***Supporting information for***

# Reactivity Studies of Corrole Germanium Hydride Complex with Aldehydes, Olefins and Alkyl halides

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## General Information

$C_6D_6$ and $CDCl_3$ were purchased from Cambridge Isotope Laboratory Inc; other solvents were distilled before used; aldehydes and olefins were purchased from Aldrich or Alfa Aesar and were distilled before used; and all other chemicals were purchased from Aldrich or Alfa Aesar unless otherwise noted and used as received. $^1$H NMR and $^{19}$F NMR spectra were recorded on a Bruker AVII$^+$-400 spectrometer at ambient temperature. Mass spectra were taken on a Bruker Apex IV FTMS.UV-Vis spectra were recorded on a SHIMADZU UV-3100 UV-Vis-NIR spectrophotometer. The FTIR microspectroscopy of complex **3** was recorded on a NICOLET iN10 MX spectrometer in the range of 4000-400cm$^{-1}$.The single-crystal X-ray diffraction data was collected on a Rigaku MM007HF Saturn724+ diffractometer.

## General Synthesis method of (TPFC)Ge-$OCH_3$ and (TPFC)Ge-$OCH_2CH_3$ complexes.

The labile axial ligand of (TPFC)Ge-L (L= -OH and –Cl, 10 mg) is easily changed toalkoxy group (-$OCH_3$, -$OCH_2CH_3$) by dissolving in alcohol (methanol, ethanol, 10 ml) at room temperature within 30 minutes. (TPFC)Ge-$OCH_2CH_3$ is crystallized from ethanol solution to give dark red crystals.

(TPFC)Ge-$OCH_3$ $^1$H NMR (400 MHz, $CDCl_3$) δ(ppm): 9.53 (d, 2H, $^3J$(H,H)=4.3 Hz; *β*-pyrrole H), 9.11 (d, 2H, $^3J$(H,H)=4.7 Hz; *β*-pyrrole H), 9.05 (d, 2H, $^3J$(H,H)=4.3 Hz; *β*-pyrrole H), 8.92 (d, 2H, $^3J$(H,H)=4.8 Hz; *β*-pyrrole H), -1.01 (s, 3H; $CH_3$);$^{19}$F NMR (376 MHz, $C_6D_6$) δ(ppm): -137.8 (m, 3F; *ortho*-F), -138.8 (dd, 1F, $^3J$(F,F)=24.8 Hz, $^4J$(F,F)=6.6 Hz; *ortho*-F), -139.0 (dd, 2F, $^3J$(F,F)=24.5 Hz, $^4J$(F,F)=6.6 Hz; *ortho*-F), -152.2 (t, 1F, $^3J$(F,F)=21.2 Hz; *para*-F), -152.4 (t, 2F, $^3J$(F,F)=21.8 Hz; *para*-F), -161.8 (m, 3F; *meta*-F), -162.2 (td, 2F, $^3J$(F,F)=23.2 Hz, $^4J$(F,F)=8.2 Hz; *meta*-F), -162.4 (td, 1F, $^3J$(F,F)=22.9 Hz, $^4J$(F,F)=8.2 Hz; *meta*-F); UV/Vis ($CHCl_3$): $\lambda_{max}$(nm):

389.0, 411.0, 560.0, 576.5; HRMS (ESI) calcd for $C_{38}H_{12}F_{15}GeN_4O$ $[M+H]^+$ 898.9986; found 898.9997.

(TPFC)Ge-$OCH_2CH_3$$^1$H NMR (400 MHz, $C_6D_6$) δ(ppm): 9.14 (d, 2H, $^3J$(H,H)=4.4 Hz; *β*-pyrrole H), 8.89 (d, 2H, $^3J$(H,H)=5.0 Hz; *β*-pyrrole H), 8.71 (d, 2H, $^3J$(H,H)=4.4 Hz; *β*-pyrrole H), 8.69 (d, 2H, $^3J$(H,H)=4.6 Hz; *β*-pyrrole H), -1.01 (q, 2H, $^3J$(H,H)=7.0 Hz; $CH_2$), -1.69 (t, 3H, $^3J$(H,H)=7.0 Hz; $CH_3$);UV/Vis ($CHCl_3$): $\lambda_{max}$(nm): 389.5, 411.0, 560.5, 577.0; HRMS (ESI) calcd for $C_{39}H_{14}F_{15}GeN_4O$ $[M+H]^+$ 913.0143; found 913.0145.

