Highly Dispersed Zirconium–Oxo Species Anchored on Ultrathin g-C_3N_4 Nanosheets for Efficient Catalytic Transfer Hydrogenation of Furfural

*Yanan Li, Yixiao Shi, Lei Li, Lijun Wang**

School of Chemistry and Chemical Engineering, Shaoxing University, Shaoxing 312000, China. E-mail: ljwang@usx.edu.cn

Figures S1-S9 and **Table S1-S2**

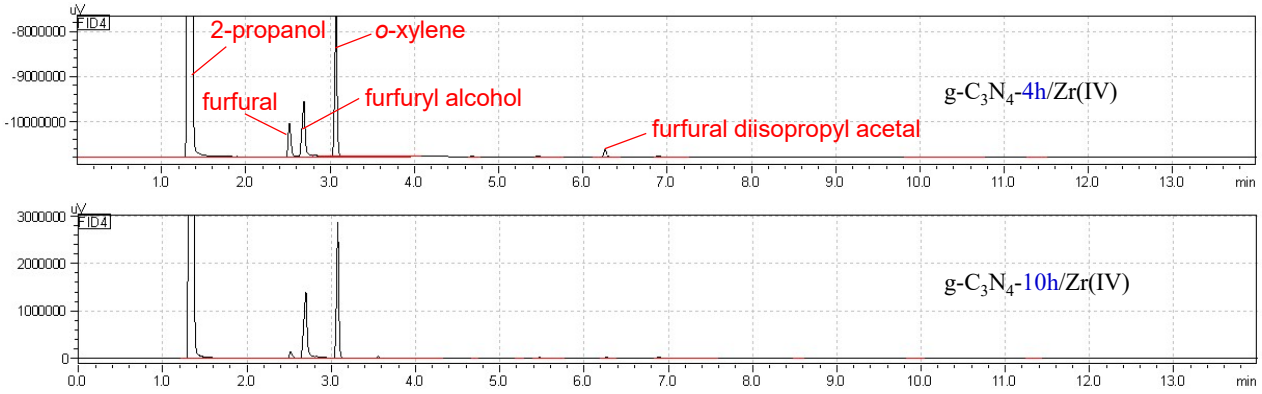

Figure S1. GC spectra of the liquid products from the reaction of furfural with 2-propanol over g-C_3N_4-*x*h/Zr(IV) catalysts. Reaction conditions: 50 mg catalyst, 1 mmol furfural, 5 mL 2-propanol, 60 μL o-xylene (internal standard), 1 MPa N_2, 120 °C, 8 h. (Note: *x* in g-C_3N_4-*x*h/Zr(IV) denotes the calcination time (in hours) for g-C_3N_4 synthesis).

