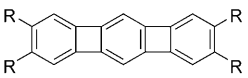
Phenylenes

Anatomy of a Cyclohexatriene: Chemical Dissection of the π and σ Frame of Angular [3]Phenylene**

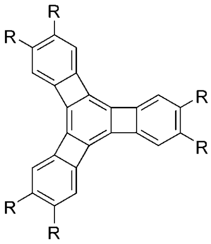
*Sriram Kumaraswamy, Satish S. Jalisatgi, Adam J. Matzger, Ognjen Š. Miljanić, and K. Peter C. Vollhardt**

The syntheses of several topological forms of the phenylenes have been reported,[1] but an exploration of their chemical behavior has been limited mainly to the parent system [2]phenylene (biphenylene),[2] the linear frame (e.g. the linear [3]phenylene **1**),[3] and the triangular variety (e.g. the C_3-symmetric [4]phenylene **2**).[4] Noticeably absent from these investigations is the behavior of angular [3]phenylene (**3**), for which only hydrogenation of the central ring[4a,5] and flash-pyrolytic isomerization have been recorded.[6]

In **3**, angular fusion minimizes cyclobutadienoid antiaromaticity by rendering the central ring extensively (62%) bond-localized and thus comparatively less diatropic,[4a,7] while leaving one double bond exposed. In contrast, and besides its distinct topology, **1** is qualitatively very different[1a,3] with a distorted but relatively more diatropic center, flanked by relatively paratropic neighbors.[7] On the other hand, **2** differs quantitatively in the degree of central cyclohexatriene character (100%) and exhibits lower steric



1a: R = H
1b: R = $SiMe_3$



2a: R = H
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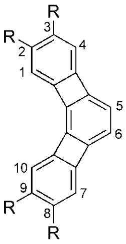

3a: R = H
3b: R = $SiMe_3$

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[*] Dr. S. Kumaraswamy, Dr. S. S. Jalisatgi, Dr. A. J. Matzger, O. Š. Miljanić, Prof. K. P. C. Vollhardt
Center for New Directions in Organic Synthesis
Department of Chemistry, University of California at Berkeley
and
Chemical Sciences Division
Lawrence Berkeley National Laboratory
Berkeley, CA 94720-1460 (USA)
Fax: (+1) 510-643-5208
E-mail: kpcv@berkeley.edu

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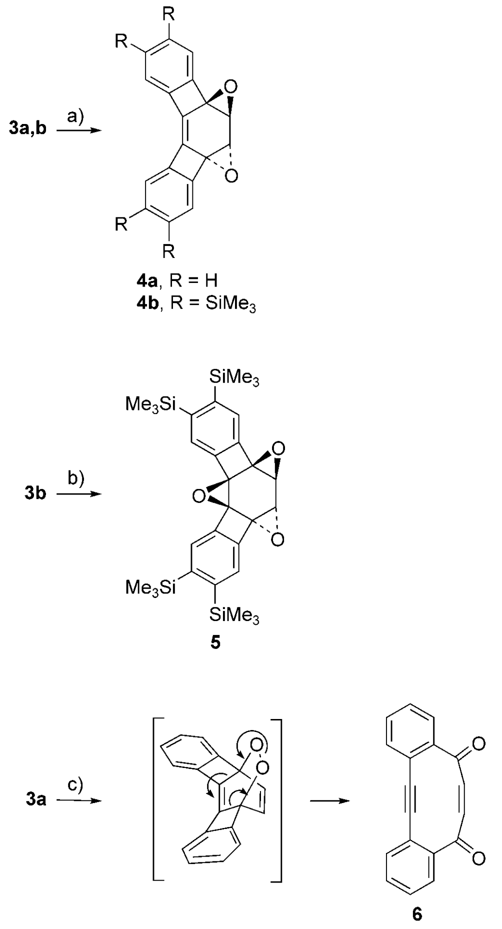
accessibility. The motif of **3** is important as the repeating structural unit of the heliphene[8] and zigzag phenylene oligomers[9] and polymers,[10] *anti*-kekulene,[11] and archimedene.[1b] Herein we compare the reactivity of **3** with that of **1** and **2** and reveal some unprecedented transformations and their novel products.

