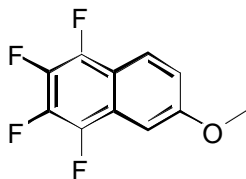


Supporting Information for:**F₈BINOL, an Electronically Perturbed Version of BINOL with Remarkable Configurational Stability**

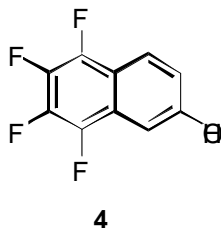
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General. Anhydrous hexanes and dichloromethane were obtained using the method described by Grubbs.¹ Chloropentafluorobenzene, *n*-butyllithium, boron tribromide, *N*-bromosuccinimide, copper powder, (-)-menthyl chloroformate, and anhydrous *N,N*-dimethylformamide (DMF) were purchased from Aldrich Chemical Company. 3-Methoxythiophene was either purchased from Aldrich Chemical Company or obtained using literature procedure.² Melting points are uncorrected. Column chromatography was carried out using 230-400 mesh silica gel.

**3**

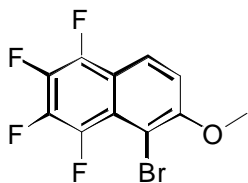
2-Methoxy-5,6,7,8-tetrafluoronaphthalene (3). To a magnetically stirred solution of chloropentafluorobenzene (20.2 g, 100 mmol) and 3-methoxythiophene (4.56 g, 40

mmol) in anhydrous hexanes (200 mL) maintained at -15 °C to -20 °C (ethylene glycol/dry ice bath) was added *n*-butyllithium (50 mL, 80 mmol, 1.6M solution in hexanes) dropwise over 1 hr under nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and stirred for another 12 h. The reaction mixture was diluted with ether and washed with aqueous HCl (5%, 100 mL), commercial 5% aqueous NaOCl (100 mL), NaOH (5%, 100 mL), and brine (200 mL). The resulting organic extract was dried over Na₂SO₄, concentrated and chromatographed (hexane:ether, 9:1) to afford a semisolid brown residue which upon sublimation (100 °C, 0.25 mm Hg) or double distillation under reduced pressure using Kugelrohr oven (160 °C, 0.25 mm Hg) furnished 6.8 g (74% yield) of **3** as white crystals. mp 67.8 °C – 68.8 °C. ¹H NMR (300 MHz, CDCl₃): δ 7.96 (dm, *J* = 8.4 Hz, 1H), 7.27 (m, 2H), 3.96 (s, 3H); ¹⁹F NMR (400 MHz, CDCl₃): δ -151.04 (t, *J* = 16.8 Hz), -152.43 (t, *J* = 18 Hz), -159.35 (t, *J* = 19.6 Hz); -163.92 (t, *J* = 19.6 Hz); ¹³C NMR (400 MHz, CDCl₃): δ 158.8, 143.6 (dm, *J* = 248.5 Hz), 142.6 (dm, *J* = 253.5 Hz), 139.8 (dm, *J* = 234.1 Hz), 137.3 (dm, *J* = 232.5 Hz); EIMS *m/z* (%): 230 (98) 187 (100); Anal. Calcd. for C₁₁H₆F₄O: C, 57.40; H, 2.63; found: C, 57.27; H, 2.70.



2-Hydroxy-5,6,7,8-tetrafluoronaphthalene (4). To a solution of 2-methoxy-5,6,7,8-tetrafluoronaphthalene (**3**) (200 mg, 1.04 mmol) in 15 mL anhydrous CH₂Cl₂ was added BBr₃ (4.2 mL 1M in CH₂Cl₂, 4.16 mmol) and the reaction mixture was stirred overnight.