**General synthesis method of (TPFC)Ge-H complex.**

Methanol (10 µl) is added to a Schlenk flask containing benzene solution (300 µl) of (TPFC)Ge-$OCH_3$ (1 mg, $1.1\times10^{-3}$mmol). After the solution is degassed for three freeze-pump-thaw cycles, excess solid $NaBH_4$ are added into the flask. The yield of the reaction reaches about 95% after 4 hours.

(TPFC)Ge-H (yield: 95%): $^1$H NMR (400 MHz, $C_6D_6$) δ(ppm): 9.09 (d, 2H, $^3J$(H,H)=4.4 Hz; *β*-pyrrole H), 8.87 (d, 2H, $^3J$(H,H)=4.3 Hz; *β*-pyrrole H), 8.65 (m, 4H,*β*-pyrrole H), -2.14 (s, 1H,Ge-H);$^{19}$F NMR (376 MHz, $C_6D_6$) δ(ppm): -139.9 (dd, 2F; $^3J$(F,F)=25.4 Hz, $^4J$(F,F)=6.2 Hz;*ortho*-F), -140.2 (dd, 1F, $^3J$(F,F)=24.8 Hz, $^4J$(F,F)=6.7 Hz; *ortho*-F), -140.6 (dd, 1F, $^3J$(F,F)=24.9 Hz, $^4J$(F,F)=6.8 Hz; *ortho*-F), -140.8 (dd, 2F, $^3J$(F,F)=24.6 Hz, $^4J$(F,F)=6.1 Hz;*ortho*-F), -154.6 (t, 1F, $^3J$(F,F)=21.7 Hz; *para*-F), -154.7 (t, 2F, $^3J$(F,F)=21.8 Hz; *para*-F), -163.9 (td, 3F, $^3J$(F,F)=23.3 Hz, $^4J$(F,F)=7.3 Hz; *meta*-F), -164.3 (td, 2F, $^3J$(F,F)=23.4 Hz, $^4J$(F,F)=8.1 Hz; *meta*-F), -164.5 (td, 1F, $^3J$(F,F)=23.4 Hz, $^4J$(F,F)=8.0 Hz; *meta*-F); UV/Vis ($CHCl_3$): $\lambda_{max}$(nm): 399.0, 419.5, 529.0, 567.5, 595.0.

**General procedure of reactions of (TPFC)Ge-H with aldehydes**.

Freshly prepared (TPFC)Ge-H (1 mg, $1.2\times10^{-3}$mmol) is dissolved in 300 µl $C_6D_6$ in J. Young Valve NMR tube. Excess aldehydes and catalytic amount of KOH are added into the NMR tube. After the solution is degassed for three freeze-pump-thaw cycles, the NMR tube is heated to 60-70°C in a water-bath for 24-33 hours.

(TPFC)Ge-$CH_2OH$ (prepared using paraformaldehyde; yield: 91%): $^1$H NMR (400 MHz, $C_6D_6$) δ(ppm): 9.12 (d, 2H, $^3J$(H,H)=4.3 Hz; *β*-pyrrole H), 8.88 (d, 2H, $^3J$(H,H)=4.6 Hz;*β*-pyrrole H), 8.68 (d, 2H, $^3J$(H,H)=4.1 Hz; *β*-pyrrole H), 8.66 (d, 2H, $^3J$(H,H)=4.7 Hz; *β*-pyrrole H), -2.20 (d, 2H,$^3J$(H,H)=5.3 Hz; $CH_2$), -3.72 (t, 1H,$^3J$(H,H)=5.5 Hz; OH);$^{19}$F NMR (376 MHz, $C_6D_6$) δ(ppm): -140.3 (dd, 2F; $^3J$(F,F)=24.9 Hz, $^4J$(F,F)=5.8 Hz;*ortho*-F), -140.6 (td, 2F, $^3J$(F,F)=22.8 Hz, $^4J$(F,F)=7.0 Hz; *ortho*-F), -140.8 (dd, 2F, $^3J$(F,F)=25.6 Hz, $^4J$(F,F)=5.7 Hz; *ortho*-F), -154.7 (m, 3F; *para*-F), -164.2 (m, 5F; *meta*-F), -164.4 (td, 1F, $^3J$(F,F)=22.9 Hz, $^4J$(F,F)=7.2 Hz; *meta*-F); UV/Vis ($CHCl_3$): $\lambda_{max}$(nm): 420.0, 530.0, 568.0, 597.0; HRMS (ESI) calcd for $C_{38}H_{11}F_{15}GeN_4NaO$ $[M+Na]^+$920.98058; found 920.98179.

