A heterogenous bifunctional silica-supported Ag_2O/Im^+Cl^- catalyst for efficient CO_2 conversion

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Supporting Information

General:

All the chemicals and solvents were commercially available and used without further purification. Aerosil-300 was obtained as a gift from Nippon Aerosil. Silver oxide [Ag_2O, Wako], N-methylimidazole and 3-Chloropropyltriethoxysilane (TCI) were used as precursors for the preparation of catalyst. The propargyl alcohols/amines and other alcohols/amines were obtained from TCI, WAKO, Sigma-Aldrich and Kanto chemicals. Deionized water was used in all experiments. Analytical thin layer chromatography (TLC) was performed with E. Merck pre-coated TLC plates, silica gel 60F-254, layer thickness 0.25 mm. Flash chromatography was performed on Kanto Chemical 60 N (0.04-0.05 mm) mesh silica gel.

^{1}H-NMR spectra were recorded on a Bruker AV400N (400 MHz) and ^{13}C-NMR were recorded on Bruker AVANCE III 500 (500 MHz) and Bruker AV400N (400 MHz). The high resolution TEM (HR-TEM) images of catalyst from 1st catalytic cycle and the recovered catalyst after reaction were recorded with JEOL, Model JEM2100F at an accelerating voltage of 200 kV, operating in the STEM mode.

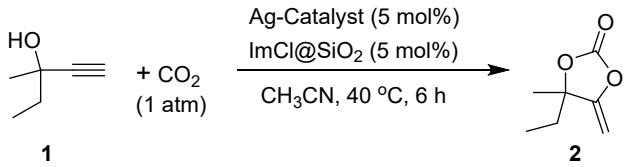
The structure and morphology of prepared catalysts were characterized using wide-angle X-ray

diffraction (WAXD, Rigaku RINT, Japan) with rotating-anode Cu Kα X-ray generator operated at 40 mA and 40 kV.

Cyclization reaction of propargyl alcohol and CO_2 (under air)

The reactions were carried out in round-bottom flasks in a water bath. To a suspension of $Im^+Cl^-@SiO_2$ (130 mg, 0.1 mmol) and CH_3CN (4mL) was added Ag_2O (11.5 mg, 0.05 mmol). To the mixture was added 3-methyl-1-pentyn-3-ol (113µl, 1.0 mmol), and the reaction mixture was stirred at 40 °C under air in open atmosphere for 24 h. After that, the mixture was diluted with ether (30 mL) and centrifuged to remove the solid catalyst. The supernatant was collected, and the remaining solid was washed three times with ether. The combined supernatants were evaporated to give crude product for NMR yields.

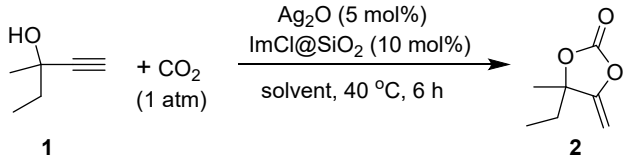
Table S1: Screening of Ag-catalysts and temperature



entry	Ag–catalyst	Yield of 2 (%)
1	Ag_2O	33
2	Ag_2CO_3	32
3	AgOAc	8
4	$AgOCOCF_3$	0
5	AgOTf	0
6	AgCl	0 (0)[a]
7	AgCl	23[b]
8	Ag_3PO_4	26
9[c]	Ag_2O	27
10[d]	Ag_2O	14

Reaction Condition: [a]reaction was conducted with AgCl and SiO_2, [b]KO*t*Bu (5 mol%), 24 h [c]80 °C, [d]$Im^+OAc^-@SiO_2$, 24 h

Table S2: Screening of solvent



1 2

entry	solvent	Yield of 2 (%)
1	CH_3CN	56
2	DCM	0
3	THF	0
4	H_2O	0
5	Toluene	0
6	DMF	13
7	DMSO	0

Table S3: Leaching Test

In a round-bottom flask, Ag_2O (0.1 mmol), $Im^+Cl^-@SiO_2$ (0.2 mmol) and CH_3CN (8 mL) were added according to the typical procedure. CO_2 gas was supplied from a CO_2 balloon after three freeze-pump-thaw cycles. To the mixture was added 3-methyl-1-pentyn-3-ol (2.0 mmol), and the reaction mixture was stirred at 40 °C. The reaction was stopped at 8.5 h and the catalyst was removed by centrifugation and filtration. The filtrate was divided into two equal portions. One portion was allowed to react for the next 24 h, and the other portion was evaporated and analyzed by NMR immediately.

Entry 1 shows the yield of product of the reaction stopped at 8.5 h.

Entry 2 shows the yield of reaction after 24 h reaction where catalyst was removed at 8.5 h.

1	49
2	50

Table S4: Reusability test

cycles	Amount of catalyst (mg)		Catalyst recovery %	TM yield%
	used	recovered		
0	945	847	90	92
1	810	738	91	92
2	675	650	96	91
3	539	425	79	96
4	405	359	89	84
5	270	252	93	86

Characterization of Catalyst

Fig. S1: XRD spectrum

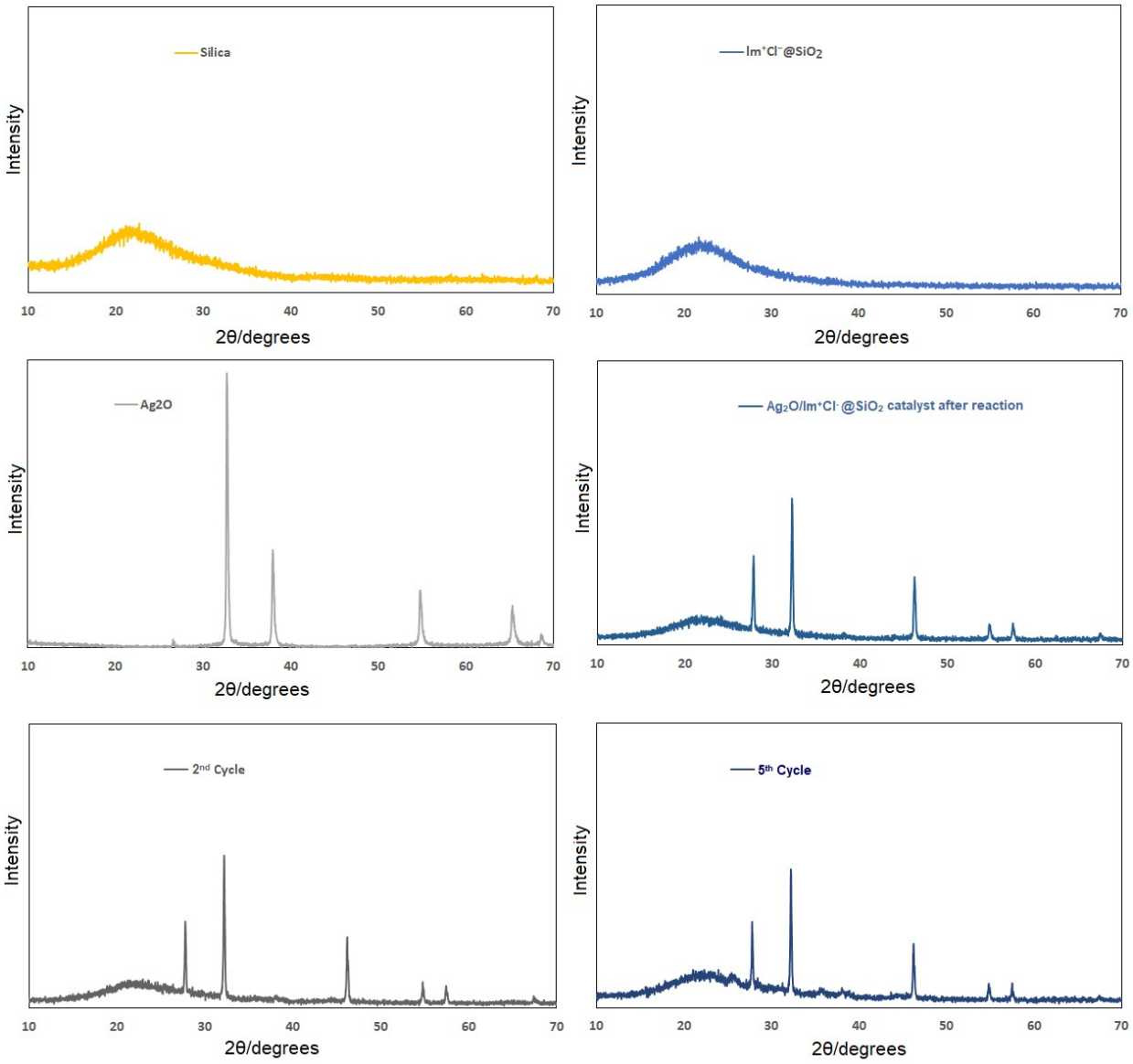
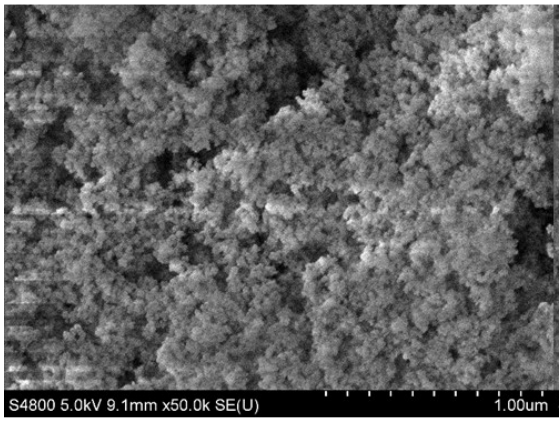
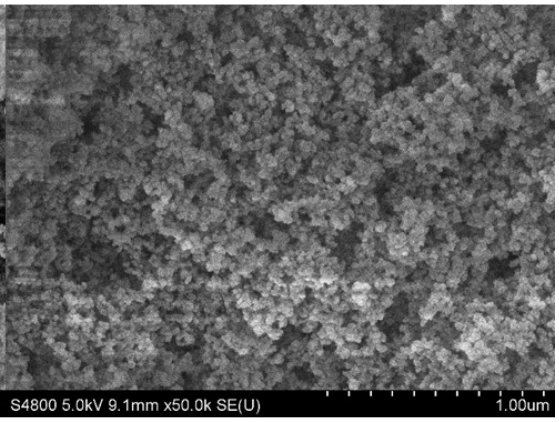


