

Supporting Information

Covalent Organic Frameworks Embedding Single Cadmium Sites for Efficient Carboxylative Cyclization of CO₂ with Propargylic Amines

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Section 1. Experimental Section

1.1 Materials

2,2'-Bipyridine-5,5'-dicarboxaldehyde (Bpy >97%) was purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co. $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (99.99%), 4-cyanoacetanilide (98%), benzylamine (99%), propargyl bromide (97%), etc. were purchased from J&K Scientific Co., Ltd., Energy Chemical Co., Ltd., or Shanghai Aladdin Biochemical Co., Ltd. All chemicals were used without further purification.

1.2. Characterization

Fourier transform infrared (FTIR) spectra were recorded with KBr pellets using Thermo Scientific Nicolet iS10 Instrument. Solid-state ^{13}C cross-polarization/magic-angle spinning solid-state nuclear magnetic resonance (CP/MAS ssNMR) spectra were collected on a Bruker AVANCE III HD 400MHz instrument. N_2 and CO_2 adsorption and desorption isotherms were measured using a Autosorb-iQ-MP system. The samples were degassed at 120 °C for 12 h before the measurements. The N_2 adsorption/desorption isotherms were measured at 77 K. Surface areas were calculated based on Brunauer-Emmett-Teller (BET) method. Pore size distribution curves were obtained via non-local density functional theory (NLDFT) method. The carbon dioxide adsorption and desorption isotherms were measured at 273 K and 298 K. Thermogravimetric analysis (TGA) was conducted on a STA449F3 instrument under N_2 atmosphere. Power X-ray diffraction (PXRD) was performed on a Bruker D8 ADVANCE instrument with the X-ray source of $\text{Cu K}\alpha$ radiation and data were collected with a scan rate of 0.1 step/s in the range of 2° - 40° . Transmission electron

microscopy (TEM) were obtained from JEOL JEM-2100 Field Emission Electron Microscope. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was carried out on a Agilent ICP-OES 730 instrument. XPS X-ray photoelectron spectra (XPS) data were collected using a Thermo Scientific K-Alpha instrument, which were analyzed by the calibration using the binding energy of 284.8 eV of C 1s. ^1H and ^{13}C NMR spectra were recorded on spectrometers at 400 and 100 MHz, respectively, by using CDCl_3 as a locking solvent. Chemical shifts were reported in ppm relative to TMS. Steady-state photoluminescence spectra were recorded on a HITACHI F-7000 spectrophotometer.

1.3. In situ ATR FT-IR spectra for carboxylative cyclization of propargylic amines with CO_2

In-situ ATR FT-IR spectra were collected on a Nicolet iS 10 Fourier transform infrared spectrometer equipped with an ATR attachment. In a typical procedure, DBU (0.25 mmol), Cu-Bpy-COF (10 mg) and CH_3CN (3.0 mL) were put into a 10 mL bottle flask, the liquid sample (10 μL) was first collected as the background prior to the reaction. After completion, CO_2 balloon (99.999%) and propargylic amines (0.5 mmol) were added and the FT-IR spectra of liquid samples (10 μL) at different times were collected by subtracting the background.

1.4. Experimental procedures

1.4.1. Synthesis of 1,3,5-tris-(4-aminophenyl)triazine (TAPT)

The TAPT was synthesized according to previous literature with a slight modification.^[1] Typically, N-(4-cyanophenyl)acetamide (5.0 g, 31.2 mmol) was added

to a stirred solution of $\text{CF}_3\text{SO}_3\text{H}$ (8.0 mL) at 0 °C. The reaction mixture was heated to room temperature and stirred for 12 h. After completion, the mixture was poured to 300 mL ice water, which was then neutralized by adding ammonia until the pH = 7. The solid product was filtered and repeatedly washed with distilled water, and obtained $\text{N,N',N''}((1,3,5\text{-triazine-2,4,6-triyl})\text{tris}(\text{benzo-4,1-diyl}))\text{triacetamide}$ in 98% yield, which was used without further purification in the next step.

$\text{N,N',N''}((1,3,5\text{-triazine-2,4,6-triyl})\text{tris}(\text{benzo-4,1-diyl}))\text{triacetamide}$ (1.0 g) and 1.8 M HCl solutions (20 mL) were taken in a round-bottom flask and the reaction mixture was degassed with N_2 and heated to 110 °C for 8 h. Subsequently, the reaction mixture was neutralized to pH=12 with 20% NaOH solutions at 0 °C. The resultant white solid product was filtered and washed several times with distilled water, finally yielding the desirable TAPT in 50% yield. The purified product was characterized by ^1H and ^{13}C NMR. ^1H NMR (400 MHz, DMSO-d_6): δH (ppm) 8.36 (d, $J = 8.0$ Hz, 6H), 6.69 (d, $J = 8.0$ Hz, 6H), 5.89 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δC (ppm) 169.56, 152.98, 130.15, 122.90, 113.10.

1.4.2. Synthesis of *M*-bipyridine complex (*Cd-Bpy*)

Cd-bipyridine complex (*Cd-Bpy*) was synthesized according to previous literature.^[2] A solution of 2,2'-bipyridine (2.72 mmol) in 10 mL DMF was added to a stirred solution of $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (4.08 mmol) in 20 mL DMF. The mixture was allowed to stir for 8 h at room temperature, and then filtered and washed with diethyl ether. The solid product was dried in vacuo at 60 °C for overnight yielded a white powder of *Cd-Bpy*.

1.4.3. Synthesis of propargylic amines

All the propargylic amines were synthesized according to previous report.^[3] The spectroscopic data was consistent with those reported previously.

1.4.4. Procedure for the cycling test

In a typical experiment, propargylic amines (0.5 mmol), DBU (0.25 mmol), Cd-Bpy-COF (10 mg) and CH₃CN (3.0 mL) were put into a 10 mL bottle flask, and then a balloon filled with CO₂ (99.999%) was installed in a bottleneck. To remove the residual air, successively excluding and charging with CO₂ several times was performed and finally purged CO₂ into the reaction system. After the reaction mixture was stirred at 60 °C for 12 h, the catalyst was collected by filtration, the liquid was calculated the product yield by GC. The catalyst was washed with 3 × 5 mL of CH₃OH and dried under vacuum at 60°C. Finally, the recovered catalyst was directly used as the recycled catalyst in the next cycling test. Two parallel experiments will be conducted concurrently to ensure the catalyst dosage remains at 10 mg.

1.5. DFT Calculation Methods.

We carried out all the DFT calculations in the Vienna *ab initio* simulation (VASP5.4.4) code^[4] The exchange-correlation is simulated with PBE functional and the ion-electron interactions were described by the PAW method.^[5,6] The vdWs interaction was included by using empirical DFT-D3 method.^[7] The Monkhorst-Pack-grid-mesh-based Brillouin zone k-points are set as 1×1×1 for all periodic structure with the cutoff energy of 400 eV. The convergence criteria are set as 0.05 eV A⁻¹ and 10⁻⁵ eV in force and energy, respectively. A 15 Å vacuum layer along the *z* direction is employed to avoid interlayer interference.

The adsorption energy (E_{ads}) calculation follows as the equation:

$$E_{\text{ads}} = E (\text{CO}_2\text{-Cd-Bpy-COF}) - E (\text{Cd-Bpy-COF}) - E (\text{CO}_2)$$

Section 2. Supplementary Figures

Table S1. Fractional atomic coordinates for the unit cell of Bpy-COF.

Bpy-COF space group :P6/m							
a=b=43.6580Å, c=3.5340Å, $\alpha=\beta=90^\circ$, $\gamma=120^\circ$							
Atom	x	y	z	Atom	x	y	z
C1	-0.08934	-0.52504	0	C13	0.24193	-0.41009	0
C2	-0.07822	-0.55017	0	C14	0.20531	-0.42957	0
N3	-0.0435	-0.53951	0	C15	0.29764	-0.35247	0
C4	-0.01852	-0.50481	0	N16	0.3168	-0.36894	0
C5	-0.02854	-0.47882	0	H17	-0.09687	-0.57829	0
C6	-0.06421	-0.48914	0	H18	-0.00913	-0.45089	0
C7	0.12681	-0.46341	0	H19	-0.07215	-0.46927	0
N8	0.14857	-0.42981	0	H20	0.13554	-0.48261	0
C9	0.18591	-0.4119	0	H21	0.18804	-0.36156	0
C10	0.20312	-0.37511	0	H22	0.25232	-0.32705	0
C11	0.23962	-0.35563	0	H23	0.25658	-0.42409	0
C12	0.25926	-0.37301	0	H24	0.19271	-0.45805	0

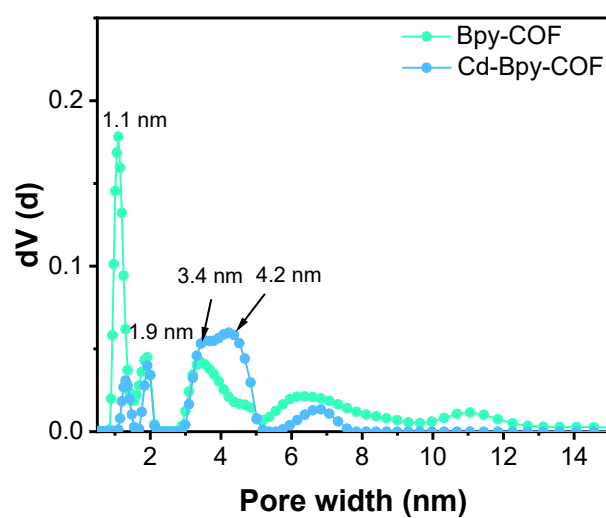


Figure S1. Pore size distribution profiles of Bpy-COF and Cd-Bpy-COF calculated by NL-DFT.

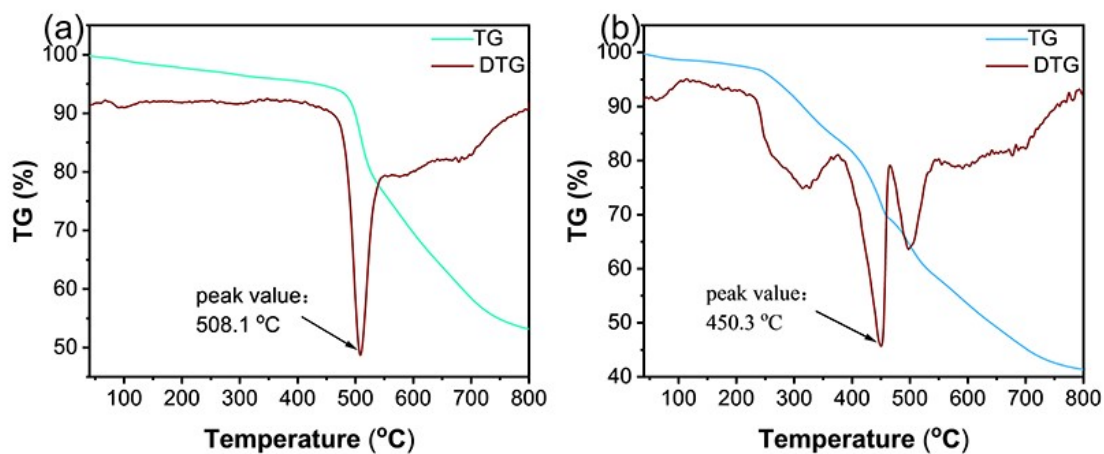


Figure S2. Thermogravimetric analysis of (a) Bpy-COF and (b) Cd-Bpy-COF.

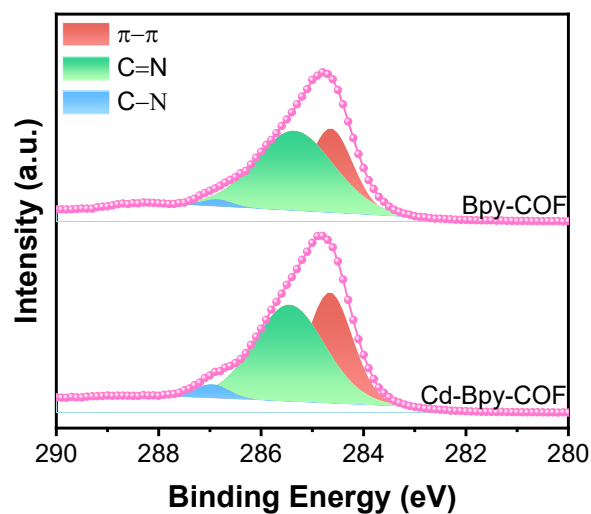


Figure S3. High-resolution C 1s XPS spectra of Bpy-COF and Cd-Bpy-COF.

