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Nickel-Promoted First Ene−Diyne Cycloaddition Reaction on C_{60}: Synthesis and Photochemistry of the Fullerene Derivatives

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Abstract: A novel method for the construction of a fused cyclohexadiene ring on C_{60} based on a nickel-promoted [2+2+2] cycloaddition of 1,6-diynes is described. Treatment of C_{60} with terminal 1,6-diynes ($HC{\equiv}CCH_2)_2X$) in the presence of $NiCl_2(PPh_3)_2$, Zn, and PPh_3 at 90 °C in toluene afforded [2+2+2] bicyclic hexadiene derivatives (X = $C(CO_2Me)_2$ (**2a**), $C(CO_2Et)_2$ (**2b**), $C(COMe)_2$ (**2c**), CH_2 (**2d**), O (**2e**), NSO_2-*p*-$C_6H_5CH_3$ (**2f**), $C(SO_2Ph)_2$ (**2g**), and $\overline{\mathrm{CC(O)CH_2C(CH_3)_2CH_2C}}\mathrm{(O)}$ (**2h**) in good yields. Spectral data for products **2a**−**h** indicated that the cycloaddition of diynes to C_{60} occurs across a 6,6-ring junction on the fullerene. On the basis of the established chemistry of metal-mediated [2+2+2] cycloaddition, a mechanism is proposed to account for the present nickel-mediated reaction. All the hexadiene derivatives **2a**−**h** in solution are readily oxidized by molecular oxygen in the presence of light at ambient temperature. The oxidation process of compound **2a** in chloroform-*d* was monitored by ^1H NMR spectroscopy, and the results showed that **2a** first reacted with molecular oxygen to form peroxide **3** and was subsequently converted to dialdehyde **4** and C_{60}-containing polymeric material. Photochemical properties of some cyclohexadiene derivatives were then investigated. Upon irradiation (350 nm), compounds **2a**−**c**, **2f**, and **2h** readily underwent [4+4] cycloaddition to give the corresponding bisfulleroids **5a**−**c**, **5f,** and **5h** in excellent yields.

Introduction

Studies on the functionalization of fullerene via cycloaddition reactions continue to draw great attention owing to the potential applications of its derivatives.[1] While numerous synthetic methodologies for the preparation of three-,[2] four-,[3] and five-membered-ring[4] derivatives have been discovered, only a few methods are known for the synthesis of six-membered derivatives of fullerene.[5,6] Diels−Alder cycloaddition appears to be most effective for the construction of a six-membered ring on the fullerene.[5,7] In all these cycloaddition reactions, one of the carbon−carbon double bonds across two six-membered rings in the fullerene serves as a dienophile and reacts with dienes to give cyclohexene-ring products. A vast number of cyclohexene derivatives of C_{60} via Diels−Alder cycloaddition have thus been reported, but only a few cyclohexadiene derivatives are known.[8] The methods developed for the synthesis of the latter required several steps[8a] or are limited to specific substrates.[8c] For example, the well-studied cyclohexadiene derivative reported by Rubin et al. was prepared from Diels−Alder cycloaddition of butadiene to C_{60}, followed by a sequence of oxidation, reduction, and dehydration reactions.

Reports on the preparation of a cyclohexadiene ring via metal-catalyzed cyclotrimerization of two alkynes with an alkene have appeared in the literature.[9−13] In general, cobalt complexes were used in these catalytic cyclizations.[13] The only nickel system

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[1] (a) Prato, M. *J. Mater. Chem.* **1997**, *7*, 1097−109. (b) Jensen, A. W.; Wilson, S. R.; Schuster, D. I. *Bioorg. Med. Chem.* **1996**, *4*, 767−79 and references therein.

[2] (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186−8. (b) Hirsch, A.; Lamparth, I.; Grosser, T.; Karfunkel, H. R. *J. Am. Chem. Soc.* **1994**, *116*, 9385−6. (c) Smith, A. B., III; Strongin, R. M.; Brard, L.; Furst, G. T.; Romanow, W. J.; Owens, K. G.; King, R. C. *J. Am. Chem. Soc.* **1993**, *115*, 5829−30. (d) Isaacs, L.; Wehrsig, A.; Diederich, F. *Helv. Chim. Acta* **1993**, *76*, 1231−50. (e) Shi, S.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 10656−7. (f) Vasella, A.; Uhlmann, P.; Waldraff, C. A.; Diederich, F.; Thilgen, C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1388−90.

[3] (a) Prato, M.; Maggini, M.; Scorrano, G.; Lucchini, V. *J. Org. Chem.* **1993**, *58*, 3613−5. (b) Wilson, S. R.; Wu, Y.; Kaprinidis, N. A.; Schuster, D. I. *J. Org. Chem.* **1993**, *58*, 6548−9. (c) Zhang, X.; Romero, A.; Foote, C. S. *J. Am. Chem. Soc.* **1993**, *115*, 11024−5. (d) Yamago, S.; Takeichi, A.; Nakamura, E. *J. Am. Chem. Soc.* **1994**, *116*, 1123−4. (e) Vassilikogiannakis, G.; Orfanopoulos, M. *J. Am. Chem. Soc.* **1997**, *119*, 7394−5.

[4] (a) Da Ros, T.; Prato, M.; Novello, F.; Maggini, M.; Banfi, E. *J. Org. Chem.* **1996**, *61*, 9070−2. (b) Prato, M.; Suzuki, T.; Foroudian, H.; Li, Q.; Khemani, K.; Wudl, F.; Leonetti, J.; Little, R. D.; White, T.; Rickborn, B.; Yamago, S.; Nakamura, E. *J. Am. Chem. Soc.* **1993**, *115*, 1594−5. (c) Meier, M. S.; Poplawska, M. *J. Org. Chem.* **1993**, *58*, 4524−5. (d) Shiu, L.-L.; Lin, T.-I.; Peng, S. M.; Her, G.-R.; Ju, D. D.; Lin, S.-K.; Hwang, J.-H.; Mou, C. Y.; Luh, T.-Y. *J. Chem. Soc., Chem. Commun.* **1994**, 647−8. (e) Shen, C. K. F.; Chien, K.-M.; Liu, T.-Y.; Lin, T.-I. Her, G.-R.; Luh, T.-Y. *Tetrahedron Lett.* **1995**, *36*, 5383−4. (f) Shu, L.-H.; Sun, W.-Q.; Zhang, D.-W.; Wu, S.-H.; Wu, H. M.; Xu, J.-F.; Lao, X.-F. *J. Chem. Soc., Chem. Commun.* **1997**, 79−80.

