

Supporting Information

for

Mechanism-Guided Design of Flow Systems for Multicomponent Reactions:

Conversion of CO₂ and Olefins to Cyclic Carbonates

Jie Wu,[†] Jennifer A. Kozak,[†] Fritz Simeon,[‡] T. Alan Hatton,^{*,‡} and Timothy F. Jamison^{*,†}

[†]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA, 02139

[‡]Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139

Table of Contents:

<i>Study to explore the interaction between NBS and DBU</i>	S2
<i>Further control experiments for mechanism study</i>	S4
<i>Condition optimization for the two-stream flow system</i>	S6
<i>Comparison between batch conditions and two-stream flow reactions</i>	S8
<i>Efforts towards multi-stream flow systems</i>	S9
<i>Exploring the conversion of epoxides to cyclic carbonates in flow</i>	S11
<i>General experimental</i>	S11
<i>Design and construction of the flow apparatus</i>	S12
<i>Flow reactor preparation and Execution</i>	S16
<i>Representative procedure for flow synthesis of cyclic carbonates</i>	S17
<i>Representative procedure for flow synthesis of ethylene carbonates</i>	S25
<i>Representative procedure for scale up reactions in flow</i>	S26
<i>Representative procedure for batch synthesis of cyclic carbonates</i>	S27
<i>¹H and ¹³C Spectra</i>	S28

Study to explore the interaction between NBS and DBU:

Table S1: Instant ^1H NMR study of NBS and DBU in D_2O

D

entry	NBS	DBU	results in D_2O (3 mL) ^a
1	0.6 mmol (not fully dissolved)	0.1 mmol	$[\text{D}]:[\text{DBU}]:[\text{NBS}]=0.81:1:2.5$
2	0.3 mmol	0.3 mmol	$[\text{D}]:[\text{DBU}]:[\text{NBS}]=0.55:1:0.38$
3	0.2 mmol	0.3 mmol	$[\text{D}]:[\text{DBU}]:[\text{NBS}]=0.5:1:0.12$
4	0.2 mmol	0.6 mmol	$[\text{D}]:[\text{DBU}]:[\text{NBS}]=0.25:1:0$

^a Ratios based on ^1H NMR spectra

^1H NMR study has been conducted to explore the interaction between NBS and DBU in D_2O . The ^1H NMR spectra indicated that complex **D** may be formed (Figure S1). However, the structure was not fully characterized since we were unable to isolate the complex. NMR experiment of water suppression using PRESAT has been conducted to exclude the possibility of deuterium exchange in D_2O under basic condition. Changing DBU to Et_3N did not have this interaction. Better solubility of NBS in the presence of DBU (compared to moderate solubility without DBU, 1.47 g / 100 mL water), and the slightly yellow color of the mixture solution again supported the interaction between DBU and NBS.

Moreover, the instant NMR study at various ratios of starting materials indicated an equilibration between the generated complex **D** and starting NBS and DBU (Table S1). However, long term NMR study (Figure S2 and S3) demonstrated that the reaction became more complicated in a several hour period. As shown in NMR, 1) one group of newly formed peaks moved down-field. 2) The proton peak of NBS became broad. 3) The proton peak integration of new compound **D** was changed by time. We were not clear about the exact reaction happened that caused the NMR change, however, dimerization or oligomerization may happened. Despite numerous attempts, these unstable intermediates could not be isolated from the reaction mixture.

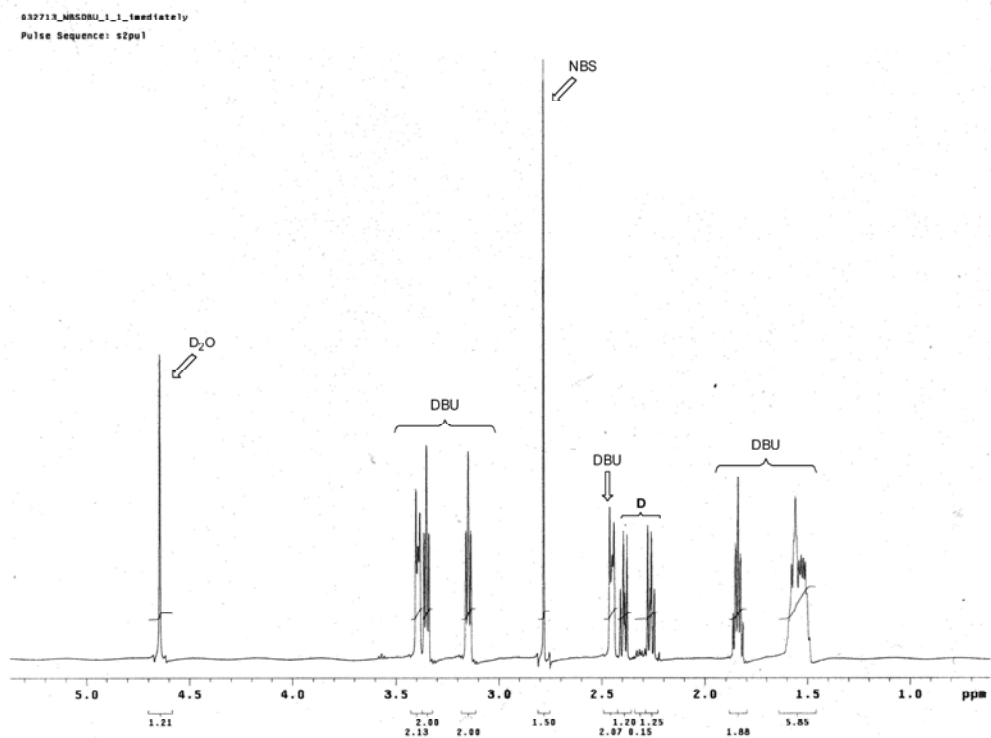


Figure S1: ¹H NMR spectra of NBS and DBU in D₂O

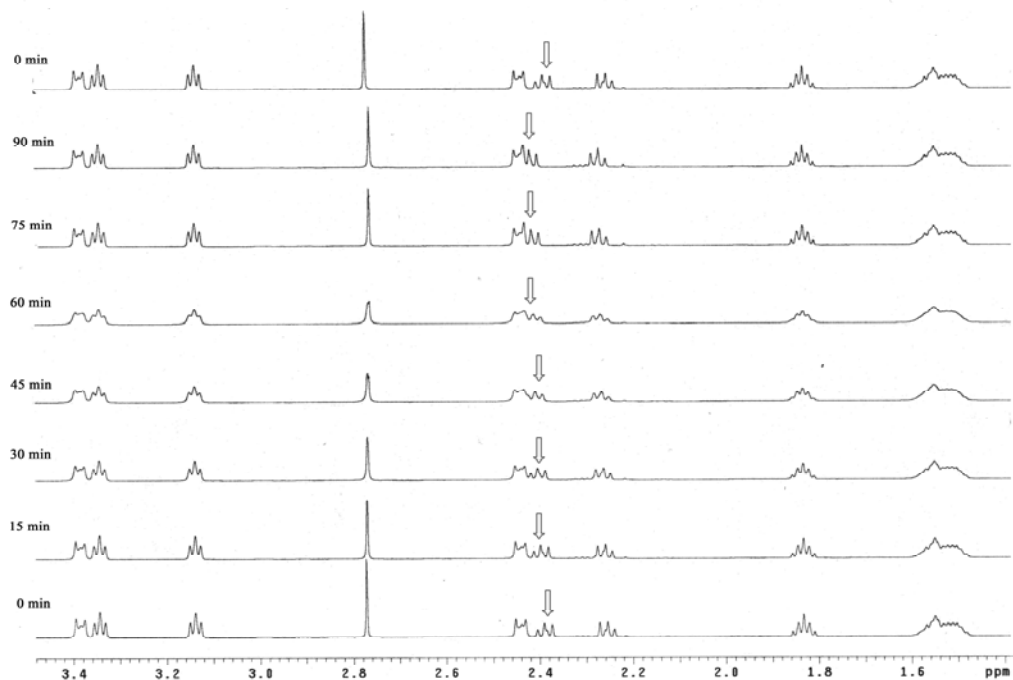


Figure S2: A two hour period ¹H NMR study of NBS and DBU in D₂O at room temperature

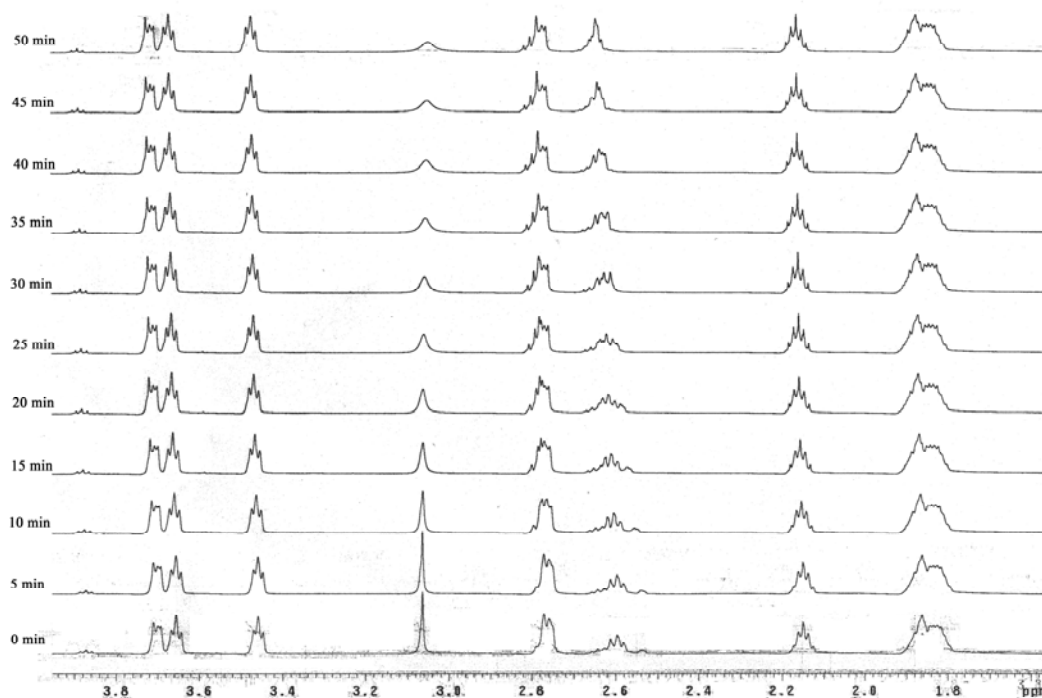


Figure S3: ^1H NMR study of NBS and DBU in D_2O at $50\text{ }^\circ\text{C}$ after mixing 2 hours at room temperature

Further control experiments for mechanism study:

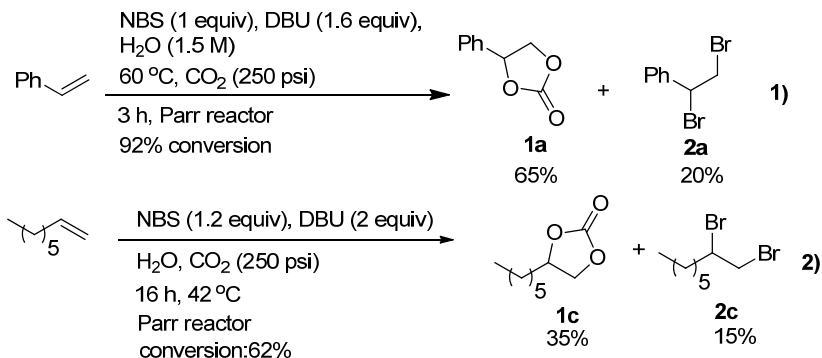
Further control experiments to explore the possible mechanism (Scheme S1) have been conducted. In our hand, both styrene and 1-octene resulted in dibromide by-products without detection of bromohydroxylation products under previous reported conditions¹ (equations 1 and 2). DBU- CO_2 bicarbonate salt **C** was prepared according to reported literature² to test whether the reaction was through pathway b. Both styrene and 1-octene were treated with **C** and NBS in a sealed tube at $50\text{ }^\circ\text{C}$ (equations 3 and 4), which exhibited similar reactivity with the reported conditions (equations 1 and 2). Water induced bicarbonate anion seemed not to be the major intermediate of this CO_2 transformation, since the reaction using NaHCO_3 resulted in various by-products (equation 5), and it also demonstrated the crucial role of DBU played in the reaction. Epoxide **4a** was tested with NBS and DBU in H_2O , which exhibited low reactivity in pressurized autoclaves and diol **5a** was observed (equation 6). Taking together reactions 6 and 7 indicated that the reaction may not go through the “bromohydrin” intermediate (path a) since that no diol

¹ N. Eghbali, C.-J. Li, *Green Chem.* **2007**, 9, 213-215.

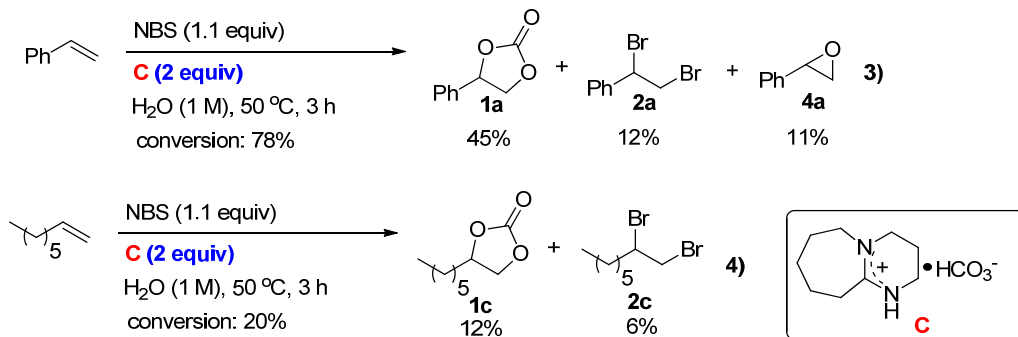
² D. J. Heldebrant, P. G. Jessop, C. A. Thomas, C. A. Eckert, C. L. Liotta, *J. Org. Chem.* **2005**, 70, 5335-5338.

product was observed in reaction 1. However, it was still highly possible that all the pathways had contribution to the formation of the final cyclic carbonates under given conditions.

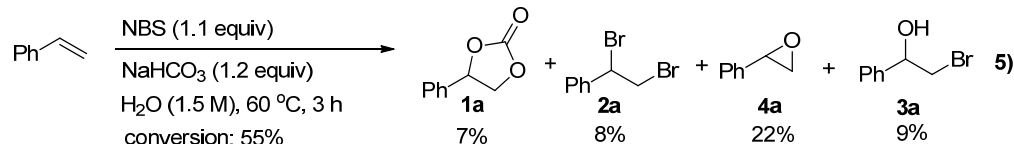
a) With reported condition



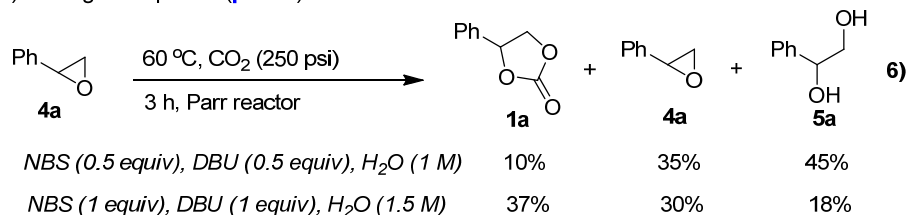
b) With DBU-CO₂ complex (**path b**)



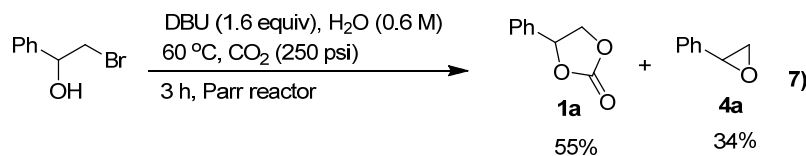
c) With bicarbonate anion (**path c**)



d) starting with epoxide (**path d**)



e) bromohydrin (**path a**)



Scheme S1: Further control experiments to explore the reaction mechanism

Condition optimization for the two-stream flow system:

A temperature study using styrene in the two-stream flow system in stainless steel tubing (SS-tubing) reactor (2 mL) exhibited that epoxide **4a** was the major product at low temperature, and reaction at 100 °C afforded the best results (80% conversion, 54% yield of carbonate **1a**, Figure S4). Temperature higher than 100 °C led to the formation of diol byproduct, and the reaction rate became unsteady. However, optimization of CO₂ pressure in flow system was fruitless, mainly because the mass flow controller stopped working at high pressure (> 200 psi) due to the high permeability of CO₂ to the polymer orifice in the controller.³

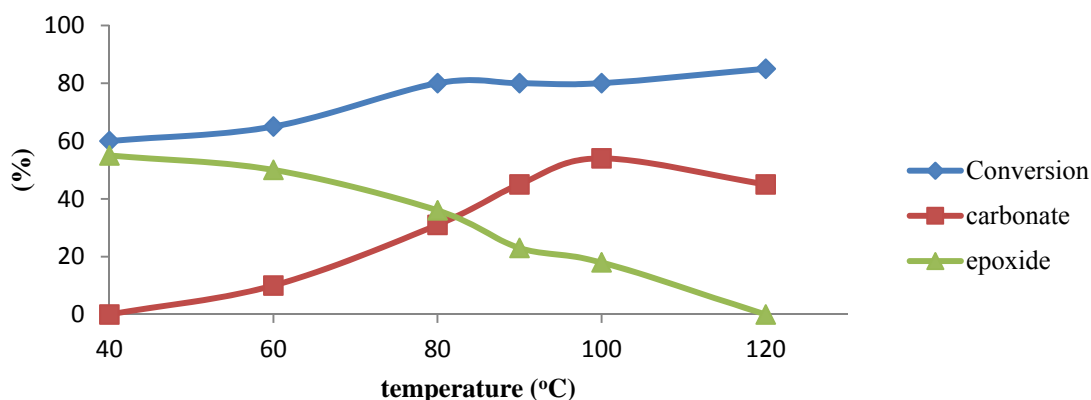


Figure S4: Temperature study in the two-stream flow system

Further optimization of the flow condition revealed that the packed-bed reactor packed with stainless powder (325 mesh, strem, 1.2 mL space volume) was more efficient than the SS-tubing reactor (Table S2, entry 1 vs 2), and the flow rate became more steady at high temperature probably due to the increased inner diameter of the reactor (0.25 inch vs 0.03 inch). Similar to SS-tubing, reactions conducted at higher temperature afforded the diol byproduct **5a** (entry 3). Diol **5a** can be directly obtained at 150 °C without formation of carbonate **1a** (entry 8). Excessive DBU was not necessary, and one equiv base resulted in an increased yield of **1a** (entry 4 vs entry 2). But sub-stoichiometric DBU decreased the yield of carbonate **1a** (entry 5). Surprisingly, longer residence time didn't help the reaction conversion (entry 6), suggesting that a small amount NBS may be decomposed during the reaction which caused the 15% unreacted starting styrene. By simply adding 1.2 equiv NBS, a full conversion was achieved within 7.5 minute reacting time to afford carbonate **1a** in 85% yield (entry 7).

³ O.M. Davies, J. C. Arnold, S. Sulley, *J. Mater. Sci.* **1999**, *34*, 417-422.

