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Supporting information

A Recyclable AgI/OAc$^-$ Catalytic System for the Efficient Synthesis of α-Alkylidene Cyclic Carbonates: Carbon Dioxide Conversion at Atmospheric Pressure

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1. General information
2. Experimental section
3. Investigations about the activation mechanism
4. Characterization of products

1. General information

All the compounds involved including the substrates, silver salts and ionic liquids were commercially purchased from Sigma-Aldrich, Aladdin, TCI, Alfa, Macklin in China and used without further dryness and purification. The purity of CO_2 used for purging and reacting was 99.999%. NMR spectra were recorded on a Bruker 500 MHz NMR (^1H NMR, 500 MHz; ^{13}C NMR, 126 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^1H NMR and against the solvent ($CDCl_3$, 77.0 ppm; DMSO-d_6, 39.9 ppm) for ^{13}C NMR, respectively. Multiplicity abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. The coupling constants, *J*, were reported in Hertz (Hz).

2. Experimental section

2.1 Synthesis of α-alkylidene cyclic carbonates by carboxylative cyclization of propargylic alcohols with CO_2 catalyzed by AgI/IL_1 system.

AgI (11.7 mg, 0.05 mmol, 1 mol%), IL_1 (1 mL, 1.102 g, 6.474 mmol), a propargylic alcohol (5 mmol) were added to a Schlenk tube equipped with a magnetic stirring bar. The system was quickly purged 3 times with CO_2. Then the mixture was stirred at 45 °C, 1 bar of CO_2 for the required time. Upon completion, the mixture was extracted with hexane (4 × 15 mL). The upper layer was combined and the solvent was removed to obtain the crude product, which could be further purified by column chromatography on silica gel using petroleum ether/ethyl acetate (100:1-20:1) as an eluent. When the reusability of the catalytic system was investigated, the lower layer (recovered IL_1 + AgI) was dried under vacuum for 10-15 minutes to evaporate the residual hexane. After dryness, the recovered IL_1 and AgI were directly reused as the catalyst for the next round.

2.2 NMR yield calculation for the reaction system of CO_2 with propargylic alcohols.

The ^1H NMR spectra of the crude reaction mixture generated by 2-methylbut-3-yn-2-ol and CO_2 (Figure S1) was used as an example for the quantitative determination of products employing 1,1,2,2-tetrachloroethane as the internal standard. The deuterated solvent is $CDCl_3$.

Two protons that belongs to the double bonds of α-alkylidene cyclic carbonates (red and green marked), which are far away from the alkyl and aryl protons and show two clear individual peaks, could be treated as characteristic protons for quantitative determination. The sharp peak at δ = 5.98 ppm (blue marked) represents two protons of 1,1,2,2-tetrachloroethane. Therefore, the exact amount and the NMR yield of the product could be calculated by the ratio of double bond proton and internal standard proton based on the exact amounts of 1,1,2,2-tetrachloroethane and the substrate.

Example: is = internal standard, p = product, s = substrate.

m (is) = 0.8668 g, M (is)= 167.86 g/mol. ⟹ n(is) = 5.164 mmol.

ratio (is/p) = 2.23/2 : 1 = 1.115. ⟹ n(p) = n(is) / ratio (is/p) = 4.631 mmol.

m(s) = 0.4187 g. M (s) = 84.12 g/mol. ⟹ n(s) = 4.977 mmol.

Therefore, NMR yield = n(p) / n(s) = 93%.

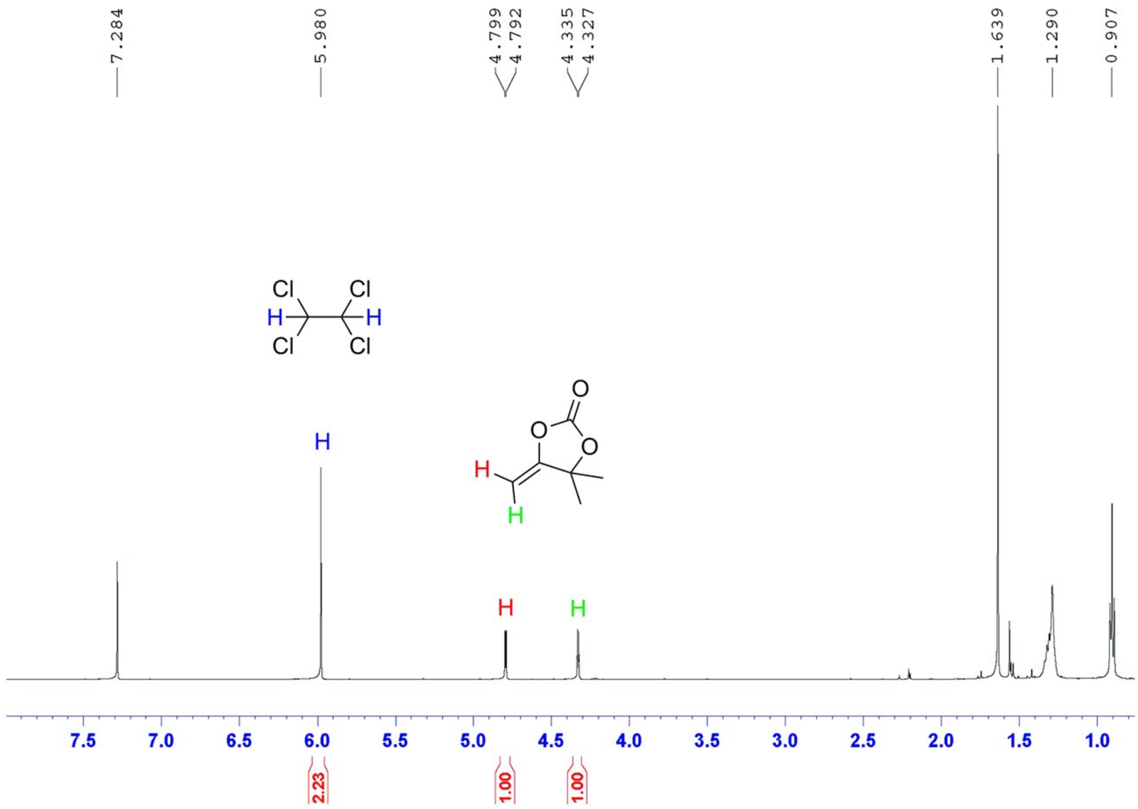
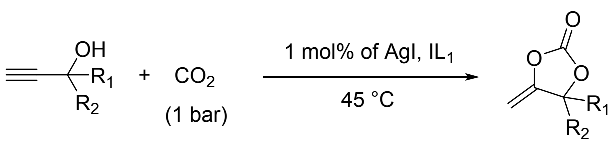


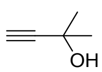
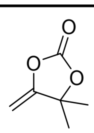
Figure S1. ^{1}**H NMR of crude product generated by 2-methylbut-3-yn-2-ol and** CO_2

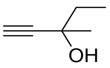
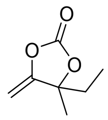
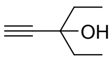
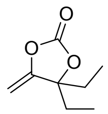
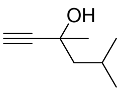
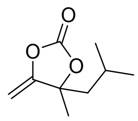
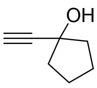
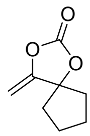
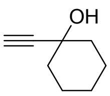
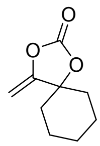
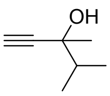
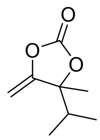
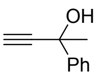
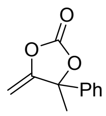
2.3 The isolated yields of 2a-2h

Table S1. The isolated yields of **2a**-**2h**.[a]



1 **2**

Substrate		Product		Time	Yield[b]	Yield[c]
1a		**2a**		3 h	93%	90%

1b		**2b**		4 h	96%	93%
1c		**2c**		3 h	91%	87%
1d		**2d**		6 h	99%	94%
1e		**2e**		8 h	88%	83%
1f		**2f**		6 h	99%	95%
1g		**2g**		6 h	97%	93%
1h		**2h**		12 h	44%	40%

[a] Reaction conditions: AgI (0.05 mmol), IL_1 (1 mL, 1.102 g, 6.474 mmol), substrate (5 mmol), CO_2 (1 bar) at 45°C.
[b] NMR Yields were determined by ^1H NMR spectroscopy using 1,1,2,2-tetrachloroethane as the internal standard.
[c] Isolated yields

2.4 The mass and the amount of ILs of Table 1.

Table S2. The mass and the amount of ILs of Table 1

	V	**m**	**n**
IL_1	1 mL	1.102 g	6.474 mmol
IL_2	1 mL	1.243 g	6.270 mmol
IL_3	1 mL	1.28 g	6.466 mmol
IL_4	1 mL	1.5 g	3.833 mmol
IL_5	/	1.5 g	6.301 mmol

2.5 Comparison of AgI/IL_1 system (this work) with the previously reported reusable silver systems.

Table S3. Comparison of AgI/IL_1 system (this work) with the previously reported reusable silver systems

Ref.	**Year**	**Authors**	**Catalytic systems**	**General reaction condition**	**CO_2 pressure**	**Recycle rounds**
1	2013	Yuan *et al.*	Polystyrene-supported -NHC-Ag	2 mol% of Polystyrene -supported-NHC-Ag	5 MPa	15
2	2014	He *et al.*	Ag_2WO_4 PPh_3	1 mol% of Ag_2WO_4 2 mol% of PPh_3	0.1 MPa	4
3	2014	Liu *et al.*	Fluorinated-MOP-Ag DBU	10 mol% of Ag 1 equiv of DBU	1 MPa	5
4	2015	Han *et al.*	Ag nanoparticles-sulfonated macroreticular resin DBU	10 mol% of Ag 1 equiv of DBU	0.1 MPa	5
5	2015	He *et al.*	$[(Ph_3P)_2Ag]_2CO_3$	1 mol% of $[(Ph_3P)_2Ag]_2CO_3$	0.1 MPa	>2
6	2016	Wang *et al.*	AgOAc $[P_{66614}]$[DEIm]	1 mol% of AgOAc 10 mol% of $[P_{66614}]$[DEIm]	0.1 MPa	>5
7	2016	Liu *et al.*	poly(PPh_3)-azo-Ag DBU	0.064 mol% of Ag 1 equiv of DBU	1 MPa	5
8	2016	Wang *et al.*	AgI@C DBU	3 mol% of Ag 20 mol% of DBU	0.1 MPa	10
		This Work	AgI IL_1	1 mol% of AgI 1.3 equiv of IL_1	0.1 MPa	20

3. Investigations about the activation mechanism

In this investigation, all the ^1H NMR spectra applied were performed in DMSO-d_6.

