Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Simple and Robust AgI/KOAc Catalytic System for the Carboxylative Assembly of Propargyl Alcohols and Carbon Dioxide at Atmospheric Pressure

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This file includes:

1. General information

Unless otherwise noted, all the compounds involved 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 (^{1}H NMR, 500 MHz; ^{13}C NMR, 126 MHz) spectrometer. Their peak frequencies were referenced versus an internal standard (TMS) shifts at 0 ppm for ^{1}H 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

General procedures of the carboxylative cyclization of propargyl alcohols with CO_2 to access the α-alkylidene cyclic carbonates:

AgI (11.7 mg, 0.05 mmol), KOAc (4.9 mg, 0.05 mmol), a propargyl alcohol (5 mmol) and DMF (10 mL) were added to a Schlenk tube equipped with a magnetic stir 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 diluted with 20 mL deionized water and extracted with diethyl ether (3 × 30 mL). The organic layers were combined and dried over $MgSO_4$. Then the solvent was removed and the crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (100:1-20:1) as an eluent to give the desired product. Other conditions employing AgI/KOAc system in Table 2 followed the same procedures and the amounts of AgI, KOAc, substrate and DMF were tuned according to the footnotes in Table 2.

Investigation experiments about the activation state

Substrate **1a**, and the mixture of **1a**/AgI, **1a**/KOAc, **1a**/AgI/KOAc were added into 5 ml of DMSO-d_6 according to the amounts below. These systems were allowed to stir at 45°C without CO_2 and monitored by NMR.

1a system: **1a** = 1 mmol

1a/AgI system: **1a** = 1 mmol, AgI = 1 mmol.

1a/KOAc system: **1a** = 1 mmol, KOAc = 1 mmol.

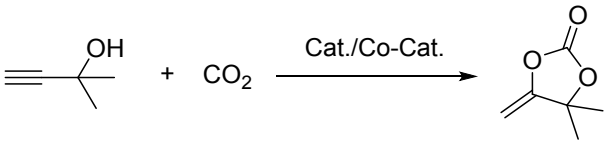
1a/AgI/KOAc system: **1a** = 1 mmol, AgI = 1 mmol, KOAc = 1mmol.

3. Further Investigation about the reaction conditions.

Further optimization of the reaction conditions of the AgI/KOAc-catalyzed carboxylative cyclization protocol were performed and the results were depicted in Table S1, Obviously, the AgI/KOAc system exhibited excellent activity in high-polar aprotic solvents of DMF and DMSO under identical conditions (entries 1, 2). Nevertheless, a detectable but much lower yield was obtained when the catalytic reaction was performed in acetonitrile (CH_3CN) (entry 3). In relatively low-polar solvents, such as toluene, THF and CH_2Cl_2, the AgI/KOAc system was ineffective for the carboxylative cyclization

(entries 4-6). This tendency implied that the AgI/KOAc system required a high-polar circumstance to interact with the substrates. On the other hand, CH_3OH was proved to be not suitable for this reaction probably due to the hydroxyl groups of the solvent which seriously interfered with the activation of the hydroxyl groups of the substrates (entry 7). Furthermore, the AgI/KOAc system couldn't catalyze this reaction under neat conditions (entry 8). Gratifyingly, when decreasing the temperature to 45°C, the CO_2 pressure to 1 bar and the Ag loading to 1 mol%, the AgI/KOAc system still exhibited excellent activity (entry 9). The yield would slightly decrease when the amounts of both AgI and KOAc were reduced to 0.5 mol% (entry 10). However, employment of a higher amount of the economical KOAc would make this AgI/KOAc system continue to exhibit excellent activity even when the Ag loading was largely decreased to 0.05 mol% (entry 11). Furthermore, the yield would also decrease obviously if the temperature was tuned to room temperature (entry 12), implying that slight heating was essential. Consequently, conditions of entry 9 and entry 11 were selected as the optimal reaction conditions for further screening of the substrates.

Table S1. Further screening of the reaction conditions [a-d]



Entry	Catalyst	Co-catalyst	Solvent	T	P(CO_2)	[Ag]	Yield[e]
1[a]	AgI	KOAc	DMF	65°C	2 bar	2 mol%	>99%
2[a]	AgI	KOAc	DMSO	65°C	2 bar	2 mol%	97%
3[a]	AgI	KOAc	CH_3CN	65°C	2 bar	2 mol%	11%
4[a]	AgI	KOAc	Toluene	65°C	2 bar	2 mol%	0
5[a]	AgI	KOAc	THF	65°C	2 bar	2 mol%	0
6[a]	AgI	KOAc	CH_2Cl_2	65°C	2 bar	2 mol%	0
7[a]	AgI	KOAc	CH_3OH	65°C	2 bar	2 mol%	0
8[a]	AgI	KOAc	/.	65°C	2 bar	2 mol%	2%
9[b]	AgI	KOAc	DMF	45°C	1 bar	1 mol%	>99%
10[c]	AgI	KOAc	DMF	45°C	1 bar	0.5 mol%	83%
11[d]	AgI	KOAc	DMF	45°C	1 bar	0.05 mol%	>99%
12[b]	AgI	KOAc	DMF	rt	1 bar	1 mol%	42%

[a] 0.1 mmol of AgI, 0.1 mmol of KOAc, 5 mmol of 2-methylbut-3-yn-2-ol, 10 mL of solvent, 12 h.

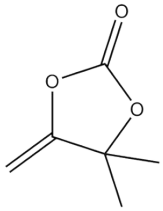
[b] 0.05 mmol of AgI, 0.05 mmol of KOAc, 5 mmol of 2-methylbut-3-yn-2-ol, 10 mL of DMF, 12 h.

[c] 0.025 mmol of AgI, 0.025 mmol of KOAc, 5 mmol of 2-methylbut-3-yn-2-ol, 10 mL of DMF, 12 h.

[d] 0.01 mmol of AgI, 20 mmol of KOAc, 20 mmol of 2-methylbut-3-yn-2-ol, 40 mL of DMF, 12 h.

[e] Yields were determined by ^1H NMR spectroscopy using 1, 1, 2, 2-tetrachloroethane as the internal standard.

4. Characterization of Products



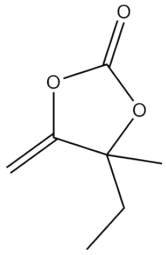
2a

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.[1]



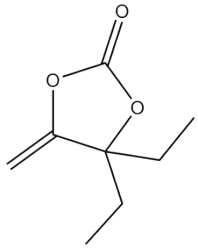
2b

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.[1]



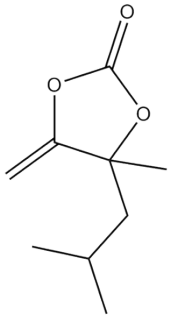
2c

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.[1]



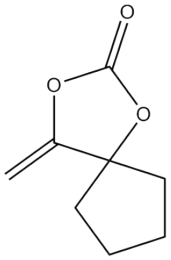
2d

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.[1]



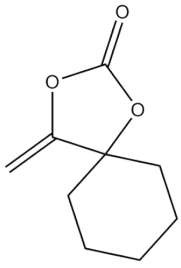
2e

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.[2]



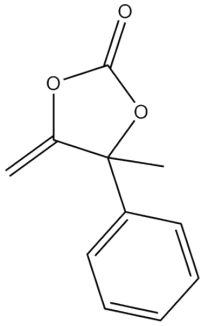
2f

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.[1]



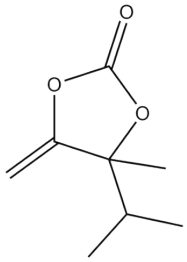
2g

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

^{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.[2]



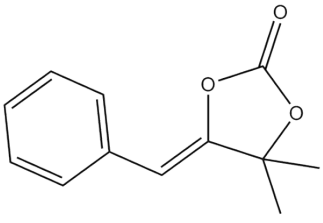
2h

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

^{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.[2]



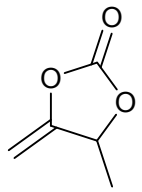
2i

4, 4-Dimethyl-5-(phenylmethylene)-1, 3-dioxolan-2-one (2i)

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.58-7.56 (m, 2H), 7.40-7.37 (m, 2H), 7.30-7.27 (m, 1H), 5.53 (s, 1H), 1.72 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ = 151.31, 150.76, 132.42, 128.67, 128.47, 127.63, 101.59, 85.54, 27.76.

The spectroscopic data matched those reported in the literature. [2]



2j

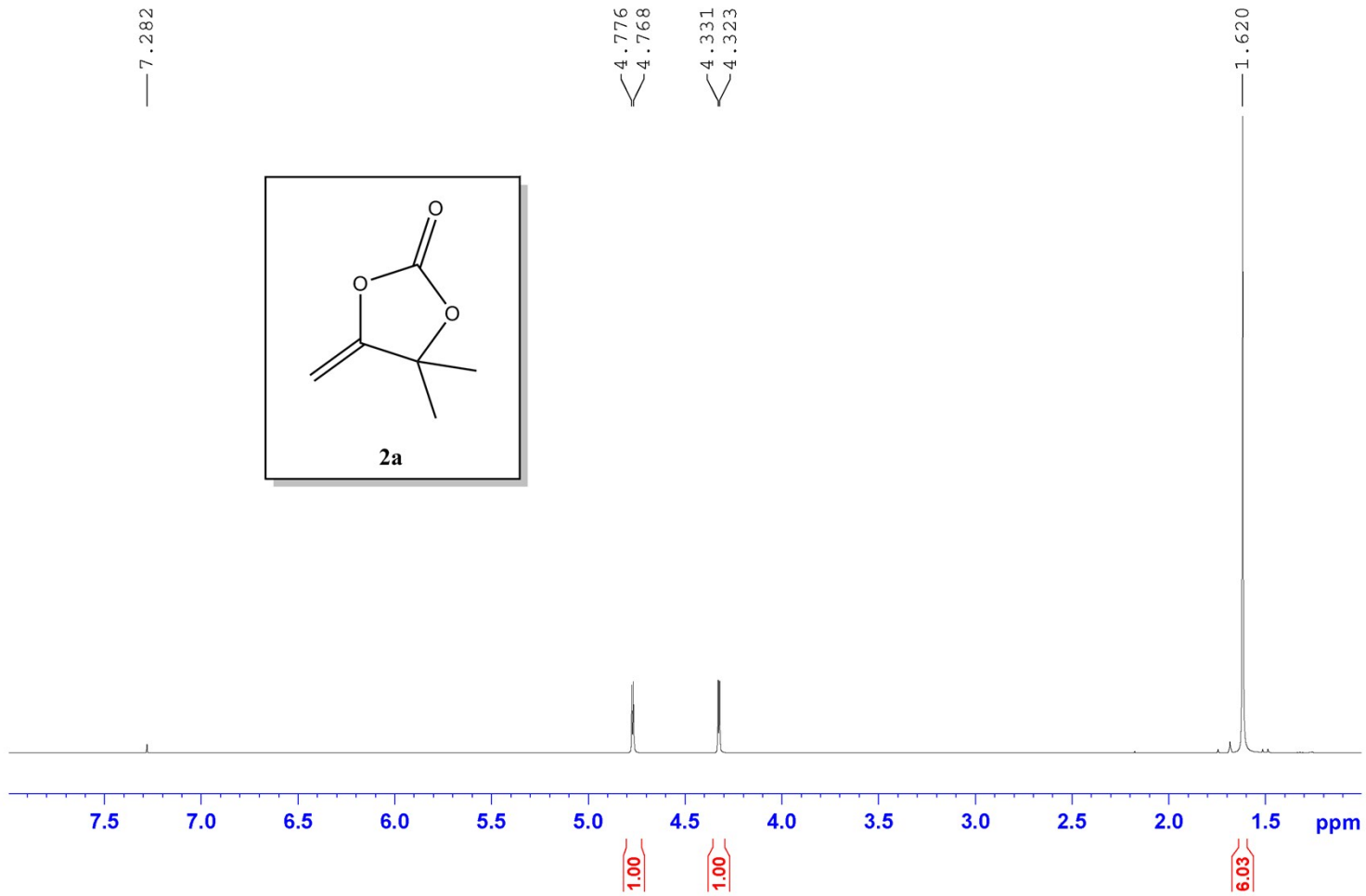
4-methyl-5-methylene-1,3-dioxolan-2-one (2j)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.30-5.26 (m, 1H), 4.86-4.84 (m, 1H), 4.38-4.37 (m, 1H), 1.60-1.59 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 154.63, 151.93, 86.58, 76.24, 20.45.

