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# The Abnormal Behavior of an Atropisomer: 3,3′-Dibromo-1,1′-difluoro-2,2′-binaphthyl Reacting with Alkyllithium Compounds

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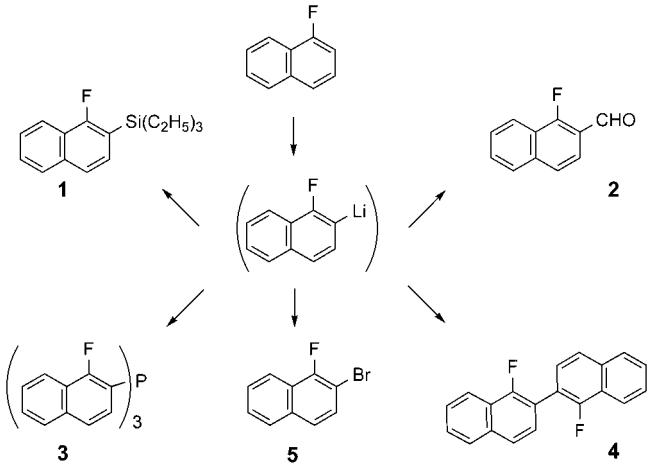
1-Fluoro-2-(triethylsilyl)naphthalene (**1**) and other 1-fluoronaphthalenes bearing a metalation-resistant substituent at the 2-position proved to be totally inert toward base attack. 3-Bromo-1-fluoronaphthalene (**6**), readily prepared from the 2-bromo isomer **5** by deprotonation-triggered heavy halogen migration, was converted into 3,3′-dibromo-1,1′-difluoro-2,2′-binaphthyl (**8**) by consecutive treatment with lithium diisopropylamide, copper(II) bromide and nitrobenzene. The dilithiated intermediate generated from the atropisomer **8** by treatment with 2 equiv. of butyllithium reacted with a variety of electrophiles to afford products such as the diacid **12** or the bis(phosphanes) **14** and **15** in high yields. The latter compound was also obtained in a straightforward manner from (4-fluoro-2-naphthyl)diphenylphosphane oxide (**16**). Unexpectedly, neither the 3,3′-dibromobinaphthyl **8** nor its 3,3′-diiodo analogue **18** were amenable to a unilateral but only to a double-sided halogen/metal permutation.



Naphthalenes carrying heteroatoms or functional groups at the 1-position may undergo a permutational hydrogen/metal interconversion ("metalation") at either the 2- or the 8-position.[1,2] When treated with phenyllithium in diethyl ether at ambient temperature[3] or with butyllithium in tetrahydrofuran at –60 °C,[4] 1-fluorononaphthalene was deprotonated at the 2-position rapidly and exclusively. Not even trace amounts of products resulting from attack at the 8-position were detected, whereas such regioisomers were invariably formed, depending on the reaction conditions, as minor or major components, when 1-methoxynaphthalene served as the substrate.[1]

We wondered whether the *peri* metalation could be forced by simply blocking the *ortho* position. To this end, 1-fluoronaphthalene was converted into a series of derivatives, two of which were selected for further studies. Trapping of the intermediate 1-fluoro-2-naphthyllithium with chlorotriethylsilane afforded the silane **1** (91%), with *N*,*N*-dimethylformamide the aldehyde **2** (66%), with triethyl phosphite the phosphane **3** (92%), with copper(II) bromide in the presence of nitrobenzene[5] the dimer **4** (84%), and with elemental bromine the dihalo compound **5** (92%).




Whereas protons may be abstracted from trimethylsilyl groups,[6,7] triethylsilyl entities were so far always found to be inert towards even the strongest organometallic reagents. Therefore, the silane **1** and the binaphthyl **4** were exposed to the action of both *sec*-butyllithium in tetrahydrofuran at –75 °C and potassium *tert*-butoxide activated butyllithium[8,9] in hexanes at +25 °C over prolonged periods of time. In either case the starting materials were recovered quantitatively.

1-Fluoronaphthalene being an inexpensive substance (retail price about 100 €/mol), we decided to explore its chemistry further. As previously accomplished with 1-fluoro-2-iodonaphthalene,[10] the bromo compound **5** was subjected to a deprotonation-triggered heavy halogen migration. The 2-bromo-1-fluoro-3-naphthyllithium initially generated

