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Preparation and NMR Characterization of $C_{70}H_{10}$: Cutting a Fullerene π-System in Half

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Three isomers of $C_{70}H_{10}$ were prepared by Zn(Cu) reduction of C_{70}. Three chromatographic bands were identified as $C_{70}H_{10}$ species by MALDI-FT mass spectrometry, and these compounds were isolated by repeated HPLC treatments. The major isomer (**2**) was characterized by ^{1}H and ^{13}C NMR, while the minor isomers **3**−**4** were isolated in such small quantities that only ^{1}H NMR analysis was possible. ^{1}H-coupled and ^{1}H-decoupled ^{13}C NMR of **2** established a 7,8,19,26,33,37,45,49,53,63-substitution pattern. This assignment was confirmed by HMBC and DFQ-COSY experiments. This structure is completely reasonable, as we found that **2** results exclusively from reduction of the 7,19,23,27,33,37,44,53-$C_{70}H_8$ that is formed in the course of the Zn(Cu) reduction of C_{70}.

Derivatization of higher fullerenes generally occurs preferentially at the more highly pyramidalized carbons.[1] This pattern of reactivity is consistent with the notion that the strain due to pyramidalization drives the reactivity of fullerenes.[2] There are some notable exceptions to the rule. Within the class of monoadducts of C_{70}, disilylenes,[3] benzyne,[4] azomethine ylides,[5] quinodimethanes,[6] and carbenes[7] have been shown to add (albeit in low yield) to some of the less pyramidalized carbons.[8] Highly subsituted octa- and decasubstituted C_{70} derivatives, prepared by nucleophilic addition of malonate anions, result from attack initially at the poles, then at positions closer to the equator.[9]

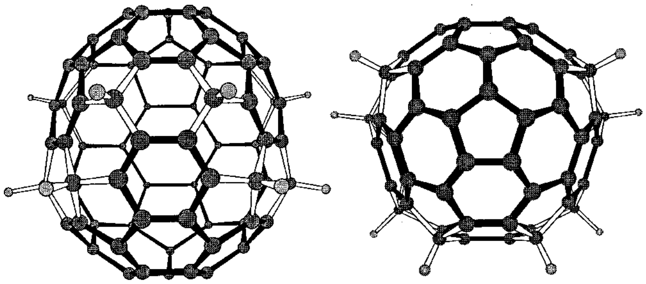

Figure 1. 7,19,23,27,33,37,44,53-$C_{70}H_8$ (**1**) as produced by Zn-(Cu) reduction: (a) side view; (b) top view.

There are some examples of reactions in which the less-pyramidalized carbons are attacked at rates equal to or greater than the rate of attack at more-pyramidalized carbons. Specifically, ICl chlorination[10] and Zn(Cu) reduction[11] of C_{70} produce structures in which the less-pyramidalized section of the molecule has reacted (Figure 1). As such, these compounds offer unique starting points for further transformations of C_{70}, and are likely to lead to novel structures that cannot be otherwise obtained directly from C_{70}. In this paper, we report the reduction of a sidewall-derivatized isomer of $C_{70}H_8$ and identification of the reactive site by NMR.

The Zn/Cu reduction of C_{70} generates a roughly 1:1:1 mixture of $C_{70}H_2$, $C_{70}H_4$, and $C_{70}H_8$ after 5 h of reaction time, but reduction does not stop at the $C_{70}H_8$ level.[11] At longer reaction times, three isomers (**2**−**4**) of $C_{70}H_{10}$ are formed in a 3:2:1 ratio. Isolation of $C_{70}H_8$ (**1**), followed by further reduction of this compound, produces only 2 of the 3 $C_{70}H_{10}$ isomers, including the major isomer **2**. Of these three isomers, isomer **2** displays an absorption spectrum that is significantly different from the others, with very low absorption at long wavelengths. In this paper, we report the isolation and structural characterization of this interesting compound.

The UV/vis absorption spectum of $C_{70}H_{10}$ (**2**) is drastically altered from that C_{70}, suggesting that the chromophore of $C_{70}H_{10}$ is composed of a much less extended π system (Figure 2). While C_{70} has strong absorbances at 334, 362, 380, and 472 nm, $C_{70}H_{10}$ has a λ_{max} at 305 nm with a nearly featureless decrease in absorption at longer wavelengths and by 480 nm no absorbance is observed. Samples of **2** in toluene are very lightly colored even when concentrated, consistent with a highly altered chromophore.