It has been reported that the activation of the hydroxyl proton of the substrate was the pivotal process to initiate the catalytic cycle, which could be monitored by ^1H NMR.[1]

Consequently, in order to recognize the species that activated the hydroxyl proton, substrate **1a** (5 mmol), and the mixture of **1a**/AgI (5 mmol of **1a**, 0.05 mmol of AgI), **1a**/IL_1 (5 mmol of **1a**, 1 mL of IL_1) were respectively added to a Schlenk tube and directly analyzed by ^1H NMR. The obtained spectra were supplied in Figure S2.

In Figure S2(a), a peak at δ = 5.29 ppm was considered as the hydroxyl proton of the substrate. When AgI was added into **1a**, no significant difference was observed, indicating that AgI individually couldn't activate the hydroxyl proton. Nevertheless, when IL_1 was mixed with **1a**, the peak of hydroxyl proton was extremely extended as a quite board peak at δ = 6.45 ppm (Figure S3). These results implied that the activation was accomplished by the IL component of the catalytic system.

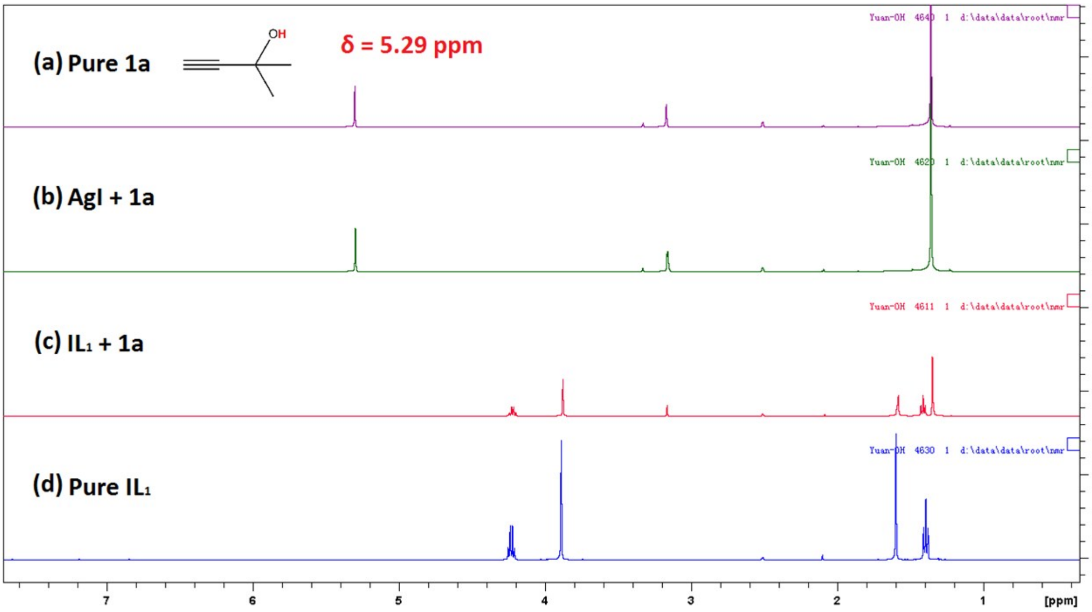


Figure S2. ^{1}H NMR of (a) pure **1a** in DMSO-d_6, (b) AgI+**1a** in DMSO-d_6, (c) IL_1+**1a** in DMSO-d_6, (d) pure IL_1 in DMSO-d_6

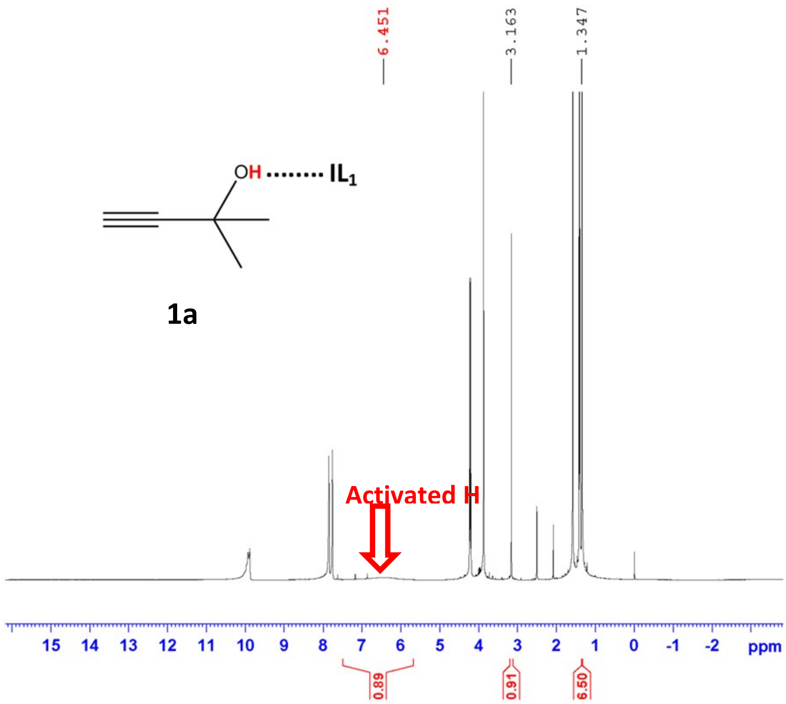
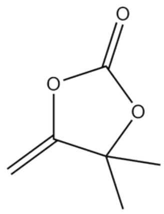


Figure S3. ^{1}H NMR of IL_1+**1a** in DMSO-d_6 (peaks marked with chemical shifts belong to **1a**)

4. Characterization of products



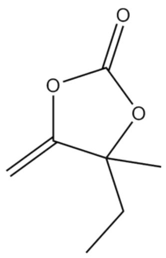
2a

4, 4-Dimethyl-5-methylene-[1,3]dioxolan-2-one (2a)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.77 (d, *J* = 4.0 Hz, 1H), 4.33 (d, *J* = 4.0 Hz, 1H), 1.62 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.74, 151.27, 85.30, 84.65, 27.56.

The spectroscopic data matched those reported in the literature.[9]



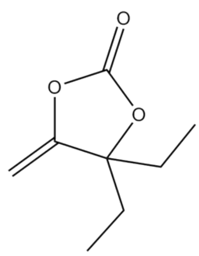
2b

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

^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.83 (d, *J* = 4.0 Hz, 1H), 4.28 (d, *J* = 3.9 Hz, 1H), 1.93 (dq, *J* = 14.6 Hz, 7.4 Hz, 1H), 1.78 (dq, *J* = 14.7 Hz, 7.4 Hz, 1H), 1.60 (s, 3H), 1.01 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 157.48, 151.53, 87.56, 85.53, 33.40, 25.95, 7.32.

The spectroscopic data matched those reported in the literature.[9]



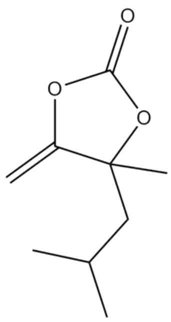
2c

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

^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.88 (d, *J* = 3.8 Hz, 1H), 4.24 (d, *J* = 3.9 Hz, 1H), 1.95 (dq, *J* = 14.6 Hz, 7.3 Hz, 2H), 1.72 (dt, *J* = 14.8 Hz, 7.4 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 155.83, 151.85, 90.83, 85.78, 31.90, 7.10.

The spectroscopic data matched those reported in the literature.[9]



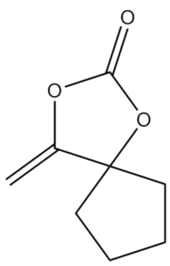
2d

4-Isobutyl-4-methyl-5-methylene-[1, 3] dioxolan-2-one (2d)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.81 (d, *J* = 3.9 Hz, 1H), 4.29 (d, *J* = 3.9 Hz, 1H), 1.90 – 1.80 (m, 2H), 1.70 – 1.66 (m, 1H), 1.60 (s, 3H), 1.00 – 0.98 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.37, 151.45, 87.30, 85.54, 48.57, 27.02, 24.29, 23.98, 23.68.

The spectroscopic data matched those reported in the literature.[9]



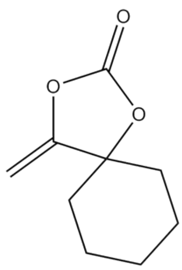
2e

4-Methylene-1, 3-dioxa-spiro [4.4] nonan-2-one (2e)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.81 (d, *J* = 3.9 Hz, 1H), 4.36 (d, *J* = 3.9 Hz, 1H), 2.28 – 2.23 (m, 2H), 1.98 – 1.83 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 157.79, 151.46, 94.21, 85.31, 40.65, 24.25.

The spectroscopic data matched those reported in the literature.[5]



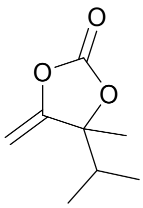
2f

4-Methylene-1, 3-dioxa-spiro [4.5] decan-2-one (2f)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.78 (d, *J* = 3.8 Hz, 1H), 4.30 (d, *J* = 3.8 Hz, 1H), 2.04 – 2.02 (m, 2H), 1.79 – 1.59 (m, 7H), 1.38 – 1.28 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 158.79, 151.48, 86.38, 85.46, 36.53, 24.37, 21.62.

The spectroscopic data matched those reported in the literature.[9]



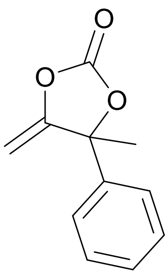
2g

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

^{1}H NMR (500 MHz, $CDCl_3$) δ = 4.84 (d, *J* = 3.8 Hz, 1H), 4.28 (d, *J* = 3.8 Hz, 1H), 1.99-1.93 (m, 1H), 1.59 (s, 3H), 1.03 (dd, *J* = 13.4 Hz, 13.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 157.14, 151.71, 89.82, 86.21, 36.99, 24.04, 16.34, 16.04.

