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PREPARATION OF BENZOHETEROCYCLES CONTAINING GROUP 14 ELEMENTS USING ZIRCONACYCLOPENTADIENES

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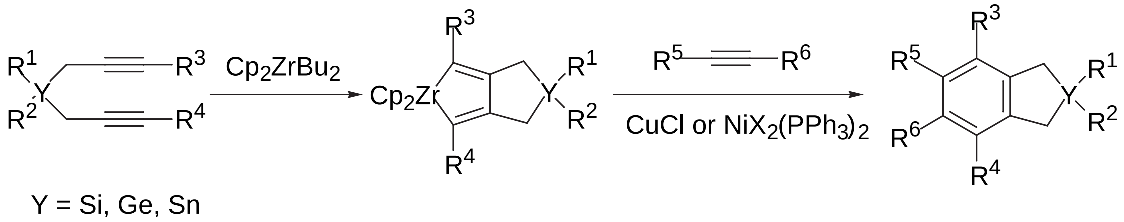
Abstract-Benzoheterocycles containing group 14 elements such as benzosilacycles, benzogermacycles and benzostannacycles were prepared from the corresponding zirconacycles and alkynes in the presence of CuCl or $NiBr_2(PPh_3)_2$. Monomers for the synthesis of benzoheterocyclic polymers containing silicon and germanium were synthesized by this method.

INTRODUCTION

Heterocycles containing group 14 elements were attractive and useful for material sciences.[1] They have been prepared by several methods.[2] Among them the fomation of benzoheterocycles containing group 14 elements are rather rare and remained to be studied,[3] although various benzoheterocycles have been investigated.[4-8] Recently we have reported benzene formation from zirconacyclopentadienes using CuCl or $NiX_2(PPh_3)_2$.[4,9] We applied this method for the formation of benzoheterocycles as shown in eq 1. In this paper we report a novel preparative method of benzoheterocycles containing group 14 elements from bis(propargyl)silanes, -germanes and -stannanes.



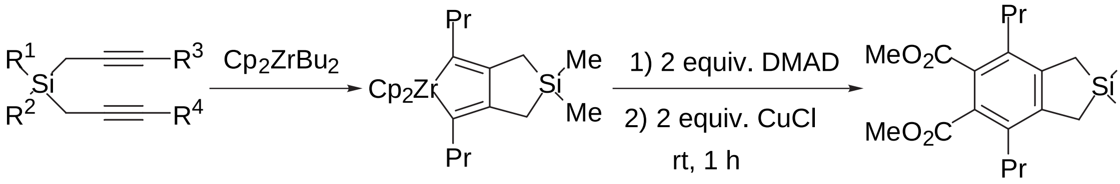
(1)

Dedicated to Prof. Sho Ito of Bunri University of Tokushima on the occasion of his 77th birthday

RESULTS AND DISCUSSION

CuCl mediated preparation of benzosilacycles, benzogermacycles and benzostannacycles

It is known that bis(2-hexynyl)silane (**1a)** can react with Cp$_2$ZrBu$_2$[10] to give bicyclic zirconacyclopentadiene (**2a)**. Zirconacyclopentadiene (**2a)** thus prepared *in situ* reacted with dimethyl acetylenedicarboxylate (**3a)** in the presence of 2 equiv of CuCl for 1 h at room temperature to give the corresponding benzosilacycle (**4a)** in 93% yield based on **1a** (eq 2).

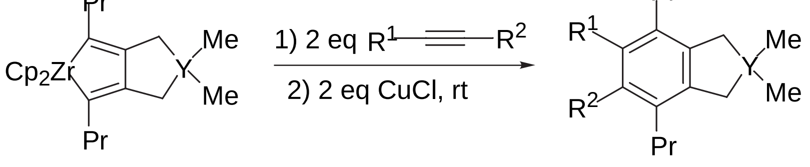


(2)

1a **2a** **4a: 93% Yield**

Various benzosilacycles, benzogermacycles and benzostannacycles could be prepared by this method. Results are summarized in Table 1. Acetylene with a one electron-withdrawing group such as ethyl phenylpropynoate (**3b)** could be used for the cycloaddition reaction, although a longer reaction time (36 h) was necessary to complete the reaction (Table 1, Entry 1). Acetylene (**3c)** with other electron-withdrawing groups such as COPh and *p*-NO$_2$Ar afforded benzosilacycle compound (**4c)** in 83% yield. For this benzoheterocycle formation from zirconacyclopentadienes, at least one electron-withdrawing group was requisite for the alkyne, since the major reaction step of this method is Michael addition of the dienylcopper species to the alkyne as reported.[9] Interestingly, when a diyne containing two silicon atoms, for example **2b**, was employed in the reaction, the corresponding benzoheterocycles (**4d)** and (**4e)** with a 6-membered ring were obtained in 88 and 91% yields, respectively.

