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Sterically Stabilized *p*-Quinodimethanes by Nucleophilic Aromatic Substitution

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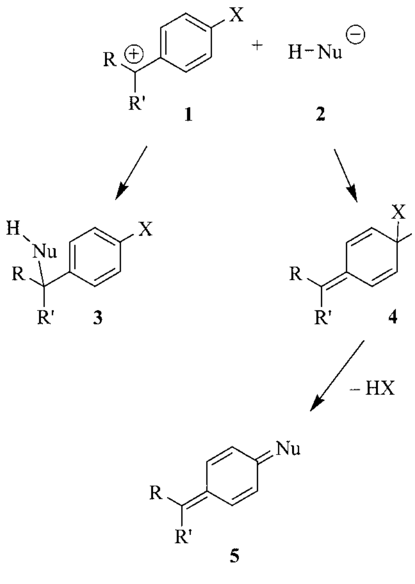
Triarylmethyl cations with a sterically shielded cationic center react with selected C- and N-nucleophiles under nucleophilic aromatic substitution. The resulting dipolar *p*-quinodimethanes represent highly functionalized extended π systems.

The importance of *p*-quinonoid compounds is based on their general tendency to aromatize, thus exhibiting a high reactivity combined with interesting electronic properties. *p*-Quinodimethanes, for instance, are regularly generated as reactive intermediates for polymerization or cyclic oligomerization reactions,[1] the latter being a versatile entry to the strained [2.2]paracyclophanes.[2] With the ultimate goal to synthesize extended conjugated π systems with multiple coordination sites[3] for transition metals, we envisioned the nucleophilic aromatic substitution at triarylmethyl cations to be a versatile entry to dipolar *p*-quinodimethanes, a concept, which is depicted in Scheme 1. The electrophilicity of benzylic cations **1** is of course strongly influenced by electronic effects of attached functional groups,[4] however, steric influence can be even more important for the regioselectivity of a nucleophilic attack: while structure **3** represents the ordinary product[5] from the reaction with nucleophiles **2**, bulky groups R and/or R′ should be able to favor attack in *para* position to give the intermediates **4**. With a remaining hydrogen atom at the nucleophilic center the final elimination should give the desired *p*-benzoquinodimethanes **5**,[6] which are anticipated to be rather dipolar because of the general acceptor character of the double-bonded "Nu"-group. Triarylmethyl cations were chosen as easily accessible model compounds. Examples for the nucleophilic aromatic substitution at triarylmethyl cations are still very rare in literature,[7] especially with C-nucleophiles.[8] A general preparative investigation of scope and limitations of the concept in Scheme 1 is clearly missing.



Scheme 1. Reaction pathways for the nucleophilic attack on benzylic cations.

Results and Discussion

The dianisyl-substituted triarylmethyl salts **8** are efficiently accessible in just two preparative steps starting from the corresponding benzophenone **6** (Scheme 2). The reaction with malononitrile under basic conditions either leads to the quarternary-centered products **9**, or to the desired *p*-quinodimethanes **10**, depending on the steric hindrance at the central carbon atom: obviously both, the mesityl- (in **8b**) and the 9-anthryl substituent (in **8d**) are bulky enough for effectively shielding the benzylic position. However, the anthryl group itself was not completely inert, allowing the formation of the semi-quinonoid by-product **11** (Scheme 3), which was identified by the diagnostic AB signal of the two methine protons at 4.23/4.44 ppm (J = 10 Hz). In order to enhance the structural diversity of applicable C-nucleophiles bis(4-nitrophenyl)methane and fluorene were tested in the reaction with **8b**, leading to the successful isolation of the extended π systems **12** and **13**.

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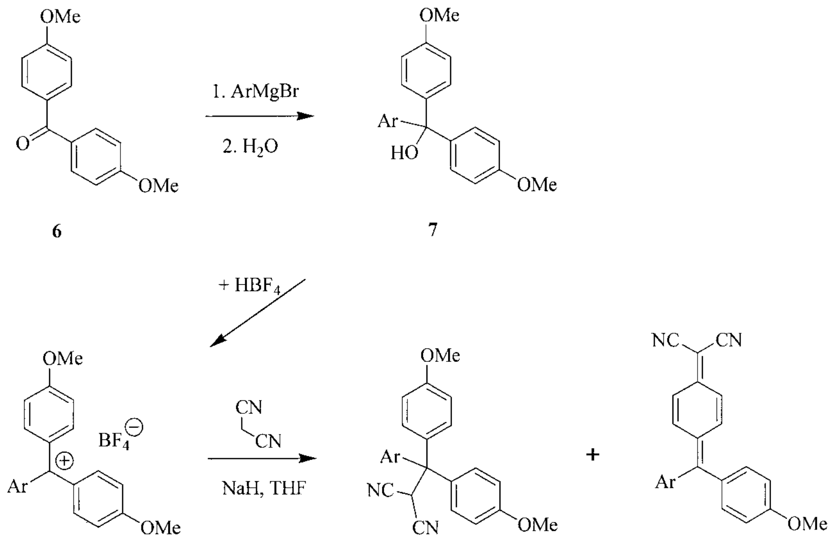
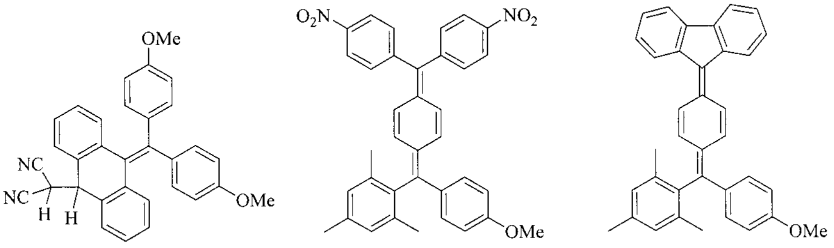


8a	(R = 2-methylphenyl)	**9a** (73%)	**10a** (0%)
8b	(R = 2,4,6-trimethylphenyl)	**9b** (0%)	**10b** (39%)
8c	(R = 1-naphthyl)	**9c** (94%)	**10c** (0%)
8d	(R = 9-anthryl)	**9d** (0%)	**10d** (60%)
8e	(R = 4-fluorophenyl)	**9e** (67%)	**10e** (0%)

Scheme 2. Dianisyl-substituted benzylic cations: product ratio in relation to steric hindrance.

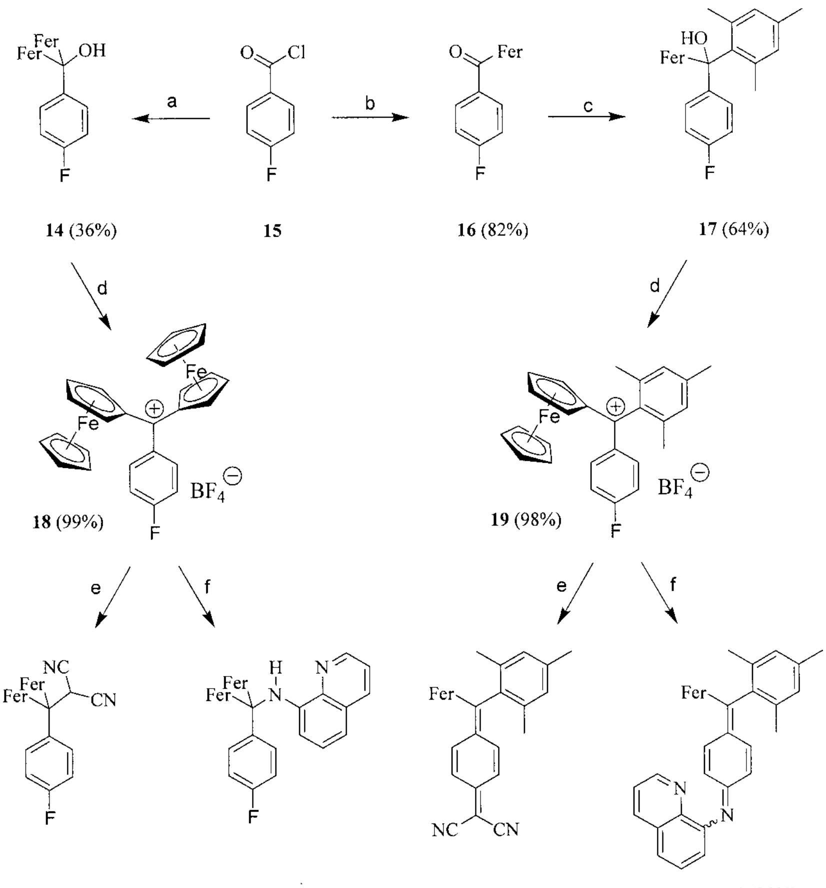


11 (~37%) **12** (39%) **13** (12%)

Scheme 3. Additional products from dianisyl-substituted carbocations.

As model substrates for the synthesis of conjugated π systems with coordinated metals we chose the ferrocenyl-substituted triarylmethyl cations **18** and **19**, which are known as being especially stabilized and might be regarded as cationic fulvene–iron complexes.[9] Nevertheless, the fluorophenyl group should guarentee a higher reactivity towards nucleophilic substitution and was compatible with the rather short synthetic pathways depicted in Scheme 4. The steric hindrance of the two ferrocenyl substituents of **18** obviously is not sufficient for preventing the conventional CC and CN bond formation[10] with relatively small nucleophiles like malononitrile and 8-aminoquinoline leading to **20** and **21**, respectively. On the other hand, the mesityl group of **19** is an effective control element leading to the desired *p*-quinonoid compounds **22** and **23**, the latter as a 1:1 mixture of stereoisomers. The metallic lustre and deep green (**22**) or purple color (**23**) of their crystals are macroscopic effects of the polar extended π systems.

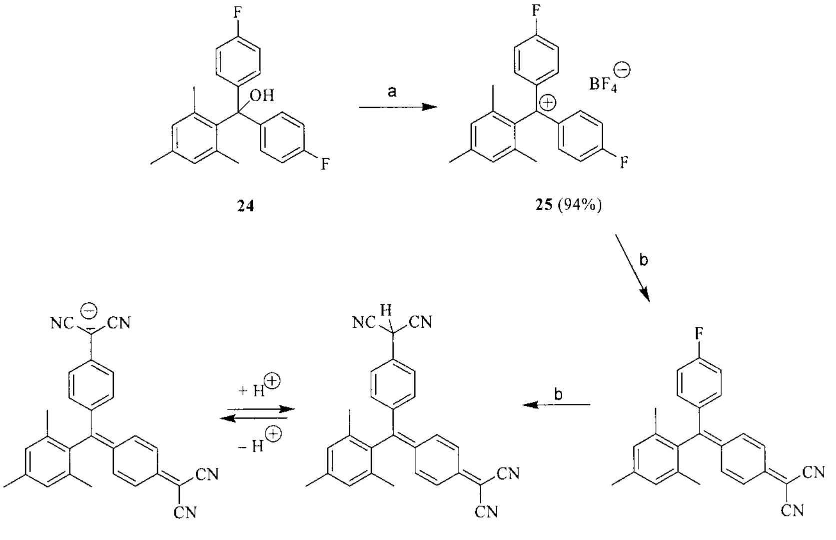
The bis(fluorophenyl)-substituted salt **25** is interesting both, from a spectroscopic and from a chemical point of view. The ^1H and ^{13}C spectra in $CDCl_3$ exhibit some broad signals and doubled sets of signals (in addition to C–F and H–F couplings); presumably reversible coordination of water is responsible for these dynamic NMR effects. Under neutral conditions **25** is not sensitive towards hydrolysis. We tested **25** as substrate for a twofold nucleophilic aromatic substitution. Indeed, at room temperature an excess of deprotonated malononitrile gives the monosubstitution product **28**. According to preliminary results the elevated temperature of refluxing tetrahydrofuran is necessary. Under the basic reaction conditions the crude product exhibits the intensive green color of the anion **26**, with two symmetrical dicyanomethyl-substituted phenylene groups according to ^1H NMR spectroscopy. Acidification leads to the orange to red neutral quinodimethane **27**, which shows signals of two distinguished phenylene groups in the ^1H NMR spectrum



14 (36%) **15** **16** (82%) **17** (64%) **18** (99%) **19** (98%) **20** (71%) **21** (35%) **22** (66%) **23** (28%)

Scheme 4. Test reactions with ferrocenyl-4-fluorophenyl-substituted benzylic cations (Fer = ferrocenyl); a: 3 equiv. ferrocenyl-Li, THF; b: $AlCl_3$, CH_2Cl_2; c: mesityllithium, THF; d: HBF_4–diethyl ether, CH_2Cl_2; e: malononitrile, NaH, THF; f: 8-aminoquinoline, NaH, THF.

in $CDCl_3$ solution. The signal of the $CH(CN)_2$-group, registered at $\delta = 5.88$ ppm, is very broad due to dynamic effects, presumably in connection with the acidity of **27**. Currently we are investigating the amphoteric behavior of **27** and the complexating ability of tetracyano-substituted anion **26** for transition metal cations (Scheme 5).



