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Nickel-Catalyzed, Cascade Cycloadditions of 1-Ethynyl-8-halonaphthalenes with Nitriles: Synthesis, Structure, and Physical Properties of New Pyrroloarenes**

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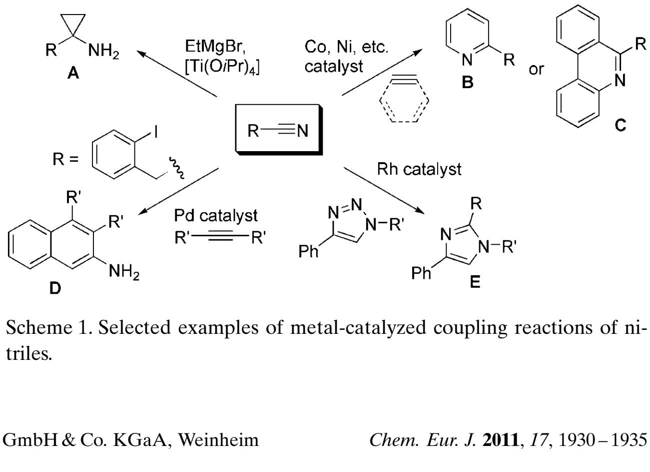
Abstract: The reaction of 1-ethynyl-8-halonaphthalenes **1** with nitriles in the presence of the catalytic system [$NiBr_2$-(dppe)]/Zn (dppe = 1,2-bis(diphenylphosphino)ethane) is found to produce unusual pyrroloarenes **2**. The carbon–nitrogen triple bond in nitrile is activated twice, and five new bonds are formed in a one-pot transformation, which causes a pyrrole and two six-membered rings to be generated simultaneously. The scope and limitations of this reaction are examined. Similarly, alkyl-bridged diynes also furnish the corresponding polycycles. Diaryl-substituted cycloadducts **2** (R^1 = Ar) are fluxional, because of the restriction in rotation of the aryl groups. The rotational barrier is studied by performing ^1H NMR experiments at various temperatures. The structures of several compounds are determined by X-ray crystallographic analysis. The photophysical and electrochemical properties of the pyrroloarenes are also investigated.

Keywords: alkynes · cascade reactions · cycloaddition · nickel · nitriles · pyrroloarenes

Introduction

Metal-catalyzed reactions for carbon–carbon bond formation are the focus of extensive research in organic synthesis. These reactions are useful tools for constructing a variety of valuable products.[1] Unsaturated substrates, such as alkenes and alkynes, are suitable for use in this type of reaction because they easily form π-complexes and then undergo migratory insertion reactions from their coordination sphere. This phenomenon makes these reactions very efficient, even under mild conditions. Similarly, nitriles can react with several types of metal complex to produce versatile nitrogen-containing molecules.[2] For example, under titanium-mediated conditions (the so-called Kulinkovich–de Meijere's protocol), nitriles are converted into cyclopropylamines **A** through 1,1-addition with Grignard reagents (Scheme 1).[3] Similar to alkynes, nitriles also react with 1-metallacyclopentadienes. Thus, the metal-catalyzed [2+2+2] cycloaddition of nitriles with two molecules of an alkyne[4] or benzyne[5] yields pyridines **B** or phenanthridines **C**, respectively. Reacting the cyano group in (*o*-iodophenyl)acetonitrile with an



Scheme 1. Selected examples of metal-catalyzed coupling reactions of nitriles.