Table S2. Solvent screening ^a

Entry	Catalyst	Solvent	Yield (%) ^b
1	Cd-Bpy-COF	MeCN	99.9
2	Cd-Bpy-COF	CH ₃ OH	57.3
3	Cd-Bpy-COF	THF	31.8
4	Cd-Bpy-COF	Toluene	59.6

^a Reaction conditions: **1a** (0.5 mmol), Cd-Bpy-COF (10 mg), DBU (0.5 equiv.), CO₂ (balloon), solvent (3 mL), 60 °C for 12 h, unless otherwise noted. ^b Yield as determined by gas chromatography using mesitylene as the internal standard.

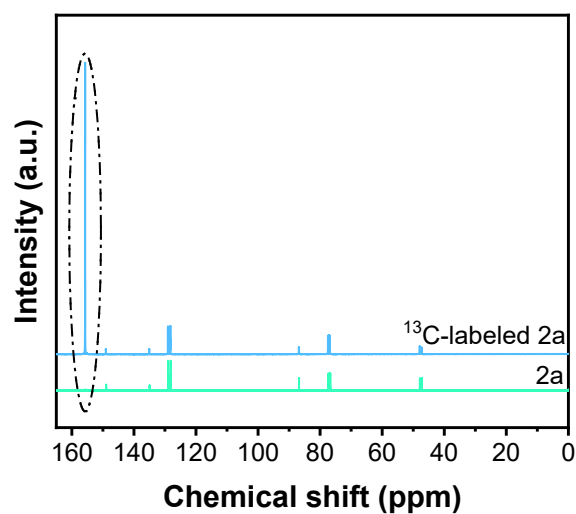


Figure S4. ¹³C NMR spectra of ¹³C-labeled **2a** and unlabeled **2a** produced from the carboxylative cyclization of **1a** using ¹³CO₂ as substrate

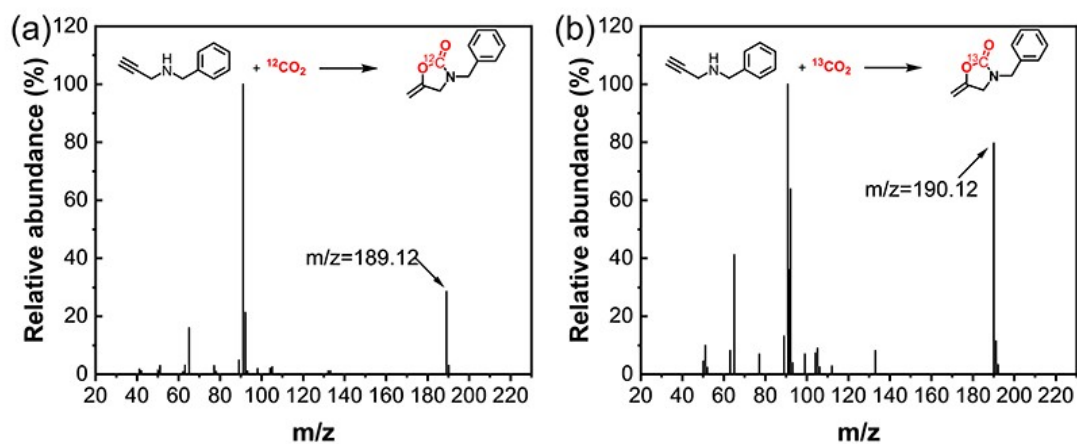


Figure S5. GC-MS spectra of ^{13}C -labeled **2a** and unlabeled **2a** produced from the carboxylative cyclization of **1a** using $^{13}\text{CO}_2$ as substrate.

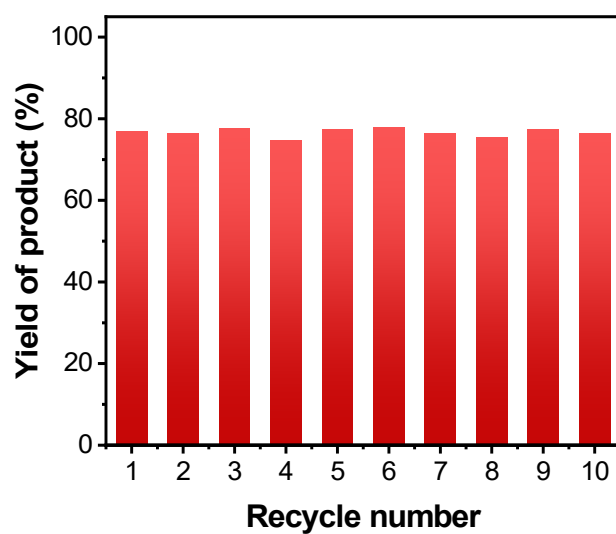


Figure S6. Recycling tests under the similar conditions (60 °C, 6 h for each run).

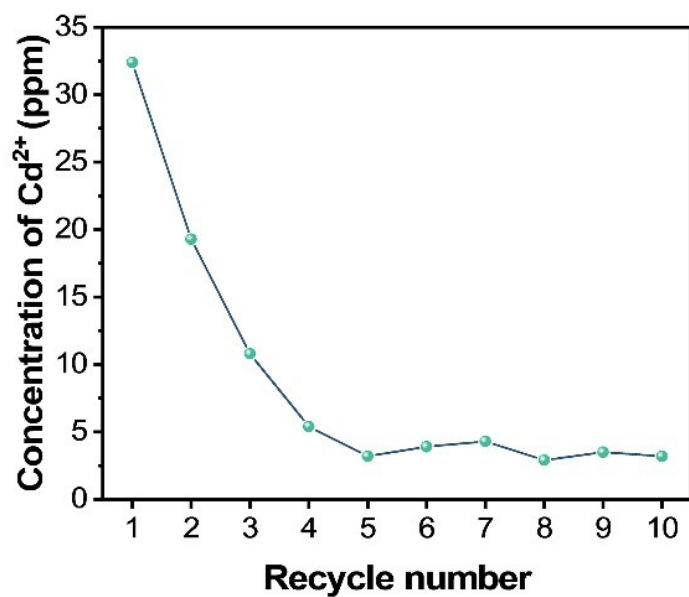


Figure S7. The Cd leaching amount for every single run in cycling tests.

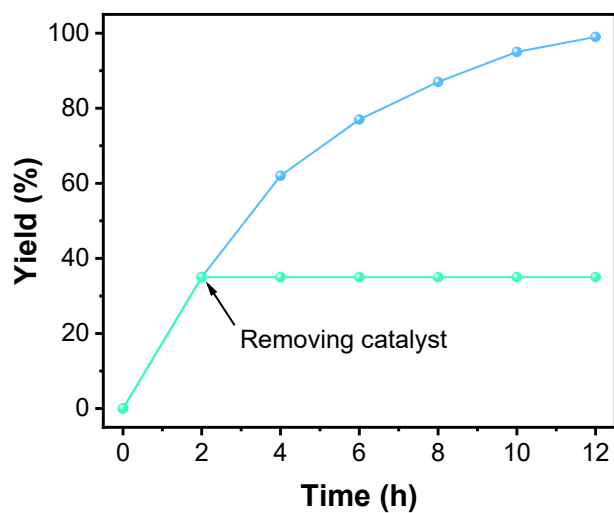


Figure S8. Hot filtration experiment using Cd-Bpy-COF for the carboxylative cyclization reaction.

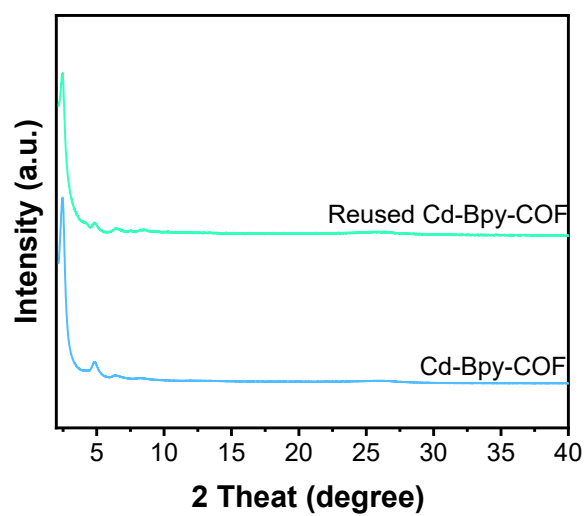


Figure S9. XRD spectra of fresh and reused Cd-Bpy-COF.

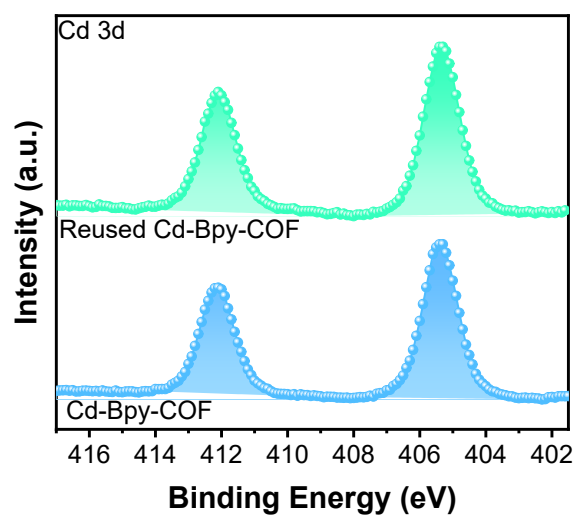


Figure S10. Cd 3d XPS spectra of fresh and reused Cd-Bpy-COF.

Table S3. Comparison with previously reported catalytic systems.

Entry	Cat.	T (°C)	Time (h)	Yield (%)	Recycle number	Ref.
1	ZnCl ₂ (TBD) ₂	60	12	96	-	8
2	[DBUH][MIm]	60	6	90	5	9
3	[Bmim][OAc]	100	12	84	5	10
4	Ag ₂₇ -MOF	25	6	97	4	11
5	Zn ₁₁₆	70	12	99	10	3
6	PdSCS	80	16	99	-	12
7	Ag@TpPa-1	60	18	96	5	13
8	AgN@COF	55	10	94	6	14
9	Cu ₂ O@MIL-101(Cr)-DABCO	25	12	97.5	5	15
10	[Ru]/PPh ₃	100	8	80	-	16
11	MOF-1a	60	24	99	4	17
12	Ag-HMP-2	60	20	95	5	18
13	Cd-Bpy-COF	60	12	99	10	This Work

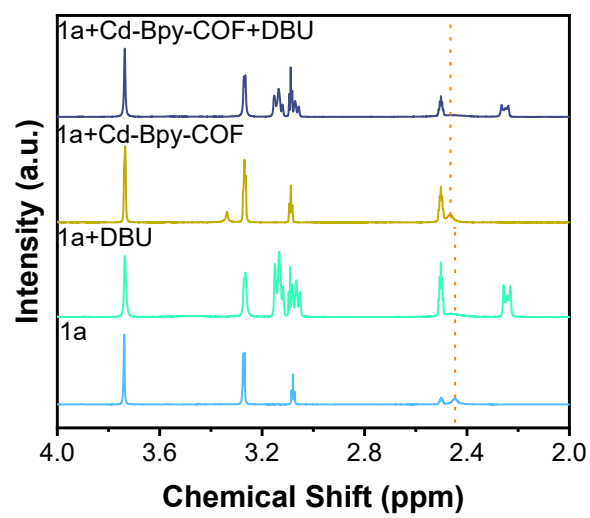
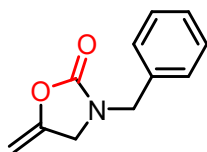
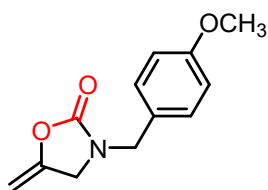


Figure S11. ¹H NMR spectral changes on different systems in DMSO-d₆.

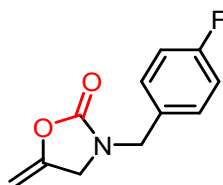
Section 3. Data of NMR Spectra



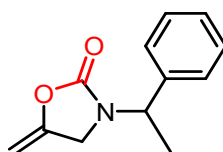
2a: pale yellow oil. ^1H NMR (400 MHz, CDCl_3), δH (ppm) 7.38 – 7.28 (m, 5H), 4.73 (s, 1H), 4.46 (s, 2H), 4.24 (s, 1H), 4.02 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3), δC (ppm) 155.74, 149.04, 135.06, 129.07, 128.26, 86.86, 47.93, 47.32.



