178. Synthesis of Functionalized Cycloprop[*f*]indenes *via* the Carbene Addition Route

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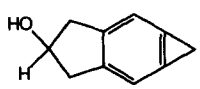
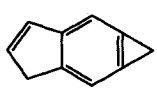
The synthesis of 4,5-dihydro-1*H*,3*H*-cycloprop[*f*]inden-4-ol (**1**) and diethyl 4,5-dihydro-1*H*,3*H*-cycloprop[*f*]-indene-4,4-dicarboxylate (**26**) starting from diene **4** is described. The cyclopentene ring is constructed by condensation of diethyl malonate to the dibromide **21**. The key-step in the synthesis of **1** consists in a twofold *Curtius* degradation of **22**, with subsequent reduction of the carbonyl group and aromatization. The skeleton of the isomer **31** is synthesized *via* cycloaddition of butadiene to cyclopent-4-ene-1,3-dione (**7**) and addition of dichlorocarbene to the adduct **27** after ketalisation. The attempted synthesis of dihydrocycloprop[*f*]indene (**2**) by base-induced elimination of several appropriately substituted precursors failed.

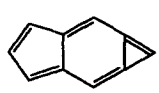
Introduction. – In [1], we have reported the synthesis of several carbo- and heterocyclic cycloprop[*f*]indenes *via* cycloaddition of dienes to di- and tetrahalogenocyclopropenes and subsequent aromatization. Of the various cycloproparenes prepared by this route, the functionalized 4-hydroxy derivative **1** was of interest as a potential precursor for the so far inaccessible dihydrocycloprop[*f*]indene (**2**), which we hoped, eventually, to convert to cycloprop[*f*]indene (**3**) itself, an isomer of dehydroazulene which has been the subject of recent theoretical interest [2].



1



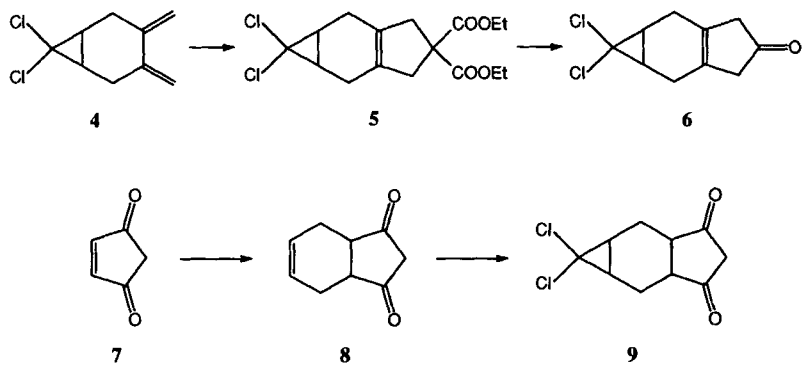
2



3

The cycloaddition approach to **1** was, however, not entirely satisfactory. The crucial step in the sequence, which involved a cycloaddition of an appropriate diene to 1-bromo-2-chlorocyclopropene at –20°, was found to be impractical for the preparation of **1** on a large scale. In this paper, we describe an alternative access to **1** and an independent synthesis of still another precursor of **2**. Both approaches use aromatization of an appropriate 1,1-dichlorocyclopropane in the last step. The synthesis of **1** is based on the construction of the tricyclic skeleton starting with synthon **4**, which has been used in the past as building block for cycloproparenes [3] [4] (*Scheme 1*). The ring system **5** is constructed by condensation of a one-atom fragment derived from malonate. The key-step of the sequence consists in a double *Curtius* degradation of **5** to the ketone **6** which, after reduction to the alcohol, was expected to undergo aromatization under the conditions developed by *Billups et al.* [5] to afford **1**. By the second approach, first the functionalized indane system **8** is constructed by cycloaddition of butadiene to cyclopent-

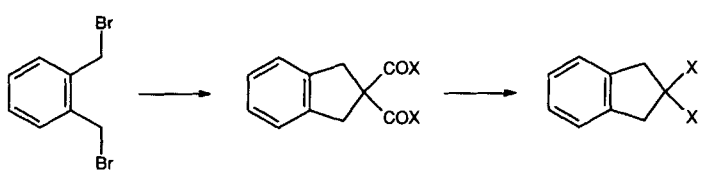
Scheme 1



4-ene-1,3-dione (**7**). Addition of dichlorocarbene followed by functional-group modification and aromatization of the adduct **9** as above should lead directly to **2**.

Results and Discussion. – *Synthesis of 4,5-Dihydro-1*H*,3*H*-cycloprop[f]inden-4-ol* (**1**) *from* **4**. The double *Curtius* degradation of geminal diesters, which is the key step in the proposed synthesis of **1**, has been used only once in the literature [6]. Model studies were carried out in order to establish the feasibility of the approach in our system. 1,2-Bis(bromomethyl)benzene (**10**) was condensed with diethyl malonate [7] to afford **11**, which was hydrolyzed [8] to the diacid **12** (*Scheme 2*). Reaction of **12** with oxalyl chloride afforded the dichloride **13**, and treatment of the latter with NaN_3 in MeCN at 25° led to the azide **14**. The azide was rearranged to the bis-isocyanate **15** by refluxing in cyclohexane. Hydrolysis of the crude **15** afforded indan-2-one (**16**) in 45–50% overall yield.

