Supporting Information

to

Tandem-Reduction of DMF with Silanes via Necklace-type Transition over Pt(0) Nanoparticles: Deciphering the Dual Si-H Effect as an Extension of Steric Effects

*Vijay P. Taori and Michael R. Buchmeiser**

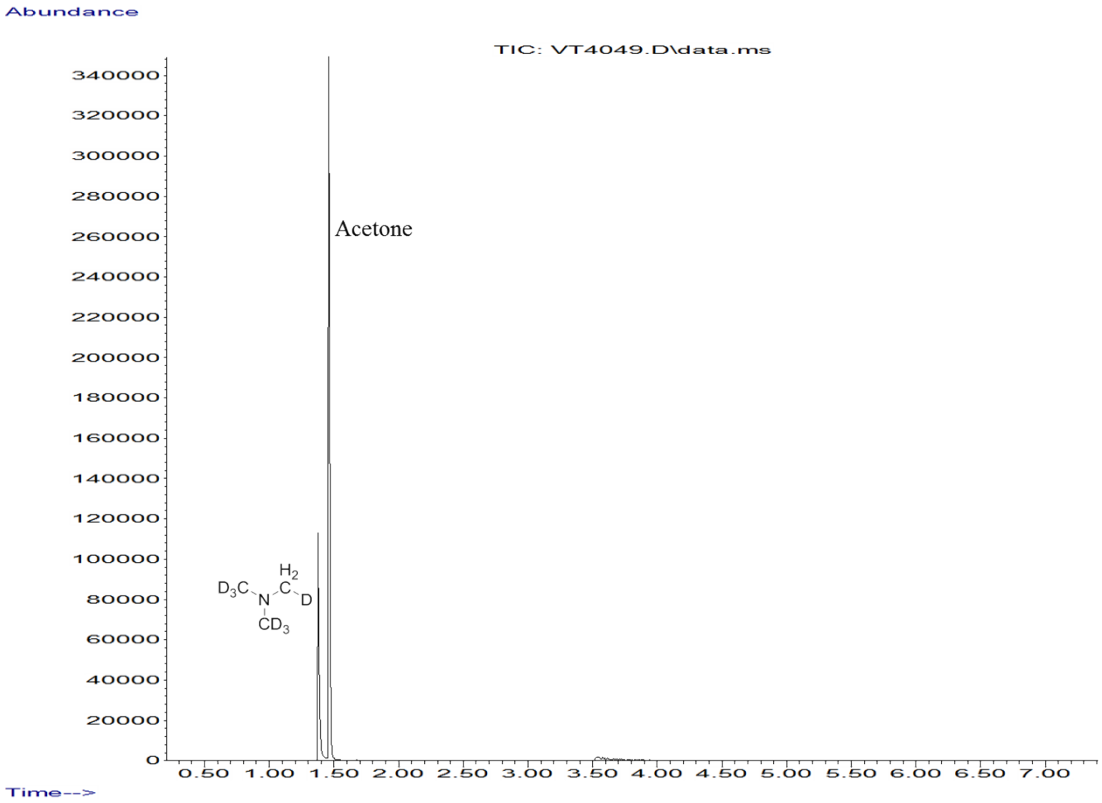

Figure S1(a). GC-MS spectrum (head-space experiment) performed on a sample of the reaction mixture containing 600 µL of DMF-d_7, 5 mg of the Pt-containing monolith (357 ppm Pt; ~9 nanomol of Pt) and 50 µL of diethylsilane. The peak at t_R = 1.393 min, corresponds to trimethylamine-d_7, $(CD_3)_2NCH_2D$ with a molecular weight of 66.1 Da.

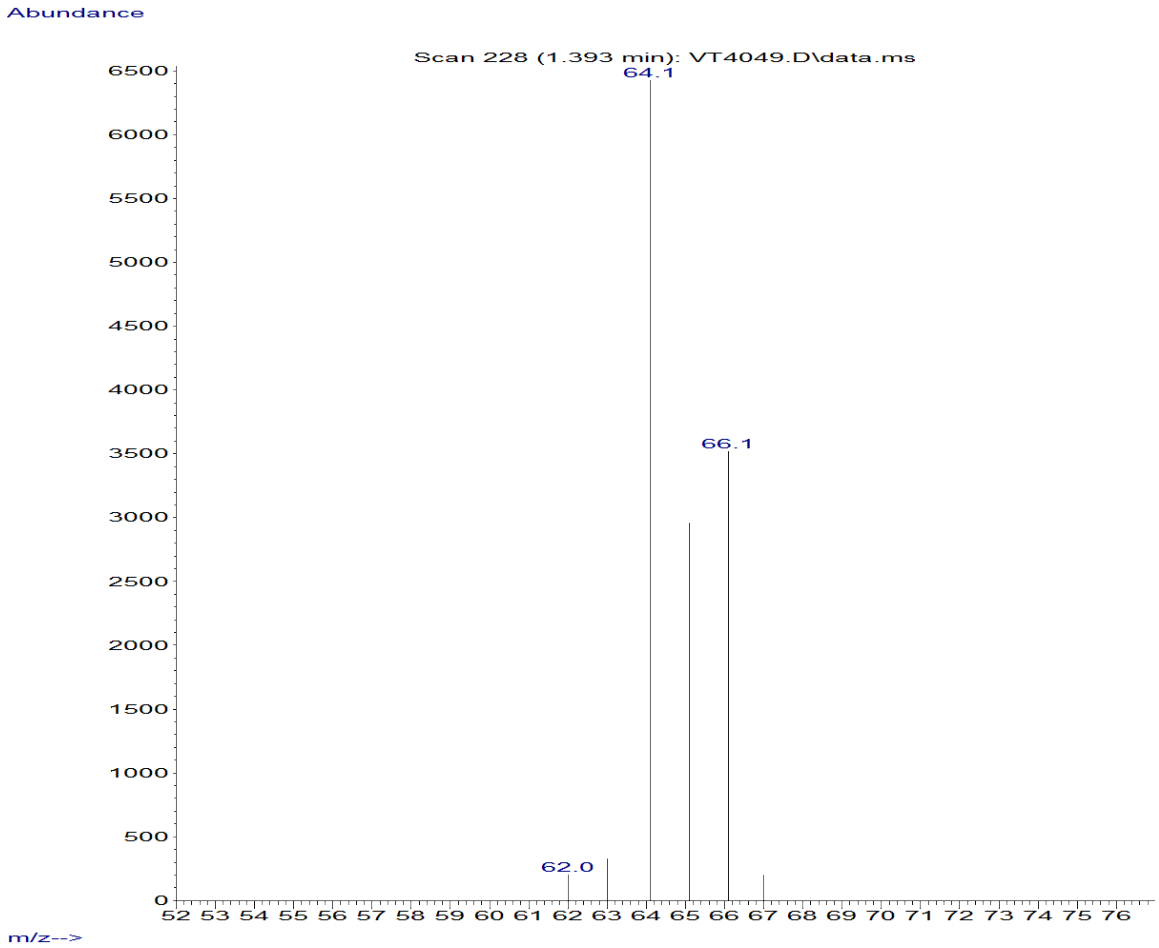

Figure S1(b). Fragmentation pattern of the peak at t_R = 1.393 min in the GC-MS spectrum shown in Figure S2(a). The molecular weight of 66.1 Da corresponds to trimethylamine-d_7, $(CD_3)_2NCH_2D$.