2b: pale yellow oil. ^1H NMR (400 MHz, CDCl_3), δH (ppm) 7.20 (d, $J = 6.9$ Hz, 2H), 6.89 (d, $J = 8.6$ Hz, 2H), 4.72 (t, $J = 2.1$ Hz, 1H), 4.40 (s, 2H), 4.28 – 4.16 (m, 1H), 4.00 (s, 2H), 3.81 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3), δC (ppm) 159.65, 155.65, 149.13, 129.70, 127.07, 114.40, 86.75, 55.40, 47.34, 47.18.

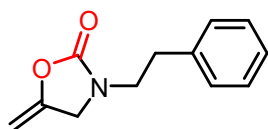


2c: pale yellow oil. ^1H NMR (400 MHz, CDCl_3), δH (ppm) 7.26 (q, $J = 4.0$ Hz, 2H), 7.05 (t, $J = 8.6$ Hz, 2H), 4.74 (q, $J = 3.0$ Hz, 1H), 4.44 (s, 2H), 4.27 (q, $J = 4.0$ Hz, 1H), 4.03 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3), δC (ppm) 163.89, 161.43, 155.66, 148.87, 130.94, 130.06, 116.08, 115.87, 87.01, 47.18.

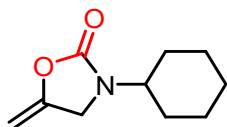


2d: pale yellow oil. ^1H NMR (400 MHz, CDCl_3), δH (ppm) 7.39 – 7.29 (m, 5H), 5.26

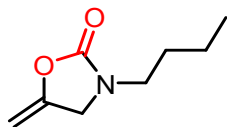
(dd, $J_1 = 12.0$ Hz, $J_2 = 4.0$, 1H), 4.70 (dt, $J_1 = 4.8$ Hz, $J_2 = 2.6$ Hz, 1H), 4.22 (d, $J = 2.1$ Hz, 1H), 4.11 (dt, $J_1 = 13.9$, $J_2 = 2.4$ Hz, 1H), 3.77 (dt, $J_1 = 14.2$ Hz, $J_2 = 2.0$ Hz, 1H), 1.60 (dd, $J_1 = 7.2$ Hz, $J_2 = 1.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δC (ppm) 155.14, 149.30, 138.86, 128.89, 128.19, 127.01, 86.59, 51.38, 43.70, 16.45.



2e: pale yellow oil. ^1H NMR (400 MHz, CDCl_3), δH (ppm) 7.32 – 7.20 (m, 5H), 4.68 (s, 1H), 4.21 (s, 1H), 3.99 (s, 2H), 3.53 (d, $J = 6.9$ Hz, 2H), 2.88 (t, $J = 7.4$ Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δC (ppm) 155.48, 149.07, 137.97, 128.79, 128.61, 126.82, 86.45, 48.37, 45.14, 33.90.

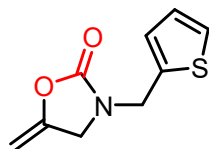


2f: pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δH (ppm) 4.72 (d, $J = 2.8$ Hz, 1H), 4.28 (d, $J = 2.7$ Hz, 1H), 4.13 (t, $J = 2.4$ Hz, 2H), 3.72 (t, $J = 7.1$ Hz, 1H), 1.82 (d, $J = 6.6$ Hz, 4H), 1.68 (d, $J = 11.6$ Hz, 1H), 1.35 (tdd, $J = 12.1, 8.9, 3.9$ Hz, 4H), 1.15 – 1.05 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δC (ppm) 154.96, 149.77, 86.22, 52.49, 44.22, 30.34, 25.36.

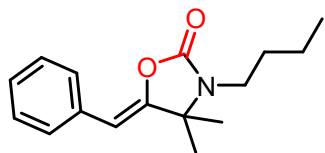


2g: pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δH (ppm) 4.74 (s, 1H), 4.29 (s, 1H), 4.16 (s, 2H), 3.31 (t, $J = 6.6$ Hz, 2H), 1.58 – 1.49 (m, 2H), 1.36 (m, 2H), 0.95 (t, $J = 6.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δC (ppm) 155.68, 149.31, 86.42, 47.90, 43.59,

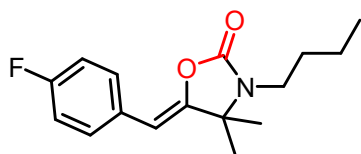
29.39, 19.87, 13.70.



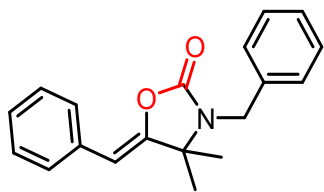
2h: pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ H 7.28 (dd, $J = 5.2, 1.4$ Hz, 1H), 7.02 (d, $J = 2.9$ Hz, 1H), 6.98 (dd, $J_1 = 5.1$ Hz, $J_2 = 3.5$ Hz, 1H), 4.73 (d, $J = 2.9$ Hz, 1H), 4.64 (s, 2H), 4.27 (d, $J = 3.2$ Hz, 1H), 4.11 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ C (ppm) 155.20, 148.91, 137.15, 127.49, 127.22, 126.28, 86.92, 47.12, 42.25.



2j: pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ H 7.58 (d, $J = 7.5$ Hz, 2H), 7.32 (t, $J = 7.6$ Hz, 2H), 7.19 (t, $J = 7.4$ Hz, 1H), 5.45 (s, 1H), 3.26-3.14 (m, 2H), 1.66 (p, $J = 7.9$ Hz, 2H), 1.49 (s, 6H), 1.37 (m, 2H), 0.96 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ C (ppm) 154.28, 153.67, 133.83, 128.56, 128.40, 126.81, 100.49, 62.28, 40.53, 31.63, 27.69, 20.34, 13.82.

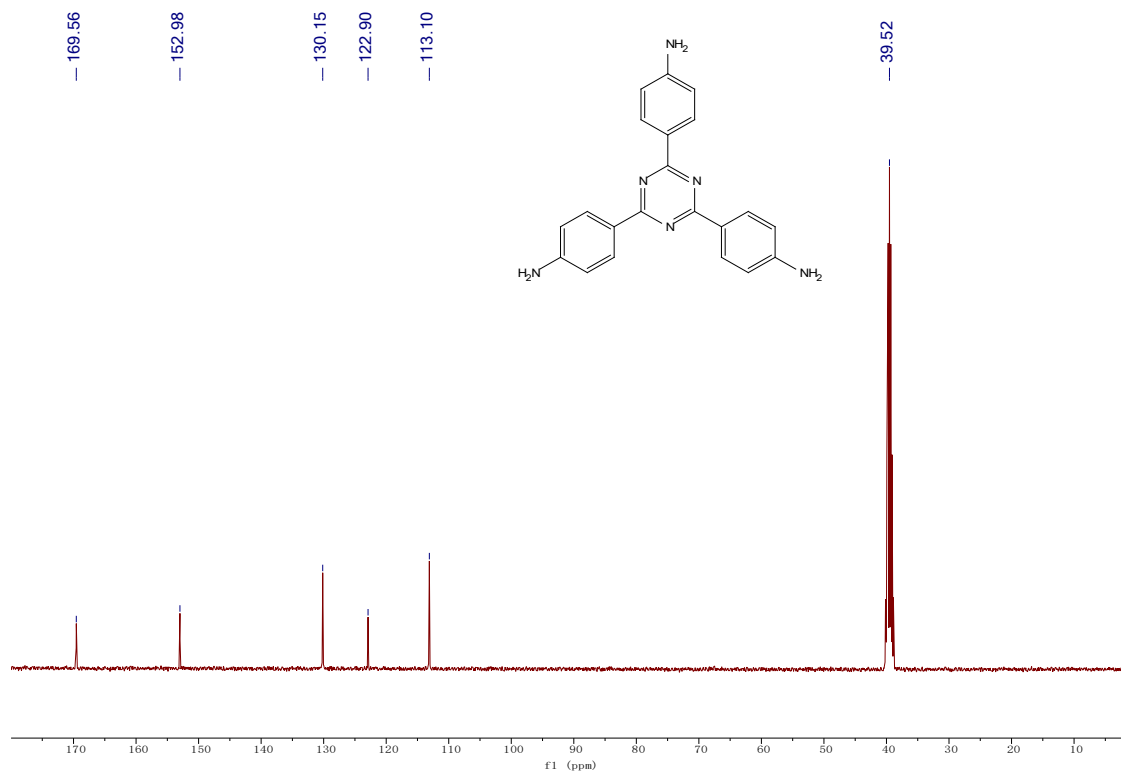
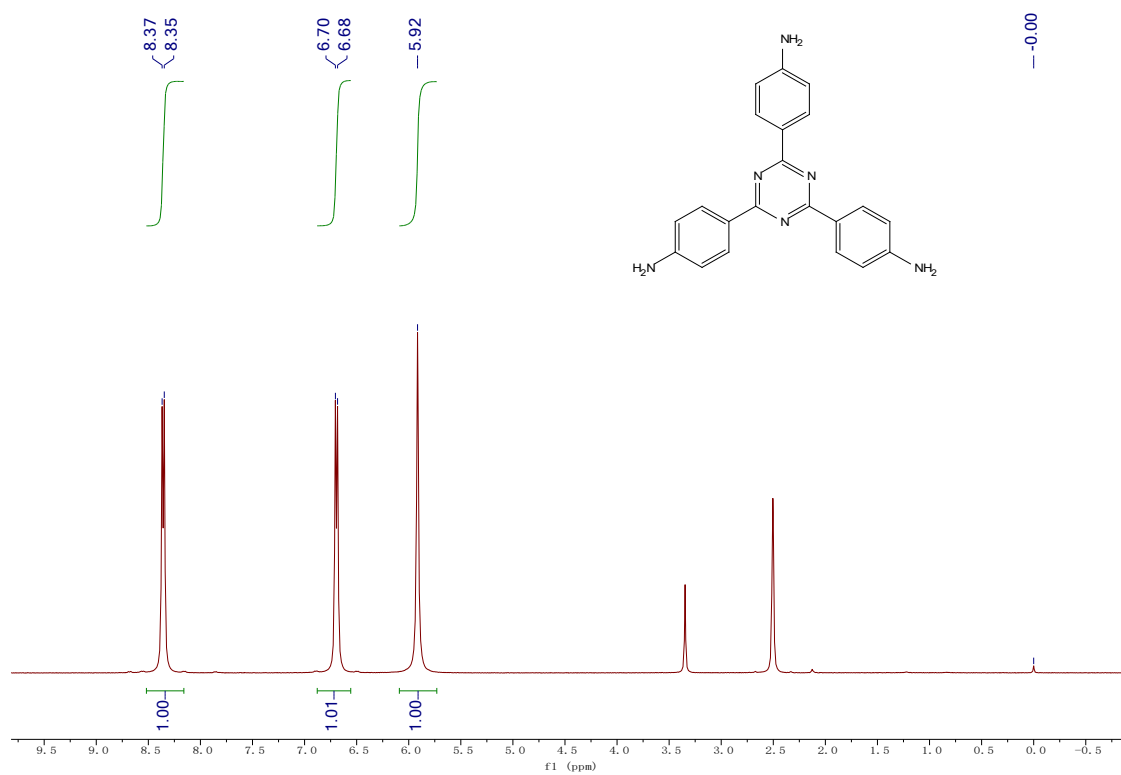