Table S2: Optimization of flow reactions with styrene

<div style="text-align: center;"> <p>NBS (1 equiv), DBU (1.6 equiv) DMF/H₂O (2:1, 0.4 M) CO₂ (130 psi), V_g/V_l = 1:1 SS-tubing or Packed-bed reactor</p> <p>1a 4a 5a</p> </div>							
entry	reactor	Temp (°C)	residence time	conversion (%) ^a	yield (%) of 1a ^b	yield (%) of 4a ^b	yield (%) of 5a ^b
1	SS-tubing	100	12 min	80	54	18	0
2	Packed-bed	100	7.5 min	85	65	5	15
3	Packed-bed	120	7 min	90	35	0	40
4 ^c	Packed-bed	100	7.5 min	85	72	5	0
5 ^d	Packed-bed	100	7.5 min	85	55	0	0
6 ^c	Packed-bed	100	15 min	85	76	0	5
7^{c,f}	Packed-bed	100	7.5 min	100	85	0	2
8 ^e	Packed-bed	150	6.5 min	100	0	0	66

^a Conversion based on GC using dodecane as the internal standard. ^b Yield were determined by ¹H NMR analysis using trichloroethylene as an external standard. ^c 1 equiv DBU was used. ^d 0.5 equiv DBU was used. ^e 2 equiv DUB was used. ^f 1.2 equiv NBS was used.

Comparison between batch conditions and two-stream flow reactions:

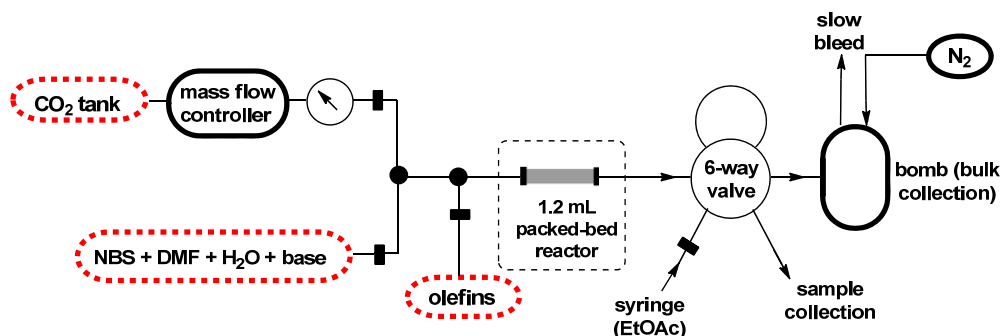
Table S3: Comparison of flow and batch reactions

entry	condition	time	conversion ^a	yield of 1a ^b	other products ^b	notes
1 ^c	CO ₂ balloon	3 h	85%	15%	36% 3a, 10% 2a 10% 4a	<ul style="list-style-type: none"> • high CO₂ permeability • low reproducibility
2 ^c	Cell tube	3 h	88%	57%	15% 3a	<ul style="list-style-type: none"> • variable pressure • low reproducibility
3 ^c	Parr reactor	3 h	92%	65%	20% 2a	<ul style="list-style-type: none"> • safety issue • cost efficiency
4 ^d	flow (SS-tubing)	12 min	80%	54%	18% 4a	<ul style="list-style-type: none"> • high surface-to-volume ratio • reduced equipment footprint • flow not always steady
5 ^d	flow (packed-bed)	7.5 min	100%	85%	no	<ul style="list-style-type: none"> • high surface-to-volume ratio • reduced equipment footprint • steady flow

^aConversion based on GC analysis using dodecane as internal standard. ^bYield based on crude ¹H NMR analysis using trichloroethylene as the external standard. ^cRxn conducted at 60 °C. ^dRxn conducted at 100 °C and DMF was applied as co-solvent to achieve a homogenous solution.

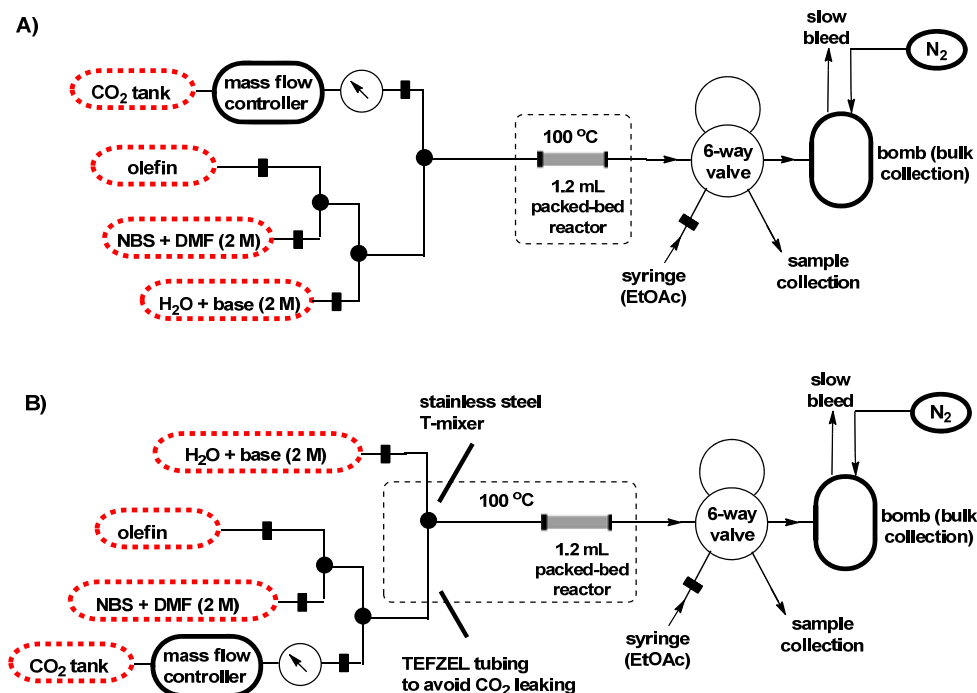
To compare the flow condition with the traditional batch condition, we carried out the same oxidative carboxylation of styrene (Table S3) in a conventional flask using a CO₂-filled balloon, a sealed cell tube with dry ice, and a pressurized autoclave (Parr reactor). Table S3 showed the results of the comparative tests where clearly demonstrated the superior of the packed-bed flow system.

Efforts towards multi-stream flow systems:



Scheme S2: The three-stream flow setup

Due to the incompatibility of NBS and olefin in DMF and the low solubility of NBS in water (1.47 g/100 mL), a three-stream flow system was designed as shown in Scheme S2. However, no matter with DBU, Cs_2CO_3 or CsHCO_3 , we encountered clogging problems. This was mainly due to the incompatibility of NBS and the bases, which slowly generated solids that were insoluble in both DMF and water. In this regards, the flow system was modified to a four-stream flow reactor (Scheme S3A). However, this setup still gave clogging problems. Once the NBS and base met in the flow system, insoluble solids started to form to block the flow tubing. Thus, following modification has been made in order to solve the clogging problems (Scheme S3B): 1) introducing CO_2 flow prior to the introduction of aqueous base solution in order to flush possibly generated solids into the heating reactor; 2) using a stainless-steel T-mixer to connect the aqueous base flow and CO_2 gas flow and maintaining it under heating; 3) changing the PFA tubing for the gas flow to TEFEZL tubing, which had less permeability of CO_2 at high temperature to avoid any possible gas leaking. In this way, the organic and inorganic solvent met at high temperature, which would help dissolve generated insoluble solids. One notable feature of the flow system described here was the switchable flow order, that the gas flow, organic flow, and inorganic flow can be introduced in any desired sequence. However, in batch conditions, especially the pressurized autoclaves, the gas flow normally had to be introduced at the last step.



Scheme S3: Switchable flow order in four-stream flow systems

Phenyl allyl ether was used to test the flow reaction in the updated four-stream flow system due to its high boiling point, and both the conversion and yield can be obtained by ^1H NMR measurement using trichloroethylene as an external standard. The reactions went smoothly with different bases (Table S4), and no clogging was observed. However, the results of conversion and yield were disappointing. Low conversion was obtained and the major product was the dibromide by-product in all the cases. Based on those results, the gas-organic-inorganic flow condition was not superior to conventional batch conditions.

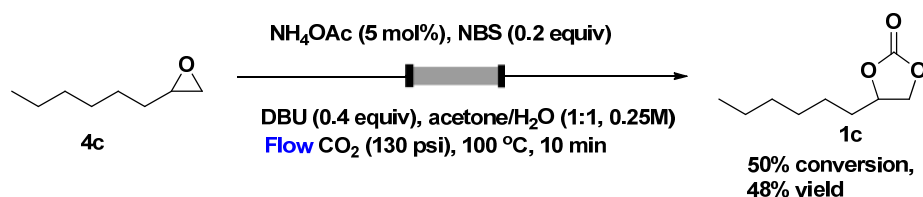
Table S4: Four-stream flow test

DMF/H ₂ O (1:1, 1 M): NBS (1.2 equiv), CO ₂ (130 psi), V _g /V _l = 1:1 R _t =10 min, 100 °C Packed-bed reactor				
entry	base	conversion (%) ^a	yield of 1d (%) ^a	Yield of 2d (%) ^a
1	DBU (2 equiv)	30	2	25

2	Cs ₂ CO ₃ (1.2 equiv)	35	5	28
3	CsHCO ₃ (1.2 equiv)	35	10	20

^a Yield and conversion are based crude ¹H NMR analysis using trichloroethylene as the external standard.

Exploring the conversion of epoxides to cyclic carbonates in flow:



Scheme S4: Conversion of epoxides in flow

Under the flow condition (Scheme S4), epoxide **4c** was converted to cyclic product **1c** in 50% conversion with only 0.2 equiv NBS and 0.4 equiv DBU. This transformation could be one reason why no epoxide by-products were observed in the flow synthesis of cyclocarbonates directly from olefins.

General Experimental Information:

All reactions sensitive to air or moisture were carried out in flame-dried glassware under an atmosphere of argon. Volumetric flasks were oven-dried and cooled in a desiccator prior to use. 5-vinylbenzo[d][1,3]dioxol-2-one and 5-vinyl-1H-indole were synthesized following a literature procedure of a similar compound.⁴ All other commercial reagents or materials were used as received without purification. Thin layer chromatography (TLC) was performed on DC-Fertigplatten SIL G-25 UV₂₅₄ pre-coated TLC plates. The developed chromatogram was visualized by UV lamp or stained using one of the following: aqueous potassium permanganate (KMnO₄) or ethanolic *para*-anisaldehyde. Selected purifications were performed using a Biotage Isolera One flash purification system, as noted in the experimental procedures.

⁴ S. N. Aslam, P. C. Stevenson, S. J. Phythian, N. C. Veitch, D. R. Hall, *Tetrahedron* **2006**, 62, 4214-4226.

Proton nuclear magnetic resonance (^1H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Varian Inova (500 MHz) in deuteriochloroform (CDCl_3) unless otherwise noted. Chemical shifts are recorded in parts per million (ppm) and are referenced to the centerline of deuteriochloroform (δ 7.24 ppm ^1H NMR; δ 77.0 ppm ^{13}C NMR). Data was recorded as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qt = quintet, m = multiplet, br = broad). Coupling constants (J values) are given in Hertz (Hz). Infrared (IR) spectra were recorded on an Agilent Cary 630 FTIR. High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR-MS) by Li Li of the Massachusetts Institute of Technology Department of Chemistry Instrumentation Facility. Gas chromatographic (GC) analysis was performed on an Agilent 7890A GC system on an Agilent HP-5 column (30 m, 0.32 mm i.d., 25 μm film thickness) with a flow rate of 1 ml/min using the following method: the oven temperature was held at 50 $^\circ\text{C}$ for 5 min and then increased linearly to 250 $^\circ\text{C}$ over 20 min with a final hold of 5 min.

Design and Construction of the Flow Apparatus:

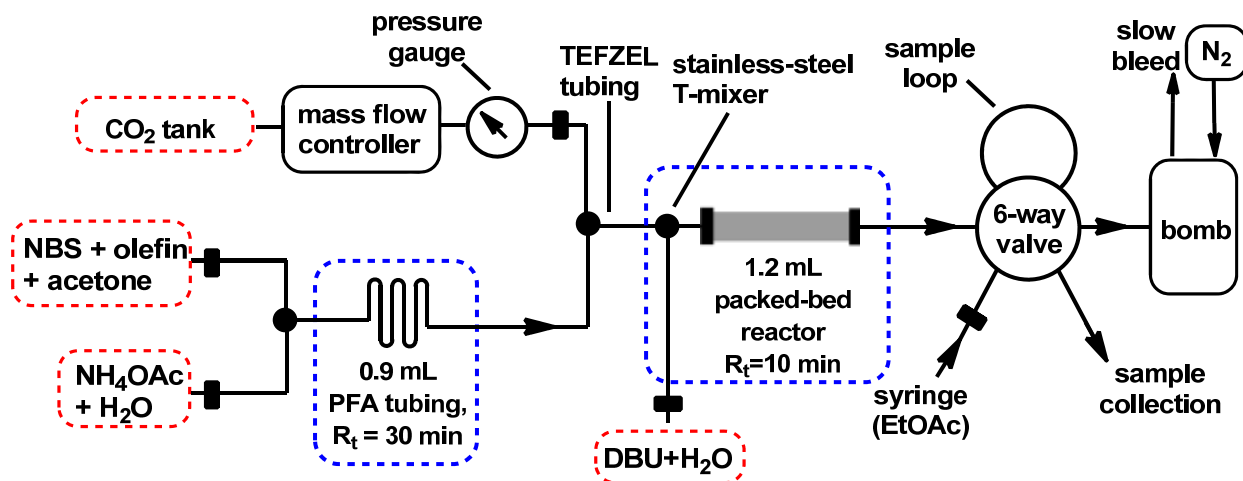


Figure S5: Schematic of the sequential continuous flow apparatus.

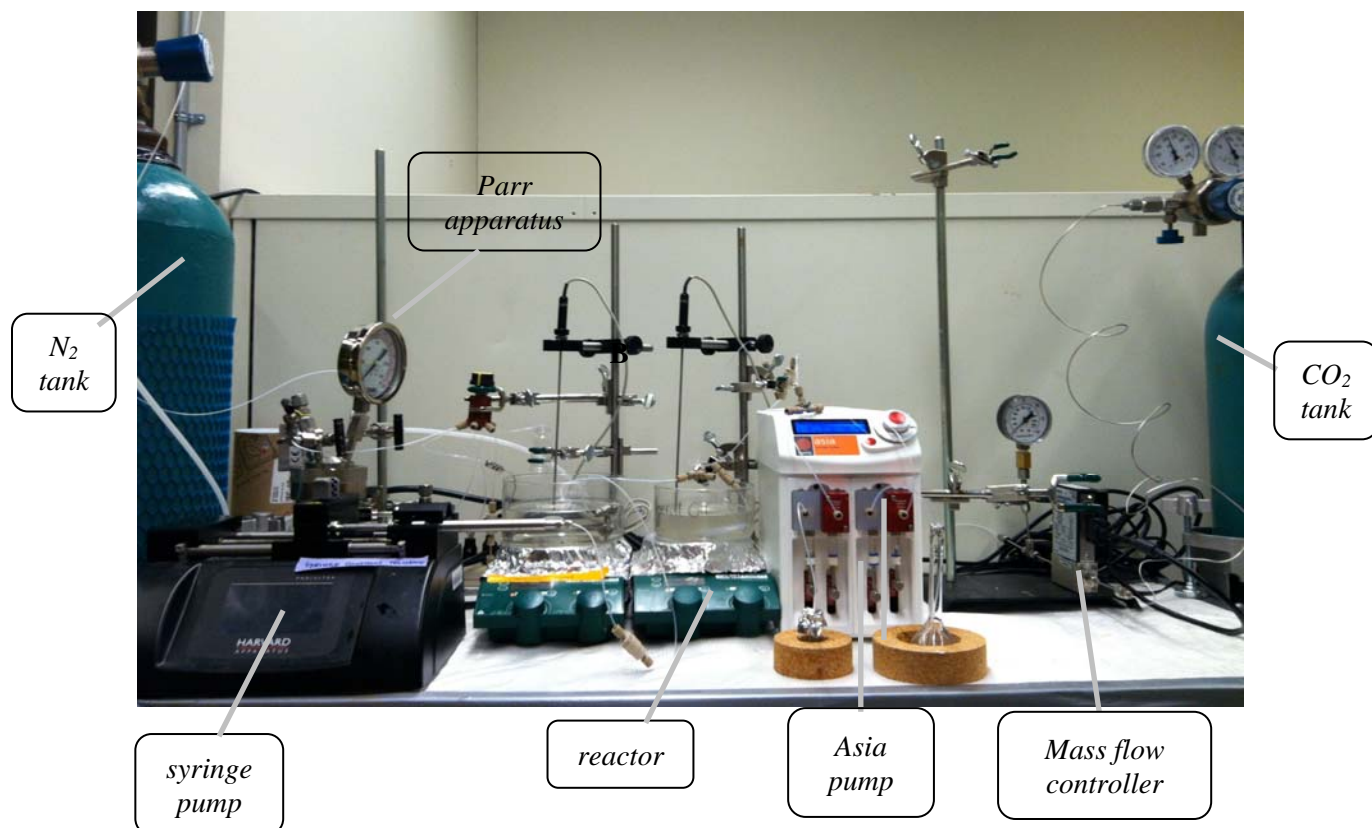


Figure S6: The full continuous flow set-up.