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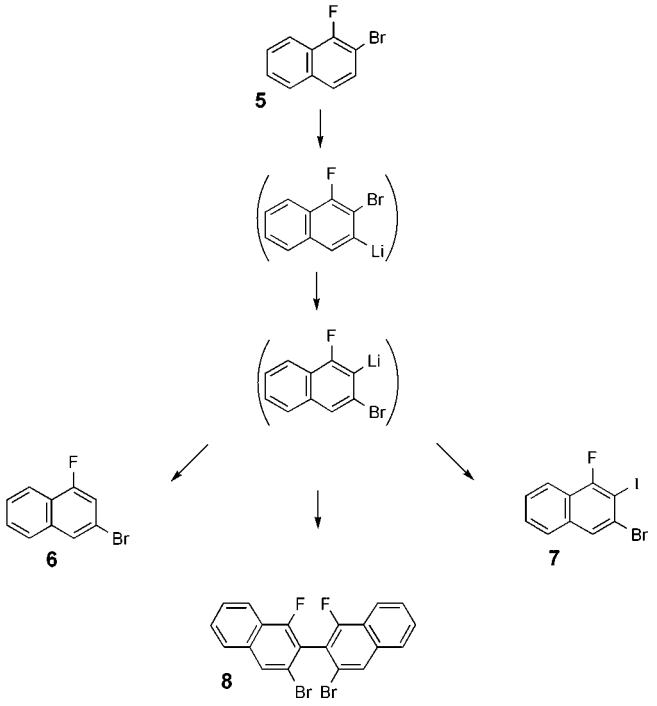
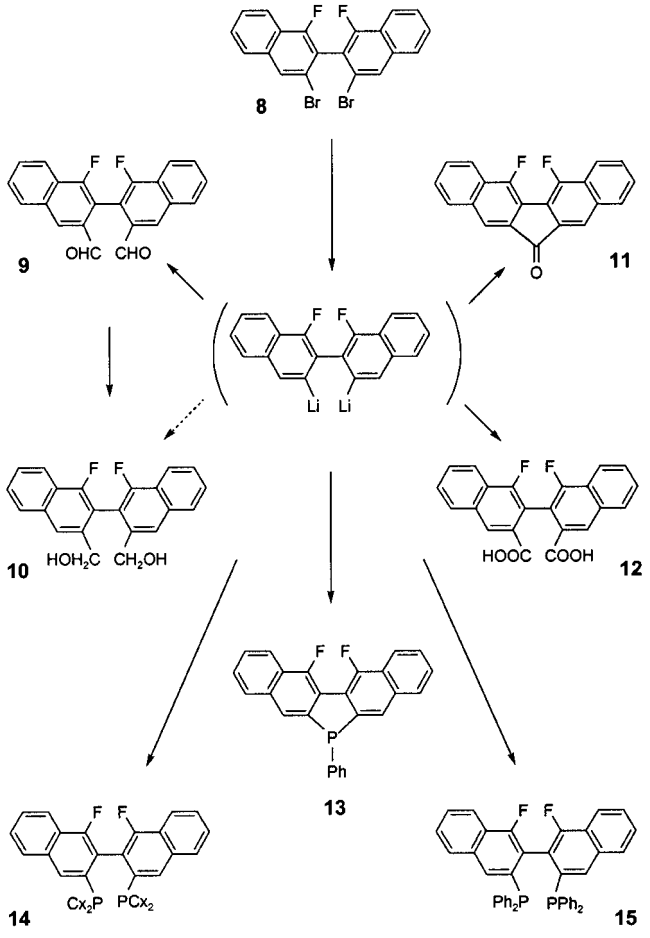
with lithium diisopropylamide instantaneously isomerized to the 3-bromo-1-fluoro-2-naphthyllithium which gave 3-bromo-1-fluoronaphthalene (**6**; 89%) upon neutralization, 3-bromo-1-fluoro-2-iodonaphthalene (**7**; 80%) upon trapping with elemental iodine, and 3,3′-dibromo-1,1′-difluoro-2,2′-binaphthyl (**8**; 66%) upon oxidative dimerization using copper(II) bromide in the presence of nitrobenzene.



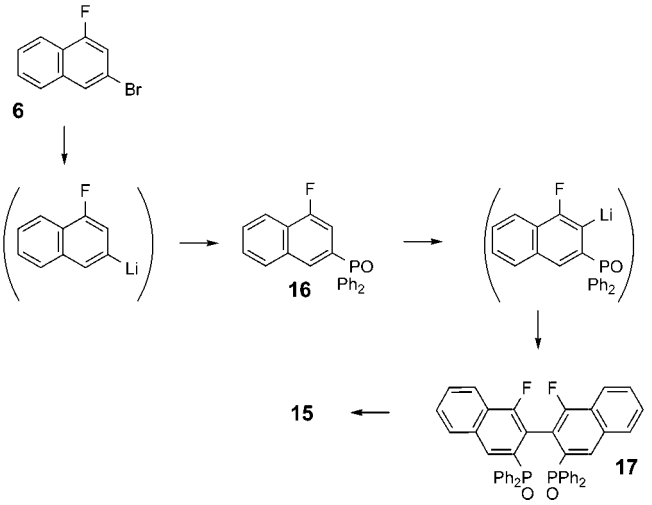

A twofold halogen/metal permutation performed with butyllithium (2.0 equiv.) or *tert*-butyllithium (4.0 equiv.) transformed the dibromo compound **8** into a dilithio species which reacted with *N*,*N*-dimethylformamide to afford the dialdehyde **9** (61%). This was reduced to the dialcohol **10** (85%). The same compound was obtained directly, although in only poor yield (<30%), when the dilithio species was treated with paraformaldehyde. The organometallic intermediate was furthermore converted into the dibenzofluorinone **11** (with methyl chloroformate; 91%), the dicarboxylic acid **12** (with dry ice; 58%), the benzonaphthophosphindene **13** [with dichloro(phenyl)phosphane; 70%], the bis(dicyclohexylphosphane) **14** (with chlorodicyclohexylphosphane; 67%) and the bis(diphenylphosphane) **15** (with chlorodiphenylphosphane; 15%).