[5] (a) Rubin, Y.; Khan, S.; Freedberg, D. I.; Yeretzian, C. *J. Am. Chem. Soc.* **1993**, *115*, 344−5. (b) Tsuda, M.; Ishida, T.; Nogami, T.; Kurono, S.; Ohashi, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1296−8. (c) Guhr, K. I.; Greaves, M. D.; Retello, V. M. *J. Am. Chem. Soc.* **1994**, *116*, 5997−8. (d) Kräutler, B.; Maynollo, J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 87−8. (e) Zhang, X.; Foote, C. S. *J. Org. Chem.* **1994**, *59*, 5235−8.

[6] Ganapathi, P. S.; Friedman, S. H.; Kenyon, G. L.; Rubin, Y. *J. Org. Chem.* **1995**, *60*, 2954−5.

[7] (a) Gugel, A.; Kraus, A.; Spickermann, J.; Belik, P.; Mullen, K. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 559−61. (b) Takeshita, H.; Liu, J.-F.; Kato, N.; Mori, A.; Isobe, R. *J. Chem. Soc., Perkin Trans. 1* **1994**, 1433−7. (c) Ohno, M.; Azuma, T.; Kojima, S.; Shirakawa, Y.; Eguchi, S. *Tetrahedron* **1996**, *52*, 4983−94.

[8] (a) An, Y.-Z.; Ellis, G. A.; Viado, A. L.; Rubin, Y. *J. Org. Chem.* **1995**, *60*, 6353−61. (b) Arce, M.-J.; Viado, A. L.; An, Y.-Z.; Khan, S. I.; Rubin, Y. *J. Am. Chem. Soc.* **1996**, *118*, 3775−6. (c) Liou, K.-F.; Cheng, C.-H. *J. Chem. Soc., Chem. Commun.* **1995**, 1603−4.

[9] (a) Suzuki, H.; Itoh, K.; Ishii, Y.; Simon, K.; Ibers, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 8494−8500. (b) Dunach, E.; Halterman, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 1664−71. (c) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49−92.

[10] Wakatsuki, Y.; Aoki, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1974**, *96*, 5284−5.

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reported for these catalyses is $Ni(CO)_2(PPh_3)_2$.[14] While coordination of fullerenes to transition metals is well established, only a few methods are known using transition metal complexes as catalysts to prepare fullerene derivatives.[4d,e] Our interest in the synthesis of C_{60} derivatives and in the metal-catalyzed cyclization of olefins and alkynes[15] led us to investigate the possibility of employing metal complexes in the cycloaddition of alkynes to C_{60}. Herein, we report a novel one-step synthesis of cyclohexadiene derivatives of C_{60} via a nickel-mediated cycloaddition of bisalkynes to C_{60}. This method is general for a variety of bisalkynes, and the cyclization products show interesting photochemical properties.[8b]

Results and Discussion

Ene−Diyne [2+2+2] Cycloaddition. In the presence of $NiCl_2(PPh_3)_2$, PPh_3, and zinc powder in toluene at 90 °C, 4,4-bis(methoxycarbonyl)hepta-1,6-diyne (**1a**) underwent a [2+2+2] ene−diyne cycloaddition reaction with C_{60} to give the six-membered-ring product **2a** in 68% yield. No reaction occurred in the absence of either $NiCl_2(PPh_3)_2$ or zinc metal. The requirement of a nickel complex for the cycloaddition (eq 1) indicates that the nickel species acts as a catalyst during the reaction. However, due to gradual decomposition of the nickel complex under the reaction conditions, more than a stoichiometric amount of the nickel complex was necessary in order to achieve a high yield of the cycloaddition product (see Experimental Section).

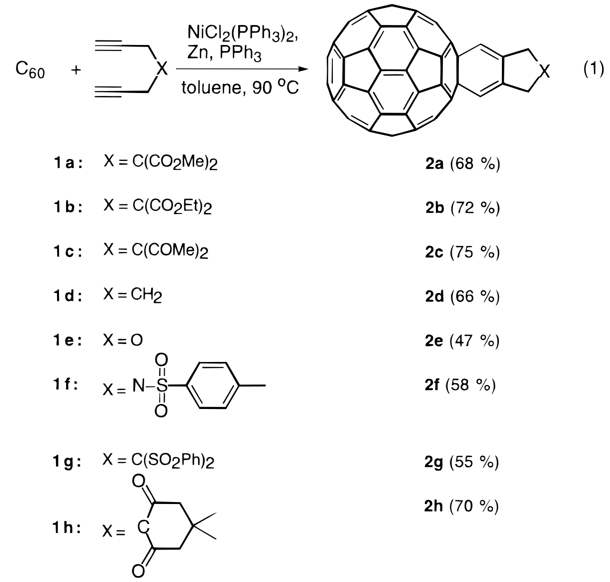

Table 1. Effect of Reaction Conditions[a] on the Yield of Cycloaddition Product **2a**

entry	**1a**:C_{60}[b]	PPh_3:Ni[b]	amt of toluene (mL)	time (h)	yield (%)	C_{60} recovered (%)
1	2.0	12	25	20	0	90
2	2.0	22	25	20	0	93
3	2.0	52	25	20	trace	85
4	2.0	202	25	9	18	13
5	1.5	202	25	9	23	20
6	1.2	202	10	4	22	26
7	1.2	202	25	9	39	27
8	1.2	202	50	9	50	38

[a] All the reactions were carried out under the following reaction conditions: C_{60}, 0.050 mmol; $NiCl_2(PPh_3)_2$, 0.0050 mmol; zinc, 2.5 mmol; diyne, triphenylphosphine, solvent, and duration of reaction, as indicated in the table; temperature, 90 °C. [b] Molar ratio.

