Supplementary Materials

HCO_3^- modified *N*-heterocyclic carbene silver organic porous polymer catalyzes the conversion of low concentration CO_2 into oxazolidinone compounds

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Table of Contents

1. CATALYST COMPARISON

Supplementary Table 1. Comparison with reported catalysts

	Catalyst	Reaction Conditions	CO_2 vol.%	Yield (%)	Cycle number
[26]	AgOAc	DMSO, 10 h, r.t.	100 vol.%	98%	-
[27]	$AgNO_3$	MeCN, base, 24 h, 60 °C	100 vol.%	95%	-
[28]	Ag-HMP-2	MeCN, base, 20 h, 60 °C	100 vol.%	97%	5 times
[29]	NiBDP-AgS	MeCN, base, 60 °C	100 vol.%	87%	10 times
This work	Ag@POP-HCO_3	DMSO, 12 h, r.t.	15 vol.%	77%	3 times

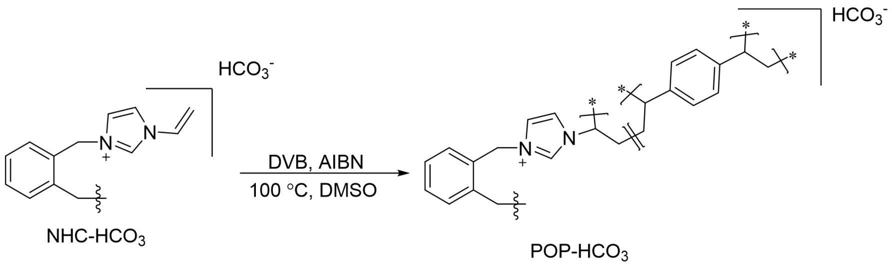
2. SYNTHESIS METHOD OF CATALYST AND SUBSTRATE

2.1 Chemical reagent

Materials 1,2-Dibromo-methyl benzene, *n*-vinylimidazole, divinylbenzene (DVB), and azodiisobutyronitrile (AIBN) were purchased from Innochem in Beijing, China. Potassium carbonate ($KHCO_3$) and silver nitrate ($AgNO_3$) were procured from Xilong Science Co., LTD. Solvents such as toluene, ethyl acetate (EA), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and methanol (MeOH) are purchased from local suppliers. The reagents used in this experiment are of analytical purity, and unless otherwise indicated, no additional purification is usually required during use.

2.2 Synthesis method of POP-HCO_3

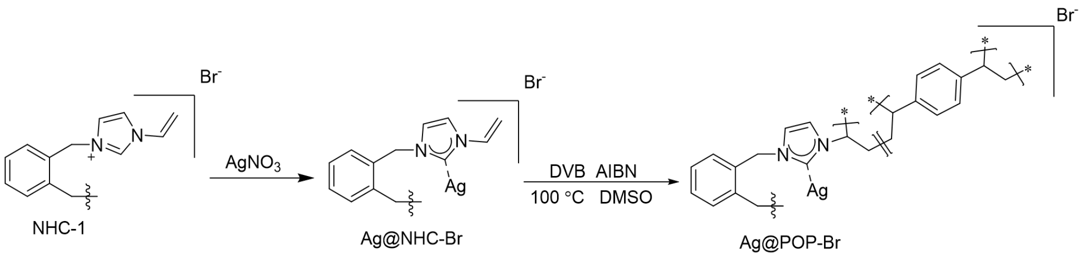
POP-HCO_3 was synthesized by high pressure reaction and DVB crosslinker and vinyl imidazole as the basic polymerization units. First, 0.2 mmol of NHC-HCO_3 monomer and 60 mg of AIBN were weighed into a reaction tube, and 3 mL of DMSO was added. Then, DVB (4 mmol, 565 μL) was added and the mixture was stirred at 50 °C until completely mixed. The solution was transferred to a Teflon high-pressure reactor for polymerization at 100 °C for 24 h and then cooled to room temperature. The resulting solid was washed with EA at least three times and then washed with MeOH several times, and finally, the polymer was dried under vacuum conditions to obtain the polymer POP-HCO_3, which was ground for use.



Supplementary Scheme 1. The synthetic pathway of POP-HCO_3.

2.3 Synthesis method of Ag@POP-Br

The precoordination method was adopted. The metal is loaded with NHC-1: $AgNO_3$ = 1:1, and Ag@NHC-1 was obtained. The polymer Ag@POP-Br was synthesized with a DVB crosslinker and vinylimidazole as the basic polymerization units in the N_2 environment. The specific steps are the same as those for the synthesis of the polymer Ag@POP-HCO_3.

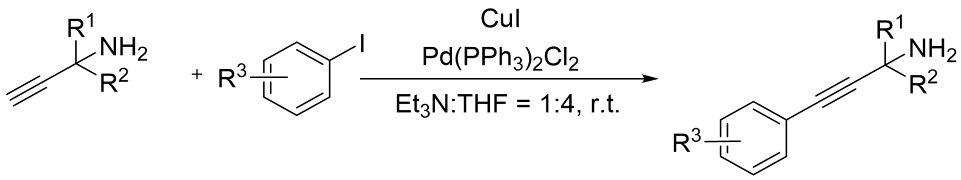


Supplementary Scheme 2. The synthetic pathway of Ag@POP-Br.

3. SYNTHESIS METHOD OF PROPARGYL AMINES

Synthesis method of 1a-1i: According to reports, the reaction substrate **1a-1i** was synthesized by Sonogashira coupling method. CuI (0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (0.1

mmol) were weighed into a side flask. Under N_2 atmosphere, 6 mL Et_3N, 24 mL THF, iodobenzene (5.2 mmol) and 2-methyl-3-butylene-2-amine (5.0 mmol) were added successively. The mixture was stirred evenly at room temperature and reacted for 12 h. After the reaction, the reaction solution was quenched with saturated NH_4Cl solution and extracted with saturated NaCl solution and EA. The organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed by vacuum evaporation to obtain crude products. The propargyl amines were purified by column chromatography (PE/EA as eluent).

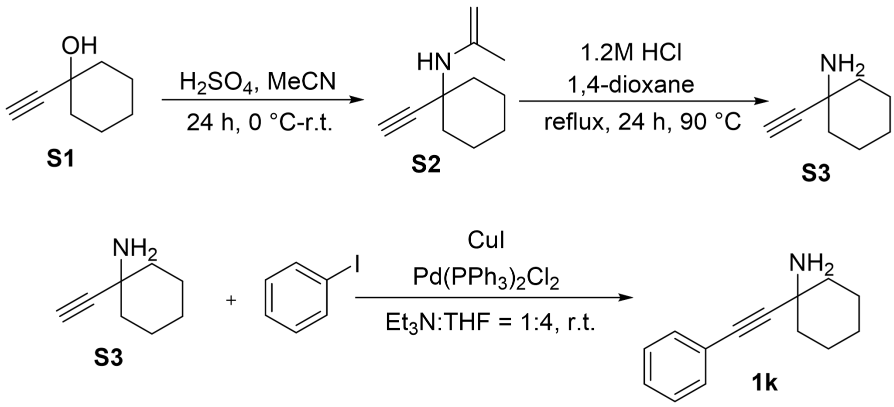


Supplementary Scheme 3. The synthetic pathway of **1a-1i.**

Synthesis method of 1k: According to the literature reports, the reaction substrate **1k** was synthesized. Concentrated sulfuric acid (6.6 mL) was dropped into 62 mL MeCN at 0 °C, and then stirred for 15 min. In a dry round-bottomed flask, Na_2SO_4 (25 mmol, 3.5 g), **S1** (1-ethylcyclohexylamine) (50 mmol, 3.3 mL) and 62 mL MeCN were added under N_2 atmosphere. The MeCN and concentrated sulfuric acid mixture was then dropped evenly into this flask. Afterward, the solution was stirred at room temperature for two hours. Following the reaction, the solvent was evaporated. The reaction liquid was quenched with ice water, and the aqueous phase was extracted with ether three times. The organic phase was dried with anhydrous Na_2SO_4. The solvent was removed by vacuum distillation to obtain the crude product **S2**, which was used for subsequent reaction without further purification.

The **S2** synthesized in the first step was dissolved in 10 mL 1, 4-dioxane, and 48 mL 1.2M HCl was added. The mixture was stirred at 90 °C for 24 h. Upon completion of the reaction, the aqueous phase was extracted once with ether. The aqueous phase was then alkalized with 2 M NaOH solution to pH = 11, followed by ether extractions twice. The organic phase was combined and dried with Na_2SO_4, and the solvent was removed by vacuum distillation to obtain the crude product **S3**, which was used for subsequent reaction without further purification.

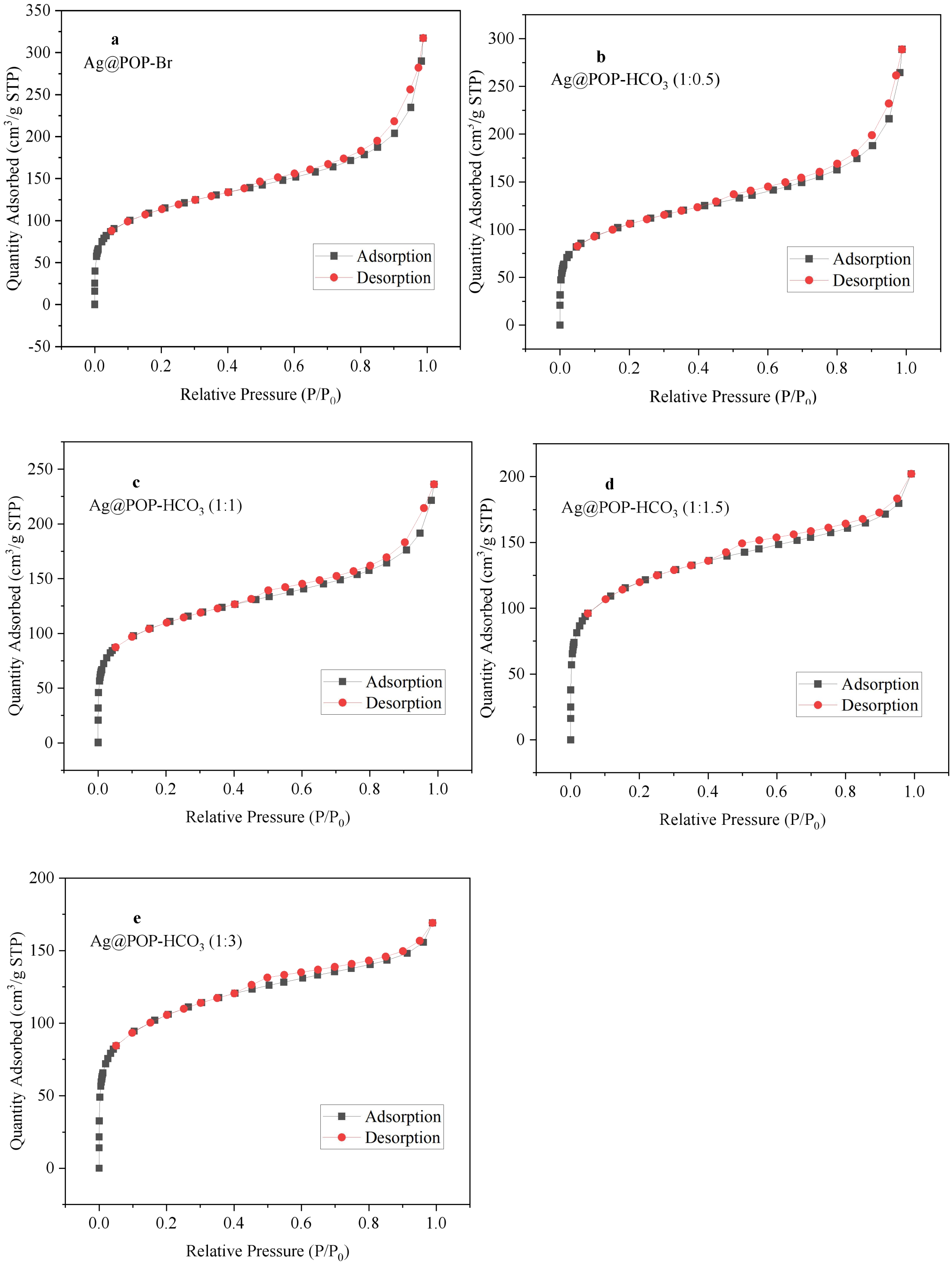
Finally, the reaction substrate **1k** was synthesized by Sonogashira coupling method. CuI (0.2 mmol) and $Pd(PPh_3)_2Cl_2$ (0.1 mmol) were weighed into a side-necked bottle. Under N_2 atmosphere, 1.5 mL Et_3N, 6 mL THF, iodobenzene (5.2 mmol) and **S3** (5.0 mmol) were added successively. The mixture was stirred evenly at room temperature and reacted for 12 h. After the reaction, the reaction solution was quenched with saturated NH_4Cl solution and extracted with saturated NaCl solution and EA. The organic phase was dried with anhydrous Na_2SO_4, and the solvent was removed by vacuum evaporation to obtain crude products. The propargyl amines **1k** were purified by column chromatography (PE/EA as eluent).