24 **25** (94%) **26** **27** **28** (62%)

Scheme 5. Twofold S_NAr reaction with a bis(fluorophenyl)-substituted benzylic cation; a: HBF_4–etherate, CH_2Cl_2; b: malononitrile, NaH, THF.

Conclusion

Functionalized *p*-quinodimethanes are easily accessible by nucleophilic aromatic substitution with triarylmethyl salts, sterically hindered at the central carbocation. This method is compatible even with ferrocenyl substituents. With two 4-fluorophenyl substituents – such as in **25** – it is possible to perform two nucleophilic substitution reactions successively, leaving the *p*-quinodimethane moiety intact. Thus, we intend to use compound **25** as key substrate for the synthesis of various donator-acceptor substituted *p*-quinodimethanes.

Experimental Section

General Remarks: M.p. (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.

Bis(4-methoxyphenyl)-(2-methylphenyl)methanol (7a): To a solution of 2-bromotoluene (700 mg, 0.49 mL, 4.05 mmol) in 20 mL of dry THF, a 15% solution of *n*-butyllithium in hexane (2.63 mL, 4.2 mmol) was added within 5 min at –70 °C under argon. After 1 h of stirring at –70 °C to –55 °C a solution of 4,4′-dimethoxybenzophenone (**6**, 1.01 g, 4.17 mmol) in 20 mL of dry THF was added dropwise within 15 min and the reaction mixture was stirred at room temperature for another 1.5 d. After hydrolysis with 20 mL of a saturated aqueous $(NH_4)_2HPO_4$ solution water layer was extracted three times with 20 mL of dichloromethane and the combined organic layers were dried with sodium sulfate. Then the solvents were evaporated to dryness at the rotary evaporator: TLC (silica/diethyl ether/hexane, 1:1) of the crude product: R_f = 0.46, 0.35. The fraction with R_f = 0.46 was isolated by flash chromatography: 920 mg (68%) of **7a** a slightly yellow solid with m.p. 104 °C. IR (KBr): $\tilde{\nu}$ = 3059 cm^{-1} (w), 3006 (w), 2957 (w), 2933 (w), 2836 (w), 1608 (m), 1508 (s), 1462 (w), 1295 (m), 1252 (s), 1178 (s), 1032 (m), 831 (m), 763 (w), 610 (w), 588 (w). UV (acetonitrile): λ_{max} (lgε) = 198 nm (4.95), 228 (4.35, sh), 276 (3.53), 284 (3.46). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.15 ppm (s, 3 H, CH_3), 2.90 (s, 1 H, O*H*), 3.79 (s, 6 H, OCH_3), 6.76 (dd, *J* = 7.8, 1.2 Hz, 1 H), 6.83 (d, *J* = 9.0 Hz, 4 H), 7.00–7.04 (m, 1 H), 7.12 (d, *J* = 9.1 Hz, 4 H), 7.15–7.20 (m, 2 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 22.14 ppm (q, CH_3), 55.25 (q, OCH_3), 82.55 (s, *C*–OH), 113.19 (d), 124.88 (d), 127.66 (d), 128.90 (d), 129.42 (d), 132.46 (d), 137.93 (s), 139.21 (s), 144.91 (s), 158.53 (s). MS (EI = 70 eV): *m*/*z* (%) = 335 (9) [M$^+$ + 1], 334 (35) [M$^+$], 318 (10), 317 (25), 244 (18), 243 (100), 227 (18), 215 (15), 135 (83), 119 (13), 108 (9), 107 (14), 91 (13), 77 (15). $C_{22}H_{22}O_3$ (334.41): calcd. C 79.01, H 6.63; found C 79.04, H 6.58

Bis(4-methoxyphenyl)(2-methylphenyl)methylium Tetrafluoroborate (8a): To a solution of the triarylmethyl alcohol **7a** (600 mg, 1.79 mmol) in 5 mL of dry dichloromethane HBF_4–diethyl ether (0.63 mL, 4.6 mmol) was added at room temperature under nitrogen. After 10 min stirring at room temperature a layer of 15 mL of diethyl ether was placed carefully on the surface of the reaction mixture, leading to the formation of a solid precipitate within 1 d, which was isolated by filtration and washing with 5 mL of diethyl ether: 607 mg (84%) of **8a** as a red to orange solid with m.p. 140 °C. IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (w), 3012 (w), 2949 (w), 2844 (w), 2727 (w), 1606 (m), 1577 (s), 1507 (m), 1449 (m), 1373 (s), 1297 (s), 1164 (s), 1124 (s), 1084 (s), 1038 (m), 1005 (m), 916 (w), 853 (w), 833 (w), 756 (w), 595 (w). UV (acetonitrile): λ_{max} (lgε) = 194 nm (4.77), 253 (3.92, sh), 268 (4.07), 417 (4.22), 503 (4.89). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.94 ppm (s, 3 H, CH_3), 4.17 (s, 6 H, OCH_3), 7.11 (dd, *J* = 7.7, 1.4 Hz, 1 H), 7.36 (d, *J* = 8.7 Hz, 4 H), 7.41 ("t", "*J*" = 7.6 Hz, 1 H), 7.47 (d, *J* = 7.0 Hz, 1 H), 7.66 ("d", br, "*J*" = 6.4 Hz, 4 H), 7.70 (dt, *J* = 7.5, 1.4 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.93 ppm (q), 57.70 (q), 117.85 (d), 126.22 (d), 132.19 (d), 132.86 (s), 135.03 (d), 135.92 (d), 139.08 (s), 141.81 (s), 143.92 (d), 173.04 (s), 194.50 (s). MS (EI = 70 eV): *m*/*z* (%) = 337 (13), 336 (54) [M$^+$ – BF_3], 319 (9), 318 (41), 317 (48) [M$^+$-BF_4], 305 (11), 303 (16), 302 (34), 287 (17), 246 (17), 245 (100), 243 (12), 229 (17), 228 (12), 227 (31), 215 (10), 209 (16), 197 (10), 179 (14), 165 (11). $C_{22}H_{21}BF_4O_2$ (404.21): calcd. C 65.37, H 5.24; found C 65.08, H 5.21.

Bis(4-methoxyphenyl)(2,4,6-trimethylphenyl)methanol (7b): To a solution of 2-bromomesitylene (818 mg, 0.62 mL, 4.13 mmol) in 15 mL of dry THF a 15% solution of *n*-butyllithium in hexane (2.8 mL, 4.5 mmol) was added within 5 min at –60 °C under argon. After 1 h of stirring at –60 °C to –35 °C a solution of 4,4′-dimethoxybenzophenone (**6**, 1.00 g, 4.13 mmol) in 20 mL of dry THF was added dropwise within 15 min, and the reaction mixture was stirred at room temperature for another 3.5 d. After hydrolysis with 20 mL of a saturated aqueous $(NH_4)_2HPO_4$ solution, the water layer was extracted three times with 20 mL of dichloromethane and the combined organic layers were dried with sodium sulfate, and the solvents evaporated to dryness at the rotary evaporator: TLC (silica/diethyl ether/hexane, 1:1) of the crude product: R_f = 0.37, 0.23. The fraction with R_f = 0.37 was isolated by flash chromatography: 1.02 g (68%) of **7b** as a reddish solid with m.p. 134–137 °C. IR (KBr): $\tilde{\nu}$ = 2997 cm^{-1} (w), 2956 (w), 2933 (w), 2836 (w), 1608 (m), 1582 (w), 1507 (s), 1462 (m, br), 1295 (m), 1249 (s), 1176 (s), 1115 (w), 1033 (m), 997 (w), 832 (m), 594 (w). UV (acetonitrile): λ_{max} (lgε) = 201 nm (4.88), 228 (4.35), 277 (3.22). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 1.87 ppm (s, 6 H), 2.26 (s, 3 H), 2.65 (s, 1 H, O*H*), 3.80 (s, 6 H), 6.80 (s, 2 H), 6.82 (d, *J* = 9.0 Hz, 4 H), 7.13 (d, *J* = 9.0 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 20.50 ppm (q), 24.31 (q), 55.32 (q), 83.08 (s, *C*–OH), 113.52 (d), 129.12 (d), 131.34 (d), 136.09 (s), 138.17 (s), 140.44 (s), 141.58 (s), 158.88 (s). MS (EI = 70 eV): *m*/*z* (%) = 363 (8) [M$^+$ + 1], 362 (28) [M$^+$], 346 (26), 345 (93), 331 (15), 330 (52), 315 (10), 255 (12), 253 (13), 244 (17), 243 (100), 237 (15), 223 (11), 222 (15), 215 (17), 214 (23), 179 (10), 165 (10), 149 (12), 147 (45), 136 (12), 135 (90), 121 (20), 77 (12). $C_{24}H_{26}O_3$ (362.47): calcd. C 79.53, H 7.23; found C 79.34, H 7.28.

Bis(4-methoxyphenyl)(2,4,6-trimethylphenyl)methylium Tetrafluoroborate (8b): To a solution of the triarylmethyl alcohol **7b** (300 mg, 0.828 mmol) in 3 mL of dry dichloromethane HBF_4–diethyl ether (0.33 mL, 2.4 mmol) was added at room temperature under nitrogen. After 10 min stirring at room temperature a layer of 9 mL of diethyl ether was placed carefully on the surface of the reaction mixture, leading to the formation of an oily precipitate within 1 d, which solidified upon washing five times with 10 mL diethyl ether and drying in vacuo (60 °C/0.04 mbar): 319 mg (89%) of **8b** as an orange solid with m.p. 160–163 °C. IR (KBr): $\tilde{\nu}$ = 2944 cm^{-1} (w), 2850 (w), 1626 (w), 1603 (m), 1576 (s), 1501 (w), 1444 (w), 1372 (s), 1316 (m), 1280 (s), 1160 (s), 1124 (s), 1084 (s), 1064 (w), 1036 (w), 1005 (w), 911 (w), 855 (w), 590 (w). UV (acetonitrile): λ_{max} (lgε) = 197 nm (4.88), 255 (3.97, sh), 270 (4.16), 330 (3.86), 442 (4.06, sh), 510 (4.96). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.81 ppm (s, 6 H), 2.42 (s, 3 H), 4.17 (s, 6 H), 7.05 (s, 2 H), 7.35

(br. s, 4 H), 7.74 (br. s, 4 H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ = 20.64 ppm (q), 21.39 (q) 57.78 (q, O*C*H$_3$), 118.29 (d, broad), 129.71 (d), 133.01 (s), 136.09 (s), 138.68 (s), 143.51 (s), 173.40 (s), 195.02 (s). MS (EI = 70 eV): *m*/*z* (%) = 346 (30) [M$^+$ + 1 – BF$_4$], 345 (100) [M$^+$-BF$_4$], 343 (10), 331 (16), 330 (51), 315 (11), 287 (9), 272 (6), 237 (9), 227 (6), 222 (11), 179 (6), 165 (7), 121 (6). $C_{24}H_{25}BF_4O_2$ (432.27): calcd. C 66.69, H 5.83; found C 66.69, H 5.81.

