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The first stereospecific arylation of (*Z*)-germyl(stannyl)ethenes with an aryl halide or heteroaryl halide under palladium-catalysis

Takumi Kataishi[a], Kotaro Kato[a], Yoshiaki Makihara[a], Yuichi Kitashima[a], Sigeru Ohara[a], Fumiaki Anzai[a], Seiich Inokuma[b], Hiroyuki Oku[b], Masa-aki Ubukata[c], Yutaka Takahashi[c] and Taichi Nakano[a]*

A combination catalyst of Pd(dba)$_2$-PPh$_3$-CuI-LiCl or Pd(dba)$_2$-P(2-furyl)$_3$-CuI-LiCl effectively catalyzed the cross-coupling of (*Z*)-germyl(stannyl)ethenes with aryl halides, providing novel triethyl(2,2-diarylethenyl)germanes in good to high yields. The reaction proceeds with retention of configuration. Cross-coupling results in the formation of phenylene or phenyleneethynylene derivatives with terminal stereochemically defined vinylgermane unit(s).

Keywords: cross-coupling; Migita–Kosugi–Stille reaction; Sonogashira–Hagihara reaction; phenylene derivatives; phenyleneethynylene derivatives; vinylgermanes

Introduction

Organic compounds possessing a high degree of conjugation such as phenylenes or phenyleneethynylenes have long been recognized as ideal materials for advanced electronics and photonic applications such as organic LEDs, liquid crystal displays, and solar cells.[1,2] (*Z*)-1-Aryl-1-(tri-*n*-butylstannyl)-2-(triethylgermyl)ethenes, (*Z*)-**1**,[3,4] seem to provide good building blocks to synthesize new types of phenyleneethynylenes with terminal (germyl)ethenyl unit(s) through a combination of a Migita–Kosugi–Stille type reaction†[5–8] and a Sonogashira–Hagihara reaction (†Organotins, organoborons and organosilicons are known to work as cross-coupling reagents in the presence of a transition metal complex catalyst; among them, organotins [e.g. tri-*n*-butyl(organo)tins] are stable in air, but reactive in palladium-catalyzed cross-coupling, while organoborons require a base for the reaction to occur, and organosilicons need a special group(s) [e.g. F, alkoxy, 2-pyridyl, or 2-(hydroxymethyl)phenyl] on silicon as well as a base such as TBAF (tetra-*n*-butylammonium fluoride) for the reaction to take place).[5,9]

In addition, according to a simple semi-empirical MO calculation (AM1) of 1,4-bis[4-((*Z*)-1-phenyl-2-germylethenyl)phenylethynyl]benzene and the parent 1,4-bis[4-(1-phenylethenyl)phenylethynyl]benzene, a germyl group seems to reduce the HOMO–LUMO gap of the phenyleneethynylene. Therefore, the synthesis of novel phenyleneethynylenes with terminal vinylgermane unit(s) is quite interesting. However, no cross-coupling of a (*Z*)-**1** vinyltin bearing a germyl group β to the tin with a halide has been reported to date, while the reaction of simple (*E*)-1-germyl-2-stannylethenes has been reported.[10,11] Herein, preliminary results of the first stereospecific arylations of (*Z*)-**1** with aryl halides, a heteroaryl halide or aryl dihalides under palladium-catalysis are reported.

The reaction of (*Z*)-1-(tri-*n*-butylstannyl)-2-(triethylgermyl)-1-phenylethene (*Z*)-**1a**[3,4] with iodobenzene was selected as a model to compare reaction conditions. Thus, a combination catalyst of Pd(dba)$_2$-PPh$_3$-CuI (dba: dibenzylideneacetone) in dry DMF (*N*,*N*-dimethylformamide) at 70 °C was examined first. The reaction produced triethyl(2,2-diphenylethenyl)germane **2a** in 40% yield. A Pd(dba)$_2$–P(2-furyl)$_3$–CuI combination catalyst was also active in the reaction, affording **2a** in 56% yield. Interestingly, Pd(dba)$_2$–PPh$_3$–CuI–LiCl and Pd(dba)$_2$–P(2-furyl)$_3$–CuI–LiCl catalyzed the reaction more efficiently, providing **2a** in 89% and 80% yields, respectively. BnPdCl(PPh$_3$)$_2$–CuI–LiCl and Pd(dba)$_2$–P(2-tol)$_3$–CuI–LiCl (2-tol: 2-methylphenyl) were, on the contrary, less effective, giving **2a** in 38 and 24% yields, respectively. Cross-coupling with bromobenzene also took place in the presence of Pd(dba)$_2$–PPh$_3$–CuI–LiCl to produce **2a** in 70% yield (Scheme 1).

Next, to shed light on the stereochemistry of the cross-coupling of (*Z*)-**1**, the reaction with 4-bromocyanobenzene was examined in the presence of the Pd(dba)$_2$–PPh$_3$–CuI-LiCl combination catalyst, producing **2b** as colorless crystals in 41% yield (Scheme 2). A NOE analysis of **2b** disclosed that it possesses (*Z*)-geometry (Fig. 1), demonstrating that the arylation of (*Z*)-**1** proceeds with retention of configuration, as does arylation of (*Z*)-silyl(stannyl)ethenes.[12]

Under similar conditions, the reaction of (*Z*)-1-(tri-*n*-butylstannyl)-1-(4-cyanophenyl)-2-(triethylgermyl)ethene (*Z*)-**1b**