(TPFC)Ge-CH(OH)$C_6H_5$(prepared using benzaldehyde; yield: 84%): $^1$H NMR (400 MHz, $C_6D_6$) δ(ppm): 9.03 (d, 2H, $^3J$(H,H)=4.2 Hz; *β*-pyrrole H), 9.02 (d, 2H,

$^3J$(H,H)=4.3 Hz; *β*-pyrrole H), 8.82 (d, 2H, $^3J$(H,H)=5.1 Hz; *β*-pyrrole H), 8.61 (d, 2H, $^3J$(H,H)=4.8 Hz; *β*-pyrrole H), 6.38 (t, 1H, $^3J$(H,H)=7.2 Hz; ε-CH), 6.21 (t, 2H, $^3J$(H,H)=7.6 Hz; δ-CH), 3.80 (d, 2H, $^3J$(H,H)=7.6 Hz; γ-CH), -1.17 (d, 1H, $^3J$(H,H)=4.0 Hz; CH), -2.69 (d, 1H, $^3J$(H,H)=4.1 Hz; OH); HRMS (ESI) calcd for $C_{44}H_{16}F_{15}GeN_4O$ [M+H]$^+$975.03011; found 975.03366.

**General procedure of reactions of (TPFC)Ge-H with olefins**.

Freshly prepared (TPFC)Ge-H is dissolved in 300 μl $C_6D_6$ in a J. Young Valve NMR tube. Olefin (100 equiv.) and a catalytic amount of KOH are added into the NMR tube. After the solution is degassed for three freeze-pump-thaw cycles, the NMR tube is heated to 60 °C in a water-bath for 24 hours.

(TPFC)Ge-$CH_2CH_2CO_2CH_3$ (prepared using methyl acrylate; yield: 95%) $^1$H NMR (400 MHz, $CDCl_3$) δ(ppm): 9.44(d, 2H, $^3J$(H,H)=4.3 Hz; *β*-pyrrole H), 9.02(d, 2H, $^3J$(H,H)=4.8 Hz; *β*-pyrrole H), 8.97(d, 2H, $^3J$(H,H)=4.2 Hz; *β*-pyrrole H), 8.82(d, 2H, $^3J$(H,H)=4.8 Hz; *β*-pyrrole H), 2.81(s, 3H; $CH_3$), -2.08(m, 2H; *β*-$CH_2$), -4.11(m, 2H; *α*-$CH_2$). $^{19}$F NMR (376 MHz, $CDCl_3$) δ(ppm): -139.4 (m, 3F; *ortho*-F), -139.9 (dd, 1F, $^3J$(F,F)=23.7 Hz, $^4J$(F,F)=5.9 Hz;*ortho*-F), -140.0 (dd, 2F, $^3J$(F,F)=23.8 Hz, $^4J$(F,F)=5.6 Hz;*ortho*-F), -154.7 (t, 2F, $^3J$(F,F)=21.0 Hz;*para*-F), -154.9 (t, 1F, $^3J$(F,F)=20.9 Hz; *para*-F), -164.0 (m, 6F; *meta*-F); UV/Vis ($CHCl_3$): $\lambda_{max}$(nm): 398.5, 419.5, 528.5, 567.5, 595.5; HRMS (ESI) calcd for $C_{41}H_{16}F_{15}GeN_4O_2$ [M+H]$^+$ 955.0249; found 955.0278.The (TPFC)Ge-$CH_2CH_2CO_2CH_3$ was crystallized from petroleum ether/chloroform solution.

(TPFC)Ge-$CH_2CHDCOOCH_3$ (yield: 95%) $^1$H NMR (400 MHz, $CDCl_3$) δ(ppm): 9.44(d, 2H, 4.3 Hz), 9.02(d, 2H, 4.8 Hz), 8.97(d, 2H, 4.2 Hz), 8.82(d, 2H, 4.8 Hz), 2.81(s, 3H), -2.10(t, 1H, 8.0 Hz), -4.12(d, 2H, 8.8 Hz). The HRMS (ESI) calcd for $C_{41}H_{14}DF_{15}GeN_4NaO_2$ [M+Na]$^+$ 978.01316; found 978.01470.

