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Supplementary Information

Formic Acid Disproportionation into Formaldehyde Trigged by Vanadium Complexes with Iridium Catalysis Under Mild Conditions in the N-methylation

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1. General Information

Ir-catalysts **2**[1], **2a**[2], Rh-catalyst **2b**[3] and compound **5**[4] were prepared according to the reported procedure. Deionized water was used for the reactions. Wheat straw was afforded by Institute of Pulp and Paper Technology, Hubei University of Technology, China. If no special indication, other reagents and solvents were used as commercially available without further purification. All the reactions were carried out by using standard Schlenk techniques under argon atmosphere in a Wattcas Thermal Parral Reactor. Column chromatographic purification of products was accomplished using 200-300 mesh silica gel. pH values were measured on an Leici PHS-25 pH meter with a glass electrode after calibration with standard buffer solutions. The ^{1}H NMR yields of formic acid (HCO_2H) after hydrolysis-oxidation were determined by using 1,4-dioxane as an internal standard. NMR spectra were measured on a Bruker Avance-400 spectrometer in the solvents indicated. Chemical shifts are reported in units (ppm) by assigning TMS resonance in the ^{1}H NMR spectrum as 0.00 ppm, $CDCl_3$ resonance in the ^{13}C NMR spectrum as 77.0 ppm. DMSO resonance in the ^{13}C NMR spectrum as 39.5 ppm. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). Mass spectra were taken at Thermo Trace 1300 gas chromatograph mass spectrometer and a TR-5MS column (0.25 mm × 30 m, Film: 0.25 μm). Error bars were calculated by dividing the range between the maximum and the minimum value by the average value.

Table S1. Components of the wheat straw

Material[a]	H_2O %	Ash %	Extraction %	Glucose %	Xylose %	Galactose %	Arabinose %	Mannose %	Cellulose %[c]	Hemicellulose %[d]	Lignin %	Element % (C)
Wheat straw[b]	2.31	5.51	13.41	41.19	14.07	1.15	0.00	0.97	41.19	16.19	18.26	43.84

[a] Wheat straw was prepared into 200 mesh. The components were analyzed according to NREL/TP-510-42618 method.[5] Cellulose contents were calculated based on the amount of glucose. Hemicellulose contents were calculated based on the amount of xylose, galactose, arabinose and mannose. [b] Extracted content is determined according to GB/T 2677.5-93 method.[6] [c] Reported as an average of three times analysis data analysis with an error margin of 3%. [d] Reported as an average of three times analysis data with an error margin of 5%.

2.1. The procedure of hydrolysis-oxidation of the wheat straw or glucose[7]

The wheat straw or glucose (containing 18 mmol or 54 mmol C-atoms of ploysaccharides), $NaVO_3$ (3.5 mol%), 0.7 wt% H_2SO_4 aqueous solution (30.00 mL/18 mmol C-atoms of polysaccharides), DMSO (1 v%) were added into an Erlenmeyer flask (150 mL) charged with a stirring bar. The flask was installed with a cap containing a small hole (0.7 cm diameter) to connect with air (the function of the cap is to avoid the volatilization of the produced HCO_2H). The reaction mixture was stirred at room temperature for about 30 min until all the $NaVO_3$ was dissolved. Meanwhile the sleeve of the autoclave was preheated for 20-30 min to 160 °C. The flask was put into the autoclave (500 mL, 7.5 cm inner diameter) prefilled with water (250 mL, to avoid the corrosion of the autoclave by the acid). Then the autoclave was charged with air or oxygen (3 MPa, used for the wheat straw containing 18 mmol C-atoms of ploysaccharides or 54 mmol C-atoms of polysaccharides, respectively). The mixture was stirred with 1000 rpm stirring rate and heated up to 160 °C (inner temperature, ± 0.5 °C) with the heating rate of 5-6 °C/ min in about 20-30 min (notably, lower reaction yields were obtained with faster or slower heating rate). Then the reaction mixture was stirred at 160 °C (inner temperature, ± 0.5 °C) for another 3 h. The autoclave was cooled by water to room temperature and the pressure was released carefully. 1,4-dioxane was added as an internal standard for the detection of ^{1}H NMR yields of the generated HCO_2H. HCO_2H was obtained in 95% yield based on the average of several experiments during all of the hydrolysis-oxidation experiments.

2.2. Procedure for prepared [V] (5 mol% or 10 mol%) by a 10 mins hydrolysis-oxidation of glucose with $NaVO_3$ as a catalyst precursor[7]

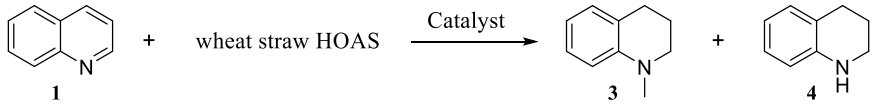
1) The glucose (0.3 mmol, 54.6 mg, containing 1.8 mmol C-atoms of ploysaccharides), $NaVO_3$ (0.066 mmol, 8.13 mg, 3.5 mol%), 0.7 wt% H_2SO_4 aqueous solution (3.00 mL/1.8 mmol C-atoms of polysaccharides), DMSO (1 v%, 0.031 mL) were added into a tube (25 mL) charged with a stirring bar. The reaction mixture was stirred at room temperature for about 30 mins until all the $NaVO_3$ was dissolved. Meanwhile the sleeve of the autoclave was preheated for 20-30 min to 160 °C. The flask was put into the autoclave (60 mL, 3.0 cm inner diameter) prefilled with water (3 mL, to avoid the corrosion of the autoclave by the acid). Then the autoclave was charged with oxygen (3 MPa). The mixture was stirred with 1200 rpm stirring rate

and heated up to 160 °C (inner temperature, ± 0.5 °C) with the heating rate of 8-10 °C/ min in about 10-15 min. Then the reaction mixture was stirred at 160 °C (inner temperature, ± 0.5 °C) for another 10 mins. The autoclave was cooled by water to room temperature and the pressure was released carefully. 3 mL of blue clear aqueous solution was obtained. 1,4-dioxane was added as an internal standard for the detection of ^{1}H NMR yield of the generated HCO_2H. HCO_2H was obtained in 40% yield based on the average of several experiments.

0.6 mL solution (contains 0.013 mmol [V] complexes) from the resulting glucose HOAS (3 mL) is used for the experiments for the N-methylation of **4** (0.25 mmol), the amount of [V] complexes are 5 mol% (Table 1, entry 5).

2) 1.2 mL solution (contains 0.026 mmol [V] complexes) from the resulting glucose HOAS (3 mL) is used for the experiments for the N-methylation of **4** (0.25 mmol), the amount of [V]) complexes are 10 mol% (Table 1, entry 6). 37.2 mL solution (contains 0.774 mmol [V] complexes) from the resulting glucose HOAS (according to the above procedure to repeat the experiments for 13 times to accumulate the [V] complexes) for the N-methylation of **1** (7.74 mol) (Figure 6 Eq. (1)).

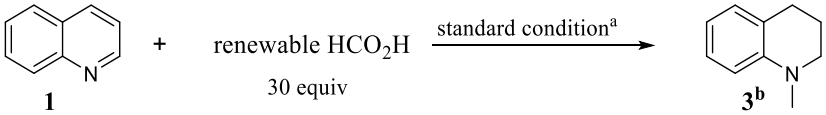
Table S2. Optimization of the reaction conditions.



Entry[a]	Catalyst (mol%)	Renewable HCO_2H (equiv)	T (°C)	Time (h)	**3**[b]	**4**[b]
1	**2** (0.5)	8	60	24	30	60
2	**2** (0.5)	12	60	24	45	49
3	**2** (1.0)	24	60	20	74	15
4	**2** (1.0)	30	60	20	91	—
5	**2** (1.0)	30	50	20	91(91)[c]	—
6	**2** (1.0)	30	50	15	86	—
7	**2** (0.5)	30	50	48	86	—

Reaction conditions: [a]quinoline **1** (0.25 mmol, 32.3 mg), **2**, renewable HCO_2H was prepared by the hydrolysis-oxidation of the wheat straw. [b]Yields were determined by ^{1}H NMR using $Cl_2CHCHCl_2$ as an internal standard. [c]Isolated yield.

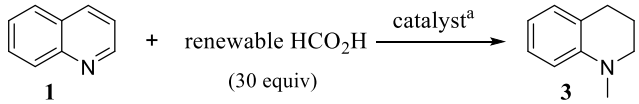
Table S3. The utilization rate of the HCO_2H.

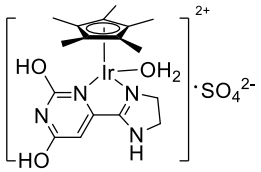


[a]Reaction conditions: quinoline **1** (0.25 mmol, 32.3 mg), **2** (1.0 mol%), 50 °C, 20 h. Renewable HCO_2H was prepared by the hydrolysis-oxidation of the wheat straw (contained HCO_2H 7.5 mmol). [b] It takes five molecules of HCO_2H to form one molecule of **3**.

$$\text{The utilization rate of HCOOH (\%)} = \frac{n_{(\text{consumed HCOOH})}}{n_{(\text{total HCOOH})}} = \frac{1.25\ \text{mmol} \times 0.91}{7.5\ \text{mmol}} = 15\%$$

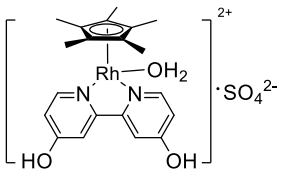
Table S4. Investigation of the catalytic activity of other catalysts.