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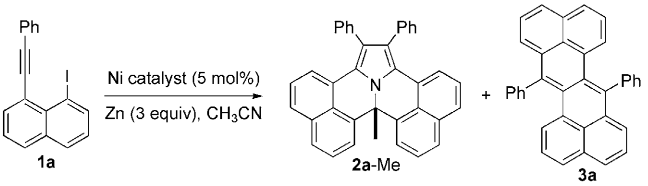
alkyne in the presence of a palladium catalyst leads to the formation of β-naphthylamines **D**.[6] Moreover, the rhodium-catalyzed transannulation of 1,2,3-triazoles with nitriles produces imidazoles **E**, with in situ generated rhodium-carbenes expected to be the key intermediates.[7] Recently, we observed that in the Ni-catalyzed cycloaddition of 1-phenylethynyl-8-iodonaphthalene in acetonitrile the carbon–nitrogen triple bond in the solvent can be activated twice to give an unexpected pyrroloarene product. This study explores the scope and limitations of this reaction and elucidates the unusual structure and physical properties of its products.

Results and Discussion

In our earlier studies, attempts were made to synthesize zethrene **3a** from 1-iodo-8-(phenylethynyl)naphthalene (**1a**) through a nickel-catalyzed cyclodimerization.[8] However, the catalyst system [$NiBr_2$(dppe)]/Zn (dppe = 1,2-bis(diphenylphosphino)ethane) gave an acetonitrile-incorporated cycloadduct **2a**-Me in 84 % yield, accompanied by traces of diphenylzethrene **3a**.[9]

In this cascade reaction, five new bonds in **2a**-Me are formed in a one-pot transformation, causing one pyrrole and two six-membered rings to be generated simultaneously.[10] Based on this result, the reaction conditions were systematically investigated (Table 1). Catalyst [$NiBr_2$(dppe)] was found to be superior to [$NiBr_2$(dme)], [Ni(acac)$_2$], [$NiCl_2$(dppp)], and [$NiCl_2(PPh_3)_2$] (Table 1, entries 3–8). Evidently, reactions conducted at 110 °C in neat acetonitrile gave the desired product in good yield. Pyrroloarene **2a**-Me was also generated in a mixed solvent system, but ten equivalents of acetonitrile, relative to the amount of alkyne **1a**, had to be used to completely consume the starting material. 1,4-Dioxane and *o*-xylene were determined to be better solvents than DMF, *N*-methylpyrrolidone (NMP), or DME, and furnished **2a**-Me in 74 and 71 % yields, respectively (Table 1, entries 9 and 10).

Table 1. The optimization of the reaction conditions for synthesizing cycloadduct **2a**-Me.[a]

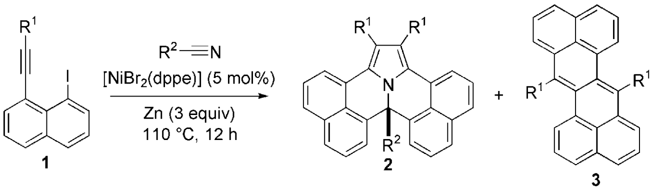


	Catalyst	Solvent	T [°C]	t [h]	Yield [%][b]
1	[$NiBr_2$(dppe)]	CH_3CN	60	12	0
2	[$NiBr_2$(dppe)]	CH_3CN	80	12	65[c]
3	[$NiBr_2$(dppe)]	CH_3CN	110	12	84[c]
4	[$NiBr_2$(dppe)]	CH_3CN	110	12	84[c,d]
5	[$NiBr_2$(dme)]	CH_3CN	110	12	0
6	[$NiCl_2$(dppp)]	CH_3CN	110	12	trace[c]
7	[$NiCl_2(PPh_3)_2$]	CH_3CN	110	12	36[c]
8	[$NiCl_2(acac)_2$]	CH_3CN	110	12	0
9	[$NiBr_2$(dppe)]	dioxane + CH_3CN[e]	110	36	71[c]
10	[$NiBr_2$(dppe)]	*o*-xylene + CH_3CN[e]	110	36	74[c]

[a] Reactions were conducted with alkyne **1a** (0.5 mmol), Zn (3 equiv) and a nickel catalyst (5 mol %) in acetonitrile (3 mL), unless otherwise mentioned; DME = dimethoxyethane; dppp = 1,3-bis(diphenylphosphino)propane; acac = acetylacetone. [b] Isolated yield of **2a**-Me. [c] Small amounts of zethrene **3a** was also obtained. [d] [$NiBr_2$(dppe)] (10 mol %) was used. [e] A mixture of 1,4-dioxane or *o*-xylene (1.5 mL) and acetonitrile (10 equiv) was used.

