Supplementary Information for

Reversible Addition of Terminal Alkenes to Digermynes

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1. General Remarks.

All manipulations were carried out under an argon atmosphere, using either Schlenk line or glove box techniques. All solvents were purified by standard methods and/or the Ultimate Solvent System, Glass Contour Company.[S1] Remaining trace amounts of water and oxygen in the solvents were thoroughly removed by bulb-to-bulb distillation from potassium mirror prior to use. ^{1}H and ^{13}C NMR spectra were measured on a JEOL JNM-ECA600 (^{1}H: 600 MHz, ^{13}C: 151 MHz) in the Joint Usage/Research Center (JURC, Institute for Chemical Research, Kyoto University) or on a JEOL AL-300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz). Signals arising from residual C_6D_5H (7.15 ppm) in the C_6D_6 or $C_6D_5CD_2H$ (2.08 ppm, $–CD_2\underline{H}$) in toluene-d_8 were used as internal standards for the ^{1}H NMR spectra, whereas the signals of C_6D_6 (128.0 ppm) and toluene-d_8 (137.48 ppm, $–\underline{C}–CD_3$) were used to reference the ^{13}C NMR spectra. High-resolution mass spectra (HRMS) were obtained from a Bruker micrOTOF focus-Kci mass spectrometer (DART). All melting points were determined on a Büchi Melting Point apparatus M-565 and are uncorrected. Digermynes BbtGe≡GeBbt and TbbGe≡GeTbb (Bbt: 2,6-[CH(SiMe$_3$)$_2$]$_2$-4-[C(SiMe$_3$)$_3$]-C$_6$H$_2$; Tbb: 4-*t*Bu-2,6-[CH(SiMe$_3$)$_2$]$_2$-C$_6$H$_2$) were prepared according to literature procedures.[S2,S3]

2. Experimental Details.

Synthesis of 1,2-Bbt$_2$-1,2-digermacyclobutene (10a): A hexane solution (0.2 mL) of digermyne **5a** (24.0 mg, 17.2 μmol) was treated with styrene (2.5 mg, 24.0 μmol, 1.4 equiv.) for 10 min at room temperature. After the solvent and residual styrene were removed under reduced pressure, 1,2-digermacyclobutene **10a** was obtained as a purple solid (24.5 mg, 16.6 μmol, 97%). **10a**: purple solid, mp 90.5-91.5 °C (dec); ^{1}H NMR (600 MHz, toluene-d_8, 253 K): δ 0.35 (s, 36H), 0.36 (s, 36H), 0.40 (s, 54H), 2.54 (bs, 2H), 2.83 (bs, 2H), 3.19 (dd, J = 13.8, 4.8 Hz, 1H), 3.26 (dd, J = 13.8, 7.8 Hz, 1H), 4.88 (dd, J = 7.8, 4.8 Hz, 1H), 6.96–7.01 (m, 5H), 7.19–7.22 (m, 2H), 7.58 (d, J = 7.2 Hz, 2H); ^{13}C NMR (151 MHz, toluene-d_8, 253 K): δ 2.08 (q), 5.63 (q), 5.64 (q), 34.98 (d), 35.03 (s), 45.41 (t), 55.39 (d), 125.26 (d), 126.57 (d), 126.83 (d), 127.61 (d), 129.15 (d), 137.40 (s), 142.46 (s), 146.09 (s), 146.27 (s), 146.89 (s), 147.56 (s), 150.45 (s), 150.98 (s); UV/vis [0.334 mM, *n*-hexane]: λ_{max} (nm, ε) = 459 (5,600); MS (DART-TOF, positive mode): *m/z* calcd for $C_{68}H_{144}Ge_2Si_{14}$ 1499.6383 ([M+H]$^+$), found 1499.6438 ([M+H]$^+$).

Synthesis of 1,2-Bbt$_2$-1,2-digermacyclobutene (11): A hexane solution (0.3 mL) of digermyne **5a** (22.5 mg, 16.1 μmol) was treated with 1-hexene (5.1 mg, 60.6 μmol, 3.8 equiv.) for 10 min at room temperature. After the solvent and residual 1-hexene were removed under reduced pressure, 1,2-digermacyclobutene **11** was obtained as a purple solid (22.7 mg, 15.4 μmol, 96%). **11**: purple solid, mp 52.4-53.4 °C (dec); ^{1}H NMR (600 MHz, C_6D_6, 273 K): δ 0.28 (s, 36H), 0.36 (s, 36H), 0.36 (s, 54H), 0.98 (t, J = 7.4 Hz, 3H), 1.36–1.49 (m, 2H), 1.59–1.79 (m, 2H), 2.18 (dd, J = 13.5, 1.8 Hz, 1H), 2.48–2.53 (m, 1H), 2.56 (bs, 2H), 2.65 (bs, 2H), 3.53 (ddd, J = 13.5, 6.6, 1.8 Hz, 1H), 6.91 (bs, 2H), 6.93 (bs, 2H); ^{13}C NMR (151 MHz, C_6D_6, 273 K): δ 1.88 (q), 5.62 (q), 5.68 (q), 14.65 (q), 23.53 (t), 34.55 (t), 34.66 (s), 34.76 (d), 39.69 (t), 45.71 (t), 52.79 (d), 126.76 (d), 126.85 (d), 145.53 (s), 145.65 (s), 146.95 (s), 149.33 (s), 150.04 (s), 150.93 (s); UV/vis [2.48 mM, *n*-hexane]: λ_{max} (nm, ε) = 473 (2,000); MS (DART-TOF, positive mode): *m*/*z* calcd for $C_{66}H_{147}Ge_2Si_{14}$ 1478.6618 ($[M]^+$), found 1478.6669 ($[M]^+$).