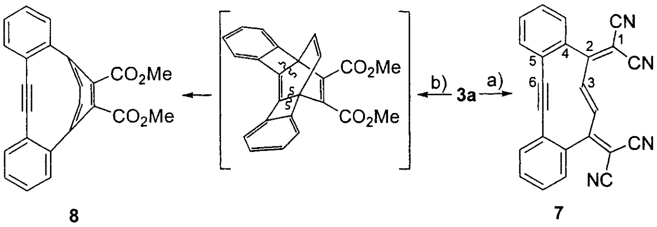
Initial experiments were directed at the reactivity of the π system, particularly the central cyclohexatriene moiety. Indeed, under conditions that convert biphenylene, albeit sluggishly,[12] and **2a** rapidly[4b] into the corresponding trisoxacyclopropanes (*trans* and *cis*, respectively), **3a** and **3b** underwent oxidation within 30 min to yield the heat-and moisture-sensitive bisoxacyclopropanated products **4a** and **4b**, respectively (Scheme 1, see Experimental Section).[13] Only **4b** could be isolated cleanly and its stereochemistry was ascertained through its conversion into the similarly sensitive, fully desymmetrized trisoxacyclopropanated product **5**. Attempts at triscyclopropanation of **3a**, as effected for **2a** and **b**,[4b] with a variety of reagents left the system intact, demonstrating its relatively lower reactivity. However, addition of singlet oxygen[14] to **3a** proceeded efficiently to furnish the (*Z*)-dione **6**, in a similar fashion to both biphenylene[12] and **1b** (whose reaction proceeded in the absence of a sensitizer),[3a] but unlike **2a** or **b**, which are inert. The unreactivity of **2** may be explained by a cycloaddition–retrocyclization sequence, analogous to that shown in Scheme 1 for **3**, which would lead to an unfavorable benzocyclobutadiene substructure.



Scheme 1. a) 3,3-Dimethyl-1,2-dioxacyclopropane, acetone, 23 °C, 30 min (**3a**), 100%; 60 min (**3b**), 100%; b) as for a) 6 h, 26%; c) methylene blue (0.09 equiv), O_2, CH_2Cl_2, $h\nu$, 23 °C, 70%.

The structure of **6** was confirmed by the spectral data (see Experimental Section), which highlight its component functional groups and symmetry, and also through comparison with a serendipitous oxidation product in the zigzag phenylene series for which an X-ray crystal structure was obtained.[9] The molecule **6** constitutes a promising entry into the elusive class of benzodehydro[10]annulenes.[15]

Having established the feasibility of cycloadditions to **3**, we then turned our attention to carbon-based dienophiles, which led to the unprecedented chemistry shown in Scheme 2.[13] When **3a** and tetracyanoethylene (TCNE) were mixed in CH_3CN, a green solution of a charge-transfer (CT) complex resulted instantly ($\lambda_{max} = 562$ nm).[16] Upon heating, the green solution gradually turned brown and was found to contain the adduct **7** in which the initial C–C bond connectivities at the center of **3a** as well as in the dienophile had been completely disrupted. As crystals suitable for X-ray crystallographic studies could not be obtained, the structural assignment was based on spectral data, particularly IR and NMR spectroscopic measurements, which point to a symmetrical structure containing the functional groups depicted in Scheme 2. Moreover, a combination of DEPT experiments on **7** and comparisons with model systems[17] allowed a complete assignment of the most important carbon signals C1–C6 (see Experimental Section).



Scheme 2. a) TCNE (1 equiv), CH_3CN, △, 8 h, 78%; b) dimethyl butynedioate (1.6. equiv), $AlCl_3$ (0.1 equiv), toluene, 23 °C, 1 h, 74%.

TCNE is known to undergo cycloaddition to double bonds, including those in activated arenes, in both a [2+2] and [4+2] manner and either with or without subsequent tetranitrile C–C bond cleavage.[18] Addition of TCNE to **3a** is envisaged to proceed along the lines depicted for singlet-oxygen addition to **3** in Scheme 1, namely [4+2] cycloaddition–[2+2+2] cycloreversal followed by double bond isomerization, with the latter perhaps facilitated by the relief of strain of the sterically encumbered nitrile groups located *cis* to the phenyl moieties.

