**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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40    **ABSTRACT:**

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42    A convenient synthesis of an octacyclic compound containing an iodo and a trimethylsilyl group in

43    vicinal doublebridgehead positions, as a possible precursor of a pyramidalized alkene, is described. The

44    key step of the synthesis consists of a double nucleophilic substitution of two neopentyl-type iodides by

45    cyclopentadienide anions followed by two intramolecular Diels–Alder cycloadditions. All attempts to

46    generate the expected pyramidalized alkene from the above precursor on reaction with different sources

47    of fluoride failed. This octacyclic compound, which contains two disubstituted C=C bonds, underwent a

48    chemo- and stereoselective Pd0-catalyzed co-cyclotrimerization with dimethyl acetylenedicarboxylate

49    give a nonacyclic cyclohexadiene derivative that can be aromatized upon reaction with CsF or

50    transformed into a related fluoride upon reaction with AgF.

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**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[3.3.1.03,7]non-3(7)-ene,[5] tricyclo[ 3.3.0.03,7]oct-1(5)-ene and derivatives,[6] pentacyclo-[4.3.0.02,4.03,8.05,7]non-4-ene,[7] and 3,4,8,9-etramethyltetracyclo[4.4.0.03,9.04,8]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).

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 generated 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]

Moreover, the preparation of the diiodide precursor in the series of tricyclo[3.3.0.03,7]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.

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 neopentyltype 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).

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 onsidered 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)·CHCl3 ([Pd2(dba)3·CHCl3], 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

126  remote from the iodine and trimethylsilyl substituents and hence less affected by the steric effect of the

127  trimethylsilyl group (Scheme 3). The structure of this compound was clearly established by X-ray

128  diffraction analysis (Figure 3) and was fully characterized on the basis of its spectroscopic data and

129  elemental analysis. Once again, the trimethylsilyl group remained unaffected under these conditions.

130  Thus, the palladium catalyst does not seem to promote the formation of pyramidalized alkene 3 or a

131  palladium complex derivative.

132  It is known that palladium(0) catalyzes the co-cyclotrimerization of acetylenes with electron-deficient or

133  some bicyclic olefins.[14] In particular, norbornene reacts with 2 equivalents of DMAD in the presence

134  of a catalytic amount of tetrakis(methoxycarbonyl) palladiacyclopentadiene to give stereoselectively a

135  cyclohexadiene derivative.[15] When compound 2 was treated with DMAD in the presence of

136  [Pd2(dba)3] (10 mol-%) in 1,4-dioxane at reflux, nonacycle 11 was obtained in high yield. As before,

137  the structure and configuration of this compound was clearly established by X-ray diffraction analysis

138  (Figure 4). It was also fully characterized on the basis of its spectroscopic data and elemental analysis.

139  As before, the more remote C=C bond in 2 with respect to the trimethylsilyl and iodine substituents is

140  the only one that reacts, in spite of using an excess of DMAD, a fact reasonably associated with the

141  steric hindrance of the trimethylsilyl group, which includes not only the carbocyclic skeleton but also

142  the vicinal iodide substituent.

143  Taking into account the fact that the conversion of 11 into 10 might require an oxidant, compound 11

144  was treated with an excess of AgF (3 equiv.) under similar reaction conditions to those used before.

145  Worthy of note, compound 13, which still contains the cyclohexadiene subunit and with the iodine atom

146  having been replaced by fluorine, was the only isolated product (47 % yield) from this reaction, the

147  formation of compound 10 not being observed. The structure and configuration of compound 13 was

148  also established by X-ray diffraction analysis (Figure 5) and fully characterized on the basis of its

149  spectroscopic data and elemental analysis. Compound 13 was also obtained, although in only 31 %

150  yield, upon reaction of octacycle 2 with excess DMAD in the presence of [Pd2(dba)3] (10 mol-%) and

151  AgF (3 equiv.) in 1,4-dioxane at reflux. As expected, when compound 2 was treated with excess AgF in

152  1,4-dioxane at reflux, octacycle fluoride 12 was obtained in 46 % yield. Bridgehead iodides have

153  previously been transformed into the corresponding fluorides upon reaction with different reagents, such

154  as XeF2,[16] elemental fluorine,[17] nitronium tetrafluoroborate/pyridine polyhydrogen fluoride or

155  sodium nitrate/pyridine polyhydrogen fluoride,[18] and HgF2,[19] the last reagent giving better results

156  than AgF for the studied halogenated adamantanes. It seems reasonable that the conversion of

157  compounds 11 and 2 into 13 and 12, respectively, takes place through an SN1-type mechanism,[19] the

158     -silicon syn effect helping to stabilize the pyramidalized intermediate carbocation.[20]

159  Worthy of note, the reaction of nonacycle 11 with excess CsF in 1,4-dioxane at reflux gave compound

160  10 in 89 % yield as the only isolated product. A possible explanation of this transformation is given in

161  Scheme 4. The fluoride could catalyze the tautomerizaton of 11 to a cis-1,4-dihydrobenzene derivative,

162  which might lose hydrogen in a concerted (4q+2)-allowed process, as recently proposed in a related

163 dehydrogenation.[21] An alternative ionic mechanism for the dehydrogenation of 11 is also shown in

164 Scheme 4. Alternatively, although this transformation was carried out under Ar, we cannot exclude the

165 possibility of an autoxidation process.[22] The inability to generate pyrimidalized alkene 3 from 2 upon

166 reaction with different sources of fluoride under different conditions, including the presence of AgF to

167 increase the leaving group capacity of the iodide group, is in striking contrast to previous works in

168 which vicinal halo-trimethylsilyl compounds were transformed into reactive intermediates such as

169 pyramidalized alkenes[3c] or benzynes[23] upon reaction with diverse fluoride sources. The steric

170 hindrance of the trimethylsilyl group in this compound might be responsible of this lack of reactivity. In

171 accord with the indications of the referees, a mixture of compound 2 and a great excess of

172 tetrabutylammonium fluoride (TBAF, from a 1 M solution in THF) was heated at 150 °C for 19 h, after

173 the solvent had been distilled off. The partial degradation of TBAF to tributylamine was observed, most

174 of the starting 2 was recovered, and some degradation products were also detected. CCDC 1522945 (for

175 2), 1522948 (for 10), 1522946 (for 11), and 1522947 (for 13) contain the supplementary

176 crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

177 Crystallographic Data Centre.

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## 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, 13C, and 19F NMR) and, in several cases, X-ray diffraction analysis. Assignments given for the NMR spectra are based on DEPT, COSY, NOESY, 1H/13C single quantum correlation (gHSQC sequence) and 1H/13C multiple bond correlation (gHMBC sequence) spectra. 1H and 13C NMR spectra were recorded with a Varian Mercury 400 (400 MHz for 1H, 100.6 MHz for 13C, and 376.28 MHz for 19F) spectrometer. Unless otherwise stated, the NMR spectra were recorded in CDCl3. Chemical shifts ($\delta$) are reported in parts per million relative to internal TMS or CDCl3 (for 1H and 13C NMR) and to external CFCl3 ($\delta$ = 0 ppm, for 19F 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 KMnO4. 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, [Pd2(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]

**[(1R\*,4S\*)-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

226    CH2Cl2 (50 mL), and the mixture was stirred for 30 min at this temperature. Bis(trimethylsilyl)

227    acetylene (5.00 g, 29.3 mmol) was added and stirring at 0 °C was continued for 2 h. The solution was

228    concentrated in vacuo at room temperature, hexane (120 mL) was added to the white oily residue, and

229    the mixture was stirred for 10 min. The solid formed was filtered, washed with Et2O (3 × 10 mL), and

230    dried in vacuo to give iodonium triflate 4 (9.28 g). The combined filtrate and washings were

231    concentrated in vacuo at room temperature to give an oily residue. Hexane (70 mL) was added to this

232    residue and the solid formed was filtered, washed with Et2O (3 × 8 mL), and dried in vacuo to give

233    more triflate 4 (1.23 g, altogether 10.51 g, 80 % yield), some of which was used as such in the next step.