Under the Zn/Cu reduction conditions, no isomerization of fullerene hydrides has been observed;[11−13] therefore, the structure of the major isomer of $C_{70}H_{10}$ must have a $C_{70}H_8$ substructure. The ^{1}H-decoupled ^{13}C NMR spectrum

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(1) For a review of the chemistry of the higher fullerenes, including C_{70}, see; Thigen, C.; Herrmann, A.; Diederich, F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2268−2280.

(2) Haddon, R. C. *Science* **1993**, *261*, 1545−1550.

(3) An unusual, photochemical addition to the equatorial belt of C_{70} has been reported. See: Akasaka, T.; Mitsuhida, E.; Ando, W.; Kobayashi, K.; Nagase, S. *J. Am. Chem. Soc.* **1994**, *116*, 2627−2628.

(4) Meier, M. S.; Wang, G. W.; Haddon, R. C.; Brock, C. P.; Lloyd, M. A.; Selegue, J. P. *J. Am. Chem. Soc.* **1998**, *120*, 2337−2342.

(5) Wang, Y.; Schuster, D. I.; Wilson, S. R.; Welch, C. J. *J. Org. Chem.* **1996**, *61*, 5198−5199.

(6) Herrmann, A.; Diederich, F.; Thilgen, C.; ter Meer, H.-U.; Meuller, W. H. *Helv. Chim. Acta* **1994**, *77*, 1689−1706.

(7) Kiely, A.; Haddon, R. C.; Meier, M. S.; Selegue, J. P.; Brock, C. P.; Wang, G.-W.; Chen, Y. *J. Am. Chem. Soc.* **1999**, *121*, 7971−7972.

(8) A 1,4 arrangement of hydrogens near the equator of $C_{70}H_2$ has been investigated at the MNDO level of theory and found to be reasonably stable. See: Henderson, C. C.; Rohlfing, C. M.; Cahill, R. A. *Chem. Phys. Lett.* **1993**, *213*, 383−388.

(9) Herrmann, A.; Rüttimann, M. W.; Gibtner, T.; Thilgen, C.; Diederich, F.; Mordasini, T.; Thiel, W. *Helv. Chim. Acta* **1999**, 261−289.

(10) Birkett, P. R.; Avent, A. G.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1995**, 683−684.

(11) Spielmann, H. P.; Wang, G.-W.; Meier, M. S.; Weedon, B. R. *J. Org. Chem.* **1998**, *9865*, 5−9871. For other methods to prepare $C_{70}H_n$ compounds, see refs 16−22.

10.1021/jo991862p CCC: $19.00

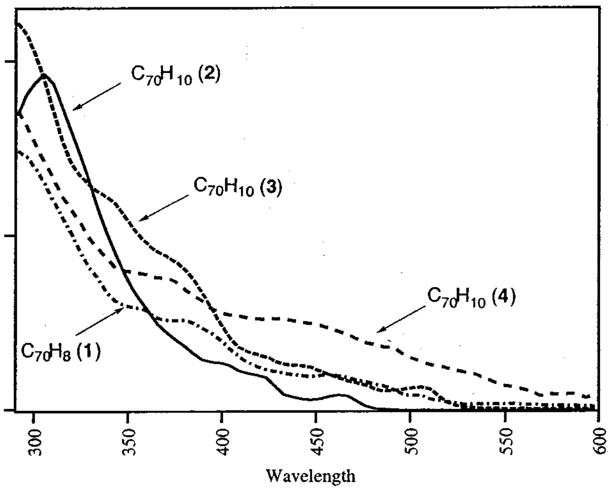

Figure 2. Absorption spectra of $C_{70}H_8$ (**1**) and $C_{70}H_{10}$ isomers **2**−**4**, measured in 60% toluene/40% hexane.

