Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supporting Information

Heterogeneous (de)chlorination-enabled control of reactivity in liquid-phase synthesis of furanic biofuel from cellulosic feedstock

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Experimental details

Materials

Diphenyl (silane-d_2) (97 atom % D), D_2O (99.9 atom % D), CD_3OD (≥99.8 atom % D), and $CDCl_3$ (>99.9 atom % D) were purchased from Sigma-Aldrich (Shanghai) Trading Co. Ltd. Poly(vinylbenzyl chloride) (PS-Cl), NH_4Cl (>99%), $NH_3 \cdot H_2O$ (28-30% in water), cyclohexane (99.5%), microcrystalline cellulose (average particle size 50 μm), *n*-butanol (>99%), 5-methyfurfuryl alcohol (MFA, 99.9%), 5-hydroxymethylfurfural (HMF, >99%), 5-methylfurfural (MFF, 98%), 2,5-dimethylfuran (DMF, >98%), 2,5-dihydroxymethylfuran (DHMF, 98%), 5 wt. % Pd/C (wetted with ca. 50% water), 4-chloromethylbenzaldehyde (98.0%), 4-chlorobenzaldehyde (99%), 4-chloro-2-methoxybenzaldehyde (97%), 3-chloro-4-methoxybenzaldehyde (98%), 4-chloro-3-methoxybenzaldehyde (98%), 4-chloro-2-(trifluoromethyl)benzaldehyde (97%), 4-chloro-3-(trifluoromethyl)benzaldehyde (98%), 3-chloro-4-(trifluoromethyl)benzaldehyde (>95%), 4-chloroacetophenone (99%), 4-chlorobenzophenone (99%), 4-chlorophenyl cyclohexyl ketone (97%) and 1,3,5-trimethoxybenzene (99%) were supplied by Beijing Innochem Sci. & Tech. Co. Ltd. Poly(methylhydrosiloxane) (PMHS), *N,N*-dimethyl formamide (99.8%), H_2PtCl_4 (>99.9%), $RuCl_3$ (99%), $Ni(NO_3)_2$ (98%), $Co(NO_3)_2$ (99%), HBr (48 wt. % in H_2O), HI (55.0-58.0% in H_2O), and activated charcoal (>99.9%) were bought from Shanghai Aladdin Industrial Inc. Prior to experiments, pulverous filter paper, waste paper, corn stover and wheat straw, as well as cellulose were completely dried and ball-milled for 120 min.

Catalyst preparation

Synthesis of PS-NH_3Cl

The PS-NH_3Cl catalyst was prepared according to a previously reported method [S1]. 1 g PS-Cl and 5.78 mmol $NH_3 \cdot H_2O$ (28-30% in water) were added into a round-bottom flask (50 mL) containing 15 mL *N,N*-dimethyl formamide, and kept stirring at 80 °C for 24 h. Upon completion, the resulting solids were washed with *N,N*-dimethyl formamide (30 mL × 3) and methanol (25 mL × 3), filtered out and dried at 60 °C overnight. Finally, the solid samples were stirred in HCl aqueous solution (5 mol/L, 30 mL) for 1 h, washed with methanol, filtered out and dried at 60 °C for 5 h. The nitrogen content of the catalyst was determined to be 0.85 mmol/g by elemental analysis.

Synthesis of metal particles on carbon

5 wt. % metal particles (Ru, Pt, Ni, Co) on activated charcoal were prepared by incipient wetness impregnation [S2]. In a typical procedure, 34 mg $RuCl_3$ was firstly dissolved in 1.2 mL water. To the resulting mixture, 0.4 g of activated charcoal was added, and kept stirring (300 rpm) at ambient temperature for 24 h. Upon completion, the obtained suspension was dried at 80 °C overnight, calcined at 450 °C (heating ramp: 10 °C/min) in air for 4 h, and reduced in hydrogen (flow rate: 20 cm^3/min) at 400 °C (heating ramp: 10 °C/min) for 2 h.

Catalysts characterization

Inductively coupled plasma-optical emission spectrometer (ICP-OES) was recorded on an Optima 5300 DV instrument (PerkinElmer Inc., Waltham, MA). Nitrogen content was measured by elemental analysis (Vario EL III, Elementar). Scanning transmission electron microscope and high-angle annular dark-field (STEM-HAADF) images were acquired with an aberration-corrected FEI Tecnai G2 F30 S-TWIN (S)TEM operating at 300 kV. FT-IR (Fourier Transform infrared spectroscopy) spectra of the samples were acquired on a Nicolet iS50 (Thermo Fisher Scientific) instrument. High-Resolution Transmission electron microscopy (HR-TEM) images were obtained on a JEM-1200EX instrument.

Reaction procedures

Catalytic conversion of cellulosic biomass to HMF and CMF

All experiments for catalytic conversion of cellulose and raw biomass materials (filter paper, waste paper, corn stover and wheat straw) to HMF and CMF were performed in a well-controlled microwave synthesis reactor (Monowave 300, Anton Paar, Graz, Austria). In a general reaction procedure, 3 mL cyclohexane and 1 mL conc. HCl or 5-50 wt% NH_4Cl aqueous solution with 0.1 g of additive (PS-Cl or PS-NH_3Cl) were added into the glass vial (10 mL) containing 5 wt. % cellulose or the raw biomass material (relative to the aqueous solution). The biphasic reaction mixture was heated to a desired temperature (100-160 ºC) within 3 min and magnetically stirred at 600 rpm for a specific reaction period. After the reaction, solid components were separated from the product mixture by centrifugation at 10000 rpm for 5 min, and the liquid samples in both aqueous and organic phases were collected and filtered with a 0.45 μm syringe filter for further analyses. The furanic mixture mainly composed of CMF and HMF could be obtained by rapid and facile recovery of the extracting solvent (cyclohexane) via rotary evaporation (60 ºC, 0.08 MPa), which can be directly used for the following HDO process.

The resulting CMF was purified from the furanic mixture as light yellow oil by column chromatography (CH_2Cl_2/Et_2O (2:1) → CH_2Cl_2/MeOH (95:5) gradient). ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm = 4.4 (s, 2H), 6.4 (d, 1H), 7.0 (d, 1H), 9.5 (s, 1H); ^{13}C NMR (500 MHz, $CDCl_3$): δ/ppm = 45.8, 125.9, 128.2, 147.8, 152.6, 177.4.

Catalytic HDO of furanic compounds to DMF

The real loading of Pd in the commercial 5 wt. % Pd/C catalyst was determined to be 4.2 wt. % by ICP analysis. All the HDO reactions were conducted in a 15 mL Ace tube. In a general reaction procedure, 0.5 mmol reactant (including the mixture of CMF and HMF obtained by simple evaporation of the extracting solvent), 2 mL *n*-butanol, 0.5 mol% Pd, 3.5 equiv. PMHS (1.75 mmol H^-) were added into the tube, which was magnetically stirred at 600 rpm for a specific reaction time. The time zero was defined as the tube was placed into an oil bath that was preheated to the desired reaction temperature. Upon completion, liquid products after syringe filtration (0.45 μm) were quantitatively analyzed by GC, HPLC and NMR.

Product analysis

Liquid products and major by-products were identified with GC-MS (Agilent 6890N GC/5973 MS, Santa Clara, CA). The reaction mixtures were quantitatively analyzed by GC (Agilent 7890B) with a HP-5 column (30 m ×320 μm × 0.25 μm or 30 m × 250 μm × 0.25 μm) and a flame ionization detector using naphthalene as internal standard and referring to the standard curves (with $R^2 \geq 0.997$) made from commercial and purified samples. For the rest products, NMR was used for quantification by using 1,3,5-trimethoxybenzene as the internal standard.

According to the standard methods reported by National Renewable Energy Laboratory (NREL) [S3-S5], the compositions of raw materials with respect to cellulose, hemicellulose, lignin and ash contents were determined (Table S6). Soluble sugars and furanic compounds were quantified by high performance liquid chromatography (HPLC), by referring to standard samples of HPLC grade bought from Sigma-Aldrich (Shanghai) Trading Co. Ltd. The sample moisture content was measured using a moisture analyzer (Sartorius Mechatronics Corp., USA). The contents of hexose sugars were set as the theoretical yields of DMF obtained from raw materials.

Catalyst recycles

After each cycle of reaction, the Pd/C catalyst in the liquid mixture was recovered by centrifugation (8000 rpm, 3 min), followed by successively washing with ethanol (30 mL × 3) and acetone (20 mL × 5) under ultrasonic conditions, and vacuum drying at 60 ºC for 6 h, which was then directly used for the next run.

Isotope labeling experiments

For isotope labeling and mechanism studies, ^{1}H, ^{13}C, and ^{1}H-^{13}C HSQC NMR (with DEPT-135) spectra of the reaction mixtures were used in the experiments under the given reaction conditions with either normal or deuterium reagents. Analyses were performed with deuterated solvents ($CDCl_3$ or CD_3OD) on a JEOL-ECX 500 NMR spectrometer. GC-MS spectra for some of the liquid mixtures were measured to determine the incorporated D in the products.

Computational methods

All the calculations were performed with Gaussian09 package [S6]. Geometry optimization of all the minima and transition states involved was carried out at the B3LYP [S7] level with the Lanl2DZ [S8] basis set for Pd and 6-31G(d) for C, H, O and Si. Default convergence criteria were used. The vibrational frequency calculations were conducted at the same level of theory as geometry optimization to confirm whether each optimized structure is an energy minimum or a saddle point. For each transition state, intrinsic reaction coordinate (IRC) [S9] analysis was performed to verify that it connects the right reactants and products on the potential energy surface. The solvent effects were considered using the PCM [S10] model with the gas-phase optimized structures as the initial geometries.

Tabular data

Table S1 Catalytic conversion of cellulose to CMF reported in previous literature

Entry	Substrate	Catalyst	Temp. (ºC)	Time (h)	Extraction solvent	Extraction times	Product yield (%)		Ref.
							CMF	HMF	
1	Cellulose	Conc. HCl + LiCl	65	18 + 12	DCE	1	71	5	S11
2	Cellulose	Conc. HCl	100	3	DCE	3	83.5	-	S12
3	Glucose	Conc. HCl	100	3	DCE	3	81.2	-	S12
4	Sucrose	Conc. HCl	100	3	DCE	3	89.7	-	S12
5	Corn stover	Conc. HCl	100	3	DCE	3	80.2	-	S12
6[a]	Cellulose	Conc. HCl	80	0.75	DCE	1	12	-	S13
7[a]	Cellulose	Conc. HCl	80	0.75	DCE	3	24	-	S13
8[a,b]	Cellulose	Conc. HCl	80	0.75	DCE	3	71	-	S13
9	Cellulose	HCl	120	2	Cyclohexane	3	54.6	12.5	This work
10	Cellulose	HBr	120	2	Cyclohexane	3	42.3[c]	16.4	This work
11	Cellulose	HI	120	2	Cyclohexane	3	35.6[d]	19.2	This work

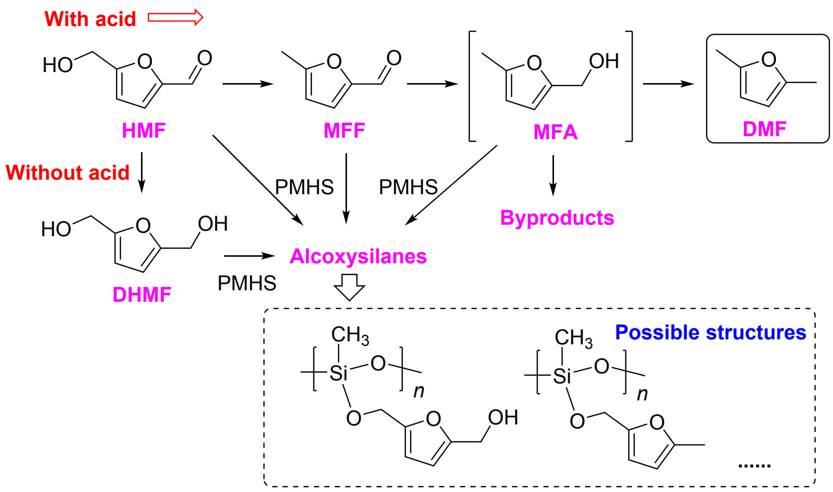
[a] Microwave irradiation; [b] Ball-milling for 110 min; DCE: 1,2-dichloroethane.
[c] Product is 5-bromomethylfurfural; [d] Product is 5-iodomethylfurfural.

Table S2 Effect of reaction temperature and time on the synthesis of HMF/CMF from cellulose

Entry	Temp. (ºC)	Time (h)	Product yield (%)	
			HMF	CMF
1	100	2	25.3	12.7
2	120	2	49.4	25.8
3	140	2	38.7	18.5
4	160	2	32.5	14.6
5	120	0.5	18.9	9.5
6	120	1	35.6	16.2
7	120	3	45.2	28.4
8	120	5	36.8	17.3

Reaction conditions: 5 wt% cellulose, 1 mL 40 wt% NH_4Cl aqueous solution, 0.1 g PS-NH_3Cl, 3 mL cyclohexane

Table S3 Conversion of HMF with PMHS over different metal catalysts



Entry	Catalyst	HMF conv.(%)	DMF yield (%)	DHMF yield (%)	Alkoxysilane yield (%)
1	Pd/C	81	1	56	14
2	Ru/C	43	<1	9	25
3	Pt/C	62	<1	25	29
4	Ni/C	33	0	2	23
5	Co/C	25	0	0	18

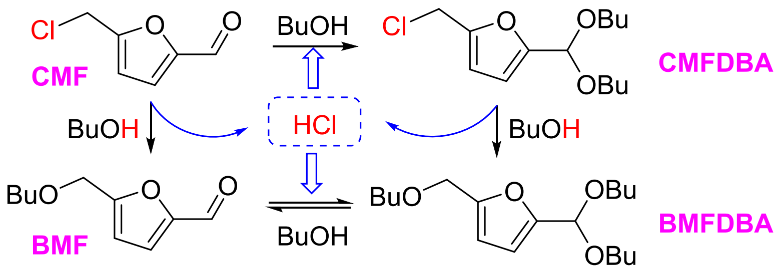
Reaction conditions: 0.5 mmol HMF, 2 mL *n*-butanol, 0.5 mol% metal, 3.5 equiv. PMHS (1.75 mmol H^{-}), 25 ºC, 60 min, acid-free. **HMF:** 5-hydroxymethylfurfural, **MFF:** 5-methylfurfural, **MFA:** 5-methylfurfuryl alcohol, **DMF:** 2,5-dimethylfuran, **DHMF:** 2,5-dihydromethylfuran

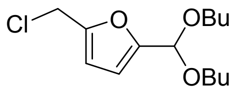
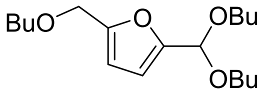
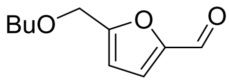
Table S4. Previous results in catalytic production of DMF from HMF