The spectroscopic data matched those reported in the literature.[3]

^{1}H NMR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O
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5.5
5.0
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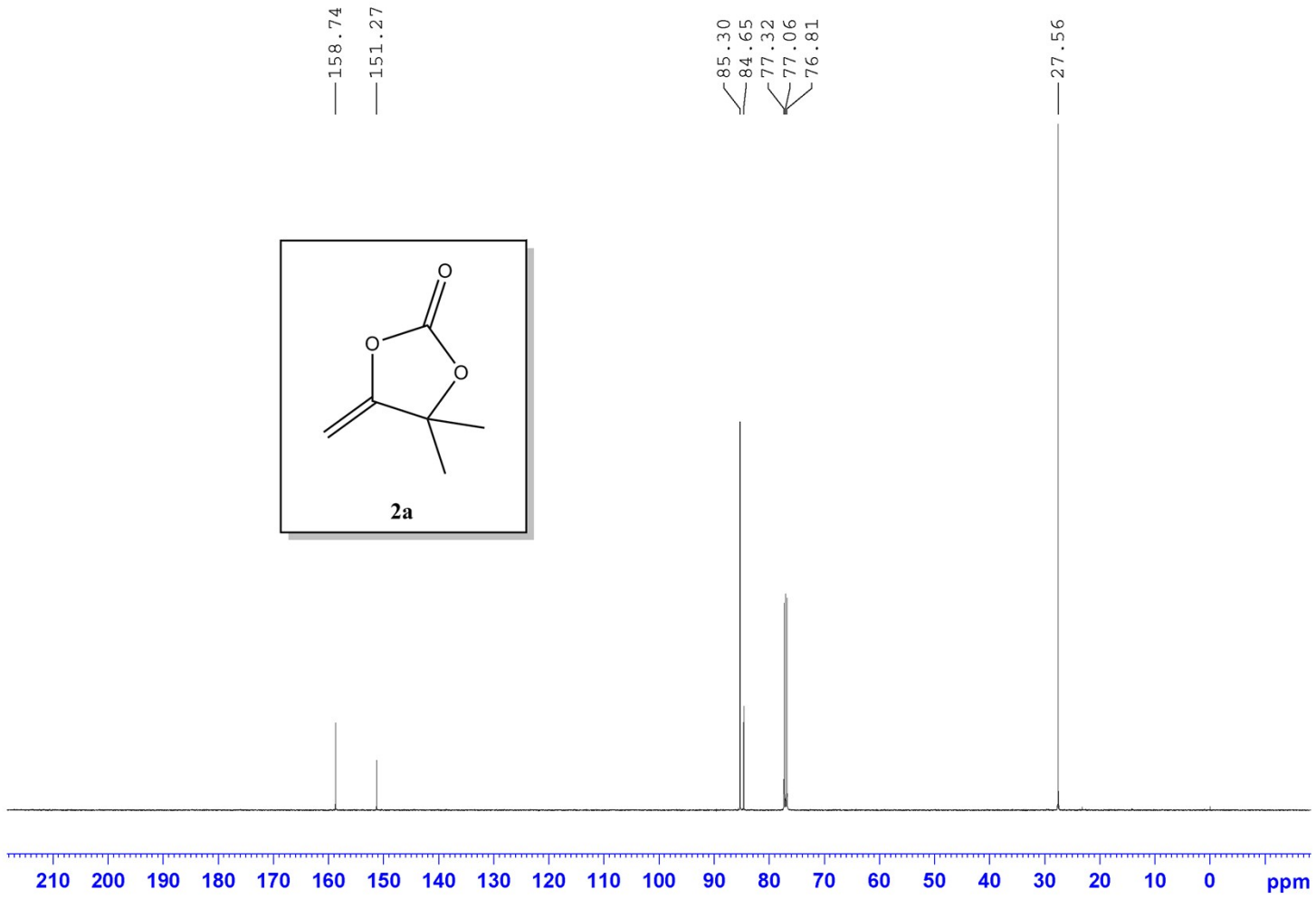
2.0
1.5
ppm
1.00
1.00
6.03

^{13}C NMR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84.65
77.32
77.06
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27.56
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O
O
2a
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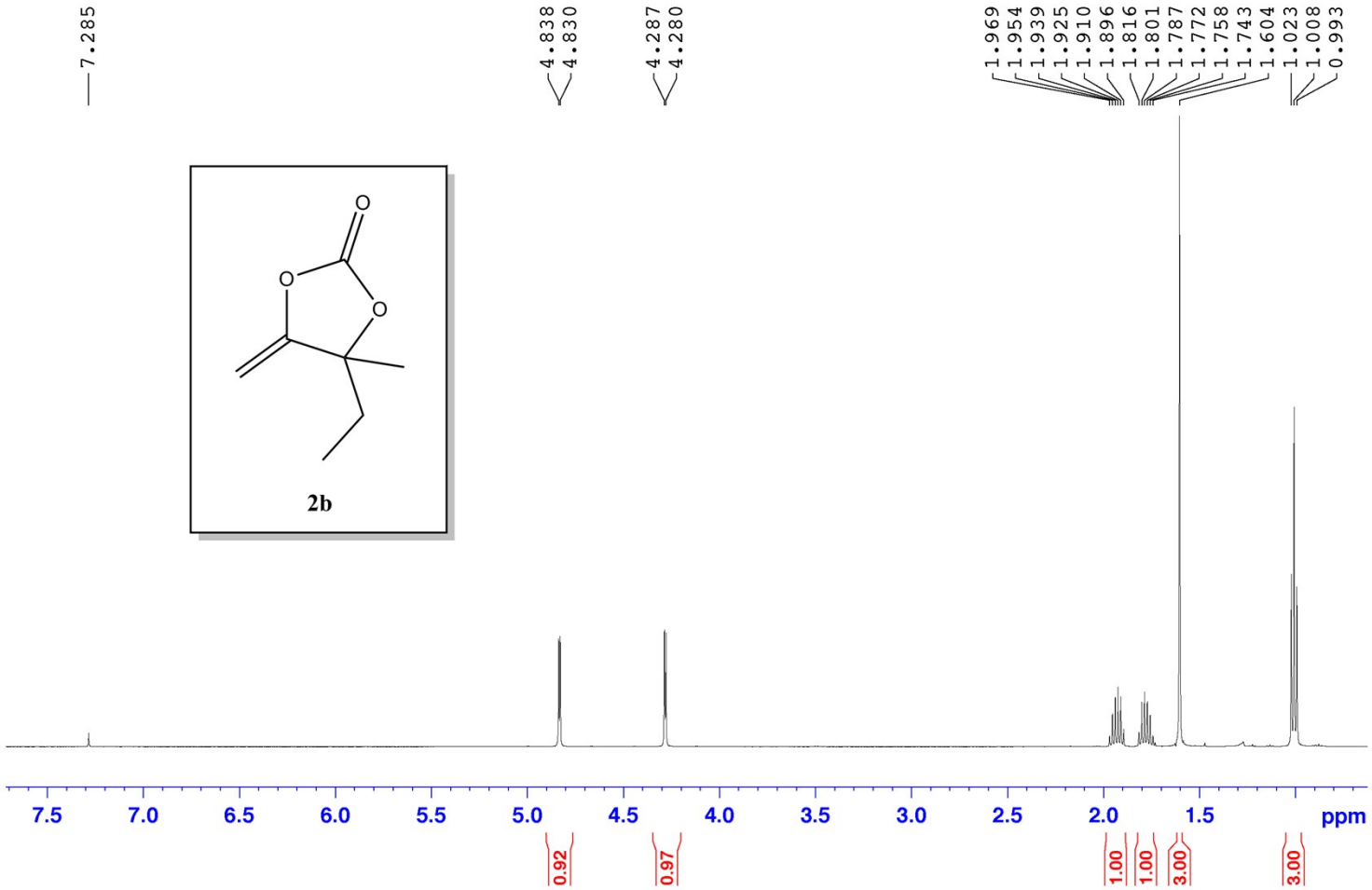
^{1}H NMR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1.787
1.772
1.758
1.743
1.604
1.023
1.008
0.993
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3.00