Supplementary Scheme 4. The synthetic pathway of **1k.**

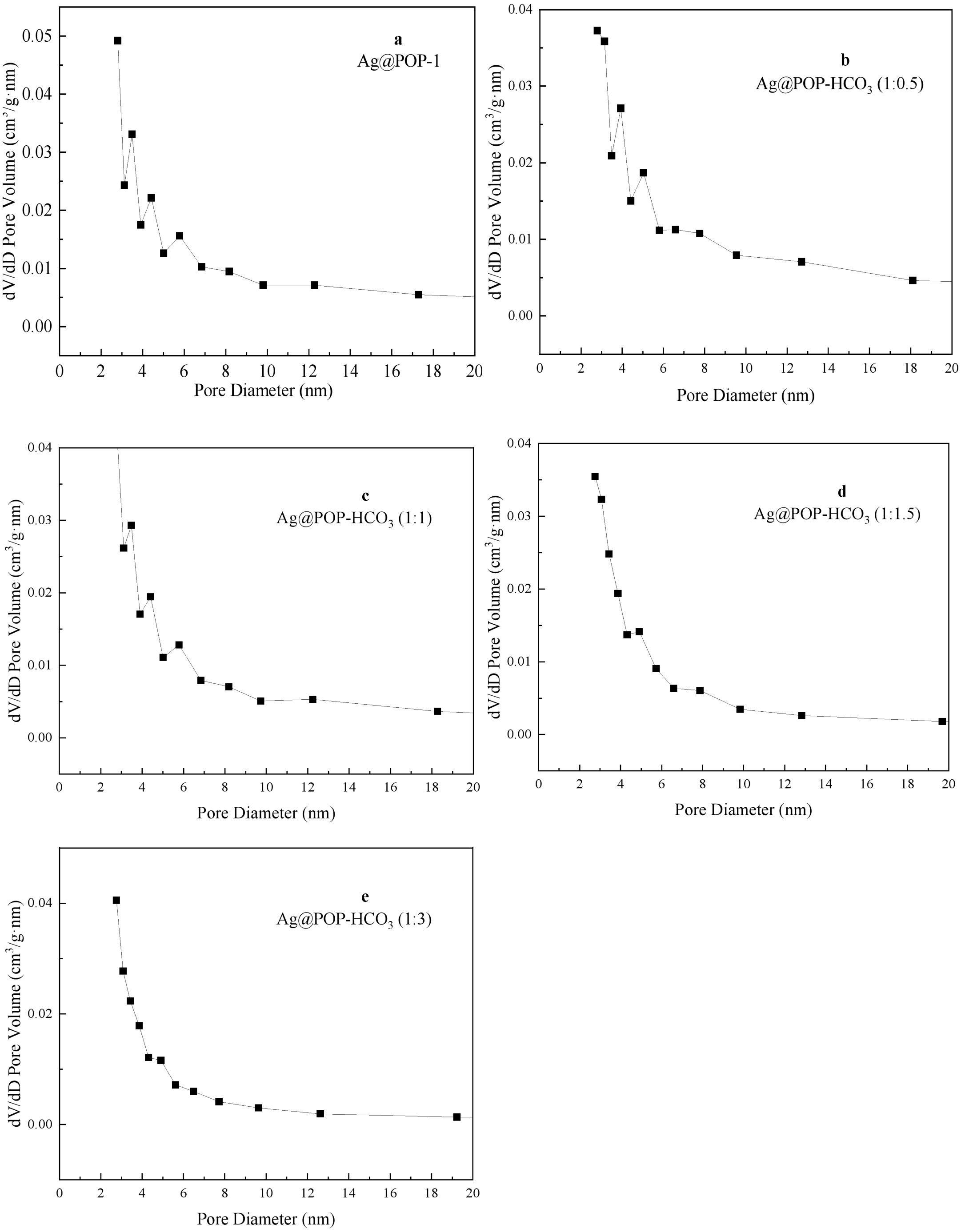
4. CATALYST CHARACTERIZATION

(1) N_2 adsorption-desorption isotherm (different HCO_3^- loadings)



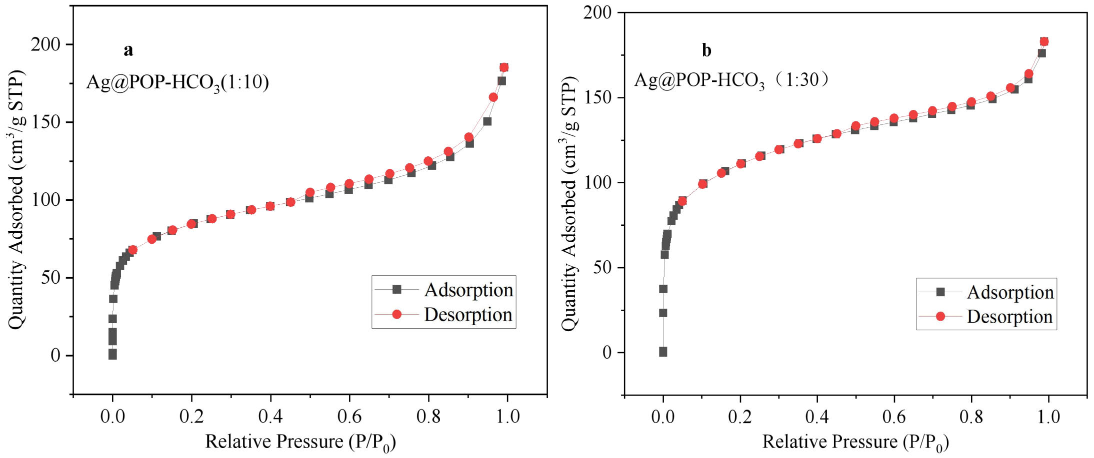
Supplementary Figure 1. N_2 adsorption-desorption isotherm with different NHC-1 and HCO_3^- ratios.(a) 1:0; (b) 1:0.5; (c) 1:1; (d) 1:1.5; (e) 1:3.

(2) Pore size distribution curve of catalyst (different HCO_3^- loadings)



Supplementary Figure 2. Pore size distribution curve of catalyst with different NHC-1 and HCO_3^- ratios.(a) 1:0; (b) 1:0.5; (c) 1:1; (d) 1:1.5; (e) 1:3.

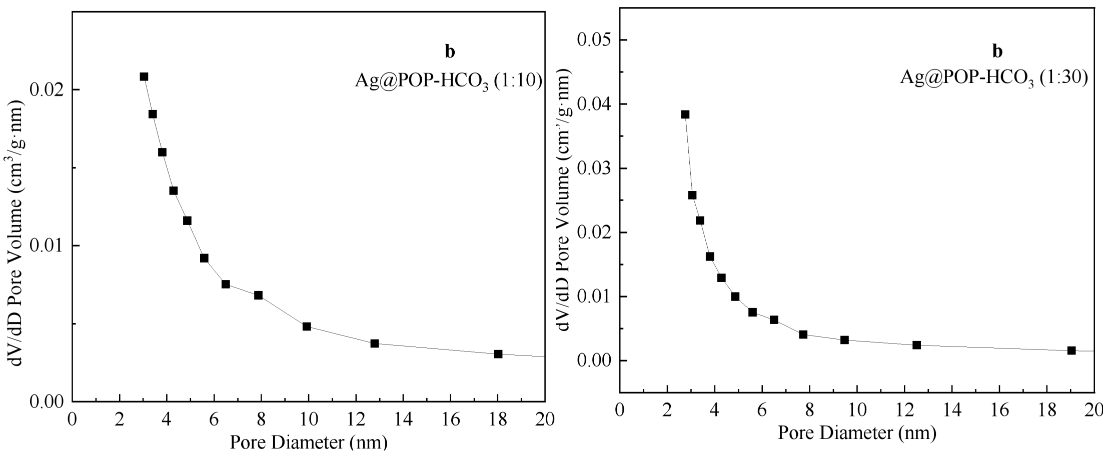
(3) N_2 adsorption desorption isotherm (different polymerization ratios)



Supplementary Figure 3. N_2 adsorption-desorption isotherm with different polymerization ratios.

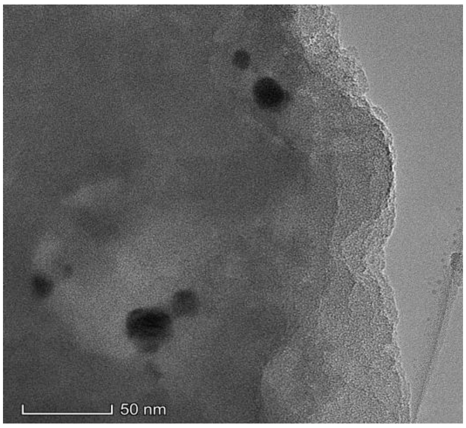
(a) Ag@POP-HCO_3 (1:10); (b) Ag@POP-HCO_3 (1:30).

(4) Pore size distribution curve of catalyst (different polymerization ratios)



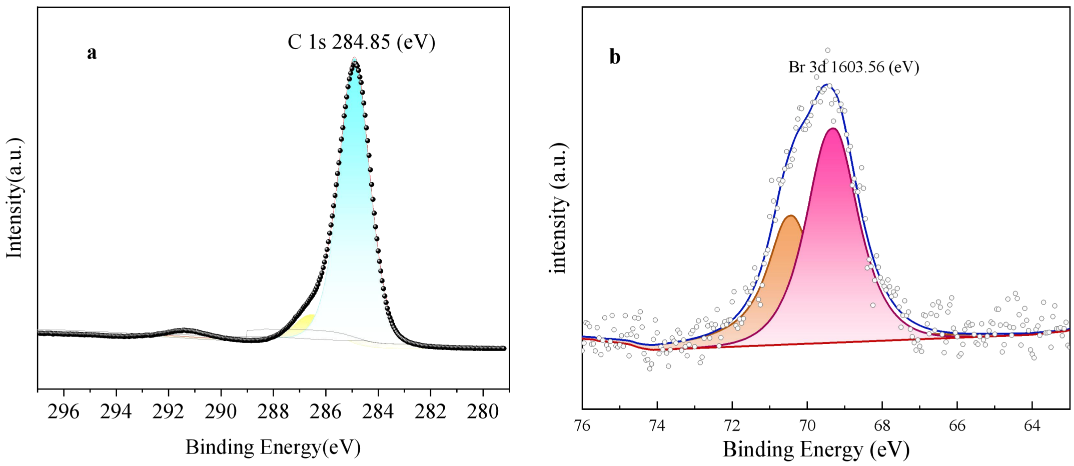
Supplementary Figure 4. Pore size distribution curve of catalyst with different polymerization ratios.(a) Ag@POP-HCO_3 (1:10); (b) Ag@POP-HCO_3 (1:30).

(5) TEM image of catalyst after cycling



Supplementary Figure 5. TEM image of catalyst after cycling.

(6) High resolution XPS spectrum



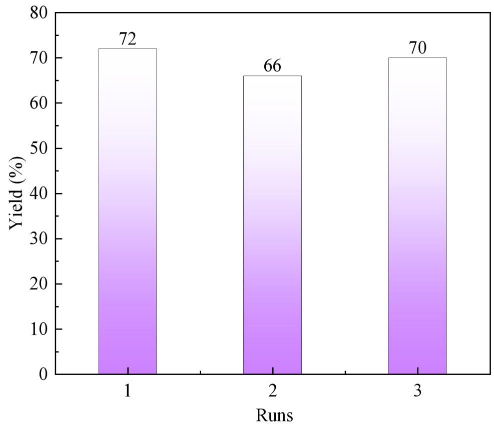
Supplementary Figure 6. High resolution XPS spectrum. (a) C 1s; (b) Br 3d.