Entry	Catalyst	Temp (ºC)	Time (h)	H-donor	Substrate	Conv. (%)	Product	Yield (%)	Ref.
1	Cu-Co@C	180	8	5.0 MPa H_2	HMF	100	DMF	99.4	S14
2	Cu-Ru	220	1	5.0 MPa H_2	HMF	96	DMF+DTHF	81	S15
3	Ni/Perovskite	230	6	5.0 MPa H_2	HMF	>99	DMF	98.3	S16
4	Pd/Zn/C	150	8	0.8 MPa H_2	HMF	>99	DMF	85	S17
5	Pd/C	120	1	6.2 MPa H_2	HMF	19	DMF	2	S18
6	Ru-NaY	220	1	1.5 MPa H_2	HMF	100	DMF	78	S19
7	Ru/Co_3O_4	130	24	0.7 MPa H_2	HMF	>99	DMF	93.4	S20
8	Ru/C	190	6	2-Propanol	HMF	100	DMF	81	S21
9	Oxidized Ru/C	190	6	2-Propanol	HMF	100	DMF	70	S22
10	Ni-Co/C	210	24	Formic acid	HMF	99	DMF	90	S23
11	Cu-PMO	260	3	Methanol	HMF	100	DMF	48.0	S24
12	Cu/Al_2O_3	240	6	Methanol	HMF	100	DMF	73.9	S25
13	NC-Cu/MgAlO	220	0.5	Cyclohexanol	HMF	100	DMF	96.1	S26
14	Pd/Fe_2O_3	180	0.4	2-Propanol	HMF	100	DMF	72	S27
15	Pt/rGO	120	2	3 MPa H_2	HMF	100	DMF	73.2	S28
16	Pt-OMD1	200	6	3 MPa H_2	HMF	99.0	DMF	62.9	S29
17	PtCo@HCS	180	2	1 MPa H_2	HMF	100	DMF	98	S30
18	Pt-Co/MWCNTs	160	8	1 MPa H_2	HMF	100	DMF	92.3	S31
19	Pd_{50}/C	60	12	0.1 MPa H_2	HMF	>99	DMF	>99	S32
20	$Pd_{50}Au_{50}$/C	60	6	0.1 MPa H_2	HMF	>99	DMF	>99	S32
21	$PdAu_4$/GC800	150	4	1 MPa H_2	HMF	86.8	DMF	81.9	S33
22	Pd/C	45	10 min	3.5 equiv. PMHS	CMF	100	DMF	96	This work
23	Pd/C	25	30 min	3.5 equiv. PMHS	CMF	94	DMF	87	This work

HMF: 5-hydroxymethylfurfural; DMF: 2,5-dimethylfuran; DTHF: 2,5-dimethyltetrahydrofuran

Table S5 Product distribution after heating CMF in *n*-butanol at 80 ºC for different reaction time



Entry	Time (min)	CMF conv. (%)	Product yield (%)		
					
1	15	96	40	54	1.5
2	30	98	36	60	2
3	60	>99	12	83	4
4	120	>99	2	92	5

Reaction conditions: 0.5 mmol CMF, 2 mL *n*-butanol, 80 ºC. **CMF:** 5-chloromethylfurfural, **BMF:** 5-butoxymethylfurfural, **CMFDBA:** 5-chloromethylfurfural dibutyl acetal, **BMFDBA:** 5-butoxymethylfurfural dibutyl acetal.

Table S6 Composition of raw materials (%) [a]

Material	Water content	Cellulose	Hemicellulose	Lignin	Soluble sugars	Ash	Others
Filter paper	1.8	55.9	21.4	7.1	5.4	2.9	5.5
Waste paper	3.5	57.1	13.8	5.6	8.7	3.2	6.1
Corn stover	2.3	33.9	23.8	15.8	12.4	4.3	7.5
Wheat straw	1.5	35.4	18.5	18.4	6.8	8.2	11.2

[a] The analytical methods were supplied in the experimental details.

Catalytic conversion of cellulosic biomass to HMF/CMF

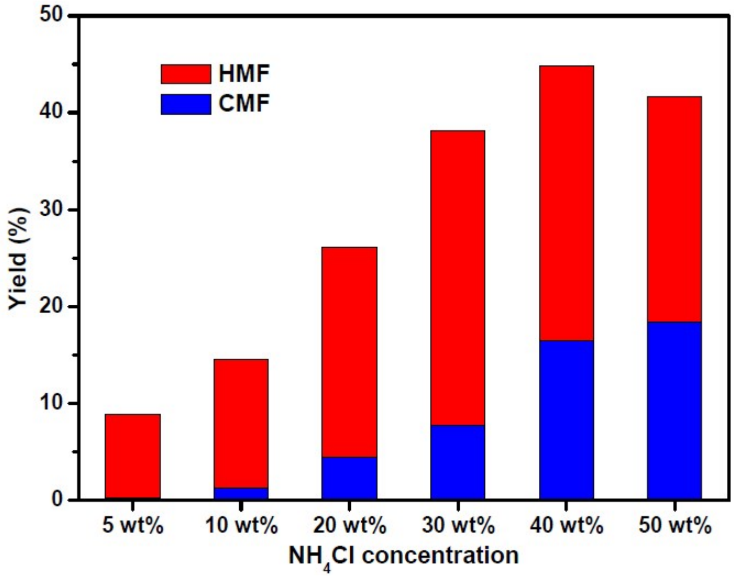


Figure S1 Effect of NH_4Cl concentration on the conversion of cellulose to HMF and CMF. Reaction conditions: 5 wt% cellulose, 1 mL NH_4Cl aqueous solution, 3 mL cyclohexane, 120 ºC, 2 h.

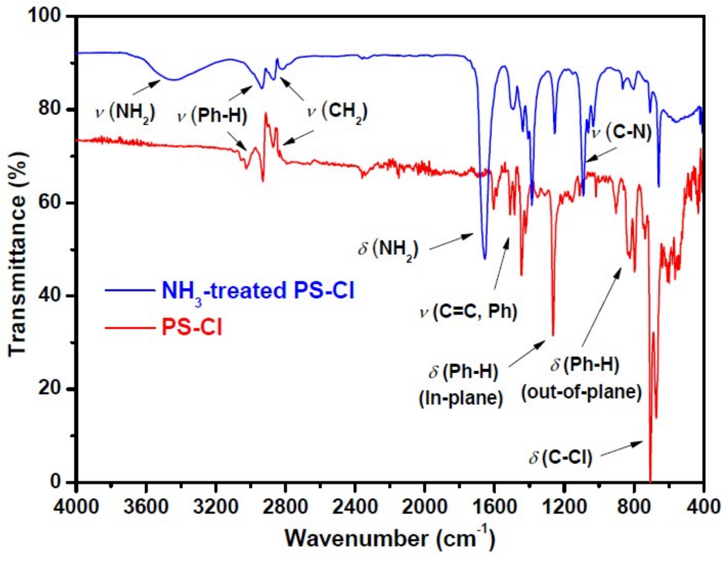


Figure S2 FT-IR spectra of PS-Cl and NH_3-treated PS-Cl.

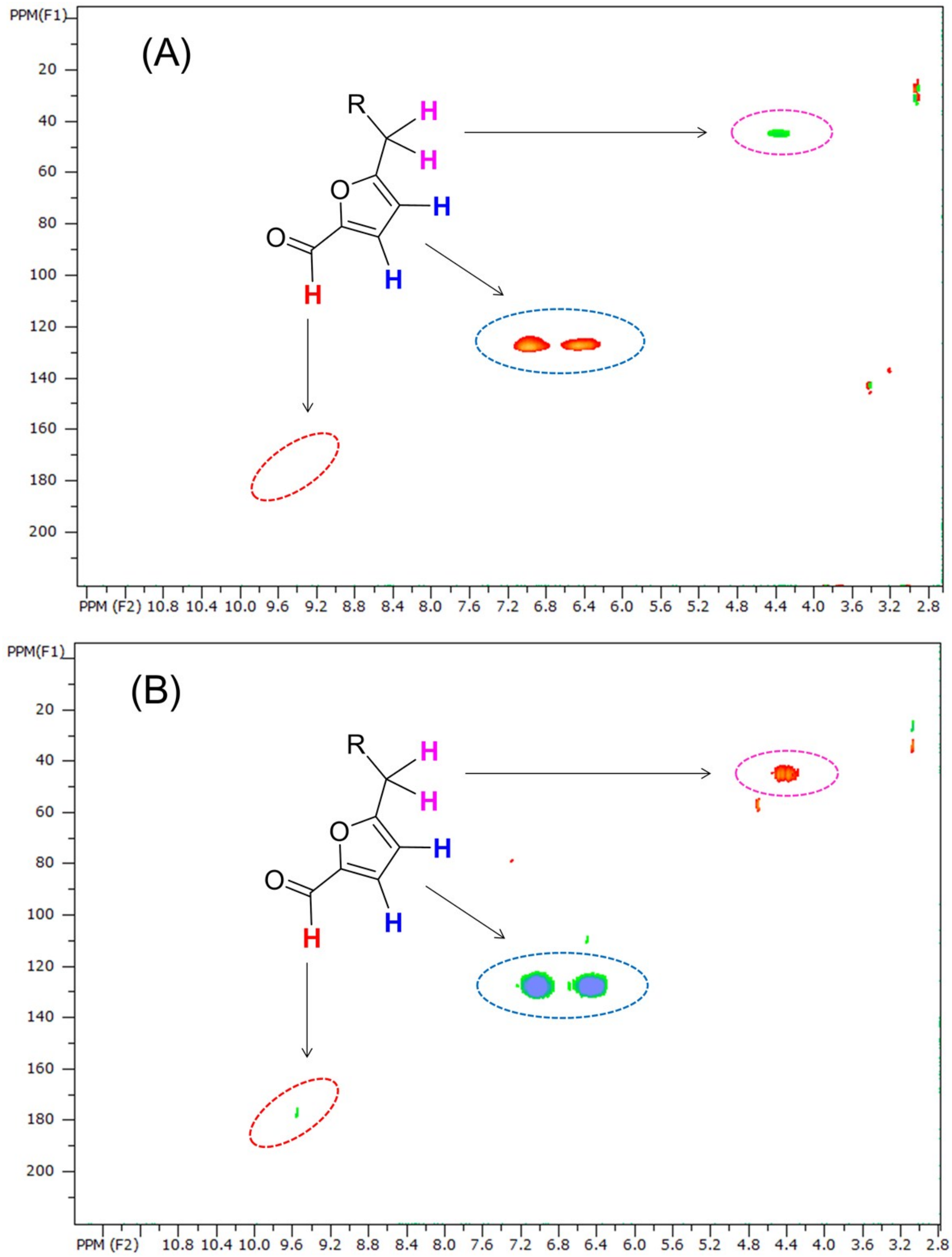
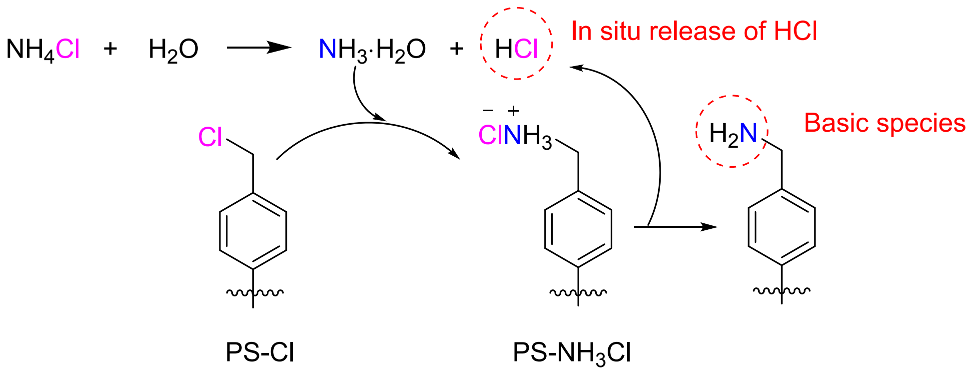


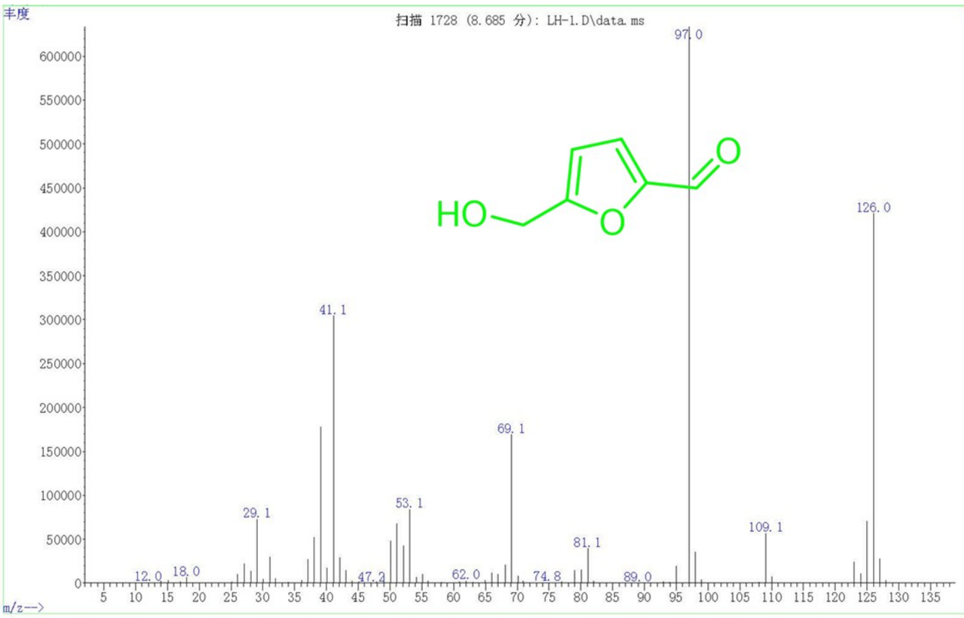
Figure S3 2D HSQC NMR spectra of the reaction mixture in the CD_3Cl phase: (A) 1 h, (B) 2 h; R = OH, Cl. Reaction conditions: 5 wt% cellulose, 1 mL 40wt% NH_4Cl aqueous (D_2O) solution, 0.1 g PS-NH_3Cl, 3 mL CD_3Cl, 120 ºC

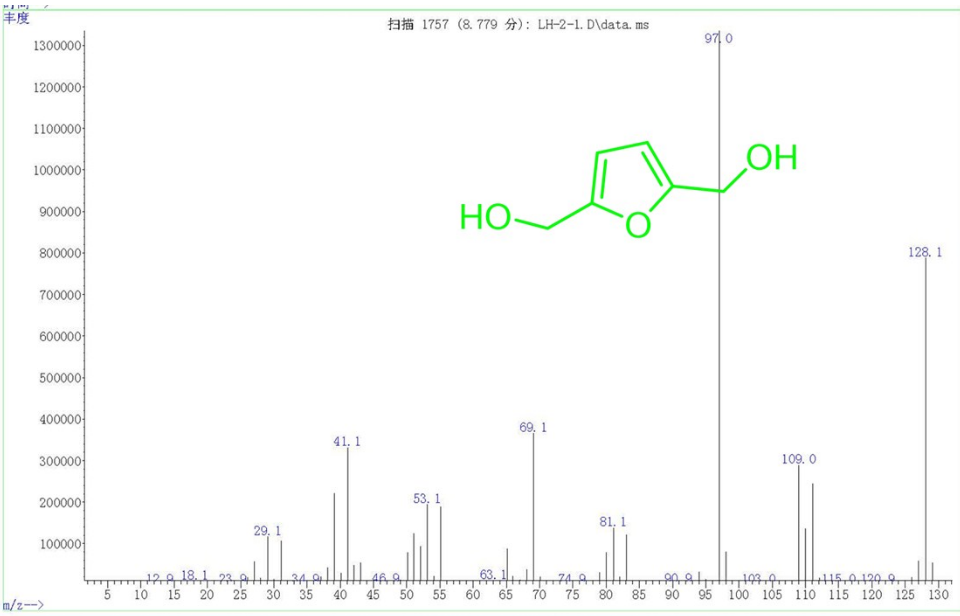
The near absence of characteristic peak of -CHO at 9.5 ppm (^{1}H NMR) and 177.4 ppm (^{13}C NMR) in 2D HSQC NMR spectra (Figure S3), which proves the substantial quantity of deuterium at C-1 position of HMF, indicating the occurrence of glucose-to-fructose isomerization [S34,S35].

