Supporting Information

Copper(I) iodide cluster-based lanthanide organic frameworks: synthesis and application as efficient catalysts for carboxylative cyclization of propargyl alcohols with CO_2 under mild conditions

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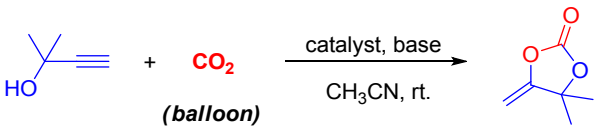
Table S1 Crystallographic data and structure refinements for compounds **1** and **2**.

	1	**2**
Formula	$C_{21}H_8Cu_2DyI_2N_4O_7$	$C_{63}H_{80}Cu_2Gd_2I_2N_{15}O_{21}$
Fw	971.69	2078.80
T/K	150(2)	150(2)
Cryst syst	Tetragonal	Triclinic
Space group	*I*-42*d*	*P*-1
a/Å	25.3670(4)	12.9904(5)
b/Å	25.3670(4)	13.0609(5)
c/Å^3	9.0667(2)	13.4710(6)
α/°	90	65.919(2)
β/°	90	86.020(2)
γ/°	90	82.341(2)
Volume/Å	7818.5(11)	2067.76(15)
Z	8	1
ρ_{calc}mg/mm^3	2.212	1.669
μ/mm^{-1}	6.139	2.910
F(000)	3584	1023
θ/°	2.539 to 26.378	2.198 to 25.010
Reflections collected	41594	30167
Unique reflns	2980 [R_{int}=0.0502]	7290 [R_{int}=0.0571]
GOF on F^2	1.087	1.054
R_1, wR_2 ($I > 2\sigma(I)$)	0.0294, 0.0635	0.0304, 0.0610
R_1, wR_2 (all data)	0.0322, 0.0647	0.0509, 0.0679

Table S2. Carboxylative cyclization of propargyl alcohol with CO_2.[a]



Entry	Catalyst	Base	Yield[b](%)
1	Dy_2O_3	DBU	<1
2	Gd_2O_3	DBU	3
3	compound **1**	Et_3N	Trace
4	compound **1**	K_2CO_3	0
5	compound **1**	Cs_2CO_3	Trace

[a]Reaction conditions: 2-methyl-3-butyn-2-ol (0.6 mmol), catalyst (30 mg), base (1.0 equiv.), CH_3CN (3 mL), CO_2 (balloon), 5 h, room temperature. [b] Determined by GC.

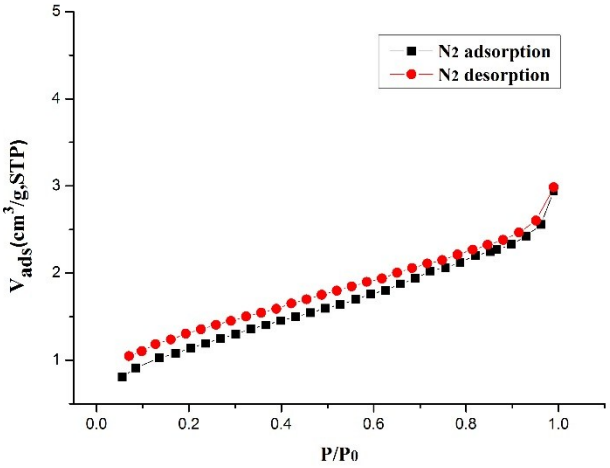


Figure. S1 N_2 sorption isotherm of compound **1** at 77 K.

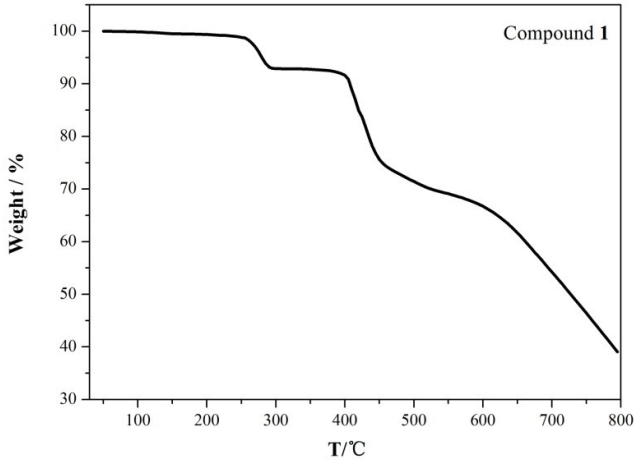


Figure. S2 The TGA curve for compound **1**.

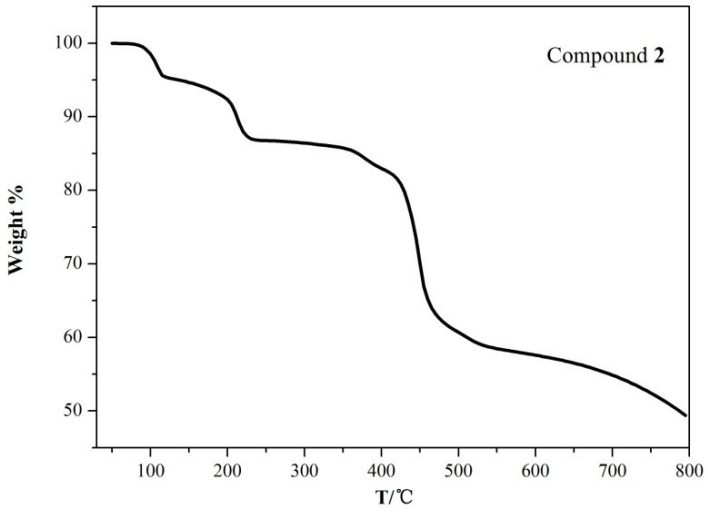


Figure. S3 The TGA curve for compound **2**.

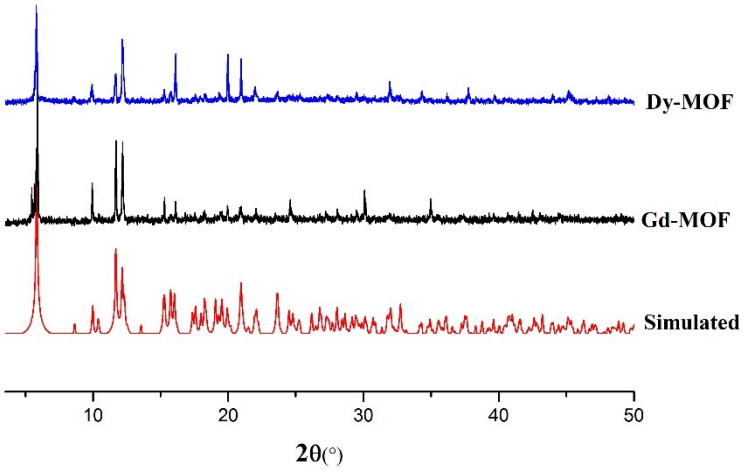


Figure. S4 The PXRD patterns of Gd-MOF and Dy-MOF.

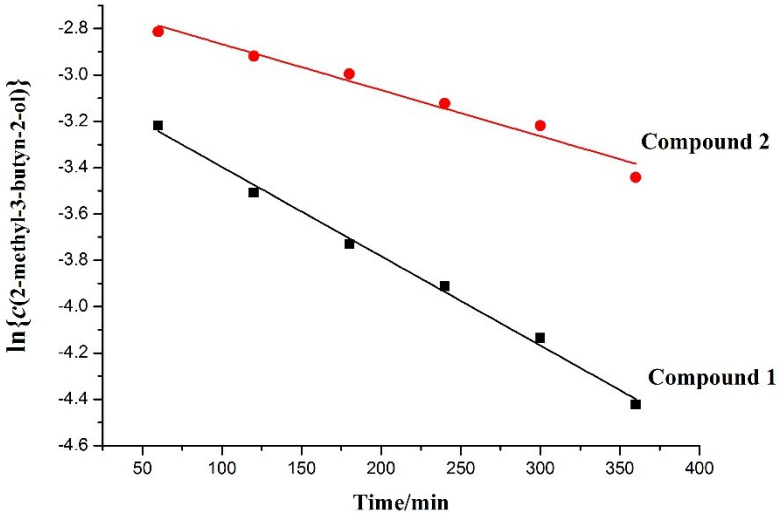


Figure. S5 The kinetic study for compounds **1** and **2** in the reactions.

