

The Abnormal Behavior of an Atropisomer: 3,3'-Dibromo-1,1'-difluoro-2,2'-binaphthyl Reacting with Alkylolithium Compounds

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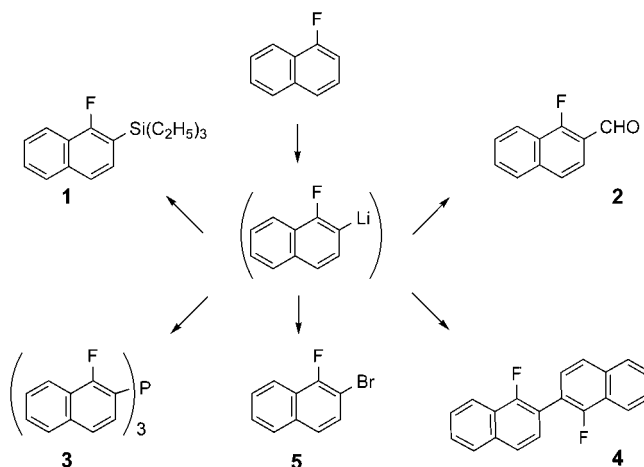
1-Fluoro-2-(triethylsilyl)naphthalene (**1**) and other 1-fluoronaphthalenes bearing a metalation-resistant substituent at the 2-position proved to be totally inert toward base attack. 3-Bromo-1-fluoronaphthalene (**6**), readily prepared from the 2-bromo isomer **5** by deprotonation-triggered heavy 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.

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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-fluoronaphthalene 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%).



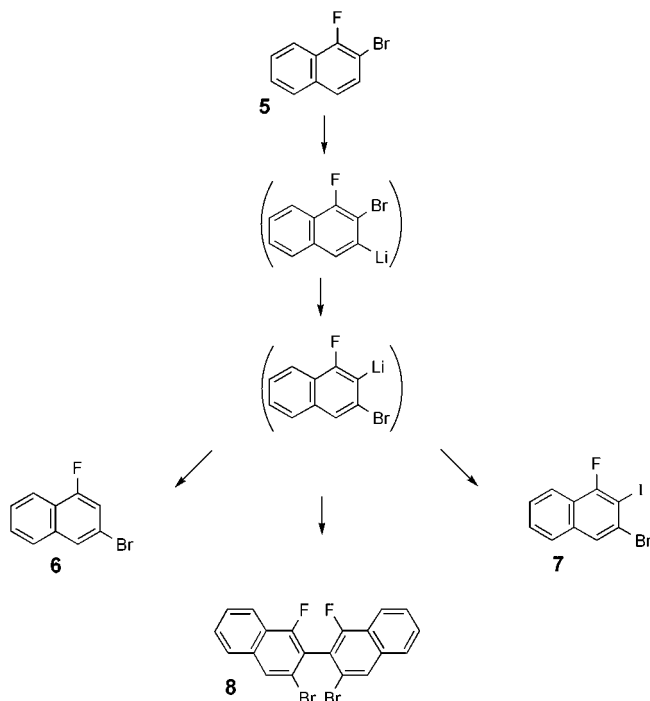
Whereas protons may be abstracted from trimethylsilyl groups,^[6,7] triethylsilyl entities were so far always found to be inert towards even the strongest organometallic reagents. Therefore, the silane **1** and the binaphthyl **4** were exposed to the action of both *sec*-butyllithium in tetrahydrofuran at -75°C and potassium *tert*-butoxide activated butyllithium^[8,9] in hexanes at $+25^{\circ}\text{C}$ 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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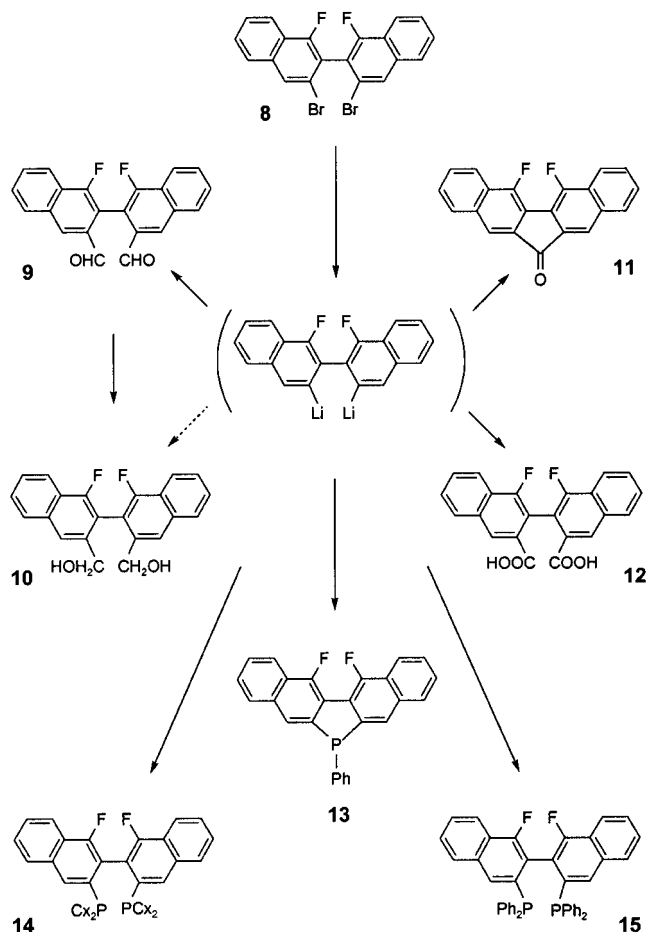
with lithium diisopropylamide instantaneously isomerized to the 3-bromo-1-fluoro-2-naphthyllithium which gave 3-bromo-1-fluoronaphthalene (**6**; 89%) upon neutralization, 3-bromo-1-fluoro-2-iodonaphthalene (**7**; 80%) upon trapping with elemental iodine, and 3,3'-dibromo-1,1'-difluoro-2,2'-binaphthyl (**8**; 66%) upon oxidative dimerization using copper(II) bromide in the presence of nitrobenzene.



