Synthesis and Properties of Kinetically Stabilized Cyclohepta[*def*]fluorene Derivatives

Udo Grieser and Klaus Hafner*

Institut für Organische Chemie der Technischen Hochschule Darmstadt,
Petersenstraße 22, D-64287 Darmstadt, Germany

Received June 22, 1994

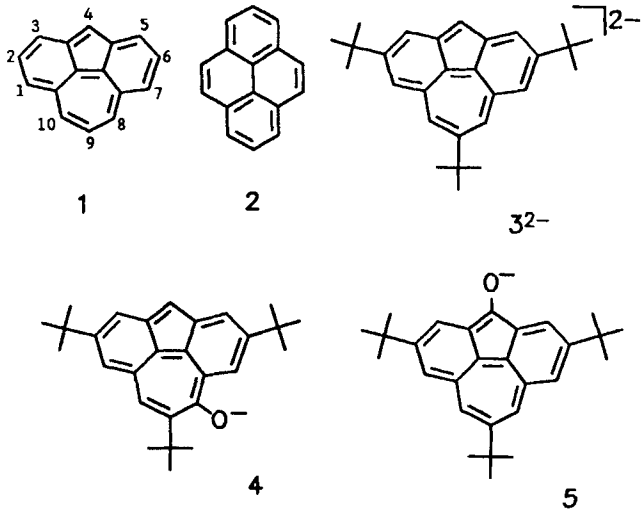
Key Words: Cyclohepta[*def*]fluorene / Non-alternant pyrene isomers / Polycyclic hydrocarbon dianions

The dihydrocyclohepta[*def*]fluorene **18** was prepared by starting from 2,7-di-*tert*-butylfluorene (**11**). Deprotonation of **18** furnished the dianion 3^{2-} in which the charge is mainly localized at the five- and seven-membered rings as evidenced by NMR investigations. Attempts to oxidize 3^{2-} to the uncharged species **3** failed. The ketones **26** and **29** were obtained by regioselective oxidation of **18**. Deprotonation of **29** and **26** furnished the anions **4** and **5**, respectively, which could be described as cyclohepta[*def*]fluorenes with a strong donor substituent. ^{13}C-NMR spectroscopic investigations, however, revealed that **4** is described best as an acyl-substituted fluorenyl anion. In contrast to this, proof of the existence of the anion **5** could be obtained only from a trapping experiment.

The polycyclic hydrocarbon cyclohepta[*def*]fluorene (**1**), a non-alternant isomer of pyrene (**2**), has been the focus of interest over the last thirty years. In contrast to **2** and six of its seven non-alternant isomers, for which Kékulé structures with cyclic conjugated benzene units (Clar sextets) exist, only two Kékulé structures are possible for **1**, both with a 14-π perimeter and a central double bond and without cyclic conjugated benzene units. Besides a few unsuccessful attempts[1] to synthesize the tetracyclic 16-π electron system **1**, several theoretical investigations of **1** have been published[2]. These predict a low-lying triplet state[2a,g], which actually could be the ground state of the molecule, and a singlet state with a large amount of charge separation[2a,c]. The resonance energy should be slightly positive[2h,i]. Heilbronner et al.[2a] suggest that the replacement of ring carbon atoms of **1** by hetero atoms or substitution of the tetracycle itself should severely influence the relative energies of the triplet state and the singlet state. According to this prediction, donor substituents in position 4 or acceptor substituents in position 8 or 10 should favor the triplet state energetically while acceptor substituents in position 4 or donor substituents in position 8 or 10 should disfavor the triplet state, which is equivalent to stabilization of the singlet state.

In this paper we report on the synthesis and properties of the 2,6,9-tri-*tert*-butylcyclohepta[*def*]fluorene dianion (3^{2-}), besides cyclohepta[*def*]fluorene-4,8-dione[3] the first derivative of **1**, which contains exclusively sp^2-hybridized carbon atoms in the tetracyclic ring system. As results of theoretical investigations[2] led to the assumption that cyclohepta[*def*]fluorene (**1**) itself should be rather unstable, we decided to synthesize cyclohepta[*def*]fluorenes which are kinetically stabilized by bulky *tert*-butyl groups. Furthermore, we were interested to prove the predicted influence of substituents on the cyclohepta[*def*]fluorene system. The anions **4** (expected to be a ground-state singlet) and **5** (expected to be a ground-state triplet), both cyclohepta[*def*]fluorenes with a strong donor substituent, appeared particularly suitable for this purpose.

Scheme 1

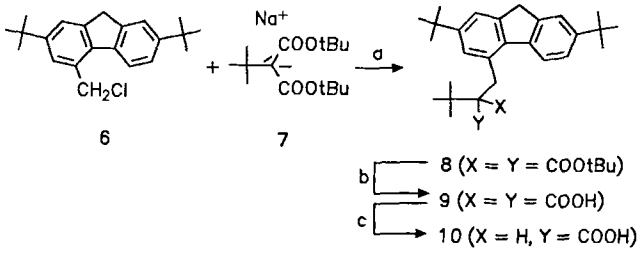


For the synthesis of 2,6,9-tri-*tert*-butyl-4,8-dihydrocyclohepta[*def*]fluorene (**18**), 2,7-di-*tert*-butyl-4-(chloromethyl)-fluorene[4] (**6**) was treated with the sodium salt of di-*tert*-butyl *tert*-butylmalonate (**7**) in refluxing toluene to yield the disubstituted malonate **8**, which was converted to acid **10**[5] by treatment with *p*-toluenesulfonic acid and decarboxylation.

Since the overall yield of this sequence was only moderate (24%), an alternative route to acid **10** was elaborated. Formylation of 2,7-di-*tert*-butylfluorene[4] (**11**) according to the method of Rieche et al.[6] resulted in the formation of aldehyde **12**, which was converted into the hydroxy ester **14**

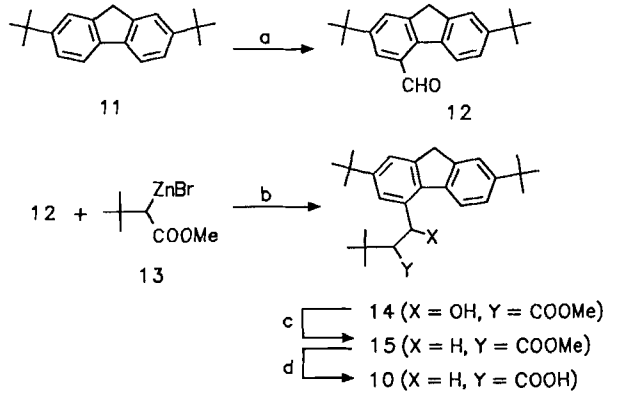
  0009–2940/94/1111–2307 $ 10.00+.25/0

Scheme 2. a: Toluene, 110°C, 1 h (48%). – b: *p*-Toluenesulfonic acid/benzene, 80°C, 4 h (53%). – c: 230°C, 20 min (95%)



(mixture of diastereomers) by reaction with the Reformatsky reagent **13** prepared from methyl 2-bromo-3,3-dimethylbutanoate. After removal of the hydroxyl group with triethylsilane/trifluoroacetic acid[7] and acid hydrolysis, the fluorenepropanoic acid **10** was obtained in an overall yield of 45%.

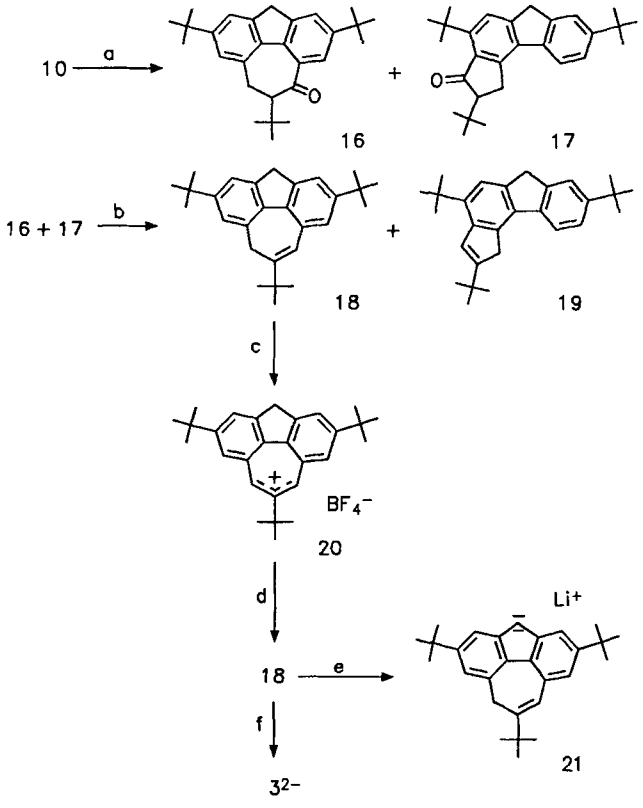
Scheme 3. a: $MeOCHCl_2/SnCl_4/CH_2Cl_2$, 1 h (70%). – b: Benzene/Et_2O (9:1), 80°C, 1 h (82%). – c: $Et_3SiH/CF_3COOH/CH_2Cl_2$, 24 h (88%). – d: HBr/AcOH/H_2O, 110°C, 3 d (90%)



Cyclization of the acyl chloride of **10** with tin(IV) chloride furnished a 2:3 mixture of the ketones **16** and **17**. Separation of this mixture by chromatography or crystallization proved to be ineffective on a larger than analytical scale. Therefore, the ketones were reduced with $LiAlH_4$ and dehydrated with acidic alumina without previous separation. The obtained mixture of the isomeric hydrocarbons **18** and **19** was treated with one equivalent (based on **18**) of trityl tetrafluoroborate furnishing the red dibenzotropylium salt **20**, which could easily be purified. Reduction of **20** with $NaBH_4$ afforded the desired dihydrocyclohepta[*def*]fluorene **18** in pure form.

