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Polycycle Synthesis

Straightforward Synthesis of a Vicinal Double-Bridgehead Iodo Trimethylsilyl Octacycle: Unprecedented Lack of Reactivity of the Silyl Group in the Presence of Fluoride Anions

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Dedicated to Professor Alejandro F. Barrero[‡]

Abstract: A convenient synthesis of an octacyclic compound containing an iodo and a trimethylsilyl group in vicinal double-bridgehead positions, as a possible precursor of a pyramidalized alkene, is described. The key step of the synthesis consists of a double nucleophilic substitution of two neopentyl-type iodides by cyclopentadienide anions followed by two intramolecular Diels–Alder cycloadditions. All attempts to generate the expected pyramidalized alkene from the above precursor on reaction with different sources of fluoride failed. This octacyclic compound, which contains two disubstituted C=C bonds, underwent a chemo- and stereoselective Pd^0-catalyzed co-cyclotrimerization with dimethyl acetylenedicarboxylate to give a nonacyclic cyclohexadiene derivative that can be aromatized upon reaction with CsF or transformed into a related fluoride upon reaction with AgF.

Introduction

The generation and reactions of highly pyramidalized alkenes have been the subject of many publications and several reviews[1] since the first alkene of this type, 9,9′-dehydrodianthracene was reported by Weinshenker and Greene in 1968.[2] Worthy of mention are 1,2-dehydrocubane (cubene),[3] 1,5-dehydroquadricyclane,[4] tricyclo[3.3.1.$0^{3,7}$]non-3(7)-ene,[5] tricyclo[3.3.0.$0^{3,7}$]oct-1(5)-ene and derivatives,[6] pentacyclo[4.3.0.$0^{2,4}$.$0^{3,8}$.$0^{5,7}$]non-4-ene,[7] and 3,4,8,9-tetramethyltetracyclo[4.4.0.$0^{3,9}$.$0^{4,8}$]dec-1(6)-ene.[8] These alkenes can be easily trapped as Diels–Alder adducts with different dienes and, in the absence of dienes, they usually dimerize to form cyclobutane derivatives (Figure 1).

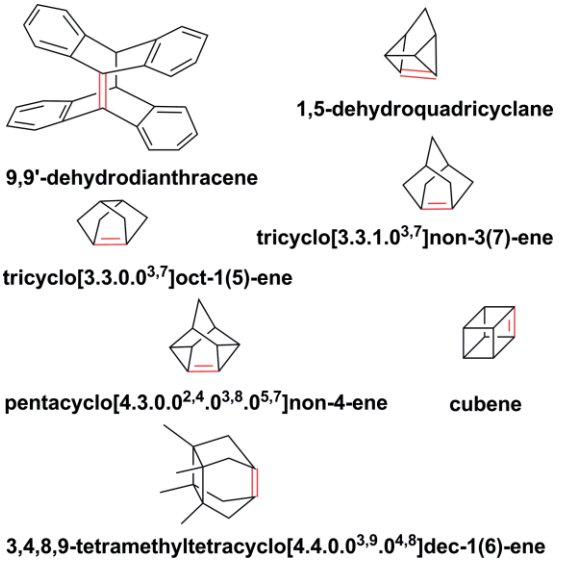

Figure 1. Structures of significant pyramidalized alkenes.

The more highly pyramidalized alkenes are usually generated by reaction of a vicinal double-bridgehead diiodide or dibromide with an organolithium reagent in THF, sodium/potassium alloy, or with molten sodium in boiling 1,4-dioxane. However, these conditions are drastic and sometimes it is desirable to apply milder conditions. For instance, when cubene was gener-

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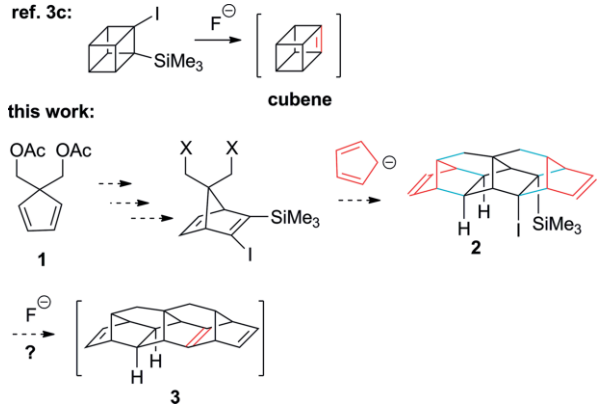
ated from 1,2-diiodocubane by reaction with an organolithium reagent, it reacted very rapidly with any of the organolithiums present at its generation.[3a] This fact restricted the study of the behavior of cubene towards other reagent probes. Only 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene was found to be a moderate organolithium-compatible trap able to compete with the organolithium addition process, and the corresponding Diels–Alder adduct could be isolated. Lukin and Eaton developed a milder procedure to generate cubene by reaction of a vicinal iodo- or bromo-trimethylsilyl precursor with fluoride (Scheme 1).[3c]



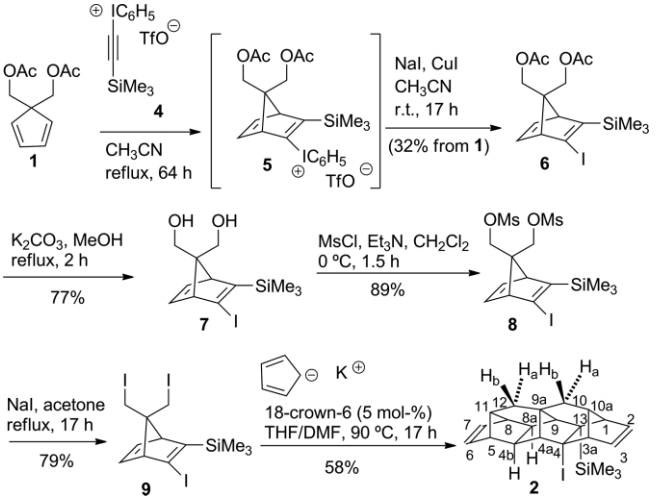
Scheme 1. Previously described generation of cubene[3c] and planned preparation of pyramidalized alkene **3** from octacycle **2**.

Moreover, the preparation of the diiodide precursor in the series of tricyclo[3.3.0.0^{3,7}]oct-1(5)-ene derivatives implies a long sequence of transformations, the key step consisting of a double iododecarboxylation of a not easily available 1,2-dicarboxylic acid upon reaction with iodosobenzene diacetate (IBDA) and iodine under photochemical conditions.[6] Also, the preparation of 1-iodo- or 1-bromo-2-(trimethylsilyl)cubane requires a long sequence of transformations, the trimethylsilyl group being introduced by the reaction of a carbanion with trimethylsilyl chloride.[3a,3b]

We planned the preparation of the vicinal double-bridgehead iodo-trimethylsilyl polycycle **2** from the recently described[9] 1,1-disubstituted cyclopentadiene **1** in a process not requiring any iododecarboxylation step or reaction of a carbanion with trimethylsilyl chloride, as well as the generation of the pyramidalized alkene **3** by a procedure similar to that used by Lukin and Eaton to generate cubene to study its reactivity (Scheme 1).

Results and Discussion

Octacycle **2** was prepared according to Scheme 2. Cyclopentadiene **1** was fully transformed into the corresponding Diels–Alder adduct **5** upon reaction with the known[10] phenyl[(trimethylsilyl)ethynyl]iodonium triflate **4** in anhydrous acetonitrile at reflux for 64 h. This adduct was directly treated with NaI and CuI[11] at room temperature for 17 h to give the substituted norbornadiene **6** in 32 % overall yield. By contrast, when diene **1** was treated with (iodoethynyl)trimethylsilane in *o*-dichlorobenzene at 180 °C for different reaction times, mixtures of **6** and the starting diene, which could not be separated by silica gel column chromatography, were always obtained.



Scheme 2. Preparation of octacycle **2** from cyclopentadiene **1**.

Basic methanolysis of diacetate **6** gave diol **7** in 77 % yield, which was mesylated under standard conditions to give dimesylate **8** in 89 % yield. The reaction of **8** with sodium iodide in acetone at reflux gave triiodide **9** in 79 % yield. Finally, the reaction of a solution of **9** in anhydrous DMF with potassium cyclopentadienide, prepared from freshly distilled cyclopentadiene and 30 % KH in mineral oil in THF, in the presence of 18-crown-6 (5 mol-%) gave octacycle **2** in 58 % yield. This transformation consists of two nucleophilic substitutions of neopentyl-type iodides by the cyclopentadienide anion followed by two intramolecular Diels–Alder reactions. The obtained yield corresponds to an average 87 % per synthetic stage. Although the intramolecular Diels–Alder reaction with the less substituted alkene moiety was to be expected,[9] this was not the case for the more substituted, non-electron-deficient, and hindered alkene. Although octacycle **2** was fully characterized by spectroscopic means as well as by elemental analysis and accurate mass measurement, its structure was confirmed by X-ray diffraction analysis (Figure 2).

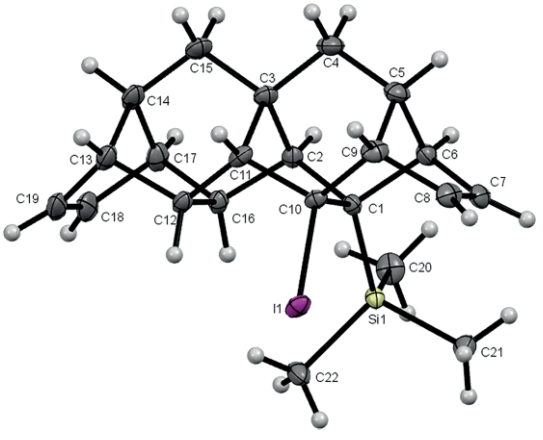
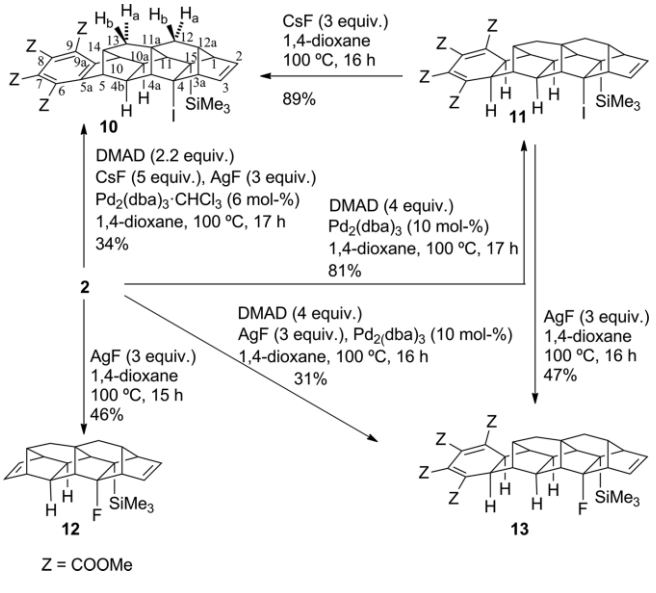


Figure 2. ORTEP representation of octacycle **2**.