234    A solution of cyclopentadiene 1 (284 mg, 1.35 mmol) in anhydrous acetonitrile (3 mL) was added

235    dropwise to a magnetically stirred and cold solution (–35 °C, cryocool) of phenyl[(trimethylsilyl)-

236    ethynyl]iodonium trifluoromethanesulfonate (4; 790 mg, 1.75 mmol) in anhydrous acetonitrile (3 mL)

237    under Ar, and the mixture was heated at reflux for 64 h. The solvent was distilled in vacuo and the black

238    oily residue was taken in acetonitrile (1.7 mL). This solution was added dropwise to a cold mixture (–35

239    °C, cryocool) of NaI (206 mg, 1.37 mmol) and CuI (263 mg, 1.38 mmol) in anhydrous acetonitrile (3.8

240    mL). The reaction mixture was allowed to warm to room temperature and then it was stirred at this

241    temperature for 17 h. The solvent was distilled in vacuo and the black solid residue was extracted with

242    CH2Cl2 (3 × 20 mL). The solvent and the formed iodobenzene were eliminated in vacuo from the

243    combined extracts. The brown oily residue (443 mg) was subjected to automated column

244    chromatography (35–70 μm silica gel, 12 g, hexane/EtOAc mixtures). On elution with hexane/EtOAc

245    (9:1, 3 min), diacetate 6 (186 mg, 32 % yield) was obtained as a yellow oil. Rf (silica gel, 10 cm,

246    hexane/EtOAc, 8:2) = 0.43. 1H NMR (400 MHz, CDCl3): δ = 0.16 [s, 9 H, Si(CH3)3], 2.02 (s, 3 H,

247    anti-CH3COO), 2.03 (s, 3 H, syn-CH3COO), 3.48 [overlapped pseudo-dt, 4J(H,H) = 0.9, 3J(H,H) =

248    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

249    H, 4-H], 4.15 [d, 2J(H,H) = 11.6 Hz, 1 H, anti-CHaOAc], 4.20 [overlapped d, 2J(H,H) = 11.6 Hz, 1 H,

250    syn-CHaOAc], 4.21 [overlapped d, 2J(H,H) = 11.6 Hz, 1 H, syn-CHbOAc], 4.24 [d, 2J(H,H) = 11.6 Hz,

251    1 H, anti-CHbOAc], 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

252    [ddd, 3J(H,H) = 5.6, 3J(H,H) = 3.2 Hz, 4J(H,H) = 0.9 Hz, 1 H, 6-H]. 13C NMR (100.6 MHz, CDCl3): δ

253    = –1.9 [CH3, Si(CH3)3], 20.79 (anti-CH3COO), 20.85 (syn- CH3COO), 59.7 (CH, C-4), 64.5 (CH2,

254    anti-CH2OAc), 64.7 (CH2, syn-CH2OAc), 68.4 (CH, C-1), 84.1 (C, C-7), 115.9 (C, C-2), 139.2 (CH, C-

255    6), 141.0 (CH, C-5), 154.2 (C, C-3), 170.6 (syn-CH3COO), 170.7 ppm (anti-CH3COO). IR (ATR): ṽ =

256    2950 (w), 1541 (m), 1739 (s), 1537 (w), 1374 (m), 1361 (m), 1232 (s), 1028 (s), 1000 (m), 977 (m), 860

257    (m), 837 (s), 754 (m), 734 (m), 692 cm–1 (m). HRMS: calcd. for C16H23IO4Si + NH4 + 452.0749;

258    found 452.0747. C16H23IO4Si (434.35): calcd. C 44.24, H 5.34, I 29.22; found C 44.05, H 5.27, I

259    29.53.

260    **[(1R*,4S*)-2-Iodo-3-(trimethylsilyl)bicyclo[2.2.1]hepta-2,5-diene-7,7-diyl]dimethanol (7):** K2CO3

261    (22 mg, 0.16 mmol) was added to a solution of diacetate 6 (271 mg, 0.62 mmol) in anhydrous MeOH

262    (6.3 mL) and the mixture was heated at reflux for 2 h. A saturated aqueous solution of NaHCO3 (0.1

263    mL) was added. The mixture was cooled to 0 °C with an ice/water bath and filtered. The solid was

264    washed with MeOH (4 × 5 mL). The combined filtrate and washings were concentrated in vacuo, the

265    oily residue was taken in $CH_2Cl_2$ (5 mL), and the solution was dried with anhydrous $Na_2SO_4$ and

266    concentrated in vacuo to give diol 7 as a brown oil (201 mg). This crude product was subjected to

267    column chromatography (35–70 μm silica gel, 5.0 g, hexane/EtOAc mixtures). On elution with

268    hexane/EtOAc (95:5), diol 7 (168 mg, 77 % yield) was obtained as a yellow oil. Crystallization of the

269    above product from pentane (1 mL) gave the analytical sample of 7 as a white solid. Rf (silica gel, 10

270    cm, hexane/EtOAc, 3:7) = 0.38; m.p. 55–56 °C (pentane). 1H NMR (400 MHz, $CDCl_3$): δ = 0.18 [s, 9

271    H, $Si(CH_3)_3$], 2.05–2.10 (br. s, 1 H) and 2.10–2.15 (br. s, 1 H, 2 OH), 3.50 [pseudo-dt, $^4J(H,H)$ = 0.8,

272    $^3J(H,H)$ = $^4J(H,H)$ = 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

273    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, $^2J(H,H)$ =

274    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

275    ppm [ddd, $^3J(H,H)$ = 5.2, $^4J(H,H)$ = 3.2, $^3J(H,H)$ = 1.1 Hz, 1 H, 6-H]. 13C NMR (100.6 MHz, $CDCl_3$):

276    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),

277    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): ṽ =

278    3100–3600 (br, m), 2952 (m), 1541 (m), 1247 (m), 1008 (s), 836 (vs), 755 (m), 727 (m), 691 cm–1 (m).

279    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

280    41.15, H 5.47, I 36.23; found C 41.17, H 5.45, I 36.15.

281    **[(1R\*,4S\*)-2-Iodo-3-(trimethylsilyl)bicyclo[2.2.1]hepta-2,5-diene-7,7-diyl]bis(methylene)**

282    **Dimethanesulfonate (8):** Methanesulfonyl chloride (50 μL, 0.60 mmol) was added dropwise to a cold

283    (0 °C, ice/water bath) and magnetically stirred solution of a mixture of diol 7 (87 mg, 0.25 mmol) and

284    $Et_3N$ (0.14 mL, 1.0 mmol) in anhydrous $CH_2Cl_2$ (2 mL) under Ar, and the mixture was stirred at this

285    temperature for 1.5 h. A saturated aqueous solution of $NaHCO_3$ (0.1 mL) was added. The organic phase

286    was separated and was washed with a saturated aqueous solution of NaHCO (3 × 2 mL). The combined

287    aqueous phases were extracted with $CH_2Cl_2$ (3 × 5 mL). The combined organic phases and extracts

288    were washed with water (3 mL) and brine (3 mL), dried (anhydrous $Na_2SO_4$), and concentrated in

289    vacuo to give dimesylate 8 as a brown oil (140 mg). This crude product was subjected to automated

290    column chromatography (35–70 μm silica gel, 4.0 g, hexane/EtOAc mixtures). On elution with

291    hexane/EtOAc (4:1) to hexane/EtOAc (1:9; 4 min), dimesylate 8 (112 mg, 89 % yield) was obtained as a

292    yellow oil. Crystallization of the above product from EtOAc/pentane (1:3, 2 mL) gave the analytical

293    sample of 8 as a white solid. Rf (silica gel, 10 cm, hexane/EtOAc, 3:7) = 0.76; m.p. 82–83 °C. 1H NMR

294    (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

295    (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,

296    1 H, syn- and anti- $CHaOMs$), 4.43 [d, $^2J(H,H)$ = 9.6 Hz, 2 H, syn- and anti-$CHbOMs$), 6.71 [dd,

297    $^3J(H,H)$ = 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-

298    H]. 13C NMR (100.6 MHz, $CDCl_3$): δ = –2.0 [$CH_3$, $Si(CH_3)_3$], 37.20 ($CH_3$, $CH_3SO_3$), 37.21 ($CH_3$,

299    $CH_3SO_3$), 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): ṽ = 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.

**[(1R*,4S*)-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. 1H NMR (400 MHz, CDCl3): δ = 0.22 [s, 9 H, Si(CH3)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- CH2I), 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]. 13C NMR (100.6 MHz, CDCl3): δ = –1.7 [CH3, Si(CH3)3], 13.88 (CH2, CH2I), 13.95 (CH2, CH2I), 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): ṽ = 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.