For the deprotonation of the dihydrocyclohepta[*def*]fluorene derivative **18** several bases were tested. Treatment with *n*-butyllithium in tetrahydrofuran at room temperture furnished anion **21** or dianion 3^{2-}, depending on the amount of base employed. At −50°C *n*-butyllithium in tetrahydrofuran (even in excess) deprotonated **18** only once as evidenced by deuterium quenching experiments. The deprotonations were rapid and complete within a few minutes. ^1H- and ^{13}C-NMR spectra of the green solution obtained after treatment of **18** with two equivalents of *n*-butyllithium

Scheme 4. a: 1. $PCl_5/CHCl_3$, 2 h; 2. $SnCl_4$, 3 d (93%, **16**:**17** = 2:3). – b: 1. $LiAlH_4/Et_2O$ (97%); 2. Al_2O_3, 240°C, 30 min (93%). – c: $Ph_3C^+BF_4^-$/MeCN (84% based on $Ph_3C^+BF_4^-$). – d: $NaBH_4$/MeCN (95%). – e: *n*BuLi (1 equiv.)/THF, room temp. – f: *n*BuLi (2 equiv.)/THF, room temp.



at room temperature are in accordance with the proposed structure of the 2,6,9-tri-*tert*-butylcyclohepta[*def*]fluorene dianion (3^{2-}). Since the chemical shifts of carbon signals in polycyclic hydrocarbon ions – in contrast to hydrogen chemical shifts – are not significantly influenced by ring current effects, ^{13}C-NMR spectroscopy is suitable for obtaining information about the charge distribution in these compounds[8]. A comparison of the ^{13}C-NMR spectra of 3^{2-} with those of the fluorenyl anion (**22**)[9] and the 1,3-diphenylallyl anion (**23**)[10] reveals only minor differences in the chemical shifts for equivalent carbon atoms, and hence the charge distribution in 3^{2-} should resemble that in **22** and **23**, respectively. Hence, 3^{2-} can be considered as a combination of a fluorenyl anion moiety and an allyl anion moiety, which influence each other only to a small degree, the negative charge being localized mainly in the positions 4 (in the five-membered ring) and 8 as well as 10 (in the seven-membered ring) of the tetracyclic ring system.

The dianions of pyrene (**2**)[8b,11] and of its non-alternant isomers cyclohept[*fg*]acenaphthylene (**24**)[8b,12] and dicyclopenta[*ef*,*kl*]heptalene (**25**)[8b] were prepared by reduction of the parent hydrocarbons with alkali metals, and the ^{13}C-NMR spectra of the dianions were measured. The charge distribution (as concluded from their ^{13}C-NMR spectra) in the dianions 2^{2-}, 24^{2-}, and 25^{2-} is different from that in 3^{2-}. In 2^{2-}, which is strongly paratropic, the negative

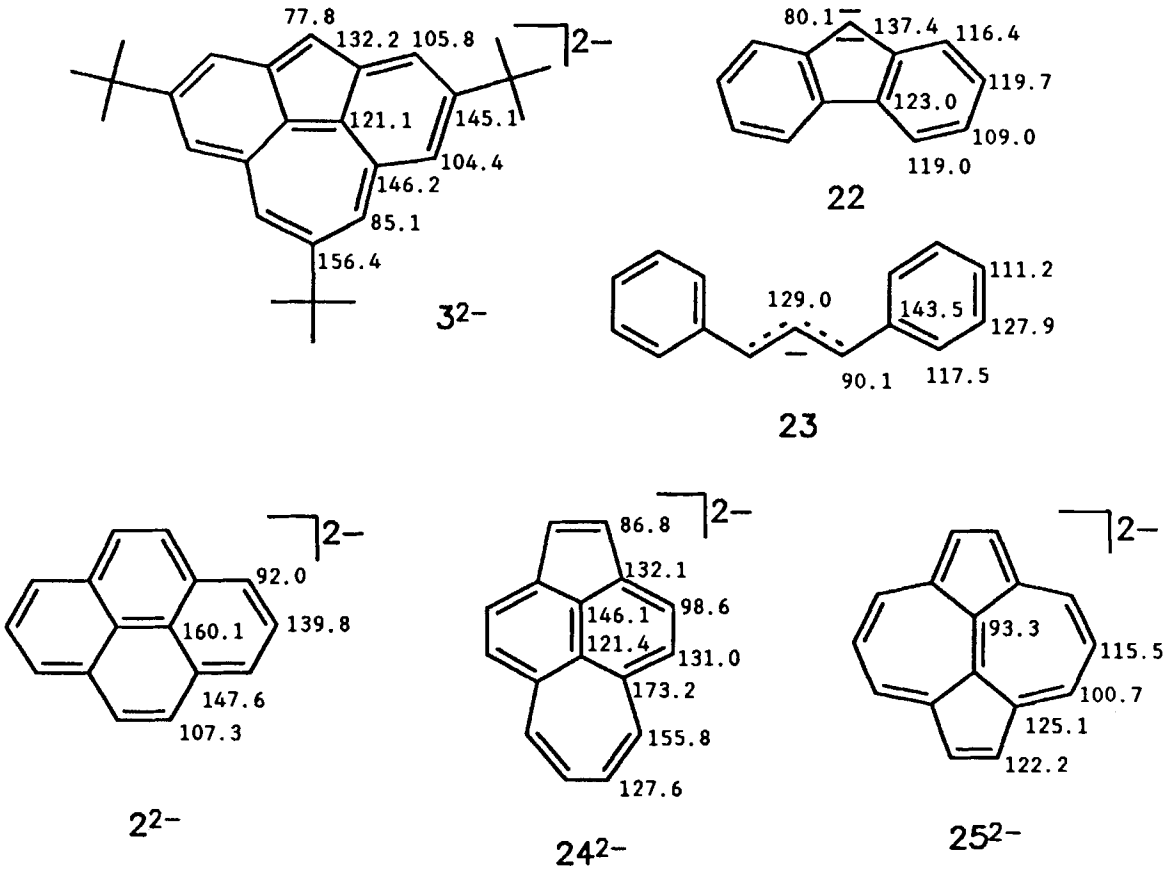


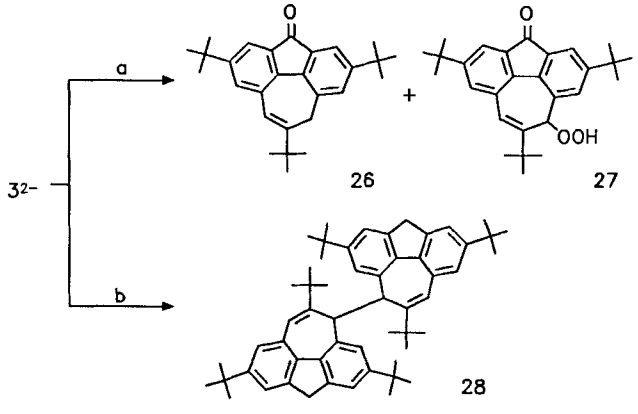
Figure 1. Selected ^{13}C-chemical shifts of 3^{2-}, **22**[9], **23**[10], 2^{2-}[8b,11], 24^{2-}[8b,12] and 25^{2-}[8b]

charge is delocalized mainly in the perimeter, in 24^{2-} it is delocalized only in the acenaphthylene substructure, and in 25^{2-} the negative charge is localized at the central double bond.

All attempts to oxidize the dianion 3^{2-} to the uncharged species **3**, which would be the first known cyclohepta[*def*]-fluorene, failed in our hands. With two exceptions all oxidants tested furnished only polymeric material. With molecular oxygen as oxidant the ketones **26** and **27** were obtained, a reaction type, which has some literature precedence[13]. Oxidation of 3^{2-} with anhydrous cadmium chloride furnished the hydrocarbon **28** (only one diastereomer) besides polymeric material. Compound **28** probably arises from a dimerization of the radical anion $3^{\cdot-}$, formed by one-electron oxidation of 3^{2-}. Attempts to obtain **3** by deprotonation of the cation **20** (the conjugate acid of **3**) were also unsuccessful and furnished only polymeric material, similar to previous attempted syntheses of cyclohepta-[*def*]fluorene (**1**)[1b,c].