The mechanism that gives rise to **7** suggests that employment of an alkyne as a dienophile might allow the isolation of the initial addition product. Indeed, biphenylene and other arenes have been reported to be converted into the corresponding bicyclo[2.2.2]octatrienes in the presence of reactive triple bonds such as those in arynes, dicyanoacetylene, and bis(fluoroalkyl)alkynes.[2,18b,19] Remarkably, dimethyl butynedioate in the presence of catalytic $AlCl_3$ smoothly converted **3a** into the cyclophane **8**. This indicates not only that the desired cycloaddition had occurred, but also that the initial adduct underwent unusually facile alkyne extrusion (Scheme 2).[19,20]

X-ray crystallographic analysis of **8** secures the structural assignment and heralds the molecule as the most distorted, completely unsaturated [6]paracyclophane (Figure 1).[18b,21,22]

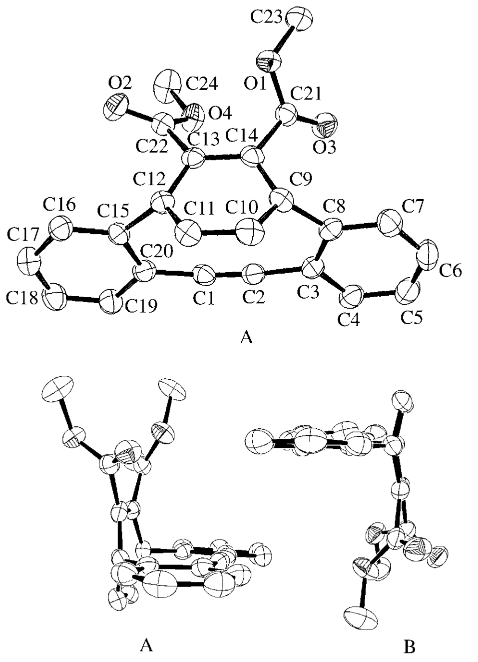
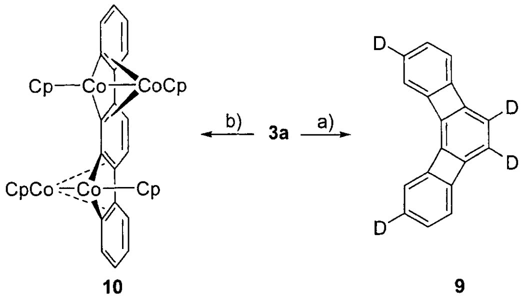


Figure 1. X-ray crystal structure of **8**. Views from above (A, top) and the side (two non-equivalent molecules A and B in the unit cell; bottom). Selected bond lengths [Å] and angles [°] for A; [average of all corresponding equivalent values in A and B in square brackets]: C1-C2 1.202(4) [1.200], C2-C3 1.461(4) [1.457], C3-C8 1.429(4) [1.427], [C1-C2 (centroid)]-[C10-C11-C13-C14 (centroid)] 2.80 [2.80]; C1-C2-C3 172.3(1) [170.3], C2-C3-C8 118.1(1) [118.49], C3-C8-C9 112.0(1) [112.28].

The bow-shaped diarenoalkyne bridges are twisted and bent with noticeable elongation of the C2–C3 and C3–C8 bonds (and their equivalents in both A and B in the unit cell).[23] Most instructive is the pronounced boat conformation of the central arene moiety, characterized by the relatively high α (16.6–18.7°) and β values (21.9–25.4°), with an average for $\alpha + \beta = 41.4°$.[24] POAV2 analysis[25] reflects the degree of pyramidalization of the arene carbon atoms (average pyramidalization angles: C9 7.62°, C12 7.31°, C13 3.39°, C14 5.23°). The NMR and UV/Vis spectral data do not reveal any unusual bridge conjugation or transannular interactions.[18b,21,24,26] The molecule is thermally robust, melts without decomposition, and is also photoinert. The strain in **8** is estimated to be $37.2\ \text{kcal mol}^{-1}$ from the calculated (B3LYP6-31G*) heat of the (homodesmotic) cycloaddition involved in its formation ($\Delta H^\circ = -62.5\ \text{kcal mol}^{-1}$), and the measured σ/π ring strain in **3a** ($99.7\ \text{kcal mol}^{-1}$).[4a] Similarly, the hypothetical reaction **8** + $2\,C_6H_6 \rightarrow$dimethyl 3,6-diphenylbenzene-1,2-dicarboxylate + diphenylethyne has a calculated $\Delta H^\circ = -35.6\ \text{kcal mol}^{-1}$, reflecting the energy gain of opening the cyclophane bridge.