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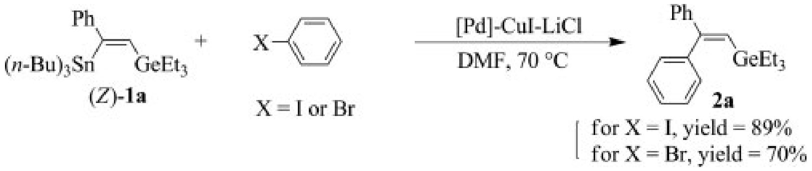
* Correspondence to: Taichi Nakano, Department of Materials Chemistry, School of High-Technology for Human Welfare, Tokai University, Numazu, Shizuoka 410-0395, Japan. E-mail: naka1214@wing.ncc.u-tokai.ac.jp

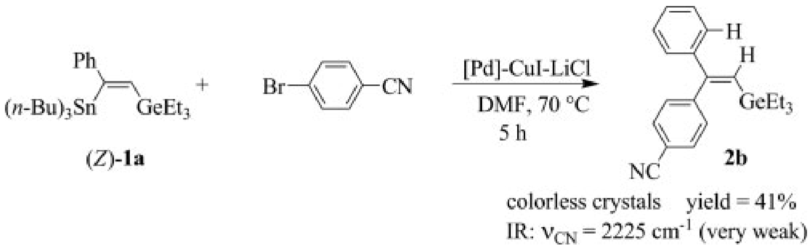
a Department of Materials Chemistry, School of High-Technology for Human Welfare, Tokai University, 317 Nishino, Numazu, Shizuoka 410-0395, Japan

b Department of Chemistry and Chemical Biology, Graduate School of Engineering, Gunma University, Kiryu, Gunma 376-8515, Japan

c Analytical Instrument Division, Jeol Ltd, 3-1-2 Musashino, Akishima, Tokyo 196-8558, Japan



Scheme 1. Palladium-catalyzed cross-coupling of (*Z*)-**1a** with iodo- or bromobenzene.



Scheme 2. Palladium-catalyzed cross-coupling of (*Z*)-**1a** with 4-cyanobromobenzene.

with bromobenzene produced **2c** as a viscous liquid in high yield (Scheme 3). The product **2c** also underwent NOE analysis, showing *E*-geometry. [NOE analysis of **2c**: upon irradiation with energy corresponding to a magnetic field at 6.56 ppm (vinylic proton), the *ortho* protons of the 4-cyanophenyl group appearing at 7.33 ppm increased by 2.3% in strength, the methyl protons in the ethyl group (0.94 ppm) by 0.25%, and the methylene protons (0.59 ppm) in the ethyl group by 0.45%.]

Thus, the reaction was reconfirmed to proceed with retention of configuration. Under similar conditions, (*Z*)-**1a** readily coupled with 3-bromopyridine to afford **2d** in 56% yield (Fig. 2). Interestingly, the reaction of (*Z*)-**1a** with 3 equiv. of 1,4-diiodobenzene or 3 equiv. of 4-bromoiodobenzene selectively produced **2e-*p*-I** (89%) and **2f-*p*-Br** (79%), respectively (Fig. 2), with the formation of small amounts of a bis-substituted product similar to **4a**. The products, **2e-*p*-I** and **2f-*p*-Br** are regarded as useful building blocks for successive coupling reactions, i.e. Migita–Kosugi–Stille or Sonogashira–Hagihara coupling. Thus, the Sonogashira–Hagihara cross-coupling of **2e-*p*-I** with phenylacetylene, 4-chlorophenylacetylene, or 4-methoxyphenylacetylene was examined, which readily occurred under mild conditions to produce **3a, 3b** and **3c** in 85, 98 and 94% yields, respectively (Fig. 2). On the other hand, the use of 2 equiv. of (*Z*)-**1a** relative to 1,4-dibromobenzene brought about the double cross-coupling reaction, affording **4a** in 89% yield (Fig. 2).

Similar double cross-coupling also occurred in the reaction of 4,4′-dibromobiphenyl with 2 equiv. of (*Z*)-**1a** or (*Z*)-1-(tri-*n*-butylstannyl)-1-(4-chlorophenyl)-2-triethylgermylethene (*Z*)-**1c**, resulting in **5a** and **5b** being produced in 50 and 62% yields, respectively (Fig. 2). Finally, the cross-coupling of (*Z*)-**1a** with (*Z*)-1-(4-iodophenyl)-1-phenyl-2-trimethylsilylethene, **2e-Si-*p*-I**, synthesized from the reaction of (*Z*)-1-(tri-*n*-butylstannyl)-2-(trimethylsilyl)-1-phenylethene[13,14] with 1,4-diiodobenzene by a procedure similar to that for **2a**, was examined, which readily took place to afford unsymmetrical product **6a** in 96% yield (Fig. 2).

In closing, Pd(dba)$_2$–PPh$_3$–CuI–LiCl and Pd(dba)$_2$–P(2-furyl)$_3$–CuI–LiCl were found for the first time to be quite active catalysts in the coupling of an aromatic ring with a vinylgermane unit by the use of (*Z*)-germyl(stannyl)ethenes. The palladium-catalyzed cross-coupling of (*Z*)-germyl(stannyl)ethenes with aryl halides proceeds with retention of configuration, producing (germyl)vinylarenes in good to high yields. This method is expected to be useful for the synthesis of a new type of oligophenyleneethynylenes with terminal stereodefined vinylgermane unit(s).

