Syntheses of Donor–Acceptor-Substituted 2,6-Stellanes

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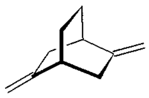
A number of condensations could be carried out using tricyclo[3.3.0.0^{3,7}]octane-2-one (stellanone, **4**) and tricyclo[3.3.0.0^{3,7}]octane-2,6-dione (2,6-stelladione, **5**) as starting materials. The components for condensations were 2-trimethylsilyl-1,3-dithiane (**6**), 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene (**7**), its 3,6-dimethoxy-substituted analogue **8**, fluorene (**12**), xanthene (**13**), diethyl malonate (**14**), and malononitrile (**15**). The condensation reactions with **5** yielded mono- and disubstituted products, among them were the donor–acceptor-substituted 2,6-stellanes **33**–**35**. The structures of **18** (prepared from stellanone and fluorene), **19**, **24**, **27**, **31** and **32** (synthesized by condensation of 2,6-stelladione and 2-trimethylsilyl-1,3-dithiane and malononitrile, respectively) were determined by X-ray crystallography.

In many model investigations concerning electron-transfer processes donor and acceptor units were used that are connected by a rigid σ scaffold. Usually, the distances and orientations of the π systems have been varied.[1] In those compounds where the two systems are separated by more than 3 Å the through-bond coupling should dominate; therefore the nature of the σ system should be important. In order to test this we have started a program in which one varies not only the distance between the two π systems, but also increases the bridging of the central σ system.[2,3] If the bridges are small the angle strain within the scaffold is intensified, which usually leads to an increase of the p character of the C−C bonds. A series of simple test systems are **1**−**3**.



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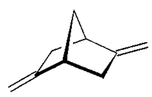

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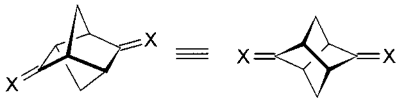
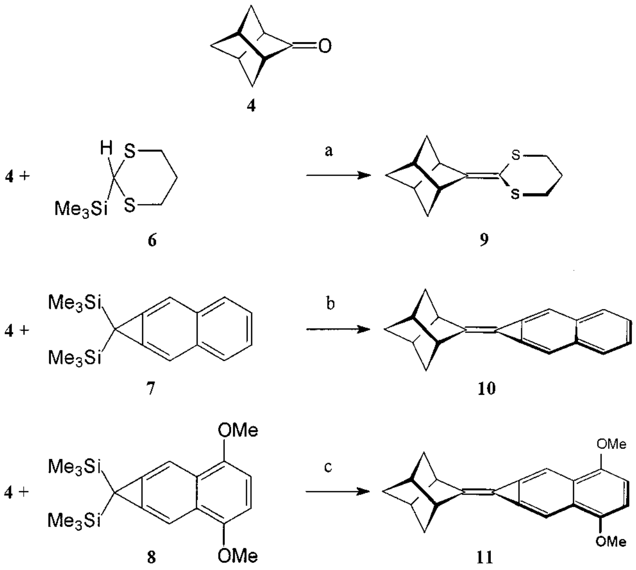


3 X = CH$_2$
5 X = O

In all three systems a central six-membered ring adopts a boat or twist-boat conformation and the angle strain increases from **1** to **3**. Investigations by PE spectroscopy of **1**−**3** have shown that the energy difference between the π ionization energies increases from 0.2 eV (**1**)[4] to 0.9 eV (**3**).[5] A key system for our further investigations is a *p*-stelladiene (**3**) unit bearing donor and acceptor units. In this paper we describe our experimental efforts to join donor and/or acceptor groups to the stellane skeleton.

Results and Discussion

In the preparation of the desired substituted stellenes and stelladienes we chose different condensation methodologies. Starting compounds were either stellanone (**4**)[6] or stelladione (**5**).[2,7,8] Their syntheses have been described in the literature.[6,8] Further components were 2-trimethylsilyl-1,3-dithiane (**6**),[9] 1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene (**7**)[10] and its 3,6-dimethoxy-substituted product **8**. Starting from 3,6-dimethoxycyclopropa[*b*]naphthalene[11] we prepared **8** as a new coupling component.



Scheme 1. a: *n*BuLi/THF, −78°C; b: *t*BuOK/THF, −70°C

A convenient method for the olefination of **4** with electron-rich systems proved to be the Peterson reaction[12] (Scheme 1). The reaction of **4** with **6**−**8** in the presence of a strong base yielded **9**−**11**, respectively, in medium to good yields.

In the case of systems with acidic hydrogen atoms a strong base was sufficient for the condensation (Scheme 2). Treatment of fluorene (**12**) or xanthene (**13**) with LDA in

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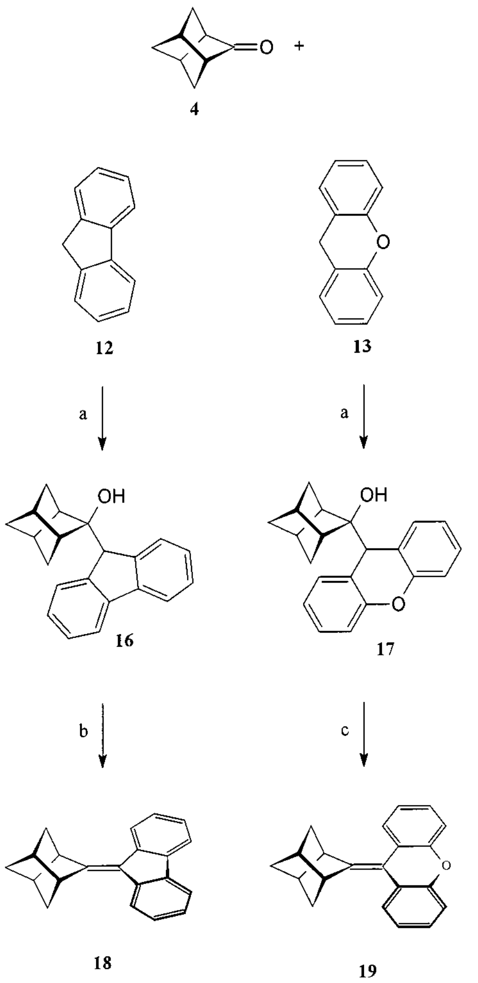
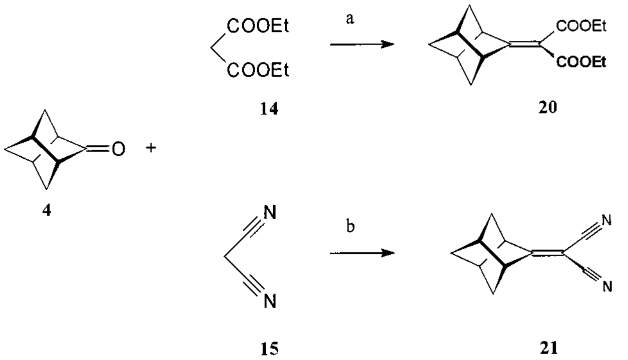


Scheme 2. a: LDA/THF, −78°C; b: LDA/Me_3SiCl/THF, 0°C; c: pyridine $POCl_3$, room temp.

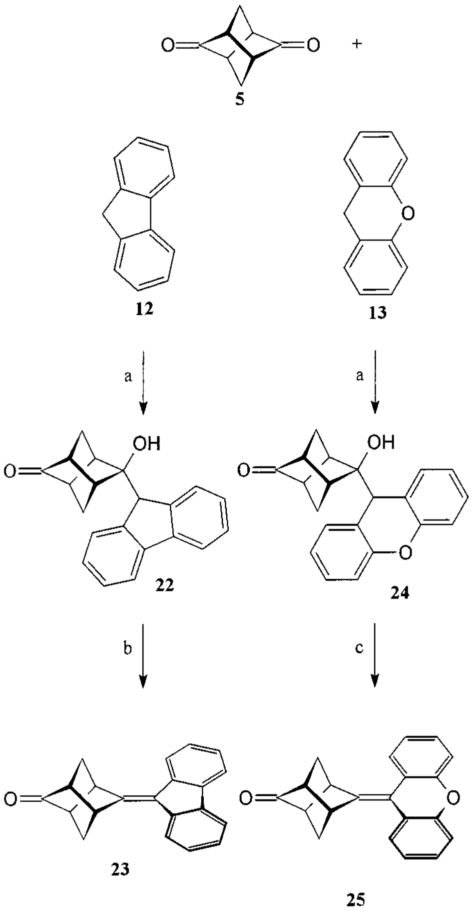


Scheme 3. a: $TiCl_4$/pyridine, 0°C; b: NH_4OAc/HOAc/toluene, reflux

THF at −78°C led to the corresponding addition products **16** and **17** in good yields. Further reaction of **16** with LDA and trimethylsilyl chloride (TMSCl) yielded **18** almost quantitatively. In the case of **17** the same procedure yielded the corresponding silyl ether, which proved to be rather stable towards strong bases. Finally, the reaction of **17** with $POCl_3$ in the presence of pyridine led to **19** in 34% yield.