Synthesis of 1,2-Bbt$_2$-1,2-digermacyclobutene (10b): A hexane solution (0.5 mL) of digermyne **5b** (28.4 mg, 27.2 μmol) was treated with styrene (3.0 mg, 28.8 μmol, 1.1 equiv.) for 10 min at room temperature. After the solvent and residual styrene were removed under reduced pressure, the residue was recrystallized from hexane to afford 1,2-digermacyclobutene **10b** as stable orange crystals in quantitative yield (31.4 mg, 27.2 μmol, quant). **10b**: orange crystals, mp 135.7-136.7 °C (dec); ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.18 (s, 36H), 0.25 (s, 36H), 1.30 (s, 18H), 2.86 (s, 4H), 2.93 (dd, J = 14.1, 8.1 Hz, 1H), 3.47 (dd, J = 14.1, 5.1 Hz, 1H), 5.13 (dd, J = 8.1, 5.1 Hz, 1H), 6.93–6.99 (m, 5H), 7.18 (t, J = 7.7 Hz, 2H), 7.55 (d, J = 7.7 Hz, 2H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 1.04 (q), 1.24 (q), 31.25 (q), 33.87 (d), 34.49 (s), 46.42 (t), 54.55 (d), 121.66 (d), 125.23 (d), 126.93 (d), 129.08 (d), 147.32 (s), 147.51 (s), 148.11 (s), 151.33 (s); UV/vis [0.383mM, *n*-hexane] λ_{max} (nm, ε) = 462 (5,700); MS (DART-TOF, positive mode): *m*/*z* calcd for $C_{64}H_{111}Ge_2Si_8$ 1151.4950 ($[M+H]^+$), found 1151.4889 ($[M+H]^+$).

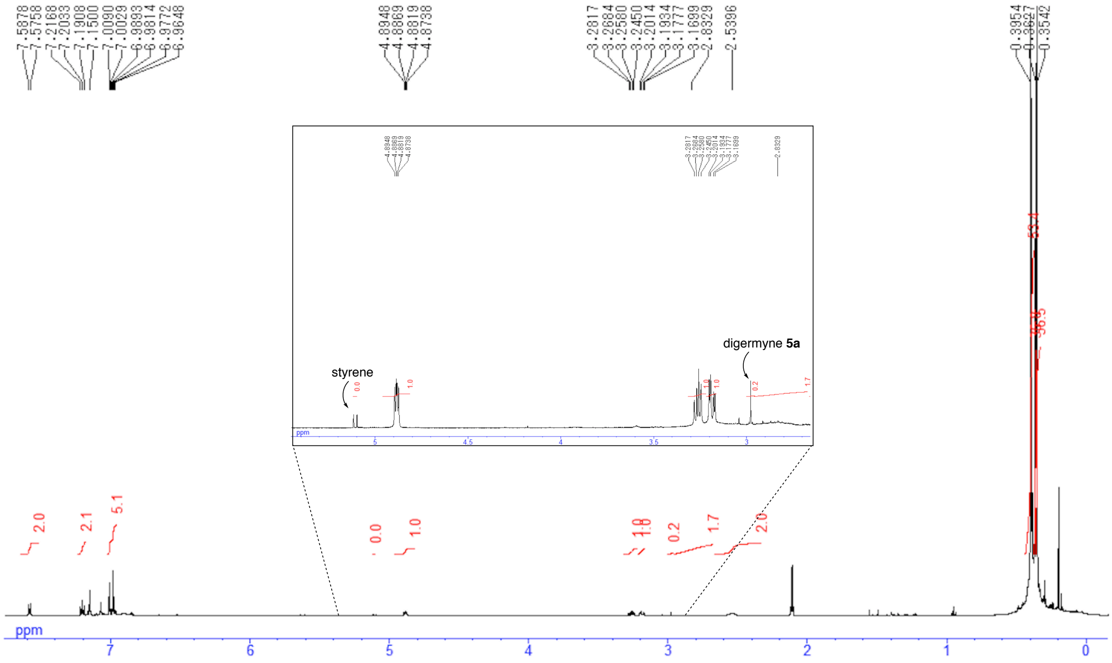


Figure S1. ^{1}H NMR spectrum of **10a** in toluene-d_8.

