Eco-Friendly Co-Catalyst-Free Cycloaddition of CO_2 and Aziridines Activated by a Porous MOF Catalyst

Ying Shi, Jian Zhao, Hang Xu, Sheng-Li Hou* & Bin Zhao*

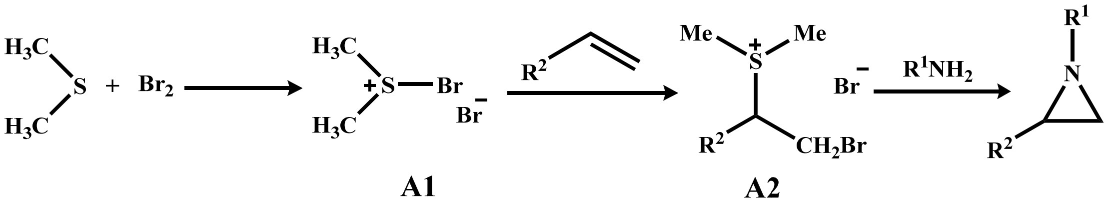
[a] Department of Chemistry, Key Laboratory of Advanced Energy Material Chemistry, Nankai University, Tianjin 300071, China.

Contents

S1. Synthesized of {[Co(DCTP)]·3.5DMA}$_n$ (2)

0.1 mmol $Co(NO_3)_2 \cdot 6H_2O$, 0.05 mmol H_2DCTP and 30 mg NaOAc were dissolved in 8 mL DMA. After adding 200 μL HOAc, the mixture was sealed in 25 mL Teflon-lined stainless autoclave, and then heated at 120 ºC for 72 h. After cooling down to room temperature, purple block crystals were obtained and washed with DMA for several times. Elemental analysis (%) for compound **2** ($CoC_{37}H_{44.5}N_{6.5}O_{7.5}$), calcd: C 58.53, H 5.91, N 11.99; Found: C 58.69, H 5.77, N 12.11.

S2. Synthesized of aziridines



The synthetic procedure was according to previous literature.[1] 40 mL CH_2Cl_2 solution with 0.2 mol bromine was slowly dropped into 40 mL CH_2Cl_2 solution with 0.2 mol dimethyl sulfide under an ice-salt bath condition. Orange solids of bromodimethyl sulfonium bromide (**A1**) were formed during stirring overnight. After filtration, **A1** was washed with diethyl ether several times. Then, 160 mmol olefin was dropped into 160 mL CH_3CN solution with 160 mmol **A1** under an ice-salt bath condition. After stirring overnight, white solid **A2** was formed, and then washed with fresh CH_3CN several times. Finally, 20-50 mmol amine solution was dropped into 20 mL H_2O solution with 10 mmol **A2**, and the mixture was stirred overnight at room temperature. Then dropping 20 mL saturated salt solution, the mixture was extracted with diethyl ether for three times and dried with anhydrous $MgSO_4$. The product aziridines were obtained by rotary evaporation.

S3. General procedure for the catalytic recyclable experiments

After completed catalytic reaction, the catalyst **1** was isolated by centrifugation, washed with fresh CH_2Cl_2 for three times and dried at 60 ºC. The recovered catalyst was used for the next cycle.

S4. General procedure for the Iodine adsorption experiments

50 mg compound **1** was immersed in fresh CH_2Cl_2 and exchanged CH_2Cl_2 three times a day for 5 days. After heating at 130 ºC, the prepared **1a** was immersed in 0.01M I_2/cyclohexane solution at room temperature for 48 h. The block crystal changed from green to dark brown. I_2@**1a** was washed with fresh cyclohexane for several times and carried out the thermogravimetric analysis.

Immersing 15 mg I_2@**1a** in fresh CH_3CN solution for 1 h, the dark brown crystals changed to green and the CH_3CN solution changed from colorless to orange.

S5. General procedure for the gas adsorption experiments

120 mg compound **1** was immersed in fresh CH_2Cl_2 for exchanging the free solvent molecules in the framework. Fresh CH_2Cl_2 was exchanged three times a day for 5 days, and then **1** was activated at 130 ºC to obtain **1a**. Activated **1a** adsorbed N_2 at 77 K and CO_2 at 273 K/298 K, respectively.

S6. X-ray single crystal structure analysis

Crystal diffraction data of compounds **1** and **2** were collected on a SuperNova Single Crystal diffractometer with graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å). The single-crystal structure was solved by direct methods and refined by full-matrix least-squares with SHELXS-97 and SHELXL-97 programs.[2] Due to the highly disordered solvent molecules in frameworks, we used PLATON/SQUEEZE programs[3] to remove, and the number of free solvent molecules was determined by elemental analysis and TG analysis. Detail single crystal data and structure refinement for **1** and **2** were recorded in Table S1.

Table S1. Crystal data and structure refinement for **1** and **2**.

Identification code	**1**	**2**
Empirical formula	$NiC_{42.5}H_{58.5}N_{9.5}O_{10.5}$	$CoC_{37}H_{44.5}N_{6.5}O_{7.5}$
Formula weight	929.17	759.22
Temperature/K	293(2)	293(2)
Crystal system	tetragonal	tetragonal
Space group	*P*-4*c*2	$P4_2/nmc$
a/Å	22.2452(2)	22.5767(6)
b/Å	22.2452(2)	22.5767(6)
c/Å	42.0696(6)	21.3815(7)
α/°	90	90
β/°	90	90
γ/°	90	90
Volume/$Å^3$	20818.1(5)	10898.3(7)
Z	16	8
F(000)	3712.0	1848.0
Goodness-of-fit on F^2	0.966	0.982
Final *R* indexes [I>=2σ (I)]	$R_1 = 0.0658$, $wR_2 = 0.1480$	$R_1 = 0.0671$, $wR_2 = 0.1729$
Final *R* indexes [all data]	$R_1 = 0.1039$, $wR_2 = 0.1646$	$R_1 = 0.1281$, $wR_2 = 0.2102$
Flack parameter	0.504(18)	-
CCDC	1887432	1945131

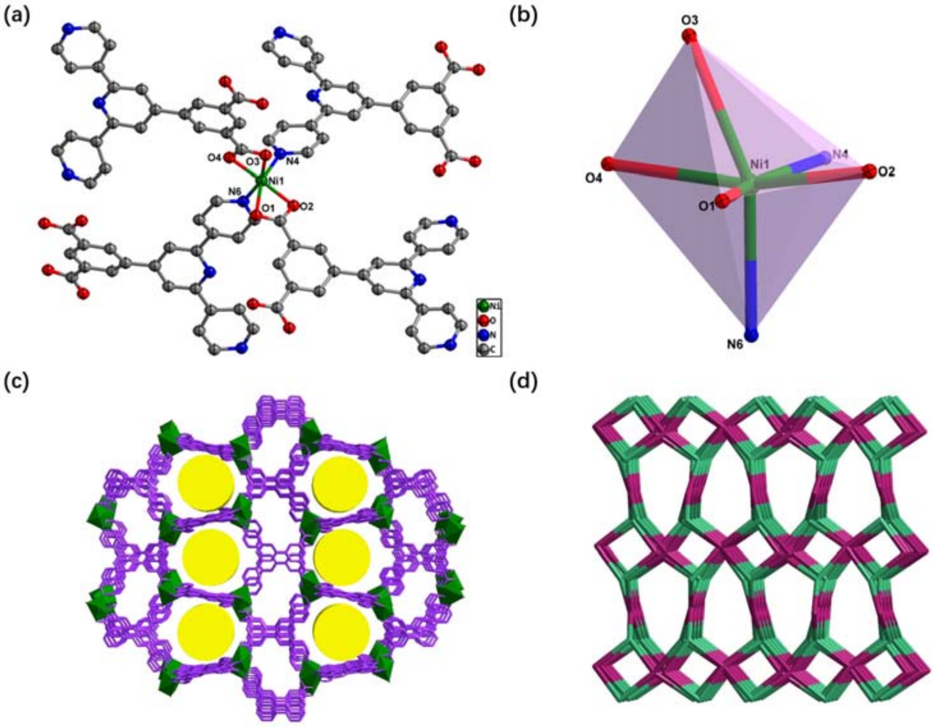


Fig. S1 (a) The asymmetric structural unit in compound **1**. (b) The deformed octahedral environments representation of Ni^{2+}. (c) The 3D framework of **1**. (d) The simplified *pts* topology of **1**.

S7. Characterization of the re-prepared compounds

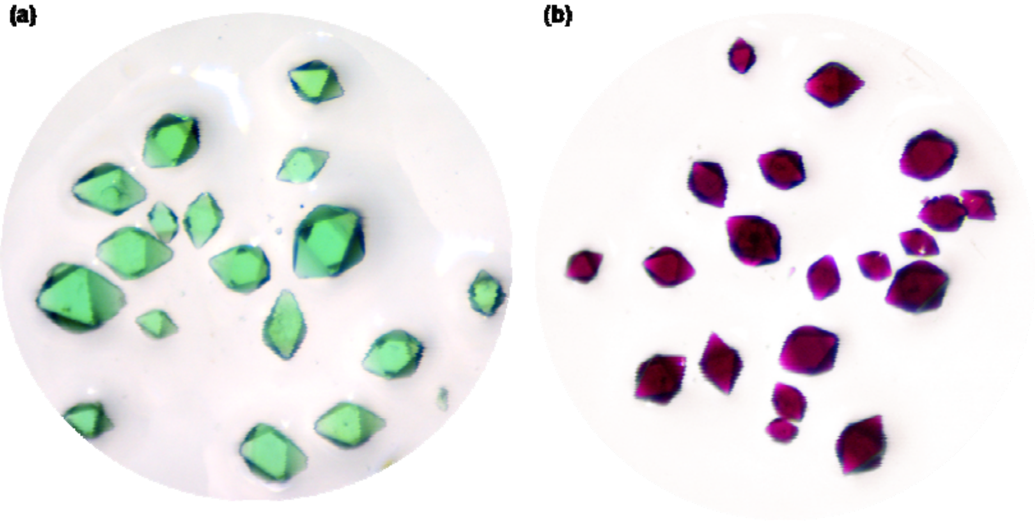


Fig. S2 Images of as-synthesized compound **1** (a) and as-synthesized compound **2** (b).

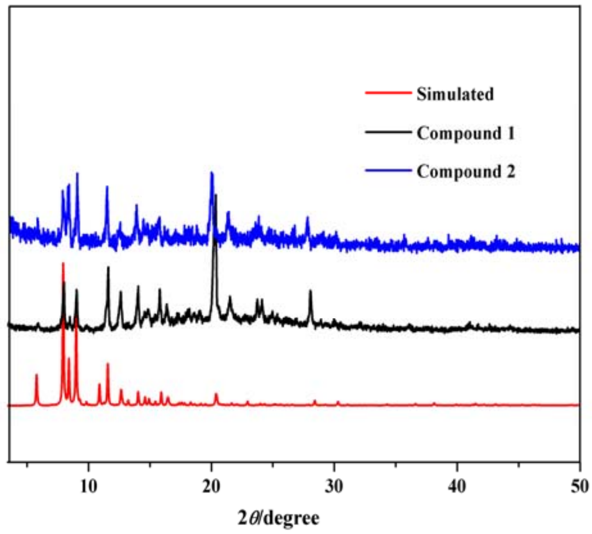


Fig. S3 The PXRD patterns of the simulated one from the single-crystal data (red), as-synthesized compound **1** (black) and compound **2** (blue).

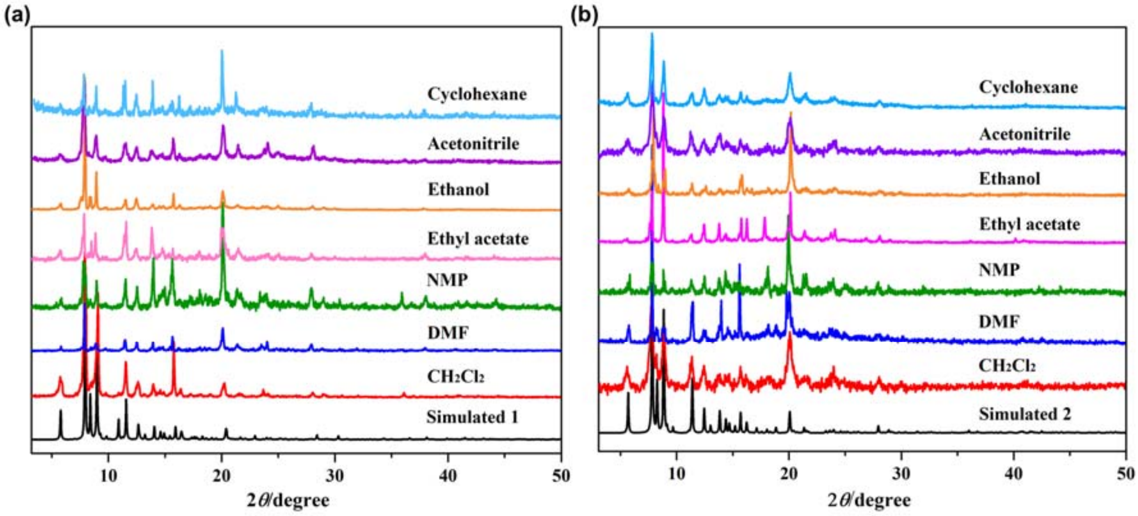


Fig. S4 The PXRD patterns of compound **1** (a) and **2** (b) after immersing different common solvents for 12 h.

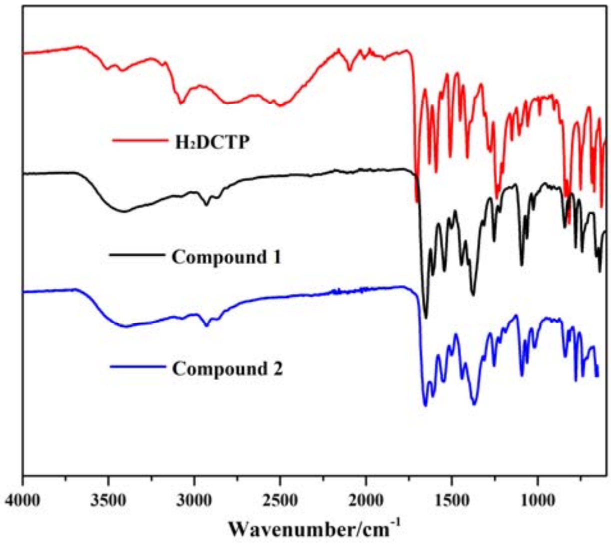


Fig. S5 The IR spectra of H_2DCTP ligand (red), compound **1** (black) and compound **2** (blue).