All attempts to generate pyramidalized alkene **3** from octacycle **2** and trap it as a Diels–Alder adduct with different dienes

left the starting compound unchanged, in spite of using excess of CsF, alone or in combination with AgF, or tetrabutylammonium fluoride as fluoride source in the presence of excess of furan, 1,3-diphenylisobenzofuran, tetraphenylcyclopentadienone, or anthracene as dienes. To the best of our knowledge, there is no precedent for this lack of reactivity of the trimethylsilyl group in the presence of fluoride anions and it might be due to the steric hindrance experienced by the silyl group.

Bearing in mind that strained cyclic intermediates can be stabilized by coordination to transition metals,[12] we considered the possibility of generating a transient palladium complex of alkene **3** initiated by the oxidative addition of palladium(0) to iodo-octacycle **2**. Subsequent reaction of the plausible palladium–alkene complex with two molecules of dimethyl acetylenedicarboxylate (DMAD) could lead to the formation of the corresponding co-cyclotrimerization product, similarly to the palladium-catalyzed [2+2+2] co-cycloaddition of arynes or cyclic alkynes with DMAD.[13] However, the reaction of **2** with an excess of DMAD in the presence of CsF, AgF, and a catalytic amount of tris(dibenzylideneacetone)dipalladium(0)·$CHCl_3$ ($[Pd_2(dba)_3$·$CHCl_3]$, 6 mol-%) in 1,4-dioxane at reflux gave in 34 % yield nonacycle **10**, a compound that contains the vicinal iodo and trimethylsilyl groups of the starting compound and a new benzene ring, fused to polycycle **2** at the C=C bond more remote from the iodine and trimethylsilyl substituents and hence less affected by the steric effect of the trimethylsilyl group (Scheme 3). The structure of this compound was clearly established by X-ray diffraction analysis (Figure 3) and was fully characterized on the basis of its spectroscopic data and elemental analysis. Once again, the trimethylsilyl group remained unaffected under these conditions. Thus, the palladium catalyst does not seem to promote the formation of pyramidalized alkene **3** or a palladium complex derivative.



Scheme 3. Several transformations of octacycle **2**.

It is known that palladium(0) catalyzes the co-cyclotrimerization of acetylenes with electron-deficient or some bicyclic olefins.[14] In particular, norbornene reacts with 2 equivalents of

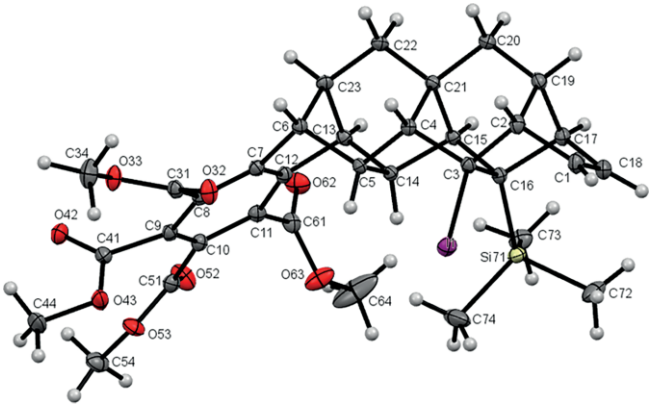


Figure 3. ORTEP representation of nonacycle **10**.

DMAD in the presence of a catalytic amount of tetrakis(methoxycarbonyl)palladiacyclopentadiene to give stereoselectively a cyclohexadiene derivative.[15] When compound **2** was treated with DMAD in the presence of $[Pd_2(dba)_3]$ (10 mol-%) in 1,4-dioxane at reflux, nonacycle **11** was obtained in high yield. As before, the structure and configuration of this compound was clearly established by X-ray diffraction analysis (Figure 4). It was also fully characterized on the basis of its spectroscopic data and elemental analysis. As before, the more remote C=C bond in **2** with respect to the trimethylsilyl and iodine substituents is the only one that reacts, in spite of using an excess of DMAD, a fact reasonably associated with the steric hindrance of the trimethylsilyl group, which includes not only the carbocyclic skeleton but also the vicinal iodide substituent.

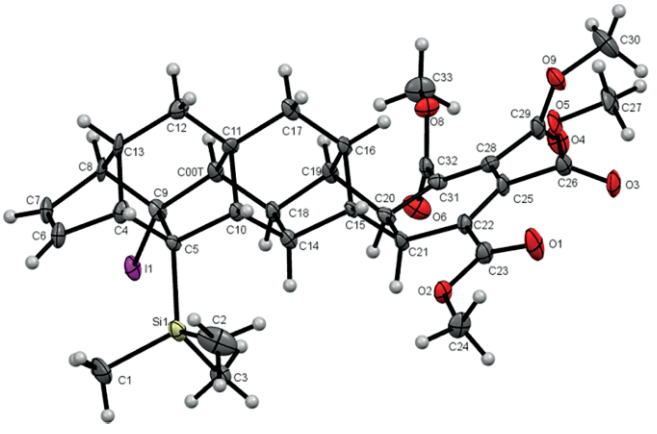


Figure 4. ORTEP representation of nonacycle **11**.

Taking into account the fact that the conversion of **11** into **10** might require an oxidant, compound **11** was treated with an excess of AgF (3 equiv.) under similar reaction conditions to those used before. Worthy of note, compound **13**, which still contains the cyclohexadiene subunit and with the iodine atom having been replaced by fluorine, was the only isolated product (47 % yield) from this reaction, the formation of compound **10** not being observed. The structure and configuration of compound **13** was also established by X-ray diffraction analysis (Figure 5) and fully characterized on the basis of its spectroscopic data and elemental analysis. Compound **13** was also obtained,

although in only 31 % yield, upon reaction of octacycle **2** with excess DMAD in the presence of $[Pd_2(dba)_3]$ (10 mol-%) and AgF (3 equiv.) in 1,4-dioxane at reflux. As expected, when compound **2** was treated with excess AgF in 1,4-dioxane at reflux, octacycle fluoride **12** was obtained in 46 % yield. Bridgehead iodides have previously been transformed into the corresponding fluorides upon reaction with different reagents, such as XeF_2,[16] elemental fluorine,[17] nitronium tetrafluoroborate/pyridine polyhydrogen fluoride or sodium nitrate/pyridine polyhydrogen fluoride,[18] and HgF_2,[19] the last reagent giving better results than AgF for the studied halogenated adamantanes. It seems reasonable that the conversion of compounds **11** and **2** into **13** and **12**, respectively, takes place through an S_N1-type mechanism,[19] the β-silicon *syn* effect helping to stabilize the pyramidalized intermediate carbocation.[20]

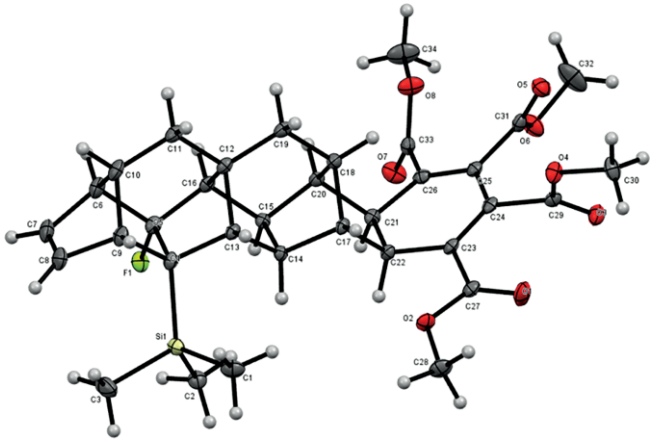
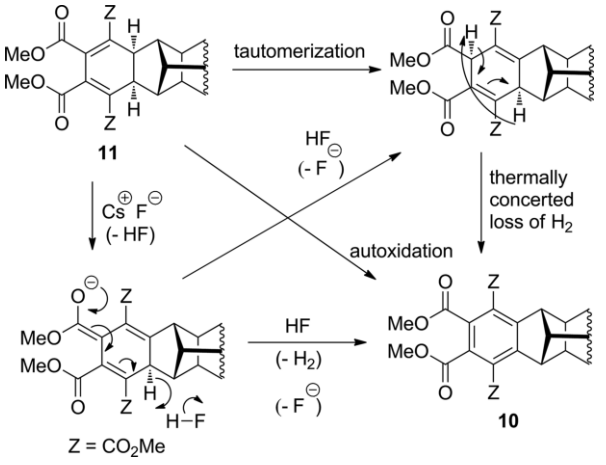


Figure 5. ORTEP representation of nonacycle **13**.

Worthy of note, the reaction of nonacycle **11** with excess CsF in 1,4-dioxane at reflux gave compound **10** in 89 % yield as the only isolated product. A possible explanation of this transformation is given in Scheme 4. The fluoride could catalyze the tautomerizaton of **11** to a *cis*-1,4-dihydrobenzene derivative, which might lose hydrogen in a concerted (4q+2)-allowed process, as recently proposed in a related dehydrogenation.[21] An alternative ionic mechanism for the dehydrogenation of **11** is also shown in Scheme 4. Alternatively, although this transformation was carried out under Ar, we cannot exclude the possibility of an autoxidation process.[22]

The inability to generate pyrimidalized alkene **3** from **2** upon reaction with different sources of fluoride under different conditions, including the presence of AgF to increase the leaving group capacity of the iodide group, is in striking contrast to previous works in which vicinal halo-trimethylsilyl compounds were transformed into reactive intermediates such as pyramidalized alkenes[3c] or benzynes[23] upon reaction with diverse fluoride sources. The steric hindrance of the trimethylsilyl group in this compound might be responsible of this lack of reactivity. In accord with the indications of the referees, a mixture of compound **2** and a great excess of tetrabutylammonium fluoride (TBAF, from a 1 M solution in THF) was heated at 150 °C for 19 h, after the solvent had been distilled off. The partial degradation of TBAF to tributylamine was observed, most of



Scheme 4. Mechanistic proposals for the CsF-promoted conversion of nonacycle **11** into compound **10**.

the starting **2** was recovered, and some degradation products were also detected.

CCDC 1522945 (for **2**), 1522948 (for **10**), 1522946 (for **11**), and 1522947 (for **13**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Conclusions

Pyramidalized alkene **3** could not be generated from polycycle **2** upon reaction with different sources of fluoride under different reaction conditions. Work is in progress to prepare a polycycle with the same skeleton as **2** but containing a second iodine atom instead of the trimethylsilyl group. Based on our previous experience, the desired pyramidalized alkene **3** might be generated from this diiodide.

