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Formation of C-C Bonds at Mild Conditions for Bio-alkanes Production

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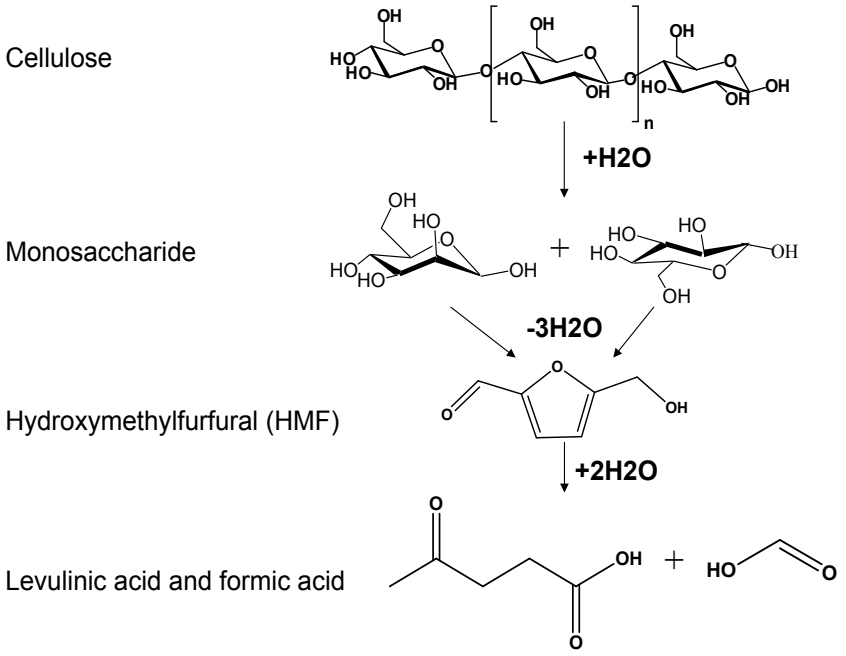


Figure S1. Proposed pathway for the conversion of levulinic acid and formic from cellulose.

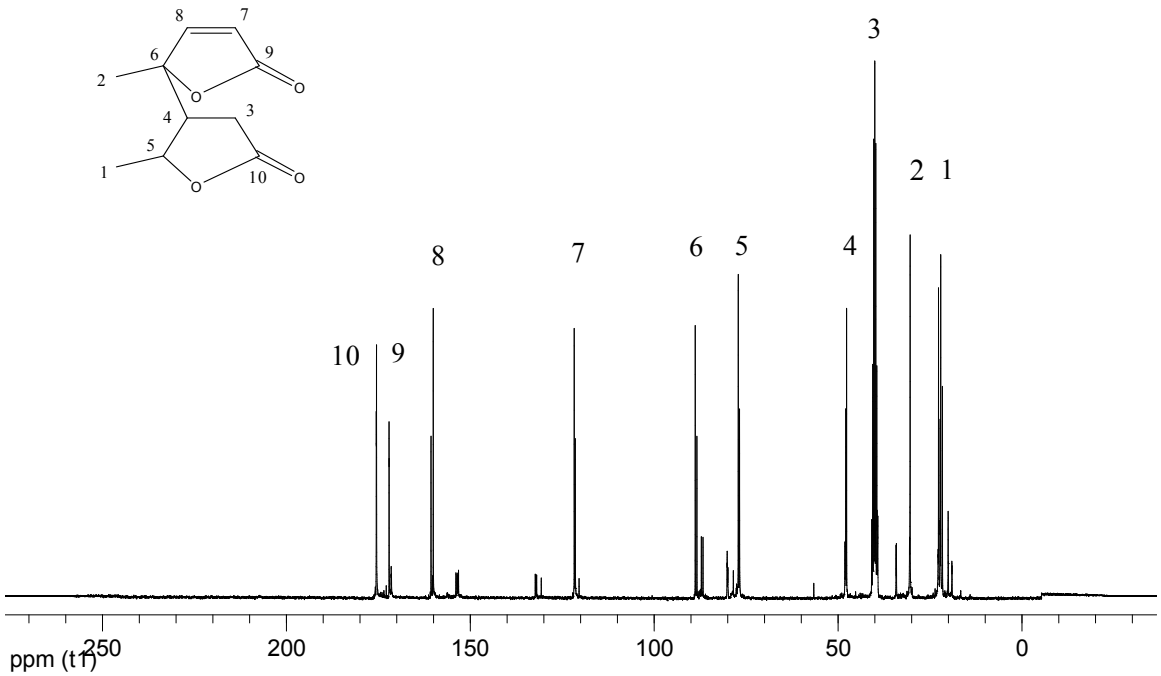


Figure S2. ^{13}C NMR spectra of di/trimerization products obtained from angelica lactone catalyzed by K_2CO_3 at 353 K**.**