(7) Elemental analysis

Supplementary Table 2. The elemental analysis data of the Ag@POP-HCO_3catalyst

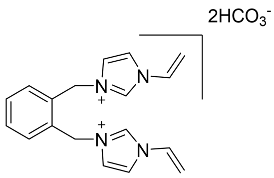
Sample	Area of N	Area of C	Area of H	N (%)	C (%)	H (%)
Ag@POP-HCO_3	746	43788	11132	0.9	71.02	5.749

(8) Cycle test of catalyst

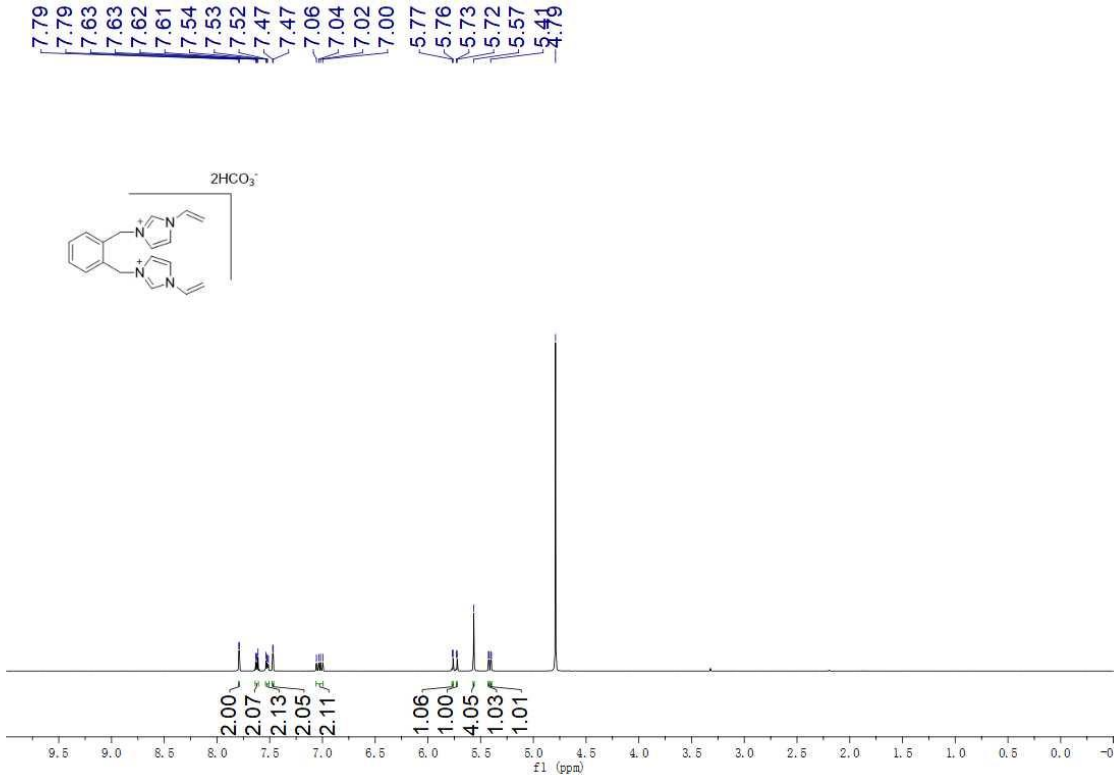


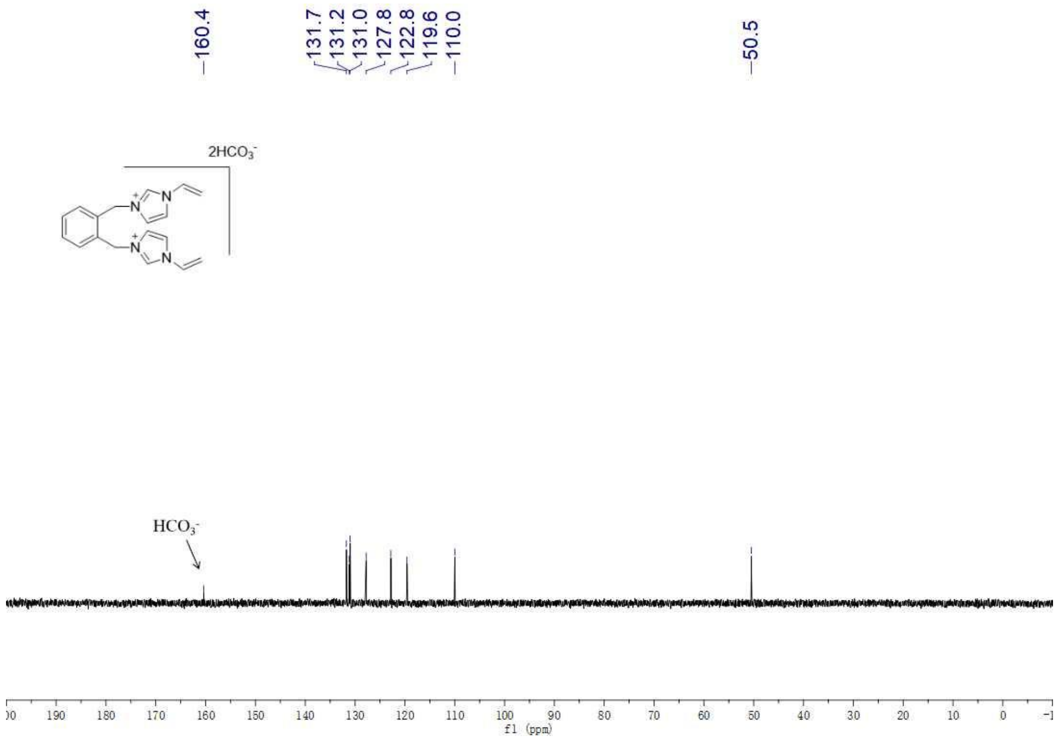
Supplementary Figure 7. Cyclic test results.

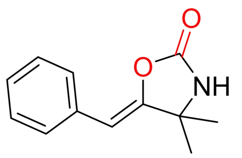
5. ^{1}H NMR, ^{13}C NMR SPECTRA OF NHC-HCO$_3$ AND ALL PRODUCTS



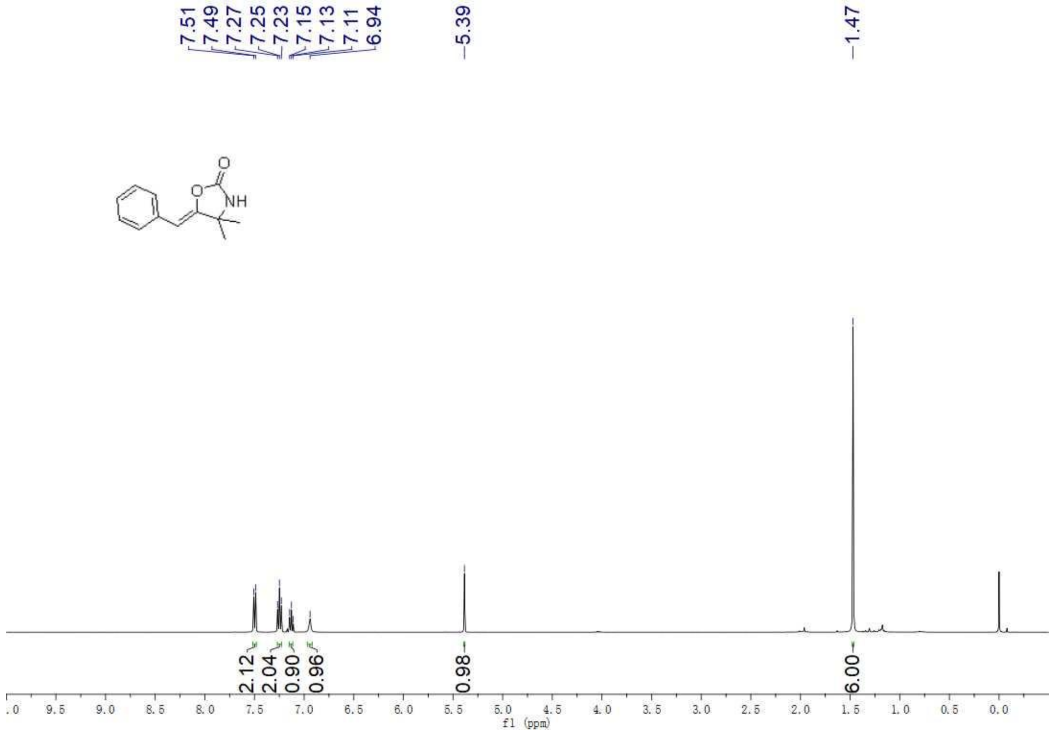
3,3'- (1,2-Phenylenebis(methylene)) bis (1-vinyl-1*H*-imidazol-3-ium) (NHC-HCO$_3$**)**, white solid; **^{1}H NMR** (400 MHz, D$_2$O) δ 7.79 (d, *J* = 2.2 Hz, 2H), 7.62 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.52 (dd, *J* = 5.6, 3.5 Hz, 2H), 7.47 (d, *J* = 2.1 Hz, 2H), 7.03 (dd, *J* = 15.6, 8.7 Hz, 2H), 5.77 (d, *J* = 3.0 Hz, 1H), 5.73 (d, *J* = 3.0 Hz, 1H), 5.57 (s, 4H), 5.42 (d, *J* = 3.0 Hz, 1H), 5.40 (d, *J* = 3.0 Hz, 1H). **^{13}C NMR** (101 MHz, D$_2$O) δ 160.4, 131.7, 131.2, 131.0, 127.8, 122.8, 119.6, 110.0, 50.5.

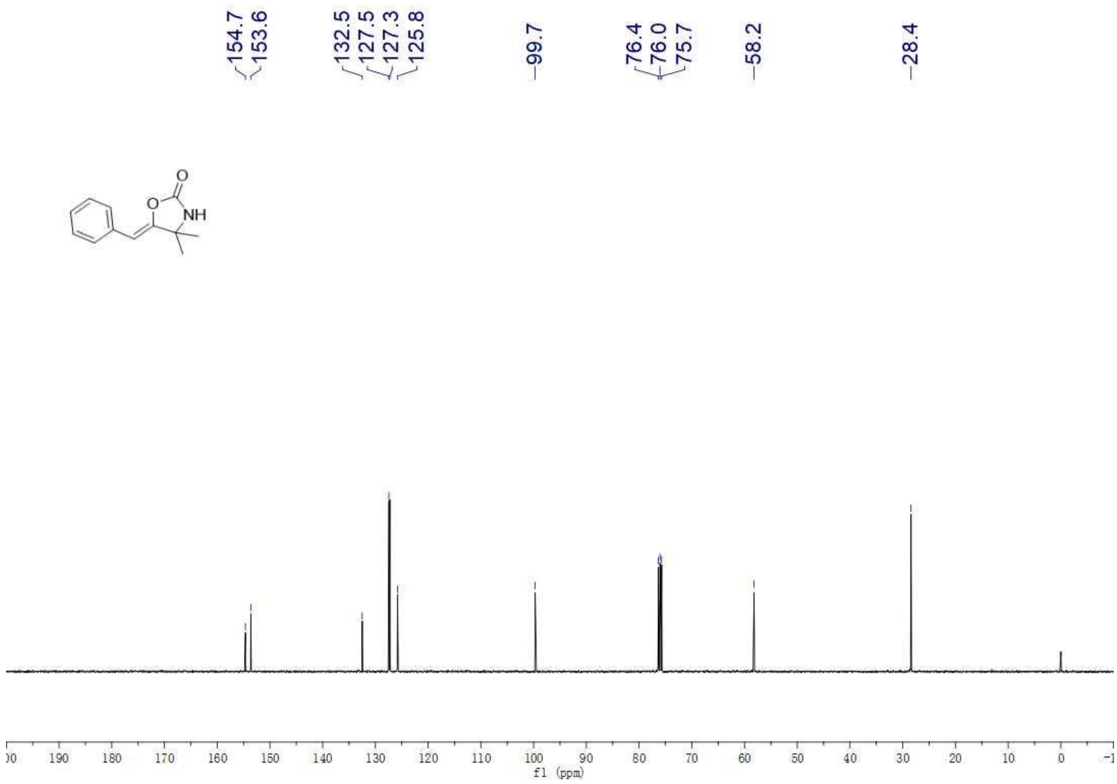

7.79 7.79 7.63 7.63 7.62 7.61 7.54 7.53 7.52 7.47 7.47 7.06 7.04 7.02 7.00 5.77 5.76 5.73 5.72 5.57 5.41 4.79
2HCO3-
2.00 2.07 2.13 2.05 2.11 1.06 1.00 4.05 1.03 1.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

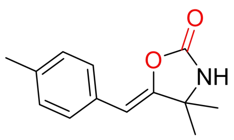

160.4
131.7 131.2 131.0 127.8 122.8 119.6 110.0
50.5
2HCO3-
HCO3-
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
NH