The same bis(phosphane) was accessed also by a different route. Consecutive treatment of 3-bromo-1-fluoronaphthalene (**6**) with *tert*-butyllithium and diphenylphosphinic chloride gave the phosphane oxide **16** (60%) which, after *ortho*-lithiation,[11] was oxidatively coupled to the bis(phosphane oxide) **17** (71%). This compound was eventually reduced with trichlorosilane to the bis(phosphane) **15** (63%).

To prepare bis(phosphanes) having two different sets of *P*-substituents, for example phenyl on one and cyclohexyl on the other side, a 3′-bromo-2,2′-binaphthyl-3-yllithium would be required. Unfortunately, all attempts to stop the



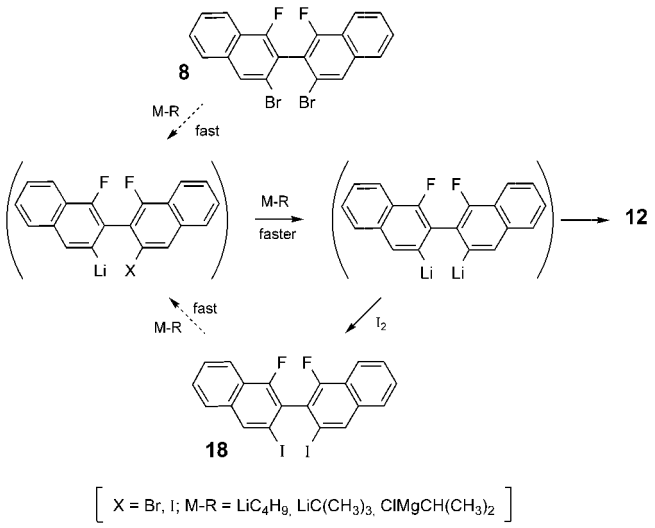

[ Cx = cyclohexyl, Ph = phenyl ]



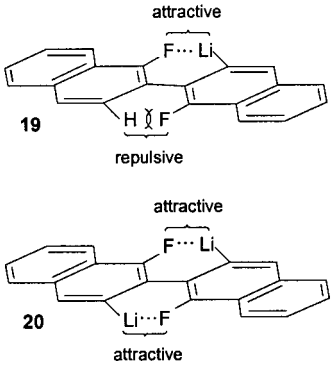

permutational halogen/metal interconversion at an intermediate stage failed. No matter what reagent and what reaction conditions were employed, roughly 50% of the 3,3′-disubstituted product (e.g., diacid **12**) was formed and half of the starting material was recovered whenever only 1 mol-equiv. of the alkyllithium was added. The same situation was encountered when the diiodo compound **18**, prepared

from the dibromo-2,2′-binaphthyl **8** by consecutive reaction with butyllithium and iodine (2 equiv. each) in 80% yield, was treated with isopropylmagnesium chloride.




This behavior contrasts strikingly with that of numerous other *o*,*o*′-dibromo-1,1′-biaryls and even of 2,2′,6,6′-tetrabromobiphenyl which enable a stepwise replacement of the two halogens without any problem.[12] At the moment, we can only offer a tentative explanation of the divergent reaction mode observed with the binaphthyl **8**. Although the planes of the two aromatic rings of biphenyl occupy a dihedral angle of approximately 45 °C[13] and are more strongly twisted in 2,2′-difluorobiphenyl[14] or in 2,2′,6,6′-tetrafluorobiphenyl derivatives[5,15–18] (dihedral angles ≥ 55°), 6,6′-difluoro-2,2′-biphenyldiyldilithium and 1,1′-difluoro-2,2′-binaphthyldiyldilithium (and analogous magnesium derivatives as well) may adopt a flattened array. Strong interactions are known to exist between fluorine and metals, both covalently bound to carbon.[19–27] The resulting gain in energy may suffice to planarize the biaryl structure already after the introduction of the first metal atom (intermediate **19**) and, all the more, after the introduction of the second metal (intermediate **20**).




## Experimental Section

**General:** Details concerning standard operations and abbreviations can be found in previous publications from this laboratory.[28–30] $^1$H and ($^1$H-decoupled) $^{13}$C NMR spectra were recorded at 400 and 101 MHz, respectively, of samples dissolved in deuterochloroform.