Fig. S2: SEM analysis

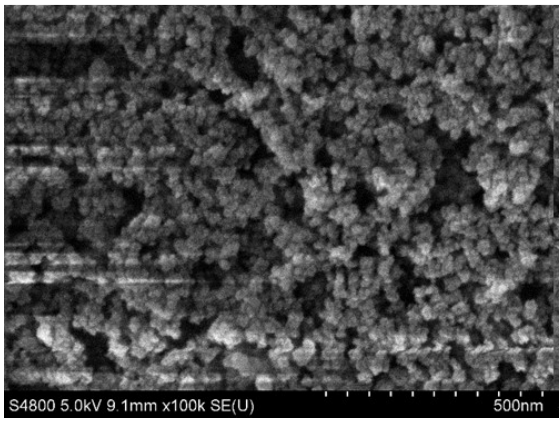
Silica



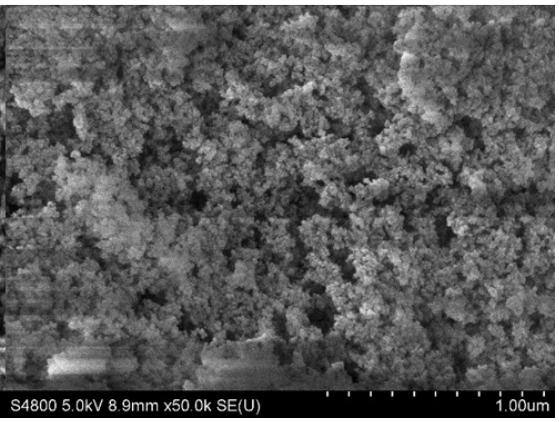
$Im^{+}Cl^{-}@SiO_2$



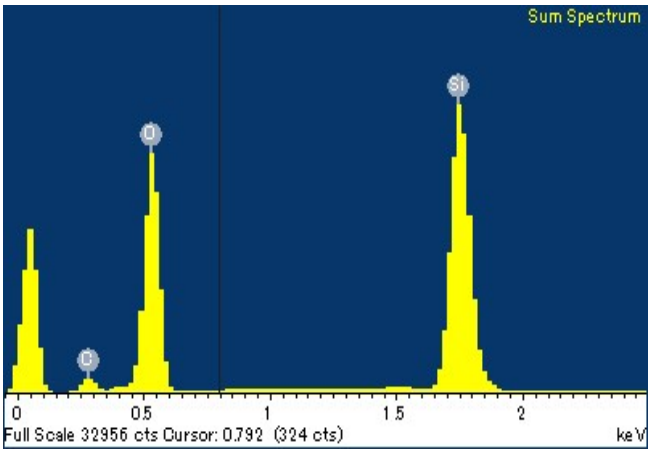
1st Cycle



5th Cycle

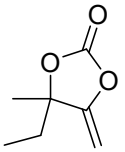


Element	Weight%	Atomic%
C K	8.04	12.92
O K	50.45	60.82
Si K	35.95	24.69
Cl K	1.58	0.86
Ag L	3.98	0.71
Totals	100.00	



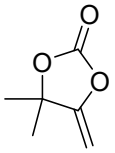
The ^{1}H NMR spectral data were in accordance with those reported in the literature.[1-3]

4-ethyl-4-methyl-5-methylene-1,3-dioxolane-2-one



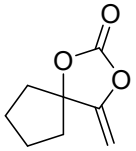
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.81 (d, *J* = 4.0 Hz, 1H), 4.25 (d, *J* = 4.0 Hz, 1H), 1.94-1.88 (m, 1H), 1.78-1.73 (m, 1H), 1.58 (s, 3H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 151.5, 87.6, 85.5, 33.4, 26.0, 7.4 ppm.

4,4-dimethyl-5-methylene-1,3-dioxolane-2-one



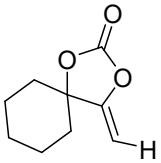
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.77 (d, J = 4.0 Hz, 1H), 4.31 (d, J = 3.6 Hz, 1H), 1.61 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 151.2, 85.3, 85.2, 84.7, 27.5 ppm.

4-methylene-1,3-dioxaspiro[4.4]nonan-2-one



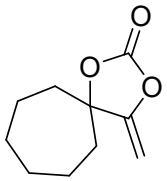
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.79 (d, J = 4.0 Hz, 1H), 4.33 (d, J = 3.6 Hz, 1H), 2.25-2.23 (m, 2H), 1.93-1.84 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 151.6, 89.9, 85.1, 40.2, 28.9, 22.1 ppm.

4-methylene-1,3-dioxa-spiro[4.5]decan-2-one



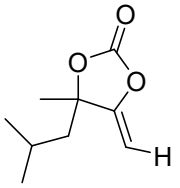
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69 (d, J = 3.2 Hz, 1H), 4.26 (d, J = 3.2 Hz, 1H), 1.96-1.92 (m, 2H), 1.79-1.55 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 151.4, 86.4, 85.5, 36.4, 24.3, 21.6 ppm.

4-methylene-1,3-dioxaspiro[4.6]undecan-2-one



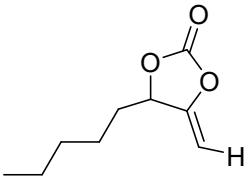
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.75 (d, J = 4.0 Hz, 1H), 4.31 (d, J = 4.0 Hz, 1H), 2.14-2.11 (m, 2H), 1.92-1.86 (m, 2H), 1.73-1.69 (m, 4H), 1.69-1.56 (m, 4H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.1, 151.6, 89.9, 85.1, 40.2, 28.9, 22.1 ppm.

4-Isobutyl-4-methyl-5-methylene-1,3-dioxolan-2-one



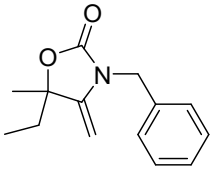
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.80 (d, *J* = 4.0 Hz, 1H), 4.26 (d, *J* = 4.0 Hz, 1H), 1.84─1.77 (m, 2H),1.68─1.65 (m, 1H), 1.57 (s, 3H), 0.98─0.96 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.4, 151.5, 87.3, 85.6, 48.6, 27.1, 24.3, 24.0, 23.7 ppm.

4-pentyl-5-methylene-1,3-dioxolan-2-one



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17–5.14 (m, 1H), 4.85 (dd, J = 2.4, 1.6 Hz, 1H), 4.34 (dd,J = 2.0 Hz, 2H), 1.86–1.76 (m, 2H), 1.55–1.40 (m, 2H), 1.34–1.32 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.5, 152.1, 86.7, 79.9, 34.7, 31.2, 23.6, 22.4, 13.9 ppm.

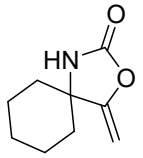
3-Benzyl-5-ethyl 5-methyl-4-methyleneoxazolidin-2-one (isomeric mixture)



^{1}H NMR (400 MHz,$CDCl_3$) δ 7.35-7.27 (m, 5H), 4.70 (d, 1H, J = 15.6 Hz), 4.60 (d, 1H, J = 16.0 Hz),

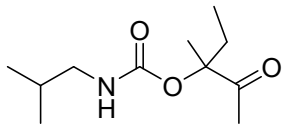
4.05 (d, 1H, J = 2.4 Hz), 3.90 (d, 1H, J = 2.8 Hz), 1.87-1.82 (m, 1H), 1.69-1.63 (m, 1H), 1.48 (s, 3H), 0.87 (t, J= 7.2, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 138.5, 138.4, 128.6, 128.5, 127.5, 127.3, 127.2, 127.0, 91.1, 91.0, 87.7, 43.6, 43.5, 29.9, 26.8, 21.5, 21.2, 20.4, 16.7, 8.4, 8.3 ppm.

