Synthesis of Symmetrically Substituted 2,6-Diphenylphenols

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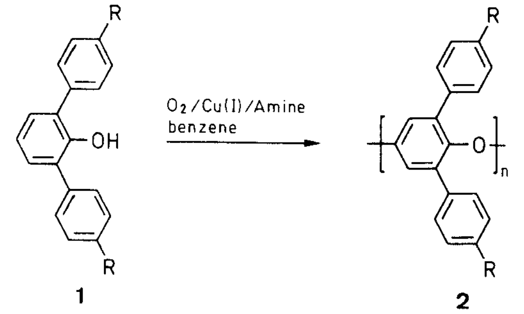
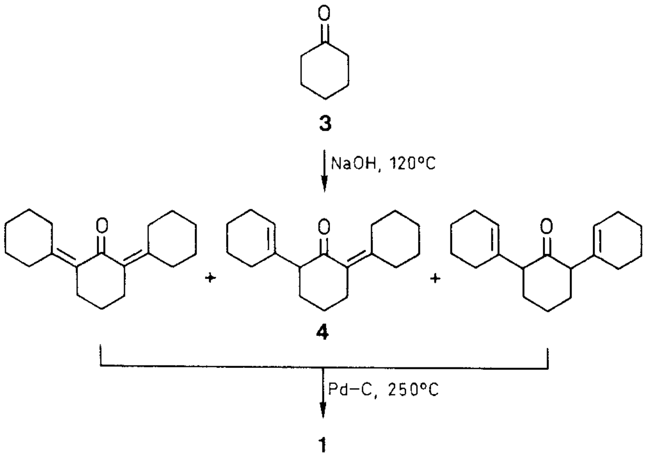
The synthesis of 2,6-diphenylphenols containing the substituents F, Cl, Br, I, *t*-Bu, CN and OPh on the para-positions of the pendant phenyl groups is described.

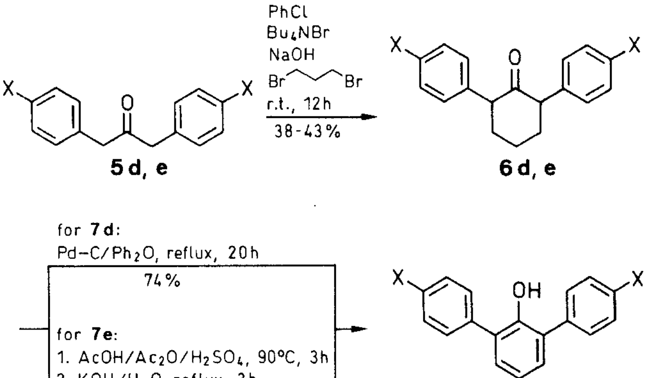
The oxidative polymerization of 2,6-diphenylphenol (**1**) (R = H) gives the polyphenylene oxide **2** (R = H), which has a glass transition temperature of 235 °C and melting point of 480 °C.[1] In an attempt to modify the properties of this polymer, a series of 2,6-diphenylphenols containing substituents (F, Cl, Br, I, *t*-Bu, CN, OPh) in both *para*-positions of the pendant phenyl groups have been prepared.



The most attractive synthesis of **1**[2] is a two-step synthesis in which cyclohexanone **3** is self-condensed in the presence of sodium hydroxide to produce a mixture of trimers **4** followed by dehydrogenation with palladium on carbon as catalyst. Obviously, this method cannot be used for the preparation of 2,6-diphenylphenols symmetrically substituted in the *para*-positions of the pendant phenyl groups.



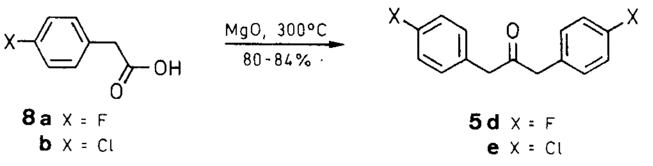
We previously reported[3] the synthesis of some symmetrically substituted diarylphenols, **7a**, **7b**, **7c**, via the condensation of dibenzyl ketones **5a**, **5b** and **5c**, respectively, with 1,3-dibromopropane followed by dehydrogenation of the intermediate cyclohexanone over palladium on carbon catalyst. We have now utilized this approach for the synthesis of fluoro and chloro substituted 2,6-diphenylphenols **7d** and **7e** since these substituents cannot be introduced directly onto the aromatic ring.



5-7[a]	X	5-7	X
a	Me	**d**	F
b	OMe	**e**	Cl
c	Ph		

[a] For the preparation of **7a**–**c** see Ref. 3.

The key step in this procedure is the preparation of the precursor dibenzyl ketones, **5**. Recently Wolfe[4] reported the preparation of bis(4-bromobenzyl) ketone in 74% yield by reacting 4-bromophenylacetic acid with magnesium oxide at high temperature under vacuum. We have found that the fluoro and chloro substituted dibenzyl ketones, **5d** and **5e**, can be prepared by this method in good yield.