For the synthesis of cyclohepta[*def*]fluorenes bearing a substituent in position 8, ketone **29** was required. This could be obtained in 85% yield by oxidation of 2,6,9-tri-*tert*-butyl-4,8-dihydrocyclohepta[*def*]fluorene (**18**) with DDQ in chloroform in the presence of a small amount of water, a procedure, which reportedly can be used to oxidize selectively that benzylic methylene group in hydroaromatic compounds that is capable of forming the most stable

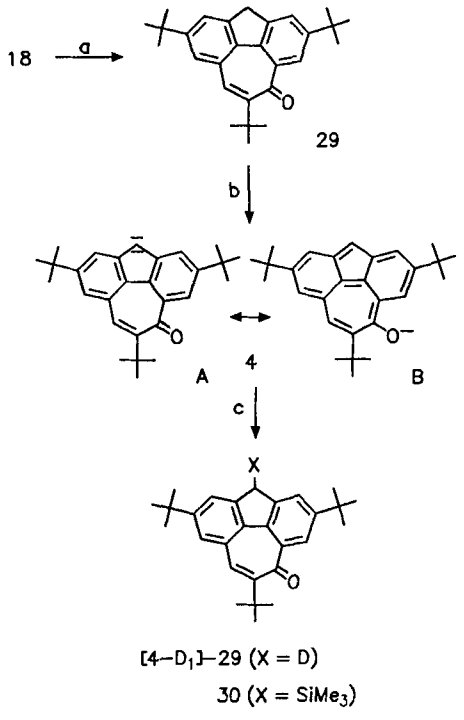
Scheme 5. a: 1. O_2/THF, −80°C; 2. H_2O, −80°C to room temp. (**26**: 26%; **27**: 53%). − b: 1. $CdCl_2$/THF, −90 to −45°C; 2. H_2O (22%)



benzylic carbocation[14]. Deprotonation of **29** with lithium diisopropylamide (LDA) or lithium hexamethyldisilazide (LiHMDS) in tetrahydrofuran furnished a solution of the lithium salt of the desired anion **4**, which is stable for several months in the absence of proton sources and air.

Compound **4** can be formulated as the anion of a cyclohepta[*def*]fluoren-8-olate (formula **B**) or as an acyl-substituted fluorenide (formula **A**). Experimental evidence of the charge distribution in **4**, which, as before, can be obtained

Scheme 6. a: DDQ (3 equiv.)/$CHCl_3/H_2O$, 17 h, (85%). – b: LiHMDS/THF. – c: D_2O or Me_3SiCl



easily by means of ^{13}C-NMR spectroscopy[8], should enable us to decide whether formula **A** or formula **B** is a better description of the bonding system. A comparison of the chemical shifts of the methine carbon signals (which were easily identified by $^1H,^{13}C$-COSY spectra) in **4**, **29**, and **21** reveals only minor differences between the chemical shifts in the fluorenyl moiety (C-1, C-3, C-4, C-5, and C-7) in **4** and **21** and between the chemical shifts for C-8 and C-10 in **4** and **29** (Table 1). Hence, anion **4** is described better by formula **A**, which represents an acyl-substituted fluorenide. This view is further supported by quenching experiments with D_2O and chlorotrimethylsilane, which furnished cleanly the deuterated compound [4-D_1]-**29** and the silylated compound **30**, respectively.

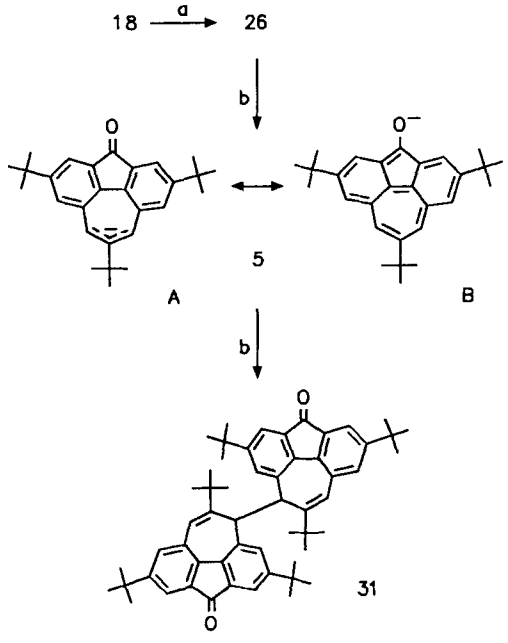
Table 1. Selected ^{13}C-chemical shifts (δ values) of **4**, **21**, and **29**

	C-1	C-3	C-4	C-5	C-7	C-8	C-10
4	109.9	111.9	82.3	112.6	103.3	193.4	138.3
21	111.7	111.4	79.3	110.2	107.1	38.0	126.6
29	126.7	122.4	36.9	125.3	123.7	190.5	135.2

The ^1H- and ^{13}C-NMR spectra of **4** exhibit sharp lines and are therefore in accordance with **4** being a singlet molecule as expected. Obviously, the donor substituent in position 8 of the cyclohepta[*def*]fluorene system, a position which should bear a large amount of positive charge in the singlet state, stabilizes the singlet state by diminishing the positive charge in position 8 and in turn the charge separation in the whole molecule.

For the synthesis of cyclohepta[*def*]fluorenes with a substituent in position 4 ketone **26** was synthesized by a method similar to known procedures for the synthesis of fluorenone[14]. 2,6,9-Tri-*tert*-butyl-4,8-dihydrocyclohepta[*def*]-fluorene (**18**) was deprotonated with *n*-butyllithium at –80°C, and the resulting lithium salt of anion **21** was treated first with oxygen and then with basic alumina to yield ketone **26**.

Scheme 7. a: 1. *n*BuLi/THF, –80°C; 2. O_2, –80°C; 3. Al_2O_3, –80°C to room temp. (84%). – b: 1. KO*t*Bu/THF; 2. O_2 (68%)



When **26** was treated with potassium *tert*-butoxide or potassium hexamethyldisilazide (KHMDS) in tetrahydrofuran, a quick color change from yellow to purple was observed indicating a fast reaction with the base, but after addition of deuterium oxide or chlorotrimethylsilane only polymeric material could be isolated. ^1H-NMR spectra of the purple solution exhibited only very broad signals and did not allow any conclusion about the species in solution. When oxygen was bubbled through this solution, the purple color disappeared, and the solution turned orange again. After workup, the ketone **31** (only one diastereomer) was isolated, the formation of which can be rationalized by oxidation of anion **5** to the corresponding radical and subsequent dimerization. Thus, this result is a hint to the existence of **5**, and the fact that **5** could be intercepted with oxygen (which is a diradical) but in contrast to **4** not with deuterium oxide or chlorotrimethylsilane could indicate its existence as a triplet molecule. However, all attempts to establish this by ESR spectroscopy, which would unambiguously prove the existence of a triplet, were unsuccessful so far.

This work has been generously supported by the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *Degussa AG*, Frankfurt/Main. We thank the *Stiftung Stipendienfonds des Verbandes der Chemischen Industrie* for a Ph. D. fellowship to U.G.

Experimental

NMR: Bruker WM 300, AC 300, ARX 300 (^{1}H: 300 MHz, ^{13}C: 75.5 MHz). ^{1}H- and ^{13}C-NMR spectra were measured with TMS as internal standard at room temp. if not stated otherwise. For the spectra recorded in [D$_8$]THF the signals of the solvent were used as standard (^{1}H: δ = 3.58 and 1.73, ^{13}C: δ = 67.4 and 25.2). – MS: Finnigan MAT 311-A/100 MS. – IR: Beckman IR 5A. – UV: Beckman DK-2A, UV 5240. – Elemental analyses: Perkin-Elmer CHN 240 B. – All experiments with moisture- or air-sensitive compounds were performed in anhydrous solvents under nitrogen in flame-dried glass ware. Solvents were dried and distilled according to standard procedures. – Column chromatography: basic alumina [activity B II–III (Brockmann) ICN Biomedicals] and silica gel [70–230 mesh (ASTM) Macherey-Nagel]. – Melting points: Kofler apparatus (Reichert, Vienna, Austria).

1) *Di-tert-butyl tert-Butylmalonate:* A pressure bottle was cooled with a salt/ice bath and filled with 32.1 g (118 mmol) of *tert*-butylmalonic acid, 25 ml of diethyl ether, 1 ml of concd. sulfuric acid, and 35 ml (0.41 mol) of liquid isobutene. The bottle was stoppered, and the content was stirred for 6 h at room temp. and then cooled again. The bottle was opened and the reaction mixture hydrolyzed with a mixture of ice (60 g), water (60 ml), and sodium hydroxide (18 g). The organic layer was separated and the aqueous layer extracted twice with diethyl ether (50 ml). The combined organic layers were dried with potassium carbonate and the solvent removed by distillation. The residue was purified by distillation in vacuo affording 19.9 g (73.2 mmol, 62%) of di-*tert*-butyl *tert*-butylmalonate as a colorless liquid, b.p. 88°C/1 Torr. – MS (70 eV), *m/z* (%): 216 (5) [M$^+$ – C$_4$H$_8$], 199 (5) [M$^+$ – OC$_4$H$_9$], 160 (33) [M$^+$ – 2 C$_4$H$_8$], 57 (100) [C$_4$H$_9^+$]. – IR (CHCl$_3$): $\tilde{\nu}$ = 2915 cm^{-1} (C–H), 1705 (C=O). – ^{1}H NMR (CDCl$_3$): δ = 3.01 (s, 1H, α-H), 1.47 (s, 18H, O–*t*Bu), 1.28 (s, 9H, C–*t*Bu). – C$_{15}$H$_{28}$O$_4$ (272.4): calcd. C 66.14, H 10.36; found C 66.37, H 10.57.

