Synthesis and Derivatization of Expanded $[n]$Radialenes ($n = 3, 4$)

Abstract: Versatile, iterative synthetic protocols to form expanded \([n]\)radialenes have been developed \((n = 3\) and \(4)\), which allow for a variety of groups to be placed around the periphery of the macrocyclic framework. The successful use of the Sonogashira cross-coupling reaction to complete the final ring closure demonstrates the ability of this reaction to tolerate significant ring strain while producing moderate to excellent product yields. The resulting radialenes show good stability under normal laboratory conditions in spite of their strained, cyclic structures. The physical and electronic characteristics of the macrocycles have been documented by UV-visible spectroscopy, electrochemical methods, and X-ray crystallography (four derivatives), and these studies provide insight into the properties of these compounds as a function of pendent substitution in terms of conjugation and donor/acceptor functionalization.

**Keywords**: cross-conjugation · cross-coupling · macrocycles · radialenes · strained molecules

**Introduction**

It is hard to debate the potential role of carbon-rich organic molecules and materials as the active components in electronic, optical, and optoelectronic devices. The commercial release of a 55-inch organic light-emitting diode (OLED) TV was announced earlier this year,[1] graphene offers an intriguing and realistic alternative to indium tin oxide (ITO) for flexible transparent electrodes,[2] and the fullerene derivative phenyl-C\(_{61}\)-butyric acid methyl ester (PCBM) is by far the most common electron acceptor in polymer solar cells.[3] Just to name a few. Although the applications of carbon-rich molecules might be the crowning jewels of years of research, it is arguably the fundamental study of new molecular designs and structures that often make these headline discoveries possible.

Conjugated macrocycles are just one small section of the general class of carbon-rich molecules.[4] In addition to their aesthetically appealing structures, conjugated macrocycles offer a rigid structure that has often been used to study aromaticity,[5] and their defined geometry provides supramolecular building blocks.[6] Radialenes (1; Figure 1) are a particular class of carbon-rich macrocycles that have drawn attention on account of their interesting structure and unusual electronic properties.[7] Expanded radialenes, on the other hand, are macrocycles that arise from the formal insertion of acetylenic spacers into the cyclic, all-carbon core of a radia-}

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diynes, vinyl triflates, and dibromoolefins shown in Figure 2. These three building blocks, when combined with our previous methodology developed for the synthesis of cross-conjugated enyne oligomers from vinyl triflates (the iso-polydiacetylenes (iso-PDAs))\(^{[20–23]}\) suggest a viable route to enyne radialenes with more diverse substitution patterns. We report herein our efforts to develop the modular synthesis of expanded \([n]\)radialenes, as well as characterization of these products by spectroscopic, electrochemical, and solid-state structural analyses.

**Results and Discussion**

As described above, dibromoolefins are important building blocks toward the synthesis of expanded radialenes. To this end, \(5a–e\) were synthesized by means of the Ramirez protocol\(^{[24]}\) from the corresponding ketones by using PPh\(_3\) and CBr\(_4\) (Scheme 1). Compounds \(5a–c\) were formed as previously reported\(^{[25–27]}\) whereas the synthesis of \(5d\) and \(5e\) was developed for the present study. It is noteworthy that in the case of \(5a, d, e\) the dibromoolefination reaction was sluggish due to steric hindrance about the ketone carbon, and the reactions were thus best conducted under reflux conditions in benzene.

The formation of mono-substituted expanded \([4]\)radialenes rested on iso-PDA \(6\) as the common precursor (Scheme 2), and this cross-conjugated precursor was readily available from a known procedure.\(^{[23]}\) Subjecting \(6\) to tetra-n-butylammonium fluoride (TBAF) in THF at room temperature cleanly gave the desilylated iso-PDA. Because of the limited stability of the terminal acetylene product, it was taken directly to the subsequent Sonogashira cross-coupling reaction with a dibromoolefin conducted in THF under reflux conditions.\(^{[28]}\) The reactions to form \(7–10\) were monitored by thin-layer chromatography (TLC), which showed that progress was no longer observed after about 18 h. Once judged completed, a standard aqueous workup and column chromatography gave the desired products. Following this protocol, aryl derivatives \(7\) and \(8\) were isolated as bright yellow solids in good yields (68 and 79%, respectively), whereas the fulvene-like derivative \(9\) was obtained as a brown solid and in slightly lower yield (64%), presumably

![Figure 2. Building blocks for enyne radialene synthesis.](image)

![Scheme 1. Synthesis of dibromoolefins 5a–e.](image)

![Scheme 2. Synthesis of expanded [4]radialenes 7–10 (yields given are over the two steps from 6).](image)
due to the sensitivity of the cross-coupling reaction to the sterically encumbered environment of the dibromoolefin moiety. Finally, the reaction with dibromoolefin 5b gave expanded [4]radialene 10 in 77% yield as a yellow solid. The successful formation of 10 in good yield is noteworthy because it opens the door to postsynthetic modification of the expanded [4]radialene skeleton by following a sequence of desilylation and Sonogashira reaction (see below).

