JOC The Journal of Organic Chemistry

J. Org. Chem., 1997, 62(5), 1419-1426, DOI:10.1021/jo9622035

Supplementary Information

We report herein the synthesis of the 1,3-diaryl-1,3-propanediones **8**, the 2,2-methyl-1,3-diaryl-1,3-propanediones **9** and of the 3,5-dimethyl-3,5-diaryl-4*H*-pyrazoles **10**.

-Insert Structures 8 - 10 here -

General Aspects. NMR spectra were recorded on the Bruker AC 200 or AC 250 spectrometer with $CDCl_3$, d_4-MeOD or d_6-DMSO as internal standard. Infrared spectra were taken on a Perkin Elmer 1420 ratio recording infrared spectrophotometer (values in cm^{-1}). Melting points were determined on a Büchi SMP 535 apparatus and are uncorrected. Combustion analyses were performed by the Microanalytical Divison of the Institute of Inorganic Chemistry, University of Würzburg. Solvents and commercially available chemicals were purified by standard procedures or used as such. Column chromatography was conducted on silica gel (0.063 - 0.200 mm, Woelm) or on basic alumina (0.063 - 0.200 mm, Merck).

General Procedure for the Preparation of the 1,3-Diaryl-1,3-propanediones (8).[14,16] 4.18 g (100 mmol) of 60% sodium hydride was dispersed in 50 mL of abs. DMSO and the mixture was stirred at ca. 20 °C for 30 min. After lowering the temperature to ca. 18 °C, 100 mmol of the corresponding methyl benzoate was added. The reaction mixture was stirred vigorously and 50 mmol of the corresponding aryl methyl ketone was added the temperature kept below 15 °C during addition. After complete addition the reaction mixture was stirred for another 1.5 h at ca. 20 °C and poured then on 100 g of crushed ice which contained 5 mL of 85% H_3PO_4. The crude product was removed by filtration and washed thoroughly with water and cyclohexane. Recrystallisation afforded the pure 1,3-propanediones **8**.

1,3-Di(4'-α,α,α–trifluoromethylphenyl)-1,3-propanedione (*p*-8g; *p*-CF_3): 10.6 g (59%) colorless powder, mp 127 - 128 °C (cyclohexane). IR (KBr): ν = 2920, 2880, 1610, 1580, 1220, 1170, 1070, 1010, 865, 850; ^{1}H NMR ($CDCl_3$): δ = 6.88 (s, 1H, enol 2-H), 7.77 (d, ^3J = 8.0 Hz, 4H, 3'-H), 8.10 (d, ^3J = 8.0 Hz, 4H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 94.1 (d, C-2), 123.6 (q, $^1J_{CF}$ = 271 Hz, CF_3), 125.8 (dq, $^3J_{CF}$ = 4 Hz, C-3'), 127.6 (d, C-2'), 134.1 (q, $^2J_{CF}$ = 33 Hz, C-4'), 138.4 (s, C-1'), 184.7 (s, C-1 and C-3).-Anal. Calcd for $C_{17}H_{10}F_6O_2$ (360.3): C, 56.68; H, 2.80. Found: C, 56.90; H, 3.11.

1,3-Di(3'-α,α,α–trifluoromethylphenyl)-1,3-propanedione (*m*-8g; *m*-CF_3): 11.2 g (61%) pale yellow powder, mp 67 - 69 °C (ethanol). IR (KBr): ν = 2920, 1610, 1580, 1430, 1330, 1220, 1170, 1120, 790, 690; ^{1}H NMR ($CDCl_3$): δ = 6.88 (s, 1H, enol 2-H), 7.66 (t, ^3J = 7.8 Hz, 2H, 5'-H), 7.84 (d, ^3J = 7.8 Hz, 2H, 4'-H or 6'-H), 8.19 (d, ^3J = 7.8 Hz, 2H, 4'-H or 6'-H), 8.25 (s, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 93.1 (d, C-2), 123.7 (q, $^1J_{CF}$ = 271 Hz, CF_3), 124.1 (dq, $^3J_{CF}$ = 4 Hz, C-2'), 129.1 (dq, $^3J_{CF}$ = 4 Hz, C-4'), 129.4 (d, C-6'), 130.4 (d, C-5'), 131.4 (q, $^2J_{CF}$ = 33 Hz, C-3'), 135.9 (s, C-1'), 184.5 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{10}F_6O_2$ (360.3): C, 56.68; H, 2.80. Found: C, 56.65; H, 3.09.

1,3-Di(3'-chlorophenyl)-1,3-propanedione (*m*-8h; *m*-Cl): 11.8 g (81%) pale yellow powder, mp 152 - 154 °C (toluene). IR (KBr): ν = 3020, 2880, 1540, 1570, 1560, 1530, 1280, 1240, 1210, 710; ^{1}H NMR ($CDCl_3$): δ = 6.89 (s, 1H, enol 2-H), 7.43 (t, ^3J = 7.9 Hz, 2H, 5'-H), 7.53 (ddd, ^3J = 7.9 Hz, ^4J = 2.0 Hz, ^4J = 1.2 Hz, 2H, 6'-H), 7.85 (dt, ^3J = 7.9 Hz, ^4J = 1.2 Hz, 2H, 4'-H), 7.95 (t, ^4J = 1.2 Hz, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 93.4 (d, C-2), 125.3 (d, C-6'), 127.3 (d, C-5'), 130.0 (d, C-2'), 132.4 (d, C-4'), 135.0 (s, C-3'), 137.0 (s, C-1'), 184.4 (s, C-1 and C-3). Anal. Calcd for $C_{15}H_{10}Cl_2O_2$ (293.1): C, 61.46, H, 3.44. Found: 61.28; H, 3.49.

1,3-Di(3'-methylphenyl)-1,3-propanedione (*m*-8m; *m*-CH_3): 8.10 g (64%) yellow solid, mp 38 - 39 °C (methylene chloride). IR (KBr): ν = 3000, 2880, 1540, 1230, 1170, 1040, 760, 720, 670, 600; ^{1}H NMR ($CDCl_3$): δ = 2.42 (s, 6H, CH_3), 6.85 (s, 1H, enol 2-H), 7.35 (m, 4H, Ph-H), 7.82 (m, 4H, Ph-H); ^{13}C-NMR ($CDCl_3$): δ = 21.0 (q, CH_3), 92.8 (d, C-2), 124.0 (d, C-6'), 127.4 (d, C-5'), 128.2 (d, C-2'), 132.9 (d, C-4'), 135.1 (s, C-3'), 138.0 (s, C-1'), 185.5 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{16}O_2$ (252.3): C, 80.93; H, 6.39. Found: C, 80.69; H, 6.30.

1,3-Di(3'-methoxyphenyl)-1,3-propanedione (*m*-8o; *m*-OCH_3): 10.8 g (76%) pale yellow powder, mp 102 - 103 °C (ethanol). IR (KBr): ν = 3000, 2880, 1540, 1230, 1170, 1040, 760, 720, 670, 600; ^{1}H NMR ($CDCl_3$): δ = 3.89 (s, 6H, OCH_3), 6.82 (s, 1H, enol 2-H), 7.10 (ddd, ^3J = 8.2 Hz, ^4J = 2.6 Hz, ^5J = 0.9 Hz, 2H, 4'-H), 7.40 (t, ^3J = 8.2 Hz, 5'-H), 7.55 (m, 4H, 2'-H and 6'-H); ^{13}C NMR ($CDCl_3$): δ = 55.4 (q, OCH_3), 93.5 (d, C-2), 111.9 (d, C-2'), 118.6 (d, C-4'), 119.6 (d, C-6'), 129.6 (d, C-5'), 136.7 (s, C-1'), 159.8 (s, C-3'), 185.5 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{16}O_4$ (284.3): C, 71.82; H, 5.67. Found: C, 71.92; H, 5.66.

1,3-Di(3'-fluorophenyl)-1,3-propanedione (*m*-8r; *m*-F): 11.0 g (85%) pale yellow needles, mp 126 - 127 °C (toluene). IR (KBr): ν = 3040, 1550, 1440, 1290, 1240, 1170, 910, 760, 720, 650; ^{1}H NMR ($CDCl_3$): δ = 6.79 (s, 1H, enol 2-H), 7.27 (ddt, ^3J = 8.2 Hz, ^5J = 1 Hz, $^4J_{HF}$ = 2.6 Hz, 2H, 5'-H), 7.48 (dt, ^3J = 8.2 Hz, $^3J_{HF}$ = 5.6 Hz, 2H, 4'-H), 7.68 (ddd, ^3J = 9.6 Hz, ^4J = 1.6 Hz, $^5J_{HF}$ = 2.5 Hz, 2H, 6'-H), 7.77 (dt, $^3J_{HF}$ = 7.8 Hz, ^4J = 1.6 Hz, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 93.5 (d, C-2), 114.1 (dd, $^2J_{CF}$ = 23 Hz, C-4'), 119.6 (dd, $^2J_{CF}$ = 21 Hz, C-2'), 122.8 (dd, $^4J_{CF}$ = 3 Hz, C-6'), 130.3 (dd, $^3J_{CF}$ = 8 Hz, C-5'), 137.5 (d, $^3J_{CF}$ = 7 Hz, C-1'), 162.9 (d, $^1J_{CF}$ = 246 Hz, C-3'), 184.5 (d, $^4J_{CF}$ = 8 Hz, C-1 and C-3). Anal. Calcd for $C_{15}H_{10}F_2O_2$ (260.2): C, 69.21; H, 3.88. Found: C, 68.95; H, 3.77.

General Procedure for the Preparation of the of the 2,2-Dimethyl-1,3-diaryl-1,3-propanediones (9).[14,16] The corresponding diketones ***p*-8g**, ***m*-8g**, ***m*-8h**, ***m*-8m**, ***m*-8o** and ***m*-8r** (10.0 mmol) were dissolved in 30 mL of DMSO and 15 mL of $CHCl_3$, and 5.0 g of potassium carbonate powder were added. The mixture was chilled by means of an ice bath and 4.27 g (30.0 mmol) of methyl iodide was added all at once. The mixture was stirred for 48 h at ca. 20 °C and 100 mL of methyl *tert*-butyl ether were added. After filtration, 40 mL of water were added to the filtrate and the aqueous DMSO layer was separated. The organic layer was washed thouroughly three times with 100 mL of water and dried over magnesium sulfate, and the solvent evaporated (40 °C, 18 torr). The crude product was purified by recrystallization or column chromatography on silica gel.