4-methylene-3-oxa-1-azaspiro[4.5]decan-2-one



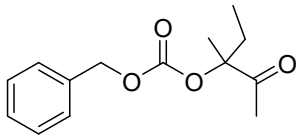
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1 H), 4.65 (d, J1 = 3.2 Hz, 1H), 4.22 (d, J = 3.2 Hz, 1H), 1.86–1.73 (m, 5 H), 1.60–1.40 (m, 4 H), 1.24–1.31 (m, 1 H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.10, 156.32, 84.70, 61.57, 38.36, 24.76, 22.22 ppm.

3-methyl-2-oxopentan-3-yl isobutylcarbamate

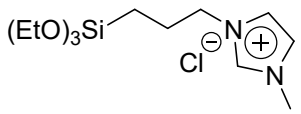


^{1}H NMR (400 MHz, $CDCl_3$): δ 3.10–3.04 (m, 1H), 2.97–2.91 (m, 1H), 1.97–1.90 (m, 1H), 1.70–1.63 (m, 1H), 1.58–1.51 (m, 1H), 1.37 (s, 3H), 1.35 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H), 0.92-0.90 (m, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.4, 91.1, 87.1, 47.7, 29.9, 28.2, 20.4, 20.2, 20.1, 16.7, 8.3 ppm.

benzyl (3-methyl-2-oxopentan-3-yl) carbonate



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.34 (m, 5H), 5.15 (d, J = 1.6 Hz, 2H), 2.11 (s, 3H), 1.95–1.90 (m, 1H), 1.80–1.74 (m, 1H), 1.52 (s, 3H), 0.89 (t, J = 7.6 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.7, 153.8, 135.0, 128.6, 128.4, 88.5, 69.8, 29.5, 24.2, 19.5, 7.5 ppm.



^{1}H NMR (400 MHz, $CDCl_3$): δ 11.02 (s, 1H), 7.23 (s, 1H), 7.21 (s, 1H), 4.34 (t, J=7.6 Hz 2H), 4.12 (s, 3H), 3.82 (q, J=7.2 Hz Hz 6H), 2.03-1.97 (m, J= 8Hz 2H), 1.22 (t, J=7.2 Hz, 12), 0.61 (t, J= 8Hz,

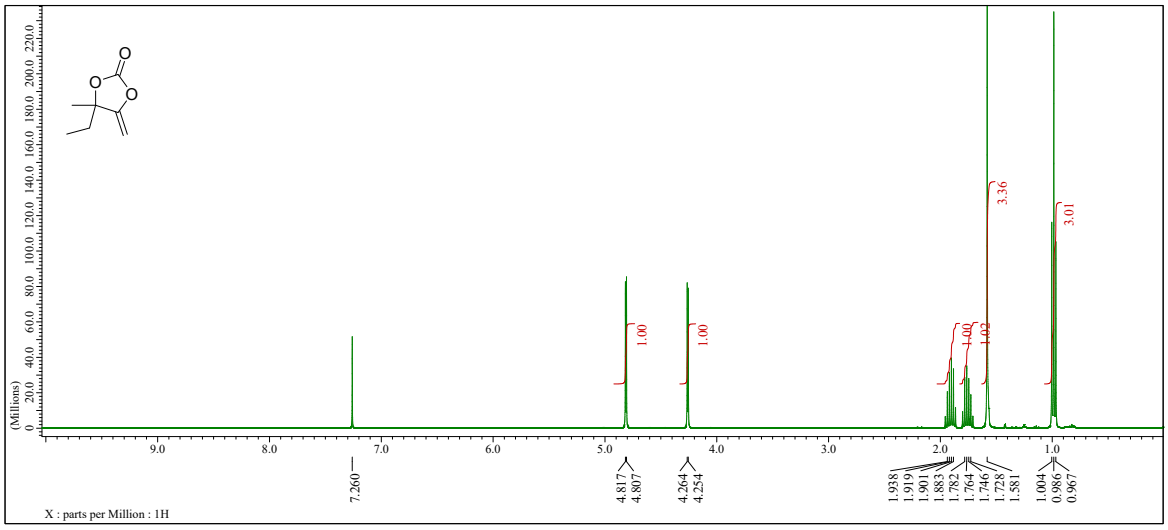
2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.0, 122.6, 121.5, 58.7, 51.9, 36.7, 24.4, 18.3, 7.2 ppm.

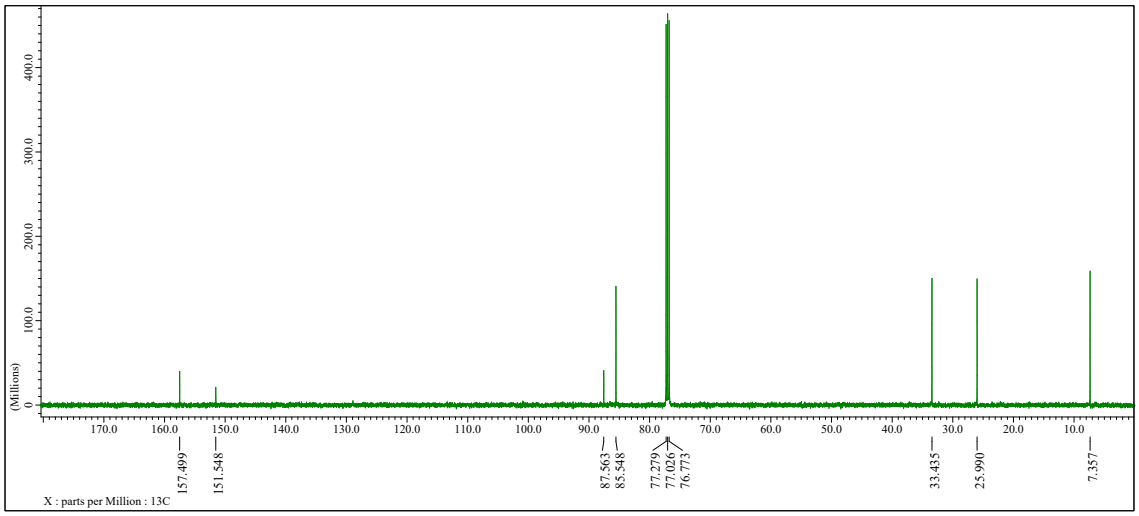
References

1) Cervantes-Reyes, A.; Farshadfar, K.; Rudolph, M; Rominger, F.; Schaub, T.; Ariafard, A.; Hashmi, S. Copper-Catalyzed Synthesis of α-Alkylidene Cyclic Carbonates from Propargylic Alcohols and CO_2. *Green Chem.*, **2021**, *23*, 889–897.

2) Yuan, G.-Q.; Zhu, G.-J.; Chang, X.-Y.; Qi, C.-R.; Jiang, H.-F. Electrochemically catalyzed synthesis of cyclic carbonates from CO_2 and propargyl alcohols. *Tetrahedron*, **2010***, 66*, 9981–9985

3) Chakraborty, D.; Shekhar, P; Singh, H. D.; Kushwaha, R.; Vinod, C. P.; Vaidhyanathan, R. Ag Nanoparticles Supported on a Resorcinol-Phenylenediamine- Based Covalent Organic Framework for Chemical Fixation of CO_2. *Chem. Asian J.* doi:10.1002/asia.201901157