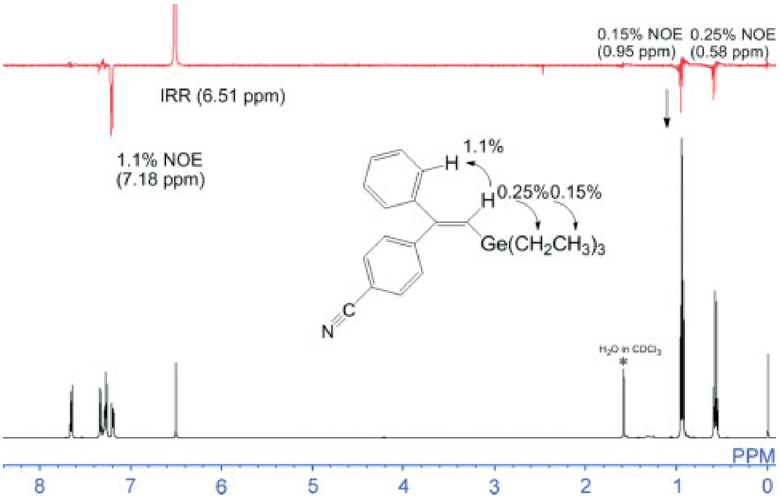
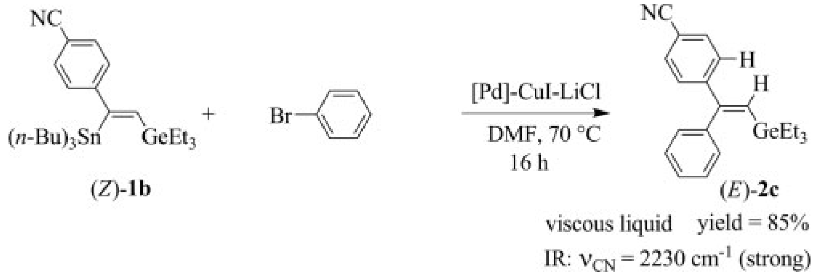


Figure 1. ^{1}H-NMR differential NOE analysis, 500 MHz, of **2b** in CDCl$_3$ at 20 °C.



Scheme 3. Palladium-catalyzed cross-coupling of (Z)-**1b** with bromobenzene.

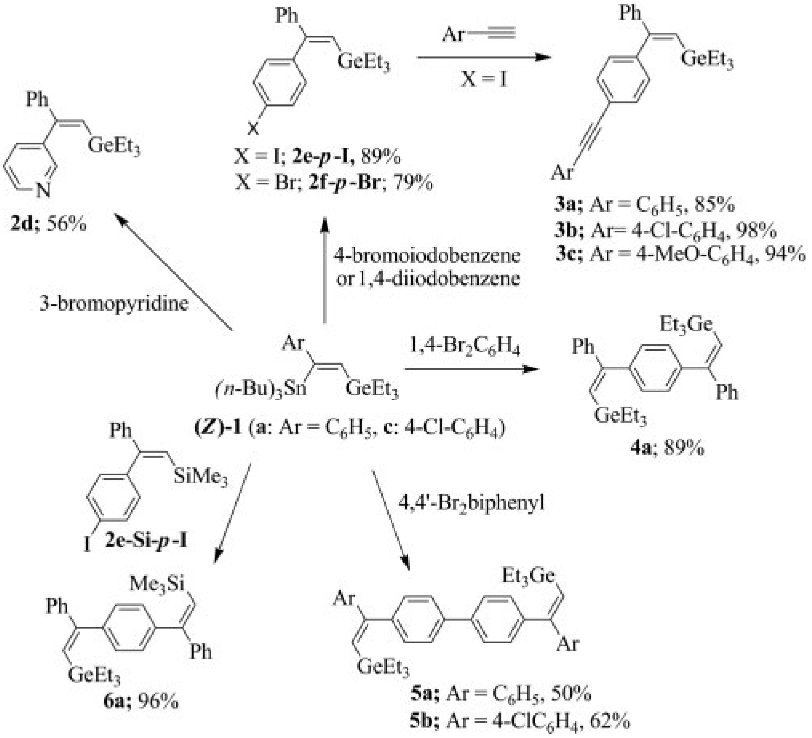


Figure 2. Synthesis of several phenylenes or phenyleneethynylenes with a terminal stereodefined vinylgermane unit(s) using (Z)-germyl(stannyl)ethenes (see Experimental for reaction conditions).

In a preliminary experiment, **3b** in hexane generated a pale blue color upon UV irradiation. Further work is in progress to exploit the arylation of (Z)-**1** with a variety of halides for the synthesis of novel symmetrical and unsymmetrical oligophenylenes or phenyleneethynylenes with terminal Z-type (germyl)ethenyl group(s).

Experimental

A typical procedure for the palladium-catalyzed reaction of (Z)-**1a** with iodobenzene is as follows: a mixture of $Pd(dba)_2$ (0.025 mmol) and PPh_3 (0.1 mmol) in dry DMF (2.0 ml) was stirred at room temperature for 5 min under nitrogen. To the mixture, CuI (0.04 mmol) and LiCl (1.20 mmol) were added and stirred. After 5 min, (Z)-**1a** (0.5 mmol)[3,4] in dry DMF (2 ml) and iodobenzene (1.5 mmol) in dry DMF (2 ml) were successively added. The mixture was stirred at 70 °C for 8 h. The resultant mixture was passed through a short silica gel column [SiO_2 (neutral), hexane]. The eluted solution was concentrated with a rotary evaporator under aspirator vacuum to a volume of *ca* 5 ml. Then, after addition of ether (5 ml) to the concentrate, the resulting solution was vigorously stirred with aqueous KF (2.15 M, 10 ml) overnight at room temperature. Filtration of the liberated crystalline Bu_3SnF and ether extraction of the organic phase, followed by drying over Na_2SO_4, evaporation with a rotary evaporator and column chromatography [silica gel (Kanto Kagaku Co. Ltd, Japan, 60N, spherical, 40–50 μm, neutral, for flash chromatography; if the same silica gel we used to purify the cross-coupling products is not available, Harrowven's method is recommended for the purification of products),[15] hexane] provided spectroscopically pure triethyl(2,2-diphenylethenyl)germane **2a** (0.1506 g, 89% yield) as a colorless viscous liquid. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.33–7.31 (m, 4H), 7.29–7.25 (m, 4H), 7.24–7.19 (m, 2H), 6.41 (s, 1H), 0.94 (t, 9H, $J = 8.0$ Hz), 0.57 (q, 6H, $J = 8.0$ Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 156.6 (vinyl carbon bearing two phenyl groups), 143.4 (quart. carbon of phenyl group *trans* to germanium), 143.0 (quart. carbon of phenyl group *cis* to germanium), 129.5 (*meta*-carbon of phenyl group *trans* to germanium), 128.9 (*meta*-carbon of phenyl group *cis* to germanium), 128 (*para*-carbon of phenyl group *trans* to germanium), 127.8 (*para*-carbon of phenyl group *cis* to germanium), 127.34 (*ortho*-carbon of phenyl group *cis* to germanium), 127.3 (*ortho*-carbon of phenyl group *trans* to germanium), 127.2 (vinyl carbon bearing germyl group), 9.0 (C1 of ethyl group) and 5.6 (C2 of ethyl group) ppm. The assignment of the aromatic carbons is based on intensity information, the additivity of the chemical shifts[16] and reported ^{13}C-NMR data of styrylgermanes[17] and -silanes.[14] IR (neat): 3070 (m), 3050 (m), 3025 (m), 2950 (s), 2900 (s), 2870 (s), 1595 (m), 1490 (s), 1460 (s), 840 (s), 780 (s), 760 (s), 700 (s) cm^{-1}. LRMS (EI, 70 eV): 340 (M$^+$), 311 (M$^+$ − 29). HRMS (EI, 70 eV): calcd for $C_{20}H_{26}Ge$, 340.1246; found, 340.1209.