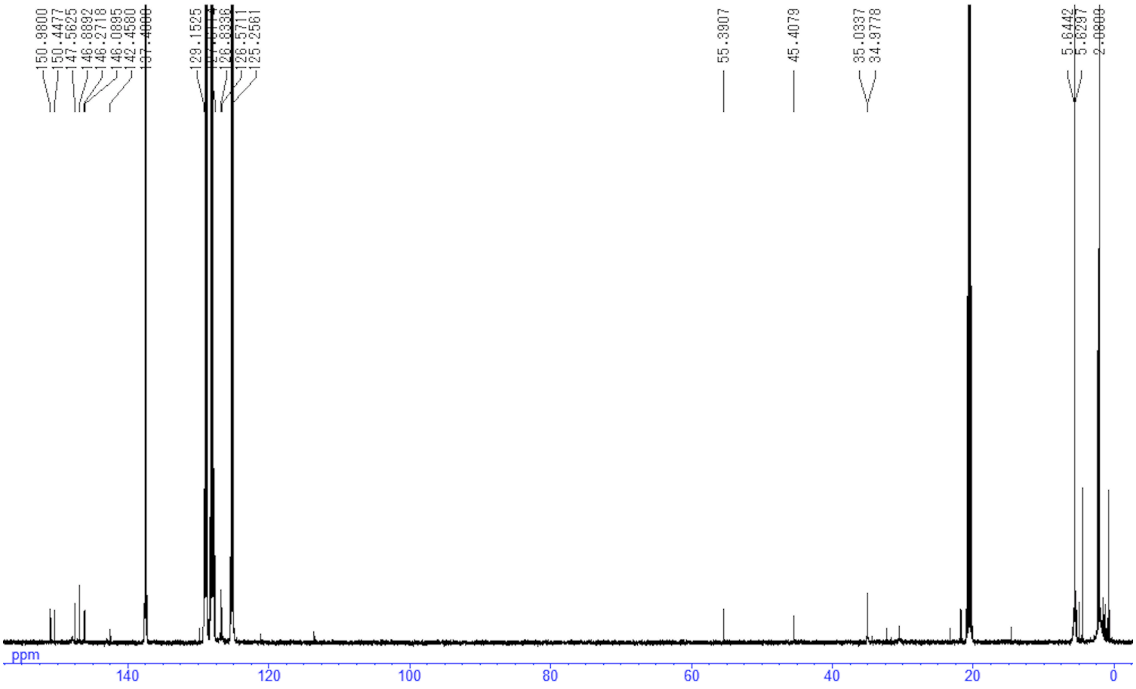
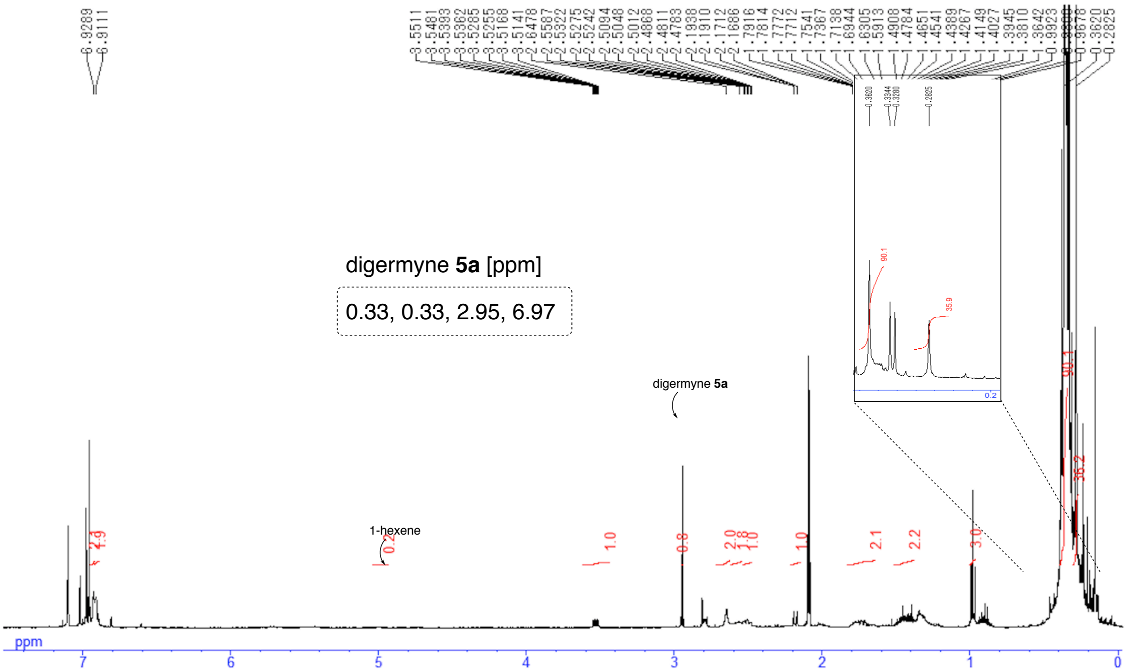