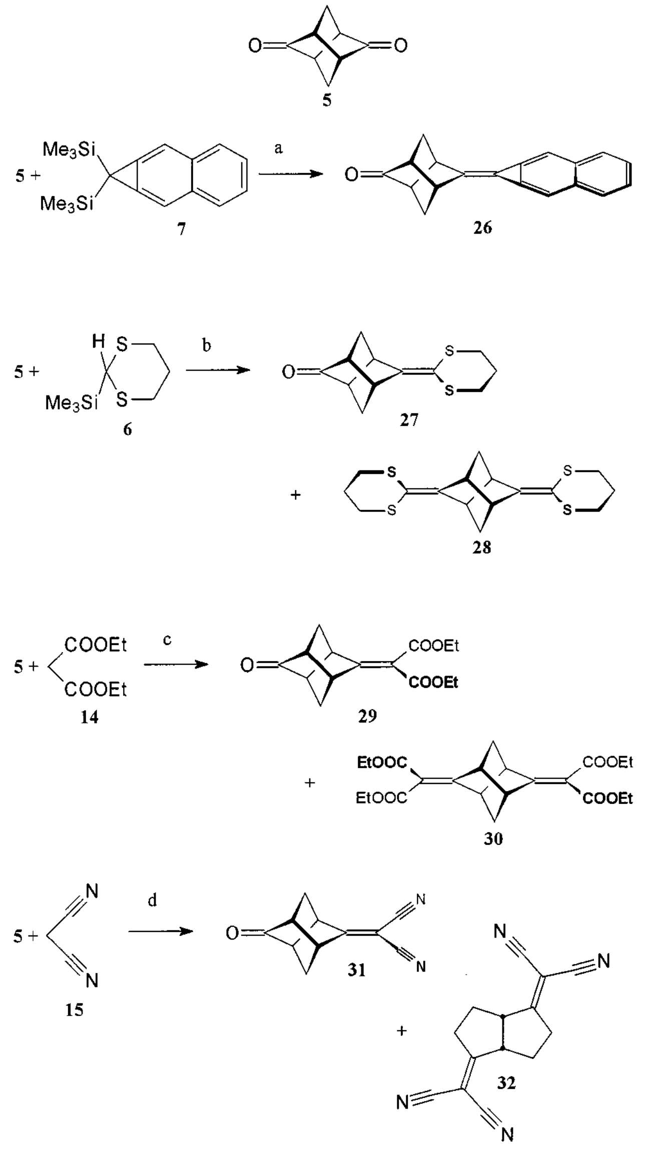
For the introduction of acceptor groups the Knoevenagel condensation proved to be very helpful (Scheme 3). The reaction of **4** with diethyl malonate (**14**) in the presence of $TiCl_4$/pyridine afforded **20** in 48% yield. In order to obtain the condensation product with malononitrile (**15**) the mixture with **4** was refluxed in toluene in the presence of ammonium acetate/acetic acid buffer. The yield of **21** was only 2%.

Our experience with stellanone could be used to treat stelladione (**5**) with fluorene (**12**) and xanthene (**13**) (Scheme 4). Treatment of **12** and **13** with freshly prepared LDA in the presence of **5** yielded the alcohols **22** and **24**, respectively. Dehydration afforded the ketones **23** and **25** in reasonable yields. The reaction of **5** with **7** afforded **26** in 62% yield. The reaction of **5** with **6**, **14** and **15** (Scheme 5) afforded the anticipated monosubstituted products **27**, **29**, and **31**, as well as the disubstituted products **28**, **30**, and **32** as minor components.



Scheme 4. a: LDA/THF, −78°C; b: LDA/Me_3SiCl/THF, 0°C. − C: pyridine /$POCl_3$, room temp.

The formation of **32** can be rationalized by assuming a rupture of one of the central C−C bonds of the tricyclo[3.3.0.$0^{3,7}$]octane skeleton. The lengths of these bonds (ca. 1.6 Å, see below) make them succeptible to breaking. The structural assignment of **32** is based on its spectroscopic properties and on X-ray investigations of single crystals. The donor−acceptor-substituted stelladienes **33**−**35** (Scheme 6) could be prepared from **23** and **25** by reaction with **6** and **14**, in an analogous way to the experiments summarized in Schemes 1−5.



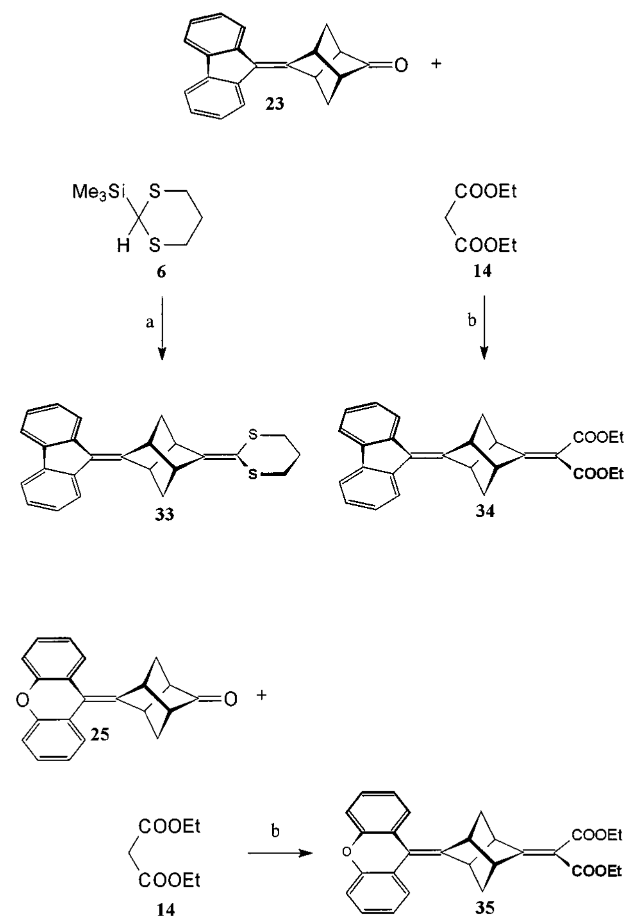
Scheme 5. a: *t*BuOK/THF, −70°C; b: *n*BuLi/THF, −78°C; c: $TiCl_4$/pyridine, 0°C; d: NH_4OAc/toluene, reflux

Structural Investigations

In the cases of **18**, **19**, **24**, **27**, **31**, and **32** single crystals suitable for X-ray analysis could be grown, which allowed more detailed studies of the structural parameters of these species. In Figure 1 the molecular structures of the three stellane and stellanone derivatives **18**, **27**, and **31** are shown, representing species with donor, acceptor−donor and acceptor−acceptor capabilities. On average the single bonds at the carbonyl groups of **24**, **27**, and **31** are shorter [1.523(3) Å; averaged from Table 1) than the corresponding bonds of **18** and **19** [1.540(3) Å].

The donor-substituted compounds of **18**, **19**, and **27** have bond lengths **e** and **f** of 1.514(3) Å, while a shortening to 1.498(2) Å was noticed in compound **31**, which is substituted by nitrile groups.

In five structures with the stellane framework we notice only small torsional angles in the range of 0.1(2)° to 5.9(2)° (Table 1) at the bridging bonds, which indicates nearly eclipsed positions along these bonds. This gives rise to steric strain that leads, in conjunction with the strain inherent in the tricyclo[3.3.0.0^{3,7}]octane system, to the long bridging bonds in the range of 1.594(3) Å to 1.606(3) Å (Table 1). Furthermore, the C−C−C angles at the CH_2 atoms are considerably smaller [93.1(2)°−94.2(2)°] than the expected angle for an sp^3-carbon atom. The same effect is found for the angles **e**−**f**/**k**−**i** [96.8(1)−98.2(2)°], which deviate considerably from the anticipated 120°. This trend is in accordance with our previous investigations on stellane compounds.[2b,8,13] In the crystals of **19** and **32** there are two independent molecules in the asymmetric unit. Further structural details are in deposition.



Scheme 6. a: *n*BuLi/THF, −78°C; b: $TiCl_4$/pyridine, 0°C

Experimental Section

General Procedures: Reactions were carried out in oven-dried (120°C) glassware under argon and with magnetic stirring. Solvents were dried and distilled under argon before use. − ^{1}H and ^{13}C NMR: Bruker AS 200 and Bruker WH 300. If not otherwise noted the ^{1}H-NMR spectra were recorded at 300 MHz and the ^{13}C-NMR spectra at 75.47 MHz. − Low-resolution mass spectra were recorded with a Hewlett-Packard HP 59970 CD GC/MS-MSD. − High-resolution mass spectra (HRMS) were obtained with a ZAB high-resolution mass spectrometer (Vacuum Generators). − Mic-

