

Supporting Information

Rhodium-Catalyzed Synthesis of Germoles via the Activation Carbon-Germanium Bonds

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I. General Information.

¹H NMR and ¹³C NMR spectra were recorded using either a JEOL JMN-270 spectrometer, a JEOL ECS-400, Varian Unity-INOVA600 spectrometer in CDCl₃. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a Horiba FT-700 spectrometer; absorptions are reported in reciprocal centimeters with the following relative intensities: s (strong), m (medium), or w (weak). Mass spectra were obtained using a Shimadzu GCMS-QP 2010 instrument with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-DX303. Melting points were determined using a Yamato melting point apparatus. Column chromatography was performed with SiO₂ (Silicycle SiliaFlash F60 (230-400 mesh)). Some compounds were purified by LC-908 HPLC (GPC). Fluorescence spectra were recorded by Shimadzu RF-5300 PC Spectrofluorophotometer.

II. Materials.

Unless otherwise noted, all reagents were obtained from commercial suppliers and were used as received. 1,4-Dioxane was distilled over benzophenone ketyl. 4-Octyne (**2**), 1-phenyl-1-propyne, 1-(trimethylsilyl)-1-propyne and DABCO (1,4-diazabicyclo[2,2,2]octane) were purchased from Wako Pure Chemical Industries, Ltd. Diphenylacetylene, 1-phenyl-1-hexyne, tetrolic acid methyl ester and methyl 3-phenylpropionate were purchased from Tokyo Chemical Industry Co., Ltd. 1,4-Dimethoxy-2-butyne were purchased from Sigma-Aldrich Co. Sodium carbonate was purchased from Nacalai Tesque. [RhCl(cod)]₂ (CAS 12092-47-6) was prepared according to literature procedures¹. Cyclododecyne (CAS 1129-90-4) was prepared by the method of Brandsma with minor modification². 4,4'-Dimethoxydiphenylacetylene (CAS 2132-62-9), 1,2-bis(4-(trifluoromethyl)phenyl)ethyne (CAS 119757-51-6), 1,2-bis(4-bromophenyl)ethyne (CAS 2789-89-1), 1,2-di(naphthalen-1-yl)ethyne (CAS 20199-29-5) and 1,2-di(thiophen-2-yl)ethyne (CAS 23975-15-7) were prepared by Sonogashira reaction³.

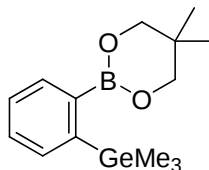
¹ Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

² Brandsma, L.; Verkruijsse, H. D. *Synthesis* **1978**, 290.

³ Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002**, *4*, 3199.

III. Synthesis of Starting Materials.

(2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)trimethylgermane (1)



A dry three-necked flask was charged with a solution of 1,2-dibromobenzene (3.85 g, 16.3 mmol) in THF/Et₂O (33 mL/33 mL) in a nitrogen atmosphere. The solution was cooled to $-110\text{ }^{\circ}\text{C}$ using an EtOH/liquid N₂ bath. A solution of *n*-BuLi in hexane (1.6 M, 12.2 mL, 19.6 mmol) was added dropwise to the solution. The reaction mixture was stirred for an additional 30 min to give a white suspension. A solution of chlorotrimethylgermane (5 g, 32.6 mmol) in Et₂O (10 mL) was added dropwise to the vigorously stirred suspension. The reaction mixture was stirred at $-110\text{ }^{\circ}\text{C}$ to $-100\text{ }^{\circ}\text{C}$ for 90 min and allowed to warm slowly to room temperature. The saturated aqueous solution of NH₄Cl was added and the mixture was extracted with Et₂O (20 mL $\times$ 3). The combined organic layers were washed (brine), dried (MgSO₄), filtered, and evaporated in vacuo. The residual yellow oil was distilled using Kugel Rohr apparatus to give (2-bromophenyl)trimethylgermane (4.35 g, 97%, $125\text{ }^{\circ}\text{C}$ – $130\text{ }^{\circ}\text{C}$, 11 mmHg) as a colorless oil.

A dry three-necked flask was charged with a solution of (2-bromophenyl)trimethylgermane (4.35 g, 15.9 mmol) in toluene/THF (100 mL/25 mL) in a nitrogen atmosphere. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ using a MeOH/dry ice bath. A solution of *n*-BuLi in hexane (1.6 M, 13.2 mL, 21.1 mmol) was added dropwise to the solution. After the mixture was stirred for an additional 60 min, triisopropyl borate (9.5 mL, 41.2 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then 1 M HCl solution (50 mL) was added at $0\text{ }^{\circ}\text{C}$. The mixture was extracted with Et₂O (20 mL $\times$ 3), and the combined organic layers were washed (brine), dried (MgSO₄), filtered, and evaporated in vacuo to produce crude 2-(trimethylgermyl)phenylboronic acid (3.26 g) as a pale yellow solid. A round-bottom flask was charged with a solution of crude 2-(trimethylgermyl)phenylboronic acid (3.26 g) and 2,2-dimethylpropane-1,3-diol (1.43 g, 13.7 mmol) in hexane. The reaction mixture was stirred overnight. Then CaCl₂ was added and the mixture was stirred for a few hours. The mixture was filtered and evaporated in vacuo. The residual yellow oil was distilled by Kugel Rohl apparatus (100 – $110\text{ }^{\circ}\text{C}$, 10 mmHg) then purified by silica gel column chromatography (hexane/EtOAc = 100/1 $\rightarrow$ 10/1) to give a titled compound (2.69 g, 8.8 mmol, 55%).

Colorless oil. R_f 0.21 (hexane/EtOAc = 100/1).

¹H NMR (CDCl₃, 270.05 MHz) δ : 0.38 (s, 9H), 1.04 (s, 6H), 3.76 (s, 4H), 7.29–7.38 (m, 2H), 7.56 (d, J = 7.2 Hz, 1H), 7.87 (d, J = 6.9 Hz, 1H).

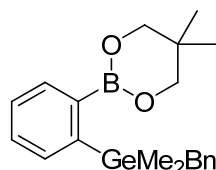
¹³C NMR (CDCl₃, 100.53 MHz) δ : 0.5, 22.0, 31.7, 72.0, 127.4, 129.4, 133.5, 134.7, 148.6.

IR (neat): 3047 w, 2964 m, 2931 m, 2906 m, 1581 w, 1556 w, 1541 w, 1481 s, 1433 m, 1415 m, 1377 m, 1336 s, 1311 s, 1252 m, 1138 s, 1070 w, 1030 w, 829 m, 764 w, 733 m, 683 w, 650 m, 596 m, 571 w, 503 w, 480 w, 420 w.

MS, m/z (relative intensity, %): 308 (M^+ , 0), 293 ($M^+ - \text{Me}$, 44), 292 (24), 291 (35), 290 (11), 289 (25), 225 (26), 224 (13), 223 (21), 221 (15), 207 (30), 206 (15), 205 (24), 203 (15), 117 (12), 91 (12), 69 (100).

Exact Mass (CI): Calcd for $\text{C}_{14}\text{H}_{24}\text{BGeO}_2^+$ 309.1076, found 309.1088.

Benzyl(2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)dimethylgermane (22)



A dry three-necked flask was charged with a solution of 1,2-dibromobenzene (1.51 g, 6.4 mmol) in THF/Et₂O (15 mL/15 mL) in a nitrogen atmosphere. The solution was cooled to $-110\text{ }^\circ\text{C}$ using an EtOH/liquid N₂ bath. A solution of *n*-BuLi in hexane (1.6 M, 4.4 mL, 7.0 mmol) was added dropwise to the solution. The reaction mixture was stirred for an additional 30 min to give a white suspension. A solution of benzylchlorodimethylgermane (3.71 g, 11.5 mmol), prepared from dichlorodimethylgermane and benzylmagnesium bromide⁴, in Et₂O (5 mL) was added dropwise to the vigorously stirred suspension. The reaction mixture was stirred at $-110\text{ }^\circ\text{C}$ to $-100\text{ }^\circ\text{C}$ for 90 min and allowed to warm slowly to room temperature. The saturated solution of NH₄Cl in water was added and the mixture was extracted with Et₂O (15 mL $\times$ 3). The combined organic layers were washed (brine), dried (MgSO₄), filtered, and evaporated in vacuo. The residual yellow oil was filtered by silica gel to give crude benzyl(2-bromophenyl)dimethylgermane (3.57 g) as a colorless oil.

A dry three-necked flask was charged with a solution of crude benzyl(2-bromophenyl)dimethylgermane (3.75 g) in Et₂O (35 mL) in a nitrogen atmosphere. The solution was cooled to $-78\text{ }^\circ\text{C}$ using a MeOH/dry ice bath. A solution of *t*-BuLi in hexane (1.59 M, 8.1 mL, 12.8 mmol) was added dropwise to the solution. After the mixture was stirred for 60 min., a solution of 2-isopropoxy-5,5-dimethyl-1,3,2-dioxaborinane (9.5 mL, 41.2 mmol) in Et₂O (7 mL) was added dropwise. The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ over 60 min. and allowed to warm to $0\text{ }^\circ\text{C}$ slowly. After the mixture was stirred for an additional 30 min., chlorotrimethylsilane (1.6 mL, 12.8 mmol) was added dropwise at $0\text{ }^\circ\text{C}$. The reaction mixture was stirred at $0\text{ }^\circ\text{C}$ for 20 min. and allowed to warm to room temperature, then stirred overnight. The reaction mixture was filtered by celite and purified by silica gel column chromatography to give a crude product. The crude product was purified by GPC to give a titled compound (2.1 g, 5.5 mmol, 86%).

