# Synthesis of new indolo[1,2-*b*]isoquinoline derivatives from *N*-(2bromobenzyl)indole

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Dedicated to Prof. Dr. Joan Bosch on the occasion of his 60<sup>th</sup> birthday

#### Abstract

Optimal conditions have been established for the generation of N-(2-lithiobenzyl)-2-lithio-1Hindole from easily available N-(2-bromobenzyl)-1H-indole. An efficient method was developed for the synthesis of 6,11-dihydroindolo[1,2-b]isoquinoline derivatives by reaction of this indole dianion with carboxylic esters. New and interesting fused indole derivatives have also been synthesized.

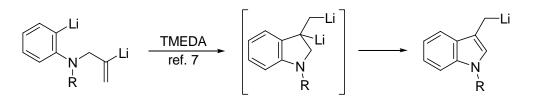
Keywords: Indoles, organolithiums, dianions, isoquinolines, carboxylic esters

### Introduction

Due to the potent biological activity exhibited by various indole derivatives, there is a continuous demand for novel synthetic methods in this area, as well as for the preparation of new indole derivatives.<sup>1</sup> Also, isoquinolines as well as their derivatives have received considerable attention due to their interesting biological properties.<sup>2</sup> Indolo[1,2-*b*]isoquinoline derivatives are of considerable pharmacological relevance because they represent C-analogues of tryptanthrin.<sup>3</sup> This kind of fused heterocyclic systems have been prepared mainly by radical cyclization,<sup>4</sup> palladium-catalyzed couplings,<sup>5</sup> and more recently, by a domino "cyclization-lactamization" reaction of functionalized nitriles.<sup>6</sup>

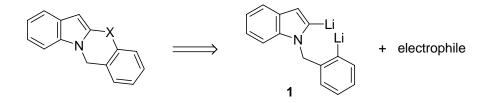
In the last years we have developed a new carbolithiation reaction of lithiated double bonds which has allowed us the easy preparation of functionalized indole and pyrrole derivatives.<sup>7</sup> For instance, N-(2-lithioallyl)-2-lithioanilines gave rise to 3-lithiomethylindoles that were trapped with electrophiles (Scheme 1). Moreover, we and others have recently reported that carboxylic

esters could undergo useful cyclization reactions with 1,4-dianions affording hydroxy cyclic derivatives, which in some cases could undergo a subsequent dehydration process.<sup>7c,8</sup>



Scheme 1. Intramolecular carbolithiation reaction of N-(2-lithioallyl)-2-lithioanilines.

Following all these investigations and in connection with our interest on the synthesis of indole derivatives,<sup>9</sup> we envisaged that *N*-(2-lithiobenzyl)-2-lithio-1*H*-indole **1** could be a useful intermediate for the synthesis of fused indoles like indolo[1,2-*b*]isoquinoline derivatives by its reaction with selected electrophiles (Scheme 2).



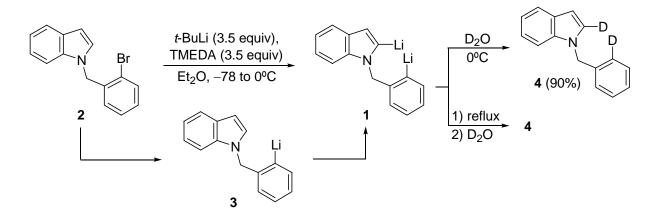
Scheme 2. Retrosynthetic analysis of indolo[1,2-*b*]isoquinoline derivatives.

In this paper, we wish to report an efficient synthesis of new indolo[1,2-*b*]isoquinoline derivatives by reaction of easily available N-(2-lithiobenzyl)-2-lithioindole **1** with carboxylic esters. Moreover, other interesting fused indole derivatives could be also prepared from this dianion.