The structure of compound **2a** was determined on the basis of its NMR, IR, and MS data. Analysis of **2a** by DCI-MS reveals clearly the molecular ion at m/z 928 supporting the presence of a mono adduct of **1a** with C_{60}. The ester group is evidenced by the strong IR absorptions at 1738 and 1257 (C=O) and 1197 (C−O) cm^{-1}. The ^1H NMR spectrum shows only three resonances at δ 3.48 (d), 3.89 (s), and 6.37 (t) corresponding to the methylene, methoxy, and olefin protons. The number of chemical shifts and the allylic coupling constant of 1.2 Hz between the methylene and the olefin protons are wholly in agreement with the proposed symmetric bicyclic structure of **2a**. Moreover, the observed magnetic equivalency of the methylene protons and the absorption maxima at 428 nm in the UV−visible spectrum of **2a** strongly indicate that the cycloaddition of diyne **1a** to C_{60} occurs across a 6,6-ring junction. The ^{13}C NMR spectrum of **2a** exhibits 23 resonances, of which 19 appear in the sp^2 and 4 appear in the sp^3 regions. These results are consistent with the number of signals predicted on the basis of the symmetry (C_{2v}) of the proposed structure. The characteristic resonances in the spectrum for the carbonyl, fused tertiary olefin, methylene, and sp^3 carbons on the 6,6-ring junction appear at 171.46, 118.09, 39.36, and 65.13 ppm, respectively.

Under similar conditions, C_{60} reacts with 1,6-diynes **1b−h** to afford the corresponding ene−diyne cotrimerization products **2b−h** in 47−75% isolated yields (eq 1). In each reaction, in addition to the mono [2+2+2] adduct, unreacted C_{60} was isolated in 11−24% yield along with traces of multiple cycloaddition products. The structures of these mono adducts were also determined on the basis of their mass, IR, and ^1H and ^{13}C NMR spectra. All the products showed their expected molecular ions in the mass spectra. In the ^1H NMR spectra, the olefinic and methylene protons appeared at ca. 6.3 and 3.4 ppm, respectively. Furthermore, their ^{13}C NMR spectra exhibited the expected number of signals, and the characteristic signals at ca. 118, 65, and 32−40 ppm corresponded to the fused tertiary olefin carbons, the sp^3 carbons on the 6,6-ring junction, and the methylene carbons, respectively. Contrary to the results of the reactions **1a−h**, mono(alkynes) such as phenylacetylene and methyl propiolate did not react with C_{60} to give the [2+2+2] adduct in the presence of $NiCl_2(PPh_3)_2$, PPh_3, and zinc.

The stability of the nickel complex and the yield of cotrimerization reaction shown in eq 1 depend greatly on the amount of PPh_3 used. Excess of PPh_3 (~15 equiv based on nickel) was used in each cycloaddition reaction to achieve a high yield of the product. In the absence of extra PPh_3, no product was obtained. A systematic study of the influence of PPh_3 on the yield of **2a** is presented in Table 1. It may be mentioned that the reaction conditions in Table 1 employed only $^1/_{12}$ the amount of nickel complex used for the preparation of cycloaddition products **2a−h**. As shown in entries 1 and 2, no product was formed at molar ratios of PPh_3 to nickel between 12:1 and

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(11) (a) Diversi, P.; Ingrosso, G.; Lucherini, A.; Minutillo, A. *J. Mol. Catal.* **1987**, *40*, 359−77. (b) Cioni, P.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Ronca, P. *J. Mol. Catal.* **1987**, *40*, 337−57. (c) Diversi, P.; Ermini, L.; Ingrosso, G.; Lucherini, A. *J. Organomet. Chem.* **1993**, *447*, 291−8.

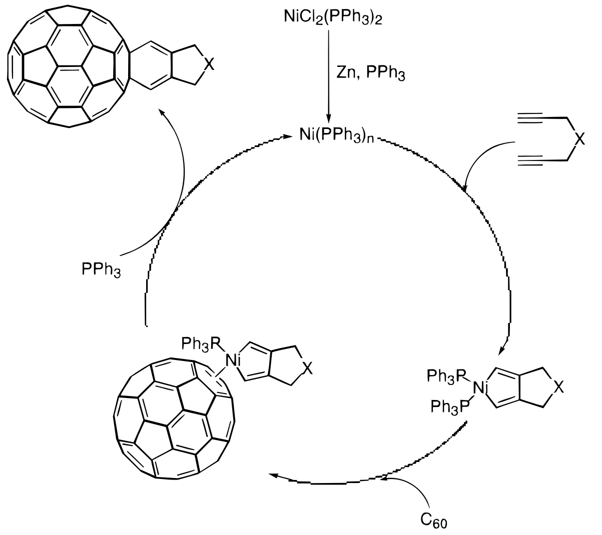
(12) Carbonaro, A.; Greco, A.; Dall'Asta, G. *Tetrahedron Lett.* **1968**, *49*, 5129−30.

(13) (a) Wakatsuki, Y.; Yamazaki, H. *J. Organomet. Chem.* **1977**, *139*, 169−77. (b) Grotjahn, D. B.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 2091−3. (c) Butenschon, H.; Winkler, M.; Vollhardt, K. P. C. *J. Chem. Soc., Chem. Commun.* **1986**, 388−90. (d) Johnson, E. P.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1991**, *113*, 381−2.

(14) Chalk, A. J. *J. Am. Chem. Soc.* **1972**, *94*, 5928−9.

(15) (a) Kong, K.-C.; Cheng, C.-H. *J. Chem. Soc., Chem. Commun.* **1991**, 423−4. (b) Kong, K.-C.; Cheng, C.-H. *Organometallics* **1992**, *11*, 1972−5. (c) Duan, I.-F.; Cheng, C.-H.; Shaw, J.-S.; Cheng, S.-S.; Liou, K.-F. *J. Chem. Soc., Chem. Commun.* **1991**, 1347−8.