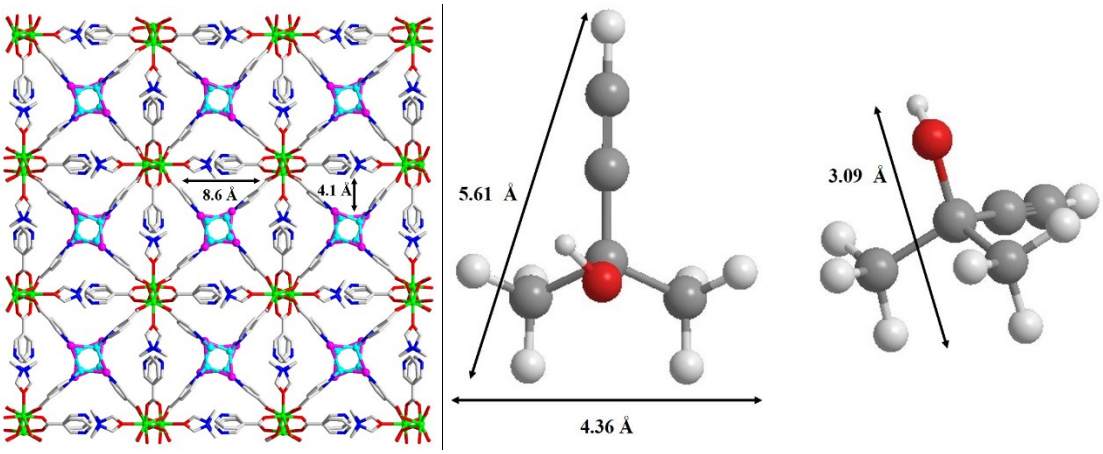


Figure. S6 Perspective view of the framework of **1** along c direction (left) and the size of 2-methyl-3-butyn-2-ol.

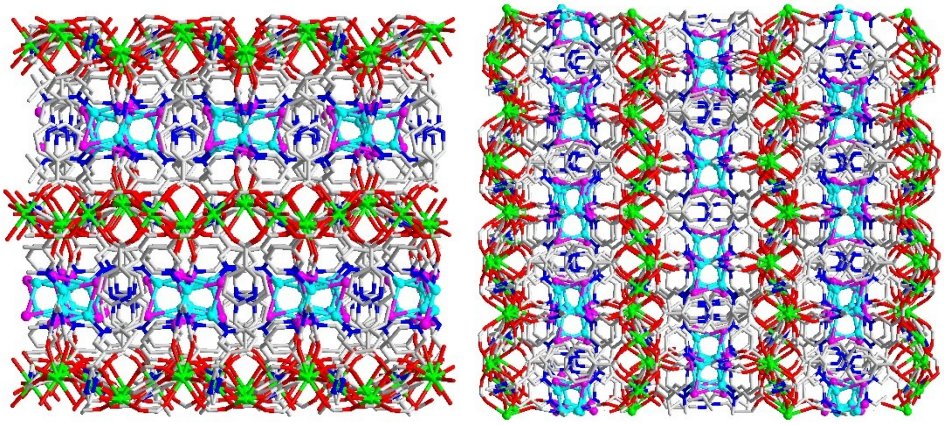


Figure. S7 Perspective view of the framework of **1** along a direction (left) and b direction (right), respectively.

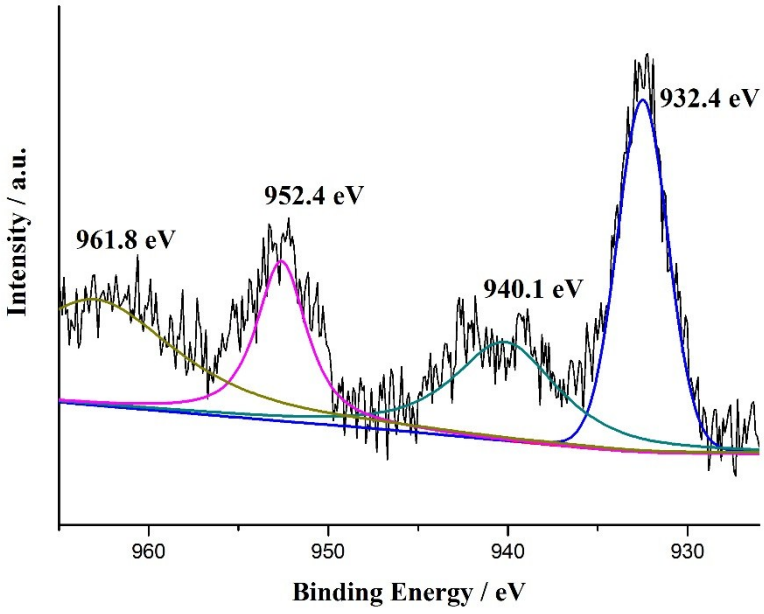
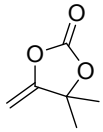


Figure. S8 The XPS spectra of Cu(I) and Cu(II) in the reused **1**.

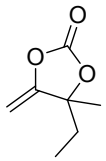
Characterization Data of All Products

*4,4-Dimethyl-5-methylene-1,3-dioxolan-2-one (**2a**):*



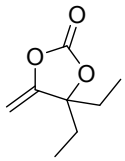
Colorless oil liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) : 4.70 (d, J = 4.20 Hz, 1H), 4.24 (d, J = 4.20 Hz, 1H), 1.55 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 158.78, 151.26, 85.26, 84.61, 27.58. GC-MS calcd. for $C_6H_8O_3$ 128.05, found 128.10.

*4-Ethyl-4-methyl-5-methylene-1,3-dioxolan-2-one(**2b**)*



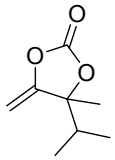
Colorless oil liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) : 4.82 (d, J = 3.60 Hz, 1H), 4.28 (d, J = 3.60 Hz, 1H), 1.95-1.89 (m, 1H), 1.80-1.74 (m, 1H), 1.59 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 157.45, 151.53, 87.57, 85.54, 33.38, 25.93, 7.30. GC-MS calcd. for $C_7H_{10}O_3$ 142.06, found 142.08.

*4,4-Diethyl-5-methylene-1,3-dioxolan-2-one (**2c**)*



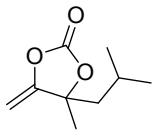
Colorless oil liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) : 4.87 (d, J = 4.2 Hz, 1H), 4.23 (d, J = 4.20 Hz, 1H), 1.97-1.91 (m, 2H), 1.75-1.69 (m, 2H), 0.98 (t, J = 7.20 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) : 155.81, 151.85, 90.83, 85.78, 31.90, 7.10. GC-MS calcd. for $C_8H_{12}O_3$ 156.08, found 156.13.

*4-Isopropyl-4-methyl-5-methylene-1,3-dioxolan-2-one (**2d**)*



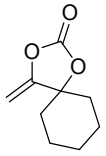
Colorless oil liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) : 4.82 (d, J = 4.20 Hz, 1H), 4.28 (d, J = 3.60 Hz, 1H), 1.97-1.93 (m, 1H), 1.58 (s, 3H), 1.03 (d, J = 7.20 Hz, 3H), 1.00 (d, J = 6.60 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 157.13, 151.68, 89.80, 86.17, 36.96, 24.00, 16.31, 16.01. GC-MS calcd. for $C_8H_{12}O_3$ 156.08, found 156.13.

*4-Isobutyl-4-methyl-5-methylene-1,3-dioxolan-2-one (**2e**)*



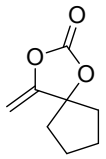
Colorless oil liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) : 4.79 (d, J = 1.80 Hz, 1H), 4.27 (d, J = 1.80, 1H), 1.85-1.79 (m, 2H), 1.68-1.65 (m, 1H), 1.58 (s, 2H), 0.97 (dd, J_1 = 6.60 Hz, J_2 = 4.20 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 158.34, 151.45, 87.32, 85.55, 48.53, 27.00, 24.28, 23.96, 23.66. GC-MS calcd. for $C_9H_{14}O_3$ 170.09, found 170.08.

*4-Methylene-1,3-dioxaspiro[4.5]decan-2-one (**2f**)*



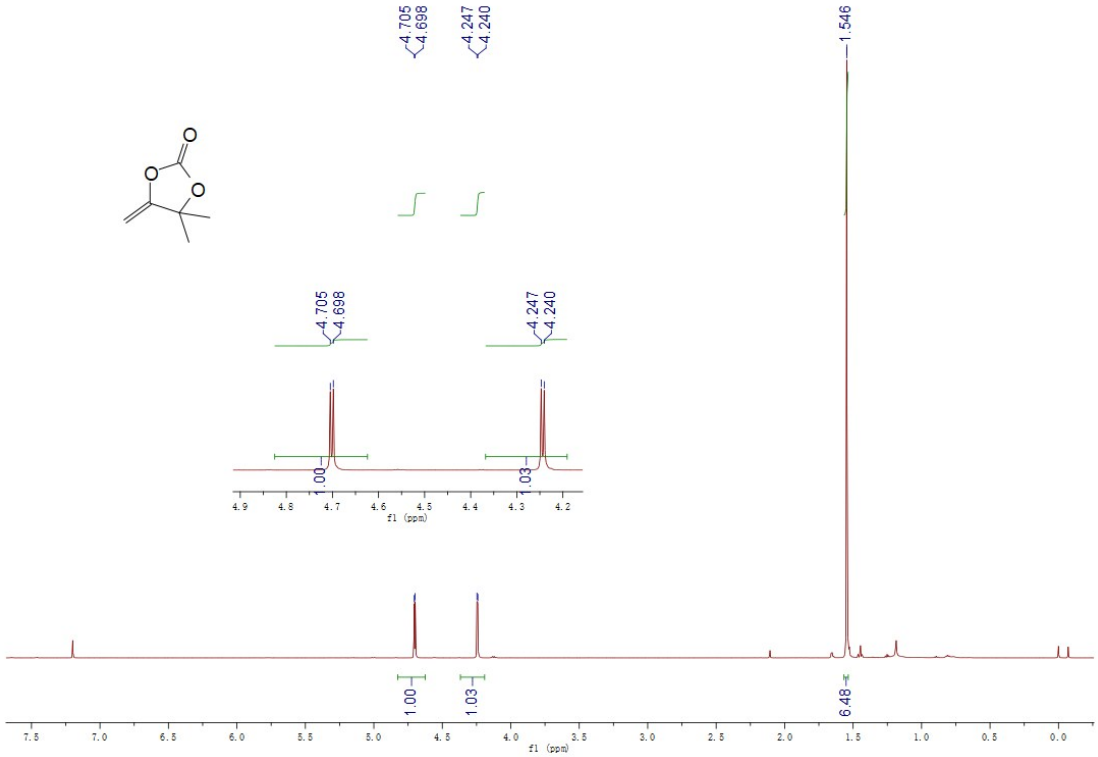
Colorless oil liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 4.76 (d, J = 3.00 Hz, 1H), 4.28 (d, J = 3.60 Hz, 1H), 2.0 (d, J = 4.80 Hz, 2H), 1.74-1.59 (m, 7H), 1.34-1.25 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm): 158.78, 151.48, 86.38, 85.46, 36.53, 24.37, 21.62. GC-MS calcd. for $C_9H_{12}O_3$ 168.08, found 168.06.