Experimental Section

General: Melting points were determined in open capillary tubes with an MFB 595010M Gallenkamp melting-point apparatus. All new compounds were fully characterized by their analytical (melting point, elemental analysis, and/or accurate mass measurement) and spectroscopic data (IR, ^1H, ^{13}C, and ^{19}F NMR) and, in several cases, X-ray diffraction analysis. Assignments given for the NMR spectra are based on DEPT, COSY, NOESY, $^1H/^{13}C$ single quantum correlation (gHSQC sequence) and $^1H/^{13}C$ multiple bond correlation (gHMBC sequence) spectra. ^1H and ^{13}C NMR spectra were recorded with a Varian Mercury 400 (400 MHz for ^1H, 100.6 MHz for ^{13}C, and 376.28 MHz for ^{19}F) spectrometer. Unless otherwise stated, the NMR spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in parts per million relative to internal TMS or $CDCl_3$ (for ^1H and ^{13}C NMR) and to external $CFCl_3$ (δ = 0 ppm, for ^{19}F NMR). Multiplicities are reported by using the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br., broad, or combinations thereof. IR spectra were recorded with an FTIR Perkin–Elmer Spectrum RX1 spectrometer using the attenuated total reflectance (ATR) technique or a Nicolet Avantar 320 FT-IR spectrometer; the intensities of the absorptions are denoted as strong (s), medium (m), or weak (w). HRMS was carried out at the Mass Spectrometry Unit of the Centres Científics i Tecnològics of the Universitat de Barcelona (CCiTUB) by

using an LC/MSD-TOF spectrometer with electrospray ionization (ESI-TOF-MS) from Agilent Technologies. Elemental analyses were carried out at the IIQAB (CSIC) of Barcelona, Spain, in Thermofinnigan model Flash 1112 series elemental microanalyzers (A5) for C, H, and N determinations and in a Methrom model 808 titroprocessor for halogen determination. For flash column chromatography, silica gel 60 AC (35–70 μm, SDS, ref. 2000027) was used. The eluents employed are reported as volume/volume percentages. Automatized chromatography was carried out with a Combiflash RF 150 psi from Teledyne Isco. TLC was performed on aluminium-backed sheets with silica gel 60 F254 (Merck, ref. 1.05554) and the spots were visualized with UV light or a 1 % aqueous solution of $KMnO_4$. X-ray diffraction analyses of compounds **2**, **11**, and **13** were performed with a D8 Venture diffractometer at the CCiTUB of the University of Barcelona and that of compound **10** was performed with a Bruker X8 APEXII CCD at Unidade de Raios X, RIAIDT, Universidade de Santiago de Compostela. DMAD, iodosobenzene diacetate, tetrabutylammonium fluoride, and CuI were purchased from Sigma–Aldrich, bis(trimethylsilyl)acetylene, methanesulfonyl chloride, 18-crown-6, and NaI from ACROS Organics, trifluoromethanesulfonic acid, CsF, and AgF from Fluorochem, $[Pd_2(dba)_3]$ from Alfa Aesar, 1,3-diphenylisobenzofuran from Fluka, tetraphenylcyclopentadienone from ABCR chemicals, and anthracene from Merck. All of them were used without further purification. An anhydrous stock solution of TBAF (1 M in acetonitrile) was prepared as described previously.[24]

[(1*R,4*S**)-2-Iodo-3-(trimethylsilyl)bicyclo[2.2.1]hepta-2,5-diene-7,7-diyl]bis(methylene) Diacetate (6):** Trifluoromethanesulfonic acid (5.16 mL, 58.7 mmol) was added through a glass pipette to a cold solution (0 °C, ice/water bath) of iodosobenzene diacetate (IBDA; 10.02 g, 31.1 mmol) in anhydrous CH_2Cl_2 (50 mL), and the mixture was stirred for 30 min at this temperature. Bis(trimethylsilyl)acetylene (5.00 g, 29.3 mmol) was added and stirring at 0 °C was continued for 2 h. The solution was concentrated in vacuo at room temperature, hexane (120 mL) was added to the white oily residue, and the mixture was stirred for 10 min. The solid formed was filtered, washed with Et_2O (3 × 10 mL), and dried in vacuo to give iodonium triflate **4** (9.28 g). The combined filtrate and washings were concentrated in vacuo at room temperature to give an oily residue. Hexane (70 mL) was added to this residue and the solid formed was filtered, washed with Et_2O (3 × 8 mL), and dried in vacuo to give more triflate **4** (1.23 g, altogether 10.51 g, 80 % yield), some of which was used as such in the next step.

A solution of cyclopentadiene **1** (284 mg, 1.35 mmol) in anhydrous acetonitrile (3 mL) was added dropwise to a magnetically stirred and cold solution (–35 °C, cryocool) of phenyl[(trimethylsilyl)ethynyl]iodonium trifluoromethanesulfonate (**4**; 790 mg, 1.75 mmol) in anhydrous acetonitrile (3 mL) under Ar, and the mixture was heated at reflux for 64 h. The solvent was distilled in vacuo and the black oily residue was taken in acetonitrile (1.7 mL). This solution was added dropwise to a cold mixture (–35 °C, cryocool) of NaI (206 mg, 1.37 mmol) and CuI (263 mg, 1.38 mmol) in anhydrous acetonitrile (3.8 mL). The reaction mixture was allowed to warm to room temperature and then it was stirred at this temperature for 17 h. The solvent was distilled in vacuo and the black solid residue was extracted with CH_2Cl_2 (3 × 20 mL). The solvent and the formed iodobenzene were eliminated in vacuo from the combined extracts. The brown oily residue (443 mg) was subjected to automated column chromatography (35–70 μm silica gel, 12 g, hexane/EtOAc mixtures). On elution with hexane/EtOAc (9:1, 3 min), diacetate **6** (186 mg, 32 % yield) was obtained as a yellow oil. R_f (silica gel, 10 cm, hexane/EtOAc, 8:2) = 0.43. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.16 [s, 9 H, $Si(CH_3)_3$], 2.02 (s, 3 H, *anti*-CH_3COO), 2.03 (s, 3 H, *syn*-CH_3COO), 3.48 [overlapped pseudo-dt, ^4J(H,H) = 0.9, ^3J(H,H) = ^4J(H,H) = 2.8 Hz, 1 H, 1-H], 3.50 [overlapped pseudo-dt, ^4J(H,H) = 0.9, ^3J(H,H) = ^4J(H,H) = 2.8 Hz, 1 H, 4-H], 4.15 [d, ^2J(H,H) = 11.6 Hz, 1 H, *anti*-CH_aOAc], 4.20 [overlapped d, ^2J(H,H) = 11.6 Hz, 1 H, *syn*-CH_aOAc], 4.21 [overlapped d, ^2J(H,H) = 11.6 Hz, 1 H, *syn*-CH_bOAc], 4.24 [d, ^2J(H,H) = 11.6 Hz, 1 H, *anti*-CH_bOAc], 6.66 [ddd, ^3J(H,H) = 5.6, ^3J(H,H) = 3.2, ^4J(H,H) = 0.9 Hz, 1 H, 5-H], 6.77 ppm [ddd, ^3J(H,H) = 5.6, ^3J(H,H) = 3.2 Hz, ^4J(H,H) = 0.9 Hz, 1 H, 6-H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.9 [CH_3, $Si(CH_3)_3$], 20.79 (*anti*-CH_3COO), 20.85 (*syn*-CH_3COO), 59.7 (CH, C-4), 64.5 (CH_2, *anti*-CH_2OAc), 64.7 (CH_2, *syn*-CH_2OAc), 68.4 (CH, C-1), 84.1 (C, C-7), 115.9 (C, C-2), 139.2 (CH, C-6), 141.0 (CH, C-5), 154.2 (C, C-3), 170.6 (*syn*-CH_3COO), 170.7 ppm (*anti*-CH_3COO). IR (ATR): $\tilde{\nu}$ = 2950 (w), 1541 (m), 1739 (s), 1537 (w), 1374 (m), 1361 (m), 1232 (s), 1028 (s), 1000 (m), 977 (m), 860 (m), 837 (s), 754 (m), 734 (m), 692 cm^{-1} (m). HRMS: calcd. for $C_{16}H_{23}IO_4Si + NH_4^+$ 452.0749; found 452.0747. $C_{16}H_{23}IO_4Si$ (434.35): calcd. C 44.24, H 5.34, I 29.22; found C 44.05, H 5.27, I 29.53.

[(1*R,4*S**)-2-Iodo-3-(trimethylsilyl)bicyclo[2.2.1]hepta-2,5-diene-7,7-diyl]dimethanol (7):** K_2CO_3 (22 mg, 0.16 mmol) was added to a solution of diacetate **6** (271 mg, 0.62 mmol) in anhydrous MeOH (6.3 mL) and the mixture was heated at reflux for 2 h. A saturated aqueous solution of $NaHCO_3$ (0.1 mL) was added. The mixture was cooled to 0 °C with an ice/water bath and filtered. The solid was washed with MeOH (4 × 5 mL). The combined filtrate and washings were concentrated in vacuo, the oily residue was taken in CH_2Cl_2 (5 mL), and the solution was dried with anhydrous Na_2SO_4 and concentrated in vacuo to give diol **7** as a brown oil (201 mg). This crude product was subjected to column chromatography (35–70 μm silica gel, 5.0 g, hexane/EtOAc mixtures). On elution with hexane/EtOAc (95:5), diol **7** (168 mg, 77 % yield) was obtained as a yellow oil. Crystallization of the above product from pentane (1 mL) gave the analytical sample of **7** as a white solid. R_f (silica gel, 10 cm, hexane/EtOAc, 3:7) = 0.38; m.p. 55–56 °C (pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.18 [s, 9 H, $Si(CH_3)_3$], 2.05–2.10 (br. s, 1 H) and 2.10–2.15 (br. s, 1 H, 2 O*H*), 3.50 [pseudo-dt, ^4J(H,H) = 0.8, ^3J(H,H) = ^4J(H,H) = 2.8 Hz, 1 H, 1-H], 3.54 [pseudo-dt, ^4J(H,H) = 0.8, ^3J(H,H) = ^4J(H,H) = 2.8 Hz, 1 H, 4-H], 3.86 (s, 2 H, *anti*-CH_2OH), 3.88 [overlapped d, ^2J(H,H) = 10.8 Hz, 1 H] and 3.92 [d, ^2J(H,H) = 10.8 Hz, 1 H, *syn*-CH_2OH), 6.65 [ddd, ^3J(H,H) = 5.2, ^4J(H,H) = 3.2, ^3J(H,H) = 0.8 Hz, 1 H, 5-H], 6.79 ppm [ddd, ^3J(H,H) = 5.2, ^4J(H,H) = 3.2, ^3J(H,H) = 1.1 Hz, 1 H, 6-H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.8 [CH_3, $Si(CH_3)_3$], 59.3 (CH, C-4), 66.2 (CH_2, CH_2OH), 66.6 (CH_2, CH_2OH), 68.1 (CH, C-1), 88.8 (C, C-7), 116.0 (C, C-2), 139.5 (CH, C-6), 140.9 (CH, C-5), 154.7 ppm (C, C-3). IR (ATR): $\tilde{\nu}$ = 3100–3600 (br, m), 2952 (m), 1541 (m), 1247 (m), 1008 (s), 836 (vs), 755 (m), 727 (m), 691 cm^{-1} (m). HRMS: calcd. for $C_{12}H_{19}IO_2Si + Na^+$ 373.0091; found 373.0106. $C_{12}H_{19}IO_2Si$ (350.27): calcd. C 41.15, H 5.47, I 36.23; found C 41.17, H 5.45, I 36.15.

