6 Experimental Section

6.1 Syntheses of the Target Compounds

6.1.1 General methods

All reagents and solvents were purchased from Acros Organics, Sigma-Aldrich, Merck, Fluka or Lancaster. Dichloromethane was dried over molecular sieve 4A for 48 hours and then stirred with phosphor(V) oxide for 8 hours and distilled. Acetonitrile was stirred with phosphor(V) oxide for 8 hours and distilled. Tetrahydrofuran was dried over potassium hydroxide for three days and distilled and then was dried over sodium/benzophenone.

Reactions were all monitored by thin-layer chromatography (TLC), performed on precoated silica gel plates (Kieselgel 60 F_{254}, Merck). Visualization on TLC was achieved by UV light at 254 and / or 366 nm. Column chromatography was performed with silica gel 60 (0.063-0.200 mm, Merck). The silica gel were first bloated in the used eluent and then filled into the column. The sample was solved in a little of the corresponding eluent unless otherwise noted and loaded onto the column.

Melting points are measured using a Büchi B-545 melting point apparatus (Flawil, Switzerland) and are uncorrected.

NMR-spectra were taken with a Bruker ADX 400 spectrometer (Rheinstetten, Germany) at 400 MHz (for ^{1}H) or 100 MHz (for ^{13}C) with TMS as internal standard.

IR-spectra (KBr pellets or film) were recorded with a Perkin Elmer Model 580 A spectrometer (Shelton, USA).

FAB-MS-spectra were determined using a CH5DF/FAB(+) instrument. EI-MS-spectra were recorded with a CH-7A-Varian MAT (70eV) instrument (Palo Alto, USA)

Elemental analyses were run with a Vario EL Elementaranalysator (Hanau, Germany).

6.1.2 Chloro-substituted benzaldehydes 3 - 5

General Procedure

The corresponding chloro-substituted anisole (0.053 mol) was dissolved in 100 ml of dry dichloromethane and stirred at 0°C. To which were added cautiously via syringe titanium tetrachloride (20 ml, 0.18 mol) and dichloromethyl methyl ether (10 ml, 0.11 mol). After stirring for 30 minutes at 0°C , the reaction mixture was hydrolyzed by adding chopped ice and then was extracted with dichloromethane. The organic phase was washed with water, dried over sodium sulfate and evaporated under vacuum. The resulting crude product was purified by column chromatography on silica gel and recrystallization.

2-Chloro-4-methoxybenzaldehyde 3

starting from 3-chloroanisole. The crude product was purified first by column chromatography on silica gel with dichloromethane as eluent and then by recrystallization from ligroin.

Yield: 2.80 g (31%, colorless needles); mp: 61.7-62.7°C

^{1}H-NMR ($CDCl_3$): δ [ppm] = 3.88 (s, 3H, OCH_3), 6.90 (dd, 1H, ^3J = 8.7Hz and ^4J = 2.4Hz, Ar-H), 6.94 (d, 1H, ^4J = 2.4Hz, Ar-H), 7.90 (d, 1H, ^3J = 8.7Hz, Ar-H), 10.34 (s, 1H, CHO)

^{1}H-NMR (DMSO-d_6): δ [ppm] = 3.89 (s, 3H, OCH_3), 7.10 (dd, 1H, ^3J = 8.7Hz and ^4J = 2.2Hz, Ar-H), 7.19 (d, 1H, ^4J = 2.2Hz, Ar-H), 7.84 (d, 1H, ^3J = 8.7Hz, Ar-H), 10.20 (s, 1H, CHO)

IR (KBr): ν (cm^{-1}) = 3080w, 3010w, 2979w, 2946w, 2844w, 1687s (CH=O), 1595s, 1492m, 1462m, 1399m, 1305m, 1244s, 1040s, 880m

MS (EI, 35°C): m/z = 170 (M^+, 78%), 169 (M^+-H, 100%), 153 (14%), 126 (20%), 111 (15%), 99 (11%), 75 (22%), 63 (31%)

Elemental analysis: $C_8H_7ClO_2$ (170.01 g/mol)

Calculated: C% 56.32 H% 4.14

Found: C% 56.35 H% 4.26

2,6-Dichloro-4-methoxybenzaldehyde 4

starting from 3,5-dichloroanisole. After removal of dichloromethane, the resulting mixture of isomers **4** and **5** was isolated by column chromatography on silica gel with dichloromethane : ligroin = 2 : 1 as eluent.

Yield: 2.95g (27%, colorless needles, R_f = 0.58); mp: 107.5-110.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.88 (s, 3H, OCH_3), 6.92 (s, 2H, Ar-H), 10.42 (s, 1H, CHO)

IR (KBr): ν (cm^{-1}) = 3085m, 2960w, 2877w, 2781w, 1700s (CH=O), 1591s, 1546s, 1470m, 1402m, 1301m, 1260s, 1209m, 1066s, 1033s, 868m, 847m

MS (EI, 50°C): m/z = 203 (M$^+$, 100%), 160 (4.5%), 111 (6%), 97 (6%), 74 (5%), 62 (6%)

Elemental analysis: $C_8H_6Cl_2O_2$ (203.97 g/mol)

Calculated:	C%	46.86	H%	2.95
Found:	C%	46.88	H%	2.89

2,4-Dichloro-6-methoxybenzaldehyde 5

starting from 3,5-dichloroanisole. After removal of dichloromethane, the resulting mixture of isomers **4** and **5** was isolated by column chromatography on silica gel with dichloromethane : ligroin = 2 : 1 as eluent.

Yield: 4.22 g (39%, colorless needles, R_f = 0.42); mp: 109-111°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.93 (s, 3H, OCH_3), 6.91 (d, 1H, ^4J = 1.7Hz, Ar-H), 7.07 (d, 1H, ^4J = 1.7Hz, Ar-H), 10.44 (s, 1H, CHO)

IR (KBr): ν (cm^{-1}) = 3091w, 2958w, 2898w, 1689s (CH=O), 1586s, 1560s, 1451m, 1394m, 1254s, 1096m, 1038s, 875m, 840s

MS (EI, 30°C): m/z = 204 (M$^+$, 100%), 187 (57%), 172 (41%), 162 (35%), 144 (26%), 111 (23%), 75 (20%)

Elemental analysis: $C_8H_6Cl_2O_2$ (203.97 g/mol)

Calculated:	C%	46.86	H%	2.95
Found:	C%	46.78	H%	3.15

6.1.3 Symmetric dimethoxystilbenes 8 - 11

General Procedure

Titanium tetrachloride (1.33 ml, 12 mmol) was added via a syringe dropwise to a stirred suspension of zinc power (1.56 g, 24 mmol) in dry tetrahydrofuran (30 ml) at –10°C under nitrogen. The resulting yellow-dark mixture was stirred at room temperature for 30 minutes and then heated under reflux for 1 hour. The dark suspension was cooled to room temperature and the starting benzaldehyde (8 mmol) in tetrahydrofuran (10 ml) was added. The reaction mixture was refluxed for 2 - 4 hours. After cooling the mixture was poured into ice-water and worked up as described responsively by each product as follows.

(*E*)-1,2-Bis(4-methoxyphenyl)ethene 8

starting from 4-methoxybenzaldehyde (1.0 ml, 8 mmol). After refluxing for 2 hours, the cooled mixture was poured into ice-water and extracted with heated dichloromethane many times until no product suspended in aqueous layer. The united organic extract was washed with water, dried over sodium sulfate and evaporated under vacuum. The residue was purified by recrystallization from chloroform.

Yield: 0.53 g (55%, colorless leaflets); mp: 215.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.82 (s, 6H, 2OCH_3), 6.88 (AA'BB', 4H, ^3J = 8.7Hz, 2Ar-H, 2Ar'-H), 6.93 (s, 2H, CH=CH), 7.42 (AA'BB', 4H, ^3J = 8.7Hz, 2Ar-H, 2Ar'-H)

IR (KBr): ν (cm^{-1}) = 3018w, 2956m, 2937w, 2911w, 2838w, 1608s, 1577m, 1514s, 1468m, 1441m, 1307m, 1270s, 1251s, 1216m, 1178s, 1031s, 968m, 835s

MS (EI, 90°C): m/z = 240 (M^+, 100%), 225 (47%), 165 (9%), 120 ($C_8H_8O^+$, 15%)

Elemental analysis: $C_{16}H_{16}O_2$ (240.12 g/mol)

Calculated: C% 79.97 H% 6.71

Found: C% 80.02 H% 6.87

(*E*)-1,2-Bis(2-fluoro-4-methoxyphenyl)ethene 9

starting from 2-fluoro-4-methoxybenzaldehyde (1.30 g, 8 mmol). After refluxing for 4 hours, the cooled mixture was poured into ice-water and extracted with diethyl ether. The united organic extract was washed with water, dried over sodium sulfate and evaporated. To the residue was added a mixture of ligroin (25 ml) and tetrahydrofuran (5 ml) and stirred under reflux for 30 minutes. After cooling at room temperature, the suspension was stayed in a refrigerator over night. The crystals were isolated by suction filtration, washed with a mixture of ligroin and dichloromethane (10 : 1) and dried to give the pure product. The filtrate was evaporated and the residue was purified by means of the same method described hereinabove with isopropanol and ligroin (2 : 1) instead of ligroin and tetrahydrofuran to afford further some desired product.

Yield: 0.90 g (82%, colorless crystals); mp: 135-136°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.81 (s, 6H, 2OCH_3), 6.62 (dd, 2H, $^3J_{(H,\,F)}$ = 12.5Hz and ^4J = 2.5Hz, Ar-H, Ar'-H), 6.70 (dd, 2H, ^3J = 8.7Hz and ^4J = 2.5Hz, Ar-H, Ar'-H), 7.13 (s, 2H, CH=CH), 7.52 (dd, 2H, ^3J = 8.7Hz and $^4J_{(H,\,F)}$ = 8.7Hz, Ar-H, Ar'-H)

IR (KBr): ν (cm^{-1}) = 3073w, 3023w, 2960w, 2838w, 2057w, 2028w, 1624s, 1578m, 1512s, 1283s, 1155s, 1105s, 1030m, 973m, 857m, 812m

MS (EI, 110°C): m/z = 276 (M^+, 100%), 261 (42%), 247 (10%), 138 ($C_8H_7FO^+$, 14%)

Elemental analysis: $C_{16}H_{14}F_2O_2$ (276.10 g/mol)

Calculated: C% 69.56 H% 5.11

Found: C% 69.47 H% 4.97

(*E*)-1,2-Bis(2-chloro-4-methoxyphenyl)ethene 10

starting from 2-chloro-4-methoxybenzaldehyde (1.36 g, 8 mmol). After refluxing for 4 hours, the cooled mixture was poured into ice-water and extracted with diethyl ether. The united organic extract was washed with water, dried over sodium sulfate and evaporated. The crude product was recrystallized from a mixture of ligroin and tetrahydrofuran (5 : 1).

Yield: 0.82 g (66%, colorless crystals); mp: 131.5-132.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.81 (s, 6H, 2OCH_3), 6.84 (dd, 2H, ^3J = 8.7Hz and ^4J = 2.6Hz, Ar-H, Ar'-H), 6.93 (d, 2H, ^4J = 2.6Hz, Ar-H, Ar'-H), 7.29 (s, 2H, CH=CH), 7.63 (d, 2H, ^4J = 8.8Hz, Ar-H, Ar'-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 55.6, 113.8, 114.6, 124.8, 127.3, 128.1, 134.0, 159.6

IR (KBr): ν (cm^{-1}) = 3071w, 2965w, 2936w, 2908w, 2835w, 1603s, 1556m, 1496s, 1465m, 1451m, 1282s, 1235s, 1206m, 1043s, 963m, 861m, 811m

MS (EI, 80°C): m/z = 308 (M^+, 100%), 293 (23%), 238 (12%), 195 (14%), 155 (18%)

Elemental analysis: $C_{16}H_{14}Cl_2O_2$ (308.04 g/mol)

Calculated: C% 62.15 H% 4.56

Found: C% 62.27 H% 4.52

(*E*)-1,2-Bis(2,6-dichloro-4-methoxyphenyl)ethane 11

2,6-Dichloro-4-methoxybenzaldehyde (1.85 g, 8.8 mmol) was dissolved in dry dioxane (20 ml). $TiCl_4$ (1.5 ml, 13.2 mmol) was added via a syringe at room temperature under stirring and nitrogen. Then zinc (1.72 g, 26.4 mmol) was added in small portions over a period of 20 minutes and the resulting mixture was heated under reflux for 4 hours. After cooling the reaction mixture was poured in ice-water and extracted with dichloromethane. The united organic phase was filtrated and the filtrate was washed with water, dried with sodium sulfate and evaporated in vacuum. To the residue 50 ml of diethyl ether was added and the desired product as precipitate was isolated by suction filtration, washed with diethyl ether and dried.

Yield: 0.65 g (39%, colorless needles); mp: 211-212.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.81 (s, 6H, 2OCH_3), 6.94 (s, 4H, 2Ar-H, 2Ar'-H), 7.05 (s, 2H, CH=CH)

IR (KBr): ν (cm^{-1}) = 3085w, 2968m, 2936m, 2836w, 1601s, 1553s, 1478s, 1430s, 1401m, 1310s, 1269s, 1212s, 1064s, 1043s, 960s, 912m, 852m, 835s, 806s

MS (EI, 45°C): m/z = 378 (M^+, 100%), 363 (12%), 306 (18%), 263 (23%), 220 (11%), 189 ($C_8H_6Cl_2O^+$, 12%)

Elemental analysis: $C_{16}H_{12}Cl_4O_2$ (378.08 g/mol)

Calculated: C% 50.83 H% 3.20

Found: C% 50.90 H% 3.36

6.1.4 2-Halo-4-methoxybenzyl alcohol 13 and 14

General Procedure

In a two-necked flask with a condensator sodium borohydride was added portion-wise to methanol under stirring and cooling in a water bath. The relative vigorous reaction between sodium borohydride and methanol led to reflux. After addition of sodium borohydride, the corresponding benzaldehyde was added portion-wise in a period of 10 minutes and then stirred at room temperature for 1 hour. The reaction mixture was diluted with water and extracted with diethyl ether. The united organic phase was washed with water, dried over sodium sulfate and evaporated under vacuum. The reside was analyzed to be the pure product, which could be directly used for the following reaction. Further purification of the product was possible by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (5 : 1) as eluent.

2-Fluoro-4-methoxybenzyl alcohol 13

starting from 2-fluoro-4-methoxybenzaldehyde (2.43 g, 15 mmol) with sodium borohydride (2.85 g, 75 mmol) in 30 ml methanol.

Yield: 2.30 g (98%, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.64 (s, 1H, OH), 3.80 (s, 3H, OCH_3), 4.68 (s, 2H, CH_2), 6.62 (dd, 1H, $^3J_{(H,F)}$ = 11.9Hz and ^4J = 2.4Hz, Ar-H), 6.69 (dd, 1H, ^3J = 8.4Hz and ^4J = 2.4Hz, Ar-H), 7.29 (dd, 1H, ^3J = 8.5Hz and $^4J_{(H,F)}$ = 8.5Hz, Ar-H)

^{1}H-NMR (DMSO-d_6): δ[ppm] = 3.75 (s, 3H, OCH_3), 4.44 (d, 2H, ^3J = 5.6Hz, CH_2), 5.10 (t, 1H, ^3J = 5.6 Hz, OH), 6.77 (m, 2H, Ar-H), 7.29 (dd, 1H, ^3J = 8.7Hz and $^4J_{(H,F)}$ = 8.7Hz, Ar-H)

^{1}H-NMR (DMSO-d_6/D_2O): δ[ppm] = 3.75 (s, 3H, OCH_3), 4.45 (s, 2H, CH_2), 6.76 (m, 2H, Ar-H), 7.34 (dd, 1H, ^3J = 8.8Hz and $^4J_{(H,F)}$ = 8.8Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3367 (s, broad), 3006w, 2942m, 2840m, 1627s, 1587s, 1509s, 1444s, 1319s, 1283s, 1193s, 1153s, 1114s, 1029s, 944s, 837s

MS (EI, 40°C): m/z = 156 (M^+, 78%), 139 (M^+-OH, 65%), 127 (41%), 112 (21%), 95 (13%), 77 (14%), 65 (11%), 39 (10%)

Elemental analysis: $C_8H_9FO_2$ (156.06 g/mol)

Calculated:	C%	61.53	H%	5.81
Found:	C%	61.35	H%	5.62

2-Chloro-4-methoxybenzyl alcohol 14

starting from 2-chloro-4-methoxybenzaldehyde (1.36 g, 8 mmol) with sodium borohydride (0.76 g, 20 mmol) in 16 ml of methanol.

Yield: 1.36 g (99%, colorless oil)

^{1}H-NMR (DMSO-d_6): δ[ppm] = 3.76 (s, 3H, OCH_3), 4.48 (d, 2H, ^3J = 5.6Hz, CH_2), 5.22 (t, 1H, ^3J = 5.6Hz, OH), 6.92 (dd, 1H, ^3J = 8.5Hz and ^4J = 2.5Hz, Ar-H), 6.98 (d, 1H, ^4J = 2.5Hz, Ar-H), 7.42 (d, 1H, ^3J = 8.5Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3366s, 3005w, 2942m, 2907w, 2837w, 1608s, 1498s, 1462m, 1439m, 1285s, 1240s, 1047s, 880m

MS (EI, 35°C): m/z = 172 (M^+, 100%), 155 (M^+-OH, 51%), 143 (32%), 137 (61%), 109 (45%), 77 (42%), 65 (28%)

Elemental analysis: $C_8H_9ClO_2$ (172.03 g/mol)

Calculated:	C%	55.67	H%	5.26
Found:	C%	55.95	H%	5.02

6.1.5 2-Halo-4-methoxybenzyl chloride 15 and 16

General Procedure

Thionyl chloride was dropwise added via a syringe to a stirred solution of corresponding benzyl alcohol in dichloromethane over a period of 15 minutes at room temperature and then heated to reflux for 6 hours. The cooled reaction mixture was neutralized with a solution of 10% $NaHCO_3$ under water-cooling and stirred for further 20 minutes. The mixture was extracted with diethyl ether. The ethereal layer was washed with water, dried over sodium sulfate and evaporated. The reside was purified by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (5 : 1) as eluent.

2-Fluoro-4-methoxybenzyl chloride 15

starting from 2-fluoro-4-methoxybenzyl alcohol (2.90 g, 18.6 mmol) with thionyl chloride (1.6 ml, 21.9 mmol) in 30 ml dichloromethane.

Yield: 2.95 g (91%, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.80 (s, 3H, OCH_3), 4.61 (s, 2H, CH_2), 6.62 (dd, 1H, $^3J_{(H, F)}$ = 11.7Hz and ^4J = 2.5Hz, Ar-H), 6.69 (dd, 1H, ^3J = 8.5Hz and ^4J = 2.5Hz, Ar-H), 7.29 (dd, 1H, ^3J = 8.6Hz and $^4J_{(H, F)}$ = 8.6Hz, Ar-H)

MS (EI, 35°C): m/z = 174 (M^+, 16%), 139 (M^+-Cl, 100%), 96 (12%)

Elemental analysis: $C_8H_9FO_2$ (174.02 g/mol)

Calculated: C% 55.03 H% 4.62

Found: C% 55.45 H% 4.26

2-Chloro-4-methoxybenzyl chloride 16

starting from 2-chloro-4-methoxybenzyl alcohol (1.35 g, 7.8 mmol) with thionyl chloride (0.67 ml, 9.2 mmol) in 13 ml dichloromethane.

Yield: 1.39 g (94%, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.80 (s, 3H, OCH_3), 4.67 (s, 2H, CH_2), 6.80 (dd, 1H, ^3J = 8.5Hz and ^4J = 2.6Hz, Ar-H), 6.95 (d, 1H, ^4J = 2.5Hz, Ar-H), 7.35 (d, 1H, ^3J = 8.5Hz, Ar-H)

MS (EI, 35°C): m/z = 190 (M^+, 18%), 155 (M^+-Cl, 100%)

Elemental analysis: $C_8H_8Cl_2O$ (190.00 g/mol)

Calculated: C% 50.29 H% 4.22

Found: C% 50.45 H% 4.64

6.1.6 Substituted benzyltriphenylphosphonium chlorides 19 - 22

General Procedure

The corresponding benzyl chloride (20 mmol) and triphenylphosphine (5.25 g, 20 mmol) were mixed and melted under nitrogen for 20 minutes. After cooling the crude product was dissolved in chloroform (10 ml) and to which diethyl ether was added under stirring to result a suspension. The precipitate was isolated by suction filtration, washed with diethyl ether several times and dried in vacuum.

3-Methoxybenzyltriphenylphosphonium chloride 19

$C_{26}H_{24}ClOP$ (418.89 g/mol); starting from 3-methoxybenzyl chloride.

Yield: 8.25 g (98%, colorless powder); mp: 255-258°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.55 (s, 3H, OCH_3), 5.44 (d, 2H, ^{2}J = 14Hz, CH_2), 6.59-7.24 (m, 4H, Ar-H), 7.54-8.07 (m, 15H, Ar-H)

4-Methoxybenzyltriphenylphosphonium chloride 20

$C_{26}H_{24}ClOP$ (418.89 g/mol); starting from 4-methoxybenzyl chloride.

Yield: 5.63 g (67%, colorless powder)

2-Fluoro-4-methoxybenzyltriphenylphosphonium chloride 21

$C_{26}H_{23}ClFOP$ (436.89 g/mol); starting from 2-fluoro-4-methoxybenzyl chloride.

Yield: 7.52 g (86%, colorless powder); mp: 219-221°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.71 (s, 3H, OCH_3), 5.39 (d, 2H, ^{2}J = 13Hz, CH_2), 6.23-6.94 (m, 2H, Ar-H), 7.22-7.94 (m, 16H, Ar-H)

2-Chloro-4-methoxybenzyltriphenylphosphonium chloride 22

$C_{26}H_{24}Cl_2OP$ (453.34 g/mol); starting from 2-chloro-4-methoxybenzyl chloride.

Yield: 8.07 g (89%, colorless powder); mp: 224-226°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.84 (s, 3H, OCH_3), 5.61 (d, 2H, ^{2}J = 14Hz, CH_2), 6.68-6.92 (m, 2H, Ar-H), 7.47-8.07 (m, 16H, Ar-H)

6.1.7 Asymmetrical dimethoxystilbenes 23 - 29*E / Z*

General Procedure

The corresponding methoxybenzyltriphenylphosphonium chloride and methoxybenzaldehyde were dissolved (or suspended in some cases) in dry methanol. To which was dropwise added at room temperature a solution of sodium methanolate in methanol and then the reaction mixture was stirred at room temperature for 24 hours to complete reaction. The work-up was performed as described respectively under each product.

1-(2-Fluoro-4-methoxyphenyl)-2-(4-methoxyphenyl)ethene 23*E / Z*

starting from (2-fluoro-4-methoxybenzyl)triphenylphosphonium chloride (2.64 g, 6.0 mmol) and 4-methoxybenzaldehye (0.78 ml, 6.0 mmol) with sodium methanolate (0.66g, 12 mmol) in 60 ml of methanol. After stirring for 24 hours, 15 ml of water was added and stirred for further 1 hour. The *E*-form isomer was precipitated as pure crystals and was isolated by suction filtration, washed with 80% methanol and dried under vacuum. The filtrate was extracted with diethyl ether. The organic phase was washed with water, dried with sodium sulfate and evaporated. The residue was purified into a mixture of *E*- and *Z*-isomer (R_f= 0.53) by column chromatography on silica gel with a mixture of ligroin and dichloromethane (1 : 1) as eluent. The *E*-isomer as crystals was less soluble in cooled ligroin, while the *Z*-isomer as oil was well mixable. Thus by repeated treatment of the isomer mixture with ligroin the *E*-isomer as colorless crystals was isolated, while the *Z*-isomer left in ligroin, which was removed to give the pure *Z*-isomer as colorless oil.

