Highly Effective CS_2 Conversion with Aziridines Catalyzed by Novel [Dy_{24}] Nano-Cages in MOFs under Mild Conditions

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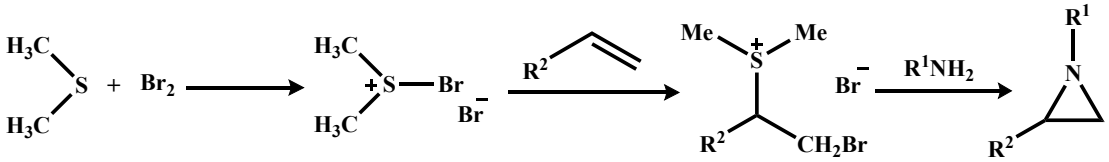
Experimental Procedures

Materials and Characterization

All of the chemical reagents were purchased commercially and used without purification. The aziridines substrates were synthesized according to the literature. Powder X-ray diffraction (PXRD) was fulfilled by an Ultima IV X-ray diffractometer with Cu-Kα radiation. Thermogravimetric analysis was completed by an EVO2G-TG TG-DTA analyzer under the air atmosphere. NMR spectra were performed on a 400 MHz Bruker 400 spectrometer in $CDCl_3$. Fourier transform infrared (FT-IR) spectra were obtained by the Nicolet IS10 instrument.

Synthesis of aziridines.



A1 **A2**

According to previous literature,[1] the common aziridines substrates have been synthesized and the specific steps are as follows: Firstly, 0.2 mol bromine immersing in 40 mL CH_2Cl_2 was slowly dropped into 40 mL CH_2Cl_2 with 0.2 mol dimethyl sulfide under an ice-salt bath condition. Orange solid **A1**, bromodimethyl sulfonium bromide, was gradually formed during stirring overnight. The resultant **A1** was washed with diethyl ether for several times and dried. Next, **A1** was dissolved in 160 mL of CH_3CN, and then 160 mmol styrene was added dropwise under ice bath conditions. White solid **A2** was obtained after stirring overnight, and then washed with fresh CH_3CN for several times. Finally, 20-50 mmol amine was dropped into 20 mL H_2O solution with 10 mmol **A2** and stirred for overnight at room temperature. After the reaction, 20 mL saturated salt solution was dropped into this system. The mixture was extracted with diethyl ether (20 mL) for three times and dried with anhydrous $MgSO_4$. The product aziridines were obtained by rotary evaporation.

Synthesis of $\{Na[Tb_2(\mu_3\text{-}OH)(BTB)_2]\cdot 6DMA\}_n$ (2)

The synthesis method of Compound **2** was similar to compound **1** except that $Dy(OAc)_3$ was replaced as $Tb(OAc)_3$. Elemental analysis (%) for compound **2** ($NaTb_2C_{78}H_{85}O_{19}N_6$), calcd: C 53.49, H 4.89, N 4.79; Found: C 53.66, H 4.68, N 4.62.

Gram-scale experiment of CS_2 and aziridines.

25 mg compound **1**, 0.05 mmol TBAB, 10 mmol aziridine substrate (1.47 g) and 50 mmol CS_2 (3.8 g) were sealed in a 50 mL Schlenk tube, and stirred at 60 ºC for 12 h. The corresponding yield was analyzed by ^1H NMR with 1,3,5-trimethoxybenzene as an internal standard.

Catalytic recyclable experiments of CS_2 and aziridines.

After the first cycle reaction, the catalyst was isolated by centrifugation, washed with fresh CH_2Cl_2 for three times and dried naturally. The recovered catalyst was used for the next cycle.

Supplemental Figures

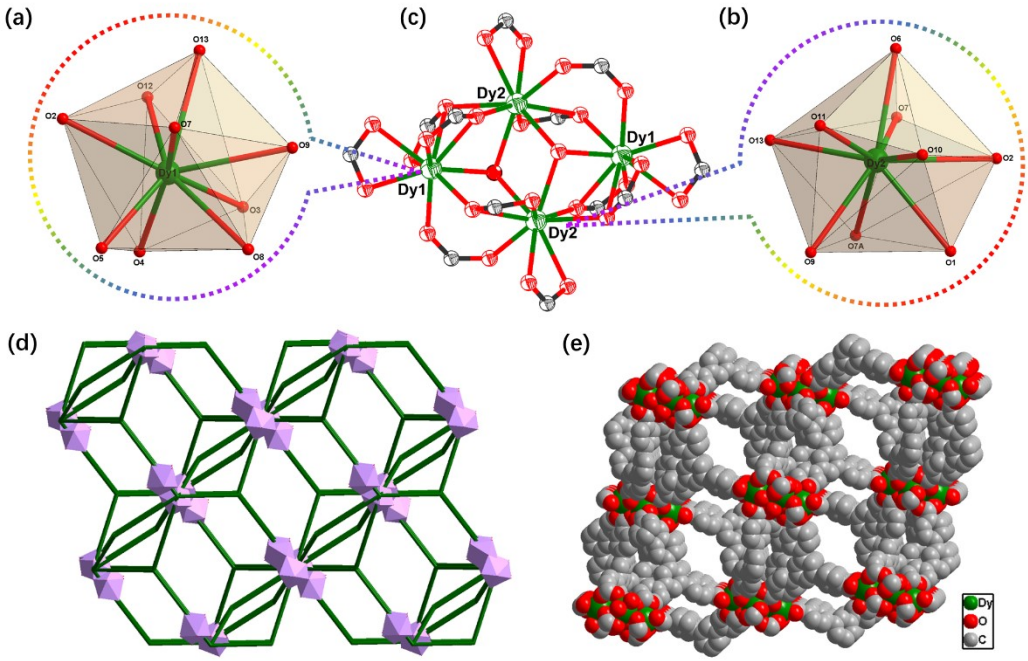


Figure S1. The coordinated environments and the polyhedral representation of Dy^{III} (a, b) and [Dy_4] cluster unit (c) in compound **1**. (d) The (3, 12)-connect topology of **1**. (e) The two different 1D channels in the 3D framework of **1** in packing mode along *b*-axis.

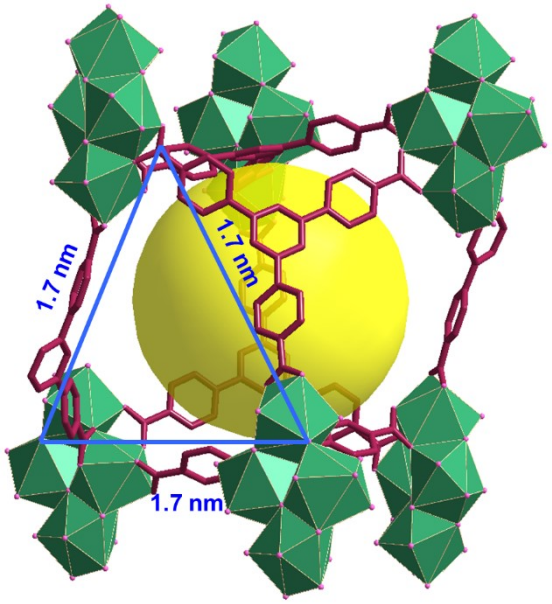


Figure S2. The [Dy_{24}]-cage in compound **1**, and the similar triangular window size of 1.7 nm ×1.7 nm ×1.7 nm.

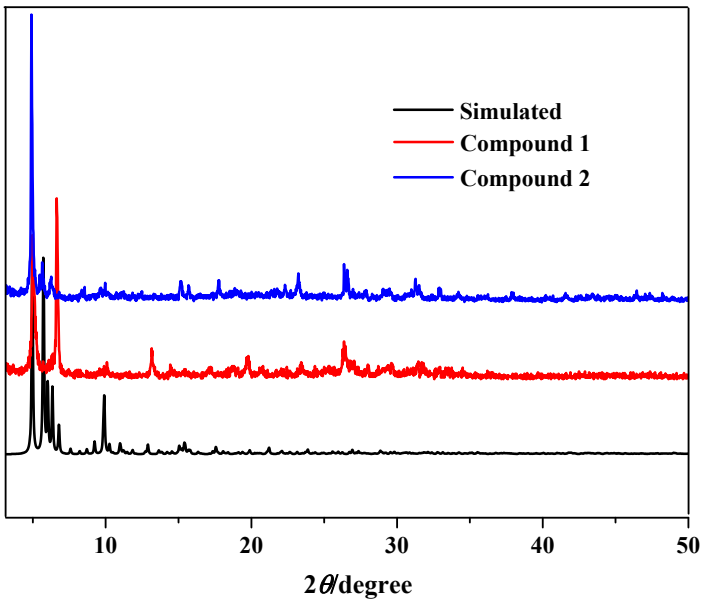


Figure S3. The PXRD patterns of the simulated one from the single-crystal data (black), as-synthesized compound **1** (red) and **2** (blue).

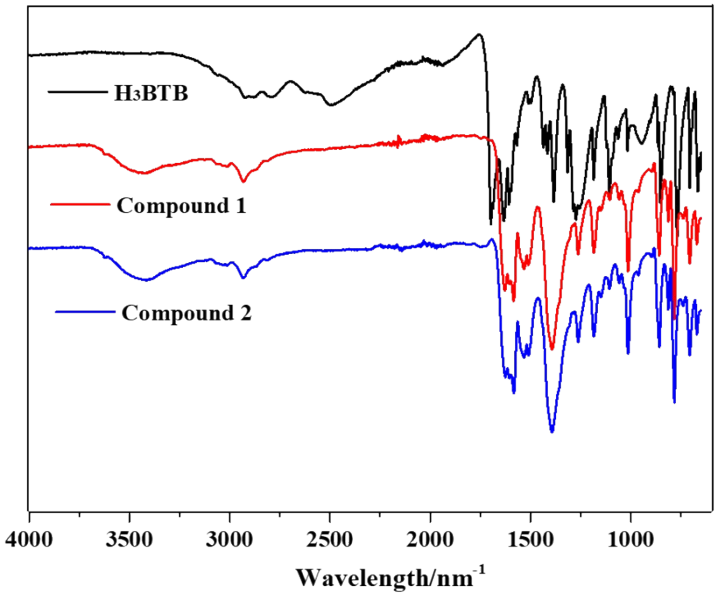


Figure S4. The IR spectra of H_3BTB ligand (black), compound **1** (red) and **2** (blue).

The peaks from 3200 to 2700 cm^{-1} belong to the stretching vibration of -OH in -COOH groups and the stretching vibration of aromatic rings in the H_3BTB ligand. In compound **1**, the position and intensity of characteristic peaks have changed, indicating that the -COOH group in the ligand coordinates with Ln^{3+}, and the characteristic peaks shift from 1700 ~ 1638 cm^{-1} to 1626 ~ 1511 cm^{-1}.

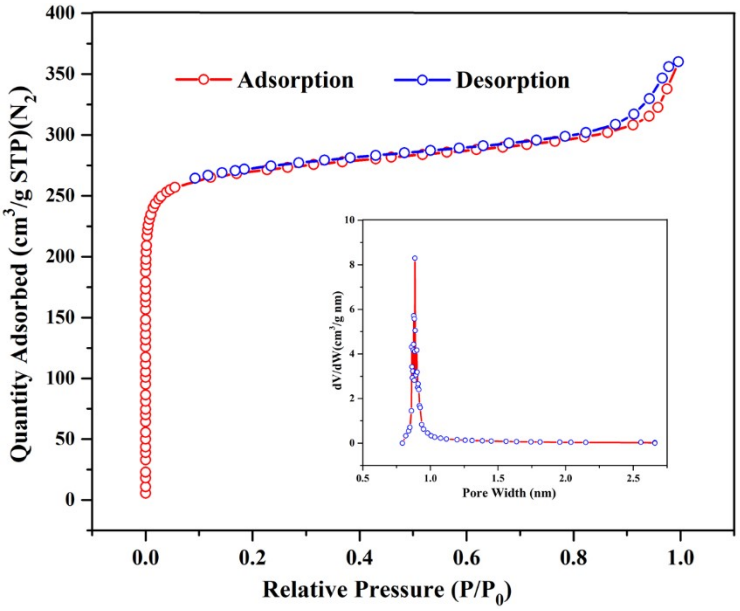


Figure S5. The N_2 adsorption/desorption of **1** at 77 K. Inset: The adsorption average pore diameter.

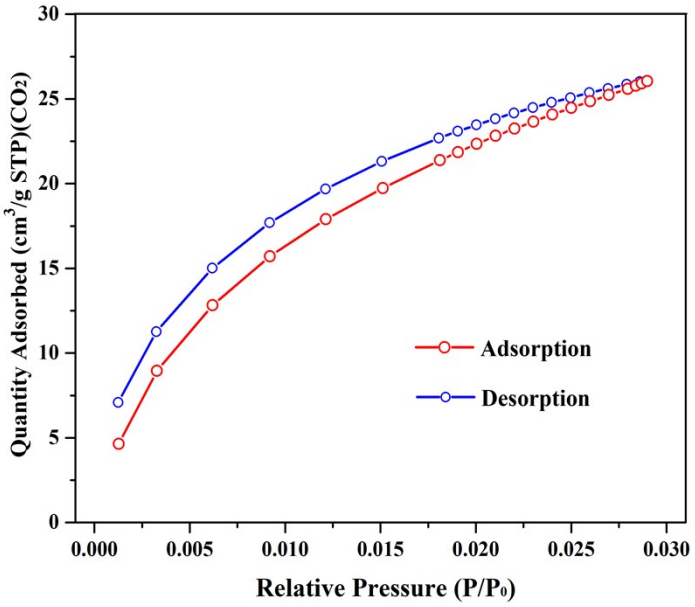


Figure S6. The CO_2 adsorption/desorption of **1** at 298 K.

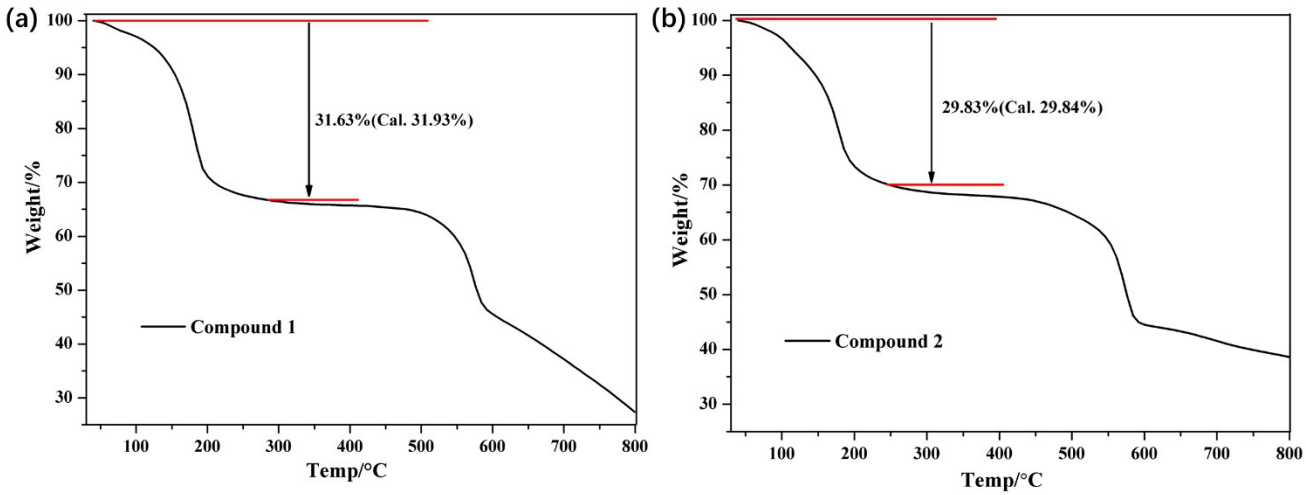


Figure S7. The thermogravimetric analyses curve of compound **1** and **2**.

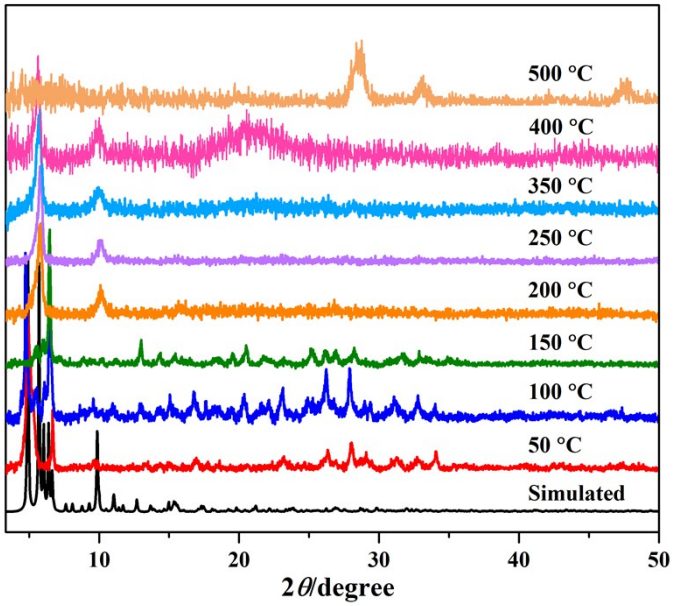


Figure S8. Variable-temperature PXRD patterns of **1**.

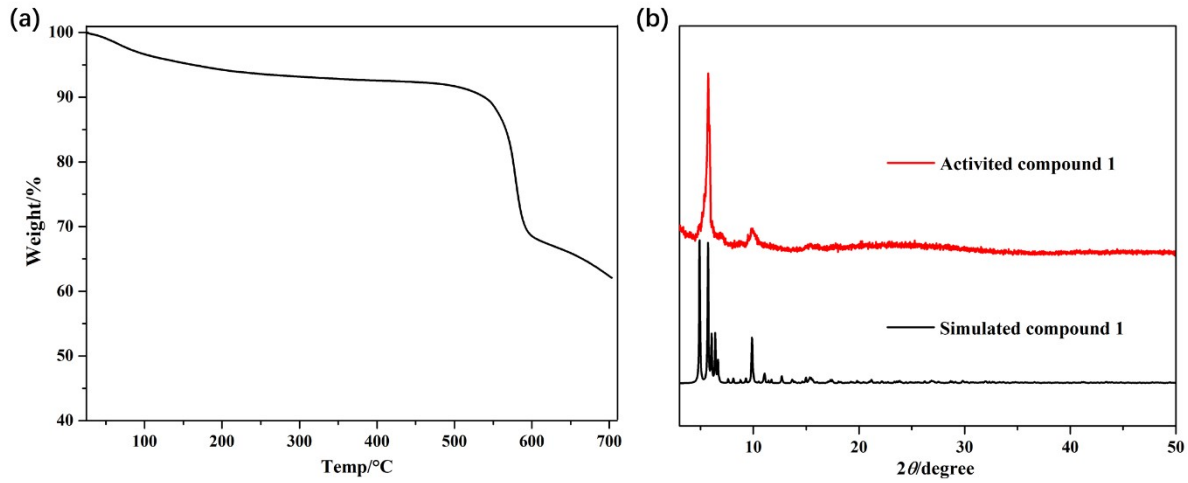


Figure S9. The thermogravimetric analyses curve (a) and the PXRD patterns (b) of compound **1** after the solvent exchange with MeOH and drying at 80 °C for 2 h.

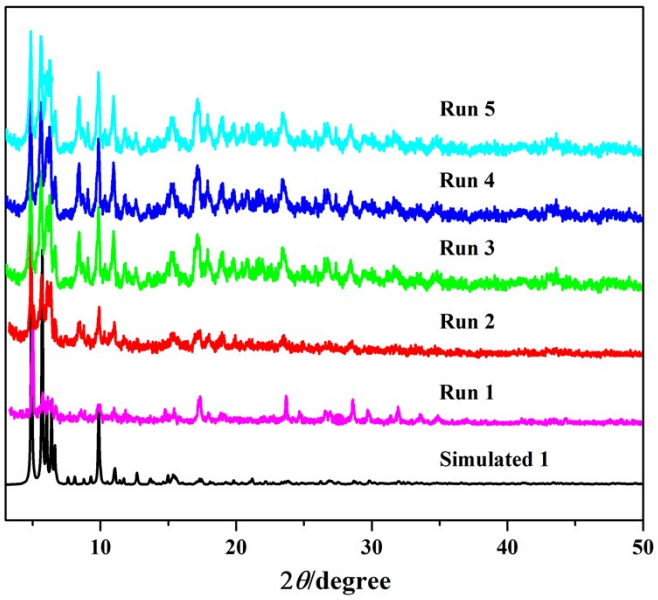


Figure S10. The consistent PXRD patterns with simulated data of **1** after five cycles for the cycloaddition of CS_2 and aziridines.

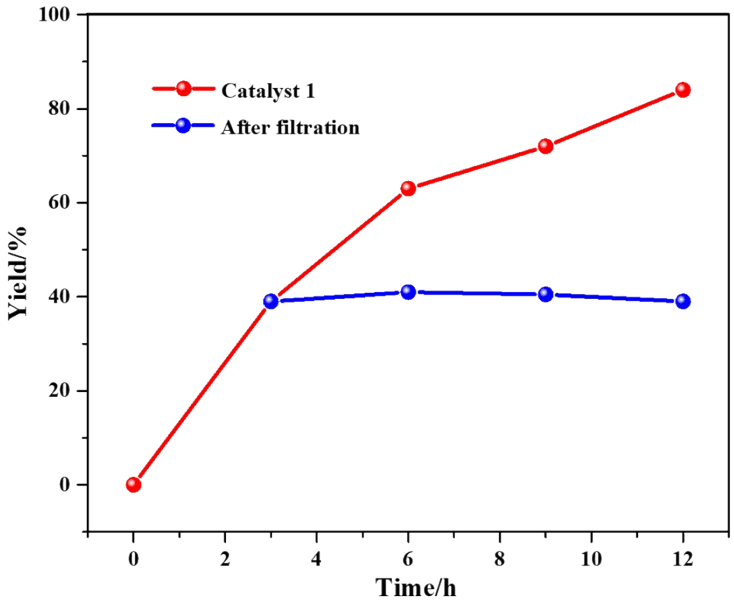


Figure S11. Catalytic filtration experiments for the cyclization reaction of CS_2 and aziridines.

