Supporting Information for

Access to 1,3-Oxazine-2,4-diones/1,3-thiazine-2,4-diones via Organocatalytic CO_2/COS Incorporation into Allenamides

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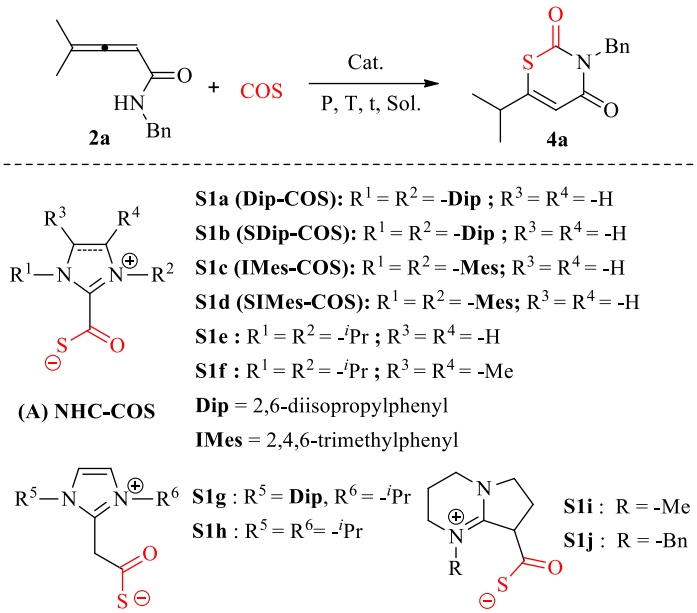
Table of Contents

1. General Procedure:

All manipulations of oxygen- and/or moisture-sensitive materials were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques. NHC-COS adducts, NHO-COS adducts and THPE-COS adducts were prepared according to the reported procedures.[S1-S3] Solvents were dried by standard methods and distilled under argon. ^{1}H, and ^{13}C NMR spectra were recorded on Varian Inova 500, Varian Inova 400 and Bruker 500 spectrometers.

2. Optimization of 4a formation catalyzed by LB-COS adducts

Table S1. Optimization of the reaction conditions[a]



Entry	Catalyst (5 mol %)	Solvent (0.5 mL)	P (MPa)	T (°C)	t (h)	Yield (%)[a)]
1	**S1a**	DMSO	1.0	60	4	14
2	**S1b**	DMSO	1.0	60	4	9
3	**S1c**	DMSO	1.0	60	4	4
4	**S1d**	DMSO	1.0	60	4	1
5	**S1e**	DMSO	1.0	60	4	19
6	**S1f**	DMSO	1.0	60	4	5
7	**S1g**	DMSO	1.0	60	4	21
8	**S1h**	DMSO	1.0	60	4	5

9	**S1i**	DMSO	1.0	60	4	21
10	**S1j**	DMSO	1.0	60	4	45
11	**S1j**	DMSO	1.0	60	12	81
12	**S1j**	DMSO	0.1	60	12	44
13	**S1j**	DMSO	1.0	25	4	0
14	**S1j**	DMF	1.0	60	4	43
15	**S1j**	DCM	1.0	60	4	0
16	**S1j**	CH_3CN	1.0	60	4	70
17	**S1j**	CH_3CN	1.0	60	6	76
18	**S1j**	CH_3CN	1.0	60	12	96
19	-	DMSO	1.0	60	4	0

[a] Reaction conditions: substrate **2a** (0.5 mmol), catalyst (5.0 mmol%). [b] Yields were determined by ^{1}H-NMR analysis.

We initially explored the annulation of COS with *N*-benzyl 4-methyl-2,3-pentadienamide (**2a**) as the model substrate using Lewis Base-COS adducts under 1.0 MPa COS. After considerable experimentation, we found that both NHC-COS adducts and NHO-COS adducts showed lower reactivity than THPE-COS adducts and especially **S1j** (5 mol%) as the catalyst in DMSO under 1 MPa COS at 60 °C for 4 h provided the best results, giving rise to 1,3-thiazine-2,4-dione (**4a**) in 45% yield (Table S1, entries 1-10). As expected, when a Lewis base-COS adduct was not added, no product was obtained (Table S1, entry 19). Some other typical results under different conditions are summarized in Table 1. Based on these results, we also examined the effect of pressure and found that the yield of the target product decreased significantly when the pressure of COS decreased (Table S1, entry 12). Then, the effect of temperature was investigated and found no product formation at 25 ^{o}C (Table S1, entry 13). Other solvents such as DMF, DCM, CH_3CN were also tested; CH_3CN were the most efficient than others (Table S1, entries 14-16). An enhancement in yield was observed when the reaction time prolonged to 12 h (Table S1, entry 18), which was defined to be our standard reaction conditions for further study.

3. Crystallography

Single crystals of complexes **4h** suitable for X-ray structural analysis were obtained from acetone solution at room temperature. Diffraction data were collected at 220 K on a Bruker SMART-CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods[S4] and refined by full-matrix least squares on F2. All nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL[S5] crystallographic software packages. CCDC: 1859584 (**4h**) contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

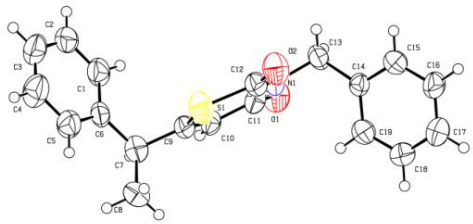


Figure S1. ORTEP Single Crystal X-Ray Diffraction of **4h**

Table S2. Crystal data and structure refinement for **4h**

Bond precision: C-C = 0.0071 A Wavelength=0.71073

Cell: a=5.5128(6) b=14.1945(18) c=20.649(3)
alpha=90 beta=90 gamma=90
Temperature: 296 K

	Calculated	Reported
Volume	1615.8(4)	1615.8(3)
Space group	P 21 21 21	P2(1)2(1)2(
Hall group	P 2ac 2ab	?
Moiety formula	C19 H17 N O2 S	?
Sum formula	C19 H17 N O2 S	C19 H17 N O2 S
Mr	323.40	323.40
Dx,g cm-3	1.329	1.329
Z	4	4
Mu (mm-1)	0.209	0.209
F000	680.0	680.0
F000'	680.77	
h,k,lmax	7,18,26	7,18,26
Nref	3723[2171]	3680
Tmin,Tmax	0.970,0.979	0.600,0.746
Tmin'	0.967	

Correction method= # Reported T Limits: Tmin=0.600 Tmax=0.746
AbsCorr = MULTI SCAN

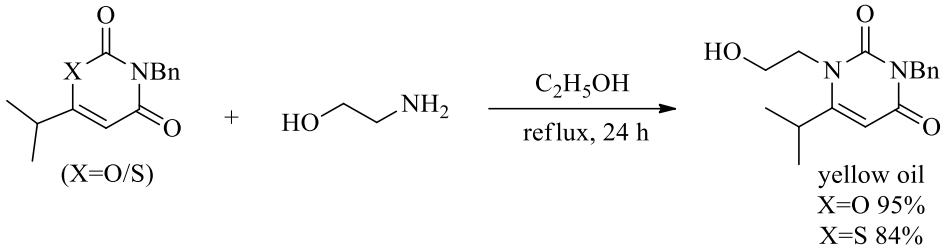
Data completeness= 1.70/0.99 Theta(max)= 27.520

R(reflections)= 0.0643(1611) wR2(reflections)= 0.1734(3680)

S = 0.964 Npar= 208

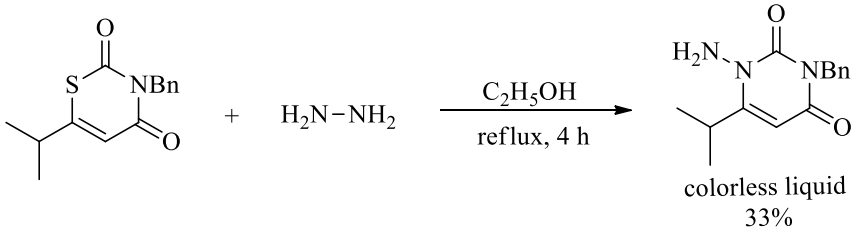
4. Experimental procedure for synthesis of 1, 3-oxazine-2, 4-dione (3a) and 1, 3-thiazine-2, 4-dione (4a) derivatives

3-benzyl-1-(2-hydroxyethyl)-6-isopropylpyrimidine-2, 4-dione (5)



The obtained product **3a** (252 mg, 1.03 mmol) and ethanol (4.0 mL) were sequentially added to a 10 mL round bottom flask, followed by dropwise addition of ethanolamine (160 mg, 2.62 mmol) to the reaction mixture. The mixture was refluxed for 24 h. The solvents were evaporated under vacuum and the residue was purified by column chromatography (silica gel, dichloromethane/methanol = 20:1) to afford the desired product (R_f = 0.40) as yellow liquid (0.28 g, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 6.7 Hz, 2H), 7.27 (dt, *J* = 12.1, 6.9 Hz, 3H), 5.66 (s, 1H), 5.07 (s, 2H), 4.03 (t, *J* = 5.3 Hz, 2H), 3.82 (dd, *J* = 10.1, 5.0 Hz, 2H), 3.28 – 2.85 (m, 2H), 1.19 (d, *J* = 6.8 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.9, 162.2, 152.9, 136.8, 129.1, 128.4, 127.6, 97.8, 60.9, 46.2, 44.5, 29.3, 21.8.**HRMS(ESI)**: calcd for $C_{16}H_{20}N_2O_3$: 289.1547 $[M+H]^+$. Found: 289.1546 $[M+H]^+$. **IR**: 3433, 2972, 2879, 1698, 1651, 1609, 1496, 1448, 1400, 1348, 1218, 1062, 827, 769, 727, 708, 613, 525 cm^{-1} (vs).

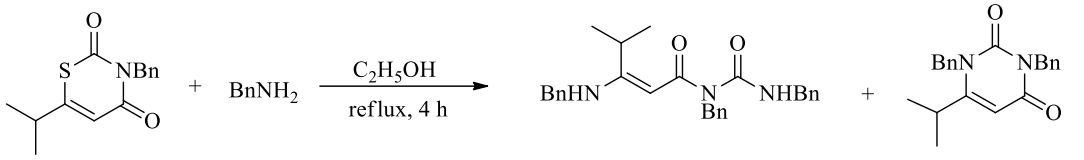
1-amino-3-benzyl-6-isopropylpyrimidine-2, 4-dione (6)



The obtained product **4a** (166 mg，0.64 mmol) and ethanol (2.0 mL) were sequentially added to a 10 mL round bottom flask, followed by dropwise addition of hydrazine (200 mg，6.24 mmol) to the reaction mixture. The mixture was refluxed for 4 h. The solvents were evaporated under vacuum and the residue was purified by

column chromatography (silica gel, dichloromethane/methanol = 40:1) to afford the desired product (R_f = 0.80) as colorless liquid (54 mg, 33%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 6.9 Hz, 2H), 7.36 – 7.22 (m, 3H), 5.60 (s, 1H), 5.11 (s, 2H), 4.35 (s, 2H), 3.46 – 3.26 (m, 1H), 1.20 (d, *J* = 6.8 Hz, 6H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.2, 162.4, 153.5, 136.9, 129.3, 128.5, 127.8, 96.6, 44.9, 29.0, 21.2.**HRMS(ESI)**: calcd for $C_{14}H_{17}N_3O_2$: 260.1394 $[M+H]^+$. Found: 260.1392 $[M+H]^+$. **IR**: 3326, 3217, 1703, 1662, 1495, 1440, 1399, 1346, 1237, 1196, 1180, 1132, 1076, 1041, 823, 756, 711, 698, 611, 522 cm^{-1} (vs).

***N*-benzyl-3-(benzylamino)-*N*-(benzylcarbamoyl)-4-methylpent-2-enamide (7a) and 1, 3-dibenzyl-6-isopropylpyrimidine-2, 4-dione (7b)**



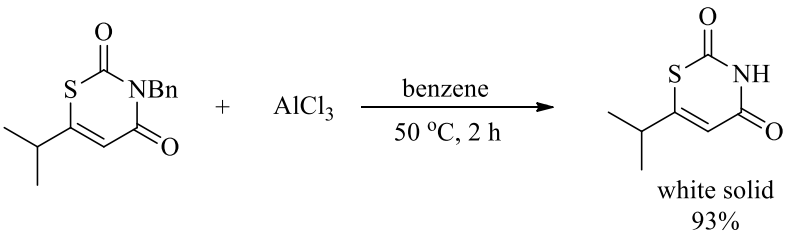
7a, colorless liquid 41%

7b, colorless liquid 58%

The obtained product **4a** (170 mg，0.65 mmol) and ethanol (4.0 mL) were sequentially added to a 10 mL round bottom flask, followed by dropwise addition of benzylamine (280 mg，2.60 mmol) to the reaction mixture. The mixture was refluxed for 22 h at 100 °C. The solvents were evaporated under vacuum and the residue was purified by column chromatography (silica gel, PE/EtOAc = 5:1) to afford the desired product **7a** (R_f = 0.60, 121 mg, 41%) and **7b** (R_f = 0.40, 391 mg, 58%) as colorless liquid. **7a. ^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.05 (s, 2H), 7.45 – 7.09 (m, 15H), 5.06 (s, 2H), 4.73 (s, 1H), 4.55 (d, *J* = 5.6 Hz, 2H), 4.38 (d, *J* = 6.3 Hz, 2H), 2.65 – 2.47 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6, 173.3, 157.0, 139.3, 139.1, 138.2, 128.8, 128.5, 128.5, 127.5, 127.5, 127.0, 126.7, 126.7, 126.3, 80.8, 47.8, 46.0, 44.5, 29.0, 21.4. **HRMS(ESI)**: calcd for $C_{28}H_{31}N_3O_2$: 442.2489 $[M+H]^+$. Found: 442.2500 $[M+H]^+$. **IR**: 3236, 3063, 3030, 2970, 2932, 2872, 1684, 1605, 1581, 1514, 1453, 1371, 1298, 1275, 1235, 1206, 1181, 1148, 1079, 1056, 1030, 934, 781, 733, 699 cm^{-1} (vs). **7b**. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.3 Hz, 2H), 7.43 – 7.23 (m, 6H), 7.12 (d, *J* = 7.4 Hz, 2H), 5.77 (s, 1H), 5.20 (s, 4H), 2.93 – 2.60 (m, 1H), 1.16 (d, *J* = 6.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.6, 161.7,

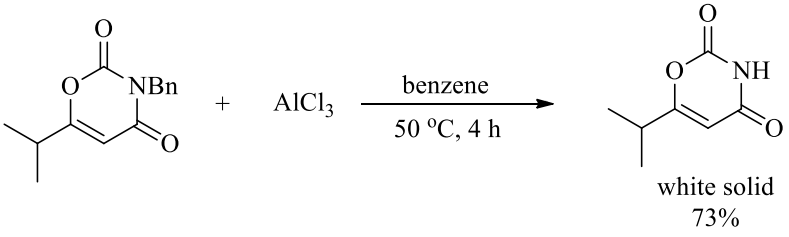
152.7, 137.0, 136.5, 129.0, 129.0, 128.4, 127.6, 127.5, 125.7, 98.3, 47.0, 44.6, 29. 5, 22.0. **HRMS(ESI)**: calcd for $C_{21}H_{22}N_2O_2$: 335.1754 $[M+H]^+$. Found: 335.1756 $[M+H]^+$. **IR**: 3088, 3063, 3032, 2972, 2877, 1703, 1656, 1614, 1496, 1442, 1395, 1351, 1218, 1182, 1074, 1026, 932, 826, 763, 730, 698, 606, 529 cm^{-1} (vs).

6-isopropyl-1, 3-thiazine-2, 4-dione (8)



In a glove box, a 25 mL Schlenk flask, equipped with a magnetic stir bar, is charged successively with **4a** (224 mg，0.86 mmol) and benzene (5.0 mL), followed by addition of aluminum chloride (1.1 g，8.25 mmol) to the reaction mixture with continuous stirring. The reaction mixture was heated to 50 °C for 2 hours. Water was added and the reaction mixture was extracted with DCM (3 × 20 mL). The collected organic layers were dried over anhydrous Na_2SO_4 and the solvents were evaporated under vacuum. Flash chromatography of the crude (silica gel, PE/EtOAc = 5:1) gave the pure product (R_f = 0.25) as a white solid (136 mg, 92%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.83 (s, 1H), 6.38 (s, 1H), 3.20 – 2.43 (hept, 1H), 1.28 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.3, 164.8, 163.8, 113.3, 113.0, 35.7, 21.8. **HRMS(ESI)**: calcd for $C_7H_9N_2O_2S$: 172.0427 $[M+H]^+$. Found: 172.0427 $[M+H]^+$. **IR**: 3150, 3051, 2971, 2934, 2852, 1766, 1691, 1595, 1463, 1442, 1367, 1290, 1260, 1225, 1129, 993, 967, 862, 749, 695, 643, 606, 574, 545, 485 cm^{-1} (vs).

6-isopropyl-1, 3-oxazine-2, 4 –dione (9)



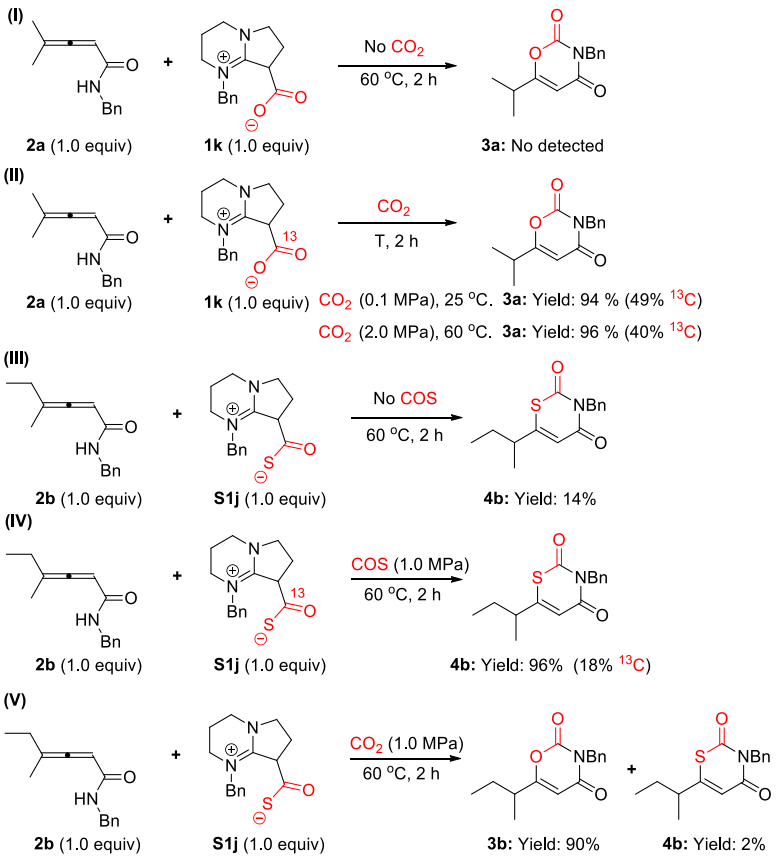
In a glove box, a 25 mL Schlenk flask, equipped with a magnetic stir bar, is charged successively with **3a** (224 mg，0.86 mmol) and benzene (5.0 mL), followed

by addition of aluminum chloride (1.1 g，8.25 mmol) to the reaction mixture with continuous stirring. The reaction mixture was heated to 50 °C for 4 hours. Water was added and the reaction mixture was extracted with DCM (3 × 20 mL). The collected organic layers were dried over anhydrous Na_2SO_4 and the solvents were evaporated under vacuum. Flash chromatography of the crude (silica gel, PE/EtOAc = 5:1) gave the pure product (R_f = 0.25) as a white solid (116 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.93 (s, 1H), 5.74 (s, 1H), 2.85 – 2.52 (m, 1H), 1.25 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.02, 162.25, 147.77, 98.31, 32.25, 19.30. **HRMS(ESI)**: calcd for $C_7H_{10}NO_3$: 154.0504 $[M-H]^-$. Found: 154.0508 $[M-H]^-$. **IR** $\nu_{C=O}$: 1727, 1650 cm^{-1} (vs).

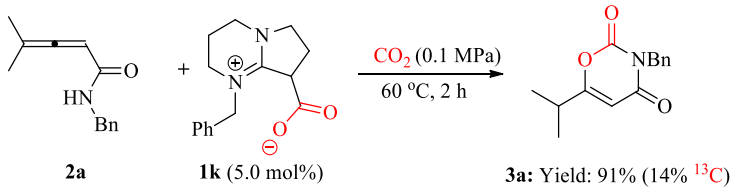
5. Mechanistic studies

5.1 Control Experiments

In order to clarify the detailed reaction mechanism, several control experiments were carried out (Scheme S1). Firstly, a stoichiometric reaction involving one equivalent of LB-CO_2 adduct **1k** and one equivalent of allenamide **2a** was carried out in the absence of CO_2 (Scheme S1, I). No desired product **3a** was generated, and allenamide **2a** was totally decomposed to unknown chemicals from the crude ^{1}H-NMR. Under ambient conditions (25 °C, and 0.1 MPa CO_2), the use of ^{13}C labelled **1k** and equivalent **2a** resulted in the formation of **3a** with 49% ^{13}C label determined by HRMS spectra (Scheme S1, II; Figure S3). When increasing the reaction temperature to 60 °C and CO_2 pressure to 2.0 MPa, **3a** with 40% ^{13}C label could also be detected (Scheme S1, II; Figure S4). For COS system, a stoichiometric reaction could carry out in the absence of COS, and the desired thiazine-2, 4-dione **4b** was obtained in 14% yield (Scheme S1, III). When introducing free COS (1.0 MPa) into isotope labeling experiment, **4b** with only 18% ^{13}C label was obtained (Scheme S1, IV; Figure S6), which preferentially comes from free COS rather than COS moiety in THPE-COS adducts. When introducing free CO_2 (1.0 MPa) into stoichiometric reaction involving one equivalent of LB-COS adduct **S1j** and one equivalent of allenamide **2b**, **4b** was obtained in 2% yield and **3b** was obtained in 90% yield (Scheme S1, V).



Scheme S1. Preliminary mechanistic studies



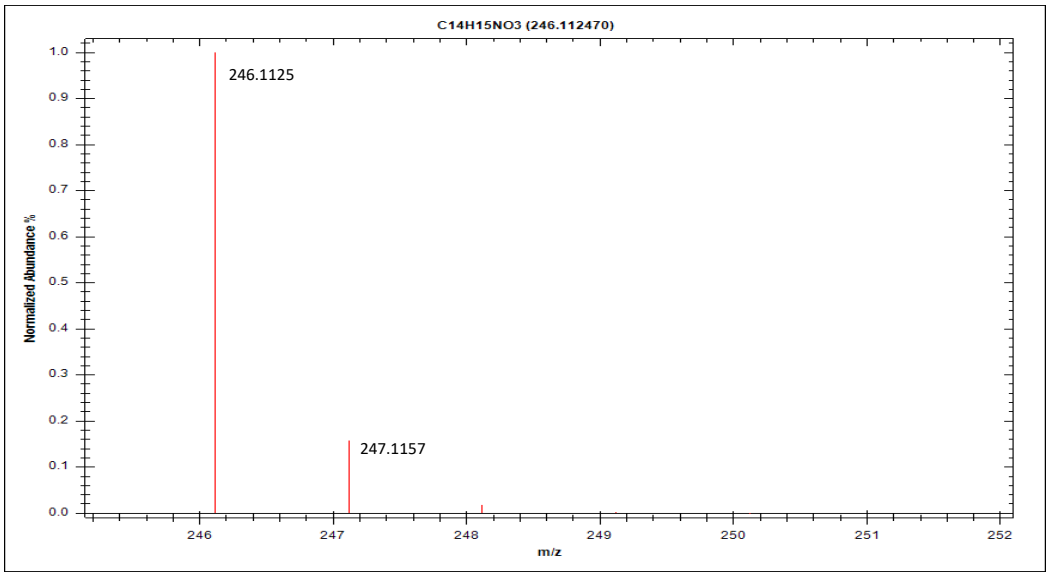
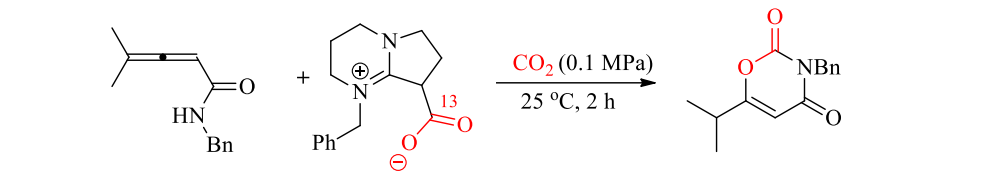


Figure S2. Enlarged HRMS Spectra of Product **3a**



2a (1.0 equiv) **1k** (1.0 equiv) **3a:** Yield: 94% (^{13}C labeled **3a**: 49%)

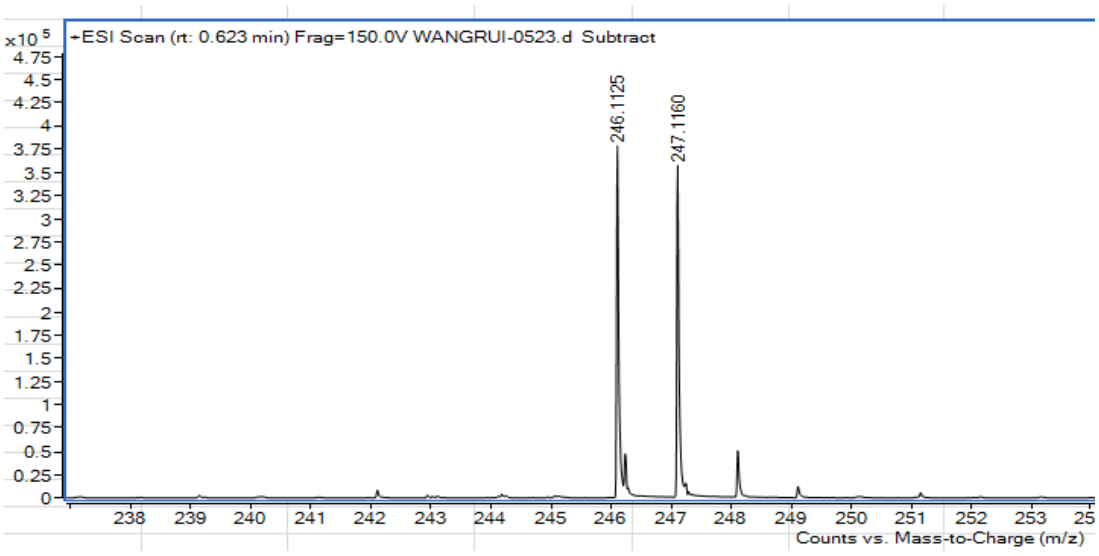
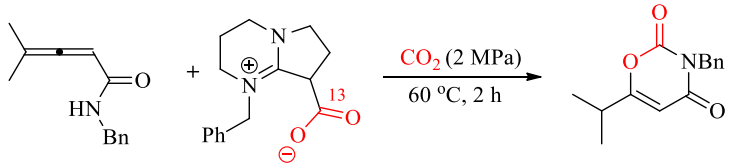


Figure S3. Enlarged HRMS Spectra of Scheme 3 **(II)**



2a (1.0 equiv) **1k** (1.0 equiv) **3a:** Yield: 96% (^{13}C labeled **3a**: 40%)

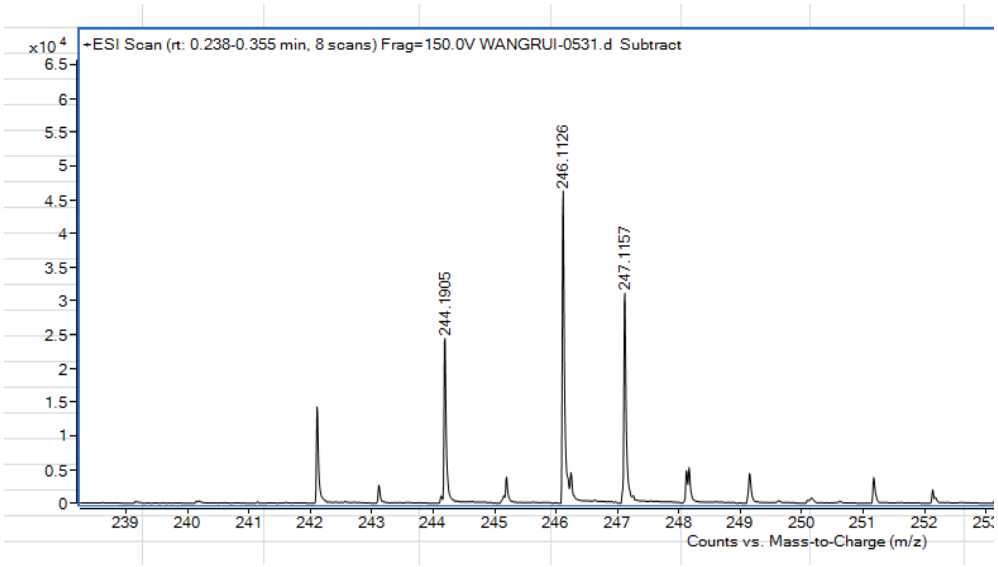
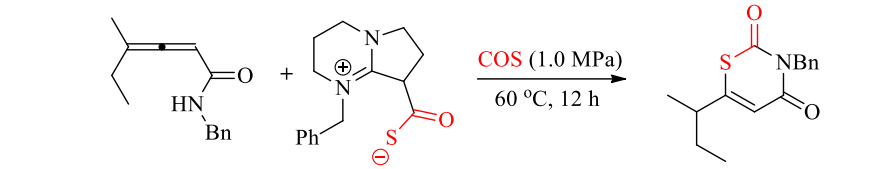


Figure S4. Enlarged HRMS Spectra of Scheme 3 **(II)**



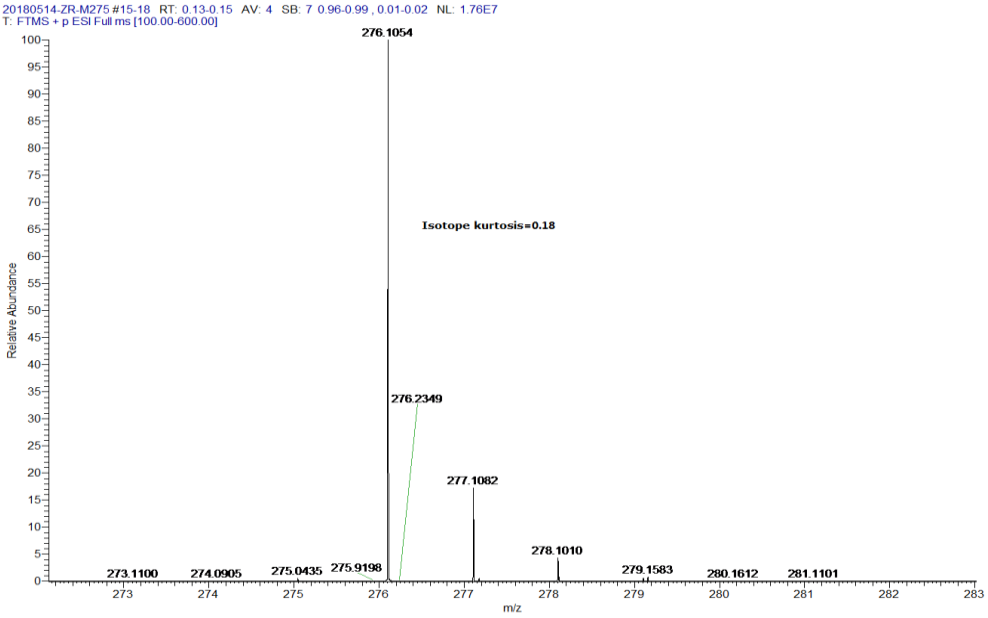
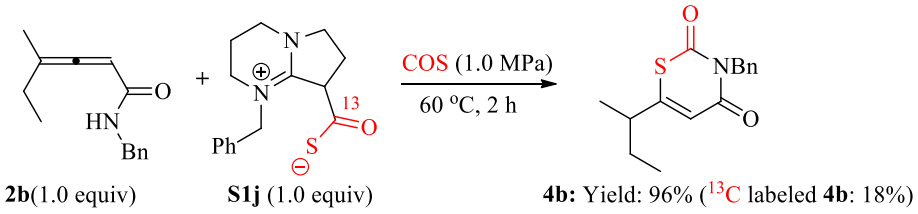


Figure S5. Enlarged HRMS Spectra of Product **4b**



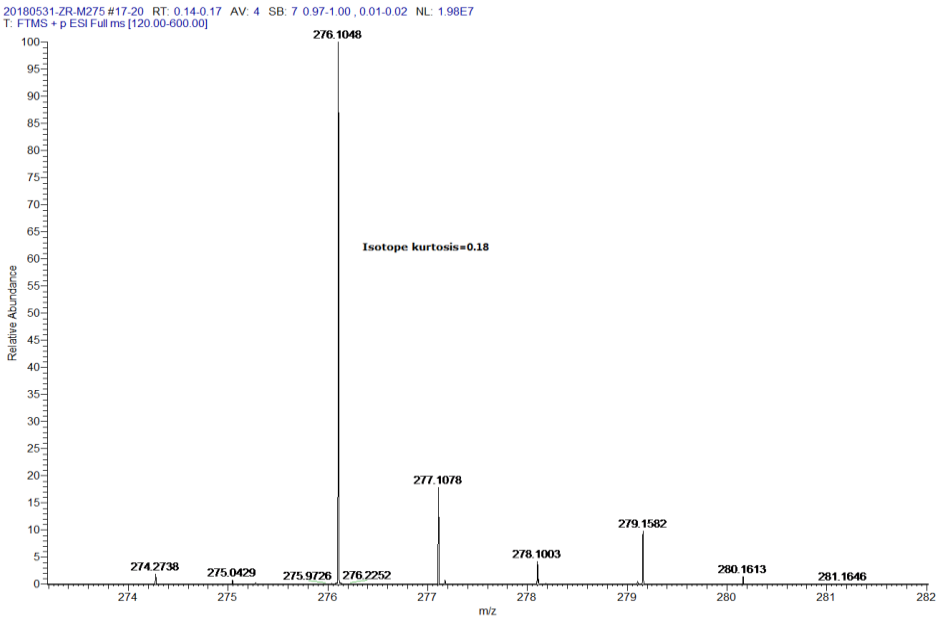


Figure S6. Enlarged HRMS Spectra of Scheme 3 **(IV)**

5.2 Exchange Experiments

In order to further understand the reaction mechanism, we further systematically investigated the exchange reaction of THPE-^{13}COX adducts with free COX by means of HRMS. First, in the glove box, a 10 mL Schlenk flask equipped with a magnetic stir bar was charged with THPE-$^{13}CO_2$ adduct (0.5 mmol) and DMSO (0.5 mL), successively. The flask was then evacuated and filled with CO_2 with a balloon and the reaction was stirred at 25 ^{o}C for 2 hours. We found that there was an exchange phenomenon between THPE-$^{13}CO_2$ adduct and free CO_2 in the absence of the substrate (Figure S8). This exchange process also occurs when the reaction temperature rises to 60 ^{o}C (Figure S9). In addition, we also found that the exchange process proceeded very quickly, and a large amount of THPE-CO_2 was detected within five minutes of reaction (Figure S10). Furthermore, the exchange process between THPE-CO_2 and free $^{13}CO_2$ can also proceed smoothly under reaction conditions, which indicates that exchange behavior is reversible (Figure S12). Moreover, we investigated the exchange process between THPE-^{13}COS and free COS in the absence of the substrate in the same way. Unlike the exchange of THPE-CO_2 adduct and free CO_2, THPE-^{13}COS is very stable in the presence COS atmosphere at room temperature (Figure S14). However, most of THPE-^{13}COS were transformed to THPE-COS under high temperature (Figure S15) and high pressure (Figure S16).