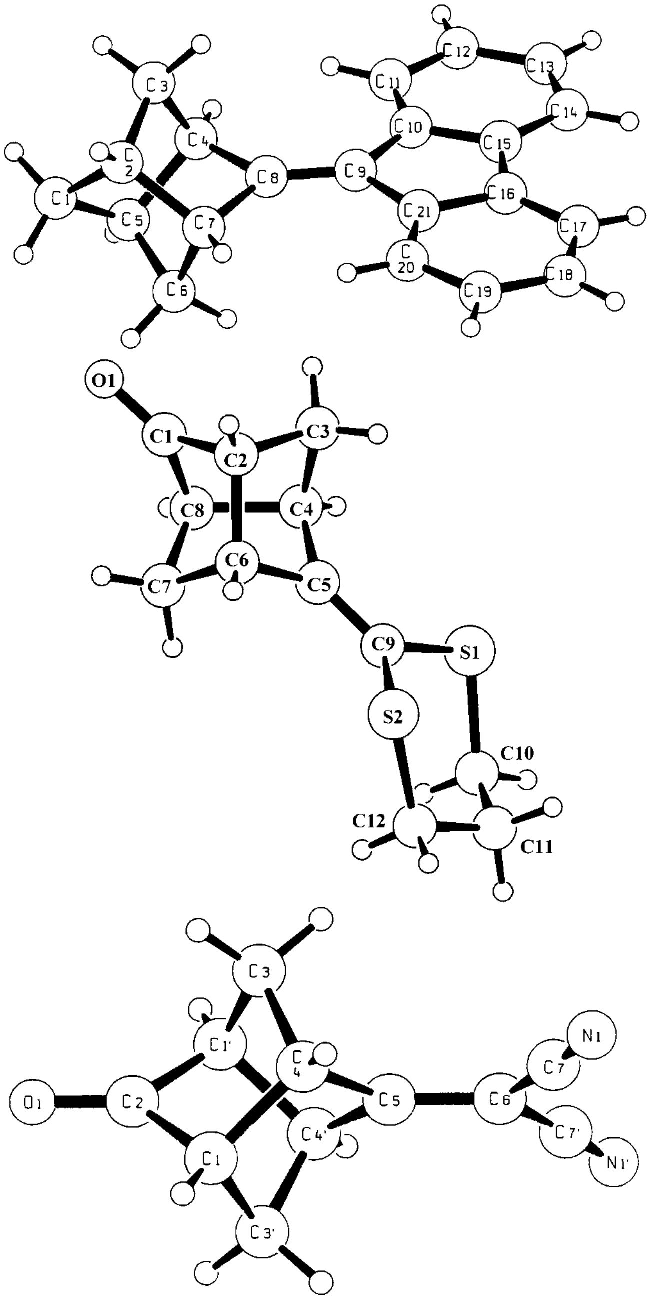


Figure 1. Molecular structures of **18** (top), **27** (middle) and **31** (bottom);[16] selected bond lengths [A] and angles [°]: **18**: C1−C2 1.546 (3), C2−C3 1.527 (3), C2−C7 1.597 (3), C3−C4 1.552 (3), C4−C5 1.606 (3), C8−C9 1.351 (2), C9−C10 1.487 (2), C10−C11 1.388 (3), C10−C15 1.411 (2); C5−C1−C2 93.3 (2), C3−C2−C1 97.6 (2), C3−C2−C7 102.0 (2), C2−C3−C4 93.8 (2), C4−C8−C7 95.5 (1); **27**: O1−C1 1.204(3), C1−C2 1.531(3), C2−C3 1.549(3), C3−C4 1.556(3), C4−C5 1.513(3), C5−C6 1.507(2), C6−C7 1.554(3), C7−C8 1.548(3), C2−C6 1.592(3), C4−C8 1.595(3), C5−C9 1.334(3), C9−S1 1.768(2), C9−S2 1.769(2); O1−C1−C2 131.4(2), C2−C1−C8 97.3(2), C1−C2−C3 93.8(2), C2−C3−C4 94.1(2), C3−C4−C5 95.7(2), C4−C5−C6 96.8(2), C1−C2−C6 101.0(2), C1−C8−C4 102.0(2), C4−C5−C9 131.8(2); **31**: O1−C2 1.204 (3), C1−C2 1.523 (2), C1−C3′ 1.552 (2), C1−C4 1.594 (2), C3−C4 1.554 (2), C4−C5 1.498 (2), C5−C6 1.335(3), N1−C7 1.144 (2), C6−C7 1.437 (2); C1−C2−C1′ 97.3 (2), C1−C4−C3 103.0 (1), C3−C4−C5 95.0 (2), C1−C3−C4 94.1 (1), C4−C5−C4′ 98.2 (2), C7−C6−C7′ 119.4 (2), N1−C7−C6 176.5 (2)

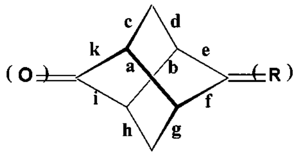
roanalyses: Analytical laboratory of the Chemische Institute der Universität Heidelberg.

3,6-Dimethoxy-1,1-bis(trimethylsilyl)-1*H*-cyclopropa[*b*]naphthalene (8): 2.1 mL (3.4 mmol) of a 1.6 M solution of *n*BuLi in *n*-hexane was slowly added at −78°C to a magnetically stirred solution of 534 mg (2.7 mmol) of 3,6-dimethoxycyclopropa[*b*]naphthalene[11] in 15 mL of THF. The mixture was allowed to warm up to −50°C during 1.5 h, maintained at that temperature for 0.5 h, and then cooled to −78°C. Chlorotrimethylsilane (0.42 mL) was added slowly and the mixture was allowed to warm to −40°C before being cooled to −70°C. The metallation and silylation procedure was repeated twice, the first time with 1.4 mmol of 1.6 M *n*-butyllithium and 0.18 mL of chlorotrimethylsilane and the second time with 0.7 mmol of 1.6 M *n*-butyllithium and 0.08 mL of chlorotrimethylsilane. After the final silylation, the reaction mixture was allowed to warm up to room temp. (2 h), before 5% aqueous $NaHCO_3$ was added. The mixture was extracted with pentane (× 2) and the combined organic layers were washed with water (× 3) and dried ($MgSO_4$). Evaporation of the solvent and purification on silica gel gave 743 mg (82%) of **8** as air-sensitive colorless crystals, m.p. 143°C. − R_f (silica gel, pentane/diethyl ether, 9:1) = 0.62. − ^1H NMR ($CDCl_3$): δ = 7.49 (2 H, s), 6.67 (2 H, s), 3.93 (6 H, s), −0.03 (18 H, s). − ^{13}C NMR ($CDCl_3$): δ = 149.8 (2 C, s), 131.2 (2 C, s), 127.3 (2 C, s), 103.2 (2 C, d), 102.0 (2 C, d), 55.6 (2 C, q), 28.8 (s), −1.5 (6 C, q). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 224 nm (4.52), 270 (4.60), 294 (3.93), 308 (3.88), 330 (3.60). − IR (KBr): $\tilde{\nu}$ = 3066 cm^{-1} (w), 3005 (w), 2952 (s), 2901 (m), 2831 (m), 1785 (w), 1611 (m), 1581 (w), 1464 (s), 1436 (m), 1363 (w), 1303 (s), 1258 (vs). − MS (70 eV); *m/z* (%): 344 (34) [$M^{•+}$] 331 (10), 330 (27), 329 (100). − $C_{19}H_{28}O_2Si_2$ (344.60): calcd. C 66.25, H 8.20; found C 65.98, H 8.17.

2-(1,3-Dithian-2-ylidene)tricyclo[3.3.0.0^{3,7}]octane (9): 1.2 mL (2.0 mmol) of a 1.6 M solution of *n*BuLi in *n*-hexane was added at −78°C to a magnetically stirred solution of 385 mg (2.0 mmol) of 2-trimethylsilyl-1,3-dithiane (**6**) in 50 mL of THF. The solution was allowed to warm up to 0°C. After cooling to −78°C, 244 mg (2.0 mmol) of **4**, dissolved in 10 mL of THF, was added and the reaction mixture was maintained at −78°C for 1 h and subsequently warmed to 0°C. The mixture was hydrolyzed with water, the solvent evaporated and the residue directly chromatographed on silica gel with pentane/diethyl ether (9:1) to yield 403 mg (90%) of **9** as a pale yellow solid, m.p. 39°C: − R_f (silica gel, pentane) = 0.28; R_f (silica gel, pentane/diethyl ether, 9:1) = 0.85. − ^1H NMR ($CDCl_3$): δ = 2.95−2.92 (2 H, m), 2.82−2.72 (4 H, m), 2.41 (2 H, s, br), 2.16−2.11 (2 H, m), 1.57−1.25 (6 H, m). − ^{13}C NMR ($CDCl_3$): δ = 163.4 (s), 99.2 (s), 44.6 (2 C, t), 44.2 (t), 40.8 (2 C, d), 36.9 (2 C, d), 30.9 (2 C, t), 26.2 (t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 224 nm (3.96), 256 (4.01). − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (s, br.), 2952 (vs), 2926 (vs), 2880 (s), 2821 (w), 1637 (m). − MS (70 EV); *m/z* (%): 224 [$M^{•+}$] (100), 196 (13), 183 (68). − $C_{12}H_{16}S_2$ (224.38): calcd. C 64.24, H 7.19; found C 64.40, H 7.41.

2-(1*H*-Cyclopropa[*b*]naphthalen-1-ylidene)tricyclo[3.3.0.0^{3,7}]octane (10): Potassium *tert*-butoxide (217 mg (1.9 mmol) in 7 mL of THF was slowly added at −70°C to a magnetically stirred solution of 427 mg (1.5 mmol) of **7** in 25 mL of THF. The reaction temp. was raised to −30°C, maintained there for 0.5 h, and then lowered to −70°C. The anion was quenched at −70°C with 220 mg (1.8 mmol) of ketone **4**, dissolved in 10 mL of THF, and the reaction mixture warmed to room temp. during 1.5 h. THF was evaporated under reduced pressure. After addition of 5% aqueous NH_4Cl, the residue was extracted with diethyl ether (× 3) and the combined organic layers were washed with water and dried ($MgSO_4$). After evaporation of the solvent, purification on silica gel (pentane) gave 218 mg (60%) of **10** as a pale yellow solid, m.p. 122°C. − R_f (silica gel, pentane) = 0.52. − ^1H NMR (CD_2Cl_2): δ = 7.79 (2 H, dd,

Table 1. Selected geometrical parameters of **18**, **19**, **24**, **27**, and **31** (geometrical parameters of **19** are averaged values of both independent molecules)



	18	19	24	27	31
Bond length [Å]					
a	1.597(3)	1.604(3)	1.602(3)	1.592(3)	1.594(2)
b	1.606(3)	1.616(3)	1.594(3)	1.595(3)	–
e	1.511(2)	1.517(3)	1.556(2)	1.513(3)	1.498(2)
f	1.516(2)	1.519(2)	1.543(2)	1.507(2)	–
i	1.534(3)	1.541(3)	1.526(3)	1.514(3)	1.523(2)
k	1.546(3)	1.537(3)	1.522(3)	1.531(3)	–
Bond angle [°]					
c–d	93.8(2)	93.8(2)	93.8(2)	94.1(2)	–
g–h	93.7(2)	93.4(2)	93.8(2)	94.2(2)	94.1(1)
e–f	95.5(1)	95.5(2)	92.6(1)	96.8(2)	98.2(2)
k–i	93.3(2)	93.1(2)	96.8(1)	97.3(2)	97.3(2)
Torsion angle					
c–a–f	2.6(2)	1.4(2)	5.9(2)	0.4(2)	0.5(1)
k–a–g	0.6(2)	1.4(2)	4.8(2)	1.8(2)	1.6(1)
d–b–i	1.8(2)	1.4(2)	4.0(2)	2.4(2)	–
e–b–h	1.4(2)	2.0(2)	3.4(2)	0.1(2)	–

