Electronic supplementary information

Low-temperature catalytic hydrogenation of bio-based furfural and relevant aldehydes using cesium carbonate and hydrosiloxane

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Table of Contents:

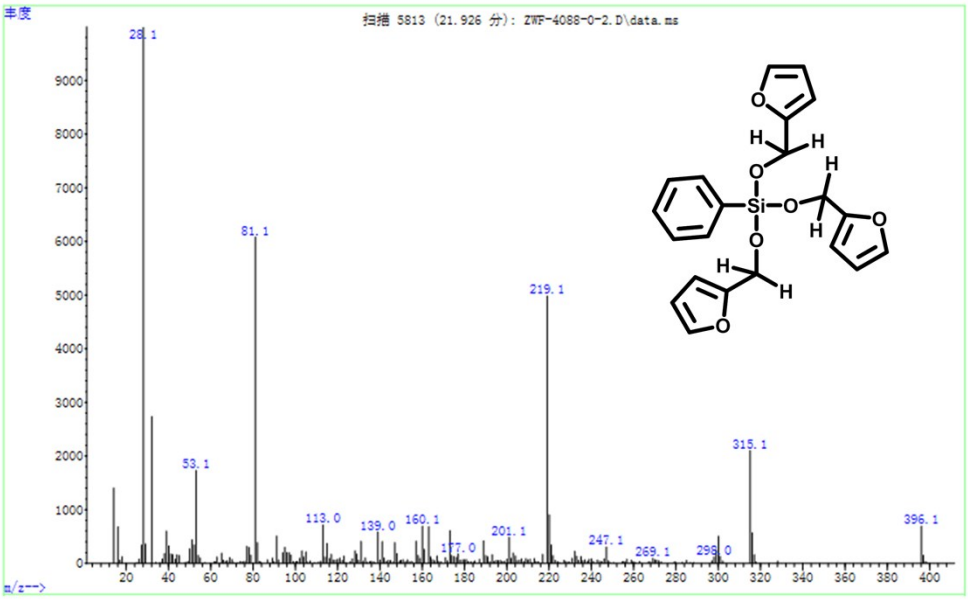


Fig. S1 GC-MS spectrum of the siloxane intermediate in hydrogenation of FUR to FFA; Reaction conditions: 0.5 mmol FUR, $PhSiH_3$ (1.47 mmol H^-), 2 mL DMF, 16 mg Cs_2CO_3, 25 ºC, and 6 h.

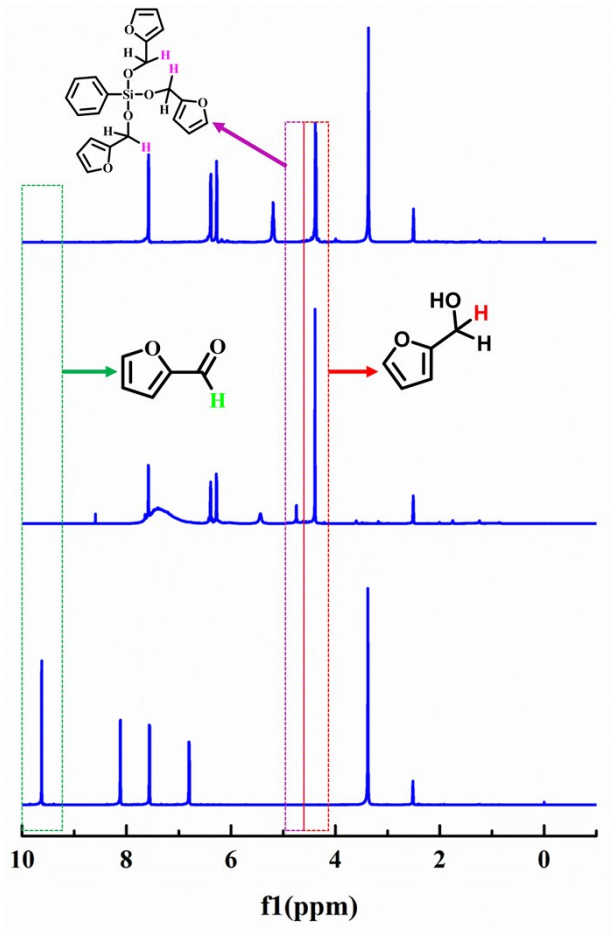


Fig. S2 ^1H NMR spectra of the siloxane intermediate in hydrogenation of FUR to FFA. Reaction conditions: 0.5 mmol FUR, $PhSiH_3$ (1.47 mmol H^-), 1 mL DMSO-d_6, 16 mg Cs_2CO_3, 25 ºC, and 6 h.

