The Superbase-Mediated Pairwise Substitution of the 2,2′- and 6,6′-Positions in a Biphenyl Derivative

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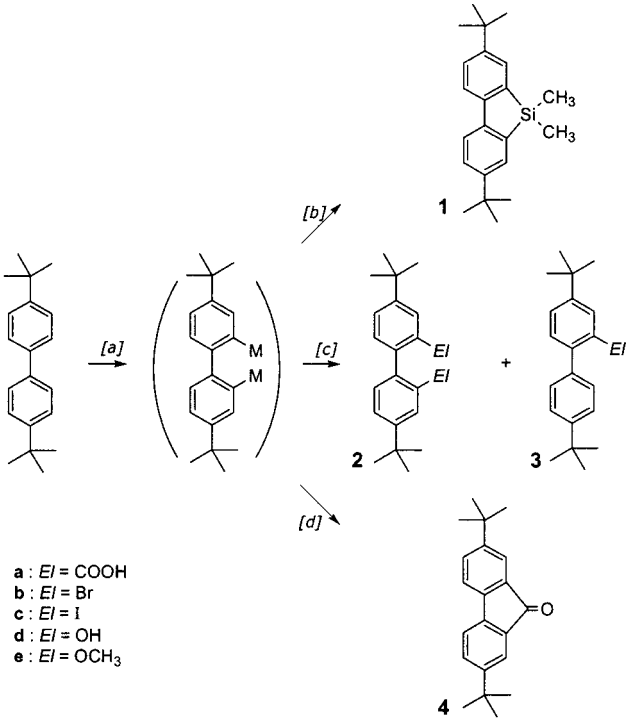
The superbasic mixture of butyllithium and potassium *tert*-butoxide is powerful enough to enable the double proton abstraction from one *ortho* and one *ortho′* position of 4,4′-di-*tert*-butylbiphenyl. In this way, a series of functionalized derivatives becomes readily accessible, among them 4,4′-di-*tert*-butylbiphenyldiyl-2,2′-dicarboxylic acid (**2a**) and 4,4′-di-*tert*-butylbiphenyl-2,2′-diol (**2d**). The latter compound can be subjected again to a superbase-promoted double metalation, thus giving rise to 2,2′,6,6′-tetrasubstituted biphenyl derivatives.

Introduction

As previously reported, benzene[1] and other arenes[2] undergo double metalation if exposed to the superbasic mixture of butyllithium and potassium *tert*-butoxide in hexanes or other paraffinic solvents. In the same context, the *tert*-butyl group was found to severely inhibit deprotonation at neighboring positions as long as other sites remain available.[1−3] This not being the case with 1,4-di-*tert*-butylbenzene, its mono- and dimetalation can be brought about only at elevated temperatures (+75 °C for 24 h) and with poor yields.[2] In contrast, *tert*-butylbenzene reacts smoothly at ambient temperature to provide *meta*- and *para*-mono- and *meta,meta′*-disubstituted derivatives in 80−90% total yields depending on the stoichiometry.[2] If an excess of the superbase is employed, 4,4′-di-*tert*-butylbiphenyl, a *para*−*para* coupled "dimer" of *tert*-butylbenzene, should consequently be exclusively and efficaciously attacked at the 2- and 2′-position. This prediction proved to be correct.

4,4′-Di-*tert*-butylbenzene, a commercial product, was dissolved in hexanes and treated for 12 h at +70 °C with two molar equivalents of butyllithium and potassium *tert*-butoxide before the reaction was quenched with dichlorodimethylsilane to afford the 2,7-di-*tert*-butyl-9,9-dimethyl-9-silafluorene[4] (**1**; 72%). Trapping of the intermediate with carbon dioxide followed by neutralization gave 2,2′-biphenyldicarboxylic acid[5] (**2a**; 53%) and 2,7-di-*tert*-butylfluorenone[6] (**4**; 15%), but no 2-biphenylylcarboxylic acid (**3a**, independently prepared from the monoiodobiphenyl **3c**) at all. Therefore, one has to impute the formation of the monosubstituted derivatives **3b**[7] (*El* = Br; 49%), **3c**[7,8] (*El* = I; 3%) and the presumed, though not unequivocally characterized, **3d** (*El* = OH; 30%), along with the disubstituted products **2b**[7,9−11] (*El* = Br; 31%), **2c**[12] (*El* = I; 60%), and **2d** (*El* = OH; 38%), to radical-generating pro-