2a

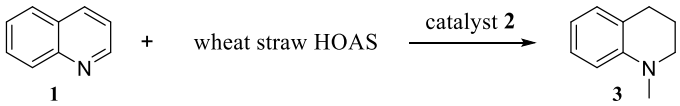
Entry[a]	Catalyst (mol%)	**3**
1	**2a** (1)	40
2	**2b** (1)	—
3	$(RhCp^*Cl_2)_2$ (1)	—
4	$[RuCl_2(benzene)]_2$ (0.5)/dppe (1)	—
5	$RuCl_3$ (1)/*m*-TPPTs (0.5)	—
6	$Fe(BF_4)_2$ (1)/$(Ph_2PCH_2CH_2)_3P$ (1)	—



2b

[a]The renewable HCO_2H was prepared by the hydrolysis-oxidation of the wheat straw. **1** (0.25 mmol), catalyst (1.0 mol%). Yields were determined by ^{1}HNMR using $Cl_2CHCHCl_2$ as an internal standard.

Table S5. Investigate the effect of pH on the activity of HCO_2H disproportionation.

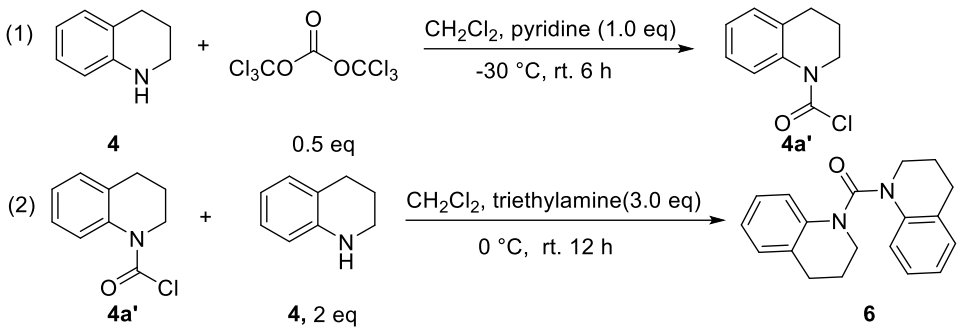


Entry[a]	pH[b]	**3** (%)[c]
1	0.90	88
2	2.25	91
3	2.50	90
4	3.00	52
5	3.30	20
6	3.50	7
7	4.00	—

Reaction conditions: [a]quinoline **1** (0.25 mmol, 32.3 mg), **2** (1.0 mol%), 50 °C. Renewable HCO_2H was prepared by the hydrolysis-oxidation of the wheat straw (contained HCO_2H 7.5 mmol). [b]pH of the solution was adjusted by NaOH aqueous solution (2 mol/L). [c]Yields were determined by ^{1}H NMR using $Cl_2CHCHCl_2$ as an internal standard.

Mechanistic studies

3. Procedure for the synthesis of compound 6[8]



A 100 mL two-necked flask with a magnetic stirring bar was evacuated and backfilled with argon for three times. Triphosgene (1.8 mmol, 534.1 mg) and CH_2Cl_2 (15.0 mL) were added to the flask. The mixture was cooled at –30 °C and dry pyridine (321.8 µL) was slowly added to the flask (*Caution: highly toxic phosgene was generated*). After stirring for 15 min at –30 °C, **4** (4.0 mmol, 532.8 mg) was slowly added to the mixture. The mixture was warmed to room temperature and stirred for 6 h at room temperature. The reaction mixture was carefully quenched by 1N HCl (10.0 mL) and was extracted with CH_2Cl_2 (5.0 mL x 3). The organic layer was washed with water and brine, then dried over $MgSO_4$. After the filtration, the solution was concentrated. The resulted residue was purified by silica gel column chromatography to afford **4a′**, which was used quickly for the next step.

A 100 mL two-necked flask with a magnetic stir bar was evacuated and backfilled with argon for three times. **4** (1.0 mmol, 133.19 mg) and CH_2Cl_2 (15.0 mL) were added to the flask. The mixture was cooled at 0 ℃ and dry triethylamine (416.0 µL) was slowly added to the flask. After stirring for 15 min at 0 ℃, **4a′** (0.5 mmol, 97.8 mg) was slowly added to the mixture. The mixture was warmed to room temperature and stirred for 12 h at 40 ℃. The solution was concentrated and the resulted residue was purified by silica gel column chromatography. Further purification was carried out by recrystallization in hexane. The solid was collected by filtration to afford **6** (100.0 mg, 90% yield) as a crystalline white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.0 Hz, 1H), 7.03 (dd, *J* = 16.0, 7.8 Hz, 2H), 6.89 (t, *J* = 7.4 Hz, 1H), 3.54 (s, 2H), 2.75 (t, *J* = 6.8 Hz, 2H), 1.98–1.92 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 139.5, 128.9, 128.5, 126.2, 122.7, 121.01, 77.3, 77.0, 76.7, 45.7, 26.9, 23.4; IR (cm^{-1}): v 2944, 2921, 2886, 2854, 1653, 1601, 1579, 1489, 1360, 1287, 1193, 754. HRMS (EI): m/z: $[M+H]^+$ calculated for $C_{19}H_{20}N_2O$, 293.1648, found 293.1650.

4.1 The procedure of Eq. 1 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **1** (0.25 mmol, 32.3 mg), **2** (2.5 µmol, 1.6 mg), wheat straw HOAS with a pH value of 2.25 (contained 30.0 equiv of HCO_2H, 12.5 mL based on the 95% yield of HCO_2H) were added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for 3 times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 5 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (91%) was determined by ^{1}H NMR using $Cl_2CHCHCl_2$ as an internal standard.

4.2 The procedure of Eq. 2 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **1** (0.25 mmol, 32.3 mg), **2** (2.5 µmol, 1.6 mg), HCO_2H (0.625 mmol, 2.5 equiv) were added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 5 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **4** (90%) was determined by ^{1}H NMR by applying $Cl_2CHCHCl_2$ as an internal standard.

4.3 The procedure of Eq. 3 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **1** (0.25 mmol, 32.3 mg), **2** (2.5 μmol, 1.6 mg), wheat straw HOAS with a pH value of 2.25 (contained 2.5 equiv of HCO_2H, 2.2 mL based on the 95% yield of HCO_2H) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 5 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yields of **4** (89%) and **3** (5%) were determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

4.4 The procedure of Eq. 4 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), wheat straw HOAS with a pH value of 2.25 (contained 2.5 equiv of HCO_2H, 2.2 mL based on the 95% yield of HCO_2H) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for 3 times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 5 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yields of **3** (25%) were determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

4.5 The procedure of Eq. 5 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), wheat straw HOAS with a pH value of 2.25 (contained 30.0 equiv of HCO_2H, 12.5 mL based on the 95% yield of HCO_2H) were added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 5 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (88%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

4.6 The procedure of Eq. 6 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 5 h. The Schlenk tube was cooled by water to room temperature. No product was detected in this reaction.

4.7 The procedure of Eq. 7 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **5** (0.25 mmol, 80.6 mg), **2** (2.5 μmol, 1.6 mg), wheat straw HOAS with a pH value of 2.25 (contained 30.0 equiv of HCO_2H, 12.5 mL based on the 95% yield of HCO_2H) was added, separately. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. No product was detected in this reaction.

4.8 The procedure of Eq. 8 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **6** (0.25 mmol, 73.3 mg), **2** (2.5 μmol, 1.6 mg), wheat straw HOAS with a pH value of 2.25 (contained 30.0 equiv of HCO_2H, 12.5 mL based on the 95% yield of HCO_2H) was added, separately. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. No product was detected in this reaction.

4.9 The procedure of Eq. 9 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (0.375 mmol, 1.5 equiv), CH_2O (0.275 mmol, 1.1 equiv, aqueous solution) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (46%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

4.10 The procedure of Eq. 10 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), CH_2O (0.275 mmol, 1.1 equiv, aqueous solution) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (49%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

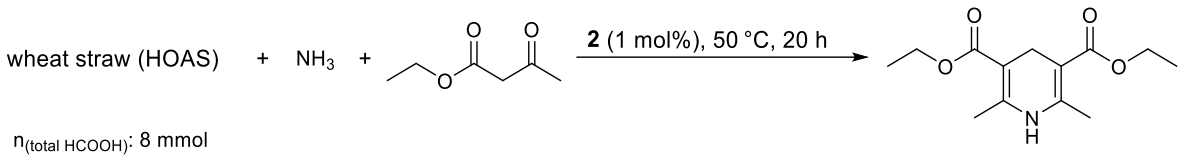
4.11 The procedure of Eq. 11 in Fig. 2

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (0.375 mmol, 1.5 equiv), CH_2O (0.5 mmol, 2 equiv, aqueous solution) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (64%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

5. The procedure of formaldehyde capture experiment [9]

(1) To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, ammonia (16 mmol, aqueous solution, 1.1 mL), acetoacetic ester (2 mmol, 260.3 mg), **2** (2.5 μmol, 1.6 mg), wheat straw HOAS contained HCO_2H (8 mmol) with the pH value of 2.25 was added to the reactor tube. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. The solution was detected by ^1H NMR (400 MHz, D_2O). 30% of the HCO_2H (2.4 mmol) is consumed in the system. 70% of the HCO_2H (5.6 mmol) is converted to ammonium formate (HCO_2NH_4). Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated and crude product was purified by silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford **7** (194.8 mg, 77% yield) as a crystalline white solid. ^1H NMR (400 MHz, DMSO) δ 8.28 (s, 1H), 4.08–4.02 (m, 4H), 3.11 (s, 2H), 2.11 (s, 6H), 1.18 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, DMSO) δ 167.1, 146.5, 97.0, 58.9, 24.7, 17.9, 14.4. The methandiol $CH_2(OH)_2$, the major form of CH_2O in aqueous solution, contained in the wheat straw HOAS (0.28 mmol, based on the average of 3.5 mol% $CH_2(OH)_2$ accompanying with per mol of HCO_2H) is deducted, the conversion rate of HCO_2H to formaldehyde is 41%.

