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Palladium-Catalyzed Germylation of Aryl Bromides and Aryl Triflates Using Hexamethyldigermane

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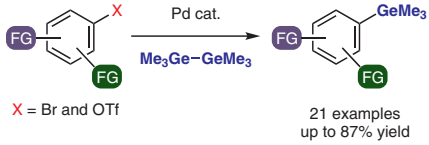

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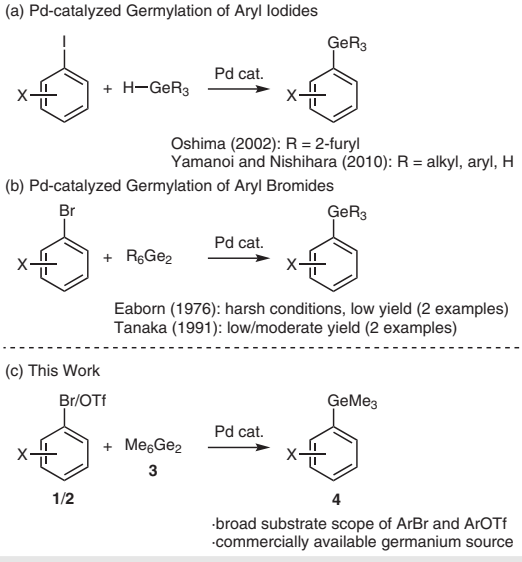
Abstract Palladium-catalyzed germylation of aryl bromides and aryl triflates using commercially available hexamethyldigermane is described. Optimized reaction conditions afforded various functionalized aryltrimethylgermanes, including drug-like molecules, in moderate to good yields, demonstrating the versatility of the presented protocols.

Key words palladium catalysis, germylation, digermane, aryl bromide, aryl triflate

Organosilicon[1] and organotin[2] compounds are useful reagents in organic synthesis and can be applied to a variety of synthetic transformations, including transition-metal-catalyzed cross-coupling reactions. Organogermanium compounds, however, have attracted much less attention. Germanium is located between silicon and tin in the periodic table, and the properties of a C–Ge bond are intermediate between a C–Si bond and a C–Sn bond.[3] Arylgermanes are expected to be more reactive toward electrophiles[4] than arylsilanes due to the stronger β-effect from the C–Ge bond compared with the C–Si bond.[5] Organotin compounds are more reactive, but highly toxic.[6] Therefore, arylgermanes are potentially attractive synthetic intermediates, but only a limited number of synthetic reactions using arylgermanes are reported.[3,4b–d,7,8] This is in part due to the high cost of germanium, but the lack of the general methods to prepare arylgermanes is also an important issue. Nucleophilic substitution of halogermanes by aryllithium or Grignard reagents is the most reliable method for accessing arylgermanes.[3b] These highly reactive organometallic reagents are, however, incompatible with sensitive functional groups.

Transition-metal-catalyzed silylation of aryl (pseudo)halides using disilanes[9] or hydrosilanes[10] has been extensively investigated over the last several decades for synthesizing arylsilanes without using aryllithium or Grignard reagents. On the other hand, studies of transition-metal-catalyzed germylation of aryl halides are scarce,[8c,9b,10h,k,11] although such reactions enable the direct synthesis of functionalized arylgermanes. Oshima achieved Pd-catalyzed germylation of aryl iodides using tri(2-furyl)germane (Scheme 1a),[8c] but electron-deficient aryl iodides were not investigated, and an aryl bromide was unreactive. Yamanoi and Nishihara reported general conditions for Pd-catalyzed coupling reactions of various aryl iodides and hydrogermanes (Scheme 1a).[10k] In contrast to aryl iodides, less reactive aryl bromides are still difficult substrates for germylation (Scheme 1b). Eaborn reported Pd-catalyzed germylation of aryl bromides with hexaethyldigermane, but the reactions required harsh conditions (140–180 °C) and re-



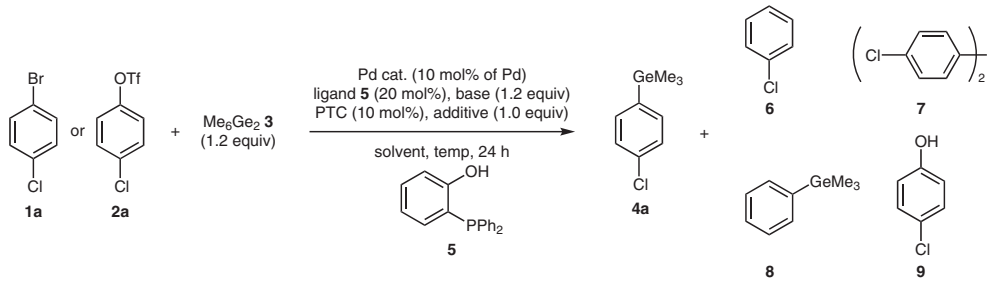
Scheme 1 Germylation of aryl (pseudo)halides

sulted in a low yield.[9b] Tanaka reported Pd-catalyzed germylation of bromobenzene and 2,5-dibromothiophene, but moisture sensitive dichlorotetramethyldigermane was required, and the results were rather complicated due to halogen exchange.[11] To date, general and practical conditions for transition-metal-catalyzed germylation of aryl bromides and aryl triflates have not been reported.

In this article, we report Pd-catalyzed germylation of aryl bromides **1** and aryl triflates **2** using commercially available hexamethyldigermane (**3**) (Scheme 1c).

