Electronic Supplementary Information

AgX@Carbon (X=Br and I) as robust and efficient catalysts for the reaction of propargylic alcohols and CO_2 to carbonates under ambient conditions

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Contents

1. Preparation of activated carbon supported Ag^0 (Ag^0@C)

Ag^0@C catalyst was prepared by using an ultrasound-assisted in situ deposition method. First, 3 ml of 0.1 M ammonia solution was added into 50 ml of 10 mM $AgNO_3$ solution. Then, 0.4g of polyvinylpyrrolidone (PVP-K30) was added and mixed by ultrasonic treatment with a frequency of 40 kHz for a few minutes. The resulting solution was heated to 45 °C in a water bath, and 1.0g of the support was immersed into the solution, followed by the addition of 0.9g glucose. After ultrasonication for 30 min, the sample was rinsed with distilled water to remove NO_3^- and glucose. Finally, the sample was dried under vacuum at 60 °C for 24 h. The silver content in Ag@C was found to be 5.1 wt%, as determined from inductively coupled plasma mass spectrometry.

2. Figures and tables

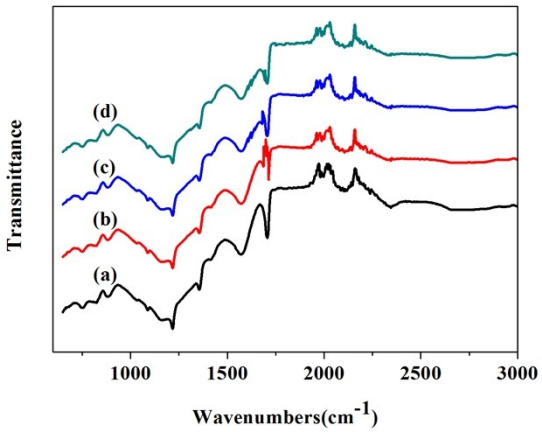
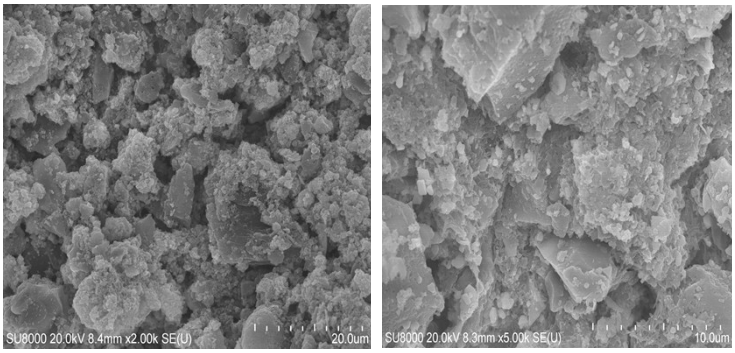
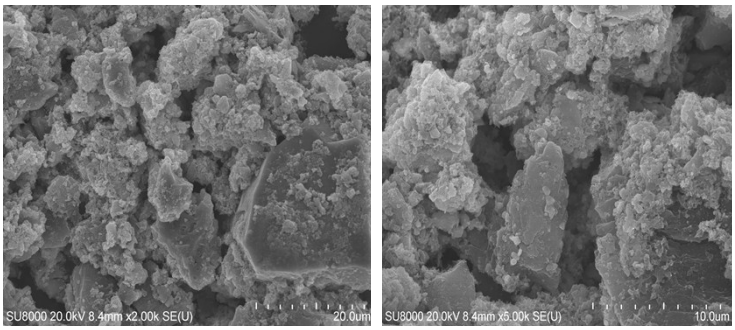


Fig. S1 FT-IR spectra of (a) pure AC, (b) AgCl@C, (c)AgBr@C and (d) AgI@C



a. b.



c. d.

Fig. S2 FESEM image of AgI@C before (a and b) and after (c and d) catalytic reaction

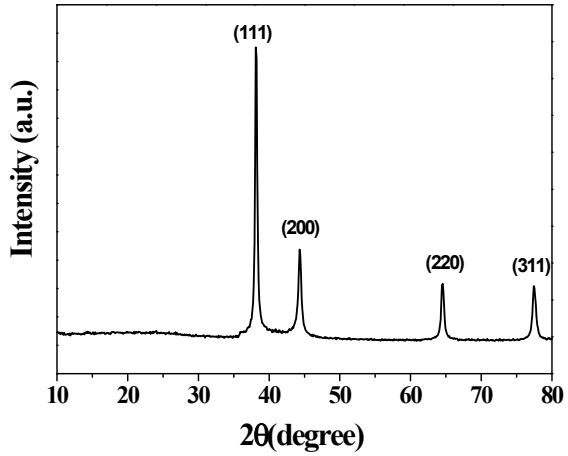


Fig. S3. XRD pattern of Ag^0@C

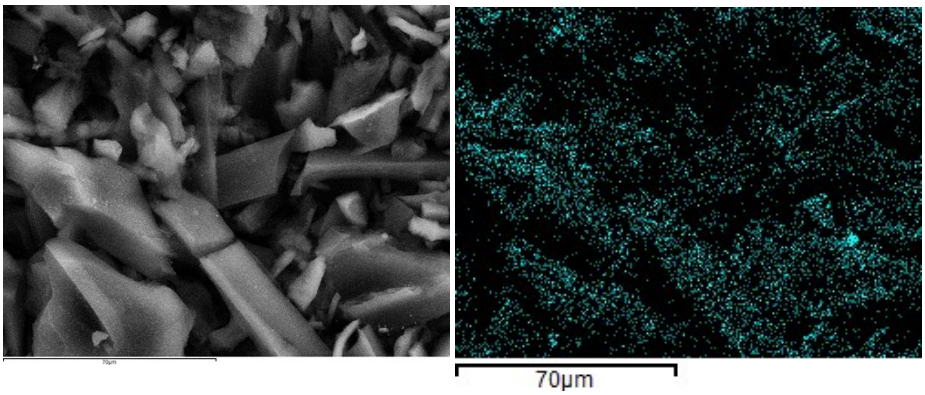


Fig. S4. Element maps for Ag^0@C sample: left, SEM image; right, EDS image of Ag (green).

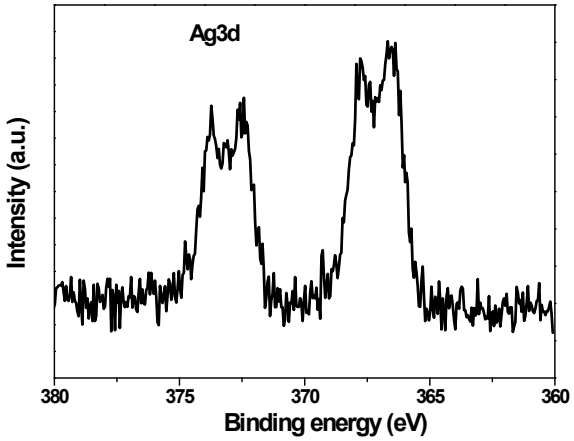


Fig. S5. XPS spectra of Ag@C exhibiting metallic Ag (0) peaks.

