Supporting Information

Stereocontrolled Synthesis of Triols Containing Four Asymmetric Centers: Application of *C*,*O*-Chelated Germyl Enolates to a Diastereoselective Aldol Reaction

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1. General

NMR spectra were recorded on JEOL-AL400 spectrometers (400 MHz for ^{1}H, and 100 MHz for ^{13}C) with TMS as an internal standard. ^{1}H and ^{13}C NMR signals of compounds were assigned using HMQC, HSQC, HMBC, COSY, NOESY, and ^{13}C off-resonance techniques. Positive and negative FAB and EI mass spectra were recorded on a JEOL JMS-700 and Shimadzu GCMS-QP2010 Ultra, respectively. High-resolution mass spectra were obtained by magnetic sector type mass spectrometer. IR spectra were recorded as thin films or as solids in KBr pellets on a HORIBA FT-720 and a JASCO FT/IR 6200 spectrophotometer.

Data collection for X-ray crystal analysis was performed on a Rigaku/ R-AXIS RAPID (MoK_α λ = 0.71075 Å, and CuK_α λ = 1.54187 Å), Rigaku/XtaLAB Synergy-S/Mo (MoK_α λ = 0.71075 Å), and Rigaku/XtaLAB Synergy-S/Cu (CuK_α λ = 1.54187 Å) diffractometers. All calculations were performed with the observed reflections [$I>2\sigma(I)$] by the program CrystalStructure crystallographic software packages.[1] All non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed at calculated positions and refined "riding" on their corresponding carbon atoms

2. Materials

Anhydrous dichloromethane, THF, acetonitrile, diethylether, toluene and hexane were purchased and used as obtained. All reagents were obtained from commercial suppliers and used as received. All reactions were carried out under nitrogen. $GeCl_2$-dioxane as prepared by the reported procedure.[2] The α,β-unsaturated ketones **1a**, **1b**, and **1d** were obtained from commercial supplies and **1c**[3] and **1e**[4] were prepared by the reported procedures.

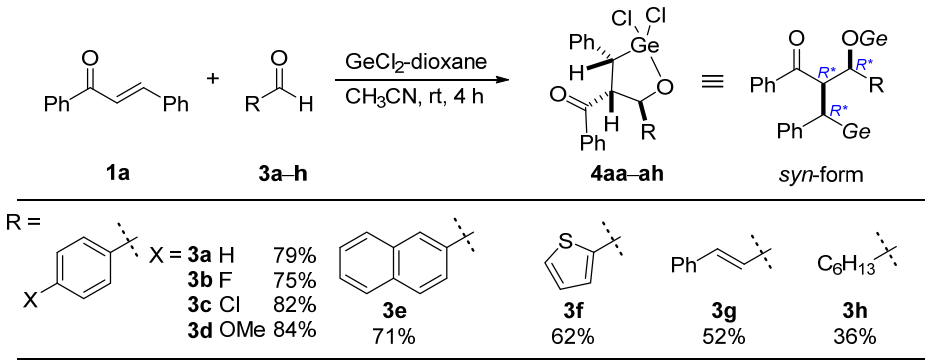
3. Synthetic procedures

3-1. *Syn*-selective aldol reaction of α,β-unsaturated ketones with arylaldehydes using $GeCl_2$-dioxane

General procedure

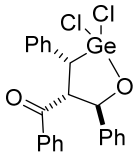
In a nitrogen-filled glove box, to a mixture of $GeCl_2$-dioxane (0.2 mmol) and arylaldehyde (0.2 mmol) in acetonitrile (2 mL) was added α,β-unsaturated ketone (0.2 mmol). After the reaction mixture was stirring at room temperature for 2 h, the solvent was removed by decantation. The obtained solid is washed with acetonitrile (5 mL × 3) and hexane (5 mL × 3). The residual solvent was removed under vacuum to give **4** as a colorless solid. Compounds **4aa**–**4ei** are too insoluble to record any NMR spectrum.

Table S1. Summary for *Syn*-selective aldol reaction[a)].



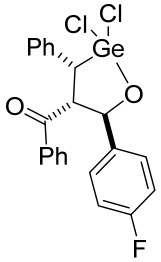
a) Isolated yield. All structures of **4aa**–**ah** were determined by X-ray analysis.

((3*R,4*R**,5*R**)-2,2-Dichloro-3,5-diphenyl-1,2-oxagermolan-4-yl)(phenyl)methanone 4aa**



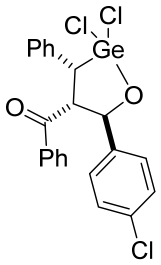
According to the general procedure, this compound was prepared from **1a** (0.0425 g, 0.204 mmol), **3a** (0.0212 g, 0.200 mmol), $GeCl_2$-dioxane (0.0477 g, 0.206 mmol), to give the product **4aa** as a colorless solid (0.0717 g, 79%). mp 181.0 °C (decomp.); IR (KBr) ν = 3060 (w), 3026 (w), 2904 (w), 1631 (s), 1596 (s), 1577 (s), 1495 (s), 1450 (s), 1350 (m), 1219 (m), 1182 (w), 1117 (w), 1055 (s), 767 (m), 744 (m), 698 (s) cm^{-1}; Analysis $C_{22}H_{18}Cl_2GeO_2$ (457.99), Calculated: C, 57.71; H, 3.96, Found: C, 57.73; H, 3.98.

((3*R,4*R**,5*R**)-2,2-Dichloro-5-(4-fluorophenyl)-3-phenyl-1,2-oxagermolan-4-yl)(phenyl)methanone 4ab**



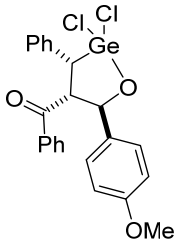
According to the general procedure, this compound was prepared from **1a** (0.0415 g, 0.199 mmol), **3b** (0.0248 g, 0.200 mmol), $GeCl_2$-dioxane (0.0485 g, 0.210 mmol), to give the product **4ab** as a colorless solid (0.0713 g, 75%). mp 175.0 °C (decomp.); IR (KBr) ν = 3063 (w), 1631 (s), 1596 (s), 1574 (m), 1509 (s), 1448 (m), 1349 (m), 1279 (m), 1225 (s), 1054 (s) 985 (m), 827 (m), 684 (s) cm^{-1}; Analysis $C_{22}H_{17}Cl_2FGeO_2$ (475.90), Calculated: C, 55.52; H, 3.60, Found: C, 55.51; H, 3.57.

((3*R,4*R**,5*R**)-2,2-Dichloro-5-(4-chlorophenyl)-3-phenyl-1,2-oxagermolan-4-yl)(phenyl)methanone 4ac**



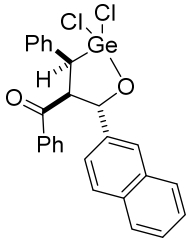
According to the general procedure, this compound was prepared from **1a** (0.0417 g, 0.200 mmol), **3c** (0.0285 g, 0.203 mmol), $GeCl_2$-dioxane (0.0417 g, 0.200 mmol), to give the product **4ac** as a colorless solid (0.0810 g, 82%). mp 170.0°C (decomp.); IR (KBr) ν = 3062 (w), 3030 (w), 1633 (s), 1595 (s), 1576 (s), 1493 (s), 1448 (m), 1352 (m), 1279 (m), 1223 (m), 1180 (m), 1090 (m), 1053 (m), 1012(m), 984 (m), 829 (m), 814 (m), 781 (m), 762 (m), 696 (s) cm^{-1}; Analysis $C_{22}H_{18}Cl_2GeO_2$ (492.36) Calculated: C, 53.67; H, 3.48, Found: C, 53.55; H, 3.48.

((3*R,4*R**,5*R**)-2,2-Dichloro-5-(4-methoxyphenyl)-3-phenyl-1,2-oxagermolan-4-yl)(phenyl)methanone 4ad**



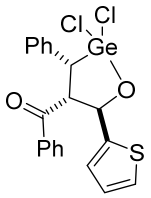
According to the general procedure, this compound was prepared from **1a** (0.0417 g, 0.200 mmol), **3d** (0.0272 g, 0.200 mmol), $GeCl_2$-dioxane (0.0463 g, 0.200 mmol), to give the product **4ad** as a colorless solid (0.0821 g, 84%). mp 141.0 °C (decomp.); IR (KBr) ν = 3060 (w), 3027 (w), 2935 (w), 1637 (s), 1597 (s), 1512 (s), 1450 (m), 1342 (m), 1300 (m), 1250 (s) 1174 (s), 1038 (s), 827 (m), 687 (s) cm^{-1}; Analysis $C_{23}H_{20}Cl_2GeO_3$ (487.94) Calculated: C, 56.62; H, 4.13, Found: C, 56.36; H, 4.27.

((3*R,4*R**,5*R**)-2,2-Dichloro-5-(naphthalen-2-yl)-3-phenyl-1,2-oxagermolan-4-yl)(phenyl)methanone 4ae**



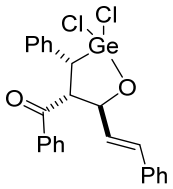
According to the general procedure, this compound was prepared from **1a** (0.0417 g, 0.200 mmol), **3e** (0.0312 g, 0.200 mmol), $GeCl_2$-dioxane (0.0463 g, 0.200 mmol), to give the product **4ae** as a colorless solid (0.0721 g, 71%). mp 140.0 °C (decomp.); IR (KBr) ν = 3050 (w), 2954 (w), 1636 (s), 1596 (s), 1577 (m), 1495 (m), 1449 (m), 1350 (m), 1332 (m), 1276 (m), 1226 (m), 1119 (m), 1051 (s) 764 (m), 683 (s) cm^{-1}; Analysis $C_{26}H_{20}Cl_2GeO_2$ (507.97) Calculated: C, 61.48; H, 3.97, Found: C, 61.26; H, 4.08.

((3*R,4*R**,5*R**)-2,2-Dichloro-3-phenyl-5-(thiophen-2-yl)-1,2-oxagermolan-4-yl)(phenyl)methanone 4af**



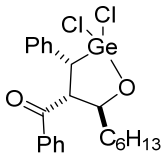
According to the general procedure, this compound was prepared from **1a** (0.0424 g, 0.204 mmol), **3f** (0.0230 g, 0.205 mmol), $GeCl_2$-dioxane (0.0478 g, 0.206 mmol), to give the product **4af** as a colorless solid (0.0578 g, 62%). mp 172.0 °C (decomp.); IR (KBr) ν = 3062 (w), 3030 (w), 1632 (s), 1597 (s), 1577 (m), 1495 (m), 1450 (m), 1348 (s), 1286 (m), 1230 (s), 1119 (w), 1055 (s), 1027 (m), 845 (m), 781 (m), 698 (s) cm^{-1}; Analysis $C_{20}H_{16}Cl_2GeO_2S$ (463.94) Calculated: C, 51.78; H, 3.48, Found: C, 51.58; H, 3.57.

((3*R,4*R**,5*S**)-2,2-Dichloro-3-phenyl-5-((*E*)-styryl)-1,2-oxagermolan-4-yl)(phenyl)methanone 4ag**



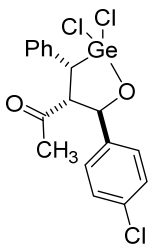
According to the general procedure, this compound was prepared from **1a** (0.0416 g, 0.200 mmol), **3g** (0.0264 g, 0.200 mmol), $GeCl_2$-dioxane (0.0467 g, 0.201 mmol), to give the product **4ag** as a colorless solid (0.0504 g, 52%). mp 120.0 °C (decomp.); IR (KBr) ν = 3059 (w), 3028 (w), 1641 (s), 1597 (s), 1495 (m), 1450 (m), 1352 (m), 1228 (m), 1084 (m), 974 (s), 877 (w), 694 (s) cm^{-1}; Analysis $C_{24}H_{20}Cl_2GeO_2$ (483.95) Calculated: C, 59.56; H, 4.17, Found: C, 59.38; H, 4.16.

((3*R,4*R**,5*S**)-2,2-Dichloro-5-hexyl-3-phenyl-1,2-oxagermolan-4-yl)(phenyl)methanone 4ah**



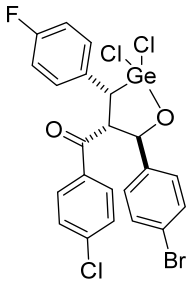
According to the general procedure, this compound was prepared from **1a** (0.0411 g, 0.197 mmol), **3h** (0.0228 g, 0.200 mmol), $GeCl_2$-dioxane (0.0476 g, 0.205 mmol), to give the product **4ah** as a colorless solid (0.0337 g, 37%). mp 149.0 °C (decomp.); IR (KBr) ν = 3060 (w), 3030 (w), 2929 (s), 2856 (s), 1647 (s), 1597 (s), 1577 (m), 1495 (m), 1450 (s), 1335 (m), 1230 (s), 1186 (m), 1028 (m), 939 (w), 893 (w), 692 (s) cm^{-1}; Analysis $C_{22}H_{26}Cl_2GeO_2$ (465.98) Calculated: C, 56.71; H, 5.62, Found: C, 56.28; H, 5.63.

1-((3*R,4*R**,5*R**)-2,2-Dichloro-5-(4-chlorophenyl)-3-phenyl-1,2-oxagermolan-4-yl)ethan-1-one 4bc**



According to the general procedure, this compound was prepared from **1b** (0.0285 g, 0.195 mmol), **3c** (0.0283 g, 0.201 mmol), $GeCl_2$-dioxane (0.0463 g, 0.200 mmol), to give the product **4bc** as a colorless solid (0.0711 g, 85%). mp 190.0 °C (decomp.); IR (KBr) ν = 3072 (w), 3030 (w), 2900 (w), 1682 (s), 1598 (w), 1493 (s), 1452 (m), 1404 (m), 1365 (m), 1331 (m), 1304 (m), 1281 (m), 1219 (m), 1182 (m), 1078 (s), 1012 (m), 941 (w), 814 (m), 773 (m), 694 (s) cm^{-1}; Analysis $C_{17}H_{15}Cl_3GeO_2$ (430.29) Calculated: C, 47.45; H, 3.51, Found: C, 47.41; H, 3.60.

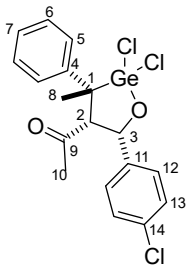
((3*R,4*R**,5*R**)-5-(4-Bromophenyl)-2,2-dichloro-3-(4-fluorophenyl)-1,2-oxagermolan-4-yl)(4-chlorophenyl)methanone 4ei**



According to the general procedure, this compound was prepared from **1e** (0.261 g, 1.00 mmol), **3i** (0.189 g, 1.02 mmol), $GeCl_2$-dioxane (0.233 g, 1.01 mmol), to give the product **4ei** as a colorless solid (0.539 g, 91%).
mp 175.0 °C (decomp.); IR (KBr) ν = 3091 (w), 3052 (w), 2955 (w), 2892 (w), 1635 (m), 1589 (s), 1510 (s), 1487 (m), 1403 (m), 1345 (w), 1233 (s), 1179 (w), 1093 (m), 1070 (m), 836 (m), 734 (w) cm^{-1}; Analysis $C_{22}H_{15}BrCl_3FGeO_2$ (589.24) Calculated: C, 44.84; H, 2.57, Found: C, 44.63; H, 2.79.