23*E*

Yield: 0.73 g (47%, colorless crystals); mp: 121-122°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.81 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.62 (dd, 1H, $^3J_{(H, F)}$ = 12.5Hz and ^4J = 2.5Hz, Ar'-H), 6.70 (dd, 1H, ^3J = 8.7Hz and ^4J = 2.5Hz, Ar'-H), 6.89 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 6.99 (d, 1H, ^3J = 16.5Hz, CH=), 7.06 (d, 1H, ^3J = 16.5Hz, =CH), 7.44 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 7.49 (dd, 1H, ^3J = 8.7Hz and $^4J_{(H, F)}$ = 8.7Hz, Ar'-H)

IR (KBr): ν (cm^{-1}) = 3037w, 2961w, 2933w, 2839w, 1617s, 1574m, 1514s, 1456m, 1445m, 1316m, 1284s, 1247s, 1210m, 1175s, 1159s, 1089m, 1028s, 970m, 950m, 828s

MS (EI, 180°C): m/z = 258 (M^+, 100%), 243 (41%), 229 (9%), 183 (8%), 129 (8%)

Elemental analysis: $C_{16}H_{15}FO_2$ (258.11 g/mol)

Calculated: C% 74.40 H% 5.85

Found: C% 74.36 H% 6.28

23*Z*

Yield: 0.39 g (25%, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.78 (s, 6H, $2OCH_3$), 6.43 (d, 1H, ^3J = 12.1Hz, CH=), 6.51 (dd, 1H, ^3J = 8.7Hz and ^4J = 2.5Hz, Ar'-H), 6.56 (d, 1H, ^3J = 12.2Hz, CH=, superimposed), 6.60 (dd, 1H, $^3J_{(H, F)}$ = 11.8Hz and ^4J = 2.5Hz, Ar'-H, superimposed), 6.76 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 7.15 (dd, 1H, ^3J = 8.7Hz and $^4J_{(H, F)}$ = 8.7Hz, Ar'-H, superimposed), 7.17 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H, superimposed)

IR (film): ν (cm^{-1}) = 3007w, 2957w, 2836w, 1615s, 1574m, 1508s, 1462m, 1443m, 1287s, 1251s, 1178m, 1154m, 1106m, 1033s, 832m

MS (EI, 35°C): m/z = 258 (M^+, 100%), 243 (51%), 229 (17%), 183 (13%)

Elemental analysis: $C_{16}H_{15}FO_2$ (258.11 g/mol)

Calculated: C% 74.40 H% 5.85

Found: C% 74.84 H% 6.02

1-(2-Chloro-4-methoxyphenyl)-2-(4-methoxyphenyl)ethene 24*E / Z*

starting from (4-methoxybenzyl)triphenylphosphonium chloride (1.67 g, 4.0 mmol) and 2-chloro-4-methoxybenzaldehye (0.68 g, 4.0 mmol) with sodium methanolate (0.44g, 8 mmol) in 40 ml of methanol. After stirring for 24 hours, 10 ml of water was added and stirred for further 1 hour. The *E*-form isomer was precipitated as pure crystals and was isolated by suction filtration, washed with 80% methanol and dried under vacuum. The filtrate was extracted with diethyl ether. The organic phase was washed with water, dried with sodium sulfate and evaporated. The residue was suspended with a mixture of ligroin and diethyl ether (5 : 1) and the by-product triphenylphosphine oxide as precipitate was isolated by suction filtration. The filtrate was evaporated and the residue was separated into the *E*- and *Z*-isomer by column chromatography on silica gel with a mixture of ligroin and diethyl ether (5 : 1) as eluent.

24*E*

Yield: 0.59 g (54%, colorless crystals, $R_f = 0.45$); mp: 101-103°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.81 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.82 (dd, 1H, ^3J = 8.8Hz and ^4J = 2.6Hz, Ar'-H), 6.85-6.95 (m, 4H, 1CH=, 2Ar-H, 1Ar'-H), 7.30 (d, 1H, ^3J = 16.3Hz, CH=), 7.46 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 7.58 (d, 1H, ^3J = 8.8Hz, Ar'-H)

IR (KBr): ν (cm^{-1}) = 3005w, 2962w, 2935w, 2838w, 2053w, 1605s, 1578m, 1512s, 1487m, 1439m, 1287s, 1250s, 1212m, 1176s, 1037s, 967m, 860m, 824s

MS (EI, 70°C): m/z = 274 (M^+, 100%), 259 (26%), 196 (9%), 152 (7%), 137 (10%)

Elemental analysis: $C_{16}H_{15}ClO_2$ (274.08 g/mol)

Calculated: C% 69.95 H% 5.50

Found: C% 70.06 H% 5.46

24*Z*

Yield: 0.08 g (7%, colorless oil, $R_f = 0.56$)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.77 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.49 (d, 1H, ^3J = 12.0Hz, CH=), 6.57 (d, 1H, ^3J = 12.0Hz, =CH), 6.63 (dd, 1H, ^3J = 8.6Hz and ^4J = 2.5Hz, Ar'-H), 6.73 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 6.95 (d, 1H, ^4J = 2.5Hz, Ar'-H), 7.12 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 7.15 (d, 1H, ^3J = 8.6Hz, Ar'-H)

IR (film): ν (cm^{-1}) = 3007m, 2957m, 2937m, 2907m, 2835m, 1604s, 1574m, 1557m, 1510s, 1492s, 1462s, 1440s, 1421m, 1403m, 1287s, 1251s, 1222s, 1200m, 1178s, 1041s, 888m, 861s, 832s, 794m, 756w, 700w

MS (EI, 60°C): m/z = 274 (M^+, 100%), 259 (M^+-CH_3, 45%), 239 (M^+-Cl, 16%), 224 (M^+-CH_3-Cl, 15%), 196 (25%), 165 (15%), 152 (22%), 135 (28%), 97 (21%), 85 (25%), 71 (40%)

Elemental analysis: $C_{16}H_{15}ClO_2$ (274.08 g/mol)

Calculated: C% 69.95 H% 5.50

Found: C% 70.09 H% 5.52

1-(2-Chloro-4-methoxyphenyl)-2-(2-fluoro-4-methoxyphenyl)ethene 25*E / Z*

starting from (2-fluoro-4-methoxybenzyl)triphenylphosphonium chloride (3.52 g, 8.0 mmol) and 2-chloro-4-methoxybenzaldehye (1.36 g, 8.0 mmol) with sodium methanolate (0.88 g, 16 mmol) in 80 ml of methanol. After stirring for 24 hours, the reaction mixture was diluted with water and extracted with diethyl ether. The organic phase was washed with water, dried with sodium sulfate and evaporated. The residue was purified into a mixture of the *E*- and *Z*-isomer by column chromatography on silica gel with a mixture of ligroin and dichloromethane (3 : 2) as eluent (R_f = 0.46). The *E*-isomer as crystals was less soluble in cooled ligroin, while the *Z*-isomer as oil was well mixable. Thus by repeated treatment of the isomer mixture with ligroin the *E*-isomer was isolated as colorless crystals, while the *Z*-isomer left in ligroin, which was removed to afford the pure *Z*-isomer as colorless oil.

25*E*

Yield: 0.98 g (47%, colorless crystals); mp: 102-103°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.82 (s, 6H, 2OCH_3), 6.63 (dd, 1H, $^3J_{(H, F)}$ = 12.4Hz and ^4J = 2.5Hz, Ar-H), 6.72 (dd, 1H, ^3J = 8.7Hz and ^4J = 2.4Hz, Ar-H), 6.83 (dd, 1H, ^3J = 8.7Hz and ^4J = 2.5Hz, Ar'-H), 6.93 (d, 1H, ^4J = 2.5Hz, Ar'-H), 7.06 (d, 1H, ^3J = 16.4Hz, CH=), 7.36 (d, 1H, ^3J = 16.4Hz, =CH), 7.55 (dd, 1H, ^3J = 8.7Hz and $^4J_{(H, F)}$ = 8.7Hz, Ar-H), 7.62 (d, 1H, ^3J = 8.8Hz, Ar'-H)

IR (KBr): ν (cm^{-1}) = 3060w, 3017w, 2957m, 2909w, 2836m, 2057w, 1875w, 1820w, 1619s, 1575s, 1505s, 1461s, 1438s, 1282s, 1238s, 1206s, 1152s, 1104s, 1036s, 969s, 857s, 811s

MS (EI, 60°C): m/z = 292 (M^+, 100%), 277 (33%), 214 (14%), 170 (14%)

Elemental analysis: $C_{16}H_{14}ClFO_2$ (292.07 g/mol)

Calculated: C% 65.65 H% 4.82

Found: C% 65.72 H% 4.97

25*Z*

Yield: 0.82 g (35%, colorless oil)

^{1}H-NMR (CDCl$_3$): δ[ppm] = 3.76 (s, 3H, OCH$_3$), 3.78 (s, 3H, OCH$_3$), 6.46 (dd, 1H, ^{3}J = 8.7Hz and ^{4}J = 2.5Hz, Ar-H), 6.53-6.63 (m, 2H, superimposed, Ar-H, Ar'-H), 6.62 (d, 1H, superimposed, ^{3}J = 12Hz, CH=), 6.65 (d, 1H, superimposed, ^{3}J = 12Hz, =CH), 6.94 (d, 1H, ^{4}J = 2.6Hz, Ar'-H), 6.99 (dd, 1H, ^{3}J = 8.7Hz and ^{4}J$_{(H, F)}$ = 8.7Hz, Ar-H), 7.10 (d, 1H, ^{3}J = 8.7Hz, Ar'-H)

IR (film over KBr): ν (cm^{-1}) = 3006w, 2959w, 2940w, 2837w, 1617s, 1574m, 1503s, 1462s, 1440s, 1288s, 1248s, 1196s, 1155s, 1106s, 1039s, 951w, 888w, 838s, 807m

MS (EI, 50°C): m/z = 292 (M$^+$, 100%), 277 (31%), 214 (12%), 170 (14%), 135 (12%)

Elemental analysis: $C_{16}H_{14}ClFO_2$ (292.07 g/mol)

Calculated:	C%	65.65	H%	4.82
Found:	C%	65.91	H%	5.31

1-(2,6-Dichloro-4-methoxyphenyl)-2-(2-fluoro-4-methoxyphenyl)ethene 26*E*

starting from (2-fluoro-4-methoxybenzyl)triphenylphosphonium chloride (2.64 g, 6.0 mmol) and 2,6-dichloro-4-methoxybenzaldehye (1.26 g, 6.0 mmol) with sodium methanolate (0.66g, 12 mmol) in 60 ml of methanol. After stirring for 24 hours, 15 ml of water was added and stirred for further 1 hour. The *E*-isomer was precipitated and was isolated by suction filtration, washed with 80% methanol and dried under vacuum. The obtained crystals were suspended in 20 ml of a mixture of methanol and ligroin (3 : 1) and stirred 30 minutes under reflux. After cooling the precipitate was isolated by suction filtration and dried under vacuum to afford the pure *E*-form crystals.

Yield: 1.36 g (69.4%, colorless crystals); mp: 109.5-110.5°C

^{1}H-NMR (CDCl$_3$): δ[ppm] = 3.81 (s, 3H, OCH$_3$), 3.82 (s, 3H, OCH$_3$), 6.63 (dd, 1H, ^{3}J$_{(H, F)}$ = 12.4Hz and ^{4}J = 2.5Hz, Ar-H), 6.72 (dd, 1H, ^{3}J = 8.7Hz and ^{4}J = 2.5Hz, Ar-H), 6.92 (s, 2H, Ar'-H), 7.00 (d, 1H, ^{3}J = 16.8Hz, CH=), 7.19 (d, 1H, ^{3}J = 16.8Hz, CH=), 7.53 (dd, 1H, ^{3}J = 8.7Hz and ^{4}J$_{(H, F)}$ = 8.7Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3081w, 3017w, 2946w, 2838w, 1623s, 1600s, 1577m, 1548m, 1507s, 1469m, 1431m, 1282s, 1239s, 1156s, 1105s, 1063m, 1030s, 969m, 853m, 792m

MS (EI, 80°C): m/z = 326 (M$^+$, 100%), 311 (M$^+$-CH$_3$, 22%), 256 (M$^+$-2Cl, 14%), 213 (21%), 170 (13%), 139 (45%)

Elemental analysis: $C_{16}H_{13}Cl_2FO_2$ (326.03 g/mol)

Calculated: C% 58.74 H% 4.00

Found: C% 58.81 H% 3.96

1-(2,6-Dichloro-4-methoxyphenyl)-2-(2-chloro-4-methoxyphenyl)ethene 27*E*

starting from (2-chloro-4-methoxybenzyl)triphenylphosphonium chloride (1.81 g, 4.0 mmol) and 2,6-dichloro-4-methoxybenzaldehye (0.84 g, 4.0 mmol) with sodium methanolate (0.44g, 8 mmol) in 40 ml of methanol. After stirring for 24 hours, 10 ml of water was added and stirred for further 1 hour. The *E*-isomer was precipitated and was isolated by suction filtration, washed with 80% methanol and dried under vacuum. The obtained crystals were suspended in 12 ml of a mixture of methanol and ligroin (3 : 1) and stirred under reflux for 30 minutes. After cooling the precipitate was isolated by suction filtration and dried under vacuum to afford the pure *E*-form crystals.

Yield: 0.72 g (52.5%, colorless crystals); mp: 110-111.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.81 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.85 (dd, 1H, ^{3}J = 8.7Hz and ^{4}J = 2.6Hz, Ar-H), 6.92 (d, 1H, superimposed, CH=), 6.93 (s, 2H, superimposed, 2Ar'-H), 6.94 (d, 1H, superimposed, Ar-H), 7.46 (d, 1H, ^{3}J = 16.6Hz, CH=), 7.64 (d, 1H, ^{3}J = 8.7Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3083w, 3007w, 2962w, 2935w, 2834w, 1605s, 1551m, 1493s, 1464m, 1432m, 1285s, 1233s, 1066m, 1045s, 956m, 867m, 835m, 790m

MS (EI, 110°C): m/z = 344 (M^+, 100%), 329 (M^+-CH_3, 17%), 272 (M^+-2Cl, 23%), 229 (27%)

Elemental analysis: $C_{16}H_{13}Cl_3O_2$ (343.63 g/mol)

Calculated: C% 55.92 H% 3.81

Found: C% 56.13 H% 4.19

1-(2-Fluoro-4-methoxyphenyl)-2-(3-methoxyphenyl)ethene 28*E / Z*

starting from (3-methoxybenzyl)triphenylphosphonium chloride (3.35 g, 8.0 mmol) and 2-fluoro-4-methoxybenzaldehye (1.23 g, 8.0 mmol) with sodium methanolate (0.88 g, 16 mmol) in 80 ml of methanol. After stirring for 24 hours, the reaction mixture was diluted with water and extracted with diethyl ether. The organic phase was washed with water, dried with sodium sulfate and evaporated. The residue was purified into a mixture of the *E*- and *Z*-isomer by column chromatography on silica gel with a mixture of ligroin and dichloromethane (1 : 1) as eluent (R_f = 0.50). The mixture of *E*- and *Z*-isomers was separated into *Z*-isomer (R_f = 0.54) and *E*-isomer (R_f = 0.45) by column chromatography on silica gel with a mixture of ligroin and diethyl ether (5 : 1) as eluent.

28*E*

Yield: 1.05 g (51%, colorless oil, $R_f = 0.45$)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.82 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.63 (dd, 1H, $^3J_{(H, F)}$ = 12.6Hz and ^4J = 2.5Hz, Ar'-H), 6.71 (dd, 1H, ^3J = 8.7Hz and ^4J = 2.4Hz, Ar'-H), 6.81 (dd, 1H, ^3J = 8.2Hz and ^4J = 2.3Hz, Ar-H), 7.02 (2d, 2H, superimposed, ^3J = 16.6Hz, CH=, Ar-H), 7.10 (d , 1H, ^3J = 7.7Hz, Ar-H), 7.19 (d, 1H, ^3J = 16.4Hz, CH=), 7.27 (t, 1H, ^3J = 7.8Hz, Ar-H), 7.51 (dd, 1H, ^3J = 8.7Hz and $^4J_{(H, F)}$ = 8.7Hz, Ar'-H)

IR (film): ν (cm^{-1}) = 3042w, 3003m, 2957m, 2938m, 2836m, 1620s, 1600s, 1575s, 1506s, 1465s, 1445s, 1306s, 1286s, 1275s, 1201s, 1155s, 1123m, 1106s, 1090s, 1048s, 1034s, 963s, 836s, 802m, 775s, 686s

MS (EI, 30°C): m/z = 258 (M^+, 100%), 183 (15%)

Elemental analysis: $C_{16}H_{15}FO_2$ (258.11 g/mol)

Calculated: C% 74.40 H% 5.85

Found: C% 74.65 H% 5.96

28*Z*

Yield: 0.62 g (30%, colorless oil, $R_f = 0.54$)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.68 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.51 (dd, 1H, ^3J = 8.7Hz and ^4J = 2.3Hz, superimposed, Ar'-H), 6.52-6.64 (3H, superimposed, CH=CH, Ar'-H), 6.75 (dd, 1H, ^3J = 8.2Hz and ^4J = 2.3Hz, Ar-H), 6.80 (s, 1H, Ar-H), 6.84 (d, 1H, ^3J = 7.6Hz, Ar-H), 7.14 (t, 1H, ^3J = 8.6Hz and $^4J_{(H, F)}$ = 8.6Hz, superimposed, Ar'-H), 7.15 (t, 1H, ^3J = 7.8Hz, superimposed, Ar-H)

IR (film): ν (cm^{-1}) = 3006m, 2957m, 2938m, 2835m, 1619s, 1597s, 1575s, 1506s, 1487s, 1464s, 1433s, 1317s, 1287s, 1262s, 1194m, 1155s, 1107s, 1092m, 1033s, 950m, 867m, 836s, 786s, 697m

MS (EI, 30°C): m/z = 258 (M^+, 100%); 183 (17%)

Elemental analysis: $C_{16}H_{15}FO_2$ (258.11 g/mol)

Calculated: C% 74.40 H% 5.85

Found: C% 74.16 H% 6.09

1-(2-Chloro-4-methoxyphenyl)-2-(3-methoxyphenyl)ethene 29*E* / *Z*

starting from (3-methoxybenzyl)triphenylphosphonium chloride (3.35 g, 8.0 mmol) and 2-chloro-4-methoxybenzaldehye (1.36 g, 8.0 mmol) with sodium methanolate (0.88 g, 16 mmol) in 80 ml of methanol. After stirring for 24 hours, the reaction mixture was diluted with water and extracted with diethyl ether. The organic phase was washed with water, dried with sodium sulfate and evaporated. The residue was purified into a mixture of the *E*- and *Z*-isomer by column chromatography on silica gel with a mixture of ligroin and dichloromethane (1 : 1) as eluent (R_f = 0.53). The mixture of *E*- and *Z*-isomer was separated into *Z*-isomer (R_f = 0.63) and *E*-isomer (R_f = 0.52) by column chromatography on silica gel with a mixture of ligroin and diethyl ether (5 : 1) as eluent.

29*E*

Yield: 1.14 g (52%, colorless oil, R_f = 0.52)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.82 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.79-6.86 (m, 2H, superimposed, Ar-H, Ar'-H), 6.93 (d, 1H, superimposed, ^{4}J = 2.5Hz, Ar'-H), 6.94 (d, 1H, superimposed, ^{3}J = 16.2Hz, CH=), 7.06 (s, 1H, Ar-H), 7.12 (d, 1H, ^{3}J = 7.7Hz, Ar-H), 7.28 (t, 1H, ^{3}J = 7.8Hz, Ar-H), 7.43 (d, 1H, ^{3}J = 16.3Hz, CH=), 7.61 (d, 1H, ^{3}J = 8.7Hz, Ar'-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 55.3, 55.6, 111.9, 113.3, 113.7, 114.6, 119.3, 124.7, 127.2, 127.9, 129.0, 129.6, 134.1, 138.8, 159.5, 159.9

IR (film): ν (cm^{-1}) = 3042w, 3003m, 2957m, 2939m, 2908w, 2834m, 1597s, 1578s, 1556m, 1495s, 1463s, 1436s, 1285s, 1256s, 1204s, 1156s, 1042s, 961s, 890m, 862m, 843m, 808m, 775m, 686m

MS (EI, 30°C): m/z = 274 (M^+, 77%), 239 (M^+-Cl, 100%), 224 (M^+-Cl-CH_3, 59%), 208 (22%), 196 (16%), 181 (14%), 169 (10%), 165 (21%), 152 (25%), 135 (16%), 120 (22%),

Elemental analysis: $C_{16}H_{15}ClO_2$ (274.08 g/mol)

Calculated:	C%	69.95	H%	5.50
Found:	C%	69.99	H%	5.85

29*Z*

Yield: 0.75 g (34%, colorless oil, R_f = 0.63)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.66 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 6.56-6.66 (m, 3H, superimposed, CH=CH, Ar'-H), 6.68-6.76 (m, 2H, Ar-H), 6.77 (d, 1H, ^{3}J = 7.7Hz, Ar-H), 6.94 (d, 1H, ^{4}J = 2.5Hz, Ar'-H), 7.06-7.17 (m, 2H, superimposed, Ar-H, Ar'-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 55.0, 55.5, 112.9, 113.2, 113.9, 114.4, 121.5, 127.0, 128.1, 129.2, 130.6, 131.4, 134.3, 138.1, 159.3

IR (film): ν (cm^{-1}) = 3005m, 2957m, 2939m, 2907w, 2834m, 1602s, 1576s, 1555m, 1494s, 1463s, 1432s, 1287s, 1257s, 1218s, 1181m, 1135m, 1045s, 882m, 842s, 783s, 691m

MS (EI, 30°C): m/z = 274 (M^+, 67%), 239 (M^+-Cl, 100%), 224 (M^+-Cl-CH_3, 62%), 208 (24%), 196 (18%), 181 (15%), 165 (19%), 152 (26%)

Elemental analysis: $C_{16}H_{15}ClO_2$ (274.08 g/mol)

Calculated: C% 69.95 H% 5.50

Found: C% 69.95 H% 5.79

6.1.8 Chloro-substituted 4-hydroxybenzaldehyde 30 and 31

General Procedure

Boron tribromide was added via a syringe to a stirred solution of the corresponding chloro-substituted 4-methoxybenzaldehyde in dry dichloromethane at 0°C. After stirring for 30 minutes at 0°C, the reaction mixture was allowed to warm to room temperature and stirred for 24 - 48 hours. If the ether cleavage was incomplete after stirring for 48 hours, the reaction mixture was refluxed. After the reaction being complete, the mixture was poured into ice-water and extracted with diethyl ether. The united organic phase was washed with water, dried over sodium sulfate and evaporated. The obtained residue was purified as described under each product.

2-Chloro-4-hydroxybenzaldehyde 30

starting from 2-chloro-4-methoxybenzaldehyde (1.19 g, 7.0 mmol), boron tribromide (2.0 ml, 21 mmol) and dichloromethane (84 ml). The reaction mixture was stirred at room temperature for 24 hours. The residue obtained from ethereal layer was purified by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (10 : 1) to yield the pure desired product.

Yield: 0.60 g (55%, light yellow-ochreous solid); mp: 146-148°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 6.89 (dd, 1H, ^3J = 8.6Hz and ^4J = 2.1Hz, Ar-H), 6.93 (d, 1H, ^4J = 2.1Hz, Ar-H), 7.76 (d, 1H, ^3J = 8.6Hz, Ar-H), 10.14 (s, 1H, CHO), 11.11 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3149s (OH), 1661s (CH=O), 1593s, 1567s, 1440s, 1358m, 1312s, 1278s, 1225s, 1205s, 1037s, 813m

MS (EI, 80°C): m/z = 156 (M^+, 67%), 155 (M^+-H^+, 100%), 127 (M^+-CHO, 12%), 99 (16%), 73 (9%), 63 (18%)

Elemental analysis: $C_7H_5ClO_2$ (156.00 g/mol)

Calculated: C% 53.70 H% 3.22

Found: C% 53.40 H% 3.68

2,6-Dichloro-4-hydroxybenzaldehyde 31

starting from 2,6-dichloro-4-methoxybenzaldehyde (1.53 g, 7.5 mmol), boron tribromide (2.25 ml, 24 mmol) and dry dichloromethane (90 ml). The reaction mixture was stirred at room temperature for 48 hours and was heated under reflux for 2 hours. The residue (1.43 g) obtained from ethereal phase was suspended in a mixture of dichoromethane (20 ml) and ligroin (12 ml) and stirred under reflux for 30 minutes. After cooling the precipitate was collected by suction filtration, washed with a mixture of dichloromethane and ligroin (1 : 1) and dried under vacuum to afford the pure desired product.

Yield: 1.11g (78%, light yellow-ochreous solid); mp: 225-226°C (decompose)

^{1}H-NMR (DMSO-d$_6$): δ[ppm] = 6.95 (s, 2H, Ar-H), 10.25 (s, 1H, CHO), 11.45 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3219s (OH), 1669s (CH=O), 1590s, 1553s, 1411m, 1276s, 1256s, 1214m, 1193m, 1067s, 863m

MS (EI, 80°C): m/z = 191 (M$^+$, 71%), 190 (M$^+$, 58%), 189 (M$^+$-H$^+$, 100%), 133 (9%), 63 (12%)

Elemental analysis: $C_7H_4Cl_2O_2$ (189.96 g/mol)

Calculated:	C%	44.02	H%	2.11
Found:	C%	44.14	H%	2.24

6.1.9 (*E*)-4-Hydroxy-4'(3')-methoxystilbenes 33 - 40

General Procedure

Titanium tetrachloride (1.33 ml, 12 mmol)) was added via a syringe dropwise to a stirred suspension of zinc power (1.56 g, 24 mmol) in dry tetrahydrofuran (30 ml) at –10°C under nitrogen. The resulting yellow-dark mixture was stirred at room temperature for 30 minutes and then heated under reflux for 1 hour. The dark suspension was cooled to room temperature and a solution of two corresponding starting benzaldehydes (8 mmol in total) in tetrahydrofuran (10 ml) was added. The reaction mixture was stirred for 48 hours at room temperature under dry nitrogen atmosphere and then was refluxed for 2 hours. After cooling the mixture was poured into ice-water and extracted with diethyl ether. The united organic phase was washed with a solution of 5% sodium chloride in water, dried over sodium sulfate and evaporated. The residue was separated into the desired product and a by-product of dimethoxystilbene by column chromatography on silica gel.

(*E*)-1-(2-Fluoro-4-methoxyphenyl)-2-(4-hydroxyphenyl)ethene 33

starting from 4-hydroxybenzaldehyde (0.49 g, 4 mmol) and 2-fluoro-4-methoxybenzaldehyde (0.62 g, 4 mmol). The residue was separated into the desired product **33** and a by-product of 1,2-bis(2-fluoro-4-methoxyphenyl)ethene (*E*-isomer, 0.14 g) by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (20 : 1) as eluent.