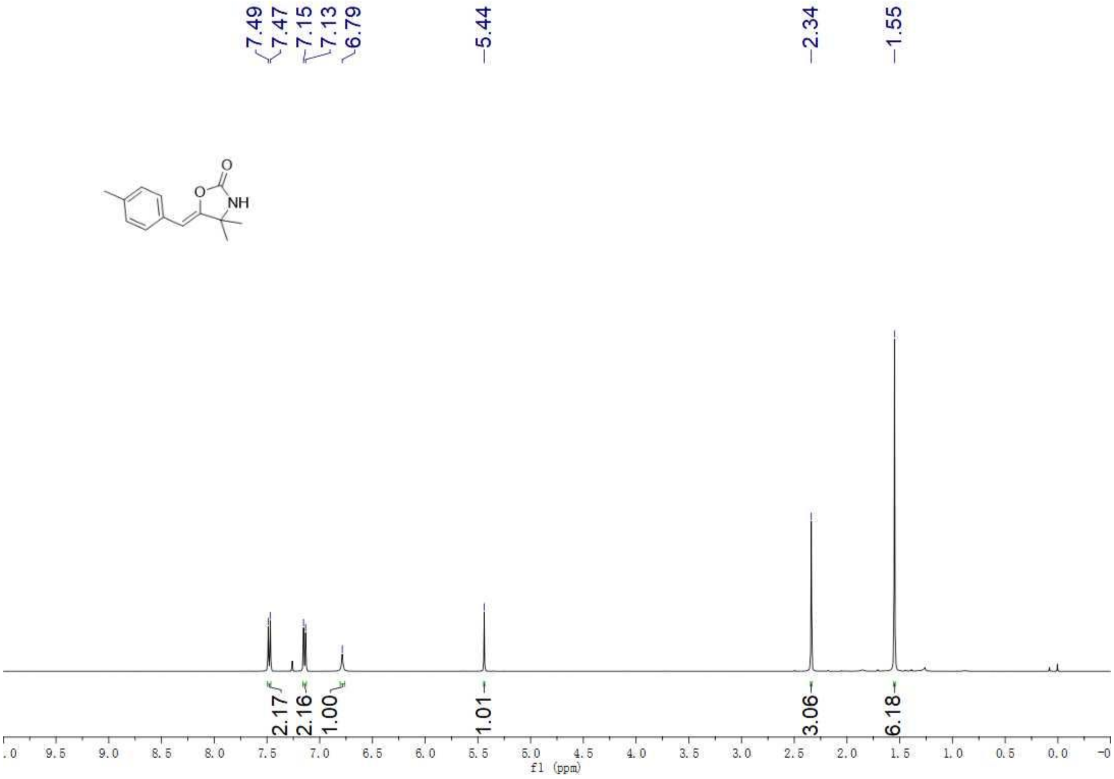
(*Z*)-5-Benzylidene-4,4-dimethyloxazolidin-2-one (2a), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51-7. 49 (m, 2H), 7.27-7.25 (m, 2H), 7.15-7.13(m, 1H), 6.95 (s, 1H), 5.40 (s, 1H), 1.48 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.7, 153.6, 132.5, 127.5, 127.3, 125.8, 99.7, 58.2, 28.4. HRMS (m/z) (ESI): calcd for $C_{12}H_{14}NO_2^+$ [M+H]$^+$ 204.1019, found 204.1023.

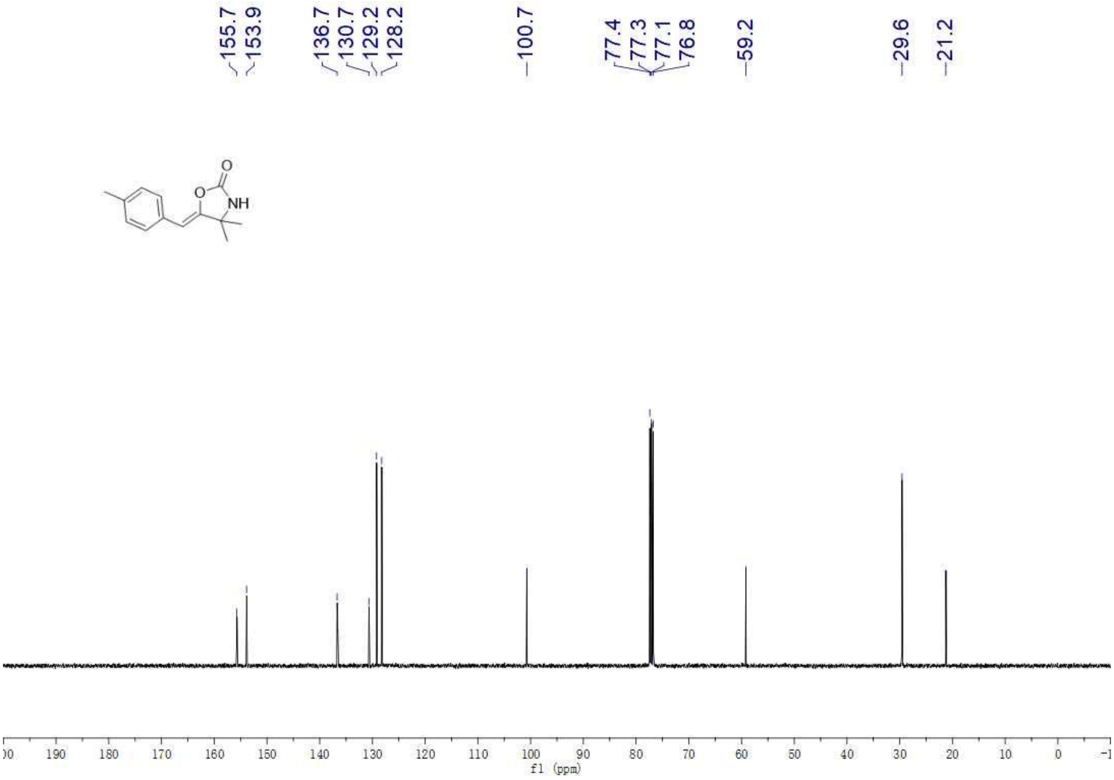


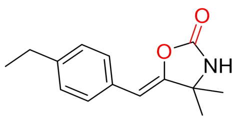




(*Z*)-4,4-Dimethyl-5-(4-methylbenzylidene)oxazolidin-2-one (2b), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.15-7.13 (m, 2H), 6.79 (s, 1H), 5.44 (s, 1H), 2.34 (s, 3H), 1.55 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.7, 153.9, 136.7, 130.7, 129.2, 128.2, 100.7, 59.2, 29.6, 21.2. HRMS (m/z) (ESI): calcd for $C_{13}H_{16}NO_2^+$ $[M+H]^+$ 218.1176, found 218.1177.

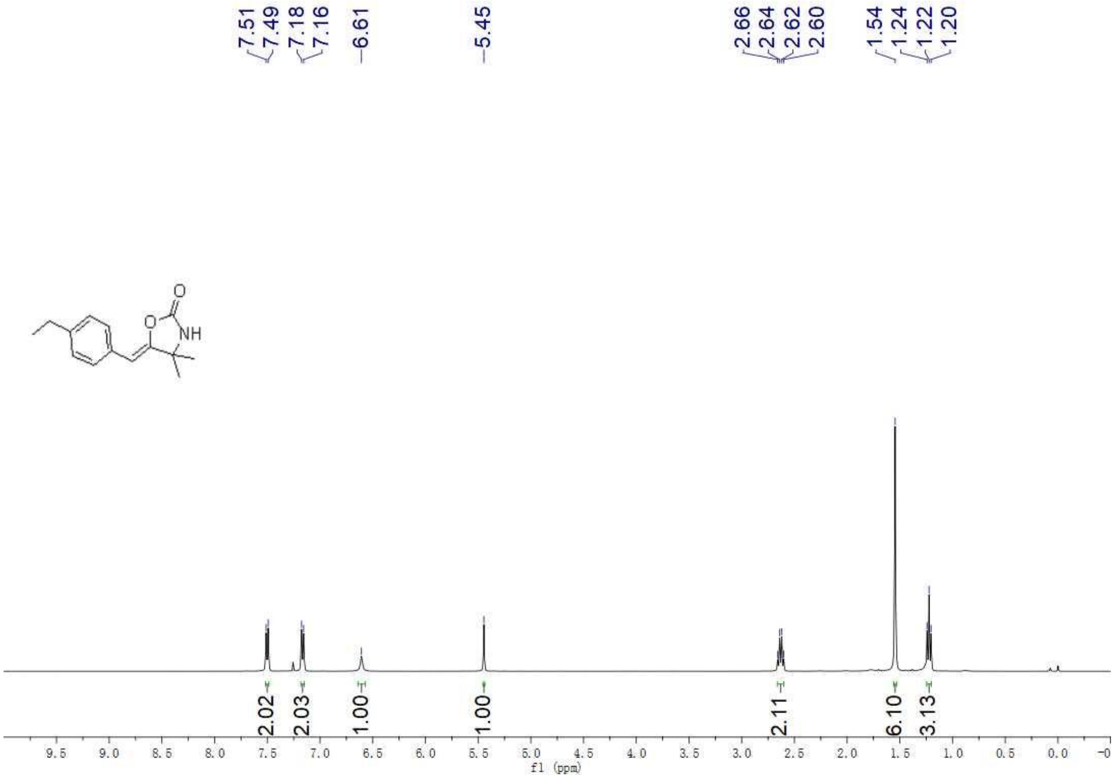


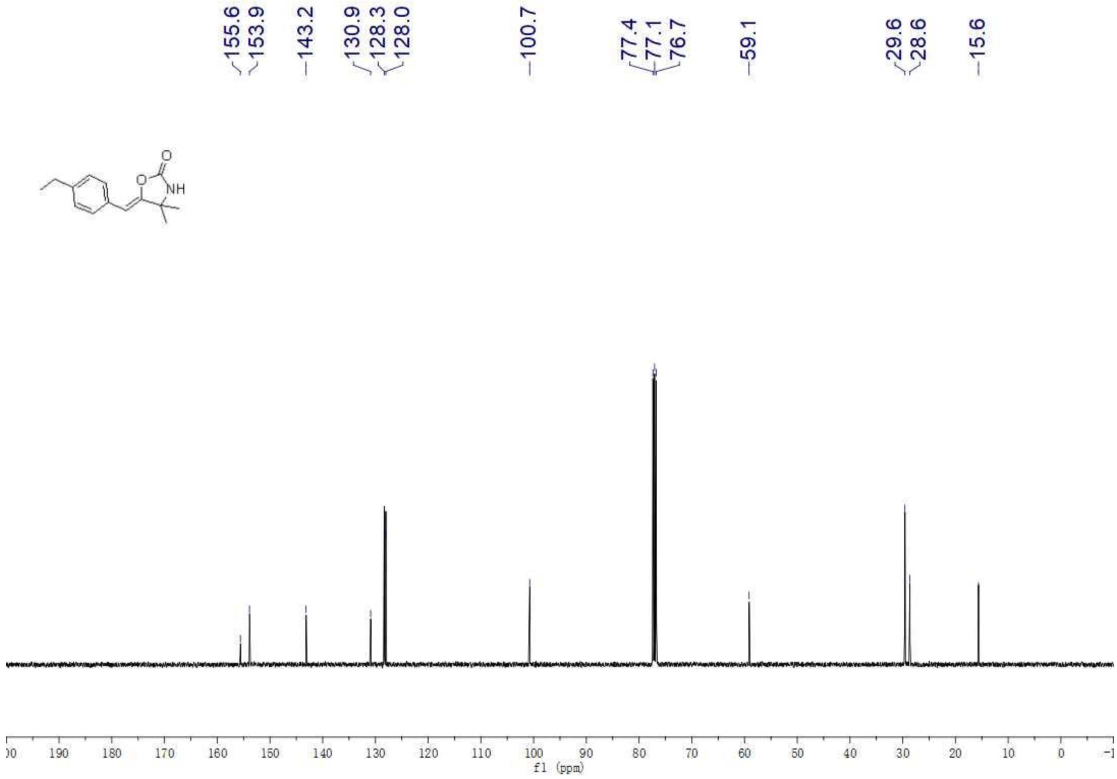


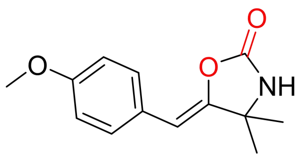


(*Z*)-5-(4-Ethylbenzylidene)-4,4-dimethyloxazolidin-2-one (2c), white solid; **^{1}H**