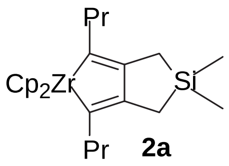
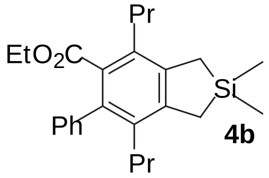
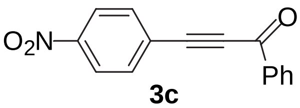
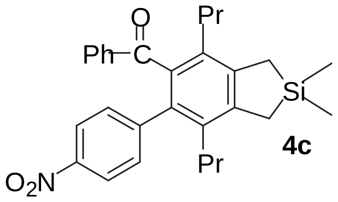
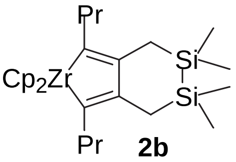
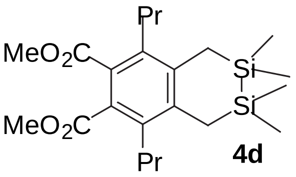
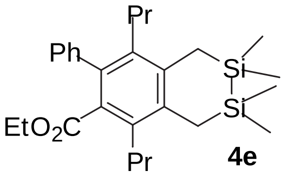
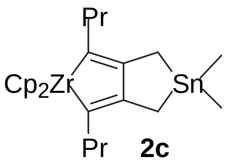
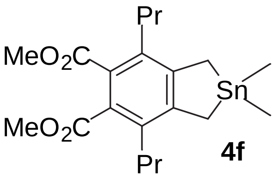
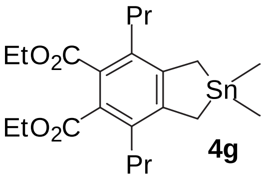
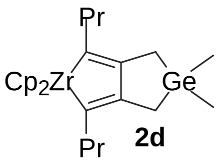
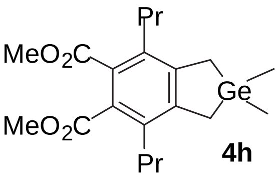
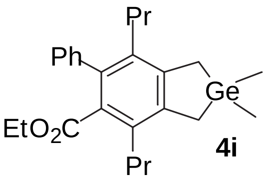
This addition reaction similarly proceeded under the same conditions for zirconacyclopentadienes containing tin and germanium such as **2c** and **2d** prepared from the corresponding diynes (eq 3). The benzoheterocycle derivatives (**4f-4i)** were obtained in good yields (Table 1, Entries 5-8).



(3)

Y = Sn, R^1 = R^2 = COOMe, 4f: 58%
Y = Sn, R^1 = R^2 = COOEt, 4g: 50%
Y = Ge, R^1 = R^2 = COOMe, 4h: 61%
Y = Ge, R^1 = Ph, R^2 = COOEt, 4i: 63%

Table 1. Cu-mediated preparation of benzoheterocycles containing group 14 elements from bicyclic zirconacyclopentadienes

Entry	Zirconacycles	Alkyne	Time (h)	Products	Yield (%)
1	 **2a**	$\mathrm{Ph{-}C{\equiv}C{-}CO_2Et}$ **3b**	36	 **4b**	83 (57)
2	**2a**	 **3c**	1	 **4c**	83 (70)
3	 **2b**	**3a**	1	 **4d**	88 (77)
4	**2b**	**3b**	12	 **4e**	91 (68)
5	 **2c**	**3a**	3	 **4f**	58 (40)
6	**2c**	$\mathrm{EtO_2C{-}C{\equiv}C{-}CO_2Et}$ **3d**	3	 **4g**	50 (32)
7	 **2d**	**3a**	1	 **4h**	61 (58)
8	**2d**	**3b**	36	 **4i**	63 (61)

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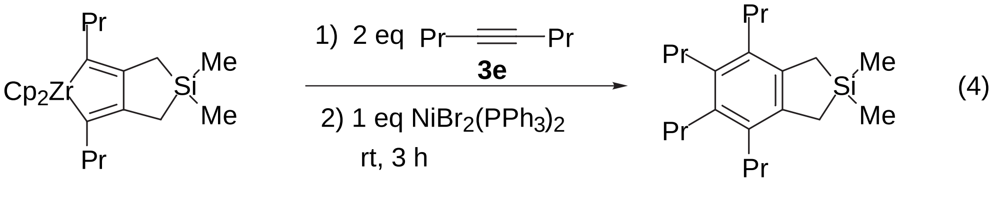
[a] GC yields; isolated yields are given in parentheses.

$NiCl_2(PPh_3)_2$ mediated preparation of benzosilacycles, benzogermacycles and benzostannacycles

As we mentioned above, the CuCl mediated benzoheterocycle formation reaction requires at least one electron-withdrawing group in the alkyne. In order to overcome this difficulty, recently, we developed novel method using nickel complexes instead of CuCl.[4] Addition of 1 equiv of $NiBr_2(PPh_3)_2$ to a mixture of silicon containing zirconacyclopentadiene (**2a)** and 4-octyne (**3e**)in THF at room temperature resulted in the formation of benzosilacycle **(4j)** in 81% after 3 h (eq 4).