In a typical experiment, 25 mg catalyst **1**, 0.05 mmol TBAB, 1 mmol 1-ethyl-2-phenylaziridine and 5 mmol CS_2 are sealed in a Schlenk tube. The mixture is stirred at 60 ºC for different times, and the products are determined by ^{1}H NMR. After 3 hours of reaction, catalyst **1** is isolated from this reaction system by centrifugation. The filtrate is placed in another new reactor to continue the reaction under optimal reaction conditions for an additional 9 hours. All of these processes have been analyzed by ^{1}H NMR and the experimental results are shown in Figure S11. The results show that the substrate can not convert after separating catalyst **1** from the reaction tube, which demonstrates compound **1** can act as an efficient heterogeneous catalyst for the cycloaddition reaction of CS_2 and aziridines.

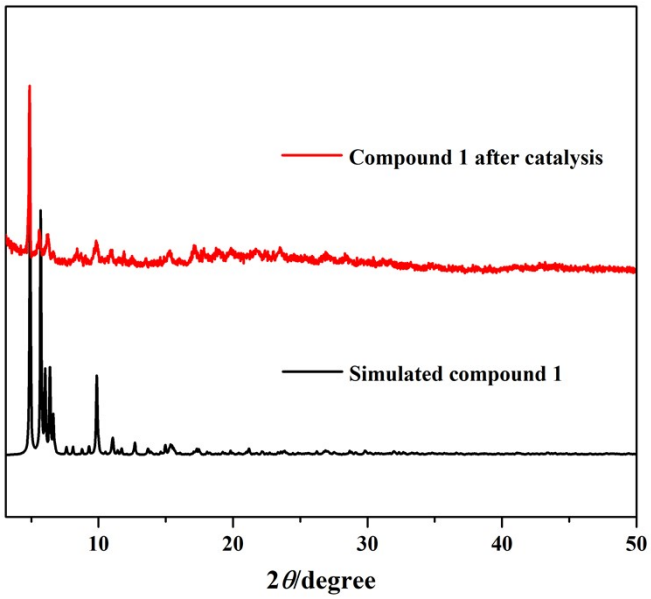


Figure S12. The PXRD patterns of compound **1** for the gram-scale catalytic experiment after 24 h.

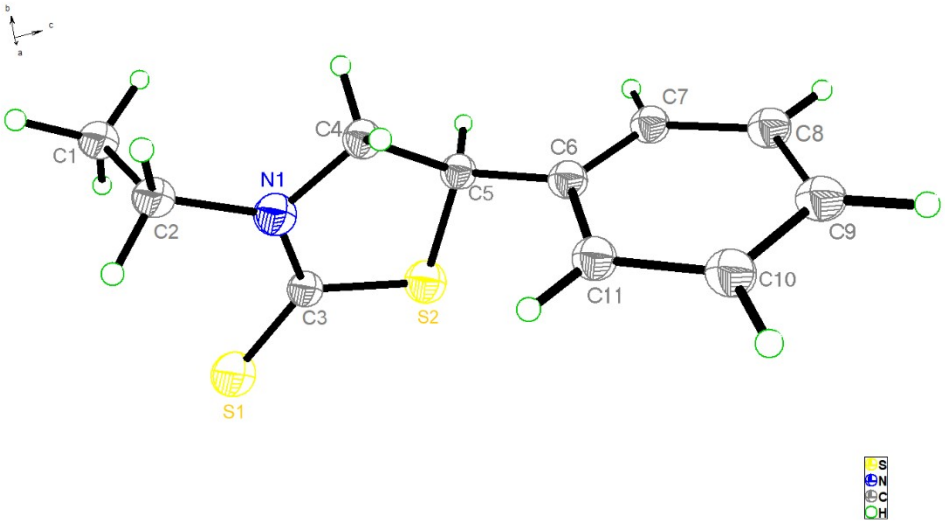


Figure S13. The single-crystal structure of 3-ethyl-5-phenylthiazolidine-2-thione. Thermal ellipsoids are set at the 50% probability level.

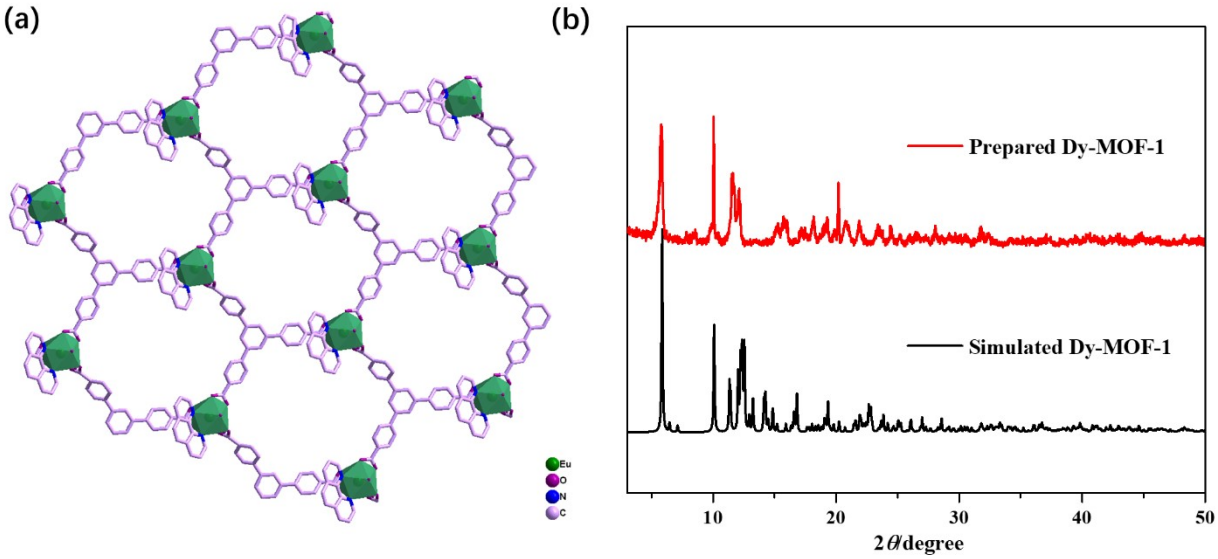


Figure S14. The 3D framework of **Dy-MOF-1** (a) and its PXRD patterns (b).[2]

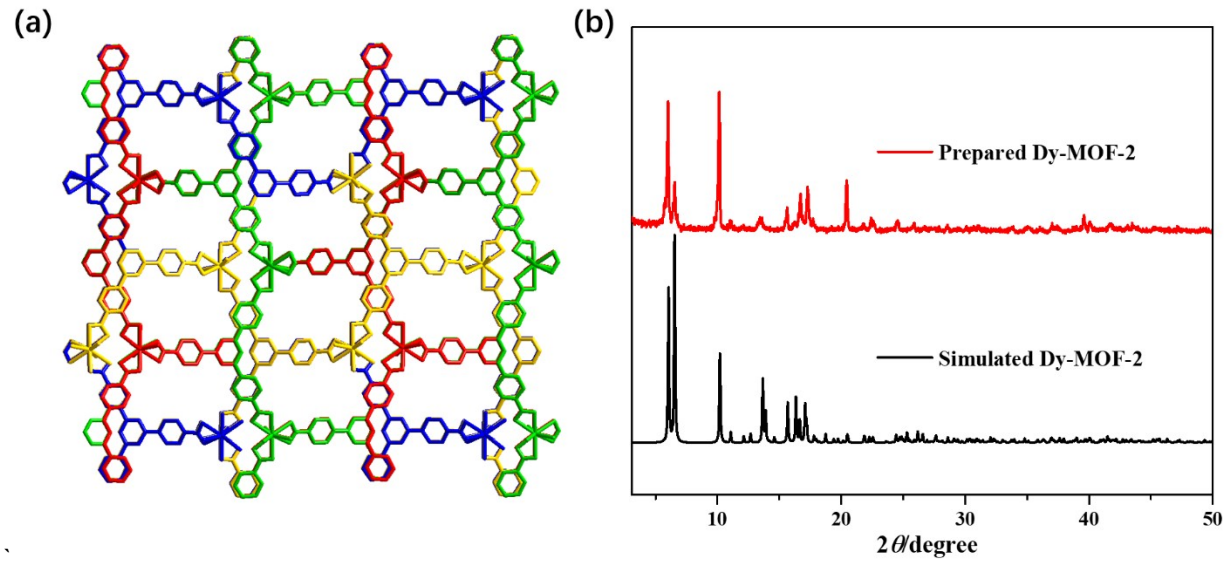


Figure S15. The 3D framework of **Dy-MOF-2** and its PXRD patterns. [3]

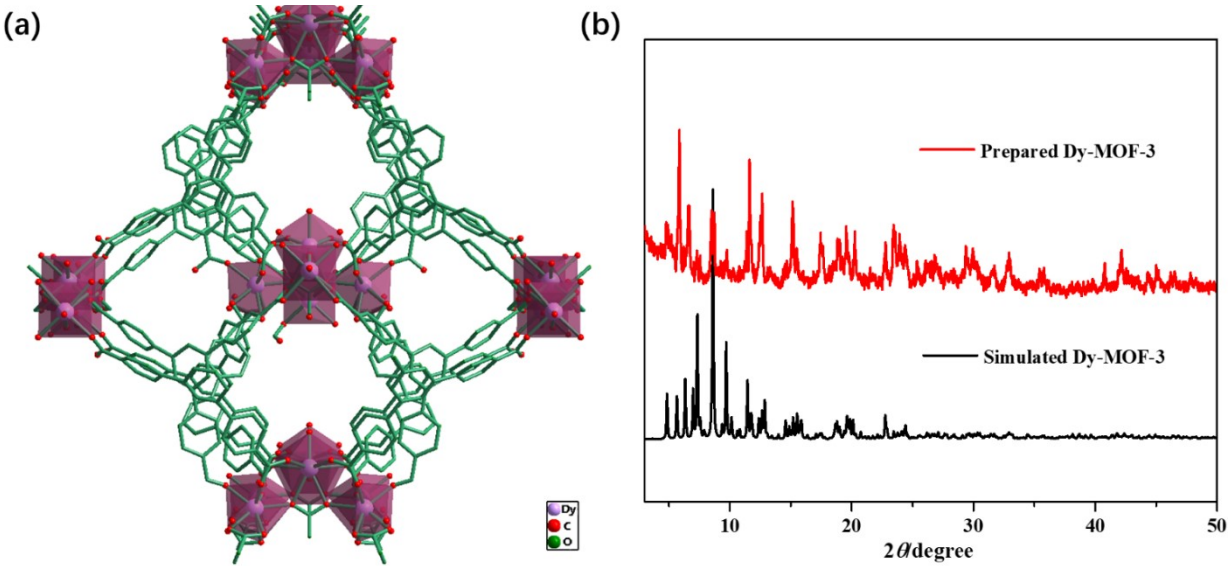


Figure S16. The 3D framework of **Dy-MOF-3** (a) and its PXRD patterns (b). [4]

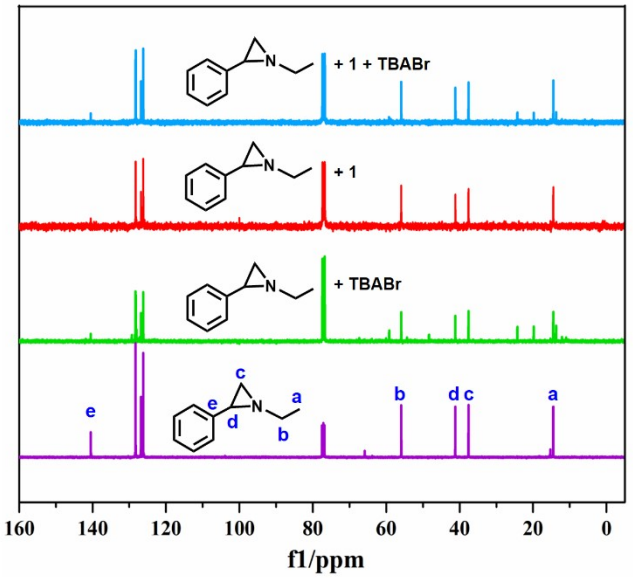


Figure S17. ^{13}C NMR spectral to analyze the activation of aziridine substrate by catalysts in different systems (in $CDCl_3$).

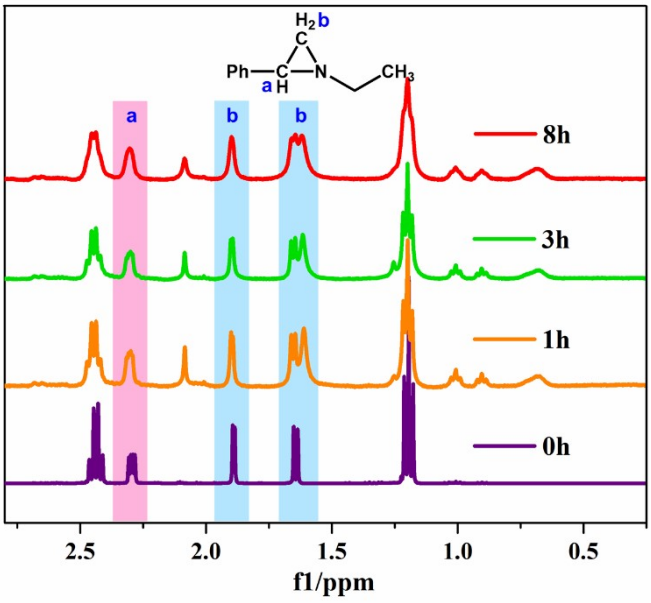


Figure S18. ^{1}H NMR spectral to analyze the activation of aziridine substrate by individual **1** for different times (in $CDCl_3$). Reaction conditions: 25 mg compound **1** and 1 mmol 1-ethyl-2-phenylaziridine are sealed in a Schlenk tube at 60 ºC for different times.

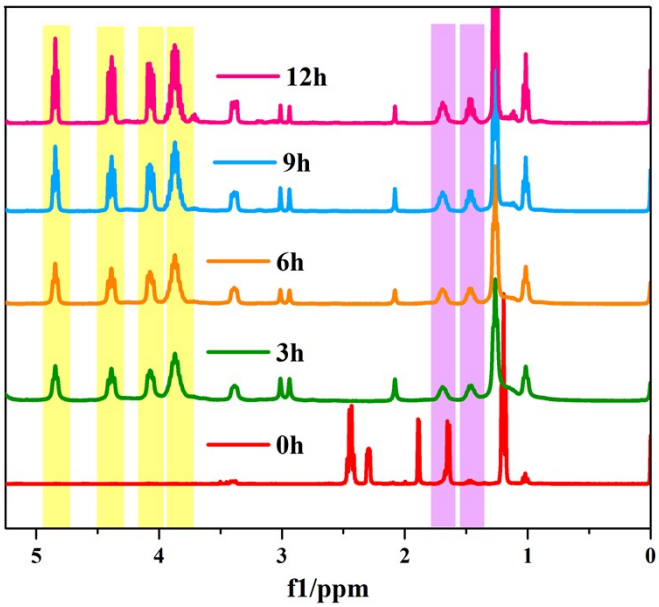


Figure S19. ^{1}H NMR spectral to monitor the entire cycloaddition process of aziridine and CS_2 by compound **1** and TBAB for different times (in $CDCl_3$).

As the time increasing, the characteristic protons of 1-ethyl-2-phenylaziridine (substrate) gradually shift from δ = 2.29 ppm to 2.08 ppm, and at the same time, the characteristic peaks of the corresponding product appear at δ = 4.84, 4.38, 4.07 and 3.87 ppm and their intensities enhance. This result indicates compound **1** can effectively catalyze the conversion of aziridines and CS_2 into 3-ethyl-5-phenylthiazolidine-2-thione.

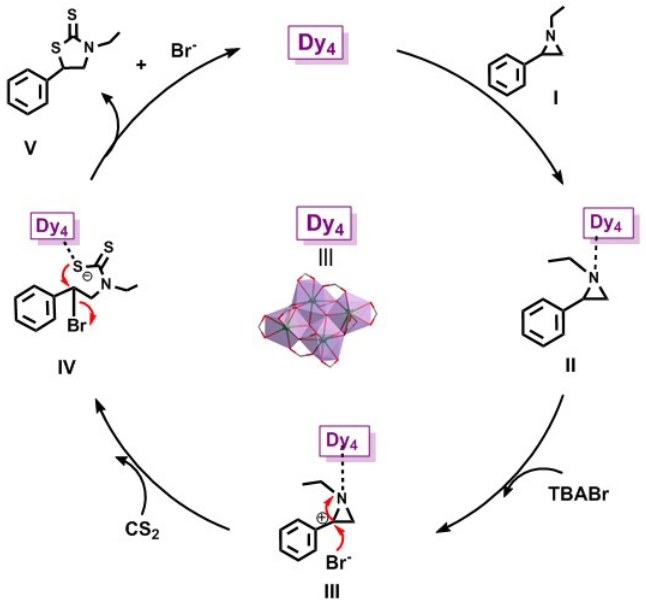


Figure S20. Possible reaction mechanism of the cycloaddition of CS_2 and aziridines by compound **1**.

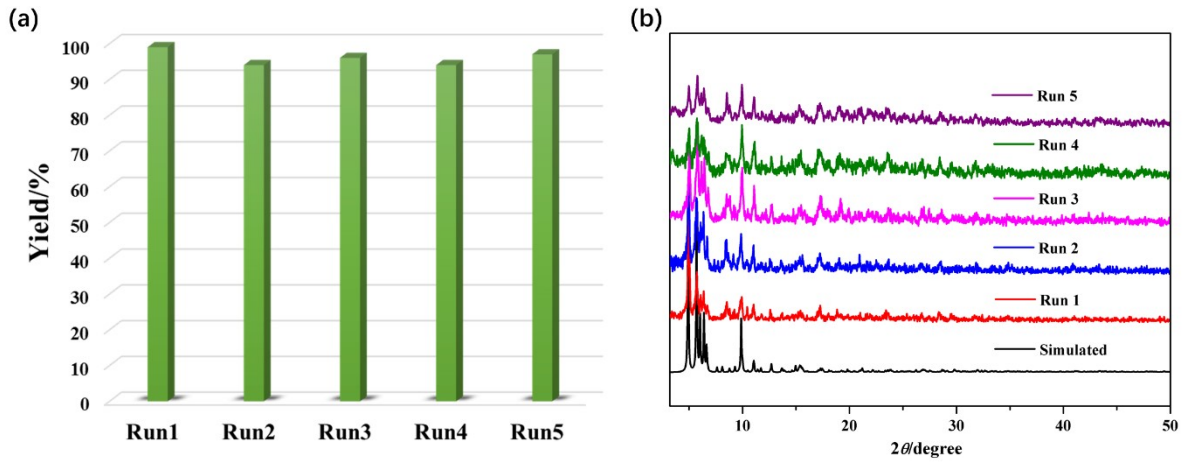


Figure S21. (a) The yields of oxazolidinones for the cycloaddition of CO_2 and aziridines by catalyst **1**. (b) The consistent PXRD patterns with simulated data of **1** after recyclable experiments.

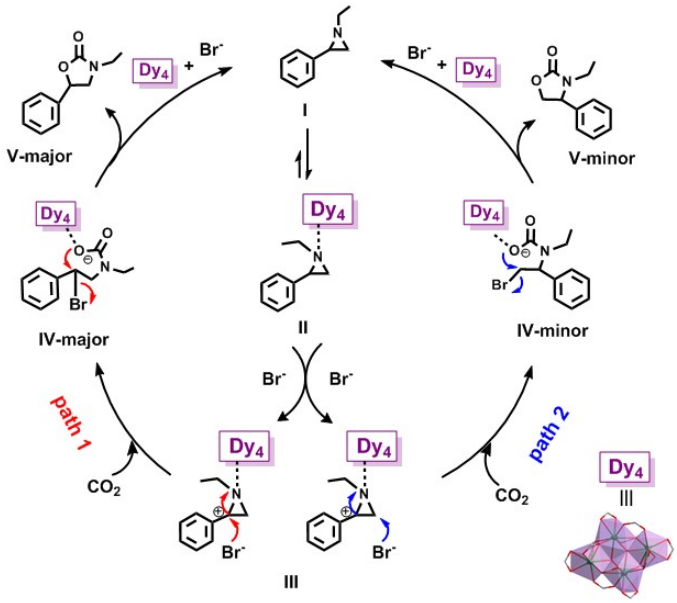


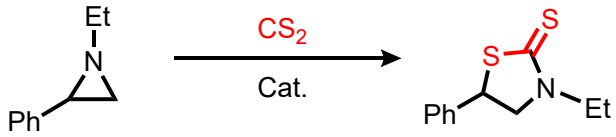
Figure S22. Possible reaction mechanism of the cycloaddition of CO_2 and aziridines by compound **1**.

Supplemental Tables

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

	1	**2**
Empirical formula	$NaDy_2C_{80}H_{91.5}O_{20.5}N_{6.5}$	$NaTb_2C_{78}H_{85}O_{19}N_6$
Formula weight	1820.10	1751.38
Temperature/K	123.10(14)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a/Å	20.5751(4)	20.7046(4)
b/Å	19.0251(4)	19.1345(3)
c/Å	27.2310(6)	26.5347(12)
α/°	90	90
β/°	102.224(2)	101.404(3)
γ/°	90	90
Volume/Å^3	10417.7(4)	10304.8(5)
Z	4	4
F(000)	2364.0	2352.0
Goodness-of-fit on F^2	1.090	1.029
Final R indexes [I>=2σ (I)]	R_1 = 0.0250, wR_2 = 0.0685	R_1 = 0.0662, wR_2 = 0.1547
Final R indexes [all data]	R_1 = 0.0312, wR_2 = 0.0712	R_1 = 0.1096, wR_2 = 0.1777
CCDC	2034446	2034449

Table S2. Control experiments of cycloaddition of CS_2 and aziridines.[a]



Entry	Catalyst **1** (mg)	Temp (°C)	Yield (%)[b]
1	25	30	74
2	25	40	78
3	25	50	79
4	25	60	87
5	25	70	87
6[c]	25	60	69
7[d]	25	60	78
8[e]	25	60	74

[a] Reaction conditions: 1-ethyl-2-phenylaziridine (1.0 mmol), CS_2 (5.0 mmol), compound **1** (25 mg based on metal center, about 2.74 mol%), TBAB (0.05 mmol), solvent-free, 12 h. [b] Using 1,3,5-trimethoxybenzene as an internal standard to determine total yield of the product by ^{1}H NMR. [c] 9 h. [d] TBAI (0.05 mmol) as co-catalyst. [e] Cs_2CO_3 (0.05 mmol) as co-catalyst.