*4-Methylene-1,3-dioxaspiro[4.4]nonan-2-one (**2g**)*

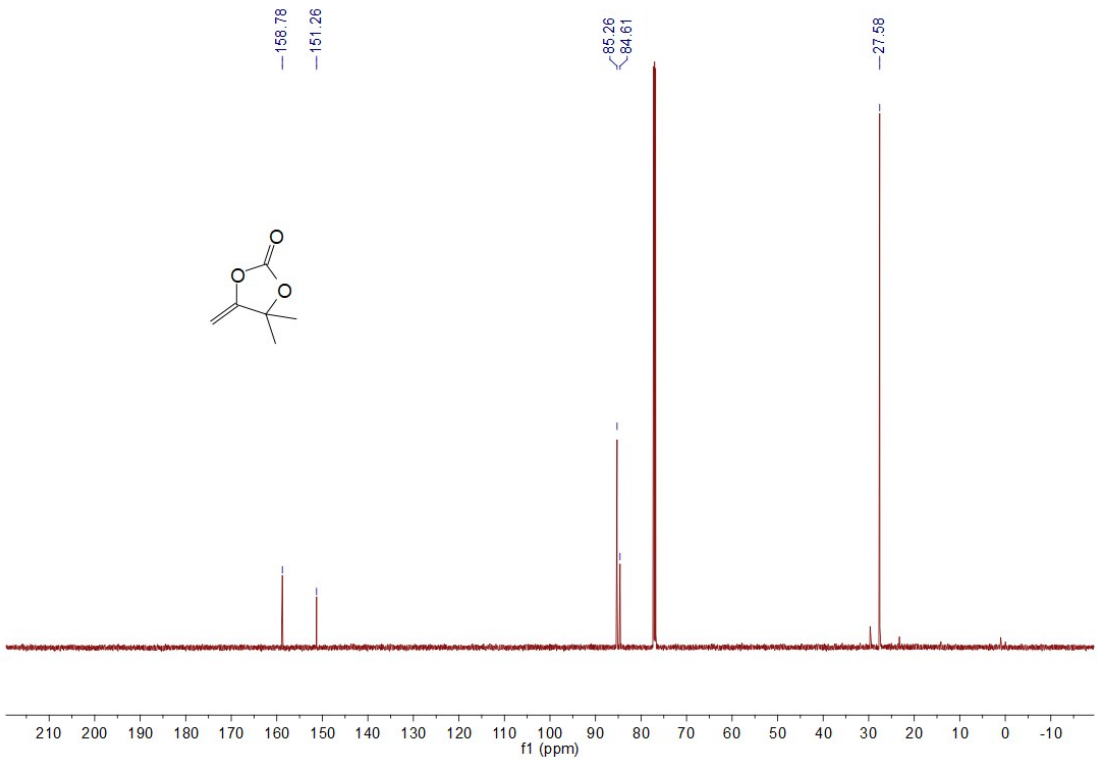


Colorless oil liquid. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) : 4.79 (d, J = 4.20 Hz, 1H), 4.33 (d, J = 4.20 Hz, 1H), 2.26-2.22 (m, 2H), 1.95-1.83 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ (ppm) : 157.82, 151.47, 94.20, 85.30, 40.66, 24.26. GC-MS calcd. for $C_8H_{10}O_3$ 154.06, found 154.03