[a] LiC_4H_9 and $KOC(CH_3)_3$ (suspension) in hexanes, 12 h at +70 °C. *[b]* $Cl_2Si(CH_3)_2$. *[c]* Electrophilic reagents *El*-X: CO_2 or Br_2 or I_2 or $FB(OCH_3)_2$ (in the latter case followed by treatment with H_2O_2). *[d]* CO_2 (**4** formed as a by-product).

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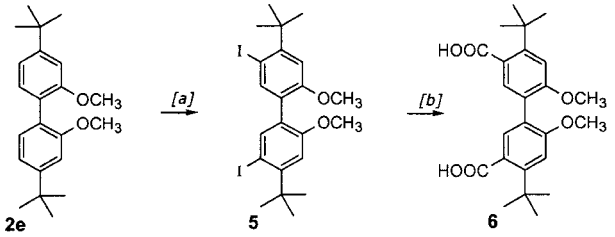
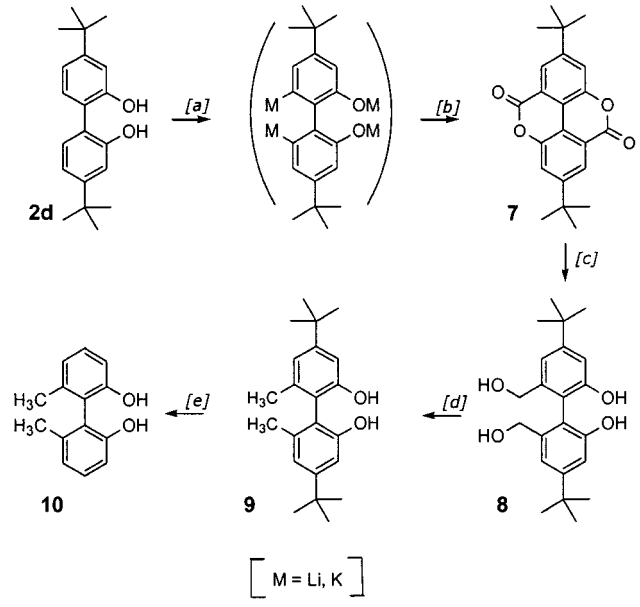
cesses unleashed in the moment of reaction with, respectively, bromine, iodine and fluorodimethoxyborane (in the latter case followed by oxidation with hydrogen peroxide). The bisphenol was quantitatively converted into the dimethoxy compound **2e** (97%).

A first attempt to introduce a second pair of substituents into the 6,6′-positions failed. Despite the steric hindrance caused by the bulky *tert*-butyl groups, iodination of the 2,2′-dimethoxybiphenyl **2e** occurred selectively at the 5,5′-positions with no effect on the 6- or 6′-positions. When the resulting diiodo derivative **5** (80%) was consecutively subjected to halogen/metal permutation and carboxylation, the diacid **6** was produced in 95% yield.



[a] I_2 and HIO_4 in H_3CCOOH and CCl_4, 2 h at +80 °C. *[b]* (1.) $LiC(CH_3)_3$ (2 equiv.) in tetrahydrofuran, 5 min at -75 °C; (2.) CO_2; (3.) H^+.