In view of the behavior of **3** towards electrophilic reagents, the question arose as to how **3** would behave upon simple protonation (deuteration). Biphenylene[2] and **2a** undergo H/D exchange with D^+ exclusively at C2 (β positions), whereas **1a** decomposes in the presence of acid.[3b] There are five potential sites for D incorporation in **3a** of which the relative reactivity of the cyclohexatrienic "α" positions, C5 and C6, was of special interest. Emulating the approach taken by Maksić and co-workers for biphenylene,[27] calculations (HF/6-31G*) of the five protonated species reveal extensively delocalized systems, the energy ranking of which is largely controlled by the avoidance of cyclobutadienoid resonance forms. Thus, attack at C5 should be most favored (relative energy $0\ \text{kcal mol}^{-1}$), followed by that at C2 ($+2.27\ \text{kcal mol}^{-1}$), C3 ($+5.10\ \text{kcal mol}^{-1}$), C4 ($+11.55\ \text{kcal mol}^{-1}$), and C1 ($+14.70\ \text{kcal mol}^{-1}$). This order of reactivity is also indicated by the decrease in the corresponding HOMO coefficients of **3a** (HF/STO-3G): 0.31, 0.25, 0.17, −0.17, −0.01. Experimental results conformed partly with these expectations (Scheme 3), in as much as deuteration of **3a** at C5 and C6 occurred before deuteration at C2 and C9 in a clearly stepwise manner to yield **9**, as observed by NMR[1a] and mass spectral analysis. Unfortunately, more stringent conditions caused decomposition.



Scheme 3. a) CF_3CO_2D (0.5 mL), $CDCl_3$ (3 mL), 60 °C, 8 h (C5,6-deuteration), 80%; then CF_3CO_2D (0.5 mL), $CDCl_3$ (3 mL), 100 °C, 8 h (C2,9-deuteration), 82%; b) $[CpCo(C_2H_4)_2]$ (10 equiv), C_6H_6, 70 °C, 6 h, 71%.

Finally, in a similar fashion to biphenylene[28] and **1b**,[3b] it was thought that **3a** would be subject to C–C bond activation in the presence of electrophilic metal fragments. Treatment of **3a** with excess $[CpCo(C_2H_4)_2]$ (Scheme 3) gave rise to **10**, the result of double regio- and stereoselective dinuclear cobalt insertion. The spectral data confirm its overall connectivity,[28] with more details obtained by X-ray crystallographic studies (Figure 2).[22] Four-membered-ring-opening thus occurs at adjacent sites and the two η^4-coordinated cobalt atoms are located *anti* with respect to the terphenyl ligand plane; both observations are probably of steric origin. The terphenyl ligand is notably planar, but shows considerable bond alternation. Fluxionality around the dinuclear moiety is not detectable as there is no observed coalescence of the ^1H NMR signals for the Cp groups upon heating to 100 °C.[28] The generation of **10** suggests interesting extensions to higher

