Palladium-catalyzed highly regio-, stereo- and chemoselective carbogermanylation of allenes: a novel method for the synthesis of 2-arylallylgermane derivatives

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Supporting Information

General procedure for the three-component assembly of aryl iodide 1, allene 2 and stannylgermane 3. A 25-mL sidearm flask containing $Pd(dba)_2$ (0.050 mmol) was evacuated and purged with nitrogen several times. Aryl iodide **1** (1.00 mmol), allene **2** (1.50 mmol), stannylgermane **3** (1.00 mmol) and toluene (2.0 mL) were added to the system and the reaction mixture was stirred at 80 °C for 8 h. The crude reaction mixture was diluted with CH_2Cl_2 (50 mL), filtered through Celite and silica gel and concentrated in vacuo. The residue was chromatographed on a silica gel column (hexane/EtOAc = 98/2) to give the desired product **4**. Compounds **4a-k** were prepared by following this procedure.

General procedure for the reaction of allene 5 with stannylgermane 3. A 25-mL sidearm flask containing $Pd(dba)_2$ (0.05 mmol) was evacuated and purged with nitrogen several times. Allene **5** (1.10 mmol), stannylgermane **3** (1.00 mmol) and toluene (2.0 mL) were added to the system and the reaction mixture was stirred at 80 °C for 8 h. The crude reaction mixture was diluted with CH_2Cl_2 (50 mL), filtered through Celite and silica gel and concentrated in vacuo. The residue was chromatographed on a silica gel column (hexane/EtOAc = 9/1) to give desired product **6**.

Spectral data of compounds **4a-k** and **6** are listed below:

[(*Z*)-3-Cyclohexyl-2-(4-methoxyphenyl)-2-propenyl](trimethyl)germane (4a): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 5.28 (d, *J* = 9.5 Hz, 1H), 3.78 (s, 3H), 2.15 (m, 1H), 2.08 (s, 2H), 1.74 – 1.13 (m, 10H), -0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.29, 137.09, 135.71, 130.34, 127.44, 113.28, 55.22, 37.90, 33.29, 26.14, 26.11, 20.49, -1.50; HRMS calcd for $C_{19}H_{30}GeO$ 348.1508, found 348.1516.

[(*Z*)-3-Cyclohexyl-2-(2-methoxyphenyl)-2-propenyl](trimethyl)germane (4b): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18 (t, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 8.5

Hz, 1H), 6.86 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 5.20 (d, *J* = 9.0 Hz, 1H), 3.78 (s, 3H), 2.21 (m , 1H), 2.16 (s, 2H), 1.73 – 1.07 (m, 10H), -0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.84, 135.97, 134.83, 133.17, 130.52, 127.67, 120.45, 110.94, 55.34, 37.21, 33.27, 26.17, 26.09, 20.86, -1.59; HRMS calcd for $C_{19}H_{30}GeO$ 348.1508, found 348.1515.

[(*Z*)-3-Cyclohexyl-2-(4-nitrophenyl)-2-propenyl](trimethyl)germane (4c): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 5.49 (d, *J* = 9.0 Hz, 1H), 2.21 (m, 1H), 2.12 (s, 2H), 1.79 – 1.09 (m, 10H), -0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.30, 146.26, 139.12, 135.22, 126.95, 123.43, 38.18, 32.84, 25.96, 25.89, 20.09, -1.48; HRMS calcd for $C_{18}H_{27}GeNO_2$ 363.1254, found 363.1259.

1-(4-{(*Z*)-2-Cyclohexyl-1-[(1,1,1-trimethylgermyl)methyl]-1-ethenyl}phenyl) -1-ethanone (4d): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 5.45 (d, *J* = 9.0 Hz, 1H), 2.58 (s, 3H), 2.21 (m, 1H), 2.12 (s, 2H), 1.67 – 1.08 (m, 10H), -0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 197.80, 149.43, 135.82, 135.17, 133.71, 128.28, 126.47, 38.07, 32.98, 26.56, 26.04, 25.98, 20.09, -1.47; HRMS calcd for $C_{20}H_{30}GeO$ 360.1508, found 360.1516.