We initiated our investigation by optimizing the reaction conditions for germylation of aryl bromide **1a** using hexamethyldigermane (**3**) (Table 1, entries 1–10). The reaction conditions of Pd-catalyzed silylation of aryl halides with hexamethyldisilane reported by Shirakawa and Hiyama[9g] were selected as the initial conditions (entries 1,2). These conditions afforded the desired germylated arene **4a** in moderate yield along with several by-products. GC/MS analysis revealed the formation of reduced product **6**, biaryl **7**, and unidentified products bearing an allyl or propenyl

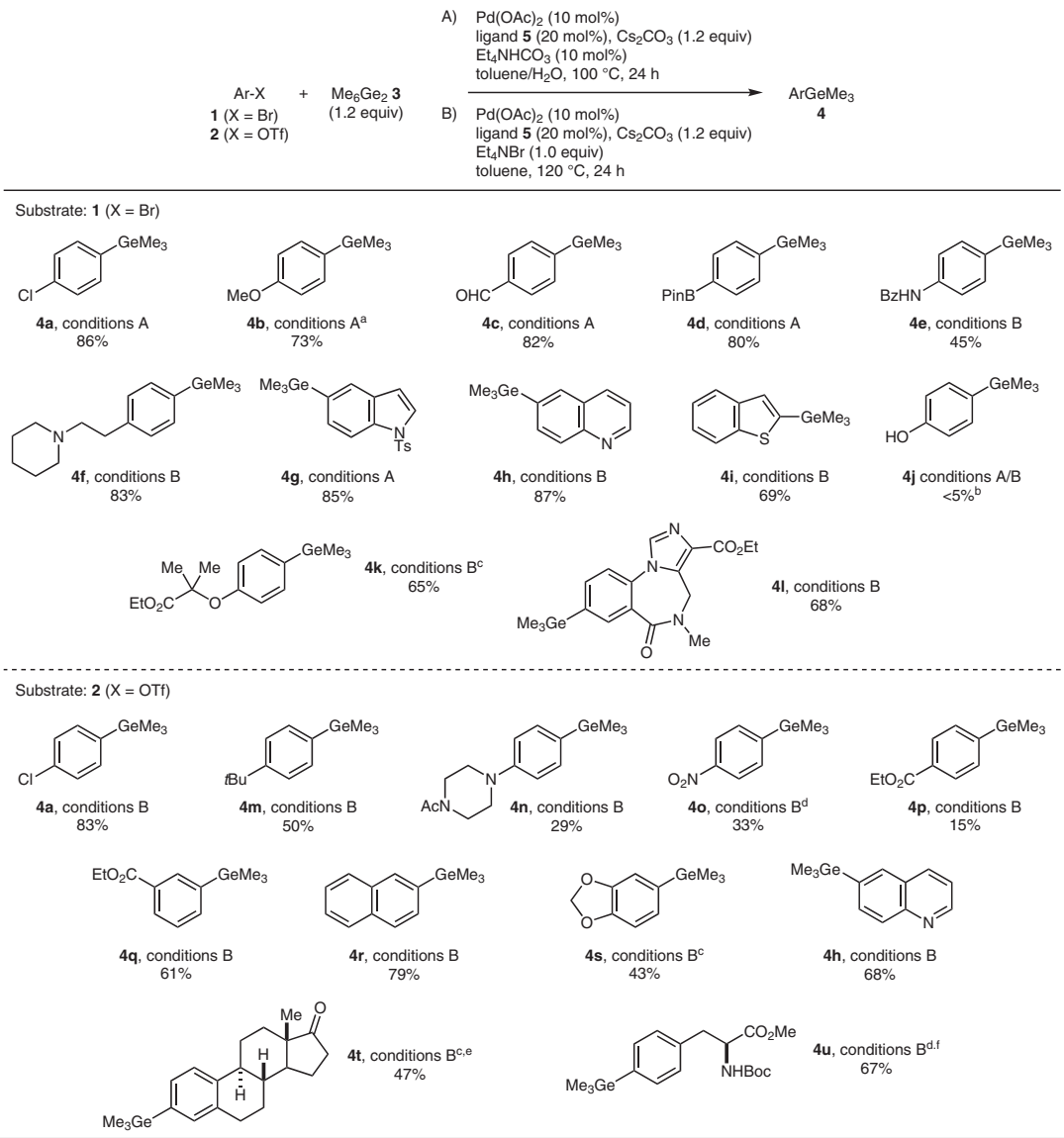
Table 1 Optimization of Reaction Conditions for Germylation of **1a** and **2a**[a]



Entry	Substrate	Pd cat.	Solvent	Base	PTC	Additive	Temp (°C)	Yield of **4a** (%)[b]	Ratio of **1a**/**2a**:**4a**:**6**:**7**:**8**:**9**[c]
1	**1a**	$[PdCl(allyl)]_2$	THF/H_2O	NaOH	Bu_4NBr	–	100	44	2:75:4:18:0:0
2	**1a**	$[PdCl(allyl)]_2$	toluene/H_2O	NaOH	Bu_4NBr	–	100	60	3:80:13:3:1:0
3	**1a**	$Pd_2(dba)_3$	toluene/H_2O	NaOH	Bu_4NBr	–	100	39	0:65:12:21:2:0
4	**1a**	$Pd(OAc)_2$	toluene/H_2O	NaOH	Bu_4NBr	–	100	62	0:73:3:23:1:0
5	**1a**	$Pd(OAc)_2$	toluene/H_2O	KO*t*-Bu	Bu_4NBr	–	100	48	0:66:2:32:1:0
6	**1a**	$Pd(OAc)_2$	toluene/H_2O	KOAc	Bu_4NBr	–	100	47	0:67:25:6:2:0
7	**1a**	$Pd(OAc)_2$	toluene/H_2O	Cs_2CO_3	Bu_4NBr	–	100	77	0:89:6:4:1:0
8	**1a**	$Pd(OAc)_2$	toluene/H_2O	Cs_2CO_3	Bu_4NOAc	–	100	56	20:59:0:21:0:0
9	**1a**	$Pd(OAc)_2$	toluene/H_2O	Cs_2CO_3	Et_4NHCO_3	–	100	93 (86)[d]	0:92:8:0:0:0
10[e]	**1a**	$Pd(OAc)_2$	toluene/H_2O	Cs_2CO_3	Et_4NHCO_3	–	100	63	0:71:3:0:26:0
11	**2a**	$Pd(OAc)_2$	toluene/H_2O	Cs_2CO_3	Et_4NHCO_3	–	100	0	99:0:0:0:0:1
12	**2a**	$Pd(OAc)_2$	toluene	Cs_2CO_3	Et_4NHCO_3	–	100	11	25:16:0:0:16:43
13	**2a**	$Pd(OAc)_2$	toluene	Cs_2CO_3	Et_4NHCO_3	LiCl	100	13	61:11:0:0:5:23
14	**2a**	$Pd(OAc)_2$	toluene	Cs_2CO_3	Et_4NHCO_3	LiBr	100	9	94:5:1:0:0:0
15	**2a**	$Pd(OAc)_2$	toluene	Cs_2CO_3	Et_4NHCO_3	Bu_4NCl	100	2	94:2:0:0:0:4
16	**2a**	$Pd(OAc)_2$	toluene	Cs_2CO_3	Et_4NHCO_3	Bu_4NBr	100	8	88:7:0:0:0:5
17	**2a**	$Pd(OAc)_2$	toluene	Cs_2CO_3	Et_4NHCO_3	Bu_4NI	100	15	57:22:0:4:1:16
18	**2a**	$Pd(OAc)_2$	toluene	Cs_2CO_3	Et_4NHCO_3	Et_4NCl	100	35	7:54:1:0:9
19	**2a**	$Pd(OAc)_2$	toluene	Cs_2CO_3	Et_4NHCO_3	Et_4NBr	100	49	30:42:0:2:14:12
20	**2a**	$Pd(OAc)_2$	toluene	Cs_2CO_3	Et_4NHCO_3	Et_4NBr	120	77	2:59:0:0:27:12
21	**2a**	$Pd(OAc)_2$	toluene	Cs_2CO_3	–	Et_4NBr	120	85 (83%)[d]	1:66:2:0:24:7