J = 6.1, J = 3.4 Hz), 7.41 (2 H, dd, J = 6.2, J = 3.3 Hz), 7.24 (2 H, s), 3.08–3.06 (2 H, m), 2.56 (2 H, s, br.), 1.67–1.58 (6 H, m). – ^{13}C NMR (CD_2Cl_2): δ = 141.2 (s), 137.9 (2 C, s), 128.6 (2 C, d), 127.8 (2 C, s), 126.1 (2 C, d), 105.6 (2 C, d), 93.6 (s), 46.3 (2 C, t), 44.9 (t), 42.5 (2 C, d), 37.7 (2 C, d). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 234 nm (4.55), 264 (4.31) 276 (4.49), 354 (4.40), 364 (4.36), 374 (4.64). – IR (KBr): $\tilde{\nu}$ = 3049 cm^{-1} (m), 2998 (vs), 2869 (s), 1577 (s), 1518 (s), 1433 (s). – MS (70 eV); *m/z* (%): 244 $[M^{\bullet +}]$ (69), 243 (13), 229 (25), 228 (36), 217 (11), 216 (41), 215 (93), 204 (18), 203 (100), 202 (96). – HRMS: calcd. for $C_{19}H_{16}$ 244.1252; found 244.1256.

2-(3,6-Dimethoxy-1*H*-cyclopropa[*b*]naphthalen-1-ylidene)tricyclo[3.3.0.0^{3,7}]octane (11): The preparation of **11** was carried out analogously to the preparation of **10**. Starting materials: 345 mg (1.0 mmol) of **8**, 141 mg (1.3 mmol) of potassium *tert*-butoxide, 159 mg (1.3 mmol) of **4**. The reaction yielded 129 mg (42%) of **11** as a yellow solid, 122°C. – R_f (silica gel, pentane/CH_2Cl_2, 1:1) = 0.77. – ^{1}H NMR (CD_2Cl_2): δ = 7.65 (2 H, s), 6.76 (2 H, s), 3.97 (6 H, s), 3.09 (2 H, dd, ^3J = 4.7, ^3J = 2.5 Hz), 2.58 (2 H, s, br.), 1.68 (2 H, m), 1.60–1.56 (4 H, m, br.). – ^{13}C NMR (CD_2Cl_2): δ = 150.8 (2 C, C–O), 139.8 (s), 129.8 (2 C, s), 127.7 (2 C, s), 104.4 (2 C, d), 100.3 (2 C, d), 93.6 (s), 56.2 (2 C, q), 46.4 (2 C, t), 44.9 (t), 42.4 (2 C, d), 37.6 (2 C, d). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 224 nm (4.45), 292 (4.58), 300 (4.65), 342 (4.13), 354 (4.32), 374 (4.47). – IR (KBr): $\tilde{\nu}$ = 2957 cm^{-1} (s), 1613 (s), 1465 (s), 1437 (w). – MS (70 eV); *m/z* (%): 304 (19), 269 (10), 263 (17), 233 (16), 201 (13), 200 (88), 186 (14), 185 (100). – HRMS: calcd. for $C_{21}H_{20}O_2$ 304.1463; found 304.1451.

2-(Fluoren-9-yl)tricyclo[3.3.0.0^{3,7}]octane-2-ol (16): To a magnetically stirred solution of lithium diisopropylamide – prepared at 0°C from 1.1 mL (8.0 mmol) of diisopropylamine and 5 mL (8 mmol) of 1.6 M *n*-butyllithium in *n*-hexane in 60 mL of THF, was added 1.2 g (8.0 mmol) of fluorene (**12**), dissolved in 170 mL of THF, at –78°C. The solution was stirred for 15 min and then added dropwise at –78°C to 489 mg (4.0 mmol) of ketone **4**, dissolved in 170 mL of THF. The solution was allowed to warm up to room temp. during 2 h and then hydrolyzed with water and the solvent evaporated under reduced pressure. Water and CH_2Cl_2 were added. The separated aqueous layer was extracted twice with CH_2Cl_2 and the combined organic layers were washed with NH_4Cl and brine and concentrated. Purification of the residue by silica gel chromatography (pentane/ethyl acetate, 20:1) gave 1.05 g (91%) of **16** as a colorless solid, m.p. 130°C. – R_f (silica gel, pentane/diethyl ether, 9:1) = 0.20. – ^{1}H NMR ($CDCl_3$): δ = 7.78–7.75 (2 H, m), 7.70–7.64 (2 H, m), 7.42–7.25 (4 H, m), 4.53 (1 H, s, br), 2.73 (1 H, m), 2.61 (1 H, s, br.), 2.54–2.50 (1 H, m), 2.41 (1 H, d, J = 2.5 Hz), 2.32 (1 H, s, br.), 1.69–1.66 (1 H, m), 1.58–1.55 (2 H, m), 1.44 (1 H, m, br.), 1.28–1.23 (1 H, m), 1.01 (1 H, m). – ^{13}C NMR ($CDCl_3$): δ = 144.5 (s), 144.4 (s), 142.6 (s), 141.9 (s), 127.7 (d), 127.5 (d), 127.0 (d), 126.9 (d), 125.4 (d), 125.3 (d), 120.1 (d), 119.9 (d), 89.2 (COH), 52.9 (CH_{Cp}), 47.4 (t), 45.2 (d), 43.7 (d), 40.0 (t), 39.8 (t), 38.7 (d), 37.8 (d). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 226 nm (3.9), 168 (4.24), 292 (3.73), 302 (3.8) nm. – IR (KBr): $\tilde{\nu}$ = 3520 cm^{-1} (w), 3396 (w, br.), 3016 (m), 2980 (m), 2937 (w), 2895 (w), 1448 (s). – MS (70 eV); *m/z* (%): 289 (1), 288 $[M^{\bullet +}]$ (1), 167 (12), 166 (90), 165 (100). – $C_{21}H_{20}O$ (288.39): calcd. C 87.46, H 6.99; found C 87.46, H 7.01.

2-(9*H*-Xanthen-9-yl)tricyclo[3.3.0.0^{3,7}]octane-2-ol (17): The preparation of **17** was accomplished in an analogous way to **16**. Starting materials: 916 mg (7.5 mmol) of **4**, 2.4 g (13.0 mmol) of **13**. The reaction yielded 2.2 g (96%) of **17** as a colorless solid, m.p. 200°C. – R_f (silica gel, pentane/diethyl ether, 9:1) = 0.25. – ^{1}H NMR ([D$_6$]DMSO) δ = 7.37–7.01 (8 H, m), 4.57 (1 H, s), 4.43 (1 H, s), 2.64–2.60 (1 H, m), 2.44 (1 H, s, br.), 2.17 (2 H, s, br.), 2.06 (1 H, s, br.), 1.63 (1 H, s), 1.43 (2 H, m), 1.24 (1 H, d, J = 8.7 Hz), 0.96 (1 H, m). – ^{13}C NMR ([D$_6$]DMSO) δ = 153.7 (s), 153.0 (s), 130.3 (d), 127.7 (d), 127.2 (d), 127.1 (d), 123.7 (s), 123.5 (s), 122.2 (t), 122.0 (d), 115.9 (d), 115.6 (d), 90.7 (s), 46.6 (t), 43.2 (d), 42.9 (d), 40.8 (d), 39.8 (t), 39.6 (t), 38.2 (d), 36.9 (d). – UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 222 nm (3.92), 246 (3.98), 286 (3.51). – IR (KBr): $\tilde{\nu}$ = 3562 cm^{-1} (m), 3486 (s), 3025 (m), 2986 (vs), 2940 (m), 2918 (m), 2901 (m), 1597 (m), 1574 (m), 1479 (vs), 1454 (vs), 1250 (vs).

− MS (70 eV); *m/z* (%): 304 [$1M^{\bullet+}$], 183 (8), 182 (60), 181 (100). − $C_{21}H_{20}O_2$ (304.39): calcd. C 82.87, H 6.62; found C 82.66, H 6.58.

2-(Fluoren-9-ylidene)tricyclo[3.3.0.0^{3,7}]octane (18): A solution of 300 mg (1.0 mmol) of **16** in 10 mL of THF was added to a magnetically stirred solution of lithium diisopropylamide − prepared at 0°C from 0.3 mL (2.0 mmol) of diisopropylamine and 1.3 mL (2.0 mmol) of 1.6 M *n*-butyllithium in *n*-hexane in 60 mL of THF. The reaction mixture was stirred at 0°C for 30 min, then 0.6 mL (5.0 mmol) of chlorotrimethylsilane was added dropwise and the mixture was allowed to warm up to room temp. The reaction mixture was hydrolyzed with water and extracted with diethyl ether (× 3). The combined organic layers were washed with 5% aqueous $NaHCO_3$, water, brine and the solvent was evaporated. Purification of the residue by silica gel chromatography (elution with pentane/diethyl ether, 20:1) gave 257mg of **18** (95%) as colorless crystals, m.p. 182°C. − R_f (silica gel, pentane/diethyl ether, 20:1) = 0.68. − ^1H NMR ($CDCl_3$): δ = 7.98−7.93 (2 H, m), 7.82−7.77 (2 H, m), 7.36−7.28 (4 H, m), 3.81 (2 H, s), 2.63 (2 H, s), 1.67 (6 H, s). − ^{13}C NMR ($CDCl_3$): δ = 162.8 (s), 139.4 (2 C, s), 139.3 (2 C, s), 126.6 (2 C, d), 126.2 (2 C, d), 123.1 (2 C, d), 119.5 (2 C, d), 115.9 (s), 44.6 (t), 44.0 (2 C, t), 40.3 (2 C, d), 37.5 (2 C, d). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 nm (4.58), 258 (4.14), 282 (4.17), 292 (4.21), 306 (4.02), 320 (4.06). − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (s, br.), 3048 (w), 2977 (s), 2957 (s), 2878 (w), 1654 (vs), 1445 (vs). − MS (70 eV); *m/z* (%): 270 [$M^{\bullet+}$] (100), 243 (12), 242 (48), 241 (33), 229 (51), 228 (28), 226 (11). − $C_{21}H_{18}$ (270.37): calcd. C 93.29, H 6.71; found C 93.03, H 6.88.

