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Generation and Reactions of Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-ene

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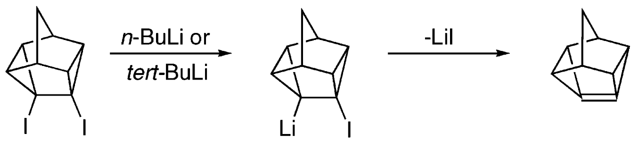

12 **10** **9**

The highly pyramidalized alkene, pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-ene (**9**), has been generated via treatment of 4,5-diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**12**) with *n*-butyllithium and *tert*-butyllithium. The title alkene has also been trapped as its Diels−Alder adduct with 1,3-diphenylisobenzofuran, 2,5-dimethylfuran, and spiro[2.4]hepta-4,6-diene. Products resulting from alkyllithium addition to the pyramidalized double bond of **9** have been isolated and fully characterized spectroscopically. The geometry, olefin strain energy, heat of hydrogenation, and relative HOMO/LUMO energies of **9** have been obtained by ab initio calculations at the MP2 and B3LYP levels using the 6-31G* basis set.

Introduction

Pyramidalized alkenes are molecules that contain carbon−carbon double bonds in which one or both of the two sp^2 carbon atoms do not lie in the same plane as the three atoms attached to it. Over the past 35−40 years, pyamidalized alkenes have received significant attention both synthetically and computationally. Since Weinshenker and Greene published the synthesis of the first substantially pyramidalized alkene **1** (Figure 1),[1] numerous other pyramidalized alkenes have been prepared. In 1981, Szeimies published the first review of pyramidalized alkenes,[2] and, since that time, other reviews by Borden[3] and Keese[4] have appeared. Most recently, Camps and Vazquez published an excellent comprehensive review of the synthesis and chemistry of pyramidalized alkenes.[5] In addition to the synthesis and chemistry summarized in the aforementioned papers, numerous computational studies of pyramidalized alkenes have also been reported.[6]

Deviations from planarity in pyramidalized alkenes can result from a combination of strain and unsymmetric steric effects, as in the *syn*-sesquinorbornenes **2** and related alkenes.[7] Such deviations from planarity are typically smaller, and the compounds are, in many cases, stable and isolable. However, deviations from planarity and pyramidalization can be substantial when the carbon−carbon double bond is located at the bridgehead positions of a polycyclic alkene. For example, cubene (**3**), prepared by Eaton and Maggini in 1988, is predicted by ab initio calculations to be the most highly pyramidalized alkene yet known and has a fleeting existence.[8] Also, in 1988,

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[6] See, for example: (a) Rasul, G.; Olah, G. A.; Prakash, G. K. S. *J. Phys. Chem. A* **2006**, *110*, 7197. (b) Williams, R. V.; Margetic, D. *J. Org. Chem.* **2004**, *69*, 7134. (c) Margtic, D.; Williams, R. V.; Warrener, R. N. *J. Org. Chem.* **2003**, *68*, 9186. (d) Can, H.; Zahn, D.; Balci, M.; Brickmann, J. *Eur. J. Org. Chem.* **2003**, 1111. (e) Vazquez, S. *J. Chem. Soc., Perkin Trans.* **2002**, *2*, 2100. (f) Yates, B. F. *J. Organomet. Chem.* **2001**, *635*, 142. (g) Mastryukov, V. S.; Chen, K.-H.; Allinger, N. L. *J. Phys. Chem. A* **2001**, *105*, 8562. (h) Mastryukov, V. S.; Boggs, J. E. *Struct. Chem.* **2000**, *11*, 97.

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[8] (a) Lukin, K.; Eaton, P. E. *J. Am. Chem. Soc.* **1995**, *117*, 7652. (b) Staneke, P. O.; Ingemann, S.; Eaton, P.; Nibbering, N. M. M.; Kass, S. R. *J. Am. Chem. Soc.* **1994**, *116*, 6445. (c) Eaton, P. E.; Maggini, M. *J. Am. Chem. Soc.* **1988**, *110*, 7230.

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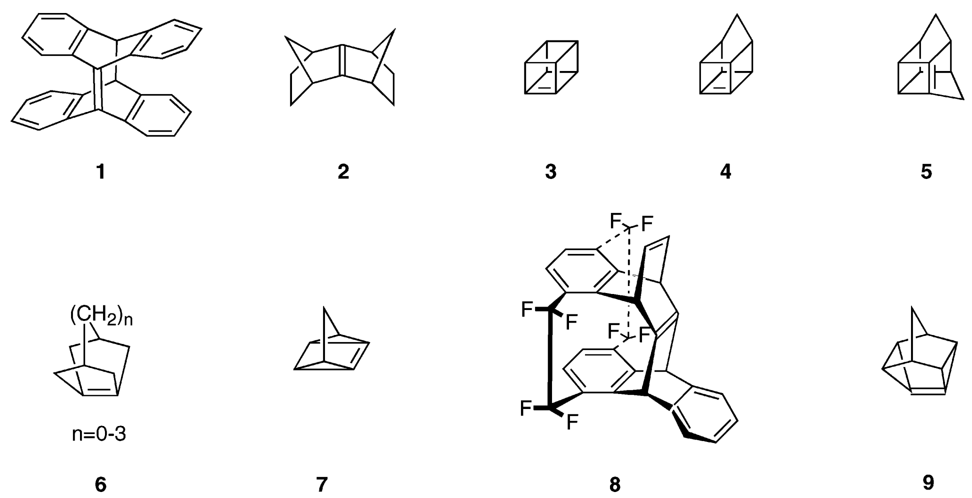

FIGURE 1. Some representative pyramidalized alkenes **1**−**8** and pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]non-4-ene (**9**).

Borden[9] and Szeimies[10] independently prepared highly reactive 4(5)-homocubene (**4**) via alkyllithium-induced dehalogenation. Subsequently, Szeimies provided evidence for the homocubene derivative, 2,5-dichloropentacyclo[4.3.0.$0^{2,5}$.$0^{3,8}$.$0^{4,7}$]non-3-ene.[11] Bishomocubene (**5**) has been prepared by Marchand and coworkers, and it is also highly unstable.[12] The Borden[13] and Camps and Vazquez[14] groups have independently synthesized and studied numerous members of a family of highly pyramidalized alkenes containing the tricyclo[3.3.*n*.$0^{3,7}$]alk-3(7)-ene skeleton **6**. Other pyramidalized alkenes with various ring systems, such as dodecahedrenes[15] and cyclopropenes with the bicyclo[*n*.1.0]-framework,[16] have also appeared. Additionally, Szeimies has thoroughly studied several different quadricyclenes,[17] all of which contain highly pyramidalized carbon−carbon double bonds. 1(5)-Quadricyclene (**7**)[18] is one example from this family of pyramidalized alkenes. Most recently, Dolbier has reported that the double Diels−Alder reaction of *syn*-4,5,13,14-bis(dehydro)octafluoroparacyclophane with anthracene furnishes a product **8** with the highest degree of pyramidalization, $\phi = 34.3°$, as measured by X-ray crystallography.[19]

As part of our continuing research on the synthesis and study of strained organic molecules, we have been interested in the synthesis of the highly pyramidalized alkene, pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]non-4-ene (**9**). Structurally, **9** is related to tricyclo[3.3.*n*.$0^{3,7}$]alk-3(7)-ene **6** with $n = 1$, although closer inspection of **9** reveals the presence of cyclopropane rings and the bicyclopropylidene ring system. In this report, we describe the synthesis of pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]non-4-ene (**9**), its trapping with 1,3-diphenylisobenzofuran, 2,5-dimethylfuran, and spiro[2.4]hepta-4,6-diene, and its reactions with multiple alkyllithiums present in the reaction mixture. We also describe preliminary attempts to synthesize **9** via dehydrohalogenation of 4-iodopentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane (**11**) and ab initio calculations that predict the geometry, olefin strain energy, heat of hydrogenation, and HOMO/LUMO energies of this alkene.

Results and Discussion

Synthesis of 4,5-Diiodopentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane (12). The dehalogenation of vicinal dihalides has proven to be a reliable method for the synthesis of a variety of strained alkenes, including ones with pyramidalized double bonds.[5] Dehalogenation is most frequently accomplished via metal−halogen exchange with alkyllithiums, although reduction with metals such as Zn, Mg, Na, or sodium amalgam has been utilized successfully in several instances. Thus, we identified 4,5-diiodopentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]nonane (**12**) as a potential precursor to **9**. On the basis of previous work, we surmised that treatment of **12** would result in iodine−lithium exchange followed by elimination of lithium iodide to give the title compound **9**. Alternatively, dehydrohalogenation of

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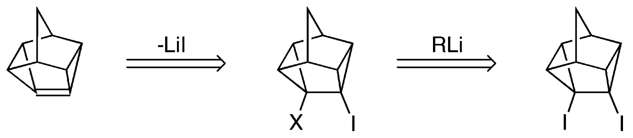
SCHEME 1. Retrosynthetic Analysis of Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-ene (9) − Dehalogenation of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with an Alkyllithium



9

10, X = Li
11, X = H

12

4-iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**11**) could give **9**, thus making **12** an attractive target.