To explore the optimal reaction system, 1-ethyl-2-phenylaziridine was selected as a model substrate to analyze under different conditions (Table S2). 25 mg compound **1**, 0.05 mmol TBAB, 1 mmol 1-ethyl-2-phenylaziridine and 5 mmol CS_2 have been sealed in a Schlenk tube without additional solvent at different temperatures (Entries 1-5). As the temperature rises, the yield of 3-ethyl-5-phenylthiazolidine-2-thione increases from 74% to 87%. However, higher temperatures do not result in more substrate conversion, so the optimal reaction temperature is 60 ºC. Additionally, the yield of the product decreased after shortening the reaction time from 12 h to 9 h (Entry 6). Finally, the types of additives are also investigated. Compared with tetrabutylammonium iodide (TBAI) and Cs_2CO_3, tetrabutylammonium bromide (TBAB) exhibits better synergistic catalytic activity due to the higher nucleophilic offensive capabilities (Entries 7 and 8). Based on the above experimental results, the optimal reaction system is that 25 mg compound **1**, 0.05 mmol TBAB, 1 mmol 1-ethyl-2-phenylaziridine and 5 mmol CS_2 react under 60 ºC for 12 h.

Table S3. The ICP results of compound **1** after catalytic recyclings for the cycloaddition of CS_2 and aziridines.

Compound **1**	Amount of Dy in filter liquor after recyclings (ppm)	Mass loss percent (%)
After first catalytic recyclings	0.039	0.03
After fifth catalytic recyclings	0.152	0.12

Table S4. The reported catalysts for the cycloaddition of CS_2 with aziridines.

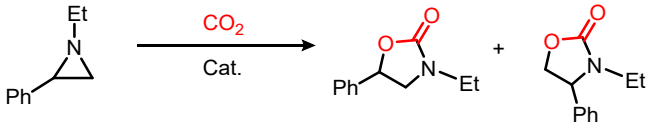
Catalyst	Amount	Temp(°C)	Time(h)	Yield(%)	TON[a]	TOF[b]	Reference
TBAB	5 mol%	r.t.	24	94	18.8	0.78	[5]
2-Pyridinecarboxaldehyde oxime	20 mol%	40	4	98	4.9	1.23	[6]
Tributylphosphine	10 mol%	Refulx	10	98	9.8	0.98	[7]
Polystyryl-supported tertiary amine	5 mol%	100	2.5	88.8	17.8	7.10	[8]
$L^1Eu[N(SiMe_3)_2]\cdot THF\}_2$	1 mol%	45	72	92	92[c]	1.27	[9]
$\{Na[Dy_2(\mu_3\text{-}OH)(BTB)_2]\cdot 6.5DMA\cdot H_2O\}_n$	2.74 mol%	60	12	84	613[d]	51.1	This work

[a] TON: Turnover number = n(product)/n(catalyst). [b] TOF: Turnover frequency = TON/t(reaction time). [c] 7 mmol substrate. [d] 10 mmol substrate.

Table S5. Crystal data and structure refinement for 3-ethyl-5-phenylthiazolidine-2-thione.

Identification code	3-ethyl-5-phenylthiazolidine-2-thione
Empirical formula	$C_{11}H_{13}NS_2$
Formula weight	223.34
Temperature/K	293(2)
Crystal system	monoclinic
Space group	*Cc*
a/Å	21.386(2)
b/Å	5.4755(6)
c/Å	10.7641(11)
α/°	90
β/°	118.825(12)
γ/°	90
Volume/Å^3	1104.3(2)
Z	4
F(000)	472.0
Goodness-of-fit on F^2	1.110
Final *R* indexes [I>=2σ (I)]	R_1 = 0.0918, wR_2 = 0.2340
Final *R* indexes [all data]	R_1 = 0.0956, wR_2 = 0.2383
CCDC	2096097

Table S6. Control experiments of cycloaddition of CO_2 with aziridines.[a]



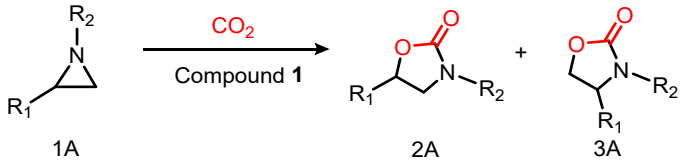
1S 2S 3S

Entry	Catalyst **1** (mg)	Temp (°C)	Yield (%)[b]	Regio-sel[c]
1	25	30	>99	97:3
2	25	40	97	97:3
3	25	50	96	97:3
4	25	60	>99	96:4
5[d]	25	30	49	87:13
6[e]	25	30	65	92:8
7[f]	25	30	10	73:27

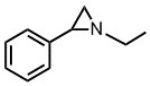
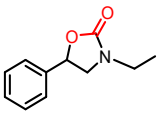
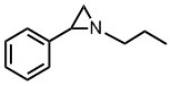
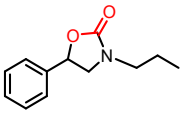
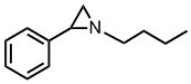
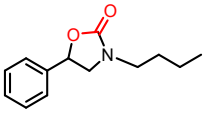
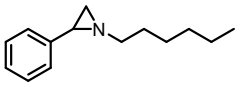
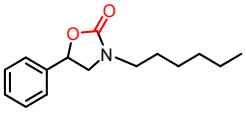
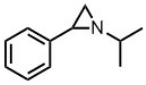
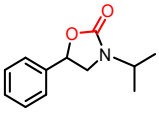
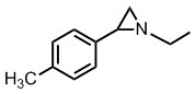
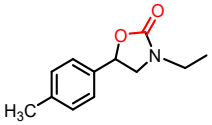
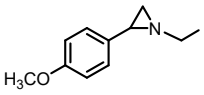
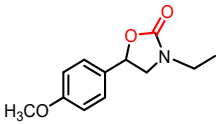
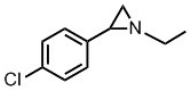
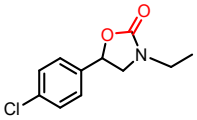
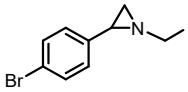
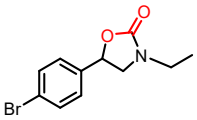
[a] Reaction conditions: 1-ethyl-2-phenylaziridine (2.0 mmol), CO_2 (2.0 MPa), compound **1** (25 mg, based on metal center, about 1.37 mol%), TBAB (0.05 mmol), solvent-free, 12 h. [b] Using 1,3,5-trimethoxybenzene as an internal standard to determine total yield of the products **2S** and **3S** by ^{1}H NMR. [c] The molar ratio of **2S** to **3S**. [d] CO_2 (0.5 MPa). [e] CO_2 (1.0 MPa). [f] Individual **1** as catalyst, without TBAB.

To identify the optimum reaction condition, 1-ethyl-2-phenylaziridine as the model substrate is selected to explore under the various conditions (Table S6). 25 mg compound **1**, 0.05 mmol TBAB and 2 mmol 1-ethyl-2-phenylaziridine are sealed in an autoclave under the different reaction systems. With the rise of temperature, the yields of 3-ethyl-5-phenyloxazolidin-2-one (**2S**) and 3-ethyl-4-phenyloxazolidin-2-one (**3S**) do not significantly increase (Entries 1-4). Hence, the reaction is performed at 30 ºC. In addition, the reaction pressure is also investigated. Under 0.5 MPa of CO_2 at 30 ºC for 12 h, **1** displays a low catalytic activity. After extending pressure to 1 MPa, the yields of **2S** and **3S** increase to 65%. Further increasing the pressure to 2 MPa, the yield of the product is close to 100% (Entries 1, 5 and 6). Finally, when no co-catalyst adds into the reaction system, the yield of the product is 10%, indicating compound **1** and TBAB can catalyze the cycloaddition of CO_2 and aziridines synergistically (Entry 7). Therefore, the optimal reaction condition is 30 ºC and 2 MPa of CO_2 for 12 h with TBAB as co-catalyst.

Table S7. Cycloaddition reactions of various aziridines with CO_2.[a]



1A 2A 3A

Entry	Substrate	Main product	Yield (%)[b]	Regio-sel[c]
1			>99	97:3
2			98	97:3
3			94	95:5
4			46	99:1
5			26	96:4
6			95	98:2
7			85	99:1
8			96	96:4
9			76	96:4

[a] Reaction conditions: aziridine (2.0 mmol), CO_2 (2.0 MPa), catalyst **1** (25 mg, based on metal center, about 1.37 mol%), TBAB (0.05 mmol), solvent-free, 30 °C, 12 h. [b] Using 1,3,5-trimethoxybenzene as an internal standard to determine by ^{1}H NMR. [c] The molar ratio of **2A** to **3A**.

Table S8. The ICP results of compound **1** after fifth catalytic recyclings for the cycloaddition of CO_2 and aziridines.

Compound **1**	Dy
Filter liquor after fifth catalytic recyclings (ppm)	0.002

Table S9. Control experiments of the cycloaddition of CO_2 and aziridines.[a]

Entry	Catalyst (mg)	Yield (%)[b]	Regio-sel[c]
1[d]	-	34	98:2
2	Compound **1**	>99	97:3
3[e]	Compound **1**	10	73:27
4[f]	TBAB	72	95:5
5[g]	$Dy(OAc)_3$	75	95:5
6[h]	H_3BTB	29	96:4
7[i]	$Dy(OAc)_3$+ H_3BTB	85	93:7

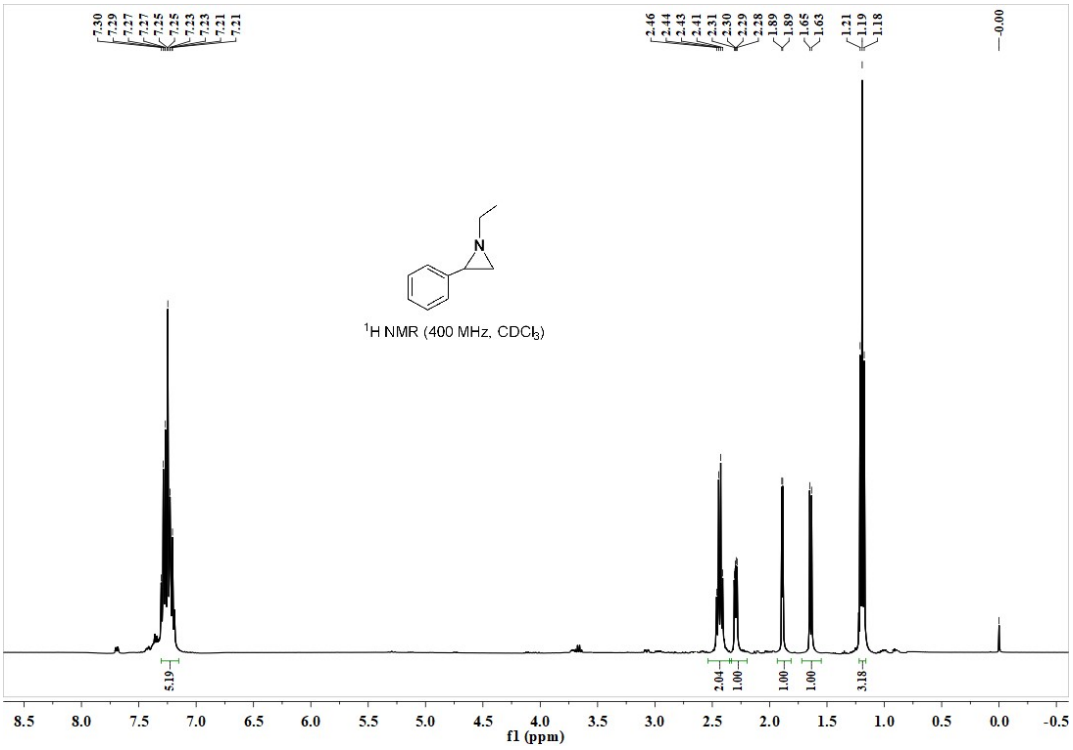
[a] Reaction conditions: 1-ethyl-2-phenylaziridine (2.0 mmol), TBAB (0.05 mmol), CO_2 (2.0 MPa), solvent-free, 30 °C, 12 h. [b] Using 1,3,5-trimethoxybenzene as an internal standard to determine total yield of the products by ^{1}H NMR. [c] The molar ratio of **2S** to **3S**. [d] No catalyst and TBAB. [e] Individual compound **1** (25 mg). [f] Individual TBAB (0.05 mmol). [g] $Dy(OAc)_3$ (14.5 mg, based on metal center, about 1.4 mol%). [h] H_3BTB (20 mg). [i] $Dy(OAc)_3$ (14.5 mg) + H_3BTB (20 mg).

Some control experiments are carried out to investigate the reasons for high catalytic ability of **1** for the cycloaddition of CO_2 and aziridines. The corresponding results were summarized in Table S8. In the absence of the additive TBAB, individual compound **1** exhibits a lower catalytic activity. After adding TBAB, the two synergistically promote this reaction and completely convert the aziridines substrate into the corresponding products (99%, Entries 3 and 4). Due to the inherent Lewis acidity of Ln^{III} ions, the catalytic ability of individual $Dy(OAc)_3$ under optimal reaction conditions is analyzed, and its catalytic performance is moderate (Entry 5). When H_3BTB ligand is added into this system and performs simple mechanical mixing, the yield of the product increases, indicating that $Dy(OAc)_3$ and H_3BTB ligand have a synergistic effect to promote the reaction (Entries 6 and 7).

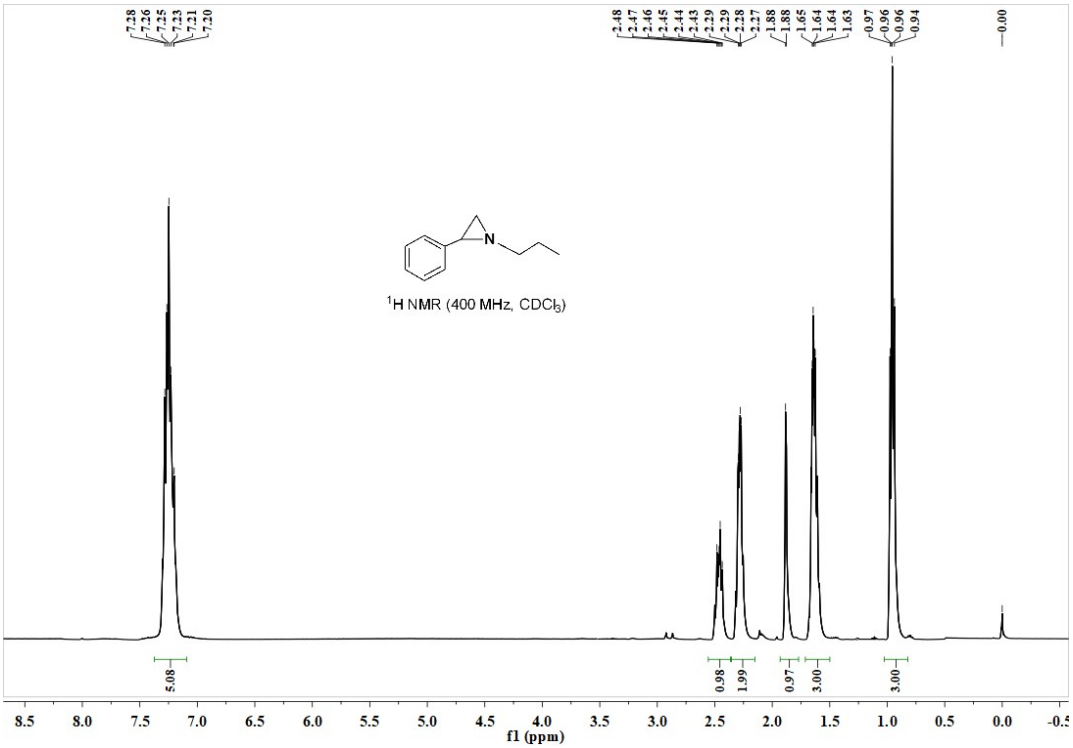
NMR spectral for re-prepared aziridines, thiazolidine-2-thiones and oxazolidinones

The ^{1}H NMR spectral for aziridines.