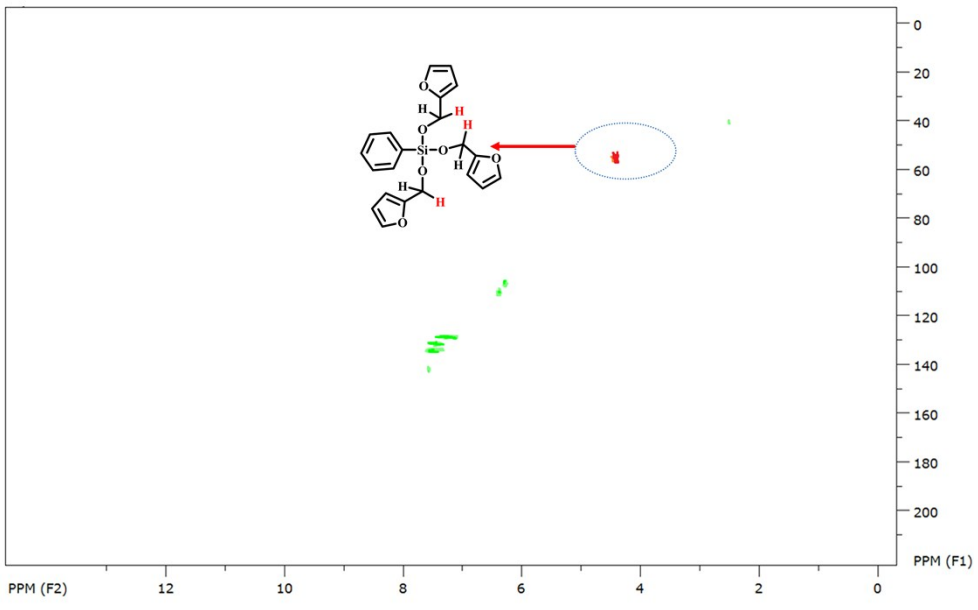


Fig. S3. ^{1}H-^{13}C HSQC NMR spectrum of the siloxane intermediate in hydrogenation of FUR to FFA. Reaction conditions: 0.5 mmol FUR, $PhSiH_3$ (1.47 mmol H^-), 1 mL DMSO-d_6, 16 mg Cs_2CO_3, 25 ºC, and 6 h.

Table S1 Effect of different hydrosilanes on the hydrogenation of FUR to FFA

Entry	H-donor	Yield (%)	Conversion (%)
1	Et_3SiH	0.2	0.6
2	$(MeO)_3SiH$	5.4	10.0
3	Me_3Si-O-MeSiH-O-$SiMe_3$	30.7	40.0
4	$(EtO)_3SiH$	32.5	42.0
5	Me_2SiH-O-$HSiMe_2$	50.7	60.0
6	Ph_2SiH_2	88.4	90.0
7	$PhSiH_3$	99.1	99.2
8	PMHS	99.5	99.5

Reaction conditions: 0.5 mmol FUR, 16 mg Cs_2CO_3, H-donor (1.47 mmol H^-), 2 mL DMF, 80 °C, and 6 h.

Table S2 The recycling study of cesium carbonate-catalyzed reduction of FUR to FFA

Entry	Time (h)	T (°C)	Catalyst dosage (mg)	Reaction cycle	Yield (%)	Conv. (%)
1	6	80	16	1	99	99
2	6	80	16	2	30.4	43.1
3	6	25	16	1	90	99
4	6	25	16	2	47	48

Reaction conditions: 0.5 mmol FUR, PMHS (1.47 mmol H^-), 2 mL DMF.