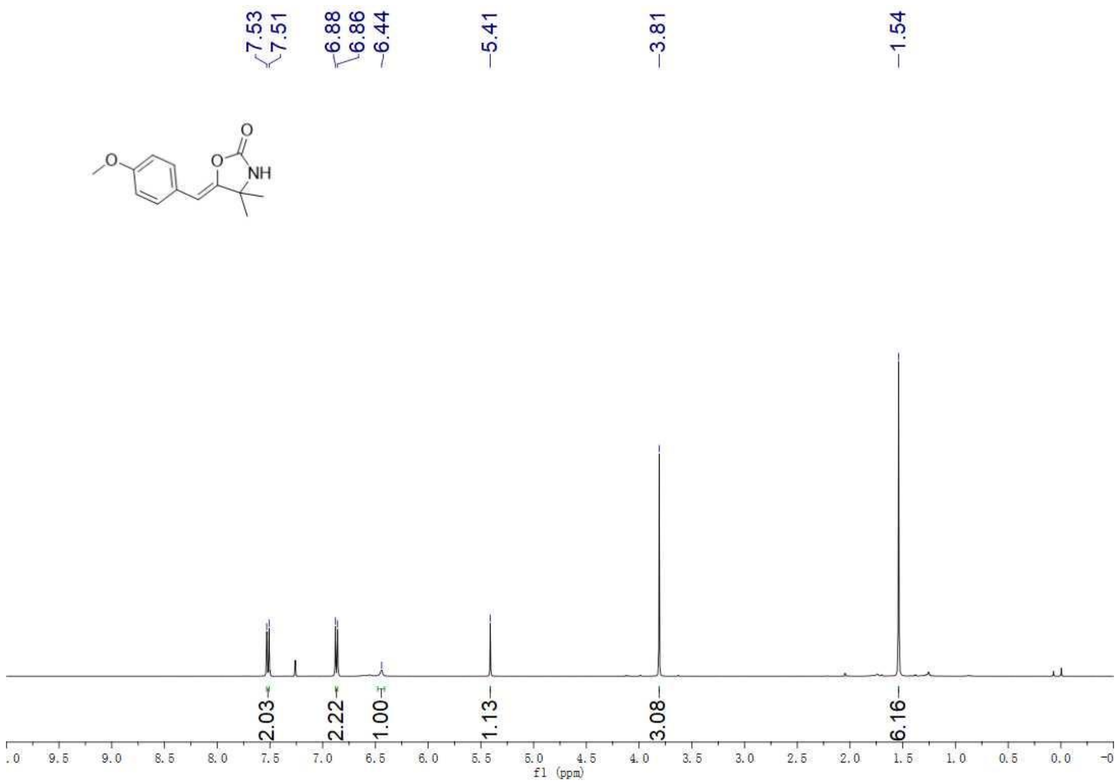
NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.18-7.16 (m, 2H), 6.61 (s, 1H), 5.45 (s, 1H), 2.63 (q, J = 7.6 Hz, 2H), 1.54 (s, 6H), 1.22 (t, J = 7.6 Hz, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 155.6, 153.9, 143.2, 130.9, 128.3, 128.0, 100.7, 59.1, 29.6, 28.6, 15.6. HRMS (m/z) (ESI): calcd for $C_{14}H_{18}NO_2^+$ $[M+H]^+$ 232.1332, found 232.1334.

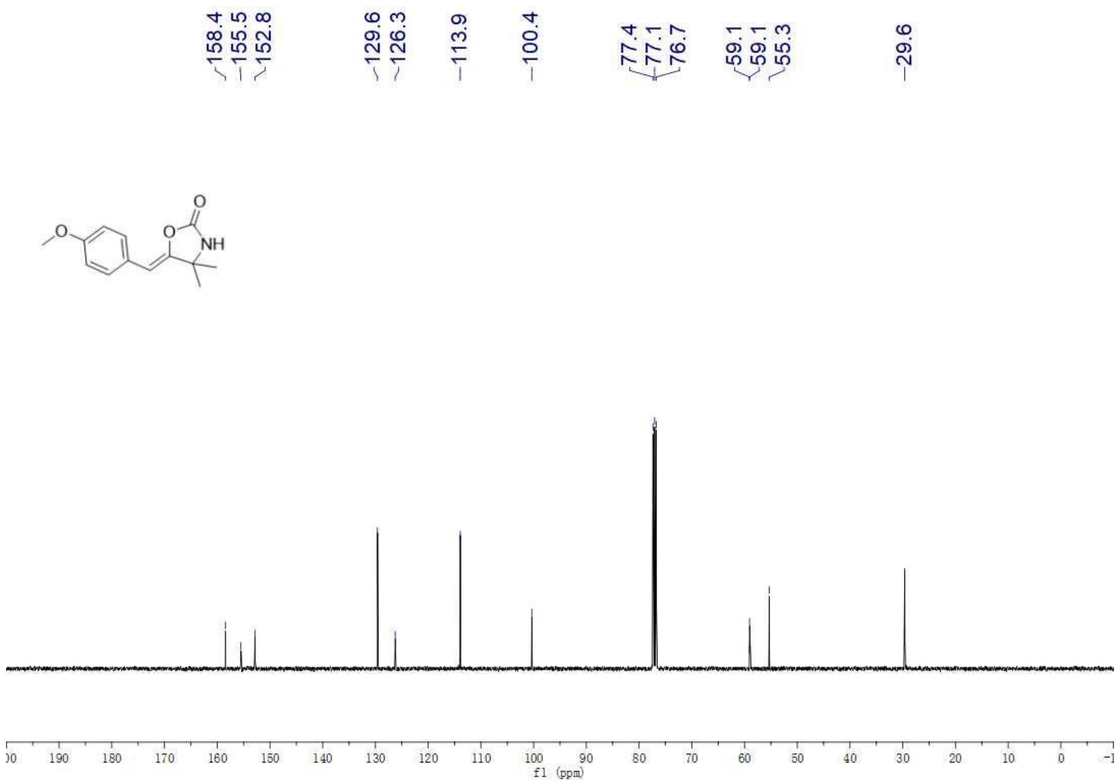


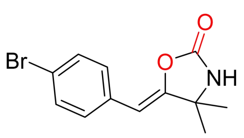




(*Z*)-5-(4-Methoxybenzylidene)-4,4-dimethyloxazolidin-2-one (2d), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.51 (m, 2H), 6.88-6.86 (m, 2H), 5.41 (s, 1H), 3.81 (s, 3H), 1.54 (s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.4, 155.5, 152.8, 129.6, 126.3, 113.9, 100.4, 59.1, 55.3, 29.6. HRMS (m/z) (ESI): calcd for $C_{14}H_{16}NO_3^+$ [M+H]$^+$ 234.1125, found 234.1126.

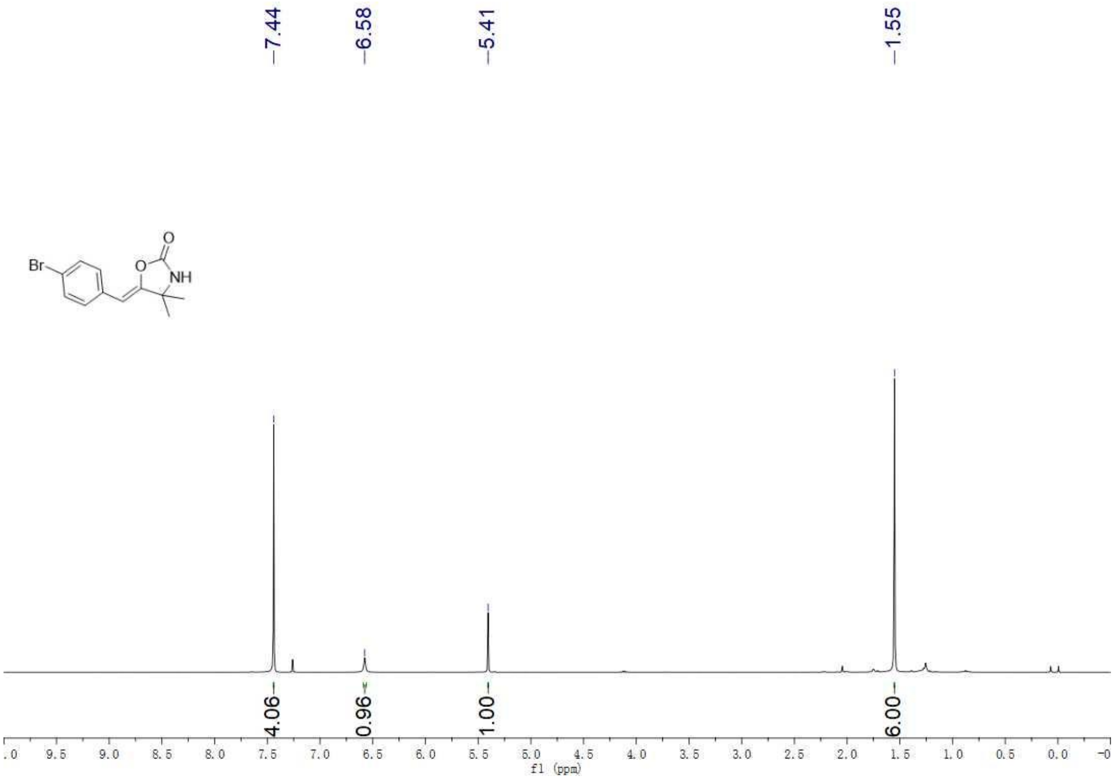


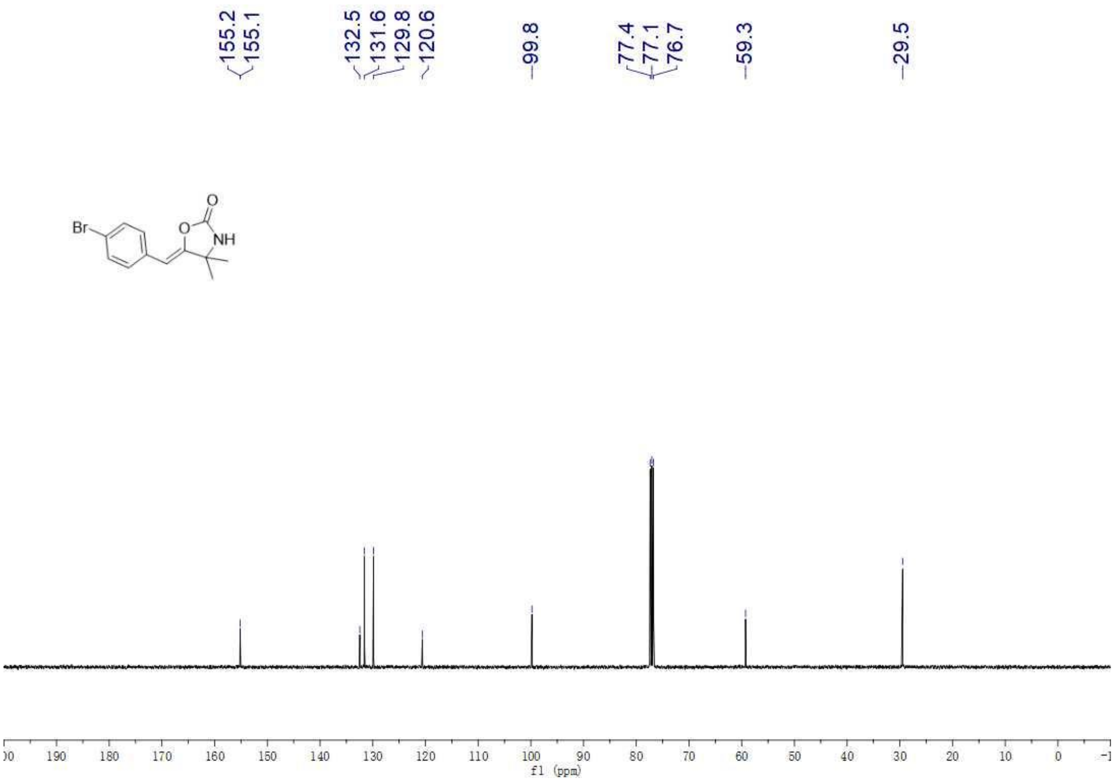


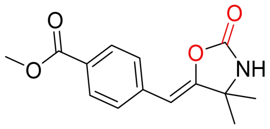


(*Z*)-5-(4-Bromobenzylidene)-4,4-dimethyloxazolidin-2-one (2e), white solid; ^{1}**H**