The synthesis of diiodide **12** may be accomplished via bis-decarboxylative iodination of the known diacid, pentacyclo-[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4,5-dicarboxylic acid (**15**).[20] Diacid **15** may be conveniently prepared in only three steps from norbornadiene and dimethylacetylene dicarboxylate, as shown in Scheme 2. Homo Diels−Alder reaction of norbornadiene with dimethylacetylene dicarboxylate furnished diester **13**. Saponification of **13** followed by intramolecular [2+2]photocycloaddition yielded pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4,5-dicarboxylic acid (**15**).

Initially, we attempted to transform diacid **15** into diiodide **12** via bis-iododecarboxylation using the Moriarty modification[21] of the Suarez method,[22] iodosobenzene diacetate/I$_2$ in standard solvents (CCl$_4$, CH$_2$Cl$_2$, benzene, cyclohexane). Indeed, Camps and Vazquez have used this method extensively for the synthesis of numerous vicinal diiodides, particularly those precursors leading to pyramidalized alkenes in the tricyclo[3.3.*n*.0^{3,7}]alk-3(7)-ene **6** family. However, in all of the aforementioned solvents, yields of **12** were either very low or afforded none of the desired vicinal diiodide product. This result is likely due to the low solubility of diacid **15** in these solvents. The highest yields of diiodide **12** were obtained in carbon tetrachloride (ca. 10−15% based on recovered diacid **15**). However, we found these samples to be contaminated with about 10−15% of the corresponding vicinal iodochloro derivative, this impurity undoubtedly resulting from radical abstraction of chlorine from the solvent. Further, we were unable to readily separate these two vicinal dihalides using conventional methods. As an alternative, we conducted stepwise iododecarboxylation.

Accordingly, diacid **15** was transformed into the corresponding anhydride **16** via treatment with dicyclohexylcarbodiimide, and reaction of the anhydride **16** with sodium methoxide in methanol gave methyl hemiester **17** in good yield.[23] Iododecarboxylation of methyl hemiester **17** using the Suarez procedure again gave low yields, so we utilized the Barton procedure for iodinative decarboxylation, as modified by Eaton and Tsanaktsidis.[24] Saponification of iodoester **18** furnished the corresponding iodo acid, which afforded the desired diiodide **12** after submission to identical conditions used for the synthesis of iodo ester **18** (Scheme 2).

Reaction of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with *n*-Butyllithium. With ample quantities of **12** available, we next investigated its dehalogenation with *n*-butyllithium to form **9**. Initial experiments afforded **11** when the reaction of **12** with *n*-butyllithium was quenched at low temperature (−78 °C) prior to lithium iodide elimination (Scheme 1). Treatment of **12** with 1.2 equiv of *n*-butyllithium in THF at −78 °C and warming to 0 °C gave a mixture of products containing **22** (58.2% area ratio by GCMS), **23** (13.9%), and **26** (1%). Two products whose molecular ions suggest structures **24** (3.5%, M$^{\bullet+}$ = 300) and **25** (11.0%, M$^{\bullet+}$ = 174) were also detected, although the structural assignments for these products are tentative, as they could not be separated from one another and isolated in pure form. As it is well known that pyramidalized alkenes react rapidly with alkyllithiums present in the reaction mixture, we propose the following mechanism for the formation of **22**−**26**. Treatment of **12** with *n*-butyllithium effects iodine−lithium exchange to give **10**, which loses lithium iodide to form pyramidalized alkene **9**. The highly reactive **9** then reacts with **10** to give **19**, which undergoes lithium−iodine exchange with either **12** or *n*-butyliodide (formed in the original iodine−lithium exchange) to furnish **22**. Alternatively, **19** may be quenched upon workup to form **23**. In addition to **10** adding across the double bond of **9**, *n*-butyllithium may also react with the pyramidalized double bond of **9** giving **20**, which may add to **9** to form **26** after abstraction of iodine from either **12** or *n*-butyliodide. Alternatively, **20** may react with **12**/*n*-butyliodide to form **24** or with H$^+$ to form **25**. We also observe monoiodide **11** (8.9% area ratio by GCMS), its formation likely resulting from reaction of **10** with H$^+$. No cyclobutane dimers were observed in the reaction of **12** with *n*-butylithium, as the highly pyramidalized double bond of **9** reacts immediately with the alkyllithiums present in the reaction mixture. This observation is consistent with the reported syntheses of other highly pyramidalized alkenes, where only alkyllithium addition products, and no cyclobutane dimers, were observed.[25]

The alkyllithium addition products shown in Scheme 3 all support the formation of **9**. More direct support for the formation of alkene **9** comes from trapping experiments with dienes. Thus, treatment of diiodide **12** with *n*-butyllithium in THF in the presence of 1.2 equiv of 1,3-diphenylisobenzofuran (DPIBF) gave crystalline Diels−Alder adduct **27** in 34% isolated yield,[26] the structure of which was confirmed by single-crystal X-ray analysis (Scheme 4). In addition to the Diels−Alder adduct **27**, we observe (5% by GCMS) monoiodide **11** in the reaction mixture and trace amounts of alkyllithium addition products **22**−**25**.

Reaction of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with *tert*-Butyllithium. We next investigated the dehalogenation of **12** with *tert*-butyllithium (Scheme 5), as we hoped that a switch to this alkyllithium might minimize some of the side reactions observed with *n*-butyllithium. Thus, reaction of diiodide **12** with *tert*-butyllithim in 20:1 heptane:ether[27] furnished a mixture of products **11** (24.3% by GCMS), **22** (46.2%),

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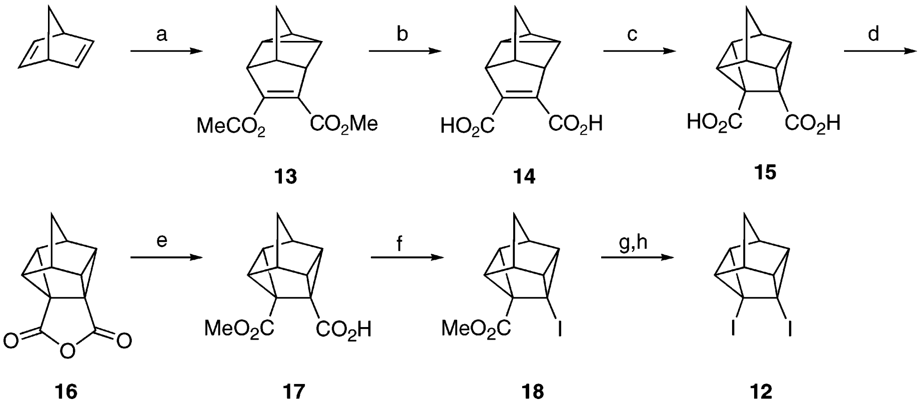
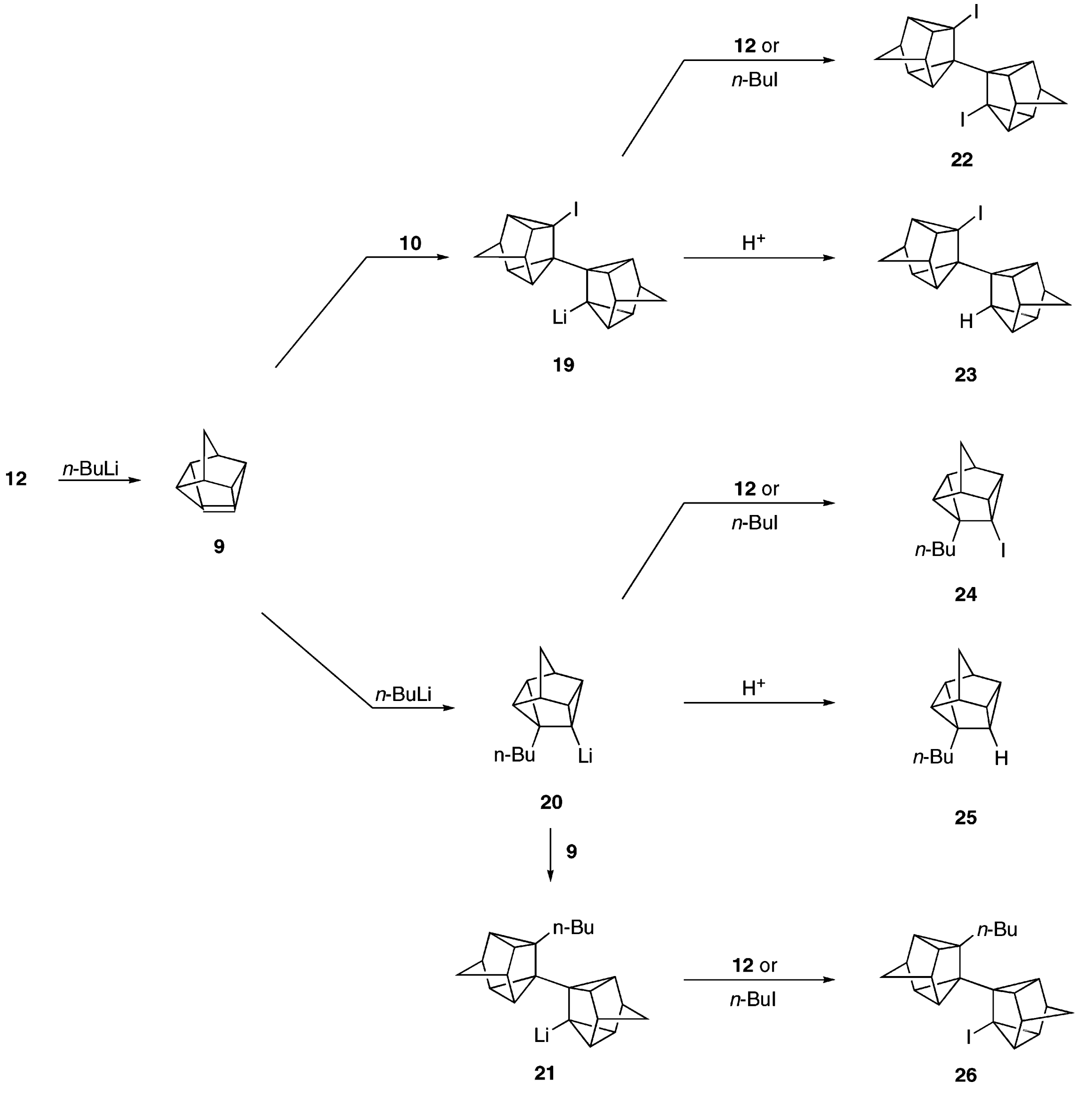
(26) This yield represents the lower bound, as **27** rearranges upon purification via flash column chromatography, even when the eluent contains 2% triethylamine to deactivate the silica gel.