3-2. *Anti*-selective aldol reaction of α,β-unsaturated ketones with 4-chlorobenzaldehyde 3c using $GeCl_2$-dioxane aldol

1-((3*R,4*R**,5*S**)-2,2-Dichloro-5-(4-chlorophenyl)-3-methyl-3-phenyl-1,2-oxagermolan-4-yl)ethan-1-one 4cc**

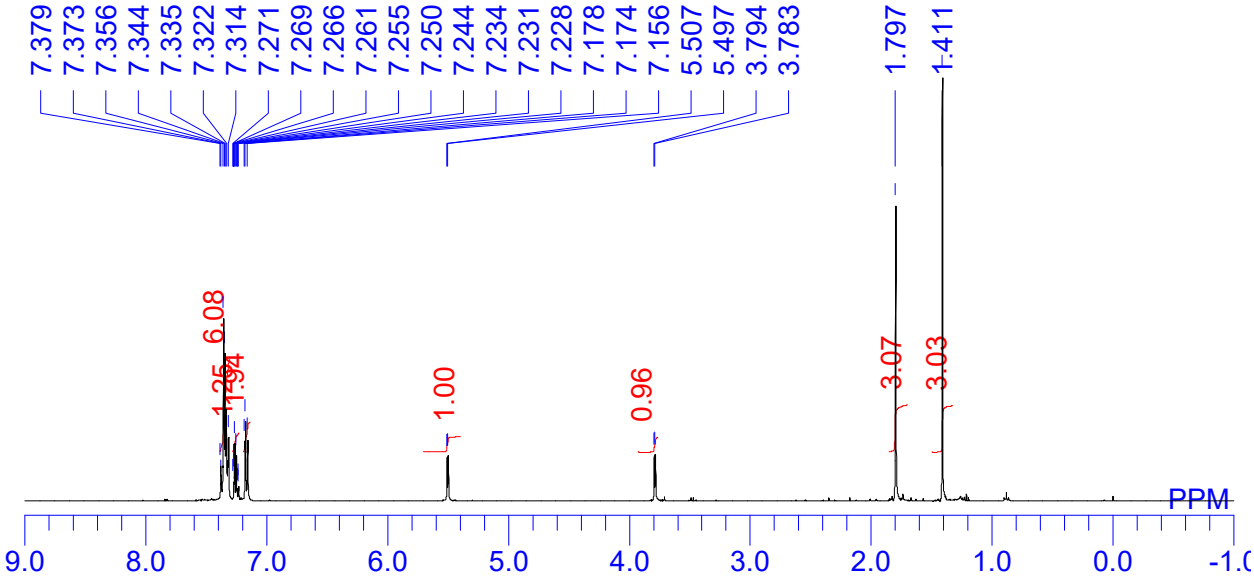


In a nitrogen-filled glove box, to a mixture of $GeCl_2$-dioxane (0.481 g, 3.00 mmol) and **3c** (0.697 g, 3.00 mmol) in acetonitrile (4 mL) was added (*E*)-4-phenylpent-3-en-2-one[3] **1c** (0.421 g, 3.00 mmol). After the reaction mixture was stirring at room temperature for 2 h, the solvent was removed by evaporation. The solid is washed with hexane (2 mL×3) and ether (2 mL×3). The residual solvent was removed under vacuum to give the product **4cc** as a

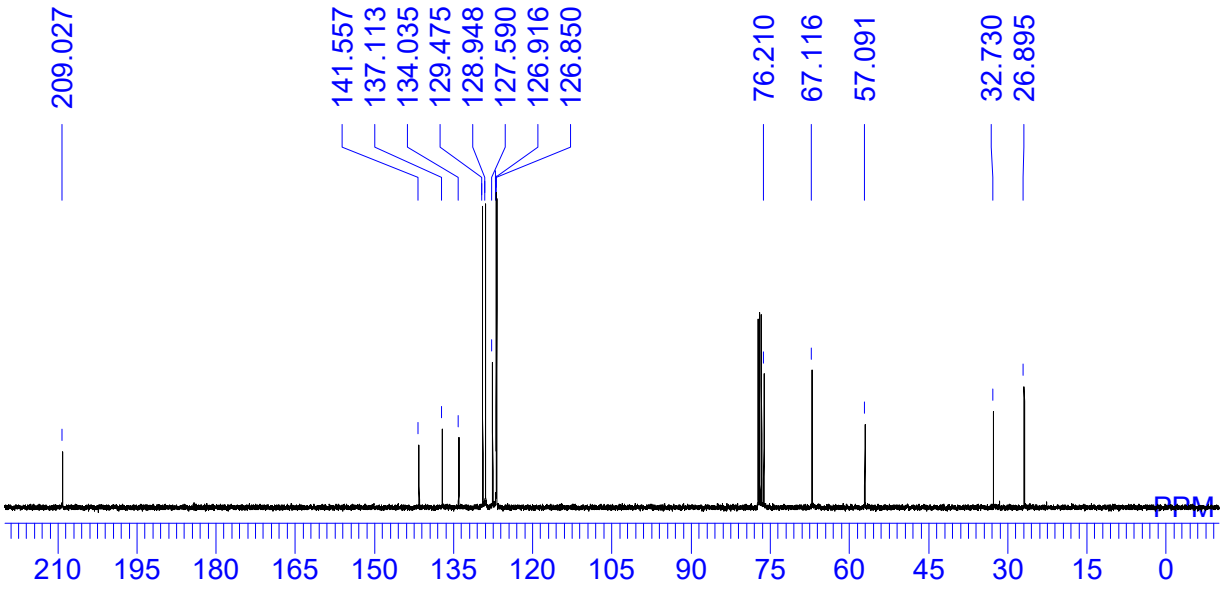
colorless solid (0.459 g, 34%). Although the NMR measurement of the crude product indicated that **4cc** was quantitatively generated, the repeated wash and recrystallization of the crude product caused the decrease in the isolated yield.

mp 139.0 °C (decomp.); IR (KBr) ν = 3017 (w), 2978 (w), 2924 (w), 1701 (s), 1598 (w), 1492 (s), 1443 (m), 1409 (w), 1364 (s), 1264 (w), 1225 (w), 1167 (s), 1088 (s), 995 (s), 831 (m), 759 (s), 735 (s), 697 (s), 673 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.38–7.31 (m, 5H, Ar), 7.27–7.23 (m, 1H, 7-H), 7.17 (d, J = 8.0 Hz, 2H, 5-H), 5.50 (d, J = 4.4 Hz, 1H, 3-H), 3.79 (d, J = 4.4 Hz, 1H, 2-H), 1.80 (s, 3H, 8-H), 1.41 (s, 3H, 10-H); ^{13}C NMR (100 MHz, $CDCl_3$) 209.0 (s, C-9), 141.6 (s, C-4), 137.1 (s, C-11), 134.0 (d, C-14), 129.5 (d), 128.9 (d), 127.6 (d), 126.9 (d) 126.9 (d), 76.2 (d, C-3), 67.1 (d, C-2), 57.1 (s, C-1), 32.7 (q, C-10), 26.9 (q, C-8); Analysis $C_{18}H_{17}Cl_3GeO_2$ (444.31) Calculated: C, 48.66; H, 3.86, Found: C, 48.45; H, 3.82.

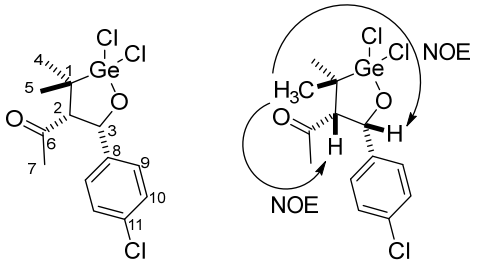
^1H NMR: (400 MHz, $CDCl_3$)



^{13}C NMR: (100 MHz, $CDCl_3$)



1-((4*R,5*S**)-2,2-Dichloro-5-(4-chlorophenyl)-3,3-dimethyl-1,2-oxagermolan-4-yl)ethan-1-one 4dc**

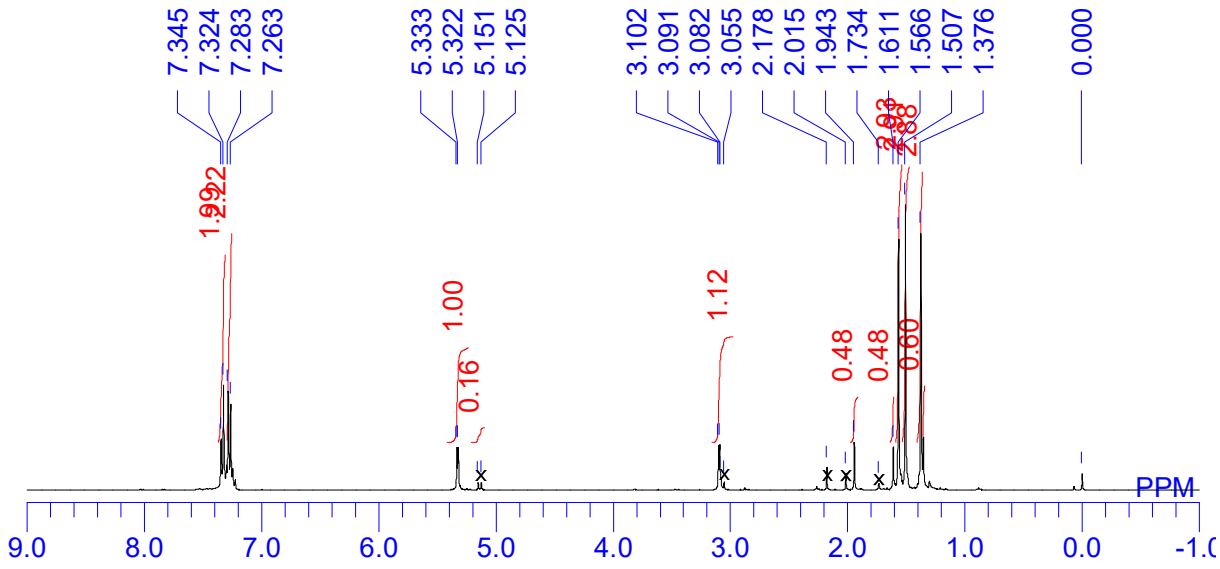


In a nitrogen-filled glove box, to a mixture of $GeCl_2$-dioxane (0.695 g, 3.00 mmol) and **3c** (0.421 g, 3.00 mmol) in acetonitrile (6 mL) was added 4-methyl-3-penten-2-one **1d** (0.295 g, 3.00 mmol). After the reaction mixture was stirring at room temperature for 2 h, the solvent was removed by evaporation. The solid is washed with hexane (6 mL×3) and acetonitrile (2 mL). The residual solvent was removed under vacuum to give the product **4dc** as a colorless solid (0.946 g, 82%).

mp 122.0 °C (decomp.); IR (KBr) ν = 3072 (w), 3056 (w), 2965 (w), 2895 (w), 1695 (s), 1492 (s), 1465 (m), 1408 (m), 1363 (s), 1178 (s), 1153 (m), 1089 (s), 1035 (s) 992 (s), 824 (s), 740 (s), 673 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.34 (d, J = 8.4 Hz, 2H, 10-H), 7.27 (d, J = 8.0 Hz, 2H, 9-H), 5.33 (d, J = 4.4 Hz, 1H, 3-H), 3.10 (d, J = 4.4 Hz, 1H, 2-H), 1.57 (s, 3H, 5-H), 1.51 (s, 3H, 7-H), 1.38 (s, 3H, 4-H); ^{13}C NMR (100 MHz, $CDCl_3$) 208.7 (s, C-6), 137.2 (s, C-8), 133.8 (s, C-11), 128.8 (d, C-10), 127.0 (d, C-9), 75.8 (d, C-3), 68.7 (d, C-2), 43.2 (s, C-1), 33.5 (q, C-7) 24.2 (q, C-5), 20.6 (q, C-4); MS (EI$^+$, 70 eV) *m/z* 384 ([M+2]$^+$, 5), 382 (M$^+$, 7), 242 (100); HRMS (EI, 70 eV) Calculated ($C_{13}H_{15}Cl_3GeO_2$): 381.9349 (M$^+$), Found: 381.9342; Analysis $C_{13}H_{15}Cl_3GeO_2$ (382.24) Calculated: 40.85; H, 3.96, Found: C, 40.64; H, 3.99.

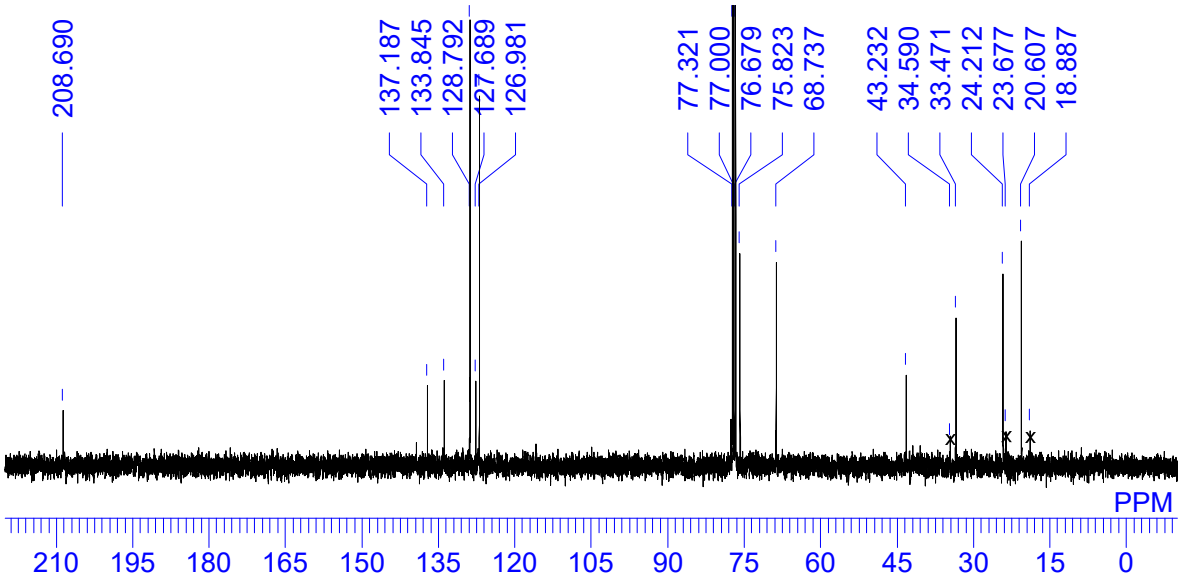
^1H NMR: (400 MHz, $CDCl_3$)

(The cross marks (x) represent the signals from the residual solvents and inseparable impurities.)



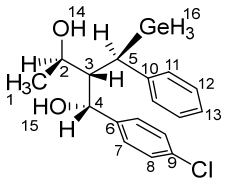
^{13}C NMR: (100 MHz, $CDCl_3$)

(The cross marks (x) represent the signals from the residual solvents and inseparable impurities.)



3-3. Reduction of aldol adducts by BH_3-THF

(1*R,2*S**,3*R**)-1-(4-Chlorophenyl)-2-((*R**)-germyl(phenyl)methyl)butane-1,3-diol 5bc**

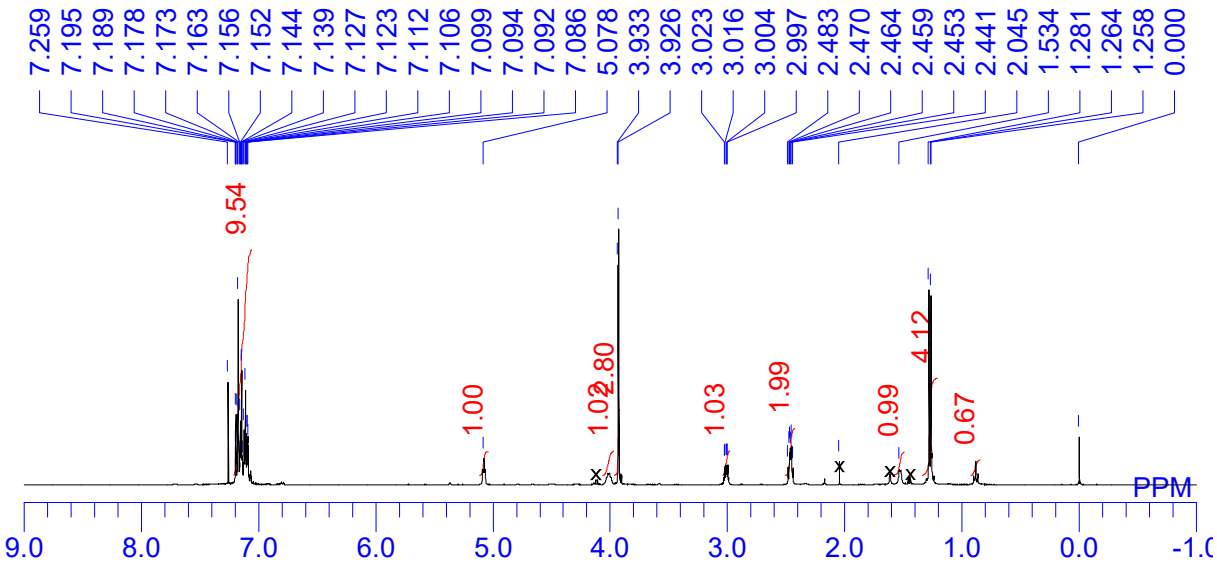


To a mixture of **4bc** (0.129 g, 0.300 mmol) in THF (1 mL) was added BH_3-THF complex (0.9 M in THF, 2.8 mL, 2.50 mmol). The reaction mixture was stirred at 40 °C for 15 h. The resulting mixture was poured into water and the organic phase was extracted with EtOAc. The organic layer was washed with water and brine, and dried over $MgSO_4$. The filtrate was evaporated under vacuum and the residue was purified by column chromatography on silica gel (hexane/AcOEt = 70:30) to give **5bc** as a colorless solid (0.0464 g, 43%).

mp 48.0–49.0 °C; IR (KBr) ν = 3369 (br), 3027 (w), 2971 (w), 2926 (w), 2095 (m), 1598 (m), 1492 (s), 1452 (m), 1381 (m), 1091 (s), 1013 (s), 905 (m), 830 (m), 786 (m), 699 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.20–7.09 (m, 9H), 5.08 (t, J = 4.4 Hz, 1H, 4-H), 4.05–3.98 (m, 1H, 2-H), 3.93 (d, J = 2.8 Hz, 3H, 16-H), 3.01 (qd, J = 4.3 Hz, 2.8 Hz, 1H, 5-H), 2.48–2.44 (m, 2H, 3-H, 15-H), 1.53 (d, J = 5.2 Hz, 1H, 14-H), 1.27 (d, J = 6.8 Hz, 3H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.9 (s), 142.2 (s), 132.6 (s), 128.7 (d), 128.4 (d), 128.2 (d), 127.3 (d), 125.5 (d), 73.5 (d, C-4), 70.3 (d, C-2), 55.1 (d, C-3) 28.9 (d, C-5), 21.4 (q, C-1); MS (FAB^-, 70 eV) *m/z* 367 ($[M-H+2]^-$, 4), 365 ($[M-H]^-$, 10), 153 (100); HRMS (FAB^-, 70 eV) Calculated ($C_{17}H_{20}ClGeO_2$): 365.0364 ($[M-H]^-$), Found: 365.0353.

