Supporting Information

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Synthesis of 2a.

To a solution of **5** (3.01 g, 5.83 mmol) in Et_2O (50 mL) was added MeLi (1.02 M Et_2O solution, 17.0 mL, 17.3 mmol) at 0 ˚C, and the mixture was stirred for 3 h at room temperature. I_2 (4.50 g, 17.7 mmol) was then added to the mixture at -78 ˚C and the mixture was stirred for 1 h. The resulting mixture was washed with $Na_2S_2O_3$ aq. (120 mL) and brine (100 mL), dried over anhydrous $MgSO_4$, and evaporated in vacuo with cooling with an acetone/CO_2 bath. The resulting crude solid was washed with *n*-hexane to afford white solid of **2a** (2.64 g, 4.86 mmol, 83.4%). Although **2a** obtained in this reaction contained 8% of **3a**, further purifications were not carried out. Mp 126-129 ˚C; **2a**: ^{1}H NMR ($CDCl_3$, δ) 7.80-7.58 (m, 8H), 2.28 (d, 3H, $^2J_{P-H}$ = 13.2 Hz); ^{19}F NMR ($CDCl_3$, δ) -75.7 (q, 6F, $^4J_{F-F}$ = 9.2 Hz), -76.5 (q, 6F, $^4J_{F-F}$ = 9.2 Hz); ^{31}P NMR ($CDCl_3$, δ) -6.3.; **3a**: ^{1}H NMR ($CDCl_3$, δ) 8.43-8.38 (m, 2H), 7.79-7.69 (m, 6H), 2.11 (d, 3H, $^2J_{P-H}$ = 16.6 Hz); ^{19}F NMR ($CDCl_3$, δ) -75.1 (q, 6F, $^4J_{F-F}$ = 9.5 Hz), -75.4 (q, 6F, $^4J_{F-F}$ = 9.5 Hz); ^{31}P NMR ($CDCl_3$, δ) -22.6.

Synthesis of 2b.

For the procedures to prepare **2b**, see note 7 in the paper.

2b: ^{1}H NMR ($CDCl_3$, δ) 7.75-7.69 (m, 2H), 7.65-7.55 (m, 6H), 2.48 (dt, 2H, $^2J_{P-H}$ = 17.1 Hz, $^3J_{H-H}$ = 6.8 Hz), 1.67-1.54 (m, 2H), 1.34 (sextet, 2H, $^3J_{H-H}$ = 7.2 Hz), 0.83 (t, 3H, $^3J_{H-H}$ = 7.2 Hz); ^{19}F NMR ($CDCl_3$, δ) -74.9 (q, 6F, $^4J_{F-F}$ = 8.5 Hz), -76.2 (q, 6F, $^4J_{F-F}$ = 8.5 Hz); ^{31}P NMR ($CDCl_3$, δ) -3.5; Mp 115-116 ˚C.

Synthesis of 2c.

To a solution of **5** (1.01 g, 1.95 mmol) in Et_2O (20 mL) was added *t*-BuLi (1.6 M pentane solution, 4.00 mL, 6.48 mmol) at 0 ˚C, and the solution was stirred for 3 h at room temperature. The solution was cooled to -78 ˚C, then I_2 (1.65 g, 6.50 mmol) was added. The

mixture was stirred for 1 h at -78 ˚C. The resulting solution was washed with $Na_2S_2O_3$ aq. (30 mL x2) and brine (30 mL x2), dried over anhydrous $MgSO_4$, and evaporated. The resulting crude solid was recrystallized from acetonitrile to afford colorless crystals of **2c** (529 mg, 0.924 mmol, 47.5%). ^{1}H NMR ($CDCl_3$, δ) 7.91-7.88 (m, 2H), 7.73-7.71 (m, 2H), 7.62-7.52 (m, 4H), 1.21 (d, 9H, $^3J_{P-H}$ = 21.0 Hz); ^{19}F NMR ($CDCl_3$, δ) -73.7 (q, 6F, $^4J_{F-F}$ = 9.2 Hz), -75.9 (q, 6F, $^4J_{F-F}$ = 9.2 Hz); ^{31}P NMR ($CDCl_3$, δ) 7.7; Mp 138-139 ˚C; Anal. calcd for $C_{22}H_{17}F_{12}O_2P$: C, 46.17; H, 2.99. Found: C, 46.32; H, 3.27.