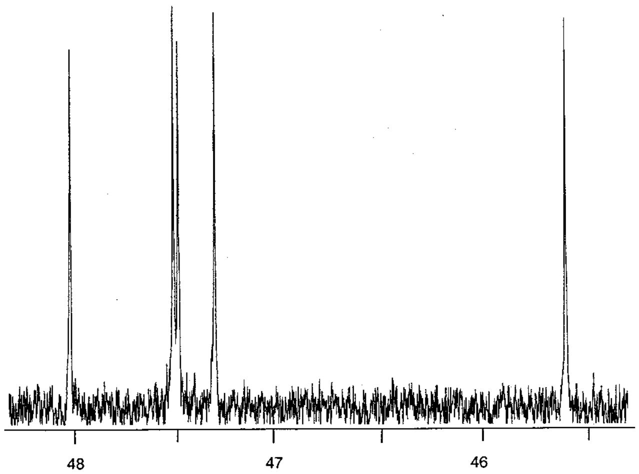

Figure 3. sp^3 region of the H-decoupled ^{13}C NMR spectrum of $C_{70}H_{10}$ (**2**).

of **2** shows 37 resonances, composed of 33 double intensity and 4 single intensity lines, consistent with C_s symmetry (a plane of symmetry containing the long axis of the molecule). The sp^3 region of the spectrum shows five double-intensity resonances, confirming that the 10 hydrogens are attached to two symmetry-related sets of five different carbons (Figure 3).

Inspection of the ^1H-coupled ^{13}C NMR spectrum shows that all these resonances have multiple, small couplings ($J \leq 2$ Hz). The upfield sp^3 resonance shows both small couplings ($J \leq 1.4$ Hz) and an additional 5.6 Hz coupling. The chemical shift and the larger splitting is characteristic of reduced C_{60} and C_{70} systems with adjacent sp^3 carbons.[11] The four downfield sp^3 ^{13}C resonances are located within a narrow 0.72 ppm window, and the chemical shift of these resonances is similar to those of **1**.

Analysis of the cross-peak connectivity pattern from an $^1H-^1H$ DQF−COSY spectrum (Figure 4) acquired at high digital resolution indicates a linear ABCDE spin system.

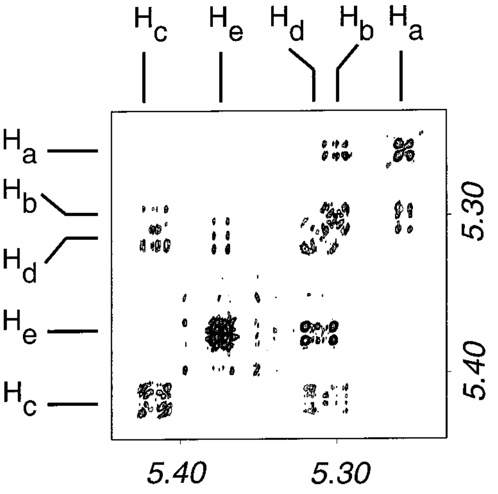

Figure 4. DQF−COSY spectrum of $C_{70}H_{10}$.

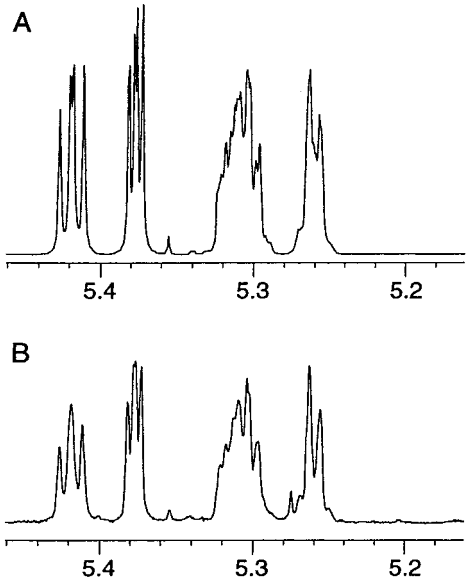

Figure 5. Simulated and experimental spectrum of $C_{70}H_{10}$. The simulated spectrum is in panel A and the experimental spectrum is in panel B. The axes are in ppm.

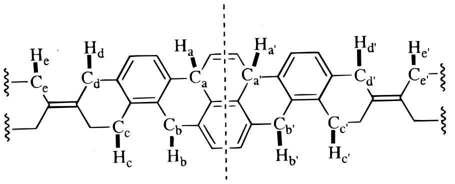

Figure 6. Spin system in $C_{70}H_{10}$ (**2**). The dashed line represents the mirror plane through the molecule.