Table S1 Influence of the reaction temperature and CO_2 pressure on the carboxylic cyclization[a]

Entry	Temperature/ ^oC	Pressure/ MPa	Yield/%[b]
1	r.t.	0.1	>99
2	50	0.1	96
3	80	0.1	84
4	r.t.	0.5	>99
5	r.t.	1.0	>99

[a]Reaction condition: 2-methyl-3-butyn-2-ol (1 mmol), catalyst (3 mol% based on Ag), DBU (0.2 mmol), CH_3CN (2 ml), CO_2 (99.999%), 4 h. [b]The yields were determined by GC with naphthalene as internal standard.

2. DFT calculations

Density functional theory (DFT) calculations were performed by GAUSSIAN 09 *D.01* program packages[1]. All the structures were optimized at B3LYP/BSI level[2], where BSI signifies basis set LANL2DZ performed for Ag and I atom and basis set 6-31G* for other non-metal main group atoms. Furthermore, all the structures were characterized and confirmed by frequency calculations to be energy minima. Solvent effect was also taken into consideration by SMD salvation model when energy was involving. Single point energy calculations were performed at B3LYP/BSI level in acetonitrile solvent, where basis set 6-311++G** was employed to C, H and O atoms while basis set LANL2DZ was employed to Ag and I atom. The binding energy[3] for a dimer (AB) complex was calculated by $\Delta E = E_{AB} - E_A - E_B$.

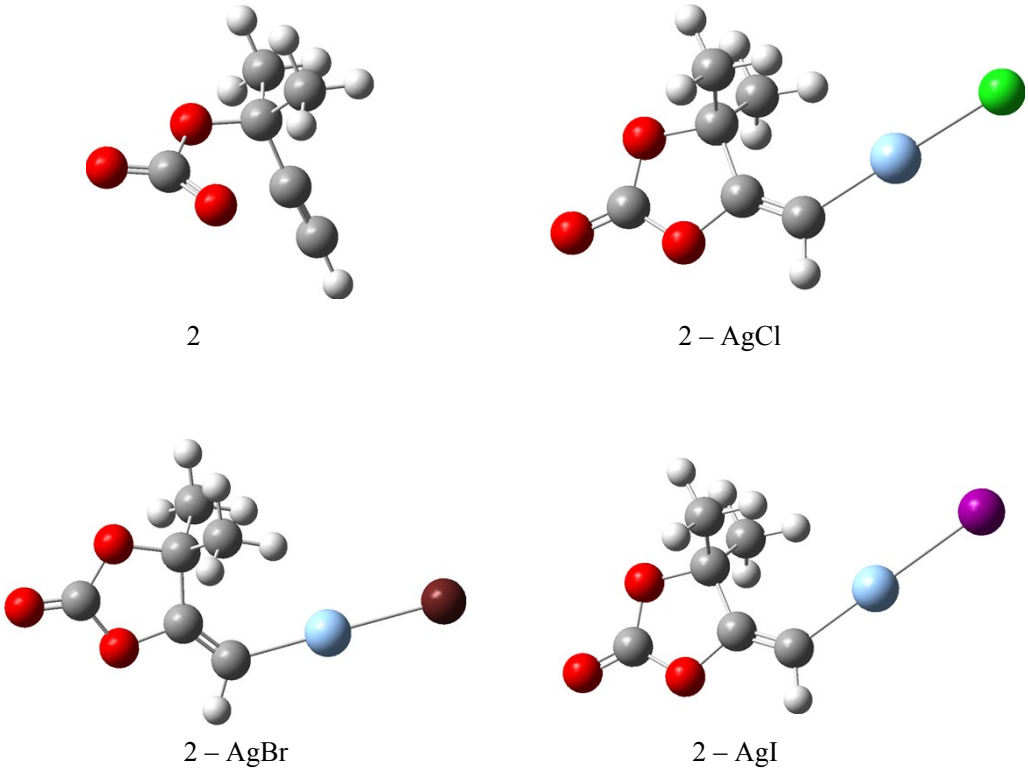


Fig. S6 Optimized geometries for 2 and its complexes with different catalysts. C atom (gray), H atom (white), O atom (red), Cl atom (green), Br atom (dark red) and I atom (red purple) are shown in different colors for clarity.

Molecular coordinates

Structure of 2

C	−1.74931700	2.02889900	−0.46872800
H	−2.10134300	3.01557600	−0.66152800
C	−1.22445900	0.96874100	−0.21114900
C	−0.75346400	−0.41999700	0.03776100
C	−0.79677200	−0.72645400	1.55136800
H	−0.49172000	−1.76897200	1.70592600
H	−0.09397200	−0.06472100	2.05773300
H	−1.80752900	−0.58828400	1.95789800
C	−1.70824500	−1.37164300	−0.71773100
H	−1.67137100	−1.15885600	−1.79039400
H	−1.37948600	−2.40463600	−0.55834400
H	−2.74229100	−1.26308800	−0.36826100
O	0.51918700	−0.68116600	−0.51899500
C	1.69788300	0.12789200	−0.06815700
O	2.71984000	−0.25084100	−0.64153000
O	1.44771700	1.00555100	0.77512200

Structure of 2 – AgCl

C	0.20931900	-1.22222300	0.00024100
H	0.30055300	-2.31147600	-0.00120800
C	1.37592100	-0.59149200	-0.00025700
C	1.73043300	0.89042300	0.00107000
C	1.27283700	1.61628100	-1.26552400
H	1.62067700	2.65622600	-1.26140000
H	1.66631300	1.11435800	-2.15510300
H	0.18011700	1.60215500	-1.31823200
C	1.27481900	1.61351900	1.27002200
H	1.67028700	1.10997600	2.15779500
H	1.62202900	2.65368000	1.26739700
H	0.18221200	1.59862000	1.32456400
O	3.19423900	0.87259800	-0.00014800
C	3.65390600	-0.40042400	-0.00243400
O	4.82338700	-0.69626000	-0.00401000
O	2.63542700	-1.28057900	-0.00267800
Cl	-3.99034800	0.48457600	-0.00575000
Ag	-1.73902300	-0.40987000	0.00255200

Structure of 2 – AgBr

C	0.76750400	-1.28026800	0.00077400
H	0.90487000	-2.36459600	0.00093500
C	1.90494100	-0.59847200	0.00054900
C	2.19068600	0.89835400	0.00024100
C	1.69981000	1.60116100	-1.26696400
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C	1.70247200	1.60104700	1.26858500
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H	0.61169900	1.53629000	1.32402600
O	3.65360900	0.94838800	-0.00115400
C	4.17170400	-0.30196500	-0.00083600
O	5.35360600	-0.54330000	-0.00155200
O	3.19507900	-1.22849500	0.00040400
Br	-3.58568500	0.34185500	-0.00040400
Ag	-1.21499600	-0.53514400	0.00024500

Structure of 2 – AgI

C	1.25959100	-1.30659200	-0.00027100
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C	2.62259800	0.91100800	0.00031300
C	2.11564600	1.60132600	-1.26744800
H	2.38830900	2.66334700	-1.26304700
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H	1.02672200	1.51023400	-1.32191700
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C	4.63517400	-0.23533700	-0.00034700
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I	-3.35250800	0.26320900	-0.00042900
Ag	-0.74710300	-0.61612200	0.00063200

