Bis(triarylmethylium)-Mediated Diaryl Ether Synthesis: Oxidative Arylation of Phenols with *N,N*-Dialkyl-4-Phenylthioanilines

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Supporting Information

General: NMR spectra were obtained on a Bruker Avance-500(500 MHz) or a JEOL AL-400 (400 MHz) spectrometer. Chemical shift values were given in ppm relative to internal Me_4Si (for ^1H NMR: δ 0.00) and $CDCl_3$ (for ^{13}C NMR: δ 77.0). IR spectra were recorded on a Horiba FT-300S spectrometer. Mass spectra were taken with a JEOL JMS-SX-102A spectrometer. Elemental analyses were performed with a YANAKO MT-6 CHN Corder apparatus. Column chromatography and preparative thin-layer chromatography (PTLC) were performed on silica gel.

Typical experimental procedure for the preparation of aniline derivatives **3a**–**c**, **g**, **h**
To a suspension of NaH (3.9 g, 60% dispersion in mineral oil, 98 mmol) in THF (50 ml) was added an aniline (40 mmol) at 0 ^oC under argon, and the reaction mixture was stirred for 0.5 h at the same temperature. After an alkyl iodide (ethyl iodide, benzyl iodide, or allyl iodide: 96 mmol) was added, the mixture was stirred at room temperature for 3 h. The reaction was quenched with water, and organic materials were extracted with EtOAc. The combined extracts were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave the crude product, which was purified by column chromatography (hexane-EtOAc).

4-Bromo-*N,N*-diethylaniline (**3a**)
a yellow oil;
^1H NMR (500 MHz, $CDCl_3$) δ 1.14 (6H, t, *J* = 7.0 Hz), 3.31 (4H, q, *J* = 7.0 Hz), 6.51 (2H, dd, *J* = 6.9, 2.1 Hz), 7.25 (2H, dd, *J* = 6.9, 2.1 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 12.4, 44.4, 106.9, 113.4, 131.4, 146.7;
IR (neat) 2968, 1589, 1493, 1354, 1265, 1192, 802 cm^{-1};
FAB HRMS calcd. for $C_{10}H_{15}{}^{79}BrN$ 228.0388 (M+1); found 228.0410.

4-Chloro-*N,N*-diethylaniline (**3b**)
a pale yellow oil;
^1H NMR (500 MHz, $CDCl_3$) δ 1.13 (6H, t, *J* = 7.1 Hz), 3.31 (4H, q, *J* = 7.1 Hz), 6.58 (2H, dd, *J* = 9.2, 1.7 Hz), 7.13 (2H, dd, *J* = 9.2, 1.7 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 12.4, 44.5, 112.9, 120.0, 128.9, 146.3;

IR (neat) 2969, 1595, 1498, 1265, 1188, 804, 741 cm^{-1};
FAB HRMS calcd. for $C_{10}H_{15}ClN$ 184.0893 (M+1); found 184.0876.

N,N-Diethyl-4-fluoroaniline (**3c**)
a pale yellow oil;
^1H NMR (500 MHz, $CDCl_3$) δ 1.12 (6H, t, J = 7.0 Hz), 3.29 (4H, q, J = 7.0 Hz), 6.59–6.64 (2H, m), 6.89–6.94 (2H, m);
^{13}C NMR (125 MHz, $CDCl_3$) δ 12.4, 44.9, 113.6 (d, J_{CF} = 34 Hz), 115.5 (d, J_{CF} = 22 Hz), 144.6, 154.5 (d, J_{CF} = 233 Hz);
IR (neat) 2970, 1508, 1227, 810 cm^{-1};
FAB HRMS calcd. for $C_{10}H_{15}FN$ 168.1189 (M+1); found 168.1179.