The objective of introducing functional substituents pairwise in the 2,2′- and 6,6′-positions was realized by the superbase-promoted metalation of the bisphenolate obtained by deprotonation of the dihydroxy compound **2d**. Upon carboxylation and neutralization, the bislactone **7** was isolated in 41% yield. It was first reduced with aluminum hydride to the bis(hydroxymethyl) compound **8** (63%) and subsequently treated with chlorotrimethylsilane in the presence of sodium iodide to yield the dimethyl derivative **9** (78%). Removal of the *tert*-butyl groups with aluminum trichloride provided 6,6′-dimethylbiphenyl-2,2′-diol (**10**; 89%), a known substance.[13]



[a] LiC_4H_9 (8.0 equiv.) and $KOC(CH_3)_3$ (8.0 equiv., suspension) in hexanes, 6 h at +70 °C. *[b]* (1.) CO_2 (excess); (2.) H^+. *[c]* (1.) AlH_3 (2.0 equiv.) in refluxing diethyl ether, 20 h; (2.) H^+. *[d]* $ClSi(CH_3)_3$ and NaH (10 equiv. each) in acetonitrile, 20 h at +25 °C. *[e]* $AlCl_3$ (3 equiv.) in benzene, 20 h at +25 °C.

Experimental Section

General: For laboratory routine and abbreviations, see recent publications[14−16] from this laboratory. ^1H and (^1H-decoupled) ^{13}C NMR spectra were recorded at 400 and 101 MHz, respectively. The samples were dissolved in deuteriochloroform unless stated otherwise. As the intensities of ^{13}C signals cannot be exactly measured, they are visually estimated. The signal intensities given (e.g., 2:2:2:18:6 rather than 1:1:1:9:3 H ratios) take into account the mass spectrometric information. To avoid redundancy, only [^{79}Br] fragments and no [^{81}Br] isotopomers are listed in the mass spectra.

2,7-Di-*tert*-butyl-9,9-dimethyl-9*H*-9-silafluorene (1): Potassium *tert*-butoxide (11 g, 0.10 mol) was added to a solution of butyllithium (0.10 mol) and 4,4′-di-*tert*-butylbiphenyl (13 g, 50 mmol) in hexanes (60 mL). The suspension was stirred for 12 h at 70 °C. At −75 °C, the mixture was treated with dichlorodimethylsilane (12 mL, 13 g, 0.10 mol) before being evaporated. The residue was crystallized from pentanes to give colorless cubes; yield: 11.6 g (72%); m.p. 166−167 °C (ref.[4] m.p. 167 °C). ^1H NMR (ppm): δ = 7.71 (d, *J* = 8.0 Hz, 2 H), 7.63 (d, *J* = 2.0 Hz, 2 H), 7.45 (dd, *J* = 8.0, 2.0 Hz, 2 H), 1.37 (s, 18 H), 0.43 (s, 6 H). ^{13}C NMR (ppm): δ = 149.8 (2 C), 145.7 (2 C), 139.0 (2 C), 129.6 (2 C), 127.5 (2 C), 120.0 (2 C), 35.0 (2 C), 31.5 (6 C), 3.0 (2 C). MS (c.i.): *m*/*z* (%) = 340 (9) [$M^+ + NH_3$], 322 (49) [M^+], 307 (100), 267 (10), 235 (6). $C_{22}H_{30}Si$ (322.57): calcd. C 81.92, H 9.37; found C 81.87, H 9.27.