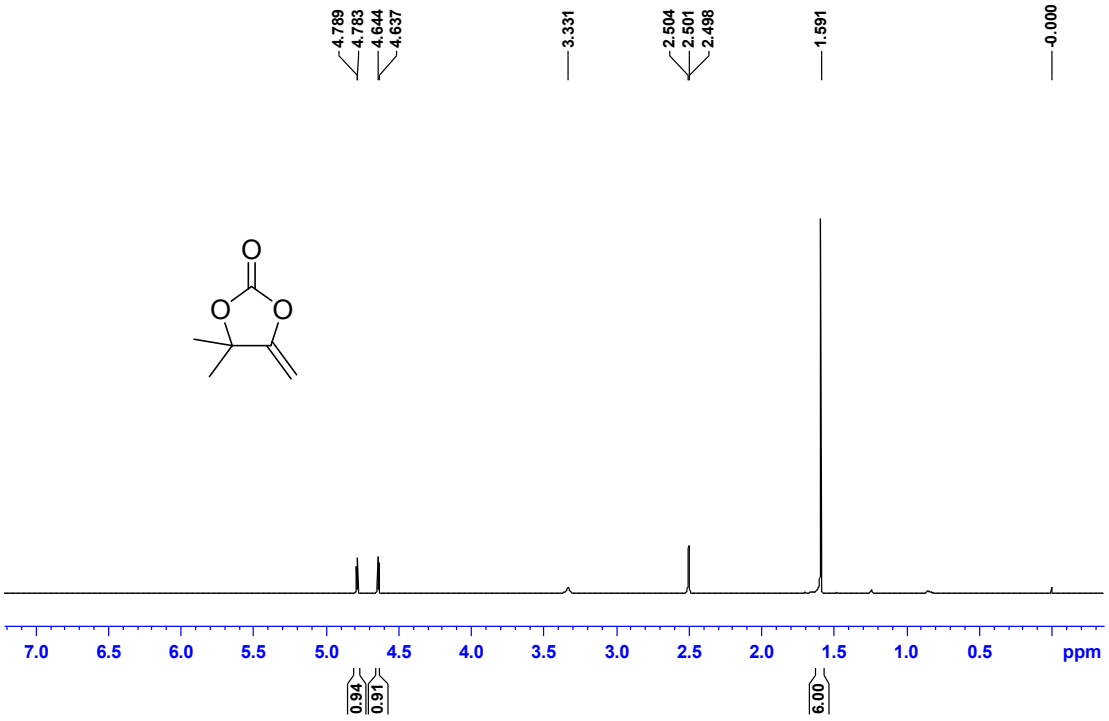
References

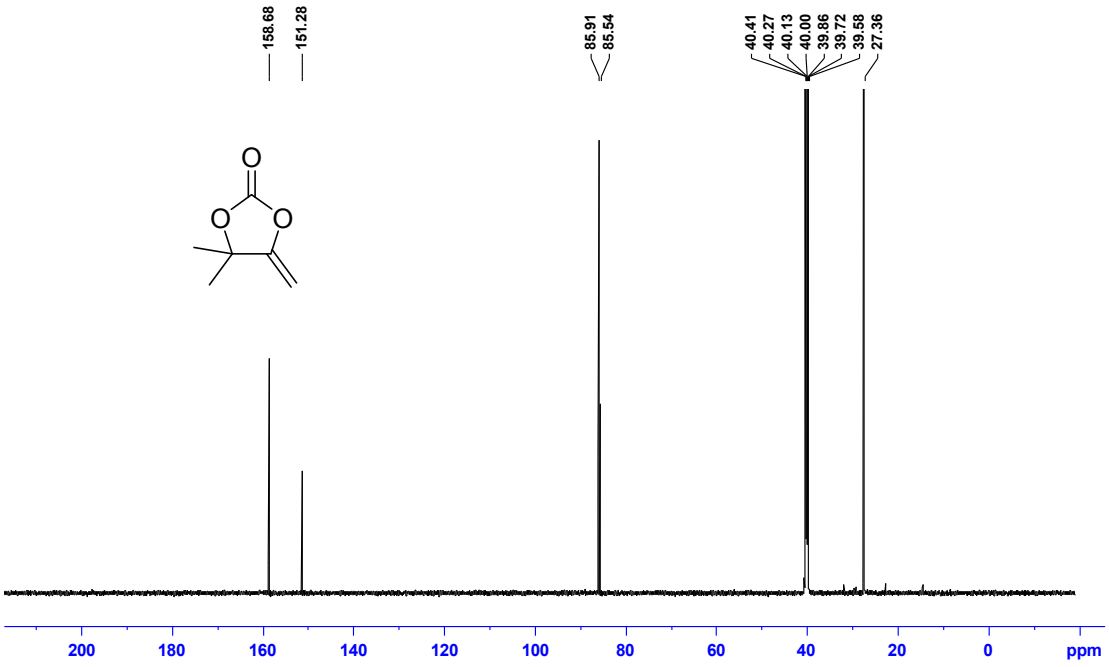
1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al. Gaussian 09, Revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

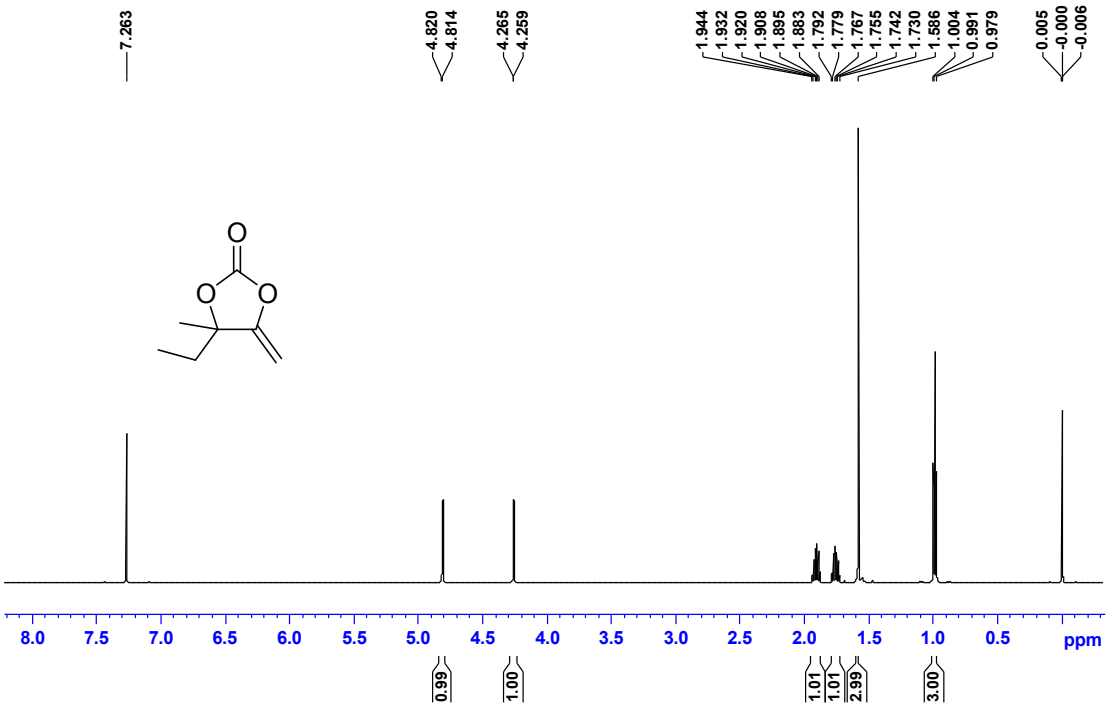
2. Q. W. Song, W. Q. Chen, R. Ma, A. Yu, Q. Y. Li, Y. Chang, L. N. He, *ChemSusChem,* **2015**, 8, 821–827.