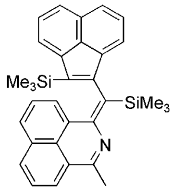
The reactivity of numerous alkynes **1** was examined and most of them produced, under these conditions, the corresponding cycloadducts **2** in moderate to good yields (Table 2). Our reaction conditions are compatible with many functional groups, including alkyl, alkoxy, ester, haloaryl, and heteroaryl groups. However, the terminal alkyne of type **1** (R^1 = H) is not suitable for this reaction because it generates unsubstituted zethrene **3** (R^1 = H) as the major product, although in low yield. The steric congestion around and electronic properties of the substituents R^1 and R^2 strongly influence the yield. In comparison to electron-rich moieties, electron-deficient aryl substituents R^1 reduce the reaction efficiency and/or increase the amount of zethrene formed (Table 2, entries 6 and 8–10). 4-Trifluoromethylphenyl-substituted alkyne **1f** is a representative example of the effect of electron-withdrawing groups on the reaction. As expected, the bulky 1-naphthyl group gave unsatisfactory results, even at higher temperatures (Table 2, entry 14). Additionally, 1-iodo-8-(trimethylsilylethynyl)naphthalene (**1m**) formed an unexpected cycloadduct **4** and zethrene **3m**.

Table 2. The preparation of pyrroloarenes **2**.[a]



	Alkyne	R^1	R^2	Product (yield [%])[b]
1	**1a**	Ph	Me	**2a**-Me (84) + **3a** (4)
2[c]	**1a**	Ph	Et	**2a**-Et (74) + **3a** (2)
3[c]	**1a**	Ph	Ph	**2a**-Ph (trace) + **3a** (3)
4[c]	**1a**	Ph	Bn	**2a**-Bn (52) + **3a** (1)
5	**1b**	4-MeC_6H_4	Me	**2b**-Me (82) + **3b** (4)
6	**1c**	4-FC_6H_4	Me	**2c**-Me (65) + **3c** (10)
7	**1d**	4-ClC_6H_4	Me	**2d**-Me (77) + **3d** (6)
8	**1e**	4-BrC_6H_4	Me	**2e**-Me (51) + **3e** (17)
9	**1f**	4-$CF_3C_6H_4$	Me	**2f**-Me (16) + **3f** (19)
10	**1g**	4-$CO_2MeC_6H_4$	Me	**2g**-Me (56) + **3g** (20)
11	**1h**	4-$OMeC_6H_4$	Me	**2h**-Me (68) + **3h** (7)
12	**1i**	2-thiophenyl	Me	**2i**-Me (65) + **3i** (2)
13	**1j**	3,5-$(CH_3)_2C_6H_3$	Me	**2j**-Me (54) + **3j** (9)
14[c]	**1k**	1-naphthyl	Me	**2k**-Me (36) + **3k** (10)
15	**1l**	*n*Bu	Me	**2l**-Me (78) + **3l** (6)
16[d]	**1m**	$SiMe_3$	Me	**2m**-Me (trace) + **3m** (6)

[a] Reactions were conducted with alkyne **1** (0.5 mmol), Zn (3 equiv) and [$NiBr_2$(dppe)] (5 mol %) in the corresponding nitrile as the solvent. [b] Isolated yields. [c] Reactions were conducted at 130 °C. [d] A mixture of **4** and **5** was obtained in 59 % yield. Compound **3m** was isolated as unsubstituted zethrene (R^1 = H).