Scheme 1

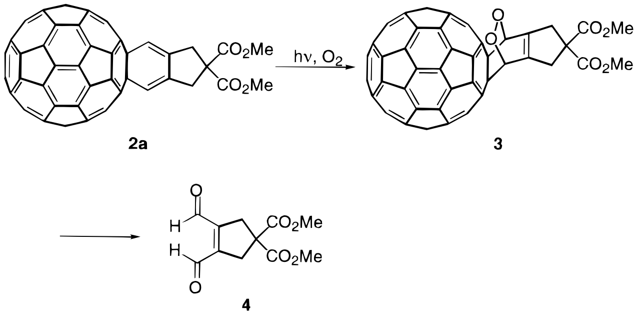


22:1. A trace of product **2a** was detected at a ratio of 52:1. However, when the ratio was raised to 200:1, **2a** was isolated in 18% yield along with the mutiple addition products. Further increase in the amount of PPh_3 did not alter the yield of **2a**. An optimum condition was achieved by adjusting the amount of diyne **1a** and the volume of solvent, to increase the yield of **2a** to 50% (entry 8). The dependence of the yield of mono cycloaddition product on the amount of triphenylphosphine may be rationalized on the basis of the stability of the nickel catalyst. At a low ratio of triphenylphosphine to nickel, dissociation of PPh_3 from the nickel(0) species occurs; the complex becomes thermally unstable and readily decomposes to nickel metal, leading to no catalytic activity. A very high ratio of triphenylphosphine to nickel is required to keep the nickel as an active catalyst in the toluene solution and to maintain the catalytic activity. Indeed, at PPh_3:Ni = 200:1, the nickel complex shows no sign of decomposition and the cycloaddition can become catalytic as shown in entry 8.

The mechanism for the cyclotrimerization of alkynes and cotrimerization of alkynes and alkenes mediated by transition metal complexes has been extensively studied.[16] On the basis of the results of mechanistic studies for these metal-mediated [2+2+2] cyclization reactions, the pathways shown in Scheme 1 were proposed to account for the present nickel-mediated cycloaddition of 1,6-diyne to C_{60} in eq 1. First, $NiCl_2(PPh_3)_2$ is reduced to a nickel(0) phosphine complex by zinc powder. Interaction of the nickel(0) species with a diyne leads to the formation of a bicyclic nickelacyclopentadiene intermediate. Coordination of C_{60} to the nickel intermediate followed by typical insertion and reductive elimination steps leads to the observed product and regeneration of the nickel(0) phosphine intermediate.

Oxidation of Cyclohexadiene Derivatives. All the hexadiene derivatives **2a**−**h** in solution were found to be air and light sensitive and to be readily oxidized by molecular oxygen in the presence of light at ambient temperature. A chloroform-*d* solution of compound **2a** was monitored by ^1H NMR spectroscopy. A freshly prepared solution of **2a** exhibited three signals at 3.48, 3.89, and 6.37 ppm for the methylene, methoxy, and olefinic protons, respectively. The solution in the NMR tube was exposed to air and ambient light for 2 days. The ^1H NMR signals of **2a** decreased in intensity drastically, and two other species, **3** and **4**, with signals at 3.80, 3.89, and 6.14 ppm and at 3.49, 3.75, and 10.51 ppm, respectively, were observed. On further exposure, the NMR signals due to **2a** disappeared completely and the signals of **4** increased in intensity with concomitant decrement of the signals of **3**. After 4 days, only **4** was left in the solution. The final product **4** was proposed as a dialdehyde on the basis of the observed characteristic resonances at 10.51 ppm for the aldehyde protons and at 3.49 and 3.75 ppm for the methylene and methoxy protons, respectively. The GC/MS spectrum of this compound showed the molecular ion at *m*/*z* 220, further supporting the proposed structure. The intermediate species **3**, which was observed on exposure to air and light for 2 days, was assigned as a peroxide on the basis of its ^1H NMR and mass spectra (Scheme 2). Only the signals due to the methoxy (3.80 and 3.89 ppm) and methine protons (6.14 ppm) were clearly observed in the ^1H NMR spectrum. The signals corresponding to the methylene protons, which should have appeared as two doublets due to the unsymmetric nature of the intermediate, were eclipsed in the region 3.8−4.0 ppm. Consistent with an adduct of molecular oxygen with **2a**, the mass spectrum of **3** showed clearly the molecular ion at *m*/*z* 960. The observed facile reaction of molecular oxygen with the present cyclohexadiene derivatives is attributed to the self-sensitizing ability of C_{60} and its derivatives.[17] Compound **2a** first acts as an $^1O_2$ sensitizer in ambient light and then reacts with $^1O_2$ generated at the diene center to give the *endo*-peroxide **3**.[8a]

Scheme 2



Photoinduced [4+4] Cycloaddition of Hexadiene Derivatives. In the absence of oxygen, the cyclohexadiene derivatives undergo interesting photoinduced intramolecular [4+4] cycloaddition, leading to the formation of bisfulleroids (eq 2).[8b] A deoxygenated toluene solution of **2a** was irradiated with 350 nm light for 2 h. The solution turned from brown to purple gradually and upon isolation afforded bisfulleroid **5a** in essentially quantitative yield as indicated by the ^1H NMR spectrum of the crude product. Compound **5a** was fully characterized by MS, NMR, and IR spectral data. The results of DCI-MS showed a strong molecular ion at *m*/*z* 928, suggesting the same molecular formula as that of compound **2a**. Consistent with the unsymmetric nature of the structure, the methylene protons appeared as an AB quartet in the range 3.51−3.58 ppm. The two methoxy groups exhibited the proton signals at 3.82 and 3.86 ppm in the ^1H NMR spectrum and are hence nonequivalent. Similarly, in the ^{13}C NMR spectrum, two different methoxy