⁴ Kondo, T.; Yamamoto, K.; Omura, T.; Kumada, M. *J. Organomet. Chem.* **1973**, 60, 287.

Colorless oil. Rf 0.14 (hexane).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.31 (s, 6H), 1.07 (s, 6H), 2.54 (s, 2H), 3.82 (s, 4H), 6.99 (d, J = 6.8 Hz, 2H), 7.04 (t, J = 7.4 Hz, 1H), 7.18 (t, J = 7.6 Hz, 2H), 7.34-7.37 (m, 2H), 7.48-7.51 (m, 1H), 7.91-7.93 (m, 1H).

^{13}C NMR (CDCl_3 , 150.83 MHz) δ : -2.0, 22.0, 26.8, 31.7, 72.1, 123.7, 127.6, 127.98, 128.00, 129.5, 133.9, 135.0, 141.7, 147.1.

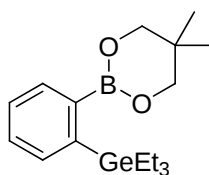
IR (neat): 3051 w, 3024 w, 2964 m, 2931 m, 1599 w, 1581 w, 1556 w, 1481 m, 1433 m, 1415 m, 1375 m, 1335 s, 1309 s, 1252 s, 1211 w, 1136 s, 1068 w, 1030 w, 999 w, 964 w, 930 w, 904 w, 810 m, 760 m, 735 m, 700 m, 683 w, 650 m, 596 w, 577 w, 503 w, 480 w, 463 w.

MS, m/z (relative intensity, %): 384 (M^+ , 0), 293 ($\text{M}^+ - \text{Bn}$, 38), 292 (21), 291 (31), 290 (10), 289 (21), 225 (23), 224 (12), 223 (19), 221 (13), 207 (26), 206 (13), 205 (21), 203 (14), 91 (46), 69 (100).

Exact Mass (CI): Calcd for $\text{C}_{20}\text{H}_{28}\text{BGeO}_2^+$ 385.1389, found 385.1389.

20, **24a** and **24b** were synthesized by the borylation of the corresponding 2-germylbromobenzenes or 2-silylbromobenzene through the procedure described for **22**.

(2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)triethylgermane (20)



Colorless oil. Rf 0.14 (hexane).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 1.02 (s, 15H), 1.05 (s, 6H), 3.76 (s, 4H), 7.30-7.35 (m, 2H), 7.48-7.50 (m, 1H), 7.84-7.87 (m, 1H).

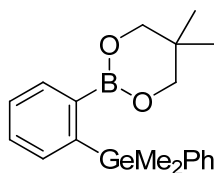
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : 5.7, 9.3, 22.0, 31.7, 72.1, 127.1, 129.1, 134.6, 134.7, 145.4.

IR (neat): 2958 m, 2906 m, 2871 m, 1579 w, 1558 w, 1541 w, 1481 m, 1458 m, 1431 m, 1377 m, 1336 m, 1311 s, 1250 m, 1138 s, 1070 w, 1014 w, 970 w, 816 w, 766 w, 739 w, 708 w, 685 w, 652 w, 575 w, 482 w, 420 w.

MS, m/z (relative intensity, %): 350 (M^+ , 0), 323 (11), 322 (10), 321 ($\text{M}^+ - \text{Et}$, 50), 320 (28), 319 (39), 318 (13), 317 (28), 253 (29), 252 (15), 251 (24), 249 (20), 235 (15), 233 (12), 279 (11), 177 (22), 175 (16), 69 (100).

Exact Mass (CI): Calcd for $\text{C}_{17}\text{H}_{30}\text{BGeO}_2^+$ 351.1545, found 351.1555.

(2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)dimethyl(phenyl)germane (24a)



White solid. mp = 89-90 °C. Rf 0.24 (hexane/EtOAc = 50/1).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.66 (s, 6H), 0.87 (s, 6H), 3.49 (s, 4H), 7.30-7.34 (m, 3H), 7.35-7.38 (m, 2H), 7.46-7.48 (m, 2H), 7.50-7.52 (m, 1H), 7.86-7.88 (m, 1H).

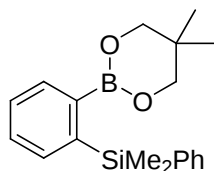
^{13}C NMR (CDCl_3 , 150.83 MHz) δ : -0.8, 21.8, 31.4, 71.6, 127.71, 127.727, 127.734, 129.4, 133.4, 134.5, 134.7, 143.2, 145.9.

IR (KBr): 3064 m, 3047 m, 3005 m, 2966 s, 2951 s, 2908 s, 2871 m, 1579 m, 1481 s, 1431 s, 1375 s, 1336 s, 1313 s, 1250 s, 1165 m, 1134 s, 1092 m, 1065 m, 1028 m, 995 w, 960 w, 810 s, 769 m, 731 s, 700 s, 667 m, 646 s, 604 m, 577 m, 501 w, 472 m.

MS, m/z (relative intensity, %): 370 (M^+ , 0), 357 (11), 356 (12), 355 ($\text{M}^+ - \text{Me}$, 51), 354 (29), 353 (40), 352 (13), 351 (28), 293 (23), 292 (12), 291 (18), 289 (14), 287 (11), 269 (24), 268 (12), 267 (19), 265 (12), 209 (32), 208 (15), 207 (31), 205 (22), 165 (14), 163 (12), 151 (11), 149 (13), 91 (26), 69 (100).

Exact Mass (CI): Calcd for $\text{C}_{19}\text{H}_{26}\text{BGeO}_2^+$ 371.1232, found 371.1234.

(2-(5,5-Dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)dimethyl(phenyl)silane (24b)



White solid. mp = 73-75 °C. Rf 0.24 (hexane/EtOAc = 50/1).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.55 (s, 6H), 0.81 (s, 6H), 3.38 (s, 4H), 7.31-7.32 (m, 3H), 7.37-7.40 (m, 2H), 7.46-7.48 (m, 2H), 7.62-7.64 (m, 1H), 7.78-7.80 (m, 1H).

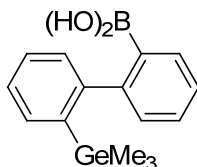
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -0.4, 21.8, 31.3, 71.5, 127.5, 128.1, 128.2, 129.0, 133.7, 133.9, 135.5, 141.0, 143.0.

IR (KBr): 3068 m, 3047 m, 2951 s, 2902 m, 1581 w, 1481 s, 1431 s, 1377 m, 1336 s, 1313 s, 1244 s, 1163 m, 1134 s, 1111 s, 1070 m, 1026 m, 995 w, 958 w, 822 s, 769 s, 735 s, 698 s, 644 s, 501 w, 480 m, 447 m, 420 w.

MS, m/z (relative intensity, %): 324 (M^+ , 0), 310 (25), 309 ($\text{M}^+ - \text{Me}$, 100), 308 (24), 267 (30), 253 (13), 247 (37), 223 (43), 211 (16), 209 (19), 189 (15), 163 (52), 162 (14), 161 (11), 120 (10), 119 (87), 105 (18), 93 (24), 69 (95), 53 (10).

Exact Mass (CI): Calcd for $\text{C}_{19}\text{H}_{26}\text{BO}_2\text{Si}^+$ 325.1790 found 325.1804.

2'-(Trimethylgermyl)biphenyl-2-ylboronic acid (**18**)



A dry three-necked flask was charged with a solution of 2,2'-dibromobiphenyl (2.03 g, 6.5 mmol) in THF (45 mL) in a nitrogen atmosphere. The solution was cooled to $-78\text{ }^{\circ}\text{C}$ using an MeOH/dry ice bath. A solution of *n*-BuLi in hexane (1.6 M, 4.2 mL, 6.6 mmol) was added dropwise to the solution. The reaction mixture was stirred for an additional 30 min. To the reaction mixture was added chlorotrimethylgermane (1 g, 6.5 mmol) dropwise. The reaction mixture was stirred for an additional 30 min and allowed to warm to room temperature. The saturated aqueous solution of NH_4Cl was added and the mixture was extracted with Et_2O . The combined organic layers were washed (brine), dried (MgSO_4), filtered, and evaporated in vacuo. The residual yellow oil was purified by silica gel column chromatography (hexane) as a colorless oil (2.1 g, 6.0 mmol, 92%).