[a] The reactions were performed using **1a** or **2a** (0.10 mmol), **3** (0.12 mmol), Pd cat. (10 mol% of Pd), ligand **5** (0.02 mmol, 20 mol%), PTC (0.01 mmol, 10 mol%), and base (0.12 mmol) in THF/H_2O (1:1) or toluene/H_2O (1:1), or toluene (0.5 mL) for 24 h, unless otherwise noted.
[b] Determined by GC/MS analysis using pentadecane as an internal standard.
[c] The radio of the TIC area in GC/MS analysis.
[d] Isolated yield in 0.50 mmol scale.
[e] PPh_3 (0.02 mmol, 20 mol%) was used as a ligand instead of **5**.

group. Other palladium sources using toluene/H_2O as the solvent were next investigated to circumvent incorporation of the C3 units derived from $[PdCl(allyl)]_2$. While $Pd_2(dba)_3$ exhibited inferior catalytic activity (entry 3), the use of $Pd(OAc)_2$ resulted in 62% yield (entry 4). In these cases, incorporation of the C3 unit was avoided, but a significant amount of **7** was produced. Several bases and phase transfer catalysts (PTC) were then screened to improve the selectivity (entries 5–9), and Cs_2CO_3 and Et_4NHCO_3 were the most effective for providing **4a** in 93% yield, with only a tiny amount of **6** (entry 9). A control experiment using PPh_3 as a ligand instead of **5** (entry 10) was performed. The reaction unexpectedly proceeded with moderate yield, but a relatively large amount of phenyl(trimethyl)germane (**8**) was observed. This by-product would be formed by reduction of **4a** or an aryl–aryl exchange between an arylpalladium intermediate and PPh_3 during the catalytic process.[12] Germylation of aryl triflate **2a** (entries 11–21) was investigated next. The optimized conditions for aryl bromide **1a** in entry 9 afforded no products, and **2a** remained intact (entry



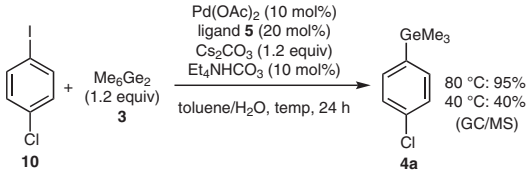
Scheme 2 Scope and limitations of the germylation of aryl bromides **1** and aryl triflates **2**. *Reagents and conditions A*: **1** (1.0 equiv), **3** (1.2 equiv), $Pd(OAc)_2$ (10 mol%), **5** (20 mol%), Et_4NHCO_3 (10 mol%), and Cs_2CO_3 (1.2 equiv) in toluene/H_2O at 100 °C for 24 h. *Reagents and conditions B*: **1** or **2** (1.0 equiv), **3** (1.2 equiv), $Pd(OAc)_2$ (10 mol%), ligand **5** (20 mol%), Cs_2CO_3 (1.2 equiv), and Et_4NBr (1.0 equiv) in toluene at 120 °C for 24 h. Isolated yields are shown. See experimental section for detailed conditions and scale of each substrate. [a] Reaction was carried out at 120 °C. [b] Only a trace amount of the desired product was observed in GC/MS analysis. [c] $Pd(OAc)_2$ (20 mol%) and **5** (40 mol%) were used. [d] KOAc instead of Cs_2CO_3 was used. [e] Reaction was carried out at 130 °C. [f] Digermane **3** (2.0 equiv) was used, 62 h.

11). The use of toluene as the sole solvent provided the desired product **3**, but the yield was low and a significant amount of **9** was observed (entry 12). We speculated the lower reactivity of **2a** compared with **1a** might be due to the absence of a halide ion in the reaction, and several halide sources were screened as potential additives (Table 1, entries 13–19). The addition of one equivalent of Et_4NBr was found to be effective, and the yield was improved to 49% (entry 19). Raising the reaction temperature to 120 °C further improved the yield (entry 20). Finally, the conditions without Et_4NHCO_3 resulted in a slightly better yield (entry 21), and were determined to be the optimal conditions for **2a**. Although a significant amount of **8** was observed at 120 °C, the yield of **4a** based on an internal standard was high (entries 20 and 21), indicating that **8** was derived from ligand **5** rather than **2a** or **4a** in these cases.