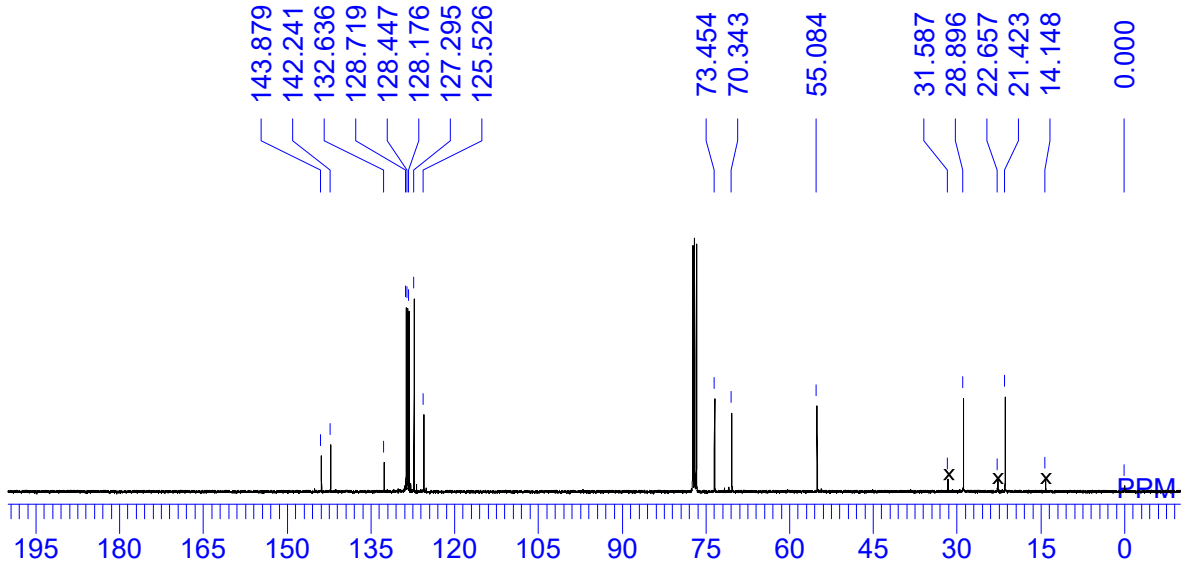
^1H NMR: (400 MHz, $CDCl_3$)

(The cross marks (x) represent the signals from the residual solvents and inseparable impurities.)

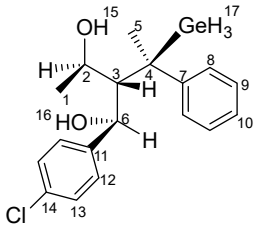


^{13}C NMR: (100 MHz, $CDCl_3$)

(The cross marks (x) represent the signals from the residual solvents and inseparable impurities.)



(1*R,2*R**,3*S**)-1-(4-Chlorophenyl)-2-((*S**)-1-germyl-1-phenylethyl)butane-1,3-diol 5cc**

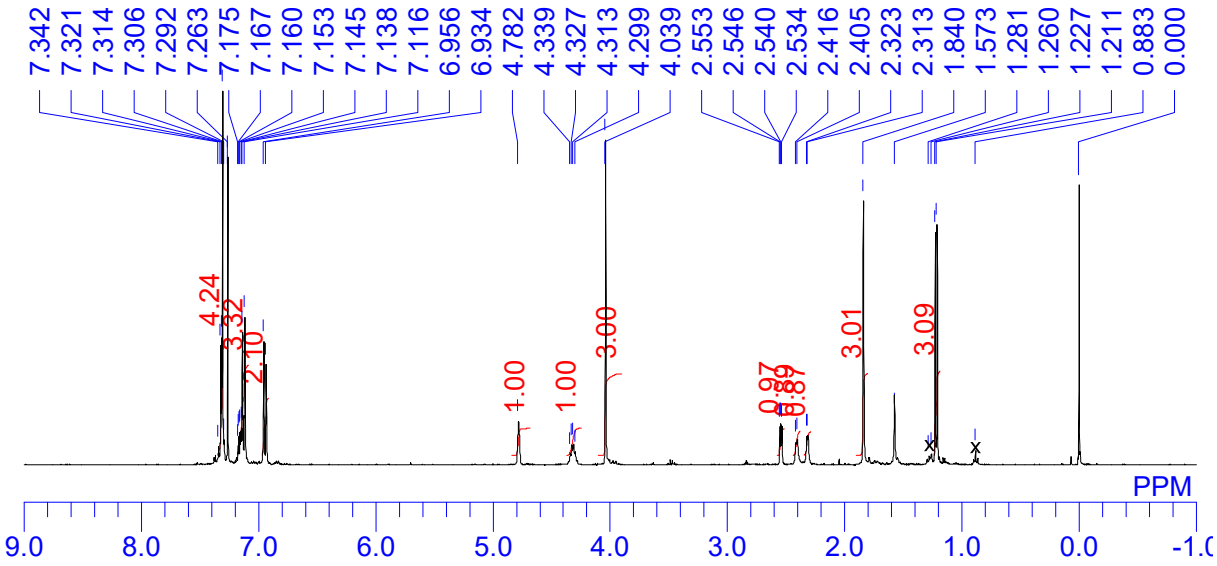


To a mixture of **4cc** (0.131 g, 0.294 mmol) in THF (1 mL) was added BH_3-THF complex (0.9 M in THF, 1.7 mL, 1.50 mmol). The reaction mixture was stirred at room temperature for 1 h. The resulting mixture was poured into water and the organic phase was extracted with EtOAc. The organic layer was washed with water and brine, and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (hexane/AcOEt = 70:30) to give **5cc** as a colorless solid (0.0381 g, 34%).

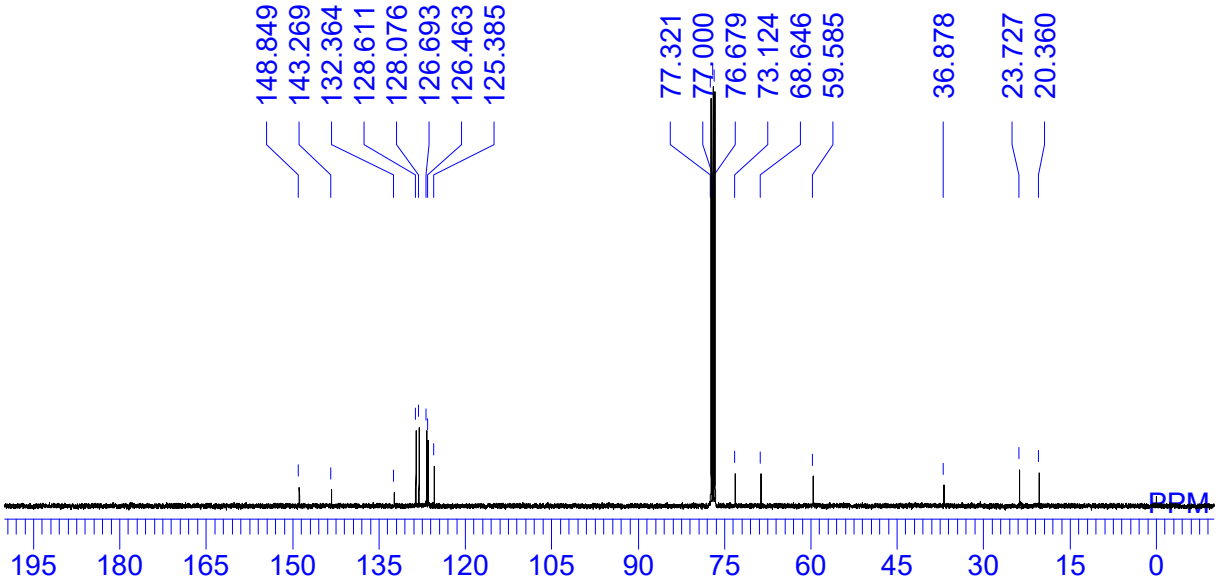
mp 120.0–121.0 °C (decomp.); IR (KBr) ν = 3361 (br), 2931 (w), 2062 (s), 2041 (s), 2027 (s), 1597 (w), 1490 (m), 1394 (w), 1121 (m), 1090 (m), 1038 (m) 980 (w), 900 (m), 821 (s), 788 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.34–7.29 (m, 4H, 8-H, 9-H), 7.18–7.15 (m, 1H, 10-H), 7.13 (d, J = 8.8 Hz, 2H, 13-H), 6.95 (d, J = 8.8 Hz, 2H, 12-H), 4.78 (s, 1H, 6-H), 4.36–4.28 (m, 1H, 2-H), 4.04 (s, 3H, 17-H), 2.54 (dd, J = 5.0, 2.8 Hz, 1H, 3-H), 2.41 (d, J = 4.4 Hz, 1H, 15-H), 2.32 (d, J = 4.0 Hz, 1H, 16-H), 1.84 (s, 3H, 5-H), 1.22 (d, J = 6.4 Hz, 3H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.8 (s, C-7), 143.3 (s, C-11), 132.4 (s, C-14), 128.6 (d), 128.1 (d, C-13), 126.7 (d, C-12), 126.5 (d), 125.4 (d, C-10), 73.1 (d, C-6), 68.6 (d, C-2), 59.6 (d, C-3) 36.9 (s, C-4), 23.7 (q, C-1), 20.4 (q, C-5); MS (FAB$^-$, 70 eV) *m/z* 379 ([M–H+2]$^-$, 2), 377 ([M–H]$^-$, 4), 153 (100); HRMS (FAB$^-$, 70 eV) Calculated ($C_{18}H_{23}ClGeO_2$+$C_7H_7NO_3$): 533.1024 ([M–H]$^-$), Found: 533.1014.

^{1}H NMR: (400 MHz, $CDCl_3$)

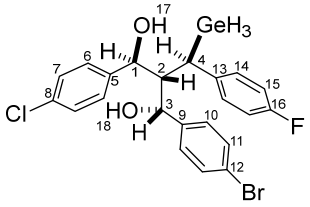
(The cross marks (x) represent the signals from the residual solvents and inseparable impurities.)



^{13}C NMR: (100 MHz, $CDCl_3$)



(1*R,2*S**,3*S**)-1-(4-Bromophenyl)-3-(4-chlorophenyl)-2-((*R**)-(4-fluorophenyl)(germyl)methyl)propane-1,3-diol 5ei**

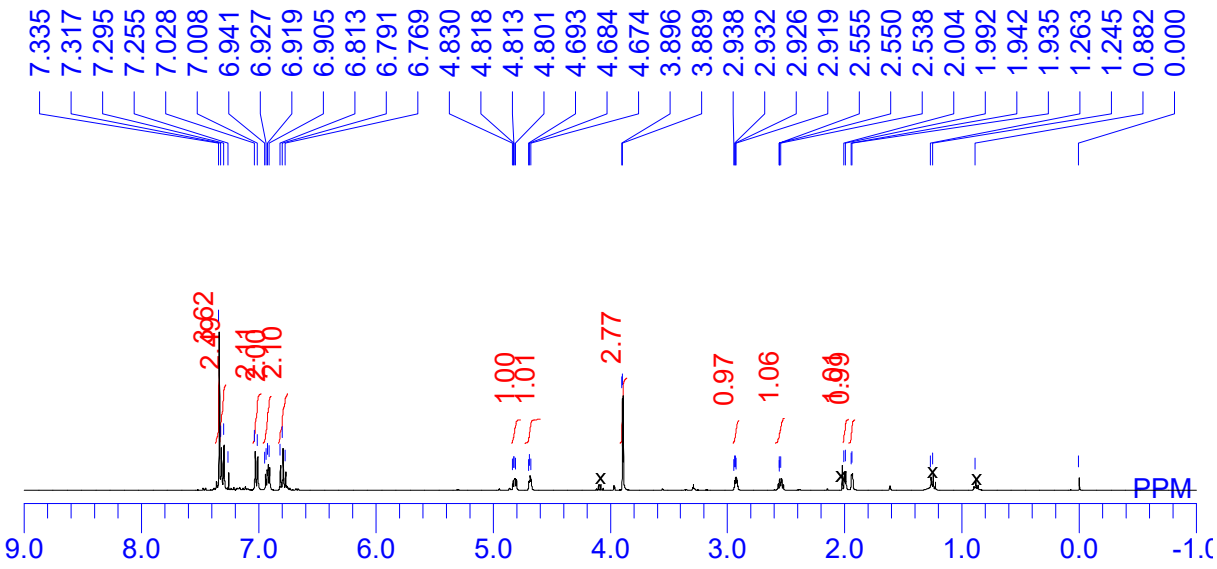


To a mixture of **4ei** (0.294 g, 0.500 mmol) in THF (1 mL) was added BH_3-THF complex (0.9 M in THF, 2.8 mL, 2.50 mmol). The reaction mixture was stirred at room temperature for 2 h. The resulting mixture was poured into water and the organic phase was extracted with EtOAc. The organic layer was washed with water and brine, and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (hexane/AcOEt = 70:30) to give **5ei** as a colorless oil (0.131 g, 50%).

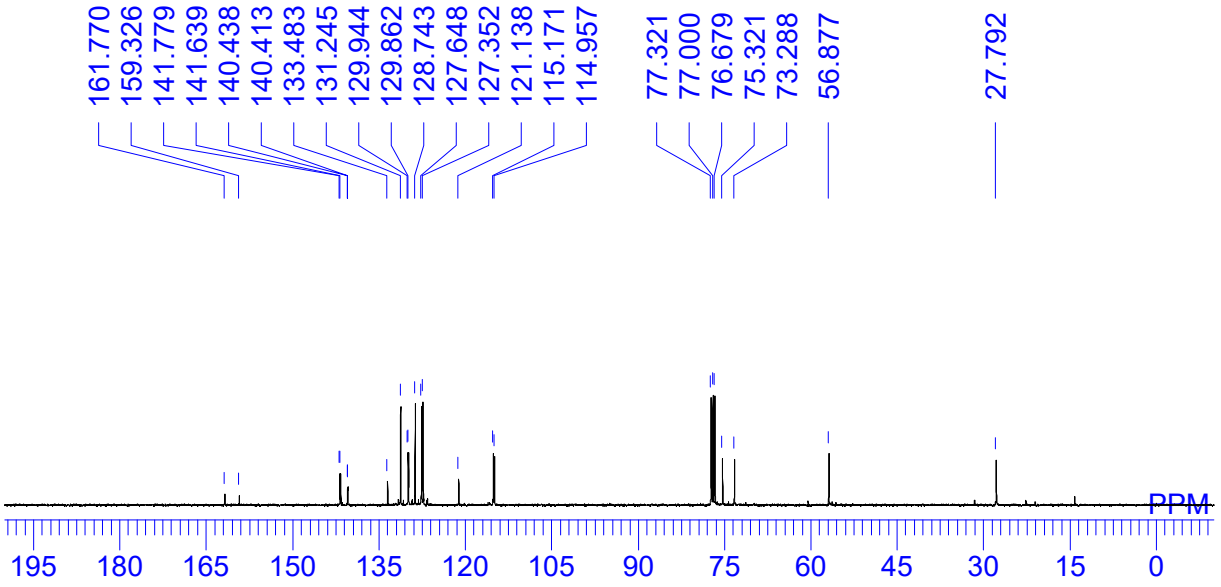
IR (KBr) ν = 3559 (m), 3426 (br), 2912 (w), 2064 (s), 1599 (w), 1505 (s), 1403 (w), 1227 (m), 1092 (m), 1011 (m) 832 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.36–7.32 (m, 4H), 7.31 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.0 Hz, 2H), 6.92 (dd, J = 5.6, 8.8 Hz, 2H, 14-H), 6.79 (t, J = 8.8 Hz, 2H, 15-H), 4.82 (dd, J = 6.8, 4.8 Hz, 1H), 4.68 (t, J = 3.8 Hz, 1H), 3.89 (d, J = 2.8 Hz, 3H, Ge-H), 2.95–2.91 (m, 1H, 4-H), 2.55 (td, J = 5.0, 6.8 Hz, 1H, 2-H), 2.00 (d, J = 4.8 Hz, 1H, O-H), 1.94 (d, J = 2.8 Hz, 1H, OH); ^{13}C NMR (100 MHz, $CDCl_3$) 160.5 (d, $^1J_{C\text{-}F}$ = 244.4 Hz, C-16), 159.3 (s), 141.8 (s), 141.6 (s), 140.4 (d, $^4J_{C\text{-}F}$ = 2.5 Hz, C-13), 133.5 (s), 131.2 (s), 129.9 (dd, $^3J_{C\text{-}F}$ = 8.2 Hz, C-14), 128.7 (d), 127.6 (d), 127.4 (d), 121.1 (d), 115.1 (dd, $^2J_{C\text{-}F}$ = 21.4 Hz, C-15), 75.3 (d), 73.3 (d), 56.9 (d, C-2) 27.8 (d, C-4); MS (FAB$^-$, 70 eV) *m/z* 525 ([M–H+2]$^-$, 26), 523 ([M–H]$^-$, 38), 153 (100); HRMS (FAB$^-$, 70 eV) Calculated ($C_{22}H_{20}BrClFGeO_2$): 522.9531 ([M–H]$^-$), Found: 522.9532.