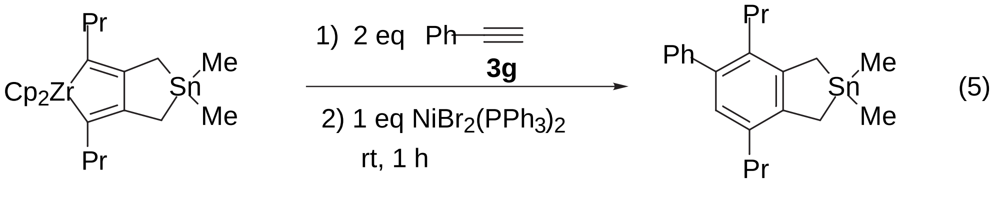


2a

4j: 81% yield

Unsymmetrical alkynes such as 2-hexyne (**3f)** reacted with **2a** in the presence of $NiBr_2(PPh_3)_2$ to give silaindane (**4k)** in 78% yield. Even terminal alkynes such as phenylacetylene (**3g)** could be used in this reaction. The desired product (**4l)** was obtained in 84% yield (Table 2, Entry 2).

This methodology could be applied to the formation of stannaindanes under the similar reaction conditions. Tin containing zirconacyclopentadiene (**2c)** reacted with phenylacetylene (**3g)** to give benzostannacycle (**4m)** in 54% isolated yield in 1 h (eq 5). Not only aryl-substituted alkynes, but also alkyl- and trimethylsilyl-substituted alkynes such as 1-pentyne (**3h)** and trimethylsilylacetylene (**3i)** could react with **2c** in the presence of 1 equiv. of $NiBr_2(PPh_3)_2$ to give **4n** and **4o** in 40 and 43% isolated yields, respectively (Table 2, Entries 3 and 4).



2c

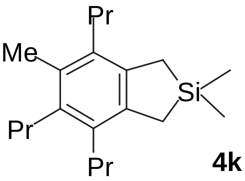
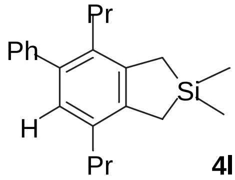
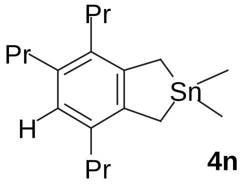
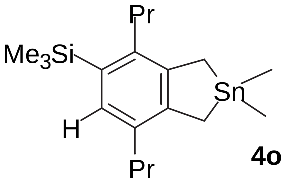
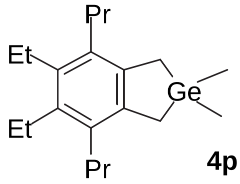
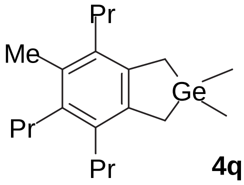
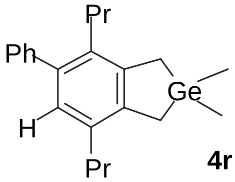
4m: 54% isolated yield

Benzogermacycles could also be prepared in high yields in a similar way (Table 2, Entries 5-7).

Formation of monomers for the synthesis of benzosilacyclic or benzogermacyclic polymers

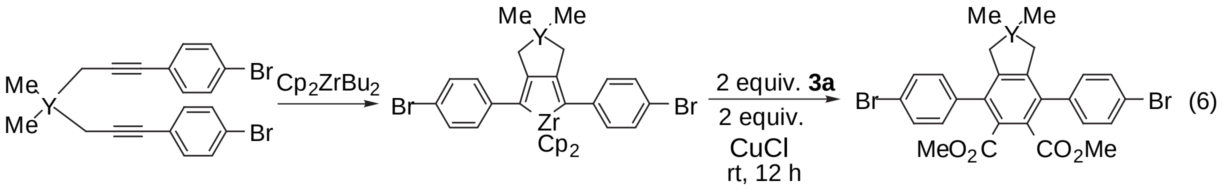
The synthesis and properties of conjugated polymers have received considerable interest in recent years. They have many potential applications, including self-contained electronic device[11] and nonlinear optical materials.[12] Very recently, we have reported the preparation of polyphenylenes from dibromoterphenyl derivatives.[14b] We used this method to prepare the polyphenylenes containing benzosilacycles or benzogermacycles. The precursor (**5**) was prepared by the reaction of terminal diynes with *p*-bromoiodobenzene in the presence of a catalytic amount of $(PPh_3)_4$, CuI and triethylamine in THF at room temperature.

