Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Calcium-based catalysis cooperative with 1,8-diazabicyclo[5.4.0]-undec-7-ene for the cycloaddition of epoxides with CO_2 at atmospheric pressure

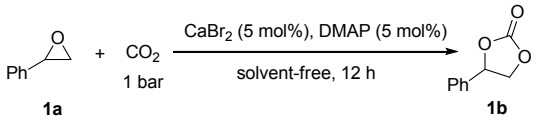
Xi Liu, Shuai Zhang, Qing-Wen Song, Xiao-Fang Liu, Ran Ma and Liang-Nian He*

State Key Laboratory and Institute of Elemento-Organic Chemistry Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin, 300071 (P. R. China)

Contents:

1. Optimization of Reaction Conditions

Table S1. Optimization of the reaction temperature[a]



Entry	T [°C]	Yield[b] [%]	Selectivity[b] [%]
1	60	56	82
2	80	74	86
3	100	78	87
4	120	59	70

[a] Reaction conditions: **1a** (0.6008 g, 5 mmol) $CaBr_2$ (5 mol%, 0.25mmol), DMAP (5 mol%, 0.25 mmol), 1 bar CO_2, 12 h. [b] GC yield using diphenyl as internal standard.

2. DFT Calculation

Molecular coordinates of optimized geometries

Complex 7 in Scheme 1

Ca	-0.00005700	-0.00006900	-0.00009200
Br	0.00086600	1.51408400	2.43676500
Br	-0.00086100	-1.51499200	-2.43651800
O	1.71466800	-1.47074400	0.66672100
O	-1.71647500	-1.46891600	0.66645600
O	-1.71433600	1.47103100	-0.66704900
O	1.71606900	1.46902300	-0.66646900
C	2.32831000	2.33969500	-0.05295100
N	3.30470100	3.08322800	-0.59277300
C	3.70493800	2.90200600	-1.97704600
C	4.00178700	4.09167500	0.18005700
H	4.74845000	2.57912600	-2.02729600
H	3.06578500	2.14657000	-2.42893400
H	3.60123100	3.84555400	-2.51905200
H	3.87259300	5.07702400	-0.27612100
H	3.60261500	4.11647300	1.19364600
H	5.07054400	3.86474500	0.22503300
H	2.09652300	2.56136900	0.99722500
C	2.32606500	-2.34191300	0.05308500
N	3.30206400	-3.08617600	0.59264200
C	3.70281000	-2.90536500	1.97679200
C	3.99813800	-4.09517800	-0.18038300
H	3.06495500	-2.14884900	2.42873400

H	3.59763600	-3.84865000	2.51899100
H	4.74686600	-2.58420100	2.02678500
H	3.86832000	-5.08039100	0.27591700
H	3.59860600	-4.11974500	-1.19383600
H	5.06705200	-3.86904900	-0.22569800
C	-2.32874000	-2.33946200	0.05280800
H	-2.09670500	-2.56123500	-0.99728600
N	-3.30545800	-3.08278500	0.59233500
C	-3.70585800	-2.90179700	1.97658900
C	-4.00230700	-4.09127300	-0.18065300
H	-3.06741100	-2.14573300	2.42842400
H	-4.74967800	-2.57990600	2.02674200
H	-3.60128900	-3.84517700	2.51873800
H	-3.60307600	-4.11587500	-1.19422300
H	-3.87297900	-5.07667600	0.27538500
H	-5.07109500	-3.86452200	-0.22564200
C	-2.32544300	2.34221200	-0.05313800
H	-2.09307700	2.56348400	0.99697800
N	-3.30127500	3.08686500	-0.59242400
C	-3.99716500	4.09570300	0.18099100
C	-3.70237100	2.90633100	-1.97651300
H	-3.59736900	4.12007300	1.19434400
H	-3.86750200	5.08100700	-0.27514900
H	-5.06606300	3.86954200	0.22654500
H	-3.59757100	3.84979700	-2.51846500
H	-3.06446100	2.15009400	-2.42883800
H	-4.74636600	2.58494000	-2.02631300
H	2.09384600	-2.56351500	-0.99699600

PO in Scheme 1

C	-1.04145900	0.61095500	-0.05102700
C	0.15029400	-0.05293000	0.49133600
H	-1.87393800	0.85154100	0.60245600
H	-0.93852000	1.23020400	-0.93767400
H	0.14519200	-0.29595300	1.55167000
O	-0.81549000	-0.77506500	-0.25704100
C	1.50152400	0.10575900	-0.14615300
H	2.07188500	-0.82201800	-0.06799900
H	1.39033200	0.35374200	-1.20297900
H	2.06682100	0.90030200	0.34591700

Complex 8 in Scheme 1

Ca	-0.15725300	-0.02771400	-0.11126600
Br	0.76437100	1.29125100	2.27187000

Br	-0.62752600	-1.91312500	-2.17026300
O	-2.42247000	-0.29911100	0.45842700
O	-0.65008600	2.11146800	-0.92922800
O	2.10692400	0.06930400	-0.70122900
C	3.14858900	0.30556200	-0.09593100
N	4.34659100	-0.16011900	-0.47560200
C	4.48072900	-0.99134700	-1.66164300
C	5.55255800	0.15275800	0.26564500
H	4.93439000	-1.94892500	-1.39219500
H	3.49204800	-1.16015500	-2.08499000
H	5.11688400	-0.49271100	-2.39768600
H	6.25635800	0.70192100	-0.36572600
H	5.30132400	0.76423500	1.13202100
H	6.03411000	-0.76654900	0.60928200
H	3.14795300	0.91136500	0.82003900
C	-3.23625200	-1.12130300	0.03898800
H	-3.00707400	-1.74929700	-0.83211100
N	-4.44005300	-1.32485700	0.58990400
C	-4.86665700	-0.57447200	1.75781700
C	-5.36394900	-2.30041400	0.04514900
H	-4.04970600	0.06965600	2.07513700
H	-5.74290900	0.03276300	1.51495400
H	-5.12694000	-1.26298100	2.56576100
H	-4.91331900	-2.78628000	-0.81976500
H	-5.59933000	-3.05928500	0.79620700
H	-6.29231300	-1.81292900	-0.26454900
C	-0.53662200	3.21584400	-0.39847100
H	-0.12090300	3.31538700	0.61278400
N	-0.89650000	4.36474400	-0.98294100
C	-0.74984500	5.63654400	-0.30194200
C	-1.46699800	4.38283800	-2.31869200
H	-0.30370500	5.47739200	0.67930700
H	-0.10614200	6.30307200	-0.88196400
H	-1.72530300	6.11379700	-0.17484300
H	-0.85133700	5.00086100	-2.97712900
H	-1.50117700	3.36426700	-2.69805900
H	-2.47763400	4.79827800	-2.28651900
O	0.33549100	-1.96696500	1.16602000
C	1.06279800	-2.41025000	2.30502000
C	1.04364200	-3.20036600	1.06069200
H	1.93125600	-1.80308400	2.54034600
H	0.43985000	-2.69417100	3.14578000
H	0.37367100	-4.05448500	1.01641700
C	2.20549100	-3.21949100	0.11034000

H	1.83822700	-3.16160600	-0.91714900
H	2.86262700	-2.36870000	0.30108500
H	2.77457000	-4.14331400	0.23935700

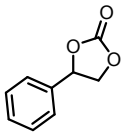
DMF in Scheme 1

C	0.86562900	-0.64451200	0.00045200
N	-0.34131200	-0.02224100	0.00022500
O	1.94237200	-0.09204600	-0.00065700
C	-0.42334400	1.42477000	0.00010900
C	-1.58528200	-0.75952700	0.00009000
H	0.76690300	-1.74403200	-0.00066400
H	0.58718300	1.82785300	0.00007700
H	-0.95627600	1.77486100	0.88917600
H	-0.95629600	1.77472000	-0.88900100
H	-1.37854700	-1.83009200	0.00013800
H	-2.17747600	-0.51780000	0.88797000
H	-2.17729200	-0.51784300	-0.88792400

3. Characterization Data for Cyclic Carbonate Products

All cyclic carbonate products have been reported previously and the characterization data are all in good agreement with literature value.

4-phenyl-1,3-dioxolan-2-one (1b)



White solid; mp: 51-53 ^{o}C, ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 4.31 (t, ^{3}J = 8.4 Hz, 1H), 4.78 (t, ^{3}J = 8.4 Hz, 1H), 5.66 (t, ^{3}J = 8.0 Hz, 1H), 7.34–7.35 (m, 2H) 7.41–7.44 (m, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 71.18, 78.02, 125.92, 129.17, 129.67, 135.80, 154.95; GS-MS (EI, 70 eV) *m/z* (%)164 (59) [M^{+}], 119 (12), 105 (34), 91 (79), 90 (100), 89 (40), 78 (96), 77 (32).

1,3-dioxolan-2-one (2b)

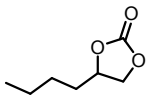
Pale yellow solid; mp: 36-37 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 4.54 (s, 4H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 64.75, 155.60.

4-methyl-1,3-dioxolan-2-one (3b)

Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.49 (d, ^{3}J = 6.0 Hz, 3H), 4.04 (t, ^{3}J = 8.4

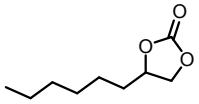
Hz, 1H), 4.58 (t, ^{3}J = 8.4 Hz, 1H), 4.84–4.92 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 19.35, 70.70, 73.65, 155.12.