The peaks from 3600 to 2800 cm^{-1} belong to the stretching vibration of -OH in -COOH groups and the stretching vibration of C-H in aromatic rings of the ligand. These peaks become broadened and weakened in compounds, indicating that metal ions coordinate with the carboxyl groups and the pyridine N atoms. The peaks of 1650~1500 cm^{-1} and 1440~1370 cm^{-1} are attributed to the stretching vibration and bending vibration absorption of the C-O bond in the -COO group, respectively. The C-H characteristic absorption zone of the pyridine ring is 850 ~ 630 cm^{-1}.

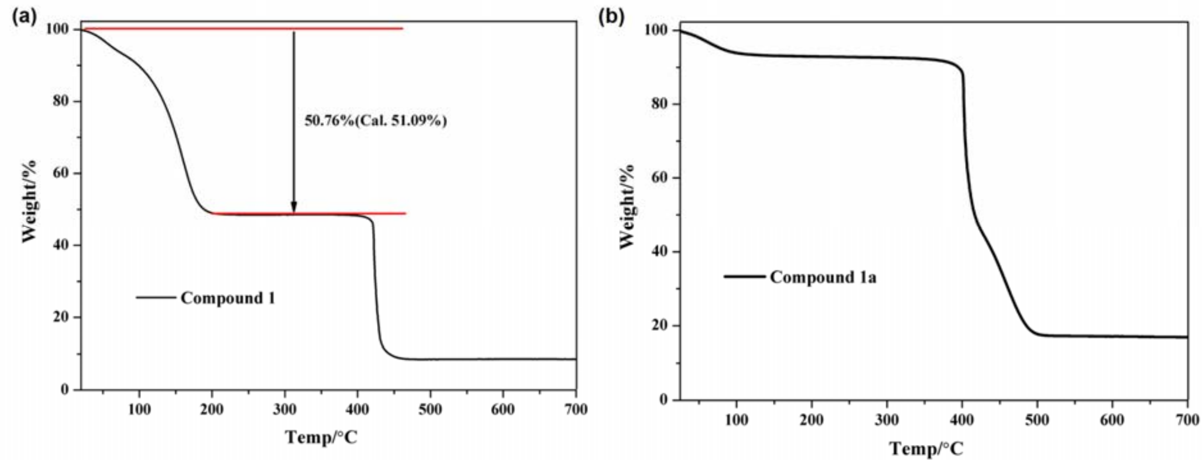


Fig. S6 The thermogravimetric analysis curves of compounds **1** (a) and **1a** (b).

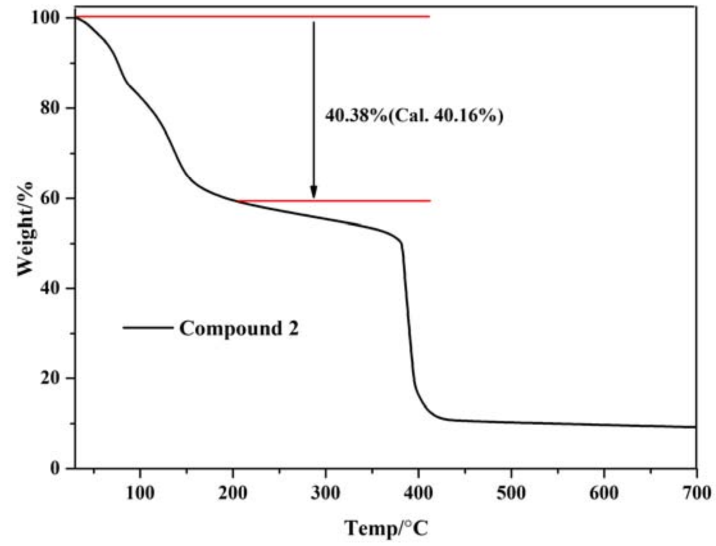


Fig. S7 The thermogravimetric analysis curve of compound **2**.

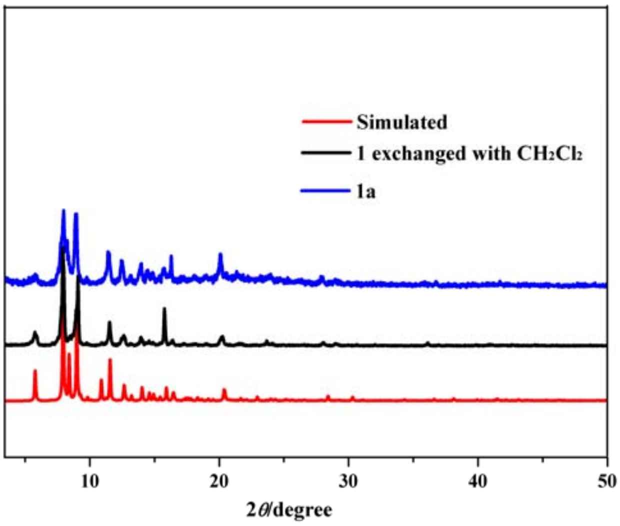


Fig. S8 The PXRD patterns of compound **1** exchanged with CH_2Cl_2 (black) and then heated at 130 °C for one hour (**1a**, blue).

S8. Iodine adsorption experiment

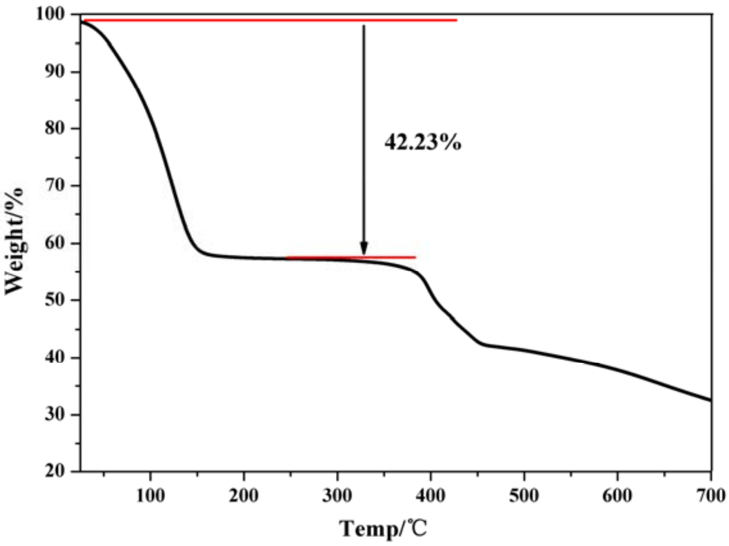


Fig. S9 The thermogravimetric analyses curve of I_2@**1a**.

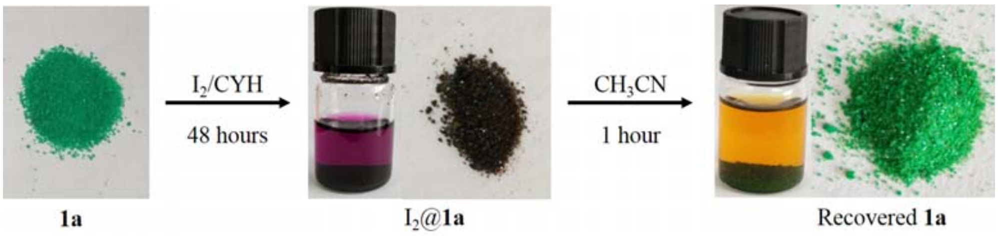


Fig. S10 Images of iodine adsorption process and iodine release process of compound **1a**. After adsorbing I_2, the green **1a** changed into dark brown to obtain I_2@**1a**. When I_2@**1a** were immersed in a fresh CH_3CN solution, the dark brown crystals changed in green and the CH_3CN solution changed from colorless to orange.

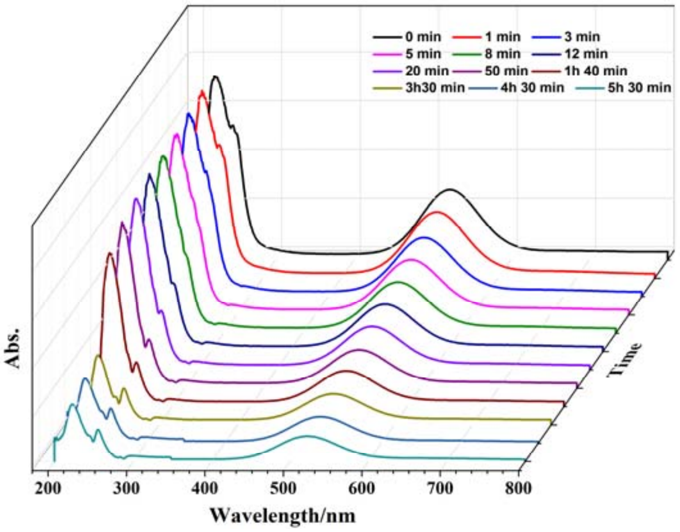


Fig. S11 The UV-Vis spectra to monitor the adsorption process of **1a** in cyclohexane solution of iodine (1.25 mM) at room temperature.

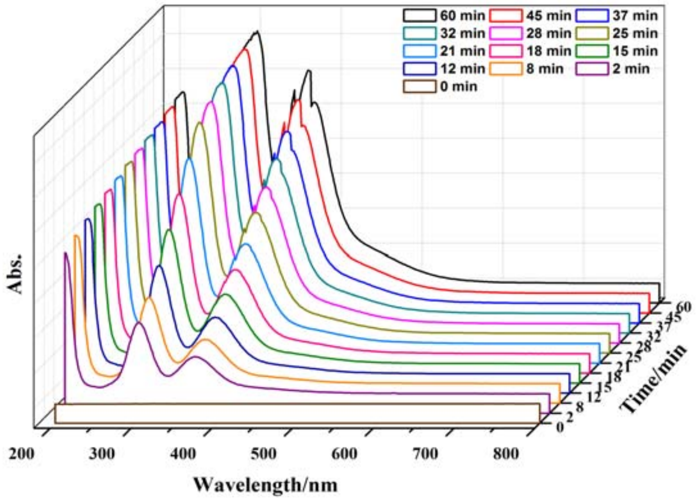


Fig. S12 The UV-Vis spectra to monitor the release process of I_2@**1a** in fresh CH_3CN solution in one hour. The characteristic peaks of I_2 and I_3^- appear at 206, 291 and 361 nm.

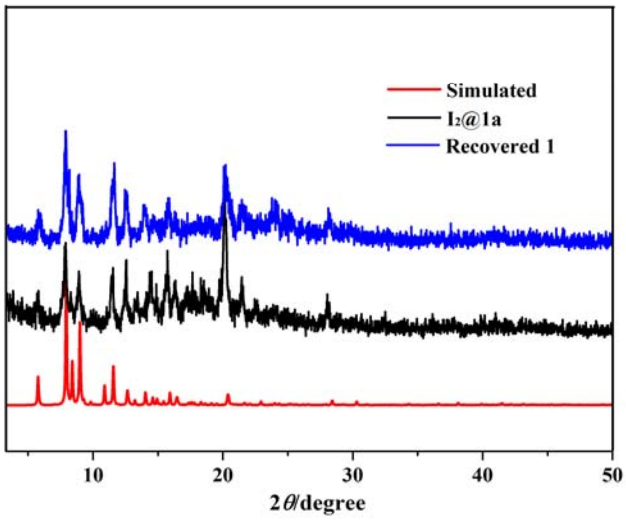


Fig. S13 The PXRD patterns of I_2@**1a** (black), and recovered **1** after the release of iodine in CH_3CN (blue).

S9. Gas adsorption experiment

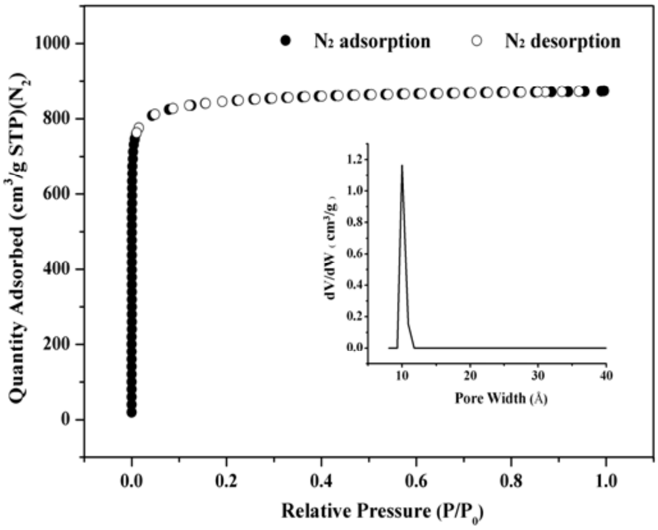


Fig. S14 The N_2 adsorption/desorption of **1a** at 77 K. Inset: The adsorption average pore diameter.

Table S2. Comparison of the CO_2 adsorption with some reported MOFs.