4,4′-Di-*tert*-butylbiphenyl-2,2′-dicarboxylic Acid (2a): A mixture (see above) formed by the reaction of 4,4′-di-*tert*-butylbiphenyl (13 g, 50 mmol) with butyllithium (0.10 mol) and potassium *tert*-butoxide (11 g, 0.10 mol) was poured onto an excess of freshly crushed dry ice covered by a layer of tetrahydrofuran. At 25 °C, it was extracted with a 10% aqueous solution (50 mL) of sodium hydroxide. The aqueous phase was washed with diethyl ether (3 × 20 mL) and acidified to pH 5. The solid precipitate was collected by filtration and crystallized from 50% aqueous ethanol to afford colorless needles; yield: 9.39 g (53%); m.p. 300−301 °C (reprod.; ref.[5] m.p. 301−304 °C). ^1H NMR (ppm): δ = 7.61 (d, *J* = 2.0 Hz, 2 H), 7.43 (t, *J* = 2.0 Hz, 2 H), 7.41 (d, *J* = 2.0 Hz, 2 H), 1.35 (s, 18 H). MS: *m*/*z* (%) = 354 (61) [M^+], 330 (100), 280 (12), 174 (3), 120 (6).

4,4′-Di-*tert*-butyl-2,2′-dibromobiphenyl (2b): This was obtained analogously (see above) after treatment of 4,4′-di-*tert*-butylbiphenyl (13 g, 50 mmol) with a solution of bromine (5.1 mL, 16 g, 0.10 mol) in hexanes (50 mL) which was added dropwise over the course of 15 min. At 25 °C, the organic phase was washed with an aqueous solution (0.10 L) of sodium sulfite (5.0 g) and the solvents evaporated. The residue was crystallized from ethanol to afford colorless needles; yield: 15.0 g (36%); m.p. 160−161 °C (ref.[6] m.p. 157−158 °C). ^1H NMR (ppm): δ = 7.90 (d, *J* = 2.0 Hz, 2 H), 7.40 (dd, *J* = 8.0, 2.0 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 1.35 (s, 18 H). MS: *m*/*z* (%) = 422 (40) [M^+], 345 (100), 310 (60), 214 (12), 134 (23), 112 (12).

4,4′-Di-*tert*-butyl-2,2′-diiodobiphenyl (2c): This was obtained analogously (see above) after treatment of 4,4′-di-*tert*-butylbiphenyl (13 g, 50 mmol) with elemental iodine (26 g, 0.10 mol) with vigorous stirring. At 25 °C, the organic phase was washed with an aque-

ous solution (0.10 L) of sodium sulfite (5.0 g) and the solvents evaporated under reduced pressure. The residue was crystallized from ethanol to afford colorless needles; yield: 31.0 g (60%); m.p. 140−141 °C (ref.[6] m.p. 140−141 °C). ^{1}H NMR (ppm): δ = 7.90 (d, *J* = 2.0 Hz, 2 H), 7.40 (dd, *J* = 8.0, 2.0 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 1.35 (s, 18 H). MS (c.i.): *m*/*z* (%) = 536 (51) [M + NH_4^+], 518 (100) [M^+], 513 (87), 512 (88), 345 (23), 312 (12), 245 (3), 124 (10).

4,4′-Di-*tert*-butylbiphenyl-2,2′-diol (2d): At −75 °C, a mixture formed (see above) by the reaction of 4,4′-di-*tert*-butylbiphenyl (13 g, 50 mmol) with butyllithium (0.10 mol) and potassium *tert*-butoxide (11 g, 0.10 mol) was treated with the fluorodimethoxyborane diethyl ether 1:1 complex[17,18] (19 mL, 17 g, 0.10 mol), which was added dropwise over 1 h. At 25 °C, sodium hydroxide pellets (2.0 g, 50 mmol) and 30% hydrogen peroxide solution (10 mL, 0.10 mmol) were added. The mixture was stirred for 2 h at 25 °C before being acidified to pH 5. The organic phase was decanted and the aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried and the solvents evaporated. The residue was crystallized from heptanes to afford colorless needles; yield: 5.67 g (38%); m.p. 190−191 °C. ^{1}H NMR (ppm): δ = 7.2 (m, 2 H), 7.1 (m, 4 H), 1.34 (s, 18 H). ^{13}C NMR (ppm): δ = 154.2 (2 C), 151.0 (2 C), 131.5 (2 C), 123.2 (2 C), 116.0 (2 C), 113.0 (2 C), 34.2 (2 C), 31.5 (6 C). MS (c.i.): *m*/*z* (%) = 316 (38) [M + NH_4^+], 300 (32), [M^+ + 2], 299 (100) [M^+ + 1], 298 (93) [M^+]. $C_{20}H_{26}O_2$ (298.43): calcd. C 80.50, H 8.78; found C 80.83, H 8.49.