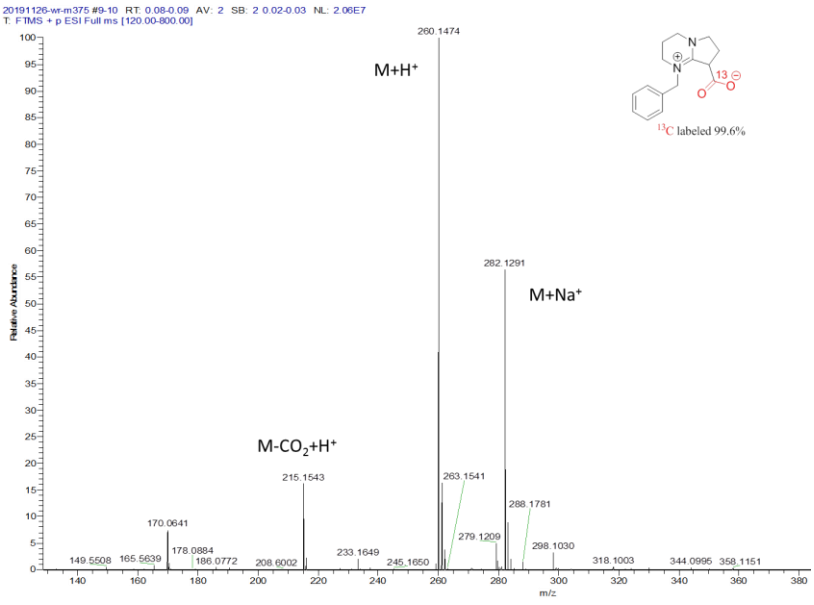


Figure S7. Enlarged HRMS Spectra of THPE-$^{13}CO_2$

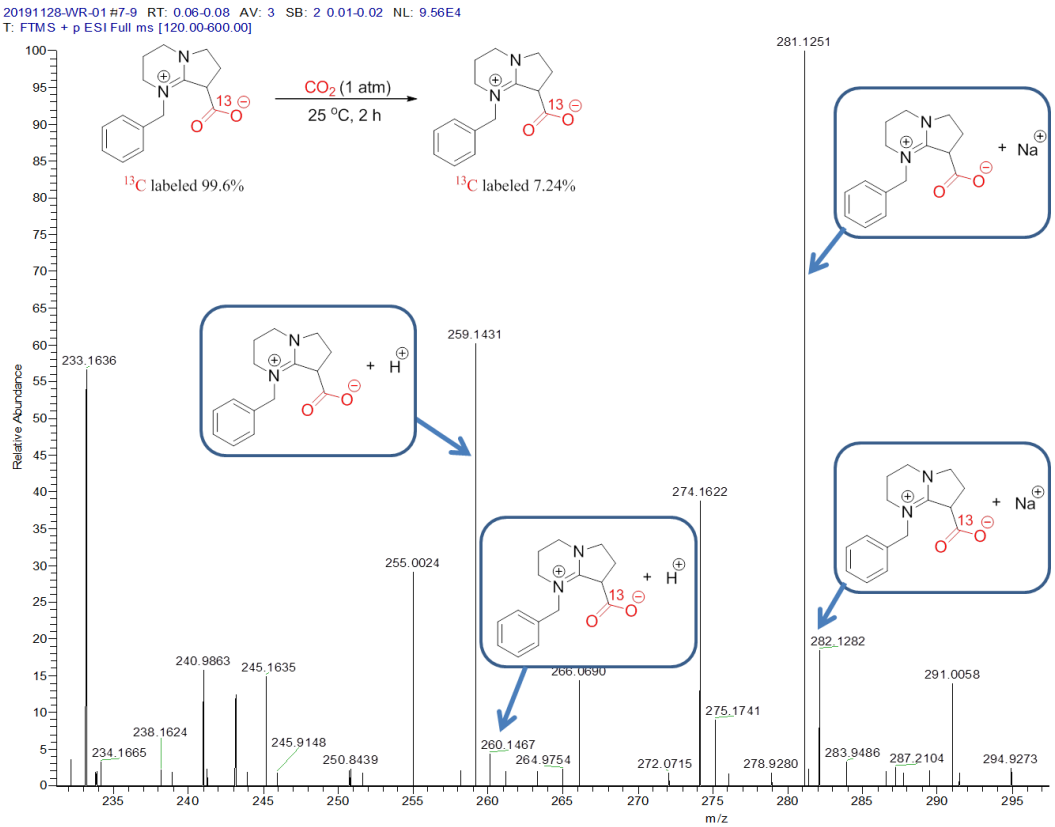


Figure S8. HRMS Spectra of the exchange process between THPE-$^{13}CO_2$ and free CO_2 at 25 °C for 2 hours

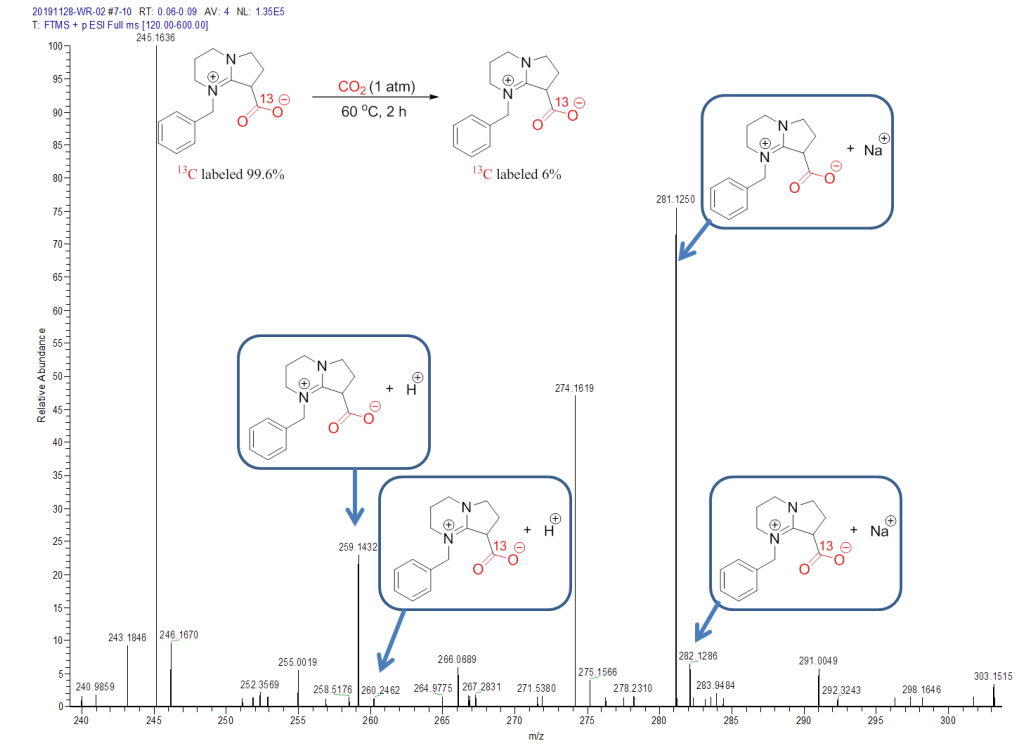


Figure S9. HRMS Spectra of the exchange process between THPE-$^{13}CO_2$ and free CO_2 at 60 °C for 2 hours

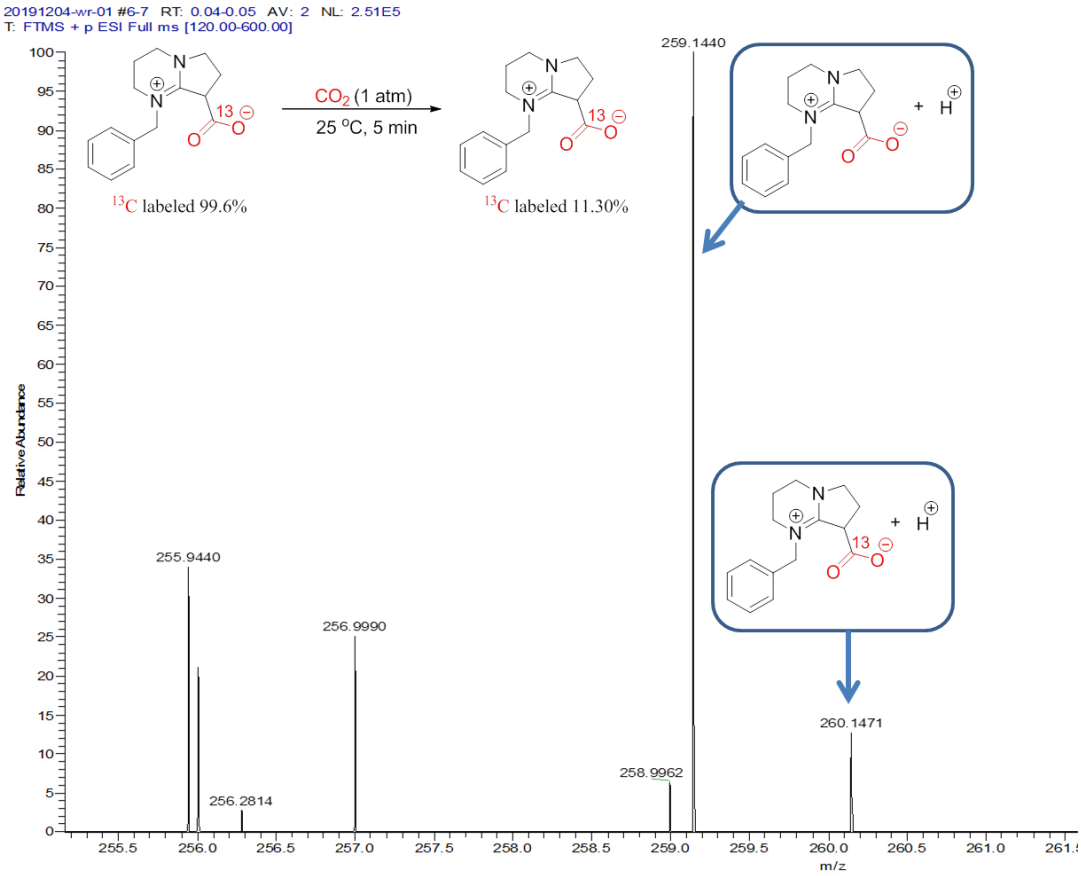


Figure S10. HRMS Spectra of the exchange process between THPE-$^{13}CO_2$ and free CO_2 at 25 °C for 5 min

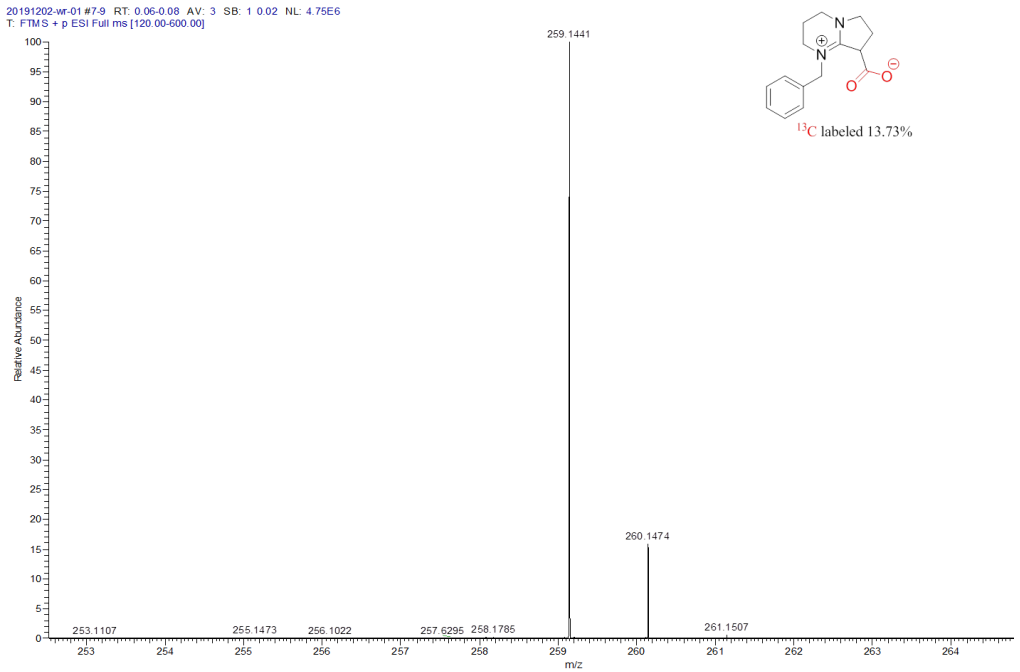


Figure S11. Enlarged HRMS Spectra of THPE-CO_2

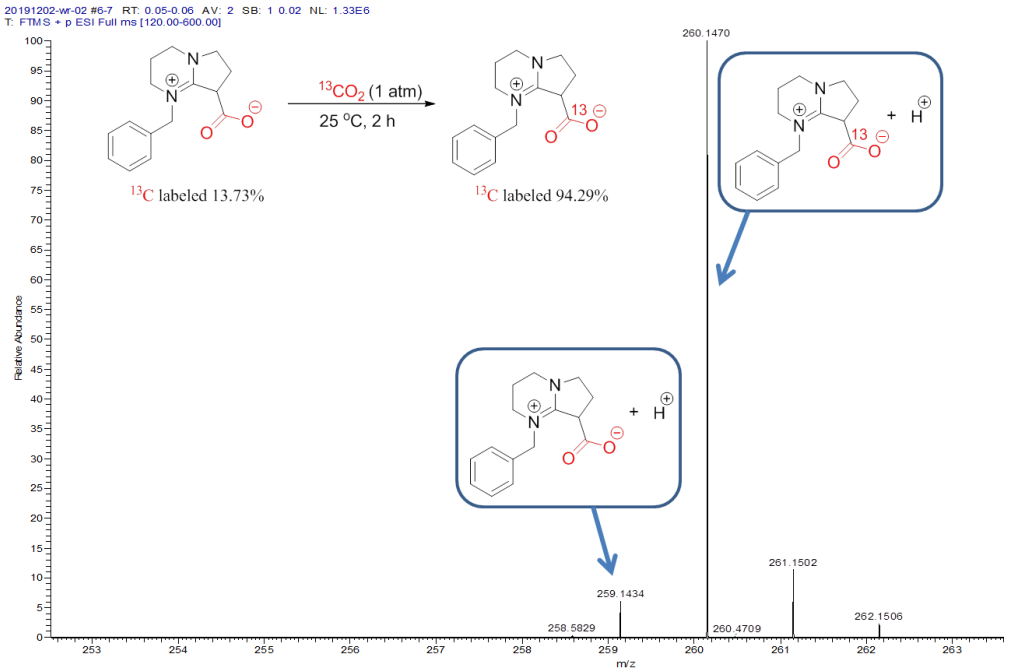


Figure S12. HRMS Spectra of the exchange process between THPE-CO_2 and free $^{13}CO_2$ at 25 °C for 2 hours

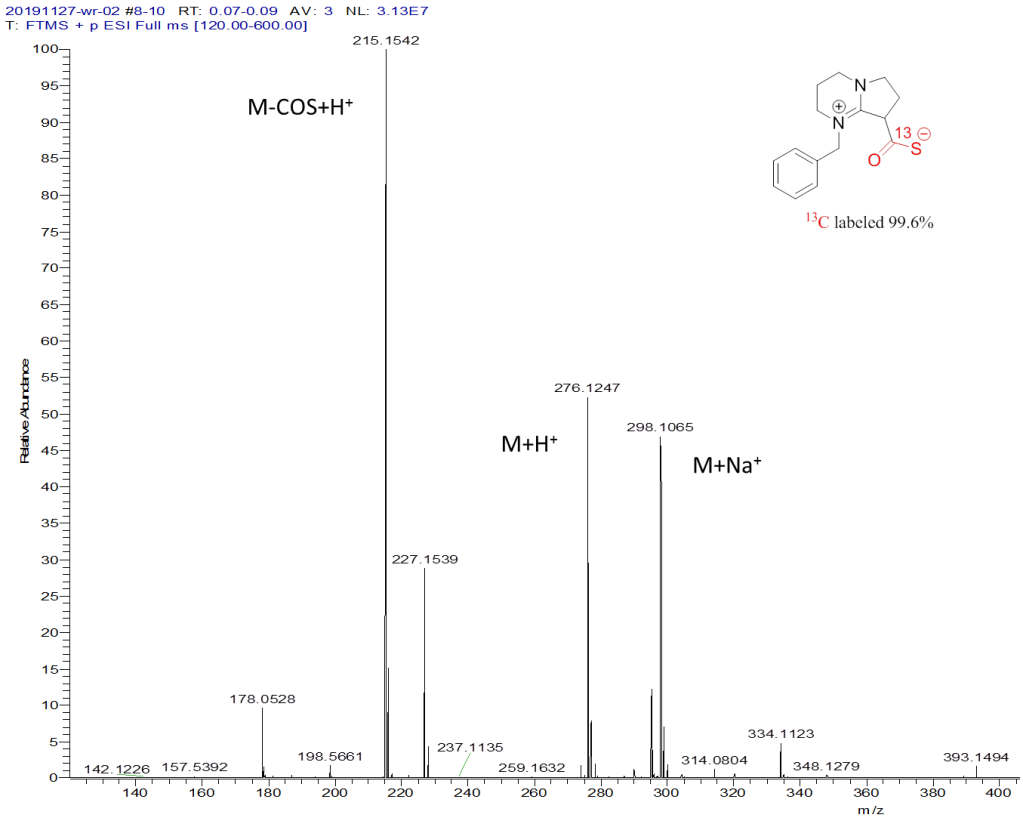


Figure S13. Enlarged HRMS Spectra of THPE-^{13}COS

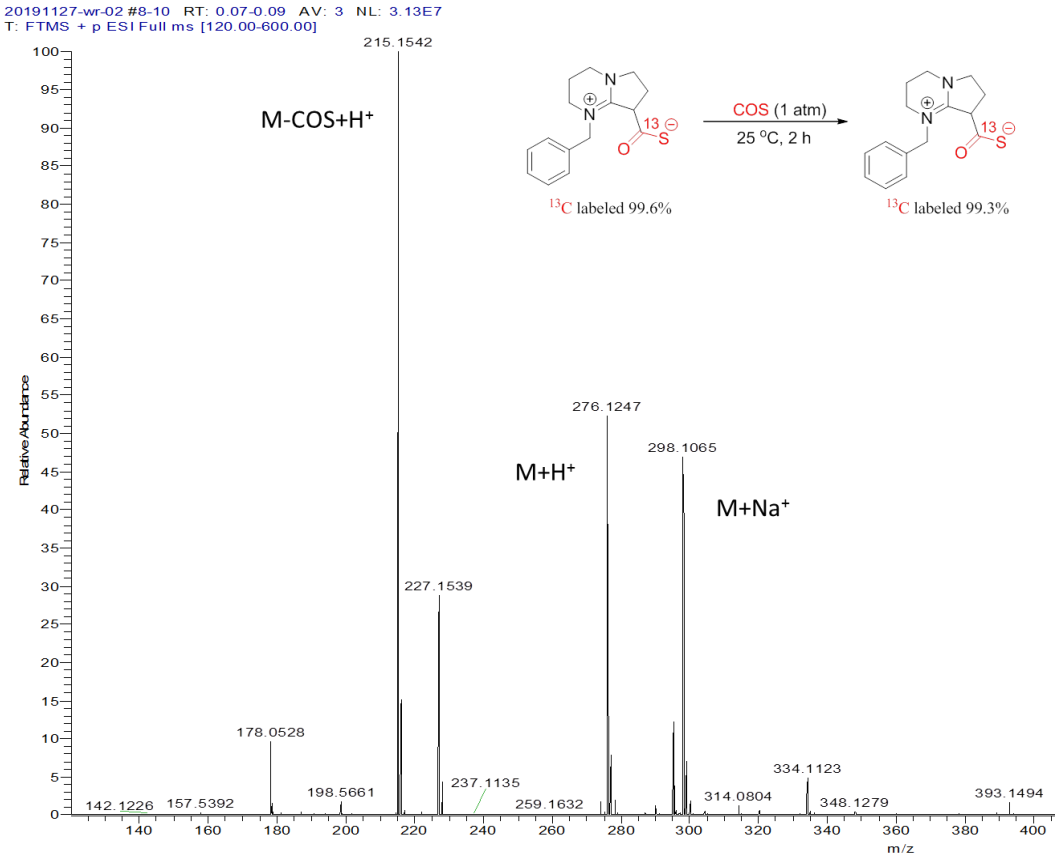


Figure S14. HRMS Spectra of the exchange process between THPE-^{13}COS and free COS at 25 °C for 2 hours

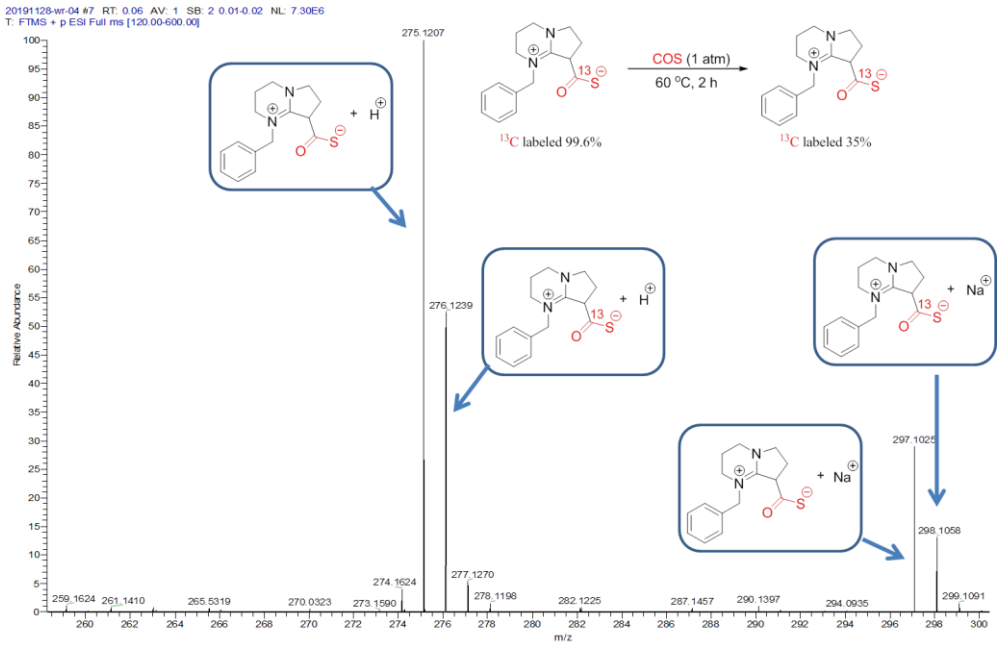


Figure S15. HRMS Spectra of the exchange process between THPE-^{13}COS and free COS at 60 °C for 2 hours

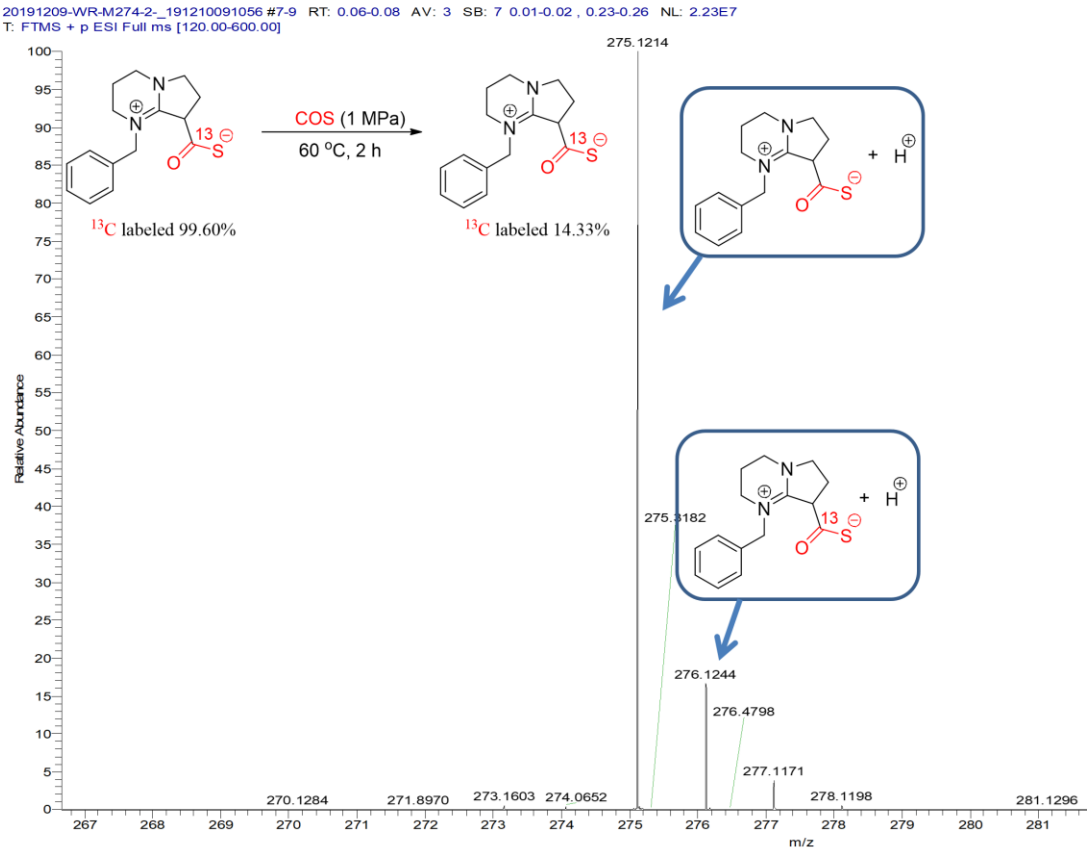


Figure S16. HRMS Spectra of the exchange process between THPE-^{13}COS and free COS (1 MPa) at 60 °C for 2 hours

5.3 Monitoring the interaction between 2a and LB-COX (X=O/S) adduct by ^{1}H-NMR experiments

Monitoring the interaction between 2a and THPE-CO_2 adduct 1k

In a glove box, a 1.0 mL vial containing a stirring bar was charged with allenamide **2a** (0.05 mmol), various concentrations of THPE-CO_2 adduct **1k** and DMSO-d^6 (0.5 mL). After 1 h with continuous stirring, the reaction mixture was detected by ^{1}H-NMR. From the data, the -NH- signal (δ 8.28 ppm) of **2a** gradually drift undergoes a modest upshift of 0.45 ppm upon addition of 1.0 equiv. of **1k** to this solution (Figure S17). ^{1}H-NMR experiments show that THPE-CO_2 adduct **1k** as base could activate allenamide.

Monitoring the interaction between 2a and THPE-COS adduct S1j

In a glove box, a 1.0 mL vial containing a stirring bar was charged with allenamide **2a** (0.05 mmol), various concentrations of THPE-COS adduct **S1j** and CD_3CN (0.5 mL). After 1 h with continuous stirring, the reaction mixture was detected by ^{1}H-NMR. From the data, the -N*H*- signal (δ 6.92 ppm) of **2a** completely

disappears, while the -*H* of –C*H*CO signal (δ 5.41 ppm) gradually drift undergoes a modest upshift of 0.11 ppm upon addition of 1.0 equiv. of THPE-COS adduct **S1j** to this solution (Figure S18). ^{1}H-NMR experiments show that THPE-COS adduct **S1j** as base could activate allenamide.

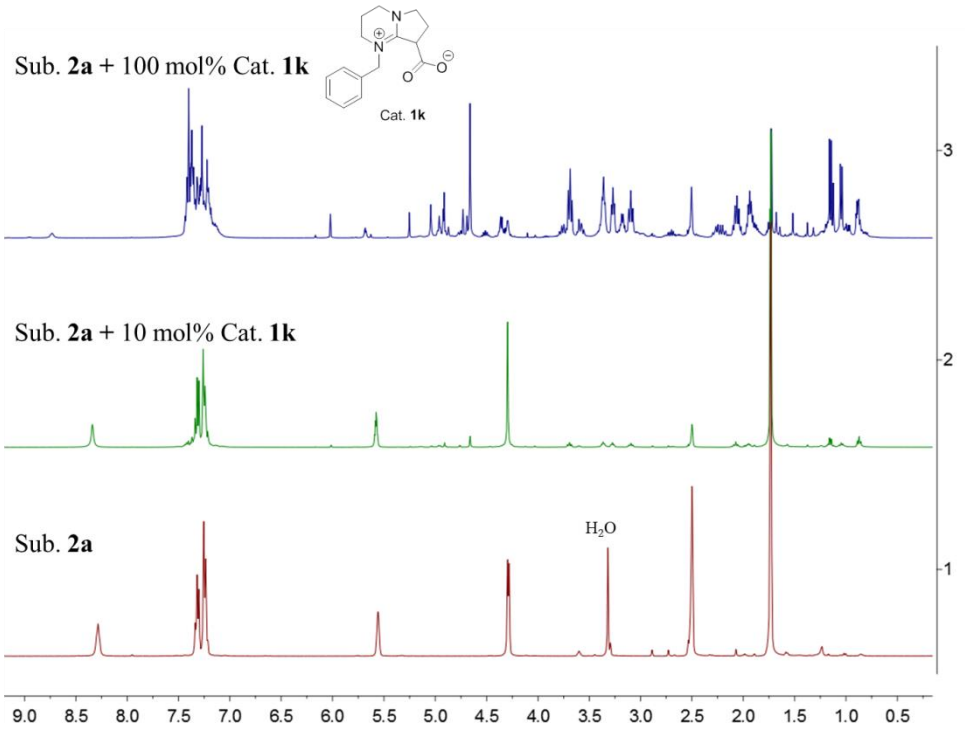


Figure S17. Monitoring the interaction between **2a** and THPE-CO_2 adduct **1k**

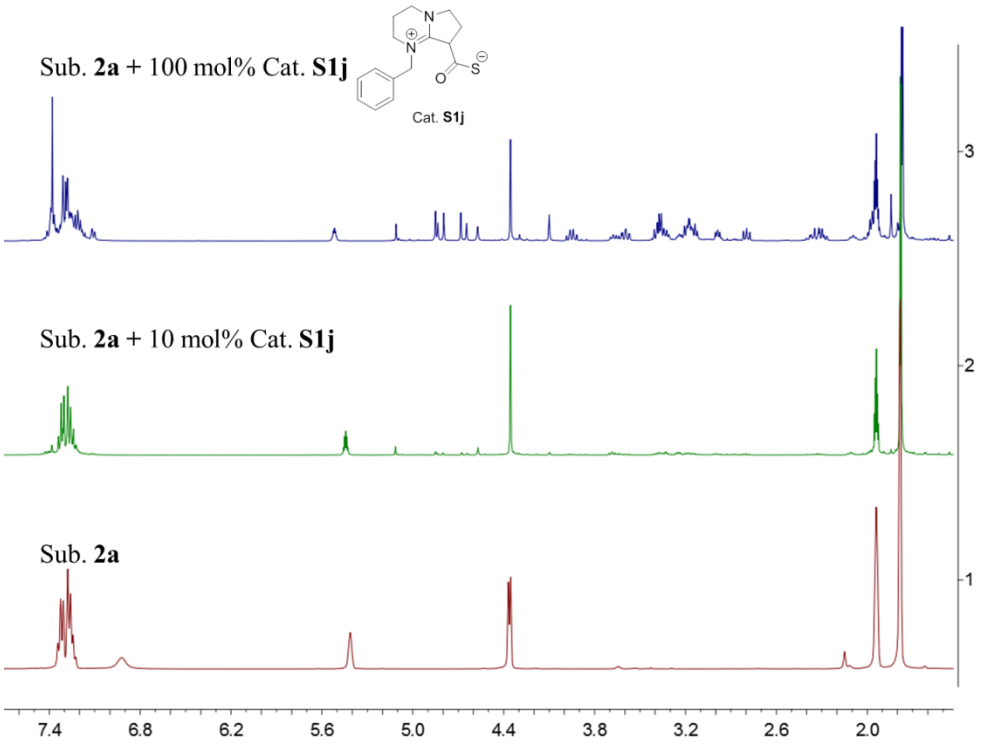


Figure S18. Monitoring the interaction between **2a** and THPE-COS adduct **S1j**

5.4 The stability of THPE-COS adduct S1j under CO_2 atmosphere

In a glove box, a 10 mL Schlenk flask containing a stirring bar was charged with THPE-COS adduct **S1j** and CD_3CN (0.5 mL). The flask was then evacuated and filled with CO_2 with a balloon and the reaction was stirred at 60 °C for 2 hours. The reaction mixture was detected by ^{1}H-NMR. THPE-COS adduct **S1j** was found to be very stable under CO_2 atmosphere by ^{1}H-NMR analysis (Figure S19).

