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p-Quinoid Compounds by Nucleophilic Aromatic Substitution with Hydride as Leaving Group

Marcel Hagel,[a] Jianhui Liu,[a] Oliver Muth,[a] Hebert Jesus Estevez Rivera,[a] Erik Schwake,[a] Lertnarong Sripanom,[a] Gerald Henkel,[b] and Gerald Dyker*[a]

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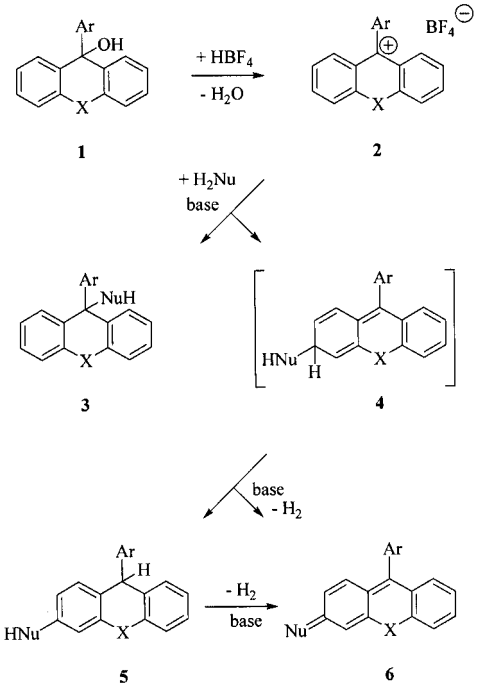
Triarylmethylium tetrafluoroborates with a sterically shielded cationic center react with selected C- and N-nucleophiles under nucleophilic aromatic substitution to give dipolar *p*-quinoid final products. The mechanistic rationale includes a hydride leaving group in analogy to the Tschitschibabin reaction.

Introduction

Triarylmethylium salts – stabilized by an extensive delocalization of the cation – found widespread application in various aspects of organic chemistry, for instance as dyes, indicators, one-electron-oxidants and activators for olefin polymerization.[1] In the course of our studies towards the construction of extended π-systems with multiple coordination sites for transition metals we tested sterically hindered triarylmethylium salts as substrates for nucleophilic aromatic substitution.[2] With methoxy- and with fluoro-substituents as leaving groups and with various pronucleophiles we obtained satisfying yields of dipolar *p*-quinoid compounds.[3] Herein we report on our observation, that this type of products is also accessible with hydride as leaving group.

Results and Discussion

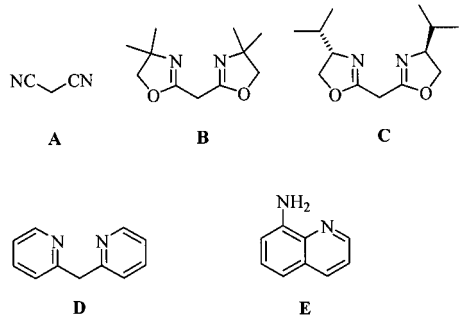
Triarylmethyl alcohols **1** are easily synthesized from the corresponding diaryl ketone and a metallated arene, generally with yields in the range of 60 to 80%, even for the sterically rather crowded mesityl-substituted xanthenol **1.1**[4] (Scheme 1). The transformation to the tetrafluoroborate **2** also follows the standard procedure with tetrafluoroboric acid as reagent. Among the eight model electrophiles **2.1** to **2.8** the reactivity of the mesityl-substituted tetrafluoroborate **2.1** was tested with all of our five model nucleophiles **A**–**E**, including 8-aminoquinoline (**E**) as N-nucleophile. Since the central carbon atom of **2.1** is sterically rather shielded, formation of products of type **3** should be impossible with these nucleophiles, and indeed, *p*-quinoid products of type **6** were isolated in good to excellent yields; with one exception: in the case of the dipyridylmethane **D** – the least acidic pronucleophile of Scheme 2 – we obtained the triarylmethane **5.1D** exclusively. As a mechanistic rationale we assume, that the cross-conjugated structures **4**[5] are intermediates for both, products of type **5** and **6**. A rearrangement analogous to the transformation of **4.1D** to **5.1D** was reported earlier by Zaugg et al.[6] refering to the reaction of triphenylmethyl tetrafluoroborate with di-*tert*-butyl malonate. If the basic reaction conditions are suitable



Scheme 1. Mechanistic rationale for the reactions of nucleophiles with triarylmethylium salts of type **2**.

[a] Fakultät für Chemie und Biochemie, Ruhr-Universität Bochum,
Universitätsstrasse 150, 44780 Bochum, Germany
E-mail: gerald.dyker@ruhr-uni-bochum.de
[b] Department Chemie, Universität Paderborn,
Warburger Strasse 100, 33098 Paderborn, Germany

for a fast deprotonation of the HNu group of **4**, the mechanistic pathway to **6** becomes possible: the anionic charge of the Nu^- group then activates hydride as leaving group, thus generating the energetically favourable dipolar π-system **6** with aromatic character. Presumably its a rather facile process, judged from the immediate change to the intensive characteristic color of the products. We consider this process to be related to the Tschitschibabin reaction,[7,8] which is known as an early example of a hydride elimination, also energetically profiting from rearomatization.



Scheme 2. List of the tested C- and N-nucleophiles (or prenucleophiles, respectively).

In order to further demonstrate the generality of this approach to products of type **6** we also varied the electrophile **1**, this time constantly with malononitrile (**A**) as nucleophile: as long as the central carbon of the triarylmethyl system is shielded by two methyl groups as in **2.2** to **2.5** (with unreactive bridging units) the *p*-quinoid compounds **6** are always isolated as the main products. The structure of **6.2A** was confirmed by X-ray crystal structure analysis (Figure 1).[9,10] The extended length of 140.1 pm of the exocyclic double bond indicates its distinct push-pull character.[11]

In the case of the thioxanthenylium salt **2.4** a test reaction in the NMR tube at –40 °C clearly showed the intermediary cross-conjugated system **4.4A**, with the diagnostic ^{1}H NMR signals of the alkyl and vinyl hydrogens at 3.75, 4.04, 5.58, 5.72 and 6.14 ppm. On a preparative scale we obtained the quinonmethide **7** as a by-product, presumably a result of basic hydrolization of **2.4**. The related compound **8** we isolated after partial hydrolization of the sensitive imine **6.1E** during chromatographic work-up on silica gel (Table 1).

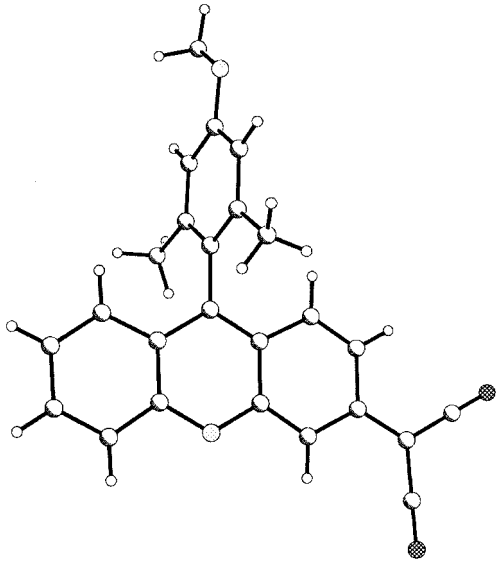


Figure 1. Structure of *p*-quinoid dibenzopyran **6.2A** in the crystal.[9]

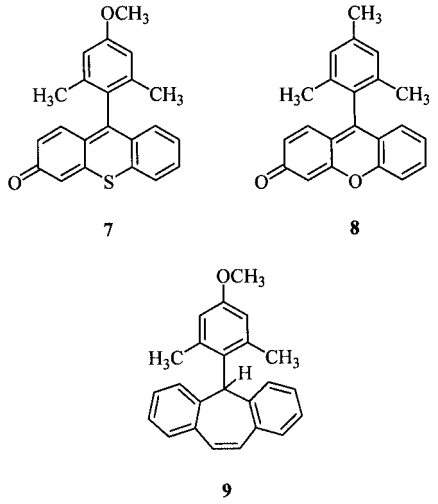
Since the cycloheptanylium tetrafluoroborate **2.5** seemed to be sensitive to oligomerization, we chose a special procedure for the synthesis of **6.5**: directly starting from the tertiary alcohol **1.5** and malononitrile in DMF as polar solvent at elevated temperature, thus saving one preparative step. In this case dissociation delivers the basic hydroxide, which deprotonates malononitrile. However, the 37% yield of **6.5** is only moderate: main reaction pathway is the transformation to the olefinic product **9** in 59% yield; obviously the intermediary cation is deprotonated at the ethandiyl bridge to give a highly reactive *o*-quinoid compound, which rearranges to the final product (Scheme 3).

The unbridged model compound **2.6** also reacts with malononitrile to the corresponding *p*-quinoid product **6.6**. Most interestingly, the xylyl-substituted xanthenylium salt **2.7** with just one shielding methyl group is still sterically hindered enough for the formation of the quinoid compound **6.7A**. The 4-tolyl-substituted xanthenylium salt **2.8**

Table 1. Yield (%) of products for the reactions of Scheme 1.

Entry	X	Ar	**1**[a]	**2**	Nucleophile	**3**	**5**	**6**
1	O	2,4,6-trimethylphenyl	79 (**1.1**)	98	**A**			96
2					**B**			94
3					**C**			61
4					**D**		93	
5					**E**			32
6	O	4-methoxy-2,6-dimethylphenyl	15 (**1.2**)	90	**A**			58
7	O	4-(dimethylamino)-2,6-dimethylphenyl	71 (**1.3**)	88	**A**			90
8	S	4-methoxy-2,6-dimethylphenyl	71 (**1.4**)	93	**A**			49
9	C_2H_4	4-methoxy-2,6-dimethylphenyl	76 (**1.5**)	not isol.	**A**			37
10	H···H[b]	4-methoxy-2,6-dimethylphenyl	60 (**1.6**)	86	**A**			30
11	O	2,4-dimethylphenyl	94 (**1.7**)	92	**A**	37		15
12	O	4-methylphenyl	43 (**1.8**)	95	**A**	65		

[a] Yield of **1** synthesized by the reaction of the aryl-Li species with the specific ketone. [b] No bridging group X.



Scheme 3. Additional isolated and identified products.

finally is sterically open for the classical reaction pathway to **3.8A**.

Our results represent a straightforward and efficient access to polar *p*-quinoid π-systems, attached with functional groups which can trigger the electronic properties: we intend to test these products as bidentate redoxactive ligands in transition metal catalysis.