Bis(4-methoxyphenyl)(1-naphthyl)methanol (7c): To a solution of 1-bromonaphthalene (500 mg, 2.42 mmol) in 10 mL of dry THF a 15% solution of *n*-butyllithium in hexane (1.6 mL, 2.6 mmol) was added within 5 min at –70 °C under argon. After 1 h of stirring at –60 °C a solution of 4,4′-dimethoxybenzophenone (**6**, 585 mg, 2.42 mmol) in 15 mL of dry THF was added dropwise within 15 min, and the reaction mixture was warmed up to room temperature within 20 h and was stirred for another 2 h at 50 °C. After hydrolysis with 20 mL of a saturated aqueous (NH$_4$)$_2$HPO$_4$ solution water layer was extracted three times with 20 mL of dichloromethane and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness at the rotary evaporator: TLC (silica/diethyl ether/hexane, 1:1) of the crude product: R_f = 0.75, 0.41, 0.33. The fraction with R_f = 0.41 was isolated by flash chromatography: 765 mg (86%) of **7c** as colorless solid with m.p. 158 °C. IR (KBr): $\tilde{\nu}$ = 3049 cm^{-1} (w), 3003 (w), 2956 (w), 2836 (w), 1607 (m), 1583 (w), 1507 (s), 1459 (w), 1297 (m), 1250 (s), 1177 (s), 1034 (m), 1005 (w), 835 (m), 805 (m), 787 (w), 778 (m), 609 (w), 589 (w). UV (acetonitrile): λ_{max} (lgε) = 197 nm (4.84), 204 (4.81, sh), 222 (4.85, sh), 227 (4.88), 273 (3.99, sh), 281 (4.05), 293 (3.80, sh). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 3.25 ppm (br. s, 1 H, O*H*), 3.79 (s, 6 H), 6.83 (d, *J* = 8.9 Hz, 4 H), 6.88 (d, *J* = 7.4 Hz, 1 H), 7.18 (d, *J* = 8.9 Hz, 4 H), 7.20–7.29 (m, 2 H), 7.38 (ddd, "*J*" = 8.1, 5.7, 1.2 Hz, 1 H), 7.81 ("dd", "*J*" = 8.2, 7.2 Hz, 2 H), 8.13 (d, *J* = 8.7 Hz, 1 H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ = 55.25 ppm (q), 82.84 (s), 113.29 (d), 124.27 (d), 125.27 (d), 125.50 (d), 128.01 (d), 128.19 (d), 128.80 (d), 128.97 (d), 129.23 (d), 131.39 (s), 134.96 (s), 139.60 (s), 142.54 (s), 158.56 (s). MS (EI = 70 eV): *m*/*z* (%) = 370 (24) [M$^+$], 354 (21), 353 (39), 263 (21), 262 (43), 261 (9), 245 (19), 244 (8), 243 (50), 231 (12), 215 (13), 202 (11), 155 (11), 136 (9), 135 (100), 128 (9), 127 (15), 107 (10), 77 (14). $C_{25}H_{22}O_3$ (370.45): calcd. C 81.06, H 5.99; found C 81.08, H 5.95.

Bis(4-methoxyphenyl)(1-naphthyl)methylium Tetrafluoroborate (8c): To a solution of the triarylmethyl alcohol **7c** (630 mg, 1.70 mmol) in 7 mL of dry dichloromethane, HBF$_4$–diethyl ether (0.85 mL, 6.3 mmol) was added at room temperature under nitrogen. After 30 min stirring at room temperature a layer of 15 mL of pentane was placed on the surface of the reaction mixture, leading to the formation of an oily precipitate within 1 d. Recrystallization from dichloromethane/diethyl ether gave 699 mg (93%) of **8c** as dark green, metallic shining needles with m.p. 182–185 °C. IR (KBr): $\tilde{\nu}$ = 3056 cm^{-1} (w), 2937 (w), 2840 (w), 1605 (m), 1577 (s), 1505 (m), 1441 (m, br), 1373 (s), 1315 (m), 1279 (s, br), 1255 (w), 1161 (s), 1124 (s), 1084 (s, br), 1006 (m), 912 (w), 851 (w, br), 807 (w), 781 (w), 578 (w). UV (acetonitrile): λ_{max} (lgε) = 204 nm (4.63, sh), 219 (4.71), 279 (4.07), 339 (3.87), 388 (3.63, sh), 494 (4.64). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.15 ppm (s, 6 H), 7.28–7.47 (m, 7 H), 7.56–7.74 (m, 6 H), 8.03 (d, *J* = 8.2 Hz, 1 H), 8.33 (d, *J* = 8.2 Hz, 1 H). ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ = 57.64 ppm (q), 117.76 (d), 125.11 (d), 125.74 (d), 127.65 (d), 129.02 (d), 129.15 (d), 133.60 (s), 133.75 (s), 134.17 (s), 137.31 (d), 137.45 (s), 137.83 (d), 143.94 (d), 172.87 (s), 192.66 (s). MS (EI = 70 eV): *m*/*z* (%) = 372 (4) [M$^+$ – BF$_3$], 355 (24), 354 (92), 353 (50), 352 (100), 337 (18), 323 (19), 321 (25), 247 (11), 246 (14), 245 (25), 227 (25), 215 (19), 202 (18), 49 (69), 48 (18). $C_{25}H_{21}BF_4O_2$ (440.24): calcd. C 68.21, H 4.81; found C 67.93, H 4.86

9-Anthryl-bis(4-methoxyphenyl)methanol (7d): To a solution of 9-bromoanthracene (1.12 g, 4.13 mmol) in 20 mL of dry THF, a 15% solution of *n*-butyllithium in hexane (2.8 mL, 4.5 mmol) was added within 5 min at –60 °C under argon. After 30 min of stirring at –35 °C a solution of 4,4′-dimethoxybenzophenone (**6**, 1.00 g, 4.13 mmol) in 25 mL of dry THF was added dropwise within 15 min, and the reaction mixture was warmed up to room temperature within 1.5 d and was stirred for another 2 h at 50 °C. After hydrolysis with 20 mL of a saturated aqueous (NH$_4$)$_2$HPO$_4$ solution water layer was extracted three times with 20 mL of dichloromethane and the combined organic layers were dried with sodium sulfate, and the solvents evaporated to dryness at the rotary evaporator: TLC (silica/diethyl ether/hexane, 1:1) of the crude product: R_f = 0.74 (anthracene), 0.49, 0.43 (**6**). The fraction with R_f = 0.43–0.49 was isolated by flash chromatography and recrystallized from diethyl ether/*n*-hexane (2:3): 1.14 g (66%) of **7d** as colorless solid with m.p. 101 °C. IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1} (w), 3002 (w), 2933 (w), 2836 (w), 1604 (m), 1506 (s), 1459 (w), 1443 (w), 1304 (m, sh), 1251 (s), 1176 (s), 1033 (m), 929 (w), 890 (w), 833 (m), 771 (w), 739 (w), 606 (w), 583 (w). UV (acetonitrile): λ_{max} (lgε) = 196 nm (4.86), 226 (4.48), 258 (4.85), 284 (4.24), 337 (3.34), 353 (3.55), 371 (3.70), 392 (3.65). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 2.99 ppm (s, 1 H, O*H*), 3.78 (s, 6 H), 6.81 (d, *J* = 8.9 Hz, 4 H), 7.05 ("ddd", "*J*" = 7.9, 6.5, 1.4 Hz, 2 H), 7.21 (d, *J* = 9.0 Hz, 4 H), 7.23–7.31 (m, 2 H), 7.90–7.95 (m, 4 H), 8.42 (s, 1 H). ^{13}C NMR (CDCl$_3$, 75.5 MHz): δ = 55.26 ppm (q, O*C*H$_3$), 83.49 (s, *C*–OH), 113.70 (d), 123.93 (d), 124.17 (d), 128.17 (d), 128.65 (d), 128.93 (d), 129.12 (d), 130.75 (s), 132.09 (s), 139.49 (s), 141.05 (s), 158.82 (s). MS (EI = 70 eV): *m*/*z* (%) = 420 (20) [M$^+$], 404 (34), 403 (76), 389 (32), 388 (100), 387 (9), 359 (14), 315 (10), 313 (28), 312 (79), 295 (11), 281 (24), 253 (23), 252 (26), 243 (11), 178 (18), 135 (79). $C_{29}H_{24}O_3$ (420.51): calcd. C 82.83, H 5.75; found C 82.64, H 5.84

9-Anthryl-bis(4-methoxyphenyl)methylium Tetrafluoroborate (8d): To a solution of the triarylmethyl alcohol **7d** (450 mg, 1.07 mmol) in 3 mL of dry dichloromethane, HBF$_4$–diethyl ether (0.50 mL, 3.7 mmol) was added at room temperature under nitrogen. After 5 min stirring at room temperature a layer of 10 mL of diethyl ether was carefully placed on the surface of the reaction mixture, leading to the formation of an oily precipitate within 1 d, which solidified upon washing five times with 10 mL diethyl ether in the ultrasonic bath: 363 mg (69%) of **8d** as dark green, metallic shining solid with m.p. 115–120 °C. IR (KBr): $\tilde{\nu}$ = 3050 cm^{-1} (w), 2933 (w), 2847 (w), 2731 (w), 1624 (m), 1605 (m), 1575 (s), 1443 (m), 1369 (s), 1280 (s), 1157 (s), 1123 (m), 1084 (s), 1003 (m), 910 (m), 863 (w), 841 (m), 742 (w), 600 (w). UV (acetonitrile): λ_{max} (lgε) = 253 nm (5.09), 342 (4.14, sh), 369 (4.22), 388 (4.17, sh), 519 (4.90), 685 (3.70). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 4.16 ppm (s, 6 H, OC*H*$_3$), 7.29 (dd, *J* = 8.9, 0.7 Hz, 4 H), 7.27–7.32 (br. m, 2 H), 7.41 ("ddd", "*J*" = 7.9, 6.6, 1.3 Hz, 2 H), 7.54 ("ddd", "*J*" = 8.4, 6.7, 1.0 Hz, 2 H), 7.75 ("s", br, 4 H), 8.14 (d, *J* = 8.5 Hz, 2 H), 8.83 (s, 1 H). ^{13}C NMR (CDCl$_3$, 125.8 MHz): δ = 57.85 ppm (q, O*C*H$_3$), 118.49 (d), 125.53 (d), 126.25 (d), 129.11 (d), 130.79 (s), 132.58 (s), 132.70 (s), 134.30 (d), 134.88 (s), 173.51 (s), 191.50 (s). MS (EI = 70 eV): *m*/*z* (%) = 404 (10), 403 (13) [M$^+$ – BF$_4$], 402 (11), 389 (32), 388 (100), 387 (11), 359 (15), 313 (10), 281 (21), 253 (18), 252 (21), 150 (12). $C_{29}H_{23}BF_4O_2$ (490.31): calcd. C 71.04, H 4.73; $C_{29}H_{23}BF_4O_2$ 0.25 H_2O (494.81): calcd. C 70.39, H 4.79; found C 70.43, H 4.59. HRMS: calcd. 403.1698; found 403.1628.