Scheme 2



10

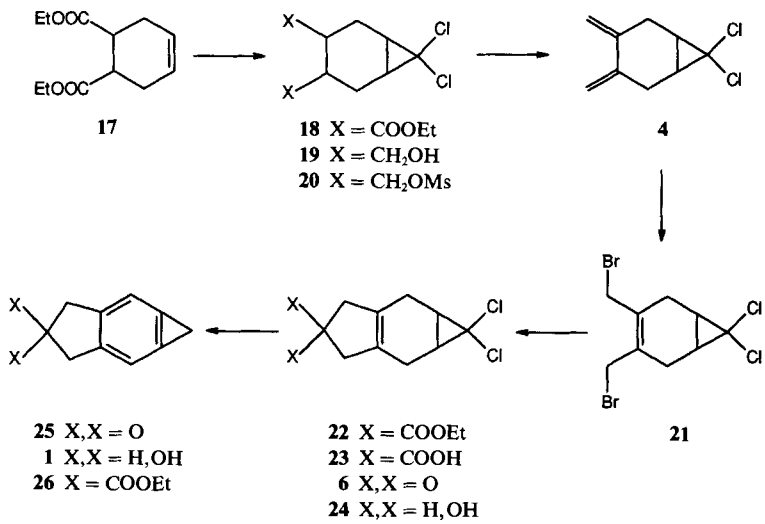
11 X = EtO
12 X = OH
13 X = Cl
14 X = N_3

15 X = NCO
16 X,X = O

The synthesis of **1** is outlined in *Scheme 3*. The synthon **4** was prepared according to the sequence described in [3] with only minor modifications: addition of dichlorocarbene, generated under phase-transfer conditions ($CHCl_3$ and conc. NaOH in the presence of (benzyl)(triethyl)ammonium chloride) to diethyl *cis*-cyclohexene-4,5-dicarboxylate (**17**) furnished **18** as a single stereoisomer which was reduced with $LiAlH_4$ to afford the diol **19**. Mesylation followed by elimination of **20** with *t*-BuOK in THF at 0° afforded the diene **4** in 50% yield. The diene **4**, in turn, underwent bromination in pentane to afford **21**, which

reacted with diethyl malonate in the presence of K_2CO_3 [7] to form **22**. Hydrolysis to **23** was carried out with KOH in 80% EtOH [8]. Double *Curtius* degradation as described above afforded the ketone **6** in 50% yield. When **6** was subjected to strong base (*t*-BuOK/DMSO), no aromatization occurred, however, and only unidentified decomposition products rather than the expected ketone **25** were formed. However, the alcohol **24**, obtained *via* reduction of **6** with $LiAlH_4$, could be aromatized to afford **1** in 72% yield. When **22** was subjected to the elimination conditions, the substituted cycloproparene **26** was formed (49% yield).

Scheme 3



17

18 X = COOEt
19 X = CH_2OH
20 X = CH_2OMs

4

21

25 X,X = O
1 X,X = H,OH
26 X = COOEt

22 X = COOEt
23 X = COOH
6 X,X = O
24 X,X = H,OH

Construction of the Skeleton of **2** via *Cycloaddition to Cyclopent-4-ene-1,3-dione* (**7**). The synthesis is outlined in *Scheme 4*. The cycloaddition of butadiene to **7** has been reported in [9], but we found that the procedure is significantly improved, when the reaction is carried out in Et_2O in the presence of 5M of $LiClO_4$ [10]. The addition of dichlorocarbene to **8** could not be realized as planned, and required ketalisation of the carbonyl groups. The bis-ketal **27** underwent carbene addition under phase-transfer conditions to yield **28** in 89% yield. Exposure of **28** to EtOH with acid catalysis afforded the enol ether **29** which was reduced with $LiAlH_4$ in Et_2O to the unsaturated ketone **30**. Further reduction with $LiAlH_4$ in Et_2O afforded the alcohol **31** (when THF was used as solvent, the C=C bond of **30** was also reduced). The configuration of **31** was investigated by COSY and NOE spectra [11] which revealed *trans*-orientation of the cyclopropane and cyclopentane rings, with the OH in *endo*-configuration (*Fig.*). Only a trace of isomeric products, having *cis*-configurated rings was detected in the reaction mixture.

Attempts to convert **31** into the methanesulfonate or 4-toluenesulfonate failed, and so did the conversion to the chloride with Bu_3P and CCl_4. The chloride **32** could, however, be prepared as a *ca.* 5:1 mixture of stereoisomers by bubbling dry HCl into a $CHCl_3$ solution of **31** [13].

Scheme 4

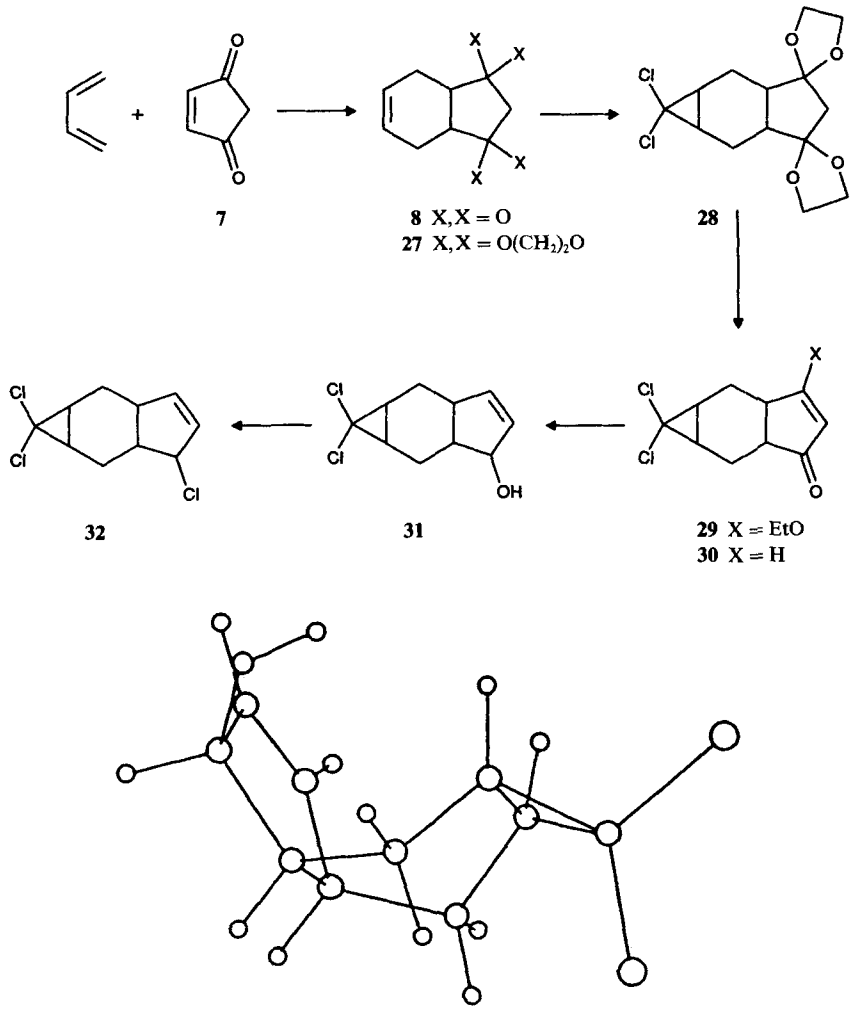
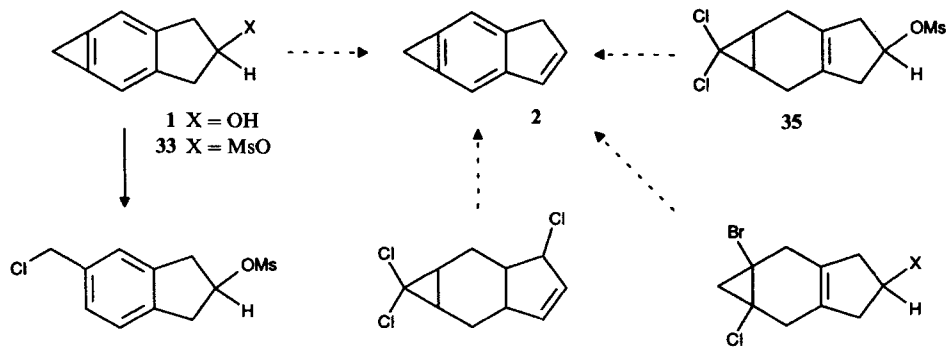