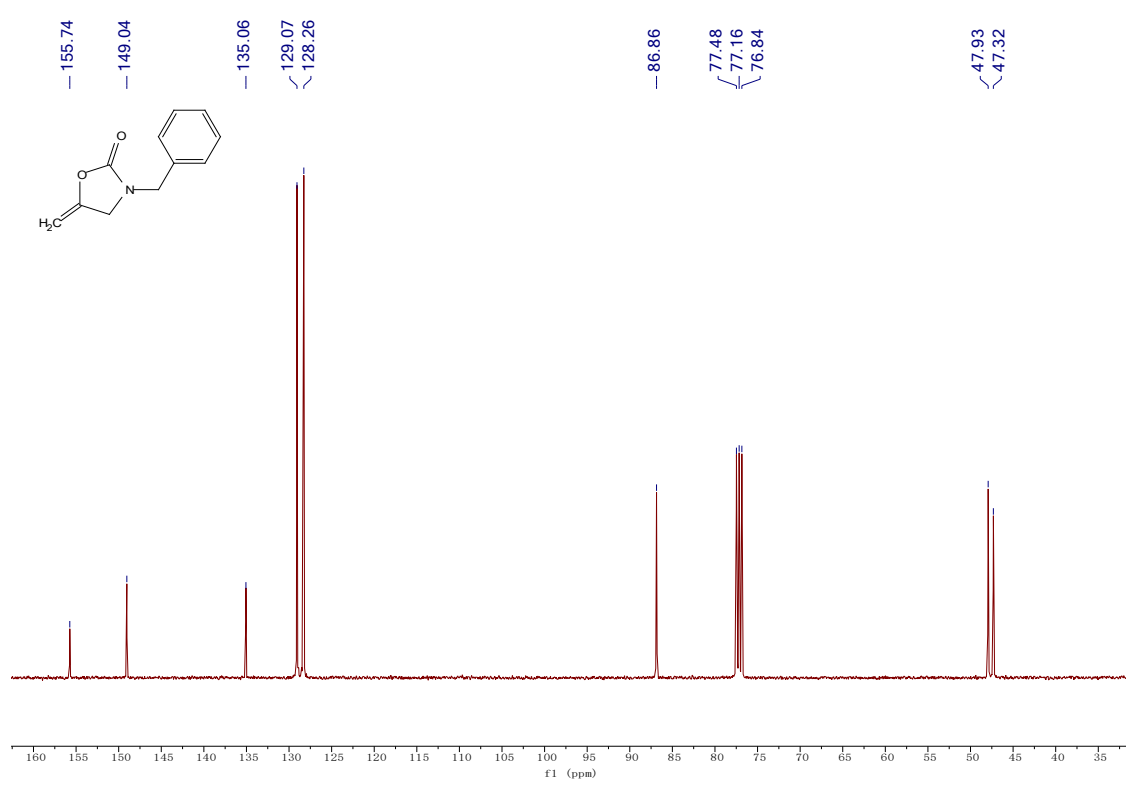
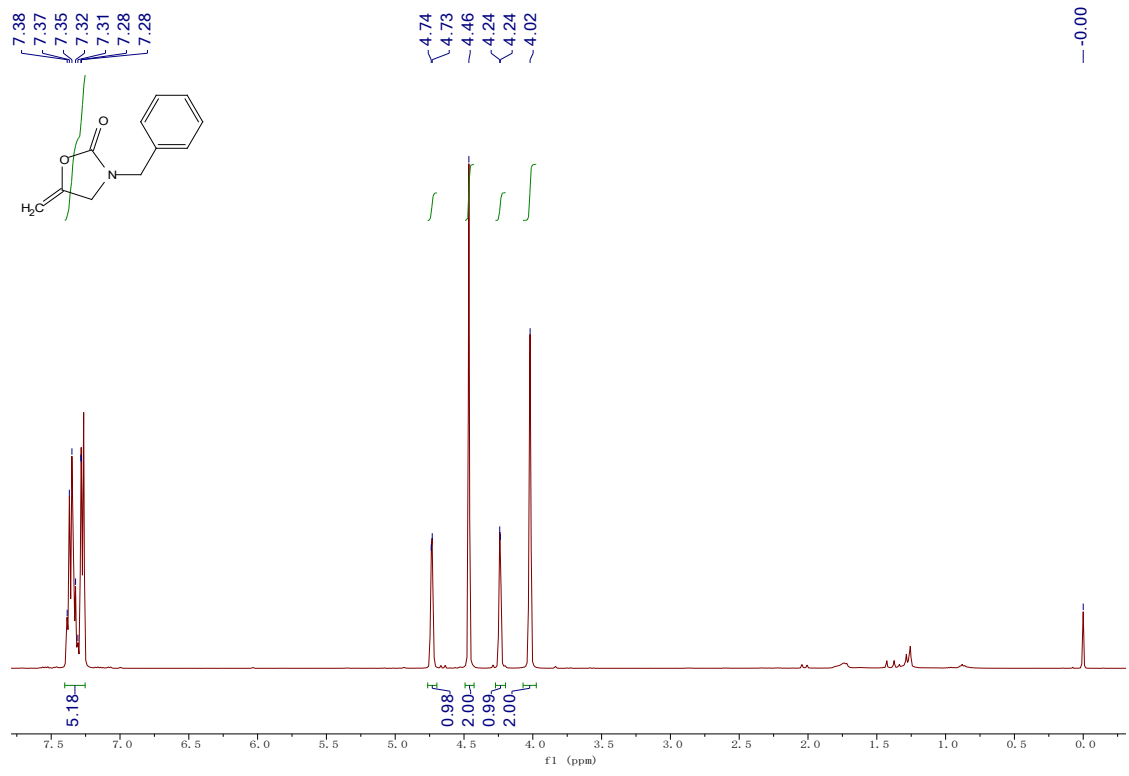
2k : pale yellow oil. ^1H NMR (400 MHz, CDCl_3) δ H 7.56 (dd, $J = 8.8, 5.5$ Hz, 2H), 7.00 (t, $J = 8.8$ Hz, 2H), 5.42 (s, 1H), 3.25-3.11 (m, 2H), 1.69-1.62 (m, 2H), 1.49 (s, 6H), 1.38 (dt, $J = 15.1, 7.5$ Hz, 2H), 0.96 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ C (ppm) 162.27, 154.05, 153.18, 153.17, 129.91, 129.86, 115.38, 115.24, 99.28, 62.13, 40.42, 31.49, 27.56, 20.21, 13.70.

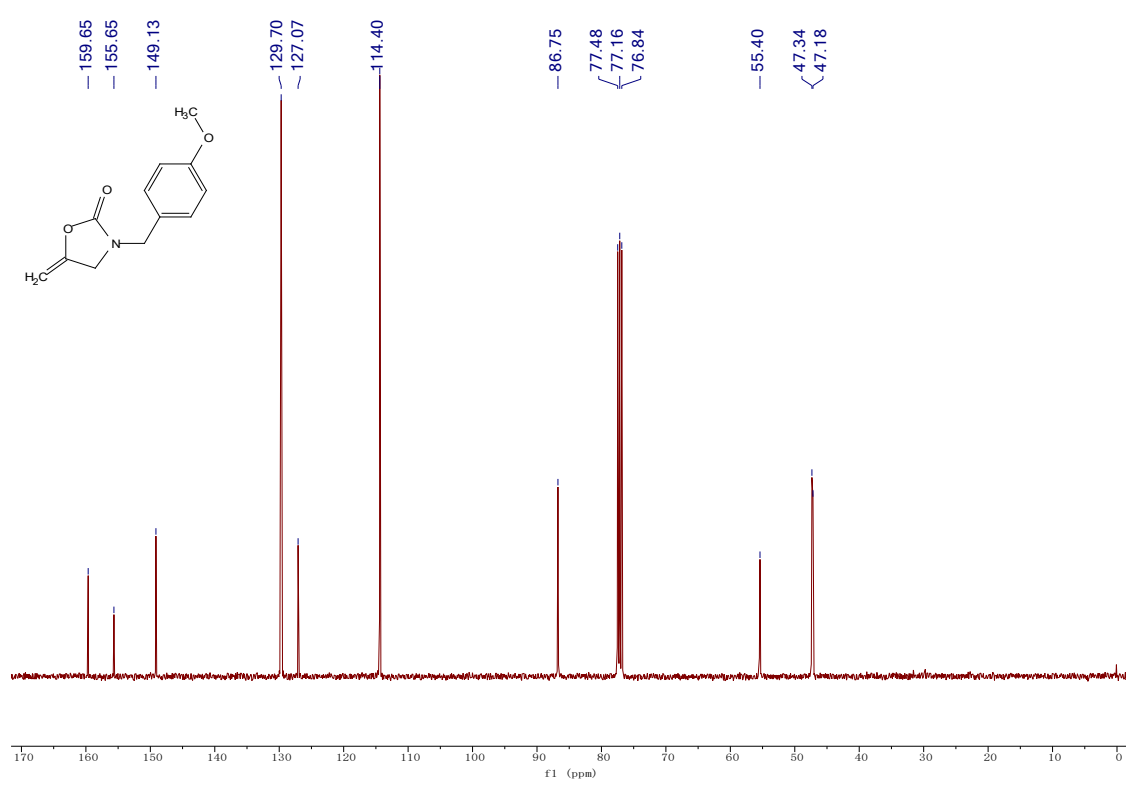
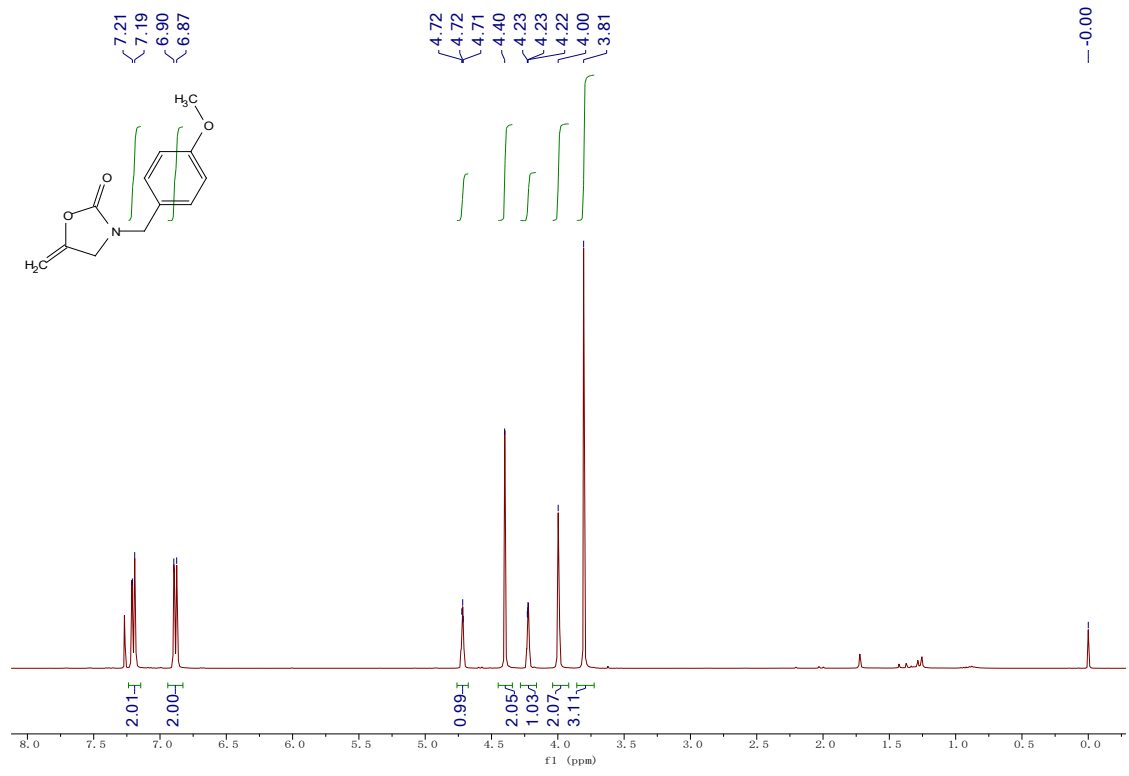