A dry three-necked flask was charged with a solution of (2'-bromobiphenyl-2-yl)trimethylgermane (1.05 g, 3 mmol) in toluene/THF (5 mL/5 mL) in a nitrogen atmosphere. The solution was cooled to $-110\text{ }^{\circ}\text{C}$ using a EtOH/ N_2 bath. A solution of *n*-BuLi in hexane (1.6 M, 2.3 mL, 3.6 mmol) was added dropwise to the solution. After the mixture was stirred for an additional 30 min., triisopropyl borate (3.5 mL, 15 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight. Then 1 M HCl solution (20 mL) was added at $0\text{ }^{\circ}\text{C}$. The mixture was extracted with Et_2O (15 mL $\times$ 3) and the combined organic layers were washed (brine), dried (MgSO_4), filtered, and evaporated in vacuo. The residual pale yellow solid was washed with cooled hexane to give 633.4 mg (2.01 mmol, 67%) of a titled compound as a white solid.

White solid. mp = $129\text{--}132\text{ }^{\circ}\text{C}$.

^1H NMR (CDCl_3 , 399.78 MHz) δ : -0.07-0.07 (m, 9H), 6.53-6.60 (m, 1H), 7.10-7.16 (m, 3H), 7.29-7.44 (m, 3H), 7.60-7.64 (m, 1H).

^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -0.2, 125.9, 126.0, 127.6, 129.2, 129.3, 130.1, 130.8, 133.3, 137.3, 140.0, 150.8.

IR (KBr): 3219 m, 3053 w, 2972 w, 2906 w, 1591 w, 1562 w, 1431 m, 1346 s, 1296 m, 1246 m, 1198 w, 1161 w, 1117 w, 1039 w, 1003 w, 827 s, 758 m, 729 w, 706 m, 652 w, 598 m, 567 w, 552 w, 455 w.

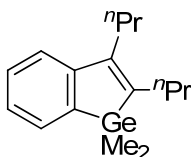
IV. Typical Procedure.

Procedure for the Rh-Catalyzed Synthesis of **3.** An oven-dried 5 mL screw-capped vial was charged with (2-(5,5-dimethyl-1,3,2-dioxaborinan-2-yl)phenyl)trimethylgermane (**1**, 153.4 mg, 0.5 mmol), 4-octyne (**2**, 110.2 mg, 1.0 mmol), DABCO (112.2 mg, 1.0 mmol), $[\text{RhCl}(\text{cod})]_2$ (12.3 mg,

0.025 mmol), 1,4-dioxane (1 mL) and H₂O (100 μ L) under a gentle stream of nitrogen. The vessel was heated in an oil bath at 80 °C for 15 h followed by cooling. The contents were subjected to flash chromatography (hexane) to give 1,1-dimethyl-2,3-dipropyl-1H-benzo[b]germole (**3**) (135.7 mg, 94%) as a white solid.

V. Spectroscopic Data.

1,1-Dimethyl-2,3-dipropyl-1H-benzo[b]germole (**3**)



Colorless oil. Rf 0.63 (hexane).

¹H NMR (CDCl₃, 270.05 MHz) δ : 0.47 (s, 6H), 0.88-1.01 (m, 6H), 1.46-1.60 (m, 4H), 2.43-2.55 (m, 4H), 7.14-7.20 (m, 1H), 7.30-7.32 (m, 2H), 7.49 (d, J = 5.5 Hz, 1H).

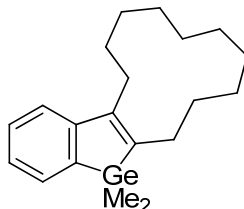
¹³C NMR (CDCl₃, 67.80 MHz) δ : -2.7, 14.39, 14.42, 22.1, 24.0, 29.1, 33.1, 121.7, 125.6, 128.8, 131.4, 140.6, 144.7, 147.1, 149.0.

IR (neat): 3053 m, 2958 s, 2927 s, 2870 s, 1583 m, 1556 w, 1462 s, 1441 s, 1377 m, 1336 w, 1298 w, 1271 m, 1234 m, 1186 w, 1161 w, 1122 w, 1093 w, 1032 w, 835 s, 796 s, 762 s, 725 s, 648 w, 602 s, 582 m, 428 w.

MS, m/z (relative intensity, %): 292 (M^+ +2, 12), 290 (M^+ , 69), 289 (M^+ -1, 20), 288 (M^+ -2, 49), 286 (M^+ -4, 36), 277 (14), 276 (10), 275 (81), 274 (23), 273 (58), 271 (43), 261 (11), 259 (11), 247 (27), 246 (10), 245 (21), 243 (16), 233 (18), 231 (18), 229 (14), 219 (12), 217 (19), 215 (16), 186 (14), 185 (43), 184 (17), 157 (55), 155 (35), 143 (71), 142 (23), 141 (38), 129 (72), 128 (58), 127 (13), 115 (67), 107 (17), 105 (100), 104 (21), 103 (79), 101 (62), 91 (39), 89 (77), 88 (13), 87 (55), 85 (37).

Exact Mass (EI): Calcd for C₁₆H₂₄Ge 290.1090, found 290.1092.

5,5-Dimethyl-6,7,8,9,10,11,12,13,14,15-decahydro-5H-benzo[b]cyclo[10.10.0]germole (**4**)



White solid. mp = 68-70 °C. Rf 0.43 (hexane).

¹H NMR (CDCl₃, 399.78 MHz) δ : 0.48 (s, 6H), 1.29-1.74 (m, 16H), 2.52 (t, J = 7.6 Hz, 2H), 2.64 (t, J = 6.6 Hz, 2H), 7.17-7.20 (m, 1H), 7.31-7.38 (m, 2H), 7.52 (d, J = 6.8 Hz, 1H).

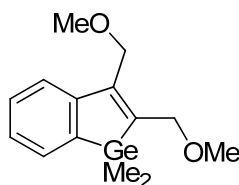
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -2.8, 21.9, 23.1, 23.5, 23.9, 25.0, 25.6, 25.8, 26.8, 27.7, 27.8, 122.3, 125.5, 128.8, 131.3, 140.6, 145.4, 146.4, 149.1.

IR (KBr): 3064 w, 3051 w, 2968 m, 2916 s, 2848 s, 1581 w, 1466 m, 1441 m, 1292 w, 1273 w, 1115 w, 831 m, 795 m, 760 m, 725 m, 652 w, 600 m, 580 m, 482 w.

MS, m/z (relative intensity, %): 346 ($\text{M}^+ + 2$, 16), 345 ($\text{M}^+ + 1$, 17), 344 (M^+ , 81), 343 ($\text{M}^+ - 1$, 29), 342 ($\text{M}^+ - 2$, 59), 340 ($\text{M}^+ - 4$, 44), 331 (18), 330 (18), 329 (87), 328 (31), 327 (67), 325 (50), 245 (23), 243 (21), 241 (17), 240 (19), 239 (42), 238 (12), 237 (20), 233 (22), 231 (26), 229 (22), 227 (11), 221 (14), 220 (67), 219 (44), 218 (55), 217 (41), 216 (43), 215 (32), 213 (19), 211 (12), 207 (21), 205 (58), 204 (17), 203 (49), 201 (39), 197 (11), 195 (11), 193 (15), 191 (24), 189 (24), 187 (15), 183 (16), 181 (21), 169 (23), 167 (20), 165 (12), 157 (15), 155 (47), 153 (14), 143 (38), 142 (29), 141 (83), 131 (16), 130 (17), 129 (67), 128 (50), 127 (13), 117 (31), 115 (61), 107 (22), 105 (89), 104 (25), 103 (67), 101 (53), 95 (17), 91 (61), 89 (100), 88 (20), 87 (74), 85 (53), 81 (28), 79 (11), 69 (13), 67 (36), 55 (54).

Exact Mass (EI): Calcd for $\text{C}_{20}\text{H}_{30}\text{Ge}$ 344.1559, found 344.1555.

2,3-Bis(methoxymethyl)-1,1-dimethyl-1H-benzo[b]germole (5)



Colorless oil. R_f 0.43 (hexane/EtOAc = 10/1).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.54 (s, 6H), 3.38 (s, 6H), 4.38 (s, 2H), 4.51 (s, 2H), 7.19-7.23 (m, 1H), 7.30-7.35 (m, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 6.8 Hz, 1H).

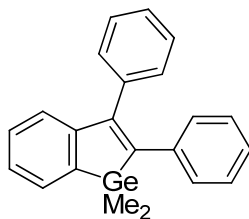
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -2.8, 57.9, 58.4, 67.1, 72.4, 122.6, 126.4, 128.9, 131.6, 141.1, 142.1, 147.5, 148.9.

IR (neat): 3051 m, 2981 s, 2914 s, 2885 s, 2816 s, 1583 m, 1560 w, 1444 s, 1362 s, 1302 m, 1273 m, 1232 m, 1192 s, 1161 s, 1103 s, 955 s, 908 m, 837 s, 802 s, 764 s, 725 s, 607 s, 584 s, 526 w, 484 w, 424 w.

