163. Synthesis of Carbo- and Heterocyclic Cycloprop[*f*]indenes *via* Cycloaddition of Dienes to Cyclopropenes

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The heterocyclic cycloprop[*f*]indene **19** was synthesized *via* cycloaddition of diene **10** to the cyclopropene **11a** and subsequent base-induced aromatization. While **19** is isolable, although very short-lived, the oxa analogue **18** decomposed under the conditions required for its preparation. The difluoro derivatives **14** and **15**, in which the heterocyclic moiety is saturated, are accessible by the cycloaddition approach, but the corresponding dichlorides are again not isolable. Cycloprop[*f*]indenes carrying substituents at C(4) have been obtained *via* cycloaddition of **22b** to 1-bromo-2-chlorocyclopropene. The key step of the sequence is a double *Curtius* degradation of the cycloadduct **23b** to the ketone **27a**. While aromatization of the alcohol **27b** provided the cycloprop[*f*]indenol **28b**, the reaction failed with **27a**. Attempts to convert **28b** to 1,3-dihydrocycloprop[*f*]indene (**25**) *via* the methanesulfonate **28d** failed.

Introduction. – Since their discovery, some 30 years ago, cycloproparenes have been systematically investigated in several laboratories [1]. Most of the efforts were directed towards the synthesis of still larger and/or more strained, or otherwise destabilized isocyclic compounds. With the exception of a few halogeno and silyl derivatives, the number of functionalized cycloproparenes is still limited. Notable exceptions are 2,6-dimethoxy-1*H*-cyclopropa[*b*]naphthalene and 1*H*-cyclopropa[*b*]naphthalene-2,6-dione [2], 2-methoxycyclopropene [3], and some products obtained by electrophilic substitution of 1,1-bis-silylated benzocyclopropene [4] or by metallation of 1,1-difluorobenzocyclopropene [5]. The effect of heteroatoms in cycloproparenes has been the subject of more recent studies. While derivatives of cyclopropapyridine [6], -quinoline [7], and -isoquinoline [8] are isolable species, the introduction of oxygen or sulfur into the system appar-

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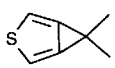

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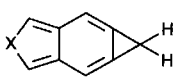

3 X=O
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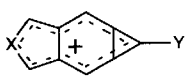
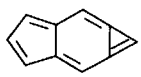


5 X = O, Y = Cl, F
6 X = S, Y = Cl, F



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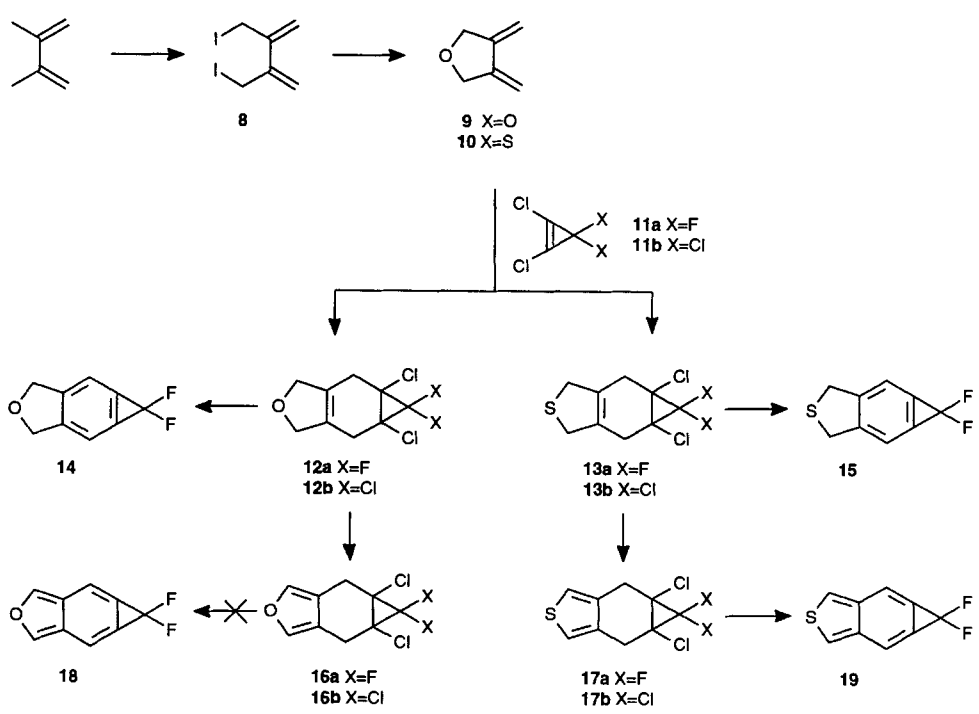
ently leads to destabilization. Thus, the synthesis of cyclopropa[*c*]furan (**1**) *via* the *Billups* route failed [9]. Similarly 4,4-dimethyl-4*H*-cyclopropa[*c*]thiophene (**2**) could not be isolated, but was trapped as adduct with isobenzofuran [10]. On the other hand, the benzo-fused analogues, 5*H*-cycloprop[*f*]isobenzofuran (**3**) and 5*H*-cyclopropa[*f*][2]-benzothiophene (**4**) have been synthesized by *Anthony* and *Wege* [11]. Both compounds are isolable, although highly reactive, and they decompose rapidly at room temperature.

This communication deals with the synthesis of several isocyclic and heterocyclic cycloprop[*f*]indenes and some substituted or functionalized derivatives using the classical approach involving cycloaddition of appropriately substituted butadienes to 1,2-dihalogeno- and tetrahalogenocyclopropenes, followed by *bis*(hydro,halogeno) elimination. This research was inititated with the long-term objective of preparing precursors for cycloprop[*f*]indenium cations **5** and **6** and for 1*H*-cycloprop[*f*]indene **7** [12] which, so far, remain both elusive.

Results and Discussion. – 1. *5,5-Difluoro-5*H*-cyclopropa[f][2]benzothiophene and Related Compounds.* The heterocyclic cycloproparenes **3** and **4** are highly reactive, and it was impossible, at the outset, to predict whether their 1,1-dihalogeno derivatives would be isolable compounds. However, we have repeatedly observed in the past, that 1,1-difluorocycloproparenes are often at least as easily isolable as their parent analogues, while the corresponding 1,1-dichloro derivatives may be synthesized only in a few exceptional cases [13] [14]. We, therefore, undertook the synthesis of the difluoro derivatives of **3** and **4** hoping that the inductive effect of the difluoro substituents would stabilize the heterocyclic system and, therefore, open the access to the heterocyclic cyclopropabenzenium ions **5** and **6**.