Synthesis of 2d.

To a solution of bromomesitylene (0.42 mL, 2.7 mmol) in Et_2O (5 mL) was added *n*-BuLi (1.46 mL, 2.33 mmol, *c* 1.62 M in hexane) at -78 ˚C. The mixture was allowed to warm to rt and was stirred for 3 hours. To the mixture was added a solution of **5** (200 mg, 0.388 mmol) in Et_2O (5 mL) at -78 ˚C, and stirring was continued at rt for an hour followed by the addition of I_2 (591 mg, 2.33 mmol). After quenching with aqueous $Na_2S_2O_3$, the mixture was extracted with Et_2O (20 mL x3) and the collected organic layer was dried over $MgSO_4$. The solvent was evaporated in vacuo. The crude product (**2d**:**3d** = 1:1) was purified by TLC (silica gel, hexane-CH_2Cl_2 = 3:1), followed by recrystallization from hexane/CH_2Cl_2. **2d** completely isomerized to **3d** during recrystallization. Only **3d** was isolated as colorless crystals (158 mg, 0.249 mmol, 64.2%). **2d**: ^{1}H NMR ($CDCl_3$, δ) 7.81 (d, 1H, *J* = 7.3 Hz), 7.64-7.60 (m, 3H), 7.56-7.42 (m, 4H), 6.84 (d, 1H, $^4J_{P-H}$ = 5.8 Hz), 6.76 (d, 1H, $^4J_{P-H}$ = 7.8 Hz), 2.67 (s, 3H), 2.22 (s, 3H), 2.13 (s, 3H); ^{19}F NMR ($CDCl_3$, δ) -74.5 (q, 3F, $^4J_{F-F}$ = 9.7 Hz), -75.1 (br s, 6F), -76.1 (q, 3F, $^4J_{F-F}$ = 9.7 Hz); ^{31}P NMR ($CDCl_3$, δ) -5.2. **3d**: ^{1}H NMR ($CDCl_3$, δ) 8.49-8.45 (m, 2H), 7.72-7.66 (m, 6H), 6.67 (d, 2H, $^4J_{P-H}$ = 6.4 Hz), 2.19 (s, 3H), 2.18 (s, 6H); ^{13}C NMR ($CDCl_3$, δ) 138.6 (d, $^4J_{P-C}$ = 3.7 Hz), 137.8 (d, $^2J_{P-C}$ = 12.9 Hz), 137.7, 136.8 (d, $^3J_{F-C}$ = 22.1 Hz), 136.7 (d, $^1J_{P-C}$ = 174.6 Hz), 133.6 (d, *J* = 3.7 Hz), 132.3 (d, $^1J_{P-C}$ = 156.2 Hz), 131.1 (d, *J* = 12.9 Hz), 130.0 (d, *J* = 16.5 Hz), 124.8 (d, $^2J_{P-C}$ = 14.7 Hz), 122.7 (q, $^1J_{F-C}$ = 288.6 Hz), 122.3 (q, $^1J_{F-C}$ = 288.6 Hz), 81.9 (sept, $^2J_{F-C}$ = 31.2 Hz), 23.9 (d, $^3J_{P-C}$ = 5.5 Hz), 20.8; ^{19}F NMR ($CDCl_3$, δ) -74.2 (q, 6F, $^4J_{F-F}$

= 9.8 Hz), -75.7 (q, 6F, $^4J_{F\text{-}F}$ = 9.8 Hz); ^{31}P NMR ($CDCl_3$, δ) -27.0; Mp 175 ˚C (sublimation); Anal. calcd for $C_{27}H_{19}F_{12}O_2P$: C, 51.12; H, 3.02. Found: C, 51.02; H, 2.90.