2,2-Dimethyl-1,3-di(4'-α,α,α–trifluoromethylphenyl)-1,3-propanedione (*p*-9g; *p*-CF_3): 2.38 g (61%) colorless needles, mp 96 - 97 °C, R_f = 0.90 (SiO_2, methylene chloride). IR (KBr): ν = 2980, 2900, 1650, 1560, 1490, 1440, 1390, 1300, 1230, 1150, 1000, 930; ^{1}H NMR ($CDCl_3$): δ = 1.68 (s, 6H, 2-CH_3), 7.60 (d, ^3J = 8.3 Hz, 4H, 3'-H), 8.93 (d, ^3J = 8.3 Hz, 4H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 24.9 (q, 2-CH_3), 59.9 (s, C-2), 123.4 (q, $^1J_{CF}$ = 268 Hz, CF_3), 125.9 (dq, $^3J_{CF}$ = 4 Hz, C-3'), 129.4 (d, C-2'), 134.5 (q, $^2J_{CF}$ = 33 Hz, C-4'), 138.1 (s, C-1'), 198.8 (s, C-1 and C-3). Anal. Calcd for $C_{19}H_{14}F_6O_2$ (388.3): C, 58.77; H, 3.63. Found: C, 58.75; H, 4.13.

2,2-Dimethyl-1,3-di(3'-α,α,α–trifluoromethylphenyl)-1,3-propanedione (*m*-9g; *m*-CF_3): 1.72 g (45%) colorless oil, R_f = 0.90 (SiO_2, methylene chloride). IR (KBr): ν = 2990, 2910, 1630, 1530, 1470, 1440, 1380, 1300, 1270, 1110, 1050, 990; ^{1}H NMR ($CDCl_3$): δ = 1.70 (s, 6H, 2-CH_3), 7.45 (t, ^3J = 7.9 Hz, 2H, 5'-H), 7.69 (d, ^3J = 7.9 Hz, 2H, 4'-H), 7.90 (d, ^3J = 7.9 Hz, 2H, 6'-H), 8.16

(s, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 25.1 (q, 2-CH_3), 59.6 (s, C-2), 123.3 (q, $^1J_{CF}$ = 271 Hz, CF_3), 126.1 (dq, $^3J_{CF}$ = 4 Hz, C-2'), 129.4 (d, C-5'), 129.6 (dq, $^3J_{CF}$ = 4 Hz, C-4'), 130.9 (q, $^2J_{CF}$ = 33 Hz, C-3'), 131.8 (d, C-6'), 135.9 (s, C-1'), 198.6 (s, C-1 and C-3).). Anal. Calcd for $C_{19}H_{14}F_6O_2$ (388.3): C, 58.77; H, 3.63. Found: C, 58.50; H, 3.70.

2,2-Dimethyl-1,3-di(3'-chlorophenyl)-1,3-propanedione (*m*-9h; *m*-Cl): 1.21 g (38%) colorless needles, mp 82 - 83 °C (methanol). IR (KBr): ν = 3020, 2960, 2880, 1660, 1630, 1550, 1440, 1390, 1230, 1210, 1150; ^1H NMR ($CDCl_3$): δ = 1.65 (s, 6H, 2-CH_3), 7.24 (dt, ^3J = 8.0 Hz, ^5J = 0.3 Hz, 2H, 5'-H), 7.41 (ddd, ^3J = .8.0 Hz, ^4J = 2.1 Hz, ^4J = 1.1 Hz, 2H, 6'-H), 7.59 (ddd, ^3J = 8.0 Hz, ^4J = 1.7 Hz, ^4J = 1.1 Hz, 2H, 4'-H), 7.87 (dt, ^4J = 1.9 Hz, ^5J = 0.3 Hz, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 25.1 (q, 2-CH_3), 59.6 (s, C-2), 126.9 (d, C-6'), 129.2 (d, C-2'), 129.9 (d, C-5'), 133.2 (d, C-4'), 135.2 (s, C-3'), 136.7 (s, C-1'), 198.6 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{14}Cl_2O_2$ (321.2): C, 63.57; H, 4.39. Found: C, 63.30; H, 4.38.

2,2-Dimethyl-1,3-di(3'-methylphenyl)-1,3-propanedione (*m*-9m; *m*-CH_3): 1.12 g (40%) colorless needles, mp 121 - 122 °C (methanol). IR (KBr): ν = 3020, 2840, 2810, 1650, 1630, 1570, 1460, 1440, 1400, 1250, 1140; ^1H NMR ($CDCl_3$): δ = 1.64 (s, 6H, 2-CH_3), 2.30 (s, 6H, CH_3), 7.18 (m, 4H, Ph-H), 7.58 (m, 2H, Ph-H), 7.69 (m, 2H, Ph-H); ^{13}C NMR ($CDCl_3$): δ = 21.3 (q, CH_3), 25.5 (q, 2-CH_3), 59.5 (s, C-2), 126.3 (d, C-6'), 128.4 (d, C-5'), 128.6 (d, C-2'), 133.7 (d, C-4'), 135.6 (s, C-3'), 138.4 (s, C-1'), 200.5 (s, C-1 and C-3). Anal. Calcd for $C_{19}H_{20}O_2$ (280.4): C, 81.40; H, 7.19. Found: C, 81.65; H, 6.81.

2,2-Dimethyl-1,3-di(3'-methoxyphenyl)-1,3-propanedione (*m*-9o; *m*-OCH_3): 1.69 g (54%) colorless rhombes, mp 98 - 100 °C (methanol). IR (KBr): ν = 3020, 2920, 2820, 1660, 1570, 1480, 1430, 1280, 1240, 1050, 1010, 970; ^1H NMR ($CDCl_3$): δ = 1.64 (s, 2-CH_3), 3.76 (s, 6H, OCH_3), 6.96 (ddd, ^3J = 8.1 Hz, ^4J = 2.6 Hz, ^4J = 1.0 Hz, 2H, 4'-H), 7.19 (t, ^3J = 8.1 Hz, 5'-H), 7.33 (dt, ^3J = 8.1 Hz, ^4J = 1.0 Hz, 2H, 6'-H), 7.43 (t, ^4J = 1.0 Hz, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 25.4 (q, 2-CH_3), 55.3 (q, OCH_3), 59.5 (s, C-2), 113.2 (d, C-2'), 119.7 (d, C-4'), 121.6 (d, C-6'), 129.6 (d, C-5'), 136.7 (s, C-1'), 159.6 (s, C-3'), 200.0 (s, C-1 and C-3). Anal. Calcd for $C_{19}H_{20}O_4$ (312.37): C, 73.06; H, 6.45. Found: C, 72.70; H, 6.20.

2,2-Dimethyl-1,3-di(3'-fluorophenyl)-1,3-propanedione (*m*-9r; *m*-F): 1.47 g (50%) colorless needles, mp 66 - 67 °C (methanol). IR (KBr): ν = 3040, 2940, 2890, 1640, 1560, 1460, 1410, 1240, 1190, 1120; ^{1}H NMR ($CDCl_3$): δ = 1.66 (s, 6H, 2-CH_3), 7.12 (ddt, $^3J = {}^3J_{HF}$ = 8.1 Hz, ^4J = 2.6 Hz, ^4J = 1.1 Hz, 2H, 4'-H), 7.29 (dt, $^3J = {}^3J_{HF}$ = 8.1 Hz, ^5J = 0.5 Hz, 2H, 5'-H), 7.56 (m, 4H, 2'-H/ 6'-H).- ^{13}C NMR ($CDCl_3$): δ = 25.2 (q, 2-CH_3), 59.7 (s, C-2), 116.0 (dd, $^2J_{CF}$ =23 Hz, C-4'), 120.3 (dd, $^2J_{CF}$ = 22 Hz, C-2'), 124.7 (dd, $^4J_{CF}$ = 3 Hz, C-6'), 130.4 (dd, $^3J_{CF}$ = 8 Hz, C-5'), 137.5 (d, $^3J_{CF}$ = 6 Hz, C-1'), 162.8 (d, $^1J_{CF}$ = 249 Hz, C-3'), 198.8 (s, C-1 and C-3). Anal. Calcd. for $C_{17}H_{14}F_2O_2$ (288.3): C, 70.82; H, 4.89. Found: C, 70.53; H, 4.84.

2,2-Dimethyl-1,3-di(3'-phenylacetylenophenyl)-1,3-propanedione (*m*-9t; *m*-C≡CPh).[31] 550 mg (1.09) of the diketone ***m*-9k** (X = *m*-I)[16] was dissolved under a nitrogen atmosphere in 30 mL of dry pyridine. To this solution 359 mg (2.18 mmol) of Cu(I) C≡CPh was added and the reaction mixture was then refluxed for 7 h. After hydrolysis with 50 mL of water, the aqueous layer was extracted with methylene chloride (3 x 100 mL). The organic layer was then washed with water (50 mL), 10% hydrochloric acid (20 mL) and saturated sodium carbonate solution (50 mL) and dried over magnesium sulfate. After evaporation of the solvent (40 °C, 18 torr) 400 mg of a pale yellow oil was obtained, which contained ca. 70% of the desired diketone ***m*-9t** (^{1}H NMR analysis). Several attempts of purification failed and the crude material was used as such for the further synthesis. R_f = 0.90 (silicagel, methylene chloride). ^{1}H NMR ($CDCl_3$): δ = 1.72 (s, 6H, 2-CH_3), 7.35 (m, 8H, Ph-H), 7.55 (m, 6H, Ph-H), 7.71 (m, 2H, 4'-H or 6'-H), 8.09 (t, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 25.2 (q, 2-CH_3), 59.5 (s, C-2), 88.0 (s, C≡C), 90.6 (s, C≡C), 121.7 (s, C-3'), 124.2 (s, Ph-*ipso*), 128.3 - 128.7 (d, C-6' and Ph-C), 129.2 (d, C-5'), 131.6 (d, C-2'), 132.4 (d, Ph-*ortho*), 135.6 (s, C-1'), 135.7 (d, C-4'), 199.4 (s, C-1 and C-3).-

General Procedure for the Preparation of the 4,4-Dimethyl-3,5-diaryl-4*H*-pyrazoles (10). [14,16] The corresponding dimethylated diketones ***p*-9g**, ***m*-9g**, ***m*-9h**, ***m*-9m**, ***m*-9o**, ***m*-9r** and ***m*-9t** (5.00 mmol) were dissolved in 30 mL $CHCl_3$ and 258 mg (5.16 mmol) of hydrazine hydrate were added. The mixture was refluxed for 24 h and chilled and 3 g of magnesium sulfate were added. After brief stirring, filtration and evaporation of the solvent (ca. 40 °C, 18 torr), the crystalline crude material was obtained, which was further purified by recrystallization or column chromatography on silica gel.

4,4-Dimethyl-3,5-di(4'-α,α,α–trifluoromethylphenyl)-4*H*-pyrazole (*p*-10g; *p*-CF_3): 1.58 g (83%) colorless powder, mp 259 - 261 °C (benzene/hexane 1:1). IR (KBr): ν = 3020, 2960, 1600, 1510, 1490, 1440, 1390, 1300, 1150, 1120, 1020, 1010; ^{1}H NMR ($CDCl_3$): δ = 1.72 (s, 6H, 4-CH_3), 7.77 (d, ^3J = 8.3 Hz, 4H, 3'-H), 8.20 (d, ^3J = 8.3 Hz, 4H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 22.3 (q, 4-CH_3), 59.0 (s, C-4), 123.7 (q, $^1J_{CF}$ = 270 Hz, CF_3), 125.9 (dq, $^3J_{CF}$ = 4 Hz, C-3'), 128.3 (d, C-2'), 132.1 (q, $^2J_{CF}$ = 25 Hz, C-4'), 133.0 (s, C-1'), 178.4 (s, C-3 and C-5). Anal. Calcd for $C_{19}H_{14}F_6N_2$ (384.3): C, 59.38; H, 3.67; N, 7.29. Found: C, 58.85; H, 3.55; N, 7.08.