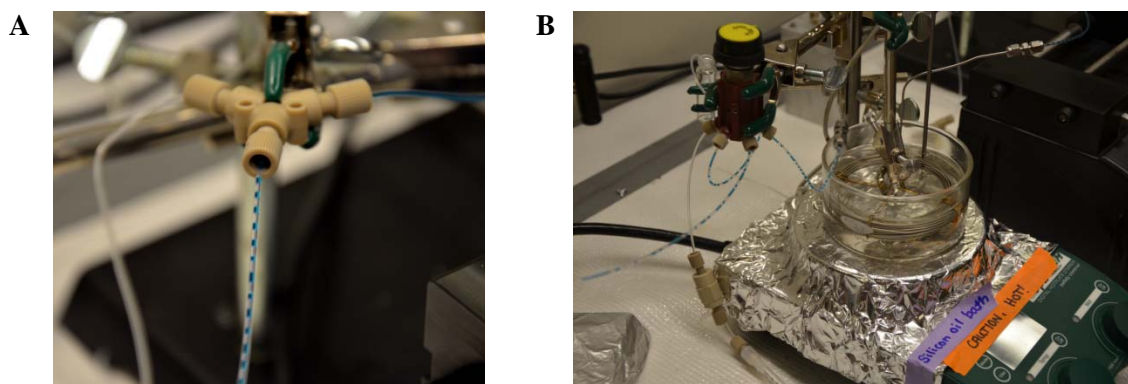
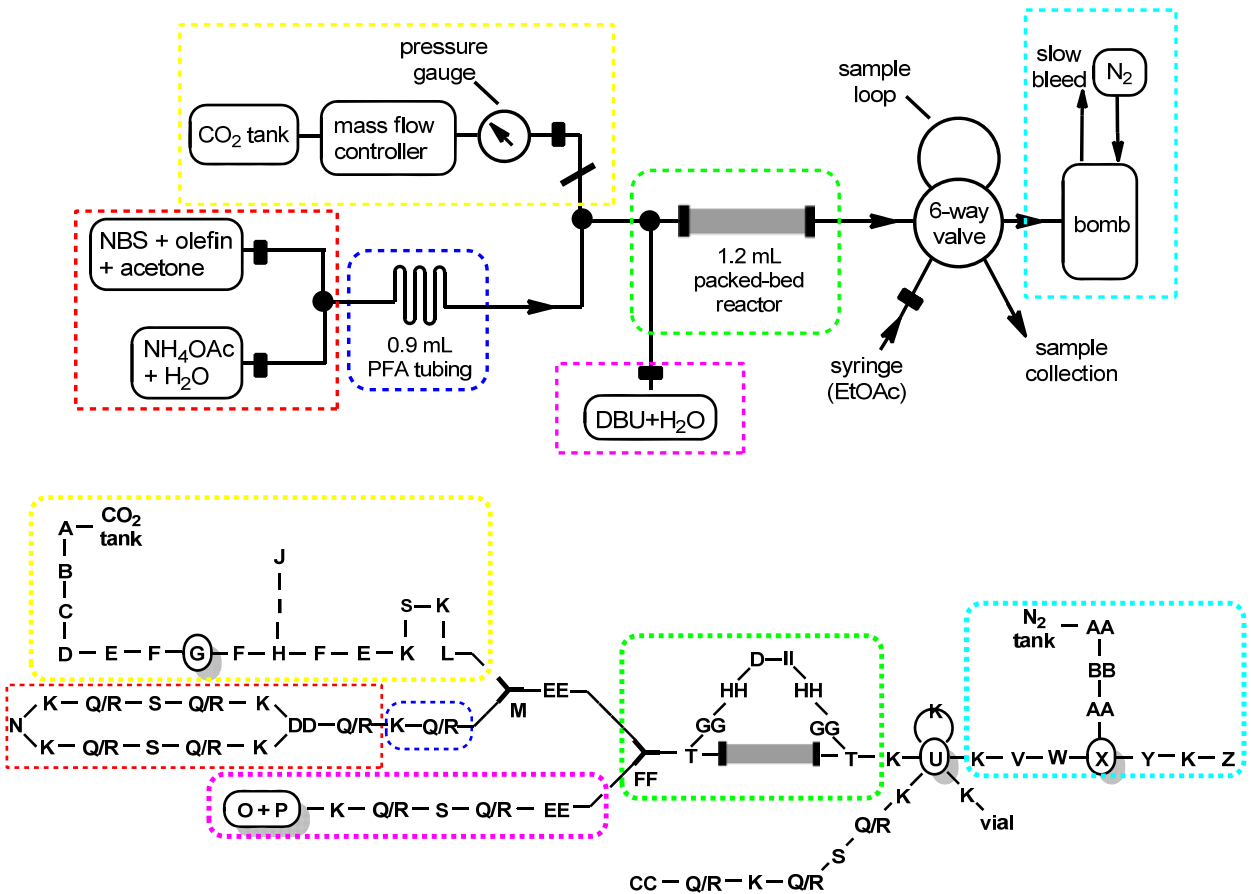


Figure S7: A. Demonstration of slug-flow (blue food coloring was added to the liquid phase).
B. Close-up of the reactor and the 6 way valve.

Table S5: Sequential continuous flow apparatus components and order of construction



Item	Vendor	Part #	Part Description
A	Airgas	Y12215F320	two stage brass 0-400 psi general regulator
B	Swagelok	SS-4-HRCG-2	hex reducing coupling 1/4" female NPT x 1/8" female NPT
C	Swagelok	SS-100-1-2	tube fitting; male connector 1/16" tube OD x 1/8" male NPT
D	McMASTER-CARR	89895K414	Type 304 Smooth-Bore Seamless SS Tubing 1/4" OD, .18" ID, .035" Wall, 6" Length
E	Swagelok	SS-200-6-1	tube fitting; reducing union 1/8" x 1/16" tube OD
F	McMaster-Carr	89895K114	SS Tubing 1/8" OD, .055" ID, .035" wall, 3" length
G	Sierra Instruments	C101-DD-1-OV1-SV1-PV2-V3-S3-C10	mass flow controller

H	Swagelok	SS-200-3	tube fitting; union tee 1/8" tube OD
I	Swagelok	SS-400-R-2	tube fitting; reducer 1/4" x 1/8" tube OD
J	Swagelok	PG1-63C-PG300-LAQX	0-300 psi gauge; 1/4" tube ADP lower mount
K	Upchurch Scientific	1912L	Tubing, Teflon® HPFA; .030" x 1/16" x 50 ft
L	Upchurch Scientific	P-732	shut off valve
M	Upchurch Scientific	P-514	Y-connector; 0.060" thru hole
N	Syrris Asia	ASP-3.0	Syrris Asia Pump
O	Harvard Apparatus	703305	PHD Ultra Remote RS485 Infuse only syringe pump
P	Harvard Apparatus	702267	8 mL stainless steel syringe with a 1/16" fitting
Q	Upchurch Scientific	P-255X	super flangeless nut, PEEK, natural
R	Upchurch Scientific	P-259X	super flangeless ferrule, 1/16", ETFE, yellow
S	Upchurch Scientific	CV-3330	check valve
T	Swagelok	SS-100-6	tube fitting, union, 1/16" tube OD
U	Upchurch Scientific	V-541	6-port injection valve
V	Swagelok	SS-102-1	nut for 1/16" Swagelok tube fitting
W	Swagelok	SS-100-7-2	tube fitting, female connector, 1/16" tube OD x 1/8" female NPT
X	Parr Instrument Company	4790 Model No. 4793	general purpose 100 mL pressure vessel (bomb)
Y	Swagelok	SS-200-6-1	tube fitting, reducing union, 1/8" x 1/16" tube OD
Z	Upchurch Scientific	P-445	micro metering valve
AA	Swagelok	SS-400-7-4	tube fitting, female connector 1/4" tube OD x 1/4" female NPT
BB	McMaster-Carr	5033K31	Teflon® PTFE 1/8" ID, 1/4" OD, " 1/16 wall, semi-clear white
CC	Upchurch Scientific	P-628	adapter, female slip luer to female, TEFZEL® (ETFE)

DD	Upchurch Scientific	P-712	TEE, WITH P-200/P-235, 1/16 IN, 1/4-28, .020 IN (.5mm) THRU HOLE, PEEK™
EE	Upchurch Scientific	1528L	TUBING, TEFZEL® (ETFE), .030 IN x 1/16 IN x 50 FT, NATURAL
FF	Swagelok	23171	Swagelok Fitting, Stainless Steel, 1/16", Tee
GG	Swagelok	SS-400-6-1	SS Swagelok Tube Fitting, Reducing Union, 1/4 in. x 1/16 in. Tube OD
HH	Upchurch Scientific	A-122x	Frits.188 in x .074 in x .254 in, stainless steel, 20 um
II	Strem Chemicals, Inc.	93-2671	Stainless steel powder, type 316

Flow Reactor Preparation and Execution:

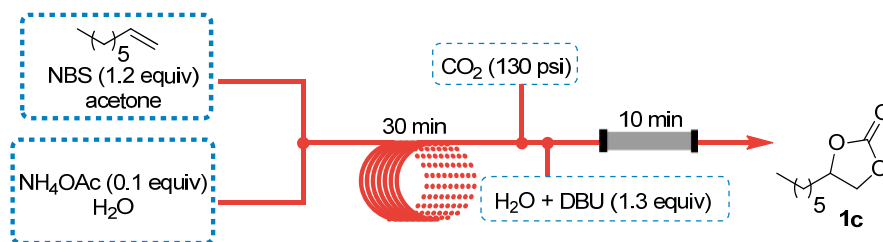
First, the CO₂ tank is pressurized to ~20 psi higher (~150 psi) than the desired back-pressure of the system (130 psi). The system must be pressurized and all the air expelled prior to the start of the reaction. To do this, the shut-off valve is closed and the mass flow controller set to purge. When the pressure gauge reads the same value as the CO₂ tank regulator gauge, it is fully pressurized. At this point the shut-off valve can be opened and closed to expel any air in the system. The back-pressure of the system (the nitrogen tank) is set to the desired pressure (130 psi). A Syrris Asia pump is pumped with olefins (10 mmol, 1.0 equiv) and NBS (2.13 g, 12 mmol, 1.2 equiv) in acetone (total 20 mL) and NH₄OAc (77 mg, 1 mmol, 0.1 equiv) in H₂O (10 mL). A stainless steel Harvard Apparatus syringe (8 mL) is filled with DBU (1.3 M, 1.3 equiv) water solution and placed in the syringe pump. Once the back-pressure is set, the Syrris Asia pump is started with 20 µL/min of acetone solution and 10 µL/min of water solution. Harvard syringe pump is started (10 µL/min) and the mass flow controller is switched from purge to the desired setting (in sccm). The system will take approximately 30 minutes to equilibrate. During this time the reactor coil is brought to the desired temperature using a silicon oil bath (40 °C and 100 °C for aliphatic olefins, 30 °C and 85 °C for aromatic olefins), and the flow rates adjusted to obtain 1:1 v:v liquid/gas slug flow. The 6-way valve must be in the LOAD position.

Once a steady flow rate is observed, the system then must reach equilibrium. This is approximately three reactor volumes plus the volume of the reagent loop located on the 6-way

valve. For example, if a reaction has a t_R of 30 minutes, the equilibration time is approximately 2 h. When the system has reached its equilibrium, a collection vial is placed under the sample collection tube, and the 6-way valve can be switched to the INJECT position. The vial must be in place as the pressurized CO₂ in the reagent loop will expel some of the liquid rapidly. A syringe filled with ethyl acetate then pushes out any remaining product into the vial. After the sample is collected, the 6-way valve can be switched back to LOAD. At this point, the parameters of the system can be changed and the process repeated.

Quantitative yields were obtained as follows: Due to non-linear effects observed for the cyclic carbonate product on the GC instrument, ¹H NMR was used to determine the yields of the products. After collection of a sample from the 6-way valve, a known amount of the solution (400 µL) was accurately measured into a new vial. The solution was then diluted with ethyl acetate and water and brine added. After mixing the biphasic solution, a pipette was used to withdraw the organic layer, and filter it through a pipette containing sodium sulfate, into a 25 mL round-bottomed flask. The aqueous layer was extracted a further three times. The combined organic fractions were concentrated *in vacuo* to afford a brown liquid. A known amount of an external standard trichloroethylene (9 µL, 0.1 mmol) was added to the round-bottomed flask, and the mixture was taken into CDCl₃ for ¹H NMR analysis.

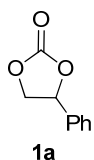
Representative Continuous Flow Procedure for Cyclic Carbonate Formation:



4-Hexyl-1,3-dioxolan-2-one (1c)

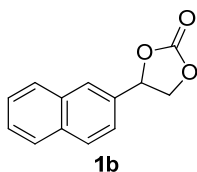
A 20 mL volumetric flask was charged with 1-octene (1.56 mL, 10 mmol, 1 equiv), NBS (2.13 g, 12 mmol, 1.2 equiv) and acetone. The volumetric flask was filled to the mark with acetone (0.5 M). A 10 mL volumetric flask was charged with NH₄OAc (77 mg, 1 mmol, 0.1 equiv) and 10 mL H₂O. Another 10 mL volumetric flask was charged with 1.94 mL DBU (13 mmol, 1.3

equiv), and was filled to the mark with water. A Syrris Asia pump was pumped with the acetone solution and $\text{NH}_4\text{OAc}/\text{H}_2\text{O}$ solution, and then attached to the flow system. An 8 mL, stainless steel Harvard Apparatus syringe was filled with the DBU/ H_2O solution and then attached to the flow apparatus (syringe pump). The flow apparatus itself was set up as described above. After the system running approximately $4 t_R$ (~ 2 h), a sample was taken using the 6-way valve. The sample was analyzed by ^1H NMR, which indicated a yield of 75% of the title compound **1c**. IR (neat): 2928, 2859, 1788, 1384, 1165, 1059, 774 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 4.67 (qd, $J = 7.5, 5.5$ Hz, 1H), 4.50 (t, $J = 8.1$ Hz, 1H), 4.04 (dd, $J = 8.3, 7.3$ Hz, 1H), 1.79-1.73 (m, 1H), 1.68-1.61 (m, 1H), 1.45-1.27 (m, 10H), 0.86 (t, $J = 6.9$ Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 155.1, 77.1, 69.4, 33.9, 31.5, 28.8, 24.3, 22.5. HRMS (DART) m/z calcd for $\text{C}_9\text{H}_{20}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$: 190.1438. Found: 190.1438.



4-Phenyl-1,3-dioxolan-2-one (**1a**)

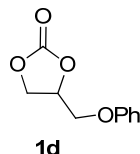
Styrene (1.1 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 80% yield to the title compound **1a**. IR (neat): 1784, 1670, 1160, 1050 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 7.44-7.36 (m, 3H), 7.36-7.28 (m, 2H), 5.64 (t, $J = 8.0$ Hz, 1H), 4.7867 (t, $J = 8.4$ Hz, 1H), 4.30 (dd, $J = 8.6, 7.9$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 154.9, 135.8, 129.8, 129.3, 125.9, 78.0, 71.2. HRMS (DART) m/z calcd for $\text{C}_9\text{H}_{12}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$: 182.0812. Found: 182.0810.



4-(Naphthalen-2-yl)-1,3-dioxolan-2-one (**1b**)

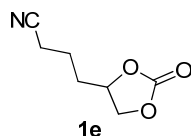
1-vinylnaphthalene (1.54g, 10 mmol) was added according to the representative procedure. 30 mL volumetric flask was used to introduce 10 mL more acetone to help dissolving. Acetone solution flow rate at 30 $\mu\text{L}/\text{min}$. ^1H NMR analysis of the final sample indicated 85% yield to the

title compound **1b**. IR (neat): 2925, 2855, 1795, 1712, 1165, 1058 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 7.88 (d, $J = 8.5\text{Hz}$, 1H), 7.83 (m, 3H), 7.53 (m, 2H), 7.39(dd, $J = 8.4\text{ Hz}$, 2Hz, 1H), 5.79(t, $J = 8.0\text{ Hz}$, 1H), 4.82(t, $J = 8.5\text{ Hz}$, 1H), 4.38(t, $J = 8.0\text{ Hz}$, 1H). ^{13}C NMR (125 MHz, CDCl_3): 154.9, 133.5, 132.8, 132.8, 129.4, 128.0, 127.7, 127.0, 126.9, 125.7, 122.3, 78.1, 71.0. HRMS (DART) m/z calcd for $\text{C}_{13}\text{H}_{11}\text{O}_3$ $[\text{M}+\text{H}]^+$: 215.0708. Found: 215.0704.



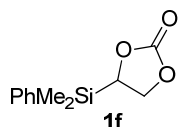
4-(Phenoxymethyl)-1,3-dioxolan-2-one (**1d**)

Allyl phenyl ether (1.372 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 80% yield to the title compound **1d**. IR (solid film): 2927, 1783, 1600, 1490, 1396, 1161, 1081, 1009 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 7.34-7.20 (m, 2H), 7.03-6.94 (m, 1H), 6.93-6.82 (m, 2H), 5.04-4.98 (m, 1H), 4.60 (t, $J = 8.4\text{ Hz}$, 1H), 4.51 (dd, $J = 8.5, 5.9$, 1H), 4.21 (dd, $J = 10.6, 4.2\text{ Hz}$, 1H), 4.12 (dd, $J = 10.6, 3.6\text{ Hz}$, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 157.8, 154.7, 129.7, 122.0, 114.6, 74.1, 66.9, 66.3. HRMS (DART) m/z calcd for $\text{C}_{10}\text{H}_{14}\text{NO}_4$ $[\text{M}+\text{NH}_4]^+$: 212.0917. Found: 212.0916.



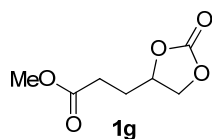
4-(2-Oxo-1,3-dioxolan-4-yl)butanenitrile (**1e**)

Hex-5-enenitrile (1.135 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 71% yield to the title compound **1e**. IR (solid film): 2927, 2247, 1781, 1390, 1164, 1057 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 4.71 (m, 1H), 4.55(t, $J = 8.5\text{ Hz}$, 1H), 4.06 (t, $J = 7.0\text{ Hz}$, 1H), 2.42 (m, 2H), 1.85(m, 3H), 1.74 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 154.6, 118.9, 75.9, 69.0, 32.5, 20.8, 16.6. HRMS (DART) m/z calcd for $\text{C}_7\text{H}_{10}\text{NO}_3$ $[\text{M}+\text{H}]^+$: 156.0661. Found: 156.0661.



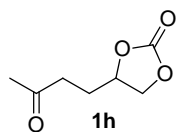
4-(Dimethyl(phenyl)silyl)-1,3-dioxolan-2-one (**1f**)

Dimethyl(phenyl)(vinyl)silane (1.82 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 75% yield to the title compound **1f**. IR (solid film): 2962, 1782, 1378, 1254, 1160, 1044, 910 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 7.50(m, 2H), 7.39(m, 3H), 4.46 (m, 2H), 4.18 (dd, $J=13.5, 12.5$ Hz, 1H), 0.44 (s, 3H), 0.43 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 156.3, 133.7, 132.4, 130.1, 128.1, 70.7, 67.0, -6.2, -6.8. HRMS (DART) m/z calcd for $\text{C}_{11}\text{H}_{18}\text{NO}_3\text{Si}$ $[\text{M}+\text{NH}_4]^+$: 240.1056. Found: 240.1055.



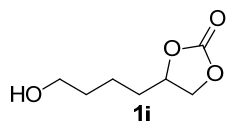
Methyl 3-(2-oxo-1,3-dioxolan-4-yl)propanoate (**1g**)

Methyl pent-4-enoate (1.14 g, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 82% yield to the title compound **1g**. IR (solid film): 1786, 1729, 1360, 1158, 1059, 980 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 4.77 (m, 1H), 4.54 (t, $J = 8.1$ Hz, 1H), 4.07 (dd, $J = 6.9, 15.6$ Hz, 1H), 3.67 (s, 3H), 2.51 (m, 2H), 2.03 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 172.4, 154.6, 75.8, 69.2, 51.8, 28.9. HRMS (DART) m/z calcd for $\text{C}_7\text{H}_{14}\text{NO}_5$ $[\text{M}+\text{NH}_4]^+$: 192.0872. Found: 192.0855.



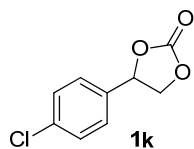
4-(3-Oxobutyl)-1,3-dioxolan-2-one (**1h**)

Hex-5-en-2-one (1.2 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 85% yield to the title compound **1h**. IR (solid film): 2920, 1782, 1394, 1159, 1055 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 4.72 (m, 1H), 4.52 (dd, $J = 8.5, 8.0$ Hz, 1H), 4.04 (dd, $J = 9.0, 7.0$ Hz, 1H), 2.64 (t, $J = 7.0$ Hz, 2H), 2.14 (s, 3H), 2.01 (m, 1H), 1.87 (m, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 206.8, 154.7, 76.0, 69.4, 38.0, 29.9, 27.6. HRMS (DART) m/z calcd for $\text{C}_7\text{H}_{14}\text{NO}_4$ $[\text{M}+\text{NH}_4]^+$: 176.0923. Found: 176.0914.