SCHEME 2. Synthesis of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12)[a]



[a] Key: (a) dimethylacetylene dicarboxylate, MeOH, Δ, 73%; (b) KOH, MeOH, H_2O then 10% HCl, 97%; (c) *hν*, diethylether, 25%; (d) DCC, THF; (e) NaOMe, MeOH, 98% 2 steps; (f) (i) $(COCl)_2$, CH_2Cl_2, DMF, (ii) 2-mercaptopyridine-*N*-oxide sodium salt, benzene, 2-iodo-1,1,1-trifluoroiodoethane, DMAP, 66%; (g) KOH, MeOH, H_2O then 10% HCl, 94%; (h) (i) $(COCl)_2$, CH_2Cl_2, DMF, (ii) 2-mercaptopyridine-*N*-oxide sodium salt, benzene, 2-iodo-1,1,1-trifluoroiodoethane, DMAP, 53%.

SCHEME 3. Reaction of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with *n*-Butyllithium

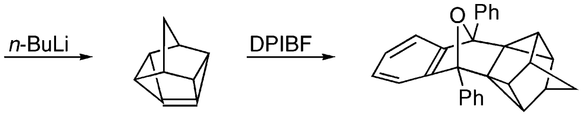


23 (11.7%), and **28** (6.9%). In contrast to what was observed when dehalogenation was conducted with *n*-butyllithium, no products resulting from *tert*-butyllithium addition to the pyramidalized double bond of **9** were observed. Alkyllithium addition products **22**, **23**, and **28** are proposed to form in a manner similar to that proposed in Scheme 3.

The addition of several different Diels−Alder trapping agents to the dehalogenation reaction of **12** with *tert*-butyllithium led

SCHEME 4. Trapping of Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-ene (9) with 1,3-Diphenylisobenzofuran (DPIBF)

12



9 27

to the corresponding Diels−Alder adducts in moderate to low yields. Thus, reaction of diiodide **12** with 3 equiv of *tert*-butyllithium in 20:1 heptane:ether at 0 °C in the presence of 1,3-diphenylisobenzofuran, 2,5-dimethylfuran, and spiro[2.4]-hepta-4,6-diene led to the formation of cycloadducts **27**, **29**, and **30**, in 45%, 22%, and 13% isolated yields, respectively (Scheme 6). In each of these trapping reactions, small amounts ($<$5% by GCMS) of **11**, **22**, **23**, and **28** were present as side products.

Interestingly, we were unable to effectively trap and isolate the Diels−Alder adduct resulting from the reaction of **12** with *tert*-butyllithium in the presence of 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene. This diene has been successfully employed to trap other highly pyramidalized alkenes in several cases,[5] and it was reported by Eaton to be the most effective diene for trapping cubene (when generated by treatment of the corresponding diiodide with butyllithium).[8] In the dehalogenation of **12** with *tert*-butyllithium in the presence of 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene, the major products of this reaction are those resulting from addition of *tert*-butyllithium to the diene moiety of this molecule.[28] We do observe what appears by GCMS to be the Diels−Alder adduct of this reaction ($M^{\bullet+}$ 346); however, this adduct is formed only in very small amounts (ca. less than 5% by GCMS) and could not be separated from the major products in the reaction mixture. Apparently, addition of *tert*-butyllithium to the 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene trap is faster than dehalogenation of **12** under the reaction conditions required for generation of **9**.

Attempted Dehydrohalogenation of 4-Iodopentacyclo-[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (11). Whereas the dehalogenation of vicinal dihalides has proven to be a useful procedure for the formation of highly pyramidalized alkenes, the elimination of hydrogen halide from appropriately substituted precursors has been much less successful. There are exceptions, however, but most of these involve the treatment of bridgehead-halogen-substituted bicyclo[1.1.0]butanes or quadricyclanes with a strong base,[29] and pyramidalized alkenes synthesized by this method thus have substantial s-character in the C−H bond of the precursors. The percent s-character in the carbon-4 (or carbon-5) C−H bond of pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**33**) has been experimentally estimated to be 34.2%[30] and has been calculated to be 30.1% at the HF/6-31G* level of theory.[31] In addition, the ^{13}C NMR spectrum of **11** shows a coupling constant $^1J(^{13}C(5)-H) = 173.7$ Hz, which corresponds to 34.8% s-character in the C(5)−H bond.[32] These values are close to, but slightly less than, the amount of s-character present in the C−H bonds of the aforementioned bicyclo[1.1.0]butane and quadricyclane precursors. Nonetheless, we were interested to see if **9** could be prepared via dehydroiodination of 4-iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**11**).

Monoiodide **11** was synthesized as shown in Scheme 7. Initially, we attempted to prepare monoacid **32** by analogy to the synthesis of diacid **15** (Scheme 3). Indeed, Prinzbach and co-workers previously reported that the irradiation of tetracyclo-[4.3.0.0^{2,4}.0^{3,7}]non-8-ene-8-carboxylic acid in carbon tetrachloride led to pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-carboxylic acid (**32**) in 52% yield via intramolecular [2+2]photocycloaddition. Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene-8-carboxylic acid was, in turn, synthesized via homo Diels−Alder reaction of 2,5-norbornadiene with propynoic acid.[20b] In our hands, however, the intramolecular photocycloaddition of tetracyclo[4.3.0.0^{2,4}.0^{3,7}]-non-8-ene-8-carboxylic acid leading to pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-carboxylic acid (**32**) was problematic, as product mixtures were often intractable and little, if any, **32** could be isolated. Given that we had already prepared iodo ester **18** in conjunction with the synthesis of diiodide **12**, we elected to synthesize monoacid **32** by reduction of **18** with tri-*n*-butylstannane[33] followed by saponification. Barton iododecarboxylation then furnished 4-iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]-nonane (**11**).

Reaction of **11** with *tert*-butyllithium followed by quenching with methanol gave pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**33**) as the only reaction product. Evidently, the kinetic acidity of the C-5 hydrogen in **11** is not high enough to compete with iodine−lithium exchange under these conditions. This is similar to what was observed by Eaton and Maggini in their attempted synthesis of cubene (**3**) via treatment of iodocubane with *tert*-butyllithium. Alternatively, reaction of **11** with a variety of strong bases such as LDA and potassium *tert*-butoxide gave only unreacted starting material **11** even after prolonged reaction time. There is no evidence to invoke the formation of **9** under these conditions.