2) *Di-tert-butyl tert-Butyl[(2,7-di-tert-butylfluoren-4-yl)methyl]-malonate* (**8**): 31.8 g (117 mmol) of di-*tert*-butyl *tert*-butylmalonate was added to a suspension of 2.95 g (123 mmol) of sodium hydride in 70 ml of toluene, and the suspension was refluxed for 30 min. Then a solution of 38.2 g (117 mmol) of 2,7-di-*tert*-butyl-4-(chloromethyl)fluorene (**6**) in 70 ml of toluene was added over 45 min and refluxing continued for 1 h. The mixture was hydrolyzed with 140 ml of water and extracted three times with diethyl ether (50 ml). The combined organic layers were dried with magnesium sulfate, and the solvent was evaporated. The residue was purified by chromatography (*n*-hexane/diethyl ether, 20:1) on alumina to yield 31.3 g (55.8 mmol, 48%) of **8** as colorless crystals, m.p. 164°C (*n*-hexane). – UV (*n*-hexane): λ_{max} (lg ε) = 227 nm (4.28) sh, 233 (4.06) sh, 265 (4.35), 271 (4.38) sh, 275 (4.44), 281 (4.30) sh, 287 (4.28), 294 (4.00), 306 (3.90). – MS (70 eV), *m/z* (%): 562 (8) [M$^+$], 506 (5) [M$^+$ – C$_4$H$_8$], 450 (28) [M$^+$ – 2 C$_4$H$_8$], 291 (36), 57 (39) [C$_4$H$_9^+$]. – IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1} (C–H), 1705 (C=O), 1465, 1450. – ^{1}H NMR (CDCl$_3$): δ = 7.90 (d, *J* = 8.4 Hz, 1H, 5-H), 7.53 (d, *J* = 1.3 Hz, 1H, Ar-H), 7.39–7.36 (m, 3H, Ar-H), 3.83 (s, 2H, 9-H), 3.77 (s, 2H, ArC*H*$_2$), 1.37 (s, 9H, *t*Bu), 1.33 (s, 9H, *t*Bu), 1.31 (s, 9H, *t*Bu), 1.21 (s, 18H, O–*t*Bu). – C$_{37}$H$_{54}$O$_4$ (562.8): calcd. C 78.96, H 9.67; found C 79.19, H 9.64.

3) *tert-Butyl[(2,7-di-tert-butylfluoren-4-yl)methyl]malonic Acid* (**9**): A solution of 3.45 g (6.14 mmol) of ester **8** and 0.10 g (0.53 mmol) of *p*-toluenesulfonic acid in 20 ml of benzene was refluxed for 1 h. The resulting precipitate was filtered by suction and recrystallized from benzene to yield 1.46 g (3.25 mmol, 53%) of **9** as colorless crystals, m.p. 190°C (dec.). – UV (methanol): λ_{max} (lg ε) = 218 nm (4.47), 255 (4.16) sh, 265 (4.38), 270 (4.41) sh, 274 (4.47), 280 (4.34) sh, 285 (4.31), 290 (4.25), 301 (3.93). – MS (70 eV), *m/z* (%): 450 (63) [M$^+$], 435 (10) [M$^+$ – CH$_3$], 406 (19) [M$^+$ – CO$_2$], 391 (24) [M$^+$ – CH$_3$ – CO$_2$], 291 (47), 57 (100) [C$_4$H$_9^+$]. – IR (KBr): $\tilde{\nu}$ = 3060 cm^{-1} (OH, br.), 2930 (C–H), 1730 (C=O), 1630, 1410. – ^{1}H NMR (CDCl$_3$): δ = 7.79 (d, *J* = 8.3 Hz, 1H, 5-H), 7.56 (d, *J* = 1.7 Hz, 1H, 8-H), 7.43 (dd, *J* = 1.7, 8.3 Hz, 1H, 6-H), 7.35 (s, 1H, 1-H or 3-H), 6.86 (s, 1H, 1-H or 3-H), 3.89 (s, 2H, 9-H or ArC*H*$_2$), 3.84 (s, 2H, 9-H or ArC*H*$_2$), 1.38 (s, 9H, *t*Bu), 1.26 (s, 9H, *t*Bu), 1.25 (s, 9H, *t*Bu). – C$_{29}$H$_{38}$O$_4$ (450.6): calcd. C 77.30, H 8.50; found C 77.54, H 8.52.

4) *Decarboxylation of Malonic Acid* **9**: 2.21 g (4.91 mmol) of **9** was heated to 230°C for 25 min. After recrystallization of the crude product from *n*-hexane 1.90 g (4.68 mmol, 95%) of *2-tert-butyl-3-(2,7-di-tert-butylfluoren-4-yl)propanoic acid* (**10**) was obtained as colorless crystals, m.p. 246°C. – UV (methanol): λ_{max} (lg ε) = 218 nm (4.51) sh, 224 (4.33) sh, 232 (4.04) sh, 254 (4.12) sh, 264 (4.36), 273 (4.45), 285 (4.28), 291 (4.12), 303 (3.98). – MS (70 eV), *m/z* (%): 406 (60) [M$^+$], 391 (43) [M$^+$ – CH$_3$], 291 (20), 57 (100) [C$_4$H$_9^+$]. – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1} (C–H and OH), 1690 (C=O), 1450. – ^{1}H NMR (CDCl$_3$): δ = 7.77 (d, *J* = 8.3 Hz, 1H, 5'-H), 7.56 (d, *J* = 1.2 Hz, 1H, Ar-H), 7.39–7.36 (m, 2H, Ar-H), 7.18 (d, *J* = 1.4 Hz, 1H, Ar-H), 3.84 (s, 2H, 9'-H), 3.43 (dd, *J* = 13.8, 3.2 Hz, 1H, 3-H), 3.16 (dd, *J* = 12.3, 13.8 Hz, 1H, 3-H), 2.78 (dd, *J* = 12.3, 3.2 Hz, 1H, 2-H), 1.38 (s, 9H, *t*Bu), 1.27 (s, 9H, *t*Bu), 1.16 (s, 9H, *t*Bu). – C$_{28}$H$_{38}$O$_2$ (406.6): calcd. C 82.71, H 9.42; found C 82.90, H 9.46.

5) *2,7-Di-tert-butylfluorene-4-carbaldehyde* (**12**): A solution of 27.8 g (100 mmol) of 2,7-di-*tert*-butylfluorene (**11**) in 70 ml of dichloromethane was cooled to 0°C. Then 52.2 g (200 mmol) of tin(IV) chloride and 11.7 g (100 mmol) of dichloromethyl methyl ether were added slowly. After stirring for 1 h at room temp. the mixture was hydrolyzed with 200 g of ice; subsequently 100 ml of dichloromethane was added. The organic layer was separated, washed successively twice with water (100 ml), twice with a saturated solution of sodium hydrogen carbonate (100 ml), and with water (100 ml), dried with magnesium sulfate and concentrated. The residue was recrystallized from *n*-hexane to yield 21.4 g (70 mmol, 70%) of aldehyde **12** as colorless needles, m.p. 175°C. – UV (*n*-hexane): λ_{max} (lg ε) = 244 nm (4.35), 251 (4.37), 277 (4.16), 282 (4.11) sh, 285 (4.08) sh, 340 (4.08), 352 (4.06). – MS (70 eV), *m/z* (%): 306 (42) [M$^+$], 291 (100) [M$^+$ – CH$_3$], 57 (32) [C$_4$H$_9^+$]. – IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1} (C–H), 1665 (C=O), 1600, 1450, 1390. – ^{1}H NMR (CDCl$_3$): δ = 10.68 (s, 1H, CHO), 8.40 (d, *J* = 8.3 Hz, 1H, 5-H), 7.90 (d, *J* = 1.5 Hz, 1H, 8-H), 7.77 (d, *J* = 1.1 Hz, 1H, 1-H or 3-H), 7.60 (d, *J* = 1.1 Hz, 1H, 1-H or 3-H), 7.45 (dd, *J* = 8.3, 1.5 Hz, 1H, 6-H), 3.92 (s, 2H, 9-H), 1.41 (s, 9H, *t*Bu), 1.39 (s, 9H, *t*Bu). – C$_{22}$H$_{26}$O (306.5): calcd. C 86.23, H 8.55; found C 86.27, H 8.51.

6) *Methyl 2-tert-Butyl-3-(2,7-di-tert-butylfluoren-4-yl)-3-hydroxypropanoate* (**14**): A suspension of 8.24 g (126 mmol) of zinc turnings in 25 ml of benzene/diethyl ether (9:1) was heated to reflux and a solution of 20.2 g (96.8 mmol) of methyl 2-bromo-3,3-dimethylbutanoate in 25 ml of the same solvent was added. Heating was continued for 30 min, then a suspension of 14.8 g (48.4 mmol) of aldehyde **12** in 150 ml of the same solvent was added over 45 min, and heating was continued for 1 h. The mixture was cooled to 0°C, hydrolyzed with 100 ml of 2 N HCl and extracted three times with 50 ml of diethyl ether each. The combined organic layers were dried with magnesium sulfate, and the solvent was evaporated. Chromatography of the residue on alumina with *n*-hexane/diethyl ether (19:1) yielded two fractions.