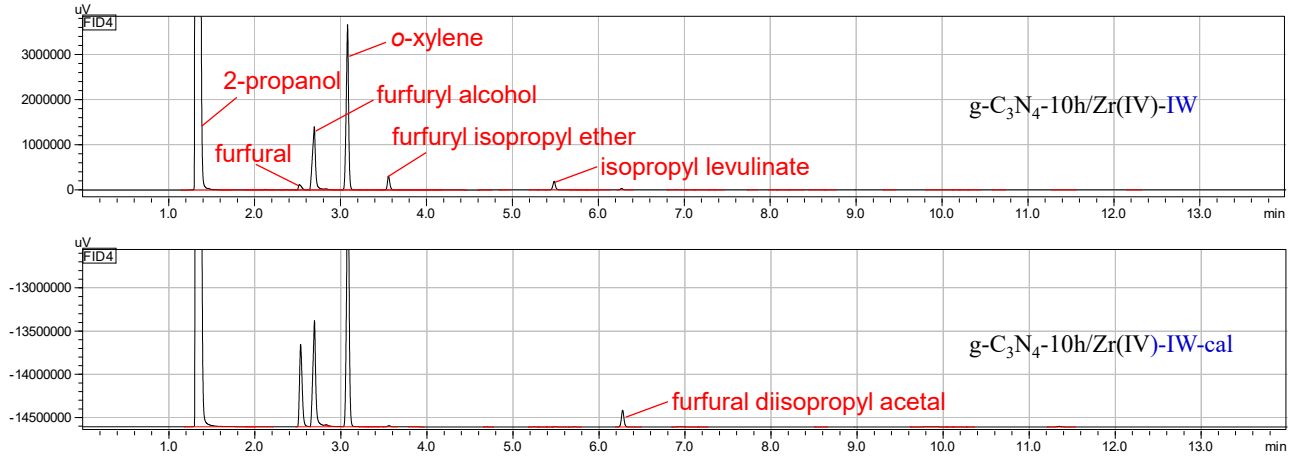

Figure S2. GC spectra of the liquid products from the reaction of furfural with 2-propanol over g-C_3N_4-10h/Zr(IV)-IW prepared by conventional incipient wetness impregnation and its calcined derivative g-C_3N_4-10h/Zr(IV)-IW-cal. Reaction conditions: 50 mg catalyst, 1 mmol furfural, 5 mL 2-propanol, 60 μL o-xylene (internal standard), 1 MPa N_2, 120 °C, 8 h.

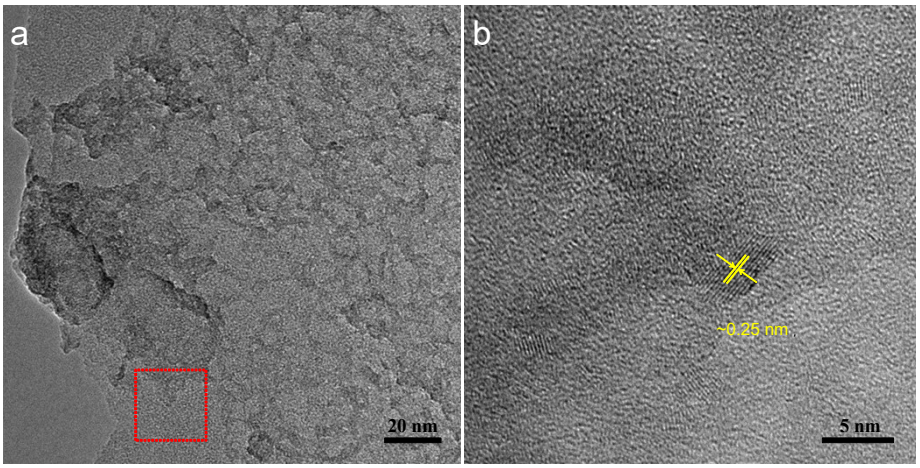

Figure S3. (a) TEM image of g-C_3N_4-4h/Zr(IV). (b) HRTEM image of the region marked by the dashed red box in (a).

Table S1. The contents of Brønsted and Lewis acidic sites of the catalysts obtained from pyridine-IR analysis with pyridine desorption at 150 °C, 250 °C, 350 °C, respectively.[a]

Samples	T (°C)	Brønsted acid (μmol·g^{-1})	Lewis acid (μmol·g^{-1})	Total acid (μmol·g^{-1})	Brønsted/Lewis acid molar ratios
g-C_3N_4-4h/Zr(IV)	150	14.5	111.3	125.8	0.13
	250	12.3	80.8	93.1	0.15
	350	6.3	40.8	47.1	0.15
g-C_3N_4-10h/Zr(IV)	150	18.0	157.5	175.5	0.11
	250	12.2	83.6	95.8	0.15
	350	5.8	39.7	45.5	0.15

[a] The acidic site amounts at the desorption temperatures of 150 °C, 250 °C, and 350 °C, respectively, represent all strength of the specific acidic sites, moderately and strongly acidic sites, and strongly acidic sites, respectively (*Inorg. Chem. 2024, **63**, 13775-13784*).