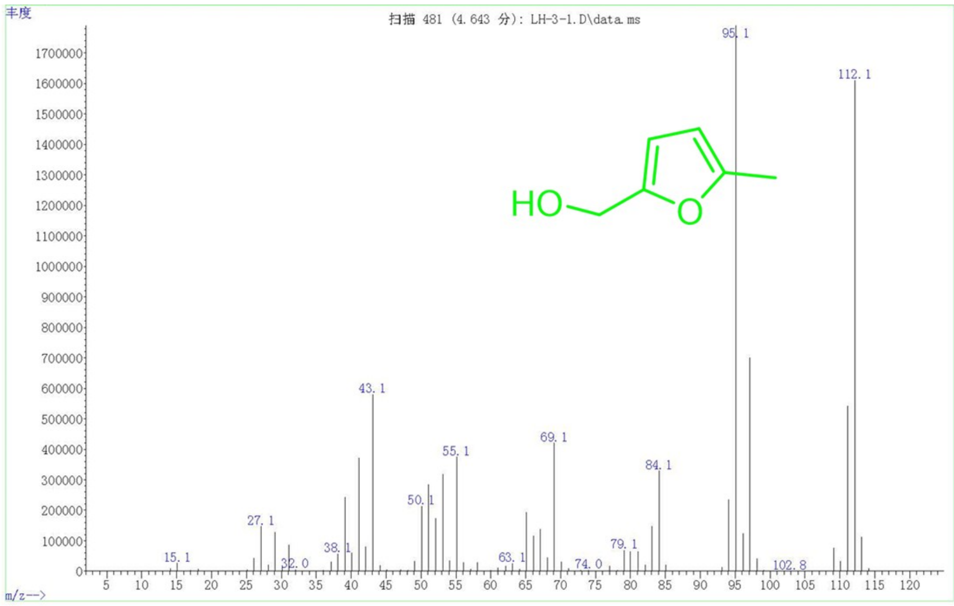


Scheme S1 Schematic illustration of HCl release and basic site (-NH_2) formation assisted by PS-Cl and PS-NH_3Cl

Product identification for the reaction starting from HMF







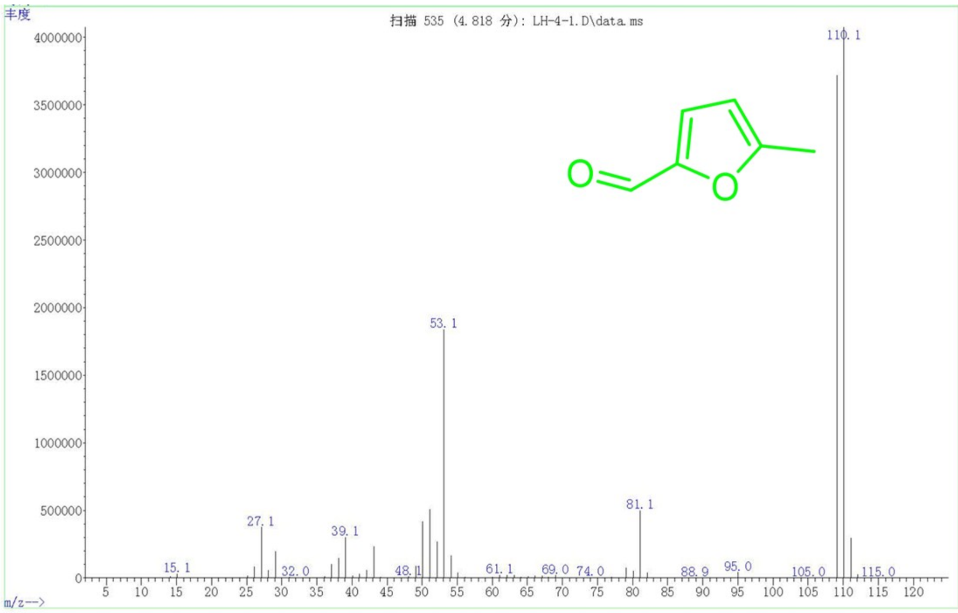


Figure S4 Representative MS spectra for the reactant and dominant compounds detected in the reaction mixture of HMF conversion; Reaction conditions: 0.5 mmol HMF, 2 mL *n*-butanol, 0.5 mol% Pd, 3.5 equiv. PMHS (1.75 mmol H^-), 25 ºC, 60 min.

Control experiments

Obtained products of the reaction mixtures are identified by GC and MS spectra, which are further cross-checked with NMR.

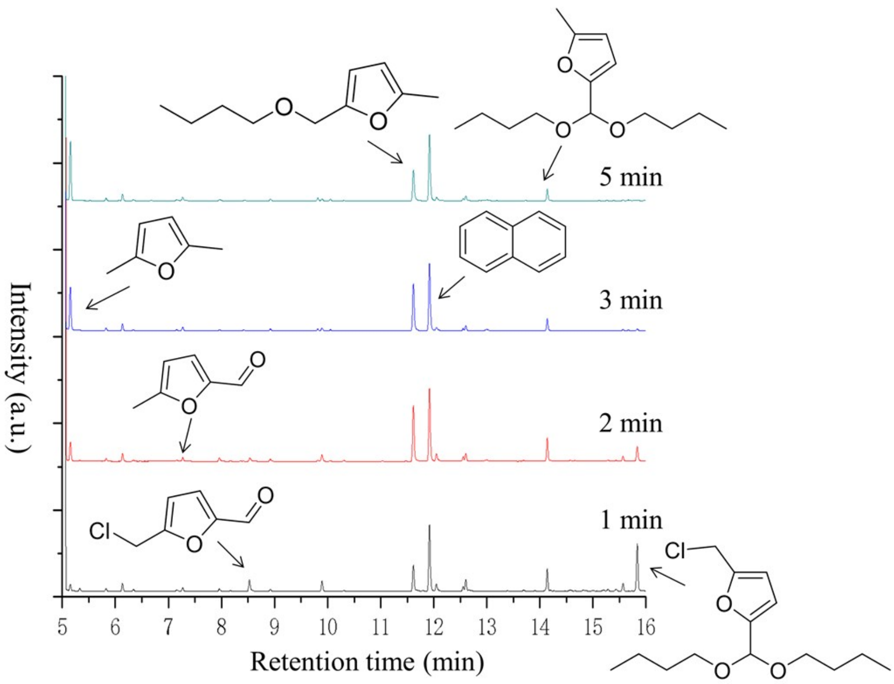
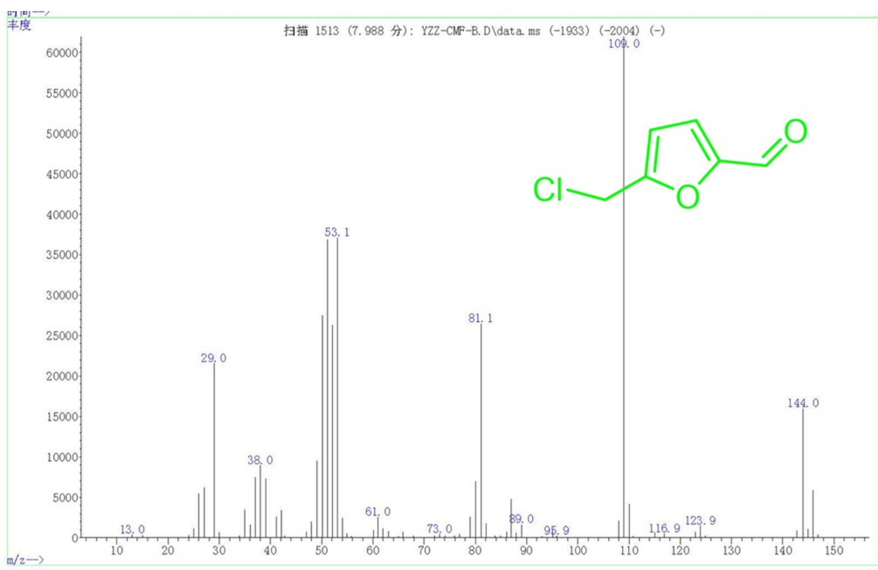
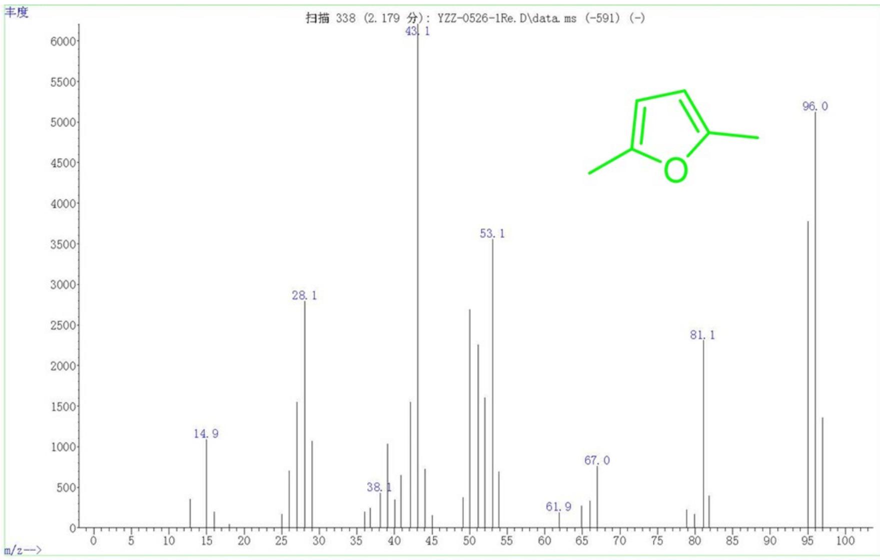


Figure S5 GC spectra for the reaction mixture starting from CMF over Pd/C at 45 ºC after variable reaction times (1-5 min); Reaction conditions: 0.5 mmol CMF, 2 mL *n*-butanol, 0.5 mol% Pd, 3.5 equiv. PMHS (1.75 mmol H^-), 45 ºC.

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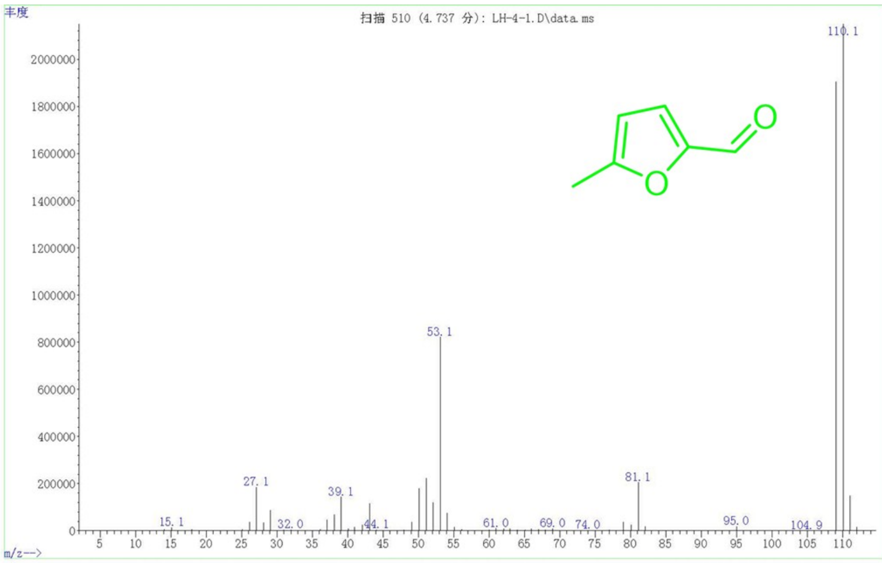
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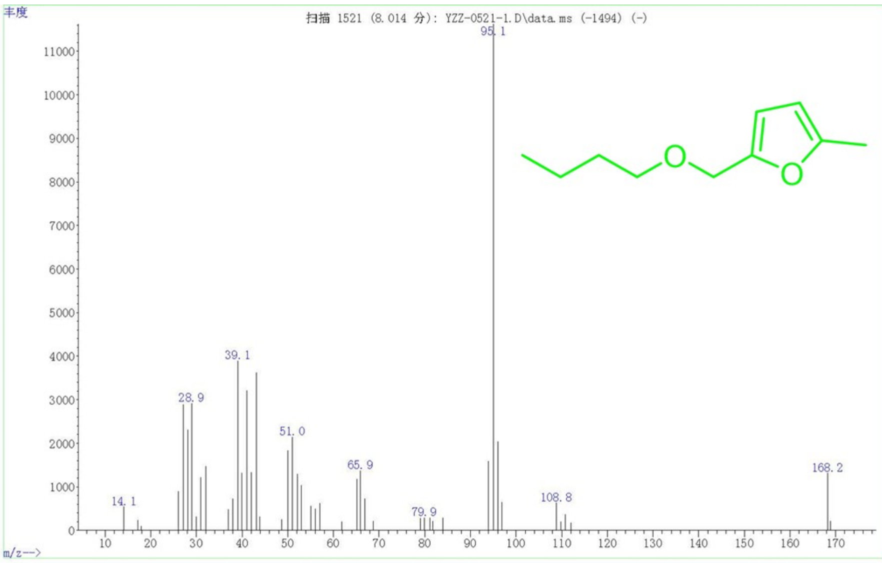
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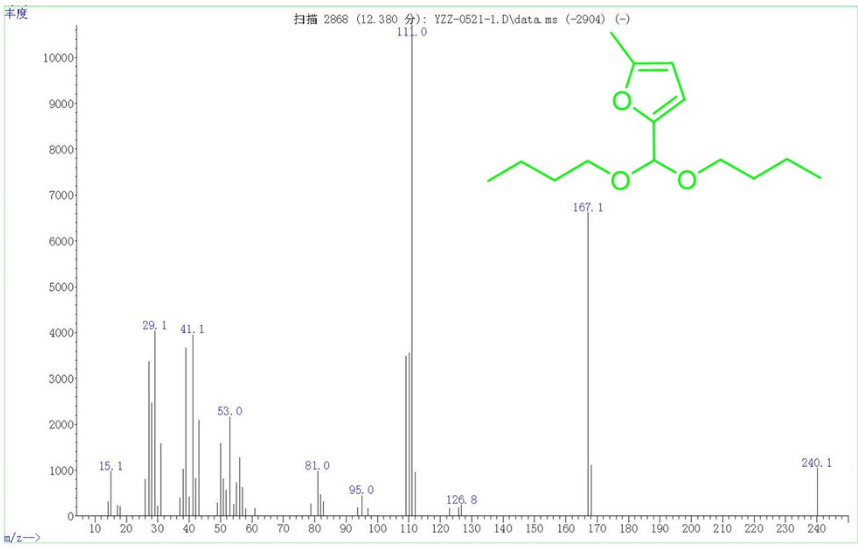


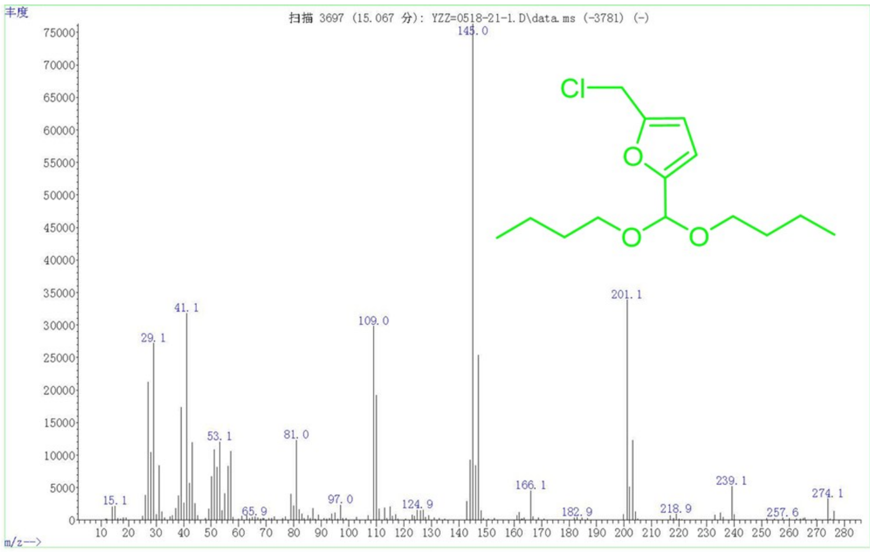


Figure S6 Representative MS spectra of the reactant and dominant products in the reaction mixture listed in Figure S5.