Experimental Section

General Remarks: Melting points (uncorrected): Reichert Thermovar. IR: Perkin–Elmer 841 and 983. NMR: Bruker DPX-200, WM-300, DRX-400, AM-500. ^{1}H NMR spectra were recorded in $CDCl_3$ with TMS as the internal standard. ^{13}C NMR spectra were measured by using $CDCl_3$ as the solvent and the internal standard. MS: MAT 700 ITD (70 eV) and Varian MAT 311 A. For analytical TLC precoated plastic sheets "POLYGRAM SIL G/UV254" from "Macherey–Nagel" were used. EA: Elementar/Hanau Vario EL.

9-Hydroxy-9-(2,4,6-trimethylphenyl)xanthene (1.1): To a solution of 1.49 g (1.13 mL, 7.50 mmol) 2-bromomesitylene in 17 mL of dry THF was added 3.30 mL (8.26 mmol) of *n*-butyllithium (2.5 M in hexane) at –30 °C. The colorless solution was stirred for 30 min and a solution of 0.98 g (5.00 mmol) xanthone in 28 mL of dry dioxane was added dropwise within 15 min. The reaction mixture was stirred at room temperature for 24 h and hydrolyzed with 20 mL of saturated aqueous diammonium hydrogen phosphate solution. After extraction with CH_2Cl_2 (3 × 20 mL) and concentration of the combined organic layer in vacuo the crude product was purified by flash chromatography (silica, PE/Et_2O, 10:1, R_f = 0.25) and dried in vacuo (50 °C, 0.5 mbar, 4 h): 1.24 g (79%) of the colorless solid **1.1** with m.p. 193–194 °C (ref.[4,12] m.p. 192.5–193.5 °C dec.). IR (KBr): $\tilde{\nu}$ = 3518 (s), 3037 (w), 2970 (m), 2921 (m), 2859 (w), 1602 (s), 1574 (m), 1479 (s), 1446 (s), 1315 (s), 1293 (s), 1242 (s), 1203 (m), 1099 (m), 1043 (m), 1026 (m), 1002 (s), 894 (s), 874 (s), 747 (s), 629 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.08 (s, 1 H), 2.13 (br. s, 6 H), 2.28 (s, 3 H), 6.83 (br. s, 2 H), 7.02 ("t", "*J*" = 7.5 Hz, 2 H), 7.16 (dd, *J* = 7.8, *J* = 1.65 Hz, 2 H), 7.20 (dd, *J* = 8.25, *J* = 1.2 Hz, 2 H), 7.31 ("t", "*J*" = 7.7 Hz, 2 H) ppm. ^{13}C NMR {^{1}H}: δ = ($CDCl_3$, 125 MHz): δ = 20.58 (q), 24.20 (q, br.), 74.31 (s), 116.39 (d), 123.60 (d), 127.94 (s), 128.35 (d), 129.10 (d), 131.75 (d), 136.61 (s), 137.35 (s), 138.40 (s), 149.45 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 316 (14) [M$^+$], 299 (33), 197 (100). $C_{22}H_{20}O_2$ (316.40): calcd. C 83.52, H 6.37; found C 83.55, H 6.45.

9-Hydroxy-9-(4-methoxy-2,6-dimethylphenyl)xanthene (1.2): To a solution of 500 mg (2.25 mmol) of 4-bromo-3,5-dimethylanisol in 10 mL of dry THF was added 1.6 mL (2.5 mmol) of *n*-butyllithium (15% in hexane) at –30 °C. The colorless solution was stirred for 1 h and a solution of 455 mg (2.32 mmol) xanthone in 20 mL of dry dioxane was added dropwise within 15 min. The reaction mixture was stirred at reflux temperature for 21 h and was hydrolyzed with 20 mL of saturated aqueous diammonium hydrogen phosphate solution. After extraction with CH_2Cl_2 (three times 20 mL) and concentration of the combined organic layer in vacuo the crude product was purified by flash chromatography (silica, *n*-hexane/Et_2O, 4:1, R_f = 0.44 (**1.2**), 0.37 (xanthone)) and dried in vacuo (50 °C, 0.5 mbar, 4 h): 110 mg (15%) of a brownish needles **1.2** with m.p. 183–185 °C (in addition to 340 mg (75%) recovered starting material xanthone). IR (KBr): $\tilde{\nu}$ = 3512 (s), 3071 (w), 2937 (w), 2835 (w), 1601 (s), 1571 (m), 1477 (s), 1447 (s), 1315 (s), 1302 (s), 1241 (m), 1193 (w), 1138 (m), 1124 (m), 1099 (w), 1071 (w), 1043 (w), 1005 (w), 894 (w), 874 (w), 750 (s) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 194 (4.73, sh), 203 (4.79), 239 (4.35), 281 (3.59), 290 (3.59) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.06 (s, 1 H, O*H*), 2.13 (s, 6 H, C*H*$_3$), 3.77 (s, 3 H, OC*H*$_3$), 6.54 (s, 2 H, 3-H/5-H), 7.01 ("dt", "*J*" = 8.0, 7.3, 1.1 Hz, 2 H), 7.13–7.19 (m, 4 H), 7.29 (ddd, *J* = 8.4, 7.2, 1.7 Hz, 2 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 75.5 MHz): δ = 24.61 (q), 54.96 (q), 74.11 (s, *C*–OH), 115.90 (d), 116.39 (d), 123.58 (d), 128.06 (s), 128.33 (d), 129.08 (d), 133.80 (s), 139.06 (s), 149.40 (s), 157.85 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 333 (8) [M$^+$ + 1], 332 (34) [M$^+$], 316 (10), 315 (37), 198 (19), 197 (100), 136 (43). $C_{22}H_{20}O_3$ (332.40): calcd. C 79.50, H 6.06; found C 79.50, H 6.05.

9-(4-Dimethylamino-2,6-dimethylphenyl)-9-hydroxyxanthene (1.3): To a solution of 550 mg (2.00 mmol) of 3,5,*N*,*N*-tetramethyl-4-iodoaniline in 5 mL of dry THF was added 0.88 mL (2.2 mmol) of *n*-butyllithium (2.5 M in hexane) at –78 °C. The colorless solution was stirred for 0.5 h and a solution of 314 mg (1.60 mmol) xanthone in 10 mL of dry dioxane was added at –60 °C. The reaction mixture was stirred at reflux temperature for 6 h and was hydrolyzed with 25 mL of saturated aqueous ammonium chloride solution. After extraction with diethyl ether (twice 20 mL) and concentration of the combined organic layer in vacuo the crude product was purified by flash chromatography (silica, petroleum ether/Et_2O, 5:1, R_f = 0.63 (**1.3**), 0.35 (xanthone)): 390 mg (71%) of a colorless solid **1.3** which decomposes at 182–185 °C. IR (KBr): $\tilde{\nu}$ = 3407 (m), 3079 (w), 2963 (m), 2930 (m), 1657 (m), 1606 (s), 1574 (m), 1477 (s), 1459 (s), 1447 (s), 1347 (m), 1332 (m), 1311 (m), 1239 (s), 1113 (s), 830 (m), 758 (s) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 213 (4.72), 244 (4.33), 265 (3.65) nm. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.02 (s, 1 H), 2.12 (br. s, 6 H), 2.93 (s, 6 H), 6.38 (s, 2 H), 6.99–7.02 (m, 2 H), 7.16–7.21 (m, 4 H), 7.28 ("t", "*J*" = 7.73 Hz, 2 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 125 MHz): δ = 24.79 (q), 40.24 (q), 74.03 (s), 114.61 (d), 116.23 (d), 123.45 (d), 128.40 (d), 128.41 (d), 128.84 (s), 129.80 (s), 138.15 (s), 148.92 (s), 149.33 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 345 (10) [M$^+$], 328 (38), 312 (14), 197 (100), 149 (93), 134 (16). $C_{23}H_{23}NO_2$ (345.44): calcd. C 79.97, H 6.71, N 4.05; found C 79.99, H 6.97, N 4.00.

9-Hydroxy-9-(4-methoxy-2,6-dimethylphenyl)thioxanthene (1.4): To a solution of 1.00 g (4.51 mmol) of 4-bromo-3,5-dimethylanisol in 20 mL of dry THF was added 2.8 mL (4.5 mmol) of *n*-butyllithium (15% in hexane) at –45 °C. The colorless solution was stirred for 1 h and a solution of 637 mg (3.00 mmol) thioxanthone in 25 mL of dry dioxane/THF (4:1) was added dropwise within 15 min. The

orange suspension was stirred at reflux temperature for 5 d and was hydrolyzed with 20 mL of saturated aqueous diammonium hydrogen phosphate solution. After extraction with CH_2Cl_2 (three times 20 mL) and concentration of the combined organic layer in vacuo a crude product was obtained, containing 750 mg (71%) of thioxanthenol **1.4**. Purification by flash chromatography (silica, *n*-hexane/acetone, 10:1, R_f = 0.31 (thioxanthone), 0.20 (**1.4**)) gave an analytically pure sample of 133 mg (13%) of the greenish solid **1.4** with m.p. 132 °C. IR (KBr): $\tilde{\nu}$ = 3520 (m), 3059 (w), 2963 (w), 2937 (w), 2835 (w), 1600 (s), 1467 (s), 1438 (s), 1305 (s), 1270 (m), 1159 (w), 1140 (m), 1125 (m), 1069 (m), 1043 (w), 995 (w), 957 (w), 867 (w), 769 (s), 738 (s), 632 (s) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 197 (4.78), 205 (4.74, sh), 241 (4.12, sh), 271 (4.15), 285 (3.95, sh), 378 (2.21) nm. ^1H NMR ($CDCl_3$, 300 MHz): δ = 2.09 (s, 6 H), 2.17 (s, 1 H, O*H*), 3.81 (s, 3 H, OC*H*$_3$), 6.59 (s, 2 H, 3-H/5-H), 7.04–7.13 (m, 4 H), 7.22 (ddd, *J* = 8.8, 6.6, 2.0 Hz, 2 H), 7.35 (dd, *J* = 7.9, 0.9 Hz, 2 H) ppm. ^{13}C NMR {^1H} ($CDCl_3$, 75.5 MHz): δ = 24.65 (q, *C*H$_3$), 55.01 (q, O*C*H$_3$), 79.94 (s, *C*-OH), 115.84 (d), 125.40 (d), 126.31 (d), 127.70 (d), 128.96 (s), 129.02 (d), 133.80 (s), 138.61 (s), 139.31 (s), 157.87 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 349 (8) [M^+ + 1], 348 (33) [M^+], 332 (14), 331 (50), 214 (16), 213 (100), 212 (21), 184 (21), 136 (17). $C_{22}H_{20}O_2S$ (348.46): calcd. C 75.83, H 5.79; found C 75.78, H 5.80.