Table 2. Ni-mediated formation of benzoheterocycles containing group 14 elements from bicyclic zirconacyclopentadienes

Entry	Zirconacycles	Alkynes	Time (h)	Product	Yields (%) [a]
1	**2a**	Pr—≡—Me **3f**	3	 **4k**	78 (65)
2	**2a**	Ph—≡ **3g**	3	 **4l**	84 (71)
3	**2c**	Pr—≡ **3h**	1	 **4n**	(40)
4	**2c**	Me_3Si—≡ **3i**	1	 **4o**	50 (43)
5	**2d**	Et—≡—Et **3j**	3	 **4p**	69 (63)
6	**2d**	**3f**	3	 **4q**	87 (68)
7	**2d**	**3g**	3	 **4r**	73 (65)

[a] GC yields; isolated yields are given in parentheses.

Treatment of **5** with Cp_2ZrBu_2led to the quantitative formation of zirconacyclopentadienes (**6)**. No debromination of aromatic bromide was observed.[13] Reaction of **6** with **3a** gave monomer, 4, 4'-dibromo-*p*-terphenyl derivatives (**7)** (eq 6).



5

6

7a: Y = Si, 69%
7b: Y= Ge, 56%

Treatment of monomer (7) with a catalytic amount of NiCl and bipyridine in the presence of zinc powder in DMF at 80˚C led to the formation of polyphenylenes as we reported.[14]

In conclusion, two one-pot procedures for the synthesis of benzosilacycles, benzogermacycles and benzostannacycles were developed *via* zirconacyclopentadienes.

EXPERIMENTAL

All reactions involving organometallic compounds were carried out using standard Schlenk techniques under nitrogen. Tetrahydrofuran (THF) was dried over sodium and benzophenone. Zirconocene dichloride was purchased from Aldrich Chemical Co., Inc. *n*-Butyllithium (1.6 M solution in hexane), ethylmagnesium bromide (0.96 M solution in tetrahydrofuran) and alkynes were purchased from Tokyo Chemical Industry Co. Ltd. Copper (I) chloride was purchased from Wako Pure Chemical Industries Ltd. Diynes containing group 14 element were prepared according to previously published procedures.[16]

^1H and ^{13}C NMR spectra were recorded for $CDCl_3$ (containing 1% TMS) solutions at 25°C on Bruker ARX-400 spectrometer. GC analysis was performed on SHIMADZU GC-14A equipped with fused silica capillary column SHIMADZU CBP1-M25-O25 and SHIMADZU C-R6A-Chromatopac integrator.

A typical procedure for the preparation of benzoheterocycles mediated by CuCl.

To a solution of Cp_2ZrC_2 (0.292 g; 1.0 mmol) in THF (5 mL) was added BuLi (1.60 M, 1.25 mL; 2.0 mmol) at -78 °C. After stirring for 1 h at the same temperature silicon containing diyne (1.0 mmol) was added and the reaction mixture was allowed to be warmed to rt for 1 h. DMAD (0.284 g; 2.0 mmol) and CuCl(0.198 g; 2.0 mmol) were added and stirred for 1 h. Then the reaction mixture was quenched with 3N

HCl and extracted with ether (3 x 30 mL). The extract was washed with water and dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was purified by chromatography on silica using hexane. A yellow oil **4a** (272 mg, 75 %) was obtained.

Dimethyl 2,2-Dimethyl-4,7-dipropyl-2-silaindane-5,6-dicarboxylate (4a)

GC yield 93%. Isolated yield: 75%. A yellow oil : ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.23(s, 6H), 0.96(t, *J* = 7.3Hz, 6H), 1.45-1.6(m, 4H), 2.02(s, 4H), 2.60-2.70(m, 4H), 3.83(s, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -2.56(2C), 14.46(2C), 19.42(2C), 23.41(2C), 39.77(2C), 51.96(2C), 129.68(2C), 137.51(2C), 144.44(2C), 169.57(2C); HRMS calcd for $C_{20}H_{30}O_4Si$ 362.1922, found 362.1913.

Ethyl 2,2-Dimethyl-4,7-dipropyl-6-phenyl-2-silaindane-5-carboxylate (4b)

GC yield: 83%. Isolated yield: 57%. A yellow oil: ^{1}H NMR ($CDCl_3$,) δ 0.18 (s, 6H), 0.65 (t, *J* =7.2 Hz, 3H), 0.80 (t, *J* = 6.9 Hz, 3H), 0.89 (t, *J* = 7.2 Hz, 3H), 1.20-1.28 (m, 2H), 1.46-1.54 (m, 2H), 1.96 (s, 4H), 2.25-2.31 (m, 2H), 2.48-2.52 (m, 2H), 3.73, 3.75, 3.77, 3.80 (q, *J* =7.2 Hz, 2H), 7.13-7.25 (m, 2H); ^{13}C NMR ($CDCl_3$,) δ -2.20 (2C), 13.61, 14.25, 14.69 18.95, 19.52, 23.12, 23.50, 33.62, 34.44, 60.26, 126.69, 127.35 (2C), 129.94 (2C), 132.85, 134.90, 136.54, 137.58, 139.93, 140.74, 142.62, 170.28. IR(neat): 2959.1, 2932.1, 2901.2, 2872.3, 1724.5, 1466.0, 1365,7, 1300.1, 1267.3, 1182.5, 1043.6, 831.4, 725.3, 702.1 cm^{-1}; HRMS calced for $C_{25}H_{34}Si$: 394.2328, found: 394.2340.