**(1R*,3aS*,4R*,4aR*,4bS*,5R*,8S*,8aR*,9S*,9aS*,10aR*, 11S*,13S*)-4-Iodo-13-(trimethylsilyl)-3a,4,4a,4b,5,8,8a,9, 10,10a-decahydro-1H-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 NaHCO3 (3 × 10 mL), water (2 × 10 mL), and brine (10 mL), dried (anhydrous Na2SO4), 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 CH2Cl2/MeOH (1:3; 2 mL). Rf (silica gel, 10 cm, hexane/EtOAc, 9:1) = 0.74; m.p. 108.7–109.5 °C (CH2Cl2/MeOH). 1H NMR (400 MHz, CDCl3): δ = 0.19 [s, 9 H, Si(CH3)3], 1.33 [dd, 2J(H,H) = 14.2, 3J(H,H) = 2.6 Hz, 1 H, 12-Ha], 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-Hb], 1.53 [overlapped dd, 2J(H,H) = 14.8, 3J(H,H) = 2.8 Hz, 1 H, 10-Ha], 1.57 [overlapped dd, 2J(H,H) = 14.8, 3J(H,H) = 3.2 Hz, 1 H, 10-Hb], 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]. 13C NMR (100.6 MHz, CDCl3): δ = 4.0 [CH3, Si(CH3)3], 35.0 (CH2, C-10), 35.4 (CH2, 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): ṽ = 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 C22H27ISi + H+ 447.0999; found 447.0991; calcd. for C22H27ISi – I+ 319.1877; found 319.1873. C22H27ISi (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

374 mmol) and tetraphenylcyclopentadienone (65 mg, 0.17 mmol) in a mixture of anhydrous THF (1.5 mL)

375 and acetonitrile (1.5 mL), and the mixture was heated at 60 °C for 17 h.

376 **Reaction with Tetrabutylammonium Fluoride in the Presence of Tetraphenylcyclopentadienone:**

377 Procedure 1: Tetraphenylcyclopentadienone (65 mg, 0.17 mmol) was added to a cold (0 °C) suspension

378 of tetrabutylammonium fluoride (1 M in acetonitrile, 0.34 mL, 0.34 mmol). Then octacycle 2 (50 mg,

379 0.11 mmol) in anhydrous THF (50 μL) was added and the mixture was stirred at 0 °C for 1 h.

380 Procedure 2: A suspension of tetrabutylammonium fluoride (1 M in acetonitrile, 70 μL, 70 μmol) was

381 added to a solution of octacycle 2 (10 mg, 22 μmol) and tetraphenylcyclopentadienone (17 mg, 44 μmol)

382 in anhydrous 1,4-dioxane (0.5 mL), and the mixture was heated at 100 °C for 19 h.

383 **Reaction with CsF and AgF in the Presence of Anthracene:** Anhydrous CsF (85 mg, 0.56 mmol) and

384 AgF (43 mg, 0.34 mmol) were added to a solution of octacycle 2 (50 mg, 0.11 mmol) and anthracene

385 (40 mg, 0.22 mmol) in a mixture of anhydrous 1,4-dioxane (2.5 mL) and acetonitrile (1 mL), and the

386 mixture was heated at 100 °C for 20 h.

387 **Tetramethyl (1R*,3aS*,4R*,4aR*,4bR*,5R*,10S*,10aS*, 11S*,11aS*,12aR*,14S*,15S*)-**

388 **3a,4,4a,4b,5,10,10a,11,12,12a-Decahydro-4-iodo-15-(trimethylsilyl)-1H-5,10,11a-(epiethane-**

389 **[1,1,2]triyl)-1,4,11-(epimethanetriyl)benzo[b]cyclopenta[h]-fluorene-6,7,8,9-tetracarboxylate (10):**

390 A 10 mL Schlenk tube equipped with a reflux condenser and magnetic stirrer was charged with a

391 solution of octacycle 2 (50 mg, 0.11 mmol) in anhydrous 1,4-dioxane (2.5 mL) under Ar. Then DMAD

392 (0.03 mL, 0.24 mmol), tris(dibenzylideneacetone)dipalladium(0)·CHCl3 (6 mg, 6 μmol), anhydrous CsF

393 (85 mg, 0.56 mmol), and AgF (43 mg, 0.34 mmol) were successively added and the mixture was stirred

394 and heated at 100 °C for 17 h. The reaction mixture was cooled to room temperature and concentrated in

395 vacuo to give a brown solid (196 mg), which was submitted to column chromatography [35–70 μm

396 silica gel (7 g), hexane/EtOAc mixtures] to give, on elution with hexane/ EtOAc (8:2), adduct 10 (28

397 mg, 34 % yield) as a white solid. An analytical sample of 10 (20 mg) was obtained as a white solid by

398 crystallization of the above product from CH2Cl2/pentane (1:4, 1 mL). Rf (silica gel, 10 cm,

399 hexane/EtOAc, 8:2) = 0.22; m.p. 117– 118 °C (CH2Cl2/pentane). 1H NMR (400 MHz, CDCl3): δ =

400 0.14 [s, 9 H, Si(CH3)3], 1.48 [dd, 2J(H,H) = 14.4, 3J(H,H) = 2.8 Hz, 1 H, 13-Hb], 1.60 [overlapped dd,

401 2J(H,H) = 14.8, 3J(H,H) = 3.2 Hz, 1 H, 13-Ha], 1.65 [overlapped d, 4J(H,H) = 0.8 Hz, 1 H, 11-H], 1.62–

402 1.68 [complex signal, 2 H, 12-Ha, 12-Hb], 1.90–1.93 (br. s, 1 H, 12a-H), 2.14–2.18 (br. s, 2 H, 14-H,

403 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–

404 3.28 (br. s, 1 H, 10-H), 3.48–3.50 (br. s, 1 H, 5-H), 3.86 (s, 3 H, OCH3), 3.88 (s, 3 H, OCH3), 3.90 (s, 3

405 H, OCH3), 3.93 (s, 3 H, OCH3), 5.99 [dd, 3J(H,H) = 6.0, 3J(H,H) = 3.2 Hz, 1 H, 3-H], 6.33 ppm [dd,

406 3J(H,H) = 6.0, 3J(H,H) = 3.2 Hz, 1 H, 2-H]. 13C NMR (100.6 MHz, CDCl3): δ = 3.9 [CH3,

407 Si(CH3)3],34.1 (CH2, C-13), 34.8 (CH2, C-12), 42.9 (C, C-11a), 43.2 (CH, C-10a), 45.9 (C, C-15), 48.6

408 (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 (CH3), 52.8

409 (CH3), 52.91 (CH3), 52.94 (CH3, 4 COOCH3), 53.4 (CH, C-11), 54.6 (CH, C-12a), 63.2 (CH, C-4a),

410 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),

411  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),

412  167.4 ppm (C, 4 COOCH3). IR (NaCl): ṽ = 2951 (m), 2918 (m), 1733 (s), 1444 (m), 1361 (m), 1321

413  (m), 1249 (s), 1212 (s), 1166 (m), 1143 cm–1 (m). HRMS: calcd. for $C_{34}H_{37}IO_8Si + NH_4^+$ 746.1641;

414  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

415  17.54.

416  **Tetramethyl (1R\*,3aS\*,4R\*,4aR\*,4bS\*,5R\*,5aR\*,9aR\*,**

417  **10S\*,10aS\*,11R\*,11aS\*,12aR\*,14S\*,15S\*)-3a,4,4a,4b,5,5a,9a, 10,10a,11,12,12a-Dodecahydro-4-**

418  **iodo-15-(trimethylsilyl)-1H-5,10,11a-(epiethane[1,1,2]triyl)-1,4,11-(epimethanetriyl)-**

419  **benzo[b]cyclopenta[h]fluorene-6,7,8,9-tetracarboxylate (11):** DMAD (0.1 mL, 0.79 mmol) and

420  tris(dibenzylideneacetone)dipalladium(0) (18 mg, 20 μmol) were added to a solution of octacycle 2 (88

421  mg, 0.20 mmol) in anhydrous 1,4-dioxane (4.4 mL) and the mixture was stirred and heated at 100 °C for

422  17 h. The reaction mixture was cooled to room temperature and concentrated in vacuo to give a brown

423  solid (190 mg), which was submitted to automated column chromatography [35–70 μm silica gel (4 g),

424  hexane/ EtOAc mixtures]. On elution with hexane/AcOEt (3:1) to hexane/ AcOEt (7:3, 4 min), adduct