4,4-Dimethyl-3,5-di(3'-α,α,α–trifluoromethylphenyl)-4*H*-pyrazole (*m*-10g; *m*-CF_3): 1.40 g (74%) pale yellow needles, mp 112 - 113 °C (benzene/cyclohexane 1:1). IR (KBr): ν = 3040, 2880, 1590, 1510, 1470, 1440, 1420, 1320, 1300, 1150, 1110; ^{1}H NMR ($CDCl_3$): δ = 1.73 (s, 6H, 4-CH_3), 7.65 (t, ^3J = 7.8 Hz, 2H, 5'-H), 7.78 (d, ^3J = 7.8 Hz, 2H, 4'-H), 8.25 (d, ^3J = 7.8 Hz, 2H, 6'-H), 8.34 (br s, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 22.5 (q, 4-CH_3), 58.8 (s, C-4), 123.7 (q, $^1J_{CF}$ = 271 Hz, CF_3), 124.7 (dq, $^3J_{CF}$ = 4 Hz, C-2'), 127.6 (dq, $^3J_{CF}$ = 4 Hz, C-4'), 129.5 (d, C-5'), 130.4 (s, C-1'), 131.0 (d, C-6'), 132.1 (q, $^2J_{CF}$ = 31 Hz, C-3'), 178.2 (s, C-3 and C-5). Anal. Calcd for $C_{19}H_{14}F_6N_2$ (384.3): C, 59.38; H, 3.67; N, 7.29. Found: C, 59.09; H, 3.79; N, 7.16.

4,4-Dimethyl-3,5-di(3'-chlorophenyl)-4*H*-pyrazole (*m*-10h; *m*-Cl): 1.31 g (83%) pale yellow powder, mp 164 - 165 °C (benzene/cyclohexane 1:1). IR (KBr): ν = 3020, 2920, 2890, 1570, 1550, 1490, 1450, 1440, 1400, 1320, 1140; ^{1}H NMR ($CDCl_3$): δ = 1.68 (s, 6H, 4-CH_3), 7.46 (m, 4H, 5'-H and 6'-H), 7.93 (dt, ^3J = 7.2 Hz, ^4J = 1.7 Hz, 2H, 4'-H), 8.05 (t, ^4J = 1.7 Hz, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 22.5 (q, 4-CH_3), 58.8 (s, C-4), 125.9 (d, C-6'), 127.9 (d, C-5'), 130.1 (d, C-2'), 131.0 (d, C-4'), 131.5 (s, C-1'), 134.9 (s, C-3'), 178.2 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{14}Cl_2N_2$ (317.2): C, 64.37; H, 4.45; N, 8.83. Found: C, 64.15; H, 4.47; N, 8.77.

4,4-Dimethyl-3,5-di(3'-methylphenyl)-4*H*-pyrazole (*m*-10m; *m*-CH_3): 0.90 g (65%) pale yellow needles, mp 114 - 115 °C (benzene/cyclohexane 1:1). IR (KBr): ν = 3020, 2980, 2910, 1600, 1520, 1470, 1460, 1350, 1140, 800, 720; ^{1}H NMR ($CDCl_3$): δ = 1.69 (s, 6H, 4-CH_3), 2.44 (s, 6H, CH_3), 7.35 (m, 4H, Ph-H), 7.86 (m, 2H, Ph-H), 7.93 (m, 2H, Ph-H); ^{13}C NMR ($CDCl_3$): δ = 21.5 (q, CH_3), 22.8 (q, 4-CH_3), 58.7 (s, C-4), 124.8 (d, C-6'), 128.55 (d, C-5'), 128.57 (d, C-2'), 130.0 (s,

C-1'), 131.5 (d, C-4'), 138.5 (s, C-3'), 179.1 (s, C-3 and C-5). Anal. Calcd for $C_{19}H_{20}N_2$ (276.4): C, 82.57; H, 7.29; N, 10.14. Found: C, 82.75; H, 7.27; N, 9.90.

4,4-Dimethyl-3,5-di(3'-methoxyphenyl)-4*H*-pyrazole (*m*-10o; *m*-OCH_3): 1.30 g (85%) pale yellow needles, mp 95 - 96 °C (benzene/hexane 1:1). IR (KBr): ν = 3020, 2980, 1570, 1510, 1500, 1470, 1440, 1400, 1220, 1020, 1010; ^{1}H NMR ($CDCl_3$): δ = 1.69 (s, 4-CH_3), 3.89 (s, 6H, OCH_3), 7.05 (ddd, ^3J = 8.2 Hz, ^4J = 2.6 Hz, ^4J = 1.0 Hz, 2H, 4'-H), 7.40 (t, ^3J = 8.2 Hz, 5'-H), 7.57 (dt, ^3J = 8.2 Hz, ^4J = 2.6 Hz, 2H, 6'-H), 7.70 (t, ^4J = 1.0 Hz, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 22.9 (q, 4-CH_3), 55.4 (q, OCH_3), 58.7 (s, C-4), 112.9 (d, C-2'), 117.1 (d, C-4'), 120.2 (d, C-6'), 129.7 (d, C-5'), 131.2 (s, C-1'), 159.8 (s, C-3'), 179.0 (s, C-3 and C-5). Anal. Calcd for $C_{19}H_{20}N_2O_2$ (308.4): C, 74.00; H, 6.54; N, 9.08. Found: C, 74.04; H, 6.33; N, 8.86.

4,4-Dimethyl-3,5-di(3'-fluorophenyl)-4*H*-pyrazole (*m*-10r; *m*-F): 1.23 g (86%) pale yellow needles, mp 178 - 180 °C (benzene/cyclohexane 1:1), R_f = 0.87 (SiO_2, methylene chloride/methanol 20:1). IR (KBr): ν = 3020, 2940, 2900,1590, 1560, 1490, 1460, 1420, 1200, 1180; ^{1}H NMR ($CDCl_3$): δ = 1.69 (s, 6H, 4-CH_3), 7.21 (ddt, $^3J = {}^3J_{HF}$ = 8.3 Hz, ^4J = 2.6 Hz, ^4J = 1.0 Hz, 2H, 4'-H), 7.48 (dt, ^3J = 8.3 Hz, $^4J_{HF}$ = 6.0 Hz, 2H, 5'-H), 7.80 (m, 4H, 2'-H/6'-H); ^{13}C NMR ($CDCl_3$): δ = 22.6 (q, 4-CH_3), 58.7 (s, C-4), 114.8 (dd, $^2J_{CF}$ = 23 Hz, C-2'), 118.0 (dd, $^2J_{CF}$ = 21 Hz, C-4'), 123.6 (dd, $^5J_{CF}$ = 3 Hz, C-6'), 130.4 (dd, $^3J_{CF}$ = 8 Hz, C-5'), 131.8 (d, $^3J_{CF}$ = 8 Hz, C-1'), 162.8 (d, $^1J_{CF}$ = 245 Hz, C-3'), 178.3 (s, C-1 and C-3). Anal. Calcd for $C_{17}H_{14}F_2N_2$ (284.3): C, 71.82; H, 4.96; N, 9.85. Found: C, 71.59; H, 4.94; N, 9.76.

4,4-Dimethyl-3,5-di(3'-phenylacetylenophenyl)-4*H*-pyrazole (*m*-10t; *m*-C≡CPh): 1.35 g (60%) pale yellow solid, mp 54 - 55°C, R_f = 0.26 (87 (SiO_2, methylene chloride/petroleum ether 99:1). IR (KBr): ν = 3020, 2980, 2930, 1600, 1515, 1490, 1460, 1440, 1350, 880; ^{1}H NMR ($CDCl_3$): δ = 1.74 (s, 6H, 4-CH_3), 7.38 (m, 6H, Ph-H), 7.50 (t, ^3J = 7.9 Hz, 5'-H), 7.58 (m, 4H, Ph-H), 7.67 (dt, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 4'-H), 8.07 (dt, ^3J = 7.9 Hz, ^4J = 1.5 Hz, 6'-H), 8.19 (t, ^4J = 1.5 Hz, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 22.6 (q, 4-CH_3), 58.8 (s, C-4), 88.5 (s, C≡C), 90.2 (s, C≡C), 122.3 (s, C-3'), 124.0 (s, *ipso*-Ph), 127.7 - 128.9 (C-6' and Ph-C), 130.1 (d, C-5'), 130.7 (s, C-1'), 131.5 (d, *ortho*-Ph), 131.6 (d, C-2'), 133.7 (d, C-4'), 178.6 (s, C-3 and C-5). Anal. Calcd for $C_{33}H_{24}N_2$ (448.6): C, 88.36; H, 5.39; N, 6.25. Found: C, 88.40; H, 5.16; N, 5.99.

General Procedure for the Preparation of the 4*H*-Pyrazoles *p*-10p and *m*-10p.[32] 30.0 mmol of BBr_3 were dissolved in 25 mL of dry methylene chloride and chilled by means of an ice bath. To this solution, 3.00 mmol of the 4*H*-pyrazoles ***p*-10o**[14] or ***m*-10o** were added dropwise keeping the temperature at 0° C. The orange-colored reaction mixture was stirred afterwards for 5 h at ambient temperature. Hydrolysis with 100 mL of crushed ice afforded the crude product, which was filtered of by suction and washed thoroughly with cyclohexane. The precipitate was recristallized from benzene/cyclohexane (1:1).

4,4-Dimethyl-3,5-di(4'-hydroxyphenyl)-4*H*-pyrazole (*p*-10p; *p*-OH): 665 mg (79%) yellow powder, mp 259 - 260 °C (benzene/cyclohexane 1:1). IR (KBr): ν = 3220, 2980, 1610, 1580, 1540, 1510, 1460, 1360, 1290, 1230, 1170; ^{1}H NMR (d_4-MeOD): δ = 1.67 (s, 6H, 4-CH_3), 6.91 (dd, ^3J = 9.0 Hz, ^4J = 4.5 Hz, 4H, 3'-H), 7.91 (dd, ^3J = 9.0 Hz, ^4J = 4.5 Hz, 4H, 2'-H); ^{13}C NMR (d_4-MeOD): δ = 23.8 (q, 4-CH_3), 59.6 (s, C-4), 117.0 (d, C-3'), 121.7 (s, C-1'), 130.9 (d, C-2'), 162.1 (s, C-4'), 180.5 (s, C-3 and C-5). Anal. Calcd for $C_{17}H_{16}N_2O_2$ (280.3): C, 72.84; H, 5.75; N, 9.99.