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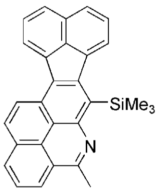

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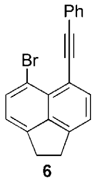

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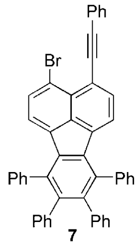

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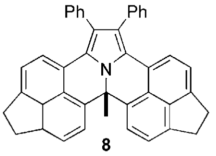

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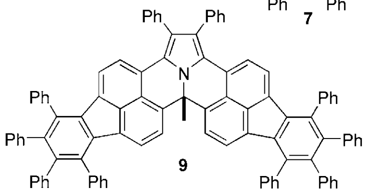
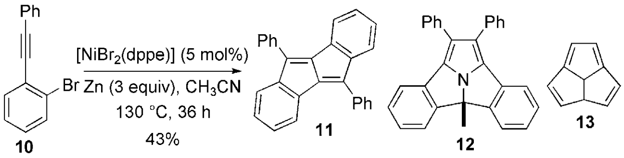




Scheme 2. The cyclodimerization of alkyne **10**.

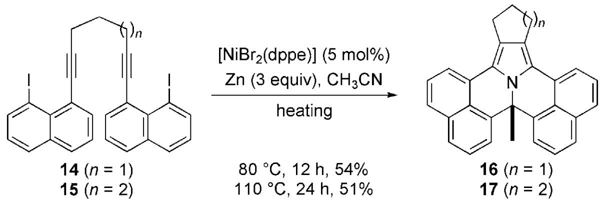
When the mixture was slowly purified by column chromatography, zethrene **3m** underwent desilylation to produce unsubstituted zethrene (**3**, $R^1 = H$), and some of compound **4** was converted into **5** through desilylation and subsequent aromatization (Table 2, entry 16). The structure of **5** was verified by X-ray crystallographic analysis (Table 3).[11] Other nitriles, such as propionitrile and benzylnitrile, can also participate in this reaction, but they are not as reactive as acetonitrile. Steric effects are responsible for these unsatisfactory results. Unlike other examples, pure compound **2a**-Bn could not be obtained because it contained an inseparable impurity (approximately 15%).

Table 3. The X-ray crystal-structure data for compounds **2d**-Me, **2j**-Me, **5**, and **8**.

	2d-Me	**2j**-Me	**5**	**8**
formula	$C_{39}H_{25}Cl_4N$	$C_{42}H_{33}N$	$C_{29}H_{23}NSi$	$C_{42}H_{29}N$
M_r	649.40	551.69	413.57	547.66
solvent	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH	CH_2Cl_2/MeOH
T [K]	295(2)	295(2)	100(2)	100(2)
crystal system	triclinic	monoclinic	monoclinic	othorhombic
space group	$P\bar{1}$	$P2_1/n$	$P12_1/n1$	$P2_1/c$
Z	2	4	4	4
a [Å]	9.2014(5)	16.2850(10)	11.6358(6)	14.4121(11)
b [Å]	13.2634(7)	8.7183(5)	7.7698(4)	11.9728(9)
c [Å]	14.1819(7)	22.2079(13)	24.8346(13)	16.7720(12)
α [°]	99.5140(10)	90	90	90
β [°]	104.1500(10)	106.6990(10)	101.0970(10)	105.608(3)
γ [°]	107.1950(10)	90	90	90
V [Å^3]	1549.64(14)	3020.1(3)	2203.3(2)	2787.3(4)