4-Bromo-*N,N*-dibenzylaniline (**3g**)
white crystals, m.p. 124–126 °C (EtOH)
^1H NMR (500 MHz, $CDCl_3$) δ 4.63 (4H, s), 6.59 (2H, d, J = 9.0 Hz), 7.19–7.28 (8H, m), 7.30–7.35 (4H, m);
^{13}C NMR (125 MHz, $CDCl_3$) δ 54.4, 108.6, 114.1, 126.5, 127.0, 128.7, 131.8, 138.0, 148.1;
IR (neat) 1591, 1493, 1360, 1230, 729 cm^{-1};
Anal. calcd. for $C_{20}H_{18}NBr$: C, 68.19; H, 5.15; N, 3.98%. Found: C, 68.04; H, 5.34; N, 3.80%.

4-Bromo-*N,N*-diallylaniline (**3h**)
a pale yellow oil;
^1H NMR (400 MHz, $CDCl_3$) δ 3.86 (4H, d, J = 3.4 Hz), 5.09–5.20 (4H, m), 5.73–5.88 (2H, m), 6.53 (2H, d, J = 8.8 Hz), 7.23 (2H, d, J = 8.8 Hz);
^{13}C NMR (100 MHz, $CDCl_3$) δ 52.8, 108.0, 113.8, 116.1, 131.5, 133.3, 147.4;
IR (neat) 1589, 1493, 1230, 916, 802 cm^{-1}.

Typical experimental procedure for the preparaton of 4-substituted *N,N*-diethylanilines **3d**–**h**
To a solution of 4-bromo-*N,N*-dialkylaniline (8.8 mmol) in THF (35 ml) was added *n*-BuLi (3.4 ml, 2.71 M in hexane, 9.2 mmol) at –78 °C under argon. The reaction mixture was stirred for 1 h at the same temperture and then an electrophile (*n*-Bu_3SnCl, PhSSPh, or MeSSMe: 8.8 mmol) was added. After stirring for 2 h, the reaction was quenched with saturated aqueous NH_4Cl. Organic materials were extracted with EtOAc. The combined extracts were washed with brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure gave the crude product.

N,N-Diethyl-4-tributylstannylaniline (**3d**)
The crude product was purified by distillation under reduced pressure to give **3d** in 63% yield.
a colorless oil, b.p. 190 °C/2 mmHg (bath temp.)
^1H NMR (500 MHz, C_6D_6) δ 0.98 (9H, t, J = 7.4 Hz), 1.01 (6H, t, J = 7.3 Hz), 1.23 (6H, t, J = 7.3 Hz), 1.50 (6H, tt, J = 7.4, 7.3 Hz), 1.77 (6H, tq, J = 7.4, 7.4 Hz), 3.09 (4H, q, J = 7.3 Hz), 6.79 (2H, d, J = 8.5 Hz), 7.56–7.61 (2H, m);
^{13}C NMR (125 MHz, C_6D_6) δ 9.6, 12.4, 13.7, 27.6, 29.4, 43.9, 112.4, 124.4, 137.5, 147.9;
IR (neat) 2924, 1587, 1502, 1263, 1080, 798 cm^{-1};
Anal. calcd. for $C_{22}H_{41}NSn$: C, 60.29; H, 9.43; N, 3.20%. Found: C, 60.13; H, 9.31; N, 2.97%.

N,N-Diethyl-4-methylthioaniline (**3e**)
The crude product was purified by distillation under reduced pressure to give **3e** in 70% yield.

a pale yellow oil, b.p. 100 °C/2 mmHg (bath temp.)
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (6H, t, *J* = 7.0 Hz), 2.40 (3H, s), 3.32 (4H, q, *J* = 7.0 Hz), 6.61 (2H, dd, *J* = 6.8, 2.1 Hz), 7.26 (2H, dd, *J* = 6.8, 2.1 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 19.6, 44.3, 112.3, 121.6, 132.0, 146.7;
IR (neat) 2968, 1592, 1500, 1354, 1263, 1194, 806 cm^{-1};
FAB HRMS calcd. for $C_{11}H_{18}NS$ 196.1160 (M+1); found 196.1144.