MS, m/z (relative intensity, %): 294 (M^+ , 0), 264 ($\text{M}^+ + 1 - \text{OMe}$, 15), 262 (27), 260 (20), 258 (10), 251 (16), 250 (11), 249 (83), 248 (30), 247 (100), 246 (21), 245 (75), 243 (26), 232 (10), 219 (16), 217 (38), 216 (13), 215 (44), 213 (29), 211 (11), 189 (14), 187 (12), 159 (12), 141 (12), 135 (17), 133 (13), 131 (13), 129 (34), 128 (81), 127 (13), 123 (10), 121 (31), 119 (25), 117 (23), 116 (13), 115 (52), 107 (13), 105 (55), 104 (15), 103 (45), 101 (36), 91 (17), 89 (36), 87 (25), 85 (17), 75 (11).

Exact Mass (EI): Calcd for $\text{C}_{14}\text{H}_{20}\text{GeO}_2$ 294.0675, found 294.0677.

1,1-Dimethyl-2,3-diphenyl-1H-benzo[b]germole (6)



White solid. mp = 103-104 °C. Rf 0.21 (hexane).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.66 (s, 6H), 6.95-6.97 (m, 2H), 7.02-7.07 (m, 2H), 7.10-7.14 (m, 2H), 7.19-7.21 (m, 2H), 7.25-7.27 (m, 2H), 7.30-7.37 (m, 3H), 7.61-7.63 (m, 1H).

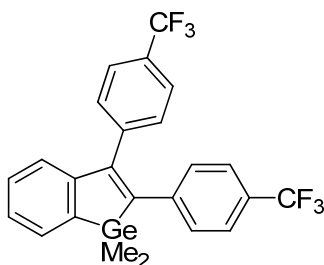
^{13}C NMR (CDCl_3 , 67.80 MHz) δ : -2.5, 124.8, 125.7, 126.7, 126.9, 127.9, 128.4, 128.7, 129.0, 129.8, 131.6, 138.7, 140.37, 140.41, 144.9, 149.76, 149.82.

IR (KBr): 3072 m, 3051 m, 3018 w, 2991 w, 2968 w, 2906 w, 1595 w, 1547 w, 1489 m, 1441 m, 1415 w, 1296 w, 1236 w, 1153 w, 1120 w, 1074 w, 1030 w, 978 w, 908 w, 835 m, 800 m, 766 s, 746 m, 725 m, 700 s, 665 w, 596 m, 482 w, 413 w.

MS, m/z (relative intensity, %): 360 ($\text{M}^+ + 2$, 13), 359 ($\text{M}^+ + 1$, 14), 358 (M^+ , 61), 357 (22), 356 ($\text{M}^+ - 2$, 44), 354 (32), 345 (22), 344 ($\text{M}^+ - 4$, 22), 343 (100), 342 (38), 341 (76), 340 (14), 339 (60), 254 (22), 253 (43), 252 (73), 250 (13), 151 (11).

Exact Mass (EI): Calcd for $\text{C}_{22}\text{H}_{20}\text{Ge}$ 358.0777, found 358.0774.

1,1-Dimethyl-2,3-bis(4-(trifluoromethyl)phenyl)-1H-benzo[b]germole (7)



White solid. mp = 130-131 °C. Rf 0.40 (hexane).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.67 (s, 6H), 6.97-6.99 (m, 1H), 7.01 (d, J = 8.0 Hz, 2H), 7.29-7.32 (m, 4H), 7.39 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.64-7.66 (m, 1H).

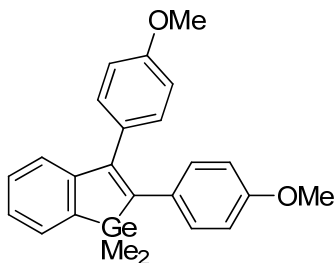
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -2.7, 124.9, 124.1 (q, J = 272.1 Hz), 124.2 (q, J = 272.1 Hz), 125.1 (q, J = 2.8 Hz), 125.5 (q, J = 2.8 Hz), 127.5, 127.7 (q, J = 31.6 Hz), 128.4, 129.3, 129.4 (q, J = 32.6 Hz), 130.1, 132.0, 140.2, 141.8, 144.0, 145.2, 148.4, 150.0.

IR (KBr): 3059 w, 2995 w, 2924 w, 1610 m, 1574 w, 1550 w, 1441 w, 1408 w, 1323 s, 1242 w, 1167 s, 1113 s, 1066 s, 1016 w, 980 w, 849 m, 800 w, 756 w, 727 w, 692 w, 669 w, 609 w, 418 w.

MS, m/z (relative intensity, %): 494 (M^+ , 47), 493 (15), 492 ($\text{M}^+ - 2$, 33), 490 ($\text{M}^+ - 4$, 22), 481 (18), 480 (20), 479 (100), 478 (36), 477 (76), 476 (12), 475 (59), 372 (10), 371 (53), 351 (12), 320 (12), 301 (21), 252 (10).

Exact Mass (EI): Calcd for C₂₄H₁₈F₆Ge 494.0524, found 454.0529.

2,3-Bis(4-methoxyphenyl)-1,1-dimethyl-1H-benzo[b]germole (8)



White solid. mp = 114-115 °C. Rf 0.37 (hexane/CH₂Cl₂ = 2/1).

¹H NMR (CDCl₃, 399.78 MHz) δ: 0.65 (s, 6H), 3.75 (s 3H), 3.85 (s, 3H), 6.68-6.71 (m, 2H), 6.91-6.94 (m, 4H), 7.02-7.04 (m, 1H), 7.12-7.15 (m, 2H), 7.23-7.26 (m, 2H), 7.59-7.61 (m, 1H).

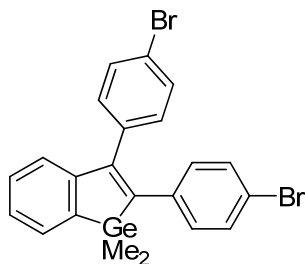
¹³C NMR (CDCl₃, 100.53 MHz) δ: -2.3, 55.1, 55.2, 113.4, 114.0, 124.5, 126.4, 129.0, 130.1, 130.9, 131.2, 131.5, 132.8, 140.0, 143.8, 148.0, 150.3, 157.5, 158.4.

IR (KBr): 3057 m, 3030 m, 3002 m, 2929 m, 2904 m, 2835 m, 1604 s, 1576 m, 1545 m, 1504 s, 1458 s, 1441 s, 1414 m, 1282 s, 1248 s, 1176 s, 1151 m, 1107 m, 1032 s, 978 m, 835 s, 802 s, 783 m, 754 m, 727 m, 604 m, 577 m, 501 w, 418 w.

MS, *m/z* (relative intensity, %): 420 (M⁺+2, 21), 419 (M⁺+1, 23), 418 (M⁺, 100), 417 (37), 416 (M⁺-2, 72), 415 (11), 414 (M⁺-4, 51), 405 (19), 404 (20), 403 (88), 402 (32), 401 (63), 399 (47), 328 (11), 327 (22), 314 (12), 299 (20), 283 (17), 252 (21), 240 (21), 239 (52), 227 (12), 226 (16), 181 (17), 179 (13), 157 (16), 121 (26), 105 (26), 103 (19), 101 (17), 89 (12).

Exact Mass (EI): Calcd for C₂₄H₂₄GeO₂ 418.0988, found 418.0991.

2,3-Bis(4-bromophenyl)-1,1-dimethyl-1H-benzo[b]germole (9)



White solid. mp = 173-174 °C. Rf 0.31 (hexane).

¹H NMR (CDCl₃, 399.78 MHz) δ: 0.64 (s, 6H), 6.80 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 4.4 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 7.26-7.28 (m, 4H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.61 (t, *J* = 4.4 Hz, 1H).

¹³C NMR (CDCl₃, 100.53 MHz) δ: -2.7, 119.7, 121.2, 124.7, 127.1, 129.2, 130.0, 131.2, 131.5, 131.7, 131.8, 137.0, 139.2, 140.2, 144.5, 148.8, 149.1.

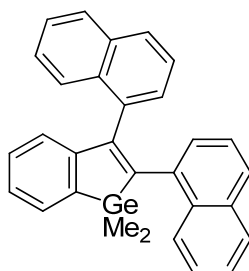
IR (KBr): 3055 m, 2908 w, 1587 m, 1545 m, 1481 s, 1441 m, 1389 m, 1300 m, 1230 w, 1149 w,

1103 m, 1070 s, 1011 s, 839 s, 820 s, 777 s, 725 s, 694 m, 673 w, 602 m, 582 m, 538 w, 503 m, 488 m, 424 m.

MS, m/z (relative intensity, %): 519 (11), 518 (45), 517 (28), 516 (M^{+2} , 94), 515 (M^{+1} , 35), 514 (M^{+} , 93), 513 (21), 512 (M^{+2} , 57), 510 (M^{+4} , 17), 504 (11), 503 (48), 502 (28), 501 (98), 500 (36), 499 (100), 498 (20), 497 (61), 495 (18), 412 (15), 368 (12), 366 (10), 265 (12), 253 (20), 252 (86), 251 (17), 250 (45).

Exact Mass (EI): Calcd for $C_{22}H_{18}Br_2Ge$ 513.8987, found 513.8984.