A single crystal of radialene 9 suitable for X-ray crystalgraphic analysis was grown in THF at 4–5 °C (Figure 3). The macrocyclic framework of 9 is clearly strained, with acetylenic bond angles spanning from 164.14(18)° for C6-C7-C8 to 170.70(18)° for C3-C4-C5. This structure is, however, consistent with that reported for perphenylated expanded [4]radialene 2b.[17] Unlike 2b, which is planar, the steric demands of the tetraphenylcyclopentadienylidene group have a dramatic effect on the planarity of radialene 9. As shown in Figure 3b, steric repulsion between phenyl rings leads to a puckering of the ring system (38.5°), similar to that found for cyclobutane.

The syntheses of the smallest members of the expanded [n]radialene series were then targeted, namely, the expanded [3]radialenes shown in Scheme 3. This required the synthesis of iso-PDA dimer 11, which was achieved by using the reported literature procedure.[23] With 11 in hand, a sequence of desilylation using TBAF and Sonogashira cross-coupling with dibromoolefins 5a–e gave the desired expanded radialene products 12–15 in a manner similar to that developed for [4]radialenes 7–10. Despite their strained acetylenic framework, the [3]radialene products 12–15 showed no particular instability under normal laboratory conditions, and they could be purified by column chromatography to give the products as yellow or orange solids. The isolated yields for 12–15 were substantially lower over the two steps from 11 than those of the analogous cyclic tetramers 7–10. This is likely a result of the rather significant strain incorporated into the conjugated structure during the final ring-closing event, as well as, in the case of 12, the steric demands of the dibromoolefin 5e[23] (relative to the less hindered 5a–c).

The successful formation of 12–15, however, offers an excit-
ing testament to the ability of the Sonogashira cross-coupling reaction to tolerate significant ring strain on the way to forming interesting macrocyclic structures.[29]

Single crystals of expanded [3]radialene 14 were grown from a mixture of acetone and dichloromethane maintained at a temperature of 4–5°C. The most notable parameters from the solid-state structure of 14 (Figure 4) are the planar radialene skeleton and the alkyne bond angles found for C4-C5-C6 at 155.59(14), C1-C2-C3 at 156.20(15), and C2-C1-C9 at 156.30(15). These are amongst the smallest alkyne angles characterized by X-ray crystallography to date. [30] Finally, it is interesting to note the difference in twist angles of the two phenyl groups appended to the tetraethynylethene (TEE) section of 14. In one case, the phenyl ring is almost coplanar with the enyne skeleton of the radialene (15°) to permit π-conjugation, and it is severely twisted (79°) in the other case.[31]

Further functionalization of the radialene core was available through selective use of enediyne and dibromoolefin building blocks to assemble iso-PDAs with varied structures. As described in Scheme 4, this goal was readily achieved through derivatization of enediyne 16 by using a sequence of desilylation and subsequent Sonogashira coupling with vinyl triflate 17.[23] iso-PDA 18 was thus formed in good yield, and then carried on to the synthesis of the C2-symmetric [4]radialene 19 by means of desilylation with TBAF and cross-coupling with 5e. The disubstituted expanded [4]radialene 19 was isolated as a bright yellow solid that is stable under ambient conditions.

Single crystals of 19 suitable for crystallography were grown by the diffusion of pentane into a solution of 19 in chloroform at 4–5°C. The centrosymmetric framework of the radialene is practically planar (Figure 5), including exocyclic alkylidene carbon atoms C3/C3', whereas the alkylidene carbon atoms C7/C7 lie 0.33 Å above/below this plane.[32] The acetylenic bonds angles fall in a narrow range that spans from 167.85(18) for C1-C8-C6 to 170.63(18) for C4-C5-C6. The two CF3C6H4 rings are rotated by approximately 43 and 81° from the plane of the radialene, whereas the phenyl rings are twisted by 43–46°.

Finally, the protocol developed for 19 was easily adapted to the formation of the analogous system with two tetraethynylethene units (Scheme 5). In this case, the trimethylsilyl group of enediyne 20 was carefully removed to give 21, which was then utilized in a cross-coupling reaction with dibromoolefin 5b to give iso-PDA 22. With 22 in hand, a second iteration of desilylation and cross-coupling with 5b gave the radialene 23 as a stable yellow solid (m.p. 235°C) in excellent yield of 78% over the two steps from 22.

Single crystals for X-ray analysis were grown from a solution of 23 in CHCl3 at 4–5°C; the ORTEP plot of radialene 23 is shown in Figure 5. Overall, bond lengths and angles for the centrosymmetric structure are unremarkable in comparison to the structures of expanded [4]radialenes 2b, 9, and 19 as described earlier. The framework of 23 is slightly twisted, with alkylidene carbon atoms C4/C4' that lie approximately 0.4 Å out of a plane generated from the twelve carbon atoms of the radialene core. This twisting also forces the

![Figure 4. ORTEP drawing of expanded [3]radialene 14 (ORTEP shown at 30% probability; hydrogen atoms removed for clarity).](image)

![Scheme 4. Synthesis of C2-symmetric expanded [4]radialene 19 (yields of 18 and 19 are over the two steps from 16 and 18, respectively).](image)
pendent alkyne units to positions slightly above and below this plane, although the deviation is not particularly significant (see the Supporting Information).