It may be possible that the corresponding chloro derivative, 4-chloropentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane, will give **9** upon treatment with *tert*-butyllithium. The chlorine atom of 4-chloropentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane should enhance the acidity of the hydrogen on adjacent C-5. Moreover, chlorine−lithium exchange is much slower than iodine−lithium exchange, possibly giving dehydrohalogenation a chance to compete with the exchange reaction. We are currently investigating this possibility.

Calculations. To calculate the geometric parameters of the title alkene **9** as well as predict the olefin strain energy, heat of hydrogenation, and relative HOMO/LUMO energies, we carried out ab initio calculations on this molecule. Recent studies have shown that density functional theory (DFT) can be used to reliably model highly pyramidalized alkenes and gives results similar to those obtained using more costly correlated (MP2) methods.[34] In this study, we have used both the B3LYP/6-31G*

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(27) We are grateful to Professor William Bailey (University of Connecticut) for calling our attention to the importance of this solvent for effecting lithium−iodine exchange with *tert*-butyllithium. See: *J. Org. Chem.* **1990**, *55*, 5404.

(28) (a) Herres, J. P.; Forman, M. A.; Wheeler, K. A. *Acta Crystallogr., Sect. E* **2005**, *E61*, o3961. (b) Herres, J. P.; Forman, M. A.; Wheeler, K. A.; Yap, G. P. A. *Acta Crystallogr., Sect. E* **2005**, *E61*, o1223. We also observe this same reaction with *n*-butyllithium.

(29) See, for example, refs 16 and 17.

(30) Hamlin, J. E.; Toyne, K. J. *J. Chem. Soc., Perkin Trans.* **1981**, *1*, 2731.

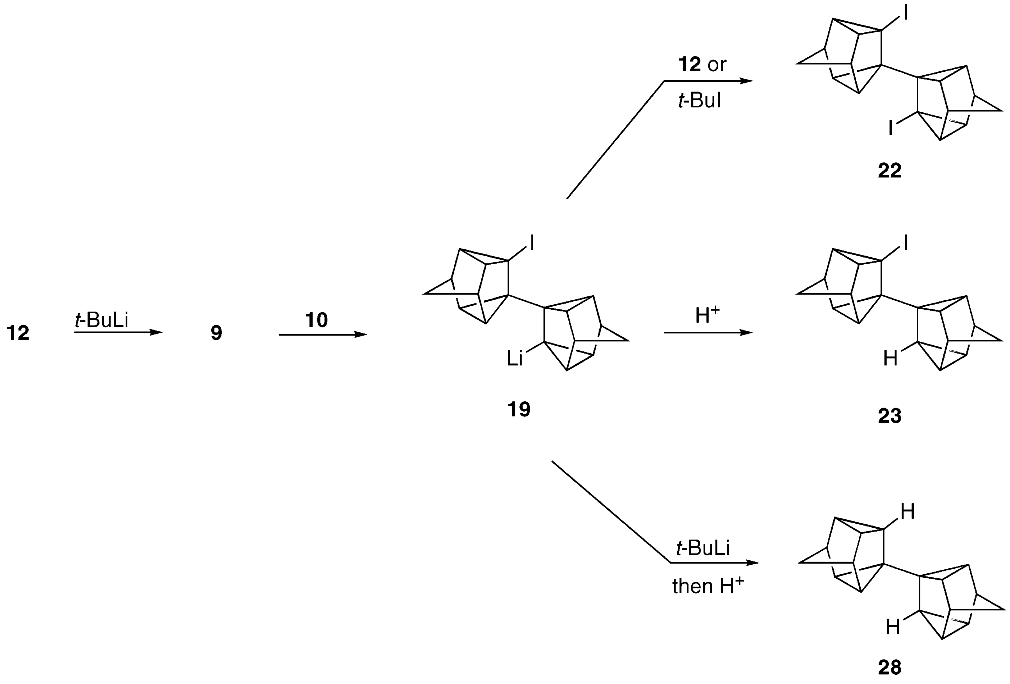
(31) Craciun, L.; Jackson, J. E. *J. Phys. Chem. A* **1998**, *102*, 3738.

(32) We used the relationship between $^1J_{^{13}C-H}$ and the % s character in the carbon hybrid orbital, as proposed by Muller and Pritchard. (a) Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 1471. (b) Muller, N.; Pritchard, D. E. *J. Chem. Phys.* **1959**, *31*, 768.

(33) Leibner, J. E.; Jacobus, J. *J. Org. Chem.* **1979**, *44*, 449.

(34) See, for example, refs 6f and 14a−c.

SCHEME 5. Reaction of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with *tert*-Butyllithium

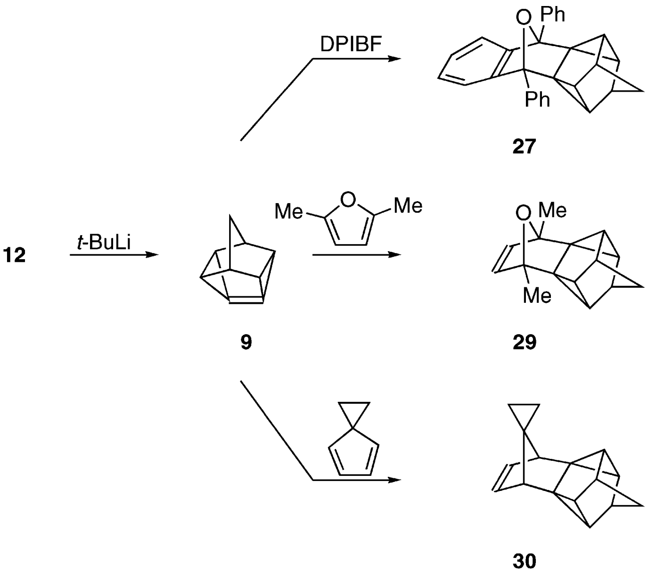


and the MP2/6-31G* methods, as implemented in Gaussian 03,[35] to calculate the structures and energies of **9**.

Figure 2 shows the carbon−carbon bond lengths for the ring bonds of **9** and the pyramidalization angle, ϕ, calculated at both the B3LYP/6-31G* and the MP2/6-31G* levels of theory. Not surprisingly, the optimized geometries for **9** using the two methods give similar bond lengths (maximum difference of 0.023 Å) and pyramidalization angles. It is known that the MP2 method generally overestimates carbon−carbon double bond lengths, and this lengthening was observed in the calculated geometry for **9** (1.354 Å for B3LYP/6-31G* and 1.377 Å for MP2/6-31G*). Additionally, we observe the expected lengthening of the carbon−carbon double bond of **9** as compared to the unbridged alkene, bicyclo[3.3.0]oct-1(5)-ene (1.337 Å for bicyclo[3.3.0]oct-1(5)-ene[25b] vs 1.354 Å for **9** using B3LYP/6-31G*). Moreover, the carbon−carbon double bond lengths calculated for **9** are similar to those previously calculated for other highly pyramidalized alkenes. The pyramidalization angle calculated for **9** (64.2° using B3LYP/6-31G* and 65.1° using MP2/6-31G*) is among the highest for a molecule where evidence for its formation exists.

The olefin strain energy (OSE)[36] provides a measure of the extra strain introduced into a system upon introduction of a double bond. As first pointed out by Hrovat and Borden,[9] the OSE of pyramidalized alkenes (the olefin pyramidalization energy) may be calculated by taking the difference between the hydrogenation energy of the alkene and that of a bicyclic reference compound. For the tricyclo[3.3.*n*.0^{3,7}]alk-3(7)-enes **6**, the unbridged alkene bicyclo[3.3.0]oct-1(5)-ene has been used as the reference compound, and we have used this alkene as the reference compound in the current study. The OSE for **9** was calculated to be 75.8 and 73.4 kcal/mol at the B3LYP/6-31G* and MP2/6-31G* levels of theory, respectively. These values are very close to those calculated for the tricyclo[3.3.*n*.0^{3,7}]alk-3(7)-enes **6**. Nonetheless, these calculated values

SCHEME 6. Trapping of Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-ene (9) with 1,3-Diphenylisobenzofuran (DPIBF), 2,5-Dimethylfuran, and Spiro[2.4]hepta-4,6-diene To Furnish 27, 29, and 30, Respectively



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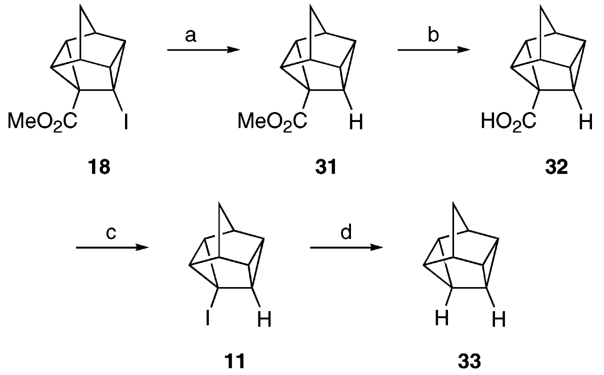
[35] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, revision C.02; Gaussian, Inc.: Wallingford, CT, 2004.