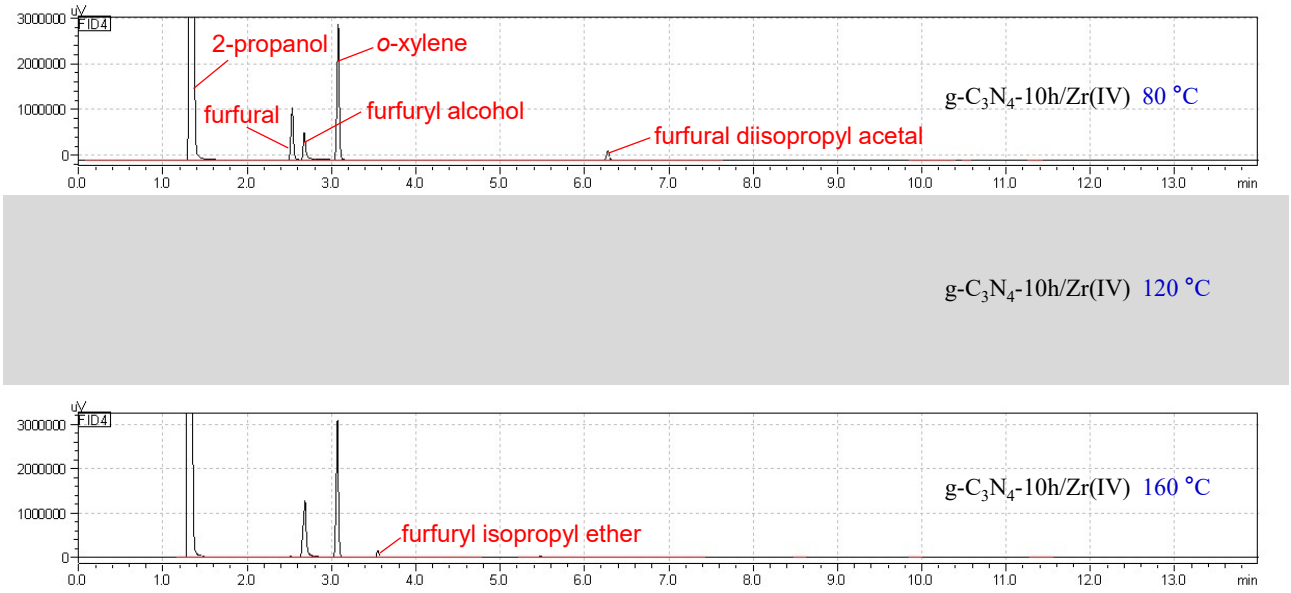

Figure S4. GC spectra of the liquid products from the reaction of furfural with 2-propanol over g-C_3N_4-10h/Zr(IV) at different temperatures. Reaction conditions: 50 mg g-C_3N_4-*10*h/Zr(IV), 1 mmol furfural, 5 mL 2-propanol, 60 μL o-xylene (internal standard), 1 MPa N_2, 8 h.

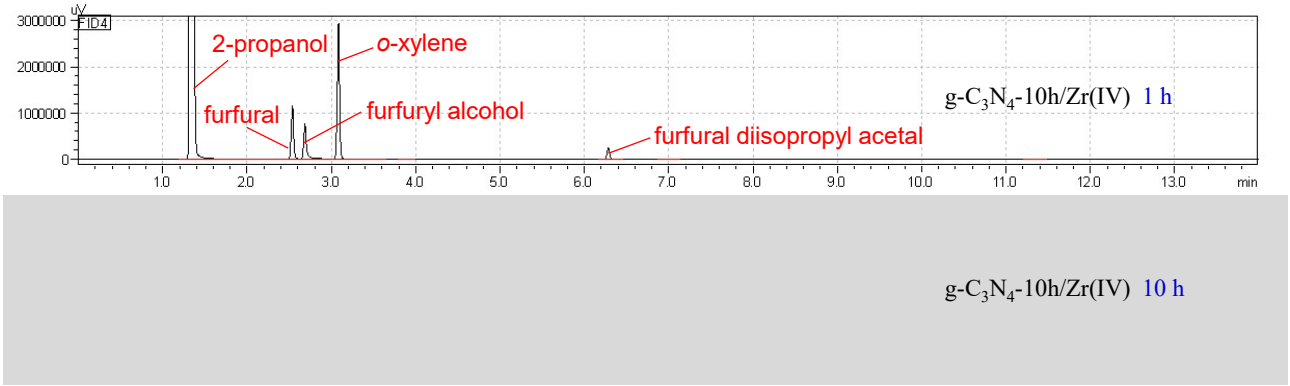

Figure S5. GC spectra of the liquid products from the reaction of furfural with 2-propanol over g-C_3N_4-10h/Zr(IV) at different reaction times. Reaction conditions: 50 mg g-C_3N_4-*10*h/Zr(IV), 1 mmol furfural, 5 mL 2-propanol, 60 μL o-xylene (internal standard), 1 MPa N_2, 120 °C.