The scope and limitations of the optimized conditions for germylation are summarized in Scheme 2. Both electron-deficient and electron-rich aryl bromides afforded the desired products in good yields (**4a**, **4b**). Various functional groups were well tolerated, providing germylated building blocks that are useful for further transformation (**4c–f**). Heteroaryl bromides were reactive to give the corresponding germylated products (**4g**, **4h**, **4i**). The conditions optimized for aryl triflates (Conditions B) were more effective for less reactive aryl bromides to afford **4f**, **4h** and **4i**. 4-Bromophenol (**1j**), however, failed to give the germylated product **4j**, and phenol was detected as a major product under both reaction conditions. Germylated drug-like structures (**4k**,[13] **4l**[14]) were accessible from the corresponding aryl bromides under Conditions B. In addition to aryl bromides, various types of aryl triflates afforded the desired germylated arenes. Electron-rich arenes such as **2n** and **2s** exhibited low reactivity (**4n**, **4s**), while highly electron-deficient substrates resulted in low yields due to fast hydrolysis of the sulfonate group (**4o**, **4p**). In some cases, the use of KOAc instead of Cs_2CO_3 was beneficial for avoiding the hydrolysis (**4o**, **4u**). Moderately electron-deficient aryl triflates were good substrates, and the products were obtained in good yield (**4a**, **4q**, **4r**, **4h**) under the standard conditions. The triflate of estrone **2t** exhibited low reactivity, but moderate yield was obtained using 20 mol% of $Pd(OAc)_2$ (**4t**).

We also investigated germylation of aryl iodide **10** under the optimized conditions for aryl bromides (Scheme 3). The conditions for aryl bromides were effective to provide **4a** in 95% yield at 80 °C, but the lower reaction temperature resulted in lower conversion.

When β-bromostyrene was used as a substrate, both Conditions A and Conditions B in Scheme 2 afforded a dimerized product as a major product (see Supporting Information). Thus, the developed conditions were not suitable for germylation of alkenyl bromides.



Scheme 3 Germylation of aryl iodide **10**

The exact catalytic cycle was not elucidated, but a plausible cycle comprises oxidative addition of **1** or **2** to Pd(0), transmetalation with digermane **3**, and reductive elimination to release arylgermane **4**. The use of PPh_3 as a ligand also afforded the product in moderate yield (Table 1, entry 10), and therefore a hydroxy group of **5** would only have minor effects for the desired catalytic cycle, in contrast to the dramatic ligand effects observed in silylation.[9g] The role of Et_4NBr in germylation of aryl triflates was unclear. A tetraethylammonium ion might be important rather than a bromide ion (entries 13–19).

In summary, we have developed general conditions for the germylation of aryl bromides **1** and aryl triflates **2** using hexamethyldigermane (**3**) under palladium catalysis. Various functionalized substrates, including drug-like molecules, afforded the germylated products in moderate to good yields, demonstrating the versatility of the presented protocols. These methods enable easy access to functionalized arylgermanes, and may encourage further investigation of the properties and reactivity of arylgermane derivatives.

Reported melting points are uncorrected. IR spectra were recorded on a JASCO FT/IR-5300 spectrophotometer and absorbance bands are reported in wave numbers (cm^{-1}). NMR spectra were recorded on JEOL JNM-ECS400 spectrometers operating at 391.78 MHz for ^1H NMR and 98.52 MHz for ^{13}C NMR, JEOL JNM-ECX400 spectrometers operating at 395.88 MHz for ^1H NMR and 99.55 MHz for ^{13}C NMR, and JNM-ECA500 spectrometers operating at 500.16 MHz for ^1H NMR and 125.77 MHz for ^{13}C NMR. Chemical shifts were reported in the scale relative to TMS (0.00 ppm for ^1H NMR), $CHCl_3$ (7.26 ppm for ^1H NMR), $CDCl_3$ (77.0 ppm for ^{13}C NMR), C_6HD_5 (7.15 ppm for ^1H NMR), and C_6D_6 (128.06 ppm for ^{13}C NMR) as an internal reference, respectively. ESI mass spectra were recorded on JEOL JMS-T100LCP spectrometer. Silica gel column chromatography was performed with Kanto Silica gel 60 N (40–50 mesh). Gel permeation chromatography was performed with YMC LC-forte/R using $CHCl_3$ as an eluent. Commercially available THF, toluene (Wako Ltd., deoxidized grade) were used without further manipulation unless otherwise stated. All aryl triflates **2** were prepared from the corresponding commercially available phenol. Aryl bromides **1a**, **1b**, **1c**, **1d**, **1h**, **1i** were commercially available and distilled under reduced pressure or recrystallized before use. 1-(4-Bromophenethyl)piperidine (**1f**),[15] 5-bromo-1-tosyl-1*H*-indole (**1g**),[16] 2-bromobenzo[*b*]thiophene (**1i**),[17] and ethyl 8-bromo-5-methyl-6-oxo-5,6-dihydro-4*H*-benzo[*f*]imidazo[1,5-*a*][1,4]diazepine-3-carboxylate (**1l**)[14] were synthesized according to the literature. Structures of bromides **1** and aryl triflates **2** are listed in Figure S1 in Sup-

porting Information. Hexamethyldigermane (**3**) was purchased from Sigma-Aldrich and used as received. All other reagents were commercially available and used as received.

Germylation of Aryl Bromides 1 and Triflates 2; General Procedure

Conditions A: To a screw vial with a septum cap were added aryl bromide **1** (0.50 mmol), $Pd(OAc)_2$(11.2 mg, 0.05 mmol, 10 mol%), ligand **5** (27.8 mg, 0.10 mmol, 20 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol, 1.2 equiv), Et_4NHCO_3 (9.5 mg, 0.05 mmol, 10 mol%), hexamethyldigermane (**3**; 120 µL, 0.60 mmol, 1.2 equiv), and toluene (1.25 mL) under argon atmosphere in a glove box. The vial was capped and removed from the glove box, and then H_2O (1.25 mL) was injected via syringe. The vial was heated at 100 °C for 24 h with stirring. After cooling to r.t., the organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 3 mL). The combined organic layers were washed with brine (3 mL) and dried (Na_2SO_4). After filtration and evaporation, purification of the crude product by silica gel column chromatography afforded the corresponding product **4**.