1,1-Dimethyl-2,3-di(naphthalen-1-yl)-1H-benzo[b]germole (10)



White solid. mp = 169-170 °C. Rf 0.21 (hexane/ CH_2Cl_2 = 10/1).

1H NMR ($CDCl_3$, 270.05 MHz) δ : 0.61 (s, 3H), 0.67 (s, 3H), 6.64 (d, J = 7.6 Hz, 1H), 6.91 (d, J = 7.0 Hz, 1H), 7.07-7.18 (m, 4H), 7.28-7.42 (m, 5H), 7.47 (d, J = 8.1 Hz, 1H), 7.58-7.62 (m, 1H), 7.68-7.75 (m, 3H), 7.88 (d, J = 7.6 Hz, 1H), 8.02-8.05 (m, 1H).

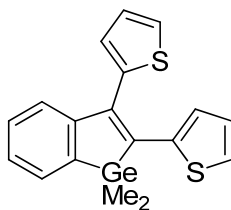
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ : -2.8, -2.1, 123.4, 125.0, 125.3, 125.4, 125.5, 125.6, 126.4, 126.5, 126.8, 127.2, 128.0, 128.1, 129.2, 131.4, 131.7, 131.9, 133.2, 133.3, 136.0, 139.2, 140.7, 147.6, 149.4, 150.6.

IR (KBr): 3049 m, 2991 m, 2904 m, 1581 m, 1502 m, 1437 m, 1389 s, 1331 w, 1292 m, 1248 m, 1155 w, 1119 w, 1093 w, 1053 w, 1012 m, 949 m, 904 w, 839 m, 798 s, 775 s, 723 s, 669 m, 634 w, 609 m, 580 m, 522 m, 503 m, 424 m.

MS, m/z (relative intensity, %): 460 (M^{+2} , 24), 459 (M^{+1} , 31), 458 (M^{+} , 100), 457 (42), 456 (M^{+2} , 71), 455 (17), 454 (M^{+4} , 51), 444 (13), 443 (42), 442 (18), 441 (33), 439 (23), 354 (15), 353 (37), 352 (45), 351 (25), 350 (32), 315 (42), 314 (15), 313 (31), 311 (23), 277 (19), 276 (24), 226 (10).

Exact Mass (EI): Calcd for $C_{30}H_{24}Ge$ 458.1090, found 458.1088.

1,1-Dimethyl-2,3-di(thiophen-2-yl)-1H-benzo[b]germole (11)



White solid. mp = 124-125 °C. Rf 0.26 (hexane).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.76 (s, 6H), 6.95-7.01 (m, 4H), 7.19-7.21 (m, 1H), 7.24-7.32 (m, 3H), 7.58-7.61 (m, 2H).

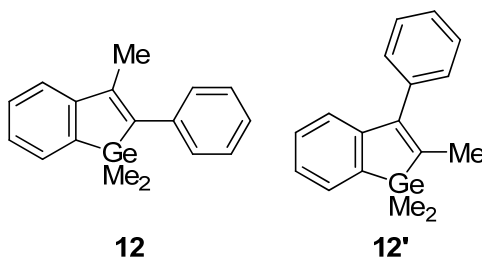
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -1.8, 124.4, 126.1, 126.7, 127.2, 127.5, 127.99, 128.05, 128.8, 129.5, 131.4, 138.1, 138.3, 139.2, 141.3, 142.9, 150.5.

IR (KBr): 3059 w, 2904 w, 1576 w, 1437 m, 1415 w, 1275 m, 1236 w, 1209 w, 1115 w, 1057 w, 1034 w, 850 m, 827 m, 800 m, 773 m, 704 s, 606 m, 582 m, 476 w, 424 w.

MS, m/z (relative intensity, %): 372 ($\text{M}^+ + 2$, 29), 371 ($\text{M}^+ + 1$, 22), 370 (M^+ , 100), 369 (35), 368 ($\text{M}^+ - 2$, 73), 367 (11), 366 ($\text{M}^+ - 4$, 51), 355 (39), 354 (12), 353 (30), 351 (20), 321 (22), 319 (15), 316 (10), 266 (48), 265 (12), 249 (25), 235 (19), 234 (99), 233 (17), 232 (18), 221 (17), 215 (10), 208 (25), 189 (19), 117 (17), 104 (21), 89 (17), 87 (13).

Exact Mass (EI): Calcd for $\text{C}_{18}\text{H}_{16}\text{GeS}_2$ 369.9905, found 369.9913.

1,1,3-Trimethyl-2-phenyl-1H-benzo[b]germole (**12**)



This compound was obtained as a regioisomeric mixture of **12** and **12'** (15:1) determined by NMR.

White solid. mp = 61-63 °C. Rf 0.43 (hexane).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.54 (s, 6H), 2.16 (s, 3H), 7.16-7.29 (m, 4H), 7.35-7.46 (m, 4H), 7.57 (d, $J = 7.4$ Hz, 1H).

^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -3.1, 14.6, 122.6, 125.5, 126.6, 127.9, 128.2, 129.1, 131.4, 140.4, 141.8, 143.9, 144.2, 149.6.

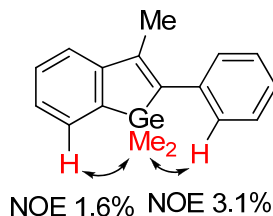
IR (KBr): 3074 w, 3049 s, 3018 m, 2985 m, 2933 m, 2906 m, 1593 m, 1487 m, 1439 s, 1365 m, 1279 m, 1232 m, 1157 w, 1122 m, 1070 m, 1028 m, 926 w, 894 w, 839 m, 793 s, 760 s, 723 s, 702 s, 602 s, 582 s, 540 w, 499 m, 472 m, 440 w.

MS, m/z (relative intensity, %): 296 (M^+ , 49), 295 (16), 294 ($\text{M}^+ - 2$, 36), 292 ($\text{M}^+ - 4$, 26), 283 (21), 282 (16), 281 (100), 280 (34), 279 (78), 278 (10), 277 (60), 265 (19), 263 (16), 261 (12), 191 (29),

189 (16), 165 (10), 115 (12), 89 (15).

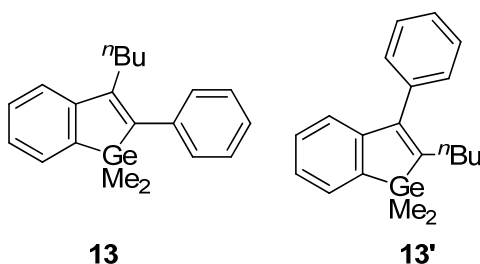
Exact Mass (EI): Calcd for $C_{17}H_{18}Ge$ 296.0620, found 296.0617.

The regiochemistry of **12** was determined based on NOE experiments.



The formation of **12'** was confirmed by GCMS m/z (relative intensity, %): 296 (M^+ , 41), 295 (11), 294 (M^+-2 , 29), 292 (M^+-4 , 20), 283 (18), 282 (12), 281 (100), 280 (30), 279 (75), 277 (56), 265 (11), 191 (30), 189 (16), 165 (11), 115 (12), 89 (20), 87 (12).

3-Butyl-1,1-dimethyl-2-phenyl-1H-benzo[b]germole (**13**)



This compound was obtained as a regioisomeric mixture of **13** and **13'** (14:1) determined by NMR.

Colorless oil. R_f 0.43 (hexane).

1H NMR ($CDCl_3$, 399.78 MHz) δ : 0.51 (s, 6H), 0.84-0.88 (m, 3H), 1.30-1.36 (m, 2H), 1.52-1.60 (m, 2H), 2.53 (t, $J = 8.0$ Hz, 2H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.18-7.28 (m, 2H), 7.33-7.41 (m, 3H), 7.44 (d, $J = 8.0$ Hz, 1H), 7.57 (d, $J = 7.2$ Hz, 1H).

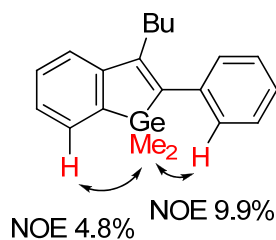
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ : -3.3, 13.9, 23.0, 27.8, 31.7, 122.9, 125.4, 126.3, 127.4, 128.2, 129.0, 131.7, 141.1, 142.1, 144.1, 148.5, 149.0.

IR (neat): 3055 m, 3020 m, 2956 s, 2927 s, 2864 s, 1599 m, 1579 m, 1554 w, 1489 m, 1462 m, 1441 m, 1415 w, 1379 w, 1273 w, 1234 w, 1124 w, 1070 w, 1032 w, 920 w, 837 m, 796 m, 762 s, 727 s, 700 s, 606 m, 584 m, 542 w, 484 w, 426 w.

MS, m/z (relative intensity, %): 340 (M^++2 , 10), 339 (M^++1 , 10), 338 (M^+ , 49), 337 (17), 336 (M^+-2 , 35), 334 (M^+-4 , 26), 325 (21), 324 (19), 323 (100), 322 (35), 321 (74), 320 (10), 319 (54), 296 (40), 295 (15), 294 (29), 292 (22), 281 (30), 280 (11), 279 (29), 277 (23), 265 (29), 264 (10), 263 (28), 261 (19), 205 (11), 203 (14), 202 (13), 192 (14), 191 (59), 189 (20), 165 (13), 115 (11), 91 (25), 90 (26), 87 (18), 85 (12).