10,11-Dihydro-5-(4-methoxy-2,6-dimethylphenyl)-5*H*-dibenzo[*a*,*d*]-cyclohepten-5-ol (1.5): To a solution of 2.50 g (11.3 mmol) of 4-bromo-3,5-dimethylanisol in 20 mL of dry THF was added 15.3 mL (22.5 mmol) of *tert*-butyllithium (15% in *n*-pentane) at –60 °C. The yellow suspension was stirred for 1 h and a solution of 2.42 (11.3 mmol) of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one in 100 mL of dry dioxane was added dropwise within 30 min at –40 °C. The reaction mixture was stirred at reflux temperature for 6 d and was hydrolyzed with 20 mL of saturated aqueous diammonium hydrogen phosphate solution. After extraction with diethyl ether (three times 20 mL) and with CH_2Cl_2 (three times 20 mL) and concentration of the combined organic layer in vacuo the crude product was purified by flash chromatography (silica, *n*-hexane/toluene, 1:1, R_f = 0.26 (diaryl ketone), 0.14 (**1.5**)) and dried in vacuo (50 °C, 0.5 mbar, 4 h): 2.95 (76%) of colorless solid **1.5** with m.p. 143–145 °C. IR (KBr): $\tilde{\nu}$ = 3493 (s), 3056 (w), 3003 (w), 2963 (m), 2935 (m), 2838 (w), 1599 (s), 1476 (s), 1443 (s), 1304 (s), 1196 (m), 1166 (m), 1140 (m), 1108 (m), 1070 (m), 1033 (m), 1017 (m), 962 (w), 944 (w), 852 (m), 781 (w), 764 (m), 753 (s) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 205 (4.85), 238 (4.19, sh) nm. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.75 (s, 6 H, C*H*$_3$), 2.39 (s, 1 H, O*H*), 2.70–2.80 (m, 4 H, C*H*$_2$), 3.77 (s, 3 H, OC*H*$_3$), 6.48 (s, 2 H, 3-H/5-H), 6.92 (dd, *J* = 7.3, 1.4 Hz, 2 H), 7.04–7.16 (m, 4 H), 7.79 ("d", "*J*" = 6.6 Hz, 2 H, br.) ppm. ^{13}C NMR {^1H} ($CDCl_3$, 75.5 MHz): δ = 24.03 (q), 31.66 (t), 55.01 (q, O*C*H$_3$), 115.83 (d), 124.30 (s, br.), 126.44 (d), 126.92 (d), 130.62 (d), 135.87 (s, br.), 139.72 (s), 148.15 (s, br.), 158.00 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 344 (16) [M^+], 209 (10), 208 (28), 207 (7), 179 (6), 165 (9), 164 (23), 163 (100), 103 (8). $C_{24}H_{24}O_2$ (344.45): calcd. C 83.69, H 7.02; found C 83.86, H 7.03. An attempt to synthesize the corresponding cycloheptenylium tetrafluoroborate **2.5** by treating the tertiary alcohol **1.5** with $HBF_4{\cdot}O(C_2H_5)_2$ led to the isolation of a brown to black presumably polymeric material, which exhibited only broad signals in the ^1H NMR spectroscopy.

(4-Methoxy-2,6-dimethylphenyl)diphenylmethanol (1.6): To a solution of 500 mg (2.25 mmol) of 4-bromo-3,5-dimethylanisol in 10 mL of dry THF was added 1.55 mL (2.5 mmol) of *n*-butyllithium (15% in *n*-hexane) at –60 °C. The colorless suspension was stirred for 1 h and a solution of 424 mg (2.33 mmol) of benzophenone in 20 mL of dry THF was added dropwise within 5 min at –60 °C. The reaction mixture was stirred at room temperature for 3 h and at reflux temperature for 18 h and was hydrolyzed with 20 mL of saturated aqueous diammonium hydrogen phosphate solution. After extraction with diethyl ether (three times 20 mL) and with CH_2Cl_2 (three times 20 mL) and concentration of the combined organic layer in vacuo the crude product was purified by flash chromatography (silica, diethyl ether/*n*-hexane, 1:5): R_f = 0.42, 0.28 (**1.6**)) and dried in vacuo (50 °C, 0.5 mbar, 4 h): 428 mg (60%) of colorless crystals **1.6** with m.p. 110–115 °C. IR (KBr): $\tilde{\nu}$ = 3503 (s), 3054 (w), 3011 (w), 2983 (w), 2961 (w), 2935 (w), 2917 (w), 2836 (w), 1598 (br. s, sh), 1449 (br. s, sh), 1341 (m), 1299 (s), 1163 (s), 1132 (s), 1067 (s), 1045 (m), 1030 (m), 1008 (m), 1001 (m), 959 (m), 851 (s), 772 (s), 698 (s) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 198 (4.83), 207 (4.77, sh), 235 (3.96, sh) nm. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.87 (s, 6 H), 2.73 (s, 1 H, O*H*), 3.78 (s, 3 H), 6.54 (s, 2 H, 3-H/5-H), 7.21–7.34 (m, 10 H) ppm. ^{13}C NMR {^1H} ($CDCl_3$, 75.5 MHz): δ = 24.71 (q, *C*H$_3$), 54.99 (q, O*C*H$_3$), 83.38 (s, *C*-OH), 115.51 (d), 127.30 (d), 127.87 (d), 128.18 (d), 136.67 (s), 139.89 (s), 147.85 (s), 157.64 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 319 (10) [M^+ + 1], 318 (38) [M^+], 301 (29), 300 (11), 241 (31), 223 (24), 183 (26), 165 (19), 163 (25), 136 (21), 105 (100), 77 (35). $C_{22}H_{22}O_2$ (318.42): calcd. C 82.99, H 6.96; found C 83.07, H 6.95.

9-(2,6-Dimethylphenyl)-9-hydroxyxanthene (1.7): To a solution of 5.55 g (30.0 mmol) of 1-bromo-2,4-dimethylbenzene in 30 mL of dry THF was added 40.9 mL (60.0 mmol) of *n*-butyllithium (1.6 M in *n*-hexane) at –78 °C within 15 min. The colorless suspension was stirred for 1 h and 5.88 g (30.0 mmol) of xanthone was added in one portion. The reaction mixture was stirred at room temperature for 2 h and was hydrolyzed with 30 mL of water. After extraction with CH_2Cl_2 (three times 30 mL) the combined organic layer was dried with sodium sulfate and was concentrated in vacuo. The crude product was purified by flash chromatography (silica, ethyl acetate/petroleum ether, 1:5: R_f = 0.27) and dried in vacuo (70 °C, 0.5 mbar, 1 h): 8.49 g (94%) of **1.7** as colorless crystals with m.p. 172–173 °C. IR (KBr): $\tilde{\nu}$ = 3510 (m), 2914 (m), 1924 (w), 1700 (w), 1601 (m), 1573 (m), 1477 (s), 1446 (m), 1380 (m), 1357 (m), 1312 (s), 1291 (s), 1237 (s), 1205 (s), 1176 (m), 1153 (m), 1116 (m), 1001 (m), 1040 (m), 991 (s), 946 (m), 929 (m), 896 (m), 874 (s), 824 (m), 798 (m), 759 (s) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 239 (3.64), 281 (3.45), 289 (3.51) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 1.48 (s, 3 H), 2.41 (s, 3 H), 2.44 (s, 1 H, OH), 6.90 (br. s, 1 H), 7.06 ("t", "*J*" = 7.8 Hz, 2 H), 7.15 (dd, *J* = 7.8, 1.8 Hz, 2 H) 7.24–7.28 (m, 3 H), 7.37 ("t", "*J*" = 7.8 Hz, 2 H), 8.28 (d, *J* = 7.8 Hz, 1 H) ppm. ^{13}C NMR {^1H} ($CDCl_3$, 125 MHz): δ = 20.52 (q), 20.93 (q), 69.85 (s), 116.29 (d), 123.52 (d), 125.88 (d), 125.90 (d), 126.05 (s), 128.77 (d), 129.21 (d), 132.83 (d), 135.46 (s), 137.34 (s), 140.98 (s), 150.10 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 302 (13) [M^+], 286 (4), 285 (20), 198 (13), 197 (100), 181 (3), 141 (4), 115 (4), 77(6). $C_{12}H_{18}O_2$ (194.27): calcd. C 83.42, H 6.00; found C 83.38, H 5.98.

9-Hydroxy-9-(4-methylphenyl)xanthene (1.8): To a solution of 3.70 mL (30.0 mmol) of 4-bromotoluene in 80 mL of dry THF was added 23.4 mL (37.5 mmol) of *n*-butyllithium (15% in hexane) at –78 °C within 5 min. After 30 min additional stirring 5.89 g (30.0 mmol) of xanthone was added and the reaction mixture was warmed up to room temperature overnight. After hydrolysis with 20 mL of water and extraction with CH_2Cl_2 (three times 20 mL) the organic layer was concentrated to dryness and the residue recrystallized from pentane. After drying in vacuo for (2 h at 0.5 mbar and 70 °C) 3.75 g (43%) of xanthenol **1.8** as a colorless solid with m.p. 140–141 °C was obtained (ref.[13–15] m.p. between 141 and 150 °C). ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.29 (s, 3H), 2.59 (s, 1 H, OH), 7.09–7.03 (m, 4 H), 7.19 (dd, *J* = 8.3, 1.0 Hz, 2 H), 7.31–7.26 (m, 5 H), 7.38 (dd, *J* = 8.1, 1.8 Hz, 2 H) ppm. ^{13}C

NMR {^{1}H} ($CDCl_3$, 100 MHz): δ = 21.03 (q), 70.44 (s), 116.43 (d), 123.58 (d), 126.17 (d), 127.48 (s), 128.72 (d), 128.98 (d), 129.03 (d), 136.40 (s), 145.22 (s), 149.77 (s) ppm.

9-(2,4,6-Trimethylphenyl)xanthenylium Tetrafluoroborate (2.1): 0.98 g (3.10 mmol) of xanthenol **1.1** in 40 mL of dry diethyl ether was treated with 1 mL (7.4 mmol) of HBF_4 etherate (15% in Et_2O). After 1 h of stirring at room temperature, the slightly yellow precipitate was collected, washed with Et_2O and dried in vacuo (100 °C, 0.5 mbar, 2 H): 1.16 g (98%) of the yellow solid **2.1** with m.p. 251–254 °C. IR (KBr): $\tilde{\nu}$ = 3075 (vw), 1623 (w), 1599 (s), 1576 (w), 1536 (w), 1508 (s), 1436 (w), 1373 (s), 1084 (s), 1053 (s), 761 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 197 (4.42), 258 (4.30), 372 (4.20), 444 (3.23) nm. ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 1.83 (s, 6 H), 2.48 (s, 3 H), 7.18 (s, 2 H), 7.27–8.00, (m, 4 H), 8.56–8.67 (m, 4 H) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): {^{1}H} δ = 20.13 (q), 21.25 (q), 121.11 (d), 124.43 (s), 127.42 (s), 129.23 (d), 129.93 (d), 130.11 (d), 135.34 (s), 141.71 (s), 145.12 (d), 158.49 (s), 177.90 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 299 (100) [M^+ – BF_4], 154 (20), 136 (14). $C_{22}H_{19}BF_4O$ (386.20): calcd. C 68.42, H 4.96; found C 68.20, H 4.91.