Chemical formula	Surface area (m^2/g)[a]		CO_2 adsorption (cm^3/g)		Ref.
	BET	Langmuir	273 K	298 K	
[Cu(Me-4py-trz-ia)]	1473	-	206.08	136.64	4
$\{[Zn(btz)]\cdot DMF\cdot 0.5H_2O\}_n$	1151[b]	1222[b]	181.22	111.78	5
$[Cu_2(L3)]_n$ (**NTU-113**)	3095	-	166.8	-	6
$[Cu_2(bdcppi)]_n$ (**SNU-50'**)	2300	2450	120	50	7
$\{[Ni(DCTP)]\cdot 6.5DMF\}_n$	2525	3789	103.98	53.71	**This work**
polyILs@MIL-101	2462	-	103	62	8
$\{[Sr(BDPO)_{0.5}(H_2O)]\cdot 2H_2O\}_n$	621	694	98.1	68.3	9
$[Yb_5(\mu_3\text{-}OH)_6(DDPY)_2(H_2O)_6](NO_3)\cdot(solv)_x$	1226	-	76.07	-	10
$[Cu(bpy)_2(EDS)]_n$ (**TMOF-1**)	256	-	47.1	32.4	11
$[Ni_2(dobdc)]_n$ (**Ni-MOF-74**)	936	1356	-	160.11	12
$[Cu_3(BTC)_2(H_2O)_3]_n$ (**HKUST-1**)	692.2	917.6	-	72	13

[a]Based on N_2 adsorption at 77 K. [b]Based on Ar adsorption at 87 K.

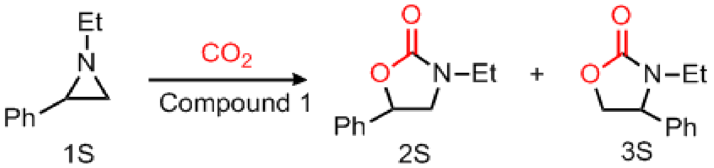
S10. Catalytic experiments for the cycloaddition of CO_2 and aziridines

Table S3. Comparison of the catalytic activity of compound **1** with some reported MOFs-based catalysts.

Chemical formula	Temp (°C)	Pressure (MPa)	Time (h)	Co-catalyst	Yield (%)	Recycled times	TOF (h^{-1})[a]	Ref.
$\{[Cu_2(BCP)(H_2O)_2]\cdot 3DMF\}_n$	100	2	12	TBAB	>99	Ten	0.83	1
$\{[Co_2(XN)_2(IPA)_2]\cdot 2H_2O\}_n$	30	1	10	TBAB	89	Five	2.45	14
$\{[Zn(btz)]\cdot DMF\cdot 0.5H_2O\}_n$	70	2	12	TBAB	>99	Ten	2.97	15
$\{[Zn(H_2O)(C_5H_7NO_4)]\cdot H_2O\}_n$	r.t.	1	24	TBAB/ H_2O	94	-	4.89[b]	16
$\{Cu_4(CuTBCPPP)(H_2O)_4\}_n$	100	2	10	TBAB	>99	Two	16[b]	17
$\{[Ni(DCTP)]\cdot 6.5DMF\}_n$	70	2	10	No	95	Five	32[c]	**This work**

[a]TOF: Turnover frequency represented the number of transformations at a single active site per hour. [b]1-Methyl-2-phenylaziridine as substrate. [c]20 mmol Substrate, 0.05 mmol catalyst, 70 °C, 10 h, 2 MPa of CO_2.

Table S4. Control experiments of cycloaddition of CO_2 with aziridines.[a]



Entry	Catalyst **1** (mg)	Temp (°C)	Yield (%)[b]	Regio-sel[c]
1	45	30	60	97:3
2	45	50	85	99:1
3	45	60	87	99:1
4	45	70	95	98:2
5	45	80	89	98:2
6	45	100	88	98:2
7[d]	45	70	12	74:26
8[e]	45	70	18	85:15
9[f]	45	70	81	95:5

[a]Reaction conditions: 1-Ethyl-2-phenylaziridine (2.0 mmol), solvent-free, compound **1** (45 mg based on metal center, about 2.4 mol%), CO_2 (2.0 MPa), 10 h. [b]Using 1,3,5-trimethoxybenzene as an internal standard to determine the total yield of the products **2S** and **3S** by ^{1}H NMR. [c]The molar ratio of **2S** to **3S**. [d]CO_2 (0.1 MPa, 10 h). [e]CO_2 (0.1 MPa, 72 h). [f]CO_2 (1 MPa, 10 h). The above experiments were repeated twice.

To explore the optimum reaction conditions, 1-ethyl-2-phenylaziridine was selected as the model substrate to investigate under various conditions (Table S4). 45 mg compound **1** and 2 mmol 1-ethyl-2-phenylaziridine were sealed in an autoclave without additional solvent and co-catalyst at different temperatures (entries 1-6). With the rise of temperature, the yields of 3-ethyl-5-phenyloxazolidin-2-one (**2S**) and 3-ethyl-4-phenyloxazolidin-2-one (**3S**) were significantly increased. However, higher temperature caused the yield to decrease a little owing to the self-polymerization of partial substrates. Hence, the reaction was carried out at 70 ºC. The pressure was also investigated. Under 0.1 MPa of CO_2 at 70 ºC for 10 h, **1** displayed low catalytic activity. After extending reaction time to 72 h, the yields of **2S** and **3S** increased slightly. Further increasing the pressure to 1 MPa, the yield of product was 81%. When the pressure of CO_2 reached 2 MPa, the catalytic efficiency increased to 95% (entries 7-9). So, we chose the optimal condition was 70 ºC and 2 MPa of CO_2 for 10 h without any solvent and co-catalyst.

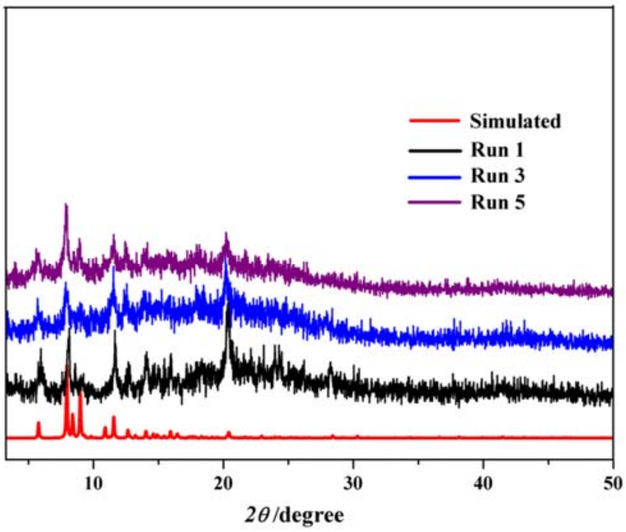


Fig. S15 The consistent PXRD patterns of **1** with the simulated data after five cycles.

Table S5. The ICP results of compound **1** after recyclable recyclings and mass loss percent.

Compound **1**	Ni
Filter liquor after fifth catalytic recyclings (ppm)	1.84
Mass loss percent (%)	1.8

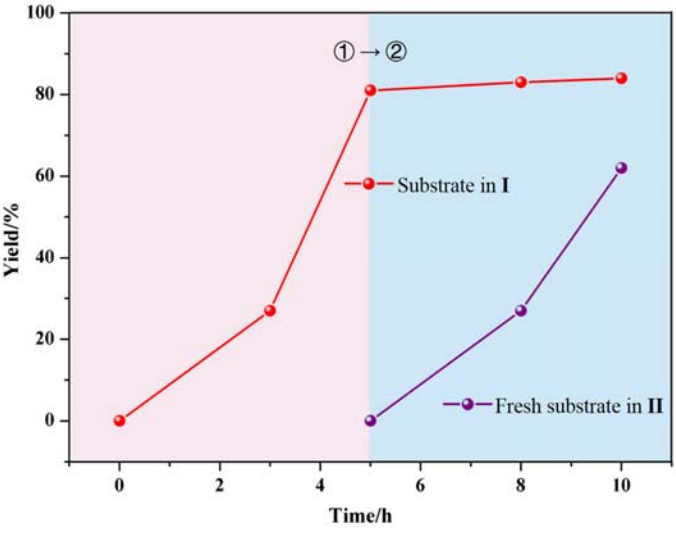


Fig. S16 Catalytic filtration experiments for the cycloaddition reaction of CO_2 and aziridines. Reaction conditions: 45 mg compound **1** and 2 mmol 1-ethyl-2-phenylaziridine were sealed in an autoclave at 70 ºC and 2 MPa CO_2 for different times. The yields were analyzed by ^{1}H NMR with 1,3,5-trimethoxybenzene as an internal standard.

In a typical experiment, catalyst **1** and 1-ethyl-2-phenylaziridine (substrate) were sealed in an autoclave **I** without additional co-catalyst. The mixture was stirred at 70 ºC and 2 MPa CO_2, and the products were determined by ^{1}H NMR. ① After 5 hours of reaction, the catalyst **1** was isolated from **I** by centrifugation and placed in another new reactor **II**. At the same time, fresh 1-ethyl-2-phenylaziridine was added into **II** and reacted for 5 hours. ② The filtrate in **I** was stirred for an additional 5 hours under optimal reaction conditions. All of these processes were analyzed by ^{1}H NMR and the experimental results were shown in Figure S15. In autoclave **I**, the substrate 1-ethyl-2-phenylaziridine could quickly convert into corresponding oxazolidinones, while the yield of product hardly increased after isolating catalyst **1**. Meanwhile, the separated catalyst **1** in autoclave **II** still exhibited effective catalytic ability for this cycloaddition. The results mentioned above demonstrated compound **1** could serve as an efficient heterogeneous catalyst for the cycloaddition reaction of CO_2 and aziridines.

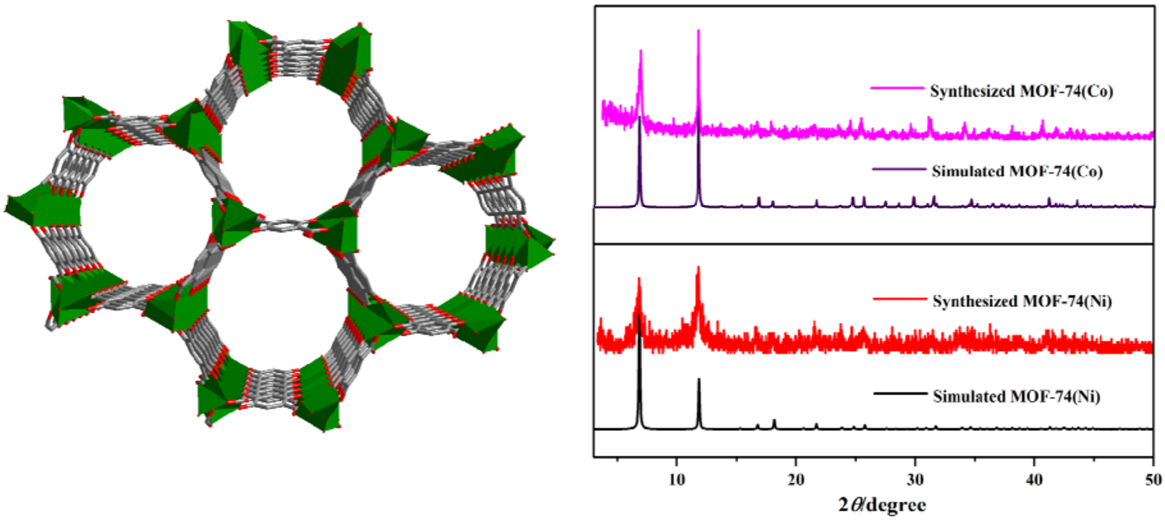


Fig. S17 The 3D framework MOF-74(Ni), and the PXRD patterns of MOF-74(Ni) (red) and MOF-74-(Co) (rosy).[12]

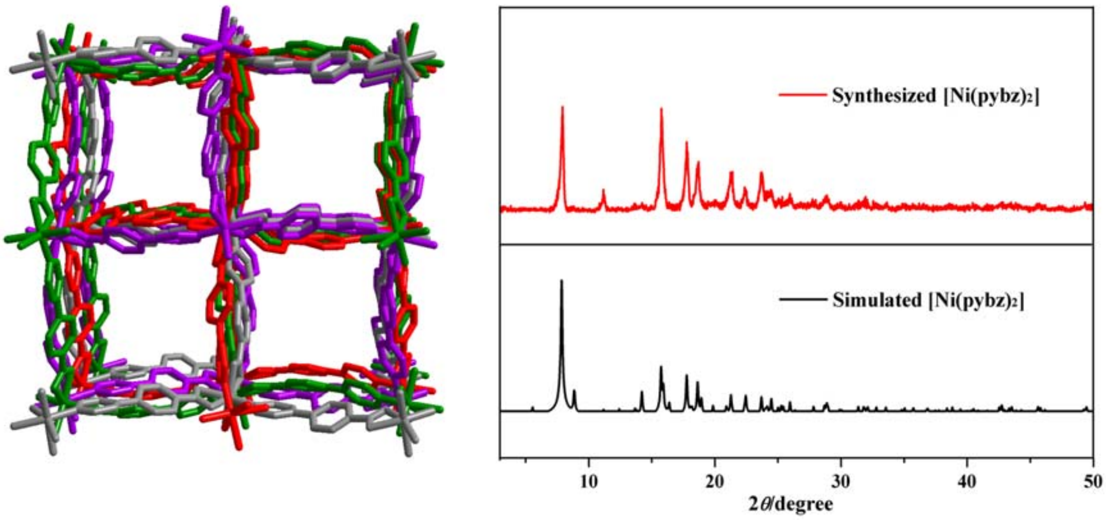


Fig. S18 The 3D framework with 1D square channels in [Ni(pybz)$_2$] and its PXRD patterns.[18]

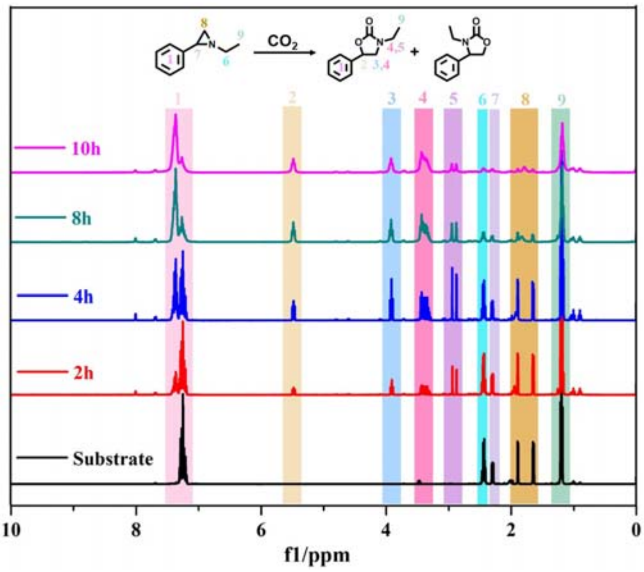


Fig. S19 ^{1}H NMR spectral to monitor the entire cycloaddition reaction of CO_2 and 1-ethyl-2-phenylaziridine by compound **1** for different times (in $CDCl_3$). Reaction conditions: 45 mg compound **1** and 2 mmol 1-ethyl-2-phenylaziridine were sealed in an autoclave at 70 ºC and 2 MPa CO_2 for different times.