The spectroscopic data matched those reported in the literature.[5]



2h

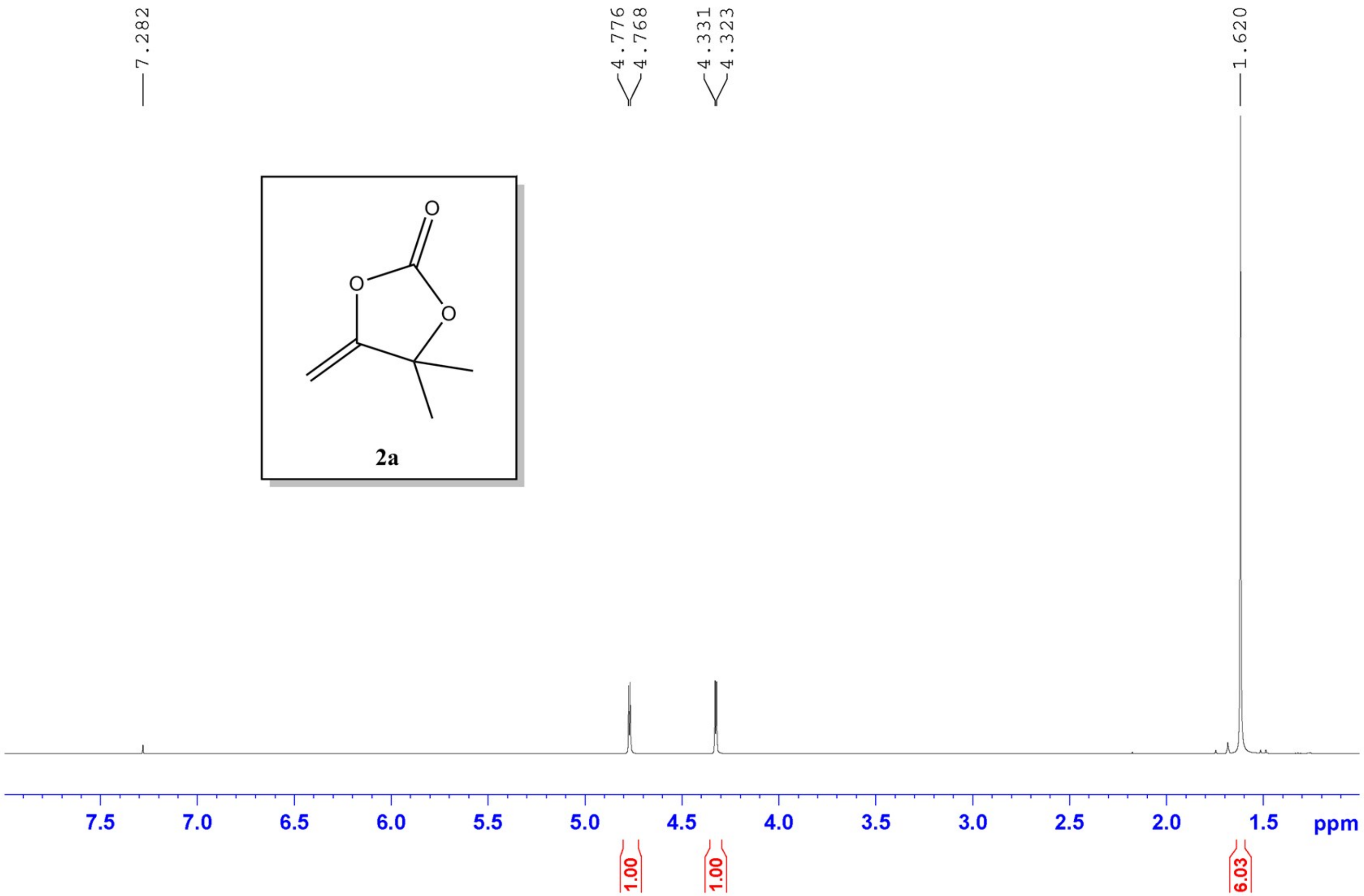
4-Methyl-5-methylene-4-phenyl-1, 3-dioxolan-2-one (2h)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.51 – 7.50 (m, 2H), 7.47 – 7.40 (m, 3H), 4.98 (d, *J* = 4.0 Hz, 1H), 4.49 (d, *J* = 4.0 Hz, 1H). 2.00 (s, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) δ = 157.49, 151.16, 139.30, 129.19, 128.93, 124.70, 88.16, 87.16, 27.47

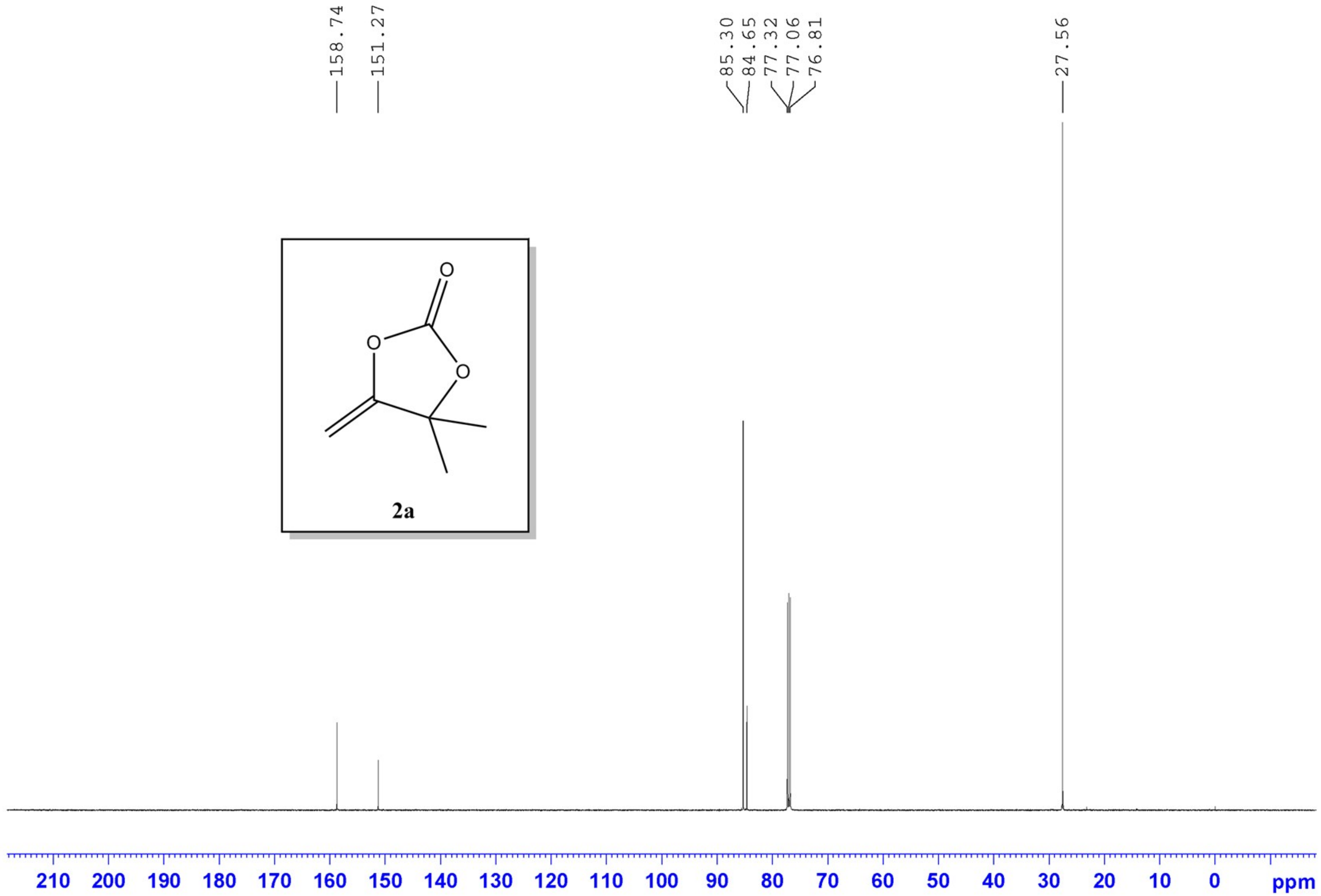
The spectroscopic data matched those reported in the literature.[5]

^1H NMR



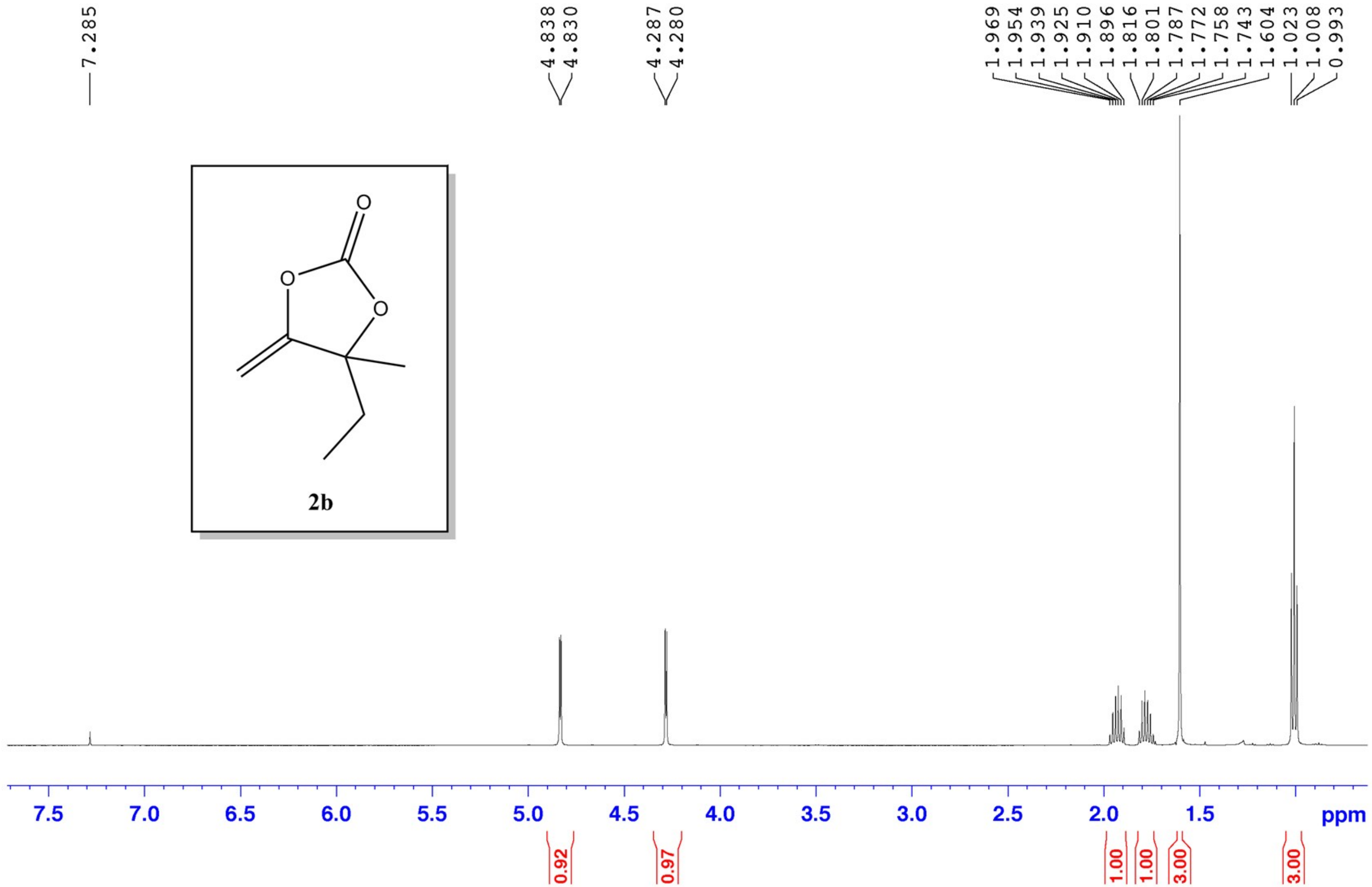
7.282
4.776
4.768
4.331
4.323
1.620
2a
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
ppm
1.00
1.00
6.03

^{13}C NMR



158.74
151.27
85.30
84.65
77.32
77.06
76.81
27.56
2a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

