

# 3-Bromopentadienylsilane: A New Reagent for the Introduction of a Functional Pentadienyl Unit with Fixed Configuration

Maryline Roux, Maurice Santelli, Jean-Luc Parrain

## Supporting information

All reactions were carried out under argon atmosphere. Dichloromethane was dried by distillation over  $P_2O_5$ . Flash chromatography was carried out with Merck silica gel (silica gel, 230–400 mesh).  $^1H$  NMR and  $^{13}C$  NMR spectra were recorded on a Bruker AC 200 or a Bruker AMX 400 (nuclear magnetic resonance) spectrometer. Chemical shifts are given in ppm referring to  $Me_4Si$  used as internal standard for  $^1H$  and  $^{13}C$  NMR spectra (solvent =  $CDCl_3$ ). Coupling constants are given in Hertz.

**3-bromopenta-2,4-dienyltrimethylsilane (3) :** At 0° C, to 1,4-bis(trimethylsilyl)but-2-ene (50.0 g, 0.25 mol) and potassium *tert*-butoxide (84.2 g, 0.75 mol) in pentane (300 mL) was slowly added bromoform (65.5 mL, 0.75 mol). The mixture was stirred for 1 hour, and warmed to room temperature for 30 min. The solution is then filtered on celite and washed with a saturated aqueous  $NaCl$  solution (150 mL). The aqueous phase was extracted with ether (3 x 50 mL). The organic phase was dried over  $MgSO_4$ . and the solvents were eliminated in *vacuo*. The crude product is warmed at 100-130 °C in a distillation assembly under vacuum (10 mm Hg). After elimination of the formed trimethylsilyl bromide and elimination of the excess of bromoform, **3** is purified by distillation.  $bp(10\text{ mm Hg}) = 60\text{ }^\circ C$ . 75 %.

$^1H$  NMR ( $CDCl_3$ , 200 MHz) 0.07 (s, 9H), 1.83 (d,  $J = 8.9$  Hz, 2H), 5.07 (d,  $J = 10.6$  Hz, 1H), 5.40 (d,  $J = 16.0$  Hz, 1H), 6.00 (t,  $J = 8.9$  Hz, 1H), 6.33 (dd,  $J = 16.0$  Hz, 10.6, 1H).  $^{13}C$  NMR ( $CDCl_3$ , 50 MHz) -1.3(3C), 23.7, 115.3, 123.9, 132.7, 136.1.

General procedure for the synthesis of bromodienyl alcohols **4**: At  $-78^\circ C$ , boron trifluoride etherate (0.14 mL, 1.12 mmol) and **3** (0.41 g, 1.86 mmol) were successively added to a solution of 2-bromo-4-methoxybenzaldehyde (0.2 g, 0.93 mmol) in dry dichloromethane (3 mL). The reaction was monitored by TLC. The mixture was allowed to warm up and after 1.5 hours was poured into a saturated aqueous  $NaCl$  solution (1.5 mL). The aqueous phase was extracted with dichloromethane and the organic phase was dried over  $MgSO_4$ . After evaporation of the solvents, the crude product **4d** was purified by chromatography on silica gel (petroleum ether/ether 9/1 then 8/2). Yield : 60%

**1-(2-bromo-4-methoxyphenyl)-4-bromohexa-3,5-dienyl-1-ol (4d).**  $^1H$  NMR ( $CDCl_3$ , 200 MHz): 2.1 (bs, 1H), 2.78 (m, 2H), 3.80 (s, 3H), 5.17 (m, 1H), 5.19 (d,  $J = 10.6$ , 1H), 5.54 (d,  $J = 16.3$ , 1H), 6.12 (t,  $J = 6.9$ ,

1H), 6.33 (dd,  $J = 16.3, 10.3$ ), 6.70 (dd,  $J = 8.9, 3.1, 1H$ ), 7.12 (d,  $J = 3.1, 1H$ ), 7.4 (d,  $J = 8.6, 1H$ ).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 50 MHz) 39.5, 55.5, 71.8, 122.0, 122.7, 115.1, 118.2, 128.0, 130.2, 133.3, 135.6, 143.5, 159.2.