4-Fluorophenyl-bis(4-methoxyphenyl)methanol (7e): To a solution of 4-bromofluorobenzene (2.00 g, 11.4 mmol) in 5 mL of dry THF, magnesium (340 mg, 14 mmol) was added, and the mixture stirred at reflux temperature for 45 min. A solution of 4,4′-dimethoxybenzophenone (**6**, 2.00 g, 8.25 mmol) in 35 mL of dry THF was added, and the reaction mixture was stirred at reflux temperature for 3.5 h and at room temperature for another 4 d. After hydrolysis with of a saturated aqueous $(NH_4)_2HPO_4$ solution (20 mL), the water layer was extracted three times with 20 mL of dichloromethane, and the combined organic layers were dried with sodium sulfate, and the solvents evaporated to dryness at the rotary evaporator: TLC (silica/diethyl ether/hexane, 1:2) of the crude product: R_f = 0.30, 0.19. The fraction with R_f = 0.30 was isolated by flash chromatography: 1.754 g (63%) of **7e** as a highly viscous yellow oil. IR (film): $\tilde{\nu}$ = 3039 cm^{-1} (w), 3001 (w), 2954 (w), 2933 (w), 2906 (w), 2836 (w), 1606 (m), 1582 (w), 1503 (s), 1460 (m), 1442 (w), 1298 (m, sh), 1250 (s), 1225 (m), 1177 (m), 1158 (m), 1034 (m, sh), 906 (w), 828 (s). UV (acetonitrile): λ_{max} (lgε) = 198 nm (5.12), 230 (4.54), 266 (3.62, sh), 275 (3.71), 283 (3.61). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 2.77 ppm (s, 1 H, O*H*), 3.78 (s, 6 H), 6.82 ("dd", "*J*" = 6.8, 2.3 Hz, 4 H), 6.94–6.99 (m, 2 H), 7.14 ("dd", "*J*" = 6.8, 2.2 Hz, 4 H), 7.21–7.16 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 55.29 ppm (q), 81.11 (s), 113.30 (d), 114.59 (d, $^2J_{CF}$ = 21.1 Hz), 129.07 (d), 129.58 (d, $^3J_{CF}$ = 8.0 Hz), 139.34 (s), 143.21 (s, $^4J_{CF}$ = 3.3 Hz), 158.76 (s), 161.86 (s, $^1J_{CF}$ = 246.3 Hz). MS (EI = 70 eV): *m*/*z* (%) = 339 (13) [M$^+$ + 1], 338 (56) [M$^+$], 322 (11), 321 (33), 244 (16), 243 (89), 231 (43), 215 (16), 136 (9), 135 (100), 123 (67), 108 (11), 107 (10), 95 (17). HRMS calcd. for $C_{21}H_{19}FO_3$ (338.38): 338.1318; found 338.1284.

4-Fluorophenyl-bis(4-methoxyphenyl)methylium Tetrafluoroborate (8e): To a solution of the triarylmethyl alcohol **7e** (571 mg, 1.69 mmol) in 5 mL of dry dichloromethane, HBF_4–diethyl ether (0.75 mL, 5.5 mmol) was added at room temperature under nitrogen. After 10 min stirring at room temperature a layer of 10 mL of diethyl ether was placed carefully on the surface of the reaction mixture, leading to the formation of a solid precipitate within 1 d, which was isolated by filtration and washing with 5 mL of diethyl ether: 634 mg (92%) of **8e** as a orange solid with m.p. 171–177 °C. IR (KBr): $\tilde{\nu}$ = 3057 cm^{-1} (w), 2953 (w), 2837 (w), 1581 (s, br), 1504 (m), 1443 (w), 1414 (w), 1366 (m), 1316 (w), 1280 (s, br), 1251 (m), 1163 (s), 1124 (s), 1084 (s, br), 1037 (m), 917 (w), 831 (m). UV (acetonitrile): λ_{max} (lgε) = 196 nm (4.72), 228 (4.03, sh), 264 (3.87), 414 (4.29), 495 (4.65). ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 4.14 ppm (s, 6 H), 7.36 (d, *J* = 9.1 Hz, 4 H), 7.39–7.45 (m, 2 H), 7.53–7.58 (m, 2 H), 7.64 (d, *J* = 8.8 Hz, 4 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 57.51 ppm (q), 117.44 (d), 117.45 (d, $^2J_{CF}$ = 2.3 Hz), 132.24 (s), 135.21 (s), 140.98 (d, $^3J_{CF}$ = 10.4 Hz), 144.25 (d), 168.93 (s, $^1J_{CF}$ = 266.4 Hz), 172.39 (s), 192.81 (s). MS (EI = 70 eV): *m*/*z* (%) = 341 (19), 340 (84) [M$^+$ – BF_3], 322 (38), 321 (54) [M$^+$ – BF_4], 309 (29), 291 (19), 246 (21), 245 (100), 234 (12), 233 (63), 227 (15), 215 (17), 214 (21), 213 (12), 199 (12), 189 (10), 183 (12), 171 (13), 170 (16), 135 (20). $C_{21}H_{18}BF_5O_2$ (408.17): calcd. C 61.79, H 4.44; found C 61.58, H 4.50.

1,1-Dicyano-2,2-bis(4-methoxyphenyl)-2-(2-methylphenyl)ethane (9a): Malononitrile (67 mg, 1.0 mmol) in 3 mL of dry THF was deprotonated at room temperature with 60% sodium hydride/mineral oil (24 mg, 0.6 mmol). A deep red suspension of the tetrafluoroborate **8a** (300 mg, 0.742 mmol) in 9 mL of dry THF was added, and the reaction mixture was stirred for 21 h at room temperature. After hydrolysis with 20 mL of a saturated aqueous $(NH_4)_2HPO_4$ solution, the water layer was extracted three times with 20 mL of diethyl ether and the combined organic layers were dried with sodium sulfate, and the solvents evaporated to dryness at the rotary evaporator. The residue was recrystallized from diethyl ether/*n*-pentane (1:5) to give 206 mg (73%) of **9a** as purple needles with m.p. 163–167 °C. IR (KBr): $\tilde{\nu}$ = 3059 cm^{-1} (w), 3006 (w), 2935 (w), 2839 (w), 1608 (m), 1511 (s), 1462 (w), 1293 (w), 1258 (s), 1185 (m), 1032 (m), 827 (m), 757 (w). UV (acetonitrile): λ_{max} (lgε) = 199 nm (4.90), 234 (4.32), 275 (3.53), 286 (3.34, sh), 322 (2.90), 511 (2.75). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.78 ppm (s, 3 H), 3.82 (s, 6 H), 5.08 (s, 1 H), 6.89 (d, *J* = 8.9 Hz, 4 H), 7.16–7.28 (m, 4 H), 7.23 (d, *J* = 8.7 Hz, 4 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 22.70 ppm (q), 37.20 (d), 55.30 (q), 58.94 (s), 112.80 (s), 114.03 (d), 126.32 (d), 128.18 (d), 128.55 (d), 130.19 (d), 132.50 (s), 133.51 (d), 137.60 (s), 140.57 (s), 159.22 (s). MS (EI = 70 eV): *m*/*z* (%) = 382 (0.2) [M$^+$], 350 (5), 319 (5), 318 (33), 317 (100) [M$^+$ – C_3HN_2], 302 (6), 287 (6), 227 (8), 209 (8), 165 (5). $C_{25}H_{22}N_2O_2$ (382.46): calcd. C 78.51, H 5.80, N 7.32; found C 78.54, H 5.82, N 7.57.

1,1-Dicyano-2,2-bis(4-methoxyphenyl)-2-(1-naphthyl)ethane (9c): Malononitrile (37 mg, 0.55 mmol) in 3 mL of dry THF was deprotonated at room temperature with 60% sodium hydride/mineral oil (24 mg, 0.6 mmol. A deep red suspension of the tetrafluoroborate **8c** (180 mg, 0.409 mmol) in 7 mL of dry THF was added, and the reaction mixture was stirred for 24 h at room temperature. After hydrolysis with a saturated aqueous $(NH_4)_2HPO_4$ solution (20 mL), the water layer was extracted three times with 20 mL of diethyl ether and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness at the rotary evaporator: 160 mg (94%) of **9c** as purple colored crystals (purity according to ^{1}H NMR > 95%); an analytically pure sample with m.p. 177–180 °C was obtained by recrystallization from diethyl ether/pentane (1:3). IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1} (w), 3005 (w), 2931 (w), 2838 (w), 1608 (m), 1510 (s), 1461 (w), 1293 (m), 1258 (s), 1185 (m), 1033 (m), 830 (m), 802 (m), 790 (m), 777 (m). UV (acetonitrile): λ_{max} (lgε) = 199 nm (4.62), 225 (4.58), 274 (3.69, sh), 284 (3.76), 295 (3.53). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.80 ppm (s, 6 H), 5.35 (s, 1 H), 6.87 (d, *J* = 9.1 Hz, 4 H), 7.15 (t, *J* = 7.5 Hz, 1 H), 7.32 (d, *J* = 9.0 Hz, 4 H), 7.33–7.39 (m, 2 H), 7.49 (t, *J* = 7.6 Hz, 2 H), 7.86 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 8.7 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): (two doublets are superimposed): δ = 37.65 ppm (d), 55.36 (q), 59.18 (s), 112.91 (s), 114.02 (d), 124.86 (d), 125.58 (d), 125.82 (d), 126.85 (d), 129.61 (d), 130.32 (d), 130.50 (d), 131.01 (s), 132.71 (s), 135.22 (s), 137.88 (s), 159.44 (s). MS (EI = 70 eV): *m*/*z* (%) = 417 (6) [M$^+$ – 1], 416 (19), 386 (16), 379 (10), 355 (33), 354 (100) [M$^+$ – C_3N_2], 353 (26), 323 (20), 247 (14), 246 (15), 245 (24), 227 (35), 226 (10), 215 (21), 202 (13), 66 (6). $C_{28}H_{22}N_2O_2$ (418.49): calcd. C 80.36, H 5.30, N 6.69; found C 80.16, H 5.30, N 6.70.

1,1-Dicyano-2-(4-fluorophenyl)-2,2-bis(4-methoxyphenyl)ethane (9e): Malononitrile (38 mg, 0.57 mmol) in 3 mL of dry THF was deprotonated at room temperature with 60% sodium hydride/mineral oil (26 mg, 0.65 mmol). A deep orange suspension of the tetrafluoroborate **8e** (166 mg, 0.407 mmol) in 13 mL of dry THF was added, and the reaction mixture was stirred for 24 h at room temperature. After hydrolysis with 20 mL of a saturated aqueous $(NH_4)_2HPO_4$ solution, the water layer was extracted three times with 20 mL of diethyl ether, and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness at the rotary evaporator: TLC (silica; diethyl ether/*n*-hexane, 1:2): R_f = 0.44 (**7e**), 0.27 (**9e**). The fraction with R_f = 0.27 was isolated by flash chromatography to give 105 mg (67%) of **9e** as slightly yellow solid with m.p. 52 °C. IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1} (w), 3005 (w), 2959 (w), 2935 (w), 1606 (m), 1582 (w), 1508 (s), 1461 (m), 1299 (m), 1258 (s), 1186 (m), 826 (s), 738 (w). UV (acetonitrile): λ_{max} (lgε) = 198 nm (4.95), 225 (4.32), 275 (3.68). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.81 ppm (s, 6 H), 5.05 (s, 1 H), 6.89 (d, *J* = 8.9 Hz, 4 H), 7.02–7.08 (m, 2 H), 7.13 (d, *J* = 8.9 Hz, 4 H), 7.21–7.27 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 35.96 ppm (d), 55.32 (q), 58.17 (s), 112.63 (s), 114.07 (d), 115.63 (d, $^2J_{CF}$ = 21.4 Hz), 129.85 (d), 130.62 (d, $^3J_{CF}$ = 8.0 Hz), 133.73 (s), 138.09 (s), 159.20 (s), 162.13 (s, $^1J_{CF}$ = 248.8 Hz). MS (EI = 70 eV):

m/*z* (%) = 386 (0.6) [M$^+$], 322 (29), 321 (100), 142 (15), 135 (23), 86 (31), 84 (52), 66 (19). HMRS calcd. for $C_{24}H_{19}FN_2O_2$ (386.42): 321.12908 (for M – $C_3H_2N_2$) and 66.02180 (for malononitrile fragment); found 321.128586 and 66.012988.