As the reaction proceeds, 1-ethyl-2-phenylaziridine (substrate) reacted with CO_2 to produce the major product 3-ethyl-5-phenyloxazolidin-2-one, whose characteristic proton signals appeared at δ = 5.48 ppm and gradually enhanced. At the same time, the proton signals of 1-ethyl-2-phenylaziridine at δ = 2.29 and 1.89/1.65 ppm decreased and further disappeared. All these results indicate compound **1** can effectively promote the cycloaddition of CO_2 and aziridines without co-catalyst.

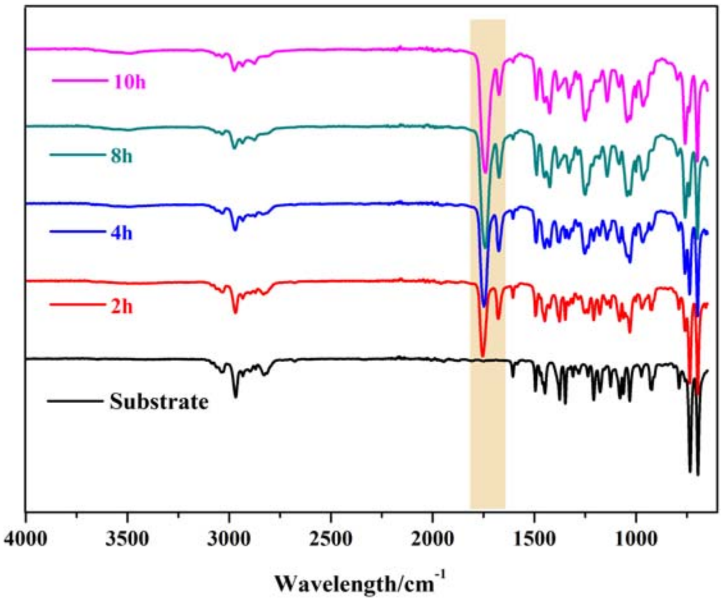


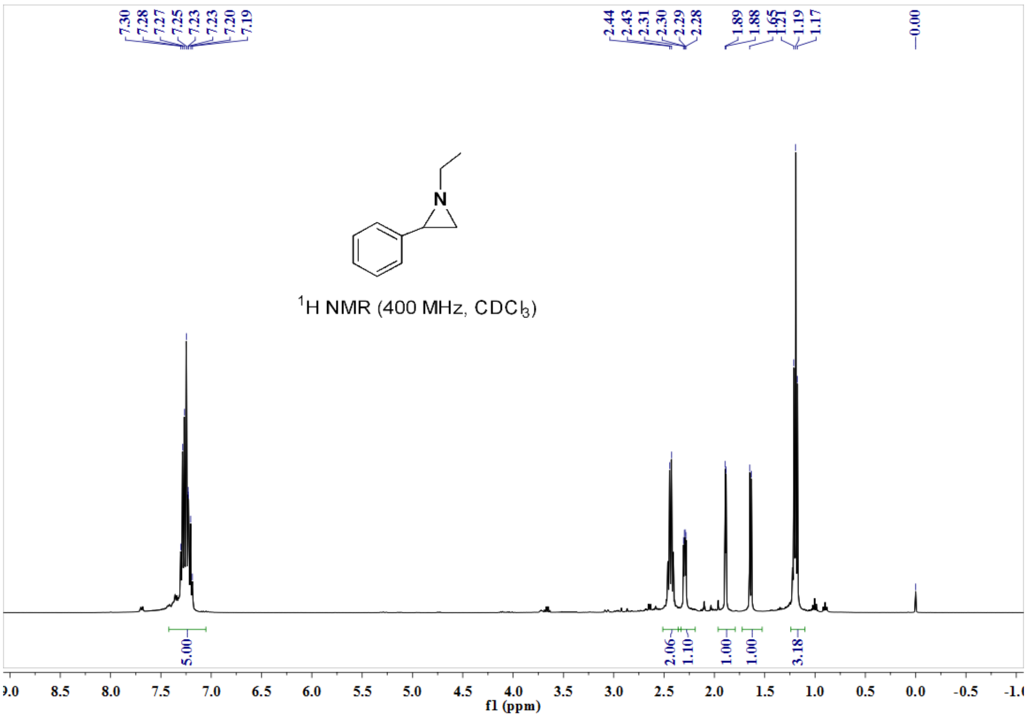
Fig. S20 IR spectra for monitoring this cycloaddition reaction of CO_2 and 1-ethyl-2-phenylaziridine by compound **1** at different times. Reaction conditions: 45 mg compound **1** and 2 mmol 1-ethyl-2-phenylaziridine were heated at 70 ºC and 2 MPa CO_2.

The stretching vibration peaks of -CH groups at 2983 and 2965 cm^{-1} gradually became weak with the reaction time increasing, which indicated compound **1** could activate the substrate and promote the cycloaddition reaction. Meanwhile, the new characteristic peaks of product appeared at 1753 and 1678 cm^{-1} and gradually enhanced, belonging to the C=O bond of oxazolidinones.

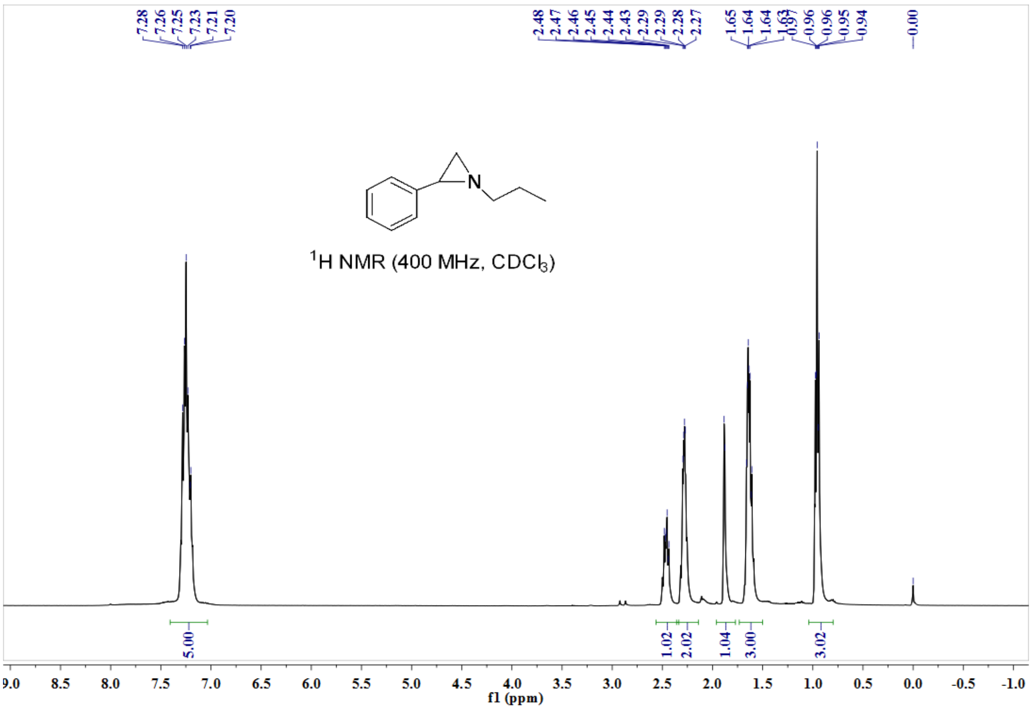
S11. ^{1}H NMR spectral for re-prepared aziridines and oxazolidinones

The ^{1}H NMR spectral for aziridines.