Yield: 0.46 g (47%, $R_f = 0.68$, colorless crystals); mp: 143.5-145.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.81 (s, 3H, OCH_3), 4.75 (s, 1H, OH), 6.62 (dd, 1H, $^3J_{(H,\,F)}$ = 12.5Hz and ^4J = 2.5Hz, Ar-H), 6.70 (dd, 1H, ^3J = 8.7Hz and ^4J = 2.5Hz, Ar-H), 6.82 (AA'BB', 2H, ^3J = 8.6Hz, Ar'-H), 7.00 (d, 1H, ^3J = 16.5Hz, CH=), 7.03 (d, 1H, ^3J = 16.5Hz, CH=), 7.40 (AA'BB', 2H, ^3J = 8.6Hz, Ar'-H), 7.48 (dd, 1H, ^3J = 8.7Hz and $^4J_{(H,\,F)}$ = 8.7Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3434s (OH), 3042w, 3021w, 2955w, 2915w, 2839w, 2051w, 1891w, 1618s, 1590m, 1573m, 1512s, 1443s, 1439m, 1313s, 1283s, 1251s, 1192s, 1157s, 1088m, 1030m, 965m, 948m, 831s

MS (EI, 110°C): m/z = 244 (M^+, 100%), 229 (M^+-CH_3, 40%), 215 (10%), 122 (17%)

Elemental analysis: $C_{15}H_{13}FO_2$ (244.09 g/mol)

Calculated:	C%	73.76	H%	5.36
Found:	C%	73.67	H%	5.51

(*E*)-1-(2-Chloro-4-methoxyphenyl)-2-(4-hydroxyphenyl)ethene 34

starting from 4-hydroxybenzaldehyde (0.58 g, 4.8 mmol) and 2-chloro-4-methoxybenzaldehyde (0.54 g, 3.2 mmol). The residue was separated into the desired product **34** and a by-product of 1,2-bis(2-chloro-4-methoxyphenyl)ethene (*E*-isomer, 0.096 g) by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (20 : 1) as eluent.

Yield: 0.44 g (53%, $R_f = 0.70$, colorless crystals); mp: 136-138°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.81 (s, 3H, OCH_3), 4.74 (broad, 1H, OH), 6.79-6.95 (5H, superimposed, 1CH=, 2Ar-H, 2Ar'-H), 7.30 (d, 1H, ^3J = 16.3Hz, CH=), 7.42 (d, 2H, ^3J = 8.6Hz, Ar-H), 7.58 (d, 1H, ^3J = 8.7Hz, Ar'-H)

IR (KBr): ν (cm^{-1}) = 3400s, 3007w, 2943w, 2836w, 1605s, 1578m, 1513s, 1493s, 1439m, 1266s, 1202s, 1177s, 1022m, 842m, 822m

MS (EI, 100°C): m/z = 260 (M^+, 100%), 245 (22%), 181 (22%), 155 ($C_8H_7ClO^+$, 40%), 107 ($C_7H_7O^+$, 35%)

Elemental analysis: $C_{15}H_{13}ClO_2$ (260.06 g/mol)

Calculated:	C%	69.10	H%	5.03
Found:	C%	68.73	H%	5.11

(*E*)-1-(2,6-Dichloro-4-methoxyphenyl)-2-(4-hydroxyphenyl)ethene 35

starting from 4-hydroxybenzaldehyde (0.49 g, 4 mmol) and 2,6-dichloro-4-methoxybenzaldehyde (0.82 g, 4 mmol). The residue was separated into the desired product **35** by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (20 : 1) as eluent.

Yield: 0.48 g (41%, $R_f = 0.59$, colorless crystals); mp: 130-131°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.79 (s, 3H, OCH_3), 5.05 (broad, 1H, OH), 6.82 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 6.91 (s, 2H, Ar'-H), 6.93 (d, 1H, ^3J = 16.6Hz, CH=), 7.01 (d, 1H, ^3J = 16.6Hz, CH=), 7.41 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H)

^{1}H-NMR (DMSO-d_6): δ[ppm] = 3.81 (s, 3H, OCH_3), 6.78 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 6.86 (d, 1H, ^3J = 16.6Hz, CH=), 6.90 (d, 1H, ^3J = 16.6Hz, CH=), 7.14 (s, 2H, Ar'-H), 7.41 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 9.65 (s, 1H, OH)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 55.7, 114.7, 115.6, 120.3, 127.3, 128.1, 130.1, 134.9, 135.3, 155.6, 158.1

IR (KBr): ν (cm^{-1}) = 3396s, 3078w, 2934w, 1602s, 1552m, 1510m, 1465m, 1434m, 1264m, 1235m, 1170m, 1064m, 1040m, 818m

MS (EI, 60°C): m/z = 294 (M^+, 100%), 224 (33%), 206 (94%), 189 (63%), 171 (58%), 143 (51%), 108 (26%), 71 (35%)

Elemental analysis: $C_{15}H_{12}Cl_2O_2$ (294.02 g/mol)

Calculated:	C%	61.04	H%	4.10
Found:	C%	60.98	H%	4.07

(*E*)-1-(2,4-Dichloro-6-methoxyphenyl)-2-(4-hydroxyphenyl)ethene 36

starting from 4-hydroxybenzaldehyde (0.49 g, 4 mmol) and 2,4-dichloro-6-methoxybenzaldehyde (0.82 g, 4 mmol). The residue was separated into the desired product **36** by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (20 : 1) as eluent.

Yield: 0.69 g (58%, $R_f = 0.70$, colorless crystals); mp: 124.5-126°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.89 (s, 3H, OCH_3), 4.74 (s, 1H, OH), 6.80-6.85 (3H, superimposed, 2Ar-H, Ar'-H), 7.06 (d, 1H, ^4J = 2.0Hz, Ar'-H), 7.12 (d, 1H, ^3J = 16.5Hz, CH=), 7.35-7.46 (3H, superimposed, 1CH=, 2Ar-H)

^{1}H-NMR (DMSO-d_6): δ[ppm] = 3.90 (s, 3H, OCH_3), 6.78 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 6.99 (d, 1H, ^3J = 16.5Hz, CH=), 7.14 (d, 1H, ^4J = 1.9Hz, Ar'-H), 7.22 (d, 1H, ^4J = 1.9Hz, Ar'-H), 7.31 (d, 1H, ^3J = 16.5Hz, CH=), 7.38 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 9.65 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3307s, 3086w, 3019w, 2964w, 2939w, 1606s, 1592s, 1578s, 1556s, 1512s, 1455s, 1443s, 1397s, 1257s, 1228s, 1172s, 1046s, 968s, 830s, 817s

MS (EI, 90°C): m/z = 294 (M$^+$, 100%), 244 (27%), 181 (18%), 120 (92%), 107 (47%)

Elemental analysis: $C_{15}H_{12}Cl_2O_2$ (294.02 g/mol)

Calculated:	C%	61.04	H%	4.10
Found:	C%	61.13	H%	4.12

(*E*)-2-(2-Chloro-4-hydroxyphenyl)-1-(2,4-dichloro-6-methoxyphenyl)ethene 37

starting from 2-chloro-4-hydroxybenzaldehyde (0.62 g, 4 mmol) and 2,4-dichloro-6-methoxybenzaldehyde (0.82 g, 4 mmol). The residue was separated into the desired product **37** by column chromatography on silica gel with dichloromethane as eluent.

Yield: 0.28 g (21%, R_f = 0.45, light pink crystals); mp: 140.5-141.5°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 3.92 (s, 3H, OCH_3), 6.82 (dd, 1H, ^3J = 8.6Hz and ^4J = 2.4Hz, Ar-H), 6.87 (d, 1H, ^4J = 2.4Hz, Ar-H), 7.03 (d, 1H, ^3J = 16.4Hz, CH=), 7.18 (d, 1H, ^4J = 1.6Hz, Ar'-H), 7.25 (d, 1H, ^4J = 1.7Hz, Ar'-H), 7.65 (d, 1H, ^3J = 8.6Hz, Ar-H), 7.69 (d, 1H, ^3J = 16.4Hz, CH=), 10.14 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3393m (broad), 3092w, 2963w, 2937w, 1602s, 1578s, 1556s, 1493s, 1455s, 1441m, 1399m, 1255s, 1211m, 1045s, 965m, 904s, 832m

MS (EI, 250°C): m/z = 330 (M$^+$, 100%), 285 (10%), 278 (23%), 215 (23%), 187 (20%), 154 (86%), 141 (34%)

Elemental analysis: $C_{15}H_{11}Cl_3O_2$ (329.60 g/mol)

Calculated:	C%	54.66	H%	3.36
Found:	C%	54.37	H%	3.58

(*E*)-1-(2,6-Dichloro-4-hydroxyphenyl)-2-(4-methoxyphenyl)ethene 38

starting from 2,6-dichloro-4-hydroxybenzaldehyde (0.76 g, 4 mmol) and 4-methoxybenzaldehyde (0.70 ml, 5 mmol). The residue of the ethereal extract was taken up in methanol. A by-product of 1,2-bis(4-methoxyphenyl)ethene (*E*-isomer) was insoluble in methanol and thus was precipitated as white crystals. After isolation of this by-product (0.25 g), the solution containing the crude desired product **38** was evaporated under vacuum and the residue was purified by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (20 : 1) as eluent.

Yield: 0.25 g (21%, R_f = 0.52, light yellow crystals); mp: 112-114°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.84 (s, 3H, OCH_3), 4.94 (s, 1H, OH), 6.87 (s, 2H, Ar-H), 6.90 (d, 1H, ^{3}J = 16.6Hz, CH=), 6.91 (AA'BB', 2H, ^{3}J = 8.7Hz, Ar'-H), 7.03 (d, 1H, ^{3}J = 16.6Hz, CH=), 7.46 (AA'BB', 2H, ^{3}J = 8.7Hz, Ar'-H)

IR (KBr): ν (cm^{-1}) = 3368s (OH), 3080w, 2938w, 2840w (OCH_3), 1607s, 1566m, 1512s, 1440m, 1428m, 1264s, 1244, 1178s, 1020m, 968m, 955m, 815m

MS (EI, 190°C): m/z = 294 (M^+, 100%), 279 (M^+-CH_3, 15%), 224 (M^+-2Cl, 27%), 176 (46%), 141 (31%)

Elemental analysis: $C_{15}H_{12}Cl_2O_2$ (294.02 g/mol)

Calculated: C% 61.04 H% 4.10

Found: C% 60.87 H% 4.12

(*E*)-1-(2,6-Dichloro-4-hydroxyphenyl)-2-(2-fluoro-4-methoxyphenyl)ethene 39

starting from 2,6-dichloro-4-hydroxybenzaldehyde (0.76 g, 4 mmol) and 2-fluoro-4-methoxybenzaldehyde (0.62 g, 4 mmol). The residue of the ethereal extract was taken up in methanol. A by-product of 1,2-bis(2-fluoro-4-methoxyphenyl)ethene (*E*-isomer) was less soluble in methanol and was precipitated as white crystals. After isolation of this by-product (0.16 g in total), the solution containing the crude desired product **39** was evaporated under vacuum and the residue was isolated by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (20 : 1) as eluent.

Yield: 0.19 g (15%, R_f = 0.61, colorless needles); mp: 121.5-123.5°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 3.80 (s, 3H, OCH_3), 6.80-6.95 (m, 4H, superimposed, 2Ar-H, 2CH=), 7.02 (s, 2H, Ar'-H), 7.68 (dd, 1H, ^{3}J = 8.8Hz and $^4J_{(H, F)}$ = 8.8Hz, Ar-H), 10.45 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3454s (OH), 3080w, 2982w, 2953w, 2840w (OCH_3), 1611s, 1569m, 1503s, 1471m, 1444m, 1425m, 1280m, 1260s, 1227m, 1193m, 1155m, 1092m, 1027m, 947s, 834s, 799m

MS (EI, 130°C): m/z = 312 (M^+, 100%), 297 (M^+-CH_3, 18%), 242 (M^+-2Cl, 31%), 199 (27%), 170 (20%), 139 (45%)

Elemental analysis: $C_{15}H_{11}Cl_2FO_2$ (312.01 g/mol)

Calculated: C% 57.53 H% 3.54

Found: C% 57.12 H% 3.85

(*E*)-1-(2,6-Dichloro-4-hydroxyphenyl)-2-(2-chloro-4-methoxyphenyl)ethene 40

starting from 2,6-dichloro-4-hydroxybenzaldehyde (0.76 g, 4 mmol) and 2-chloro-4-methoxybenzaldehyde (0.68 g, 4 mmol). The residue of the ethereal extract was taken up in methanol. A by-product of 1,2-bis(2-chloro-4-methoxyphenyl)ethene (*E*-isomer) was less soluble in methanol and thus was precipitated as white crystals. After isolation of this by-product (0.24 g in total), the solution containing the crude desired product **40** was evaporated under vacuum and the residue was isolated by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (20 : 1) as eluent.

Yield: 0.24 g (18%, $R_f = 0.60$, colorless crystals); mp: 147-148.5°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 3.81 (s, 3H, OCH_3), 6.93 (s, 2H, Ar-H), 6.98 (d, 1H, ^3J = 16.7, superimposed, CH=), 6.99 (dd, 1H, superimposed, Ar'-H), 7.09 (d, 1H, ^4J = 2.5Hz, Ar'-H), 7.27 (d, 1H, ^3J = 16.7Hz, CH=), 7.79 (d, 1H, ^3J = 8.7Hz, Ar'-H), 10.49 (s, 1H, OH)

^{13}C-NMR (DMSO-d_6): δ[ppm] = 55.6, 114.3, 116.0, 122.7, 124.2, 125.3, 126.6, 127.4, 130.2, 132.9, 133.8, 157.1, 159.6

IR (KBr): ν (cm^{-1}) = 3428s (OH), 3079w, 2970w, 2945w, 2839w (OCH_3), 1606s, 1567s, 1492s, 1461m, 1440m, 1424s, 1308m, 1280s, 1261s, 1246m, 1206s, 1168m, 1063m, 1044s, 1028m, 969s, 954m, 890w, 857m, 837m, 804m, 789m

MS (EI, 130°): m/z = 328 (M^+, 100%), 313 (M^+-CH_3, 12%), 258 (M^+-2Cl, 46%), 215 (24%)

Elemental analysis: $C_{15}H_{11}Cl_3O_2$ (327.98 g/mol)

Calculated:	C%	54.66	H%	3.36
Found:	C%	54.56	H%	3.51

6.1.10 (*E*)-Dihydroxystilbenes 41 - 51

General Procedure

Boron tribromide (1.5 ml, 16 mmol) was added via a syringe to a stirred solution of corresponding dimethoxystilbene (2.5 mmol) in dry dichloromethane (60 ml) at 0°C. After stirring for 30 minutes at 0°C, the reaction mixture was stirred at room temperature for 1 - 48 hours. If the demethylation was incomplete (TLC control), the reaction mixture was refluxed for further demanded time. After the complete reaction, the mixture was poured into ice-water and extracted with either ethyl acetate or diethyl ether. The united organic phase was washed with either brine (with ethyl acetate) or water (diethyl ether), dried over sodium sulfate and evaporated. The residue was purified by column chromatography on silica gel.

(*E*)-1,2-Bis(4-hydroxyphenyl)ethene 41

starting from (*E*)-1,2-bis(4-methoxyphenyl)ethane **8**; Reaction time at room temperature : 1 hour.

The reaction mixture was extracted with ethyl acetate and the residue was dissolved in a mixture of tetrahydrofuran (4 ml) and ligroin (2 ml) and was purified by column chromatography on silica gel with a mixture of diethyl ether and ligroin (4 : 1) as eluent.

Yield: 0.52 g (98%, $R_f = 0.67$, white crystals); mp: 278.5°C (decompose)

^{1}H-NMR (CD_3OD): δ[ppm] = 6.75 (AA'BB', 4H, $^3J = 8.6$Hz, 2Ar-H, 2Ar'-H), 6.88 (s, 2H, CH=CH), 7.33 (AA'BB', 4H, $^3J = 8.6$Hz, 2Ar-H, 2Ar'-H)

IR (KBr): ν (cm^{-1}) = 3403s (OH), 3016w, 1608s, 1595s, 1513s, 1450m, 1375m, 1247s, 1213m, 1174m, 961m, 835s

MS (EI, 80°C): m/z = 212 (M^+, 100%), 197 (14%), 165 (21%)

Elemental analysis: $C_{14}H_{12}O_2$ (212.08 g/mol)

Calculated: C% 79.22 H% 5.70

Found: C% 78.67 H% 5.75

(*E*)-1-(2-Fluoro-4-hydroxyphenyl)-2-(4-hydroxyphenyl)ethene 42

starting from dimethoxystilbene **23*E***; Reaction time at room temperature: 4 hours.

The reaction mixture was extracted with diethyl ether and the residue was purified by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (6 : 3 : 1) as eluent.

Yield: 0.20 g (34%, $R_f = 0.64$, light pink crystals); mp: 232-233.5°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 6.57 (dd, 1H, $^3J_{(H, F)} = 12.7$Hz and $^4J = 2.3$Hz, Ar'-H), 6.63 (dd, 1H, $^3J = 8.6$Hz and $^4J = 2.3$Hz, Ar'-H), 6.75 (AA'BB', 2H, $^3J = 8.6$Hz, Ar-H), 6.93 (d, 1H, $^3J = 16.5$Hz, CH=), 7.00 (d, 1H, $^3J = 16.5$Hz, =CH), 7.36 (AA'BB', 2H, $^3J = 8.6$Hz, Ar-H), 7.52 (dd, 1H, $^3J = 8.9$Hz and $^4J_{(H, F)} = 8.9$Hz, Ar'-H), 9.54 (s, 1H, OH), 9.96 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3429s (OH), 3047w, 1616s, 1589m, 1510s, 1457m, 1439m, 1353m, 1301m, 1281s, 1235s, 1199m, 1174m, 1146m, 1093m, 964m, 859m, 833m

MS (EI, 190°C): m/z = 230 (M^+, 100%), 215 (7%), 183 (6%), 115 (5 %)

Elemental analysis: $C_{14}H_{11}FO_2$ (230.07 g/mol)

Calculated: C% 73.03 H% 4.82

Found: C% 72.83 H% 4.99

(*E*)-1-(2-Chloro-4-hydroxyphenyl)-2-(4-hydroxyphenyl)ethene 43

starting from dimethoxystilbene **24*E***; Reaction time at room temperature: 4 hours.

The reaction mixture was extracted with diethyl ether and the residue was purified by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (6 : 3 : 1) as eluent.

Yield: 0.28 g (45%, $R_f = 0.66$, white crystals); mp: 208-210°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 6.76 (3H, superimposed, 2Ar-H, Ar'-H), 6.83 (d, 1H, ^4J = 2.4Hz, Ar'-H), 6.98 (d, 1H, ^3J = 16.3Hz, CH=), 7.11 (d, 1H, ^3J = 16.3Hz, =CH), 7.38 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 7.64 (d, 1H, ^3J = 8.6Hz, Ar'-H), 9.59 (s, 1H, OH), 9.96 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3269s (OH), 3021w, 1594s, 1511s, 1469s, 1385m, 1244s, 1204s, 1188m, 1172s, 1043m, 964s, 907m, 857m, 824s, 777m

MS (EI, 290°C): m/z = 246 (M^+, 100%), 211 (M^+-Cl, 11%), 193 (M^+-Cl-H_2O, 17%), 181 (11%), 165 (16%)

Elemental analyse: $C_{14}H_{11}ClO_2$ (246.04 g/mol)

Calculated: C% 68.16 H% 4.49

Found: C% 68.01 H% 4.56

(*E*)-1,2-Bis(2-fluoro-4-hydroxyphenyl)ethene 44

starting from (*E*)-1,2-bis(2-fluoro-4-methoxyphenyl)ethene **9**; Reaction time at room temperature: 16 hours.

The reaction mixture was extracted with diethyl ether and the residue was purified by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (6 : 3 : 1) as eluent.

Yield: 0.14 g (22%, $R_f = 0.76$, off-white crystals); mp: 235-236.5°C

^{1}H-NMR (CD_3OD): δ[ppm] = 6.50 (dd, 2H, $^3J_{(H,\,F)}$ = 12.7Hz and ^4J = 2.3Hz, Ar-H, Ar'-H), 6.60 (dd, 2H, ^3J = 8.6Hz and ^4J = 2.3Hz, Ar-H, Ar'-H), 7.06 (s, 2H, CH=CH), 7.44 (dd, 2H, ^3J = 8.8Hz and $^4J_{(H,\,F)}$ = 8.8Hz, Ar-H, Ar'-H)

IR (KBr): ν (cm^{-1}) = 3304s (OH), 3057w, 1623s, 1597s, 1514s, 1474s, 1395w, 1290s, 1237s, 1200m, 1153s, 1095m, 964s, 850m

MS (EI, 130°C): m/z = 248 (M^+, 100%), 233 (6%), 124 (11%)

Elemental analysis: $C_{14}H_{10}F_2O_2$ (248.06 g/mol)

Calculated: C% 67.74 H% 4.06

Found: C% 67.23 H% 4.16

(*E*)-1-(2-Chloro-4-hydroxyphenyl)-2-(2-fluoro-4-hydroxyphenyl)ethene 45

starting from dimethoxystilbene **25*E***; Reaction time at room temperature: 16 hours.

The reaction mixture was extracted with diethyl ether and the residue was purified by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (6 : 3 : 1) as eluent.

Yield: 0.40 g (61%, $R_f = 0.53$, off-white crystals); mp: 209-211°C

^{1}H-NMR (DMSO-d$_6$): δ[ppm] = 6.59 (dd, 1H, $^3J_{(H, F)}$ = 12.8Hz and ^4J = 2.3Hz, Ar-H), 6.65 (dd, 1H, ^3J = 8.5Hz and ^4J = 2.3Hz, Ar-H), 6.77 (dd, 1H, ^3J = 8.6Hz and ^4J = 2.4Hz, Ar'-H), 6.84 (d, 1H, ^4J = 2.4Hz, Ar'-H), 7.00 (d, 1H, ^3J = 16.5Hz, CH=), 7.23 (d, 1H, ^3J = 16.5Hz, =CH), 7.50 (dd, 2H, ^3J = 8.9Hz and $^4J_{(H, F)}$ = 8.9Hz, Ar-H), 7.66 (d, 1H, ^3J = 8.6Hz, Ar'-H), 10.05 (s, 2H, 2OH)

IR (KBr): ν (cm^{-1}) = 3304s (OH), 3052w, 1622s, 1594s, 1509s, 1471s, 1388m, 1277s, 1247s, 1200s, 1155s, 1093s, 1044m, 964s, 908s, 858s, 813s, 793m

MS (EI, 250°C): m/z = 264 (M$^+$, 100%), 228 (10%), 199 (10%), 183 (10%)

Elemental analysis: $C_{14}H_{10}ClFO_2$ (264.04 g/mol)

Calculated: C% 63.53 H% 3.81

Found: C% 63.55 H% 4.02

(*E*)-1,2-Bis(2-chloro-4-hydroxyphenyl)ethene 46

starting from (*E*)-1,2-bis(2-chloro-4-methoxyphenyl)ethene **10**; Reaction time at room temperature: 16 hours.

The reaction mixture was extracted with diethyl ether and the residue was purified by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (6 : 3 : 1) as eluent.

Yield: 0.52 g (74%, $R_f = 0.70$, white crystals); mp: 230-232°C

^{1}H-NMR (CD$_3$OD): δ[ppm] = 6.75 (dd, 2H, ^3J = 8.6Hz and ^4J = 2.5Hz, Ar-H, Ar'-H), 6.83 (d, 2H, ^4J = 2.5Hz, Ar-H, Ar'-H), 7.24 (s, 2H, CH=CH), 7.56 (d, 2H, ^3J = 8.6Hz, Ar-H, Ar'-H)

^{13}C-NMR (CD$_3$OD): δ[ppm] = 116.0, 117.2, 125.4, 128.1, 128.4, 134.8,159.2

IR (KBr): ν (cm^{-1}) = 3293s (OH), 3055w, 1597s, 1496s, 1469s, 1372w, 1253s, 1199s, 1043m, 964s, 900s, 859s, 815m, 788m

MS (EI, 130°C): m/z = 280 (M$^+$, 100%), 244 (8%), 210 (63%), 181 (17%), 152 (13%), 105 (11%), 90 (11%), 76 (12%)

Elemental analysis: $C_{14}H_{10}Cl_2O_2$ (280.01 g/mol)

Calculated: C% 59.81 H% 3.59

Found: C% 59.75 H% 3.86

(*E*)-1-(2,6-Dichloro-4-hydroxyphenyl)-2-(2-fluoro-4-hydroxyphenyl)ethene 47

starting from dimethoxystilbene **26*E***; Reaction time at room temperature: 48 hours.

The reaction mixture was extracted with diethyl ether and the residue was purified by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (4 : 4 : 1) as eluent.