425  11 (117 mg, 81 % yield) was obtained as a white solid. An analytical sample of 11 (93 mg) was obtained

426  as a white solid by crystallization of the above product from CH2Cl2/pentane (1:3, 1.5 mL). Rf (silica

427  gel, 10 cm, hexane/ EtOAc, 3:2) = 0.19; m.p. 117–118 °C (CH2Cl2/pentane). 1H NMR (400 MHz,

428  CDCl3): δ = 0.22 [s, 9 H, Si(CH3)3], 1.43 (overlapped s, 1 H, 11-H), 1.46 [overlapped dd, 2J(H,H) =

429  10.2, 3J(H,H) = 2.8 Hz, 1 H, 13-Hb], 1.51–1.60 [complex signal, 3 H, 12-Ha, 12-Hb, 13-Ha], 1.82–1.84

430  (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-

431  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,

432  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],

433  3.08 [d, 3J(H,H) = 12.4 Hz, 1 H, 5a-H], 3.74 (s, 3 H, OCH3), 3.75 (s, 3 H, OCH3), 3.76 (s, 3 H, OCH3),

434  3.79 (s, 3 H, OCH3), 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) =

435  5.8, 3J(H,H) = 3.0 Hz, 1 H, 2-H]. 13C NMR (100.6 MHz, CDCl3): δ = 4.0 [CH3, Si(CH3)3], 33.0

436  (CH2, C-13), 34.6 (CH2, C-12), 40.2 (CH, C-14), 43.60 (CH) and 43.64 (CH, C-5a, C-9a), 45.1 (C, C-

437  15), 46.3 (CH, C-10a), 51.1 (CH, C-4b), 52.46 (CH, C-1), 52.47 (CH3), 52.59 (CH3), 52.62 (CH3), (4

438  COOCH3), 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-

439  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),

440  139.2 (CH, C-3), 140.4 (CH, C-2), 166.5 (C) and 166.6 (C, 8-COOMe, 9-COOMe), 166.9 (C) and 167.0

441  ppm (C, 6-COOMe, 7-COOMe); according to the gHMBC spectrum, C-11a might be under the signals

442  at δ = 43.60 and 43.64 ppm. IR (NaCl): ṽ = 2949 (m), 2916 (m), 2840 (w), 1732 (s), 1644 (w), 1591

443  (w), 1434 (s), 1342 (m), 1243 (s), 1117 (m), 993 (m), 849 (m), 836 (m), 727 cm–1(m). HRMS: calcd.

444  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

445  5.14; found C 52.55, H 5.11.

446  **Preparation of Compound 10 from 11**: A solution of nonacycle 11 (51 mg, 0.07 mmol) in anhydrous

447  1,4-dioxane (1.5 mL) was placed in a 10 mL flask equipped with a reflux condenser and magnetic stirrer

448   under Ar. Then anhydrous CsF (32 mg, 0.21 mmol) was added and the mixture was stirred and heated at

449   100 °C for 16 h. The reaction mixture was cooled to room temperature and concentrated in vacuo to give

450   a white solid (87 mg), which was submitted to column chromatography [35–70 μm silica gel (2 g),

451   hexane/ EtOAc mixtures] to give, on elution with hexane/EtOAc (8:2), adduct 10 (45 mg, 89 % yield) as

452   a white solid.

453   **(1R*,3aS*,4R*,4aR*,4bS*,5R*,8S*,8aR*,9S*,9aS*,10aR*,11S*, 13S*)-4-Fluoro-13-**

454   **(trimethylsilyl)-3a,4,4a,4b,5,8,8a,9,10,10adecahydro-1H-5,8,9a-(epiethane[1,1,2]triyl)-1,4,9-**

455   **(epimethanetriyl) cyclopenta[b]fluorene (12):** A solution of octacycle 2 (63 mg, 0.14 mmol) in

456   anhydrous dioxane (3 mL) was added to a 10 mL flask equipped with a reflux condenser and magnetic

457   stirrer under Ar. Then anhydrous AgF (54 mg, 0.43 mmol) was added and the mixture was stirred and

458   heated at 100 °C for 15 h. The reaction mixture was cooled to room temperature and concentrated in

459   vacuo to give a residue (130 mg), which was submitted to column chromatography [35–70 μm silica gel

460   (1.0 g), hexane/EtOAc mixtures] to give, on elution with hexane, product 12 (22 mg, 46 % yield) as a

461   colorless oil. Rf (silica gel, 10 cm, hexane/EtOAc, 9:1) = 0.63. 1H NMR (400 MHz, CDCl3): $\delta$ = 0.05

462   [s, 9 H, Si(CH3)3], 1.37–1.44 (complex signal, 3 H, 10-Ha, 10-Hb, 12-Ha), 1.48 [dd, $^2J$(H,H) = 14.2,

463   $^3J$(H,H) = 3.0 Hz, 1 H, 12-Hb], 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.

464   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–

465   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

466   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]. 13C NMR

467   (100.6 MHz, CDCl3): $\delta$ = 3.1 [d, $^4J$(C,F) = 2.2 Hz, CH3, Si(CH3)3], 34.7 [d, $^4J$(C,F) = 2.3 Hz, CH2, C-

468   10], 35.4 (CH2, 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

469   (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),

470   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,

471   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,

472   $^1J$(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),

473   142.3 ppm (CH, C-2). 19F NMR (376.28 MHz, CDCl3): $\delta$ = –174.0 ppm. IR (NaCl): $\tilde{v}$ = 3062 (w),

474   2950 (m), 2916 (m), 2838 (w), 1329 (w), 1249 (m), 1135 (w). 858 (m), 836 (s), 721 (m), 712 (s), 627

475   cm–1 (m). HRMS: calcd. for C22H27FSi + NH4 + 356.2204; found 356.2191; calcd. For C22H27FSi –

476   F+ 319.1877; found 319.1875. C22H27FSi (338.54): calcd. C 78.05, H 8.04; found C 78.08, H 8.07.

477   **Tetramethyl (1R*,3aS*,4R*,4aR*,4bS*,5R*,5aR*,9aS*,10S*,**

478   **10aR*,11S*,11aR*,12aS*,14R*,15S*)-4-Fluoro-3a,4,4a,4b,5,5a, 9a,10,10a,11,12,12a-dodecahydro-**

479   **15-(trimethylsilyl)-1H-5,10,11a-(epiethane[1,1,2]triyl)-1,4,11-(epimethanetriyl)-**

480   **benzo[b]cyclopenta[h]fluorene-6,7,8,9-tetracarboxylate (13):** A solution of iodo nonacycle 11 (90

481   mg, 0.12 mmol) in anhydrous 1,4-dioxane (2.6 mL) was placed in a 10 mL flask equipped with a reflux

482   condenser and magnetic stirrer under Ar. Then anhydrous AgF (47 mg, 0.37 mmol) was added and the

483   mixture was stirred and heated at 100 °C for 16 h. The reaction mixture was cooled to room temperature

484   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). 1H NMR (400 MHz, $CDCl_3$): δ = 0.09 [s, 9 H, $Si(CH_3)_3$], 1.38–1.48 (complex signal, 2 H, 12-Ha, 12-Hb), 1.54 [overlapped pseudo-dt, $^2J(H,H)$ = 14.0, $^3J(H,H)$ = $^5J(H,F)$ = 2.8 Hz, 1 H, 13-Ha], 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-Hb], 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]. 13C 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-COOMe, 7-COOMe, 8-COOMe and 9-COOMe). 19F NMR (376.28 MHz, $CDCl_3$): δ = –173.8 ppm. IR (NaCl): ṽ = 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 %, Rint = 3.13 %, Rsig = 1.76 %) and 5168 (89.44 %) were greater than 2σ(F2). The final cell constants of a = 10.6974(5), b = 11.8520(5), c = 15.1773(7) Å, ꞵ = 101.230(2)°, V = 1887.42(15) Å3 are based upon the refinement of the XYZ centroids of reflections above 20σ(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 P21/n with Z = 4 for the formula unit C22H27ISi. The final anisotropic full-matrix least-squares refinement on F2 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 andthelargestholewas–0.546e Å–3withanRMSdeviationof0.095e 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 C34H37IO8Si, 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-Kα (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 12.72, completeness = 99.1 %, Rint = 6.26 %, Rsig = 4.33 %) and 10896 (79.11 %) were greater than 2σ(F2). The final cell constants of a = 9.4212(4), b = 12.9967(6), c = 13.3746(5) Å, α = 76.241(2), ꞵ = 82.033(2), γ = 84.308(3)°, V = 1571.56(12) Å3 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 P1‾ with Z = 2 for the formula unit C34H37IO8Si. The final anisotropic full-matrix least-squares refinement on F2 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 C34H39IO8Si·CH2Cl2, 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

559  equipped with a multilayer monochroma-tor and a Mo microfocus ($\lambda = 0.71073$ Å). The frames were

560  integrated by using the Bruker SAINT software package[25] using a narrow-frame algorithm. The

561  integration of the data using a monoclinic unit cell yielded a total of 58589 reflections to a maximum $\theta$

562  angle of 26.45° (0.80 Å resolution) of which 6901 were independent (average redundancy 8.490,

563  completeness = 98.4 %, Rint = 10.58 %, Rsig = 7.23 %) and 5378 (77.93 %) were greater than $2\sigma(F2)$.