**1-phenyl-4-bromohexa-3,5-dienyl-1-ol (4a).**  $^1\text{H}$  NMR (CDCl<sub>3</sub>, 200 MHz) 2.03 (bs, 1H), 2.78 (t,  $J = 6.9, 2\text{H}$ ), 4.83 (t,  $J = 6.9, 1\text{H}$ ), 5.19 (d,  $J = 10.3, 1\text{H}$ ), 5.55 (d,  $J = 16.1, 1\text{H}$ ), 6.05 (t,  $J = 6.85, 1\text{H}$ ), 6.30 (dd,  $J = 16.1, 10.3$ ), 7.30 (m, 5H).  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 50 MHz) 41.6, 73.8, 118.6, 126.3(2C), 128.4(2C), 129.1(2C), 131.0, 136.1, 144.1.

Typical procedure for the synthesis of symmetrical ethers **5a-d**. At -78 °C, under argon atmosphere, TMSOTf (0.014 mL, 0.07 mol) and **3** (0.2 g, 0.91 mmol) were successively added to a solution of propanal (0.055 mL, 0.76 mmol) in dry dichloromethane (2 mL). The reaction mixture was allowed to warm up. The reaction was monitored by TLC. After stirring for 3 hours the mixture was poured into a saturated aqueous NaCl solution (1 mL). The aqueous phase was then extracted with ether (3 x 5 mL) and the organic phases were dried over MgSO<sub>4</sub>. After evaporation of the solvents, the crude product **5b** obtained as a 50/50 mixture of diastereoisomers was purified by silica gel column chromatography (petroleum ether/ ether 9/1). Yield : 67%

#### **Di(4-bromo-1-phenylhexa-3,5-dien-1-yl)oxyde (5a)**

$^1\text{H}$  NMR (CDCl<sub>3</sub>, 200 MHz) 2.70 (m, 4H), 4.19 (dd,  $J = 8.2, 5.5, 2\text{H}$ ), 5.16 (d,  $J = 10.3, 2\text{H}$ ), 5.49 (d,  $J = 16.1, 2\text{H}$ ), 5.96 (t,  $J = 6.8, 2\text{H}$ ), 6.26 (dd,  $J = 10.3, 16.1, 2\text{H}$ ), 7.25 (m, 10H); meaningful signals for the other diastereoisomer: 4.54 (t,  $J = 6.2, 2\text{H}$ ), 5.53 (d,  $J = 16.1, 2\text{H}$ ), 5.98 (t,  $J = 6.8, 2\text{H}$ ), 6.27 (dd,  $J = 10.3, 16.1, 2\text{H}$ ),  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 50 MHz) 39.1(2C), 77.9(2C), 117.7(2C), 126.4(4C), 127.4(2C), 127.9(2C), 128.4(4C), 131.0(2C), 135.7(2C), 141.6(2C); meaningful signals for the other diastereoisomer: 77.4, 117.5, 126.9, 127.1, 127.5, 128.2, 130.6, 135.6, 141.2.

#### **Di(6-bromooceta-5,7-dien-3-yl)oxyde (5b)**

$^1\text{H}$  NMR (CDCl<sub>3</sub>, 200 MHz) 0.88 (t,  $J = 5.7, 6\text{H}$ ), 1.50 (m, 4H), 2.50 (m, 4H), 3.45 (m, 2H), 5.14 (d,  $J = 11.1, 2\text{H}$ ), 5.46 (d,  $J = 16.7, 2\text{H}$ ), 6.06 (t,  $J = 6.9, 2\text{H}$ ), 6.30 (dd,  $J = 11.1, 16.6, 2\text{H}$ ); meaningful signals for the other diastereoisomer: 6.07 (t,  $J = 6.9, 2\text{H}$ ), 6.31 (dd,  $J = 16.6, 11.1, 2\text{H}$ );  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 50 MHz) 10.1(2C), 27.4(2C), 36.0(2C), 77.6(2C), 117.6(2C), 127.3(2C), 131.3(2C), 135.9(2C). meaningful signals for the other diastereoisomer: 9.9, 27.3, 36.1, 131.5.