Figure. *Structure of* **31**, *conformational energy minimum, as calculated with ALCHEMY II* [12]

Attempted Synthesis of 1,5-dihydrocycloprop[f]indene (**2**). When **1** was exposed to MsCl in the presence of Et_3N, ring opening to **34** occurred (*Scheme 5*). Reaction of **1** with 1 equiv. of *t*-BuOK, followed by MsCl, afforded the methanesulfonate **33**, which was identified by its ^1H- and ^{13}C-NMR spectra and characterized *via* its conversion to the ring-opened product **34**. The elimination of MsOH from **33** with *t*-BuOK to **2** could not be brought to completion, however. Direct introduction of the cyclopentene C=C bond under the condition of aromatization of the cycloproparene was attempted with the methanesulfonates **35** and **37**, both being available from the appropriate alcohols **24** and **36** [1], respectively, and from the chlorides **32** and **38**. In all cases, decomposition

Scheme 5



products were obtained, and the desired cyclopropparene **2** was either not formed, or decomposed upon the attempted isolation. In the light of the observation that the corresponding saturated tetrahydrocycloprop[*f*]indene or even more strained cyclopropparenes such as the cyclobutacyclopropabenzenes are isolable species, the difficulties encountered in the synthesis of **2** are surprising. Experiments to overcome them by working with appropriate protecting groups of the cyclopropparene are under way.

We are indebted to the *Swiss National Science Foundation* (grants No. 20-32117.91 and 2000-038907/1) for financial support.

Experimental Part

General. See [14].

Model Reactions: Synthesis of Indan-2-one (**15**). *Diethyl Indane-2,2-dicarboxylate* (**10**). A mixture of diethyl malonate (1.60 g, 10 mmol) *1,2-bis(bromomethyl)benzene* (**10**; 2.64 g, 10 mmol), and K_2CO_3 (6.0 g, 43.5 mmol) in butan-2-one (50 ml) was heated to reflux for 24 h. The mixture was filtered and the filtrate was concentrated. The residue was subjected to CC (silica gel; AcOEt/pentane 1:5) to yield 3.8 g (90%) of **11**. IR ($CHCl_3$): 3071*m*, 2983*s*, 2905*s*, 1721*s*, 1605*w*, 1461*m*, 1368*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.20–7.15 (*m*, 4 H); 4.25–4.10 (*q*, 4 H); 3.58 (*s*, 4 H); 1.30–1.20 (*t*, 6 H). ^{13}C-NMR ($CDCl_3$): 171.6 (C); 140.0 (C); 126.9 (CH); 124.2 (CH); 61.7 (CH_2); 60.1 (C); 40.5 (CH_2); 14.0 (CH_3). MS: 262 (13, M^+), 217 (19), 188 (73), 161 (18), 143 (22), 129 (39), 115 (100), 91 (11), 57 (14). HR-MS: 262.12045 ($C_{15}H_{18}O_4^+$, calc. 262.12055).

Indane-2,2-dicarboxylic Acid (**12**). A soln. of KOH (1.0 g, 17.8 mmol) and **11** (2.47 g, 9.4 mmol) in 80% EtOH (20 ml) was heated to reflux during 12 h. After evaporation of the solvent, the residue was dissolved in H_2O (100 ml) and acidified to pH 2 with conc. HCl under cooling. The resulting slurry was extracted with Et_2O (4 × 100 ml), the extracts were dried ($MgSO_4$) and the solvent evaporated. Recrystallization from toluene afforded **11** (1.80 g, 92%). M.p. 191–193° (dec.). IR (KBr): 3026 (br.), 1698*s*, 1483*w*, 1409*s*, 1221*s*, 1069*w*. ^{1}H-NMR (200 MHz, DMSO): 7.20–7.00 (*m*, 4 H); 5.10 (*s*, 2 H); 3.50 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 175.1 (C); 141.5 (C); 127.9 (CH); 125.1 (CH); 60.1 (C); 41.5 (CH_2). MS: 206 (23, M^+), 160 (67), 116 (100), 91 (11), 77 (5), 57 (12). HR-MS: 206.05673 ($C_{11}H_{10}O_4^+$, calc. 206.05793).

Indan-2-one (**16**) via Curtius *Degradation of* **12**. To a suspension of **12** (0.70 g, 3.4 mmol) in anh. benzene (50 ml), containing a catalytic amount of pyridine was added oxalyl chloride (2.0 g, 15 mmol). The mixture was heated to reflux for 5 h. After evaporation of the solvent and unreacted oxalyl chloride, the resulting oil was dissolved in MeCN (30 ml), to which commercial NaN_3 (2.0 g, 30.8 mmol) was added. The suspension was stirred

overnight. The mixture was filtered and concentrated at 25° under reduced pressure. The azide **14** was obtained as a gummy golden residue. It was heated in cyclohexane (30 ml) to reflux for 2 h. After concentration and re-dissolution in THF (30 ml), hydrolysis of the rearranged **15** was effected with 3.0 ml of 50% AcOH during 8 h to afford **16** (220 mg, 49%) as an amorphous solid after CC (silica gel; CH_2Cl_2).