1. Fraction: 4.22 g (9.68 mmol, 20%) of *methyl 2-tert-butyl-3-(2,7-di-tert-butylfluoren-4-yl)-3-hydroxypropanoate* (**14**) (first dia-

stereomer), colorless crystals, m.p. 158–160°C (*n*-hexane). – UV (methanol): λ_{max} (lg ε) = 264 nm (4.34) sh, 269 (4.37) sh, 273 (4.39), 284 (4.23) sh, 295 (4.10), 306 (4.15), 337 (1.85). – MS (70 eV), *m/z* (%): 436 (8) [M^+], 307 (10), 291 (13), 251 (41), 57 (100) [$C_4H_9^+$]. – IR (KBr): $\tilde{\nu}$ = 3485 cm^{-1} (OH), 2900 (C–H), 1705 (C=O). – ^1H NMR ($CDCl_3$, 323 K): δ = 8.15 (d, *J* = 8.3 Hz, 1H, 5′-H), 7.54 (d, *J* = 1.2 Hz, 1H, Ar-H), 7.44–7.39 (m, 3H, Ar-H), 5.71 (dd, *J* = 3.6, 10.1 Hz, 1H, 3-H), 3.84 (s, 2H, 9′-H), 3.22 (s, 3H, OMe), 3.18 (d, *J* = 10.1 Hz, 1H, 2-H), 1.90 (d, *J* = 3.6 Hz, 1H, OH), 1.38 (s, 9H, *t*Bu), 1.35 (s, 9H, *t*Bu), 1.25 (s, 9H, *t*Bu). On addition of deuterium oxide the signal at δ = 1.90 disappeared; the signal at δ = 5.71 became a doublet (*J* = 10.1 Hz). – $C_{29}H_{40}O_3$ (436.6): calcd. C 79.77, H 9.23; found C 79.53, H 9.31.

2. Fraction: 13.1 g (30.0 mmol, 62%) of **14** (second diastereomer), colorless crystals, m.p. 120°C (ethanol). – UV (methanol): λ_{max} (lg ε) = 265 nm (4.34) sh, 269 (4.37) sh, 273 (4.39), 285 (4.20) sh, 295 (4.03), 306 (4.05). – MS (70 eV), *m/z* (%): 436 (19) [M^+], 308 (18), 291 (23), 251 (100), 57 (94) [$C_4H_9^+$]. – IR (KBr): $\tilde{\nu}$ = 3410 cm^{-1} (OH), 2905 (C–H), 1700 (C=O). – ^1H NMR ($CDCl_3$): δ = 7.85 (d, *J* = 8.3 Hz, 1H, 5′-H), 7.58 (s, 1H, Ar-H), 7.44 (s, 1H, Ar-H), 7.42–7.39 (m, 2H, Ar-H), 5.89 (dd, *J* = 4.0, 8.7 Hz, 1H, 3-H), 3.95 (d, *J* = 8.7 Hz, 1H, OH), 3.86 (s, 2H, 9′-H), 3.50 (s, 3H, OMe), 2.88 (d, *J* = 4.0 Hz, 1H, 2-H), 1.39 (s, 9H, *t*Bu), 1.36 (s, 9H, *t*Bu), 1.17 (s, 9H, *t*Bu). On addition of deuterium oxide the signal at δ = 3.95 disappeared; the signal at δ = 5.89 became a doublet (*J* = 4.0 Hz). – $C_{29}H_{40}O_3$ (436.6): calcd. C 79.77, H 9.23; found C 79.56, H 9.21.

7) *Reduction of Hydroxy Ester* **14**: A solution of 1.16 g (2.66 mmol) of **14** (first diastereomer), 0.37 g (3.14 mmol) of triethylsilane, and 0.98 g (8.64 mmol) of trifluoroacetic acid in 5 ml of dichloromethane was stirred at room temp. After 24 h the solution was neutralized with solid sodium carbonate, filtered, and the filtrate was concentrated. After recrystallization from ethanol the residue furnished 0.99 g (2.35 mmol, 88%) of *methyl 2-tert-butyl-3-(2,7-di-tert-butylfluoren-4-yl)propanoate* (**15**) as colorless crystals, m.p. 128°C (ethanol). An analogous reduction of the second diastereomer of **14** afforded the same yield. – UV (*n*-hexane): λ_{max} (lg ε) = 218 nm (4.46) sh, 224 (4.34) sh, 231 (4.07) sh, 254 (4.11) sh, 264 (4.35), 270 (4.39) sh, 274 (4.45), 280 (4.29) sh, 286 (4.28), 292 (4.11), 304 (4.00). – MS (70 eV), *m/z* (%): 420 (39) [M^+], 405 (22) [$M^+ - CH_3$], 283 (40), 57 (100) [$C_4H_9^+$]. – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (C–H), 1725 (C=O), 1455. – ^1H NMR ($CDCl_3$): δ = 7.80 (d, *J* = 8.2 Hz, 1H, 5′-H), 7.57 (d, *J* = 1.3 Hz, 1H, Ar-H), 7.41–7.37 (m, 2H, Ar-H), 7.13 (d, *J* = 1.5 Hz, 1H, Ar-H), 3.85 (s, 2H, 9′-H), 3.45 (dd, *J* = 13.5, 3.3 Hz, 1H, 3-H), 3.39 (s, 3H, OMe), 3.18 (dd, *J* = 13.5, 12.7 Hz, 1H, 3-H), 2.80 (dd, *J* = 3.3, 12.7 Hz, 1H, 2-H), 1.38 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu), 1.17 (s, 9H, 2-*t*Bu). – $C_{29}H_{40}O_2$ (420.6): calcd. C 82.81, H 9.59; found C 83.01, H 9.74.

8) *Hydrolysis of Ester* **15**: A solution of 17.0 g (40.5 mmol) of **15** in 150 ml of a mixture of 48% hydrobromic acid and a 33% solution of hydrogen bromide in acetic acid (1:1) was refluxed for 3 d. Then the solution was evaporated to dryness and the residue recrystallized from *n*-hexane to yield 14.8 g (36.5 mmol, 90%) of acid **10**, identical in all respects with that obtained from experiment 4).

9) *Cyclization of Acid* **10**: 8.69 g (41.8 mmol) of phosphorus pentachloride was added to a solution of 7.07 g (17.4 mmol) of **10** in 80 ml of chloroform, and the mixture was stirred for 2 h. The solution of the obtained acyl chloride was diluted with 140 ml of chloroform and added to a solution of 43.1 g (165 mmol) of tin(IV) chloride in 80 ml of chloroform over a period of 1 h. The resulting mixture was stirred for 3 d and hydrolyzed with 200 ml of 2 N HCl. The organic layer was separated, washed four times with 0.1 N HCl (80 ml) and twice with water (80 ml), then dried with magnesium sulfate. The solvent was evaporated, the residue dissolved in *n*-hexane and the solution filtered through a short column of alumina. Evaporation of the solvent furnished 6.28 g (16.2 mmol, 93%) of a mixture (3:2 as concluded from its ^1H-NMR spectrum) of cyclopenta[*c*]fluorene derivative **17** and cyclohepta[*def*]fluorene derivative **16**, which could not be separated on a preparative scale. For the following experiments this mixture was used without separation. Analytically pure samples of both ketones **16** and **17** could be obtained by fractional crystallization from ethanol.

2,4,8-Tri-tert-butyl-1,6-dihydrocyclopenta[c]fluoren-3(2H)-one (**17**): Colorless crystals, m.p. 143–144°C. – UV (*n*-hexane): λ_{max} (lg ε) = 216 nm (4.40), 239 (4.34) sh, 248 (4.64), 253 (4.62) sh, 256 (4.80), 268 (4.23), 273 (4.26), 285 (4.30), 289 (4.23) sh, 296 (4.23), 320 (3.41), 331 (3.38). – MS (70 eV), *m/z* (%): 388 (100) [M^+], 373 (53) [$M^+ - CH_3$], 345 (30), 332 (50), 317 (33), 57 (69) [$C_4H_9^+$]. – IR (KBr): $\tilde{\nu}$ = 2890 cm^{-1} (C–H), 1690 (C=O), 1445. – ^1H NMR ($CDCl_3$): δ = 7.77 (d, *J* = 8.1 Hz, 1H, 10-H), 7.62 (d, *J* = 1.6 Hz, 1H, 7-H), 7.54 (s, 1H, 5-H), 7.47 (dd, *J* = 8.1, 1.6 Hz, 1H, 9-H), 3.92 (s, 2H, 6-H), 3.42 (dd, *J* = 17.4, 8.1 Hz, 1H, 1-H), 3.22 (dd, *J* = 17.4, 3.5 Hz, 1H, 1-H), 2.52 (dd, *J* = 8.1, 3.5 Hz, 1H, 2-H), 1.52 (s, 9H, *t*Bu), 1.40 (s, 9H, *t*Bu), 1.05 (s, 9H, *t*Bu). – $C_{28}H_{36}O$ (388.6): calcd. C 86.54, H 9.34; found C 86.67, H 9.47.

2,6,9-Tri-tert-butyl-9,10-dihydrocyclohepta[def]fluoren-8(4H)one (**16**): Colorless crystals, m.p. 155–156°C. – UV (*n*-hexane): λ_{max} (lg ε) = 218 nm (4.47), 236 (4.21) sh, 245 (4.39), 252 (4.39), 276 (4.18), 285 (4.18), 297 (3.56), 335 (3.98). – MS (70 eV), *m/z* (%): 388 (100) [M^+], 373 (82) [$M^+ - CH_3$], 332 (25), 57 (57) [$C_4H_9^+$]. – IR (KBr): $\tilde{\nu}$ = 2925 cm^{-1} (C–H), 1670 (C=O), 1590, 1455. – ^1H NMR ($CDCl_3$): δ = 7.81 (d, *J* = 1.8 Hz, 1H, 5-H or 7-H), 7.69 (d, *J* = 1.8 Hz, 1H, 5-H or 7-H), 7.46 (s, 1H, 1-H or 3-H), 7.22 (s, 1H, 1-H or 3-H), 3.98 (d, *J* = 21.7 Hz, 1H, 4-H), 3.87 (d, *J* = 21.7 Hz, 1H, 4-H), 3.22–3.05 (m, 3H, 9-H and 10-H), 1.39 (s, 9H, *t*Bu), 1.38 (s, 9H, *t*Bu), 1.14 (s, 9H, *t*Bu). – $C_{28}H_{36}O$ (388.6): calcd. C 86.54, H 9.34; found C 86.17, H 9.54.