4,4-Dimethyl-3,5-di(3'-hydroxyphenyl)-4*H*-pyrazole (*m*-10p; *m*-OH): 793 mg (94%) colorless powder, mp 285 - 286 °C (benzene/cyclohexane 1:1). IR (KBr): ν = 3200, 1570, 1510, 1480, 1430, 1300, 1210, 980, 870, 780, 710; ^{1}H NMR (d_6-DMSO): δ = 1.58 (s, 6H, 4-CH_3), 6.95 (dt, ^3J = 7.8 Hz, ^4J = 1.1 Hz, 2H, 4'-H), 7.34 (t, ^3J = 7.8 Hz, 2H, 5'-H), 7.48 (m, 4H, 2'-H and 6'-H); ^{13}C NMR (d_6-DMSO): δ = 22.1 (q, 4-CH_3), 58.2 (s, C-4), 114.1 (d, C-2'), 118.0 (d, C-4'), 118.5 (d, C-6'), 130.1 (d, C-5'), 130.6 (s, C-1'), 157.6 (s, C-3'), 178.5 (s, C-3 and C-5). Anal. Calcd for $C_{17}H_{16}N_2O_2$ (280.3): C, 72.84; H, 5.75; N, 9.99.

General Procedure for the Preparation of the 4*H*-Pyrazoles *p*-10q and *m*-10q. 5.00 mmol of the 4*H*-pyrazoles ***p*-10p** or ***m*-10p** were suspended in 40 mL of dry methylene chloride and 1.06 g (10.5 mmol) of acetic anhydride were added. After dropwise addition of 0.02 mL of concentrated sulfuric acid the reaction mixture was refluxed for 5 h. After hydrolysis with 100 mL of cracked ice the aqueous layer was extracted twice with 50 mL of methylene chloride. The organic layer was dried over magnesium sulfate and the solvent removed under vacuo affording the crude product which was purified by column chromatography on silica gel or recristallization.

4,4-Dimethyl-3,5-di(4'-acetoxyphenyl)-4*H*-pyrazole (*p*-10q; *p*-OCOCH$_3$): 1.43 g (79%) pale yellow needles, mp 196 - 197 °C (benzene/cyclohexane 1:1). IR (KBr): ν = 2880, 1730, 1580, 1480, 1430, 1340, 1320, 1200, 1180, 1140, 980, 900; ^{1}H NMR ($CDCl_3$): δ = 1.69 (s, 6H, 4-CH_3), 2.34 (s, 6H, $OCOCH_3$), 7.23 (dd, ^3J = 8.9 Hz, ^4J = 5.0 Hz, 4H, 3'-H), 8.11 (dd, ^3J = 8.9 Hz, ^4J = 5.0 Hz, 4H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 21.2 (q, $OCO\underline{C}H_3$), 22.8 (q, 4-CH_3), 58.5 (s, C-4), 122.8 (d, C-3'), 121.4 (s, C-1'), 129.2 (d, C-2'), 152.6 (s, C-4'), 169.1 (s, $O\underline{C}OCH_3$), 178.1 (s, C-3 and C-5). Anal. Calcd for $C_{21}H_{20}N_2O_4$ (364.4): C, 69.22; H, 5.53; N, 7.69. Found: C, 69.14; H, 5.51; N, 7.60.

4,4-Dimethyl-3,5-di(3'-acetoxyphenyl)-4*H*-pyrazole (*m*-10q; *m*-OCOCH$_3$): 1.40 g (76%) colorless powder, mp 124 - 125 °C, R_f = 0.32 (SiO_2, methylene chloride/methanol 20:1). IR (KBr): ν = 3020, 2940, 1740, 1560, 1500, 1460, 1430, 1350, 1190, 1000, 910; ^{1}H NMR ($CDCl_3$): δ = 1.69 (s, 6H, 4-CH_3), 2.35 (s, 6H, $OCOCH_3$), 7.25 (ddd, ^3J = 8.1 Hz, ^4J = 2.4 Hz, ^4J = 0.9 Hz, 2H, 4'-H), 7.51 (t, ^3J = 8.1 Hz, 2H, 5'-H), 7.83 (t, ^4J = 0.9 Hz, 2H, 2'-H), 7.91 (dt, ^3J = 8.1 Hz, ^4J =, 2.5 Hz, 2H, 6'-H); ^{13}C NMR ($CDCl_3$): δ = 21.2 (q, $OCO\underline{C}H_3$), 22.7 (q, 4-CH_3), 58.6 (s, C-4), 121.2 (d, C-2'), 124.2 (d, C-6'), 125.2 (d, C-4'), 129.8 (d, C-5'), 131.2 (s, C-1'), 150.7 (s, C-3'), 169.3 (s, $O\underline{C}OCH_3$), 178.3 (s, C-3 and C-5). Anal. Calcd for $C_{21}H_{20}N_2O_4$ (364.4): C, 69.22; H, 5.53; N, 7.69. Found: C, 68.97; H, 5.66; N, 7.44.

The preparation of the azoalkanes ***p*-5a - c, h, j, k, l, m - o,** r and ***m*-5a - b, k** has been reported previously,[8b,14,16a] while the synthesis of the new azoalkanes **5** are given below.

General Procedure for the Preparation of the Azoalkanes (5).[16a] The corresponding 4*H*-pyrazoles ***p*-10g, *p*-10q, *m*-10g, *m*-10h, *m*-10m, *m*-10o, *m*-10q, *m*-10r** and ***m*-10t** (1.00 mmol) and 102.7 mg (0.90 mmol) of trifluoracetic acid were dissolved in methylene chloride (20 mL), the mixture chilled in an ice bath, and 10 mL of freshly recondensed cyclopentadiene was added. After the mixture was allowed to stand overnight at ca. 0 °C, 2.0 g of patassium carbonate and 2.0 g of silica gel (0.2 - 0.5 mm) were added, and stirring was continued for 30 min at 0 °C. The mixture was filtered and the solvent removed (ca. 20 °C, 18 Torr) to afford the crude solid product. Purification was accomplished by column chromatography. The atom numbering for the NMR assingments of the azoalkanes **5** is shown in Scheme 1.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(4'-α,α,α–trifluoromethyl-phenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*p*-5g; *p*-CF_3): 355 mg (79%) colorless powder, mp 186 - 188 °C, dec. R_f = 0.66 (SiO_2, methylene chloride); IR (KBr): ν = 3020, 2980, 2820, 1600, 1450, 1430, 1400, 1210, 1150, 1100, 1050, 1000; UV (C_6H_6): λ_{max} (log ε) = 360 nm (2.262), 348 (2.033, sh), 327 (1.813, sh); ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 3H, 9-H), 1.06 (s, 3H, 10-H), 2.22 (m_c, ^2J = 9.3 Hz, ^3J = 5.5 Hz, ^4J = 2.1 Hz, 2H, 7-H), 3.67 (dt, ^3J = 8.7 Hz, ^3J = 5.5 Hz, 1H, 7a-H), 4.14 (m_c, ^3J = 8.7 Hz, 1H, 4a-H), 5.47 (m_c, ^3J = 6.0 Hz, 1H, 5-H), 5.54 (mc, ^3J =6.0 Hz, 6-H), 7.77 (m, 4H, 3'-H/3"-H), 7.93 (m, 4H, 2'-H/2"-H); ^{13}C NMR ($CDCl_3$): δ = 16.7 (q, C-9), 17.4 (q, C-10), 31.5 (t, C-7), 43.5 (d, C-7a), 57.1 (d, C-4a), 64.7 (s, C-8), 96.6 (s, C-1), 97.7 (s, C-4), 123.5 (q, $^1J_{CF}$ = 280 Hz, CF_3), 125.5 (dq, $^3J_{CF}$ = 4 Hz, C-3'), 126.5 (d, C-6), 127.5 and 127.9 (2 × d, C-2'), 133.1 (q, $^2J_{CF}$ = 32 Hz, C-4'), 134.0 (d, C-5), 139.6 (s, C-1'). Anal. Calcd for $C_{24}H_{20}F_6N_2$ (450.4): C, 64.00; H, 4.48; N, 6.22. Found: C, 64.28; H, 4.50; N, 5.85.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(4'-acetoxyphenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*p*-5q; *p*-$OCOCH_3$): 165 mg (38%) colorless powder, mp 174 - 175 °C dec. R_f = 0.60 (SiO_2, methylene chloride/methanol 20:1); IR (KBr): ν = 3020, 2920, 2800, 1730, 1490, 1440, 1350, 1190, 1150, 1000, 900; UV (C_6H_6): λ_{max} (log ε) = 360 nm (2.328), 346 (2.185, sh), 327 (2.086, sh); ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 3H, 9-H), 1.01 (s, 3H, 10-H), 2.20 (dd, ^3J = 6.8 Hz, ^3J = 3.0 Hz, 2H, 7-H), 2.34 (s, 6H, $OCOCH_3$), 3.60 (dt, ^3J = 8.3 Hz, ^3J = 6.8 Hz, 1H, 7a-H), 4.05 (m_c, ^3J = 8.3 Hz, 1H, 4a-H), 5.50 (m_c, 2H, 5-H und 6-H), 7.22 (m, 4H, 3'-H/3"-H), 7.78 (m, 4H, 2'-H/2"-H); ^{13}C NMR ($CDCl_3$): δ = 16.9 (q, C-9), 17.3 (q, C-10), 21.2 (q, $OCO\underline{C}H_3$), 31.6 (t, C-7), 43.4 (d, C-7a), 56.9 (d, C-4a), 64.2 (s, C-8), 96.5 (s, C-1), 97.6 (s, C-4), 121.5 (d, C-3'), 126.9 (d, C-6), 128.2 and 128.6 (2 × d, C-2'), 133.2 and 133.3 (2 × s, C-1'), 133.7 (d, C-5), 150.31 and 150.38 (2 × s, C-4'), 169.4 (s, $O\underline{C}OCH_3$). Anal. Calcd for $C_{26}H_{26}N_2O_4$ (430.5): C, 72.54; H, 6.09; N, 6.51. Found: C, 72.14; H, 6.02; N, 6.98.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(3'-α,α,α–trifluoromethyl-phenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5g; *m*-CF_3): 357 mg (79%) colorless powder, mp 114 - 116 °C dec. R_f = 0.63 (SiO_2, methylene chloride); IR (KBr): ν = 3020, 2980, 2890, 1570, 1470, 1420, 1360, 1330, 1290, 1255, 1240, 1140; UV (C_6H_6): λ_{max} (log ε) = 360 nm (2.277), 347 (2.152, sh); ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 3H, 9-H), 1.05 (s, 3H, 10-H), 2.24 (m_c,