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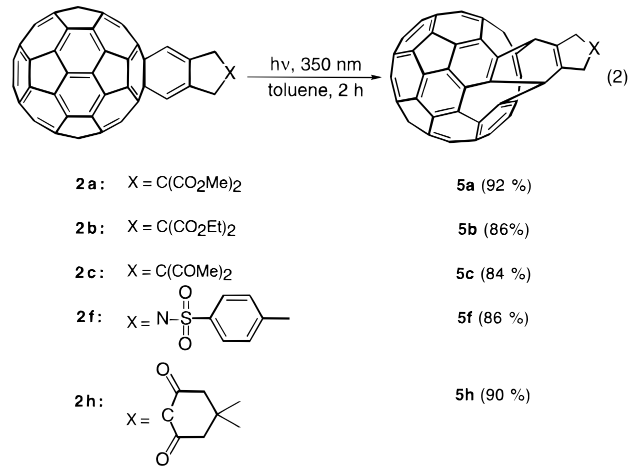
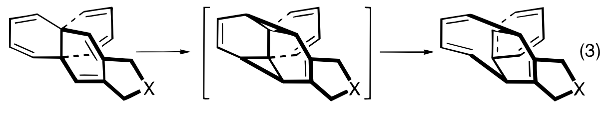
(16) (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539−40. (b) Schore, N. E. *Chem. Rev.* **1988**, *88*, 1081−119. (c) Okuda, J.; Zimmermann, K. H.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 430−1. (d) McAlister, D. R.; Bercaw, J. E.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 1666−8. (e) Rappoli, B. J.; Churchill, M. R.; Janik, T. S.; Rees, W. M.; Atwood, J. D. *J. Am. Chem. Soc.* **1987**, *109*, 5145−9.

(17) (a) Arbogast, J. W.; Foote, C. S.; Kao, M. *J. Am. Chem. Soc.* **1992**, *114*, 2277−9. (b) Tokuyama, H.; Nakamura, E. *J. Org. Chem.* **1994**, *59*, 1135−8. (c) Orfanopoulos, M.; Kambourakis, S. *Tetrahedron Lett.* **1995**, *36*, 435−8. (d) Wu, S. H.; Shu, L. H.; Fan, K. N. *Tetrahedron Lett.* **1994**, *35*, 919−22.



and ester carbonyl carbons at 52.94 and 53.04 ppm and at 171.62 and 171.95 ppm, respectively, were observed. Strong evidence supporting a bisfulleroid structure instead of a bismethanofullerene is from the observation of an extremely downfield ^{1}H NMR singlet at 6.51 ppm for the methine protons and a resonance at 43.69 ppm for the bridgehead sp^3 carbon in the ^{13}C NMR spectrum. The absence of an sp^3 carbon signal for the C_{60} moiety also is in accordance with the bisfulleroid structure. It is known that the NMR signal of a methano proton pointing to a five-membered ring in a fulleroid appears much more downfield than a normal proton with the same hybridization and substituent.[18] The photocyclization is a general reaction for all the cyclohexadiene derivatives. Under similar photolytic conditions, **2b**, **2c**, **2f,** and **2h** were converted to bisfulleroids **5b**, **5c**, **5f**, and **5h**, respectively, in excellent yields (eq 2). These products are thermally and photochemically more stable than their corresponding [2+2+2] parent compounds.

The formation of **5** likely occurs via an intramolecular photoinduced [4+4] cyclization reaction of **2** to give an intermediate bismethanofullerene (**I**). This, upon subsequent carbon−carbon bond cleavage and rearrangement yielded the bis(fulleroid) product as presented in eq 3. For clarity, the structures shown in eq 3 are simplified, with the main part of the fullerene moiety being omitted. It should be noted that the methano groups in intermediate **I** are across 5,6-ring junctions of the C_{60} moiety. The rearrangement of **I** to **5** is expected in view of the fact that a bisfulleroid is generally more stable than the corresponding methanofullerene. Examples of such rearrangement are known.[19] Intramolecular [4+4] photocyclization of organic compounds has been studied previously.[20] Prior to our present [4+4] photocyclization reaction in fullerene chemistry, only Rubin[8b] has made a similar report.



2 **I** **5**

Conclusion

We have demonstrated that nickel phosphine complexes can successfully promote cycloaddition of 1,6-diynes to C_{60}. The method provides a new and convenient way for constructing various fused cyclohexadiene rings on a C_{60} framework. These [2+2+2] derivatives undergo facile photooxidation and [4+4] cycloaddition. The latter serves as an efficient synthetic route for unusual bisfulleroids that consist of a "dimethano[12]-annulene" on the C_{60} framework. Investigation on further functionalization of cyclohexadiene derivatives and bisfulleroids is underway.

Experimental Section

Reagent chemicals were purchased from commercially available sources and used without further purification. $Ni(PPh_3)_2Cl_2$,[21] 4,4-bis-(methoxycarbonyl)hepta-1,6-diyne (**1a**), 4,4-bis(ethoxycarbonyl)hepta-1,6-diyne (**1b**), 3,3-di-2-propynyl-2,4-pentanedione (**1c**), dipropargyl ether (**1e**), *N*,*N*-di-2-propynyl-*p*-toluenesulfonamide (**1f**), 4,4-bis-(phenylsulfonyl)hepta-1,6-diyne (**1g**), and 5,5-dimethyl-2,2-di-2-proynyl-1,3-cyclohexanedione (**1h**) were prepared according to reported methods.[22]

General Procedure for the Synthesis of Cyclohexadiene Derivatives of C_{60}. To a 100 mL side arm flask were added C_{60} (0.0360 g, 0.0500 mmol), appropriate hepta-1,6-diyne (0.0600 mmol; see eq 1), $NiCl_2(PPh_3)_2$ (0.0392 g, 0.0600 mmol), PPh_3 (0.21 g, 0.80 mmol), and zinc (0.164 g, 2.60 mmol). The system was evacuated and then purged with nitrogen five times. To this system was added toluene (50 mL). The reaction mixture was heated at 90 °C for 3 h. The solution was concentrated, and the residue was isolated on a silica gel column using toluene as eluent. The fractions containing C_{60} and fused hexadiene product were collected separately. After removal of the solvent, the solid residues were washed with ether and acetone and then dried in vacuo to afford the respective hexadiene derivatives of C_{60} and recovered C_{60}.