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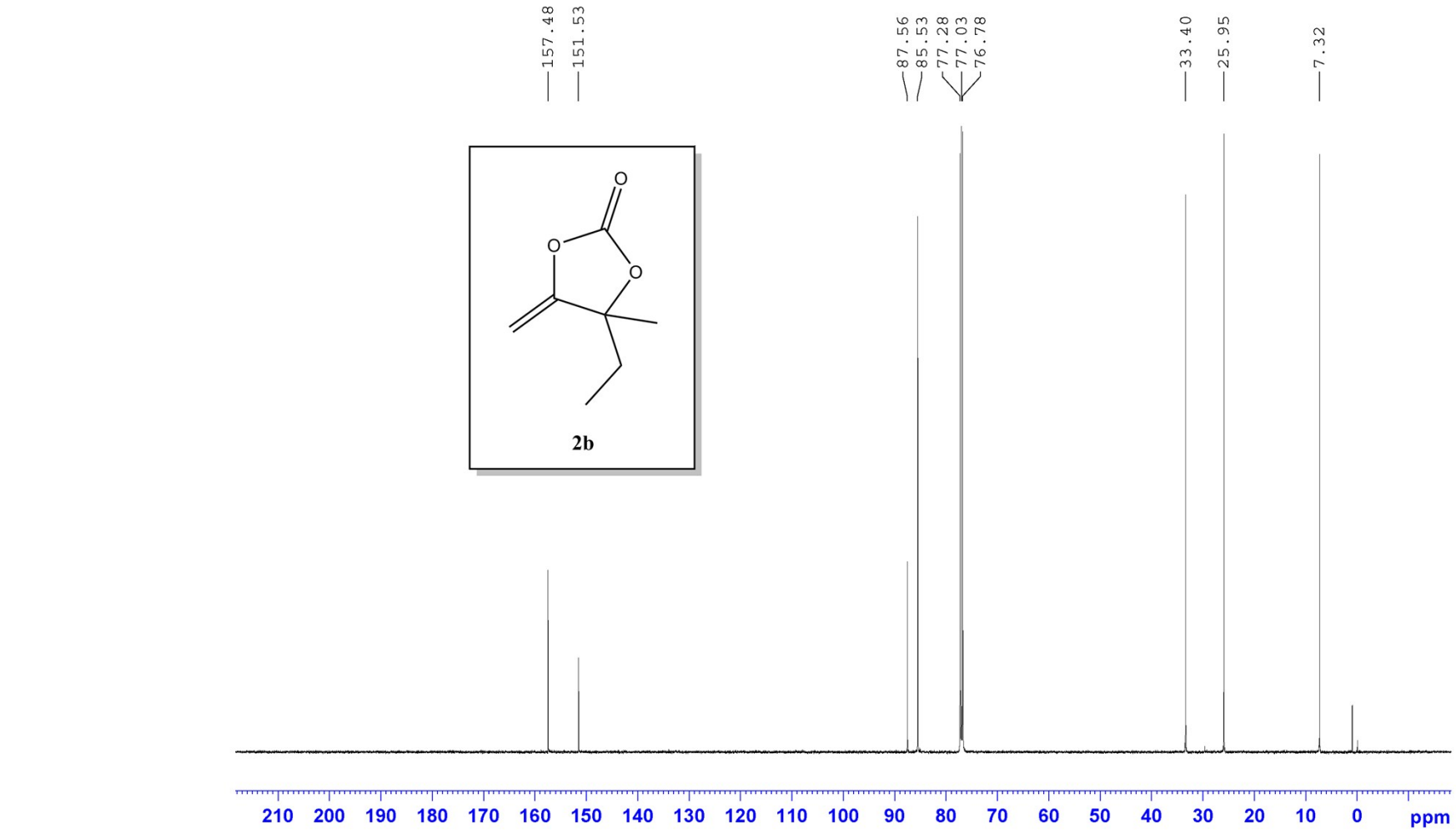
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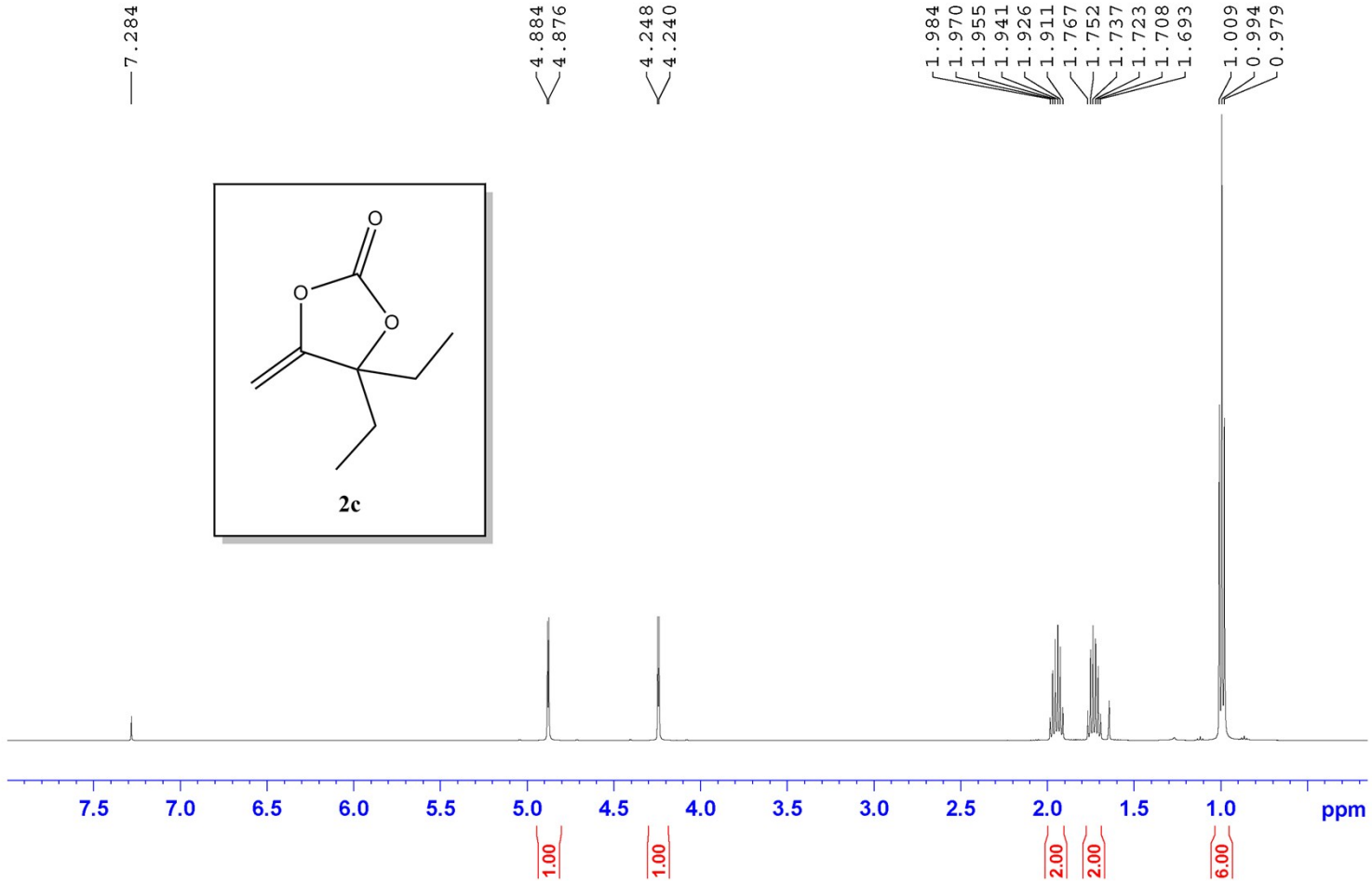
^{1}H NMR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1.737
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1.708
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0.979
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6.0
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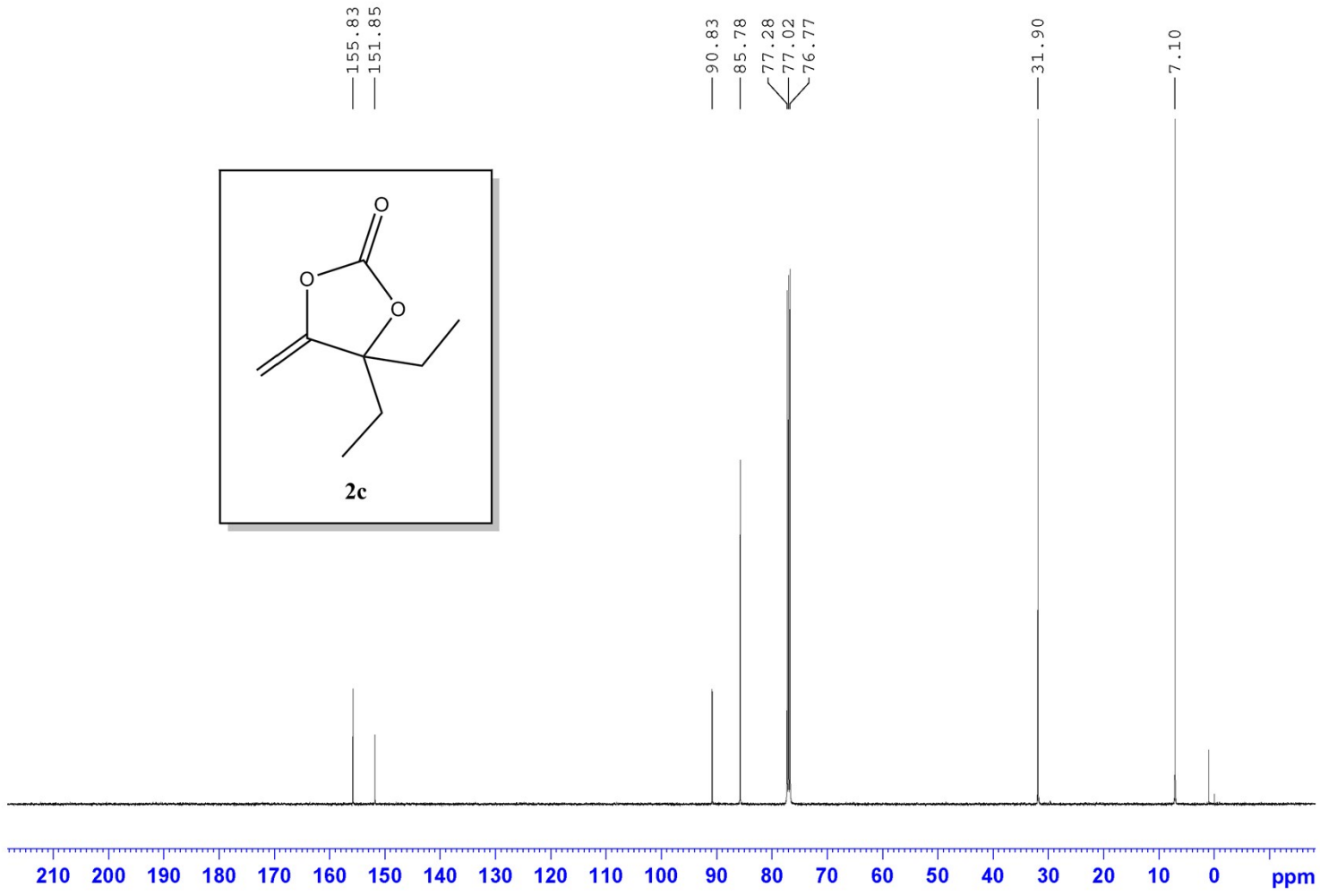
2.00
6.00