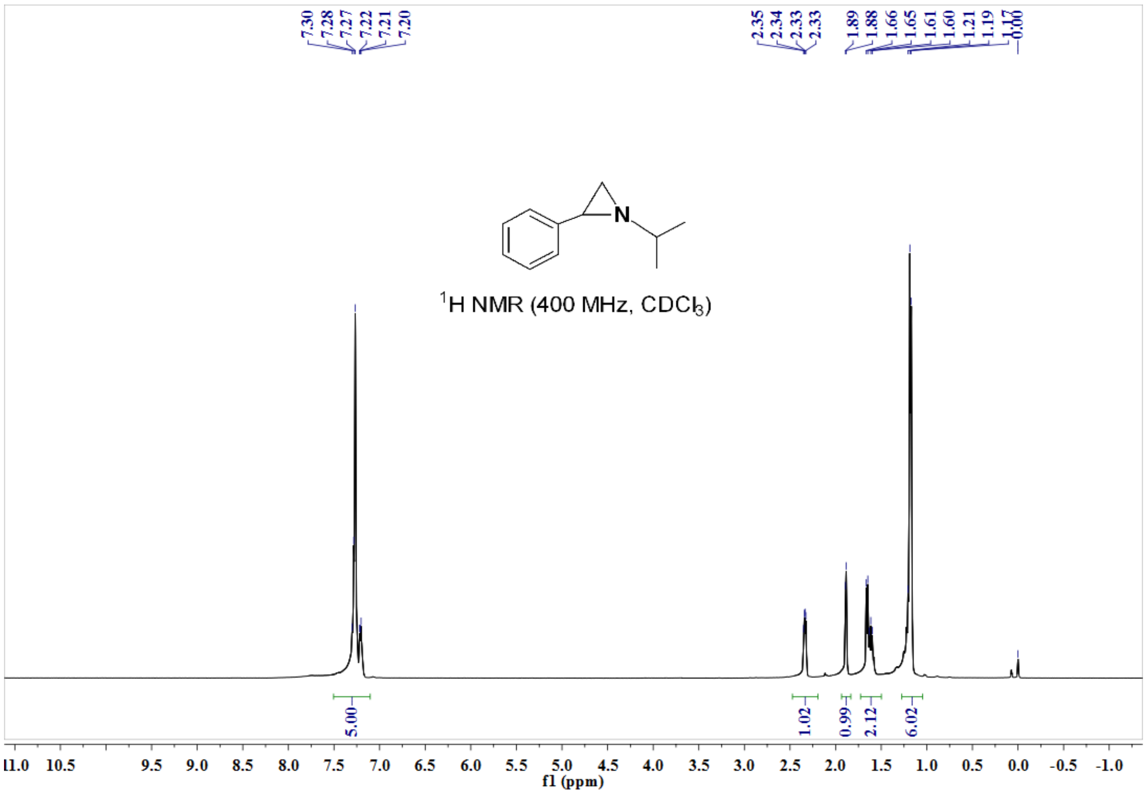
1-Ethyl-2-phenylaziridine



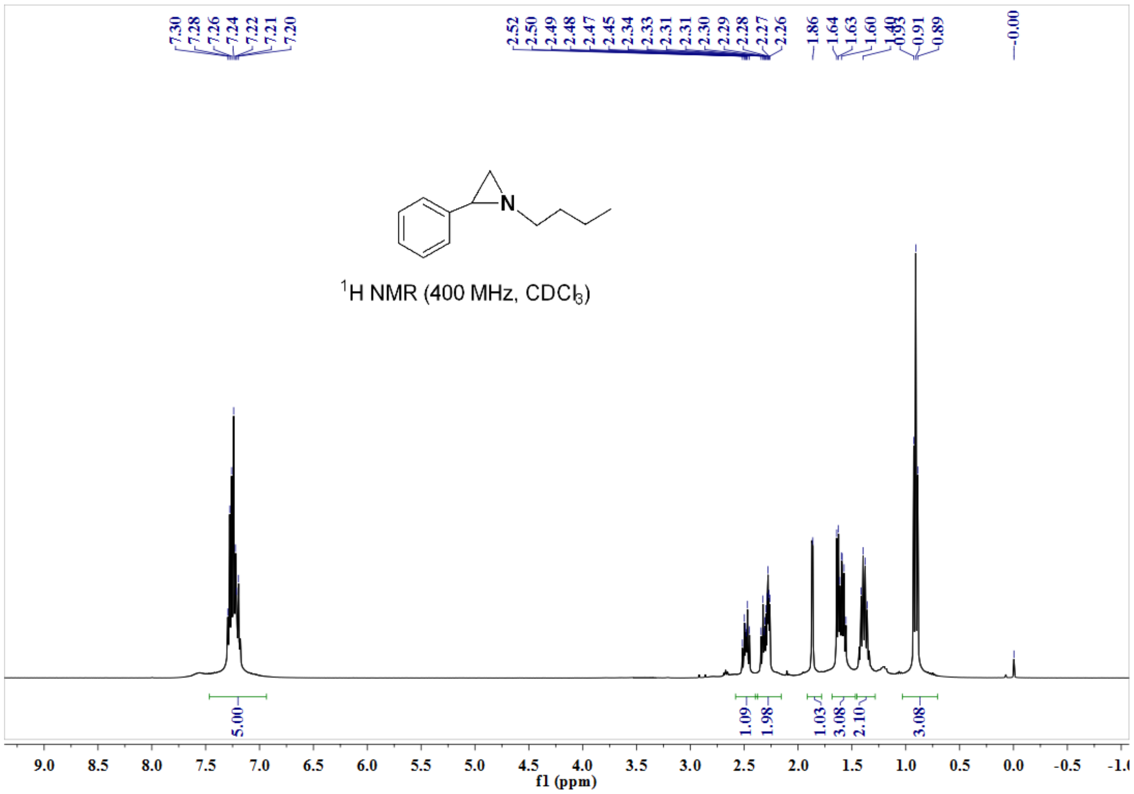
1-Propyl-2-phenylaziridine



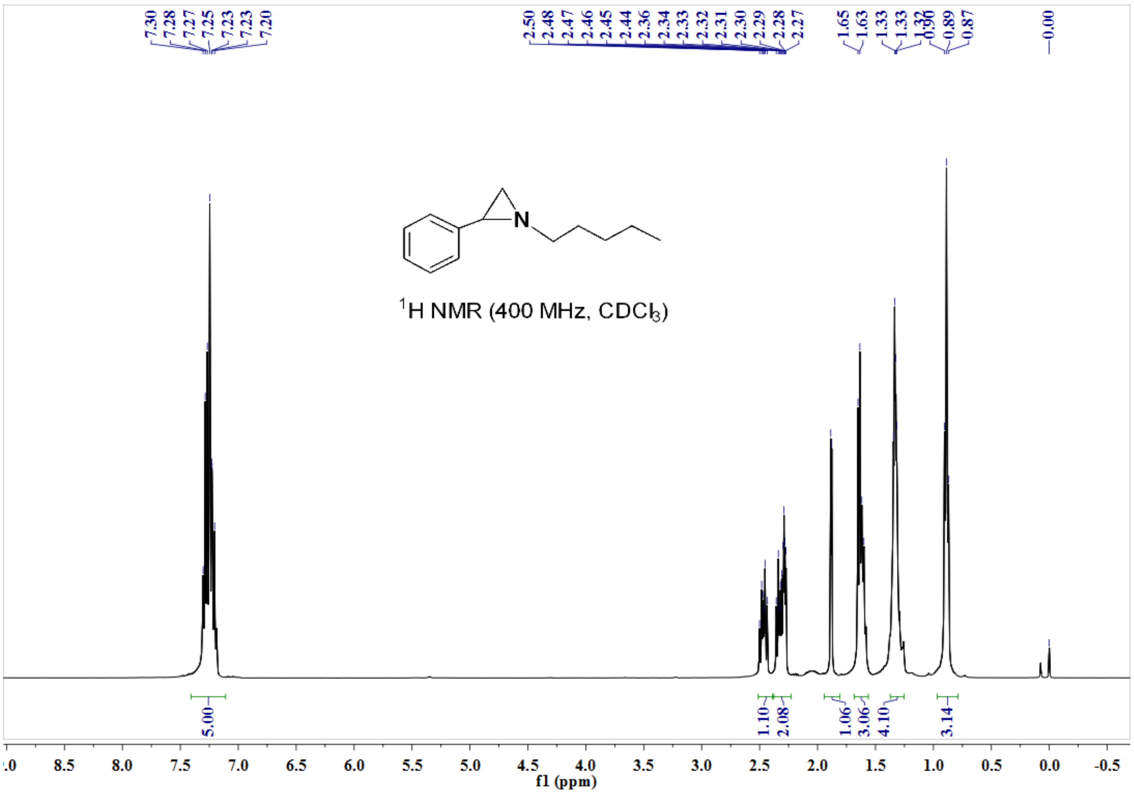
1-Isopropyl-2-phenylaziridine



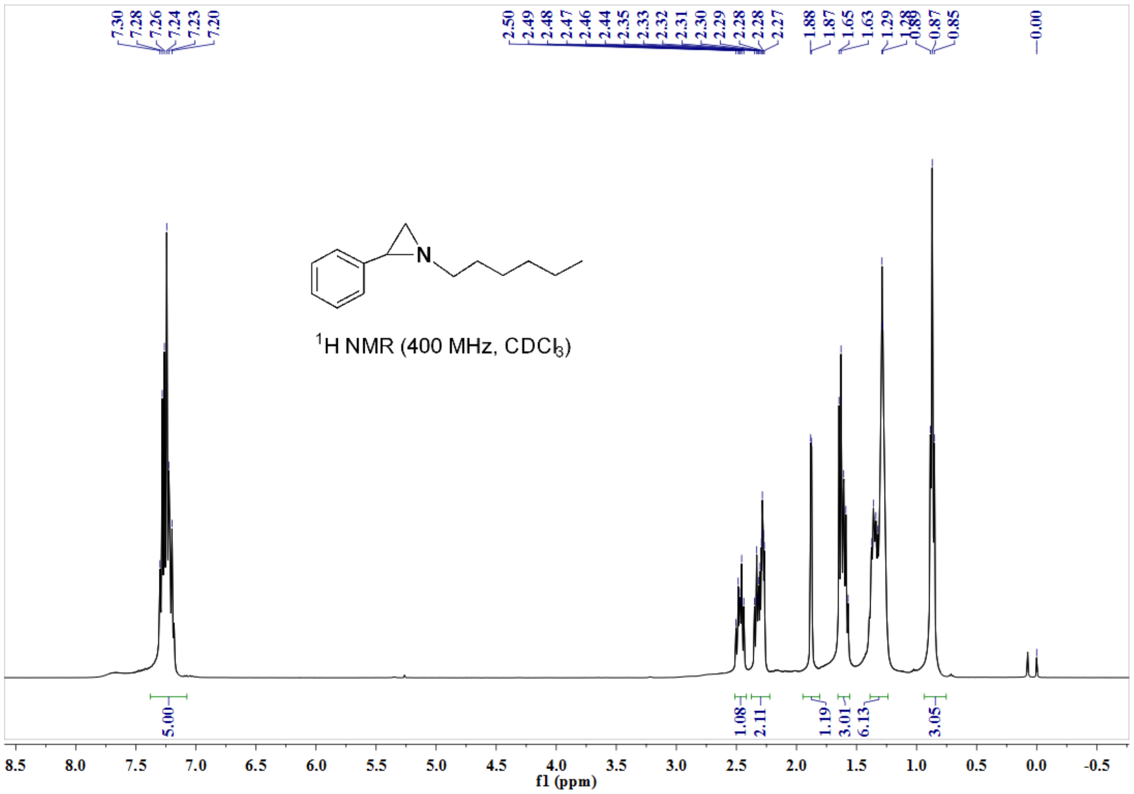
1-Butyl-2-phenylaziridine



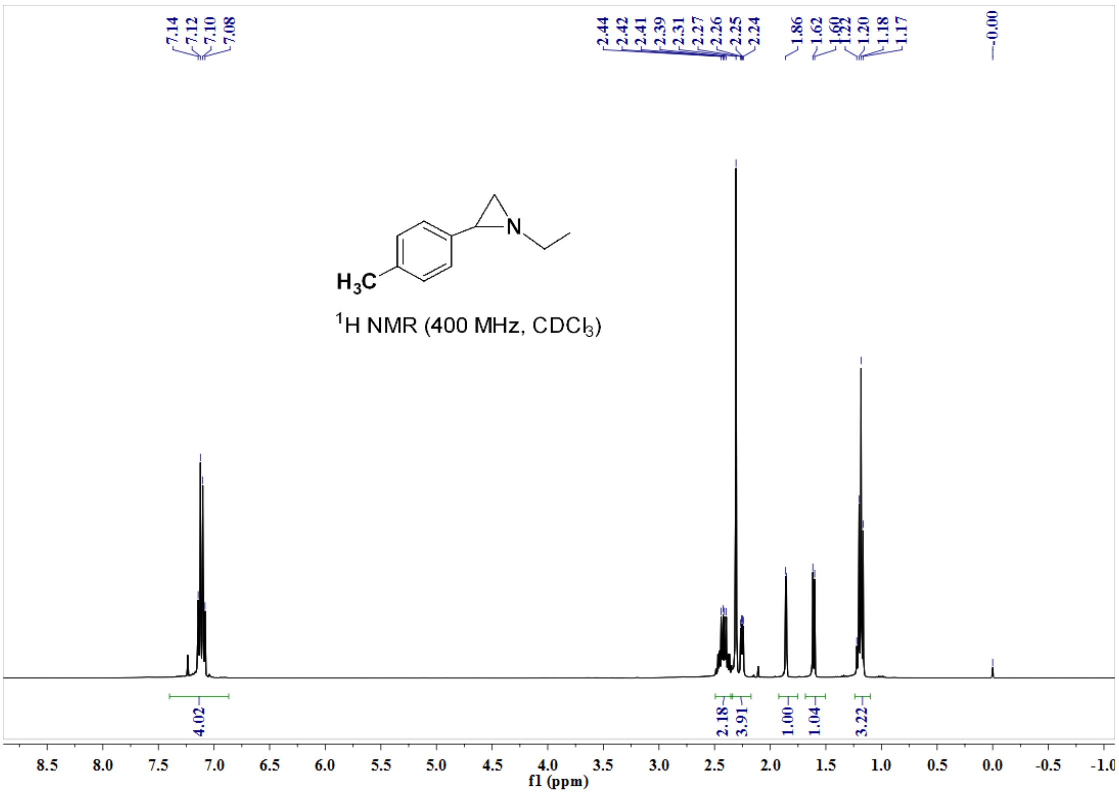