3. Y. Zhao, J. Wang, H. Wang, Z. Li, X. Liu, S. Zhang, *J. Phys. Chem. B*, **2015**, 119, 6686−6695.

3. The ^{1}H and ^{13}C NMR charts for products 2a-2i



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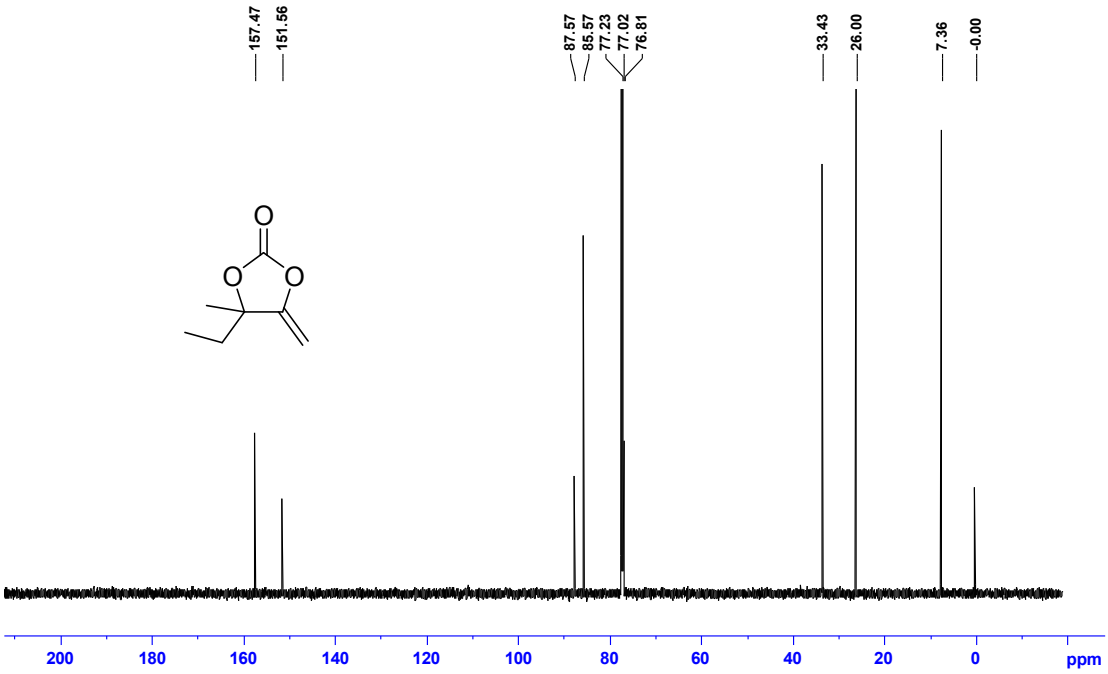
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