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Germanium(II) Hydride Mediated Reduction of Carbon Dioxide to Formic Acid and Methanol with Ammonia Borane as the Hydrogen Source

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1: **Preparation of LGeO^{13}C(O)H**. A solution of **LGeH** (0.49 g, 1.00 mmol) in toluene (30 mL) was cooled to -78 ^{o}C, and the N_2 atmosphere was exchanged with $^{13}CO_2$ gas. The solution was allowed to warm up to ambient temperature and stirred for another 12 h. All volatiles were removed in vacuum, giving **LGeO^{13}C(O)H**. ^{1}H NMR (500.13 MHz, C_6D_6): δ 8.64 (d, $^{1}J_{CH}$ = 203 Hz, 1H, C*H*), 7.05-7.19 (m, 6H, Ar-*H*), 5.06 (s, 1H, γ-C*H*), 3.53 (sept, 2H, C*H*$(CH_3)_2$), 3.08 (sept, 2H, C*H*$(CH_3)_2$), 1.54 (s, 6H, CH_3), 1.28 (d, 6H, CH(CH_3)$_2$), 1.20 (d, 6H, CH(CH_3)$_2$), 1.14 (d, 6H, CH(CH_3)$_2$), 1.12 (d, 6H, CH(CH_3)$_2$) ppm.

2: **Preparation of LSnO^{13}C(O)H**. A solution of **LSnH** (0.54 g, 1.00 mmol) in toluene (30 mL) was cooled to -78 ^{o}C, and the N_2 atmosphere was exchanged with $^{13}CO_2$ gas. The solution was allowed to warm up to ambient temperature and stirred for another 12 h. All volatiles were removed in vaccum, giving a **LSnO^{13}C(O)H**. ^{1}H NMR (500.13 MHz, C_6D_6): δ 8.97 (d, $^{1}J_{CH}$ = 202 Hz, 1H, C*H*), 7.02-7.15 (m, 6H, Ar-*H*), 4.96 (s, 1H, γ-C*H*), 3.61 (sept, 2H, C*H*$(CH_3)_2$), 3.06 (sept, 2H, C*H*$(CH_3)_2$), 1.58 (s, 6H, CH_3), 1.32 (d, 6H, CH(CH_3)$_2$), 1.18 (d, 12H, CH(CH_3)$_2$), 1.15 (d, 6H, CH(CH_3)$_2$), 1.05 (d, 6H, CH(CH_3)$_2$) ppm.

3: Preparation of $^{13}CH_3OD$. (a) An NMR tube was loaded with LGeO^{13}C(O)H (0.053 g, 0.10 mmol) and NH_3BH_3 (0.009 g, 0.30 mmol), and C_6D_6 (0.6 mL) was added at room temperature. Then the NMR tube was heated to 60 ^{o}C inside the NMR magnet, and ^{1}H NMR spectra were recorded every hour. After 18 h, the NMR tube was removed from the magnet and 1 mL of D_2O was added. The D_2O phase was separated and contained $^{13}CH_3OD$. ^{1}H

NMR δ3.25 (d, $^1J_{CH}$ = 142 Hz) ppm. ^{13}C NMR δ48.7 (q, $^1J_{CH}$ = 142 Hz) ppm. (b) An NMR tube was loaded with LGeO^{13}C(O)H (0.053 g, 0.10 mmol) and NH_3BH_3 (0.009 g, 0.30 mmol), and THF-d_8 (0.6 mL) was added at room temperature. Then the NMR tube was heated to 60 ^{o}C inside the NMR magnet, and ^{1}H NMR spectra were recorded every hour. After 3 h, the NMR tube was removed from the magnet and 1 mL of D_2O was added. The D_2O phase was separated and contained $^{13}CH_3OD$. ^{1}H NMR δ3.25 (d, $^1J_{CH}$ = 142 Hz) ppm. ^{13}C NMR δ48.7 (q, $^1J_{CH}$ = 142 Hz) ppm. (c) An NMR tube was loaded with LSnO^{13}C(O)H (0.058 g, 0.10 mmol), and NH_3BH_3 (0.009 g, 0.30 mmol), and C_6D_6 (0.6 mL) was added at room temperature. ^{1}H NMR spectra were recorded every hour for 24 h. Afterwards 1 mL of D_2O was added to the grey suspension. The D_2O phase was separated and contained $^{13}CH_3OD$. ^{1}H NMR δ3.25 (d, $^1J_{CH}$ = 142 Hz) ppm. ^{13}C NMR δ48.7 (q, $^1J_{CH}$ = 142 Hz) ppm.