(TPFC)Ge-$CH_2CH_2CH_2CH_2CH_3$ (prepared using 1-pentene; yield: 50%) $^1$H NMR (400 MHz, $CDCl_3$) δ(ppm): 9.41 (d, 2H, $^3J$(H,H)=4.2 Hz; *β*-pyrrole H), 9.00 (d, 2H, $^3J$(H,H)=4.8 Hz; *β*-pyrrole H), 8.95 (d, 2H, $^3J$(H,H)=4.2 Hz; *β*-pyrrole H), 8.80 (d, 2H, $^3J$(H,H)=4.7 Hz; *β*-pyrrole H), -0.05 (t, 3H, $^3J$(H,H)=7.3 Hz; $CH_3$), -0.20 (m, 2H; *δ*-$CH_2$), -1.17 (m, 2H; *γ*-$CH_2$), -3.07 (m, 2H; *β*-$CH_2$), -4.40 (m, 2H; *α*-$CH_2$); $^{19}$F NMR (376 MHz, $CDCl_3$) δ(ppm): -139.8 (m, 6F; *ortho*-F), -155.0 (t, 2F, $^3J$(F,F)=20.8 Hz; *para*-F), -155.2 (t, 1F, $^3J$(F,F)=20.9 Hz; *para*-F), -164.2 (m, 6F; *meta*-F);UV/Vis ($CHCl_3$): $\lambda_{max}$(nm): 400.0, 421.0, 529.5, 568.5, 598.0; HRMS (ESI) calcd for $C_{42}H_{19}F_{15}GeN_4$ M$^+$ 938.0586; found 938.0599.

**General method for synthesis of (TPFC)Ge-alkyl complexes using alkyl halides as alkylation reagents.**

(TPFC)Ge-$OCH_3$(10 mg) is dissolved in 5 mL ethanol in a Schlenk flask. After the solution was degassed for three freeze-pump-thaw cycles, NaOH (20 mg, 0.50 mmol) and $NaBH_4$ (20 mg, 0.54 mmol) are injected into the flask. The solution is vigorously stirred at room temperature for 30 min, and then excess alkyl halide (> 100 equiv.)is injected into the frozen flask followed by a degassing procedure. The (TPFC)Ge-alkyl complex is obtained by chromatography on silica gel using $CHCl_3$/petroleum ether (1:3) as eluent.

(TPFC)Ge-$CH_3$ (prepared using $CH_3I$; yield: 90%; crystallized from acetone/$H_2O$ solution) $^1$H NMR (400 MHz, $C_6D_6$) δ(ppm): 9.11 (d, 2H, $^3J$(H,H)=4.3 Hz; *β*-pyrroleH), 8.87(d, 2H, $^3J$(H,H)=5.5 Hz; *β*-pyrrole H), 8.67(d, 2H, $^3J$(H,H)=4.3 Hz; *β*-pyrrole H), 8.65(d, 2H, $^3J$(H,H)=4.7 Hz; *β*-pyrrole H), -5.13(s, 3H; $CH_3$); $^{19}$F NMR (376 MHz, $CDCl_3$) δ(ppm): -139.7 (dd, 2F, $^3J$(F,F)=24.4 Hz, $^4J$(F,F)=5.6 Hz; *ortho*-F), -139.8 (dd, 2F, $^3J$(F,F)=24.3 Hz, $^4J$(F,F)=6.4 Hz; *ortho*-F), -139.9 (dd, 2F, $^3J$(F,F)=23.9 Hz, $^4J$(F,F)=5.4 Hz; *ortho*-F), -154.9 (t, 2F, $^3J$(F,F)=20.8 Hz; *para*-F), -155.1 (t, 1F, $^3J$(F,F)=20.8 Hz; *para*-F), -164.2 (m, 6F; *meta*-F); UV/Vis ($CHCl_3$): $\lambda_{max}$(nm): 398.0, 419.5, 529.0, 568.0, 595.5; HRMS (ESI) calcd for $C_{38}H_{11}F_{15}GeN_4$ $M^+$881.9959; found 881.9974.