4-*n*Butyl-1,3-dioxolan-2-one (4b)



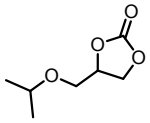
Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 0.93 (t, ^{3}J = 7.2 Hz, 3H), 1.26–1.48 (m, 4H), 1.64–1.87 (m, 2H), 4.08 (dd, ^{3}J = 7.3 Hz, ^{2}J = 8.0 Hz, 1H), 4.54 (t, ^{3}J = 8.0 Hz, 1H), 4.68–4.75 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 13.90, 22.35, 26.53, 33.66, 69.51, 76.84, 155.22.

4-Hexyl-1,3-dioxolan-2-one (5b)



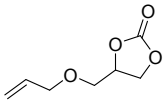
Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 0.89 (t, ^{3}J = 6.9 Hz, 3H), 1.30–1.48 (m, 8H), 1.65–1.79 (m, 2H), 4.07 (dd, ^{3}J = 8.4 Hz, ^{2}J = 7.2 Hz, 1H), 4.53 (dd, ^{3}J = 8.3 Hz, ^{2}J = 7.9 Hz, 1H), 4.67–4.72 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 14.12, 22.59, 24.45, 28.92, 31.64, 34.02, 69.52, 77.48, 155.21.

4-isopropoxy-1,3-dioxolan-2-one (6b)



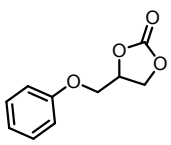
Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 1.16 (t, ^{3}J = 6.4 Hz, 6H), 3.58–3.70 (m, 3H), 4.38 (dd, ^{3}J = 8.0 Hz, ^{2}J = 15.6 Hz, 1H), 4.50 (t, ^{3}J = 8.0 Hz, 1H), 4.82 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 21.76, 21.88, 66.41, 67.11, 72.87, 75.32, 155.19.

4-((allyloxy)methyl)-1,3-dioxolan-2-one (7b)



Colourlesss liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 3.61–3.72 (m, 2H), 4.06–4.07 (m, 2H), 4.39–4.43 (m, 1H), 4.51 (t, ^{3}J = 8.4 MHz, 1H), 4.80–4.86 (m, 1H), 5.22–5.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 66.41, 68.95, 72.74, 75.11, 118.11, 133.76, 155.03.

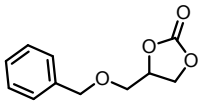
4-phenoxymethyl-1,3-dioxolan-2-one (8b)



White solid; mp: 99-100 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 4.16 (dd, ^{3}J = 4.4 Hz, ^{2}J = 10.8 Hz, 1H), 4.24 (dd, ^{3}J = 3.6 Hz, ^{2}J = 10.8 Hz, 1H), 4.55 (dd, ^{3}J = 8.4 Hz, ^{2}J = 6 Hz, 1H), 4.62 (t, ^{3}J = 8.4 Hz, 1H), 5.03 (m, 1H), 6.91 (d, ^{3}J = 8.0 Hz, 2H), 7.02 (t, ^{3}J = 7.4 Hz, 1H), 7.31 (t, ^{3}J = 8.0 Hz, 2H); ^{13}C NMR (CDCl3, 100.6 MHz) δ (ppm) 66.40, 67.08, 74.20, 76.37, 114.80, 122.20,

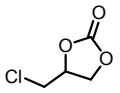
129.86, 157.93.

4-(Benzyloxy)methyl-1,3-dioxolan-2-one (9b)



Colorless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 3.61 (dd, ^{3}J = 10.8 Hz, ^{2}J = 3.6 Hz, 1H), 3.70 (dd, ^{3}J = 11.2 Hz, ^{2}J = 3.6 Hz, 1H), 4.38 (dd, ^{3}J = 8.2 Hz, ^{2}J = 6.0 Hz, 1H), 4.48 (t, ^{3}J = 8.4 Hz, 1H), 4.58 (q, J = 11.6 Hz, 1H), 4.79–4.83 (m, 1H), 7.32–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 66.38, 68.92, 73.78, 75.11, 127.85, 128.17, 128.67, 137.17, 155.04.

4-Chloromethyl-1,3-dioxolan-2-one (10b)

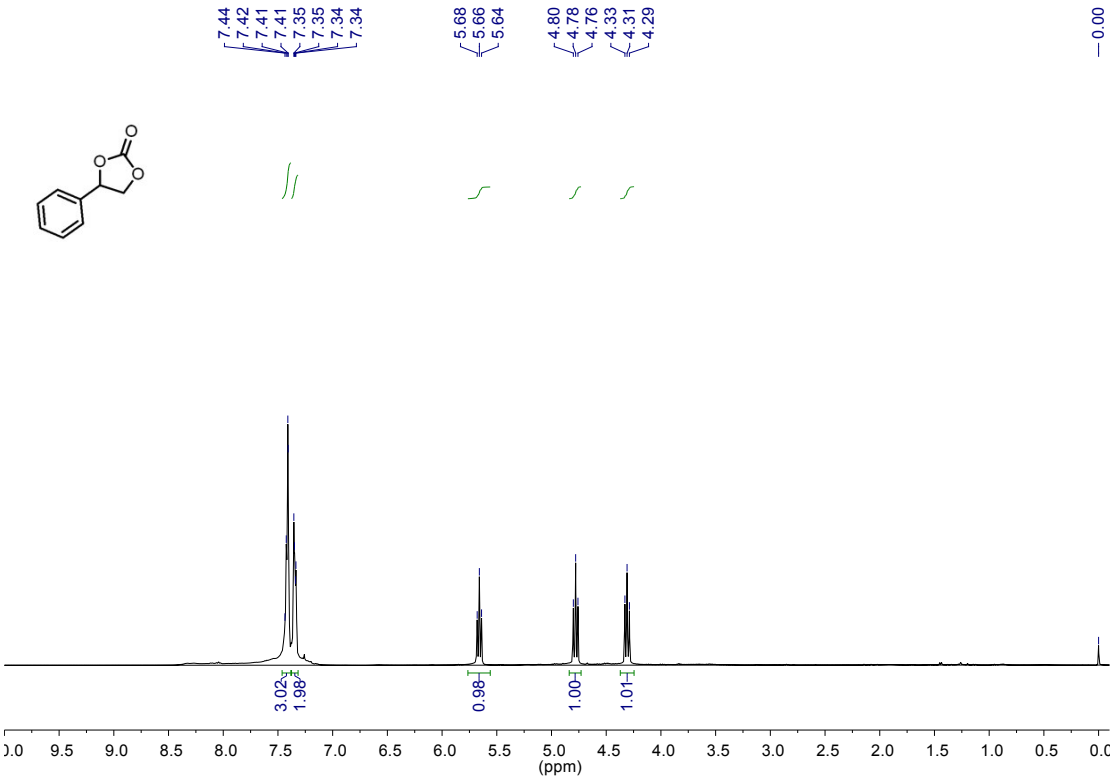


Pale yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm) 3.81 (dd, ^{3}J = 3.2 Hz, ^{2}J = 12.0 Hz, 1H), 3.82 (dd, ^{3}J = 5.2 Hz, ^{2}J = 12.0 Hz, 1H), 4.43 (dd, ^{3}J = 6.0 Hz, ^{2}J = 8.4 Hz, 1H), 4.60 (t, ^{3}J = 8.4 Hz, 1H), 4.99-5.05 (m, 1H); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ (ppm) 43.99, 67.00, 74.44, 154.44.

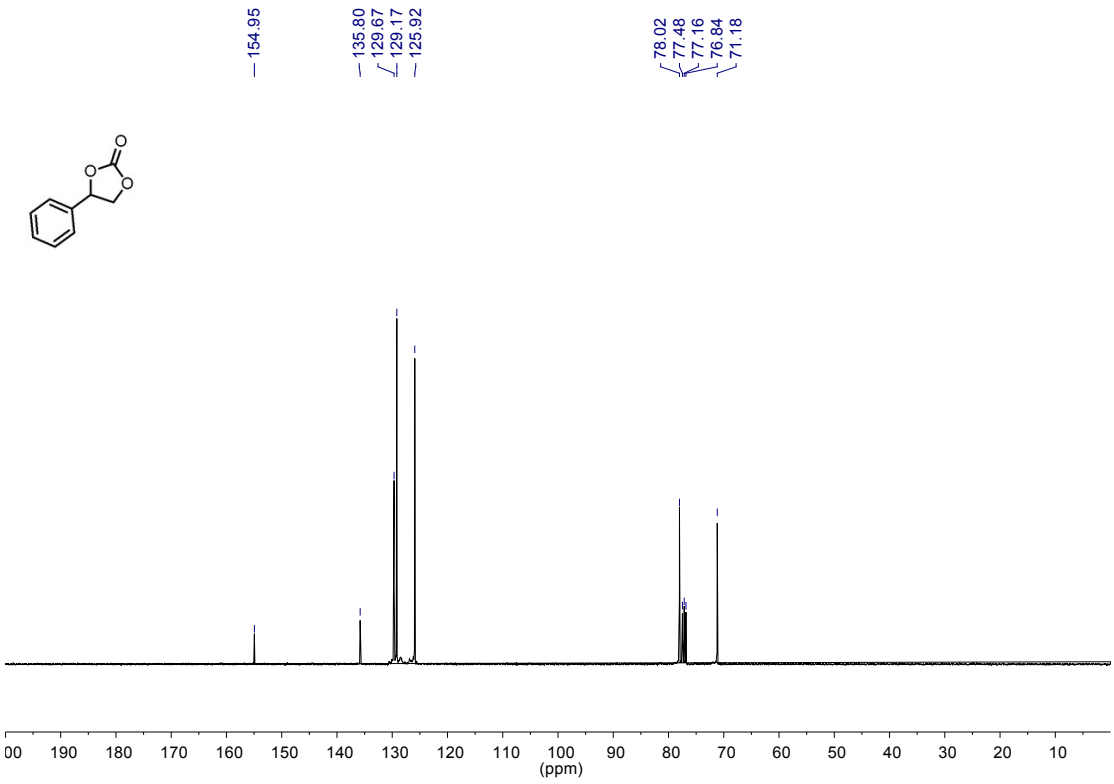
4,4-dimethyl-1,3-dioxolan-2-one (11b)

Pale yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm) 1.53 (s, 6H), 4.17 (s, 2H); ^{13}C NMR ($CDCl_3$, 100.6 MHz), δ (ppm): 26.01, 60.37, 75.41, 81.82, 154.68.