### **Results and Discussion**

Due to the fact that *N*-protected indoles are easily lithiated at the C-2 position,<sup>10</sup> *N*-(2-bromobenzyl)-1*H*-indole **2** was chosen as precursor of the desired dianion **1**. Indole derivative **2** was easily prepared by alkylation of indole with 2-bromobenzylbromide and KOH in dimethylsulfoxide.<sup>11</sup> First, reaction of **2** with 2 equiv of *t*-BuLi in Et<sub>2</sub>O at low temperature afforded organolithium **3**, which is stable up to room temperature and could be trapped with deuterium oxide.<sup>12</sup> After several attempts, we found that the addition to **2** of 3.5 equiv of *t*-BuLi at  $-78^{\circ}$ C in Et<sub>2</sub>O,<sup>13</sup> and further evolution to 0°C for 1 h in the presence of TMEDA, led to an almost complete lithiation of the C-2 position,<sup>14</sup> and formation of dianion **1**. Treatment of the so

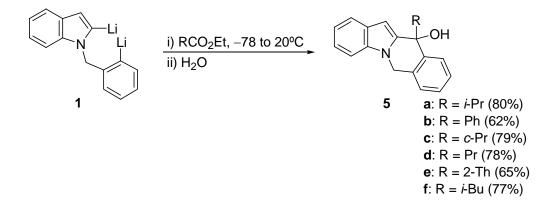
generated dianion **1** with deuterium oxide at 0°C allowed the isolation of dideuterated indole **4** in very good yield (Scheme 3).



Scheme 3. Reaction conditions for generation of 1-(2-lithiobenzyl)-2-lithio-1*H*-indole 1.

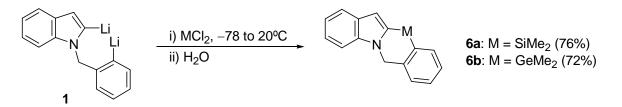
In order to attempt an intramolecular carbolithiation reaction on dianion  $\mathbf{1}$ , similar to that shown in Scheme 1,<sup>7</sup> the ethereal solution of this dianion was refluxed for 1 h. However, after deuteriolysis no cyclization product was obtained and the dideuteriated indole  $\mathbf{4}$  was again exclusively obtained (Scheme 3).

Once we had found the conditions for the selective double lithiation of 2 as well as we had checked that this dianion does not undergo intramolecular carbolithiation, we decided to investigate the reaction of 1 with carboxylic esters to get the indolo[1,2-*b*]isoquinoline skeleton. Thus, as shown in Scheme 4 a wide range of aliphatic or aromatic carboxylic esters were useful electrophiles for the trapping of dianion 1, and dihydroindolo[1,2-*b*]isoquinolin-11-ol derivatives 5 were isolated in good yields.





Finally, treatment of dianion **1** with silicon or germanium dichlorides gave rise to the indolo silicium derivative **6a** or indolo germanium derivative **6b**, respectively, in good yields referred to the starting benzylindole **2** (Scheme 5).



Scheme 5. Synthesis of dihydroindolo[1,2-*b*]isoquinoline derivatives 6.

From the results described in this work we can conclude that although 1-(2-lithiobenzyl)-2-lithio-1H-indole **1** does not undergo an intramolecular carbolithiation reaction, this easily generated dianion reacts with carboxylic esters and metallodichlorides to afford new and interesting fused indole derivatives. Moreover, this route could provide a general method for the preparation of various substituted derivatives of *b*-fused indolo-isoquinolines using appropriately substituted *N*-benzylindoles.

# **Experimental Section**

General Procedures. All reactions were carried out under a nitrogen atmosphere in oven-dried glassware and with dry, freshly distilled solvents using standard procedures. N,N,N',N'-Tetramethylethylenediamine (TMEDA) was distilled from potassium/benzophenone in vacuo. All reagents were commercially available (Acros, Aldrich) and were used without further purification. TLC was performed on aluminum-backed plates coated with silica gel 60 with F<sub>254</sub> indicator (Merck) and compounds were viewed by use of UV light (254 nm), iodine, or phosphomolybdic acid. Chromatography refers to flash column chromatography and was carried out on SiO<sub>2</sub> (silica gel 60, Merck, 230-400 mesh). Melting points were determined in a capillary tube and are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> at 400 (100.6) or 300 (75.4) MHz on Varian spectrometers. Chemical shifts ( $\delta$ ) are reported in ppm from tetramethylsilane with the residual solvent resonance (7.16 ppm, 76.95 ppm) as the internal standard. Data are reported as follows: chemical shift, multiplicity (s: singlet; d: doublet; t: triplet; q: quartet; dd: doublet of doublets; td: triplet of doublets; m: multiplet; br: broad), coupling constants (J in Hz) and integration. Low-resolution electron impact mass spectra (EI-LRMS) were obtained at 70 eV on a HP 6890N/5973. High-resolution mass spectra (HRMS) were performed on a Micromass Autospec spectrometer.