By a procedure similar to that for **2a**, other arylation products were obtained from the corresponding (*Z*)-**1**. Spectral data of the products are shown below.

Triethyl[(*Z*)-2-(4-cyanophenyl)-2-phenylethenyl]germane: 2b, colorless crystals, m.p. 68.7–69.8 °C. Reaction conditions: (*Z*)-1a (0.5 mmol), 4-bromobenzonitrile (1 mmol), Pd(dba)$_2$ (5 mol%), PPh$_3$ (20 mol%), CuI (8 mol%) and LiCl (2.2 equiv); DMF (4 ml); 70 °C; 5 h; yield = 41%

^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.64 (dd, 2H, $J = 8.0, 0.4$ Hz), 7.33 (dd, 2H, $J = 8.0, 0.4$ Hz), 7.29–7.18 (m, 5H), 6.51 (s, 1H), 0.95 (t, 9H, $J = 8.0$ Hz), 0.58 (q, 6H, $J = 8.0$ Hz) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 154.9 (vinyl carbon bearing two aromatic rings), 148 (quart. aromatic carbon *para* to cyano group), 142.3 (quart. phenyl carbon bearing vinyl group), 131.7 (aromatic carbon *ortho* to cyano group), 131.1 (phenyl carbon *meta* to vinyl group), 130.3 (phenyl carbon *para* to vinyl group), 128.2 (aromatic carbon *meta* to cyano group), 127.8 (phenyl carbon *ortho* to vinyl group), 127.1 (vinyl carbon bearing germyl group), 118.8 (cyano carbon), 111.2 (aromatic carbon bearing CN group), 8.9 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. IR (KBr disk): 3050 (w), 2950 (s), 2925 (s), 2850 (s), 2225 (very weak), 1460 (s), 850 (w), 700 (w) cm^{-1}. LRMS (EI, 70 eV): 365 (M$^+$), 336 (M$^+$ − 29). HRMS (EI, 70 eV): calcd for $C_{21}H_{25}GeN$, 365.1199; found, 365.1227.

Triethyl[(*E*)-2-(4-cyanophenyl)-2-phenylethenyl]germane: 2c, colorless viscous liquid. Reaction conditions: (*Z*)-1b (0.5 mmol), bromobenzene (1 mmol), Pd(dba)$_2$ (5 mol%), PPh$_3$ (20 mol%), CuI (8 mol%) and LiCl (2.2 equiv); DMF (4 ml); 70 °C; 16 h; yield = 85%

^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.54 (dd, 2H, $J = 6.6, 1.4$ Hz), 7.37–7.33 (m, 5H), 7.18–7.15 (m, 2H), 6.56 (s, 1H), 0.94 (t, 9H, $J = 8.0$ Hz), 0.59 (q, 6H, $J = 8.0$ Hz) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 154.9 (vinyl carbon bearing two aromatic rings), 147.4 (quart. aromatic carbon *para* to cyano group), 141.7 (quart. phenyl carbon bearing vinyl group), 133.5 (aromatic carbon *meta* to vinyl group), 131.9 (phenyl carbon *meta* to vinyl group), 129.4 (phenyl carbon *para* to vinyl group), 128.1 (aromatic carbon *ortho* to vinyl group), 127.8 (phenyl carbon *ortho* to vinyl group), 127.7 (vinyl carbon bearing germyl group), 119.0 (cyano carbon), 110.6 (aromatic carbon bearing CN group), 10.0 (C1 of ethyl group), 5.5 (C2 of ethyl group) ppm. IR (neat): 3050 (m), 3030 (m), 2950 (s), 2900 (s), 2860 (s), 2230 (s), 1600 (s), 1580 (m), 1500 (s), 1460 (s), 820 (s), 700 (s) cm^{-1}. LRMS (FD): 365 (M$^+$). HRMS (FD): calcd for $C_{21}H_{25}GeN$, 365.1199; found, 365.1222.