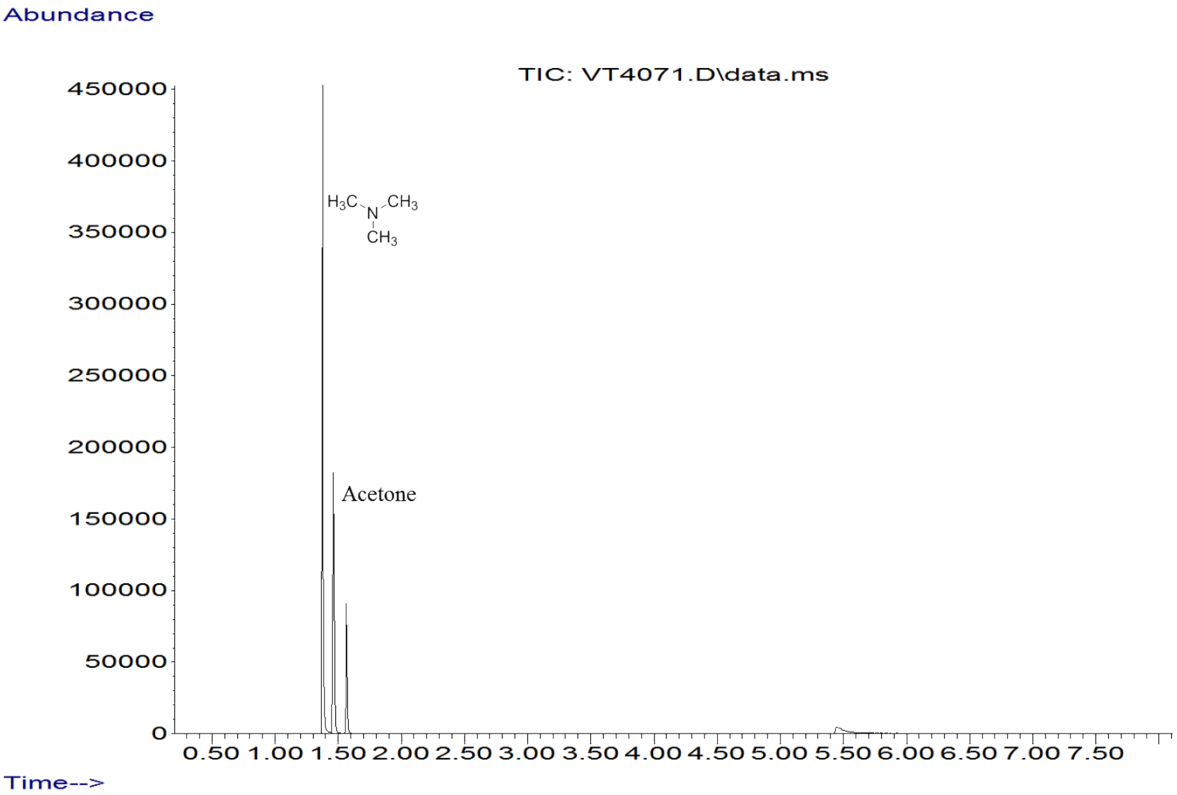

Figure S2(a). GC-MS spectrum, head-space experiment performed on commercially purchased trimethylamine in ethanol. The peak at t_R = 1.393 min, corresponds to trimethylamine with a molecular weight of 59.1 Da.

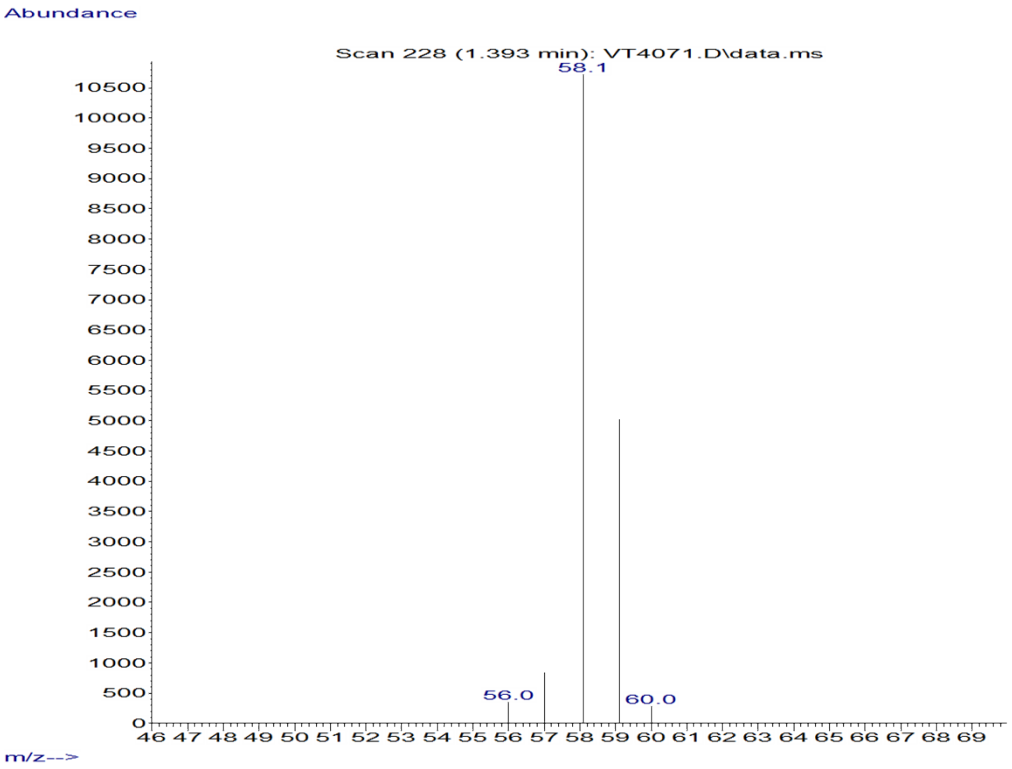

Figure S2(b). Fragmentation pattern of the peak at t_R = 1.393 min in the GC-MS spectrum shown in Figure S3(a) containing commercially purchased trimethylamine in ethanol. The molecular weight of 59.1 Da corresponds to trimethylamine.