5.5 The stability of THPE-COS adduct S1j at 60 °C

^{1}H-NMR (Figure S20) and ^{13}C -NMR (Figure S21) of THPE-COS adduct **S1j** were detected at 60 °C. THPE-COS adduct **S1j** was found to be stable at 60 °C by NMR analysis (Figure S20).

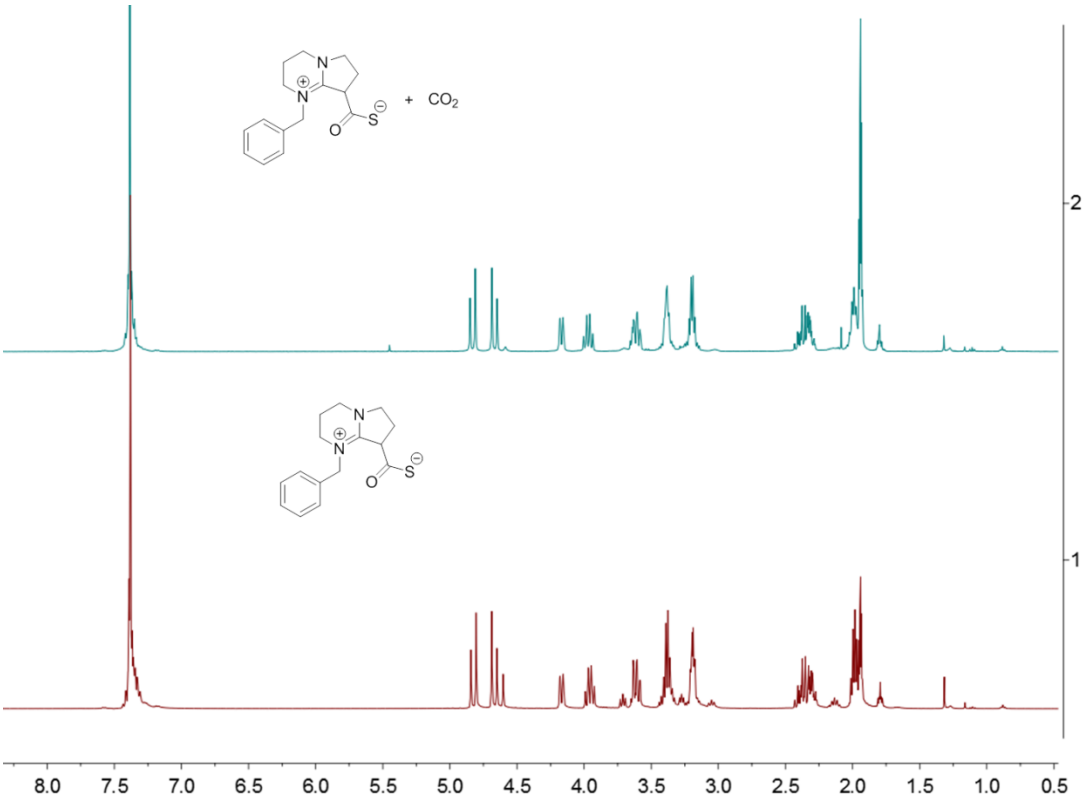


Figure S19. THPE-COS adduct **S1j** in the presence of CO_2 atmosphere

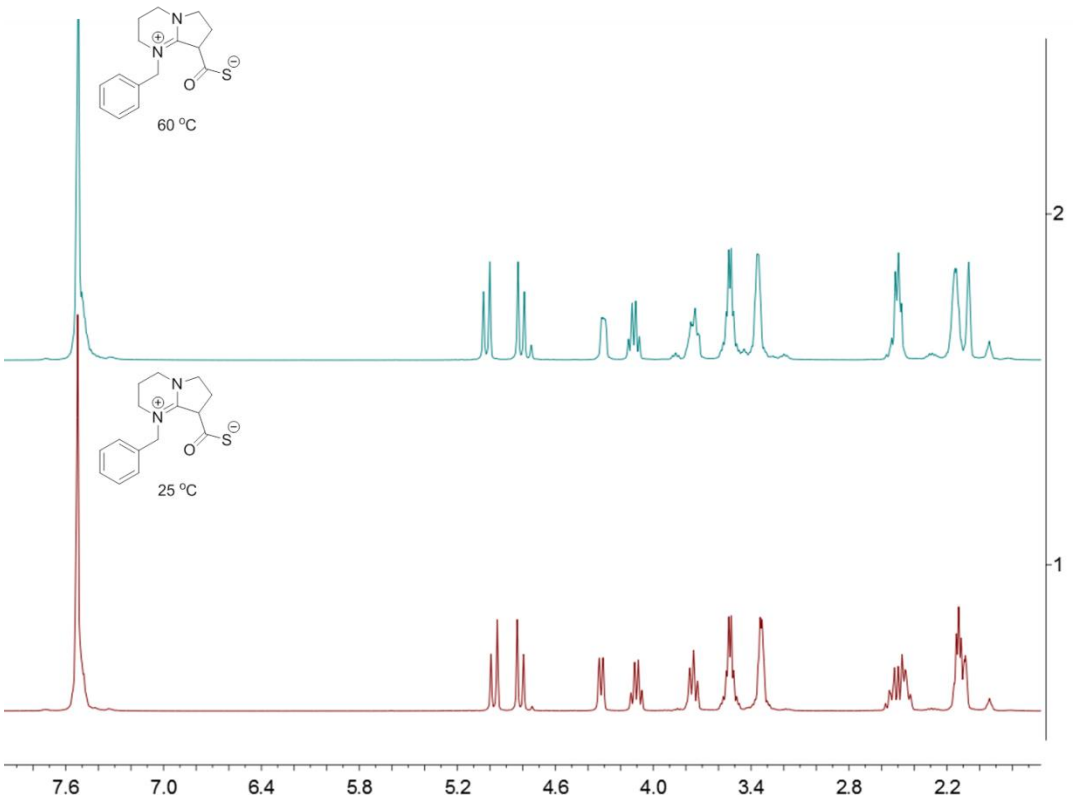


Figure S20. THPE-COS adduct **S1j** at 60 °C

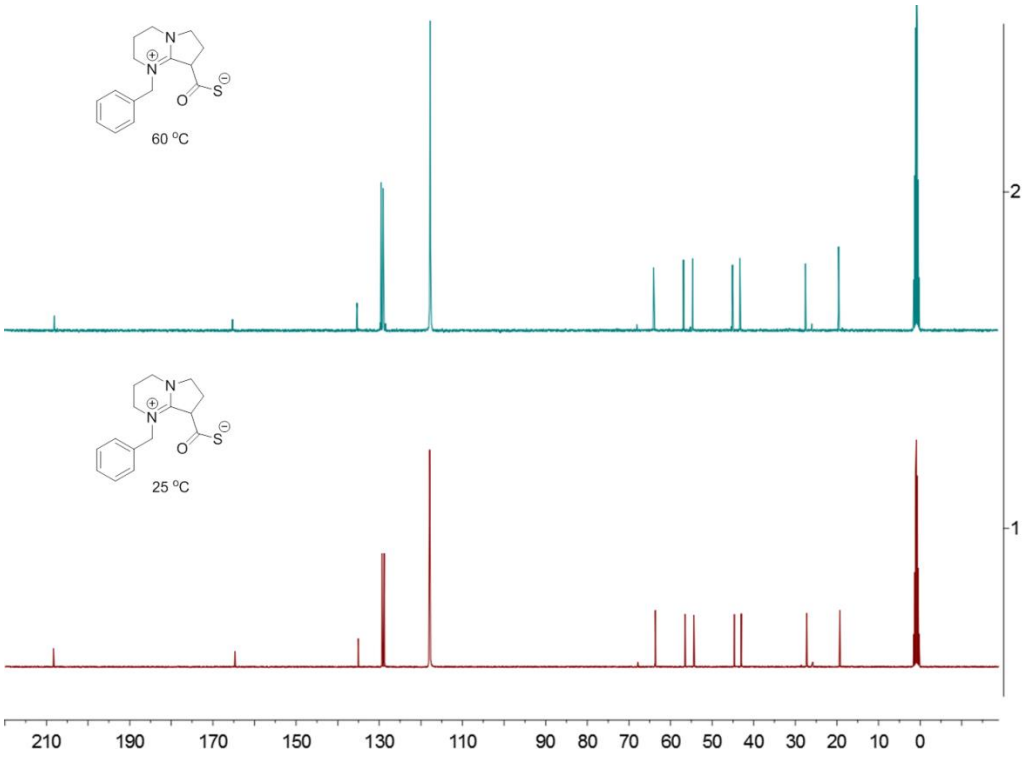
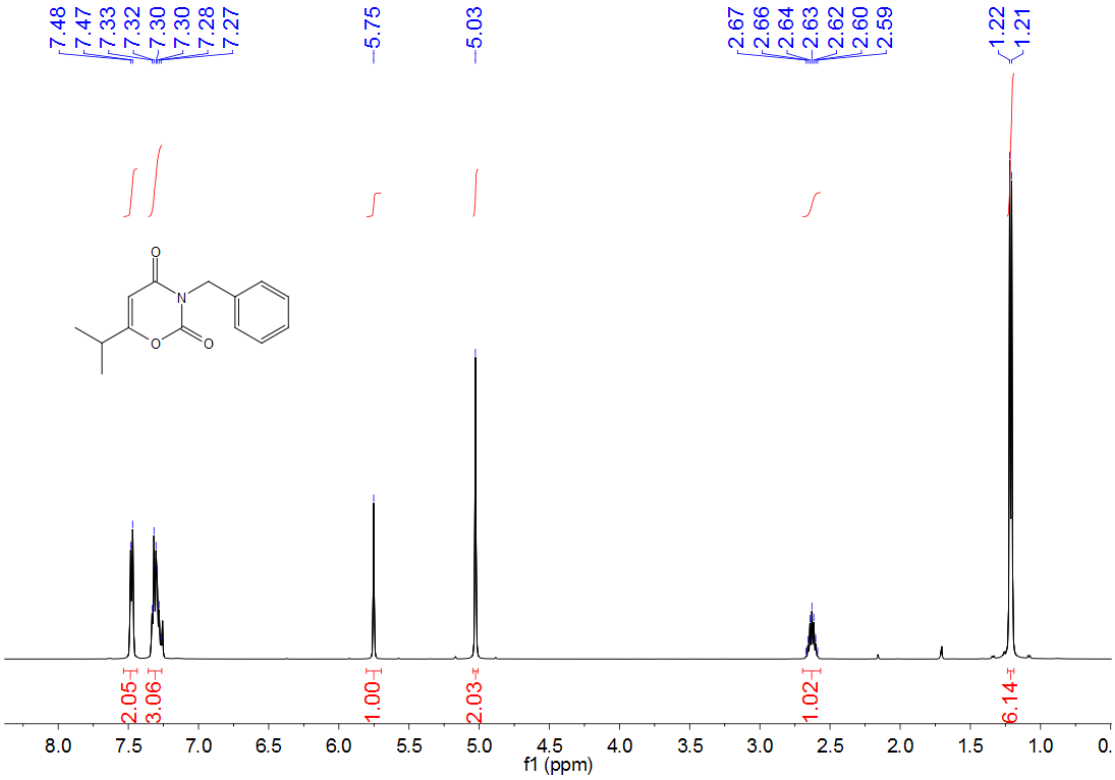
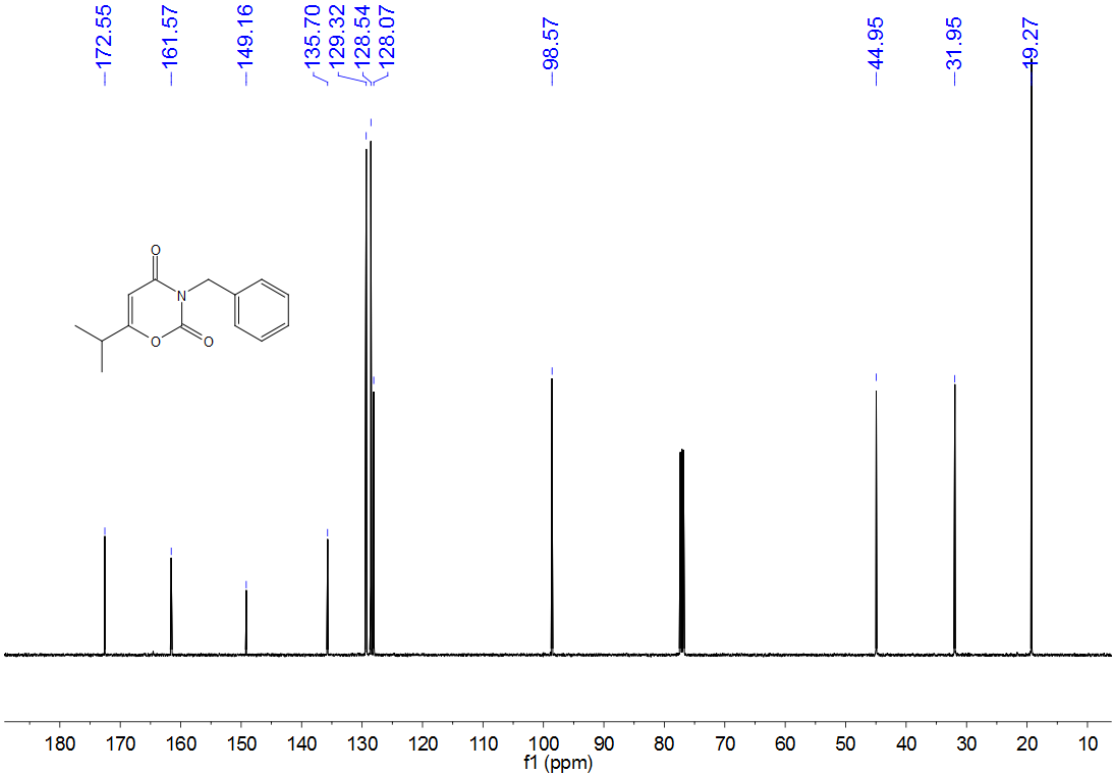
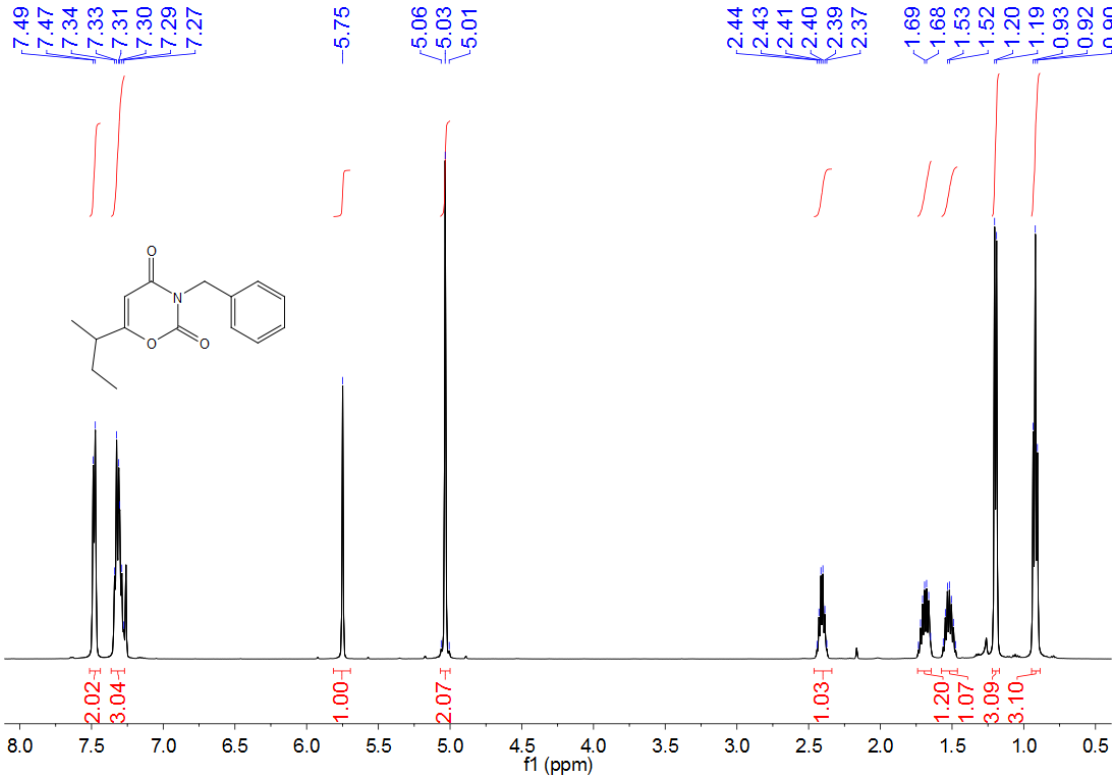