#### **Di(4-bromo-1-(4-fluorophenyl)-hexa-3,5-dien-1-yl)oxyde (5c)**

$^1\text{H}$  NMR (CDCl<sub>3</sub>, 200 MHz) 2.70 (m, 4H), 4.14 (dd,  $J = 7.9, 5.8, 2\text{H}$ ), 5.15 (d,  $J = 10.6, 2\text{H}$ ), 5.50 (d,  $J = 16.5, 2\text{H}$ ), 5.86 (t,  $J = 7.2, 2\text{H}$ ), 6.25 (dd,  $J = 16.5, 10.6, 2\text{H}$ ), 6.29-7.20 (m, 8H). meaningful signals for the other diastereoisomer: 4.47 (t,  $J = 6.2, 2\text{H}$ ), 5.53 (d,  $J = 16.5, 2\text{H}$ ), 5.90 (t,  $J = 7.2, 2\text{H}$ ), 6.26 (dd,  $J = 16.5, 10.4, 2\text{H}$ )  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 50 MHz) 39.6(2C), 78.2(2C), 115.7(4C), 118.3, 128.3(2C), 129.0(4C), 130.5(2C), 137.1(2C), 137.7(2C), 162.3 (2C,  $J_{\text{C}-\text{F}} = 207$ ); meaningful signals for the other diastereoisomer: 40.6, 78.0, 116.0, 118.4, 128.1, 129.3, 130.8, 137.2, 137.6.

#### **Di(4-bromo-1-(2-bromo-4-methoxyphenyl)-hexa-3,5-dien-1-yl)oxyde (5d)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) 2.64-2.82 (m, 4H), 3.78 (s, 6H), 4.64 (dd, *J* = 7.20, 5.8, 2H), 5.15 (d, *J* = 10.3, 2H), 5.50 (d, *J* = 16.1, 2H), 5.96 (t, *J* = 6.9, 2H), 6.25 (dd, *J* = 16.1, 10.3, 2H), 6.73 (dd, *J* = 8.6, 3.1, 2H), 7.09 (d, *J* = 3.1, 2H), 7.30 (d, *J* = 8.6, 2H); meaningful signals for the other diastereoisomer: 3.80 (s, 6H), 4.89 (t, *J* = 5.8, 2H), 5.18 (d, *J* = 10.3, 2H), 5.53 (d, *J* = 16.5, 2H), 6.06 (t, *J* = 6.9, 2H), 6.32 (dd, *J* = 16.5, 10.3, 2H), 6.63 (dd, *J* = 8.6, 3.1, 2H), 6.93 (d, *J* = 3.1, 2H), 7.51 (d, *J* = 8.6, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 39.1(2C), 55.6(2C), 76.7(2C), 113.3(2C), 113.8(2C), 115.6(2C), 118.0(2C), 127.7(2C), 130.3(2C), 133.4(2C), 135.7(2C), 141.2(2C), 159.4(2C); meaningful signals for the other diastereoisomer: 38.1, 55.4, 77.7, 113.2, 115.8, 117.9, 127.9, 130.2, 133.1, 135.9, 141.6, 159.1.

Typical procedure for the synthesis of **6a-b**. At -78 °C, boron trifluoride etherate (0.07 mL, 0.49 mmol) and **3** (0.12 g, 0.55 mmol) were successively added to a solution of phenylacetaldehyde dimethylacetal (0.075 g, 0.45 mmol) in dry dichloromethane (5 mL). The reaction mixture was allowed to warm up to room temperature. The reaction was monitored by TLC. After stirring for 3 hours, the mixture was poured into a saturated aqueous NH<sub>4</sub>Cl solution (2 mL). The aqueous phase was then extracted with dichloromethane (3 x 20 mL) and the organic phase was dried over MgSO<sub>4</sub>. After evaporation of the solvent, the crude product **6a** was purified by silica gel column chromatography (petroleum ether then petroleum ether/ ether 95/5). Yield: 75%.

### **3-bromo-6-methoxy-7-phenylhepta-1,3-diene (6a)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): 2.48 (dd, *J* = 11.6, 6.0, 2H), 2.80 (m, 2H), 3.32 (s, 3H), 3.54 (m, 1H), 5.18 (d, *J* = 10.8, 1H), 5.54 (d, *J* = 16.2, 1H), 6.08 (t, *J* = 8.1, 1H), 6.32 (dd, *J* = 16.2, 10.8), 7.24 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 35.4, 40.4, 57.1, 81.1, 117.7, 126.3, 127.5, 128.3(2C), 129.5(2C), 130.8, 135.8, 138.5.

### **6-bromo-3-ethoxyocta-5,7-dien-1-yne (6b)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): 1.20 (t, *J* = 7.8, 3H), 2.47 (s, 1H), 2.73 (t, *J* = 7.9, 2H), 3.43 (q, *J* = 7.8, 2H), 4.10 (t, *J* = 7.9, 1H), 5.18 (d, *J* = 10.6, 1H), 5.55 (d, *J* = 15.6, 1H), 6.10 (t, *J* = 7.9, 1H), 6.32 (dd, *J* = 15.6, 10.6). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 15.2, 37.3, 60.9, 64.4, 67.5, 82.3, 118.0, 127.8, 129.6, 135.6.