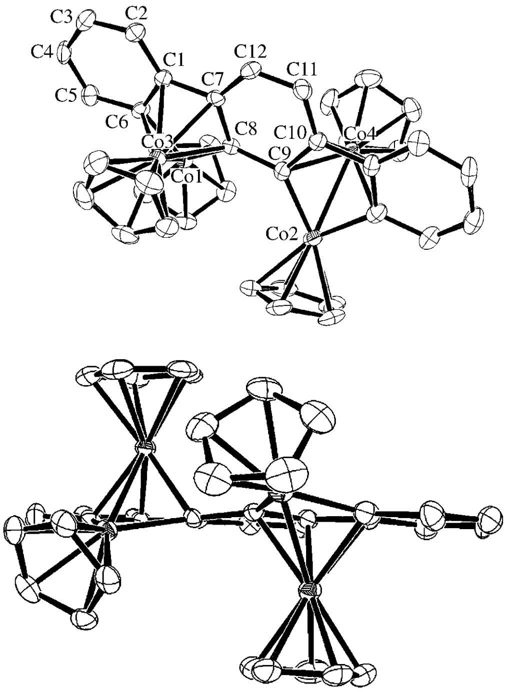


Figure 2. X-ray crystal structure of **10**·C_6H_6 (solvent molecule omitted). Views from above (top) and the side (bottom). Selected bond lengths [Å]: Co1-Co3 2.4498(6), Co2-Co4 2.4800(7), Co1-C6 1.886(30, Co1-C8 1.937(3), Co3-C6 2.054(3), Co3-C1 2.067(3), Co3-C7 2.081(3), Co3-C8 2.070(3), C1-C2 1.434(4), C1-C6 1.428(5), C1-C7 1.453(5), C2-C3 1.354(5), C3-C4 1.415(5), C4-C5 1.366(5), C5-C6 1.437(5), C7-C8 1.454(4), C7-C12 1.435(5), C8-C9 1.491(5), C9-C10 1.449(5), C10-C11 1.440(5), Co_n-Cp(centroid) 1.66, 1.71, 1.68, 1.72.

phenylenes for the construction of novel organometallic oligomers.[29]

In summary, although the central ring in the angular [3]phenylene (**3**) may stay intact on exposure to electrophilic reagents, it mostly behaves as a "loaded spring" ready to unravel into a remarkable array of products. The chemistry reported herein, which places the reactivity of angular phenylene between those of its linear and triangular relatives, significantly expands the potential of the angular motif to give rise to a plethora of novel structures.

Experimental Section

4a: sensitive, colorless oil ($t_{1/2}$ ~ 2 min); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.36$ (dt, $J = 7.9$, 0.9 Hz, 2H), 7.08 (td, $J = 7.9$, 0.9 Hz, 2H), 7.00 (td, $J = 7.9$, 0.9 Hz, 2H), 6.86 (dt, $J = 7.9$, 0.9 Hz, 2H), 3.68 ppm (s, 2H); MS (70 eV): *m*/*z* (%): 258 (6) [M^+], 226 (100).

4b: sensitive, light-orange wax; ^{1}H NMR (500 MHz, CD_2Cl_2): $\delta =$ 7.77 (s, 2H), 7.64 (s, 2H), 4.49 (s, 2H), 0.42 (s, 18H), 0.38 ppm (s, 18H); $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): $\delta = 150.6$, 150.0, 146.6, 146.3, 129.4, 128.5, 126.7, 69.3, 56.4, 1.84, 1.80 ppm; IR (film): $\tilde{\nu} =$ 2953, 2922, 2853, 1251, 1083, 840, 757 cm^{-1}; MS (70 eV): *m*/*z* (%): 546 (41) [M^+], 531 (18), 514 (54), 73 (100); HRMS: calcd for $C_{30}H_{42}O_2Si_4$: 546.2262; found: 546.2241.

5: sensitive, light-yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta =$ 7.84 (d, $J = 0.9$ Hz, 1H), 7.79 (d, $J = 0.9$ Hz, 1H), 7.65 (d, $J = 0.9$ Hz, 1H), 7.56 (d, $J = 0.9$ Hz, 1H), 4.48 (d, $J = 1.4$ Hz, 1H), 4.36 (d, $J =$ 1.4 Hz, 1H), 0.42 (s, 18H), 0.42 (s, 9H), 0.39 (s, 9H), 0.39 ppm (s, 18H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): $\delta = 150.8$, 150.2, 149.54, 148.4, 147.0, 145.8, 143.5, 141.9, 128.8, 128.7, 128.6, 128.4, 72.2, 71.7, 70.9, 70.4, 58.2, 58.0, 1.95, 1.88, 1.86, 1.76 ppm; MS (70 eV): *m*/*z* (%): 562 (34) [M^+], 547 (26), 531 (12), 199 (75), 73 (100); HRMS: calcd for $C_{30}H_{42}O_3Si_4$: 562.2211; found: 562.2219.