A final question to be answered in this study was the prospect of postsynthetic modification of the radialene framework, such as desilylation of expanded [4]radialene 10 followed by Sonogashira cross-coupling to an aryl iodide (Scheme 6). Thus, removal of the triisopropylsilyl groups of 10 was effected by treatment with TBAF (2.2 equiv) at 0°C, and this reaction proceeded without significant decomposition. After the removal of the triisopropylsilyl groups, attempts to introduce aryl groups by means of Sonogashira cross-coupling at room temperature resulted in long reaction times and the formation of numerous byproducts that complicated purification. When the analogous reactions were carried out under reflux conditions, however, the situation improved dramatically and the desired radialenes 24–26 were obtained in 75–94% yield after purification by either column chromatography or recrystallization.

Although the primarily goals of this study were concerned with the development of efficient synthetic protocols, some comments on the physical properties of these new and rather unique molecules are also worth noting. Thus, in addition to X-ray crystallographic analysis of 9, 14, 19, and 23 as described above, all new radialenes were also characterized by typical spectroscopic methods to confirm their structure (see the Experimental Section and the Supporting Information), as well as by UV-visible spectroscopy and electrochemical methods to provide a preliminary overview of their electronic characteristics (spectra and electrochemical traces are provided in the Supporting Information).

UV-visible spectroscopy in solution gives an empirical picture of changes in the electronic structure as a function of pendent substituents (Table 1). Salient points of this analysis include the following observations:

1) The spectra of all the radialenes show a strong absorption in the higher-energy range from 363 nm (e.g., 2a and 12) to approximately 400 nm (e.g., 9, 23–26).
2) UV-visible spectra for expanded [3]radialenes typically show more resolved signals than the [4]radialenes. This is likely the result of the centrosymmetric (2b, 19, 23) or pseudo-centrosymmetric structure (7–10, and to a lesser extent 24–26) of the [4]radialenes and the resulting selection rules.[33] For example, CF 3-substituted [3]radialene 12 shows strong, defined absorptions at 363 and 412 nm, whereas [4]radialenes 7 and 19 both show a similar high-energy absorption (376 nm) but only a weak absorption at lower energy (≈430 nm, shoulder). A similar observation can be found for the series of triisopropylsilylethynyl-substituted radialenes, 10, 15, and 23.
3) Switching from aryl alkylidene substitution (2a/2b or 7/12) to the cyclic fluorenylidene (8/13) affords a significant redshift in $\lambda_{\text{max}}$, as the pendent aryl rings of the latter are formally made coplanar with the radialene skeleton through annulation of the aryl rings. This trend has been previously observed for radiaannulenes.[10e]
4) As expected, the largest changes in $\lambda_{\text{max}}$ are found in derivatives with pendent groups that extend $\pi$-conjugation beyond the radialene core, including the fluorenylidene (8 and 13), the tetraphenylcyclopentadienyl (9), and phenylethynyl (14) moieties. The contribution of the trii-
opropylsilylthynyl substituents (10, 15, 23) to the π-systems is less dramatic.

5) The addition of π-acceptors and π-donors in radialenes 24–26 has the expected effect of decreasing the energy of \( \lambda_{\text{max}} \), especially in the case of 26, which features the disopropylaniline donors.

Electrochemical analysis by Osteryoung square-wave and cyclic voltammetry were used to complement analysis of the electronic properties determined by UV-visible spectroscopy. The [4]radialenes show two one-electron oxidative steps, except for 7 and those decorated with the electron-deficient triisopropylsilylthynyl groups (10 and 23). The first oxidative step is reversible for 2b, 8, and 10, and irreversible for the other [4]radialenes. The [4]radialenes in general show two or three reduction events (except 25), and the first reduction potential is reversible in all cases except for 7 and 25. All substituted [4]radialene derivatives are easier to reduce than 2b, whereas the value of first oxidation potential of each radialene relative to 2b is dependent on the electron-donating or -accepting nature of the pendant substituents.

Expanded [3]radialenes 2a and 12–15 generally exhibit similar electrochemical behavior to the analogous [4]radialenes. All [3]radialenes except 12 show two one-electron oxidative steps, and the first oxidative step is reversible for 2a, 13, and 15, but it is irreversible for 12 and 14. All of the expanded [3]radialenes studied exhibit three one-electron reductive steps, and the first reduction event is reversible except for 12. In comparison to the parent radialene 2a, the first oxidation potentials of 12–15 are rendered more difficult, especially through either the presence of electron-deficient CF3 groups or through the extension of the acetylenic scaffold by means of addition of the pendant ethynyl groups.

On the other hand, the initial reduction potential for [3]radialenes 13–15 is dramatically lower than 2a, thus highlighting the influence of the fluorenylidene and ethynyl substituents on the electronic makeup of the radiaene framework, particularly for the increase in electron-accepting ability brought on by attachment of the phenylethynyl groups of 14. Perhaps most surprising is the fact that the two CF3 substituents in 12 do not appreciably shift the reduction potentials anodically relative to 2a.