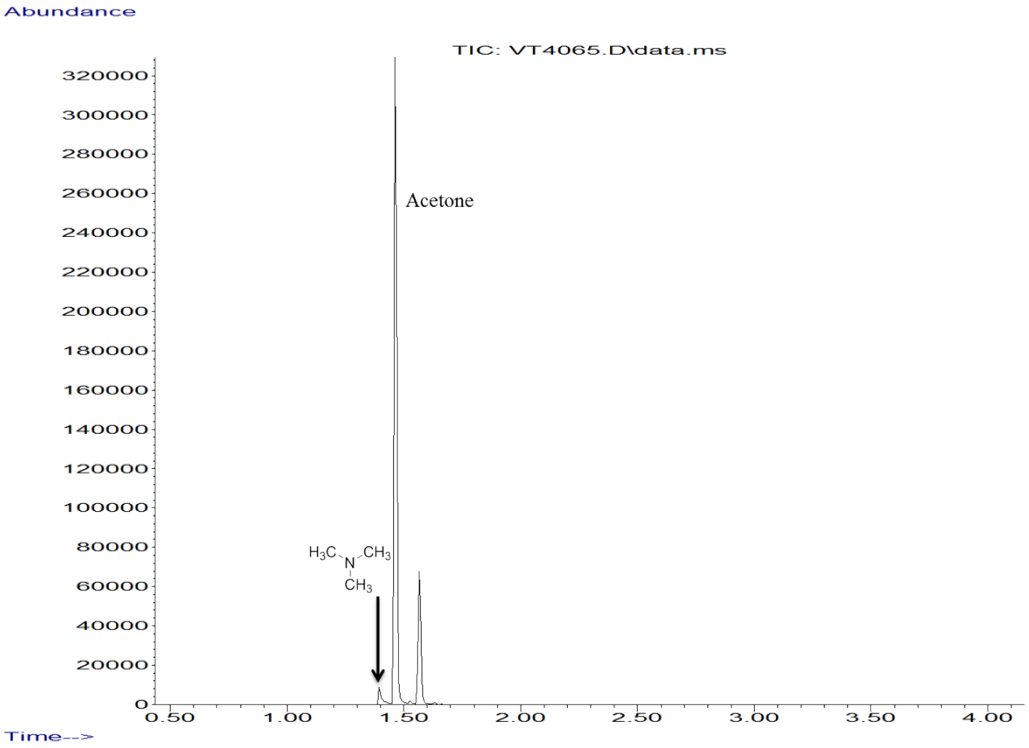

Figure S3(a). GC-MS spectrum (head-space experiment) performed on a sample of the reaction mixture containing 50 µL of DMF, 10 mg of Pt-containing monolith (357 ppm Pt loading; ~18 nanomole), 50 µL of diethylsilane and 600 µL of DMSO-d_6. The peak at t_R = 1.393 min corresponds to trimethylamine with a molecular weight of 59.1 Da.

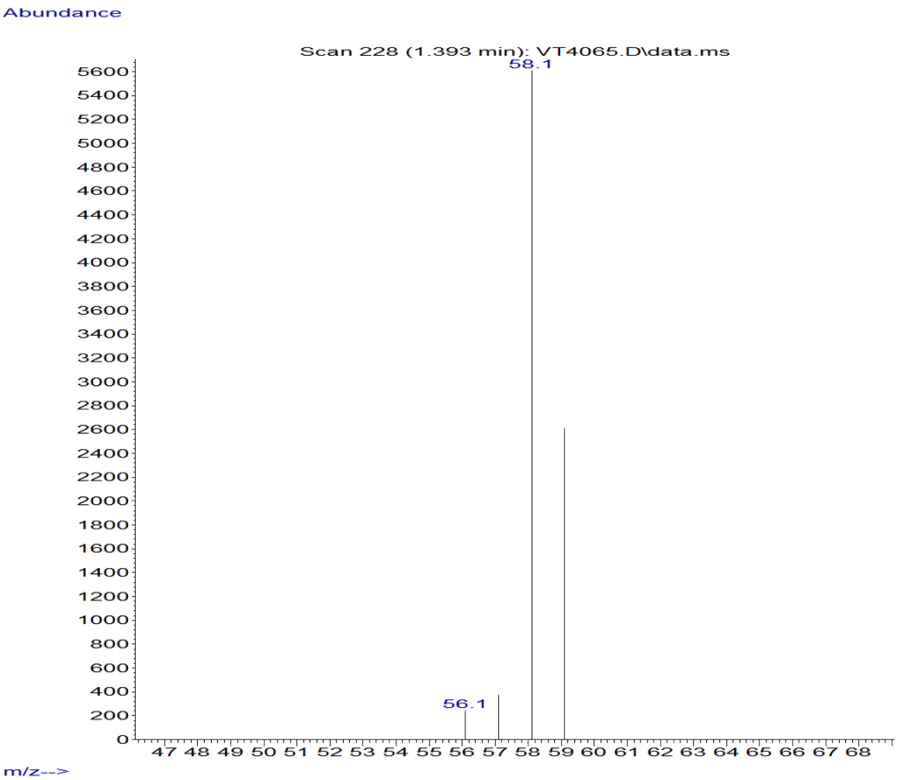

Figure S3(b). Fragmentation pattern of the peak at t_R = 1.393 min in the GC-MS spectrum shown in Figure S4(a). The molecular weight of 59.1 Da corresponds to the one of trimethylamine.

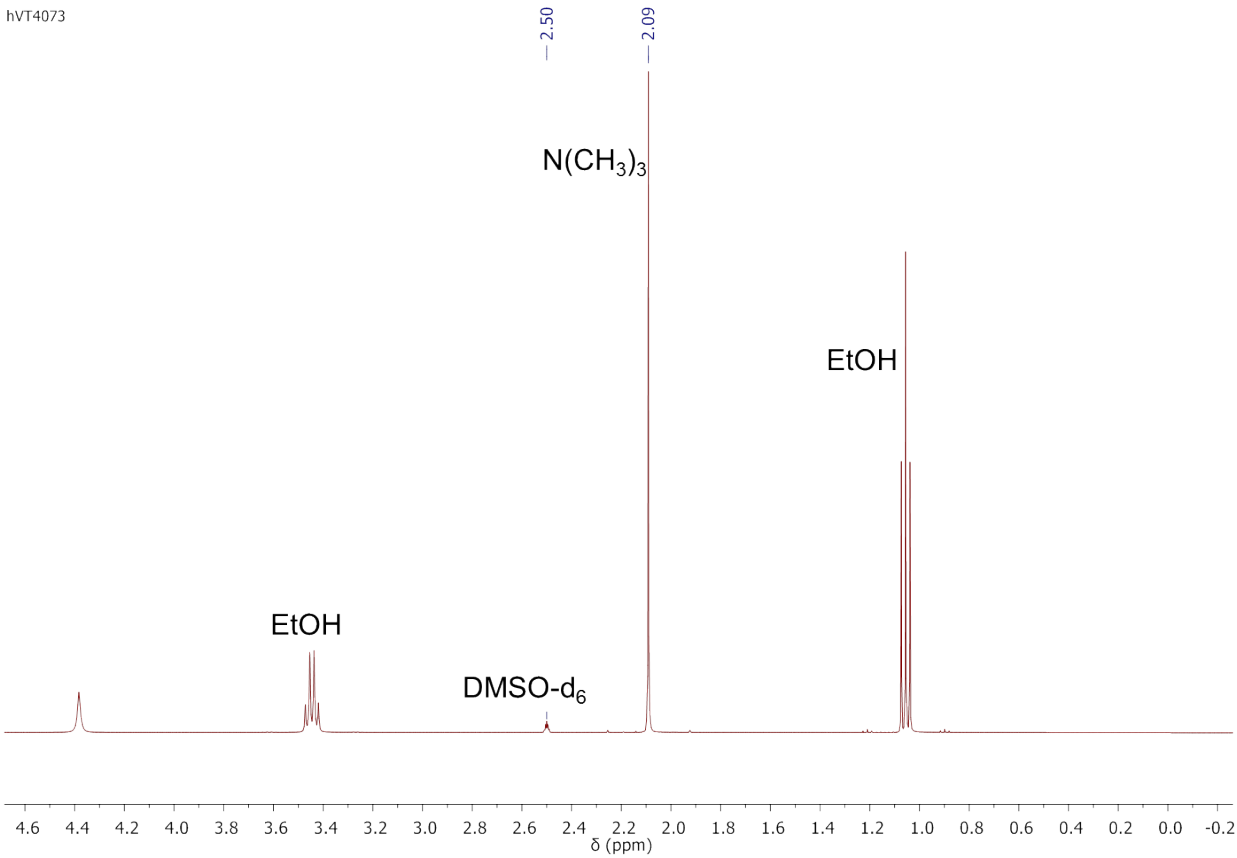

Figure S4. ^{1}H NMR acquired for commercially purchased trimethylamine in ethanol.

