Supporting Information

Sustainable synthesis of diethyl carbonate from carbon dioxide and ethanol featuring acetals as regenerable dehydrating agent

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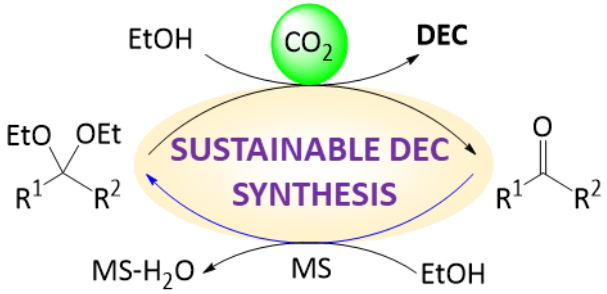

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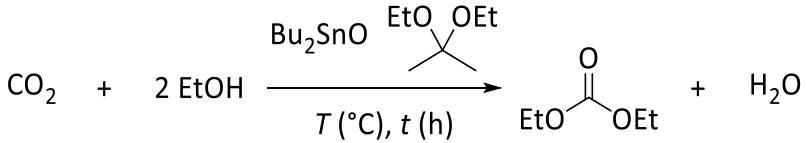
Table S1 Investigation of optimum condition for the synthesis of DEC using Bu_2SnO catalyst



EtOH/ acetal	T (°C)	t (h)	EtOH (mmol)	Acetal (mmol)	Acetone (mmol)	2-Ethoxypropene (mmol)	Mesityl oxide (mmol)	DEC (mmol)[a]	DEC (%)[b]	DEC (%)[c]	MB (%)[d]		
											①	②	③
2/1	160	20	29.4	14.7	1.90	0.79	0.01	0.48	3	3	92	98	98
2/1	180	20	29.4	14.8	2.44	1.54	0.03	0.92	6	6	85	95	95
4/1	160	20	41.9	10.9	1.99	0.51	0.01	0.85	4	8	90	95	95
4/1	180	20	41.1	10.6	2.90	0.70	0.05	1.59	8	15	85	92	92
10/1	180	20	58.5	5.63	2.03	0.32	0.01	1.33	5	23	85	90	90
20/1	180	20	66.1	3.09	1.42	0.10	0.00	0.79	3	26	85	88	88
20/1	200	20	66.2	3.17	1.47	0.13	0.01	1.03	3	32	77	81	81
20/1	200	48	65.4	3.22	1.58	0.09	0.03	1.31	4	41	65	68	69
20/1	220	20	65.9	3.21	1.42	0.24	0.01	0.83	3	26	71	79	79

Reaction conditions: 5 MPa CO_2 at room temperature, 20 mol% Bu_2SnO relative to acetal. [a] DEC was determined by GC using *tert*-butyl toluene as internal standard. [b] DEC yield was calculated based on EtOH. [c] DEC yield was calculated based on acetal. [d] MB = material balance (%). ① = 100 x (remaining acetal + acetone)/initial acetal. ② = 100 x (remaining acetal + acetone + 2-ethoxypropene)/initial acetal. ③ = 100 x (remaining acetal + acetone + 2-ethoxypropene + 2 x mesityl oxide)/initial acetal

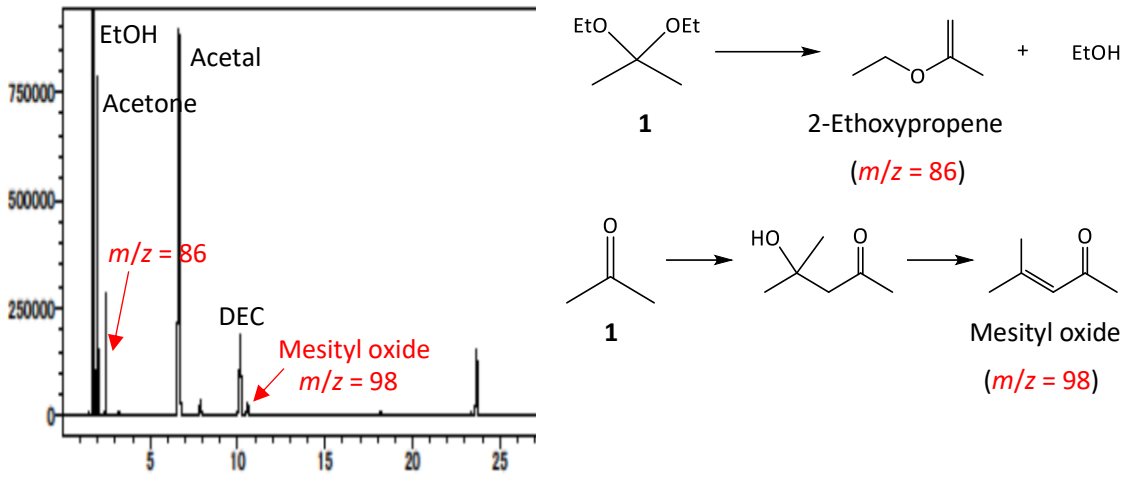
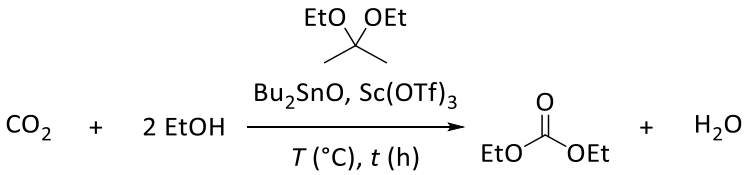


Fig. S1 GC chart of DEC synthesis using acetal **1** and the corresponding byproduct

Table S2 The effect of co-catalyst ($Sc(OTf)_3$) for the synthesis of DEC using Bu_2SnO catalyst



EtOH/ Acetal	*T* (°C)	$Sc(OTf)_3$ (mol%)	EtOH (mmol)	Acetal (mmol)	Acetone (mmol)	DEC (mmol)[a]	DEC (%)[b]	DEC (%)[c]	MB (%)[d]
2/1	160	—	29.4	14.7	1.90	0.48	3	3	92
2/1	160	0.04	28.9	14.6	2.86	1.48	10	10	86
2/1	180	—	29.4	14.8	2.44	0.92	6	6	85
2/1	180	0.04	29.5	14.6	3.62	2.57	17	18	73
4/1	160	—	41.9	10.9	1.99	0.85	4	8	90
4/1	160	0.04	41.8	10.8	2.90	1.46	7	14	89
4/1	180	—	41.1	10.6	2.90	1.59	8	15	85
4/1	180	0.04	42.5	10.7	3.80	2.84	13	26	79
10/1	180	—	59.0	5.72	1.44	0.83	3	14	86
10/1	180	0.04	57.9	5.68	2.12	1.00	3	18	84
10/1	180	—	58.5	5.63	2.03	1.33	5	23	85
10/1	180	0.04	59.9	5.99	2.76	2.15	7	36	81

Reaction conditions: 5 MPa CO_2 at room temperature, 20 mol% Bu_2SnO relative to acetal, 0.04 mol% $Sc(OTf)_3$ relative to acetal amount. [a] DEC was determined by GC using *tert*-butyl toluene as internal standard. [b] DEC yield was calculated based on EtOH. [c] DEC yield was calculated based on acetal. [d] MB = material balance (%).

Table S3 Equilibrium constant from acetal formation in anhydrous methanol and the rate constant of the acetal hydrolysis

Ketone + 2 MeOH ⇌ Acetal + H_2O		Acetal + H_2O → Ketone	DEC formation (mmol)	
K = [Acetal][H_2O]/[Ketone][MeOH]^2		k of acetal hydrolysis		
Ketone	K / 10^{-3} mol·L^{-1} [a]	k [b]	Without $Sc(OTf)_3$	With $Sc(OTf)_3$
Acetone **1a**	0.4 ± 0.02	4.45	1.59	2.84
Butanone **2a**	0.13 ± 0.01	7.82	2.03	3.12
2-Pentanone **3a**	—	8.97	2.42	3.51
3-Pentanone **4a**	0.034 ± 0.002	8.89	1.74	3.09
Cyclohexanone **5a**	6.7 ± 0.4	0.67	0.21	0.26

[a] K is the equilibrium constant of acetal formation from methanol observed at 25 °C as referred from J. M. Bell, D. G. Kubler, *et al.*, *J. Org. Chem.*,1965, **30**, 4284-4292. [b] k is the rate constant for acetal hydrolysis observed 25 °C referred from M. J. Huggins and D. G. Kubler, *et al.*, *J. Org. Chem.*,1975, **40**, 2813-2815

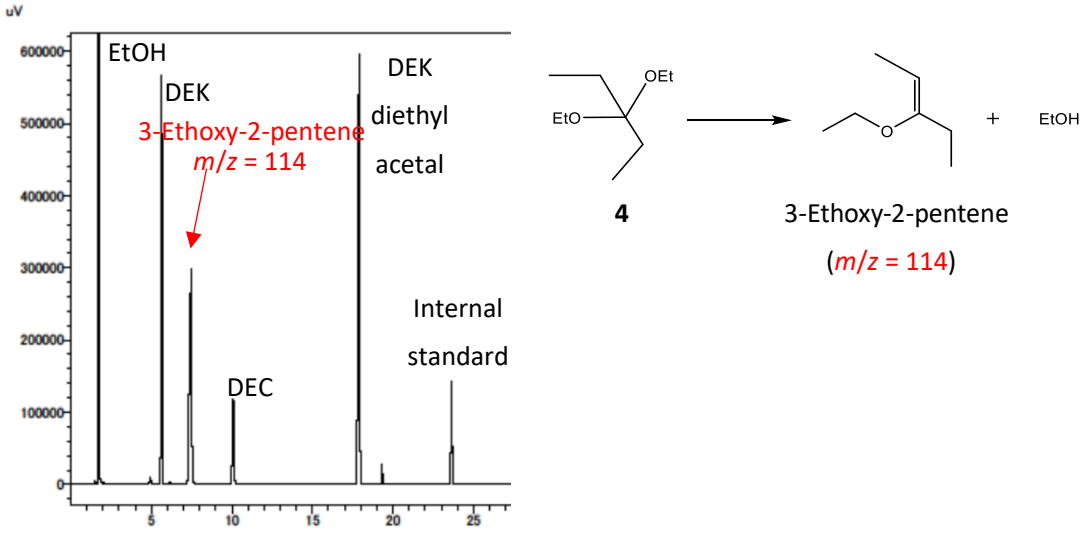
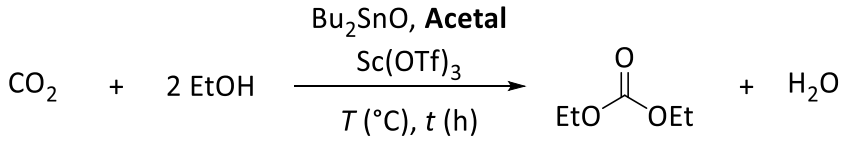
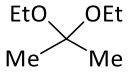
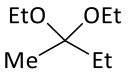
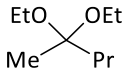
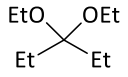
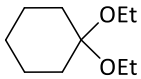


Fig. S2 GC chart of DEC synthesis using acetal **4** and the corresponding byproduct

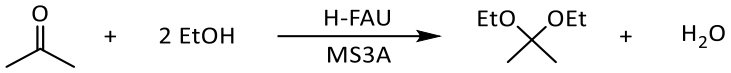
Table S4 Acetal screening for the direct synthesis of DEC from CO_2 using Bu_2SnO catalyst with or without $Sc(OTf)_3$ co-catalyst



Acetal	$Sc(OTf)_3$ (mol%)	EtOH (mmol)	Acetal (mmol)	Ketone (mmol)	DEC (mmol)[a]	DEC (%)[b]	DEC (%)[c]	MB (%)[d]
 **1**	—	41.1	10.6	2.90	1.59	8	15	85
	0.04	42.5	10.7	3.80	2.84	13	26	79
 **2**	—	41.9	10.6	3.40	2.03	10	19	80
	0.04	41.8	10.3	4.42	3.12	15	30	81
 **3**	—	41.5	10.2	3.82	2.42	12	24	76
	0.04	42.4	10.4	4.89	3.51	17	34	75
 **4**	—	42.5	10.6	3.77	1.74	8	16	70
	0.04	42.2	10.8	4.61	3.09	15	29	67
 **5**	—	41.7	10.6	3.36	0.21	1	2	72
	0.04	42.2	10.7	2.25	0.26	1	2	37

Reaction conditions: 5 MPa CO_2 at room temperature, 40 mmol EtOH, 10 mmol acetal, 20 mol% Bu_2SnO relative to acetal, 0.04 mol% $Sc(OTf)_3$ relative to acetal, 180 °C, 20 h. [a] Percentage is DEC yield determined by GC using *tert*-butyl toluene as internal standard. [b] DEC yield was calculated based on EtOH. [c] DEC yield was calculated based on acetal. [d] MB = Material balance (%).

Table S5 The effect of EtOH/acetone ratio on the synthesis of acetal from acetone



EtOH / Acetone	Acetone (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal (%)	Conv. (%)	MB (%)[c]	H_2O (%)[d]	Adsorbed H_2O (%)[e]
0.1/0.2	154.3	41.3	21.8	44[a]	23	88	0.015	99
0.1/0.1	65.9	41.1	22.1	44[a]	34	88	0.034	99
0.2/0.1	48.7	92.8	40.1	40[b]	51	89	0.038	99
0.4/0.1	46.0	282.9	46.1	46[b]	51	92	0.047	99
0.6/0.1	43.6	464.8	48.1	48[b]	56	92	0.055	98
1.0/0.1	44.3	890.8	49.6	50[b]	56	94	0.064	95
1.5/0.1	42.2	1354.3	50.7	51[b]	58	93	0.085	96

Reaction conditions: 1.275 g H-FAU, 10 g MS3A, 1 h, ambient conditions. [a] Yield based on EtOH, and [b] yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [c] Material balance. [d] H_2O content was determined by Karl-Fischer titration. [e] H_2O adsorbed by MS.

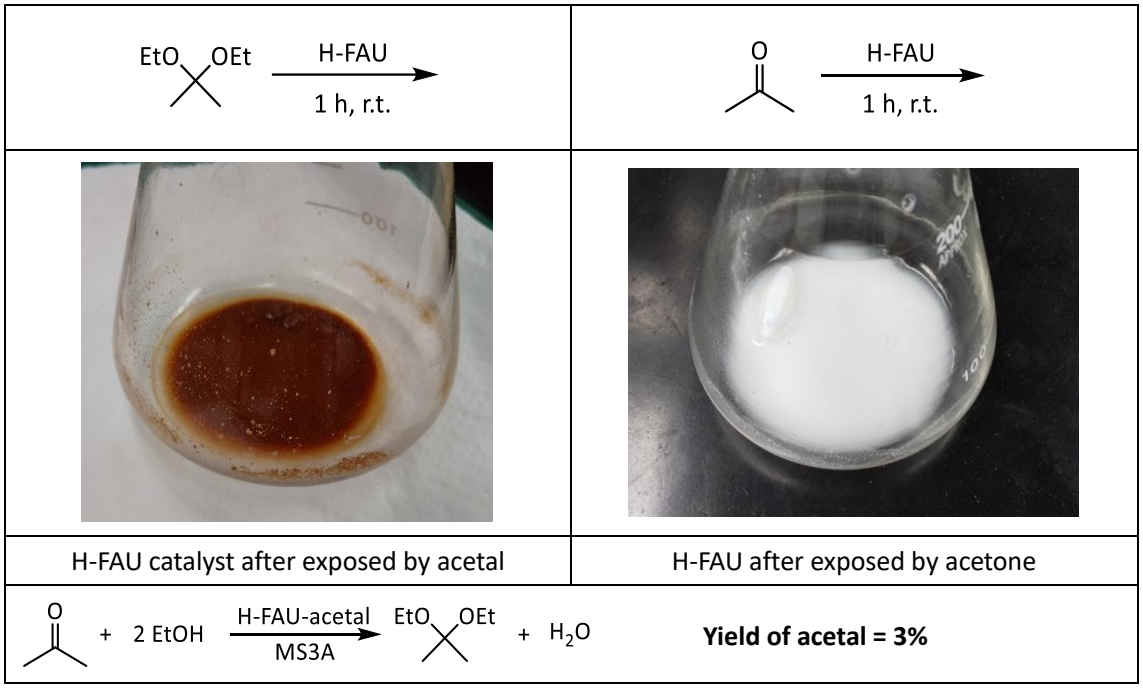
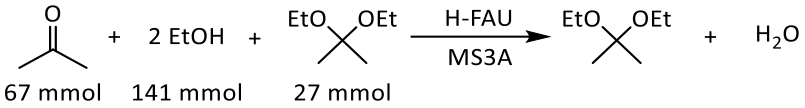


Fig. S3 The photograph of H-FAU catalyst after exposed by acetal and acetone and its catalytic activity for formation of acetal

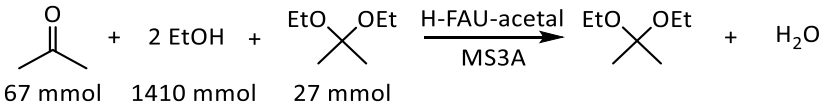
Table S6 The effect of acetal addition on time profile results of the synthesis of acetal from acetone



Reaction time (h)	Acetone (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal (%)[a]	Acetal difference (%)	MB (%)[b]
Start	67.2	1410	27.9	28	–	–
1	53.9	1369	38	38	10	95
2	51.9	1361	37	37	9	91
3	53.2	1362	38	38	10	94
18	53.2	1329	38	38	10	96
20	50.8	1351	37	37	9	94

Reaction conditions: 0.067 mol acetone, 1.41 mol ethanol, 0.027 mol 2,2-ethoxypropane, 10 g MS3A, 0.85 g H-FAU, ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] MB = Material balance (%).

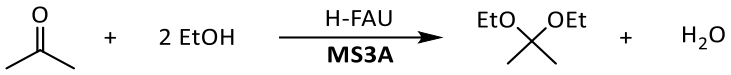
Table S7 The effect of acetal addition with acetal-pretreated catalyst on time profile results of the synthesis of acetal from acetone



Reaction time (h)	Acetone (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal (%)[a]	Acetal difference (%)	MB (%)[b]
Start	67.2	1413	27	27	–	–
1	78.8	1415	17	17	-10	102
2	63.5	1369	24	24	-3	93
3	65.7	1393	24	24	-3	95
90	68.3	1423	23	23	-4	95

Reaction conditions: 0.067 mol acetone, 1.41 mol ethanol, 0.027 mol 2,2-ethoxypropane, 10 g MS3A, 0.85 g H-FAU exposed by acetal (H-FAU-acetal), ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] MB = Material balance (%).

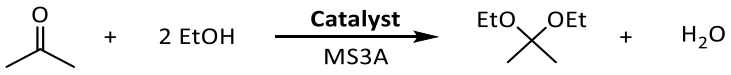
Table S8 The effect of MS amount on the synthesis of acetal from acetone



MS3A (g)	Acetone (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal (%)[a]	Conv. (%)	MB (%)[b]	H_2O (%)[c]	Adsorbed H_2O (%)[d]
5	64.0	322.9	27.6	28	36	92	0.218	89
7	55.4	300.2	36.6	37	45	89	0.176	93
8	51.8	292.8	41.3	41	48	93	0.056	98
10	46.0	282.9	46.1	46	51	92	0.047	99
12	40.0	262.2	48.1	48	60	88	0.032	99

Reaction conditions: 0.1 mol acetone, 0.4 mol ethanol, 1.275 g H-FAU, 1 h, ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] Material balance. [c] H_2O content was determined by Karl-Fischer titration. [d] H_2O adsorbed by MS.

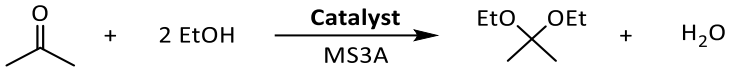
Table S9 Catalyst screening for the synthesis of acetal from acetone



Catalyst	Acetone (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal Yield (%)[a]	Conv. (%)	MB (%)[b]	H_2O (%)[c]
H-FAU	46.0	282.9	46.1	46	54	92	0.047
SZ	71.1	326.8	27.3	27	60	90	0.041
Dowex	26.6	271.0	26.6	27	44	82	0.132
Nafion	56.1	284.8	40.6	41	44	97	0.098
Amberlyst	49.8	282.5	45.3	45	50	95	0.062

Reaction conditions: 0.1 mol acetone, 0.4 mol ethanol, 10 g MS3A, 0.09 mmol H^+, H-FAU ⟶ 1 h, SO_4^{2-}/ZrO_2, Dowex ⟶ 2 h, Nafion ⟶ 3 h, and Amberlyst ⟶ 2 h, ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] MB = Material balance (%). [c] H_2O content was determined by Karl-Fischer titration.

Table S10 Catalyst screening for the synthesis of acetal from acetone



Catalyst	Acetone (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal Yield (%)[a]	Conv. (%)	MB (%)[b]	H_2O (%)[c]
H-FAU	46.0	282.9	46.1	46	54	92	0.047
SZ	71.1	326.8	27.3	27	60	90	0.041
Dowex	26.6	271.0	26.6	27	44	82	0.132
Nafion	56.1	284.8	40.6	41	44	97	0.098
Amberlyst	49.8	282.5	45.3	45	50	95	0.062

Reaction conditions: 0.1 mol acetone, 0.4 mol ethanol, 10 g MS3A, 0.09 mmol H^+, H-FAU ⟶ 1 h, SO_4^{2-}/ZrO_2, Dowex ⟶ 2 h, Nafion ⟶ 3 h, and Amberlyst ⟶ 2 h, ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] MB = Material balance (%). [c] H_2O content was determined by Karl-Fischer titration.

Table S11 Proton amount and chemical structure of the used ion exchange resins

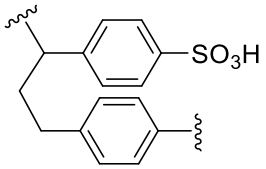
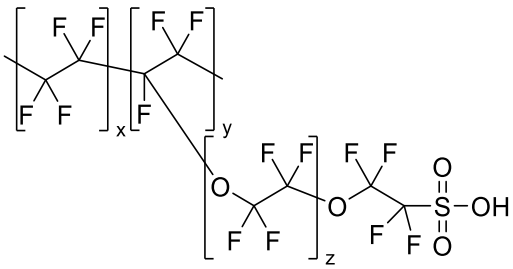
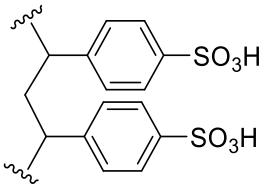
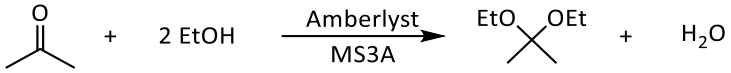
Catalyst	H^+ (mmol/g)	Chemical structure
Dowex 50Wx2	0.6	
Nafion-NR50	0.8	
Amberlyst-15	4.7	

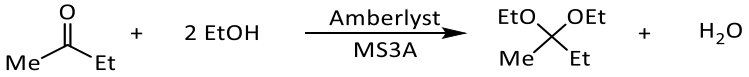
Table S12 Synthesis of acetal from acetone using Amberlyst catalyst



Time (h)	Acetone (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal yield (%)[a]	Conversion (%)	MB (%)[b]
1	53.8	294.5	42.3	42	46	96
2	49.8	282.5	45.3	45	50	95
3	54.8	288.4	40.0	40	45	95
4	54.8	288.9	36.6	37	45	91
5	58.2	294.5	34.6	35	42	93
22	57.3	288.7	27.2	27	43	85
24	58.8	289.5	27.6	28	41	86

Reaction conditions: 0.1 mol acetone, 0.4 mol ethanol, 10 g MS3A, 0.2 g Amberlyst, ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] MB = Material balance (%). H_2O content determined by Karl-Fischer titration was 0.004% (at 0 h) ⟶ 0.062% (24 h).

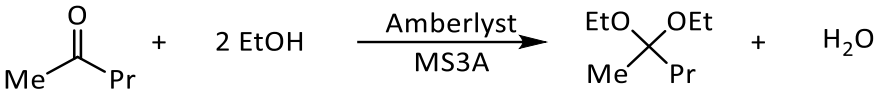
Table S13 Synthesis of acetal from methyl ethyl ketone (MEK) using Amberlyst catalyst



Time (h)	MEK (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal yield (%)[a]	Conversion (%)	MB (%)[b]
1	71.7	284.5	34.6	35	28	106
2	62.1	260.7	43.8	44	38	106
3	59.4	250.9	46.3	46	41	106
5	63.9	255.8	41.7	42	36	106
22	70.5	261.0	30.1	30	29	101
24	69.7	257.9	30.3	30	30	100

Reaction conditions: 0.1 mol MEK, 0.4 mol ethanol, 10 g MS3A, 0.2 g Amberlyst, ambient conditions. [a] Yield based on acetone determined by GC using *tert*-butyl toluene as an internal standard. [b] MB = Material balance (%). H_2O content determined by Karl-Fischer titration was 0.004% (0 h) ⟶ 0.043% (24 h).

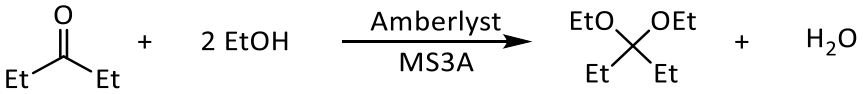
Table S14 Synthesis of acetal from methyl propyl ketone (MPK) using Amberlyst catalyst



Time (h)	MPK (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal yield (%)[a]	Conversion (%)	MB (%)[b]
1	71.1	322.3	32.3	32	29	103
2	67.7	312.9	37.7	38	32	105
3	66.0	298.2	36.8	37	34	103
5	70.0	302.7	32.6	33	30	103
22	75.4	304.4	24.3	24	25	100
24	75.7	304.3	24.3	24	24	100

Reaction conditions: 0.1 mol methyl propyl ketone, 0.4 mol ethanol, 10 g MS3A, 0.2 g Amberlyst, ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] MB = Material balance (%). H_2O content determined by Karl-Fischer titration was 0.004% (at 0 h) ⟶ 0.030% (24 h).

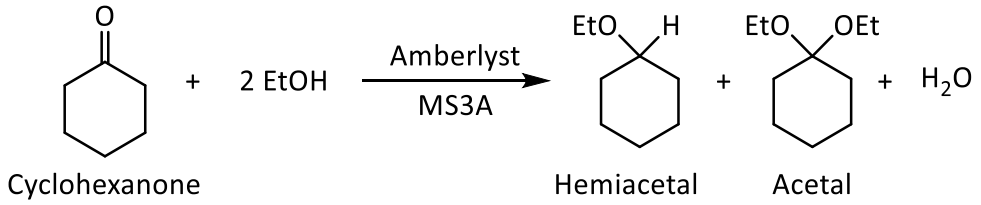
Table S15 Synthesis of acetal from diethyl ketone using Amberlyst catalyst



Time (h)	Diethyl ketone (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal yield (%)[a]	Conversion (%)	MB (%)[b]
1	44.8	178.6	5.8	12	10	101
2	42.1	168.8	8.0	16	16	100
3	41.1	164.7	9.1	18	18	100
5	40.1	158.8	9.7	19	20	100
22	39.5	153.8	9.7	19	21	98
24	39.2	152.7	9.7	19	22	98

Reaction conditions: 0.05 mol diethyl ketone, 0.2 mol ethanol, 5 g MS3A, 0.1 g Amberlyst, ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] MB = Material balance (%). H_2O content determined by Karl-Fischer titration was 0.004% (at 0 h) ⟶ 0.020% (24 h).

Table S16 Synthesis of acetal from cyclohexanone using Amberlyst catalyst

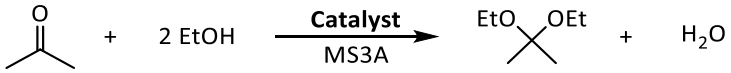


Cyclohexanone Hemiacetal Acetal

Time (h)	Cyclohexanone (mmol)	Ethanol (mmol)	Hemiacetal (mmol)	Acetal (mmol)	Acetal yield (%)[a]	Conversion (%)	MB (%)[b]
1	22.4	227.9	18.7	59.0	59	78	100
2	25.8	231.3	16.4	57.8	58	74	100
5	31.1	237.3	16.8	52.2	52	69	100
22	32.1	246.2	1.2	66.8	67	68	99
24	31.5	216.5	1.4	67.5	68	68	100

Reaction conditions: 0.1 mol cyclohexanone, 0.4 mol ethanol, 10 g MS3A, 0.2 g Amberlyst, ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] Material balance = [(mole of acetal + mole of hemiacetal + mole of cyclohexanone)/initial mole of cyclohexanone] × 100 %. H_2O content determined by Karl-Fischer titration was 0.004% (at 0 h) ⟶ 0.208% (24 h).

Table S17 Results of catalytic reusability on acetal synthesis using normal method

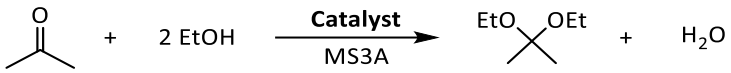


Run	Reaction scale	Acetone (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal yield (%)[a]	MB (%)[b]	H_2O content (%)[c]
H-FAU							
1	1	49.3	299.6	50.0	50	99	0.036
2	0.98	68.0	327.7	26.1	27	96	0.006
3	0.96	87.7	361.7	6.1	6	98	0.000
Nafion							
1	1	50.1	256.9	44.2	44	94	0.026
2	1	53.3	271.0	44.1	44	97	0.019
3	1	48.5	261.5	45.3	45	94	0.024
4	1	52.6	266.0	43.0	43	96	0.031
5	1	48.9	136.2	46.3	46	97	0.042

Amberlyst							
1	1	51.5	271.6	46.7	47	98	0.028
2	0.89	47.3	245.7	40.5	45	99	0.028
3	0.76	38.5	207.3	36.5	48	99	0.033
4	0.30	14.9	84.7	15.3	50	101	0.042
5	0.13	6.3	33.4	5.3	42	99	0.040

Reaction conditions: 0.1 mol acetone, 0.4 mol ethanol, 10 g MS3A, H-FAU ⟶ 1.275 g, Nafion ⟶ 5.1 g, and Amberlyst ⟶ 0.2 g, 2 h, ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] MB = Material balance (%). [c] H_2O content was determined by Karl-Fischer titration.

Table S18 Results of catalytic reusability on acetal synthesis using SpinChem method



Run	Reaction scale	Acetone (mmol)	Ethanol (mmol)	Acetal (mmol)	Acetal yield (%)[a]	MB (%)[b]	H_2O content (%)[c]
H-FAU							
1	1	55.1	346.7	27.2	27	82	0.089
2	0.89	53.3	312.6	22.3	25	85	0.165
3	0.70	39.5	243.3	19.0	27	84	0.280
4	0.61	26.1	223.1	15.7	26	83	0.367
5	0.53	36.7	193.1	5.9	11	81	0.236
Nafion							
1	1	73.7	371.2	19.8	20	94	0.080
2	1	56.4	318.4	25.0	25	81	0.062
3	1	59.9	341.1	25.0	25	85	0.075
4	1	61.3	345.4	26.3	26	88	0.052
5	1	58.2	334.9	29.4	29	88	0.047
Amberlyst							
1	1	55.2	340.1	30.8	31	86	0.049
2	1	61.9	332.9	33.9	34	96	0.047
3	1	61.0	331.2	35.9	36	97	0.067
4	1	61.2	334.6	36.6	37	98	0.062

5	1	63.4	338.4	35.2	35	99	0.067

Reaction conditions: 0.1 mol acetone, 0.4 mol ethanol, 10 g MS3A, H-FAU ⟶ 1.275 g, Nafion ⟶ 5.1 g, and Amberlyst ⟶ 1.0 g, 24 h, ambient conditions. [a] Yield based on acetone was determined by GC using *tert*-butyl toluene as an internal standard. [b] MB = Material balance (%). [c] H_2O content was determined by Karl-Fischer titration.

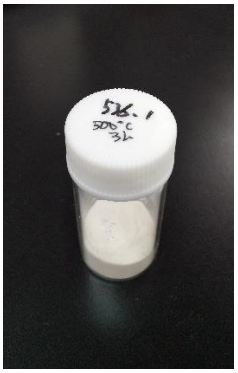
	
H-FAU catalyst after catalysis	H-FAU after treated at 500 °C for 3 h

Fig. S4 The photograph of used catalyst and its appearance after heating treatment at 500 °C.

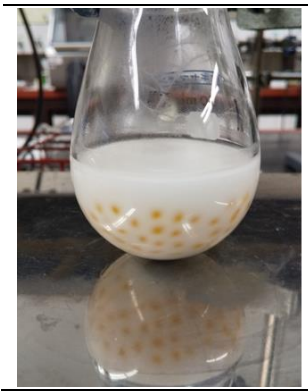
Normal reaction	**SpinChem reaction**
	

Fig. S5 The photograph of normal and SpinChem reactor system

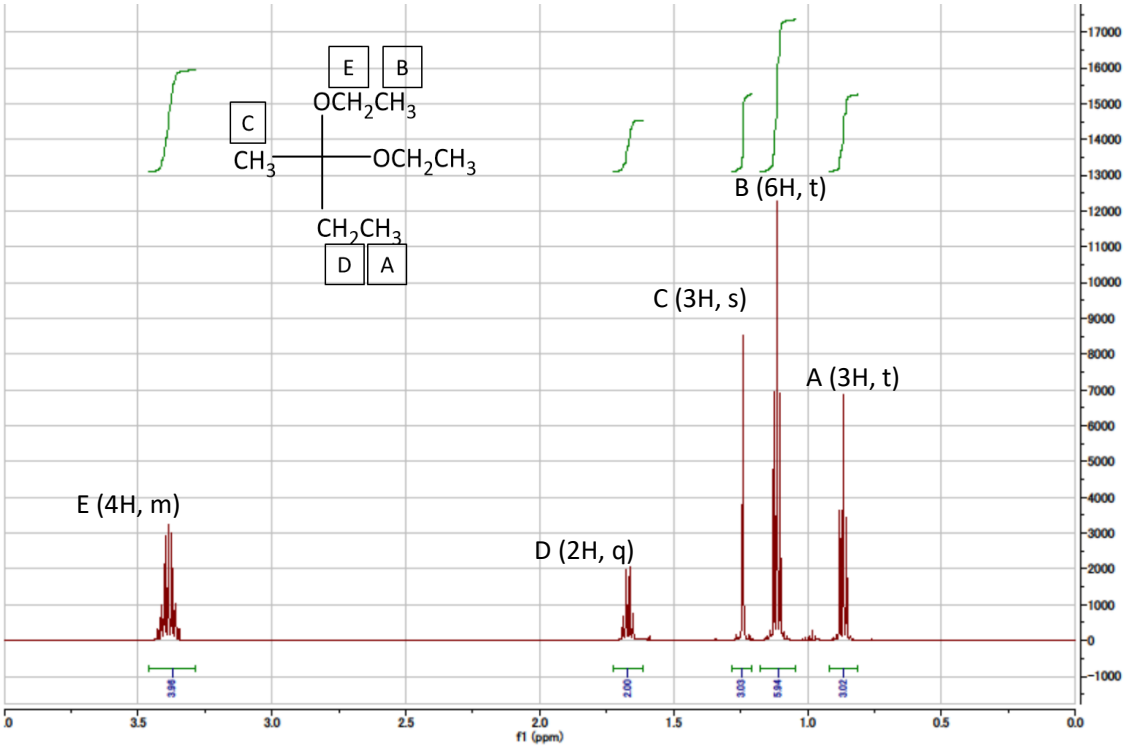


Fig. S6 ^{1}H NMR of acetal **2** synthesized from **2a**

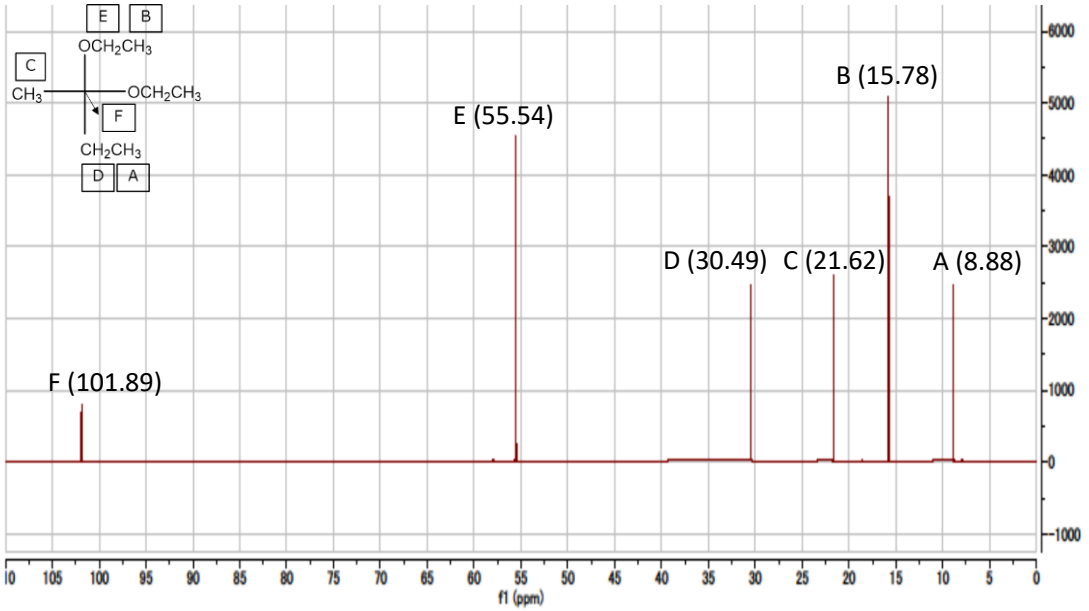


Fig. S7 ^{13}C{^{1}H} NMR of acetal **2** synthesized from **2a**

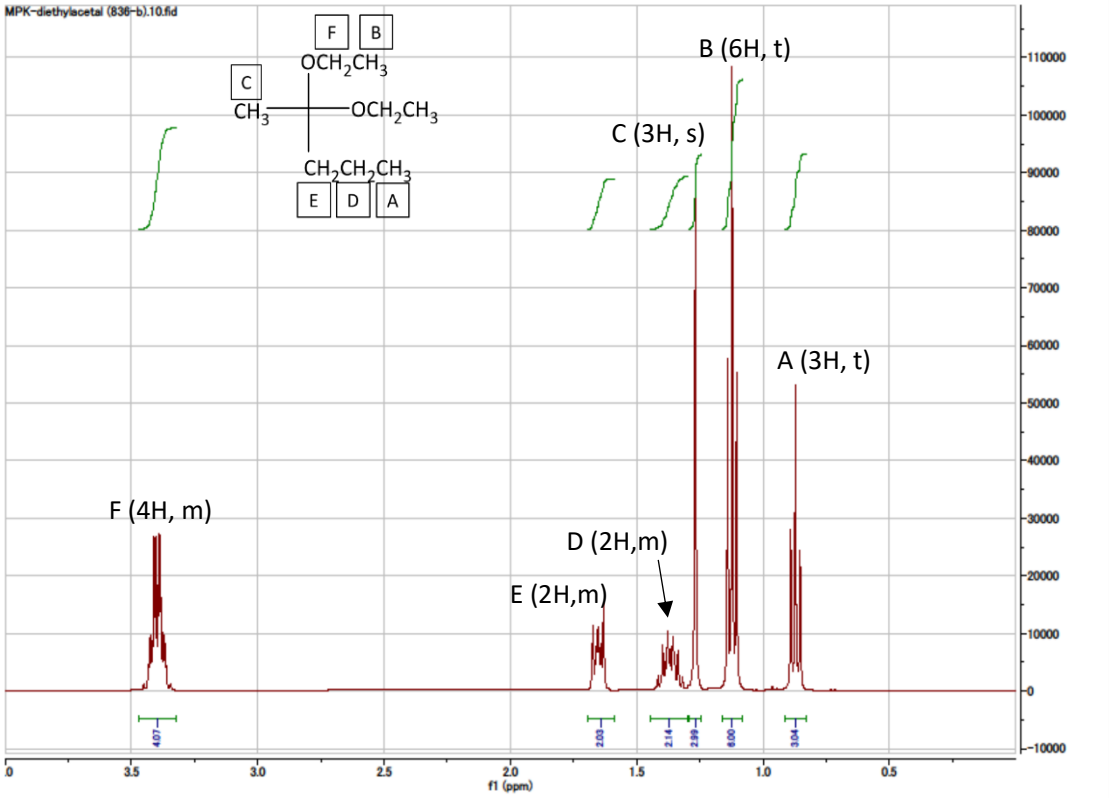


Fig. S8 ^{1}H NMR of acetal **3** synthesized from **3a**

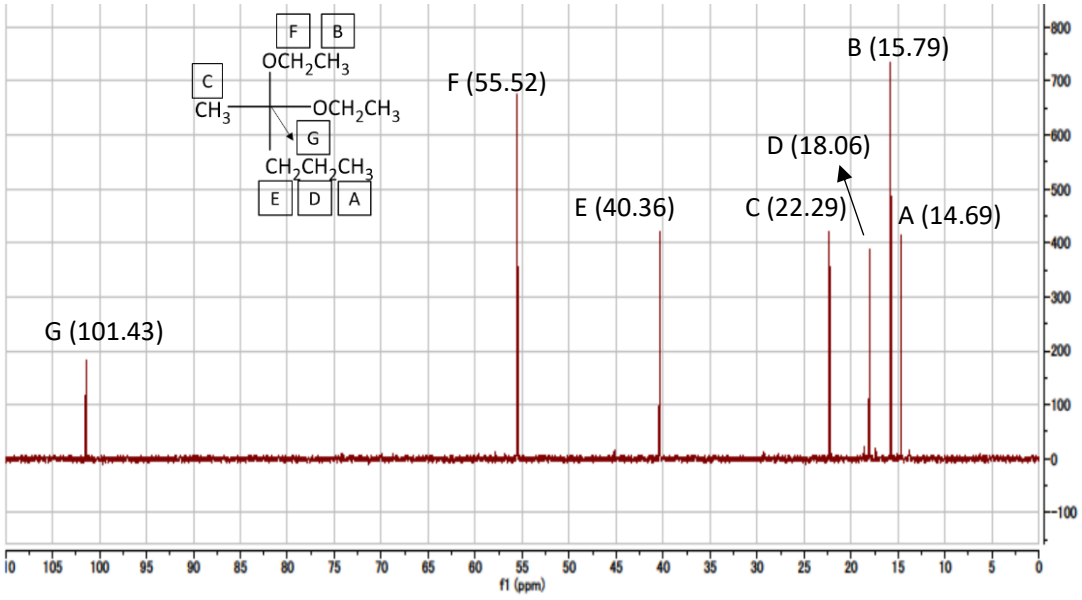


Fig. S9 ^{13}C{^{1}H} NMR of acetal **3** synthesized from **3a**

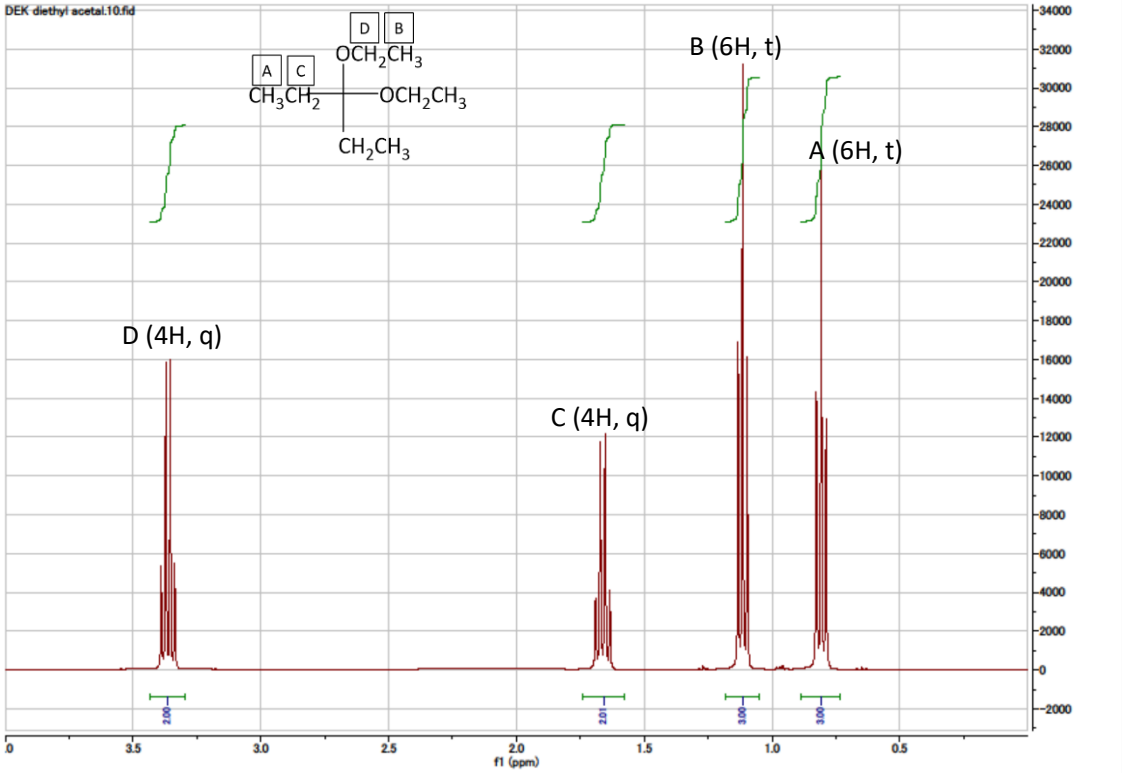


Fig. S10 ^{1}H NMR of acetal **4** synthesized from **4a**

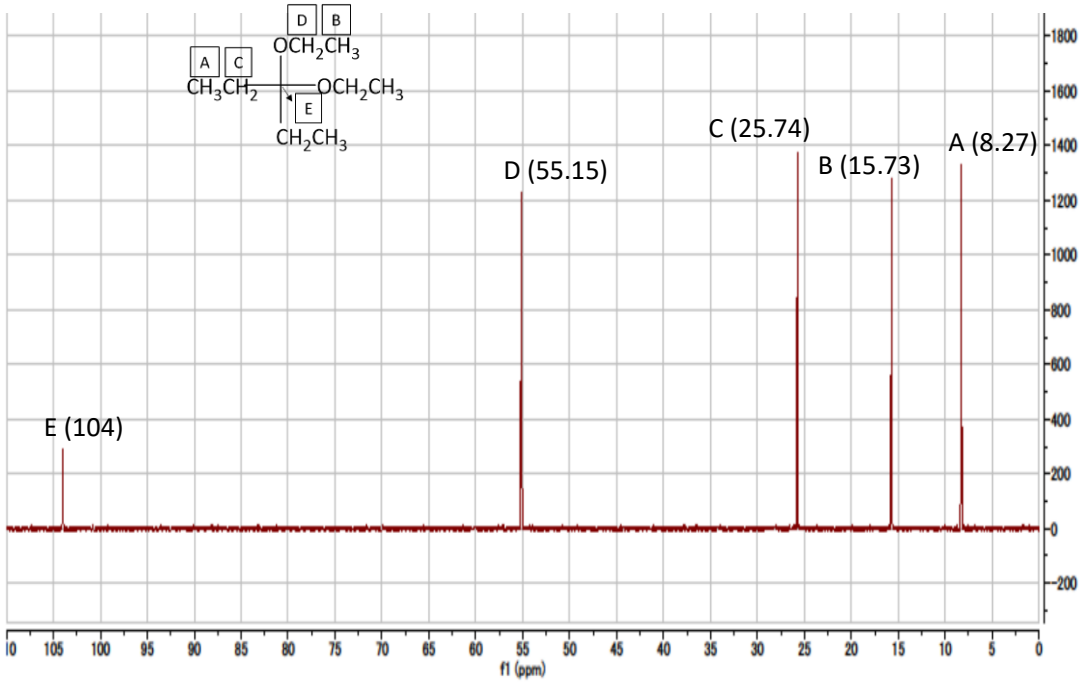


Fig. S11 ^{13}C{^{1}H} NMR of acetal **4** synthesized from **4a**

Table S19. Comparison of the direct synthesis of DEC based on previous reports and present work

No	Catalyst	Co-catalyst	Reaction condition				DEC (mmol)	Yield (%)	Ref.
			Dehydrating agent or reactant	CO_2 (MPa)	T (K)	Time (h)			
1	Bu_2SnO	–	–	5	433	24	n.d.	n.d.	This work
2	Bu_2SnO	$Sc(OTf)_3$	–	5	433	24	n.d.	n.d.	This work
3	–	–	2,2-diethoxypropane	5	433	24	0.01	0.1	This work
4	–	$Sc(OTf)_3$	2,2-diethoxypropane	5	433	24	0.12	1.1	This work
5	Bu_2SnO	–	2,2-diethoxypropane	5	433	24	1.59	15	This work
6	Bu_2SnO	$Sc(OTf)_3$	2,2-diethoxypropane	5	433	24	2.84	26	This work
7	Bu_2SnO	–	Tetraethyl orthosilicate (TEOS)	5	453	24	2.1	40	S1
8	Bu_2SnO	–	Triethyl orthoacetate	5	453	24	7.8	68	S1
9	$Zr(OEt)_4$	–	Tetraethyl orthosilicate (TEOS)	5	453	20	3.8	48	S2
10	CeO_2	–	2,2-diethoxypropane	5	393	4	0.8	4	S3
11	CeO_2	H-FAU	2,2-diethoxypropane	5	393	4	13.1	62	S3
12	CeO_2	–	Triethyl orthoacetate	5	433	24	6.3	64	S4
13	CeO_2	–	2-cyanopyridine	5	393	24	9.1	91	S5

Reference

S1 W. S. Putro, Y. Munakata, S. Shigeyasu, S. Hamur, S. Matsumoto, J. C. Choi and N. Fukaya, *Mendeleev Commun.*, 2022, **32**, 54–56.

S2 W. S. Putro, A. Ikeda, S. Shigeyasu, S. Hamura, S. Matsumoto, V. Y. Lee, J.-C. Choi and N. Fukaya, *ChemSusChem*, 2020, **14**, 842–846.

S3 T. Chang, M. Tamura, Y. Nakagawa, N. Fukaya, J.-C. Choi, T. Mishima, S. Matsumoto, S. Hamura and K. Tomishige, *Green Chem.*, 2020, **22**, 7321–7327.

S4 W. S. Putro, Y. Munakata, S. Ijima, S. Shigeyasu, S. Hamura, S. Matsumoto, T. Mishima, K. Tomishige, J.-C. Choi and N. Fukaya, *J. CO_2 Util.*, 2022, **55**, 101818.

S5 M. Honda, M. Tamura, Y. Nakagawa, K. Nakao, K. Suzuki and K. Tomishige, *J. Catal.*, 2014, **318**, 95–107.