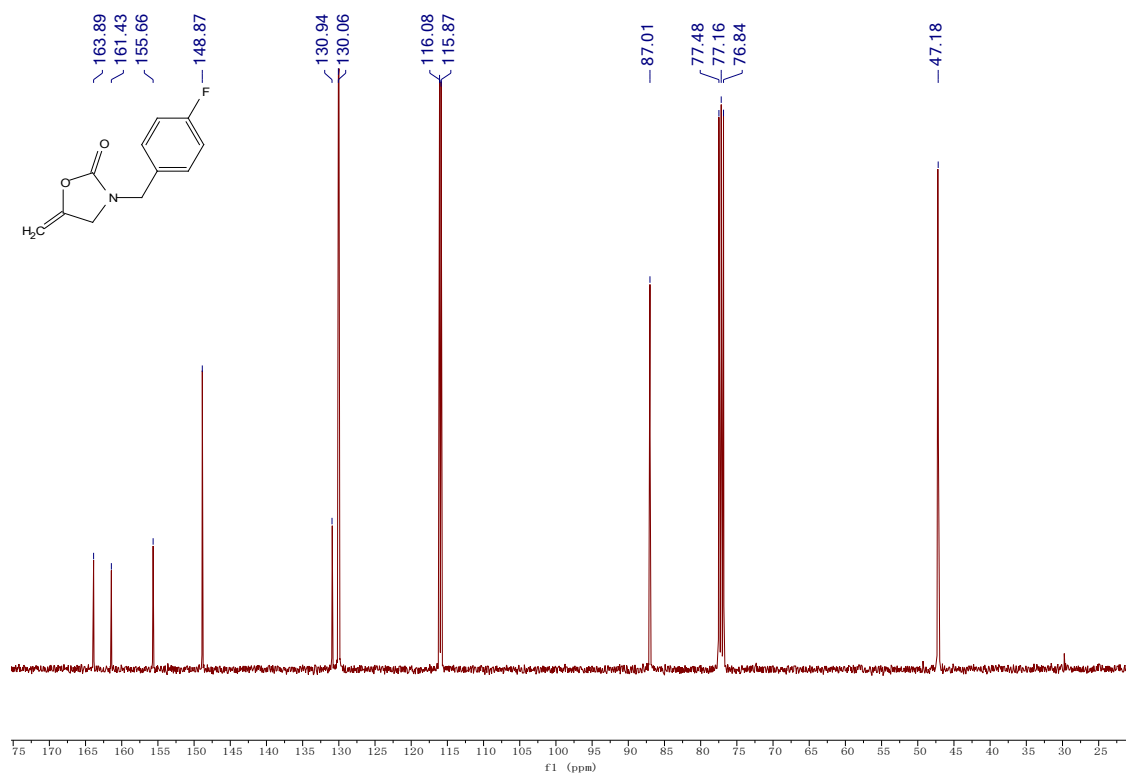
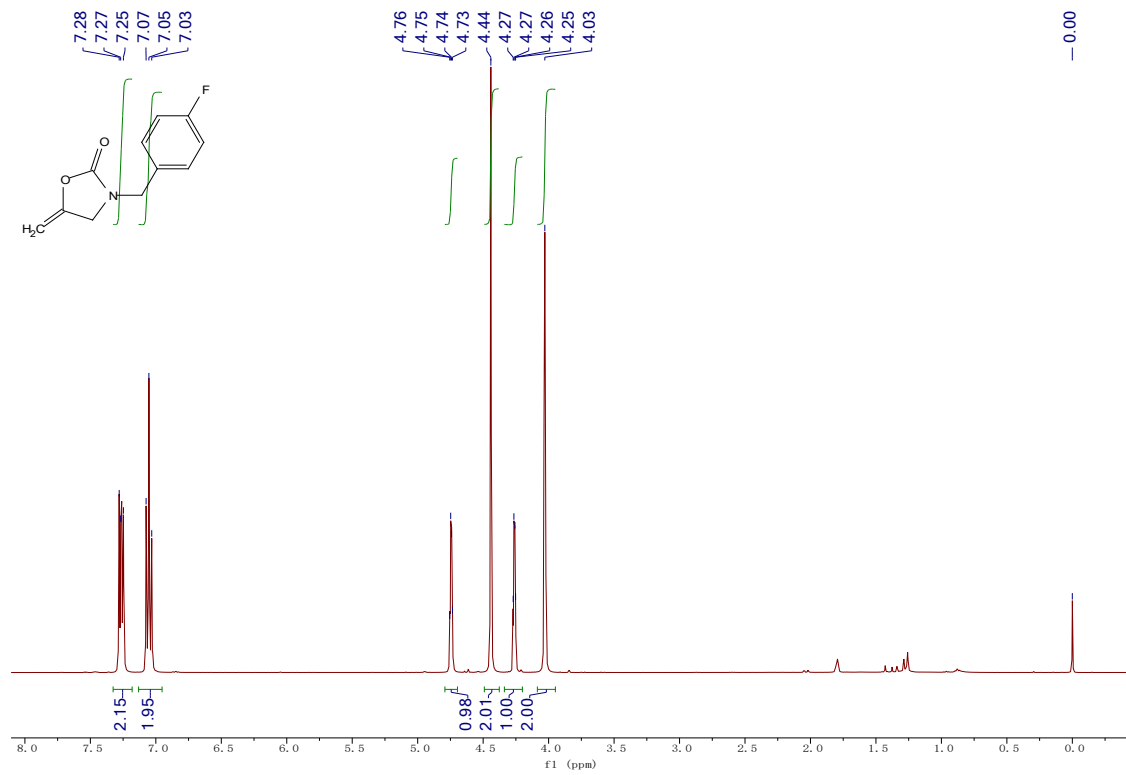
21 : white solid. ^1H NMR (400 MHz, CDCl_3) δ H 7.59 (d, $J = 6.9$ Hz, 2H), 7.39-7.27 (m, 7H), 7.20 (t, $J = 7.4$ Hz, 1H), 5.44 (s, 1H), 4.51 (s, 2H), 1.38 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ C (ppm) 154.79, 153.42, 137.52, 133.58, 128.73, 128.50, 128.35, 127.82, 127.77, 126.83, 100.67, 62.44, 44.18, 27.72.

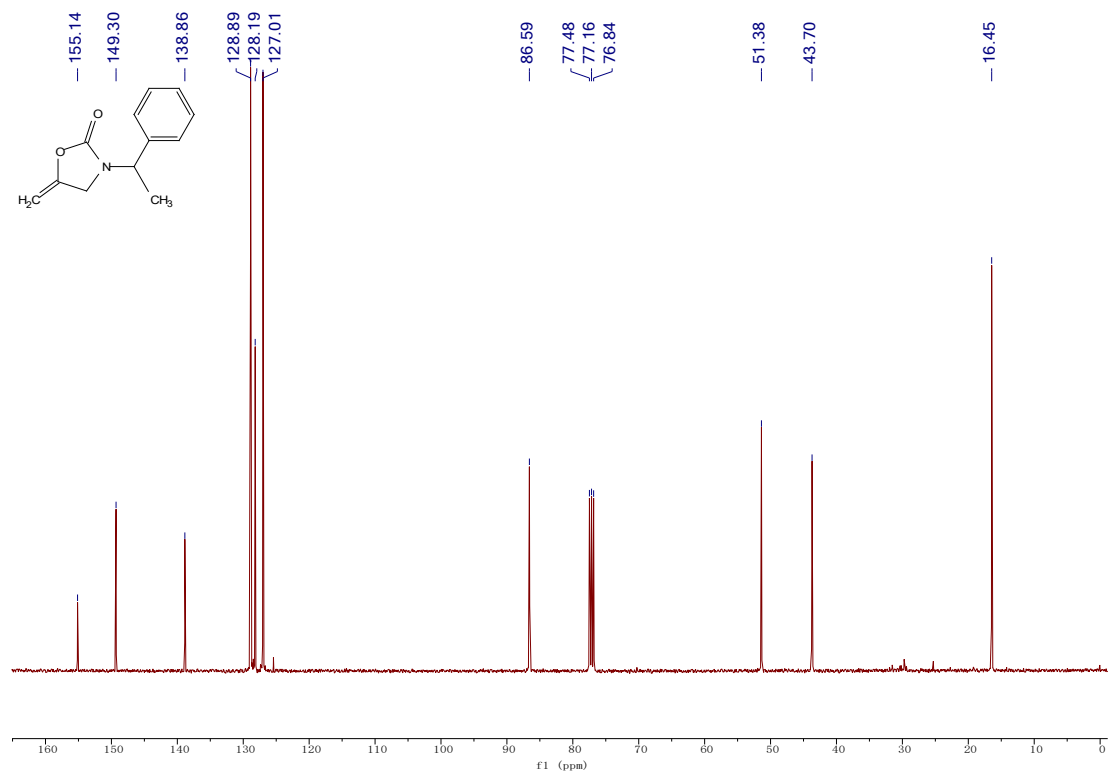
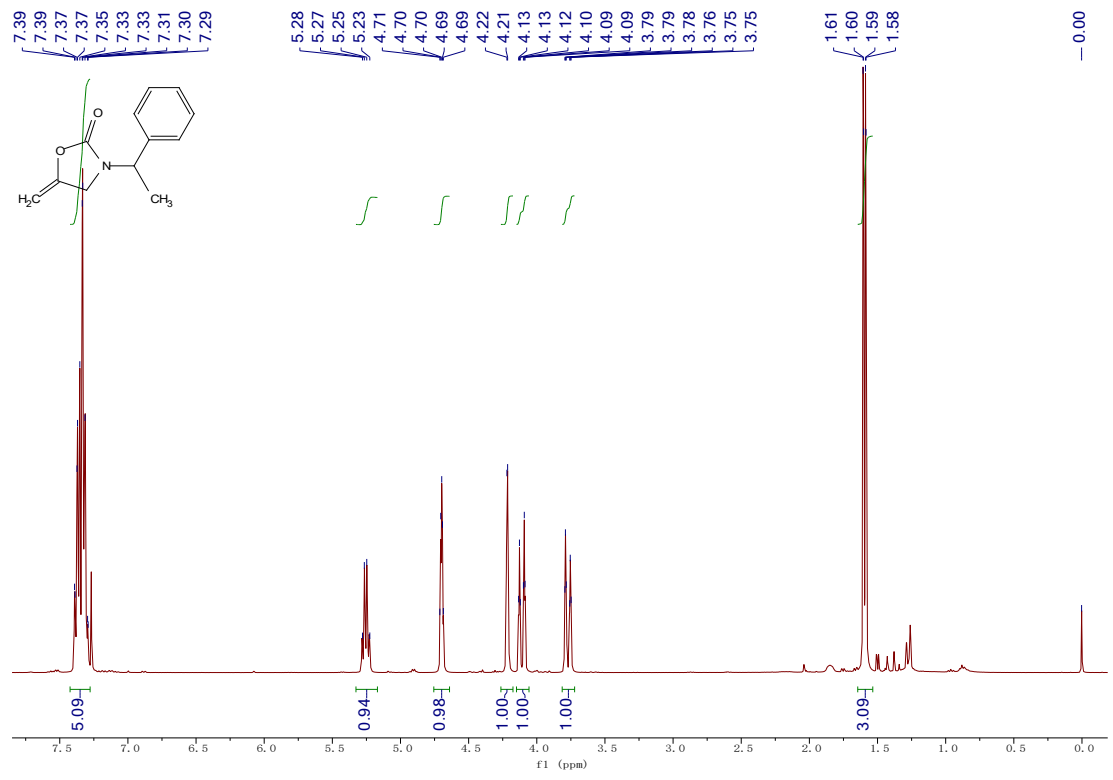
Section 4. Copies of NMR Spectra