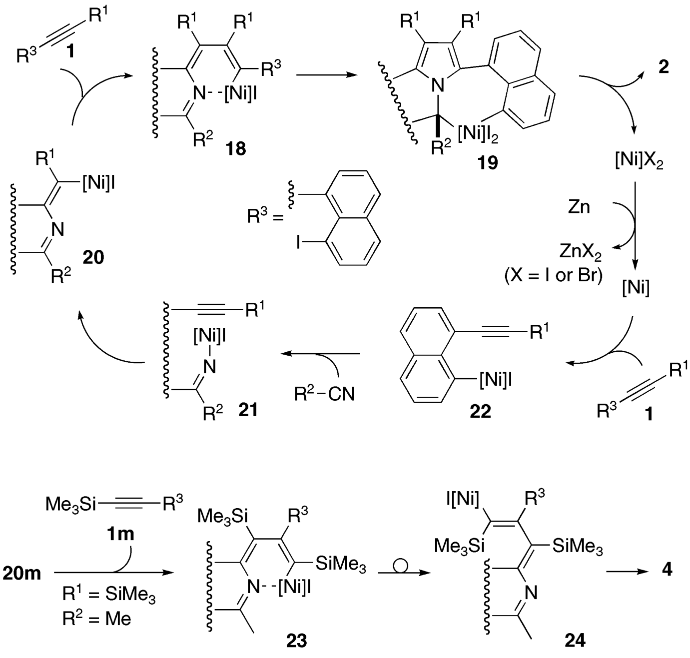
Reactions with bromo-substituted alkynes **6** and **7** had to be conducted at higher temperatures and over longer reaction times (130 °C, 36 h) to ensure complete conversion of the starting material and form cycloadducts **8** and **9** in 61 and 36% yields, respectively. Under the conditions described above, 1-bromo-2-(phenylethynyl)benzene (**10**), however, underwent cyclodimerization, rather than the formation of the acetonitrile-insertion cycloadduct (Scheme 2). Consequently, 5,10-diphenylindeno[2,1-*a*]indene (**11**) was isolated in 43% yield, with 40% of alkyne **10** recovered. Similar procedures have been developed by Tilley[12a] and Kubo.[12b] The formation of the desired product **12**, the backbone of which contains an analogue of dihydroacepentalene **13**,[13] is inhibited by the high strain energy.

The cycloaddition of alkyl-bridged diynes **14** and **15** with acetonitrile produced compounds **16** and **17**, respectively, in moderate yields (Scheme 3). The reaction conditions required reveal the difference in their reactivity, and diyne **14** (80 °C, 12 h) was consumed more easily than **15** (110 °C, 24 h).



Scheme 3. The cycloaddition of diynes with acetonitrile.

The putative reaction mechanisms for the formation of compounds **2** and **3** are very similar, but the generation of the latter involves the insertion of a molecule of nitrile, as presented in Scheme 4. Zinc reduces the precatalyst [Ni]X_2 to generate a Ni^0 species, which undergoes oxidative addition with iodonaphthalene **1** to give complex **22**. The *syn*-addition of the Ar–Ni bond in **22** to the C–N triple bond of a nitrile molecule yields imine derivative **21**.[14] This process is followed by the insertion of the alkynyl moiety to produce **20**, which subsequently reacts with another molecule of alkyne **1** to afford intermediate **18**. The desired product **2** is eventually obtained from **18**, via complex **19**, through cyclization and reductive elimination. The successful formation of *n*-butyl-substituted cycloadduct **21**-Me reveals that the insertion of the second alkyne in complex **20** ($R^1 = n$Bu) is faster than the β-hydride elimination. The formation of compound **4** may arise from a variation in the regioselectivity of the insertion of the second alkyne. The trimethylsilyl group in **1m** is bulkier than the naphthyl moiety and thus allows the reaction of **20m** with **1m** to generate **23**, which isomerizes and subsequently cyclizes to yield **4** via complex **24**.



Scheme 4. The proposed mechanism for the formation of cycloadducts **2** and **4**.

Diaryl-substituted cycloadducts **2** are fluxional molecules that give broad signals in their ^{1}H NMR spectra at room temperature, perhaps because of the restriction in rotation of the aryl groups. The less bulky substituents, such as thiophenyl and *n*-butyl groups, do not exhibit this property. Variable-temperature NMR experiments on **2a**-Me to determine the rotational barrier of the phenyl group provided a coalescence temperature of 313 K, which correlates to an estimated barrier of 14.8 kcal mol^{-1}[15] and is less than the barriers in 3,4,5,6-tetraphenyl-1,2-di(3-tolyl)benzene (16.4 kcal mol^{-1})[16a] and 9,10-di(3-tolyl)phenanthrene (20.6 kcal mol^{-1}).[16b] This result can be explained with reference to the complex NMR spectra of 1-naphthyl-substituted cycloadduct **2k**-Me, which should have three conformers at room temperature.