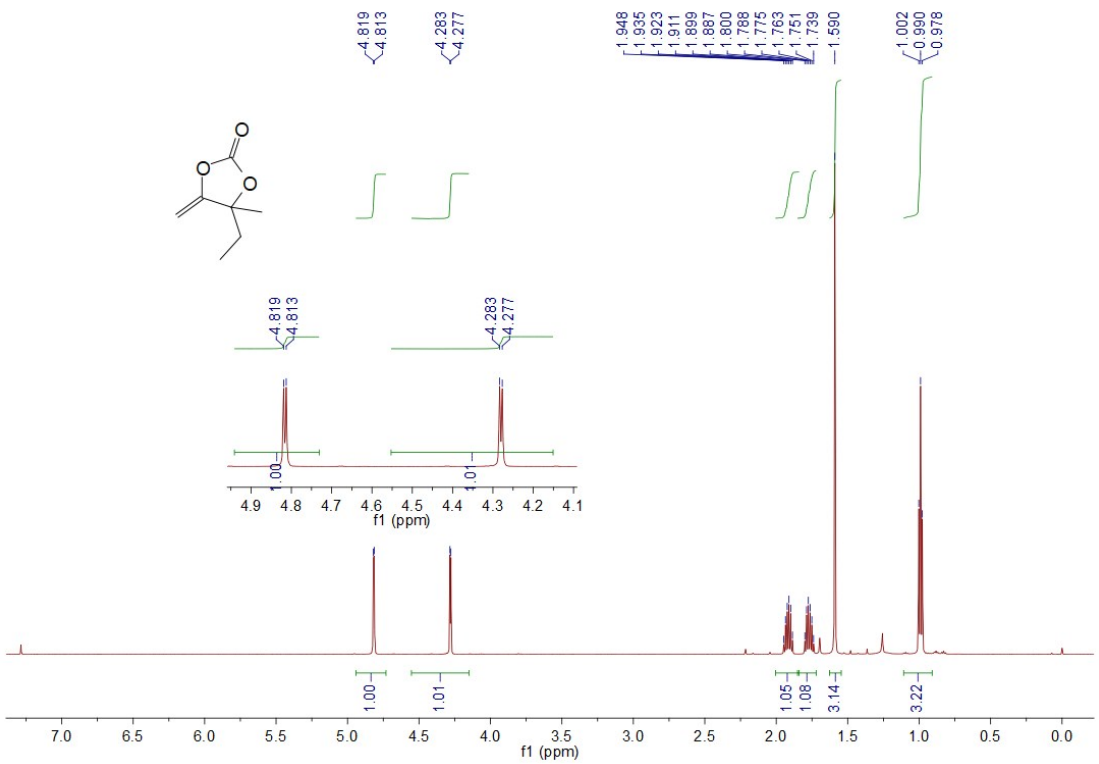
Copies of NMR Spectra of All Products



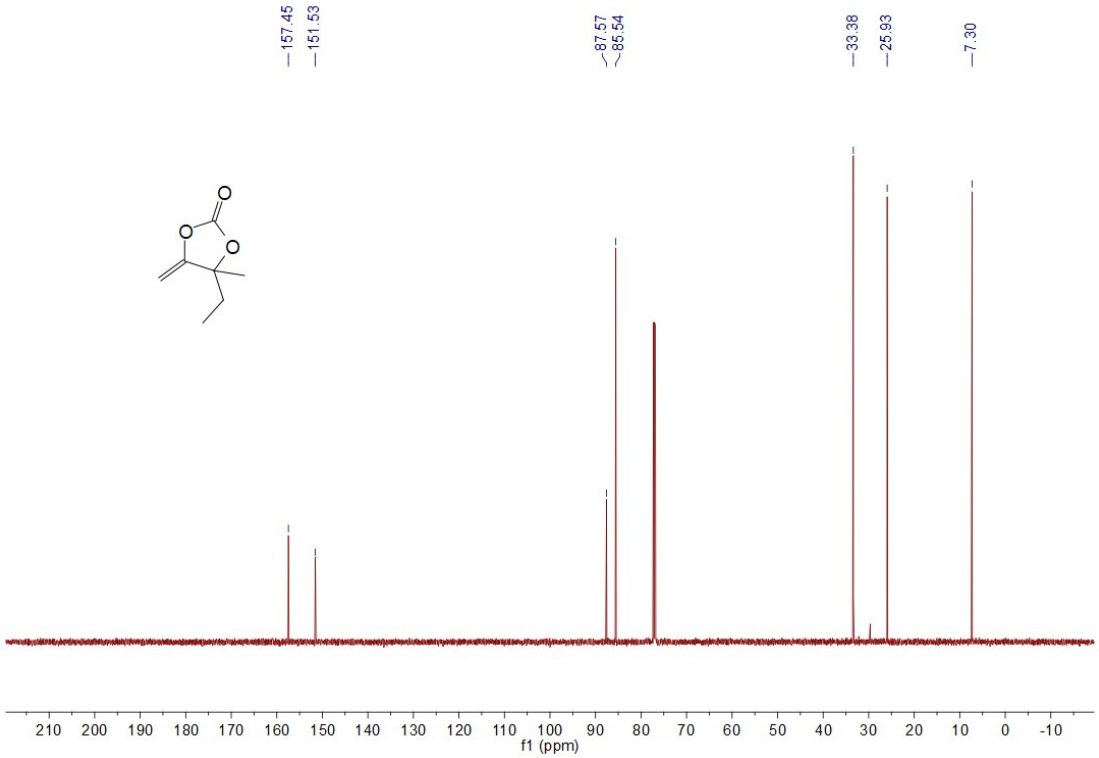
^{1}H NMR spectrum of product ***2a***



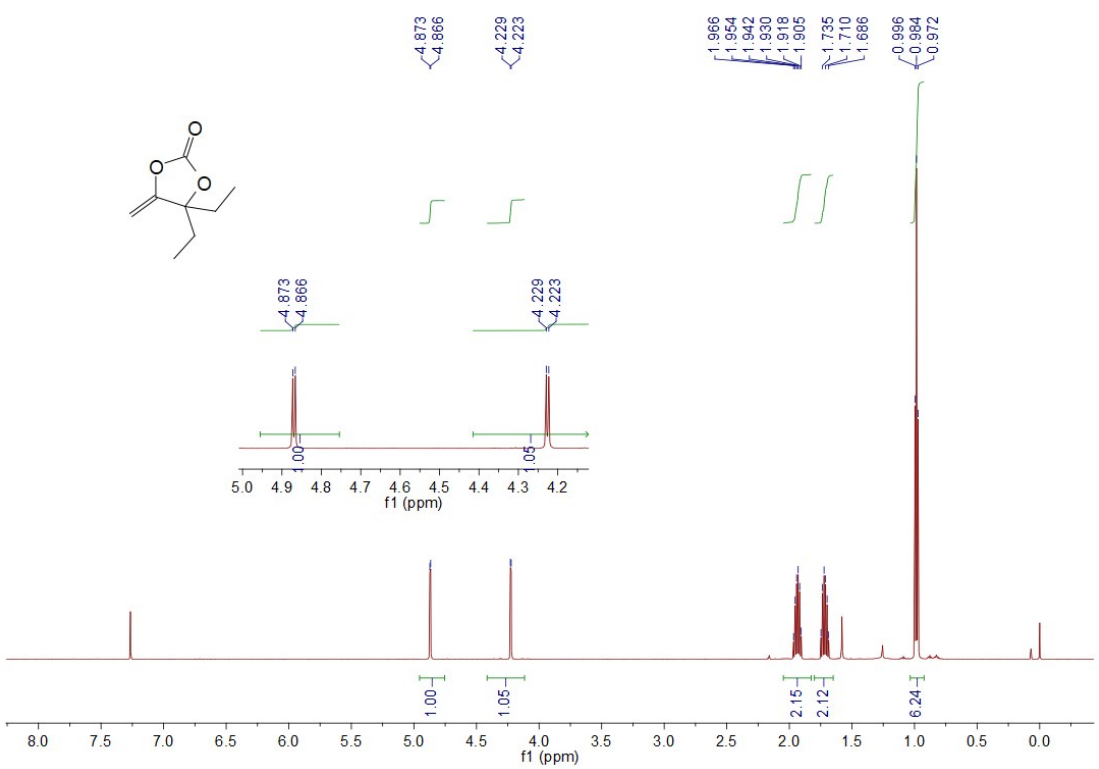
^{13}C NMR spectrum of product ***2a***



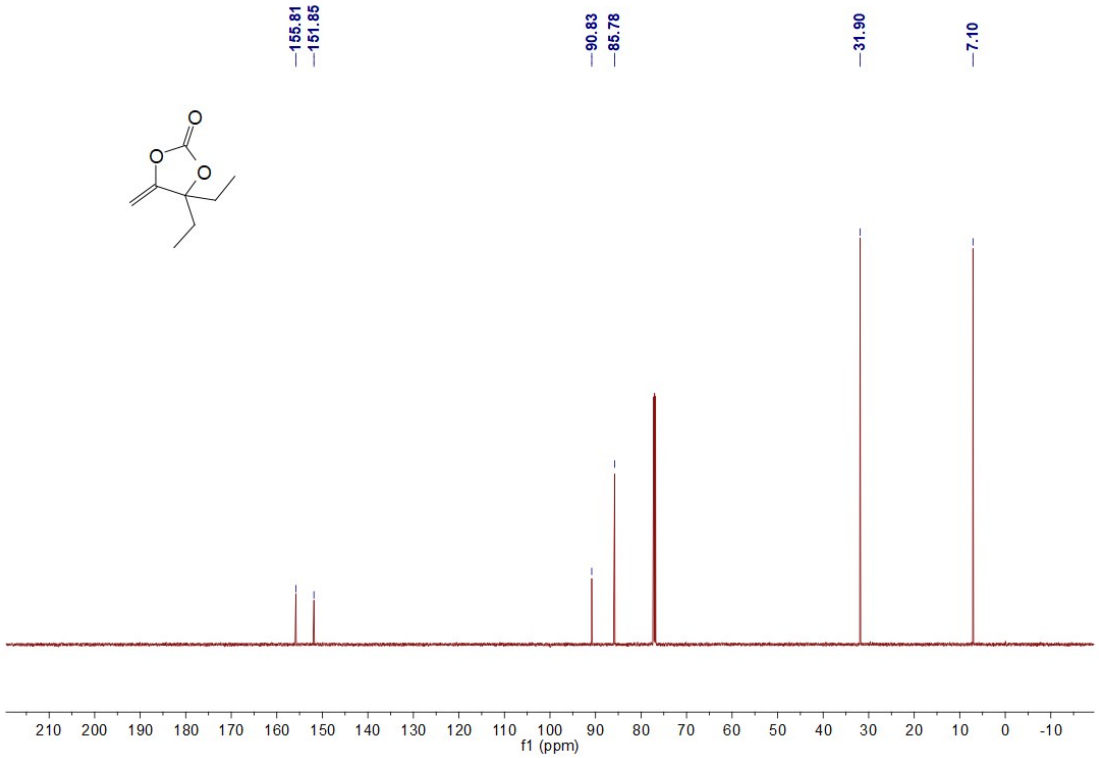
^{1}H NMR spectrum of product ***2b***