Figure S21. THPE-COS adduct **S1j** at 60 °C

6. NMR spectra



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2.43
2.41
2.40
2.39
2.37
1.69
1.68
1.53
1.52
1.20
1.19
0.93
0.92
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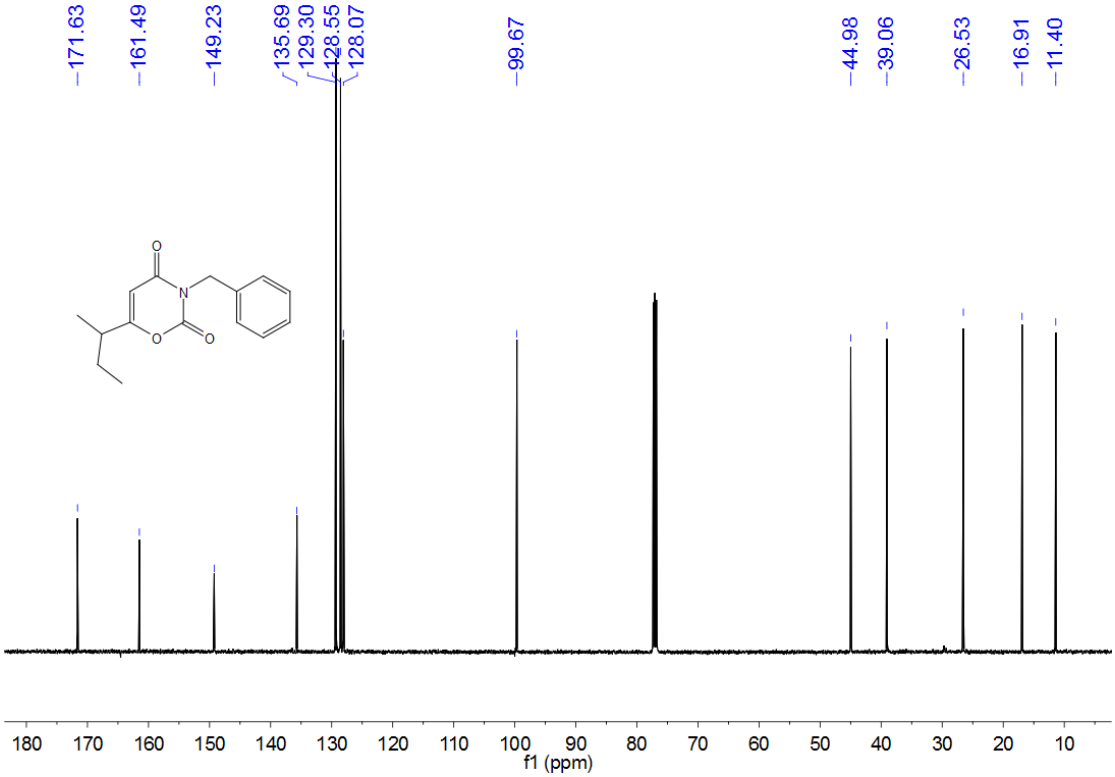
3.04
1.00
2.07
1.03
1.20
1.07
3.09
3.10
f1 (ppm)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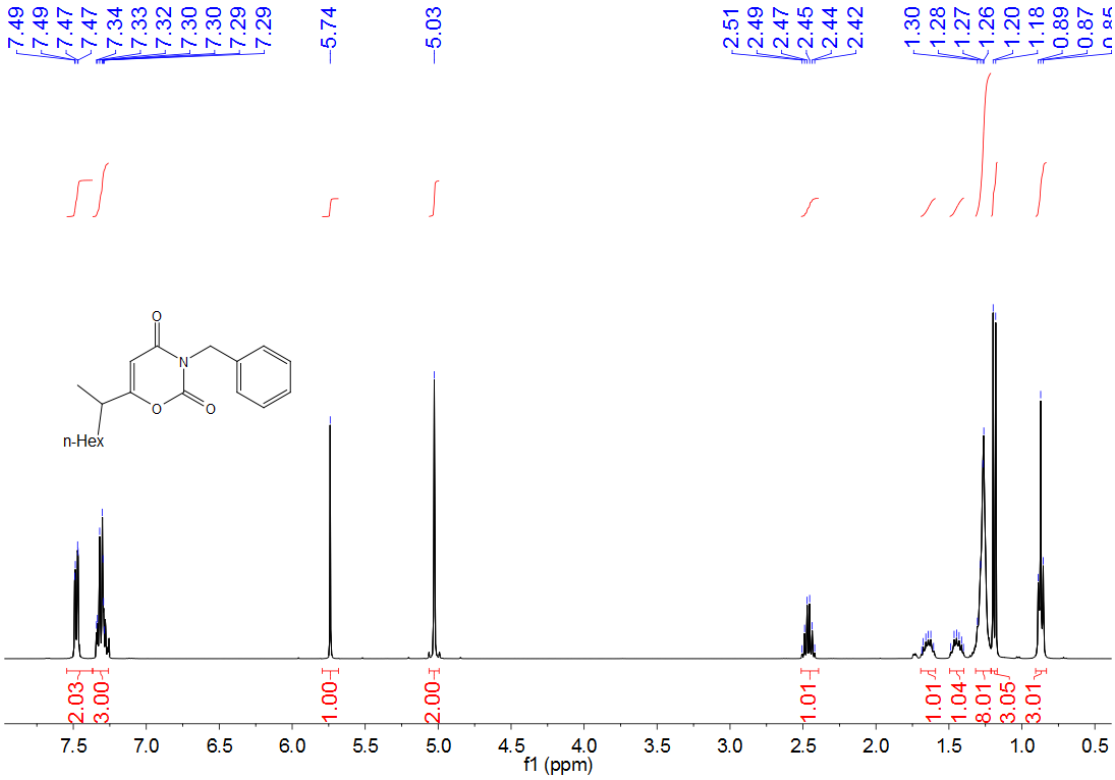
11.40
f1 (ppm)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2.49
2.47
2.45
2.44
2.42
1.30
1.28
1.27
1.26
1.20
1.18
0.89
0.87
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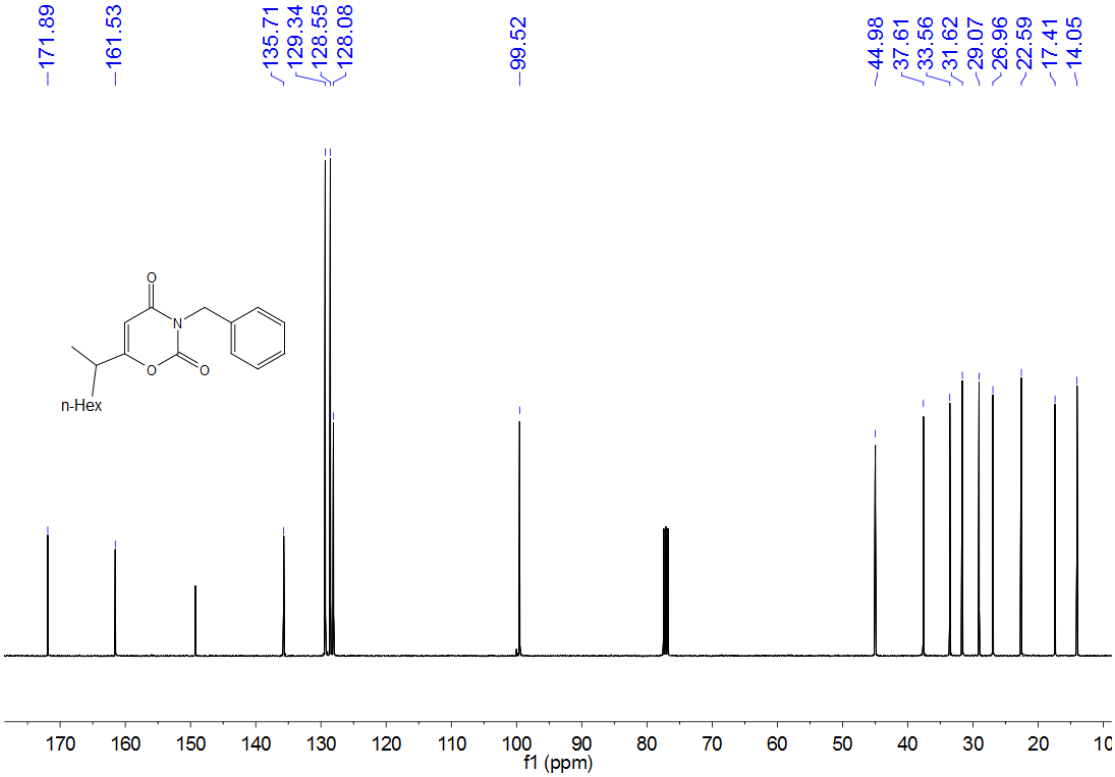
1.00
2.00
1.01
1.01
1.04
8.01
3.05
3.01
f1 (ppm)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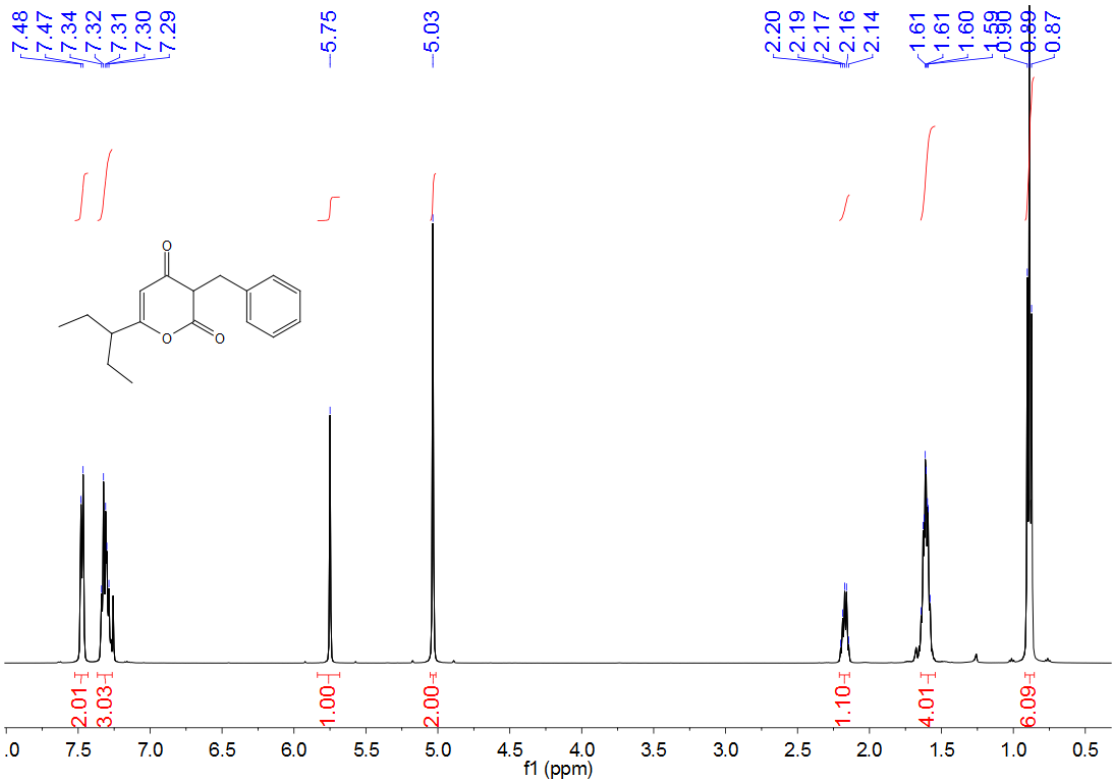
22.59
17.41
14.05
n-Hex
f1 (ppm)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2.16
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1.61
1.61
1.60
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3.03
1.00
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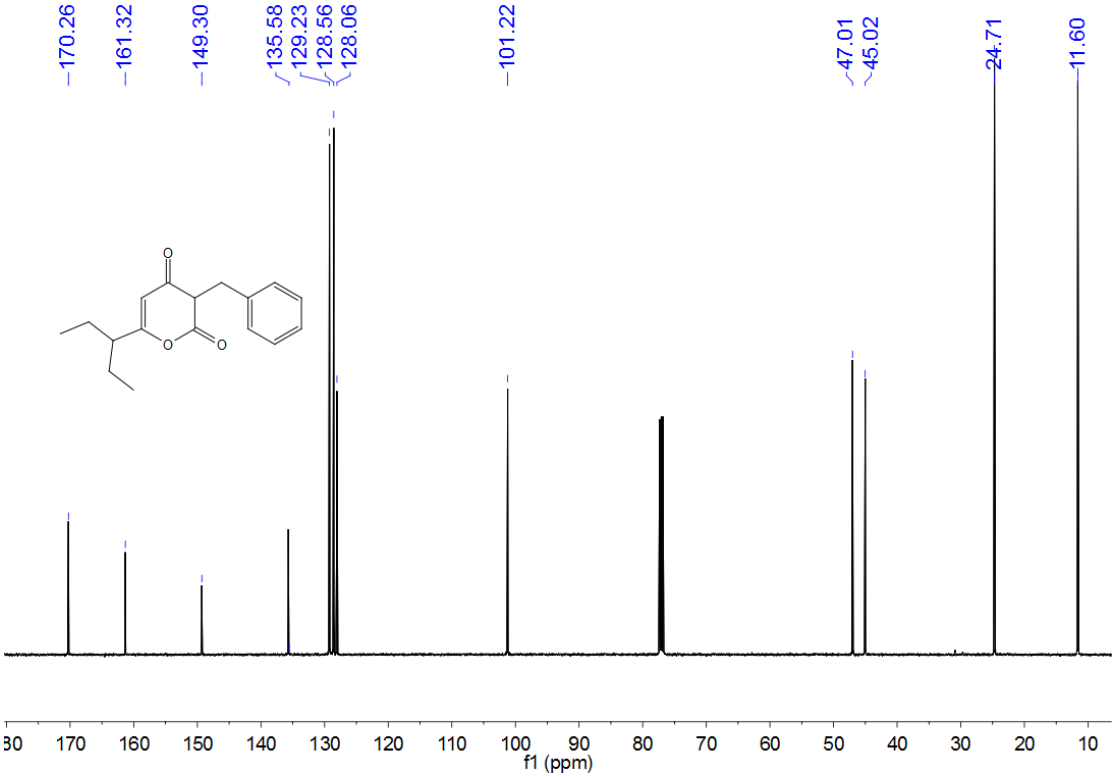
6.09
f1 (ppm)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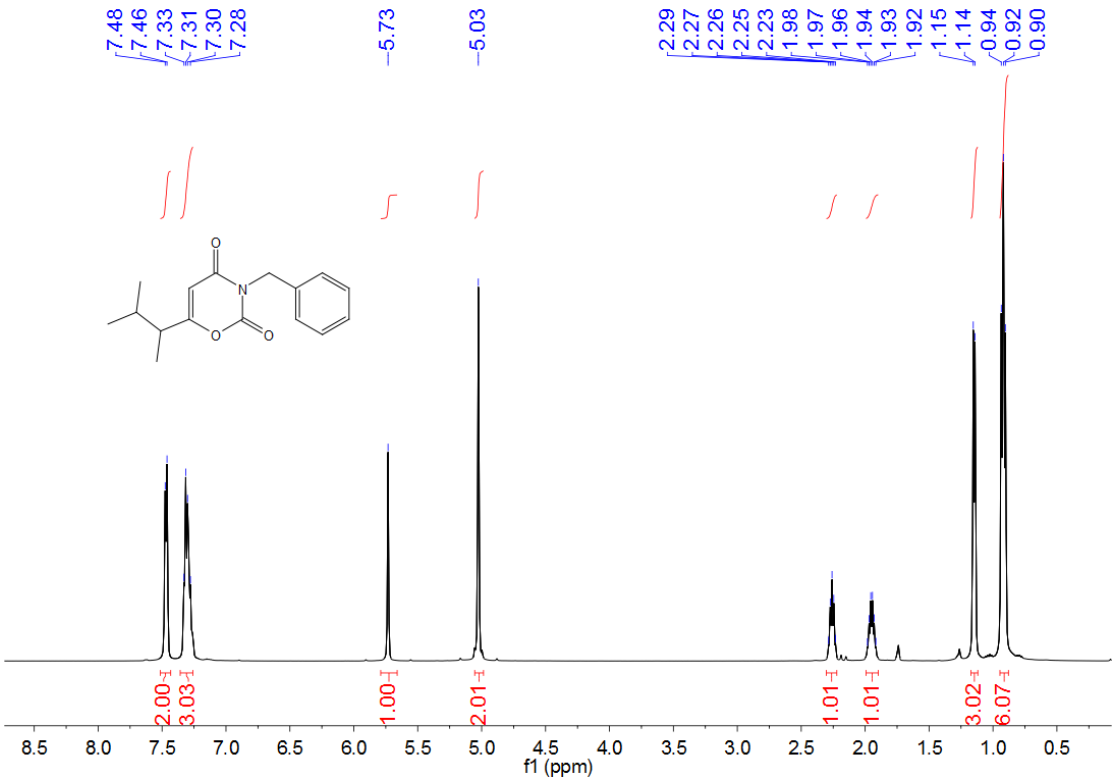
f1 (ppm)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1.97
1.96
1.94
1.93
1.92
1.15
1.14
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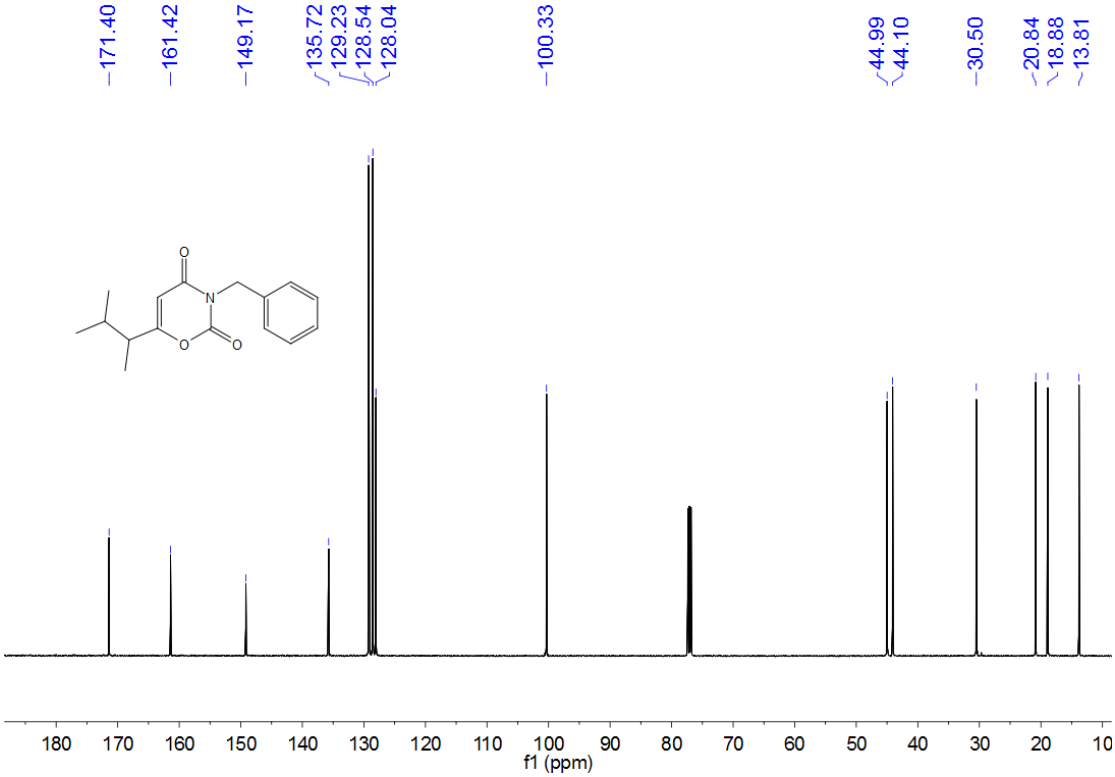
f1 (ppm)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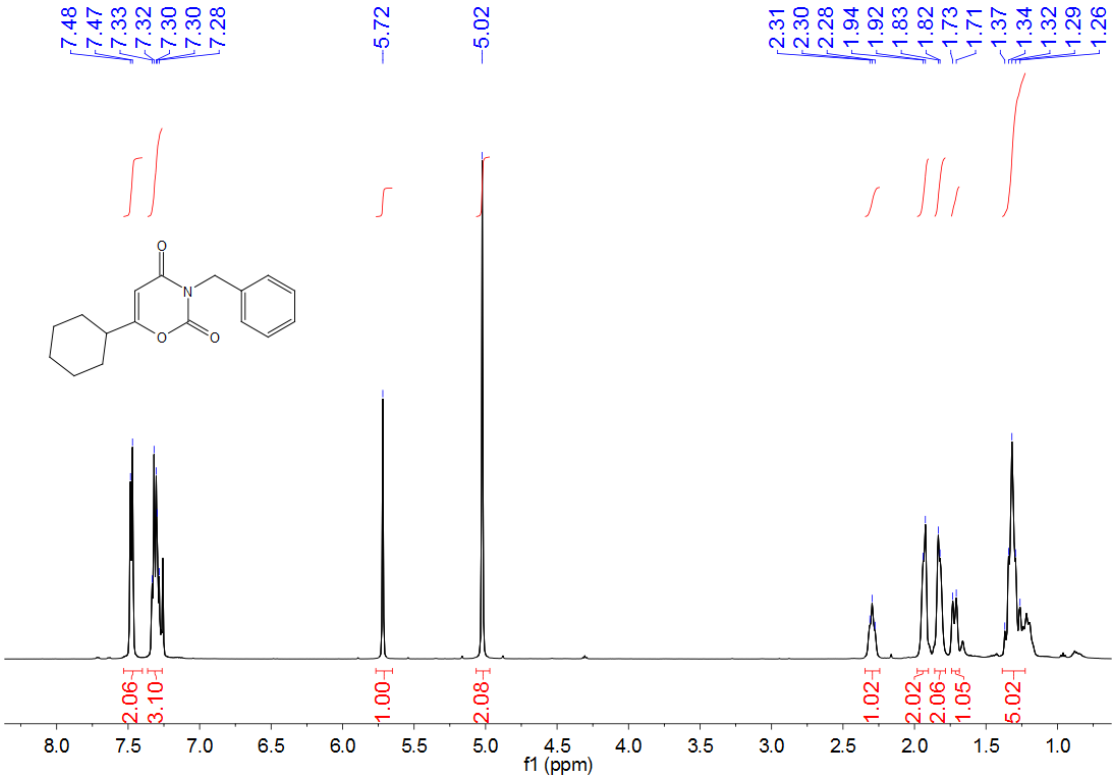
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1.82
1.73
1.71
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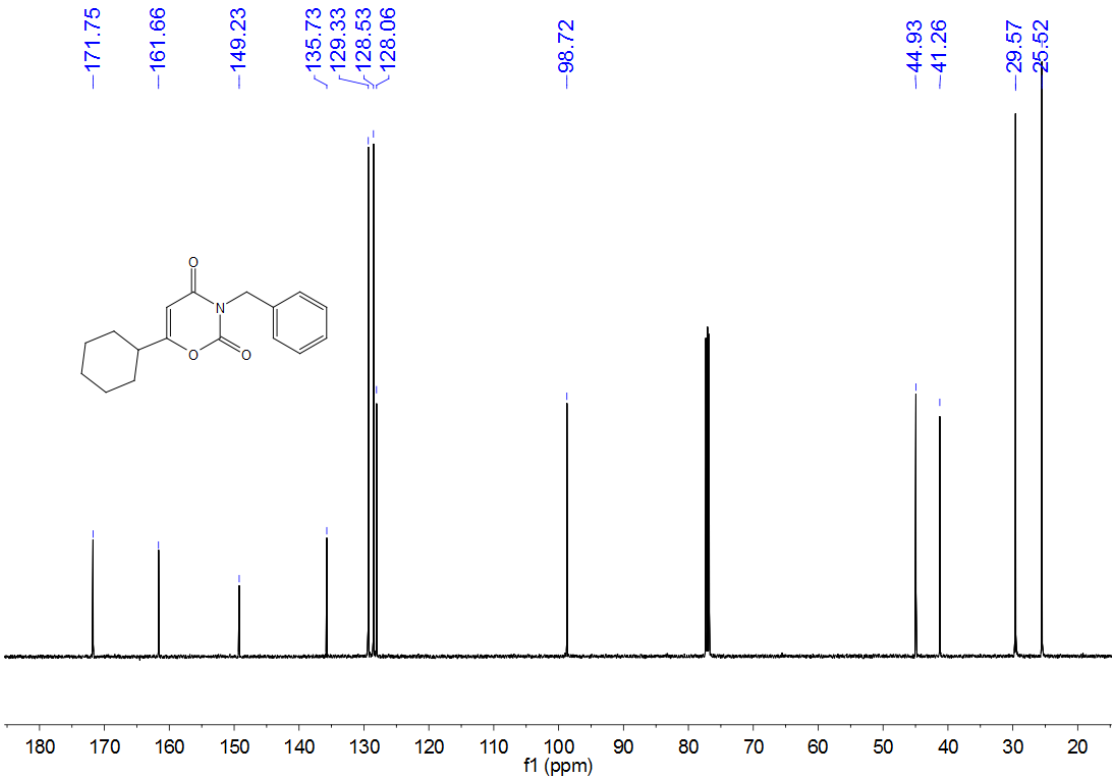
5.02
f1 (ppm)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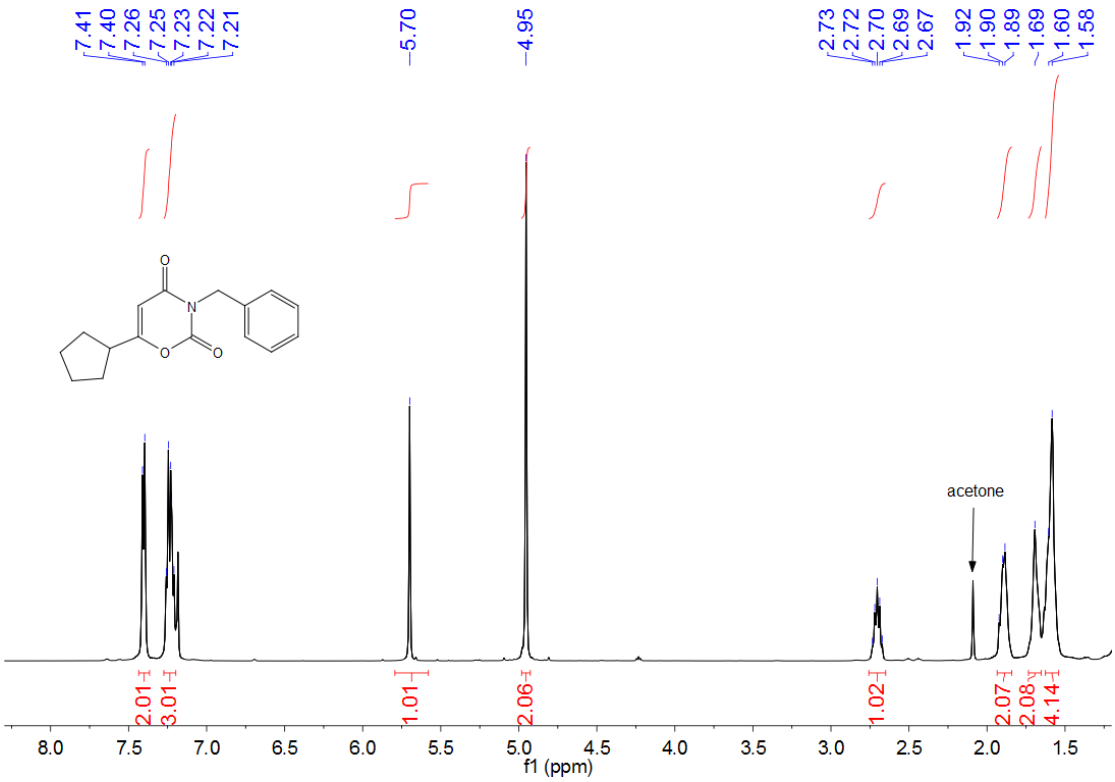
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1.89
1.69
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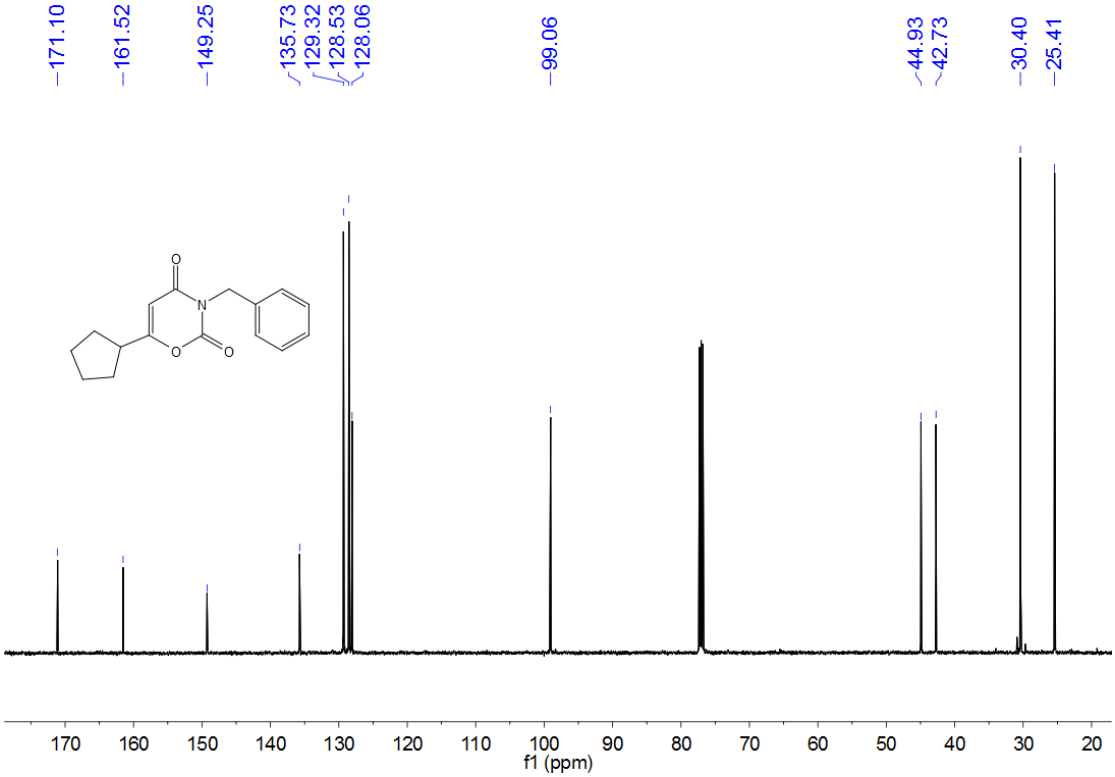
f1 (ppm)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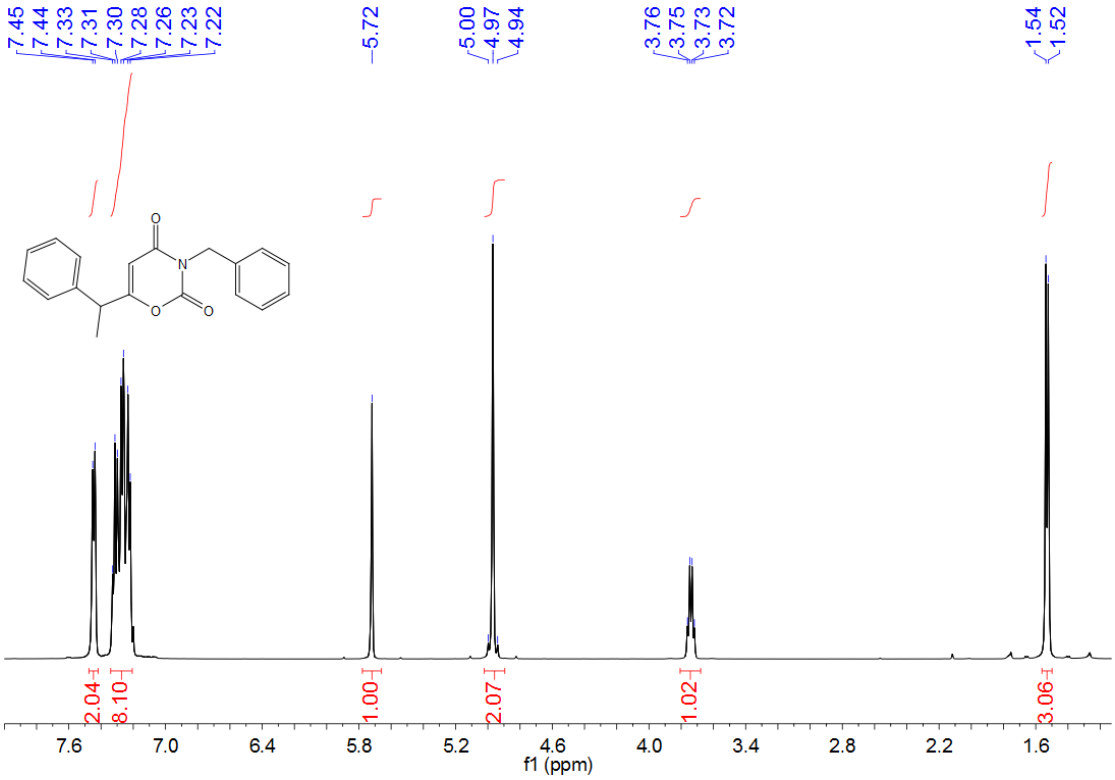
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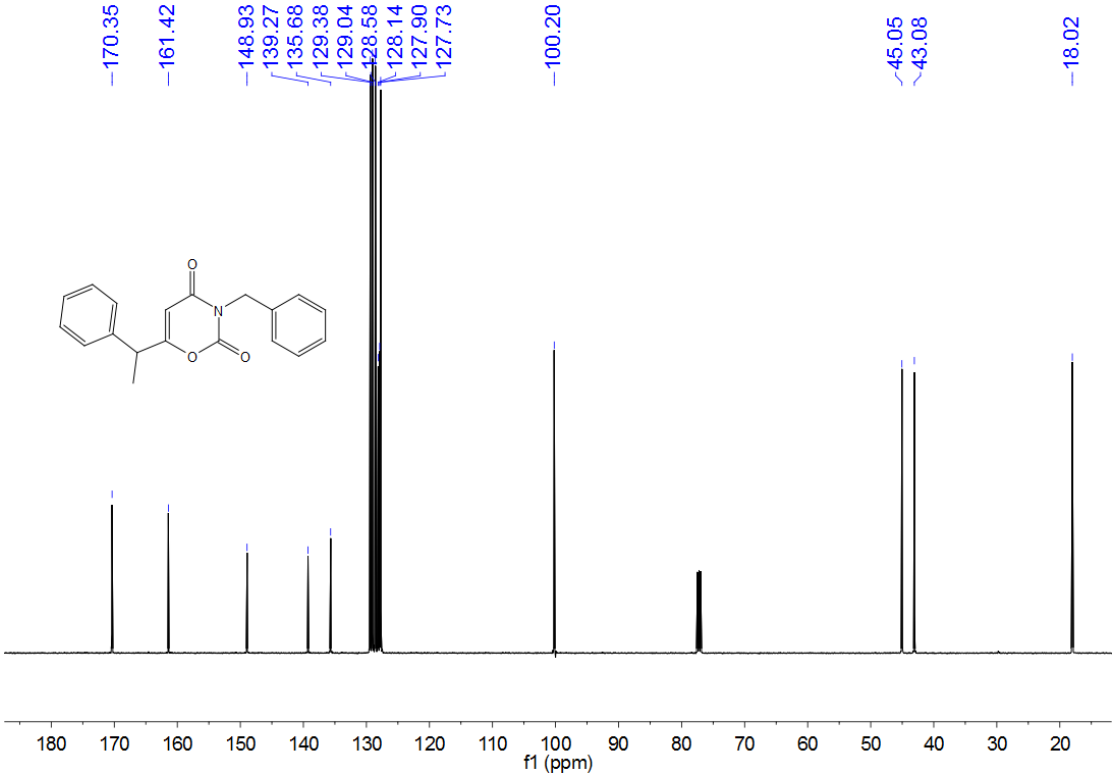
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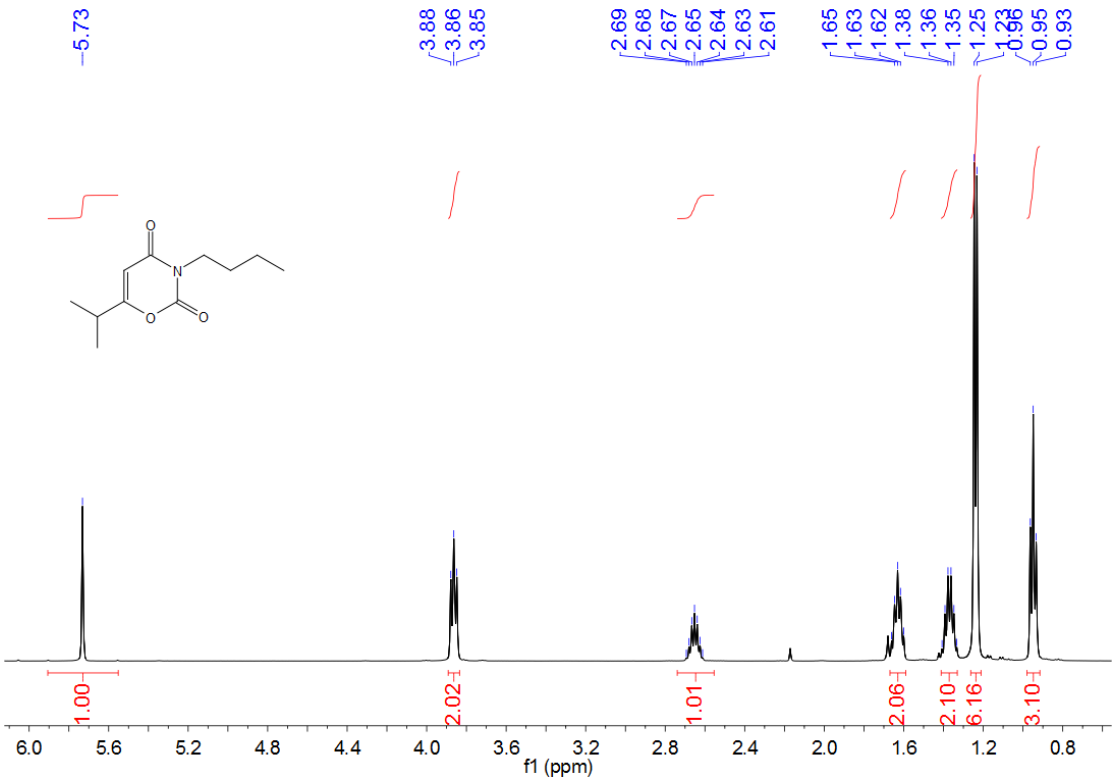
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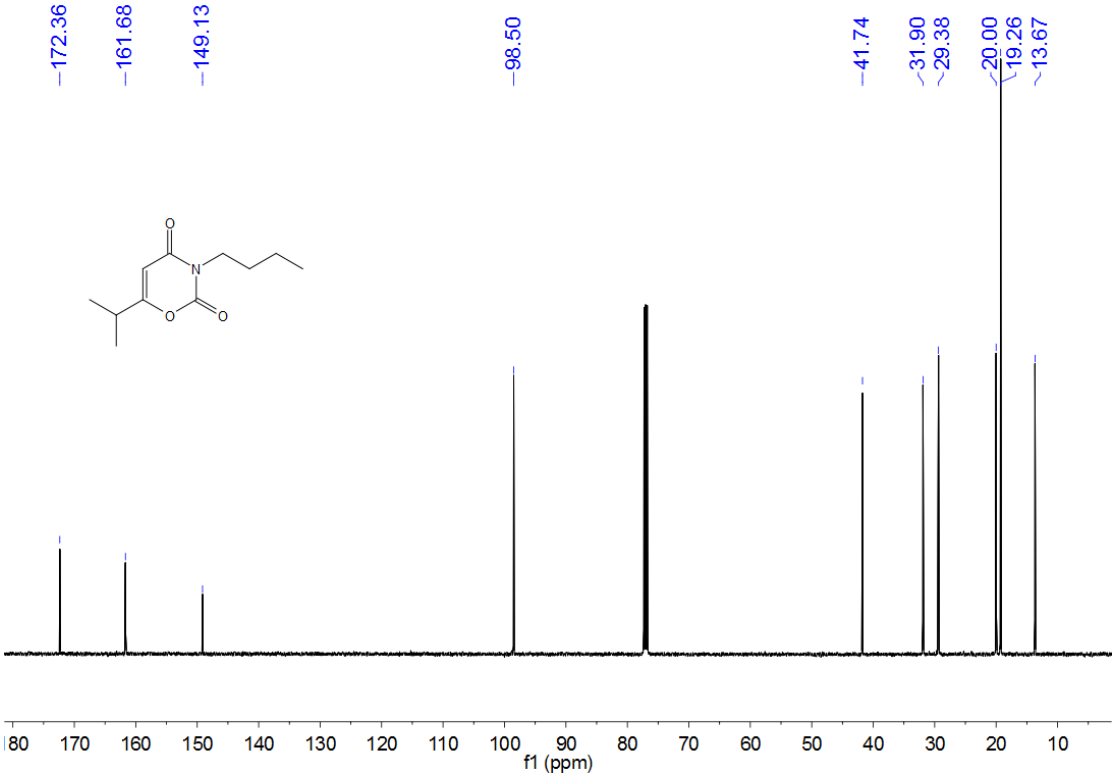
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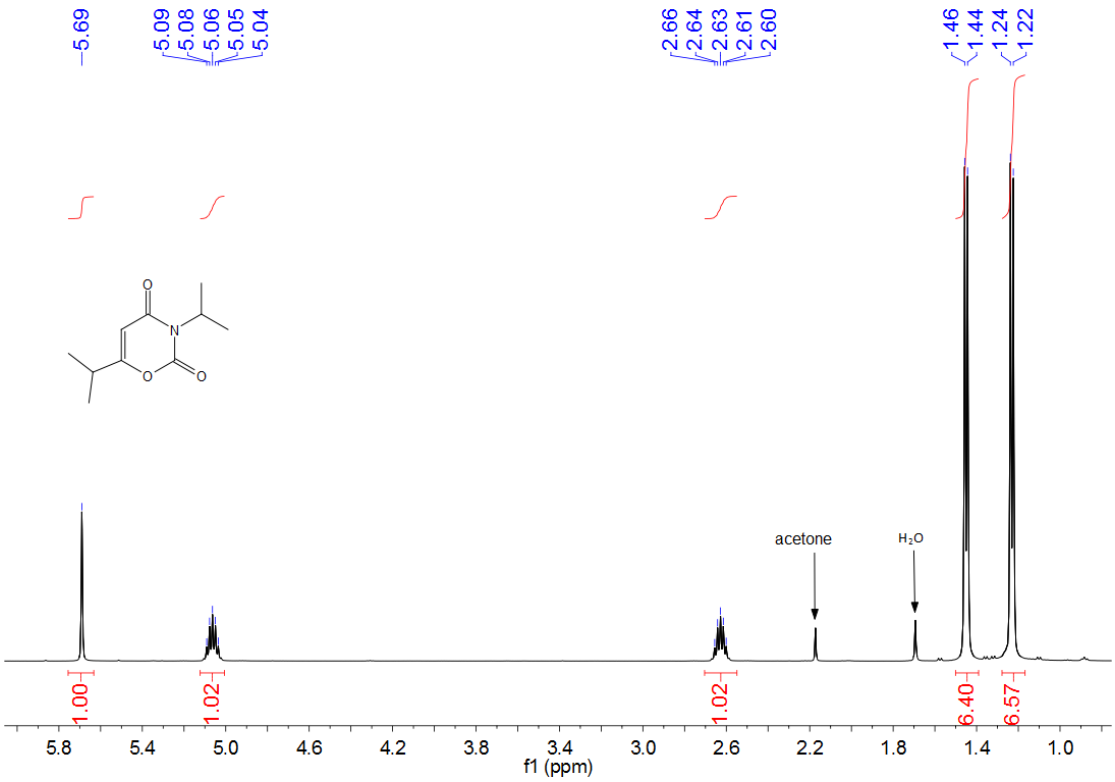
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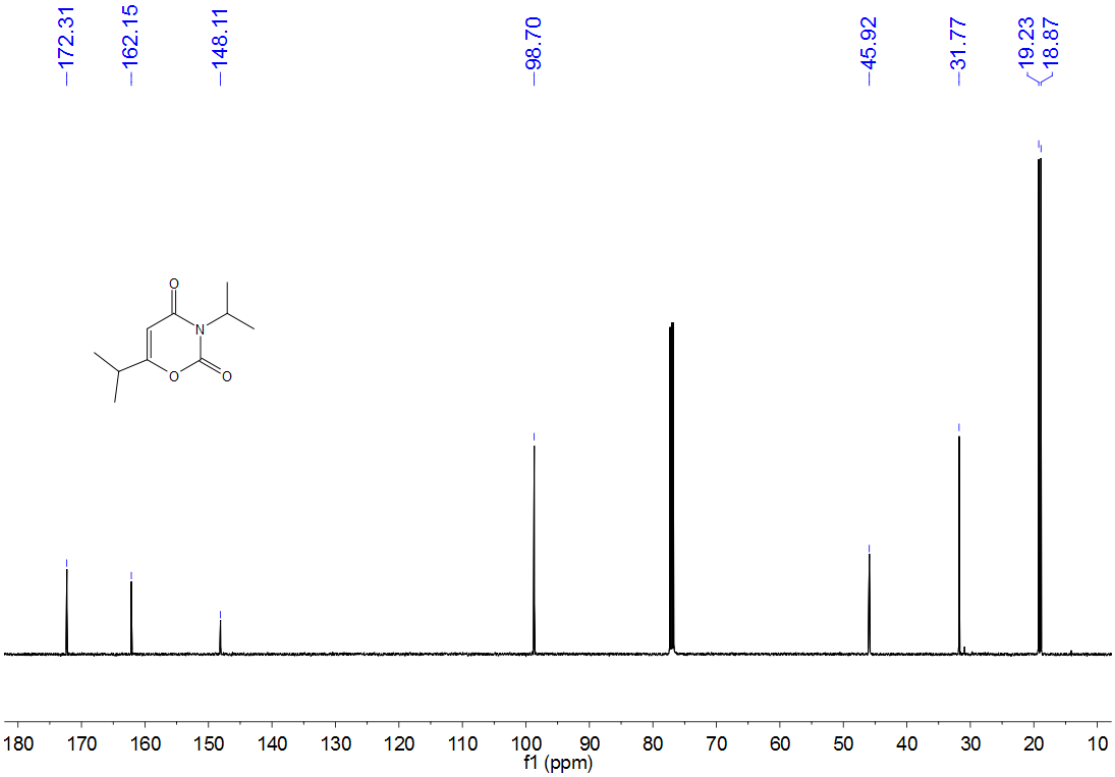
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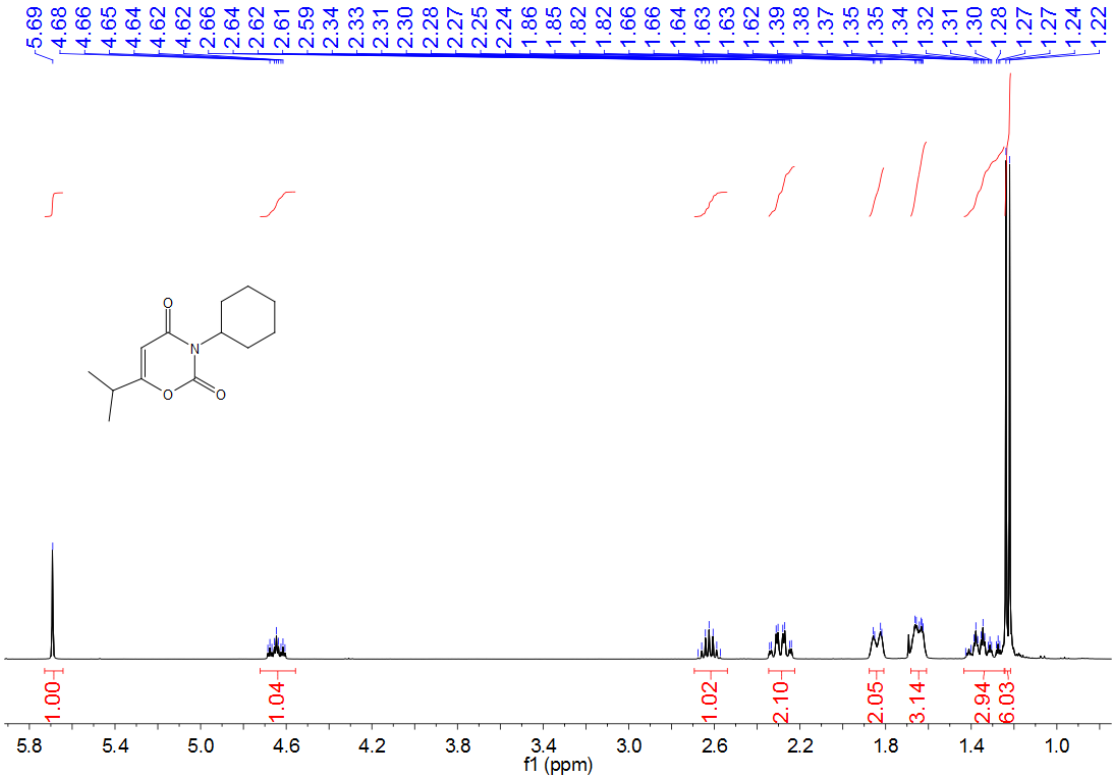
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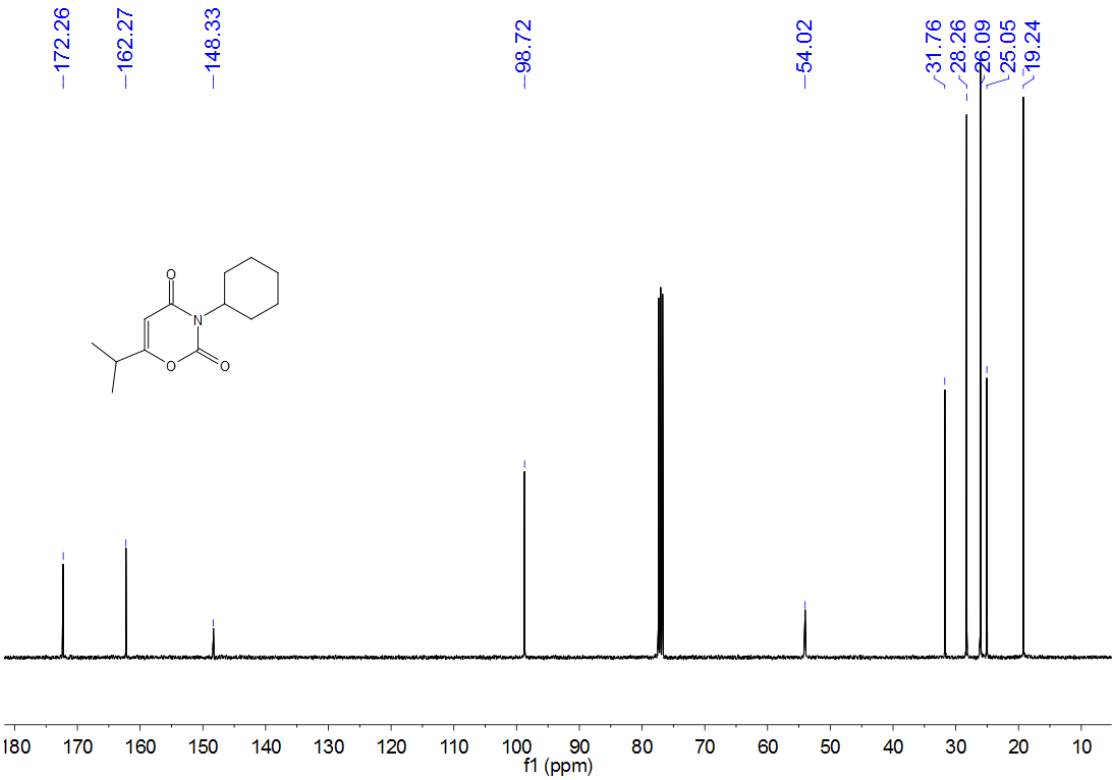
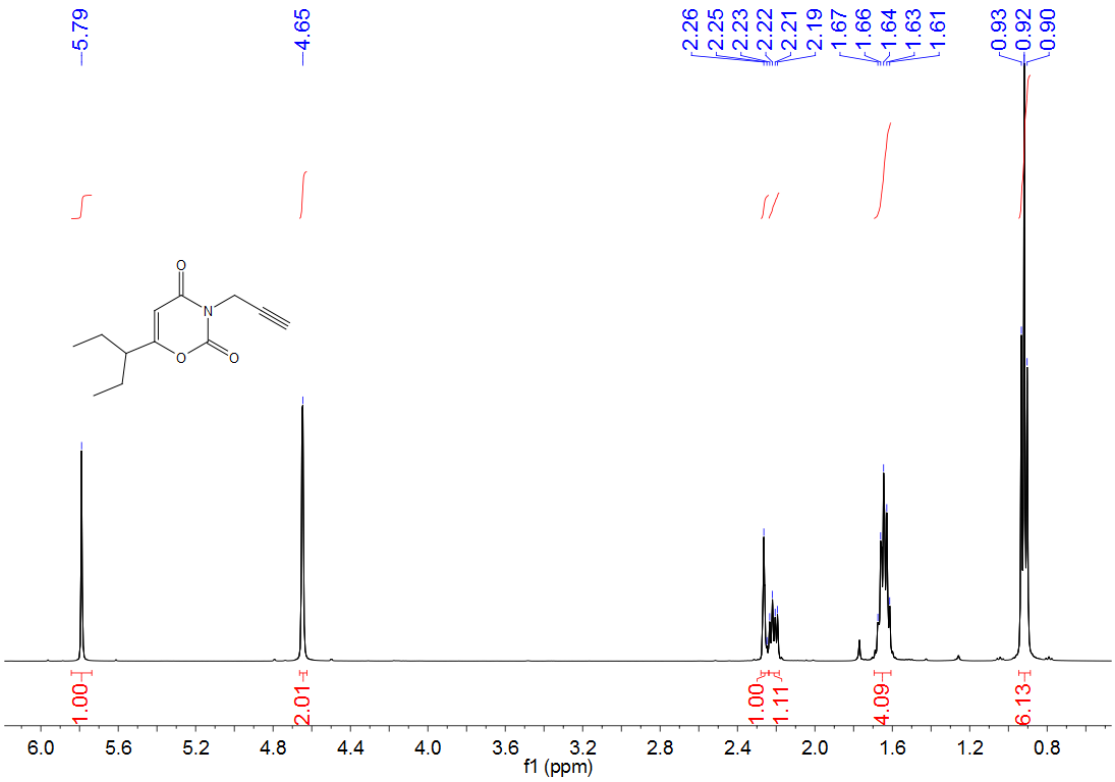
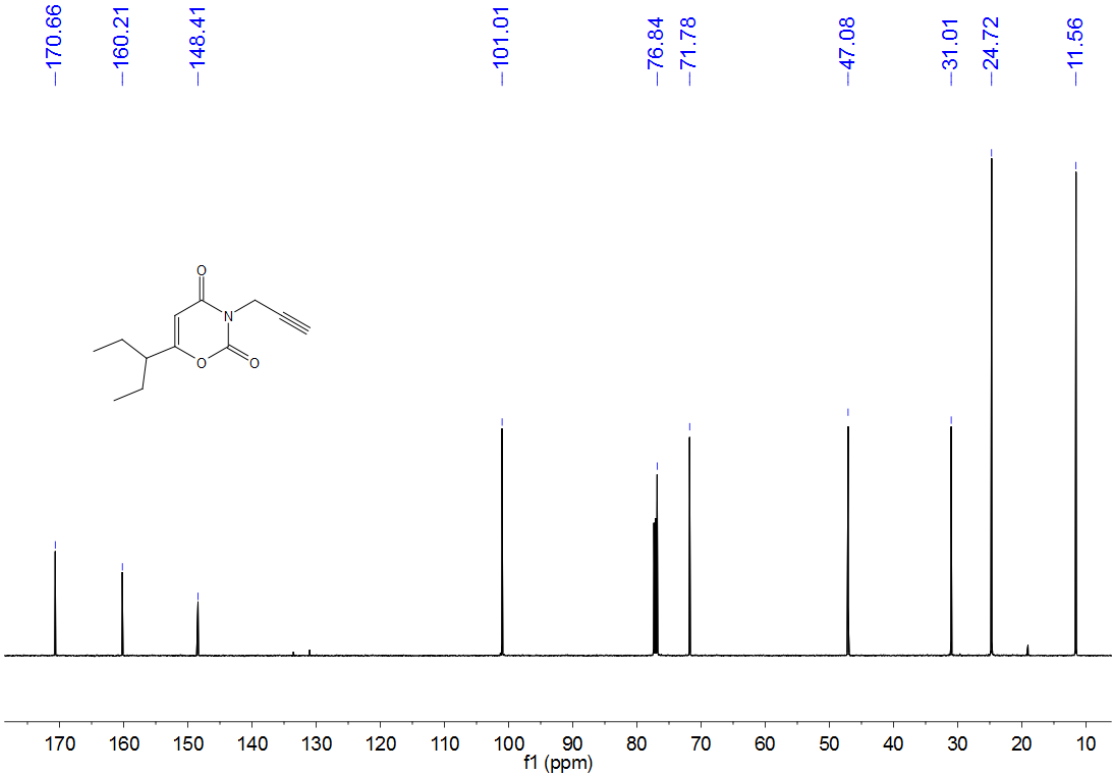
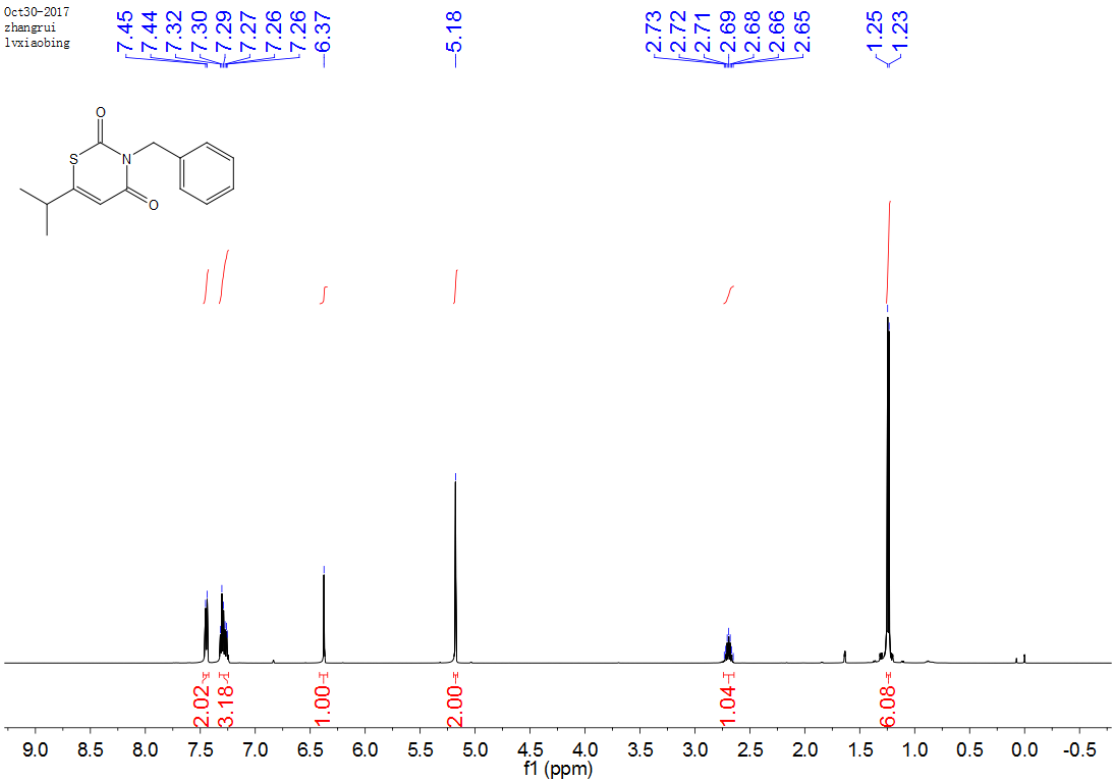
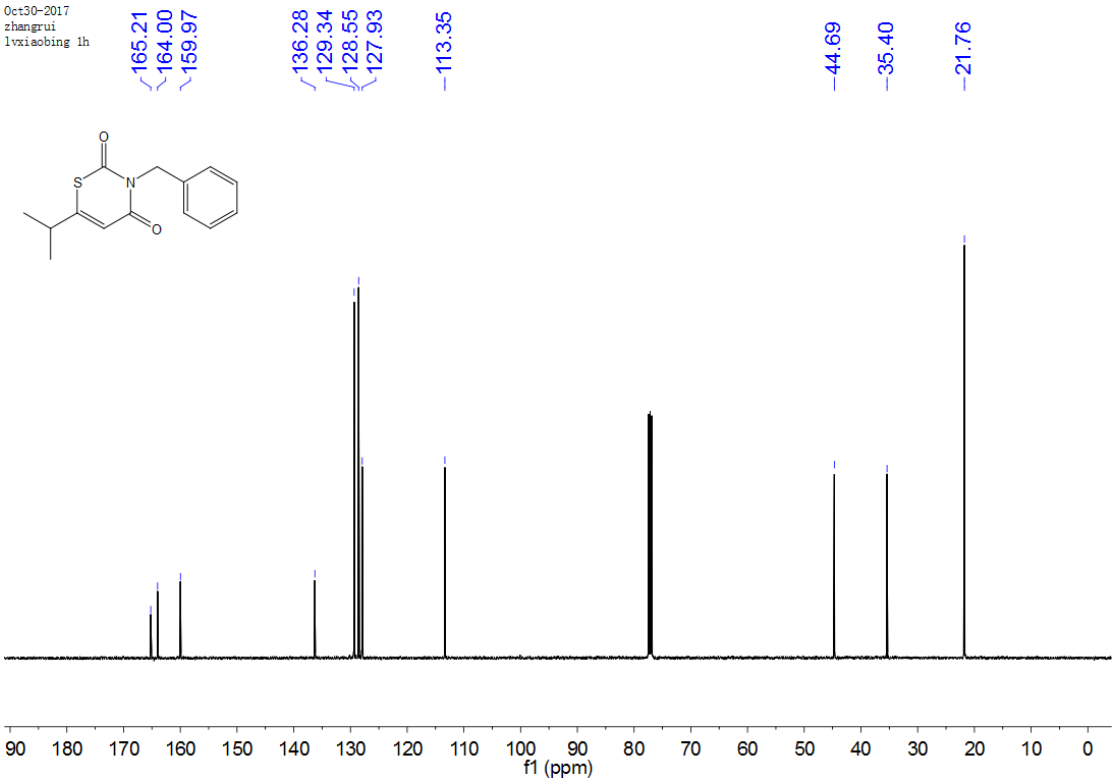
1.0
f1 (ppm)