**Triethyl(1-fluoro-2-naphthyl)silane (1):** 1-Fluoronaphthalene (5.5 mL, 7.3 g, 50 mmol) was added to a solution of *sec*-butyllithium (50 mmol) in tetrahydrofuran (0.10 L) and hexanes (40 mL), cooled in a methanol/dry ice bath. After 2 h at –75 °C, the mixture was treated with chlorotriethylsilane (8.4 mL, 7.5 g, 50 mmol) and distilled without any further workup; colorless liquid; b.p. 188–190 °C/15 Torr; $n_D^{20}$ = 1.5553; yield: 11.8 g (91%). $^1$H NMR: δ = 8.09 (dd, *J* = 5.8, 3.4 Hz, 1 H), 7.81 (symm. m, 1 H), 7.59, (d, *J* = 8.0 Hz, 1 H), 7.49 (dt, *J* = 9.5, 3.2 Hz, 2 H), 7.41 (dd, *J* = 8.2, 5.2 Hz, 1 H), 1.00 (q, *J* = 6.9 Hz, 9 H), 0.93 (t, *J* = 6.9 Hz, 6 H). $^{13}$C NMR: *δ* = 165.3, 162.8, 136.0, 131.0, 127.5, 127.2, 126.5, 123.2, 121.0, 116, 10.3, 4.1 ppm. $C_{16}H_{21}FSi$ (260.43): calcd. C 73.79, H 8.13; found C 73.74, H 8.23.

**1-Fluoronaphthalene-2-carbaldehyde (2):** The reaction was started as described above, but chlorotriethylsilane was replaced by *N*,*N*-dimethylformamide (3.9 mL, 3.7 g, 50 mmol). The mixture was poured into water (0.15 L) and extracted with diethyl ether (3 × 20 mL). After evaporation of the volatiles, the residue was crystallized from ethanol; yellow prisms; m.p. 35–36 °C; 2,4-dinitrophenylhydrazone: m.p. 262–265 °C (decomp.) (ref.[31] 265 °C); yield: 5.7 g (66%). $^1$H NMR: *δ* = 10.59 (d, *J* = 0.6 Hz, 1 H), 8.23 (d, *J* = 5.5 Hz, 1 H), 7.88 (d, *J* = 5.5 Hz, 1 H), 7.84 (dd, *J* = 5.9, 4.5 Hz, 1 H), 7.65 (symm. m, 3 H) ppm. $^{13}$C NMR: *δ* = 164.9, 162.0, 138.2, 130.0, 128.0, 127.5, 124.5, 123.5, 123.0, 122.0, 119.0 ppm.

**Tris(1-fluoronaphth-2-yl)phosphane (3):** Analogously, using 1-fluoronaphthalene (11 mL, 15 g, 0.10 mol), *sec*-butyllithium (0.10 mol) and phosphorus trichloride (2.4 mL, 4.5 g, 33 mmol). After 2 h at –75 °C, the mixture was poured into water. The organic layer was separated and the aqueous one was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were dried and concentrated under reduced pressure. The residue was crystallized from a 1:1 (v/v) ethyl acetate/pentane mixture to obtain fine colorless needles; m.p. 173–174 °C; yield: 14.2 g (92%). $^1$H NMR: *δ* = 8.1 (m, 3 H), 7.8 (m, 3 H), 7.5 (m, 9 H), 7.1 (m, 3 H) ppm. $^{13}$C NMR: *δ* = 162.3 (d, *J* = 17.5 Hz), 159.7 (d, *J* = 17.5 Hz), 136, 129.3, 127.8 (d, *J* = 22.5 Hz), 126.8, 124.0, 123.4 (d, *J* = 17.5 Hz), 121.0, 115.5 ppm. $C_{30}H_{18}F_3P$ (466.43): calcd. C 77.25, H 3.89; found C 77.14, H 3.89.

**1,1′-Difluoro-2,2′-binaphthyl (4):** After treating 1-fluoronaphthalene (0.10 mol) with *sec*-butyllithium (0.10 mol) at –75 °C for 2 h, cupric bromide (22 g, 0.10 mol) was added under vigorous stirring and 45 min later, still at –75 °C, nitrobenzene (10 mL, 12 g, 0.10 mol). At +25 °C, the mixture was filtered through basic alumina (0.30 kg) and the filter cake was washed with hexane (3 × 0.20 L). After evaporation of the volatiles, the residue was crystallized from ethanol; colorless platelets; m.p. 152–153 °C; yield: 12.0 g (84%). $^1$H NMR: *δ* = 8.21 (d, *J* = 7.5 Hz, 2 H), 7.90 (d, *J* = 7.5 Hz, 2 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 7.58 (symm. m, 6 H) ppm. $^{13}$C NMR: *δ* = 155.6, 134.6, 128.4, 127.5, 127.4, 124.1, 123.7, 121.4, 118.0, 113.1 ppm. $C_{20}H_{12}F_2$ (290.31): calcd. C 82.75, H 4.17; found C 82.76, H 4.16.