The ^1H resonances of **2** fall in a narrow 0.2 ppm range, giving a second-order spectrum which must be analyzed by simulation. The coupling constants J_{ab} (4.3 Hz), J_{bc} (3.4 Hz), J_{cd} (4.4 Hz), J_{de} (4.4 Hz), and J_{ad} (1.3 Hz) were determined directly from the COSY cross-peak multiplet structure (Figure 4). Successful simulation[14] of the 1-D spectrum requires inclusion of couplings between the symmetry related spins: AA′ ($J_{aa'} = 4.1$ Hz), BB′ ($J_{bb'} = 1.0$ Hz), and EE′ ($J_{ee'} = 10.5$ Hz) (Figure 5). The requirement for coupling between AA′ and EE′ proton

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[12] Meier, M. S.; Weedon, B. R.; Spielmann, H. P. *J. Am. Chem. Soc.* **1996**, *118*, 11682−11683.

[13] Bergosh, R. G.; Laske Cooke, J. A.; Meier, M. S.; Spielmann, H. P.; Weedon, B. R. *J. Org. Chem.* **1997**, *62*, 7667−7672.

[14] Balacco, G. *J. Chem. Inf. Comput. Sci.* **1994**, *34*, 1235−1241.

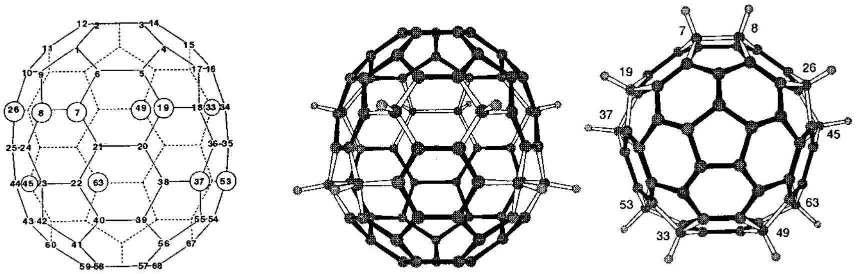

Figure 7. Structure of $C_{70}H_{10}$ (**2**) as produced by Zn(Cu) reduction: (a) numbering system with protonated carbons circled; (b) front view showing symmetry plane; (c) top view. Note the vicinal arrangement of the new hydrogens and the nonadjacent arrangement of the remaining **8**.

resonances indicates that the two symmetry-related ABCDE spin systems are connected into a ABCDEE′D′C′B′A′ system. There is no evidence of J_{ac}, J_{bd}, or J_{ce} couplings greater than 0.5 Hz in the spectra of $C_{70}H_{10}$. The best fit for $J_{ee'} = 10.5$ Hz is consistent with the spectra of the $C_{60}H_x$ and $C_{70}H_x$ series of fullerenes where J-coupling constants for protons on adjacent carbons are between 10 and 15.5 Hz.[12,13,15] Simulations where $J_{ee'}$ is left out or set in the range of 4 Hz yield spectra that poorly approximate the experimental spectrum.

The topology of the $C_{70}H_{10}$ spin system is shown in Figure 6. We find that the 5-bond *J*-couplings are between 3.4 and 4.4 Hz and the 7-bond J-couplings for **2** are about 1 Hz, consistent with those observed in $C_{70}H_8$.[11] The proposed spin topology is supported by the similarity of the derived $J_{bb'}$ and J_{ad} coupling constants, both of which are smaller than the 5-bond couplings. Cahill has found a 1.8 Hz ^5J coupling in 1,2,3,4-$C_{60}H_4$, lending further support for the observation of small $^1H-^1H$ couplings between protons arranged in a 1,4-fashion (5 bond) on a fullerene.[15] In the $C_{60}H_4$ system, the 1,3 *J* coupling (4-bond) was determined to be 0 Hz.

Consistent with the ^1H ABCDEE′D′C′B′A′ spin system, the protonated carbons in $C_{70}H_{10}$ show couplings to several magnetically inequivalent protons, and most of the sp^2 carbons show small couplings to protons. Unlike the pattern observed in $C_{70}H_2$ and $C_{70}H_4$ and $C_{70}H_8$ (**1**),[11] only one of the most downfield sp^2 resonances shows a large multibond (>2 Hz) C−H coupling. Instead, there are 6−10 Hz, presumably 2-bond, ^1H couplings to some of the most *upfield* sp^2 carbon resonances.