^{1}H NMR


7.285
4.838
4.830
4.287
4.280
1.969
1.954
1.939
1.925
1.910
1.896
1.816
1.801
1.787
1.772
1.758
1.743
1.604
1.023
1.008
0.993
O
O
O
2b
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
ppm
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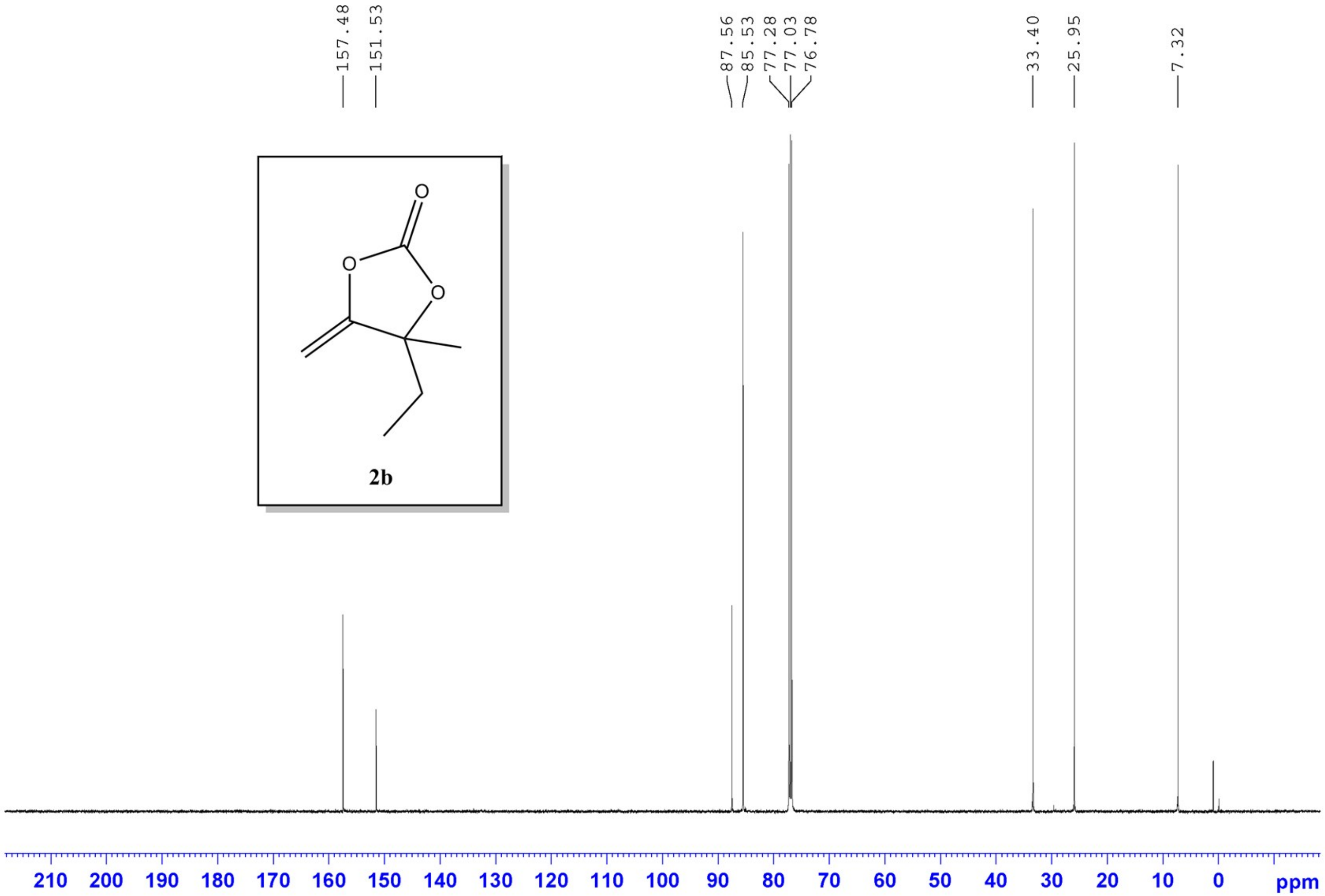
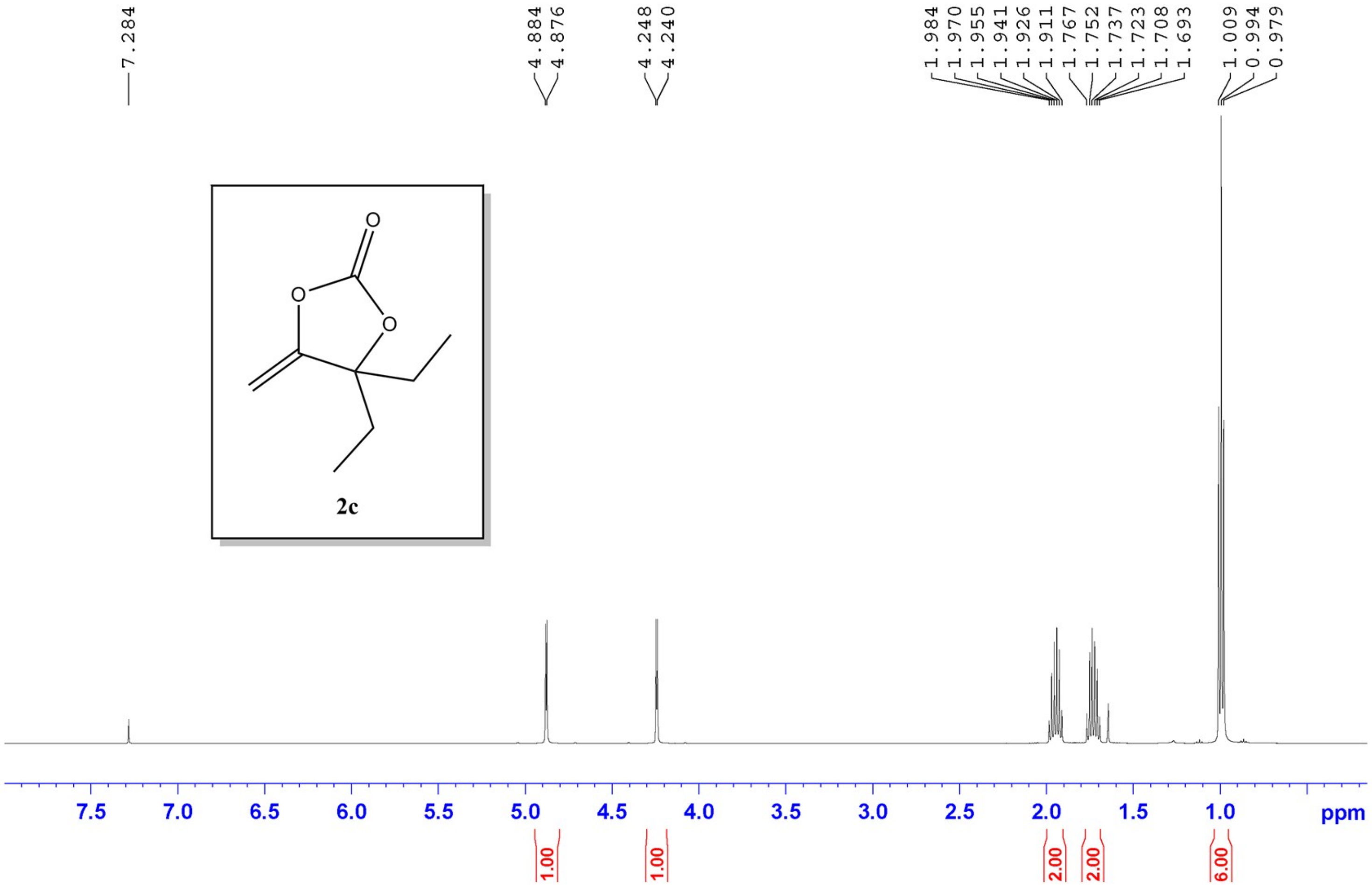
0.97
1.00
1.00
3.00
3.00

^{13}C NMR



157.48
151.53
87.56
85.53
77.28
77.03
76.78
33.40
25.95
7.32
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