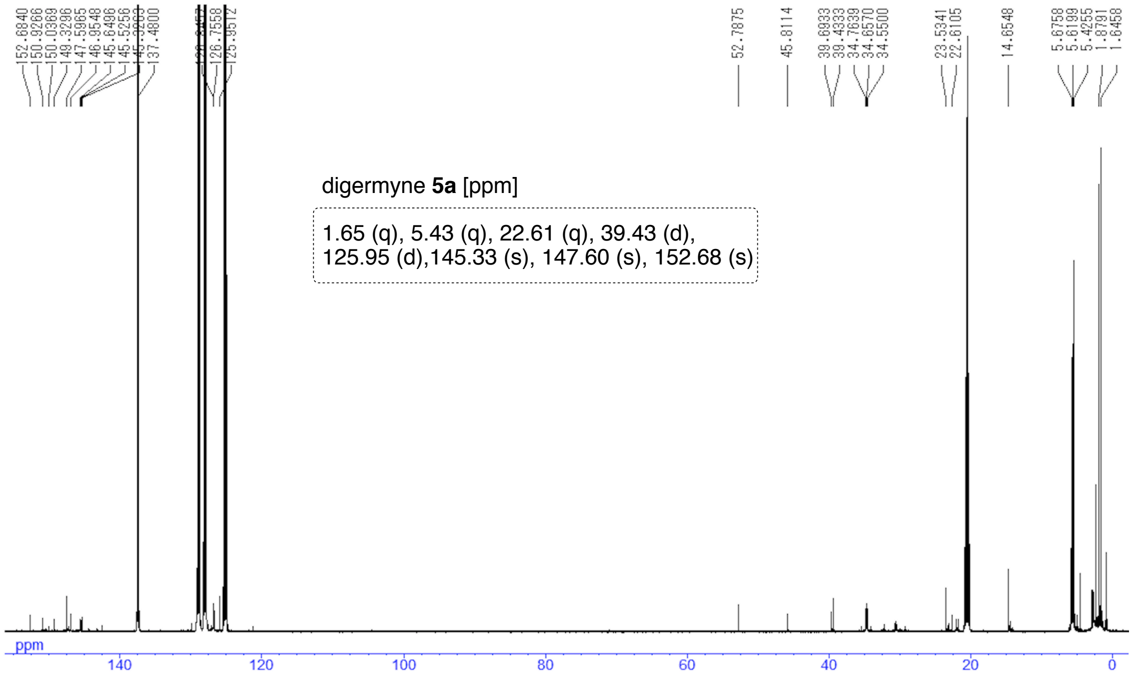
Figure S2. ^{13}C NMR spectrum of **10a** in toluene-d_8.



digermyne **5a** [ppm]

0.33, 0.33, 2.95, 6.97

Figure S3. ^{1}H NMR spectrum of **11** in toluene-d_8.



digermyne **5a** [ppm]

1.65 (q), 5.43 (q), 22.61 (q), 39.43 (d),
125.95 (d),145.33 (s), 147.60 (s), 152.68 (s)

Figure S4. ^{13}C NMR spectrum of **11** in toluene-d_8.

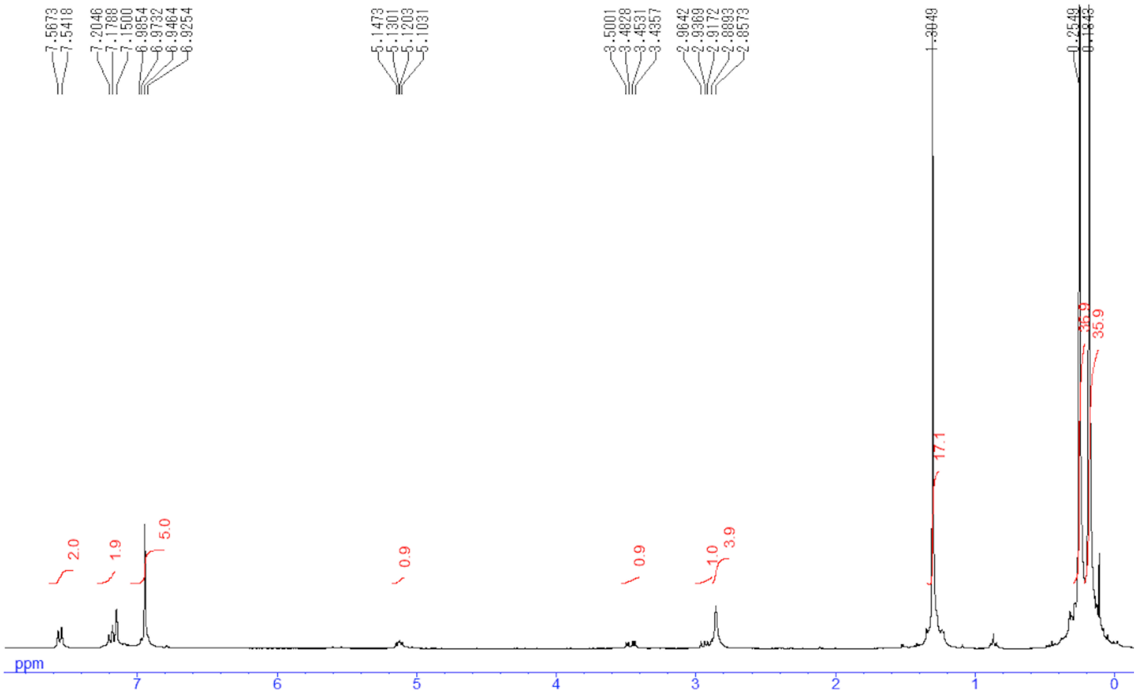


Figure S5. ^{1}H NMR spectrum of **10b** in C_6D_6.