Yield: 0.11 g (15%, $R_f = 0.54$, white crystals); mp: 175.5-176°C

^{1}H-NMR (DMSO-d$_6$): δ[ppm] = 6.59 (dd, 1H, $^3J_{(H, F)}$ = 12.8Hz and ^{4}J = 2.3Hz, Ar-H). 6.66 (dd, 1H, ^{3}J = 8.5Hz and ^{4}J = 2.3Hz, Ar-H), 6.91 (s, 2H, Ar′-H), 6.93 (d, 1H, ^{3}J = 16.6Hz, CH=), 7.24 (d, 1H, ^{3}J = 16.8Hz, CH=), 7.56 (dd, 1H, ^{3}J = 8.9Hz and $^4J_{(H, F)}$ = 8.9Hz, Ar-H), 10.14 (s, 1H, OH), 10.49 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3255s (broad), 2759w, 1606s, 1595s, 1571s, 1505s, 1472s, 1447s, 1379m, 1292s, 1275s, 1239s, 1204m, 1151s, 1114m, 1095m, 1065m, 969s, 953s, 850s, 798m

MS (EI, 90°C): m/z = 298 (M$^+$, 100%), 228 (M$^+$-2Cl, 74%), 199 (24%), 170 (14%)

Elemental analysis: $C_{14}H_9Cl_2FO_2$ (298.00 g/mol)

Calculated: C% 56.21 H% 3.03

Found: C% 56.44 H% 3.81

(*E*)-1-(2,6-Dichloro-4-hydroxyphenyl)-2-(2-chloro-4-hydroxyphenyl)ethene 48

starting from dimethoxystilbene **27*E***; Reaction time at room temperature: 48 hours.

The reaction mixture was extracted with diethyl ether and the residue was purified by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (4 : 4 : 1) as eluent.

Yield: 0.42 g (54%, $R_f = 0.63$, white crystals); mp: 195.5-196.5°C

^{1}H-NMR (DMSO-d$_6$): δ[ppm] = 6.81 (dd, 1H, ^{3}J = 8.6Hz and ^{4}J = 2.4Hz, Ar-H), 6.86 (d, 1H, ^{4}J = 2.4Hz, Ar-H), 6.90 (d, 1H, superimposed, CH=), 6.92 (s, 2H, superimposed, Ar′-H), 7.24 (d, 1H, ^{3}J = 16.6Hz, CH=), 7.68 (d, 1H, ^{3}J = 8.6Hz, Ar-H), 10.13 (s, 1H, OH), 10.45 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3233s (broad), 2783w, 1599s, 1584s, 1570s, 1489s, 1467s, 1447s, 1369w, 1262s, 1248s, 1231s, 1204s, 963m, 950s, 905s, 852s, 793m

MS (EI, 110°C): m/z = 314 (M$^+$, 100%), 244 (M$^+$-2Cl, 91%), 215 (22%), 152 (21%)

Elemental analysis: $C_{14}H_9Cl_3O_2$ (313.97 g/mol)

Calculated: C% 53.28 H% 2.87

Found: C% 53.70 H% 3.20

(*E*)-1,2-Bis(2,6-dichloro-4-hydroxyphenyl)ethene 49

starting from (*E*)-1,2-bis(2,6-dichloro-4-methoxyphenyl)ethene **11**; Reaction time at room temperature: 48 hours, further under reflux: 12 hours.

The reaction mixture was extracted with diethyl ether and the residue was suspended in a mixture of ligroin and dichloromethane (2 : 1). The precipitate was collected by suction filtration, washed with the same mixture and dried under vacuum to afford the pure desired product **49**. The filtrate was evaporated and purified by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (4 : 4 : 1) as eluent.

Yield: 0.78 g (89%, $R_f = 0.61$, white crystals); mp: 225-227°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 6.93 (s, 6H, 2Ar-H, 2Ar'-H, CH=CH), 10.50 (s, 2H, 2OH)

IR (KBr): ν (cm^{-1}) = 3413s (broad), 1604s, 1575m, 1468m, 1434m, 1270m, 1228m, 1172w, 1066w, 951m, 841m, 806m

MS (EI, 45°C): m/z = 350 (M^+, 100%), 348 (M^+, 74%), 278 (53%), 249 (15%), 215 (11%), 186 (12%)

Elemental analysis: $C_{14}H_8Cl_4O_2$ (350.02 g/mol)

Calculated: C% 48.04 H% 2.30

Found: C% 47.95 H% 2.41

(*E*)-1-(2-Fluoro-4-hydroxyphenyl)-2-(3-hydroxyphenyl)ethene 50

starting from dimethoxystilbene **28*E*** (0.96 g, 3.72 mmol) with boron tribromide (2.1 ml, 22.3 mmol) in dichloromethane (84 ml); Reaction time at room temperature: 5 hours.

The reaction mixture was extracted with diethyl ether and the residue was purified by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (6 : 3 : 1) as eluent.

Yield: 0.26 g (30%, $R_f = 0.47$, white crystals); mp: 151-153°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 6.58 (dd, 1H, $^3J_{(H, F)}$ = 12.8Hz and ^4J = 2.3Hz, Ar'-H), 6.65 (m, 2H, superimposed, Ar-H, Ar'-H), 6.92 (s, 1H, Ar-H), 6.97 (d, 1H, ^3J = 7.7Hz, Ar-H), 7.02 (d, 1H, ^3J = 16.4Hz, CH=), 7.07 (d, 1H, ^3J = 16.4Hz, =CH), 7.15 (t, 1H, ^3J = 7.7Hz, Ar-H), 7.58 (dd, 1H, ^3J = 8.9Hz and $^4J_{(H, F)}$ = 8.9Hz, Ar'-H), 9.42 (s, 1H, OH), 9.99 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3367s, 3048s, 1621s, 1583s, 1508s, 1456s, 1358m, 1294s, 1280s, 1243s, 1222s, 1194s, 1154s, 1096s, 964s, 840s, 807w, 775m, 682m

MS (EI, 130°C): m/z = 230 (M^+, 100%), 210 (19%), 182 (20%)

Elemental analysis: $C_{14}H_{11}FO_2$ (230.07 g/mol)

Calculated:	C%	73.03	H%	4.82
Found:	C%	73.05	H%	5.04

(*E*)-1-(2-Chloro-4-hydroxyphenyl)-2-(3-hydroxyphenyl)ethene 51

starting from dimethoxystilbene **29*E*** (0.96 g, 3.5 mmol) with boron tribromide (2.0 ml, 21 mmol) in dichloromethane (80 ml); Reaction time at room temperature: 5 hours.

The reaction mixture was extracted with diethyl ether and the residue was purified by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (6 : 3 : 1) as eluent.

Yield: 0.25 g (29%, $R_f = 0.45$, off-white crystals); mp: 173-176°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 6.68 (dd, 1H, ^3J = 7.9Hz and ^4J = 1.8Hz, Ar'-H), 6.78 (dd, 1H, ^3J = 8.6Hz and ^4J = 2.4Hz, Ar-H), 6.85 (d, 1H, ^4J = 2.4Hz, Ar-H), 6.94 (s, 1H, Ar'-H), 6.97 (d, 1H, ^3J = 7.8Hz, Ar'-H), 7.03 (d, 1H, ^3J = 16.3Hz, CH=), 7.17 (t, 1H, ^3J = 7.8Hz, Ar'-H), 7.26 (d, 1H, ^3J = 16.3Hz, CH=), 7.70 (d, 1H, ^3J = 8.7Hz, Ar-H), 9.43 (s, 1H, OH), 10.06 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3367s, 3305s, 3043w, 3003w, 1594s, 1573s, 1494s, 1450s, 1435s, 1358m, 1335m, 1295s, 1281s, 1257s, 1222s, 1196s, 1158s, 1038s, 950s, 910s, 848s, 833s, 799m, 766s, 676s

MS (EI, 90°C): m/z = 246 (M^+, 100%), 211 (M^+-Cl, 98%), 193 (52%), 181 (23%), 165 (44%), 152 (15%), 105 (10%), 91 (13%), 82 (14%), 76 (12%)

Elemental analysis: $C_{14}H_{11}ClO_2$ (246.04 g/mol)

Calculated:	C%	68.16	H%	4.49
Found:	C%	68.12	H%	4.69

6.1.11 Cyclopropyl-(4-methoxyphenyl)methanone 53

A solution of γ-chloro-4-methoxybutyrophenone (1.06 g, 5 mmol) and potassium tert-butoxide (0.67 g, 6 mmol) in tetrahydrofuran (28 ml) was stirred under reflux for 3 hours. After cooling the reaction mixture was poured into water and extracted with diethyl ether. The united organic phase was washed with water, dried over sodium sulfate and evaporated under vacuum to afford the pure oil product, which was used directly for the following reaction.

Yield: 0.80 g (91%, pale yellow oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.00, 1.21 (2m, 4H, $2CH_2$), 2.63 (m, 1H, CH), 3.88 (s, 3H, OCH_3), 6.95 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 8.01 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 11.2 ($2CH_2$), 16.6, 55.5, 113.7, 130.2, 131.1, 163.3, 199.0

IR (KBr): ν (cm^{-1}) =3076w, 3008m, 2963w, 2936w, 2840w, 1661s, 1601s, 1576m, 1510m, 1457m, 1420s, 1385s, 1310m, 1260s, 1232s, 1171s, 1030s, 991s, 838s

MS (EI, 35°C): m/z = 176 (M^+, 34%), 135 (100%), 105 (40%), 77 (27%)

Elemental analyse: $C_{11}H_{12}O_2$ (176.08 g/mol)

Calculated: C% 74.98 H% 6.86
Found: C% 75.21 H% 6.63

6.1.12 1,2-Dialkyl-1,2-diarylethene 54 and 55

(*E*)-1,2-Bis(cyclopropyl)-1,2-bis(4-methoxyphenyl)ethene 54

Titanium tetrachloride (1.0 ml, 9 mmol) was added via a syringe to a stirred suspension of zinc power (1.17 g, 18 mmol) in dry tetrahydrofuran (30 ml) at –10°C under nitrogen over a period of 15 minutes. The resulting yellow-dark mixture was stirred at room temperature for 30 minutes and then heated under reflux for 1 hour. The dark suspension was cooled to room temperature and cyclopropyl-(4-methoxyphenyl)methanone **53** (1.06 g, 6 mmol) in tetrahydrofuran (7.5 ml) was added. The reaction mixture was refluxed for 4 hours. After cooling the mixture was poured into ice-water and extracted with diethyl ether. The united organic phase was washed with water, dried over sodium sulfate and evaporated under vacuum. The residue (0.93 g) was separated by column chromatography on silica gel with a mixture of ligroin and dichloromethane (3 : 2) as eluent into two fractions: a mixture of colourless crystals (R_f = 0.62) together with a little oil and a viscous oily mixture (R_f = 0.48 ~ 0.62). The crystals were washed two times with each 3 ml of a mixture of ligroin and diethyl ether (5 : 1) to obtain the pure **54** (0.108 g). The combined oily mixture was heated in 10 ml of ligroin (or ethanol) and stood at room temperature over 24 hours, from which more product **54** crystallized out and was isolated by suction filtration. This process was repeated until no crystals were isolated. The obtained crystals was purified by recrystallization with ethanol to afford the pure product **54 (*E*)**. The rest oil substance (0.11 g) was still a mixture which could not be separated.

Yield: 0.35 g (36%, R_f = 0.62, white crystals); mp: 175.5-176°C

^{1}H-NMR (CDCl$_3$): δ[ppm] = 0.12, 0.32 (2m, 8H, 4CH$_2$), 1.35 (m, 2H, 2CH), 3.82 (s, 6H, 2OCH$_3$), 6.88 (AA'BB', 4H, ^{3}J = 8.6Hz, 2Ar-H, 2Ar′-H), 7.09 (AA'BB', 4H, ^{3}J = 8.6Hz, Ar-H, Ar′-H)

^{13}C-NMR (CDCl$_3$): δ[ppm] = 4.4 (4CH$_2$), 15.4 (2CH), 55.2 (2OCH$_3$), 113.1 (Ar-CH), 131.1 (C), 131.4 (Ar-CH), 138.0 (C), 158.0 (C)

IR (KBr): ν (cm^{-1}) = 3089w, 3011m, 2954m, 2932w, 2833w, 1607s, 1508s, 1465m, 1455m, 1439w, 1418w, 1287s, 1244s, 1175s, 1105m, 1031s, 1018m, 998m, 841s, 820m, 750m

MS (EI, 35°C): m/z = 320 (M$^+$, 47%), 292 (100%), 279 (64%), 261 (12%), 186 (22%), 171 (20%), 121 (80%)

Elemental analysis: $C_{22}H_{24}O_2$ (320.18 g/mol)

Calculated: C% 82.46 H% 7.55

Found: C% 82.41 H% 7.59

(*E*)-1,2-Bis(3-bromopropyl)-1,2-bis(4-hydroxyphenyl)ethene 55

Boron tribromide (0.23 ml, 2.4 mmol) was added via a syringe to a stirred solution of (*E*)-1,2-bis(cyclopropyl)-1,2-bis(4-methoxyphenyl)ethene **54** (0.128 g, 0.4 mmol) in dry dichloromethane (10 ml) at 0°C. After stirring at 0°C for 30 minutes, the reaction mixture was stirred at room temperature for 48 hours. Then the mixture was poured into ice-water and extracted with diethyl ether. The united organic phase was washed with water, dried over sodium sulfate and evaporated. The dark residue was taken up in 8 ml of a mixture of dichloromehane and diethyl ether (3 : 1) and was filtrated to remove some insoluble dark material. The filtrate was evaporated and isolated by column chromatography on silica gel with the same mixture as eluent to afford a main fraction (R_f = 0.77), which was purified once again by column chromatography with a mixture of ligroin, diethyl ether and dichloromethane (1 : 1 : 1, R_f = 0.51) as eluent to give pure **55**.

Yield: 18 mg (10%, pale brown solid); mp: 114-116°C

^{1}H-NMR (DMSO-d$_6$): δ[ppm] = 1.61 (m, 4H, 2CH$_2$), 2.22 (t, 4H, ^{3}J = 7.6Hz, 2CH$_2$), 3.27 (t, 4H, ^{3}J = 6.7Hz, 2CH$_2$), 6.76 (AA'BB', 4H, ^{3}J = 8.3Hz, 2Ar-H, 2Ar′-H), 6.99 (AA'BB', 4H, ^{3}J = 8.3Hz, Ar-H, Ar′-H), 9.35 (s, 2H, 2OH)

MS (EI, 115°C): m/z = 454 (M$^+$, 84%), 452 (M$^+$, 48%), 347 (27%), 224 (28%), 107 (100%), 82 (29%), 81 (13%), 80 (24%)

Elemental analysis: $C_{20}H_{22}Br_2O_2$ (454.20 g/mol)

Calculated: C% 52.89 H% 4.88

Found: C% 53.20 H% 5.28

6.1.13 1,2-Diarylethanone 58 and 59

General Procedure

Arylacetyl chloride (0.162 mol) was added dropwise to a stirred suspension of aluminium chloride (26.1 g, 0.195 mol) and anisole (18 ml, 0.165 mol) in 60 ml of dry 1,2-dichloroethane at 0±5°C within 1 hour. After addition the mixture was stirred at room temperature for 1 hour and then was refluxed for further 2 hours. Under cooling in ice bath 100 ml of water was added and extracted with further more 1,2-dichloroethane. The combined organic phase was washed with water, dried over sodium sulfate and evaporated under vacuum. The crude product was purified by recrystallisation.

1-(4-Methoxyphenyl)-2-phenylethanone 58

starting from phenylacetyl chloride (22 ml, 0.162 mol) and anisole. The crude product was purified by recrystallisation from a mixture of ethanol and ligroin (1 : 1).

Yield: 22.3 g (61%, colorless crystals); mp: 68-69°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.85 (s, 3H, OCH_3), 4.22 (s, 2H, CH_2), 6.91 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 7.17-7.35 (m, 5H, Ar'-H), 7.98 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 45.3, 55.5, 113.8, 126.8, 128.6, 129.4, 129.7, 130.9, 135.0, 163.5, 196.2

IR (KBr): ν (cm^{-1}) = 3011w, 2973w, 2932w, 2904w, 2839w, 1674s, 1602s, 1575s, 1507m, 1452m, 1420m, 1335s, 1260s, 1222s, 1204s, 1173s, 1111m, 1032s, 990s, 836s, 731s

MS (EI, 35°C): m/z = 226 (M^+, 1.4%), 135 (100%), 77.1 (13%)

Elemental analysis: $C_{15}H_{14}O_2$ (226.10 g/mol)

Calculated: C% 79.62 H% 6.24

Found: C% 79.57 H% 6.40

1,2-Bis(4-methoxyphenyl)ethanone 59

starting from 4-methoxyphenylacetyl chloride (30 g, 0.162 mol) and anisole. The crude product was purified by recrystallisation from a mixture of ethanol and ethyl acetate (9 : 1).

Yield: 23.6 g (57%, colorless crystals); mp: 109-110.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.77 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.16 (s, 2H, CH_2), 6.84 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 6.91 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 7.17 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 7.98 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 44.4, 55.2, 55.4, 113.8, 114.1, 127.0, 129.7, 130.4, 130.9, 158.5, 163.5, 196.5

IR (KBr): ν (cm^{-1}) = 3009w, 2967w, 2938w, 2900w, 2839w, 1679s, 1599s, 1574m, 1517s, 1466m, 1441m, 1418m, 1337m, 1314m, 1249s, 1222s, 1208s, 1171s, 1027s, 994m, 833

MS (EI, 80°C): m/z = 256 (M^+, 37%), 135 (100%)

Elemental analysis: $C_{16}H_{16}O_3$ (256.11 g/mol)

Calculated: C% 74.98 H% 6.29

Found: C% 74.91 H% 6.32

6.1.14 2-Alkyl-1,2-diarylethanones 63 - 65

General Procedure

A mixture of potassium tert-butoxide (1.12 g, 0.01 mol) and 1,2-bis(4-methoxyphenyl)-ethenone (2.56 g, 0.01 mol) in dry tetrahydrofuran (15 ml) was stirred at room temperature for 30 minutes. To this was added dropwise under stirring and nitrogen the corresponding alkyl halide. After the complete reaction (see each product), the reaction mixture was diluted with water and extracted with diethyl ether. The combined organic phase was washed with water, dried over sodium sulfate and evaporated under vacuum to give the desired product.

1,2-Bis(4-methoxyphenyl)propanone 63

starting from 1,2-bis(4-methoxyphenyl)ethenone (0.01 mol) with methyl iodide (1.25 ml, 0.02 mol). After addition of methyl iodide, the mixture was stirred at room temperature for 1 hour to complete reaction. The residue obtained from the ethereal layer was analysed as the pure product.

Yield: 2.61 g (97%, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.48 (d, 3H, ^3J = 6.9Hz, CH_3), 3.74 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 4.59 (q, 1H, ^3J = 6.9Hz, CH), 6.81 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 6.85 (AA'BB', 2H, ^3J = 8.9Hz, Ar-H), 7.19 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 7.93 (AA'BB', 2H, ^3J = 8.9Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 19.9, 47.0, 55.6, 55.8, 114.0, 114.7, 129.1, 129.9, 131.4, 134.4, 158.8, 163.5, 199.5

IR (KBr): ν (cm^{-1}) = 3060w, 2969m. 2932m, 2837m, 1673s, 1600s, 1574m, 1510s, 1461m, 1420m, 1337m, 1303m, 1256s, 1169s, 1114m, 1031s, 954m, 834m, 781m

MS (EI, 35°C): m/z = 270 (M^+, 5%), 135 (100%)

Elemental analysis: $C_{17}H_{18}O_3$ (270.13 g/mol)

Calculated: C% 75.53 H% 6.71

Found: C% 75.28 H% 6.80

1,2-Bis(4-methoxyphenyl)butanone 64

starting from 1,2-bis(4-methoxyphenyl)ethenone (0.01 mol) with ethyl iodide (1.20 ml, 0.015 mol). After addition of ethyl iodide, the mixture was stirred at room temperature for 1 hour to complete reaction. The residue obtained from the ethereal layer was analysed as the pure product.

Yield: 2.72 g (96%, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 0.88 (t, 3H, ^3J = 7.4Hz, CH_3), 1.81 (m, 1H, CH_2), 2.15 (m, 1H, CH_2), 3.74 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 4.34 (t, 1H, ^3J = 7.3Hz, CH), 6.81 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 6.85 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 7.20 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 7.95 (AA'BB', 2H, ^3J = 8.9Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 14.4, 29.2, 56.3, 57.3, 57.5, 115.8, 116.3, 131.3, 132.2, 133.0, 134.2, 160.6, 165.3, 201.0

IR (KBr): ν (cm^{-1}) = 3060w, 3001m, 2963s, 2934s, 2837s, 1671s, 1599s, 1574s, 1510s, 1461s, 1441s, 1420s, 1351s, 1303s, 1254s, 1168s, 1113m, 1031s, 988m, 908m, 824s, 784s

MS (EI, 50°C): m/z = 284 (M^+, 8%), 149 (29%), 135 (100%), 121 (12%)

Elemental analysis: $C_{18}H_{20}O_3$ (284.14 g/mol)

Calculated: C% 76.03 H% 7.09

Found: C% 76.06 H% 7.36

3-(Tetrahydropyran-2-yl)-1,2-bis(4-methoxyphenyl)propanone 65 (a mixture of two diastereomers)

starting from 1,2-bis(4-methoxyphenyl)ethenone (0.01 mol) with 2-bromomethyl-tetrahydro-2H-pyran (1.30 ml, 0.01 mol). After addition of alkyl bromide, the mixture was refluxed for 6 hours under nitrogen to complete reaction. The residue obtained from ethereal layer was separated by column chromatography on silica gel with dichloromethane as eluent to afford a mixture of two diastereomers.

Yield: 1.54 g (44%, R_f = 0.45, colorless oil)

(All of the signals in ^{1}H- and ^{13}C-NMR are double)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.15-3.35 (m, 10H, 5CH_2), 3.73 / 3.75 (2s, 3H, OCH_3), 3.80 / 3.82 (2s, 3H, OCH_3), 3.87-4.02 (m, 1H, CH, tetrahydropyran-H), 4.76-4.94 (m, 1H, CH), 6.73-6.90 (AA'BB', 4H, Ar-H), 7.16-7.24 (AA'BB', 2H, Ar-H), 7.89-8.03 (AA'BB', 2H, Ar-H)
^{13}C-NMR ($CDCl_3$): δ[ppm] = 23.4 (2C), 26.2 (2C), 32.3, 32.4, 39.9, 41.5, 47.5, 48.0, 55.1, 55.2, 55.3, 55.4, 68.3, 68.4, 74.5, 75.8, 113.5, 113.6, 114.2 (2C), 129.0, 129.5, 129.7, 130.3, 131.0, 131.1, 131.6, 132.6, 158.4, 158.5, 163.1, 163.3, 198.9, 199.2
IR (KBr): ν (cm^{-1}) = 2934m, 2840m, 1671s, 1601s, 1510s, 1461w, 1304w, 1251s, 1171s, 1086m, 1033m, 832m
MS (EI, 35°C): m/z = 354 (M^+, 4%), 256 (12%), 135 (85%), 85 ($C_5H_9O^+$, 100%)
Elemental analysis: $C_{22}H_{26}O_4$ (354.18 g/mol)

Calculated:	C%	74.55	H%	7.39
Found:	C%	74.81	H%	7.39

6.1.15 2-Alkyl-1,1,2-triarylethenes 66 - 69

General Procedure

2 ml of a solution of the corresponding aryl bromide (12 mmol) in dry tetrahydrofuran (8 ml) was added to magnesium (0.273 g, 11.2 mmol) and a small piece of iodine and was heated under nitrogen until the purplish red faded away. To which was added dropwise the rest solution of aryl bromide without heating. After addition the mixture was stirred at 60 ~ 70°C until the magnesium disappeared.

To above-prepared Grignard reagent was added dropwise under stirring and nitrogen at room temperature a solution of the corresponding ketone (9.3 mmol) in tetrahydrofuran (10 ml) and the resulting mixture was refluxed for 1.5 ~ 4 hours. After cooling 7 ml of 48% hydrobromide was added dropwise at 0°C and then stirred for further 2 hours. The work-up was described under each product.

After dehydration with hydrobromide, the crude product **66** was directly precipitated from the reaction mixture, isolated by suction filtration and was purified by recrystallisation from ethanol. The other products **67 - 69** were extracted with dichloromethane and purified by column chromatography on silica gel, respectively.

1,1,2-Tris(4-methoxyphenyl)prop-1-ene 66

starting from 1,2-bis(4-methoxyphenyl)propanone **63** (2.53 g, 9.3 mmol) and Grignard reagent prepared from magnesium (11.2 mmol) and 4-bromoanisole (1.5 ml, 12 mmol).

The mixture was refluxed for 1.5 hours. After dehydration with hydrobromide, the crude product **66** was directly precipitated from the reaction mixture, isolated by suction filtration, washed successively with 80% methanol (5 ml), more water many times until neutrality and 80% methanol (5 ml) and dried. The crude **66** was purified by recrystallisation from ethanol.

Yield: 2.29 g (68%, colorless crystals); mp: 118.5-120°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 2.10 (s, 3H, CH_3), 3.69 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.57 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 6.70 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 6.79 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 6.87 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 7.05 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 7.14 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 23.4, 55.0, 55.1, 55.2, 112.8, 113.3, 113.4, 130.4, 131.2, 132.0, 133.7, 136.1, 136.5, 136.7, 137.8, 157.4, 157.7, 158.1

IR (KBr): ν (cm^{-1}) = 3006w, 2954w, 2933w, 2907w, 2836w, 1606s, 1511s, 1463m, 1293s, 1274m, 1242s, 1174s, 1034s, 832s

MS (EI, 50°C): m/z = 360 (M^+, 100%), 345 (4%), 330 (5%), 135 (12%)

Elemental analysis: $C_{24}H_{24}O_3$ (360.17 g/mol)

Calculated: C% 79.97 H% 6.71

Found: C% 79.78 H% 6.50

1,1,2-Tris(4-methoxyphenyl)but-1-ene 67

starting from 1,2-bis(4-methoxyphenyl)butanone **64** (2.64 g, 9.3 mmol) and Grignard reagent prepared from magnesium (11.2 mmol) and 4-bromoanisole (1.5 ml, 12 mmol).