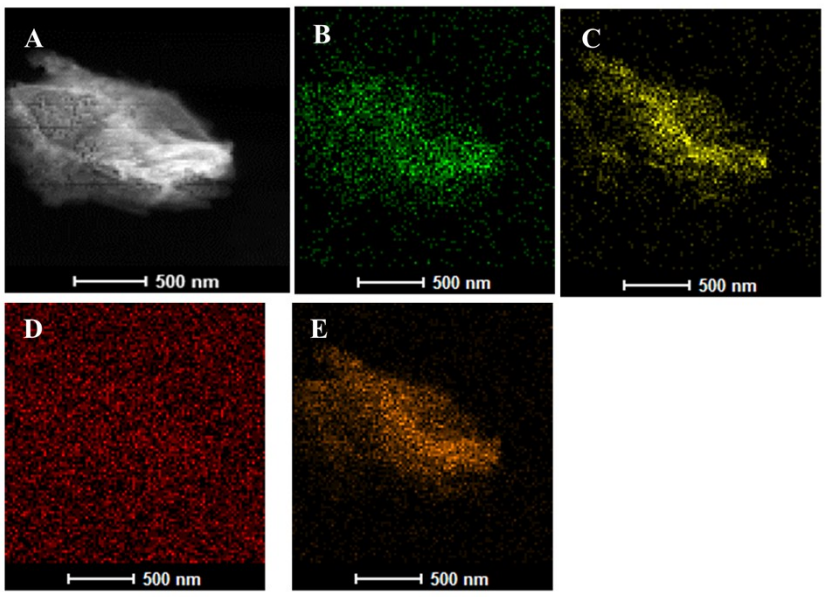


Fig. S4 STEM and elemental mapping profiles of recovered Cs_2CO_3 catalyst. (A) STEM-HAADF image and elemental mappings of (B) Cs, (C) Si, (D) C and (E) O

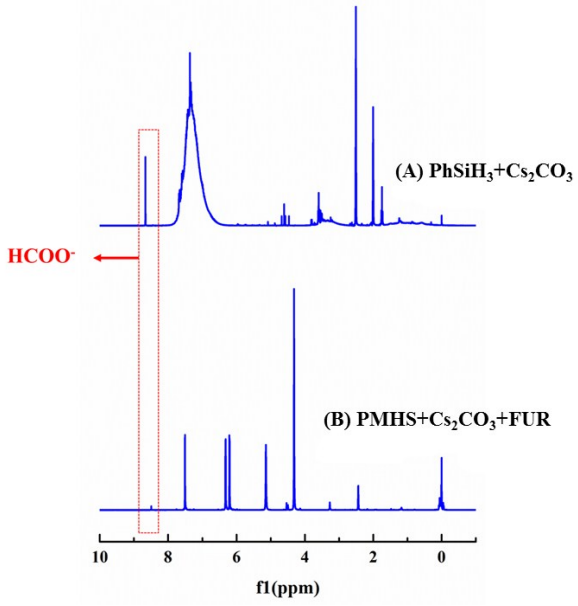


Fig. S5 ^{1}H NMR spectra of the formation of formate during hydrosilylation reaction. Reaction conditions (A): $PhSiH_3$ (1.47 mmol H^-), 1 mL DMSO-d_6, 16 mg Cs_2CO_3, 25 ºC, and 6 h; Reaction conditions (B): 0.5 mmol FUR, PMHS (1.47 mmol H^-), 1 mL DMSO-d_6, 16 mg Cs_2CO_3, 25 ºC, and 6 h.

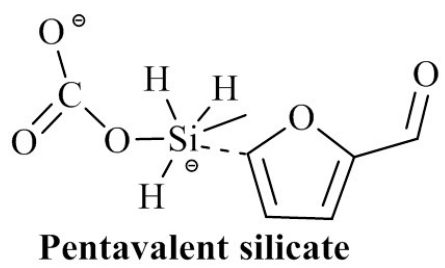


Fig. S6 The possible structure of pentavalent silicate intermediate in the hydrogenation of FUR to FFA.