There are several observable trends based on comparisons amongst all derivatives that have been studied (Table 2):

1) For radialenes with analogous substituents, 2a/2b, 8/13, and 10/15 there is little variance in either the first reduction or oxidation potential on the basis of radialene size. Thus, ring strain does not appear to play a significant role in dictating redox behavior.

2) Likewise, the greater degree of functionalization for 23 has little effect on the first initial redox events (ox 1 = 0.95 V and red 1 = −1.61 V), which are essentially the same as that measured for 10 and 15.

3) The outlier to general oxidation trends seems to be 7, which shows a remarkably facile first oxidation potential (0.79 V) in comparison to both 12 and 19 (both at 0.93 V). Equally puzzling is the fact that the first reduction of 12 (red 1 = −1.87 V) comes at a surprising similar potential compared to 2a (red 1 = −1.9 V), in spite of the increased electron deficient substitution of the former. On the other hand, reduction of 7 (red 1 = −1.79 V) and 19 (red 1 = −1.8 V) occurs more readily than 12. The origin of this strange behavior is currently not understood.

4) The facile reduction of 8 and 13 also deserves comment, and these results are nicely in line with that reported by Iyoda and co-workers for fluorenylidene-substituted radialenes, which suggests that this reduction occurs at the electron-accepting cyclopentadienyl moiety.
Expanded [n]Radialenes

By using a combination of building blocks based on enediynes, vinyl triflates, and dibromoolefins, ten new expanded [3]- and [4]radialenes have been constructed with a Sonogashira cross-coupling as the final, ring-closing step. The synthesis of expanded [3]radialenes is especially noteworthy in that it clearly demonstrates that the Sonogashira reaction is suitable for constructing strained, conjugated macrocyclic systems. When using [4]radialene, desilylation and subsequent Sonogashira coupling confirms that postsynthetic modification of the radiadene skeleton can be quite successful, thereby providing donor or acceptor radiadenes 24-26 in good to excellent yield. X-ray crystallographic analysis of four derivatives was used to confirm that the [3]- and [4]radialenes are predominantly planar molecules, although sterically demanding groups can be accommodated through deformation of the planar structure, as observed in [4]radialene 9. UV-visible spectroscopy and electrochemistry show that the electronic effects based on pendant substituents follow patterns that can be generally explained by expected paradigms with regard to the extension of the conjugated framework and/or the electron-donating or -accepting potential of the group.

Table 1. Selected UV/Vis spectroscopic details for expanded [3]- and [4]radialenes.

<table>
<thead>
<tr>
<th>No.</th>
<th>Absorption energies [nm] (ε: [M^−1.cm^−1])</th>
<th>Absorption cutoff [eV]</th>
<th>HOMO–LUMO gap [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2b-d</td>
<td>415 (25500)</td>
<td>475 (2.61)</td>
<td>2.71</td>
</tr>
<tr>
<td>377 (99300)</td>
<td>470 (2.64)</td>
<td>2.58</td>
<td></td>
</tr>
<tr>
<td>376 (81800)</td>
<td>505 (2.46)</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>393 (86500)</td>
<td>550 (2.25)</td>
<td>1.91</td>
<td></td>
</tr>
<tr>
<td>403 (20600)</td>
<td>480 (2.58)</td>
<td>2.50</td>
<td></td>
</tr>
<tr>
<td>400 (107500)</td>
<td>470 (2.64)</td>
<td>2.72</td>
<td></td>
</tr>
<tr>
<td>364 (105300)</td>
<td>475 (2.61)</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td>363 (19200)</td>
<td>505 (2.46)</td>
<td>2.43</td>
<td></td>
</tr>
<tr>
<td>338 (16100)</td>
<td>520 (2.38)</td>
<td>2.34</td>
<td></td>
</tr>
<tr>
<td>388 (35100)</td>
<td>495 (2.50)</td>
<td>2.53</td>
<td></td>
</tr>
<tr>
<td>450 (23300)</td>
<td>495 (2.50)</td>
<td>2.53</td>
<td></td>
</tr>
<tr>
<td>430 (31800)</td>
<td>465 (2.67)</td>
<td>2.73</td>
<td></td>
</tr>
<tr>
<td>378 (42800)</td>
<td>480 (2.58)</td>
<td>2.56</td>
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</tr>
<tr>
<td>376 (122000)</td>
<td>560 (2.21)</td>
<td>2.30</td>
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</tr>
<tr>
<td>498 (17800)</td>
<td>580 (2.14)</td>
<td>2.24</td>
<td></td>
</tr>
<tr>
<td>497 (13200)</td>
<td>610 (2.03)</td>
<td>2.07</td>
<td></td>
</tr>
</tbody>
</table>

[a] As was estimated from the intercept of a tangent line to the lowest energy absorption of the UV-visible spectrum with the x axis. [b] As was estimated from cyclic voltammetry, \( E_{\text{red}} - E_{\text{red}} \). [c] Spectrum acquired in THF. [d] Values taken from Ref. [17]. [e] Estimated by assuming that the observed shoulder (sh) absorption has a Gaussian shape. [f] Spectrum acquired in CH2Cl2.

5) Radialene 9 shows a notably low-value first reduction potential (\( \text{red}1 = -1.26 \text{V} \)), likely dominated by the cyclopentadienyl group directly appended to the radialene framework.