Data of Indane-2,2-dicarbonyl Dichloride (**13**): IR ($CHCl_3$): 3032*m*, 2962*m*, 2858*m*, 1788*s*, 1487*s*, 1261*s*, 1100*s*, 1059*s*, 800*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.24 (*s*, 4 H); 3.77 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 170.0 (C); 137.2 (C); 127.9 (CH); 124.5 (CH); 79.4 (C); 40.6 (CH).

Data of Indane-2,2-dicarbonyl Diazide (**14**): IR ($CHCl_3$): 3075*w*, 3028*w*, 2959*w*, 2257*s*, 2144*s*, 1706*s*, 1485*m*, 1202*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.20 (*s*, 4 H); 3.59 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 177.7 (C); 139.0 (C); 127.3 (CH); 124.3 (CH); 63.8 (C); 40.1 (CH_2).

Data of Indane-2,2-diisocyanate (**15**): IR ($CHCl_3$): 2962*w*, 2263*s*, 1726*m*, 1482*w*, 1429*w*, 1272*w*, 1218*w*, 1026*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.28 (*s*, 4 H); 3.44 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 175.3 (C); 138.2 (C); 127.8 (CH); 125.0 (CH); 79.2 (C); 50.6 (CH_2).

Data of **16**: IR ($CHCl_3$): 3029*w*, 2917*w*, 1759*s*, 1480*w*, 1389*w*, 1184*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.35–7.25 (*m*, 4 H); 3.56 (*s*, 4 H). ^{13}C-NMR ($CDCl_3$): 215.1 (C); 137.8 (C); 127.4 (CH); 125.0 (CH); 44.1 (CH_2). MS: 132 (2, M^+), 104 (7), 84 (100), 68 (12), 48 (18). HR-MS: 132.05899 ($C_9H_8O^+$, calc. 132.05749).

Synthesis of 4,5-Dihydro-1H,3H-cyclopropa[f]inden-4-ol (**1**). *Diethyl 7,7-Dichlorobicyclo[4.1.0]heptane-3,4-dicarboxylate* (**18**) [3]. A chilled soln. of 50% NaOH (100 ml) was added to **17** (10.0 g, 50 mmol), (benzyl)-(triethyl)ammonium chloride (5.0 g) and alcohol-free $CHCl_3$ (60 g) with stirring at 25°. After 4 h of stirring at 40–50°, the mixture was worked up. FC (silica gel; CH_2Cl_2) gave 7.0 g (50%) of **18**. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.63 (*s*, 6 H); 2.80–2.70 (*m*, 2 H); 2.55–2.35 (*m*, 2 H); 1.90–1.70 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 173.1 (C); 66.3 (C); 51.9 (CH_3); 38.4 (CH); 25.2 (CH); 19.9 (CH_2).

7,7-Dichlorobicyclo[4.1.0]heptane-3,4-dimethanol (**19**) [3]. To a stirred soln. of **17** (12.0 g, 42.7 mmol) in Et_2O (100 ml) was added $LiAlH_4$ (3.2 g, 84.3 mmol) at 25° under N_2. The mixture was refluxed for 2 h. Excess $LiAlH_4$ was decomposed by addition of 50 g of ice. Workup yielded **19** (8.0 g, 83%) as a colorless oil. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.65 (*s*, 2 H); 3.45 (*s*, 4 H); 2.00–1.80 (*m*, 2 H); 1.70–1.55 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 67.1 (C); 63.1 (CH_2); 36.1 (CH); 25.1 (CH); 20.6 (CH_2).

(7,7-Dichlorobicyclo[4.1.0]heptane-3,4-diyl)dimethyl Bis(methanesulfonate) (**20**) [3] [15]. MsCl (4.7 g, 58.5 mmol) in CH_2Cl_2 (20 ml) was added slowly to a stirred soln. of **19** (5.0 g, 22.2 mmol) and Et_3N (6.6 g, 5.85 mmol) in CH_2Cl_2 (80 ml) under N_2. The mixture was washed with chilled H_2O (50 ml), sat. $NaHCO_3$ (50 ml), and H_2O (100 ml), and the org. layer was dried ($MgSO_4$). After evaporation of the solvent, the resulting solid was recrystallized from CH_2Cl_2/pentane to give 8.0 g (80%) of **20**. M.p. 95–97° ([3]: 99–100°). ^{1}H-NMR (200 MHz, $CDCl_3$): 4.20–4.00 (*m*, 4 H); 3.00 (*s*, 6 H); 2.20–1.70 (*m*, 8 H). ^{13}C-NMR ($CDCl_3$): 69.5 (C); 66.0 (CH_2); 37.4 (CH); 32.3 (CH); 24.3 (CH_2); 19.9 (Me). MS: 246 (11), 209 (13), 165 (72), 129 (100), 115 (23), 91 (16), 79 (22), 65 (11).

7,7-Dichloro-3,4-dimethylidenebicyclo[4.1.0]heptane (**4**) [3]. To a stirred soln. of **20** (5.0 g, 13.1 mmol) in dry THF (50 ml) was added *t*-BuOK (5.0 g, 44.6 mmol). After 1.5 h of stirring, workup and purification by FC gave **4** (1.30 g, 50%) as a colorless liquid. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.30–5.25 (*t*, 2 H); 4.90–4.80 (*t*, 2 H); 2.85–2.70 (*m*, 2 H); 2.35–2.20 (*m*, 2 H); 1.90–1.80 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 142.0 (C); 110.0 (CH_2); 66.9 (C); 28.5 (CH); 27.6 (CH).