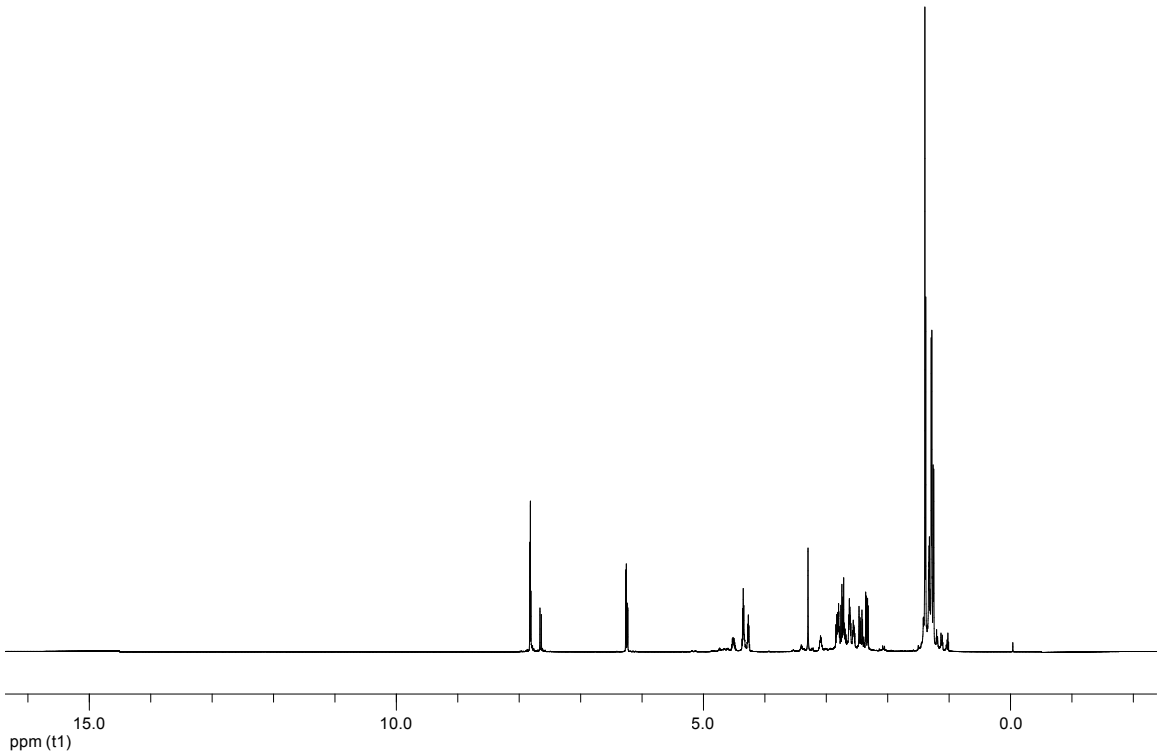


Figure S3. ^{1}H NMR spectra of di/trimerization products obtained from angelica lactone catalyzed by K_2CO_3 at 353 K**.**

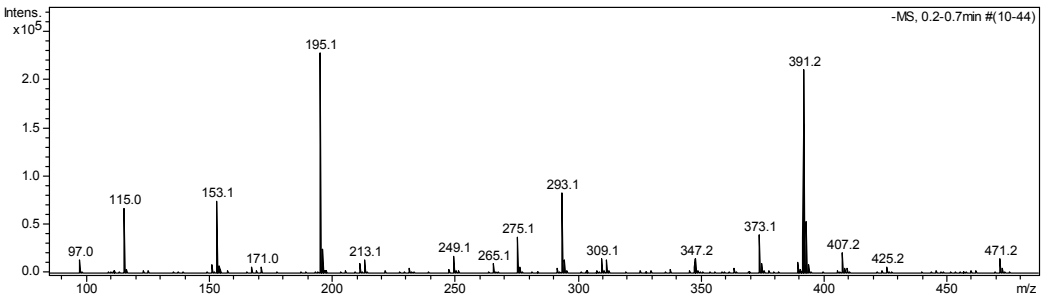


Figure S4. Mass spectra of di/trimerization products obtained from angelica lactone catalyzed by K_2CO_3 at 353 K**.**