1-Pentyl-2-phenylaziridine



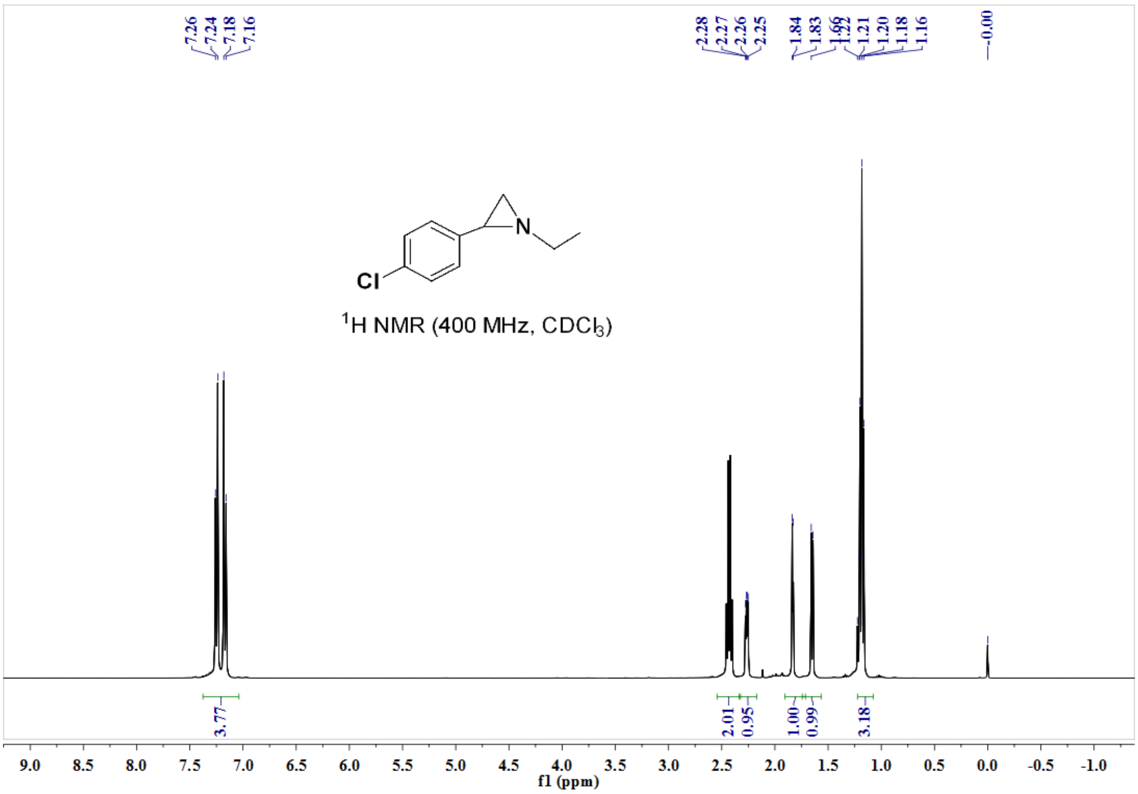
1-Hexyl-2-phenylaziridine



Ethyl-2-p-tolylaziridine

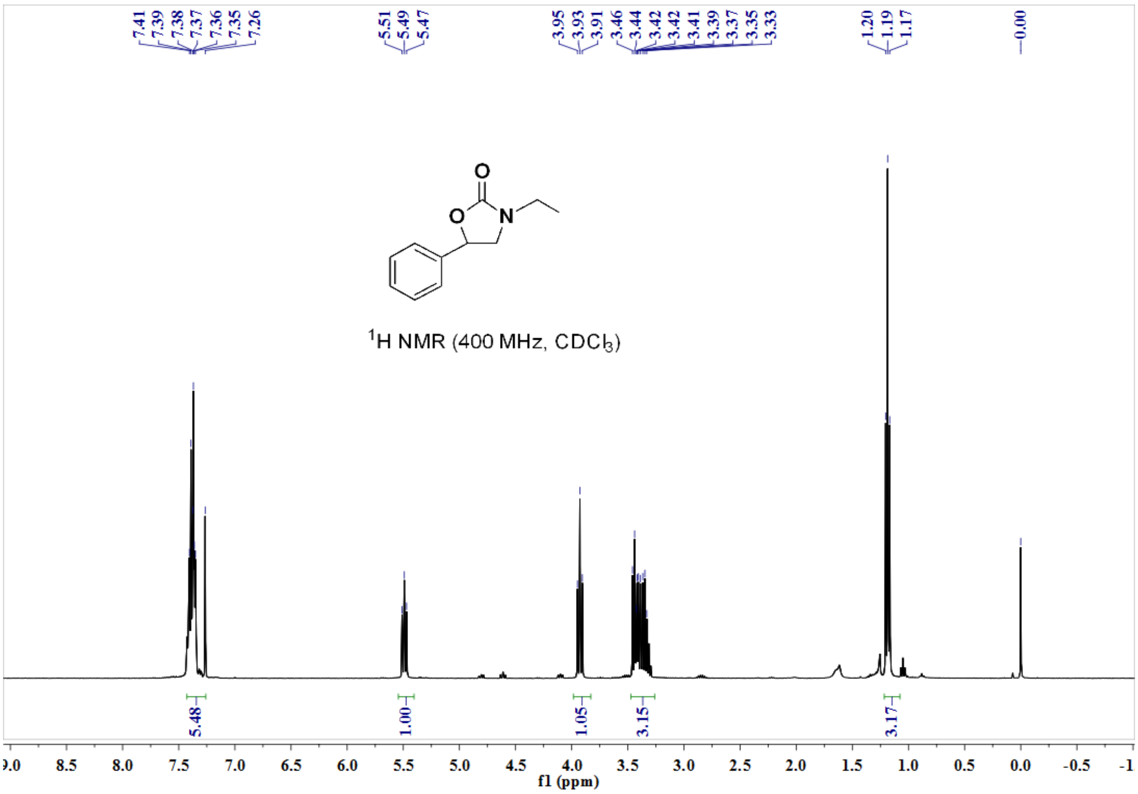


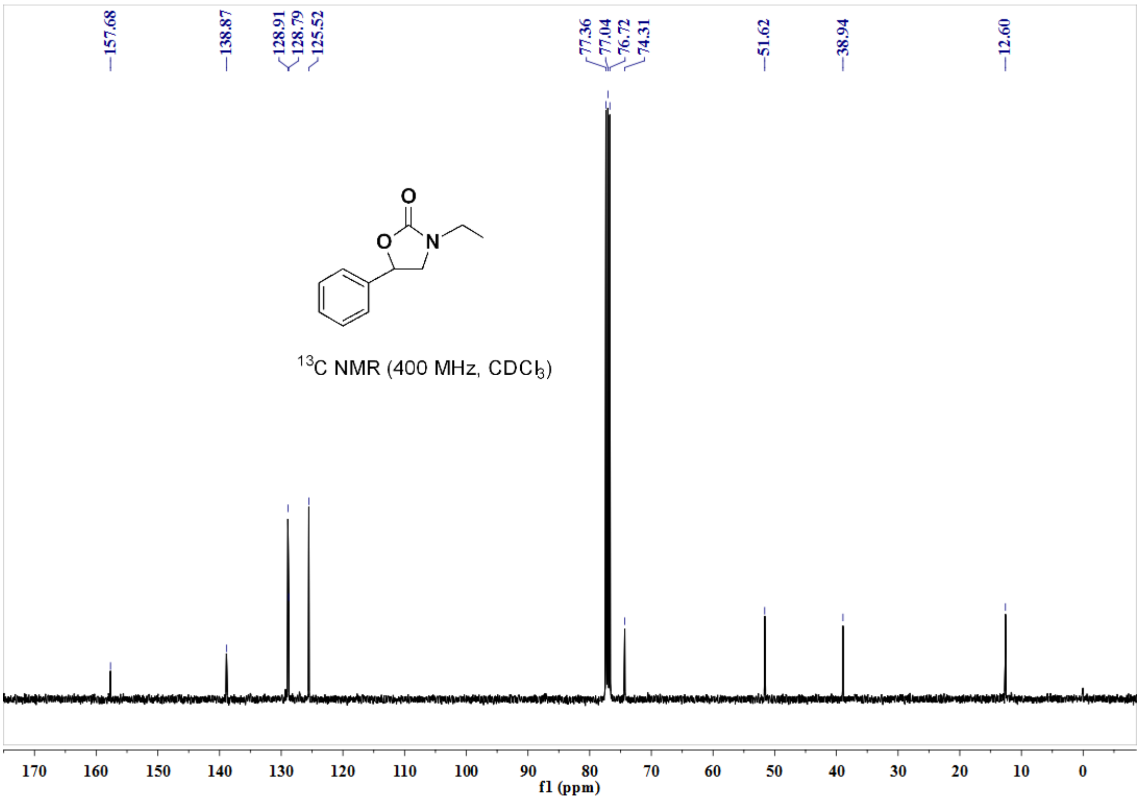
(4-Chlorophenyl)-1-ethylaziridine



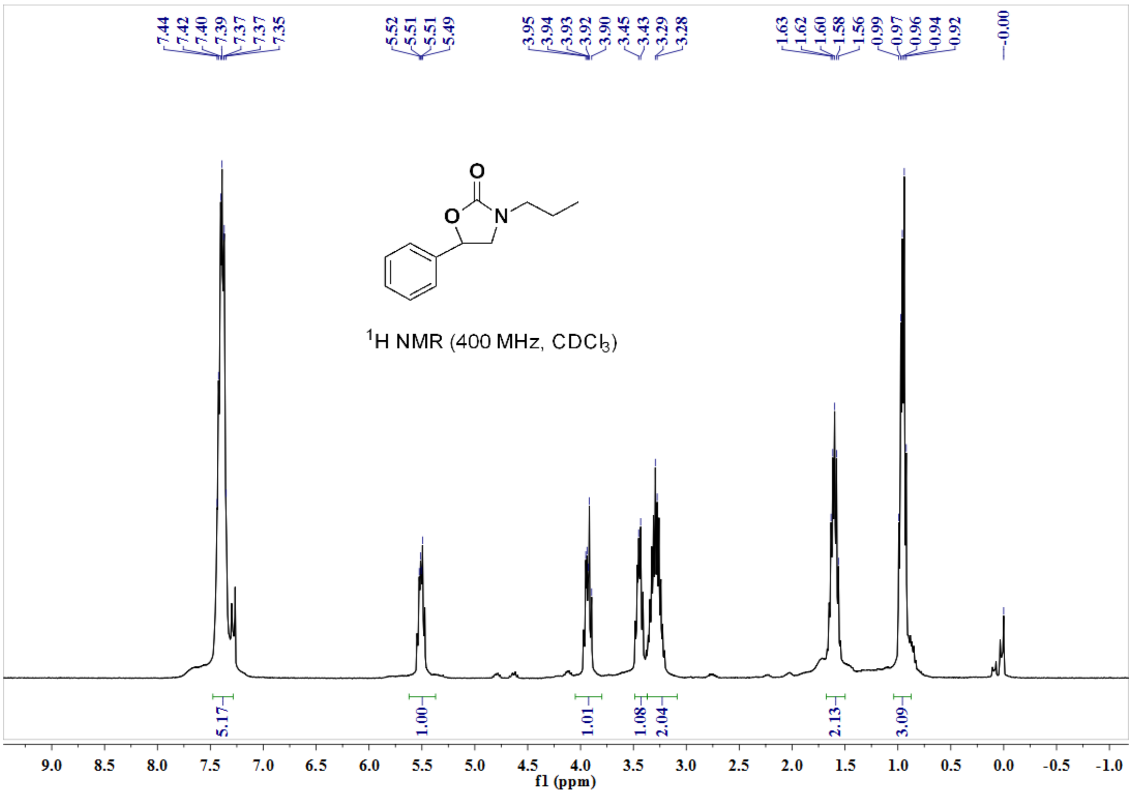
The ^{1}H NMR and ^{13}C NMR spectral for oxazolidinones.