Synthesis of 2e.

To a solution of 1-bromo-2,4,6-triethylbenzene (655 mg, 2.72 mmol) in Et_2O (5 mL) was added *n*-BuLi (1.46 mL, 2.33 mmol, *c* 1.62 M in hexane) at -78 ˚C. The mixture was allowed to warm to rt and was stirred for 3 hours. To the mixture was added a solution of **5** (200 mg, 0.388 mmol) in Et_2O (5 mL) at -78 ˚C, and stirring was continued at rt for an hour followed by the addition of I_2 (591 mg, 2.33 mmol). After quenching with aqueous $Na_2S_2O_3$, the mixture was extracted with Et_2O (20 mL x3) and the collected organic layer was dried over $MgSO_4$. The solvent was evaporated in vacuo. The crude product (**2e**:**3e** = 3:2) was purified by TLC (silica gel, hexane-CH_2Cl_2 = 3:1), followed by recrystallization from hexane/CH_2Cl_2. **2e** completely isomerized to **3e** during recrystallization. Only **3e** was isolated as colorless crystals (41.3 mg, 0.0611 mmol, 15.7%). **2e**: ^{1}H NMR ($CDCl_3$, δ) 7.96-7.90 (m, 1H), 7.88-7.84 (m, 3H), 7.58-7.52 (m, 4H), 7.39 (d, 1H, $^4J_{P\text{-}H}$ = 6.4 Hz), 7.36 (d, 1H, $^4J_{P\text{-}H}$ = 6.4 Hz), 2.96-2.64 (m, 6H), 1.42 (t, 3H, $^3J_{H\text{-}H}$ = 7.3 Hz), 1.32 (t, 3H, $^3J_{H\text{-}H}$ = 7.3 Hz), 1.29 (t, 3H, $^3J_{H\text{-}H}$ = 7.3 Hz); ^{19}F NMR ($CDCl_3$, δ) -73.7 (q, 3F, $^4J_{F\text{-}F}$ = 9.8 Hz), -74.6 (q, 3F, $^4J_{F\text{-}F}$ = 9.8 Hz), -75.1 (q, 3F, $^4J_{F\text{-}F}$ = 9.8 Hz), -75.2 (q, 3F, $^4J_{F\text{-}F}$ = 9.8 Hz); ^{31}P NMR ($CDCl_3$, δ) -3.7. **3e**: ^{1}H NMR ($CDCl_3$, δ) 8.52-8.44 (m, 2H), 7.76-7.64 (m, 6H), 6.76 (d, 2H, $^4J_{P\text{-}H}$ = 6.4 Hz), 2.79 (dq, 2H, $^2J_{H\text{-}H}$ = 14.6 Hz, $^3J_{H\text{-}H}$ = 7.3 Hz), 2.74 (dq, 2H, $^2J_{H\text{-}H}$ = 14.6 Hz, $^3J_{H\text{-}H}$ = 7.3 Hz), 2.54 (q, 2H, $^3J_{H\text{-}H}$ = 7.3 Hz), 1.17 (t, 3H, $^3J_{H\text{-}H}$ = 7.3 Hz), 0.71 (t, 6H, $^3J_{H\text{-}H}$ = 7.3 Hz); ^{19}F NMR ($CDCl_3$, δ) -74.1 (q, 3F, $^4J_{F\text{-}F}$ = 9.8 Hz), -75.1 (q, 6F, $^4J_{F\text{-}F}$ = 9.8 Hz); ^{31}P NMR ($CDCl_3$, δ) -26.6; Mp 156-157 ˚C (sublimation); Anal. calcd for $C_{30}H_{25}F_{12}O_2P$: C, 53.27; H, 3.72. Found: C, 53.29; H, 3.53.