9-(4-Methoxy-2,6-dimethylphenyl)xanthenylium Tetrafluoroborate (2.2): To a solution of 180 mg (0.542 mmol) of xanthenol **1.2** in 4 mL of dry dichloromethane was added 0.25 mL (1.8 mmol) of HBF_4·OEt_2 (15% in Et_2O). After 5 min of stirring at room temperature a layer of 10 mL of diethyl ether is carefully placed on the reaction mixture. Slow diffusion led to the formation of a red precipitate (2 d), which was collected, washed with Et_2O and dried in vacuo (60 °C, 0.5 mbar, 2 h): 195 mg (90%) of the red solid **2.2** with m.p. 293–296 °C. IR (KBr): $\tilde{\nu}$ = 3050 (w), 3013 (w), 2963 (w), 1621 (w), 1600 (s), 1576 (m), 1535 (m), 1501 (m), 1467 (m), 1371 (m), 1352 (w), 1314 (m), 1200 (w), 1166 (w), 1145 (w), 1125 (m), 1084 (s, br.), 882 (w), 805 (w), 764 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 202 (4.80), 225 (4.41, sh), 257 (4.70), 274 (3.80), 354 (4.24), 372 (4.63), 443 (3.53) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.85 (s, 6 H, *C*H_3), 3.95 (s, 3 H, O*C*H_3), 6.95 (s, 2 H, 3-H/5-H), 7.99 ("d", "*J*" = 4.0 Hz, 4 H), 8.51 (d, *J* = 8.8 Hz, 2 H), 8.60–8.66 (m, 2 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 75.5 MHz): δ = 20.42 (q), 55.65 (q), 114.20 (d), 120.55 (d), 122.47 (s), 124.68 (s), 130.35 (d), 130.76 (d), 137.44 (s), 145.37 (d), 158.34 (s), 162.19 (s), 178.76 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 334 (4) [M^+ – BF_3], 316 (32), 315 (100) [M^+ – BF_4], 313 (5), 300 (6), 299 (5), 272 (9), 271 (6), 257 (8), 256 (5), 255 (10), 199 (12), 181 (8). $C_{22}H_{19}BF_4O_2$ (402.20): calcd. C 65.70, H 4.76; found C 65.54, H 4.81.

9-(4-Dimethylamino-2,6-dimethylphenyl)xanthenylium Tetrafluoroborate (2.3): To a solution of 104 mg (0.300 mmol) of xanthenol **1.3** in 5.5 mL of dry dichloromethane was added 0.041 mL (0.3 mmol) of HBF_4·OEt_2 (15% in Et_2O). After 5 min of stirring at room temperature a layer of 12 mL of diethyl ether is carefully placed on the reaction mixture. Slow diffusion led to the formation of a red precipitate (24 h), which was collected, washed with Et_2O and dried in vacuo (60 °C, 0.5 mbar, 2 h): 110 mg (88%) of green crystals **2.3** with m.p. 260 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3060 (w), 2536 (w), 2440 (w), 1623 (m), 1598 (s), 1534 (m), 1508 (s), 1480 (m), 1374 (s), 1084 (vs, br.), 767 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 201 (4.76), 275 (3.80), 374 (4.63) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.88 (s, 6 H), 3.15 (s, 6 H), 6.66 (s, 2 H), 7.80–8.00 (m, 4 H), 8.40–8.50 (m, 4 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 125 MHz): δ = 21.33 (q), 40.40 (q), 112.15 (d), 120.75 (d), 124.87 (s), 129.61 (d), 131.15 (d), 137.53 (s), 144.11 (d), 152.29 (s), 157.86 (s), 178.41 ppm. MS (70 eV, EI): *m*/*z* (%) = 328 (72) [M^+ – BF_4], 312 (20), 181 (100), 163 (20), 49 (52).

9-(4-Methoxy-2,6-dimethylphenyl)thioxanthenylium Tetrafluoroborate (2.4): To a solution of 110 mg (0.316 mmol) of thioxanthenol **1.4** in 2 mL of dry dichloromethane was added 0.13 mL (0.96 mmol) of HBF_4·OEt_2 (15% in Et_2O). After 10 min of stirring at room temperature a layer of 15 mL of diethyl ether is carefully placed on the reaction mixture. Slow diffusion (1 d) led to the formation of a red precipitate, which was collected, washed with Et_2O and dried in vacuo (80 °C, 0.04 mbar, 2 h): 123 mg (93%) of the deep red solid **2.4** with m.p. 255–260 °C. IR (KBr): $\tilde{\nu}$ = 3047 (w), 3003 (w), 2965 (w), 2935 (w), 1632 (w), 1604 (m), 1544 (w), 1451 (m), 1372 (m), 1320 (m), 1198 (w), 1157 (m), 1124 (m), 1084 (s, br.), 1037 (m), 859 (w), 803 (w), 743 (m), 624 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 201 (4.76), 225 (4.43), 247 (4.12, sh), 280 (4.88), 361 (3.74, sh), 381 (4.29), 495 (3.60), 521 (3.57) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.73 (s, 6 H), 3.96 (s, 3 H, O*C*H_3), 6.92 (s, 2 H, 3-H/5-H), 8.07 (ddd, *J* = 7.9, 6.8, 1.1 Hz, 2 H), 8.19 (dd, *J* = 8.7, 0.7 Hz, 2 H), 8.44 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 2 H), 8.94 (d, *J* = 8.5 Hz, 2 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 75.5 MHz): δ = 20.43 (q, *C*H_3), 55.54 (q, O*C*H_3), 114.06 (d), 125.89 (s), 128.82 (d), 130.25 (s), 132.03 (d), 133.76 (d), 137.29 (s), 138.14 (d), 148.25 (s), 161.34 (s), 172.80 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 333 (8), 332 (327), 331 (100) [M^+ – BF_4], 273 (13), 271 (10), 197 (7). $C_{22}H_{19}BF_4OS$ (418.26): calcd. C 63.18, H 4.58; found C 63.15, H 4.50.

(4-Methoxy-2,6-dimethylphenyl)diphenylmethyl Tetrafluoroborate (2.6): To a solution of 210 mg (0.66 mmol) of triarylmethanol 1.6 in 5 mL of dry dichloromethane was added 0.25 mL (1.8 mmol) of HBF_4·OEt_2 (15% in Et_2O). After 5 min of stirring at room temperature a layer of 15 mL of diethyl ether is carefully placed on the reaction mixture. Slow diffusion (1 d) led to the formation of a red precipitate, which was collected, washed with Et_2O and dried in vacuo (80 °C, 0.04 mbar, 2 h): 219 mg (86%) of violet crystals **2.6** with m.p. 139–142 °C. IR (KBr): $\tilde{\nu}$ = 3059 (w), 2936 (w), 1598 (s), 1583 (s), 1482 (w), 1450 (m), 1352 (m), 1291 (s, sh), 1182 (m), 1155 (m), 1124 (m), 1084 (s, br.), 1038 (m), 995 (w), 771 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 199 (4.80), 253 (3.93), 310 (3.65), 413 (4.31), 528 (4.26) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.81 (s, 6 H, C*H*$_3$), 4.12 (s, 3 H), 7.01 (s, 2 H), 7.59 (d, *J* = 7.2 Hz, 4 H), 7.80 (t, *J* = 7.7 Hz, 4 H), 8.13 (t, *J* = 6.9 Hz, 2 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 75.5 MHz): δ = 23.42 (q), 57.33 (q), 118.84 (d), 130.50 (s), 130.89 (d), 139.49 (d), 139.80 (s), 141.67 (d), 142.33 (s), 152.36 (s), 170.53 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 302 (38), 301 (82) [M^+ – BF_4], 300 (46), 299 (100), 287 (20), 285 (20), 284 (16), 269 (11), 253 (13), 252 (15), 241 (14), 239 (20), 223 (13), 179 (20), 166 (13), 165 (39), 126 (12). $C_{22}H_{21}BF_4O$ (388.21): calcd. C 68.07, H 5.45; found C 68.01, H 5.39.

9-(2,4-Dimethylphenyl)xanthenylium Tetrafluoroborate (2.7): To a solution of 300 mg (0.99 mmol) of triarylmethanol **1.7** in 10 mL of dry dichloromethane was added 0.41 mL (2.9 mmol) of HBF_4·OEt_2 (15% in Et_2O). After 10 min of stirring at room temperature a layer of 20 mL of diethyl ether is carefully placed on the reaction mixture. Slow diffusion (1 d) led to the formation of a yellow precipitate, which was collected, washed with Et_2O and dried in vacuo (100 °C, 0.5 mbar, 3 h): 280 mg (92%) of **2.7** as yellow solid with m.p. 225–230 °C. IR (KBr): $\tilde{\nu}$ = 3511 (w), 3073 (w), 1625 (m), 1599 (s), 1577 (m), 1537 (m), 1508 (s), 1436 (m), 1402 (s), 1373 (m), 1285 (w), 1234 (w), 1211 (w), 1150 (m), 1097 (s), 1053 (s), 879 (s), 829 (w), 805 (w), 759 (s) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 205 (4.57), 258 (4.60), 290 (2.76), 368 (4.45), 371 (4.45), 449 (3.74) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.99 (s, 3 H), 2.52 (s, 3 H), 7.30–7.36 (m, 3 H), 7.90–7.97 (m, 4 H), 8.47 ("d", *J* = 8.6 Hz, 2 H), 8.54 ("t", *J* = 8.6 Hz, 2 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 125 MHz): δ = 20.16 (q), 21.51 (q), 120.61 (d), 124.37 (s), 127.24 (d), 127.87 (s), 129.53 (d), 129.83 (d), 131.14 (d), 131.98 (d), 135.87 (s), 142.48 (s), 144.45 (d), 158.63 (s), 176.67 (s) ppm. MS (70 eV, EI): *m*/*z* (%) =

304 (29) [$M^+ - BF_4$], 286 (18), 285 (63), 269 (11), 255 (6), 199 (100), 181 (16), 49 (10). $C_{21}H_{17}BF_4O$ (372.17): calcd. C 67.74, H 4.56; found C 67.74, H 4.74.