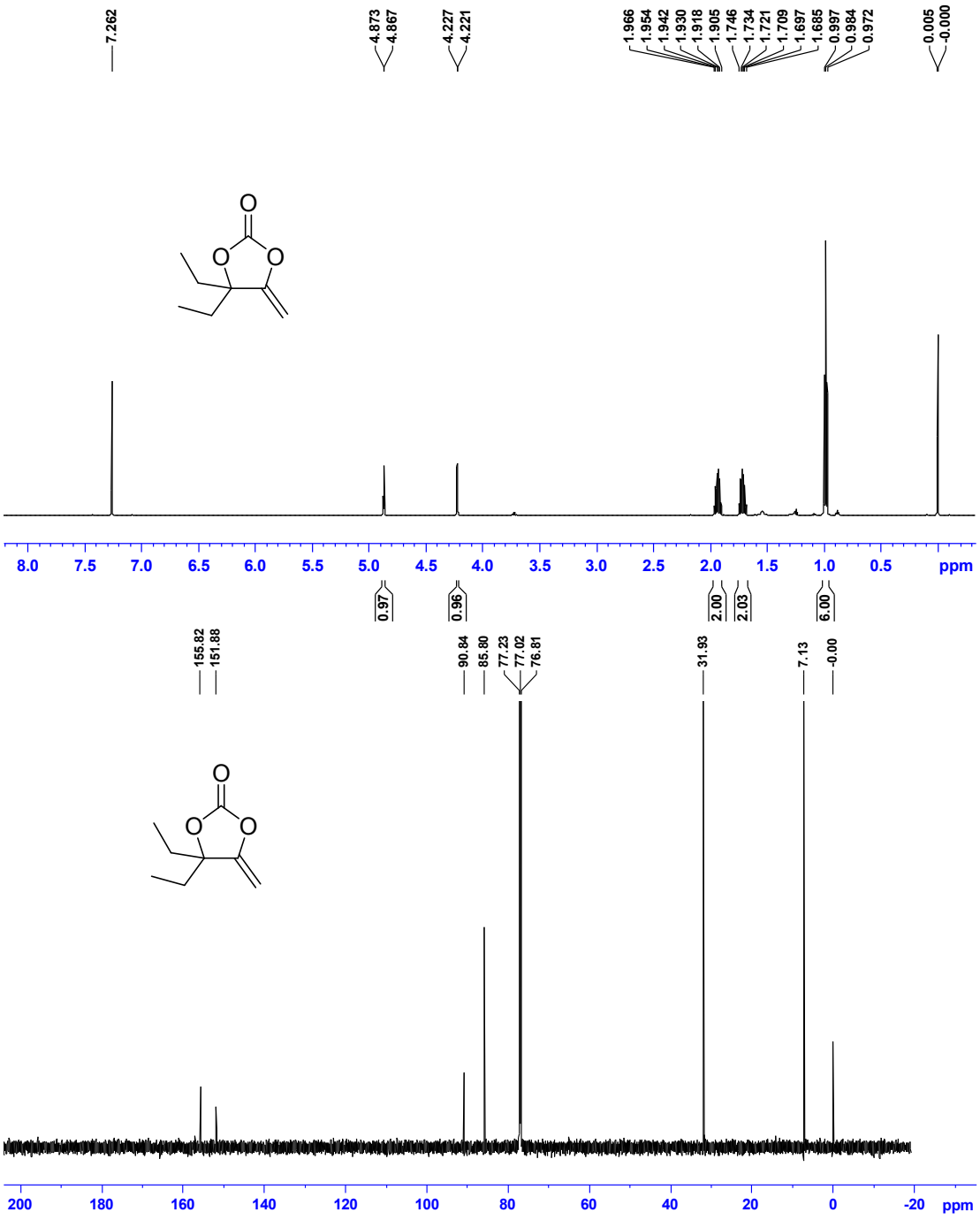
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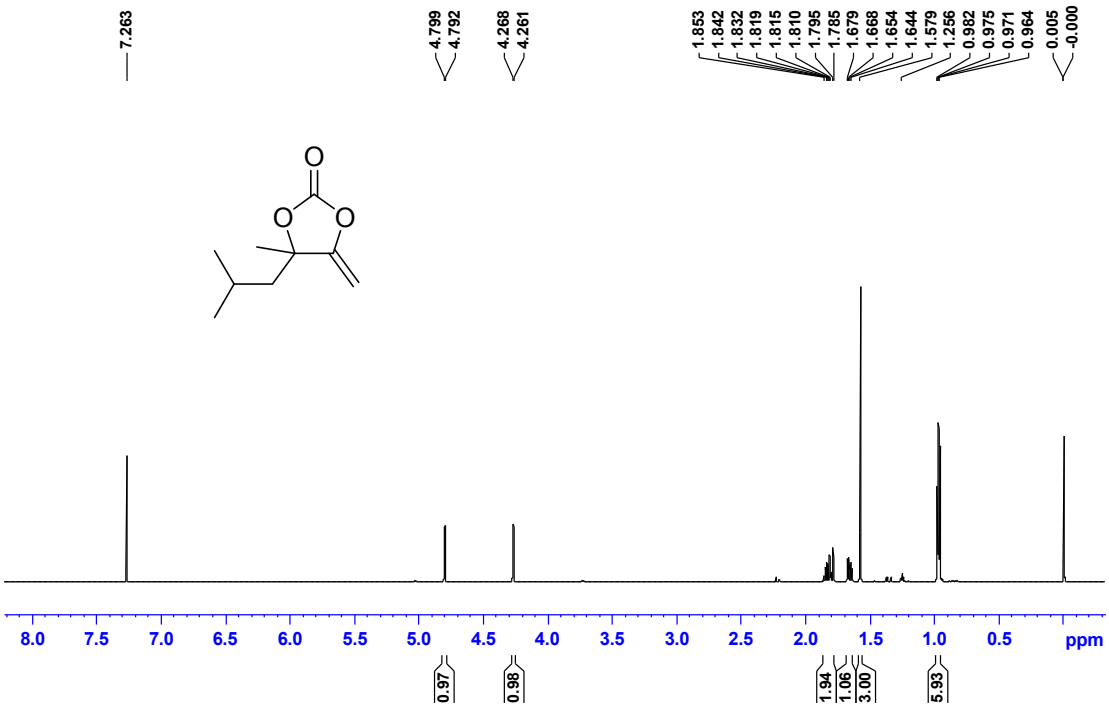
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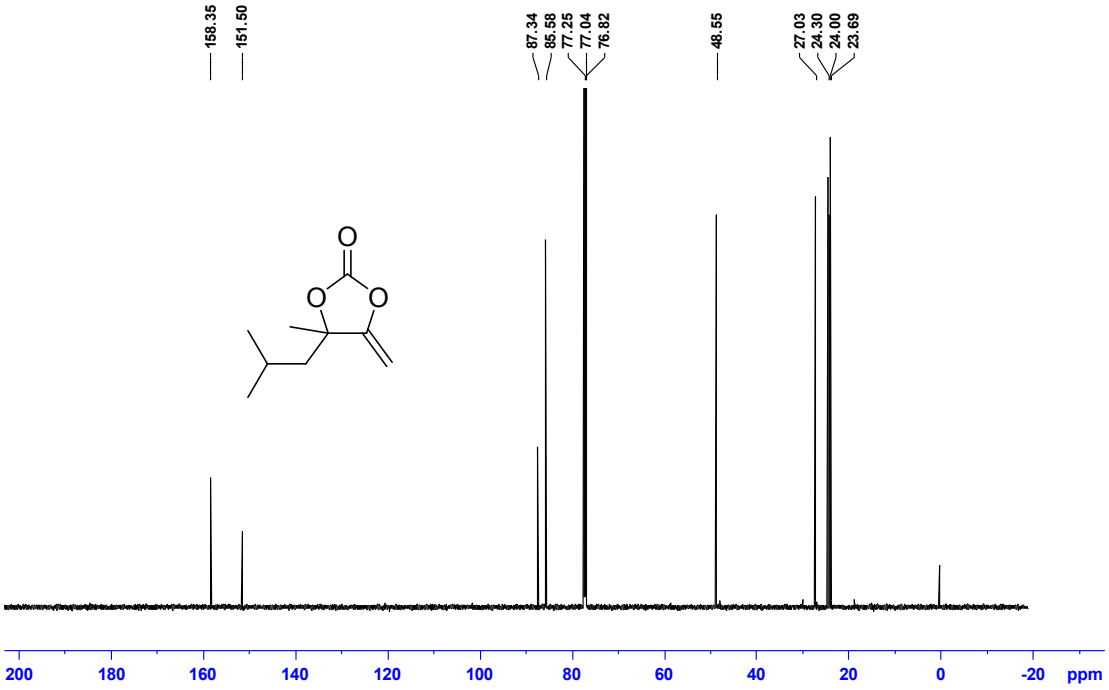
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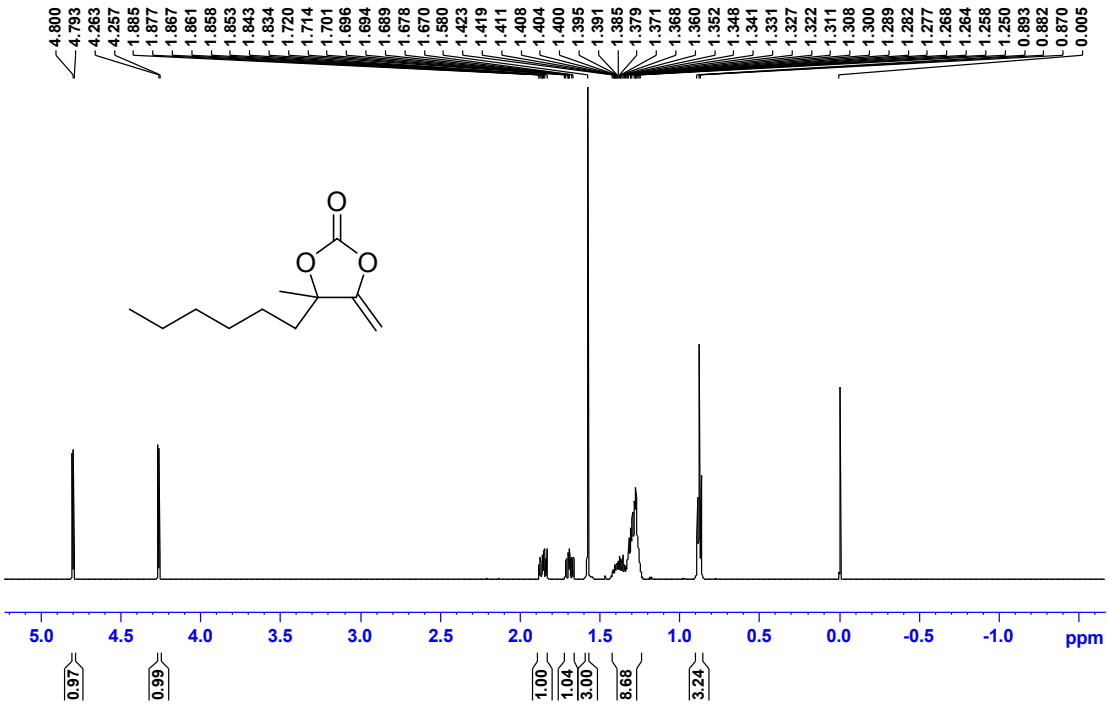