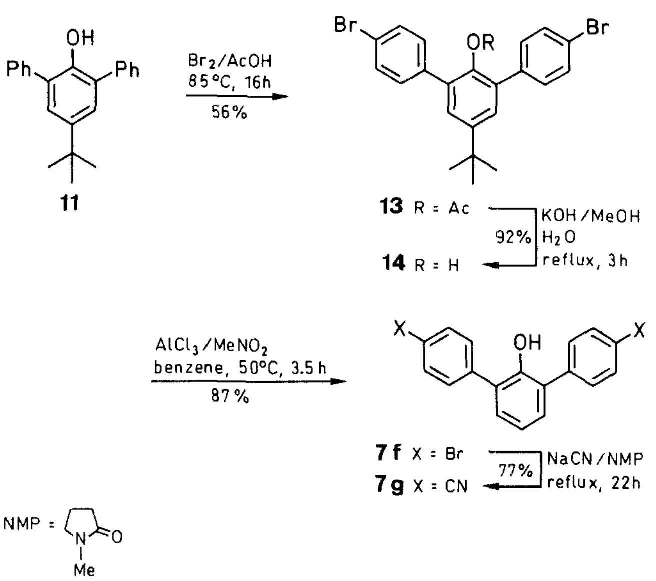
In this reaction it is critical that the temperature be maintained as low as possible in order to avoid decomposition of the salt and this requires that the vaccum be maintained as low as possible. Methoxy-substituted phenylacetic acid gives only a very low yield in this process because of extensive decomposition during the reaction at the elevated temperatures. The fluoro and chloro substituted dibenzyl ketones **5d** and **5e** were converted to the corresponding cyclohexanones **6d** (38 %) and **6e** (43 %). During the aromatization step 2,6-bis(4-fluorophenyl)phenol **7d** was obtained in good yield (74 %) but the chloro substituted diphenylphenol **7e** was obtained in very low yield because of hydrogenolysis to **1**. We found that the aromatization of **6e** can be accomplished in good yield by using sulfuric acid/acetic anhydride as the aromatization reagent to afford the acetate derivative of **7e** followed by hydrolysis to give **7e**.

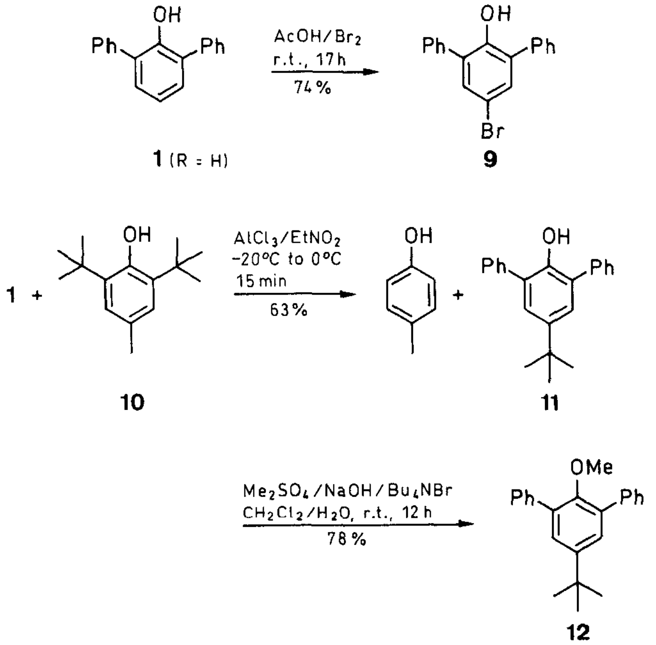
This synthesis is not a general one since it depends on the availability of the substituted dibenzyl ketones and in addition some substituents will not survive the aromatization of the intermediate cyclohexanone. In this paper we would like to report some new approaches to the synthesis of 2,6-diarylphenols substituted in the *para*-position of the pendant phenyl groups (**7**; X = Br, I, CN, *t*-Bu, OPh).

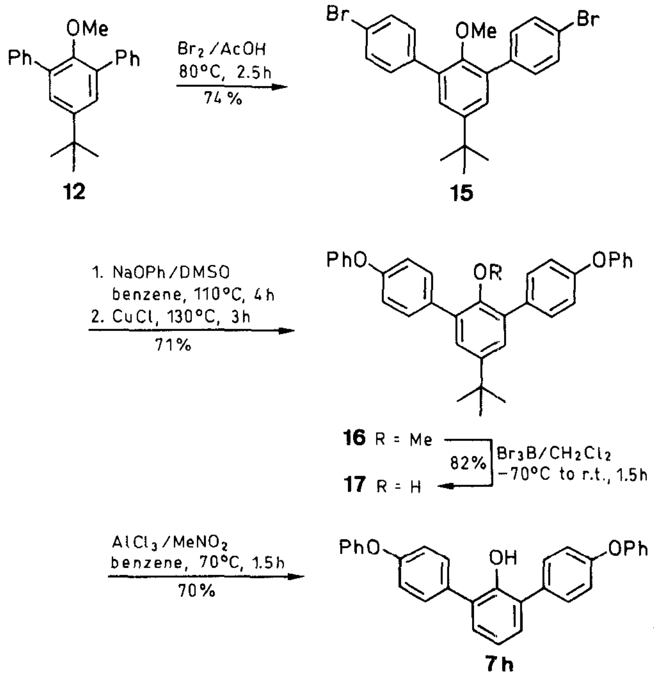
Our approach to the synthesis of other symmetrically substituted 2,6-diarylphenols is based on the use of the parent molecule **1** as a readily available starting material. By blocking and deblocking the center phenolic moiety of **1** in the 4-position with bromo or *tert*-butyl groups we have been able to readily introduce substituents like bromo, iodo and *tert*-butyl groups onto the *para*-positions of the pendant rings of **1** by simple chemistry and with readily available reagents. Further reaction of the bromo-substituted 2,6-diarylphenol **7f** serves to introduce substituents such as cyano, **7g**, and the phenoxy group, **7h** onto the 4-position of the pendant phenyl groups.