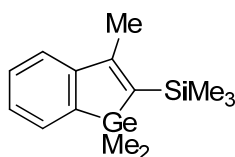
Exact Mass (EI): Calcd for $C_{20}H_{24}Ge$ 338.1090, found 338.1082.

The regiochemistry of **13** was determined based on NOE experiments.



The formation of **13'** was confirmed by GCMS m/z (relative intensity, %): 338 (M^+ , 50), 205 (23), 191 (100).

Trimethyl(1,1,3-trimethyl-1*H*-benzo[*b*]germol-2-yl)silane (14**)**



Colorless oil. Rf 0.80 (hexane).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.24 (s, 9H), 0.49 (s, 6H), 2.33 (s, 3H), 7.26 (t, $J = 7.2$ Hz, 1H), 7.36 (t, $J = 7.4$ Hz, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.56 (d, $J = 6.8$ Hz, 1H).

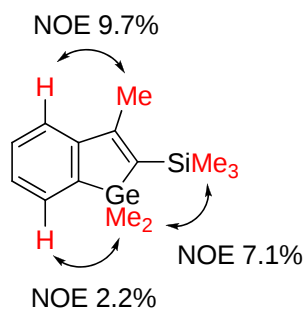
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -2.3, 0.9, 19.6, 122.1, 126.7, 128.8, 131.0, 140.5, 143.2, 149.6, 158.4.

IR (neat): 3060 w, 2954 m, 2908 w, 1537 m, 1437 m, 1369 w, 1250 s, 1128 w, 1093 w, 1030 w, 1005 w, 895 s, 839 s, 795 w, 764 m, 723 w, 688 w, 636 w, 602 w, 584 w, 488 w, 420 w.

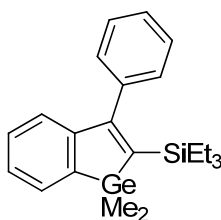
MS, m/z (relative intensity, %): 292 (M^+ , 28), 290 ($M^+ - 2$, 20), 288 ($M^+ - 4$, 14), 279 (23), 278 (18), 277 (93), 276 (31), 275 (70), 273 (52), 189 (12), 188 (35), 187 (10), 174 (14), 173 (84), 145 (46), 131 (19), 115 (19), 97 (10), 89 (14), 73 (100), 59 (27).

Exact Mass (EI): Calcd for $\text{C}_{14}\text{H}_{22}\text{GeSi}$ 292.0703, found 292.0710.

The regiochemistry of **14** was determined based on NOE experiments.



(1,1-Dimethyl-3-phenyl-1*H*-benzo[*b*]germol-2-yl)triethylsilane (15**)**



Colorless oil. Rf 0.49 (hexane).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.41 (q, $J = 7.8$ Hz, 6H), 0.65 (s, 6H), 0.88 (t, $J = 7.8$ Hz, 9H), 6.85-6.86 (m, 1H), 7.22-7.30 (m, 4H), 7.40-7.45 (m, 3H), 7.64-7.66 (m, 1H).

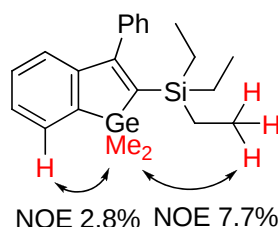
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -1.8, 4.4, 7.6, 124.7, 126.8, 127.0, 127.8, 128.66, 128.74, 131.1, 141.5, 142.0, 143.0, 150.0, 164.8.

IR (neat): 3055 s, 2953 s, 2908 s, 2873 s, 2808 m, 1574 m, 1523 s, 1485 s, 1460 s, 1439 s, 1417 s, 1377 m, 1273 s, 1234 s, 1159 m, 1120 m, 1070 m, 1007 s, 974 s, 910 s, 839 s, 787 s, 741 s, 723 s, 700 s, 677 s, 598 s, 582 s, 496 m, 482 m, 413 s.

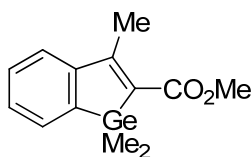
MS, m/z (relative intensity, %): 396 (M^+ , 0), 369 ($\text{M}^+ + 2\text{-Et}$, 23), 368 ($\text{M}^+ + 1\text{-Et}$, 25), 367 ($\text{M}^+ - \text{Et}$, 100), 366 (37), 365 (73), 364 (12), 363 (53), 339 (28), 337 (20), 335 (15), 311 (26), 309 (21), 307 (16), 221 (25), 207 (11), 151 (12), 149 (11), 148 (12), 147 (34), 146 (18), 145 (16), 135 (16), 105 (13), 87 (12), 73 (16), 59 (34).

Exact Mass (EI): Calcd for $\text{C}_{22}\text{H}_{30}\text{GeSi}$ 396.1329, found 396.1328.

The regiochemistry of **15** was determined based on NOE experiments.



Methyl 1,1,3-trimethyl-1H-benzo[b]germole-2-carboxylate (**16**)



Colorless oil. Rf 0.20 (hexane/EtOAc = 50/1).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.55 (s, 6H), 2.61 (s, 3H), 3.79 (s, 3H), 7.37-7.42 (m, 2H), 7.55-7.61 (m, 2H).

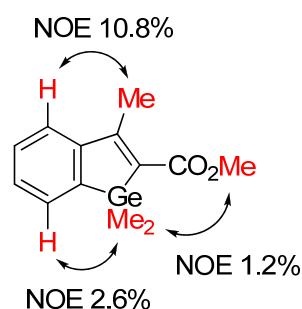
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -3.2, 15.4, 51.5, 124.3, 129.0, 129.1, 131.7, 131.8, 141.5, 148.1, 161.8, 169.5.

IR (neat): 3053 w, 2987 w, 2947 w, 2912 w, 1703 s, 1585 m, 1554 m, 1437 m, 1369 w, 1302 m, 1273 m, 1211 s, 1105 m, 1055 m, 957 w, 841 w, 800 w, 773 m, 723 w, 611 w, 588 w.

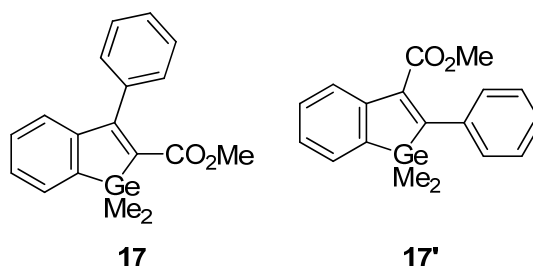
MS, m/z (relative intensity, %): 278 (M^+ , 30), 276 (M^+-2 , 22), 274 (M^+-4 , 15), 265 (15), 263 (73), 262 (22), 261 (53), 259 (40), 247 (16), 245 (11), 235 (22), 234 (12), 233 (100), 232 (31), 231 (80), 229 (60), 220 (15), 219 (12), 218 (19), 217 (16), 216 (16), 215 (13), 203 (13), 201 (10), 189 (18), 187 (16), 185 (11), 129 (12), 128 (23), 116 (27), 115 (95), 114 (13), 105 (20), 103 (18), 101 (16), 91 (14), 89 (42), 87 (28), 85 (18).

Exact Mass (EI): Calcd for $C_{13}H_{16}GeO_2$ 278.0362, found 278.0363.

The regiochemistry of **16** was determined based on NOE experiments.



Methyl 1,1-dimethyl-3-phenyl-1*H*-benzo[*b*]germole-2-carboxylate (**17**)



This compound was obtained as a regioisomeric mixture of **17** and **17'** (5:1) determined by NMR.

White solid. mp = 51-54 °C. Rf 0.26 (hexane/EtOAc = 50/1).

The followings are the data for **17**.

1H NMR ($CDCl_3$, 399.78 MHz) δ : 0.69 (s, 6H, **17**), 3.64 (s, 3H, **17**), 7.05 (d, J = 8.0 Hz, 1H), 7.26-7.31 (m, 2H), 7.35-7.49 (m, 5H), 7.63 (d, J = 6.8 Hz, 1H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ : -3.0, 51.4, 126.9, 127.5, 127.9, 128.0, 128.96, 129.04, 131.9, 134.0, 137.9, 141.4, 148.0, 163.3, 168.5.

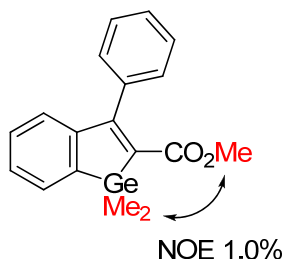
IR (KBr): 3053 w, 2985 w, 2945 w, 2910 w, 1714 s, 1601 w, 1577 m, 1552 m, 1491 w, 1439 m, 1286 m, 1207 s, 1155 m, 1120 w, 1070 m, 1024 w, 843 w, 806 m, 775 m, 727 m, 702 m, 611 m, 586 w, 424 w.