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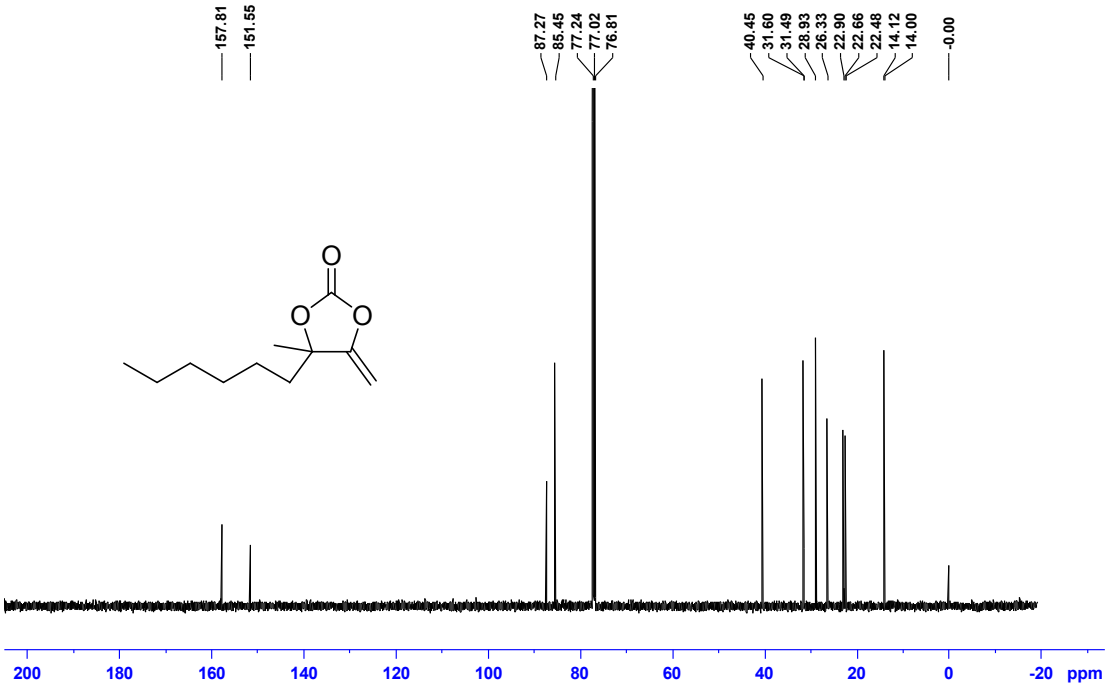
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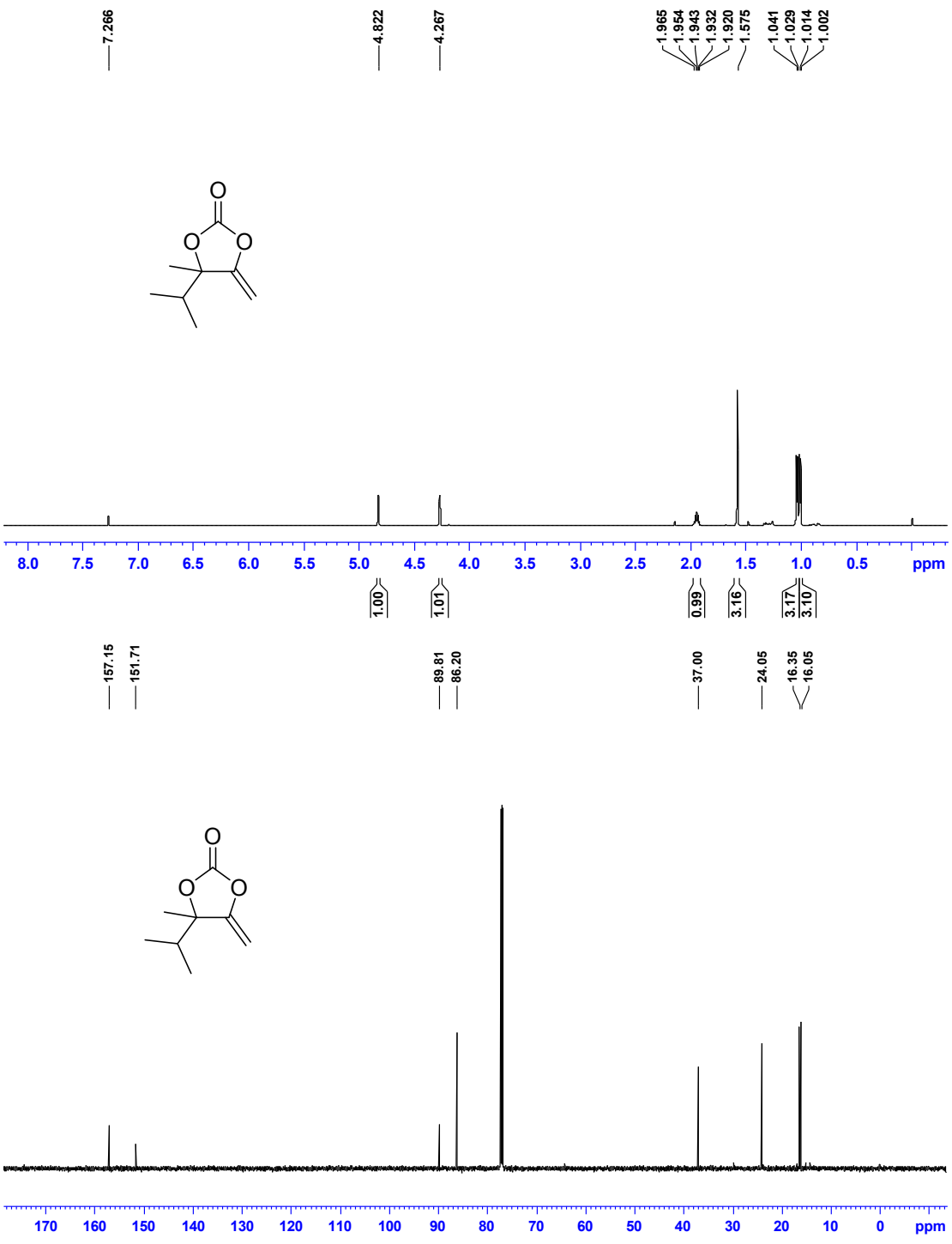
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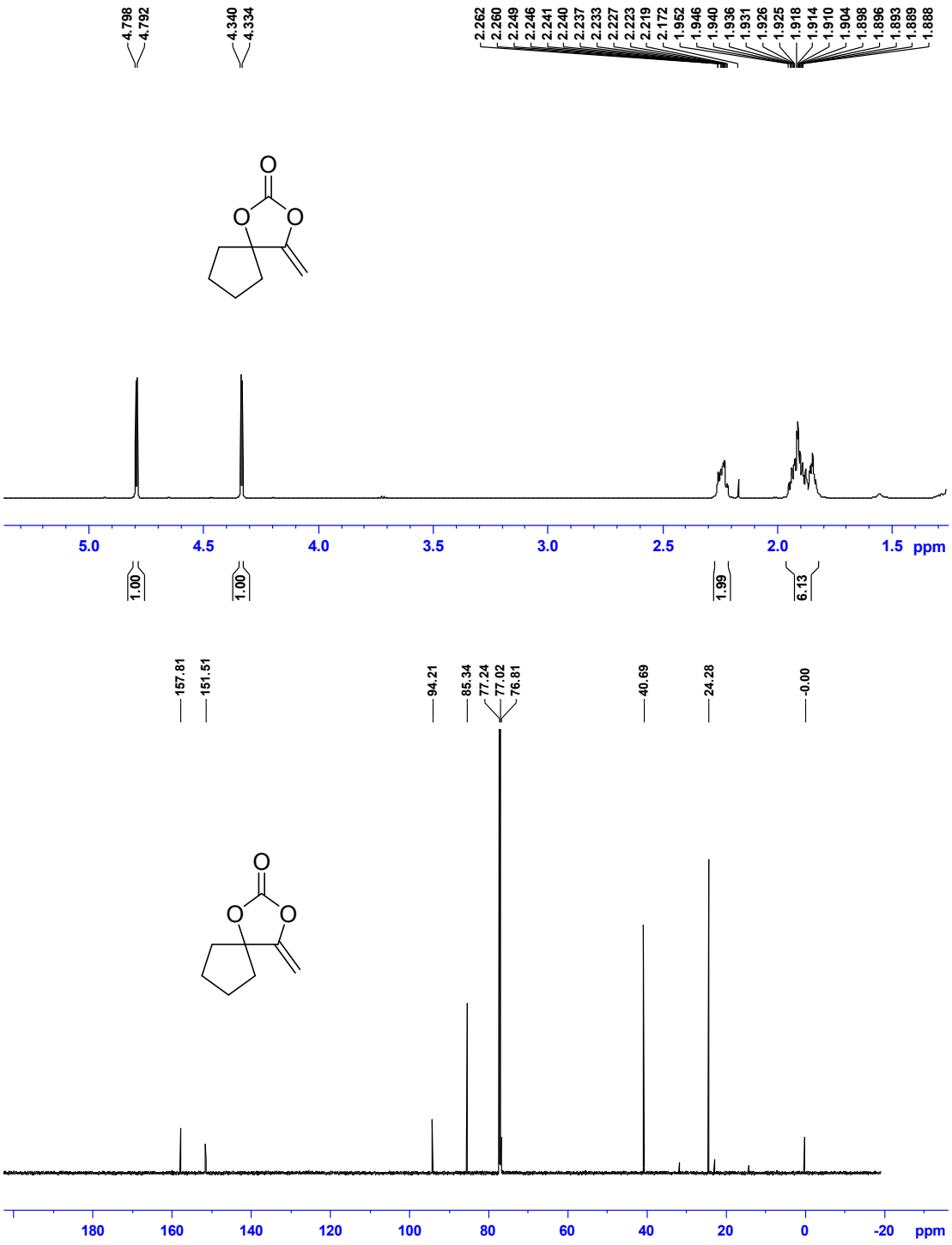