Calculation of the conversion rate of HCO_2H to CH_2O:



$n_{(total\ HCOOH)}$: 8 mmol

$n_{(methandiol\ contained\ in\ the\ wheat\ straw\ HOAS)}$: 0.28 mmol

$n_{(caputured\ HCHO)}$: **7**, 77 % (0.77 mmol)

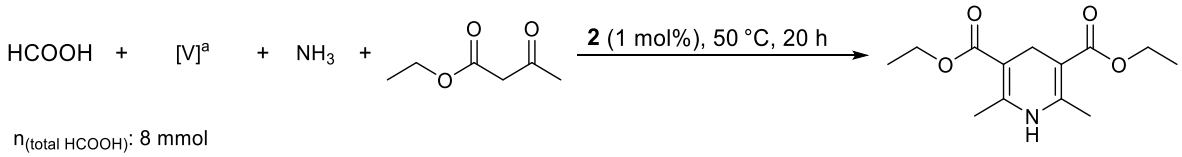
$2HCOOH^{a} \longrightarrow CH_2O + CO_2 + H_2O$

[a] It takes two molecules of formic acid to form one molecule of formaldehyde.

$$\text{The conversion rate of HCOOH to HCHO (\%)} = \frac{n_{(caputured\ HCHO)} - n_{(methandiol\ contained\ in\ the\ wheat\ straw\ HOAS)}}{n_{(total\ HCOOH)} - n_{(residual\ HCOOH)}} \times 2$$
$$= \frac{0.77\ mmol - 0.28\ mmol}{8\ mmol\ - 5.6\ mmol} \times 2 = 41\%$$

(2) To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, ammonia (16 mmol, aqueous solution, 1.1 mL), acetoacetic ester (2 mmol, 260.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (8 mmol), with the pH value of 2.25 was added to the reactor tube[V] solution from wheat straw HOAS with the pH value of 2.25 was added to the reactor tube. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. The solution was detected by ^1H NMR (400 MHz, D_2O). 28% of the HCO_2H (2.24 mmol) is consumed in the system. 72% of the HCO_2H (5.76 mmol) is converted to ammonium formate (HCO_2NH_4). Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solution was concentrated and crude product was purified by silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford **7** (58.2 mg, 23% yield) as a crystalline white solid, the conversion rate of HCO_2H to formaldehyde is 21%.

Calculation of the conversion rate of HCO_2H to CH_2O:



$n_{(total\ HCOOH)}$: 8 mmol

$n_{(caputured\ HCHO)}$: **7**, 23 % (0.23 mmol)

$2HCOOH^{b} \longrightarrow CH_2O + CO_2 + H_2O$

[a] The wheat straw HOAS was extracted by EtOAc to remove HCOOH and the other minor components to afford the [V] solution.

[b] It takes two molecules of formic acid to form one molecule of formaldehyde.

$$\text{The conversion rate of HCOOH to HCHO (\%)} = \frac{n_{(caputured\ HCHO)}}{n_{(total\ HCOOH)} - n_{(residual\ HCOOH)}} \times 2 = \frac{0.23\ mmol}{8\ mmol\ - 5.76\ mmol} \times 2$$
$$= 21\%$$

6. The procedure of preparation of [V] solution from wheat straw HOAS with removal of HCO_2H and other minor organic components

According to the procedure of hydrolysis-oxidation of wheat straw,[7] the wheat straw HOAS (30 mL) was prepared. Then the solution was extracted by EtOAc (10.0 mL × 10). The solution was detected by ^1H NMR (400 MHz, $(CD_3)_2SO$). As shown in Fig S1, HCO_2H, DMSO, HOAc, MeOH, $DMSO_2$ in wheat straw HOAS were removed. Deionized water (about 5 mL) was added to keep the volume as 30 mL to give the [V] solution.

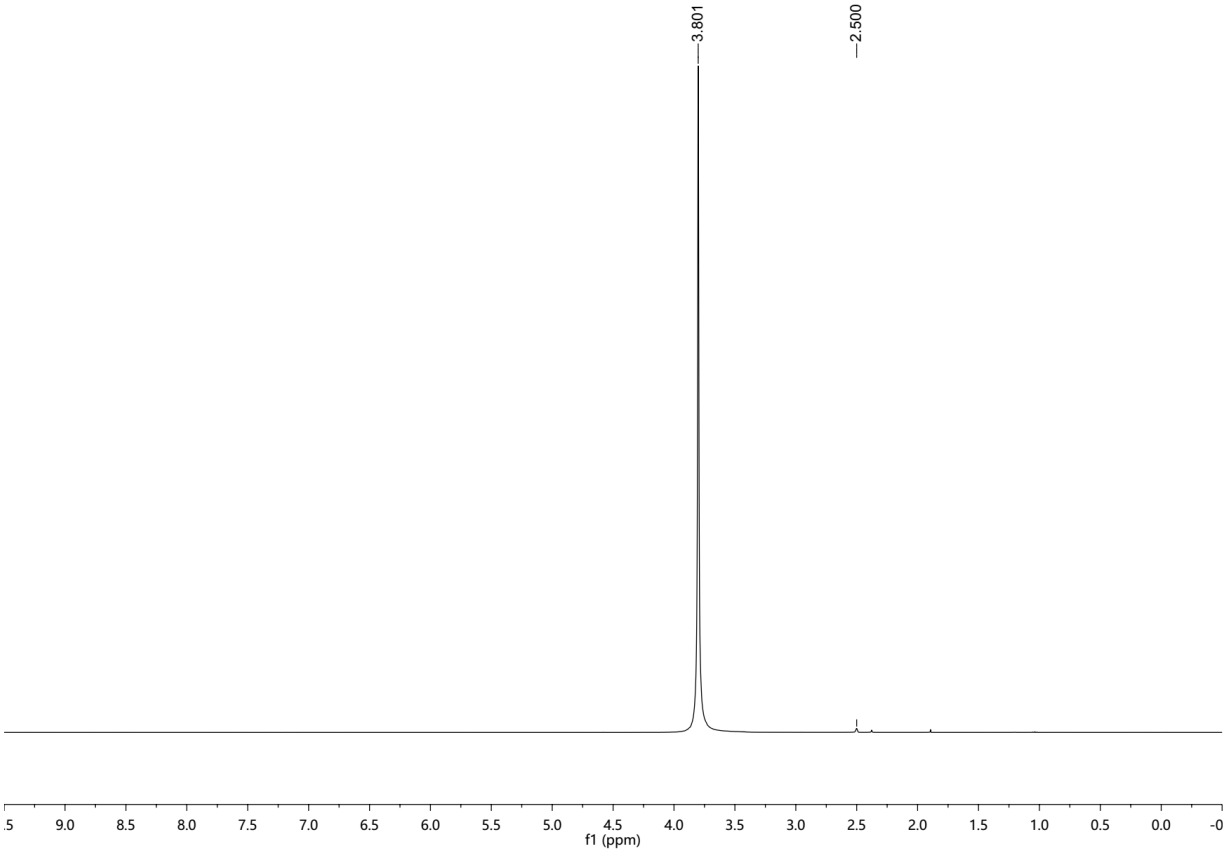


Fig S1. ^1H NMR (400 MHz, $(CD_3)_2SO$) of the [V] solution from wheat straw HOAS with removal of HCO_2H and other minor organic components.

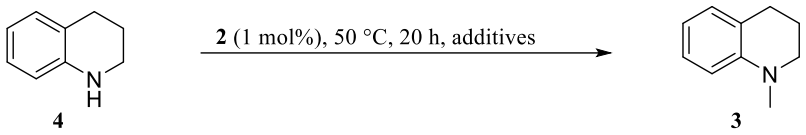
Table S6. Detection of the influence of other minor components for the N-methylation

1 or 4 —**2** (1.0 mol%), 50 °C, 20 h, additives→ **4 or 3**

Entry[a]	Substrate	Additives	**4** (%)	**3** (%)
1	**1**	-	90	–
2	**1**	$DMSO_2$ (0.58 mmol)	90	–
3	**1**	DMSO (0.52 mmol)	90	–
4	**1**	Na_2SO_4 (0.93 mmol)	91	–
5	**1**	HOAc (0.52 mmol)	91	–
6	**1**	1,4-dioxane (0.97 mmol)	93	–
7	**1**	MeOH (0.17 mmol)	92	–
8	**4**	–	–	–
9	**4**	$DMSO_2$ (0.58 mmol)	–	–
10	**4**	DMSO (0.52 mmol)	–	–
11	**4**	Na_2SO_4 (0.93 mmol)	–	–
12	**4**	HOAc (0.52 mmol)	–	–
13	**4**	1,4-dioxane (0.97 mmol)	–	–
14	**4**	MeOH (0.17 mmol)	–	–

[a]Reaction conditions: **1** or **4** (0.25 mmol), **2** (1.0 mol%), HCO_2H (7.5 mmol, 30 equiv).