**Preparation of 1-(2-bromobenzyl)-1***H***-indole (2).<sup>11</sup> DMSO (40 mL) was added to KOH (4.49 g, 80 mmol) (crushed pellets) and the mixture was stirred for 5 min. Indole (2.34 g, 20 mmol) was then added and the mixture was stirred for 45 min. 2-Bromobenzyl bromide (6.25 g, 25 mmol) was added and the resulting mixture was stirred for 2 h. Water (40 mL) was added and the mixture was extracted with Et<sub>2</sub>O (3 x 40 mL). The organic layers were combined, washed with H<sub>2</sub>O, and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvents were removed under reduced pressure and the resulting residue was purified by column chromatography (hexane/EtOAc, 10:1) affording the title compound (4.46 g, 78%) as a pale yellow solid. Mp 38-40°C (lit.<sup>15</sup> 39°C); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) \delta 7.71-7.68 (m, 1H, ArH), 7.63-7.59 (m, 1H, ArH), 7.27-7.09 (m, 6H, ArH), 6.61 (d,** *J* **= 3.1 Hz, 1H, NCH=), 6.55-6.51 (m, 1H, NCH=CH), 5.40 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100.6 MHz) \delta 136.6 (C), 136.2 (C), 132.6 (CH), 129.0 (CH), 128.6 (C), 128.3 (CH), 127.9 (CH), 127.7 (CH), 122.1 (CH), 121.8 (C), 121.0 (CH), 119.7 (CH), 109.6 (CH), 102.0 (CH), 50.1 (CH<sub>2</sub>); MS-EI** *m/z* **287 (M<sup>+</sup>+2, 42), 285 (M<sup>+</sup>, 43), 287 (42), 285 (44), 206 (70), 204 (35), 171 (97), 169 (100); HRMS calcd for C<sub>15</sub>H<sub>12</sub>BrN 285.0153, found 285.0160.** 

#### General procedure for the synthesis of compounds 4-6

*t*-BuLi (2.33 mL of a 1.5M solution in pentane, 3.5 mmol) was added to a solution of indole **2** (286 mg, 1 mmol) in Et<sub>2</sub>O (5 mL) at  $-78^{\circ}$ C. After stirring the solution for 10 min at this temperature, TMEDA (0.53 mL, 3.5 mmol) was added. The mixture was stirred at  $-78^{\circ}$ C for 10 min, the cooling bath was removed and stirring was continued for 1 h at 0°C. The ethereal suspension of the generated dianion **1** was again cooled to  $-78^{\circ}$ C and the corresponding electrophile (carboxylic ester or metallodichloride, 1 mmol) was added (for the synthesis of **4** excess of deuterium oxide was added at 0°C). After the addition of the electrophile, the mixture was stirred for 5 h at low temperature (from -78 to ca.  $-40^{\circ}$ C), then it was allowed to warm to room temperature, quenched with water, and extracted with EtOAc (3 x 10 mL). The combined organic layers were dried (Na<sub>2</sub>SO<sub>4</sub>) and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel to afford the corresponding indole derivatives **4-6**.

**2-Deuterio-1-(2-deuteriobenzyl)-1***H***-indole (4).** White solid; Mp 43-45°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.76-7.73 (m, 1H, ArH), 7.38-7.30 (m, 4H, ArH), 7.28-7.15 (m, 3H, ArH), 6.64 (s, 1H, NCD=CH), 5.38 (s, 2H, CH<sub>2</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100.6 MHz)  $\delta$  137.3 (C), 136.1 (C), 128.61 (CH), 128.58 (C), 128.5 (CH), 128.2 (t, *J* = 7.5 Hz, C), 127.4 (CH), 126.6 (CH), 121.5 (CH), 120.8 (CH), 119.4 (CH), 119.3 (t, *J* = 21.9 Hz, C), 109.6 (CH), 101.4 (CH), 49.8 (CH<sub>2</sub>); MS-EI *m*/*z* 209 (M<sup>+</sup>, 76), 92 (100); HRMS calcd for C<sub>17</sub>H<sub>11</sub>D<sub>2</sub>N 209.1172, found 209.1167.