^1H NMR: (400 MHz, $CDCl_3$)

(The cross marks (x) represent the signals from the residual solvents and inseparable impurities.)

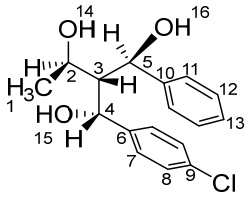


^{13}C NMR: (100 MHz, $CDCl_3$)



3-4. Synthesis of triol derivatives 6

(1*R,2*R**,3*R**)-1-(4-Chlorophenyl)-2-((*R**)-hydroxy(phenyl)methyl)butane-1,3-diol 6bc**

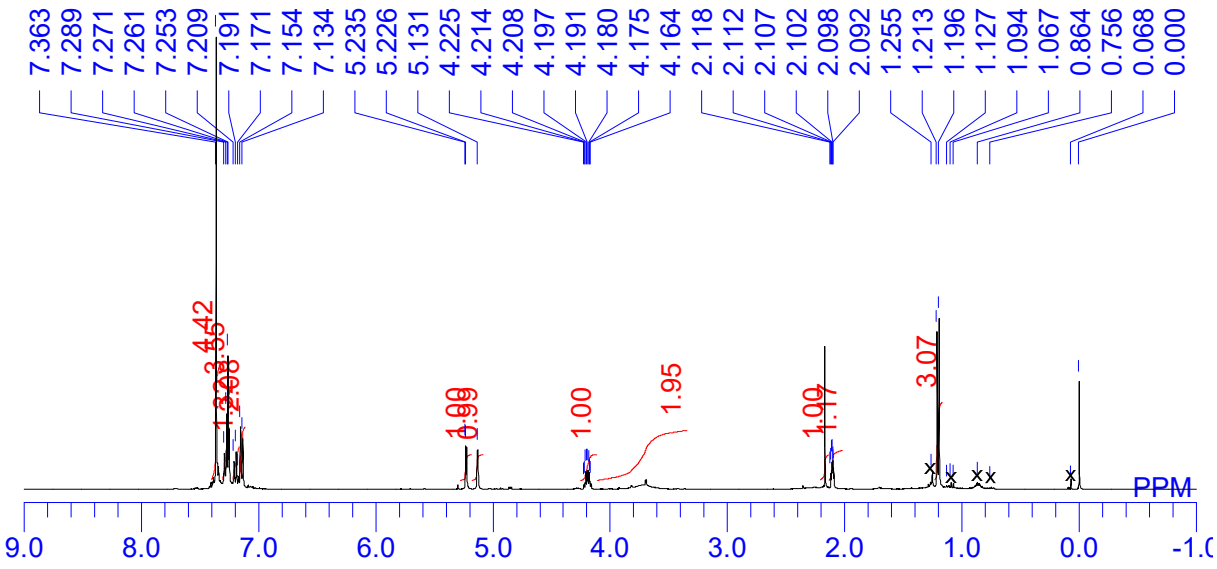


To a mixture of **5bc** (0.0776 g, 0.212 mmol) in THF (1 mL) and methanol (1 mL) was added KF (0.0618 g, 1.06 mmol), $KHCO_3$ (0.511 g, 0.510 mmol) and 30% H_2O_2 aq. (0.350 mL). The reaction mixture was stirred at 40 °C for 24 h. The resulting mixture was poured into water and the organic phase was extracted with ether. The organic layer was washed with water and brine, and dried over $MgSO_4$. The filtrate was evaporated under vacuum to give the product **6bc** as a colorless oil (0.0581 g, 89%).

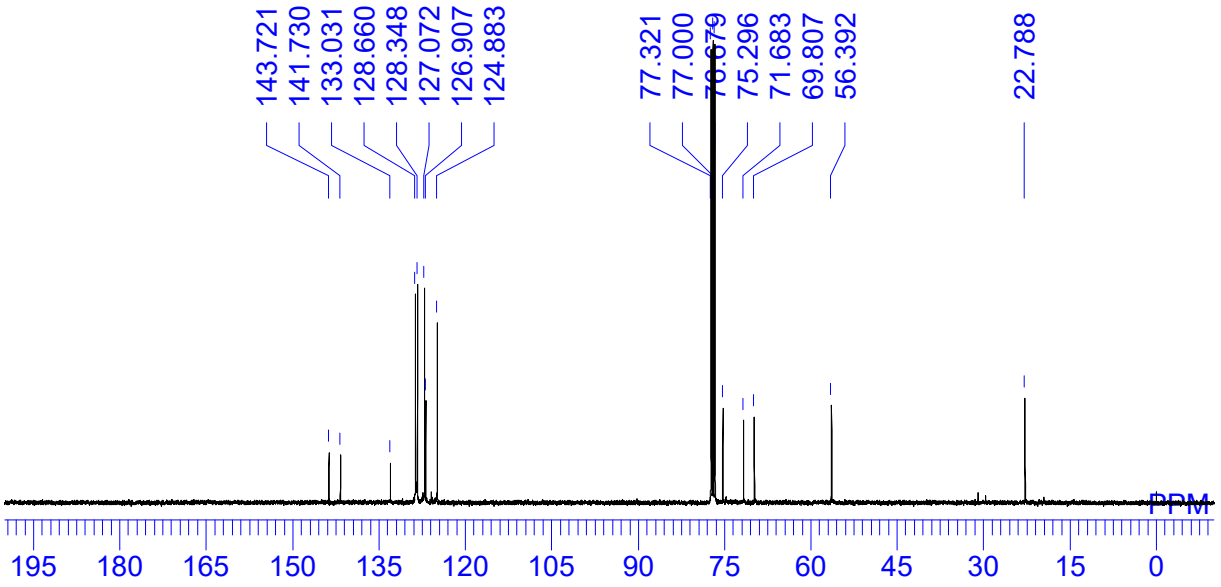
IR (KBr) ν = 3367 (br), 3062 (w), 3028 (w), 2972 (w), 2929 (w), 1492 (s), 1452 (m), 1399 (m), 1329 (m), 1091 (s), 1013 (s), 826 (m), 701 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.39–7.34 (m, 4H, 7-H, 8-H), 7.29–7.25 (m, 2H, 12-H), 7.19 (t, J = 8.0 Hz, 1H, 13-H), 7.14 (d, J = 8.0 Hz, 11-H), 5.23 (d, J = 3.6 Hz, 1H, 4-H), 5.13 (s, 1H, 5-H), 4.19 (qd, J = 6.8, 4.4 Hz, 1H, 2-H), 3.71 (bs, 2H, D_2O-exchangeable), 2.17 (s, 1H, OH, D_2O-exchangeable), 2.12–2.09 (m, 1H, 3-H), 1.20 (d, J = 6.8 Hz, 3H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) 143.7 (s, C-10), 141.7 (s, C-6), 133.0 (s, C-9), 128.7 (d, C-8), 128.3 (d, C-12), 127.1 (d, C-7), 126.9 (d, C-13), 124.9 (d, C-11), 75.3 (d, C-4), 71.7 (d, C-5), 69.8 (d, C-2) 56.4 (d, C-3), 22.8 (q, C-1); MS (FAB$^-$, 70 eV) *m/z* 307 ([M–H+2]$^-$, 19), 305 ([M–H]$^-$, 51), 183 (100); HRMS (FAB$^-$, 70 eV) Calculated ($C_{17}H_{18}ClO_3$): 305.0944 ([M-H]$^-$), Found: 305.0942.

^1H NMR: (400 MHz, $CDCl_3$)

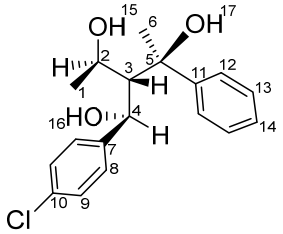
(The cross marks (x) represent the signals from the residual solvents and inseparable impurities.)



^{13}C NMR: (100 MHz, $CDCl_3$)



(2*R,3*S**,4*R**)-3-((*S**)-(4-Chlorophenyl)(hydroxy)methyl)-2-phenylpentane-2,4-diol 6cc**

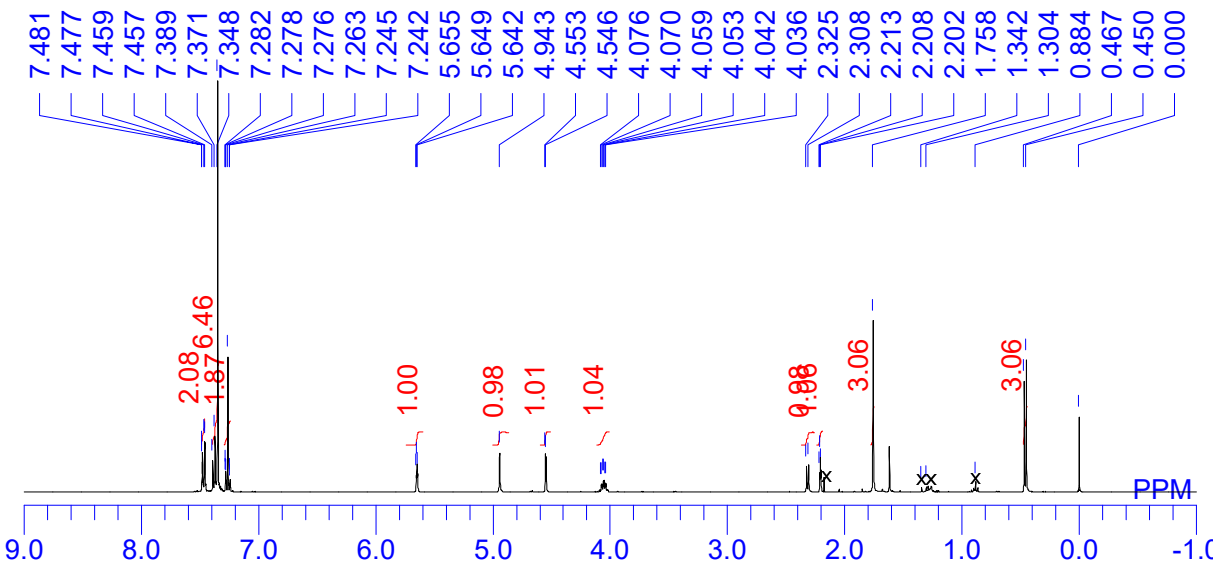


To **5cc** (0.112 g, 0.296 mmol) in THF (1 mL) and methanol (1 mL) was added KF (0.0573 g, 0.988 mmol), $KHCO_3$ (0.0511 g, 0.510 mmol) and 30% H_2O_2 aq. (0.350 mL). The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched by sodium thiosulfate aq. and the organic phase was extracted with ether. The organic layer was washed with water and brine, and dried over $MgSO_4$. The filtrate was evaporated under vacuum and the residue was purified by column chromatography on silica gel (hexane/AcOEt = 50:50) to give the product **6cc** as a colorless solid (0.0473 g, 50%).

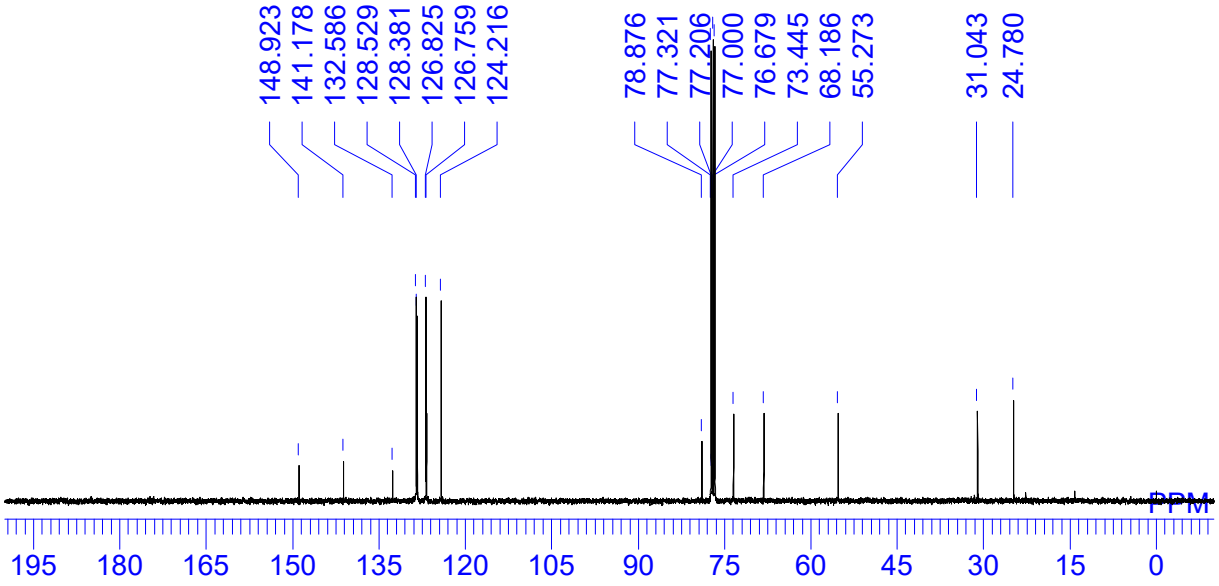
mp 1310–132.0 °C; IR (KBr) ν = 3365 (br), 2975 (w), 2932 (w), 1600 (w), 1492 (s), 1447 (m), 1402 (m), 1377 (m), 1215 (w), 1119 (m), 1092 (s), 1013 (m), 907 (w), 816 (m), 755 (m), 703 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.47 (dd, J = 8.8, 1.6 Hz, 2H, 12-H), 7.39–7.34 (m, 6H), 7.28–7.24 (m, 1H, 14-H), 5.65 (t, J = 2.8 Hz, 1H, 4-H), 4.94 (s, 1H, 17-H), 4.55 (d, J = 2.8 Hz, 1H, 16-H), 4.06 (ddq, J = 6.8, 6.8, 2.4 Hz, 1H, 2-H), 2.32 (d, J = 6.8 Hz, 1H, 15-H), 2.21 (t, J = 2.4 Hz, 1H, 3-H), 1.76 (s, 3H, 6-H), 0.46 (d, J = 6.8 Hz, 3H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) 148.9 (s, C-11), 141.2 (s, C-7), 132.6 (s, C-10), 128.6 (d), 128.4 (d), 126.83 (d, C-8), 126.76 (d, C-14), 124.2 (d, C-12), 78.9 (s, C-5), 73.4 (d, C-4), 68.2 (d, C-2), 55.3 (d, C-3), 31.0 (q, C-6), 24.8 (q, C-1); MS (FAB^-, 70 eV) *m*/*z* 321[M–H+2]$^-$, 37), 319 ([M–H]$^-$, 100); HRMS (FAB^-, 70 eV) Calculated ($C_{18}H_{20}ClO_3$): 319.1101 ([M-H]$^-$), Found: 319.1100.

^{1}H NMR: (400 MHz, $CDCl_3$)

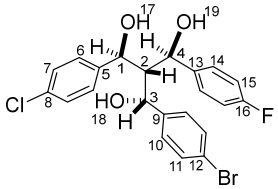
(The cross marks (x) represent the signals from the residual solvents and inseparable impurities.)