**2-Bromo-1-fluoronaphthalene (5):** Analogously, using 1-fluoronaphthalene (50 mmol), *sec*-butyllithium (50 mmol) and, after 2 h at –75 °C, bromine (2.6 mL, 8.0 g, 50 mmol) in precooled hexanes (0.10 L). The mixture was washed with a 10% aqueous solution (0.20 L) of sodium sulfite. Distillation under reduced pressure af-

forded a colorless liquid; b.p. 120–121 °C/15 Torr (ref.[4] 93 °C/0.1 Torr; m.p.[4] –4 to –2 °C); $n_D^{20}$ = 1.6328 (ref.[4] 1.6322); yield: 10.3 g (92%). $^1$H NMR: $\delta$ = 8.0 (m, 1 H), 7.8 (m, 1 H), 7.5 (m, 4 H) ppm. $^{13}$C NMR: $\delta$ = 158.1, 151.3, 134.0, 129.6, 127.9, 127 (m), 125.0, 124.5 (d, $J$ = 25.0 Hz), 120.0, 103.9 (d, $J$ = 25.0 Hz) ppm.

**3-Bromo-1-fluoronaphthalene (6):** 2,2,6,6-Tetramethylpiperidine (8.5 mL, 7.1 g, 50 mmol) and 2-bromo-1-fluoronaphthalene (**5**; 11 g 50 mmol) were added consecutively to a solution of butyllithium (50 mmol) in tetrahydrofuran (0.10 L) and hexanes (25 mL), cooled in a methanol/dry ice bath. After 6 h at –75 °C, the mixture was poured into brine (0.10 L). The organic layer was concentrated. Upon distillation of the residue, a colorless liquid was collected; b.p. 85–86 °C/10 Torr (ref.[32] 74–78 °C/0.3 Torr), $n_D^{20}$ = 1.6318 (ref.[32] 1.6314); yield: 10.0 g (89%). $^1$H NMR: $\delta$ = 8.01 (dd, $J$ = 6.4, 3.3 Hz, 1 H), 7.76 (s, 1 H), 7.71 (symm. m, 1 H), 7.51 (dd, $J$ = 9.7, 3.3 Hz, 2 H), 7.25 (dd, $J$ = 9.8, 1.7 Hz, 1 H) ppm. $^{13}$C NMR: $\delta$ = 160.3, 154.1, 135.9, 129.2, 127.6, 126.2, 121.9, 119.8, 115.0 (dd, $J$ = 23.4, 7.8 Hz), 113.2 (dd, $J$ = 23.4, 7.8 Hz) ppm.

**3-Bromo-1-fluoro-2-iodonaphthalene (7):** Diisopropylamine (7.0 mL, 5.0 g, 50 mmol) and 3-bromo-1-fluoronaphthalene (**6**; 11 g, 50 mmol) were added consecutively to a solution of butyllithium (50 mmol) in tetrahydrofuran (0.10 L) and hexanes (25 mL), kept in a methanol/dry ice bath. After 2 h at –75 °C, the mixture was treated with iodine (13 g, 50 mmol) in tetrahydrofuran (50 mL) before being washed with a 10% aqueous solution (50 mL) of sodium sulfite. The aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried and the solvents evaporated. Crystallization of the residue from ethanol gave colorless fine needles; m.p. 109–110 °C; yield: 14.0 g (80%). $^1$H NMR: $\delta$ = 8.0 (m, 2 H), 7.8 (m, 1 H), 7.6 (m, 2 H) ppm. $^{13}$C NMR: $\delta$ = 161.0, 155.1, 135.5, 128.9, 127.5, 127.0, 122.0, 120.9, 112.2, 85.2 (d, $J$ = 30.0 Hz) ppm. $C_{10}H_5BrFI$ (350.95): calcd. C 34.22, H 1.44; found C 34.41, H 1.04.

**3,3′-Dibromo-1,1′-difluoro-2,2′-binaphthyl (8):** 3-Bromo-1-fluoro-2-iodonaphthalene (**7**; 18 g, 50 mmol) was consecutively treated with butyllithium (50 mmol), cupric bromide (50 mmol) and nitrobenzene (50 mmol) as described above for the preparation of the difluorobinaphthyl **4**. The same workup procedure gave colorless prisms (from methanol); m.p. 201–202 °C (reprod.); yield: 7.39 g (66%). $^1$H NMR: $\delta$ = 8.1 (m, 2 H), 8.05 (s, 2 H), 7.8 (m, 2 H), 7.6 (m, 4 H) ppm. $^{13}$C NMR: $\delta$ = 160, 157.7, 134.7, 128.5, 127.2, 126.6, 125.5, 122.1, 121.8, 120.5 ppm. $C_{20}H_{10}F_2Br_2$ (448.10): calcd. C 53.61, H 2.25; found C 53.52, H 2.63.