^{13}C NMR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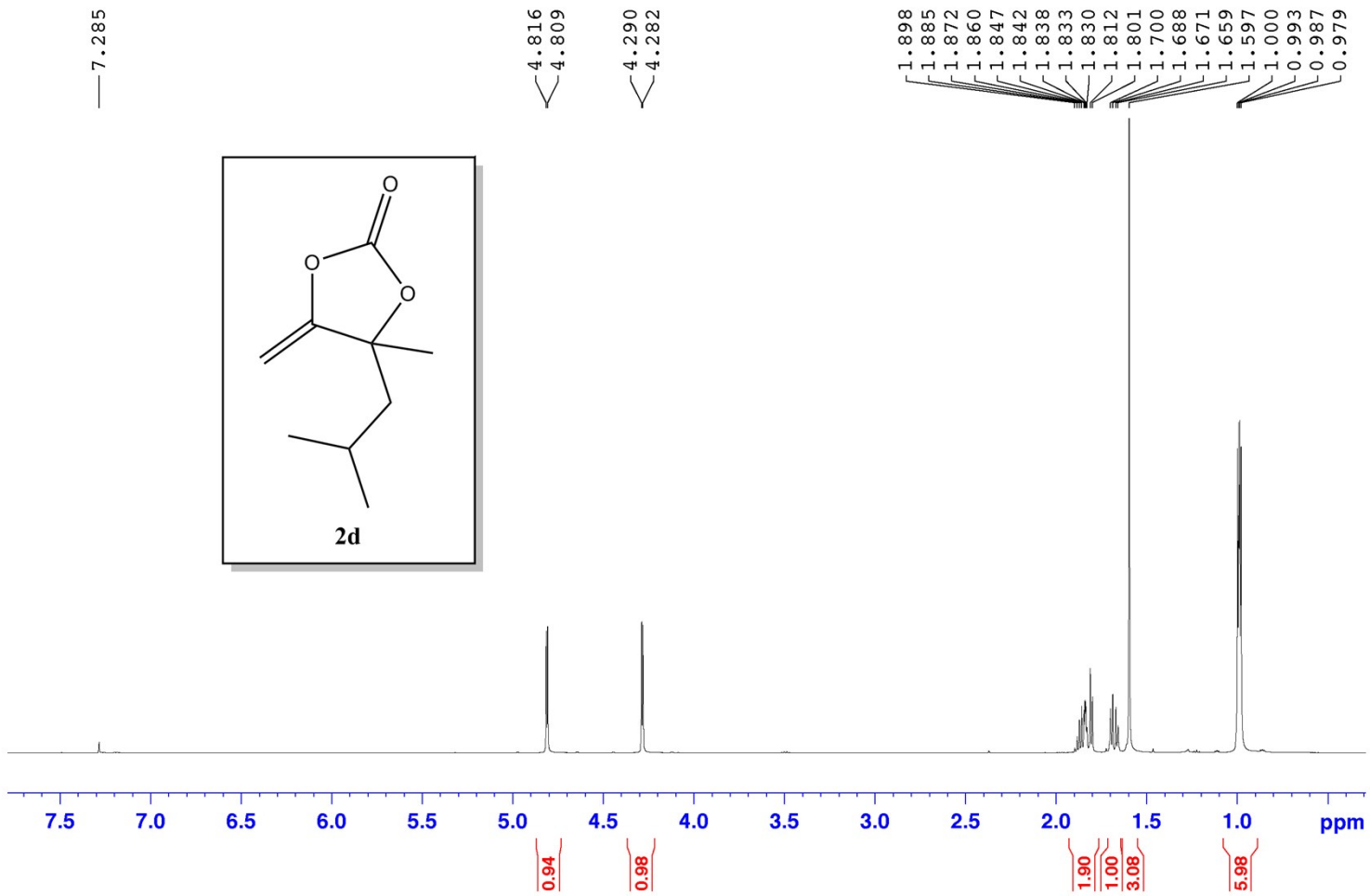
^{1}H NMR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1.830
1.812
1.801
1.700
1.688
1.671
1.659
1.597
1.000
0.993
0.987
0.979
2d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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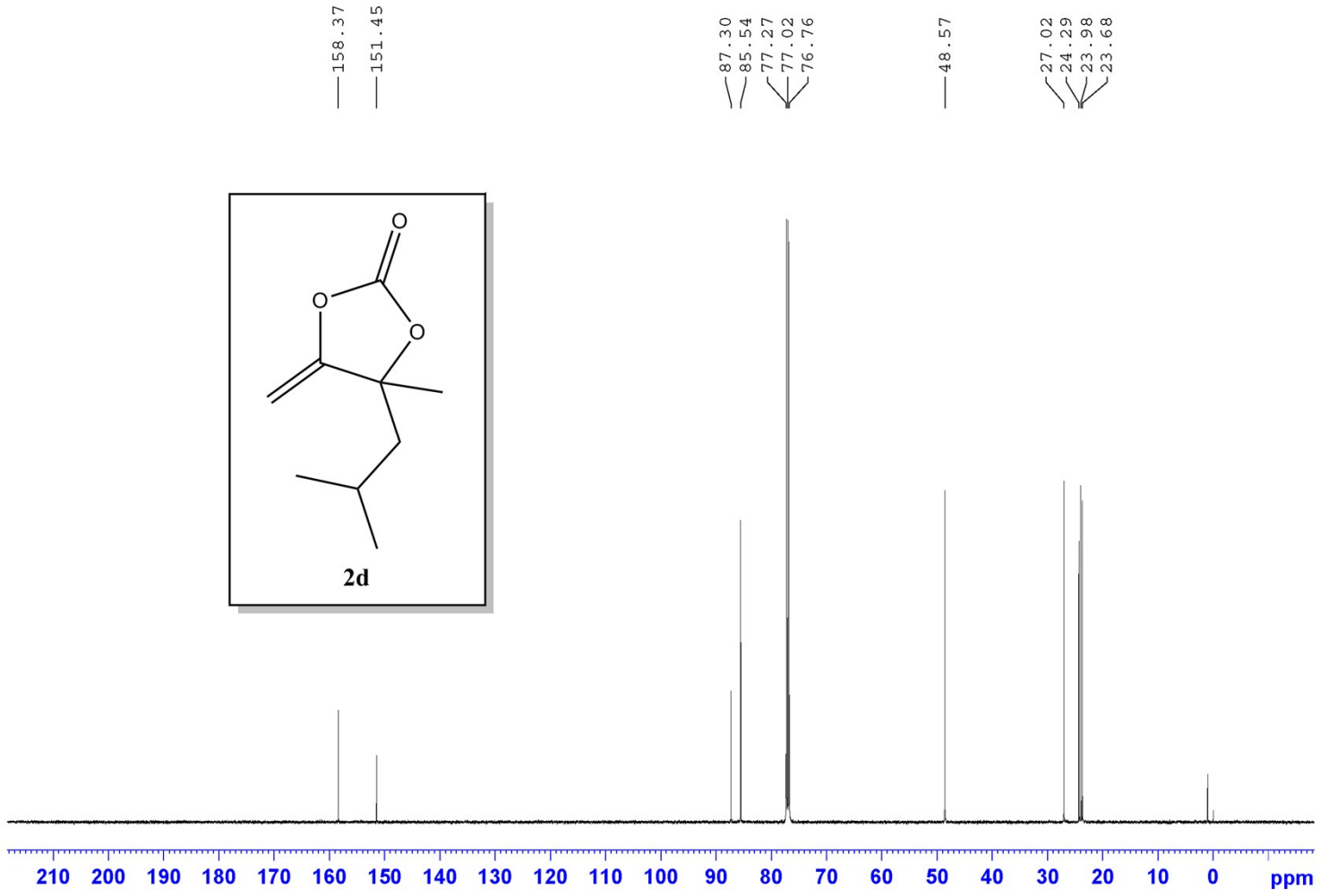
^{13}C NMR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77.27
77.02
76.76
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27.02
24.29
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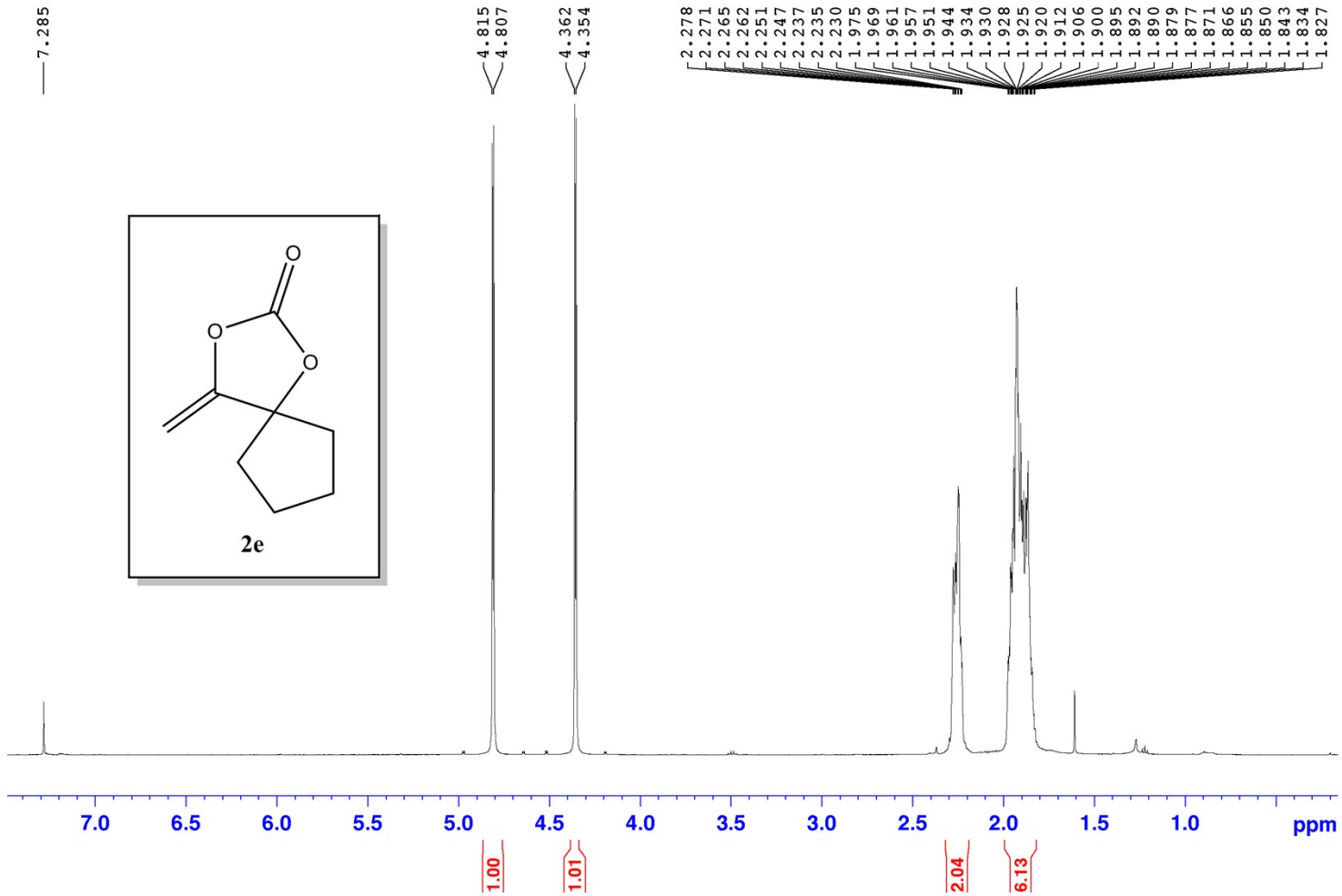
2d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