^2J = 10.3 Hz, ^3J = 4.8 Hz, ^4J = 2.1 Hz, 2H, 7-H), 3.68 (dt, ^3J = 9.0 Hz, ^3J = 4.8 Hz, 1H, 7a-H), 4.14 (ddd, ^3J = 9.0 Hz, ^3J = 3.7 Hz, ^4J = 2.1 Hz, 1H, 4a-H), 5.52 (m_c, 2H, 5-H and 6-H), 7.68 (m, 4H, 5'-H/5"-H and 4'-H/4"-H), 8.01 (m, 4H, 6'-H/6"-H and 2'-H/2"-H); ^{13}C NMR ($CDCl_3$): δ = 16.8 (q, C-9), 17.3 (q, C-10), 31.5 (t, C-7), 43.4 (d, C-7a), 56.9 (d, C-4a), 64.5 (s, C-8), 96.5 (s, C-1), 97.6 (s, C-4), 124.1 (q, $^1J_{CF}$ = 271 Hz, CF_3), 123.8 and 124.1 (2 × dq, $^3J_{CF}$ = 4 Hz, C-2'), 124.9 (dq, $^3J_{CF}$ = 4 Hz, C-4'), 126.4 (d, C-6), 129.1 (d, C-5'), 130.5 and 130.9 (2 × d, C-6'), 131.0 (q, $^2J_{CF}$ = 32 Hz, C-3'), 134.0 (d, C-5), 136.6 (s, C-1'). Anal. Calcd for $C_{24}H_{20}F_6N_2$ (450.4): C, 64.00; H, 4.48; N, 6.22. Found: C, 63.84, H, 4.54; N, 5.74.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(3'-chlorophenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5h; *m*-Cl): 319 mg (83%) colorless needles, mp 153 - 155 °C dec.; IR (KBr): ν = 3020, 2960, 2880, 2820, 1580, 1560, 1470, 1460, 1400, 1280, 1070; UV (C_6H_6): λ_{max} (log ε) = 360 nm (2.261), 347 (1.977, sh), 327 (1.505, sh); ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 3H, 9-H), 1.03 (s, 3H, 10-H), 2.21 (ddd, ^2J = 10.3 Hz, ^3J = 4.1 Hz, ^4J = 1.9 Hz, 2H, 7-H), 3.59 (dt, ^3J = 8.8 Hz, ^3J = 5.7 Hz, 1H, 7a-H), 4.06 (m_c, ^3J = 8.8 Hz, 1H, 4a-H), 5.51 (m_c, 2H, 5-H and 6-H), 7.42 (m, 4H, 5'-H/5"-H and 6'-H/6"-H), 7.65 (m, 2H, 4'-H/4"-H), 7.77 (m, 2H, 2'-H/2"-H); ^{13}CNMR $CDCl_3$): δ = 16.9 (q, C-9), 17.4 (q, C-10), 31.5 (t, C-7), 43.4 (d, C-7a), 56.9 (d, C-4a), 64.4 (s, C-8), 96.4 (s, C-1), 97.5 (s, C-4), 125.4 and 125.8 (2 × d, C-6'), 126.3 (d, C-6), 127.3 and 127.6 (2 × d, C-5'), 128.1 and 128.2 (2 × d, C-2'), 129.8 (d, C-4'), 133.9 (d, C-5), 134.6 (s, C-3'), 137.7 (s, C-1'). Anal. Calcd for $C_{22}H_{20}Cl_2N_2$ (383.3): C, 68.94; H, 5.26; N, 7.31. Found: C, 68.71; H, 5.45; N, 7.19.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(3'-methylphenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5m; *m*-CH_3): 232 mg (68%) colorless powder, mp 136 - 138 °C dec. R_f = 0.50 (SiO_2, methylene chloride); IR (KBr): ν = 3040, 2980, 2920, 2860, 1605, 1585, 1490, 1465, 1370, 785, 775; UV (C_6H_6): λ_{max} (log ε) = 362 nm (2.223), 349 (1.977, sh), 328 (1.433, sh); ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 3H, 9-H), 1.01 (s, 3H, 10-H), 2.22 (m_c, ^3J = 6.8 Hz, ^4J = 3.0 Hz, 2H, 7-H), 2.44 and 2.45 (s, 6H, CH_3), 3.63 (dt, ^3J = 7.8 Hz, ^3J = 6.8 Hz, 1H, 7a-H), 4.09 (dt, ^3J = 7.8 Hz, ^4J = 3.0 Hz, 1H, 4a-H), 5.51 (m_c, 2H, 5-H and 6-H), 7.20 - 7.63 (m, 8H, Ph-H); ^{13}C NMR ($CDCl_3$): δ = 17.1 (q, C-9), 17.4 (q, C-10), 21.7 (q, CH_3), 31.7 (t, C-7), 43.1 (d, C-7a), 56.6 (d, C-4a), 64.0 (s, C-8), 96.8 (s, C-1), 97.9 (s, C-4), 124.1 and 124.5 (2 × d, C-2'), 127.2 (d, C-6), 128.0

(d, C-4'), 128.2 and 128.4 (2 × d, C-6'), 128.5 and 128.6 (2 × d, C-5'), 133.5 (d, C-5), 135.8 (s, C-3'), 137.88 and 137.91 (2 × s, C-1'). Anal. Calcd for $C_{24}H_{26}N_2$ (342.5): C, 84.17; H, 7.65; N, 8.18. Found: C, 83.87; H, 7.60; N, 8.03.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(3'-methoxyphenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5o; *m*-OCH_3): 214 mg (60%) colorless powder, mp 144 - 145 °C dec. R_f = 0.50 (Al_2O_3, methylene chloride); IR (KBr): ν = 2980, 2820, 2700, 1590, 1510, 1470, 1420, 1380, 1210, 1040, 1010; UV (C_6H_6): λ_{max} (log ε) = 361 nm (2.344), 346 (2.246, sh), 327 (2.162, sh); ^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 3H, 9-H), 1.03 (s, 3H, 10-H), 2.21 (dd, ^2J = 7.5 Hz, ^3J = 2.6 Hz, 2H, 7-H), 3.59 (dt, ^3J = 7.9 Hz, ^3J = 3.5 Hz, 1H, 7a-H), 3.88 (s, 6H, OCH_3), 4.06 (m_c, ^3J = 7.9 Hz, 1H, 4a-H), 5.51 (m_c, 2H, 5-H and 6-H), 6.96 (m, 2H, 2'-H/2"-H), 7.29 - 7.44 (m, 6H, 4'-H/4"-H, 5'-H/ 5"-H, 6'-H/6"-H); ^{13}C NMR ($CDCl_3$): δ = 17.1 (q, C-9), 17.5 (q, C-10), 31.7 (t, C-7), 43.4 (d, C-7a), 55.3 (q, OCH_3), 56.9 (d, C-4a), 64.3 (s, C-8), 96.8 (s, C-1), 97.8 (s, C-4), 113.0 and 113.1 (2 × d, C-2'), 113.3 and 113.6 (2 × d, C-4'), 119.5 and 119.9 (2 × d, C-6'), 127.2 (d, C-6), 129.4 (d, C-5'), 133.6 (d, C-5), 137.5 (s, C-1'), 159.6 (s, C-3'). Anal. Calcd. for $C_{24}H_{26}N_2O_2$ (374.5): C, 76.98; H, 7.00; N, 7.48. Found: C, 76.63; H, 6.99; N, 7.21.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(3'-acetoxyphenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5q; *m*-$OCOCH_3$): 110 mg (25%) colorless powder, mp 124 - 125 °C dec. R_f = 0.58 (SiO_2, methylene chloride/methanol 20:1); IR (KBr): ν = 3020, 2940, 2880, 1740, 1590, 1560, 1470, 1410, 1350, 1190, 1000, 910; UV (C_6H_6): λ_{max} (log ε) = 360 nm (2.241), 347 (1.952, sh), 326 (1.533, sh); ^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 3H, 9-H), 1.03 (s, 3H, 10-H), 2.21 (dd, ^2J = 7.0 Hz, ^3J = 4.2 Hz, 2H, 7-H), 2.238 and 2.335 (s, 6H, $OCOCH_3$), 3.58 (dt, ^3J = 8.3 Hz, ^3J = 5.4 Hz, 1H, 7a-H), 4.03 (m_c, ^3J = 8.3 Hz, 1H, 4a-H), 5.50 (m_c, 2H, 5-H and 6-H), 7.17 (m, 2H, 4'-H/4"-H), 7.50 (m, 4H, 5'-H/5"-H and 2'-H/2"-H), 7.62 (m, 2H, 6'-H/6"-H); ^{13}C NMR ($CDCl_3$): δ = 16.9 (q, C-9), 17.3 (q, C-10), 21.2 (q, $OCO\underline{C}H_3$), 31.6 (t, C-7), 43.3 (d, C-7a), 56.9 (d, C-4a), 64.5 (s, C-8), 96.5 (s, C-1), 97.6 (s, C-4), 120.5 and 120.9 (2 × d, C-2'), 121.1 and 121.2 (2 × d, C-4'), 124.5 and 124.8 (2 × d, C-6'), 126.8 (d, C-6), 129.4 (d, C-5'), 133.7 (d, C-5), 137.40 and 137.44 (s, C-1'), 150.8 (s, C-3'), 169.4 (s, $O\underline{C}OCH_3$). Anal. Calcd for $C_{26}H_{26}N_2O_4$ (430.5): C, 72.54; H, 6.09; N, 6.51. Found: C, 72.54; H, 6.19; N, 6.76.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(3'-fluorophenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5r; *m*-F): 175 mg (50%) colorless needles, mp 129 - 130 °C dec. R_f = 0.63 (SiO_2, methylene chloride); IR (KBr): ν = 3020, 2920, 2800, 1590, 1570, 1490, 1460, 1410, 1280, 1250; UV (C_6H_6): λ_{max} (log ε) = 360 (2.265), 346 (1.943, sh), 327 (1.353, sh); ^{1}H NMR ($CDCl_3$): δ = 0.21 (s, 3H, 9-H), 1.04 (s, 3H, 10-H), 2.21 (m_c, ^3J = 8.7 Hz, 2H, 7-H), 3.59 (dt, ^3J = 8.7 Hz, ^3J = 6.1 Hz, 1H, 7a-H), 4.06 (m_c, 1H, 4a-H), 5.50 (m_c, 2H, 5-H and 6-H), 7.12 (m, 2H, 4'-H/4"-H), 7.51 (m, 6H, 2'-H/2''-H, 4'-H/4"-H and 6'-H/6''-H); ^{13}C NMR ($CDCl_3$): δ = 16.9 (q, C-9), 17.4 (q, C-10), 31.5 (t, C-7), 43.4 (d, C-7a), 57.0 (d, C-4a), 64.4 (s, C-8), 96.4 (d, $^4J_{CF}$ = 2 Hz, C-1), 97.5 (d, $^4J_{CF}$ = 2 Hz, C-4), 114.4 and 114.8 (2 × dd, $^2J_{CF}$ = 23 Hz, C-2'), 114.6 and 115.0 (2 × dd, $^2J_{CF}$ = 21 Hz, C-4'), 122.8 and 123.2 (2 × dd, $^4J_{CF}$ = 3 Hz, C-6'), 126.7 (d, C-6), 130.0 (dd, $^3J_{CF}$ = 9 Hz, C-5'), 133.8 (d, C-5), 138.2 (d, $^3J_{CF}$ = 7 Hz, C-1'), 162.9 (d, $^1J_{CF}$ = 244 Hz, C-3'). Anal. Calcd for $C_{22}H_{20}F_2N_2$ (350.4): C, 75.41; H, 5.75; N, 7.99. Found: C, 75.11; H, 5.76; N, 7.90.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(3'-phenylacetylenophenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5t; *m*-C≡CPh): 288 mg (56%) colorless powder, mp 139 - 140 °C dec. R_f = 0.59 (SiO_2, methylene chloride); IR (KBr): ν = 3040, 2940, 2920, 2830, 1580, 1480, 1450, 1440, 710, 690; UV (C_6H_6): λ_{max} (log ε) = 360 nm (2.467), 347 (2.326), 328 (2.575); ^{1}H NMR ($CDCl_3$): δ = 0.25 (s, 3H, 9-H), 1.08 (s, 3H, 10-H), 2.24 (m_c, ^2J = 12.1 Hz, 2H, 7-H), 3.66 (dt, ^3J = 8.4 Hz, ^3J = 6.1 Hz, 1H, 7a-H), 4.13 (m_c, ^3J = 8.4 Hz, 1H, 4a-H), 5.53 (m_c, 2H, 5-H and 6-H), 7.22 - 7.97 (m, 18H, $H_{arom.}$); ^{13}C NMR ($CDCl_3$): δ = 17.0 (q, C-9), 17.5 (q, C-10), 31.6 (t, C-7), 43.2 (d, C-7a), 56.8 (d, C-4a), 64.3 (s, C-8), 89.3 (s, C≡C), 89.6 (s, C≡C), 96.6 (s, C-1), 97.7 (s, C-4), 123.1 and 123.5 (2 × d, C-2'), 126.9 (d, C-6'), 127.3 (2 × d, *p*-Ph), 127.7 (d, C-6), 128.4 (4 × d, *m*-Ph), 130.1 (d, C-5'), 131.1 (2 × d, C-4'), 131.6 (4 × d, *o*-Ph), 133.8 (d, C-5), 136.0 (s, C-1'). Anal. Calcd for $C_{38}H_{30}N_2$ (514.7): C, 88.68; H, 5.88; N, 5.44. Found: C, 88.55; H, 6.18; N, 5.00.