564  The final cell constants of a = 13.492(2), b = 7.9880(14), c = 31.941(5) Å, $\beta$ = 98.032(5)°, V =

565  3408.6(10) Å3 are based upon the refinement of the XYZ centroids of reflections above $20\sigma(I)$. Data

566  were corrected for absorption effects by using the multiscan method (SADABS).[25] The calculated

567  minimum and maximum transmission coefficients (based on crystal size) are 0.5356 and 0.7454. The

568  structure was solved and refined by using the Bruker SHELXTL software package[26] by using the

569  space group P21/c with Z = 4 for the formula unit $C34H39IO8Si \cdot CH2Cl2$. The final anisotropic full-

570  matrix least-squares refinement on F2 with 425 variables converged at R1 = 6.86 % for the observed

571  data and wR2 = 14.90 % for all data. The goodness-of-fit was 1.118. The largest peak in the final

572  difference electron density synthesis was 1.874 e Å–3 and the largest hole was –1.610 e Å–3 with an

573  RMS deviation of 0.153 e Å–3. On the basis of the final model, the calculated density was 1.589 g cm–3

574  and F(000) = 1664 e (Table 1).

575  **X-ray Crystal Structure Determination of Compound 13**: A colorless prism-like specimen of

576  $C34H39FO8Si$, approximate dimensions 0.059 mm × 0.096 mm × 0.451 mm, was used for the X-ray

577  crystallographic analysis. The X-ray intensity data were measured on a D8 Venture system equipped

578  with a multilayer monochromator and a Mo microfocus ($\lambda = 0.71073$ Å). The frames were integrated by

579  using the Bruker SAINT software package[25] using a narrow-frame algorithm. The integration of the

580  data by using a monoclinic unit cell yielded a total of 16671 reflections to a maximum $\theta$ angle of 26.42°

581  (0.80 Å resolution), of which 6171 were independent (average redundancy 2.702, completeness = 99.7

582  %, Rint = 3.17 %, Rsig = 3.74 %) and 5537 (89.73 %) were greater than $2\sigma(F2)$. The final cell constants

583  of a = 13.5766(8), b = 7.8653(4), c = 14.9087(8) Å, $\beta$ = 108.082(2)°, V = 1513.39(14) Å3 are based

584  upon the refinement of the XYZ centroids of reflections above $20\sigma(I)$. Data were corrected for

585  absorption effects by using the multiscan method (SADABS).[25] The calculated minimum and

586  maximum transmission coefficients (based on crystal size) are 0.7188 and 0.7454. The structure was

587  solved and refined by using the Bruker SHELXTL software package[26] and the space group P21 with

588  Z = 2 for the formula unit $C34H39FO8Si$. The final anisotropic full-matrix least-squares refinement on

589  F2 with 404 variables converged at R1 = 3.38 % for the observed data and wR2 = 8.06 % for all data.

590  The goodness-of-fit was 1.047. The largest peak in the final difference electron density synthesis was

591  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

592  of the final model, the calculated density was 1.367 g cm–3 and F(000) = 660 e (Table 1).