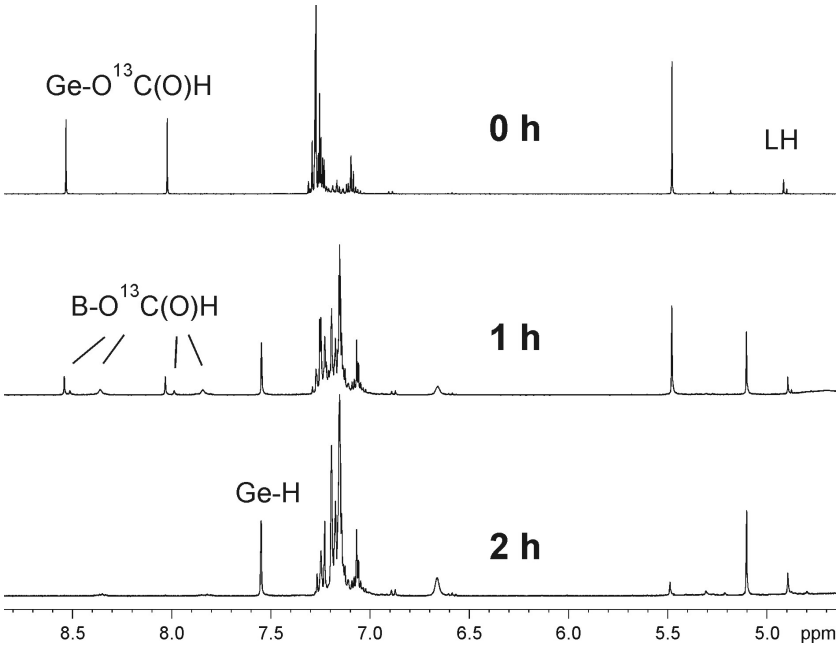

Figure S1 ^{1}H NMR spectra of LGeO^{13}C(O)H with 3 eq. ammonia borane in thf-d_8 recorded directly, 1 h and 2 h after heating to 60 °C.

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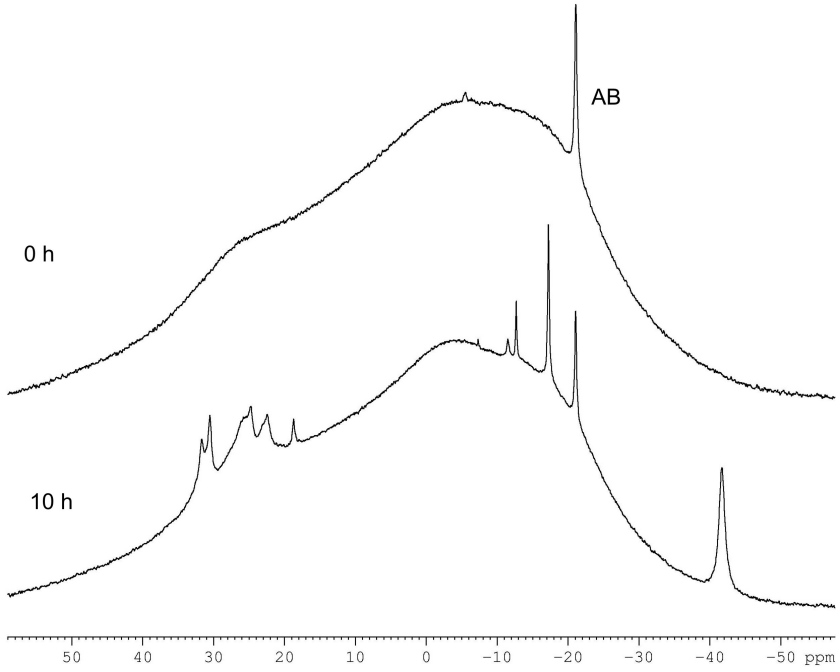

Figure S2 ^{11}B NMR spectra of LGeO^{13}C(O)H with 3 eq. ammonia borane in C_6D_6 at recorded directly and 10 h after heating to 60 °C.