Compound 2a. Yield: 68%. Recovered C_{60}: 12%. $R_f = 0.56$ (TLC, SiO_2, toluene). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.48 (d, $J = 1.2$ Hz, 4 H, CH_2), 3.89 (s, 6 H, CH_3), 6.37 (t, $J = 1.2$ Hz, 2 H, ${=}CH$). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ 39.36 (CH_2), 53.27 (CH_3), 58.47, 65.13, 118.09 ($=CH$), 134.21, 135.48, 140.54, 141.38, 142.17, 142.47, 142.58, 143.30, 144.46, 145.01, 145.25, 145.47, 146.25, 146.36, 146.43, 147.85, 151.03, 171.46. IR (KBr): 1738, 1430, 1257, 1197, 1066, 766, 735, 526 cm^{-1}. UV−vis ($CHCl_3$) λ_{max}: 257, 325, 428, 696 nm. DCI-MS *m/z* (relative intensity): 931 ($M^+ + 3$, 25), 930 ($M^+ + 2$, 40), 929 ($M^+ + 1$, 39), 928 (M^+, 46), 722 (32), 721 (73), 720 (100). HRMS (FAB^+) *m/z*: calcd for $C_{71}H_{13}O_4$, 929.0814; found, 929.0827.

Compound 2b. Yield: 72%. Recovered C_{60}: 15%. $R_f = 0.56$ (TLC, SiO_2, toluene).^{1}H NMR (300 MHz, $CDCl_3$): δ 1.36 (t, $J = 7.1$ Hz, 6 H, CH_3), 3.46 (d, $J = 1.4$ Hz, 4 H, CH_2), 4.34 (q, $J = 7.1$ Hz, 4 H, CH_2), 6.36 (t, $J = 1.4$ Hz, 2 H, $=CH$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 14.18 (CH_3), 39.38 (CH_2), 58.65, 62.05 (OCH_2), 65.24, 117.94 ($=CH$), 134.25, 135.83, 140.59, 141.42, 142.19, 142.53, 142.63, 143.35, 144.51, 145.05, 145.30, 145.52, 146.29, 146.40, 146.48, 147.90, 151.16, 171.05. IR (KBr): 1728, 1251, 1184, 901, 727, 525 cm^{-1}. FAB-MS *m/z* (relative intensity): 959 ($M^+ + 3$, 7), 958 ($M^+ + 2$, 14), 957 ($M^+ + 1$, 20), 956 (M^+, 17), 722 (36), 721 (79), 720 (100). HRMS (FAB^+), *m/z*: calcd for $C_{73}H_{17}O_4$, 957.1126; found, 957.1113.

Compound 2c. Yield: 75%. Recovered C_{60}: 11%. $R_f = 0.26$ (TLC, SiO_2, toluene). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.35 (s, 6 H, CH_3), 3.40 (d, $J = 1.6$ Hz, 4 H, CH_2), 6.39 (t, $J = 1.6$ Hz, 2 H, $=CH$). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): δ 26.89 (CH_3), 36.78 (CH_2), 65.13, 72.90, 118.55 ($=CH$), 134.21, 135.39, 140.60, 141.41, 142.18, 142.49, 142.63, 143.34, 144.48, 145.06, 145.21, 145.52, 146.29, 146.41, 147.89, 150.91, 204.41. IR (KBr): 1698, 1426, 1355, 1183, 846, 766, 526 cm^{-1}. UV−vis ($CHCl_3$) λ_{max}: 260, 326, 427, 696 nm. DCI-MS *m/z* (relative intensity): 899 ($M^+ + 3$, 46), 898 ($M^+ + 2$, 78), 897 ($M^+ + 1$, 86), 896 (M^+, 100), 722 (17), 721 (43), 720 (61). HRMS (FAB^+) *m/z*: calcd for $C_{71}H_{12}O_2$, 896.0837; found, 896.0838.

Compound 2d. Yield: 66%. Recovered C_{60}: 18%. $R_f = 0.91$ (TLC, SiO_2, toluene). ^{1}H NMR (300 MHz, 1:1 $CDCl_3/CS_2$): δ 2.10

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[18] Suzuki, T.; Li, Q.; Khemani, K. C.; Wuld, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301−2.

[19] Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243−55 and references therein.

[20] (a) Masamune, S.; Seidner, R. T.; Zenda, H.; Wiesel, M.; Nakatsuka, N.; Bigam, G. *J. Am. Chem. Soc.* **1968**, *90*, 5286−8. (b) Babad, E.; Ginsburg, D.; Rubin, M. B. *Tetrahedron Lett.* **1968**, 2361−3.

[21] Hayter, R. G.; Humiec, F. S. *Inorg. Chem.* **1965**, *4*, 1701−6.

[22] Grigg, R.; Scott, R.; Stevenson, P. *J. Chem. Soc., Perkin Trans. 1*, **1998**, 1357−64.

(d, J = 7.2 Hz, 2 H, CH_2), 2.27 (td, J = 7.2 Hz, J = 1.6 Hz, 4 H, CH_2), 6.30 (t, J = 1.6 Hz, 2 H, ═CH). $^{13}C\{^1H\}$ NMR (150.8 MHz, $CDCl_3$): δ 24.84 (CH_2), 32.30 (CH_2), 64.38, 116.01, 133.82 (═CH), 138.89, 140.29, 141.09, 141.84, 142.27, 142.78, 142.90, 144.16, 144.66, 144.72, 145.03, 145.07, 145.95, 146.01, 146.07, 151.06. FAB-MS m/z (relative intensity): 814 ($M^+ + 2$, 10), 813 ($M^+ + 1$, 15), 812 (M^+, 15), 722 (41), 721(85), 720 (100).

Compound 2e. Yield: 47%. Recovered C_{60}: 13%. R_f = 0.50 (TLC, SiO_2, toluene). ^1H NMR (300 MHz, 1:1 $CDCl_3/CS_2$): δ 4.91 (d, J = 1.6 Hz, 4 H, CH_2), 6.38 (t, J = 1.6 Hz, 2 H, ═CH). IR (KBr): 1459, 1425, 1039, 756, 660, 553, 525 cm^{-1}. DCI-MS m/z (relative intensity): 817 ($M^+ + 3$, 32), 816 ($M^+ + 2$, 61), 815 ($M^+ + 1$, 76), 814 (M^+, 100), 722 (29), 721 (57), 720 (82).