Conditions B: To a dried screw capped vial were added aryl bromide **1** or aryl triflate **2** (0.50 mmol), $Pd(OAc)_2$(11.2 mg, 0.05 mmol, 10 mol%), ligand **5** (27.8 mg, 0.10 mmol, 20 mol%), Cs_2CO_3 (195.5 mg, 0.60 mmol, 1.2 equiv), Et_4NBr (105.1 mg, 0.5 mmol, 1.0 equiv), hexamethyldigermane (**3**; 120 µL, 0.60 mmol, 1.2 equiv), and toluene (2.5 mL) under argon atmosphere in a glove box. The vial was capped and heated at 120 °C for 24 h with stirring. After cooling to r.t., H_2O (2 mL) was added. After dilution with EtOAc, the organic layer was separated, and the aqueous layer was extracted with EtOAc (3 × 3 mL). The combined organic layers were washed with brine (3 mL) and dried (Na_2SO_4). After filtration and evaporation, purification of the crude product by silica gel column chromatography afforded the corresponding product **4**.

(4-Chlorophenyl)trimethylgermane (4a)

Conditions A using 1-bromo-4-chlorobenzene (**1a**; 0.50 mmol) and purification of the crude product by silica gel column chromatography (hexane) followed by gel permeation chromatography afforded **4a** as a colorless oil (98.6 mg, 86%). Conditions B using 4-chlorophenyl trifluoromethanesulfonate (**2a**; 0.50 mmol) and purification of the crude product by silica gel column chromatography (hexane) afforded **4a** as a colorless oil (95.1 mg, 83%); R_f = 0.75 (hexane).

IR (neat): 2972, 2907,1481, 1381, 1238, 1077, 1015, 825, 602, 571 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.38 (m, 2 H), 7.33–7.30 (m, 2 H), 0.38 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 134.5, 134.3, 128.1, –1.83.

HRMS (EI): *m*/*z* (M^+) calcd for $C_9H_{13}Cl^{70}Ge$: 225.9948; found: 225.9945.

(4-Methoxyphenyl)trimethylgermane (4b)

Conditions A using 1-bromo-4-methoxybenzene (**1b**) at 120 °C and purification of the crude product by silica gel column chromatography (hexane/EtOAc 20:1) afforded **4b** as a colorless oil (82.0 mg, 73%); R_f = 0.59 (hexane/EtOAc 8:1).

IR (neat): 2969, 2905, 1592, 1568, 1499, 1461, 1279, 1246, 1180, 1094, 1032, 823, 599, 567 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.37 (m, 2 H), 6.94–6.90 (m, 2 H), 3.81 (s, 3 H), 0.36 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 134.1, 133.2, 113.7, 55.0, –1.66.

HRMS (EI): *m*/*z* (M^+) calcd for $C_{10}H_{16}{}^{70}GeO$: 222.0444; found: 222.0444.

4-(Trimethylgermyl)benzaldehyde (4c)

Conditions A using 4-bromobenzaldehyde (**1c**) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 30:1 to 20:1) followed by gel permeation chromatography afforded **4c** as a colorless oil (91.2 mg, 82%); R_f = 0.65 (hexane/EtOAc 5:1).

IR (neat): 2979, 2911, 2825, 1703, 1594, 1211, 1172, 825, 679, 603, 571 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.01 (s, 1 H), 7.83 (d, *J* = 8.1 Hz, 2 H), 7.65 (d, *J* = 8.1 Hz, 2 H), 0.43 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.7, 151.9, 136.1, 133.5, 128.8, –1.93.

HRMS (EI): *m*/*z* (M^+) calcd for $C_{10}H_{14}{}^{70}GeO$: 220.0287; found: 222.0286.

Trimethyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]germane (4d)

Conditions A using 2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**1d**) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 20:1) afforded **4d** as a colorless solid (128.3 mg, 80%); mp 119.3–120.2 °C; R_f = 0.73 (hexane/EtOAc 5:1).

IR (KBr): 2977, 1598, 1327, 1296, 1108, 859, 656, 602 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.2 Hz, 2 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 1.34 (s, 12 H), 0.38 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.6, 134.0, 132.3, 83.7, 24.8, –1.91; the carbon directly attached to the boron atom was not detected.

HRMS (ESI): *m*/*z* (M + Na^+) calcd for $C_{15}H_{25}B^{70}GeO_2Na$: 340.1124; found: 340.1134.

N-[4-(Trimethylgermyl)phenyl]benzamide (4e)

Conditions B using *N*-(4-bromophenyl)benzamide (**1e**) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 10:1 to 5:1) afforded **4e** as a colorless solid (70.1 mg, 45%); mp 114.6–115.3 °C; R_f = 0.65 (hexane/EtOAc 2:1).

IR (KBr): 3311, 2972, 1578, 1525, 1504, 1388, 1322, 1285, 819, 720, 694, 593 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.85 (m, 2 H), 7.76 (br s, 1 H), 7.63 (d, *J* = 8.2 Hz, 2 H), 7.58–7.47 (m, 5 H), 0.39 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.8, 138.4, 138.0, 134.9, 133.7, 131.8, 128.7, 127.0, 119.7, –1.78.

HRMS (ESI): *m*/*z* (M + Na^+) calcd for $C_{16}H_{19}{}^{70}GeNONa$: 334.0601; found: 334.0603.

1-[4-(Trimethylgermyl)phenethyl]piperidine (4f)

Conditions B using 1-(4-bromophenethyl)piperidine (**1f**; 268 mg, 1.0 mmol) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 6:1, 3% Et_3N) afforded **4f** as a yellow oil (255 mg, 83%); R_f = 0.38 (hexane/EtOAc 6:1, 3% Et_3N).

IR (neat): 2969, 2934, 2853, 2798, 1758, 1235, 1155, 1120, 1090, 823, 757, 600, 572 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (d, *J* = 8.2 Hz, 2 H), 7.20 (d, *J* = 8.2 Hz, 2 H), 2.83–2.77 (m, 2 H), 2.59–2.53 (m, 2 H), 2.51–2.44 (m, 4 H), 1.67–1.59 (m, 4 H), 1.50–1.42 (m, 2 H), 0.36 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 140.6, 139.5, 132.9, 128.3, 61.3, 54.5, 33.5, 25.9, 24.4, –1.84.

HRMS (ESI): *m*/*z* (M + H^+) calcd for $C_{16}H_{28}{}^{70}GeN$: 304.1459; found: 304.1461.