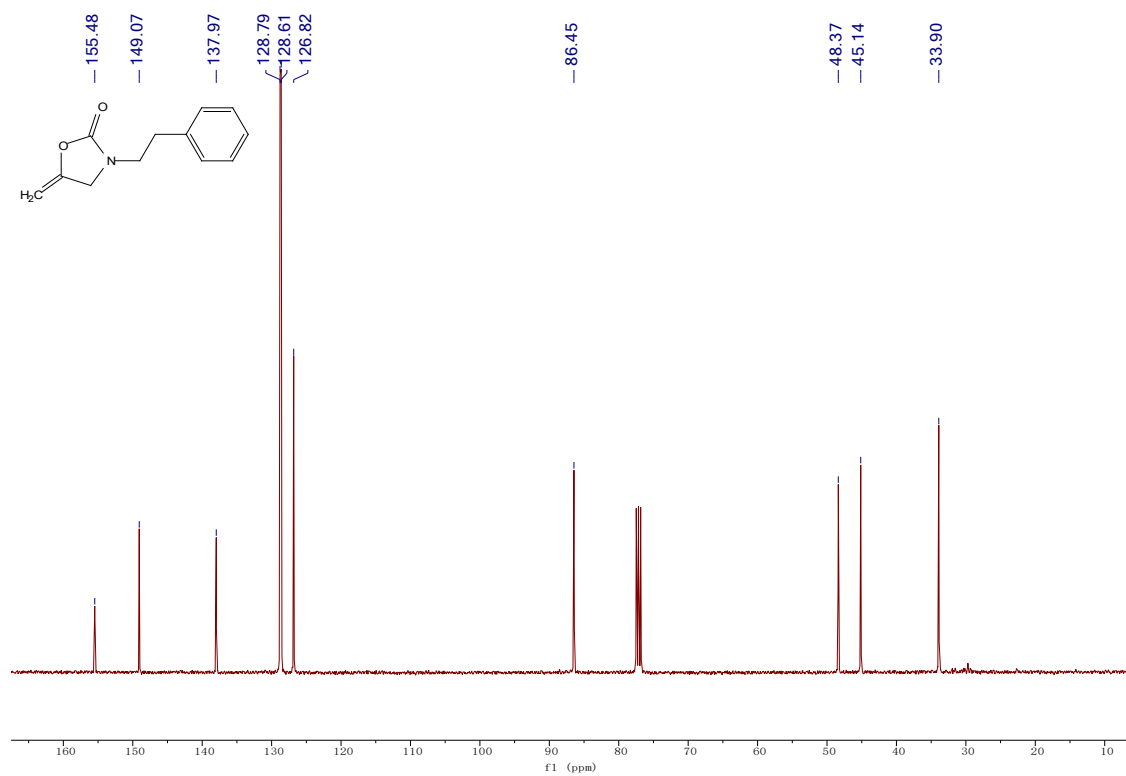
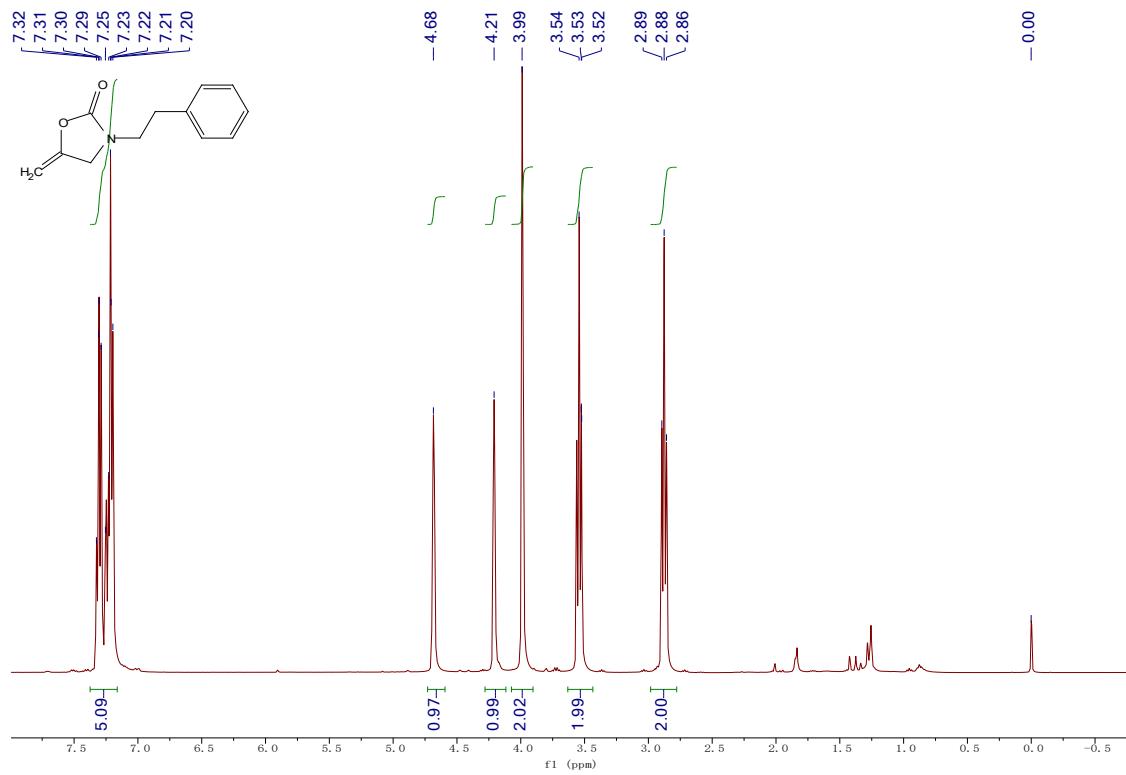


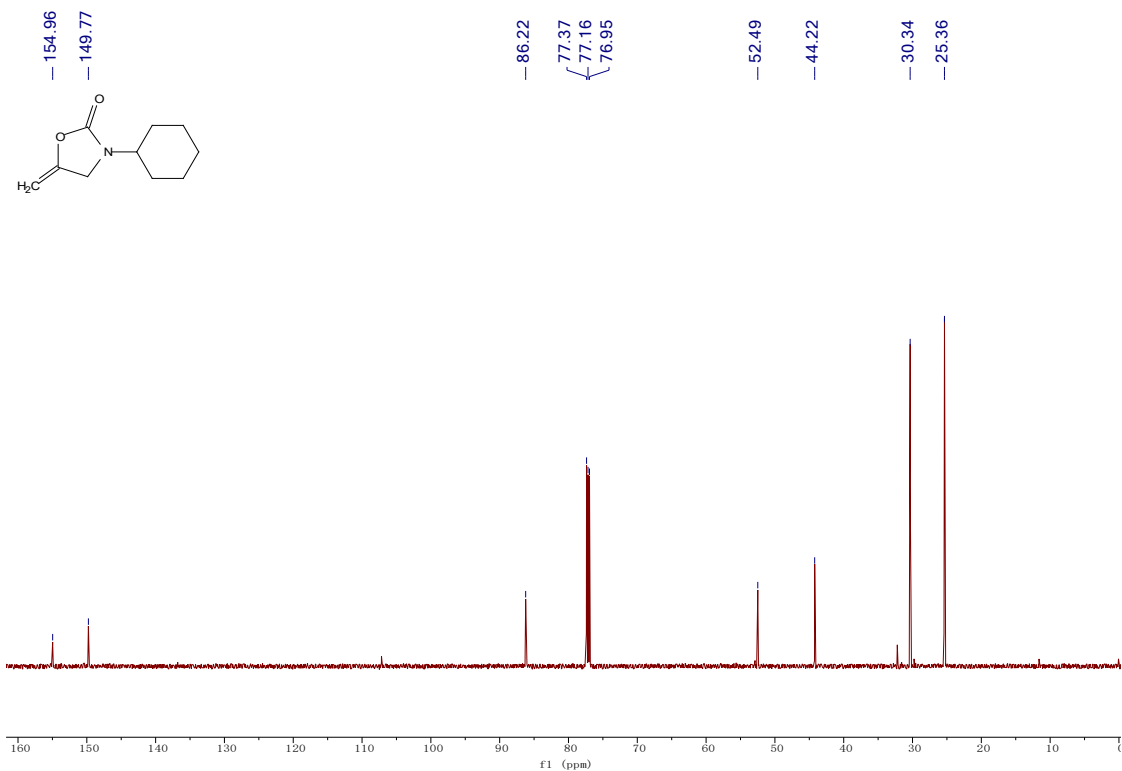
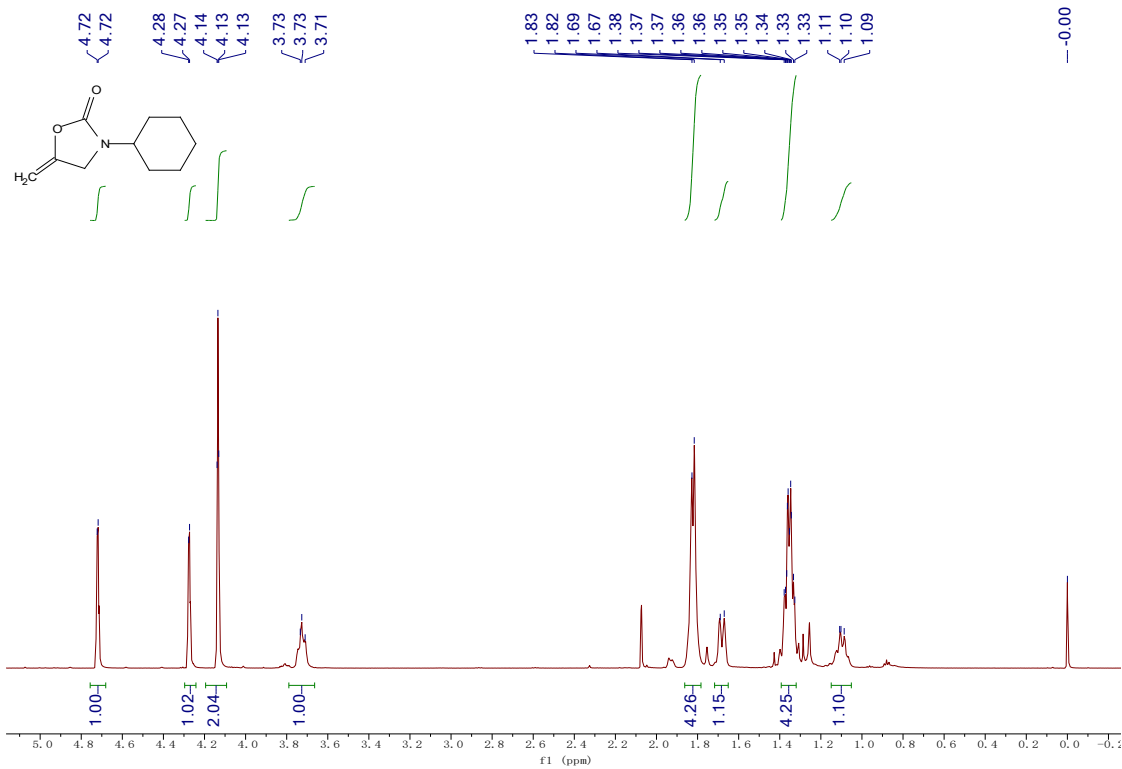


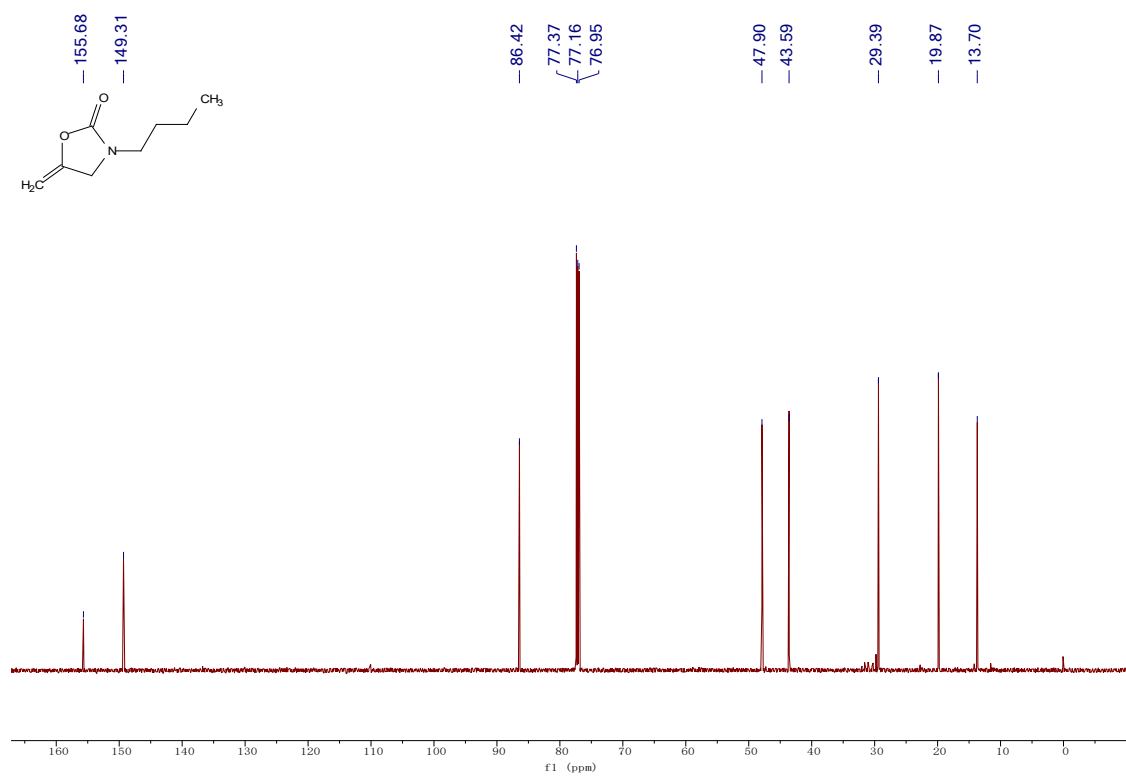
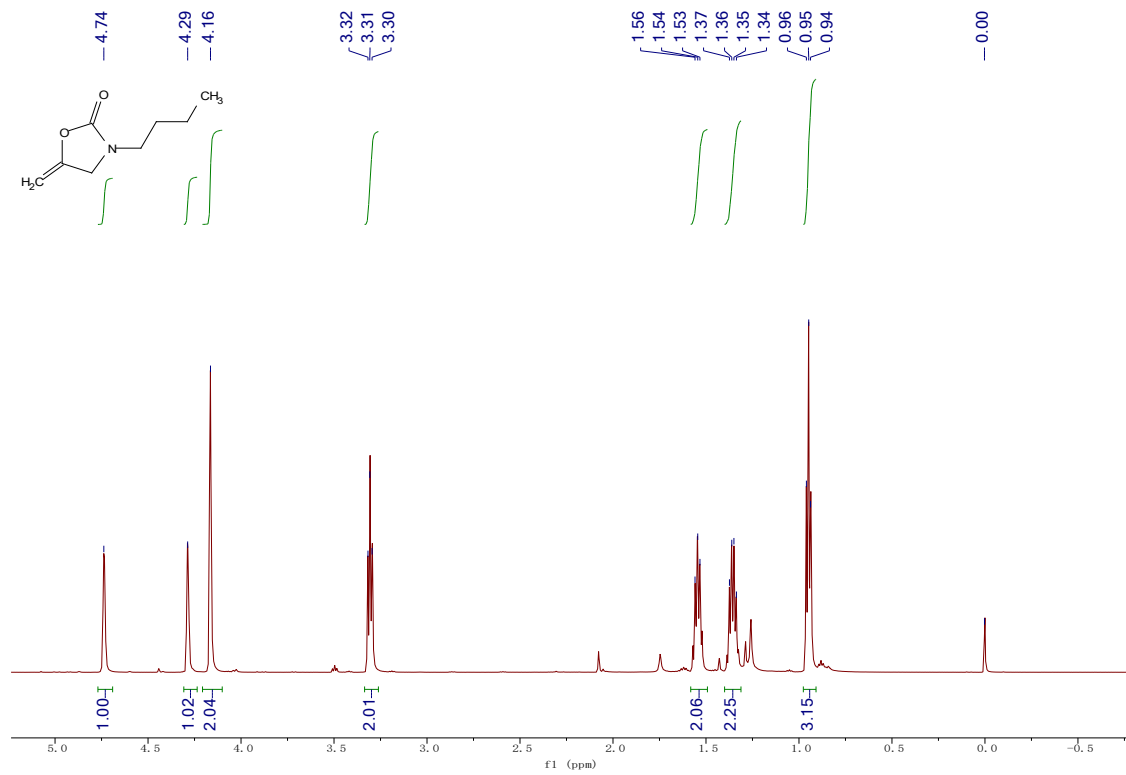