[(1*R,4*S**)-2-Iodo-3-(trimethylsilyl)bicyclo[2.2.1]hepta-2,5-diene-7,7-diyl]bis(methylene) Dimethanesulfonate (8):** Methanesulfonyl chloride (50 μL, 0.60 mmol) was added dropwise to a cold (0 °C, ice/water bath) and magnetically stirred solution of a mixture of diol **7** (87 mg, 0.25 mmol) and Et_3N (0.14 mL, 1.0 mmol) in anhydrous CH_2Cl_2 (2 mL) under Ar, and the mixture was stirred at this temperature for 1.5 h. A saturated aqueous solution of $NaHCO_3$ (0.1 mL) was added. The organic phase was separated and was washed with a saturated aqueous solution of $NaHCO_3$ (3 × 2 mL). The combined aqueous phases were extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phases and extracts were washed with water (3 mL) and brine (3 mL), dried (anhydrous Na_2SO_4), and concentrated in vacuo to give dimesylate **8** as a brown oil (140 mg). This crude product was subjected to automated column chromatography (35–70 μm silica gel, 4.0 g, hexane/EtOAc mixtures). On

elution with hexane/EtOAc (4:1) to hexane/EtOAc (1:9; 4 min), dimesylate **8** (112 mg, 89 % yield) was obtained as a yellow oil. Crystallization of the above product from EtOAc/pentane (1:3, 2 mL) gave the analytical sample of **8** as a white solid. R_f (silica gel, 10 cm, hexane/EtOAc, 3:7) = 0.76; m.p. 82–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.20 [s, 9 H, $Si(CH_3)_3$], 3.00 (s, 3 H) and 3.02 (s, 3 H, 2 CH_3SO_3), 3.55–3.58 (m, 1 H, 1-H), 3.57–3.60 (m, 1 H, 4-H), 4.38 [d, ^2J(H,H) = 10.4 Hz, 1 H] and 4.39 [d, ^2J(H,H) = 9.6 Hz, 1 H, *syn*- and *anti*-CH_aOMs), 4.43 [d, ^2J(H,H) = 9.6 Hz, 2 H, *syn*- and *anti*-CH_bOMs), 6.71 [dd, ^3J(H,H) = 5.2, ^4J(H,H) = 3.2 Hz, 1 H, 5-H], 6.85 ppm [pseudo-t, ^3J(H,H) = ^4J(H,H) = 4.0 Hz, 1 H, 6-H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –2.0 [CH_3, $Si(CH_3)_3$], 37.20 (CH_3, CH_3SO_3), 37.21 (CH_3, CH_3SO_3), 59.2 (CH, C-4), 67.6 (CH, C-1), 69.4 (CH_2) and 69.6 (CH_2, *syn*- and *anti*-CH_2OMs), 83.2 (C, C-7), 115.0 (C, C-2), 139.4 (CH, C-6), 141.0 (CH, C-5), 154.8 ppm (C, C-3). IR (ATR): $\tilde{\nu}$ = 3028 (w), 2949 (w), 1349 (s), 1328 (s), 1245 (m), 1170 (s), 940 (s), 840 (s), 822 (s), 775 (m), 754 (m), 729 cm^{-1} (m). HRMS: calcd. for $C_{14}H_{23}IO_6S_2Si + NH_4^+$ 524.0088; found 524.0104. $C_{14}H_{23}O_6S_2Si$ (379.54): calcd. C 33.20, H 4.58, S 12.66; found C 33.64, H 4.61, S 12.17.

[(1*R,4*S**)-2-Iodo-7,7-bis(iodomethyl)bicyclo[2.2.1]hepta-2,5-dien-2-yl]trimethylsilane (9):** Powdered NaI (365 mg, 2.43 mmol) was added to a solution of dimesylate **8** (103 mg, 0.20 mmol) in anhydrous acetone (2 mL) under Ar and the mixture was heated at reflux for 17 h. The reaction mixture was concentrated in vacuo and the yellow solid residue was subjected to column chromatography (35–70 µm silica gel, 1.0 g, hexane/EtOAc mixtures). On elution with hexane/EtOAc (90:10), diiodide **9** (92 mg, 79 % yield) was obtained as a light-yellow oil. R_f (silica gel, 10 cm, hexane/EtOAc, 1:1) = 0.84. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.22 [s, 9 H, $Si(CH_3)_3$], 3.54 [overlapped pseudo-dt, ^4J(H,H) = 1.2, ^3J(H,H) = ^4J(H,H) = 2.8 Hz, 1 H, 4-H], 3.56 [overlapped pseudo-dt, ^4J(H,H) = 1.2, ^3J(H,H) = ^4J(H,H) = 2.8 Hz, 1 H, 1-H], 3.65 [d, ^2J(H,H) = 10.0 Hz, 1 H], 3.70 [d, ^2J(H,H) = 10.8 Hz, 1 H] and 3.71–3.76 (complex signal, 2 H, *anti*- and *syn*-CH_2I), 6.68 [ddd, ^3J(H,H) = 5.6, ^3J(H,H) = 3.2, ^4J(H,H) = 1.2 Hz, 1 H, 5-H], 6.85 ppm [ddd, ^3J(H,H) = 5.2, ^3J(H,H) = 3.2, ^4J(H,H) = 1.4 Hz, 1 H, 6-H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = –1.7 [CH_3, $Si(CH_3)_3$], 13.88 (CH_2, CH_2I), 13.95 (CH_2, CH_2I), 63.8 (CH, C-4), 71.9 (CH, C-1), 85.6 (C, C-7), 115.9 (C, C-2), 139.9 (CH, C-6), 141.2 (CH, C-5), 155.6 ppm (C, C-3). IR (ATR): $\tilde{\nu}$ = 2949 (w), 1567 (w), 1536 (m), 1418 (m), 1281 (m), 1245 (m), 1198 (m), 1006 (m), 867 (m), 834 (s), 791 (m), 751 (m), 727 (m), 637 (m), 626 cm^{-1} (m). $C_{12}H_{17}I_3Si$ (570.07): calcd. C 25.28, H 3.01, I 66.78; found C 25.38, H 2.93, I 66.94.

(1*R,3a*S**,4*R**,4a*R**,4b*S**,5*R**,8*S**,8a*R**,9*S**,9a*S**,10a*R**,11*S**,13*S**)-4-Iodo-13-(trimethylsilyl)-3a,4,4a,4b,5,8,8a,9,10,10a-decahydro-1*H*-5,8,9a-(epiethane[1,1,2]triyl)-1,4,9-(epimethanetriyl)cyclopenta[*b*]fluorene (2):** In a 10 mL flask, KH (30 % in mineral oil, 267 mg, 2.00 mmol) was washed with anhydrous THF (5 × 10 mL) under Ar. Anhydrous THF (10 mL) was added to the washed KH and the suspension was cooled to 0 °C in an ice/water bath. Freshly distilled cyclopentadiene (0.25 mL, 198 mg, 3.0 mmol) was added and the mixture was stirred at this temperature for 10 min. 18-Crown-6 (26 mg, 0.10 mmol, 5 % with respect to KH) was added and the mixture was stirred at 0 °C for 10 min and at room temperature for 15 min.

A solution of diiodide **9** (415 mg, 0.73 mmol) in anhydrous DMF (4.1 mL) was prepared in a 25 mL flask equipped with a magnetic stirrer and reflux condenser under Ar. The solution was cooled to 0 °C in an ice/water bath and then part of the above potassium cyclopentadienide solution (8.0 mL, 1.6 mmol) was added dropwise. The mixture was stirred at 0 °C for 5 min, at room temperature for 10 min, and then it was heated at 90 °C for 17 h. The mixture was cooled to room temperature, MeOH (0.1 mL) was added, and the mixture was stirred for 10 min. Then EtOAc (5 mL) and water (5 mL) were added and the organic phase was separated. The aqueous phase was extracted with EtOAc (3 × 10 mL) and the combined organic phases were washed with a saturated aqueous solution of $NaHCO_3$ (3 × 10 mL), water (2 × 10 mL), and brine (10 mL), dried (anhydrous Na_2SO_4), and concentrated in vacuo to give a crude brown oily residue (339 mg), which was subjected to column chromatography [35–70 µm silica gel (20 g) pentane/EtOAc mixtures] to give, on elution with pentane, octacycle **2** (188 mg, 58 % yield) as a white solid. An analytical sample of **2** (136 mg) was obtained as a white solid by crystallization of the above product from CH_2Cl_2/MeOH (1:3; 2 mL). R_f (silica gel, 10 cm, hexane/EtOAc, 9:1) = 0.74; m.p. 108.7–109.5 °C (CH_2Cl_2/MeOH). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.19 [s, 9 H, $Si(CH_3)_3$], 1.33 [dd, ^2J(H,H) = 14.2, ^3J(H,H) = 2.6 Hz, 1 H, 12-H_a], 1.43 (overlapped s, 1 H, 9-H), 1.45 [overlapped dd, ^2J(H,H) = 14.2, ^3J(H,H) = 2.6 Hz, 1 H, 12-H_b], 1.53 [overlapped dd, ^2J(H,H) = 14.8, ^3J(H,H) = 2.8 Hz, 1 H, 10-H_a], 1.57 [overlapped dd, ^2J(H,H) = 14.8, ^3J(H,H) = 3.2 Hz, 1 H, 10-H_b], 1.74–1.78 (br. s, 1 H, 11-H), 1.88–1.92 (br. s, 1 H, 10a-H), 1.96 (s, 1 H, 4a-H), 2.01 [d, ^3J(H,H) = 6.4 Hz, 1 H, 8a-H], 2.07 [d, ^3J(H,H) = 6.4 Hz, 1 H, 4b-H], 2.31–2.35 (br. s, 1 H, 8-H), 2.40–2.44 (br. s, 1 H, 5-H), 2.47–2.51 (br. s, 1 H, 1-H), 3.00–3.04 (br. s, 1 H, 3a-H), 5.98 [dd, ^3J(H,H) = 5.6, ^3J(H,H) = 3.2 Hz, 1 H, 3-H], 6.05 [dd, ^3J(H,H) = 6.0, ^3J(H,H) = 2.8 Hz, 1 H, 7-H], 6.10 [dd, ^3J(H,H) = 6.0, ^3J(H,H) = 2.8 Hz, 1 H, 6-H], 6.33 ppm [dd, ^3J(H,H) = 5.6, ^3J(H,H) = 3.2 Hz, 1 H, 2-H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 4.0 [CH_3, $Si(CH_3)_3$], 35.0 (CH_2, C-10), 35.4 (CH_2, C-12), 42.6 (C, C-9a), 43.0 (CH, C-8a), 46.3 (C, C-13), 48.4 (CH, C-4b), 49.0 (CH, C-8), 49.7 (CH, C-5), 52.3 (CH, C-11), 52.5 (CH, C-1), 53.1 (CH, C-9), 55.0 (CH, C-10a), 63.2 (CH, C-4a), 63.4 (CH, C-3a), 72.2 (C, C-4), 137.2 (CH, C-7), 137.3 (CH, C-6), 139.4 (CH, C-3), 140.7 ppm (CH, C-2). IR (ATR): $\tilde{\nu}$ = 3055 (w), 2944 (m), 2910 (m), 2893 (m), 2833 (w), 1326 (w), 1245 (m), 937 (m), 921 (m), 856 (m), 842 (s), 829 (s), 810 (m), 794 (m), 724 (m), 708 (s), 680 cm^{-1} (m). HRMS: calcd. for $C_{22}H_{27}ISi + H^+$ 447.0999; found 447.0991; calcd. for $C_{22}H_{27}ISi - I^+$ 319.1877; found 319.1873. $C_{22}H_{27}ISi$ (446.45): calcd. C 59.19, H 6.10, I 28.43; found C 59.18, H 5.98, I 28.58.