The mixture was refluxed for 2 hours. After dehydration with hydrobromide, the reaction mixture was diluted with water (20 ml) and extracted with dichloromethane. The combined organic layer was washed with water, dried over sodium sulfate and evaporated. The residue was purified by column chromatography on silica gel with a mixture of ligroin and diethyl ether (3 : 1, R_f = 0.60) and then by recrystallization from a mixture of ethanol and ligroin (1 : 1) to obtain pure **67**.

Yield: 2.55 g (74%, colorless crystals); mp: 90.2-91.2°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 0.92 (t, 3H, ^3J = 7.4Hz, CH_3), 2.45 (q, 2H, ^3J = 7.4Hz, CH_2), 3.68 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 6.55 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 6.70 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 6.78 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 6.87 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 7.02 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 7.14 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 13.7, 28.9, 55.0, 55.1, 55.2, 112.8, 113.3, 113.5, 130.6, 130.7, 131.9, 134.8, 136.1, 136.6, 137.4, 140.5, 157.4, 157.7, 158.2

IR (KBr): ν (cm^{-1}) = 3038m, 2946m, 2928m, 2904m, 2832m, 1607s, 1573m, 1506s, 1461s, 1439m, 1284s, 1243s, 1173s, 1106m, 1034s, 836m, 813s

MS (EI, 110°C): m/z = 374 (M$^+$, 100%), 359 (21%), 345 (12%), 251 (19%), 227 (12%), 121 (19%)

Elemental analyse: $C_{25}H_{26}O_3$ (374.19 g/mol)

Calculated: C% 80.18 H% 7.00

Found: C% 80.08 H% 6.91

3-(Tetrahydropyran-2-yl)-1,1,2-tris(4-methoxyphenyl)prop-1-ene 68

starting from 1,2-bis(4-methoxyphenyl)-2-(tetrahydropyran-2-yl)propanone **65** (3.29 g, 9.3 mmol) and Grignard reagent prepared from magnesium (11.2 mmol) and 4-bromoanisole (1.5 ml, 12 mmol).

The mixture was refluxed for 4 hours. After dehydration with hydrobromide, the reaction mixture was diluted with water (20 ml) and extracted with dichloromethane. The combined organic layer was washed with water, dried over sodium sulfate and evaporated. The residue was purified by column chromatography on silica gel with a mixture of ligroin and diethyl ether (2 : 1, R_f = 0.60) to give pure **68**.

Yield: 2.18 g (49%, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.09-1.78 (m, 6H, 3CH_2, tetrahydropyran-H), 2.48 (dd, 1H, CH_2), 2.52 (dd, 1H, CH_2), 3.05-3.25 (m, 2H, CH_2, tetrahydropyran-H), 3.68 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.86-3.94 (m, 1H, CH, tetrahydropyran-H), 6.54 (AA'BB', 2H, ^{3}J = 8.7Hz, Ar-H), 6.70 (AA'BB', 2H, ^{3}J = 8.7Hz, Ar-H), 6.78 (AA'BB', 2H, ^{3}J = 8.7Hz, Ar-H), 6.85 (AA'BB', 2H, ^{3}J = 8.6Hz, Ar-H), 7.02 (AA'BB', 2H, ^{3}J = 8.6Hz, Ar-H), 7.22 (AA'BB', 2H, ^{3}J = 8.6Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 23.6, 26.0, 31.7, 42.1, 55.0, 55.1, 55.2, 68.4, 76.2, 112.7, 113.2, 113.4, 130.7, 131.1, 131.8, 134.8, 135.5, 136.1, 136.2, 139.6, 157.3, 157.7, 158.1

IR (KBr): ν (cm^{-1}) = 3031w, 2998w, 2933m, 2834m, 1606s, 1510s, 1462m, 1440m, 1289m, 1244s, 1174s, 1089m, 1085s, 831m

MS (EI, 35°C): m/z = 444 (M$^+$, 43%), 359 (M$^+$-C_5H_9O, 100%), 290 (7%), 251 (16%), 121 (14%), 85 ($C_5H_9O^+$, 16%)

Elemental analysis: $C_{29}H_{32}O_4$ (444.23 g/mol)

Calculated: C% 78.35 H% 7.26

Found: C% 79.02 H% 7.33

(*E* / *Z*)-1-(Benzo[1,3]dioxole-5-yl-)-1,2-bis(4-methoxyphenyl)but-1-ene 69

starting from 1,2-bis(4-methoxyphenyl)butanone **64** (2.64 g, 9.3 mmol) and Grignard reagent prepared from magnesium (11.2 mmol) and 5-bromobenzo[1,3]dioxole (1.5 ml, 12 mmol). The mixture was refluxed for 3.5 hours. After dehydration with hydrobromide, the reaction mixture was diluted with water (20 ml) and extracted with dichloromethane. The combined organic layer was washed with water, dried over sodium sulfate and evaporated. The residue was purified by column chromatography on silica gel with a mixture of ligroin and dichloromethane (2 : 3, $R_f = 0.70$) to give **69** as a mixture of two isomers.

Yield: 1.48 g (41%, colorless oil), stored in refrigerator for 2 months, solid.

The NMR-spectra relate to two isomers.

^{1}H-NMR ($CDCl_3$): δ[ppm] = 0.91 (2t, 6H, superimposed, $2CH_3$), 2.45 (2q, 4H, superimposed, $2CH_2$), 3.69 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 3.77 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 5.82 (s, 2H, OCH_2O), 5.95 (s, 2H, OCH_2O), 6.32-6.39 (m, 2H, 2Ar-H), 6.47 (d, 1H, ^3J = 8.0Hz, Ar-H), 6.56 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 6.65-6.82 (m, 9H, superimposed, Ar-H), 6.87 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 7.01 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 7.03 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 7.13 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 21.3, 36.6, 62.6, 62.7, 62.8, 108.2, 108.5, 115.0, 115.6, 117.7, 118.9, 120.4, 120.9, 121.1, 121.3, 130.3, 132.1, 137.5, 138.1, 138.2, 138.3, 139.4, 142.2(d), 143.4, 143.9, 144.9, 145.0, 145.4, 145.6, 148.4, 148.6, 152.9, 153.7, 154.3, 155.0, 165.0, 165.4(d), 165.9,

IR (film): ν (cm^{-1}) = 3029w, 3001w, 2960m, 2932m, 2900m, 2835m, 1606s, 1573w, 1508s, 1484s, 1463s, 1433s, 1287s, 1244s, 1175s, 1106w, 1038s, 937m, 834m, 807s, 757s

MS (EI, 35°C): m/z = 388 (M^+, 100%), 373 (M^+-CH_3, 15%), 359 (M^+-C_2H_5, 15%), 241 (10%), 135 (13%), 121 (10%)

Elemental analysis: $C_{25}H_{24}O_4$ (388.17 g/mol)

Calculated: C% 77.30 H% 6.23

Found: C% 77.28 H% 6.12

6.1.16 2-Alkyl-1,1,2-triarylethenes 75 - 77

General Procedure

Titanium tetrachloride (1.33 ml, 12 mmol)) was added via a syringe dropwise to a stirred suspension of zinc power (1.56 g, 24 mmol) in dry tetrahydrofuran (30 ml) at –10°C under nitrogen. The resulting yellow-dark mixture was stirred at room temperature for 30 minutes and then heated under reflux for 1 hour. The dark suspension was cooled to room temperature and a solution of two corresponding starting ketones (8 mmol in total) in tetrahydrofuran (10 ml) was added. The reaction mixture was refluxed under dry nitrogen atmosphere for 4 hours. After cooling to room temperature, the mixture was poured into ice-water and extracted with diethyl ether. The united organic phase was washed with water, dried over sodium sulfate and evaporated. The residue was separated by column chromatography on silica gel to obtain the desired product.

2-(4-Methoxyphenyl)-1,1-diphenylprop-1-ene 75

starting from benzophenone (0.73 g, 4 mmol) and 4'-mehoxyacetophenone (0.60 g, 4 mmol). The residue was separated by column chromatography on silica gel with a mixture of ligroin and dichloromethane (3 : 2) as eluent to obtain **75**.

Yield: 0.89 g (74%, white solid); mp: 107.5-108.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 2.11 (s, 3H, CH_3), 3.75 (s, 3H, OCH_3), 6.66-7.38 (m, 14H, Ar-H)

IR (KBr): ν (cm^{-1}) = 3074w, 3021m, 2960w, 2934w, 2911w, 2841w, 1607s, 1509s, 1460s, 1289s, 1246s, 1180s, 1029s, 832m, 762m, 670s

MS (EI, 50°C): m/z = 300 (M^+, 100%), 285 (11%), 192 (12%), 165 (10%), 191 (38%), 165 (33%), 121 (30%), 91 (20%), 28 (22%, N_2)

Elemental analysis: $C_{22}H_{20}O$ (300.15 g/mol)

Calculated:	C%	87.96	H%	6.71
Found:	C%	87.19	H%	6.94

2-(4-Hydroxyphenyl)-1,1-bis(4-methoxyphenyl)prop-1-ene 76

starting from 4,4'-dimethoxybenzophenone (1.00 g, 4 mmol) and 4'-hydroxyacetophenone (0.56 g, 4 mmol). The residue was separated by column chromatography on silica gel with a mixture of dichloromethane and tetrahydrofuran (60 : 1, R_f = 0.39) as eluent to obtain crude **76**, which was heated to reflux in a mixture of ligroin (5 ml) and tetrahydrofuran (1 ml) and then cooled in a refrigerator to give pure **76** as white precipitate, which was isolated by suction filtration and dried under vacuum.

Yield: 0.52 g (38%, off-white solid); mp: 148.5-149.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 2.10 (s, 3H, CH_3), 3.70 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 4.72 (broad, 1H, OH), 6.57 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 6.62 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 6.79 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 6.87 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 7.01 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 7.13 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3363m, 3028w, 3003w, 2964w, 2936w, 2909w, 2837w, 1607s, 1508s, 1264m, 1243s, 1172s, 832s

MS (EI, 70°C): m/z = 346 (M^+, 3%), 205 (3%), 84 (4%), 72 (60%), 42 (100%), 27 (18%)

Elemental analysis: $C_{23}H_{22}O_3$ (346.16 g/mol)

Calculated:	C%	79.74	H%	6.40
Found:	C%	79.88	H%	6.41

3,3,3-Trifluoro-1,1-bis(4-methoxyphenyl)-2-phenylprop-1-ene 77

starting from 4,4'-dimethoxybenzophenone (1.00 g, 4 mmol) and α,α,α-trifluoroacetophenone (0.56 ml, 4 mmol). The residue was separated by column chromatography on silica gel with a mixture of dichloromethane and ligroin (1 : 1, R_f = 0.64) as eluent to obtain **77**.

Yield: 0.51 g (74%, yellow viscous oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.67 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.55 (AA'BB', 2H, ^3J = 8.9Hz, Ar-H), 6.80 (AA'BB', 2H, ^3J = 8.9Hz, Ar-H), 6.89 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 7.16-7.26 (m, 7H, Ar-H)

MS (EI, 95°C): m/z = 384 (M^+, 100%)

Elemental analysis: $C_{23}H_{19}F_3O_2$ (384.13 g/mol)

Calculated:	C%	71.87	H%	4.98
Found:	C%	71.54	H%	5.43

6.1.17 Hydroxylated 2-alkyl-1,1,2-triarylethenes 78 - 80

General Procedure

The methyl ether protected compound was dissolved in dry dichloromethane and cooled to –50°C. At this temperature boron tribromide was added via syringe under nitrogen and stirred for 2 hours. Then the reaction mixture was allowed to warm to room temperature and stirred for further 24 ~ 48 hours. After cooling at –10°C, methanol was added dropwise and stirred at room temperature for 3 hours. The resulting mixture was evaporated under vacuum. The residue was separated by column chromatography on silica gel.

1,1,2-Tris(4-hydroxyphenyl)prop-1-ene 78

starting from 1,1,2-tris(4-methoxyphenyl)propene **66** (0.36 g, 1.0 mmol) with boron tribromide (0.57 ml, 6 mmol) in dichloromethane (38 ml); reaction time at room temperature: 48 hours; added methanol: 10 ml.

The residue was separated by column chromatography with diethyl ether as eluent. The desired fraction (R_f = 0.9) was evaporated and the resulting residue was refluxed for 30 minutes in a mixture of ligroin (10 ml) and diethyl ether (5 ml). After cooling the precipitate was isolated by suction filtration and dried under vacuum to give pure **78**.

Yield: 0.28 g (88%, off-white solid); mp: 205-206°C

^{1}H-NMR (CD_3OD): δ[ppm] = 2.04 (s, 3H, CH_3), 6.43 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 6.55 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 6.66 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 6.74 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 7.92 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 6.98 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3368s (OH), 3030w, 2936w, 2909w, 1892w, 1608s, 1510s, 1437m, 1249s, 1226s, 1171s, 832s

MS (EI, 100°C): m/z = 318 (M^+, 100%), 224 ($C_{15}H_{12}O_2^+$, 7%), 199 ($C_{13}H_{11}O_2^+$, 8%), 159 (8%), 107 (6%)

Elemental analysis: $C_{21}H_{18}O_3$ (318.13 g/mol)

Calculated:	C%	79.22	H%	5.70
Found:	C%	79.10	H%	5.75

4,8-Dibromo-1,1,2-tris(4-hydroxyphenyl)oct-1-ene 79

starting from 3-(tetrahydropyran-2-yl)-1,1,2-tris(4-methoxyphenyl)propene **68** (175 mg, 0.39 mmol) with boron tribromide (0.30 ml, 3.17 mmol) in dichloromethane (15 ml); reaction time at room temperature: 24 hours; added methanol: 5 ml.

The residue was separated by column chromatography with diethyl ether as eluent. The desired fraction (R_f = 0.74) was evaporated and the resulting residue was refluxed for 30 minutes in ligroin (10 ml) and diethyl ether (3 ml). After cooling in a refrigerator for 2 days, the precipitate was isolated by suction filtration and dried under vacuum to give pure **79**.

Yield: 27 mg (17%, pale pink solid); mp: 156-157°C (decompose)

^{1}H-NMR (CD_3OD): δ[ppm] = 1.73-2.01 (m, 6H, 3CH_2), 2.42-2.57 (m, 1H, CH_2), 2.57-2.74 (m, 1H, CH_2), 3.34-3.42 (m, 2H, CH_2), 3.87-3.99 (m, 1H, CH), 6.43 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 6,59 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 6.67 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 6.76 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 6.92 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 7.01 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H)

MS (EI, 250°C): m/z = 546 (M^+, 0.7%), 466 (M^+-HBr, 2.2%), 384 (M^+-2HBr, 3.1%), 317 ($C_{21}H_{17}O_3^+$, 2.5%), 266 ($C_{13}H_{15}BrO^+$, 3.2%), 199 ($C_{13}H_{11}O_2^+$, 3.6%), 187 ($C_{13}H_{15}O^+$, 3.7%), 157 (10%), 107 (7.2%), 94 (100%), 82 (29%), 81 (14%), 80 (37%)

Elemental analysis: $C_{26}H_{26}Br_2O_3$ (546.29 g/mol)

Calculated:	C%	57.16	H%	4.80
Found:	C%	57.38	H%	4.79

(*E* / *Z*)-1-(3,4-Dihydroxyphenyl)-1,2-bis(4-hydroxyphenyl)but-1-ene 80

starting from (*E* / *Z*)-1-(benzo[1,3]dioxole-5-yl-)-1,2-bis(4-methoxyphenyl)but-1-ene **69** (155 mg, 0.4 mmol) with boron tribromide (0.30 ml, 3.17 mmol) in dichloromethane (15 ml); reaction time at room temperature: 24 hours; added methanol: 5 ml.

The residue was separated by column chromatography with diethyl ether as eluent. The desired fraction (R_f = 0.73) was evaporated and the resulting residue was cooled in a refrigerator and then led to solid by addition of ligroin (5 ml). The precipitate was isolated and dried under vacuum to give **80**.

Yield: 116 mg (83%, pink solid)

The NMR-spectrum relates to two isomers.

^{1}H-NMR (CD_3OD): δ[ppm] = 0.96 (m, 6H, 2CH_3), 2.48 (m, 4H, 2CH_2), 6.19-7.10 (m, 22H, Ar-H)

IR (KBr): ν (cm^{-1}) = 3389s (broad, OH), 3030w, 2967w, 2932w, 1605s, 1582s, 1559m, 1512s, 1429m, 1320m, 1276s, 1235s, 1179s, 834s

MS (EI, 35°C): m/z = 348 (M^+, 100%), 333 (18%), 319 (23%), 239 (13%), 223 (12%), 215 (20%), 199 (10%), 107 (13%)

Elemental analysis: $C_{21}H_{18}O_3$ (348.14 g/mol)

Calculated:	C%	75.84	H%	5.79
Found:	C%	75.73	H%	6.13

6.1.18 Hydroxylated 1,2-diaryl-1,2-diazidoethanes 81 - 95

General Procedure

To a stirred slurry of sodium azide (0.20 g, 3.0 mmol) in acetonitile (4 ml) was added via a syringe at –15±5°C under nitrogen a solution of iodmonochloride (0.17 g, 1.0 mmol) in acetonitrile (2 ml) over a period of 15 minutes. After stirring for 1 hour at this temperature, the mixture was cooled to –50°C and the corresponding hydroxystilbene (1.0 mmol) was added. After stirring for 4 hours at –50±10°C, the reaction mixture was stirred at room temperature for further 20 hours and then the mixture was refluxed for 2 hours. After cooling the red-brown slurry was diluted with water and extracted with diethyl ether. The united organic phase was washed with 50 ml of 5% sodium thiosulfate, 50 ml of 5% sodium chloride and with water three times, then was dried over sodium sulfate and evaporated under vacuum. The residue was separated by column chromatography on silica gel.

1,2-Diazido-1-(2-fluoro-4-methoxyphenyl)-2-(4-hydroxyphenyl)ethane 81 (*threo*)

starting from (*E*)-hydroxystilbene **33**. The residue was separated into the pure product by column chromatography on silica gel with a mixture of ligroin, tetrahydrofuran and dichloromethane (4 : 1 : 1) as eluent.

Yield: 45 mg (14%, $R_f = 0.51$, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.75 (s, 3H, OCH_3), 4.68 (d, 1H, $^3J = 8.5$Hz, CHN_3), 4.80 (broad, 1H, OH), 4.88 (d, 1H, $^3J = 8.5$Hz, CHN_3), 6.47 (dd, 1H, $^3J_{(H,\ F)} = 12.1$Hz and $^4J = 2.5$Hz, Ar-H), 6.65 (dd, 1H, $^3J = 8.6$Hz and $^4J = 2.4$Hz, Ar-H), 6.71 (AA'BB', 2H, $^3J = 8.5$Hz, Ar'-H), 7.03 (AA'BB', 2H, $^3J = 8.6$Hz, Ar'-H), 7.15 (dd, 1H, $^3J = 8.4$Hz and $^4J_{(H,\ F)} = 8.4$Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3399m (broad, OH), 3019w, 2938w, 2839w, 2106s (N_3), 1625s, 1587m, 1511s, 1444m, 1258s, 1157s, 1104m, 834m

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 351 ($[M+Na]^+$, 4%), 258 (M^+-N_3-N_2, 15%), 244 (M^+-$2N_3$, 25%), 231 (100%), 180 ($C_8H_7FN_3O^+$, 8%), 152 ($C_8H_7FNO^+$, 60%), 148 ($C_7H_6N_3O^+$, 22%), 139 ($C_8H_8FO^+$, 28%), 120 ($C_7H_6NO^+$, 63%)

MS (EI, 100°C): m/z = 285 (M^+-HN_3, 2%), 257 (M^+-HN_3-N_2, 7%), 244 (M^+-$2N_3$, 12%), 180 ($C_8H_7FN_3O^+$, 14%), 152 ($C_8H_7FNO^+$, 100%), 148 ($C_7H_6N_3O^+$, 15%), 120 ($C_7H_6NO^+$, 66%)

Elemental analysis: $C_{15}H_{13}FN_6O_2$ (328.11 g/mol)

Calculated:	C%	54.88	H%	3.99	N%	25.60
Found:	C%	55.32	H%	3.75	N%	25.67

1,2-Diazido-1-(2-chloro-4-methoxyphenyl)-2-(4-hydroxyphenyl)ethane 82 (*threo*)

starting from (*E*)-hydroxystilbene **34**. The residue was separated by column chromatography on silica gel two times, respectively, firstly with a mixture of ligroin, tetrahydrofuran and dichloromethane (4 : 1 : 1) as eluent into the crude product ($R_f = 0.51$) and then with a mixture of ligroin, diethyl ether, dichloromethane and acetonitrile (8 : 2 : 2 : 1) as eluent into the pure product ($R_f = 0.32$).

Yield: 75 mg (22%, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.78 (s, 3H, OCH_3), 4.71 (d, 1H, ^3J = 7.1Hz, CHN_3), 4.82 (broad, 1H, OH), 5.15 (d, 1H, ^3J = 7.1Hz, CHN_3), 6.75 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 6.79-6.86 (m, 2H, superimposed, Ar'-H), 7.12 (AA'BB', 2H, ^3J = 8.5Hz, Ar-H), 7.33 (d, 1H, ^3J = 8.5Hz, Ar'-H)

IR (KBr): ν (cm^{-1}) = 3368m (broad, OH), 3023w, 2942w, 2838w, 2104s (N_3), 1607s, 1514s, 1497s, 1241s, 1174m, 1041s, 834m

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 367 ($[M+Na]^+$, 6%), 301 (M^+-HN_3, 4%), 274 (M^+-N_3-N_2, 22%), 260 (M^+-$2N_3$, 28%), 247 (100%), 196 ($C_8H_7ClN_3O^+$, 15%), 168 ($C_8H_7ClNO^+$, 81%), 148 ($C_7H_6N_3O^+$, 13%), 120 ($C_7H_6NO^+$, 74%)

MS (EI, 120°C): m/z = 309 (M^+-Cl, 6%), 301 (M^+-HN_3, 8%), 273 (M^+-HN_3-N_2, 26%), 260 (M^+-$2N_3$, 51%), 196 ($C_8H_7ClN_3O^+$, 16%), 168 ($C_8H_7ClNO^+$, 100%), 148 ($C_7H_6N_3O^+$, 21%), 120 ($C_7H_6NO^+$, 73%)

Elemental analysis: $C_{15}H_{13}ClN_6O_2$ (344.08 g/mol)

Calculated:	C%	52.26	H%	3.80	N%	24.38
Found:	C%	52.07	H%	3.57	N%	24.28

1,2-Diazido-1-(2,6-dichloro-4-methoxyphenyl)-2-(4-hydroxyphenyl)ethane 83 (*threo*)

starting from (*E*)-hydroxystilbene **35**. The residue was separated into the pure product by column chromatography on silica gel with a mixture of ligroin and diethyl ether (1 : 1) as eluent.

Yield: 87 mg (23%, R_f = 0.38, pale yellow solid); mp: 88-89°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 3.73 (s, 3H, OCH_3), 5.53 (d, 1H, ^3J = 10.3Hz, CHN_3), 5.58 (d, 1H, ^3J = 10.3Hz, CHN_3), 6.61 (AA'BB', 2H, ^3J = 8.4Hz, Ar-H), 6.89-7.05 (s, broad, 2H, Ar'-H), 7.08 (AA'BB', 2H, ^3J = 8.4Hz, Ar-H), 9.54 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3312m (broad, OH), 3088w, 3021w, 2941w, 2838w, 2104s (N_3), 1599s, 1554m, 1514m, 1467m, 1434m, 1249s, 1173m, 1056m, 834m

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 401 ($[M+Na]^+$, 8%), 336 (M^+-HN_3, 3%), 308 (M^+-N_3-N_2, 11%), 294 (M^+-$2N_3$, 14%), 281 (63%), 230 ($C_8H_6Cl_2N_3O^+$, 6%), 202 ($C_8H_6Cl_2NO^+$, 41%), 148 ($C_7H_6N_3O^+$, 31%), 120 ($C_7H_6NO^+$, 100%), 107 ($C_7H_7O^+$, 90%)

MS (EI, 60°C): m/z = 335 (M^+-HN_3, 2%), 310 (21%); 309 (44%), 307 (M^+-HN_3-N_2, 37%), 294 (M^+-$2N_3$, 100%), 224 (24%), 203 (79%), 148 ($C_7H_6N_3O^+$, 21%), 120 ($C_7H_6NO^+$, 46%)

Elemental analysis: $C_{15}H_{12}Cl_2N_6O_2$ (378.04 g/mol)

Calculated:	C%	47.51	H%	3.19	N%	22.16

Found: C% 47.70 H% 3.30 N% 22.06

1,2-Diazido-1-(2,6-dichloro-4-hydroxyphenyl)-2-(4-methoxyphenyl)ethane 84 (*threo*) starting from (*E*)-hydroxystilbene **38**. The residue was separated into the pure product by column chromatography on silica gel with a mixture of ligroin and diethyl ether (1 : 2) as eluent.