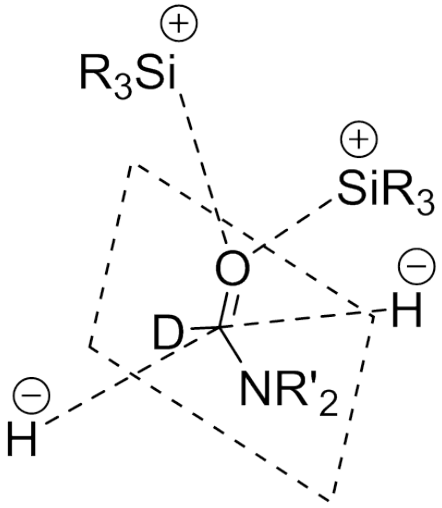

Figure S5(a). Transition state which depicts the concerted attack of two hydrides on the DMF-d_7 molecule (R'=CD_3) implying simultaneous breaking of a C(sp2)=O bond, formation of two new C(sp3)-H bonds and formation of two new Si-O bonds to form compound **2** in **Scheme 2**.

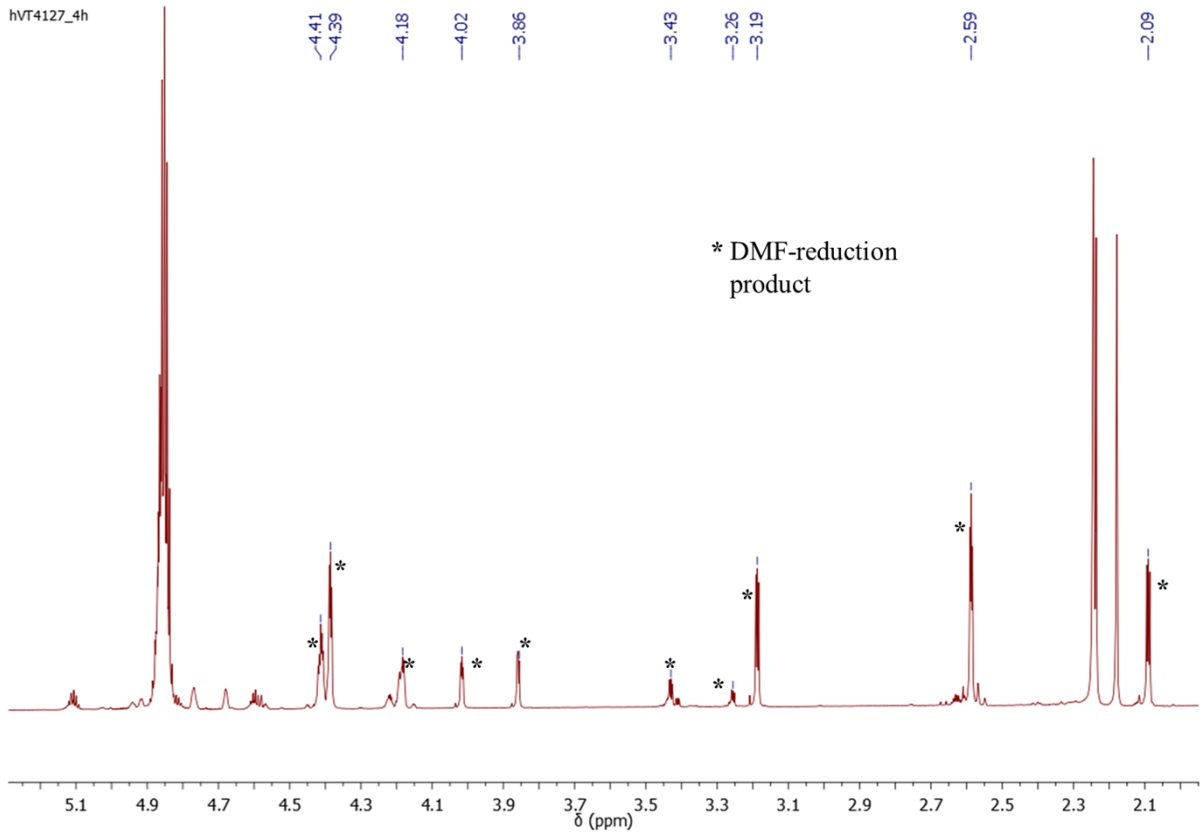

Figure S5(b). ^{1}H-NMR of the reduction of DMF-d_7 in presence of Karstedt's catalyst gives multiple DMF-reduction products. δ = 2.09 ppm, trimethylamine-d_7. Reaction conditions used from Pannell's study.[1]

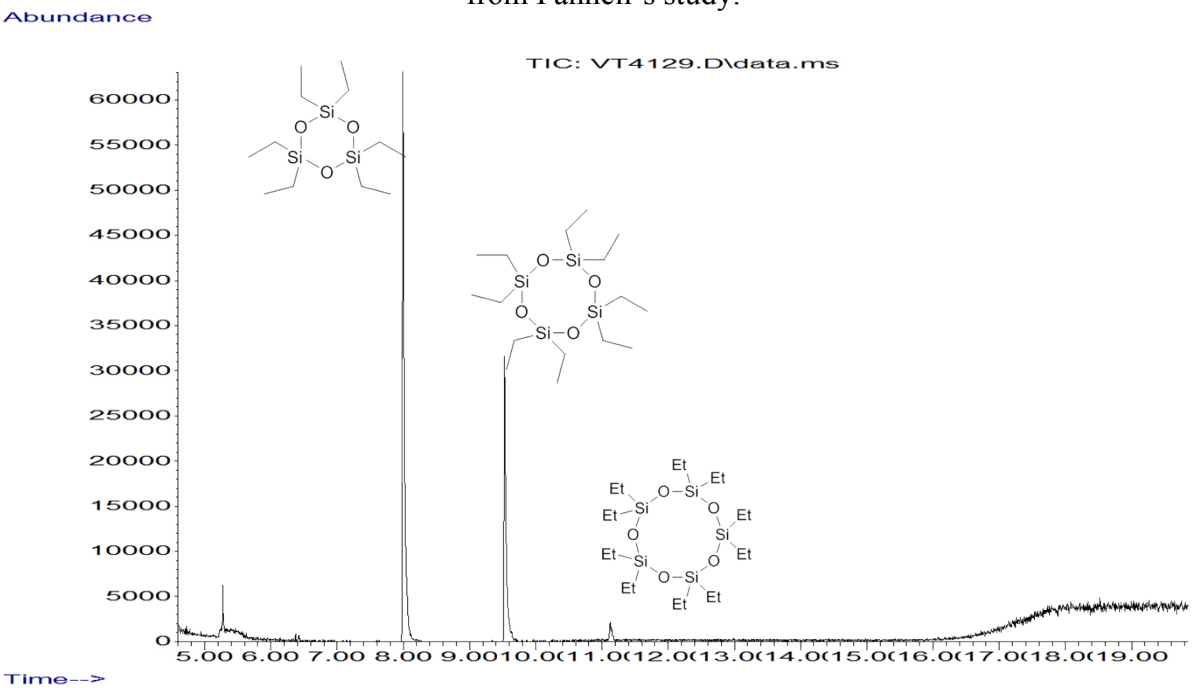

Figure S6(a). GC-MS spectrum. Experiment performed on the sample of the reaction mixture containing 600 µL of DMF-d_7, 5 mg of the Pt-containing monolith (357 ppm Pt; ~9 nanomol of Pt) and 50 µL of diethylsilane. The peak at t_R = 7.997 min, corresponds to a six-membered siloxane ring with a molecular weight of 306.1 Da formed as the side product in the reduction reaction. A peak at t_R = 9.531 min, corresponds to an eight-membered

ring with a molecular weight of 408.2 Da. There is also formation of a peak at t_R = 11.127 min which corresponds to a ten-membered siloxane ring.