Crystals suitable for X-ray analysis of **2d**-Me, **2j**-Me, and **8** were obtained by slow evaporation of a CH_2Cl_2/MeOH solvent mixture (Table 3).[11] The two acenaphthyl or naphthyl moieties are not coplanar because they are in sterically congested environments (Figure 1). The torsion angles measured between carbon atoms A-B-C-D in **2d**-Me, **2j**-Me, and **8** are 37.3, 36.6, and 28.1°, respectively. The crowded nature of these molecules is also shown by the non-bonded contact between adjacent carbon atoms A and D, the distances between which in **2d**-Me, **2j**-Me, and **8** are 3.113, 3.097, and 3.106 Å, respectively. All of these values are smaller than the sum of the van der Waals radii of two carbon atoms (3.40 Å).[17]

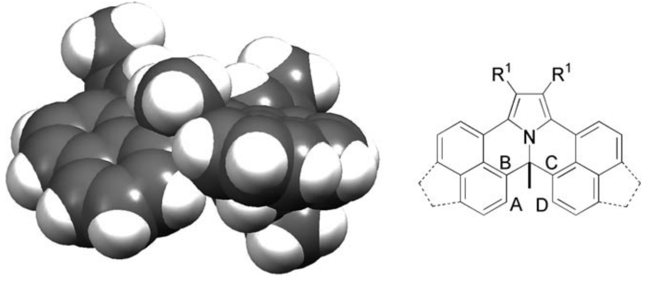


Figure 1. The molecular structure of **2j**-Me shown in space filling mode.

The photophysical properties of the compounds (Table 4) are strongly influenced by the aromatic π system in the backbone rather than by the substituents. For compound **9** both the absorption and emission bands are significantly redshifted, in contrast to cycloadducts **2** and **8**. However, the effect of the alkyl substituents in the R^1 and R^2 positions in **2** or the ethylene bridges in **8** is not as important, as shown by the similarity in the photophysical properties of compounds **2a**-Me, **2a**-Et, **2l**-Me, and **8** (Table 4, entries 1, 2, 6, and 7). In the subclass of diaryl-substituted pyrroloarenes **2**, the aryl moieties slightly change the absorption and emission bands. This phenomenon is probably caused by the twisting of the two aryl rings in the main core, as revealed in their X-ray crystal structures (Table 4, entries 1 and 3–6). Notably, diluted solutions of these pyrroloarenes are strongly fluorescent, even under ambient light.[15]

Table 4. Physical properties of the pyrroloarenes.[a]

		Photophysical properties			Electrochemistry[d]
		$\lambda_{max(abs)}$ [nm][b]	$\lambda_{max(em)}$ [nm][b]	Φ_f[c]	oxidation potential E_{pa} [V]
1	**2a**-Me	438	480	0.45 (0.53)	0.27, 0.94 (ir.)
2	**2a**-Et	438	480	0.48 (0.55)	0.26, 0.98 (ir.)
3	**2g**-Me	441	480	0.53 (0.62)	0.35, 0.97 (ir.)
4	**2h**-Me	441	480	0.40 (0.47)	0.23, 0.92 (ir.)
5	**2i**-Me	430	481	0.45 (0.52)	0.34, 0.98 (ir.)
6	**2l**-Me	446	481	0.38 (0.44)	0.16, 0.94 (ir.)
7	**8**	438	481	0.52 (0.61)	0.07, 0.70 (ir.), 0.97 (ir.), 1.20 (ir.)
8	**9**	563	603	0.21	0.26