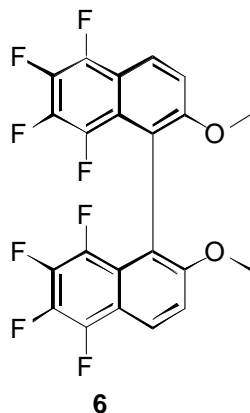
The reaction was diluted with ether and washed with water. The organic layer was dried and concentrated. The resulting solid was purified by column chromatography (hexane:ethyl acetate, 3:1) to provide **4** as a white solid (mp 82-84 °C). ^1H NMR (400 MHz, CDCl_3): δ 7.95 (dm, 1H, $J = 9.2$ Hz, $J = 1.2$ Hz), 7.29 (m, 1H), 7.20 (dd, 1H, $J = 9.2$ Hz, $J = 2.4$ Hz) 6.03 (m, 1H); ^{19}F NMR (400 MHz, CDCl_3): δ -150.90 (t, $J = 18.0$ Hz), -152.42 (t, $J = 18.0$ Hz), -159.04 (t, $J = 19.6$ Hz); -163.87 (t, $J = 19.6$ Hz); EIMS m/z (%): 216 (100) 187 (52).

**5**

1-Bromo-2-methoxy-5,6,7,8-tetrafluoronaphthalene (5). To a magnetically stirred solution of 2-methoxy-5,6,7,8-tetrafluoronaphthalene (**3**) (6.8 g, 29.56 mmol) in acetonitrile (100 mL) was added *N*-bromosuccinimide (6.5 g, 36.5 mmol, freshly recrystallized from hot water). After one hour, the reaction mixture was concentrated under reduced pressure, diluted with water and extracted with ether (2 x 150 mL). The combined organic extracts were dried over Na_2SO_4 , concentrated and recrystallized (ethanol:ether, 8:2) to afford 8 g (88% yield) of **5** as pale yellow crystals (mp 144-145 °C). ^1H NMR (400 MHz, CDCl_3): δ 8.01 (d, 1H, $J = 9.6$ Hz), 7.31 (d, 1H, $J = 9.2$ Hz), 4.03 (s, 3H); ^{19}F NMR (400 MHz, CDCl_3): δ -143.04 (t, $J = 16.8$ Hz), -149.11 (t, $J = 18$ Hz), -155.97 (t, $J = 19.6$ Hz); -161.33 (t, $J = 20.8$ Hz); ^{13}C NMR (400 MHz, CDCl_3): δ 155.7, 143.5 (dm, $J = 256.1$ Hz), 142.9 (dm, $J = 250.0$ Hz), 141.6 (dm, $J = 250.8$ Hz),

137.4 (dm, $J = 250.8$ Hz); EIMS m/z (%): 310 (98), 308 (100), 267 (76), 265 (77); Anal.

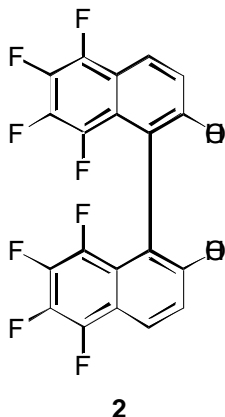
Calcd. for $C_{11}H_5BrF_4O$: C, 42.75; H, 1.63; found: C, 42.56; H, 1.65.



5,5',6,6',7,7',8,8'-Octafluoro-2,2'-bis(methoxy)-1,1'-binaphthyl (6). A heterogeneous mixture of 1-bromo-2-methoxy-5,6,7,8-tetrafluoronaphthlene (**5**) (3.08 g, 10 mmol) and copper powder (6.5 g, 100 mmol, freshly activated) in anhydrous DMF (7 mL) was heated at 155 °C under nitrogen atmosphere. After 30 min., the reaction mixture was concentrated under reduced pressure, diluted with ether (200 mL) and washed successively with saturated NH_4Cl solution (50 mL), 2N HCl (50 mL) and water (100 mL). The organic extract was dried over $MgSO_4$, concentrated, and column chromatographed (hexane : ethyl acetate, 1:1) to afford 1.78 g (83% yield) of **6** as white crystals (mp 218-219 °C, recrystallized from hexane:ethyl acetate). 1H NMR (400 MHz, $CDCl_3$): δ 8.17 (d, $J = 9.2$ Hz, 2H), 7.47 (d, $J = 9.2$ Hz, 2H), 3.77 (s, 6H); ^{19}F NMR (400 MHz, $CDCl_3$): δ -147.56 (t, $J = 16.8$ Hz), -150.54 (t, $J = 16.8$ Hz), -158.89 (t, $J = 19.6$ Hz), -163.56 (t, $J = 19.6$ Hz); ^{13}C NMR (400 MHz, CD_3OD): δ 156.0, 144.0 (dm, $J = 251.5$ Hz), 143.4 (dm, $J = 248.5$ Hz), 140.7 (dm, $J = 249.2$ Hz), 137.1 (dm, $J = 248.4$ Hz), 122.0 (m), 120.3 (m), 116.5, 115.6 (dd, $J = 14.4$ Hz, $J = 3.8$ Hz), 114.4;