**1,1′-Difluoro-2,2′-binaphthyl-3,3′-dicarbaldehyde (9):** 3,3′-Bromo-1,1′-difluoro-2,2′-binaphthyl (**8**; 8.9 g, 20 mmol) was added to a solution of butyllithium (40 mmol) in tetrahydrofuran (80 mL) and hexanes (25 mL), cooled in a methanol/dry ice bath. The mixture was transferred through a stainless steel capillary into a solution of *N*,*N*-dimethylformamide (2.0 mL, 2.9 g, 40 mmol) in tetrahydrofuran (25 mL), kept at –75 °C, before being poured into water (0.10 L). Extraction of the aqueous phase with diethyl ether (3 × 20 mL), concentration of the combined organic layers after drying and crystallization of the residue from a 1:1 (v/v) mixture of ethyl acetate and pentanes afforded colorless platelets; m.p. 352–353 °C (decomp.); yield: 4.23 g (61%). $^1$H NMR: $\delta$ = 8.37 (s, 2 H), 8.18 (d, $J$ = 8.0 Hz, 3 H), 8.10 (d, $J$ = 8.0 Hz, 3 H) ppm. $^{13}$C NMR: $\delta$ = 165.5, 134.5, 134.0, 132.8, 131.5, 130.7, 129.9, 127.3, 121.5, 113.7, 109.2 ppm. $C_{22}H_{12}F_2O_2$ (346.33): calcd. C 76.30, H 3.49; found C 75.96, H 3.62. All attempts failed to accomplish unilateral substitution by employing butyllithium in equimolar amounts (1.0 equiv.), in the presence or absence of *N*,*N*,*N*′,*N*′′,*N*′′-pentamethyldiethylenetriamine, *tert*-butyllithium (1.0 and 2.0 equiv.) or phenyllithium (1.0 equiv.) as the exchange reagent, diethyl ether instead of tetrahydrofuran as the solvent, and –125 or –100 °C rather than –75 °C as the reaction temperature (standard exposure time 15 min). According to the $^1$H and $^{19}$F NMR spectra, a mixture of unconsumed starting material **8** and dialdehyde **9** was obtained in all these cases.

**1,1′-Difluoro-3,3′-hydroxymethyl-2,2′-binaphthyl (10):** 1,1′-Difluoro-2,2′-binaphthyl-3,3′-dicarbaldehyde (**9**; 6.9 g, 20 mmol) and lithium aluminum hydride (1.5 g, 40 mmol) were dissolved in tetrahydrofuran (0.20 L). The reaction mixture was heated at 65 °C for 2 h under vigorous stirring. Methanol (20 mL) was added dropwise and the resulting suspension was filtered through a Celite filter pad (30 g). The yellow orange solid residue obtained after evaporation of the volatiles was crystallized from a 1:1 (v/v) ethyl acetate/pentane mixture; colorless platelets; m.p. 130–132 °C; yield: 5.96 g (85%). $^1$H NMR: $\delta$ = 8.0 (m, 2 H), 7.8 (m, 2 H), 7.69 (s, 2 H), 7.5 (m, 4 H), 4.38 (s, 4 H) ppm. $^{13}$C NMR: $\delta$ = 156.8, 154.3, 138.0, 134.7, 127.9, 127.5, 126.7, 123.7, 123.0, 120.8, 63.3 ppm. $C_{22}H_{16}F_2O_2$ (350.36): calcd. C 75.42, H 4.60; found C 75.06, H 4.70.

**5,6-Difluoro-12*H*-dibenzo[*b*,*h*]fluoren-12-one (11):** At –75 °C, 3,3′-dibromo-1,1′-difluoro-2,2′-binaphthyl (8.9 g, 20 mmol) was added to a solution of butyllithium (40 mmol) in tetrahydrofuran (80 mL) and hexanes (26 mL). After 5 min, the mixture was treated with methyl chloroformate (1.5 mL, 1.9 g, 20 mmol), before being poured into water (0.10 L). The aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried and the solvents evaporated. The residue was recrystallized from a 1:1 (v/v) ethyl acetate/pentanes mixture; yellow prisms; m.p. 290–291 °C (decomp.); yield: 5.70 g (91%). $^1$H NMR: $\delta$ = 7.6 (m, 2 H), 7.5 (m, 4 H), 7.4 (m, 4 H) ppm. $^{13}$C NMR: $\delta$ = 164.2, 142.5, 136.0, 133.7, 128.7, 128.2, 128 (m), 127.4, 124.5, 121.6, 120.7 ppm. $C_{21}H_{10}F_2O$ (316.30): calcd. C 79.74, H 3.19; found C 77.40, H 3.96.