2,2-Dimethyl-4,7-dipropyl-5-benzoyl-6-(4’-nitrophenyl)-2-silaindane (4c)

GC yield 83%. Isolated yield: 70%. A yellow solid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.31(s, 6H), 0.73(t, *J* = 7.2 Hz, 3H), 0.83(t, *J* = 7.3 Hz, 3H), 1.20-1.60(m, 4H), 2.09(s, 4H), 2.20-2.70(m, 4H), 7.00-8.20(m, 9H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -2.15, -0.03, 14.08, 14.61, 19.12, 19.59, 23.15, 23.57, 33.46, 34.23, 122.34(2C), 128.16(2C), 129.20(2C), 132.29(2C), 133.07(2C), 134.19, 135.82, 136.86, 137.25, 138.27, 142.28, 142.82, 145.45, 146.80, 199.98; HRMS calcd for $C_{29}H_{33}NO_4Si$ 471.2228, found 471.2247.

Dimethyl 2,2,3,3-Tetramethyl-4,7-dipropyl-2,3-disilatetralin-5,6-dicarboxylate (4d)

GC yield 88%. Isolated yield: 77%. A yellow oil: ^{1}H NMR ($CDCl_3$, Me_4Si), δ 0.03(s, 12H), 0.94(t, *J* = 7.4 Hz, 6H), 1.40-1.60(m, 4H), 2.11(s, 4H), 2.40-2.60(m, 4H), 3.79(s, 6H); ^{13}C NMR δ -4.69(4C), 14.45(2C), 20.47(2C), 23.68(2C), 33.36(2C), 51.92(2C), 128.77(2C), 135.18(2C), 139.57(2C), 169.98(2C); HRMS calcd for $C_{22}H_{36}O_4Si_2$, 420.2150, found 420.216.

Ethyl 2,2,3,3-Tetramethyl-4,7-dipropyl-2,3-disilatetralin-5-phenyl-6-carboxylate (4e)

GC yield 91%. Isolated yield: 68%. A colorless oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.07(s, 6H), 0.10(s, 6H), 0.71(t, J = 7.4 Hz, 3H), 0.90(t, J = 7.1 Hz, 3H), 0.98(t, J = 7.3 Hz, 3H), 1.20-1.45(m, 2H), 1.50-1. 70(m, 2H), 2.14(s, 2H), 2.15(s, 2H), 2.20-2.35(m, 2H), 2.40-2.55(m, 2H), 3.84(q, J = 7.1 Hz, 2H), 7.20-7.30(m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -4.60(2C), -4.43(2C), 13.65, 14.47, 14.68, 19.89, 20.48, 23.61, 23.88, 33.06, 34.16, 60.18, 126.57, 127.27(2C), 130.07(2C), 132.05, 132.77, 135.35, 135.59, 135.68, 137.66, 140.56, 170.68; HRMS calcd for $C_{27}H_{40}O_2Si$ 452.2565, found 452.2559.

Dimethyl 2,2-Dimethyl-4,7-dipropyl-2-stannaindane-5,6-dicarboxylate (4f)

GC yield 58%. Isolated yield: 40%. A white solid: ^{1}H NMR ($CDCl_3$,Me_4Si), δ 0.36(s, J_{SnH} = 56.5 Hz, 6H), 0.97(t, J = 7.4 Hz, 6H), 1.50-1.70(m, 4H), 2.25(s, J_{SnH} = 44 Hz, 4H), 2.60-2.80(m, 4H), 3.82(s, 6H); ^{13}C NMR δ -9.87(J_{SnC} = 335 Hz, 320 Hz, 2C), 14.57(2C), 15.34(J_{SnC} = 305 Hz, 294 Hz, 2C), 23.40(2C), 34.40(2C), 51.94(2C), 129.30(2C), 138.35(J_{SnC} = 50 Hz, 2C), 145.91(J_{SnC} = 20 Hz, 2C), 169.76(2C); HRMS calcd for $C_{20}H_{30}O_4Sn$, 454.1164, found 454.1157.

Diethyl 2,2-Dimethyl-4,7-dipropyl-2-stannaindane-5,6-dicarboxylate (4g)

GC yield 50%. isolated yield: 32%. A colorless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.35 (s, satellites, J_{SnH} = 55 Hz, 57 Hz, 6H), 0.98 (t, J = 7.3 Hz, 6H), 1.35 (t, J = 7.1 Hz, 6H), 1.55-1.61 (m, 4H), 2.24 (s, satellites, J_{SnH} = 44 Hz, 4H), 2.69-2.73 (m, 4H), 4.30 (q, J = 7.1 Hz, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -9.76, 14.12, 14.70, 15.33, 23.50, 34.57, 61.11, 129.55, 138.17, 145.80, 169.51; IR (neat) 2961, 2934, 2872, 1728, 1549, 1468, 1420, 1364, 1298, 1267, 1192, 1115, 1096, 1076, 1046, 781, 748 cm^{-1}; HRMS calcd for $C_{22}H_{34}O_4Sn$ 482.1477, found 482.1485.