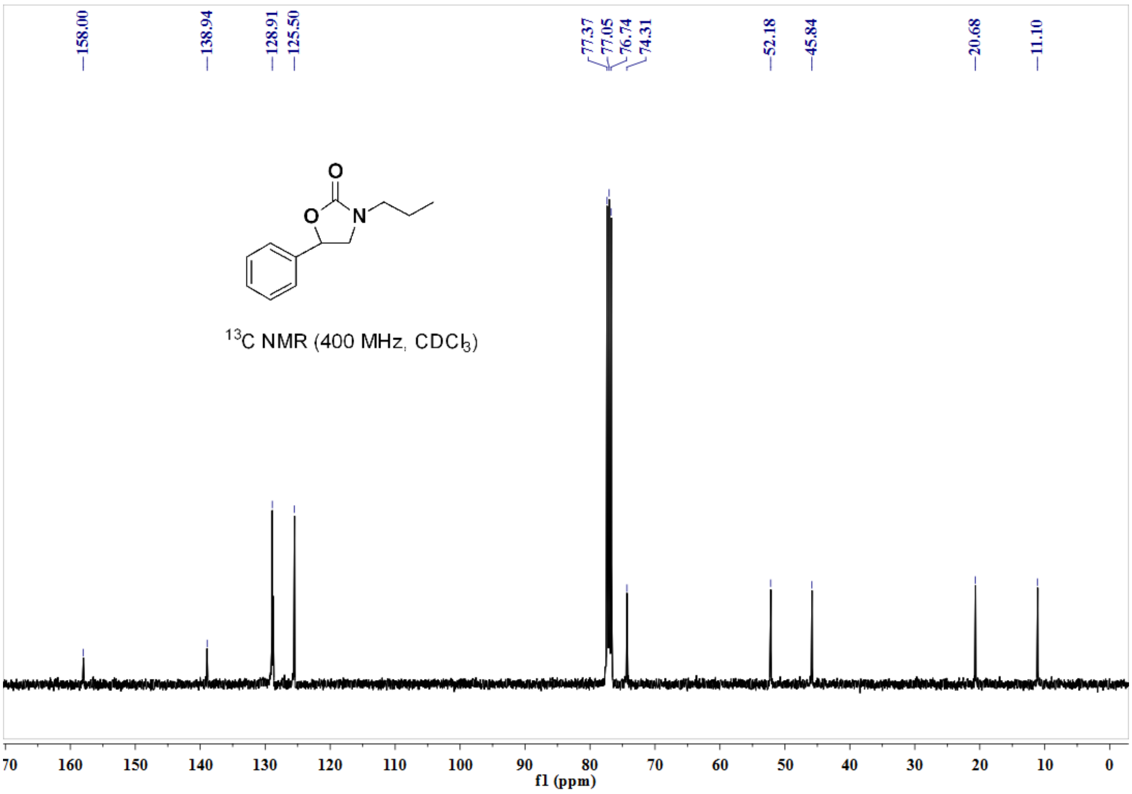
3-Ethyl-5-phenyloxazolidin-2-one



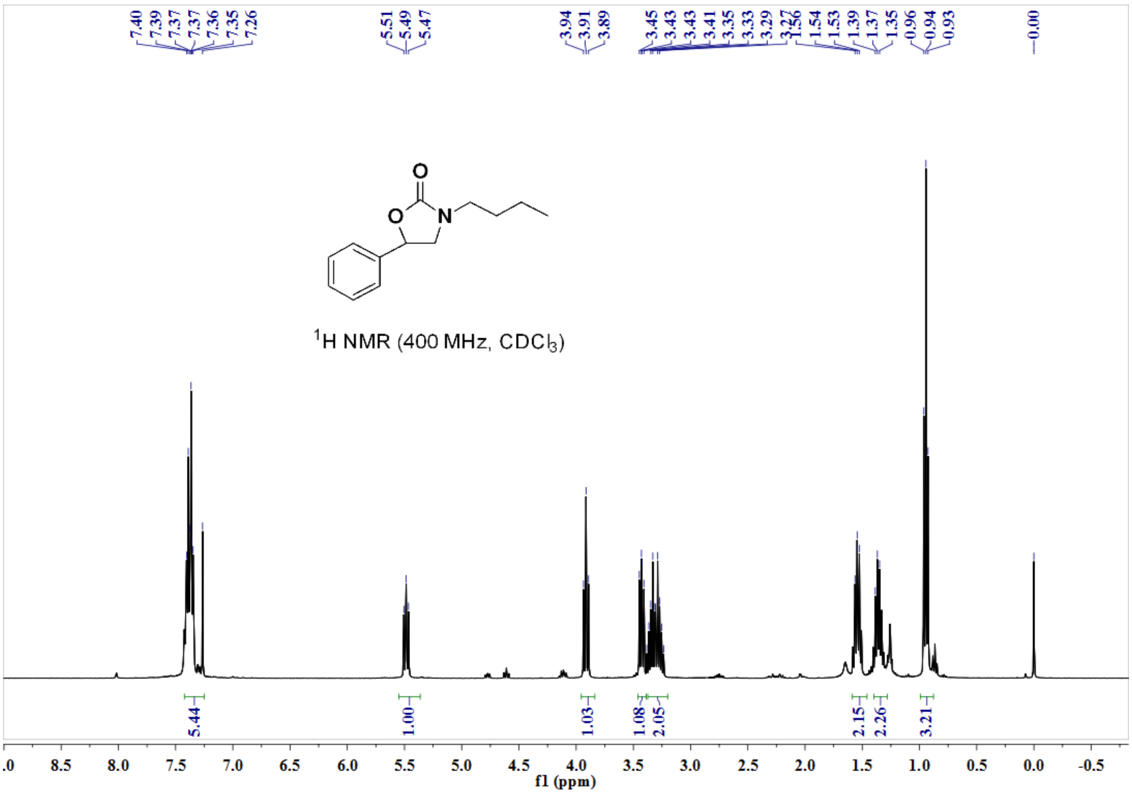


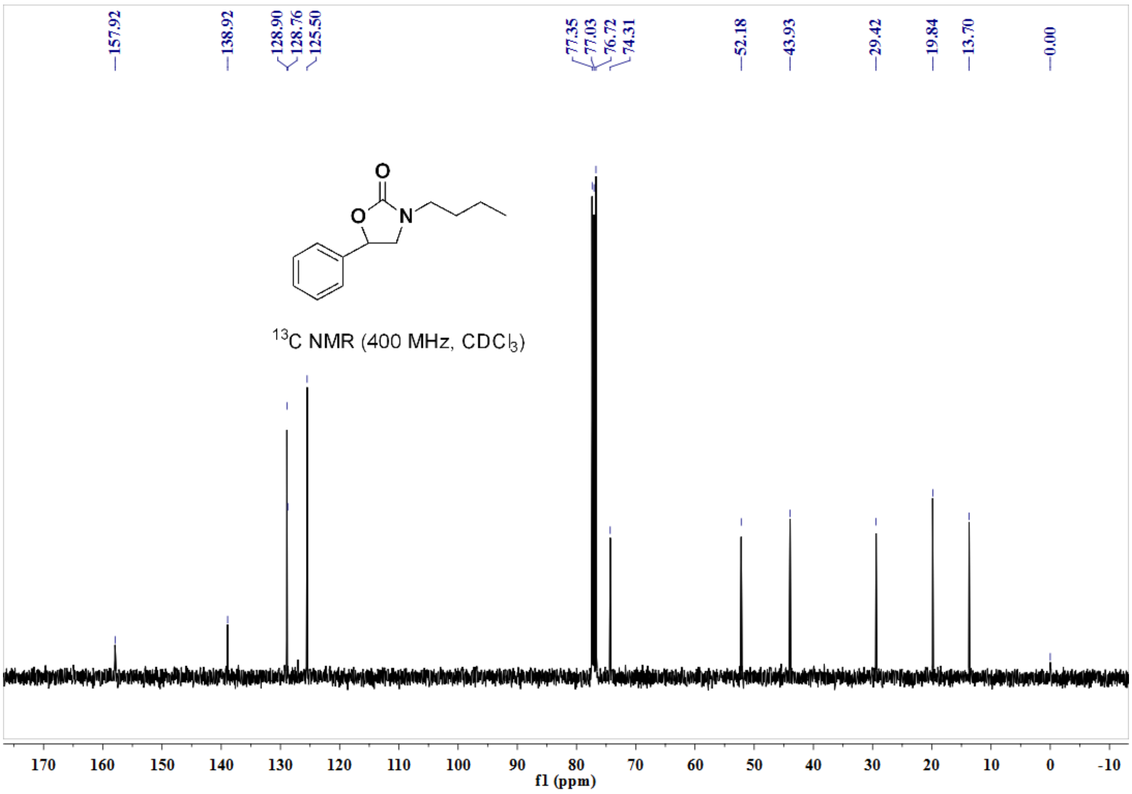
3-Phenyl-5-propyloxazolidin-2-one



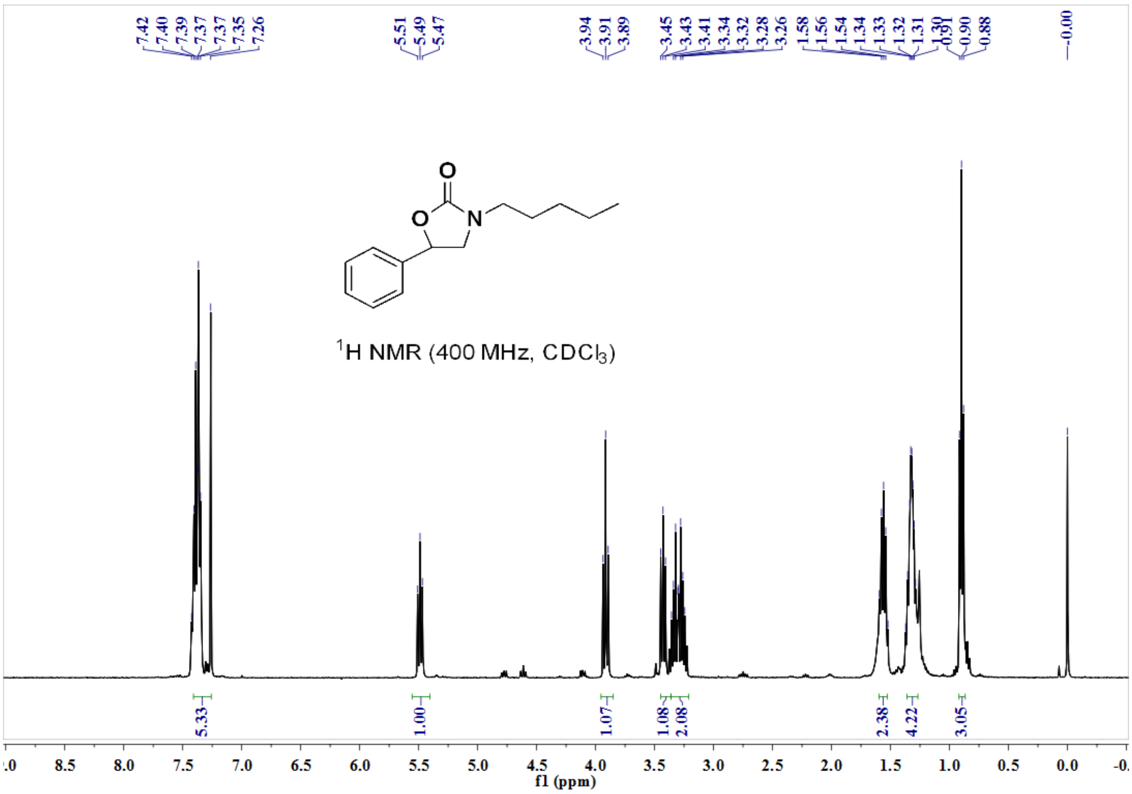


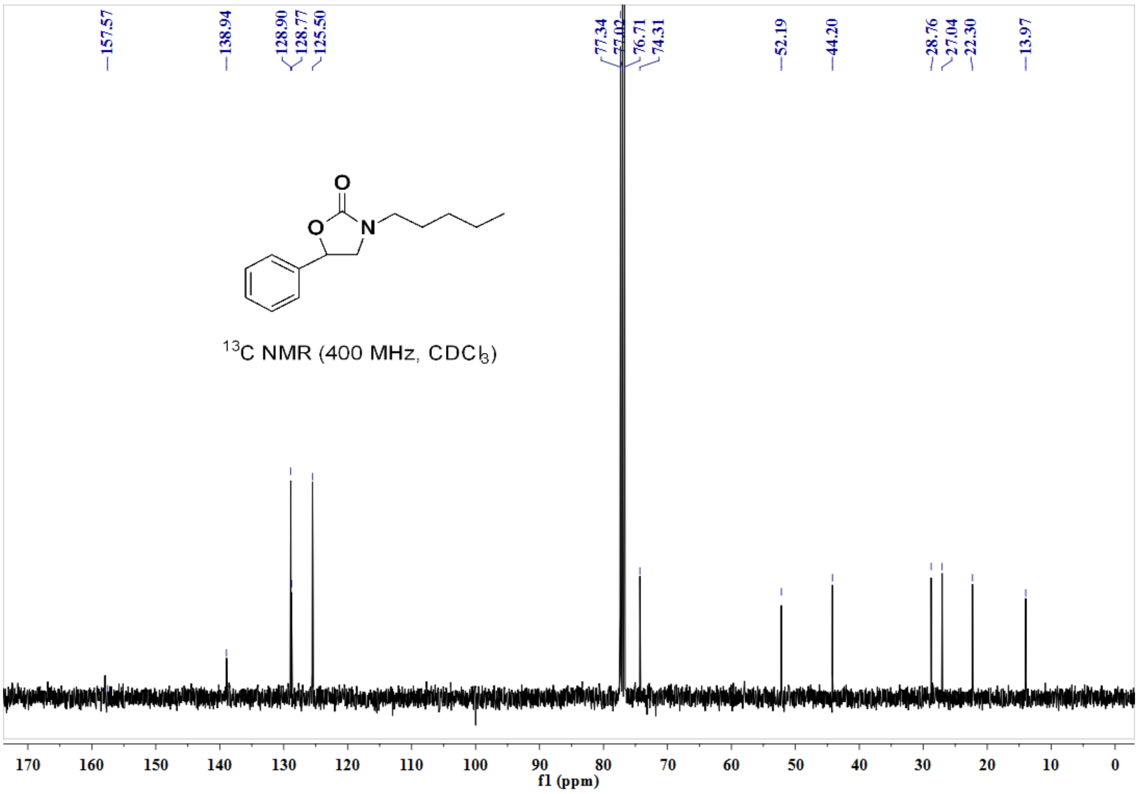
3-Butyl-5-phenyloxazolidin-2-one



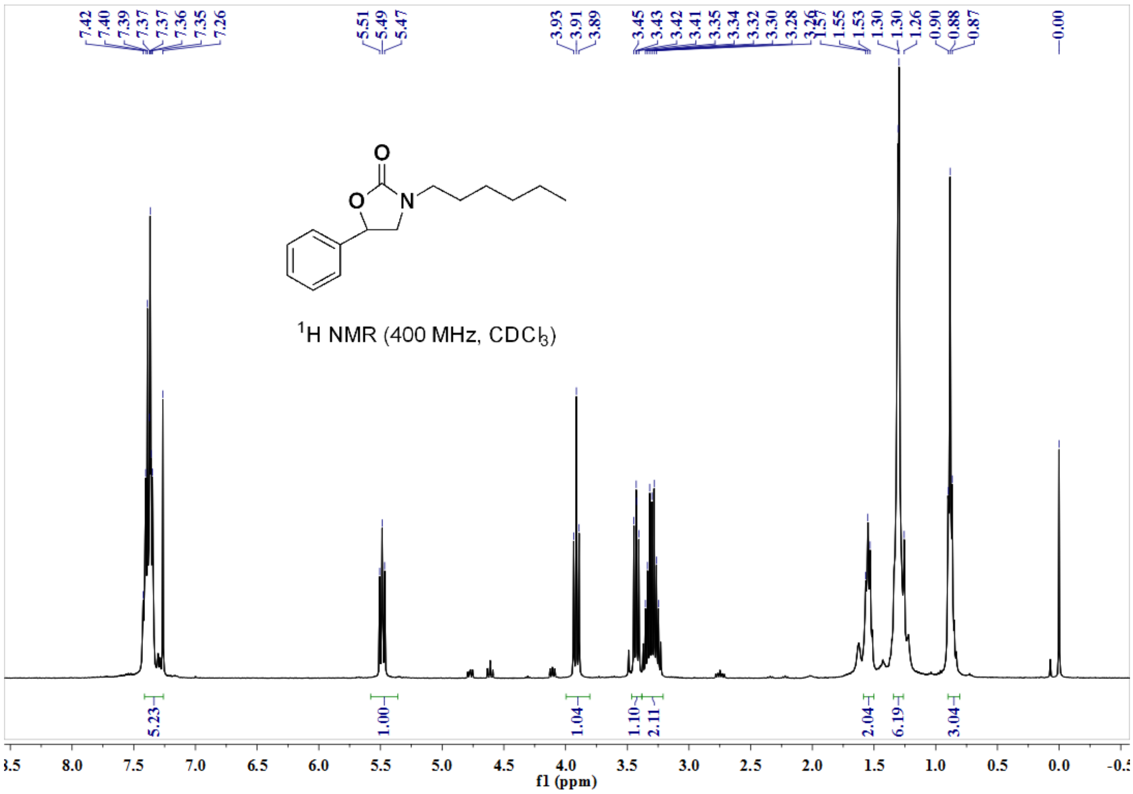


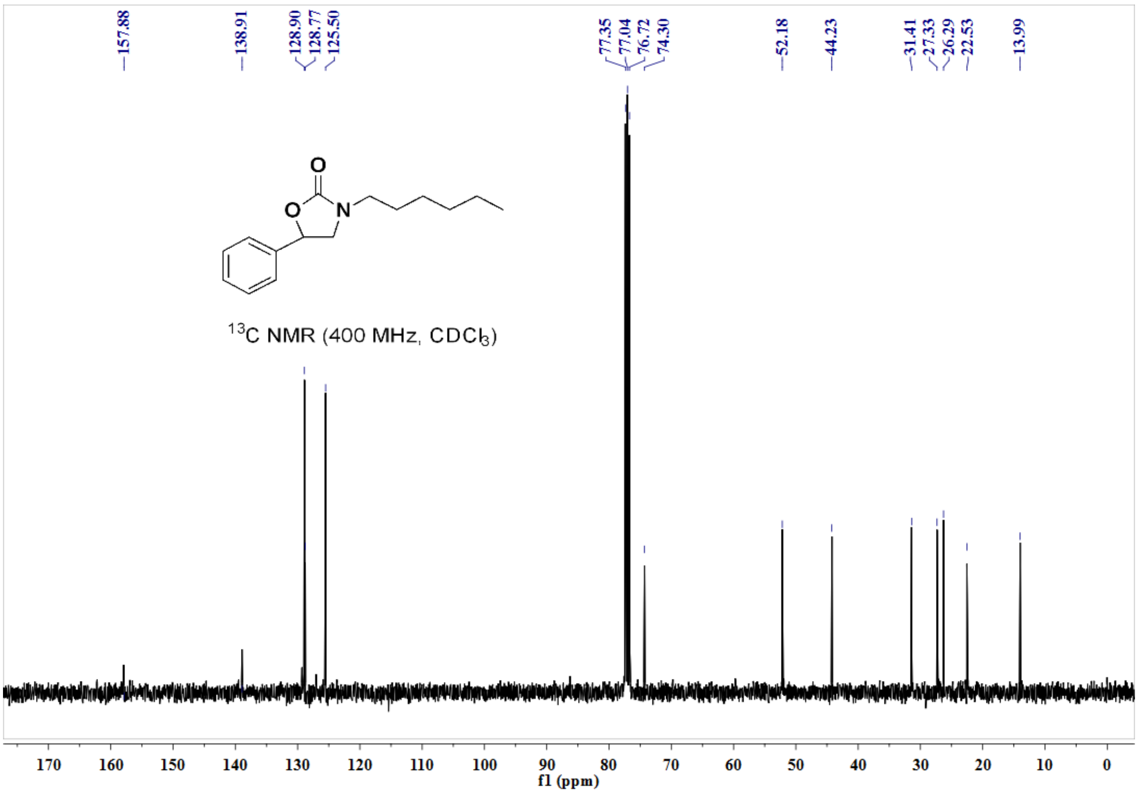
3-Pentyl-5-phenyloxazolidin-2-one



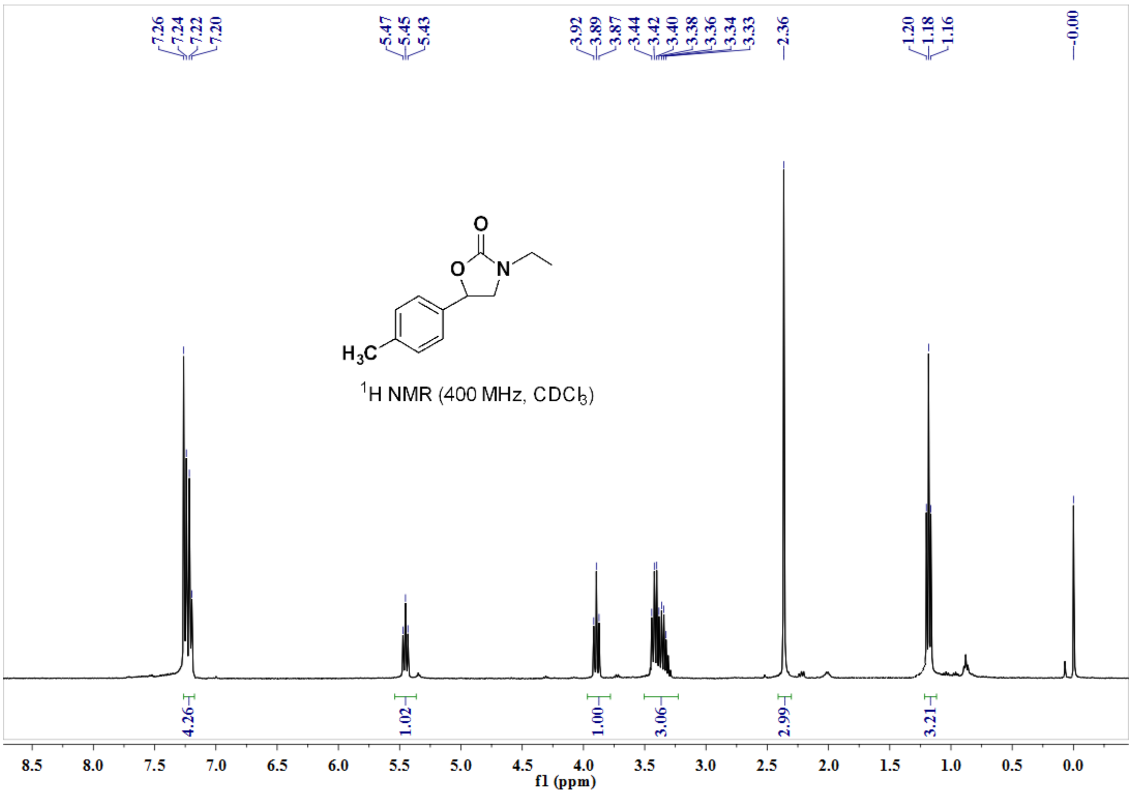


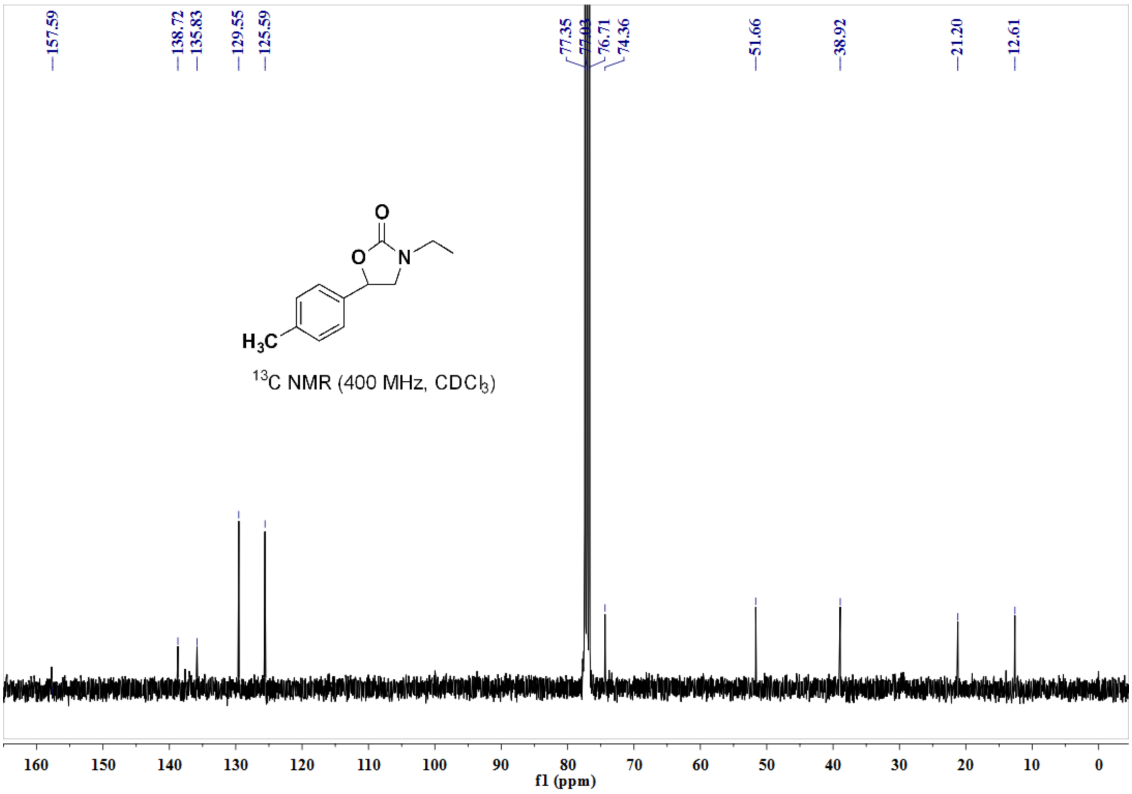
3-Hexyl-5-phenyloxazolidin-2-one



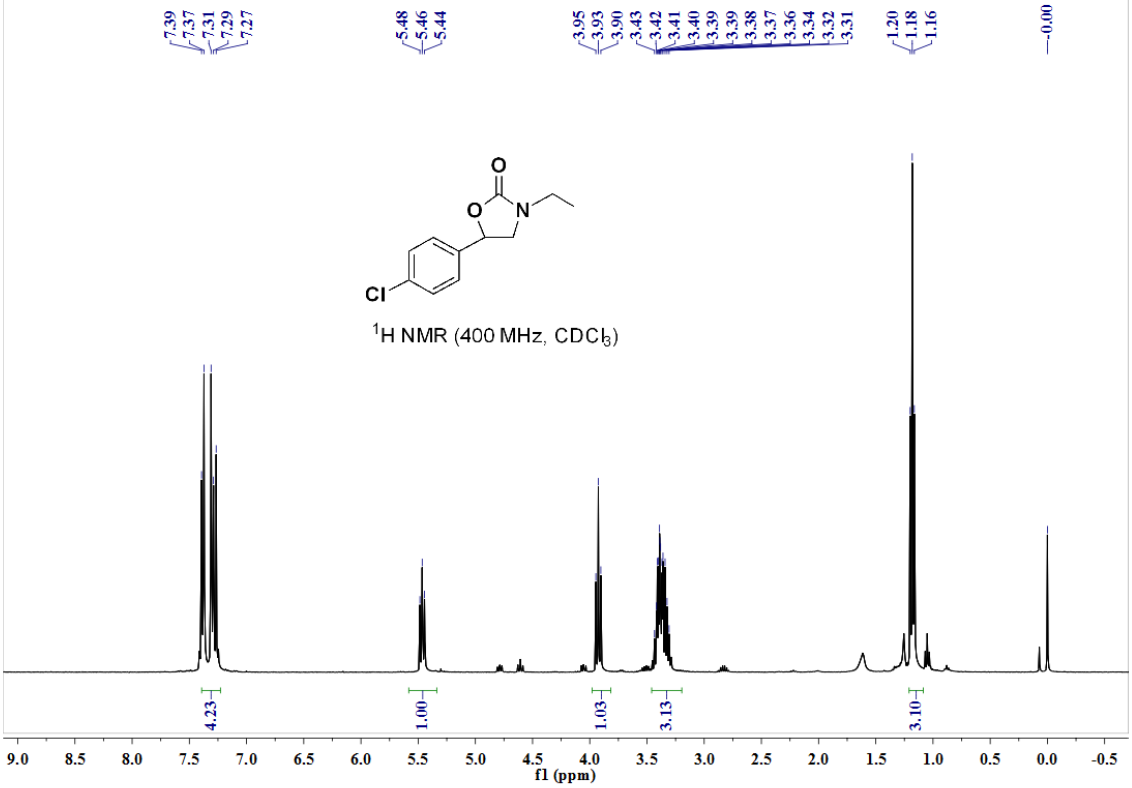


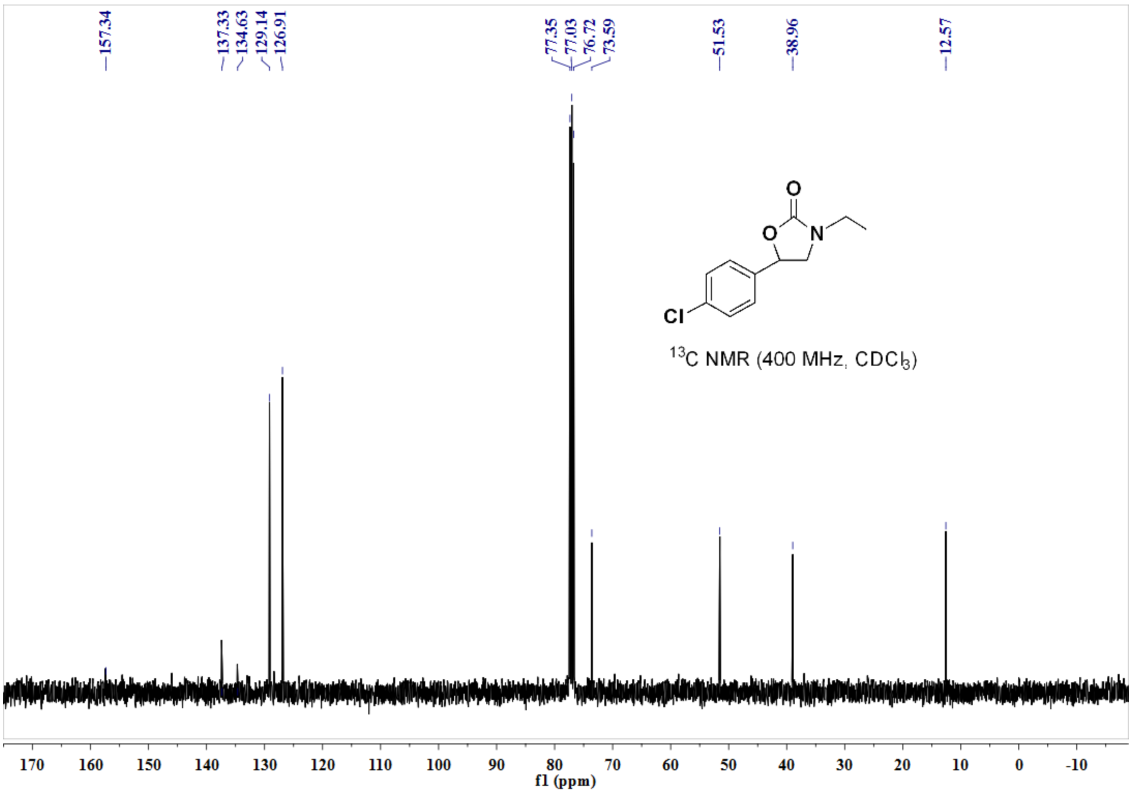
Ethyl-5-*p*-tolyloxazolidin-2-one





Ethyl-5-(4-chlorophenyl)oxazolidin-2-one





References

1 Xu H, Liu XF, Cao CS, Zhao B, Cheng P, He LN. *Adv Sci*, 2016, 3: 1600048

2 Sheldrick GM, Schneider TR. *Method Enzymol*, 1997, 277: 319-343

3 Spek AL. *Acta Crystallogr*, 2015, C71: 9

4 Lässig D, Lincke J, Moellmer J, Reichenbach C, Moeller A, Gläser R, Kalies G, Cychosz KA, Thommes M, Staudt R, Krautscheid H. *Angew Chem Int Ed*, 2011, 50: 10344-10348

5 Cui P, Ma YG, Li HH, Zhao B, Li JR, Cheng P, Balbuena PB, Zhou HC. *J Am Chem Soc*, 2012, 134: 18892-18895