9-(4-Methylphenyl)xanthenylium Tetrafluoroborate (2.8): 3.72 g (12.9 mmol) of xanthenol **1.8** was dissolved in 25 mL of dry CH_2Cl_2 and 5.0 mL (36 mmol) of $HBF_4{\cdot}OEt_2$ (15% in diethyl ether) was added. After 10 min of stirring at room temperature a layer of 40 mL of diethyl ether was carefully placed on the reaction mixture. Slow diffusion (1 d) led to the formation of a yellow to orange precipitate, which was collected, washed with diethyl ether and dried in vacuo (50 °C, 0.5 mbar, 4 h): The formed yellow solid was removed by filtration, washed with diethyl ether (3×10 mL) and dried in vacuo (100 °C, 0.5 mbar, 3 h): 4.60 g (95%) of the orange solid (a hydrate according to NMR) with m.p. 210–215 °C (ref.[13] m.p. 200 °C, dec.). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.59 (s, 3 H), 2.80 (broad s, hydrate), 7.58 ("d", J = 8.0 Hz, 2 H), 7.62 ("d", J = 8.0 Hz, 2 H), 7.92 ("t", J = 7.7 Hz, 2 H), 8.18 (dd, J = 8.2, 1.3 Hz, 2 H), 8.33 (d, J = 8.7 Hz, 2 H), 8.36–8.54 (m, 4 H) ppm.

Reaction of 2.1 with Nucleophile A. 2-[9-(2,4,6-Trimethylphenyl)-xanthen-3-yliden]malononitrile (6.1A): To 132 mg (2.00 mmol) of malononitrile (**A**) in 20 mL of dry THF at –78 °C 1.0 mL of *n*-butyllithium (2.5 M in hexane) were slowly added and the reaction mixture was stirred for 30 min. 750 mg (2.00 mmol) of the mesityl-substituted xanthenylium salt **2.1** was added in the cold and the reaction mixture was stirred for 24 h at room temperature. After hydrolysis with 20 mL of saturated aqueous diammonium hydrogen phosphate solution and extraction with CH_2Cl_2 (three times 20 mL) the organic layer was concentrated and the residue was purified by flash chromatography (silica, petroleum ether/ethyl acetate, 1:1, R_f = 0.29): 695 mg (96%) of the *p*-quinoid compound **6.1A** as a deep purple solid with m.p. 228–231 °C. IR (KBr): $\tilde{\nu}$ = 2923 (w), 2203 (s), 1635 (m), 1599 (m), 1469 (s), 1414 (m), 1322 (m), 1152 (m), 843 (m), 754 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 197 (4.82), 292 (3.97), 370 (3.81), 529 (4.39), 568 (4.48), 617 (4.31) nm. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.94 (s, 6 H), 2.42 (s, 3 H), 6.84 (d, J = 9.4 Hz, 1 H), 7.04 (d, J = 1.8 Hz, 1 H), 7.06 (s, 2 H), 7.09 (dd, J = 8.1 Hz, J = 1.5 Hz, 1 H), 7.21 (dd, J = 9.4 Hz, J = 1.8 Hz, 1 H), 7.24("t", "J" = 8.2 Hz, 1 H), 7.51 (dd, J = 8.5 Hz, J = 0.8 Hz, 1 H), 7.67 ("t", "J" = 7.8 Hz, 1 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 125 MHz): δ = 19.80 (q), 21.17 (q), 64.55 (d), 102.52 (d), 115.90 (s), 116.07 (s), 117.23 (d), 121.23 (s), 122.74 (s), 125.48 (d), 125.93 (s), 127.66 (s), 128.22 (d), 128.84 (d), 128.96 (d), 134.60 (d), 135.90 (s), 139.53 (s), 150.65 (s), 153.06 (s), 155.98 (s), 157.35 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 362 (22) [M^+], 332 (7), 299 (30), 181 (25), 66 (100). $C_{25}H_{18}N_2O$ (362.43): calcd. C 82.85, H 5.01, N 7.73; found C 82.63, H 5.04, N 7.72.

Reaction of 2.1 with Nucleophile B. 3-Bis[(4,4-dimethyl-4,5-dihydrooxazol-2-yl)methylene]-9-(2,4,6-trimethylphenyl)-3*H*-xanthene (6.1B): 210 mg (1.00 mmol) of bis(4,4-dimethyl-4,5-dihydrooxazol-2-yl)methane (**D**) in 20 mL of dry THF was treated with 40 mg of NaH (60% in mineral oil, 1.00 mmol) for 30 min at room temperature. 386 mg (1.00 mmol) of the mesityl-substituted xanthenylium salt **2.1** was added and the reaction mixture stirred for 24 h at room temperature. After hydrolysis with 20 mL of saturated aqueous diammonium hydrogen phosphate solution and extraction with CH_2Cl_2 (three times 20 mL) the organic layer was concentrated and the residue was purified by flash chromatography (silica, petroleum ether/ethyl acetate, 1:1, R_f = 0.46): 475 mg (94%) of the *p*-quinoid compound **6.1B** as a deep red solid with m.p. 226 °C. IR (KBr): $\tilde{\nu}$ = 2963 (w), 1656 (m), 1605 (m), 1577 (m), 1473 (s), 1260 (m), 1187 (m), 1011 (m), 725 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 261 (4.12), 268 (4.10), 355 (3.83), 577 (3.90) nm. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.25 (s, 6 H), 1.34 (s, 6 H), 1.90 (s, 6 H, *o*-CH_3), 2.28 (s, 3 H, *p*-CH_3), 4.24 ("d", 4 H, CH_2), 6.27 (d, J = 9 Hz, 1 H), 6.65 (d, J = 9 Hz, 1 H), 6.84 (m, 1 H), 6.90 (s, 2 H), 7.07 (d, J = 8 Hz, 1 H), 7.23 (m, 2 H), 7.37 ("d", 1 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 100 MHz): δ = 19.64 (q), 21.14 (q), 28.20 (q), 28.45 (q), 67.61 (s), 67.81 (s), 74.75 (s), 78.08 (t), 78.32 (t), 103.66 (d), 105.53 (s), 116.02 (d), 122.20 (s), 123.60 (d), 124.23 (s), 125.81 (d), 125.94 (d), 128.42 (d), 128.80 (d), 128.75 (s), 131.02 (d), 136.69 (s), 137.44 (s), 138.16 (s), 144.55 (s), 152.99 (s), 153.14 (s), 161.12 (s) ppm. MS (FAB): *m*/*z* (%) = 507 (47), 507 (100), 506 (43) [M^+], 136 (60). $C_{33}H_{34}N_2O_3$ (506.64): calcd. C 78.23, H 6.76, N 5.53; found C 77.91, H 6.67, N 5.49.

Reaction of 2.1 with Nucleophile C. *S*,*S*-3-Bis[(4-isopropyl-2-methyl-4,5-dihydrooxazolyl)methylene]-9-(2,4,6-trimethylphenyl)-3*H*-xanthene (6.1C): 57 mg (0.24 mmol) of bisoxazoline **E** in 2.5 mL of dry DMF was treated with 11 mg of NaH (60% in mineral oil, 0.28 mmol) for 30 min at room temperature. 78 mg (0.2 mmol) of the mesityl-substituted xanthenylium salt **2.1** in 1.5 mL DMF was added and the red solution stirred at 70 °C for 6 h. After hydrolysis with 20 mL of water and extraction with CH_2Cl_2 (three times 25 mL) the organic layer was washed with water (20 mL), brine (20 mL), dried with Na_2SO_4 and concentrated and the residue was fractionated by flash chromatography (silica, petroleum ether/diethyl ether/methanol, 50:25:2; R_f = 0.78, 0.69, 0.31). The fraction with R_f = 0.69 gave 65 mg (61%) of the *p*-quinoid compound **6.1C** as a deep red solid with m.p. 226–231 °C. IR (KBr): $\tilde{\nu}$ = 2963 (s), 2909 (m), 1622 (m), 1470 (s), 1351 (m), 1312 (m), 1265 (m), 1201 (m), 1113 (w), 992 (m), 850 (w), 756 (w), 653 (w), 616 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 211 (4.21), 361 (3.75), 506 (3.95) nm. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.91 (d, J = 5.9 Hz, 3 H), 0.98 (t, J = 6.8 Hz, 6 H), 1.07 (d, J = 6.65 Hz, 3 H), 1.87–1.92 (m, 2 H), 1.97 (s, 6 H), 2.36 (s, 3 H), 4.00–4.13 (m, 4 H), 4.27–4.34 (m, 2 H), 6.33 (d, J = 9.7 Hz, 1 H), 6.71 (dd, J = 7.85, 1.45 Hz 1 H), 6.93 (td, J = 7.25, 1.05 Hz, 1 H), 6.98 (s, 2 H), 7.14 (dd, J = 8.3, 1.0 Hz, 1 H), 7.28–7.32 (m, 2 H), 7.42 (dd, J = 9.8, 1.75 Hz, 1 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 125 MHz): δ = 18.36 (q), 18.43 (q), 19.09 (q), 19.64 (q), 21.12 (q), 32.83 (d), 32.94 (d), 69.34 (t), 69.52 (t), 72.77 (d), 103.53 (d), 105.68 (s), 115.96 (d), 122.12 (s), 123.58 (d), 124.07 (s), 125.66 (d), 125.90 (d), 128.39 (d), 128.72 (d), 129.64 (s), 131.00 (d), 136.62 (s), 136.69 (s), 137.46 (s), 138.12 (s), 143.89 (s), 152.91 (s), 152.96 (s), 162.57 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 535 (63), 491 (100) [M^+], 405 (37), 380 (21), 337 (11), 314 (25), 299 (12), 285 (14), 237 (18), 41 (13). $C_{35}H_{38}N_2O_3$ (534.70) + 0.5H_2O: calcd. C 77.32, H 7.23, N 5.15; found C 76.95, H 7.47, N 4.97.