General Procedure for the Preparation of the Azoalkanes *p*-5d and *m*-5d. 121 mg (300 μmol) of the NO_2-substituted azoalkanes ***p*-5a**[16a] or ***m*-5a**[14] were dissolved in 40 mL of methanol and 18.0 mg (600 μmol) of a 39% aqueous formaldehyde solution were added. After addition of ca. 1 mg of PtO_2 catalyst the reaction mixture was placed under a hydrogen atmosphere and stirred for

36 h at ambient temperature. Removal of the catalyst by filtration and evaporation of the solvent afforded the crude product, which was purified by column chromatography on basic alumina.

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1,4-di(4'-N,N-dimethylamino-phenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*p*-5d; *p*-N(CH$_3$)$_2$): 94.7 mg (78%) colorless powder, mp 101 - 102 °C dec. R_f = 0.75 (Al_2O_3, methylene chloride); IR (KBr): ν = 2910, 2890, 2810, 1590, 1510, 1440, 1420, 1330, 1180, 780; UV (C_6H_6): λ_{max} (log ε) = 361 nm (2.246), 352 (2.230); ^{1}H NMR ($CDCl_3$): δ = 0.17 (s, 3H, 9-H), 0.90 (s, 3H, 10-H), 1.57 (m, 6H, 5-H, 6-H and 7-H), 3.00 (s, 12H, N(C$\underline{H}_3$)$_2$), 3.42 (m, 2H, 4a-H/7a-H), 6.85 (d, ^3J = 8.9 Hz, 4H, 3'-H), 7.60 (d, ^3J = 8.9 Hz, 4H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 17.1 (q, C-9), 17.8 (q, C-10), 25.6 (t, C-5 and C-7), 28.6 (t, C-6), 40.6 (q, N(C$\underline{H}_3$)$_2$), 48.6 (d, C-4a and C-7a), 65.2 (s, C-8), 98.0 (s, C-1 and C-4), 112.3 (d, C-3'), 128.3 (d, C-2'), 128.5 (s, C-1'), 149.9 (s, C-4'). Anal. Calcd for $C_{26}H_{36}N_4$ (404.6): C, 77.18; H, 8.97; N, 13.95. Found: C, 77.50; H, 8.80; N, 13.67.

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1,4-di(3'-N,N-dimethylamino-phenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5d; *m*-N(CH$_3$)$_2$): 76.4 mg (63%) colorless powder, mp 82 - 83 °C dec. R_f = 0.85 (Al_2O_3, methylene chloride); IR (KBr): ν = 2920, 2840, 2780, 1590, 1570, 1480, 1410, 1340, 1220, 980, 720; UV (C_6H_6): λ_{max} (log ε) = 364 nm (2.297), 351 (2.210); ^{1}H NMR ($CDCl_3$): δ = 0.20 (s, 3H, 9-H), 0.88 (s, 3H, 10-H), 1.58 (m, 6H, 5-H, 6-H and 7-H), 3.01 (s, 12H, N(C$\underline{H}_3$)$_2$), 3.47 (m, ^3J = 3.4 Hz, 2H, 4a-H/7a-H), 6.78 (dd, ^3J = 7.5 Hz, ^4J = 2.6 Hz, 2H, 4'-H), 7.02 (d, ^3J = 7.5 Hz, 2H, 6'-H),7.26 (br s, 2H, 2'-H), 7.33 (t, ^3J = 7.5 Hz, 2H, 3'-H); ^{13}C NMR ($CDCl_3$): δ = 17.3 (q, C-9), 18.1 (q, C-10), 25.6 (t, C-5 and C-7), 28.6 (t, C-6), 40.7 (q, N(C$\underline{H}_3$)$_2$), 49.0 (d, C-4a and C-7a), 66.2 (s, C-8), 98.5 (s, C-1 and C-4), 111.8 (d, C-2'), 112.5 (d, C-4'), 115.5 (d, C-6'), 128.8 (d, C-5'), 137.2 (s, C-1'), 150.5 (s, C-3'). Anal. Calcd for $C_{26}H_{36}N_4$ (404.6): C, 77.18; H, 8.97; N, 13.95. Found: C, 77.05; H, 8.90; N, 13.80.

General Procedure for the Preparation of the Azoalkanes *p*-5p and *m*-5p. 129 mg (300 μmol) of the acetoxy-substituted azoalkanes ***p*-5q** or ***m*-5q** were dissolved in 30 mL dry methylene chloride and 0.5 mL of 100% hydrazine hydrate were added. The reaction mixture was refluxed for 3 h and the solvent was evaporated afterwards. The crude product was purified by column chromatography on silica gel.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(4'-hydroxyphenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*p*-5p; *p*-OH): 102 mg (93%) colorless powder, mp 267 - 268 °C dec. R_f = 0.59 (SiO_2, methylene chloride/methanol 10:1); IR (KBr): ν = 3420, 3000, 2920, 1590, 1570, 1490, 1420, 1220, 1160, 990, 800; UV (CH_3CN): λ_{max} (log ε) = 360 nm (2.129), 347 (2.048, sh), 327 (1.851, sh); ^{1}H NMR (d_4-MeOD): δ = 0.15 (s, 3H, 9-H), 0.92 (s, 3H, 10-H), 2.17 (m_c, 2H, 7-H), 3.73 (dt, ^3J = 10.5 Hz, ^3J = 8.4 Hz, ^3J = 4.5 Hz, 1H, 7a-H), 4.17 (m_c, ^3J = 8.4 Hz, 1H, 4a-H), 5.45 (m_c, 2H, 5-H and 6-H), 6.90 (m, 4H, 3'-H/3"-H), 7.54 (m, 4H, 2'-H/2"-H); ^{13}C NMR (d_4-MeOD): δ = 17.6 (q, C-9), 17.7 (q, C-10), 32.7 (t, C-7), 44.0 (d, C-7a), 57.6 (d, C-4a), 65.4 (s, C-8), 98.5 (s, C-1), 99.7 (s, C-4), 116.3 (d, C-3'), 127.56 and 127.62 (2 × s, C-1'), 128.6 (d, C-6), 129.5 and 130.0 (2 × d, C-2'), 134.1 (d, C-5), 158.48 and 158.53 (2 × s, C-4'). Anal. Calcd for $C_{22}H_{22}N_2O_2$ (364.4): C, 72.51; H, 6.08; N, 7.69. Found: C, 72.05; H, 5.91; N, 7.72.

(1α,4α,4aα,7aα)-4,4a,7,7a-Tetrahydro-8,8-dimethyl-1,4-di(3'-hydroxyphenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5p; *m*-OH): 93.1 mg (85%) colorless powder, mp 137 - 139 °C dec. R_f = 0.48 (SiO_2, methylene chloride/methanol 10:1); IR (KBr): ν = 3400, 2920, 1580, 1570, 1430, 1290, 1200, 870, 770, 710, 690; UV (CH_3CN): λ_{max} (log ε) = 359 nm (2.385), 347 (2.002, sh), 327 (1.752, sh); ^{1}H NMR (d_4-MeOD): δ = 0.17 (s, 3H, 9-H), 1.00 (s, 3H, 10-H), 2.20 (m_c, 2H, 7-H), 3.74 (ddd, ^3J = 10.2 Hz, ^3J = 8.4 Hz, ^3J = 4.6 Hz, 1H, 7a-H), 4.17 (m_c, ^3J = 8.4 Hz, 1H, 4a-H), 5.46 (m_c, 2H, 5-H and 6-H), 6.83 (m, 2H, 4'-H/4"-H), 7.20 (m, 4H, 2'-H/2"-H and 6'-H/6"-H), 7.31 (t, ^3J = 8.1 Hz, 2H, 5'-H/5"-H); ^{13}C NMR (d_4-MeOD): δ = 17.8 (q, C-9), 17.9 (q, C-10), 32.6 (t, C-7), 44.3 (d, C-7a), 57.9 (d, C-4a), 65.6 (s, C-8), 98.6 (s, C-1), 99.7 (s, C-4), 115.4 (d, C-2'), 115.9 and 116.0 (2 × d, C-4'), 119.4 and 119.8 (2 × d, C-6'), 128.5 (d, C-6), 130.6 (d, C-5'), 134.2 (d, C-5), 138.3 (s, C-1'), 158.7 (s, C-3'). Anal. Calcd for $C_{22}H_{22}N_2O_2$ (364.4): C, 72.51; H, 6.08; N, 7.69. Found: C, 72.31; H, 6.00; N, 7.54.

General Procedure for the Preparation of the Azoalkanes *p*-5e, *m*-5e and *m*-5s. 300 μmol of the azoalkanes ***p*-5a**,[16a] ***m*-5a**[14] or ***m*-5t** were dissolved in 20 mL of ethyl acetate and 20 mL of ethanol and ca. 1 mg of a 10% Pd/charcoal catalyst was added. The reaction mixture was put then under a hydrogen atmosphere and stirred for 48 h at ambient temperature. After filtration of the catalyst and evaporation of the solvent the crude product was purified by column chromatography.