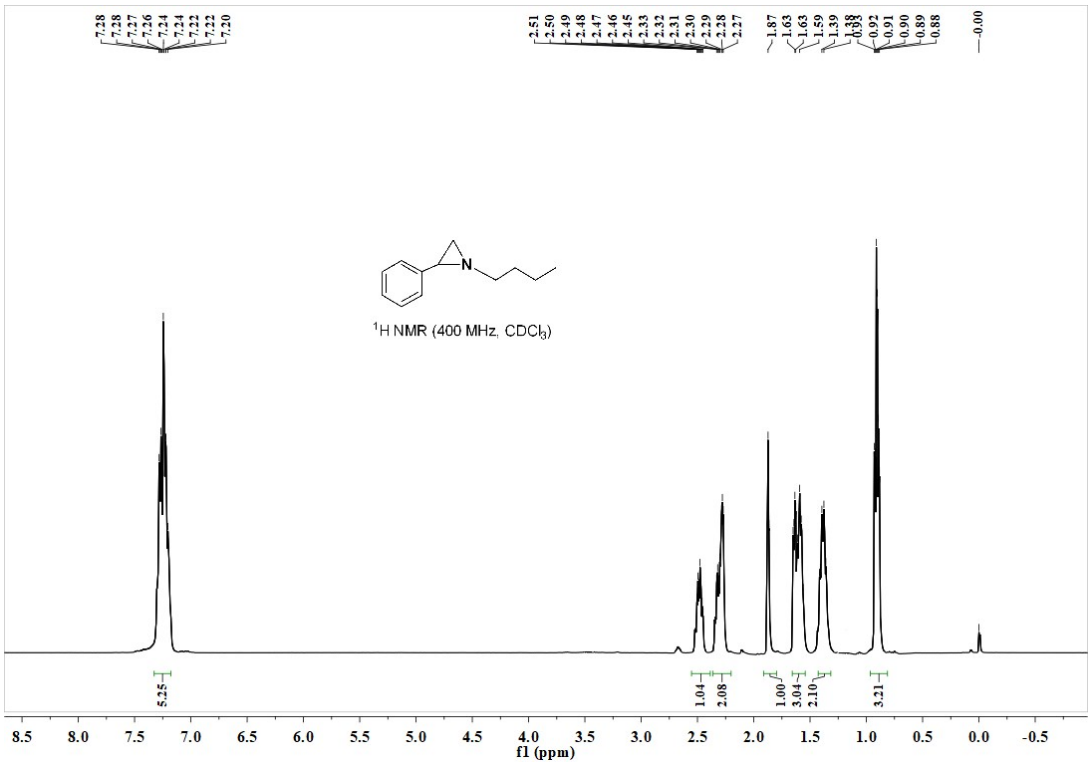
1-Ethyl-2-phenylaziridine



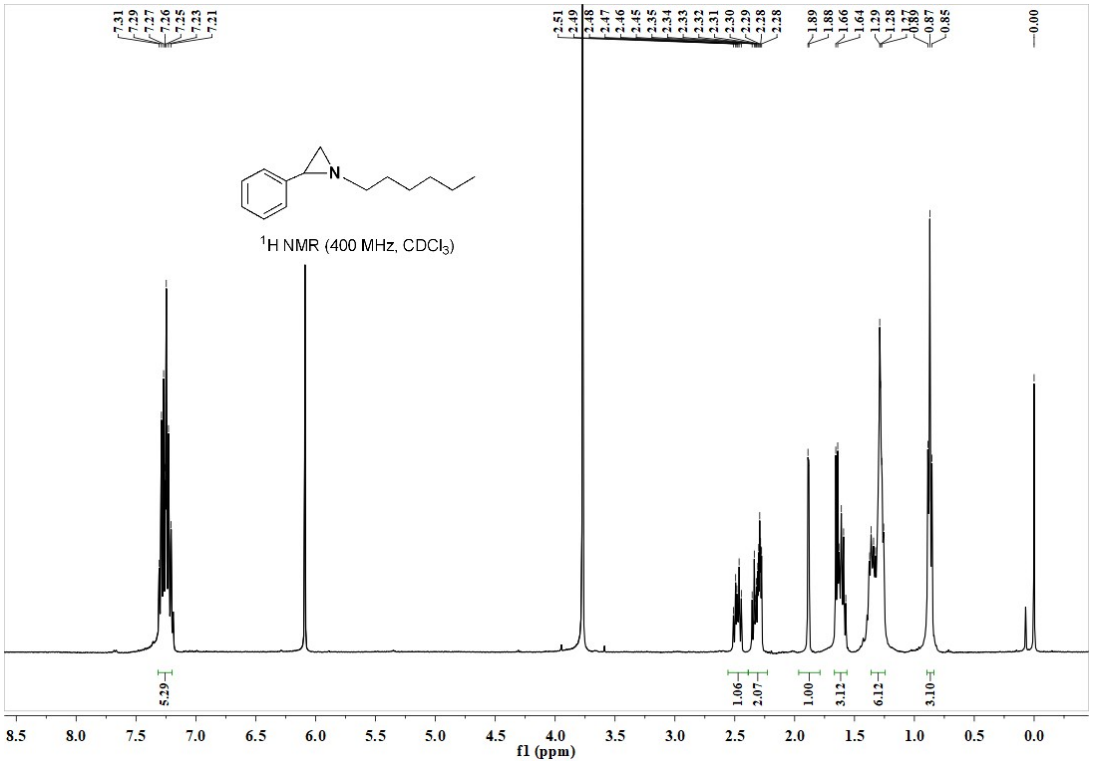
1-Propyl-2-phenylaziridine



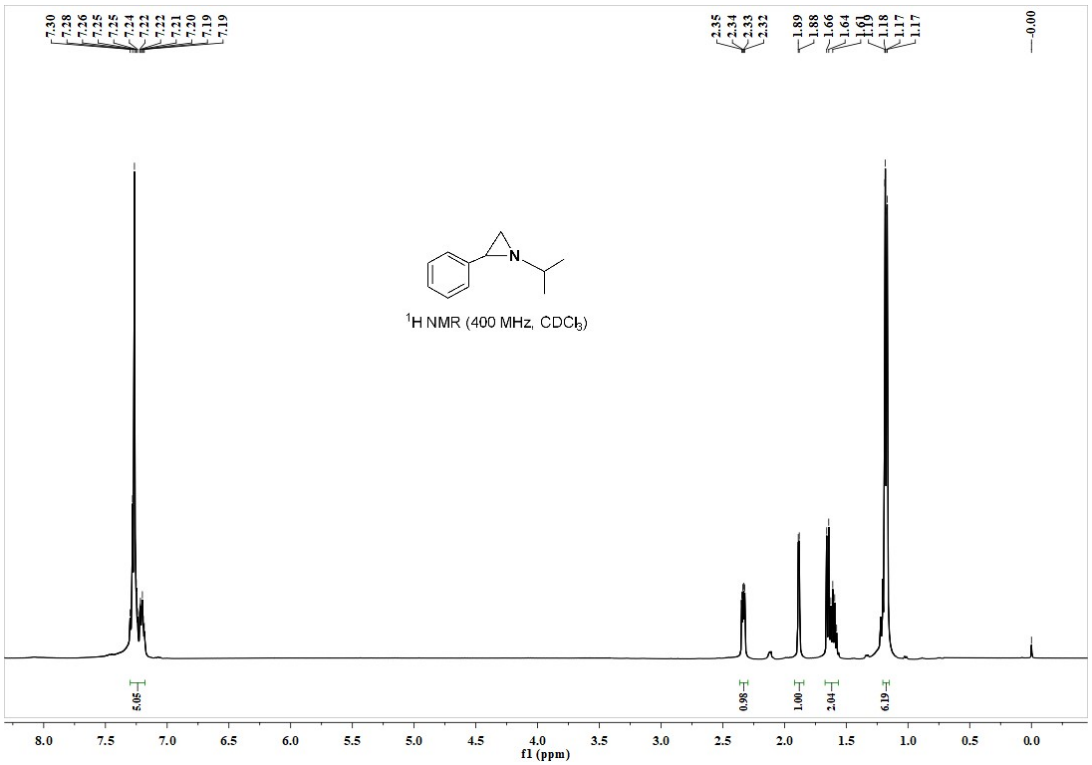
1-Butyl-2-phenylaziridine



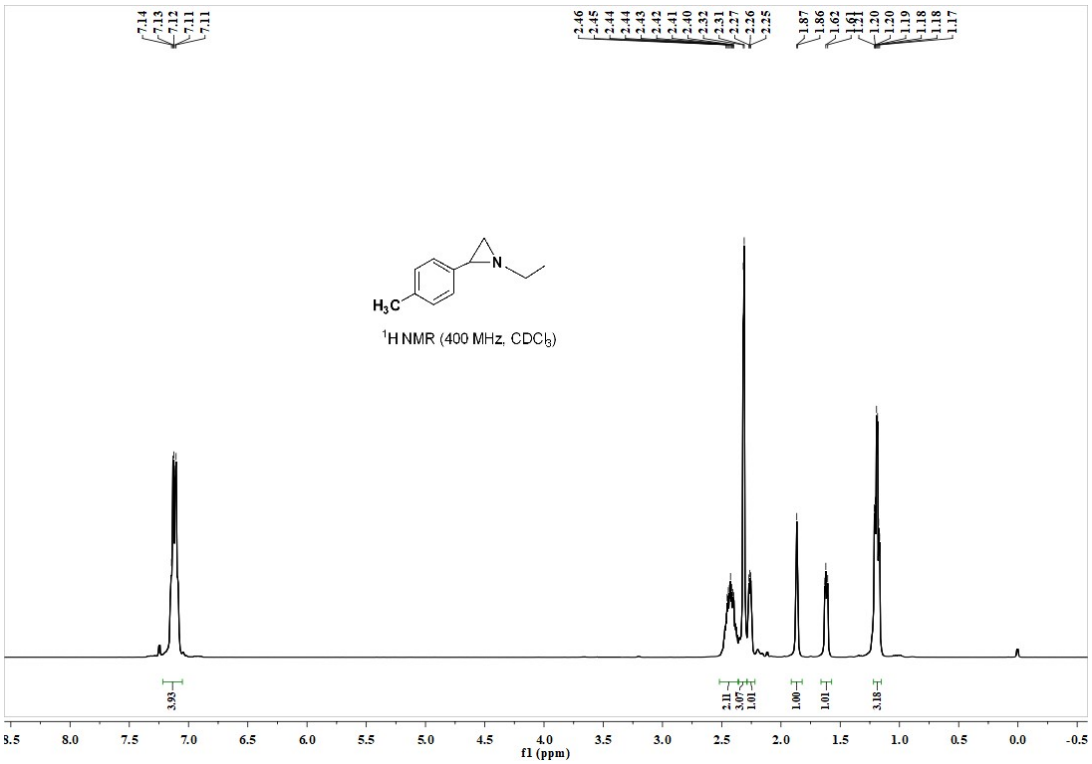
1-Hexyl-2-phenylaziridine



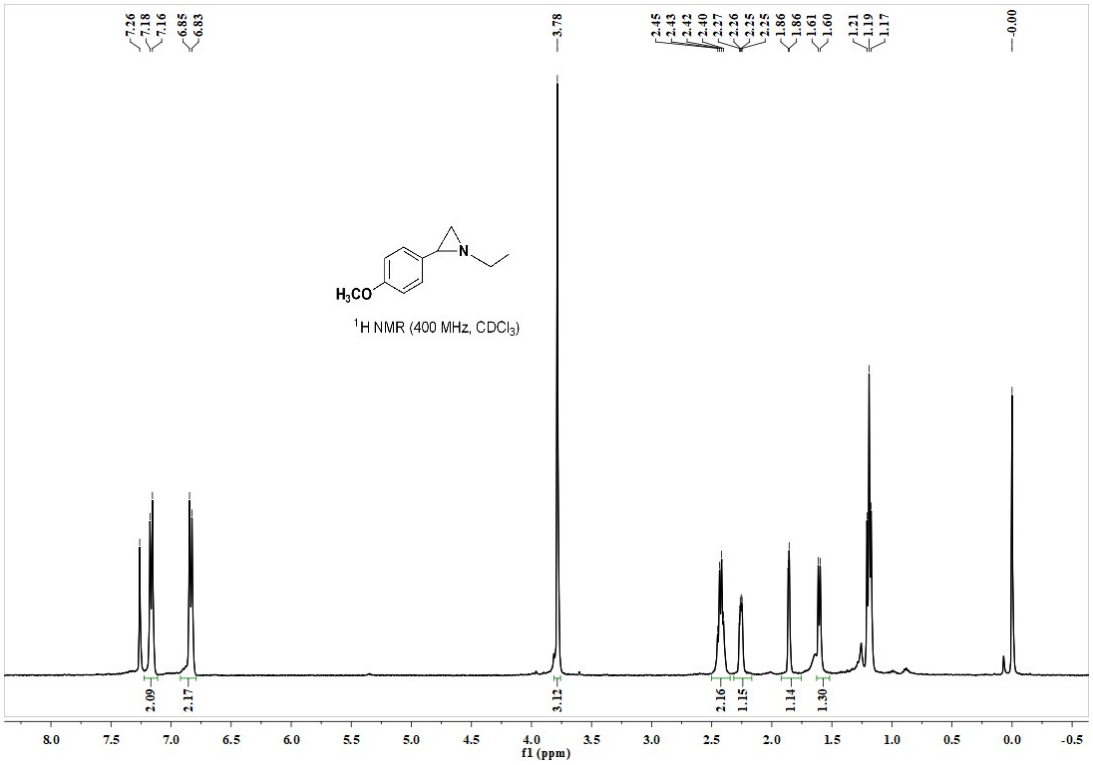
1-Isopropyl-2-phenylaziridine



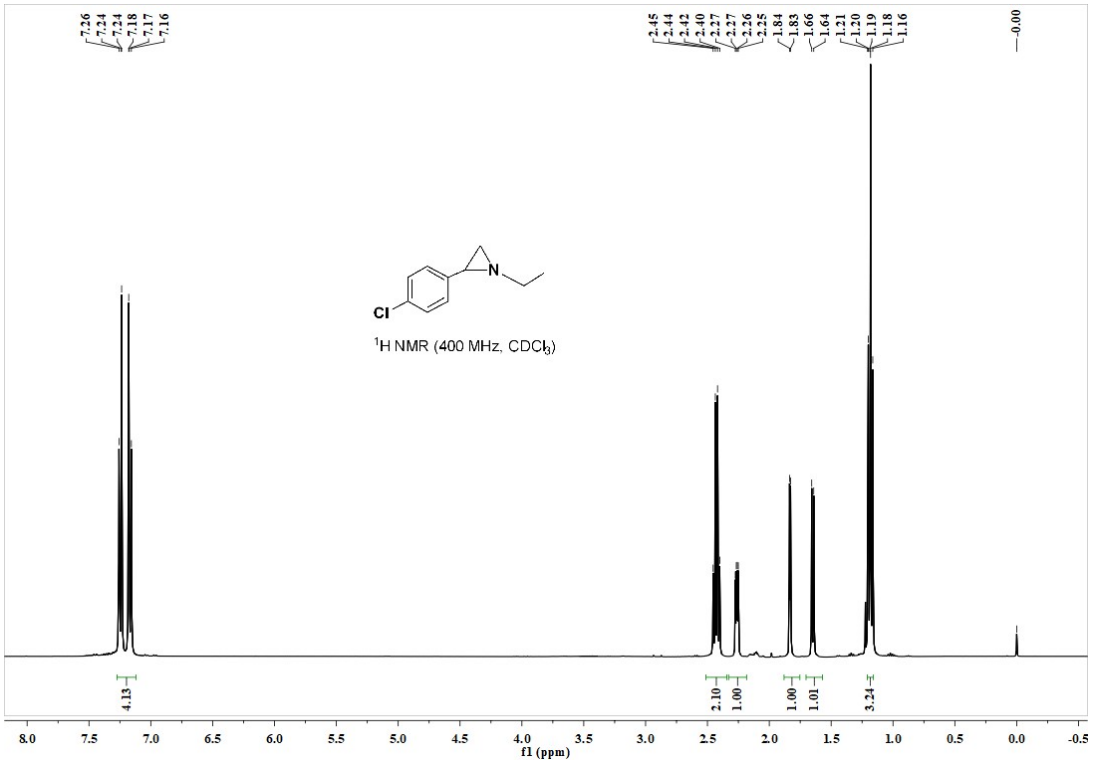
Ethyl-2-*p*-tolylaziridine



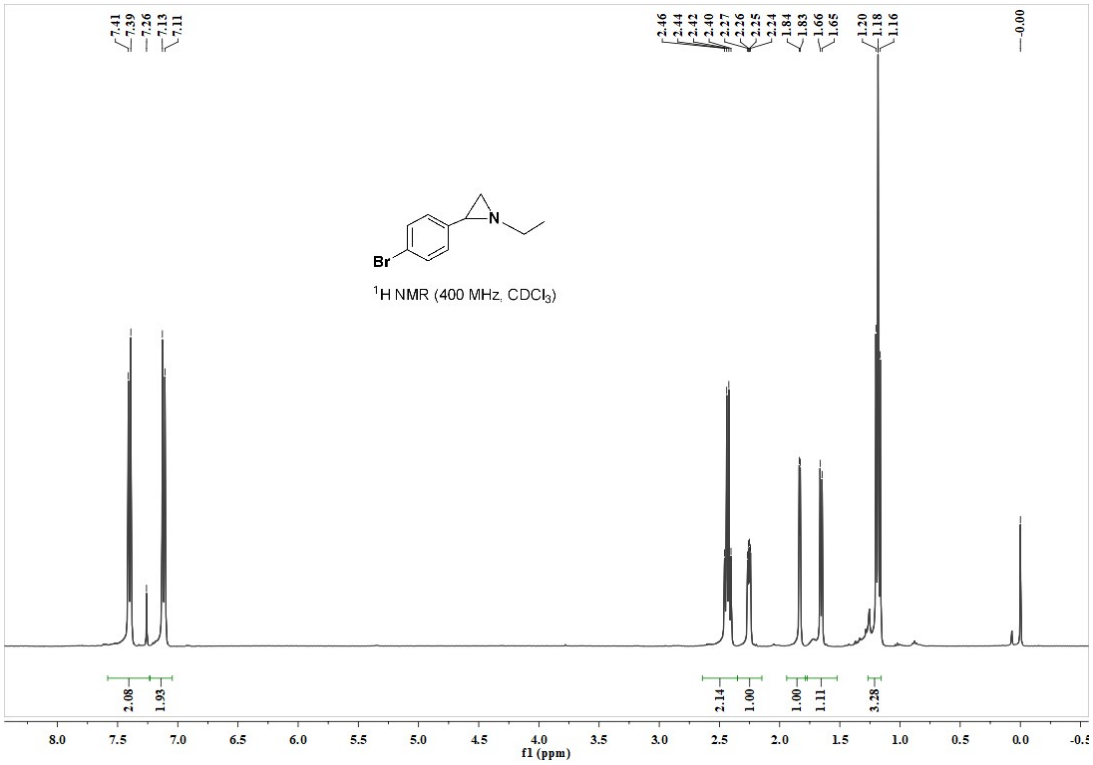
(4-Methoxyphenyl)-1-ethylaziridine



(4-Chlorophenyl)-1-ethylaziridine

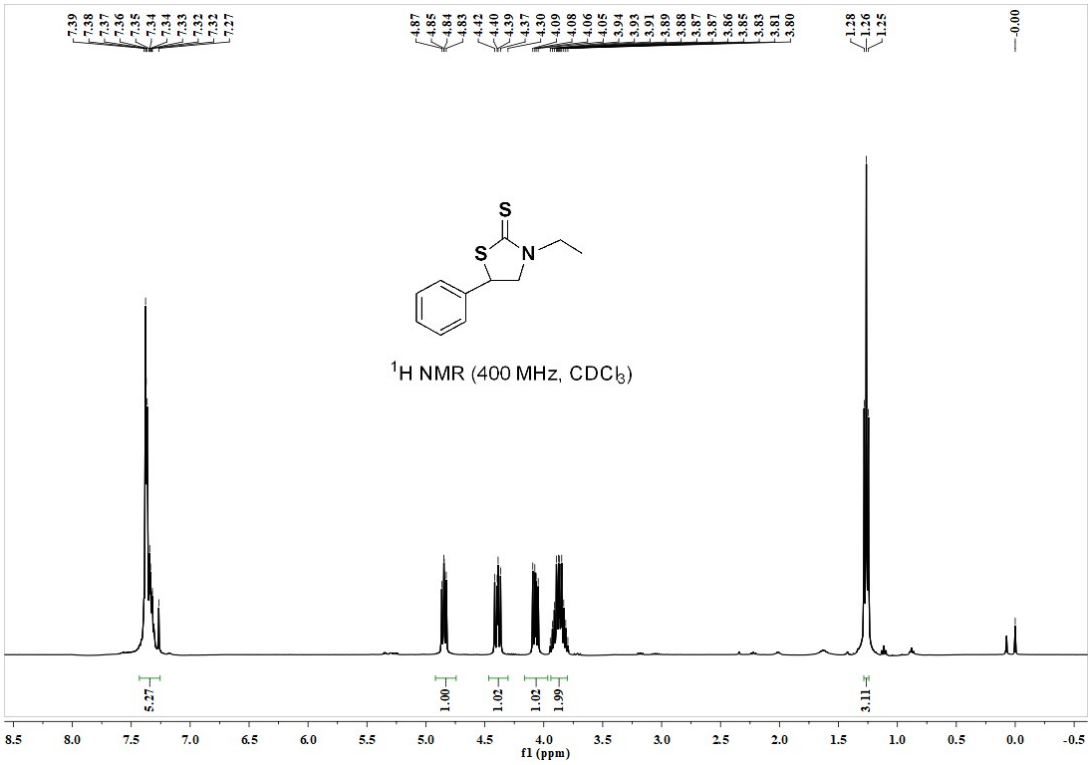


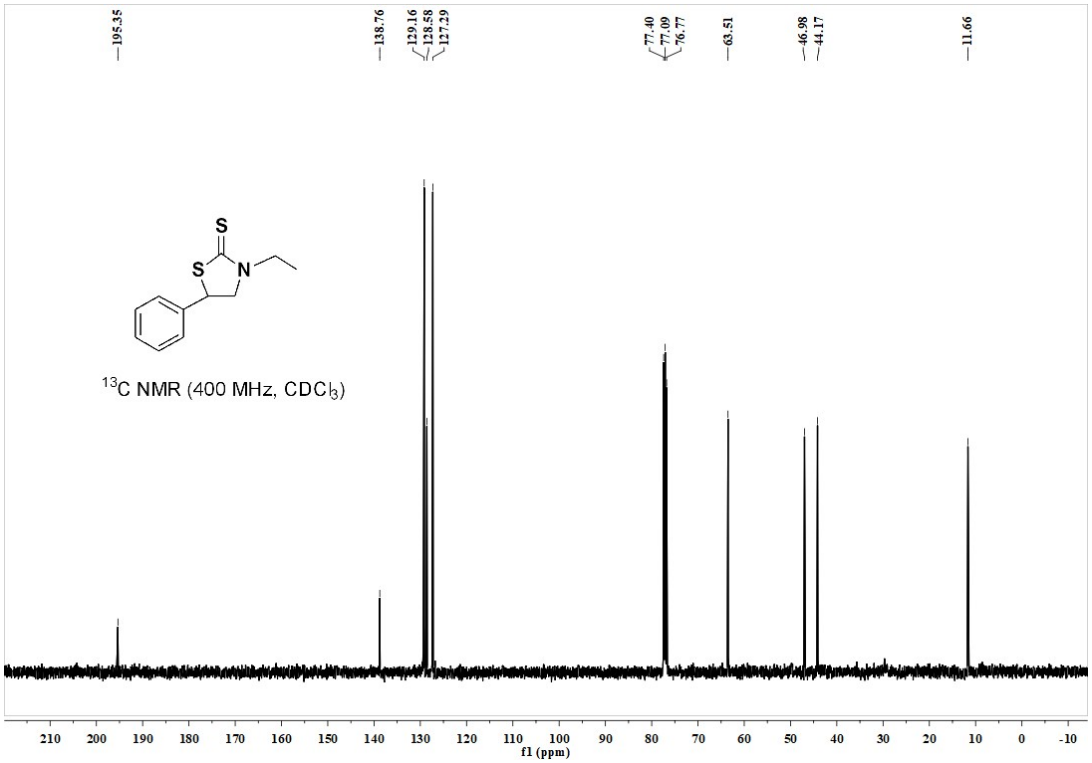
(4-Bromophenyl)-1-ethylaziridine



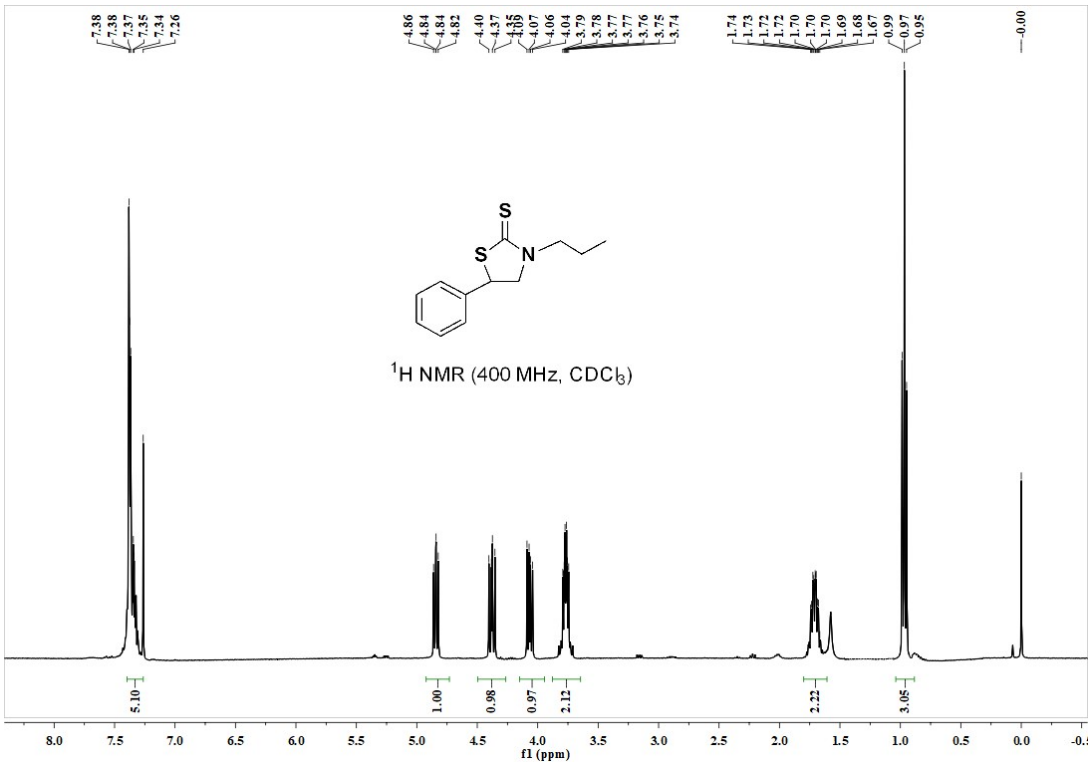
The ^{1}H NMR and ^{13}C NMR spectral for thiazolidine-2-thiones.