Reaction of 2.1 with Nucleophile D. 3-(Dipyridin-2-ylmethyl)-9-(2,4,6-trimethylphenyl)xanthene (5.1D): To 900 mg (5.30 mmol) of 2-(pyridin-2-ylmethyl)pyridine **D** in 20 mL of dry THF at –78 °C was added 2.1 mL (5.30 mmol) of *n*-butyllithium (2.5 M in hexane) within 2 min, then the reaction mixture was stirred for 30 min. A suspension of 772 mg (2.00 mmol) of the mesityl-substituted xanthenylium salt **2.1** in of dry THF was added and the reaction mixture was stirred at room temperature for 16 h. After hydrolysis with 25 mL of aqueous ammonium chloride solution and extraction with diethyl ether (three times 25 mL) the organic layer was dried with Na_2SO_4 and concentrated. 370 mg of starting material **D** were recovered by distillation in the kugelrohr oven at 160 °C and 0.3 mbar. The residue was fractionated by flash chromatography (silica, petroleum ether/ethyl acetate, 1:3; R_f = 0.71, 0.46, 0.23, 0.11): The fraction with R_f = 0.23 gave 870 mg (93%) of compound **5.1D** as a colorless solid with m.p. 200 °C. IR (KBr): $\tilde{\nu}$ = 3427 (m, br.), 3005 (w), 2963 (w), 2917 (w), 2868 (w), 1588 (s), 1567 (s), 1484 (s), 1470 (m), 1456 (m), 1419 (s), 1322 (m), 1272 (m), 1244 (m),

1102 (w), 996 (w), 979 (w), 859 (w), 788 (w), 752 (s), 699 (w), 620 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 220 (4.68, sh), 257 (4.18), 270 (4.02, sh), 285 (3.57), 295 (3.59) nm. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.63 (s, 3 H), 2.27 (s, 3 H), 2.50 (s, 3 H), 5.77 (s, 1 H), 5.83 (s, 1 H), 6.67 (dd, *J* = 7.9, 1.1 Hz, 1 H), 6.73 (m, 2 H), 6.79 (dd, *J* = 8.1, 1.7 Hz, 1 H), 6.85 (td, *J* = 7.5, 1.3 Hz, 1 H), 6.95 (br. s, 1 H), 6.96 (d, *J* = 1.8 Hz, 1 H), 6.98 (dd, *J* = 8.2, 1.3 Hz, 1 H), 7.11–7.15 (m, 3 H), 7.25–7.27 (m, 2 H), 7.63 (m, 2 H), 8.58 (m, 2 H) ppm. ^{13}C NMR {^1H} ($CDCl_3$, 125 MHz): δ = 20.77 (q), 20.88 (q), 21.21 (q), 36.97 (d), 61.28 (d), 115.99 (d), 116.77 (d), 121.63 (d), 122.18 (s), 123.06 (d), 123.78 (s), 124.03 (d), 124.16 (d), 127.59 (d), 128.09 (d), 128.18 (d), 128.62 (d), 131.42 (d), 136.48 (s), 136.54 (d), 137.01 (s), 137.34 (s), 137.75 (s), 141.56 (s), 149.46 (d), 150.87 (s), 150.89 (s), 161.90 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 469 (33), 468 (100) [M^+], 389 (22), 349 (75), 299 (69), 270 (54), 174 (26), 169 (6). $C_{33}H_{28}N_2O$ (468.60): calcd. C 84.59, H 6.02, N 5.98; found C 84.51, H 6.02, N 5.99.

Reaction of 2.1 with Nucleophile E. Quinolin-8-yl-[9-(2,4,6-trimethylphenyl)xanthen-3-ylidene]amine (6.1E): 288 mg (2.00 mmol) 8-aminoquinoline (**E**) in 20 mL of dry THF was treated with 80 mg of NaH (60% in mineral oil, 2.00 mmol) for 4 h at room temperature. 388 mg (1.00 mmol) of the xanthenylium salt **2.8** was added and the reaction mixture was stirred at room temperature for 24 h. After hydrolysis with a saturated aqueous solution of Na_2HPO_4, extraction with CH_2Cl_2 (3 × 20 mL) and removal of the solvent and the excess of nucleophile in vacuo (100 °C, 0.5 mbar), the product was isolated by flash chromatography (silica, methyl *tert*-butyl ether/CH_2Cl_2, 1:10, R_f = 0.44): 139 mg (32%) of the metallic shiny black solid **6.1E** with m.p. 172–174 °C. IR (KBr): $\tilde{\nu}$ = 2921 (vw), 1637 (s), 1596 (s), 1559 (m), 1542 (m), 1507 (s), 1490 (a), 1486 (s), 1472 (s), 1386 (m), 1326 (m), 1326 (m), 1149 (m), 1058 (m), 827 (w), 759 (w) cm^{-1}. UV ($CHCl_3$) λ_{max} (log ε): 243 (4.17), 274 (3.90), 362 (3.77), 515 (4.02) nm. ^1H NMR ($CDCl_3$, 400 Hz): δ = 1.90 (s, 6 H, *o*-CH_3), 2.43 (s, 3 H, *p*-CH_3), 7.10 (s, 2 H), 7.35–7.53 (m, 5 H), 7.68 (t, *J* = 8.6 Hz, 1 H), 7.83–7.86 (m, 2 H), 7.95 (t, *J* = 8.6 Hz, 1 H), 8.05 (d, *J* = 8.60 Hz, 1 H), 8.25 (dd, *J* = 8.3, 1.5 Hz, 1 H), 8.90 (dd, *J* = 8.3, 1.5 Hz, 1 H) ppm. ^{13}C NMR {^1H} ($CDCl_3$, 100 MHz): δ = 19.97 (d), 21.24 (d), 118.49 (d), 120.86 (d), 121.08 (s), 122.46 (d), 123.91 (q), 126.90 (d), 126.95 (d), 127.63 (s), 127.86 (s), 128.81 (d), 129.10 (d), 129.14 (d), 131.79 (s), 133.44 (s), 135.52 (d), 136.61 (d), 137.60 (d), 140.54 (s), 141.74 (q), 150.44 (d), 154.34 (s), 161.60 (s) ppm, two signals are missing. MS (70 eV, EI): *m*/*z* (%) = 442 (37), 441 (100) [M + H^+], 154 (27), 136 (25). $C_{31}H_{24}N_2O$ (440.54): calcd. C 84.52, H 5.49, N 6.36; found C 84.49, H 5.41, N 6.74.

Reaction of 2.2 with Nucleophile A. 2-[9-(4-Methoxy-2,6-dimethylphenyl)xanthen-3-ylidene]malononitrile (6.2A): 26 mg (0.39 mmol) of malononitrile (**A**) in 3 mL of dry THF was treated with 18 mg (60% in mineral oil, 0.45 mmol) of NaH for 20 min at room temperature. 100 mg (0.249 mmol) of the (4-methoxy-2,6-dimethylphenyl)-substituted xanthenylium salt **2.2** in 5 mL of THF was added and the reaction mixture was stirred at room temperature for 18 h. After hydrolysis with 20 mL of saturated aqueous diammonium hydrogen phosphate solution and extraction with CH_2Cl_2 (three times 20 mL) the organic layer was concentrated and the residue (91 mg of a slightly impure crude product) was purified by flash chromatography (silica, *n*-hexane/diethyl ether, 2:3, R_f = 0.35): 56 mg (58%) of the *p*-quinoid compound **6.2A** as dark green crystals with m.p. 239–243 °C. IR (KBr): $\tilde{\nu}$ = 3067 (w), 2936 (w), 2841 (w), 2204 (s), 1630 (s), 1596 (s), 1546 (w), 1525 (w), 1467 (s), 1413 (m), 1361 (m), 1325 (m), 1311 (s), 1251 (w), 1211 (w), 1196 (w), 1149 (m), 1131 (m), 1112 (w), 1063 (w), 843 (w), 758 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 201 (4.79), 229 (4.51), 261 (3.88), 282 (3.88), 296 (3.95), 311 (3.98), 345 (4.36), 388 (3.77), 460 (3.82, sh), 489 (4.13, sh), 528 (4.39), 569 (4.49), 619 (4.31) nm. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.96 (s, 6 H, C*H*$_3$), 3.89 (s, 3 H, OC*H*$_3$), 6.79 (s, 2 H, 3-H/5-H), 6.86 (d, *J* = 9.4 Hz, 1 H), 7.04 (s, 1 H, 4-H), 7.11 (dd, *J* = 8.0, 1.4 Hz, 1 H), 7.20–7.28 (m, 2 H), 7.51 (d, *J* = 8.4 Hz, 1 H), 7.67 ("t", "*J*" = 8.5 Hz, 1 H) ppm. ^{13}C NMR {^1H} ($CDCl_3$, 75.5 MHz): δ = 20.25 (q), 55.33 (q), 64.82 (s), 102.61 (d), 113.60 (d), 115.91 (s), 116.08 (s), 117.30 (d), 121.62 (s), 123.27 (s), 123.46 (s), 125.53 (d), 126.06 (d), 127.75 (d), 129.05 (d), 134.60 (d), 137.77 (s), 150.39 (s), 153.15 (s), 156.07 (s), 157.39 (s), 160.41 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 379 (28), 378 (100) [M^+], 335 (3), 320 (8), 319 (6), 318 (4), 305 (3), 255 (3), 189 (10). $C_{25}H_{18}N_2O_2$ (378.43): calcd. C 79.35, H 4.79, N 7.40; found C 79.40, H 4.75, N 7.37.

Reaction of 2.3 with Nucleophile A. 2-{9-[2,6-Dimethyl-4-(dimethylamino)phenyl]xanthen-3-ylidene}malononitrile (6.3A): 13 mg (0.20 mmol) of malononitrile (**A**) in 2 mL of dry THF was treated with 9 mg (60% in mineral oil, 0.225 mmol) of NaH for 30 min at room temperature. 34 mg (0.10 mmol) of the [2,6-dimethyl-4-(dimethylamino)phenyl]-substituted xanthenylium salt **2.3** was added and the reaction mixture was stirred at room temperature for 21 h. After hydrolysis with 20 mL of saturated aqueous diammonium hydrogen phosphate solution and extraction with CH_2Cl_2 (three times 20 mL) the organic layer was concentrated and the residue was purified by flash chromatography (silica, petroleum ether/diethyl ether, 1:1, R_f = 0.25): 35 mg (90%) of the *p*-quinoid compound **6.3A** as purple solid with m.p. 238–242 °C. IR (KBr): $\tilde{\nu}$ = 3050 (w), 2628 (w), 2208 (s), 1678 (m), 1634 (s), 1594 (s), 1530 (w), 1471 (s), 1416 (m), 1205 (s), 1143 (s), 842 (w), 799 (w), 743 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 216 (4.57), 261 (4.36), 309 (4.19), 370 (3.86), 528 (4.40), 568 (4.48), 621 (4.32) nm. ^1H NMR ($CDCl_3$, 500 MHz): δ = 1.93 (s, 6 H), 3.05 (s, 6 H), 6.56 (s, 2 H), 6.94(d, *J* = 9.35 Hz, 1 H), 7.03 (d, *J* = 1.95 Hz, 1 H), 7.20("t", "*J*" = 8 Hz, 1 H), 7.24 (dd, *J* = 7 Hz, *J* = 1 Hz, 1 H), 7.26 (s, 1 H), 7.50 (dd, *J* = 8.5 Hz, *J* = 0.7 Hz, 1 H), 7.66 ("t", "*J*" = 7.8 Hz, 1 H) ppm. ^{13}C NMR {^1H} ($CDCl_3$, 125 MHz): δ = 20.53 (q), 40.27 (q), 63.61(s), 102.36 (d), 111.40 (d), 116.16 (s), 116.31 (s), 117.14 (s), 118.83 (d), 122.04 (s), 123.37 (s), 125.33 (d), 125.58 (d), 128.16 (d), 129.49 (d), 134.41 (d), 136.86 (s), 151.03 (s), 152.15 (s), 153.06 (s), 156.17 (s), 157.47 (s) ppm. MS (70 eV, EI): *m*/*z* (%) = 392 (27), 391 (100) [M^+], 375 (11), 195 (22). $C_{26}H_{21}N_3O$ (391.47): C 79.77, H 5.41, N 10.73; found C 79.70, H 5.06, N 10.55.