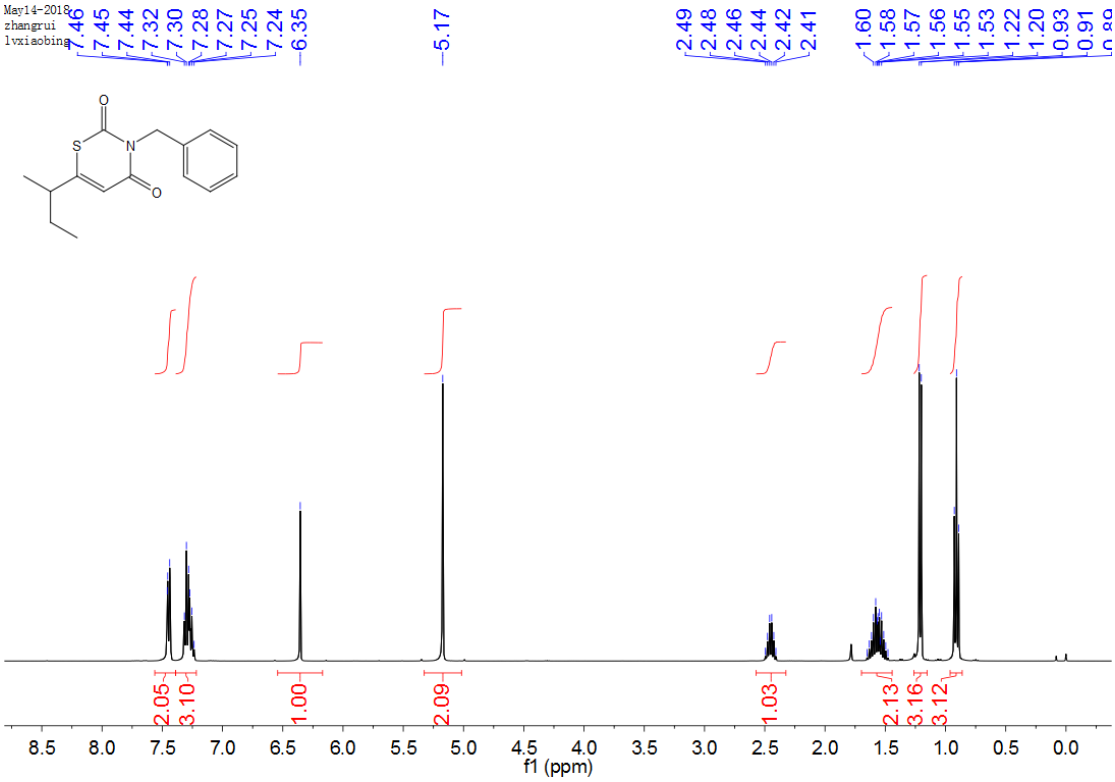

172.26
162.27
148.33
98.72
54.02
31.76
28.26
26.09
25.05
19.24
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

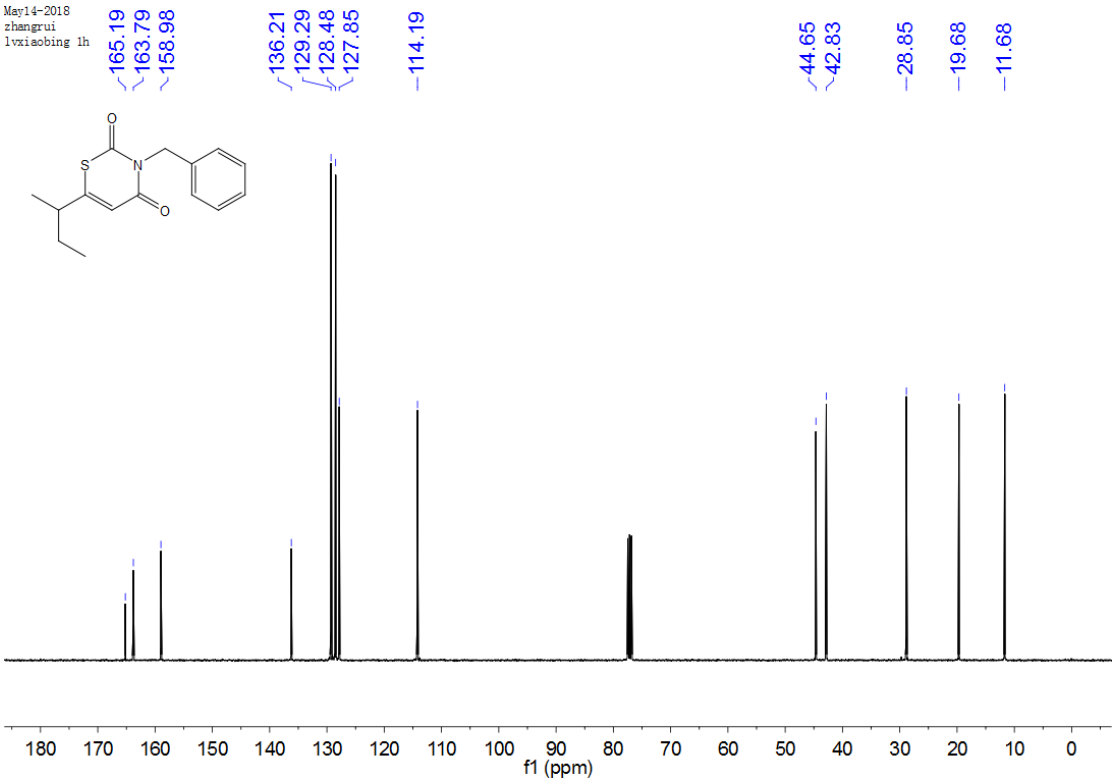

5.79
4.65
2.26
2.25
2.23
2.22
2.21
2.19
1.67
1.66
1.64
1.63
1.61
0.93
0.92
0.90
1.00
2.01
1.00
1.11
4.09
6.13
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
0.8
f1 (ppm)

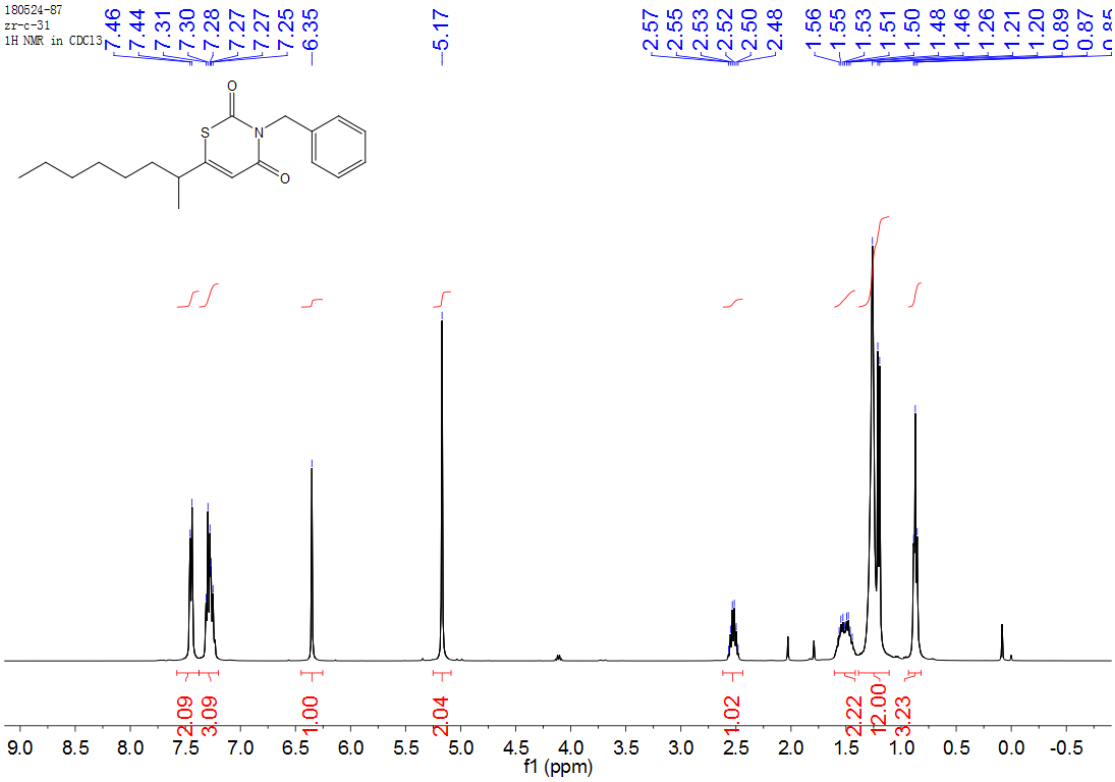

170.66
160.21
148.41
101.01
76.84
71.78
47.08
31.01
24.72
11.56
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

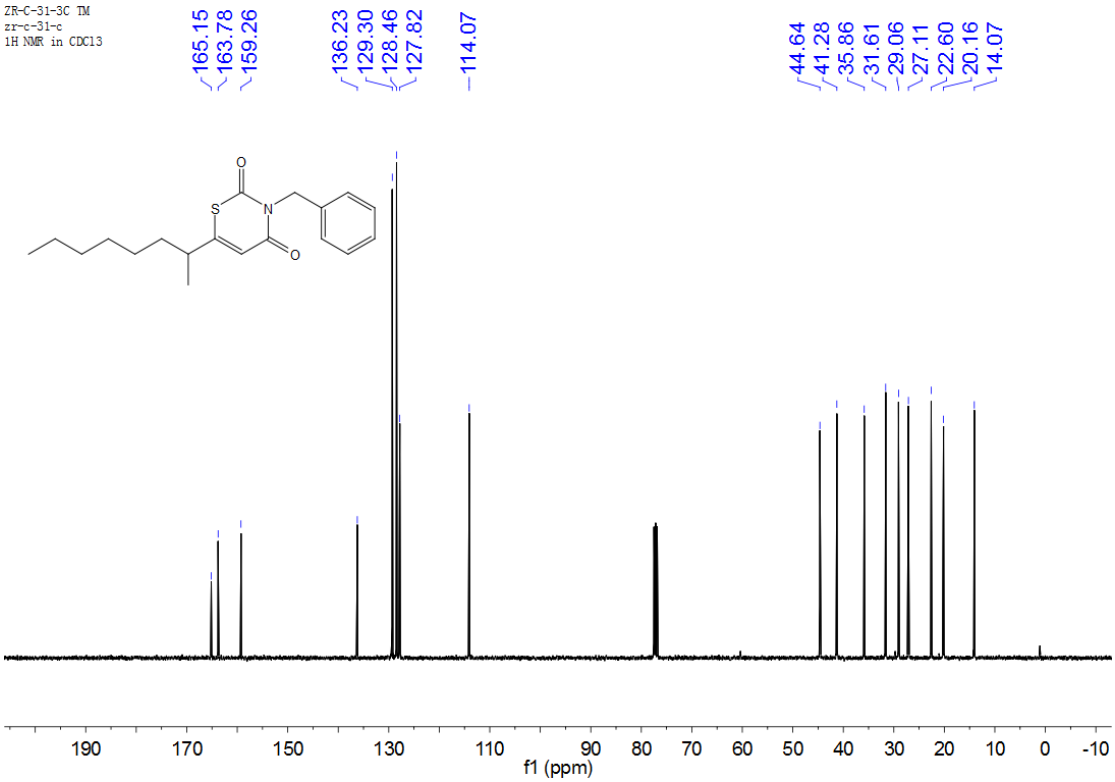

Oct30-2017
zhangrui
lvxiaobing
7.45
7.44
7.32
7.30
7.29
7.27
7.26
7.26
6.37
5.18
2.73
2.72
2.71
2.69
2.68
2.66
2.65
1.25
1.23
2.02
3.18
1.00
2.00
1.04
6.08
f1 (ppm)

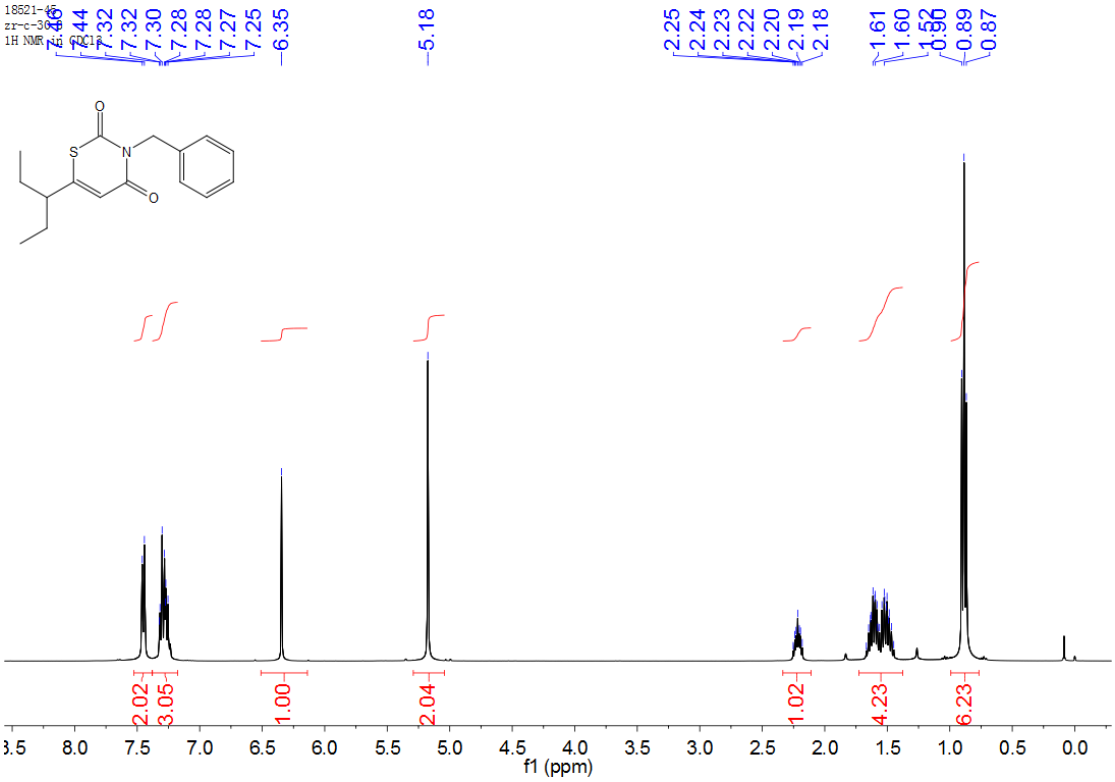

Oct30-2017
zhangrui
lvxiaobing 1h
165.21
164.00
159.97
136.28
129.34
128.55
127.93
113.35
44.69
35.40
21.76
f1 (ppm)

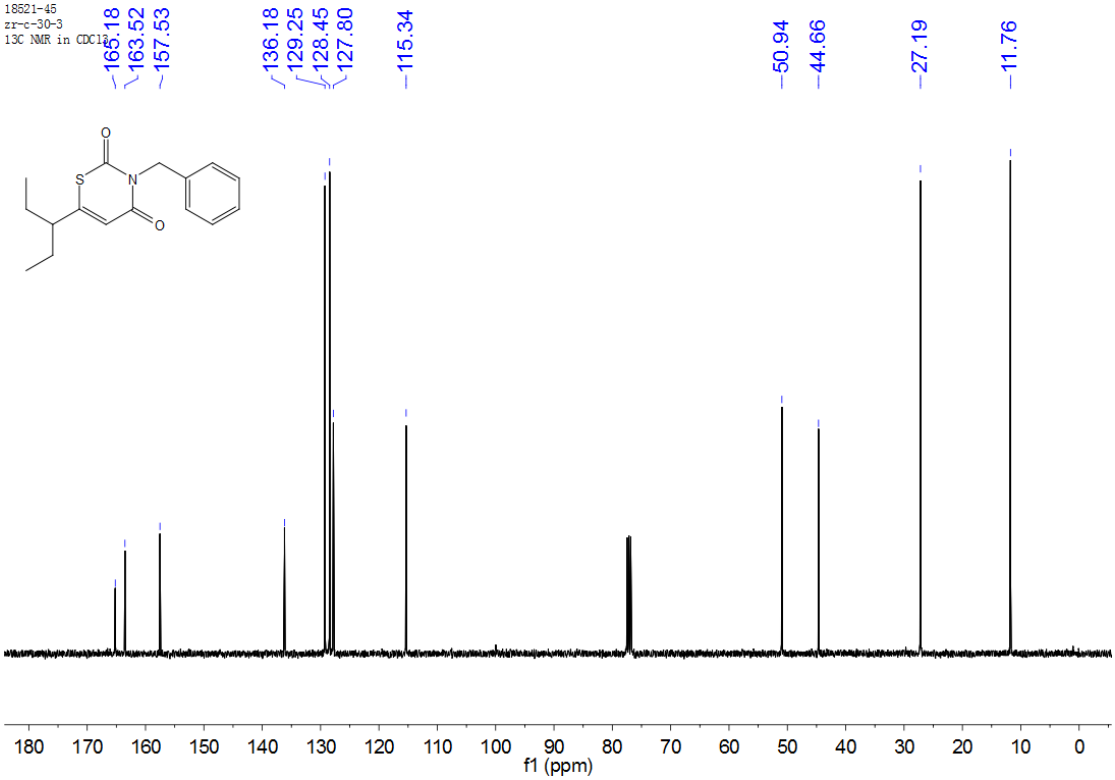

May14-2018
zhangrui
lvxiaobing
7.46
7.45
7.44
7.32
7.30
7.28
7.27
7.25
7.24
6.35
5.17
2.49
2.48
2.46
2.44
2.42
2.41
1.60
1.58
1.57
1.56
1.55
1.53
1.22
1.20
0.93
0.91
O
S
N
O
2.05
3.10
1.00
2.09
1.03
2.13
3.16
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

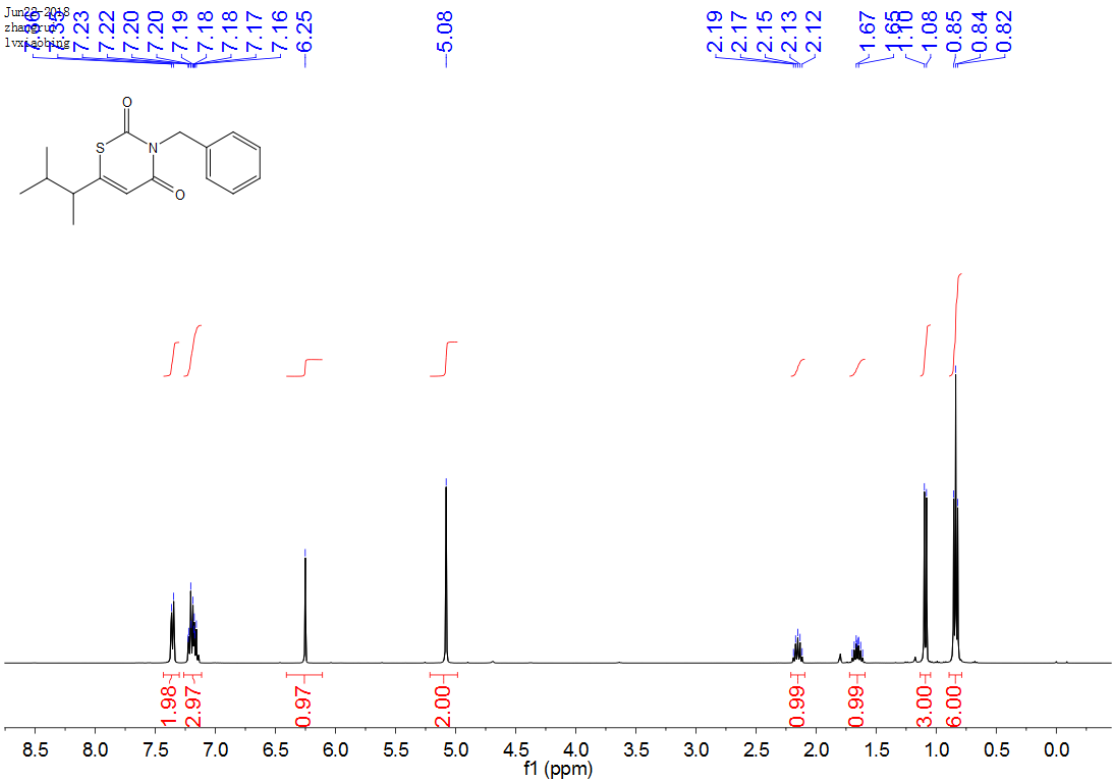

May14-2018
zhangrui
lvxiaobing 1h
165.19
163.79
158.98
136.21
129.29
128.48
127.85
114.19
44.65
42.83
28.85
19.68
11.68
O
S
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