**1,1′-Difluoro-2,2′-binaphthyl-3,3′-dicarboxylic Acid (12):** An analogous reaction was carried out but the mixture was poured onto freshly crushed dry ice, covered by a tetrahydrofuran layer (rather than treated with methyl chloroformate). The semisolid product was dissolved in a 10% aqueous solution of potassium hydroxide (20 mL). Washing with diethyl ether (3 × 20 mL) and acidification of the aqueous phase to pH = 5 gave a white precipitate that was crystallized from a 1:1 (v/v) mixture of toluene and heptanes; colorless platelets; m.p. >350 °C; yield: 4.40 g (58%). $^1$H NMR: $\delta$ = 8.68 (s, 2 H), 8.36 (d, $J$ = 8.0 Hz, 2 H), 8.20 (d, $J$ = 8.0 Hz, 2 H), 7.87 (symm. m, 4 H) ppm. $^{13}$C NMR: $\delta$ = 167.9, 156.9, 154.5, 133.8, 130.8, 130.4, 129.3, 128.1, 125.4, 121.5, 118.1 ppm. $C_{22}H_{12}F_2O_4$ (378.33): calcd. C 69.84, H 3.20; found C 69.78, H 3.34.

**1,13-Difluoro-7-phenyl-7*H*-benzo[*f*]naphtho[2,3-*b*]phosphindole (13):** An analogously prepared reaction mixture was treated dropwise, at –75 °C, with dichloro(phenyl)phosphane (2.7 mL, 3.6 g, 20 mmol) in tetrahydrofuran (40 mL). The solvents were evaporated and the orange-yellow residue repetitively extracted with a hot 1:1 (v/v) mixture of ethyl acetate and methanol. Upon concentration and cooling, colorless platelets were obtained; m.p. 214–215 °C (reprod.); yield: 5.55 g (70%). $^1$H NMR: $\delta$ = 8.29 (d, $J$ = 8.2 Hz, 2 H), 7.93 (d, $J$ = 7.5 Hz, 2 H), 7.79 (d, $J$ = 8.2 Hz, 2 H), 7.5 (m, 4 H), 7.3 (m, 1 H), 7.2 (m, 4 H) ppm. $^{13}$C NMR: $\delta$ = 134.5, 133.0, 132.5, 131.4, 131.1, 129.7, 129.0, 128.6, 127.6, 127.1, 126.9, 126.6, 122.0, 121.6 ppm. $C_{26}H_{15}F_2P$ (396.37): calcd. C 78.78, H 3.81; found C 78.46, H 4.10.

**3,3′-Bis(dicyclohexylphosphanyl)-1,1′-difluoro-2,2′-binaphthyl (14):** Prepared analogously, using chlorodicyclohexylphosphane (8.8 mL, 9.3 g, 40 mmol) in tetrahydrofuran (40 mL). The orange-

yellow solid left behind upon evaporation of the volatiles was crystallized from a 1:1 (v/v) mixture of ethyl acetate and methanol; colorless platelets; m.p. 240–242 °C (reprod.); yield: 9.15 g (67%). $^1$H NMR: $\delta$ = 8.0 (m, 2 H), 7.91 (s, 2 H), 7.76 (s, 2 H), 7.5 (m, 4 H), 1.9 (m, 4 H), 1.8 (m, 8 H), 1.5 (m, 8 H), 1.4 (m, 8 H), 1.3 (m, 8 H), 1.0 (m, 8 H) ppm. $^{13}$C NMR: $\delta$ = 134.0, 127.9, 127.0, 126.6, 123.5, 121.0, 36.0, 32.7, 30.8, 30.0, 29.1, 28.3, 27.0, 26.2 ppm. $C_{44}H_{54}F_2P_2$ (682.84): calcd. C 77.39, H 7.97; found C 77.78, H 8.04.

**1,1′-Difluoro-3,3′-bis(diphenylphosphanyl)-2,2′-binaphthyl (15):** Prepared essentially as described in the preceding paragraph by treatment of the reaction mixture with chlorodiphenylphosphane (7.2 mL, 8.8 g, 40 mmol) in tetrahydrofuran (40 mL) at +25 °C. Water (0.10 L) was added, the organic layer was separated and the aqueous phase was extracted with diethyl ether (3 × 20 mL). The combined organic phases were dried and the solvents evaporated. The yellow solid was recrystallized from a 1:1 (v/v) ethyl acetate/hexanes mixture to afford colorless prisms; m.p. 68–70 °C; yield: 1.97 g (15%). $^1$H NMR: $\delta$ = 8.1 (m, 2 H), 7.7 (m, 2 H), 7.60 (d, $J$ = 9.0 Hz, 2 H), 7.51 (dquint, $J$ = 6.0, 2.0 Hz, 4 H), 7.35 (d, $J$ = 5.0 Hz, 18 H), 7.03 (dq, $J$ = 6.0, 1.0 Hz, 2 H) ppm. $^{13}$C NMR: $\delta$ = 160.0 (d, $J$ = 7 Hz), 157.8 (d, $J$ = 7.0 Hz), 137.0 (d, $J$ = 10 Hz), 136.0 (d, $J$ = 20 Hz), 135 (m), 134.0 (dd, $J$ = 25, 5 Hz), 130.0 (d, $J$ = 7.0 Hz), 129.4, 129 (m), 128.0, 127.4 (d, $J$ = 30 Hz), 124 (m), 120.9, 113 (m) ppm. $C_{44}H_{30}F_2P_2$ (658.67): calcd. C 80.24, H 4.59; found C 79.99, H 4.84.