**11-Isopropyl-6,11-dihydroindolo**[**1,2-***b*]**isoquinolin-11-ol** (**5a**). White solid; Mp 83-85°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.83 (dd, *J* = 7.8, 1.1 Hz, 1H, ArH), 7.66 (d, *J* = 7.8 Hz, 1H, ArH), 7.44-7.28 (m, 4H, ArH), 7.27-7.20 (m, 1H, ArH), 7.15 (td, *J* = 7.5, 1.0 Hz, 1H, ArH), 6.65 (s, 1H, NC=CH), 5.31 (d, *J* = 16.0 Hz, 1H, NCHH), 5.11 (d, *J* = 16.0 Hz, 1H, NCHH), 2.34 (br s, 1H, OH), 2.22 (hept, *J* = 6.9 Hz, 1H, C*H*(CH<sub>3</sub>)<sub>2</sub>), 0.96 (d, *J* = 6.9 Hz, 3H, CHCH<sub>3</sub>), 0.72 (d, *J* = 6.9 Hz, 3H, CHCH<sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100.6 MHz)  $\delta$  140.4 (C), 139.6 (C), 135.4 (C), 130.8

(C), 127.9 (C), 127.3 (CH), 127.0 (CH), 126.1 (CH), 125.4 (CH), 120.8 (CH), 120.5 (CH), 119.8 (CH), 109.0 (CH), 97.9 (CH), 74.4 (C), 44.7 (CH<sub>2</sub>), 41.9 (CH), 17.0 (CH<sub>3</sub>), 16.9 (CH<sub>3</sub>); MS-EI *m*/*z* 277 (M<sup>+</sup>, 6), 259 (52), 258 (57), 234 (100), 217 (20); HRMS calcd for C<sub>19</sub>H<sub>19</sub>NO 277.1467, found 277.1462.

**11-Phenyl-6,11-dihydroindolo**[**1**,2-*b*]isoquinolin-11-ol (5b). Light yellow oil;  $R_f$  0.19 (hexane/EtOAc 5:1); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.70-7.62 (m, 2H, ArH), 7.46-7.15 (m, 11H, ArH), 6.52 (s, 1H, NC=CH), 5.29 (d, *J* = 15.6 Hz, 1H, NC*H*H), 5.07 (d, *J* = 15.6 Hz, 1H, NCH*H*), 3.00 (br s, 1H, OH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100.6 MHz)  $\delta$  144.4 (C), 142.0 (C), 140.0 (C), 135.6 (C), 131.4 (C), 128.1 (CH), 128.0 (CH), 127.9 (CH), 127.8 (CH), 127.6 (CH), 127.4 (CH), 126.3 (CH), 126.0 (CH), 121.4 (CH), 121.0 (CH), 119.9 (CH), 109.0 (CH), 97.8 (CH), 73.6 (C), 44.5 (CH<sub>2</sub>); MS-EI *m*/*z* 311 (M<sup>+</sup>, 2), 294 (28), 293 (100), 292 (64), 291 (40), 145 (27); HRMS calcd for C<sub>22</sub>H<sub>17</sub>NO 311.1310, found 311.1314.

**11-Cyclopropyl-6,11-dihydroindolo**[**1,2-***b*]**isoquinolin-11-ol** (**5c**). Brown oil; R<sub>f</sub> 0.13 (hexane/EtOAc 5:1); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.86 (dd, *J* = 7.4, 1.6 Hz, 1H, ArH), 7.65 (d, *J* = 7.4 Hz, 1H, ArH), 7.44-7.22 (m, 5H, ArH), 7.17 (t, *J* = 7.6 Hz, 1H, ArH), 6.59 (s, 1H, NC=CH), 5.21 (d, *J* = 15.7 Hz, 1H, NCHH), 5.08 (d, *J* = 15.7 Hz, 1H, NCHH), 2.47 (br s, 1H, OH), 1.43-1.32 (m, 1H, C(OH)CH), 0.57-0.16 (m, 4H, CH<sub>2</sub>CH<sub>2</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75.4 MHz)  $\delta$  141.0 (C), 140.3 (C), 135.8 (C), 131.0 (C), 128.2 (C), 127.9 (CH), 127.5 (CH), 126.0 (CH), 125.5 (CH), 121.4 (CH), 121.0 (CH), 120.0 (CH), 109.1 (CH), 97.3 (CH), 71.6 (C), 44.7 (CH<sub>2</sub>), 23.8 (CH), 1.6 (CH<sub>2</sub>), 1.1 (CH<sub>2</sub>); MS-EI *m*/*z* 257 (M<sup>+</sup>-H<sub>2</sub>O, 72), 256 (100), 254 (73); HRMS calcd for C<sub>19</sub>H<sub>17</sub>NO 275.1310, found 275.1302.