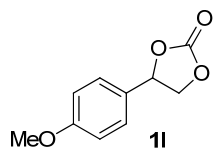
4-(4-Hydroxybutyl)-1,3-dioxolan-2-one (**1i**)

Hex-5-en-1-ol (1.2 mL, 10 mmol), DBU (2.3 equiv) were added according to the representative procedure. ^1H NMR analysis of the final sample indicated 73% yield to the title compound **1i**. IR (solid film): 3414, 2932, 2868, 1775, 1165, 1055 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): 4.70 (m, 1H), 4.51(t, $J = 8.0$ Hz, 1H), 4.06 (t, $J = 7.0$ Hz, 1H), 3.64 (t, $J = 5.5$ Hz, 2H), 1.81 (m, 1H), 1.73 (m, 1H), 1.64 (br, 1H), 1.56(m, 3H), 1.46(m, 1H). ^{13}C NMR (125 MHz, CDCl_3): 155.2, 77.0, 69.3, 61.9, 33.4, 31.8, 20.7. HRMS (DART) m/z calcd for $\text{C}_7\text{H}_{16}\text{NO}_4$ $[\text{M}+\text{NH}_4]^+$: 178.1079. Found: 178.1070.



4-(3-Chlorophenyl)-1,3-dioxolan-2-one (**1k**)

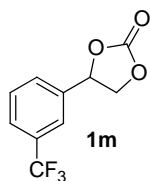
1-Chloro-4-vinylbenzene (1.2 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 85% yield to the title compound **1k**. IR (solid film): 3577, 2966, 2126, 1789, 1489, 1162, 1048, 955 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 7.37 (m, 2H), 7.26 (m, 2H), 5.64 (t, $J = 8.0$ Hz, 1H), 4.78 (t, $J = 8.0$ Hz, 1H), 4.27 (t, $J = 8.0$ Hz, 1H). ^{13}C NMR (125MHz, CDCl_3): δ 154.5, 135.5, 134.2, 129.3, 127.2, 77.2, 70.9. HRMS (DART) m/z calcd for $\text{C}_9\text{H}_8\text{ClO}_3$ $[\text{M}+\text{H}]^+$: 199.0162. Found: 199.0156.



4-(4-Methoxyphenyl)-1,3-dioxolan-2-one (**1l**)

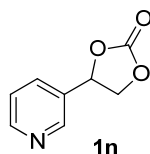
1-Methoxy-4-vinylbenzene (1.33 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 57% yield to the title compound **1l**. IR (solid film): 2962, 2925, 1783, 1250, 1161, 1050 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): 7.27 (m, 2H), 6.93 (m, 2H), 5.60 (t, $J = 8.5$ Hz, 1H), 4.73 (t, $J = 8.5$ Hz, 1H), 4.32 (t, $J = 8.0$ Hz, 1H), 3.80

(s, 3H). ^{13}C NMR (125 MHz, CDCl_3): 160.7, 154.9, 127.8, 127.3, 114.5, 78.1, 71.1, 55.3. HRMS (DART) m/z calcd for $\text{C}_{10}\text{H}_{14}\text{NO}_4$ $[\text{M}+\text{NH}_4]^+$: 212.0923. Found: 212.0918.



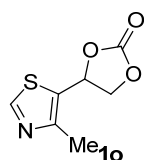
4-(3-(Trifluoromethyl)phenyl)-1,3-dioxolan-2-one (1m)

1-(Trifluoromethyl)-3-vinylbenzene (1.48 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 86% yield to the title compound **1m**. IR (solid film): 2923, 1793, 1326, 1066, 902 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 7.67(d, J = 7.0 Hz, 1H), 7.56 (m, 3H), 5.74(t, J = 8.0 Hz, 1H), 4.85(t, J = 8.5 Hz, 1H), 4.31 (t, J = 8.0 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 154.4, 136.9, 131.6 (q), 129.9, 129.0, 126.4, 123.5 (q), 122.6, 77.1, 70.9 (q). HRMS (DART) m/z calcd for $\text{C}_{10}\text{H}_7\text{F}_3\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 255.0245. Found: 255.0255.



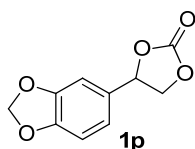
4-(Pyridin-3-yl)-1,3-dioxolan-2-one (1n)

3-Vinylpyridine (1.07 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 48% yield to the title compound **1n**. IR (solid film): 2924, 2854, 1795, 1434, 1165, 1071, 968 cm^{-1} . ^1H NMR (300 MHz, CDCl_3): δ 8.68 (dd, J = 1.8, 4.8 Hz, 2H), 8.6 (d, J = 2.4 Hz, 2H), 7.74 (dt, J = 2.1, 8.1 Hz, 1H), 7.40 (dd, J = 4.8, 8.4 Hz, 1H), 5.72(t, J = 8.1 Hz, 1H), 4.84 (t, J = 8.7 Hz, 1H), 4.35 (dd, J = 7.8, 9.0 Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 154.2, 151.2, 147.6, 133.4, 131.5, 124.0, 75.7, 70.7. HRMS (DART) m/z calcd for $\text{C}_8\text{H}_8\text{NO}_3$ $[\text{M}+\text{H}]^+$: 166.0504. Found: 166.0502.



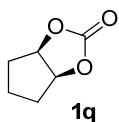
4-(2-Oxo-1,3-dioxolan-4-yl)butanenitrile (**1o**)

4-Methyl-5-vinylthiazole (1.15 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 62% yield to the title compound **1o**. IR (solid film): 2923, 2854, 1796, 1710, 1157, 1056, 949 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 8.79 (s, 1H), 7.24 (s, 1H), 5.99 (t, $J = 8.0$ Hz, 1H), 4.82 (t, $J = 8.0$ Hz, 1H), 4.38 (t, $J = 8.0$ Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3): δ 183.0, 153.7, 153.1, 125.9, 71.7, 71.0, 15.5. HRMS (DART) m/z calcd for $\text{C}_7\text{H}_8\text{NO}_3\text{S}$ $[\text{M}+\text{H}]^+$: 186.0225. Found: 186.0217.



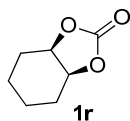
4-(Benzo[d][1,3]dioxol-5-yl)-1,3-dioxolan-2-one (**1p**)

5-Vinylbenzo[d][1,3]dioxole (1.48 g, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 72% yield to the title compound **1p**. IR (solid film): 2920, 1787, 1447, 1247, 1162, 1033, 923 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 6.8 (m, 3H), 5.96 (s, 2H), 5.55 (t, $J = 8.0$ Hz, 1H), 4.71 (t, $J = 8.5$ Hz, 1H), 4.27 (t, $J = 8.5$ Hz, 1H). ^{13}C NMR (125 MHz, CDCl_3): δ 154.7, 148.7, 148.4, 129.1, 120.4, 108.5, 106.1, 101.5, 78.1, 71.0. HRMS (DART) m/z calcd for $\text{C}_{10}\text{H}_9\text{O}_5$ $[\text{M}+\text{H}]^+$: 209.0450. Found: 209.0447.



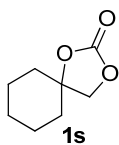
cis-Tetrahydro-3aH-cyclopenta[d][1,3]dioxol-2-one (**1q**)

Cyclopentene (0.882 mL, 10 mmol) was added according to the representative procedure. ^1H NMR analysis of the final sample indicated 85% yield to the title compound **1q**. IR (solid film): 2970, 1784, 1717, 1373, 1165, 1043, 929 cm^{-1} . ^1H NMR (500 MHz, CDCl_3): δ 5.08 (dd, $J = 4.0, 2.0$ Hz, 1H), 2.14 (m, 2H), 1.78 (m, 2H), 1.64 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3): δ 155.4, 81.8, 33.2, 21.5. HRMS (DART) m/z calcd for $\text{C}_6\text{H}_{12}\text{NO}_3$ $[\text{M}+\text{NH}_4]^+$: 146.0817. Found: 146.0817.



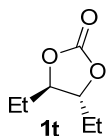
***cis*-Hexahydrobenzo[d][1,3]dioxol-2-one (1r)**

Cyclohexene (1.01 mL, 10 mmol) was added according to the representative procedure. ¹H NMR analysis of the final sample indicated 49% yield to the title compound **1r**. IR (solid film): 2942, 1796, 1523, 1166, 1030, 996 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 4.66 (m, 2H), 1.88 (q, *J* = 5.5 Hz, 4H), 1.60 (m, 2H), 1.41 (m, 2H). ¹³C NMR (125 MHz, CDCl₃): δ 155.3, 75.7, 26.8, 19.2. HRMS (DART) *m/z* calcd for C₇H₁₄NO₃ [M+NH₄]⁺: 160.0974. Found: 160.0965.



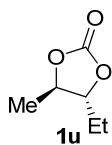
1,3-Dioxaspiro[4.5]decan-2-one (1s)

Methylenecyclohexane (1.2 mL, 10 mmol) was added according to the representative procedure. ¹H NMR analysis of the final sample indicated 52% yield to the title compound **1s**. IR (solid film): 2936, 2864, 1786, 1200, 1052, 965 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 4.10 (s, 2H), 1.88 (m, 2H), 1.75 (m, 2H), 1.63 (m, 2H), 1.5 (m, 3H), 1.38 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 154.6, 83.2, 74.4, 35.4, 24.4, 22.2. HRMS (DART) *m/z* calcd for C₈H₁₃O₃ [M+NH₄]⁺: 157.0865. Found: 157.0859.



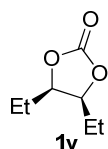
***trans*-4,5-Diethyl-1,3-dioxolan-2-one (1t)**

trans-Hex-3-ene (1.24 mL, 10 mmol) was added according to the representative procedure. ¹H NMR analysis of the final sample indicated 81% yield to the title compound **1t**. IR (solid film): 2974, 1786, 1463, 1374, 1174, 1035, 913 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 4.19 (m, 2H), 1.72 (m, 4H), 1.02 (t, *J* = 7.5 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 154.7, 82.5, 26.8, 8.7. HRMS (DART) *m/z* calcd for C₇H₁₆NO₃ [M+NH₄]⁺: 162.1130. Found: 162.1131.



***cis*-4-Ethyl-5-methyl-1,3-dioxolan-2-one (1u)**

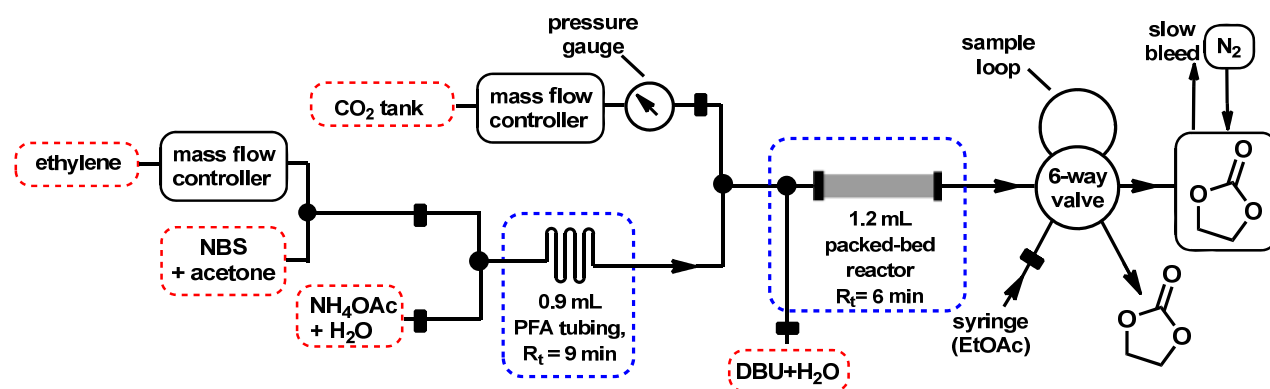
(*E*)-Pent-2-ene (1.079 mL, 10 mmol) was added according to the representative procedure. ¹H NMR analysis of the final sample indicated 83% yield to the title compound **1u** as a pure *trans* isomer. IR (solid film): 2975, 1786, 1373, 1186, 1010 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 4.35 (m, 1H), 4.11 (m, 1H), 1.71 (m, 2H), 1.41 (d, *J* = 3.5 Hz, 4H), 0.99 (t, *J* = 7.0 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃): δ 154.5, 84.4, 78.0, 26.1, 19.1, 8.7. HRMS (DART) *m/z* calcd for C₆H₁₄NO₃ [M+NH₄]⁺: 148.0974. Found: 148.0976.



cis-4,5-Diethyl-1,3-dioxolan-2-one (**1v**)

cis-Hex-3-ene (1.23 mL, 10 mmol) was added according to the representative procedure. ¹H NMR analysis of the final sample indicated 80% yield to the title compound **1v** as a mixture of 4:1 *cis/trans* isomers. IR (solid film): 2975, 1785, 1367, 1186, 1027, 999 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 4.54 (m, 2H), 1.64 (m, 4H), 1.03 (m, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 154.8, 81.2, 22.1, 10.1. HRMS (DART) *m/z* calcd for C₇H₁₃O₃ [M+H]⁺: 145.0865. Found: 145.0858.

Representative procedure for flow synthesis of ethylene carbonates



First, the CO₂ tank was pressurized to ~30 psi higher (~120 psi) than the desired back-pressure of the system (90 psi); ethylene tank was pressurized to ~20 psi higher (~110 psi) than the back-pressure. The back-pressure of the system (the nitrogen tank) was set to 90 psi. A Syrris

Asia pump was pumped with NBS (1.78 g, 10 mmol, 1 equiv) in acetone (total 20 mL) and NH₄OAc (77 mg, 1 mmol, 0.1 equiv) in H₂O (10 mL). A stainless steel Harvard Apparatus syringe (8 mL) was filled with DBU (1.3 M, 1.3 equiv) water solution and placed in the syringe pump. Both the CO₂ tank and ethylene tank were opened and the mass flow controllers were set at “purge”. Once the back-pressure was set, the Syrris Asia pump was started with 20 µL/min of acetone solution and 10 µL/min of water solution. Harvard syringe pump was started (10 µL/min) and the mass flow controllers were switched from purge to the desired setting (in sccm). The system would take approximately 30 minutes to equilibrate. During this time the reactor coil was brought to the desired temperature using a silicon oil bath (40 °C and 100 °C). The ethylene and CO₂ flow rates were adjusted to give 9 and 6 min residence time in each reactor. After approximately 1 hour, a sample was taken using the 6-way valve. The sample was analyzed by ¹H NMR, which indicated a yield of 72% of ethylene carbonate **1j** based on the amount of NBS.

Representative procedure for scale up reactions in flow

A 20 mL volumetric flask was charged with styrene (1.1 mL, 10 mmol, 1 equiv) or 1-octene (1.56 mL, 10 mmol, 1 equiv), NBS (2.13 g, 12 mmol, 1.2 equiv) and acetone. The volumetric flask was filled to the mark with acetone (0.5 M). A 10 mL volumetric flask was charged with NH₄OAc (77 mg, 1 mmol, 0.1 equiv) and 10 mL H₂O. Another 10 mL volumetric flask was charged with 1.94 mL DBU (13 mmol, 1.3 equiv), and was filled to the mark with water. A Syrris Asia pump was pumped with the acetone solution and NH₄OAc/H₂O solution, and then attached to the flow system. An 8 mL, stainless steel Harvard Apparatus syringe was filled with the DBU/H₂O solution and then attached to the flow apparatus (syringe pump). Once the back-pressure was set (130 psi), the Syrris Asia pump was started with 20 µL/min of acetone solution and 10 µL/min of water solution. Harvard syringe pump was started (10 µL/min) and the mass flow controller was switched from purge to the desired setting (0.6 sccm). The system will take approximately 30 minutes to equilibrate. During this time the reactor coil is brought to the desired temperature using a silicon oil bath (40 °C and 100 °C for 1-octene, 30 °C and 85 °C for styrene), and the flow rates adjusted to obtain 10 min residence time in the packed-bed reactor. After approximately 4 *t_R* (~ 2 h), the valve on the sample collecting container was opened, and the solvent mixture in the container was pressurized out by the N₂ back-pressure without a big

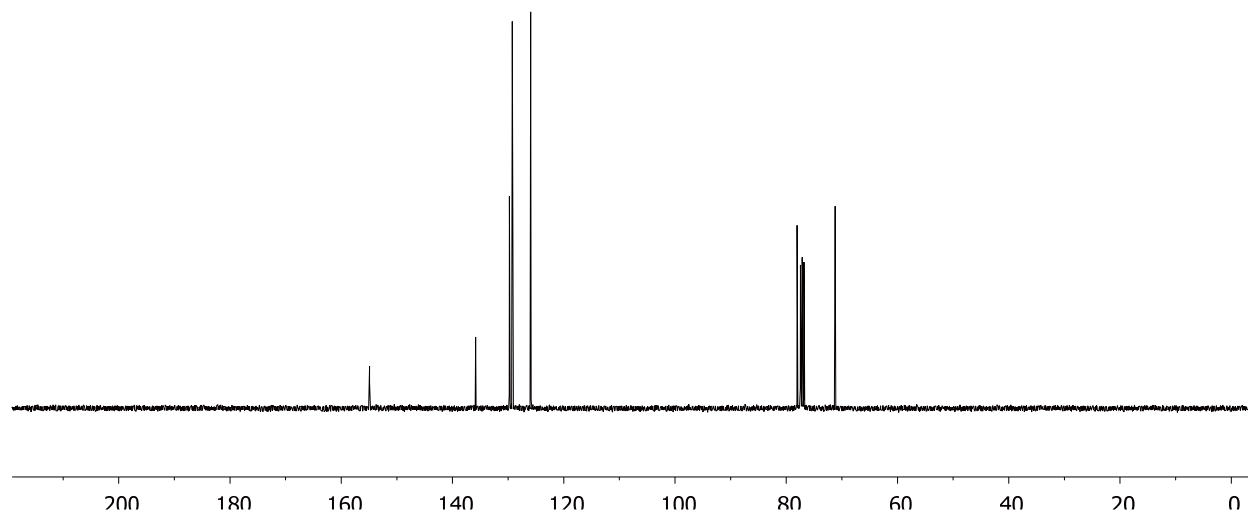
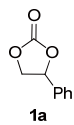
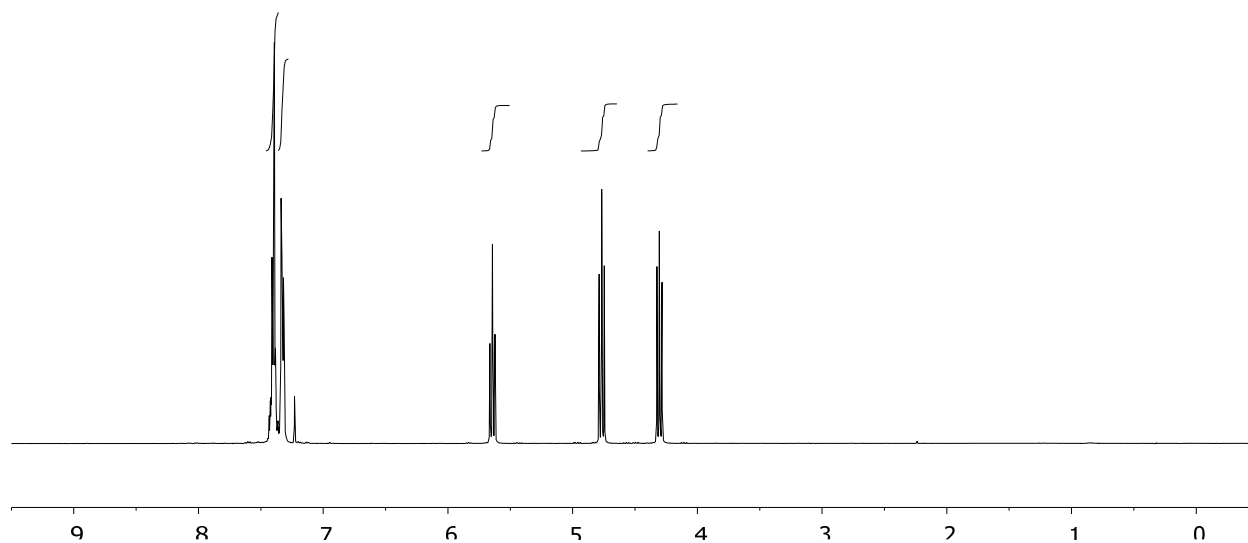
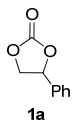
disturbing of the current equilibrated flow. Then the valve was closed and the product was collected for 8 hours. After that, the valve on the container was opened again to collect all the solvent mixture. The solvent mixture was then extracted with saturated NaCl solution and CH₂Cl₂ twice. The organic phase was combined, dried with Na₂SO₄. The solution was then filtered and concentrated. Further purification was performed using a Biotage Isolera One flash purification system to afford the desired cyclic carbonates **1a** (621 mg, 79% yield) or **1c** (643 mg, 78% yield) as a white solid.