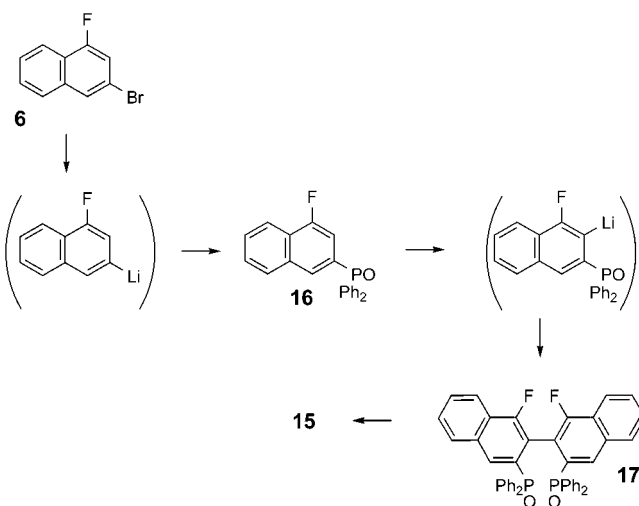
A twofold halogen/metal permutation performed with butyllithium (2.0 equiv.) or *tert*-butyllithium (4.0 equiv.) transformed the dibromo compound **8** into a dilithio species which reacted with *N,N*-dimethylformamide to afford the dialdehyde **9** (61%). This was reduced to the dialcohol **10** (85%). 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

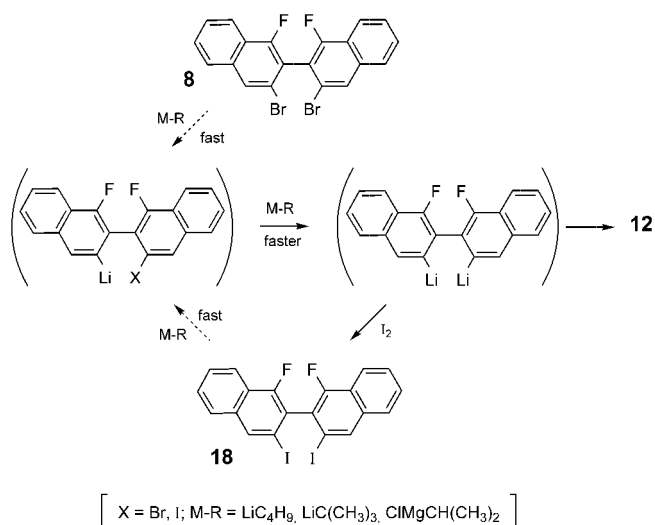


[Cx = cyclohexyl, Ph = phenyl]

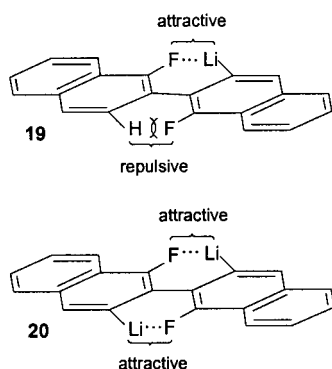


permutational halogen/metal interconversion at an intermediate stage failed. No matter what reagent and what reaction conditions were employed, roughly 50% of the 3,3'-disubstituted product (e.g., diacid **12**) was formed and half of the starting material was recovered whenever only 1 mol-equiv. of the alkylolithium 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 $\geq 55^\circ$), 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] ¹H and (¹H-decoupled) ¹³C NMR spectra were recorded at 400 and 101 MHz, respectively, of samples dissolved in deuteriochloroform.

