Supporting Information for

A General Strategy for the Facile Synthesis of 2,7-Dibromo-9-heterofluorenes

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Materials: Commercially available chemicals (Acros) were used without further purification.

Measurements: Both ^1H and ^{13}C NMR spectra were collected on a Varian Mercury Plus 400 spectrometer with chloroform-*d* or DMSO-*d* as the solvent and tetramethylsilane as the internal standard. MALDI-TOF experiments were carried out using a Shimadzu AXIMA-CFRTM plus time-of-flight mass spectrometer (Kratos Analytical, Manchester, U.K.). GC-MS experiments were recorded on a Shimadzu GCMS-QP2010 plus equipped with DB-5 ms column.

4,4'-Dibromo-3,3'-dimethoxybiphenyl (1)

o-Dianisidine (5.0 g) was dissolved in a hot mixture of 40% hydrobromic acid (20 ml), water (80 ml) and acetonitrile (80 ml). The solution was cooled to 0°C and sodium nitrite (3.6 g) in cold water (7 ml) was added with stirring, the temperature being kept below 10 °C. Cuprous bromide (6.5 g) in hydrobromic acid (80 ml) was added to the cold diazonium compound with vigorous stirring, and after the mixture warmed up to the room temperature it was heated until the evolution of nitrogen ceased. The precipitate was extracted with chloroform, washed with water, chromatographed on alumina, and dried. Evaporation of the extract gave the crude product with almost 100% yield. ¹H NMR (CDCl₃, 400 MHz, ppm): δ7.60 (d, 2H, ³*J* = 7.6 Hz); δ7.04 (d, 2H, ⁴*J* = 1.6 Hz); δ7.03 (dd, 2H, ³*J* = 8.0 Hz, ⁴*J* = 2.0 Hz); δ3.97 (s, 6H).

4,4'-Dibromo-6,6'-diiodo-3,3'-dimethoxybiphenyl (2)

A mixture of 4,4'-dibromo-3,3'-dimethoxybiphenyl (7.5 g, 20 mmol), KIO₃ (1.9 g, 8.8 mmol), I₂ (5.6 g, 22 mmol), and 20% H₂SO₄ (15 ml) in AcOH (150 ml) was heated at 80 °C overnight. When cooled to room temperature, water (200 ml) was added. The precipitate was collected, dissolved in chloroform and washed with aqueous Na₂S₂O₃ and brine, and dried over magnesium sulfate. After removal of the solvent, the product was purified through silica gel chromatography and by recrystallization twice from ethanol to afford 11.6 g (yield: 93%) of the compound as colorless crystal. ¹H NMR (CDCl₃, 400 MHz, ppm): δ8.05 (s, 2H); δ6.72 (s, 2H); δ3.88 (s, 6H).

General procedure for the synthesis of 2,7-dibromo-3,6-dimethoxy-9-heterofluorene

To the mixture of 4,4'-dibromo-6,6'-diiodo-3,3'-dimethoxybiphenyl (5.3 g, 8.5 mmol) and dry THF (80 ml) was added a 1.6 M *n*-butyllithium/hexane solution (10.7 ml, 17.1 mmol) at -100°C . The resulting mixture was allowed to stir at this temperature for 30 min and then suitably disubstituted heteroatom reactant (9 mmol) was added into the mixture. After the addition, the mixture was allowed to warm to room temperature and stirred overnight. Then the reaction mixture was hydrolyzed with water and extracted with ether. The combined organic layers were dried over Na_2SO_4 and the solvent was evaporated. The crude product was chromatographed on a silica gel column with petroleum ether/ethyl acetate (7:1) as eluent. Recrystallize several times from ethanol or dichloromethane/hexane to afford the compounds as crystals.

2,7-Dibromo-3,6-dimethoxyl-9,9'-dimethyl-9-silafluorene (3)

Yield: 63%. ^1H NMR (DMSO, 400 MHz, ppm): δ 7.86 (s, 2H); δ 7.72 (s, 2H); δ 3.98 (s, 6H); δ 0.35 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ -2.91; δ 56.54; δ 105.01; δ 112.25; δ 132.68; δ 137.39; δ 148.15; δ 157.90. GC-MS (EI- m/z): 428 (M^+).

2,7-Dibromo-3,6-dimethoxyl-9,9'-methyloctadecyl-9-silafluorene (4)

Yield: 23%. ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.71 (s, 2H); δ 7.26 (s, 2H); δ 4.03 (s, 6H); δ 1.36-1.17 (b, 35H); δ 0.87 (t, 2H, $^3J = 7.2$ Hz); δ 0.36 (s, 3H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ -4.60; δ 13.92; δ 14.36; δ 22.92; δ 24.02; δ 29.35; δ 29.59; δ 29.77; δ 29.89; δ 29.93; δ 32.16; δ 33.49; δ 56.51; δ 105.01; δ 112.20; δ 132.20; δ 137.54; δ 148.39; δ 157.84. MALDI-TOF, m/z : 666.4, 588.5, 508.5.