10) *2,6,9-Tri-tert-butyl-4H-cyclohepta[def]fluorenium Tetrafluoroborate* (**20**): A solution of 5.44 g (14.0 mmol) of ketones **16** and **17** (3:2 mixture from previous experiment) in 20 ml of diethyl ether was added slowly to a suspension of 147 mg (3.86 mmol) of $LiAlH_4$ in 10 ml of diethyl ether at room temp., and the mixture was heated to reflux for 1 h. After hydrolysis with 20 ml of water, the resulting precipitate of aluminium hydroxide was dissolved with a small amount of concd. hydrochloric acid. The organic layer was separated and the aqueous layer extracted twice with diethyl ether (10 ml). The combined organic layers were dried with magnesium sulfate and evaporated to dryness, furnishing 5.30 g of a mixture of alcohols. The mixture was heated to 240°C for 30 min with 5.00 g of acidic alumina. After cooling to room temp., the obtained solid mass was extracted with diethyl ether and the alumina was filtered off. After evaporation of diethyl ether 4.70 g (12.65 mmol, 90%) of a mixture of crude dihydrocyclohepta[*def*]fluorene **18** and dihydrocyclopenta[*c*]fluorene **19** was obtained. – 0.80 g (2.44 mmol) of trityl tetrafluoroborate was added to a solution of 2.27 g (6.10 mmol) of the mixture of the hydrocarbons **18** and **19** in 50 ml of boiling acetonitrile. The solution immediately turned red on addition of the trityl tetrafluoroborate. Then the acetonitrile was evaporated and the solid residue washed with diethyl ether until the washings were colorless. Tetrafluoroborate **20** (0.94 g, 2.05 mmol, 84%) was obtained as red crystals, m.p. 245°C (dec.). – UV (acetonitrile): λ_{max} (lg ε) = 232 nm (4.20), 252 (4.20), 286 (4.78), 317 (4.64), 328 (4.57), 491 (3.97). – MS (70 eV), *m/z* (%): 371 (100) [M^+], 356 (29) [$M^+ - CH_3$], 328 (31), 315 (52), 57 (39) [$C_4H_9^+$]. – IR (KBr): $\tilde{\nu}$ =

2915 cm^{-1} (C–H), 1600, 1570, 1450, 1400, 1365. – ^1H NMR ($CDCl_3$): δ = 9.88 (s, 2H, 8,10-H), 8.82 (d, *J* = 1.2 Hz, 2H, 3,5-H), 8.67 (d, *J* = 1.2 Hz, 2H, 1,7-H), 4.83 (s, 2H, 4-H), 1.81 (s, 9H, 9-*t*Bu), 1.62 (s, 18H, 2,6-*t*Bu). – $C_{28}H_{35}BF_4$ (458.4): calcd. C 73.37, H 7.70; found C 73.19, H 7.61.

11) *2,6,9-Tri-tert-butyl-4,8-dihydrocyclohepta[def]fluorene* (**18**): 8.1 mg (0.214 mmol) of $NaBH_4$ was added to a solution of 98.0 mg (0.214 mmol) of **20** in 10 ml of acetonitrile. The resulting colorless mixture was neutralized with 2 N HCl and extracted three times with 5 ml of *n*-hexane each. The combined *n*-hexane layers were dried with magnesium sulfate, concentrated in vacuo, the residue was filtered through a short column of silica gel, and the filtrate evaporated to dryness. Recrystallization of the residue from ethanol afforded 75.6 mg (0.203 mmol, 95%) of **18** as colorless crystals, m.p. 135–136°C. – UV (*n*-hexane): λ_{max} (lg ε) = 224 nm (4.41), 229 (4.41), 246 (4.48) sh, 253 (4.57), 261 (4.67), 300 (4.02), 307 (4.00) sh, 315 (3.95) sh, 331 (3.64) sh. – MS (70 eV), *m/z* (%): 372 (21) [M^+], 371 (5) [M^+ – H], 357 (13) [M^+ – CH_3], 315 (100) [M^+ – C_4H_9], 57 (39) [$C_4H_9^+$]. – IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1} (C–H), 1680, 1590, 1450, 1355. – ^1H NMR ($CDCl_3$): δ = 7.42 (s, 1H, Ar-H), 7.41 (s, 1H, Ar-H), 7.22 (s, 1H, Ar-H), 7.12 (s, 1H, Ar-H), 6.47 (s, 1H, 10-H), 3.87 (s, 2H, 4-H), 3.57 (s, 2H, 8-H), 1.39 (s, 9H, *t*Bu), 1.38 (s, 9H, *t*Bu), 1.28 (s, 9H, *t*Bu). – ^{13}C NMR ($CDCl_3$): δ = 151.17, 149.33, 145.19, 143.25, 142.24, 138.98, 137.00, 132.10, 131.44 (C-2,3a,4a,6,7a,9,10a,10b,10c), 125.03, 122.51, 121.96, 119.57, 119.18 (C-1,3,5,7,10), 38.24 [*C*(CH_3)], 37.01 (C-4 or C-8), 34.91, 34.76 [*C*(CH_3)], 34.58 (C-4 or C-8), 31.76, 31.67, 29.25 [C(*CH*$_3$)]. – $C_{28}H_{36}$ (372.6): calcd. C 90.26, H 9.74; found C 90.22, H 9.75.

12) *Deprotonation of Dihydrocyclohepta[def]fluorene* **18**

a) *Synthesis of Anion* **21**: 0.11 ml (0.16 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane was added to a solution of 53.5 mg (0.14 mmol) of **18** in 2 ml of THF. After removal of the solvent in vacuo the residue was dissolved in 1 ml of [D_8]THF and the solution transferred into a NMR tube. – ^1H NMR ([D_8]THF): δ = 7.22 (d, *J* = 1.4 Hz, 1H, 3-H), 7.13 (d, *J* = 1.5 Hz, 1H, 5-H), 6.56 (s, 1H, 10-H), 6.48 (d, *J* = 1.4 Hz, 1H, 1-H), 6.33 (d, *J* = 1.5 Hz, 1H, 7-H), 5.72 (s, 1H, 4-H), 3.74 (s, 2H, 8-H), 1.40 (s, 9H, 2-*t*Bu or 6-*t*Bu), 1.38 (s, 9H, 2-*t*Bu or 6-*t*Bu), 1.30 (s, 9H, 9-*t*Bu). – ^{13}C NMR ([D_8]THF): δ = 142.99, 141.04, 140.92, 138.29, 137.44, 131.00 (C-2,3a,4a,6,7a,9,10a,10b,10c), 126.61 (C-10), 122.27, 119.90 (C-2,3a,4a,6,7a,9,10a,10b,10c), 111.67 (C-1), 111.40 (C-3), 110.16 (C-5), 107.11 (C-7), 79.31 (C-4), 38.85 [*C*(CH_3)], 37.99 (C-8), 35.47, 35.34 [*C*(CH_3)], 33.15, 32.94 [2,6-C(*CH*$_3$)], 30.28 [9-C(*CH*$_3$)].

b) *Synthesis of Dianion* 3^{2-}: The experiment was carried out as described under a) with 0.23 ml (0.34 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane and 44 mg (0.12 mmol) of **18**. – ^1H NMR ([D_8]THF): δ = 5.48 (d, *J* = 1.3 Hz, 2H, 3,5-H), 4.49 (s, 1H, 4-H), 4.32 (d, *J* = 1.3 Hz, 2H, 1,7-H), 2.41 (s, 2H, 8,10-H), 0.98 (s, 18H, 2,6-*t*Bu), 0.84 (s, 9H, 9-*t*Bu). – ^{13}C NMR ([D_8]THF): δ = 156.43 (C-9), 146.22 (C-7a,10a), 145.06 (C-2,6), 132.19 (C-3a,4a), 121.12 (C-10b,10c), 105.77 (C-3,5), 104.36 (C-1,7), 85.14 (C-8,10), 77.83 (C-4), 36.41 [9-*C*(CH_3)$_3$], 34.18 [2,6-*C*(CH_3)$_3$], 31.75 [2,6-C(*CH*$_3$)$_3$], 31.25 [9-C(*CH*$_3$)$_3$].

13) *Oxidation of the Dianion* 3^{2-}

a) *With Oxygen:* 0.31 ml (0.46 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane was added to a solution of 168 mg (0.451 mmol) of **18** in 20 ml of THF. The mixture was stirred at room temp. for 5 min and cooled to –80°C. Then oxygen was bubbled through the solution until the brown color disappeared (5 min). After addition of 0.5 ml of water the reaction mixture was allowed to warm up to room temp. The solution was dried with magnesium sulfate and concentrated in vacuo. Chromatography of the residue was carried out on alumina with *n*-hexane/diethyl ether (4:1) (first fraction) and diethyl ether (second fraction).