3,4-Bis(bromomethyl)-7,7-dichlorobicyclo[4.1.0]hept-3-ene (**21**). To **4** (300 mg, 1.5 mmol) in Et_2O (15 ml) was added Br_2 (250 mg, 1 equiv.) in CCl_4 (5.0 ml) at 0°. Stirring was continued at 25° for 20 min. Evaporation of the solvent followed by FC (silica gel; pentane) and recrystallization from Et_2O afforded **21** (500 mg, 92%). M.p. 110°. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.25–4.10 (*m*, 4 H); 2.85–2.30 (*m*, 4 H); 2.10–2.00 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 130.7 (C); 65.9 (C); 31.8 (CH_2); 25.2 (CH); 24.1 (CH). MS: 384 (5, M^+), 269 (17), 233 (13), 187 (49), 151 (80), 91 (65), 79 (89), 65 (59), 51 (100). HR-MS: 345.85185 ($C_9H_{10}{}^{79}Br^{35}Cl^+$, calc. 345.85259).

Diethyl 1,1-Dichloro-1a,2,4,5,6,6a-hexahydro-1H,3H-cyclopropa[f]indene-4,4-dicarboxylate (**22**) [7]. A mixture of diethyl malonate (1.0 g, 6.3 mmol), **21** (2.2 g, 6.3 mmol) and K_2CO_3 (5.0 g) in butan-1-one (50 ml) was refluxed for 12 h. It was then filtered, and the filtrate was concentrated. The residue was purified by CC (silica gel; AcOEt/pentane 1:5) to give **22** (2.5 g, 78%). M.p. 84–86°. IR ($CHCl_3$): 2983*m*, 2903*m*, 1727*s*, 1258*s*, 1183*s*, 1018*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.20–4.00 (*m*, 4 H); 2.85–2.75 (*m*, 4 H); 2.45–1.95 (*m*, 4 H); 1.85–1.75 (*m*, 2 H); 1.25–1.10 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 172.2, 171.8 (C); 127.5 (C); 65.0 (C); 61.6, 61.4 (CH_2); 57.1 (C); 43.1 (CH_2); 25.3, 20.5 (CH_2); 14.0 (Me). MS: 349 (21), 348 (14), 347 (29), 346 (16, M^+), 301 (13), 272 (54), 237 (51), 189 (44), 163 (73), 150 (26), 129 (100), 115 (58), 91 (57), 77 (39), 65 (24), 51 (33). HR-MS: 346.07556 ($C_{16}H_{20}O_4{}^{35}Cl^+$, calc. 346.07386).

1,1-Dichloro-1a,2,4,5,6,6a-hexahydro-1H,3H-cyclopropa[f]indene-4,4-dicarboxylic Acid (**23**). A soln. of **22** (300 mg, 0.87 mmol) and KOH (300 mg, 5.4 mmol) in 80% EtOH (25 ml) was refluxed for 12 h, then evaporated to

dryness. The residue was dissolved in H_2O (100 ml) and acidified with conc. HCl to pH 2 with cooling. The resulting slurry was extracted wit Et_2O, the extracts were washed with H_2O and dried ($MgSO_4$). Evaporation of the solvent and recrystallization of the residue from toluene afforded **23** (0.24 g, 95%). M.p. 190–193° (dec.). IR (KBr): 3149*s* (br.), 1721*s*, 1402*m*, 1241*s*, 1117*w*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.2 (*s*, 2 H); 3.0–2.0 (*m*, 8 H); 1.97–1.85 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 175.7, 175.5 (C); 128.8 (C); 66.3 (C); 58.4 (C); 44.4 (CH_2); 26.8 (CH); 21.3 (CH_2). MS: 290 (12, M^+), 244 (51), 209 (25), 161 (37), 129 (73), 115 (45), 91 (53), 77 (56), 65 (28), 55 (22). HR-MS: 290.00848 ($C_{16}H_{12}O_4{}^{35}Cl_2^+$, calc. 290.01128).

*1,1-Dichloro-1a,2,4,5,6,6a-hexahydro-1*H,*3*H-*cycloprop[f]inden-4-one* (**6**). To a suspension of **23** (500 mg, 1.7 mmol) in benzene (50 ml), containing a catalytic amount of pyridine, was added oxalyl chloride (2.0 g, 15 mmol). The mixture was heated to reflux for 5 h. After evaporation of the solvent and unreacted oxalyl chloride, the residue was stirred with NaN_3 (5.0 g, 78 mmol) in MeCN (30 ml) overnight at 25°. It was filtered, and the filtrate was concentrated at 25° under reduced pressure to afford a gummy residue which was heated to reflux for 2 h in cyclohexane (30 ml). The solvent was evaporated and the residue dissolved in THF (30 ml). Hydrolysis was accomplished using 5 ml of 50% AcOH for 10 h and afforded **6** (167 mg, 45%) as amorphous solid after CC (silica gel; AcOEt/pentane 1:10).

The ketone **6** was also produced (43% yield), when NaN_3 was replaced by Me_3SiN_3 (4 equiv., 5 h of reflux in cyclohexane). IR ($CHCl_3$): 2977*m*, 2989*s*, 2833*m*, 1753*s*, 1427*s*, 1188*s*, 1068*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.80–2.15 (*m*, 8 H); 2.00–1.85 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 214.6 (C); 128.0 (C); 65.1 (C); 45.8 (CH_2); 24.9 (CH); 20.4 (CH_2). MS: 216 (47, M^+), 188 (32), 155 (96), 117 (96), 105 (40), 91 (67), 65 (26), 51 (46). HR-MS: 216.00667 ($C_{10}H_{10}O^{32}Cl_2^+$, calc. 216.01087).

*1,1-Dichloro-1a,2,4,5,6,6a-hexahydro-1*H,*3*H-*cycloprop[f]inden-4-ol* (**24**). To **7** (50 mg, 0.23 mmol) in Et_2O (5.0 ml) was added $LiAlH_4$ (30 mg, 0.79 mmol). After 1 h of stirring at 25°, 1 drop of H_2O was added. The mixture was stirred for 5 min and passed through a small column of $MgSO_4$. After evaporation of the solvent, the residue was subjected to CC (silica gel; CH_2Cl_2) to afford **24** (40 mg, 80%) as an amorphous solid. IR ($CHCl_3$): 3434*w*, 2926*s*, 2854*s*, 1430*w*, 1262*s*, 1097*s*, 1016*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.45–4.30 (*m*, 1 H); 2.60–1.95 (*m*, 9 H); 1.95–1.82 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 127.7 (C); 70.2 (CH); 65.5 (C); 45.4 (CH_2); 25.7 (CH); 20.9 (CH_2). MS: 218 (50, M^+), 200 (12), 165 (100), 117 (95), 91 (82), 77 (65), 65 (35), 51 (60). HR-MS: 218.02696 ($C_{12}H_{12}O^{35}Cl_2^+$, calc. 218.02656).