α,α-Dicyano-β-(4-methoxyphenyl)-β-(2,4,6-trimethylphenyl)-*p*-benzoquinodimethane (10b): Malononitrile (17 mg, 0.25 mmol) in 1.5 mL of dry THF was deprotonated at room temperature with 60% sodium hydride/mineral oil (11 mg, 0.28 mmol). A solution of the tetrafluoroborate **8b** (80 mg, 0.19 mmol) in 2.5 mL of dry THF was added, and the reaction mixture was stirred for 20 h at room temperature. After hydrolysis with 20 mL of water the aqueous layer was extracted three times with 30 mL of diethyl ether and the combined organic layers were dried with sodium sulfate and the solvents evaporated. The residue was fractionated by flash chromatography (silica/diethyl ether/*n*-hexane, 2:3). The fraction with R_f = 0.35 was isolated to give **10b** (27 mg, 39%) as purple solid with m.p. 188–190 °C. IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1} (w), 2926 (w), 2849 (w), 2209 (s), 1607 (m), 1591 (s), 1437 (s), 1414 (m), 1308 (w), 1291 (w), 1259 (m), 1203 (w), 1173 (s), 1028 (w), 841 (m), 604 (w). UV (acetonitrile): λ_{max} (lgε) = 196 nm (4.85), 220 (4.23, sh), 244 (3.80, sh), 276 (3.74. sh), 301 (4.10), 391 (3.79), 508 (4.55). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.92 ppm (s, 6 H), 2.35 (s, 3 H), 3.88 (s, 3 H), 6.81 (dd, *J* = 9.6, 2.0 Hz, 1 H), 6.94 (d, ü, *J* = 8.8 Hz, 2 H), 6.95 (s, 2 H), 7.04 (dd, *J* = 9.6, 2.0 Hz, 1 H), 7.21 (dd, *J* = 9.7, 2.0 Hz, 1 H), 7.25 (d, *J* = 8.9 Hz, 2 H), 7.58 (dd, *J* = 9.6, 2.0 Hz, 1 H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 20.24 ppm (q), 21.19 (q), 55.62 (q), 69.91 (s), 114.51 (d), 114.91 (s, *C*°N), 115.00 (s, *C*°N), 124.03 (d), 124.13 (d), 128.92 (d), 130.94 (s), 131.94 (s), 133.79 (d), 136.22 (s), 136.34 (d), 136.58 (s), 136.81 (d), 139.20 (s), 155.86 (s), 162.42 (s), 162.61 (s). MS (EI = 70 eV): *m*/*z* (%) = 380 (4), 379 (29), 378 (100) [M$^+$], 363 (4), 348 (5), 305 (3), 270 (3), 258 (4), 255 (6), 237 (4), 222 (3), 189 (4). $C_{26}H_{22}N_2O$ (378.48): calcd. C 82.51, H 5.86, N 7.40; found C 82.60, H 5.90, N 7.38.

β-(9-Anthryl)-α,α-dicyano-β-(4-methoxyphenyl)-*p*-benzoquinodimethane (10d): Malononitrile (37 mg, 0.55 mmol) in 3 mL of dry THF were deprotonated at room temperature with 60% sodium hydride/mineral oil (24 mg, 0.60 mmol). A suspension of the tetrafluoroborate **8d** (200 mg, 0.408 mmol) in 7 mL of dry THF was added, and the reaction mixture was stirred for 21 h at room temperature. After hydrolysis with 20 mL of water the aqueous layer was extracted three times with 30 mL of diethyl ether, and the combined organic layers were dried with sodium sulfate and the solvents evaporated. The residue was fractionated by flash chromatography (silica/diethyl ether/*n*-hexane, 3:2). The fraction with R_f = 0.39 gave 177 mg of a mixture of two-products, identified by NMr analysis to consist of *p*-quinodimethane **10d** as main component (60% yield according to integrals) and of the tetraarylethane **11** as byproduct (≈ 37%). By recrystallization from diethyl ether/*n*-hexane (1:3) a pure sample of 88 mg (49%) of **10d** as green to purple metallic shining solid with m.p. 256 °C was obtained. IR (KBr): $\tilde{\nu}$ = 3054 cm^{-1} (w), 2935 (w), 2839 (w), 2209 (s), 1609 (m), 1589 (s), 1505 (w), 1440 (s), 1414 (m), 1358 (w), 1308 (w), 1291 (w), 1261 (m), 1196 (w), 1173 (s), 1025 (m), 907 (w), 890 (w), 834 (m), 787 (w), 738 (w). UV (acetonitrile): λ_{max} (lgε) = 190 nm (4.61), 223 (4.23), 253 (4.86), 305 (3.97), 348 (3.73), 366 (3.87), 387 (3.95), 499 (4.35). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.81 ppm (s, 3 H), 6.47 (dd, *J* = 9.6, 2.0 Hz, 1 H), 6.84 (dd, *J* = 9.6, 2.1 Hz, 1 H), 6.87 (d, *J* = 9.0 Hz, 2 H), 7.31 (d, *J* = 8.9 Hz, 2 H), 7.33 (dd, *J* = 9.7, 2.0 Hz, 1 H), 7.39 (ddd, *J* = 7.8, 5.4, 1.3 Hz, 2 H), 7.48 (ddd, *J* = 7.6, 5.5, 1.0 Hz, 2 H), 7.63 (dd *J* = 8.8, 0.8 Hz, 2 H), 7.86 (dd, *J* = 9.7, 1.9 Hz, 1 H), 8.07 (d, *J* = 8.5 Hz, 2 H), 8.60 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.55 ppm (q), 71.14 (s), 114.56 (s), 114.60 (d), 114.80 (s), 124.15 (d), 124.59 (d), 125.62 (d), 125.65 (d), 127.23 (d), 128.84 (d), 129.26 (d), 130.51 (s), 131.23 (s), 132.21 (s), 133.31 (s), 133.62 (d), 133.95 (s), 136.02 (d), 137.23 (d), 155.59 (s), 159.47 (s), 162.31 (s). MS (EI = 70 eV): *m*/*z* (%) = 438 (6), 437 (34) [M$^+$ + 1], 436 (100) [M$^+$], 329 (7), 328 (12), 252 (5). $C_{31}H_{20}N_2O$ (436.51): calcd. C 85.30, H 4.62, N 6.42; found C 85.06, H 4.70, N 6.30.

α-(4-Methoxyphenyl)-α-(2,4,6-trimethylphenyl)]-β,β-bis(4-nitrophenyl)-*p*-benzoquinodimethane (12): To a solution of bis(4-nitrophenyl)methane (168 mg, 0.65 mmol) in 6 mL of dry THF, a solution of *n*-butyllithium (15% in *n*-hexane, 0.41 mL, 0.65 mmol) was added at –20 °C under argon. The solution was warmed to room temperature within 15 min, and a suspension of the tetrafluoroborate **8b** (265 mg, 0.613 mmol) in 6 mL of dry THF was added. The reaction mixture was stirred for another 4 d at room temperature and was hydrolyzed with 20 mL of a saturated aqueous $(NH_4)_2HPO_4$ solution. The water layer was extracted three times with 20 mL of diethyl ether, and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness at the rotary evaporator: TLC (silica; diethyl ether/*n*-hexane, 1:2): R_f = 0.44, 0.17–0.05. The fraction with R_f = 0.44 was isolated by flash chromatography to give **12** (84 mg, 39%) of as an orange solid with m.p. 211–214 °C. IR (KBr): $\tilde{\nu}$ = 3045 cm^{-1} (w), 2920 (w), 1596 (m), 1582 (m), 1512 (m), 1451 (w), 1340 (s), 1252 (m), 1174 (m), 1108 (w), 1032 (w), 846 (m), 702 (w). UV (CH_3CN): λ_{max} (lgε) = 199 nm (4.97), 221 (4.39, sh), 277 (4.29), 361 (4.06), 474 (4.55). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.03 ppm (s, 6 H), 2.31 (s, 3 H), 3.81 (s, 3 H, OC*H*$_3$), 6.33 (dd, *J* = 10.0, 2.0 Hz, 1 H), 6.64 (dd, *J* = 10.0, 2.1 Hz, 1 H), 6.77 (dd, *J* = 10.1, 2.1 Hz, 1 H), 6.85 (d, *J* = 8.9 Hz, 2 H), 6.91 (s, 2 H), 7.20 (d, *J* = 8.9 Hz, 2 H), 7.24 (dd, *J* = 10.1, 2.1 Hz, 1 H), 7.36 (ddd, *J* = 9.0, 2.1, 1.5 Hz, 2 H), 7.40 (ddd, *J* = 8.9, 2.4, 2.0 Hz, 2 H), 8.17 (dd, *J* = 8.9, 2.0 Hz, 2 H), 8.21 (dd, *J* = 8.9, 2.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 298 K, 125.8 MHz): δ = 20.24 ppm (q), 21.12 (q), 55.35 (q, O*C*H$_3$), 113.73 (d), 123.66 (d), 123.74 (d), 126.67 (d), 126.95 (d), 128.54 (d), 130.04 (d), 131.18 (d), 131.67 (s), 131.70 (d), 131.83 (s), 132.02 (d), 132.04 (d), 132.57 (s), 136.11 (s), 136.65 (s), 137.41 (s), 143.56 (s), 143.57 (s), 146.71 (s), 146.77 (s), 147.98 (s), 148.16 (s), 159.63 (s). MS (70 eV): *m*/*z* (%) = 571 (39), 570 (100) [M$^+$], 524 (5), 285 (6), 237 (4), 222 (5), 150 (6). $C_{36}H_{30}N_2O_5$ (570.64): calcd. C 75.77, H 5.30, N 4.91; found C 75.52, H 5.34, N 4.94.

4-(Fluoren-9-ylidene)-1-[(4-methoxyphenyl)(2,4,6-trimethylphenyl)]-methylidenecyclohexa-2,5-diene (13): Fluorene (266 mg, 1.60 mmol) and lithium (11 mg, 1.60 mmol) in 5 mL of dry THF were treated in the ultrasonic bath for 1 h at 50 °C. Unreacted lithium was removed, and a suspension of the tetrafluoroborate **8b** (460 mg, 1.06 mmol) in 7 mL of dry THF was added. The reaction mixture was stirred for another 20 h at room temperature and was hydrolyzed with a saturated aqueous $(NH_4)_2HPO_4$ solution (20 mL). The water layer was extracted three times with 20 mL of diethyl ether, and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness at the rotary evaporator: TLC (silica; diethyl ether/*n*-hexane, 1:9): R_f = 0.63 (fluorene), 0.38, 0.11–0.00. The fraction with R_f = 0.38 was isolated by flash chromatography and recrystallized from diethyl ether/pentane (1:3) to give 60 mg (12%) of **13** as dark green crystals with m.p. 102–108 °C, pure enough for collecting significant spectroscopic data: IR (KBr): $\tilde{\nu}$ = 3052 cm^{-1} (w), 2920 (w), 2853 (w), 1731 (w), 1627 (s), 1599 (s), 1501 (m), 1474 (m), 1443 (s), 1391 (w), 1378 (w), 1346 (w), 1335 (w), 1288 (m), 1252 (s), 1173 (s), 1032 (m), 834 (m), 728 (m). UV (CH_3CN): λ_{max} (lgε) = 199 nm (4.96), 247 (4.45), 256 (4.57), 383 (4.05), 490 (4.33). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 ppm (s, 6 H), 2.35 (s, 3 H), 3.83 (s, 3 H), 6.56 (dd, *J* = 9.8, 1.6 Hz, 1 H), 6.89 (d, *J* = 8.8 Hz, 2 H), 6.95 (s, 2 H), 7.18–7.30 (m, 6 H), 7.49 (dd, *J* = 9.8, 1.5 Hz, 1 H), 7.68 (d, *J* = 8.8 Hz, 1 H), 7.73 ("d", "*J*" = 5.4 Hz, 2 H), 7.81 (d, *J* = 9.7 Hz, 1 H), 7.93 (d, *J* = 7.6 Hz, 1 H), 8.03 ("dd", "*J*" = 8.4, 3.2 Hz, 1 H). ^{13}C NMR ($CDCl_3$, 298 K, 125.8 MHz): (one d is superimposed): δ = 20.32 ppm (q), 21.17 (q), 55.36 (q), 113.78 (d), 119.85 (d), 124.64 (d), 124.67 (d), 126.73 (d), 126.74 (d), 126.81 (d), 126.85 (d), 127.63 (d), 127.90 (d), 128.54 (d), 129.69 (d), 130.76 (d), 131.90 (d), 132.29 (s), 132.31 (s), 132.67 (s), 136.42 (s), 137.02 (s), 137.38 (s), 137.71 (s), 138.31 (s), 138.35 (s), 139.78 (s), 139.80 (s), 143.77 (s), 159.62 (s). MS (70 eV): *m*/*z* (%) = 478 (3) [M^+], 332 (4), 331 (25), 330 (100), 315 (5), 287 (10), 272 (7), 271 (3), 257 (3), 250 (4), 237 (4), 229 (5), 222 (4), 180 (5), 179 (7), 178 (3), 165 (5), 136 (3), 121 (5).