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665

**FIGURE 1**

9,9'-dehydrodianthracene

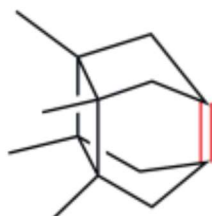1,5-dehydroquadricyclane

tricyclo[3.3.1.0$^{3,7}$]non-3(7)-ene

tricyclo[3.3.0.0$^{3,7}$]oct-1(5)-ene

pentacyclo[4.3.0.0$^{2,4}$.0$^{3,8}$.0$^{5,7}$]non-4-ene

cubene

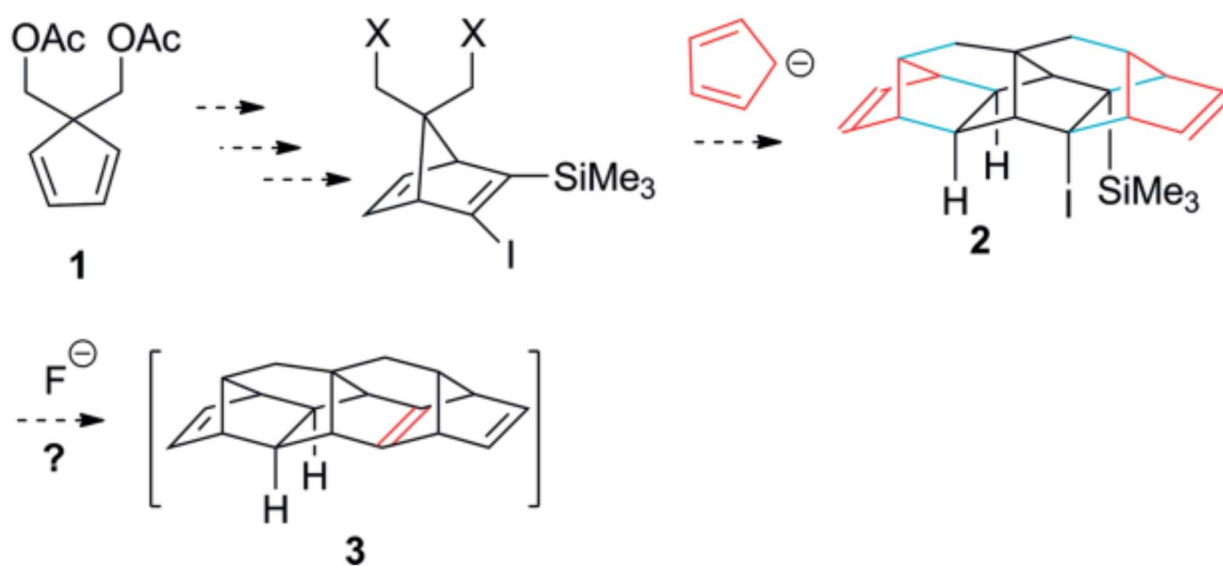3,4,8,9-tetramethyltetracyclo[4.4.0.0$^{3,9}$.0$^{4,8}$]dec-1(6)-ene
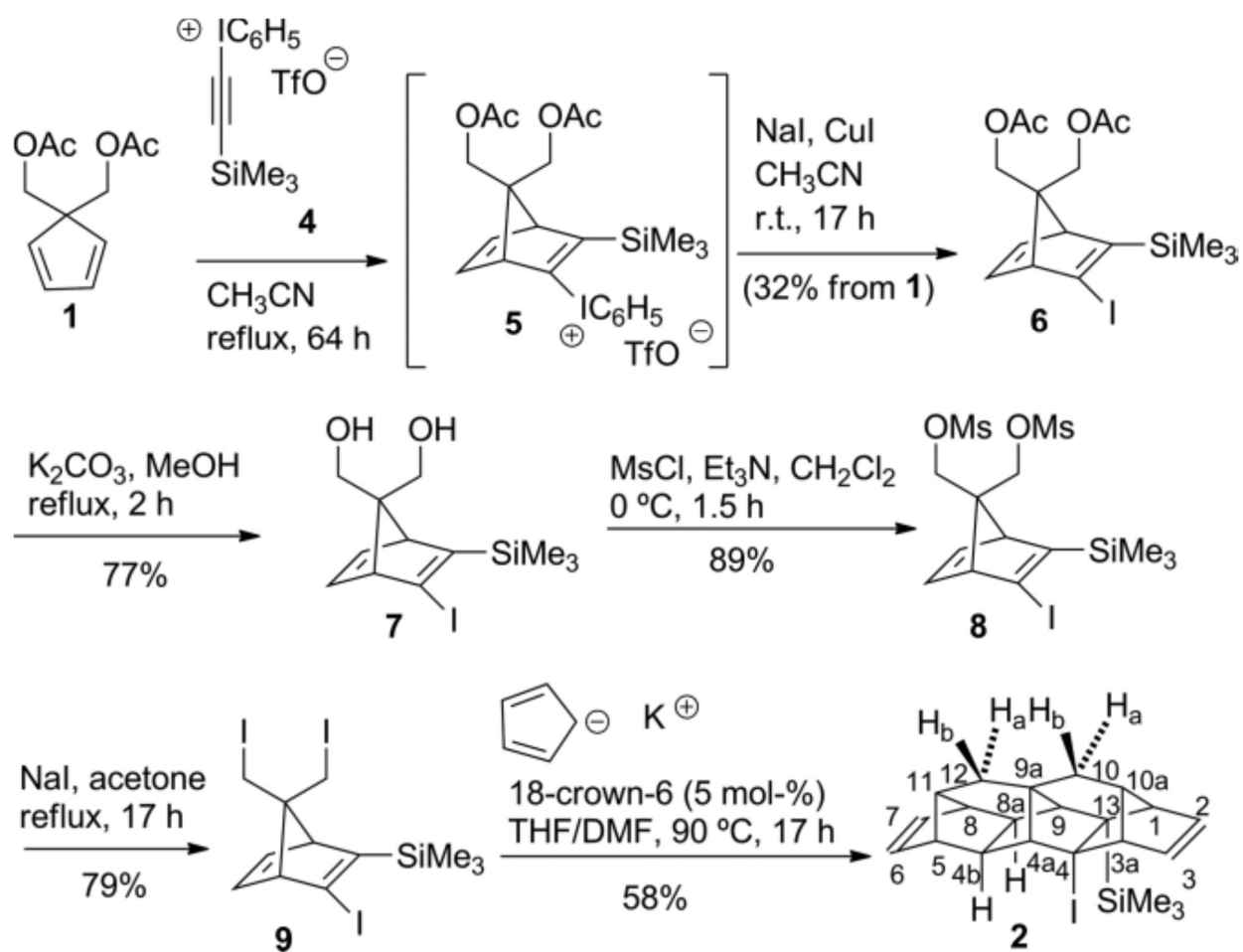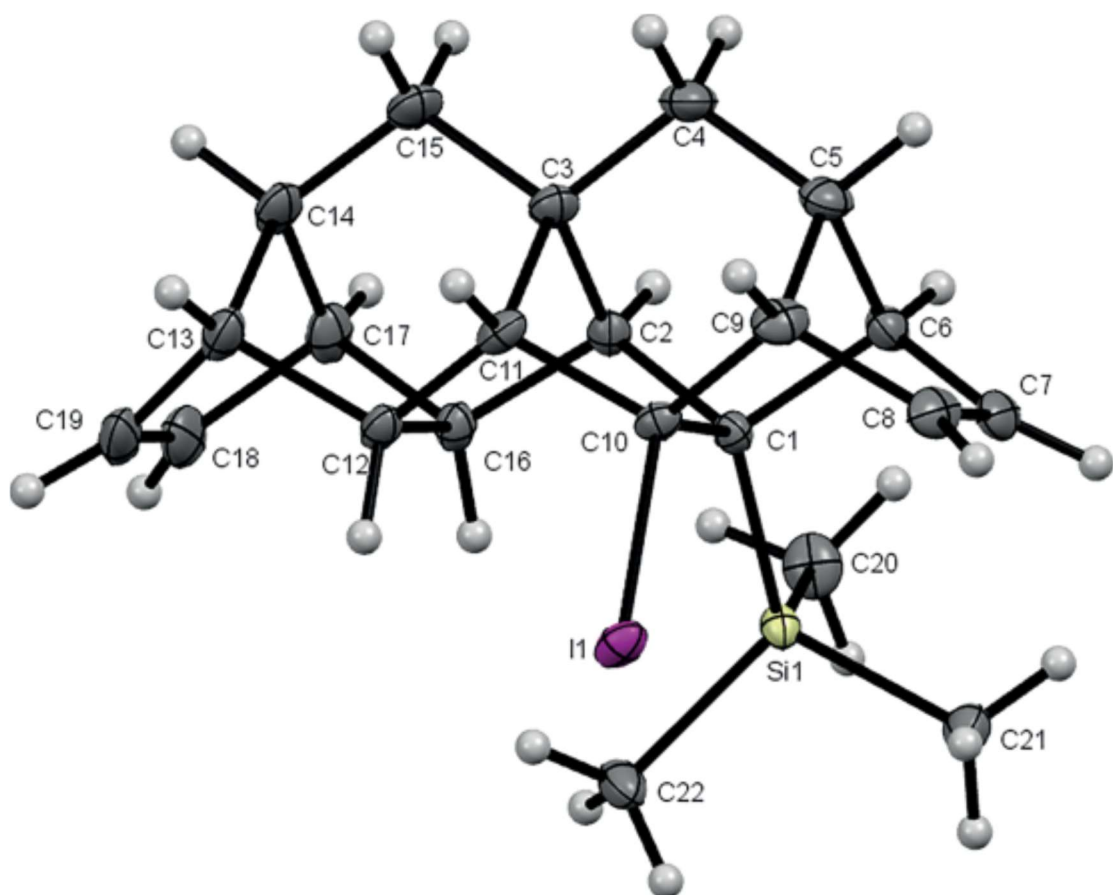
**SCHEME 1.**

**ref. 3c:**

**this work:**

**1**

**2**

**3**

**FIGURE 2**

**SCHEME 3**

CsF (3 equiv.)
1,4-dioxane
100 ºC, 16 h

89%

DMAD (2.2 equiv.)
CsF (5 equiv.), AgF (3 equiv.)
Pd$_2$(dba)$_3$·CHCl$_3$ (6 mol-%)
1,4-dioxane, 100 ºC, 17 h
34%

DMAD (4 equiv.)
Pd$_2$(dba)$_3$ (10 mol-%)
1,4-dioxane, 100 ºC, 17 h
81%

DMAD (4 equiv.)
AgF (3 equiv.), Pd$_2$(dba)$_3$ (10 mol-%)
1,4-dioxane, 100 ºC, 16 h
31%