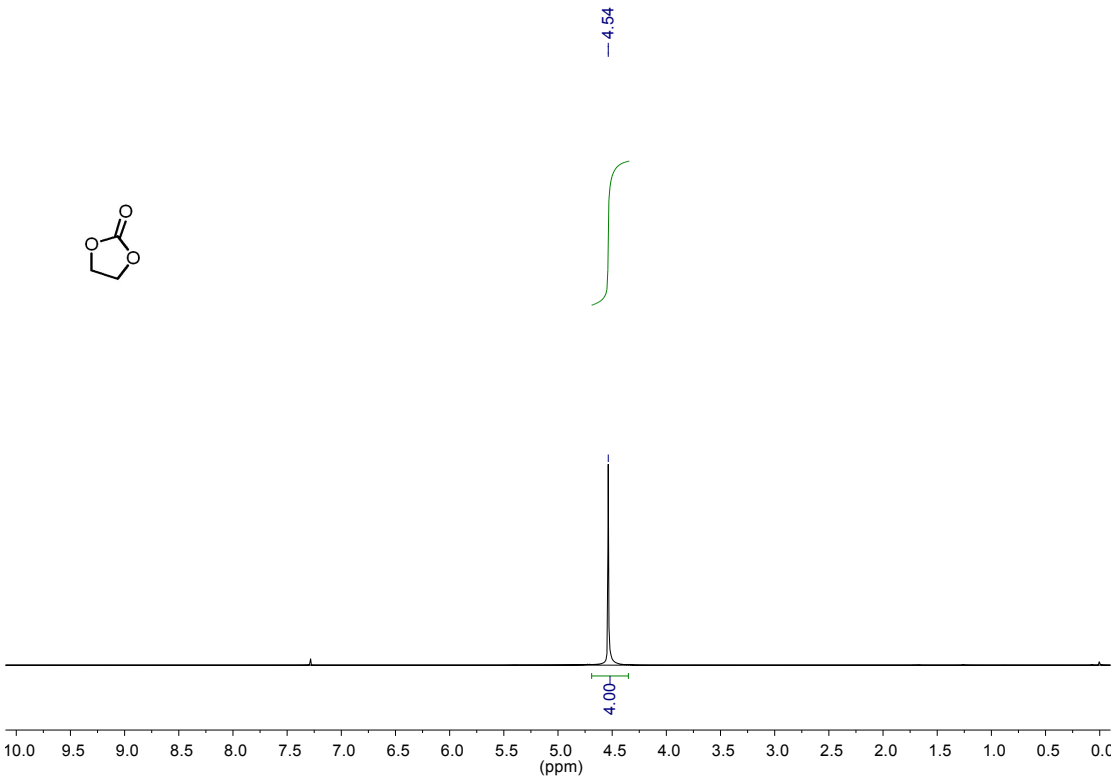
4. Characterization Spectra for Cyclic Carbonate Products



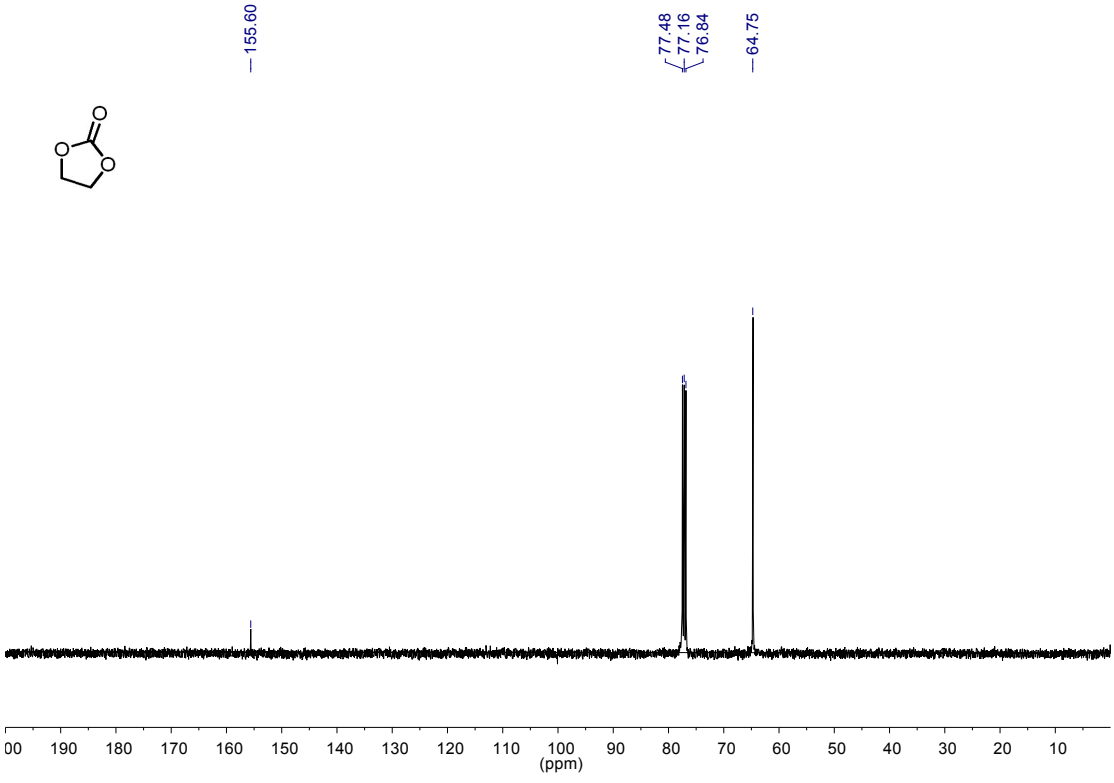
^{1}H NMR ($CDCl_3$, 400 MHz)



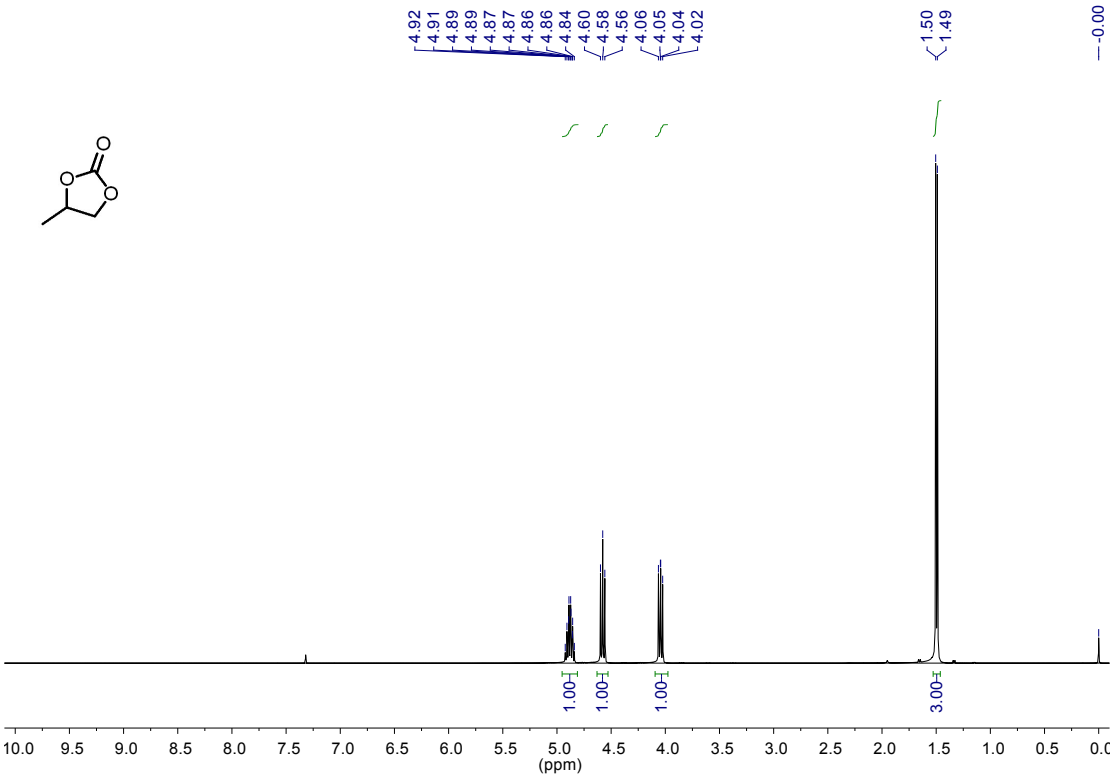
^{13}C NMR ($CDCl_3$, 100.6 MHz)