4,4′-Di-*tert*-butyl-2,2′-dimethoxybiphenyl (2e): A slurry of potassium hydride (0.8 g, 20 mmol) in a solution of 4,4′-di-*tert*-butylbiphenyl-2,2′-diol (**2d**; 3.0 g, 10 mmol) and methyl iodide (1.2 mL, 2.7 g, 20 mmol) in tetrahydrofuran (50 mL) was stirred for 2 h at 25 °C. Upon evaporation of the volatiles a white solid was obtained, which was crystallized from 50% aqueous ethanol to afford colorless platelets; yield: 3.17 g (97%); m.p. 142−143 °C. ^{1}H NMR (ppm): δ = 7.2 (s, 2 H), 7.0 (m, 4 H), 3.79 (s, 6 H), 1.36 (s, 18 H). ^{13}C NMR (ppm): δ = 157.0 (2 C), 152.0 (2 C), 131.5 (2 C), 125.0 (2 C), 117.8 (2 C), 109.0 (2 C), 56.0 (2 C), 35.0 (2 C), 31.7 (6 C). MS: *m*/*z* (%) = 328 (12) [M^+ + 2], 327 (56) [M^+ + 1], 326 (100) [M^+], 311 (85). $C_{22}H_{30}O_2$ (326.47): calcd. C 80.9, H 9.26; found C 81.03, H 9.19.

4,4′-Di-*tert*-butylbiphenyl-2-carboxylic Acid (3a): At −75 °C 4,4′-di-*tert*-butyl-2-iodobiphenyl[7] (**3c**; 7.8 g, 20 mmol) in tetrahydrofuran (50 mL) was added to *tert*-butyllithium (40 mmol) in hexanes (25 mL). The mixture was poured, 5 min later, onto an excess of freshly crushed dry ice covered by a layer of tetrahydrofuran. The product was isolated as described above (see diacid **2a**) to afford colorless needles (from 50% aqueous ethanol); yield: 5.28 g (85%); m.p. 221−222 °C (reprod.). ^{1}H NMR (ppm): δ = 7.94 (d, *J* = 2.1 Hz, 1 H), 7.55 (dd, *J* = 8.1, 2.1 Hz, 1 H), 7.38 (d, *J* = 8.1 Hz, 2 H), 7.30 (d, *J* = 8.1 Hz, 1 H), 7.27 (d, *J* = 8.1 Hz, 2 H), 1.36 (s, 9 H), 1.34 (s, 9 H). ^{13}C NMR (ppm): δ = 174.3, 150.0, 140.3, 137.8, 132.3, 131.1, 129.1, 128.9, 128.2, 127.5 (2 C), 125.0 (2 C), 34.6, 34.5, 31.4 (3 C), 31.2 (3 C). MS: *m*/*z* (%) = 310 (22) [M^+], 295 (100) 237 (6), 178 (3), 112 (3). $C_{21}H_{26}O_2$ (310.43): calcd. C 81.25, H 8.44; found C 81.48, H 8.11.

This acid was converted into its methyl ester by exhaustive treatment with ethereal diazomethane. The crude reaction mixture from which diacid **2a** was isolated (see above) was esterified in the same manner and examined by gas chromatography (2 m, 5% C-20M, 120 °C; 30 m, DB-1, 100 °C). Not even trace amounts (< 3%) of the monoester were detected by comparison of the retention times.