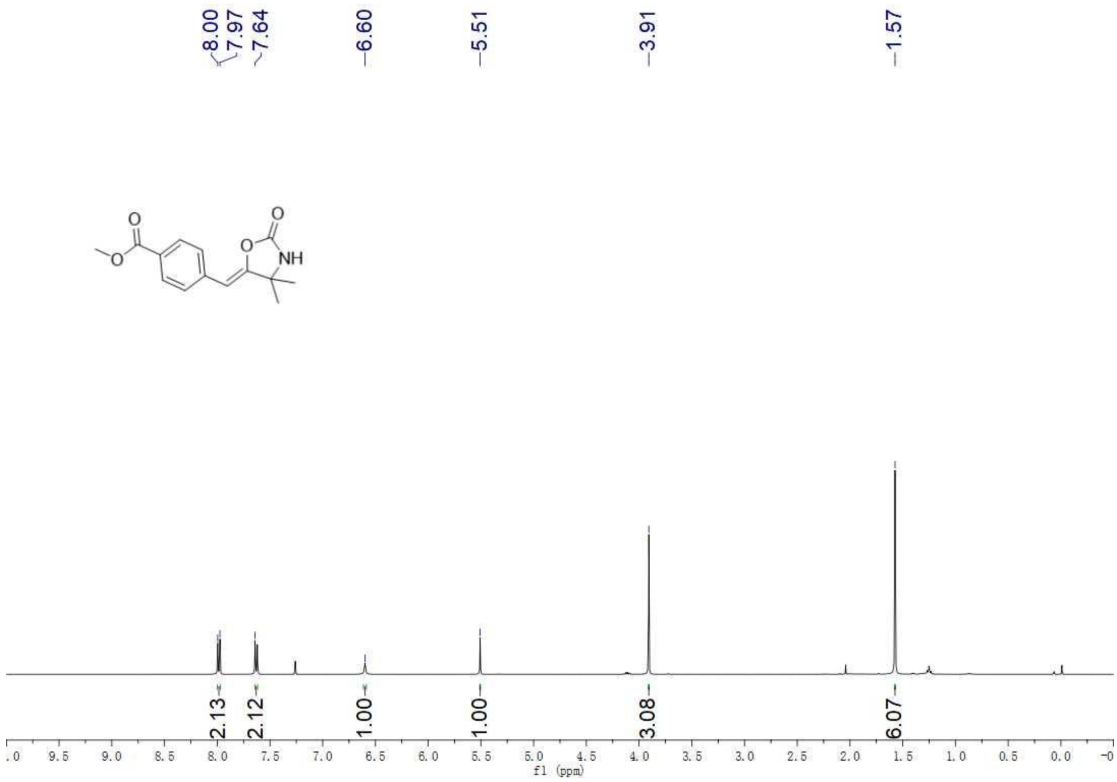
NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 4H), 6.58 (s, 1H), 5.41 (s, 1H), 1.55 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.2, 155.1, 132.5, 131.6, 129.8, 120.6, 99.8, 59.3, 29.5. HRMS (m/z) (ESI): calcd for $C_{12}H_{13}BrNO_2^+$ $[M+H]^+$ 282.0124, found 282.0128.

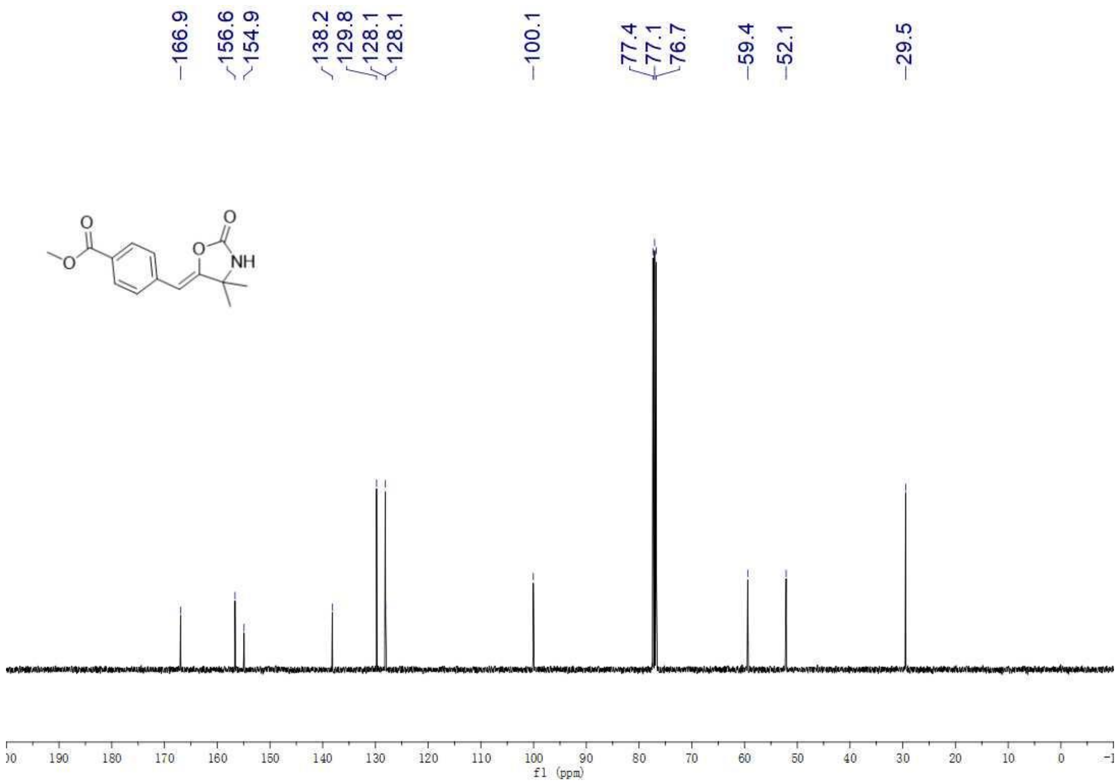


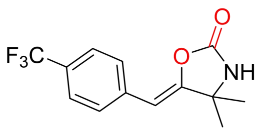




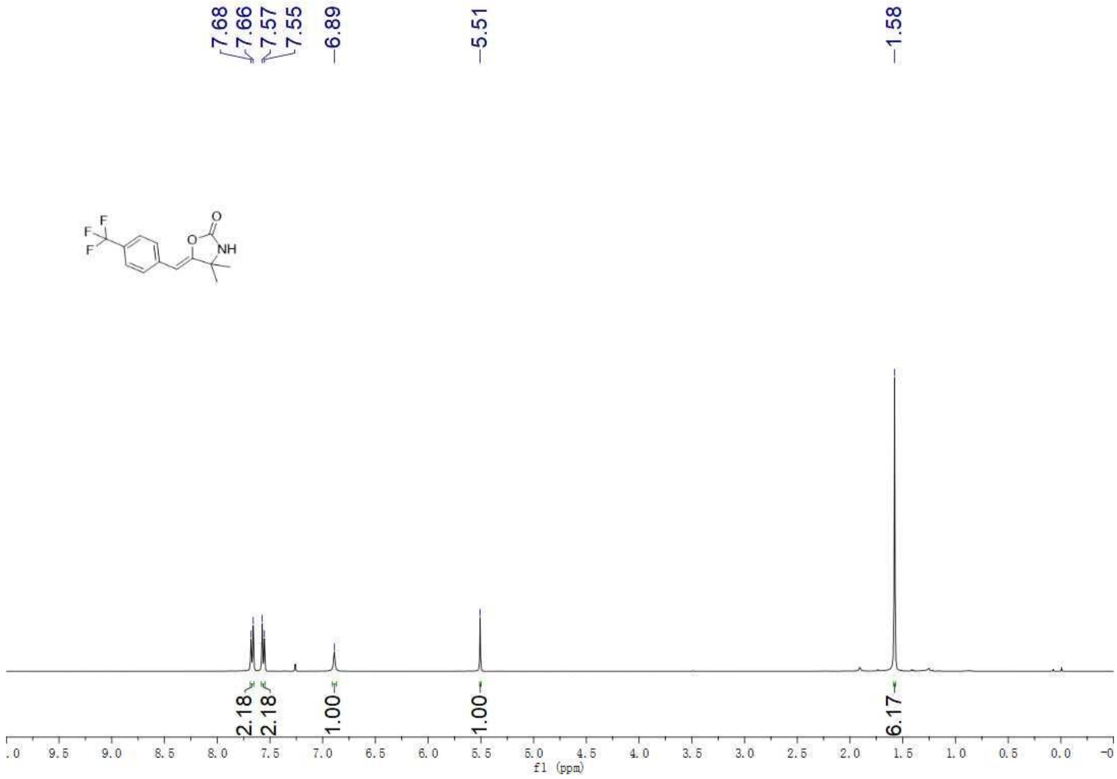
Methyl (*Z*)-4-((4,4-dimethyl-2-oxooxazolidin-5-ylidene)methyl) benzoate (2f), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00-7.97 (m, 2H), 7.64 (m, 2H), 6.60 (s, 1H), 5.51 (s, 1H), 3.91 (s, 3H), 1.57 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.9, 156.6, 154.9, 138.2, 129.8, 128.1 100.1, 59.4, 52.1, 29.5. HRMS (m/z) (ESI): calcd for $C_{14}H_{16}NO_4^+$ [M+H]$^+$ 262.1074, found 262.1072.

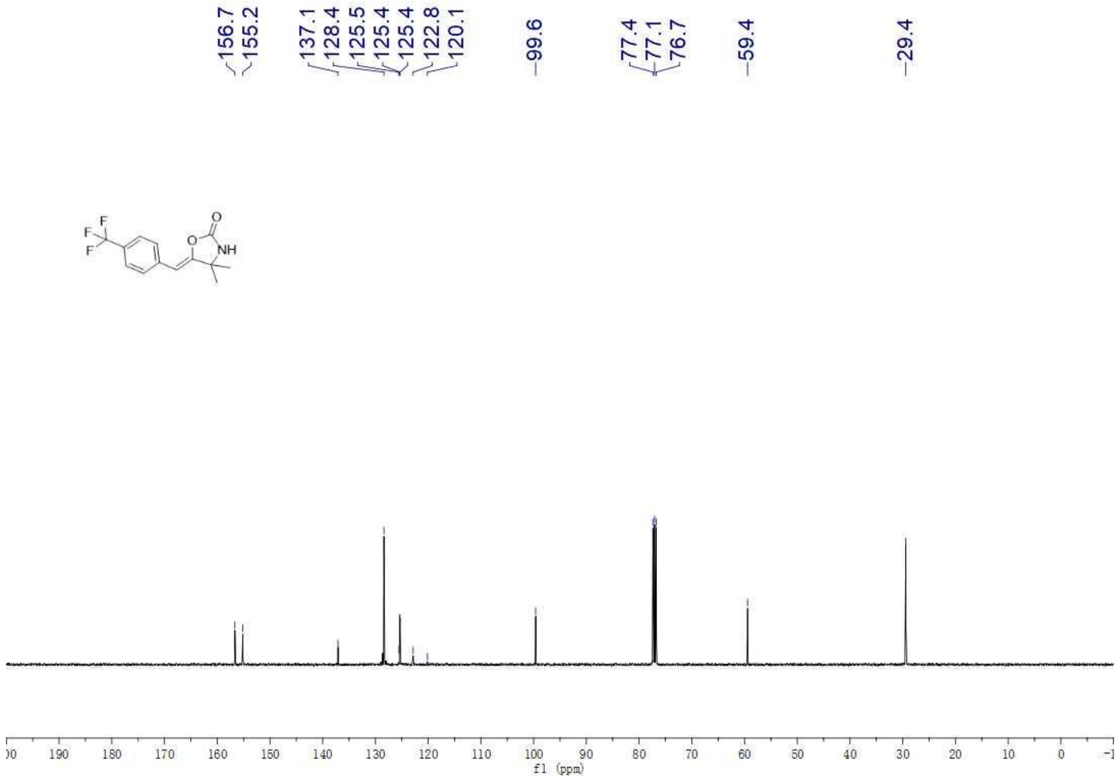


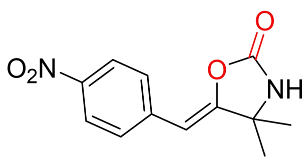




(*Z*)-4,4-Dimethyl-5-(4-(trifluoromethyl) benzylidene)oxazolidin-2-one (**2g**), white solid; **[1]H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 2H), 7.57-7.55 (m, 2H), 6.89 (s, 1H), 5.51 (s, 1H), 1.58 (s, 6H). **[13]C NMR** (101 MHz, $CDCl_3$) δ 156.7, 155.2, 137.1, 128.4, 125.4, 124.2(q, J = 272.2 Hz, 3F), 99.6, 59.4, 29.4. HRMS (m/z) (ESI): calcd for $C_{13}H_{13}F_3NO_2^+$ $[M+H]^+$ 272.0893, found 272.0900.