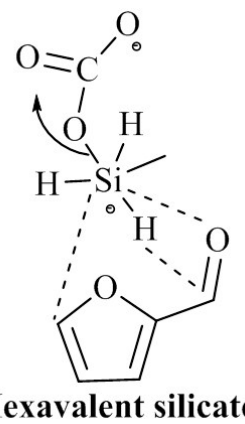


Fig. S7 The possible structure of hexavalent silicate intermediate in the hydrogenation of FUR to FFA.

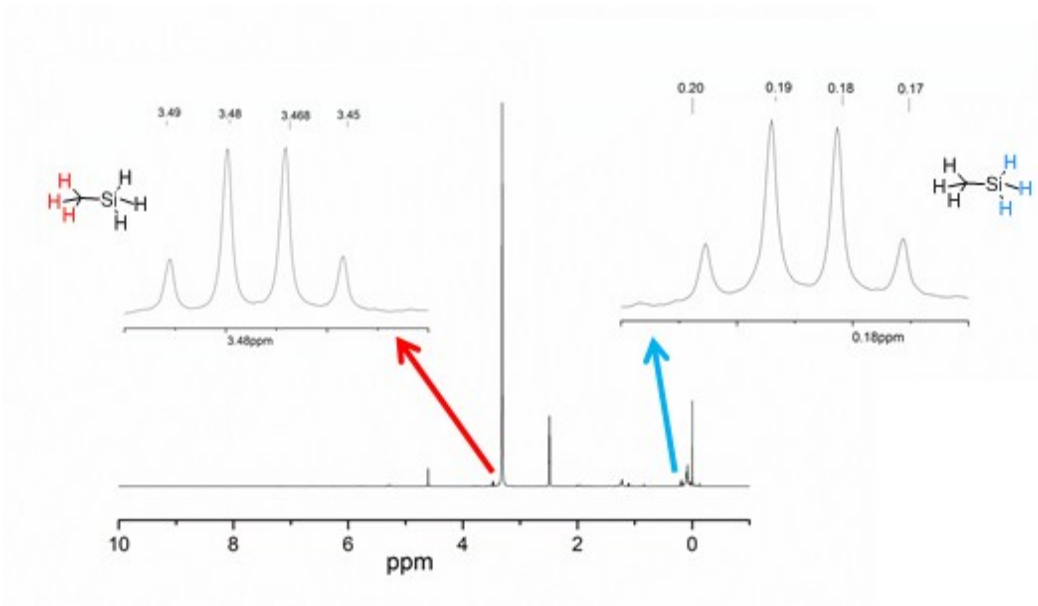