2-Bromo-4,4′-di-*tert*-butylbiphenyl (3b) and **4,4′-di-*tert*-butyl-2-iodobiphenyl (3c)**, formed as by-products along with the 2,2′-disubstituted analogs **2b** and **2c**, were equally identified by gas chromatographic comparison of their retention times with those of authentic samples[7] (2 m, 5% C-20M, 120 °C; 30 m, DB-1, 100 °C).

4,4′-Di-*tert*-butyl-2-hydroxybiphenyl (3d): The mother liquor from which the main product 4,4′-di-*tert*-butylbiphenyl-2,2′-diol (**2d**; see above) had been removed by crystallization was evaporated and the residue was crystallized from methanol to afford colorless needles; yield: 4.24 g (30%); m.p. 113−114 °C. ^{1}H NMR (ppm): δ = 7.5 (m, 2 H), 7.3 (m, 2 H), 7.14 (d, *J* = 7.2 Hz, 1 H), 7.03 (dd, *J* = 7.5, 2.0 Hz, 1 H), 6.77 (d, *J* = 2.0 Hz, 1 H), 1.29 (s, 9 H), 1.23 (s, 9 H). ^{13}C NMR (ppm): δ = 155.5, 147.1, 146.3, 133.2, 131.3, 128.1, 127.2 (2 C), 125.3 (2 C), 118.3, 113.0, 35.2, 34.9, 31.5 (6 C). MS: *m*/*z* (%) = 282 (23) [M^+], 220 (100), 187 (56), 151 (41), 123 (14), 108 (3).

2,7-Di-*tert*-butylfluoren-9-one (4): This compound was isolated as a by-product from the reaction in which di-*tert*-butylbiphenyl was mainly converted into the diacid **2a** (see above). After alkaline extraction, the organic solution was evaporated and the residue crystallized from pentanes to afford yellow platelets; yield: 2.19 g (15%); m.p. 111−112 °C (ref.[6] m.p. 109−110 °C). ^{1}H NMR (ppm): δ = 7.6 (m, 3 H), 7.1 (m, 3 H), 1.33 (s, 18 H). MS: *m*/*z* (%) = 292 (12) [M^+], 287 (34), 210 (100), 167 (1), 156 (3), 123 (5).

4,4′-Di-*tert*-butyl-5,5′-diiodo-2,2′-dimethoxybiphenyl (5): A biphasic mixture composed of 4,4′-di-*tert*-butyl-2,2′-dimethoxybiphenyl (16 g, 50 mmol), periodic acid dihydrate (2.3 g, 10 mmol), iodine (51 g, 0.20 mol), 98% sulfuric acid (1.0 mL), glacial acetic acid (26 mL), tetrachloromethane (20 mL), and water (4.5 mL) was heated to 80 °C for 2 h before being poured into a saturated solution (0.20 L) of sodium sulfite. The aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were dried and the solvents evaporated under reduced pressure. The residue was crystallized from ethanol to afford white cubes; yield: 23.1 g (80%); m.p. 120−121 °C. ^{1}H NMR (ppm): δ = 7.78 (s, 2 H), 7.04 (s, 2 H), 3.77 (s, 6 H), 1.57 (s, 18 H). ^{13}C NMR (ppm): δ = 157.0 (2 C), 151.0 (2 C), 145.5 (2 C), 125.5 (2 C), 111.5 (2 C), 82.8 (2 C), 55.9 (2 C), 37.0 (2 C), 29.9 (6 C). MS: *m*/*z* (%) = 578 (79) [M^+ + 1], 452 (100), 326 (53), 215 (5), 128 (6). $C_{22}H_{28}I_2O_2$ (578.26): calcd. C 45.70, H 4.88; found C 45.64, H 4.90.