2-(9*H*-Xanthen-9-ylidene)tricyclo[3.3.0.0^{3,7}]octane (19): 0.8 mL of $POCl_3$ (8.7 mmol) was added at 0°C to a solution of 609 mg (2.0 mmol) of **17** in 10.2 mL of pyridine. The brown mixture was stirred for 90 h at room temp. and was then poured into a mixture of ice/water and ethyl acetate. After extraction, the organic layer was washed with 5% aqueous $NaHCO_3$ and with brine. The residue was chromatographed on silica gel (elution with benzene) to yield 194 mg of **19** (34%) as colorless crystals, 197°C. − R_f (silica gel, benzene) = 0.80. − ^1H NMR (CD_2Cl_2): δ = 7.51−7.12 (8 H, m), 3.32 (2 H, s, br.), 2.54 (2 H, s, br.), 1.58 (6 H, s, br.). − ^{13}C NMR (CD_2Cl_2): δ = 154.9 (s), 152.4 (2 C, s), 125.8 (2 C, d), 125.6 (2 C, d), 124.8 (2 C, s), 121.8 (2 C, d), 114.9 (2 C, d), 105.3 (s), 43.4 (2 C, t), 43.2 (t), 38.7 (2 C, d), 35.9 (2 C, d). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 230 nm (3.85), 244 (3.90), 284 (3.45), 314 (3.23). − IR (KBr): $\tilde{\nu}$ = 3074 cm^{-1} (w), 3025 (m), 2966 (s), 2880 (w), 1656 (w), 1590 (w), 1469 (m), 1445 (s), 1254 (vs), 1200 (s). − MS (70 eV); *m/z* (%): 286 [$M^{\bullet+}$] (100), 285 (30), 267 (11), 258 (18), 257 (35), 246 (15), 245 (74), 244 (10), 243 (12), 231 (13). − $C_{21}H_{18}O$ (286.37): calcd. C 88.08, H 6.33; found C 88.16, H 6.32.

Diethyl 2-(Tricyclo[3.3.0.0^{3,7}]octan-2-ylidene)propanedioate (20): 0.9 mL of $TiCl_4$ (9.0 mmol) was added at 0°C to a mixture of 2.0 mL of CCl_4 and 4.0 mL of THF. A solution of 0.6 mL (4.0 mmol) of diethyl malonate and 489 mg (4.0 mmol) of **4** in 3 mL of THF was added to the cooled precipitate. This addition was followed by a solution of 1.3 mL (16.0 mmol) of pyridine in 9.0 mL of THF. The reaction mixture was allowed to warm up to room temp and stirred for 3 d before it was poured into ice-cold water. Extraction was effected with ethyl acetate (× 3). The combined organic layers were washed with 5% aqueous NH_4Cl and with brine. The solvent from the organic layer was evaporated and after purification of the residue by silica gel chromatography (pentane/ethyl acetate, 20:1) yielded 510 mg (48%) of **20** as a yellow solid, m.p. 30°C. − R_f (silica gel, pentane/ethyl acetate, 20:1) = 0.24. − ^1H NMR (CD_2Cl_2): δ = 4.22 (4 H, dq, ^3J = 7.1, J = 1.6 Hz), 3.23 (2 H, dd, ^3J = 5.0, ^3J = 2.5 Hz), 2.50 (2 H, m, br.), 1.62−1.49 (6 H, m), 1.31 (6 H, t, ^3J = 7.1 Hz). − ^{13}C NMR (CD_2Cl_2): δ = 177.8 (s), 165.6 (2 C, C=O), 108.2 (s), 61.0 (2 C, CH_2−O−), 44.6 (t), 43.8 (2 C, t), 41.6 (2 C, d), 37.2 (2 C, d), 14.4 (2 C, q). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 226 nm (4.39), 246 (4.03), 260 (3.81), 314 (3.92). − IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1} (s), 2883 (w), 1719 (vs), 1662 (m), 1466 (w). − MS (70 eV); *m/z* (%): 264 [$M^{\bullet+}$] (7), 219 (68), 218 (48), 199 (11), 198 (98), 190 (36), 177 (32), 173 (23), 172 (100), 170 (55). − HRMS: calcd. for $C_{15}H_{20}O_4$ 264.1225; found 264.1293.

(Tricyclo[3.3.0.0^{3,7}]octan-2-ylidene)propanedinitrile (21): A mixture of 2.0 g (16.4 mmol) of **4**, 5.3 g (80.0 mmol) of malononitrile, 5.3 g (69.0 mmol) of ammonium acetate, and 15.8 mL of acetic acid in 120 mL of toluene was refluxed for 42 h in a Dean−Stark apparatus. After addition of 5% aqueous $NaHCO_3$, the phases were separated. Extraction was effected twice with toluene and the combined organic layers were washed with water and dried with $MgSO_4$ and the solvent was evaporated. Purification by silica gel chromatography (elution with pentane/diethyl ether, 4:1) gave 65 mg of **21** (2.3%) as a colorless solid. − R_f (silica gel, pentane/diethyl ether, 4:1) = 0.27. − ^1H NMR (CD_2Cl_2): δ = 3.09 (2 H, dd, $^3J_1$ = 5.2, $^3J_2$ = 2.6 Hz), 2.64 (2 H, m, br.), 1.73−1.54 (6 H, m). − ^{13}C NMR (CD_2Cl_2): δ = 186.5 (C), 112.1 (2 C, CN), 100.0 (C), 44.1 (2 C, d), 44.0 (t), 43.9 (2 C, t), 38.1 (2 C, d). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 240 nm (4.17). − IR (KBr): $\tilde{\nu}$ = 3012 cm^{-1} (m), 2960 (m), 2882 (m), 2234 (s), 1634 (vs), 1301 (w), 1142 (w), 1083 (w). − MS (70 eV); *m/z* (%): 170 [$M^{\bullet+}$] (26), 169 (24), 155 (21), 143 (19), 142 (76), 129 (27), 128 (29), 115 (23), 105 (12). − HRMS: calcd. for $C_{11}H_{10}N_2$ 170.0844; found 170.0825.

(Fluoren-9-yl)-6-hydroxytricyclo[3.3.0.0^{3,7}]octane-2-one (22): The preparation of **22** was accomplished in an analogous way to that of **16**. Starting materials: Lithium salt of fluorene, prepared from 1.3 g (8.0 mmol) of **12** and 544 mg (4.0 mmol) of **5**. The reaction yielded 572 mg (47%) of **22** as a colorless solid. − R_f (silica gel, pentane/diethyl ether, 1:1) = 0.17. − ^1H NMR ($CDCl_3$): δ = 7.81−7.28 (8 H, m), 4.40 (1 H, s), 2.97 (1 H, br., m), 2.71 (1 H, dd, J = 11.7, J = 3.0 Hz), 2.64−2.60 (3 H, m), 2.42 (1 H, br., m), 1.65−1.61 (1 H, m), 1.49 (1 H, dd, J = 11.8, J = 2.1 Hz), 1.37−1.22 (1 H, m). − ^{13}C NMR ($CDCl_3$): δ = 208.9 (s), 143.3 (s), 142.9 (s), 142.6 (s), 141.9 (s), 128.2 (d), 127.9 (d), 127.3 (2 C, d), 125.4 (d), 125.1 (d), 120.3 (d), 120.2 (d), 87.1 (s), 52.6 (d), 46.0 (d), 45.8 (d), 44.5 (d), 41.7 (d), 34.2 (t), 33.5 (t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 220 nm (4.21), 268 (4.2), 292 (3.59), 302 (3.64), 342 (316). − IR (KBr): $\tilde{\nu}$ = 3426 cm^{-1} (s, br.), 3014 (w), 1768 (vs). − MS (70 eV); *m/z* (%): 303 (10), 302 [$M^{\bullet+}$] (44), 222 (8), 167 (17), 166 (100), 165 (91). − $C_{21}H_{18}O_2$ (302.37): calcd. C 83.42, H 6.00; found C 83.25, H 5.92.