*4,5-Dihydro-1*H,*3*H-*cycloprop[f]inden-4-ol* (**1**). To **24** (107 mg, 0.49 mmol) in freshly distilled DMSO (from CaH_2; 2.0 ml) was added *t*-BuOK (240 mg, 2.1 mmol) in DMSO (3.0 ml) at 0°. The mixture was stirred at 25° for 30 min. After addition of H_2O (20 ml), it was extracted with Et_2O (5 × 10 ml). Tbe combined org. layers were washed with H_2O and dried ($MgSO_4$). Evaporation of the solvent afforded **24** (40 mg, 72%). Data: see [1].

*Diethyl 4,5-Dihydro-1*H,*3*H-*cycloprop[f]indene-4,4-dicarboxylate* (**26**). To **22** (200 mg, 0.578 mmol) in dry DMSO (2.0 ml) was added *t*-BuOK (150 mg, 1.34 mmol) in DMSO (3.0 ml) at 25°. After stirring for 10 min, 20 ml of H_2O was added, and the soln. was extracted with Et_2O (5 × 10 ml). The org. layer was washed (H_2O) and dried ($MgSO_4$). After evaporation of the solvent, the residue was passed through a silica-gel column with pentane/AcOEt 20:1. The crude product was dissolved in EtOH (15 ml) to which NaOEt (10 mg) was added. After 2 h at 25°, the solvent was evaporated, and the product was purified by CC (silica gel; pentane/AcOEt 20:1) to give **26** (80 mg, 50.5%). Data: see [1].

*Synthesis of 1,1,3-Trichloro-1a,2,3a,5a,6,6a-hexahydro-1*H,*3*H-*cycloprop[f]indene* (**32**). cis-*2,3,3a,4,7,7a-Hexahydro-1*H-*indane-1,3-dione* (**8**) [9]. Buta-1,3-diene (4.40 g, 81.5 mmol) and **7** (2.0 g, 20.8 mmol) were stirred in 5M $LiClO_4$ in Et_2O (50 ml) in an autoclave for 72 h at 25°. After evaporation of the volatiles, the residue was washed with H_2O (50 ml) and Et_2O (100 ml) and afforded **8** (2.8 g, 90%). M.p. 159–160° ([9]: 160–161.5°). IR (KBr): 3030*m*, 2950*m*, 1600*s*, 1550*s*, 1530*s*, 1450*s*, 1300*s*, 1250*s*, 1245*s*, 1240*s*, 1050*m*, 830*s*, 700*s*, 650*s*. ^{1}H-NMR (200 MHz, DMSO): 5.78–5.70 (*m*, 2 H); 5.50 (*s*, 1 H); 2.80–2.72 (*m*, 2 H); 2.80–1.98 (*m*, 4 H). ^{13}C-NMR (100 MHz, DMSO): 127.4 (CH); 105.7 (CH); 41.5 (CH); 23.7 (CH_2). MS: 150 (5, M^+), 132 (3), 122 (4), 108 (19), 107 (11), 104 (115), 77 (31), 69 (9), 65 (7), 51 (27).

cis-*2,3,3a,4,7,7a-Hexahydro-1*H-*indene-1,3-dione Bis(ethylene ketal)* (**27**). The dione **8** (2.80 g, 18.7 mmol) was heated with ethyleneglycol (3.0 g, 48.4 mmol) and 0.20 g of TsOH to reflux in benzene (50 ml) in a 250-ml flask fitted with a *Dean-Stark* trap. After evaporation of the solvent, the residue was subjected to CC (silica gel; pentane/Et_2O 3:1) and gave **27** (4.0 g, 90%) as an amorphous solid. IR ($CHCl_3$): 3022*m*, 2965*m*, 1590*s*, 1224*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.67–5.62 (*m*, 2 H); 4.00–3.80 (*m*, 8 H); 2.15 (*s*, 2 H); 2.30–1.90 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 126.1 (CH); 113.7 (C); 65.0 (CH_2); 65.0 (CH_2); 49.1 (CH_2); 45.0 (CH); 24.6 (CH_2). MS: 238 (11, M^+), 194 (8), 152 (100), 113 (8), 86 (64), 79 (77). HR-MS: 238.11813 ($C_{13}H_{18}O_4^+$, calc. 238.12051).

1,1-Dichloroperhydrocycloprop[f]indene-3,5-dione Bis(ethylene ketal) (**28**). To a soln. of **27** (1.0 g, 4.2 mmol) and (benzyl)(triethyl)ammonium chloride (0.3 g) in alcohol-free $CHCl_3$ (20 ml) were added 3.0 ml of 50% NaOH

dropwise with vigorous stirring. The resulting mixture was stirred at 50° for 3 h. H_2O (50 ml) was added, and the product continuously extracted with CH_2Cl_2 for 10 h. After evaporation of the solvent, the residue was subjected to CC (silica gel; CH_2Cl_2) to afford **28** (1.20 g, 89%) as amorphous solid. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.00–3.85 (*m*, 8 H); 2.25–2.18 (*m*, 2 H); 2.18–2.17 (*d*, 2 H); 2.21–1.95 (*m*, 4 H); 1.90–1.65 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 111.0, 110.0 (C); 64.7 (C); 65.0, 64.95, 64.90, 64.88 (CH_2); 49.8 (CH_2); 45.4 (CH); 43.7 (CH); 27.9 (CH); 26.8 (CH); 18.6 (CH_2); 18.4 (CH_2). MS: 320 (3, M^+), 234 (50), 199 (67), 157 (15), 125 (84), 112 (100), 99 (36), 87 (61), 68 (27), 55 (32). HR-MS: 320.05775 ($C_{14}H_{18}O_4{}^{35}Cl_2^+$, calc. 320.05821).