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1,4-di(4'-aminophenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*p*-5e; *p*-NH_2): 94.7 mg (91%) colorless powder, mp 189 - 191 °C dec. R_f = 0.57 (Al_2O_3, methyl *tert*-butyl ether); IR (KBr): ν = 3290, 2910, 1600, 1495, 1445, 1350, 1260, 1170, 1020, 830; UV (C_6H_6): λ_{max} (log ε) = 364 nm (2.079), 353 (sh, 2.000); ^1H NMR ($CDCl_3$): δ = 0.15 (s, 3H, 9-H), 0.88 (s, 3H, 10-H), 1.56 (m_c, 6H, 5-H, 6-H and 7-H), 3.41 (m_c, 2H, 4a-H and 7a-H), 3.72 (br s, 4H, NH_2), 6.79 (d, ^3J = 8.5 Hz, 2H, 3'-H), 7.51 (d, ^3J = 8.5 Hz, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 17.0 (q, C-9), 17.7 (q, C-10), 25.6 (t, C-5 and C-7), 28.5 (t, C-6), 48.5 (d, C-4a and C-7a), 65.7 (s, C-8), 98.0 (s, C-1 and C-4), 114.9 (d, C-3'), 126.4 (s, C-1'), 128.5 (d, C-2'), 145.8 (s, C-4'). Anal. Calcd for $C_{22}H_{26}N_4$ (346.5): C, 76.26; H, 7.56; N, 16.17. Found: C, 76.04; H, 8.06; N, 15.68.

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1,4-di(3'-aminophenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5e; *m*-NH_2): 102 mg (98%) colorless powder, mp 82 - 84 °C dec. R_f = 0.56 (Al_2O_3, methylene chloride); IR (KBr): ν = 3390, 3290, 3180, 2920, 2820, 1580, 1560, 1470, 1430, 1300; UV (C_6H_6): λ_{max} (log ε) = 363 nm (2.395), 350 (sh, 2.297); ^1H NMR ($CDCl_3$): δ = 0.17 (s, 3H, 9-H), 0.97 (s, 3H, 10-H), 1.57 (m_c, 6H, 5-H, 6-H and 7-H), 3.43 (m_c, 2H, 4a-H and 7a-H), 3.76 (br s, 4H, NH_2), 6.72 (ddd, ^3J = 7.8 Hz, ^4J = 2.0 Hz, ^5J = 0.9 Hz, 2H, 4'-H), 7.05 (dt, ^3J = 7.8 Hz, ^5J = 0.9 Hz, 2H, 6'-H), 7.18 (t, ^4J = 2.0 Hz, 2H, 2'-H), 7.25 (t, ^3J = 7.8 Hz, 2H, 5'-H); ^{13}C NMR ($CDCl_3$): δ = 16.8 (q, C-9), 18.0 (q, C-10), 25.6 (t, C-5 und C-7), 28.5 (t, C-6), 48.7 (d, C-4a and C-7a), 66.0 (s, C-8), 98.3 (s, C-1 and C-4), 114.4 (d, C-2'), 114.7 (d, C-4'), 117.6 (d, C-6'), 129.1 (d, C-5'), 137.4 (s, C-1'), 146.3 (s, C-3'). Anal. Calcd for $C_{22}H_{26}N_4$ (346.5): C, 76.26; H, 7.56; N, 16.17. Found: C, 76.67;H, 7.72; N, 15.95.

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1,4-di(3'-phenethylphenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5s; *m*-CH_2CH_2Ph): 36.4 mg (99%) colorless oil; IR (CCl_4): ν = 3020, 2980, 2920, 2880, 2820, 1570, 1470, 1430, 1350, 690; UV (C_6H_6): λ_{max} (log ε) = 363 nm (2.651); ^1H NMR ($CDCl_3$): δ = 0.08 (s, 3H, 9-H), 0.87 (s, 3H, 10-H), 1.65 (m, 6H, 5-H, 6-H and 7-H), 2.98 (m, 8H, CH_2CH_2), 3.45 (m, 2H, 4a-H/7a-H), 7.23 (m, 12H, Ph-H), 7.40 (t, ^3J = 7.7 Hz, 2H, 5'-H), 7.57 (m, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 17.0 (q, C-9), 17.8 (q, C-10), 25.5 (t, C-5 und C-7), 28.5 (t, C-6), 37.95 and 38.01 (2 x t, Ph-CH_2CH_2-Ar), 48.8 (d, C-4a and C-7a), 66.1 (s, C-8), 98.3 (s, C-1 and C-4), 125.0 (d, C-2'), 125.9 (d, C-4'), 127.8 (d, C-6'), 128.2 (d, C-5'), 128.3

and 128.5 (Ph-C), 136.1 (s, C-1'), 141.6 (s, C-3'). Anal. Calcd. for $C_{38}H_{40}N_2$ (524.8): C, 86.98; H, 7.68; N, 5.34. Found: C, 87.26; H, 7.76; N, 5.67.

General Procedure for the Preparation of the Azoalkanes *p*-5f and *m*-5f. 104 mg (300 µmol) of the NH_2-substituted azoalkanes ***p*-5e** or ***m*-5e** were dissolved in 30 mL of dry methylene chloride and 61.4 mg (600 µmol) of acetic anhydride were added. The reaction mixture was kept at reflux for 4 h and the solvent removed. The crude product was purified by column chromatography on basic alumina.

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1,4-di(4'-N-acetanilid)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*p*-5f; *p*-NHCOCH$_3$): 111 mg (86%) colorless powder, mp 132 - 133 °C dec. R_f = 0.20 (Al_2O_3, methylene chloride); IR (KBr): ν = 3260, 2920, 2820, 1690, 1570, 1510, 1490, 1380, 1340, 1300, 800; ^{1}H NMR (d_4-MeOD): δ = 0.12 (s, 3H, 9-H), 0.94 (s, 3H, 10-H), 1.51 (m, 6H, 5-H, 6-H und 7-H), 2.15 (s, 6H, COC$\underline{H}_3$), 3.66 (m, 2H, 4a-H/7a-H), 7.56 (br s, 8H, 2'-H/3'-H); ^{13}C NMR (d_4-MeOD): δ = 17.6 (q, C-9), 18.2 (q, C-10), 23.9 (q, CO$\underline{C}H_3$), 26.5 (t, C-5 and C-7), 29.4 (t, C-6), 50.0 (d, C-4a and C-7a), 67.6 (s, C-8), 100.0 (s, C-1 and C-4), 121.1 (d, C-2'), 129.1 (d, C-3'), 132.8 (s, C-1'), 139.7 (s, C-4'), 171.8 (s, $\underline{C}OCH_3$). Anal. Calcd for $C_{26}H_{30}N_4O_2$ (430.6): C, 72.53; H, 7.02; N, 13.01. Found: C, 72.66; H, 7.00; N, 12.89.

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1,4-di(3'-N-acetanilid)-1,4-methano-1*H*-cyclopenta[d]pyridazine (*m*-5f; *m*-NHCOCH$_3$): 96.5 mg (74%) colorless powder, mp 135 - 136 °C dec. R_f = 0.19 (Al_2O_3, methylene chloride); IR (KBr): ν = 3280, 2940, 2840, 1700, 1600, 1570, 1530, 1470, 1420, 1300; UV (C_6H_6): λ_{max} (log ε) = 363 nm (1.945), 349 (1.878); ^{1}H NMR ($CDCl_3$): δ = 0.14 (s, 3H, 9-H), 1.00 (s, 3H, 10-H), 1.57 (m, 6H, 5-H, 6-H and 7-H), 2.22 (s, 6H, COC$\underline{H}_3$), 3.48 (m, 2H, 4a-H/7a-H), 7.44 (m, 4H, 5'-H/6'-H), 7.67 (m, 2H, 4'-H), 7.83 (br s, 2H, 2'-H); ^{13}C NMR ($CDCl_3$): δ = 17.0 (q, C-9), 17.8 (q, C-10), 24.7 (q, CO$\underline{C}H_3$), 25.4 (t, C-5 and C-7), 28.5 (t, C-6), 48.8 (d, C-4a and C-7a), 66.5 (s, C-8), 98.4 (s, C-1 und C-4), 119.0 (d, C-2'), 119.2 (d, C-4'), 122.9 (d, C-6'), 129.0 (d, C-5'), 136.8 (s, C-1'), 138.2 (s, C-3'), 168.9 (s, $\underline{C}OCH_3$). Anal. Calcd for $C_{26}H_{30}N_4O_2$ (430.6): C, 72.53; H, 7.02; N, 13.01. Found: C, 72.11; H, 6.88; N, 13.45.

General Procedure for the Preparation of the Azoalkanes *p*-5i and *m*-5i. 17.3 mg (50 μmol) of the NH_2-substituted azoalkanes ***p*-5e** or ***m*-5e** were dissolved in 30 mL of dry methyl *tert*-butyl ether and 10.0 mg (100 μmol) of a 70% $HClO_4$ solution were added. The mixture was stirred for 20 min at ambient temperature and the precipitated salt collected by filtration and washed with cyclohexane.

(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1,4-di(4'-ammoniumphenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine diperchlorate (*p*-5i; *p*-NH_3^+): 26.0 mg (95%) pale yellow powder, mp 189 - 190 °C dec.; IR (KBr): ν = 3360, 2920, 2820, 2560, 1590, 1500, 1120, 1090, 1070, 800; UV (CH_3CN): λ_{max} (log ε) = 362 nm (2.279); ^1H NMR (CD_3CN): δ = 0.07 (s, 3H, 9-H), 0.93 (s, 3H, 10 H), 1.49 (m, 6H, 5-H, 6-H, 7-H), 3.57 (m, 2H, 4a-H, 7a-H), 4.86 (br s, 6H, NH_3^+), 7.24 (dt, ^3J = 8.8 Hz, ^4J = 2.6 Hz, 4H, 3'-H), 7.77 (dt, ^3J = 8.8 Hz, ^4J = 2.6 Hz, 4H, 2'-H); ^{13}C NMR (CD_3CN): δ = 17.5 (q, C-9), 18.1 (q, C-10), 26.0 (t, C-5 and C-7), 29.3 (t, C-6), 49.7 (d, C-4a and C-7a), 67.0 (s, C-8), 98.9 (s, C-1 and C-4), 121.6 (d, C-3'), 130.0 (d, C-2'), 134.9 (s, C-4'), 135.8 (s, C-1'). Anal. Calcd for $C_{22}H_{28}Cl_2N_4O_8$ (547.4): C, 48.27; H, 5.16; N, 10.24.