N,N-Diethyl-4-phenylthioaniline (**3f**)
The crude product was purified by column chromatography (hexane-EtOAc 50/1), followed by recrystallization from ethanol to give **3f** in 83% yield.
white crystals, m.p. 68–69 °C (EtOH);
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (6H, t, *J* = 7.1 Hz), 3.37 (4H, d, *J* = 7.1 Hz), 6.63–6.67 (2H, m), 6.99–7.12 (3H, m), 7.17–7.22 (2H, m), 7.35–7.38 (2H, m);
^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 44.3, 112.2, 115.7, 124.8, 126.6, 128.7, 136.6, 140.6, 148.1;
IR (neat) 2970, 1590, 1504, 1267, 1194, 912, 794, 734 cm^{-1};
Anal. calcd. for $C_{16}H_{19}NS$: C, 74.66; H, 7.44; N, 5.44%. Found: C, 74.63; H, 7.51; N, 5.33%.

N,N-Dibenzyl-4-phenylthioaniline (**3g**)
The crude product was purified by column chromatography (hexane-EtOAc 50/1), followed by recrystallization from ethanol to give **3g** in 66% yield.
white crystals, m.p. 107–109°C (EtOH);
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.67 (4H, s), 6.72 (2H, d, *J* = 8.9 Hz), 7.06–7.15 (3H, m), 7.15–7.37 (14H, m);
^{13}C NMR (125 MHz, $CDCl_3$) δ 54.1, 113.1, 118.2, 125.1, 126.5, 127.0, 127.2, 128.7, 128.7, 135.9, 137.9, 139.7, 149.4;
IR (neat) 1594, 1582, 1502, 1477, 1451, 1361, 1233 cm^{-1};
Anal. calcd. for $C_{26}H_{23}NS$: C, 81.85; H, 6.08; N, 3.67%. Found: C, 81.70; H, 6.26; N, 3.43%.

N,N-Diallyl-4-phenylthioaniline (**3h**)
The crude product was purified by column chromatography (hexane-EtOAc 50/1) to give **3h** in 40% yield.
a pale yellow oil;
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.91 (4H, d, *J* = 2.9 Hz), 5.10–5.21 (4H, m), 5.75–5.90 (2H, m), 6.66 (2H, d, *J* = 8.3 Hz), 7.05 (1H, d, *J* = 7.1 Hz), 7.10 (2H, d, *J* = 7.8 Hz), 7.18 (2H, dd, *J* = 7.8, 7.1 Hz), 7.32 (2H, d, *J* = 8.3 Hz);
^{13}C NMR (100 MHz, $CDCl_3$) δ 52.7, 112.9, 116.2, 117.2, 124.9, 126.8, 128.6, 133.2, 136.0, 140.1, 148.9;
IR (neat) 1590, 1500, 1232, 916, 734 cm^{-1};

Typical experimental procedure for the synthesis of diaryl ether **5a**
To a solution of 4-methoxyphenol (**4a**, 12.6 mg, 0.10 mmol) in acetonitrile (2.0 ml) was added dication **1a** (77 mg, 0.12 mmol) at –40 °C. After the reaction mixture was stirred for 0.5 h at –40 °C, **3f** (52 mg, 0.20 mmol) was added at –40 °C. After stirring for 0.5 h at –40 °C, the reaction was quenched with saturated aqueous $NaHCO_3$. Organic materials were extracted with EtOAc. The combined extracts were washed with brine and dried over Na_2SO_4. After removal of the solvent under reduced pressure, the

resulting residue was purified by preparative TLC to give 4-diethylaminophenyl 4-methoxyphenyl ether (**5a**, 26 mg, 93%).

4-Diethylaminophenyl 4-methoxyphenyl ether (**5a**)

pale yellow crystals, m.p. 53–54 ^{o}C (EtOH);

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (6H, t, *J* = 7.1 Hz), 3.25 (4H, q, *J* = 7.1 Hz), 3.78 (3H, s), 6.63–6.67 (2H, m), 6.79–6.84 (2H, m), 6.86–6.91 (4H, m);

^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 44.8, 55.6, 113.6, 114.6, 118.8, 120.0, 144.4, 147.8, 152.4, 154.8;

IR (neat) 2968, 2360, 1495, 1219, 1036 cm^{-1};

Anal. calcd. for $C_{17}H_{21}NO_2$: C, 75.25; H, 7.80; N 5.16%. Found: C, 75.13; H, 7.84; N, 4.95%.