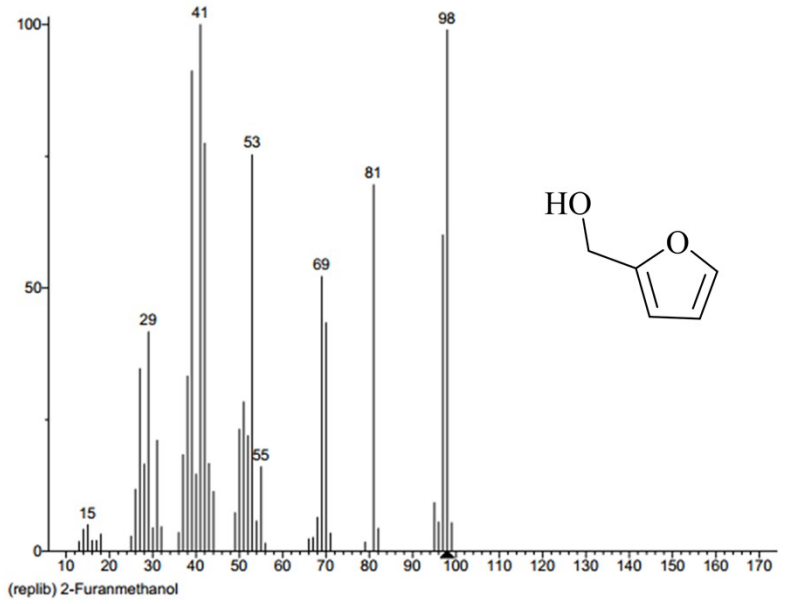
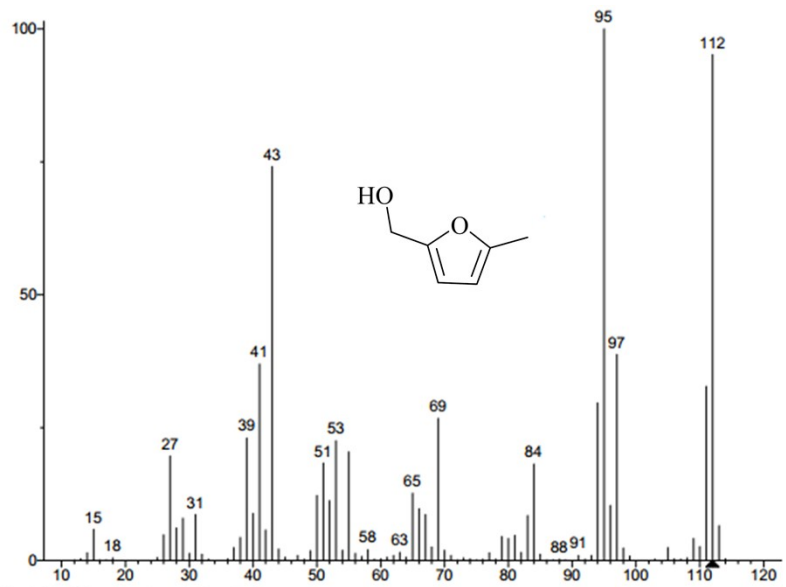
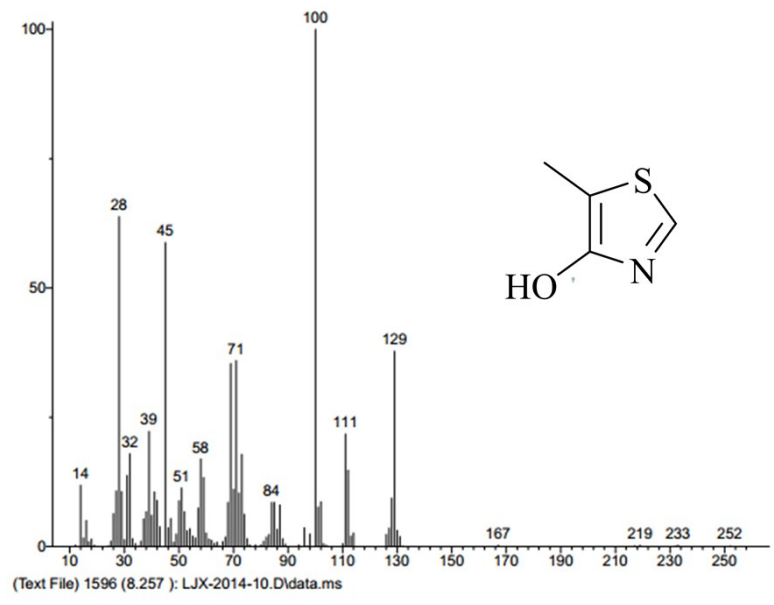
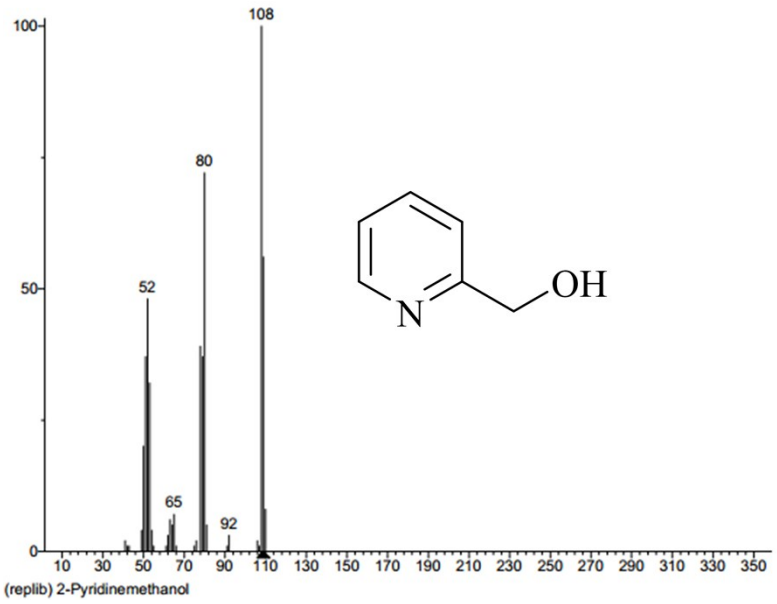