4,4′-Di-*tert*-butyl-6,6′-dimethoxybiphenyl-3,3′-dicarboxylic Acid (6): At −75 °C, *tert*-butyllithium (80 mmol) in pentanes (54 mL) was added to 4,4′-di-*tert*-butyl-5,5′-diiodo-2,2′-dimethoxybiphenyl **5** (12 g, 20 mmol) in tetrahydrofuran (40 mL). After 5 min the mixture was poured onto an excess of freshly crushed dry ice covered by a layer of tetrahydrofuran. The product was isolated as described for diacid **2a** to afford colorless needles (from 50% aqueous ethanol); yield: 7.88 g (95%); m.p. 210−211 °C (reprod.). ^{1}H NMR (D_3CSOCD_3, ppm): δ = 7.20 (s, 2 H), 7.22 (s, 2 H), 3.89 (s, 6 H), 1.57 (s, 18 H). ^{13}C NMR (D_3CSOCD_3, ppm): δ = 174.2 (2 C), 158.5 (2 C), 149.8 (2 C), 132.6 (2 C), 127.7 (2 C), 124.5 (2 C), 101.1 (2 C), 56.7 (2 C), 37.1 (2 C), 32.1 (6 C). MS: *m*/*z* (%) = 414 (1) [M^+], 215 (1), 84 (100). $C_{24}H_{30}O_6$ (414.50): calcd. C 69.55, H 7.30; found C 69.51, H 7.33.

2,7-Di-*tert*-butyl-5,10-dihydro-[1]benzopyrano[5,4,3-*cde*][1]benzopyran-5,10-dione (7): At −75 °C, potassium *tert*-butoxide (9.0 g, 80 mmol) and 4,4′-di-*tert*-butylbiphenyl-2,2′-diol (**2d**; 3.3 g, 10 mmol) were added to butyllithium (80 mmol) in hexanes (50 mL). The suspension was stirred at 70 °C for 6 h. After cooling to 25 °C, the mixture was poured onto an excess of freshly crushed dry ice covered with a layer of tetrahydrofuran. A 10% aqueous

solution (50 mL) of sodium hydroxide was then added and the aqueous phase was washed with diethyl ether (3 × 20 mL) before being acidified to pH 5 and extracted with ethyl acetate (3 × 20 mL). The organic layer was dried and the volatiles were evaporated. The residue was crystallized from a 1:1 (v/v) ethyl acetate/pentane mixture to afford white platelets; yield: 1.44 g (41%); m.p. 190−191 °C. ^{1}H NMR (ppm): δ = 8.23 (s, 2 H), 7.75 (s, 2 H), 1.44 (s, 18 H). ^{13}C NMR (ppm): δ = 173.3 (2 C), 159.9 (2 C), 156.2 (2 C), 149.7 (2 C), 119.5 (2 C), 115.5 (2 C), 112.5 (2 C), 36.0 (2 C), 31.5 (6 C). MS: *m*/*z* (%) = 350 (34) [M$^+$], 263 (100), 222 (37), 180 (3), 165 (5), 138 (2). $C_{22}H_{22}O_4$ (350.41): calcd. C 75.41, H 6.33; found C 75.39, H 6.25.

4,4′-Di-*tert*-butyl-6,6′-bis(hydroxymethyl)biphenyl-2,2′-diol (8): A suspension of bislactone **7** (3.9 g, 10 mmol), aluminum trichloride (2.7 g, 20 mmol), and lithium aluminum hydride (0.8 g, 20 mmol) in diethyl ether (0.10 L) was stirred at 35 °C for 20 h. A saturated aqueous solution (50 mL) of sodium sulfate was added dropwise over 15 min followed by 10% hydrochloric acid (50 mL). The mixture was stirred for 1 h at 25 °C and filtered through a pad of diatomaceous earth. The filter cake was washed with ethyl acetate (5 × 20 mL). The white solid obtained after evaporation of the volatiles was crystallized from a 1:1 (v/v) ethyl acetate/pentane mixture to afford colorless needles; yield: 2.26 g (63%); m.p. 249−250 °C. ^{1}H NMR (ppm): δ = 8.71 (s, 2 H), 7.04 (d, *J* = 1.4 Hz, 2 H), 6.79 (s, d, *J* = 1.4 Hz, 2 H), 4.13 (d, *J* = 14.5 Hz, 2 H), 3.97 (d, *J* = 14.5 Hz, 2 H), 1.30 (s, 18 H). ^{13}C NMR (ppm): δ = 153.2 (2 C), 149.5 (2 C), 141.2 (2 C), 118.1 (2 C), 114.0 (2 C), 110.8 (2 C), 61.1 (2 C), 34.2 (2 C), 31.2 (6 C). MS: *m*/*z* (%) = 359 (70) [M$^+$ + 1], 358 (30) [M$^+$], 291 (100), 220 (32), 218 (1), 156 (12), 120 (3). $C_{22}H_{30}O_4$ (358.47): calcd. C 73.71, H 8.44; found C 73.94, H 8.03.