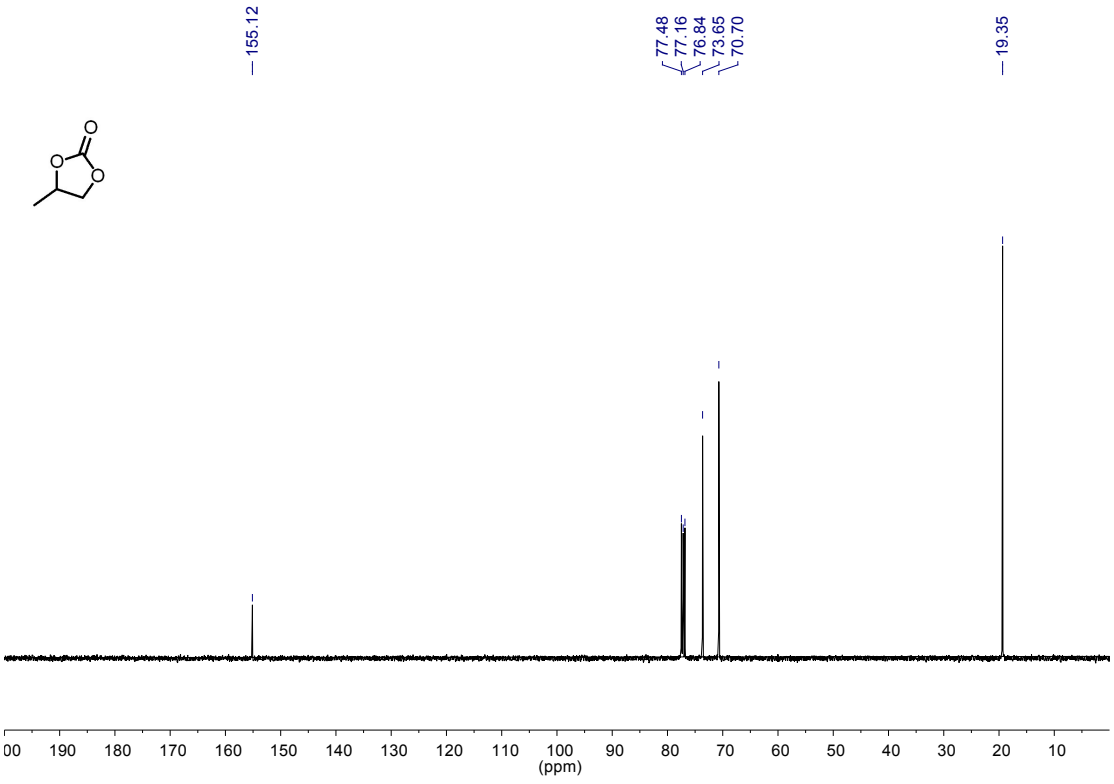
^{1}H NMR ($CDCl_3$, 400 MHz)



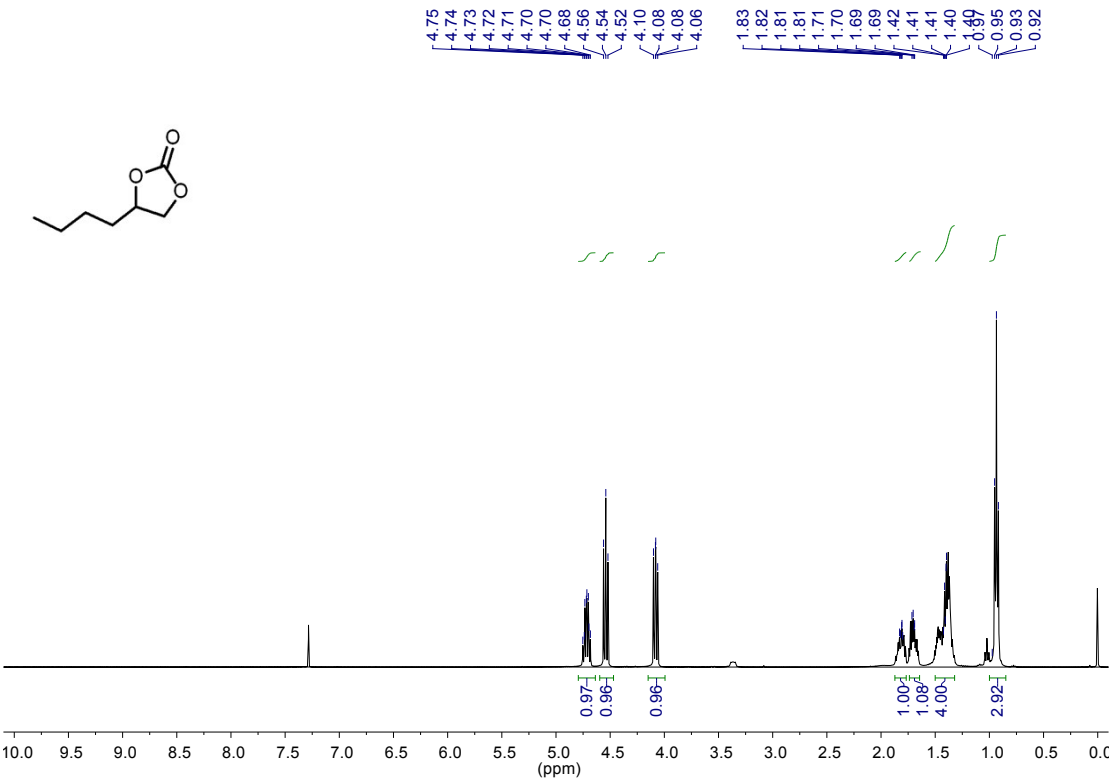
^{13}C NMR ($CDCl_3$, 100.6 MHz)



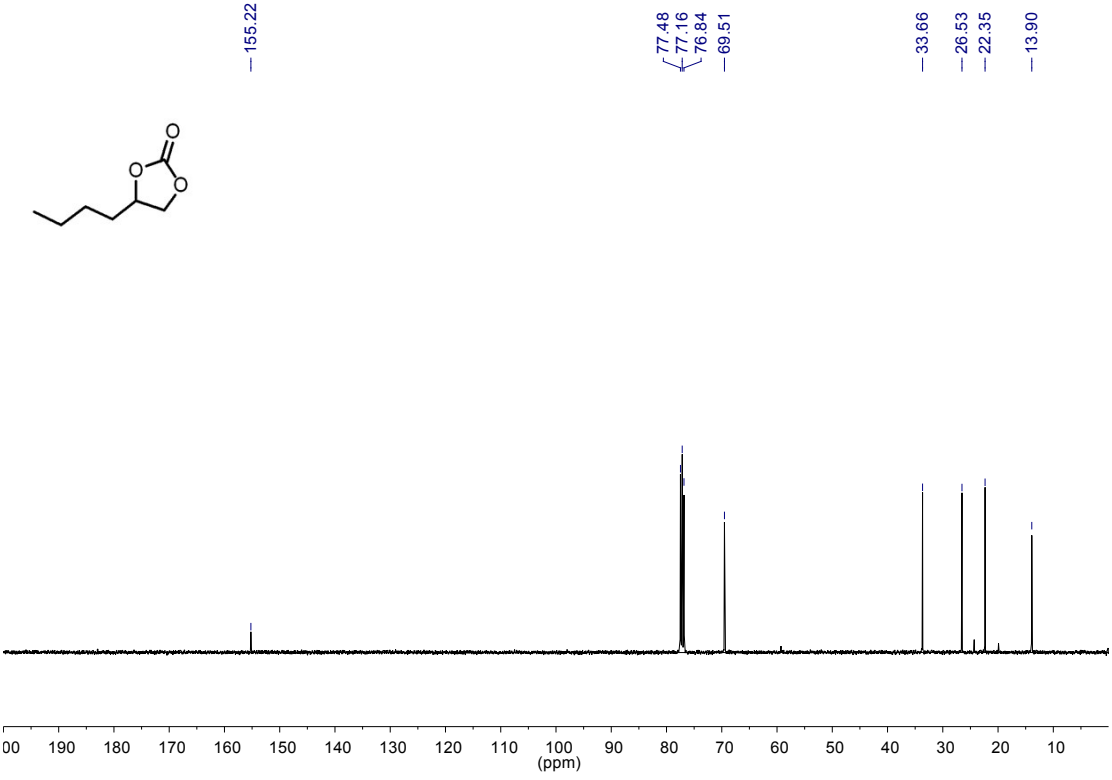
^{1}H NMR ($CDCl_3$, 400 MHz)



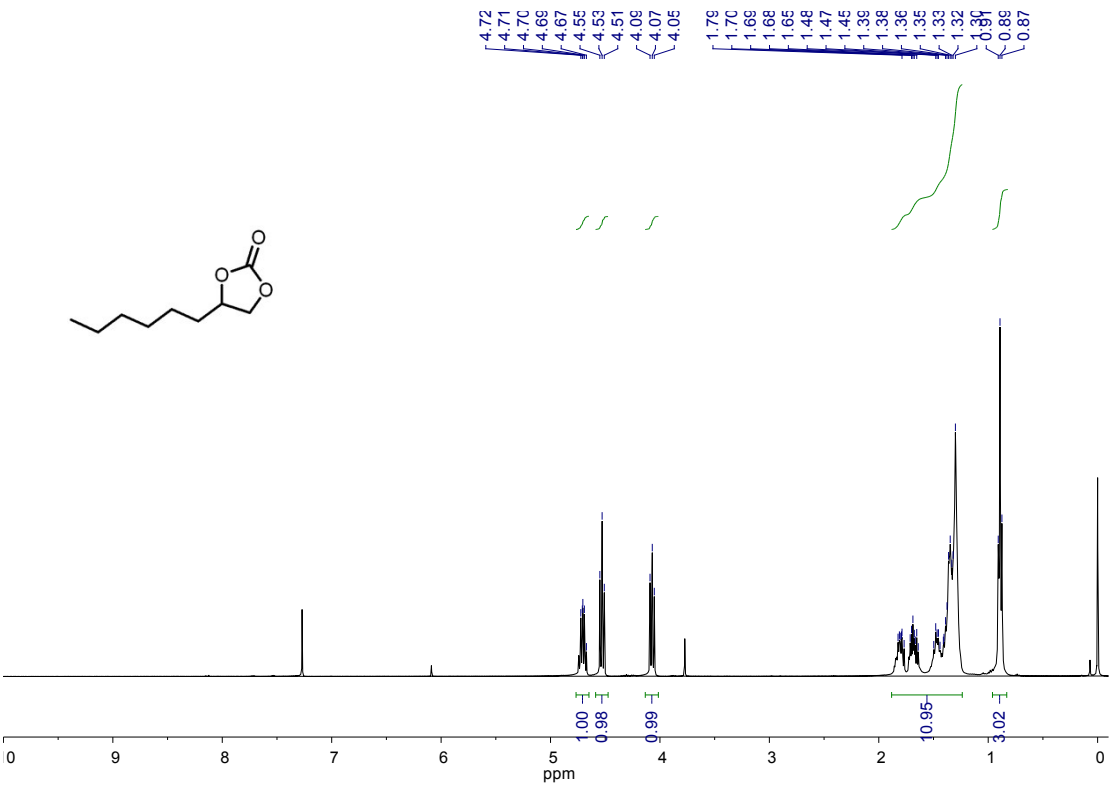
^{13}C NMR ($CDCl_3$, 100.6 MHz)