Typical procedure for the synthesis of **6c-g**. At 0 °C, boron trifluoride etherate (0.06 mL, 0.45 mmol) was added to a solution of **3** (0.25 g, 1.14 mmol), benzaldehyde (0.048 g, 0.45 mmol) and benzylalcohol (0.049 g, 0.45 mmol) in dry dichloromethane (5 mL). The reaction mixture was allowed to warm up to room temperature. The reaction was monitored by TLC. After stirring for 3 hours, the mixture was poured into a saturated aqueous NH<sub>4</sub>Cl solution (2 mL) and the aqueous phase was extracted with dichloromethane (3 x 20 mL) and the organic phase was dried over MgSO<sub>4</sub>. After evaporation of the solvent, the crude product **6f** was purified by silica gel column chromatography (petroleum ether then petroleum ether/ ether 9/1). Yield: 79%

### **3-bromo-6-methoxyocta-1,3-diene (6c)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) 0.90 (t, *J* = 7.2, 3H), 1.51 (m, 2H), 2.51 (m, 2H), 3.23 (q, *J* = 6.0, 1H), 3.30 (s, 3H), 5.15 (d, *J* = 10.6, 1H), 5.52 (d, *J* = 16.1, 1H), 6.05 (t, *J* = 6.0, 1H), 6.31 (dd, *J* = 16.1, 10.6). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 9.6, 26.3, 35.0, 56.6, 81.0, 117.5, 127.2, 131.1, 135.8.

### **3-bromo-6-methoxy-6-(2-bromo-4-methoxyphenyl)-hexa-1,3-diene (6d)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) 2.70 (m, 2H), 3.25 (s, 3H), 3.78 (s, 3H), 4.65 (m, 1H), 5.15 (d, *J* = 10.3, 1H), 5.51 (d, *J* = 16.1, 1H), 6.09 (t, *J* = 6.9, 1H), 6.31 (dd, *J* = 16.1, 10.3, 1H), 6.68 (dd, *J* = 8.6, 3.1, 1H), 7.00 (d, *J* = 3.1, 1H), 7.4 (d, *J* = 8.6, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 38.8, 55.4, 57.1, 80.9, 112.5, 113.2, 115.2, 117.7, 127.4, 130.5, 133.3, 135.7, 141.3, 159.4.

**6-benzyloxy-3-bromodeca-1,3-diene (6e)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): 0.90 (t, *J* = 7.6, 3H), 1.23-1.50 (m, 6H), 2.57 (m, 2H), 3.50 (m, 1H), 4.49 (d, *J* = 11.6, 1H), 4.57 (d, *J* = 11.6, 1H), 5.17 (d, *J* = 10.6, 1H), 5.55 (d, *J* = 16.5, 1H), 6.09 (t, *J* = 6.9, 1H), 6.32 (dd, *J* = 16.5, 10.6), 7.30 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 14.1, 22.8, 27.7, 33.9, 36.0, 70.9, 77.8, 117.5, 127.3, 127.6, 127.8(2C), 128.4(2C), 131.2, 135.9, 138.7.

**6-benzyloxy-3-bromo-6-phenylhexa-1,3-diene (6f)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): 2.82 (m, 2H), 4.41 (d, *J* = 12.0, 1H), 4.45 (d, *J* = 12.0, 1H), 4.55 (t, *J* = 6.7, 1H), 5.19 (d, *J* = 10.3, 1H), 5.56 (d, *J* = 17.1, 1H), 6.08 (t, *J* = 6.7, 1H), 6.32 (dd, *J* = 17.1, 10.3, 1H), 7.25-7.42 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 40.4, 70.5, 80.0, 117.7, 126.7, 127.3, 127.6, 127.7(2C), 127.9, 128.4(2C), 128.6 (3C), 131.8, 135.8, 138.3, 141.5.