[(*Z*)-3-Cyclohexyl-2-phenyl-2-propenyl](trimethyl)germane (4e): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 5.34 (d, *J* = 9.5 Hz, 1H), 2.20 (m, 1H), 2.13 (s, 2H), 1.72 – 1.12 (m, 10H), -0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.57, 136.44, 131.60,

127.97, 126.50, 126.38, 37.94, 33.19, 26.12, 26.09, 20.44, -1.52; HRMS calcd for $C_{18}H_{28}Ge$ 318.1403, found 318.1407.

[(*Z*)-3-Cyclohexyl-2-(1-naphthyl)-2-propenyl](trimethyl)germane (4f): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 7.0, 2.5 Hz, 1H), 7.80 (dd, *J* = 7.0, 2.5 Hz, 1H), 7.68 (d, *J* = 7.0 Hz, 1H), 7.44 - 7.40 (m, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.0 Hz, 1H), 5.21 (d, *J* = 9.0 Hz, 1H), 2.31 (m, 1H), 2.18 (s, 2H), 1.82 – 1.13 (m, 10H), -0.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.91, 135.49, 134.31, 133.31, 133.82, 131.40, 128.27, 126.13, 125.35, 125.32, 125.22, 37.69, 33.29, 26.14, 26.11, 23.74, -1.39; HRMS calcd for $C_{22}H_{30}Ge$ 368.1559, found 368.1568.

[(*Z*)-3-Cyclohexyl-2-(2-thienyl)-2-propenyl](trimethyl)germane (4g): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (d, *J* = 5.0 Hz, 1H), 6.90 (t, *J* = 3.5 Hz, 1H), 6.85 (d, *J* = 3.0 Hz, 1H), 5.58 (d, *J* = 9.5 Hz, 1H), 2.19 (m, 1H), 2.03 (s, 2H), 1.74 – 1.10 (m, 10H), 0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.53, 130.26, 129.95, 126.94, 122.62, 122.15, 37.79, 33.01, 26.4, 26.02, 20.84, -1.40; HRMS calcd for $C_{16}H_{26}GeS$ 324.0967, found 324.0970.

[(*Z*)-2-(4-Bromophenyl)-3-cyclohexyl-2-propenyl](trimethyl)germane (4h): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 9.0 Hz, 2H), 5.32 (d, *J* = 9.0 Hz, 1H), 2.17 (m, 1H), 2.06 (s, 2H), 1.76 – 1.24 (m, 10H), -0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.49, 135.48, 132.17, 131.00, 128.12, 120.11, 37.97, 33.07, 26.07, 26.05, 20.27, -1.47; HRMS calcd for $C_{18}H_{27}BrGe$ 396.0508,

found 396.0510.

[(*Z*)-3-Cyclopentyl-2-(4-methoxyphenyl)-2-propenyl](trimethyl)germane (4i): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 5.35 (d, *J* = 9.0 Hz, 1H), 3.79 (s, 3H), 2.61 (m, 1H), 2.09 (s, 2H), 1.83 – 1.24 (m, 8H), -0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.27, 137.09, 136.15, 129.87, 127.43, 113.30, 55.22, 39.85, 33.81, 25.43, 20.61, -1.54; HRMS calcd for $C_{18}H_{28}GeO$ 334.1352, found 334.1355.

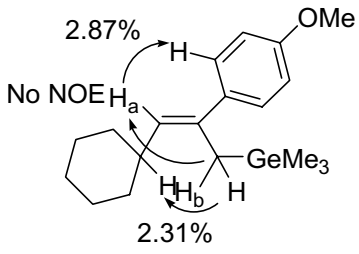
[(*Z*)-2-(4-Methoxyphenyl)-2-heptenyl](trimethyl)germane (4j): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 5.42 (t, *J* = 6.0 Hz, 1H), 3.78 (s, 3H), 2.07 (q, *J* = 7.0 Hz, 2H), 2.05 (s, 2H), 1.40 – 1.36 (m, 4H), 0.91 (t, *J* = 6.5 Hz, 3H), -0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.27, 137.56, 137.12, 127.33, 124.30, 113.46, 55.21, 32.07, 28.83, 22.58, 20.63, 14.09, -1.42; HRMS calcd for $C_{17}H_{28}GeO$ 322.1352, found 322.1355.