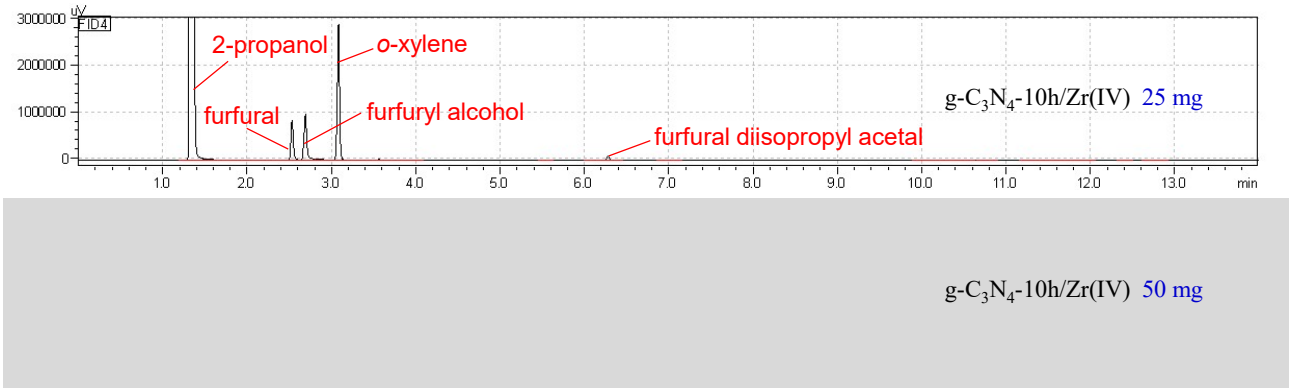

Figure S6. GC spectra of the liquid products from the reaction of furfural with 2-propanol over varying amounts of g-C_3N_4-10h/Zr(IV). Reaction conditions: 1 mmol furfural, 5 mL 2-propanol, 60 μL o-xylene (internal standard), 1 MPa N_2, 120 °C, 8 h.

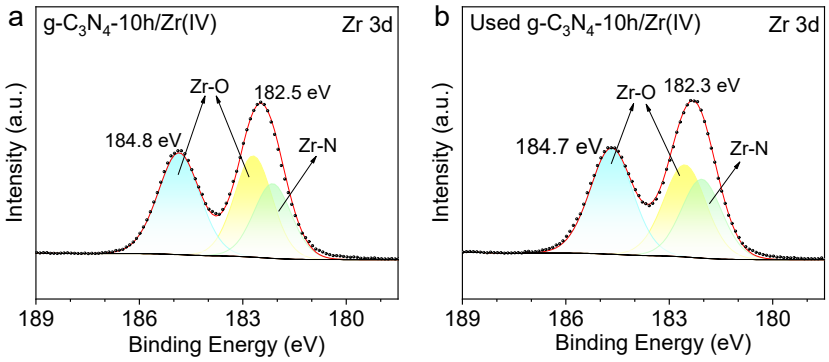

Figure S7. Zr 3d XPS spectra of (a) fresh g-C_3N_4-10h/Zr(IV) and (b) Used g-C_3N_4-10h/Zr(IV) after recycling.

Table S2. Surface elemental composition determined by XPS analysis.