Additional evidence for a 1,2-arrangement of the newly introduced hydrogen atoms is provided by coupling constants and ^{13}C chemical shifts. One of the five sp^3 ^{13}C resonances is significantly offset (1.73 ppm upfield) from the other four resonances, consistent with the arrangement shown in Figure 6. In this arrangement, one sp^3 resonance ($H_{E,E'}$) is doubly allylic while the other four sp^3 resonances are triply allylic. The most upfield resonance (doubly allylic) exhibits a large 5.6 Hz H−C coupling (in addition to a 1-bond coupling), which is very similar to the 4.7−5 Hz 2-bond H−C couplings seen in 1,2-$C_{70}H_2$.[11] Finally, the $J_{EE'}$ obtained through simulation is 10.5 Hz, consistent with a 3-bond arrangement. These data indicate that the most upfield sp^3 resonance is due to a pair of *adjacent* symmetry-related carbons.

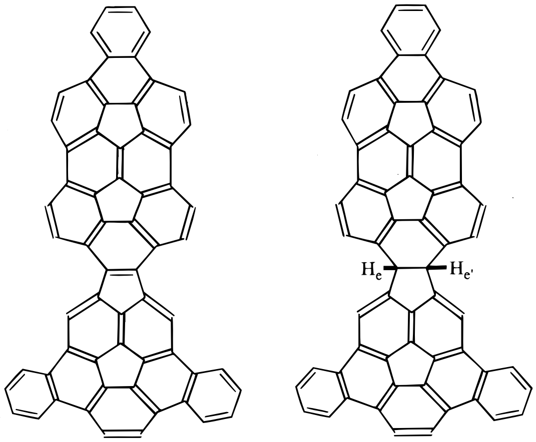

Figure 8. Chromophores of $C_{70}H_8$ and $C_{70}H_{10}$ (**2**).

Taken together, these data indicate that in the structure of this isomer of $C_{70}H_{10}$, the protonated carbons are neither on the poles nor on the equator and that only one pair of protonated carbons are adjacent to each other. There are relatively few structures that are consistent with this collection of data.

Knowing that **2** is formed from **1**, and knowing the symmetry of **2**, we assign the structure of this isomer is 7,8,19,26,33,37,45,49,53,63, as shown in Figure 7.[23]

Examination of the structure of $C_{70}H_8$ (**1**) reveals two distinct regions, a dibenzocorannulene and dibenzobicorannulene unit, connected through an etheno bridge. Shown in Figure 8 is the C_{62} buckybowl that is the chromophore of **1**. The etheno bridge is essentially cross-conjugated, and reduction of this double bond preserves the maximum amount of aromaticity in the $C_{70}H_{10}$ product. The positions of the two new sp^3 carbons in $C_{70}H_{10}$ isolate the two corannulene units. This is consistent with the attenuated UV/Vis spectrum shown in Figure 2.

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[15] Henderson, C. C.; Rohlfing, C. M.; Assink, R. A.; Cahill, P. A. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 786−788.

[16] Attalla, M. I.; Vassallo, A. M.; Tattam, B. N.; Hanna, J. V. *J. Phys. Chem.* **1993**, *97*, 6329−6331.

[17] Other methods also produce much lower amounts of the 5,6 isomer. See: Avent, A. G.; Darwish, A. D.; Heimbach, D. K.; Kroto, H. W.; Meidine, M. F.; Parsons, J. P.; Remars, C.; Roers, R.; Ohashi, O.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1994**, 15−22.

[18] Darwish, A. D.; Abdul-Sada, A. K.; Langley, J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2359−2365.

[19] Gerst, M.; Beckhaus, H.-D.; Rüchardt, C.; Campbell, E. E. B.; Tellgmann, R. *Tetrahedron Lett.* **1993**, *34*, 7729−7732.

[20] Jin, C.; Hettich, R.; Compton, R.; Joyce, D.; Blencoe, J.; Burch, T. *J. Phys. Chem.* **1994**, *98*, 4215−4217.

[21] Shigematsu, K.; Abe, K.; Mitani, M.; Tanaka, K. *Chem. Express* **1992**, *7*, 957−960.

[22] For an extensive review of reduced fullerenes, see: Gol'dshleger, N. F.; Moravshii, A. P. *Russ. Chem. Rev.* **1997**, *66*, 323−342.

[23] For two examples of this addition pattern, see ref 10 and: Avent, A. G.; Birkett, P. R.; Darwish, A. D.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Tetrahedron* **1996**, *52*, 5235−5246.