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110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
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87.563
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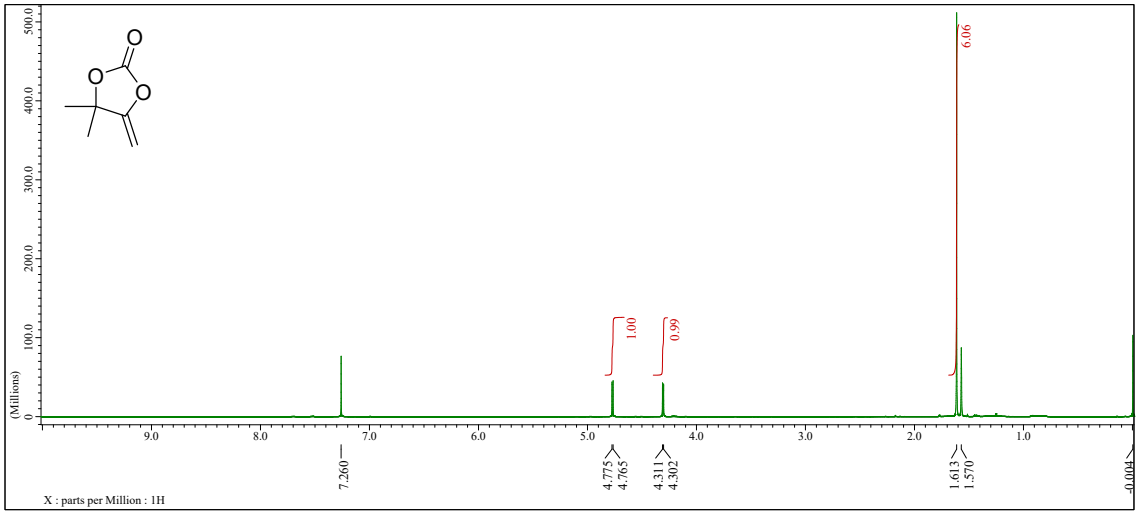
7.357
X : parts per Million : 13C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3.0
2.0
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6.06
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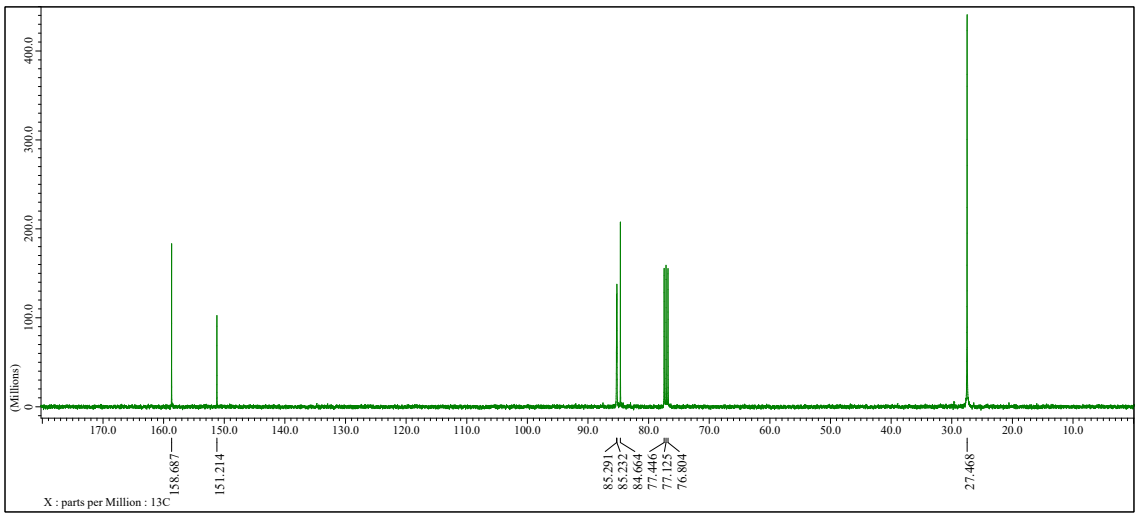
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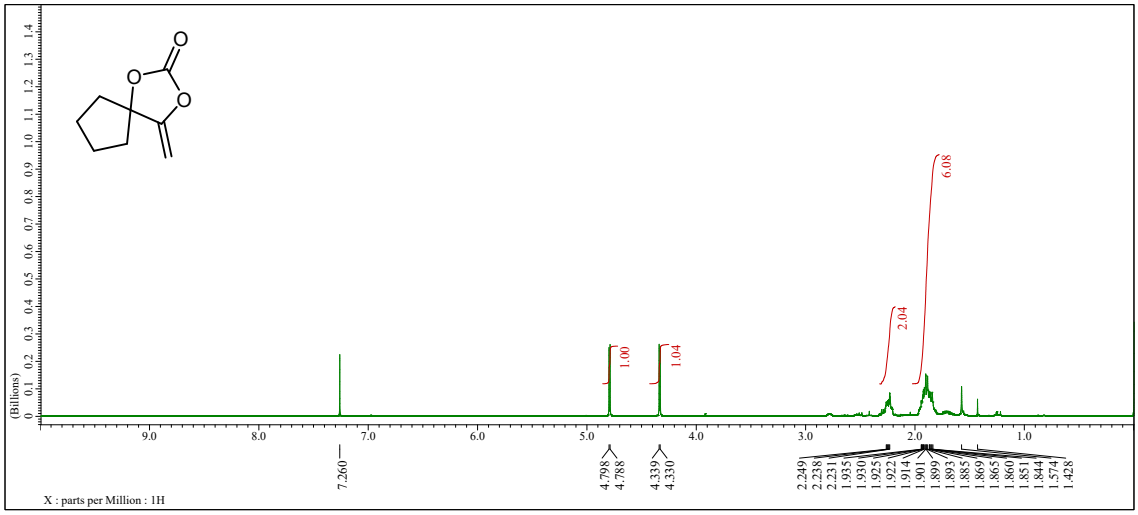
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1.925
1.922
1.914
1.901
1.899
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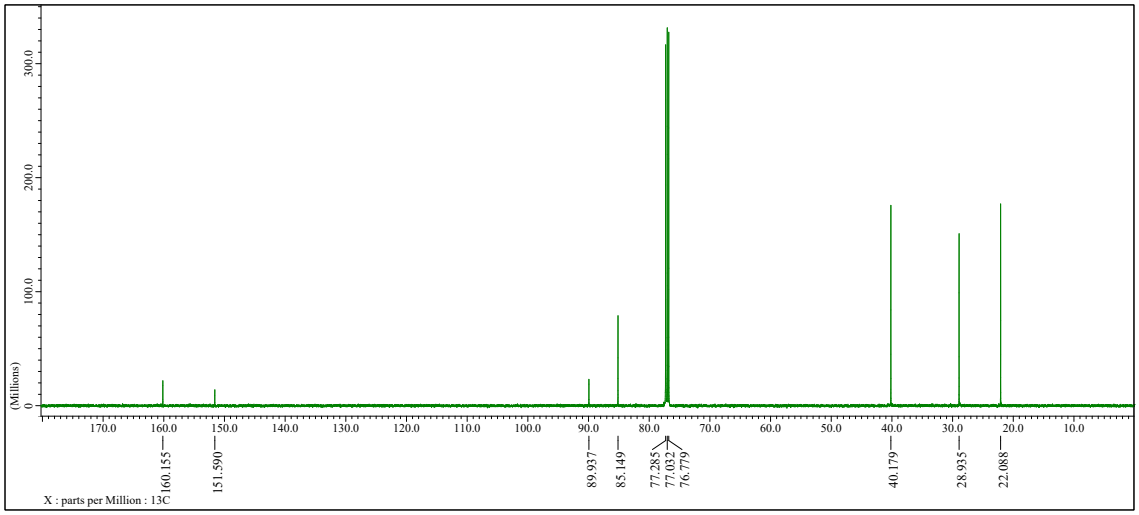
1.865
1.860
1.851
1.844
1.574
1.428
X : parts per Million : 1H