MS, m/z (relative intensity, %): 342 (M^++2 , 11), 341 (M^++1 , 10), 340 (M^+ , 64), 339 (M^+-1 , 24), 338 (M^+-2 , 46), 336 (M^+-4 , 34), 327 (20), 326 (16), 325 (94), 324 (32), 323 (70), 321 (52), 309 (33), 308 (14), 307 (24), 305 (17), 297 (23), 296 (17), 295 (100), 294 (36), 293 (77), 292 (12), 291 (57), 283 (12), 282 (32), 281 (32), 280 (38), 279 (33), 278 (30), 277 (20), 267 (33), 265 (38), 263 (30), 252 (12), 251 (34), 250 (22), 249 (30), 248 (11), 247 (20), 205 (16), 191 (22), 189 (19), 178 (26), 177

(10), 176 (19), 175 (17), 165 (18), 151 (13), 147 (14), 105 (33), 103 (23), 101 (22), 91 (18), 89 (54), 87 (41), 85 (28).

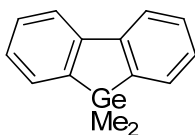
Exact Mass (EI): Calcd for C₁₈H₁₈GeO₂ 340.0519, found 340.0521.

The regiochemistry of **17** was determined based on NOE experiments.



The formation of **17** was confirmed by GCMS, *m/z* (relative intensity, %): 340 (M⁺, 100), 338 (55), 336 (33), 325 (76), 323 (51), 321 (10), 267 (22), 265 (35), 263 (56).

5,5-Dimethyl-5H-dibenzo[*b,d*]germole (**19**) [64526-49-4]



White solid. mp = 70-73 °C. R_f 0.43 (hexane).

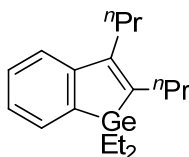
¹H NMR (CDCl₃, 270.05 MHz) δ: 0.60 (s, 6H), 7.26-7.32 (m, 2H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 6.8 Hz, 2H), 7.87 (d, *J* = 7.8 Hz, 2H).

¹³C NMR (CDCl₃, 67.80 MHz) δ: -2.7, 121.3, 127.4, 129.4, 132.8, 141.1, 146.2.

MS, *m/z* (relative intensity, %): 256 (M⁺, 28), 254 (M⁺-2, 20), 252 (M⁺-4, 15), 243 (21), 242 (13), 241 (100), 240 (32), 239 (81), 237 (64), 226 (22), 225 (15), 224 (19), 222 (13), 165 (19), 152 (35), 121 (11).

Exact Mass (EI): Calcd for C₁₄H₁₄Ge 256.0307, found 256.0306.

1,1-Diethyl-2,3-dipropyl-1H-benzo[*b*]germole (**21**)



Colorless oil R_f 0.51 (hexane).

¹H NMR (CDCl₃, 399.78 MHz) δ: 0.95-1.00 (m, 6H), 1.02-1.16 (m, 10H), 1.46-1.58 (m, 4H), 2.43 (t, *J* = 8.0 Hz, 2H), 2.54 (t, *J* = 8.0 Hz, 2H), 7.13-7.18 (m, 1H), 7.30 (t, *J* = 3.6 Hz, 2H), 7.47 (d, *J* = 6.8 Hz, 1H).

¹³C NMR (CDCl₃, 100.53 MHz) δ: 6.2, 9.3, 14.3, 14.5, 22.2, 24.1, 29.1, 33.7, 121.7, 125.3, 128.6,

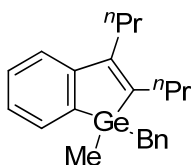
132.2, 138.8, 143.3, 148.2, 149.8.

IR (neat): 3055 m, 2956 s, 2927 s, 2870 s, 1581 w, 1556 w, 1458 s, 1377 m, 1338 w, 1271 w, 1219 w, 1093 w, 1018 m, 964 w, 766 m, 733 m, 698 m, 577 m, 484 w, 428 w.

MS, m/z (relative intensity, %): 318 (M^+ , 26), 316 (M^+-2 , 19), 314 (M^+-4 , 13), 291 (20), 290 (17), 289 (100), 288 (33), 287 (75), 285 (57), 261 (28), 259 (23), 257 (16), 185 (10), 143 (16), 141 (13), 129 (22), 128 (18), 115 (23), 103 (11), 91 (11), 89 (13).

Exact Mass (EI): Calcd for $C_{18}H_{28}Ge$ 318.1403, found 318.1402.

1-Benzyl-1-methyl-2,3-dipropyl-1H-benzo[b]germole (23)



Colorless oil. Rf 0.34 (hexane).

1H NMR ($CDCl_3$, 399.78 MHz) δ : 0.43 (s, 3H), 0.91-0.98 (m, 6H), 1.41-1.56 (m, 4H), 2.27-2.35 (m, 1H), 2.42-2.57 (m, 5H), 7.04 (d, $J = 7.6$ Hz, 2H), 7.07-7.14 (m, 2H), 7.20-7.23 (m, 3H), 7.28-7.33 (m, 2H).

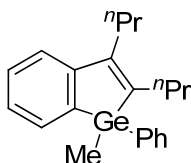
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ : -4.7, 14.37, 14.43, 22.1, 24.2, 24.5, 29.1, 33.3, 121.8, 124.3, 125.6, 127.9, 128.2, 129.0, 132.1, 139.0, 140.0, 143.4, 147.7, 148.8.

IR (neat): 3059 m, 3024 m, 2958 s, 2927 s, 2870 m, 1599 m, 1581 w, 1556 w, 1493 m, 1456 m, 1415 w, 1377 w, 1338 w, 1273 w, 1234 w, 1207 w, 1057 w, 1030 w, 812 m, 762 s, 725 m, 698 m, 590 w, 465 m, 424 w.

MS, m/z (relative intensity, %): 366 (M^+ , 8), 277 (22), 276 (16), 275 (100), 274 (33), 273 (76), 272 (10), 271 (60), 143 (12), 129 (15), 128 (11), 115 (13), 91 (33), 89 (24), 87 (18), 85 (12).

Exact Mass (EI): Calcd for $C_{22}H_{28}Ge$ 366.1403, found 366.1402.

1-Methyl-1-phenyl-2,3-dipropyl-1H-benzo[b]germole (25a)



Colorless oil. Rf 0.34 (hexane).

1H NMR ($CDCl_3$, 399.78 MHz) δ : 0.81 (d, $J = 0.8$ Hz, 3H), 0.90 (t, $J = 7.2$ Hz, 3H), 1.04 (t, $J = 7.2$ Hz, 3H), 1.40-1.53 (m, 2H), 1.54-1.65 (m, 2H), 2.38-2.45 (m, 1H), 2.50-2.57 (m, 1H), 2.61 (t, $J = 7.8$ Hz, 2H), 7.17-7.20 (m, 1H), 7.32-7.39 (m, 5H), 7.44-7.50 (m, 3H).

^{13}C NMR ($CDCl_3$, 100.53 MHz) δ : -5.0, 14.38, 14.42, 22.2, 24.1, 29.2, 33.2, 121.9, 125.9, 128.2,

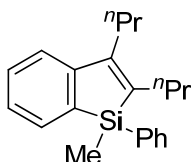
128.8, 129.1, 131.9, 133.7, 137.8, 139.0, 143.2, 148.6, 149.5.

IR (neat): 3064 m, 3051 m, 2958 s, 2927 s, 2868 s, 1583 m, 1556 w, 1458 m, 1435 s, 1377 w, 1335 w, 1304 w, 1271 w, 1236 w, 1186 w, 1159 w, 1122 w, 1092 m, 1066 w, 1028 w, 999 w, 912 w, 793 s, 766 s, 733 s, 698 s, 673 w, 648 w, 594 m, 484 w, 463 m, 426 w.

MS, m/z (relative intensity, %): 354 ($M^{+}+2$, 18), 353 ($M^{+}+1$, 18), 352 (M^{+} , 100), 351 (35), 350 ($M^{+}-2$, 76), 348 ($M^{+}-4$, 55), 339 (13), 338 (12), 337 (82), 336 (26), 335 (58), 333 (43), 310 (14), 309 (50), 308 (22), 307 (40), 305 (26), 295 (19), 293 (16), 291 (11), 279 (17), 277 (13), 245 (12), 243 (11), 233 (17), 231 (17), 229 (19), 226 (21), 219 (13), 217 (12), 215 (13), 205 (14), 203 (20), 202 (12), 191 (36), 189 (18), 185 (20), 167 (62), 166 (20), 165 (60), 163 (35), 157 (32), 155 (20), 153 (25), 151 (75), 150 (16), 149 (57), 147 (42), 143 (37), 142 (19), 141 (34), 129 (53), 128 (50), 115 (67), 105 (20), 91 (77), 89 (75), 88 (11), 87 (54), 85 (39), 77 (13).

Exact Mass (EI): Calcd for $C_{21}H_{26}Ge$ 352.1246, found 352.1247.

1-Methyl-1-phenyl-2,3-dipropyl-1H-benzo[b]silole (25b)



Colorless oil. R_f 0.54 (hexane).