^{1}H NMR



7.284
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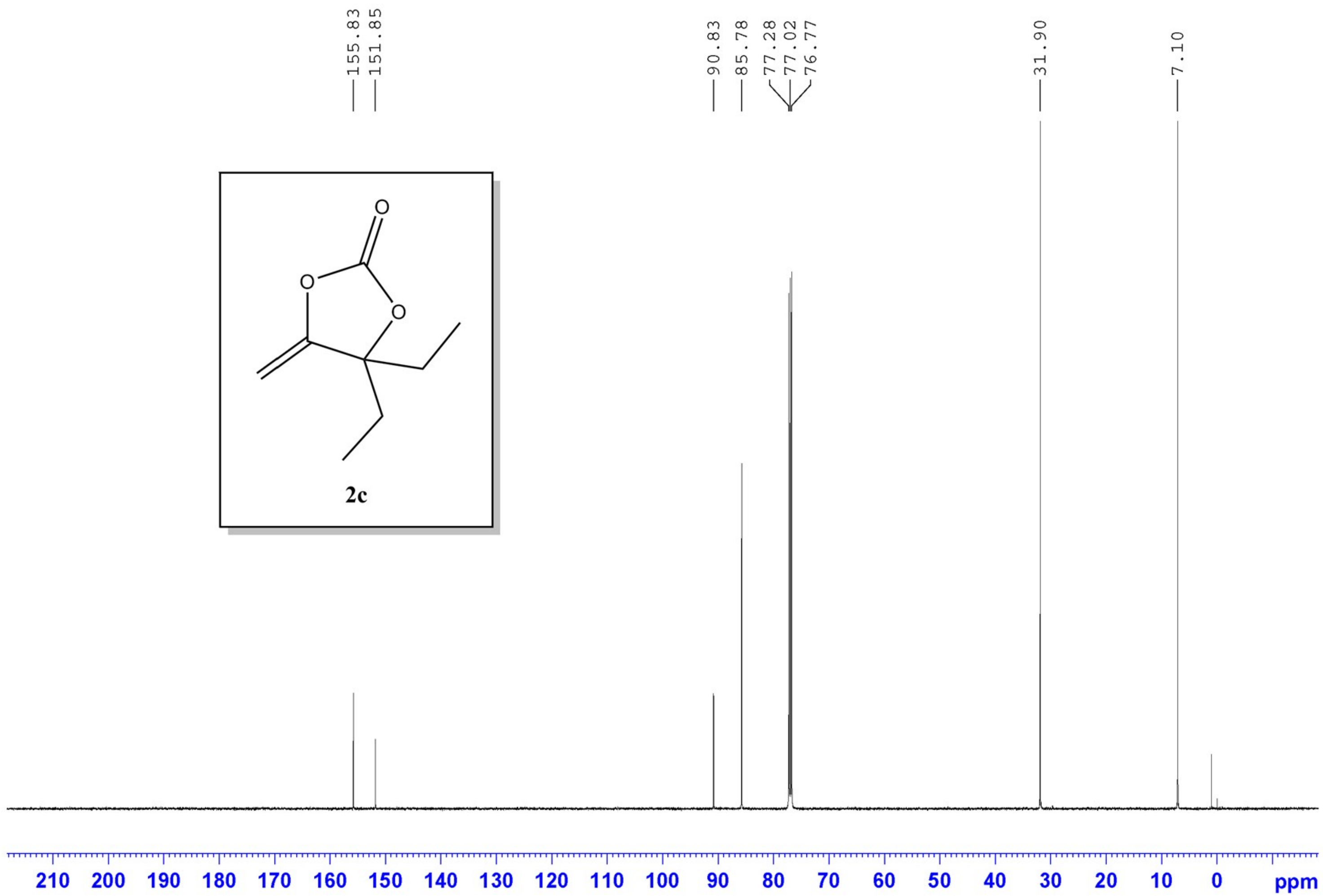
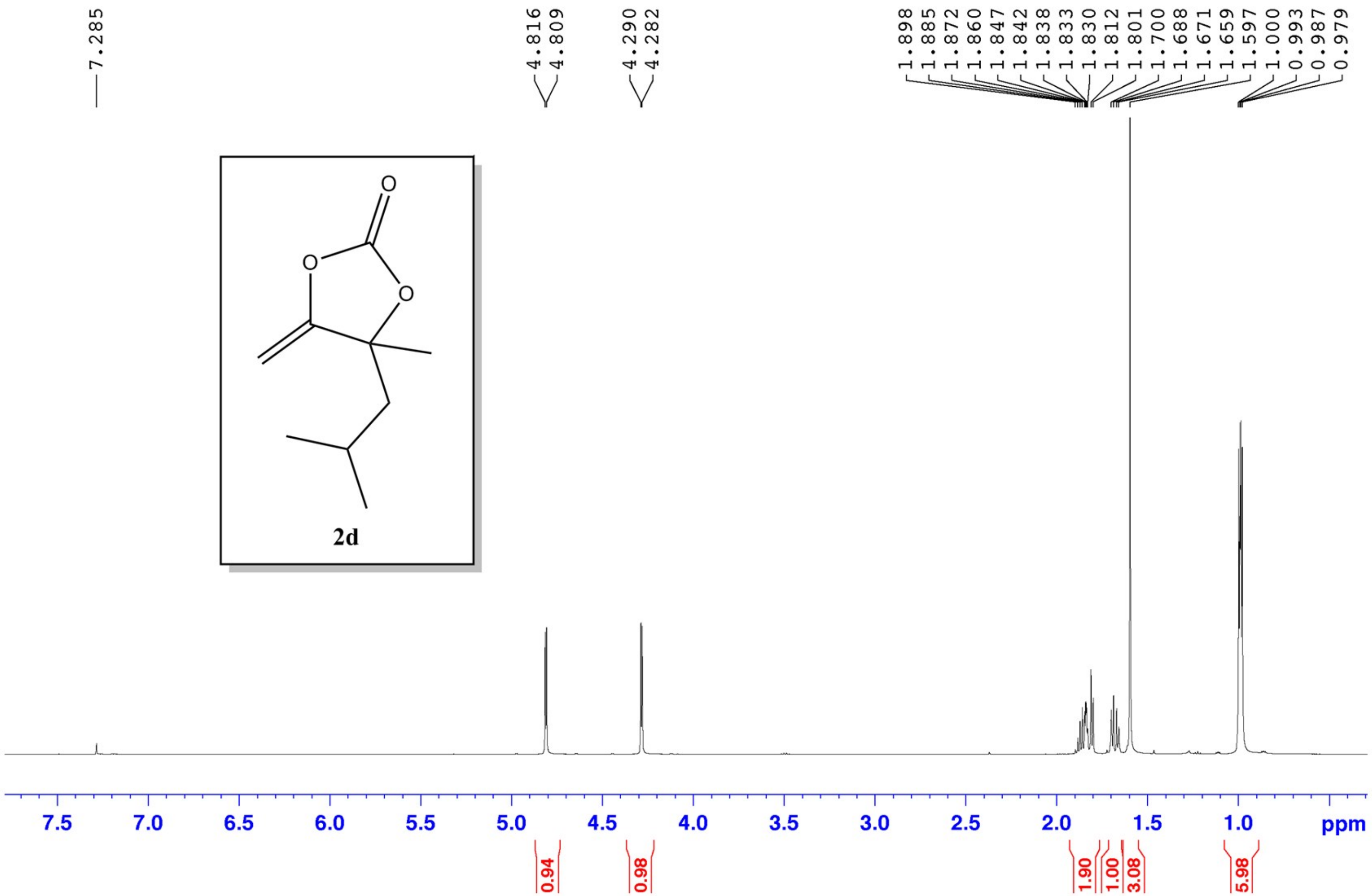
4.876
4.248
4.240
1.984
1.970
1.955
1.941
1.926
1.911
1.767
1.752
1.737
1.723
1.708
1.693
1.009
0.994
0.979
O
O
O
2c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
2.00
2.00
6.00

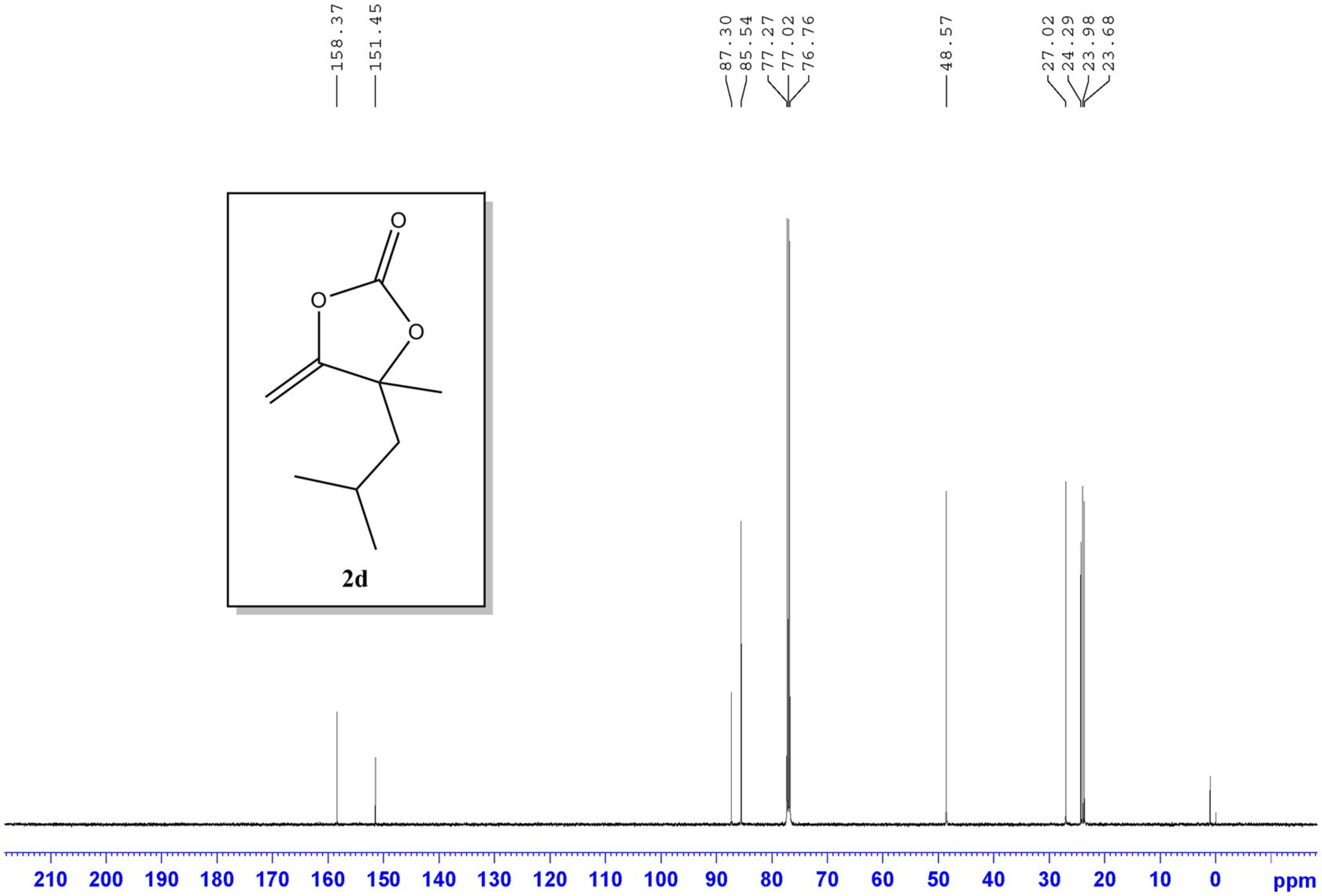
^{13}C NMR


155.83
151.85
90.83
85.78
77.28
77.02
76.77
31.90
7.10
O
O
O
2c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