[36] Schleyer, P. v. R.; Maier, W. F. *J. Am. Chem. Soc.* **1981**, *103*, 1891.

SCHEME 7. Synthesis of 4-Iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (11) and Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (33)^{a}



^{a} (a) Bu_3SnH, benzene, Δ, 93%; (b) KOH, MeOH, H_2O then 10% HCl, 96%; (c) (i) $(COCl)_2$, CH_2Cl_2, (ii) 2-mercaptopyridine-*N*-oxide sodium salt, benzene, 2-iodo-1,1,1-trifluoroiodoethane, DMAP, 65%; (d) *tert*-butyllithium, 20:1 heptane:diethylether, 0 °C.

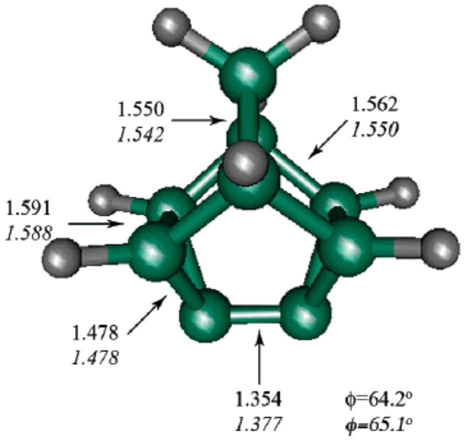


FIGURE 2. B3LYP/6-31G* and MP2/6-31G* (in italics) optimized geometries with carbon−carbon bond lengths (Å) and pyramidalization angles, ϕ, for pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-ene (**9**).

are only as good as the suitability of bicyclo[3.3.0]oct-1(5)-ene as the reference compound.

The heat of hydrogenation for **9** was calculated as the difference between the heat of formation of it and the corresponding alkane, pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (**33**). The calculated heats of hydrogenation, −101.0 kcal/mol (B3LYP/6-31G*) and −99.9 kcal/mol (MP2/6-31G*), have been corrected for the difference in zero-point energies of reactants and products and for the changes in heats of formation on going from 0 to 298 K. These values are similar to, although slightly more exothermic than, those computed for the tricyclo[3.3.*n*.0^{3,7}]-alk-3(7)-enes **6**.

As pointed out by Hrovat and Borden, the HOMO/LUMO gap in pyramidalized alkenes is much lower than that in normal alkenes. The observed bathochromic shifts in these compounds reflect a small decrease in the HOMO energy coupled with a much larger decrease in the LUMO energy. In the case of **9**, the calculated HOMO/LUMO energy gap is smaller (3.71 eV using B3LYP/6-31G*) than the related alkene **6** with $n = 1$ (4.79 eV using B3LYP/6-31G*). As noted by Borden,[13c] *tert*-butyllithium may transfer one electron into the very low-lying LUMO of pyramidalized alkenes such as **9** giving reduction products such as **33**. However, we have not observed **33** in any of the reactions of **12** with *tert*-butyllithium leading to **9**.

Finally, as first noted by Borden, highly pyramidalized alkenes such as **9** can be expected to have some diradical character, and thus at least a two-configuration wave function should be used. A coupled cluster ((CCSDCT)/6-31G*) single point energy was computed at the B3LYP/6-31G* optimized geometry to gauge the degree of multireference character in **9**. The configuration with the largest amplitude corresponds to the promotion of both electrons from the HOMO to the LUMO. The magnitude of this amplitude is significant (0.16) and indicates a notable degree of multireference character. We are currently investigating the thermodynamic properties of **9** and related alkenes comparing CCSD(T) and (2/2)CASPT2 methods and will report these results in due course.

Conclusions

In summary, we have provided strong evidence for the generation of the highly pyramidalized alkene, pentacyclo-[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-ene (**9**). Although **9** is highly reactive and undergoes rapid reaction with alkyllithiums present in the reaction mixture, we were able to trap this alkene as its Diels−Alder adduct with 1,3-diphenylisobenzofuran, 2,5-dimethylfuran, and spiro[2.4]hepta-4,6-diene. Even in the cases where **9** was trapped as its Diels−Alder adduct, alkyllithium addition products were present in the product mixture as side products. Thus, we are currently investigating the synthesis of precursors to **9** that do not utilize alkyllithiums for its generation. Attempted dehydrohalogenation of 4-iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]-nonane (**11**) to form **9** was unsuccessful.

Ab initio calculations on **9** predict pyramidalization angles (ϕ) of 64.2° and 65.1° at the B3LYP/6-31G* and MP2/6-31G* levels of theory, respectively. Thus, **9** is predicted to be one of the most highly pyramidalized alkenes for which there are experimental results to support its existence.

Experimental Section

Dimethyl Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene-8,9-dicarboxylate (13). A solution of 2,5-norbornadiene (129.5 mL, 117.3 g, 1.27 mol), dimethylacetylene dicarboxylate (48.3 mL, 56.0 g, 0.394 mol), and hydroquinone (0.631 g, 5.73 mmol) in 4 mL of methanol was heated under mild reflux for 14 h. The solvent and excess 2,5-norbornadiene were removed in vacuo, and the orange oil was recrystallized from absolute ethanol to yield diester **13** (67.4 g, 73.0%). mp 64−66 °C (lit.[20] 66 °C). IR (KBr): 1731, 1640 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.77 (s, 6H), 3.01 (t, $J = 1.1$ Hz, 2H), 2.24 (brs, 1H), 1.86 (m, 1H), 1.60 (m, 4H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 165.7 (C═O), 144.7 (C═), 57.0 (CH), 52.0 (CH), 51.6 (CH_3), 32.6 (CH_2), 27.2 (CH), 23.7 (CH). MS (EI) *m/z* (%): 234 ($M^{\bullet +}$, 2), 203 [$(M - MeO)^+$, 14], 187 (31), 174 [(M − HCOOMe), 46], 143 (22), 129 (18), 115 [(M− (COOMe− COOMe), 100). Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.64; H, 6.05.

Tetracyclo[4.3.0.0^{2,4}.0^{3,7}]non-8-ene-8,9-dicarboxylic Acid (14). To a solution of diester **13** (21.0 g, 89.7 mmol) in methanol (435 mL) was added a solution of KOH (52.3 g, 0.934 mol) in 171 mL of water. The yellow solution was stirred overnight at room temperature under nitrogen. The methanol was removed in vacuo, and the remaining solution was acidified to pH 2 with ca. 76.2 mL of 12 N HCl, diluted with 209 mL of water, extracted with ethyl acetate (3 × 100 mL), dried (anhydrous Na_2SO_4), and concentrated in vacuo to give **14** as an off-white solid (17.8 g, 96.3%). This solid was used without further purification in the following photochemical step. An analytical sample was obtained by recrystallization from acetone. mp 228−230 °C (lit.[20] 230 °C; 228−230 °C). IR (KBr): 1704, 1620, 1571 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD) δ: 3.30 (m, 2H), 2.21 (br d, 1H), 1.92 (m, J = 1.5 Hz, 1H), 1.67 (t, J = 1.5 Hz, 2H), 1.61 (dd, 2H). ^{13}C NMR (100.5 MHz, CD_3OD) δ: 167.3 (C═O), 148.3 (C═), 55.8 (CH), 52.1 (CH), 47.0 (CH_2), 27.3 (CH), 23.5 (CH). Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.11; H, 5.00.

Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4,5-dicarboxylic Acid (15). A vigorously stirred solution/suspension of **14** (7.50 g, 36.4 mmol) in anhydrous ether (1000 mL) was irradiated in a Rayonet photochemical reactor under nitrogen for 14 h. Most of the solvent was removed in vacuo (leaving ca. 100 mL of ether), and the suspended product was cooled in an ice bath and filtered under vacuum to furnish **15**. Yields were variable and ranged from 10% to 30% with typical yields around 20−25%. Diacid **15** was used in the following step without further purification. An analytical sample was obtained by recrystallization from acetone. mp 228−230 °C (lit.[20] 228−229 °C). IR (KBr): 3436, 1686, 1611, 1469, 1320, 1245 cm^{-1}. ^{1}H NMR (400 MHz, CD_3OD) δ: 2.88 (t, J = 2.6 Hz, 4H), 2.80 (brm, 2H), 1.98 (brs, 2H). ^{13}C NMR (100.5 MHz, CD_3OD) δ: 173.7 (C═O), 60.5 (CH_2), 52.0 (CH), 49.6 (C), 41.0 (CH). Anal. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89. Found: C, 64.13; H, 5.01.