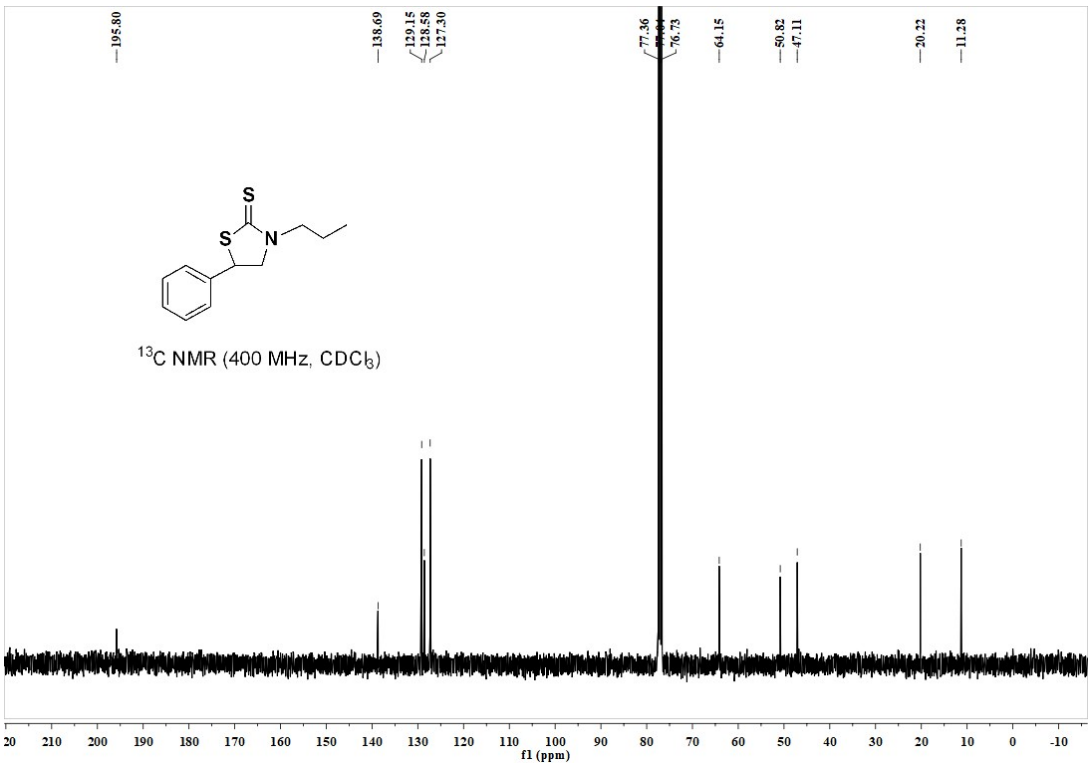
3-Ethyl-5-phenylthiazolidine-2-thione



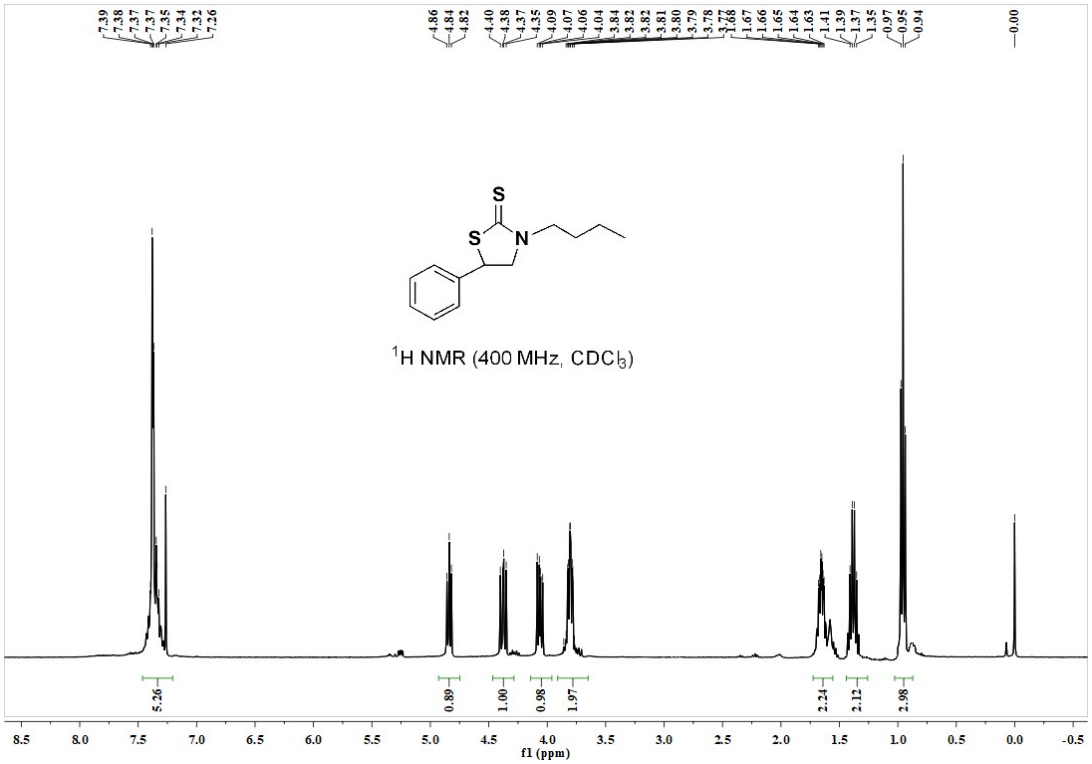


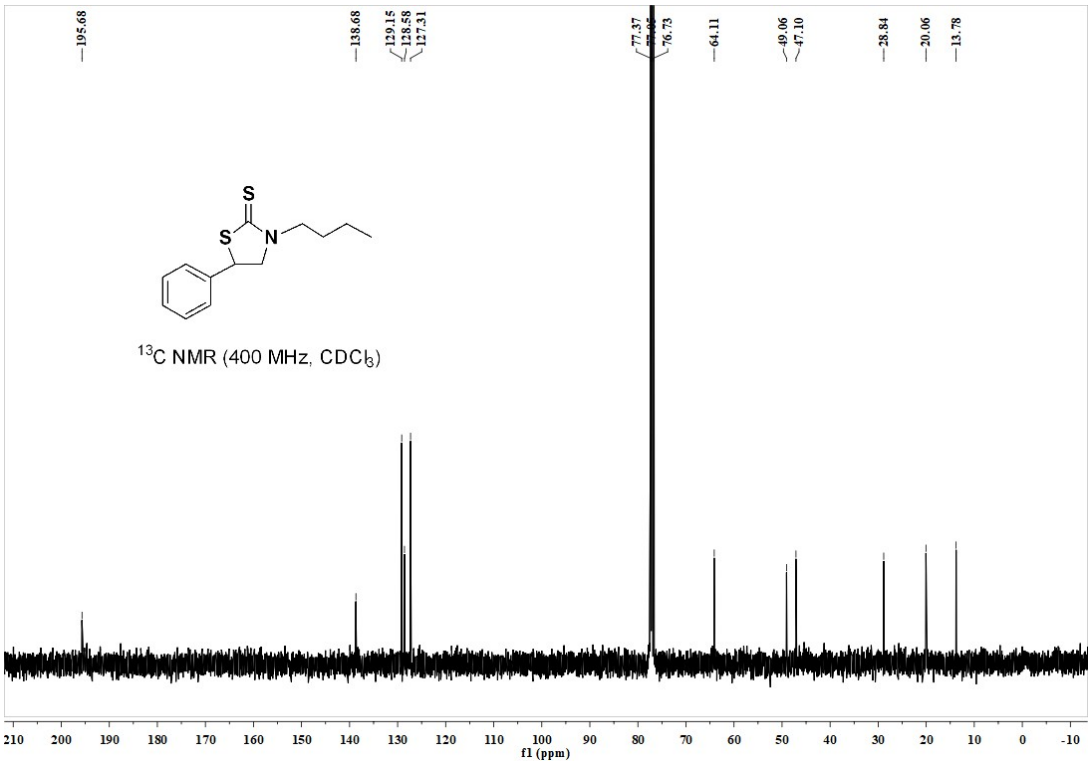
3-Propyl-5-phenylthiazolidine-2-thione



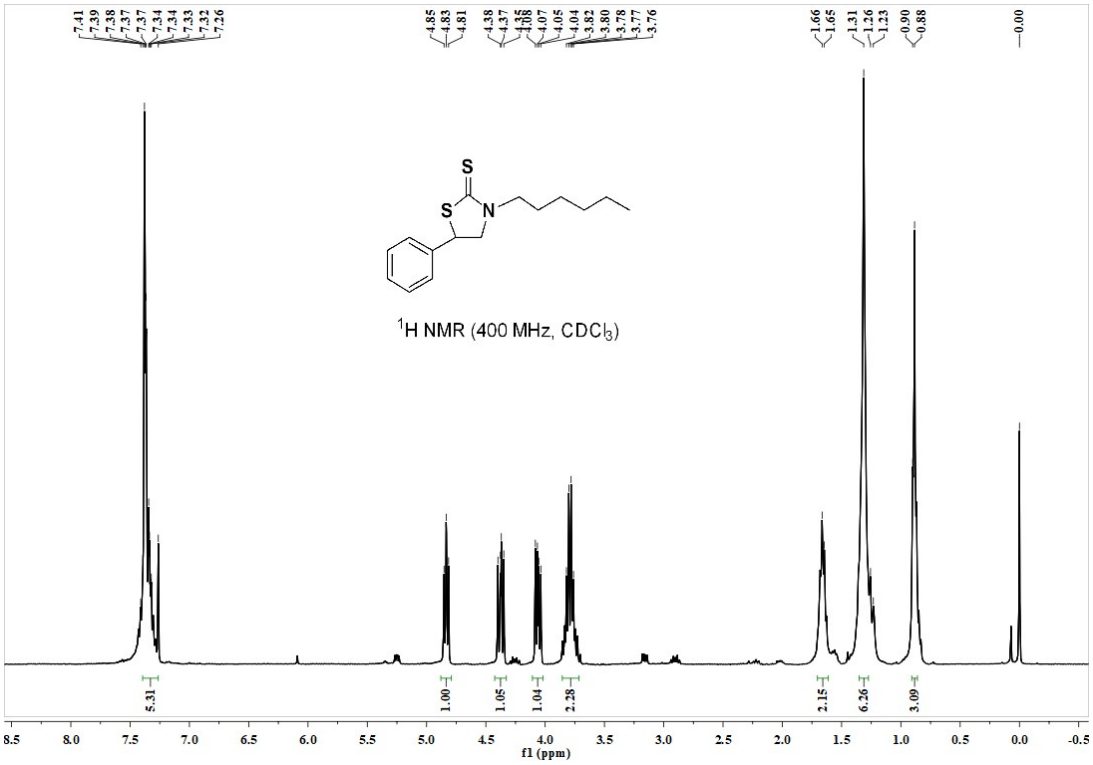


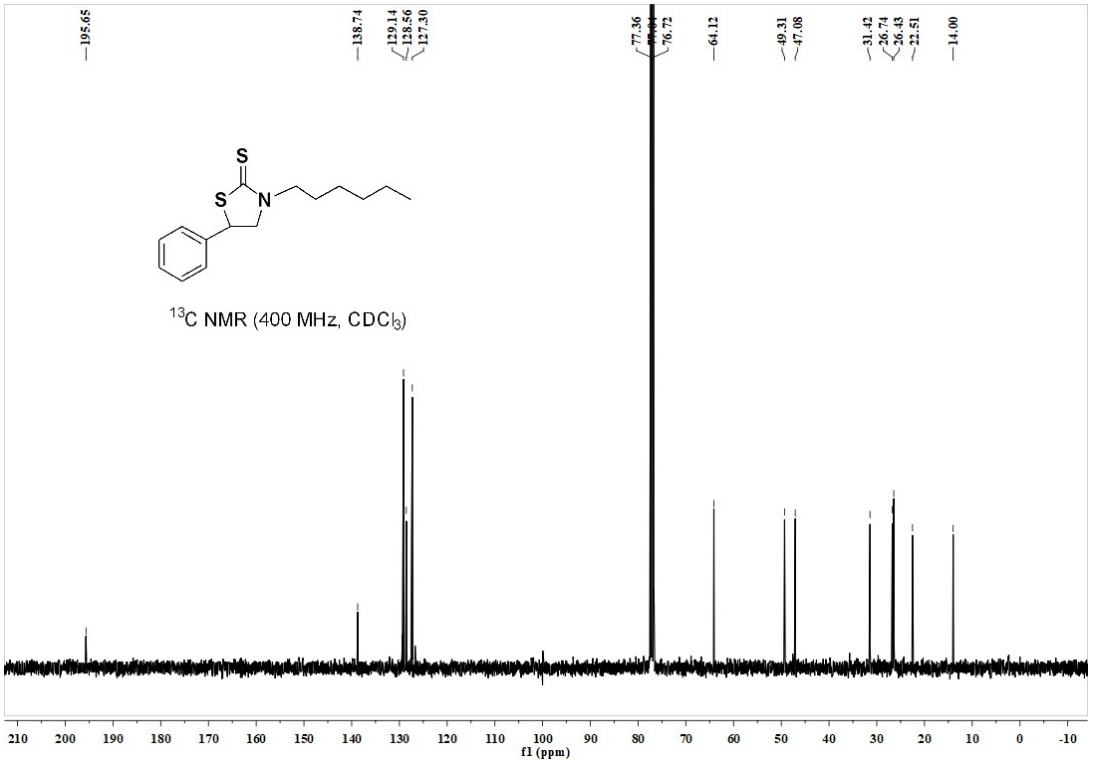
3-Butyl-5-phenylthiazolidine-2-thione



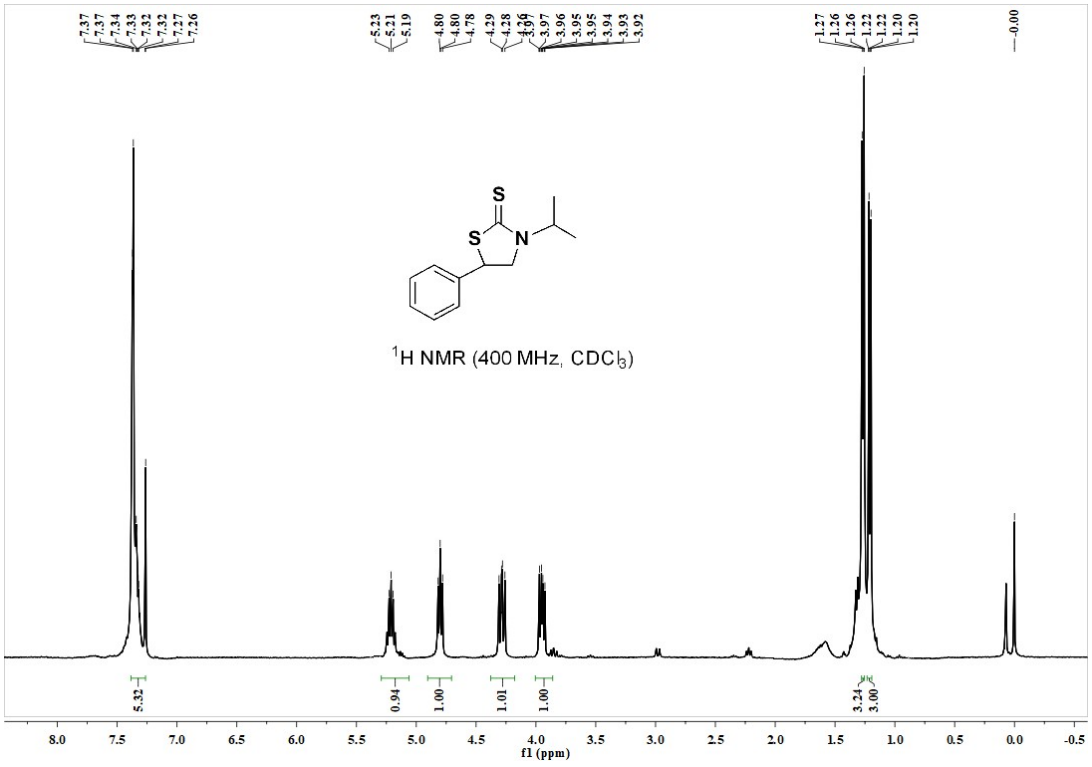


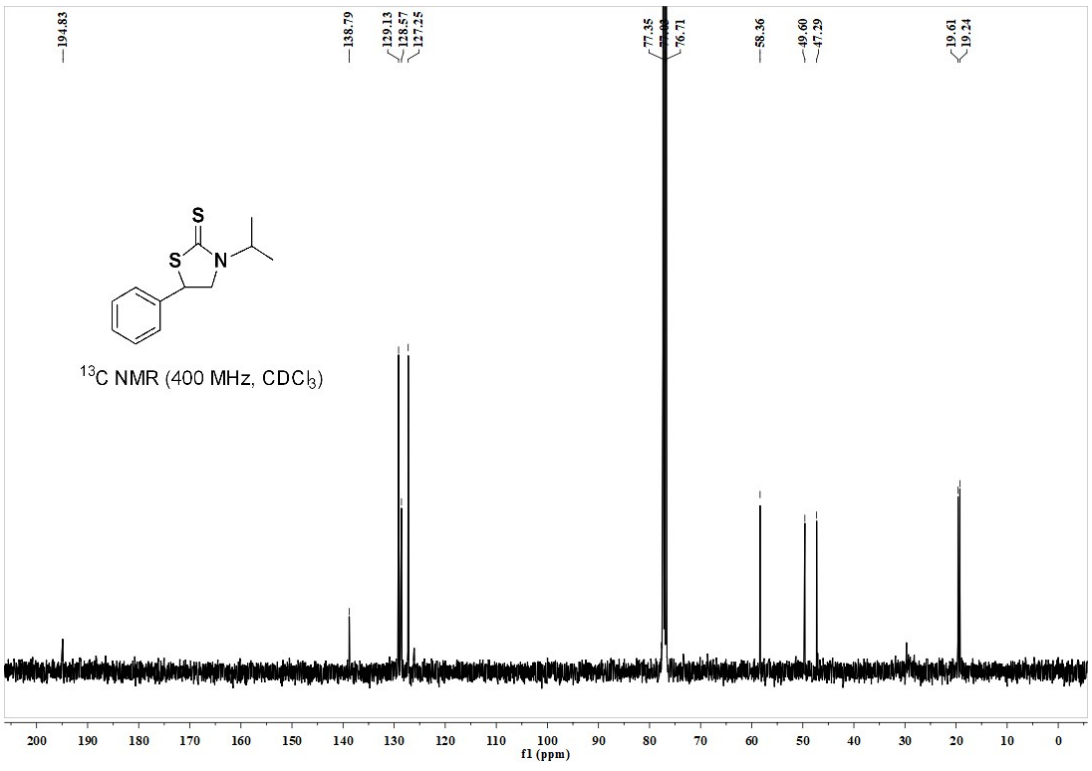
3-Hexyl-5-phenylthiazolidine-2-thione



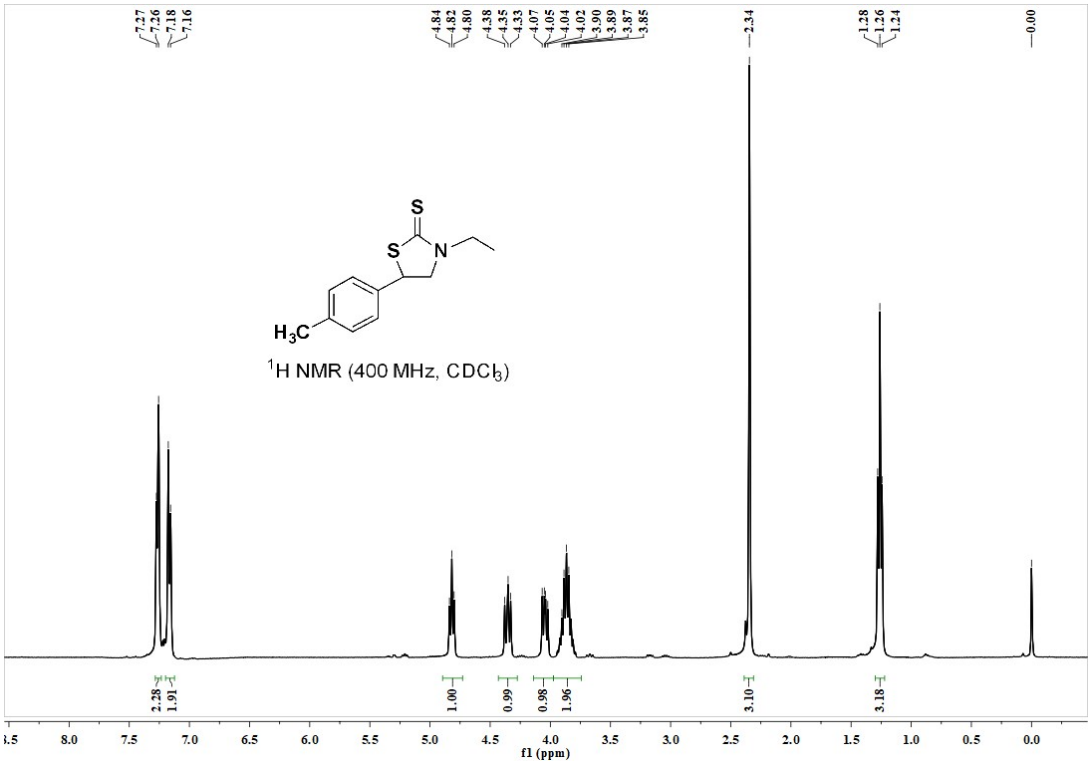


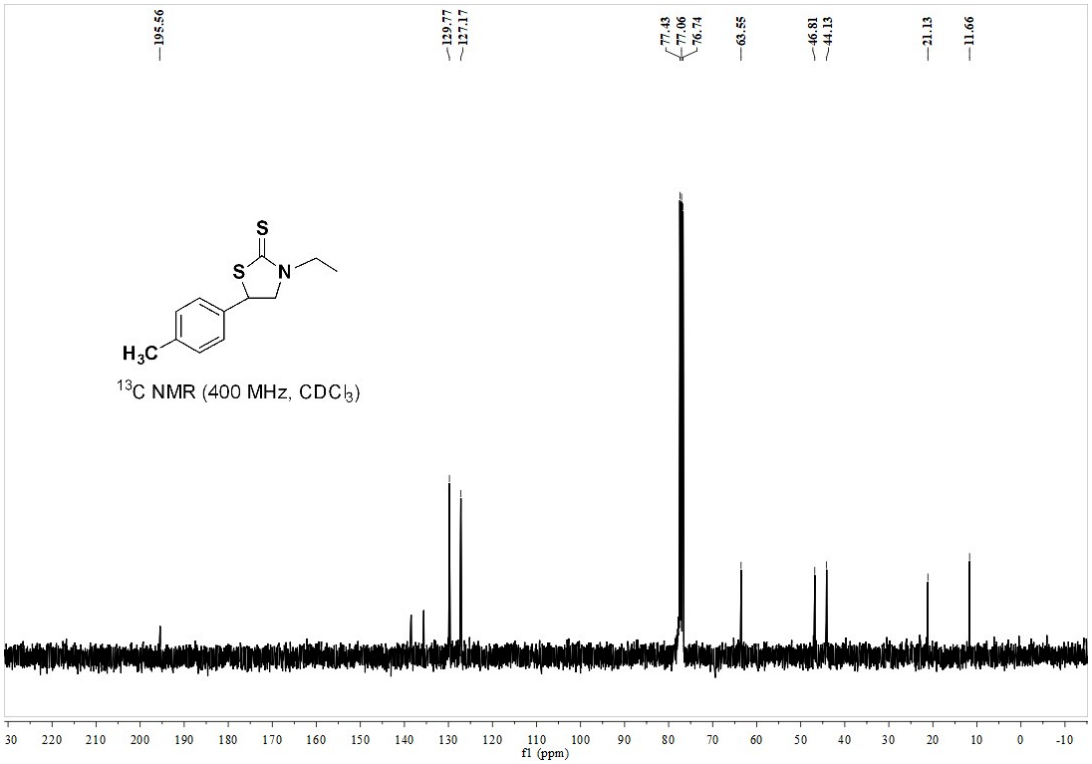
3-Isopropyl-5-phenylthiazolidine-2-thione