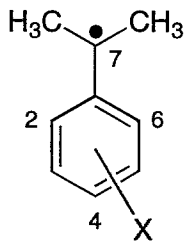
(1α,4α,4aα,7aα)-4,4a,5,6,7,7a-Hexahydro-8,8-dimethyl-1,4-di(3'-ammoniumphenyl)-1,4-methano-1*H*-cyclopenta[d]pyridazine diperchlorate (*m*-5i; *m*-NH_3^+): 25.4 mg (93%) pale yellow powder, mp 170 - 172 °C dec.; IR (KBr): ν = 3380, 2920, 2820, 2540, 1570,1480, 1130, 1100, 1070, 780; UV (CH_3CN): λ_{max} (log ε) = 364 nm (2.230); ^1H NMR (D_4-MeOD): δ = 0.15 (s, 3H, 9-H), 1.02 (s, 3H, 10 H), 1.53 (m, 6H, 5-H, 6-H, 7-H), 3.72 (m, 2H, 4a-H, 7a-H), 4.91 (br s, 6H, NH_3^+), 7.42 (d, ^3J = 7.9 Hz, 2H, 6'-H), 7.69 (t, ^3J = 7.9 Hz, 2H, 5'-H), 7.80 (d, ^3J = 7.9 Hz, 2H, 4'-H), 7.87 (br s, 2H, 2'-H); ^{13}C NMR (D_4-MeOD): δ = 16.2 (q, C-9), 17.0 (q, C-10), 25.1 (t, C-5 and C-7), 28.7 (t, C-6), 49.8 (d, C-4a and C-7a), 67.7 (s, C-8), 98.6 (s, C-1 and C-4), 122.1 (d, C-2'), 122.3 (d, C-4'), 127.7 (d, C-6'), 130.4 (d, C-5'), 131.9 (s, C-3'), 138.6 (s, C-1'). Anal. Calcd for $C_{22}H_{28}Cl_2N_4O_8$ (547.4): C, 48.27; H, 5.16; N, 10.24. Found: C, 48.00; H, 5.33; N, 9.99.

Additional References

31) In analogy to Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313.

32) In analogy to McOmie, J. F. W.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289.

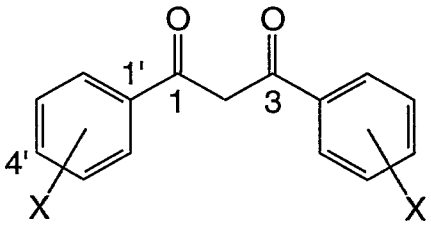
Table S-1: Calculated spin density distributions for the substituted cumyl radicals 7 [a]



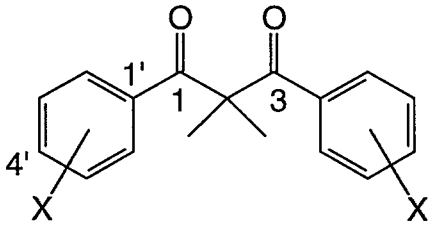
X	C-2	C-4	C-6	C-7	ρ_X [b]	$\langle S^2 \rangle$ [c]
p-H	0.121	0.123	0.121	0.542	—	0.780
p-NO_2 [d]	0.114	0.136	0.114	0.492	0.055	0.767
p-NH_2	0.117	0.131	0.117	0.521	0.011	0.759
p-NMe_2	0.118	0.128	0.118	0.520	0.012	0.768
p-NHAc	0.117	0.129	0.119	0.526	0.003	0.768
p-CN	0.116	0.132	0.116	0.513	0.033	0.778
p-CO_2Me	0.116	0.132	0.116	0.513	0.014	0.770
p-CF_3	0.118	0.127	0.116	0.529	—	0.772
p-CH_3	0.118	0.128	0.118	0.539	—	0.776
p-OH	0.119	0.128	0.119	0.537	—	0.778
p-OMe	0.120	0.128	0.120	0.536	—	0.776
p-OAc	0.120	0.126	0.120	0.542	—	0.775
p-SMe	0.116	0.128	0.118	0.526	0.010	0.757
p-SOMe	0.119	0.127	0.114	0.529	0.005	0.756
p-SO_2Me	0.114	0.128	0.117	0.525	0.006	0.768
p-F	0.119	0.130	0.119	0.532	—	0.778
p-Cl	0.119	0.129	0.119	0.529	—	0.772
p-Br	0.119	0.122	0.119	0.539	—	0.756
p-I	0.119	0.122	0.119	0.536	—	0.750
m-NO_2	0.121	0.123	0.117	0.543	—	0.772
m-NH_2	0.119	0.118	0.118	0.552	—	0.775
m-NMe_2	0.116	0.118	0.119	0.553	—	0.770
m-NHAc	0.119	0.121	0.115	0.548	—	0.774
m-CN	0.119	0.122	0.120	0.545	—	0.779
m-CF_3	0.118	0.122	0.120	0.543	—	0.776
m-CH_3	0.120	0.120	0.120	0.545	—	0.779
m-C≡CH	0.119	0.121	0.119	0.551	—	0.779
m-CH_2CH_3	0.119	0.120	0.121	0.544	—	0.779
m-OH	0.113	0.118	0.121	0.552	—	0.774
m-OMe	0.112	0.118	0.124	0.550	—	0.774
m-OAc	0.119	0.121	0.119	0.547	—	0.779
m-F	0.118	0.120	0.118	0.547	—	0.779
m-Cl	0.119	0.123	0.120	0.544	—	0.764
m-I	0.119	0.121	0.118	0.548	—	0.752

a) Geometry optimization was carried out with the PM3 method by using the AUHF Hamiltonian; spin densities were determined with a single-point *CI* (5×5) calculation; b) total spin density at the substituent, values < 0.001 are not considered; c) $\langle S^2 \rangle = S(S+1)$; d) the only case with a spin density at C-1 (0.011).

Structures 8 - 10



8



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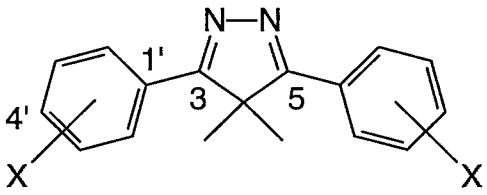

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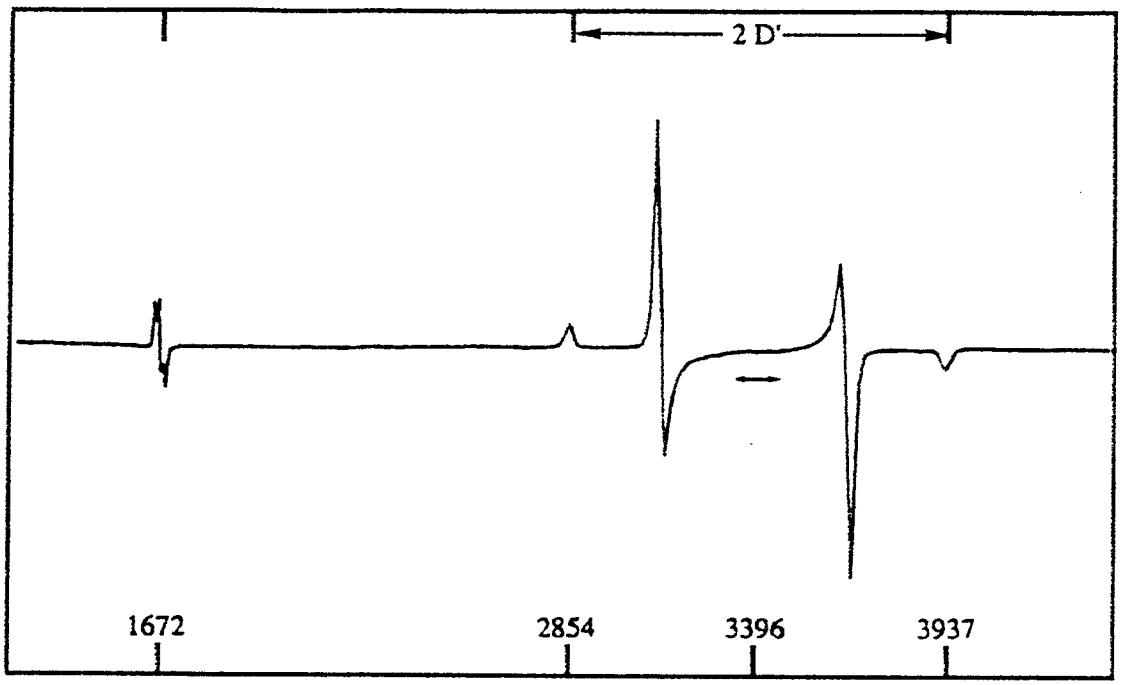
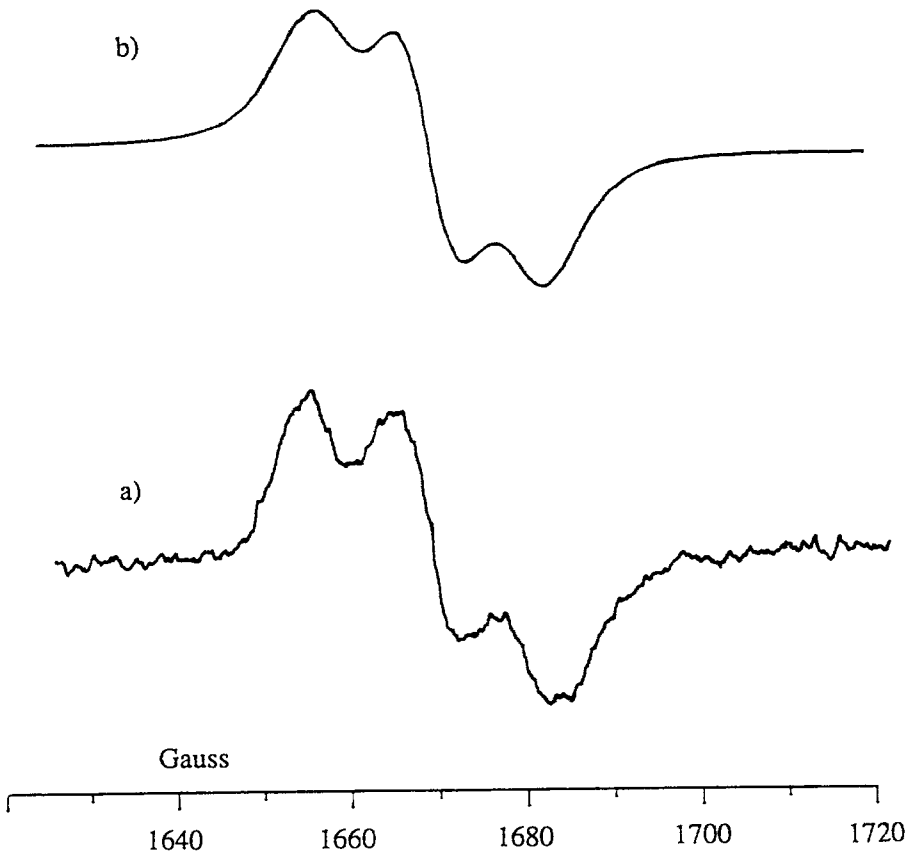


Typical EPR spectrum for the triplet diradicals **6** (i.e. ***p*-6n**).



$\Delta m_s = \pm 2$ region of the *triplet diradical* ***p*-6o**; a) recorded spectrum and b) simulated spectrum, a Lorentz function was used with a line broadening of 0.756 G and one half of the hyperfine splitting constants of the *p*-methoxycumyl monoradical,[13] i.e. 9.40 G for β-H, 2.80 G for *ortho*-H and 0.90 G for *meta*-H.