6: colorless crystals (from ethyl acetate); m.p. 160–162 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.45$–7.39 (m, 8H), 6.59 (s, $^{H-H}J = 12$ Hz (from the ^{13}C satellites), 2H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 196.8$, 142.3, 136.1, 131.1, 129.6, 129.5, 127.2, 120.5, 95.6 ppm; UV/Vis (hexane): λ_{max} ($\log\varepsilon$) = 238 (3.34), 254 (3.28), 293 (3.09), 312 (3.04), 324 nm (3.04); IR (KBr): $\tilde{\nu} = 3061$, 3020, 1687, 1589, 1479, 1449, 1274, 1260, 1213, 1007, 996, 755 cm^{-1}; MS (70 eV): *m*/*z* (%): 258 (25) [M^+], 230 (100), 202 (57); HRMS: calcd for $C_{18}H_{10}O_2$: 258.0681; found: 258.0684.

7: green crystals (from CH_2Cl_2); m.p. 185–187 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.81$–7.76 (m, 2H), 7.66–7.56 (m, 6H), 6.90 (s, $^{H-H}J = 16$ Hz (from the ^{13}C satellites), 2H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): $\delta = 168.1$ (C2), 138.2 (C3), 134.3 (C4), 133.4, 133.2, 131.12, 130.4, 123.2 (C5), 112.8 (CN), 112.7 (CN), 98.0 (C6), 86.3 ppm (C1); UV/Vis (hexane): λ_{max} ($\log\varepsilon$) = 264 (4.59), 283 (4.45), 325 (4.34), 398 (3.83), 486 nm (3.19); IR (KBr): $\tilde{\nu} = 3062$, 2917, 2849, 2231, 1589, 1563, 1478, 1267, 1182, 969, 762, 736 cm^{-1}; MS (70 eV): *m*/*z* (%): 354 (100) [M^+], 327 (50), 300 (22), 289 (35), 150 (18), 137 (16); HRMS: calcd for $C_{24}H_{10}N_4$: 354.0905; found: 354.0906.

8: colorless crystals (from ethyl acetate); m.p. 165–167 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.59$ (br d, $J = 7.2$ Hz, 2H), 7.55 (s, 2H), 7.36 (td, $J = 7.2$, 1.3 Hz, 2H), 7.22 (td, $J = 7.2$, 1.3 Hz, 2H), 7.10 (br d, $J = 7.2$ Hz, 2H), 3.60 ppm (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta = 168.8$, 144.5, 144.4, 135.7, 135.7, 129.6, 128.1, 127.8, 127.5, 125.1, 93.9, 52.2 ppm; UV/Vis (methanol): λ_{max} ($\log\varepsilon$) 278 (5.16), 295 (5.32), 301 (5.26), 313 nm (5.31); IR (KBr): $\tilde{\nu} = 3065$, 2990, 2945, 1723, 1460, 1428, 1362, 1288, 1260, 1193, 1152, 1120, 1041, 749 cm^{-1}; MS (70 eV): *m*/*z* (%): 368 (100) [M^+], 337 (35), 224 (48), 212 (28), 59 (16); elemental analysis: calcd for $C_{24}H_{16}O_4$: C 78.25, H 4.38; found: C 78.10, H 4.54.

10: black-brown crystals (from benzene/pentane, 4:1); m.p. 178–179 °C; ^{1}H NMR (400 MHz, [D_8]THF): $\delta = 8.69$ (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.7$ Hz, 2H), 7.58 (s, 2H), 7.12 (ddd, $J = 8.7$, 8.4, 0.7 Hz, 2H), 6.91 (ddd, $J = 8.7$, 8.4, 0.7 Hz, 2H), 5.10 (s, 10H), 4.37 ppm (s, 10H); $^{13}C\{^1H\}$ NMR (100 MHz, [D_8]THF): $\delta = 155.2$, 129.2, 127.6, 126.9, 121.5, 117.1, 108.2, 81.4, 81.3 ppm; MS (70 eV): *m*/*z* (%): 722 (45) [M^+], 189 (100).

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