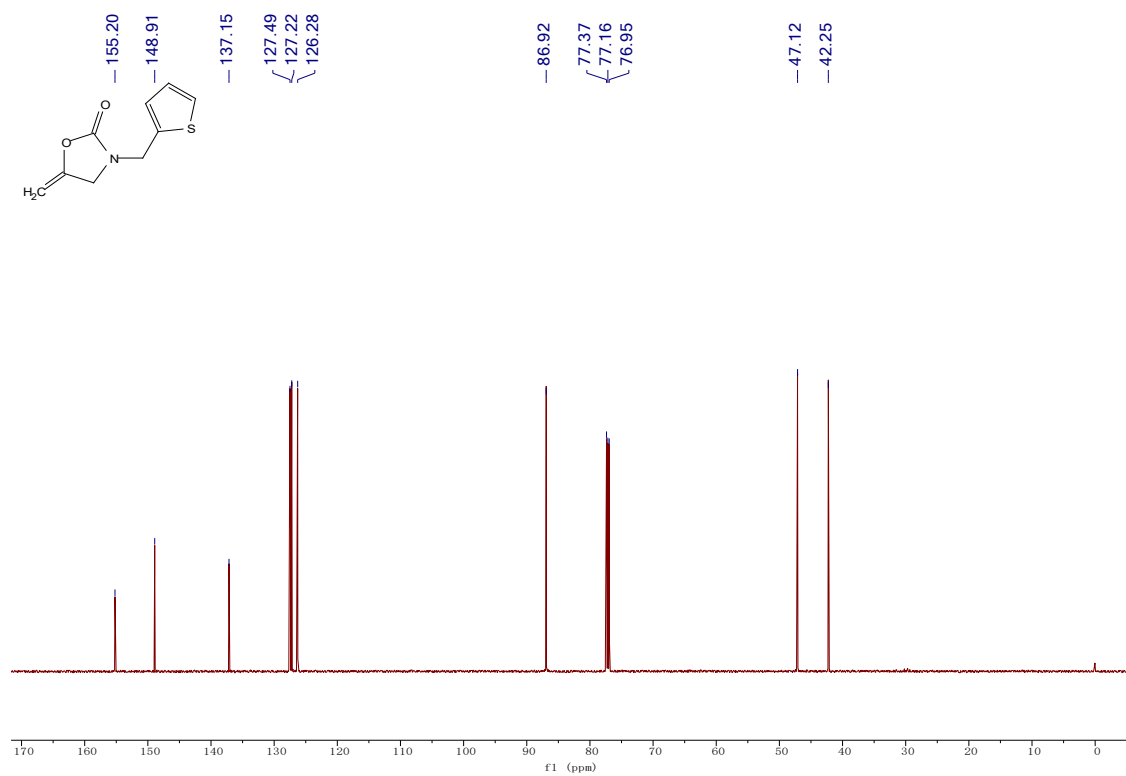
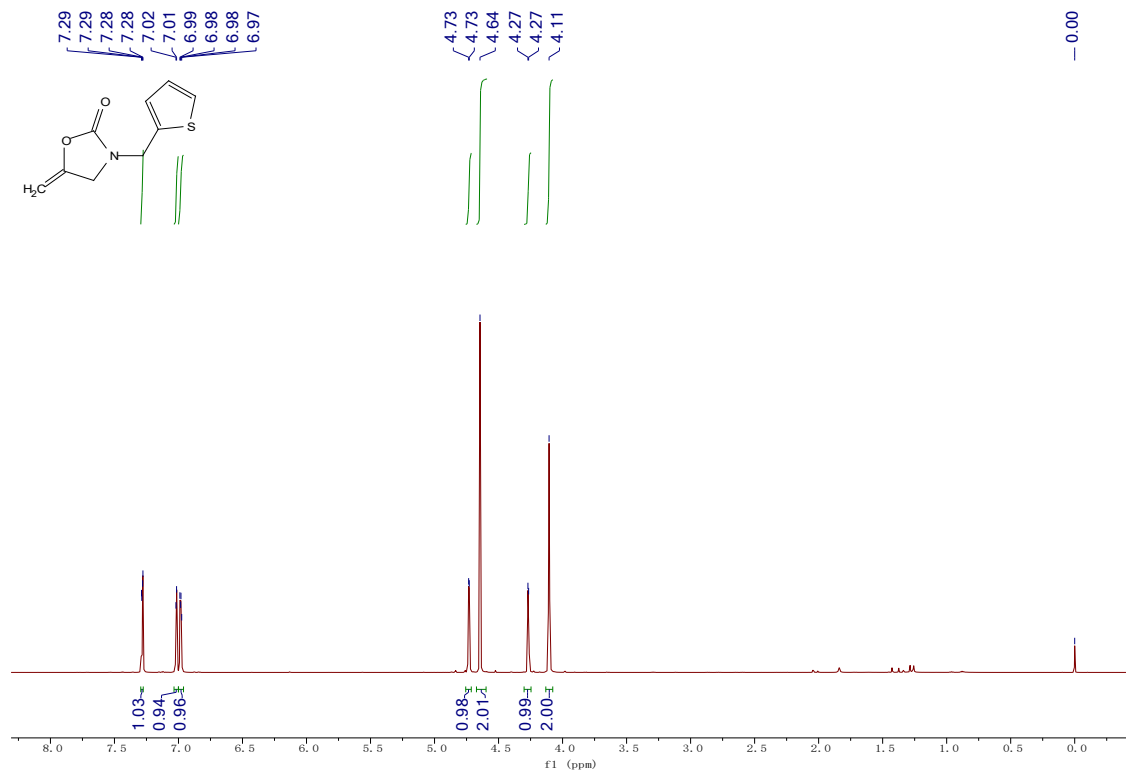


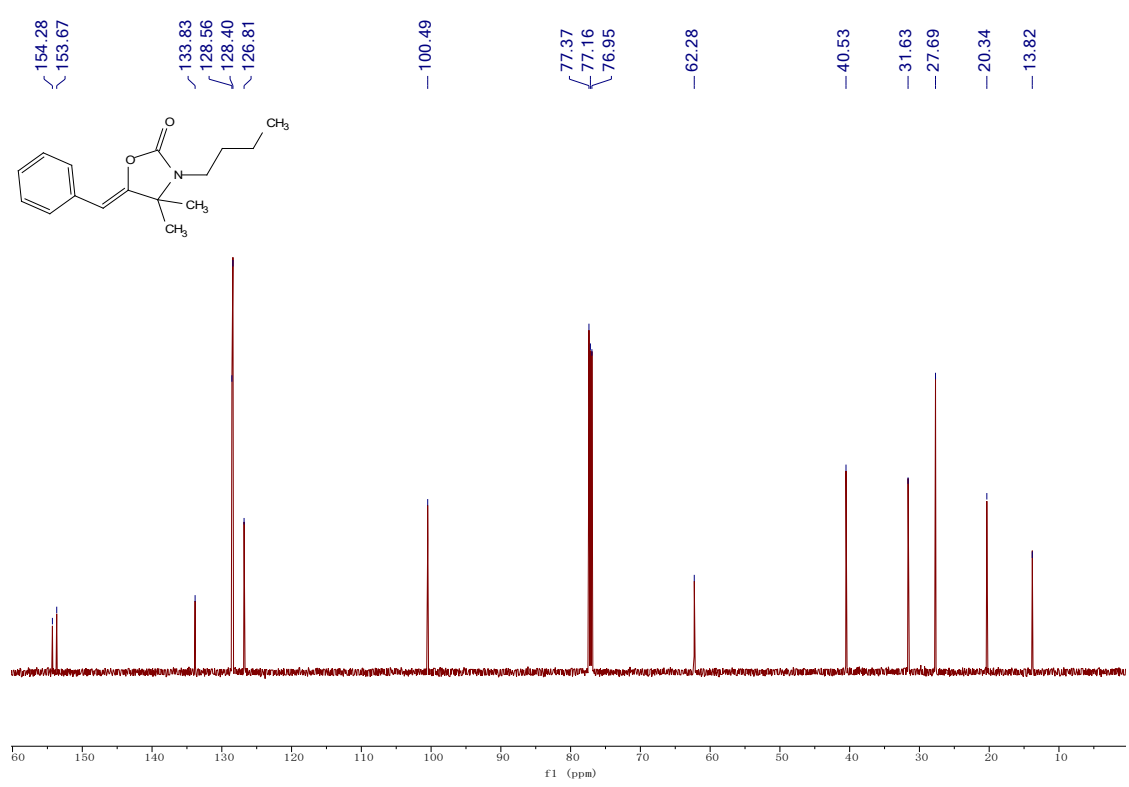
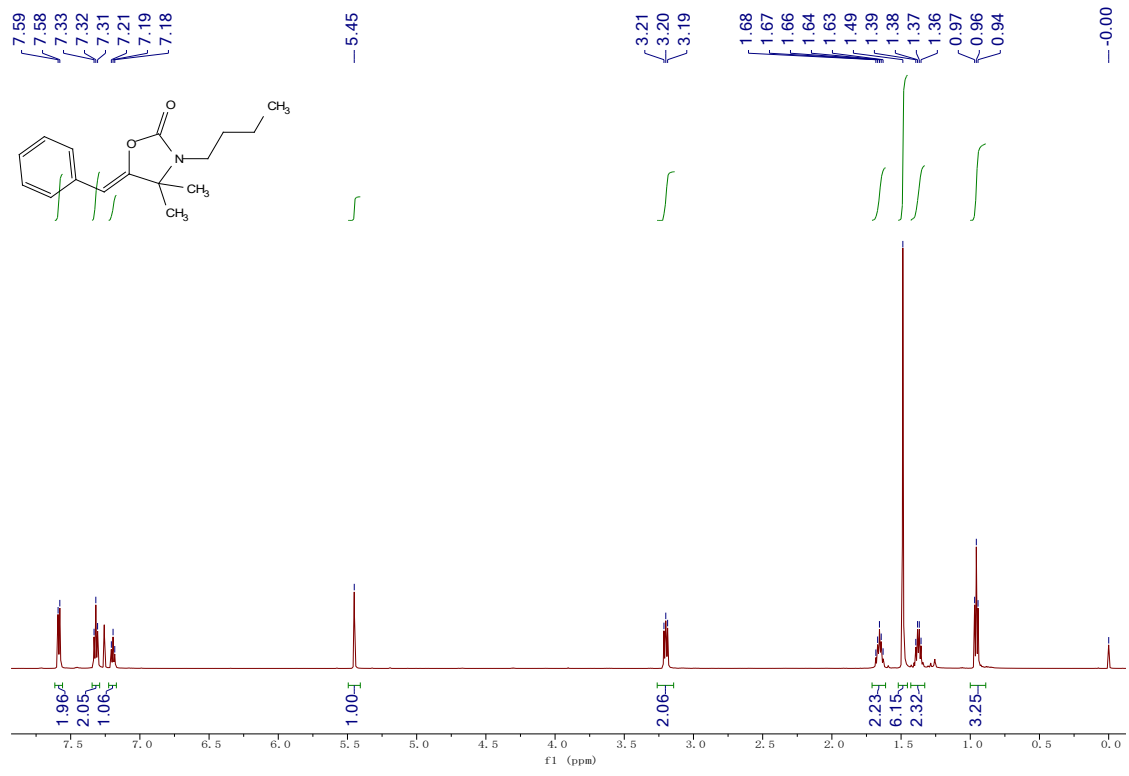