*1,1-Dichloro-5-ethoxy-1a,2,3a,5a,6,6a-hexahydro-1*H,*3*H-*cycloprop[*f*]*inden-3-one* (**29**). To **28** (200 mg, 0.64 mmol) in EtOH (10 ml) was added 5 drops of conc. HCl. The soln. was stirred for 12 h at 25°. It was then added dropwise, with stirring, to 20 ml of aq. K_2CO_3. After extraction with Et_2O, the org. layer was dried ($MgSO_4$) and concentrated. Purification with a silica-gel column (Et_2O) afforded 100 mg (60%) of **29** as wax-like solid. IR ($CHCl_3$): 3015*m*, 1641*m*, 1598*s*, 1474*w*, 1345*m*, 1297*w*, 1187*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.28 (*s*, 1 H); 4.10–3.95 (*dq*, 2 H); 3.00–2.90 (*m*, 1 H); 2.60–2.30 (*m*, 3 H); 1.40–1.30 (*t*, 3 H); 1.60–1.10 (*m*, 3 H). ^{13}C-NMR ($CDCl_3$): 207.0 (C); 190.7 (C); 195.09 (?) (CH); 67.9 (CH_2); 66.0 (C); 42.0 (CH); 37.8 (CH); 23.7 (CH); 19.2 (CH_2); 19.1 (CH_2); 14.1 (Me). MS: 260 (7, M^+), 225 (25), 197 (11), 177 (59), 151 (20), 123 (15), 91 (26), 69 (100), 55 (19). HR-MS: 260.03754 ($C_{12}H_{14}O_2{}^{35}Cl_2^+$, calc. 260.03709).

*1,1-Dichloro-1a,2,2a,5a,6,6a-hexahydro-1*H,*3*H-*cycloprop[*f*]*inden-3-one* (**30**). To a cooled soln. of **29** (250 mg, 0.96 mmol) in Et_2O (20 ml) was added $LiAlH_4$ (26 mg, 0.68 mmol) in 10 ml of Et_2O with stirring. The mixture was stirred at 25° for 1 h, then H_2O (10 ml) was added. It was poured into 20 ml of 2N HCl, which was extracted with Et_2O. The crude product was purified by CC (silica gel; Et_2O) and gave **30** (100 mg, 45%) as colorless liquid. IR ($CHCl_3$): 3024*m*, 2978*s*, 2872*s*, 1708*s*, 1489*m*, 1383*s*, 1351*s*, 1161*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.60–7.50 (*m*, 1 H); 6.30–6.20 (*m*, 1 H); 3.25–3.10 (*m*, 1 H); 2.55–2.35 (*m*, 2 H); 2.30–2.10 (*m*, 1 H); 1.55–1.20 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$): 212.2 (C); 168.4 (CH); 134.4 (CH); 66.0 (C); 41.6 (CH); 38.7 (CH); 24.5 (CH); 23.9 (CH); 21.1 (CH_2); 19.9 (CH_2). MS: 216 (15, M^+), 181 (55), 145 (25), 117 (48), 91 (48), 79 (100), 66 (85), 51 (77). HR-MS: 216.01384 ($C_{10}H_{10}O^{35}Cl_2^+$, calc. 216.01087).

*1,1-Dichloro-1a,2,2a,5a,6,6a-hexahydro-1*H,*3*H-*cycloprop[*f*]*inden-3-ol* (**31**). To **30** (200 mg, 0.86 mmol) in Et_2O (30 ml) was added $LiAlH_4$ (38 mg, 1.0 mmol). The resulting mixture was stirred at 25° for 2 h, then 3 drops of H_2O were added. The liquid was filtered through a column filled with $MgSO_4$ and concentrated. Purification by CC (silica gel; CH_2Cl_2) afforded **31** (90 mg, 45%) as amorphous solid. ^{1}H-NMR (400 MHz, $CDCl_3$): 5.80–5.70 (*m*, 2 H); 4.95–4.85 (*d*, 1 H); 2.92–2.80 (*m*, 1 H); 2.70–2.50 (*m*, 1 H); 2.35–2.20 (*m*, 1 H); 2.15–2.00 (*m*, 1 H); 1.80–1.55 (*m*, 1 H); 1.75 (*s*, 1 H); 1.50–1.40 (*m*, 1 H); 1.30–1.15 (*m*, 1 H); 1.15–1.00 (*m*, 1 H). ^{13}C-NMR ($CDCl_3$): 137.9 (CH); 133.1 (CH); 79.0 (CH); 67.7 (C); 41.3 (CH); 36.0 (CH); 26.0 (CH); 25.1 (CH); 22.3 (CH_2); 17.5 (CH_2). MS: 200 (15, $[M - OH]^+$), 167 (25), 139 (70), 128 (50), 117 (100), 91 (65), 78 (100), 65 (45), 51 (45). HR-MS: 200.01183 ($C_{10}H_{10}{}^{35}Cl_2^+$ ($[M - H_2O]^+$), calc. 200.01596).

*1,1,3-Trichloro-1a,2,2a,5a,6,6a-hexahydro-1*H,*3*H-*cycloprop[*f*]*indene* (**32**). Dry HCl was bubbled in a $CHCl_3$ soln. (3.0 ml) of **31** (100 mg, 0.46 mmol) for 2 h. Evaporation of the solvent followed by CC (silica gel; pentane) afforded **32** (100 mg, 93%) as pale-yellow oil. IR ($CHCl_3$): 2974*s*, 2870*s*, 1445*s*, 1383*s*, 1239*s*, 1120*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.90–5.75 (*m*, 2 H); 4.85–4.75 (*m*, 1 H); 3.30–3.15 (*m*, 1 H); 2.80–2.65 (*m*, 1 H); 2.25–2.00 (*m*, 2 H); 1.60–1.20 (*m*, 4 H). ^{13}C-NMR ($CDCl_3$, major isomer): 139.9 (CH); 131.6 (CH); 71.4 (CH); 66.8 (C); 43.8 (CH); 41.2 (CH); 25.0 (CH); 24.1 (CH); 22.0 (CH_2); 21.1 (CH_2); minor isomer: 137.4 (CH); 132.5 (CH); 69.8 (CH); 44.7 (CH); 41.3 (CH); 25.4 (CH); 25.0 (CH); 22.2 (CH_2); 20.6 (CH_2). MS: 236 (3, M^+), 201 (30), 165 (40), 129 (55), 113 (37), 91 (100), 79 (80), 65 (70), 51 (55). HR-MS: 235.98874 ($C_{10}H_{11}{}^{35}Cl_3^+$, calc. 235.99263).