We have used bromo and *tert*-butyl groups to initially block the center phenolic moiety of **1**. Bromination in acetic acid yielded 4-bromo-2,6-diphenylphenol (**9**) in high yield. We were not able to selectively introduce the *tert*-butyl group onto the center ring of **1** in several different attempts by direct *tert*-butylation, however, by trans-*tert*-butylation with 2,6-di-*tert*-butyl-4-methylphenol (**10**) as the *tert*-butyl donor and with aluminum chloride/nitroethane as catalyst we obtained the desired product, 4-*tert*-butyl-2,6-diphenylphenol (**11**). Methylation of **11** with dimethyl sulfate in the presence of a phase transfer catalyst afforded the fully protected intermediate **12**.

In the preparation of 2,6-bis(4-bromophenyl)phenol (**7f**), **11** was first brominated with excess bromine in acetic acid and, suprisingly, a moderate yield of the acetate derivative **13** was obtained instead of the free phenol **14**. The only other product in the reaction was the mono bromination product which could be recycled. Saponification of **13** yielded phenol **14**. The *tert*-butyl group was successfully removed by a trans-*tert*-butylation reaction with benzene as the *tert*-butyl acceptor to afford **7f**. The cyano-substituted diphenylphenol **7g** was obtained in good yield by reacting **7f** with sodium cyanide in *N*-methyl-2-pyrrolidinone.

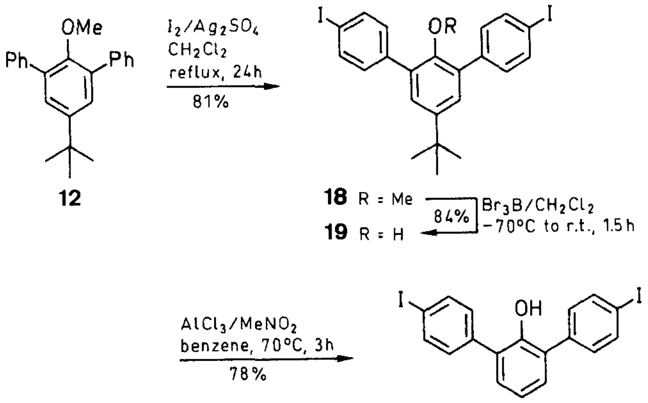




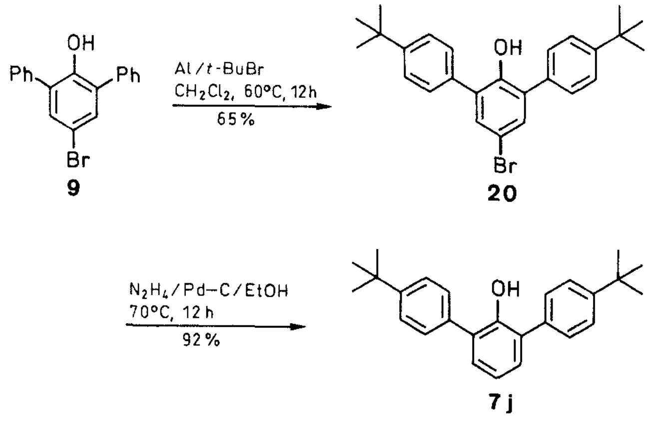


The phenoxy substituted derivative **7h** was obtained by reacting sodium phenoxide with intermediate **15**. Demethylation of **16** with tribromoborane in dichloromethane yielded **17** and the *tert*-butyl group of **17** was removed by a trans-*tert*-butylation reaction as described above to afford **7h** in good yield.

Recently[5] Wing-Wah reported simple and mild reaction conditions for the iodination of aromatics with iodine using silver sulfate as catalyst in dichloromethane at room temperature. The conversion of **12** to **19** was carried out as described above in good yield. Dealkylation with aluminum chloride/nitromethane gave **7i**.



Introduction of the *tert*-butyl group onto the pendant ring of **1** could be accomplished most efficiently by reacting **9** with *tert*-butyl bromide using aluminum metal as catalyst, a method which in this case is greatly superior to the traditional Friedel–Crafts alkylation reaction conditions using aluminum trichloride as catalyst. The use of aluminum as a Friedel–Crafts catalyst in the alkylation of toluene has been previously described.[6] The bromo group was removed by hydrogenolysis with hydrazine in the presence of palladium on carbon to give the final product **7j** in good yield.



Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. Flash chromatography was done on silica gel 60 (32–63 μm) from BDH. ^1H NMR spectra were recorded in $CDCl_3$ solution at 200 MHz on a Varian XL-200 NMR spectrometer with TMS as internal standard. Mass spectra were recorded at 70 eV with a direct insertion probe. Microanalyses were obtained from the Galbraith Laboratory Inc., TN. All chemicals and solvents were reagent grade and used without further purification. The reactions were routinely monitored on a Milton Roy HPLC instrument, using a Spherisorb ODS2 reverse-phase column (250 × 4.6 mm, 5 μm) and MeOH as an eluent at a flow rate of 1.0 mL per minute with a UV detector set at 254 nm wavelength.

1,3-Bis(4-fluorophenyl)-2-propanone (5d):

A mixture of 4-fluorophenylacetic acid (4.62 g, 30 mmol) and MgO (1.33 g, 33 mmol) was finely ground and added into a 25 mL three neck flask with a short-neck distillation tube. The flask was put in a sand bath and the temperature was slowly raised while the mixture was held under vacuum (2 mmHg). When the temperature reached about 300 °C, the product began to come out as colorless oil and the temperature was maintained until no further product distilled out. The solidified product was recrystallized from EtOH to give **5d** as white needle crystals; yield: 2.96 g (80 %); mp 64 °C.