(Millions)
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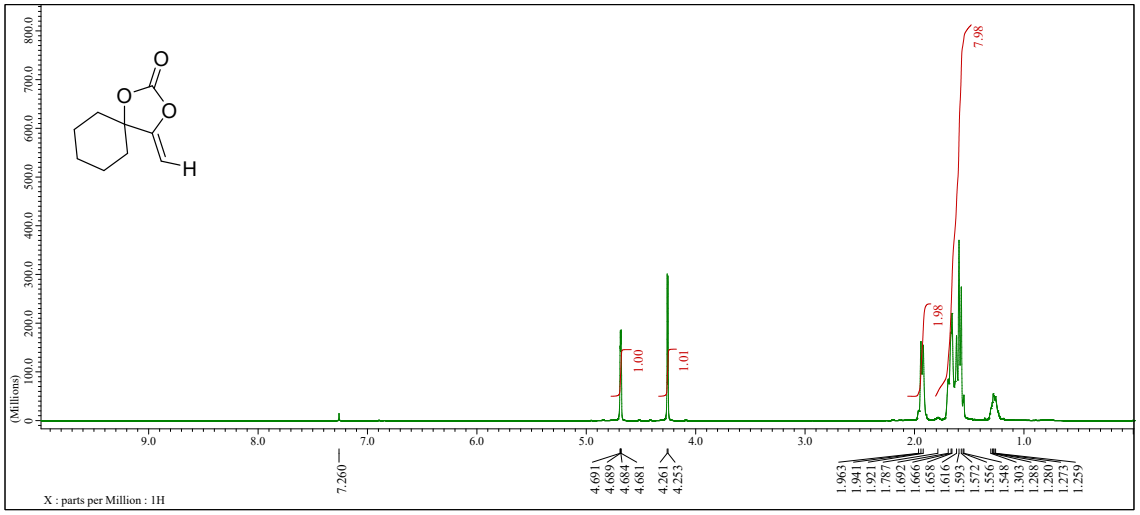
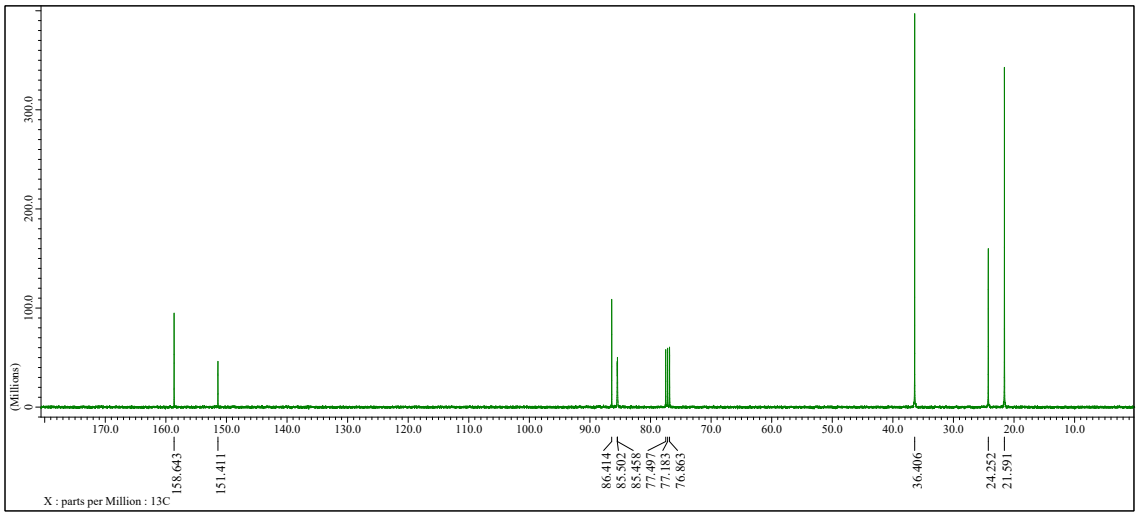
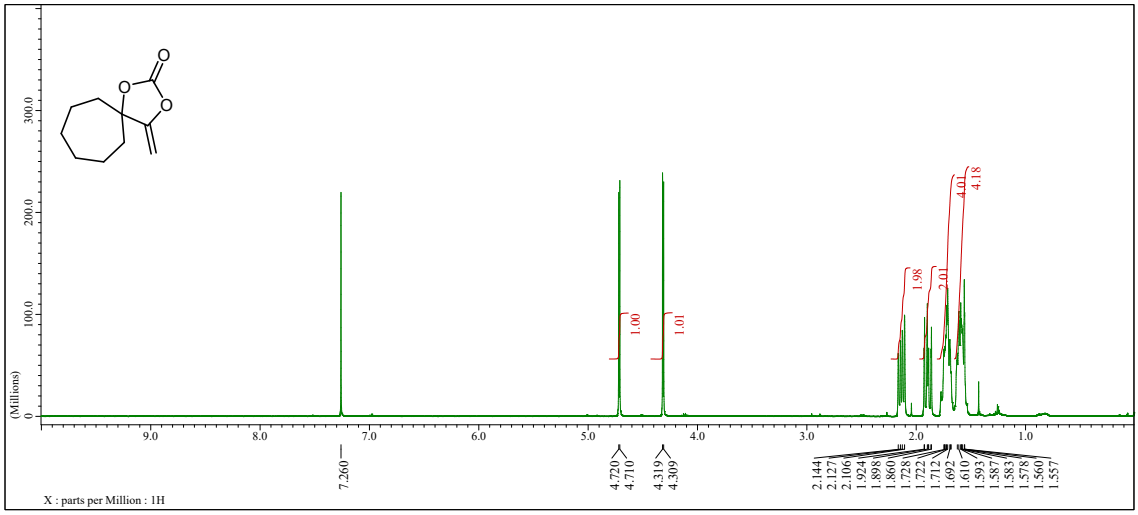
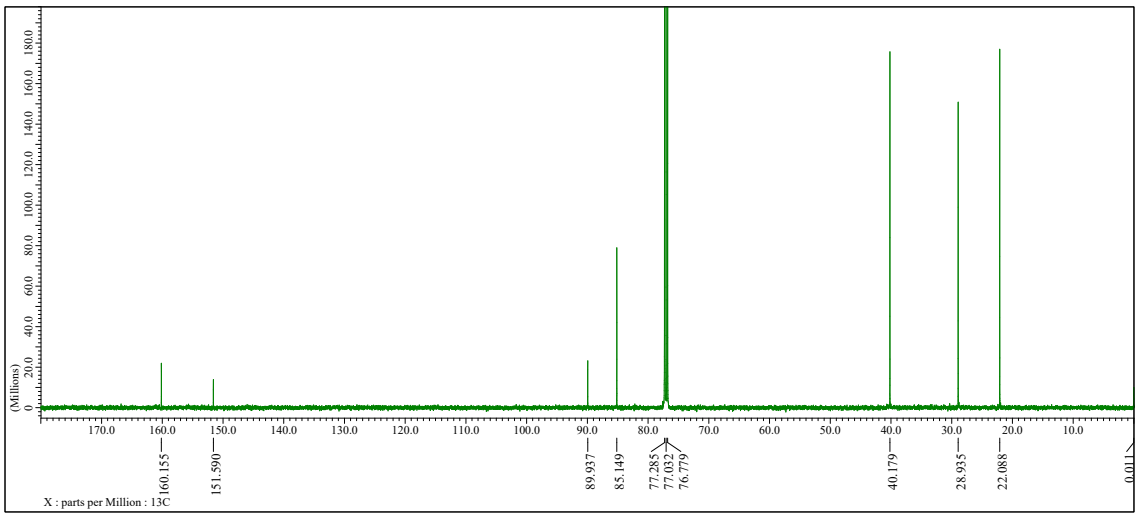
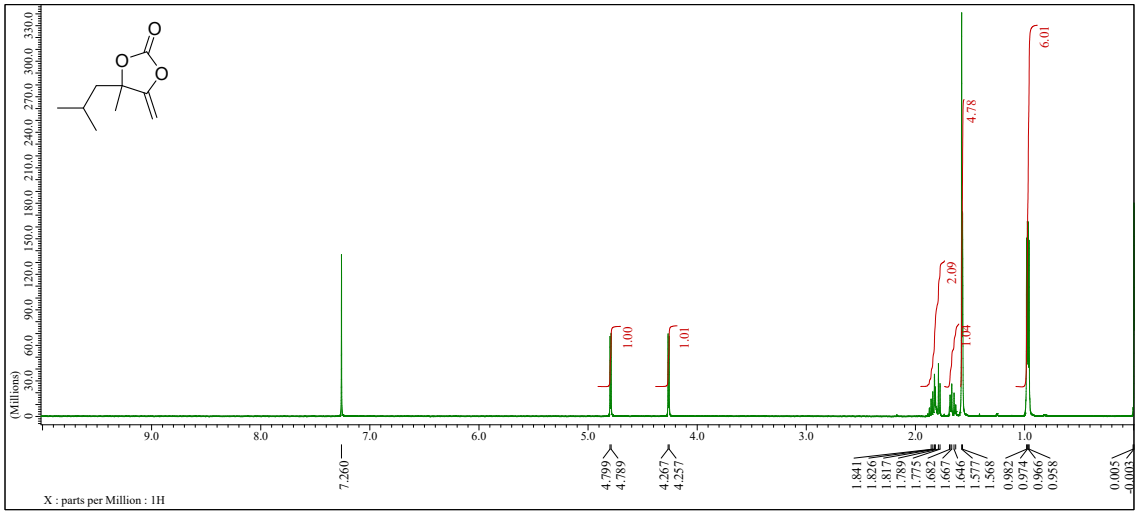
28.935
22.088
X : parts per Million : 13C

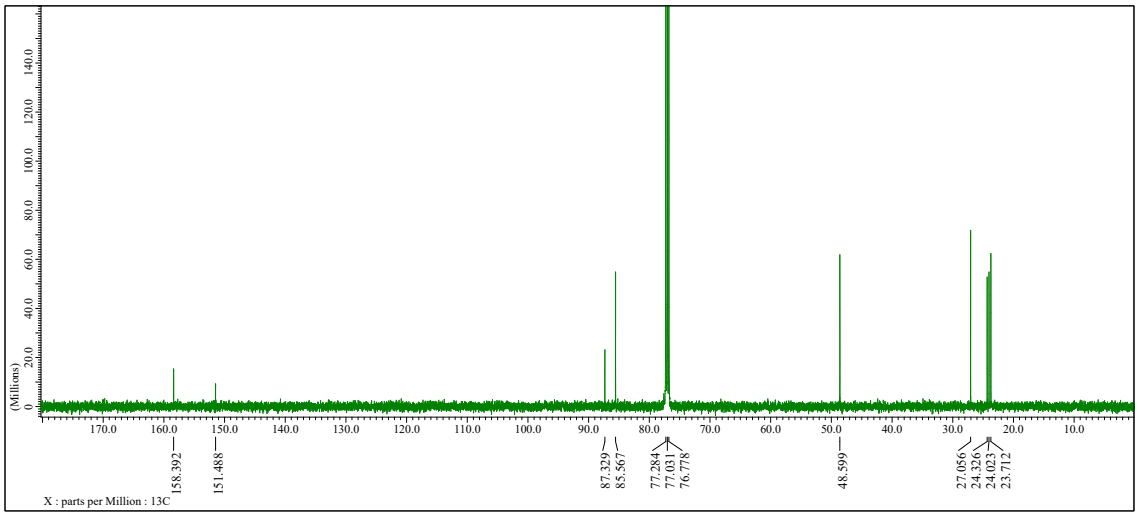

O
O
O
H
(Millions)
800.0
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.98
1.98
1.00
1.01
7.260
4.691
4.689
4.684
4.681
4.261
4.253
1.963
1.941
1.921
1.787
1.692
1.666
1.658
1.616
1.593
1.572
1.556
1.548
1.303
1.288
1.280
1.273
1.259
X : parts per Million : 1H