**11-Propyl-6,11-dihydroindolo**[**1**,**2**-*b*]**isoquinolin-11-ol** (**5d**). White solid; Mp 113-115°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.78 (dd, *J* = 7.8, 1.7 Hz, 1H, ArH), 7.61 (dt, *J* = 7.8, 1.0 Hz, 1H, ArH), 7.44-7.23 (m, 5H, ArH), 7.19 (td, *J* = 7.4, 1.3 Hz, 1H, ArH), 6.57 (s, 1H, NC=CH), 5.18 (d, *J* = 16.0 Hz, 1H, NCHH), 5.03 (d, *J* = 16.0 Hz, 1H, NCHH), 2.59 (br s, 1H, OH), 1.99-1.83 (m, 2H, CCH<sub>2</sub>CH<sub>2</sub>), 1.20-1.05 (m, 2H, CH<sub>2</sub>CH<sub>3</sub>), 0.74 (t, *J* = 7.2 Hz, 3H, CH<sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75.4 MHz)  $\delta$  142.2 (C), 140.5 (C), 135.6 (C), 130.4 (C), 128.3 (C), 127.9 (CH), 127.4 (CH), 125.9 (CH), 125.5 (CH), 121.2 (CH), 120.8 (CH), 120.1 (CH), 109.2 (CH), 96.8 (CH), 72.1 (C), 48.2 (CH<sub>2</sub>), 44.5 (CH<sub>2</sub>), 17.3 (CH<sub>2</sub>), 14.0 (CH<sub>3</sub>); MS-EI *m*/*z* 259 (M<sup>+</sup>-H<sub>2</sub>O, 56), 231 (82), 230 (100), 202 (13); HRMS calcd for C<sub>19</sub>H<sub>19</sub>NO 277.1467, found 277.1468.

**11-(2-Thienyl)-6,11-dihydroindolo[1,2-***b***]isoquinolin-11-ol (5e).** White solid; Mp 60-62°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.89 (dd, J = 7.5, 1.6 Hz, 1H, ArH), 7.67 (dt, J = 7.5, 1.0 Hz, 1H, ArH), 7.47-7.13 (m, 7H, ArH), 6.80 (dd, J = 5.2, 3.6 Hz, 1H, SCH=), 6.72 (s, 1H, NC=CH), 6.58 (dd, J = 3.9, 1.4 Hz, 1H, SC=CH), 5.27 (d, J = 15.7 Hz, 1H, NCHH), 4.98 (d, J = 15.7 Hz, 1H, NCH*H*), 3.14 (br s, 1H, OH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75.4 MHz)  $\delta$  149.4 (C), 141.5 (C), 139.9 (C), 135.7 (C), 131.3 (C), 128.03 (CH), 127.99 (CH), 127.9 (CH), 126.2 (CH), 126.0 (CH), 125.6 (CH), 125.4 (CH), 121.6 (CH), 121.2 (CH), 120.0 (CH), 109.0 (CH), 97.2 (CH), 71.7 (C), 44.4 (CH<sub>2</sub>); MS-EI *m*/*z* 299 (M<sup>+</sup>-H<sub>2</sub>O, 100); HRMS calcd for C<sub>20</sub>H<sub>15</sub>NOS 317.0874, found 317.0863. **11-Isobutyl-6,11-dihydroindolo[1,2-***b***]isoquinolin-11-ol (5f).** White solid; Mp 107-109°C; <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.81 (dd, J = 7.7, 1.7 Hz, 1H, ArH), 7.67 (d, J = 7.7 Hz, 1H, ArH),