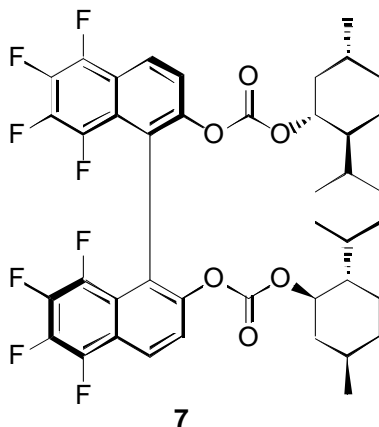
EIMS m/z (%): 458 (100) 412 (60); HRMS (+EI) calculated for $C_{22}H_{10}F_8O_2$ (M^+)

458.05531, found 458.05444.



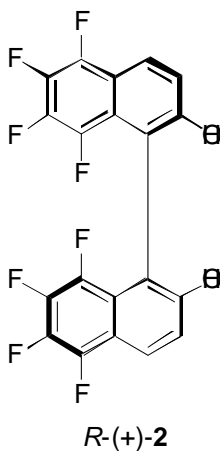
5,5',6,6',7,7',8,8'-Octafluoro-2,2'-dihydroxy-1,1'-binaphthyl (2). To a dilute solution of 2,2'-bis(methoxy)-5,5',6,6',7,7',8,8'-octafluoro-1,1'-binaphthyl (2.15 g, 5 mmol) in anhydrous CH_2Cl_2 (15 mL) was added BBr_3 (15 mmol) at room temperature under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 18 h. The reaction mixture was then poured onto ice diluted with 2N HCl (25 mL), and extracted with CH_2Cl_2 . The organic layer was dried over $MgSO_4$, concentrated and recrystallized (chlorobenzene:hexane, 1:1) to furnish **2** as pale yellow powder (mp 234 -235 °C) in 91% yield. IR: 3852.9, 3548.1; 1H NMR (400 MHz, $CDCl_3$): δ 8.15 (d, $J = 9.2$ Hz, 2H), 7.39 (d, $J = 9.2$ Hz, 2H), 5.25 (s, 2H); ^{19}F NMR (400 MHz, $CDCl_3$): δ -148.31 (t, $J = 16.8$ Hz), -149.11 (t, $J = 16.8$ Hz), -156.60 (t, $J = 21.2$ Hz), -161.79 (t, $J = 19.6$ Hz); ^{13}C NMR (400 MHz, CD_3OD): δ 156.2, 145.4 (dm, $J = 259.9$ Hz), 144.9 (dm, $J = 246.2$ Hz), 141.7 (dm, $J = 246.2$ Hz), 137.6 (dm, $J = 245.4$ Hz), 122.4 (m), 120.9, 116.4 (dd, $J = 13.7$ Hz, $J = 3.0$ Hz), 114.5; EIMS m/z (%): 430 (100) 215 (13) 187 (18); HRMS (+EI) calculated for

$C_{20}H_6F_8O_2$ (M^+) 430.02401, found 430.02480. Anal. Calcd. for $C_{20}H_6F_8O_2$: C, 55.83; H, 1.41; found: C, 55.54; H, 1.41.