AgF (3 equiv.)
1,4-dioxane
100 ºC, 15 h
46%

AgF (3 equiv.)
1,4-dioxane
100 ºC, 16 h
47%

Z = COOMe

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**FIGURE 3**



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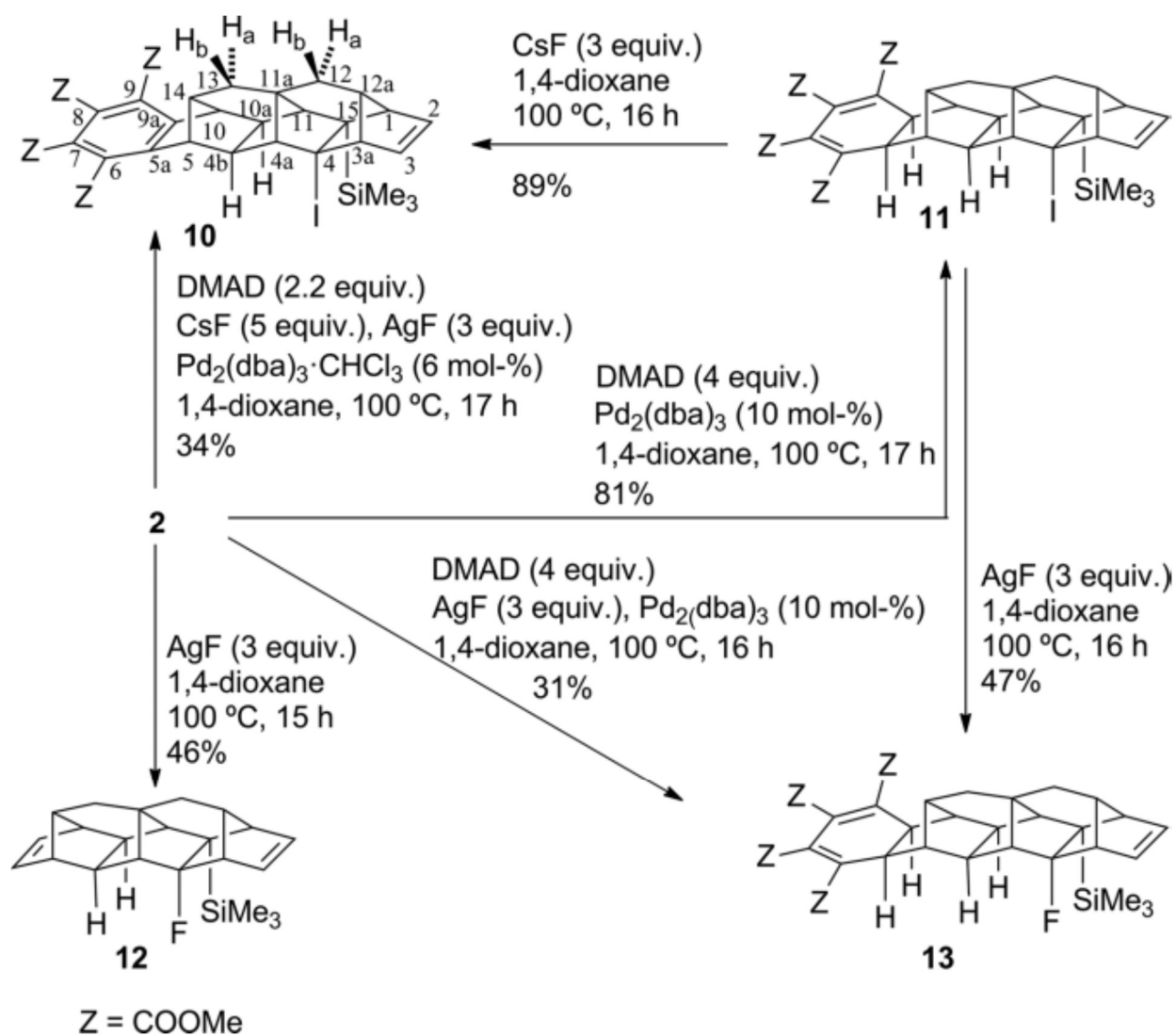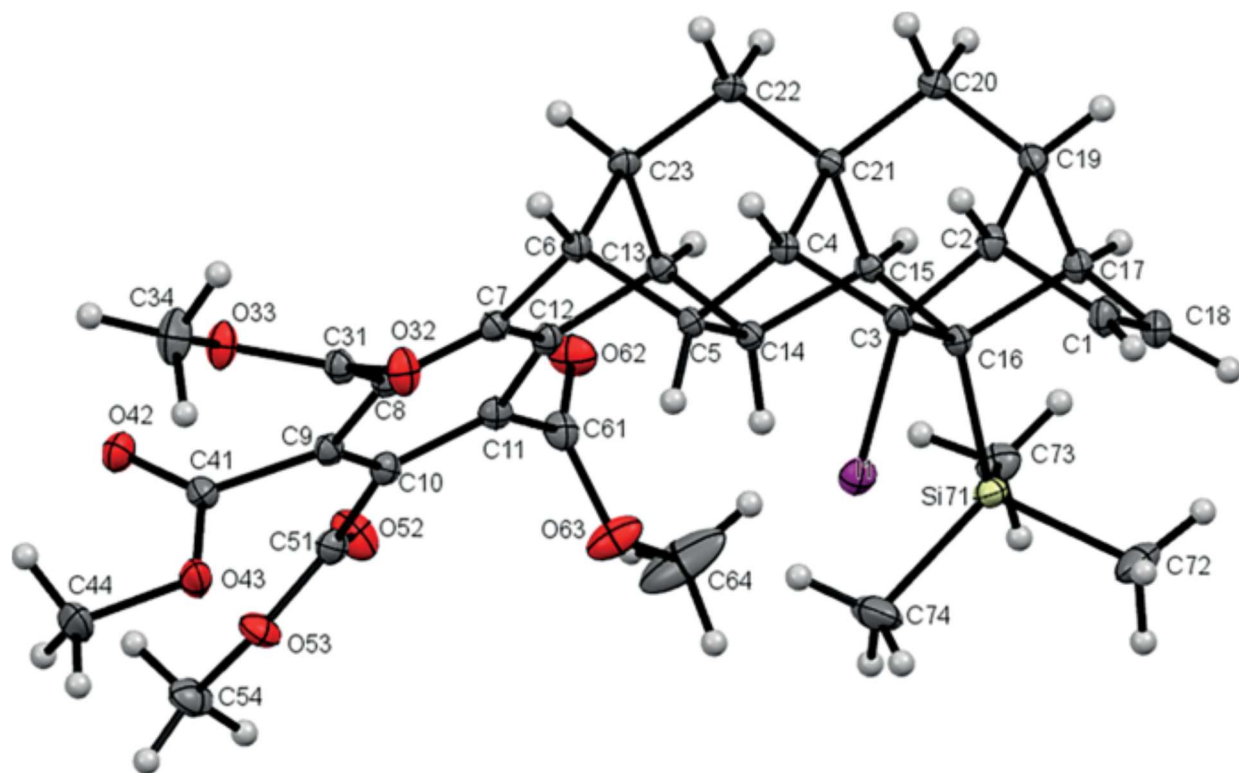
**FIGURE 4**