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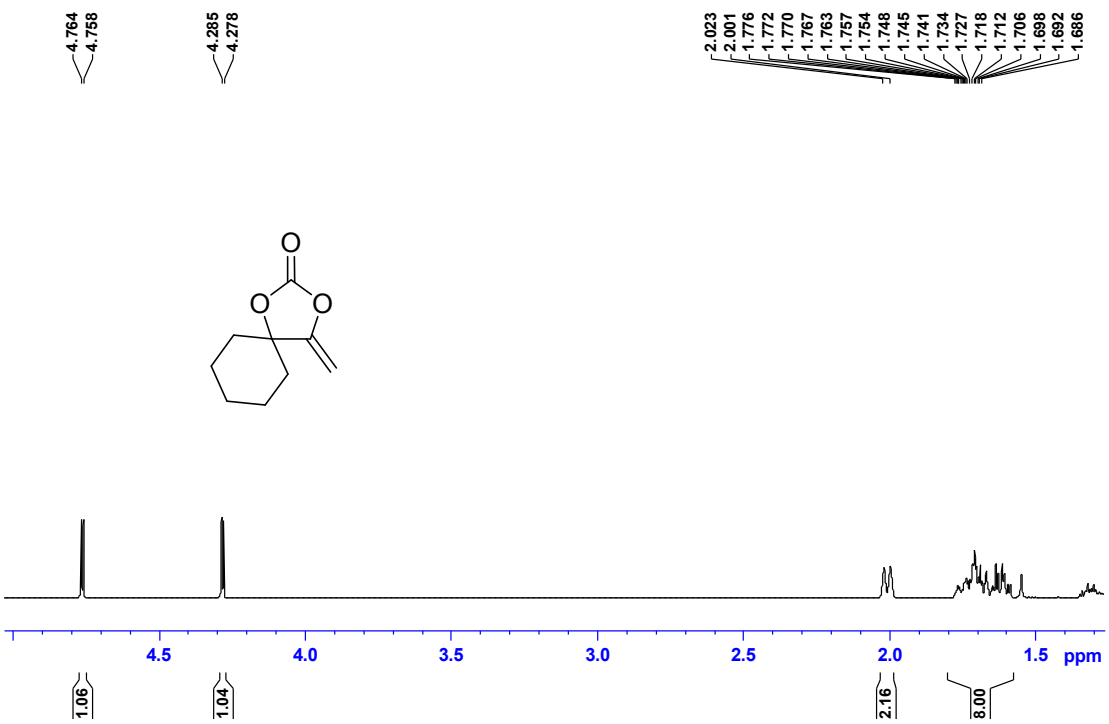
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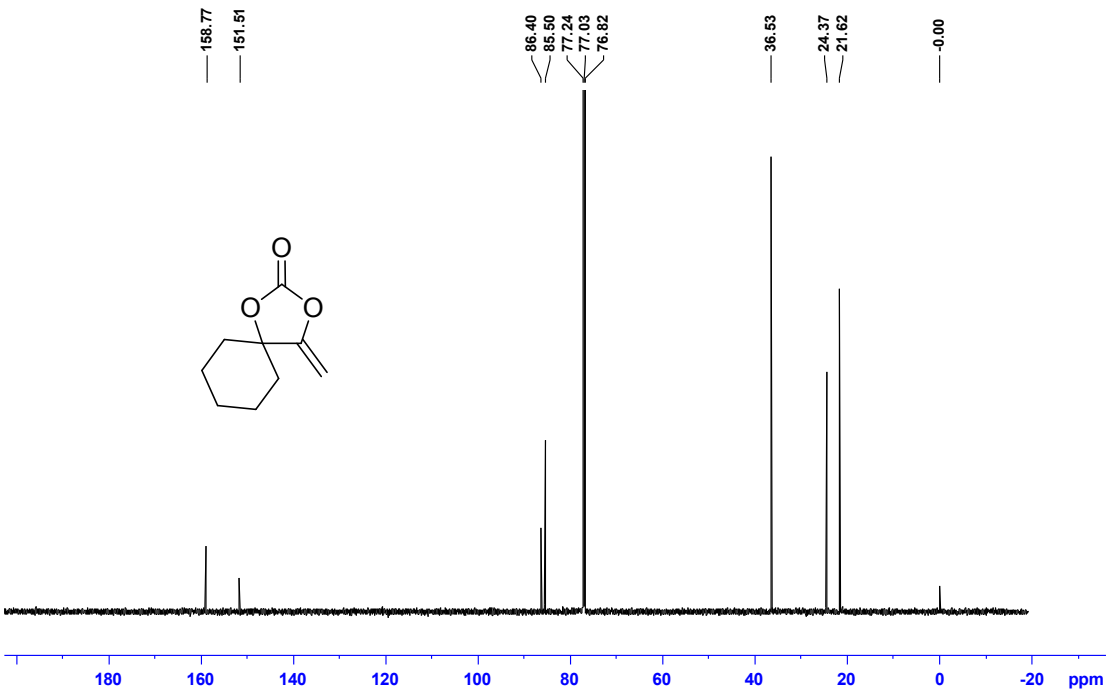
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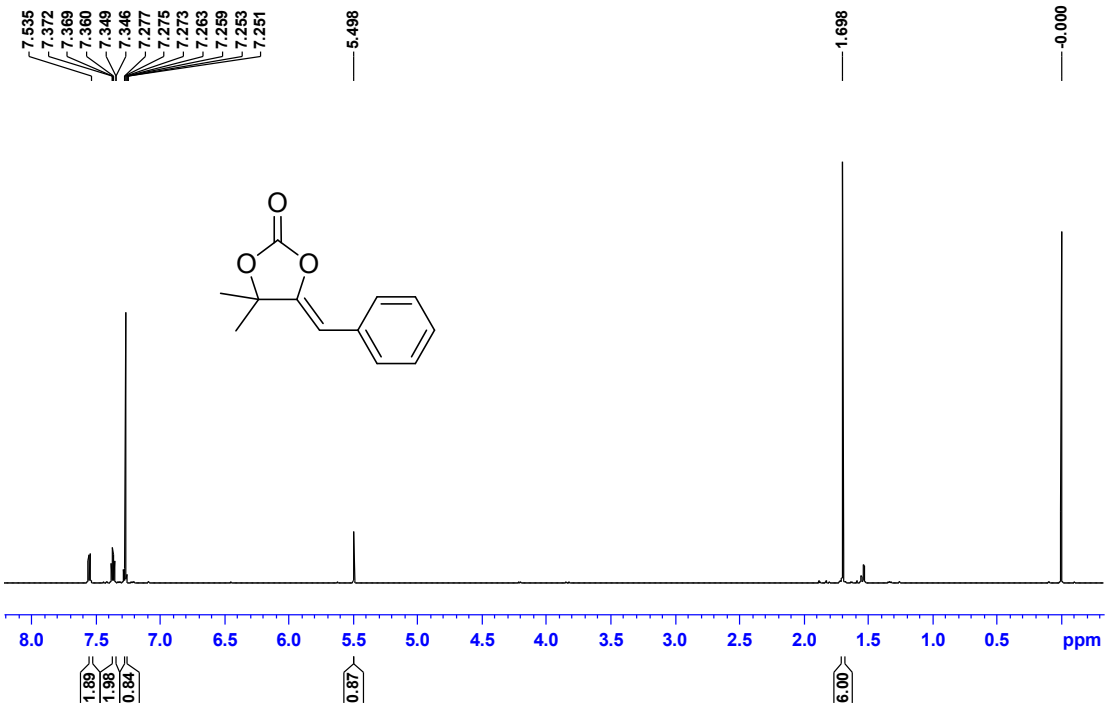