6) For radialenes 24-26, the values found for first oxidation and reduction potentials are determined predominantly by donor or acceptor aryl groups appended to the radialene, which has been observed in numerous similar systems.[36]

7) Finally, it is important to note the rather strong correlation between the HOMO–LUMO gaps determined by electrochemical methods and those estimated from the UV-visible absorption spectra (Table 1).

Conclusion

By using a combination of building blocks based on enediynes, vinyl triflates, and dibromoolefins, ten new expanded [3]- and [4]radialenes have been constructed with a Sonogashira cross-coupling as the final, ring-closing step. The synthesis of expanded [3]radialenes is especially noteworthy in that it clearly demonstrates that the Sonogashira reaction is suitable for constructing strained, conjugated macrocyclic systems. When using [4]radialene, desilylation and subsequent Sonogashira coupling confirms that postsynthetic modification of the radiadene skeleton can be quite successful, thereby providing donor or acceptor radialenes 24-26 in good to excellent yield. X-ray crystallographic analysis of four derivatives was used to confirm that the [3]- and [4]radialenes are predominantly planar molecules, although sterically demanding groups can be accommodated through deformation of the planar structure, as observed in [4]radialene 9. UV-visible spectroscopy and electrochemistry show that the electronic effects based on pendant substituents follow patterns that can be generally explained by expected paradigms with regard to the extension of the conjugated framework and/or the electron-donating or -accepting potential of the group.

Experimental Section

General: Reagents were purchased in reagent grade from commercial suppliers and used without further purification. THF was distilled from sodium benzenephone ketyl. Anhydrous MgSO4 was used as the drying agent after aqueous workup. Filtration, evaporation, and concentration under vacuum were done at water aspirator pressure. All reactions were performed in standard dry glassware under an inert atmosphere of argon. Column chromatography: silica gel (230–400 mesh). Thin-layer chromatography: precoated plastic sheets covered with 0.20 mm silica gel with fluorescent indicator UV 254 nm; visualization by UV light or KMnO4 stain. Melting points are uncorrected. Aqueous workup for reactions refers to the following general procedure: Et2O (5–25 mL) and saturated aqueous NaCl (2×5–15 mL) were added to the reaction mixture at room temperature. The organic phase was separated and washed successively with saturated aqueous NaOH (2×5–15 mL) and saturated aqueous NaCl (2×5–25 mL), then dried over MgSO4 and filtered.

\(^1H, \(^13C\) and \(^19F\) NMR spectra were collected at 27°C in CDCl3, CD2Cl2, or CD3OD; solvent peaks as reference. Coupling constants are reported as observed (±0.5 Hz). For simplicity, the coupling constants of the aryl protons for para-substituted aryl groups have been reported as pseudo-first-order (i.e., doublets), even though they are second-order (AA’XX’) spin systems. UV/Vis spectra were acquired at RT using a Varian Cary 400 Scan spectrometer. The shape of shoulder absorptions in the spectra are approximated to be Gaussian curves, and the value of both the \( A_{max} \) for the absorption and molar absorptivity were estimated on the basis of this approximation. For mass spectral analyses, low- and high-resolution data are provided in cases when \( M^+ \) was not the base peak. Otherwise, only high-resolution data are provided. The samples for ESI mass spectrometry were dissolved in CH3Cl and made use of a 3:1 MeOH/toluene mixture as the carrier solvent. MALDI mass spectrometry used the matrix trans-2-[3(4-tert-butylphenyl)-2-methyl-1-propionylidenemalononitrile (DCTB). Differential scanning calorimetry (DSC) measurements were carried out using a Perkin-Elmer Pyris 1 DSC instrument. All thermal analyses were carried out under a flow of nitrogen with a heating rate of 10°C/min. Melting points from DSC analysis are reported as the peak maxima, except in cases when the sample decomposed, in which case the onset temperature of the decomposition exothermic peak is reported, as well as the exothermic maxima that correspond to the decomposition. Cyclic voltammetry and Osteryoung electrochemical analyses were generally performed in CH3Cl that contained 0.1 M of NBut4PF6 as the supporting electrolyte. The concentration in analyte was about 5 ×
The crude reaction product was filtered, and the residue washed with benzene (2 × 40 mL). Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂, 1:1 to 5:1) afforded 5a (86 mg, 0.080 mmol), Cul (5.5 mg, 0.028 mmol), [Pd(PPh₃)₂Cl₂] (4 mg, 0.003 mmol), iPr₄NH (3 mL) and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂, 5:1 to 1:2) afforded 7 (56 mg, 68%) as a bright yellow solid. Rf = 0.7 (hexanes/CH₂Cl₂, 1:1); mp > 245–250°C;