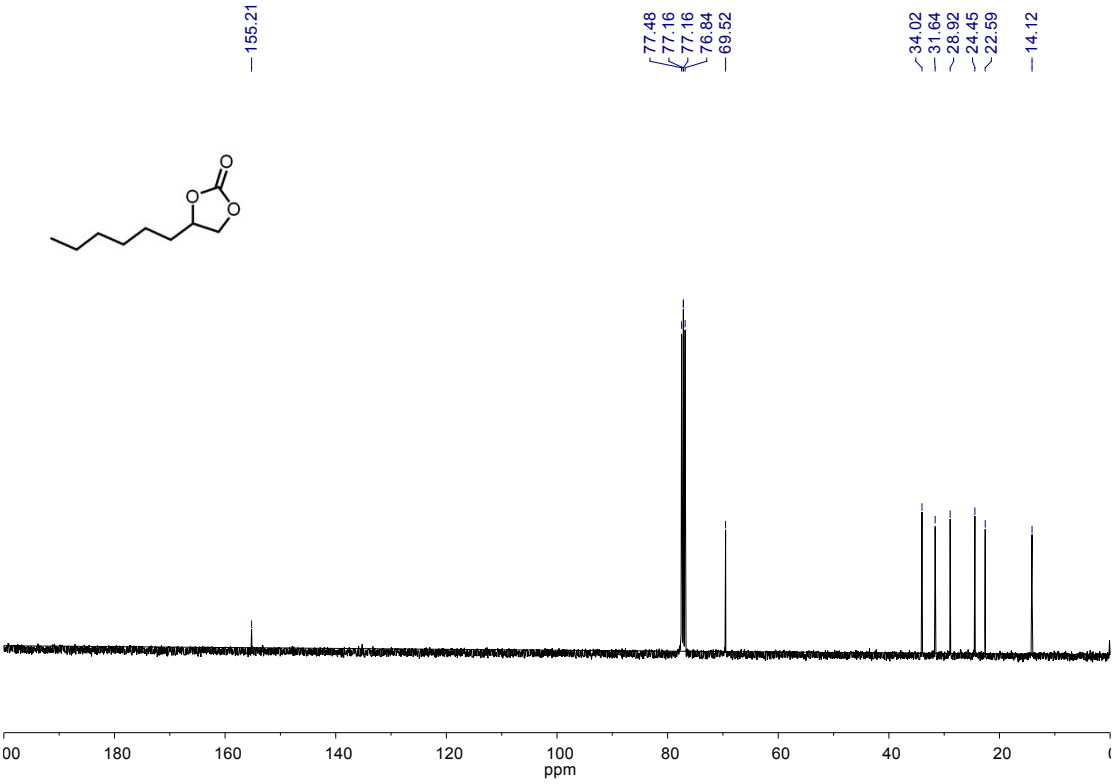
^{1}H NMR ($CDCl_3$, 400 MHz)



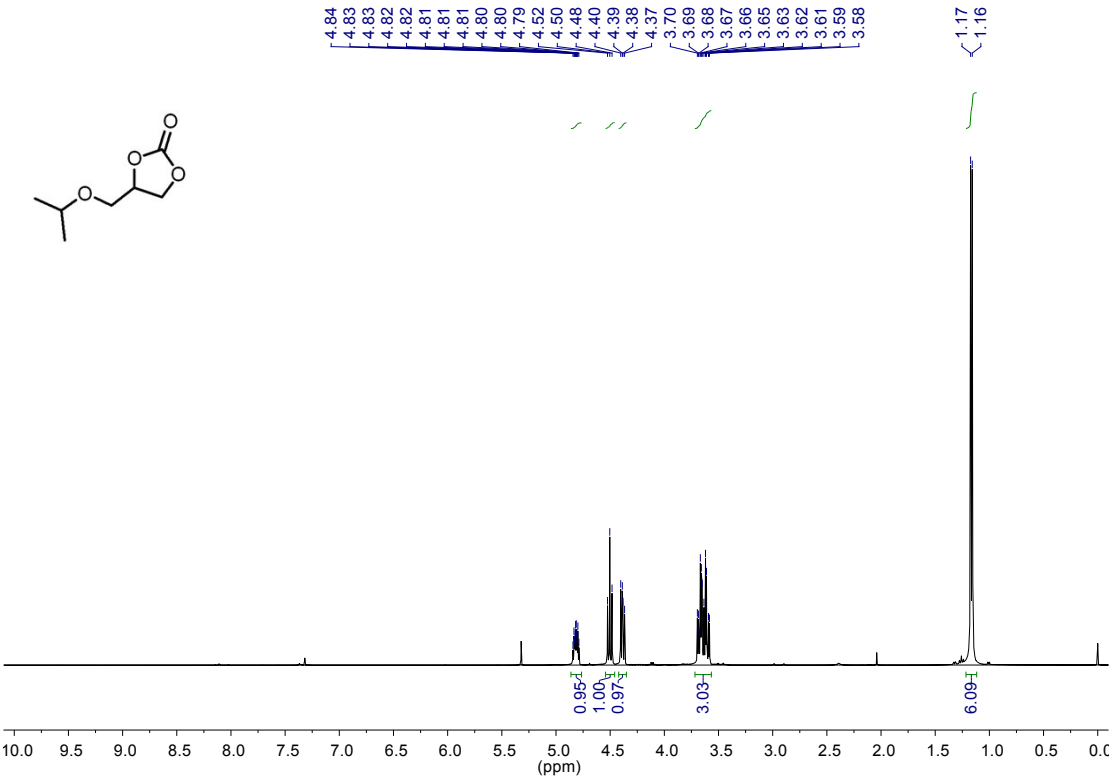
^{13}C NMR ($CDCl_3$, 100.6 MHz)



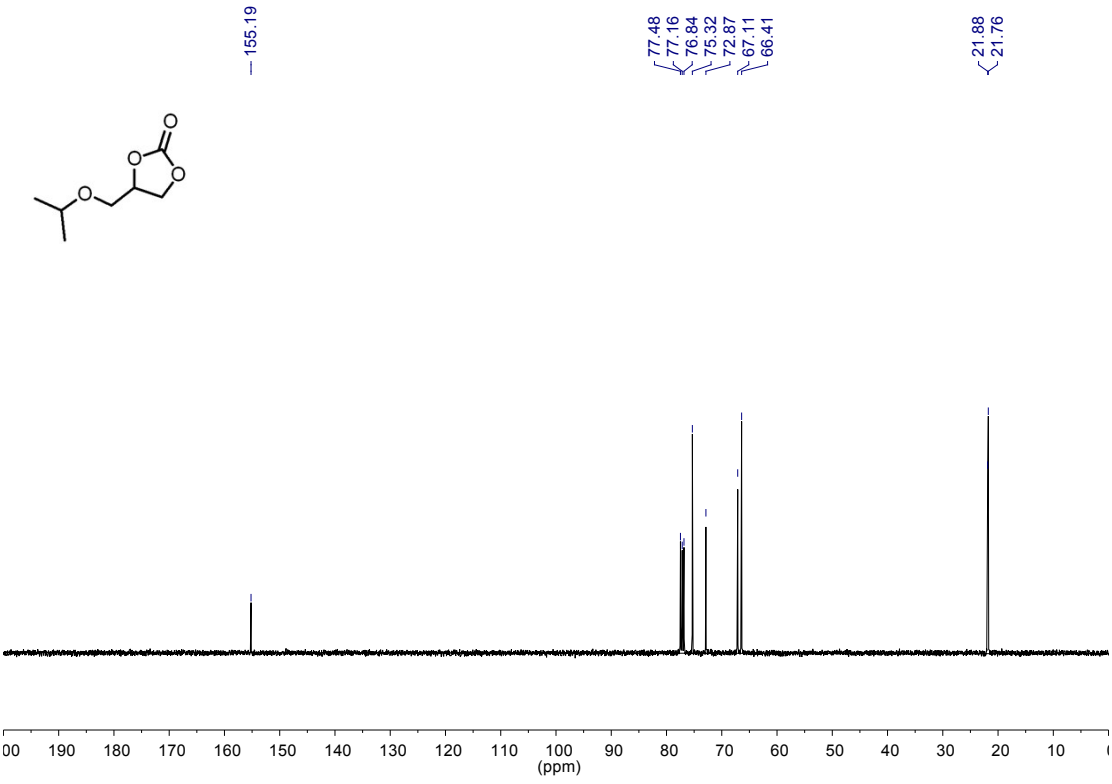
^{1}H NMR ($CDCl_3$, 400 MHz)