Sample	C (Atomic %)	N (Atomic %)	C/N atomic ratio	Zr (Atomic %)
Fresh g-C_3N_4-10h/Zr(IV)	52.6	44.0	1.195	3.4
Used g-C_3N_4-10h/Zr(IV)	48.2	48.3	0.998	3.5

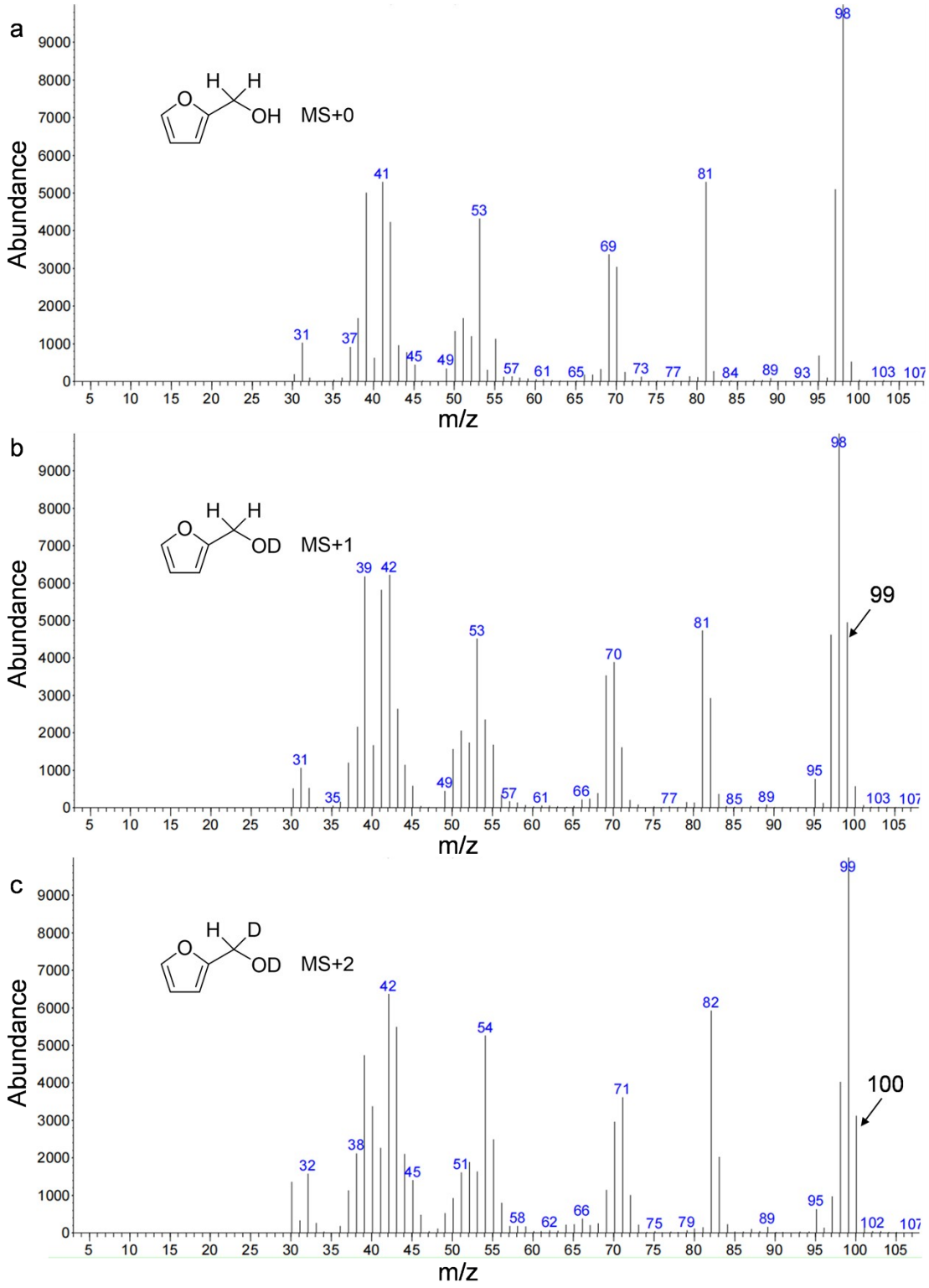

Figure S8. MS spectra of furfuryl alcohol obtained from the reaction of furfural with (a) 2-propanol, (b) 2-propanol-OD, and (c) 2-propanol-d8 catalyzed by g-C_3N_4-10h/Zr(IV) at 120°C.