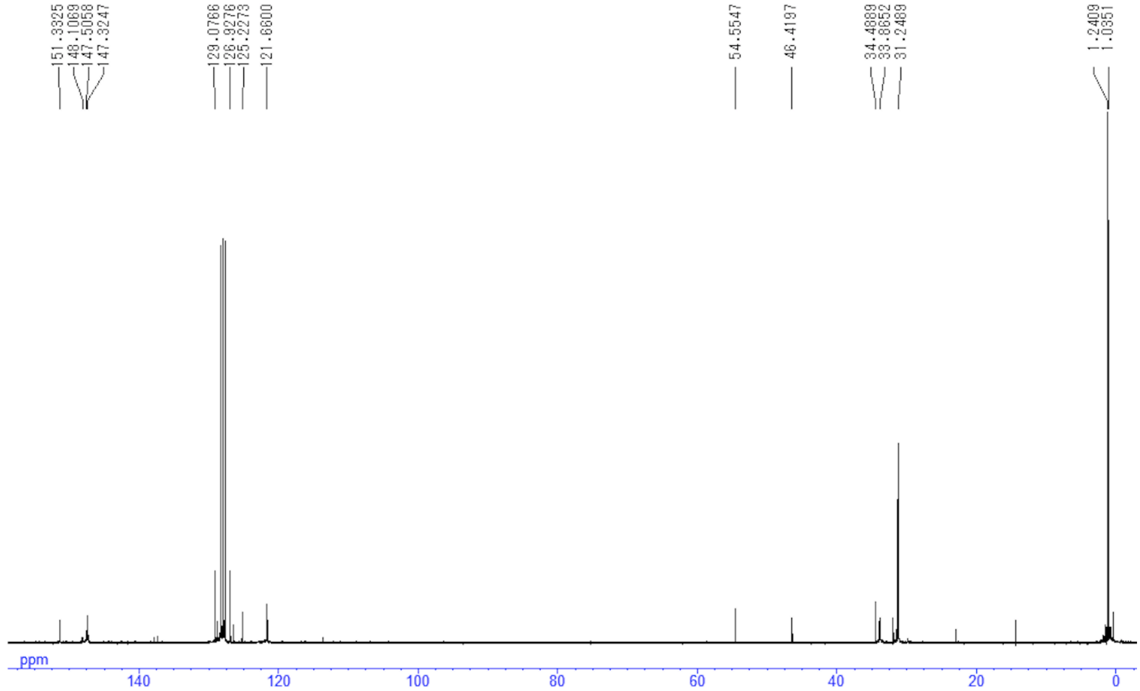


Figure S6. ^{13}C NMR spectrum of **10b** in C_6D_6.

Regeneration of 1,2-Bbt$_2$-1,2-digermyne (5a) from 1,2-Bbt$_2$-1,2-digermacyclobutenes 10a/11: Solutions of **10a** or **11** (**10a**: 7.2 μmol, **11**: 4.2 μmol) in toluene-*d*$_8$ (**10a**: 0.38 mL, **11**: 0.40 mL) were heated for 1 h under reduced pressure (**10a**: 80 ºC, **11**: 60 ºC). Judging from the ^{1}H NMR spectra, **5a** was regenerated in high NMR yield (**10a**: 81%, **11**: 97%).