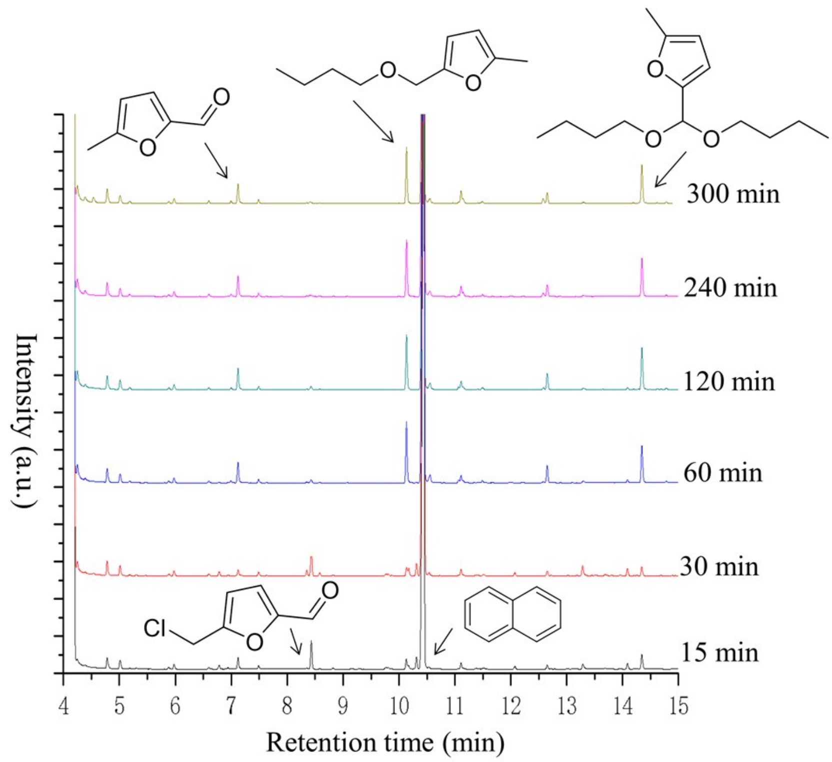


Figure S7 GC spectra for the reaction mixture starting from CMF at 0 ºC in variable reaction times; Reaction conditions: 0.5 mmol CMF, 2 mL *n*-butanol, 0.5 mol% Pd, 3.5 equiv. PMHS (1.75 mmol H^-), 0 ºC. Other unmarked peaks are attributed to alkoxysilanes.

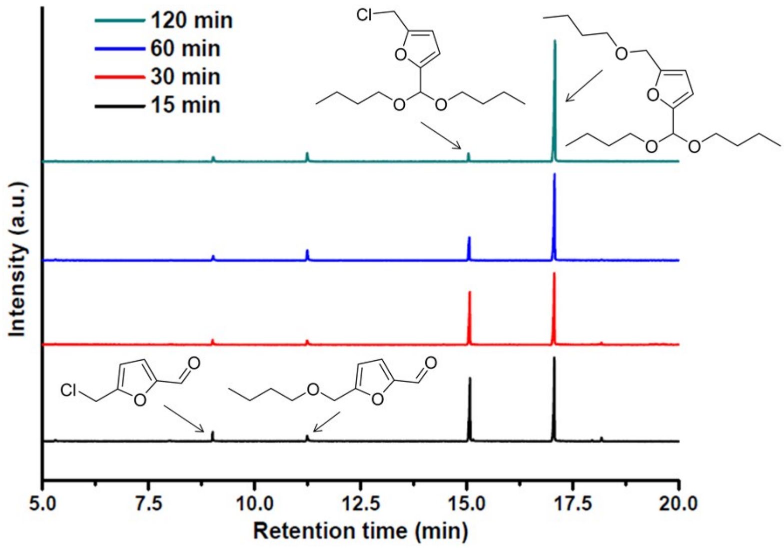
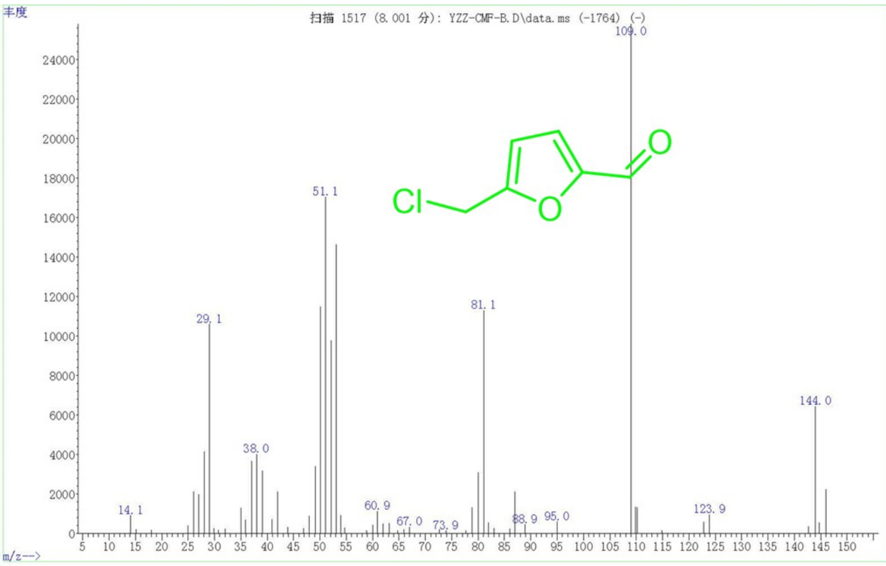


Figure S8 GC spectra for the reaction mixture of CMF and *n*-butanol without a catalyst at 80 ºC after variable reaction times; Reaction conditions: 0.5 mmol CMF, 2 mL *n*-butanol, 80 ºC.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95.0
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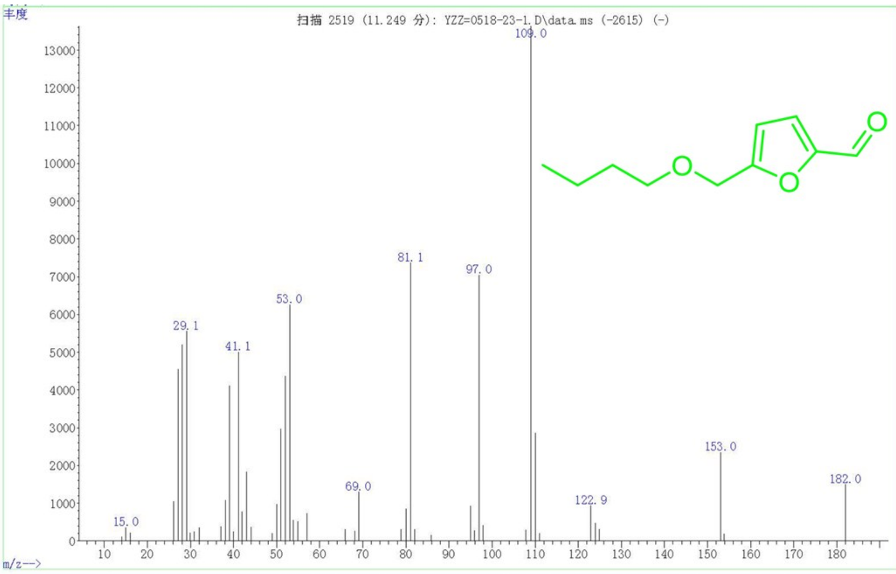
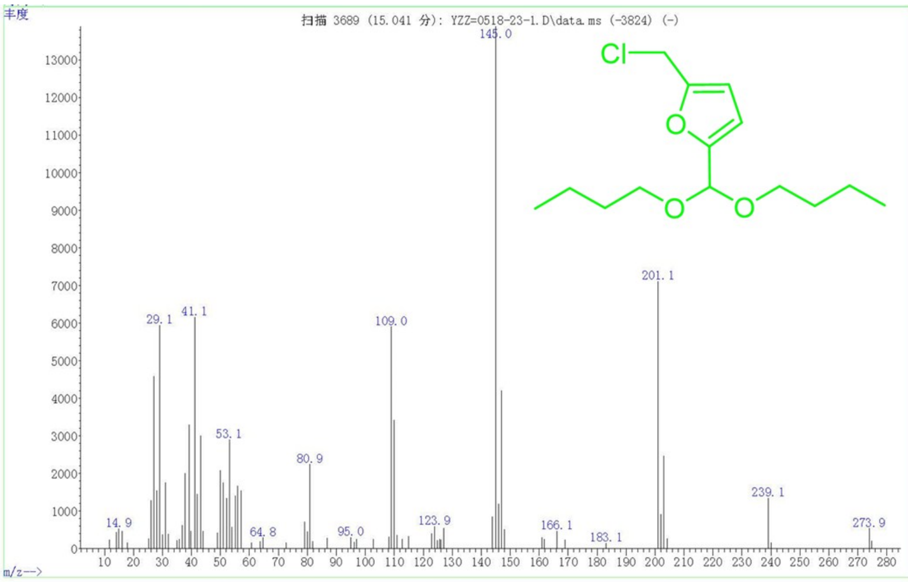
Cl
O
O
m/z-->


丰度
扫描 2519 (11.249 分): YZZ=0518-23-1.D\data.ms (-2615) (-)
109.0
81.1
97.0
53.0
29.1
41.1
153.0
182.0
69.0
122.9
15.0
O
O
O
m/z-->


丰度
扫描 3689 (15.041 分): YZZ=0518-23-1.D\data.ms (-3824) (-)
145.0
201.1
29.1
41.1
109.0
53.1
80.9
239.1
14.9
64.8
95.0
123.9
166.1
183.1
273.9
Cl
O
O
O
m/z-->

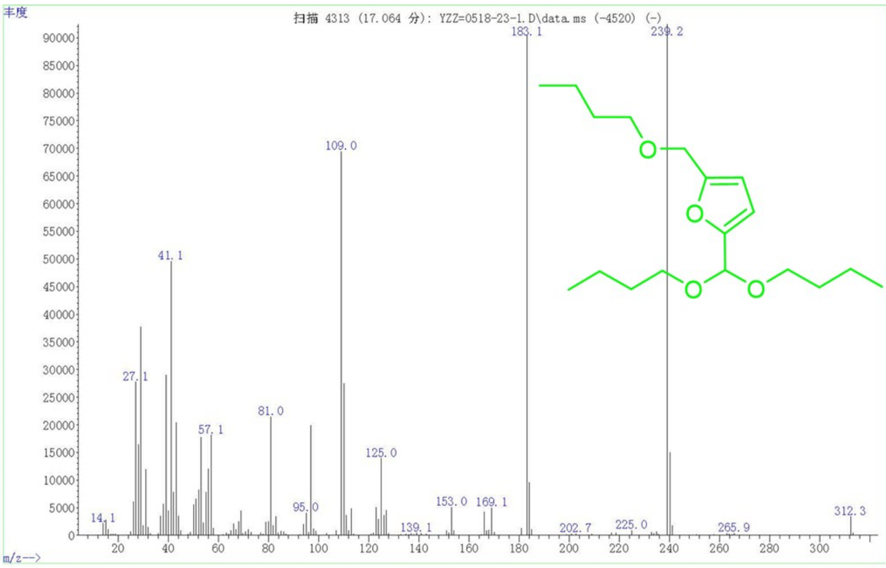
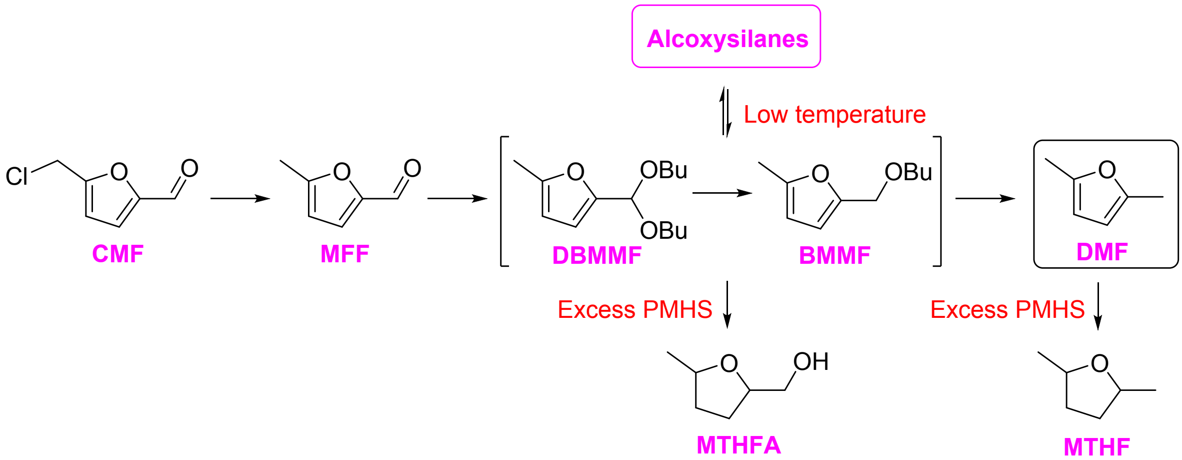


Figure S9 Representative MS spectra of the reactant and dominant products in the reaction mixture listed in Figure S8.



Scheme S2 Schematic illustration of CMF conversion at low temperatures or using excess/less PMHS; **CMF:** 5-chloromethylfurfural, **DMF:** 2,5-dimethylfuran, **MTHFA:** 5-methyl tetrahydrofurfuryl alcohol, **MTHF:** 5-methyltetrahydrofuran, **MFF:** 5-methylfurfural, **DBMMF:** 2-dibutoxymethyl-5-methylfuran, **BMMF:** 2-butoxymethyl-5-methylfuran.

As collected in Scheme S2, low temperatures are favorable for the formation of alkoxysilanes, while excess PHMS leads to the generation of MTHFA and MTHF.