5-(Methoxycarbonyl)pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-carboxylic Acid (17). The synthesis of **17** was accomplished using the method of Zwanenburg et al.,[23] with modifications. To a solution of diacid **15** (2.0 g, 9.7 mmol) in dry THF (50 mL) was added DCC (2.0 g, 9.7 mmol) all at once. The bright yellow suspension was stirred for 2 h, and the precipitated dicyclohexylurea (DCU) was filtered under vacuum. The filtrate was diluted with water (30 mL), extracted with CH_2Cl_2 (1 × 60 mL), dried (anhydrous Na_2SO_4), and concentrated in vacuo to give the anhydride **16** as an off-white solid. Yields for this reaction were often above 100% (105−110%), as not all of the precipitated DCU was removed via this procedure. Nonetheless, **16** was used without any further treatment or purification in the synthesis of the hemi ester **17**.

To a stirred solution of the anhydride **16** from the previous step in methanol (60 mL) was added a catalytic amount of sodium methoxide. After the mixture was stirred for 7.5 h, water (25 mL) was added and the mixture was extracted with CH_2Cl_2 (5 × 20 mL). The organic layer was dried (anhydrous Na_2SO_4) and concentrated in vacuo to yield an off-white crystalline solid (2.1 g, 98% two-step crude yield). The spectroscopic properties of **17** obtained by this procedure were identical to those previously reported.[23] This solid was used without further purification in the synthesis of **18**.

Methyl 5-Iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-carboxylate (18). A mixture of hemi ester **17** (2.02 g, 9.17 mmol), oxalyl chloride (11.5 mL, 23.0 mmol, 2.0 M in CH_2Cl_2, 2.5 equiv), and *N*,*N*-dimethylformamide (cat.) in dry CH_2Cl_2 (2.7 mL) was stirred at room temperature under argon for 1 h. The resulting mixture was concentrated in vacuo, and the residue was redissolved in dry thiophene-free benzene (16.2 mL). In a separate flask, a stirred suspension of *N*-hydroxypyridine-2-thione sodium salt (1.51 g, 10.12 mmol), 2,2,2-trifluoroiodoethane (4.5 mL, 9.59 g, 45.7 mmol), and DMAP (cat.) in dry thiophene-free benzene (33.1 mL) was brought to reflux and irradiated with a 300 W tungsten lamp under argon. The benzene solution of the acid chloride was added dropwise via cannula over 10−15 min, and the reaction was refluxed for an additional 1 h. After the reaction mixture was cooled, the solution was washed with water (1 × 15 mL), 12 N HCl (1 × 15 mL), water (1 × 15 mL), dried (50:50 anhydrous $MgSO_4$:K_2CO_3), and concentrated in vacuo to give **18** as a light brown oil. The iodoester was purified via column chromatography (silica gel). Elution with 95:5 petroleum ether/diethyl ether gave pure **18** (1.82 g, 65.6%). mp 47−48 °C. R_f 0.25 (95:5 pet ether/ether). IR: 2949, 1734, 1435, 1347, 1293, 1087 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.63 (s, 3H), 2.72−2.75 (m, 4H), 2.39 (q, 2H), 2.07 (d, 1H, J = 8.8 Hz), 1.77 (d of t, 1H, J = 8.8 Hz, 1.46 Hz). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 168.3 (C═O), 59.6 (CH_2), 53.8 (C), 51.8 (CH_3), 51.0 (CH), 49.5 (CH), 42.9 (CH), 7.4 (C−I). HRMS calcd for $C_{11}H_{11}IO_2$ ($M^{\bullet+}$) 301.9804, found 301.9814. Anal. Calcd for $C_{11}H_{11}IO_2$: C, 43.73; H, 3.67. Found: C, 43.80; H, 3.71.

5-Iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-carboxylic Acid. To a solution of iodoester **18** (420 mg, 1.39 mmol) in methanol (3.4 mL) was added a solution of sodium hydroxide (390 mg, 9.75 mmol) in 1.3 mL of water. The reaction mixture was stirred under nitrogen at room temperature for 12 h. At this time, the methanol was removed in vacuo, and the remaining solution was acidified to pH 2 with 12 N HCl (ca. 1.2 mL). The mixture was then extracted with ethyl acetate (4 × 10 mL), dried (anhydrous Na_2SO_4), and concentrated in vacuo to give the iodoacid as a white crystalline solid (374 mg, 93.5%). This solid was used without further purification in the synthesis of diiodide **12**.

4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12). A mixture of the crude iodoacid (1.17 g, 4.16 mmol) from the previous step, oxalyl chloride (5.1 mL, 2.0 M in CH_2Cl_2, 2.5 equiv), and *N*,*N*-dimethylformamide (cat.) in dry CH_2Cl_2 (3.1 mL) was stirred at room temperature under argon for 1 h. The resulting mixture was concentrated in vacuo, and the residue was redissolved in dry thiophene-free benzene (6.0 mL). In a separate flask, a stirred suspension of *N*-hydroxypyridine-2-thione sodium salt (670 mg, 4.49 mmol), 2,2,2-trifluoroiodoethane (2.0 mL, 4.26 g, 20.3 mmol, 5 equiv), and DMAP (cat.) in dry thiophene-free benzene (15 mL) was brought to reflux and irradiated with a 300 W tungsten lamp under argon. The benzene solution of the acid chloride was added dropwise via cannula over 10−15 min, and the reaction was refluxed for an additional 1 h. After the reaction mixture was cooled, the solution was washed with water (1 × 15 mL), 12 N HCl (1 × 15 mL), water (1 × 15 mL), dried (50:50 anhydrous $MgSO_4$:K_2CO_3), and concentrated in vacuo to give **12** as a light brown oil. The diiodide was purified via column chromatography (silica gel). Elution with petroleum ether gave pure **12** (0.800 g, 53.1%) as a colorless oil. Crystallization from pentane at −30 °C yielded colorless crystals. mp 47−48 °C. R_f 0.5 (petroleum ether). IR, no significant bands. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.75 (s, 2H), 2.39 (t, 4H, J = 2.6 Hz), 1.97 (s, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 58.2 (CH_2), 49.9 (CH), 43.8 (CH), 22.9 (C−I). HRMS calcd for $C_9H_8I_2$ ($M^{\bullet+}$) 369.8715, found 369.8721.

Reaction of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with *n*-Butyllithium To Form Bi(5-iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-yl) (22), 4-Iodo-5-{pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-yl}pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (23), 4-Butyl-5-iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (24), 4-Butylpentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (25), and 4-*n*-Butyl-5-{5-iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-yl}pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (26). To a solution of diiodide **12** (320 mg, 0.865 mmol) in dry THF (9.4 mL) at −78 °C was added dropwise a solution of *n*-butyllithium in hexanes (850 μL, 1.20 equiv, 1.04 mmol, 1.22 M) under argon. The mixture was allowed to warm to 0 °C, stirred at this temperature for 2 h, and quenched with methanol (5 mL). Water (15 mL) was added, and the mixture was extracted with CH_2Cl_2 (2 × 25 mL), dried (Na_2SO_4), and concentrated in vacuo. GCMS of the crude reaction mixture showed the following product mixture: **22** (58.2% area ratio), **23** (13.9%), **24** (3.5%, $M^{\bullet+}$ = 300), **25** (11.0% , $M^{\bullet+}$ = 174), **26** (1%). The entire mixture was subjected to silica gel chromatography using petroleum ether as the eluent. Additional product **22** (white crystalline solid) was obtained pure from this first column. To obtain pure samples of **23** and **26**, a second silica gel column was performed.

22: mp 103−104 °C. IR, no significant bands. ^{1}H NMR (600 MHz, $CDCl_3$) δ: 2.84−2.85 (m, 2H), 2.59−2.60 (m, 2H), 2.38−2.39 (m, 2H), 2.33−2.34 (m, 2H), 2.28−2.29 (m, 2H), 1.95−1.97 (d of m, 2H), 1.71−1.72 (d of m, 2H), 1.66 (m, 2H). ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 58.8 (CH_2), 55.1 (C), 50.6 (CH), 49.4 (CH), 46.2 (CH), 46.1 (CH), 43.5 (CH), 43.1 (CH), 19.0 (C−I). HRMS calcd for $C_{18}H_{16}I_2$ ($M^{\bullet+}$) 485.9342, found 485.9332. Anal. Calcd for $C_{18}H_{16}I_2$: C, 44.47; H, 3.32. Found: C, 44.15; H, 3.37.

23: IR, no significant bands. ^{1}H NMR (600 MHz, C_6D_6) δ: 2.64 (m, 2H), 2.36 (m, 1H), 2.35 (m, 2H), 2.20−2.21 (q, 2H, $J = 4$ Hz), 2.02 (m, 2H), 1.90 (br d, 2H), 1.85 (m, 2H), 1.77 (m, 2H), 1.75 (d of t, 1H), 1.49 (d of t, 1H, $J = 1.5$ Hz). ^{13}C NMR (150.9 MHz, C_6D_6) δ: 60.3 (CH_2), 59.4 (CH_2), 55.5 (C) 53.7 (C), 50.4 (CH), 46.6 (CH), 45.4 (CH), 43.9 (CH), 43.3 (CH), 42.5 (CH), 40.9 (CH), 18.1 (C−I). HRMS calcd for $C_{18}H_{17}I$ $[(M + H)^+]$ 361.0453, found 361.0527.