The synthetic sequence outlined in *Scheme 1* follows that of *Anthony* and *Wege* [11] for **3** and **4**. It is based on 2,3-bis(iodomethyl)buta-1,3-diene (**8**) [15] which, in turn, is readily accessible from 2,3-dimethylbuta-1,3-diene [16]. Reaction with OH^- or SH^-, afforded the heterocyclic dienes **9** and **10**, respectively [17]. As expected, the dienes

Scheme 1

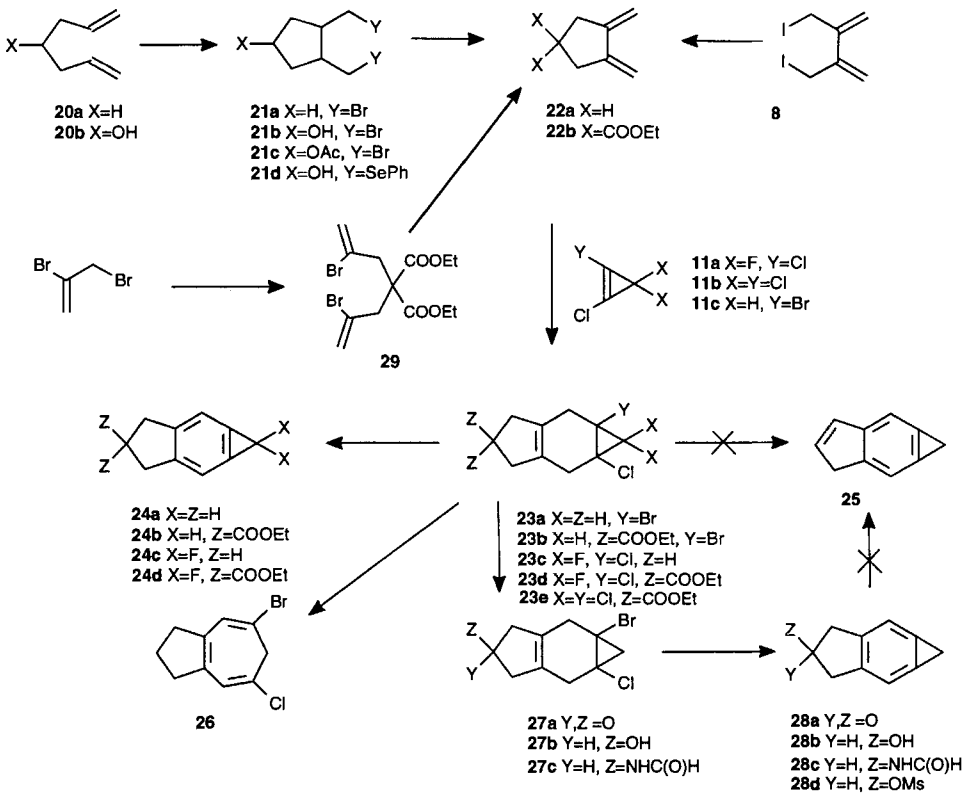


underwent cycloaddition to 1,2-dichloro-3,3-difluoro- (**11a**) [18] or tetrachlorocyclopropene (**11b**) to afford '*exo*'-adducts **12a, b** and **13a, b**, respectively. The '*exo*'-configuration of the adducts follows from the similarity of their ^{19}F-NMR spectra with that of adducts to simple dienes, the structures of which are firmly established [19]. The F-substituent *cis* to the Cl-atoms of **12a** resonates at 30.39 ppm, while the *trans*-orientied one appears at 17.48 ppm. In **13a**, the corresponding signals occur at 30.72 (*cis*) and 17.89 (*trans*). Upon treatment with *t*-BuOK in THF, the difluoro derivatives **12a** and **13a** were converted to the isolable cyclopropparenes **14** and **15**, respectively. When the dichloro compounds **12b** and **13b** were exposed to the same reaction conditions, only decomposition products were isolated.

The adducts **12** and **13** were dehydrogenated with DDQ in the usual manner [20] to the annulated furans **16a, b** and thiophenes **17a, b**, respectively. The aromatization of the heterocyclic ring resulted in a downfield shift of the ^{19}F resonance lines of the difluoro derivatives by *ca.* 5 ppm. Thus, the lines corresponding to those of **12a** (30.4 and 17.5) appear at 35.0 and 21.6 ppm in **16a**, and those of **13a** (30.7 and 17.9) are shifted to 35.2 and 22.2 ppm in **17a**. Reaction of **17a** with base (*t*-BuOK in THF) produced the very labile 1,1-difluoro-1*H*-4-thiacycloprop[*f*]indene (= 5,5-difluoro-5*H*-cyclopropa[*f*][2]-benzothiophene; **19**), which decomposed so rapidly in $CHCl_3$ solution, that it was impossible to record its ^{13}C-NMR spectrum. Owing to the high reactivity of **13b**, its ionization to the heterocyclic cyclopropabenzenium ion was not attempted. The isobenzofuran analogue **18** proved even more labile and could not be isolated. No decomposition products could be characterized for both compounds. The difficulties encountered in the isolation of **18** and **19** are best ascribed to the reduced aromatic stabilization of the heterocyclic system in comparison to that of the corresponding cyclopropa[*b*]-naphthalene, from which isolable 1,1-difluoro- and even 1,1-dichloro derivatives have been prepared. In addition, positive charge developing at C(1) upon departure of the halogen substituents of **18** and **19** which is one of the major pathways for decomposition, may be efficiently stabilized in **5** and **6**, respectively, owing to resonance involving the lone pair of the heteroatom.

2. *Functionalized Tetrahydrocycloprop[f]indenes.* 4,5-Dihydro-1*H*,3*H*-cycloprop[*f*]-indene (**24a**) has been synthesized by *Billups* and *Rodin* [21] some years ago starting from 1,2-dimethylidenecyclopentane (**22a**; *Scheme 2*). The diene, in turn, was obtained in a lengthy synthesis starting from pimelic acid [22] [23]. We have now developed a two-step synthesis of **24a**, based on Zr-mediated cyclization of hepta-1,6-diene (**20a**) [24] to the *trans*-dibromide **21a**, which reacted with KOH/CaO [25] in high yield to **22a**. The subsequent steps to the desired cyclopropparene **24a** proceeded as described *via* cycloaddition to 1-bromo-2-chlorocyclopropene (**11c**) [26] and base-induced elimination of the adduct **23a**. The synthesis of the difluoro derivative **24c** *via* an analogous route has been reported some years ago [14] [23]. Compound **23a** is of some interest as precursor for 1,3-dihydrocycloprop[*f*]indene (**25**) which, in turn, should open the access to cycloprop[*f*]indene (**7**). However, reaction of **23a** with Br_2, even at −78°, or with NBS, resulted only in formation of the cycloheptatriene **26**. Other attempts towards functionalized of **23a** (singlet oxygen, SeO_2, *m*-chloroperbenzoic acid) produced either unreacted starting material or unidentifiable decomposition products. To circumvent these difficulties, it was attempted to introduce appropriate functionalities into the precursor of the diene. Zr-Mediated cyclization of hepta-1,6-dien-4-ol (**20b**) afforded **21b**, but attempts to trans-