(TPFC)Ge-$CH_2C_6H_5$ (prepared using $C_6H_5Br$; yield: 50%) $^1$H NMR (400 MHz, $CDCl_3$) δ(ppm): 9.31(d, 2H, $^3J$(H,H)=4.3 Hz; *β*-pyrrole H), 8.98(d, 2H, $^3J$(H,H)=4.7 Hz; *β*-pyrrole H), 8.91(d, 2H, $^3J$(H,H)=4.2 Hz; *β*-pyrrole H), 8.77(d, 2H, $^3J$(H,H)=4.8; *β*-pyrrole H), 6.41(t, 1H, $^3J$(H,H)=7.3 Hz; ε-CH), 6.16(t, 2H, $^3J$(H,H)=7.6 Hz; δ-CH), 3.60(d, 2H, $^3J$(H,H)=7.4 Hz; γ-CH), -3.04(s, 2H; $CH_2$); $^{19}$F NMR (376 MHz, $CDCl_3$) δ(ppm): -139.2 (dd, 1F, $^3J$(F,F)=24.3 Hz, $^4J$(F,F)=7.3 Hz; *ortho*-F), -139.3 (dd, 2F, $^3J$(F,F)=24.7 Hz, $^4J$(F,F)=6.4 Hz; *ortho*-F), -139.7 (dd, 1F, $^3J$(F,F)=24.6 Hz, $^4J$(F,F)=6.6 Hz; *ortho*-F), -139.8 (dd, 2F, $^3J$(F,F)=24.5 Hz, $^4J$(F,F)=6.0 Hz; *ortho*-F), -154.9 (t, 2F, $^3J$(F,F)=20.9 Hz; *para*-F), -155.1 (t, 1F, $^3J$(F,F)=20.9 Hz; *para*-F), -164.2 (m, 6F; *meta*-F); UV/Vis ($CHCl_3$): $\lambda_{max}$(nm): 402.5, 423.0, 530.0, 569.5, 599.5; HRMS (ESI) calcd for $C_{44}H_{16}F_{15}GeN_4$ $[M+H]^+$ 959.0352; found 959.0370.

**Summary of $^1$H NMR data of complexes 1-9.**

**Table S1.** $^1$H NMR parameters for the organic substituents in alkyl germanium corrolates

| compd. no. | structure of substituent | solvent | organic group $^1$H NMR parameters |
|---|---|---|---|
| **1** | $-OCH_3$ | $CDCl_3$ | $CH_3$, s, -1.01 |
| **2** | $-OCH_2CH_3$ | $C_6D_6$ | $CH_2$, q, -1.01, *J*=7.0; $CH_3$, t, -1.69, *J*=7.0 |
| **3** | -H | $C_6D_6$ | Ge-H, s, -2.14 |
| **4** | $-CH_2OH$ | $C_6D_6$ | OH, t, -3.72, *J*=5.5; $CH_2$, d, -2.20, *J*=5.3 |
| **5** | $-CH(OH)C_6H_5$ | $C_6D_6$ | OH, d, -2.69, *J*=4.1; CH, d, -1.17, *J*=4.0; *γ*-CH, d, 3.80, *J*=7.6;*δ*-CH, t, 6.21, *J*=7.6;*ε*-CH, t, 6.38, *J*=7.2 |
| **6** | $-CH_2CH_2CO_2CH_3$ | $CDCl_3$ | *α*-$CH_2$, m, -4.11; *β*-$CH_2$, m, -2.08; $CH_3$, s, 2.81 |
| **7** | $-CH_2(CH_2)_3CH_3$ | $CDCl_3$ | *α*-$CH_2$, m, -4.40; *β*-$CH_2$, m, -3.07; *γ*-$CH_2$, m, -1.17; *δ*-$CH_2$, m, -0.20; $CH_3$, t, -0.05, *J*=7.3 |
| **8** | $-CH_3$ | $C_6D_6$ | $CH_3$, s, -5.13 |
| **9** | $-CH_2C_6H_5$ | $CDCl_3$ | $CH_2$, s, -3.04; *γ*-CH, d, 3.60, *J*=7.4; *δ*-CH, t, 6.16, *J*=7.6; *ε*-CH, t, 6.41, *J*=7.3 |