Tosyl-5-(trimethylgermyl)-1*H*-indole (4g)

Conditions A using 5-bromo-1-tosyl-1*H*-indole (**1g**) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 10:1 to 8:1) afforded **4g** as a colorless solid (165 mg, 85%); mp 110.2–110.8 °C; R_f = 0.50 (hexane/EtOAc 5:1)

IR (KBr): 3140, 3111, 2968, 2916, 1447, 1371, 1257, 1188, 1172, 1131, 1095, 996, 585, 576 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.97 (d, *J* = 8.3 Hz, 1 H), 7.77 (d, *J* = 8.3 Hz, 2 H), 7.63 (s, 1 H), 7.54 (d, *J* = 3.7 Hz, 1 H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1 H), 7.22 (d, *J* = 8.3 Hz, 2 H), 6.64 (d, *J* = 3.7 Hz, 1 H), 2.34 (s, 3 H), 0.38 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 144.9, 136.6, 135.4, 135.0, 130.6, 129.9, 128.9, 126.8, 126.1, 126.0, 113.0, 108.7, 21.5, –1.62.

HRMS (ESI): *m*/*z* (M + Na^+) calcd for $C_{18}H_{21}{}^{70}GeNO_2SNa$: 408.0428; found: 408.0442.

6-(Trimethylgermyl)quinoline (4h)

Conditions A using 6-bromoquinoline (**1h**) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 5:1) afforded **4h** as a colorless oil (107 mg, 87%). Conditions B using quinolin-6-yl trifluoromethanesulfonate (**2h**) and purification of the crude product by silica gel column chromatography (hexane/EtOAc = 5:1) afforded **4h** as a colorless oil (83.5 mg, 68%); R_f = 0.30 (hexane/EtOAc 4:1).

IR (neat): 2970, 2906, 1564, 1491, 1341, 1237, 1071, 856, 831, 799, 771, 623, 601, 587, 567 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.91 (dd, *J* = 4.0, 1.7 Hz, 1 H), 8.15 (d, *J* = 8.0 Hz, 1 H), 8.08 (d, *J* = 8.0 Hz, 1 H), 7.92 (s, 1 H), 7.82 (dd, *J* = 8.0, 1.1 Hz, 1 H), 7.40 (dd, *J* = 8.0, 4.0 Hz, 1 H), 0.48 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 150.4, 148.3, 141.4, 135.8, 133.5, 132.8, 128.5, 127.9, 121.1, –1.77.

HRMS (ESI): *m*/*z* (M + H^+) calcd for $C_{12}H_{16}{}^{70}GeN$: 244.0520; found: 244.0523.

Benzo[*b*]thiophen-2-yltrimethylgermane (4i)

Conditions B using 2-bromobenzo[*b*]thiophene (**1i**) and purification of the crude product by silica gel column chromatography (hexane) followed by gel permeation chromatography afforded **4i** as a colorless oil (87.1 mg, 69%); R_f = 0.67 (hexane/EtOAc 20:1).

IR (neat): 3056, 2973, 2907, 1453, 1240, 945, 826, 761, 744, 726, 605, 574, 561 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, *J* = 7.7 Hz, 1 H), 7.79 (d, *J* = 7.7 Hz, 1 H), 7.38 (s, 1 H), 7.35–7.26 (m, 2 H), 0.51 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.7, 143.4, 141.1, 129.6, 124.1, 123.9, 123.2, 122.2, –0.53.

HRMS (EI): *m*/*z* (M^+) calcd for $C_{11}H_{14}{}^{70}GeS$: 248.0059; found: 248.0057.

Ethyl 2-(4-Bromophenoxy)-2-methylpropanoate (1k)

4-Bromophenol (519 mg, 3.0 mmol) and Cs_2CO_3 (2.44 g, 7.5 mmol, 2.5 equiv) were dissolved in anhyd DMF (10 mL). The solution was stirred for 10 min, and then ethyl 2-bromoisobutyrate (1.17 g, 6.0 mmol, 2.0 equiv) was added. The resulting reaction mixture was stirred at 100 °C for 23 h. After cooling to r.t., the residue was taken up in EtOAc (50 mL). The solution was successively washed with H_2O (2 × 20 mL) and brine (20 mL), and dried (Na_2SO_4). After filtration and evaporation, the crude product was purified by silica gel column chromatography to give **1k** as a colorless oil (818 mg, 95%); R_f = 0.50 (hexane/EtOAc 5:1).

IR (neat): 2987, 2938, 1734, 1587, 1486, 1468, 1383, 1284, 1238, 1177, 1140, 1073, 1023, 1007, 825, 647 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.31 (m, 2 H), 6.75–6.71 (m, 2 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 1.58 (s, 6 H), 1.25 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.9, 154.5, 132.0, 120.8, 114.5, 79.4, 61.5, 25.2, 14.1.

HRMS (ESI): *m*/*z* (M + Na^+) calcd for $C_{12}H_{15}BrO_3Na$: 24 309.0097; found: 309.0100.

Ethyl 2-Methyl-2-[4-(trimethylgermyl)phenoxy]propanoate (4k)

Conditions B using ethyl 2-(4-bromophenoxy)-2-methylpropanoate (**1k**; 114.9 mg, 0.40 mmol), $Pd(OAc)_2$(20 mol%), and ligand **5** (40 mol%), and purification of the crude product by silica gel column chromatography (hexane/EtOAc = 10:1) followed by gel permeation chromatography afforded **4k** as a colorless oil (84.4 mg, 65%); R_f = 0.63 (hexane/EtOAc 5:1).

IR (neat): 2977, 2906, 1733, 1590, 1498, 1382, 1272, 1237, 1178, 1142, 1093, 1024, 824, 761, 599, 569 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.30 (m, 2 H), 6.84–6.80 (m, 2 H), 4.24 (q, *J* = 7.1 Hz, 2 H), 1.60 (s, 6 H), 1.25 (t, *J* = 7.1 Hz, 3 H), 0.34 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.3, 155.7, 134.8, 133.8, 118.4, 78.8, 61.4, 25.4, 14.0, –1.69.