7.45-7.24 (m, 5H, ArH), 7.19 (td, J = 7.2, 1.2 Hz, 1H, ArH), 6.61 (s, 1H, NC=CH), 5.24 (d, J = 15.9 Hz, 1H, NCHH), 5.05 (d, J = 15.9 Hz, 1H, NCHH), 2.52 (br s, 1H, OH), 1.92 (dd, J = 13.8, 6.3 Hz, 1H, C(OH)CHH), 1.83 (dd, J = 13.8, 6.3 Hz, 1H, C(OH)CHH), 1.59-1.42 (m, 1H, CH(CH<sub>3</sub>)<sub>2</sub>), 0.70 (d, J = 6.2 Hz, 3H, CHCH<sub>3</sub>), 0.62 (d, J = 6.2 Hz, 3H, CHCH<sub>3</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75.4 MHz)  $\delta$  142.1 (C), 140.9 (C), 135.5 (C), 130.1 (CH), 128.2 (C), 127.8 (CH), 127.2 (CH), 125.8 (CH), 125.3 (CH), 121.0 (CH), 120.7 (CH), 119.9 (C), 109.0 (CH), 96.9 (CH), 72.3 (C), 53.6 (CH<sub>2</sub>), 44.3 (CH<sub>2</sub>), 24.3 (CH), 24.0 (CH<sub>3</sub>), 23.9 (CH<sub>3</sub>); MS-EI *m*/*z* 273 (M<sup>+</sup>-H<sub>2</sub>O, 35), 230 (100); HRMS calcd for C<sub>20</sub>H<sub>21</sub>NO 291.1623, found 291.1616.

**11,11-Dimethyl-6,11-dihydrobenzo**[*d*]indolo[1,2-*a*]-1,3-azasiline (6a). Colourless oil; R<sub>f</sub> 0.21 (hexane/EtOAc 50:1); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.77 (dd, *J* = 7.9, 0.7 Hz, 1H, ArH), 7.72 (dd, *J* = 7.0, 1.0 Hz, 1H, ArH), 7.59 (d, *J* = 8.4 Hz, 1H, ArH), 7.48-7.39 (m, 3H, ArH), 7.38-7.31 (m, 1H, ArH), 7.24-7.17 (m, 1H, ArH), 6.98 (s, 1H, NC=CH), 5.45 (s, 2H, CH<sub>2</sub>), 0.64 (s, 6H, Si(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100.6 MHz)  $\delta$  141.8 (C), 138.8 (C), 135.8 (C), 134.1 (C), 133.4 (CH), 129.3 (CH), 128.8 (C), 127.0 (CH), 126.9 (CH), 121.8 (CH), 120.8 (CH), 119.4 (CH), 109.7 (CH), 109.1 (CH), 48.4 (CH<sub>2</sub>), -1.8 (CH<sub>3</sub>); MS-EI *m*/*z* 263 (M<sup>+</sup>, 79), 248 (100), 232 (23); HRMS calcd for C<sub>17</sub>H<sub>17</sub>NSi 263.1130, found 263.1136.

**11,11-Dimethyl-6,11-dihydrobenzo**[*d*]**indolo**[**1,2**-*a*]**-1,3-azagermine** (**6b**). Colourless oil; R<sub>f</sub> 0.20 (hexane/EtOAc 50:1); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz)  $\delta$  7.72 (dd, *J* = 8.0, 0.7 Hz, 1H, ArH), 7.66-7.63 (m, 1H, ArH), 7.57 (d, *J* = 8.3 Hz, 1H, ArH), 7.49-7.39 (m, 3H, ArH), 7.34-7.29 (m, 1H, ArH), 7.20-7.16 (m, 1H, ArH), 6.86 (s, 1H, NC=CH), 5.38 (s, 2H, CH<sub>2</sub>), 0.77 (s, 6H, Ge(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 100.6 MHz)  $\delta$  141.1 (C), 138.4 (C), 137.6 (C), 137.2 (C), 133.2 (CH), 128.8 (CH), 128.7 (C), 127.5 (CH), 127.2 (CH), 121.3 (CH), 120.4 (CH), 119.2 (CH), 108.8 (CH), 108.3 (CH), 48.6 (CH<sub>2</sub>), -2.4 (CH<sub>3</sub>); MS-EI *m*/*z* 309 (M<sup>+</sup>, 79), 294 (100); HRMS calcd for C<sub>17</sub>H<sub>17</sub>GeN 309.0573, found 309.0568.

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