Fig. S8 ^{1}H NMR spectra of the interaction between PMHS and Cs_2CO_3. Reaction conditions: PMHS (1.47 mmol H^-), 1 mL DMSO-d_6, 16 mg Cs_2CO_3, 25 ºC, and 6 h.









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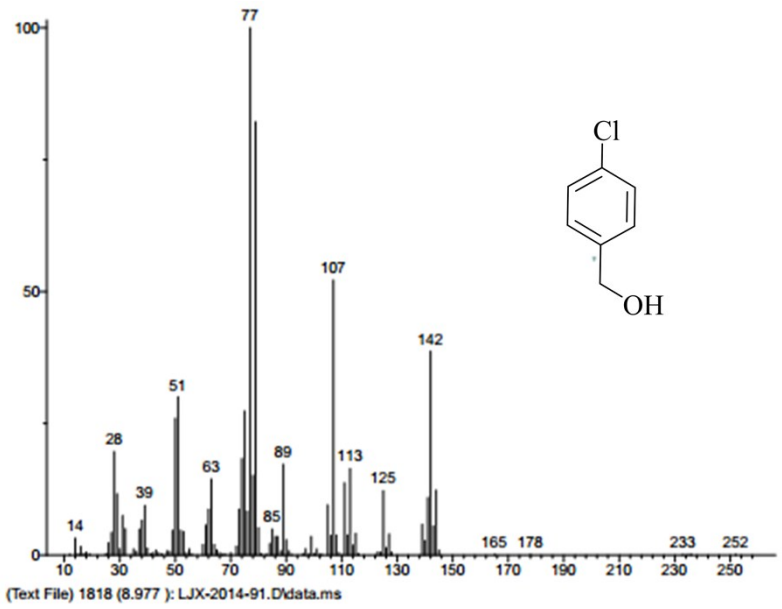