Table S7. Investigation of the influence factors of the prepared catalytic [V] species.



4 **3**

Entry[a]	Additives	T (°C)	Time (h)	Yield (%)
1	HCO_2H (30 equiv), glucose (0.24 equiv)	50	20	—
2	HCO_2H (30 equiv), glucose (0.24 equiv), $NaVO_3$ (0.05 equiv)	50	20	—
3	HCO_2H (30 equiv), glucose (0.24 equiv), $NaVO_3$ (0.05 equiv), DMSO (1v%)	50	20	—
4	HCO_2H (30 equiv), glucose (0.24 equiv), $NaVO_3$ (0.05 equiv), DMSO (1v%), the reaction mixture was stirred at 30 °C for about 30 mins in the unsealed tube.	50	20	—
5	HCO_2H (30 equiv), glucose (0.24 equiv), $NaVO_3$ (0.05 equiv), DMSO (1v%), the reaction mixture was stirred at 50 °C for about 30 mins in the unsealed tube.	50	20	—
6	Glucose (0.24 equiv), $NaVO_3$ (0.05 equiv), DMSO (1v%), the reaction mixture was prepared by a 10 mins hydrolysis-oxidation according to the procedure Supplementary 2.2, then HCO_2H (30 equiv) was added.	50	20	55
7	Glucose (0.24 equiv), $NaVO_3$ (0.05 equiv), DMSO (1v%), the reaction mixture was prepared by a 10 mins hydrolysis-oxidation according to the procedure Supplementary 2.2, then HCO_2H (30 equiv) was added.	30	25	81

[a]Reaction conditions: **4** (0.25 mmol), **2** (1.0 mol%), HCO_2H (7.5 mmol, 30 equiv), H_2O (8 mL).

7. The procedure of stirring the possible intermediates of the hydrolysis-oxidation biomass with $NaVO_3$ or $VOSO_4$

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, the possible intermediates of the hydrolysis-oxidation biomass (0.025 mmol), $NaVO_3$ (0.025 mmol, 3.1 mg) or $VOSO_4$ (0.025 mmol, 4.1 mg), 0.7% of H_2SO_4 (4 mL) were added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate at room temperature for 30 min. Then HCO_2H (7.5 mmol) was added to the mixture which was stirred with 1000 rpm stirring rate for another 10 mins.

8.1 The procedure of Entry 1 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), H_2O (8 mL) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. The solvents were removed in vacuo. No product was detected in this reaction.

8.2 The procedure of Entry 2 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), $NaVO_3$ (1.1 eq, 33.5 mg) and H_2O (8 mL) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times.

The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. No product was detected in this reaction.

8.3 The procedure of Entry 3 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), $VOSO_4$ (1.1 eq, 44.8 mg) and H_2O (8 mL) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (7%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.4 The procedure of Entry 4 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), [V] (1.1 eq) solution from wheat straw HOAS with removal of HCO_2H and other minor organic components was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (45%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.5 The procedure of Entry 5 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv) was added, 5% [V] solution from glucose HOAS (for the details, see the procedure for prepared [V] (5 mol%) by a 10 mins hydrolysis-oxidation of glucose with $NaVO_3$ as a catalyst precursor as mentioned above) and H_2O (8 mL) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1200 rpm stirring rate and heated up to 30 °C (inner temperature, ± 0.5 °C) for 25 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (83%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.6 The procedure of Entry 6 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv) was added, 10% [V] solution from glucose HOAS (for the details, see the procedure for prepared [V] (10 mol%) by a 10 mins hydrolysis-oxidation of glucose with $NaVO_3$ as a catalyst precursor as mentioned above) and H_2O (8 mL) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1200 rpm stirring rate and heated up to 30 °C (inner temperature, ± 0.5 °C) for 25 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (86%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.7 The procedure of Entry 7 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), $VOSO_4$ (0.1 eq, 4.5 mg), 1.3-dihydroxyacetone (0.1 eq, 3.1 mg) and 0.7% of H_2SO_4 (4 mL) were added. Next, the Schlenk tube was

degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (7%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.8 The procedure of Entry 8 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), $VOSO_4$ (0.1 eq, 4.5 mg), glyceraldehyde (0.1 eq, 3.1 mg) and 0.7% of H_2SO_4 (4 mL) were added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (13%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.9 The procedure of Entry 9 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), $VOSO_4$ (0.1 eq, 4.5 mg), glycolaldehyde (0.1 eq, 1.5 mg, the dimer of glycolaldehyde was used) and 0.7% of H_2SO_4 (4 mL) were added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. No product was detected in this reaction.

8.10 The procedure of Entry 10 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), $VOSO_4$ (0.1 eq, 4.5 mg), glyoxal (0.1 eq, 40% aqueous solution, 3.1 uL) and 0.7% of H_2SO_4 (4 mL) were added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (42%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.11 The procedure of Entry 11 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), $VOSO_4$ (0.1 eq, 4.5 mg), glycolic acid (0.1 eq, 1.9 mg) and 0.7% of H_2SO_4 (4 mL) were added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (12%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.12 The procedure of Entry 12 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), HCO_2H (7.5 mmol, 30 equiv), $NaVO_3$ (0.1 eq, 3.1 mg), glyoxal (0.1 eq, 40% aqueous solution, 3.1 uL) and 0.7% of H_2SO_4 (4 mL) were added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature,

± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (35%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.13 The procedure of Entry 13 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), $Zn(OTf)_2$ (0.1 eq, 9.1 mg), HCO_2H (7.5 mmol, 30 equiv), H_2O (8 mL) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 70 °C (inner temperature, ± 0.5 °C) for 30 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (3%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.14 The procedure of Entry 14 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), $Zn(OTf)_2$ (1.1 eq, 99.9 mg), HCO_2H (7.5 mmol, 30 equiv), H_2O (8 mL) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 70 °C (inner temperature, ± 0.5 °C) for 30 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (5%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.15 The procedure of Entry 15 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), $Cu(OTf)_2$ (0.1 eq, 9.0 mg), HCO_2H (7.5 mmol, 30 equiv), H_2O (8 mL) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 70 °C (inner temperature, ± 0.5 °C) for 30 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (5%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

8.16 The procedure of Entry 16 in Table 1

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **4** (0.25 mmol, 33.3 mg), **2** (2.5 μmol, 1.6 mg), $Cu(OTf)_2$ (1.1 eq, 99.5 mg), HCO_2H (7.5 mmol, 30 equiv), H_2O (8 mL) was added. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 70 °C (inner temperature, ± 0.5 °C) for 30 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The yield of **3** (10%) was determined by ^1H NMR using $Cl_2CHCHCl_2$ as an internal standard.

9. The procedure of Hg (0) poisoning test and result[10]

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **1** (0.25 mmol, 32.3 mg), **2** (2.5 μmol, 1.6 mg), wheat straw HOAS with a pH value of 2.25 (contained 30.0 equiv of HCO_2H, 12.5 mL based on the 95% yield of HCO_2H) was added to the reaction tube. Mercury 5 g (10000 eq to [Ir]) was then added to the tube. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The resulted residue was purified by silica gel column chromatography with eluting (petroleum ether/EtOAc = 20/1), **3** was obtained in 87% yield.

10. General procedure for the N-methylation of quinolines

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, **2** (2.5 μmol, 1.6 mg), compound **1** (0.25 mmol, 32.3 mg), and wheat straw HOAS with a pH value of 2.25 (contained 30.0 equiv of HCO_2H, 12.5 mL based on the 95% yield of HCO_2H) were added in sequence. Next, the Schlenk tube was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 20 h. The Schlenk tube was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc (5.0 mL × 3). The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The residue was purified by flash chromatography (silica gel, petroleum ether/ EtOAc) to afford compound **3**.

11. Gram-scale application of in-situ generated CH_2O by HCO_2H disproportionation in Fig. 6.

Eq 1: Compound **1** (7.74 mmol, 1.0 g), **2** (0.0774 mmol, 1 mol%, 48.8 mg), 10% [V] solution from glucose HOAS (for the details, see the procedure for prepared [V] (10 mol%) in Supplementary 2.2), HCO_2H (232.2 mmol, 30 equiv, 10.7 g, 8.8 mL) and H_2O (250 mL) were added into a flask (500 mL) charged with a stirring bar under argon atmosphere. Next, the flask was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1200 rpm stirring rate at 30 °C (inner temperature, ± 0.5 °C) for 65 h. The flask was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc/methanol = 10:1 (50 mL × 5). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc = 20:1) to afford **3** in 75% yield (0.854 g).