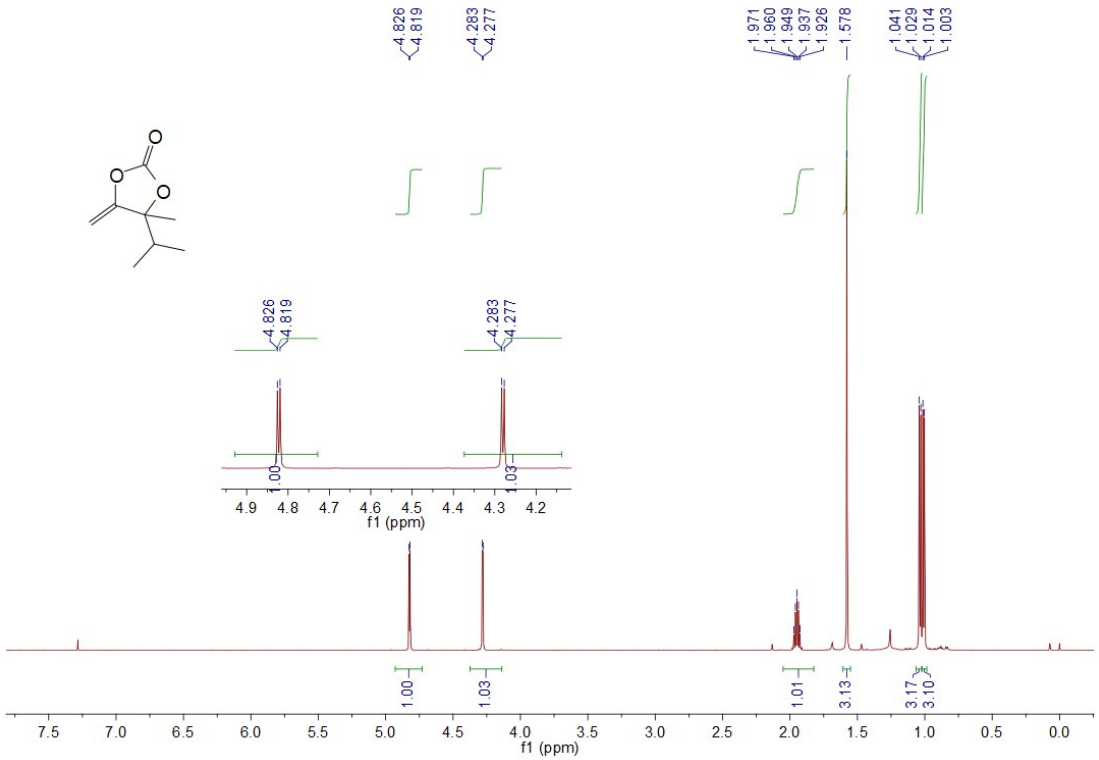
^{13}C NMR spectrum of product ***2b***



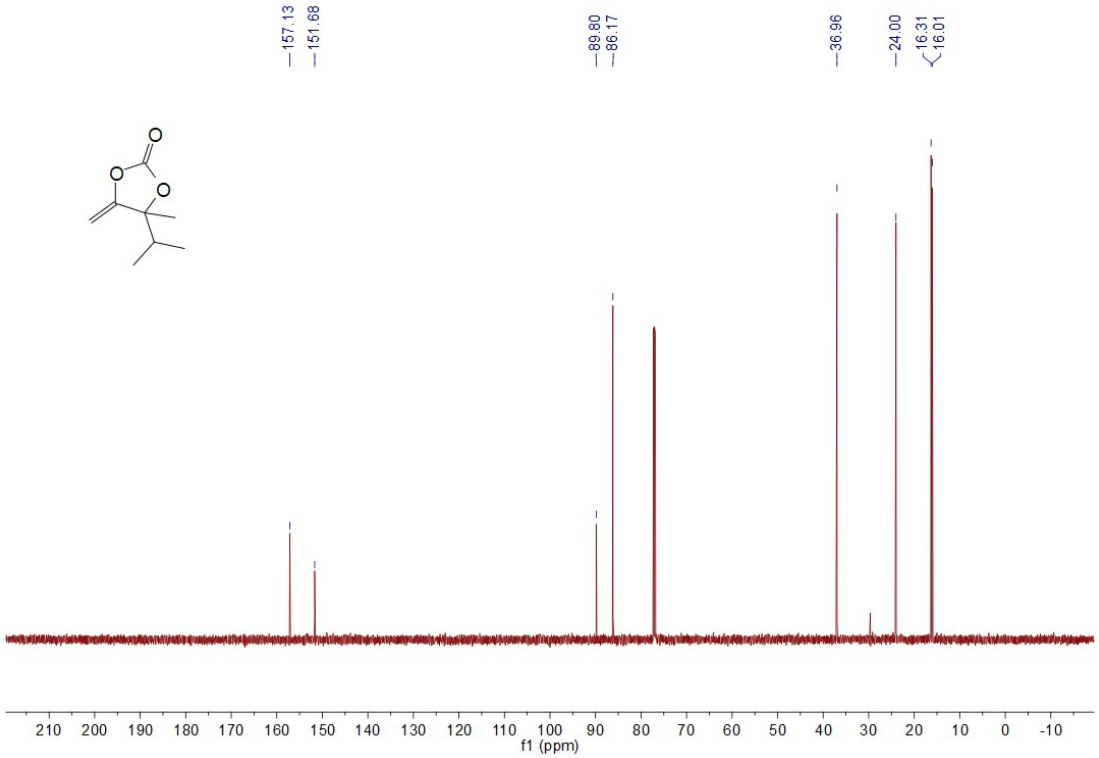
^{1}H NMR spectrum of product ***2c***



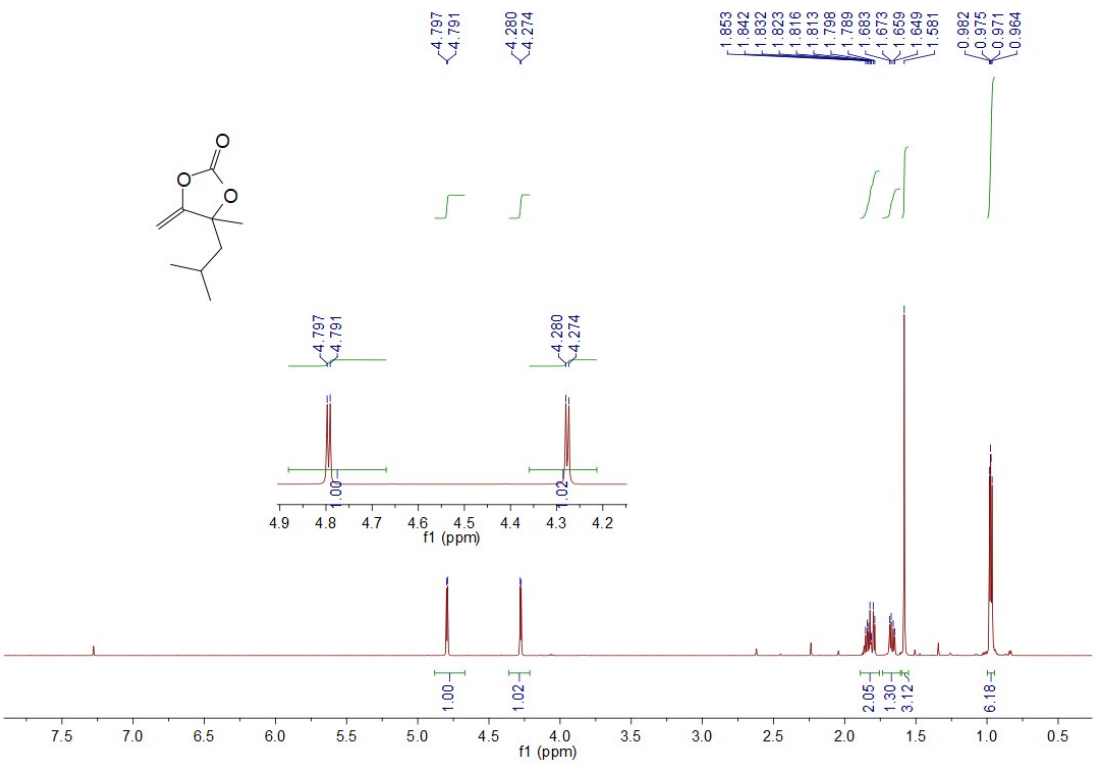
^{13}C NMR spectrum of product ***2c***



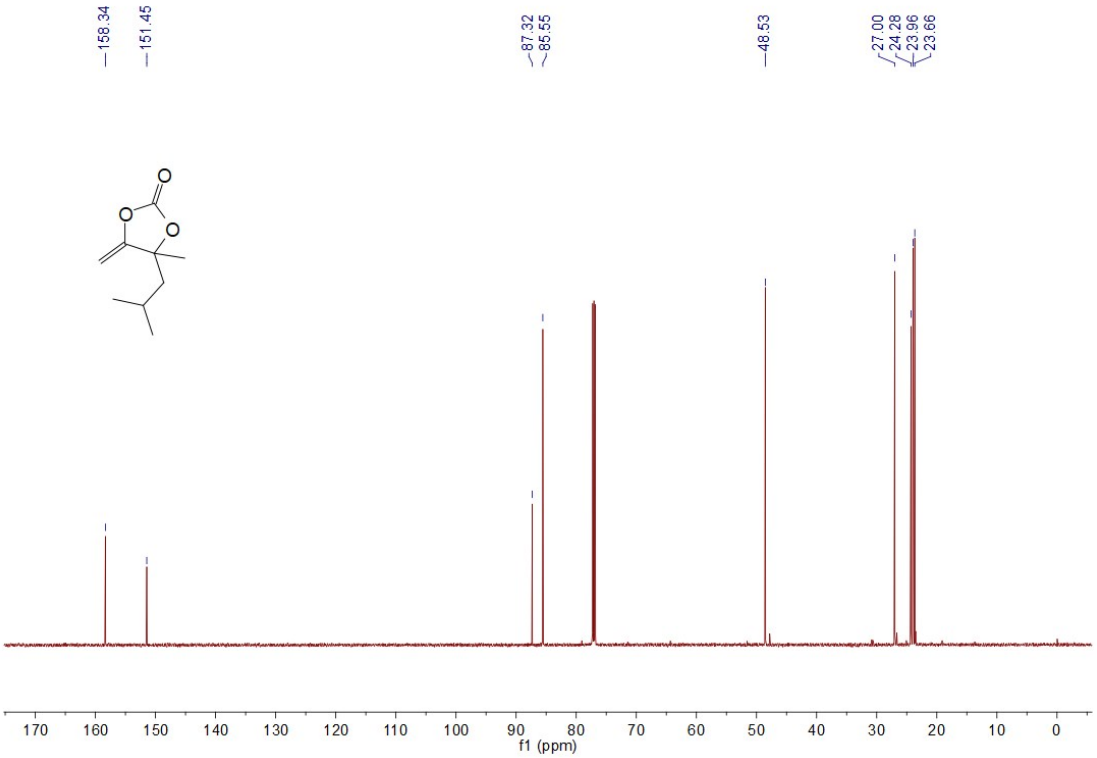
^{1}H NMR spectrum of product ***2d***