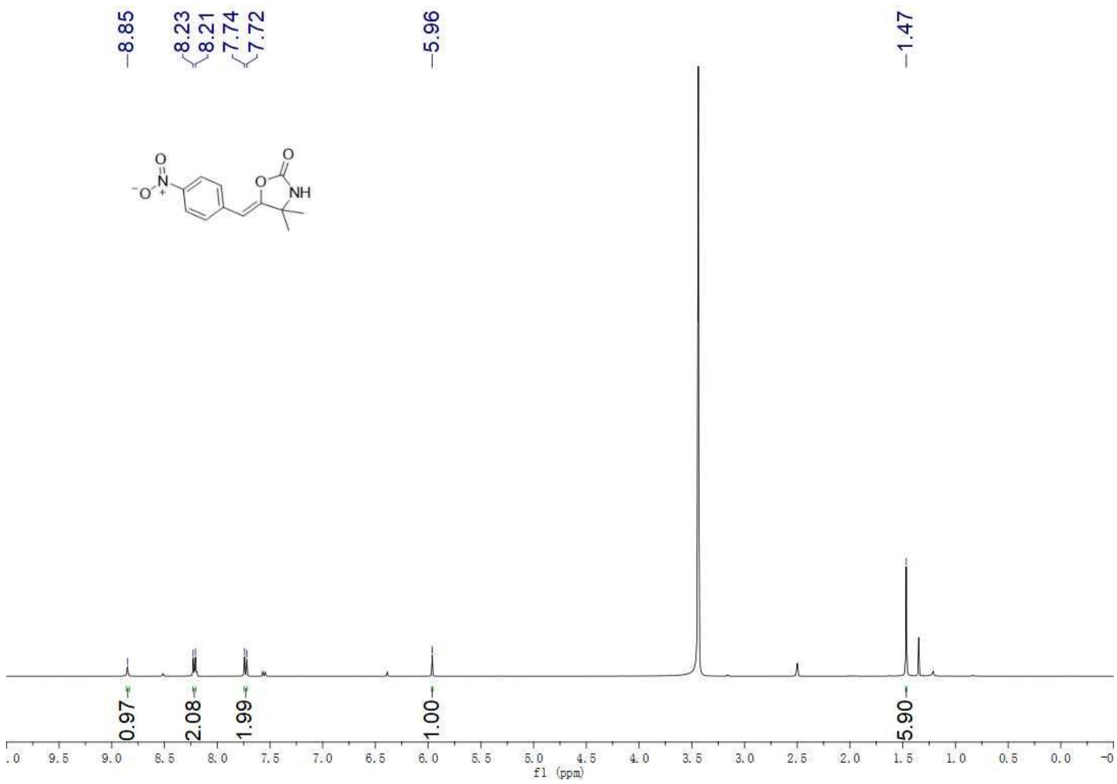


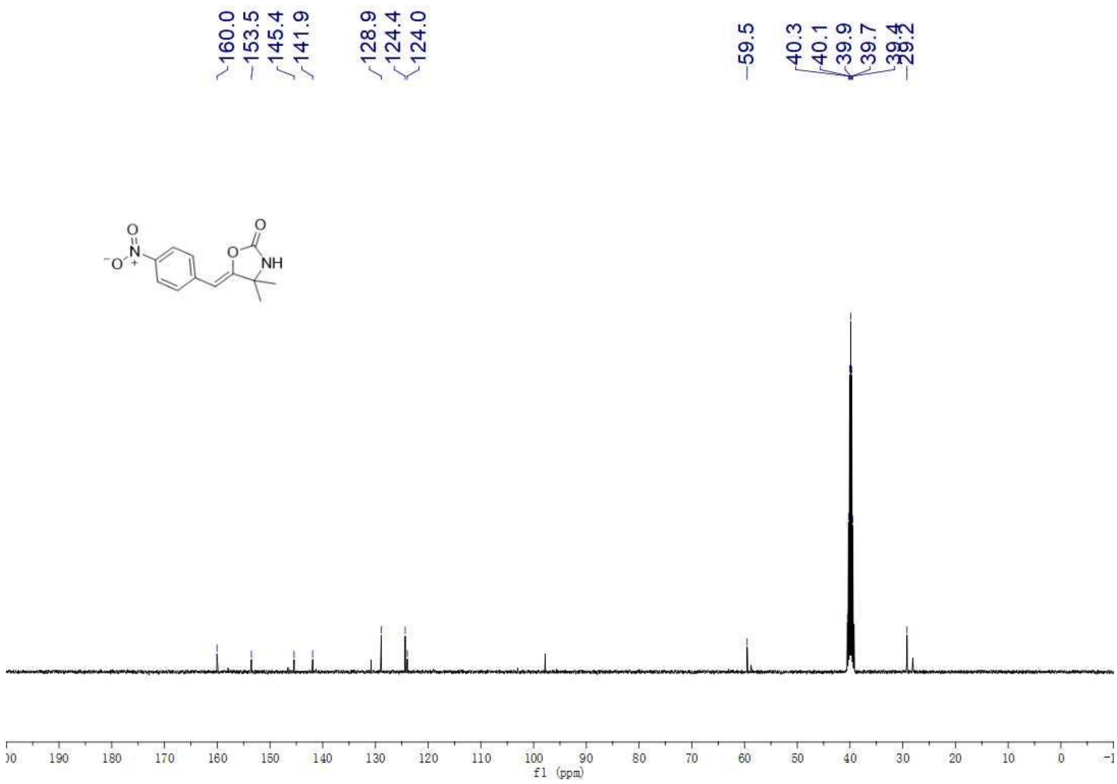


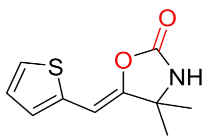


(*Z*)-4,4-Dimethyl-5-(4-nitrobenzylidene)oxazolidin-2-one (**2h**), white solid; **^{1}H**

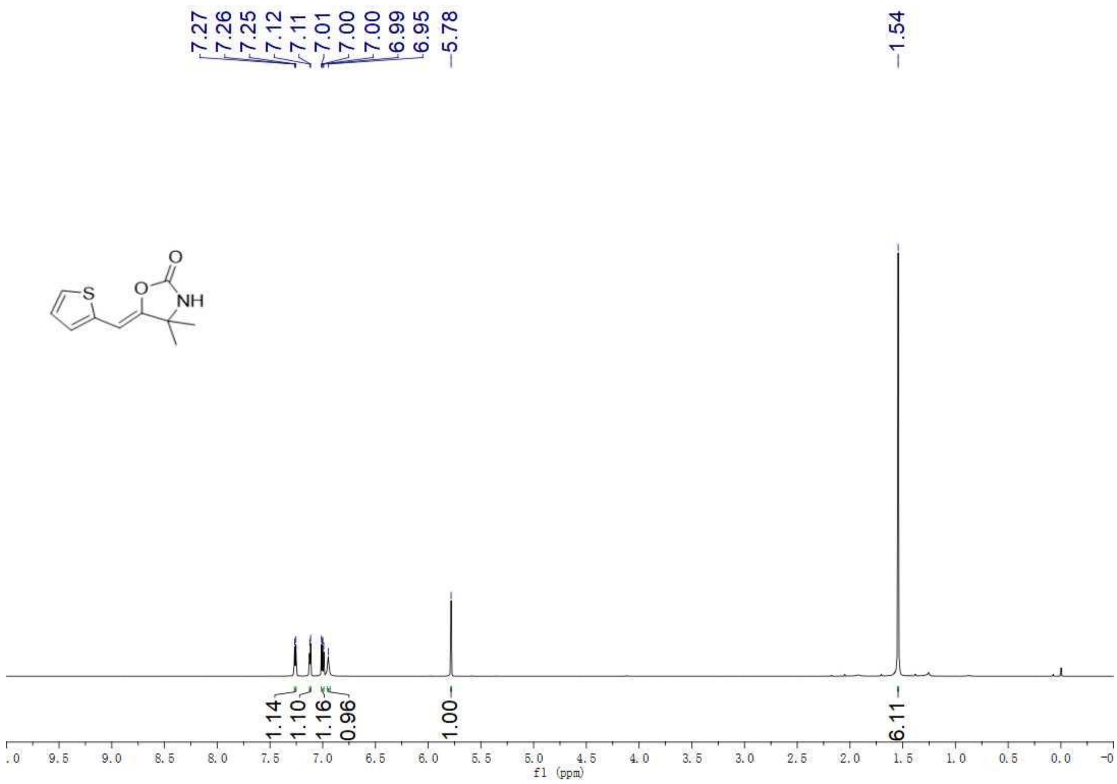
NMR (400 MHz, DMSO-d_6) δ 8.85 (s, 1H), 8.23-8.21 (m, 2H), 7.74-7.72 (m, 2H), 5.96 (s, 1H), 1.47 (s, 6H). ^{13}**C NMR** (101 MHz, DMSO-*d6*) δ 160.0, 153.5, 145.4, 141.9, 128.9, 124.4, 124.0, 59.5, 29.2. HRMS (m/z) (ESI): calcd for $C_{12}H_{13}N_2O_4^+$ $[M+H]^+$ 249.0870, found 249.0869.