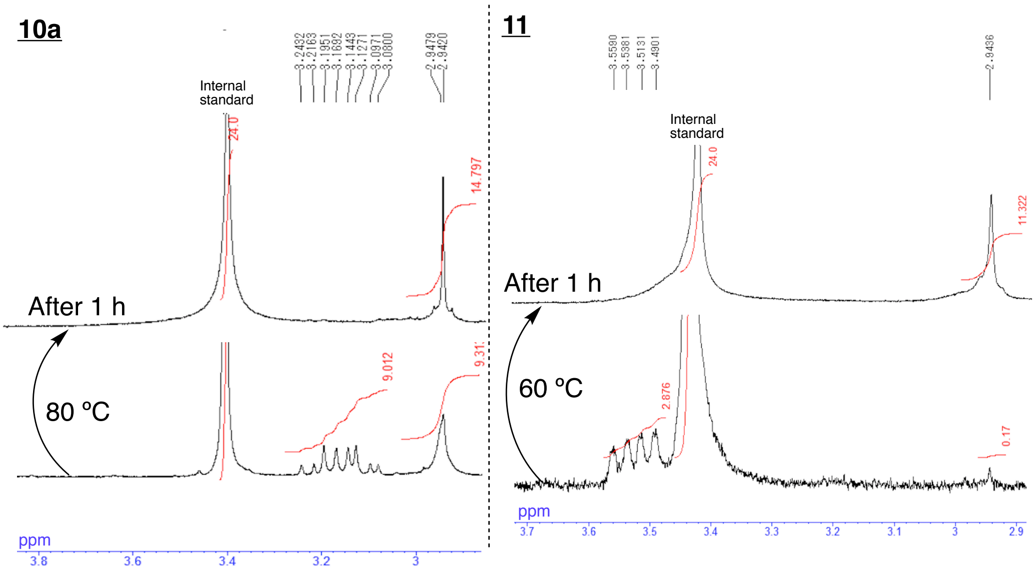


Figure S7. Regeneration of 1,2-Bbt$_2$-1,2-digermyne (**5a**) from **10a** or **11**.

VT ^{1}H NMR spectra of 1,2-Bbt$_2$-1,2-digermacyclobutenes 10a or 11 in toluene-*d*$_8$: Solutions of **10a** or **11** (**10a**: 8.1 mg, 5.4 μmol, **11**: 22.5 mg, 15.4 μmol) in toluene-*d*$_8$ (**10a**: 0.45 mL, **11**: 0.50 mL) were monitored by ^{1}H NMR spectroscopy at various temperatures. A van't Hoff analysis established sufficiently small values for the Gibbs free energy values of the equilibrium reactions between **10a** or **11** and alkenes **8** and **9** (**10a**: ΔH = –20.4 kcal/mol, ΔS = –58.2 cal/mol·K, ΔG$_{298K}$ = –3.1 kcal/mol, **11**: ΔH = –21.0 kcal/mol, ΔS = –55.0 cal/mol, ΔG$_{298K}$ = –4.5 kcal/mol), respectively.

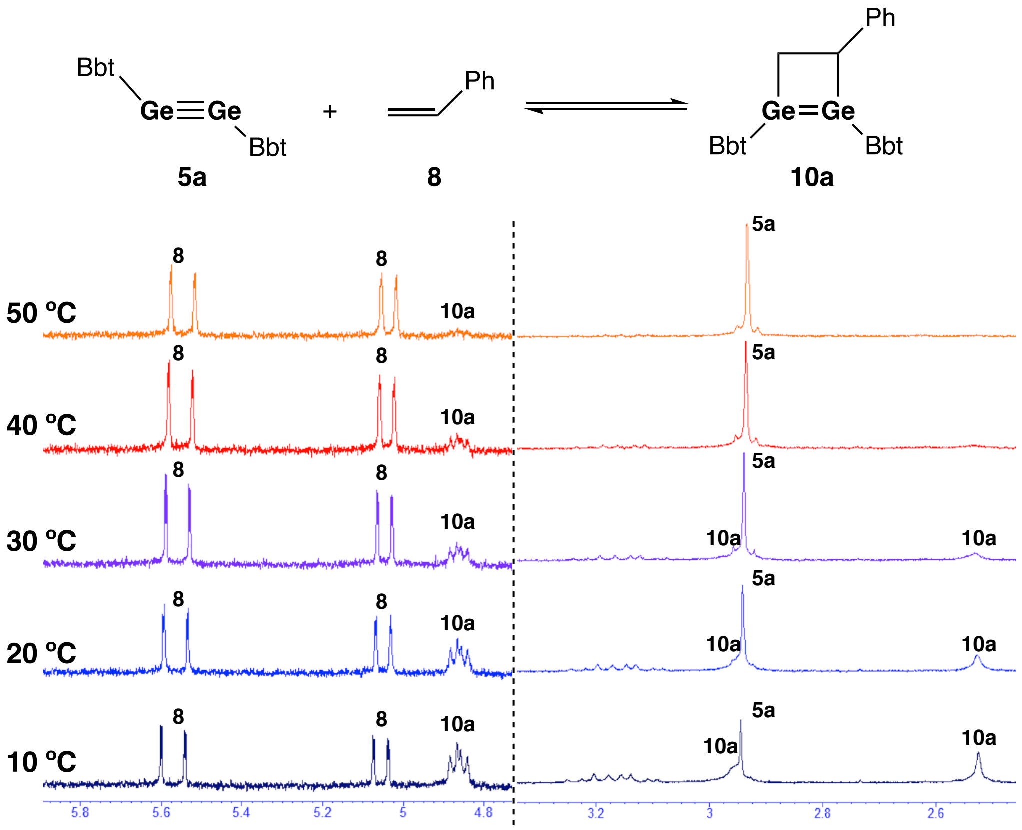


Figure S8. VT ^{1}H NMR spectra of **5a** + **8** ⇄ **10a** in toluene-d_8 (left: 4.7–5.9 ppm; right: 2.5–3.3 ppm).

Table S1. VT ^{1}H NMR and temperature data for the reaction **5a** + **8** ⇄ **10a**.