H NMR (CDCl₃, 400 MHz): δ = 7.60 (d, J = 7.6 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.27–7.02 ppm (m, 34 Hz); ¹³C NMR (376 MHz, CDCl₃); δ = −63.4 ppm; ¹²⁷⁷ CNMR (125 MHz, CDCl₃); δ = 152.8, 152.4, 147.4, 140.13, 140.70, 140.32, 139.7, 133.4, 130.6, (q, J(CF) = 32 Hz) 130.3, 130.2, 129.4, 129.3, 129.22, 129.20, 128.4, 128.3, 128.2, 126.9 (q, J(CF) = 4 Hz) 125.9 (q, J(CF) = 14 Hz) 124.3 (q, J(CF) = 27 Hz) 120.5, 102.4, 97.2, 97.4, 96.7, 95.8 ppm (one signal coincident or not observed); IR (CH₂Cl₂, cast): δ = 3053, 2921, 2849, 1610, 1449, 1276, 1259, 1250, 1249, 1210, 108, 97, 94.6, 93.5 ppm (three signals coincident or not observed); IR (CH₂Cl₂, cast): δ = 3053, 2921, 2849, 1610, 1449, 1276, 1259, 1250, 1249, 1210, 108, 97, 94.6, 93.5 ppm (three signals coincident or not observed); IR (CH₂Cl₂, cast): δ = 3053, 2921, 2849, 1610, 1449, 1276, 1259, 1250, 1249, 1210, 108, 97, 94.6, 93.5 ppm (three signals coincident or not observed); IR (CH₂Cl₂, cast): δ = 3053, 2921, 2849, 1610, 1449, 1276, 1259, 1250, 1249, 1210, 108, 97, 94.6, 93.5 ppm (three signals coincident or not observed); IR (CH₂Cl₂, cast): δ = 3053, 2921, 2849, 1610, 1449, 1276, 1259, 1250, 1249, 1210, 108, 97, 94.6, 93.5 ppm (three signals coincident or not observed); IR (CH₂Cl₂, cast): δ = 3053, 2921, 2849, 1610, 1449, 1276, 1259, 1250, 1249, 1210, 108, 97, 94.6, 93.5 ppm (three signals coincident or not observed); IR (CH₂Cl₂, cast): δ = 3053, 2921, 2849, 1610, 1449, 1276, 1259, 1250, 1249, 1210, 108, 97, 94.6, 93.5 ppm (three signals coincident or not observed); IR (CH₂Cl₂, cast): δ = 3053, 2921, 2849, 1610, 1449, 1276, 1259, 1250, 1249, 1210, 108, 97, 94.6, 93.5 ppm (three signals coincident or not observed);
ing mixture was heated to reflux for 18 h. Solvent removal and purifica-


tion by column chromatography (silica gel, hexanes/CH2Cl2, 5:1 to 3:1) af-

forded radiaene 9 (52 mg, 64 %) as a brown solid. Rf = 0.7 (hexanes/

CH2Cl2, 1:1); m.p. >300 °C (decomp). [(CH2Cl2, 400 MHz); δ = 

7.35–7.37, 7.69 ppm (m, 24H); 13C NMR (125 MHz, CDCl3); δ = 

139.5, 132.3, 131.0, 130.8, 129.7, 129.2, 128.0, 127.5, 127.4, 126.9, 126.3, 113.5, 108.7, 102.5, 101.7, 98.1, 97.4, 95.3 ppm; IR (CH2Cl2, cast): ν = 3080, 3058, 3028, 2953, 2924, 2853, 2517, 2139, 1947, 1884, 1801, 1734 cm–1; UV/Vis (THF): λmax (ε) = 455 (sh; 10 000 mε cm–1); 403 nm (20600); HRMS (MALDI-TOF; DCTB): m/z calcd for C62H62F6 = 814.4386 [M+]; found: 814.4386.