$C_{15}H_{12}F_2O$	calc.	73.16	H 4.91
(246.3)	found	73.63	4.97

MS (70 eV): m/z (%) 246 (M^+, 12), 137 (M^+ − $FPhCH_2$, 23), 109 ($FPhCH_2{}^+$, 100).

^1H NMR ($CDCl_3$): δ = 3.70 (s, 4 H, CH_2), 7.05 (m, 8 H_{arom}).

1,3-Bis(4-chlorophenyl)-2-propanone (5e):

A mixture of 4-chlorophenylacetic acid (5.12 g, 30 mmol) and MgO (1.33 g, 33 mmol) was finely ground and added into a 25 mL flask with a short-neck distillation tube. The flask was put in a sand bath and the temperature was slowly raised while the mixture is maintained under vacuum (2 mmHg). The temperature was maintained at 300 °C until no further product distilled out.The solidified product was recrystallized from EtOH giving **5e** as light yellow crystals; yield: 3.52 g (84 %); mp 96–97 °C.

$C_{15}H_{12}Cl_2O$	calc.	C 64.54	H 4.33
(279.2)	found	64.52	4.53

MS (70 eV): m/z (%) = 278 (M^+ − H, 8), 153 (M^+ − $ClPhCH_2$ − H, 16), 125 ($ClPhCH_2{}^+$, 100).

^1H NMR ($CDCl_3$): δ = 3.69 (s, 4 H, CH_2), 7.06 (d, 4 H_{arom}, J = 8.5 Hz), 7.29 (d, 4 H_{arom}, J = 8.5 Hz).

2,6-Bis(4-fluorophenyl)cyclohexanone (6d):

To a stirred suspension of **5d** (23.2 g, 94 mmol), Bu_4NBr (12.9 g, 40 mmol), NaOH (50 mL, 50 %) and chlorobenzene (30 mL), is added 1,3-dibromopropane (18.9 g, 94 mmol) very slowly under N_2 atmosphere at r.t. Following the addition, the reaction was allowed to stir overnight (12 h) at r.t. and the color of the organic phase changes from dark brown to yellow. The mixture was then poured into H_2O (400 mL) and the organic phase was diluted with $CHCl_3$ (100 mL), washed with H_2O until neutral and dried ($MgSO_4$). The solvent was evaporated and the yellow oil was recrystallized from hexane/EtOH giving **6d** as white crystals; yield: 10.2 g (38 %); mp 139–140 °C.

$C_{18}H_{16}F_2O$	calc.	C 75.51	H 5.63
(286.3)	found	75.87	5.62

MS (70 eV): m/z (%) = 286 (M^+, 85), 258 (M^+ − CO, 14), 135 (100).

^1H NMR ($CDCl_3$): δ = 2.12 (m, 4 H, 2 CH_2), 2.38 (m, 2 H, CH_2), 3.80 (m, 2 H, 2 CH), 6.95–7.16 (m, 8 H_{arom}).

2,6-Bis(4-chlorophenyl)cyclohexanone (6e):

To a stirred suspension of **5e** (27.9 g, 100 mmol), Bu_4NBr (12.9 g, 40 mmol), NaOH (50 mL, 50 %), and chlorobenzene (30 mL), was added 1,3-dibromopropane (20.2 g, 100 mmol) very slowly under N_2 at r.t. Following the addition, the reaction was allowed to stir overnight (12 h). The mixture was then poured into H_2O (400 mL) and the organic phase was diluted with $CHCl_3$ (100 mL). The $CHCl_3$ solution was washed with H_2O until neutral and dried ($MgSO_4$). The solvent was distilled in vacuo and to the crude yellow oil was added hexane (30 mL) and the mixture was agitated. The oil quickly solidified into crystals and further recrystallization from EtOH gave **6e** as white crystals; yield: 13.7 g (43 %); mp 159–160 °C.

$C_{18}H_{16}Cl_2O$	calc.	C 67.72	H 5.05
(319.2)	found	67.76	5.06

MS (70 eV): m/z (%) = 318 ($M^+ - H$, 62), 290 ($M^+ - CO - H$, 16), 138 (100).

^1H NMR ($CDCl_3$): δ = 2.07 (m, 4H, $2CH_2$), 2.40 (m, 2H, CH_2), 3.77 (m, 2H, 2CH), 7.08 (d, $4H_{arom}$, J = 8.5 Hz), 7.28 (d, $4H_{arom}$, J = 8.5 Hz).

2,6-Bis(4-fluorophenyl)phenol (7d):

A mixture of compound **6d** (7.99 g, 27.9 mmol), Pd–C (2 g, 5%) and Ph_2O (25 mL) was heated under reflux for 20 h. After cooling to r.t, the mixture was diluted with acetone (50 mL) and the catalyst was removed by filtration. The solvent was evaporated on a rotovap under pressure to give a light yellow oil. The oil was dissolved in warm hexane and set in refrigerator overnight to give **7d** as white crystals; yield: 5.8 g (74%); mp 62–65 °C.

$C_{18}H_{12}F_2O$	calc.	C 76.57	H 4.29
(282.3)	found	76.81	4.36

MS (70 eV): m/z (%) = 282 ($^+$, 100).

^1H NMR ($CDCl_3$): δ = 5.22 (s, 1H, OH), 7.10–7.30 (m, $8H_{arom}$), 7.48–7.58 (m, $3H_{arom}$).