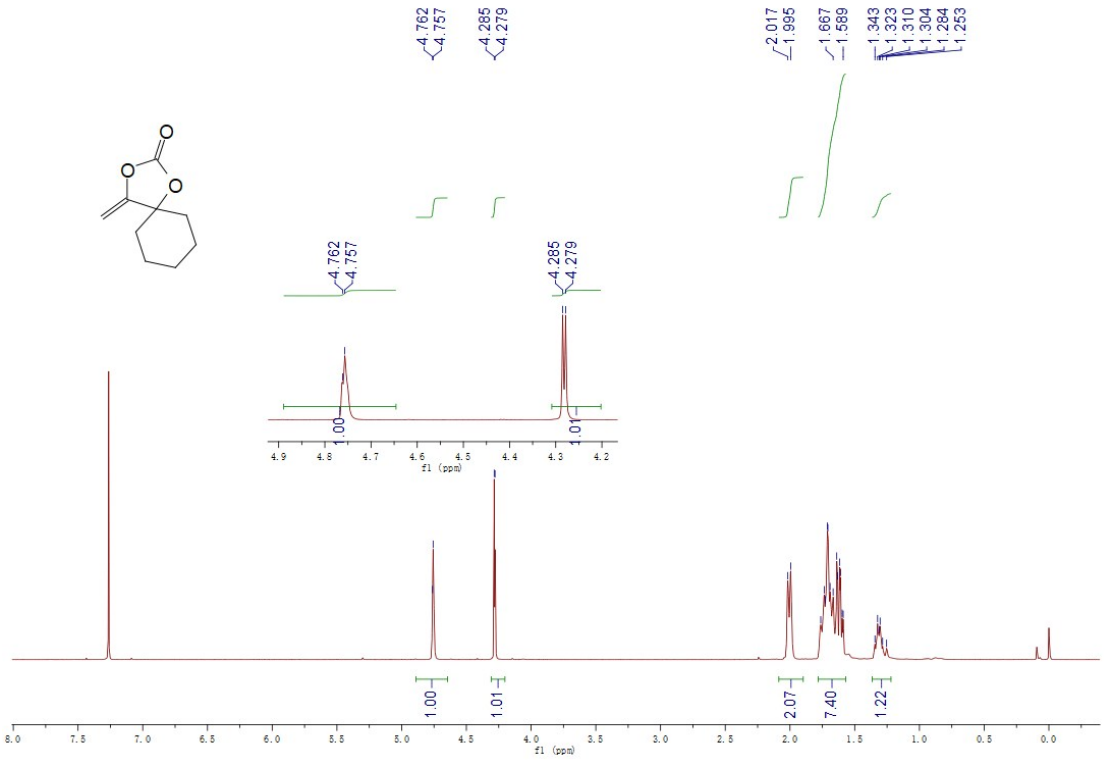
^{13}C NMR spectrum of product ***2d***



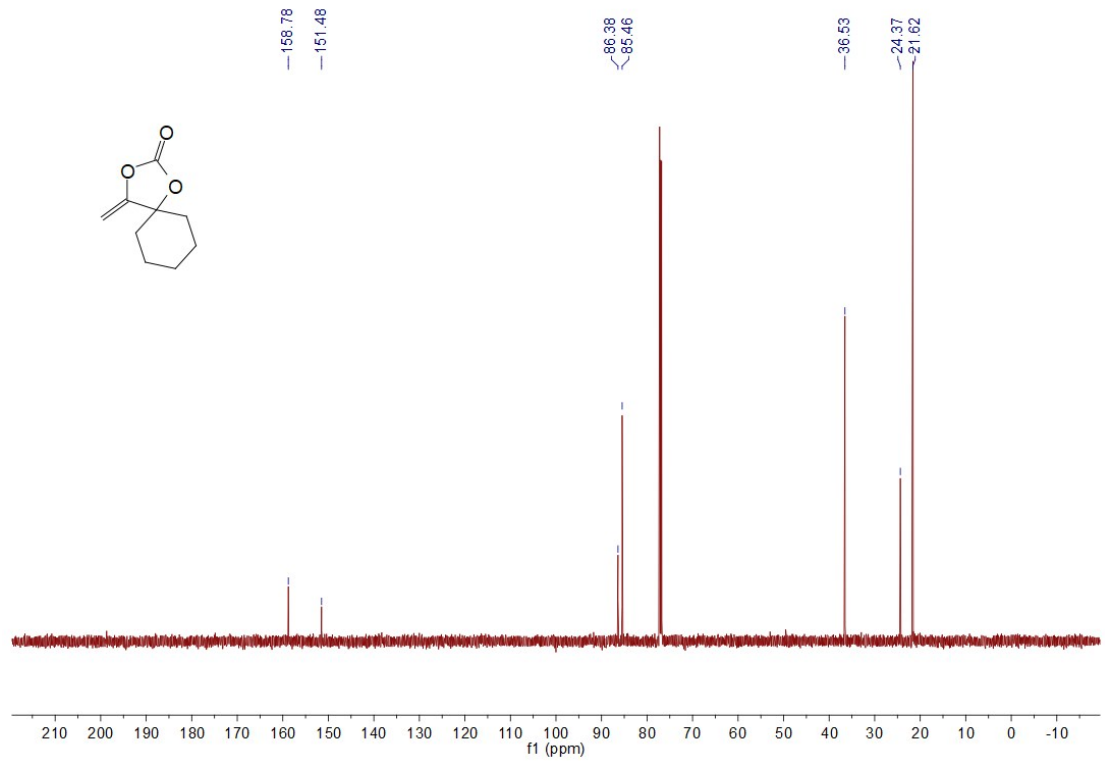
^{1}H NMR spectrum of product ***2e***



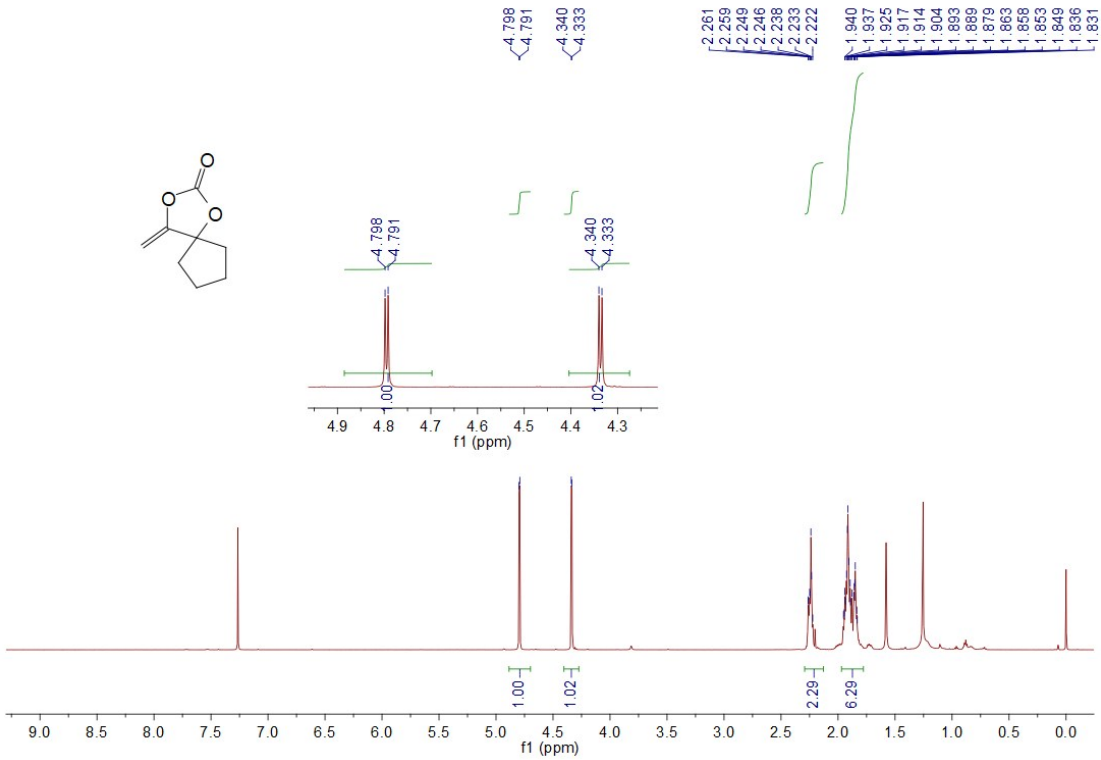
^{13}C NMR spectrum of product ***2e***



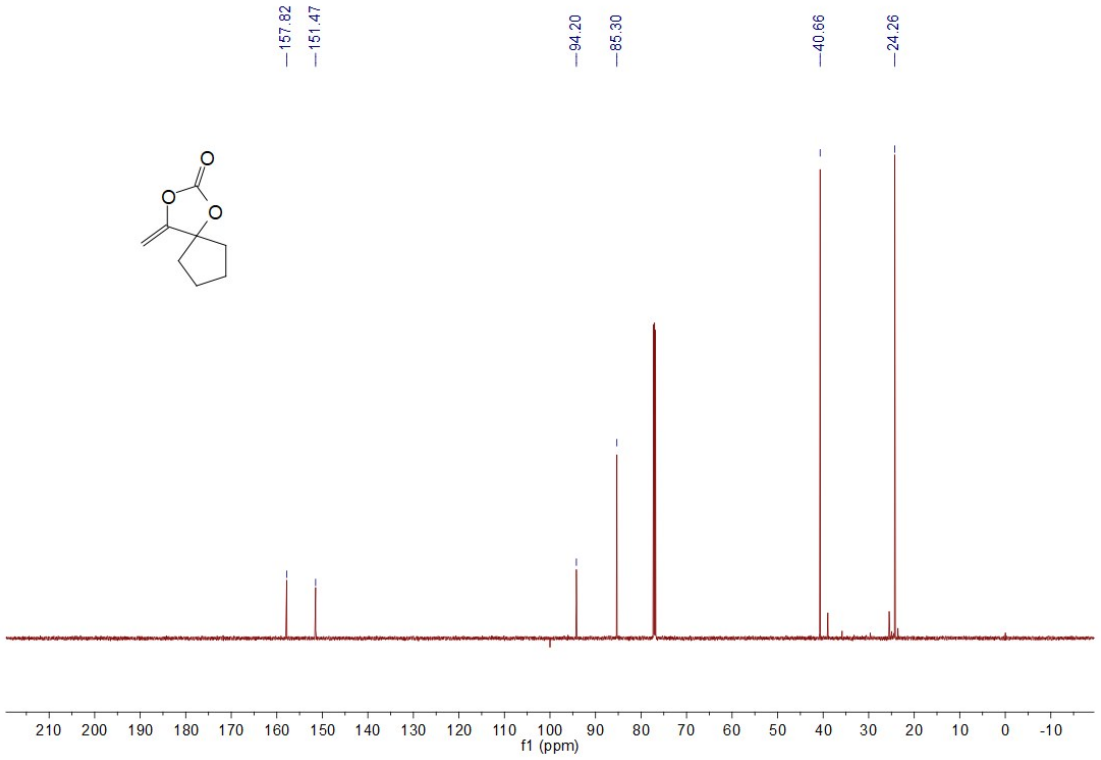
^{1}H NMR spectrum of product ***2f***