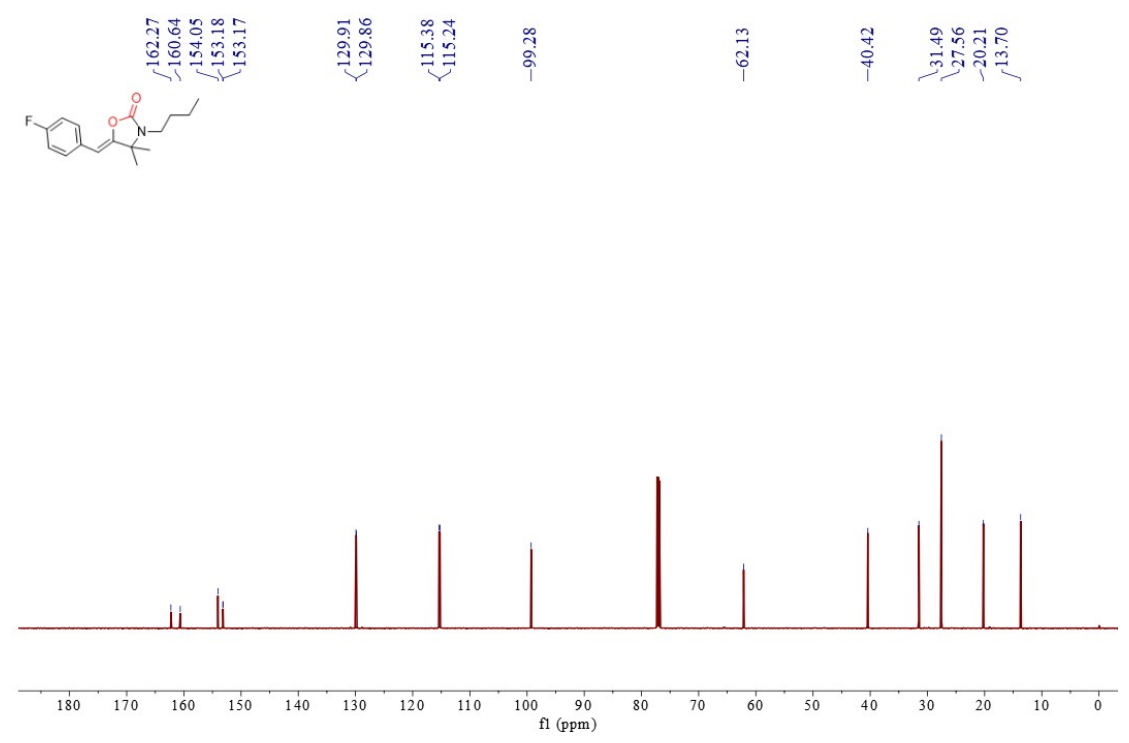
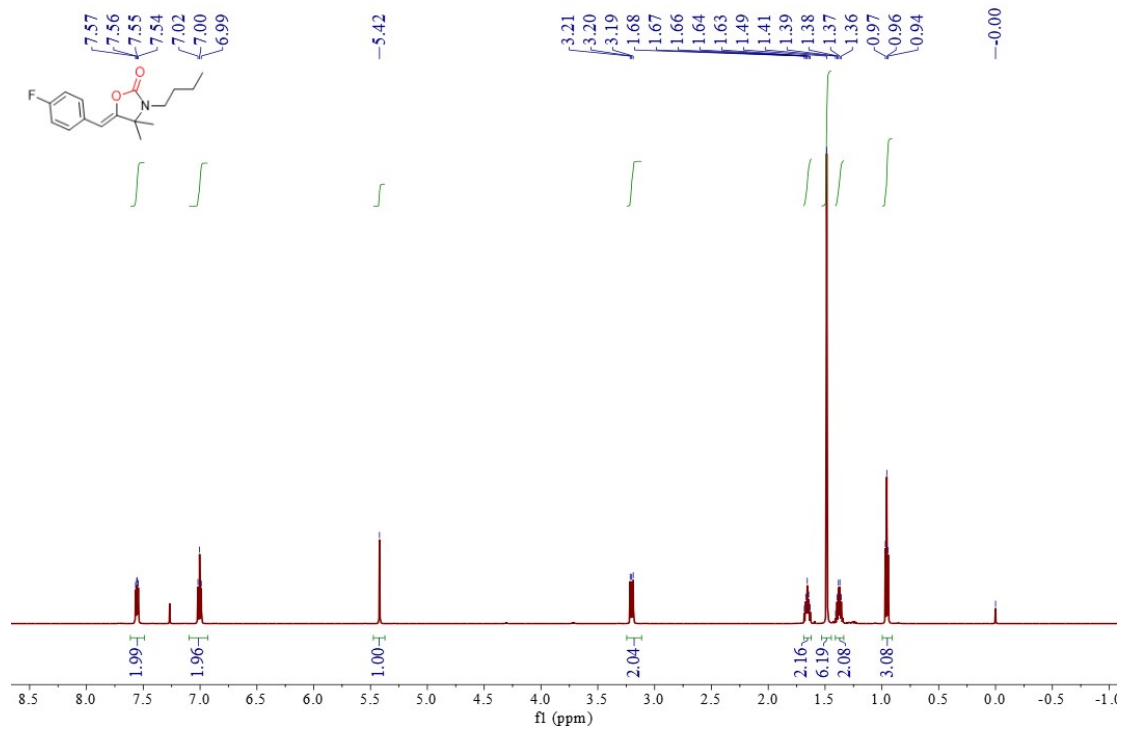


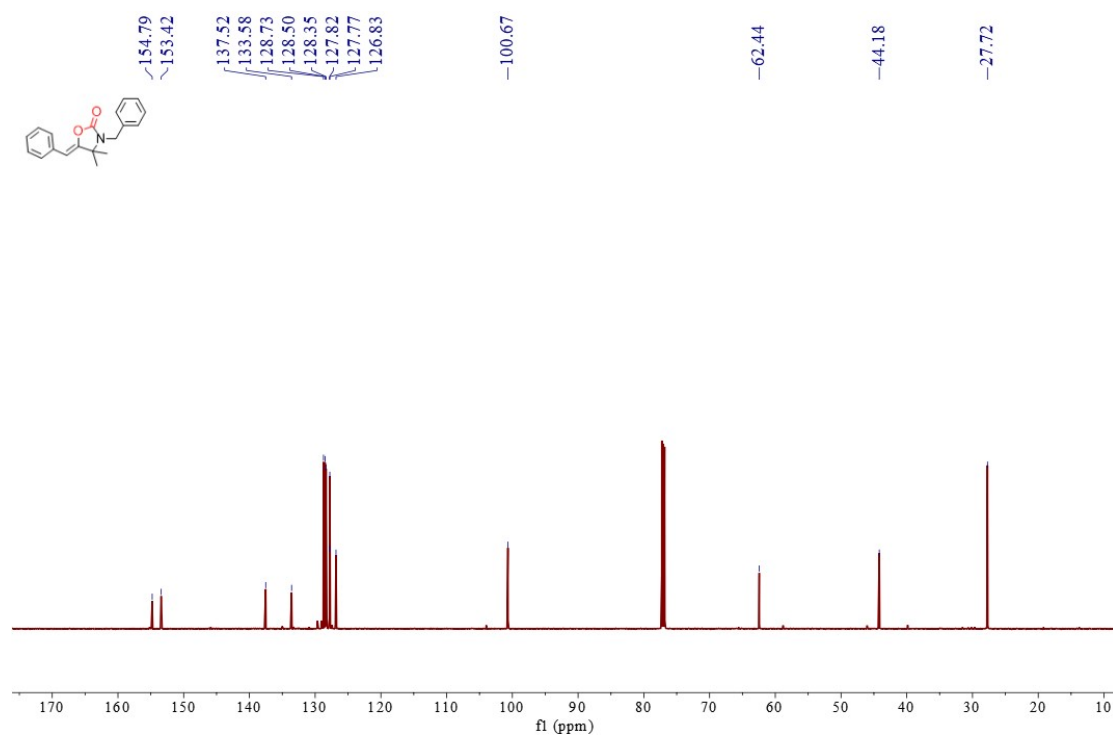
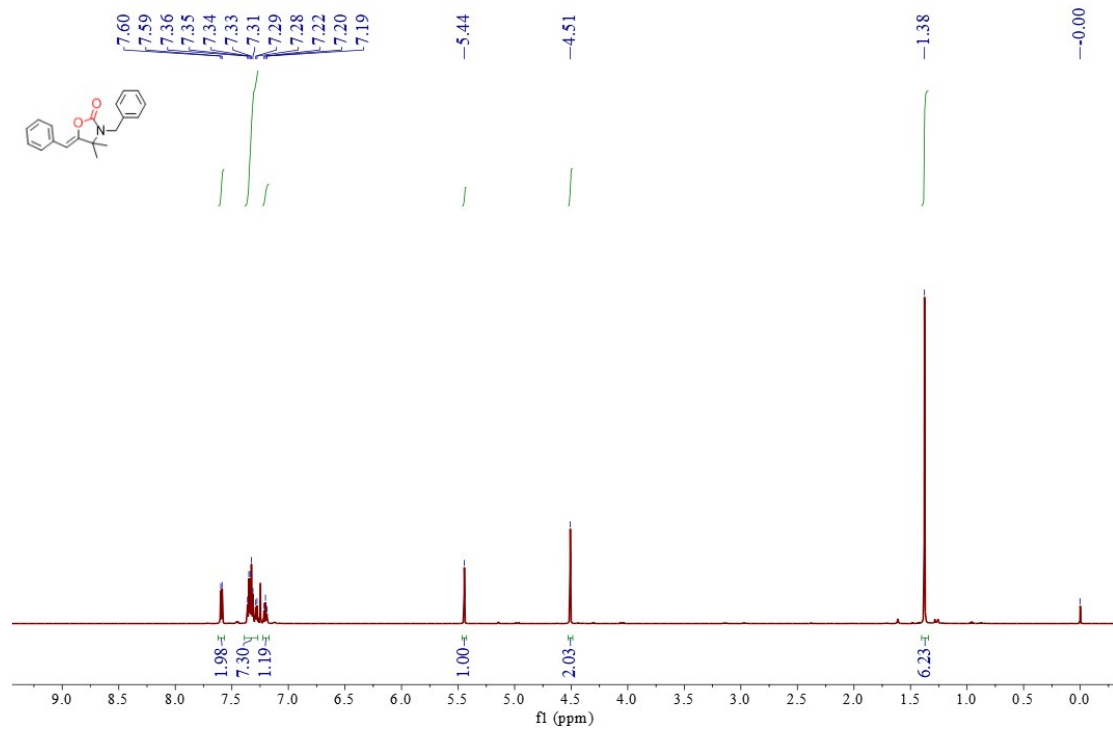












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