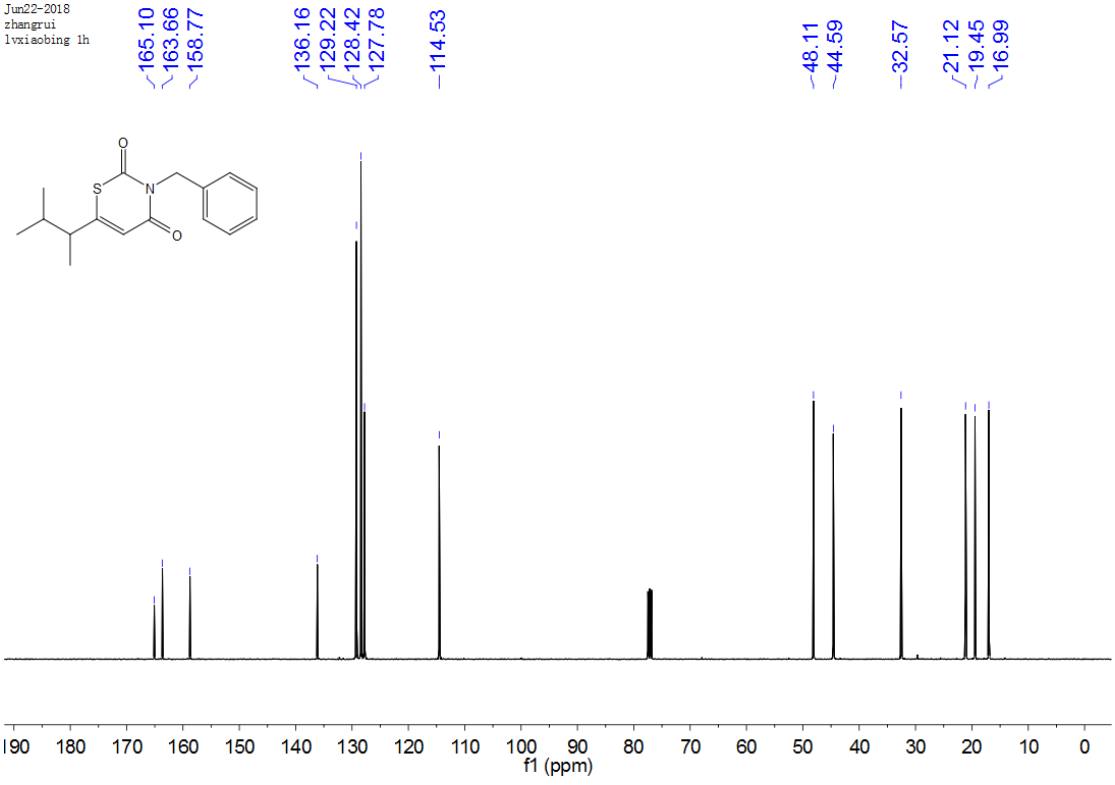

180524-87
zr-c-31
1H NMR in CDCl3
7.46
7.44
7.31
7.30
7.28
7.27
7.27
7.25
6.35
5.17
2.57
2.55
2.53
2.52
2.50
2.48
1.56
1.55
1.53
1.51
1.50
1.48
1.46
1.26
1.21
1.20
0.89
0.87
2.09
3.09
1.00
2.04
1.02
2.22
12.00
3.23
f1 (ppm)

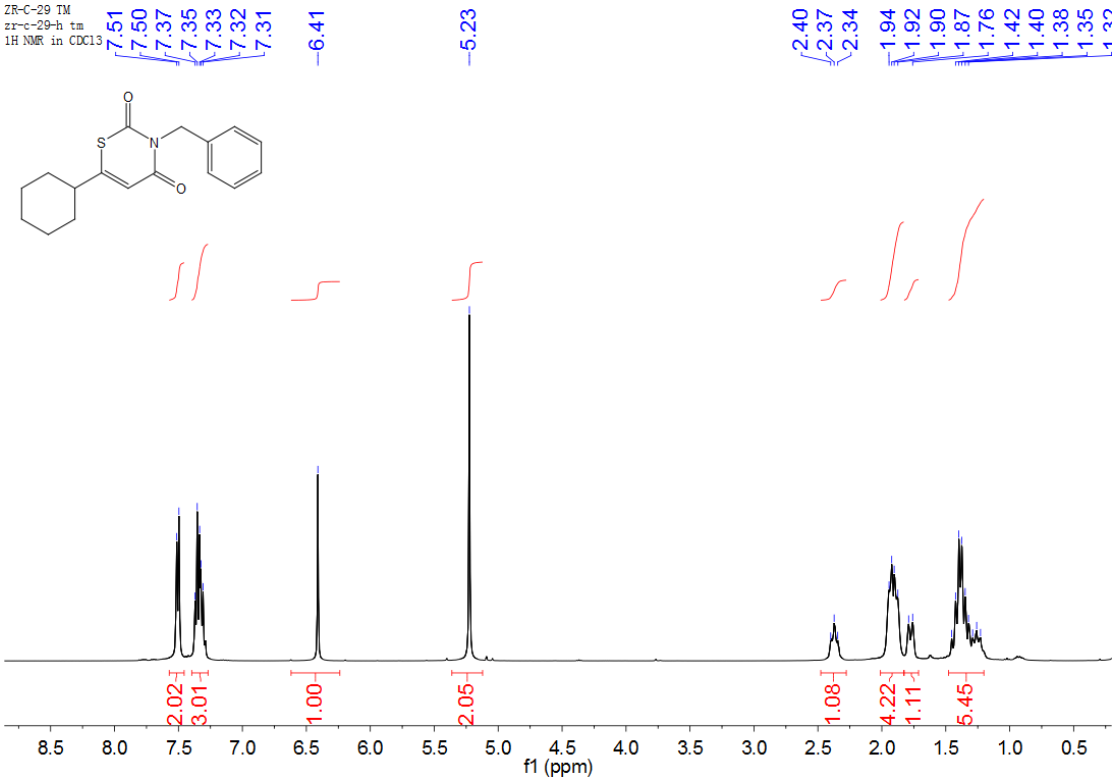

ZR-C-31-3C TM
zr-c-31-c
1H NMR in CDCl3
165.15
163.78
159.26
136.23
129.30
128.46
127.82
114.07
44.64
41.28
35.86
31.61
29.06
27.11
22.60
20.16
14.07
f1 (ppm)

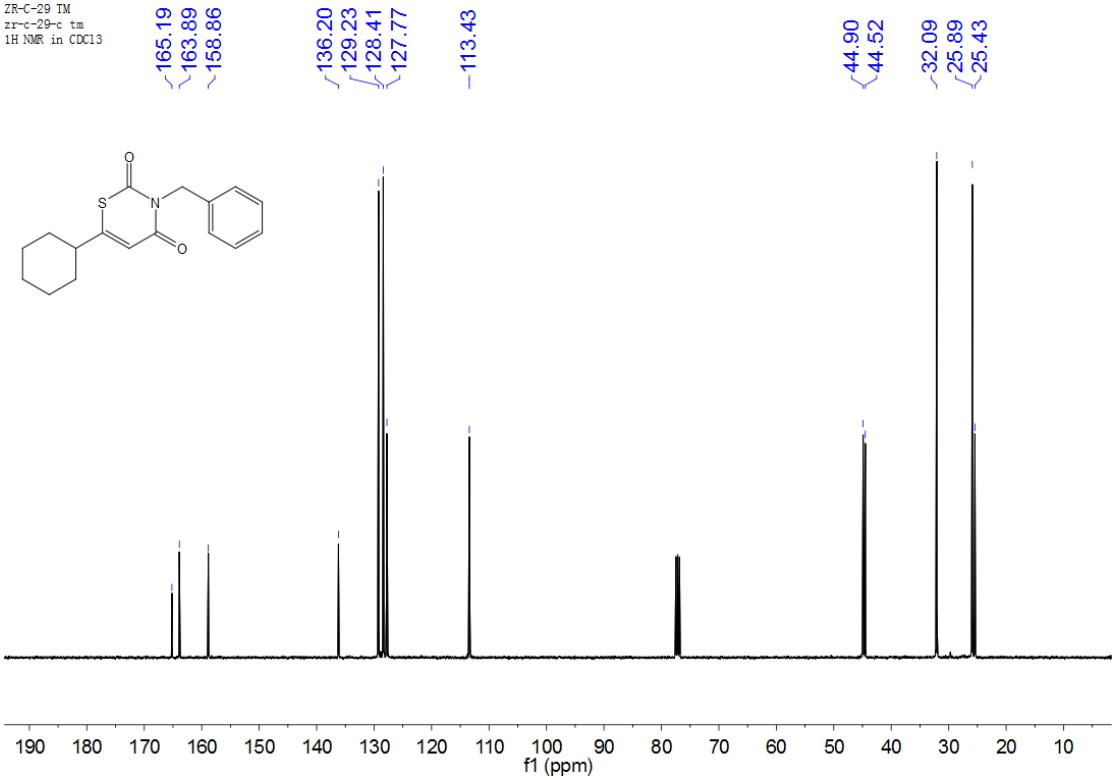

18521-45
zr-c-30-3
1H NMR in CDCl3
7.46
7.44
7.32
7.32
7.30
7.28
7.28
7.27
7.25
6.35
5.18
2.25
2.24
2.23
2.22
2.20
2.19
2.18
1.61
1.60
1.52
0.90
0.89
0.87
2.02
3.05
1.00
2.04
1.02
4.23
6.23
f1 (ppm)

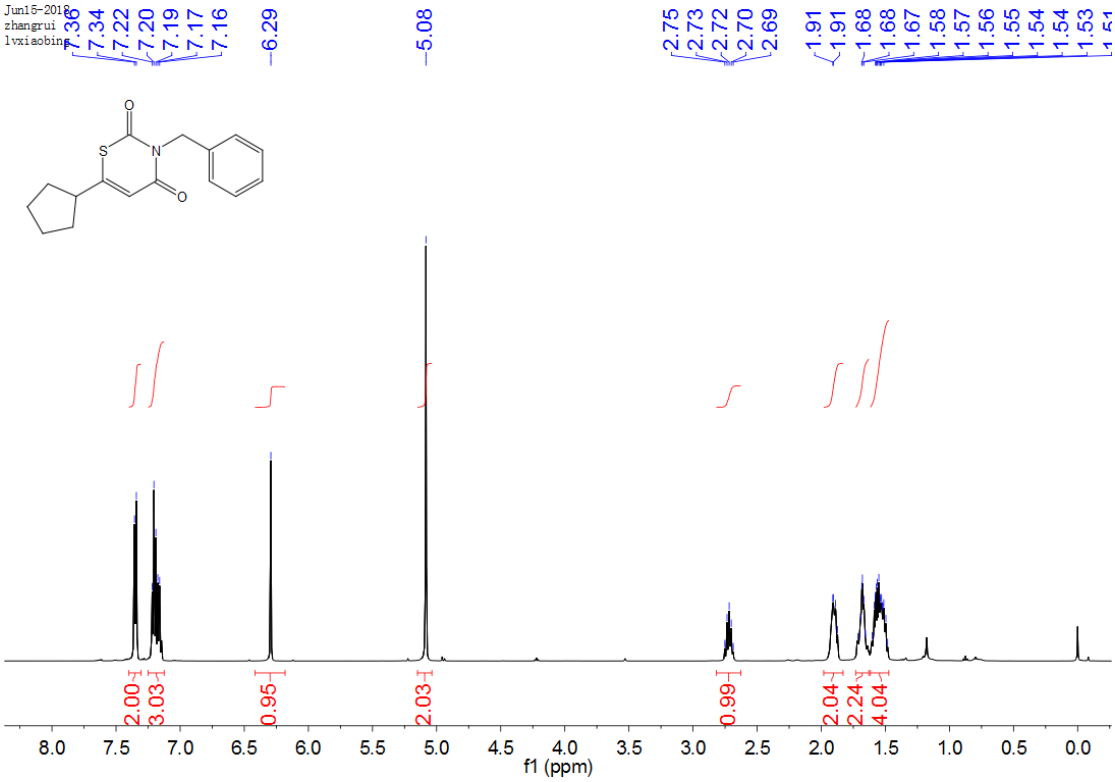

18521-45
zr-c-30-3
13C NMR in CDCl3
165.18
163.52
157.53
136.18
129.25
128.45
127.80
115.34
50.94
44.66
27.19
11.76
f1 (ppm)

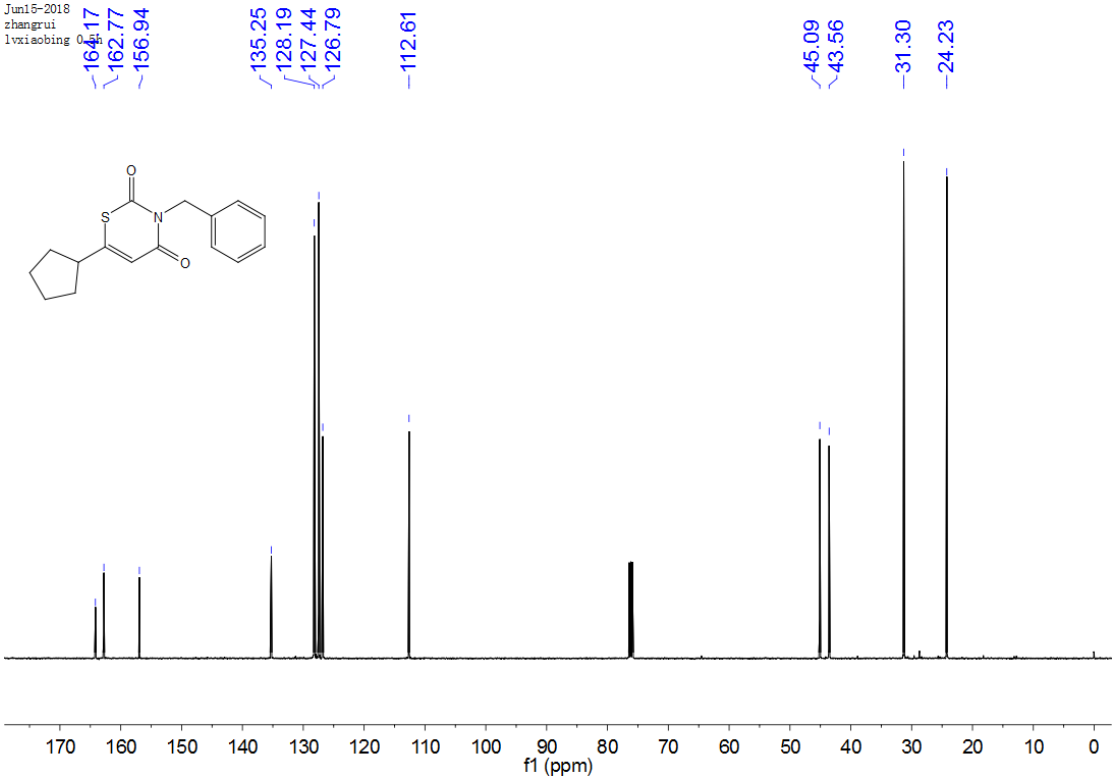

Jun22-2018
zhangrui
lvxiaobing
7.23
7.22
7.20
7.20
7.19
7.18
7.18
7.17
7.16
6.25
5.08
2.19
2.17
2.15
2.13
2.12
1.67
1.65
1.10
1.08
0.85
0.84
0.82
1.98
2.97
0.97
2.00
0.99
0.99
3.00
6.00
f1 (ppm)

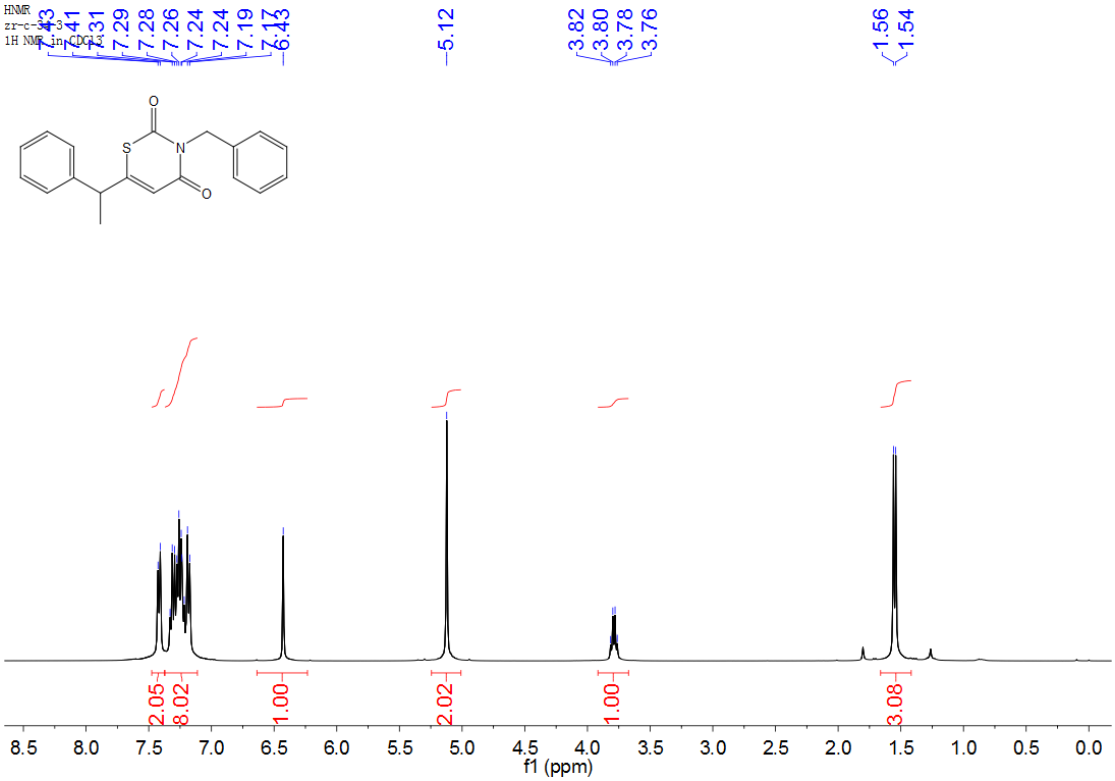

Jun22-2018
zhangrui
lvxiaobing 1h
165.10
163.66
158.77
136.16
129.22
128.42
127.78
114.53
48.11
44.59
32.57
21.12
19.45
16.99
f1 (ppm)

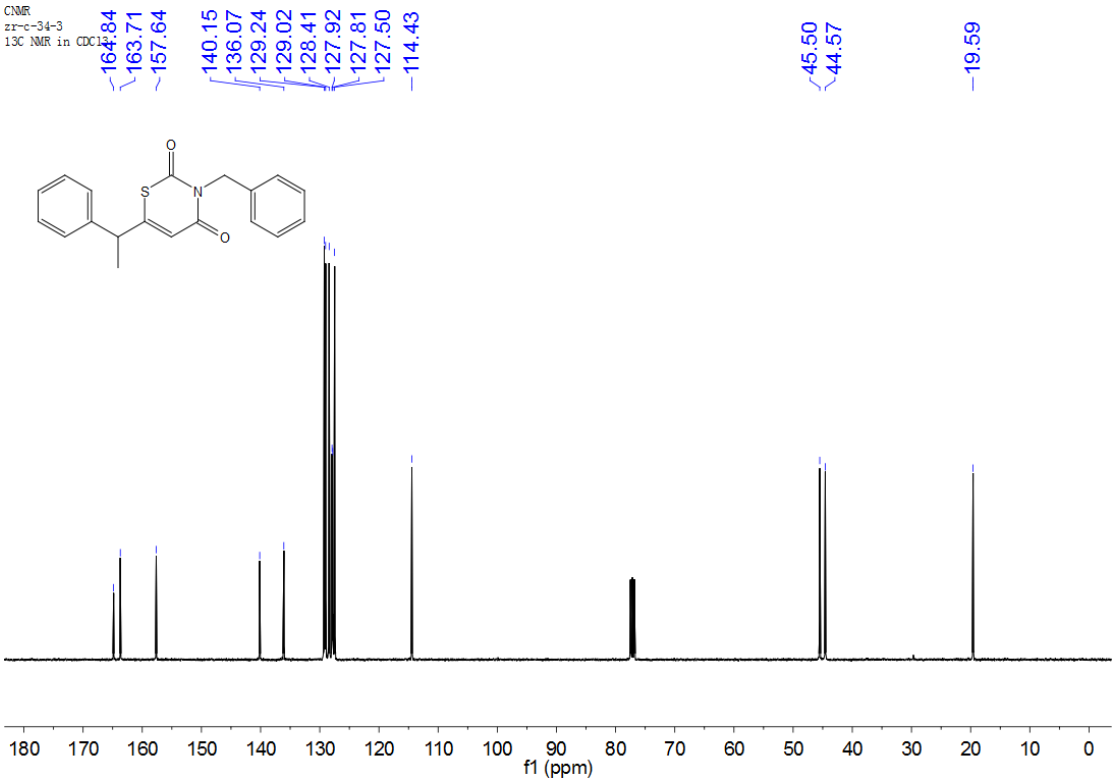

ZR-C-29 TM
zr-c-29-h tm
1H NMR in CDCl3
7.51
7.50
7.37
7.35
7.33
7.32
7.31
6.41
5.23
2.40
2.37
2.34
1.94
1.92
1.90
1.87
1.76
1.42
1.40
1.38
1.35
2.02
3.01
1.00
2.05
1.08
4.22
1.11
5.45
f1 (ppm)


ZR-C-29 TM
zr-c-29-c tm
1H NMR in CDCl3
165.19
163.89
158.86
136.20
129.23
128.41
127.77
113.43
44.90
44.52
32.09
25.89
25.43
f1 (ppm)

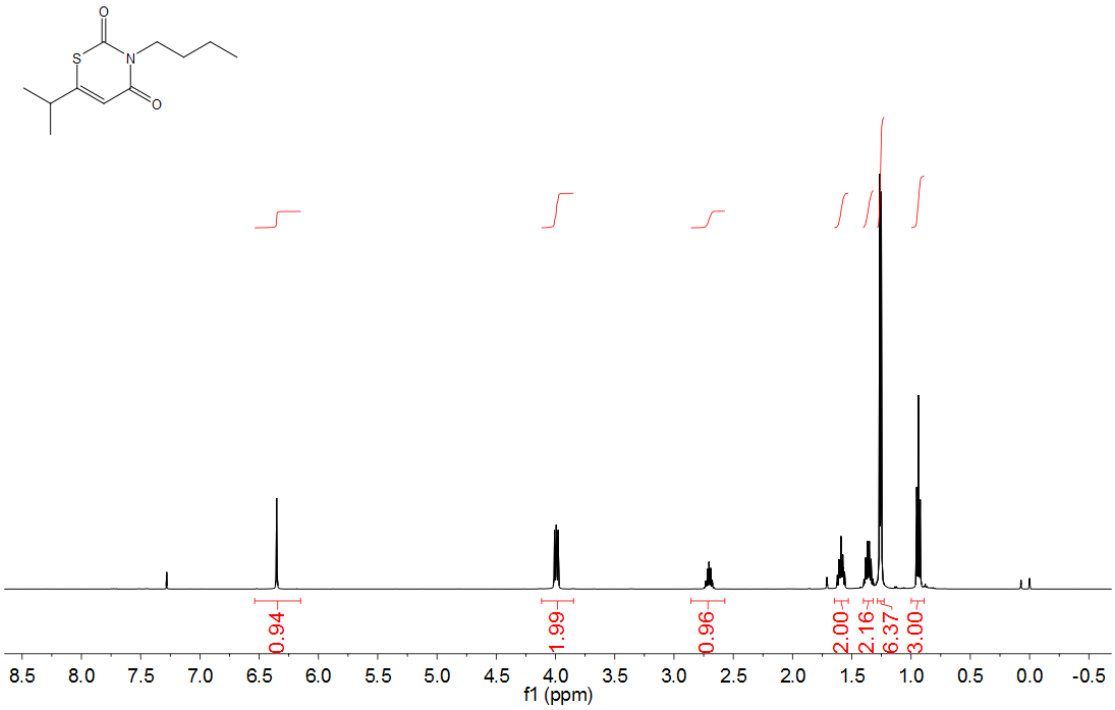

Jun15-2018
zhangrui
lvxiaobing
7.36
7.34
7.22
7.20
7.19
7.17
7.16
6.29
5.08
2.75
2.73
2.72
2.70
2.69
1.91
1.91
1.68
1.67
1.58
1.57
1.56
1.55
1.54
1.54
1.53
2.00
3.03
0.95
2.03
0.99
2.04
2.24
4.04
f1 (ppm)


Jun15-2018
zhangrui
lvxiaobing 0-1
164.17
162.77
156.94
135.25
128.19
127.44
126.79
112.61
45.09
43.56
31.30
24.23
f1 (ppm)

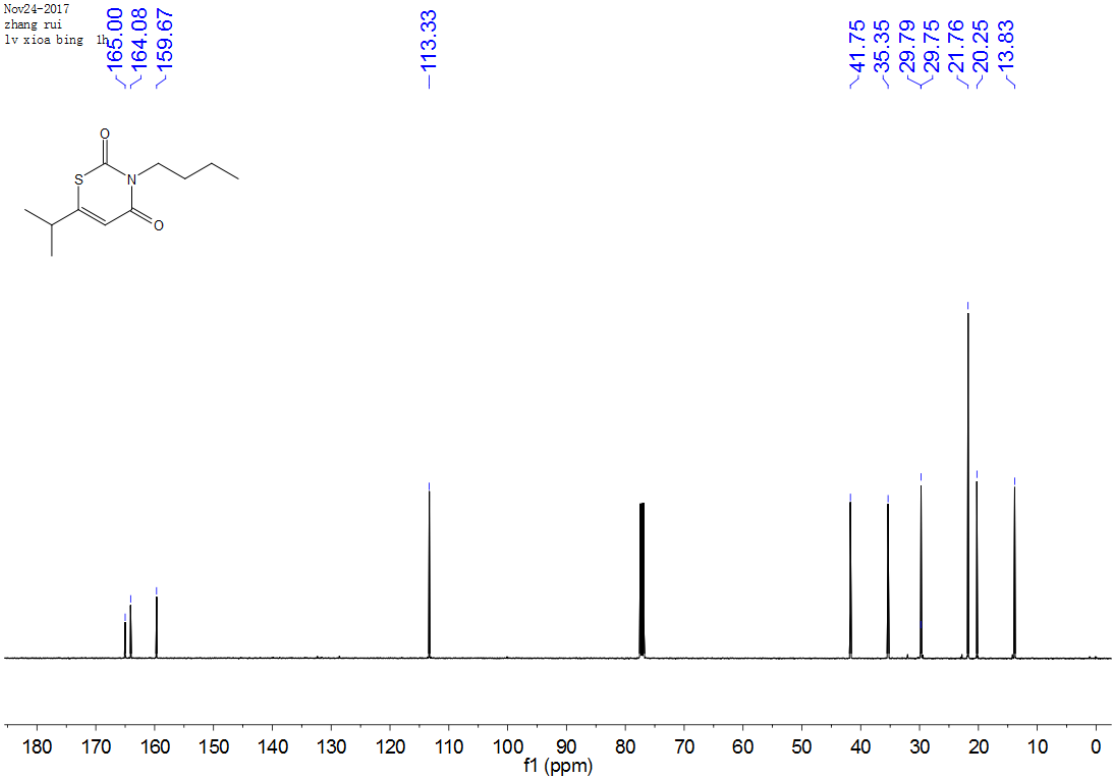

HNMR
zr-c-34-3
1H NMR in CDCl3
7.43
7.41
7.31
7.29
7.28
7.26
7.24
7.24
7.19
7.17
7.13
6.43
5.12
3.82
3.80
3.78
3.76
1.56
1.54
O
S
N
O
2.05
8.02
1.00
2.02
1.00
3.08
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

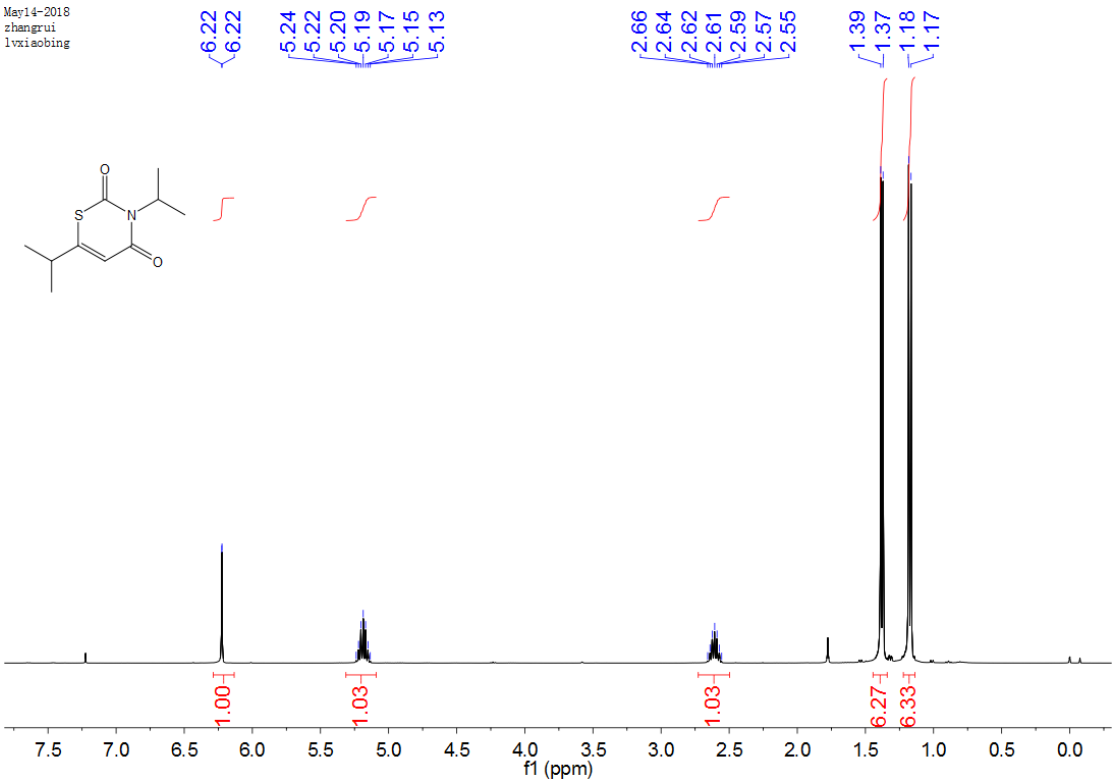

CNMR
zr-c-34-3
13C NMR in CDCl3
164.84
163.71
157.64
140.15
136.07
129.24
129.02
128.41
127.92
127.81
127.50
114.43
45.50
44.57
19.59
O
S
N
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