Eq 2: Compound **1** (7.74 mmol, 1.0 g), **2** (0.0387 mmol, 0.5 mol%, 24.4 mg) and wheat straw HOAS [334.5 mL, HCO_2H (185.7 mmol, 24 equiv) was contained] with a pH value of 2.25 were added into a polytetrafluoroethylene container (500 mL) charged with a stirring bar. The polytetrafluoroethylene container was put into the autoclave. Then the autoclave was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 50 °C (inner temperature, ± 0.5 °C) for 35 h. The autoclave was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc/methanol = 10:1 (50 mL × 5). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc = 20:1) to afford **3** in 90% yield (1.036 g).

Eq 3: Compound **1** (7.74 mmol, 1.0 g), **2** (0.0387 mmol, 0.5 mol%, 24.4 mg) and wheat straw HOAS [334.5 mL, HCO_2H (185.7 mmol, 24 equiv) was contained] with a pH value of 2.25 were added into a polytetrafluoroethylene container (500 mL) charged with a stirring bar. The polytetrafluoroethylene container was put into the autoclave. Then the autoclave was degassed in vacuo and filled with Ar for three times. The mixture was stirred with 1000 rpm stirring rate and heated up to 30 °C (inner temperature, ± 0.5 °C) for 65 h. The autoclave was cooled by water to room temperature. Then the reaction mixture was extracted by EtOAc/methanol = 10:1 (50 mL × 5). The combined organic extracts were washed with brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo. The residue was purified by flash chromatography (petroleum ether/EtOAc = 20:1) to afford **3** in 72% yield (0.819 g).

12. The recycling experiment of the [V] species in the wheat straw HOAS for the N-methylation.

To a Schlenk tube (50.0 mL) equipped with a magnetic stirring bar, compound **1** (0.25 mmol, 32.3 mg), **2** (2.5 μmol, 1.6 mg), wheat straw HOAS with a pH value of 2.25 (contained 30.0 equiv of HCO_2H, 12.5 mL based on the 95% yield of HCO_2H) was added to the reactor tube. After the standard reaction of N-methylation, **3** was extracted by dichloromethane (5.0 mL × 4) and the aqueous phase is retained. Then adjust the pH of the aqueous solution to 0.95 by 0.7% H_2SO_4. The wheat straw (containing 18 mmol C-atoms of ploysaccharides) were added into the aqueous solution

with a stirring bar. The reaction mixture was stirred at room temperature for about 30 min. The flask was put into the autoclave (500 mL, 7.5 cm inner diameter) prefilled with water (250 mL, to avoid the corrosion of the autoclave by the acid). Then the autoclave was charged with O_2 (3 MPa). The mixture was stirred with 1000 rpm stirring rate and heated up to 160 °C (inner temperature, ± 0.5 °C) with the heating rate of 5-6 °C / min in about 20-30 min. Then the reaction mixture was stirred at 160 °C (inner temperature, ± 0.5 °C) for another 3 h. The autoclave was cooled by water to room temperature and the pressure was released carefully. 1, 4-dioxane was added as an internal standard for the detection of 1H NMR yields of the generated formic acid in 66% yield. Then the resulted wheat straw HOAS for the further N-methylation of **1** (0.25 mmol) afforded resulted **3** in 85% yield.

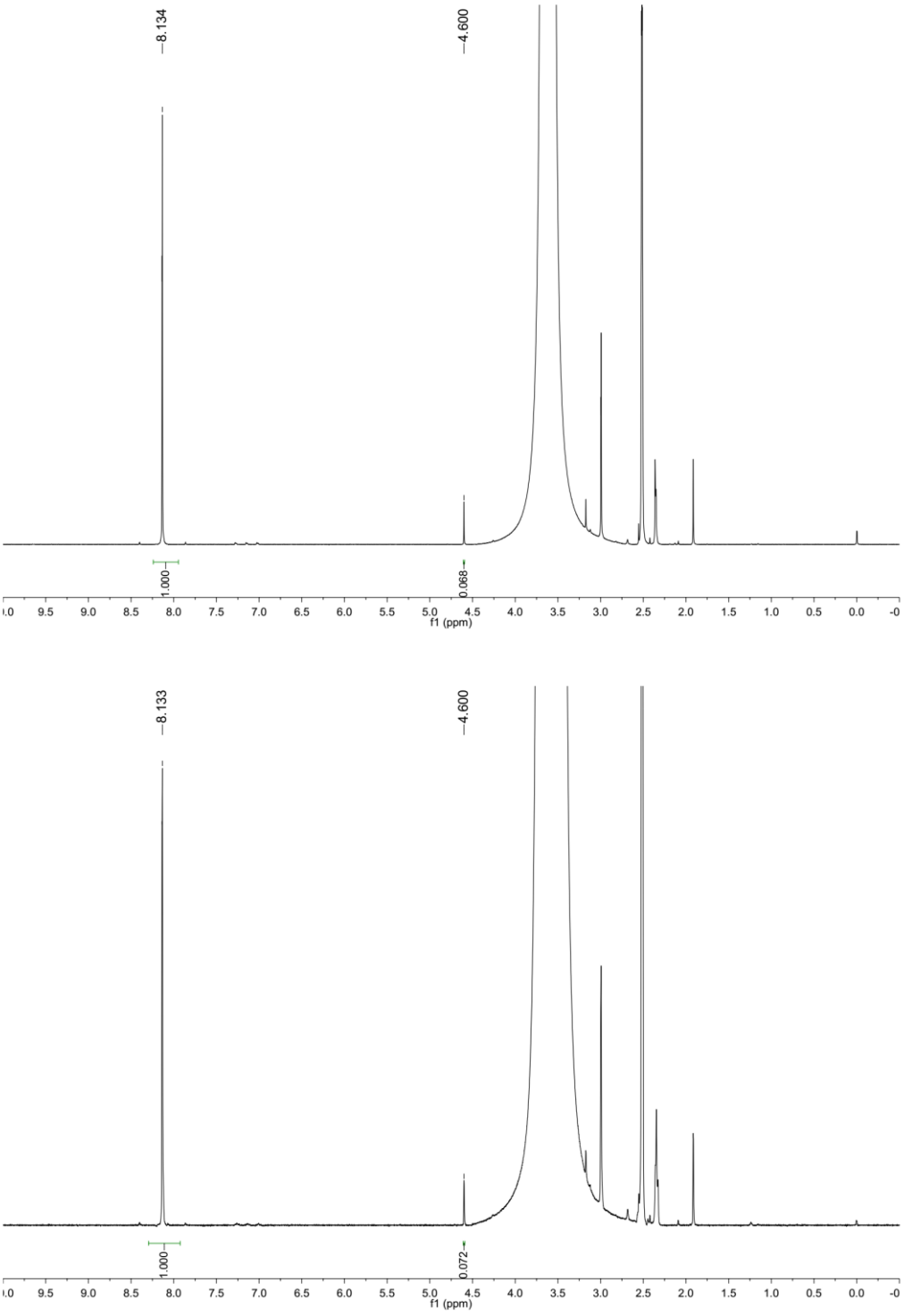


Fig S2. Wheat straw HOAS was detected by ^{1}H NMR (400 MHz, $(CD_3)_2SO$), 3.4-3.6 % of $CH_2(OH)_2$ was contained in the system. [7]

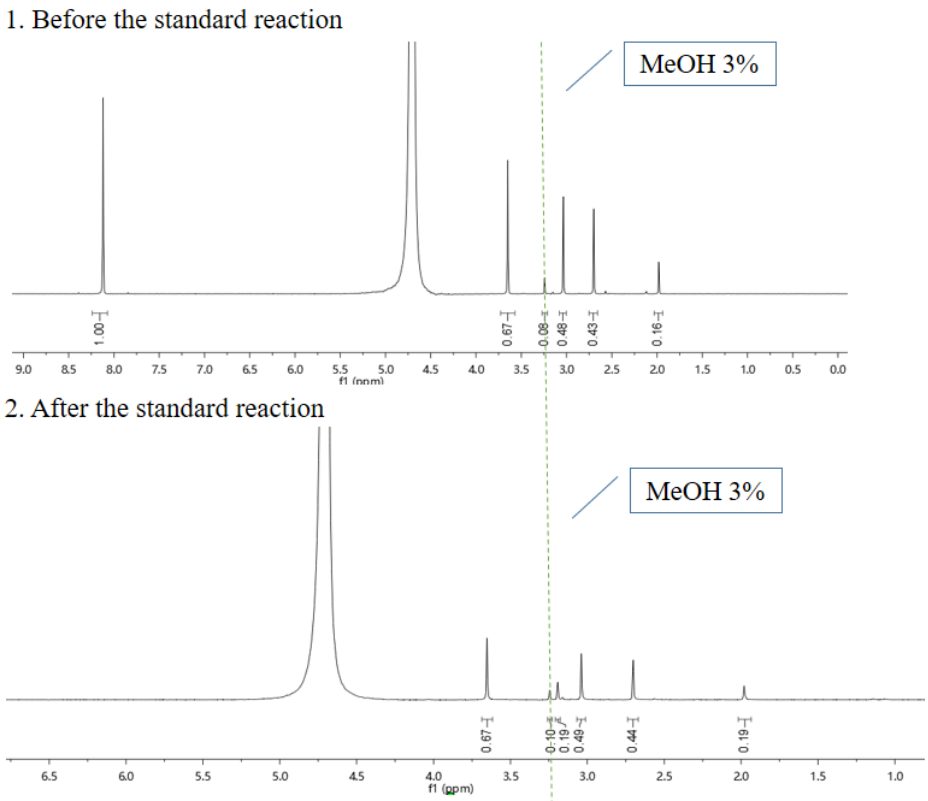
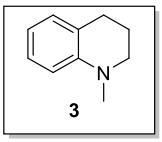


Fig S3. The MeOH in the solution was detected by ^{1}H NMR (400 MHz, D_2O)

1. There was about 3% MeOH in the renewable HCO_2H from hydrolysis-oxidation of biomass, which derived from the oxidation of DMSO.
2. After the reaction, the aqueous mixture was detected by crude ^{1}H NMR, the content of MeOH was still determined as about 3%.