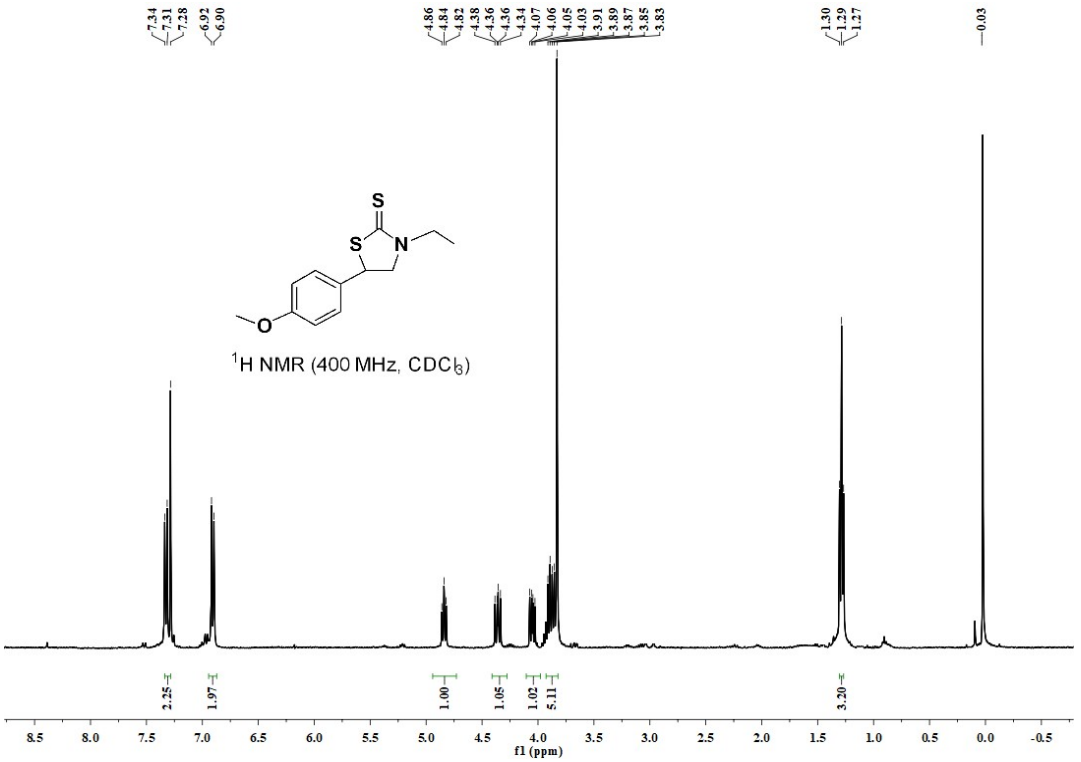


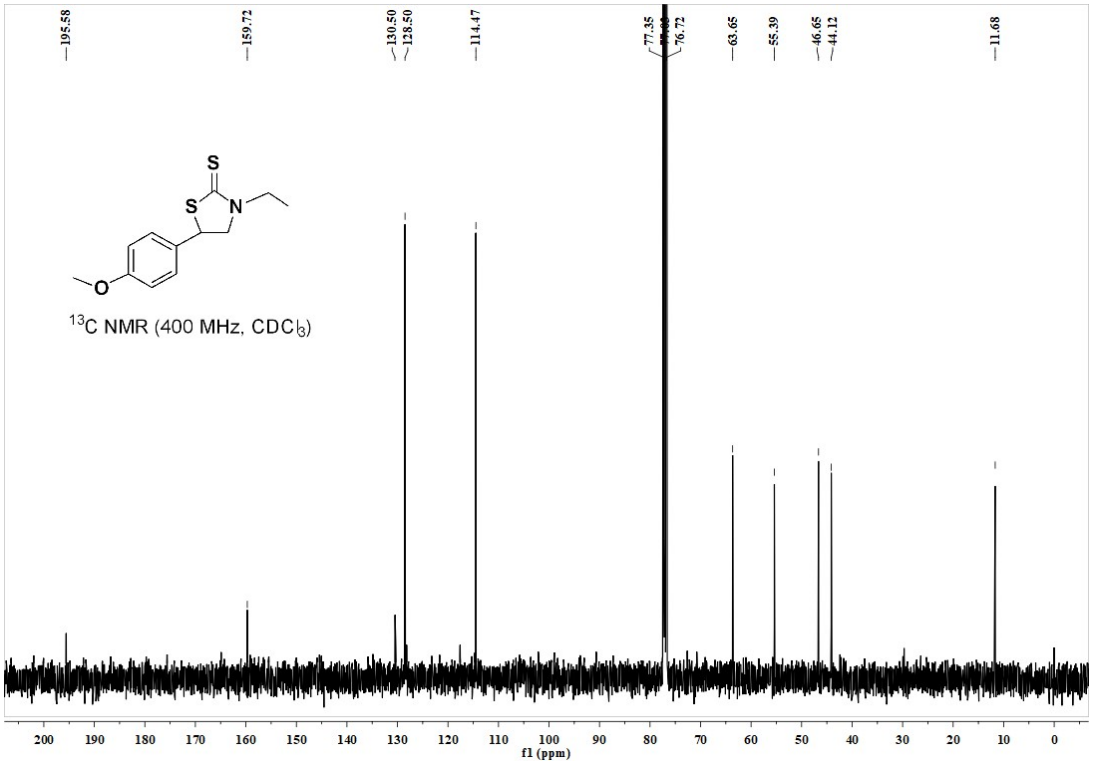
3-Ethyl-5-(*p*-tolyl)thiazolidine-2-thione



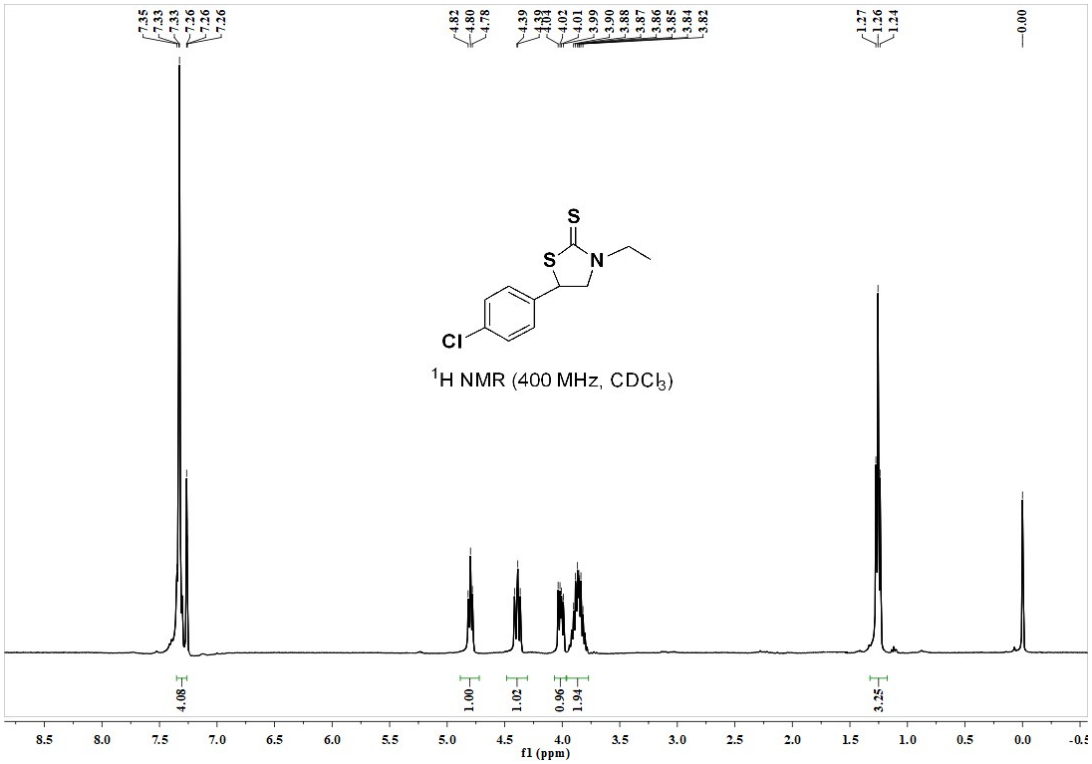


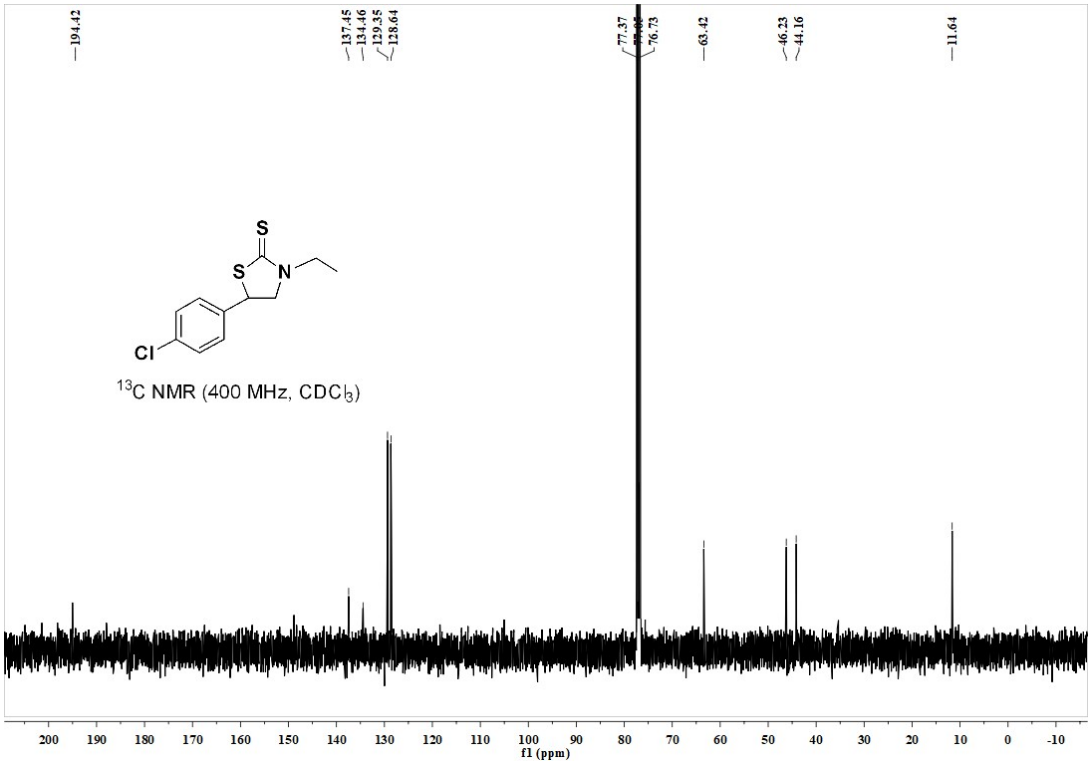
Ethyl-5-(4-methoxyphenyl)thiazolidine-2-thione



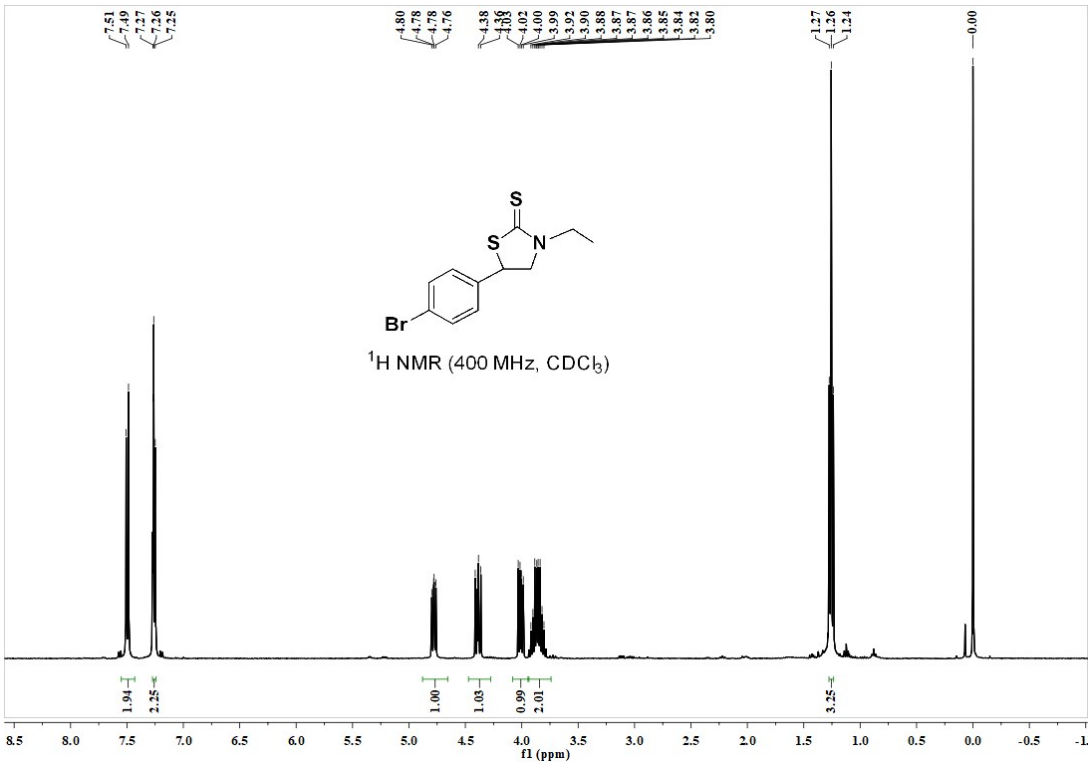


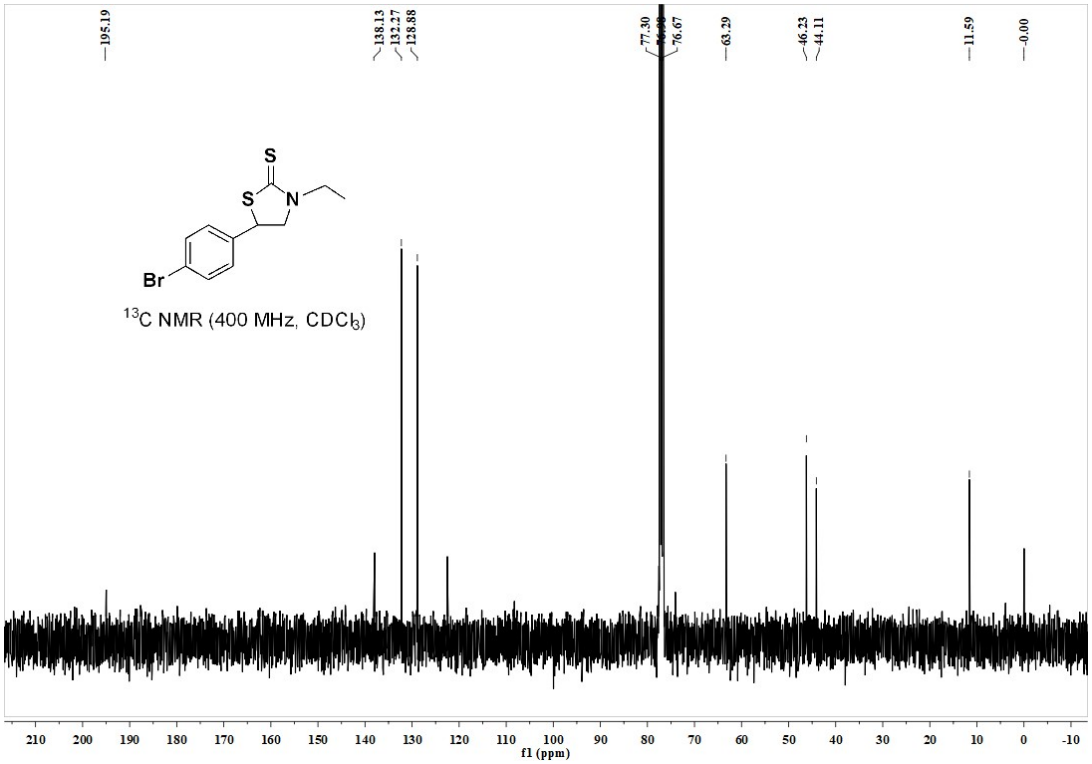
Ethyl-5-(4-chlorophenyl)thiazolidine-2-thione





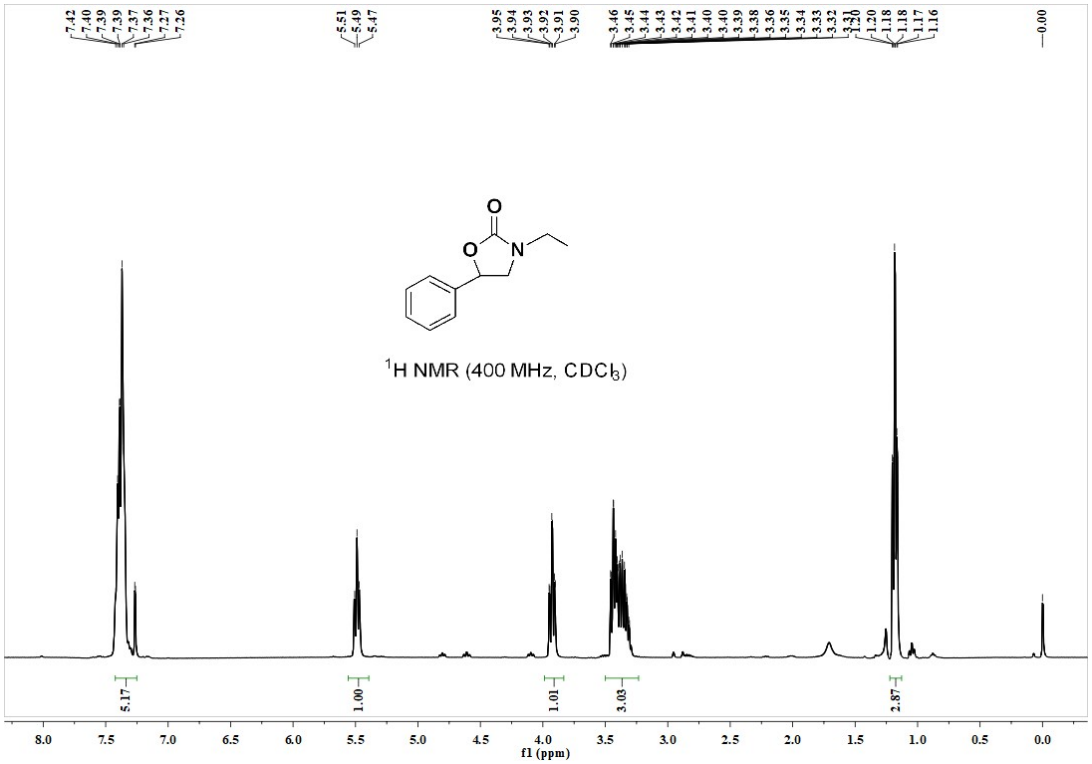
Ethyl-5-(4-Bromophenyl)thiazolidine-2-thione

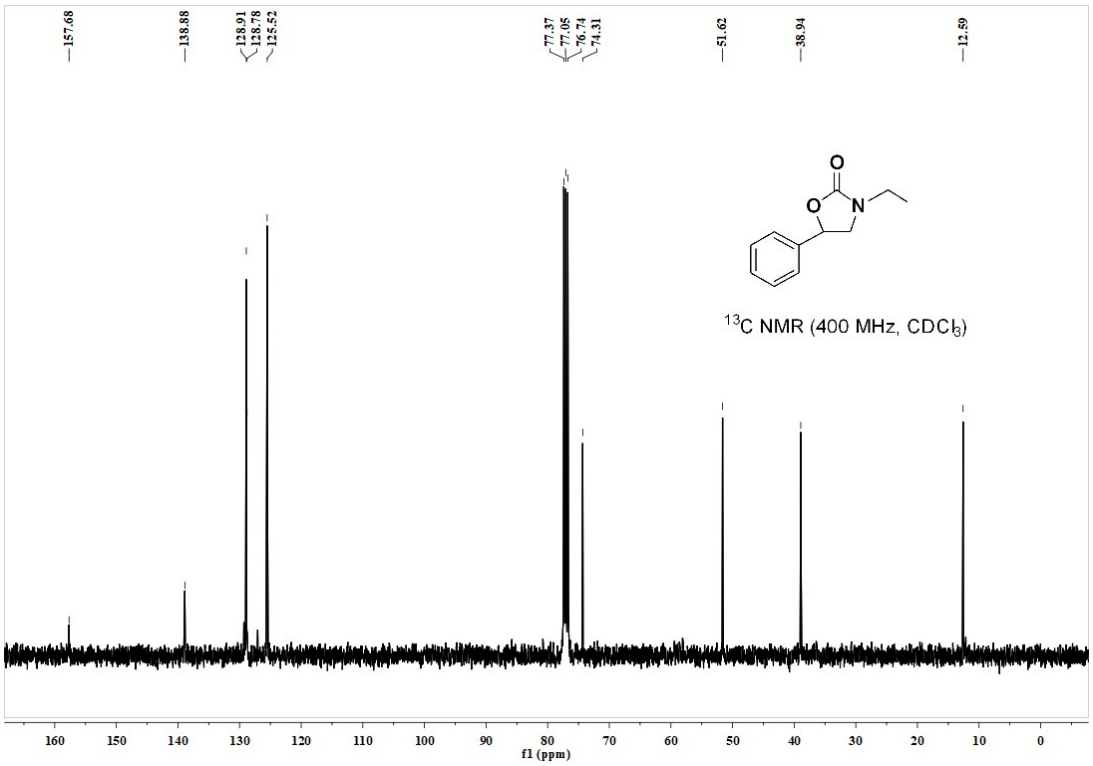




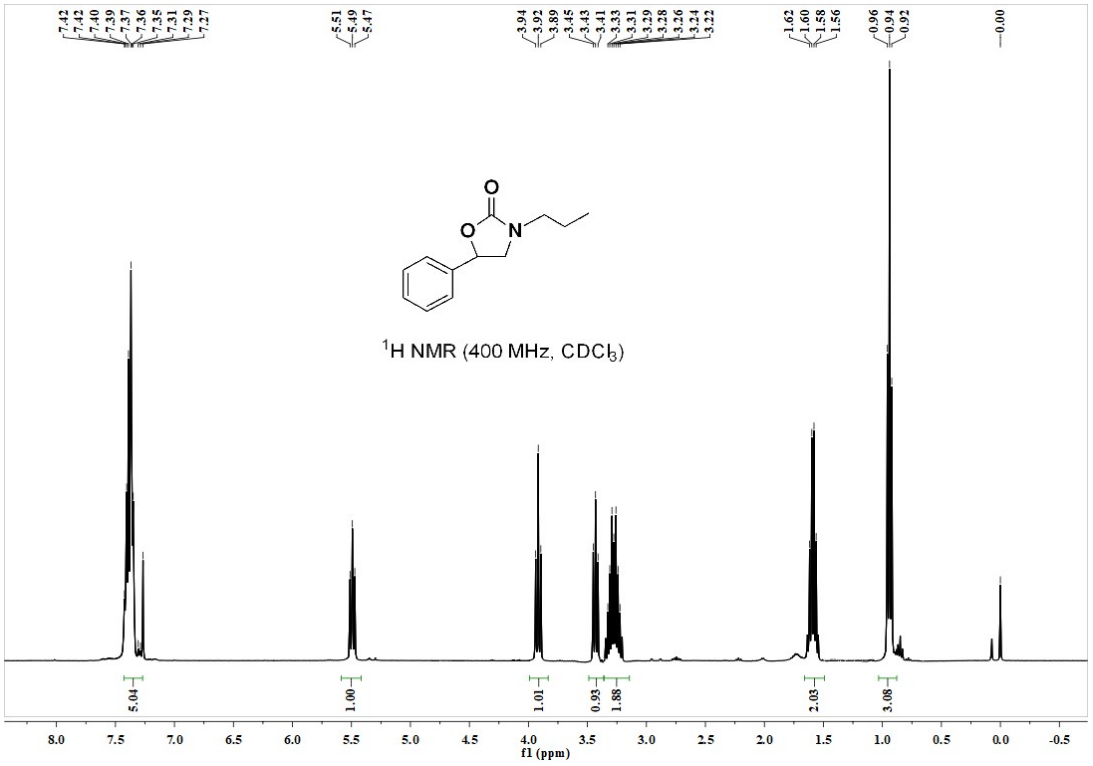
The ^{1}H NMR and ^{13}C NMR spectral for oxazolidinones.