Representative procedure for batch synthesis of cyclic carbonates

1) Representative procedure for reactions conducted in Parr reactors (e.g. reactions in Scheme 2): In a vial containing a stir bar, NBS (266 mg, 1.5 mmol, 1 equiv) was mixed with 1 mL of water. Styrene (172 μ L, 1.5 mmol, 1 equiv) was added to the mixture followed immediately by the addition of DBU (0.35 mL, 2.4 mmol, 1.6 equiv). The reaction mixture was stirred and the vial placed in a stainless steel autoclave (Parr reactor). The reactor was pressurized with CO₂ gas at an overall pressure of 300 psi. The temperature was maintained at 60 °C for 3 hour, and the reactor was cooled down to room temperature and depressurized. Ethyl acetate was used to extract any organic material. Further purification was performed using a Biotage Isolera One flash purification system to afford cyclic carbonate **1a** (160 mg, 65% yield) and dibromide **2a** (78 mg, 20% yield).

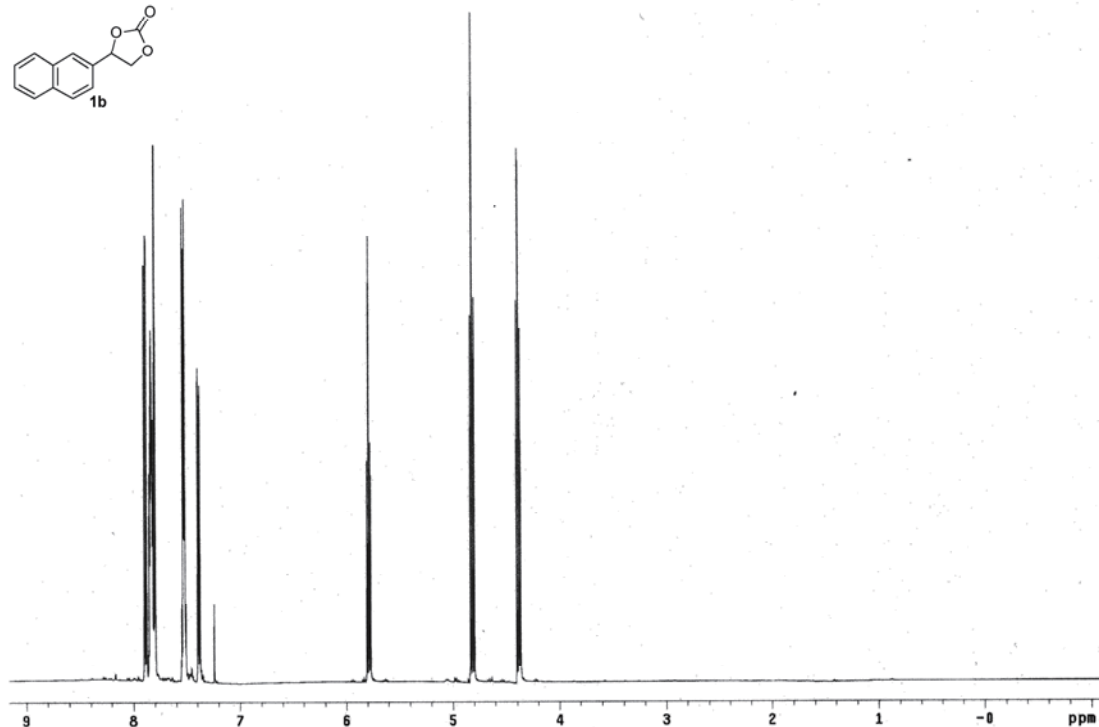
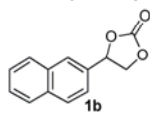
2) Representative procedure for reactions conducted in sealed tubes (e.g. reactions in Table 1): In a sealed tube containing a stir bar, NBS (266 mg, 1.5 mmol, 1 equiv) was mixed with 1 mL of water. Vinyl naphthalene (231 mg, 1.5 mmol, 1 equiv) was added to the mixture followed immediately by the addition of DBU (0.35 mL, 2.4 mmol, 1.6 equiv). Then (330 mg, 7.5 mmol, 5 equiv) dry ice was quickly weighed and added into the tube followed by immediate sealing of the tube. The reaction mixture was heated at 60 °C for 3 hour, and the reactor was cooled down to room temperature. Ethyl acetate was used to extract the organic material. The organic phase was separated, dried, and vacuumed. The result was analyzed by the crude ¹H NMR using trichloroethylene as an external standard.

^1H and ^{13}C NMR Spectra:



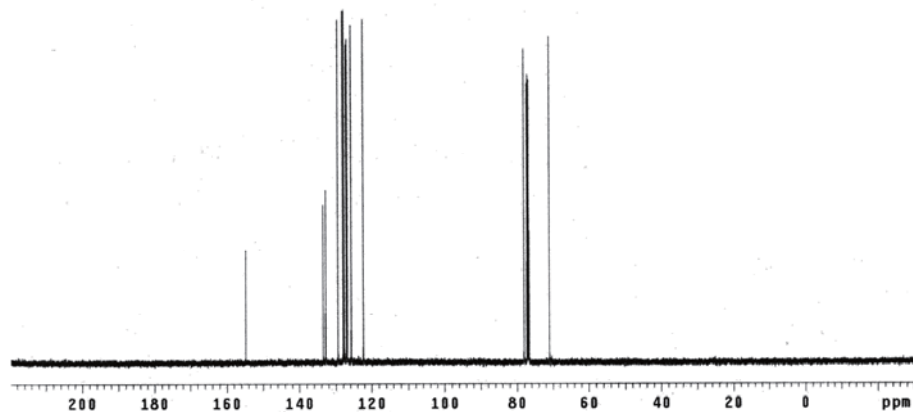
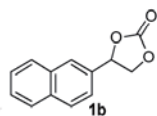
STANDARD PROTON PARAMETERS

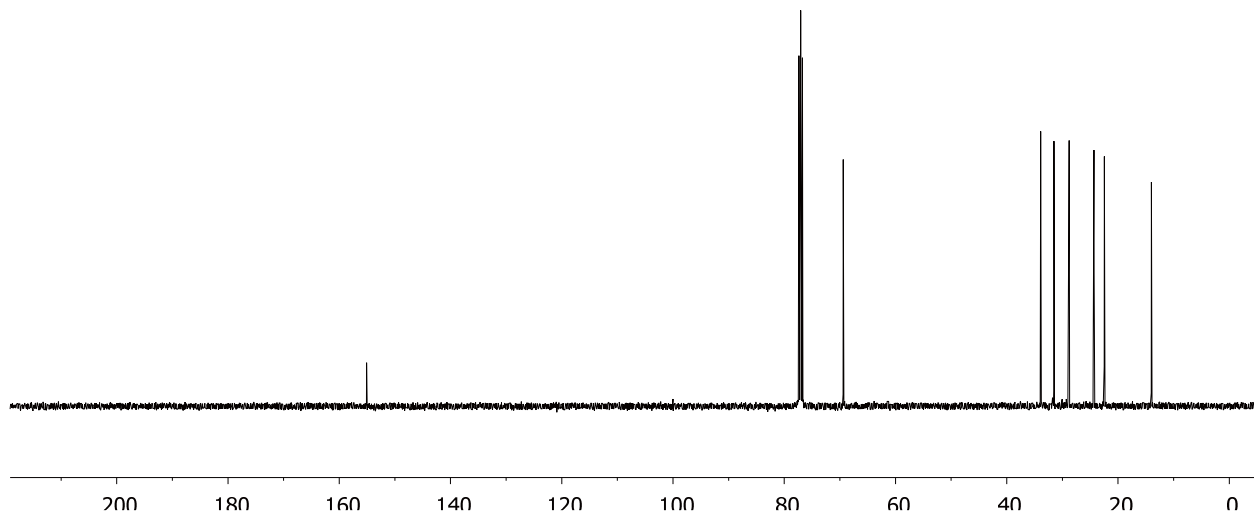
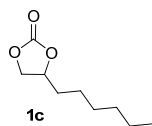
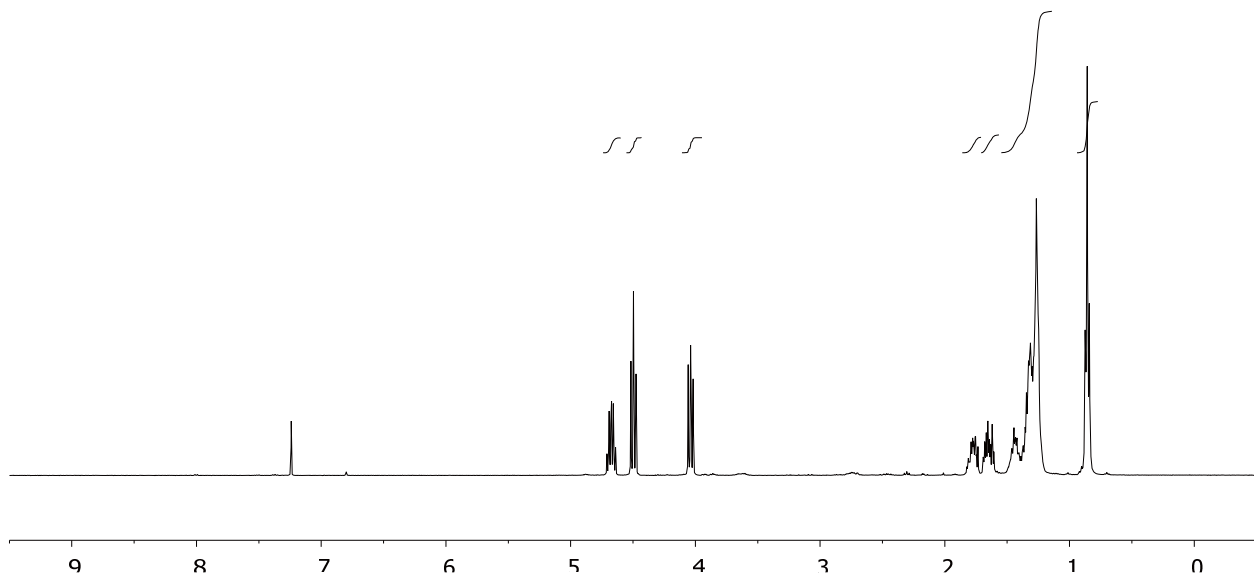
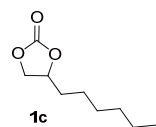
Pulse Sequence: s2pu1

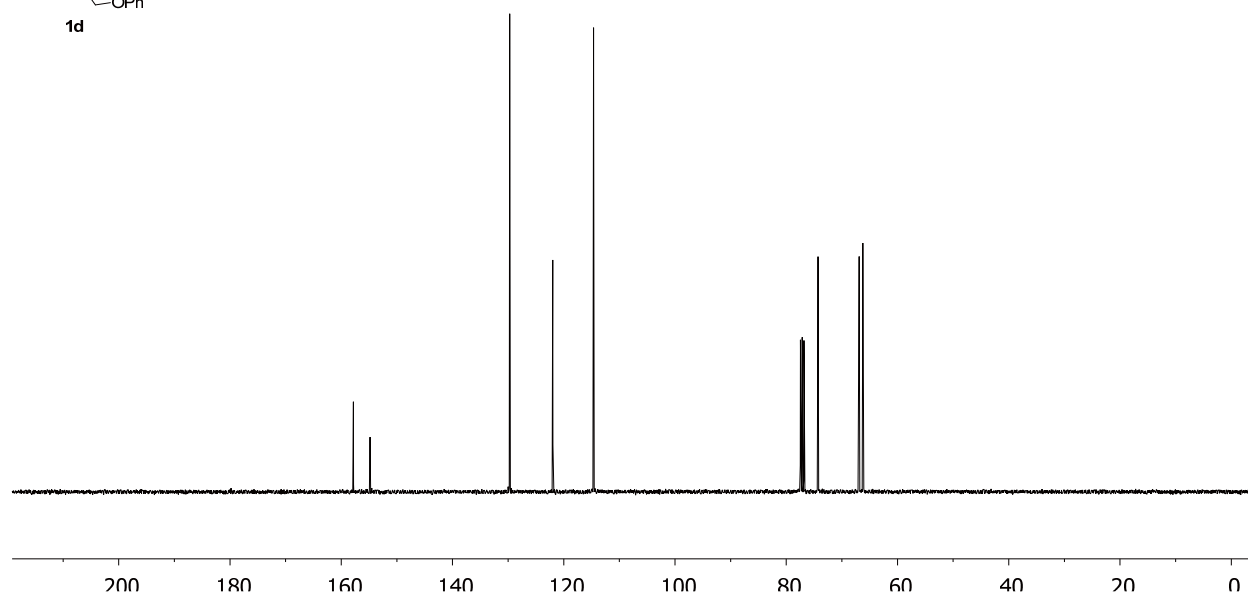
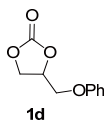
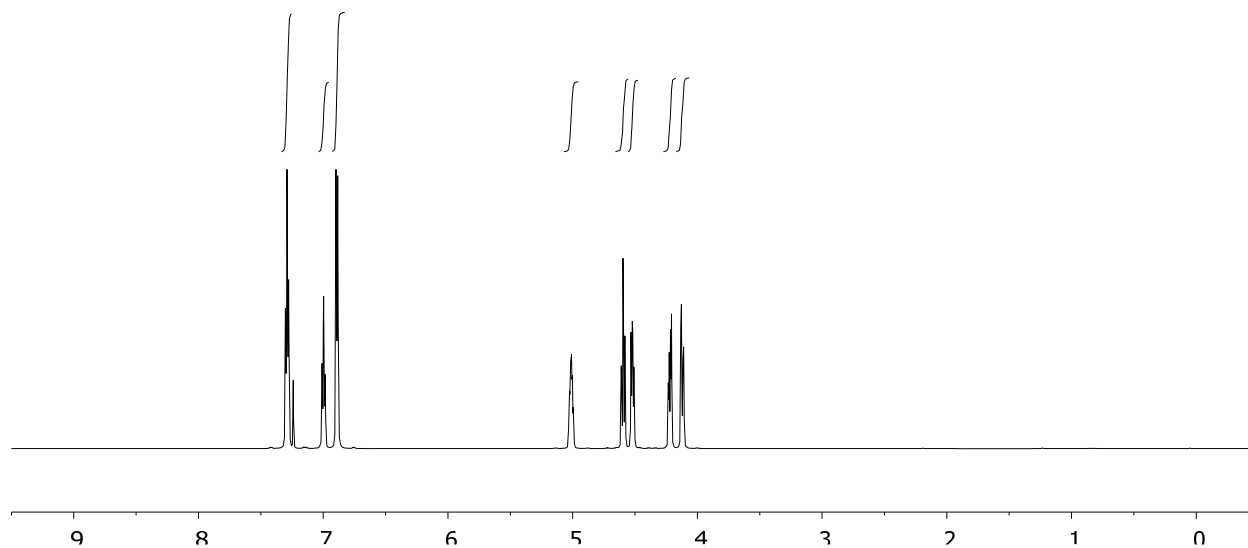
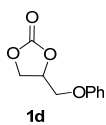


STANDARD CARBON PARAMETERS

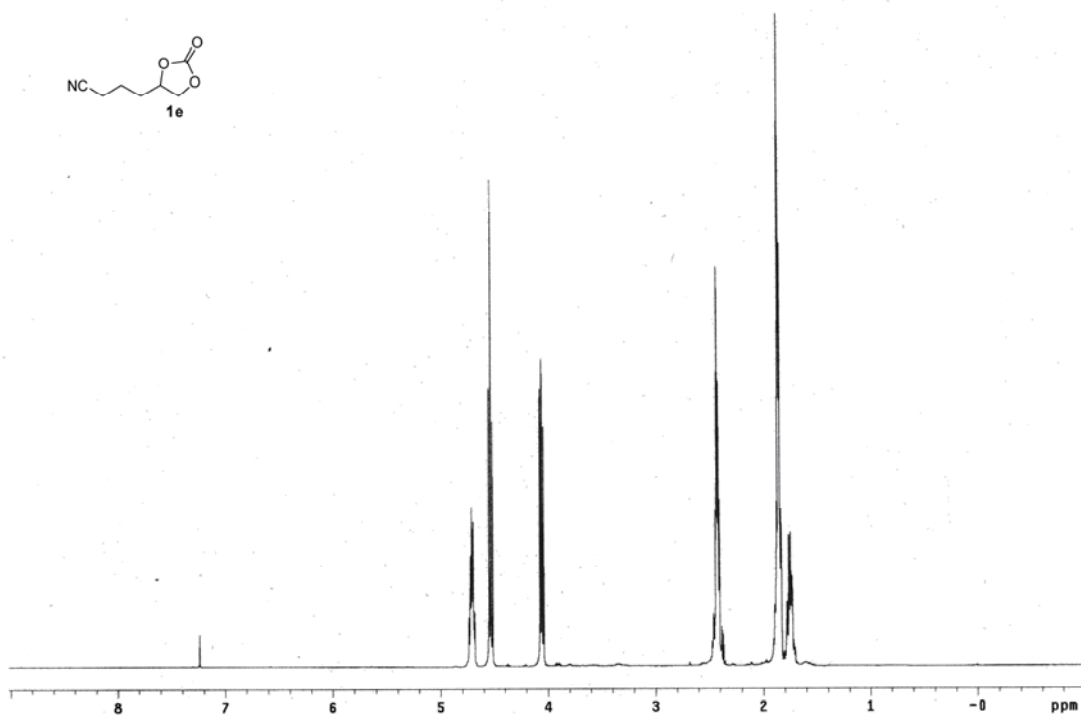
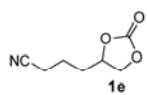
Pulse Sequence: s2pu1