10. Characterization data



1-methyl-1,2,3,4-tetrahydroquinoline (3)[11]

According to the general procedure, **3** (33.4 mg) was obtained by column chromatography with eluting (petroleum ether/EtOAc = 20/1) in 91% yield as a pale oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–7.05 (m, 1H), 6.95 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.63–6.59 (m, 2H), 3.21 (t, *J* = 5.6 Hz, 2H), 2.88 (s, 3H), 2.76 (t, *J* = 6.4 Hz, 2H), 2.01–1.95 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.7, 128.8, 127.0, 122.8, 116.2, 110.9, 51.3, 39.1, 27.8, 22.4; GC-MS (EI, m/z): $[M]^+$ 147.1.

Supplementary References

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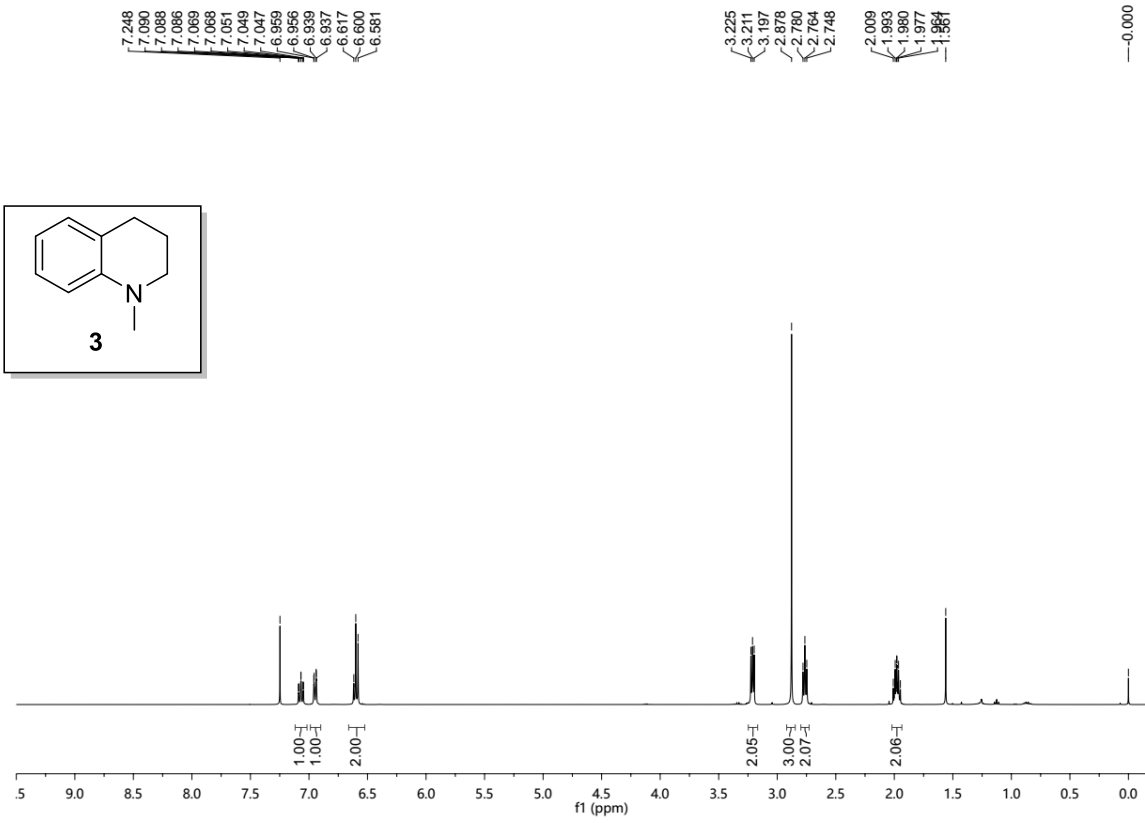
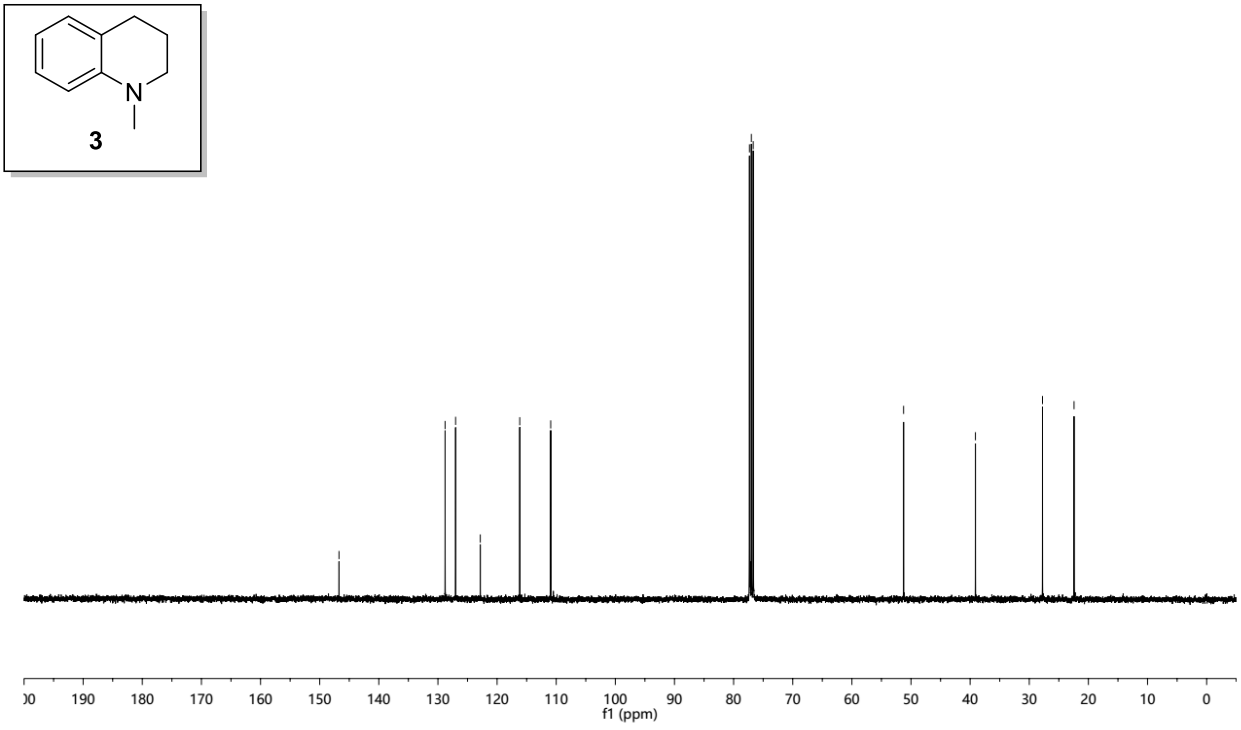
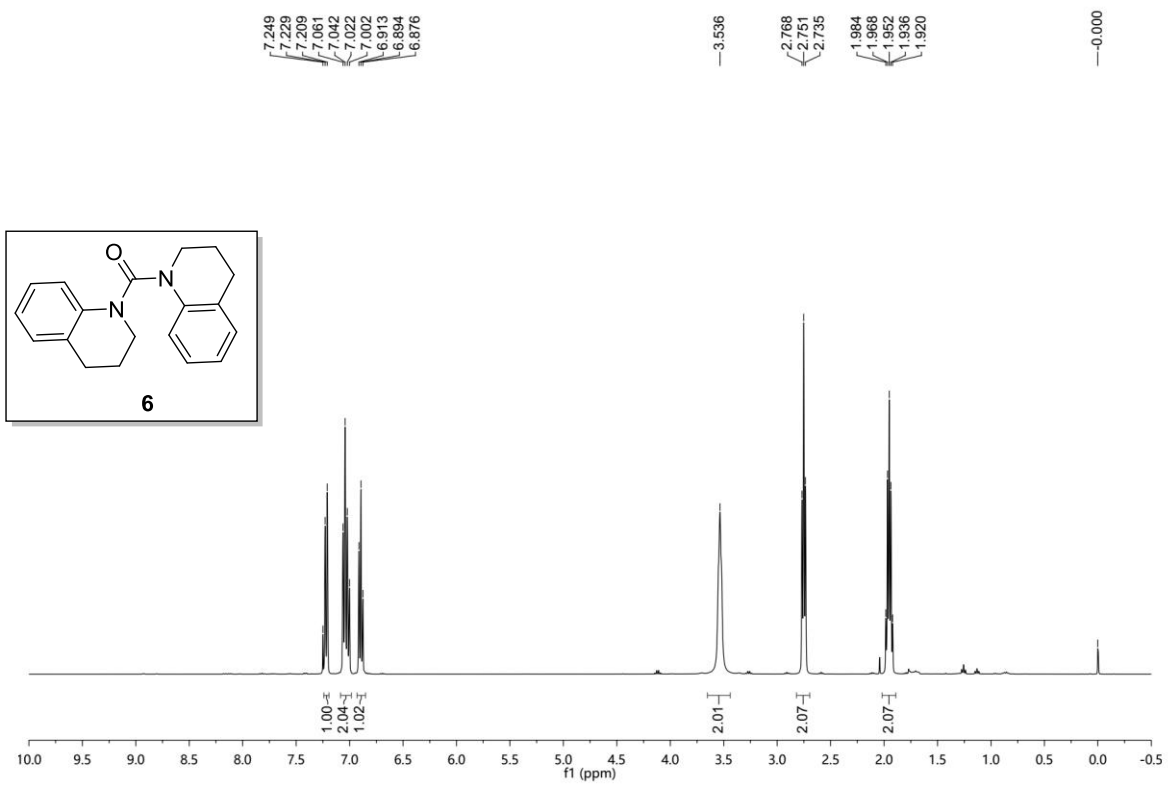
NMR Spectrum