The Zn(Cu) reduction of fullerenes can produce highly derivatized fullerene products. While an enormous number of isomers are possible, even with all of the addends being the same as in reduced fullerenes, Zn(Cu) produces very simple mixtures of isomers. This is in contrast to many other methods for chemical modification of fullerenes. Reactions that convert a fullerene to a highly modified derivative (addition to 3 or more double bonds) generally result in intractable isomeric mixtures of highly substituted products unless intermediate, less substituted products are separated and purified individual isomers are subjected to further reaction.

Experimental Section

Preparation of $C_{70}H_{10}$ (2) from C_{70}. C_{70} (49.2 mg, 0.0586 mmol) and toluene (50 mL) were combined in a 100 mL, three-neck flask equipped with a stir bar. The resulting solution was deoxygenated with argon. The Zn/Cu couple was prepared by treating zinc dust (1.028 g, 15.72 mmol) five times with 5 mL portions of each 3% HCl and H_2O, followed by five 10 mL treatments with 2% $CuSO_4$. The resulting Zn/Cu couple was then washed five times with 1 mL portions of each H_2O, ethanol, THF, and toluene. The couple was rinsed into the reaction flask using 5 mL toluene. Water (1 mL) was added. The mixture was heated at 70 °C for 22 h. The supernate was then cooled, filtered (0.2 μm), and concentrated. Purification of the resulting solution was performed by HPLC using a 21.1 × 250 mm Buckyclutcher I column (6:4 toluene/hexane mobile phase, 15 mL/min. flow rate, monitored at 400 nm), then concentrating the $C_{70}H_{10}$ fraction, which was further purified using a 10 × 250 mm Buckyclutcher I column (6:4 toluene/hexane mobile phase, 4.5 mL/min. flow rate, monitored at 400 nm). $C_{70}H_{10}$ (**2**) was isolated in 5% (2.7 mg) overall yield from C_{70}.

7,8,19,26,33,37,45,49,53,63-$C_{70}H_{10}$ (2): ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 5.25−5.27 (m, 2H), 5.29−5.33 (m, 4H), 5.375 (m, 2H), 5.42 (m, 2H); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) (rel intensity) δ 45.64 (2), 47.37 (2), 47.55 (2), 47.58 (2), 48.09 (2), 129.13 (2), 129.39 (2), 130.99 (2), 131.56 (2), 132.16 (2), 141.09 (1), 143.42 (2), 144.86 (2), 146.98 (2), 148.31 (2), 148.72 (2), 148.44 (2), 148.95 (2), 149.20 (2), 149.50 (1), 149.70 (2), 150.07 (2), 150.32 (2), 150.66 (2), 150.89 (2), 151.03 (2), 151.05 (2), 151.08 (2), 151.54 (2), 151.85 (2), 152.24 (2), 152.30 (2), 152.55 (1), 153.07 (2), 153.23 (2), 153.94 (1), 154.43 (2).

Preparation of 2 from $C_{70}H_8$ (1). $C_{70}H_8$ (61.7 mg, 0.0728 mmol) was dissolved in 1.5 mL of *o*-dichlorobenzene and transferred to a 100 mL, three-neck flask equipped with a stir bar. The solution was diluted to 50 mL with toluene and deoxygenated with argon. Zn/Cu couple was prepared by treating the zinc dust (1.008 g, 15.42 mmol) five times with 1 mL portions of each 3% HCl and H_2O followed by five 3 mL treatments with 2% $CuSO_4$ solution. The metal was rinsed five times with 1 mL portions of H_2O, THF, and toluene. The couple was added to the reaction flask and water (0.5 mL) added. The mixture was heated at 90 °C for 17 h. The mixture was cooled to room temperature, filtered (0.2 μm), and analyzed by HPLC using a 7.8 × 300 mm Regis Buckyclutcher I column and a 6:4 toluene/hexane mobile phase at 4.5 mL/min flow rate. The chromatogram was monitored at 335 nm, and rentention times for the various species were the following: **1** 19.82 min, **2** 22.33 min, **3** 25.1 min, and **4** 25.86 min. The mixture was purified on a 25 × 210 mm Buckyclutcher column in the same mobile phase at 15 mL/min. Yields based upon HPLC integration: unreacted $C_{70}H_8$ (**1**, 47%), $C_{70}H_{10}$ (**2**, 35%), $C_{70}H_{10}$ (**3**, 15%).

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