^{1}H NMR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1.879
1.877
1.871
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1.855
1.850
1.843
1.834
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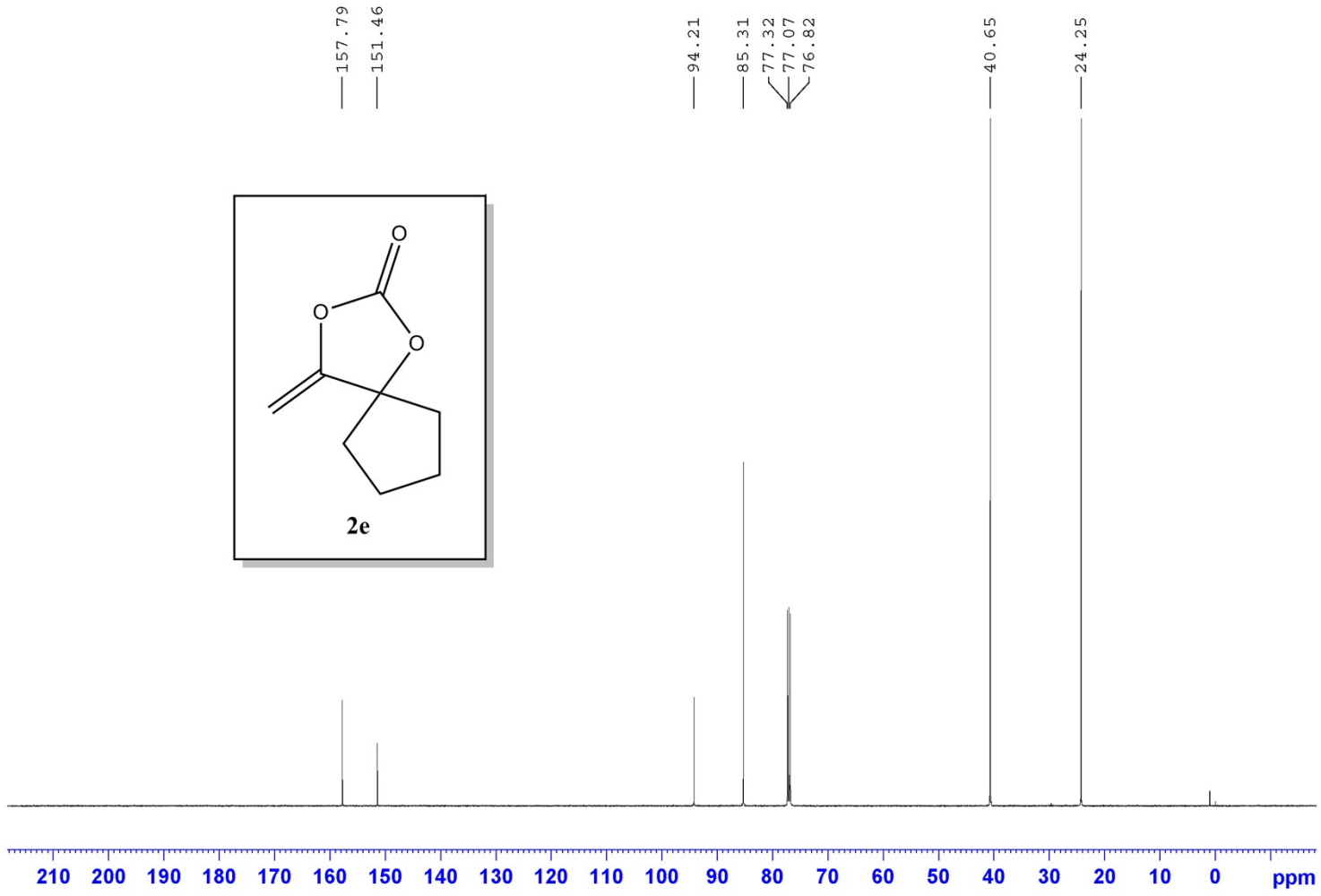
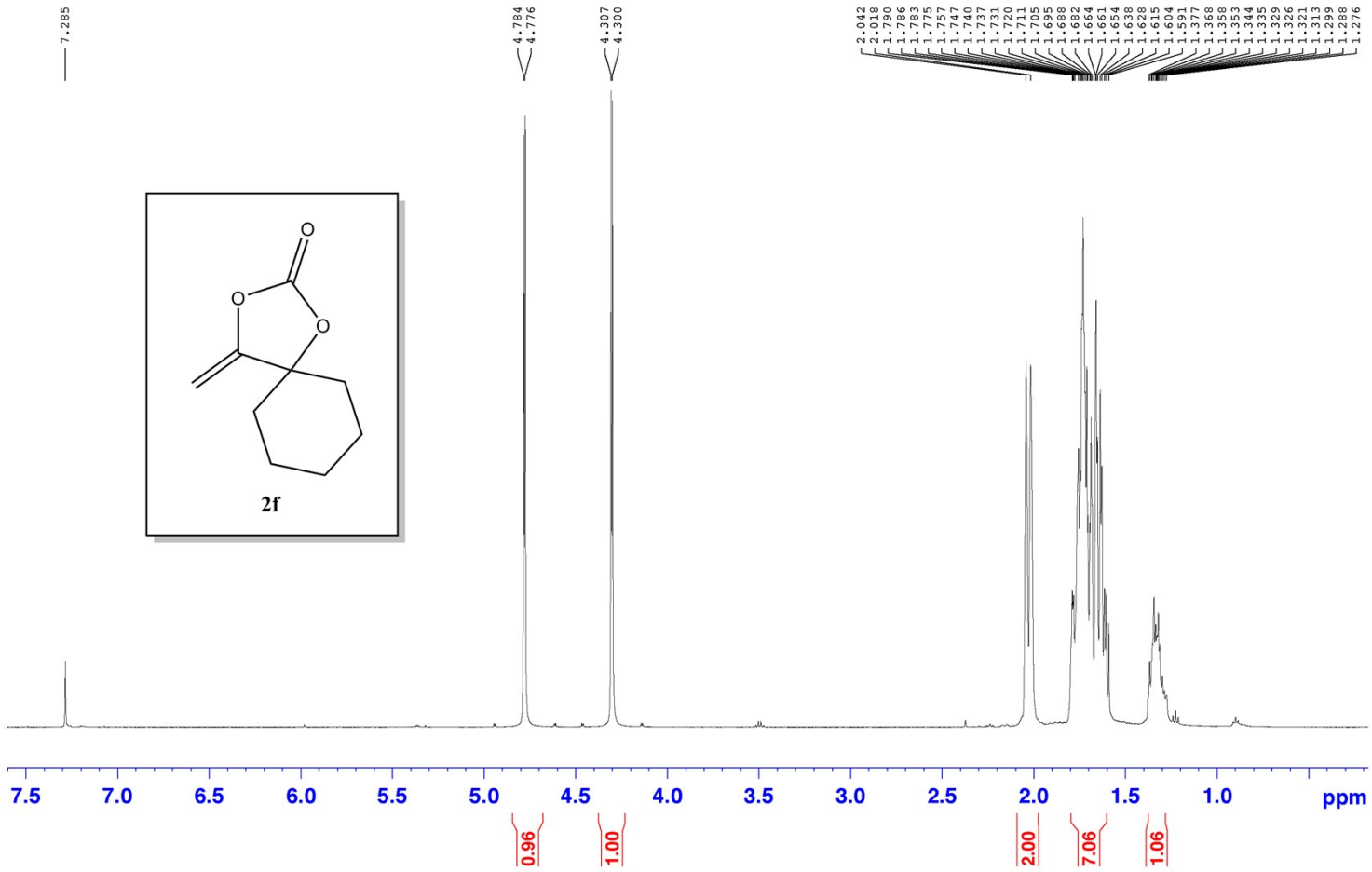
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
1.00
1.01
2.04
6.13

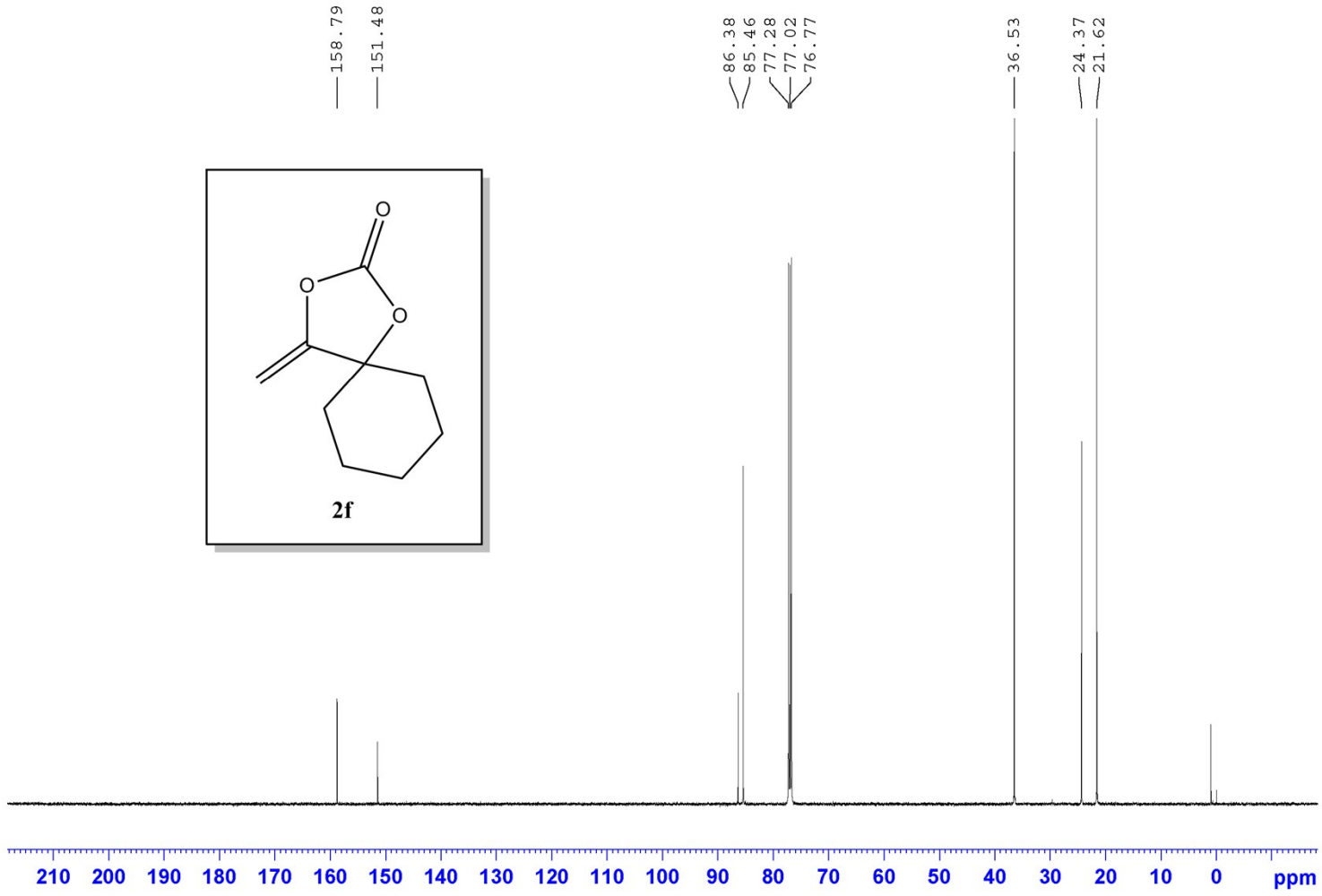
^{13}C NMR


157.79
151.46
94.21
85.31
77.32
77.07
76.82
40.65
24.25
O
O
O
2e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