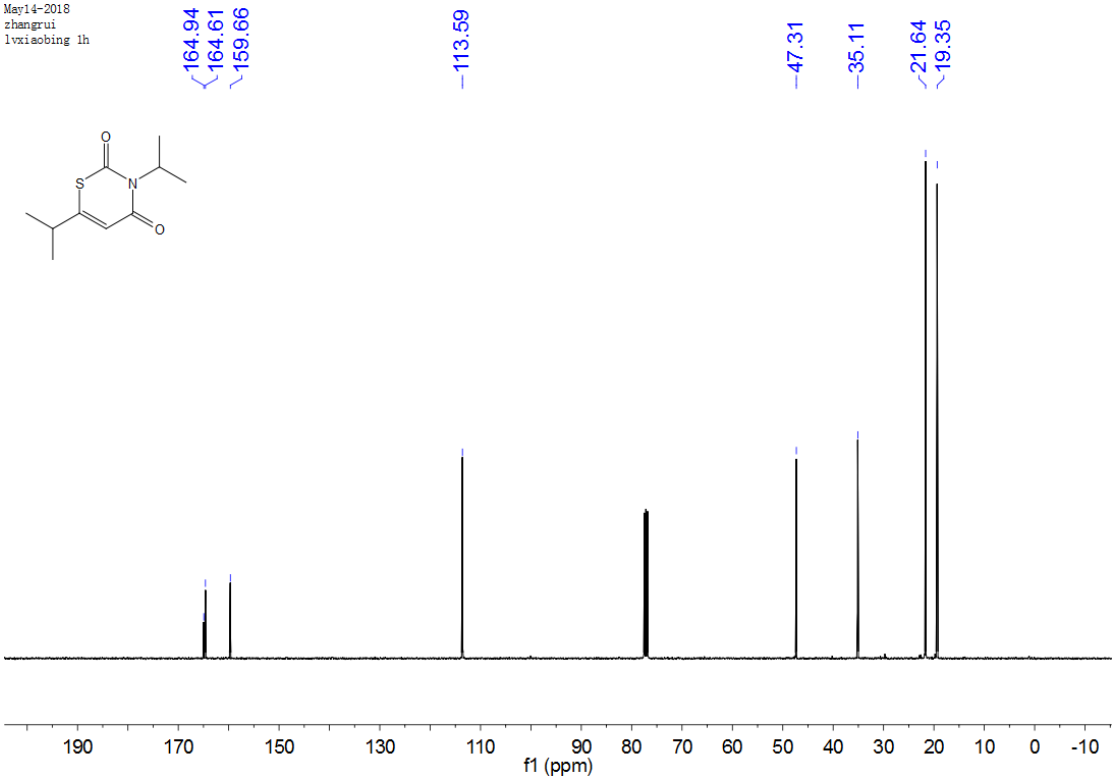
Nov24-2017
zhang rui
lv xioa bing

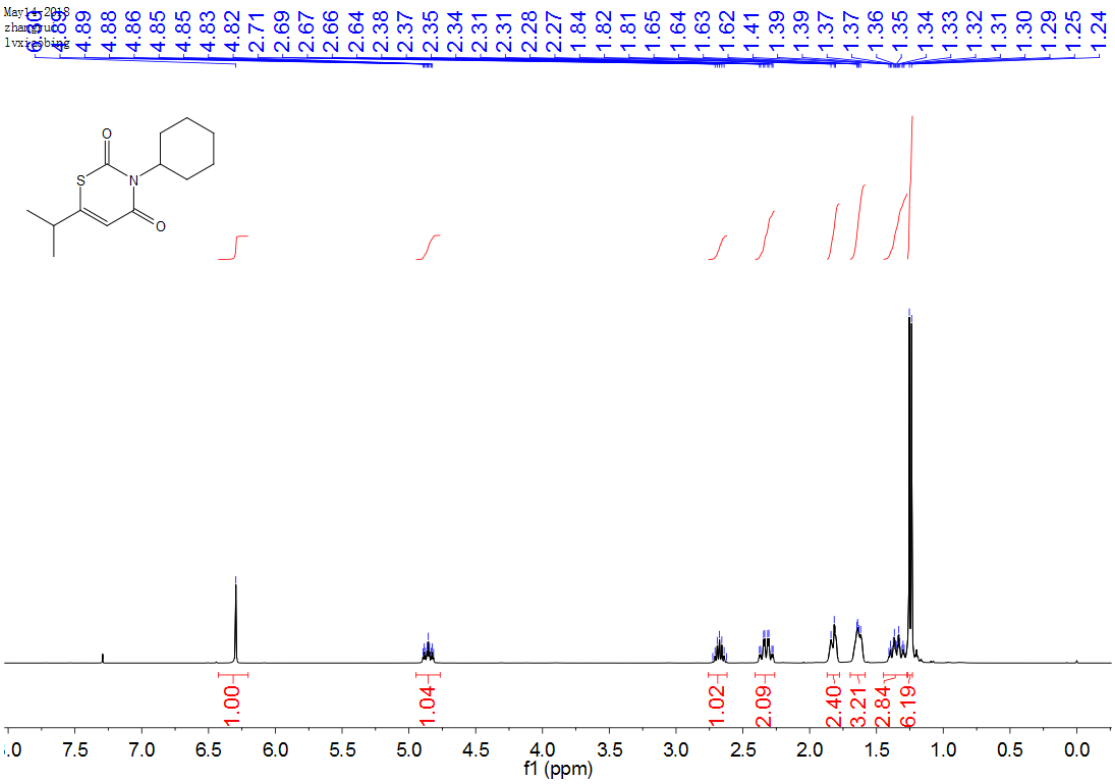


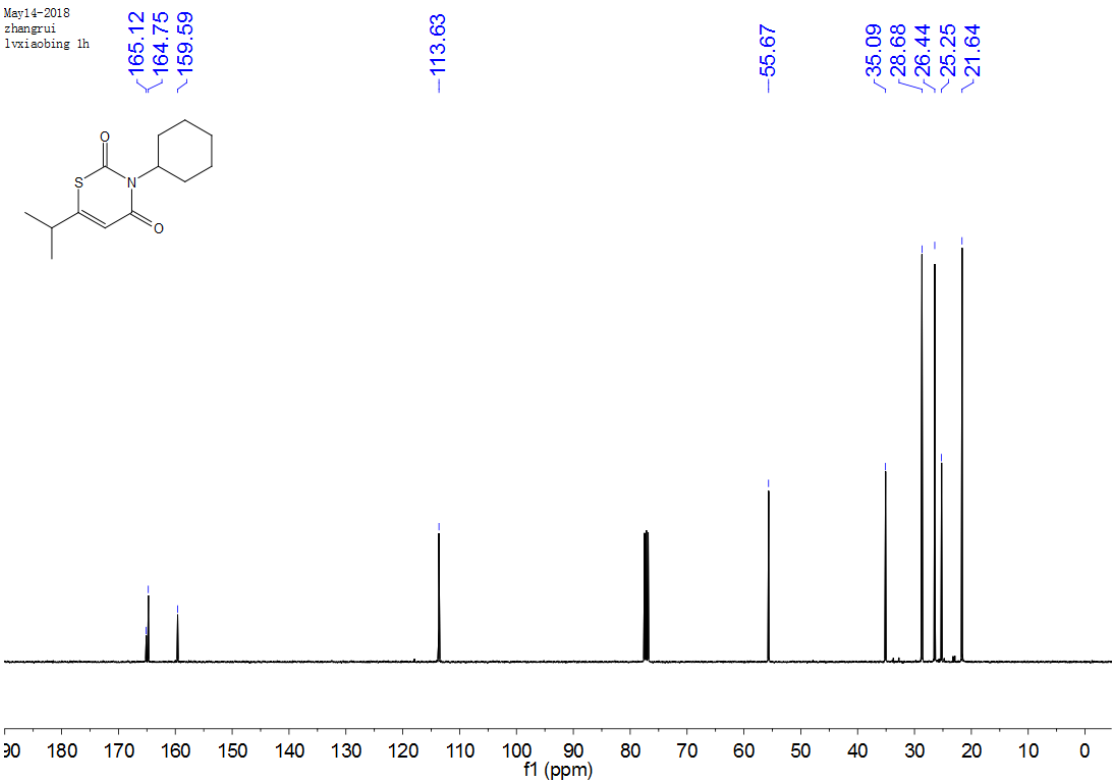
Nov24-2017
zhang rui
lv xioa bing 1h

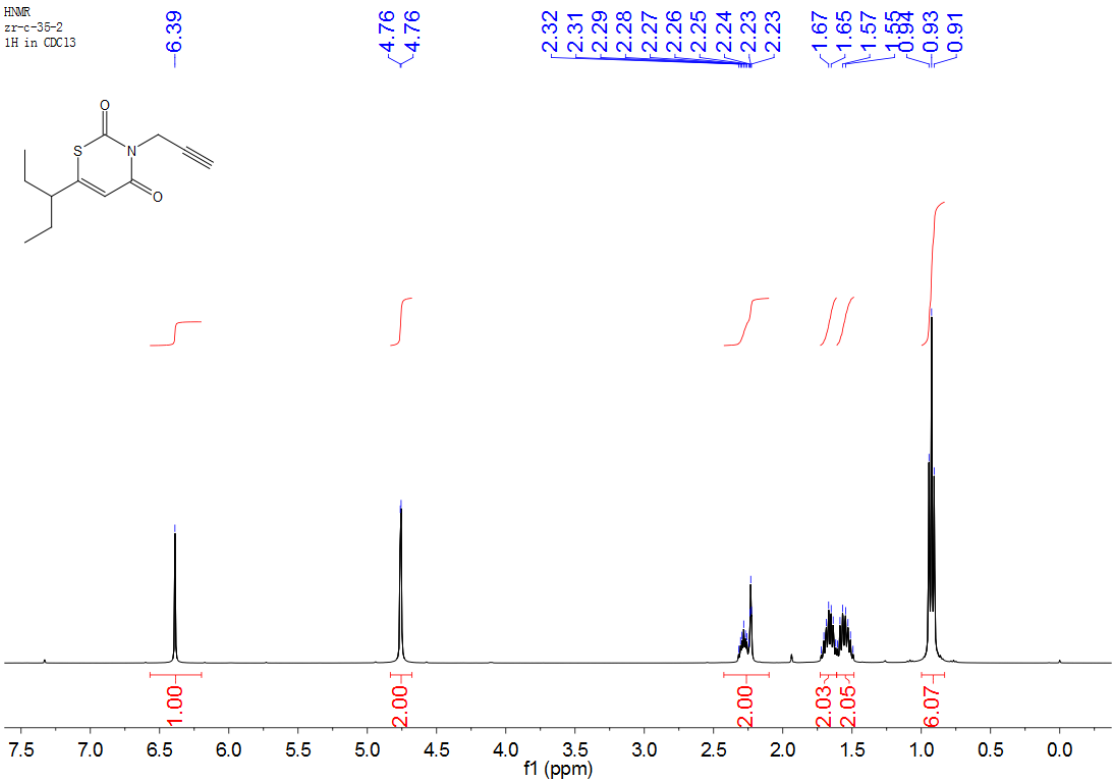


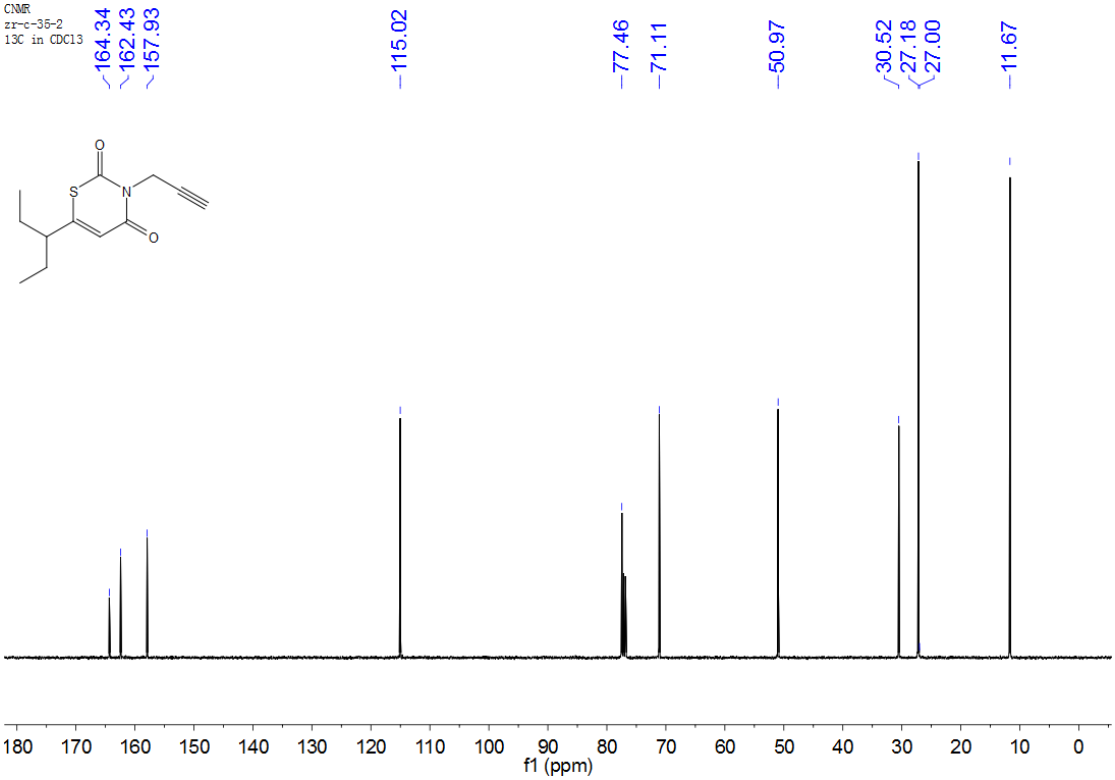

May14-2018
zhangrui
lvxiaobing
6.22
6.22
5.24
5.22
5.20
5.19
5.17
5.15
5.13
2.66
2.64
2.62
2.61
2.59
2.57
2.55
1.39
1.37
1.18
1.17
1.00
1.03
1.03
6.27
6.33
f1 (ppm)

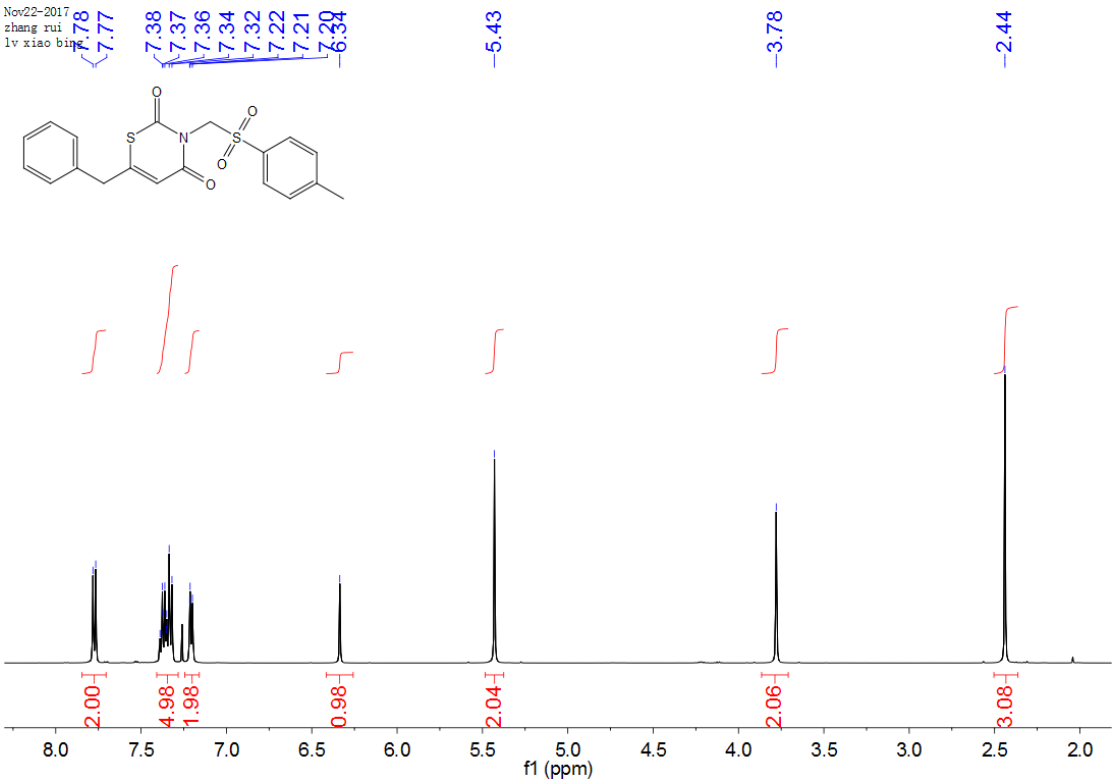

May14-2018
zhangrui
lvxiaobing 1h
164.94
164.61
159.66
113.59
47.31
35.11
21.64
19.35
f1 (ppm)

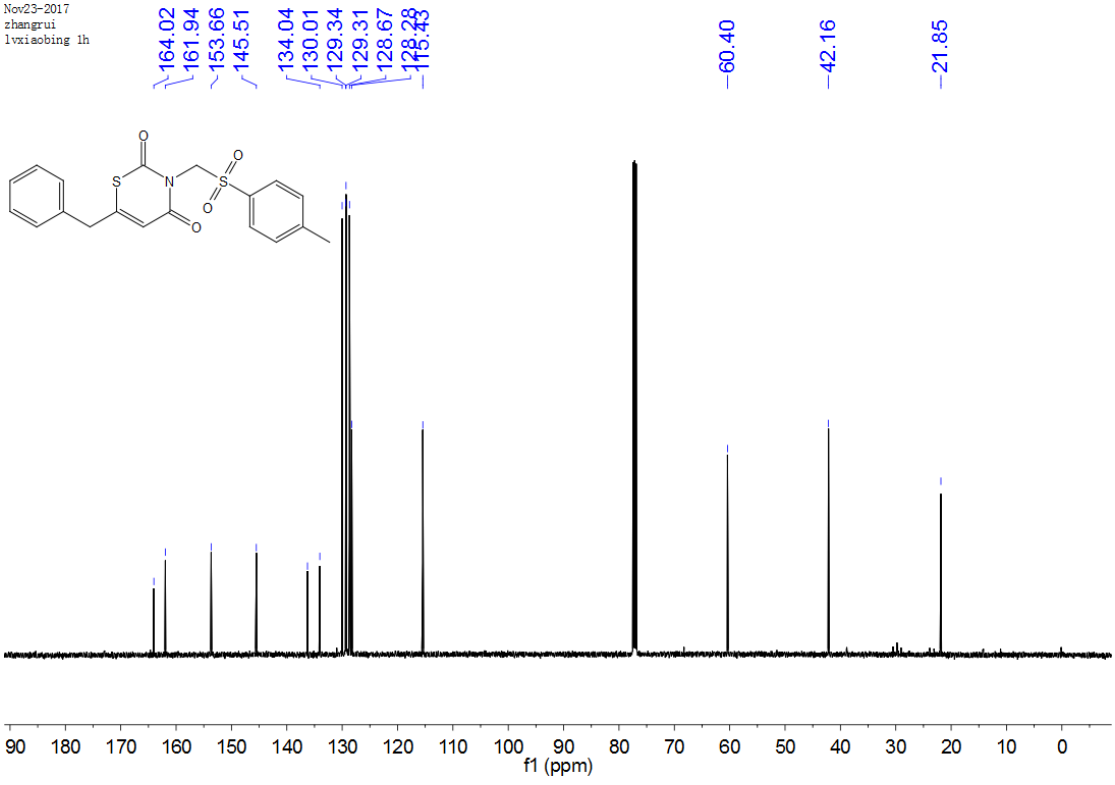

May14-2018
zhangrui
lvxiaobing
4.89
4.88
4.86
4.85
4.85
4.83
4.82
2.71
2.69
2.67
2.66
2.64
2.38
2.37
2.35
2.34
2.31
2.31
2.28
2.27
1.84
1.82
1.81
1.65
1.64
1.63
1.62
1.41
1.39
1.39
1.37
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.30
1.29
1.25
1.24
1.00
1.04
1.02
2.09
2.40
3.21
2.84
6.19
f1 (ppm)

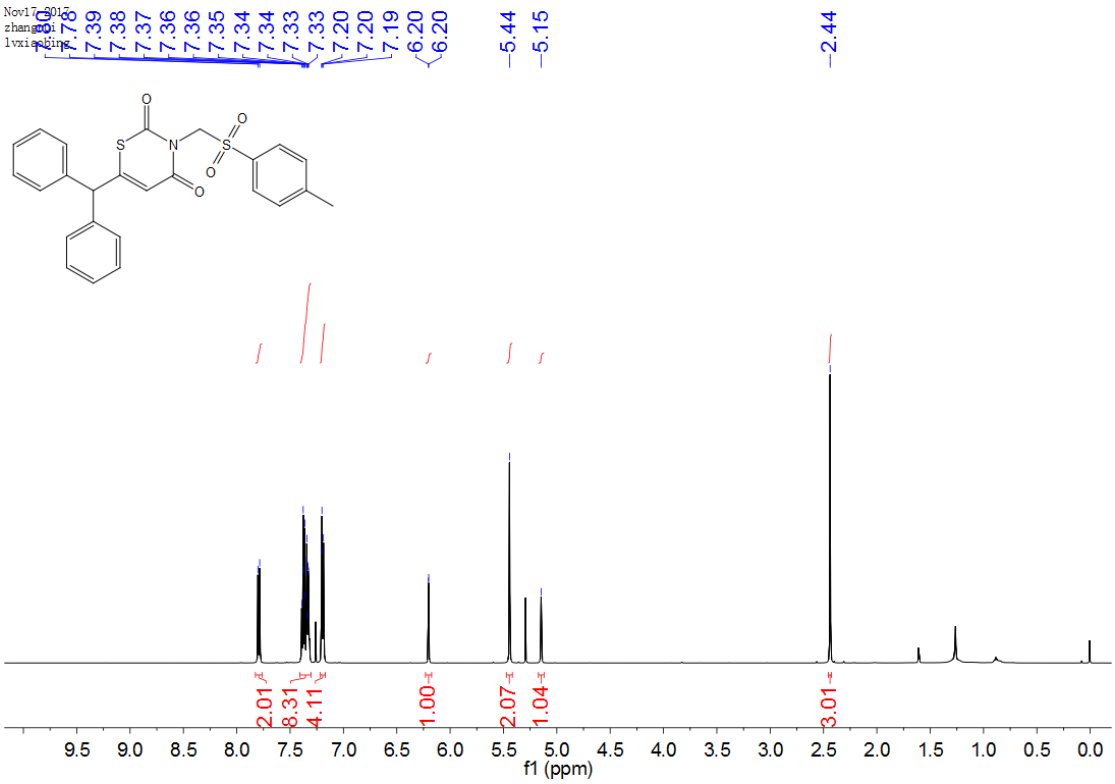

May14-2018
zhangrui
lvxiaobing 1h
165.12
164.75
159.59
113.63
55.67
35.09
28.68
26.44
25.25
21.64
f1 (ppm)

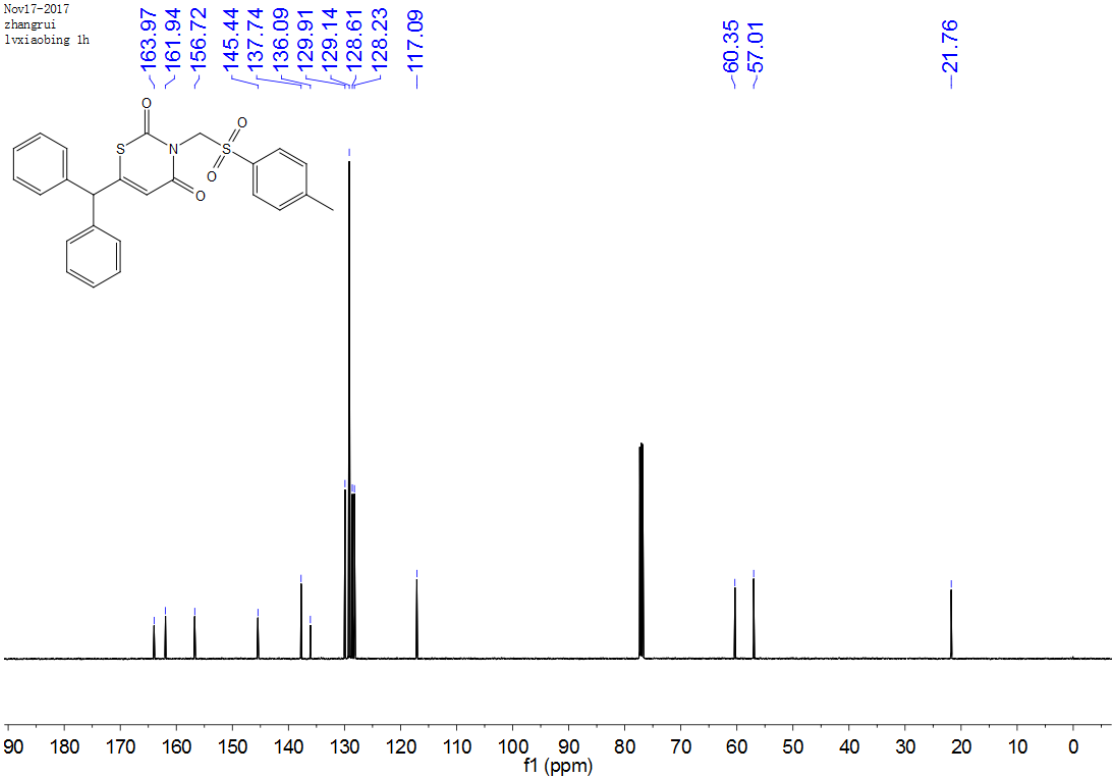

HNMR
zr-c-35-2
1H in CDCl3
6.39
4.76
4.76
2.32
2.31
2.29
2.28
2.27
2.26
2.25
2.24
2.23
2.23
1.67
1.65
1.57
1.55
0.94
0.93
0.91
1.00
2.00
2.00
2.03
2.05
6.07
f1 (ppm)

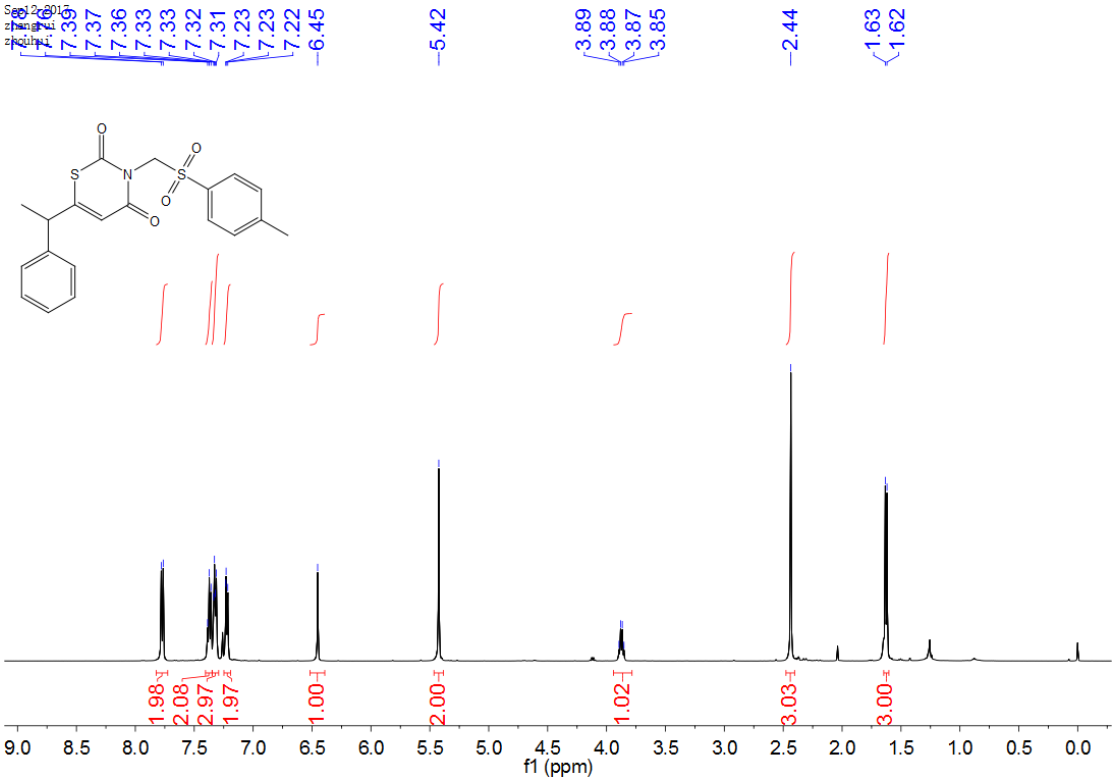

CNMR
zr-c-35-2
13C in CDCl3
164.34
162.43
157.93
115.02
77.46
71.11
50.97
30.52
27.18
27.00
11.67
f1 (ppm)

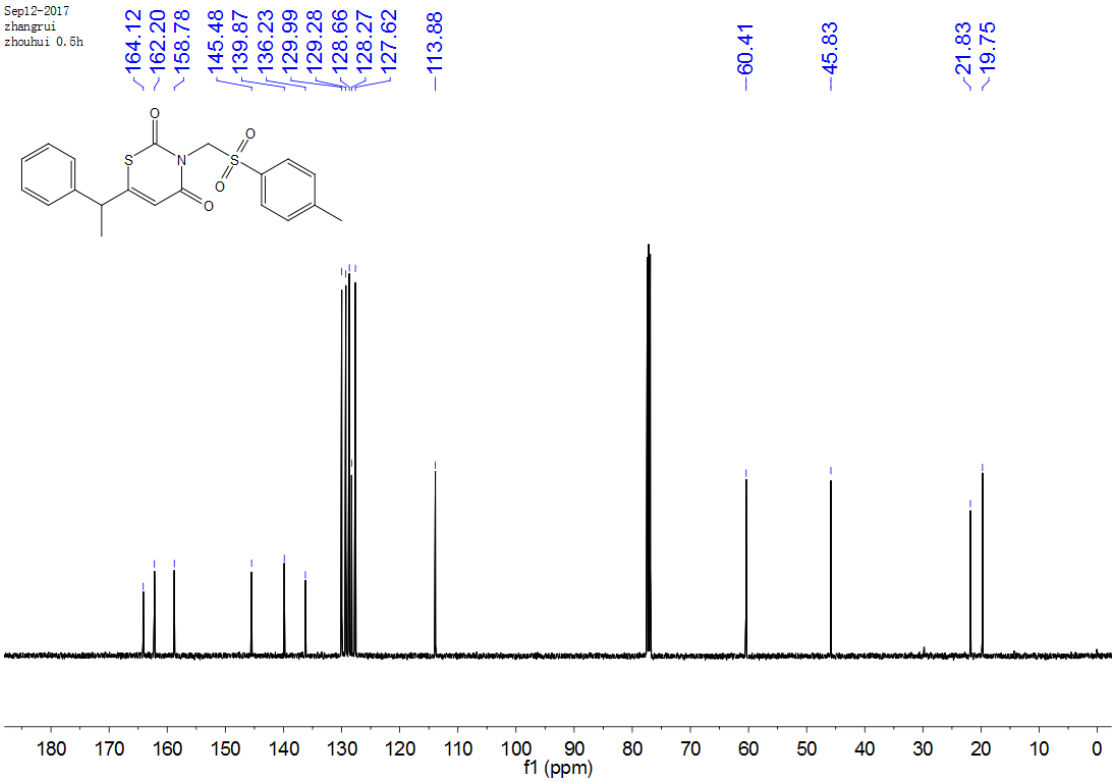

Nov22-2017
zhang rui
lv xiao bing
7.78
7.77
7.38
7.37
7.36
7.34
7.32
7.22
7.21
7.20
6.34
5.43
3.78
2.44
2.00
4.98
1.98
0.98
2.04
2.06
3.08
f1 (ppm)

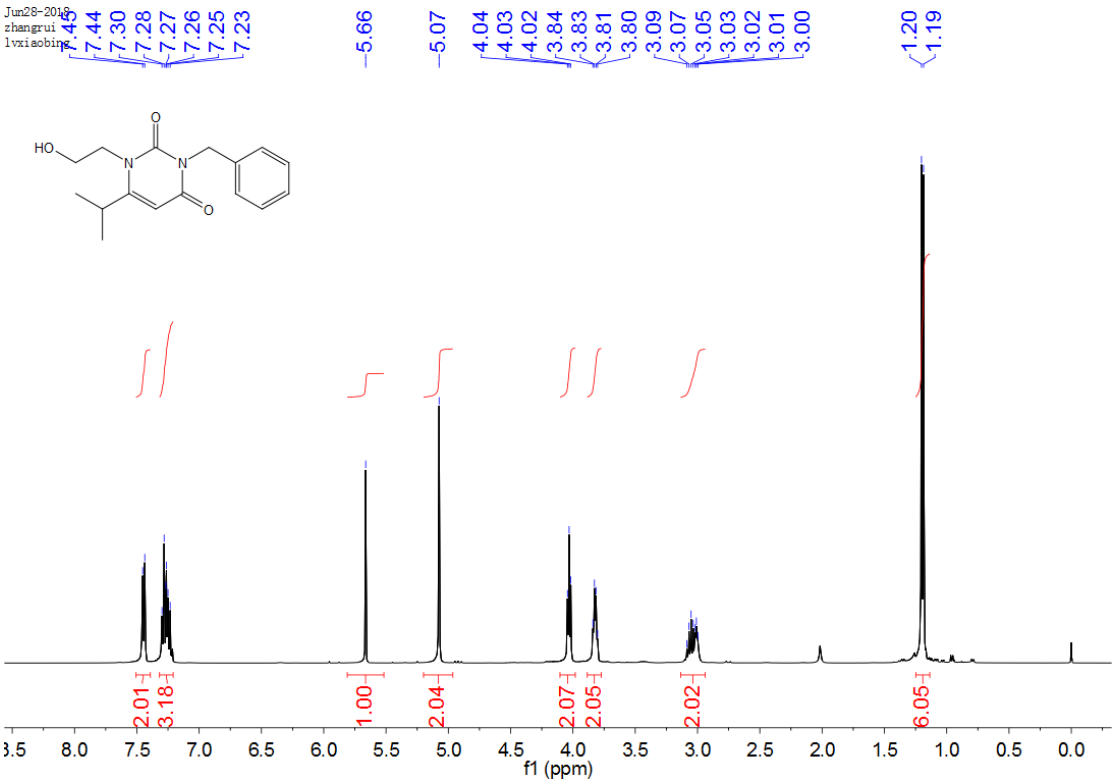

Nov23-2017
zhangrui
lvxiaobing 1h
164.02
161.94
153.66
145.51
134.04
130.01
129.34
129.31
128.67
60.40
42.16
21.85
f1 (ppm)