**Compound 14:** A mixture of 11 (85 mg, 0.13 mmol) and TBAF (0.30 mmol, 1.0 mM in THF) was stirred for 1 h. EtOAc and H2O were added; the organic phase was separated, washed with saturated NH4Cl (2 × 20 mL), dried (MgSO4), and reduced to 0.2 mL. The resulting crude solution was added to a degassed mixture of dibromo-9-furan 5a (26.5 mg, 0.05 mmol), dpPE (6.0 mg, 0.03 mmol), and dry THF (5.0 mL). The resulting mixture was heated to reflux for 2 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH2Cl2, 5:1 to 2:1) afforded 14 (32.5 mg, 48 %) as a yellow oil. Rf = 0.6 (hexanes/CH2Cl2, 1:1); m.p. >300 °C (decomp). [(CH2Cl2, 400 MHz); δ = 7.84 (d, J = 7.6 Hz, 2H), 7.73–7.65 (m, 10H), 7.55–7.53 (m, 6H), 7.46–7.43 (m, 6H), 7.39 (td, J = 6.8, 0.8 Hz, 2H), 7.31 ppm (td, J = 6.8, 1.2 Hz, 2H); 13C NMR (125 MHz, CDCl3); δ = 147.5, 140.8, 139.8, 137.4, 137.3, 130.9, 130.8, 129.6, 129.5, 128.9, 128.7 (m, 4H); IR (CH2Cl2, cast): ν = 3085, 3021, 3016, 2916, 1716 cm–1; UV/Vis (THF): λmax (ε) = 474 (12000), 447 (14000), 383 (160 mε cm–1); HRMS (EI): m/z calcd for C62H62F6: 864.2191 [M+]; found: 864.2191.
Compound 18: A mixture of 16 (55 mg, 0.11 mmol) and K₂CO₃ (2.9 mg, 0.020 mmol) in wet THF (1 mL) and MeOH (1 mL) was stirred for 1 h. Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. The resulting solution was added to a degassed mixture of triflate 17 (101 mg, 0.206 mmol), Cul (6.4 mg, 0.033 mmol), [Pd(PPh₃)₄] (7 mg, 0.006 mmol), pPr₂NH (3 mL), and dry THF (5 mL). The resulting mixture was heated to reflux for 18 h. Solvent removal and purification by column chromatography (silica gel, hexanes/CH₂Cl₂:1:10 by volume) afforded 18 (81 mg, 74%) as a bright yellow solid. Rᵢ = 0.5 (hexanes/CH₂Cl₂:1:2); m.p. 85°C; [H NMR (CDCl₃, 400 MHz); δ = 7.5-7.55 (m, 4H), 7.35-7.40 (m, 2H), 7.39-7.19 (m, 24H), 0.79 (s, 18H), 0.01 ppm (s, 12H); 1³C NMR (100.6 MHz, CDCl₃); δ = 157.8, 150.8, 140.2, 140.0, 139.6, 133.5, 130.5, 130.3, 130.2, 128.7, 128.5, 128.3, 127.7, 126.9 (q, J = 4 Hz); 125.4 (J = 32 Hz); 125.9 (J = 273 Hz); 125.0 (J = 171 Hz); 104.8, 103.3, 101.5, 96.3, 92.2, 88.6, 26.1, 16.7, -0.49 ppm (one J = 171 Hz quartet cannot be discerned due to low S/N or coincident signals); IR (CH₂Cl₂, cast); ν = 3056, 2958, 2865, 2824, 2134 cm⁻¹; UV/Vis (THF), λmax (%) = 430 (sh, 1600), 399 nm (sh, 25000 cm⁻¹); HRMS (MALDI-TOF): m/z calcd for C₁₄H₁₂N₂O₂S: 292.0729; found: 292.0726.

Crystal data for 23: C₃₀H₂₂Ni₃S₈, M_r = 1226.03; crystal dimensions 0.26 × 0.16 × 0.04 mm; triclinic space group P̅1/a (no. 14); a = 21.031(3), b = 13.0172(17), c = 15.0482(16) Å; β = 108.7882(28)°; V = 3943.99(9) Å³; Z = 2; ρcalc = 1.032 g·cm⁻³; ρfound = 1.011 g·cm⁻³; λ = 0.17037 Å; θ = 80°; 2θmax = 50.0°, total data collected = 26076; R₁(F) = 0.0648 (4989 observations); F₂(peak) = 2.05(2); wR(F) = 0.1955 for 397 variables and 6944 unique data; residual electron density = 0.389 and -0.205 e·Å⁻³.

**Compound 24:** BTAF (0.1 mmol, 1.0 mL) and THF (10 mL) was added to a solution of rac-30 (25 mg, 0.025 mmol) in wet THF (10 mL) at 0°C, and the solution was stirred until the starting material was no longer visible by TLC analysis (tą = 5-10 min). Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. This THF solution was then added to a degassed solution of 3-idobensonitrile (11 mg, 0.050 mmol) in THF (3 mL), pPr₂NH (2 mL), [Pd(PPh₃)₄] (1.4 mg, 0.0012 mmol), and Cul (1.6 mg, 0.003 mmol) were added sequentially to this solution, and the solution was stirred at approximately 50°C under N₂. Under TLC analysis no longer showed the presence of the deprotected rac-30 (t₆ = 15-18 h). Aqueous workup, solvent removal, flash column chromatography (silica gel, CH₂Cl₂), and precipitation from CH₂Cl₂ by the addition of Et₂O afforded 24 as an orange solid (17 mg, 75%); Rᵢ = 0.49 (CH₂Cl₂); m.p. 286-288°C (dec; discombs); DSC: decomposition, 304°C (onset), 319°C (peak). ³H NMR (500 MHz, CDCl₃); δ = 7.56 (d, J = 8.6 Hz, 4H), 7.45-7.43 (m, 4H), 7.31-7.18 (m, 25H), 7.02-6.99 ppm (m, 21H); ¹³C NMR (125 MHz, CDCl₃); δ = 154.0, 151.3, 140.1, 140.7, 139.7, 132.7, 132.3, 131.0, 130.4, 130.3, 129.7, 129.6, 129.3, 128.4, 128.9, 128.3, 127.0, 120.4, 118.7, 112.6, 108.9, 106.6, 102.2, 102.0, 97.3, 96.6, 96.4, 96.2, 90.1 ppm; IR (CH₂Cl₂, cast) ν = 3062, 2225, 1517, 1602 cm⁻¹; UV/Vis (CH₂Cl₂), λmax (%) = 495 (sh, 13000), 401 (76800), 359 (52300), 261 nm (48000 cm⁻¹); HRMS (MALDI-TOF): m/z calcd for C₄₃H₂₃Cl₃N₉O₈: 806.3030; found: 906.3026.