**FIGURE 5**

SCHEME 4

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731

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Z = CO₂Me

733

734
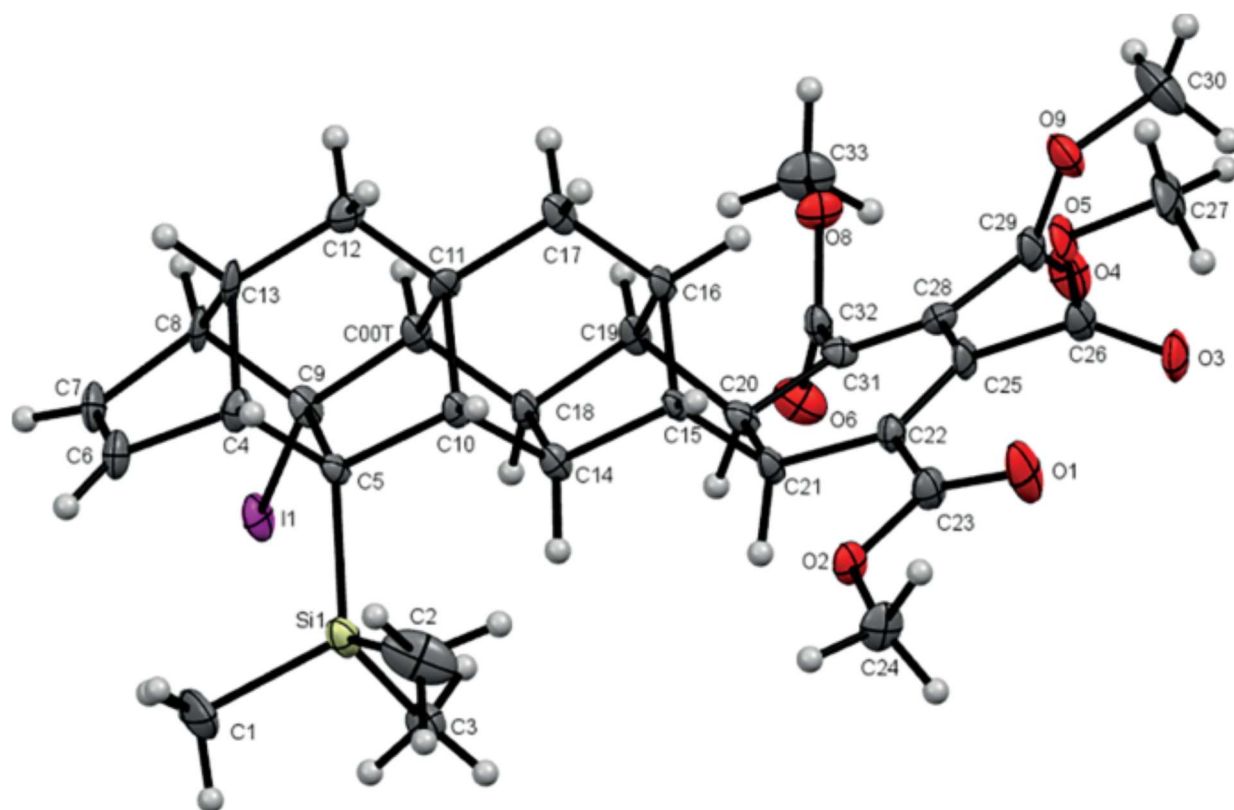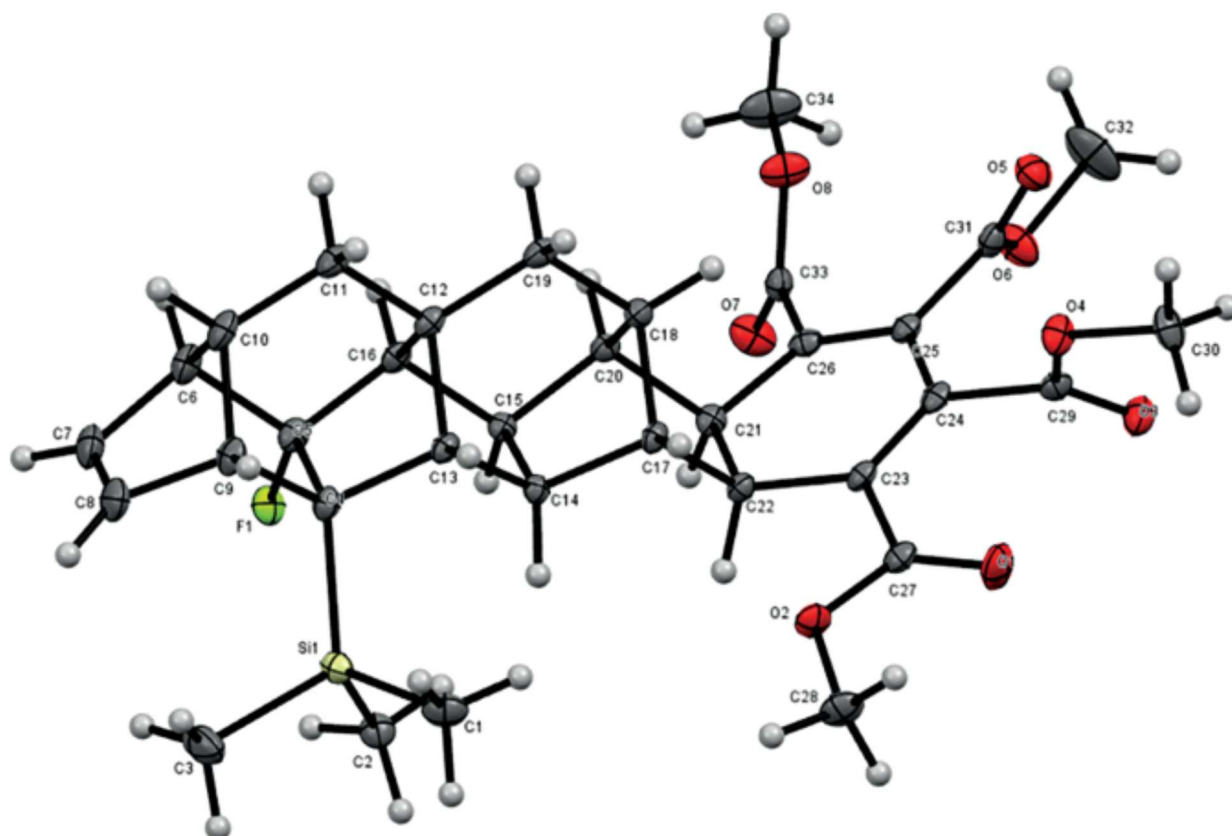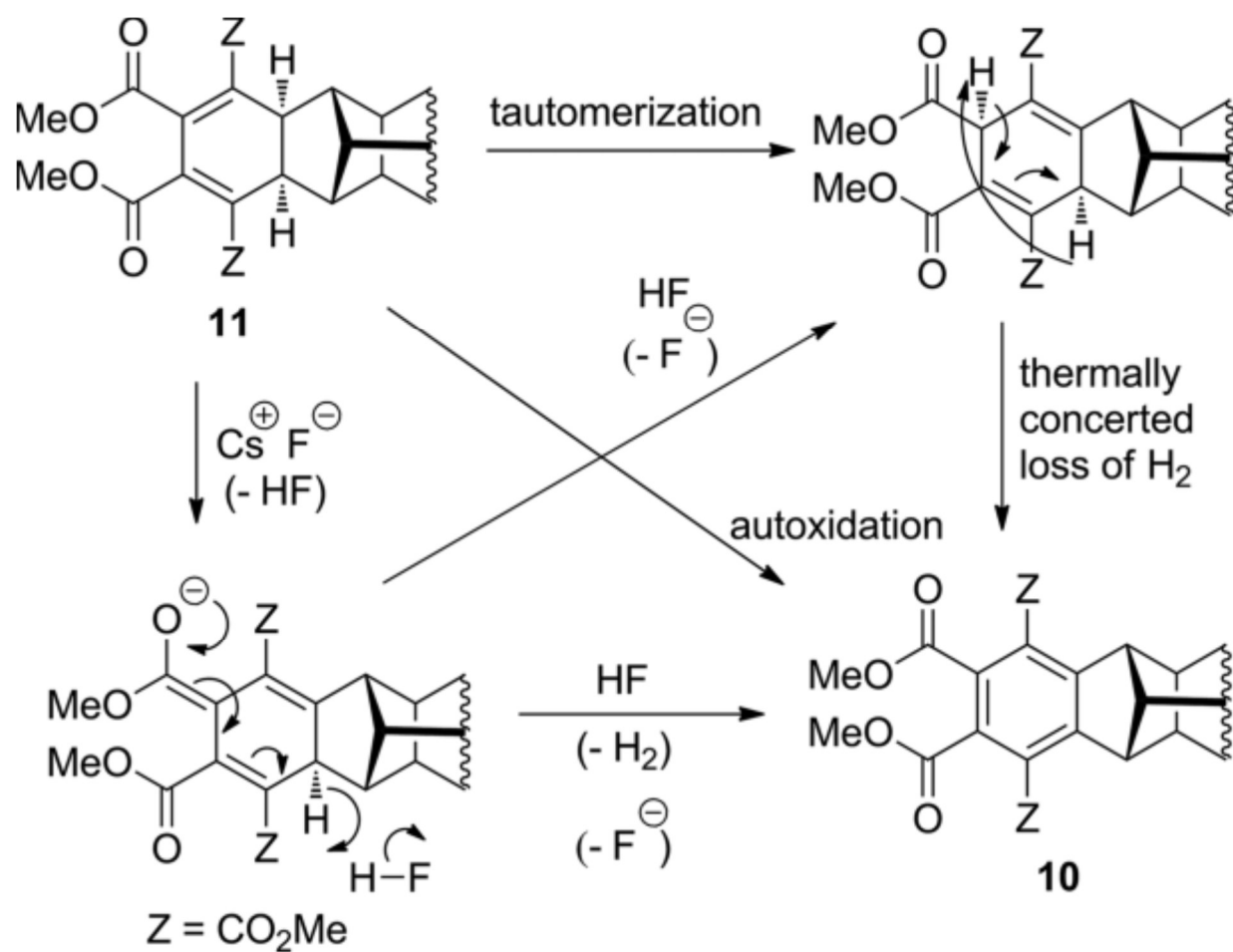
735 **Table 1** Experimental data[a] from the X-ray crystal-structure determinations of compounds 2, 10, 11,
736 and 13.

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738

| Compound | 2 | 10 | 11 | 13 |
|---|---|---|---|---|
| Molecular formula | $C_{22}H_{27}ISi$ | $C_{34}H_{27}IO_8Si$ | $C_{34}H_{39}IO_8Si\cdot CH_2Cl_2$ | $C_{34}H_{39}FO_8Si$ |
| 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) |
| $\alpha$ [°] | 90 | 76.241(2) | 90 | 90 |
| $\beta$ [°] | 101.230(2) | 82.033(2) | 98.032(5) | 108.082(2) |
| $\gamma$ [°] | 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 |
| $\theta$ 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 |
| | $[R_{int} = 0.0213]$ | $[R_{int} = 0.0626]$ | $[R_{int} = 0.1058]$ | $[R_{int} = 0.0317]$ |
| Completeness to $\theta$ [°] | 25.242 (99.9 %) | 25.242 (100.0 %) | 25.242 (99.0 %) | 25.242 (99.8 %) |
| Absorption | semi-empirical | semi-empirical | multiscan | semi-empirical |
| correction | from equivalents | from equivalents | | from equivalents |
| Max. and min. transmission | 0.7461 and 0.5829 | 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).

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