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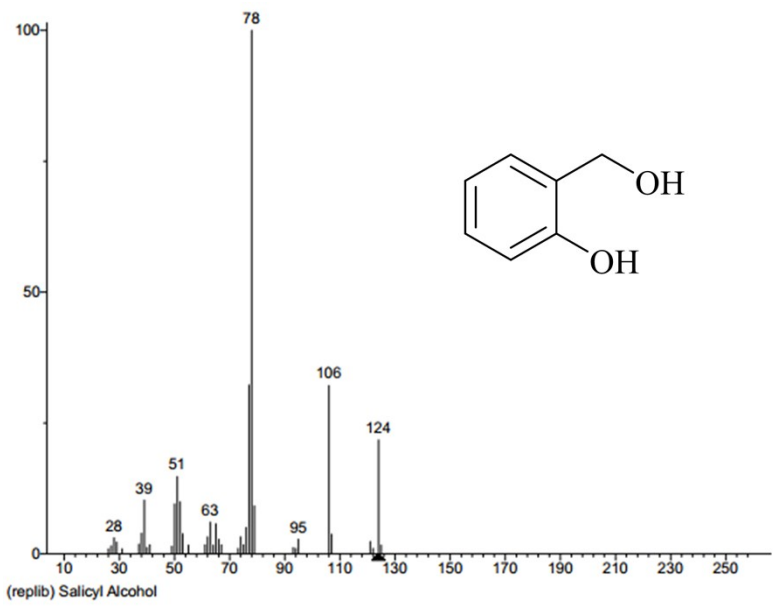
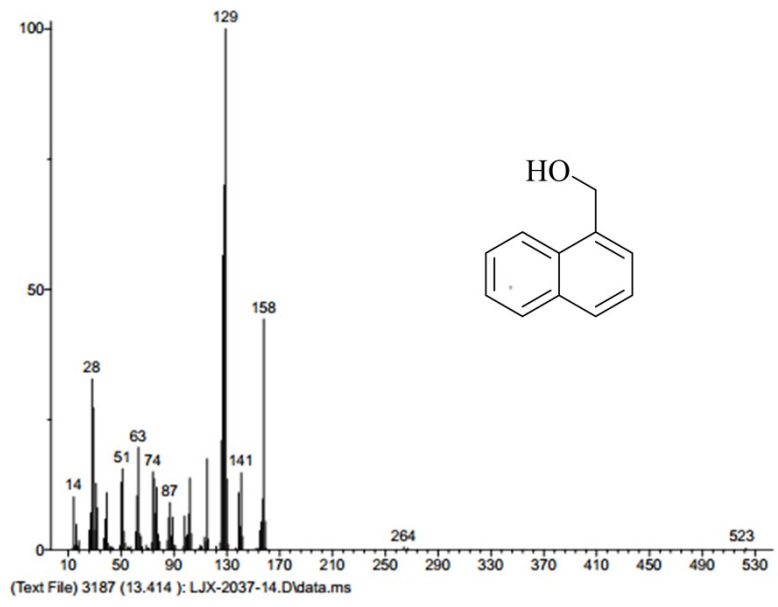


(replib) Salicyl Alcohol



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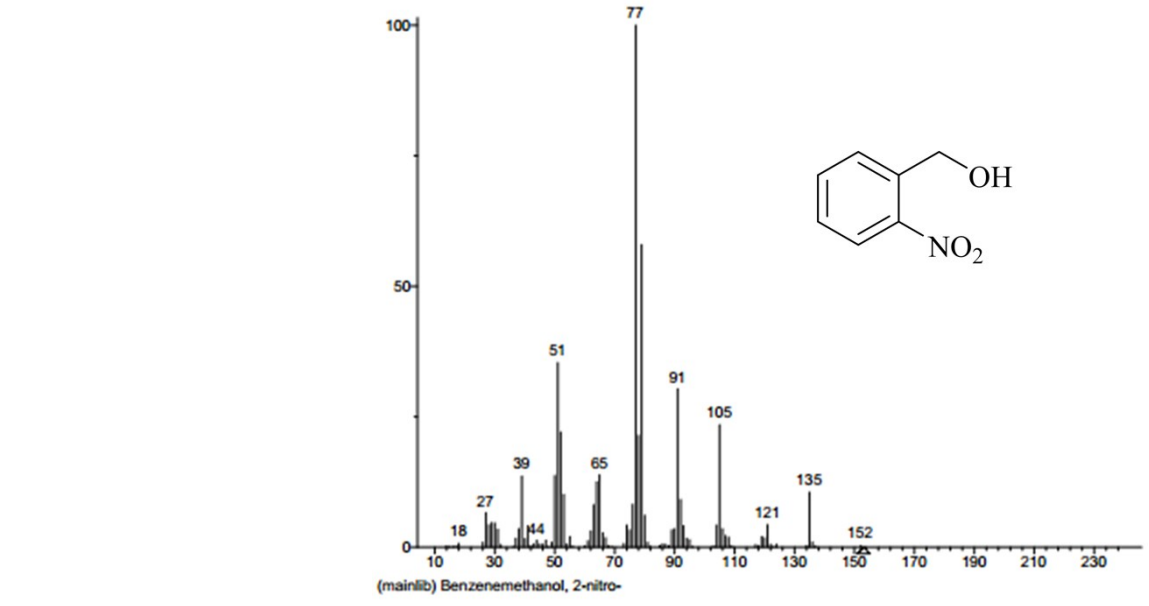