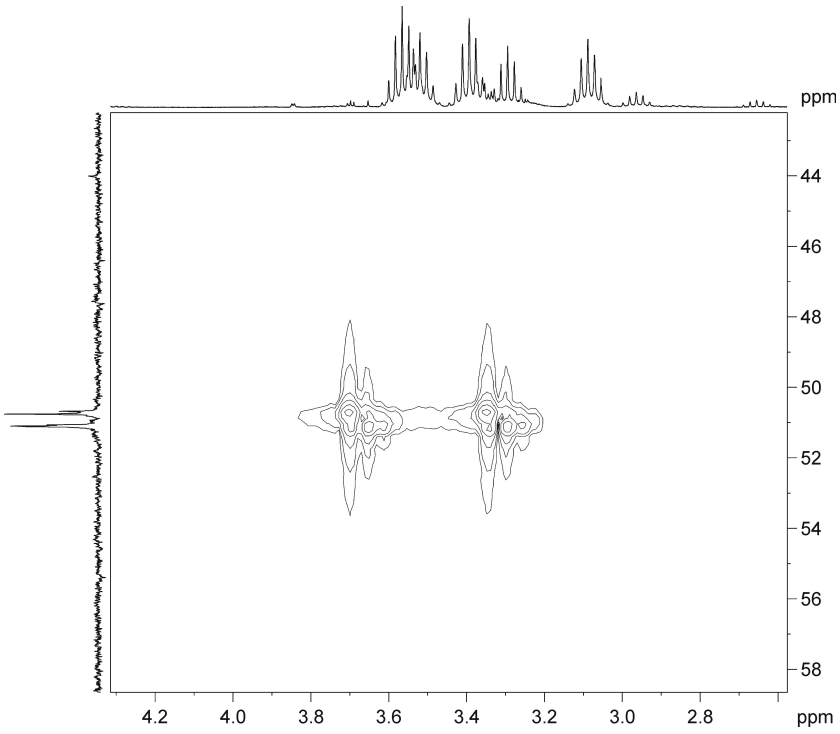

Figure S3 B-O-CH_3 region of the ^{13}C-HSQC spectrum (no decoupling in the ^{1}H dimension) of LGeO^{13}C(O)H with 3 eq. ammonia borane in C_6D_6 recorded 18 h after heating to 60 °C.

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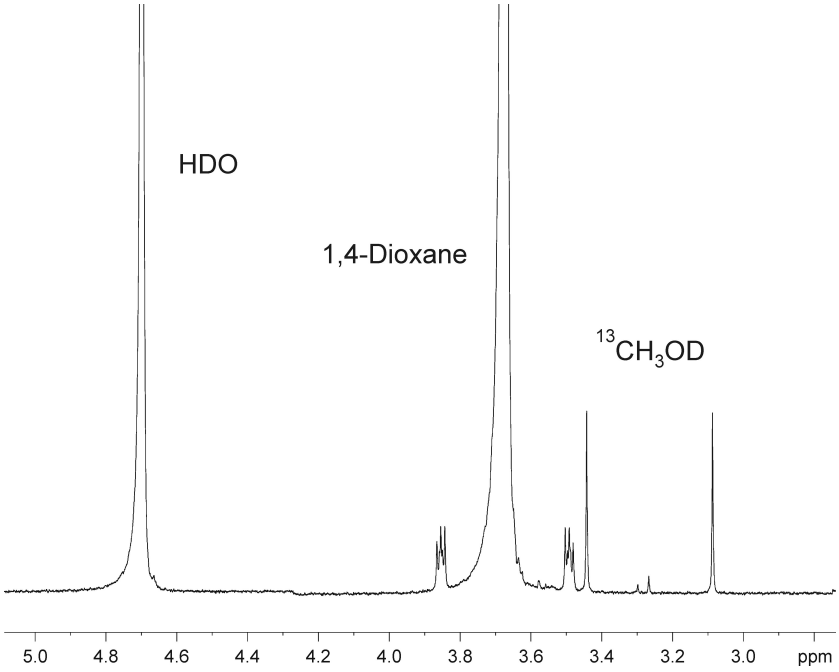

Figure S4 ^{1}H NMR spectrum of the reaction of LGeO^{13}C(O)H with 3 eq. ammonia borane after workup in D_2O.