1H NMR ($CDCl_3$, 399.78 MHz) δ : 0.65 (s, 3H), 0.89 (t, $J = 7.0$ Hz, 3H), 1.03 (t, $J = 7.4$ Hz, 3H), 1.37-1.49 (m, 2H), 1.56-1.65 (m, 2H), 2.29-2.36 (m, 1H), 2.41-2.48 (m, 1H), 2.57-2.61 (m, 2H), 7.14-7.17 (m, 1H), 7.30-7.39 (m, 5H), 7.46 (d, $J = 7.2$ Hz, 1H), 7.49-7.51 (m, 2H).

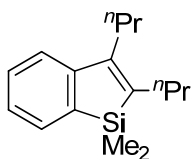
^{13}C NMR ($CDCl_3$, 100.53 MHz) δ : -5.5, 14.4, 14.5, 22.1, 23.7, 29.1, 32.0, 121.1, 125.8, 127.9, 129.5, 129.8, 131.9, 134.3, 135.1, 137.1, 140.7, 150.9, 152.9.

IR (neat): 3064 m, 3051 m, 2958 s, 2929 s, 2868 s, 1583 m, 1552 m, 1460 m, 1433 m, 1377 w, 1304 w, 1273 w, 1250 m, 1190 w, 1163 w, 1130 m, 1109 m, 1061 w, 1030 w, 916 w, 796 s, 768 s, 725 s, 698 s, 476 m, 465 m, 422 m.

MS, m/z (relative intensity, %): 307 ($M^{+}+1$, 12), 306 (M^{+} , 46), 263 (19), 235 (10), 199 (18), 185 (16), 184 (22), 145 (19), 122 (12), 121 (100), 105 (22).

Exact Mass (EI): Calcd for $C_{21}H_{26}GSi$ 306.1804, found 306.1802.

1,1-Dimethyl-2,3-dipropyl-1H-benzo[b]silole (26b) [1160757-32-3]



Colorless oil. Rf 0.69 (hexane).

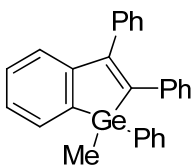
^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.29 (s, 6H), 0.95-1.03 (m, 6H), 1.49-1.57 (m, 4H), 2.38 (t, J = 7.8 Hz, 2H), 2.51 (t, J = 8.0 Hz, 2H), 7.15 (t, J = 7.2 Hz, 1H), 7.26-7.35 (m, 2H), 7.48 (d, J = 6.4 Hz, 1H).

^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -3.4, 14.4, 14.6, 22.0, 23.7, 29.0, 31.9, 120.9, 125.5, 129.5, 131.2, 138.4, 142.0, 150.2, 151.0.

MS, m/z (relative intensity, %): 244 (M^+ , 30), 215 (11), 201 (19), 184 (12), 173 (12), 155 (10), 145 (24), 73 (32), 59 (100).

Exact Mass (EI): Calcd for found $\text{C}_{16}\text{H}_{24}\text{Si}$ 244.1647, found 244.1640.

1-Methyl-1,2,3-triphenyl-1H-benzo[b]germole (27a)



Colorless oil. Rf 0.11 (hexane).

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.97 (s, 3H), 6.94-6.97 (m, 2H), 7.01-7.12 (m, 4H), 7.25-7.33 (m, 4H), 7.34-7.41 (m, 6H), 7.55-7.58 (m, 2H), 7.62-7.64 (m, 1H).

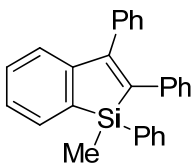
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -5.0, 125.0, 125.8, 127.0, 127.1, 127.8, 128.4, 128.5, 128.9, 129.2, 129.3, 129.8, 132.2, 133.8, 137.1, 138.5, 138.6, 140.0, 143.1, 150.2, 151.0.

IR (neat): 3055 s, 3024 m, 2958 m, 1593 m, 1541 m, 1489 m, 1441 s, 1404 w, 1300 m, 1248 s, 1153 w, 1128 m, 1070 m, 1030 m, 995 m, 910 m, 876 m, 841 s, 800 s, 779 s, 756 s, 727 s, 702 s, 650 m, 611 w, 590 w, 544 w, 490 w, 417 m.

MS, m/z (relative intensity, %): 422 (17), 421 (21), 420 (M^+ , 74), 419 (30), 418 ($\text{M}^+ - 2$, 53), 417 (12), 416 ($\text{M}^+ - 4$, 38), 407 (23), 406 (27), 405 (100), 404 (40), 403 (75), 402 (17), 401 (56), 330 (20), 329 (11), 254 (21), 253 (46), 252 (79), 250 (15), 227 (19), 226 (13), 225 (17), 223 (11), 153 (12), 151 (56), 150 (16), 149 (42), 147 (33).

Exact Mass (EI): Calcd for $\text{C}_{27}\text{H}_{22}\text{Ge}$ 420.0933, found 420.0938.

1-Methyl-1,2,3-triphenyl-1H-benzo[b]silole (27b)



Colorless oil. Rf 0.11 (hexane)

^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.82 (s, 3H), 6.95 (d, J = 6.4 Hz, 2H), 7.02-7.10 (m, 3H), 7.14 (d,

$J = 7.2$ Hz, 1H), 7.25-7.44 (m, 10H), 7.63 (d, $J = 6.8$ Hz, 3H).

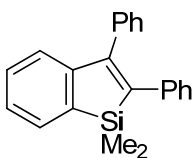
^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -5.8, 124.1, 125.7, 126.9, 127.2, 127.8, 128.1, 128.4, 128.8, 129.6, 129.8, 130.0, 132.3, 134.2, 134.5, 136.7, 138.0, 139.5, 141.2, 151.2, 154.4.

IR (neat): 3053 s, 3022 s, 2962 m, 1593 s, 1543 m, 1489 s, 1437 s, 1302 s, 1250 s, 1184 m, 1153 m, 1109 s, 1068 s, 1030 m, 993 s, 908 s, 874 m, 810 s, 791 s, 768 s, 733 s, 700 s, 667 m, 615 w, 592 m, 546 w, 488 s, 467 s, 428 m.

MS, m/z (relative intensity, %): 375 ($\text{M}^+ + 1$, 35), 374 (M^+ , 100), 360 (29), 359 (87), 252 (11), 181 (17), 105 (30).

Exact Mass (EI): Calcd for $\text{C}_{27}\text{H}_{22}\text{Si}$ 374.1491, found 374.1491.

1,1-Dimethyl-2,3-diphenyl-1H-benzo[b]silole (28b) [1016642-73-1]



White solid. R_f 0.17 (hexane).

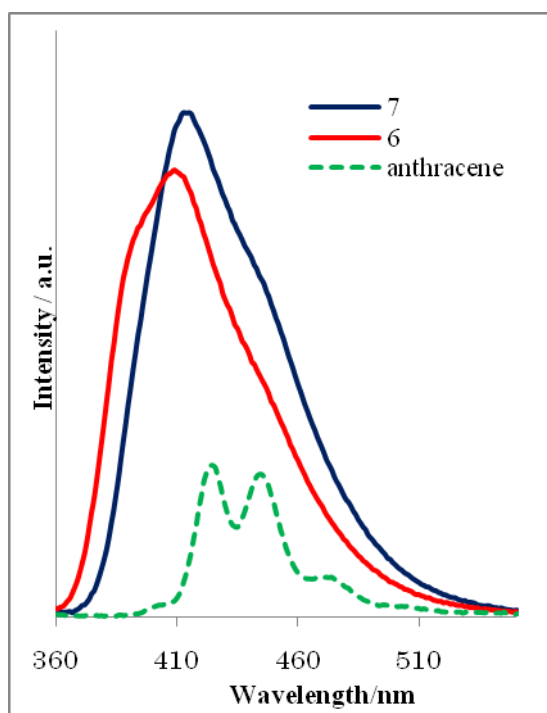
^1H NMR (CDCl_3 , 399.78 MHz) δ : 0.49 (s, 6H), 6.98-7.00 (m, 2H), 7.05-7.09 (m, 2H), 7.14 (t, $J = 7.6$ Hz, 2H), 7.20-7.22 (m, 2H), 7.25-7.37 (m, 5H), 7.62-7.64 (m, 1H).

^{13}C NMR (CDCl_3 , 100.53 MHz) δ : -3.5, 123.9, 125.6, 126.6, 127.0, 127.9, 128.3, 128.6, 129.6, 129.7, 131.6, 138.0, 138.1, 139.9, 142.9, 150.6, 153.0.

MS, m/z (relative intensity, %): 313 ($\text{M}^+ + 1$, 29), 312 (M^+ , 100), 298 (27), 297 (96), 252 (12), 121 (26), 119 (30), 105 (10), 93 (17).

Exact Mass (EI): Calcd for $\text{C}_{22}\text{H}_{20}\text{Si}$ 312.1334, found 312.1334.

VI. Photoluminescence spectra in the solid state.



Fluorescence spectra of **7,6** and anthracene in the solid-state upon excitation at 350 nm.

VII. Copies of ^1H and ^{13}C NMR Spectra.