4-Diethylaminophenyl 2,4-dimethylphenyl ether (**5b**)

a colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (6H, t, *J* = 7.1 Hz), 2.25 (3H, s), 2.28 (3H, s), 3.29 (4H, q, *J* = 7.1 Hz), 6.65 (2H, dd, *J* = 9.1, 2.3 Hz), 6.70 (1H, d, *J* = 8.2 Hz), 6.83 (2H, dd, *J* = 9.1, 2.3 Hz), 6.89 (1H, d, *J* = 8.2 Hz), 7.02 (1H, s);

^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 16.2, 20.6, 44.9, 113.9, 117.6, 119.3, 127.2, 128.5, 131.7, 131.9, 144.1, 148.2, 154.0;

IR (neat) 2970, 1510, 1495, 1248, 1222 cm^{-1};

Anal. calcd. for $C_{18}H_{23}NO$: C, 80.26; H, 8.61; N, 5.20%. Found: C, 80.04; H, 8.79; N, 4.92%.

4-Diethylaminophenyl 2,6-dimethylphenyl ether (**5c**)

a colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.97 (6H, t, *J* = 7.1 Hz), 2.14 (6H, s), 3.25 (4H, q, *J* = 7.1 Hz), 6.61–6.66 (4H, m), 6.99–7.08 (3H, m);

^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 16.4, 45.0, 114.5, 115.2, 124.5, 128.8, 131.7, 143.1, 149.4, 151.8;

IR (neat) 2969, 2360, 1506, 1194; cm^{-1};

FAB HRMS calcd. for $C_{18}H_{24}NO$ 270.1858 (M+1); found 270.1830.

4-Diethylaminophenyl 2,4,6-trimethylphenyl ether (**5d**)

a colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (6H, t, *J* = 7.1 Hz), 2.10 (6H, s), 2.28 (3H, s), 3.24 (4H, q, *J* = 7.1 Hz), 6.59–6.66 (4H, m), 6.87 (2H, d, *J* = 0.5 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 16.4, 20.8, 45.0, 114.6, 115.2, 129.4, 131.2, 133.9, 143.0, 149.5, 149.7;

IR (neat) 2968, 1506, 1479, 1220 cm^{-1};

Anal. calcd. for $C_{19}H_{25}NO$: C, 80.52; H, 8.89; N, 4.94%. Found: C, 80.42; H, 9.08; N, 4.75%.

4-Diethylaminophenyl 4-chlorophenyl ether (**5e**)

a colorless oil;

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (6H, t, *J* = 7.1 Hz), 3.33 (4H, q, *J* = 7.1 Hz), 6.66 (2H, dd, *J* = 6.8, 2.3 Hz), 6.86 (2H, dd, *J* = 6.8, 2.2 Hz), 6.91 (2H, dd, *J* = 6.8, 2.3 Hz), 7.21 (2H, dd, *J* = 6.8, 2.2 Hz);

^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 44.7, 113.1, 118.1, 121.1, 123.5, 126.5, 129.3, 145.0, 157.9;

IR (neat) 2970, 1508, 1483, 1236 cm^{-1};

Anal. calcd. for $C_{16}H_{18}ClNO$: C, 69.69; H, 6.58; N, 5.08%. Found: C, 69.56; H, 6.69; N, 4.83%.

4-Diethylaminophenyl 4-bromophenyl ether (**5f**)
a colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 (6H, t, J = 7.1 Hz), 3.33 (4H, q, J = 7.1 Hz), 6.65 (2H, dd, J = 6.8, 2.2 Hz), 6.81 (2H, dd, J = 6.8, 2.2 Hz), 6.91 (2H, dd, J = 6.9, 2.4 Hz), 7.35 (2H, dd, J = 6.9, 2.4 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 44.7, 113.1, 113.9, 118.6, 121.2, 132.2, 145.1, 145.7, 158.5;
IR (neat) 2973, 2869, 1508, 1479, 1236 cm^{-1};
Anal. calcd. for $C_{16}H_{18}BrNO$: C, 60.01; H, 5.67; N 4.37%. Found: C, 59.92; H, 5.80; N, 4.20%.