2,6-Bis(4-chlorophenyl)phenol (7e):

To a mixture of **6e** (6.38 g, 20 mmol), AcOH (60 mL), conc. H_2SO_4 (8 mL) was added slowly at r.t. The mixture was heated at 90 °C for 3 h. The reaction mixture was then poured into ice-water (200 mL), followed by extraction with Et_2O (2 × 100 mL). The combined ether extracts were washed with H_2O (2 × 200 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue was dissolved in EtOH (100 mL). A solution of KOH (15 g) in H_2O (50 mL) was added to above solution. The mixture was heated at reflux for 3 h under N_2 atmosphere. The mixture was then poured into cold H_2O (200 mL) with agitation. The solid was collected by filtration and purified by recrystallization from EtOH to give **7e** as white crystals; yield: 3.9 g (62%); mp 135–136 °C.

$C_{18}H_{12}Cl_2O$	calc.	C 68.59	H 3.84
(315.2)	found	68.18	3.98

MS (70 eV): m/z (%) = 316 ($M^+ + H$, 21), 178 (100).

^1H NMR ($CDCl_3$): δ = 5.22 (s, 1H, OH), 7.05 (t, $1H_{arom}$, J = 7.4 Hz), 7.46 (m, $8H_{arom}$).

4-Bromo-2,6-diphenylphenol (9):

To a stirred solution of **1** (123 g, 500 mmol) in AcOH (500 mL), Br_2 (80 g, 500 mmol) was added dropwise over 1 h at r.t. The reaction was continued for 16 h. The light yellow solution was poured into aq $NaHSO_3$ (1%, 1 L) with agitation. The white oil at the bottom of the flask solidified in the refrigerator overnight. The solid was collected by filtration and washed thoroughly with H_2O, then recrystallized from EtOH to give **9** (152 g, HPLC purity 96%) as white crystals. Further purification by recrystallization from petroleum ether gave **9** as white crystals; yield: 120 g (74%); mp 66 °C.

$C_{18}H_{13}BrO$	calc.	C 66.48	H 4.03
(325.2)	found	66.41	4.08

MS (70 eV): m/z (%) = 326 ($M^+ + H$, 97), 325 (M^+, 25), 324 (M^+, -H, 100).

^1H NMR ($CDCl_3$): δ = 5.39 (s, 1H, OH), 7.50 (m, $13H_{arom}$).

4-*tert*-Butyl-2,6-diphenylphenol (11):

A suspension of 2,6-diphenylphenol (**1**, 24.6 g, 100 mmol) and 2,6-bis(*tert*-butyl)-4-methylphenol (**10**; 12.0 g, 55 mmol) in $EtNO_2$ (100 mL) was cooled to −20 °C in a cooling bath. To the mixture solution of $AlCl_3$ (13.3 g, 100 mmol) in $EtNO_2$ (30 mL) was added with stirring and the solution instantly became dark colored. The reaction was continued for 15 min and then quenched by pouring the reaction mixture into ice-water (500 mL). The organic phase was separated and the solvent was distilled in vacuo. The residue was dissolved in CH_2Cl_2 (200 mL) and washed with HCl (18%, 200 mL), H_2O (150 mL), aq NaOH (10%, 150 mL) and H_2O (150 mL). The organic phase was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was dissolved in warm hexane and set in the refrigerator for 24 h to give **11** as white crystals; yield: 18.9 g (63%); mp 91–92.5 °C.

$C_{22}H_{22}O$	calc.	C 87.38	H 7.33
(302.4)	found	87.59	7.51

MS (70 eV) m/z (%) = 302 ($^+$, 41), 287 ($M^+ - CH_3$, 100).

^1H NMR ($CDCl_3$): δ = 1.36 (s, 9H, t-C_4H_9), 5.26 (s, 1H, OH), 7.29 (s, $2H_{arom}$), 7.40–7.60 (m, $10H_{arom}$).

4-*tert*-Butyl-2,6-diphenylanisole (12):

To a solution of **11** (30.2 g, 100 mmol), Me_2SO_4 (18.9 g, 150 mmol) and Bu_4NBr (2 g) in CH_2Cl_2 (250 mL), was added a solution of NaOH (6 g) in H_2O (250 mL). The mixture was stirred at r.t. temperature overnight (12 h). The organic layer was washed thoroughly with H_2O until neutral and dried ($MgSO_4$). The solvent was evaporated and the light yellow oil was dissolved in warm hexane and set in the refrigerator overnight to give **12** as white crystals; yield: 24.7 g (78%); mp 86–87 °C.

$C_{23}H_{24}O$	calc.	C 87.30	H 7.64
(316.5)	found	87.04	7.81

MS (70 eV): m/z (%) = 316 (M^+, 48), 301 ($M^+ - CH_3$, 100).

^1H NMR ($CDCl_3$): δ = 1.36 (s, 9H, t-C_4H_9), 3.14 (s, 3H, OCH_3), 7.34–7.63 (m, $12H_{arom}$).

2,6-Bis(4-bromophenyl)4-*tert*-butylphenyl Acetate (13):

To a suspension of **11** (16.3 g, 54 mmol) in AcOH (100 mL), Br_2 (43.5 g, 270 mmol) was added at r.t. The mixture was heated to 85 °C when a clear solution was obtained. The reaction was continued for 16 h and during the reaction the product separated out from the solution. The mixture was cooled to r.t. and the product was collected by filtration. The solid was washed with AcOH and the recrystallization from EtOH gave **13** as white crystals; yield: 15.3 g (56%); mp 212–213 °C.