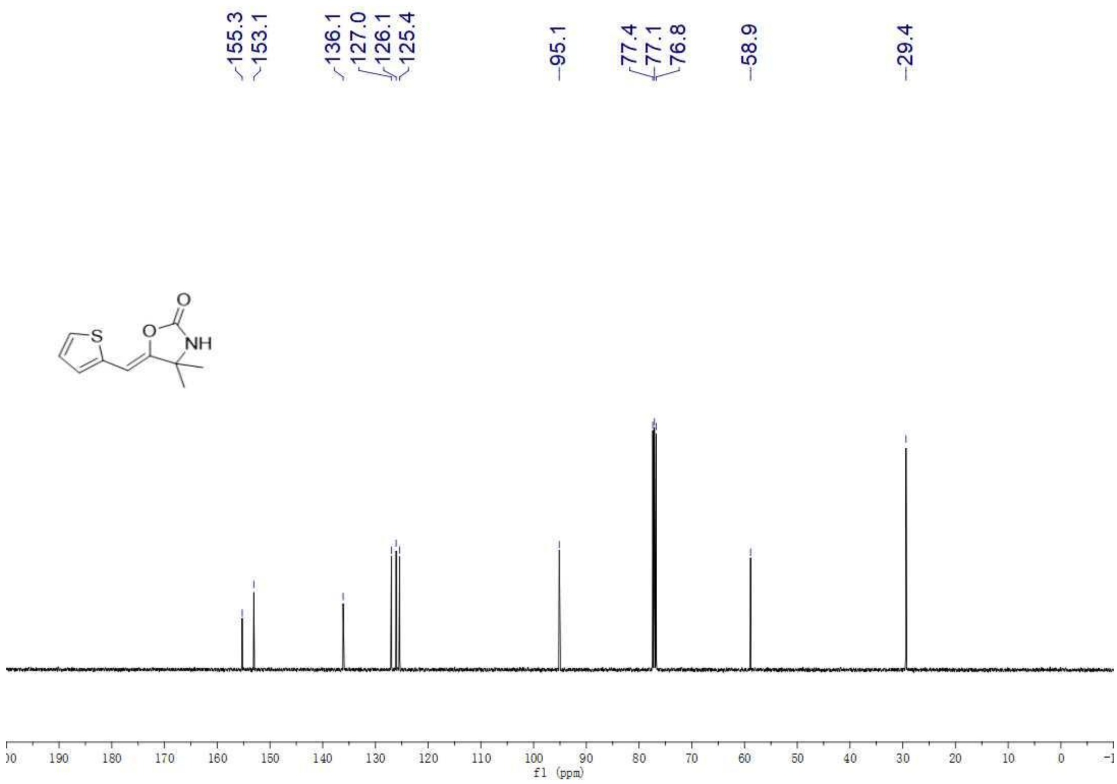


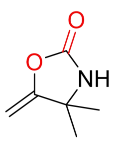




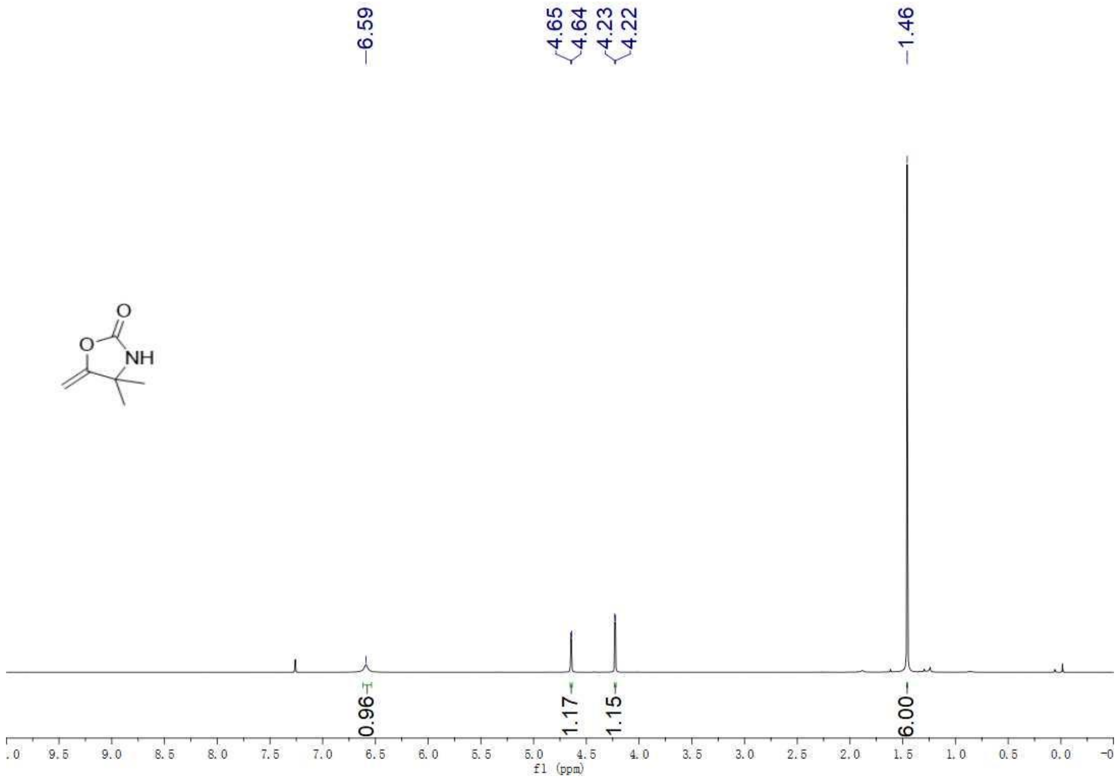
(*Z*)-4,4-Dimethyl-5-(thiophen-2-ylmethylene)oxazolidin-2-one (2i), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27-7.25 (m, 1H), 7.12-7.11 (m, 1H), 7.01-6.99 (m, 1H), 6.95 (s, 1H), 5.78 (s, 1H), 1.54 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.3, 153.1, 136.1, 127.0, 126.1, 125.4, 95.1, 58.9 29.4. HRMS (m/z) (ESI): calcd for $C_{10}H_{12}NO_2S^+$ $[M+H]^+$ 210.0583, found 210.0586.

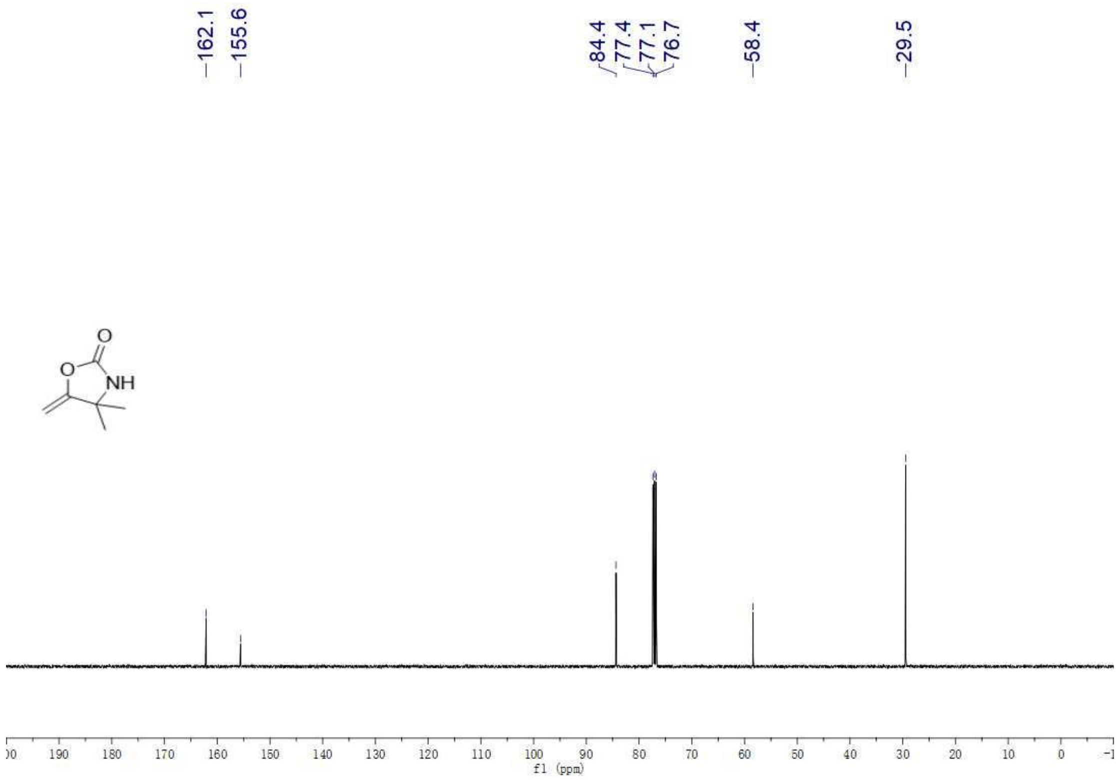


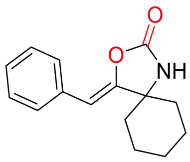




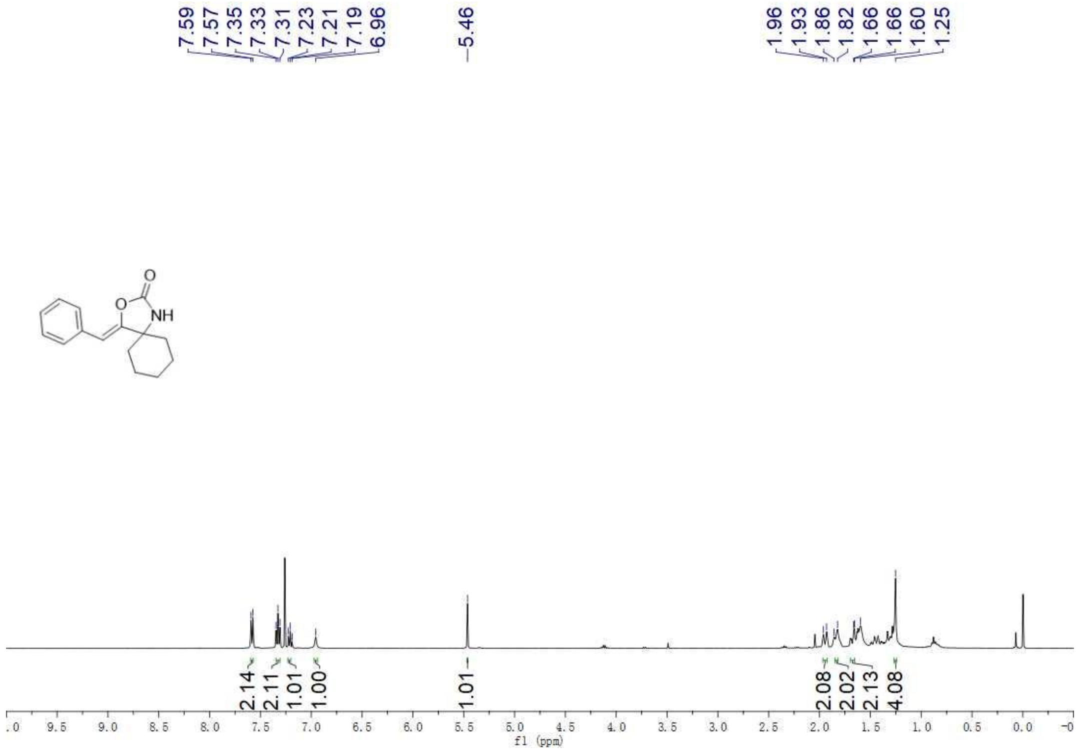
4,4-Dimethyl-5-methyleneoxazolidin-2-one (2j), white solid; ^{1}**H NMR** (400 MHz, CDCl3) δ 6.59 (s, 1H), 4.64 (d, *J* = 4.3 Hz, 1H), 4.23 (d, *J* = 3.4 Hz, 1H), 1.46 (s, 6H). ^{13}**C NMR** (101 MHz, CDCl3) δ 162.1, 155.6, 84.4, 58.4, 29.5. HRMS (m/z) (ESI): calcd for $C_6H_{10}NO_2^+$ $[M+H]^+$ 128.0706, found 128.0709.

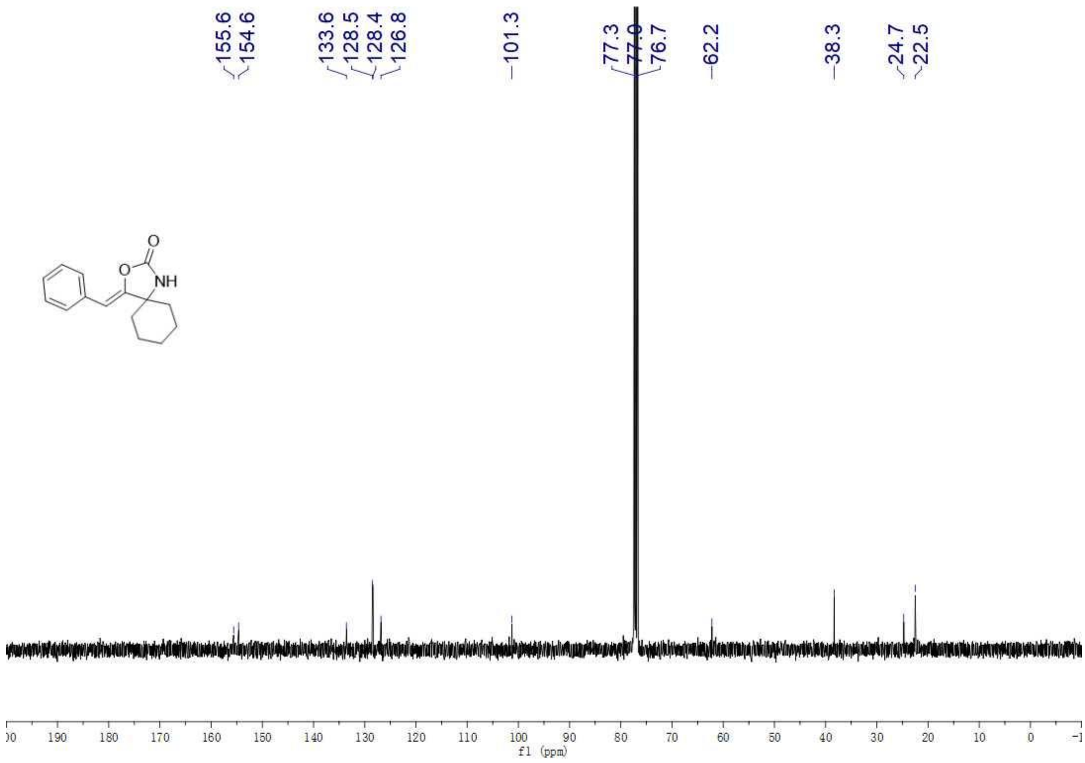






(*Z*)-4-Benzylidene-3-oxa-1-azaspiro [4.5] decan-2-one (2k), white solid; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59-7.57 (m, 2H), 7.35-7.31 (m, 2H), 7.23-7.19 (m, 1H), 6.96 (s, 1H), 5.46 (s, 1H), 1.95 (d, J = 12.4 Hz, 2H), 1.82 (s, 2H), 1.66 (d, *J* = 3.4 Hz, 2H), 1.25 (s, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.6, 154.6, 133.6, 128.5, 128.4, 126.8, 101.3, 62.2, 38.4, 24.7, 22.5. HRMS (m/z) (ESI): calcd for $C_{15}H_{18}NO_2^+$ [M+H]$^+$ 244.1332, found 244.1336.




155.6
154.6
133.6
128.5
128.4
126.8
101.3
77.3
77.0
76.7
62.2
38.3
24.7
22.5
O
O
NH
200
190
180
170
160
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140
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120
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80
70
60
50
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10
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-1
f1 (ppm)