Attempts to Generate and Trap Pyramidalized Alkene 3

General: All of the following reactions were performed under argon in a 10 mL Schlenk tube equipped with a magnetic stirrer. The reactions were followed by TLC and GC. In all cases, no evolution of the reaction mixtures was observed. At the end of the reactions, the solutions were concentrated in vacuo and the products were submitted to column chromatography (silica gel, 35–70 µm, hexane/EtOAc mixtures). On elution with hexane, the starting compound **2** was recovered unchanged. No products derived from **2** were detected.

Reaction with CsF in the Presence of Furan: Anhydrous CsF (54 mg, 0.36 mmol) was added to a solution of octacycle **2** (50 mg, 0.11 mmol) and furan (40 µL, 0.55 mmol) in anhydrous acetonitrile (3 mL), and the mixture was stirred at room temperature for 18 h. Then, the mixture was heated at 45 °C for 5 h. Finally, 18-crown-6 (6 mg, 23 µmol) was added and the mixture was heated at 45 °C for 16 h.

Reaction with CsF and AgF in the Presence of 1,3-Diphenylisobenzofuran: Anhydrous CsF (85 mg, 0.56 mmol) and AgF (43 mg, 0.34 mmol) were added to a solution of octacycle **2** (50 mg, 0.11 mmol) and 1,3-diphenylisobenzofuran (45 mg, 0.17 mmol) in anhydrous acetonitrile (3 mL), and the mixture was heated at reflux for 20 h.

Reaction with CsF and AgF in the Presence of Tetraphenylcyclopentadienone: Anhydrous CsF (85 mg, 0.56 mmol) and AgF (43 mg,

0.34 mmol) were added to a solution of octacycle **2** (50 mg, 0.11 mmol) and tetraphenylcyclopentadienone (65 mg, 0.17 mmol) in a mixture of anhydrous THF (1.5 mL) and acetonitrile (1.5 mL), and the mixture was heated at 60 °C for 17 h.

Reaction with Tetrabutylammonium Fluoride in the Presence of Tetraphenylcyclopentadienone: Procedure 1: Tetraphenylcyclopentadienone (65 mg, 0.17 mmol) was added to a cold (0 °C) suspension of tetrabutylammonium fluoride (1 M in acetonitrile, 0.34 mL, 0.34 mmol). Then octacycle **2** (50 mg, 0.11 mmol) in anhydrous THF (50 µL) was added and the mixture was stirred at 0 °C for 1 h.

Procedure 2: A suspension of tetrabutylammonium fluoride (1 M in acetonitrile, 70 µL, 70 µmol) was added to a solution of octacycle **2** (10 mg, 22 µmol) and tetraphenylcyclopentadienone (17 mg, 44 µmol) in anhydrous 1,4-dioxane (0.5 mL), and the mixture was heated at 100 °C for 19 h.

Reaction with CsF and AgF in the Presence of Anthracene: Anhydrous CsF (85 mg, 0.56 mmol) and AgF (43 mg, 0.34 mmol) were added to a solution of octacycle **2** (50 mg, 0.11 mmol) and anthracene (40 mg, 0.22 mmol) in a mixture of anhydrous 1,4-dioxane (2.5 mL) and acetonitrile (1 mL), and the mixture was heated at 100 °C for 20 h.

Tetramethyl (1*R,3a*S**,4*R**,4a*R**,4b*R**,5*R**,10*S**,10a*S**,11*S**,11a*S**,12a*R**,14*S**,15*S**)-3a,4,4a,4b,5,10,10a,11,12,12a-Decahydro-4-iodo-15-(trimethylsilyl)-1*H*-5,10,11a-(epiethane-[1,1,2]triyl)-1,4,11-(epimethanetriyl)benzo[*b*]cyclopenta[*h*]-fluorene-6,7,8,9-tetracarboxylate (10):** A 10 mL Schlenk tube equipped with a reflux condenser and magnetic stirrer was charged with a solution of octacycle **2** (50 mg, 0.11 mmol) in anhydrous 1,4-dioxane (2.5 mL) under Ar. Then DMAD (0.03 mL, 0.24 mmol), tris(dibenzylideneacetone)dipalladium(0)·$CHCl_3$ (6 mg, 6 µmol), anhydrous CsF (85 mg, 0.56 mmol), and AgF (43 mg, 0.34 mmol) were successively added and the mixture was stirred and heated at 100 °C for 17 h. The reaction mixture was cooled to room temperature and concentrated in vacuo to give a brown solid (196 mg), which was submitted to column chromatography [35–70 µm silica gel (7 g), hexane/EtOAc mixtures] to give, on elution with hexane/EtOAc (8:2), adduct **10** (28 mg, 34 % yield) as a white solid. An analytical sample of **10** (20 mg) was obtained as a white solid by crystallization of the above product from CH_2Cl_2/pentane (1:4, 1 mL). R_f (silica gel, 10 cm, hexane/EtOAc, 8:2) = 0.22; m.p. 117–118 °C (CH_2Cl_2/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.14 [s, 9 H, $Si(CH_3)_3$], 1.48 [dd, ^2J(H,H) = 14.4, ^3J(H,H) = 2.8 Hz, 1 H, 13-H_b], 1.60 [overlapped dd, ^2J(H,H) = 14.8, ^3J(H,H) = 3.2 Hz, 1 H, 13-H_a], 1.65 [overlapped d, ^4J(H,H) = 0.8 Hz, 1 H, 11-H], 1.62–1.68 [complex signal, 2 H, 12-H_a, 12-H_b], 1.90–1.93 (br. s, 1 H, 12a-H), 2.14–2.18 (br. s, 2 H, 14-H, 4a-H), 2.24–2.28 (m, 2 H, 10a-H, 4b-H), 2.52–2.55 (br. s, 1 H, 1-H), 3.02–3.05 (br. s, 1 H, 3a-H), 3.26–3.28 (br. s, 1 H, 10-H), 3.48–3.50 (br. s, 1 H, 5-H), 3.86 (s, 3 H, OCH_3), 3.88 (s, 3 H, OCH_3), 3.90 (s, 3 H, OCH_3), 3.93 (s, 3 H, OCH_3), 5.99 [dd, ^3J(H,H) = 6.0, ^3J(H,H) = 3.2 Hz, 1 H, 3-H], 6.33 ppm [dd, ^3J(H,H) = 6.0, ^3J(H,H) = 3.2 Hz, 1 H, 2-H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 3.9 [CH_3, $Si(CH_3)_3$], 34.1 (CH_2, C-13), 34.8 (CH_2, C-12), 42.9 (C, C-11a), 43.2 (CH, C-10a), 45.9 (C, C-15), 48.6 (CH, C-4b), 50.5 (CH, C-10), 51.0 (CH, C-5), 52.0 (CH, C-14), 52.59 (CH, C-1), 52.61 (CH_3), 52.8 (CH_3), 52.91 (CH_3), 52.94 (CH_3, 4 $COOCH_3$), 53.4 (CH, C-11), 54.6 (CH, C-12a), 63.2 (CH, C-4a), 63.4 (CH, C-3a), 68.8 (C, C-4), 126.6 (C) and 126.8 (C, C-7, C-8), 129.8 (C) and 130.4 (C, C-6, C-9), 139.5 (CH, C-3), 140.7 (CH, C-2), 150.8 (C, C-9a), 151.3 (C, C-5a), 166.2 (C), 166.3 (C), 166.9 (C), 167.4 ppm (C, 4 $COOCH_3$). IR (NaCl): $\tilde{\nu}$ = 2951 (m), 2918 (m), 1733 (s), 1444 (m), 1361 (m), 1321 (m), 1249 (s), 1212 (s), 1166 (m), 1143 cm^{-1} (m). HRMS: calcd. for $C_{34}H_{37}IO_8Si + NH_4^+$ 746.1641; found 746.1635. $C_{34}H_{37}IO_8Si$ (728.65): calcd. C 56.05, H 5.12, I 17.42; found C 55.97, H 5.17, I 17.54.