Reaction of 2.4 with Nucleophile A. 2-[9-(4-Methoxy-2,6-dimethylphenyl)thioxanthen-3-ylidene]malononitrile (6.4A) and 9-(4-Methoxy-2,6-dimethylphenyl)thioxanthen-3-one (7): 26 mg (0.39 mmol) of malononitrile (**A**) in 3 mL of dry THF was treated with 18 mg (60% in mineral oil, 0.45 mmol) of NaH for 20 min at room temperature. 100 mg (0.239 mmol) of the thioxanthenylium salt **2.4** was added and the reaction mixture was stirred at room temperature for 18 h. After hydrolysis with 20 mL of saturated aqueous diammonium hydrogen phosphate solution and extraction with CH_2Cl_2 (three times 20 mL) the organic layer was concentrated and the residue was purified by flash chromatography (silica, *n*-hexane/diethyl ether, 1:1, R_f = 0.29, 0.10).

1st Fraction: R_f = 0.29, 46 mg (49%) of the *p*-quinoid compound **6.4A** as brown metallic shiny crystals with m.p. 249–254 °C. IR (KBr): $\tilde{\nu}$ = 3060 (w), 2917 (w), 2840 (w), 2202 (s), 1605 (s), 1583 (s), 1490 (s), 1444 (s), 1408 (s), 1316 (m), 1287 (m), 1236 (m), 1195 (m), 1161 (m), 1146 (m), 1128 (m), 1083 (m), 1054 (m), 912 (w), 850 (w), 747 (w), 639 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 201 (4.77), 228 (4.23), 253 (4.41), 270 (4.05, sh), 306 (3.93, sh), 360 (4.45), 405 (3.92, sh), 427 (4.00), 490 (3.66, sh), 523 (4.02, sh), 565

(4.30), 610 (4.42), 664 (4.27) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.90 (s, 6 H), 3.90 (s, 3 H), 6.79 (s, 2 H, 3-H/5-H), 7.02 (d, J = 9.6 Hz, 1 H), 7.22 (dd, J = 9.6, 1.9 Hz, 2 H), 7.28–7.36 (m, 2 H), 7.55 ("dt", "J" = 7.0, 1.4 Hz, 1 H), 7.64 (dd, J = 8.1, 7.3 Hz, 1 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 125 MHz): δ = 20.13 (q), 55.30 (q), 63.46 (s), 113.53 (d), 113.55 (d), 115.99 (s), 116.25 (s), 125.76 (d), 126.09 (s), 126.38 (d), 126.78 (s), 127.71 (d), 128.80 (s), 131.17 (d), 131.96 (d), 132.99 (d), 135.70 (s), 137.65 (s), 142.61 (s), 152.93 (s), 153.00 (s), 160.04 (s) ppm. MS (70 eV, EI): m/z (%) = 396 (11), 395 (39), 394 (100) [M$^+$], 378 (6), 336 (8), 335 (6), 334 (4), 321 (5). $C_{25}H_{18}N_2OS$ (394.49): calcd. C 76.12, H 4.60, N 7.10; found C 76.00, H 4.68, N 7.01.

2nd Fraction: R_f = 0.10, ca. 37 mg (45%) of thioxanthenone **7** as dark orange oil, which still contains THF after 2 h at 150 °C in vacuo. IR (KBr): $\tilde{\nu}$ = 2941 (s), 2857 (s), 1608 (m), 1588 (w), 1486 (w), 1454 (w), 1383 (w), 1317 (w), 1115 (s, br.), 811 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 200 (4.56), 238 (4.29), 271 (4.03, sh), 283 (4.09), 295 (4.12), 306 (4.07), 360 (3.91), 377 (3.80, sh), 496 (3.74), 609 (4.08) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.91 (s, 6 H), 3.89 (s, 3 H, OCH_3), 6.65 (dd, 1 H), 6.78 (s, 2 H, 3-H/5-H), 6.86 ("d", "J" = 3.6 Hz, 1 H), 7.17–7.27 (m, 3 H), 7.50 (dd, 1 H), 7.61 (dd, 1 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 125 MHz): δ = 20.14 (q), 26.50 (t), 55.26 (q), 70.61 (t), 113.33 (d), 118.17 (d), 123.44 (s), 125.49 (d), 126.85 (d), 127.45 (s), 128.06 (s), 130.92 (d), 131.08 (d), 131.29 (d), 135.46 (s), 135.51 (d), 137.59 (s), 144.36 (s), 152.17 (s), 159.82 (s), 181.73 (s) ppm. MS (70 eV, EI): m/z (%) = 348 (10), 347 (28), 346 (100) [M$^+$], 319 (13), 318 (49), 317 (36), 303 (20), 285 (10), 271 (7), 259 (13), 258 (9), 245 (7), 129 (8). HMRS calcd. for $C_{22}H_{18}O_2S$: 346.10275; found 346.1021.

NMR Spectroscopic Test for the Intermediate 2-[9-(4-Methoxy-2,6-dimethylphenyl)-3*H*-thioxanthen-3-yl]malononitrile (4.4A): To a solution of 6 mg (0.09 mmol) of malononitrile (**A**) in 2 mL of dry $CDCl_3$ was added 4 mg (60% in mineral oil, 0.1 mmol) of NaH at –40 °C. After 10 min 35 mg (0.084 mmol) of the thioxanthenylium salt **2.4** was added and the reaction mixture was kept at –40 °C for additional 20 min, before a ^{1}H NMR spectrum of the red to brown reaction mixture was measured, which is in accord with structure **4.4A**. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.00 (s, 3 H, CH_3) 2.04 (s, 3 H, CH_3), 3.75 (d, J = 5.2 Hz, 1 H), 3.84 (s, 3 H, OCH_3), 4.02–4.06 (m, 1 H, 3′-H), 5.58 (dd, J = 4.8, 2.0 Hz, 1 H, 4′–H), 5.69–5.75 (m, 1 H), 6.14 (dd, J = 10.0, 1.2 Hz, 1 H), 6.57 (d, J = 7.9 Hz, 1 H), 6.69 (s, 2 H, 3-H/5-H), 6.86–6.91 (m, 1 H), 7.07–7.13 (m, 2 H) ppm. After 2 weeks at room temperature the colour of the reaction mixture had changed to blue and the ^{1}H NMR revealed that a clean transformation to **6.4A** had taken place.

Reaction of 1.5 with Nucleophile A. 2-[5-(4-Methoxy-2,6-dimethylphenyl)-10,11-dihydro-dibenzo[*a*,*d*]cyclohepten-2-ylidene]malononitrile (6.5A) and 5-(4-Methoxy-2,6-dimethylphenyl)-5*H*-dibenzo-[*a*,*d*]cycloheptene (8). Special Procedure: 200 mg (0.581 mmol) of triarylmethanol **1.5** and 157 mg (2.32 mmol) malononitrile in 10 mL abs. DMF were stirred at 150 °C for 19 h. The deep orange red solution was cooled to room temperature and 100 mL of H_2O was added. The aqueous layer was extracted with diethyl ether (5 times 50 mL) and the combined organic layer was reextracted with water (4 times 50 mL) and dried with sodium sulfate. After evaporation of the solvent in vacuo 215 mg of a reddish residue was obtained, which was fractionated by flash chromatography; TLC (silica, diethyl ether/*n*-hexane, 1:1): R_f = 0.64, 0.35.

1st Fraction: 112 mg (59%) of dibenzocycloheptatriene **8** as a yellow solid with 256–262 °C. IR (KBr): $\tilde{\nu}$ = 3012 (w), 2935 (w), 2837 (w), 1601 (m), 1580 (w), 1482 (m), 1378 (w), 1306 (s), 1284 (w), 1140 (m), 1066 (m), 996 (w), 857 (w), 836 (w), 813 (w), 802 (m), 780 (w), 737 (m) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 203 (4.80), 224 (4.49), 237 (4.29, sh), 256 (3.76), 288 (3.99) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.27 (s, 6 H), 3.86 (s, 3 H), 5.66 (s, 1 H, 5′-H), 6.78 (s, 2 H), 6.96 (s, 2 H), 7.05–7.30 (m, 8 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 75.5 MHz): δ = 23.54 (q), 46.63 (d), 55.12 (q), 114.71 (d), 126.10 (d), 127.52 (d), 128.86 (d), 129.35 (s), 129.44 (d), 132.74 (d), 136.46 (s), 140.13 (s, presumably 2 s), 157.94 (s) ppm. MS (70 eV, EI): m/z (%) = 327 (19), 326 (71) [M$^+$], 312 (10), 311 (16), 192 (16), 191 (56), 190 (11), 189 (18), 149 (15), 148 (100). $C_{24}H_{22}O$ (326.44): calcd. C 88.31, H 6.79; found C 88.34, H 6.75.

2nd Fraction: 83 mg (37%) of the *p*-quinoid compound **6.5A** as deep red solid with m.p. 230–233 °C. IR (KBr): $\tilde{\nu}$ = 2961 (w), 2209 (s), 1604 (s), 1527 (w), 1451 (w), 1412 (s), 1378 (w), 1316 (s), 1299 (m), 1265 (m), 1192 (m), 1172 (m), 1148 (m), 1107 (w), 1062 (w), 870 (w), 851 (w), 815 (w), 789 (w), 766 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 199 (4.81), 233 (4.06, sh), 283 (3.86), 347 (3.68, sh), 487 (4.52) nm. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.90 (br. s, 6 H), 3.09 (br. s, 4 H), 3.86 (s, 3 H), 6.69 (s, 2 H), 6.85–6.97 (m, 4 H), 7.09 ("t", "J" = 7.7 Hz, 1 H), 7.25 ("d", "J" = 7.3 Hz, 1 H), 7.32 (dt, J = 7.4, 1.0 Hz, 1 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 125 MHz): δ = 20.14 (q), 33.67 (t), 37.80 (t), 55.23 (q, OCH$_3$), 71.38 (s), 113.29 (d), 114.61 (s), 114.77 (s), 122.46 (d), 122.54 (d), 127.00 (d), 128.53 (d), 131.63 (d), 133.12 (s), 133.86 (d), 134.31 (s), 136.74 (s), 137.32 (s), 139.18 (d), 144.79 (s), 149.59 (s), 155.83 (s), 159.25 (s), 159.45 (s) ppm. MS (70 eV, EI): m/z (%) = 391 (27), 390 (100) [M$^+$], 375 (9), 360 (5), 254 (11), 195 (3), 180 (3). $C_{27}H_{22}N_2O$ (390.48): calcd. C 83.05, H 5.68, N 7.17; found C 82.76, H 5.74, N 7.02.