^{13}C NMR: (100 MHz, $CDCl_3$)



(1*R,2*S**,3*S**)-1-(4-Bromophenyl)-3-(4-chlorophenyl)-2-((*R**)-(4-fluorophenyl)(hydroxy)methyl)propane-1,3-diol 6ei**

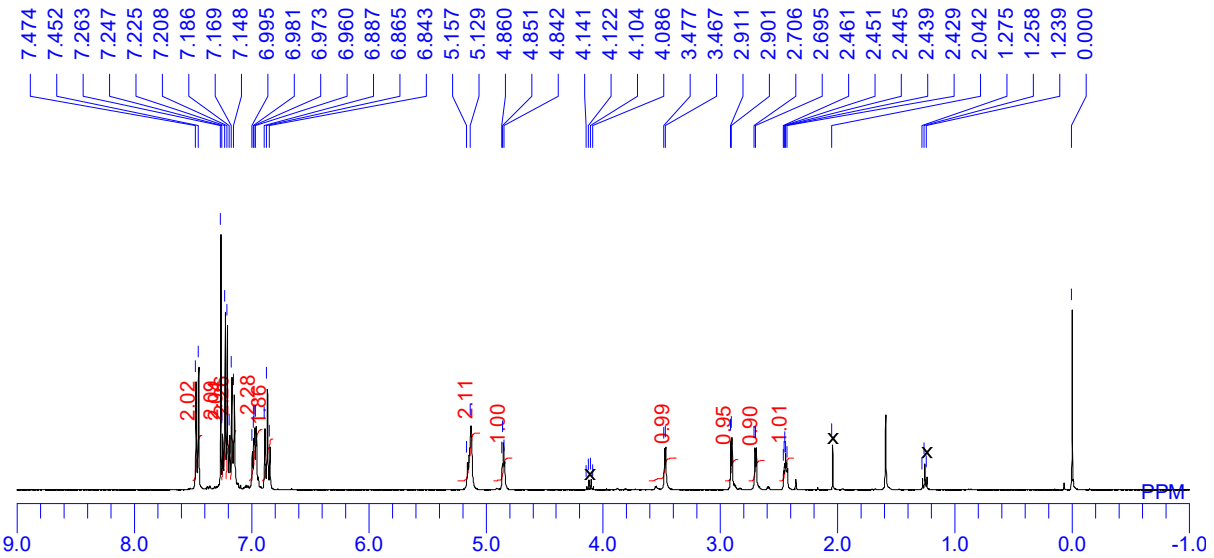


To a mixture of **4ei** (0.251 g, 0.427 mmol) in THF (1 mL) was added BH_3-THF complex (0.9 M in THF, 2.8 mL, 2.50 mmol). The reaction mixture was stirred at room temperature for 2 h. The resulting mixture was poured into water and the organic phase was extracted with EtOAc. The organic layer was washed with water and brine, and dried over $MgSO_4$. The filtrate was evaporated under vacuum. To a crude **5ei** in THF (1 mL) and methanol (1 mL) was added KF (0.0484 g, 0.830 mmol), $KHCO_3$ (0.0420 g, 0.420 mmol) and 30% H_2O_2 aq. (0.350 mL). The reaction mixture was stirred at room temperature for 24 h. The resulting mixture was quenched by sodium thiosulfate aq. and the organic phase was extracted with ether. The organic layer was washed with water and brine, and dried over $MgSO_4$. The filtrate was evaporated under vacuum and the residue was purified by column chromatography on silica gel (hexane/AcOEt = 50:50) to give the product **6ei** as a colorless solid (0.0792 g, 40%).

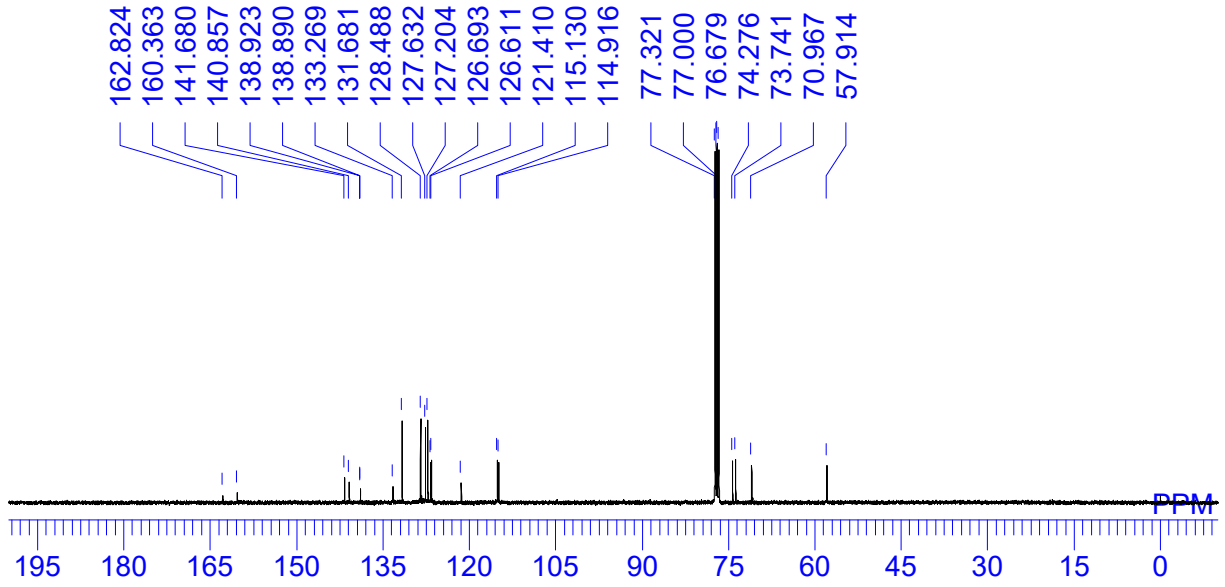
mp 147.0–148.0 °C; IR (KBr) ν = 3367 (br), 2923 (w), 1604 (w), 1510 (s), 1489 (s), 1405 (m), 1225 (s), 1159 (w), 1068 (s), 1011 (s), 830 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 7.46 (d, J = 8.8 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.98 (dd, J = 8.4, 5.4 Hz, 2H, 14-H), 6.87 (t, J = 8.8 Hz, 2H, 15-H), 5.13 (bs, 2H), 4.85 (t, J = 3.6 Hz, 1H), 3.47 (d, J = 4.0 Hz, 1H), 2.91 (d, J = 4.0 Hz, 1H), 2.70 (d, J = 4.4 Hz, 1H), 2.46–2.43 (m, 1H, 2-H); ^{13}C NMR (100 MHz, $CDCl_3$) 161.6 (d, $^1J_{C\text{-}F}$ = 246.1 Hz C-16), 141.7 (s), 140.9 (s), 138.9 (d, $^4J_{C\text{-}F}$ = 3.3 Hz, C-13), 133.3 (s), 131.7 (d), 128.5 (d), 127.6 (d), 127.2 (d), 126.7 (dd, $^3J_{C\text{-}F}$ = 8.2 Hz, C-14), 121.4 (s), 115.0 (dd, $^2J_{C\text{-}F}$ = 21.4 Hz, C-15), 74.3 (d), 73.7 (d), 71.0 (d, C-4), 57.9 (d, C-2); MS (FAB$^-$, 70 eV) *m/z* 467 ([M–H+2]$^-$, 6), 465 ([M–H+2]$^-$, 21), 463 ([M–H]$^-$, 16), 153 (100); HRMS (FAB$^-$, 70 eV) Calculated ($C_{22}H_{18}BrClFO_3$): 463.0112 (M^+), Found: 463.0105.

^1H NMR: (400 MHz, $CDCl_3$)

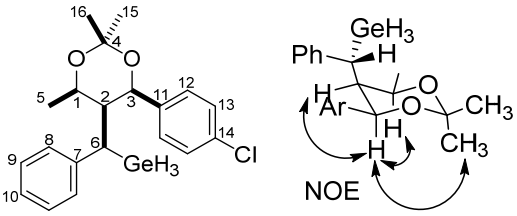
(The cross marks (x) represent the signals from the residual solvents and inseparable impurities.)



^{13}C NMR: (100 MHz, $CDCl_3$)



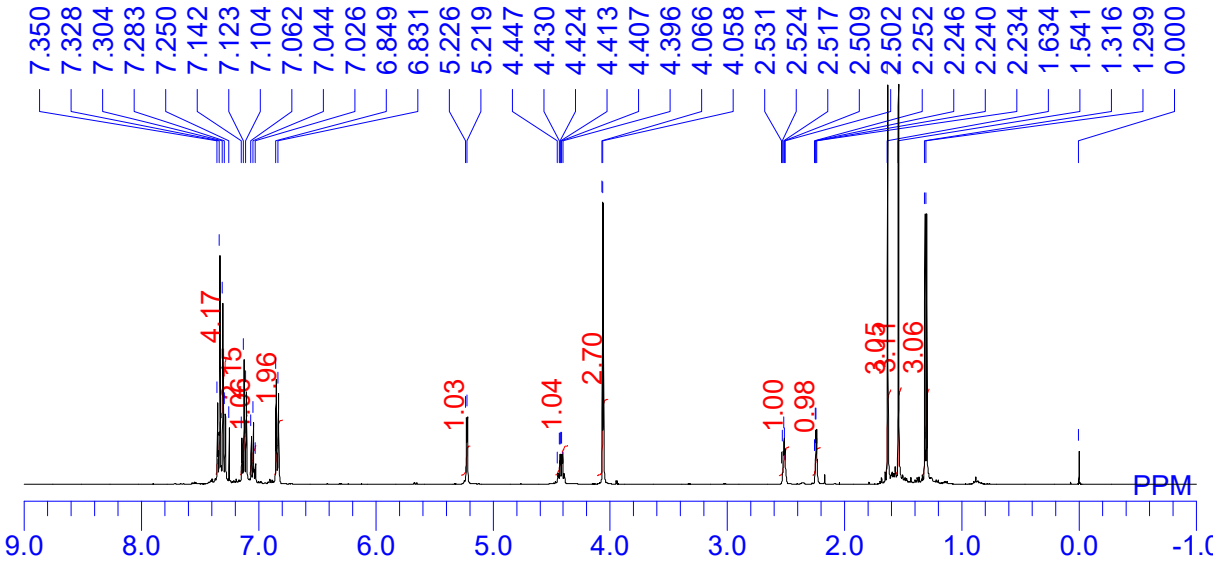
((*R)-((4*R**,5*S**,6*R**)-4-(4-Chlorophenyl)-2,2,6-trimethyl-1,3-dioxan-5-yl)(phenyl)methyl)germane 7bc**



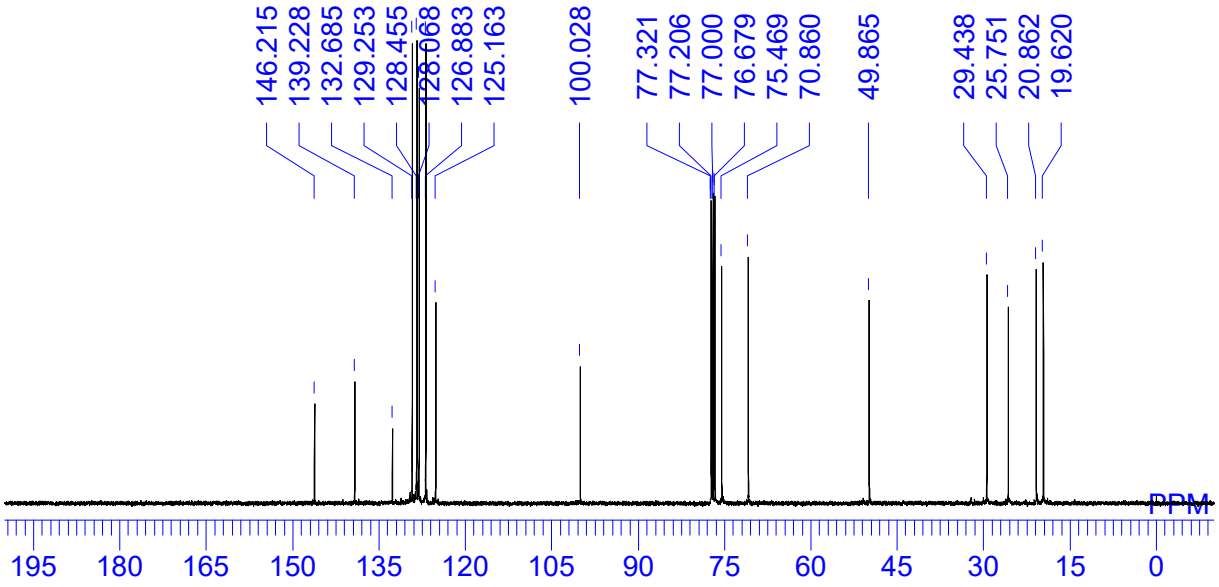
To a mixture of **5bc** (0.122 g, 0.330 mmol) and dimethoxypropane (0.5 mL, 4.00 mmol)) in acetone (2 mL) was added pyridinium *p*-toluenesulfonate (0.0300 g, 0.150 mmol). After the solution was heated under reflux for 24 h, the solvent was removed and the residue was partitioned between water and ether. The aqueous phase was extracted with ether. The organic layer was washed with water and brine, and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel (hexane/AcOEt = 80:20) to give the product **7bc** (0.0642 g, 41%) as a colorless solid (from ethanol).

mp. 92.0 °C (decomp.); IR (KBr) ν = 3055 (w), 2997 (w), 2991 (w), 2014 (s), 2051 (s), 1493 (s), 1380 (s), 1254 (s), 1202 (s), 1176 (m), 1133 (m), 1086 (m), 1067 (s) 1034 (w), 1012 (m), 986 (m), 953 (m) 891 (m), 825 (s), 774 (m), 703 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.34 (d, J = 8.8 Hz, 2H, 13-H), 7.29 (d, J = 8.8 Hz, 2H, 12-H), 7.12 (t, J = 7.6 Hz, 2H, 9-H), 7.04 (t, J = 7.2 Hz, 1H, 10-H), 6.84 (d, J = 7.2 Hz, 2H, 8-H), 5.22 (d, J = 2.8 Hz, 1H, 3-H), 4.42 (qd, J = 6.8, 2.4 Hz, 1H, 1-H), 4.06 (d, J = 3.2 Hz, 3H, Ge-H) , 2.53–2.50 (m, 1H, 6-H), 2.24 (q, J = 2.4 Hz, 1H, 2-H), 1.63 (s, 3H, 16-H) 1.54 (s, 3H, 15-H), 1.31 (d, J = 6.8 Hz, 3H, 5-H); ^{13}C NMR (100 MHz, $CDCl_3$) 146.2 (s, C-7), 139.2 (s, C-11), 132.6 (s, C-14), 129.3 (d, C-8), 128.5 (d, C-13), 128.1 (d, C-9), 126.9 (d, C-12), 125.1 (d, C-10) 100.0 (s, C-4), 75.5 (d, C-3), 70.9 (d, C-1), 49.9 (d, C-2), 29.4 (q, C-16), 25.8 (d, C-6), 20.9 (q, C-5), 19.6 (q, C-15); MS (FAB$^-$, 70 eV) *m/z* 407 ([M–H+2]$^-$), 405 ([M–H]$^-$, 13), 153 (100); HRMS (FAB$^-$, 70 eV) Calculated ($C_{20}H_{24}ClO_2Ge$): 405.0677([M–H]$^-$), Found: 405.0678.