[(*Z*)-2-(4-Methoxyphenyl)-4,4-dimethyl-2-pentenyl](trimethyl)germane (4k): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (d, *J* = 8.5 Hz, 2H), 6.79 (d, *J* = 8.5 Hz, 2H), 5.36 (s, 1H), 3.78 (s, 3H), 2.25 (s, 2H), 1.16 (s, 9H), -0.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.26, 138.74, 137.72, 135.16, 127.86, 113.17, 55.20, 32.47, 31.32, 21.63, -1.27; HRMS calcd for $C_{17}H_{28}GeO$ 322.1352, found 322.1359.

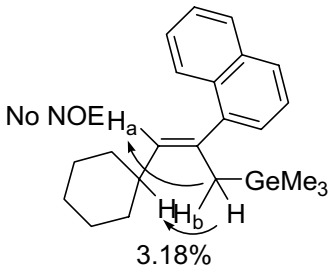
(1*H*-4-Isochromenylmethyl)(trimethyl)germane (6): colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (t, *J* = 7.5, 1H), 7.14 (t, *J* = 7.0 Hz, 1H), 7.03 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.38 (s, 1H), 4.91 (s, 2H), 1.85 (s, 2H), 0.05 (s, 9H); ^{13}C

NMR (125 MHz, $CDCl_3$): δ 140.27, 132.15, 129.17, 127.76, 126.50, 123.79, 120.84, 114.90, 68.47, 15.81, -1.80; HRMS cacld for $C_{13}H_{18}GeO$ 264.0569, found 264.0566.

The regio- and stereochemistry of products **4** were established by typical ^1H NMR NOE experiments. For example, selective irradiation of the vinylic proton H_a at δ 5.28 in **4a** caused 2.87 % enhancement of the signal at δ 7.24 for the aromatic proton and caused no enhancement of the signal for the methylene protons H_b at δ 2.08. Irradiation of the methylene protons H_b at δ 2.08 caused 2.31 % enhancement of the signal at δ 2.15 for the cyclohexyl methine proton and no enhancement of the signal for the vinylic proton H_a at δ 5.28. These NOE results strongly confirm the regio- and stereochemistry of **4a**. Similar results are obtained for other derivatives **4f**, **4g**, **4i**, **4j** and **4k** and the results are shown below.



4a



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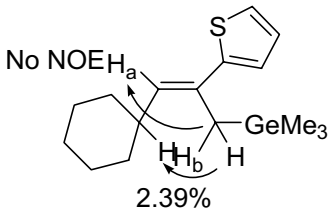

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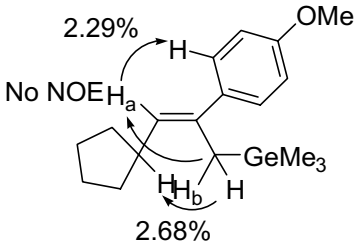

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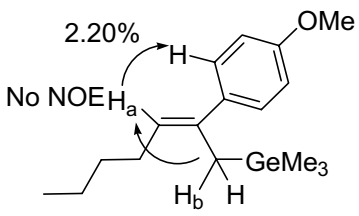
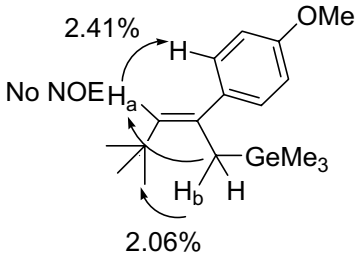


4j



4k