Diferrocenyl-(4-fluorophenyl)methanol (14): To a solution of ferrocene (2.23 g, 12.0 mmol) in 10 mL of dry THF, a solution of *tert*-butyllithium in pentane (5.9 mL, 10.0 mmol, 1.7 M) was added within 5 min at 0 °C under argon. After 1 h of stirring at 0 °C and 10 min at room temperature the reaction mixture was cooled to –78 °C and a solution of 4-fluorobenzoyl chloride (**15**, 0.5 mL, 4.0 mmol) in 5 mL of dry THF was added dropwise within 10 min, and the mixture was stirred for another 2 h at dry-ice temperature, and then for 14 h at room temperature. After hydrolysis with 20 mL of water, the water layer was extracted three times with 20 mL of dichloromethane and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness at the rotary evaporator: TLC (toluene/silica) of the crude product: R_f = 0.86, 0.52, 0.36. The fraction with R_f = 0.52 was isolated by flash chromatography (column with length of 15 cm and diameter of 2.5 cm). Compound **14** (0.72 g, 36%) was obtained as orange crystals, decomposing at 180 °C. IR (KBr): $\tilde{\nu}$ = 3520 cm^{-1} (m), 3095 (w), 1600 (w), 1500 (m), 1390 (w), 1310 (w), 1225 (m), 1160 (w), 1105 (w), 1040 (w), 1000 (w), 850 (w), 820 (m), 795 (w), 670 (w), 660 (w). UV (acetonitrile): λ_{max} (lg ε) = 205 nm (4.83), 249 (3.82), 446 (2.30). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.29 ppm (s, 1 H, OH), 3.82 (m, 2 H, Cp-H), 4.11–4.19 (m, 16 H, Cp-H), 6.98 (m, 2 H), 7.39 (m, 2 H). ^{13}C NMR ($CDCl_3$, 75.5 MHz): δ = 67.17, 67.21, 68.09, 69.66 (all d, Cp), 73.36 (s), 99.75 (s), 113.66 [d, d_{CF}, ^2J(C,F) = 21.5 Hz], 127.94 [d, d_{CF}, ^3J(C,F) = 7.7 Hz], 142.66 [s, d_{CF}, ^4J(C,F) = 3.1 Hz], 161.46 [s, d_{CF}, ^1J(C,F) = 244.6 Hz]. MS (EI = 70 eV): *m*/*z* (%) = 494 (51) [M^+], 356 (100), 233 (18), 215 (10). $C_{27}H_{23}FFe_2O$ (494.17): calcd. C 65.62, H 4.69; found C 65.54, H 4.49.

Diferrocenyl-(4-fluorophenyl)methylium Tetrafluoroborate (18): To a solution of the triarylmethanol **14** (0.74 g, 1.5 mmol) in 15 mL of dry dichloromethane HBF_4–diethyl ether (0.6 mL, 4.5 mmol) was added under nitrogen. After 10 min stirring at room temperature an overlayer of 15 mL of dry diethyl ether was carefully placed on the surface of the reaction mixture. After one day of crystallization in the refrigerator the precipitate wass isolated by filtration, washed with 30 mL of dry diethyl ether and dried for 1 h at 90 °C in vacuo (0.055 mbar). Compound **18** (0.83 g, 99%) was obtained as dark blue metallic shining needles, with m.p. 241–247 °C. IR (KBr): $\tilde{\nu}$ = 3104 cm^{-1} (m), 1594 (m), 1469 (s), 1412 (m), 1386 (m), 1332 (m), 1296 (m), 1227 (m), 1160 (m), 1084 (s), 1035 (s), 946 (w), 833 (m), 738 (m), 681 (m). UV (acetonitrile): λ_{max} (lg ε) = 194 nm (3.66), 261 (2.95), 376 (3.22), 728 (2.91). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.47 ppm (br. s, 12 H, Cp-H), 5.10 (br. s, 2 H, Cp-H), 5.86 (br. s, 4 H, Cp-H), 7.12 (2 H), 7.48 (2 H); throughout broad signals. MS (LSIMS, NBA): *m*/*z* (%) = 477 (100) [M^+], 356 (12), 123 (16), 108 (22). $C_{27}H_{22}$ BF_5Fe_2 (563.97): calcd. C 57.50, H 3.93; found C 57.11, H 3.86.

Ferrocenyl 4-Fluorophenyl Ketone (16): To a solution of 4-fluorobenzoyl chloride (**15**, 3.6 mL, 30.0 mmol) and aluminium chloride (4.00 g, 30.0 mmol) in 30 mL of dry dichloromethane, a solution of ferrocene (5.58 g, 30.0 mmol) in 30 mL of dry dichloromethane was added dropwise within 1 h at room temperature. After 14 h of additional strirring the reaction mixture was poured on 100 g of crushed ice, and the precipitated aluminium hydroxide was solubilized carefully by titrating with hydrochloric acid. The water layer was extracted three times with 40 mL of dichloromethane and the combined organic extracts were washed successively with 100 mL of brine, 100 mL of 2 N aqueous sodium hydroxide solution and again with 100 mL of brine. After drying with potassium carbonate the solvent was removed at the rotary evaporator, and the residue was treated with 50 mL of dry diethyl ether. Crystallization for 1 d in the refrigerator, washing of the crystals with 10 mL of dry diethyl ether and drying for 1 h at 70 °C in vacuo (0.056 mbar) gave 7.63 g (82%) of orange to red plates of **16** with m.p. 114–116 °C. IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1} (w), 3080 (w), 1625 (s), 1595 (s), 1500 (w), 1495 (m), 1375 (w), 1295 (m), 1220 (m), 1170 (w), 1150 (m), 1095 (w), 1025 (w), 1005 (w), 965 (w), 850 (m), 825 (m), 770 (m), 670 (w), 635 (w), 620 (m). UV (acetonitrile): λ_{max} (lg ε) = 201 nm (4.57), 244 (4.12), 276 (3.85, sh), 358 (3.10), 474 (2.85). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.21 ppm (s, 5 H, Cp-H), 4.60 (s, 2 H, Cp-H), 4.89 (s, 2 H, Cp-H), 7.15 (m, 2 H), 7.95 (m, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 70.26 ppm, 71.44, 72.56 (all d, Cp), 78.10 (s), 115.26 [d, d_{CF}, ^2J(C,F) = 21.4 Hz], 130.53 [d, d_{CF}, ^3J(C,F) = 7.9 Hz], 135.97 [s,d_{CF}, ^4J(C,F) = 4.0 Hz], 164.78 [s, d_{CF}, ^1J(C,F) = 250.7 Hz], 197.40 (s). MS (EI = 70 eV): *m*/*z* (%) = 309 (20), 308 (100) [M^+], 306 (7), 280 (6), 243 (7), 215 (6), 185 (7), 151 (7), 139 (13), 131 (5), 129 (5), 121 (9), 56 (11). $C_{17}H_{13}FFeO$ (308.13): calcd. C 66.27, H 4.25; found C 66.04, H 4.28.

Ferrocenyl(4-fluorophenyl)mesitylmethanol (17): To a *tert*-butyllithium solution in pentane (14.1 mL, 24.0 mmol, 1.7 M), a solution of 2-bromomesitylene (1.8 mL, 12.0 mmol) in 25 mL of dry THF was added at –78 °C within 5 min. After 1.5 h stirring at this temperature a solution of the ketone **16** (3.08 g, 10.0 mmol) in 15 mL of dry THF was added within 10 min. After 2 h additional stirring at –78 °C and 14 h at room temperature the mixture was hydrolyzed with 25 mL of water and the water layer was extracted three times with 40 mL of dichloromethane. The combined organic layers were dried with sodium sulfate and the solvent was evaporated. The residue was recrystallized from dichloromethane/diethyl ether to give 2.74 g (64%) orange crystals of **17** with m.p. 164–166 °C. IR (KBr): $\tilde{\nu}$ = 3470 (s), 3070 (w), 2910 (w), 1595 (m), 1500 (m), 1475 (w), 1415 (w), 1380 (w), 1355 (w), 1225 (s), 1160 (w), 1105 (w), 1005 (w), 945 (w), 850 (w), 805 (m), 670 (w), 610 (w). UV (acetonitrile): λ_{max} (lg ε) = 205 nm (4.90), 249 (3.72, sh), 459 (2.11). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.95 ppm (s, 6 H), 2.21 (s, 3 H), 3.58 (br. s, 1 H, OH) 4.05 (br. s, 1 H, Cp-H), 4.21 (br. s, 1 H, Cp-H), 4.29 (br. s, 6 H, Cp-H) 4.42 (br. s, 1 H, Cp-H), 6.73 (s, 2 H), 7.01 (m, 2 H), 7.43 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.47 ppm (q), 24.21 (q), 67.24, 68.42, 68.78, 69.15 (all d, Cp), 72.64 (s), 106.71 (s), 114.17 [d, d_{CF}, ^2J(C,F) = 21.3 Hz], 128.50 [d, d_{CF}, ^3J(C,F) = 7.9 Hz], 131.19 (d), 136.04, 137.54, 140.10 (all s), 141.74 [s,d_{CF}, ^4J(C,F) = 3.1 Hz], 161.77 [s, d_{CF}, ^1J(C,F) = 245.1 Hz]. MS (EI = 70 eV): *m*/*z* (%) = 429 (25), 428 (76) [M^+], 364 (17), 363 (67), 345 (25), 343 (26), 341 (11), 291 (14), 290 (60), 287 (16), 285 (15), 275 (36), 260 (15), 259 (13), 257 (10), 193 (9), 186 (10), 179 (11), 121 (9), 86 (43), 84 (76), 74 (23), 59 (46), 51 (27), 49 (100), 48 (9), 47 (15), 45 (26), 41 (16). $C_{26}H_{25}FFeO$ (428.33): calcd. C 72.91, H 5.88; found C 72.90, H 5.64.

Ferrocenyl(4-fluorophenyl)mesitylmethylium Tetrafluoroborate (19): To a solution of the triarylmethanol **17** (2.57 g, 6.00 mmol) in 25 mL of dry dichloromethane HBF_4–diethyl ether (1.8 mL, 13.0 mmol) was added under nitrogen. After 10 min stirring at room temperature an overlayer of 25 mL of dry diethyl ether was carefully placed on the surface of the reaction mixture. After one day of crystallization in the refrigerator the precipitate was isolated by filtration, washed with 30 mL of dry diethyl ether and dried for 1 h at 70 °C in vacuo (0.064 mbar): 2.93 g (98%) dark green crystals of **19** with m.p. 212–215 °C. IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1} (w), 2920 (w), 1605 (m), 1590 (s), 1475 (m), 1340 (m), 1320 (m), 1230 (m), 1165 (m), 1070 (s), 1035 (s), 850 (m). UV (methanol): λ_{max} (lgε) = 216 nm (4.42, sh), 229 (4.28, sh), 318 (4.19). ^{1}H NMR: throughout broad signals. MS (LSIMS, NBA): *m*/*z* (%) = 456 (6), 411 (100) [M$^+$], 290 (6), 194 (4), 136 (5), 121 (4). $C_{26}H_{24}$ BF_5Fe (498.12): calcd. C 62.69, H 4.86; found C 62.86, H 5.11.