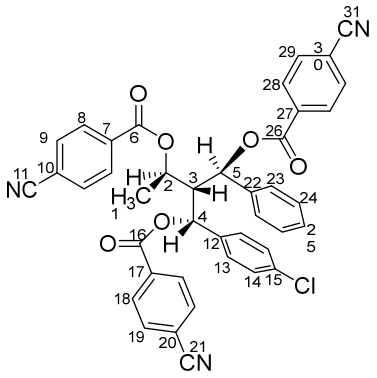
^{1}H NMR: (400 MHz, $CDCl_3$)



^{13}C NMR: (100 MHz, $CDCl_3$)



(1*R,2*R**,3*R**)-2-((*R**)-(4-Chlorophenyl)((4-cyanobenzoyl)oxy)methyl)-1-phenylbutane-1,3-diyl bis(4-cyanobenzoate) 8bc**

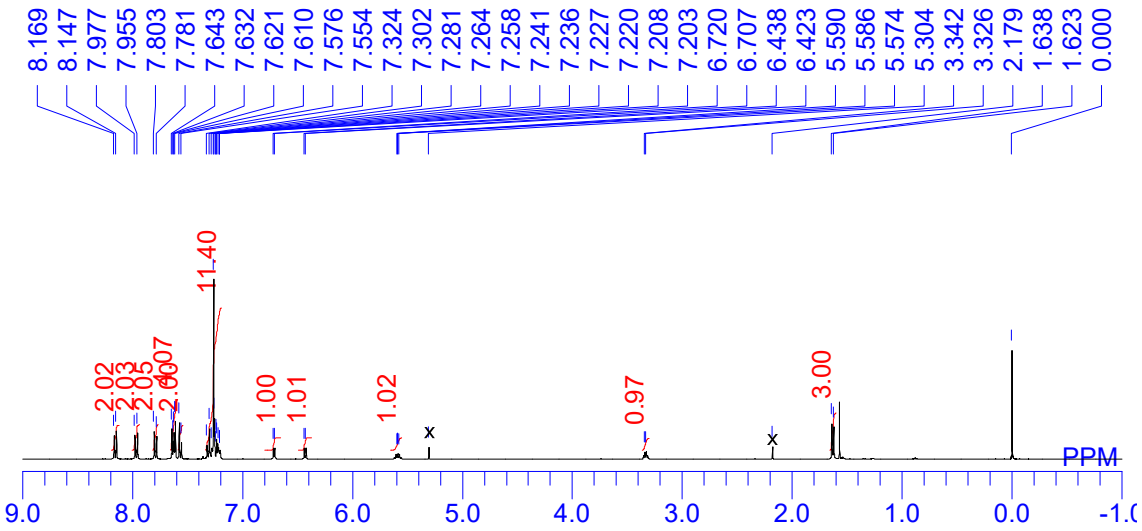


A solution of **6bc**, 4-cyanobenzoyl chloride (0.288 g, 1.74 mmol), DMAP (0.002 g, 0.02 mmol) and pyridine (0.16 mL) in acetonitrile (5 mL) was stirred at room temperature for 72 h. The mixture was diluted with water, extracted with CH_2Cl_2 (3 ×20 mL) and the combined extracts were dried over $MgSO_4$. The filtrate was evaporated under vacuum and the residue was purified by column chromatography on silica gel (hexane/AcOEt = 80:20) to give the product **8bc** (0.0993 g, 41%) as a colorless solid. Recrystallization from toluene/dichloromethane furnished a single crystal suitable for the X-ray crystallographic analysis.

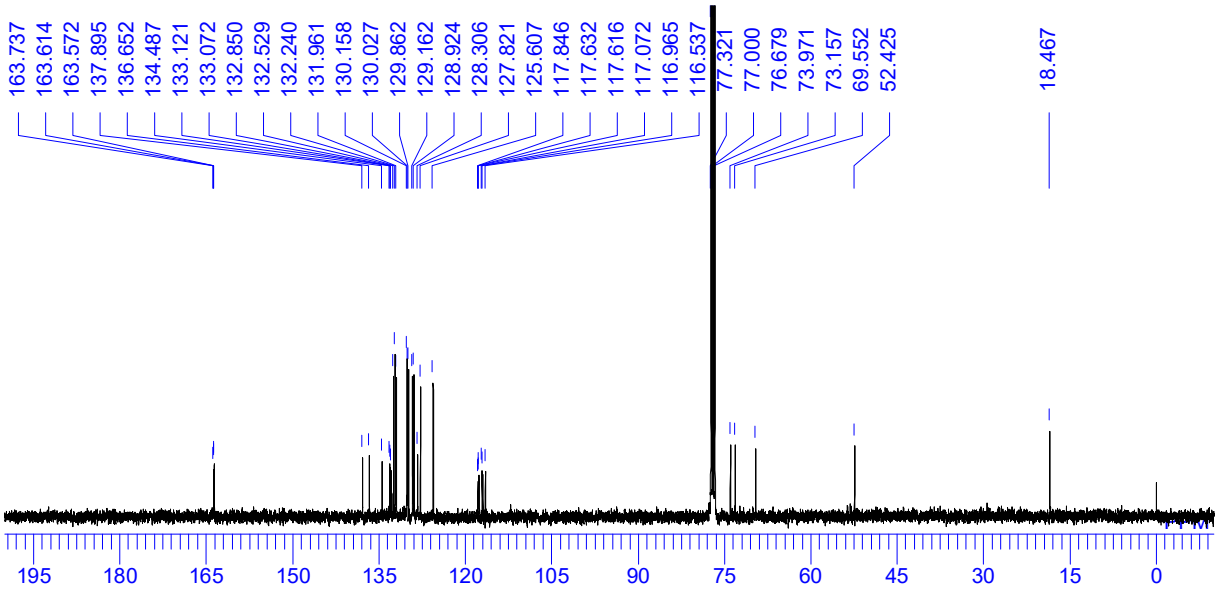
mp 235.0–236.0 °C; IR (KBr) ν = 3104 (w), 3063 (w), 2979 (w), 2951 (w), 2228 (s), 1724 (s), 1609 (m), 1571 (w), 1492 (s), 1453 (m), 1405 (m), 1390 (m), 1262 (s), 1175 (m), 1157 (m), 1102 (s), 1017 (m), 940 (m), 856 (m), 767 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 8.16 (d J = 8.8 Hz, 2H), 7.97 (d, J = 8.8 Hz, 2H), 7.79 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.57 (d, J = 8.8 Hz, 2H), 7.32–7.20 (m, 9H), 6.71 (d, J = 5.2 Hz, 1H), 6.43 (d, J = 6.0 Hz, 1H), 5.62–5.56 (m, 1H, 2-H), 3.35–3.31 (m, 1H, 3-H), 1.63 (d, J = 6.0 Hz, 3H, 1-H); ^{13}C NMR (100 MHz, $CDCl_3$) 163.7 (s), 163.61 (s), 163.57 (s), 137.9 (s), 136.7 (s), 134.5 (s), 133.12 (s), 133.07 (s), 132.9 (s), 132.5 (d), 132.2 (d), 132.0 (d), 130.2 (d), 130.0 (d), 129.9 (d), 129.2 (d), 128.9 (d), 128.3 (d), 127.8 (d), 125.6 (d), 117.8 (s), 117.63 (s), 117.62 (s), 117.1 (s), 117.0 (s), 116.5 (s), 74.0 (d), 73.2 (d), 69.6 (d, C-2), 52.4 (d, C-3), 18.5 (q, C-1); MS (FAB^+, 70 eV) m/z 718 ($[M+Na+2]^+$, 1), 716 ($[M+Na]^+$, 2), 176 (100); HRMS (FAB^+, 70 eV) Calculated ($C_{41}H_{28}ClN_3O_6$): 716.1559 ($[M+Na]^+$), Found: 716.1577; Analysis $C_{41}H_{28}ClN_3O_6$ (694.14) Calculated: C, 70.94; H, 4.07, Found: C, 70.67; H, 3.83; N, 5.98.

^{1}H NMR: (400 MHz, $CDCl_3$)

(The cross marks (x) represent the signals from the residual solvents and inseparable impurities.)



^{13}C NMR: (100 MHz, $CDCl_3$)



4. X-ray crystallographic data

4-1. ((3*R**,4*R**,5*R**)-2,2-Dichloro-3,5-diphenyl-1,2-oxagermolan-4-yl)(phenyl)methanone 4aa: CCDC 1837677

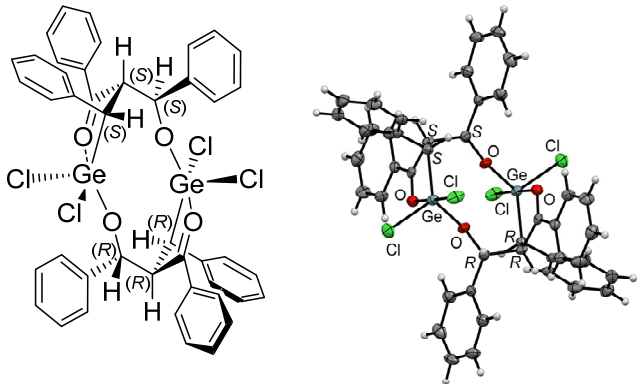


Figure S1. ORTEP drawings of **4aa** at the 50% probability level.

Empirical Formula	$C_{22}H_{18}Cl_2GeO_2$	D_{calc}	1.558 g/cm^3
Formula Weight	457.88	F_{000}	928.00
Crystal Color, Habit	colorless, prism	μ(MoK$_\alpha$)	18.562 cm^{-1}
Crystal Dimensions	0.300 X 0.300 X 0.300 mm	Temperature	-150.0 °C
Crystal System	monoclinic	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Lattice Type	Primitive	Least Squares Weights	$1/\sigma^2(F_o^2) = 1/\sigma^2(F_o)/(4F_o^2)$
Lattice Parameters	a = 9.8841(7) Å	No. Observations ($I > 2.00\sigma(I)$)	3573
	b = 17.4704(10) Å	No. Variables	262
	c = 11.5796(7) Å	Reflection/Parameter Ratio	13.64
	β = 102.4957(19) °	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0444
	V = 1952.2(2) Å^3	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0640
Space Group	$P2_1/c$ (#14)	Goodness of Fit Indicator	1.940
Z value	4	Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	0.84 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-0.66 e$^-$/Å^3

4-2. ((3*R**,4*R**,5*R**)-2,2-Dichloro-5-(4-fluorophenyl)-3-phenyl-1,2-oxagermolan-4-yl)(phenyl)methanone 4ab: CCDC 1837678

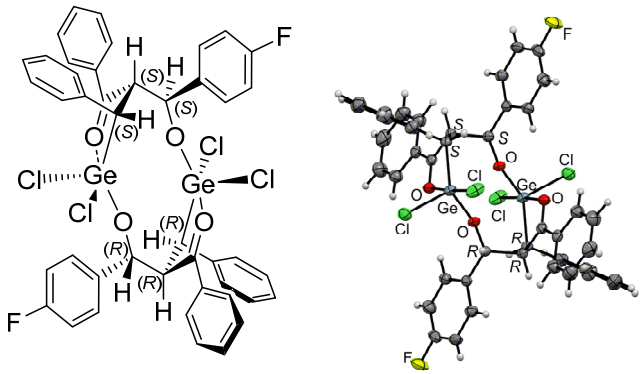


Figure S2. ORTEP drawings of **4ab** at the 50% probability level.

Empirical Formula	$C_{22}H_{17}Cl_2FGeO_2$	D_{calc}	1.645 g/cm^3
Formula Weight	475.87	F_{000}	960.00
Crystal Color, Habit	translucent, light, colorless, block	μ(MoK$_\alpha$)	18.969 cm^{-1}
		Temperature	-150.0 °C
Crystal Dimensions	0.223 X 0.164 X 0.131 mm	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Crystal System	monoclinic	Least Squares Weights	Chebychev polynomial with 3
Lattice Type	Primitive	parameters	94.3217, 127.5530, 35.0137,
Lattice Parameters	a = 8.6342(4) Å	No. Observations ($I > 2.00\sigma(I)$)	3828
	b = 22.7005(11) Å	No. Variables	321
	c = 10.0073(5) Å	Reflection/Parameter Ratio	11.93
	β = 101.649(5) °	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0385
	V = 1921.04(16) Å^3	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0554
Space Group	$P2_1/c$ (#14)	Goodness of Fit Indicator	1.150
Z value	4	Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	0.88 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-0.28 e$^-$/Å^3

4-3. ((3*R**,4*R**,5*R**)-2,2-Dichloro-5-(4-chlorophenyl)-3-phenyl-1,2-oxagermolan-4-yl)(phenyl)methanone

4ac: CCDC 1837679

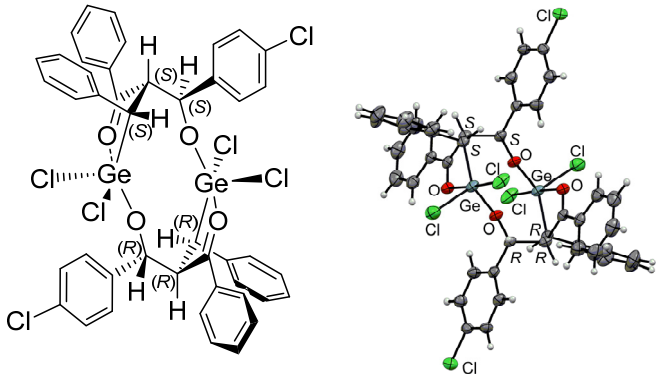


Figure S3. ORTEP drawings of **4ac** at the 50% probability level.

Empirical Formula	$C_{22}H_{17}Cl_3GeO_2$	D_{calc}	1.613 g/cm^3
Formula Weight	492.32	F_{000}	992.00
Crystal Color, Habit	translucent, light, colorless, block	μ(MoK$_\alpha$)	19.206 cm^{-1}
		Temperature	-150.0 °C
Crystal Dimensions	0.162 X 0.105 X 0.091 mm	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Crystal System	monoclinic	Least Squares Weights	Chebychev polynomial with 3
Lattice Type	Primitive	parameters	28.8153, 38.3285, 10.2984,
Lattice Parameters	a = 8.7644(4) Å	No. Observations ($I > 2.00\sigma(I)$)	3699
	b = 22.8849(10) Å	No. Variables	270
	c = 10.3481(5) Å	Reflection/Parameter Ratio	13.70
	β = 102.344(5) °	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0444
	V = 2027.56(17) Å^3	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0722
Space Group	$P2_1/c$ (#14)	Goodness of Fit Indicator	1.115
Z value	4	Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	1.18 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-0.35 e$^-$/Å^3

4-4. ((3*R**,4*R**,5*R**)-2,2-Dichloro-5-(4-methoxyphenyl)-3-phenyl-1,2-oxagermolan-4-yl)(phenyl)methanone

4ad: CCDC 1837680

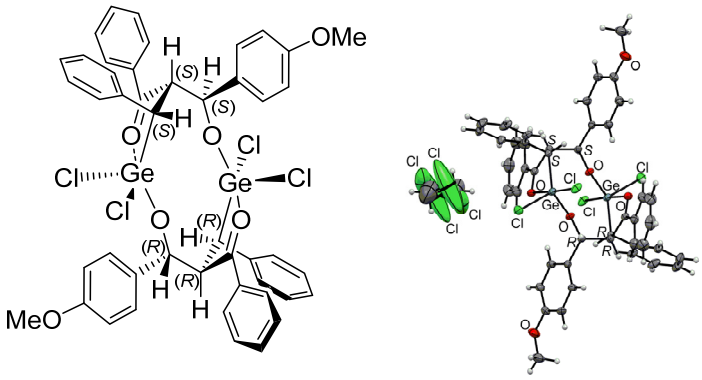


Figure S4. ORTEP drawings of **4ad** at the 50% probability level.

Empirical Formula	$C_{23.5}H_{21}Cl_3GeO_3$	D_{calc}	1.484 g/cm^3
Formula Weight	530.37	F_{000}	538.00
Crystal Color, Habit	Translucent, intense, colorless, plated	μ(MoK$_\alpha$)	16.496 cm^{-1}
		Temperature	-150.0 °C
Crystal Dimensions	0.150 X 0.127 X 0.058 mm	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Crystal System	triclinic	Least Squares Weights	$w = 1/[\sigma^2(F_o^2) + (0.0590 \cdot P)^2 + 0.9622 \cdot P]$ where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$
Lattice Type	Primitive		
Lattice Parameters	a = 9.6035(3) Å	No. Observations ($I > 2.00\sigma(I)$)	6043
	b = 11.3751(3) Å	No. Variables	283
	c = 12.2291(4) Å	Reflection/Parameter Ratio	21.35
	α = 115.083(3) °	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0400
	β = 93.191(3) °	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.1098
	γ = 98.394(3) °	Goodness of Fit Indicator	1.021
	V = 1186.63(7) Å^3	Max Shift/Error in Final Cycle	0.001
Space Group	P-1 (#2)	Maximum peak in Final Diff. Map	1.06 e$^-$/Å^3
Z value	2	Minimum peak in Final Diff. Map	-0.69 e$^-$/Å^3

4-5. ((3*R,4*R**,5*R**)-2,2-Dichloro-5-(naphthalen-2-yl)-3-phenyl-1,2-oxagermolan-4-yl)(phenyl)methanone 4ae: CCDC 1837681**

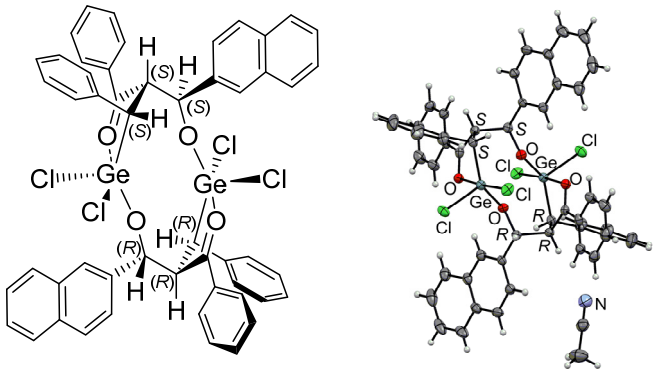


Figure S5. ORTEP drawings of **4ae** at the 50% probability level.