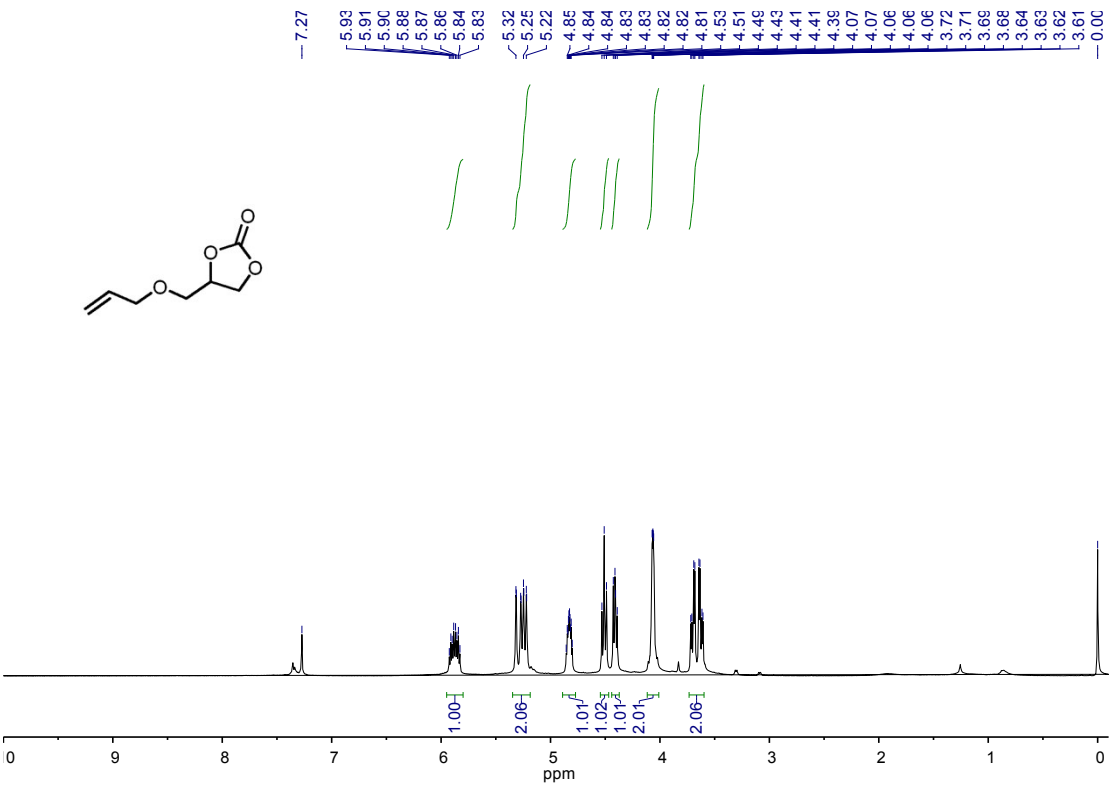
^{13}C NMR ($CDCl_3$, 100.6 MHz)



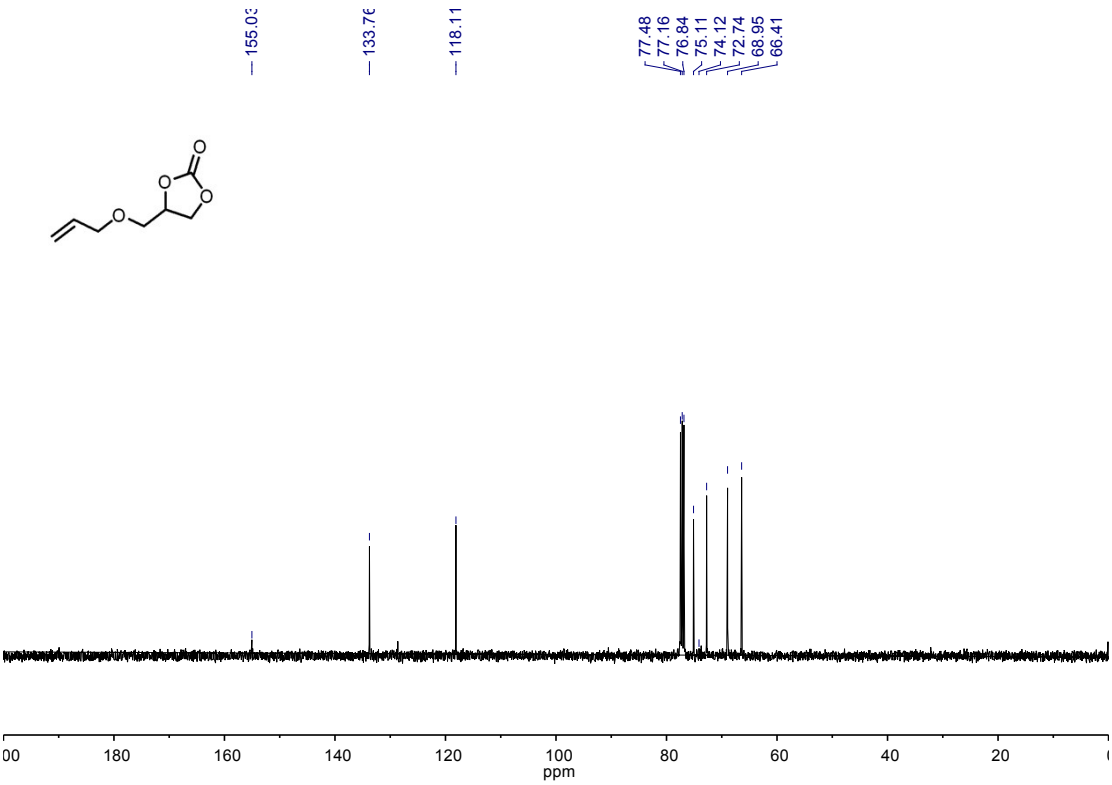
^{1}H NMR ($CDCl_3$, 400 MHz)



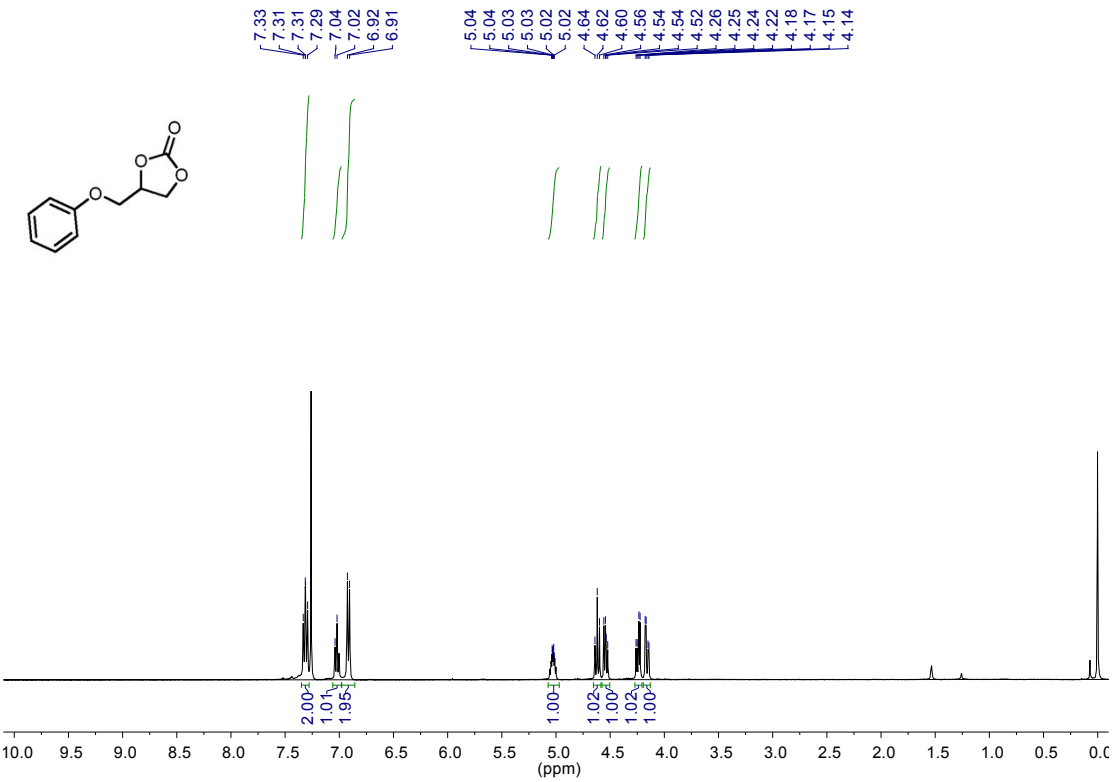
^{13}C NMR ($CDCl_3$, 100.6 MHz)