$C_{24}H_{22}Br_2O_2$	calc.	C 57.40	H 4.42
(502.3)	found	57.24	4.45

MS (70 eV): m/z (%) = 502 (M^+, 6), 460 ($M^+ - CH_3CO + H$, 100)

^1H NMR ($CDCl_3$): δ 1.36 (s, 9H, t-C_4H_9), 1.83 (s, 3H, $COCH_3$), 7.33 (s, $2H_{arom}$), 7.31 (d, $4H_{arom}$, J = 8.0 Hz), 7.54 (d, $4H_{arom}$, J = 8.0 Hz).

2,6-Bis(4-bromophenyl)4-*tert*-Butylphenol (14):

To a mixture of compound **13** (41.2 g, 82 mmol) and MeOH (400 mL), a solution of KOH (30 g) in H_2O (100 mL) was added. The temperature was raised to reflux and a clear solution was formed. The reaction was continued for 3 h. The solution was poured into cold H_2O (500 mL) with vigorous agitation. The white solid was filtered and washed with H_2O. Recrystallization from EtOH/$CHCl_3$ gave a first portion of white crystals (30.0 g). Further concentration gave another portion of white crystals (4.8 g) of **14**; yield: 34.8 g (92%); mp 161–162 °C.

$C_{22}H_{20}Br_2O$	calc.	C 57.42	H 4.38
(460.2)	found	58.05	4.58

MS (70 eV) m/z (%) = 460 ($M^+ - CH_3$, 100).

^1H NMR ($CDCl_3$): δ = 1.34 (s, 9H, t-C_4H_9), 5.07 (s, 1H, OH), 7.24 (s, $2H_{arom}$), 7.42 (d, $4H_{arom}$, J = 8.5 Hz), 7.60 (d, $4H_{arom}$, J = 8.5 Hz).

2,6-Bis(4-bromophenyl)phenol (7f):

To a stirred solution of compound **14** (34.5 g, 75 mmol) in benzene (250 mL) at 50 °C, a solution of $AlCl_3$ (11.33 g, 85 mmol) in $MeNO_2$ (50 mL) was added. The reaction was continued at 50 °C for 3.5 h. The mixture was poured into ice-water (500 mL). The organic layer was separated and the solvent was distilled in vacuo. Recrystallization from EtOH/$CHCl_3$ gave **7f** as white crystals; yield: 26.5 g (87%); mp 147–148.5 °C.

$C_{18}H_{11}Br_2O$	calc.	C 53.64	H 2.75
(403.1)	found	53.46	2.99

MS (70 eV) m/z (%) = 404 ($M^+ + H$, 79), 244 ($M^+ - 2Br - H$, 100).

^1H NMR ($CDCl_3$): δ = 5.21 (s, 1H, OH), 7.06 (t, $1H_{arom}$, J = 7.6 Hz), 7.25 (d, $2H_{arom}$, J = 7.6 Hz), 7.41 (d, $4H_{arom}$, J = 8.7 Hz), 7.65 (d, $4H_{arom}$, J = 8.7 Hz).

2,6-Bis(4-cyanophenyl)phenol (7 g):
In a 250 mL flask equipped with magnetic stirring, N_2 inlet and condenser, a mixture of compound **7f** (8.06 g, 20 mmol), CuCN (5.37 g, 60 mmol) and *N*-methyl-2-pyrrolidinone (NMP, 100 mL) was added. The mixture was heated at reflux under a N_2 atmosphere for 22 h. The brown colored solution was cooled to 100 °C and poured into warm aq NaCN (10 %, 250 mL). The grey colored solid was collected by filtration and washed with warm aq NaCN (10 %, 200 mL) and H_2O (2 x 200 mL). Recrystallization from EtOH afforded 2.0 g of light yellow crystals. The filtrate was concentrated and purified by flash chromatography (CH_2Cl_2/hexane, 1 : 1) giving another 2.6 g of **7 g** as light yellow crystals; yield: 4.6 g (77 %); mp 261–262.5 °C.

$C_{20}H_{12}N_2O$	calc.	C 81.07	H 4.08
(296.3)	found	80.55	4.13

MS (70 eV): *m*/*z* (%) = 196 (M^+, 100).

^{1}H NMR ($CDCl_3$): δ = 5.19 (s, 1 H, OH), 7.13 (t, 1 H_{arom}, $J = 7.6$ Hz), 7.29 (d, 2 H_{arom}, $J = 7.6$ Hz), 7.66 (d, 4 H_{arom}, $J = 8.3$ Hz), 7.77 (d, 4 H_{arom}, $J = 8.3$ Hz).

2,6-Bis(4-bromophenyl)-4-*tert*-butylanisole (15):
To a stirred suspension of **12** (15.8 g, 50 mmol) in AcOH (100 mL), Br_2 (12.9 mL, 250 mmol) was added. The solution was heated to 80 °C and a clear solution was formed. The reaction was continued for 2.5 h. The product continuously separated out of the solution during the reaction. The mixture was cooled to r. t. and the solid was collected by filtration and washed with cool AcOH. Recrystallization from EtOH/$CHCl_3$ gave **15** as white crystals; yield: 17.6 g (74 %); mp 145–146 °C.

$C_{23}H_{22}Br_2O$	calc.	C 58.25	H 4.68
(474.2)	found	58.32	4.72

MS (70 eV): *m*/*z* (%) = 474 (M^+, 68), 459 ($M^+ - CH_3$, 100).

^{1}H NMR ($CDCl_3$): δ = 1.35 (s, 9 H, *t*-C_4H_9), 3.13 (s, 3 H, OCH_3), 7.30 (s, 2 H_{arom}), 7.47 (d, 4 H_{arom}, $J = 8.7$ Hz), 7.56 (d, 4 H_{arom}, $J = 8.7$ Hz).