Synthesis of 2f.

For the procedures to prepare **2f**, see note 7 in the paper.

2f: White solid; Mp 107 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.75 (m, 2H), 7.66-7.63 (m, 2H), 7.57-7.52 (m, 2H), 7.47-7.42 (m, 1H), 7.20 (dd, 1H, $^3J_{PH}$ = 11.7 Hz,

$^{3}J_{HH}$ = 7.8 Hz), 7.08 (dd, 1H, $^{4}J_{PH}$ = 4.4 Hz, $^{4}J_{HH}$ = 1.9 Hz), 6.95 (dd, 1H, $^{4}J_{PH}$ = 8.8 Hz, $^{4}J_{HH}$ = 1.9 Hz), 3.94 (sept, 1H, $^{3}J_{HH}$ = 6.8 Hz), 3.39 (sept, 1H, $^{3}J_{HH}$ = 6.8 Hz), 2.83 (sept, 1H, $^{3}J_{HH}$ = 6.8 Hz), 1.41 (d, 3H, $^{3}J_{HH}$ = 6.8 Hz), 1.36 (d, 3H, $^{3}J_{HH}$ = 6.8 Hz), 1.21 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz), 1.04 (d, 3H, $^{3}J_{HH}$ = 6.8 Hz), 0.39 (d, 3H, $^{3}J_{HH}$ = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1 (d, J_{PC} = 9.3 Hz), 149.1, 142.7 (d, $^{1}J_{PC}$ = 44.5 Hz), 142.3 (d, J_{PC} = 21.7 Hz), 137.5 (d, J_{PC} = 115.9 Hz), 136.9 (d, J_{PC} = 19.7 Hz), 134.2 (d, J_{PC} = 125.2 Hz), 133.4 (d, J_{PC} = 2.1 Hz), 133.2 (d, J_{PC} = 16.6 Hz), 130.9 (d, J_{PC} = 15.5 Hz), 130.7 (d, J_{PC} = 19.7 Hz), 130.6, 130.4 (d, J_{PC} = 7.2 Hz), 130.3 (d, J_{PC} = 9.3 Hz), 125.5 (d, J_{PC} = 12.4 Hz), 125.0 (d, J_{PC} = 7.4 Hz), 123.6 (d, J_{PC} = 14.0 Hz), 122.7 (q, J_{CF} = 287.6 Hz), 122.3 (q, J_{CF} = 287.6 Hz), 122.2 (d, J_{CP} = 17.6 Hz), 121.8 (q, J_{CF} = 287.6 Hz), 121.7 (q, J_{CF} = 287.6 Hz), 81.4 (sept, J_{CF} = 31.3 Hz), 79.7 (sept, J_{CF} = 31.3 Hz), 33.7 (d, J_{CP} = 1.6 Hz), 32.9 (d, J_{CP} = 5.7 Hz), 31.7 (d, J_{CP} = 5.2 Hz), 25.4, 24.6, 24.4 (d, J_{CP} = 1.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.1 (q, 3F, $^{4}J_{FF}$ = 9.8 Hz), -74.2 (q, 3F, $^{4}J_{FF}$ = 9.8 Hz), -74.3 (q, 3F, $^{4}J_{FF}$ = 9.8 Hz), -74.6 (q, 3F, $^{4}J_{FF}$ = 9.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -2.76; Anal. calcd for $C_{33}H_{31}F_{12}O_2P$: C, 55.16; H, 4.35. Found: C, 55.16, H, 4.09.

Thermal conversion of **2f** to **3f**. A solution of **2f** (50 mg, 0.07 mmol) in Et_2O (3 mL) was heated at 60 °C for 12 hours. After removal of solvent under reduced pressure, the residue was recrystallized from hexane/CH_2Cl_2 to afford **3f**, quantitatively (50 mg, 0.07 mmol, 99%).