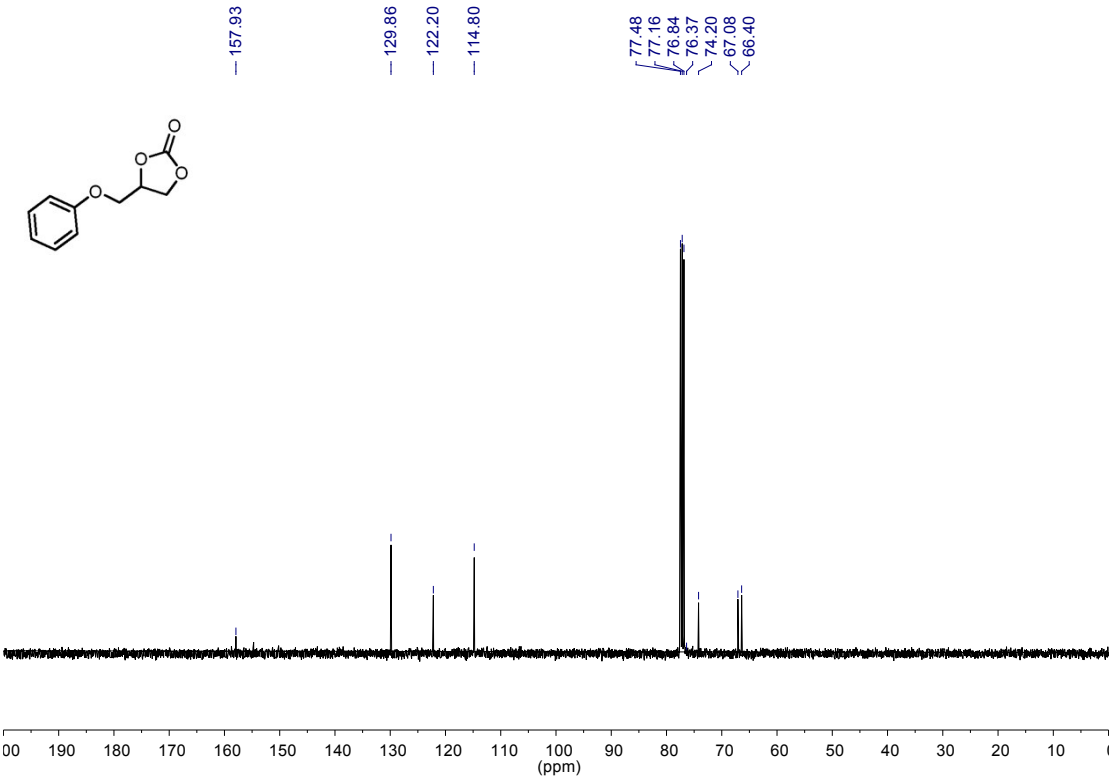
^{1}H NMR ($CDCl_3$, 400 MHz)



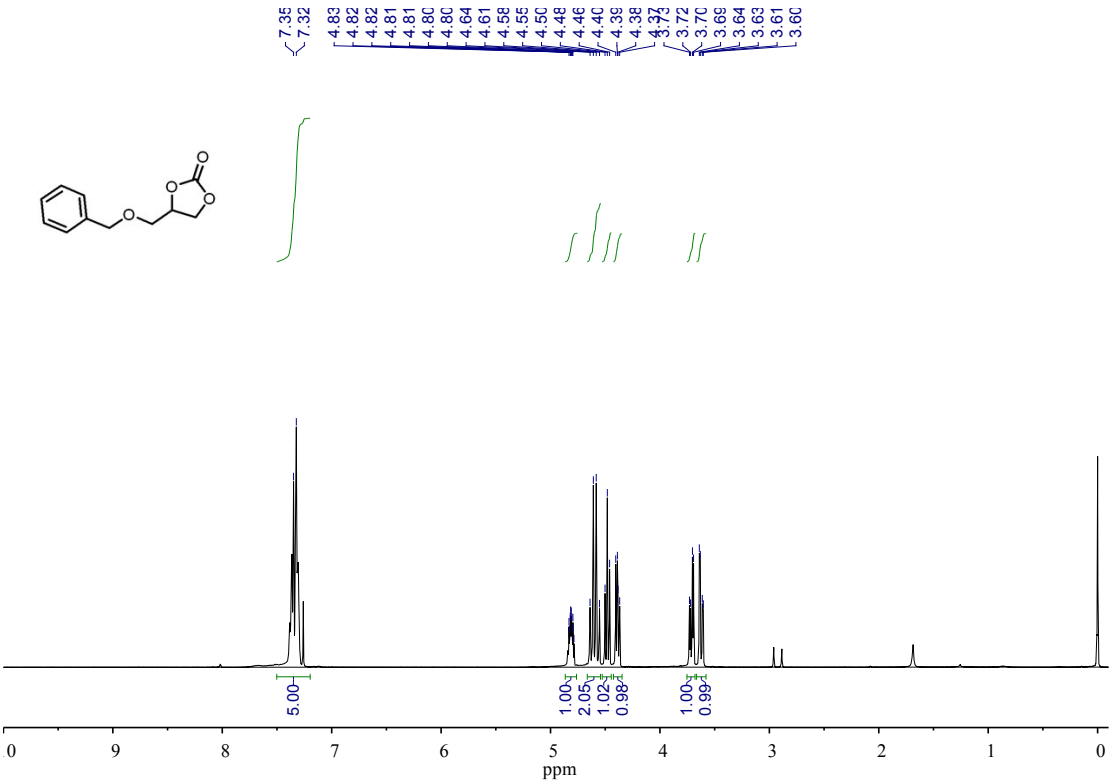
^{13}C NMR ($CDCl_3$, 100.6 MHz)



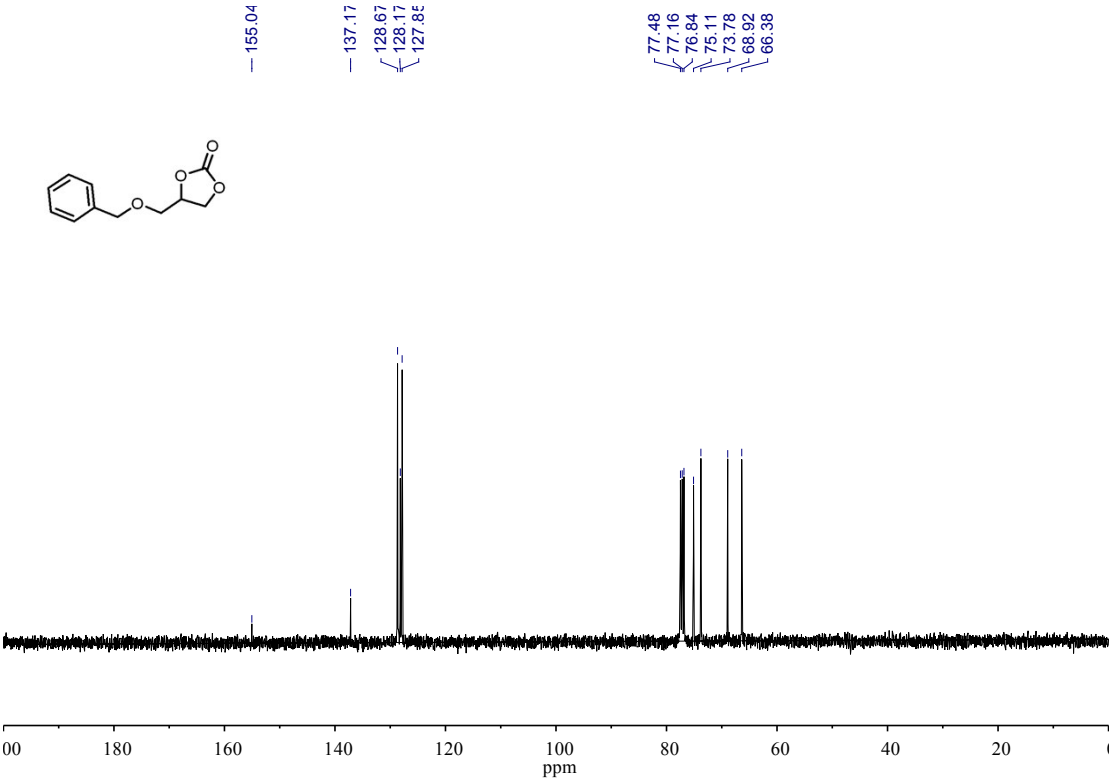
^{1}H NMR ($CDCl_3$, 400 MHz)



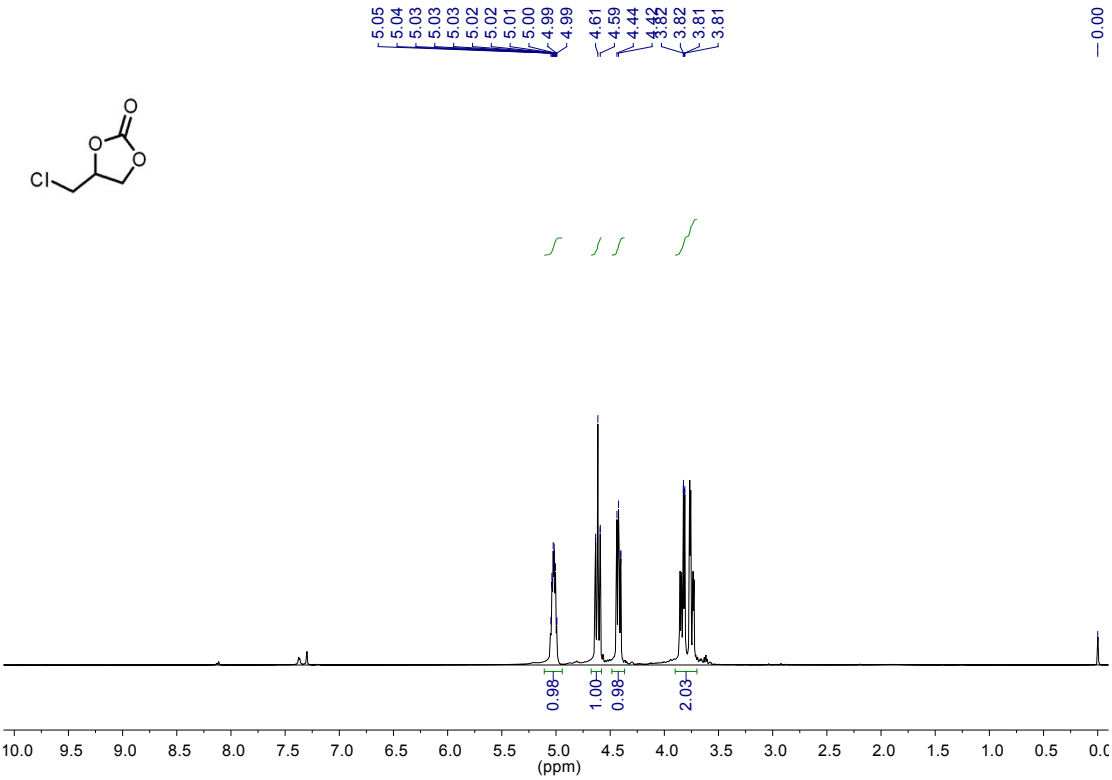
^{13}C NMR ($CDCl_3$, 100.6 MHz)