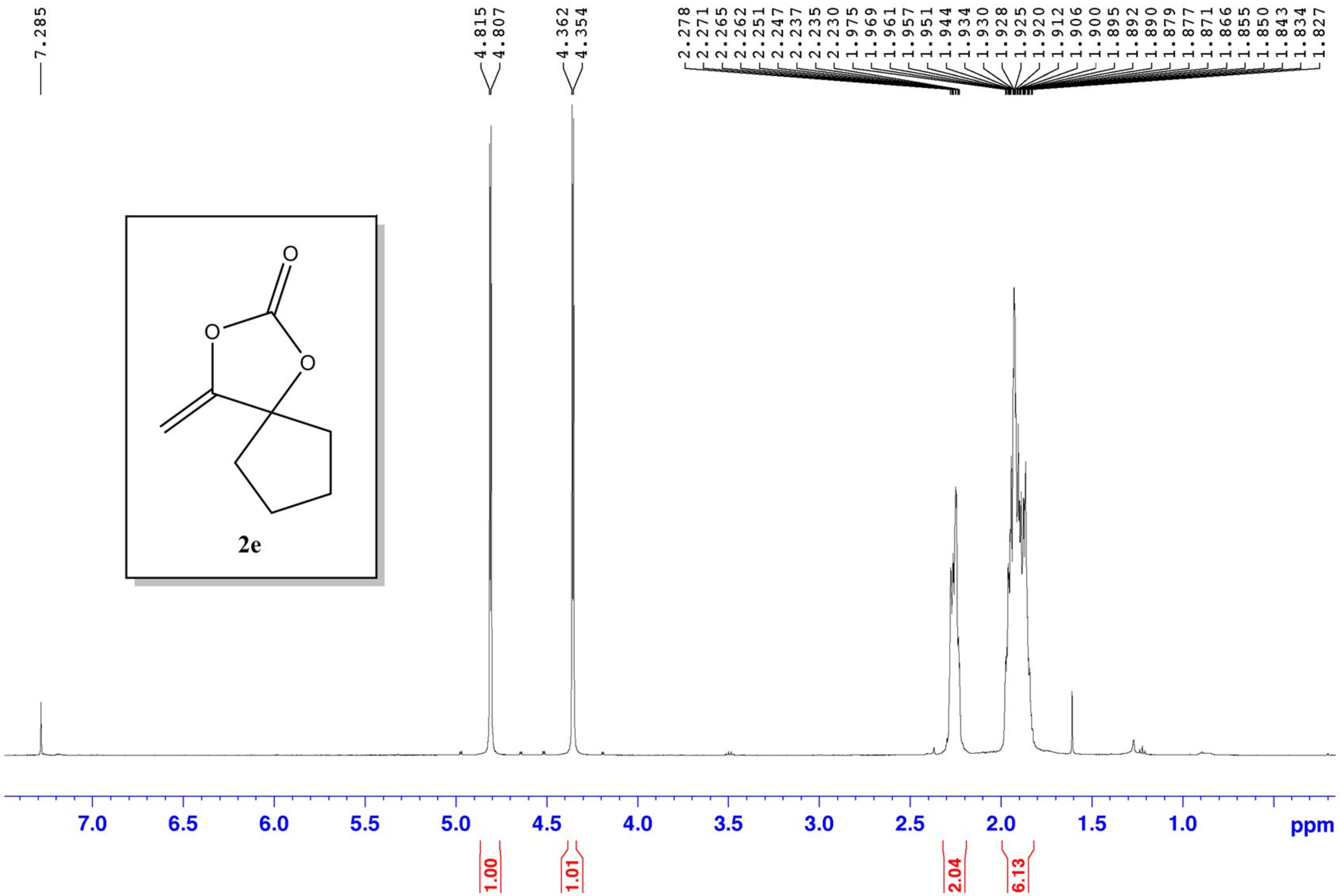
^{1}H NMR


7.285
4.816
4.809
4.290
4.282
1.898
1.885
1.872
1.860
1.847
1.842
1.838
1.833
1.830
1.812
1.801
1.700
1.688
1.671
1.659
1.597
1.000
0.993
0.987
0.979
O
O
O
2d
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
ppm
0.94
0.98
1.90
1.00
3.08
5.98

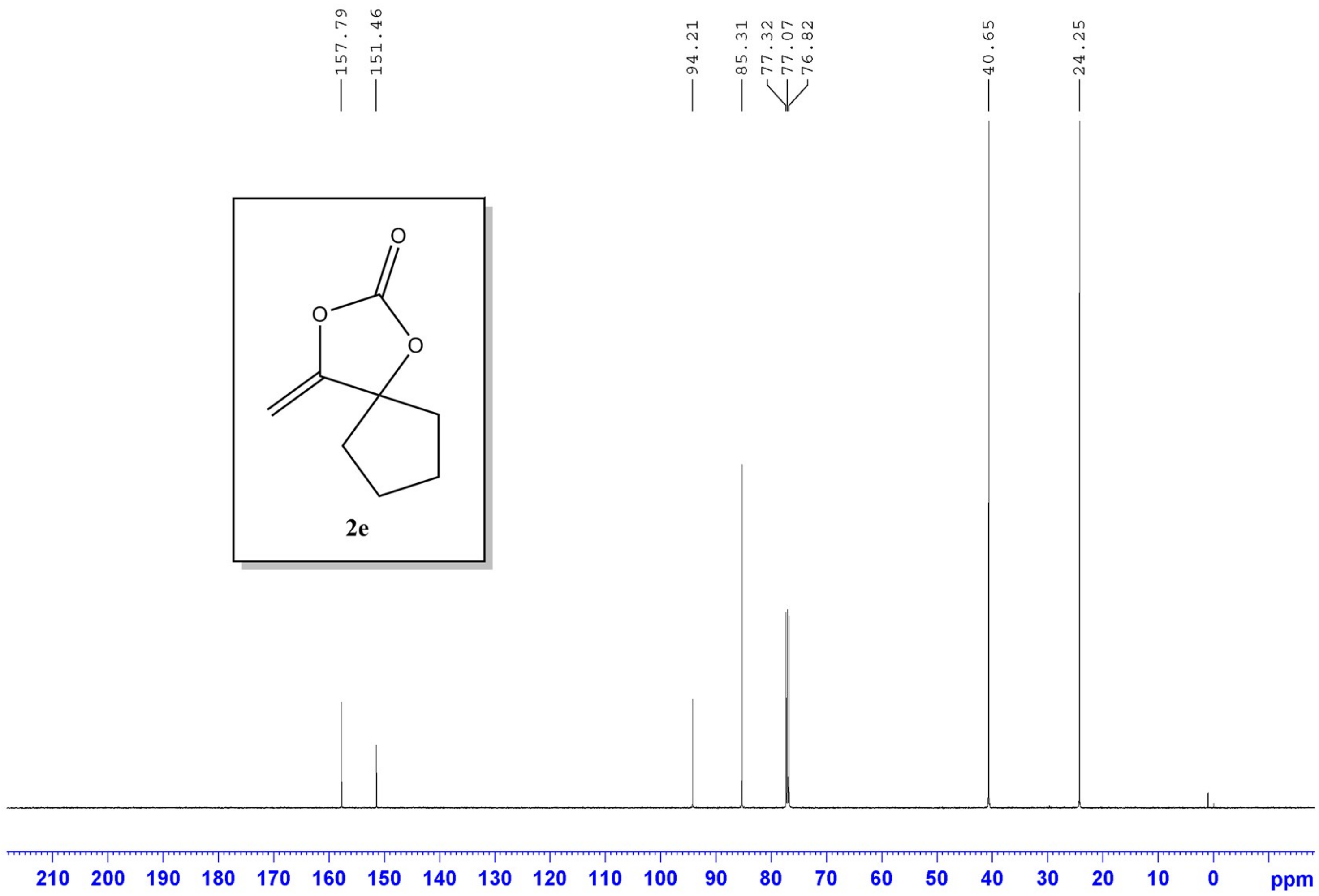
^{13}C NMR


158.37
151.45
87.30
85.54
77.27
77.02
76.76
48.57
27.02
24.29
23.98
23.68
O
O
O
2d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

¹H NMR


7.285
4.815
4.807
4.362
4.354
2.278
2.271
2.265
2.262
2.251
2.247
2.237
2.235
2.230
1.975
1.969
1.961
1.957
1.951
1.944
1.934
1.930
1.928
1.925
1.920
1.912
1.906
1.900
1.895
1.892
1.890
1.879
1.877
1.871
1.866
1.855
1.850
1.843
1.834
1.827
O
O
O
2e
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
ppm
1.00
1.01
2.04
6.13