6-(Fluoren-9-ylidene)tricyclo[3.3.0.0^{3,7}]octane-2-one (23): The preparation of **23** was carried out as described for **18**. Starting materials: 216 mg (0.7 mmol) of **22** and 0.45 mL (3.6 mmol) of chlorotrimethylsilane. This reaction yielded 173 mg (85%) of **23**. Alternatively, **23** was prepared in a one-pot reaction: To a magnetically stirred solution of lithium diisopropylamide − prepared at 0°C from 6.75 mL (48.0 mmol) of diisopropylamine and 4.8 mL (48.0 mmol) of 10 M *n*-butyllithium in *n*-hexane in 150 mL of THF was added 4.0 g (24.0 mmol) of **5**, dissolved in 100 mL of THF, at −78°C. The solution was allowed to warm up to −40°C for 15 min and then cooled to −78°C again. The resulting solution was added dropwise to 3.0 g (22.0 mmol) of **5**, dissolved in 200 mL of THF, at −78°C. The solution was allowed to warm up to −45°C for 1 h, recooled to −78°C, and chlorotrimethylsilane (15.2 mL, 120.0 mmol) was added dropwise. After 30 min, the mixture was allowed to warm to room temp. The reaction mixture was hydrolyzed with water and extracted with diethyl ether (× 3). The combined organic layers were washed with 5% aqueous $NaHCO_3$, water, and with brine and then the solvent was evaporated. The product was purified using flash column chromatography (pentane to remove fluorene and then pentane/diethyl ether, 1:1 to elute the desired product). The reaction yielded 3.9 g (58%) of **23** as a colorless solid, m.p. 159°C. − R_f (silica gel, pentane/diethyl ether, 1:1) = 0.56. − ^1H NMR (CD_2Cl_2): δ = 7.93 (2 H, dd, *J* = 6.7, *J* = 1.6 Hz), 7.80 (2 H, dd, *J* = 6.6, *J* = 1.9 Hz), 7.40−7.30 (4 H, m), 4.10 (2 H, m), 2.50−2.49 (2 H, m), 1.93−1.81 (4 H, m). − ^{13}C NMR (CD_2Cl_2): δ = 211.0 (s), 154.1, 139.7 (2 C, s), 138.2 (2 C, s), 127.1 (2 C, d), 126.8 (d), 122.9 (2 C, d), 121.4 (2 C), 119.6 (2 C, d), 43.8 (2 C, d), 38.5 (2 C, d), 36.0 (2 C, t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 234 nm (4.55), 248 (4.27), 258 (4.34), 278 (4.17), 286 (4.19), 302 (4.09), 314 (4.1). − IR (KBr): $\tilde{\nu}$ = 3041 cm^{-1} (w), 2935 (w), 2864 (w), 1768 (vs), 1668 (w), 1475 (s), 779 (m), 733 (s). − MS (70 eV); *m/z* (%): 285 (8), 284 [$M^{\bullet+}$] (32), 256 (16), 155 (15), 241 (14), 239 (11), 229 (29), 228 (29), 227 (12), 226 (15), 215 (16), 202 (13), 202 (25), 191 (10), 190 (10), 189 (18), 178 (17), 166 (17), 165 (100). − HRMS: calcd. for $C_{21}H_{16}O$ 284.1201; found 284.1186.

6-Hydroxy-6-(xanthen-9-yl)tricyclo[3.3.0.0^{3,7}]octane-2-one (24): The preparation of **24** was carried out as described for **17**. Starting materials: lithium salt of **13**, prepared from 5.8 g (32.0 mmol) of **13**, and 4 g (29.0 mmol) of **5**. This reaction yielded 7.5 g (81%) of **24** as a colorless solid, m.p. 184°C. − R_f (silica gel, pentane/ether, 1:2) = 0.42. − ^1H NMR ([D_6]DMSO): δ = 7.35−7.23 (4 H, m), 7.12−7.06 (4 H, m), 5.01 (1 H, s), 4.41 (1 H, s), 2.88 (1 H, m), 2.46 (1 H, s), 2.36 (1 H, d, *J* = 11.4 Hz), 2.29 (1 H, s), 2.15 (1 H, s), 1.99 (1 H, s), 1.39 (1 H, d, *J* = 11.3 Hz), 1.13 (1 H, d, *J* = 11.4 Hz). − ^{13}C NMR (D_6]DMSO): δ = 208.0 (s), 153.8 (s), 153.1 (s), 130.2 (d), 127.8 (d), 127.5 (d), 127.4 (d), 123.1 (s), 122.9 (s), 122.6 (d), 122.3 (d), 116.0 (d), 115.8 (d), 88.6 (s), 46.2 (d), 44.5 (d), 42.74 (d), 42.66 (d), 39.3 (d), 34.0 (t), 33.5 (t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 222 nm (3.88), 244 (3.98), 286 (3.51). − IR (KBr): $\tilde{\nu}$ = 3397 cm^{-1} (vs), 3010 (s), 2938 (m), 2878 (m), 2361 (w), 1751 (vs), 1598 (m), 1577 (m), 1479 (vs), 1456 (vs). − MS (70 eV); *m/z* (%): 318 [$M^{\bullet+}$] (1), 182 (59), 181 (100), 180 (1), 153 (2), 152 (13), 151 (3), 150 (1). − $C_{21}H_{18}O_2$ (302.37): calcd. C 79.23, H 5.70; found C 79.24, H 5.72.

6-(9*H*-Xanthen-9-ylidene)tricyclo[3.3.0.0^{3,7}]octane-2-one (25): The preparation of **25** was accomplished analogously to that of **19**. Starting materials: 6.4 g (20.0 mmol) of **24**, 8.14 mL (87.0 mmol) of $POCl_3$ and 102 mL (1.3 mmol) of pyridine. This reaction yielded 3.3 g (56%) of **25** as a colorless solid, 169°C. − R_f (silica gel, pentane/CH_2Cl_2 1:1) = 0.26. − ^1H NMR ($CDCl_3$): δ = 7.43−7.09 (8 H, m), 3.57 (2 H, s, br.), 2.41 (2 H, s, br.), 1.82−1.74 (4 H, m). − ^{13}C NMR ($CDCl_3$): δ = 211.8 (s), 153.5 (2 C, s), 148.3 (2 C, s), 128.0 (2 C, d), 126.5 (2 C, d), 124.9 (s), 123.3 (2 C, d), 116.6 (2 C, d), 113.3 (s), 44.0 (2 C, d), 38.6 (2 C, d), 37.1 (2 C, t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 224 nm (4.49), 256 (4.09), 312 (4.01). − IR (KBr): $\tilde{\nu}$ = 3025 cm^{-1} (m), 2970 (m), 2932 (m), 2866 (m), 1771 (vs), 1593 (w), 1566 (w), 1448 (vs). − MS (70 eV); *m/z* (%): 300 [$M^{\bullet+}$] (18), 299 (12), 293 (25), 280 (25), 271 (22), 269 (11), 255 (17), 245 (12), 244 (13), 243 (26), 242 (20), 240 (11), 231 (10), 219 (10), 218 (22), 217 (24), 212 (17), 205 (10), 193 (13), 182 (23), 181 (100). − HRMS: calcd. for $C_{21}H_{16}O_2$ 300.1166; found 300.1158.

6-(1*H*-Cyclopropa[*b*]naphthalen-2-ylidene)tricyclo[3.3.0.0^{3,7}]octan-2-one (26): The preparation of **26** was accomplished analogously to that of **10**. Starting materials: 360 mg (1.2 mmol) of **7** and 164 mg (1.2 mmol) of **5**. This reaction yielded 192 mg (62%) of **26** as a pale yellow solid, m.p. 105°C. − R_f (silica gel, pentane/diethyl ether, 4:1) = 0.44. − ^1H NMR ($CDCl_3$): δ = 7.85 (2 H, dd, *J* = 6.2, *J* = 3.3 Hz), 7.46 (2 H, td, *J* = 6.3, *J* = 3.0 Hz), 7.39 (2 H, s), 3.38 (2 H, d, ^3J = 0.9 Hz), 2.48 (2 H, dd, ^2J = 5.1, ^3J = 2.5 Hz), 1.91 (2 H, dd, ^2J = 11.3, ^3J = 1.4 Hz), 1.82 (2 H, dd, ^2J = 11.4, ^3J = 2.3 Hz). − ^{13}C NMR ($CDCl_3$): δ = 211.8 (C=O), 137.8 (2 C, s), 131.7 (s), 128.6 (d), 126.3 (2 C, d), 125.8 (2 C, s), 107.1 (2 C, d), 98.5 (2 C, s), 44.2 (2 C, d), 40.8 (2 C, d), 38.9 (2 C, t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 232 nm (4.6), 262 (3.34), 274 (4.50), 320 (3.82), 336 (4.06), 350 (4.38), 362 (4.35), 372 (4.65). − IR (KBr): $\tilde{\nu}$ = 3439 cm^{-1} (m, br.), 3017 (w), 2931 (w), 2865 (w), 1779 (vs), 1768 (vs), 1628 (w), 1607 (w), 1517 (w). − MS (70 eV): *m/z* = 259 (3), 258 [$M^{\bullet+}$] (14), 202 (10), 179 (15), 178 (100). − HRMS: calcd. for $C_{19}H_{14}O$ 258.1045; found 258.0998.