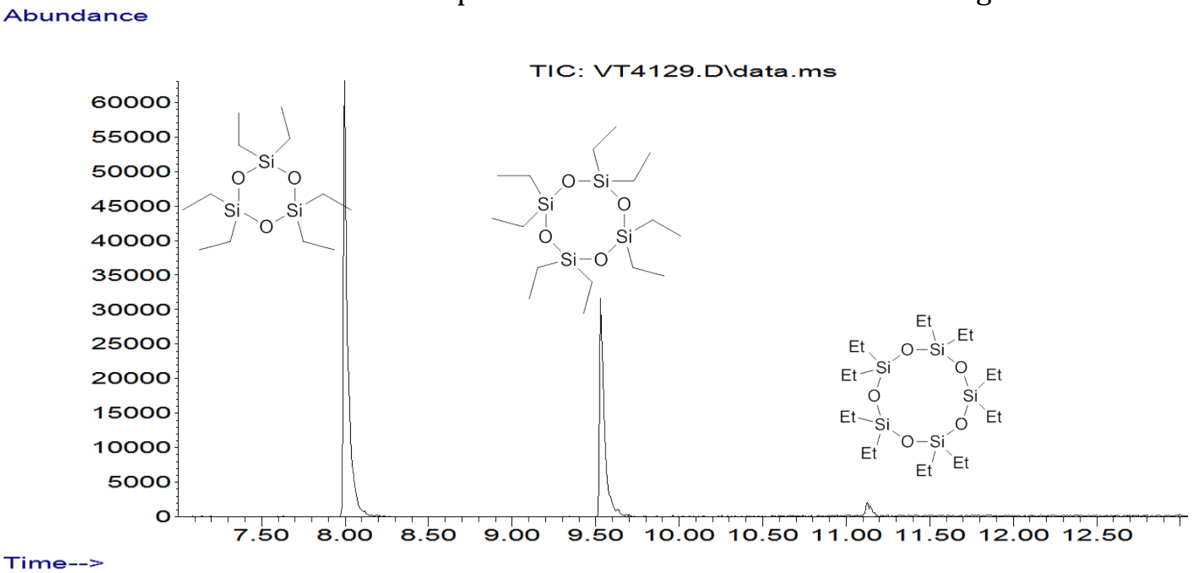

Figure S6(b). GC-MS spectrum. Expansion of the spectrum shown in Figure S6(a).

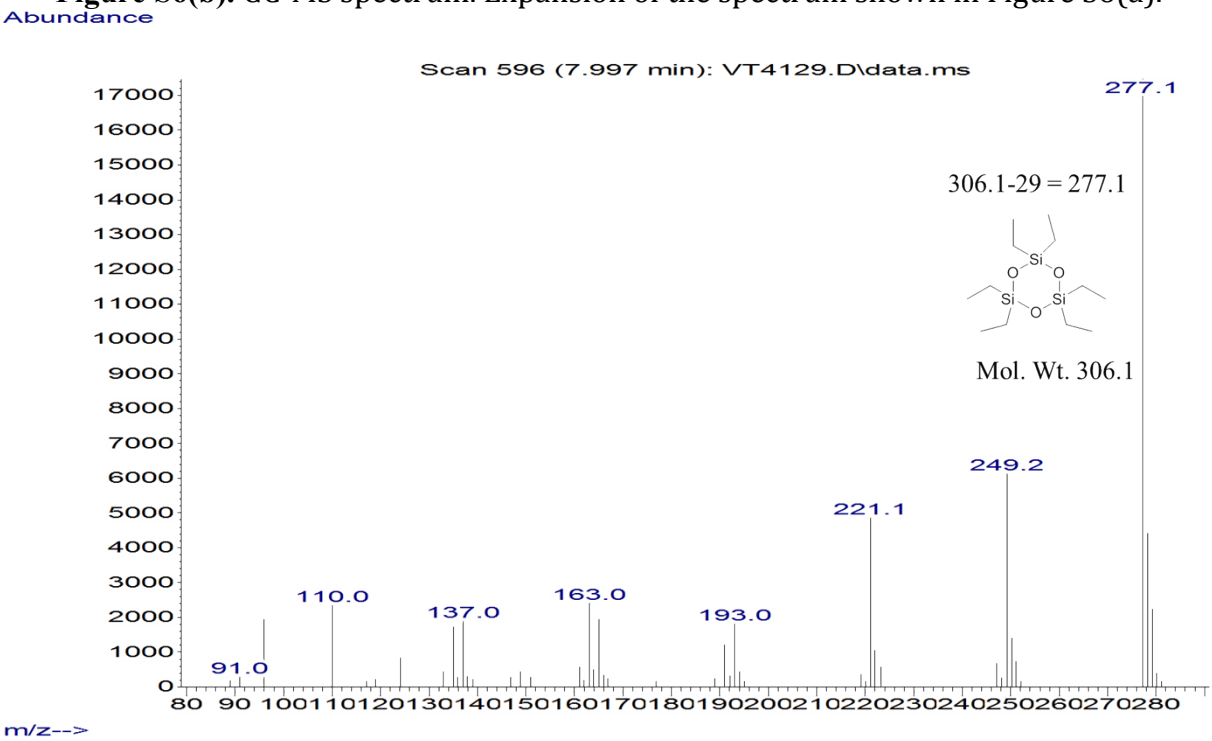

Figure S6(c). Fragmentation pattern of the peak at t_R = 7.997 min in the GC-MS spectrum shown in Figure S6(a). The molecular weight of 277.1 Da corresponds to a six-membered siloxane ring minus the molecular weight of the ethyl group.

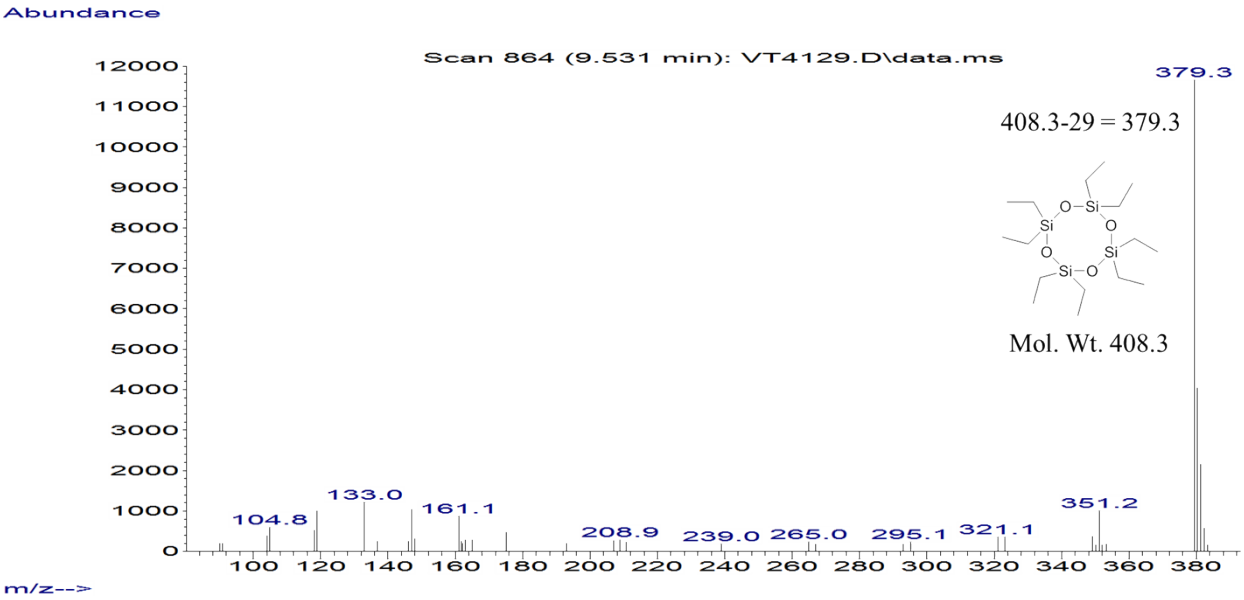

Figure S6(d). Fragmentation pattern of the peak at t_R = 9.531 min in the GC-MS spectrum shown in Figure S6(a). The molecular weight of 379.3 Da corresponds to an eight-membered siloxane ring minus the molecular weight of the ethyl group.