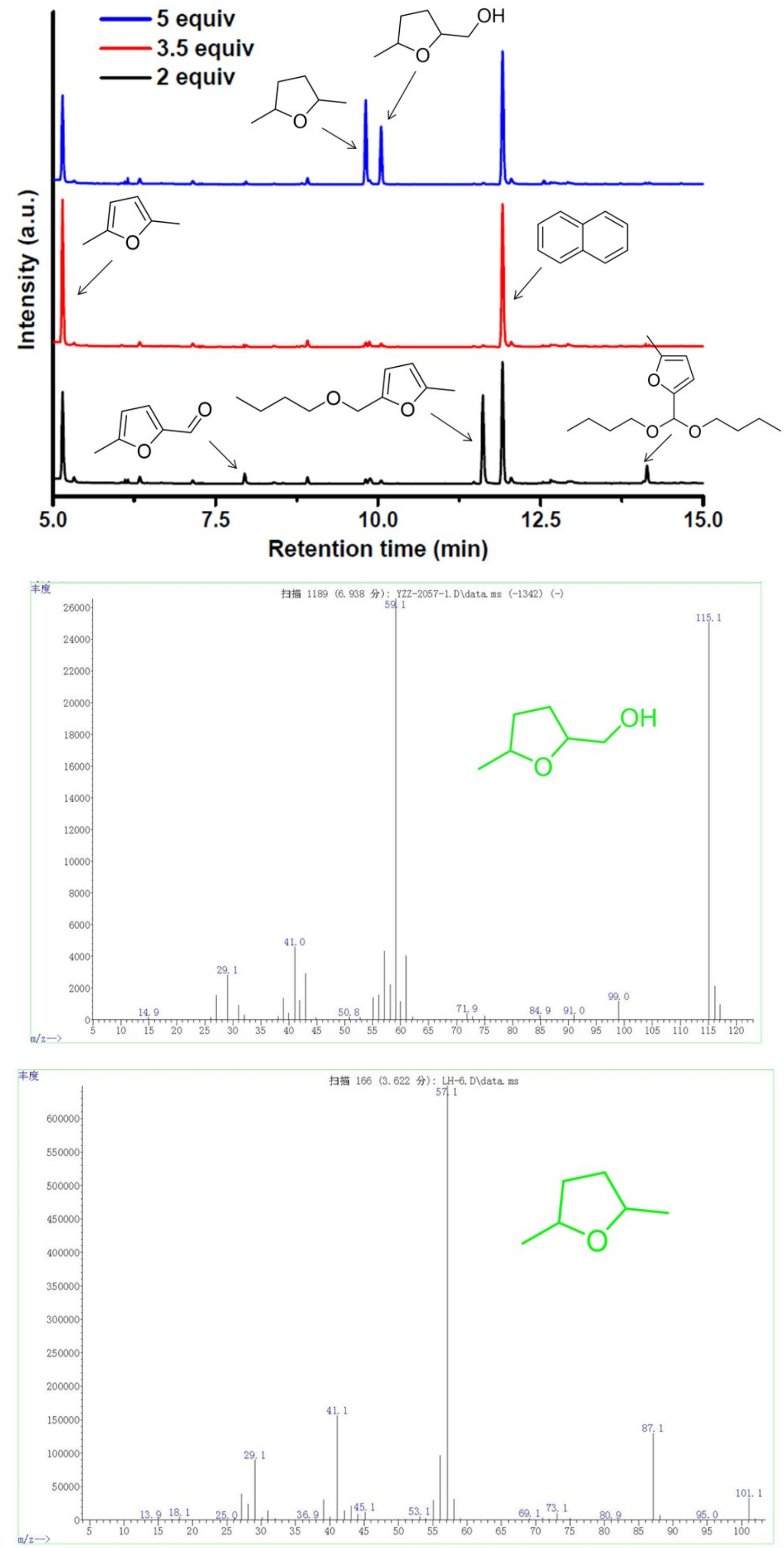
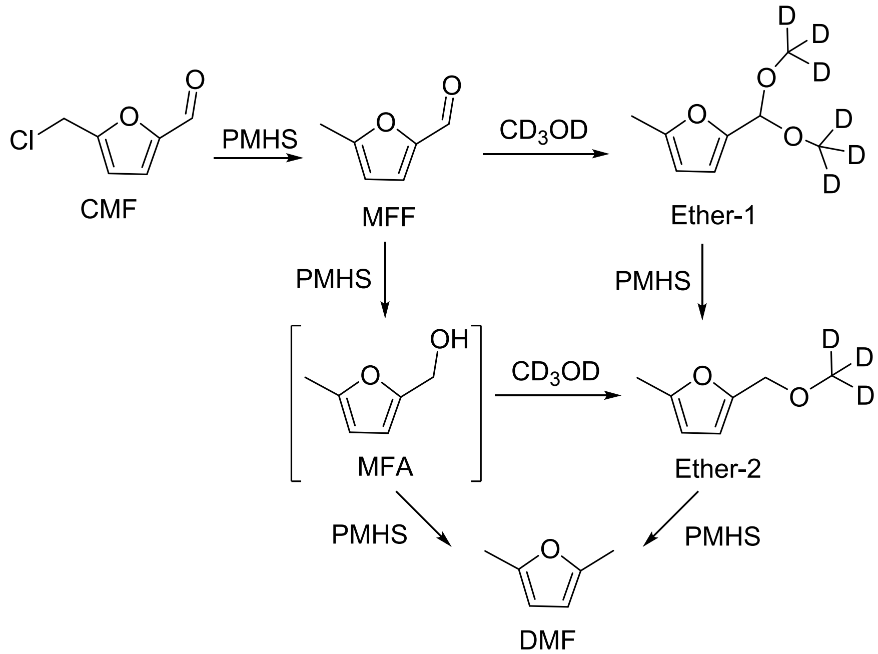


Figure S10 GC-MS spectra for the reaction mixture starting from CMF with different dosages of PMHS relative to CMF; Reaction conditions: 0.5 mmol CMF, 2 mL *n*-butanol, 0.5 mol% Pd, 45 ºC, 10 min.

Identification of reaction pathways



Scheme S3 Schematic illustration of CMF-to-DMF conversion in CD_3OD with PMHS catalyzed Pd/C.

Furanic acetal (derived from one mole of MFF with two mole of alcohol) and ether (derived from one mole of MFA with one mole of alcohol) can be confirmed by ^1H-^{13}C HSQC NMR to be the key intermediates toward DMF from CMF (Figure S11), and their structures are identified by GC-MS (Figure S12).

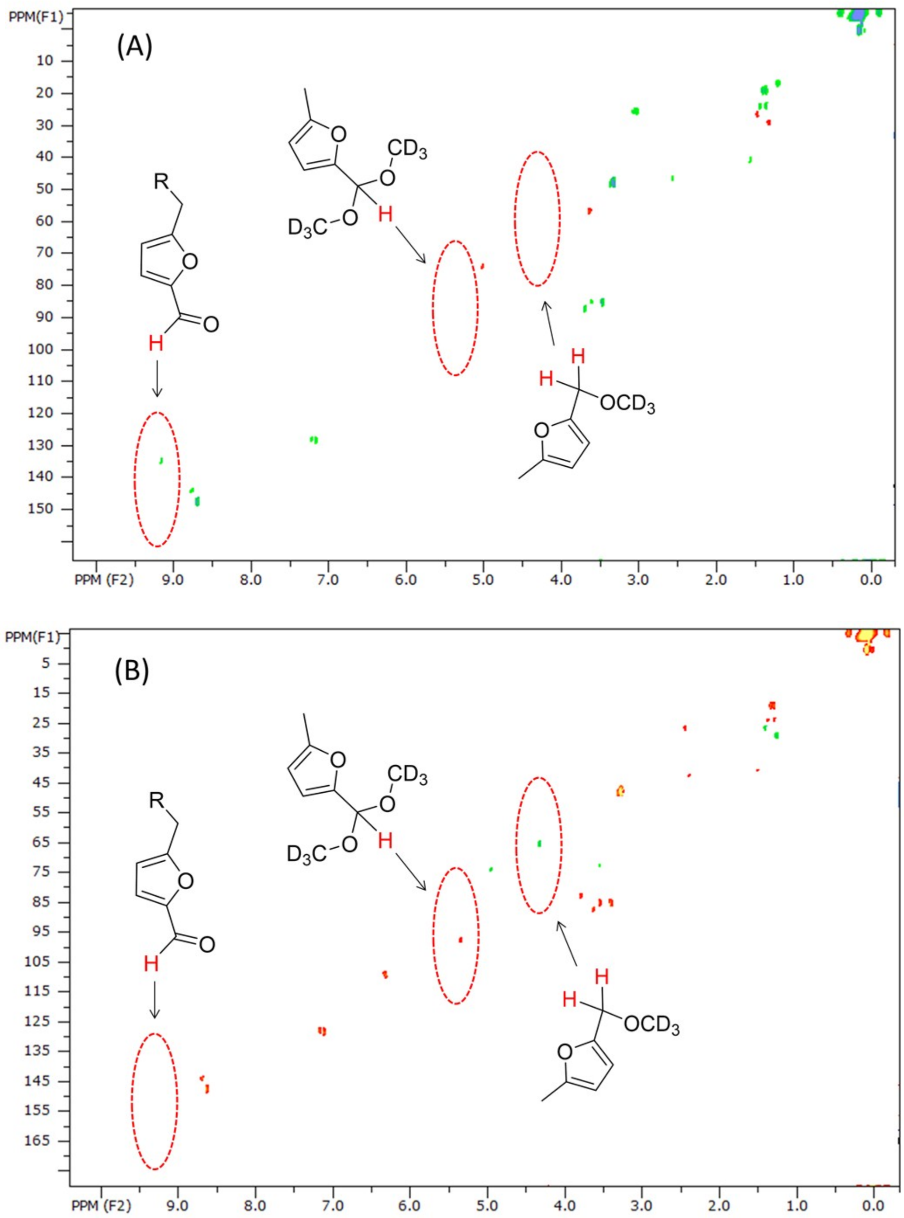


Figure S11 ^{1}H-^{13}C HSQC NMR spectra of the reaction mixture starting from CMF over Pd/C after (A) 5 min and (B) 30 min (R = H, Cl); Reaction conditions: 0.5 mmol CMF, 2 mL CD_3OD, 0.5 mol% Pd, 3.5 equiv. PMHS (1.75 mmol H^{-}), 25 ºC.

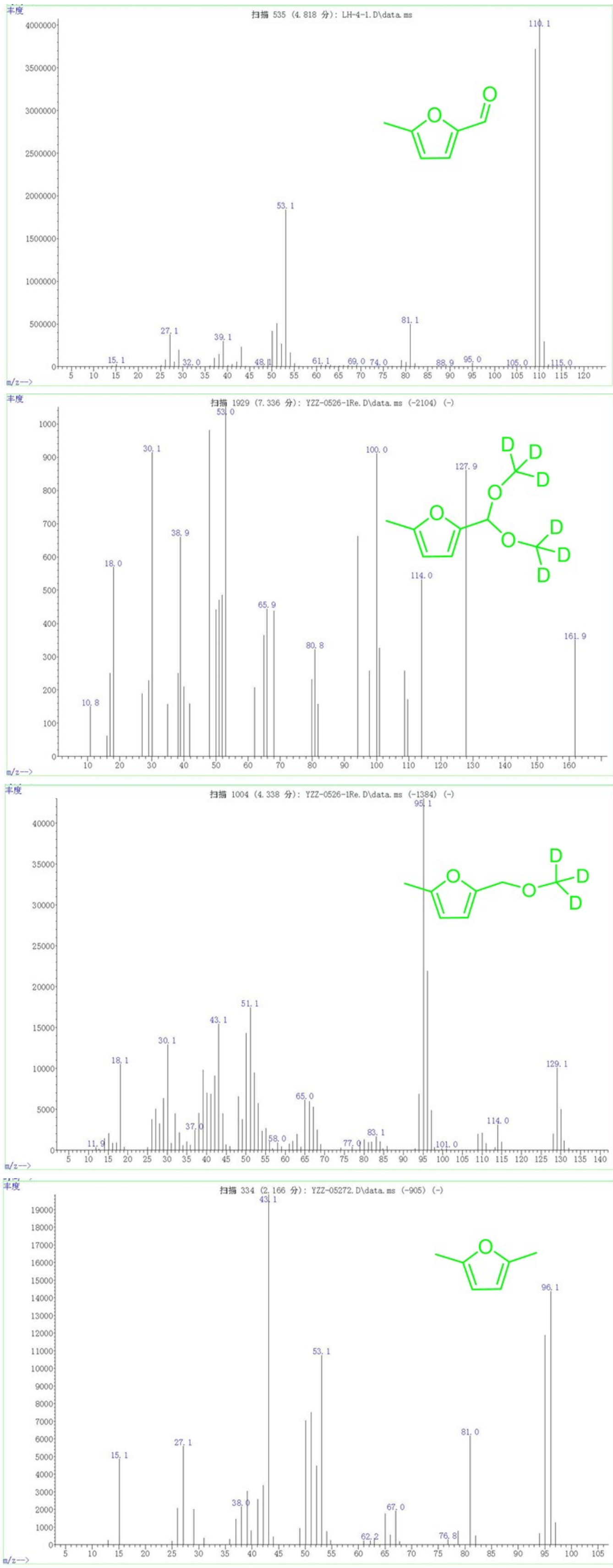


Figure S12 Representative MS spectra for the products formed in the reaction mixtures listed in Figure S11.

Isotope labeling study

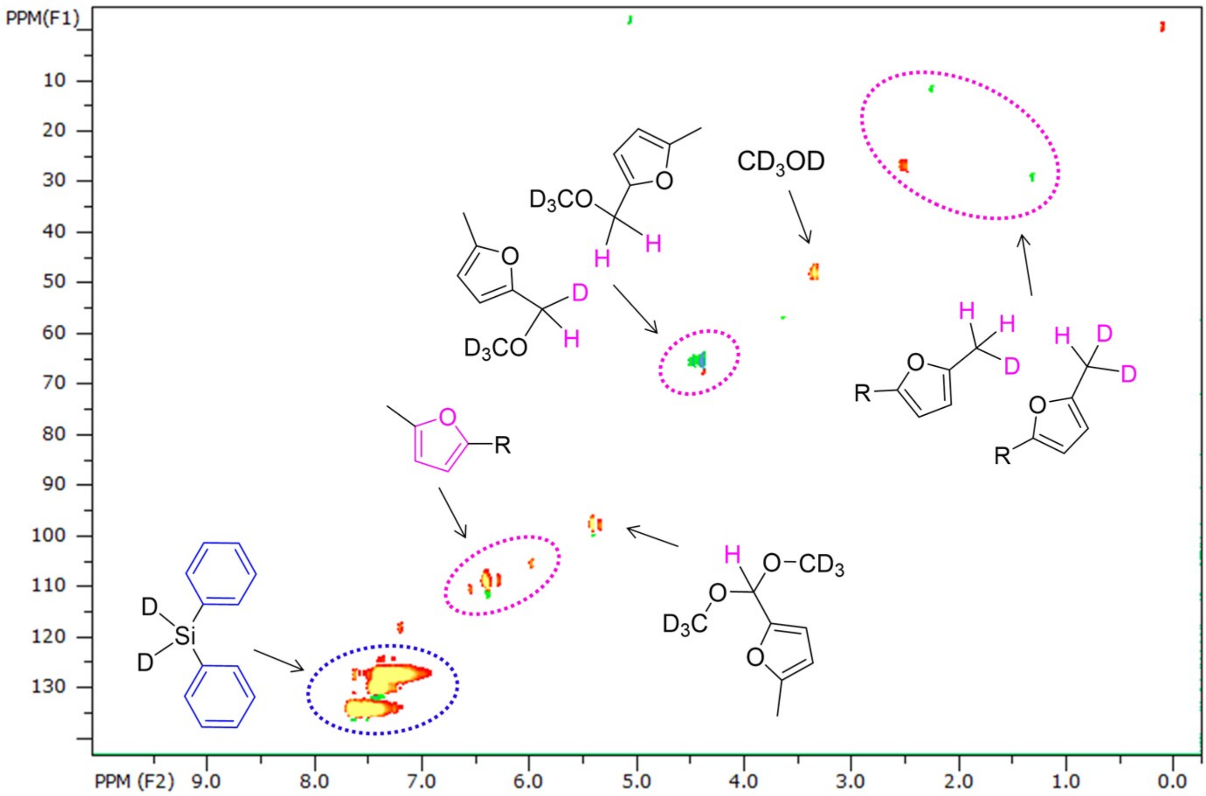


Figure S13 ^1H-^{13}C HSQC NMR spectrum of the reaction mixture starting from CMF over Pd/C; R = CH_3, CHO. Reaction conditions: 0.5 mmol CMF, 2 mL CD_3OD, 0.5 mol% Pd, 3.5 equiv. diphenylsilane-d_2 (1.75 mmol D^-), 25 ºC, 30 min.