Empirical Formula	$C_{28}H_{23}Cl_2GeNO_2$	D_{calc}	1.468 g/cm^3
Formula Weight	548.99	F_{000}	560.00
Crystal Color, Habit	Translucent, light, colorless, block	μ(MoK$_\alpha$)	14.737 cm^{-1}
		Temperature	-150.0 °C
Crystal Dimensions	0.211 X 0.170 X 0.106 mm	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Crystal System	triclinic	Least Squares Weights	Chebychev polynomial with 3
Lattice Type	Primitive	parameters	86.2290, 116.4080, 31.7769,
Lattice Parameters	a = 10.1136(5) Å	No. Observations ($I > 2.00\sigma(I)$)	5132
	b = 11.2995(4) Å	No. Variables	390
	c = 11.3342(4) Å	Reflection/Parameter Ratio	13.16
	α = 85.182(3) °	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0331
	β = 84.582(3) °	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0564
	γ = 74.782(3) °	Goodness of Fit Indicator	1.059
	V = 1241.89(9) Å^3	Max Shift/Error in Final Cycle	0.000
Space Group	P-1 (#2)	Maximum peak in Final Diff. Map	0.49 e$^-$/Å^3
Z value	2	Minimum peak in Final Diff. Map	-0.42 e$^-$/Å^3

4-6. ((3*R,4*R**,5*R**)-2,2-Dichloro-3-phenyl-5-(thiophen-2-yl)-1,2-oxagermolan-4-yl)(phenyl)methanone 4af: CCDC 1837682**

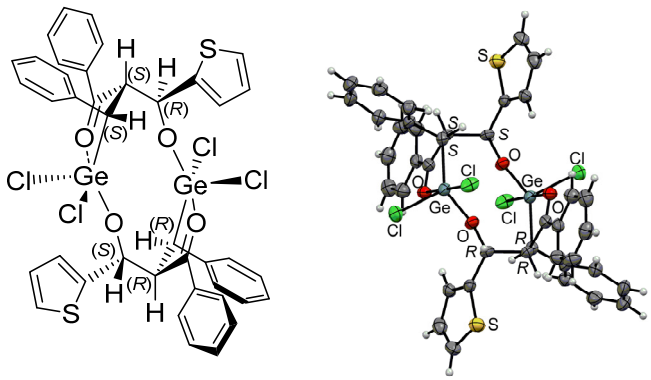


Figure S6. ORTEP drawings of **4af** at the 50% probability level.

Empirical Formula	$C_{20}H_{16}Cl_2GeO_2S$	D_{calc}	1.655 g/cm^3
Formula Weight	463.90	F_{000}	936.00
Crystal Color, Habit	colorless, prism	μ(MoK$_\alpha$)	20.559 cm^{-1}
Crystal Dimensions	0.400 X 0.400 X 0.400 mm	Temperature	-150.0 °C
Crystal System	monoclinic	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Lattice Type	Primitive	Least Squares Weights	Chebychev polynomial with 3
Lattice Parameters	a = 9.9694(15) Å	parameters	2523.2300, 3539.6900, 1165.2000,
	b = 16.935(2) Å	No. Observations ($I > 2.00\sigma(I)$)	2747
	c = 11.1790(16) Å	No. Variables	251
	β = 99.521(4) °	Reflection/Parameter Ratio	10.94
	V = 1861.3(5) Å^3	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0499
Space Group	$P2_1/c$ (#14)	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0930
Z value	4	Goodness of Fit Indicator	0.996
		Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	0.61 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-0.64 e$^-$/Å^3

4-7. ((3*R,4*R**,5*S**)-2,2-Dichloro-3-phenyl-5-((*E*)-styryl)-1,2-oxagermolan-4-yl)(phenyl)methanone 4ag: CCDC 1837683**

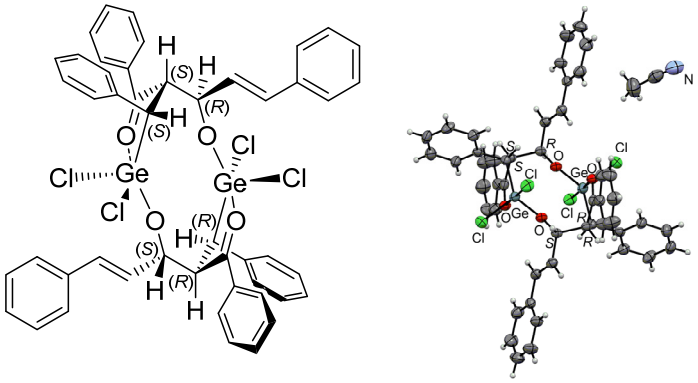


Figure S7. ORTEP drawings of **4ag** at the 50% probability level.

Empirical Formula	$C_{26}H_{23}Cl_2GeNO_2$	D_{calc}	1.458 g/cm^3
Formula Weight	524.97	F_{000}	536.00
Crystal Color, Habit	colorless, prism	μ(MoK$_\alpha$)	15.266 cm^{-1}
Crystal Dimensions	0.100 X 0.100 X 0.100 mm	Temperature	-150.0 °C
Crystal System	triclinic	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Lattice Type	Primitive	Least Squares Weights	$1/\sigma^2(F_o^2) = 1/\sigma^2(F_o)/(4F_o^2)$
Lattice Parameters	a = 10.3751(8) Å	No. Observations ($I > 2.00\sigma(I)$)	6233
	b = 10.7935(9) Å	No. Variables	312
	c = 12.5572(9) Å	Reflection/Parameter Ratio	19.98
	α = 65.093(2) °	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0439
	β = 69.7194(19) °	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0615
	γ = 83.035(2) °	Goodness of Fit Indicator	1.872
	V = 1195.84(16) Å^3	Max Shift/Error in Final Cycle	0.000
Space Group	P-1 (#2)	Maximum peak in Final Diff. Map	0.66 e$^-$/Å^3
Z value	2	Minimum peak in Final Diff. Map	-0.43 e$^-$/Å^3

4-8. ((3*R,4*R**,5*S**)-2,2-Dichloro-5-hexyl-3-phenyl-1,2-oxagermolan-4-yl)(phenyl)methanone 4ah: CCDC 1837684**

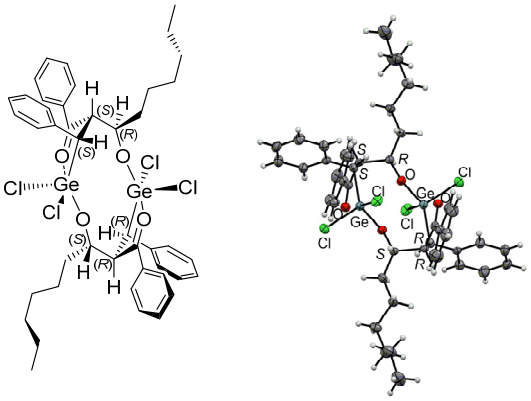


Figure S8. ORTEP drawings of **4ah** at the 50% probability level.

Empirical Formula	$C_{22}H_{26}Cl_2GeO_2$	D_{calc}	1.435 g/cm^3
Formula Weight	465.94	F_{000}	960.00
Crystal Color, Habit	colorless, prism	μ(MoK$_\alpha$)	16.814 cm^{-1}
Crystal Dimensions	0.300 X 0.300 X 0.300 mm	Temperature	-150.0 °C
Crystal System	monoclinic	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Lattice Type	Primitive	Least Squares Weights	Chebychev polynomial with 3
Lattice Parameters	a = 11.7814(4) Å	parameters	2848.3300, 3964.2900, 1257.5800,
	b = 13.6254(3) Å	No. Observations ($I > 2.00\sigma(I)$)	4921
	c = 13.9935(9) Å	No. Variables	270
	β = 106.2710(0) °	Reflection/Parameter Ratio	18.23
	V = 2156.378(98) Å^3	Residuals: R_1 ($I > 2.00\sigma(I)$)	0. 0572
Space Group	$P2_1/n$ (#14)	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0753
Z value	4	Goodness of Fit Indicator	1.157
		Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	0.84 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-0.57 e$^-$/Å^3

4-9. 1-((3*R,4*R**,5*R**)-2,2-Dichloro-5-(4-chlorophenyl)-3-phenyl-1,2-oxagermolan-4-yl)ethan-1-one 4bc: CCDC 1837685**

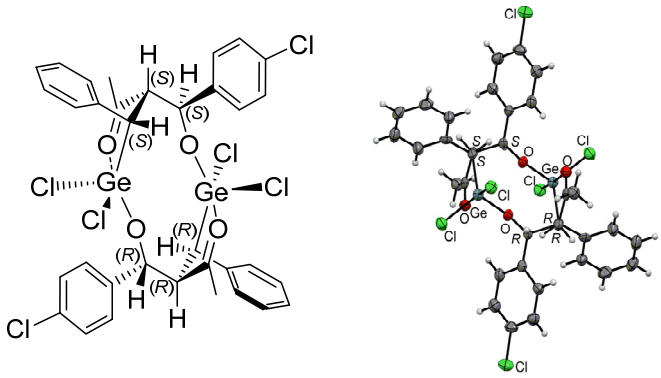


Figure S9. ORTEP drawings of **4bc** at the 50% probability level.

Empirical Formula	$C_{17}H_{15}Cl_3GeO_2$	D_{calc}	1.650 g/cm^3
Formula Weight	430.25	F_{000}	1728.00
Crystal Color, Habit	colorless, platelet	μ(MoK$_\alpha$)	22.350 cm^{-1}
Crystal Dimensions	0.300 X 0.100 X 0.100 mm	Temperature	-150.0 °C
Crystal System	monoclinic	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Lattice Type	*C*-centered	Least Squares Weights	$1/\sigma^2(F_o^2) = 1/\sigma^2(F_o)/(4F_o^2)$
Lattice Parameters	a = 23.911(14) Å	No. Observations ($I > 2.00\sigma(I)$)	2385
	b = 9.882(6) Å	No. Variables	223
	c = 16.166(9) Å	Reflection/Parameter Ratio	10.70
	β = 114.930(10) °	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0681
	V = 3464(3) Å^3	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.1012
Space Group	*C*2/*c* (#15)	Goodness of Fit Indicator	1.658
Z value	8	Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	1.16 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-0.99 e$^-$/Å^3

4-10. ((3*R,4*R**,5*R**)-5-(4-Bromophenyl)-2,2-dichloro-3-(4-fluorophenyl)-1,2-oxagermolan-4-yl)(4-chlorophenyl)methanone 4ei: CCDC 1837688**

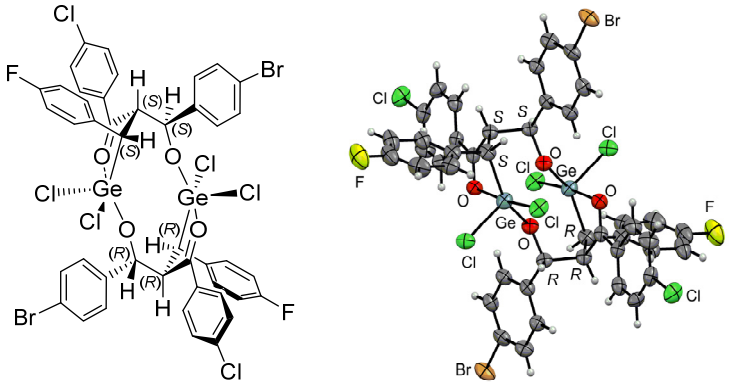


Figure S10. ORTEP drawings of **4ei** at the 50% probability level.

Empirical Formula	$C_{22}H_{15}BrCl_3FGeO_2$	F_{000}	2320.00
Formula Weight	589.21	μ(MoK$_\alpha$)	37.166 cm^{-1}
Crystal Color, Habit	Translucent, light colorless, block	Temperature	-150.0 °C
		Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Crystal Dimensions	0.163 X 0.147 X 0.083 mm	Least Squares Weights	Chebychev polynomial with 3
Crystal System	monoclinic	parameters	26.6108, 35.4729, 9.4751,
Lattice Type	*C*-centered	No. Observations ($I > 2.00\sigma(I)$)	3970
Lattice Parameters	a = 23.7288(13 Å	No. Variables	286
	b = 9.4007(4) Å	Reflection/Parameter Ratio	13.88
	c = 19.4853(7) Å	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0696
	β = 101.090(4) °	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.1243
	V = 4265.4(3) Å^3	Goodness of Fit Indicator	1.158
Space Group	*C*2/*c* (#15)	Max Shift/Error in Final Cycle	0.000
Z value	8	Maximum peak in Final Diff. Map	2.97 e$^-$/Å^3
D_{calc}	1.835 g/cm^3	Minimum peak in Final Diff. Map	-1.16 e$^-$/Å^3

4-11. 1-((3*R,4*R**,5*S**)-2,2-Dichloro-5-(4-chlorophenyl)-3-methyl-3-phenyl-1,2-oxagermolan-4-yl)ethan-1-one 4cc: CCDC 1837686**

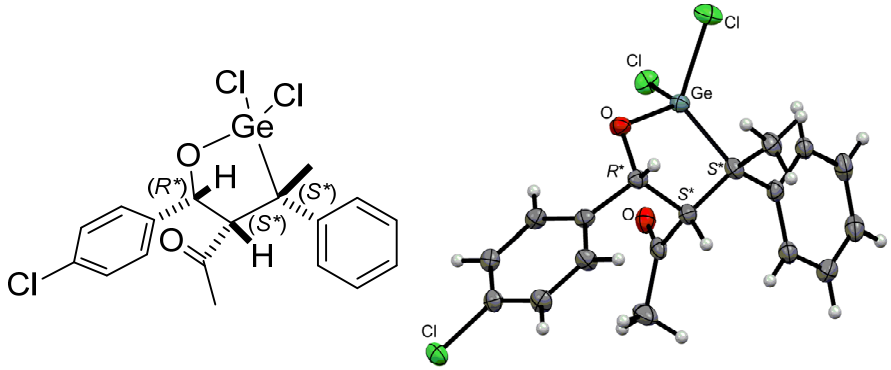


Figure S11. ORTEP drawings of **4cc** at the 50% probability level.

Empirical Formula	$C_{18}H_{17}Cl_3GeO_2$	D_{calc}	1.613 g/cm^3
Formula Weight	444.28	F_{000}	896.00
Crystal Color, Habit	colorless, prism	μ(MoK$_\alpha$)	21.184 cm^{-1}
Crystal Dimensions	0.300 X 0.200 X 0.200 mm	Temperature	-150.0 °C
Crystal System	monoclinic	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Lattice Type	Primitive	Least Squares Weights	Chebychev polynomial with 3
Lattice Parameters	a = 14.9729(9) Å	parameters	1358.2800,1899.7700,589.9290,
	b = 10.0356(6) Å	No. Observations ($I > 2.00\sigma(I)$)	3243
	c = 12.3580(7) Å	No. Variables	234
	β = 99.8410(18) °	Reflection/Parameter Ratio	13.86
	V = 1829.62(18)) Å^3	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0442
Space Group	$P2_1/c$ (#14)	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0761
Z value	4	Goodness of Fit Indicator	0.917
		Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	0.63 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-0.70 e$^-$/Å^3

4-12. 1-((4*R,5*S**)-2,2-Dichloro-5-(4-chlorophenyl)-3,3-dimethyl-1,2-oxagermolan-4-yl)ethan-1-one 4dc: CCDC 1837687**

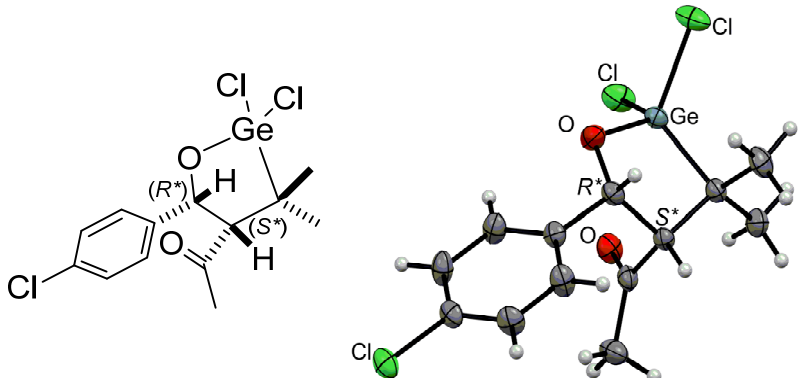


Figure S12. ORTEP drawings of **4dc** at the 50% probability level.