26: IR, no significant bands. ^{1}H NMR (600 MHz, $CDCl_3$, −55 °C) δ: 2.68 (br s, 1H), 2.57 (br s, 1H), 2.46 (br s, 1H), 2.34 (br s , 1H), 2.28 (m, 1H), 2.22 (m, 1H), 2.08 (m, 2H), 1.84−1.96 (m, 3H), 1.75 (s, 1H), 1.62−1.69 (m, 3H), 1.52−1.53 (m, 1H), 1.48−1.51 (m, 1H), 1.18−1.28 (m, 2H), 0.88−0.96 (m, 1H), 0.83−0.88 (m, 1H), 0.81 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (150.9 MHz, $CDCl_3$) δ: 59.6 (CH_2), 58.8 (CH_2), 53.2 (C), 53.2 (C), 51.1 (C), 50.3 (CH), 48.5 (CH), 46.6 (CH), 45.5 (CH), 44.4 (CH), 44.2 (CH), 43.6 (CH), 42.9 (CH), 42.2 (CH), 42.1 (CH), 42.1 (CH), 41.9 (CH), 29.5 (CH_2), 28.9 (CH_2), 23.4 (CH_2), 19.8 (C−I), 14.3 (CH_3). HRMS calcd for $C_{22}H_{25}I$ $[(M + H)^+]$ 417.1079, found 417.1245.

24: MS (EI), *m*/*z* % 300 ($M^{\bullet+}$, 14), 257 $[(M - Pr)^+$, 11], 131 (55), 117 (100), 91 (43).

25: MS (EI), *m*/*z* % 174 ($M^{\bullet+}$, 7), 131 $[(M - Pr)^+$, 56], 117 (100), 91 (43).

Reaction of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with *n*-Butyllithium in the Presence of DPIBF To Form 1,11-Diphenyl-18-oxa-octacyclo[9.6.1.0^{2,4}.0^{2,10}.0^{3,7}.0^{5,9}.0^{8,10}.0^{12,17}]octadeca-12,14,16-triene (27). To a solution of diiodide **12** (275 mg, 0.744 mmol) and 1,3-diphenylisobenzofuran (241 mg, 0.893 mmol, 1.2 equiv) in dry THF (8.0 mL) at −78 °C was added dropwise a solution of *n*-butyllithium in hexanes (732 μL, 0.893 mmol, 1.2 equiv, 1.22 M in hexanes) under argon. The mixture was allowed to warm to 0 °C, stirred at this temperature for 2 h, and quenched with methanol (5 mL). Water (30 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 30 mL), dried (Na_2SO_4), and concentrated in vacuo. The Diels−Alder adduct is moderately unstable to silica gel chromatography, and thus isolation and purification was carried out in one of two ways. (1) The crude product was dissolved in CH_2Cl_2 and maleic anhydride was added, and the mixture was allowed to stand at room temperature for 1 h. Pentane (5 mL) was added to precipitate out the maleic anhydride−DPIBF adduct and excess maleic anhydride. This mixture was filtered, and the filtrate was concentrated in vacuo. The resultant off-white solid was recrystallized by slow evaporation from benzene to yield pure product. (2) The crude product was subjected to silica gel chromatography using gradient elution of 100% petroleum ether to 80:20 petroleum ether:diethyl ether. mp 243−244 °C. IR: 3043, 2973, 1602, 1499, 1448, 964, 742, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.3−7.5 (m, 10H), 6.94−7.16 (m, 4H), 2.79−2.88 (brs, 2H), 2.07−2.3 (m, 4H), 1.65−1.74 (brs, 2H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 149.0 (C), 136.6 (C), 128.3 (CH), 127.5 (CH), 126.3 (CH), 125.2 (CH), 118.9 (CH), 87.7 (C), 69.6 (C), 58.3 (CH_2), 50.7 (CH), 48.7 (CH), 41.6 (CH), 37.6 (CH). Anal. Calcd for $C_{29}H_{22}O$: C, 90.12; H, 5.74. Found: C, 90.03; H, 5.84.

Reaction of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with *tert*-Butyllithium To Form 11, 22, 23, and Bi(pentacyclo-[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]non-4-yl) (28). To a solution of diiodide **12** (609 mg, 1.65 mmol) in dry heptane (20.6 mL) and dry ether (1.5 mL) at −78 °C was added dropwise a solution of *tert*-butyllithium in heptane (2.40 mL, 3.61 mmol, 1.53 M) under argon. The mixture was allowed to warm to 0 °C, stirred at this temperature for 2 h, and quenched with methanol (10 mL). Water (40 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 60 mL), dried (Na_2SO_4), and concentrated in vacuo to yield a crude mixture of **11**, **22**, **23**, and **28** (332 mg total) as a light brown oil. GCMS of the crude reaction mixture showed the following products: **11** (24.3% by GCMS), **22** (46.2%), **23** (11.7%), and **28** (6.9%). The entire mixture was subjected to silica gel chromatography using petroleum ether as the eluent. Additional product **22** (white crystalline solid) was obtained pure from this first column. To obtain pure samples of **11**, **23**, and **28**, a second silica gel column was performed. Dimer **28** was obtained as a colorless oil.

28: IR, no significant bands. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.54−2.55 (br m, 4H), 2.03−2.06 (t of d, 2H, $J = 1.8$ Hz, $J = 6.5$ Hz), 1.90−1.95 (m, 4H), 1.73−1.83 (m, 8H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 59.7 (CH_2), 51.8 (C), 44.8 (CH), 42.8 (CH), 40.6 (CH), 39.3 (CH). HRMS calcd for $C_{18}H_{18}$ ($M^{\bullet+}$) 234.1409, found 234.1408.

Reaction of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with *tert*-Butyllithium in the Presence of DPIBF To Form 1,11-Diphenyl-18-oxa-octacyclo[9.6.1.0^{2,4}.0^{2,10}.0^{3,7}.0^{5,9}.0^{8,10}.0^{12,17}]-octadeca-12,14,16-triene (27). To a solution of diiodide **12** (304 mg, 0.822 mmol) and 1,3-diphenylisobenzofuran (267 mg, 0.986 mmol, 1.2 equiv) in dry heptane (10.3 mL) and dry ether (731 μL) at −78 °C was added dropwise a solution of *tert*-butyllithium in heptane (1.2 mL, 1.40 mmol, 1.53 M) under argon. The mixture was allowed to warm to 0 °C, stirred at this temperature for 2 h, and quenched with methanol (6 mL). Water (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 20 mL), dried (Na_2SO_4), and concentrated in vacuo to yield crude **27** (418 mg). The Diels−Alder adduct is moderately unstable to silica gel chromatography, and it was purified as described previously to furnish 143 mg (45%) of pure, crystalline **27**.

Reaction of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with *tert*-Butyllithium in the Presence of 2,5-Dimethylfuran To Form 1,11-Dimethyl-14-oxa-heptacyclo[9.2.1.0^{2,4}.0^{2,10}.0^{3,7}.0^{5,9}.0^{8,10}]-tetradec-12-ene (29). To a solution of 2,5-dimethylfuran (2.2 mL, 20.8 mmol, 20 equiv) in dry pentane (250 μL) and dry ether (209 μL) at −78 °C was added dropwise a solution of *tert*-butyllithium in pentane (1.8 mL, 3.12 mmol, 1.70 M, 3 equiv) under argon. To this solution was added a solution of diiodide **12** (385 mg, 1.04 mmol) in dry pentane (3.0 mL). The mixture was stirred at −78 °C for 30 min, then allowed to warm to 0 °C, stirred at this temperature for 2 h, and quenched with methanol (6.6 mL). Water (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 30 mL), dried (Na_2SO_4), and concentrated in vacuo to yield crude **29** (128 mg). The Diels−Alder adduct is unstable to silica gel chromatography, and thus isolation and purification was carried out by chromatography using a C-18 stationary phase. Elution with 75:25 methanol:water gave pure **29** (47.5 mg, 22.0%) as a semi-volatile liquid (care must be taken not to subject **29** to high vacuum). IR (gas phase): 3038, 2981, 2953, 2867, 1445, 1384, 1312, 1253, 1144, 859 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.39 (s, 2H), 2.99−3.01 (m, 1H), 2.86−2.87 (m, 1H), 2.10−2.12 (m, 2H), 1.79−1.81 (m, 2H), 1.73 (s, 2H), 1.33 (s, 6H). ^{13}C NMR (100.5 MHz, $CDCl_3$) δ: 140.8 (CH), 85.3 (C), 70.3 (C), 58.5 (CH_2), 50.8 (CH), 50.8 (CH), 38.3 (CH), 36.1 (CH), 15.8 (CH_3). HRMS calcd for $C_{15}H_{16}O$ ($M^{\bullet+}$) 212.1201, found 212.1200.