[a] The purity (>97 %) of samples for physical studies was determined by HPLC, see reference [15]; ir. = irreversible. [b] Samples (concentration $\approx 10^{-5}$ M) were measured in CH_2Cl_2. [c] Standards for the determination of quantum yields: rhodamine 110 for entries 1–7 and rhodamine 101 for compound **9**. The value in parentheses refers to results if coumarin was used as the standard. [d] Compounds (concentration $\approx 10^{-3}$ M) in a background electrolyte solution of 0.1 M $TBAPF_6$ (tetrabutylammonium hexafluorophosphate) in CH_2Cl_2; working electrode: glass carbon (GC) electrode; reference electrode: $Ag/AgNO_3$ (0.1 M $AgNO_3$ and 0.1 M N-(nBu)$_4$ClO$_4$ in acetonitrile); counter electrode: platinum wire; scan rate: 50 mV s^{-1}; internal standard: ferrocene; oxidation potentials were measured versus Fc/Fc$^+$.

The first oxidation potential of the cycloadducts depends upon the substituents directly bound to the main core (Table 4). In contrast to **2a**-Me (0.27 V vs. Fc/Fc$^+$), the *n*-butyl groups in **2l**-Me (0.16 V) and ethylene bridges in **8** (0.07 V) strongly reduce the oxidation potential. However, the addition of an alkyl substituent at the R^2 position in **2** or the extension of the π system of the backbone does not significantly change the first oxidation potential of compounds **2a**-Et and **9** relative to **2a**-Me. As was determined for the photophysical properties, neither the presence of electron-rich nor electron-deficient aryl moieties at the R^1 position of pyrroloarenes **2** plays a critical role in the electrochemical properties (Table 4, entries 1, 3, and 4).

Conclusion

A new cascade reaction of nitriles was explored and the products generated exhibit interesting structural and physical properties. The electroluminescence properties of these compounds are currently being investigated, as they may potentially be used as organic light-emitting diodes (OLEDs). Moreover, the synthesis of heteroatom-substituted bowl-shaped molecules from these pyrroloarenes is underway.

Experimental Section

Instruments: ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 (300 and 75.5 MHz) and 500 (500 and 125 MHz) spectrometers. Mass spectra were collected with a Bruker Daltonics Apex II30. X-ray crystal-structure determination data were collected on a Stoe–Siemens-AED diffractometer. Melting points were determined with a Büchi B545 melting point apparatus and are uncorrected. The electrochemical experiments were accomplished by using a Princeton Applied Research Corporation (PAR) model 263 A potentiostat controlled by PAR model 270 software. A three-electrode cell was used for the electrochemical experiments. UV spectra were recorded by HP 8453. Photoluminescence experiments were accomplished by Jasco FP-6300 and a Cary Eclipse fluorescence spectrophotometer. Rhodamine 110 ($\Phi_f = 0.95$),[18] rhodamine 101 ($\Phi_f = 0.96$),[19] and coumarin ($\Phi_f = 0.73$)[20] were used as the standards for the determination of quantum yields.

General procedure for the preparation of pyrroloarenes: A mixture of the appropriate alkyne (0.50 mmol), [$NiBr_2$(dppe)] (15.4 mg, 25.0 μmol), Zn (97.5 mg, 1.50 mmol), and nitrile (3 mL) in a thick-walled Pyrex tube was purged with nitrogen for 5 min. The sealed tube was kept in an oil bath at 110 °C for 12 h (or at 130 °C for 36 h). After cooling to room temperature, the suspension was filtered through a layer of Celite and the Celite was rinsed with CH_2Cl_2 (30 mL). The solvent was removed from the filtrate under reduced pressure. The residue was subjected to column chromatography on silica gel and elution with hexane/CH_2Cl_2 afforded the pyrroloarene. A suitable crystal for the X-ray diffraction analysis was grown from CH_2Cl_2/MeOH (ca 20:1).

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