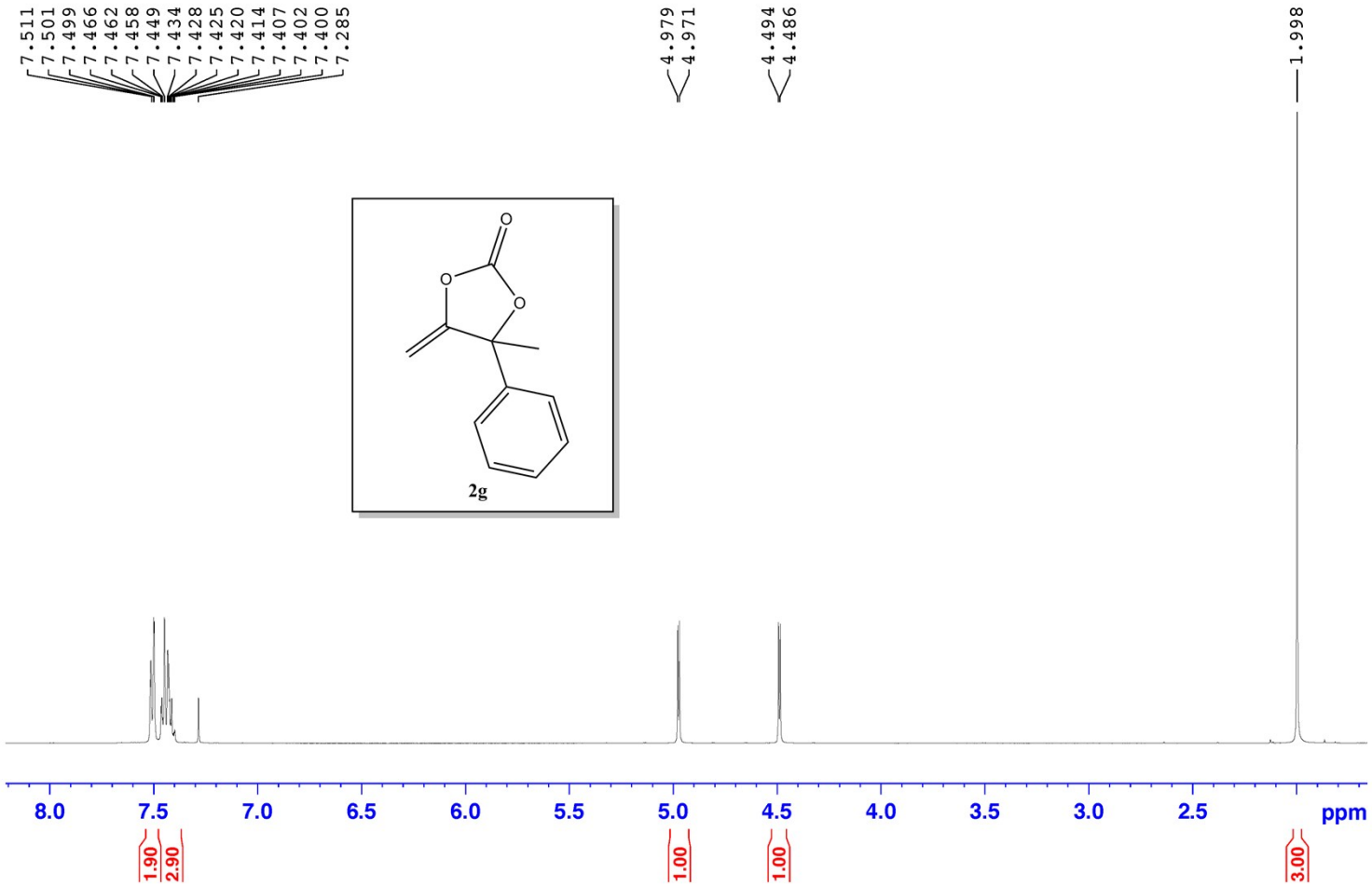
^{1}H NMR


7.285
4.784
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

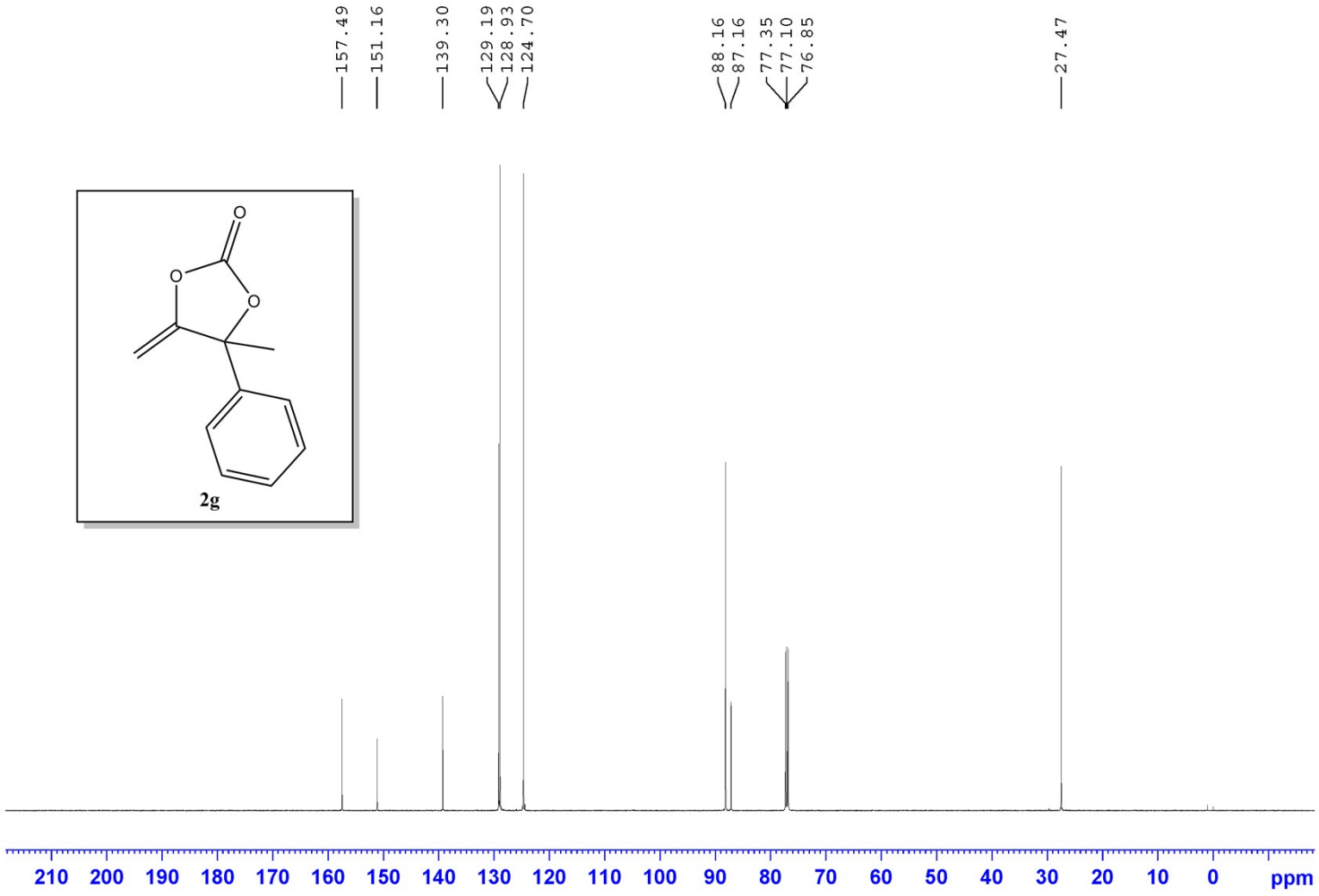
^{13}C NMR


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

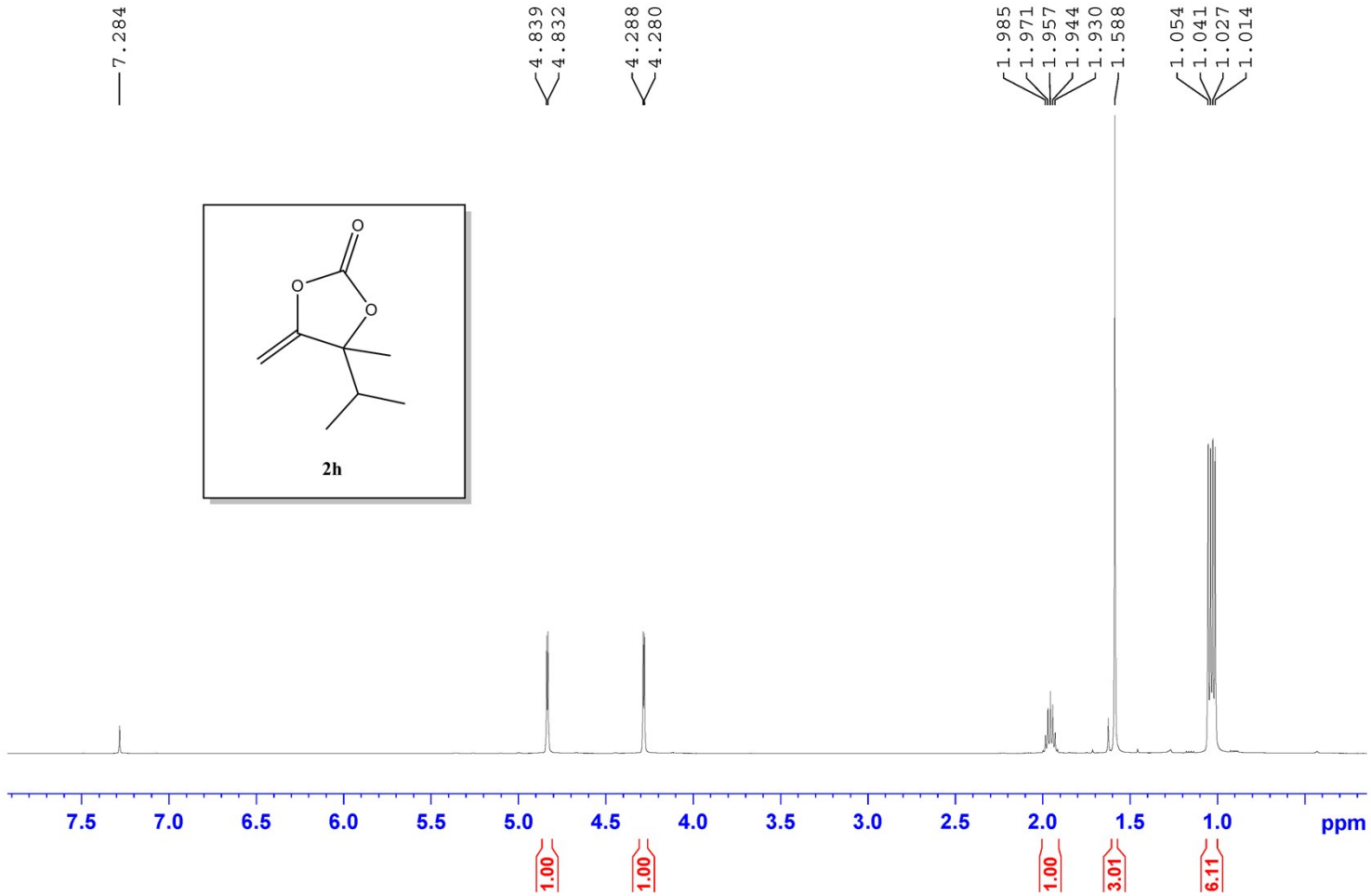
^{1}H NMR


7.511
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
2g
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