Triethyl[(*Z*)-2-phenyl-2-(3-pyridyl)ethenyl]germane: 2d. colorless viscous liquid. Reaction conditions: (*Z*)-1a (0.5 mmol), 3-bromopyridyne (2 mmol), Pd(dba)$_2$ (6 mol%), PPh$_3$ (20 mol%), CuI (8 mol%) and LiCl (2.2 equiv); DMF (4 ml); 70 °C; 17 h; yield = 56%

^{1}H-NMR (CDCl$_3$, 400 MHz): δ 8.59 (dd, 1H, $J = 4.8, 1.6$ Hz), 8.51 (dd, 1H, $J = 2.4, 0.8$ Hz), 7.50 (dt, 1H, $J = 8.0, 2.0$ Hz), 7.31–7.23 (m, 6H), 6.54 (s, 1H), 0.95 (t, 9H, $J = 8.0$ Hz), 0.59 (q, 6H, $J = 8.0$ Hz) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 152.9 (vinyl carbon bearing two aromatic rings), 150.2 (pyridyl carbon *ortho* to vinyl group and to nitrogen), 148.7 (pyridyl carbon *para* to vinyl group), 142.6 (quart. phenyl carbon bearing vinyl group), 138.6 (quart. pyridyl carbon bearing vinyl group), 136.7 (pyridyl carbon *ortho* to vinyl group and *para* to nitrogen), 131.4 (phenyl carbon *meta* to vinyl group), 128.2 (phenyl carbon *para* to vinyl group), 127.7 (phenyl carbon *ortho* to vinyl group), 127.1 (vinyl carbon bearing germyl group), 122.8 (pyridyl carbon *meta* to vinyl group), 8.9 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. IR (neat): 3075 (m), 3050 (m), 3025 (m), 2950 (s), 2900 (s), 2875 (s), 1660 (m), 1595 (m), 1565 (m), 1495 (m), 1470 (m), 1460 (m), 1440 (m), 845 (m), 818 (m), 765 (s), 750 (m), 700 (s) cm^{-1}. LRMS (EI, 70 eV): 341 (M$^+$), 312 (M$^+$ − 29). HRMS (EI, 70 eV): calcd for $C_{19}H_{25}GeN$, 341.1199; found, 341.1213.

Triethyl[(*Z*)-2-(4-iodophenyl)-2-phenylethenyl]germane: 2e-*p*-I, colorless viscous liquid. Reaction conditions: (*Z*)-1a (0.5 mmol), 1,4-diiodobenzene (1 mmol), Pd(dba)$_2$ (5 mol%), PPh$_3$ (10 mol%), CuI (8 mol%) and LiCl (2.2 equiv); DMF (4 ml); 70 °C; 6 h; yield = 89%

^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.67 (dd, 2H, $J = 6.4, 2.0$ Hz), 7.26–7.23 (m, 5H), 6.96 (dd, 2H, $J = 6.4, 2.0$ Hz), 6.41 (s, 1H), 0.95 (t, 9H, $J = 7.6$ Hz), 0.59 (q, 6H, $J = 7.6$ Hz) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 155.5 (vinyl carbon bearing two aromatic rings), 142.9 (quart. phenyl carbon bearing vinyl group), 142.5 (aromatic carbon *ortho* to iodine), 137.0 (aromatic carbon *meta* to iodine), 131.5 (phenyl carbon *meta* to vinyl group), 129.7 (quart. aromatic carbon bearing vinyl group), 128.1 (phenyl carbon *para* to vinyl group), 127.6 (phenyl carbon *ortho* to vinyl group), 127.2 (vinyl carbon bearing germyl group), 92.9 (quart. aromatic carbon bearing iodine), 9.0 (C1 of ethyl group), 5.6 (C2 of ethyl group) ppm. IR (neat): 3050 (w), 3010 (w), 2950 (s), 2900 (s), 1590 (m), 1560 (m), 1490 (s), 1490 (m), 1459 (m), 840 (m), 820 (s), 760 (s), 700 (s) cm^{-1}. LRMS (FD): 466 (M$^+$). HRMS (FD): calcd for $C_{20}H_{25}GeI$, 466.0213; found, 466.0215.

Trimethyl[(*Z*)-2-(4-iodophenyl)-2-phenylethenyl]silane: 2e-Si-*p*-I, colorless crystals, m.p. 48.5–49.2 °C

Title compound **2e-Si-*p*-I** was synthesized from (*Z*)-1-(tri-*n*-butylstannyl)-1-phenyl-2-(trimethylsilyl)ethene[13,14] and 1,4-diiodobenzene in 82% yield (conditions; 70 °C, 6 h) by the procedure similar to that for**2e-*p* -I**.

^{1}H-NMR (CDCl$_3$, 400 MHz): δ 7.68 (d, 2H, $J = 8.0$ Hz), 7.26–7.23 (m, 5H), 6.95 (d, 2H, $J = 8.0$ Hz), 6.30 (s, 1H), 0.09 (s, 9H) ppm. ^{13}C-NMR (CDCl$_3$, 100.7 MHz): δ 155.8 (vinyl carbon bearing two aromatic rings), 142.7 (quart. phenyl carbon bearing vinyl group), 142.1 (aromatic carbon *ortho* to iodine), 137.0 (aromatic carbon *meta* to iodine), 131.6 (phenyl carbon *meta* to vinyl group), 130.4 (quart. aromatic carbon bearing vinyl group), 128.1 (phenyl carbon *para* to vinyl group), 127.8 (phenyl carbon *ortho* to vinyl group), 127.1 (vinyl carbon bearing silyl group, $J_{\mathrm{Si,C}} = 65.9$ Hz), 93.0 (quart. aromatic carbon bearing iodine), 0.05 (methyl carbon of SiMe$_3$, $J_{\mathrm{Si,C}} = 52.3$ Hz) ppm. ^{29}Si-NMR (CDCl$_3$, 79.6 Hz): $\delta - 8.83$ ppm. IR (neat): 3050 (m), 3025 (m), 2950 (s), 1590 (m), 1560 (m), 1490 (m), 1480 (s), 1240 (s), 840 (s), 760 (s) cm^{-1}. LRMS (FD): 378 (M$^+$). HRMS (FD): calcd for $C_{20}H_{25}ISi$, 378.0301; found, 378.0311.