Reaction of 2.6 with Nucleophile A. 2-{4-[(4-Methoxy-2,6-dimethylphenyl)phenylmethylene]cyclohexa-2,5-dienylidene}malononitrile (6.6A): 44 mg (0.65 mmol) of malononitrile (**A**) in 4 mL of dry THF was treated with 28 mg (60% in mineral oil, 0.70 mmol) of NaH for 10 min at room temperature. 150 mg (0.386 mmol) of the triarylmethylium salt **2.6** in 6 mL of dry THF was added and the reaction mixture was stirred at room temperature for 20 h. After hydrolysis with 20 mL of saturated aqueous diammonium hydrogen phosphate solution and extraction with CH_2Cl_2 (three times 20 mL) the organic layer was concentrated and the residue was fractionated by flash chromatography (silica, *n*-hexane/diethyl ether, 1:1, R_f = 0.42 (**1.6**), 0.24 (**6.6A**)): The fraction with R_f = 0.24 gave 42 mg (30%) of the *p*-quinoid compound **6.6A** as a red to brown solid with m.p. 192–194 °C (crystallized from THF/*n*-pentane, 1:3). IR (KBr): $\tilde{\nu}$ = 3058 (w), 2961 (w), 2839 (w), 2211 (s), 1604 (s), 1449 (s), 1432 (s), 1346 (w), 1313 (s), 1201 (m), 1193 (m), 1173 (s), 1144 (m), 1064 (w), 841 (w), 775 (w), 748 (w), 705 (w), 699 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 195 (4.84), 235 (4.07, sh), 282 (4.08), 371 (3.97), 484 (4.56) nm. ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.96 (s, 6 H, CH_3), 3.84 (s, 3 H, OCH_3), 6.68 (s, 2H. 3′-H/5′-H), 6.87 (dd, J = 9.6, 1.8 Hz, 1 H, 6-H), 7.08 (dd, J = 9.6, 2.0 Hz, 1 H, 5-H), 7.21 (dd, J = 9.7, 2.0 Hz, 1 H, 3-H), 7.28 (dd, J = 9.3, 1.6 Hz, 2 H, 2-H), 7.40–7.48 (m, 3 H), 7.55 (dd, J = 9.7, 1.9 Hz, 1 H) ppm. ^{13}C NMR {^{1}H} ($CDCl_3$, 75.5 MHz): δ = 20.81 (q), 55.23 (q), 71.73 (s), 113.61 (d), 114.48 (s), 114.54 (s), 124.42 (d), 124.49 (d), 128.74 (d), 130.91 (d), 131.55 (s), 131.67 (d), 133.15 (s), 136.26 (d), 136.84 (d), 138.53 (s), 138.63 (s), 155.69 (s), 160.14 (s), 161.94 (s) ppm. MS (70 eV, EI): m/z (%) = 365 (28), 364 (100) [M$^+$], 349 (6), 334 (5), 228 (6), 223 (5), 182 (3), 165 (4), 136 (4), 90 (4). $C_{25}H_{20}N_2O$ (364.45): calcd. C 82.39, H 5.53, N 7.69; found C 82.16, H 5.55, N 7.65.

Reaction of 2.7 with Nucleophile A. 2-[9-(2,4-Dimethylphenyl)-9*H*-xanthen-9-yl]malononitrile (3.7A) and 2-[9-(2,4-Dimethylphenyl)-xanthen-3-ylidene]malononitrile (6.7A): 264 mg (4.00 mmol) of malononitrile (**A**) in 20 mL of dry THF was treated with 160 mg (60%

in mineral oil, 4.00 mmol) of NaH for 1 h at room temperature. 372 mg (1.00 mmol) of the xanthenylium salt **2.7** was added and the reaction mixture was stirred at reflux temperature for 2 d. After hydrolysis with 20 mL of saturated aqueous diammonium hydrogen phosphate solution and extraction with CH_2Cl_2 (three times 50 mL) the organic layer was concentrated and the residue was fractionated by flash chromatography (silica, toluene: R_f = 0.67, 0.14).

1st Fraction: R_f = 0.67, 274 mg (78%) of **3.7A** as a white solid with m.p. 165 °C. IR (KBr): $\tilde{\nu}$ = 3044 (vw), 2969 (w), 2932 (m), 2265 (vw), 1600 (w), 1573 (w), 1479 (s), 1143 (s), 1310 (m), 1294 (w), 1250 (m), 1229 (m), 1189 (vw), 1129 (vw), 940 (vw), 908 (vw), 874 (m), 812 (vw), 745 (s) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 220 (4.32), 247 (4.08), 290 (3.58) nm. ^1H NMR (400 MHz, $CDCl_3$, 25 °C): mixture of rotamers; δ = 1.44 (s, 3 H, CH_3), 2.39 (br. s, 3 H, CH_3), 4.08 (br. s, 0.38 H), 4.51 (br. s, 0.62 H), 6.94–7.05 (m, 5 H), 7.24–7.28 (m, 3 H), 7.37–7.42 (t, 2 H), 7.51 (br. s, 0.62 H), 7.90 (br. s, 0.38 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): mixture of rotamers, δ = 20.82 (q), 21.59 (q, br.), 34.88 (br.), 38.93 (br.), 50.11 (br.), 111.60 (s), 116.98 (d), 120.68 (br.), 124.00 (d), 125.62 (br.), 126.32 (br.), 128.26 (br.), 129.07 (br.), 130.40 (d), 135.01 (d, br.), 137.53 (s), 138.00 (s), 151.20 (s) ppm. MS (EI, 70eV): *m*/*z* (%) = 351 (0.3), 350 (1.2) [M^+], 285 (100), 255 (5), 181 (5), 134 (4). $C_{24}H_{18}N_2O$ (350.41): calcd. C 82.26, H 5.18, N 7.99; found C 82.17, H 5.30, N 7.80.

2nd Fraction: 53 mg (15%) of the *p*-quinoid compound **6.7A** as deep violet solid with m.p. 280–285 °C. IR (KBr): $\tilde{\nu}$ = 2922 (w), 2203 (s), 1631 (m), 1595 (m), 1523 (w), 1467 (s), 1414 (m), 1361 (w), 1320 (w), 1139 (w), 1113 (w), 840 (w), 754 (w) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 228 nm (4.38), 297 (3.94), 308 (3.97), 349 (4.09), 369 (3.81), 390 (3.79), 528 (4.35), 562 (4.37), 618 (4.22) nm. ^{1}HnNMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.02 (s, 3 H), 2.46 (s, 3 H), 6.89 (d, J = 9.6 Hz, 1 H), 7.02–7.06 (m, 2 H), 7.16 (dd, J = 8.1, 1.5 Hz, 1 H), 7.19–7.26 (m, 4 H), 7.48 (d, J = 8.3 Hz, 1 H), 7.65 ("t", "J" = 7.8 Hz, 1 H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 19.63 (q), 21.29 (q), 64.63 (s), 102.53 (d), 115.89 (s), 116.04 (s), 117.10 (d), 121.77 (s), 122.77 (s), 125.23 (d), 125.66 (d), 127.08 (d), 128.46 (d), 128.73 (s), 129.17 (d), 129.51 (d), 131.61 (d), 134.43 (d), 136.09 (s), 140.06 (s), 150.39 (s), 152.95 (s), 156.07 (s), 157.26 (s) ppm. MS (EI, 70 EV): *m*/*z* (%) = 349 (28), 348 (100) [M^+], 332 (4), 318 (4), 166 (4), 59 (6). $C_{24}H_{16}N_2O$ (348.40) + $0.5H_2O$: calcd. C 80.65, H 4.79, N 7.84; found: C 81.01, H 5.00, N 7.45.

Reaction of 2.8 with Nucleophile A. 2-[9-(4-Methylphenyl)-9*H*-xanthen-9-yl]malononitrile (3.8A): 264 mg (4.00 mmol) of malononitrile (**A**) in 20 mL of dry THF was treated with 160 mg (60% in mineral oil, 4.00 mmol) of NaH for 30 min at room temperature. 357 mg (1.00 mmol) of the 4-methylphenyl-substituted xanthenylium salt **2.2** was added and the reaction mixture was stirred at reflux temperature for 2 h. After hydrolysis with 50 mL of water and extraction with CH_2Cl_2 (three times 50 mL) the organic layer was concentrated and the residue was purified by flash chromatography (silica, petroleum ether/methyl *tert*-butyl ether 1:10, R_f = 0.67): 229 mg (68%) of compound **3.8A** as a colorless solid with m.p. 83–85 °C. IR (KBr): $\tilde{\nu}$ = 2032 (w), 2901 (w), 2265 (vw), 1600 (w), 1673 (w), 1478 (s), 1443 (s), 1313 (m), 1280 (m), 874 (w), 756 (s) cm^{-1}. UV (acetonitrile): λ_{max} (log ε) = 231 (4.47), 243 (4.44), 268 (3.83), 274 (3.89), 290 (3.99) nm. ^1H NMR ($CDCl_3$, 400 MHz): δ = 2.40 (s, 3 H), 4.40 (s, 1 H), 6.98 (d, J = 8.2 Hz, 2 H), 7.07 (m, 2 H), 7.2–7.3 (m, 6 H), 7.39 (m, 2 H) ppm. ^{13}C NMR {^1H} ($CDCl_3$, 100 MHz): δ = 21.04 (q), 36.09 (s), 50.70 (d), 111.43 (d), 117.05 (d), 122.37 (s), 123.85 (d), 128.63 (s), 129.47 (d), 129.87 (d), 130.28 (d), 138.15 (s), 151.36 (s) ppm, one s is missing. MS (70 eV, EI): *m*/*z* (%) = 336 (0.72) [M^+], 271 (100), 255 (16), 181 (8), 128 (14). $C_{23}H_{16}N_2O$ (336.39): calcd. C 82.12, H 4.79, N 8.33; found C 81.92, H 5.03, N 7.86.

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[9] X-ray crystal structure analysis of **6.2A**: A single crystal was mounted on top of a glass capillary. Diffraction data were collected at 150 K with a Siemens P4RA four-cyrcle diffractometer utilizing monochromated Mo-K_α radiation. The data were corrected for absorption (ψ-scan method) as well as for Lorentz and polarisation effects. The structure was solved by direct methods and refined by full-matrix least-squares methods based on F_2 with anisotropic displacement parameters for all non-hydrogen atoms using the SHELX-97* program suite. Hydrogen atoms were fixed on ideal positions and refined with a common isotropic temperature factor. The final refinement converged to R_1 = 0.0431 for 3201 data with $F_o > 4\sigma(F_o)$ and wR_2 = 0.1229 for all 4099 data and 263 parameters. CCDC-644405 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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