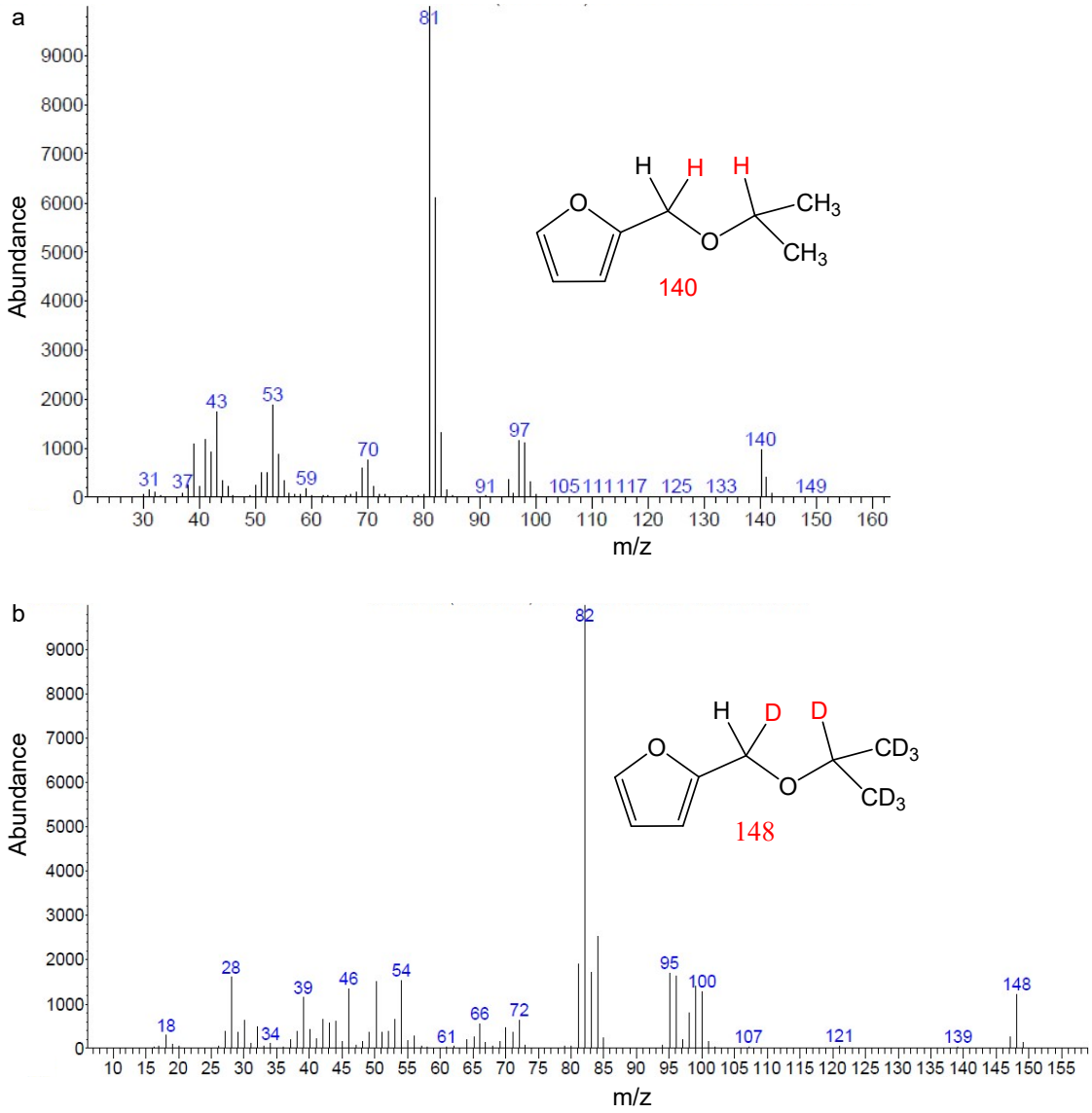

Figure S9. MS spectra of furfuryl isopropyl ether obtained from the reaction of furfural with (a) 2-propanol-OD and (b) 2-propanol-d8 catalyzed by g-C_3N_4-10h/Zr(IV) at 120°C.