Compound 2f. Yield: 58%. Recovered C_{60}: 13%. R_f = 0.38 (TLC, SiO_2, toluene). ^1H NMR (300 MHz, $CDCl_3$): δ 2.53 (s, 3 H, CH_3), 4.44 (d, J = 1.6 Hz, 4 H, CH_2), 6.32 (t, J = 1.6 Hz, 2 H, ═CH), 7.44 (d, J = 8.8 Hz, 2 H, CH), 7.87 (d, J = 8.8 Hz, 2 H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): δ 21.69 (CH_3), 51.84 (CH_2), 64.51, 117.76 (═CH), 127.99 (Ph), 129.84 (Ph), 132.60, 133.29, 134.00, 140.53, 141.26, 142.02, 142.24, 142.54, 142.96, 143.90, 144.28, 144.78, 145.00, 145.39, 146.17, 146.29, 147.72, 149.78. IR (KBr): 1508, 1460, 1427, 1348, 1181, 1093, 928, 765, 664, 603, 569, 547, 526 cm^{-1}. UV−vis ($CHCl_3$) λ_{max}: 257, 325, 428, 697 nm. DCI-MS m/z (relative intensity): 968 ($M^+ + 1$, 8), 967 (M^+, 10), 815 (36), 814 (66). 813 (100), 722 (34), 721 (66), 720 (98). HRMS (FAB^+) m/z: calcd for $C_{73}H_{13}O_2NS$, 967.0697; found, 967.0697.

Compound 2g. Yield: 55%. Recovered C_{60}: 18%. R_f = 0.23 (TLC, SiO_2, toluene). ^1H NMR (300 MHz, $CDCl_3$): δ 3.84 (s, 4 H, CH_2), 6.14 (s, 2 H, ═CH), 7.59 (t, J = 7.3 Hz, 4 H, CH), 7.80 (t, J = 7.3 Hz, 2 H, CH), 8.16 (d, J = 7.3 Hz, 4 H, CH). $^{13}C\{^1H\}$ NMR (75 MHz, 1:1 $CDCl_3/CS_2$): δ 37.88 (CH_2), 64.46, 90.06, 118.61 (═CH), 128.85 (Ph), 131.03 (Ph), 133.81, 134.07, 135.04 (Ph), 136.49, 140.45, 141.21, 141.97, 142.13, 142.49, 143.21, 144.25, 144.77, 144.96, 145.34, 146.12, 146.24, 147.65, 149.94. IR (KBr): 1508, 1323, 1146, 1076, 757, 723, 684, 605, 526 cm^{-1}. FAB-MS m/z (relative intensity): 1093 ($M^+ + 1$, 6), 936 (M^+, 100), 722 (38), 721 (81), 720 (100).

Compound 2h. Yield: 70%. Recovered C_{60}: 11%. R_f = 0.33 (TLC, SiO_2, toluene). ^1H NMR (600 MHz, $CDCl_3$): δ 1.12 (s, 6 H, CH_3), 2.80 (s, 4 H, CH_2), 3.32 (d, J = 1.62 Hz, 4 H, CH_2), 6.34 (t, J = 1.62 Hz, 2 H, ═CH). $^{13}C\{^1H\}$ NMR (150.8 MHz, 1:1 $CDCl_3/CS_2$): δ 28.37 (CH_3), 30.68, 37.79 (CH_2), 51.68 (CH_2), 65.01, 69.12, 117.77 (═CH), 134.16, 135.61, 140.46, 141.28, 142.05, 142.39, 142.48, 143.20, 144.36, 144.92, 145.11, 145.36, 146.13, 146.25, 146.33, 147.72, 150.87, 206.07. IR (KBr): 1696, 1425, 1184, 905, 728, 526 cm^{-1}. UV−vis ($CHCl_3$) λ_{max}: 257, 325, 428, 696 nm. DCI-MS m/z (relative intensity): 939 ($M^+ + 3$, 41), 938 ($M^+ + 2$, 72), 937 ($M^+ + 1$, 86), 936 (M^+, 100), 722 (17), 721 (41), 720 (60). HRMS (FAB^+) m/z: calcd for $C_{74}H_{17}O_2$, 937.1229; found, 937.1233.

Synthesis of 2a Using a Catalytic Amount of $NiCl_2(PPh_3)_2$. To a 100-mL side arm flask were added C_{60} (0.0360 g, 0.0500 mmol), 4,4-bis(methoxycarbonyl)hepta-1,6-diyne (0.0125 g, 0.0600 mmol), $NiCl_2(PPh_3)_2$ (0.00326 g, 0.00500 mmol), PPh_3 (0.262 g, 1.00 mmol), and zinc (0.163 g, 2.50 mmol). The system was evacuated and then purged with nitrogen five times. To this mixture was added toluene (50 mL), and the reaction mixture was heated at 90 °C for 9 h. The solution was then concentrated, and the residue was isolated on a silica gel column using toluene as eluent. The fractions containing C_{60} and product **2a** were collected separately. After removal of the solvent, the solid residues were washed with ether and acetone and then dried in vacuo to afford C_{60} (0.0137 g) in 38% yield and **2a** (0.0232 g, 0.0250 mmol) in 50% yield.

General Procedure for the Synthesis of Bisfulleroids. A cyclohexadiene derivative of C_{60} (0.025 mmol) was dissolved in toluene (20 mL). The solution was transferred to a quartz tube and was degassed by bubbling argon for 1 h. The solution was irradiated for 2 h in a Rayonet photoreactor using a 350 nm UV lamp. After removal of solvent, the residue was purified by column chromatography using toluene as eluent. The fraction containing the product was evaporated, and the solid obtained was washed with ether and dried in vacuo to give the bisfulleroid.

Bisfulleroid 5a. Yield: 92%. R_f = 0.56 (TLC, SiO_2, toluene). ^1H NMR (600 MHz, $CDCl_3$): δ 3.51−3.58 (AB q, J = 16.08 Hz, 4 H), 3.82 (s, 3 H), 3.86 (s, 3 H), 6.51 (s, 2 H). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ 41.68, 43.69, 52.94, 53.05, 59.09, 126.61, 134.46, 134.50, 134.67, 136.37, 136.67, 137.61, 138.90, 140.06, 140.26, 140.33, 140.44, 140.50, 140.94, 142.82, 143.12, 143.25, 143.37, 143.60, 143.63, 143.69, 143.76, 143.81, 143.92, 143.93, 143.96, 144.18, 144.36, 144.42, 145.12, 145.19, 145.54, 147.98, 149.17, 171.62, 171.95. IR (KBr): 1731, 1420, 1255, 1159, 728, 526 cm^{-1}. UV−vis ($CHCl_3$) λ_{max}: 232, 262, 327, 501 nm. DCI-MS m/z (relative intensity): 930 ($M^+ + 2$, 52), 928 (M^+, 100), 720 (5.8). HRMS (FAB^+) m/z: calcd for $C_{71}H_{13}O_4$, 929.0814; found, 929.0827.