Triethyl[(*Z*)-2-(4-bromophenyl)-2-phenylethenyl]germane: 2f-*p*-Br, colorless viscous liquid. Reaction conditions: (*Z*)-1a (0.5 mmol), 4-iodobromobenzene (1 mmol), $Pd(dba)_2$ (5 mol%), PPh_3 (10 mol%), CuI (8 mol%) and LiCl (2.2 equiv); DMF (4 ml); 70 °C; 48 h; yield = 79%

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, 2H, $J = 8.6$ Hz), 7.28–7.20 (m, 5H), 7.08 (d, 2H, $J = 8.6$ Hz), 6.42 (s, 1H), 0.95 (t, 9H, $J = 8.0$ Hz), 0.59 (q, 6H, $J = 8.0$ Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 155.5 (vinyl carbon bearing two aromatic rings), 142.9 (quart. phenyl carbon bearing vinyl group), 142.0 (quart. aromatic carbon bearing vinyl group), 131.3 (aromatic carbon *ortho* to bromine), 131.0 (phenyl carbon *meta* to vinyl group), 129.7 (aromatic carbon *meta* to bromine), 128.1 (phenyl carbon *para* to vinyl group), 127.6 (phenyl carbon *ortho* to vinyl group), 127.2 (vinyl carbon bearing germyl group), 121.4 (quart. aromatic carbon bearing bromine), 9.0 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. IR (neat): 3050 (w), 2950 (s), 2900 (m), 2860 (m), 1590 (m), 1560 (w), 1490 (m), 1480 (m), 1440 (m), 860 (m), 820 (s), 800 (s), 700 (s) cm^{-1}. LRMS (EI, 70 eV): 418 (M^+), 389 ($M^+ - 29$). HRMS (EI, 70 eV): calcd for $C_{20}H_{25}BrGe$, 418.0351; found, 418.0317.

Triethyl[(*Z*)-2-[4-(phenylethynyl)phenyl]-2-phenylethenyl]germane: 3a, yellowish viscous liquid. Reaction conditions: 2e-*p*-I (0.31 mmol), phenylacetylene (0.4 mmol), $PdCl_2(PPh_3)_2$ (3 mol%) and CuI (6 mol%); triethylamine (4 ml); 70 °C; 2 h; yield = 85%

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.56–7.54 (m, 2H), 7.52 (dd, 2H, $J = 8.4$, 0.4 Hz), 7.38–7.34 (m, 3H), 7.28–7.23 (m, 5H), 7.20 (dd, 2H, $J = 8.4$, 0.4 Hz), 6.42 (s, 1H), 0.96 (t, 9H, $J = 7.8$ Hz), 0.61 (q, 6H, $J = 7.8$ Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 156.1 (vinyl carbon bearing two aromatic rings), 143.2 (quart. phenyl carbon bearing vinyl group), 143.1 (quart. phenylene carbon bearing vinyl group), 131.6 (terminal phenyl carbon *ortho* to ethynyl group), 131.1 (phenylene carbon *meta* to vinyl group), 129.6 (phenyl carbon *meta* to vinyl group), 129.5 (terminal phenyl carbon *para* to ethynyl group), 128.3 (terminal phenyl carbon *meta* to ethynyl group), 128.2 (phenyl carbon *para* to vinyl group), 128.0 (phenyl carbon *ortho* to vinyl group), 127.5 (phenylene carbon *ortho* to vinyl group), 127.2 (vinyl carbon bearing germyl group), 123.2 (terminal quart. phenyl carbon bearing ethynyl group), 122.2 (quart. phenylene carbon *para* to vinyl group), 89.7 (acetylenic carbon), 89.4 (acetylenic carbon), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. IR (KBr disk): 3075 (m), 3050 (m), 3025 (m), 2950 (s), 2930 (s), 2900 (s), 2870 (s), 2220 (w), 1603 (m), 1595 (m), 1585 (m), 1565 (m), 1505 (s), 1490 (s), 1460 (m), 1440 (s), 850 (s), 838 (s), 735 (m), 710 (m), 690 (s) cm^{-1}. LRMS (FD): 440 (M^+). HRMS (FD): calcd for $C_{28}H_{30}Ge$, 440.1559; found, 440.1539.

Triethyl[(*Z*)-2-[4-[(4-chlorophenyl)ethynyl]phenyl]-2-phenylethenyl]germane: 3b, pale yellowish crystals, m.p. 75.3–76.6 °C. Reaction conditions: 2e-*p*-I (0.3 mmol), 4-chlorophenylacetylene (0.36 mmol), $PdCl_2(PPh_3)_2$ (3 mol%) and CuI (6 mol%); triethylamine (4 ml); 70 °C; 2.5 h; yield = 98%