HRMS (ESI): *m*/*z* (M + Na^+) calcd for $C_{15}H_{24}{}^{70}GeO_3Na$: 345.0860; found: 345.0862.

Ethyl 5-Methyl-6-oxo-8-(trimethylgermyl)-5,6-dihydro-4*H*-benzo[*f*]imidazo[1,5-*a*][1,4]diazepine-3-carboxylate (4l)

Conditions B using ethyl 8-bromo-5-methyl-6-oxo-5,6-dihydro-4*H*-benzo[*f*]imidazo[1,5-*a*][1,4]diazepine-3-carboxylate (**1l**; 109.3 mg, 0.30 mmol) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 1:2 to 1:3) afforded **4l** as a pale yellow solid (82 mg, 68%); mp 164.5–165.2 °C; R_f = 0.36 (toluene/EtOAc 1:3).

IR (KBr): 3112, 2975, 2905, 1728, 1704, 1647, 1503, 1296, 1260, 1189, 1109, 1065, 833, 605 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.15 (d, *J* = 1.4 Hz, 1 H), 7.90 (s, 1 H), 7.72 (dd, *J* = 7.7, 1.4 Hz, 1 H), 7.38 (d, *J* = 7.7 Hz, 1 H), 5.25–5.14 (m, 1 H), 4.55–4.29 (m, 3 H), 3.26 (s, 3 H), 1.46 (t, *J* = 7.2 Hz, 3 H), 0.45 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.8, 162.9, 144.1, 137.1, 136.8, 135.5, 134.8, 131.8, 128.5, 128.0, 120.9, 60.8, 42.2, 35.7, 14.3, –1.9.

HRMS (ESI): *m*/*z* (M + Na^+) calcd for $C_{18}H_{23}{}^{70}GeN_3O_3Na$: 422.0874; found: 422.0877.

[4-(*tert*-Butyl)phenyl]trimethylgermane (4m)

Conditions B using 4-(*tert*-butyl)phenyl trifluoromethanesulfonate (**2m**) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 30:1 to 10:1) afforded **4m** as a colorless oil (63.2 mg, 50%); mp 69.2–70.0 °C; R_f = 0.72 (hexane/EtOAc 8:1).

IR (KBr): 3421, 2961, 2905, 2865, 1383, 1267, 1235, 1078, 818, 760, 602, 576, 552 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 2 H), 7.40–7.37 (m, 2 H), 1.32 (s, 9 H), 0.37 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 151.1, 138.9, 132.8, 124.9, 34.6, 31.3, –1.79.

HRMS (EI): *m*/*z* (M^+) calcd for $C_{13}H_{22}{}^{70}Ge$: 248.0964; found: 248.0960.

{4-[4-(Trimethylgermyl)phenyl]piperazin-1-yl}ethan-1-one (4n)

Conditions B using 4-(4-acetylpiperazin-1-yl)phenyl trifluoromethanesulfonate (**2n**) and purification of the crude product by silica gel column chromatography (EtOAc/MeOH 19:1) followed by gel permeation chromatography afforded **4n** as a pink solid (47.2 mg, 29%); mp 66.7–67.8 °C; R_f = 0.65 (EtOAc/MeOH 9:1).

IR (KBr): 3438, 2979, 2899, 2830, 1625, 1592, 1455, 1432, 1234, 998 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.39 (d, *J* = 8.6 Hz, 2 H), 6.93 (d, *J* = 8.6 Hz, 2 H), 3.77 (t, *J* = 5.2 Hz, 2 H), 3.62 (t, *J* = 5.2 Hz, 2 H), 3.20 (t, *J* = 5.2 Hz, 2 H), 3.16 (t, *J* = 5.2 Hz, 2 H), 2.14 (s, 3 H), 0.35 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 169.0, 150.9, 133.9, 133.0, 116.2, 49.4, 49.1, 46.2, 41.3, 21.4, –1.72.

HRMS (ESI): *m*/*z* (M + Na^+) calcd for $C_{15}H_{24}{}^{70}GeN_2ONa$: 341.1023; found: 341.1025.

Trimethyl(4-nitrophenyl)germane (4o)

Conditions B using 4-nitrophenyl trifluoromethanesulfonate (**2o**) and KOAc instead of Cs_2CO_3, and purification of the crude product by silica gel column chromatography (hexane/EtOAc 8:1) and gel permeation chromatography afforded **4o** as a pale yellow solid (39.2 mg, 33%); mp 40.2–41.7 °C; R_f = 0.59 (hexane/EtOAc 8:1).

IR (KBr): 3432, 3037, 2979, 2905, 1594, 1513, 1386, 1351, 1240, 835, 730, 711, 603 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.17 (d, *J* = 8.1 Hz, 2 H), 7.64 (d, *J* = 8.1 Hz, 2 H), 0.44 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 152.5, 148.2, 133.8, 122.3, –1.91.

HRMS (EI): *m*/*z* (M^+) calcd for $C_9H_{13}{}^{70}GeNO_2$: 237.0189; found: 237.0194.

Ethyl 4-(Trimethylgermyl)benzoate (4p)

Conditions B using ethyl 4-{[(trifluoromethyl)sulfonyl]oxy}benzoate (**2p**) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 20:1) followed by reverse phase column chromatography (C18, H_2O/MeCN 15:85) afforded **4p** as a colorless oil (20 mg, 15%); R_f = 0.61 (hexane/EtOAc 8:1).

IR (neat): 2975, 2927, 2908, 1720, 1277, 1266, 1081, 602, 570 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.99 (d, *J* = 8.0 Hz, 2 H), 7.55 (d, *J* = 8.0 Hz, 2 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 1.39 (t, *J* = 7.2 Hz, 3 H), 0.41 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.9, 149.2, 132.9, 130.2, 128.6, 60.9, 14.3, –1.92.

HRMS (APCI): *m*/*z* (M + H^+) calcd for $C_{12}H_{19}{}^{70}GeO_2$: 265.0622; found: 265.0623.