^{13}C NMR spectrum of product ***2f***

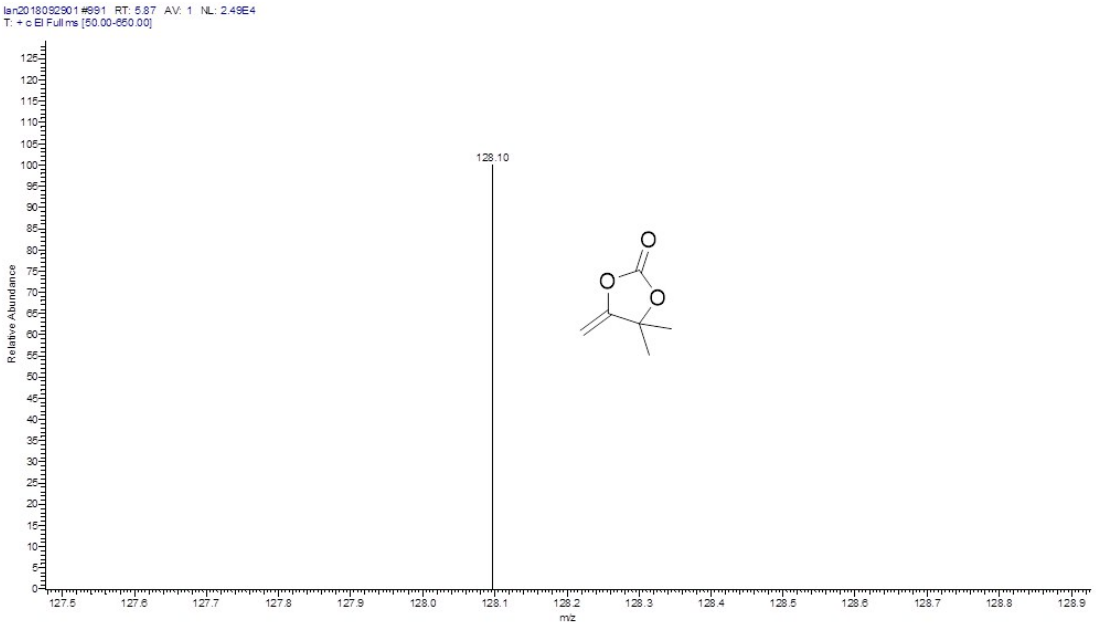


^{1}H NMR spectrum of product ***2g***

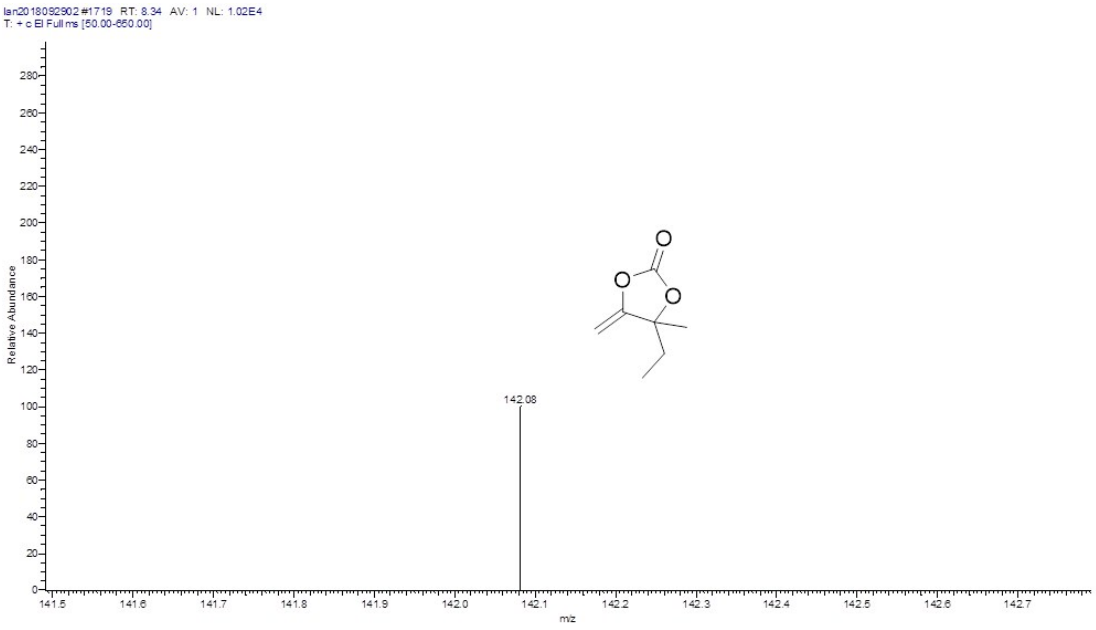


^{13}C NMR spectrum of product ***2g***

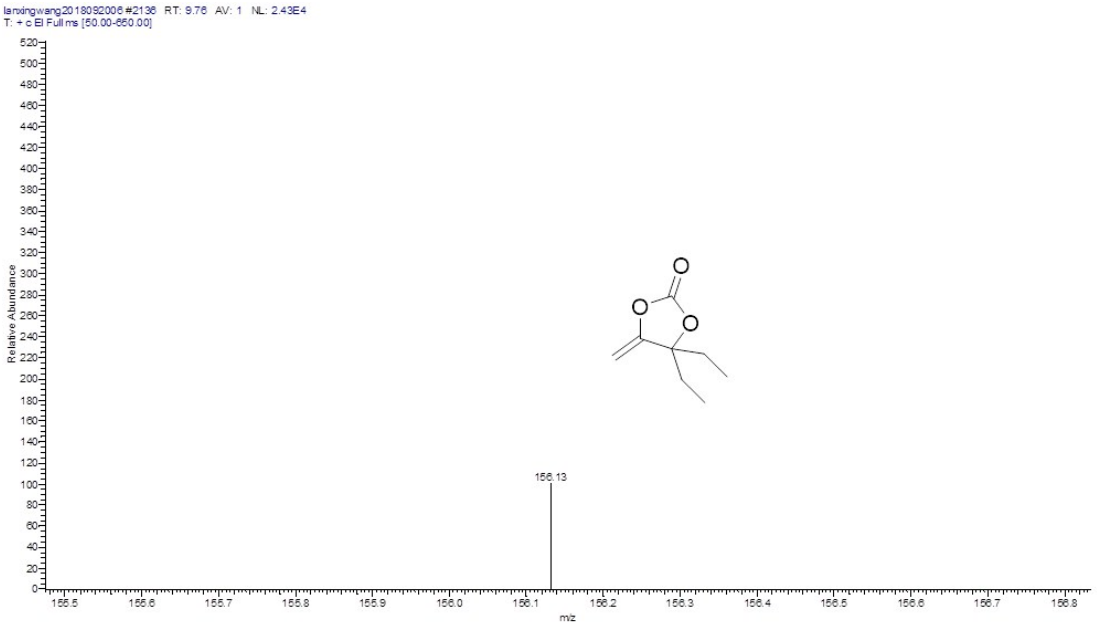
Copies of MS Spectra of All Products



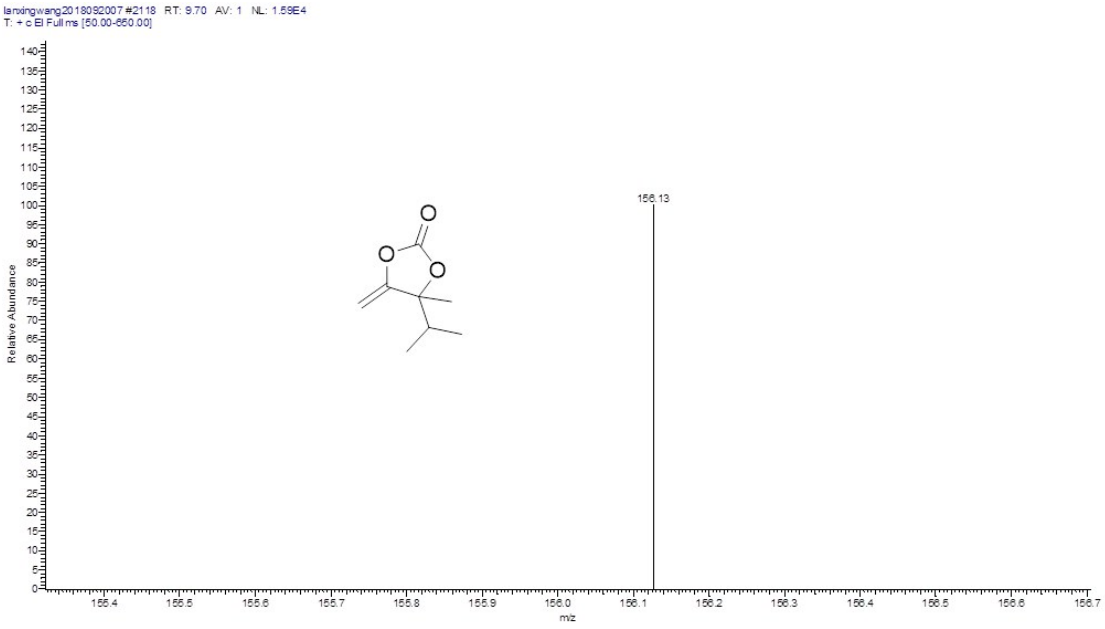
MS spectrum of product ***3a***