*4,5-Dihydro-1*H,*3*H-*cycloprop[*f*]*inden-4-yl Methanesulfonate* (**33**) *and Its Characterization as 5-(Chloromethyl)-2,3-dihydro-1*H-*inden-2-yl Methanesulfonate* (**34**). To **1** (70 mg, 0.48 mmol) in THF (5.0 ml) was added *t*-BuOK (0.5 ml, 1M in THF, 1 equiv.) at –78°. After stirring for 1 h, MsCl (60 mg, 1.2 equiv.) in THF (1.0 ml) was added at –78°, and stirring was continued for 2 h. A second portion of *t*-BuOK (1.5 ml, 3 equiv.) was added at –78°. After 2 h of stirring, standard workup revealed the presence of **33**. Addition of two drops of conc. HCl followed by CC (silica gel; CH_2Cl_2/AcOEt 3:1) gave **34** (30 mg, 24%).

Data of **33**: ^{1}H-NMR (200 MHz, $CDCl_3$): 1.10 (*s*, 2 H); 5.55–5.45 (*m*, 2 H); 3.40–3.00 (*m*, 4 H); 3.00 (*s*, 3 H); 3.00–2.80 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 139.9 (C); 125.9 (C); 112.3 (CH); 81.8 (CH); 38.5 (CH_2); 38.6 (CH_2); 22.5 (CH_2).

Data of **34**: ^{1}H-NMR (200 MHz, $CDCl_3$): 7.30–7.20 (*m*, 3 H); 5.68–5.47 (*m*, 1 H); 4.58 (*s*); 3.35–3.25 (*m*, 4 H); 3.02 (*s*, 3 H). ^{13}C-NMR ($CDCl_3$): 140.0 (C); 139.7 (C); 136.7 (C); 127.8 (CH); 125.0 (CH); 124.9 (CH); 81.8 (CH); 46.3 (CH); 40.1 (CH_2); 40.0 (CH_2); 38.6 (CH_3). MS: 164 (30, $[M - MeSO_3H]^+$), 129 (100), 115 (20), 102 (5), 91 (15), 79 (18), 63 (10), 51 (12). HR-MS: 164.03856 ($C_{10}H_9{}^{35}Cl^+$, calc. 164.03928).

1,1-Dichloro-1a,2,4,5,6,6a-hexahydro-1H,3H-cycloprop[f]inden-4-yl Methanesulfonate (**35**). The alcohol **24** (40 mg, 0.18 mmol) was stirred with MsCl (50 mg, 0.44 mmol) in 10 ml of CH_2Cl_2, containing a drop of pyridine, for 1 h at 25°. The mixture was washed with H_2O, dried ($MgSO_4$), and evaporated. The residue was purified by CC (silica gel; $CHCl_2$) and afforded **35** (15 mg, 28%) as amorphous solid. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.30–5.20 (*m*, 1 H); 3.00 (*s*, 3 H); 2.80–2.10 (*m*, 8 H); 1.95–1.87 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 127.4 (C); 79.2 (CH); 66.4 (C); 42.4 (CH_2); 38.5 (CH_3); 25.4 (CH); 20.5 (CH_2). MS: 190 (1), 128 (1), 101 (15), 86 (100), 58 (20).

1a-Bromo-6a-chloro-1a,2,4,5,6,6a-hexahydro-1H,3H-cycloprop[f]inden-4-yl Methanesulfonate (**37**). To *1a-bromo-6a-chloro-1a,2,4,5,6,6a-hexahydro-1H,3H-cycloprop[f]inden-4-ol* (**36**) [1] (90 mg, 0.34 mmol) in CH_2Cl_2 (2.0 ml) containing Et_3N (140 mg) was added MsCl (100 mg, 0.88 mmol) at 25°. After stirring for 2 h, the solvent was evaporated, and the residue was subjected to CC (silica gel; CH_2Cl_2) to afford **37** (40 mg, 32%) as an amorphous solid. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.30–5.20 (*m*, 6 H); 3.00 (*s*, 3 H); 2.95–2.40 (*m*, 8 H); 1.45–1.35 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 129.1, 128.9 (C); 79.8, 79.3 (CH); 46.1 (C); 42.9, 42.7, 42.6, 42.5 (CH_2); 38.5, 38.4 (CH_3); 38.0 (C); 37.5, 37.3, 35.3, 35.1 (CH_2); 26.2 (CH_2). MS: 246 (10, $[M - MeSO_3]^+$), 211 (12), 165 (74), 129 (100), 91 (16), 79 (19), 65 (12), 51 (12).

1a-Bromo-6a,4-dichloro-1a,2,4,5,6,6a-hexahydro-1H,3H-cycloprop[f]indene (**38**). A mixture of **36** [1] (80 mg, 0.31 mmol), Et_3N (90 mg), and SO_2Cl (80 mg, 0.67 mmol) was heated to reflux in $CHCl_3$ (5.0 ml) for 2 h. After evaporation of the solvent, the residue was purified by CC (silica gel; pentane) and gave 70 mg (82%) of **38**. IR ($CHCl_3$): 2902*m*, 2838*m*, 1435*m*, 1256*m*, 1071*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.52–4.40 (*m*, 1 H); 3.05–2.35 (*m*, 8 H); 1.60–1.40 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 129.6, 129.4 (C); 56.9, 56.0 (CH); 46.7, 46.6, 46.5, 46.4 (CH_2); 46.3 (C); 38.4 (C); 37.7, 37.5, 35.5, 35.3 (CH_2); 26.2, 26.15 (CH_2). MS: 280 (2, M^+), 247 (5), 211 (3), 201 (26), 165 (54), 129 (100), 115 (24), 103 (14), 91 (15), 77 (31), 64 (43), 51 (61). HR-MS: 279.94286 ($C_{10}H_{11}{}^{35}Cl_2{}^{79}Br^+$, calc. 279.94216).

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