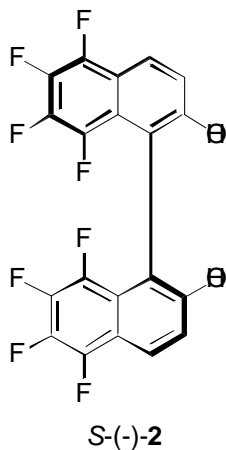
2,2'-Bis[(-)-menthoxycarbonyl]-(*R*)-(+)-5,5',6,6',7,7',8,8'-octafluoro-1,1'-binaphthyl (7). To a solution of 2,2'-dihydroxy-5,5',6,6',7,7',8,8'-octafluoro-1,1'-binaphthyl (**2**) (4.3 g, 10 mmol), pyridine (14 mL) and DMAP (5 mg) in anhydrous CH_2Cl_2 (25 mL) at 0 °C was added (-)-menthyl chloroformate (6.4 mL, 30 mmol). After stirring for 1 h at room temperature, the reaction mixture was worked up with 2N HCl, extracted with CH_2Cl_2 (2 x 25 mL), dried over $MgSO_4$, and concentrated to afford a mixture of diastereomers 2,2'-bis[(-)-menthoxycarbonyl]-(*R*)-(+)-5,5',6,6',7,7',8,8'-octafluoro-1,1'-binaphthyl (**7**) and 2,2'-bis[(-)-menthoxycarbonyl]-(*S*)-(-)-5,5',6,6',7,7',8,8'-octafluoro-1,1'-binaphthyl (**8**) in quantitative yield. Fractional recrystallization from methanol afforded 2.8 g of **7** as a single diastereomer (white crystals, mp 162-163 °C). The *R*- absolute configuration of the binaphthyl moiety in **7** was determined by X-ray analysis. 1H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, $J = 9.1$ Hz, 2H), 7.57 (d, $J = 9.3$ Hz, 2H), 4.29 (s, 2H), 1.6-1.4 (m), 1.4-1.1 (m), 1.0-0.7 (m), 0.67 (d), 0.37 (s, 2H); ^{19}F NMR (400 MHz, $CDCl_3$): δ -142.9 (t, $J = 17.7$

Hz), -149.0 (t, $J = 19.5$ Hz), -156.1 (t, $J = 19.8$ Hz), -158.5 (t, $J = 20.4$ Hz); EIMS m/z (%): 750 (1), 430 (65).



***R*-(+)-5,5',6,6',7,7',8,8'-Octafluoro-2,2'-dihydroxy-1,1'-binaphthyl (*R*-(+)-2).**

Saponification of **7** (2.4 g) using LiOH (3g) in a mixture of 20mL THF and 5mL H₂O at room temperature after 24 h afforded *R*-(+)-**2** as white crystals after single crystallization from pentane (mp 244-245°, $[\alpha]_D^{21} + 39^\circ$, $c = 1$, THF). Spectroscopic data for *R*-(+)-**2** was identical to **2**.



***S*-(-)-5,5',6,6',7,7',8,8'-Octafluoro-2,2'-dihydroxy-1,1'-binaphthyl (*S*-(-)-2).**

Saponification of **8** (2.4 g) using LiOH (3g) in a mixture of 20mL THF and 5mL H₂O at

room temperature after 24 h afforded (*S*)-(-)-5,5',6,6',7,7',8,8'-octafluoro-2,2'-dihydroxy-1,1'-binaphthyl ((*S*)-(-)-**2**) as white crystals after single crystallization from pentane (mp 244-245°, $[\alpha]_{\text{D}}^{25} - 40^\circ$, $c = 1$, THF). Spectroscopic data for *S*-(-)-**2** was identical to **2**.

Notes and references

1. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
2. S. Gronowitz, *Ark. Kemi* **1958**, *12*, 239.