**6-benzyloxy-3-bromo-6-(4-trifluoromethylphenyl)-hexa-1,3-diene (6g)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) 2.78 (m, 2H), 4.30 (d, *J* = 12.0, 1H), 4.46 (d, *J* = 12.0, 1H), 4.51 (m, 1H), 5.19 (d, *J* = 10.7, 1H), 5.54 (d, *J* = 16.5, 1H), 6.03 (t, *J* = 7.20, 1H), 6.30 (dd, *J* = 16.5, 10.7, 1H), 7.33 (m, 5H), 7.46 (d, *J* = 8.23, 2H), 7.60 (d, *J* = 8.23, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 40.2, 70.9, 79.4, 118.2, 125.6(*J*<sub>C-F</sub> = 3.8, 2C), 127.0(2C), 127.8(2C), 127.9(3C), 128.5(2C), 128.6, 130.2, 135.6, 138.1.

Typical procedure for the synthesis of protected dienyl amines **7** :

At 0 °C, boron trifluoride etherate (0.7 mL, 5.5 mmol) was added *via* a seringe to a solution of **3** (1.00 g, 4.6 mmol), benzaldehyde (0.48 g, 4.6 mmol) and benzyl carbamate (0.69 g, 4.6 mmol) in dry dichloromethane (40 mL). The reaction mixture was allowed to warm up to room temperature. The reaction was monitored by TLC. After stirring for 4 hours, the mixture was poured into a saturated aqueous NH<sub>4</sub>Cl solution (20 mL). The aqueous phase was then extracted with dichloromethane (3 x 25 mL) and the organic phase was dried over anhydrous MgSO<sub>4</sub>. After evaporation of the solvents under reduced pressure, the crude product **7b** was purified by chromatography on silica gel (petroleum ether/ ether 8/2 as eluent). 59%.

**N-(benzyloxycarbonyl)-6-bromo-octa-5,7-dien-3-ylamine (7a)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) 0.93 (t, *J* = 7.4, 3H), 1.48 (m, 2H), 2.5 (m, 2H), 3.73 (m, 1H), 4.60 (bs, 1H), 5.08 (s, 2H), 5.18 (d, *J* = 10.3), 5.53 (d, *J* = 16.5), 5.98 (t, *J* = 7.2, 1H), 6.29 (dd, *J* = 16.5, 10.3), 7.30 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 10.4, 28.0, 37.1, 52.2, 66.6, 118.1, 128.0(2C), 128.1, 128.5(3C), 130.8, 135.7, 136.6, 156.2.

**N-(benzyloxycarbonyl)-4-bromo-1-phenylhexa-3,5-dien-1-ylamine (7b)** <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) 2.81 (m, 2H), 4.89 (bq, *J* = 7.5, 1H), 5.06 (d, *J* = 12.3, 1H), 5.08 (d, *J* = 12.3, 1H), 5.1 (m, 1H), 5.19 (d, *J* = 10.3, 1H), 5.53 (d, *J* = 16.1, 1H), 5.90 (t, *J* = 7.2, 1H), 6.25 (dd, *J* = 16.1, 10.3, 1H), 7.30 (m, 10H); <sup>13</sup>C NMR

(CDCl<sub>3</sub>, 50 MHz) 38.7, 54.4, 66.9, 118.5, 126.3(2C), 127.6, 128.1, 128.3(2C), 128.5(3Car), 128.8 (3Car), 130.0, 135.5, 136.4, 155.8.

***N*-(benzyloxycarbonyl)-4-bromo-1-(4-methoxyphenyl)-hexa-3,5-dien-1-ylamine (7c)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) 2.80 (m, 2H), 3.80 (s, 3H), 4.93 (m, 1H), 5.05 (m, 1H), 5.06 (d, *J* = 12.3, 1H), 5.08 (d, *J* = 12.3, 1H), 5.17 (d, *J* = 10.3, 1H), 5.53 (d, *J* = 16.3, 1H), 5.88 (t, *J* = 7.0, 1H), 6.24 (dd, *J* = 16.3, 10.3, 1H), 6.86 (d, *J* = 10.5, 2H), 7.20 (d, *J* = 10.5, 2H), 7.30 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 38.6, 53.9, 55.3, 66.9, 114.4(2C), 118.4, 127.5(3C), 128.1(2C), 128.5(3C), 130.1, 133.6, 135.5, 136.4, 155.7, 159.0.