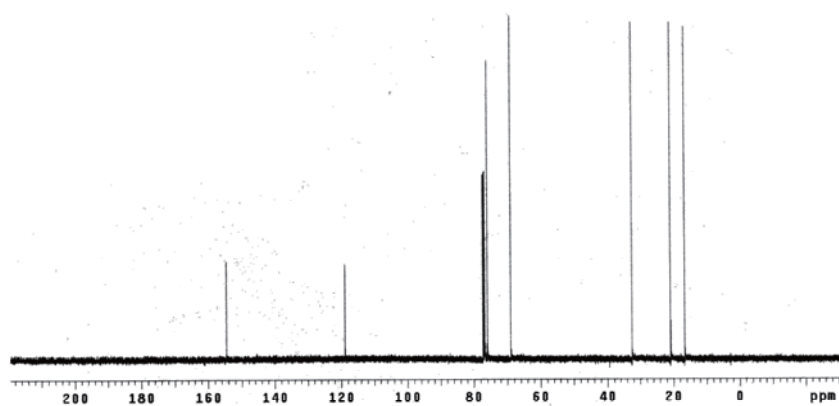
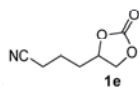


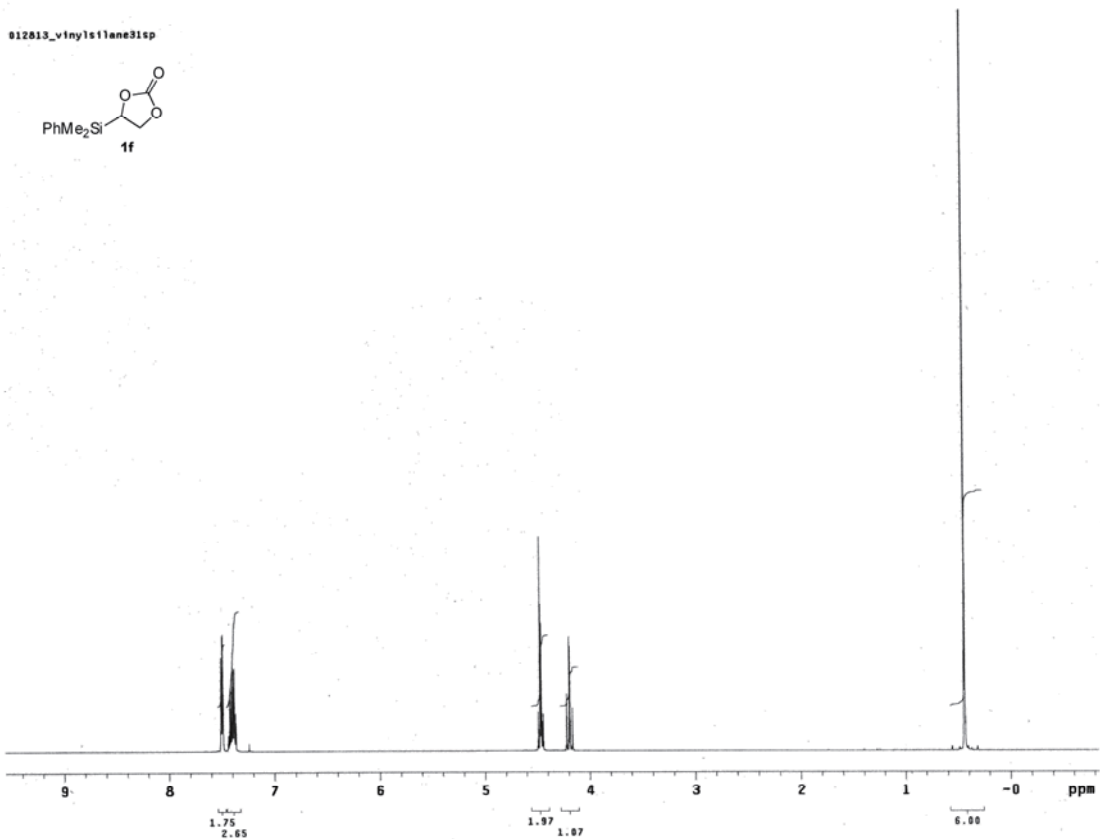


012113_C13carbonate
Pulse Sequence: s2pu1

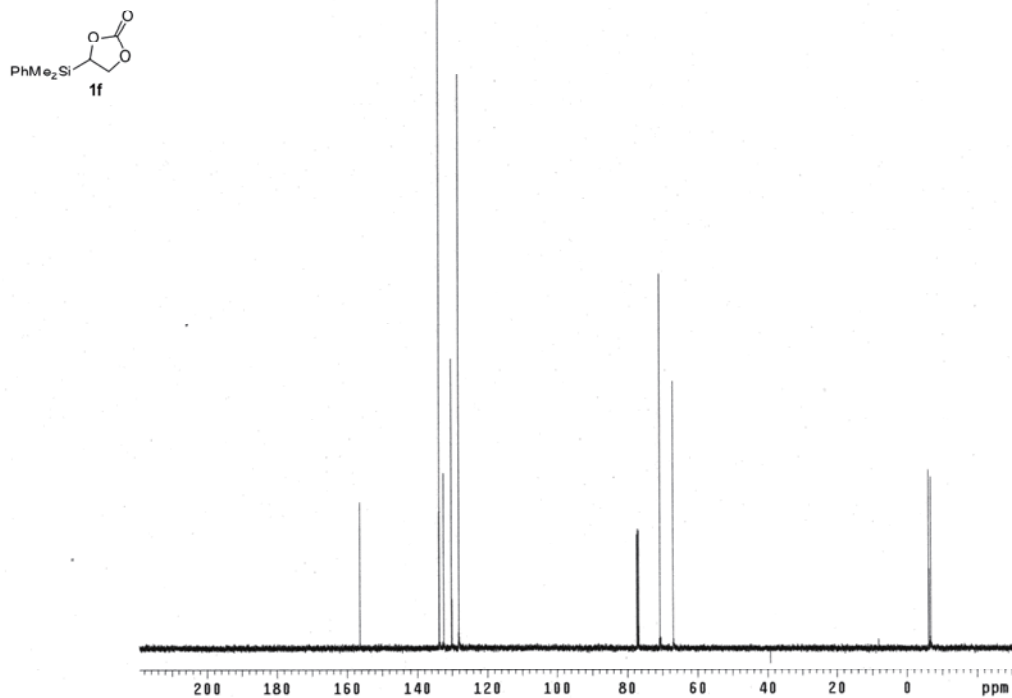


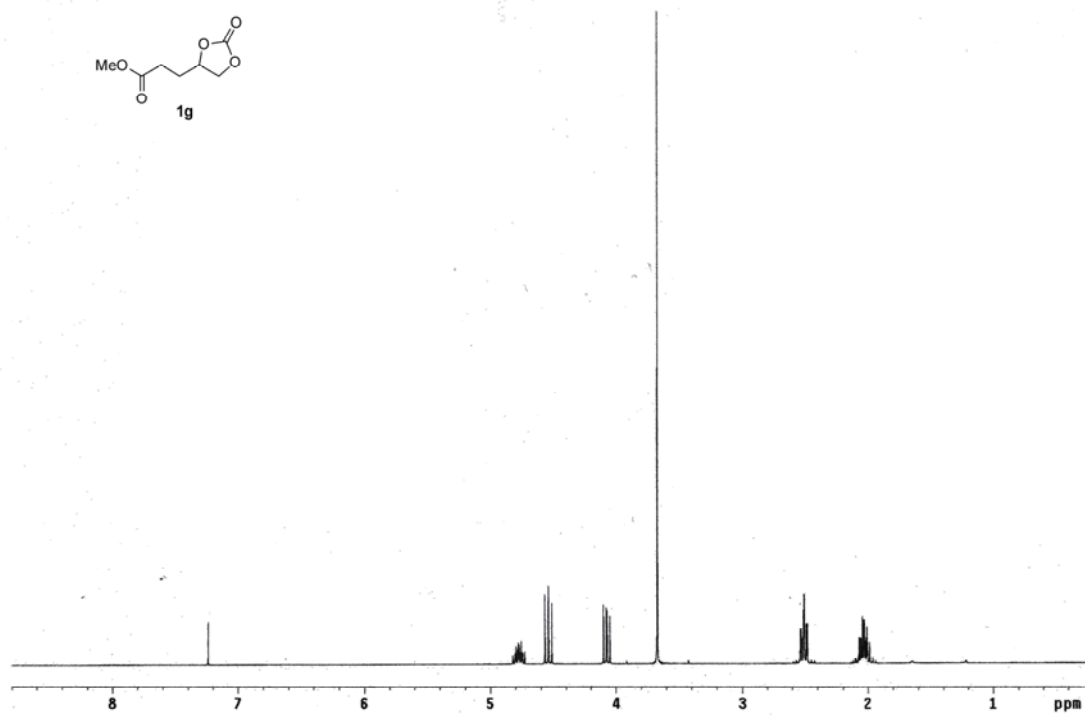
STANDARD CARBON PARAMETERS
Pulse Sequence: s2pu1





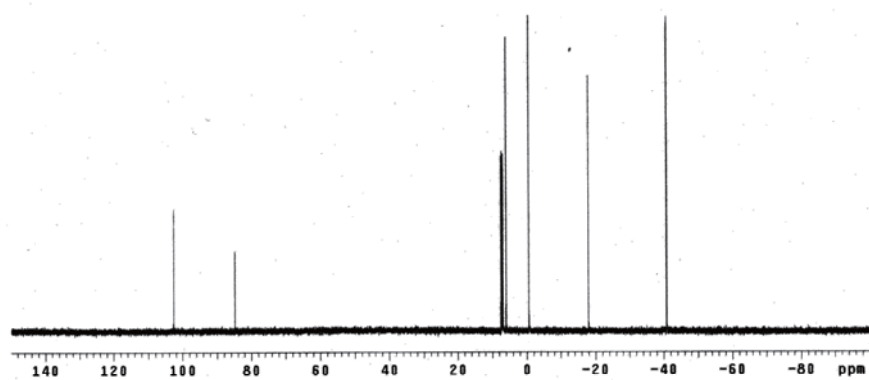
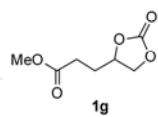
STANDARD CARBON PARAMETERS
Pulse Sequence: s2pu1

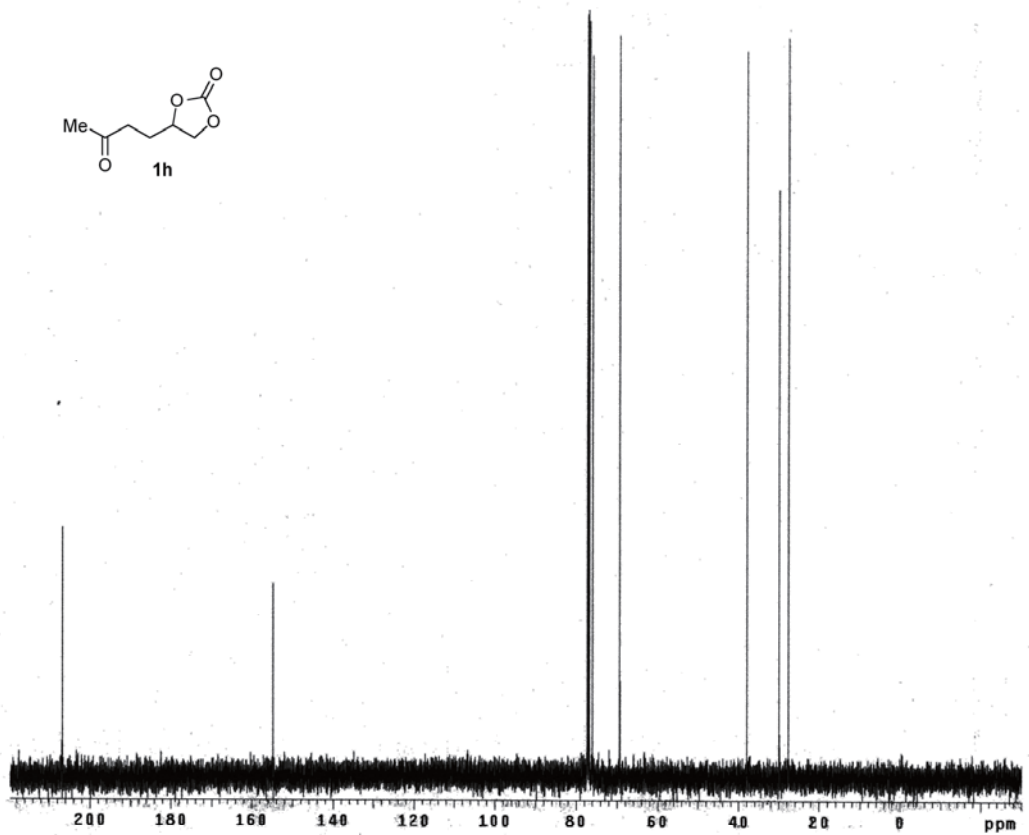
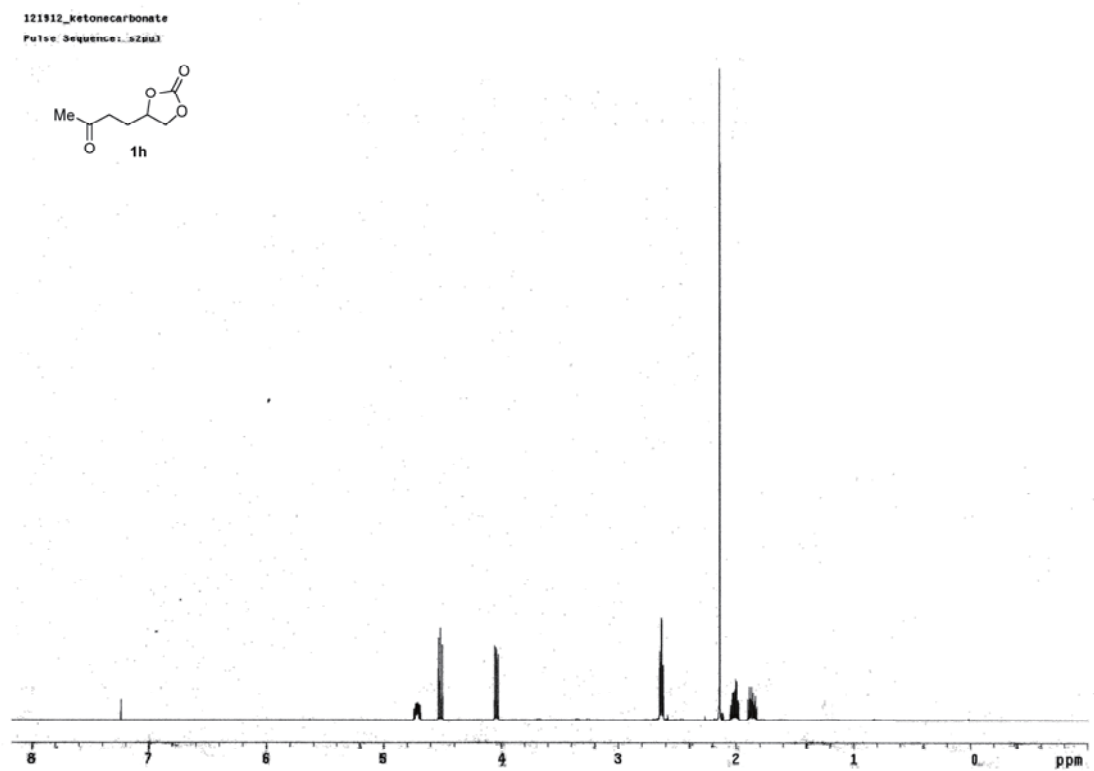




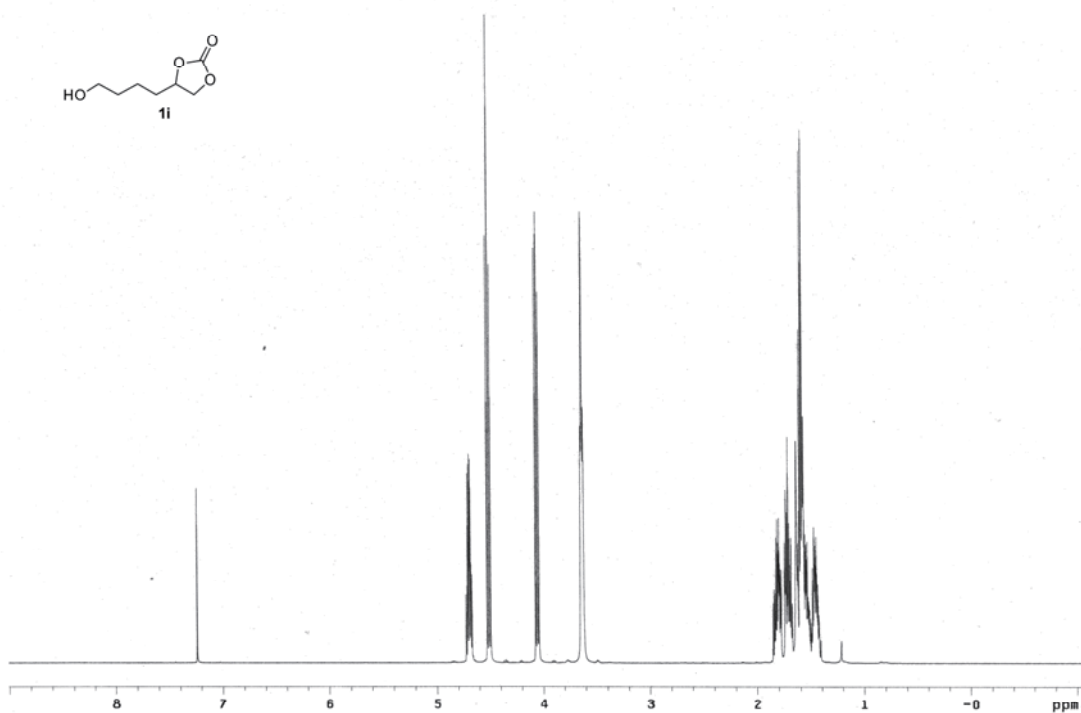
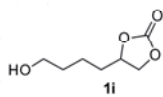
STANDARD CARBON PARAMETERS

Pulse Sequence: s2pu1

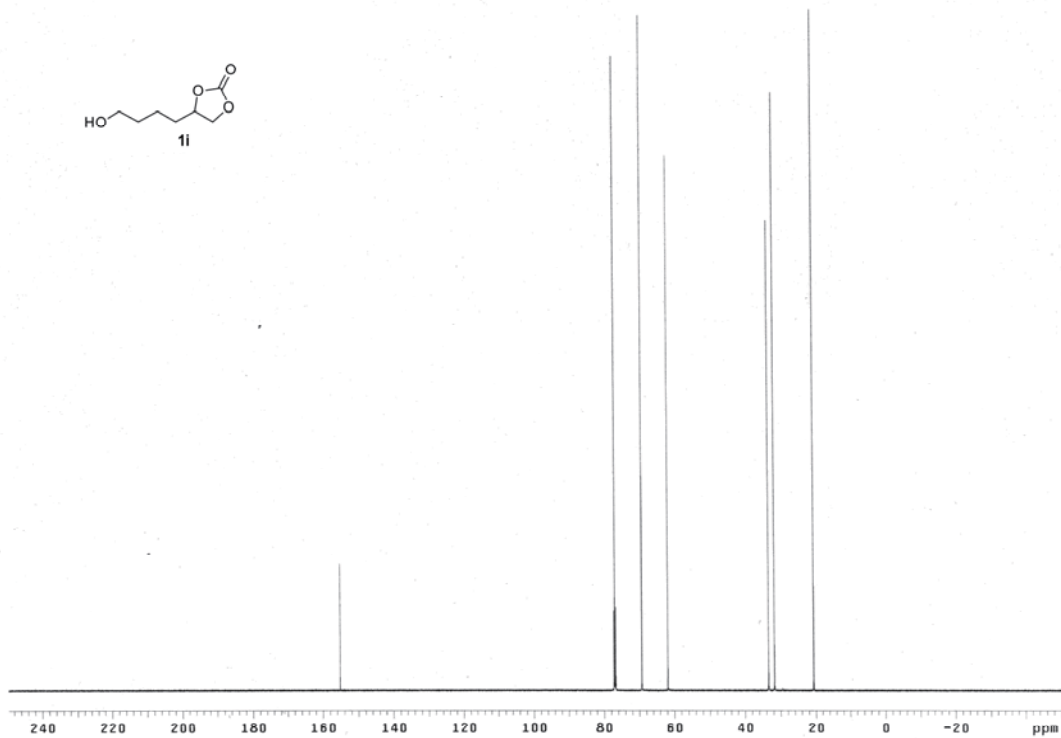
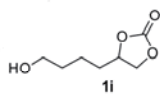