**(1-Fluoronaphth-3-yl)diphenylphosphane Oxide (16):** 3-Bromo-1-fluoronaphthalene (**6**; 2.2 g, 10 mmol) and diphenylphosphinic chloride (1.9 mL, 2.3 g, 10 mmol) were added consecutively to a solution of *tert*-butyllithium (20 mmol) in tetrahydrofuran (40 mL) and hexanes (15 mL) cooled to –75 °C. When having reached +25 °C, the reaction mixture was absorbed on silica gel (50 mL) and was eluted with ethyl acetate from a column filled with more silica (0.45 L). The material collected after evaporation of the solvent was triturated with diethyl ether and crystallized from toluene; colorless platelets; m.p. 134–135 °C; yield: 2.08 g (60%). $^1$H NMR: $\delta$ = 8.1 (m, 2 H), 7.9 (m, 1 H), 7.7 (m, 4 H), 7.6 (m, 1 H), 7.5 (m, 3 H), 7.4 (m, 4 H), 7.3 (m, 1 H) ppm. $^{13}$C NMR: $\delta$ = 160.1 (d, $J$ = 17.5 Hz), 157.6 (d, $J$ = 17.5 Hz), 135 (m), 134 (m), 133 (m), 132 (m), 131.9, 131 (m), 130 (m), 129 (m), 128.1, 125.5 (d, $J$ = 12.5 Hz), 120.9, 111.0 ppm. $C_{22}H_{16}FOP$ (346.34): calcd. C 76.29, H 4.66; found C 76.09, H 4.56.

**1,1′-Difluoro-3,3′-bis(diphenylphosphoryl)-2,2′-binaphthyl (17):** Diisopropylamine (1.4 mL, 1.0 g, 10 mmol) and (1-fluoronaphth-3-yl)-diphenylphosphane oxide (**16**; 3.5 g, 10 mmol) were added consecutively to butyllithium (10 mmol) in tetrahydrofuran (50 mL) and hexanes (6.0 mL), kept in a methanol/dry ice bath. After 15 min at –75 °C, the mixture was treated with copper(II) bromide (4.5 g, 20 mmol) and after stirring for 1 h at –75 °C, with nitrobenzene (2.5 g, 2.0 mL). The reaction mixture was filtered through an alumina pad (0.10 L) and the filter cake was washed with chloroform (3 × 50 mL). The combined organic phases were concentrated and the residue was crystallized from a 1:5 (v/v) mixture of diethyl ether and isopropyl alcohol; colorless cubes; m.p. 189–190 °C; yield: 2.45 g (71%). $^1$H NMR: $\delta$ = 7.5 (m, 8 H), 7.6 (m, 6 H), 7.68 (t, $J$ = 7.5 Hz, 2 H), 7.7 (m, 10 H), 7.85 (d, $J$ = 15.0 Hz, 2 H), 8.10 (d, $J$ = 8.0 Hz, 2 H) ppm. $^{13}$C NMR: $\delta$ = 157.5 (d, $J$ = 2.5 Hz), 155 (d, $J$ = 2.5 Hz), 133 (m), 132 (m), 131 (m), 130 (m), 129.6, 129 (m), 128.4, 128 (m), 127 (m), 126 (m), 120.6, 105 (m) ppm. $C_{44}H_{30}F_2O_2P_2$ (690.65): calcd. C 76.52, H 4.38; found C 76.34, H 4.60.

**1,1′-Difluoro-3,3′-diiodo-2,2′-binaphthyl (18):** Obtained analogously as described for the preparation of compound **9** by the treatment with a solution of iodine (10 g, 40 mmol) in tetrahydrofuran (40 mL). The mixture was washed with a 10% solution of sodium sulfite (50 mL) which was then reextracted with diethyl ether (3 × 20 mL). The combined organic layers were dried and the solvents evaporated. The white residue was crystallized from toluene; colorless prisms; m.p. 243–244 °C (reprod.); yield: 17.3 g (80%). $^1$H NMR: $\delta$ = 8.37 (s, 2 H), 8.1 (m, 2 H), 7.9 (m, 2 H), 7.6 (m, 4 H) ppm. $^{13}$C NMR: $\delta$ = 156.7, 136.4, 134.2, 128.6, 127.5, 126.9, 123.7, 123.5, 121.6, 97.0 ppm. $C_{20}H_{10}F_2I_2$ (542.10): calcd. C 44.31, H 1.86; found C 44.46, H 1.98.

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