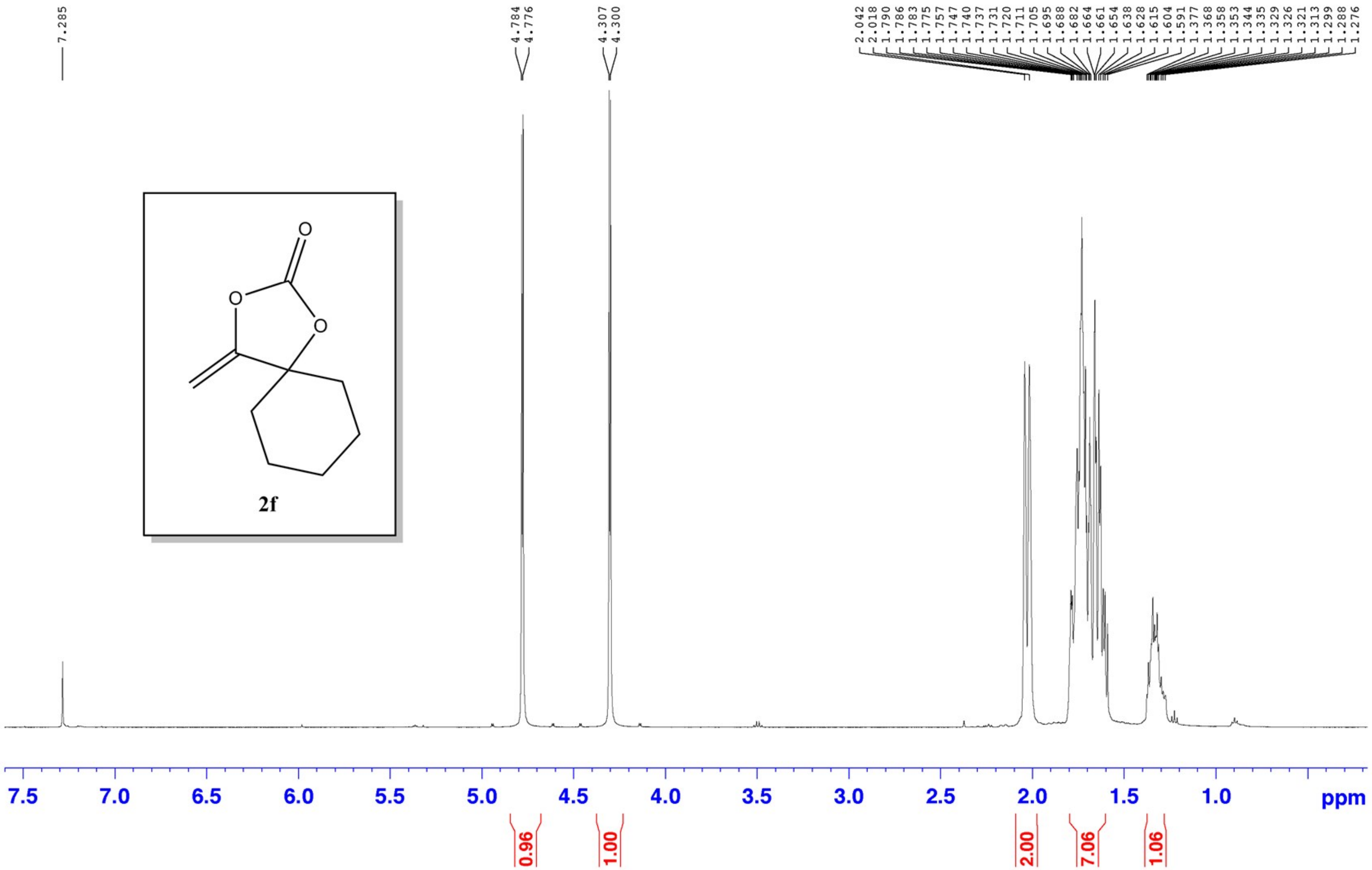
^{13}C NMR



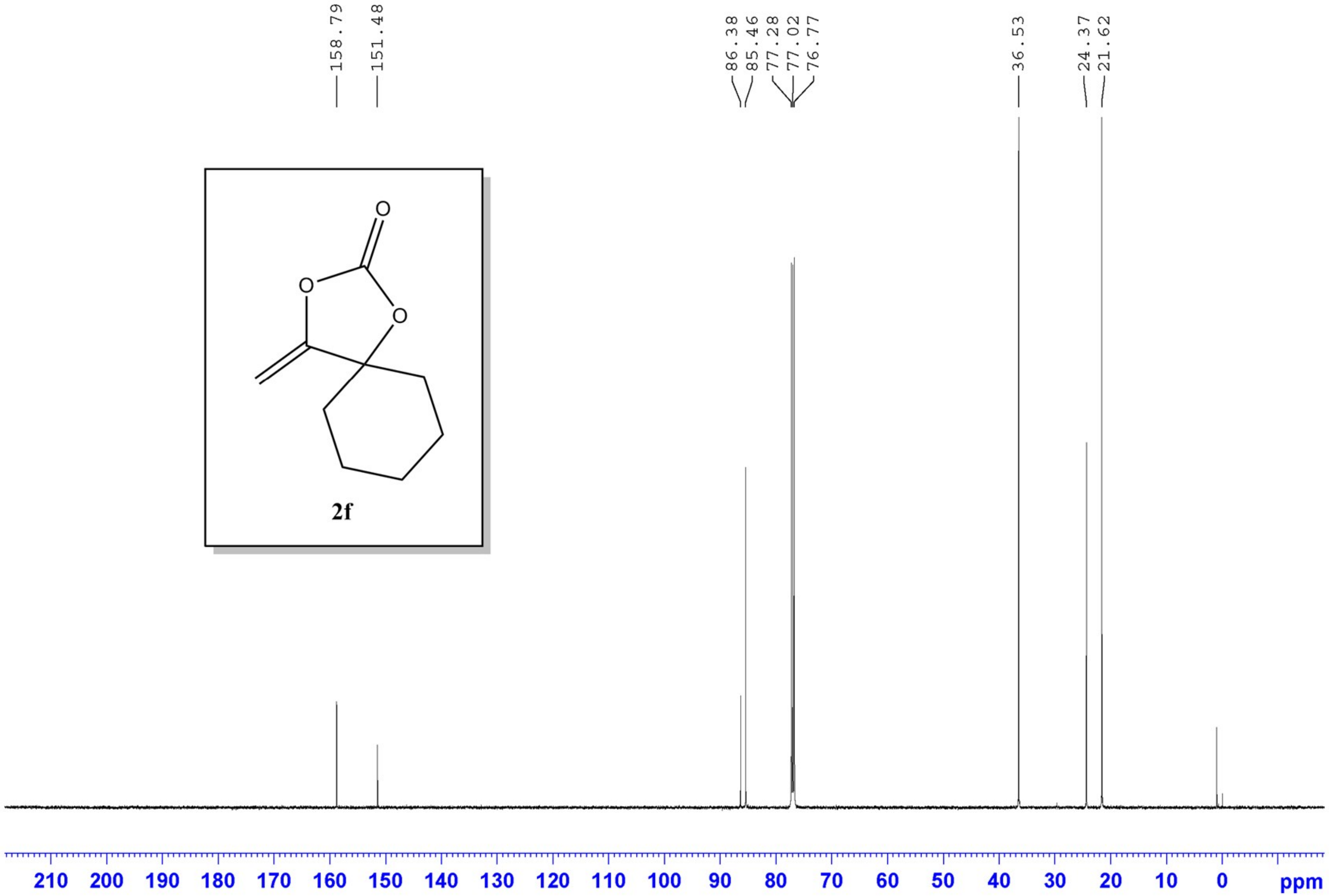
157.79
151.46
94.21
85.31
77.32
77.07
76.82
40.65
24.25
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2e

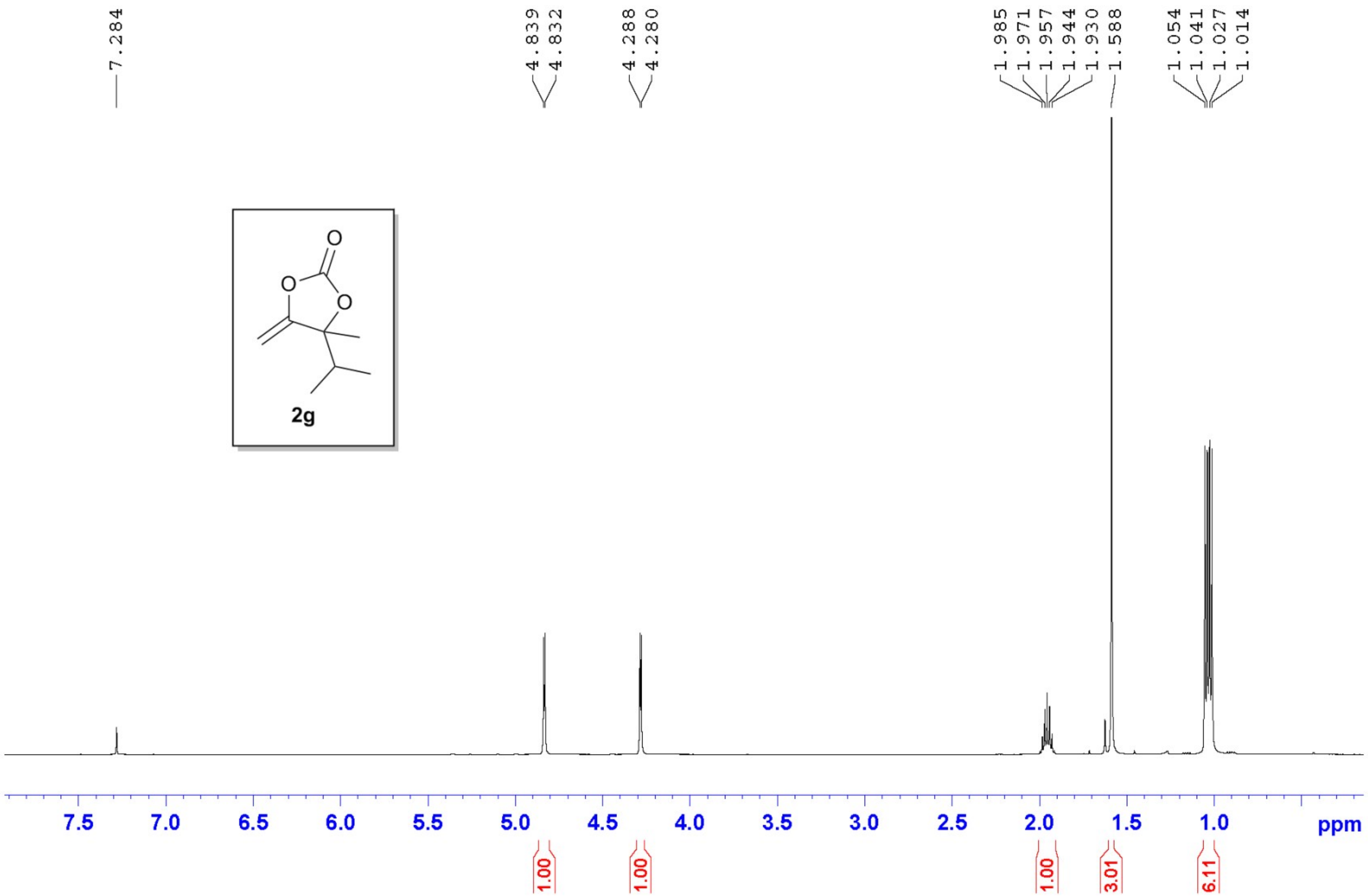
^{1}H NMR


7.285
4.784
4.776
4.307
4.300
2.042
2.018
1.790
1.786
1.783
1.775
1.757
1.747
1.740
1.737
1.731
1.720
1.711
1.705
1.695
1.688
1.682
1.664
1.661
1.654
1.638
1.628
1.615
1.604
1.591
1.377
1.368
1.358
1.353
1.344
1.335
1.329
1.326
1.321
1.313
1.299
1.288
1.276
O
O
O
2f
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
ppm
0.96
1.00
2.00
7.06
1.06

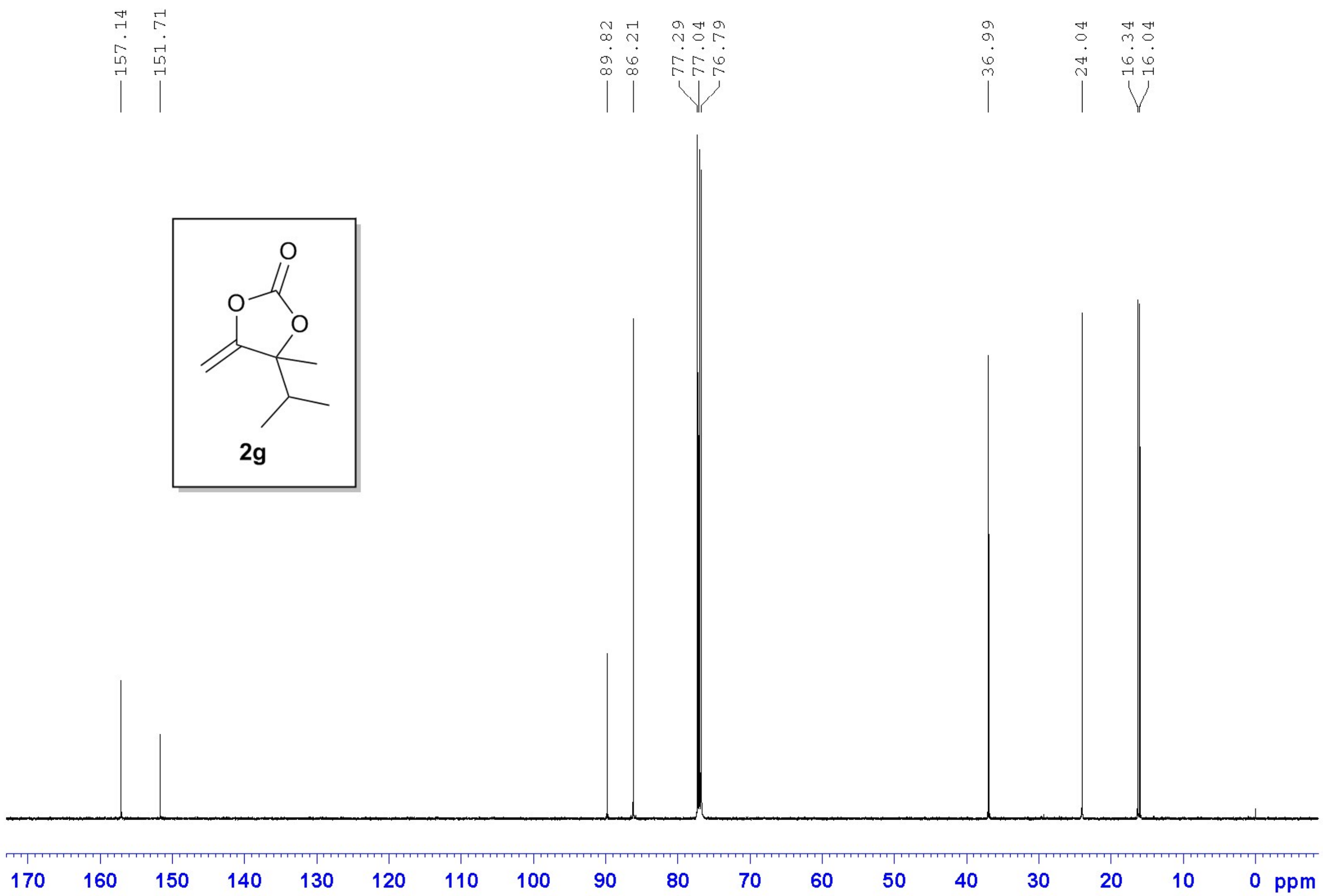
^{13}C NMR


158.79
151.48
86.38
85.46
77.28
77.02
76.77
36.53
24.37
21.62
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