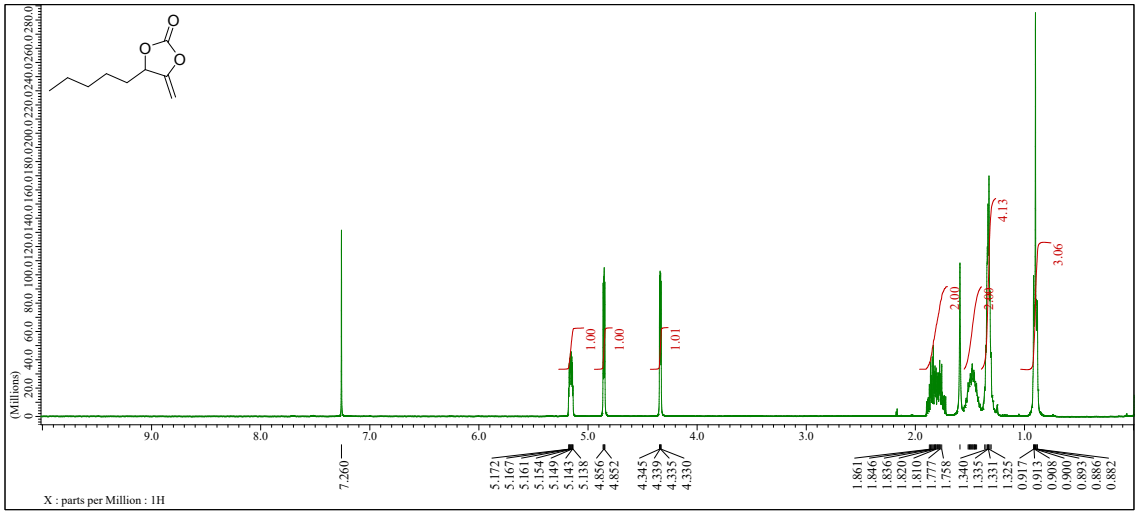

(Millions)
300.0
200.0
100.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
158.643
151.411
86.414
85.502
85.458
77.497
77.183
76.863
36.406
24.252
21.591
X : parts per Million : 13C

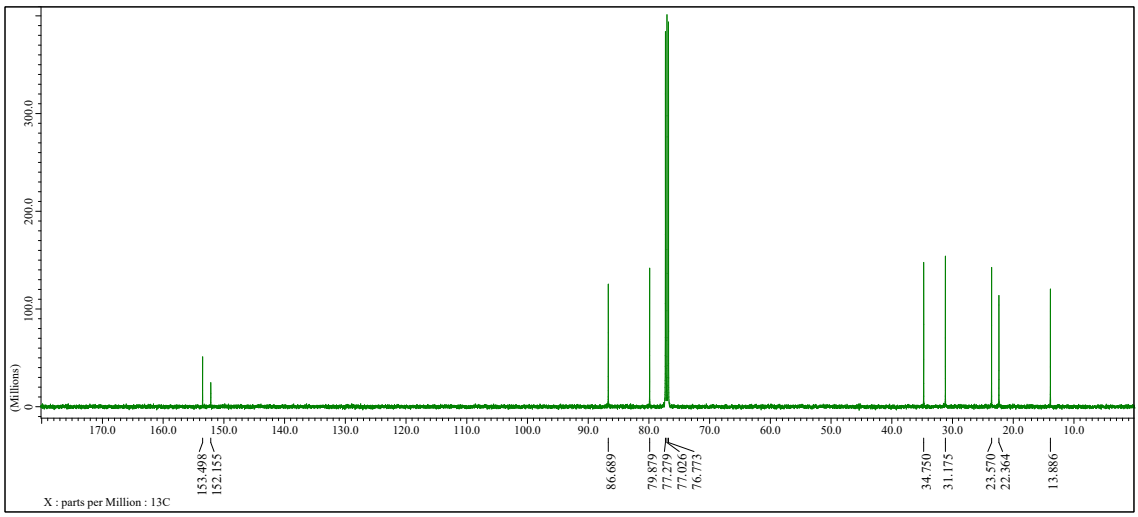

O
O
O
(Millions)
300.0
200.0
100.0
0
1.00
1.01
1.98
2.01
4.01
4.18
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.260
4.720
4.710
4.319
4.309
2.144
2.127
2.106
1.924
1.898
1.860
1.728
1.722
1.712
1.692
1.610
1.593
1.587
1.583
1.578
1.560
1.557
X : parts per Million : 1H

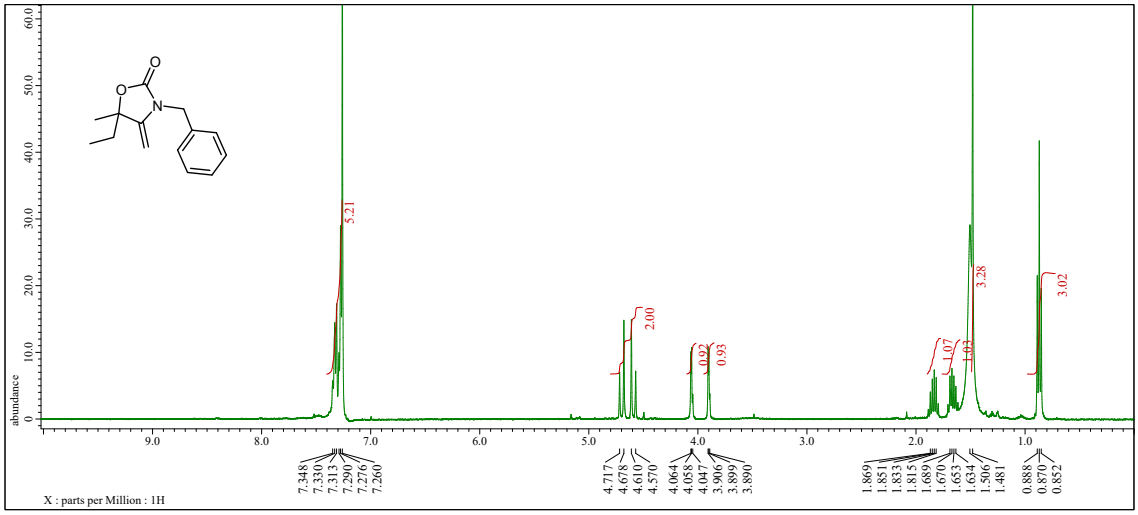

(Millions)
180.0
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0
0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
160.155
151.590
89.937
85.149
77.285
77.032
76.779
40.179
28.935
22.088
0.011
X : parts per Million : 13C

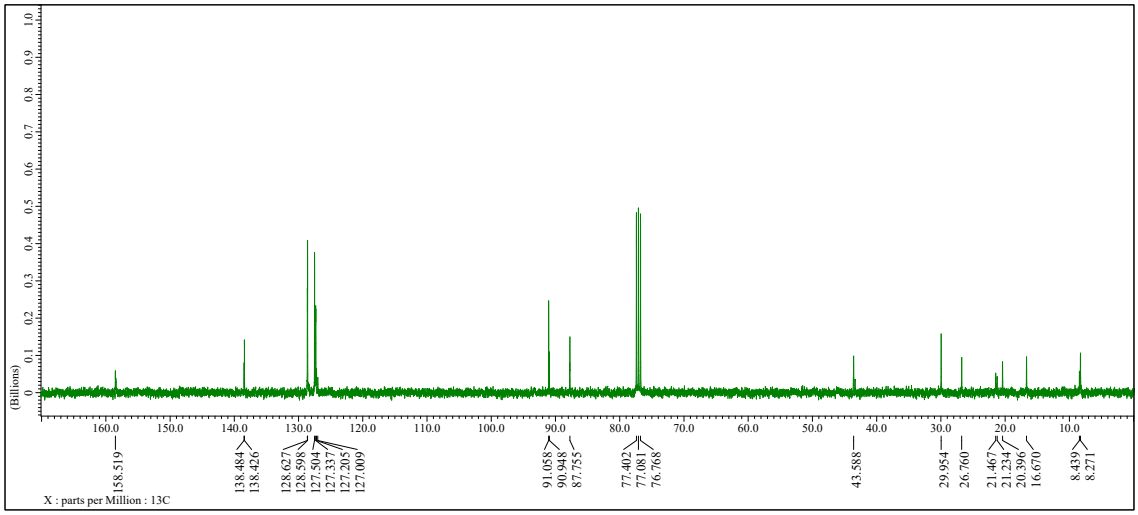

(Millions)
X : parts per Million : 1H
7.260
4.799
4.789
4.267
4.257
1.841
1.826
1.817
1.789
1.775
1.682
1.667
1.646
1.577
1.568
0.982
0.974
0.966
0.958
0.005
-0.003
1.00
1.01
2.09
4.78
1.04
6.01