Reaction of of 4,5-Diiodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (12) with *tert*-Butyllithium in the Presence of Spiro[2.4]hepta-4,6-diene To Form Spiro[cyclopropane-1,14′-heptacyclo[9.2.1.0^{2,4}.0^{2,10}.0^{3,7}.0^{5,9}.0^{8,10}]tetradecane]-12′-ene (30). To a solution of spiro[2.4]hepta-4,6-diene (0.810 μL, 8.10 mmol, 7.5 equiv) in dry pentane (250 μL) and dry ether (216 μL) at −78 °C was added dropwise a solution of *tert*-butyllithium in pentane (1.9 mL, 3.25 mmol, 1.7 M, 3 equiv) under argon. To this solution was added a solution of diiodide **12** (401 mg, 1.08 mmol) in dry pentane (3.2 mL). The mixture was stirred at −78 °C for 10 min, then allowed to warm to 0 °C, stirred at this temperature for 2 h, and quenched with methanol (6.9 mL). Water (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 30 mL), dried (Na_2SO_4), and concentrated in vacuo to yield crude **30** (470 mg). The Diels−Alder adduct is unstable to silica gel chromatography, and thus isolation and purification was carried out by chromatography using a C-18 stationary phase. Gradient elution with methanol:water from 88:12 to 100% methanol) gave semi-pure **30** (44.2 mg, 20%) as a semi-volatile liquid (care must be taken not to subject **30** to high vacuum). A second column was run to obtain an analytical sample of pure **30** (28.1 mg, 13%). IR (gas phase): 3070, 3040, 2977, 2948, 2864, 1286, 1007, 920, 815, 753, 689 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 6.40 (t, 2H, J = 1.8 Hz), 2.86−2.89 (m, 1H), 2.71−2.74 (m, 1H), 1.89−1.93 (m, 2H, J = 4.0 Hz, 3.7 Hz), 1.88 (t, 2H, J = 1.8 Hz), 1.73−1.77 (m, 2H, J = 4.0 Hz, 3.7 Hz), 1.72 (t, 2H, J = 1.5 Hz), 0.62−0.68 (m, 2H), 0.47−0.52 (m, 2H). ^{13}C NMR (100.5 MHz, CDCl$_3$) δ: 137.3 (CH), 66.0 (C), 58.4 (CH$_2$), 50.4 (C), 49.8 (CH), 49.3 (CH), 48.7 (CH), 39.7 (CH), 36.6 (CH), 8.3 (CH$_2$), 5.9 (CH$_2$). HRMS calcd for $C_{16}H_{16}$ (M$^{\bullet+}$) 208.1252, found 208.1236.

Methyl Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-carboxylate (31). A solution of iodoester **18** (651 mg, 2.15 mmol), tri-*n*-butyltin hydride (0.95 mL), and dry benzene (9.2 mL) was heated at reflux under nitrogen for 27 h. After the mixture was cooled to room temperature, the benzene was removed in vacuo and the residue was dissolved in diethyl ether (9.4 mL). The ethereal solution was then treated with excess 10% KF in water (10 mL). After the mixture was stirred for several hours, the precipitated tri-*n*-butyltin fluoride was filtered under vacuum, and the filtrate was dried (Na$_2$SO$_4$). The ether was removed in vacuo to yield an off-white solid. The ester **31** was purified via column chromatography (silica gel). Elution with 95:5 petroleum ether/diethyl ether gave pure **31** (0.352 g, 92.7%). mp 48−50 °C (lit.[23] 48−49 °C) °C. R_f 0.30 (97.5:2.5 pet ether/ether). IR: 2951, 1711, 1437, 1373, 1299, 1203, 1092, 1061 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 3.66 (s, 3H), 2.69 (brs, 4H), 2.51−2.52 (t of d, 1H), 2.08−2.09 (m, 2H), 1.89−1.91 (d of m, 1H), 1.82−1.84 (d of m, 1H). ^{13}C NMR (100.5 MHz, CDCl$_3$) δ: 171.5 (C=O), 60.3 (CH$_2$), 52.8 (C), 51.7 (CH$_3$), 51.2 (CH), 43.0 (CH), 39.5 (CH), 37.0 (CH). MS (EI), m/z % 176 (M$^{\bullet+}$, 3), 161 [(M − Me)$^+$, 4], 145 [(M − OMe), 13], 133 (4), 117 (100), 91 (23).

Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane-4-carboxylic Acid (32). To a solution of ester **31** (429 mg, 2.44 mmol) in methanol (6.0 mL) was added a solution of sodium hydroxide (1 g, 25 mmol) in 2.5 mL of water. The reaction mixture was stirred under nitrogen at room temperature overnight. At this time, the methanol was removed in vacuo and the remaining organic washed with ether (2 × 5 mL). The aqueous layer was then acidified to pH 2 with 12 N HCl. The mixture was then extracted CH$_2$Cl$_2$ (3 × 10 mL), dried (anhydrous Na$_2$SO$_4$), and concentrated in vacuo to give **32** as a white crystalline solid (378 mg, 96%). This solid was used without further purification in the synthesis of monoiodide **11**.

4-Iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (11). A mixture of monoacid **32** (378 mg, 2.33 mmol), oxalyl chloride (2.9 mL, 2 M in CH$_2$Cl$_2$, 5.84 mmol), *N*,*N*-dimethylformamide (1 drop), and dry dichloromethane (1.7 mL) was stirred at room temperature until homogeneous (1 h), then concentrated in vacuo and released to nitrogen. The residue was then taken up in dry thiophene-free benzene (4.1 mL). Separately, a well-stirred suspension of *N*-hydroxypyridine-2-thione sodium salt (381.6 mg, 2.56 mmol) in dry thiophene-free benzene (8.4 mL) containing 2,2,2-trifluoroiodoethane (1.1 mL, 11.6 mmol) and a catalytic amount of 4-*N*,*N*-dimethylaminopyridine was brought to reflux and irradiated with a 300 W tungsten lamp. The benzene solution of acid chloride was added dropwise over 10−15 min via cannula. After a further 1 h at reflux, the solution was cooled, washed successively with portions of water (1 × 15 mL), conc. HCl (1 × 15 mL), and water (1 × 15 mL), dried (50:50 anhydrous MgSO$_4$:K$_2$CO$_3$), and concentrated in vacuo. The light brown oil was purified by column chromatography with petroleum ether to furnish monoiodide **11** (371 mg, 65%) as a colorless oil. R_f 0.5 (petroleum ether). IR, no significant bands. ^{1}H NMR (400 MHz, CDCl$_3$) δ: 2.71 (m, 2H), 2.41 (t of d, 1H, J = 6.2 Hz, J = 2.2 Hz), 2.26 (d, 2H, J = 1.8 Hz), 2.05 (m, 2H), 2.02 (d, 1H, J = 8.8 Hz), 1.70 (dm, 1H, J = 8.8 Hz, 2.2 Hz, 1.5 Hz). ^{13}C NMR (100.5 MHz, CDCl$_3$) δ: 58.5 (CH$_2$), 50.0 (CH), 47.8 (CH), 43.5 (CH), 40.8 (CH), 11.4 (C−I). HRMS calcd for C_9H_9I (M$^{\bullet+}$) 243.9749, found 243.9778.

Reaction of 4-Iodopentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (11) with *tert*-Butyllithium To Form Pentacyclo[4.3.0.0^{2,4}.0^{3,8}.0^{5,7}]nonane (33). To a solution of monoiodide **11** (180 mg, 0.737 mmol) in dry heptane (7.0 mL) and dry ether (423 μL) at −78 °C was added dropwise a solution of *tert*-butyllithium in heptane (1.45 mL, 2.21 mmol, 1.53 M) under argon. The mixture was allowed to warm to 0 °C, stirred at this temperature for 30 min, and quenched with methanol (3 mL). Water (20 mL) was added, and the mixture was extracted with CH$_2$Cl$_2$ (3 × 20 mL), dried (Na$_2$SO$_4$), and carefully concentrated in vacuo to yield **33**, whose spectral properties were identical to those previously reported.[30]

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Supporting Information Available: Copies of NMR spectra, including 2-D NMR spectra for all compounds. X-ray crystallographic data (ORTEP drawing and experimental) for compound **27**. Cartesian coordinates and total energy for compound **9** [B3LYP/6-31G(d) and MP2/6-31g(d)]. This material is available free of charge via the Internet at http://pubs.acs.org.

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