	Concentration [mM] [a]					
T (K)	**5a**	**8**	**10a**	**K**	**ln(K)**	**1/T**
283	0.002692	0.002790	0.009245	1231	7.117	0.003534
293	0.004671	0.004964	0.007266	313.4	5.749	0.003413
303	0.006972	0.007256	0.004965	98.13	4.587	0.003300
313	0.009086	0.009354	0.002851	33.54	3.513	0.003195
323	0.01040	0.01072	0.001542	13.83	2.626	0.003096

[a] The uncertainty for the integrations was estimated to be typically 5%, while that of the temperatures was 1 °C (determined by monitoring the VT NMR).

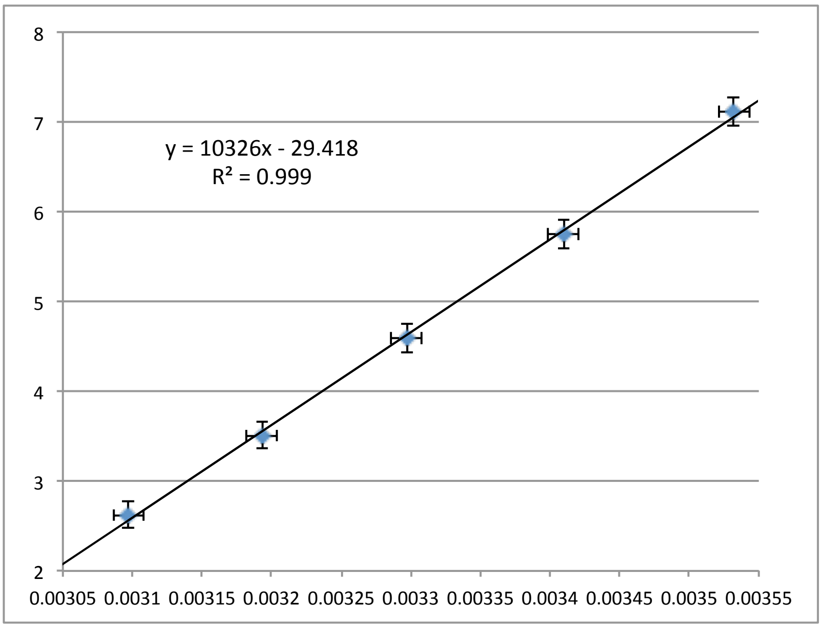


Figure S9. Plot of ln(K) as a function of T^{-1} for **5a** + **8** ⇄ **10a** [ΔH = –20.4(±1.1) kcal/mol, ΔS = –58.2(±3.8) cal/mol·K, ΔG_{298K} = –3.1(±0.2) kcal/mol].

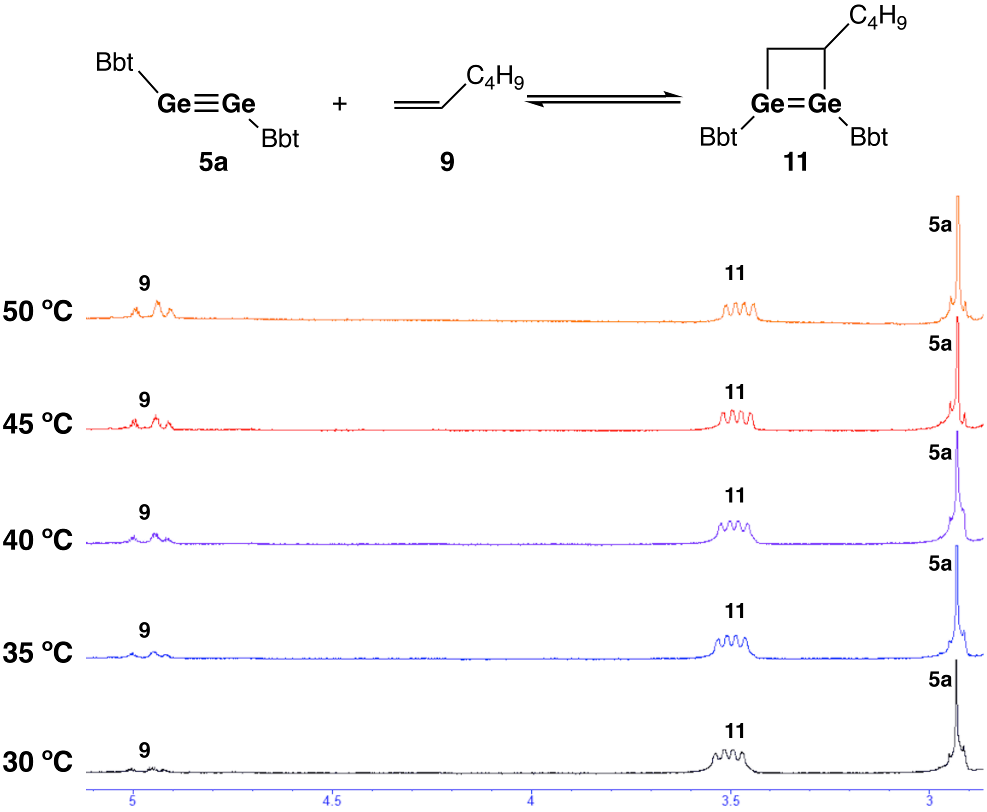


Figure S10. VT ^{1}H NMR spectra for **5a** + **9** ⇄ **11** in toluene-d_8 (2.8–5.1 ppm).