**Compound 25:** BTAF (0.1 mL, 0.1 mmol, 1.0 mL) was added to a solution of rac-30 (27 mg, 0.027 mmol) in wet THF (10 mL) at 0°C, and the solution was stirred until the starting material was no longer visible by TLC analysis (tą = 5-10 min). Et₂O and H₂O were added; the organic phase was separated, washed with saturated NH₄Cl (2 × 20 mL), dried (MgSO₄), and reduced to 2 mL. This THF solution was then added to a degassed solution of 4-iodobenzonitrile (13 mg, 0.054 mmol) in THF (10 mL), pPr₂NH (2 mL), [Pd(PPh₃)₄] (1.6 mg, 0.0014 mmol), and Cul (1 mg, 0.003 mmol) were added sequentially to this solution, and the solution was stirred at approximately 50°C under N₂. Under TLC analysis no longer showed the presence of the deprotected rac-30 (t₆ = 15-18 h). Aqueous workup, solvent removal, flash column chromatography (silica gel, CH₂Cl₂), and precipitation from CH₂Cl₂ by the addition of Et₂O afforded 25 (24 mg, 94%) as an orange solid. Rᵢ = 0.66 (CH₂Cl₂/hexanes, 7:3); m.p. 285°C (discombs); DSC: decomposition, 297°C (onset), 308°C (peak). ³H NMR (500 MHz, CDCl₃); δ = 8.11 (d, J = 9.0 Hz, 4H), 7.47-7.45 (m, 4H), 7.31-7.13 (m, 28H), 7.03-7.00 ppm (m, 2H); ¹³C NMR (125 MHz, CDCl₃); δ = 154.2, 153.2, 147.8, 140.15, 140.06, 139.7, 133.1, 131.0, 130.4, 130.3, 129.72, 129.70, 129.3, 129.0, 128.42, 128.40, 128.3, 128.0, 109.8, 107.0, 102.2, 101.9, 97.4, 96.39, 96.38, 96.2, 90.9 ppm; IR (CH₂Cl₂, cast); ν = 3099, 2924, 2853, 2167, 1342 cm⁻¹; UV/Vis (CH₂Cl₂), λmax (%) = 497 (sh, 13700), 402 (66800),
264 nm (38 300 cm−1); HRMS (MALDI-TOF; DCTB): m/z calec for C16H14N2O2·1H2O: 282.0839 [M+]; found: 282.0832.

**Compound 26**: TBAF (0.1 mL, 0.1 mmol, 1.0 M in THF) was added to a solution of radiale 10 (25 mg, 0.025 mmol) in wet THF (10 mL) at 0°C, and the solution was stirred until the starting material was no longer visible by TLC analysis (∼5–10 min). EtO and H2O were added; the organic phase was separated, washed with saturated NH4Cl (2×20 mL), dried (MgSO4), and reduced to 2 mL. This Et2O solution was then added to a degassed solution of 4-iodo-N,N-diisopropylamine (15 mg, 0.050 mmol) in THF (10 mL), p(TPPh3) (2 µL, [Pd(TPPh3)2Cl2] (1.4 mg, 0.002 mmol), and Cu (1 mg, 0.003 mmol) were added sequentially, and the solution was stirred at approximately 50°C under N2 until TLC analysis no longer showed the presence of the protected radiale (≈15–18 h). Aqueous workup, solvent removal, and flash column chromatography (silica gel, EtOAc/hexanes 1:10 to 3:1) followed by precipitation from CH2Cl2 by the addition of Et2O afforded 26 (23 mg, 87%) as a red solid. Rf = 0.31 (EtOAc/hexanes 1:4); m.p. 281°C (discolors, decomposes); DSC: decomposition, 273°C (onset), 283°C (peak); 1H NMR (500 MHz, CDCl3): δ = 7.49–7.47 (m, 7H), 7.29–7.20 (m, 16H), 7.17–7.11 (m, 10H), 6.91 (d, J = 9.1 Hz, 4H), 6.68 (d, J = 9.1 Hz, 4H), 3.92 (sept, J = 6.9 Hz, 4H), 1.31 ppm (d, J = 6.9 Hz, 24H); 13C NMR (125 MHz, CDCl3): δ = 152.2, 151.8, 149.3, 140.3, 140.23, 140.19, 133.2, 130.9, 130.4, 130.3, 129.1, 129.14, 129.07, 128.30, 128.29, 128.25, 115.6, 113.4, 112.6, 108.6, 103.0, 102.6, 102.5, 101.3, 97.7, 97.0, 96.9, 86.7, 47.8, 21.2 ppm; IR (CHCl3, cast): ν = 3082, 3053, 2969, 2928, 2170, 1603, 1295 cm−1; UV/Vis (CHCl3): Amax(ε) = (342, 3400), 495 (3700), 41 (7100), 280 nm (47 400 cm−1).

HRMS (MALDI-TOF; DCTB): m/z calec for C16H14N2O2·1H2O: 282.0832 [M+]; found: 282.0832.

CCDC-942885 (54), -942886 (9), -942887 (14), -942888 (19), and -942889 (23) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[31] Calculated from planes generated from the nine carbon atoms of the radialene and the six carbon atoms from the phenyl ring.

[32] The plane consisted of the twelve carbon atoms of the radialene ring and alkylidene carbon atoms C3/C3'.


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