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%). ¹H 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). ¹³C 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. C₁₆H₂₁FSi (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 $\times$ 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%). ¹H 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. ¹³C 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 $\times$ 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%). ¹H NMR: δ = 8.1 (m, 3 H), 7.8 (m, 3 H), 7.5 (m, 9 H), 7.1 (m, 3 H) ppm. ¹³C 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. C₃₀H₁₈F₃P (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 $\times$ 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%). ¹H 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. ¹³C NMR: δ = 155.6, 134.6, 128.4, 127.5, 127.4, 124.1, 123.7, 121.4, 118.0, 113.1 ppm. C₂₀H₁₂F₂ (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%). ¹H NMR: δ = 8.0 (m, 1 H), 7.8 (m, 1 H), 7.5 (m, 4 H) ppm. ¹³C NMR: δ = 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%). ¹H NMR: δ = 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. ¹³C NMR: δ = 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%). ¹H NMR: δ = 8.0 (m, 2 H), 7.8 (m, 1 H), 7.6 (m, 2 H) ppm. ¹³C NMR: δ = 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. C₁₀H₅BrFI (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%). ¹H NMR: δ = 8.1 (m, 2 H), 8.05 (s, 2 H), 7.8 (m, 2 H), 7.6 (m, 4 H) ppm. ¹³C NMR: δ = 160, 157.7, 134.7, 128.5, 127.2, 126.6, 125.5, 122.1, 121.8, 120.5 ppm. C₂₀H₁₀F₂Br₂ (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%). ¹H NMR: δ = 8.37 (s, 2 H), 8.18 (d, J = 8.0 Hz, 3 H), 8.10 (d, J = 8.0 Hz, 3 H) ppm. ¹³C NMR: δ = 165.5, 134.5, 134.0, 132.8, 131.5, 130.7, 129.9, 127.3, 121.5, 113.7, 109.2 ppm. C₂₂H₁₂F₂O₂ (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 ¹H and ¹⁹F 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%). ¹H NMR: δ = 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. ¹³C NMR: δ = 156.8, 154.3, 138.0, 134.7, 127.9, 127.5, 126.7, 123.7, 123.0, 120.8, 63.3 ppm. C₂₂H₁₆F₂O₂ (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%). ¹H NMR: δ = 7.6 (m, 2 H), 7.5 (m, 4 H), 7.4 (m, 4 H) ppm. ¹³C NMR: δ = 164.2, 142.5, 136.0, 133.7, 128.7, 128.2, 128 (m), 127.4, 124.5, 121.6, 120.7 ppm. C₂₁H₁₀F₂O (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%). ¹H NMR: δ = 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. ¹³C NMR: δ = 167.9, 156.9, 154.5, 133.8, 130.8, 130.4, 129.3, 128.1, 125.4, 121.5, 118.1 ppm. C₂₂H₁₂F₂O₄ (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%). ¹H NMR: δ = 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. ¹³C NMR: δ = 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. C₂₆H₁₅F₂P (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%). ¹H NMR: δ = 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. ¹³C NMR: δ = 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. C₄₄H₅₄F₂P₂ (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%). ¹H NMR: δ = 8.1 (m, 2 H), 7.7 (m, 2 H), 7.60 (d, J = 9.0 Hz, 2 H), 7.51 (dq, 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. ¹³C NMR: δ = 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. C₄₄H₃₀F₂P₂ (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%). ¹H NMR: δ = 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. ¹³C NMR: δ = 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. C₂₂H₁₆FOP (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%). ¹H NMR: δ = 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. ¹³C NMR: δ = 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. C₄₄H₃₀F₂O₂P₂ (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%). ¹H NMR: δ = 8.37 (s, 2 H), 8.1 (m, 2 H), 7.9 (m, 2 H), 7.6 (m, 4 H) ppm. ¹³C NMR: δ = 156.7, 136.4, 134.2, 128.6, 127.5, 126.9, 123.7, 123.5, 121.6, 97.0 ppm. C₂₀H₁₀F₂I₂ (542.10): calcd. C 44.31, H 1.86; found C 44.46, H 1.98.