^{1}H NMR

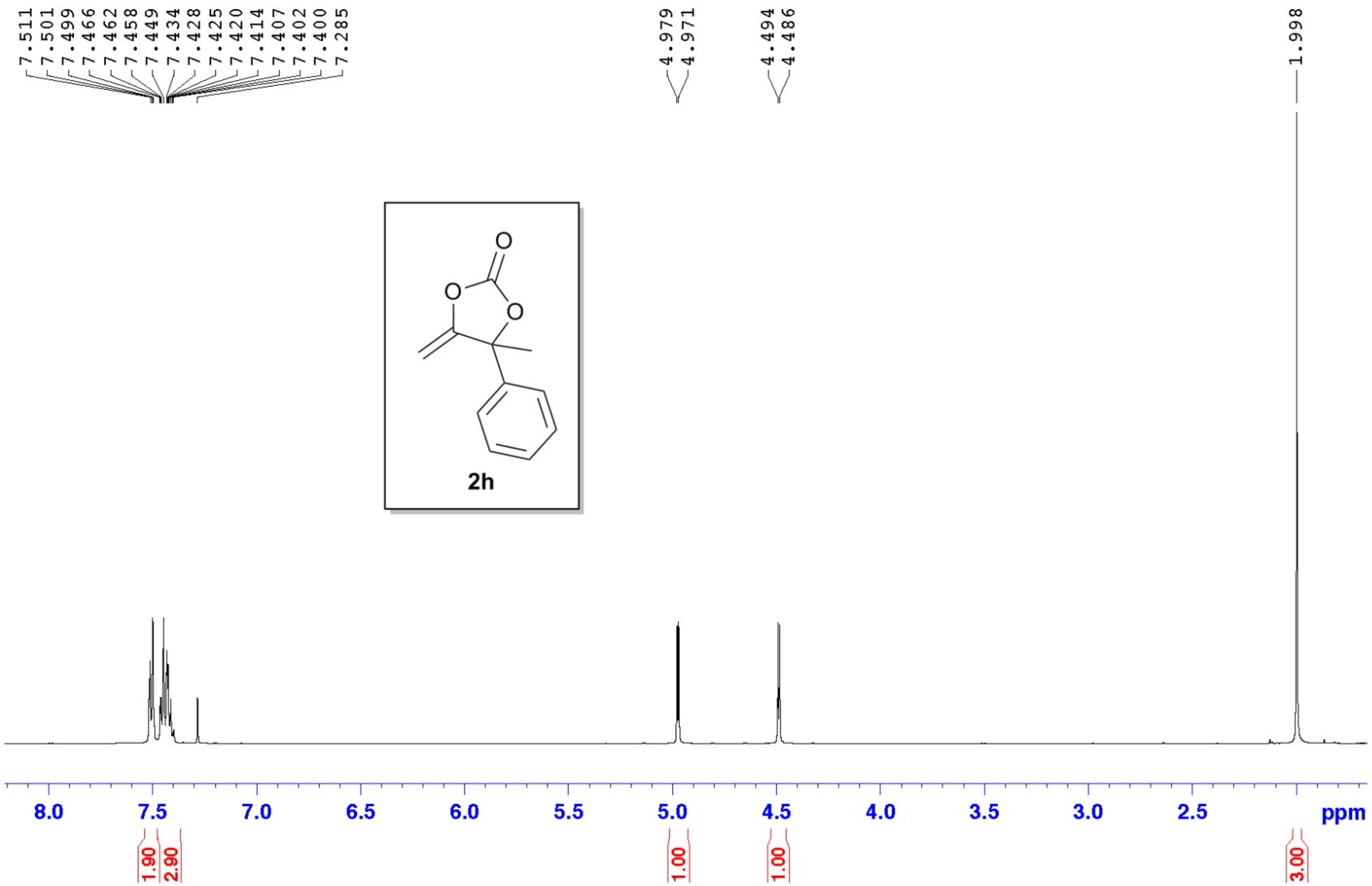

7.284
4.839
4.832
4.288
4.280
1.985
1.971
1.957
1.944
1.930
1.588
1.054
1.041
1.027
1.014
O
O
O
2g
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.00
1.00
3.01
6.11

^{13}C NMR



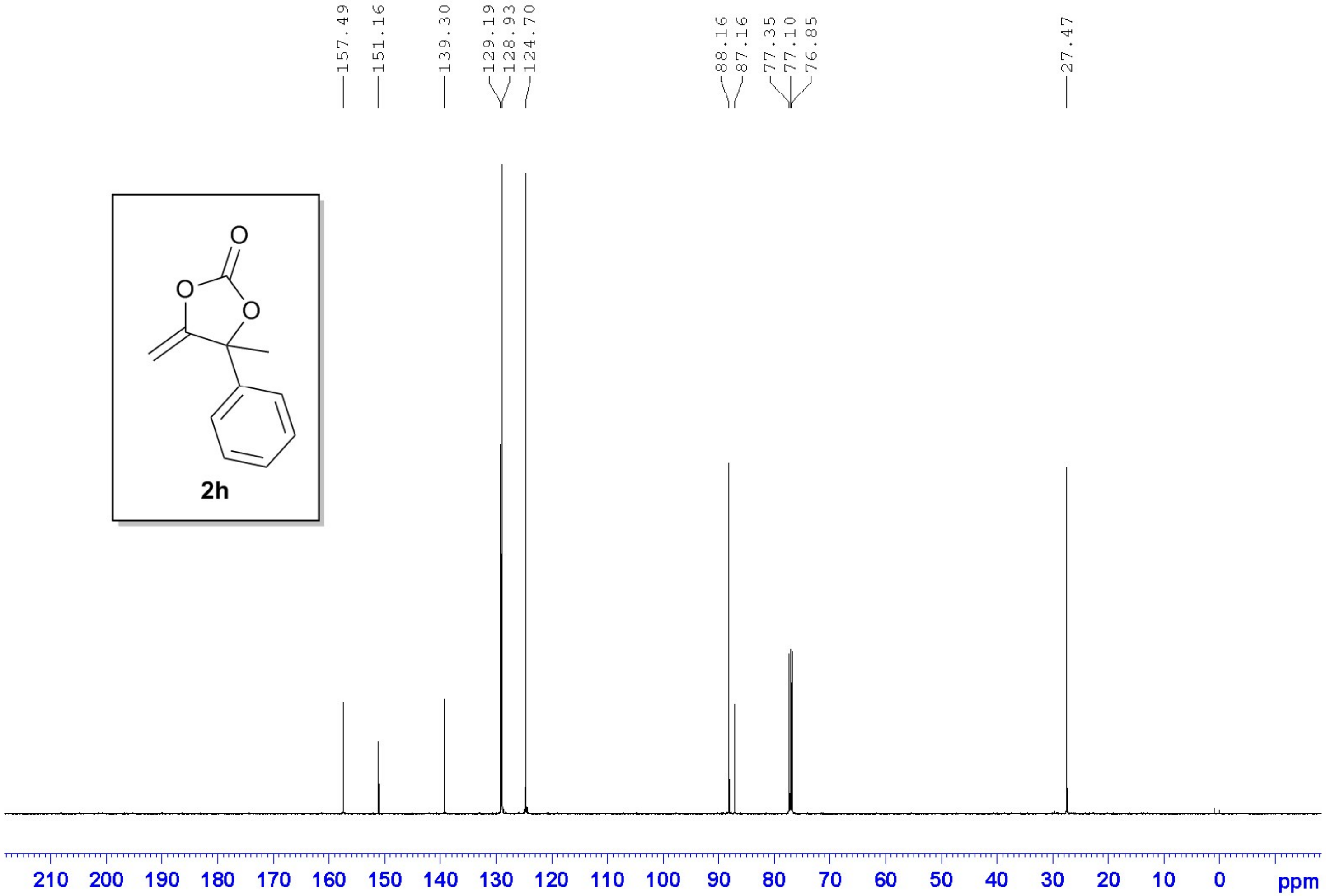
157.14
151.71
89.82
86.21
77.29
77.04
76.79
36.99
24.04
16.34
16.04
O
O
O
2g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

^{1}H NMR



7.511
7.501
7.499
7.466
7.462
7.458
7.449
7.434
7.428
7.425
7.420
7.414
7.407
7.402
7.400
7.285
4.979
4.971
4.494
4.486
1.998
O
O
O
2h
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm
1.90
2.90
1.00
1.00
3.00

^{13}C NMR


157.49
151.16
139.30
129.19
128.93
124.70
88.16
87.16
77.35
77.10
76.85
27.47
2h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

References:

1. X. Tang, C. Qi, H. He, H. Jiang, Y. Ren and G. Yuan, *Adv. Synth. Catal.*, 2013, **355**, 2019-2028.
2. Q.-W. Song, B. Yu, X.-D. Li, R. Ma, Z.-F. Diao, R.-G. Li, W. Li and L.-N. He, *Green Chem.*, 2014, **16**, 1633-1638.
3. Z.-Z. Yang, Y. Zhao, H. Zhang, B. Yu, Z. Ma, G. Ji and Z. Liu, *Chem. Commun.*, 2014, **50**, 13910-13913.
4. M. Cui, Q. Qian, Z. He, J. Ma, X. Kang, J. Hu, Z. Liu and B. Han, *Chem. Eur. J.*, 2015, **21**, 15924-15928.
5. Q. W. Song, W. Q. Chen, R. Ma, A. Yu, Q. Y. Li, Y. Chang and L. N. He, *ChemSusChem*, 2015, **8**, 821-827.
6. K. Chen, G. Shi, R. Dao, K. Mei, X. Zhou, H. Li and C. Wang, Chem. Commun., 2016, **52**, 7830-7833.
7. Z. Yang, B. Yu, H. Zhang, Y. Zhao, Y. Chen, Z. Ma, G. Ji, X. Gao, B. Han and Z. Liu, *ACS Catal.*, 2016, **6**, 1268-1273.
8. J. Qiu, Y. Zhao, H. Wang, G. Cui and J. Wang, *RSC Advances*, 2016, **6**, 54020-54026.
9. J. Hu, J. Ma, Q. Zhu, Q. Qian, H. Han, Q. Mei and B. Han, *Green Chem.*, 2016, **18**, 382-385.