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.51 (dt, 2H, $J = 8.8$, 2.0 Hz), 7.48 (dt, 2H, $J = 8.8$, 2.0 Hz), 7.34 (dt, 2H, $J = 8.4$, 2.0 Hz), 7.28–7.24 (m, 5H), 7.21 (dt, 2H, $J = 8.4$, 2.0 Hz), 6.43 (s, 1H), 0.95 (t, 9H, $J = 8.0$ Hz), 0.61 (q, 6H, $J = 8.0$ Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 156 (vinyl carbon bearing two aromatic rings), 143.4 (quart. phenyl carbon bearing vinyl group), 143.0 (quart. phenylene carbon bearing vinyl group), 134.3 (quart. aromatic carbon bearing chlorine), 132.8 (aromatic carbon *meta* to chlorine), 131.1 (phenylene carbon *meta* to vinyl group), 129.7 (phenyl carbon *meta* to vinyl group), 128.7 (aromatic carbon *ortho* to chlorine), 128.1 (phenyl carbon *para* to vinyl group), 127.5 (phenyl carbon *ortho* to vinyl group and phenylene carbon *ortho* to vinyl group), 127.2 (vinyl carbon bearing germyl group), 121.8 (quart. phenylene carbon *para* to vinyl group and quart. aromatic carbon *para* to chlorine), 90.4 (acetylenic carbon), 88.6 (acetylenic carbon), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. IR (KBr disk): 3075 (w), 3050 (w), 2950 (s), 2925 (s), 2900 (s), 2870 (s), 2220 (w), 1590 (m), 1585 (m), 1565 (m), 1508 (s), 1490 (s), 1460 (m), 1440 (m), 850 (m), 828 (s), 758 (m), 698 (s) cm^{-1}. LRMS (FD): 474 (M^+). HRMS (FD): calcd for $C_{28}H_{29}ClGe$, 474.1169; found, 474.1159.

Triethyl{(*Z*)-2-[4-[(4-methoxyphenyl)ethynyl]phenyl]-2-phenylethenyl}germane: 3c, colorless crystals, m.p. 66.2–66.7 °C. Reaction conditions: 2e-*p*-I (0.3 mmol), 4-methoxyphenylacetylene (0.4 mmol), $PdCl_2(PPh_3)_2$ (3 mol%) and CuI (6 mol%); triethylamine (4 ml); 70 °C; 2 h; yield = 94%

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.50–7.47 (m, 4H), 7.28–7.22 (m, 5H), 7.19 (dd, 2H, $J = 6.6$, 2.0 Hz), 6.89 (dd, 2H, $J = 6.6$, 2.0 Hz), 6.42 (s, 1H), 3.83 (s, 3H), 0.95 (t, 9H, $J = 8.0$ Hz), 0.60 (q, 6H, $J = 8.0$ Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 159.6 (quart. terminal aromatic carbon bearing methoxy group), 156.1 (vinyl carbon bearing two aromatic rings), 143.1 (quart. phenyl carbon bearing vinyl group), 142.8 (quart. phenylene carbon bearing vinyl group), 133.0 (terminal aromatic carbon *meta* to methoxy group), 130.9 (phenylene carbon *meta* to vinyl group), 129.6 (phenyl carbon *meta* to vinyl group), 129.4 (phenyl carbon *para* to vinyl group), 128.0 (phenyl carbon *ortho* to vinyl group), 127.5 (phenylene carbon *ortho* to vinyl group), 127.2 (vinyl carbon bearing germyl group), 122.5 (quart. phenylene carbon *para* to vinyl group), 115.3 (quart. aromatic carbon *para* to methoxy group), 113.9 (terminal aromatic carbon *ortho* to methoxy group), 89.7 (acetylenic carbon), 88.1 (acetylenic carbon), 55.2 (methoxy carbon), 9.0 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. IR (KBr disk): 3050 (w), 2950 (s), 2925 (s), 2860 (s), 2220 (w), 1605 (m), 1595 (s), 1560 (s), 1515 (s), 1500 (s), 1490 (s), 1460 (s), 1450 (s), 1440 (s), 840 (s), 825 (s), 800 (m), 765 (m), 695 (s) cm^{-1}. LRMS (FD): 470 (M^+). HRMS (FD): calcd for $C_{29}H_{32}GeO$, 470.1665; found, 470.1696.

1,4-Bis[(*Z*)-2-(triethylgermyl)-1-phenylethenyl]benzene: 4a, colorless viscous liquid. Reaction conditions: (*Z*)-1a (1.1 mmol), 1,4-dibromobenzene (0.5 mmol), $Pd(dba)_2$ (10 mol%), PPh_3 (40 mol%), CuI (16 mol%) and LiCl (4.4 equiv); DMF (8 ml); 70 °C; 2.5 h; yield = 89%

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.32–7.19 (m, 14H), 6.43 (s, 2H), 0.99 (t, 18H, $J = 8.0$ Hz), 0.66 (q, 12 H, $J = 8.0$ Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 156.4 (vinyl carbon bearing two aromatic rings), 143.5 (quart. phenyl carbon bearing vinyl group), 142.1 (quart. phenylene carbon bearing vinyl group), 129.2 (phenyl carbon *meta* to vinyl group), 128.8 (phenyl carbon *para* to vinyl group), 128 (phenyl carbon *ortho* to vinyl group), 127.4 (phenylene carbon *ortho* to vinyl group), 127.2 (vinyl carbon bearing germyl group), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. IR (neat): 3050 (m), 3025 (m), 2950 (s), 2900 (s), 2875 (s), 1580 (m), 1560 (m), 1500 (m), 1490 (m), 1460 (m), 850 (m), 760 (s), 700 (s) cm^{-1}. LRMS (FD): 600 (M^+). HRMS (FD): calcd for $C_{34}H_{46}Ge_2$, 600.2032; found, 600.2025.