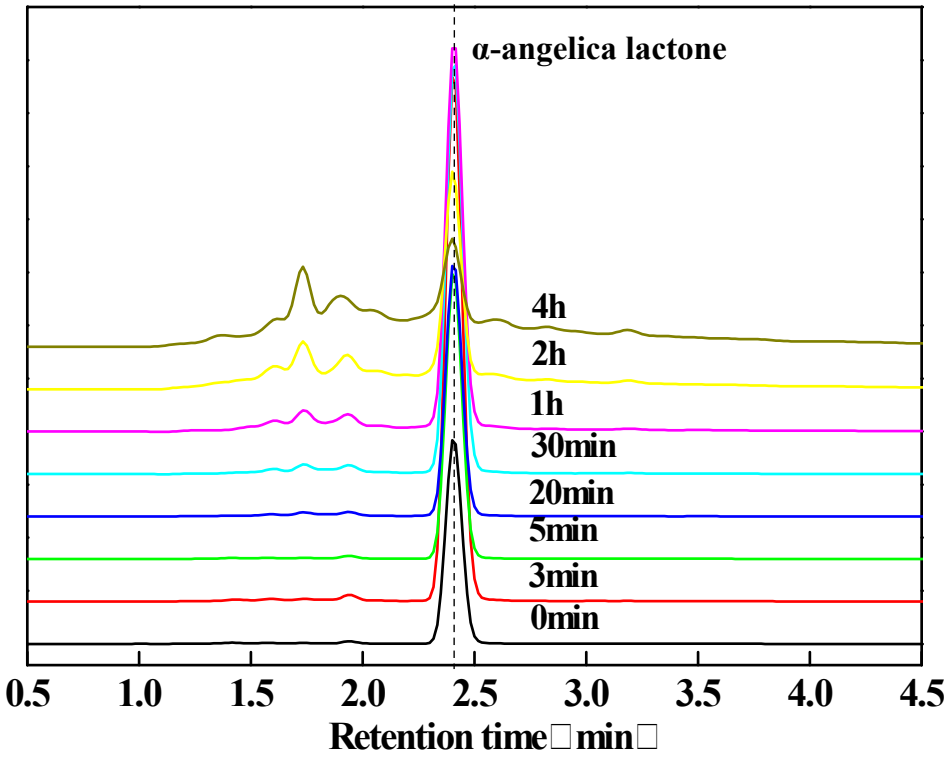


Figure S5. HPLC chromatograms of α-angelica lactone heated at 353 K for various reaction times without catalyst.

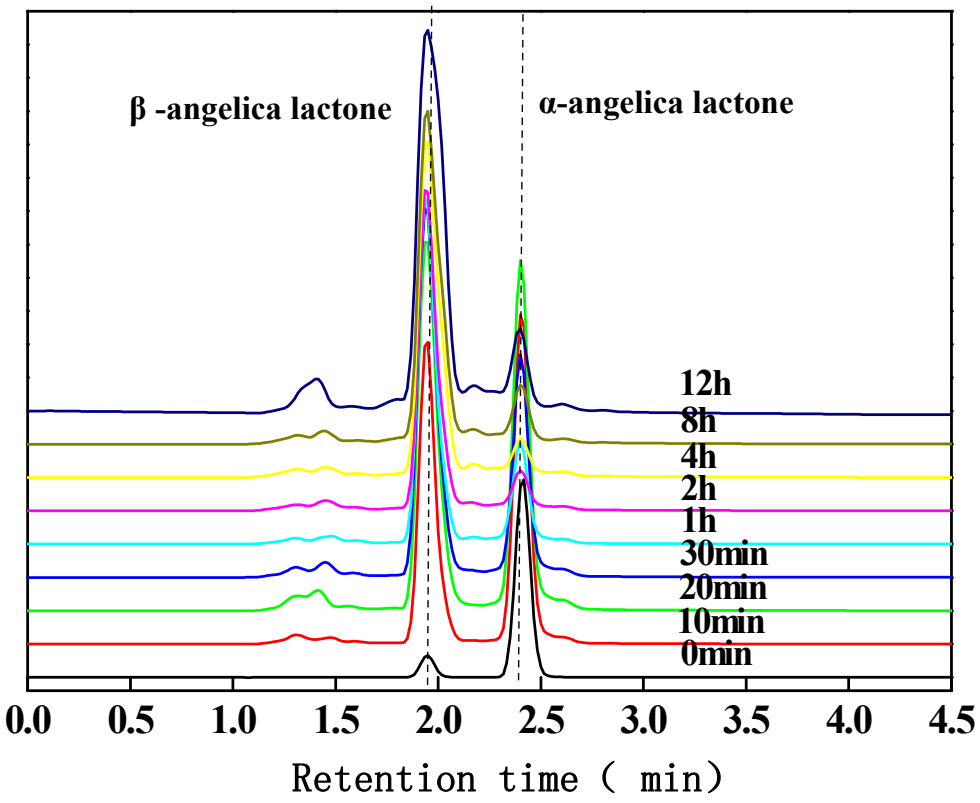


Figure S6. HPLC chromatograms of isomerization of α-angelica lactone catalyzed by 3% NaOH at 353 K.