6-(1,3-Dithian-2-ylidene)tricyclo[3.3.0.0^{3,7}]octan-2-one (27) and 2,6-Bis(1,3-dithian-2-ylidene)tricyclo[3.3.0.0^{3,7}]octane (28): The reaction of **5** with **6** was carried out analogously to the reaction of **4** with **6**. Starting materials: 544 mg (4.0 mmol) of **5** and 0.7 mL (4.0 mmol) of **6**. This reaction yielded 807 mg (85%) of **27** and 29 mg (2%) of **28** as colorless crystals. Separation was accomplished by silica gel chromatography (pentane/diethyl ether, 9:1). − **27**: M.p. 122°C. − R_f (silica gel, pentane/diethyl ether, 9:1) = 0.21. − ^1H NMR ($CDCl_3$): δ = 3.23 (2 H, s, br.), 2.89−2.76 (4 H, m), 2.33 (2 H, dd, ^3J = 5.1, $^3J_2$ = 2.5 Hz), 2.19−2.11 (2 H, m), 1.70 (2 H, d, ^2J = 11.4 Hz), 1.58 (2 H, dd, ^2J = 11.4, ^3J = 2.2 Hz). − ^{13}C NMR ($CDCl_3$): δ = 211.6 (C=O), 155.4 (C=), 107.6 (C=), 43.9 (2 C, d), 39.5 (2 C, d), 37.2 (2 C, t), 30.7 (2 C, (t), 25.6 (t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 222 nm (3.8), 256 (3.98). − IR (KBr): $\tilde{\nu}$ = 3032 cm^{-1} (w), 3017 (w), 2967 (w), 2950 (w), 2938 (m), 2916 (w), 2900 (w), 2866 (w), 1769 (vs). − MS (70 eV); *m/z* (%): 239 (1), 238 [$M^{\bullet+}$] (10), 184 (12), 183 (88), 182 (30), 163 (9), 136 (18), 135 (57), 134 (15), 121 (14), 110 (11), 109 (100), 108 (20). − $C_{12}H_{14}S_2O$ (238.36): calcd. C 60.47, H 5.92, S 26.90; found C 60.39, H 5.88, S 26.89. − **28**: M.p. 125°C. − R_f (silica gel, pentane/diethyl ether, 9:1) = 0.44. − ^1H NMR (200 MHz, $CDCl_3$): δ = 3.08 (4 H, m), 2.83−2.77 (8 H, m), 2.20−2.10 (4 H, m), 1.58−1.55 (4 H, m). − ^{13}C−NMR (50.32 MHz, $CDCl_3$): δ = 159.9 (2 C, C=), 103.4 (2 C, C=), 42.0 (2 C, t), 41.9 (4 C, d), 30.8 (4 C, t), 25.9 (2 C, t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 230 nm (3.5), 268 (3.7). − IR (KBr): $\tilde{\nu}$ = 3004 cm^{-1} (w), 2947 (m), 2927 (s), 2905 (m), 2861 (w), 2823 (w), 1638 (w), 1421 (m). − MS (70 eV); *m/z* (%): 341 (9), 340 [$M^{\bullet+}$] (23), 295 (100), 265 (13). − HRMS: calcd. for $C_{16}H_{20}S_4$ 340.0448; found 340.0448.

Diethyl 2-(6-Oxotricyclo[3.3.0.0^{3,7}]octan-2-ylidene)propanedioate (29) and Tetraethyl 2,2′-(Tricyclo[3.3.0.0^{3,7}]octane-2,6-diylidene)bis(propanedioate) (30): The reaction of **5** with diethyl malonate was carried out analogously to the reaction of **4** with **14**. Starting materials: 544 mg (4.0 mmol) of **5**, 1.22 mL (8.0 mmol) of **14** in 4.0 mL of CCl_4. This reaction yielded 347 mg (31%) of **29** and 426 mg (25%) of **30** as colorless oils. Separation was accomplished by silica gel chromatography (pentane/diethyl ether, 1:1). − **29**: R_f (silica gel, pentane/diethyl ether, 1:1) = 0.48. − ^1H NMR (CD_2Cl_2): δ = 4.26 (4 H, dq, ^3J = 7.1, *J* = 2.8 Hz), 3.55−3.54 (2 H, m), 2.41−2.40 (2 H, m), 1.81−1.72 (4 H, m), 1.35−1.30 (6 H, t, ^3J = 7.1 Hz). − ^{13}C NMR (CD_2Cl_2): δ = 210.1 (s), 171.2 (s), 165.0 (2 C, s), 114.1 (s), 61.5 (2 C, t), 43.9 (2 C, d), 40.3 (2 C, d), 35.8 (2 C, t), 14.3 (2 C, q). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 232 nm (3.75). − IR (KBr): $\tilde{\nu}$ = 2983 cm^{-1} (w), 1779 (s), 1719 (vs), 1678 (w), 1461 (w). − **30**: R_f (silica gel, pentane/diethyl ether, 1:1) = 0.12. − ^1H NMR (200 MHz, $CDCl_3$): δ = 4.18 (8 H, dq, ^3J = 7.1, *J* = 1.1 Hz), 3.38 (4 H, m), 1.65 (4 H, m), 1.24 (12 H, t, ^3J = 7.1 Hz). − ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 173.4 (2 C, s), 164.6 (4 C, s), 111.5 (2 C, s), 60.9 (4 C, t), 41.9 (4 C, d), 39.3 (2 C, t), 14.0 (4 C, q). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 238 nm (4.38). − IR (neat film): $\tilde{\nu}$ = 2982 cm^{-1} (m), 2906 (w), 1720 (vs), 1676 (s), 1463 (w), 1390 (w), 1368 (m). − MS (70 eV); *m/z* (%): 420 [$M^{\bullet+}$] (4), 375 (21), 374 (40), 329 (50), 328 (87), 301 (25), 300 (28), 283 (15), 282 (54), 256 (17), 255 (30), 254 (20), 227 (14), 215 (10), 214 (15), 210 (19), 199 (10), 155 (10), 128 (12), 127 (12), 115 (35), 107 (30), 105 (100). − $C_{22}H_{28}O_8$ (420.46): calcd. C, 62.85; H 6.71; found C 62.65; H 6.82.

2-(6-Oxotricyclo[3.3.0.0^{3,7}]octan-2-ylidene)propanedinitrile (31) and 2,6-Bis(dicyanomethylene)bicyclo[3.3.0]octane (32): A mixture 1.5 g (11.0 mmol) of **5**, 3.5 g (53.0 mmol) of malononitrile, 3.5 g (46.0 mmol) of ammonium acetate, and 10.6 mL acetic acid in 150 mL of toluene was refluxed for 2 h in a Dean−Stark apparatus, then stirred for 18 h at 80°C. After addition of 5% of aqueous $NaHCO_3$ the layers were separated. Extraction was effected twice with toluene and the combined organic layers were washed with water, dried with $MgSO_4$, and the solvent evaporated. Purification of the residue by silica gel chromatography (elution with pentane/diethyl ether, 4:1) gave 1.5 g (75%) of **31** as a colorless solid. When reflux was continued for 24 h, the yield of **31** decreased and 72 mg (3%) of **32** was obtained as colorless crystals. Compound **31**: M.p. 118°C. − R_f (silica gel, pentane/diethyl ether, 1:1) = 0.28. − ^1H NMR ($CDCl_3$): δ = 3.44 (2 H, d, ^3J = 1.5 Hz), 2.62 (2 H, dd, ^3J = 5.3, ^3J = 2.6 Hz), 1.96 (2 H, dd, ^2J = 12.5, ^3J = 1.6 Hz), 1.81 (2 H, dd, ^2J = 12.6, ^3J = 2.3 Hz). − ^{13}C NMR ($CDCl_3$): δ = 205.9 (s), 190.6 (s), 110.6 (2 C) (s), 74.8 (s), 43.4 (2 C) (d), 42.3 (2 C) (d), 35.4 (2 C) (t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 230 nm (4.26). − IR (KBr): $\tilde{\nu}$ = 3426 cm^{-1} (s, br), 3050 (w), 2951 (w), 2877 (w), 2240 (s), 1776 (vs), 1645 (s), 1462 (w). − MS (70 eV); *m/z* (%): 185 (2), 184 [$M^{\bullet+}$] (12), 156 (22), 141 (28), 129 (39), 128 (40), 102 (16), 91 (21), 78 (10), 76 (12), 75 (12), 65 (10), 55 (100). − $C_{11}H_8ON_2$ (184.20): calcd. C 71.73, H 4.38, N 15.21; found C 71.45, H 4.46, N 15.13. − Compound **32**: M.p. 163°C. − R_f (silica gel, pentane/diethyl ether, 1:1) = 0.15. − ^1H NMR ($CDCl_3$): δ = 3.81−3.72 (2 H, m), 3.17−2.95 (4 H, m), 2.68−2.57 (2 H, m), 1.99−1.86 (2 H, m). − ^{13}C NMR ($CDCl_3$): δ = 188.8 (2 C, s), 111.1 (2 C, s), 111.0 (2 C, s), 83.5 (2 C, s), 52.1 (2 C, d), 36.2 (2 C, t), 29.3 (2 C, t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 248 nm (4.42). − IR (KBr): $\tilde{\nu}$ = 2956 cm^{-1} (w), 2921 (w), 2360 (w), 2233 (s), 1616 (s). − MS (70 eV); *m/z* (%): 234 [$M^{\bullet+}$] (10), 169 (14), 144 (10), 143 (100). − HRMS: calcd. for $C_{14}H_{10}N_4$ 234.0906; found 234.0905.

[6-(Fluoren-9-ylidene)tricyclo[3.3.0.0^{3,7}]octan-2-ylidene]-1,3-dithian (33): To a magnetically stirred solution of 2-trimethylsilyl-1,3-dithiane (**6**) (258 mL, 1.4 mmol) in 10 mL of THF was added 0.9 mL (1.4 mmol) of a solution of 1.6 M *n*BuLi in *n*-hexane at −78°C. The solution was allowed to warm up to 0°C. After cooling to −78°C, the ketone **23** (160 mg, 0.6 mmol) in 10 mL of THF was added and the reaction mixture was maintained at −78°C for 1 h, then warmed to 0°C again. The reaction mixture was hydrolyzed with water, the solvent evaporated and the residue directly chromatographed on silica gel with pentane/diethyl ether (9:1) to yield 129 mg (60%) of **33** as a pale yellow solid: − R_f (silica gel, pentane/diethyl ether, 9:1) = 0.39. − ^1H NMR (200 MHz, CD_2Cl_2): δ = 7.95−7.91 (2 H, m), 7.80−7.76 (2 H, m), 7.37−7.29 (4 H, m), 3.96−3.94 (2 H, m), 3.28−3.27 (2 H, m), 2.88−2.82 (4 H, m), 2.20−2.13 (2 H, m), 1.71−1.69 (4 H, m). − ^{13}C NMR (50.32 MHz, CD_2Cl_2): δ = 160.0 (s), 159.87 (s), 139.7 (2 C, s), 139.2 (2 C, s), 127.1 (2 C, d), 126.9 (2 C, d), 126.6 (s), 125.9 (s), 123.5 (2 C, d), 119.8 (2 C, d), 42.6 (2 C, d), 41.7 (2 C, d), 41.6 (2 C, t), 31.2 (2 C, t), 26.3 (t). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 nm (4.31), 248