**The molecular structure of complex 2.**

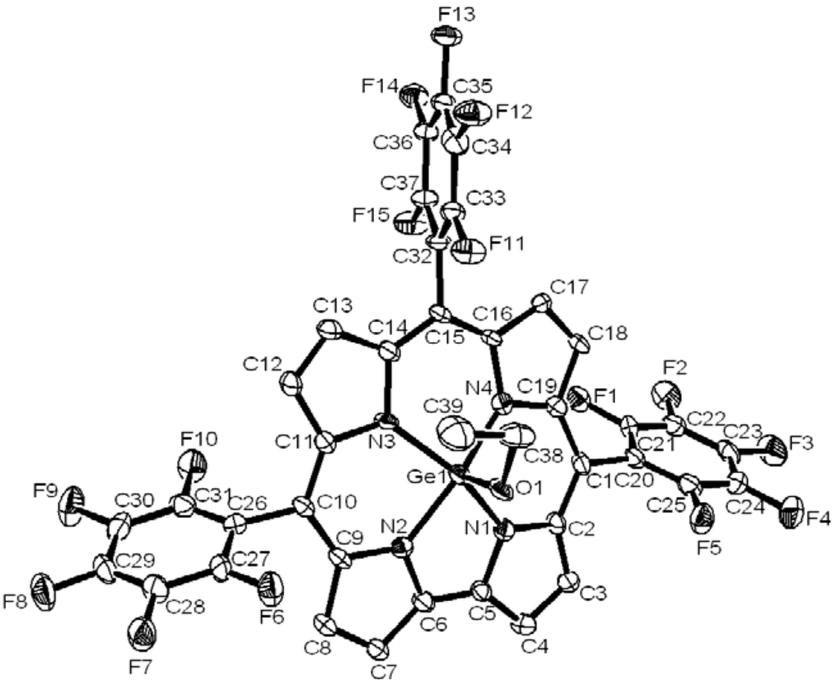

**Fig. S1** The structure of complex **2**.

**Calculation of ΔH and ΔS of eq. 2.**

A mixture of (TPFC)Ge-$CH_2OH$, (TPFC)Ge-$CH_2OCH_2OH$ and paraformaldehyde is prepared using the method mentioned above. $^1$H NMR spectra are recorded at 40 $^o$C, 50$^o$C, 60$^o$C and 70$^o$C. Equilibrium constants at different temperatures are derived from the ratios of the integrated intensity for the doublet at δ = 9.12 ppm (corresponds to the *β*-pyrrole H of (TPFC)Ge-$CH_2OH$), the doublet at δ = 9.13 ppm (corresponds to the *β*-pyrrole H of (TPFC)Ge-$CH_2OCH_2OH$) and the singlet ranging from δ = 8.75～8.84 ppm (corresponds to the H of formaldehyde). The linear fit line gives changes of ΔH and ΔS of reaction $\text{(TPFC)Ge-CH}_2\text{OH} + \text{HCHO} \rightleftharpoons \text{(TPFC)Ge-CH}_2\text{OCH}_2\text{OH}$ (Fig. S2).

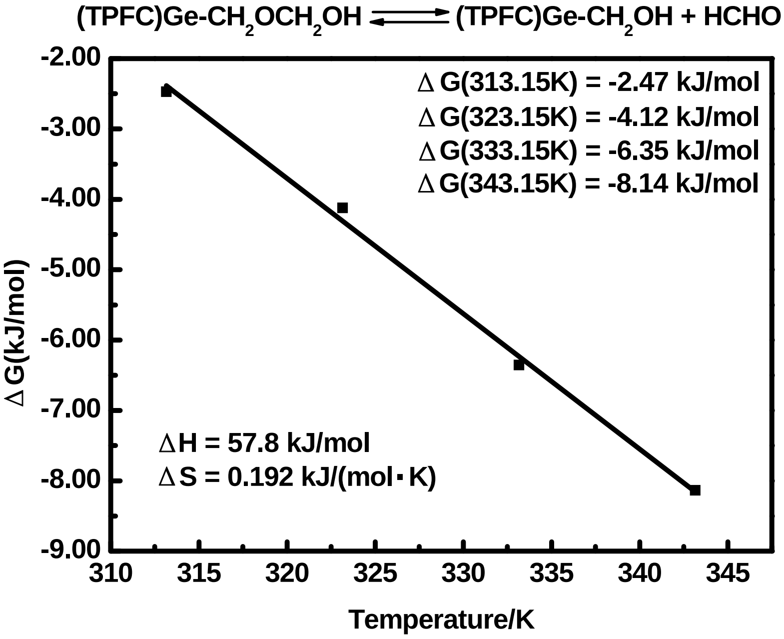

**Fig. S2** Temperature dependence of ΔG for eq. 2 ($r^2$=0.996).