Yield: 23 mg (6%, $R_f = 0.63$, pale yellow solid); mp: 84-86°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 3.68 (s, 3H, OCH_3), 5.53 (d, 1H, $^3J = 10.3$Hz, CHN_3), 5.62 (d, 1H, $^3J = 10.3$Hz, CHN_3), 6.73 (s, broad, 2H, Ar'-H), 6.81 (AA'BB', 2H, $^3J = 8.4$Hz, Ar-H), 7.19 (AA'BB', 2H, $^3J = 8.4$Hz, Ar-H), 10.57 (s, 1H, OH)

IR (film): ν (cm^{-1}) = 3335m (broad, OH), 3003w, 2933w, 2838w, 2104s (N_3), 1605s, 1571m, 1513m, 1426m, 1252s, 1177m, 1033m

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 401 ($[M+Na]^+$, 5%), 336 (M^+-HN_3, 2%), 308 (M^+-N_3-N_2, 5%), 298 (17%), 294 (M^+-$2N_3$, 7%), 281 (21%), 188 ($C_7H_4Cl_2NO^+$, 13%), 162 ($C_8H_8N_3O^+$, 11%), 134 ($C_8H_8NO^+$, 95%), 121 (100%)

MS (EI, 80°C): m/z = 309 (10%), 307 (M^+-HN_3-N_2, 5%), 294 (M^+-$2N_3$, 100%), 279 (11%), 224 (14%), 189 ($C_7H_4Cl_2NO^+$, 12%), 134 ($C_8H_8NO^+$, 72%)

Elemental analysis: $C_{15}H_{12}Cl_2N_6O_2$ (378.04 g/mol)

Calculated: C% 47.51 H% 3.19 N% 22.16

Found: C% 47.62 H% 3.35 N% 21.87

1,2-Diazido-1-(2,4-dichloro-6-methoxyphenyl)-2-(4-hydroxyphenyl)ethane 85 (*threo*) starting from (*E*)-hydroxystilbene **36**. The residue was separated into the pure product by column chromatography on silica gel with a mixture of ligroin and diethyl ether (1 : 1) as eluent.

Yield: 107 mg (28%, $R_f = 0.38$, colorless oil)

^{1}H-NMR (DMSO-d_6): δ[ppm] = 3.88 (s, 3H, OCH_3), 5.27 (d, 1H, $^3J = 10.2$Hz, CHN_3), 5.52 (d, 1H, $^3J = 10.2$Hz, CHN_3), 6.60 (AA'BB', 2H, $^3J = 8.5$Hz, Ar-H), 7.03 (AA'BB', 2H, $^3J = 8.5$Hz, Ar-H), 7.07 (s, 2H, Ar'-H), 9.54 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3370m (broad, OH), 3087w, 3025w, 2942w, 2839w, 2104s (N_3), 1613m, 1583s, 1567m, 1515m, 1459m, 1403m, 1257s, 1173m, 1041s, 899m, 832m

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 401 ($[M+Na]^+$, 2%), 336 (M^+-N_3, 1%), 308 (M^+-N_3-N_2, 6%), 294 (M^+-$2N_3$, 7%), 281 (24%), 202 ($C_8H_6Cl_2NO^+$, 11%), 148 ($C_7H_6N_3O^+$, 33%), 120 ($C_7H_6NO^+$, 70%), 107 ($C_7H_7O^+$, 100%)

MS (EI, 110°C): m/z = 335 (M^+-HN_3, 2%), 309 (9%); 307 (M^+-HN_3-N_2, 10%), 294 (M^+-$2N_3$, 15%), 202 ($C_8H_6Cl_2NO^+$, 46%), 175 (13%), 148 ($C_7H_6N_3O^+$, 42%), 120 ($C_7H_6NO^+$, 100%)

Elemental analysis: $C_{15}H_{12}Cl_2N_6O_2$ (378.04 g/mol)

Calculated: C% 47.51 H% 3.19 N% 22.16

Found: C% 47.58 H% 3.35 N% 21.91

1,2-Diazido-1,2-bis(4-hydroxyphenyl)ethane 86, 87 (*meso* and *dl*)

starting from (*E*)-dihydroxystilbene **41**. The residue was separated into two pure isomers **86** and **87** by column chromatography on silica gel with a mixture of dichloromethane and isopropanol (20 : 1) as eluent.

***Meso*-isomer 86**

Yield: 110 mg (37%, $R_f = 0.61$, white solid); mp: 136°C (decompose)

^{1}H-NMR (CD_3OD): δ[ppm] = 4.68 (s, 2H, $2CHN_3$), 6.76 (AA'BB', 4H, $^3J = 8.5$Hz, 2Ar-H, 2Ar'-H), 7.11 (AA'BB', 4H, $^3J = 8.5$Hz, 2Ar-H, 2Ar'-H)

IR (KBr): ν (cm^{-1}) = 3410s (OH), 2100s (N_3), 1613s, 1595m, 1515s, 1443m, 1343m, 1272s, 1229s, 1188s, 894m, 830m, 790s

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 319 ($[M+Na]^+$, 1.4%), 226 (M^+-N_3-N_2, 9%), 212 (M^+-$2N_3$, 11%), 199 (55%), 154 (48%), 148 ($C_7H_6N_3O^+$, 24%), 120 ($C_7H_6NO^+$, 100%)

MS (EI, 100°C): m/z = 225 (M^+-HN_3-N_2, 3%), 212 (M^+-$2N_3$, 100%), 153 (23%), 148 ($C_7H_6N_3O^+$, 20%), 120 ($C_7H_6NO^+$, 44%)

Elemental analysis: $C_{14}H_{12}N_6O_2$ (296.10 g/mol)

Calculated: C% 56.75 H% 4.08 N% 28.36

Found: C% 56.60 H% 4.03 N% 28.57

***Dl*-isomer 87**

Yield: 92 mg (31%, $R_f = 0.51$, white solid); mp: 114°C (decompose)

^{1}H-NMR (CD_3OD): δ[ppm] = 4.65 (s, 2H, $2CHN_3$), 6.63 (AA'BB', 4H, $^3J = 8.5$Hz, 2Ar-H, 2Ar'-H), 6.95 (AA'BB', 4H, $^3J = 8.5$Hz, 2Ar-H, 2Ar'-H)

IR (KBr): ν (cm^{-1}) = 3434s (OH), 2103s (N_3), 1632s, 1517s, 1447m, 1383m, 1261s, 1175m, 1144m, 1087m

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 319 ($[M+Na]^+$, 3%), 298 (5%), 253 (M^+-HN_3, 1%), 226 (M^+-N_3-N_2, 12%), 212 (M^+-$2N_3$, 18%), 199 (71%), 148 ($C_7H_6N_3O^+$, 19%), 120 ($C_7H_6NO^+$, 100%)

MS (EI, 90°C): m/z = 225 (M^+-HN_3-N_2, 1%), 212 (M^+-$2N_3$, 19%), 148 ($C_7H_6N_3O^+$, 7%), 120 ($C_7H_6NO^+$, 19%), 43 (HN_3^+, 100%)

Elemental analysis: $C_{14}H_{12}N_6O_2$ (296.10 g/mol)

Calculated:	C%	56.75	H%	4.08	N%	28.36
Found:	C%	56.80	H%	4.24	N%	28.51

1,2-Diazido-1-(2-fluoro-4-hydroxyphenyl)-2-(4-hydroxyphenyl)ethane 88, 89 (*erythro* and *threo*)

starting from (*E*)-dihydroxystilbene **42**. The residue was separated into two pure isomers **88** and **89** by column chromatography on silica gel with a mixture of diethyl ether, ligroin and dichloromethane (6 : 3 : 1) as eluent.

***Erythro*-isomer 88**

Yield: 91 mg (29%, $R_f = 0.49$, colorless crystals); mp: 114-115°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 5.00 (d, 1H, $^3J = 9.0$Hz, CHN_3), 5.09 (d, 1H, $^3J = 9.0$Hz, CHN_3), 6.54-6.71 (m, 2H, superimposed, Ar'-H), 6.78 (AA'BB', 2H, $^3J = 7.6$Hz, Ar-H), 7.24 (AA'BB', 2H, $^3J = 7.8$Hz, Ar-H), 7.31 (dd, 1H, $^3J = 8.4$Hz and $^4J_{(H, F)} = 8.4$Hz, Ar'-H), 9.62 (s, 1H, OH), 10.13 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3430s (OH), 2106s (N_3), 1625m, 1513m, 1457w, 1248m, 1100w, 967w, 843w

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 337 ($[M+Na]^+$, 3%), 244 (M^+-N_3-N_2, 9%), 230 (M^+-$2N_3$, 12%), 216 (56%), 166 ($C_7H_5FN_3O^+$, 14%), 148 ($C_7H_6N_3O^+$, 34%), 138 ($C_7H_5FNO^+$, 58%), 120 ($C_7H_6NO^+$, 100%)

MS (EI, 90°C): m/z = 230 (M^+-$2N_3$, 72%), 215 (4%), 166 ($C_7H_5FN_3O^+$, 2%), 148 ($C_7H_6N_3O^+$, 5%), 138 ($C_7H_5FNO^+$, 7%), 120 ($C_7H_6NO^+$, 10%), 43 (HN_3^+, 100%)

Elemental analysis: $C_{14}H_{11}FN_6O_2$ (314.09 g/mol)

Calculated:	C%	53.50	H%	3.53	N%	26.74
Found:	C%	53.50	H%	3.70	N%	26.57

***Threo*-isomer 89**

Yield: 114 mg (36%, $R_f = 0.41$, colorless oil)

^{1}H-NMR (DMSO-d$_6$): δ[ppm] = 5.07 (d, 1H, ^{3}J = 9.9Hz, CHN$_3$), 5.12 (d, 1H, ^{3}J = 9.9Hz, CHN$_3$), 6.41 (dd, 1H, ^{3}J$_{(H, F)}$ = 12Hz, Ar'-H), 6.51 (dd, 1H, ^{3}J = 8.3Hz, Ar'-H), 6.62 (AA'BB', 2H, ^{3}J = 7.9Hz, Ar-H), 7.06 (AA'BB', 2H, ^{3}J = 7.6Hz, Ar-H), 7.18 (dd, 1H, ^{3}J = 8.2Hz and ^{4}J$_{(H, F)}$ = 8.2Hz, Ar'-H), 9.51 (s, 1H, OH), 10.01 (s, 1H, OH)

IR (KBr): ν (cm^{-1}) = 3364s (broad, OH), 2104s (N$_3$), 1624s, 1513s, 1457m, 1332m, 1300s, 1241s, 1177s, 1154m, 1098m, 967m, 836m

MS (FAB, acetonitrile / m-NO$_2$-benzyl-OH): m/z = 337 ([M+Na]$^+$, 5%), 298 (11%), 244 (M$^+$-N$_3$-N$_2$, 13%), 230 (M$^+$-2N$_3$, 14%), 217 (55%), 166 ($C_7H_5FN_3O^+$, 10%), 148 ($C_7H_6N_3O^+$, 10%), 138 ($C_7H_5FNO^+$, 60%), 136 (100%), 120 ($C_7H_6NO^+$, 72%)

MS (EI, 200°C): m/z = 230 (M$^+$-2N$_3$, 100%), 215 (11%), 183 (7%), 137 (5%), 119 (6%)

Elemental analysis: $C_{14}H_{11}FN_6O_2$ (314.09 g/mol)

Calculated:	C%	53.50	H%	3.53	N%	26.74
Found:	C%	53.54	H%	3.79	N%	26.41

1,2-Diazido-1,2-bis(2-fluoro-4-hydroxyphenyl)ethane 90 (*dl*)

starting from (*E*)-dihydroxystilbene **44**. The residue was separated into a isomer **90** by column chromatography on silica gel with a mixture of diethyl ether and ligroin (2 : 1) as eluent.

Yield: 87 mg (26%, R$_f$ = 0.31, pale yellow oil)

^{1}H-NMR (DMSO-d$_6$): δ[ppm] = 5.23 (s, 2H, 2CHN$_3$), 6.43 (dd, 2H, ^{3}J$_{(H, F)}$ = 12.5Hz and ^{4}J = 2.0Hz, Ar-H, Ar'-H), 6.52 (dd, 2H, ^{3}J = 8.5Hz and ^{4}J = 2.1Hz, Ar-H, Ar'-H), 7.18 (dd, 2H, ^{3}J = 8.6Hz and ^{4}J$_{(H, F)}$ = 8.6Hz, Ar-H, Ar'-H), 10.05 (s, 2H, 2OH)

IR (film): ν (cm^{-1}) = 3377s (broad, OH), 2108s (N$_3$), 1627s, 1600m, 1511s, 1462m, 1303m, 1219m, 1152m, 1108m, 1194m, 967m, 759m

MS (FAB, acetonitrile / m-NO$_2$-benzyl-OH): m/z = 355 ([M+Na]$^+$, 2%), 289 (M$^+$-HN$_3$, 2%), 262 (M$^+$-N$_3$-N$_2$, 21%), 248 (M$^+$-2N$_3$, 25%), 235 (93%), 168 (16%), 149 ($C_7H_7N_3O^+$, 23%), 138 ($C_7H_5FNO^+$, 100%), 125 (42%)

MS (EI, 110°C): m/z = 261 (M$^+$-HN$_3$-N$_2$, 2%), 248 (M$^+$-2N$_3$, 100%), 188 (11%), 166 ($C_7H_5FN_3O^+$, 17%), 138 ($C_7H_5FNO^+$, 42%), 43 (HN_3^+, 55%)

Elemental analysis: $C_{14}H_{10}F_2N_6O_2$ (332.08 g/mol)

Calculated:	C%	50.61	H%	3.03	N%	25.29
Found:	C%	50.38	H%	3.20	N%	24.96

1,2-Diazido-1-(2-chloro-4-hydroxyphenyl)-2-(2-fluoro-4-hydroxyphenyl)ethane 91 (a mixture of two isomers)

starting from (*E*)-dihydroxystilbene **45**. The residue was separated into a mixture of two isomers by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (3 : 1) as eluent.

Yield: 286 mg (82%, R_f = 0.65, pale yellow oil, a mixture of two isomers **I** : **II** = 6 : 5)

^{1}H-NMR (DMSO-d_6): δ[ppm] = 5.26-5.37 (m, 4H, superimposed, 4CHN$_3$, **I** and **II**), 6.45 (dd, 1H, $^3J_{(H, F)}$ = 13.2Hz and ^4J = 2.2Hz, Ar'-H, **I**), 6.52 (dd, 1H, ^3J = 8.5Hz and ^4J = 2.1Hz, Ar-H, **I**), 6.59 (dd, 1H, $^3J_{(H, F)}$ = 12.4Hz and ^4J = 2.1Hz, Ar'-H, **II**), 6.64-6.75 (m, 3H, superimposed, Ar-H, Ar'-H, **I** and **II**), 6.80 (dd, 1H, ^3J = 8.6Hz and ^4J = 2.4Hz, Ar-H, **II**), 6.87 (d, 1H, ^4J = 2.4Hz, Ar-H, **II**), 7.19 (dd, 1H, ^3J = 8.7Hz and $^4J_{(H, F)}$ = 8.7Hz, Ar'-H, **I**), 7.30 (dd, 1H, ^3J = 8.6Hz and $^4J_{(H, F)}$ = 8.6Hz, superimposed, Ar'-H, **II**), 7.34 (2d, 2H, superimposed, 2Ar-H, **I** and **II**), 10.05 (s, 1H, OH, **I**), 10.08 (s, 1H, OH, **I**), 10.16 (s, 2H, 2OH, **II**)

IR (KBr): ν (cm^{-1}) = 3370s (broad, OH), 2979w, 2106s (N$_3$), 1624s, 1607s, 1503s, 1457s, 1299s, 1248s (broad), 1153s, 1098s, 1041w, 967m, 907m, 848m, 818w, 675w

MS (FAB, acetonitrile / m-NO$_2$-benzyl-OH): m/z = 371 ([M+Na]$^+$, 3%), 298 (3%), 278 (M$^+$-N$_3$-N$_2$, 13%), 264 (M$^+$-2N$_3$, 19%), 251 (65%), 182 ($C_7H_5ClN_3O^+$, 10%), 166 ($C_7H_5FN_3O^+$, 27%), 154 ($C_7H_5ClNO^+$, 78%), 138 ($C_7H_5FNO^+$, 100%)

MS (EI, 100°C): m/z = 264 (M$^+$-2N$_3$, 100%), 199 (16%), 182 ($C_7H_5ClN_3O^+$, 4%), 166 ($C_7H_5FN_3O^+$, 6%), 154 ($C_7H_5ClNO^+$, 10%), 138 ($C_7H_5FNO^+$, 13%), 43 (HN_3^+, 65%)

Elemental analysise: $C_{14}H_{10}ClFN_6O_2$ (348.05 g/mol)

Calculated:	C%	48.22	H%	2.89	N%	24.10
Found:	C%	48.57	H%	3.03	N%	23.78

1,2-Diazido-1,2-bis(2-chloro-4-hydroxyphenyl)ethane 92 (a mixture of two isomers)

starting from (*E*)-dihydroxystilbene **46**. The residue was separated into a mixture of two isomers by column chromatography on silica gel two times, respectively, firstly with a mixture of dichloromethane and isopropanol (20 : 1) as eluent, and then the obtained main fraction (R_f = 0.39) with a mixture of ligroin, dichloromethane and diethyl ether (2 : 2 : 1, R_f = 0.43) as eluent.

Yield: 157 mg (43%, pale brown oil, a mixture of two isomers **I** : **II** = 4 : 3)

^{1}H-NMR (CD$_3$OD): δ[ppm] = 5.31 (s, 2H, 2CHN$_3$, **I**), 5.37 (s, 2H, 2CHN$_3$, **II**), 6.67-6.80 (m, 8H, superimposed, 4Ar-H, 4Ar'-H, **I** and **II**), 7.15 (d, 2H, ^3J = 8.6Hz, Ar-H, Ar'-H, **II**), 7.31 (dd, 2H, ^3J = 9.2Hz and ^4J = 2.2Hz, Ar-H, Ar'-H, **I**)

IR (film): ν (cm^{-1}) = 3348m (OH), 2106s (N$_3$), 1608s, 1580m, 1498s, 1436m, 1252s, 1041m, 905m

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 387 ($[M+Na]^+$, 1%), 321 (M^+-HN_3, 1%), 294 (M^+-N_3-N_2, 8%), 280 (M^+-$2N_3$, 8%), 268 (27%), 182 ($C_7H_5ClN_3O^+$, 11%), 154 ($C_7H_5ClNO^+$, 100%)

MS (EI, 110°C): m/z = 294 (M^+-N_3-N_2, 4%), 280 (M^+-$2N_3$, 100%), 210 (43%), 182 ($C_7H_5ClN_3O^+$, 23%), 154 ($C_7H_5ClNO^+$, 82%)

Elemental analysis: $C_{14}H_{10}Cl_2N_6O_2$ (364.02 g/mol)

Calculated:	C%	46.05	H%	2.76	N%	23.01
Found:	C%	46.36	H%	3.23	N%	22.67

1,2-Diazido-1-(2,6-dichloro-4-hydroxyphenyl)-2-(2-chloro-4-hydroxyphenyl)ethane 93, 94 (*erythro* and *threo*)

starting from (*E*)-dihydroxystilbene **48**. After addition of **48**, further 2 ml of acetonitril was added. The residue was separated into two pure isomers **93** and **94** by column chromatography on silica gel with a mixture of dichloromethane and diethyl ether (3 : 1) as eluent.

***Erythro*-isomer 93**

Yield: 214 mg (46%, R_f = 0.73, white crystals); mp: 148-150°C (decompose)

^{1}H-NMR (DMSO-d_6): δ[ppm] = 5.75 (d, 1H, ^3J = 10.7Hz, CHN_3), 5.78 (d, 1H, ^3J = 10.7Hz, CHN_3), 6.90 (dd, 1H, ^3J = 8.5Hz and ^4J = 2.4Hz, Ar-H), 6.94 (d, 1H, ^4J = 2.4Hz, Ar-H), 6.98 (s, 2H, Ar'-H), 7.50 (d, 1H, ^3J = 8.5Hz, Ar-H). 10.27 (s, 1H, OH), 10.77 (s, 1H, OH)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 5.06 (broad, 1H, OH), 5.28 (broad, 1H, OH), 5.61 (d, 1H, ^3J = 10.4Hz, CHN_3), 5.90 (d, 1H, ^3J = 10.4Hz, CHN_3), 6.88 (dd, 1H, ^3J = 8.5Hz and ^4J = 2.5Hz, Ar-H), 6.94 (s, 2H, Ar'-H), 6.97 (d, 1H, ^4J = 2.5Hz, Ar-H), 7.41 (d, 1H, ^3J = 8.5Hz, Ar-H)

^{13}C-NMR (DMSO-d_6): δ[ppm] = 60.9, 63.1, 115.3, 116.1, 120.1, 130.0, 134.0, 158.7

IR (KBr): ν (cm^{-1}) = 3400s (broad, OH), 2104s (N_3), 1604s, 1573s, 1498s, 1429s, 1270s, 1255s, 1057m, 1041w, 953m, 908m, 853m, 799m, 785m, 678m

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 421 ($[M+Na]^+$, 2%), 355 (M^+-HN_3, 2%), 336 (3%), 328 (M^+-N_3-N_2, 4%), 314 (M^+-$2N_3$, 5%), 301 (23%), 216 ($C_7H_4Cl_2N_3O^+$, 4%), 188 ($C_7H_4Cl_2NO^+$, 25%), 182 ($C_7H_5ClN_3O^+$, 8%), 154 ($C_7H_5ClNO^+$, 100%)

MS (EI, 110°C): m/z = 314 (M^+-$2N_3$, 100%), 244 (62%), 215 ($C_7H_3Cl_2N_3O^+$, 14%), 188 ($C_7H_4Cl_2NO^+$, 29%), 182 ($C_7H_5ClN_3O^+$, 10%), 154 ($C_7H_5ClNO^+$, 60%)

Elemental analysis: $C_{14}H_9Cl_3N_6O_2$ (M = 397.99 g/mol)

Calculated:	C%	42.08	H%	2.27	N%	21.03
Found:	C%	42.10	H%	2.35	N%	21.05

Threo-isomer 94

Yield: 119 mg (32%, $R_f = 0.61$, white solid); mp: 135-136°C

^{1}H-NMR (DMSO-d_6): δ[ppm] = 5.67 (d, 1H, ^3J = 10.5Hz, CHN_3), 5.82 (d, 1H, ^3J = 10.5Hz, CHN_3), 6.68 (d, 1H, ^4J = 2.4Hz, Ar-H), 6.72 (dd, 1H, ^3J = 8.5Hz and ^4J = 2.1Hz, Ar-H), 6.76 (s, 2H, Ar'-H), 7.39 (d, 1H, ^3J = 8.5Hz, Ar-H), 10.13 (s, 1H, OH), 10.62 (s, 1H, OH)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 4.94 (broad, 1H, OH), 5.18 (broad, 1H, OH), 5.54 (d, 1H, ^3J = 10.4Hz, CHN_3), 5.87 (d, 1H, ^3J = 10.4Hz, CHN_3), 6.71 (m, 4H, superimposed, 2Ar-H, 2Ar'-H), 7.35 (d, 1H, ^3J = 9.3Hz, Ar-H)

^{13}C-NMR (DMSO-d_6): δ[ppm] = 62.2, 64.3, 114.7, 115.3, 115.6, 116.1, 119.3, 122.3, 130.7, 133.2, 158.3, 158.4, 158.7

IR (KBr): ν (cm^{-1}) = 3368s (OH), 2106s (N_3), 1604s, 1575s, 1499s, 1430s, 1314m, 1245s (broad), 1060m, 1040w, 953m, 908m, 855m, 820w, 802w, 785w, 674m

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 421 ($[M+Na]^+$, 5%), 355 (M^+-HN_3, 2%), 328 (M^+-N_3-N_2, 3%), 314 (M^+-2N_3, 6%), 301 (43%), 216 ($C_7H_4Cl_2N_3O^+$, 4%), 188 ($C_7H_4Cl_2NO^+$, 27%), 182 ($C_7H_5ClN_3O^+$, 9%), 154 ($C_7H_5ClNO^+$, 100%)

MS (EI, 110°C): m/z = 314 (M^+-2N_3, 100%), 244 (54%), 215 ($C_7H_3Cl_2N_3O^+$, 13%), 187 ($C_7H_3Cl_2NO^+$, 11%), 181 ($C_7H_5ClN_3O^+$, 6%), 154 ($C_7H_5ClNO^+$, 6%), 43 (HN_3^+, 54%)

Elemental analysis: $C_{14}H_9Cl_3N_6O_2$ (M = 397.99 g/mol)

Calculated:	C%	42.08	H%	2.27	N%	21.03
Found:	C%	42.25	H%	2.49	N%	20.65

1,2-Diazido-1,2-bis(2,6-dichloro-4-hydroxyphenyl)ethane 95 (_meso_)

starting from (*E*)-dihydroxystilbene **49**. After addition of **49**, further 5 ml of acetonitrile was added. The residue was separated into a pure isomer **95** by column chromatography on silica gel two times, respectively, firstly with a mixture of dichloromethane and methanol (12 : 1) as eluent into a main fraction ($R_f = 0.57$) and then with a mixture of dichloromethane and diethyl ether (3 : 1) as eluent into a pure isomer **95** ($R_f = 0.70$).