(4-*tert*-Butyl-2,6-bis(4-phenoxyphenyl)anisole (16):
To a 250 mL three-neck flask equipped with a condenser, Dean–Stark trap, N_2 inlet and magnetic stirring bar, phenol (10.74 g, 114 mmol), NaOH (4.44 g, 111 mmol), DMSO (45 mL) and benzene (30 mL) were added. The mixture was heated at 110 °C for 4 h until no further H_2O came out of the mixture. Compound **15** (8.54 g, 18 mmol) and CuCl (2.94 g, 30 mmol) were added under N_2 atmosphere. The temperature was raised to 130 °C and continued for 3 h. The mixture was poured into H_2O and the solid was collected by filtration. The solid was taken up in CH_2Cl_2 (2 x 100 mL) and the solution was washed with aq NaOH (10 %, 100 mL) and H_2O (2 x 100 mL). The organic layer was dried ($MgSO_4$) and the solvent was removed under reduced pressure. Recrystallization from EtOH/CH_2Cl_2 gives **16** as light yellow crystals; yield: 6.4 g (71 %); mp 169–171 °C.

$C_{35}H_{32}O_3$	calc.	83.97	H 6.44
(500.6)	found	84.16	6.37

MS (70 eV): *m*/*z* (%) = 500 (M^+, 1), 393 ($M^+ - C_6H_5 - 2CH_3$, 100).

^{1}H NMR ($CDCl_3$): δ = 1.37 (s, 9 H, *t*-C_4H_9), 3.21 (s, 3 H, OCH_3), 7.02–7.60 (m, 20 H_{arom}).

(4-*tert*-Butyl-2,6-bis(4-phenoxyphenyl)phenol (17):
To a stirred solution of **16** (5.0 mol, 10 mmol) in CH_2Cl_2 (20 mL) which was cooled to − 70 °C with an acetone/dry ice bath, was added a solution of Br_3B (1.0 M in CH_2Cl_2, 30 mL, 30 mmol) by syringe in 10 min under a N_2 atmosphere. The temperature was allowed to rise to r.t. in 1.5 h. The orange colored solution was poured into ice-water (200 mL). The organic layer was washed with H_2O (2 x 100 mL) and dried ($MgSO_4$). The solvent was distilled in vacuo and the light yellow oil was recrystallized from EtOH/$CHCl_3$ giving 3.5 g of white crystals. Further concentration gave another 0.5 g of crystals of **17**; yield: 4.0 g (82 %); mp 167–168.5 °C.

$C_{34}H_{30}O_3$	calc.	C 83.92	H 6.21
(486.6)	found	84.07	6.33

MS (70 eV): *m*/*z* (%) = 394 ($M^+ - C_6H_5 - CH_3$, 16), 83 (100).

^{1}H NMR ($CDCl_3$): δ = 1.35 (s, 9 H, *t*-C_4H_9), 5.24 (s, 1 H, OH), 7.27 (s, 2 H_{arom}), 7.08–7.54 (m, 18 H_{arom}).

2,6-Bis(4-phenoxyphenyl)phenol (7 h):
To a stirred solution of **17** (3.65 g, 7.5 mmol) in benzene (30 mL) at 70 °C, was added a solution of $AlCl_3$ (1.13 g, 8.5 mmol) in $MeNO_2$ (5 mL). A dark color rapidly developed. The reaction was continued for 1.5 h. The mixture was then poured into cold H_2O (100 mL). The organic layer was washed with aq HCl (10 %, 50 mL), then with H_2O (2 x 50 mL). The organic layer was dried ($MgSO_4$) and the solvent was distilled in vacuo and the solid was purified by recrystallization twice from EtOH to give **7h** as light yellow crystals; yield: 2.3 g (70 %); mp 118–120 °C.

$C_{30}H_{22}O_3$	calc.	C 83.70	H 5.15
(430.5)	found	83.61	5.26

MS (70 eV): *m*/*z* (%) = 430 ($^+$, 63), 244 (M^+ - $2C_6H_5O$, 12), 78 (100).

^{1}H NMR ($CDCl_3$): δ = 5.39 (s, 1 H, OH), 7.07–7.19 (m, 10 H_{arom}), 7.24 (d, 2 H_{arom}), 7.37 (t, 1 H_{arom}), 7.52 (q, 8 H_{arom}).

2,6-Bis(4-iodophenyl)-4-*tert*-butylanisole (18)
A stirred mixture of compound **12** (8.86 g, 28 mmol), Ag_2SO_4 (21.7 g, 70 mmol), I_2 crystals (17.8 g, 35 mmol) and CH_2Cl_2 (250 mL) was heated at gentle reflux under N_2 atmosphere for 24 h. The solid was removed by filtration and the solution was washed with dilute $Na_2S_2O_3$ (5 %, 300 mL), H_2O (2 x 200 mL) and dried ($MgSO_4$). The solvent was distilled in vacuo and recrystallization from EtOH/$CHCl_3$ gave **18** as light yellow crystals; yield: 12.9 g (81 %); mp 174–175 °C.

$C_{23}H_{22}I_2O$	calc.	C 48.59	H 3.90
(568.2)	found	48.63	3.91

MS (70 eV) *m*/*z* (%) = 568 (M^+, 100), 553 ($M^+ - CH_3$, 99), 426 ($M^+ - I - CH_3 - H$, 17).