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2.751
2.735
1.984
1.968
1.952
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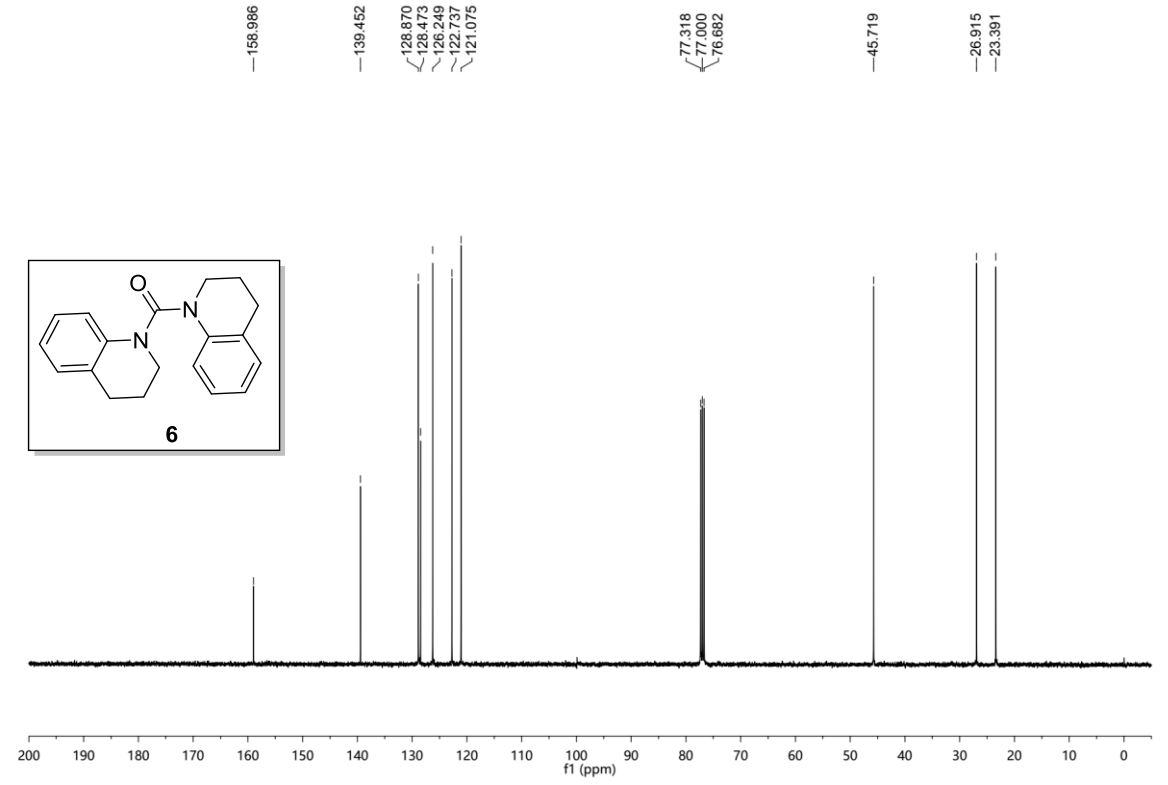
6
1.00
2.04
1.02
2.01
2.07
2.07
f1 (ppm)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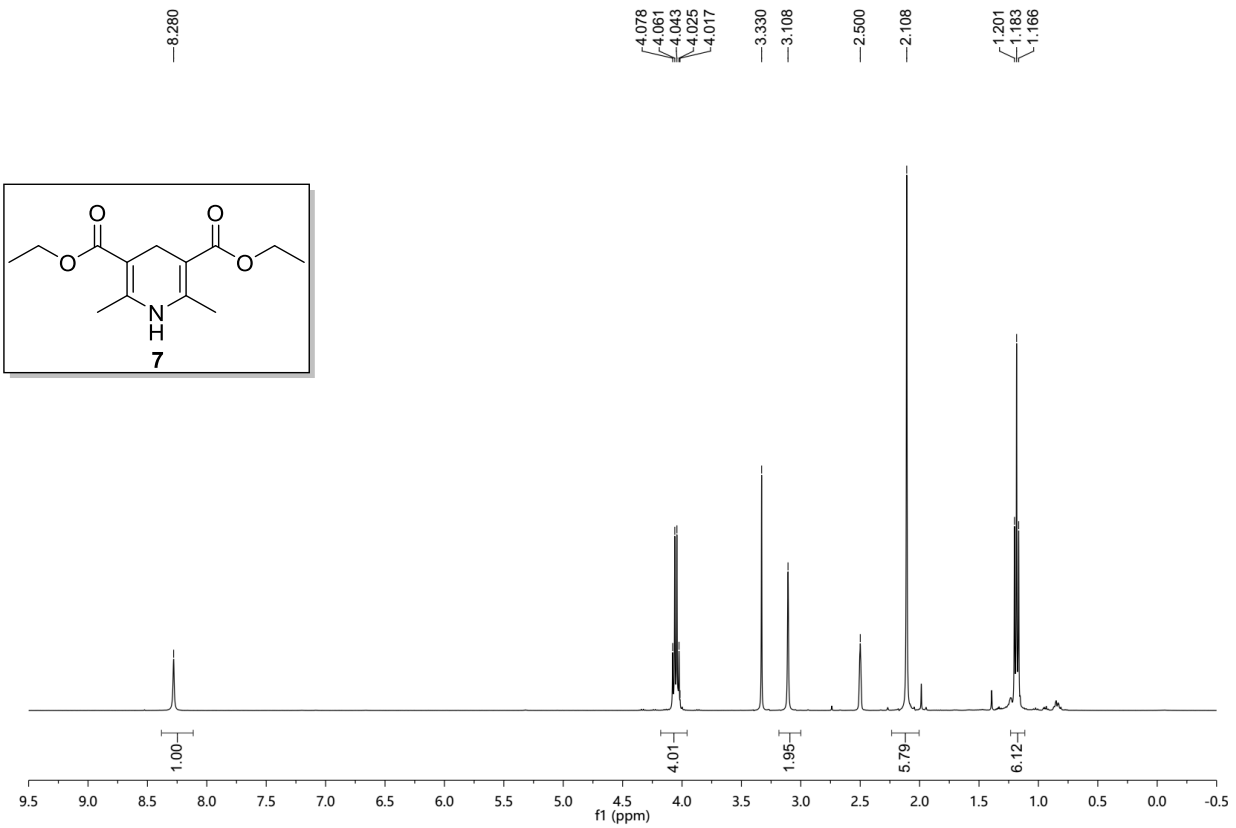