4,4′-Bis[(*Z*)-2-(triethylgermyl)-1-phenylethenyl]biphenyl:5a, colorless crystals, m.p. 116.9–118.5 °C. Reaction conditions: (*Z*)-1a (0.54 mmol), 4,4′-dibromobiphenyl (0.25 mmol), Pd(dba)$_2$ (10 mol%), PPh_3 (40 mol%), CuI (16 mol%) and LiCl (4.4 equiv); DMF (4 ml); 70 °C; 19 h; yield = 50%

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, 4H, $J = 8.0$ Hz), 7.31–7.25 (m, 14H), 6.43 (s, 2H), 0.97 (t, 18H, $J = 8.0$ Hz), 0.64 (q, 12H, $J = 8.0$ Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 156.4 (vinyl carbon bearing two phenyl groups), 143.4 (quart. phenyl carbon bearing vinyl group), 142.1 (quart. biphenylene carbons C4 and C4′ bearing germylethenyl group), 139.7 (inner quart. biphenylene carbons C1 or C1′), 130.0 (phenyl carbon *meta* to vinyl group), 129.1 (phenyl carbon *para* to vinyl), 128.0 (biphenylene carbons C2 and C2′), 127.4 (biphenylene carbons C3 and C3′), 127.3 (vinyl carbon bearing germyl group), 126.3 (phenyl carbon *ortho* to vinyl group), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. IR (KBr disk): 3073 (m), 3050 (m), 3020 (m), 2945 (s), 2895 (s), 2860 (s), 1680 (s), 1665 (s), 1595 (m), 840 (s), 820 (s), 760 (s), 690 (s) cm^{-1}. LRMS (FD): 676 (M$^+$). HRMS (FD): calcd for $C_{40}H_{50}Ge_2$, 676.2345; found, 676.2367.

4,4′-Bis[(*Z*)-2-(triethylgermyl)-1-(4-chlorophenyl) ethenyl]biphenyl:5b, colorless crystals, m.p. 89.7–97.2 °C. Reaction conditions: (*Z*)-1c (0.53 mmol), 4,4′-dibromobiphenyl (0.25 mmol), Pd(dba)$_2$ (10 mol%), PPh_3 (40 mol%), CuI (16 mol%) and LiCl (4.4 equiv); DMF (4 ml); 70 °C; 18 h; yield = 62%

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.64 (d, 4H, $J = 8.0$ Hz), 7.27 (d, 4H, $J = 8.0$ Hz), 7.30-7.20 (m, 8H), 6.42 (s, 2H), 0.97 (t, 18H, $J = 8.0$ Hz), 0.63 (q, 12H, $J = 8.0$ Hz) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 155.1 (vinyl carbon bearing two aromatic rings), 141.9 (quart. biphenylene carbons C4 and 4′ bearing vinyl group), 141.7 (quart. aromatic carbon *para* to chlorine), 139.8 (quart. biphenylene carbons C1 and C1′), 133.3 (quart. phenyl carbon bearing chlorine), 130 (phenyl carbon *ortho* to chlorine), 129.9 (phenyl carbon *meta* to chlorine), 128.6 (biphenylene carbons C2 and C2′), 128.1 (phenylene carbons C3 and C3′), 126.5 (vinyl carbon bearing germyl group), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group) ppm. IR (KBr disk): 3073 (m), 3020 (w), 2945 (s), 2895 (s), 2860 (s), 1605 (w), 1590 (m), 1555 (w), 1485 (s), 1455 (m), 825 (s), 810 (s), 740 (m), 700 (m) cm^{-1}. LRMS (FD): 744 (M$^+$). HRMS (FD): calcd for $C_{40}H_{48}Cl_2Ge_2$, 744.1566; found, 744.1520.

1-[(*Z*)-2-(Triethylgermyl)-1-phenylethenyl]-4-[(*Z*)-2-(trimethylsilyl)-1-phenylethenyl]benzene: 6a, colorless crystals, m.p. 48.8–49.4 °C. Reaction conditions: (*Z*)-1a (0.51 mmol), 2e-Si-*p*-I (0.52 mmol), Pd(dba)$_2$ (5 mol%), PPh_3 (10 mol%), CuI (8 mol%) and LiCl (2.2 equiv); DMF (4 ml); 70 °C; 5 h; yield = 96%

^{1}H-NMR ($CDCl_3$, 400 MHz): δ 7.30–7.22 (m, 10H), 7.20 (s, 4H), 6.42 (s, 1H), 6.31 (s, 1H), 0.98 (t, 9H, $J = 7.8$ Hz), 0.65 (q, 6H, $J = 7.8$ Hz), −0.03 (s, 9H) ppm. ^{13}C-NMR ($CDCl_3$, 100.7 MHz): δ 156.8 (quart. vinyl carbon β to silyl group and bearing phenylene ring), 156.4 (quart. vinyl carbon β to germyl group and bearing phenylene ring), 143.5 (quart. carbon of phenyl group *trans* to silyl group), 143.4 (quart. carbon of phenyl group *trans* to germyl group), 142.2 (quart. phenylene carbon bearing silylethenyl group), 141.7 (quart. phenylene carbon bearing germylethenyl group), 129.7 (*meta*-carbon of phenyl group *trans* to silyl group), 129.66 (*meta*-carbon of phenyl group *trans* to germyl group), 129.3 (*para*-carbon of phenyl group *trans* to silyl group), 129.2 ((*para*-carbon of phenyl group *trans* to germyl group), 129 (*ortho*-carbon of phenyl group *trans* to silyl group), 128.9 (*ortho*-carbon of phenyl group *trans* to germyl group), 128.0 (phenylene carbon *ortho* to silylethenyl group), 127.6 (phenylene carbon *ortho* to germylethenyl group), 127.4 (vinyl carbon bearing silyl group, $J_{C,Si} = 65$ Hz), 127.2 (vinyl carbon bearing germyl group), 9.1 (C1 of ethyl group), 5.7 (C2 of ethyl group), 0.1 (methyl carbon of $SiMe_3$, $J_{Si,C} = 53.3$ Hz) ppm. ^{29}Si-NMR ($CDCl_3$, 79.6 Hz): $\delta - 8.92$ ppm. IR (KBr disk): 3050 (w), 3005 (w), 2950 (s), 1590 (m), 1560 (m), 1500 (m), 1490 (m), 1480 (m), 1460 (m), 1245 (m), 830 (s), 760 (s), 700 (s) cm^{-1}. LRMS (FD): 514 (M$^+$). HRMS (FD): calcd for $C_{31}H_{40}GeSi$, 514.2111; found, 514.2103.

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