Empirical Formula	$C_{13}H_{15}Cl_3GeO_2$	D_{calc}	1.641 g/cm^3
Formula Weight	382.21	F_{000}	768.00
Crystal Color, Habit	colorless, prism	μ(MoK$_\alpha$)	24.898 cm^{-1}
Crystal Dimensions	0.600 X 0.500 X 0.400 mm	Temperature	-150.0 °C
Crystal System	monoclinic	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Lattice Type	Primitive	Least Squares Weights	Chebychev polynomial with 3
Lattice Parameters	a = 17.3147(13) Å	parameters	8374.4800,11721.9000,3694.5600,
	b = 7.8971(8) Å	No. Observations ($I > 2.00\sigma(I)$)	3810
	c = 11.8794(10) Å	No. Variables	187
	β = 107.727(3) °	Reflection/Parameter Ratio	20.37
	V = 1547.2(2) Å^3	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0344
Space Group	$P2_1/c$ (#14)	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0534
Z value	4	Goodness of Fit Indicator	1.085
		Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	0.85 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-0.37 e$^-$/Å^3

4-13. (1*R,2*R**,3*S**)-1-(4-Chlorophenyl)-2-((*S**)-1-germyl-1-phenylethyl)butane-1,3-diol 5cc: CCDC 1837689**

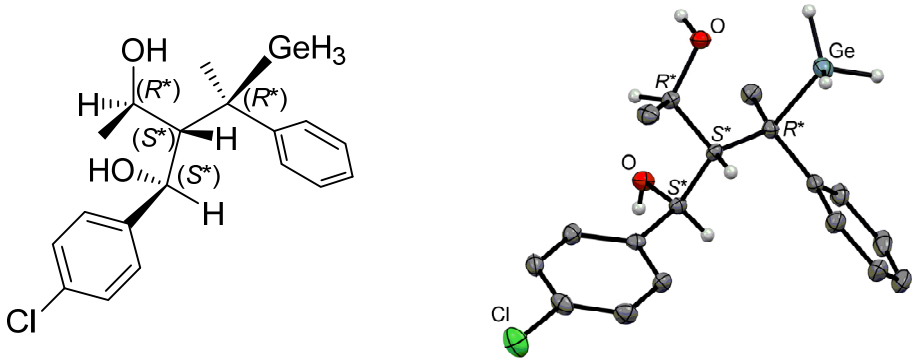
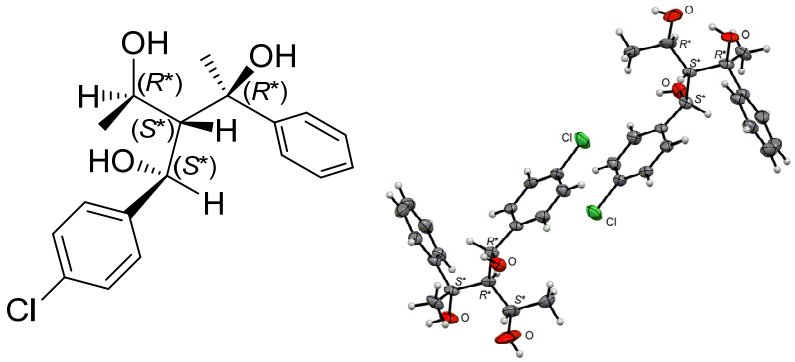


Figure S13. ORTEP drawings of **5cc** at the 50% probability level.

Empirical Formula	$C_{18}H_{23}ClGeO_2$	D_{calc}	1.475 g/cm^3
Formula Weight	379.42	F_{000}	1568.00
Crystal Color, Habit	Translucent, intense, colorless,	μ(MoKα)	19.518 cm^{-1}
Crystal Dimensions	block	Temperature	-150.0 °C
Crystal System	0.217 X 0.142 X 0.101 mm	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Lattice Type	monoclinic	Least Squares Weights	Chebychev polynomial with 3
Lattice Parameters	*C*-centered	parameters	79.3067, 106.8070, 29.1684,
	a = 19.8583(8) Å	No. Observations ($I > 2.00\sigma(I)$)	3813
	b = 6.7852(3) Å	No. Variables	291
	c = 25.7564(10) Å	Reflection/Parameter Ratio	13.10
	β = 99.975(4) °	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0340
Space Group	V = 3418.0(2) Å^3	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0476
Z value	$C2/c$ (#15)	Goodness of Fit Indicator	1.150
	8	Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	0.81 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-0.61 e$^-$/Å^3

4-14. (2*R,3*S**,4*R**)-3-((*S**)-(4-Chlorophenyl)(hydroxy)methyl)-2-phenylpentane-2,4-diol 6cc: CCDC 1837690**



FigureS14. ORTEP drawings of **6cc** at the 50% probability level.

Empirical Formula	$C_{36}H_{42}Cl_2O_6$	D_{calc}	1.334 g/cm^3
Formula Weight	320.82	F_{000}	1360.00
Crystal Color, Habit	Translucent, light, colorless,	μ(MoKα)	2.490 cm^{-1}
	block	Temperature	-150.0 °C
Crystal Dimensions	0.417 X 0.134 X 0.105 mm	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Crystal System	monoclinic	Least Squares Weights	Chebychev polynomial with 3
Lattice Type	Primitive	parameters	64.7808, 85.8503, 21.4854,
Lattice Parameters	a = 11.3744(5) Å	No. Observations ($I > 2.00\sigma(I)$)	5438
	b = 8.3853(4) Å	No. Variables	439
	c = 33.8180(15) Å	Reflection/Parameter Ratio	12.39
	β = 97.992(4) °	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0826
	V = 3194.2(3) Å^3	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.1473
Space Group	$P2_1/n$ (#14)	Goodness of Fit Indicator	1.000
Z value	4	Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	1.77 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-1.22 e$^-$/Å^3

4-15. (1*R,2*S**,3*S**)-1-(4-Bromophenyl)-3-(4-chlorophenyl)-2-((*R**)-(4-fluorophenyl)(hydroxy)methyl)propane-1,3-diol 6ei: CCDC 1837691**

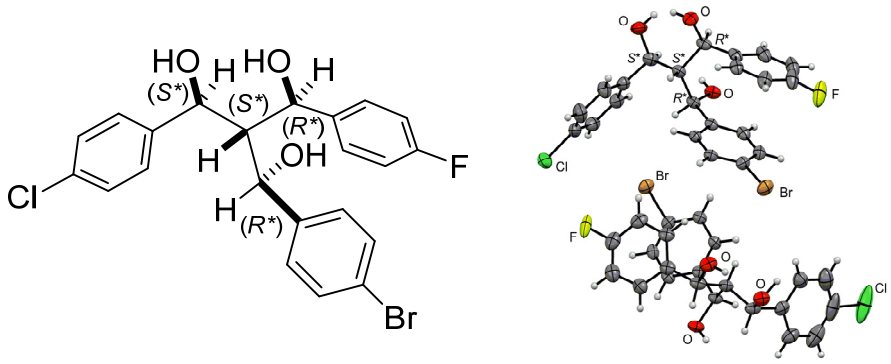


Figure S15. ORTEP drawings of **6ei** at the 50% probability level.

Empirical Formula	$C_{44}H_{38}Br_2Cl_2F_2O_6$	D_{calc}	1.548 g/cm^3
Formula Weight	931.49	F_{000}	944.00
Crystal Color, Habit	Translucent, intense, colorless, block	μ(CuK$_\alpha$)	42.951 cm^{-1}
		Temperature	-150.0 °C
Crystal Dimensions	0.083 X 0.076 X 0.054 mm	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Crystal System	Triclinic	Least Squares Weights	Chebychev polynomial with 3
Lattice Type	Primitive	parameters	4888.5700, 6769.3400, 2021.6600,
Lattice Parameters	a = 6.82290(10) Å	No. Observations ($I > 2.00\sigma(I)$)	7475
	b = 13.8363(2) Å	No. Variables	546
	c = 21.7759(3) Å	Reflection/Parameter Ratio	13.69
	α =76.9851(12) °	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0474
	β = 89.8416(12) °	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0509
	γ = 86.0436(12) °	Goodness of Fit Indicator	1.278
	V = 1997.97(5) Å^3	Max Shift/Error in Final Cycle	0.000
Space Group	P-1 (#2)	Maximum peak in Final Diff. Map	0.80 e$^-$/Å^3
Z value	2	Minimum peak in Final Diff. Map	-0.78 e$^-$/Å^3

4-16. ((*R)-((4*R**,5*S**,6*R**)-4-(4-Chlorophenyl)-2,2,6-trimethyl-1,3-dioxan-5-yl)(phenyl)methyl)germane 7bc: CCDC 1837692**

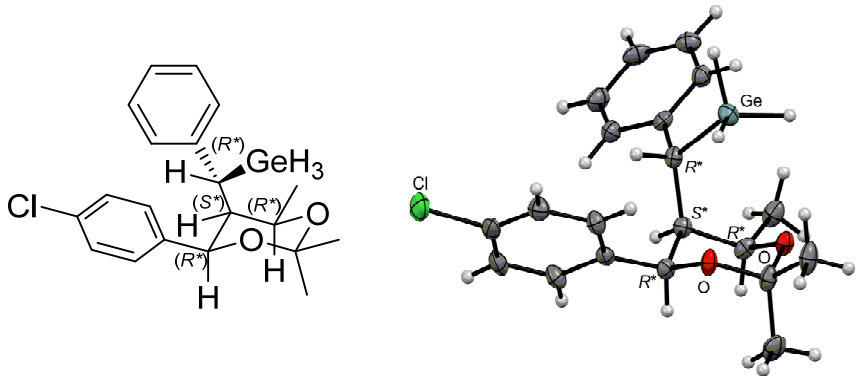


Figure S16. ORTEP drawings of **7bc** at the 50% probability level.

Empirical Formula	$C_{20}H_{25}ClGeO_2$	D_{calc}	1.385 g/cm^3
Formula Weight	405.46	F_{000}	840.00
Crystal Color, Habit	translucentintense, block	μ(CuK$_\alpha$)	34.656 cm^{-1}
Crystal Dimensions	0.351 X 0.170 X 0.137 mm	Temperature	-150.0 °C
Crystal System	monoclinic	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Lattice Type	Primitive	Least Squares Weights	Chebychev polynomial with 3 parameters
Lattice Parameters	a = 11.23541(18) Å		12574.9000,17508.1000,5331.7400,
	b = 10.13457(12) Å	No. Observations ($I > 2.00\sigma(I)$)	3753
	c = 17.7290(3) Å	No. Variables	317
	β=105.5484(16) °	Reflection/Parameter Ratio	11.84
	V = 1944.85(5) Å^3	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.0285
Space Group	$P2_1/n$ (#14)	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.0312
Z value	4	Goodness of Fit Indicator	1.281
		Max Shift/Error in Final Cycle	0.000
		Maximum peak in Final Diff. Map	0.34 e$^-$/Å^3
		Minimum peak in Final Diff. Map	-0.38e$^-$/Å^3

4-17. (1*R,2*R**,3*R**)-2-((*R**)-(4-Chlorophenyl)((4-cyanobenzoyl)oxy)methyl)-1-phenylbutane-1,3-diyl bis(4-cyanobenzoate) 8bc: CCDC 1837693**

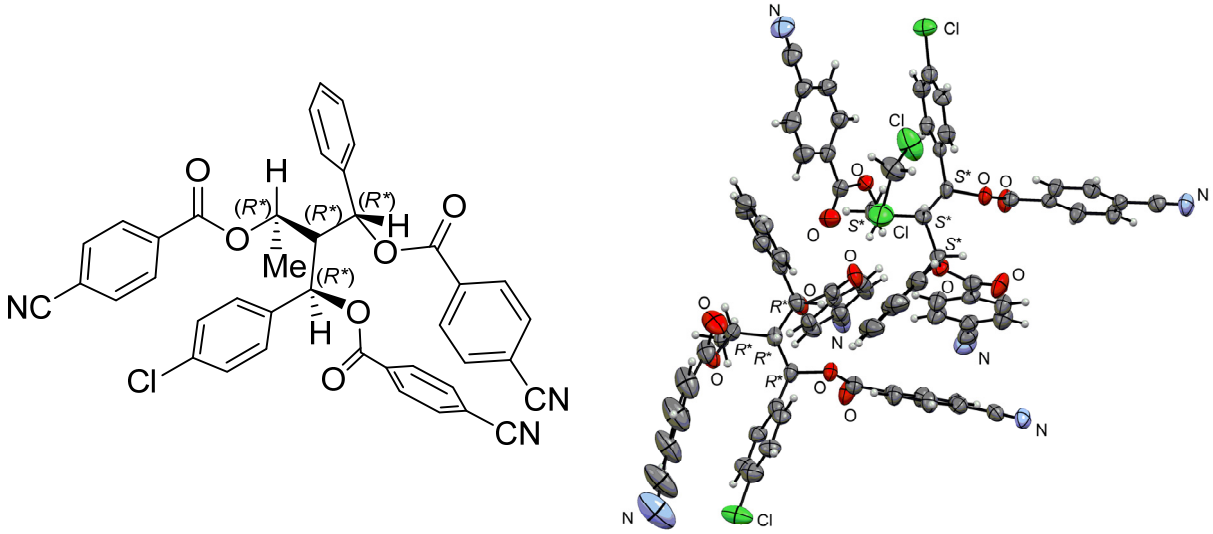
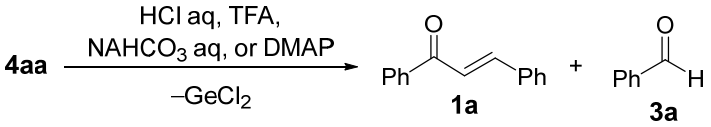


Figure S17. ORTEP drawings of **8bc** at the 50% probability level.

Empirical Formula	$C_{83}H_{58}Cl_4N_6O_{12}$	D_{calc}	1.353 g/cm^3
Formula Weight	1473.22	F_{000}	1524.00
Crystal Color, Habit	Translucent, intense, colorless, plate	μ(CuK$_\alpha$)	20.554 cm^{-1}
		Temperature	-150.0 °C
Crystal Dimensions	0.109 X 0.061 X 0.033 mm	Function Minimized	$\Sigma\, w\,(F_o^2 - F_c^2)^2$
Crystal System	triclinic	Least Squares Weights	$1/\sigma^2(F_o^2) = 1/\sigma^2(F_o)/(4F_o^2)$
Lattice Type	Primitive	No. Observations ($I > 2.00\sigma(I)$)	10199
Lattice Parameters	a = 11.2584(4) Å	No. Variables	1004
	b = 14.6929(8) Å	Reflection/Parameter Ratio	10.16
	c = 22.2536(8) Å	Residuals: R_1 ($I > 2.00\sigma(I)$)	0.1233
	α = 80.011(4) °	Residuals: wR_2 ($I > 2.00\sigma(I)$)	0.1986
	β = 86.005(3) °	Goodness of Fit Indicator	2.637
	γ = 89.135(4) °	Max Shift/Error in Final Cycle	0.001
	V = 3616.5(3) Å^3	Maximum peak in Final Diff. Map	0.86 e$^-$/Å^3
Space Group	P-1 (#2)	Minimum peak in Final Diff. Map	-0.82 e$^-$/Å^3
Z value	2		

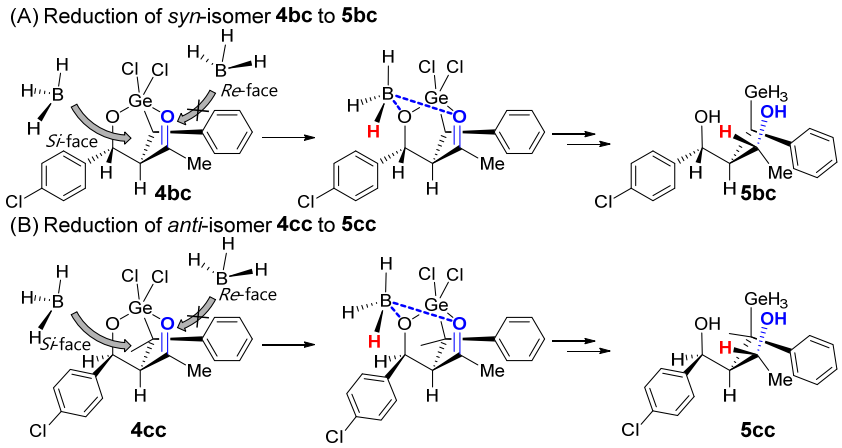
5. Retro aldol reaction of 4aa.



Scheme S1. Retro aldol reaction of **4aa**.

The aldol adduct **4aa** readily converted into the starting chalcone and benzaldehyde upon treatment with various acids/basses, such as HCl aq., TFA, $NaHCO_3$ aq., and DMAP (Scheme 3C).[5–7] In our system, the reversibility appeared to arise from the intramolecular coordination of the carbonyl groups to the Ge(IV) centers in **4aa**.

6. Facial selectivity of the reductions of 4bc and 4cc.



Scheme S2. Facial selectivity of the reductions of **4bc** and **4cc**.

The rigid cyclic structures of the aldol adducts **4bc** and **4cc** and the electrostatic interaction between the boron center and the oxygen atoms of the aldol adducts were expected to allow such a high diastereoselective transformation (Scheme S2).

7. References

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