Table 2. Crystallographic data of **18**, **19**, **24**, **27**, **31**, and **32**

Compound	**18**	**19**	**24**	**27**	**31**	**32**
Empirical formula	$C_{21}H_{18}$	$C_{21}H_{18}O$	$C_{21}H_{18}O_3$	$C_{12}H_{14}OS_2$	$C_{11}H_8N_2O$	$C_{14}H_{10}N_4$
Molecular mass [g/mol]	270.4	286.4	318.4	238.4	184.2	234.3
Crystal size [mm]	0.48 × 0.26 × 0.22	0.5 × 0.4 × 0.26	0.4 × 0.25 × 0.25	0.35 × 0.25 × 0.2	0.5 × 0.48 × 0.45	0.4 × 0.15 × 0.1
Crystal color	colorless	colorless	colorless	colorless	colorless	colorless
Crystal shape	needle	fragment	prism	prism	polyhedron	prism
Space group	*Pbca*	*P*1	$P2_1/c$	$P2_1/n$	$P4_12_12$	*P*1
a [Å]	16.1601(8)	11.2484(3)	14.726(2)	7.121(1)	6.812(1)	7.671(1)
b [Å]	9.1316(5)	11.5577(3)	9.947(1)	19.257(3)	6.812(1)	11.834(2)
c [Å]	19.307(1)	13.7313(3)	10.698(2)	8.296(1)	19.078(3)	14.884(2)
α [°]	90	91.274(1)	90	90	90	110.99(1)
β [°]	90	105.926(1)	106.86(1)	95.59(1)	90	92.42(1)
γ [°]	90	118.640(1)	90	90	90	100.37(1)
V [Å^3]	2849.1(3)	1481.4(1)	1499.7(4)	1132.2(2)	885.3(2)	1232.5(3)
$D_{calcd.}$ [Mg/m^3]	1.26	1.28	1.41	1.40	1.38	1.26
Z	8	4	4	4	4	4
F(000)	1152	608	672	504	384	488
Temperature [K]	200	200	223	223	223	223
h_{min}/h_{max}	−18/18	−11/12	−18/19	0/9	0/9	−10/10
k_{min}/k_{max}	−10/11	−13/11	0/13	0/25	0/9	−15/14
l_{min}/l_{max}	−22/18	−16/14	−14/0	−10/10	0/25	0/19
Θ range [°]	2.1−25.5	1.6−25.6	2.5−28.0	2.1−28.0	2−28	2.7−28.0
μ [mm^{-1}]	0.07	0.08	0.09	0.44	0.09	0.08
T_{max} [%]	−	97.8	−	99.1	−	−
T_{min} [%]	−	85.4	−	90.5	−	−
Refl. collected	12190	6690	3776	2922	924	6149
Refl. unique	2489	4715	3583	2718	858	5923
Refl. observed [$I > 2\sigma(I)$]	1862	3974	2462	2246	821	3247
Variables	262	541	289	192	82	405
$(\Delta/\sigma)_{max}$	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
R	0.043	0.041	0.048	0.039	0.033	0.047
R_w	0.094	0.098	0.129	0.110	0.088	0.097
S (Gof)	1.10	1.06	1.09	1.26	1.11	1.10
$(\Delta\rho)_{max}$ [e Å^{-3}]	0.22	0.43	0.33	0.59	0.18	0.23
$(\Delta\rho)_{min}$ [e Å^{-3}]	−0.18	−0.19	−0.27	−0.34	−0.30	−0.25

(4.09), 258 (4.04), 286 (3.92), 294 (3.96), 308 (3.88), 322 (3.93), 366 (3.03). − IR (KBr): $\tilde{\nu}$ = 2929 cm^{-1} (m), 1662 (s), 1445 (vs), 1268 (m). − MS (70 eV); *m/z* (%): 388 (15), 387 (30), 386 (100) $[M^{\bullet+}]$. − HRMS: calcd. for $C_{25}H_{22}S_2$ 386.11630; found 386.11596.

Diethyl 2-[6-(Fluoren-9-ylidene)tricyclo[3.3.0.0^{3,7}]octan-2-ylidene]-propanedioate (34): The reaction of **23** with diethyl malonate was carried out in an analogous way to the reaction of **4** with **14**. Starting materials: 650 mg (2.3 mmol) of **23**, 0.5 mL (3.5 mmol) of **14** in 40 mL THF. This reaction yielded 213 mg (22%) of **34** as a pale yellow solid, m.p. 53°C. − R_f (silica gel, benzene) = 0.33. − ^1H NMR (CD_2Cl_2): δ = 7.97−7.94 (2 H, m), 7.83−7.80 (2 H, m), 7.40−7.31 (4 H, m), 4.29 (4 H, dq, ^3J = 7.1, ^2J = 1.9 Hz), 4.05 (2 H, m), 3.59 (2 H, m), 1.86 (4 H, s), 1.36 (6 H, t, ^3J = 7.1 Hz). − ^{13}C NMR (CD_2Cl_2): δ = 174.5 (s), 165.2 (2 C, s), 158.3 (s), 139.9 (2 C, s), 139.0 (2 C, s), 127.2 (2 C, d), 127.1 (2 C, d), 123.6 (2 C, d), 119.9 (2 C, d), 119.8 (s), 111.6 (s), 61.3 (2 C, t), 43.1 (2 C, d), 41.4 (2 C, d), 40.4 (2 C, t), 14.3 (2 C, q). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 236 nm (4.71), 250 (4.47), 258 (4.49), 282 (4.49), 292 (4.43), 304 (4.34), 318 (4.37). − IR (KBr): $\tilde{\nu}$ = 2977 cm^{-1} (m), 1722 (s), 1663 (m), 1445 (m), 1366 (w), 1239 (s), 1221 (s). − MS (70 eV); *m/z* (%): 426 $[M^{\bullet+}]$ (20), 381 (46), 380 (100), 306 (11), 279 (17), 278 (11), 277 (12), 266 (11), 216 (11), 215 (73), 166 (12), 165 (82), 78 (22). − HRMS: calcd. for $C_{28}H_{26}O_4$ 426.1831; found 426.1821.

Diethyl 2-[6-(9*H*-Xanthen-9-ylidene)tricyclo[3.3.0.0^{3,7}]octan-2-ylidene]propanedioate (35): 1.1 mL of $TiCl_4$ (10.0 mmol) was added dropwise at 0°C to a magnetically stirred mixture of 8.0 mL of CCl_4 and 30.0 mL of THF. To the yellow precipitate which was formed, a solution of 0.8 mL (5.0 mmol) of diethyl malonate and 1.0 g (3.3 mmol) of **25** in 40 mL of THF was added within 15 min at 0°C. This addition was followed by 1.6 mL (19.8 mmol) of pyridine in 5 mL of THF. The reaction mixture was allowed to warm up to room temp. and stirred for 3 d before it was poured into ice-cold water. Extraction was effected with ethyl acetate (× 3). The combined organic layers were washed with 5% aqueous NH_4Cl and with brine. The solvent in the separated organic layer was evaporated and, after purification of the residue by silica gel chromatography (benzene), 303 mg (21%) of **35** was obtained as a pale yellow solid, m.p. 54°C. − R_f (silica gel, benzene) = 0.34. − ^1H NMR (CD_2Cl_2): δ = 7.52−7.14 (8 H, m), 4.25 (4 H, m), 3.54 (2 H, m), 3.48−3.47 (2 H, m), 1.76 (2 H, dd, ^2J = 16.6, ^3J = 10.8 Hz), 1.75 (2 H, dd, ^2J = 16.0, ^3J = 10.8 Hz), 1.33 (6 H, t, ^3J = 7.1 Hz). − ^{13}C NMR (CD_2Cl_2): δ = 175.3 (s), 165.3 (2 C, s), 153.8 (2 C, s), 151.8 (s), 128.0 (2 C, d), 127.0 (2 C, d), 125.5 (2 C, d), 123.5 (2 C, d), 116.6 (2 C, d), 111.3 (2 C, d), 61.2 (2 C, t), 42.9 (2 C, d), 41.2 (2 C, d), 41.1 (2 C, t), 14.3 (2 C, q). − UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 226 nm (4.62), 258 (4.26), 316 (4.20). − IR (KBr): $\tilde{\nu}$ = 3031 cm^{-1} (w), 2978 (m), 2868 (w), 1718 (vs), 1669 (s), 1592 (w), 1566 (w), 1474 (m), 1447 (s). − MS (70 eV); *m/z* (%): 443 $[M^{\bullet+}+1]$ (10), 442 $[M^{\bullet+}]$ (35), 398 (11), 397 (53), 396 (100). − HRMS: calcd. for $C_{28}H_{26}O_5$ 442.1780; found 442.1781.

X-ray Crystallographic Studies: Crystal data are given in Table 2. The reflections of compounds **18** and **19** were collected with a Siemens P4 diffractometer (ω scans) and the data of **24**, **27**, **31**, and **32** were collected with a Nonius-CAD4-diffractometer (Mo-K_α radiation, graphite monochromator, ω-2Θ scan). Intensities were corrected for Lorentz and polarisation effects. An empirical absorption correction was performed in the case of **19** and a numerical absorption correction was applied on compound **27**. All structures were solved by direct methods (SHELXS-86 and SHELXS-97).[14] The structural parameters of the non-hydrogen atoms were refined anisotropically and the parameters of the hydrogen atoms were refined isotropically according to a full-matrix least-squares technique (F^2). Refinement was carried out with SHELXL-93 and SHELXL-97.[15] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-101933 to -101938 for **18**, **19**, **24**, **27**, **31**, and **32**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

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