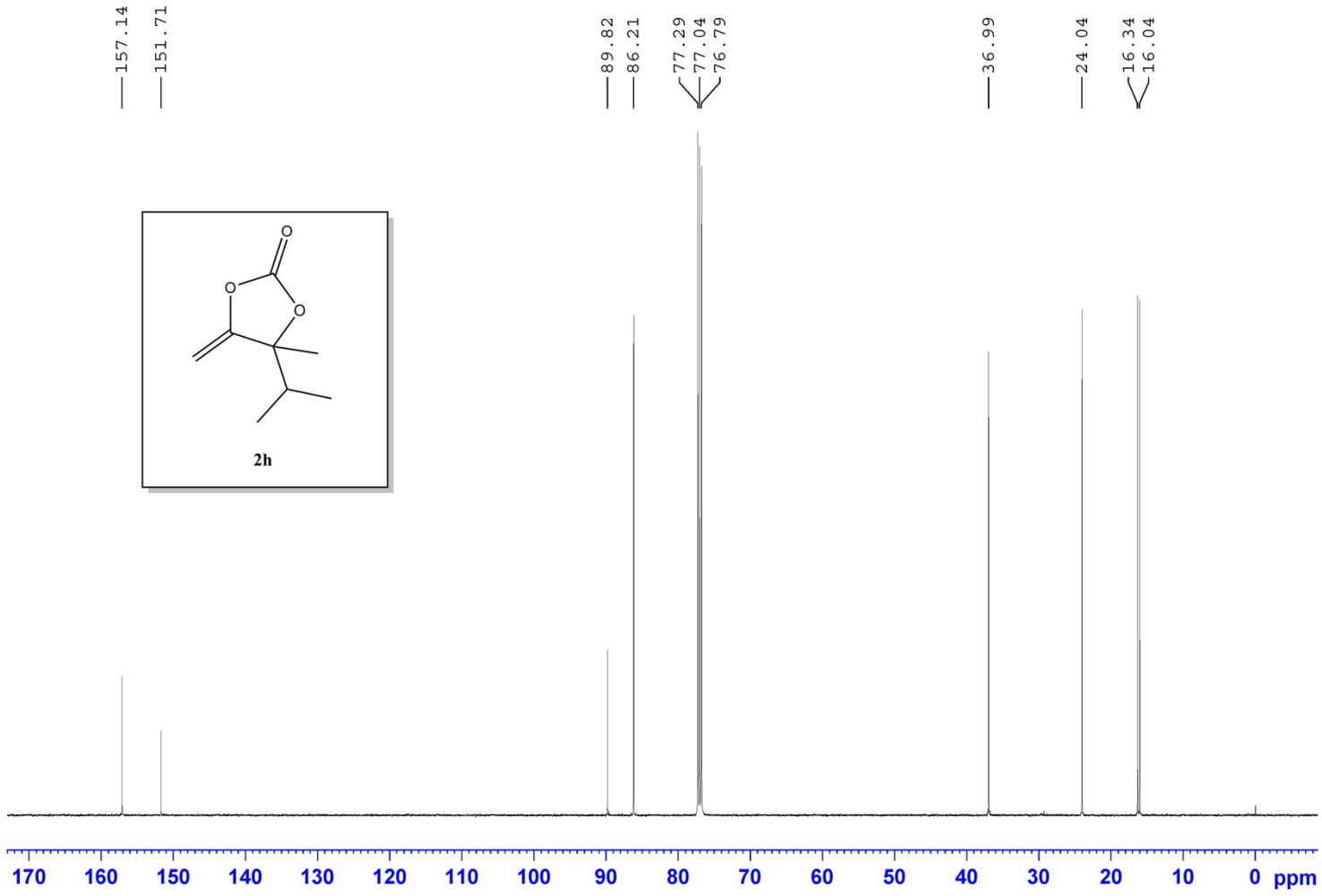
^{13}C NMR


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

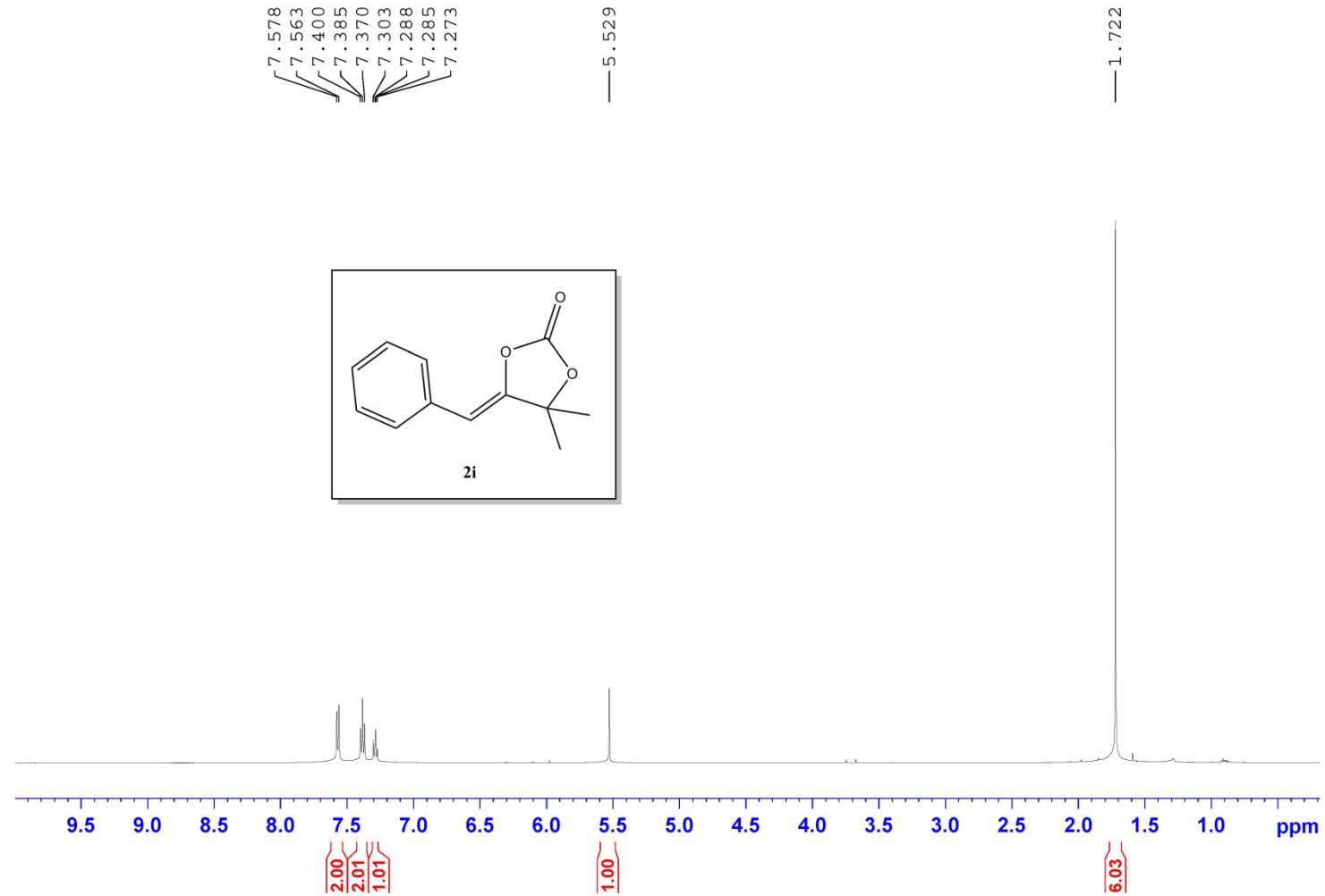
^{1}H NMR


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
2h
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