3f: White solid; m.p. 143-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45-8.40 (m, 2H), 7.71-7.65 (m, 6H), 6.88 (d, 2H, $^{4}J_{PH}$ = 6.4 Hz), 3.74 (sept, 2H, $^{3}J_{HH}$ = 6.8 Hz), 2.79 (sept, 1H, $^{3}J_{HH}$ = 6.8 Hz), 1.21 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz), 1.17 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz), 0.46 (d, 6H, $^{3}J_{HH}$ = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5 (d, J_{PC} = 3.7 Hz), 148.7 (d, J_{PC} = 14.7 Hz), 136.8 (d, J_{CF} = 20.2 Hz), 136.4 (d, J_{PC} = 11.0 Hz), 135.0 (d, J_{PC} = 178.3 Hz), 133.2 (d, J_{PC} = 3.7 Hz), 133.1 (d, J_{PC} = 154.4 Hz), 131.2 (d, J_{PC} = 14.7 Hz), 124.8 (d, J_{PC} = 14.7 Hz), 122.7 (d, J_{PC} = 16.5 Hz), 122.7 (q, J_{CF} = 288.6 Hz), 122.3 (q, J_{PC} = 288.6 Hz), 82.1 (sept, J_{CF} = 31.2 Hz), 33.7, 31.3 (d, J_{CP} = 5.5 Hz), 23.8, 23.6; ^{19}F NMR (376 MHz,

$CDCl_3$) δ -74.0 (q, 6F, $^4J_{FF}$ = 9.8 Hz), -74.8 (q, 6F, $^4J_{FF}$ = 9.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ -25.8; Anal. calcd for $C_{33}H_{31}F_{12}O_2P$: C, 55.16; H, 4.35. Found: C, 54.99, H, 4.19.

Synthesis of 2g.

To a solution of *o*-bromotoluene (0.33 mL, 2.7 mmol) in Et_2O (5 mL) was added *n*-BuLi (1.46 mL, 2.33 mmol, *c* 1.62 M in hexane) at -78 ˚C. The mixture was allowed to warm to rt and was stirred for 3 hours. To the mixture was added a solution of **5** (200 mg, 0.388 mmol) in Et_2O (5 mL) at -78 ˚C, and stirring was continued at rt for an hour followed by the addition of I_2 (591 mg, 2.33 mmol). After quenching with aqueous $Na_2S_2O_3$, the mixture was extracted with Et_2O (20 mL x3) and the collected organic layer was dried over $MgSO_4$. The solvent was evaporated in vacuo. The crude product (**2g**:**3g** = 1:3) was purified by TLC (silica gel, hexane-CH_2Cl_2 = 3:1), followed by recrystallization from hexane/CH_2Cl_2. **2g** completely isomerized to **3g** during recrystallization. Only **3g** was isolated as colorless crystals (135 mg, 0.233 mmol, 57.4%). **3g**: ^{1}H NMR ($CDCl_3$, δ) 8.64-8.58 (m, 2H), 7.80-7.74 (m, 6H), 7.40 (dd, 1H, $^3J_{P-H}$ = 18.1 Hz, $^3J_{H-H}$ = 7.8 Hz), 7.40 (t, 1H, $^3J_{H-H}$ = 7.8 Hz), 7.05-7.02 (m, 2H), 2.29 (s, 3H); ^{19}F NMR ($CDCl_3$, δ) -74.9 (q, 3F, $^4J_{F-F}$ = 9.7 Hz), -75.0 (q, 3F, $^4J_{F-F}$ = 9.7 Hz), -75.7 (q, 6F, $^4J_{F-F}$ = 9.7 Hz), -75.8 (q, 3F, $^4J_{F-F}$ = 9.7 Hz); ^{31}P NMR ($CDCl_3$, δ) -27.5; Mp 155-155.5 ˚C (sublimation); Anal. calcd for $C_{25}H_{15}F_{12}O_2P$: C, 49.52; H, 2.49. Found: C, 49.34; H, 2.31.