Fig. S9 GC-MS spectra of various alcohols obtained from hydrogenation of corresponding aldehyde

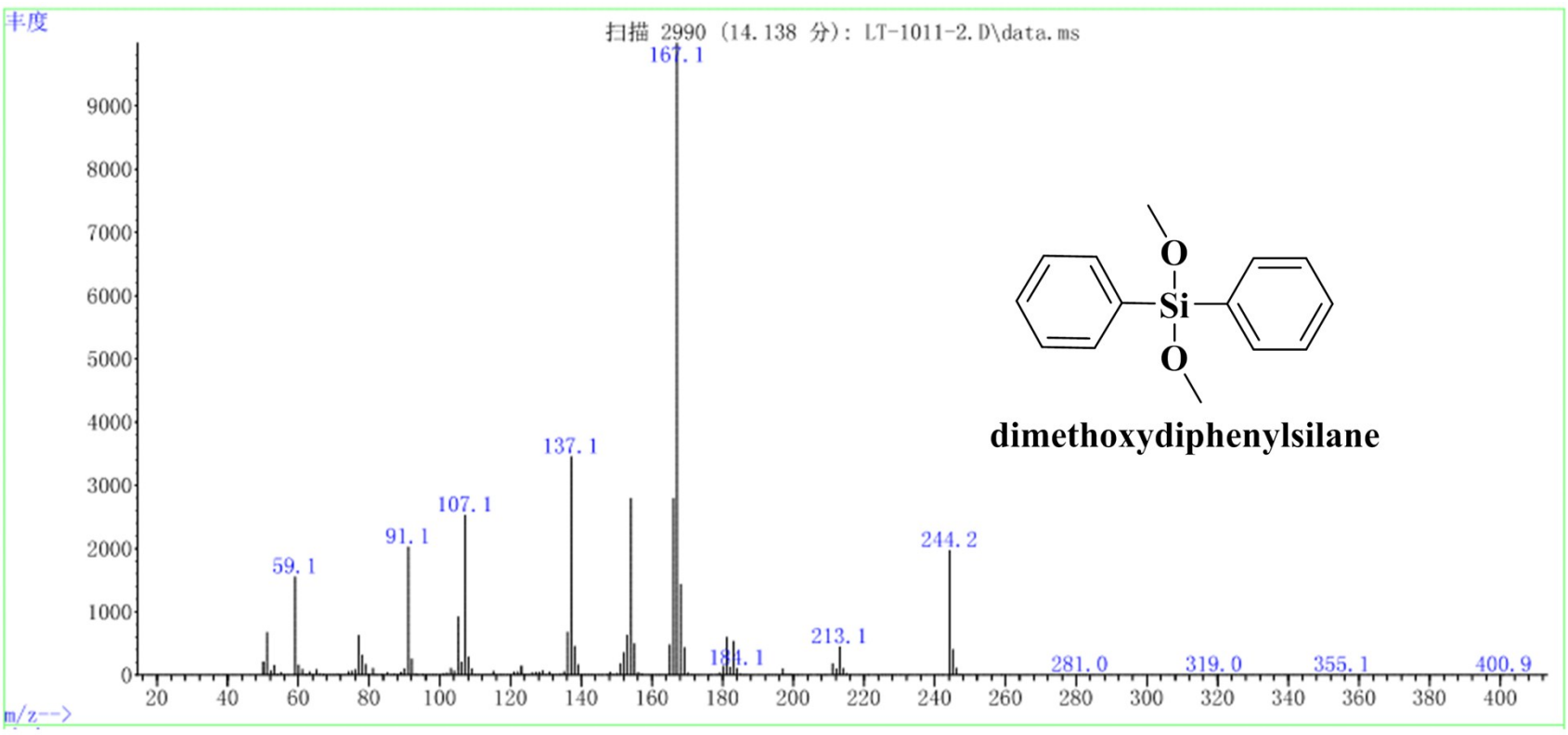

Fig. S10 GC-MS spectrum of dimethoxydiphenylsilane formed in the reaction of Ph_2SiH_2 and MeOH