Yield: 200 mg (46%, white powder); mp: 193°C (decompose)

^{1}H-NMR (DMSO-d_6): δ[ppm] = 6.30 (s, 2H, 2CHN_3), 6.99 (s, 4H, 2Ar-H, 2Ar'-H), 10.81 (s, 2H, 2OH)

IR (KBr): ν (cm^{-1}) = 3292 (s, OH), 2106s (N_3), 1603s, 1568s, 1426s, 1268s, 1225s, 1207s, 1059s, 955s, 855m, 790m

MS (FAB, acetonitrile / DMSO / m-NO_2-benzyl-OH): m/z = 455 ($[M+Na]^+$, 2%), 385 (2%), 362 (M^+-N_3-N_2, 2%), 348 (M^+-$2N_3$, 3%), 335 (12%), 216 ($C_7H_4Cl_2N_3O^+$, 2%), 188 ($C_7H_4Cl_2NO^+$, 30%), 154 (100%)

MS (EI, 120°C): m/z = 364/362 (M^+-N_3-N_2, 23%), 350/348 (M^+-$2N_3$, 100%), 278 (35%), 188 ($C_7H_4Cl_2NO^+$, 24%)

Elemental analysis: $C_{14}H_8Cl_4N_6O_2$ (M = 431.95 g/mol)

Calculated:	C%	38.74	H%	1.86	N%	19.36
Found:	C%	38.62	H%	2.17	N%	19.02

6.1.19 Tetrasubstituted 1,2-diazidoethane 96, 97 and 3-azido-2-(4-methoxyphenyl)-1,1-diphenylprop-1-ene 99

General Procedure

To a stirred slurry of sodium azide (0.78 g, 12 mmol) in acetonitile (10 ml) was added via a syringe at –15±5°C under nitrogen a solution of iodmonochloride (1.0 g, 6 mmol) in acetonitrile (8 ml) over a period of 20 minutes. After stirring at this temperature for 1 hour, the mixture was cooled to –50°C and the corresponding 2-alkyl-1,1,2-triarylethene (3.0 mmol) was added. After stirring at –50±10°C for 4 hours, the reaction mixture was stirred at room temperature for further 20 hours and then the mixture was refluxed for 1 hours. After cooling the red-brown slurry was diluted with water and extracted with diethyl ether. The united organic phase was washed with 5% sodium thiosulfate (60 ml) and water, dried over sodium sulfate and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the pure product.

1,2-Diazido-1,1,2-tris(4-methoxyphenyl)propane 96

starting from 1,1,2-tris(4-methoxyphenyl)prop-1-ene **66** (1.08 g, 3 mol); The residue was purified by column chromatography with a mixture of ligroin and diethyl ether (3 : 1) to afford the pure product.

Yield: 1.24 g (93%, R_f = 0.48, white solid); mp: 114.5-115°C (decompose)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.87 (s, 3H, CH_3), 3.79 (s, 6H, $2OCH_3$), 3.80 (s, 3H, OCH_3), 6.66-6.80 (6H, superimposed, Ar-H), 6.97 (AA'BB', 2H, ^3J = 8.9Hz, Ar-H), 7.03-7.40 (d, broad, 4H, Ar-H)

^{1}H-NMR (DMSO-d$_6$): δ[ppm] = 1.85 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 6.74-6.84 (4H, superimposed, Ar-H), 6.87 (AA'BB', 2H, ^{3}J = 8.8Hz, Ar-H), 6.97 (AA'BB', 2H, ^{3}J = 8.7Hz, Ar-H), 7.09 (broad, 2H, Ar-H), 7.24 (broad, 2H, Ar-H)

^{1}H-NMR (DMSO-d$_6$, 60°C): δ[ppm] = 1.84 (s, 3H, CH_3), 3.73 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.76 (s, 3H, OCH_3), 6.75-6.90 (6H, superimposed, Ar-H), 6.98 (AA'BB', 2H, ^{3}J = 8.9Hz, Ar-H), 7.12 (AA'BB', 2H, ^{3}J = 7.6Hz, Ar-H), 7.22 (AA'BB', 2H, ^{3}J = 8.1Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 22.5, 55.2 (3OCH_3), 73.5, 78.2, 112.5-112.6 (3C), 129.9, 131.1, 131.6, 132.1, 132.2, 158.8-159.0 (3C)

IR (film): ν (cm^{-1}) = 3005m, 2956m, 2935m, 2908w, 2837m, 2106s (-N_3), 1608s, 1579m, 1511s, 1463m, 1441m, 1299s, 1255s, 1181s, 1035s, 831m, 759s

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 467 ($[M+Na]^+$, 0.4%), 402 (M^+-N_3, 0.2%), 388 (M^+-2N_2, 0.3%), 374 (M^+-N_3-N_2, 9%), 360 (M^+-2N_3, 5%), 333 (10%), 240 ($C_{15}H_{14}NO_2^+$, 100%), 148 ($C_9H_{10}NO^+$, 52%)

MS (EI, 100°C): m/z = 415 (M^+-N_2-H^+, 0.5%), 388 (M^+-2N_2, 6%), 360 (M^+-2N_3, 8%), 240 ($C_{15}H_{14}NO_2^+$, 100%), 210 (21%), 148 ($C_9H_{10}NO^+$, 18%), 134 ($C_9H_{10}O^+$, 31%)

Elemental analysis: $C_{24}H_{24}N_6O_3$ (444.19 g/mol)

Calculated:	C%	64.85	H%	5.44	N%	18.91
Found:	C%	64.73	H%	5.32	N%	18.85

1,2-Diazido-1,1,2-tris(4-methoxyphenyl)butane 97

starting from 1,1,2-tris(4-methoxyphenyl)prop-1-ene **67** (1.12 g, 3 mol). The residue was purified by column chromatography with a mixture of ligroin and diethyl ether (3 : 1) to afford the pure product.

Yield: 1.14 g (83%, R_f = 0.44, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 0.79 (t, 3H, CH_3), 2.22 (m, 1H, CH_2), 2.50 (m, 1H, CH_2), 3.79 (s, 6H, 2OCH_3), 3.80 (s, 3H, OCH_3), 6.70-6.80 (6H, superimposed, Ar-H), 7.01 (AA'BB', 2H, ^{3}J = 8.1Hz, Ar-H), 7.18-7.35 (4H, superimposed, Ar-H)

^{1}H-NMR (DMSO-d$_6$): δ[ppm] = 0.70 (t, 3H, CH_3), 2.31 (m, 1H, CH_2), 2.40 (m, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 6.73-6.90 (6H, superimposed, Ar-H), 7.03 (AA'BB', 2H, ^{3}J = 6.6Hz, Ar-H), 7.11-7.29 (4H, superimposed, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 8.6, 28.6, 55.2 (3OCH_3), 76.5 (2C), 112.5-112.6 (3C), 128.5, 130.8, 131.3, 131.7, 131.8, 132.1, 158.8-158.9 (3C)

IR (film): ν (cm^{-1}) = 3001w, 2957w, 2936w, 2907w, 2837w, 2106s (-N_3), 1608m, 1579w, 1510s, 1463m, 1441w, 1298m, 1254s, 1181s, 1035m, 811m, 757m

MS (FAB, acetonitrile / m-NO_2-benzyl-OH): m/z = 481 ($[M+Na]^+$, 0.7%), 403 (M^+-$2N_2$+H^+, 5%), 388 (M^+-N_3-N_2, 3%), 374 (M^+-$2N_3$, 3%), 333 (14%), 268 ($C_{15}H_{14}N_3O_2^+$, 4%), 255 (12%), 240 ($C_{15}H_{14}NO_2^+$, 100%), 190 ($C_{10}H_{12}N_3O^+$, 3%), 162 ($C_{10}H_{12}NO^+$, 71%)

MS (EI, 80°C): m/z = 402 (M^+-$2N_2$, 7%), 374 (M^+-$2N_3$, 11%), 295 (10%), 268 ($C_{15}H_{14}N_3O_2^+$, 7%), 240 ($C_{15}H_{14}NO_2^+$, 100%), 210 (19%), 190 ($C_{10}H_{12}N_3O^+$, 3%), 162 ($C_{10}H_{12}NO^+$, 15%)

Elemental analysis: $C_{25}H_{26}N_6O_3$ (458.21 g/mol)

Calculated:	C%	65.49	H%	5.72	N%	18.33
Found:	C%	65.97	H%	6.09	N%	17.94

3-Azido-2-(4-methoxyphenyl)-1,1-diphenylprop-1-ene 99

starting from 2-(4-methoxyphenyl)-1,1-diphenylprop-1-ene **75** (0.90 g, 3 mol). The residue was purified by column chromatography with a mixture of ligroin and dichloromethane (2 : 1) to afford the pure product.

Yield: 0.276 g (27%, R_f = 0.38, white solid); mp: 116.5-118.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.76 (s, 3H, OCH_3), 4.16 (s, 2H, CH_2N_3), 6.70-7.43 (m, 14H, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 54.8, 55.1, 113.7, 126.6, 127.4, 127.7, 128.5, 129.7, 130.6, 130.8, 132.2, 133.4, 141.9, 142.0, 144.4, 158.7

IR (KBr): ν (cm^{-1}) = 3076w, 3032w, 2960w, 2934w, 2840w, 2098s, 1605m, 1509s, 1289m, 1250s, 1181m, 1027m, 701s

MS (EI, 30°C): m/z = 341 (M^+, 100%), 312 (87%), 299 (M^+-N_3, 83%), 221 (29%), 191 (38%), 165 (33%), 121 (30%), 91 (20%), 28 (22%, N_2)

Elemental analysis: $C_{22}H_{19}N_3O$ (341.15 g/mol)

Calculated:	C%	77.40	H%	5.61	N%	12.31
Found:	C%	77.06	H%	5.55	N%	12.20

6.1.20 1,2,4,5-Tetraarylpentane-1,5-diones 101 - 104

General Procedure

A mixture of potassium tert-butylate (1.12 g, 0.01 mol) and the corresponding 1,2-aryl-ethenone (0.01 mol) in dry tetrahydrofuran (15 ml) was stirred at room temperature for 30 minutes. Iodomethyl methyl ether (95%, 0.9 ml, 0.01 mol) was added dropwise under stirring and nitrogen and stirred over night. Then the reaction mixture was diluted with water and extracted with diethyl ether. The combined organic phase was washed with water, dried over sodium sulfate and evaporated under vacuum. The residue was separated into two pure diastereoisomers by column chromatography on silica gel with dichloromethane as eluent. Their crystals could be obtained from a mixture of ligroin, diethyl ether and dichloromethane.

1,5-Bis(4-methoxyphenyl)-2,4-diphenylpentane-1,5-dione 101 and 102

starting from 1-(4-methoxyphenyl)-2-phenylethanone (2.26 g, 0.01 mol).

***(2R,4S)/(2S,4R)*-Isomer 101**

Yield: 1.0 g (43%, $R_f = 0.30$, colorless crystals); mp: 148-149°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 2.36 (m, 1H, CH_2), 2.95 (m, 1H, CH_2), 3.82 (s, 6H, $2OCH_3$), 4.40 (t, 2H, $^3J = 7.5$Hz, 2CH), 6.84 (AA'BB', 4H, $^3J = 8.8$Hz, Ar-H), 7.10-7.30 (m, 10H, Ar-H), 7.88 (AA'BB', 4H, $^3J = 8.8$Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3058w, 3021w, 2963w, 2934w, 2837w, 1672s, 1599s, 1574m, 1510m, 1453m, 1311m, 1262s, 1241s, 1169s, 1029m, 846m, 702m

MS (EI, 100°C): m/z = 464 (M^+, 0.14%), 360 (21%), 329 (1.21%), 242 (4.48%), 226 (3.37%), 197 (3.72%); 135 (100%)

Elemental analysis: $C_{31}H_{28}O_4$ (464.20 g/mol)

Calculated:	C%	80.15	H%	6.08
Found:	C%	80.14	H%	6.03

***(2R,4R)/(2S,4S)*-Isomer 102**

Yield: 0.54 g (23%, $R_f = 0.22$, colorless crystals); mp: 108-110°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 2.65 (t, 2H, $^3J = 7.3$Hz, CH_2), 3.77 (s, 6H, $2OCH_3$), 4.52 (t, 2H, $^3J = 7.3$Hz, 2CH), 6.76 (AA'BB', 4H, $^3J = 8.9$Hz, Ar-H), 7.15-7.35 (m, 10H, Ar-H), 7.78 (AA'BB', 4H, $^3J = 8.9$Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3059w, 3025w, 2958w, 2933w, 2838w, 1671s, 1599s, 1573m, 1509m, 1493m, 1454m, 1419m, 1312m, 1258s, 1169s, 1029m, 955m, 747m, 700m

MS (EI, 80°C): m/z = 464 (M^+, 0.4%), 360 (36%), 226 (16%), 135 (100%)

Elemental analysis: $C_{31}H_{28}O_4$ (464.20 g/mol)

Calculated:	C%	80.15	H%	6.08
Found:	C%	79.95	H%	5.95

1,2,4,5-Tetra(4-methoxyphenyl)pentane-1,5-dione 103 and 104

starting from 1,2-bis(4-methoxyphenyl)ethanone (2.56 g, 0.01 mol).

_(2R,4S)/(2S,4R)_-Isomer 103

Yield: 2.02 g (26%, $R_f = 0.32$, colorless crystals); mp: 124-125°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 2.29 (m, 1H, CH_2), 2.90 (m, 1H, CH_2), 3.74 (s, 6H, $2OCH_3$), 3.81 (s, 6H, $2OCH_3$), 4.40 (t, 2H, 2CH), 6.76 (AA'BB', 4H, ^3J = 8.7Hz, Ar-H), 6.84 (AA'BB', 4H, ^3J = 9.1Hz, Ar-H), 7.07 (AA'BB', 4H, ^3J = 8.7Hz, Ar-H), 7.88 (AA'BB', 4H, ^3J = 8.8Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 38.3, 50.0, 55.6, 55.8, 114.0, 114.7, 129.7, 130.1, 131.4, 131.9, 159.0, 163.7, 198.8

IR (KBr): ν (cm^{-1}) = 3006w, 2957w, 2934w, 2837w, 1669s, 1600s, 1574m, 1510s, 1462m, 1304m, 1252s, 1170s, 1032s, 833m, 756m

MS (EI, 60°C): m/z = 524 (M^+, 4%), 390 (17%), 256 (44%), 227 (43%), 135 (100%)

Elemental analysis: $C_{33}H_{32}O_6$ (524.22 g/mol)

Calculated:	C%	75.55	H%	6.15
Found:	C%	75.42	H%	6.28

_(2R,4R)/(2S,4S)_-Isomer 104

Yield: 4.96 g (63%, $R_f = 0.25$, colorless crystals); mp: 133-135°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 2.59 (t, 2H, CH_2), 3.77 (s, 6H, $2OCH_3$), 3.78 (s, 6H, $2OCH_3$), 4.43 (t, 2H, 2CH), 6.76 (AA'BB', 4H, ^3J = 8.8Hz, Ar-H), 6.84 (AA'BB', 4H, ^3J = 8.5Hz, Ar-H), 7.22 (AA'BB', 4H, ^3J = 8.5Hz, Ar-H), 7.77 (AA'BB', 4H, ^3J = 8.8Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 38.1 (CH_2), 49.8 (CH), 55.2 (OCH_3), 55.4 (OCH_3), 113.6, 114.3, 129.5, 129.6, 130.9, 131.5, 158.6, 163.2, 198.4

IR (KBr): ν (cm^{-1}) = 3006w, 2957w, 2934w, 2837w, 1669s, 1600s, 1574m, 1510s, 1462m, 1304m, 1253s, 1169s, 1032s, 834m, 756m

MS (EI, 60°C): m/z = 524 (M^+, 3%), 390 (10%), 256 (50%), 227 (41%), 135 (100%)

Elemental analysis: $C_{33}H_{32}O_6$ (524.22 g/mol)

Calculated:	C%	75.55	H%	6.15
Found:	C%	75.34	H%	6.07

6.1.21 1,2,3,5-Tetraarylcyclopent-1-enes 106 - 108

General Procedure

Titanium tetrachloride (0.33 ml, 3 mmol)) was added via a syringe dropwise to a stirred suspension of zinc power (0.39 g, 6 mmol) in dry tetrahydrofuran (10 ml) at –10°C (icepropanol-bath) under nitrogen. The resulting yellow-dark mixture was stirred at room temperature for 30 minutes and then heated under reflux for 1 hour. The dark suspension was cooled to room temperature and a solution of the corresponding diketone (1 mmol) in tetrahydrofuran (5 ml) was added. The reaction mixture was refluxed under dry nitrogen atmosphere for 4 hours. After cooling to room temperature, the mixture was poured into ice-water and extracted with diethyl ether. The united organic phase was washed with water, dried over sodium sulfate and evaporated. The residue was treated with a suitable solvent (see each product) to give the pure desired product.

***(3R,5S)/(3S,5R)*-1,2-Bis(4-methoxyphenyl)-3,5-diphenylcyclopent-1-ene 106**

starting from 1,5-bis(4-methoxyphenyl)-2,4-diphenylpentane-1,5-dione **101** (0.46 g, 1 mmol). The residue was stirred in 10 ml ligroin under reflux until to fine crystals. After cooling the precipitate was collected by suction filtration, washed with a little ligroin and dried under vacuum to afford pure **106**.

Yield: 0.39 g (90%, white crystals); mp: 134-136°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 2.02 (m, 1H, CH_2), 3.14 (m, 1H, CH_2), 3.68 (s, 6H, $2OCH_3$), 4.36 (t, 2H, ^3J = 8.5Hz, 2CH), 6.56 (AA'BB', 4H, ^3J = 8.9Hz, Ar-H), 6.82 (AA'BB', 4H, ^3J = 8.9Hz, Ar-H), 7.15 (m, 2H, Ar-H), 7.20-7.29 (m, 8H, Ar-H)

IR (KBr): ν (cm^{-1}) = 3056w, 3024w, 2953w, 2934w, 2834w, 1604s, 1509s, 1454m, 1289s, 1248s, 1178s, 1032, 833s, 757m, 703s

MS (EI, 130°C): m/z = 432 (M^+, 100%), 355 (13%, $M^+-C_6H_5$), 341 (33%, $M^+-CH_2C_6H_5$), 314 (12%), 177 (11%), 121 (15%), 91 (11%)

Elemental analysis: $C_{31}H_{28}O_2$ (432.21 g/mol)

Calculated: C% 86.08 H% 6.52

Found: C% 85.57 H% 6.96

***(3R,5R)/(3S,5S)*-1,2-Bis(4-methoxyphenyl)-3,5-diphenylcyclopent-1-ene 107**

starting from 1,5-bis(4-methoxyphenyl)-2,4-diphenylpentane-1,5-dione **102** (0.46 g, 1 mmol). The residue was stirred in 10 ml methanol until to fine crystals. The precipitate was collected by suction filtration, washed with a little methanol and dried under vacuum to afford pure **107**.

Yield: 0.35 g (81%, white crystals); mp: 131-132°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 2.50 (t, 2H, ^3J = 7.0Hz, CH_2), 3.70 (s, 6H, $2OCH_3$), 4.55 (t, 2H, ^3J = 7.0Hz, 2CH), 6.62 (AA'BB', 4H, ^3J = 8.6Hz, Ar-H), 7.00 (AA'BB', 4H, ^3J = 8.8Hz, Ar-H), 7.11 (m, 2H, Ar-H), 7.18-7.23 (m, 8H, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 44.6 (CH_2), 54.9 (CH), 55.0 (OCH_3), 113.3, 126.0, 127.9, 128.4, 129.6, 130.2, 140.8, 145.1, 158.0

IR (KBr): ν (cm^{-1}) = 3058w, 3024m, 2999w, 2954m, 2932m, 2835m, 1604s, 1509s, 1492m, 1453m, 1290s, 1248s, 1178s, 1034s, 833s, 759m, 701s

MS (EI, 170°C): m/z = 432 (M^+, 100%), 355 (12%, M^+-C_6H_5), 341 (27%, M^+-$CH_2C_6H_5$), 311 (10%), 177 (15%), 121 (12%), 91 (10%)

Elemental analysis: $C_{31}H_{28}O_2$ (432.21 g/mol)

Calculated:	C%	86.08	H%	6.52
Found:	C%	85.87	H%	6.36

_(3R,5S)/(3S,5R)_-1,2,3,5-Tetra(4-methoxyphenyl)cyclopent-1-ene 108

starting from 1,2,4,5-tetra(4-methoxyphenyl)pentane-1,5-dione **103** (0.52 g, 1 mmol). The residue was stirred in a mixture of ligroin (10 ml) and diethyl ether (2 ml) under reflux until to fine crystals. After cooling the precipitate was collected by suction filtration, washed with a little of the same mixture and dried under vacuum to afford pure **108**.

Yield: 0.46 g (93%, white crystals); mp: 141-142.5°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 1.95 (m, 1H, CH_2), 3.09 (m, 1H, CH_2), 3.68 (s, 6H, $2OCH_3$), 3.77 (s, 6H, $2OCH_3$), 4.28 (t, 2H, ^3J = 8.3Hz, 2CH), 6.57 (AA'BB', 4H, ^3J = 8.7Hz, Ar-H), 6.80 (2AA'BB', 8H, ^3J = 8.5 and 8.7Hz, superimposed, Ar-H), 7.16 (AA'BB', 4H, ^3J = 8.5Hz, Ar-H)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 44.0, 54.3, 54.9, 55.2, 113.1, 113.7, 129.3, 130.2, 130.4, 137.8, 141.2, 157.8 (d)

IR (KBr): ν (cm^{-1}) = 3030w, 2999w, 2953m, 2934m, 2906m, 2834m, 1607s, 1510s, 1463m, 1442m, 1288m, 1248s, 1177s, 1108w, 1035s, 830s

MS (EI, 130°C): m/z = 492 (M^+, 100%), 384 (24%, M^+-$C_6H_5OCH_3$), 371 (62%, M^+-$CH_2C_6H_5OCH_3$), 253 (17%), 152 (23%), 227 (13%), 192 (13%), 145 (10%), 121 (26%)

Elemental analysis: $C_{33}H_{32}O_4$ (492.23 g/mol)

Calculated:	C%	80.46	H%	6.55
Found:	C%	80.25	H%	6.39

6.1.22 2,3,5-Triarylfuran 109 and 110

General Procedure

A mixture of the corresponding 1,2,4,5-tetraarylpentane-1,5-dione, $FeCl_3 \cdot 6H_2O$ (or iodine) and sodium acetate in acetic acid was refluxed for 24 hours. After cooling the mixture was diluted with water and extracted with dichloromethane. The united organic phase was washed with water, dried over sodium sulfate and evaporated under vacuum. The residue was separated into the desired 2,3,5-triarylfuran by column chromatography on silica gel.

2-(4-Methoxyphenyl)-3,5-diphenylfuran 109

starting from 1,5-bis(4-methoxyphenyl)-2,4-diphenylpentane-1,5-dione **102** (93 mg, 0.2 mmol), $FeCl_3 \cdot 6H_2O$ (108 mg, 0.4 mmol), sodium acetate (50 mg, 0.6 mmol) and acetic acid (4 ml). The residue was separated into the desired compound **109** by column chromatography with a mixture of dichloromethane and ligroin (5 : 1) as eluent.

Yield: 40 mg (61%, $R_f = 0.84$, colorless oil)

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.82 (s, 3H, OCH_3), 6.81 (s, 1H, furan-H), 6.85 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 7.25-7.50 (m, 8H, Ar-H), 7.54 (AA'BB', 2H, ^3J = 8.9Hz, Ar-H), 7.74 (2H, Ar-H)

MS (EI, 110°C): m/z = 326 (M^+, 100%), 311 (M^+-CH_3, 28%), 297 (8%), 221 (7%), 163 (7%), 105 (12%), 77 (10%)

Elemental analysis: $C_{23}H_{18}O_2$ (326.13 g/mol)

Calculated:	C%	84.64	H%	5.56
Found:	C%	84.56	H%	5.80

2,3,5-Tris(4-methoxyphenyl)furan 110

1) starting from 1,2,4,5-tetra(4-methoxyphenyl)pentane-1,5-dione (**103** or **104** or their mixture, 4.96 g, 9.45 mmol), $FeCl_3 \cdot 6H_2O$ (5.05 g, 18.7 mmol), sodium acetate (2.34 g, 28.5 mmol) and acetic acid (187 ml). After separation by column chromatography with dichloromethane as eluent, the product was recrystallized from ligroin.

Yield: 1.48 g (41%, colorless crystals); mp: 112-113°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.81 (s, 3H, OCH_3), 3.84 (s, 6H, $2OCH_3$), 6.63 (s, 1H, furan-H), 6.84 (AA'BB', 2H, ^3J = 8.9Hz, Ar-H), 6.91 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 6.94 (AA'BB', 2H, ^3J = 8.9Hz, Ar-H), 7.36 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 7.52 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 7.66 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3433m, 3001w, 2957w, 2931w, 2836w, 1602m, 1503s, 1462m, 1297m, 1248s, 1177m, 1030m, 835m

MS (EI, 35°C): m/z = 386 (M^+, 100%), 371 (M^+-CH_3, 22%), 193 (11%), 135 (87%)

Elemental analysis: $C_{25}H_{22}O_4$ (386.15 g/mol)

Calculated: C% 77.70 H% 5.74

Found: C% 77.63 H% 5.89

2) starting from 1,2,4,5-tetra(4-methoxyphenyl)pentane-1,5-dione (a mixture of **103** and **104**, 0.525 g, 1.0 mmol), iodine (0.508 g, 2.0 mmol), sodium acetate (0.328 g, 4.0 mmol) and acetic acid (10 ml). Before washing with water, the extract was washed first with 5% sodium thiosulfate. After separation by column chromatography with dichloromethane as eluent, the product was recrystallized from ligroin.