Tetramethyl (1*R,3a*S**,4*R**,4a*R**,4b*S**,5*R**,5a*R**,9a*R**,10*S**,10a*S**,11*R**,11a*S**,12a*R**,14*S**,15*S**)-3a,4,4a,4b,5,5a,9a,10,10a,11,12,12a-Dodecahydro-4-iodo-15-(trimethylsilyl)-1*H*-5,10,11a-(epiethane[1,1,2]triyl)-1,4,11-(epimethanetriyl)-benzo[*b*]cyclopenta[*h*]fluorene-6,7,8,9-tetracarboxylate (11):** DMAD (0.1 mL, 0.79 mmol) and tris(dibenzylideneacetone)dipalladium(0) (18 mg, 20 µmol) were added to a solution of octacycle **2** (88 mg, 0.20 mmol) in anhydrous 1,4-dioxane (4.4 mL) and the mixture was stirred and heated at 100 °C for 17 h. The reaction mixture was cooled to room temperature and concentrated in vacuo to give a brown solid (190 mg), which was submitted to automated column chromatography [35–70 µm silica gel (4 g), hexane/EtOAc mixtures]. On elution with hexane/AcOEt (3:1) to hexane/AcOEt (7:3, 4 min), adduct **11** (117 mg, 81 % yield) was obtained as a white solid. An analytical sample of **11** (93 mg) was obtained as a white solid by crystallization of the above product from CH_2Cl_2/pentane (1:3, 1.5 mL). R_f (silica gel, 10 cm, hexane/EtOAc, 3:2) = 0.19; m.p. 117–118 °C (CH_2Cl_2/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.22 [s, 9 H, $Si(CH_3)_3$], 1.43 (overlapped s, 1 H, 11-H), 1.46 [overlapped dd, ^2J(H,H) = 10.2, ^3J(H,H) = 2.8 Hz, 1 H, 13-H_b], 1.51–1.60 [complex signal, 3 H, 12-H_a, 12-H_b, 13-H_a], 1.82–1.84 (m, 1 H, 12a-H), 1.94–1.96 (br. s, 2 H, 4a-H, 10-H), 2.00–2.02 (m, 1 H, 5-H), 2.22–2.26 (br. s, 1 H, 14-H), 2.36 [d, ^3J(H,H) = 6.0 Hz, 1 H, 10a-H], 2.46 (overlapped br. s, 1 H, 1-H), 2.47 [overlapped d, ^3J(H,H) = 6.0 Hz, 1 H, 4b-H], 2.90 [d, ^3J(H,H) = 12.4 Hz, 1 H, 9a-H], 2.97 [d, ^3J(H,H) = 2.4 Hz, 3aH], 3.08 [d, ^3J(H,H) = 12.4 Hz, 1 H, 5a-H], 3.74 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 5.95 [dd, ^3J(H,H) = 6.0, ^3J(H,H) = 3.2 Hz, 1 H, 3-H], 6.29 ppm [dd, ^3J(H,H) = 5.8, ^3J(H,H) = 3.0 Hz, 1 H, 2-H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 4.0 [CH_3, $Si(CH_3)_3$], 33.0 (CH_2, C-13), 34.6 (CH_2, C-12), 40.2 (CH, C-14), 43.60 (CH) and 43.64 (CH, C-5a, C-9a), 45.1 (C, C-15), 46.3 (CH, C-10a), 51.1 (CH, C-4b), 52.46 (CH, C-1), 52.47 (CH_3), 52.59 (CH_3), 52.62 (CH_3), (4 $COOCH_3$), 53.0 (CH, C-10), 53.2 (CH, C-5), 54.60 (CH) and 54.62 (CH, C-11, C-12a), 63.3 (CH, C-3a), 64.4 (CH, C-4a), 69.5 (C, C-4), 130.6 (C, C-7), 131.6 (C, C-8), 133.1 (C, C-9), 134.7 (C, C-6), 139.2 (CH, C-3), 140.4 (CH, C-2), 166.5 (C) and 166.6 (C, 8-*C*OOMe, 9-*C*OOMe), 166.9 (C) and 167.0 ppm (C, 6-*C*OOMe, 7-*C*OOMe); according to the gHMBC spectrum, C-11a might be under the signals at δ = 43.60 and 43.64 ppm. IR (NaCl): $\tilde{\nu}$ = 2949 (m), 2916 (m), 2840 (w), 1732 (s), 1644 (w), 1591 (w), 1434 (s), 1342 (m), 1243 (s), 1117 (m), 993 (m), 849 (m), 836 (m), 727 cm^{-1} (m). HRMS: calcd. for $C_{34}H_{39}IO_8Si + NH_4^+$ 748.1797; found 748.1801. $C_{34}H_{39}IO_8Si$·0.75CH_2Cl_2: calcd. C 52.54, H 5.14; found C 52.55, H 5.11.

Preparation of Compound 10 from 11: A solution of nonacycle **11** (51 mg, 0.07 mmol) in anhydrous 1,4-dioxane (1.5 mL) was placed in a 10 mL flask equipped with a reflux condenser and magnetic stirrer under Ar. Then anhydrous CsF (32 mg, 0.21 mmol) was added and the mixture was stirred and heated at 100 °C for 16 h. The reaction mixture was cooled to room temperature and concentrated in vacuo to give a white solid (87 mg), which was submitted to column chromatography [35–70 µm silica gel (2 g), hexane/EtOAc mixtures] to give, on elution with hexane/EtOAc (8:2), adduct **10** (45 mg, 89 % yield) as a white solid.

(1*R,3a*S**,4*R**,4a*R**,4b*S**,5*R**,8*S**,8a*R**,9*S**,9a*S**,10a*R**,11*S**,13*S**)-4-Fluoro-13-(trimethylsilyl)-3a,4,4a,4b,5,8,8a,9,10,10a-decahydro-1*H*-5,8,9a-(epiethane[1,1,2]triyl)-1,4,9-(epimethanetriyl)cyclopenta[*b*]fluorene (12):** A solution of octacycle **2** (63 mg, 0.14 mmol) in anhydrous dioxane (3 mL) was added to a 10 mL flask equipped with a reflux condenser and magnetic stirrer under Ar. Then anhydrous AgF (54 mg, 0.43 mmol) was added and

the mixture was stirred and heated at 100 °C for 15 h. The reaction mixture was cooled to room temperature and concentrated in vacuo to give a residue (130 mg), which was submitted to column chromatography [35–70 μm silica gel (1.0 g), hexane/EtOAc mixtures] to give, on elution with hexane, product **12** (22 mg, 46 % yield) as a colorless oil. R_f (silica gel, 10 cm, hexane/EtOAc, 9:1) = 0.63. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.05 [s, 9 H, $Si(CH_3)_3$], 1.37–1.44 (complex signal, 3 H, 10-H_a, 10-H_b, 12-H_a), 1.48 [dd, ^2J(H,H) = 14.2, ^3J(H,H) = 3.0 Hz, 1 H, 12-H_b], 1.55–1.57 (br. s, 1 H, 9-H), 1.81–1.84 (br. s, 1 H, 11-H), 1.88–1.90 (br. s, 1 H, 4a-H), 2.00–2.04 (br. s, 1 H, 10a-H), 2.10 (s, 2 H, 4b-H, 8a-H), 2.32–2.35 (br. s, 1 H, 8-H), 2.39–2.42 (br. s, 1 H, 5-H), 2.45–2.48 (br. s, 1 H, 1-H), 2.63–2.66 (br. s, 1 H, 3a-H), 6.05–6.10 (complex signal, 3 H, 3-H, 6-H, 7-H), 6.43 ppm [dd, ^3J(H,H) = 5.8, ^3J(H,H) = 3.0 Hz, 1 H, 2-H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 3.1 [d, ^4J(C,F) = 2.2 Hz, CH_3, $Si(CH_3)_3$], 34.7 [d, ^4J(C,F) = 2.3 Hz, CH_2, C-10], 35.4 (CH_2, C-12), 38.7 [d, ^3J(C,F) = 4.6 Hz, CH, C-4b], 44.7 [d, ^3J(C,F) = 4.5 Hz, C, C-9a], 44.8 (CH, C-8a), 46.9 [d, ^2J(C,F) = 25.1 Hz, C, C-13], 49.0 (CH, C-5), 49.4 (CH, C-8), 52.5 (CH, C-11), 53.7 [d, ^3J(C,F) = 3.0 Hz, CH, C-1], 55.4 [d, ^3J(C,F) = 3.3 Hz, CH, C-9], 55.8 [d, ^2J(C,F) = 22.1 Hz, CH, C-3a], 57.4 [d, ^2J(C,F) = 20.5 Hz, CH, C-4a], 58.4 [d, ^3J(C,F) = 3.0 Hz, CH, C-10a], 114.5 [d, ^1J(C,F) = 207.6 Hz, C, C-4], 132.5 [d, ^3J(C,F) = 3.1 Hz, CH, C-3], 137.0 (CH, C-7), 137.3 (CH, C-6), 142.3 ppm (CH, C-2). ^{19}F NMR (376.28 MHz, $CDCl_3$): δ = –174.0 ppm. IR (NaCl): $\tilde{\nu}$ = 3062 (w), 2950 (m), 2916 (m), 2838 (w), 1329 (w), 1249 (m), 1135 (w). 858 (m), 836 (s), 721 (m), 712 (s), 627 cm^{-1} (m). HRMS: calcd. for $C_{22}H_{27}FSi + NH_4^+$ 356.2204; found 356.2191; calcd. for $C_{22}H_{27}FSi - F^+$ 319.1877; found 319.1875. $C_{22}H_{27}FSi$ (338.54): calcd. C 78.05, H 8.04; found C 78.08, H 8.07.