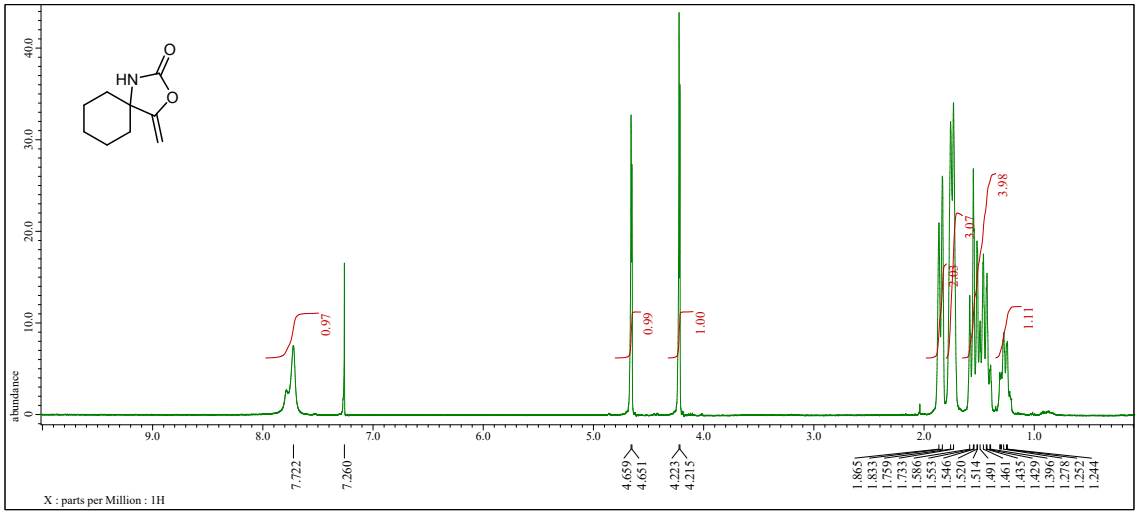

(Millions)
X : parts per Million : 13C
158.392
151.488
87.329
85.567
77.284
77.031
76.778
48.599
27.056
24.326
24.023
23.712

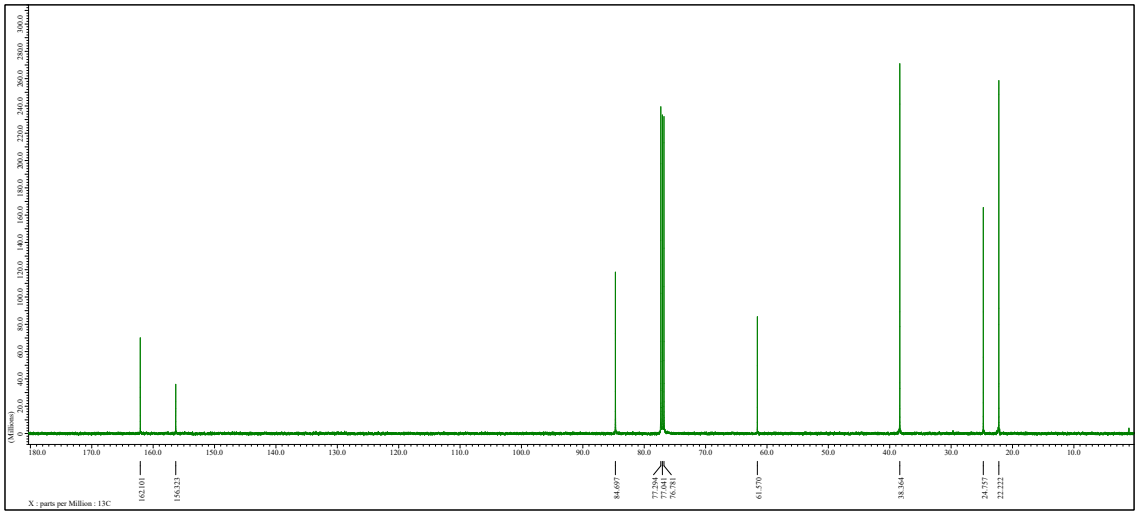

(Millions)
1.00
1.00
1.01
2.00
2.88
4.13
3.06
7.260
5.172
5.167
5.161
5.154
5.149
5.143
5.138
4.856
4.852
4.345
4.339
4.335
4.330
1.861
1.846
1.836
1.820
1.810
1.777
1.758
1.340
1.335
1.331
1.325
0.917
0.913
0.908
0.900
0.893
0.886
0.882
X : parts per Million : 1H

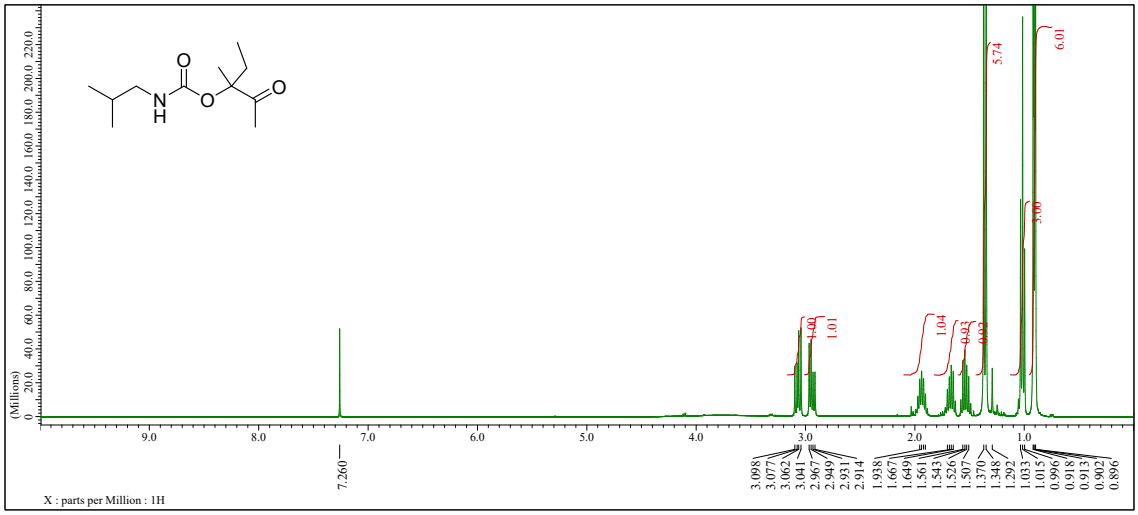

(Millions)
153.498
152.155
86.689
79.879
77.279
77.026
76.773
34.750
31.175
23.570
22.364
13.886
X : parts per Million : 13C

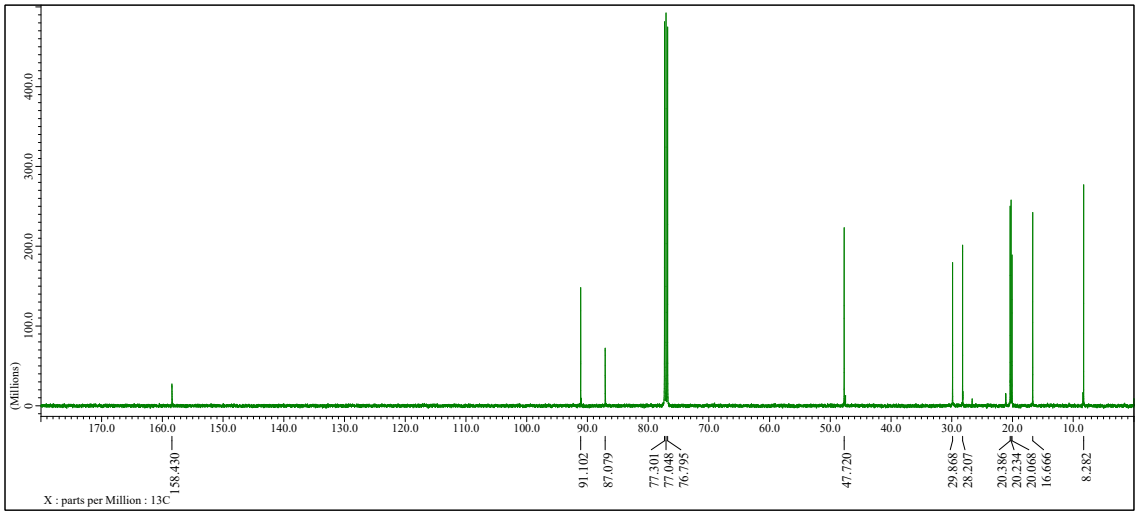

abundance
X : parts per Million : 1H
7.348
7.330
7.313
7.290
7.276
7.260
4.717
4.678
4.610
4.570
4.064
4.058
4.047
3.906
3.899
3.890
1.869
1.851
1.833
1.815
1.689
1.670
1.653
1.634
1.506
1.481
0.888
0.870
0.852
5.21
2.00
0.92
0.93
1.07
1.03
3.28
3.02

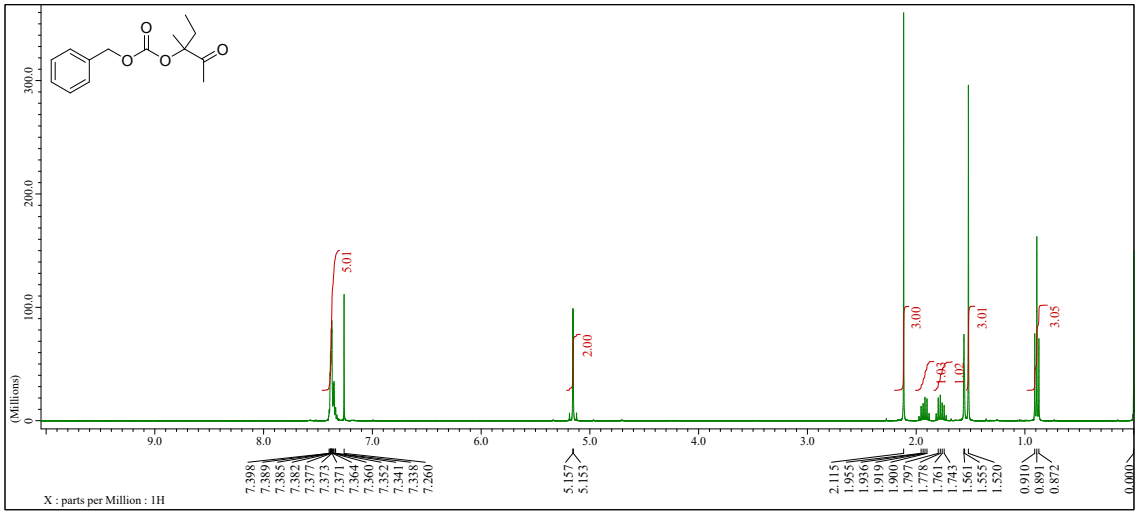

(Billions)
X : parts per Million : 13C
158.519
138.484
138.426
128.627
128.598
127.504
127.337
127.205
127.009
91.058
90.948
87.755
77.402
77.081
76.768
43.588
29.954
26.760
21.467
21.234
20.396
16.670
8.439
8.271