As recorded with ^1H-^{13}C HSQC NMR spectrum (Figure S13), the incorporation of deuterium into 2,5-positions of furanic compounds can be easily observed using diphenylsilane-d_2 together with CD_3OD. In contrast, no deuterium incorporation is detected as PMHS and CD_3OD were used for the HDO reaction (Figure S11). These results clearly indicate that the hydrosilane is the H-donor rather than the used alcoholic solvent.

Identification of Pd(111) crystal plane

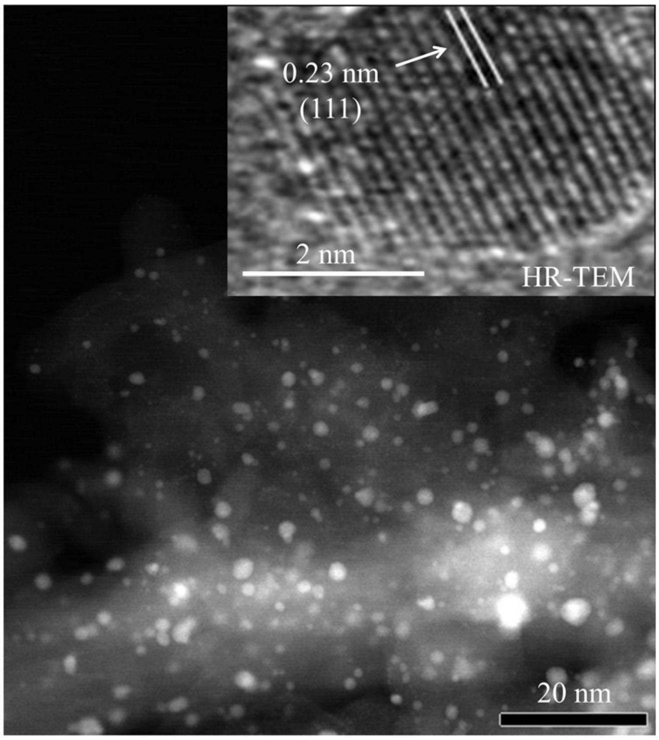


Figure S14 HR-TEM and HAADF-STEM images of the Pd/C catalyst

The dominant crystal plane on the commercial Pd/C catalyst was observed to be Pd(111) by HR-TEM, which was thus adopted for quantum-chemical calculations.

Catalyst recycling study

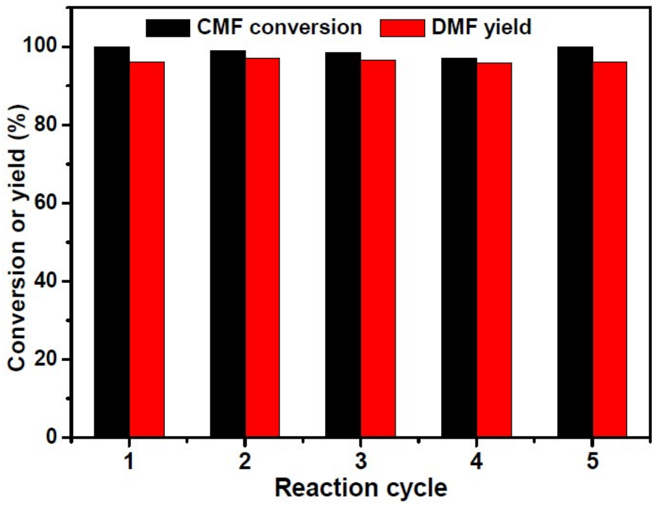


Figure S15 Reusability of Pd/C for conversion of CMF to DMF; Reaction conditions: 0.5 mmol CMF, 2 mL *n*-butanol, 0.5 mol% Pd, 3.5 equiv. PMHS (1.75 mmol H^{-}), 45 ºC, 10 min.

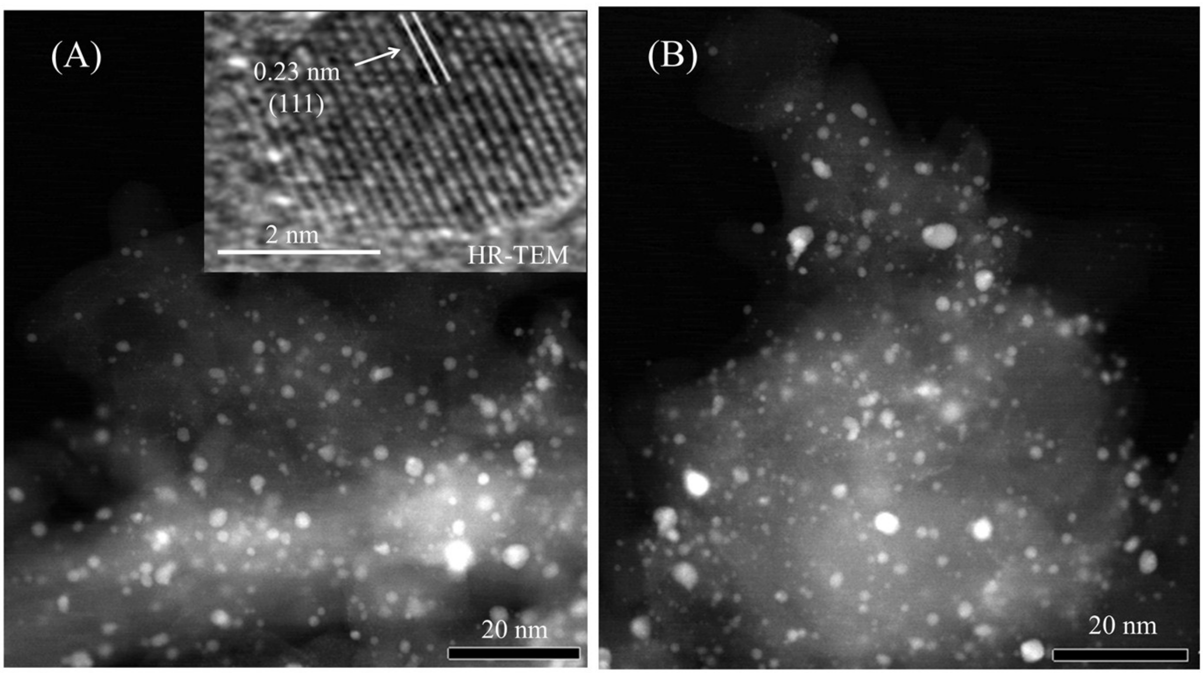


Figure S16 HR-TEM and HAADF-STEM images of (A) fresh and (B) reused Pd/C

The average particle size of Pd particles on Pd/C was estimated to be increased from 3.5 nm to 4.2 nm after five consecutive recycles, based on the STEM images in Figure S16, which can be ascribed to the slight aggregation of the metal particles during the reaction.

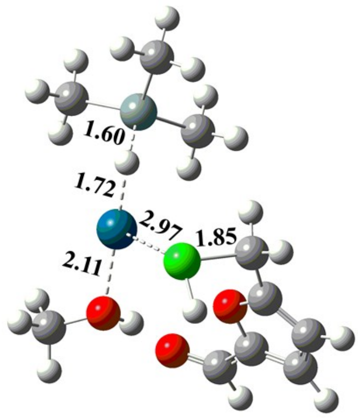
Computational Information:

Optimized geometries of reaction intermediates and transition states:

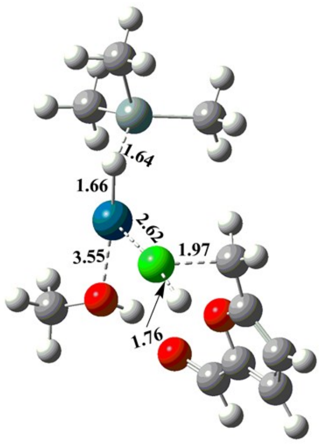
CMF as starting material

CMF→MFF

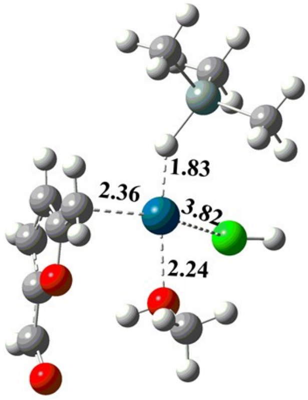
IS:



TS:

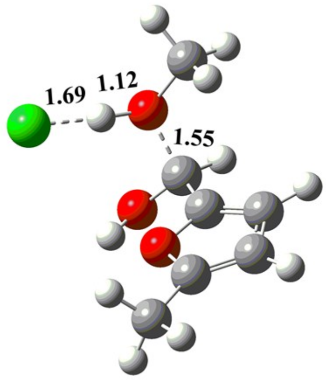


FS:

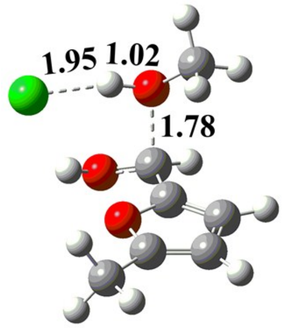


MFF→Hemiacetal

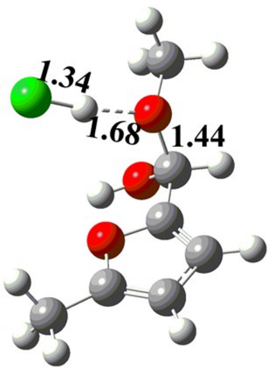
IS:



TS:

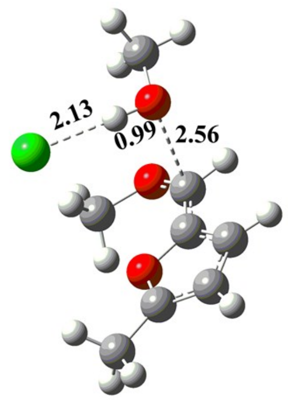


FS:



Hemiacetal→Ether-1

IS:



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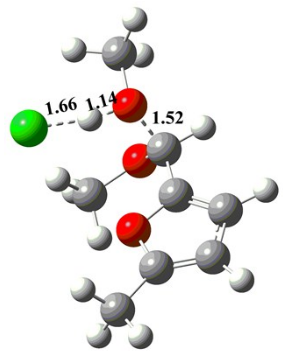
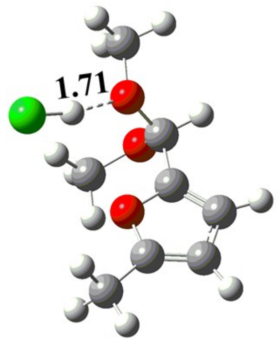
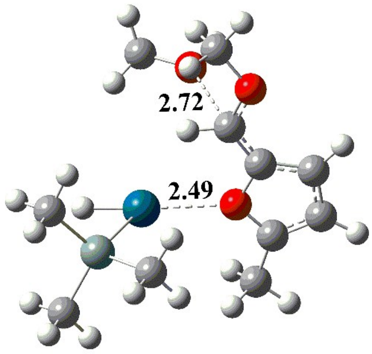


FS:

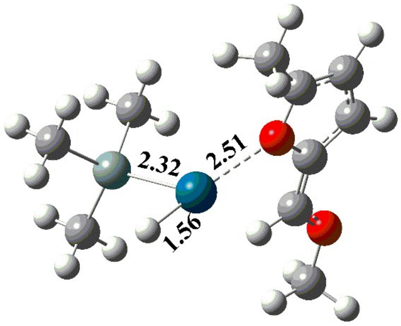


Ether-1 thermal decomposition



Ether-1→Ether-2

IS：



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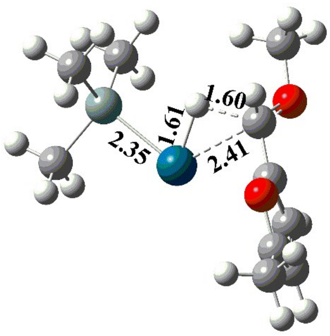

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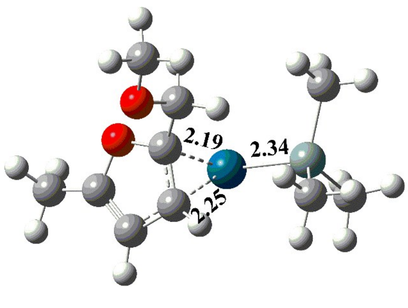
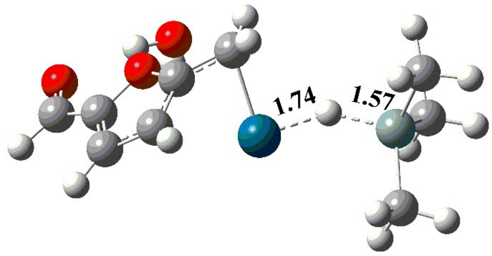


****

HMF as starting material

HMF→MFF:
IS:



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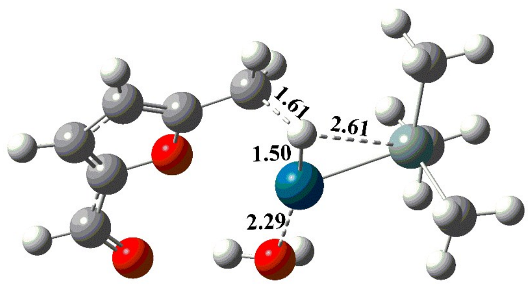
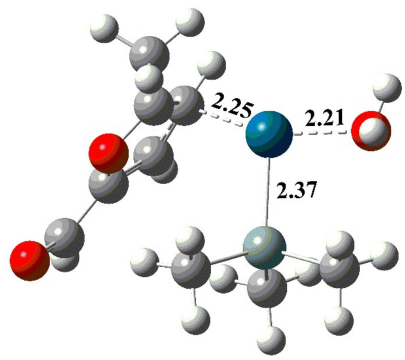
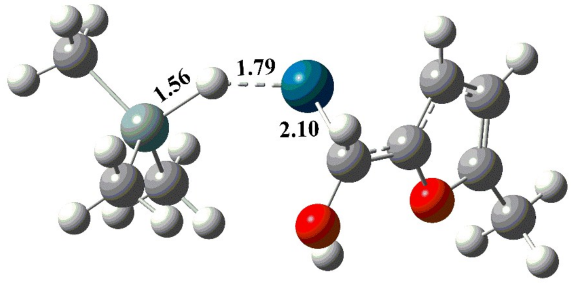


FS:



MFF→MFA:

IS:



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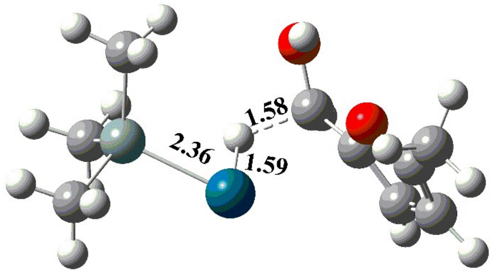
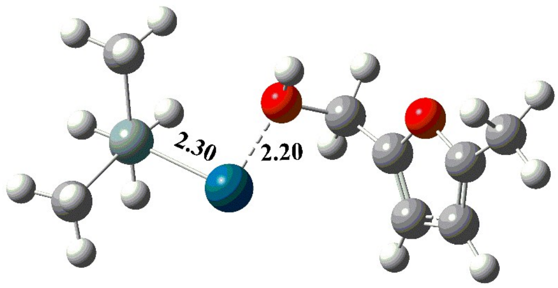


FS:



Structural coordinates of reaction intermediates and transition states:

CMF as starting material:

CMF→MFF

IS:

Si	3.10500900	-0.53421800	-0.82630200
H	2.16432700	-0.47486500	0.47045800
C	2.01582600	-0.66679900	-2.35159100
H	1.34162400	0.18963000	-2.44961200
H	2.65024900	-0.69230300	-3.24667800
H	1.41487000	-1.58042300	-2.33758600
C	4.16832600	1.01243400	-0.77546300
H	3.57275200	1.91565000	-0.91490000
H	4.71291600	1.09614700	0.16539900
H	4.90389000	0.96758600	-1.58841800
C	4.03324400	-2.11758800	-0.43112900
H	4.61068400	-2.02740600	0.49212100
H	3.35312600	-2.96706200	-0.33579500
H	4.73301100	-2.33488900	-1.24883900
C	-2.30423000	-1.63833200	-0.20848700
C	-3.58428500	-1.98767800	-0.56603800
C	-4.15500600	-0.84008700	-1.16982100
C	-3.19202800	0.14790400	-1.11910200
O	-2.05603200	-0.34819600	-0.53740600
H	-4.04804100	-2.95053600	-0.41531200
H	-5.14974000	-0.73610800	-1.57441300
C	-1.19357300	-2.40894600	0.38869200
H	-0.32643400	-2.47019200	-0.26577900
H	-1.52265100	-3.40790500	0.67197800
C	-3.20187100	1.53753200	-1.48926200
H	-4.08762400	1.87070000	-2.05427500
O	-2.30445600	2.34079600	-1.21117300
Pd	0.88528300	0.63670300	0.63493300
O	-0.72530700	1.97473000	0.95718100
H	-1.25518800	2.01735900	0.11458500
C	-0.38763900	3.31963200	1.35728900
H	-1.30504800	3.91355600	1.39966100
H	0.05511600	3.26055900	2.35273700
H	0.31669400	3.77937400	0.65507300
Cl	-0.56409100	-1.61316400	1.93176800
H	-1.76261789	-1.58907575	2.40826884

TS:

Si	-3.06327100	-0.32506800	0.74301200
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C	-2.21921600	-1.19792400	2.18695600
H	-1.34389700	-0.64752300	2.54706300
H	-2.93008500	-1.28678600	3.01918800
H	-1.90582300	-2.21212200	1.91398500
C	-3.57123400	1.44757600	1.14895300
H	-2.72716300	2.05589900	1.49023200
H	-4.02280500	1.94023400	0.28097800
H	-4.32074800	1.42709000	1.95205500
C	-4.56814500	-1.31708300	0.17436300
H	-5.05813700	-0.84274900	-0.68333400
H	-4.29160100	-2.33780400	-0.11286700
H	-5.29993100	-1.38169000	0.98971600
C	2.27601400	-1.65025400	0.22360700
C	3.57318200	-2.11567400	0.21432300
C	4.38561200	-1.02921200	0.62728500
C	3.53296200	0.03445600	0.83061800
O	2.24542600	-0.34562900	0.59980000
H	3.89102200	-3.11514400	-0.04652000
H	5.46042200	-1.01812500	0.74086500
C	0.99755900	-2.27306400	-0.06053600
H	0.19344800	-2.01112400	0.62193700
H	1.05254000	-3.33629900	-0.27505300
C	3.74401500	1.43545600	1.14522800
H	4.76995500	1.71294000	1.43402800
O	2.84729800	2.27357000	1.08400100
Pd	-0.97619200	0.49633400	-0.59034800
O	0.75055400	1.85020100	-0.77355400
H	1.37382300	1.84404200	-0.01314200
C	0.49877200	3.21897800	-1.14030600
H	1.44868000	3.73283800	-1.31924700
H	-0.08323400	3.20273200	-2.06270200
H	-0.06428300	3.74517700	-0.36194300
Cl	0.24378700	-1.53225600	-1.73034400
H	1.15054700	-2.73546900	-2.63557600

FS:

Si	3.36420100	-0.45604800	0.28346100
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C	3.93362500	-2.24285300	0.14163900
H	3.62804900	-2.68215600	-0.81444200
H	5.02772300	-2.29524500	0.20201000

H	3.52155200	-2.85702400	0.94985300
C	3.91633600	0.61082300	-1.16421800
H	3.60930400	0.17516700	-2.12158600
H	3.50016300	1.62224700	-1.09634900
H	5.01005300	0.69759900	-1.17013000
C	3.74139900	0.31873100	1.95483500
H	3.30365800	1.31952600	2.03495900
H	3.34962600	-0.29409600	2.77409800
H	4.82605300	0.41211400	2.09032900
C	-1.38571500	-1.67924600	0.26988500
C	-1.26977500	-1.66522100	1.69752600
C	-2.41690300	-1.06599400	2.19922700
C	-3.20818700	-0.70630100	1.10615600
O	-2.59554700	-1.08679800	-0.06329700
H	-0.43491700	-2.07349800	2.24927500
H	-2.66713000	-0.89164600	3.23673600
C	-0.58535800	-2.20200100	-0.73606200
H	-0.97265300	-2.28547800	-1.74563600
H	0.26248000	-2.81818100	-0.46094600
C	-4.45188000	0.01880400	1.00992800
H	-4.91941100	0.25958200	1.98139900
O	-4.95627600	0.35739500	-0.05984900
Pd	0.32132100	-0.02148200	-0.67921100
O	-1.43396000	0.96931100	-1.66646500
H	-2.22969800	0.47752400	-1.38981500
C	-1.43840200	1.11046800	-3.10267400
H	-2.31173700	1.69334000	-3.40921600
H	-0.52894300	1.65068200	-3.36668000
H	-1.44701100	0.13386900	-3.59670300
Cl	0.33999600	3.20054800	1.36711200
H	0.87493100	4.36763800	1.50723000

MFF→Hemiacetal

IS:

C	-2.31410000	0.44575400	0.13313200
C	-2.61503100	-0.75834300	0.70661100
C	-1.51216300	-1.63220600	0.44743200
C	-0.60799800	-0.90018600	-0.26526600
O	-1.08363100	0.37089900	-0.46463500
H	-3.52112600	-0.99575700	1.24590600
H	-1.41057500	-2.66779900	0.74175300
C	0.70925900	-1.20240500	-0.86254200

O	0.96833000	-0.57930000	-2.04959600
H	0.88115700	-2.27449100	-0.95352600
C	-3.02831800	1.74683800	0.03562600
H	-2.44409200	2.55531800	0.49057100
H	-3.21536600	2.02034100	-1.00959700
H	-3.98868300	1.68026500	0.55254100
H	0.52720400	0.29009900	-2.05439900
O	1.86957800	-0.77870500	0.07037400
H	1.93382200	0.33231900	0.17591500
C	1.94450800	-1.43121200	1.36741700
H	1.02053200	-1.27770300	1.92820500
H	2.12605400	-2.49254900	1.19472400
H	2.79124400	-0.97794500	1.88111900
Cl	2.10639200	2.00560700	0.35195200

TS:

C	2.29926900	0.47122900	-0.13833800
C	2.67257600	-0.83406100	-0.34255600
C	1.57808600	-1.64304900	0.06810200
C	0.60196900	-0.77904800	0.49932400
O	1.03781300	0.51549500	0.37328800
H	3.62245300	-1.16902100	-0.73401000
H	1.51764200	-2.72272300	0.05963300
C	-0.71512000	-1.01179800	1.05346900
O	-1.27680300	-0.10966300	1.85734500
H	-0.89099800	-2.02991600	1.38727200
C	2.98396200	1.77322900	-0.35316100
H	2.41372500	2.40851000	-1.04071600
H	3.09456300	2.32102100	0.59001300
H	3.97685600	1.60459900	-0.77606200
H	-1.19431900	0.79345400	1.46201300
O	-1.89617700	-1.04658400	-0.27709500
H	-2.05467300	-0.04876700	-0.45428000
C	-1.54237600	-1.72915400	-1.50101900
H	-0.61983400	-1.32723800	-1.92656900
H	-1.42221000	-2.78564800	-1.25950200
H	-2.37279300	-1.59760700	-2.19699100
Cl	-2.13289800	1.89383900	-0.37964800

FS:

C	2.35825500	0.23746100	0.04712300
C	2.66639000	-0.73816900	-0.85636100
C	1.50614500	-1.57307200	-0.98311600
C	0.56718400	-1.04810900	-0.15003700

O	1.07002000	0.05781700	0.48822800
H	3.61109700	-0.85191300	-1.36982800
H	1.39062600	-2.44661600	-1.60999200
C	-0.82979700	-1.42737700	0.20628300
O	-1.05139800	-1.46697500	1.59042800
H	-1.05163000	-2.43136400	-0.16946500
C	3.10600500	1.39262600	0.61429900
H	2.60520100	2.34239200	0.39064500
H	3.19652700	1.31589200	1.70468800
H	4.11184500	1.42588200	0.18786900
H	-0.66190500	-0.66311400	1.97735100
H	-1.51537800	1.15563800	-0.29266600
Cl	-1.48704800	2.49423700	-0.25175200
O	-1.72195400	-0.50567300	-0.44489500
C	-3.10863700	-0.86099400	-0.32499600
H	-3.42003600	-0.88177200	0.72294000
H	-3.67160400	-0.10049200	-0.86827100
H	-3.28154700	-1.84211300	-0.78273800

Hemiacetal→Ether-1

IS:

C	2.54380800	0.22563200	-0.16512900
C	2.63296800	-0.62306100	-1.26067800
C	1.51442500	-1.46132600	-1.20986000
C	0.78616400	-1.09011300	-0.07772800
O	1.43808400	-0.04931100	0.55126500
H	3.42165500	-0.61776600	-1.99867200
H	1.24488300	-2.24785100	-1.90136300
O	-1.08542200	-1.36550400	1.45552500
C	3.40974800	1.32462700	0.32345400
H	2.84710800	2.26458900	0.36039000
H	3.76628100	1.11158400	1.33784700
H	4.26903600	1.44880500	-0.33758500
C	-0.41521900	-1.62608300	0.38161100
H	-0.81797900	-2.46387000	-0.17552300
O	-2.01546900	-0.43793000	-1.22661200
C	-3.37272900	-0.67342800	-0.87817200
H	-3.53282100	-0.65175600	0.20981700
H	-4.04455400	0.06321900	-1.34075800
H	-3.64347800	-1.66750300	-1.24712800
C	-0.75575200	-0.24595000	2.33271900
H	-1.50871000	-0.28818900	3.11682700

H	0.24366800	-0.38804500	2.74428900
H	-0.82933500	0.68137600	1.75920000
H	-1.80339500	0.49244800	-0.95768400
Cl	-1.43355100	2.47665600	-0.26402300

TS:

C	2.50166000	0.27707400	-0.02048600
C	2.83528300	-0.72588800	-0.88755100
C	1.66048200	-1.51918900	-1.07341900
C	0.68748700	-0.94887800	-0.30418900
O	1.18828300	0.14967500	0.34454200
H	3.80513800	-0.87875000	-1.33965500
H	1.55166700	-2.39702000	-1.69553100
O	-1.20774100	-1.58934700	1.14933500
C	3.25243300	1.41633300	0.57333800
H	2.78056700	2.37456800	0.32603200
H	3.29406700	1.34039100	1.66661900
H	4.27551100	1.42500300	0.18939800
C	-0.72779100	-1.34729300	-0.11234100
H	-0.91254600	-2.25049100	-0.69409900
O	-1.59649700	-0.31355600	-0.81462400
C	-3.02785800	-0.60901500	-0.87438100
H	-3.55793800	0.15064400	-0.29932500
H	-3.32170200	-0.58180800	-1.92346600
H	-3.19902200	-1.59366900	-0.44321300
C	-0.97450500	-0.61358600	2.18355800
H	-1.59941000	-0.92822500	3.01999200
H	0.07599200	-0.61051600	2.48409800
H	-1.26875200	0.38829000	1.85704800
H	-1.44493400	0.78833500	-0.56225700
Cl	-1.45847900	2.42480700	-0.28981400

FS:

C	2.42392000	0.29247500	0.00737600
C	2.86473800	-0.76975300	-0.72825700
C	1.72255800	-1.59594300	-0.98904500
C	0.66068000	-0.98386600	-0.39316400
O	1.07391000	0.17122500	0.22107100
H	3.88259200	-0.94081100	-1.05040400
H	1.69579000	-2.52105200	-1.54862500
O	-1.21125700	-1.89424600	0.92314700
C	3.08885300	1.49024800	0.58992800
H	2.65506000	2.41881000	0.19951500
H	2.98857400	1.51362200	1.68202800

H	4.15371700	1.47788800	0.34361800
C	-0.78098800	-1.36918300	-0.30923600
H	-0.95303600	-2.18654900	-1.01879900
O	-1.56620400	-0.24333500	-0.71012300
C	-2.95431300	-0.54426500	-0.91636600
H	-3.42798100	0.38508800	-1.23642100
H	-3.05987000	-1.30022900	-1.70361600
H	-3.42157600	-0.90416400	0.00428000
C	-1.02878400	-1.06606200	2.07516000
H	-1.53886600	-1.57705800	2.89411600
H	0.03202100	-0.95122000	2.32300100
H	-1.47476400	-0.07538000	1.93447500
H	-1.31510300	1.40640700	-0.32558400
Cl	-1.32753700	2.72138800	-0.11698400

Ether-1 thermal decomposition

Si	2.62861800	-0.46109300	0.66563300
H	2.02248400	-1.10090700	-1.51497600
C	2.79641000	-2.26134900	1.24951000
H	3.19321800	-2.90168900	0.45347100
H	3.48039300	-2.32166700	2.10707200
H	1.82983900	-2.67457100	1.56036600
C	4.33809600	0.16475300	0.12109700
H	4.74590300	-0.44551200	-0.69276900
H	4.29156800	1.20249900	-0.22936600
H	5.04396600	0.12499100	0.96208500
C	2.05541800	0.59771000	2.14684100
H	1.98581100	1.65929200	1.88332200
H	1.07763200	0.27927400	2.52551100
H	2.78118200	0.50244600	2.96709900
C	-0.96093000	2.69325400	-0.26311400
C	-2.19827200	3.13334500	0.19036800
C	-2.85821400	2.02463300	0.72620700
C	-1.99816200	0.93533700	0.58694400
O	-0.82841100	1.36951700	-0.02627000
H	-2.56127100	4.14872500	0.12839100
H	-3.84325400	1.99028900	1.17042000
C	0.16501200	3.39006900	-0.92308400
H	1.07692800	3.29895300	-0.32151800
H	-0.07432600	4.44660400	-1.05421700
C	-2.08422900	-0.40960600	0.91541100
Pd	0.96269000	-0.12499700	-0.90977900
H	0.37083200	2.94286700	-1.90286000