Dimethyl 2,2-Dimethyl-4,7-dipropyl-2-germaindane-5,6-dicarboxylate (4h)

GC yield 61%. Isolated yield: 58%. A yellow solid: mp 83-85˚C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.40(s, 6H), 0. 97(t, J = 7.5 Hz, 3H), 1.51-1.58(m, 4H), 2.20(s, 4H), 2.65-2.70(m, 4H), 3.83(s, 6H); ^{13}C-NMR ($CDCl_3$, Me_4Si) δ -2.46(2C), 14.59(2C), 20.52(2C), 23.45(2C), 34.16(2C), 52.06(2C), 129.68(2C), 137.81(2C), 145.14(2C), 169.67(2C). IR (neat) 2953, 2926, 1773, 1736, 1559, 1300, 1120, 1177 cm^{-1}; HRMS calcd for $C_{20}H_{30}O_4Ge$ 408.1354, found 408.1359.

Ethyl 2,2-Dimethyl-4,7-dipropyl-2-germaindane-5-phenyl-6-carboxylate (4i)

GC yield 63%, Isolated yield: 61%. A yellow sticky oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.42(s, 6H), 0.73(t, J = 7.5 Hz, 3H), 0.88(t, J = 7.2 Hz, 3H), 0.98(t, J = 7.2 Hz, 3H), 1.32-1.37(m, 2H), 1.59-1.65(m, 2H), 1. 25(s, 4H), 2.38-2.44(m, 2H), 2.59-2.65(m, 2H), 3.85(q, J = 7.0 Hz, 2H), 7.22-7.32(m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -2.36(2C), 13.54, 14.53, 14.68, 20.03, 20.55, 23.03, 23.41, 33.86, 34.70, 60.15(2C), 126.63, 127.27(2C), 129.87(2C), 132.85, 135.02, 136.44, 137.75, 139.79, 141.29, 143.12, 170.11; IR (neat) 3081, 2959, 1726, 1466, 1302, 1269, 1184, 1043, 829, 702 cm^{-1}; HRMS calcd for

$C_{25}H_{34}O_2Ge$ 440.1778, found 440.1785.

Dimethyl 2,2-Dimethyl-4,7-bis(4’-bromophenyl)-2-silaindane-5,6-dicarboxylate (7a)

Isolated yield: 69%. A yellow solid: mp 260-263 ˚C : ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.13(s, 6H), 1.80(s, 4H), 3.50(s, 6H), 7.11(d, *J* = 8.1 Hz, 4H), 7.54(d, *J* = 8.1 Hz, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -2.76(2C), 21.53(2C), 52.10(2C), 121.46(2C), 129.90(2C), 130.53(4C), 131.24(4C), 138.54(2C), 138.70(2C), 144.40(2C), 168.32(2C); IR (nujol) 2926, 2857, 1740, 1493, 1233, 1009, 835 cm^{-1}; HRMS calcd for $C_{26}H_{24}O_4Br_2Si$ 585.9809, found 585.9803.

Dimethyl 2,2-Dimethyl-4,7-bis(4’-bromophenyl)-2-germaindane-5,6-dicarboxylate (7b)

Isolated yield: 56%. A yellow solid : mp 252-255°C: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.31(s, 6H), 1.95(s, 3.49(s, 6H), 7.11(d, *J* = 8.4 Hz, 4H), 7.54(d, *J* = 8.4 Hz, 4H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -2.57(2C), 22.73(2C), 52.12(2C), 121.46(2C), 129.81(2C), 130.55(4C), 131.27(4C), 138.84(2C), 139.05(2C), 145.11(2C), 168.31(2C); IR (nujol) 2964, 1736, 1462, 1377, 1225, 1009 cm^{-1}; HRMS calcd for $C_{26}H_{24}O_4Br_2Ge$ 631.9252, found 631.9281.

A typical procedure for the preparation of benzoheterocycles mediated by $NiBr_2(PPh_3)_2$

To a solution of Cp_2ZrCl_2 (0.292 g; 1.0 mmol) in THF (5 mL) was added BuLi (1.60 M, 1.25 mL; 2.0 mmol) at -78 °C. After stirring for 1 h at the same temperature silicon containing diyne (1.0 mmol) was added and the reaction mixture was allowed to be warmed to rt for 1 h. 4-Octyne (0.220 g; 2.0 mmol) and $NiBr_42(PPh_3)_2$ (0.743 g; 1.0 mmol) were added and the mixture was stirred for 3 h. Then the reaction mixture was quenched with 3N HCl and extracted with ether (3 x 30 mL). The extract was washed with water, and dried over $MgSO_4$. The solvent was evaporated *in vacuo* and the residue was purified by chromatography on silica using hexane as eluant. A yellow oil (**4j)** (78 %) was obtained.