Yield: 0.169 g (43.7%, colorless crystals); Data of analysis as described hereinabove.

6.1.23 2-Methoxy-5-[2,5-bis(4-methoxyphenyl)furan-3-yl]benzaldehyde 113

To a stirred solution of 2,3,5-tris(4-methoxyphenyl)furan **110** (1.48 g, 3.83 mmol) in dry dichloromethane (20 ml) were added carefully via syringe at 0°C titanium tetrachloride (1,36 ml, 12.35 mmol) and dichloromethyl methyl ether (0.68 ml, 7.66 mmol). After stirring at this temperature for 1 hour, the reaction mixture was hydrolyzed by adding chopped ice and then was extracted with dichloromethane. The united organic phase was washed with water, dried over sodium sulfate and evaporated under vacuum .The residue was separated by column chromatography on silica gel with a mixture of ligroin and diethyl ether (1 : 1) as eluent to obtain **113**, which crystallized out as colorless (also pale-yellow in some cases) needles from this mixture after removal of some diethyl ether in vacuum.

Yield: 0.79 g (50%, $R_f = 0.41$, colorless needles); mp: 158-160°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.85 (2s, 6H, $2OCH_3$), 3.93 (s, 3H, OCH_3), 6.63 (s, 1H, furan-H), 6.84-6.98 (5H, superimposed, Ar-H), 7.34 (AA'BB', 2H, ^3J = 8.7Hz, Ar-H), 7.62-7.72 (3H, superimposed, Ar-H), 8.15 (d, 1H, ^4J = 2.3Hz, Ar-H), 10.45 (s, 1H, CHO)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 55.3, 55.4, 55.8, 107.9, 111.7, 113.9, 114.2, 123.5, 123.8, 124.6, 124.9, 125.3, 126.2, 126.4, 129.7, 133.2, 145.6, 152.6, 158.9, 159.2, 160.8, 189.5 (CHO)

MS (EI, 250°C): m/z = 414 (M^+, 100%), 399 (M^+-CH_3, 5%), 385 (M^+-CHO, 6%), 371 (M^+-CH_3-CO, 11%)

Elemental analysis: $C_{26}H_{22}O_5$ (414.15 g/mol)

Calculated: C% 75.35 H% 5.35

Found: C% 75.35 H% 5.41

6.1.24 4,5-Diaryl-2-{5-[2,5-diarylfuran-3-yl]-2-aryl}-1H-imidazoles 117 - 119

General Procedure

A mixture of 5-[2,5-bis(4-methoxyphenyl)furan-3-yl]-2-methoxybenzaldehyde **113** (100 mg, 0.24 mmol), the corresponding benzil (0.24 mmol) and ammonium acetate (140 mg, 1.80 mmol) in acetic acid (6 ml, 0.11 mmol) was refluxed for 24 hours. After cooling the reaction mixture was diluted with 6 ml of water and was neutralized with a solution of 25% ammonia (10 ml, 0.13 mmol). The resulting suspension was stirred until the precipitate became hardend. Then the precipitate was isolated by suction filtration, washed with water and dried at 75°C under vacuum. The dried solid was refluxed in 3 ml of isopropanol for 30 minutes. After short cooling the precipitate was isolated by suction filtration, washed with 2 ml of isopropanol and dried under vacuum to afford the pure product.

4,5-Bis(4-methoxyphenyl)-2-{5-[2,5-bis(4-methoxyphenyl)furan-3-yl]-2-methoxyphenyl}-1H-imidazole 117

Corresponding benzil: 4,4'-dimethoxybenzil (65 mg, 0.24 mmol).

Yield: 132 mg (83%, white solid); mp: 192-194°C

^{1}H-NMR ($CDCl_3$): δ[ppm] = 3.82 (s, 9H, 3OCH_3), 3.84 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.63 (s, 1H, furan-H), 6.81-6.99 (9H, superimposed, Ar-H), 7.37 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 7.40-7.52 (5H, superimposed, Ar-H), 7.71 (AA'BB', 2H, ^3J = 8.6Hz, Ar-H), 8.68 (s, 1H, Ar-H), 10.50 (broad, 1H, NH)

^{13}C-NMR ($CDCl_3$): δ[ppm] = 55.19, 55.27, 55.32, 55.35, 55.09, 107.96, 111.18, 113.65, 114.03, 114.16, 114.21, 114.34, 123.68, 123.72, 125.24, 125.28, 125.49, 126.58, 126.71, 127.83, 128.58, 128.98, 129.33, 129.78, 132.39, 142.42, 146.11, 152.45, 154.95, 158.86, 159.11, 159.20

IR (KBr): ν (cm^{-1}) = 3426m (NH), 3037w, 2998w, 2936m, 2907w, 2834m, 2041w, 1613m, 1528m, 1499s, 1465m, 1441m, 1293m, 1248s, 1176s, 1031s, 834s

MS (EI): m/z = 664 (M^+, 100%), 332 (60%)

Elemental analysis: $C_{42}H_{36}N_2O_6$ (664.26 g/mol)

Calculated: C% 75.89 H% 5.46 N% 4.21

Found: C% 75.77 H% 5.32 N% 4.32

4,5-Bis(4-fluorophenyl)-2-{5-[2,5-bis(4-methoxyphenyl)furan-3-yl]-2-methoxyphenyl}-1H-imidazole 118

Corresponding benzil: 4,4'-difluorobenzil (59 mg, 0.24 mmol).

Yield: 0.12 g (78%, off-white solid), mp: 198-199°C

^{1}H-NMR (CDCl$_3$): δ[ppm] = 3.83 (s, 3H, OCH$_3$), 3.84 (s, 3H, OCH$_3$), 4.00 (s, 3H, OCH$_3$), 6.64 (s, 1H, furan-H), 6.86-7.10 (9H, superimposed, Ar-H), 7.39 (AA'BB', 2H, ^{3}J = 8.6Hz, Ar-H), 7.43-7.55 (5H, superimposed, Ar-H), 7.70 (AA'BB', 2H, ^{3}J = 8.7Hz, Ar-H), 8.67 (d, 1H, ^{4}J = 1.6Hz, Ar-H), 10.65 (broad, 1H, NH)

IR (KBr): ν (cm^{-1}) = 3431m (NH), 3038w, 2998w, 2936w, 2908w, 2836w, 2040w, 1889w, 1610m, 1597m, 1528m, 1499s, 1466m, 1441m, 1300m, 1246s, 1176m, 1031s, 836s, 813m

MS (EI, 250°C): m/z = 640 (M$^+$, 100%), 622 (M$^+$-F, 18%), 320 (29%)

Elemental, analysis: $C_{40}H_{30}F_2N_2O_4$ (640.22 g/mol)

Calculated:	C%	74.99	H%	4.72	N%	4.37
Found:	C%	75.00	H%	4.61	N%	4.58

4,5-Bis(2-chlorophenyl)-2-{5-[2,5-bis(4-methoxyphenyl)furan-3-yl]-2-methoxyphenyl}-1H-imidazole 119

Corresponding benzil: 2,2'-dichlorobenzil (67 mg, 0.24 mmol).

Yield: 0.13 g (81%, off-white solid); mp: 251-252°C

^{1}H-NMR (CDCl$_3$): δ[ppm] = 3.83 (s, 3H, OCH$_3$), 3.84 (s, 3H, OCH$_3$), 4.05 (s, 3H, OCH$_3$), 6.64 (s, 1H, furan-H), 6.86-6.98 (5H, superimposed, Ar-H), 7.14-7.48 (13H, superimposed, Ar-H), 7.74 (AA'BB', 2H, ^{3}J = 8.7Hz, Ar-H), 8.86 (s, 1H, Ar-H), 11.60 (broad, 1H, NH)

IR (KBr): ν (cm^{-1}) = 3412m (NH), 3059w, 3002w, 2938m, 2907w, 2836m, 2042w, 1885w, 1616m, 1596m, 1509s, 1499s, 1474s, 1455s, 1440m, 1301m, 1279m, 1250s, 1175s, 1107m, 1033s, 834s, 815s, 759s

MS (EI, 250°C): m/z = 672 (M$^+$, 100%), 638 (M$^+$-Cl, 12%), 414 (14%), 336 (21%)

Elemental analysis: $C_{40}H_{30}Cl_2N_2O_4$ (672.16 g/mol)

Calculated:	C%	71.32	H%	4.49	N%	4.16
Found:	C%	71.09	H%	4.44	N%	4.14

6.1.25 4,5-Diaryl-2-{5-[2,5-diarylfuran-3-yl]-2-aryl}-1H-imidazole 120 and 121

The methyl ether protected compound **117** (130 mg, 0.2 mmol) was dissolved in dry dichloromethane (10 ml) and cooled to –50°C. At this temperature boron tribromide (0.20

ml, 2.1 mmol) was added via a syringe under nitrogen and stirred for 2 hours. Then the reaction mixture was allowed to warm to room temperature and stirred for further 24 hours. After cooling at –10°C, methanol (10 ml) was added dropwise and stirred at room temperature for 3 hours. The resulting mixture was evaporated under vacuum. The residue was first separated by column chromatography on silica gel with acetone as eluent to obtain a mixture, which was then separated by column chromatography with a mixture of diethyl ether and tetrahydrofuran (5 : 1) as eluent into pure **120** ($R_f = 0.63$) and **121** ($R_f = 0.50$).

4,5-Bis(4-hydroxyphenyl)-2-{5-[2,5-bis(4-hydroxyphenyl)furan-3-yl]-2-methoxyphenyl}-1H-imidazole 120

Yield: 25 mg (21%, yellow powder); mp: >300°C

^{1}H-NMR (CD_3OD): δ[ppm] = 3.83 (s, 3H, OCH_3), 6.75 (s, 1H, furan-H), 6.76-7.01 (9H, superimposed, Ar-H), 7.23-7.40 (7H, superimposed, Ar-H), 7.77 (AA'BB', 2H, ^3J = 8.9Hz, Ar-H), 8.23 (d, 1H, J = 2.1Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3428s (broad, OH, NH), 2953w, 1616s, 1502s, 1440m, 1383m, 1249s, 1174s, 834s

MS (EI, 340°C): m/z = 608 (M^+, 100%), 593 (M^+-CH_3, 10%), 304 (24%)

Elemental analysis: $C_{38}H_{28}N_2O_6$ (608.19 g/mol)

Calculated: C% 74.99 H% 4.64 N% 4.60

Found: C% 74.84 H% 4.62 N% 4.49

4,5-Bis(4-hydroxyphenyl)-2-{5-[2,5-bis(4-hydroxyphenyl)furan-3-yl]-2-hydroxyphenyl}-1H-imidazole 121

Yield: 74 mg (62%, yellow powder); mp: >300°C

^{1}H-NMR (CD_3OD): δ[ppm] = 6.69 (s, 1H, furan-H), 6.74-6.93 (9H, superimposed, Ar-H), 7.23-7.40 (7H, superimposed, Ar-H), 7.68 (AA'BB', 2H, ^3J = 8.8Hz, Ar-H), 8.21 (d, 1H, J = 2.10Hz, Ar-H)

IR (KBr): ν (cm^{-1}) = 3407s (broad, OH, NH), 2958w, 1614s, 1502s, 1435m, 1383m, 1251s, 1172s, 834s

MS (EI, 360°C): m/z = 594 (M^+, 100%), 344 (12%), 297 (31%), 121 (11%), 94 (10%)

Elemental analysis: $C_{37}H_{26}N_2O_6$ (594.18 g/mol)

Calculated: C% 74.74 H% 4.41 N% 4.71

Found: C% 74.56 H% 4.62 N% 4.35

6.2 Pharmacological Tests

The pharmacological tests* were performed to study the transcriptional activation of the novel compounds in luciferase assays with the MCF-7-2a cells according to the known procedure that was represented as following [Gust, 150] and so that the agonistic / antagonistic effects of the tested compounds in this luciferase assay system were evaluated (see also chapter 4.1 and 4.2).

6.2.1 Biochemicals, chemicals and materials

Dextran, 17ß-estradiol, L-glutamine (L-glutamine solution: 29.2 mg/ml PBS) and Minimum Essential Medium Eagle (EMEM) were purchased from Sigma (Munich, Germany); Dulbecco's Modified Eagle Medium without phenol red (DMEM) from Gibco (Eggenstein, Germany); Fetal calf serum (FCS) from Bio whittaker (Verviers, Belgium); N-Hexamethylpararosaniline (crystal violet) and gentamycin sulfate from Fluka (Deisenhofen, Germany); Glutardialdehyde (25%) from Merck (Darmstadt, Germany); Trypsin (0.05%) in ethylenediaminetetraacetic acid (0.02%) (trypsin/EDTA) from Boehringer (Mannheim, Germany); Penicillin-streptomycin gold standard (10000 IE penicillin/mL, 10 mg streptomycin/mL) and geneticin disulfate (geneticin solution: 35.71 mg/mL PBS) from ICN Biomedicals GmbH (Eschwege, Germany); Norit A (charcoal) from Serva (Heidelberg, Germany); Cell culture lysis reagent (5×) (diluted 1:5 with purified water before use) and the luciferase assay reagent from Promega (Heidelberg, Germany); $CDCl_3$, and [D_6]-DMSO from Aldrich (Steinheim, Germany); Phosphate buffered saline (PBS) was prepared by dissolving 8.0 g NaCl, 0.2 g KCI, 1.44 g $Na_2HPO_4 \times 2\ H_2O$ and 0.2 g KH_2PO_4 (all purchased from Merck or Fluka) in 1000 mL of purified water. Deionized water - produced by means of a Millipore Milli-Q Water System, resistance > 18 MΩ. T-75 flasks, reaction tubes and 96-well plates were purchased from Renner GmbH (Dannstadt, Germany).

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* The tests were accomplished by technical assistant S. Bergmann.

6.2.2 Cell lines and growth conditions

MCF-7-2a cells were maintained as a monolayer culture at 37°C in a humidified atmosphere (95% air, 5% CO_2) in T-75 flasks using phenol red free DMEM supplemented with penicillin/streptomycin 1% (V/V), L-glutamine (2 mM), FCS 5% (V/V) and geneticin solution 0.5% (V/V) as growth media. Cell line banking and quality control were performed according to the seed stock concept reviewed by Hay [Hay, 177].

6.2.3 Transcriptional binding assay, luciferase assay

One week before starting the experiment, MCF-7-2a cells were cultivated in DMEM supplemented with L-glutamine, antibiotics, and dextran/charcoal-treated FCS (ct-DMEM, 5 % V/V). Cells from an almost confluent monolayer were removed by trypsinization and suspended in ct-DMEM to approximately 5×10^4 cells/mL. 100 µL of the cell suspension was seeded in the sixty inner wells of a white flat-bottomed 96-well plate (suitable for measuring luminescence). The border wells were filled with 200 µL of isoosmotic liquid (medium, PBS, e.g.) in order to avoid boundary problems. After 24 hours, the media was replaced by 180 µL of ct-DMEM and 20 µL of medium containing either E2 or the test compounds in appropriate amounts to achieve final concentrations ranging from 10^{-7} to 10^{-12} M (E2) or 10^{-5} to 10^{-10} M (test compounds). The concentration of the solvent (ethanol abs.) used to prepare stock solutions amounts to 0.1% (V/V).

After 50 hours of incubation under growth conditions, the medium was removed and 50 µL of cell culture lysis reagent was added into each well. The plate was incubated at roomtemperature under vigorous shaking (600 rpm, TiMix, Thistle Scientific Uddingston, Glasgow, Scotland). Luciferase was assayed using the Promega luciferase assay reagent. 50 µL of substrate reagent was added into each well and luminescence (in relative light units, RLU) was measured for 10 seconds by use of a microlumat (Bethold Technologies, Bad Wildungen, Germany). Measurements were corrected correlating the RLU with the cell mass of each sample.

The cell mass was determined in a crystal violet assay [Gillies, 178; Kueng, 179] in crystal flat-bottomed 96-well plates analogously to the transactivation assay. After incubation for 50 hours, the medium was removed and glutaric dialdehyde (1% in PBS; 100 µL/well) was added for fixation. After 15 minutes the solution of the aldehyde was replaced by 180 µL

PBS/well. The plates were stored at 4 °C until staining. Cells were stained treating them for 30 minutes with 100 µL of an aqueous solution of crystal violet (0.02% (m/V)). After decanting, cells were washed several times with water to remove the adherent dye. After addition of 180 µL of ethanol (70% (V/V)), plates were gently shaken for 4 hours. Optical density of each well was measured in a microplate autoreader at 590 nm (Fash scan, Jena Analytik, Jena, Germany).

The estrogenic activity was expressed as % activation of a 10^{-9} M E2 control (100%). The determined and calculated gene activation by all of the tested compounds are summarized in table 21 and 22.

The antiestrogenic activity was determined by incubation of the MCF-7-2a cells with the test compounds in concentrations from 10^{-5}-10^{-10} M along with a constant concentration of E2 (10^{-9} M). The gene activation (%) by the corresponding compounds with E2 of 10^{-9} M are summarized in table 23 and table 24.

Table 21. Transcriptional Activation (%) by the tested Compounds in a Concentration Range of 10^{-10} - 10^{-5} M in Luciferase Assays with MCF-7-2a Cells.
The Activity of E2 (10^{-8} M) was set as 100%. (Test for Agonistic Effect)

	Activation (%) of the tested Compound in a Concentration Range (mol/l)					
	10^{-10}	**10^{-9}**	**10^{-8}**	**10^{-7}**	**10^{-6}**	**10^{-5}**
33	-0.25	-0.93	-0.69	8.93	58.31	102.55
34	-0.24	0.63	0.74	27.09	162.43	153.54
35	4.25	5.96	18.76	21.52	95.57	178.13
36	-2.73	0.70	2.71	0.47	33.28	65.40
37	10.35	-8.09	-0.86	5.70	8.86	75.47
38	6.50	-3.99	4.43	9.42	83.58	148.70
39	8.29	-1.41	-4.58	29.62	97.64	186.17
40	-11.84	-7.29	-13.86	39.60	92.07	47.22
41	-5.29	-4.15	-4.31	7.50	118.94	133.21
42	6.76	9.21	-0.08	13.02	43.88	167.55
43	10.82	9.63	15.10	72.81	130.83	343.74
44	-0.86	-2.09	5.31	60.01	212.51	385.08
45	5.70	-9.19	4.09	18.59	83.65	245.49
46	-0.06	1.80	9.37	46.36	96.55	121.57
47	9.74	21.18	-3.30	35.20	74.81	33.27
48	14.63	20.55	12.66	24.78	35.54	33.36
49	6.99	20.57	25.93	51.34	82.30	21.19
50	1.35	2.09	4.34	4.55	155.85	312.16
51	3.78	4.79	-1.54	4.4	49.18	426.23
54	6.71	4.61	2.53	11.84	39.39	47.13
55	12.47	5.97	15.93	38.02	60.02	65.38
76	6.58	6.37	1.95	-3.78	-6.07	-10.12
79	5.45	3.59	3.59	-0.80	19.44	6.70
80	3.47	2.73	-9.27	-2.81	5.14	1.66
99	9.76	7.31	-0.23	7.76	28.01	17.01

Table 22. Transcriptional Activation (%) by the tested Compounds in a Concentration Range of 10^{-10} - 10^{-5} M in Luciferase Assays with MCF-7-2a Cells. The Activity of E2 (10^{-8} M) was set as 100%. (Test for Agonistic Effect)

	Activation (%) by the tested Compound in a Concentration Range (mol/l)					
	10^{-10}	**10^{-9}**	**10^{-8}**	**10^{-7}**	**10^{-6}**	**10^{-5}**
81	2.51	0.51	1.33	-0.65	0.10	10.31
82	15.53	9.30	8.46	14.66	16.23	36.16
83	0.37	2.79	3.43	2.72	24.58	64.35
84	11.71	10.84	8.83	15.44	26.86	20.64
85	1.94	2.55	5.78	7.52	10.46	13.26
86	-1.08	3.36	1.14	3.62	31.29	128.59
87	14.14	13.70	10.57	18.21	35.81	52.37
88	42.66	27.93	16.61	24.69	76.69	73.00
89	2.12	1.75	6.03	16.16	68.19	123.9
90	3.71	2.19	6.60	37.10	78.88	101.26
91	-0.98	3.61	8.26	22.10	77.80	114.65
92	-8.20	-0.95	9.74	31.98	65.26	86.88
93	1.36	6.05	14.34	60.92	100.97	81.18
94	3.48	4.11	7.7	40.03	61.13	37.53
95	11.47	10.29	15.66	59.77	77.62	142.69
96	9.29	-5.66	-4.36	0.55	-5.03	-13.02
97	7.27	2.99	-0.11	-1.42	0.66	3.97
106	6.28	0.67	3.19	4.39	16.84	27.03
107	6.75	1.34	0.31	-0.32	0.31	11.96
108	2.11	4.31	-2.82	0.10	-9.47	-14.34
117	6.98	11.93	6.85	26.41	46.11	92.39
118	-8.14	-7.22	-4.88	-2.82	33.62	55.00
119	0.11	3.48	10.26	5.04	3.38	2.61
120	2.28	-0.65	-2.57	2.83	17.58	-5.54
121	3.09	-2.70	-3.22	3.04	19.39	-16.23

Table 23. Transcriptional Activation (%) by the tested Compounds in a Concentration Range of 10^{-10} - 10^{-5} M separately with 10^{-9} M of E2 in Luciferase Assays with MCF-7-2a Cells. (Test for Antagonistic Effect)

	Activation (%) of the tested Compound with E2 of 10^{-9} M in a Concentration Range (mol/l)					
	10^{-10}	**10^{-9}**	**10^{-8}**	**10^{-7}**	**10^{-6}**	**10^{-5}**
33	113.41	116.61	101.38	113.17	187.93	174.66
34	82.25	99.59	97.69	90.47	150.63	149.33
35	130.91	97.59	90.67	96.57	79.02	92.92
36	124.42	122.92	116.21	100.59	93.15	55.73
37	123.00	128.63	115.98	103.56	90.64	61.04
38	131.39	116.07	111.93	112.25	113.21	149.20
39	110.01	111.41	111.05	102.96	118.91	128.67
40	120.54	144.07	102.30	123.26	117.98	122.24
41	109.23	90.44	112.51	118.88	96.27	161.74
42	86.48	87.50	84.32	87.16	91.84	354.13
43	144.14	146.66	138.07	140.61	152.95	330.10
44	75.58	76.49	80.37	78.97	90.42	397.88
45	75.85	74.67	89.33	82.26	106.20	341.72
46	74.04	86.11	85.89	76.93	85.96	349.69
47	87.60	83.74	84.99	93.99	94.83	198.12
48	84.55	86.92	102.95	82.61	99.66	211.99
49	73.30	68.92	88.58	105.42	96.33	181.61
50	126.19	141.11	122.17	116.24	138.94	292.60
51	112.55	128.99	118.09	106.92	108.78	400.67
54	113.59	99.26	115.12	93.68	97.01	77.00
55	125.80	116.05	99.15	83.21	69.37	53.57
76	96.18	89.58	104.74	99.88	26.76	-12.51
79	96.55	83.54	70.27	50.05	16.79	-6.29
80	107.65	108.30	79.37	74.06	38.75	22.76
99	125.32	117.43	132.88	109.45	98.86	25.09

Table 24. Transcriptional Activation (%) by the tested Compounds in a Concentration Range of 10^{-10} - 10^{-5} M separately with 10^{-9} M of E2 in Luciferase Assays with MCF-7-2a Cells. (Test for Antagonistic Effect)

	Activation (%) of the tested Compound with E2 of 10^{-9} M in a Concentration Range (mol/l)					
	10^{-10}	**10^{-9}**	**10^{-8}**	**10^{-7}**	**10^{-6}**	**10^{-5}**
81	65.77	69.04	83.57	74.03	104.76	80.80
82	65.62	75.76	90.24	75.81	93.45	73.26
83	104.38	95.78	117.37	122.39	109.87	100.35
84	137.84	100.40	118.17	116.12	124.57	99.24
85	121.89	126.52	139.87	150.51	135.24	141.21
86	98.65	74.29	69.22	53.75	49.05	34.99
87	111.38	91.83	81.83	70.75	69.22	51.82
88	235.30	201.54	186.81	188.49	144.95	109.57
89	120.20	120.62	126.63	107.09	96.24	131.56
90	93.39	82.38	86.11	79.71	80.59	75.72
91	136.28	120.7	121.62	107.41	116.99	145.55
92	160.52	134.3	128.42	104.34	98.46	102.82
93	126.54	118.38	107.56	127.33	96.96	66.66
94	111.77	109.68	140.28	91.97	91.86	47.34
95	128.20	108.73	114.83	108.46	106.85	135.40
96	145.97	103.79	83.33	71.85	50.87	18.15
97	115.84	98.28	103.19	89.25	83.79	70.44
106	115.92	126.21	106.50	124.48	101.37	92.05
107	106.99	114.90	114.11	129.69	104.73	93.52
108	123.60	124.79	120.00	112.86	95.34	47.86
117	143.79	131.40	114.91	105.09	100.50	83.49
118	124.32	128.67	122.44	97.70	89.80	82.38
119	133.88	119.84	125.61	97.82	90.22	72.88
120	114.57	85.12	101.31	110.64	86.51	-13.54
121	145.09	144.39	108.35	89.97	57.13	126.53