1. Fraction: recrystallization from *n*-hexane furnished 46 mg (0.11 mmol, 26%) of *2,6,9-tri-tert-butylcyclohepta[def]fluoren-4(8H)-one* (**26**) as yellow crystals, m.p. 151°C. – UV (*n*-hexane): λ_{max} (lg ε) = 237 nm (4.65), 247 (4.61), 254 (4.53) sh, 276 (3.97) sh, 286 (4.11), 297 (4.13), 309 (3.99) sh, 320 (3.81) sh, 359 (2.62) sh, 389 (2.73) sh, 413 (2.95) sh, 430 (3.01), 454 (2.85) sh. – MS (70 eV), *m/z* (%): 386 (34) [M^+], 385 (24) [M^+ – H], 371 (22) [M^+ – CH_3], 329 (100) [M^+ – C_4H_9], 57 (31) [$C_4H_9^+$]. – IR (KBr): $\tilde{\nu}$ = 2900 cm^{-1} (C–H), 1705 (C=O), 1590, 1450. – ^1H NMR ($CDCl_3$): δ = 7.56 (d, *J* = 1.7 Hz, 1H, Ar-H), 7.54 (d, *J* = 1.7 Hz, 1H, Ar-H), 7.28 (d, *J* = 1.6 Hz, 1H, Ar-H), 7.21 (d, *J* = 1.5 Hz, 1H, Ar-H), 6.38 (s, 1H, 10-H), 3.51 (s, 2H, 8-H), 1.35 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu), 1.27 (s, 9H, 9-*t*Bu). – $C_{28}H_{34}O$ (386.6): calcd. C 87.00, H 8.87; found C 87.21, H 8.99.

2. Fraction: After recrystallization from *n*-hexane 101 mg (0.241 mmol, 53%) of *2,6,9-tri-tert-butyl-8-hydroperoxycyclohepta[def]fluoren-4(8H)-one* (**27**) was obtained as yellow crystals, m.p. 133–135°C. Due to the instability of this compound a correct elemental analysis could not be obtained. – UV (*n*-hexane, qual.): λ_{max} = 245 nm sh, 249 (max.), 264 sh, 275 sh, 283 sh, 294, 306 sh, 355 sh, 422, 439. – MS (70 eV), *m/z* (%): 418 (2) [M^+], 402 (4) [M^+ – O], 400 (2) [M^+ – H_2O], 385 (63) [M^+ – OOH], 57 (100) [$C_4H_9^+$]. – IR (KBr): $\tilde{\nu}$ = 3270 cm^{-1} (OH), 2915 (C–H), 1700 (C=C), 1600 (C=C), 1450. – ^1H NMR ($CDCl_3$): δ = 8.27 (s, 1H, OOH), 7.71 (d, *J* = 1.6 Hz, 1H, 5-H), 7.58 (d, *J* = 1.6 Hz, 1H, 1-H or 3-H), 7.57 (d, *J* = 1.6 Hz, 1H, 7-H), 7.35 (d, *J* = 1.6 Hz, 1H, 1-H or 3-H), 6.75 (s, 1H, 10-H), 5.75 (s, 1H, 8-H), 1.41 (s, 9H, 6-*t*Bu), 1.35 (s, 9H, *t*Bu), 1.34 (s, 9H, *t*Bu).

b) *With Anhydrous Cadmium Chloride:* A solution of dianion 3^{2-} in 2 ml of THF was prepared as described under a) from 128 mg (0.344 mmol) of **18** and added to a suspension of 160 mg (0.874 mmol) of anhydrous cadmium chloride in 20 ml of THF at –90°C. The mixture was stirred and allowed to warm up to –45°C within 1.5 h. Then 0.5 ml of water was added, and the solution was allowed to warm up to room temp. After drying with magnesium sulfate the solvent was removed in vacuo, and the residue was chromatographed on alumina. Elution with *n*-hexane afforded 28 mg (0.037 mmol, 22%) of *4,4',8,8'-tetrahydro-8,8'-bi(cyclohepta[def]fluorene)* **28** as colorless crystals, m.p. 260°C. Further elution with *n*-hexane/diethyl ether (1:1) furnished only polymeric material. – UV (*n*-hexane): λ_{max} (lg ε) = 228 nm (4.68), 240 (4.71), 258 (4.78) sh, 266 (4.90), 289 (4.23) sh, 308 (4.15) sh, 333 (3.79) sh. – MS (FD 0–5 mA), *m/z*: 371 [M^+/2, only peak]. – IR (KBr): $\tilde{\nu}$ = 2865 cm^{-1} (C–H), 1585, 1445, 1400. – ^1H NMR (C_6D_6, 353 K): δ = 7.48 (s, 2H, Ar-H), 7.46 (s, 2H, Ar-H), 7.08 (d, *J* = 1.3 Hz, 2H, Ar-H), 6.90 (s, 2H, Ar-H), 6.16 (s, 2H, 10-H), 4.27 (s, 2H, 8-H), 3.87 (d, *J* = 21.0 Hz, 2H, 4-H), 3.60 (d, *J* = 21.0 Hz, 2H, 4-H), 1.44 (s, 18H, *t*Bu), 1.30 (s, 18H, *t*Bu), 1.14 (s, 18H, *t*Bu). – $C_{56}H_{70}$ (743.2): calcd. C 90.51, H 9.49; found C 90.63, H 9.53.

14) *2,6,9-Tri-tert-butylcyclohepta[def]fluoren-8(4H)-one* (**29**): A solution of 0.50 g (1.34 mmol) of dihydrocyclohepta[*def*]fluorene **18** and 0.92 g (4.03 mmol) of DDQ in a mixture of 30 ml of chloroform and 1.5 ml of water was stirred for 17 h at room temp. Then the reaction mixture was filtered through a short column of silica gel and the solvent removed from the filtrate in vacuo. Chromatography of the residue on silica gel with *n*-hexane/diethyl ether (9:1) afforded 0.44 g (1.13 mmol, 85%) of ketone **29** as colorless crystals, m.p. 169–170°C (ethanol). – UV (*n*-hexane): λ_{max} (lg ε) = 223 nm (4.33) sh, 231 (4.28) sh, 259 (4.59), 268 (4.61), 280 (4.37) sh, 295 (4.16) sh, 307 (4.15), 312 (4.15), 325 (4.01) sh, 343 (3.63). – MS (70 eV), *m/z* (%): 386 (71) [M^+], 385 (12) [M^+ – H], 371 (100) [M^+ – CH_3], 369 (37) [M^+ – OH], 57 (79) [$C_4H_9^+$]. – IR (KBr): $\tilde{\nu}$ = 2915 cm^{-1} (C–H), 1600 (br., C=O and C=C), 1450. – ^1H NMR ($CDCl_3$): δ = 8.22 (d, *J* = 1.6

Hz, 1H, 7-H), 7.86 (d, J = 1.6 Hz, 1H, 5-H), 7.70 (d, J = 1.3 Hz, 1H, 3-H), 7.63 (s, 1H, 10-H), 7.56 (d, J = 1.3 Hz, 1H, 1-H), 4.09 (s, 2H, 4-H), 1.51 (s, 9H, 9-*t*Bu), 1.45 (s, 9H, *t*Bu), 1.44 (s, 9H, *t*Bu). – ^{13}C NMR ($CDCl_3$): δ = 190.45 (C-8), 151.38, 151.05, 150.40, 143.37, 137.83, 137.65 (C-2,3a,4a,6,7a,9,10a,10b,10c), 135.20 (C-10), 134.49, 130.18 (C-2,3a,4a,6,7a,9,10a,10b,10c), 126.66 (C-1), 125.34 (C-5), 123.66 (C-7), 122.38 (C-3), 38.86 [*C*(CH_3)], 36.93 (C-4), 35.45, 35.19 [*C*(CH_3)], 31.74 [2 and 6-C(*CH*$_3$)], 31.22 [9-C(*CH*$_3$)]. – $C_{28}H_{34}O$ (386.6): calcd. C 87.00, H 8.87; found C 87.26, H 8.77.

15) *Synthesis of Anion* **4**: 0.21 ml (0.31 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane and 50.0 mg (0.31 mmol) of hexamethyldisilazane were stirred for 1 h, then the solvent was removed in vacuo. A solution of 59.9 mg (0.155 mmol) of ketone **29** in 1 ml of [D_8]THF was added to the residue and the resulting black solution transferred into a NMR tube. – ^{1}H NMR ([D_8]THF): δ = 7.99 (s, 1H, 10-H), 7.78 (d, J = 1.4 Hz, 1H, 5-H), 7.77 (d, J = 1.1 Hz, 1H, 3-H), 7.49 (d, J = 1.4 Hz, 1H, 7-H), 7.07 (d, J = 1.1 Hz, 1H, 1-H), 6.38 (s, 1H, 4-H), 1.57 (s, 9H, 9-*t*Bu), 1.51 (s, 9H, 2-*t*Bu), 1.48 (s, 9H, 6-*t*Bu). – ^{13}C NMR ([D_8]THF): δ = 193.36 (C-8), 142.14, 139.69, 139.39 (C-2,3a,4a,6,7a,9,10a,10b,10c), 138.28 (C-10), 137.02, 135.90, 130.91, 126.44, 118.23, 115.35 (C-2,3a,4a,6,7a,9,10a,10b,10c), 112.57 (C-5), 111.92 (C-3), 109.92 (C-1), 103.25 (C-7), 82.32 (C-4), 36.33, 33.02, 32.80 [*C*(CH_3)], 30.35 [2 and 6-C(*CH*$_3$)], 29.46 [9-C(*CH*$_3$)].