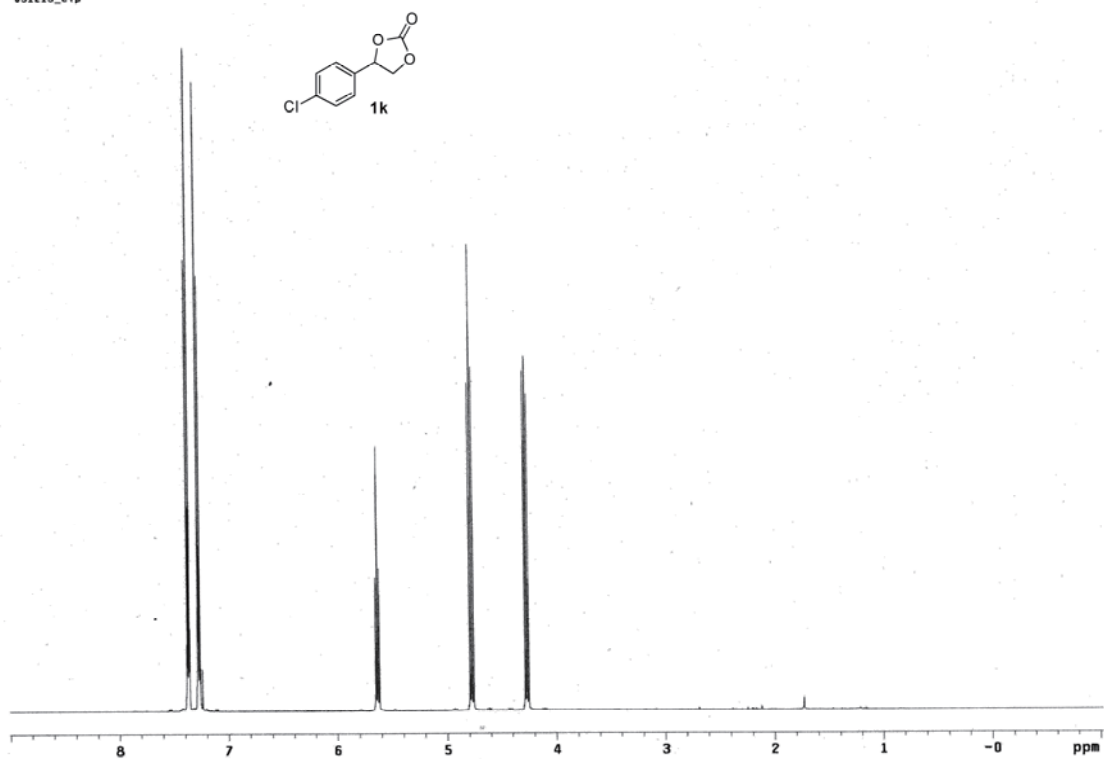
#41213_OHproduct



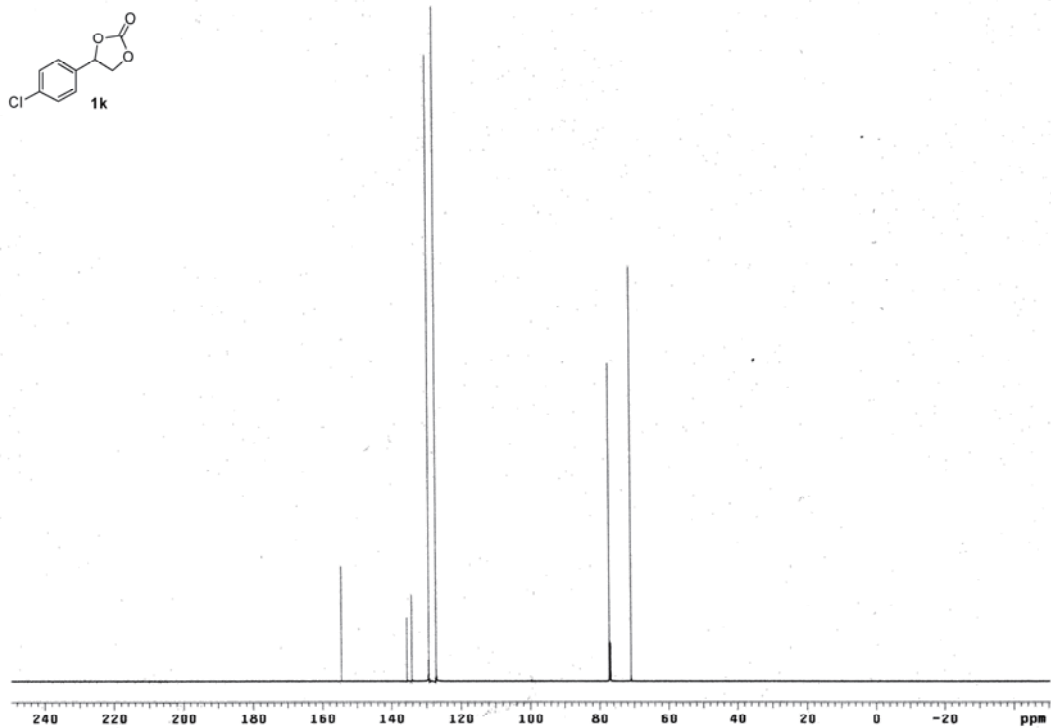
#41613_OHcarbon



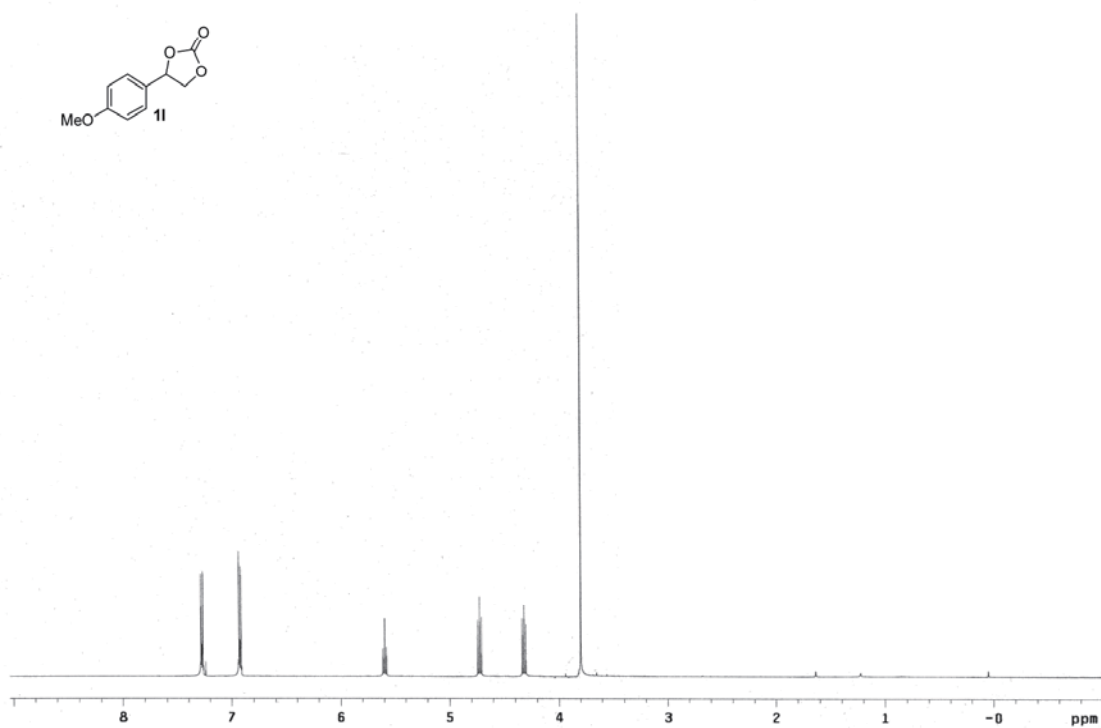
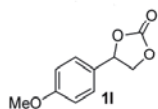
031213_c1p



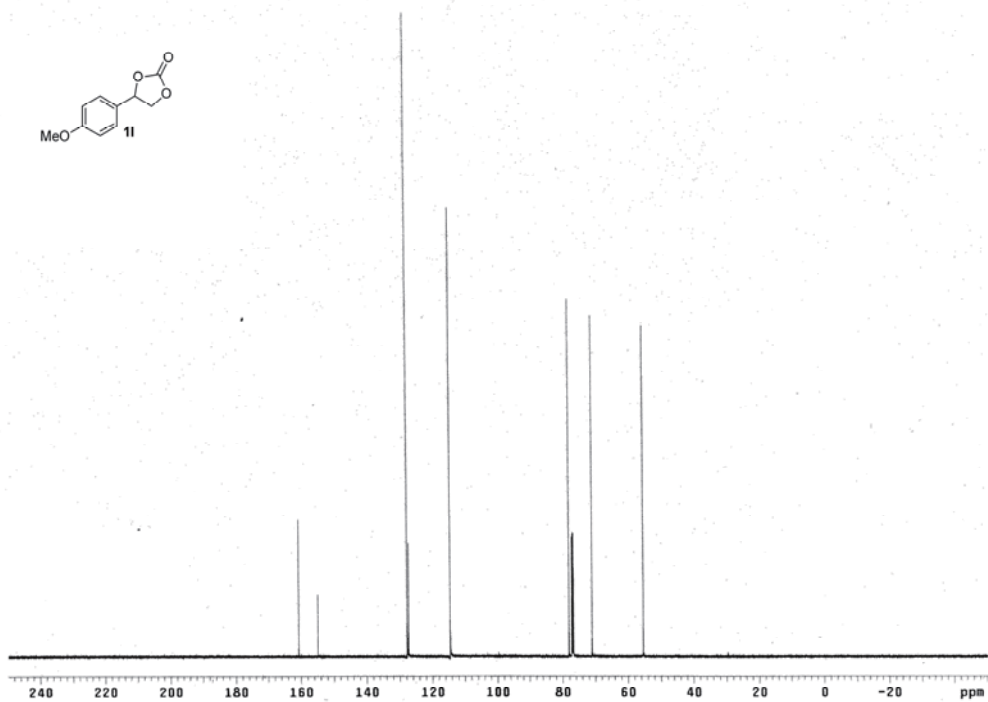
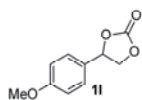
STANDARD CARBON PARAMETERS

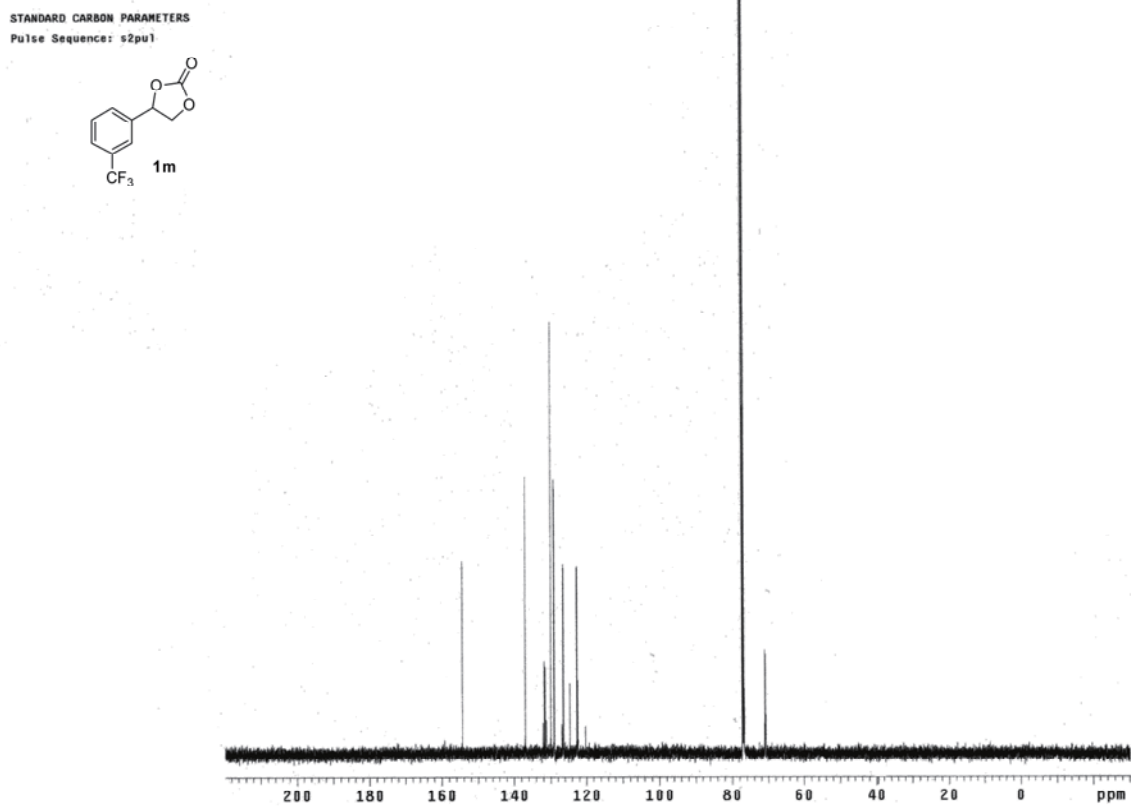
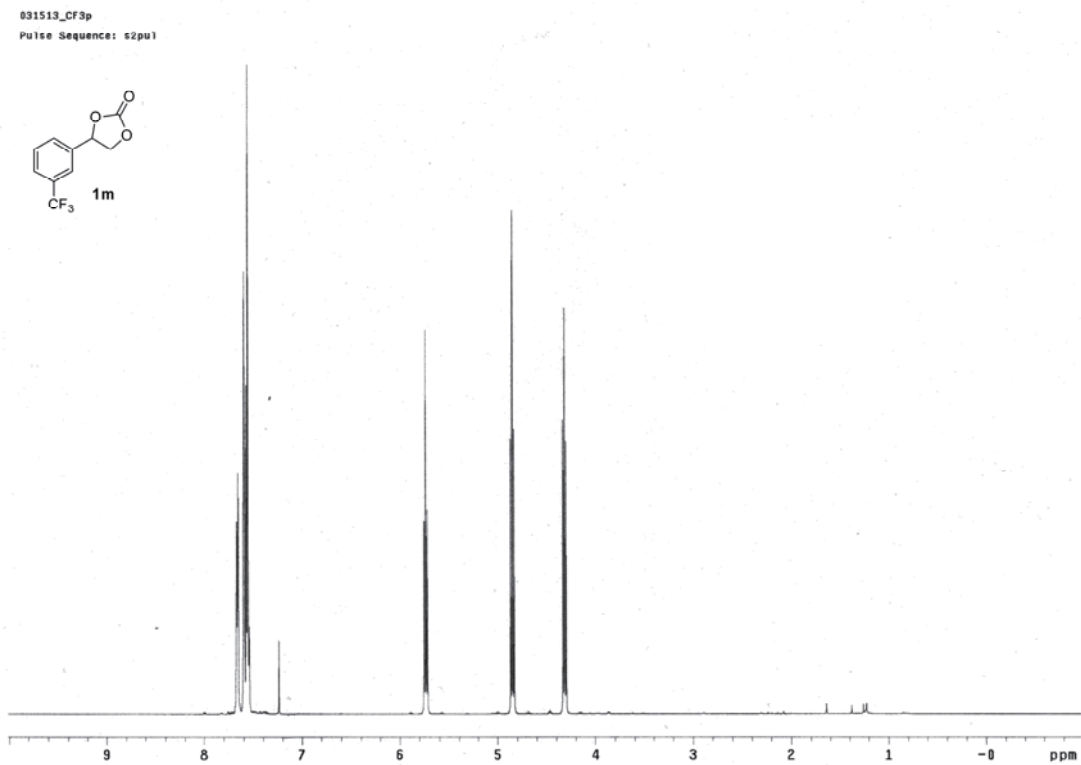


041613_0Meprone

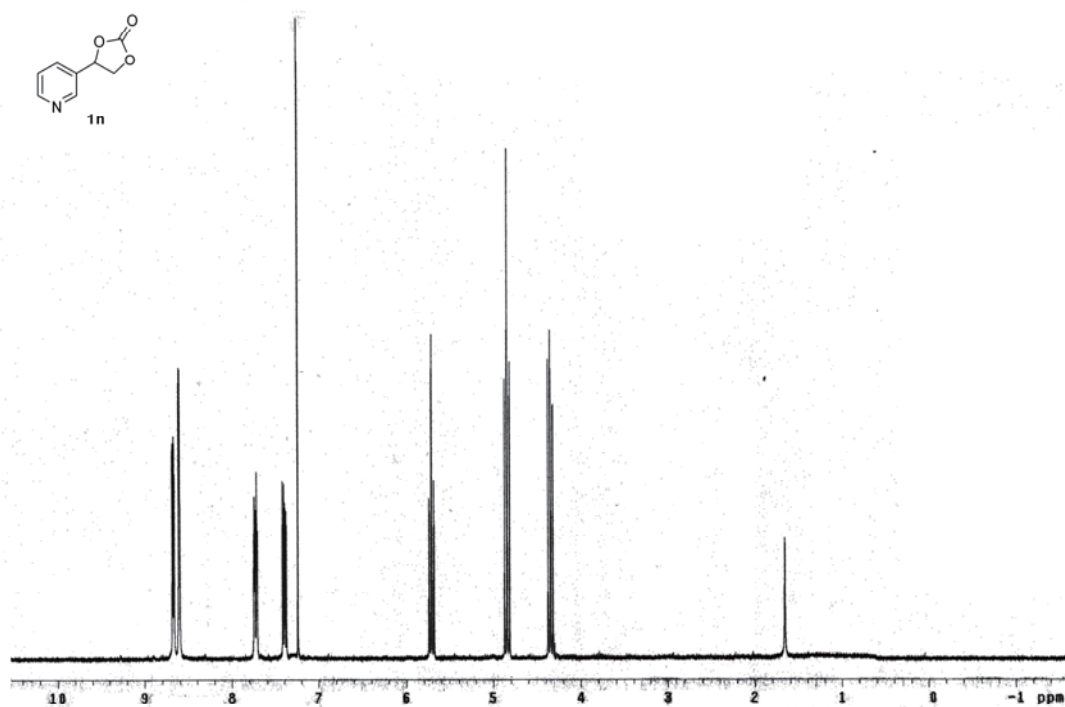
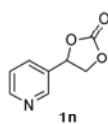