2,2-Dimethyl-4,5,6,7-tetrapropyl-2-silaindane (4j)

GC yield 81 %. Isolated yield: 78%. A white-yellow oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.00 (s, 6H), 0.82 (t, *J* = 7.2 Hz, 6H), 0.84(t, *J* =7.2 Hz, 6H), 1.26-1.36 (m, 8H), 1.77 (s, 4H), 2.28-2.38 (m, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.72 (2C), 15.10 (2C), 19.44 (2C), 23.49 (2C), 25.14 (2C), 32.21 (2C), 33.64 (2C), 136.52(2C), 137.73 (2C), 138.98 (2C); IR(neat): 2957.2, 2930.2, 2870.4, 1466.0, 1248.0, 1147.7, 842.9, 831.4 cm^{-1}; Anal. Calcd for $C_{22}H_{38}Si$: C, 79.92; H, 11.58. Found: C, 79.56; H, 11.61.

2,2-Dimethyl-4,6,7-tripropyl-5-methyl-2-silaindane (4k)

GC yield 78 %. Isolated yield: 65%. A white oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.27 (s, 6H) 1.08 (t, *J* = 7.5 Hz, 3H), 1.09 (t, *J* = 7.2 Hz, 3H), 1.10 (t, *J* = 6.9 Hz, 3H),1.50-1.60 (m, 6H), 2.05 (s, 4H), 2.30 (s, 3H), 2.60-2.70 (m, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.86 (2C), 14.8, 14.96, 15.05, 15.38, 19.51, 19.564, 22.54, 23.64, 23.95, 32.62, 33.67, 34.03, 131.74, 136.98, 137.44, 138.11, 138.58, 138.67; IR(neat): 2955.3, 2932.1, 2872.3, 1466.0, 1377.3, 1248.0, 1147.7, 831.4 cm^{-1}; HRMS calcd for $C_{20}H_{34}Si$ 302.2430, found 302.2431.

2,2-Dimethyl-4,7-dipropyl-5-phenyl-2-silaindane (4l)

GC yield: 84 %. Isolated yield: 71%. A yellow oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.34 (s, 6H), 0.86 (t, *J*= 7.5 Hz, 3H), 1.05 (t, *J* = 7.5 Hz, 3H), 1.44-1.73 (m, 4H), 2.09(s, 2H), 2.13 (s, 2H), 2.56-2.68 (m, 4H), 6.93 (s, H), 7.34-7.43 (m, 5H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -1.88 (2C), 14.36, 14.60, 18.80, 19.33, 23.14, 23.44, 33.44, 36.33, 126.25, 127.72 (2C), 128.07, 129.39 (2C), 136.81, 138.51, 139.75,140.32, 1411.46, 143.21; IR: 2957.2, 2930.2, 2870.4, 1448.2, 1445.7,1441.0, 1250.0, 1145.8, 831.4, 767.7cm^{-1}; HRMS calcd for $C_{22}H_{30}Si$ 322.2117, found: 322.2143.

2,2-Dimethyl-4,7-dipropyl-5-phenyl-2-stannaindane (4m)

Isolated yield: 54%. A colorless sticky oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.36 (s, satellites, J_{SnH} = 54 and 57 Hz, 6H), 0.79 (t, *J* = 7.3 Hz, 3H), 1.00 (t, *J* = 7.3 Hz, 3H), 1.39-1.48 (m, 2H), 1.59-1.68 (m, 2H), 2.26 (s, satellites, J_{SnH} = 43 Hz, 2H), 2.30 (s, satellites, J_{SnH} = 43 Hz, 2H), 2.56-2.60 (m, 2H), 2.64-2.68 (m, 2H), 6.86 (s,1H), 7.28-7.39 (m, 5H); ^{13}C-NMR ($CDCl_3$, Me_4Si) δ -9.72 (satellites, J_{SnC} = 315 Hz, 330 Hz), 14.50, 14.72, 14.83, 15.16, 23.11, 23.43, 34.00, 37.09, 126.26, 127.71, 127.78, 129.38, 138.15, 139.50, 139.72, 141.89, 142.98, 143.29; IR (neat) 2955, 2926, 2859, 1460, 1377, 1026, 770, 702 cm^{-1}; HRMS calcd for $C_{22}H_{30}Sn$ 414.1368, found 414.1367.