Scheme 2



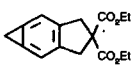
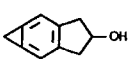
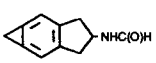
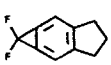
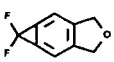
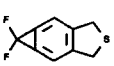
form **21b** into the corresponding diene either directly with KOH/CaO, *via* the acetate **21c**, or the selenide **21d** were not successful. Still another approach, where the required functionality was masked, was, therefore, developed: reaction of 2,3-bis(iodomethyl)buta-1,3-diene (**8**) with diethyl malonate in the presence of base [27] afforded diethyl 3,4-dimethylidenecyclopentane-1,1-dicarboxylate (**22b**) which was converted to the corresponding cycloproparene **24b** and to its 1,1-difluoro derivative **24d** by treatment with *t*-BuOK in THF in analogy to the synthesis of **24c** from **23c** [28]. Some ester exchange occurred, however, under the conditions of the elimination. Pure **24b** was obtained by reaction of the product of elimination of **23b** with EtONa in EtOH. The procedure could not be applied to **24d**, however, which decomposed in the presence of EtONa. Alternatively, the exocyclic diene **22b** was also synthesized from 1,2-dibromoprop-1-ene *via* reaction with malonate [29], followed by reductive coupling of **28** [30]. Finally, **23b** was subjected to a double *Curtius* degradation [31], which afforded the ketone **21a** in moderate yield. Exposure of the latter to *t*-BuOK resulted in a decomposition so that the desired ketone, 4,5-dihydro-1*H*,3*H*-cycloprop[*f*]inden-4-one (**28a**) could not be isolated. In contrast, the stable, functionalized cycloprop[*f*]indenol **28b** was synthesized *via* reduction of **27a** to **27b** with $NaBH_4$, followed by aromatization with strong base.

The double *Curtius* degradation of **23b** involves a transformation of the ester groups by reaction of the carboxylic acids with oxalyl chloride at 25°. When this reaction was carried out at 80°, one of the carboxyl groups was lost by decarboxylation, and the procedure afforded the amide **27c**, which was aromatized in the usual manner to **28c**.

An attempt was made to introduce a C=C bond into the cyclopentane ring of cycloprop[*f*]indene by conversion of **28b** into its methanesulfonate **28d** and exposure of the latter to strong base. However, **28d** failed to react further to **25** under the conditions tried (3 equiv. of *t*-BuOK, THF).

The ^{13}C-NMR spectra of cycloproparenes exhibit a characteristic resonance in the range of 110–115 ppm, attributed to C(2,5). This is also the case with the compounds prepared in this investigation (*Table*), and it applied in particular to the saturated heterocycles **14** and **15**. The corresponding ^{13}C-NMR resonances of **3** and **4**, however, appear at 101.9 and 106.1, respectively [11]. This shift must be appreciated in the light of the shifts of the corresponding C-atoms of the aromatic heterocycles isobenzofuran (118.5 ppm) and isobenzothiophene (121.6 ppm), respectively, in comparison to that of benzene (128.5 ppm) or naphthalene (128.0 ppm). In benzene and naphthalene, *ortho*-fu-

Table. *^{13}C-NMR Data of Cycloprop[f]indenes and Related Compounds*

Compound		C(1)	C(1a)/C(5)	C(2)/C(5)	C(3)/C(4)	Others	^{19}F-NMR	Ref.
		18.4	125.4	114.7	128.8			[1]
		19.2	122.8	110.0	145.5	29.0		[1]
	**24a**	22.8	124.7	111.9	145.3	32.2 (α) 25.6 (β)		[a]
	**24b**	22.7	125.5	111.9	140.8	39.8 (α) 60.3 (β)		
	**28b**	22.4	125.3	112.6	141.7	42.1 (α) 73.1 (β)		[a]
	**28c**	22.5	125.5	112.4	141.6	39.3 (α) 49.4 (β)		[a]
	**24c**	103.9	128.3	111.7	153.0	32.5 (α) 25.2 (β)	83.6	[22]
	**14**	103.9	129.4	109.4	147.5	72.4	82.9	[a]
	**15**	103.9	129.0	112.9	148.8	36.6	82.9	[a]

[a]) This work.

sion by a cyclopropene unit results in an upfield shift of 14 and 16 ppm, respectively. In **4**, the corresponding shift amounts to 16.5 ppm, and in **5**, it is 15.5 ppm, which is consistent with the direction and the trend observed in the isocyclic cycloproparenes.

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Experimental Part

General. See [32].

*1a,6a-Dichloro-1,1-difluoro-1a,2,3,5,6,6a-hexahydro-1*H*-4-oxacycloprop[f]indene* (**12a**). A soln. of **9** (0.54 g, 5.6 mmol) and **11a** (1.0 g, 6.9 mmol) in CCl_4 (20 ml) containing 4-(*tert*-butyl)phenol (20 mg) and $NaHCO_3$ (50 mg) was stirred in a sealed tube at 70° during 20 h. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel; pentane/CH_2Cl_2 1:1) to give 1.0 g (74%) of pure **12a**. M.p. 65–80°. IR ($CHCl_3$): 2920*w*, 2849*s*, 1450*s*, 1419*s*, 1203*s*, 950*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 4.58–4.46 (*m*, 4 H); 3.05–2.82 (*m*, 4 H). ^{13}C-NMR: 126.87 (C); 107.09 (CF_2); 76.64 (CH_2); 47.03 (C); 28.03 (CH_2). ^{19}F-NMR: 30.4 (*dtt*, J = 156, 5, 2); 17.48 (*d*, J = 156). MS: 240 (30, M^+), 205 (77), 175 (85), 157 (30), 141 (95), 125 (45), 101 (33), 91 (67), 68 (100). HR-MS: 239.98983 ($C_9H_8O^{35}Cl_2F_2^+$; calc., 239.99203).

*1,1,1a,6a-Tetrachloro-1a,2,3,5,6,6a-hexahydro-1*H*-4-oxacycloprop[f]indene* (**12b**). A soln. of **9** (0.60 g, 6.25 mmol) and **11b** (1.63 g, 9.21 mmol) in CCl_4 (20 ml) containing 4-(*tert*-butyl)phenol (20 mg) and $NaHCO_3$ (50 mg) was stirred at 40° under N_2 for 48 h. After evaporation of the solvent, the residue was purified by chromatography (silica gel; pentane/Et_2O 3:1) and yielded 1.4 g (82%) of **12b**. M.p. 103–106°. IR ($CHCl_3$): 2951*w*, 2896*m*, 2847*m*, 1425*m*, 1042*m*, 908*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.65–4.37 (*m*, 4 H); 3.05–2.95 (*d*, 4 H). ^{13}C-NMR: 127.77 (C); 76.45 (CH_2); 68.44 (C); 52.64 (C); 30.84 (CH_2). MS: 274 (5, M^+), 239 (16), 209 (23), 173 (70), 137 (30), 102 (50), 75 (60), 63 (55), 51 (100). HR-MS: 271.93240 ($C_9H_8O^{35}Cl_4^+$; calc., 271.93294).

*1a,6a-Dichloro-1,1-difluoro-1a,2,3,5,6,6a-hexahydro-1*H*-4-thiacycloprop[f]indene* (**13a**). A soln. of **10** (1.4 g, 12.5 mmol) and **11a** (1.5 g, 10.5 mmol) in CCl_4 (20 ml) containing 4-(*tert*-butyl)phenol (20 mg) and $NaHCO_3$ (50 mg) was stirred in a sealed tube at 80° for 24 h. After evaporation, the residue was purified by column chromatography (silica gel; pentane/Et_2O 3:1) and afforded 1.19 g (45%) of **13a**. M.p. 115–118°. IR ($CHCl_3$): 2930*m*, 2840*m*, 1460*s*, 1430*s*, 1259*s*, 1210*s*, 970*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.58–3.64 (*m*, 4 H); 2.88–2.96 (*m*, 4 H). ^{13}C-NMR: 128.23 (C); 107.04 (CF_2); 47.07 (C); 40.97 (CH_2); 31.99 (CH_2). ^{19}F-NMR: 31.1, 30.3 (*dtt*, J = 155, 4); 17.9 (*d*, J = 2). MS: 256 (50, M^+), 221 (40), 185 (54), 165 (25), 134 (20), 97 (27), 84 (100), 63 (18), 51 (28). HR-MS: 255.96809 ($C_9H_8{}^{32}S^{35}Cl_2F_2^+$; calc., 255.96921).