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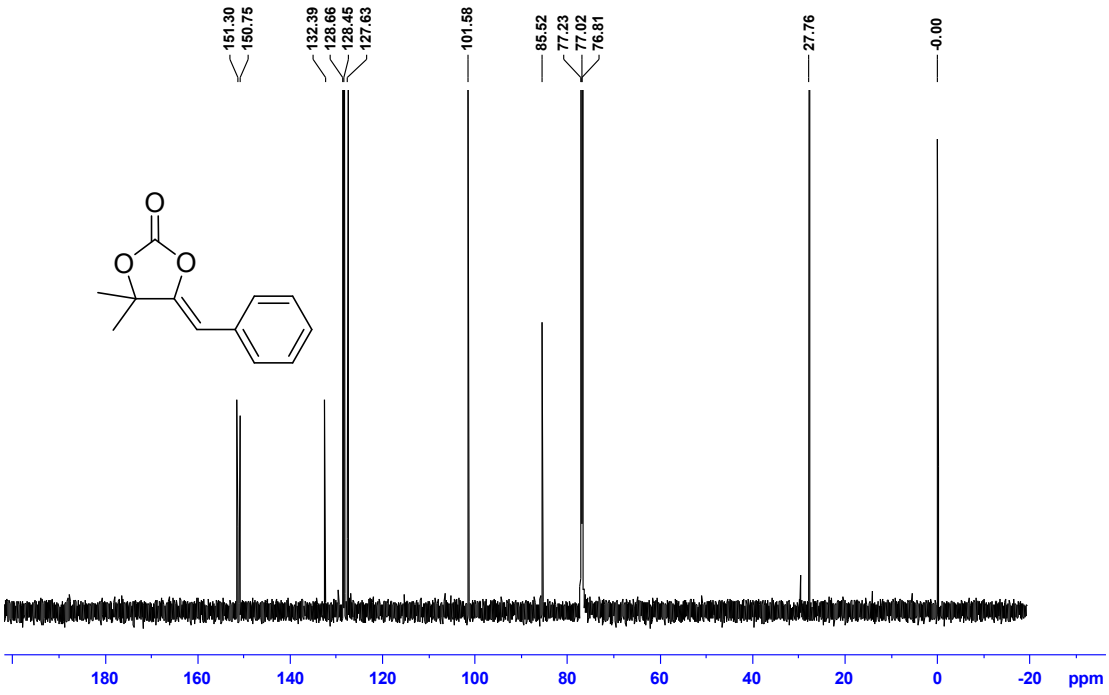
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.89
1.98
0.84
0.87
6.00


151.30
150.75
132.39
128.66
128.45
127.63
101.58
85.52
77.23
77.02
76.81
27.76
-0.00
180
160
140
120
100
80
60
40
20
0
-20
ppm