Tetramethyl (1*R,3a*S**,4*R**,4a*R**,4b*S**,5*R**,5a*R**,9a*S**,10*S**,10a*R**,11*S**,11a*R**,12a*S**,14*R**,15*S**)-4-Fluoro-3a,4,4a,4b,5,5a,9a,10,10a,11,12,12a-dodecahydro-15-(trimethylsilyl)-1*H*-5,10,11a-(epiethane[1,1,2]triyl)-1,4,11-(epimethanetriyl)-benzo[*b*]cyclopenta[*h*]fluorene-6,7,8,9-tetracarboxylate (13):** A solution of iodo nonacycle **11** (90 mg, 0.12 mmol) in anhydrous 1,4-dioxane (2.6 mL) was placed in a 10 mL flask equipped with a reflux condenser and magnetic stirrer under Ar. Then anhydrous AgF (47 mg, 0.37 mmol) was added and the mixture was stirred and heated at 100 °C for 16 h. The reaction mixture was cooled to room temperature and concentrated in vacuo to give a gray residue (145 mg), which was submitted to automated column chromatography [35–70 μm silica gel (12 g), hexane/EtOAc mixtures]. On elution with hexane/EtOAc (4:1) to hexane/EtOAc (7:3, 4 min), product **13** (36 mg, 47 % yield) was obtained as a white solid. An analytical sample of **13** (30 mg) was obtained as a white solid by crystallization of the above product from CH_2Cl_2/pentane (1:3, 1.2 mL). R_f (silica gel, 10 cm, hexane/EtOAc, 6:4) = 0.37; m.p. 192–193 °C (CH_2Cl_2/pentane). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.09 [s, 9 H, $Si(CH_3)_3$], 1.38–1.48 (complex signal, 2 H, 12-H_a, 12-H_b), 1.54 [overlapped pseudo-dt, ^2J(H,H) = 14.0, ^3J(H,H) = ^5J(H,F) = 2.8 Hz, 1 H, 13-H_a], 1.56–1.58 (br. s, 1 H, 11-H), 1.62 [dd, ^2J(H,H) = 14.0, ^3J(H,H) = 2.8 Hz, 1 H, 13-H_b], 1.88–1.90 (br. s, 1 H, 4a-H), 1.94–1.98 (br. s, 2 H, 10-H, 12a-H), 1.98–2.00 (br. s, 1 H, 5-H), 2.30–2.34 (br. s, 1 H, 14-H), 2.43–2.45 (overlapped br. s, 1 H, 1-H), 2.45 (overlapped d, 1 H, 10a-H), 2.48 [d, ^3J(H,F) = 6.4 Hz, 1 H, 4b-H], 2.60–2.63 (br. s, 1 H, 3aH), 2.94 [d, ^3J(H,H) = 12.6 Hz, 1 H, 9a-H], 3.06 [d, ^3J(H,H) = 12.6 Hz, 1 H, 5a-H], 3.74 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 3.78 (s, 3 H, OCH_3), 6.05 [dd, ^3J(H,H) = 5.8, ^3J(H,H) = 3.0 Hz, 1 H, 3-H], 6.41 ppm [dd, ^3J(H,H) = 5.8, ^3J(H,H) = 3.0 Hz, 1 H, 2-H]. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 3.1 [d, ^4J(C,F) = 2.2 Hz, CH_3, $Si(CH_3)_3$], 32.9 (CH_2, C-13), 34.2 (CH_2, C-12), 40.3 (CH, C-14), 42.0 [d, ^3J(C,F) = 4.6 Hz, CH, C-4b], 43.6 (CH) and 43.7 (CH, C-5a, C-9a), 45.7 [d, ^2J(C,F) = 24.4 Hz, C, C-15], 45.8 [d, ^3J(C,F) = 4.6 Hz, C, C-11a], 48.1 (CH, C-10a), 52.5 (CH_3) and 52.6 (3 CH_3, 4 $COOCH_3$), 52.6 (CH, C-5), 53.5 (CH, C-10), 53.7 [d, ^3J(C,F) = 3.0 Hz, CH, C-1], 55.7 [d, ^2J(C,F) = 21.4 Hz, CH, C-3a], 56.9 [d, ^3J(C,F) = 2.3 Hz, CH, C-11], 58.0 [d, ^3J(C,F) = 3.7 Hz, CH, C-12a], 58.8 [d, ^2J(C,F) = 20.6 Hz, CH, C-4a], 113.5 [d, ^1J(C,F) = 206.6 Hz, C, C-4], 130.9 (C, C-7), 131.7 (C, C-8), 132.3 [d, ^3J(C,F) = 3.0 Hz, CH, C-3], 133.1 (C, C-9), 134.5 (C, C-6), 142.1 (CH, C-2), 166.55 (C), 166.61 (C), 166.89 (C) and 166.90 ppm (C, 6-*C*OOMe, 7-*C*OOMe, 8-*C*OOMe and 9-*C*OOMe). ^{19}F NMR (376.28 MHz, $CDCl_3$): δ = –173.8 ppm. IR (NaCl): $\tilde{\nu}$ = 3064 (w), 2950 (s), 2918 (s), 2844 (m), 1739 (s), 1733 (s), 1645 (w), 1686 (w), 1435 (s), 1343 (m), 1243 (s), 1115 (s), 994 (m), 860 (s), 839 (s), 734 cm^{-1} (s). HRMS: calcd. for $C_{34}H_{39}FO_8Si + NH_4^+$ 640.2736; found 640.2727. $C_{34}H_{39}FO_8Si$ (622.76): calcd. C 65.57, H 6.31, F 3.05; found C 65.51, H 6.38.

Preparation of Compound 13 from 2: A solution of octacycle **2** (50 mg, 0.11 mmol) in anhydrous 1,4-dioxane (2.5 mL) was added to a 10 mL flask equipped with a reflux condenser and magnetic stirrer under Ar. Then DMAD (0.06 mL, 0.45 mmol), tris(dibenzylideneacetone)dipalladium(0) (10 mg, 11 μmol), and AgF (43 mg, 0.34 mmol) were successively added and the mixture was stirred and heated at 100 °C for 16 h. The reaction mixture was cooled to room temperature and concentrated in vacuo to give a gray solid (117 mg), which was submitted to automated column chromatography [35–70 μm silica gel (12 g), hexane/EtOAc mixtures]. On elution with hexane/EtOAc (3:1) to hexane/EtOAc (3:2, 3 min), adduct **13** (21 mg, 31 % yield) was obtained as a white solid.

X-ray Crystal Structure Determination of Compound 2: A colorless prism-like specimen of $C_{22}H_{27}ISi$, approximate dimensions 0.143 mm × 0.177 mm × 0.568 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured with a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å). The frames were integrated by using the Bruker SAINT software package[25] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 50804 reflections to a maximum θ angle of 30.62 (0.70 Å resolution), of which 5778 were independent (average redundancy 8.793, completeness = 99.4 %, R_{int} = 3.13 %, R_{sig} = 1.76 %) and 5168 (89.44 %) were greater than $2\sigma(F^2)$. The final cell constants of a = 10.6974(5), b = 11.8520(5), c = 15.1773(7) Å, β = 101.230(2)°, V = 1887.42(15) Å^3 are based upon the refinement of the *XYZ* centroids of reflections above $20\sigma(I)$. Data were corrected for absorption effects by using the multiscan method (SADABS).[26] The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5839 and 0.7461. The structure was solved and refined by using the Bruker SHELXTL software package using the space group $P2_1/n$ with Z = 4 for the formula unit $C_{22}H_{27}ISi$. The final anisotropic full-matrix least-squares refinement on F^2 with 220 variables converged at $R1$ = 2.12 % for the observed data and $wR2$ = 5.18 % for all data. The goodness-of-fit was 1.090. The largest peak in the final difference electron density synthesis was 0.606 *e* Å^{-3} and the largest hole was –0.546 *e* Å^{-3} with an RMS deviation of 0.095 *e* Å^{-3}. On the basis of the final model, the calculated density was 1.571 g cm^{-3} and F(000) = 904 *e* (Table 1).

X-ray Crystal Structure Determination of Compound 10: A colorless prism-like specimen of $C_{34}H_{37}IO_8Si$, approximate dimensions 0.41 mm × 0.20 mm × 0.17 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured with a Bruker X8 APEXII CCD system equipped with a graphite monochromator and Mo-K_α (λ = 0.71073 Å) sealed tube. The frames were integrated by using the Bruker SAINT V8.37A software package[25] using a narrow-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 176875 reflections to a maximum θ angle of 35.1° and a minimum θ angle of 1.6° (0.62 Å resolution), of which 13773 were independent (average redundancy

Table 1. Experimental data[a] from the X-ray crystal-structure determinations of compounds **2**, **10**, **11**, and **13**.

Compound	**2**	**10**	**11**	**13**
Molecular formula	$C_{22}H_{27}ISi$	$C_{34}H_{37}IO_8Si$	$C_{34}H_{39}IO_8Si{\cdot}CH_2Cl_2$	$C_{34}H_{39}FO_8Si$
Molecular mass	446.42	728.62	815.57	622.74
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$P2_1$
Unit cell dimensions				
a [Å]	10.6974(5)	9.4212(4)	13.492(2)	13.5766(8)
b [Å]	11.8520(5)	12.9967(6)	7.9880(14)	7.8653(4)
c [Å]	15.1773(7)	13.3746(5)	31.941(5)	14.9087(8)
α [°]	90	76.241(2)	90	90
β [°]	101.230(2)	82.033(2)	98.032(5)	108.082(2)
γ [°]	90°	84.308(3)	90	90
V [Å^3]	1887.42(3)	1571.56(12)	3408.7(10)	1513.39(14)
Z	4	2	4	2
Density [Mg/m^3]	1.571	1.540	1.589	1.367
Absorption coefficient [mm^{-1}]	1.761	1.109	1.183	0.137
F(000)	904	744	1664	660
Crystal size [mm^3]	0.568 × 0.177 × 0.143	0.410 × 0.200 × 0.170	0.258 × 0.095 × 0.075	0.451 × 0.096 × 0.059
θ range for data collection [°]	2.196–30.618	1.579–35.056	2.129–26.446	2.442–26.417
Index ranges	$-15 \le h \le 15$	$-15 \le h \le 15$	$-16 \le h \le 16$	$-16 \le h \le 16$
	$-16 \le k \le 16$	$-20 \le k \le 20$	$-9 \le k \le 9$	$-9 \le k \le 9$
	$-21 \le l \le 21$	$-21 \le l \le 21$	$-40 \le l \le 39$	$-18 \le l \le 18$
Reflections collected	50804	176875	58589	16671
Independent reflections	5778	13773	6901	6171
	[R_{int} = 0.0313]	[R_{int} = 0.0626]	[R_{int} = 0.1058]	[R_{int} = 0.0317]
Completeness to θ [°]	25.242 (99.9 %)	25.242 (100.0 %)	25.242 (99.0 %)	25.242 (99.8 %)
Absorption correction	semi-empirical from equivalents	semi-empirical from equivalents	multiscan	semi-empirical from equivalents
Max. and min. transmission	0.7461 and 0.5839	0.7190 and 0.8138	0.7454 and 0.5356	0.7454 and 0.7188
Data/restraints/parameters	5778/0/220	13773/0/404	6901/0/425	6171/1/404
Goodness-of-fit on F^2	1.090	1.084	1.118	1.047
Final R indices	R_1 = 0.0212	R_1 = 0.0346	R_1 = 0.0686	R_1 = 0.0338
[$I > 2\sigma(I)$]	wR_2 = 0.0498	wR_2 = 0.0750	wR_2 = 0.1369	wR_2 = 0.0765
R indices (all data)	R_1 = 0.0266	R_1 = 0.0523	R_1 = 0.0966	R_1 = 0.0414
	wR_2 = 0.0518	wR_2 = 0.0795	wR_2 = 0.1490	wR_2 = 0.0806
Largest diff. peak and hole [e Å^{-3}]	0.606 and –0.546	1.873 and –1.486	1.874 and –1.610	0.229 and –0.230

[a] Temperature: 100(2) K; refinement method: full-matrix least-squares on F^2; extinction coefficient: n/a; absolute structure parameter for compound **13**: –0.02(5).