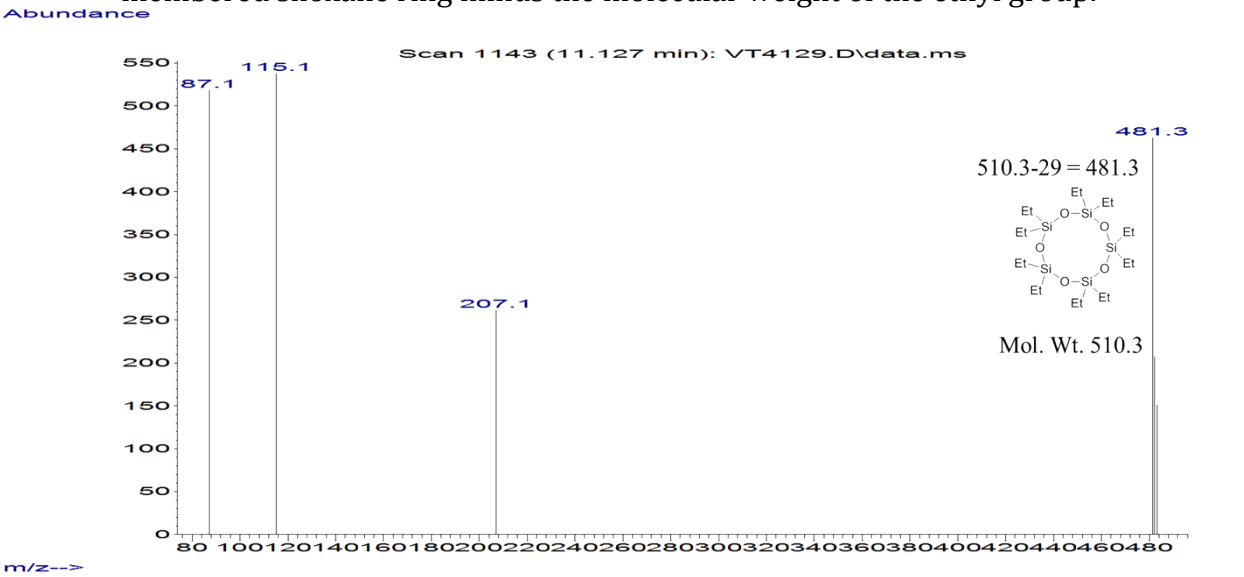

Figure S6(e). Fragmentation pattern of the peak at t_R = 11.127 min in the GC-MS spectrum shown in Figure S6(a). The molecular weight of 481.3 Da corresponds to a ten-membered siloxane ring minus the molecular weight of the ethyl group.

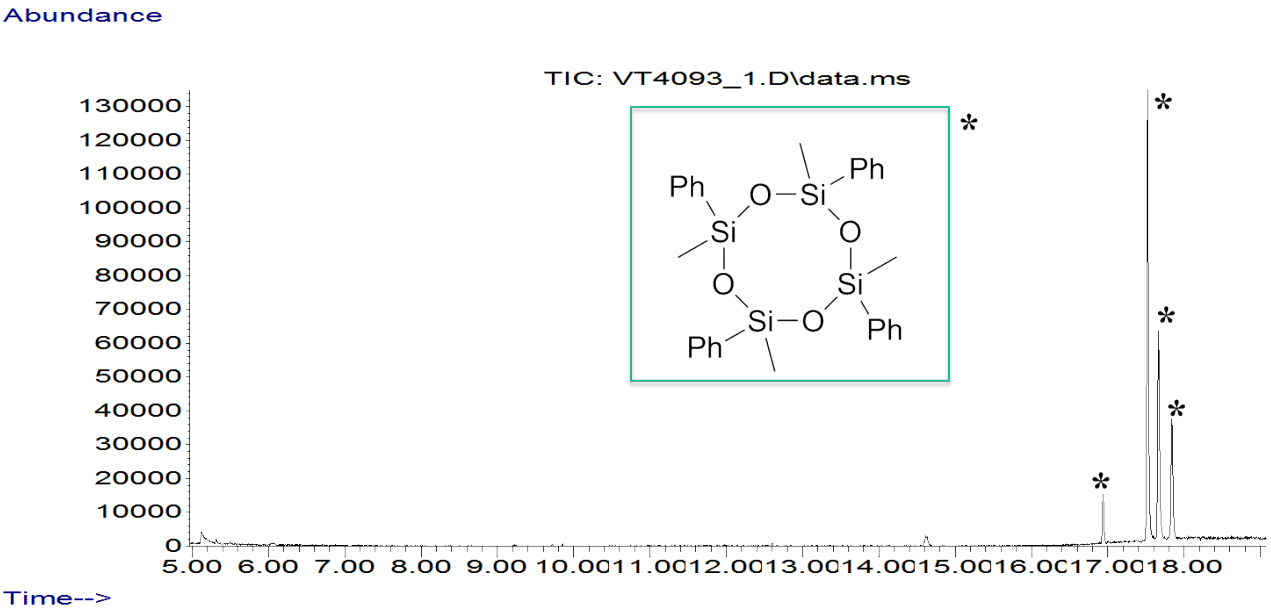

Figure S7(a). GC-MS spectrum. Experiment performed on a sample of the reaction mixture containing 600 µL of DMF-d_7, 5 mg of the Pt-containing monolith (357 ppm Pt; ~9 nanomol of Pt) and 50 µL of methylphenylsilane. The different peaks from t_R = 16.0 min onwards correspond to eight-membered siloxane ring with molecular weight of 544.2 Da formed as the side product in the reduction reaction. No six-membered siloxane ring was formed in this process.