Table S2. VT ^{1}H NMR and temperature data for **5a** + **9** $\rightleftarrows$ **11**.

	Concentration [mM] [a]					
T (K)	**5a**	**9**	**11**	**K**	**ln(K)**	**1/T**
303	0.005019	0.003193	0.02569	1315	7.192	0.003299
308	0.006647	0.003892	0.02406	648.5	6.475	0.003245
313	0.008062	0.005583	0.02265	401.0	5.994	0.003193
318	0.009887	0.007004	0.02082	228.4	5.431	0.003143
323	0.01167	0.009222	0.01904	151.4	5.020	0.003095

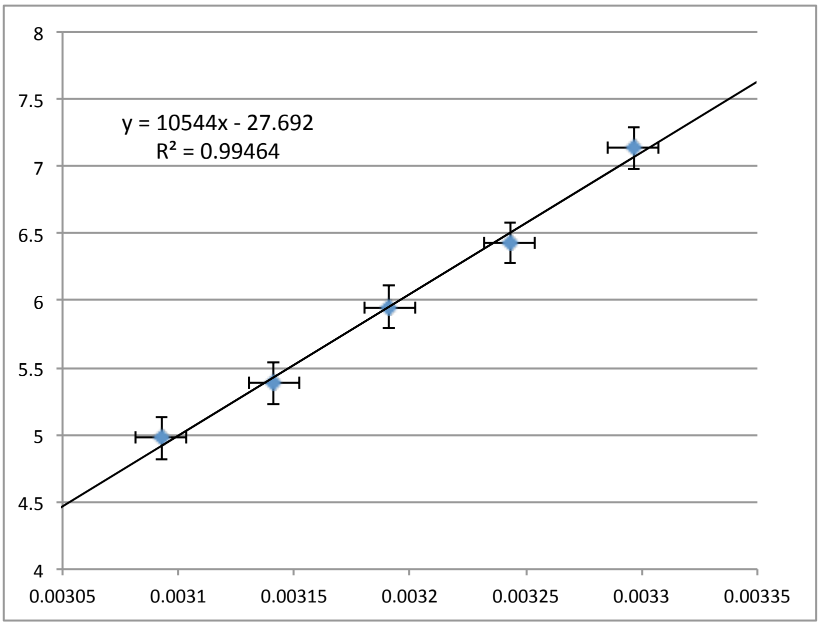


Figure S11. Plot of ln(K) as a function of T^{-1} for **5a** + **9** $\rightleftarrows$ **11** [$\Delta H = -21.0(\pm 2.4)$ kcal/mol, $\Delta S = -55.0(\pm 7.9)$ cal/mol·K, $\Delta G_{298K} = -4.5(\pm 0.3)$ kcal/mol].

Reaction of 1,2-Bbt$_2$-1,2-digermacyclobutene 10a with an excess of ethylene in C_6D_6: In a *J*-Young Schlenk tube, a solution of **10a** (12.2 mg, 8.8 µmol) in C_6D_6 (0.5 mL) was degassed by several freeze-pump-thaw cycles. Subsequently, the degassed solution was exposed to an excess of ethylene (~1 atm.) at room temperature for 20 min, before all volatiles were removed *in vacuo* at room temperature to afford 1,2-Bbt$_2$-1,2-digermacyclobutene **6** in quantitative yield (12.3 mg, 8.8 µmol).

3. X-Ray Crystallographic Analysis.

Single crystals of [**10a**·C_6H_6], **11**, and **10b** were obtained from recrystallization of the respective target compounds in benzene (**10a**) or *n*-hexane (**11**, **10b**) at room temperature (**10a**) or –20 ºC (**11**, **10b**) in an argon-filled glove box. Intensity data were collected on a RIGAKU Saturn70 CCD system with VariMax Mo optics using MoK$_\alpha$ radiation (**10a**: λ = 0.71069 Å, **11**: λ = 0.71075 Å, **10b**: λ = 0.71073 Å). The crystal data are shown in reference 20 of the main manuscript. All structures were solved by direct methods (SIR2004[S4]) and refined by a full-matrix least square method on F^2 for all reflections (SHELXL-97).[S5] All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC; reference numbers: CCDC-1583291 for [**10a**·C_6H_6], CCDC-1583292 for **11**, and CCDC-1583293 for **10b**), and can be obtained free of charge from *via* www.ccdc.cam.ac.uk/data_request.cif.

4. Theoretical calculations.

The level of theory and the basis sets used for the structural optimization are contained within the main text. Frequency calculations confirmed minimum energies for all optimized structures. All calculations were carried out on the *Gaussian 09* (Revision D.01) program package.[S6] Computational time was generously provided by the Supercomputer Laboratory in the Institute for Chemical Research (Kyoto University).

5. References

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S6) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E.

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