2,2-Dimethyl-4,6,7-tripropyl-2-stannaindane (4n)

Isolated yield: 40%. A colorless liquid: ^{1}H NMR (C_6D_6) δ 0.21 (s, satellites, J_{SnH} = 54 and 56 Hz, 6H), 1.04 (t, *J* = 7.3 Hz, 3H), 1.08 (t, *J* = 7.3 Hz, 3H), 1.11 (t, *J* = 7.3 Hz, 3H), 1.62-1.78 (m, 6H), 2.15 (s, satellites, J_{SnH}= 44 Hz, 2H), 2.20 (s, satellites, J_{SnH} = 44 Hz, 2H), 2.68-2.77 (m, 4H), 2.83-2.87 (m, 2H), 6.98 (s,1H); ^{13}C NMR (C_6D_6) δ -10.29 (satellites, J_{SnC} = 308 Hz, 323 Hz), 14.52, 14.61, 14.73, 15.14, 15.33, 23.93, 25.53, 33.53, 35.77, 37.65, 128.06, 137.27, 138.32, 139.71, 139.86, 142.60; HRMS calcd for $C_{19}H_{32}Sn$ 380.1524, found 380.1521.

2,2-Dimethyl-4,7-dipropyl-5-trimethylsilyl-2-stannaindane (4o)

GC yield 50%, isolated yield: 43%. A pale brown liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.31 (s, 9H), 0.33 (s, satellites, J_{SnH} = 54 and 56 Hz, 6H), 1.01 (t, J = 7.3 Hz, 3H), 1.04 (t, J = 7.3 Hz, 3H), 1.50-1.66 (m, 4H), 2.20 (s, satellites, J_{SnH} = 43 Hz, 2H), 2.25 (s, satellites, J_{SnH} = 44 Hz, 2H), 2.61-2.65 (m, 2H), 2.73-2.77 (m, 2H), 7.11 (s,1H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -9.81, 1.01, 14.55, 14.65, 14.77, 14.86, 23.28, 24.00, 37.42, 38.15, 132.50, 134.35, 139.67, 142.64, 144.28, 146.69; IR (neat) 2957, 2932, 2899, 2870, 1468, 1456, 1248, 837, 758, 689, 629 cm^{-1}; HRMS calcd for $C_{19}H_{34}SiSn$ 410.1450, found 410.1464.

2,2-Dimethyl-4,7-dipropyl-5,6-diethyl-2-germaindane (4p)

GC yield 69%. Isolated yield: 63%. A yellow oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.48 (s, 6H), 1.16 (t, J = .5 Hz, 6H), 1.29 (t, J = 7.5 Hz, 6H), 2.30 (s, 4H), 1.60-1.68 (m, 4H), 2.71-2.79 (m, 8H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 1.97 (2C), 15.11 (2C), 15.99 (2C), 20.75 (2C), 23.45 (2C), 33.75 (2C), 137.60 (2C), 137.91 (2C), 139.72; IR(neat): 2959.1, 2932.1, 2872.3, 1466.0, 1375.4, 1236.5, 1140.0, 1060.9, 827.5, 794.7 cm^{-1}; HRMS calcd for $C_{20}H_{34}Ge$ 348.1880, found 348.1881.

2,2-Dimethyl-4,6,7-tripropyl-5-methyl-2-germaindane (4q)

GC yield 87 %. Isolated yield: 68%. A white oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.37 (s, 6H), 1.01-1.07 (m, 9H), 1.48-1.56 (m, 6H), 2.19 (s, 2H), 2.25 (s, 2H), 2.54-2.68 (m, 6H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ -2.09(2C), 14.97, 15.01, 15.13, 15.39, 20.79, 20.90, 22.48, 23.60, 23.95, 32.61, 33.97, 34.36, 1311.78, 136.99,137.66, 138.37, 139.23, 139.33; IR(neat): 2955.3, 2930.2, 2872.3, 1468.0, 1377.3, 12343.5, 1140.0, 827.5, 794.7 cm^{-1}; HRMS calcd for $C_{20}H_{34}Ge$ 348.1880, found: 348.1893.

2,2-Dimethyl-4,7-dipropyl-5-phenyl-2-germaindane (4r)

GC yield: 73 %. Isolated yield: 65%. A yellow oil: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 0.48, (s, 6H), 0.85(t, J =7.2 Hz, 3H), 1.05 (t, J =7.2 Hz, 3H), 1.44-1.73 (m, 4H), 2.27 (s, 2H), 2.32(s, 2H), 2.58-2.70 (m, 4H), 6.93 (s, 1H), 7.33-7.44 (m, 5H); ^{13}C NMR, ($CDCl_3$, Me_4Si) δ -2.04 (2C), 14.42, 14.67, 20.08, 20.50, 23.08, 23.41,

33.73, 36.63, 126.29, 127.73, 128.02, 129.39, 137.08, 138.75, 139.75, 140.98, 142.09, 143.15; IR(neat): 2957.2, 2930.2, 2870.4, 2361.1, 1456.4, 1140.0, 1087.9, 827.5, 792.8, 769.8, 702.1 cm^{-1}; HRMS calcd for $C_{22}H_{30}Ge$: 368.1567, found: 368.1563.

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