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- [1] M. Schlosser, *Eur. J. Org. Chem.* **2001**, 3975–3984, spec. pp. 3977–3978.
- [2] F. Cottet, E. Castagnetti, M. Schlosser, *Synthesis* **2005**, 798–803.
- [3] R. Huisgen, H. Rist, *Justus Liebigs Ann. Chem.* **1955**, 594, 137–158.
- [4] G. Wittig, E. Benz, *Chem. Ber.* **1959**, 92, 1999–2013.
- [5] F. Leroux, T. U. Hutschenreuter, C. Charrière, R. Scopelliti, R. W. Hartmann, *Helv. Chim. Acta* **2003**, 86, 2671–2686.
- [6] A. Mordini, M. Schlosser, *Chimia* **1986**, 40, 309–310.
- [7] J. E. Macdonald, G. S. Poindexter, *Tetrahedron Lett.* **1987**, 28, 1851–1852.
- [8] M. Schlosser, *J. Organomet. Chem.* **1967**, 8, 9–16.
- [9] M. Schlosser, in: *Organometallics in Synthesis: A Manual*, Wiley, Chichester, **2002**, pp. 1–352; spec. pp. 211–256.
- [10] T. Rausis, M. Schlosser, *Eur. J. Org. Chem.* **2002**, 3351–3358.
- [11] B. Schaub, T. Jenny, M. Schlosser, *Tetrahedron Lett.* **1984**, 25, 4097–4100.
- [12] F. Leroux, H. Mettler, manuscript in preparation.
- [13] A. Almennigen, O. Bastiansen, L. Fernholt, B. N. Cyvin, S. J. Cyvin, S. Samdal, *J. Mol. Struct. (Theochem)* **1985**, 128, 59–76.
- [14] F. Grein, *J. Phys. Chem. A* **2002**, 106, 3823–3827.
- [15] T.-h. Tang, M. Nowakowska, J. E. Guillet, I. G. Csizmadia, *J. Mol. Struct. (Theochem)* **1991**, 232, 133–146.
- [16] J. Cioslowski, S. T. Mixon, *J. Am. Chem. Soc.* **1992**, 114, 4382–4387.
- [17] F. Leroux, *ChemBioChem* **2004**, 5, 644–649.
- [18] F. Leroux, M. Maurin, N. Nicod, R. Scopelliti, *Tetrahedron Lett.* **2004**, 45, 1899–1902.
- [19] R. J. Kulawiec, E. M. Holt, M. Lavin, R. H. Crabtree, *Inorg. Chem.* **1987**, 26, 2559–2561.
- [20] H. Plenio, *Chem. Rev.* **1997**, 97, 3363–3384.
- [21] E. F. Murphy, R. Murugavel, H. W. Roesky, *Chem. Rev.* **1997**, 97, 3425–3468.
- [22] T. Ooi, N. Kagoshima, K. Maruoka, *J. Am. Chem. Soc.* **1997**, 119, 5754–5755.
- [23] J. Karl, G. Erker, R. Fröhlich, *J. Am. Chem. Soc.* **1997**, 119, 11165–11173.
- [24] T. Ooi, N. Kagoshima, D. Uruguchi, K. Maruoka, *Tetrahedron Lett.* **1998**, 39, 7105–7108.
- [25] H. Takemura, N. Kon, M. Yasutake, H. Kariyazono, T. Shimmyozu, T. Inazu, *Angew. Chem.* **1999**, 111, 1012–1014; *Angew. Chem. Int. Ed.* **1999**, 38, 959–961.

- [26] D. R. Click, B. L. Scott, J. G. Watkin, *J. Chem. Soc., Chem. Commun.* **1999**, 633–634.
- [27] H.-J. Buschmann, J. Hermann, M. Kaupp, H. Plenio, *Chem. Eur. J.* **1999**, 5, 2566–2572.
- [28] C. Bobbio, M. Schlosser, *Eur. J. Org. Chem.* **2001**, 4533–4536.
- [29] C. Heiss, M. Schlosser, *Eur. J. Org. Chem.* **2003**, 447–451.
- [30] M. Schlosser, M. Marull, *Eur. J. Org. Chem.* **2003**, 1569–1575.
- [31] J. Blum, F. Grauer, E. D. Bergmann, *Tetrahedron* **1969**, 25, 3501–3507.
- [32] W. Adcock, M. J. S. Dewar, *J. Am. Chem. Soc.* **1967**, 89, 386–390.

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