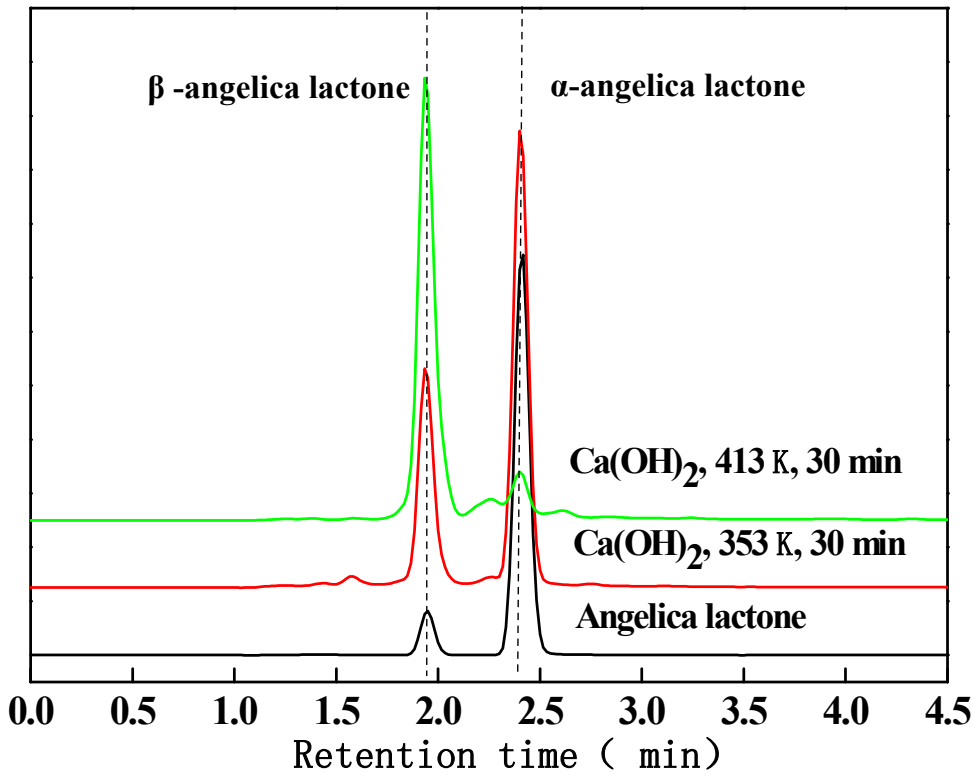


Figure S7. HPLC chromatograms of isomerization of α-angelica lactone catalyzed by 3% $Ca(OH)_2$ at 353 and 413 K for 30 min.

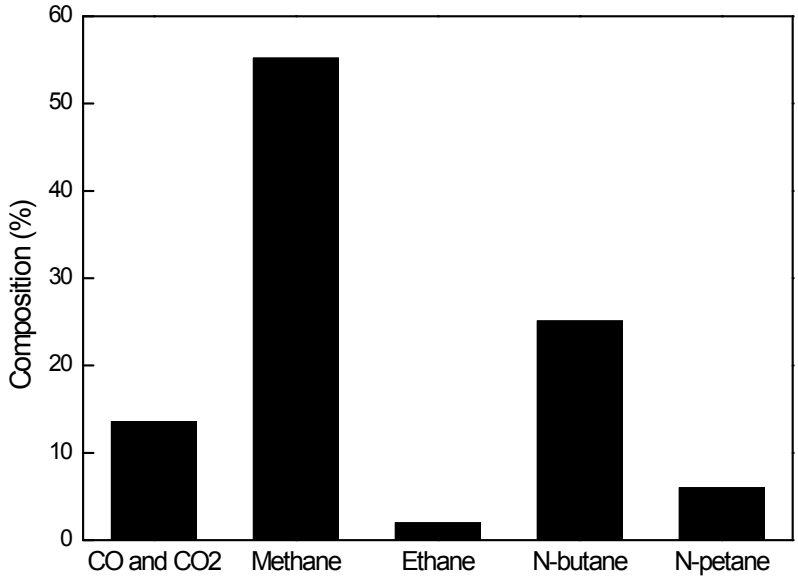
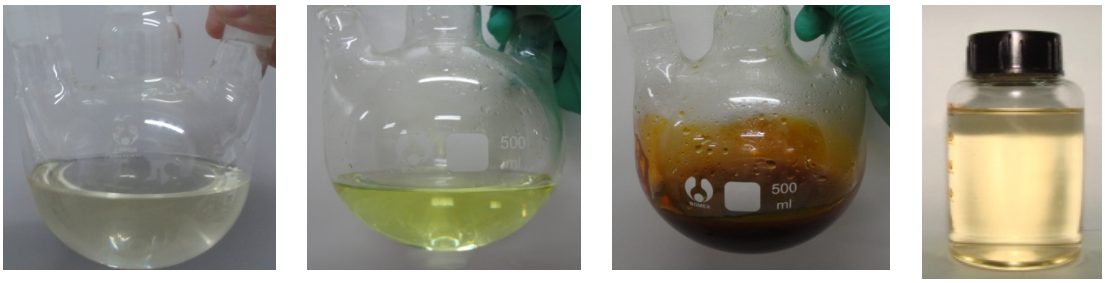


Figure S8. Composition of the gaseous products (8% carbon in C-C formation of angelica lactone) from hydrodeoxygenation for entry 8 of Table S3



Levulinic acid **Angelica lactone** **C-C formation of angelica lactone** **Bio-alkanes**

Figure S9. Pictures of the products of each step

Table S1. Results of element composition of C-C formation products obtained from angelica lactone catalyzed by K_2CO_3 at various temperatures

Reaction temperature (K)	N (%)	C (%)	H (%)	S (%)
353	0.00	61.10	6.28	—
363	0.02	61.31	6.18	0.02
373	0.00	61.16	6.27	0.01
383	0.04	60.76	6.34	0.02
393	0.00	60.86	6.47	0.03

Table S2. Conversion of cellulose, cotton, cornstalk, fructose, glucose and starch into levulinic acid and formic acid by catalyzed by HCl.

Entry	Materials and amount (wt%)	Catalyst concentration (wt%)	Reaction time (min)	T (K)	Yield (mol%)	
					Levulinic acid	Formic acid
1	Cellulose, 10	5	5	473	50	13
2	Cellulose, 10	5	10	473	46	11
3	Cellulose, 10	5	20	473	45	9
4	Cellulose, 10	5	30	473	42	8
5	Cellulose, 10	5	60	473	46	10
6	Cellulose, 10	5	120	473	42	6
7	Cellulose, 10	5	240	473	36	7
8	Cellulose, 10	5	10	413	4	14
9	Cellulose, 10	5	10	433	29	67
10	Cellulose, 10	5	10	453	52	78
11	Cellulose, 10	5	10	493	50	42
12	Cellulose, 10	2.5	10	473	43	83
13	Cellulose, 10	7.5	10	473	51	55
14	Cellulose, 10	10	10	473	56	64
15	Cellulose, 2.5	5	10	473	15	30
16	Cellulose, 5	5	10	473	29	44
17	Cellulose,7.5	5	10	473	45	71
18	Cotton, 10	5	10	473	51	71
19	Cornstalk, 10	5	10	473	28	63
20	Fructose, 10	5	10	473	57	104
21	Glucose, 10	5	10	473	52	70
22	Starch, 10	5	10	473	50	75

Table S3. Product selectivities of the organic phase produced in the hydrodeoxygenation reaction of addition reaction products from angelica lactone.

Entry		Reaction conditions		Products distribution (wt%)									
	Catalyst	Temp. (K)	Time (h)	C5	C6	C7	C8	C9	C10	C11	C12	C13+	Oxygenated products
1	10% Pd/C	573	12	5	1	1	2	6	2	8	2	22	51
2	10% Pd/C	573	60	7	13	51	10	3	6	2	0	0	8
3	10% Pd/C	623	12	5	16	6	20	31	3	3	5	2	11
4	10% Pd/C	623	18	3	3	2	10	24	5	9	13	11	20
5	10% Pd/C	623	60	4	10	7	14	30	12	8	6	4	5
6	10% Pd/C	648	4	6	4	1	7	21	7	12	4	5	33
7	10% Pd/C	648	30	1	2	3	20	36	5	4	23	3	3
8	10% Pd/C	648	60	0	3	4	15	37	11	11	10	7	2
9*	NiFeCr	648	12	7	3	7	20	16	14	10	8	11	4
10*	NiFeCr	648	18	0	5	8	30	24	15	15	3	0	0

* Pre-hydrogenated at 648 K with NiCrFe as catalyst for 12 h.