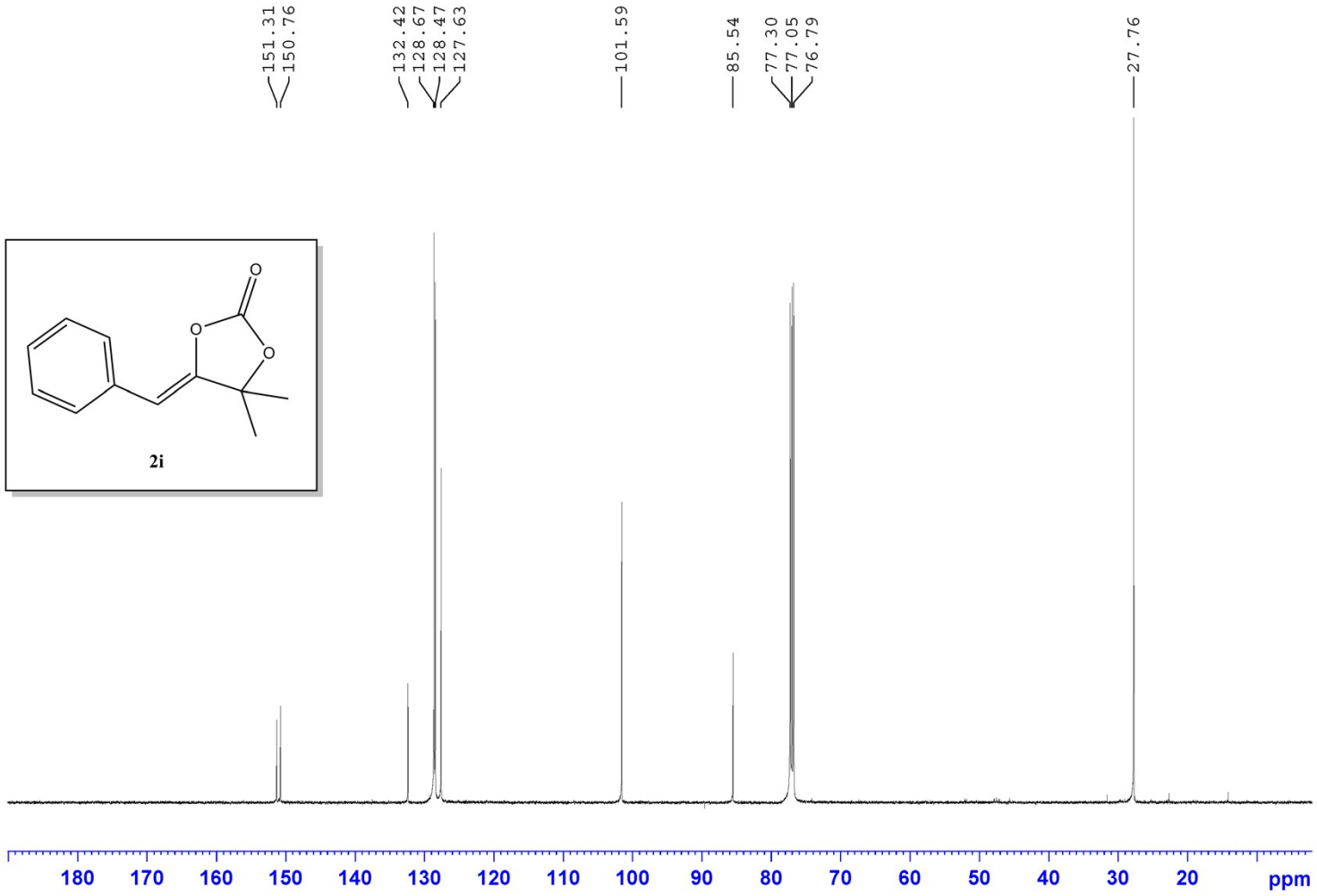
^{13}C NMR

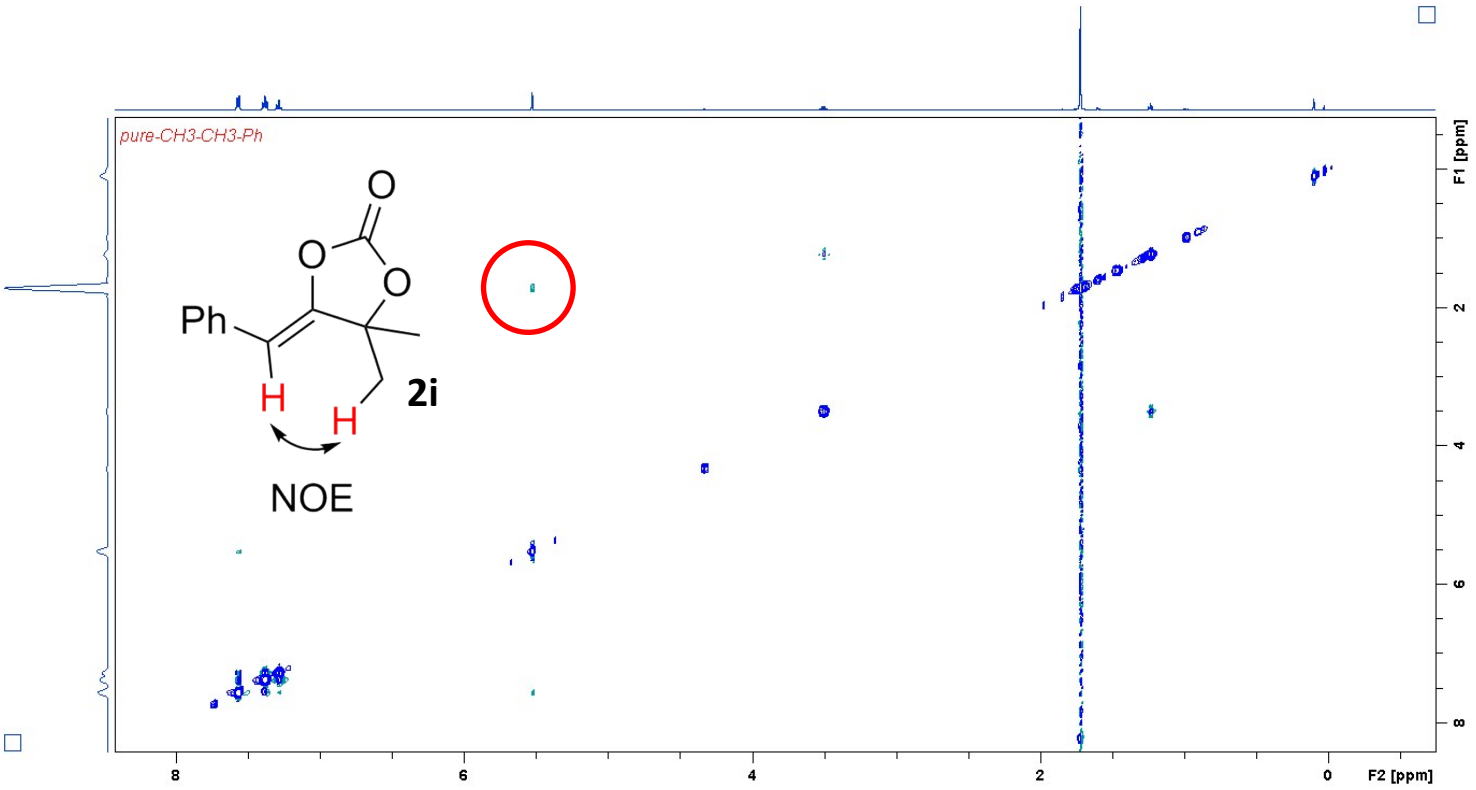

157.14
151.71
89.82
86.21
77.29
77.04
76.79
36.99
24.04
16.34
16.04
2h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

^{1}H NMR

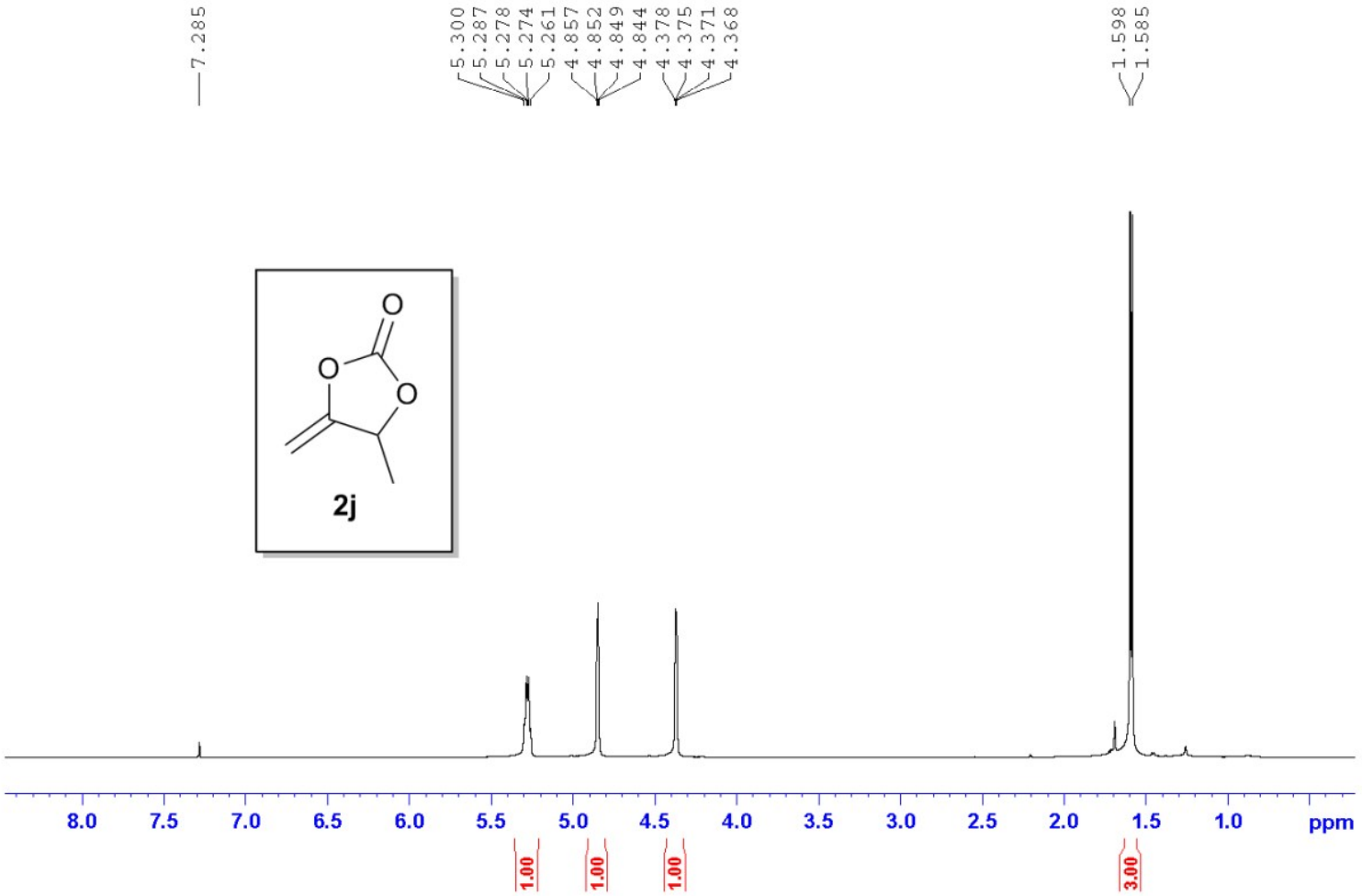

7.578
7.563
7.400
7.385
7.370
7.303
7.288
7.285
7.273
5.529
1.722
O
O
O
2i
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.00
2.01
1.01
1.00
6.03

^{13}C NMR

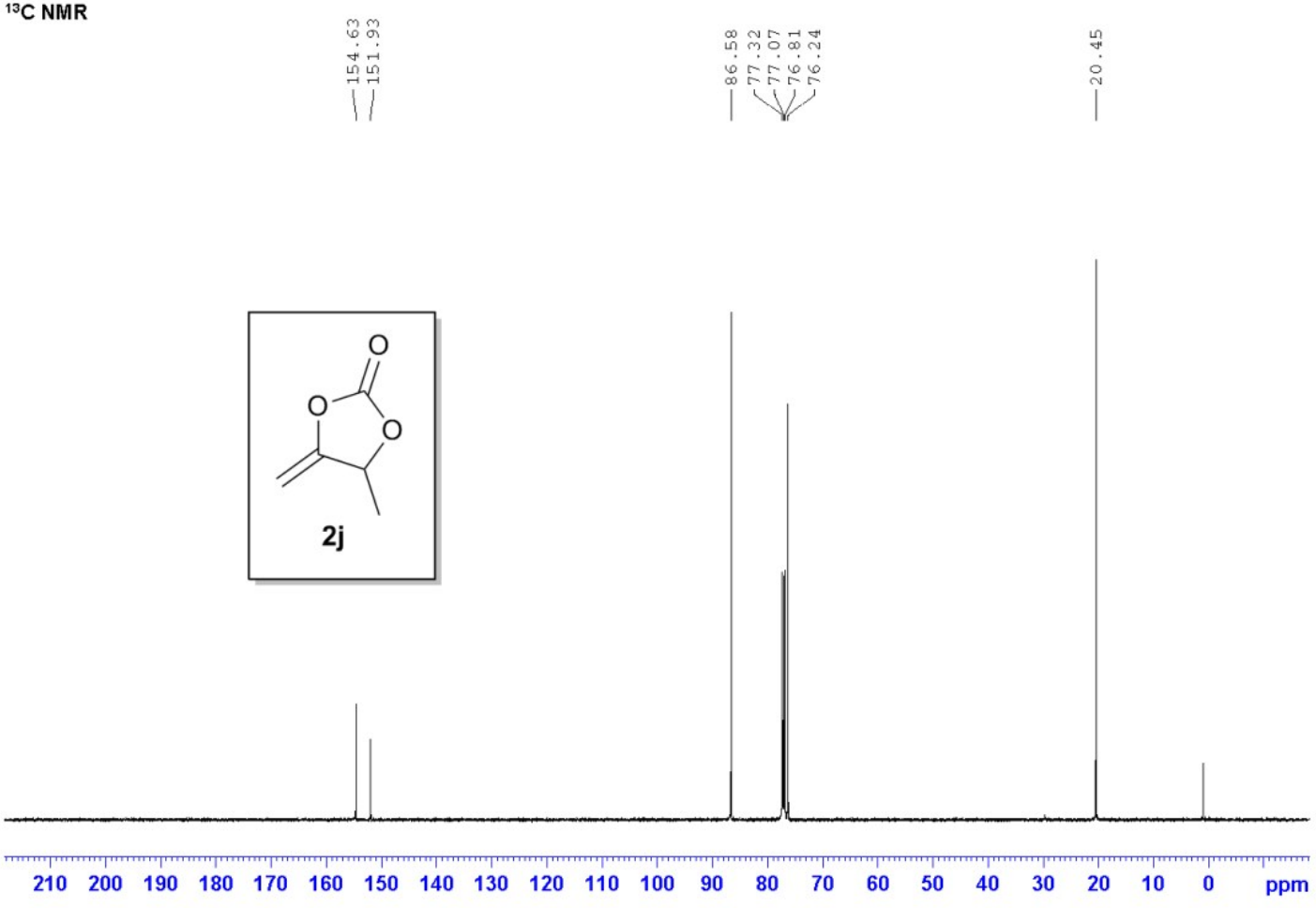

151.31
150.76
132.42
128.67
128.47
127.63
101.59
85.54
77.30
77.05
76.79
27.76
O
O
O
2i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


pure-CH3-CH3-Ph
O
O
O
Ph
H
H
2i
NOE
F1 [ppm]
F2 [ppm]
8
6
4
2
0

^{1}H NMR


7.285
5.300
5.287
5.278
5.274
5.261
4.857
4.852
4.849
4.844
4.378
4.375
4.371
4.368
1.598
1.585
O
O
O
2j
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
ppm
1.00
1.00
1.00
3.00

^{13}C NMR


154.63
151.93
86.58
77.32
77.07
76.81
76.24
20.45
O
O
O
2j
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. J. Hu, J. Ma, Q. Zhu, Q. Qian, H. Han, Q. Mei and B. Han, *Green Chem.*, 2016, **18**, 382-385.
2. Q. W. Song, W. Q. Chen, R. Ma, A. Yu, Q. Y. Li, Y. Chang and L. N. He, *ChemSusChem*, 2015, **8**, 821-827.
3. A. Buzas and F. Gagosz, *Organic Letters*, 2006, **8**, 515-518.