4-Diethylaminophenyl 2-fluorophenyl ether (**5g**)
a colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (6H, t, J = 7.1 Hz), 3.32 (4H, q, J = 7.1 Hz), 6.66 (2H, dd, J = 6.8, 2.3 Hz), 6.89–7.00 (4H, m), 7.00–7.14 (2H, m);
^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 44.7, 113.3, 116.6 (d, J_{CF} = 18 Hz), 119.2, 120.0, 122.7 (d, J_{CF} = 7 Hz), 124.1 (d, J_{CF} = 4 Hz), 144.8, 146.2 (d, J_{CF} = 11.0 Hz), 146.5, 153.4 (d, J_{CF} = 246 Hz);
IR (neat) 2976, 1508, 1498, 1257, 1213 cm^{-1};
Anal. calcd. for $C_{16}H_{18}FNO$: C, 74.11; H, 7.00; N, 5.40%. Found: C, 74.12; H, 7.00; N, 5.19%.

4-Diethylaminophenyl 2,6-dichlorophenyl ether (**5h**)
a colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (6H, t, J = 7.0 Hz), 3.27 (4H, q, J = 7.0 Hz), 6.62 (2H, dd, J = 6.9, 2.3 Hz), 6.73 (2H, dd, J = 6.9, 2.3 Hz), 7.09 (1H, t, J = 8.2 Hz), 7.36 (2H, d, J = 8.2 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 12.5, 44.8, 113.5, 115.8, 125.8, 129.0, 130.2, 143.9, 148.0, 148.1;
IR (neat) 2970, 1506, 1441, 1245, 1203 cm^{-1};
Anal. calcd. for $C_{16}H_{17}Cl_2NO$: C, 61.95; H, 5.52; N, 4.52%. Found: C, 61.74; H, 5.78; N, 4.26%.

4-Dibenzylaminophenyl 4-methoxyphenyl ether (**5i**)
a colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.77 (3H, s), 4.61 (4H, s), 6.65–6.69 (2H, m), 6.78–6.83 (4H, m), 6.87–6.92 (2H, m), 7.21–7.28 (6H, m), 7.28–7.34 (4H, m);
^{13}C NMR (125 MHz, $CDCl_3$) δ 54.8, 55.6, 113.8, 114.6, 119.2, 119.6, 126.7, 126.8, 128.5, 138.6, 145.4, 148.8, 151.9, 155.0;
IR (neat) 1513, 1496, 1222, 1203 cm^{-1};
Anal. calcd. for $C_{27}H_{25}NO_2$: C, 82.00; H, 6.37; N, 3.54%. Found: C, 81.76; H, 6.65; N, 3.26%.

4-Diallylaminophenyl 4-methoxyphenyl ether (**5j**)
a colorless oil;
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.77 (3H, s), 3.88 (4H, d, J = 4.9 Hz), 5.12–5.25 (4H, m), 5.80–5.90 (2H, m), 6.65 (2H, d, J = 9.0 Hz), 6.82 (2H, d, J = 9.1 Hz), 6.85 (2H, d, J = 9.1 Hz), 6.90 (2H, d, J = 9.0 Hz);
^{13}C NMR (125 MHz, $CDCl_3$) δ 53.3, 55.6, 113.6, 114.6, 116.1, 119.0, 119.7, 134.2, 145.1, 148.4, 152.2, 154.9;
IR (neat) 1498, 1222, 1035 cm^{-1};
Anal. calcd. for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17; N, 4.74%. Found: C, 77.07; H, 7.38; N, 4.61%.

The ESR spectrum of the mixture of **3f** and **1a** in CH_2Cl_2 at 5 K: