Supporting information

Direct Conversion of C6 Sugars to Methyl Glycerate and Glycolate in Methanol

Lei Feng, Gang Li, Yueer Yan, Wenrong Hou, Yahong Zhang* and Yi Tang*
Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Laboratory of Advanced Materials, Collaborative Innovation Centre of Chemistry for Energy Materials (*i*ChEM), Fudan University, Shanghai 200433, China

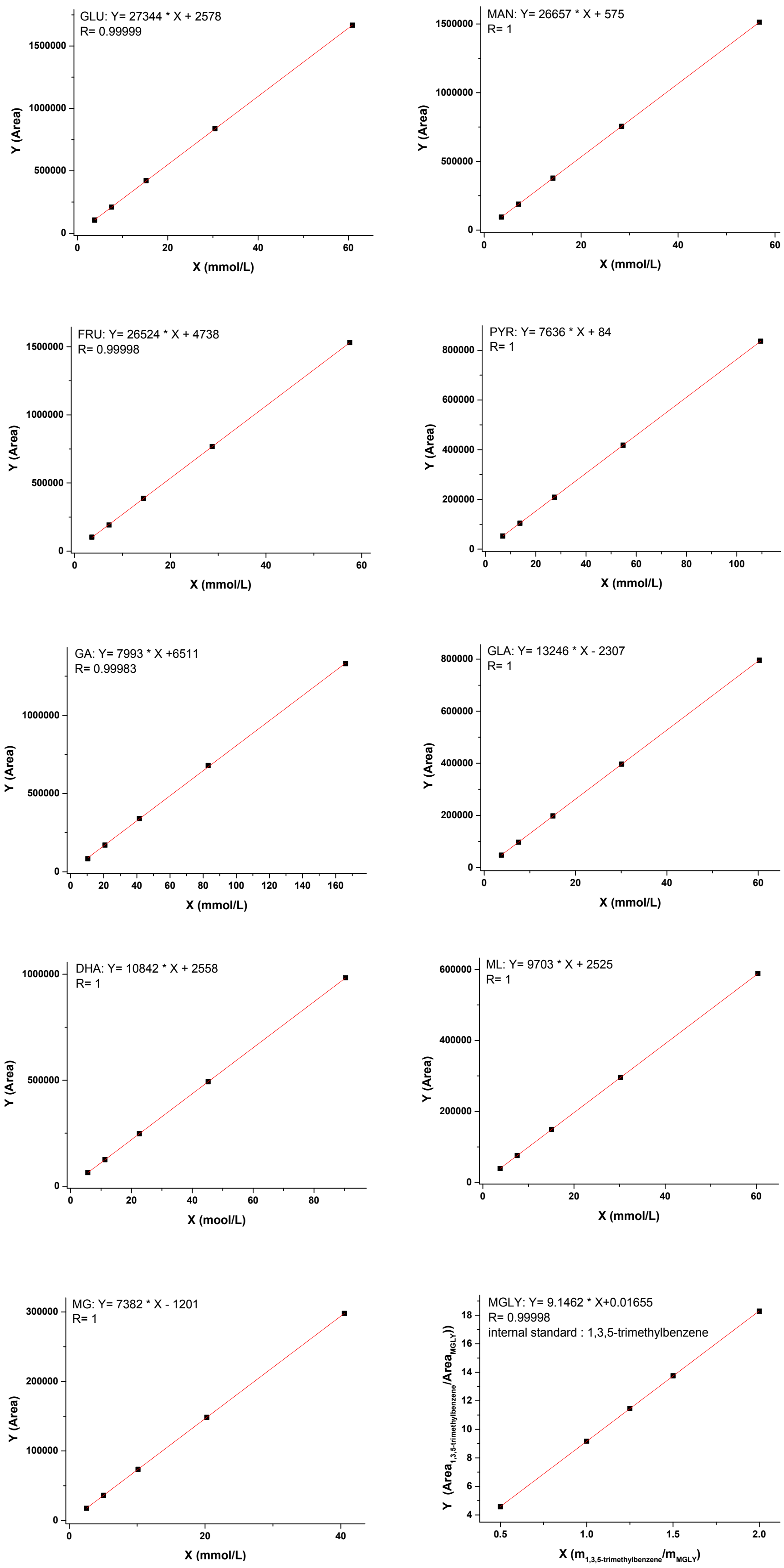


Fig. S1. Standard curves of all substrates and products

Table S1

Conversion of GA to MG catalyzed by different catalyst.

Cat.	t. (h)	Conv. (mol%)	Product yield (C mol%)		Carbon balance (mol%)
			Others	MG	
Pt/C	1	15.8	3.0	6.1	93.3
	2	31.9	13.7	7.4	89.2
Pd/C	1	45.3	5.8	33.6	94.1
	2	51.4	2.9	36.2	87.7
Ru/C	1	9.1	4.9	0	95.8
	2	16.2	7.6	0	91.4
Au/TiO_2	0.5	97.4	9.6	82.7	94.9
	1	98.8	5.5	84.8	91.5

Reaction condition: 50 mg of GA, 5 g of methanol, 100 mg of catalyst, 393 K, 1 MPa O_2. Yields of MG and others are calculated by carbon atom yield from GA. Carbon balance is calculated by [1 – Conv. + $Y_{\cdot MG}$ + $Y_{\cdot Others}$] × 100%, others: FRU, PYR, DHA.

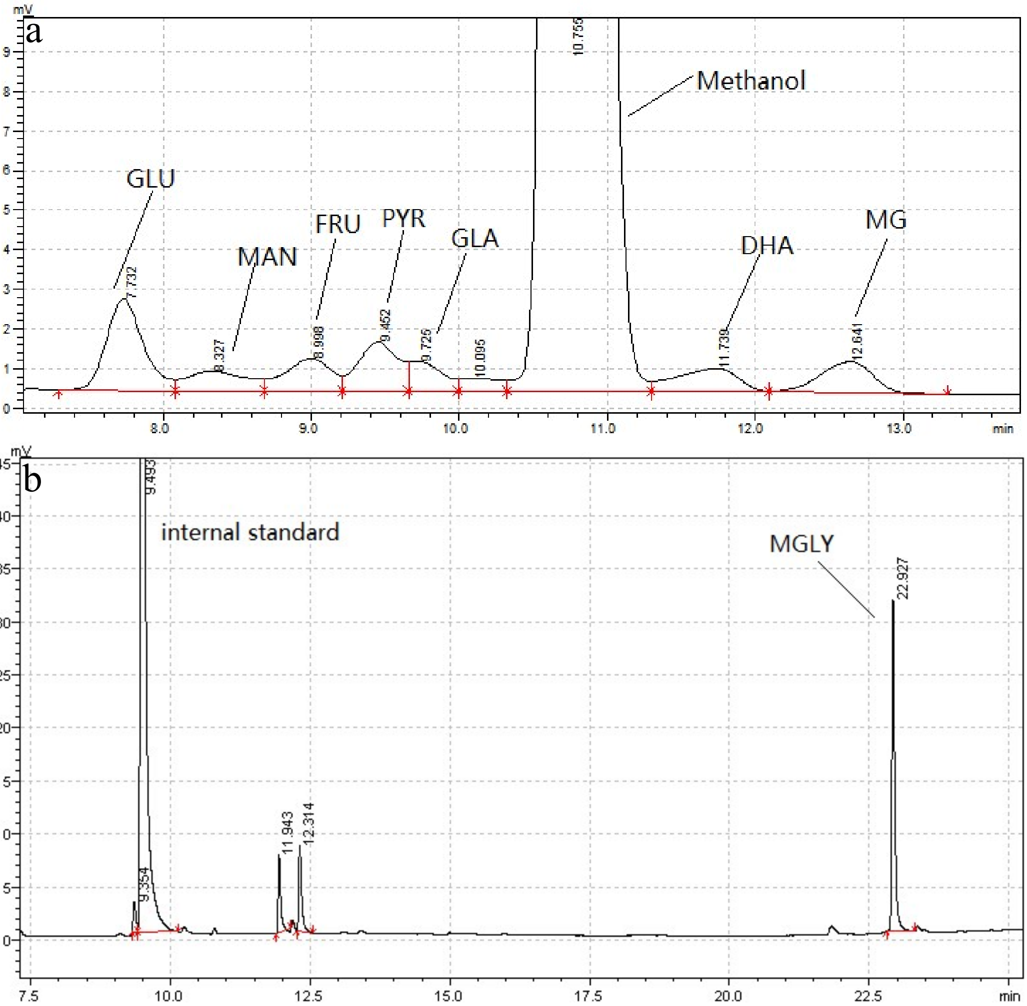


Fig. S2. HPLC (a) and GC (b) chromatograms of the reaction mixture of FRU in the presence of MoO_3 and Au/TiO_2. (reaction conditions: 50 mg of FRU, 5 g of methanol, 50 mg of MoO_3, 100 mg of Au/TiO_2 and 3 mg of K_2CO_3, 363 K, 1 MPa O_2, 5 h). Internal standard: 1,3,5-trimethylbenzene.

Table S2

Results and product distributions of FRU conversion in the presence of MoO_3 and Au/TiO_2.

T. (K)	t. (h)	Conv.$_{Retro-aldol}$ (mol%)	Product yield (C mol%)					Carbon balance (mol%)
			GLA	DHA	PYR+ML	MG	MGLY	
353	5	73.9	3.1	7.7	9.6	5.4	22.3	74.2
363	1	45.7	2.2	5.2	7.3	3.9	9.8	82.7
	3	72.4	3.6	7.1	7.6	7.1	20.9	73.9
	5	85.3	2.4	8.9	9.1	7.7	27.6	70.4
	6	87.2	1.7	8.2	10.7	7.8	27.4	68.6

Reaction condition: 50 mg of FRU, 5 g of methanol, 50 mg of MoO_3, 100 mg of Au/TiO_2 and 3 mg of K_2CO_3, 1 MPa O_2. Yields (Y.) of all products are calculated by carbon atom yield from FRU. Carbon balance is calculated by $[1 - \text{Conv.}_{Retro\text{-}aldol} + \text{Y.}_{GLA} + \text{Y.}_{DHA} + \text{Y.}_{PYR+ML} + \text{Y.}_{MG} + \text{Y.}_{MGLY}] \times 100\%$.

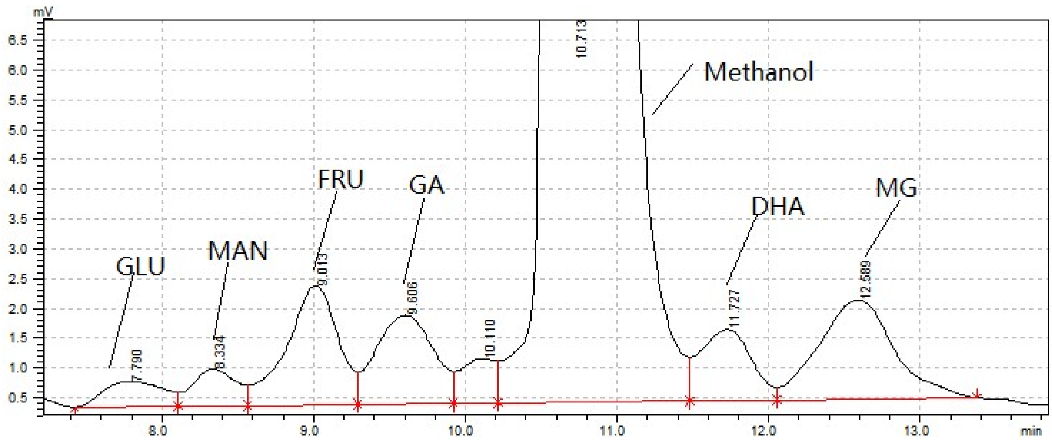


Fig. S3. HPLC chromatogram of the reaction mixture of MAN in the presence of MoO_3 and Au/TiO_2. (reaction conditions: 50 mg of MAN, 5 g of methanol, 37.5 mg of MoO_3, 80 mg of Au/TiO_2, 393 K, 1 MPa O_2, 5 h).

Table S3

Results and product distributions of MAN/GLU conversion in the presence of MoO_3 and Au/TiO_2.

Substrate	T. (K)	t. (h)	$Conv._{Retro\text{-}aldol}$ (mol%)	Product yield (C mol%)			Carbon balance (mol%)
				GA	DHA	MG	
MAN[a]	373	1	22.8	3.8	2.2	11.9	95.1
		2	41.9	8.9	3.1	21.4	91.5
		3	53.8	11.2	4.8	27.2	89.4
		4	55.2	5.2	7.5	31.2	88.7
		5	55.8	2.1	8.9	32.3	87.5
MAN[b]	393	1	72.5	17.2	9.1	24.2	78.0
		2	77.8	10.5	9.4	32.7	74.8
		3	79.7	8.2	9.2	36.2	73.9
		4	80.2	4.0	8.8	39.2	71.8
		5	80.3	3.7	8.9	38.4	70.7
GLU[c]	393	1	39.5	3.9	2.5	14.2	81.1
		2	50.8	4.9	5.0	18.8	77.9
		3	52.5	4.3	6.3	19.6	77.7
		4	54.2	3.1	4.4	21.0	74.3
		5	56.9	4.3	3.1	20.7	71.2

Reaction conditions [a]: 50 mg of MAN, 5 g of methanol, 50 mg of MoO_3, 100 mg of Au/TiO_2, 1 MPa O_2. Reaction conditions [b]: 50 mg of MAN, 5 g of methanol, 37.5 mg of MoO_3, 80 mg of Au/TiO_2, 1 MPa O_2. Reaction conditions [c]: 50 mg of GLU, 5 g of methanol, 50 mg of MoO_3, 100 mg of Au/TiO_2, 1 MPa O_2,. Yields (Y.) of all products are calculated by carbon atom yields from the original hexoses. Carbon balance is calculated by $[1 - Conv._{Retro\text{-}aldol} + Y._{MG} + Y._{GA} + Y._{DHA}] \times 100\%$.

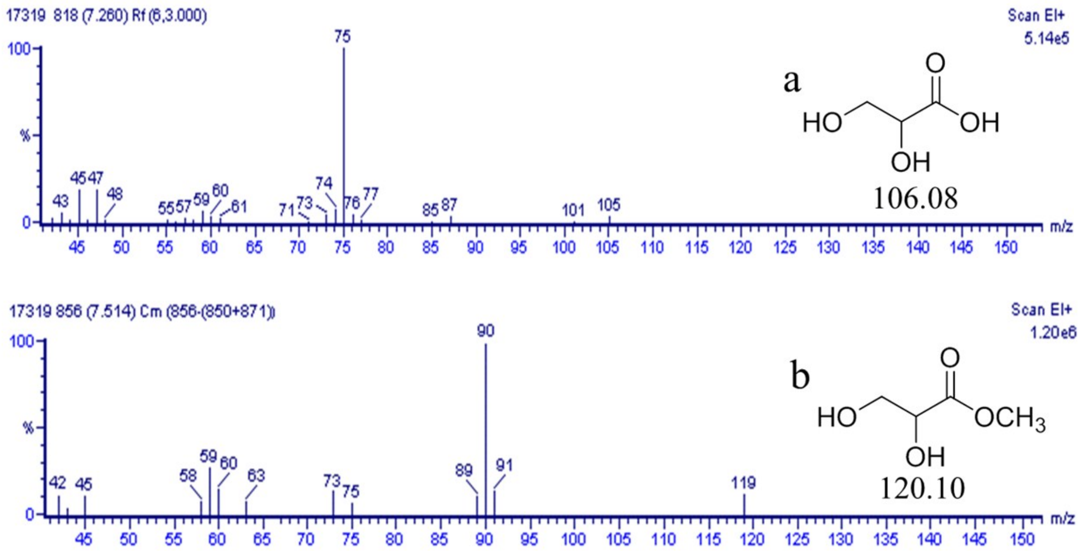


Fig. S4. GC-MS spectra of products from the conversion of FRU to MGLY. (a) glyceric acid, (b) MGLY.

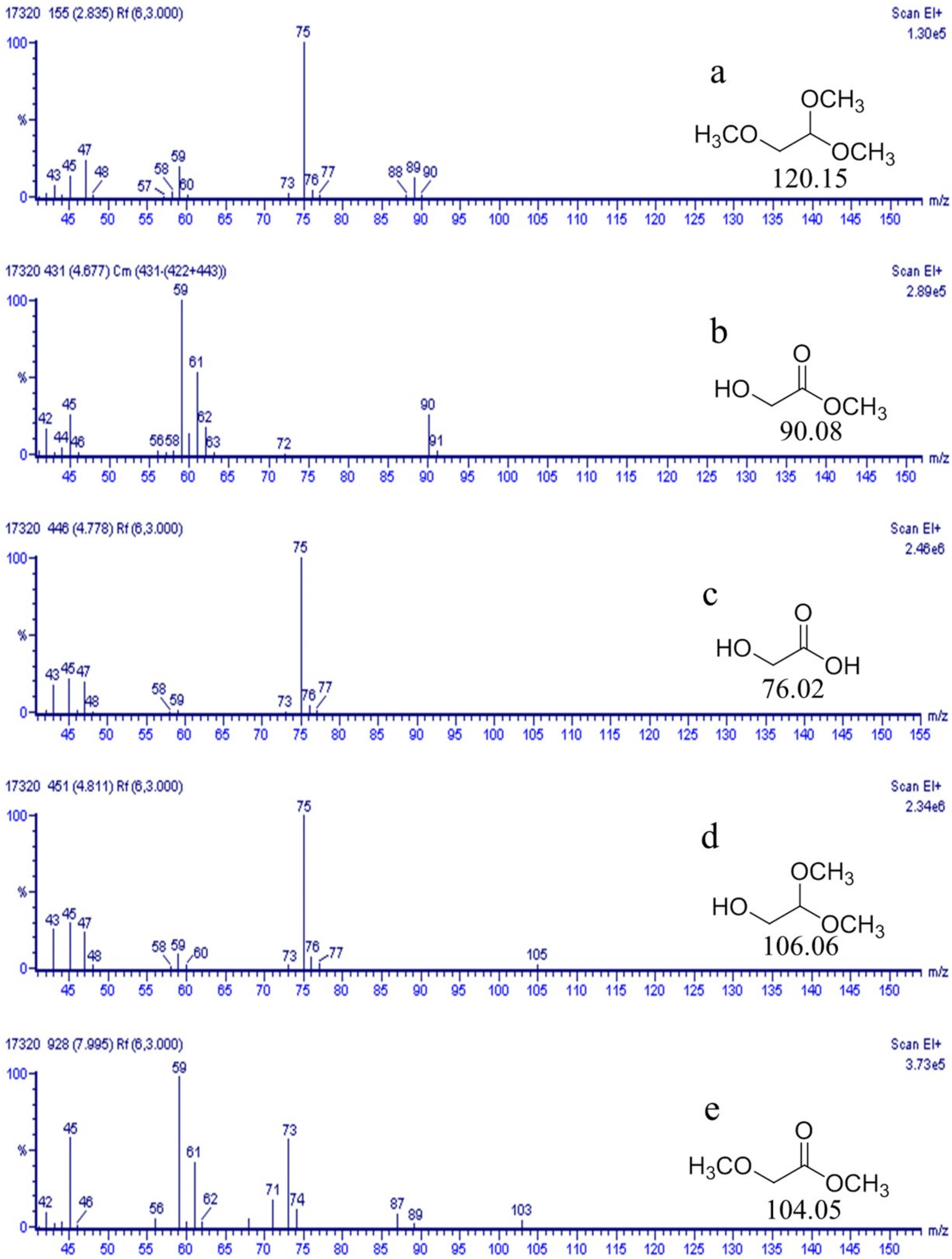
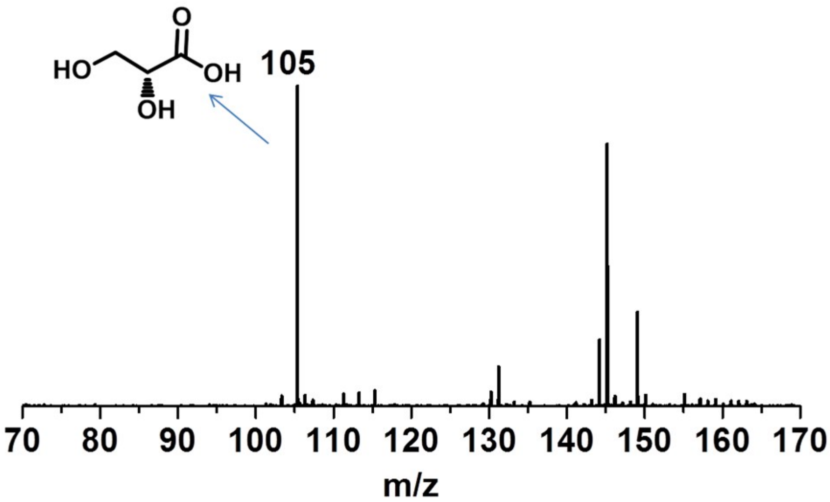


Fig. S5. GC-MS spectra of products from the conversion of MAN to MG. (a) 1,1,2-trimethoxyethane, (b) MG, (c) glycolic acid, (d) 2,2-dimethoxyethanol, (e) methyl methoxyglycolate.

a



b

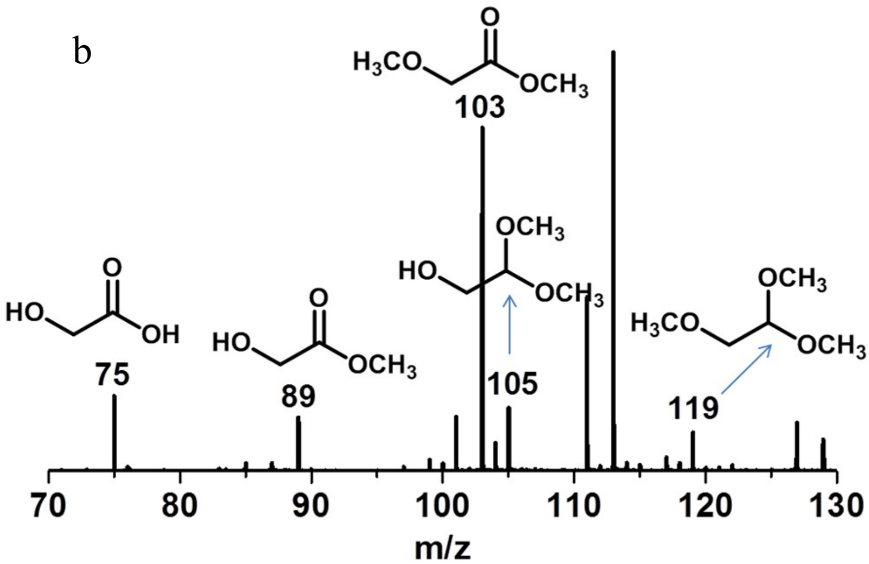


Fig. S6. MS spectra of the reaction solution of FRU (a) and MAN (b) conversion in methanol. Reaction conditions: (a) 50 mg of FRU, 5 g of methanol, 50 mg of MoO_3, 100 mg of Au/TiO_2 and 3 mg of K_2CO_3, 363 K, 1 MPa O_2, 4 h; Reaction conditions : (b) 50 mg of MAN, 5 g of methanol, 37.5 mg of MoO_3, 80 mg of Au/TiO_2, 393 K, 1 MPa O_2, 3 h.

Table S4

Conversion of FRU to GLA in methanol under different temperature.

T. (K)	t. (h)	$Conv._{Retro-aldol}$ (mol%)	Product yield (C mol%)		Carbon balance (mol%)
			PYR+ML+DHA	GLA	
353	1	17.2	0.0	0.8	83.6
	2	24.0	0.0	2.2	78.2
	3	33.8	0.0	3.5	69.7
363	1	30.7	8.2	2.8	80.3
	2	45.8	14.2	3.3	71.7
	3	47.6	12.7	3.3	68.4
373	1	40.2	11.1	4.8	75.7
	2	49.8	14.2	5.3	69.7
	3	52.5	13.9	5.2	66.6

Reaction condition: 50 mg of FRU, 5 g of methanol, 50 mg of MoO_3. Yields of products are calculated by carbon atom yield from FRU. Carbon balance is calculated by $[1 - Conv._{Retro\text{-}aldol} + Y._{GLA} + Y._{PYR+ML+DHA}] \times 100\%$.

Table S5

Conversion of GLA to MGLY in methanol under different temperature.

T. (K)	t. (h)	Conv. (mol%)	Product yield (C mol%)			Carbon balance (mol%)
			Others	DHA	MGLY	
353	1	68.8	14.1	9.3	40.9	95.5
	2	89.7	23.0	8.1	44.8	86.2
	3	94.3	26.5	6.5	44.5	83.2
363	1	79.1	23.9	7.9	41.3	94.0
	2	92.0	30.9	7.7	46.1	92.7
	3	96.1	32.2	6.1	47.3	89.5
373	1	88.1	35.6	3.2	41.5	92.2
	2	94.6	37.1	2.3	45.3	90.1
	3	98.2	37.9	0.8	48.2	88.7

Reaction condition: 50 mg of GLA, 5 g of methanol, 100 mg of Au/TiO_2, 1 MPa O_2. Yields of products are calculated by carbon atom yield from GLA. Carbon balance is calculated by [1 – Conv. + $Y_{\cdot MGLY}$ + $Y_{\cdot DHA}$ + $Y_{\cdot Others}$] × 100%, others: GLU, MAN, FRU, PYR, ML, MG.

Table S6

Direct conversion of MAN to GA in methanol under different temperature.

T. (K)	t. (h)	Conv.$_{Retro\text{-}aldol}$ (mol%)	Yield of GA (C mol%)	Carbon balance (mol%)
373	1	10.3	3.7	93.4
	2	25.4	17.2	91.8
	3	39.1	30.1	91.0
393	1	71.2	45.4	74.2
	2	73.6	38.6	65.0
	3	75.2	36.9	61.7

Reaction condition: 50 mg of MAN, 5 g of methanol, 50 mg of MoO_3. Yield of GA is calculated by carbon atom yield from MAN. Carbon balance is calculated by [1 – Conv.$_{Retro\text{-}aldol}$ + Y.$_{GA}$] × 100%.

Table S7

Conversion of GA to MG under different temperature.

T. (K)	t. (h)	Conv. (mol%)	Product yield (C mol%)		Carbon balance (mol%)
			Others	MG	
353	1	82.3	8.4	71.6	97.7
	2	95.4	9.3	78.2	92.1
	3	98.8	8.7	80.9	90.8
373	1	95.7	7.9	86.9	99.1
	2	96.3	4.9	88.7	97.3
	3	99.1	4.6	90.2	95.7
393	0.5	97.4	9.6	82.7	94.9
	1	98.8	5.5	84.8	91.5
	1.5	98.8	5.3	81.1	87.6
413	0.5	98.2	6.9	78.3	87.0
	1	99.7	2.1	72.4	74.8
	1.5	100.0	0.0	68.7	68.7

Reaction condition: 50 mg of GA, 5 g of methanol, 100 mg of Au/TiO_2, 1 MPa O_2. Yields of MG and others are calculated by carbon atom yield from GA. Carbon balance is calculated by $[1 - \text{Conv.} + Y_{\cdot MG} + Y_{\cdot Others}] \times 100\%$, others: FRU, PYR, DHA.

Table S8

Conversion of MAN to MG catalyzed by MoO_3.

Cat.	t. (h)	$Conv._{Retro\text{-}aldol}$ (mol%)	Product yield (C mol%)			Carbon balance (mol%)
			DHA	GA	MG	
MoO_3	1	65.2	3.4	39.7	0.9	78.8
	3	73.6	5.5	32.6	2.8	77.3
	5	77.5	8.4	29.7	8.9	69.5
	9	92.9	8.3	17.3	10.8	43.5

Reaction condition : 50 mg of MAN, 5 g of methanol, 50 mg of MoO_3, 1 MPa O_2, 393 K; Yields (Y.) of all products are calculated by carbon atom yields from the mannose and the corresponding carbon balance is calculated by $[1 - Conv._{Retro\text{-}aldol} + Y._{DHA} + Y._{GA} + Y._{MG}] \times 100\%$.

Table S9

Effect of mass ratio of MoO_3 to Au/TiO_2 on the yield of MGLY in methanol.

MoO_3:Au/TiO_2 (mg:mg)	$Conv._{Retro\text{-}aldol}$ (mol%)	$Y._{MGLY}$ (C mol%)	$Selec._{MGLY}$ (C mol%)	Carbon balance (mo%)
50:50	83.2	21.2	25.5	68.5
50:100	85.3	27.6	32.4	70.4
25:100	53.4	18.1	33.9	90.3

Reaction condition: 50 mg of FRU, 5 g of methanol, 3 mg of K_2CO_3, 363 K, 1 Mpa O_2, 5 h. Yield (Y.) of MGLY is calculated by carbon atom yield from FRU. Selectivity (Selec.) of MGLY is calculated by $Y._{MGLY}/Conv._{Retro\text{-}aldol} \times 100\%$. Carbon balance is calculated by $[1 - Conv._{Retro\text{-}aldol} + Y._{MGLY} + Y._{others}] \times 100\%$, others: GLA, DHA, PYR, ML.

Table S10

Effect of mass ratio of MoO_3 to Au/TiO_2 on the yield of MG in methanol.

MoO_3:Au/TiO_2 (mg:mg)	$Conv._{Retro\text{-}aldol}$ (mol%)	$Y._{MG}$ (C mol%)	$Selec._{MG}$ (C mol%)	Carbon balance (mol%)
50.0:100	80.1	37.1	46.3	65.0
37.5:100	79.5	36.2	45.5	70.0
25.0:100	77.4	28.9	37.3	65.4
12.5:100	74.3	27.7	37.2	71.5
37.5:80	80.2	39.2	48.9	71.8
37.5:60	72.9	28.2	38.7	73.7
37.5:40	73.6	23.2	31.5	76.8

Reaction condition: 50 mg of MAN, 5 g of methanol, 393 K, 1 Mpa O_2, 4 h. Yield (Y.) of MG is calculated by carbon atom yield from MAN. Selectivity (Selec.) of MG is calculated by $Y._{MG}/Conv._{Retro\text{-}aldol} \times 100\%$. Carbon balance is calculated by $[1 - Conv._{Retro\text{-}aldol} + Y._{MG} + Y._{GA} + Y._{DHA}] \times 100\%$.

Table S11

Effect of FRU concentration on the yield of MGLY in methanol.

C_{FRU} (wt%)	$Conv._{Retro\text{-}aldol}$ (mol%)	$Y._{MGLY}$ (C mol%)	$Selec._{MGLY}$ (C mol%)	Carbon balance (mol%)
1.0	85.3	27.6	32.4	70.4
2.0	79.7	25.2	31.6	74.8
5.0	75.3	21.7	28.8	71.6
10.0	68.9	18.3	26.6	79.7

Reaction condition: 5 g of methanol, 50 mg of MoO_3, 100 mg of Au/TiO_2, 3 mg of K_2CO_3, 363 K, 1 Mpa O_2, 5 h. Yield (Y.) of MGLY is calculated by carbon atom yield from FRU. Selectivity (Selec.) of MGLY is calculated by $Y._{MGLY}/Conv._{Retro\text{-}aldol} \times 100\%$. Carbon balance is calculated by $[1 - Conv._{Retro\text{-}aldol} + Y._{MGLY} + Y._{others}] \times 100\%$, others: GLA, DHA, PYR, ML.

Table S12

Effect of MAN concentration on the yield of MG in methanol.

C_{MAN} (wt%)	$Conv._{Retro\text{-}aldol}$ (mol%)	$Y._{MG}$ (C mol%)	$Selec._{MG}$ (C mol%)	Carbon balance (mol%)
1.0	80.2	39.2	48.9	71.8
2.0	75.7	39.8	52.6	78.7
5.0	72.5	29.1	40.1	70.7
10.0	63.9	20.7	32.4	72.6

Reaction condition: 5 g of methanol, 37.5 mg of MoO_3, 80 mg of Au/TiO_2, 393 K, 1 Mpa O_2, 4 h. Yield (Y.) of MG is calculated by carbon atom yield from MAN. Selectivity (Selec.) of MG is calculated by $Y._{MG}/Conv._{Retro\text{-}aldol} \times 100\%$. Carbon balance is calculated by $[1 - Conv._{Retro\text{-}aldol} + Y._{MG} + Y._{GA} + Y._{DHA}] \times 100\%$.

Table S13

Reuse of MoO_3 and Au/TiO_2 catalysts.

Reuse	$Conv._{Retro-aldol}$ (mol%)	$Y._{GA}$ (C mol%)	$Y._{MG}$ (C mol%)	$Selec._{MG}$ (C mol%)	Carbon balance (mol%)
1st	80.2	4.0	39.2	48.9	71.8
2nd	74.4	5.5	37.5	50.4	78.9
3rd	70.3	4.9	34.2	48.6	78.5
4th	71.6	6.7	30.7	42.9	75.1

Reaction condition: 100 mg of MAN, 5 g of methanol, 37.5 mg of MoO_3, 80 mg of Au/TiO_2, 393 K, 1 Mpa O_2, 4 h. Yield (Y.) of MG is calculated by carbon atom yield from MAN. Selectivity (Selec.) of MG is calculated by $Y._{MG}/Conv._{Retro\text{-}aldol} \times 100\%$. Carbon balance is calculated by $[1 - Conv._{Retro\text{-}aldol} + Y._{MG} + Y._{GA} + Y._{DHA}] \times 100\%$.

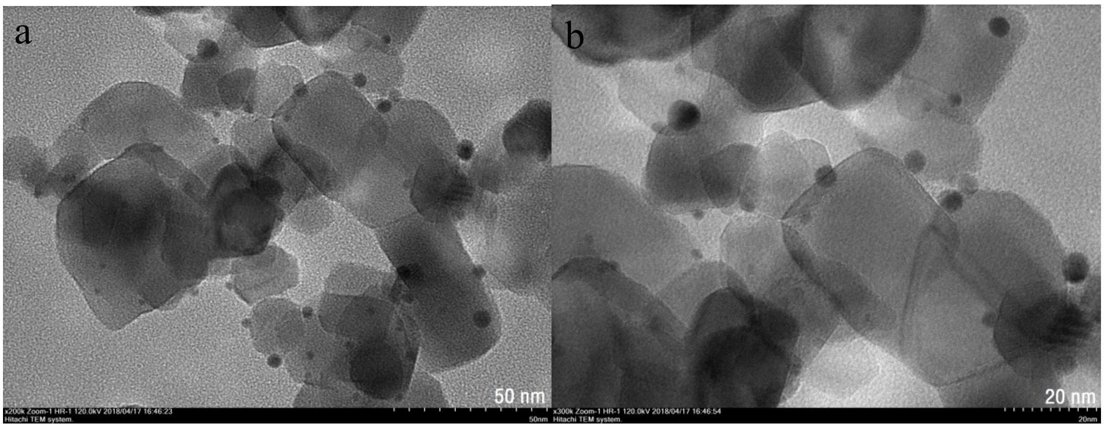


Fig. S7. TEM images of Au/TiO_2 catalyst after the fourth cycle.

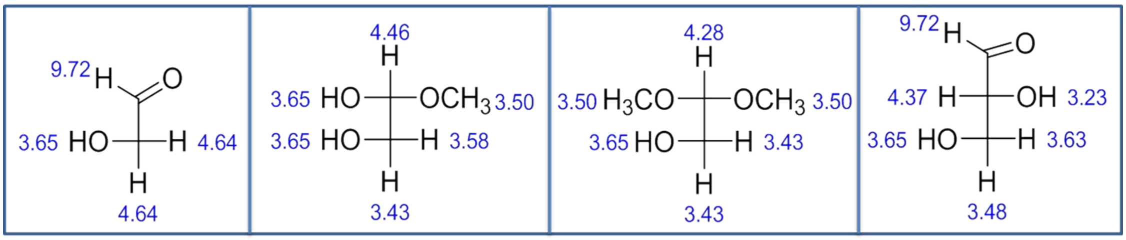


Fig. S8. Predict of ^{1}H-NMR shifts of GA and its hemiacetal, acetal as well as GLA.

Table S14

Conversion of GA in methanol.

time [min]	$Con._{GA}$ in HPLC [mol %]	Acetal product inGC [C mol %]
40	5.5	82.1
80	2.7	94.4

Reaction condition: 100 mg of GA, 5 g of methanol, 463 K.