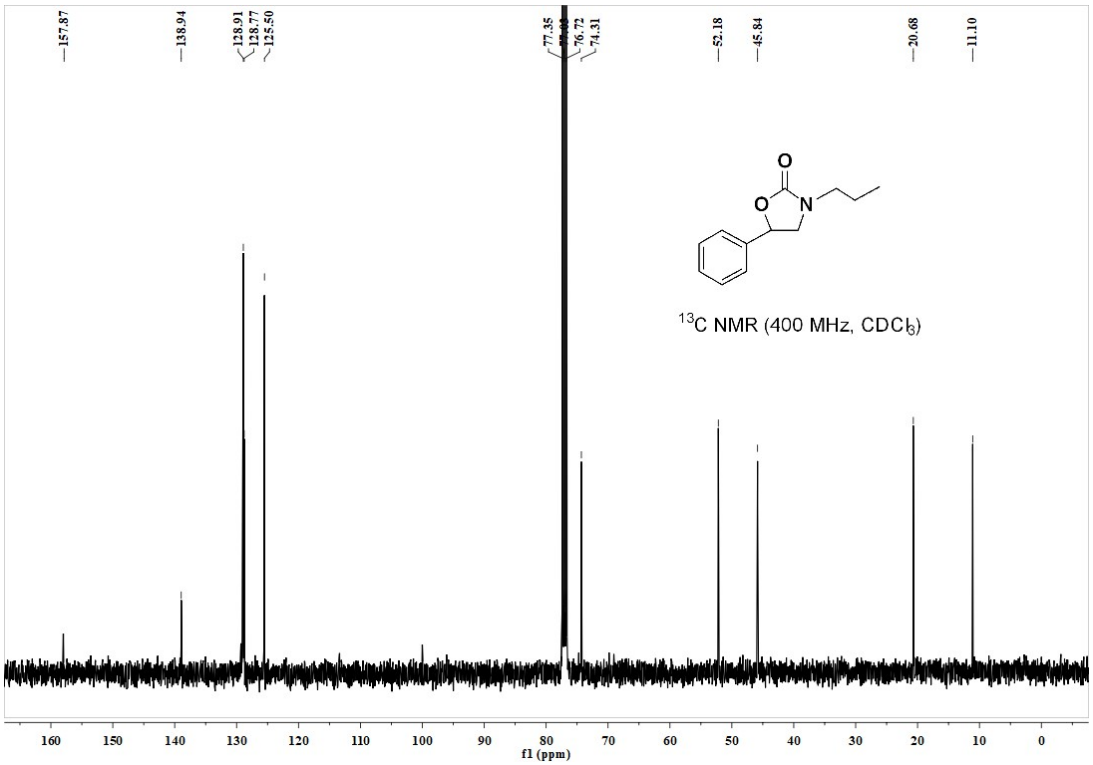
3-Ethyl-5-phenyloxazolidin-2-one



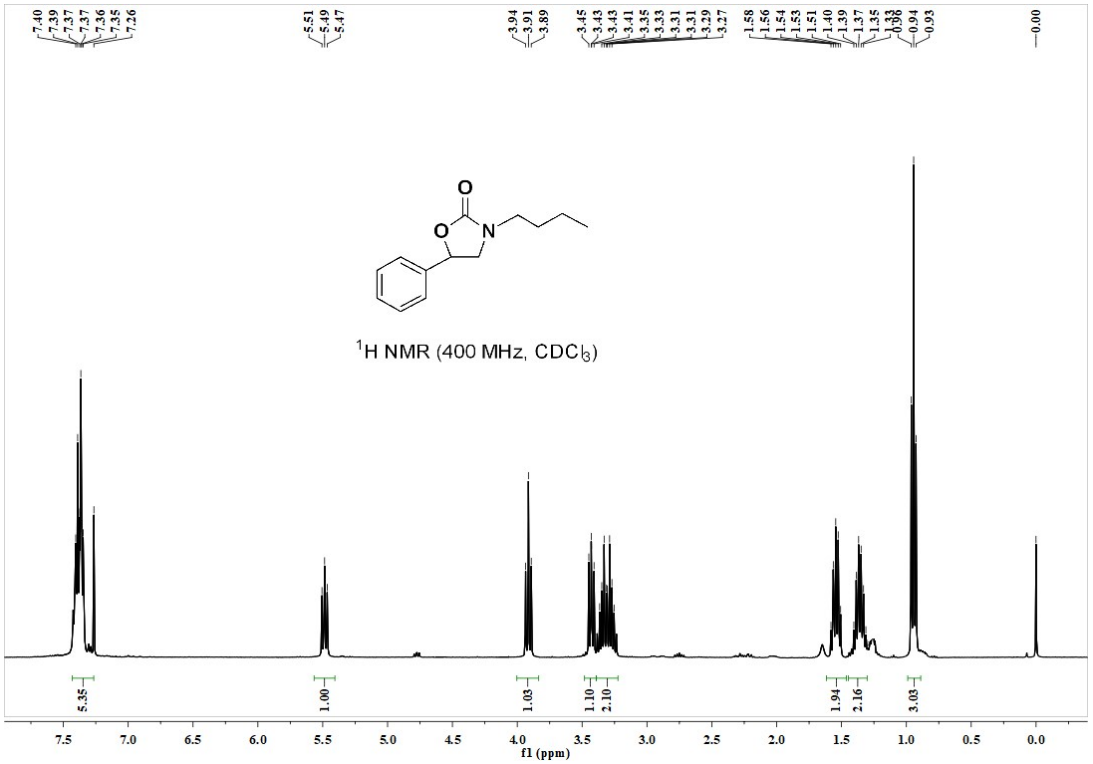


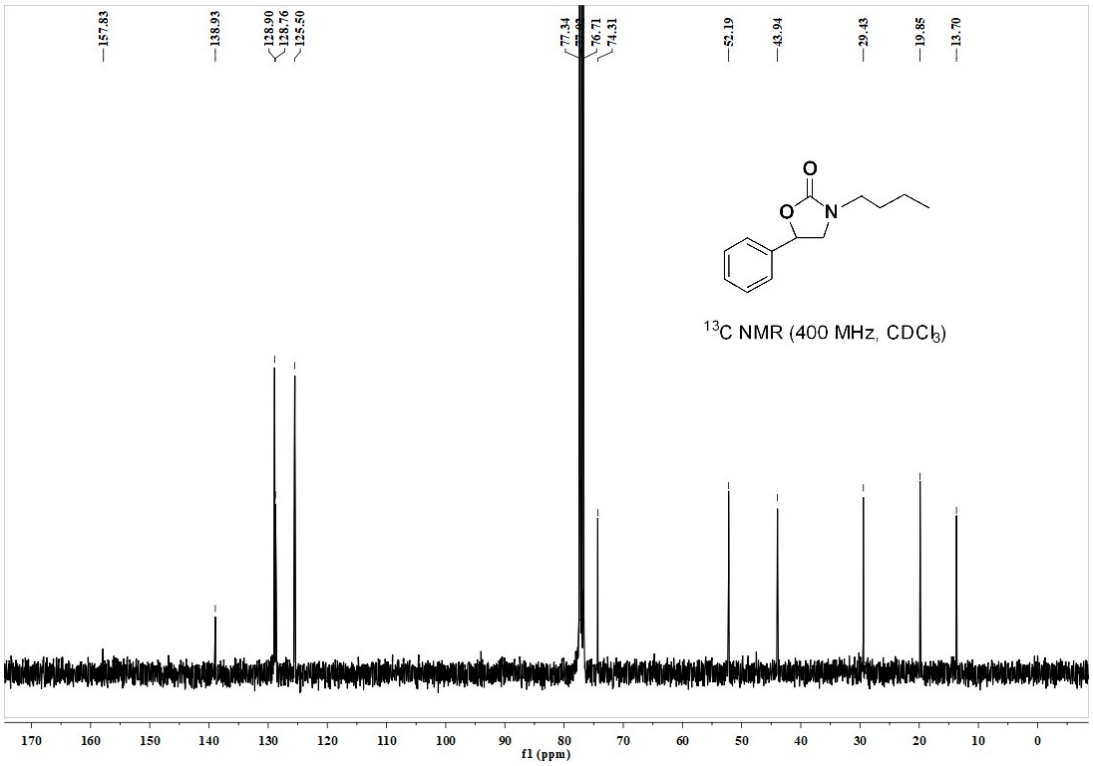
3-Phenyl-5-propyloxazolidin-2-one



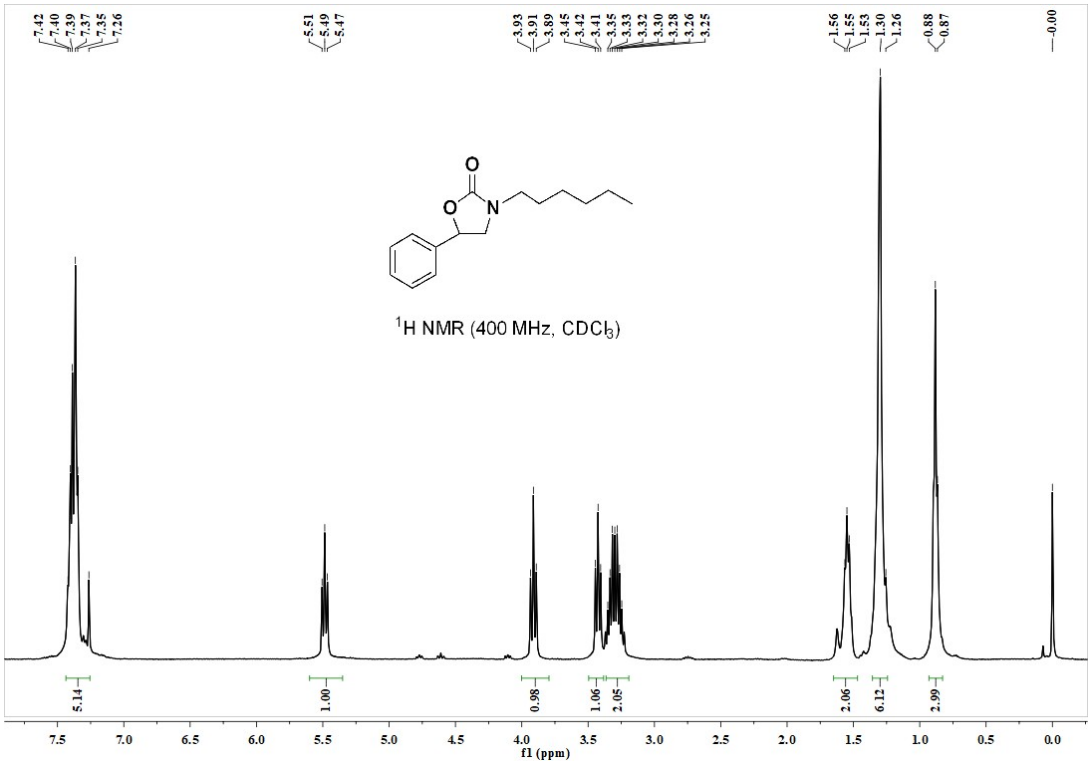


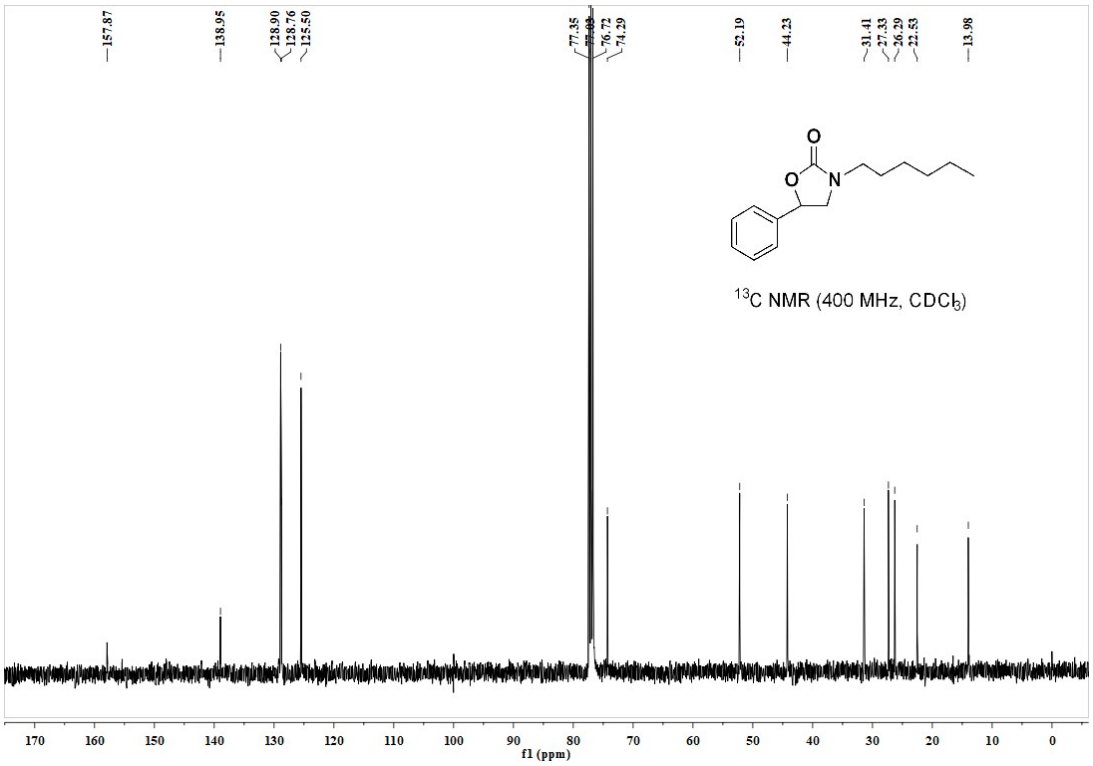
3-Butyl-5-phenyloxazolidin-2-one



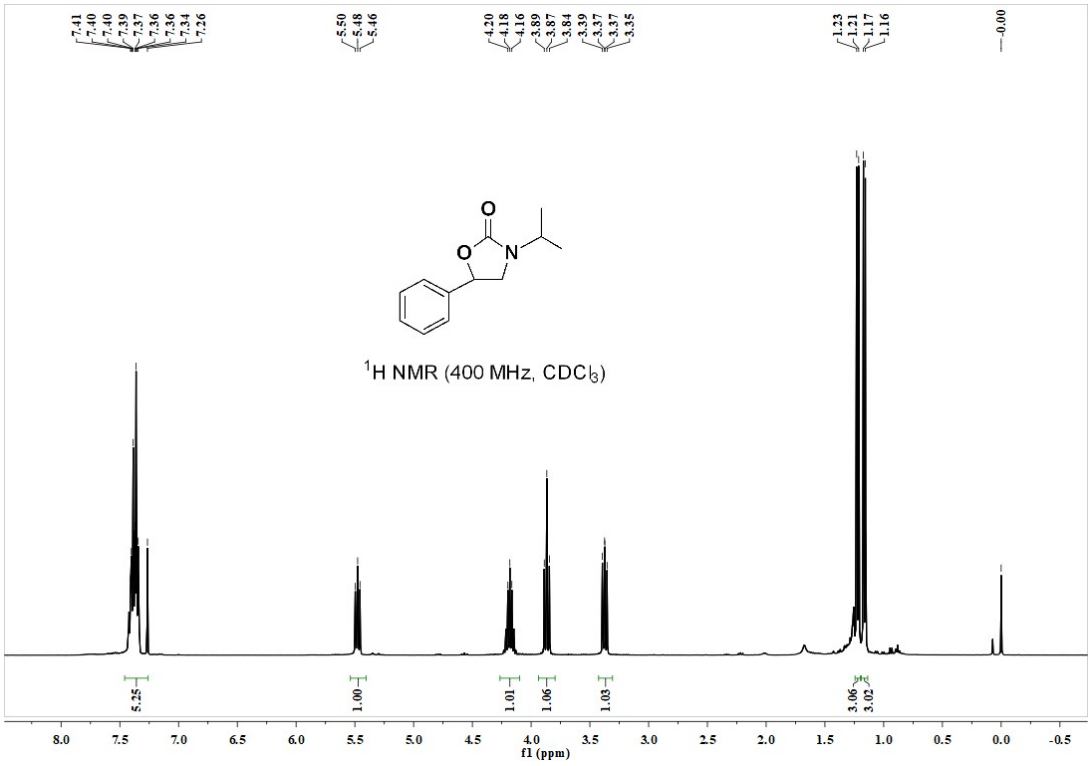


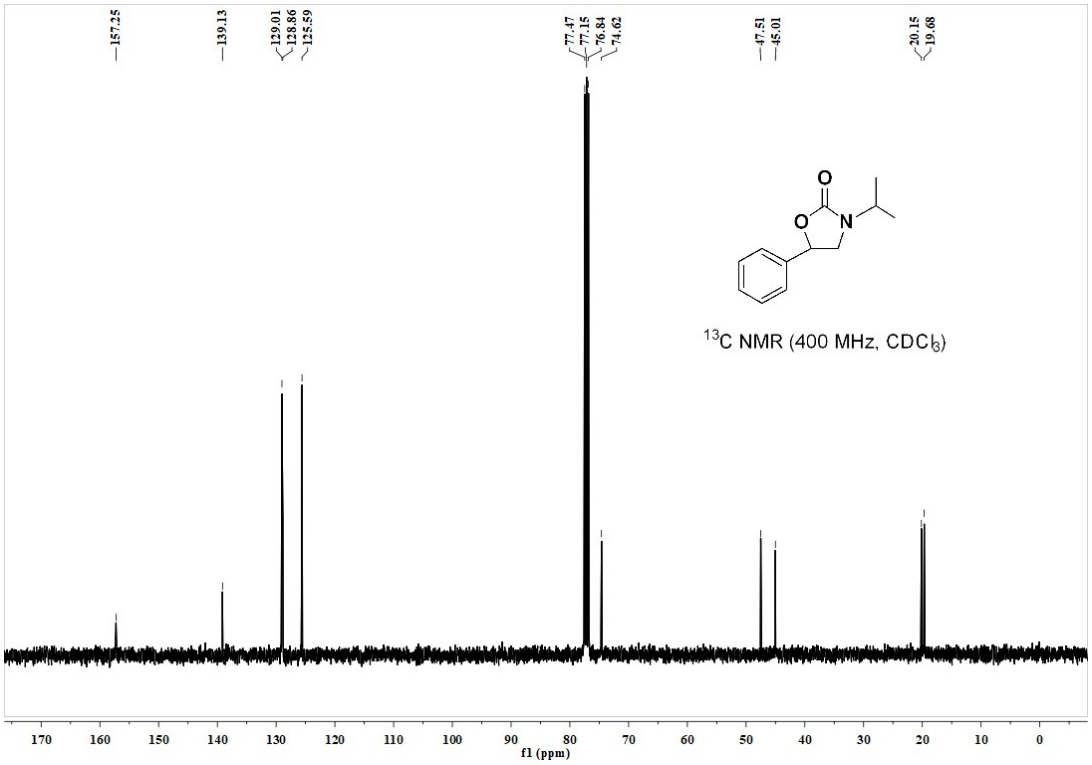
3-Hexyl-5-phenyloxazolidin-2-one


7.42
7.40
7.39
7.37
7.35
7.26
5.51
5.49
5.47
3.93
3.91
3.89
3.45
3.42
3.41
3.35
3.33
3.32
3.30
3.28
3.26
3.25
1.56
1.55
1.53
1.30
1.26
0.88
0.87
0.00
O
O
N
^{1}H NMR (400 MHz, CDCl$_3$)
5.14
1.00
0.98
1.06
2.05
2.06
6.12
2.99
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)