12.72, completeness = 99.1 %, R_{int} = 6.26 %, R_{sig} = 4.33 %) and 10896 (79.11 %) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.4212(4), b = 12.9967(6), c = 13.3746(5) Å, α = 76.241(2), β = 82.033(2), γ = 84.308(3)°, V = 1571.56(12) Å^3 are based upon the refinement of the *XYZ* centroids of 9157 reflections between θ angular values of 2.5 and 30.9°. Data were corrected for absorption effects by using the multiscan method (SADABS2014/5),[26] Bruker AXS area detector, and absorption correction. The calculated minimum and maximum transmission coefficients are 0.7190 and 0.8138. The structure was solved and refined by using the Bruker SHELX-2014 software package[15] using the space group $P\bar{1}$ with Z = 2 for the formula unit $C_{34}H_{37}IO_8Si$. The final anisotropic full-matrix least-squares refinement on F^2 with 404 variables converged at $R1$ = 3.46 % for the observed data and $wR2$ = 7.95 % for all data. The goodness-of-fit was 1.084. The largest peak in the final difference electron density synthesis was 1.783 e Å^{-3} and the largest hole was –1.486 e Å^{-3} with an RMS deviation of 0.110 e Å^{-3}. On the basis of the final model, the calculated density was 1.540 g cm^{-3} and F(000) = 744 e (Table 1).

X-ray Crystal Structure Determination of Compound 11: A colorless prism-like specimen of $C_{34}H_{39}IO_8Si{\cdot}CH_2Cl_2$, approximate dimensions 0.075 mm × 0.095 mm × 0.258 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured with a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å). The frames were integrated by using the Bruker SAINT software package[25] using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 58589 reflections to a maximum θ angle of 26.45° (0.80 Å resolution) of which 6901 were independent (average redundancy 8.490, completeness = 98.4 %, R_{int} = 10.58 %, R_{sig} = 7.23 %) and 5378 (77.93 %) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.492(2), b = 7.9880(14), c = 31.941(5) Å, β = 98.032(5)°, V = 3408.6(10) Å^3 are based upon the refinement of the *XYZ* centroids of reflections above $20\sigma(I)$. Data were corrected for absorption effects by using the multiscan method (SADABS).[25] The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.5356 and 0.7454. The structure was solved and refined by using the Bruker SHELXTL software package[26] by using the space group $P2_1/c$ with Z = 4 for the formula unit $C_{34}H_{39}IO_8Si{\cdot}CH_2Cl_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 425 variables converged at $R1$ = 6.86 % for the observed data and wR_2 = 14.90 % for all data. The goodness-of-fit was 1.118. The largest peak in the final difference electron density synthesis was 1.874 e Å^{-3} and the largest hole was –1.610 e Å^{-3} with an RMS deviation of 0.153 e Å^{-3}. On the basis of the final model, the calculated density was 1.589 g cm^{-3} and F(000) = 1664 e (Table 1).

X-ray Crystal Structure Determination of Compound 13: A colorless prism-like specimen of $C_{34}H_{39}FO_8Si$, approximate dimensions

0.059 mm × 0.096 mm × 0.451 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped with a multilayer monochromator and a Mo microfocus (λ = 0.71073 Å). The frames were integrated by using the Bruker SAINT software package[25] using a narrow-frame algorithm. The integration of the data by using a monoclinic unit cell yielded a total of 16671 reflections to a maximum θ angle of 26.42° (0.80 Å resolution), of which 6171 were independent (average redundancy 2.702, completeness = 99.7 %, R_{int} = 3.17 %, R_{sig} = 3.74 %) and 5537 (89.73 %) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.5766(8), b = 7.8653(4), c = 14.9087(8) Å, β = 108.082(2)°, V = 1513.39(14) Å^3 are based upon the refinement of the XYZ centroids of reflections above $20\sigma(I)$. Data were corrected for absorption effects by using the multiscan method (SADABS).[25] The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.7188 and 0.7454. The structure was solved and refined by using the Bruker SHELXTL software package[26] and the space group $P2_1$ with Z = 2 for the formula unit $C_{34}H_{39}FO_8Si$. The final anisotropic full-matrix least-squares refinement on F^2 with 404 variables converged at $R1$ = 3.38 % for the observed data and $wR2$ = 8.06 % for all data. The goodness-of-fit was 1.047. The largest peak in the final difference electron density synthesis was 0.229 e Å^{-3} and the largest hole was –0.230 e Å^{-3} with an RMS deviation of 0.047 e Å^{-3}. On the basis of the final model, the calculated density was 1.367 g cm^{-3} and $F(000)$ = 660 e (Table 1).

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[1] a) G. Szeimies, *Chimia* **1981**, *35*, 243–248; b) W. T. Borden, *Chem. Rev.* **1989**, *89*, 1095–1109; c) W. T. Borden, *Synlett* **1996**, 711–719; d) J. P. Melder, H. Weber, A. Weller, E. Sackers, H. Fritz, D. Hunkler, H. Prinzbach, *Res. Chem. Intermed.* **1996**, *22*, 667–702; e) S. Vázquez, P. Camps, *Tetrahedron* **2005**, *61*, 5147–5208; f) H. Hopf, *Classics in Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**, pp. 122–137; g) A. Nicolaides in *Strained Hydrocarbons* (Ed. H. Dodziuk), Wiley-VCH, Weinheim, **2009**, pp. 112–121.

[2] N. M. Weinshenker, F. D. Greene, *J. Am. Chem. Soc.* **1968**, *90*, 506.

[3] a) P. E. Eaton, M. Maggini, *J. Am. Chem. Soc.* **1988**, *110*, 7230–7232; b) P. E. Eaton, C.-H. Lee, Y. Xiong, *J. Am. Chem. Soc.* **1989**, *111*, 8016–8018; c) K. Lukin, P. E. Eaton, *J. Am. Chem. Soc.* **1995**, *117*, 7652–7656.

[4] J. Kenndoff, K. Polborn, G. Szeimies, *J. Am. Chem. Soc.* **1990**, *112*, 6117–6118.

[5] G. E. Renzoni, T. K. Yin, W. T. Borden, *J. Am. Chem. Soc.* **1986**, *108*, 7121–7122.

[6] a) P. Camps, M. Font-Bardia, F. Pérez, X. Solans, S. Vázquez, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 912–914; *Angew. Chem.* **1995**, *107*, 1011–1012; b) P. Camps, M. Font-Bardia, F. Pérez, L. Solà, X. Solans, S. Vázquez, *Tetrahedron Lett.* **1996**, *37*, 8601–8604; c) P. Camps, F. J. Luque, M. Orozco, F. Pérez, S. Vázquez, *Tetrahedron Lett.* **1996**, *37*, 8605–8608; d) P. Camps, J. A. Fernández, S. Vázquez, M. Font-Bardia, X. Solans, *Angew. Chem. Int. Ed.* **2003**, *42*, 4049–4051; *Angew. Chem.* **2003**, *115*, 4183–4185; e) P. Camps, M. R. Muñoz, S. Vázquez, *J. Org. Chem.* **2005**, *70*, 1945–1948; f) P. Camps, M. R. Muñoz, S. Vázquez, *Tetrahedron* **2006**, *62*, 7645–7652.

[7] M. A. Forman, C. Moran, J. P. Herres, J. Stairs, E. Chopko, A. Pozzessere, M. Kerrigan, C. Kelly, L. Lowehyj, K. Salandria, A. Gallo, E. Loutzenhiser, *J. Org. Chem.* **2007**, *72*, 2996–3005.

[8] M. Rey-Carrizo, M. Barniol-Xicota, M. Font-Bardia, S. Vázquez, *Angew. Chem. Int. Ed.* **2014**, *53*, 8195–8199; *Angew. Chem.* **2014**, *126*, 8334–8338.

[9] P. Camps, D. Lozano, M. Font-Bardia, *Eur. J. Org. Chem.* **2015**, 5013–5020.

[10] K. Tanaka, K. Takeishi, *Synthesis* **2007**, 2920–2923.

[11] P. J. Stang, A. Schwarz, T. Blume, V. V. Zhdankin, *Tetrahedron Lett.* **1992**, *33*, 6759–6762.

[12] a) W. M. Jones, J. Klosin, "Transition-metal complexes of arynes, strained cyclic alkynes, and strained cyclic cumulenes" in *Advances in Organometallic Chemistry, Vol. 42*, (Eds.: F. G. A. Stone, R. West), Academic Press, San Diego **1998**, p. 147; b) A. Nicolaides, J. M. Smith, A. Kumar, D. M. Barnhart, W. T. Borden, *Organometallics* **1995**, *14*, 3475–3485.

[13] a) D. Peña, D. Pérez, E. Guitián, L. Castedo, *J. Am. Chem. Soc.* **1999**, *121*, 5827–5828; b) D. Peña, B. Iglesias, I. Quintana, D. Pérez, E. Guitián, L. Castedo, *Pure Appl. Chem.* **2006**, *78*, 451–455.

[14] G. Domínguez, J. Pérez-Castells, *Chem. Eur. J.* **2016**, *22*, 6720–6739.

[15] a) H. Suzuki, K. Itoh, Y. Ishii, K. Simon, J. A. Ibers, *J. Am. Chem. Soc.* **1976**, *98*, 8494–8500; b) L. D. Brown, K. Itoh, H. Suzuki, K. Irai, J. A. Ibers, *J. Am. Chem. Soc.* **1978**, *100*, 8232–8238.

[16] a) E. W. Della, N. J. Head, *J. Org. Chem.* **1992**, *57*, 2850–2855; b) E. W. Della, N. J. Head, W. K. Janowski, C. H. Schiesser, *J. Org. Chem.* **1993**, *58*, 7876–7882.

[17] S. Rozen, M. Brand, *J. Org. Chem.* **1981**, *46*, 733–736.

[18] G. A. Olah, J. G. Shih, B. P. Singh, B. G. B. Gupta, *Synthesis* **1983**, 713–715.

[19] M. Bremer, P. S. Gregory, P v. R. Schleyer, *J. Org. Chem.* **1989**, *54*, 3796–3799.

[20] J. B. Lambert, E. C. Chelius, *J. Am. Chem. Soc.* **1990**, *112*, 8120–8126.

[21] L. S. Kocsis, H. N. Kagalwala, S. Mutto, B. Godugu, S. Bernhard, D. J. Tantillo, K. M. Brummond, *J. Org. Chem.* **2015**, *80*, 11686–11698.

[22] Q.-B. Zhang, W.-L. Jia, Y.-L. Ban, Y. Zheng, Q. Liu, L.-Z. Wu, *Chem. Eur. J.* **2016**, *22*, 2595–2598.

[23] a) J. A. Crossley, J. D. Kirkman, D. L. Browne, J. P. A. Harrity, *Tetrahedron Lett.* **2010**, *51*, 6608–6610; b) D. Rodríguez-Lojo, D. Pérez, D. Peña, E. Guitián, *Chem. Commun.* **2013**, *49*, 6274–6276.

[24] E. Yoshioka, H. Miyabe, *Tetrahedron* **2012**, *68*, 179–189.

[25] *APEX3* (version 2016-1-0), *SAINT* (version 8.35A), *SADABS* (version 2014/5), Bruker AXS Inc., Madison, Wisconsin, USA, **2016**.

[26] G. M. Sheldrick, *Acta Crystallogr., Sect. C* **2015**, *71*, 3–8.

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