1,1-Dicyano-2,2-diferrocenyl-2-(4-fluorophenyl)ethane (20): Malononitrile (132 mg, 2.00 mmol) in 20 mL of dry THF was deprotonated at room temperature with 60% sodium hydride/mineral oil (60 mg, 1.5 mmol). A solution of the tetrafluoroborate **18** (564 mg, 1.00 mmol) in 50 mL of dry THF was added within 10 min, and the reaction mixture was stirred for 19 h. After hydrolysis with 20 mL of water the aqueous layer was extracted three times with 30 mL of dichloromethane and the combined organic layers were dried with sodium sulfate and the solvents evaporated. The residue was crystallized from 20 mL dichloromethane/diethyl ether (1:1) to give 385 mg (71%) of **20** as orange crystals with mp. 200 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3073 cm^{-1} (w), 2911 (w), 1604 (m), 1508 (s), 1412 (w), 1235 (m), 1172 (m), 1109 (m), 1039 (m), 1004 (m), 824 (s), 794 (s). UV (acetonitrile): λ_{max} (lgε) = 205 nm (4.85), 244 (3.93, sh). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 4.18 ppm (br. s, 12 H, Cp-H), 4.32–4.36 (m, 6 H, Cp-H), 5.48 [s, 1 H, –C*H*(CN)$_2$], 7.07 (m, 2 H), 7.53 (m, 2 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 38.57 ppm [d, –*C*H(CN)$_2$], 50.32 [s, *C*–CH(CN)$_2$], 67.67, 68.56, 68.69, 69.21, 69.76 (all d), 94.82 (s), 113.14 (s, CN), 114.64 [d, d_{CF}, ^2J(C,F) = 21.4 Hz], 129.73 [d, d_{CF}, ^3J(C,F) = 8.0 Hz], 137.38 [s, d_{CF}, ^4J(C,F) = 3.0 Hz], 162.00 [s, d_{CF}, ^1J(C,F) = 248.8 Hz]. MS (EI = 70 eV): *m*/*z* (%) = 543 (12), 542 (34) [M$^+$], 478 (42), 477 (100), 475 (13), 409 (6), 357 (22), 356 (84), 355 (16), 354 (17), 291 (31), 235 (12), 234 (32), 233 (44), 215 (21), 186 (22), 139 (5), 121 (25), 86 (32), 84 (57), 74 (15), 66 (67), 59 (17), 56 (11), 51 (21), 49 (64), 45 (15), 39 (13), 38 (10). $C_{30}H_{23}FFe_2N_2$ (542.22): calcd. C 66.45, H 4.28, N 5.17; found C 66.30, H 4.34, N 5.08.

8-[Diferrocenyl-(4-fluorophenyl)methylamino]quinoline (21): 8-Aminoquinoline (288 mg, 2.00 mmol) in 30 mL of dry THF were deprotonated with 60% sodium hydride/mineral oil (60 mg, 1.5 mmol) within 3 h at reflux temperature. A solution of the tetrafluoroborate **18** (564 mg, 1.00 mmol) in 60 mL of dry THF was added within 5 min, and the reaction mixture was stirred for 7 h at reflux temperature. After hydrolysis with 30 mL of water the aqueous layer was extracted three times with 30 mL of dichloromethane, and the combined organic layers were dried with sodium sulfate and the solvents evaporated. The residue was fractionated by flash chromatography; TLC (toluene/silica) R_f = 0.87, 0.60, 0.33, 0.20. The fraction with R_f = 0.87 crystallized from 30 mL of diethyl ether to give 220 mg (35%) of **21** as golden to yellow crystals with m.p. 225 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3364 cm^{-1} (m), 3092 (w), 1603 (w), 1571 (m), 1511 (s), 1478 (s), 1380 (s), 1337 (w), 1226 (m), 1159 (m), 1107 (m), 1000 (w), 818 (s), 748 (w). UV (acetonitrile): λ_{max} (lgε) = 201 nm (5.02), 254 (4.48), 374 (3.67). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.99 ppm (br. s, 2 H, Cp-H), 4.10 (m, 2 H, Cp-H), 4.12 (s, 10 H, Cp-H), 4.20 (m, 2 H, Cp-H), 4.43 (br. s, 2 H, Cp-H), 6.11 (dd, ^3J = 7.7, ^4J = 1.2 Hz, 1 H, H-7), 6.93 (dd, ^3J = 8.2, ^4J = 1.2 Hz, 1 H, H-5), 7.01 (m, 1 H), 7.05 (m, 2 H), 7.39 (m, 1 H), 7.76 (m, 2 H), 8.05 (dd, ^3J = 8.3, ^4J = 1.7 Hz, 1 H, H-4), 8.25 (s, 1 H, N–H), 8.85 (dd, ^3J = 4.2, ^4J = 1.7 Hz, 1 H, H-2). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 61.25 (s), 66.77, 68.78, 68.86, 69.19 (all d), 99.52 (s), 108.71 (d), 113.19 (d), 114.00 [d, d_{CF}, ^2J(C,F) = 21.4 Hz], 121.21 (d), 127.02 (d), 128.68 (q), 130.68 [d, d_{CF}, ^3J(C,F) = 7.5 Hz], 136.10 (d), 137.27 [s, d_{CF}, ^4J(C,F) = 3.0 Hz], 138.78 (q), 141.67 (q), 146.73 (d), 161.91 [s, d_{CF}, ^1J(C,F) = 245.3 Hz]. MS (EI = 70 eV): *m*/*z* (%) = 621 (7), 620 (16) [M$^+$], 479 (6), 478 (30), 477 (71), 475 (9), 409 (4), 356 (9), 291 (17), 265 (19), 264 (100), 262 (7), 235 (5), 234 (8), 233 (12), 215 (6), 199 (23), 144 (7), 121 (5). $C_{36}H_{29}FFe_2N_2$ (620.33): calcd. C 69.70, H 4.71, N 4.52; found C 69.53, H 4.65, N 4.49.

α,α-Dicyano-β-ferrocenyl-β-mesityl-*p*-benzoquinodimethane (22): Malononitrile (132 mg, 2.00 mmol) in 20 mL of dry THF was deprotonated at room temperature with 60% sodium hydride/mineral oil (60 mg, 1.5 mmol). A solution of the tetrafluoroborate **19** (498 mg, 1.00 mmol) in 60 mL of dry THF was added within 10 min, and the reaction mixture was stirred for 20 h. After hydrolysis with 20 mL of water the aqueous layer was extracted three times with 30 mL of dichloromethane, and the combined organic layers were dried with sodium sulfate and the solvents evaporated. The residue was recrystallized from 25 mL diethyl ether to give 300 mg (66%) of **22** as dark green metallic shining crystals with m.p. 204 °C. IR (KBr): $\tilde{\nu}$ = 3070 cm^{-1} (w), 2910 (w), 2200 (s), 1595 (s), 1435 (s), 1395 (m), 1370 (m), 1340 (w), 1320 (w), 1320 (w), 1260 (w), 1210 (m), 1180 (s), 935 (w), 830 (m), 680 (m). UV (acetonitrile): λ_{max} (lgε) = 196 nm (3.91), 282 (3.02), 357 (2.82), 467 (3.27), 512 (3.32), 720 (3.01). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 1.97 ppm (s, 6 H), 2.33 (s, 3 H), 4.29 (s, 5 H, Cp-H), 4.47 (s, 2 H, Cp-H), 4.79 (s, 2 H, Cp-H), 6.60 (dd, *J* = 9.5 Hz, 1.9 Hz), 6.90 (s, 2 H), 6.95 (dd, *J* = 9.5 Hz, 2.0 Hz), 7.35 (dd, *J* = 9.6 Hz, 1.9 Hz), 8.53 (dd, *J* = 9.7 Hz, 1.7 Hz). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 20.02 ppm (q), 21.07 (q), 67.50 (s), 71.38 (d, several C), 73.72 (d), 74.62 (d), 81.96 (s), 116.10 (s, CN), 116.30 (s, CN), 122.34 (d), 122.98 (d), 128.44 (d, mesityl-H), 130.68 (s), 134.80 (d), 135.37 (s), 136.26 (d), 136.94 (s), 138.54 (s), 155.88 (s), 169.74 (s). MS (EI = 70 eV): *m*/*z* (%) = 456 (100) [M$^+$], 315 (12), 186 (7), 121 (23). $C_{29}H_{24}FeN_2$ (456.37): calcd. C 76.32, H 5.30, N 6.14; found C 76.13, H 5.38, N 6.05.

4-[Ferrocenyl(mesityl)methylene]-1-[(quinolin-8-yl)imino]cyclohexa-2,5-diene (23): 8-Aminoquinoline (288 mg, 2.00 mmol) in 30 mL of dry THF was deprotonated with 60% sodium hydride/mineral oil (60 mg, 1.5 mmol) for 3 h at reflux temperature. A solution of the tetrafluoroborate **19** (498 mg, 1.00 mmol) in 60 mL of dry THF was added within 5 min at room temperature, and the reaction mixture was stirred for 6 h at room temperature. After hydrolysis with 30 mL of water the aqueous layer was extracted three times with 30 mL of dichloromethane and the combined organic layers were dried with sodium sulfate and the solvents evaporated. The residue was fractionated by flash chromatography with first toluene, then ethyl acetate as eluent; TLC (toluene/silica) R_f = 0.87, 0.77, 0.62, 0.38, 0.13–0.00. The fraction with R_f = 0.52 (ethyl acetate/silica) was isolated and crystallized from 20 mL diethyl ether at –18° to give 150 mg (28%) of **23** as dark purple metallic crystals with m.p. 193 °C (dec.). IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1} (w), 3040 (w), 2910 (w), 2850 (w), 1605 (rn), 1565 (rn), 1490 (s), 1445 (rn), 1380 (rn), 1335 (w), 1310 (w), 1285 (w), 1245 (w), 1180 (rn), 1105 (w), 1080 (w), 1050 (w), 1000 (w), 940 (w), 835 (rn), 800 (rn), 750 (w), 665 (w). UV (acetonitrile): λ_{max} (lgε) = 198 nm (4.93), 243 (4.43), 283 (3.98), 397 (4.35), 551 (3.66). ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.02 ppm (s, 6 H), 2.29 (s, 3 H), 4.22 (s, 5 H, Cp-H), 4.30 (s, 2 H, Cp-H), 4.48 (s, 2 H, Cp-H), 6.44 (rn, br, 1 H), 6.60 (very br, 1 H), 6.86 (s, 2 H), 7.00 (very br, 1 H), 7.22 (m, lH), 7.39–7.58 (m, 3 H), 8.15 (d, *J* = 8.2 Hz, 1 H), 8.47 (rn, br, 1 H), 8.91 (br. s, 1 H). ^{13}C NMR (125 MHz, CDCl$_3$): δ = 20.05 ppm (q), 21.11 (q), 70.43 (d), 71.03 (d), 72.93 (d), 82.60 (s), 118.12 (d), 121.35 (d), 123.41 (s), 126.65 (d), 128.00 (d), 128.18 (d, mesityl-H), 129.26 (s), 129.41 (s), 132.53 (d), 135.51 (s), 136.05 (d), 137.36 (s), 137.86 (s), 142.06 (s), 149.74 (d), 160.94 (s). MS (EI = 70 eV): *m*/*z* (%) = 534 (0.1) [M$^+$], 186 (100), 144 (35), 121 (57), 93 (8), 56 (22). $C_{35}H_{30}FeN_2$ (534.48): calcd. C 78.65, H 5.66, N 5.24; found C 78.43, H 5.94, N 5.04.