f1 (ppm)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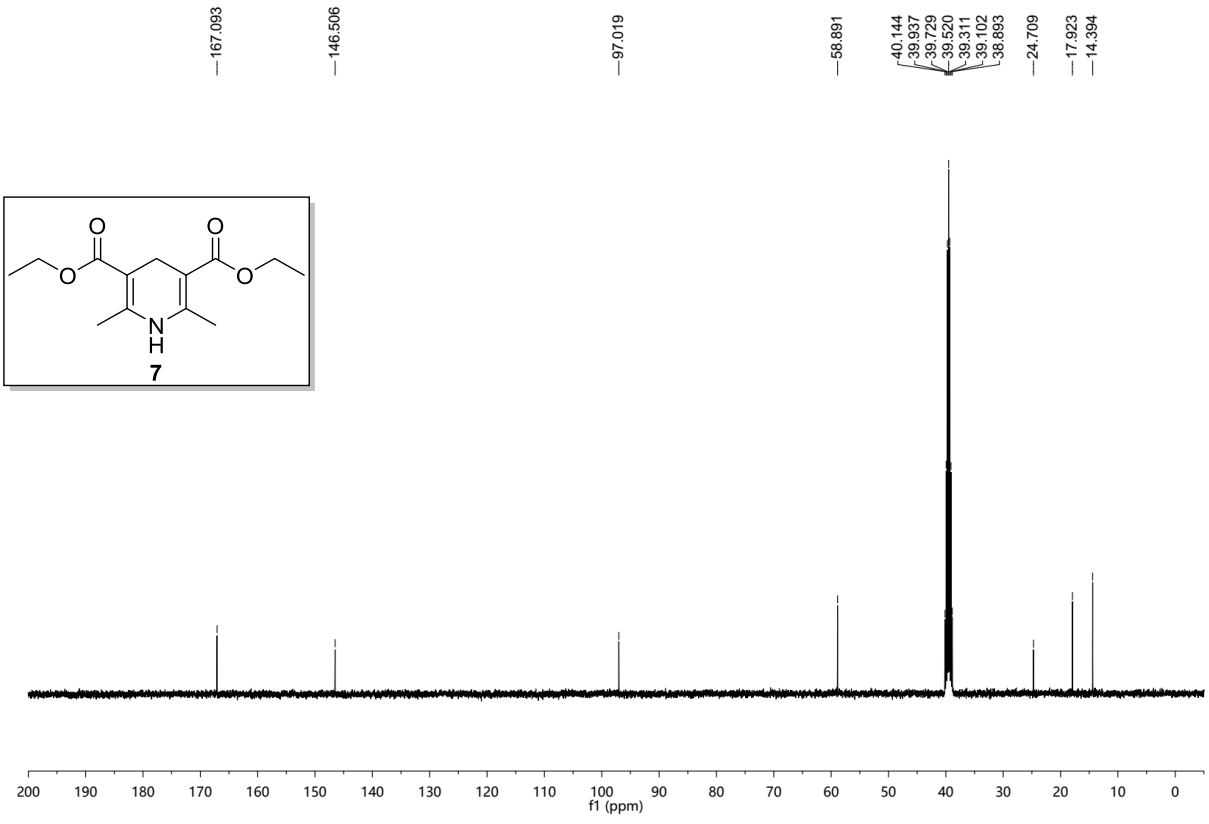
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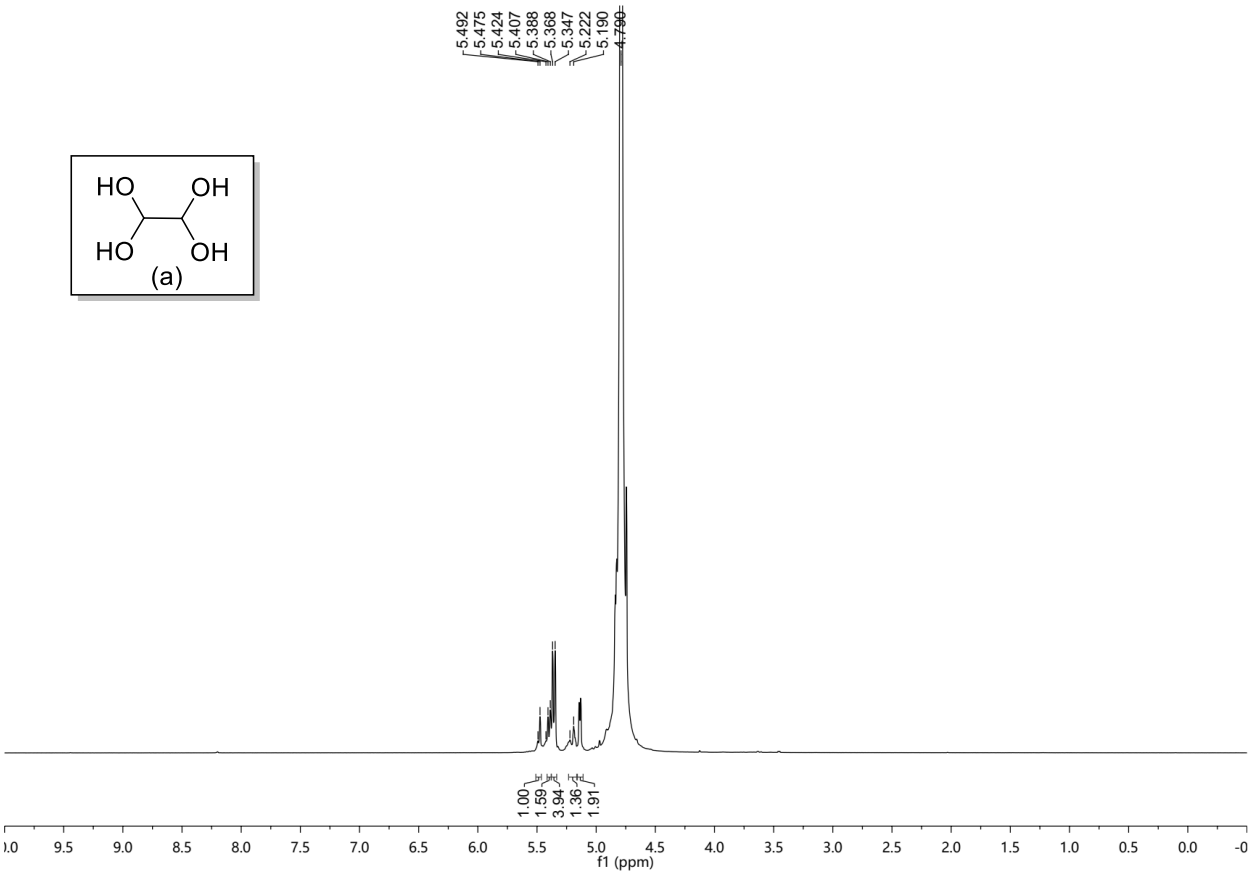
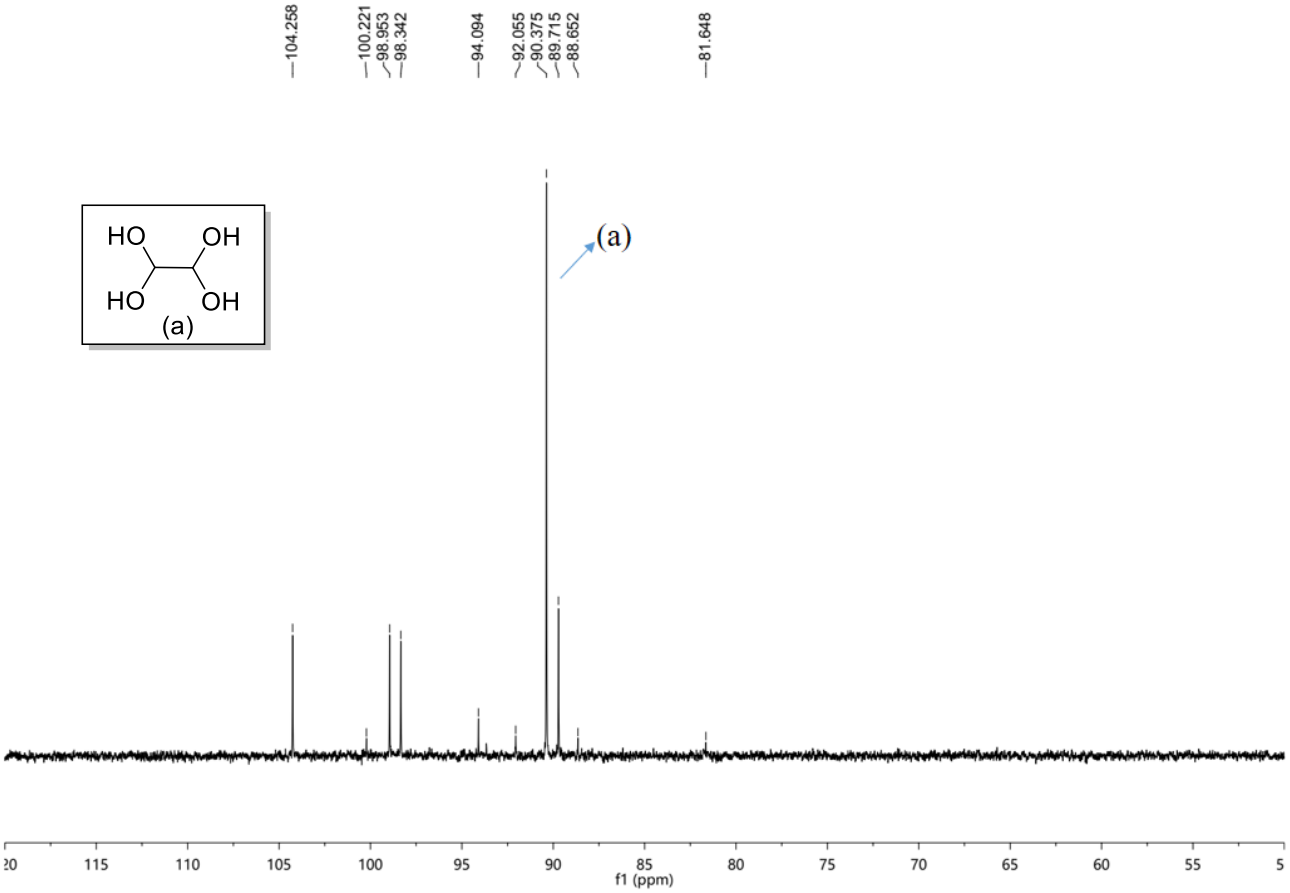


The ^{1}H NMR spectrum of glyoxal aqueous solution in D_2O



The ^{13}C NMR spectrum of glyoxal aqueous solution in D_2O