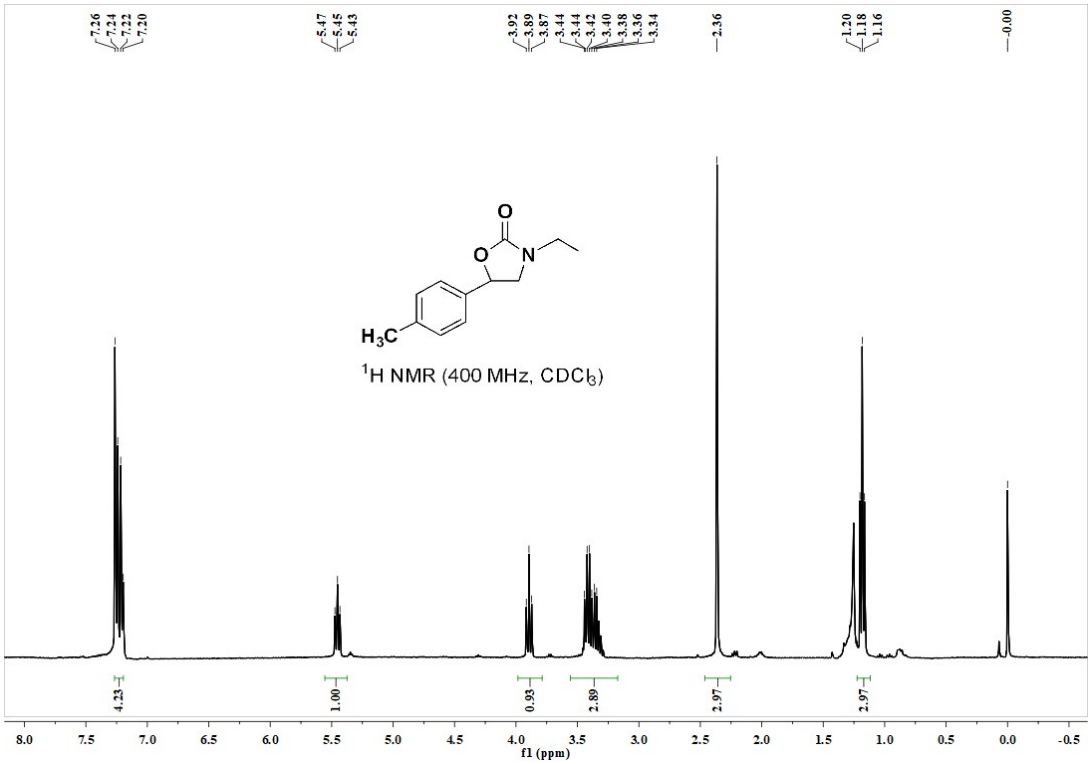

157.87
138.95
128.90
128.76
125.50
77.35
77.00
76.72
74.29
52.19
44.23
31.41
27.33
26.29
22.53
13.98
O
O
N
^{13}C NMR (400 MHz, CDCl$_3$)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

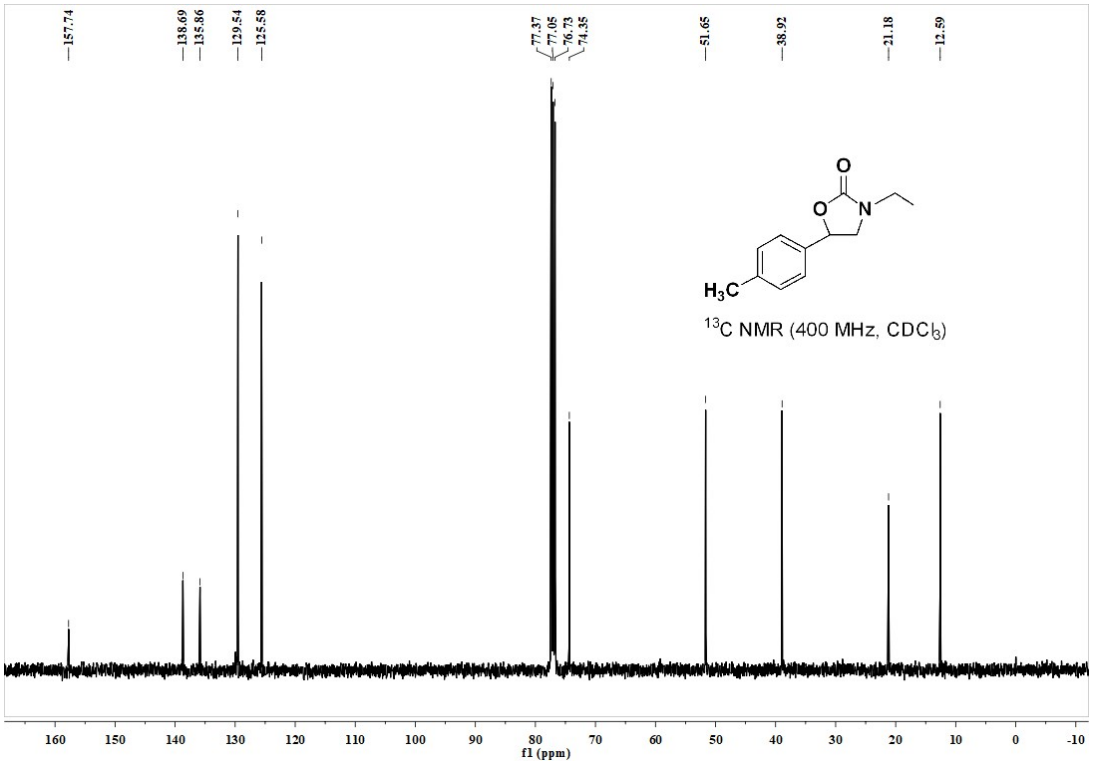
3-Isopropyl-5-phenyloxazolidin-2-one



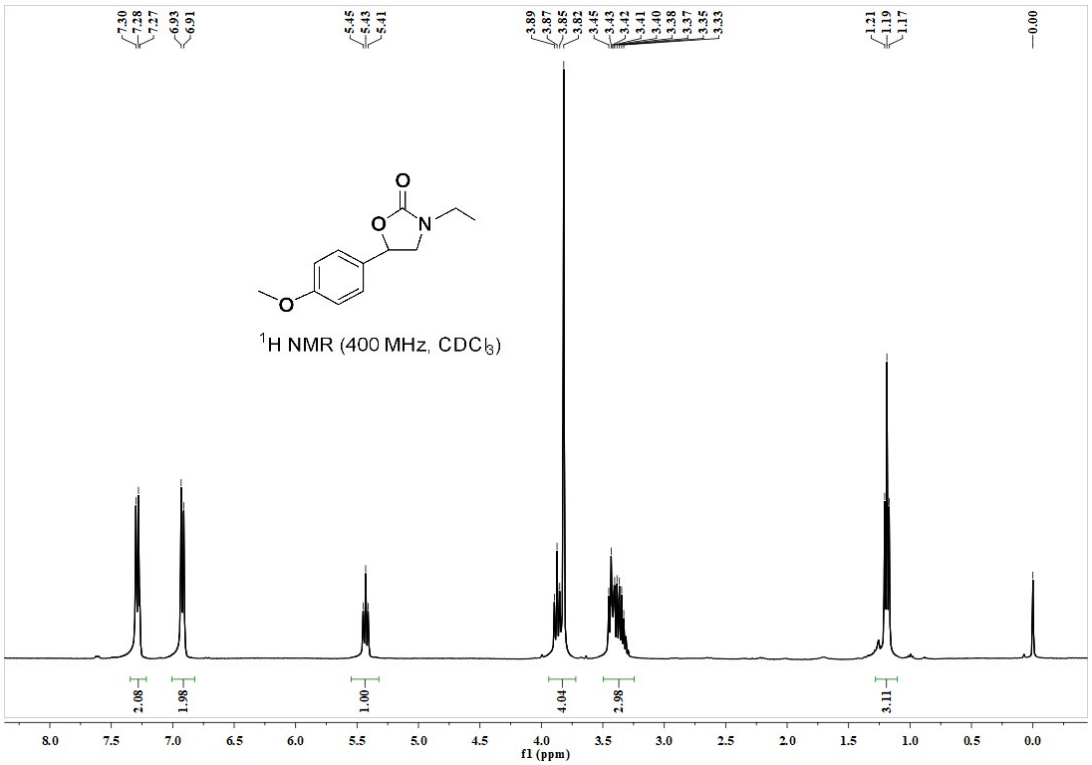


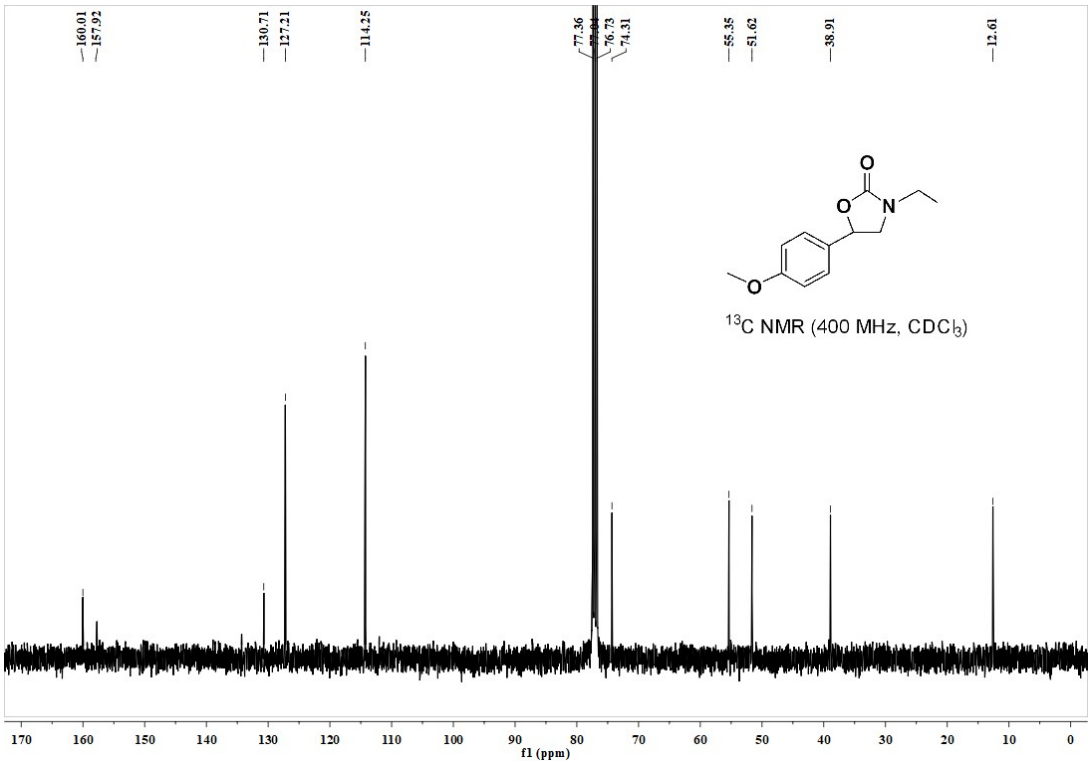
Ethyl-5-*p*-tolyloxazolidin-2-one



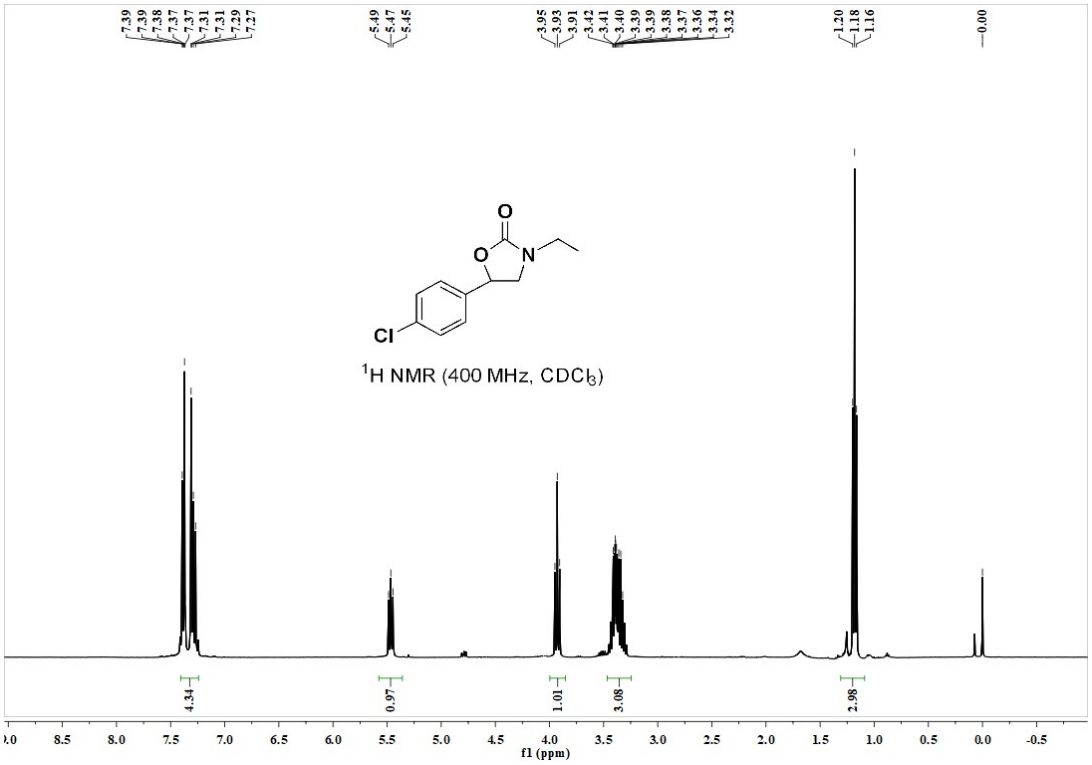


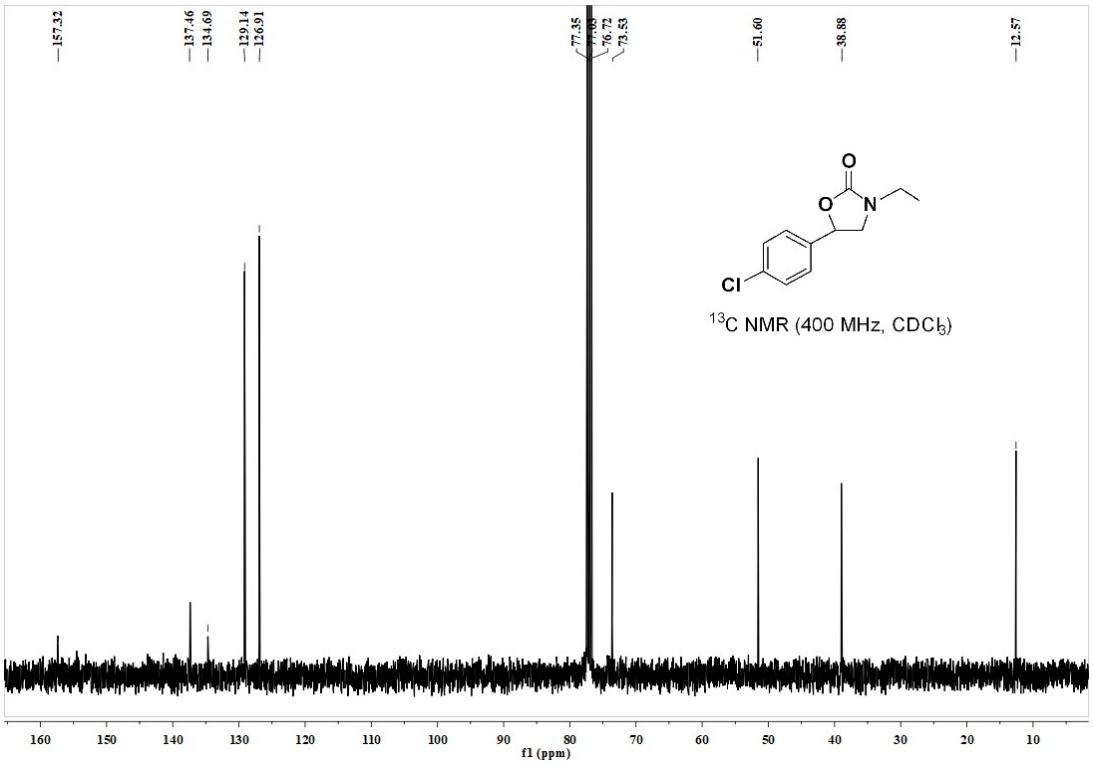
Ethyl-5-(4-methoxyphenyl)oxazolidin-2-one



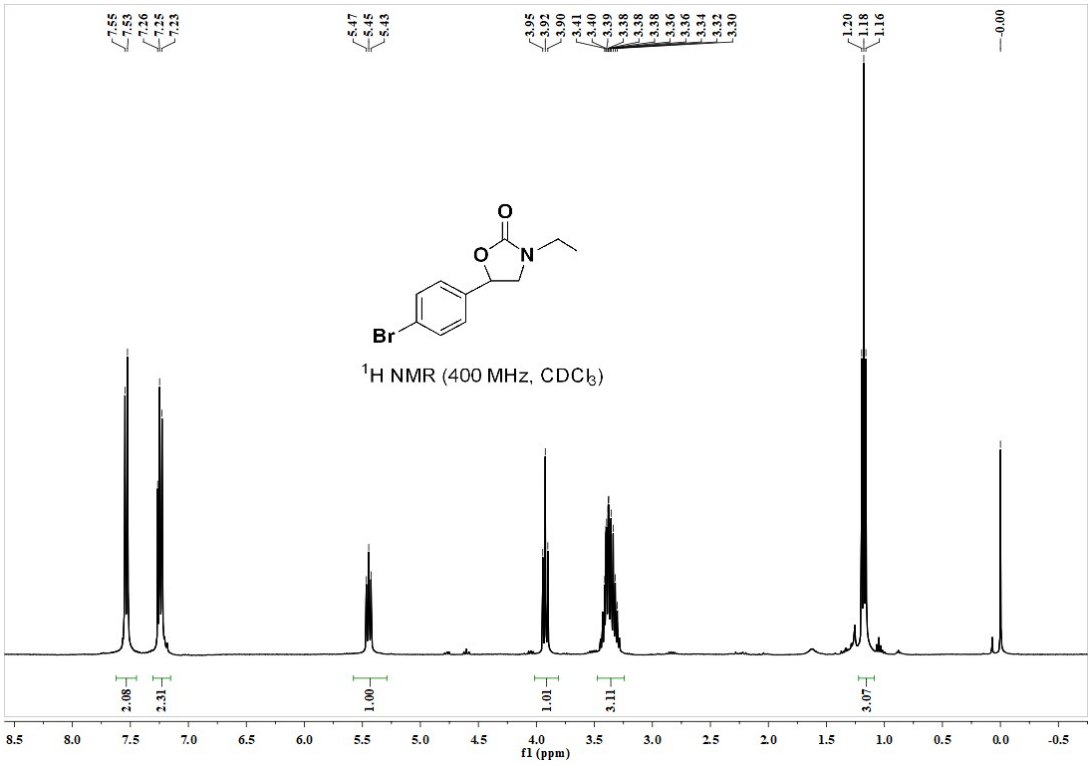


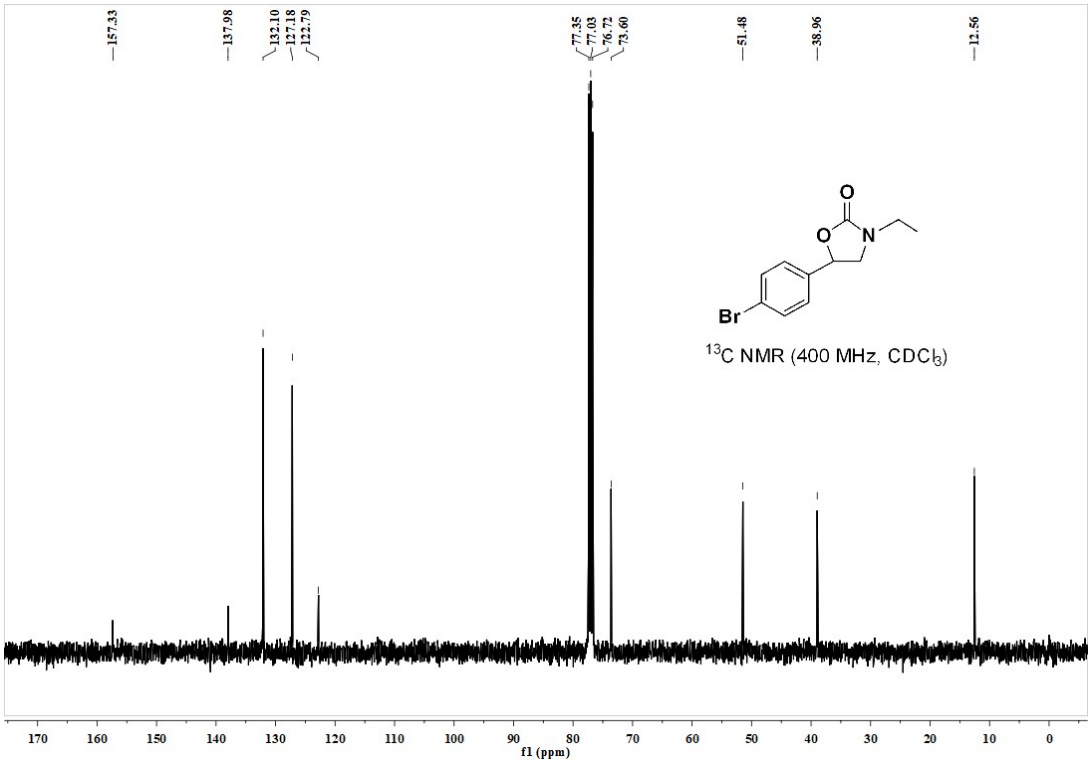
Ethyl-5-(4-chlorophenyl)oxazolidin-2-one





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





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