2,7-Dibromo-3,6-dimethoxyl-9,9'-diphenyl-9-silafluorene (5)

Yield: 12%. ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.87 (s, 2H); δ 7.61 (d, 4H, $^3J = 7.2$ Hz); δ 7.44 (t, 2H, $^3J = 8.0$ Hz); δ 7.37 (t, 4H, $^3J = 8.0$ Hz); δ 7.34 (s, 2H); δ 4.05 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 56.58; δ 105.30; δ 112.74; δ 128.52; δ 129.76; δ 130.69; δ 131.96; δ 135.66; δ 138.40; δ 149.15; δ 158.41. MALDI-TOF, m/z : 549.7, 469.8, 393.8.

2,7-Dibromo-3,6-dimethoxyl-9,9'-dibutyl-9-germafluorene (6)

Yield: 36%. ^1H NMR (CDCl_3 , 400 MHz, ppm): δ 7.69 (s, 2H); δ 7.32 (s, 2H); δ 4.02 (s, 6H); δ 1.36 (b, 4H); δ 1.28 (b, 4H); δ 1.17 (t, 4H, $^3J = 8.0$ Hz); δ 0.83 (t, 6H, $^3J = 6.8$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 13.84; δ 14.41; δ 26.28; δ 27.56; δ 56.54; δ 105.70; δ 112.34; δ 133.89; δ 137.61; δ 147.23; δ 157.22. GC-MS (EI- m/z): 557 (M^+).

2,7-Dibromo-3,6-dimethoxyl-9-phenyl-9-phosphafluorene (7)

Yield: 54%. ^1H NMR (DMSO, 400 MHz, ppm): δ 7.98 (s, 2H); δ 7.95 (d, 2H, $^3J_{\text{H,P}} = 4.8$ Hz); δ 7.32-7.21 (b, 5H); δ 4.01 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz, ppm): δ 56.72; δ 104.67; δ 112.50; δ 129.08; δ 129.99; δ 131.30; δ 133.06; δ 135.01; δ 136.40; δ 143.90; δ 157.03. GC-MS (EI- m/z): 478 (M^+). MALDI-TOF, m/z : 875.2, 795.3, 555.2, 478.0.

2,7-Dibromo-3,6-dimethoxyl-9-phenyl-9-phosphafluorene oxide (8)

^1H NMR (DMSO, 400 MHz, ppm): δ 7.97 (s, 2H); δ 7.88 (d, 2H, $^3J_{\text{H,P}} = 8.8$ Hz); δ 7.58-7.42 (b, 5H); δ 4.05 (s, 6H).
MALDI-TOF m/z : 494.6, 226.9.

Figure 1. ^1H NMR of 4,4'-dibromo-3,3'-dimethoxybiphenyl (1) in CDCl_3 .

Figure 2. ^1H NMR of 4,4'-dibromo-6,6'-diiodo-3,3'-dimethoxybiphenyl (2) in CDCl_3 .

Figure 3. ^1H NMR of 2,7-dibromo-3,3'-dimethoxyl-9,9-dimethyl-9-silafluorene (3) in DMSO.

Figure 4. ^{13}C NMR of 2,7-dibromo-3,3'-dimethoxyl-9,9-dimethyl-9-silafluorene (3) in CDCl_3 .

Figure 5. ^1H NMR of 2,7-dibromo-3,3'-dimethoxyl-9,9-methyloctadecyl-9-silafluorene (4) in CDCl_3 .

Figure 6. ^{13}C NMR of 2,7-dibromo-3,3'-dimethoxyl-9,9-methyloctadecyl-9-silafluorene (4) in CDCl_3 .

Figure 7. ^1H NMR of 2,7-dibromo-3,3'-dimethoxyl-9,9-diphenyl-9-silafluorene (5) in CDCl_3 .

Figure 8. ^{13}C NMR of 2,7-dibromo-3,3'-dimethoxyl-9,9-diphenyl-9-silafluorene (5) in CDCl_3 .

Figure 9. ^1H NMR of 2,7-dibromo-3,3'-dimethoxyl-9,9-dibutyl-9-germafluorene (6) in CDCl_3 .

Figure 10. ^{13}C NMR of 2,7-dibromo-3,3'-dimethoxyl-9,9-dibutyl-9-germafluorene (6) in CDCl_3 .

Figure 11. ^1H NMR of a mixture of 2,7-dibromo-3,3'-dimethoxyl-9-phenyl-9-phosphafluorene (7) and 2,7-dibromo-3,3'-dimethoxyl-9-phenyl-9-phosphafluorene oxide (8) in DMSO.

Figure 12. ^{13}C NMR of a mixture of 2,7-dibromo-3,3'-dimethoxyl-9-phenyl-9-phosphafluorene (7) and 2,7-dibromo-3,3'-dimethoxyl-9-phenyl-9-phosphafluorene oxide (8) in CDCl_3 .