16) *Deuteration of Anion* **4**: A solution of **4** in 1 ml of THF was prepared as described in experiment 15) from 57.4 mg (0.149 mmol) of ketone **29** and added to 1 ml of deuterium oxide with vigorous stirring. The mixture was extracted twice with diethyl ether (3 ml), the extracts were combined, dried with magnesium sulfate and evaporated to dryness. The residue was identified as the deuterated ketone [4-D_1]-**29** by its ^{1}H-NMR spectrum, which is identical with the ^{1}H-NMR spectrum of **29** except for the signal of the methylene group at C-4, which only has an intensity corresponding to one proton, and by its mass spectrum, which exhibits a molecular ion and fragment peaks with a mass one amu higher than that of **29**.

17) *Silylation of Anion* **4**: A solution of **4** was prepared as described in experiment 15) from 100 mg (0.26 mmol) of ketone **29**. 84.6 mg (0.78 mmol) of chlorotrimethylsilane was added, the mixture was stirred for 10 min and evaporated to dryness. Chromatography of the residue on silica gel with *n*-hexane/diethyl ether (19:1) afforded 112 mg (0.245 mmol, 94%) of the silylated ketone **30** contaminated with 5% ketone **29** according to its ^{1}H-NMR spectrum. Because ketone **29** could not be removed by chromatography, a satisfactory elemental analysis of compound **30** could not be obtained. – UV (qual., *n*-hexane): λ_{max} = 219 nm, 252 sh, 258 (max.), 267, 292 sh, 308, 316 sh, 347. – MS (70 eV), *m/z* (%): 458 (64) [M^+], 73 (100) [$SiMe_3^+$]. – IR ($CHCl_3$): $\tilde{\nu}$ = 2860 cm^{-1} (C–H), 1580 (br., C=C, C=O). – ^{1}H NMR ($CDCl_3$): δ = 8.24 (d, J = 1.6 Hz, 1H, Ar-H), 7.81 (d, J = 1.6 Hz, 1H, Ar-H), 7.69 (s, 1H, 10-H), 7.65 (d, J = 1.4 Hz, 1H, Ar-H), 7.56 (d, J = 1.4 Hz, 1H, Ar-H), 4.05 (s, 1H, 4-H), 1.53 (s, 9H, *t*Bu), 1.46 (s, 9H, *t*Bu), 1.45 (s, 9H, *t*Bu), −0.07 (s, 9H, $SiMe_3$).

18) *2,6,9-Tri-tert-butylcyclohepta[def]fluoren-4(8H)-one* (**26**): To a solution of 0.60 g (1.61 mmol) of dihydrocyclohepta[*def*]fluorene **18** in 25 ml of THF 1.2 ml (1.8 mmol) of a 1.5 M solution of *n*-butyllithium in *n*-hexane was added at −80°C, and the mixture was stirred for 20 min at the same temp. Then oxygen was bubbled through the solution until the red color disappeared (5 min). Subsequently 1 g of basic alumina (B II–III) was added and the mixture allowed to warm up to room temp. The alumina was filtered off and the filtrate evaporated to dryness. Chromatography of the residue on alumina with *n*-hexane/diethyl ether (9:1) afforded 0.52 g (1.35 mmol, 84%) of ketone **26**, identical in all respects with that obtained in experiment 13a).

19) *Reaction of Ketone* **26** *with Base and Oxygen:* A solution of 0.22 g (0.57 mmol) of **26** in 10 ml of THF was added to a solution of 0.13 g (1.0 mmol) of potassium *tert*-butoxide in 10 ml of THF, and the mixture was stirred for 10 min. Then oxygen was bubbled through the solution until the purple color disappeared (2 min), and 0.5 ml of water was added. The solution was dried with magnesium sulfate and the solvent removed in vacuo. The residue was dissolved in *n*-hexane/diethyl ether (2:1) and the solution filtered through a short column of silica gel to afford 0.15 g (0.195 mmol, 68%) of 8,8'-bi(cyclohepta[*def*]fluorene)-4,4'(8H,8'H)-dione **31** as orange crystals, m.p. 215–216°C. – UV (*n*-hexane): λ_{max} (lg ε) = 226 nm (4.72) sh, 249 (4.87), 265 (4.59) sh, 294 (4.22) sh, 315 (4.05) sh, 427 (3.13). – MS (FD 0–12 mA), *m/z* (%): 770 (17) [M^+], 385 (100) [M^+/2]. – IR (KBr): $\tilde{\nu}$ = 2905 cm^{-1} (C–H), 1705 (C=O), 1600, 1450. – ^{1}H NMR (C_6D_6, 353 K): δ = 7.74 (s, 2H, Ar-H), 7.40 (d, J = 1.6 Hz, 2H, Ar-H), 7.21 (s, 2H, Ar-H), 6.74 (s, 2H, Ar-H), 6.64 (s, 2H, 10-H), 4.17 (s, 2H, 8-H), 1.29 (s, 18H, *t*Bu), 1.25 (s, 18H, *t*Bu), 1.16 (s, 18H, *t*Bu). – $C_{56}H_{66}O_2$ (771.1): calcd. C 87.22, H 8.63; found C 87.23, H 8.94.

[1] [1a] D. H. Reid, N. G. Stafford, J. P. Ward, *J. Chem. Soc.* **1955**, 1193–1201. – [1b] R. Munday, I. O. Sutherland, *J. Chem. Soc., Chem. Commun.* **1967**, 569–570; *J. Chem. Soc. C* **1969**, 1427–1434. – [1c] K. Hafner, J. Flach, *Erdöl Kohle Erdgas Petrochem.* **1978**, *31*, 89; J. Flach, Dissertation, Technische Hochschule Darmstadt, **1976**. – [1d] R. Neidlein, W. Kramer, *Helv. Chim. Acta* **1981**, *64*, 939–942. – [1e] B. Freiermuth, J. Wirz, *Angew. Chem.* **1988**, *100*, 589–590; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 585–587.

[2] [2a] P. Baumgartner, E. Weltin, G. Wagniere, E. Heilbronner, *Helv. Chim. Acta* **1965**, *48*, 751–764. – [2b] R. Zahradnik, J. Michl, J. Pancir, *Tetrahedron* **1966**, *22*, 1355–1366. – [2c] A. Dasgupta, N. K. Dasgupta, *Can. J. Chem.* **1974**, *52*, 155–166. – [2d] N. K. Dasgupta, F. W. Birss, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1211–1219. – [2e] J. Aihara, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3540–3543. – [2f] J. Aihara, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2689–2694. – [2g] H. Vogler, *Int. J. Quantum Chem.* **1986**, *30*, 97–107. – [2h] B. A. Hess, L. J. Schaad, *J. Org. Chem.* **1971**, *36*, 3418–3423. – [2i] Z. Zhou, R. G. Parr, *J. Am. Chem. Soc.* **1989**, *111*, 7371–7379.

[3] Cyclohepta[*def*]fluorene-4,8-dione[15b,15a] and its 1,5-dichloro derivative[15b] behave like ordinary aromatic ketones and obviously do not possess the unusual electronic properties predicted for **1**.

[4] S. Kajigaeshi, T. Kadowaki, A. Nishida, S. Fujisaki, M. Noguchi, *Synthesis* **1984**, 335–337; S. Kajigaeshi, T. Kadowaki, A. Nishida, S. Fujisaki, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 97–103.

[5] This compound like all other chiral compounds mentioned in this paper were obtained or employed as racemate.

[6] A. Rieche, H. Gross, E. Höft, *Chem. Ber.* **1960**, *93*, 88–94.

[7] D. N. Kursanov, Z. N. Parnes, N. M. Loim, *Synthesis* **1974**, 633–651.

[8] [8a] M. Rabinovitz, *Top. Curr. Chem.* **1988**, *146*, 99–169. – [8b] K. Müllen, *Angew. Chem.* **1987**, *99*, 192–205; *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 204–217.

[9] D. H. O'Brien, C. R. Russell, A. J. Hart, *J. Am. Chem. Soc.* **1979**, *101*, 633–639.

[10] S. Bradamante, G. A. Pagani, *J. Org. Chem.* **1984**, *49*, 2863–2870; R. J. Bushby, G. J. Ferber, *Tetrahedron Lett.* **1974**, 3701–3702; *J. Chem. Soc., Perkin Trans. 2*, **1976**, 88–95.

[11] C. Schnieders, K. Müllen, W. Huber, *Tetrahedron* **1984**, *40*, 1701–1711; B. Eliasson, T. Lejon, U. Edlund, *J. Chem. Soc., Chem. Commun.* **1984**, 591–593.

[12] B. C. Becker, W. Huber, K. Müllen, *J. Am. Chem. Soc.* **1980**, *102*, 7803–7805.

[13] Y. Sprinzak, *J. Am. Chem. Soc.* **1958**, *80*, 5449–5455; R. G. Harvey, E. Abu-shqara, C. X. Yang, *J. Org. Chem.* **1992**, *57*, 6313–6317.

[14] H. Lee, R. G. Harvey, *J. Org. Chem.* **1983**, *48*, 749–751; **1988**, *53*, 4587–4589.

[15] [15a] N. Hock, Dissertation, Technische Hochschule Darmstadt, **1991**. – [15b] R. A. Pascal, Jr., D. M. Ho, *Tetrahedron Lett.* **1992**, *33*, 13–16.

[242/94]