H	-1.24879900	-1.07548100	0.70662700
O	-3.14219300	-0.86132000	1.50016900
O	-2.53306200	-1.76233800	-1.40626900
C	-3.21611200	-2.29557500	1.76411400
H	-3.20215400	-2.81145800	0.80384300
H	-2.37425400	-2.58919300	2.39340600
H	-4.15969200	-2.44068000	2.28453400
C	-1.87263000	-2.81265900	-2.11893400
H	-1.87488800	-2.62953300	-3.20084600
H	-0.83745000	-2.82433400	-1.76938400
H	-2.32831300	-3.79097300	-1.91911600
H	-3.44874300	-1.71112800	-1.72333300

Ether-1→Ether-2

IS:

Si	-2.35787000	0.47442900	0.59525100
H	-2.21907700	0.30967500	-1.76887400
C	-2.68561900	2.34643500	0.60061000
H	-3.26789500	2.65151200	-0.27628500
H	-3.25237500	2.62811800	1.49875900
H	-1.75197700	2.92104200	0.59950100
C	-4.02824300	-0.43083000	0.61434400
H	-4.64095400	-0.15299300	-0.25079500
H	-3.89658800	-1.51894400	0.59570900
H	-4.58875400	-0.17490800	1.52393400
C	-1.42482600	0.02849300	2.19920000
H	-1.25285900	-1.05050700	2.28519400
H	-0.45392700	0.53261500	2.26221100
H	-2.02311100	0.34255000	3.06637600
C	1.63412200	-2.18278300	0.25596600
C	2.94338300	-2.18221700	0.72822400
C	3.39419600	-0.86374200	0.68680700
C	2.34110700	-0.08958600	0.18985200
O	1.25984200	-0.92706900	-0.06673000
H	3.48843900	-3.05474900	1.05694400
H	4.36482500	-0.48473900	0.97518500
C	0.65248700	-3.26938700	0.04964000
H	-0.29955900	-3.02259700	0.53296800
H	1.03814000	-4.20551100	0.45650300
C	2.18700400	1.25932000	-0.08164800
Pd	-0.91776900	-0.21675900	-1.08424500
H	0.45343600	-3.40201500	-1.02119100

H	1.24240900	1.63328100	-0.48158300
O	3.16015700	2.07869700	0.13224100
C	2.99063600	3.49894400	-0.14652400
H	3.81021200	3.77978700	-0.80667600
H	2.02363700	3.67972700	-0.61837800
H	3.06806700	4.01665700	0.80935300

TS:

Si	-2.65582100	-0.57249200	0.19958700
H	-0.60758300	0.75662800	0.67005400
C	-3.69908700	0.87515800	-0.41770300
H	-3.45937200	1.13429800	-1.45448300
H	-4.76181400	0.60008100	-0.37518400
H	-3.56051800	1.76772200	0.20165600
C	-2.98736800	-2.13826100	-0.82037900
H	-2.82695100	-1.97577500	-1.89176800
H	-2.36929600	-2.98321500	-0.49811100
H	-4.04089400	-2.42056900	-0.67881900
C	-2.91656600	-0.87660400	2.04342400
H	-2.27335700	-1.68291900	2.41198500
H	-2.70703100	0.02445500	2.63002000
H	-3.96049400	-1.16507800	2.22642800
C	3.60429800	-0.75689600	0.24985000
C	3.54481100	-0.44208300	-1.08517900
C	2.45470700	0.45452700	-1.25275000
C	1.91259800	0.63986000	0.00435300
O	2.61373000	-0.10334700	0.92290500
H	4.20951800	-0.80938800	-1.85385100
H	2.12173900	0.92849200	-2.16533100
C	4.50116900	-1.62646700	1.05447200
H	5.00463100	-1.05147800	1.84050100
H	5.26051700	-2.07417900	0.40951200
C	0.82405300	1.45113700	0.52361700
Pd	-0.39047600	-0.41280800	-0.41397800
H	3.93774500	-2.43124200	1.54132300
H	0.81418700	1.54155600	1.61214600
O	0.57185700	2.57112200	-0.17478500
C	-0.42483600	3.44009200	0.38503900
H	-0.41536700	4.34240600	-0.22450800
H	-1.40622000	2.95624000	0.32826100
H	-0.18341700	3.68105600	1.42548700

FS:

Si	-2.39571100	0.27391800	-0.13564100

C	-2.37188000	1.14480900	-1.80509300
H	-2.18363600	0.44352900	-2.62469100
H	-3.35942800	1.59701400	-1.97032700
H	-1.63100200	1.94957400	-1.85503000
C	-3.58878500	-1.19760900	-0.10235200
H	-3.51645400	-1.79754900	-1.01454300
H	-3.43125900	-1.85319000	0.76294900
H	-4.61138100	-0.80096700	-0.02801600
C	-2.69074400	1.45956000	1.30198800
H	-2.64671000	0.93860000	2.26419800
H	-1.97059500	2.28333900	1.32001900
H	-3.69504200	1.89369300	1.19805700
C	2.64400500	-1.32205700	-0.21248300
C	1.84835900	-1.42364400	-1.31737800
C	0.88036200	-0.36311300	-1.23733600
C	1.15429700	0.33784000	-0.02918600
O	2.25611800	-0.26141100	0.56637000
H	1.93266000	-2.16490500	-2.09882300
H	0.27970500	0.00914300	-2.05597500
C	3.78705400	-2.12768600	0.28791300
H	4.66299800	-1.49296000	0.46291800
H	4.04832100	-2.89844300	-0.44031300
C	0.98466400	1.78376000	0.33244400
Pd	-0.51800200	-1.02174600	0.39159700
H	3.53518900	-2.61455400	1.23782900
H	0.96868100	1.89656000	1.42675300
O	2.07158900	2.49917300	-0.23007000
C	2.04791500	3.87513300	0.12269400
H	2.91561000	4.33861000	-0.35188800
H	1.13272500	4.36773900	-0.23763800
H	2.11540200	4.01094500	1.21217800
H	0.02910700	2.15523800	-0.05979800

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HMF as starting material:

HMF→MFF

IS:

Si	3.37221100	0.47868400	-0.09967700
H	1.81050100	0.46769800	0.09202300
C	3.68544100	2.29216100	-0.48467400
H	3.32594000	2.93813400	0.32343300

H	4.76212500	2.46599000	-0.60526400
H	3.18806200	2.59152500	-1.41364100
C	4.07277800	-0.07114000	1.55387600
H	3.70219000	0.55832300	2.37014800
H	3.81053900	-1.11182800	1.77269500
H	5.16713100	0.00598800	1.53782200
C	3.80944000	-0.66453000	-1.52578300
H	3.54467000	-1.70426100	-1.30483000
H	3.29867400	-0.36458600	-2.44741700
H	4.89000000	-0.62471000	-1.71321200
Pd	0.46669000	-0.59444200	-0.23393700
C	-1.44982800	-0.80804600	0.99461900
C	-1.64065800	-1.98586800	0.24429100
C	-2.82795400	-1.78204800	-0.51039100
C	-3.28048100	-0.52662400	-0.18385000
O	-2.44895400	0.07774400	0.71634400
H	-1.07487900	-2.90219300	0.34823100
H	-3.29930000	-2.47540300	-1.19223600
C	-0.26922000	-0.40718300	1.68466800
H	-0.23364800	0.59979400	2.09209000
C	-4.44102000	0.22254500	-0.65439300
H	-5.11440100	-0.34387800	-1.31883300
O	-4.66559400	1.38726700	-0.35466100
H	0.26441400	-1.16656000	2.25428400
O	-2.49084700	3.25015700	0.26075700
H	-2.62246800	3.78288600	-0.53829600
H	-3.20604000	2.58890900	0.20989400

TS:

Si	-2.78251100	-0.04311800	-0.22184800
H	-0.79849800	-1.43647400	0.76167600
C	-3.33515500	-1.77000400	-0.71577000
H	-3.26580500	-2.47510700	0.11872000
H	-4.38563800	-1.72076900	-1.03261400
H	-2.75417200	-2.16331500	-1.55659500
C	-3.64096500	0.60719000	1.32448200
H	-3.60100200	-0.11973400	2.14153800
H	-3.20380500	1.55009300	1.66930700
H	-4.69686600	0.79505800	1.08284300
C	-2.82836800	1.15958900	-1.67148500
H	-2.56137000	2.17828400	-1.37268500
H	-2.16436800	0.84340800	-2.48243900
H	-3.85412200	1.18457900	-2.06580600
Pd	-0.51516800	0.09665800	0.50250800

C	1.65899400	-1.47472600	-0.24242900
C	2.73869100	-2.21087500	0.19906300
C	3.85263500	-1.32988400	0.20729600
C	3.38336900	-0.09903200	-0.20157200
O	2.05542200	-0.19724000	-0.50029500
H	2.72646300	-3.25428000	0.48010600
H	4.86655900	-1.56046600	0.50403600
C	0.22940000	-1.73566100	-0.44730600
H	-0.13477200	-1.47925000	-1.44319500
C	3.91805100	1.24452700	-0.21233800
H	5.00717600	1.33484800	-0.07225700
O	3.20676700	2.24234400	-0.34105200
H	-0.03766800	-2.76586000	-0.21278600
O	0.29997700	2.21527400	0.17435200
H	-0.10360600	2.67662700	-0.57861900
H	1.25713700	2.13996700	-0.05440000

FS:

Si	0.90622600	1.54729200	-0.18499700
C	0.42426000	2.33577100	1.45934000
H	1.13392200	2.06558600	2.24843200
H	0.45210800	3.42793700	1.33911400
H	-0.58099000	2.05575600	1.78373700
C	2.62269700	2.12762100	-0.71586000
H	3.38458400	1.93780800	0.04440400
H	2.94208800	1.67537100	-1.66109100
H	2.56137700	3.21339800	-0.87576700
C	-0.30629500	1.87730000	-1.59135300
H	-0.02114800	1.32357700	-2.49207000
H	-1.34914200	1.65442900	-1.36170300
H	-0.23390600	2.94983200	-1.82308400
Pd	1.09679500	-0.78226600	0.22045600
C	-1.13996900	-1.57763800	-0.40542400
C	-0.87864000	-1.55465500	0.97935700
C	-1.78983700	-0.59147100	1.53878200
C	-2.50363300	-0.08085500	0.49343300
O	-2.11047600	-0.66958200	-0.68933300
H	-0.38046700	-2.34103700	1.53816300
H	-1.89399700	-0.32722900	2.58165800
C	-0.84096900	-2.57118100	-1.47926100
H	0.01119200	-3.19468500	-1.20014800
C	-3.52972400	0.95330600	0.44338600
H	-3.83684300	1.32820300	1.43757100
O	-4.01898400	1.38152400	-0.59045300

H	-1.71453100	-3.21886600	-1.62829600
O	3.30625800	-0.65580100	0.14434800
H	3.63419800	-1.51252800	0.47178700
H	3.61407500	-0.60234300	-0.77729000
H	-0.62395600	-2.07139900	-2.42734900

MFF→MFA

IS:

Si	2.94071400	-0.11904400	0.41371000
H	1.84793300	0.66263000	-0.37354800
C	3.43907300	-1.52128100	-0.73699400
H	3.82570100	-1.13513400	-1.68678800
H	4.22444700	-2.13168000	-0.27456400
H	2.58350700	-2.16996100	-0.95292800
C	4.29783000	1.16548100	0.64581600
H	4.63909400	1.56147000	-0.31696700
H	3.95081300	2.00444400	1.25925600
H	5.16031500	0.71268800	1.15064900
C	2.24954300	-0.73483600	2.05365800
H	1.88317100	0.09371900	2.66976100
H	1.42565700	-1.44030000	1.90008700
H	3.03561500	-1.25214000	2.61825300
C	-3.39456000	-0.17764600	0.71464900
C	-3.35416300	1.06359900	0.13617200
C	-2.35524800	1.02177200	-0.88046300
C	-1.83672900	-0.28220300	-0.84810000
O	-2.46624700	-1.00330200	0.13250900
H	-3.98446900	1.90258700	0.39258400
H	-2.15588400	1.76866700	-1.63793600
C	-4.21922500	-0.76965900	1.79655400
H	-4.77421600	-1.64087200	1.43030600
H	-4.93029200	-0.02994000	2.16976300
C	-0.65283000	-0.78827400	-1.47477500
H	-0.40900300	-0.46532600	-2.48456600
O	-0.19538900	-2.03324400	-1.21926400
Pd	0.06248300	0.80664000	-0.29721400
H	-3.58784900	-1.10338900	2.62848800
H	-0.52781600	-2.34561600	-0.35703500

TS:

Si	-2.60776900	0.02617500	0.37113500
H	-0.73551900	0.73579800	-1.08097600

C	-2.40304900	1.42605900	1.61924600
H	-1.93704900	2.30419400	1.16023500
H	-3.38650100	1.72505800	2.00648600
H	-1.78480300	1.11419500	2.46815400
C	-3.79492800	0.49469700	-1.01896400
H	-3.49416700	1.42963700	-1.50378900
H	-3.84430400	-0.28754500	-1.78415700
H	-4.80485100	0.63333800	-0.60999800
C	-3.12260300	-1.59852700	1.20504300
H	-3.21432600	-2.41771100	0.48370300
H	-2.41933900	-1.90024800	1.98859400
H	-4.10613600	-1.45200700	1.67425000
C	3.50082600	-0.22141700	0.59235400
C	3.68800600	-0.78058700	-0.64572400
C	2.64652700	-0.29766800	-1.48672400
C	1.87715400	0.53477900	-0.70455500
O	2.39055700	0.57996700	0.56899100
H	4.48899000	-1.45100100	-0.92270300
H	2.48890700	-0.51318200	-2.53451200
C	4.24087800	-0.30465800	1.87755200
H	4.59775400	0.68369500	2.19079800
H	5.10286800	-0.96605400	1.76538900
C	0.71347400	1.36804800	-0.96524800
H	0.57454000	1.62340500	-2.01239900
O	0.49519700	2.43287900	-0.15879500
Pd	-0.49232100	-0.67418200	-0.39149500
H	3.60215800	-0.69606000	2.67814000
H	0.86356400	2.25326700	0.72622300

FS:

Si	-2.86681200	0.16646900	0.17937600
C	-2.94967400	1.25144200	1.71666100
H	-2.29266200	2.12271500	1.62572100
H	-3.97718600	1.61812000	1.84662800
H	-2.67225300	0.69580600	2.61846800
C	-3.26344100	1.11203800	-1.40041900
H	-2.59084100	1.96661600	-1.52773400
H	-3.18347700	0.47068000	-2.28433100
H	-4.29223500	1.49450500	-1.34997500
C	-3.84149200	-1.44567200	0.34902500
H	-3.67620800	-2.11505700	-0.50243300
H	-3.58923100	-1.97900200	1.27140900
H	-4.91386800	-1.20442300	0.37996400
C	4.08030600	-0.15982200	0.36472300

C	3.88851800	-0.93417900	-0.74591900
C	2.74621600	-0.40429500	-1.42634100
C	2.31518100	0.66286600	-0.68937100
O	3.12695300	0.82139600	0.40940700
H	4.49599800	-1.77679600	-1.04561800
H	2.30790500	-0.75907500	-2.34946000
C	5.07856000	-0.17778700	1.46890800
H	5.64496200	0.76040500	1.51071300
H	5.78370300	-0.99888600	1.31742100
C	1.18750500	1.60706200	-0.83344800
H	1.48488000	2.63602800	-0.60864200
O	0.04548500	1.30367800	0.04465300
Pd	-0.75899200	-0.74011700	-0.03120000
H	4.59457600	-0.31462800	2.44357600
H	0.31579200	1.46855900	0.96524600
H	0.77957900	1.55872700	-1.84240800

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