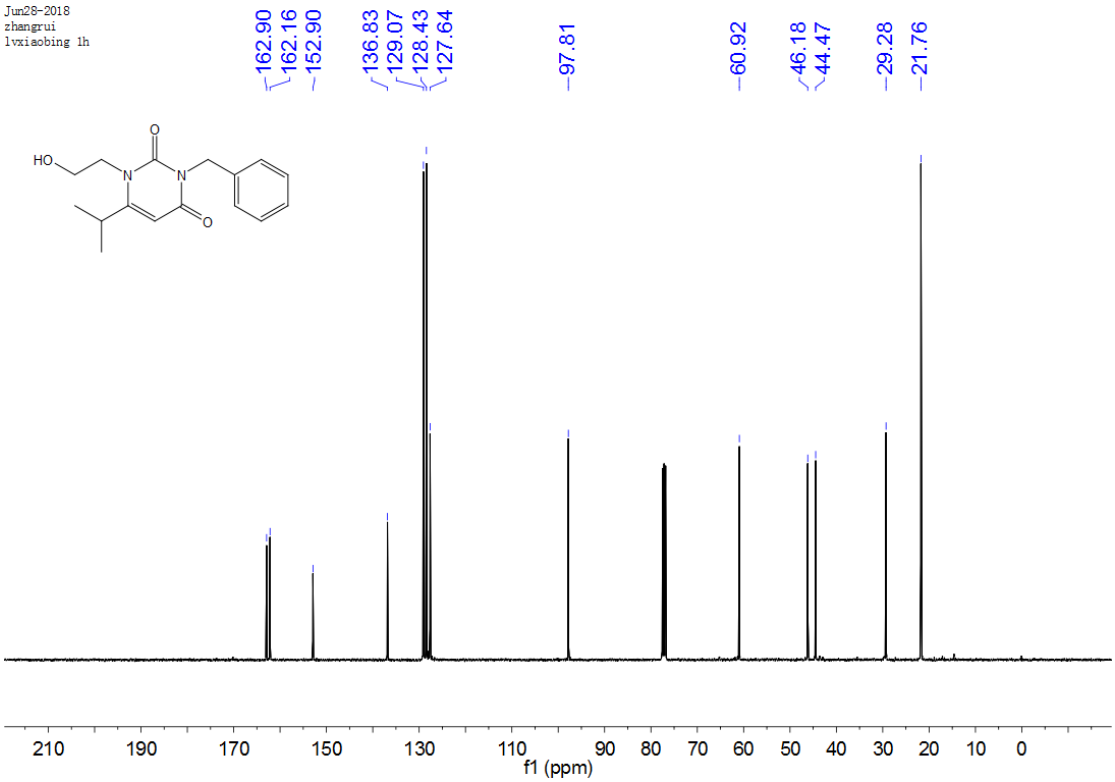

Nov17-2017
zhangrui
lvxiaobing
7.78
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.33
7.20
7.20
7.19
6.20
6.20
5.44
5.15
2.44
2.01
8.31
4.11
1.00
2.07
1.04
3.01
f1 (ppm)

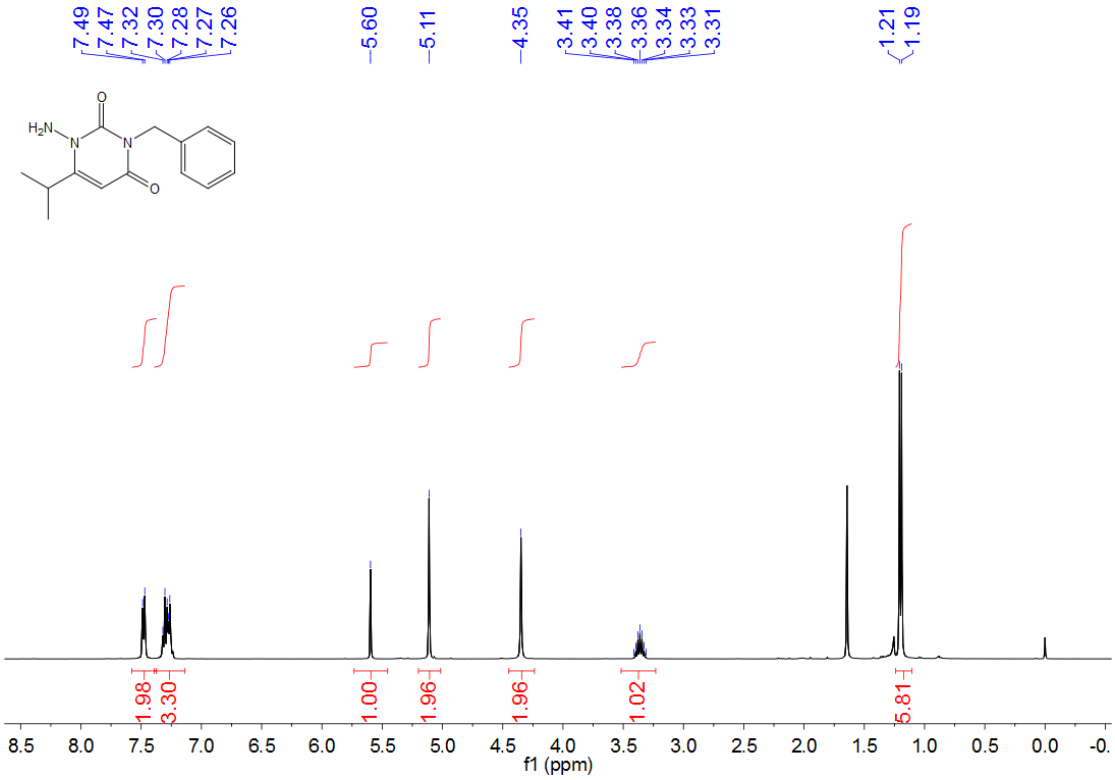

Nov17-2017
zhangrui
lvxiaobing 1h
163.97
161.94
156.72
145.44
137.74
136.09
129.91
129.14
128.61
128.23
117.09
60.35
57.01
21.76
f1 (ppm)

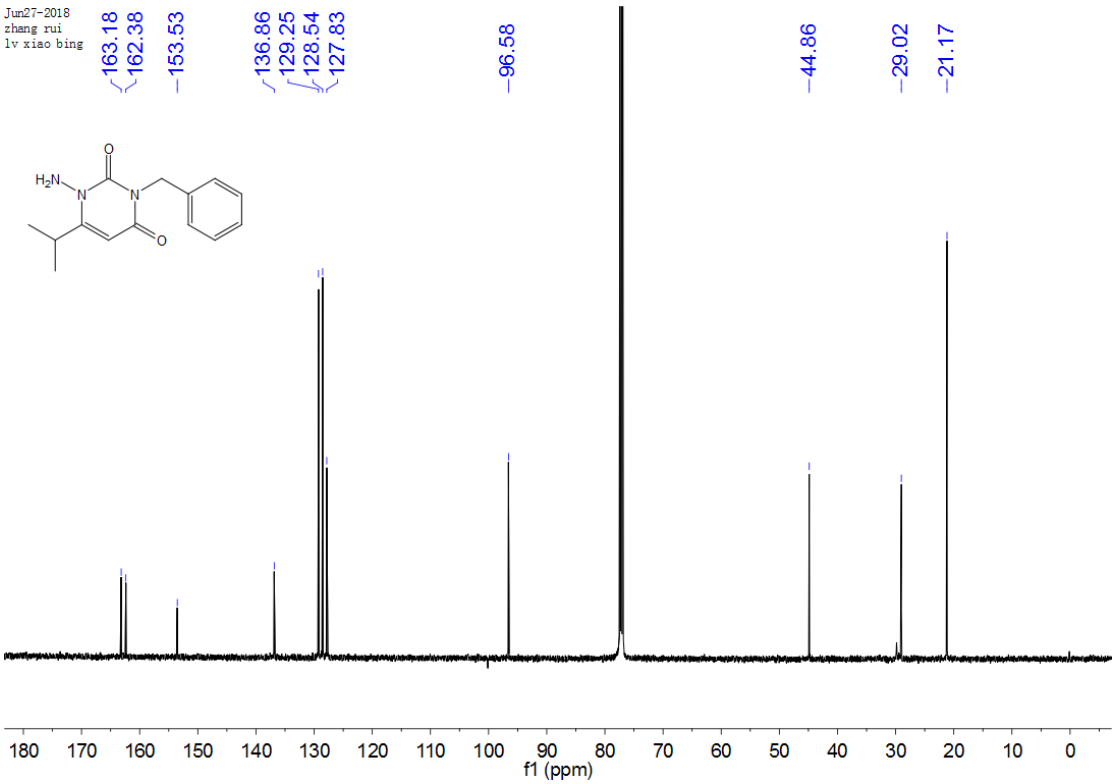

7.40
7.39
7.37
7.36
7.33
7.33
7.32
7.31
7.23
7.23
7.22
6.45
5.42
3.89
3.88
3.87
3.85
2.44
1.63
1.62
1.98
2.08
2.97
1.97
1.00
2.00
1.02
3.03
3.00
f1 (ppm)

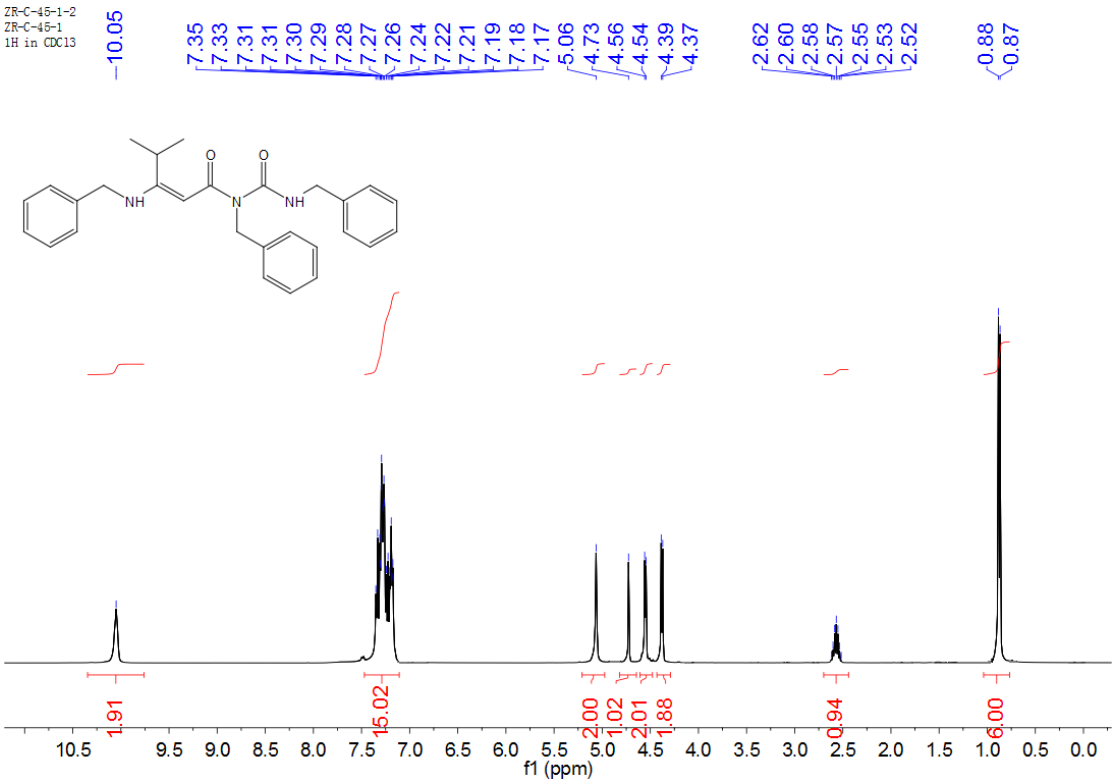

Sep12-2017
zhangrui
zhouhui 0.5h
164.12
162.20
158.78
145.48
139.87
136.23
129.99
129.28
128.66
128.27
127.62
113.88
60.41
45.83
21.83
19.75
f1 (ppm)

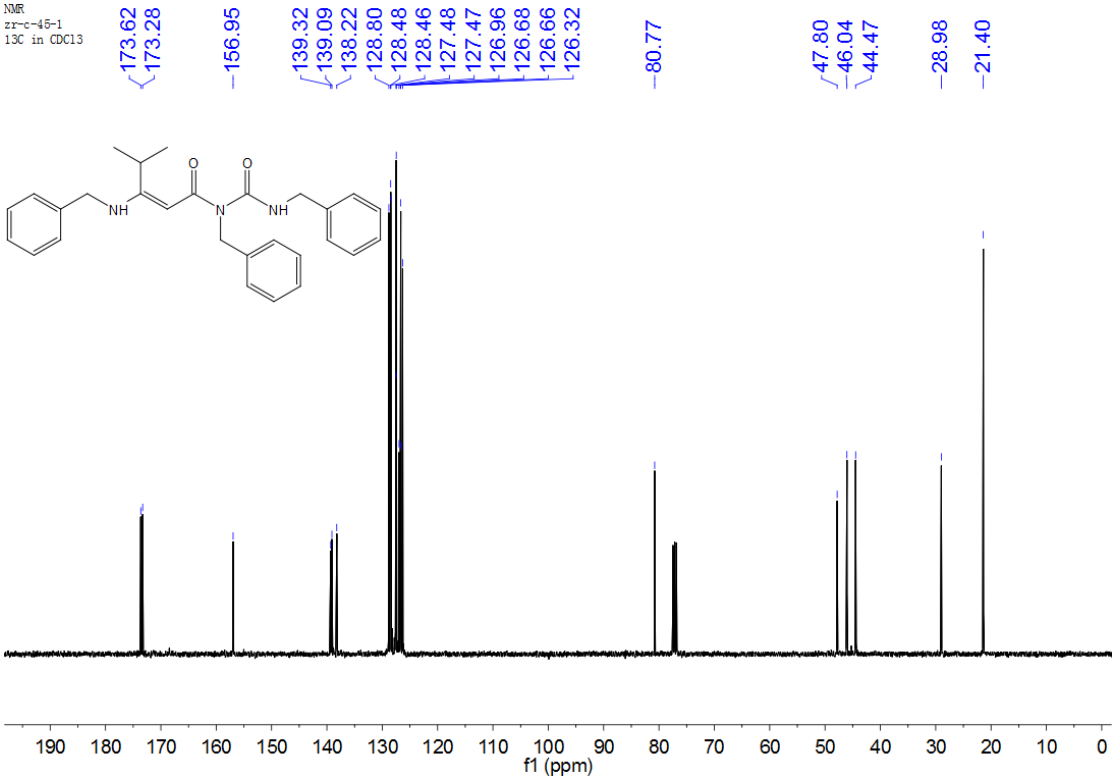

Jun28-2018
zhangrui
lvxiaobing
7.45
7.44
7.30
7.28
7.27
7.26
7.25
7.23
5.66
5.07
4.04
4.03
4.02
3.84
3.83
3.81
3.80
3.09
3.07
3.05
3.03
3.02
3.01
3.00
1.20
1.19
HO
N
N
O
O
2.01
3.18
1.00
2.04
2.07
2.05
2.02
6.05
f1 (ppm)

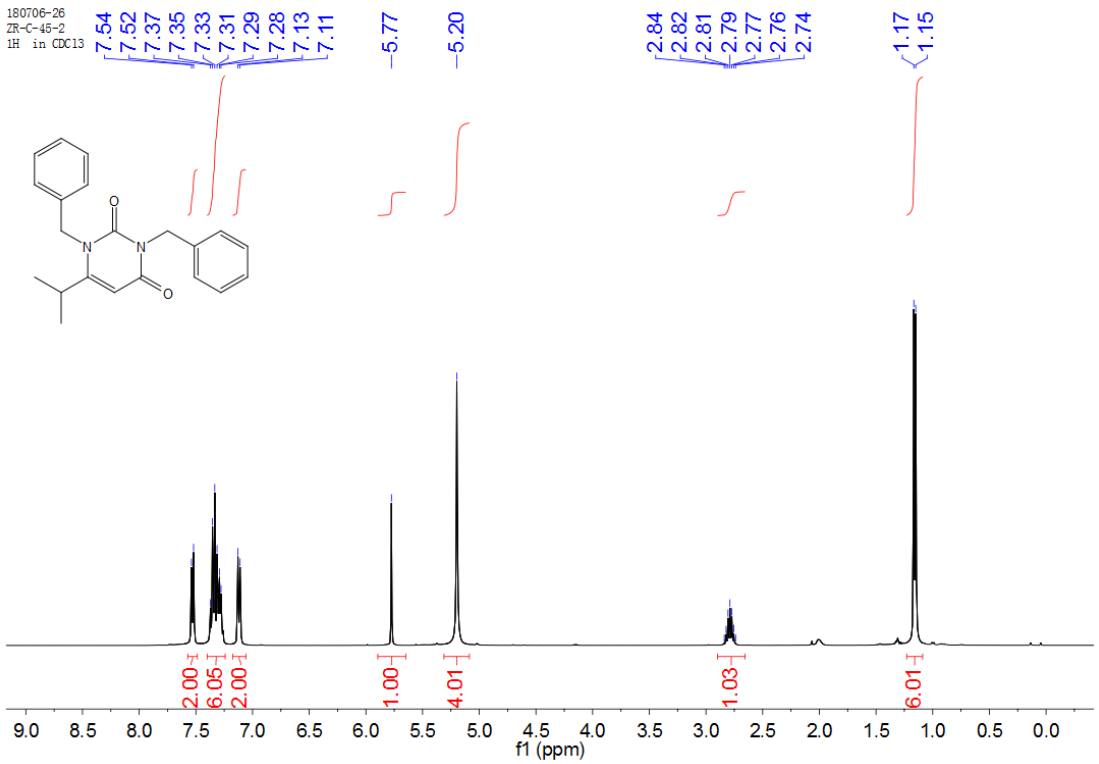

Jun28-2018
zhangrui
lvxiaobing 1h
162.90
162.16
152.90
136.83
129.07
128.43
127.64
97.81
60.92
46.18
44.47
29.28
21.76
HO
N
N
O
O
f1 (ppm)

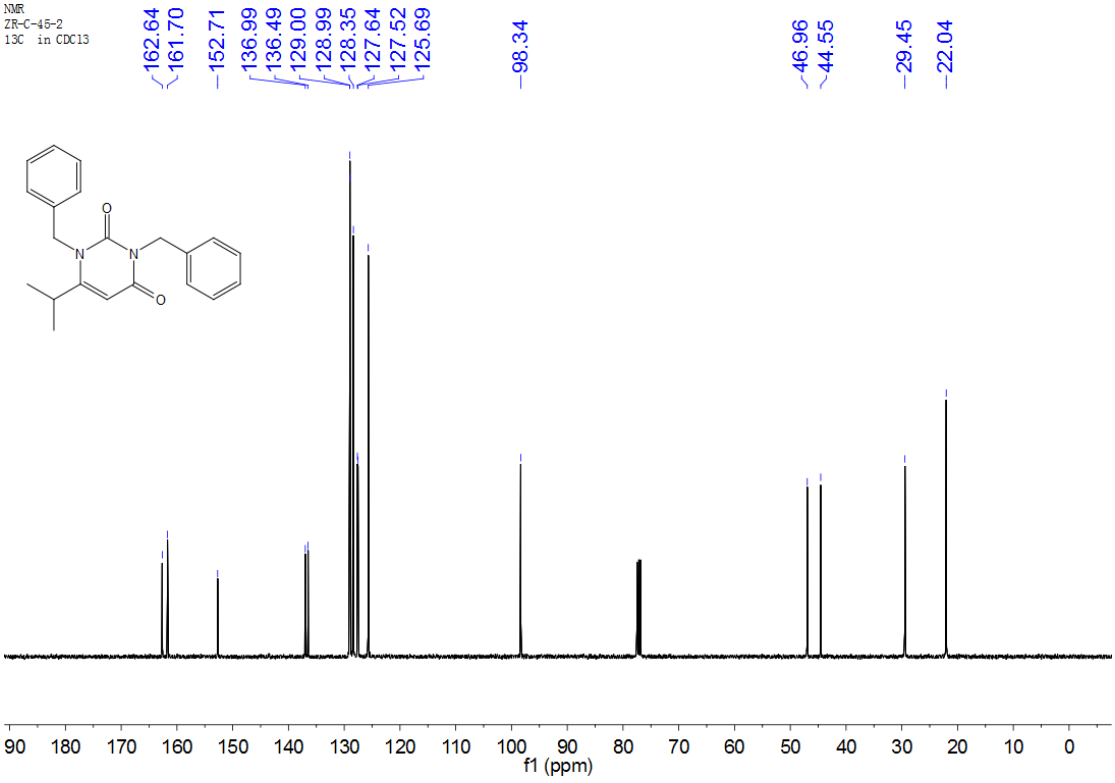

7.49
7.47
7.32
7.30
7.28
7.27
7.26
5.60
5.11
4.35
3.41
3.40
3.38
3.36
3.34
3.33
3.31
1.21
1.19
H2N
O
N
N
O
1.98
3.30
1.00
1.96
1.96
1.02
5.81
f1 (ppm)

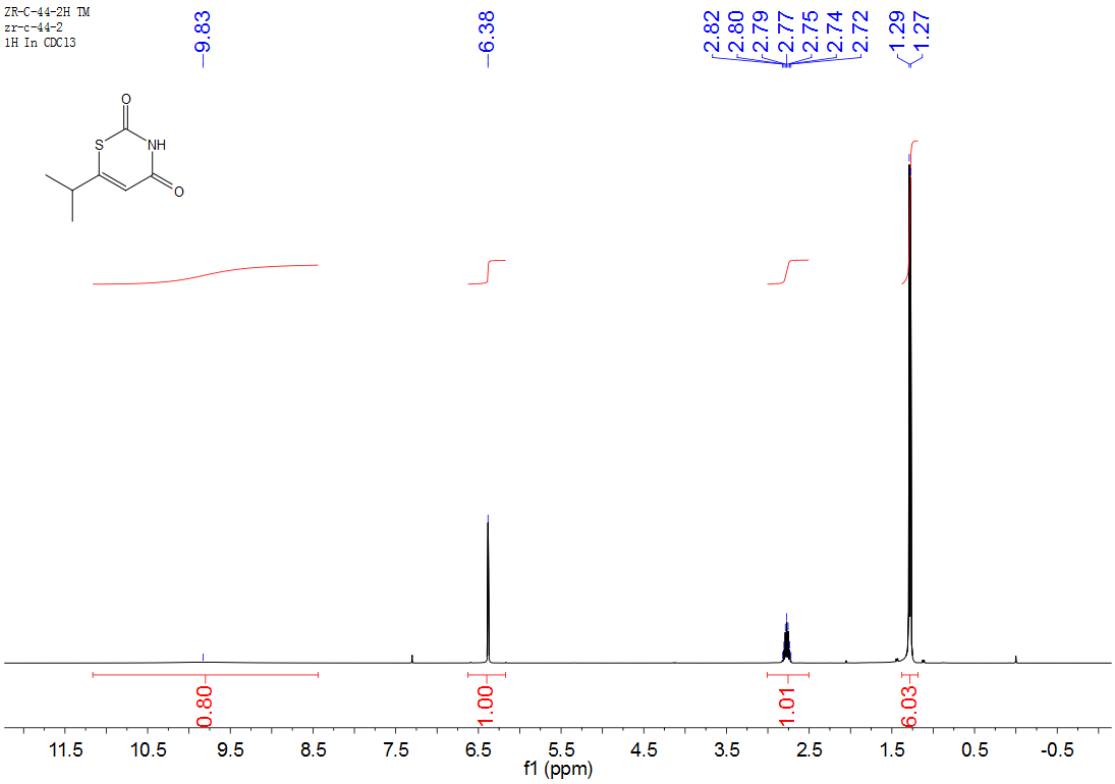

Jun27-2018
zhang rui
lv xiao bing
163.18
162.38
153.53
136.86
129.25
128.54
127.83
96.58
44.86
29.02
21.17
H2N
O
N
N
O
f1 (ppm)

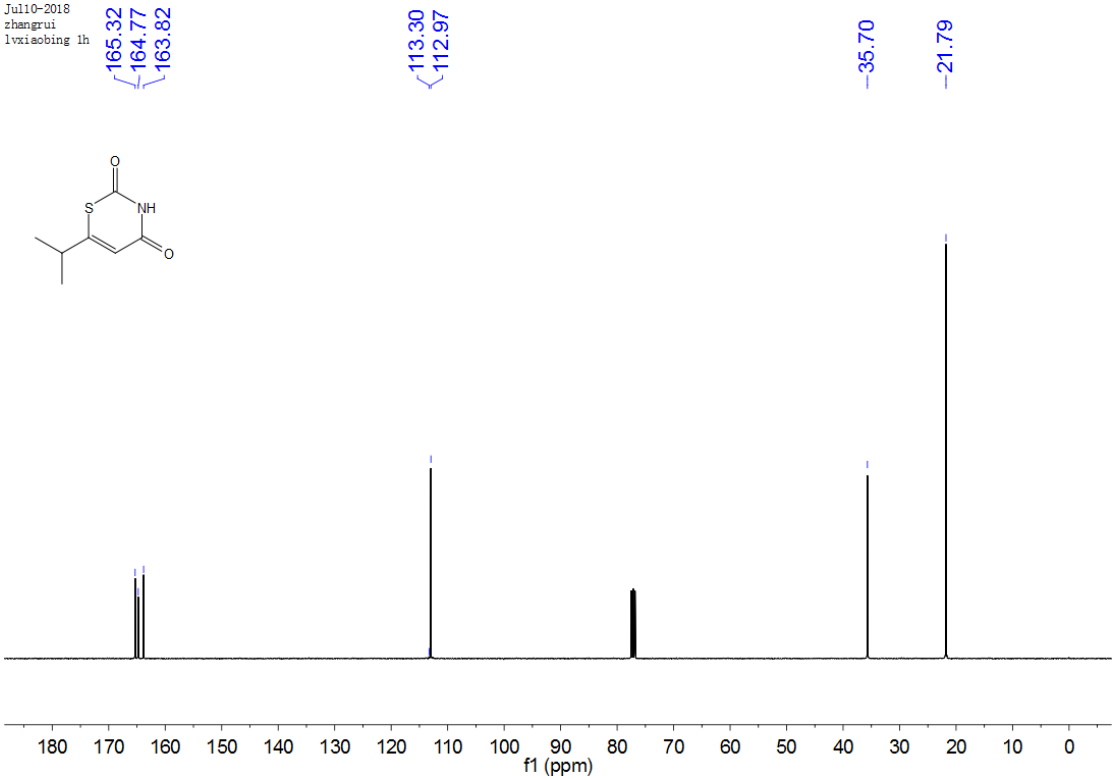

ZR-C-45-1-2
ZR-C-45-1
1H in CDC13
10.05
7.35
7.33
7.31
7.31
7.30
7.29
7.28
7.27
7.26
7.24
7.22
7.21
7.19
7.18
7.17
5.06
4.73
4.56
4.54
4.39
4.37
2.62
2.60
2.58
2.57
2.55
2.53
2.52
0.88
0.87
NH
O
N
O
NH
1.91
15.02
2.00
1.02
2.01
1.88
0.94
6.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

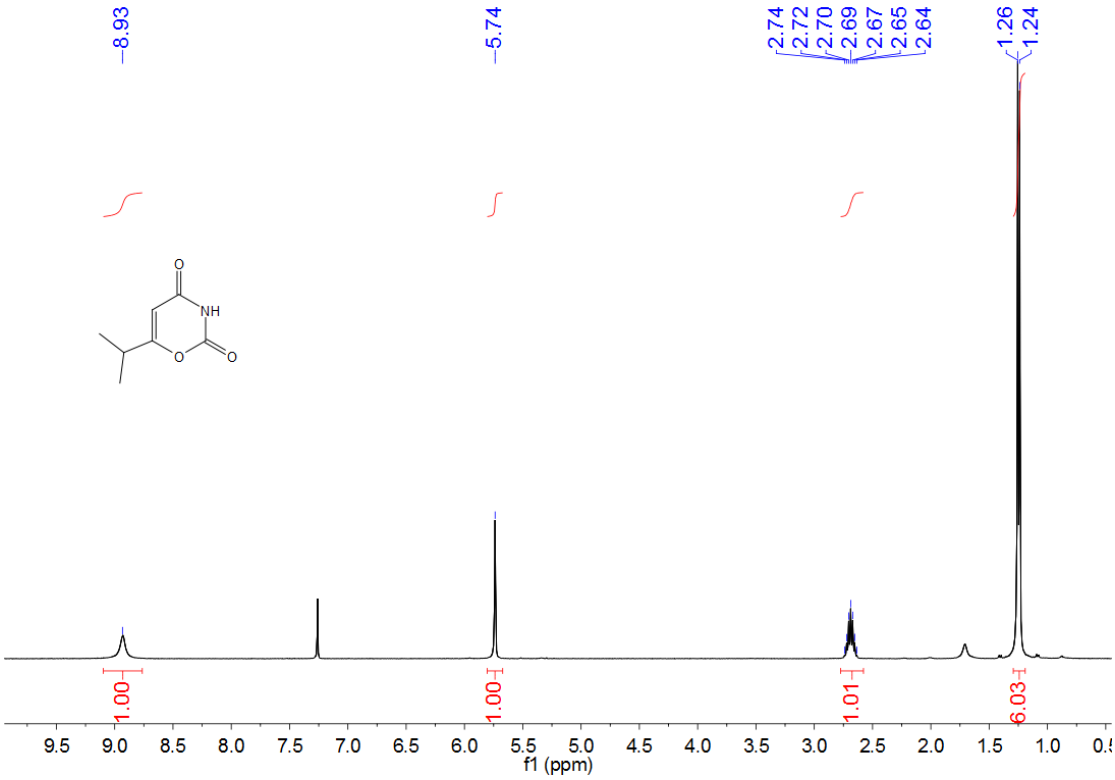

NMR
zr-c-45-1
13C in CDC13
173.62
173.28
156.95
139.32
139.09
138.22
128.80
128.48
128.46
127.48
127.47
126.96
126.68
126.66
126.32
80.77
47.80
46.04
44.47
28.98
21.40
NH
O
N
O
NH
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

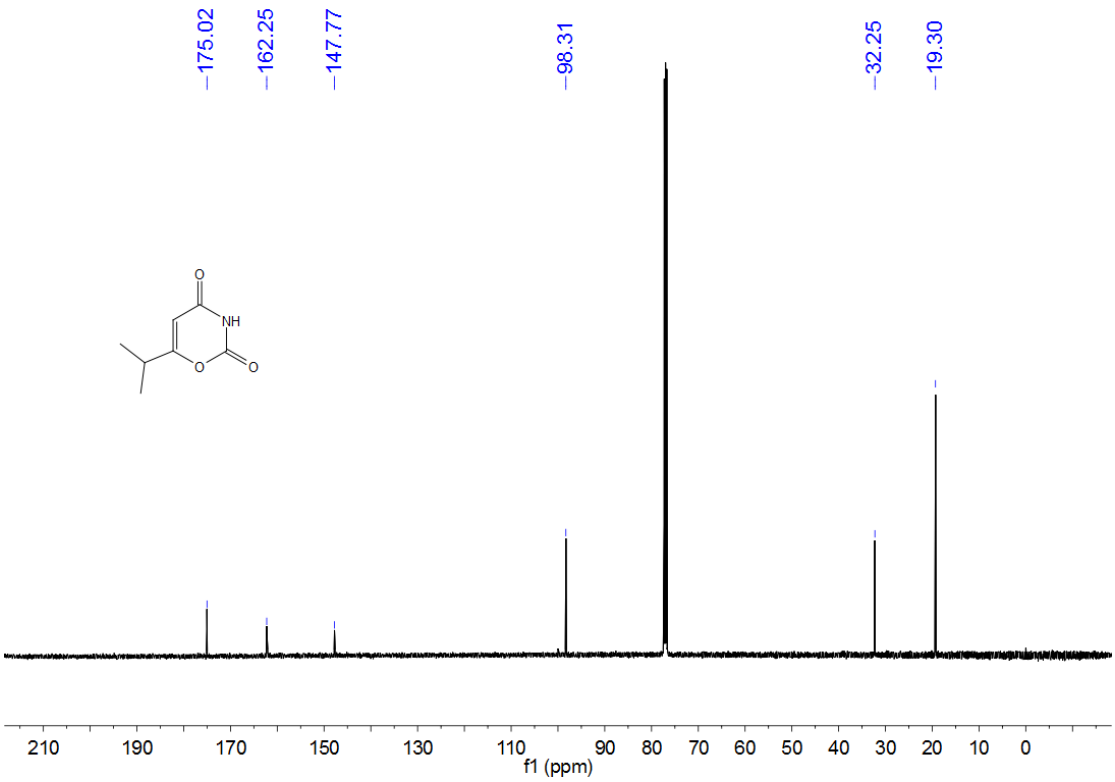

180706-26
ZR-C-45-2
1H in CDCl3
7.54
7.52
7.37
7.35
7.33
7.31
7.29
7.28
7.13
7.11
5.77
5.20
2.84
2.82
2.81
2.79
2.77
2.76
2.74
1.17
1.15
2.00
6.05
2.00
1.00
4.01
1.03
6.01
f1 (ppm)


NMR
ZR-C-45-2
13C in CDCl3
162.64
161.70
152.71
136.99
136.49
129.00
128.99
128.35
127.64
127.52
125.69
98.34
46.96
44.55
29.45
22.04
f1 (ppm)


ZR-C-44-2H TM
zr-c-44-2
1H In CDCl3
9.83
6.38
2.82
2.80
2.79
2.77
2.75
2.74
2.72
1.29
1.27
O
S
NH
O
0.80
1.00
1.01
6.03
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


Jul10-2018
zhangrui
lvxiaobing 1h
165.32
164.77
163.82
113.30
112.97
35.70
21.79
O
S
NH
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.93
5.74
2.74
2.72
2.70
2.69
2.67
2.65
2.64
1.26
1.24
NH
O
O
O
1.00
1.00
1.01
6.03
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
f1 (ppm)


175.02
162.25
147.77
98.31
32.25
19.30
NH
O
O
O
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

7. References

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[S2] Y.-B. Wang, D.-S. Sun, H. Zhou, W.-Z. Zhang and X.-B. Lu, Green Chem., 2015, 17, 4009–4015

[S3] H. Zhou, R. Zhang, H. Zhang, S. Mu, X.-B. Lu Catal. Sci. Technol. 2019, 9, 1457-1463.

[S4] SHELXTL PC; Siemens Analytical X-ray Instruments, Madison, WI, 1993.

[S5] Sheldrick, G. M. SHELXTL Structure Determination Programs, version 5.0, PC; Siemens Analytical Systems, Madison, WI, 1994.