***N*-(benzyloxycarbonyl)-4-bromo-1-(4-fluorophenyl)-hexa-3,5-dien-1-ylamine (7d)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): 2.80 (t, *J* = 6.7, 2H), 4.86 (m, 1H), 5.05 (m, 3H), 5.20 (d, *J* = 10.3, 1H), 5.55 (d, *J* = 16.5, 1H), 5.87 (t, *J* = 6.7, 1H), 6.24 (dd, *J* = 16.5, 10.3, 1H), 7.05 (t, *J* = 8.6, 2H), 7.25 (m, 7H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 38.6, 53.8, 66.9, 115.5(2C), 118.6, 127.8(2C), 128.0(2C), 128.1(2C), 128.5(3C), 129.6, 135.4, 136.2, 155.8, 162.1 (*J*<sub>C-F</sub> = 244).

***N*-(benzyloxycarbonyl)-6-bromo-2-phenylocta-5,7-dien-3-ylamine (7e)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): 1.32 (d, *J* = 6.8, 3H), 2.37 (m, 1H), 2.78 (m, 2H), 4.00 (m, 1H), 4.67 (m, 1H), 5.13 (s, 2H), 5.18 (d, *J* = 10.3, 1H), 5.50 (d, *J* = 16.5, 1H), 5.89 (t, *J* = 7.2, 1H), 6.24 (dd, *J* = 16.5, 10.3), 7.10-7.45 (m, 10H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 18.6, 35.3, 45.0, 56.1, 66.7, 118.0, 126.9, 127.3, 127.8(2C), 128.0(2C), 128.6(3C), 128.7(2C), 131.0, 131.1, 135.7, 143.7, 155.5.

***N*-(benzyloxycarbonyl)-6-bromooceta-5,7-dien-1-yn-3-ylamine (7f)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): 2.32 (s, 1H), 2.74 (m, 2H), 4.64 (m, 1H), 4.85 (m, 1H), 5.10 (s, 2H), 5.23 (d, *J* = 10.3, 1H), 5.57 (1H, d, *J* = 16.1), 6.05 (t, *J* = 7.2, 1H), 6.32 (dd, *J* = 16.1, 10.3), 7.35 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 37.8, 65.7, 66.9, 72.1, 82.2, 118.7, 128.0(2C), 128.1(2C), 128.4(2C), 128.6, 135.4, 136.1, 155.3.

Typical procedure for the synthesis of protected dienyl amines **8a-b** :

At 0 °C, boron trifluoride etherate (0.7 mL, 5.5 mmol) was added *via* a seringe to a solution of **3** (2.00 g, 9.2 mmol), benzaldehyde (0.48 g, 4.6 mmol) and 1,3-oxazolidin-2-one (0.40 g, 4.6 mmol) in dry dichloromethane (40 mL). The reaction mixture was allowed to warm up to room temperature. The reaction was monitored by TLC. After stirring for 4 hours, the mixture was poured into a saturated aqueous NH<sub>4</sub>Cl solution (20 mL). The aqueous phase was then extracted with dichloromethane (3x 25 mL) and the organic phase was dried over anhydrous MgSO<sub>4</sub>. After evaporation of the solvents under reduced pressure, the crude product **8a** was purified by chromatography on silica gel (petroleum ether/ ether 9/1 then 4/6 as eluent). Yield = 66 %.

***N*-(4-bromo-1-phenylhexa-3,5-dien-1-yl)-1,3-oxazolidin-2-one (8a)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): 2.8-3.2 (m, 4H), 4.20 (m, 2H), 5.18 (m, 1H), 5.19 (d, *J* = 10.4, 1H), 6.00 (t, *J* = 7.6, 1H), 6.29 (dd, *J* = 16.1, 10.3, 1H), 7.35 (m, 5H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 32.9, 40.2, 55.2, 61.9, 118.4, 127.3, 127.9, 128.1(2C), 128.7(2C), 129.9, 135.2, 137.5, 158.0.

***N*-(6-bromooceta-5,7-dien-3-yl)-1,3-oxazolidin-2-one (8b)**

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): 0.94 (t, *J* = 7.1, 3H), 1.55 (m, 2H), 2.50 (m, 2H), 3.42 (m, 2H), 3.88 (m, 1H), 4.30 (m, 2H), 5.17 (d, *J* = 10.3, 1H), 5.50 (d, *J* = 16.5, 1H), 5.93 (t, *J* = 6.5, 1H), 6.28 (dd, *J* = 16.5, 10.3, 1H).  
<sup>13</sup>C NMR (CDCl<sub>3</sub>, 50 MHz) 10.0, 29.1, 32.5, 40.1, 54.9, 60.0, 118.1, 128.2, 131.0, 135.3, 157.9.