*1,1,1a,6a-Tetrachloro-1a,2,3,5,6,6a-hexahydro-1*H*-4-thiacycloprop[f]indene* (**13b**). A soln. of **10** (1.6 g, 14.3 mmol) and **11b** (2.0 g, 11.25 mmol) in CCl_4 (20 ml) containing 4-(*tert*-butyl)phenol (20 mg), and $NaHCO_3$ (50 mg) was stirred at 40° during 48 h. Evaporation of the solvent and purification of the residue by column chromatography (silica gel; pentane/Et_2O 4:1) afforded 1.17 g (36%) of **13b**. M.p. 123–126°. IR ($CHCl_3$): 2911*m*, 2845*m*, 1439*m*, 1424*m*, 1126*w*, 919*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.65–3.50 (*m*, 4 H); 3.05–2.95 (*m*, 4 H). ^{13}C-NMR: 129.0 (C); 68.3 (C); 52.7 (C); 40.7 (CH_2); 34.8 (CH_2). MS: 290 (50, M^+), 253 (35), 217 (100), 181 (45), 145 (33), 119 (25), 97 (50), 63 (20), 51 (28). HR-MS: 287.90718 ($C_9H_8{}^{32}S^{35}Cl_4^+$; calc., 287.91011).

*1,1-Difluoro-3,5-dihydro-1*H*-4-oxacycloprop[f]indene* (**14**). To a soln. of **12a** (70 mg, 0.29 mmol) in dry THF (5.0 ml) was added, at −78°, freshly sublimed *t*-BuOK (130 mg, 0.58 mmol) in THF (5 ml) within 5 min. The mixture was stirred at −78° for 2 h, and then warmed to r.t. The solvent was evaporated *in vacuo* and the residue was extracted with pentane. After filtration and evaporation, **14** (30 mg, 43%) was obtained as pale yellow oil. IR ($CHCl_3$): 3067*w*, 2915*w*, 2860*m*, 1646*s*, 1384*s*, 1318*s*, 1177*s*, 1057*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.36 (*tt*, J = 3.7, 1, 2 H); 5.15 (*t*, J = 1.5, 4 H). ^{13}C-NMR: 147.57 (C); 129.36 (C); 109.43 (CH); 103.91 (CF_2); 72.45 (CH_2). ^{19}F-NMR: 82.9 (*m*). MS: 168 (100, M^+), 140 (50), 119 (50), 99 (20), 81 (22), 75 (15), 63 (27), 63 (27), 51 (15). HR-MS: 168.03894 ($C_9H_6OF_2^+$; calc., 168.03868).

*1,1-Difluoro-3,5-dihydro-1*H*-4-thiacycloprop[f]indene* (**15**). To a soln. of **13a** (100 mg, 0.38 mmol) in dry THF (5.0 ml) was added, at −78°, freshly sublimed *t*-BuOK (160 mg, 1.43 mmol) in THF (5 ml) within 10 min. The brown mixture was stirred at −78° during 2 h, then warmed to r.t. The solvent was evaporated under reduced pressure. The residue was extracted with pentane, the pentane filtered, and the filtrate evaporated *in vacuo* to afford 50 mg (50%) of **15** as pale yellow oil. IR ($CHCl_3$): 2933*m*, 1650*m*, 1446*w*, 1383*s*, 1152*s*, 1110*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.41 (*t*, J = 3.8, 2 H); 4.27 (*t*, J = 1.5, 4 H). ^{13}C-NMR: 148.79 (C); 129.04 (C); 112.90 (CH); 103.89 (CF_2); 36.61 (CH_2). ^{19}F-NMR: 82.93 (*m*). MS: 184 (20, M^+), 134 (8), 119 (30), 84 (100). HR-MS: 184.01573 ($C_9H_6SF_2^+$; calc., 184.01585).

1a,6a-Dichloro-1,1-difluoro-1a,2,6,6a-tetrahydro-1H-4-oxacylcoprop[f]indene (**16a**). A mixture of **12a** (350 mg, 1.45 mmol) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ, 350 mg, 1.54 mmol) in CCl_4 (10 ml) was stirred under reflux for 1 h. After filtration and evaporation of the filtrate, the residue was subjected to column chromatography (silica gel; pentane/CH_2Cl_2 1:1) and yielded 300 mg (86%) of **16a**. M.p. 57–60°. IR ($CHCl_3$): 2930*w*, 1764*s*, 1456*s*, 1416*m*, 1229*m*, 1197*m*, 1043*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.21–7.17 (*m*, 2 H); 3.65–3.30 (*m*, 4 H). ^{13}C-NMR: 137.3 (CH); 116.9 (C); 107.8 (CF_2); 48.26 (C); 26.45 (CH_2). ^{19}F-NMR: 34.96 (*dtt*, J = 160, 5.9, 1.5); 21.60 (*dtt*, J = 160, 1.8, 1.3). MS: 240 (40, M^+), 203 (100), 175 (68), 153 (65), 139 (30), 125 (50), 91 (30), 68 (50). HR-MS: 237.97592 ($C_9H_6O^{35}Cl_2F_2^+$; calc., 237.97638).

1,1a,6,6a-Tetrachloro-1a,2,6,6a-tetrahydro-1H-4-oxacycloprop[f]indene (**16b**). The procedure described for **16a** afforded **16b** after column chromatography (silica gel; pentane/Et_2O 10:1) in 90% yield. M.p. 85–88°. IR ($CDCl_3$). 2932*w*, 1761*s*, 1702*m*, 1415*m*, 1345*m*, 1257*m*, 1134*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.18 (*t*, J = 1, 2 H); 3.75–3.50 (*m*, 4 H). ^{13}C-NMR: 136.9 (CH); 117.2 (C); 68.4 (C); 53.4 (C); 28.6 (CH_2). MS: 272 (7, M^+), 237 (22), 199 (37), 152 (52), 136 (55), 118 (30), 99 (45), 75 (70), 63 (40), 51 (100). HR-MS: 269.91737 ($C_9H_6O^{35}Cl_4^+$; calc., 269.01729).

1a,6a-Dichloro-1,1-difluoro-1a,2,6,6a-tetrahydro-1H-4-thiacycloprop[f]indene (**17a**). The procedure described for **16a** afforded **17c** in 70% yield. M.p. 70–73°. IR ($CHCl_3$): 2914*w*, 1456*m*, 1418*m*, 1233*m*, 1114*m*, 982*s*, 902*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.96 (*s*, 2 H); 3.75–3.40 (*m*, 4 H). ^{13}C-NMR: 132.29 (C); 120.05 (CH); 107.94 (CF_2); 48.68 (C); 31.69 (CH_2). ^{19}F-NMR: 35.15 (*dtt*, J = 163, 5.70, 1.5); 22.15 (*dt*, J = 163, 2). MS: 255 (20, M^+), 219 (75), 219 (75), 183 (78), 169 (60), 133 (90), 109 (10), 80 (20), 69 (50), 51 (30), 45 (100). HR-MS: 253.95363 ($C_9H_6{}^{32}S^{35}Cl_2{}^{19}F_2^+$; calc., 253.95356).

1,1a,6,6a-Tetrachloro-1a,2,6,6a-tetrahydro-1H-4-thiacylcoprop[f]indene (**17b**). The procedure described for **16a** afforded **17b** in 75% yield after chromatography (silica gel, pentane). M.p. 92–95°. IR ($CHCl_3$): 2914*w*, 1468*m*, 1427*s*, 1150*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 6.93 (*s*, 2 H); 3.72 (*s*, 4 H). ^{13}C-NMR: 132.8 (C); 119.8 (CH); 68.9 (C); 54.2 (C); 34.1 (CH_2). MS: 288 (4, M^+), 253 (15), 215 (25), 181 (25), 168 (30), 145 (15), 134 (20), 111 (50), 90 (10), 73 (15), 63 (20), 51 (25), 45 (100). HR-MS: 285.89084 ($C_9H_6{}^{32}S^{35}Cl_4^+$; calc., 285.89446).

1,1-Difluoro-1H-4-thiacycloprop[f]indene (**19**). To **17a** (37.5 mg, 0.15 mmol) in dry THF (5.0 ml) was added, at −78°, freshly sublimed *t*-BuOK (39.6 mg, 0.35 mmol) in THF (5.0 ml) within 5 min. The brown mixture was stirred at −78° during 2 h, then warmed to r.t. The solvent was evaporated at r.t. *in vacuo* and the residue extracted with pentane. Filtration of the pentane followed by evaporation under vacuum afforded **19** as pale-yellow oil (20 mg), which decomposed within a few. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.98 (*s*, 2 H); 7.84 (*t*, J = 3.2, 2 H). MS: 182 (14, M^+), 163 (5), 138 (19), 121 (16), 109 (10), 89 (25), 77 (5), 67 (100), 51 (32). HR-MS: 181.99359 ($C_9H_4{}^{32}SF_2^+$; calc., 182.00020).

trans-*1,2-Bis(bromomethyl)cyclopentane* (**21a**). To a soln. of **20a** (385 mg, 4.0 mmol) and zirconocene dichloride (1.17 g, 4.0 mmol) in dry THF (50 ml) was added, *via* syringe, BuLi (5.0 ml, 8 mmol) in hexane (1.6M) at −78°. After 10 min, the mixture was allowed to warm to r.t., and stirring was continued for 2 h. It was then cooled to −78°, and a soln. of Br_2 (1.5 g, 9.4 mmol) in CCl_4 was added. The reaction was quenched at r.t. with 10% H_2SO_4 (50 ml), the mixture extracted with Et_2O, which was washed with aq. $NaHCO_3$ and H_2O, and was dried ($MgSO_4$). Evaporation of the solvent followed by flash chromatography (silica gel; hexane) afforded 0.71 g (70%) of **21a**. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.60–3.30 (*m*, 4 H); 2.20–2.00 (*m*, 2 H); 2.00–1.80 (*m*, 2 H); 1.07–1.04 (*m*, 4 H). ^{13}C-NMR: 46.0 (CH); 38.2 (CH_2); 32.2 (CH_2); 24.1 (CH_2).

trans-*3,4-Bis(bromomethyl)cyclopentan-1-ol* (**21b**). To a soln. of **20b** (896 mg, 8.0 mmol) and zirconocene dichloride (3.34 g, 8.0 mmol) in THF, at −78°, was added, *via* syringe, BuLi (15 ml, 24 mmol) in hexane (1.6M). After 10 min, the mixture was allowed to warm to r.t., where stirring was continued for 2 h. The mixture was cooled to −78°, and a soln. of Br_2 (3.0 g, 18 mmol) in CCl_4 (10 ml) was added. The reaction was quenched at r.t. with 10% H_2SO_4 (100 ml), and the mixture extracted with Et_2O. The org. layer was washed with aq. $NaHCO_3$ and H_2O, dried ($MgSO_4$), and evaporated. Flash chromatography (silica gel; CH_2Cl_2) gave 1.43 g (66%) of **21b** as a light yellow oil. IR ($CHCl_3$): 3345*s* (br.), 2958*s*, 2856*m*, 1436*s*, 1232*m*, 1023*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.40–4.38 (*m*, 1 H); 3.65–3.40 (*m*, 4 H); 2.25 (*s*, 1 H); 2.50–1.50 (*m*, 6 H). ^{13}C-NMR: 72.0 (CH); 44.4 (CH); 44.0 (CH); 43.5 (CH_2); 41.0 (CH_2); 38.5 (CH_2); 38.2 (CH_2). MS: 270 (0.5, M^+), 175 (90), 173 (100), 150 (44), 148 (48), 11 (10), 95 (15), 93 (48), 69 (35), 53 (20). HR-MS: 270.91981 ($C_7H_{11}{}^{79}Br^{81}BrO^+$ ([M − 1]$^+$); calc., 270.91567).

2,3-Dimethylidenecyclopentane (**22a**). Compound **21a** (1.0 g, 3.9 mmol) was mixed with powdered KOH (2.0 g) and powdered CaO (2.0 g), and the mixture was heated to 150° under vacuum (100 Torr) under N_2 during 3 h. The pyrolysate was collected in a trap cooled to −78°, and dried with $CaCl_2$. Distillation afforded 300 mg (81%) of **22a**. IR (liquid): 3050*m*, 2950*s*, 1630*m*, 1450*m*, 1250*s*, 880*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.34 (*t*, J = 2.4, 2 H); 4.87 (*t*, J = 2.0, 2 H); 2.42 (*tt*, J = 7.0, 2.0, 4 H); 1.66 (*quint.*, J = 7.4, 2 H). ^{13}C-NMR ($CDCl_3$): 148.7 (C); 103.4 (CH_2); 34.1 (CH_2); 24.0 (CH_2).

Diethyl 3,4-Dimethylidenecyclopentane-1,1-dicarboxylate (**22b**) *from* **8** [27]. A soln. of **8** (1.20 g, 3.59 mmol), diethyl malonate (0.57 g, 3.59 mmol) and Bu_4NCl (0.1 g) in Et_2O (10 ml) was added to a mixture of KOH (0.40 g, 7.2 mmol) in H_2O (2.0 ml) and MeOH (20 ml). After stirring during 10 h, H_2O (30 ml) was added, and the resulting soln. was extracted with Et_2O. After usual workup, the crude product was subjected to column chromatography (silica gel; pentane/Et_2O 3:1) to give **22b** (0.50 g, 58%). ^{1}H-NMR (200 MHz, $CDCl_3$): 5.40–5.35 (*t*, 2 H); 4.95–4.90 (*t*, 2 H); 4.25–4.10 (*q*, 4 H); 3.05–2.95 (*t*, 4 H); 1.30–1.20 (*t*, 6 H). ^{13}C-NMR: 171.2 (C); 144.6 (C); 105.5 (CH_2); 61.6 (CH_2); 57.6 (C); 41.1 (CH_2); 14.0 (Me).

Diester **22b** *from* **28** [29] [30]. A mixture of diethyl malonate (10.0 g, 50 mmol), 2,3-dibromoprop-1-ene (4.0 g, 25 mmol) and anh. K_2CO_3 (15 g, 110 mmol) in 100 ml of butan-2-one was heated to reflux for 50 h. The mixture was filtered, the filtrate concentrated and subjected to column chromatography (silica gel; AcOEt/pentane 1:5) to afford 11.5 g (82%) of *diethyl bis(2-bromoallyl)malonate* (**29**).

A mixture of **28** (9.30 g, 23.4 mmol), $Pd(OAc)_2$ (0.30 g, 1.3 mmol), Ph_3P (7.70 g, 29.4 mmol), K_2CO_3 (10.0 g, 72.5 mmol), and anh. MeCN (150 ml) was heated to reflux under N_2 for 6 h (TLC monitoring). The mixture was filtered and the filtrate was concentrated. The residue was subjected to column chromatography (silica gel; pentane/AcOEt 4:1) to afford **22b** (2.50 g, 45%) as colorless oil.

*1a-Bromo-6a-chloro-1a,2,4,5,6,6a-hexahydro-1*H,*3*H-*cyclopropa[f]indene* (**23a**) [21]. Compound **22a** (200 mg, 2.13 mmol) in THF (5.0 ml) was added to a soln. of *1-bromo-2-chlorocycloprop-1-ene* (**11c**) [26] and stirred at −20° for 15 h. After evaporation of the solvent, the residue was subjected to column chromatography (silica gel; pentane/Et_2O 50:1), and afforded 170 mg (32%) of **23a** as a yellow oil. IR ($CHCl_3$): 2900*s*, 1650*m*, 1450*m*, 1100*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 3.00–2.65 (*m*, 4 H); 2.35–2.05 (*m*, 4 H); 1.80–1.70 (*m*, 2 H); 1.42 (*AB*, *J* = 7.5, 2 H). ^{13}C-NMR ($CDCl_3$): 131.6 (C); 131.4 (C); 46.8 (C); 39.2 (C); 38.1 (CH_2); 35.7 (CH_2); 35.4 (CH_2); 35.3 (CH_2); 26.2 (CH_2); 21.8 (CH_2). MS: 248, 246 (4, M^+), 213, 211 (5), 167 (25), 131 (100), 115 (22), 103 (19), 91 (55), 77 (37), 65 (29). HR-MS: 247.97753 ($C_{10}H_{12}{}^{81}Br^{35}Cl^+$; calc., 247.97909).

*Diethyl 1a-Bromo-6a-chloro-1a,2,4,5,6,6a-hexahydro-1*H,*3*H-*cycloprop[f]indene-4,4-dicarboxylate* (**23b**). To a soln. of 1-bromo-2,2-dichloro-1-(trimethylsilyl)cyclopropane (3.0 g, 11.45 mmol) and 0.1 g of 4-(*tert*-butyl)-phenol in anh. THF (10 ml) was added, dropwise, at −30°, Bu_4NF (10 ml, 1.1M, in THF). The mixture was stirred for 3 h at the same temp. The diene **22b** (1.9 g, 7.98 mmol) in 5 ml of THF was added dropwise. The resulting mixture was stirred for 7 d at −30°. After evaporation, the residue was subjected to column chromatography (silica gel; AcOEt/pentane 1:20) to afford **23b** (1.30 g, 46%) as a colorless oil. IR ($CHCl_3$): 2983*s*, 2839*s*, 1718*s*, 1445*s*, 1368*s*, 1256*s*, 1185*s*, 1081*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.22–4.10 (*m*, 4 H); 3.00–2.70 (*m*, 8 H); 1.47–1.37 (*m*, 2 H); 1.27–1.50 (*t*, 6 H). ^{13}C-NMR ($CDCl_3$): 171.8, 171.7 (C); 129.1, 128.9 (C); 62.7 (CH_2); 57.8 (C); 46.2 (C); 43.1, 42.9 (CH_2); 38.3 (C); 37.4, 35.1 (CH_2); 26.1 (CH_2); 14.0 (CH_3). MS: 392 (5, M^+), 347 (3), 318 (7), 275 (6), 237 (36), 201 (31), 163 (27), 129 (100), 115 (26), 91 (12), 77 (20), 65 (9), 51 (21). HR-MS: 390.02441 ($C_{16}H_{20}O^{79}Br^{35}Cl^+$; calc., 390.02336).

*Diethyl 1,6a-Dichloro-1,1-difluoro-1a,2,4,5,6,6a-hexahydro-1*H,*3*H-*cycloprop[f]indene-4,4-dicarboxylate* (**23d**). A mixture of **22a** (0.5 g, 2.1 mmol), **11a** (0.40 g, 2.7 mmol), $NaHCO_3$ (50 mg), and 4-(*tert*-butyl)phenol (20 mg) was heated in toluene (5.0 ml) to 80° for 2 d with stirring. After evaporation, the residue was subjected to column chromatography (silica gel; AcOEt/pentane 1:10) to afford 0.60 g (75%) of **23d** as amorphous solid. IR ($CHCl_3$): 1729*s*, 1146*m*, 1368*m*, 1262*s*, 1095*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.20–4.05 (*m*, 4 H); 2.95–2.70 (*m*, 8 H); 1.25–1.10 (*m*, 6 H). ^{13}C-NMR ($CDCl_3$): 171.3, 171.25 (C); 107.2 (*dd*, *J* = 296, CF_2); 61.6, 61.6 (CH_2); 57.4 (C); 47.1 (*dd*, *J* = 10, C); 42.5 (CH_2); 31.0 (*dd*, *J* = 2, CH_2); 13.9 (Me). ^{19}F-NMR: 30.21 (*dm*, *J* = 155); 17.19 (*d*, *J* = 155). MS: 382 (14, M^+), 337 (20), 312 (35), 288 (95), 235 (45), 199 (45), 165 (100), 115 (45), 92 (14), 77 (9), 65 (10), 51 (12). HR-MS: 382.05119 ($C_{16}H_{18}O_4{}^{35}Cl_2{}^{19}F_2^+$; calc., 382.05499).

*Diethyl 1,1a,6,6a-Tetrachloro-1a,2,4,5,6,6a-hexahydro-1*H,*3*H-*cycloprop[f]indene* (**23e**). Diene **22b** (0.14 g, 0.59 mmol) and **11b** (0.20 g, 1.12 mmol) were heated to reflux in CCl_4 (15 ml) during 10 h. The adduct **23e** (0.20 g, 81%) was obtained after evaporation and recrystallization of the residue from Et_2O. M.p. 108–110°. IR ($CHCl_3$): 2983*s*, 2929*s*, 1728*s*, 1445*m*, 1367*m*, 1260*s*, 1182*s*, 1071*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.30–4.10 (*m*, 4 H); 3.10–2.70 (*m*, 8 H); 1.30–1.15 (*m*, 6 H). ^{13}C-NMR: 172.0, 171.8 (C); 128.2 (C); 68.9 (C); 61.8, 61.7 (CH_2); 57.8 (C); 52.8 (C); 42.5 (CH_2); 33.8 (CH_2); 14.0 (Me). MS: 416 (30, M^+), 371 (20), 342 (55), 305 (100), 269 (85), 197 (65), 162 (60), 1217 (25), 77 (15). HR-MS: 413.99146 ($C_{16}H_{18}O_4{}^{35}Cl_4^+$; calc., 413.99595).

*4,5-Dihydro-1*H,*3*H-*cycloprop[f]indene* (**24a**) [21]. The adduct **23a** (45 mg, 0.18 mmol) in THF (0.5 ml) was treated at −78° with *t*-BuOK (200 mg, 1.8 mmol) in THF (1.0 ml) for 2 h, whereupon the mixture was allowed to warm to 25°. The solvent was evaporated and the residue extracted with pentane. The extracts were filtered through a column of $MgSO_4$. Concentration gave 13 mg (55%) of **24a** as amorphous solid. UV (hexane): 279, 283. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.50 (*s*, 2 H); 3.25 (*t*, *J* = 1, 2 H); 2.84 (*t*, *J* = 7, 4 H); 2.00 (*m*, 2 H). ^{13}C-NMR: 143.3

(C); 124.7 (C); 111.9 (CH); 32.2 (CH_2); 25.6 (CH_2); 22.8 (CH_2). MS: 130 (4, M^+), 117 (100), 193 (20), 91 (63), 77 (25), 63 (40), 51 (55). HR-MS: 130.07779 ($C_{19}H_{10}^+$; calc., 130.07825).

*Diethyl 4,5-Dihydro-1*H,*3*H-*cycloprop[*f*]indene-4,4-dicarboxylate* (**24b**). To **23b** (440 mg, 1.13 mmol) in anh. THF (10 ml) was added a soln. of *t*-BuOK (300 mg, 2.68 mmol) in THF (10 ml) under N_2 at −78°. The resulting mixture was stirred for 2 h at −78°, and at 25° for 2 h. After evaporation, the residue was subjected to column chromatography (silica gel; AcOEt/pentane 1:20) to give **24b** as a mixture of ethyl and *tert*-butyl esters, which was redissolved in EtOH (15 ml) and treated with 20 mg of NaOEt. After 3 h of stirring, the solvent was evaporated and the residue purified by column chromatography as described above to afford pure **24b** (150 mg, 49%) as a colorless oil. IR ($CHCl_3$): 2983*m*, 1727*s*, 1251*s*, 1067*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.05 (*s*, 2 H); 4.25–4.10 (*q*, 4 H); 3.54 (*s*, 4 H); 3.28 (*m*, 2 H); 1.30–1.20 (*t*, 6 H). ^{13}C-NMR ($CDCl_3$): 171.7 (C); 140.8 (C); 125.6 (C); 111.9 (CH); 61.7 (CH_2); 60.3 (C); 39.8 (CH_2); 22.7 (CH_2); 14.0 (Me). MS: 274 (67, M^+), 272 (100), 237 (55), 201 (25), 163 (47), 129 (95), 115 (49), 91 (26), 76 (28), 65 (14), 57 (39), 51 (16). HR-MS: 274.11998 ($C_{16}H_{18}O_4^+$; calc., 274.12048).

3-Bromo-5-chlorobicyclo[5.3.0]hepta-1(7),2,5-triene (**26**). To **23a** (50 mg, 0.20 mmol) in THF (10 ml) was added Br_2 (40 mg, 0.25 mmol) in THF (5.0 ml) at −78°. After stirring for 1 h, the temp. was raised to −20° for 1 h. The mixture was cooled again to −78°, and *t*-BuOK (45 mg, 0.4 mmol) in THF (5.0 ml) was added. The temp. was allowed to raise to −20° within 2 h, then stirring was continued for an addition h at r.t. H_2O (20 ml) was added, and the mixture extracted with Et_2O. Evaporation afforded a dark blue amorphous solid **26** (23 mg, 46%). IR ($CHCl_3$): 2925*w*, 1657*s*, 1396*m*, 1267*m*, 1183*m*, 1071*m*, 922*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 5.5–6.3 (*d*, 2 H); 3.2 (*s*, 2 H); 2.6 (*m*, 4 H); 2.0–1.8 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 140.35 (C); 139.78 (C); 128.52 (CH); 124.21 (CH); 117.55 (C); 105.44 (C); 47.37 (CH_2); 36.49 (CH_2); 36.34 (CH_2); 22.88 (CH_2). MS: 246 (16, M^+), 211 (19), 209 (18), 165 (85), 129 (67), 115 (40), 63 (73), 51 (100). HR-MS: 243.970985 ($C_{10}H_{10}{}^{79}Br_{35}Cl^+$; calc., 243.96545).

*1a-Bromo-6a-chloro-1a,2,4,5,6,6a-hexahydro-1*H,*3*H-*cycloprop[*f*]inden-4-one* (**27a**). A mixture of **23b** (1.0 g, 25.5 mmol) and KOH (1.0 g, 178 mmol) in 80% EtOH (50 ml) was heated to reflux for 8 h, then evaporated to dryness. The residue was dissolved in H_2O (100 ml) and acidified to pH 2 with conc. HCl with cooling. The resulting slurry was extracted with Et_2O (4 × 100 ml), the extracts were washed (H_2O and dried ($MgSO_4$). Removal of the solvent and recrystallization from toluene afforded 800 mg (90%) of diacid. M.p. 191–193° (dec.). IR (KBr): 3500 (br.), 1704*s*, 1407*w*, 1287*w*, 1201*w*, 1061*w*. ^{1}H-NMR ($CDCl_3$): 5.60–5.20 (2 H); 3.0–2.70 (*m*, 8 H); 2.01 (*s*, 1 H); 1.99 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 175.3, 175.2 (C); 130.55, 130.53 (C); 59.1 (C); 47.6 (C); 44.2, 44.1 (CH_2); 39.47 (C); 38.7, 36.1 (CH_2); 26.9 (CH_2). MS: 336 (1, M^+), 291 (6), 255 (9), 211 (42), 193 (9), 165 (79), 129 (100), 115 (25), 91 (27), 77 (21), 64 (26), 51 (23). HR-MS: 333.96016 ($C_{12}H_{12}O_4{}^{35}Cl^{79}Br^+$; calc., 333.96076).

To a suspension of the diacid (300 mg, 0.89 mmol) in anh. benzene (10 ml) containing 170 mg of pyridine was added oxalyl chloride (0.80 g, 6.3 mmol). The mixture was stirred at 25° for 8 h. After removal of the solvent, and unreacted oxalyl chloride and pyridine, the residue was redissolved in dry MeCN (30 ml), and 2.5 g (38.5 mmol) of commercial NaN_3 was added. The suspension was stirred at 25° overnight. The mixture was quickly filtered and concentrated at 25° under reduced pressure to afford a gummy golden residue of acyl azide, which was redissolved in THF (1.0 ml). After addition of cyclohexane (30 ml), the suspension was heated to reflux for 2 h, then concentrated and redissolved in 30 ml of THF. Hydrolysis was accomplished using AcOH/H_2O 1:1 (3 ml). Usual workup, followed by column chromatography (AcOEt/pentane 1:25) afforded **27a** (120 mg, 50%). M.p. 81–83°. IR ($CHCl_3$): 2980*w*, 2898*w*, 1751*s*, 1218*m*, 1106*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 2.60–2.30 (*m*, 8 H); 1.54–1.48 (*d*, 2 H). ^{13}C-NMR ($CDCl_3$): 213.4 (C); 129.7, 129.5 (C); 45.8 (C); 45.7, 45.5 (CH_2); 37.7 (C); 37.6, 35.4 (CH_2); 26.3 (CH_2). MS: 262 (8, M^+), 234 (3), 227 (3), 181 (41), 153 (27), 117 (100), 103 (16), 91 (50), 77 (21), 51 (40). HR-MS: 259.96046 ($C_{10}H_{10}O^{79}Br^{35}Cl^+$; calc., 259.96038).

*1a-Bromo-6a-chloro-1a,2,4,5,6,6a-hexahydro-1*H,*3*H-*cycloprop[f]inden-4-ol* (**27b**). To **27a** (130 mg, 0.5 mmol) in EtOH (10 ml) was added $NaBH_4$ (300 mg, 8 mmol) at 25°. The mixture was stirred to 50° for 3 h, then H_2O (50 ml) was added. Usual workup, followed by column chromatography (silica gel; CH_2Cl_2) afforded **27b** (110 mg, 85%). M.p. 61–63°. IR ($CHCl_3$): 3609*w*, 2903*m*, 2838*w*, 1435*w*, 1208*m*, 1077*m*, 1027*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 4.45–4.35 (*m*, 1 H); 3.00–2.00 (*m*, 8 H); 1.55–1.35 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 129.5, 129.3, 129.2, 129.1 (C); 70.4, 70.3 (CH); 46.51 (C); 45.4, 45.3, 45.2 (CH_2); 38.7 (C); 38.0, 37.8, 35.8, 35.6 (CH_2); 26.22, 26.19 (CH_2). MS: 264 (12), 262 (10, M^+), 229 (12), 227 (11), 211 (16), 209 (11), 183 (40), 165 (100), 129 (94), 103 (41), 91 (52), 77 (49), 65 (22), 51 (50). HR-MS: 261.97417 ($C_{10}H_{12}O^{79}Br^{35}Cl^+$; calc., 261.97603).

N-*(1a-Bromo-6a-chloro-1a,2,4,5,6,6a-hexahydro-1*H,*3*H-*cycloprop[f]inden-4-yl)formamide* (**27c**). To 300 mg of diacid (prepared from **23b** as above; 0.89 mmol) in anh. benzene containing pyridine (170 mg) was added oxalyl chloride (0.80 g, 6.3 mmol). The mixture was heated to reflux for 5 h. After removal of the solvent, and of the unreacted oxalyl chloride and pyridine, the residue was redissolved in dry MeCN (30 ml), and NaN_3 (2.5 g, 38.5 mmol) was added. The suspension was stirred at 25° overnight. The mixture was then quickly filtered and

concentrated at 25° under reduced pressure to afford a gummy residue of acyl azide, which was redissolved in THF (1.0 ml). After addition of cyclohexane (30 ml), the mixture was heated to reflux for 2 h, then concentrated and redissolved in THF (30 ml), Hydrolysis was carried out with 3.0 ml of 50% aq. AcOH during 5 h at 25°. After evaporation of the volatiles under reduced pressure, the residue was dissolved in EtOH (20 ml), and $NaBH_4$ (0.5 g, 13 mmol) was added. The mixture was heated to 50° during 2 h, standard workup, followed by column chromatography, afforded **27c** (150 mg, 45%) as an amorphous solid. IR ($CHCl_3$): 3427*s* (br.), 2975*s*, 2895*s*, 1682*s*, 1492*s*, 1390*s*, 1086*s*, 1046*m*. ^{1}H-NMR (200 MHz, $CDCl_3$): 8.01 (*s*, 1 H); 6.33 (*s*, 1 H); 4.60–4.40 (*m*, 1 H); 2.95–2.50 (*m*, 6 H); 2.20–1.95 (*m*, 2 H); 1.50–1.35 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 160.72, 160.67 (C); 129.8, 129.6 (C); 46.6, 46.55 (CH); 46.23, 46.20 (C); 42.7, 42.65, 42.55, 4.25 (CH_2); 38.35, 38.30 (C); 37.7, 37.6, 35.5, 35.3 (CH_2); 26.2, 26.1 (CH_2). MS: 292 (2), 290 (4, M^+), 246 (22), 244 (17), 211 (9), 167 (17), 165 (51), 129 (100), 115 (19), 103 (11), 91 (12), 77 (20), 65 (10), 51 (23). HR-MS: 292.98238 ($C_{11}H_{13}ON^{81}Br^{37}Cl^+$; calc., 292.9815).

*4,5-Dihydro-1*H*,3*H*-cycloprop[*f*]inden-4-ol* (**28b**). To **27b** (150 mg, 0.57 mmol) in THF (3.0 ml) was added *t*-BuOK (2.0 ml, 1M in THF) at −78°. The mixture was stirred under N_2 at −78° for 3 h. After evaporation under reduced pressure, the residue was extracted with Et_2O. The combined extracts were washed (H_2O) and dried ($MgSO_4$). Evaporation of the solvent provided **28b** (60 mg, 72%) as amorphous solid. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.11 (*s*, 2 H); 4.80–4.60 (*m*, 1 H); 3.35–3.10 (*m*, 4 H); 2.96–2.80 (*m*, 2 H). ^{13}C-NMR ($CDCl_3$): 141.7 (C); 125.3 (C); 112.6 (CH); 73.1 (CH); 42.1 (CH_2); 22.4 (CH_2). MS: 146 (75, M^+), 117 (100), 103 (20), 91 (60), 77 (25), 63 (40), 51 (55). HR-MS: 146.07202 ($C_{10}H_{10}O^+$; calc., 146.07317).

*N-(4,5-Dihydro-1*H*,3*H*-cycloprop[*f*]inden-4-yl)formamide* (**28c**). To **27c** (150 mg, 0.50 mmol) in THF (3.0 ml) was added, at −78° *t*-BuOK (2.0 ml, 1M in THF), and the mixture was stirred for 3 h under N_2. After evaporation at 25° under reduced pressure, the residue was extracted with Et_2O. Workup afforded **28c** (50 mg, 56%) as amorphous solid. IR ($CHCl_3$): 3387*s* (br.), 2983*s*, 1681*s*, 1505*m*, 1385*s*, 1227*m*, 1042*s*. ^{1}H-NMR (200 MHz, $CDCl_3$): 7.99 (*s*, 1 H); 7.05 (*s*, 2 H); 6.60 (*s*, 1 H); 4.80–4.65 (*s*, 1 H); 3.26 (*s*, 2 H); 2.99 (*AB* of *AA'BB'X*, *J* = 16, 5, 3 H). ^{13}C-NMR ($CDCl_3$): 161.1 (C); 141.6 (C); 125.5 (C); 112.4 (CH); 49.4 (CH); 39.3 (CH_2); 22.5 (CH_2). MS: 173 (1.5, M^+), 128 (100), 115 (8), 102 (11), 91 (6), 77 (8), 63 (8), 51 (14). HR-MS: 272.07622 ($C_{11}H_{10}ON^+$ ([M − 1]$^+$); calc., 272.07624).

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