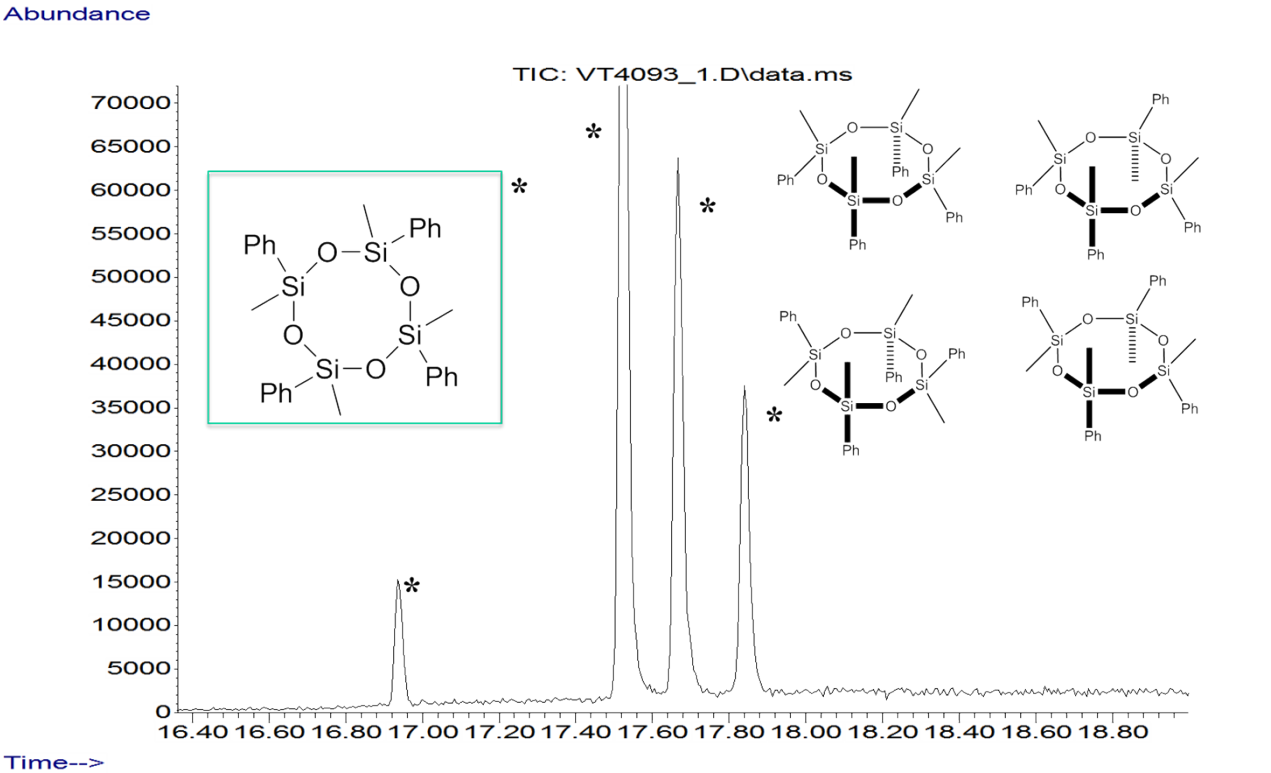

Figure S7(b). GC-MS spectrum. Expansion of spectrum in Figure S7(a). Four peaks are realized for the four enantiomers.

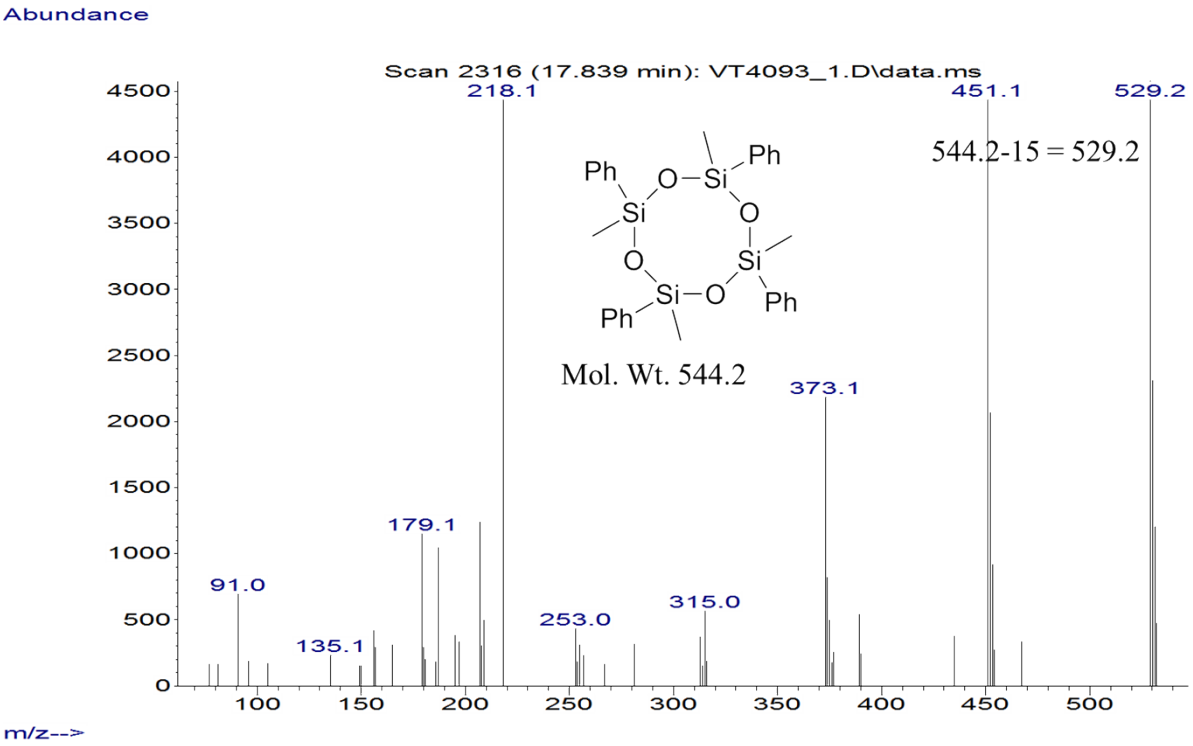

Figure S7(c). Fragmentation pattern of the peak at t_R = 17.839 min in the GC-MS spectrum shown in Figure S7(b). The molecular weight of 529.2 Da corresponds to an eight-membered siloxane ring minus the molecular weight of the methyl group. All the peaks in Figure S7(b) show similar fragmentation pattern.

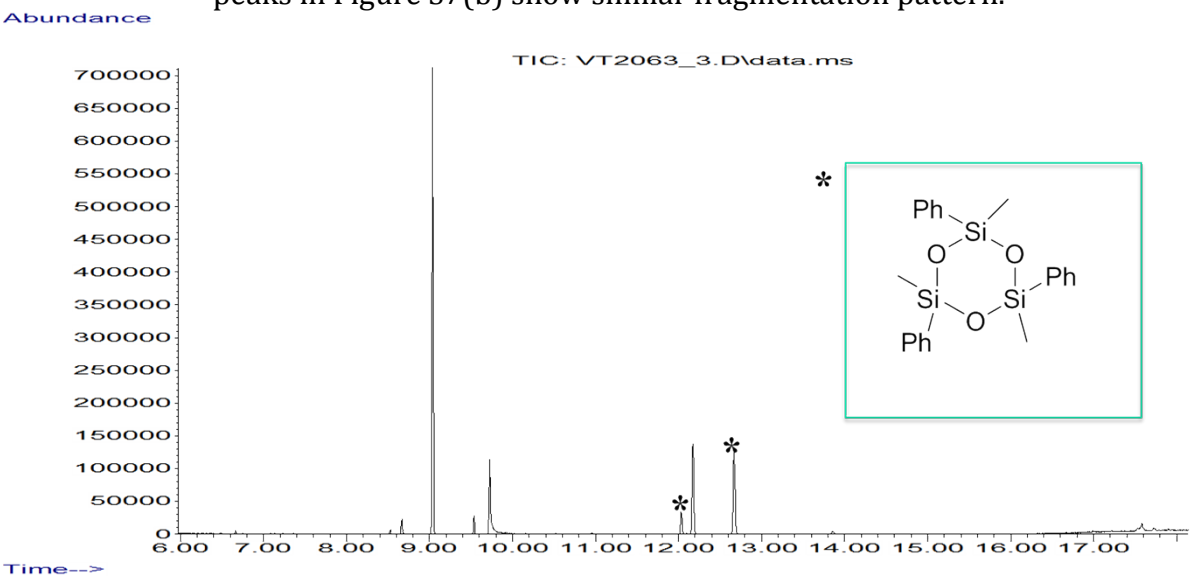

Figure S8(a). GC-MS spectrum. CO_2 reduction[2] with 10 mg of Pt-containing monolith (~28 nanomole of Pt) and 25 mg of methylphenylsilane. Two peaks at t_R = 12.037 min and t_R = 12.672 min correspond to six-membered siloxane rings with molecular weights of 408.1 Da formed as the side product in the reduction reaction. No eight-membered siloxane ring was formed in this process.