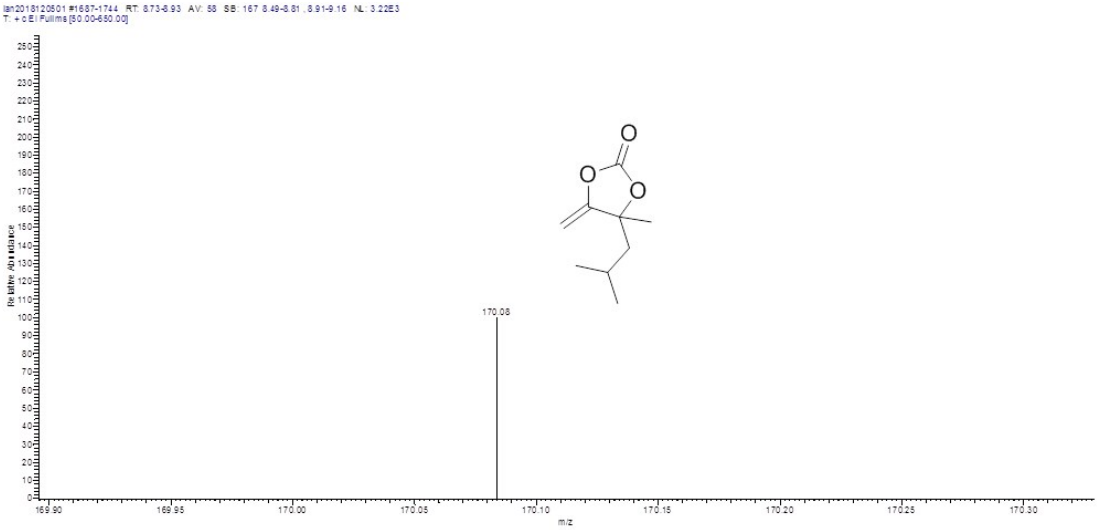
MS spectrum of product ***3b***



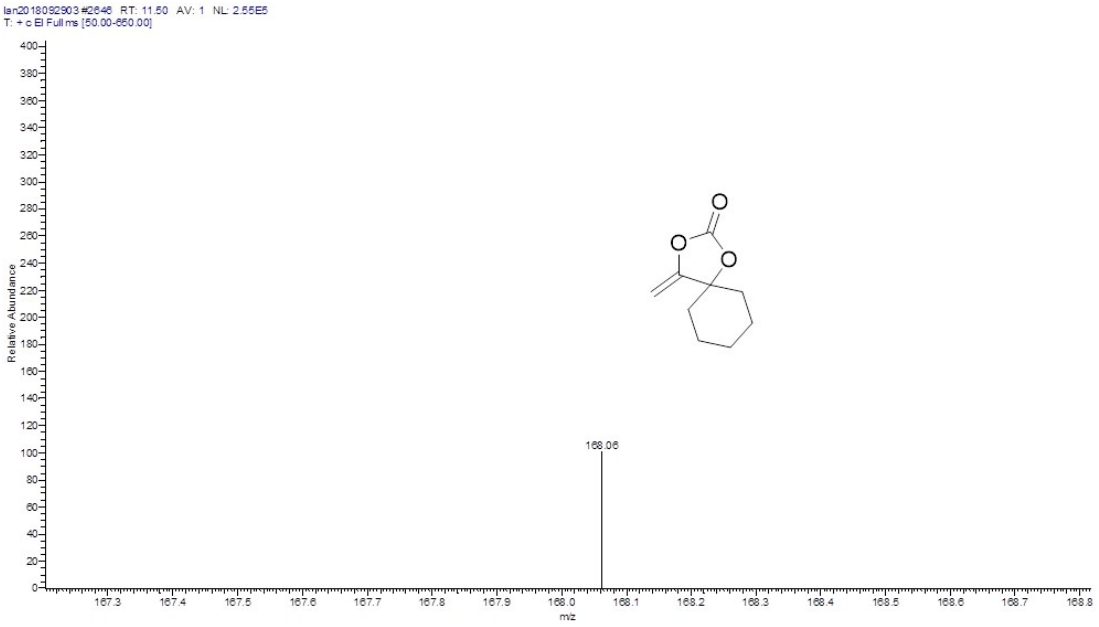
MS spectrum of product ***3c***



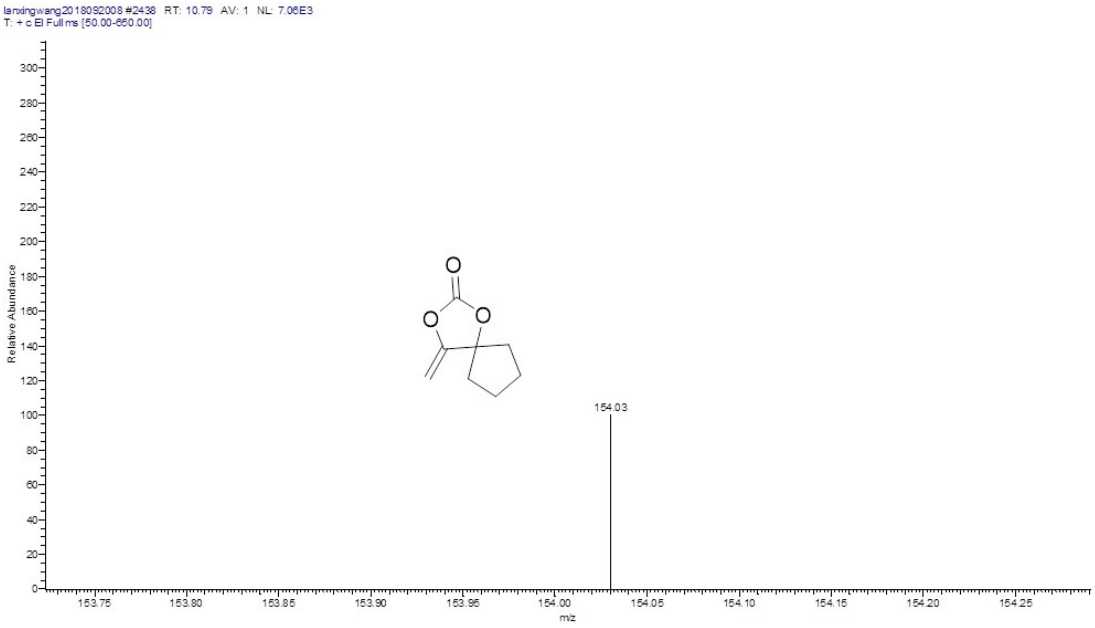
MS spectrum of product ***3d***



MS spectrum of product ***3e***



MS spectrum of product ***3f***



MS spectrum of product ***3g***