4,4′-Di-*tert*-butyl-6,6′-dimethylbiphenyl-2,2′-diol (9): A heterogeneous mixture of 6,6′-bis(hydroxymethyl)-4,4′-di-*tert*-butylbiphenyl-2,2′-diol (**8**; 2.4 g, 5.0 mmol), chlorotrimethylsilane (6.3 mL, 5.4 g, 50 mmol), and sodium iodide (7.5 g, 50 mmol) in dry acetonitrile (20 mL) was stirred at 25 °C for 20 h before being poured into a 10% aqueous solution (50 mL) of sodium sulfite. The aqueous phase was extracted with ethyl acetate (3 × 20 mL) and the combined organic phases evaporated. The residue was crystallized from pentanes to afford colorless cubes; yield: 1.27 g (78%); m.p. 182−183 °C. ^{1}H NMR (ppm): δ = 7.01 (s, 2 H), 6.91 (s, 2 H), 2.01 (s, 6 H), 1.33 (s, 18 H); integrals in the ratio of 1.0:1.0:3.0:9.0. ^{13}C NMR (ppm): δ = 154.0 (2 C), 151.3 (2 C), 147.4 (2 C), 127.0 (2 C), 124.5 (2 C), 116.0 (2 C), 35.0 (2 C), 31.0 (2 C), 20.1 (6 C). MS (c.i.): *m*/*z* (%) = 344 (5) [M + NH_4^+], 327 (17) [M$^+$ + 1], 326 (22) [M$^+$], 325 (61) [M$^+$ − 1], 324 (100) [M$^+$ − 2], 323 (93), 322 (61), 321 (17). $C_{22}H_{30}O_2$ (326.48): calcd. C 80.93, H 9.26; found C 81.04, H 9.29.

2,2′-Dihydroxy-6,6′-dimethylbiphenyl (10): A suspension of aluminum trichloride (2.0 g, 15 mmol) and 4,4′-di-*tert*-butyl-6,6′-dimethylbiphenyl-2,2′-diol (**9**; 1.6 g, 5.0 mmol) in benzene (89 mL, 78 g, 1.0 mol) was stirred at 25 °C for 20 h. After the addition of 10% hydrochloric acid (0.10 L) the stirring was continued for an additional 10 min before the organic layer was decanted and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The volatiles were evaporated and the residue was crystallized from methanol to afford colorless platelets; yield: 0.95 g (89%); m.p. 160−161 °C (ref.[13] m.p. 161.0−162.5 °C). ^{1}H NMR (ppm): δ = 7.2 (m, 2 H), 6.9 (m, 4 H), 2.01 (s, 6 H). ^{13}C NMR (ppm): δ = 154.0 (2 C), 139.1 (2 C), 130.0 (2 C), 122.8 (2 C), 119.9 (2 C), 113.4 (2 C), 19.5 (2 C). MS: *m*/*z* (%) = 214 (100) [M$^+$], 201 (32), 156 (12), 120 (2), 96 (12).

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