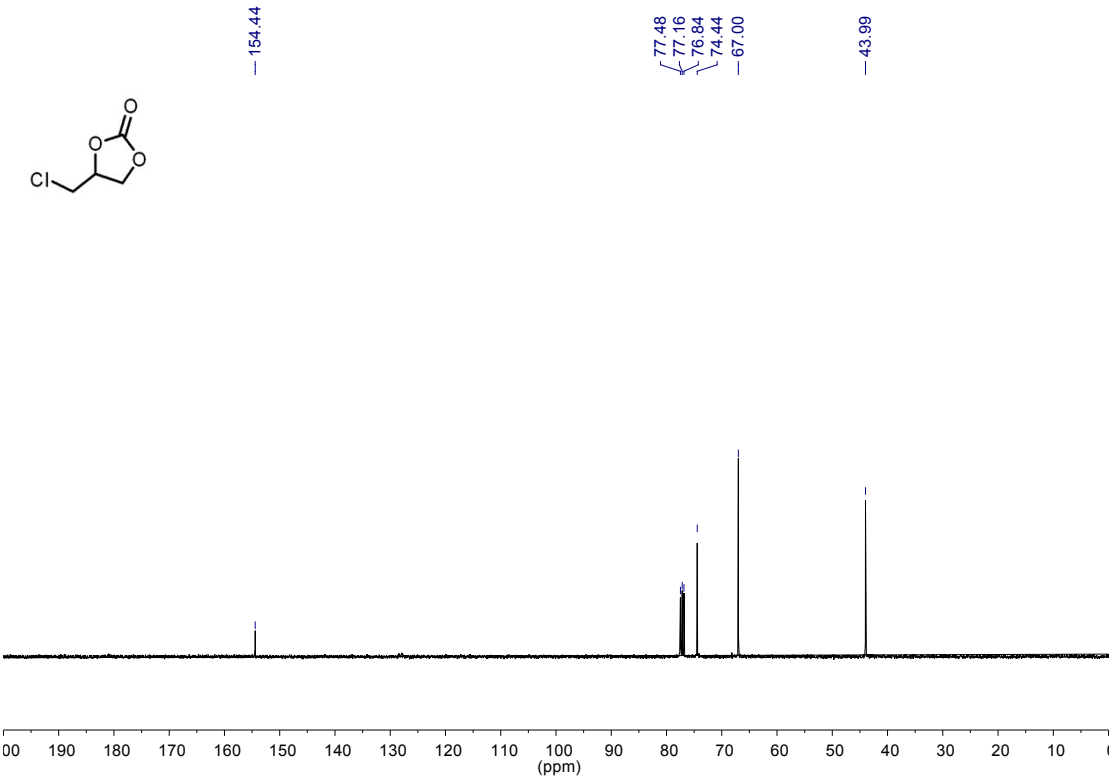
^{1}H NMR ($CDCl_3$, 400 MHz)



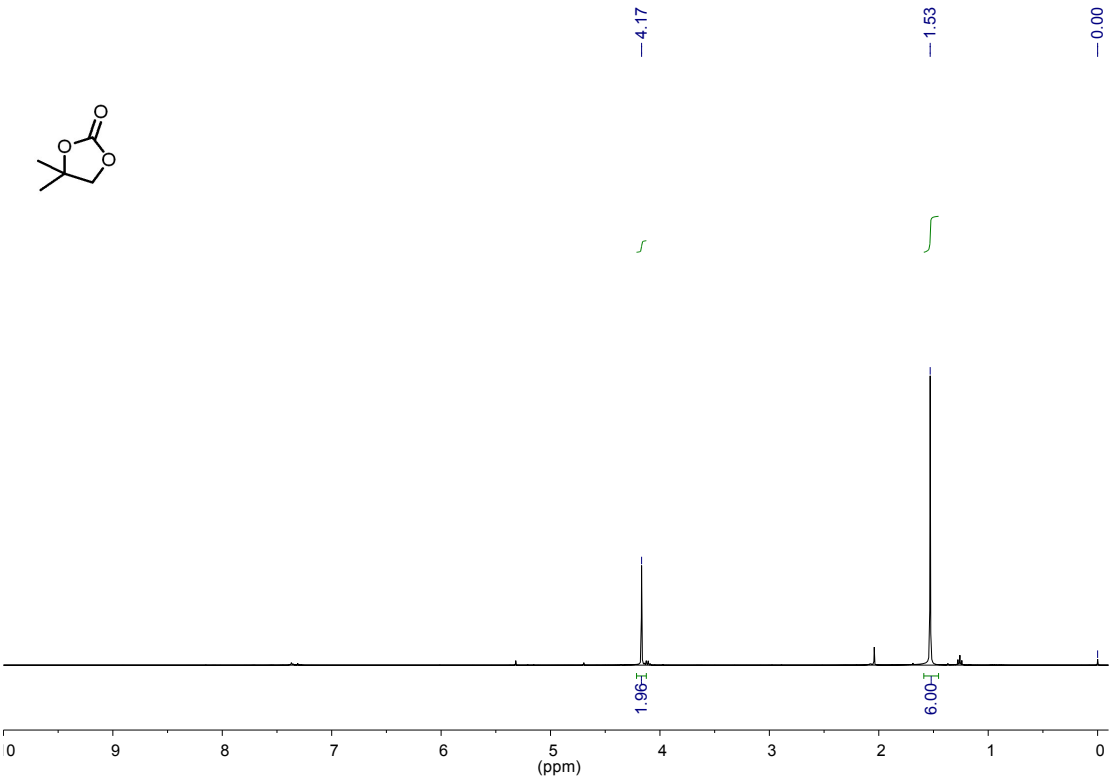
^{13}C NMR ($CDCl_3$, 100.6 MHz)



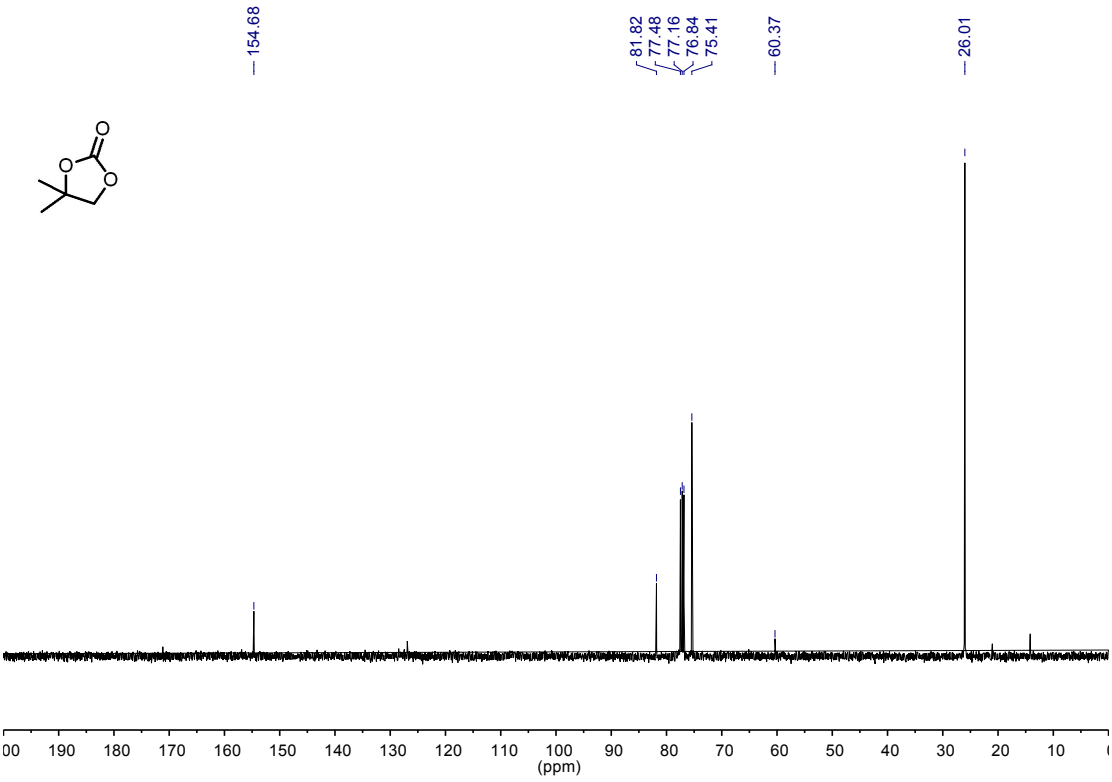
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 100.6 MHz)



^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C NMR ($CDCl_3$, 100.6 MHz)