Bis(4-fluorophenyl)(2,4,6-trimethylphenyl)methanol (24): To a solution of 1-bromomesitylene (2.74 g, 2.10 mL, 13.7 mmol) in 20 mL of dry THF a 15% solution of *n*-butyllithium in hexane (5.2 mL, 13.0 mmol) was added within 5 min at –55 °C under argon. After 30 min of stirring at –55 °C a solution of 4,4′-difluorobenzophenone (2.00 g, 9.16 mmol) in 30 mL of dry THF was added dropwise at –30 °C within 15 min, and the reaction mixture was stirred at room temperature for another 5 d. After hydrolysis with 20 mL of a saturated aqueous $(NH_4)_2HPO_4$ solution water layer was extracted three times with 40 mL of dichloromethane and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness at the rotary evaporator: TLC (silica/toluene) of the crude product: R_f = 0.56, 0.48. The fraction with R_f = 0.56 was isolated by flash chromatography: 2.46 g (79%) of **24** as colorless crystals with m.p. 137–140 °C. IR (KBr): $\tilde{\nu}$ = 3555 cm^{-1} (m, OH), 3045 (w), 2967 (w), 2934 (w), 1600 (s), 1502 (s), 1375 (w), 1231 (s), 1263 (s), 1155 (m), 1032 (w), 1014 (w), 1002 (m), 851 (m), 835 (s), 826 (s). 812 (w), 586 (m). UV (acetonitrile): λ_{max} (lgε) = 196 nm (4.92), 217 (4.44, sh), 265 (3.25), 274 (3.11). ^{1}H NMR (CDCl$_3$, 500 MHz): δ = 1.85 ppm (s, 6 H), 2.26 (s, 3 H), 2.69 (s, 1 H, O*H*), 6.81 (s, 2 H), 6.96–7.04 (m, 4 H), 7.15–7.22 (m, 4 H). ^{13}C NMR (CDCl$_3$, 125 MHz): δ = 20.51 ppm (q), 24.34 (q), 82.75 (s, *C*–OH), 115.05 (d, $^2J_{CF}$ = 21.0 Hz), 129.50 (d, $^3J_{CF}$ = 8.0 Hz), 131.54 (d), 136.62 (s), 137.85 (s), 140.74 (s), 143.41 (s, $^4J_{CF}$ = 3.5 Hz), 162.03 (s, $^1J_{CF}$ = 246.8 Hz). MS (EI = 70 eV): *m*/*z* (%) = 338 (10) [M$^+$], 321 (23), 320 (62), 305 (36), 243 (16), 226 (10), 225 (46), 224 (31), 220 (14), 219 (87), 210 (14), 148 (9), 147 (54), 123 (100), 120 (24), 105 (11), 95 (30). $C_{22}H_{20}F_2O$ (338.40): calcd. C 78.09, H 5.96; found C 78.13, H 5.88.

Bis(4-fluorophenyl)(2,4,6-trimethylphenyl)methylium Tetrafluoroborate (25): To a solution of the triarylmethyl alcohol **24** (1.09 g, 3.23 mmol) in 14 mL of dry dichloromethane HBF$_4$–diethyl ether (1.26 mL, 9.26 mmol) was added at room temperature under nitrogen. After 5 min stirring at room temperature a layer of 40 mL of diethyl ether was placed carefully on the surface of the reaction mixture, leading to the formation of a solid precipitate within 1 d, which was isolated by filtration and was washed with 10 mL of diethyl ether: Compound **25** (1.160 g, 88%) was obtained as dark green, metallic shining crystals with m.p. 144–150 °C. IR (KBr): $\tilde{\nu}$ = 3039 cm^{-1} (w), 2919 (w), 2856 (w), 1627 (m), 1599 (s), 1582 (s, sh), 1496 (w, sh), 1421 (m), 1375 (s), 1349 (m), 1240 (m), 1172 (m), 1156 (s), 1123 (m), 1084 (s, br), 910 (w), 864 (w). UV (acetonitrile): λ_{max} (lgε) = 196 nm (4.85), 247 (4.04), 266 (3.55, sh), 307 (3.80), 435 (4.68), 482 (4.21). ^{1}H NMR (CDCl$_3$, 500 MHz): partially broadened double set of signals; δ = 1.81 ppm (s, 6 H$_a$), 1.83 (s, 6 H$_b$), 2.42 (s, 3 H$_b$), 2.47 (s, 3 H$_a$), 7.07 (s, 2 H$_b$), 7.16 (s, 2 H$_a$), 7.33 (dd, *J* = 9.2, 2.4 Hz, 1 H$_b$), 7.40 ("t", "*J*" = 8.4 Hz), 7.52 (dd, *J* = 9.3, 2.4 Hz, 1 H$_b$), 7.58–7.61 (m), 7.69 (s, br), 8.04 (dd, *J* = 9.2, 2.4 Hz, 1 H$_b$), 8.15 (br. s, 1 H). MS (EI = 70 eV): *m*/*z* (%) = 340 (24) [M$^+$ – BF$_3$], 321 (34) [M$^+$ – BF$_4$], 319 (25), 318 (100), 303 (14), 275 (22), 260 (14), 225 (14), 221 (33), 210 (14), 201 (11). $C_{22}H_{19}BF_6$ (408.19): calcd. C 64.73, H 4.69; found C 64.41, H 4.69.

α,α-Dicyano-β-(4-fluorophenyl)-β-mesityl-*p*-benzoquinodimethane (28): Malononitrile (66 mg, 0.98 mmol) in 5 mL of dry THF were deprotonated at room temperature with 60% sodium hydride/mineral oil (40 mg, 1.0 mmol). A suspension of the tetrafluoroborate **25** (200 mg, 0.490 mmol) in 8 mL of dry THF was added, and the reaction mixture was stirred for 20 h. After hydrolysis with 20 mL of water the aqueous layer was extracted three times with 20 mL of diethyl ether and the combined organic layers were dried with sodium sulfate and the solvents evaporated to dryness at the rotary evaporator: TLC (silica; diethyl ether/*n*-hexane, 1:3): R_f = 0.26, 0.10. Fractionated by flash chromatography.

First Fraction: R_f = 0.26. Compound **28** (100 mg, 62%) was obtained as dark green crystals with metallic lustre and m.p. 75 °C. IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1} (w), 2212 (s), 1607 (m), 1592 (s), 1501 (w), 1444 (s), 1235 (m), 1202 (m), 1181 (m), 1159 (m), 843 (m). UV (acetonitrile): λ_{max} (lgε) = 196 nm (4.99), 283 (4.12), 357 (3.98, sh), 470 (4.70). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 1.95 ppm (s, 6 H), 2.35 (s, 3 H), 6.83 (dd, *J* = 9.7, 1.7 Hz, 1 H), 6.96 (s, 2 H), 7.05–7.15 (m, 3 H), 7.20–7.32 (m, 3 H), 7.52 (dd, *J* = 9.7, 1.7 Hz, 1 H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 20.29 ppm (q), 21.14 (q), 72.24 (s), 114.34 (s, *C*°N), 114.40 (s, *C*°N), 116.12 (d, $^2J_{CF}$ = 21.8 Hz), 124.58 (d), 124.68 (d), 129.05 (d), 132.68 (s), 133.59 (d, $^3J_{CF}$ = 8.8 Hz), 134.39 (s, $^4J_{CF}$ = 3.3 Hz), 135.68 (d), 135.88 (s), 136.38 (s), 136.61 (d), 139.40 (s), 155.55 (s), 160.32 (s), 164.17 (s, $^1J_{CF}$ = 255.0 Hz). MS (EI = 70 eV): *m*/*z* (%) = 367 (27) [M$^+$ + 1], 366 (100) [M$^+$], 351 (8), 336 (6), 270 (7), 246 (5), 225 (10), 219 (6), 210 (7), 147 (6), 123 (12), 109 (5). $C_{25}H_{19}FN_2$ (366.44): calcd. C 81.94, H 5.23, N 7.64; found C 81.70, H 5.17, N 7.45.

Second Fraction: with R_f = 0.10: 25 mg (16%) of a yellow solid with 119–123 °C, identified as the hydrolysis product 4-[(4-fluorophenyl)-(2,4,6-trimethylphenyl)]methylidene-2,5-cyclohexadien-1-one.

4-[(4-Fluorophenyl)-(2,4,6-trimethylphenyl)]methylidene-2,5-cyclohexadien-1-one: IR (KBr): $\tilde{\nu}$ = 3049 cm^{-1} (w), 2920 (w), 1629 (s), 1608 (w), 1595 (m), 1500 (m, sh), 1430 (w), 1379 (w), 1230 (m), 1159 (m), 865 (m), 839 (w), 811 (w), 586 (w). UV (acetonitrile): λ_{max} (lgε) = 196 nm (4.85), 220 (4.23, sh), 250 (4.22), 367 (4.47). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 2.00 ppm (s, 6 H, C*H*$_3$), 2.34 (s, 3 H, C*H*$_3$), 6.35 (dd, *J* = 10.0, 2.0 Hz, 1 H), 6.51 (dd, *J* = 10.0, 2.0 Hz, 1 H), 6.95 (s, 2 H), 6.96 (dd, *J* = 9.9, 2.7 Hz, 1 H), 7.06–7.14 (m, 2 H), 7.24–7.30 (m, 2 H), 7.61 (dd, *J* = 10.0, 2.7 Hz, 1 H). ^{13}C NMR (75.5 MHz, CDCl$_3$): δ = 20.27 ppm (q), 21.10 (q), 115.71 (d, $^2J_{CF}$ = 21.8 Hz, C-3′′/C-5′′), 128.84 (d), 129.06 (d), 129.38 (d), 130.45 (s), 133.24 (d, $^3J_{CF}$ = 8.2 Hz, C-2′′/C-6′′), 134.29 (s, $^4J_{CF}$ = 3.5 Hz, C-1′′), 136.01 (s), 136.21 (s), 137.66 (d), 138.49 (d), 138.80 (s), 157.92 (s), 163.62 (s, $^1J_{CF}$ = 252.7 Hz, C-4′′), 187.10 (s, *C*=O). MS (EI = 70 eV): *m*/*z* (%) = 319 (24) [M$^+$ + 1], 318 (100) [M$^+$], 303 (15), 275 (26), 260 (18), 259 (11). $C_{22}H_{19}OF$ (318.39): calcd. C 82.99, H 6.01; found C 82.86, H 5.96.

α,α-Dicyano-β-(4-dicyanomethylphenyl)-β-mesityl-*p*-benzoquinodimethane (27): In an orientating experiment malononitrile (142 mg, 2.11 mmol) in 3 mL of dry THF was deprotonated at room temperature with 60% sodium hydride/mineral oil (84 mg , 2.11 mmol). A solution of the monosubstitution product **28** (200 mg, 0.528 mmol) in 5 mL of dry THF was added, and the reaction mixture was stirred under reflux for 20 h, resulting in a dark green reaction mixture. The solvent was removed at the rotatory evaporator. The residue was solubilized in 20 mL methanol, the solution was filtered through silica and concentrated to give a dark green solid with m.p. > 330 °C, whose ^{1}H NMR spectrum is in agreement with the resonance stabilized symmetrical anion **26**. ^{1}H NMR (300 MHz, [D$_4$]MeOH): δ = 1.88 ppm (s, 6 H), 2.34 (s, 3 H), 6.98 (s, 2 H), 6.99 (d, *J* = 8.7, 4 H), 7.18 (d, *J* = 8.7, 4 H). Acidifying the dark green THF solution with half concentrated hydrochloric acid let to a change in color to deep orange. Isolation of the neutral product by flash chromatography failed due to a tendency to decomposition by hydrolysis, however, mass spectrum and ^{1}H NMR spectrum of the crude product with about 90% purity were in agreement with structure **28** (which is of course less mesomeric stabilized compared to structures **10** and **22**): ^{1}H NMR (300 MHz,

$CDCl_3$): δ = 1.97 ppm (s, 6 H), 2.35 (s, 3 H), 5.88 (s, very broad, 1 H), 6.86 (dd, J = 9.6, 1.8 Hz, 1 H), 6.91 ("d", J = 8.8 Hz, 2 H), 6.94 (s, 2 H), 7.04 (dd, J = 9.6, 2.1 Hz, 1 H), 7.16–7.24 (m, 3 H), 7.57 (dd, J = 9.6, 1.8 Hz, 1 H). MS (EI = 70 eV): m/z (%) = 413 (34) [M^+ + 1], 412 (100) [M^+], 387 (43), 270 (12), 255 (10), 241 (10), 206 (13), 166 (12), 165 (11), 97 (12), 78 (46), 66 (17).

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