^{1}H NMR ($CDCl_3$): δ = 1.35 (s, 9 H, *t*-C_4H_9), 3.13 (s, 3 H, OCH_3), 7.29 (s, 2 H_{arom}), 7.35 (d, 4 H_{arom}, $J = 8.5$ Hz), 7.76 (d, 4 H_{arom}, $J = 8.5$ Hz).

(4-*tert*-Butyl-2,6-bis(4-iodophenyl)phenol (19):
To a stired solution of **18** (4.43 g, 7.8 mmol) in CH_2Cl_2 (10 mL) which was cooled to − 70 °C with an acetone/dry ice bath, was added a solution of Br_3B/CH_2Cl_2 (1.0 M in CH_2Cl_2, 23.4 mL, 23.4 mmol) by syringe in 10 min. The temperature rose to 0 °C in 1 h and the reaction was quenched by pouring the solution into ice-water (100 mL.) The organic layer was washed with H_2O (2 x 50 mL) and dried ($MgSO_4$). The solvent was evaporated and the residue was purified by recrystallization from EtOH to give **19** as light yellow crystals; yield: 3.6 g (84 %); mp 160–161 °C.

$C_{22}H_{20}I_2O$	calc.	C 47.68	H 3.64
(554.2)	found	47.80	3.61

MS (70 eV): *m*/*z* (%) = 554 (M^+, 88), 539 ($M^+ - CH_3$, 100), 412 ($M^+ - I - CH_3 - H$, 17).

^{1}H NMR ($CDCl_3$): δ = 1.33 (s, 9 H, *t*-C_4H_9), 5.09 (s, 1 H, OH), 7.24 (s, 2 H_{arom}), 7.29 (d, 4 H_{arom}, $J = 8.4$ Hz), 7.80 (d, 4 H_{arom}, $J = 8.4$ Hz).

2,6-Bis(4-iodophenyl)phenol (7 i):
To a stirred solution of **19** (2.99 g, 5.4 mmol) in benzene (30 mL) at 70 °C, a solution of $AlCl_3$ (0.93 g, 7.0 mmol) in $MeNO_2$ (5 mL) was added. The reaction was continued at 70 °C for 3 h. The mixture was poured into ice-water (100 mL). The organic layer was separated, dried ($MgSO_4$) and the solvent was evaporated. The crude solid was purified by recrystallization from EtOH/$CHCl_3$ giving **7i** as light yellow crystals; yield: 2.1 g (78 %); mp 151–153 °C.

$C_{18}H_{12}I_2O$	calc.	C 43.40	H 2.43
(498.1)	found	43.83	2.43

MS (70 eV) *m*/*z* (%) = 498 (M^+, 100), 372 (M^+ −I, 5).

^{1}H NMR ($CDCl_3$): δ = 5.23 (s, 1 H, OH), 7.04 (q, 1 H_{arom}), 7.23 (d, 2 H_{arom}), 7.28 (d, 4 H_{arom}, $J = 8.5$ Hz), 7.80 (d, 4 H_{arom}, $J = 8.5$ Hz).

4-Bromo-2,6-bis(4-*tert*-butylphenyl)phenol (20):

A solution of **9** (65 g, 200 mmol) and *t*-BuBr (100 mL) in CH_2Cl_2 (100 mL) was heated to 60 °C. Al foil (cut in small pieces, 0.4 g) was added. In 1.5 h, a dark color developed and HBr evolution began. The reaction was stopped at 2 h and the reaction was quenched by pouring the mixture into ice-water (500 mL). The organic layer was washed with HCl (10 %, 2 x 200 mL), then with brine (2 x 200 mL). then with brine (2 x 200 mL). The organic phase was dried ($MgSO_4$) and the solvent was distilled in vacuo. The light yellow oil was purified by recrystallization from petroleum ether giving **20** as white crystals; yield: 57 g (65 %); mp 176–177 °C.

$C_{26}H_{29}BrO$	calc.	C 71.39	H 6.68
(437.4)	found	71.73	6.72

MS (70 eV): *m*/*z* (%) = 438 ($^+$ + H, 64), 423 (M^+ $-CH_3$ + H, 78).

^1H NMR ($CDCl_3$): δ = 1.36 (s, 18 H, 2 *t*-C_4H_9), 5.45 (s, 1 H, OH), 7.37 (s, 2 H_{arom}), 7.48d, 8 H_{arom}).

2,6-Bis(4-*tert*-butylphenyl)phenol (7j):

To a suspension of **20** (43.7 g, 100 mmol) and Pd–C (10 g, 10 %) in abs. EtOH (400 mL), was added anhydrous hydrazine (30 mL) by syringe under a N_2 atmosphere. The mixture was heated to 70 °C and the reaction was continued overnight (12 h). The catalyst was removed by filtration and the product crystallized rapidly from the filtrate by cooling. The solid was dissolved in CH_2Cl_2 (300 mL), and washed with aq HCl (10 %, 2 x 300 mL), then by H_2O (2 x 300 mL). The organic phase was dried ($MgSO_4$) and the solvent was distilled in vacuo. Recrystallization from petroleum ether gave **7j** as white crystals; yield: 33 g (92 %); mp 137–138 °C.

$C_{26}H_{30}O$	calc.	C 87.09	H 8.44
(358.5)	found	87.51	8.55

MS (70 eV): *m*/*z* (%) = 358 (M^+, 65), 343 (M^+ - CH_3, 100).

^1H NMR ($CDCl_3$): δ = 1.36 (s, 18 H, 2 *t*-C_4H_9), 5.47 (s, 1 H, OH), 7.05 (t, 1 H_{arom}), 7.24 (d, 2 H_{arom}), 7.49 (s, 8 H_{arom}).

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