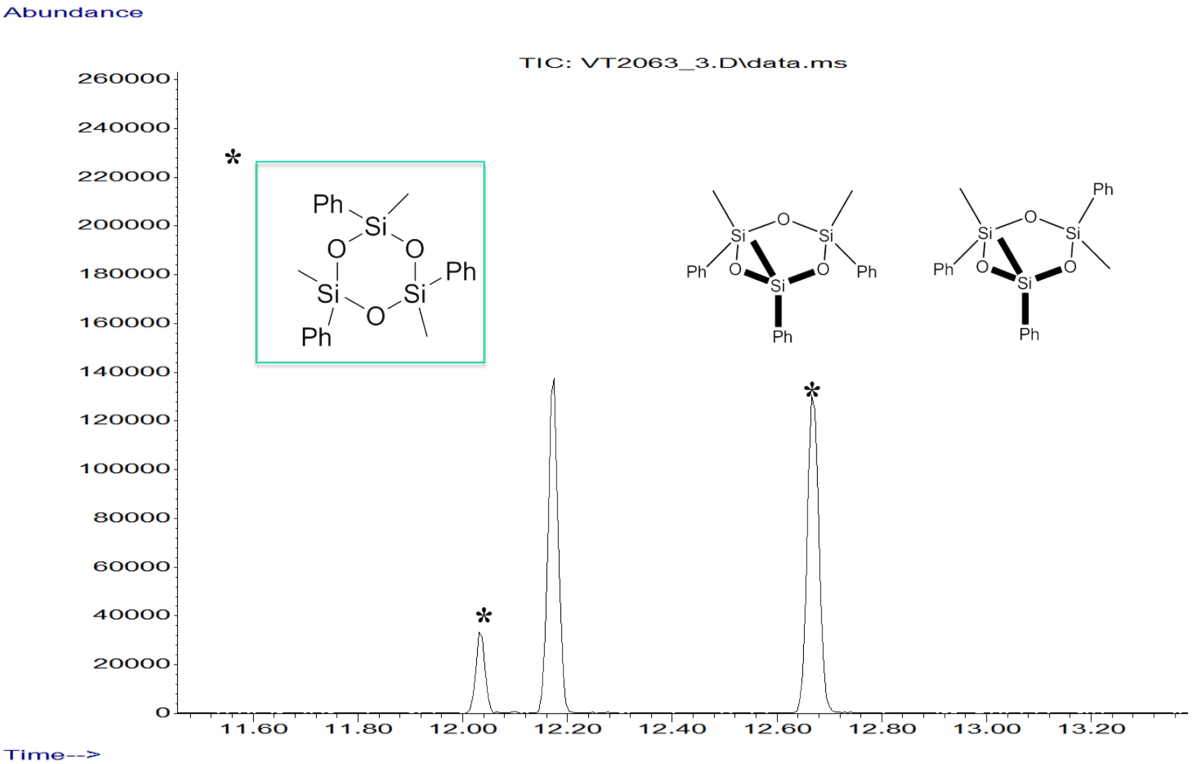

Figure S8(b). GC-MS spectrum. Expansion of spectrum shown in Figure S8(a). Two peaks are realized for the two enantiomers.

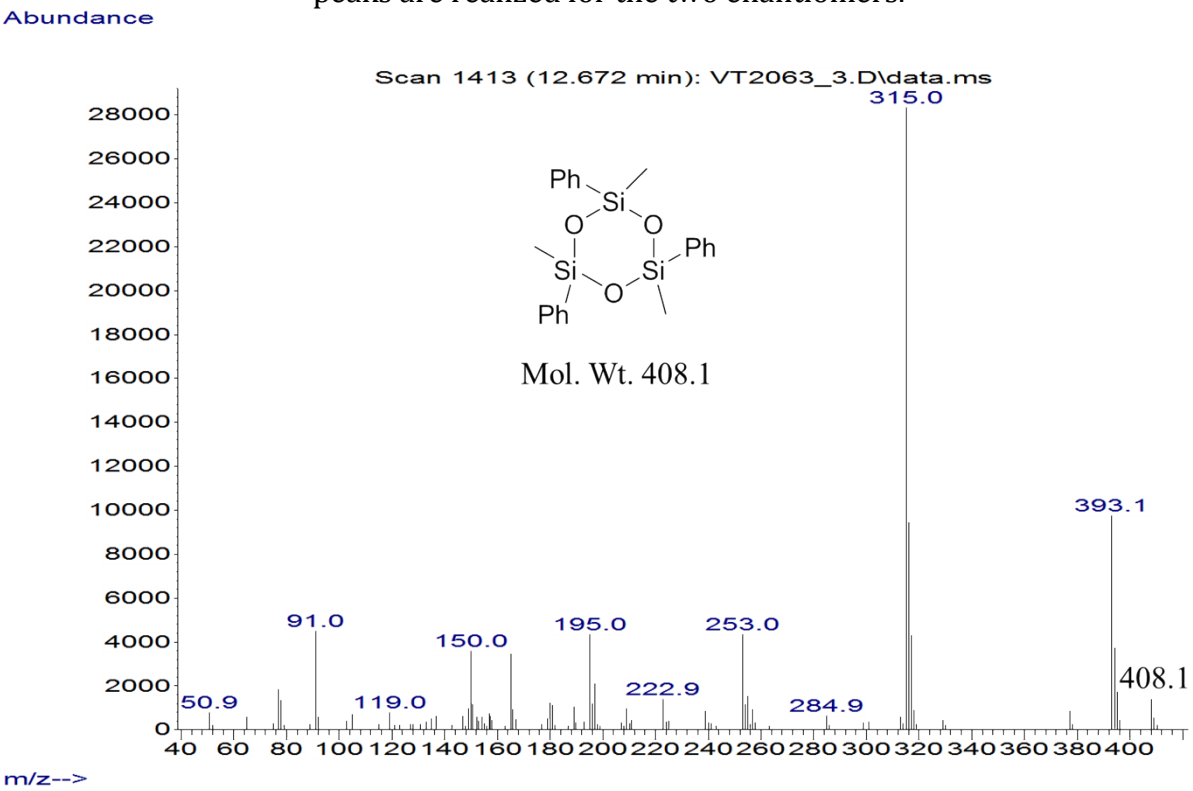

Figure S8(c). Fragmentation pattern of the peak at t_R = 12.672 min in the GC-MS spectrum shown in Figure S8(b). The molecular weight of 408.1 Da corresponds to a six-membered siloxane ring. Both the peaks at t_R = 12.037 min and t_R = 12.672 min in Figure S8(b) show similar fragmentation patterns.

(1) Arias-Ugarte, R.; Sharma, H. K.; Morris, A. L. C.; Pannell, K. H. *J. Am. Chem. Soc.* **2011**, *134*, 848.

(2) Taori, V. P.; Bandari, R.; Buchmeiser, M. R. *Chem. Eur. J.* **2014**, *20*, 3292.