Ethyl 3-(Trimethylgermyl)benzoate (4q)

Conditions B using ethyl 3-{[(trifluoromethyl)sulfonyl]oxy}benzoate (**2q**) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 20:1) afforded **4q** as a colorless oil (81.4 mg, 61%); R_f = 0.54 (hexane/EtOAc 8:1).

IR (neat): 2976, 2906, 1719, 1410, 1365, 1261, 1172, 1116, 1071, 826, 742, 602, 570 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.99 (d, *J* = 7.4 Hz, 1 H), 7.66 (d, *J* = 7.4 Hz, 1 H), 7.41 (dd, *J* = 7.4, 7.4 Hz, 1 H), 4.39 (q, *J* = 7.3 Hz, 2 H), 1.40 (t, *J* = 7.3 Hz, 3 H), 0.41 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.0, 143.0, 137.4, 133.9, 129.8, 129.4, 127.8, 60.9, 14.4, –1.83.

HRMS (EI): *m*/*z* (M^+) calcd for $C_{12}H_{18}{}^{70}GeO_2$: 264.0549; found: 264.0551.

Trimethyl(naphthalen-2-yl)germane (4r)

Conditions B using 2-naphthyl trifluoromethanesulfonate (**2r**) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 20:1) afforded **4r** as a colorless oil (97 mg, 79%); R_f = 0.77 (hexane/EtOAc 8:1).

IR (neat): 3051, 2971, 2906, 1236, 1073, 815, 757, 738, 630, 600, 579, 564 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.94 (s, 1 H), 7.84–7.80 (m, 3 H), 7.57 (d, *J* = 7.4 Hz, 1 H), 7.49–7.44 (m, 2 H), 0.46 (s, 9 H).

^{13}C NMR (100 MHz, C_6D_6): δ = 133.7, 127.8, 127.5, 127.1, 123.8, 121.8, 121.8, 121.3, 119.9, 119.8, –8.13.

HRMS (EI): *m*/*z* (M^+) calcd for $C_{13}H_{16}{}^{70}Ge$: 242.0495; found: 242.0496.

Benzo[*d*][1,3]dioxol-5-yltrimethylgermane (4s)

Conditions B using benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate (**2s**), $Pd(OAc)_2$(20 mol%), and ligand **5** (40 mol%) and purification of the crude product by silica gel column chromatography (hexane/EtOAc 20:1) afforded **4s** as a colorless oil (50.8 mg, 43%); R_f = 0.64 (hexane/EtOAc 8:1).

IR (KBr): 2974, 2905, 1482, 1414, 1232, 1050, 1040, 937, 881, 825, 590 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 6.94–6.92 (m, 2 H), 6.86–6.83 (m, 1 H), 5.93 (s, 2 H), 0.35 (s, 9 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.7, 147.4, 135.4, 126.3, 112.5, 108.6, 100.4, –1.61.

HRMS (EI): *m*/*z* (M^+) calcd for $C_{10}H_{14}{}^{70}GeO_2$: 236.0236; found: 236.0232.

(8*R*,9*S*,13*S*)-13-Methyl-3-(trimethylgermyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (4t)

Conditions B using (8*R*,9*S*,13*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl trifluoromethanesulfonate (**2t**; 402.4 mg, 1.0 mmol), $Pd(OAc)_2$ (20 mol%), and ligand **5** (40 mol%) at 130 °C and purification of the crude product by silica gel column chromatography (hexane/EtOAc 20:1 to 10:1) afforded **4t** as a colorless solid (174.0 mg, 47%); mp 119.3–120.2 °C; R_f = 0.75 (hexane/EtOAc 7:3).

IR (KBr): 3454, 2969, 2928, 2866, 2837, 1739, 1452, 1235, 1081, 828, 603 cm^{-1}.

^1H NMR ($CDCl_3$, 500 MHz): δ = 7.32–7.27 (m, 2 H), 7.22 (s, 1 H), 2.94 (dd, *J* = 8.9, 4.3 Hz, 2 H), 2.51 (dd, *J* = 18.9, 8.6 Hz, 1 H), 2.47–2.41 (m, 1 H), 2.36–2.29 (m, 1 H), 2.19–1.94 (m, 4 H), 1.68–1.59 (m, 2 H), 0.90 (s, 3 H), 0.37 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 220.7, 139.8, 139.4, 135.9, 133.7, 130.4, 124.9, 50.4, 47.9, 44.4, 38.0, 35.8, 31.5, 29.3, 26.5, 25.5, 21.5, 13.7, –1.84.

HRMS (ESI): *m*/*z* (M + Na^+) calcd for $C_{21}H_{30}{}^{70}GeONa$: 391.1431; found: 391.1431.

Methyl (*S*)-2-[(*tert*-Butoxycarbonyl)amino]-3-[4-(trimethylgermyl)phenyl]propanoate (4u)

Conditions B using methyl (*S*)-2-[(*tert*-butoxycarbonyl)amino]-3-(4-{[(trifluoromethyl)sulfonyl]oxy}phenyl)propanoate (**2u**) and KOAc instead of Cs_2CO_3 for 62 h, and purification of the crude product by silica gel column chromatography (hexane/EtOAc 10:1) afforded **4u** as a colorless solid (132.6 mg, 67%); mp 55.5–56.2 °C; R_f = 0.50 (EtOAc/MeOH 9:1).

IR (KBr): 3370, 2975, 1747, 1717, 1500, 1437, 1366, 1248, 1214, 1168, 825, 757, 600, 568 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$,50 °C): δ = 7.39 (d, *J* = 8.0 Hz, 2 H), 7.10 (d, *J* = 8.0 Hz, 2 H), 4.96–4.87 (m, 1 H), 4.62–4.52 (m, 1 H), 3.71 (s, 3 H), 3.13–3.06 (m, 1 H), 3.05–2.93 (m, 1 H), 1.40 (s, 9 H), 0.36 (s, 9 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 172.3, 155.0, 140.9, 135.9, 133.1, 128.9, 79.8, 54.3, 52.2, 38.2, 28.3, –1.85.

HRMS (ESI): *m*/*z* (M + Na^+) calcd for $C_{18}H_{29}{}^{70}GeNO_4Na$: 416.1231; found: 416.1234.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1609301.

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