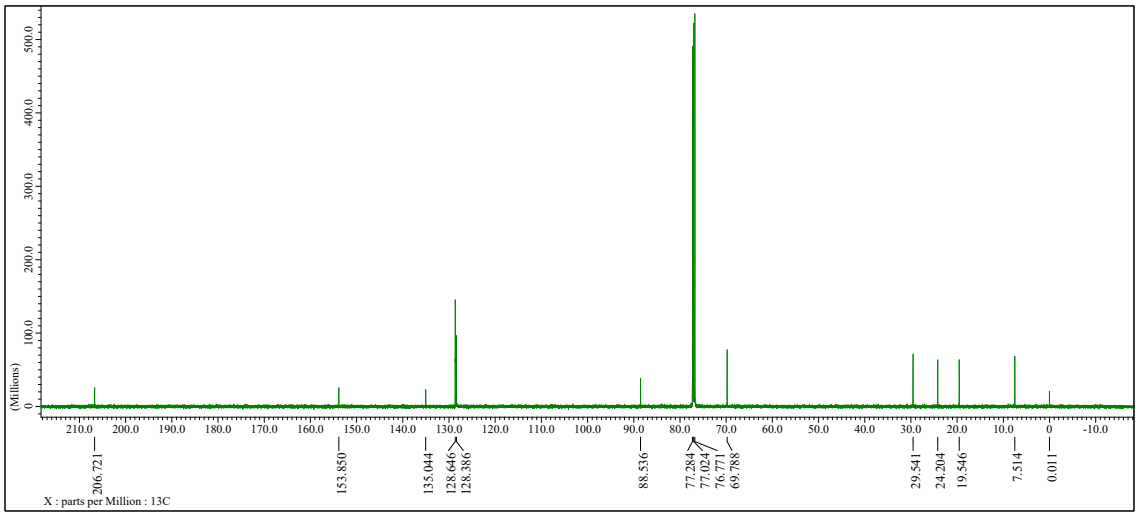

HN
O
O
abundance
40.0
30.0
20.0
10.0
0.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.97
0.99
1.00
2.83
3.07
3.98
1.11
7.722
7.260
4.659
4.651
4.223
4.215
1.865
1.833
1.759
1.733
1.586
1.553
1.546
1.520
1.514
1.491
1.461
1.435
1.429
1.396
1.278
1.252
1.244
X : parts per Million : 1H

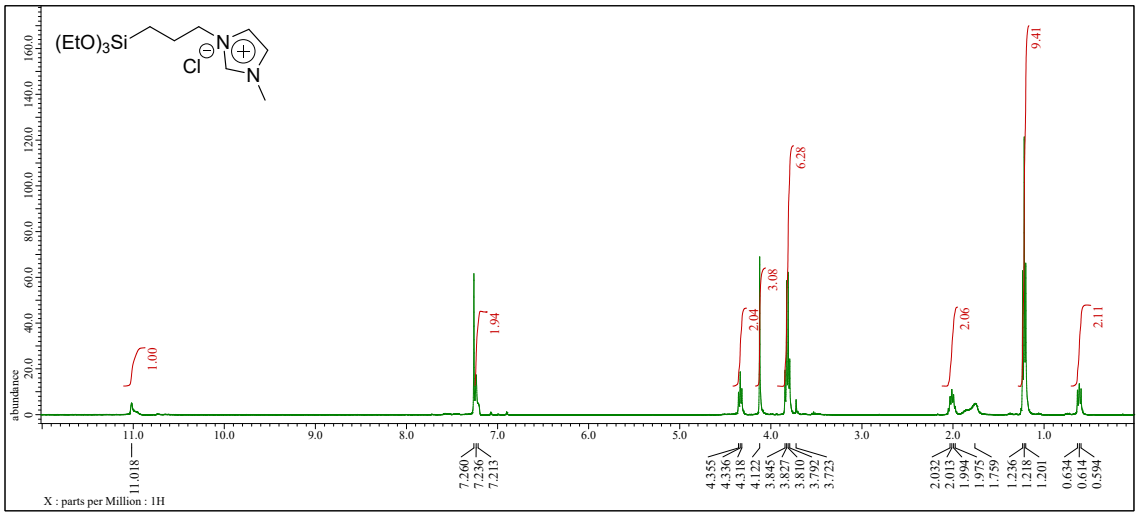

(Millions)
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
162.101
156.323
84.697
77.294
77.041
76.781
61.570
38.364
24.757
22.222
X : parts per Million : 13C

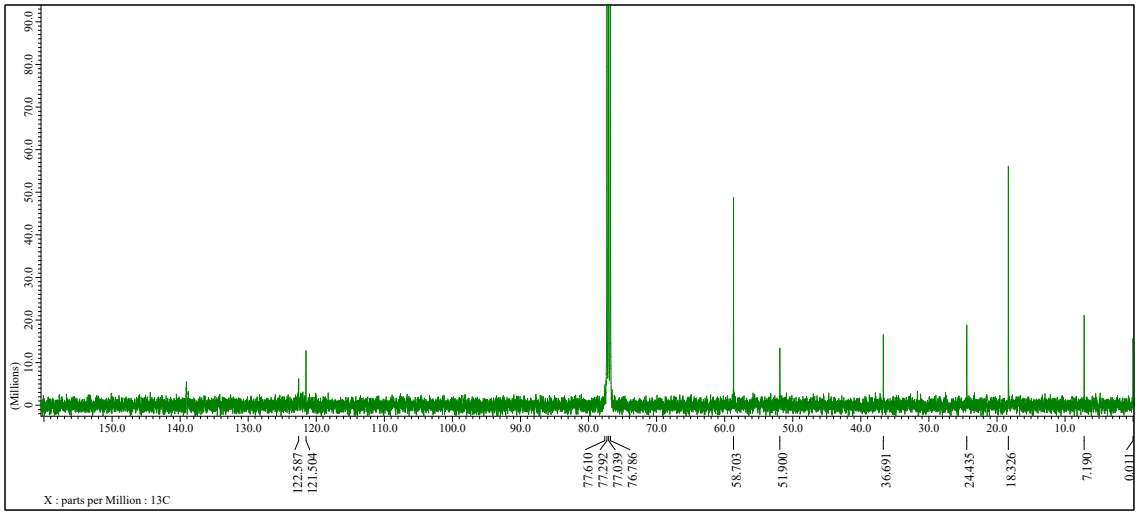

(Millions)
X : parts per Million : 1H
7.260
3.098
3.077
3.062
3.041
2.967
2.949
2.931
2.914
1.938
1.667
1.649
1.561
1.543
1.526
1.507
1.370
1.348
1.292
1.033
1.015
0.996
0.918
0.913
0.902
0.896
1.00
1.01
1.04
0.93
0.92
5.74
3.00
6.01


(Millions)
X : parts per Million : 13C
158.430
91.102
87.079
77.301
77.048
76.795
47.720
29.868
28.207
20.386
20.234
20.068
16.666
8.282


(Millions)
300.0
200.0
100.0
0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
5.01
2.00
3.00
1.03
1.02
3.01
3.05
7.398
7.389
7.385
7.382
7.377
7.373
7.371
7.364
7.360
7.352
7.341
7.338
7.260
5.157
5.153
2.115
1.955
1.936
1.919
1.900
1.797
1.778
1.761
1.743
1.561
1.555
1.520
0.910
0.891
0.872
0.000
X : parts per Million : 1H


(Millions)
500.0
400.0
300.0
200.0
100.0
0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
206.721
153.850
135.044
128.646
128.386
88.536
77.284
77.024
76.771
69.788
29.541
24.204
19.546
7.514
0.011
X : parts per Million : 13C


(EtO)3Si
Cl
N
N
abundance
1.00
1.94
2.04
3.08
6.28
2.06
9.41
2.11
11.018
7.260
7.236
7.213
4.355
4.336
4.318
4.122
3.845
3.827
3.810
3.792
3.723
2.032
2.013
1.994
1.975
1.759
1.236
1.218
1.201
0.634
0.614
0.594
X : parts per Million : 1H


(Millions)
122.587
121.504
77.610
77.292
77.039
76.786
58.703
51.900
36.691
24.435
18.326
7.190
0.011
X : parts per Million : 13C