Bisfulleroid 5b. Yield: 86%. R_f = 0.56 (TLC, SiO_2, toluene). ^1H NMR (600 MHz, $CDCl_3$): δ 1.28−1.319 (t, J = 7.02 Hz, 3 H), 1.33−1.35 (t, J = 7.02 Hz, 3 H), 3.45−3.57 (AB q, J = 15.90 Hz, 4 H), 4.25−4.29 (q, J = 7.02 Hz, 2 H), 4.30−4.34 (q, J = 7.02, Hz, 2 H), 6.51 (s, 2 H). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ 14.12, 14.15, 41.88, 44.02, 59.46, 62.05, 62.07, 126.91, 134.77, 134.95, 136.66, 136.94, 137.96, 139.18, 140.37, 140.59, 140.73, 140.77, 141.21, 143.10, 143.40, 143.52, 143.64, 143.87, 143.93, 143.97, 144.06, 144.10, 144.21, 144.23, 144.45, 144.64, 144.71, 145.40, 145.46, 148.33, 149.49, 171.47. 171.77. IR (KBr): 1730, 1439, 1254, 1171, 1074, 528 cm^{-1}. FAB^+-MS m/z (relative intensity): 959 ($M^+ + 3$, 14), 957 ($M^+ + 1$, 46), 720 (100). HRMS (FAB^+) m/z: calcd for $C_{73}H_{17}O_4$, 957.1126; found, 957.1124.

Bisfulleroid 5c. Yield: 84%. R_f = 0.26 (TLC, SiO_2, toluene). ^1H NMR (600 MHz, $CDCl_3$): δ 2.24 (s, 3 H), 2.27 (s, 3 H), 3.40 (s, 4 H), 6.45 (s, 2 H). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ 26.53, 26.62, 38.63, 44.02, 73.97, 126.84, 134.72, 134.81, 134.90, 136.64, 136.97, 137.75, 139.19, 140.30, 140.35, 140.62, 140.71, 140.81, 141.23, 143.09, 143.41, 143.55, 143.68, 143.89, 143.99, 144.11, 144.21, 144.32, 144.46, 144.66, 144.71, 145.39, 145.45, 145.83, 148.15, 149.45, 203.79, 204.07. IR (KBr): 1691, 1457, 1261, 668, 528 cm^{-1}. UV−vis ($CHCl_3$) λ_{max}: 233, 261, 326, 491 nm. FAB^+-MS m/z (relative intensity): 899 ($M^+ + 3$, 6), 897 ($M^+ + 1$, 12), 720 (100). HRMS (FAB^+) m/z: calcd for $C_{71}H_{12}O_2$, 896.0837; found, 896.0878.

Bis(fulleroid) 5f. Yield: 86%. R_f = 0.38 (TLC, SiO_2, toluene). ^1H NMR (600 MHz, $CDCl_3$): δ 2.40 (s, 3 H), 4.57 (s, 4 H), 6.42 (s, 2 H), 7.29−7.31 (d, J = 7.56 Hz, 1 H), 7.72−7.74 (d, J = 7.56 Hz, 1 H). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ 21.51, 41.90, 55.27, 126.32, 127.31, 129.66, 132.86, 134.06, 134.25, 134.62, 136.12, 136.33, 136.71, 138.95, 139.53, 139.92, 140.21, 140.42, 140.69, 140.95, 142.75, 143.09, 143.28, 143.35, 143.41, 143.54, 143.71, 143.82, 143.86, 143.94, 144.01, 144.37, 145.08, 145.51, 146.29, 148.88. IR (KBr): 1343 1155, 1096, 687, 525 cm^{-1}. UV−vis ($CHCl_3$) λ_{max}: 234, 260, 326 nm. FAB^+-MS m/z (relative intensity): 970 ($M^+ + 3$, 17), 968 ($M^+ + 1$, 36), 720 (100). HRMS (FAB^+) m/z: calcd for $C_{73}H_{13}O_2NS$, 967.0667; found, 967.0641.

Bisfulleroid 5h. Yield: 90%. R_f = 0.33 (TLC, SiO_2, toluene). ^1H NMR (600 MHz, $CDCl_3$): δ 1.09 (s, 6 H), 2.74 (s, 2 H), 2.79 (s, 2 H), 3.32−3.44 (AB q, J = 15.12 Hz, 4 H), 6.48 (s, 2 H). ^{13}C NMR (150.8 MHz, $CDCl_3$): δ 28.14, 30.06, 39.49, 43.96, 51.06, 51.34, 69.98, 126.66, 134.02, 134.53, 134.60, 136.47, 136.73, 137.52, 138.97, 140.04, 140.41, 140.46, 140.64, 140.99, 142.87, 143.15, 143.29, 143.43, 143.66, 143.73, 143.77, 143.85, 143.96, 143.97, 144.01, 144.23, 144.41, 144.48, 145.17, 145.24, 145.57, 147.83, 149.28, 204.28, 204.89. IR (KBr): 1696, 1425, 1238, 903, 728, 525 cm^{-1}. UV−vis ($CHCl_3$) λ_{max}: 261, 234, 326, 505 nm. DCI-MS m/z (relative intensity): 939 ($M^+ + 3$, 47), 936 (M^+, 100), 720 (5.46). HRMS (FAB^+) m/z: calcd for $C_{74}H_{17}O_2$, 937.1229; found, 937.1233.

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Supporting Information Available: ^1H and ^{13}C NMR with DEPT and mass spectra of compounds **2a**, **2h**, **5b**, and **5h** (20 pages, print/PDF). See any current masthead pages for ordering information and Web access instructions.

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