6 Li PZ, Wang XJ, Zhang K, Nalaparaju A, Zou RY, Zou RQ, Jiang JW, Zhao YL. *Chem Commun*, 2014, 50: 4683-4685

7 Prasad TK, Hong DH, Suh MP. *Chem Eur J*, 2010, 16: 14043-14050

8 Ding ML, Jiang HL. *ACS Catal*, 2018, 8: 3194-3201

9 Li XY, Li YZ, Yang Y, Hou L, Wang YY, Zhu ZH. *Chem Commun*, 2017, 53: 12970-12973

10 Wei N, Zhang Y, Liu L, Han ZB, Yuan DQ. *Appl Catal B*, 2017, 219: 603-610

11 Zhang GY, Wei GF, Liu ZP, Oliver SRJ, Fei HH. *Chem Mater*, 2016, 28: 6276-6281

12 Yazaydin AÖ, Snurr R, Park TH, Koh K, Liu J, LeVan MD, Benin AI, Jakubczak P, Lanuza M, Galloway DB, Low JJ, Willis RR. *J Am Chem Soc*, 2009, 131: 18198-18199

13 Wang QM, Shen DM, Bülow M, Lau ML, Deng SG, Fitch FR, Lemcoff NO, Semanscin J. *Micropor Mesopor Mater*, 2002, 55: 217-230

14 Kang XM, Shi Y, Cao CS, Zhao B. *Sci China Chem*, 2019, 62: 622-628

15 Cao CS, Shi Y, Xu H, Zhao B. *Dalton Trans*, 2018, 47: 4545-4553

16 Kathalikkattil AC, Roshan R, Tharun J, Babu R, Jeong GS, Kim DW, Choc SJ, Park DW. *Chem Commun*, 2016, 52: 280-283

17 Wang X, Gao WY, Niu Z, Wojas L, PermanJ A, Chen YS, Li Z, Aguila B, Ma SQ. *Chem Commun*, 2018, 54: 1170-1173

18 Zhang Y, Wang L, Yao RX, Zhang XM. *Inorg Chem*, 2017, 56: 8912-8919