STANDARD CARBON PARAMETERS

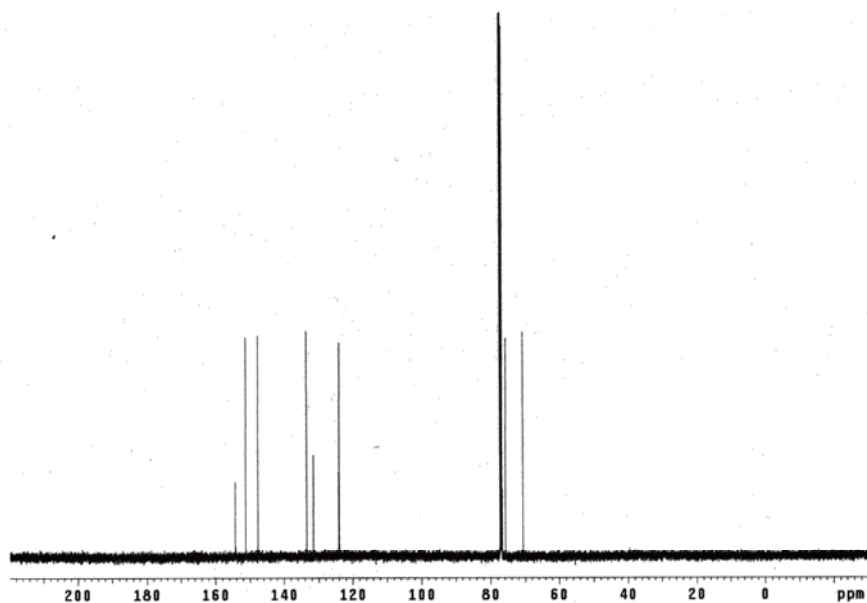
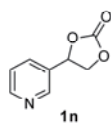


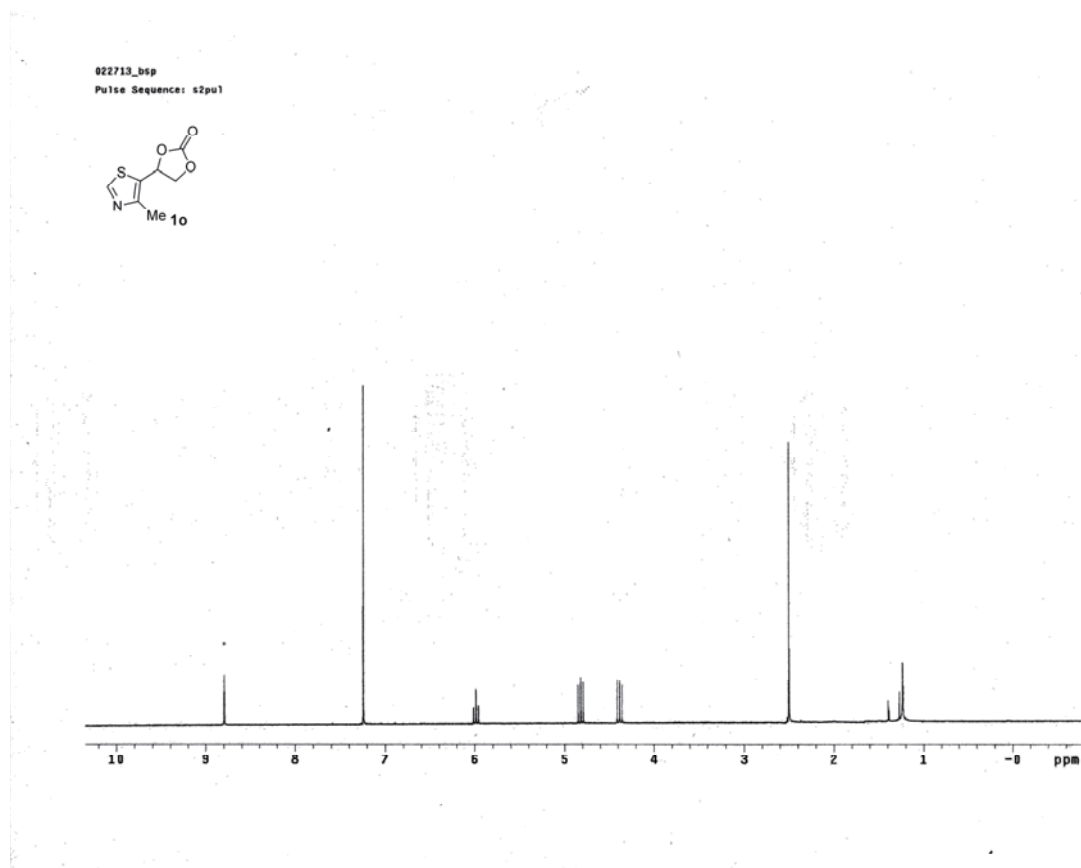


030113_check
Pulse Sequence: s2pu1

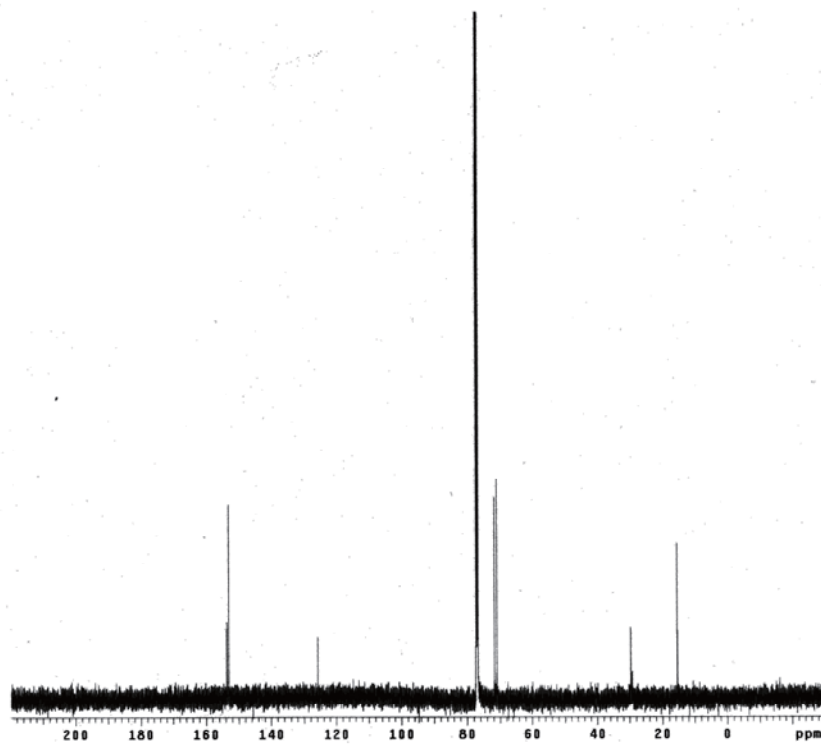
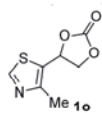


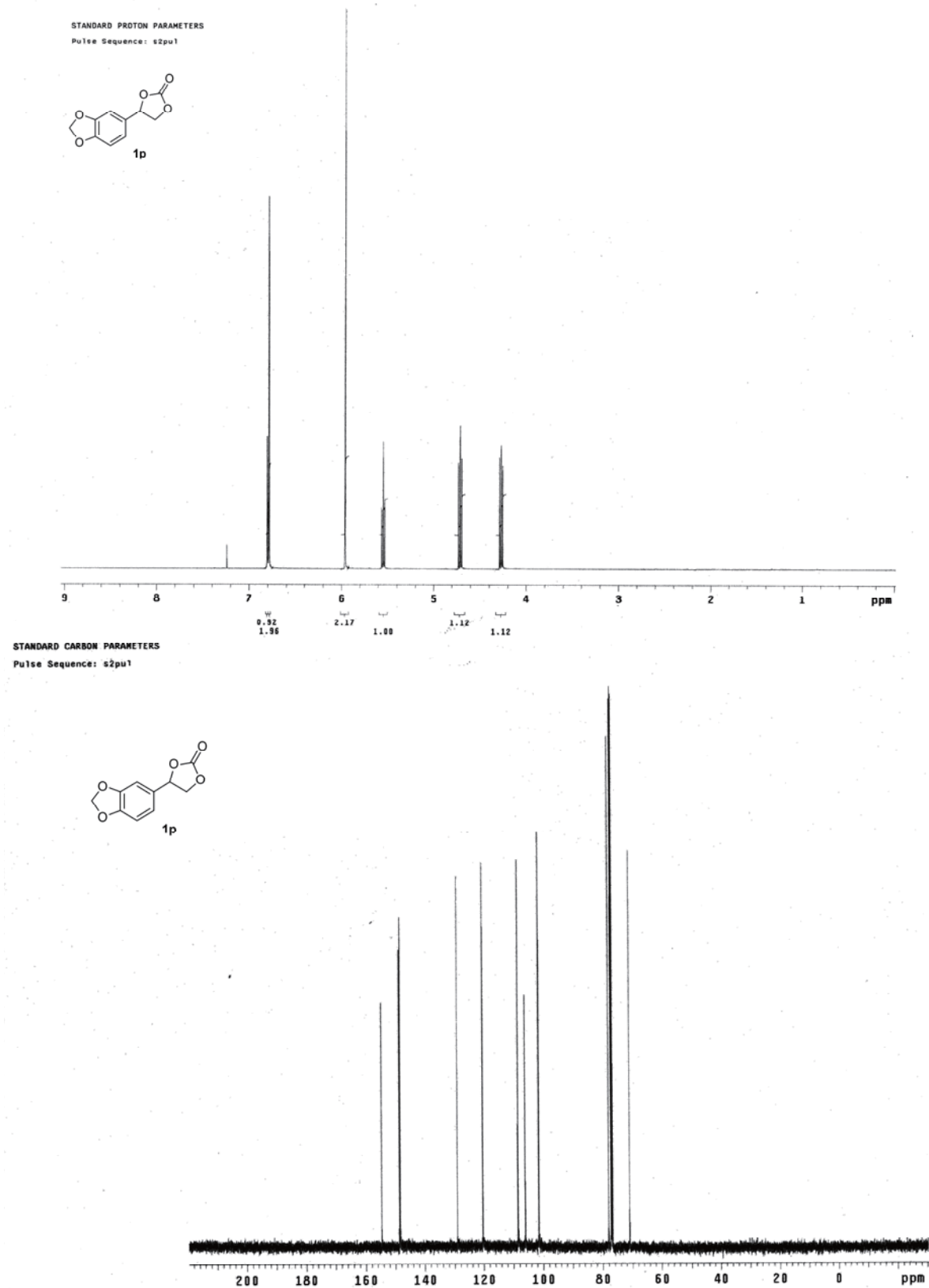
STANDARD CARBON PARAMETERS
Pulse Sequence: s2pu1



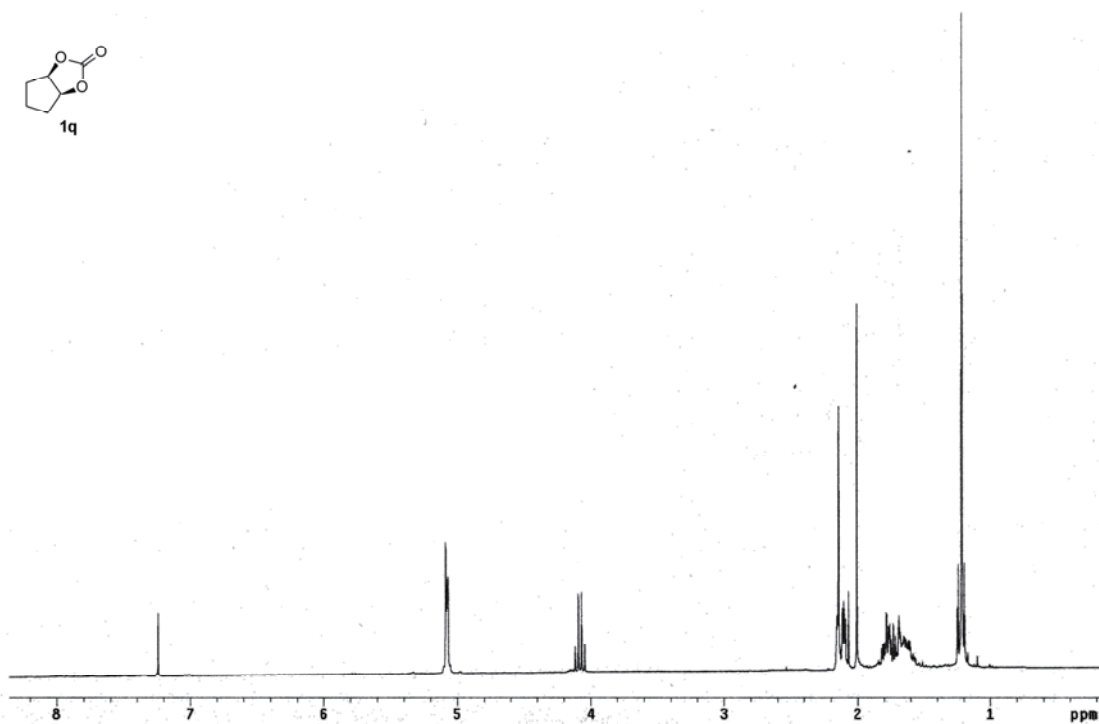


STANDARD CARBON PARAMETERS
Pulse Sequence: s2pul

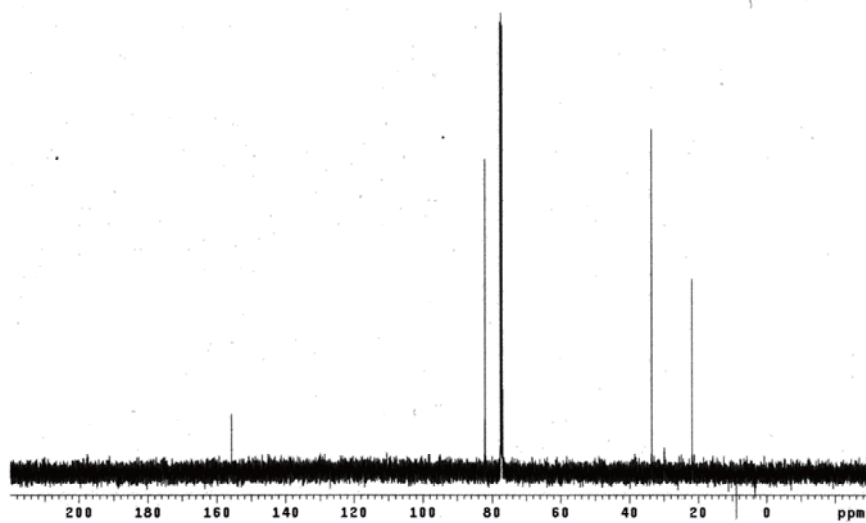




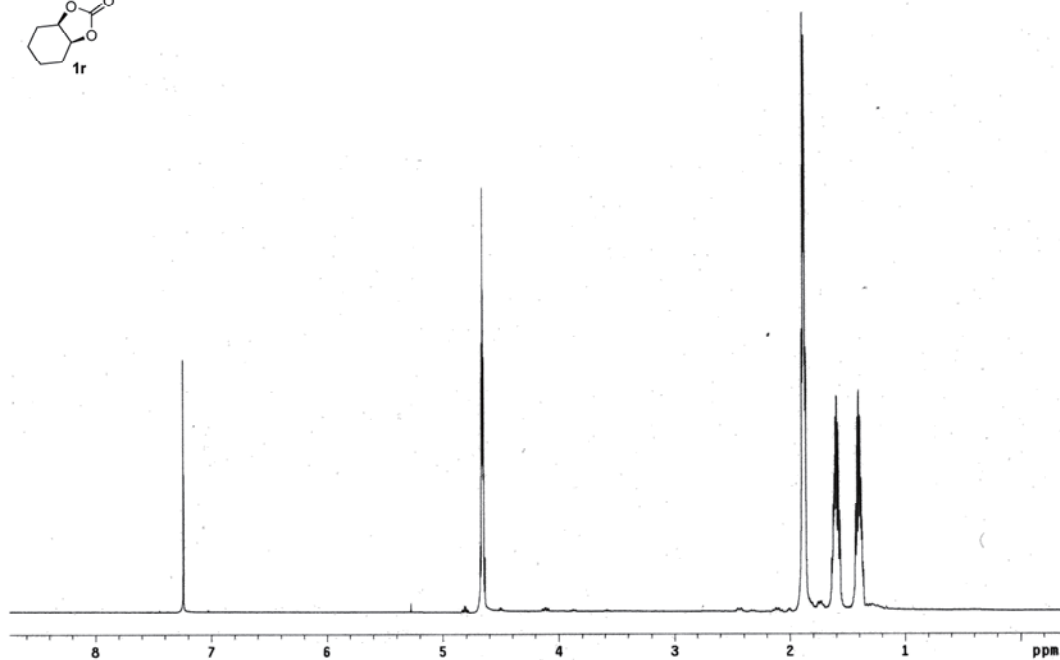
010713_foursp
Pulse Sequence: s2pu1



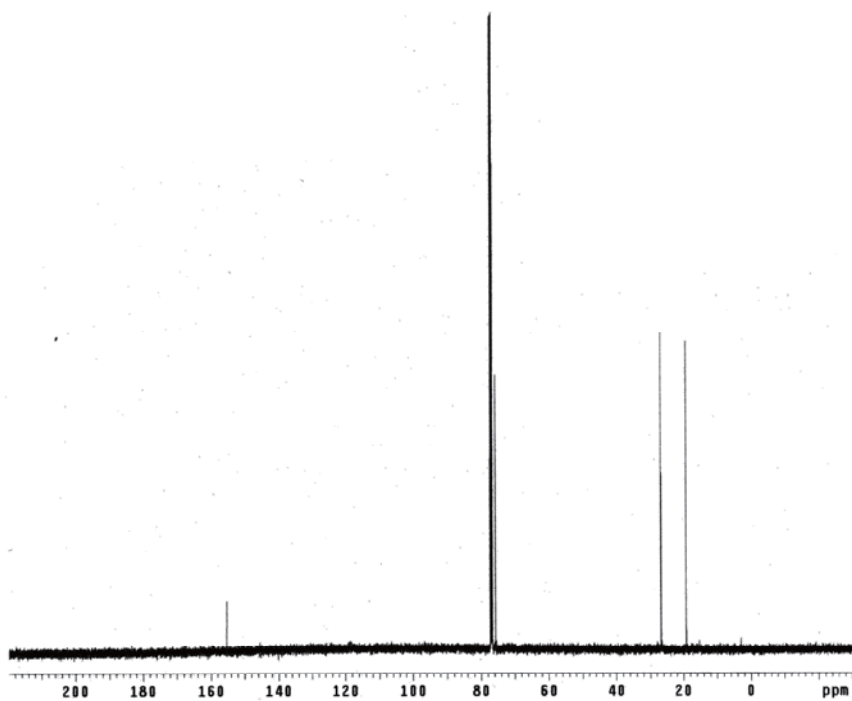
STANDARD CARBON PARAMETERS
Pulse Sequence: s2pu1



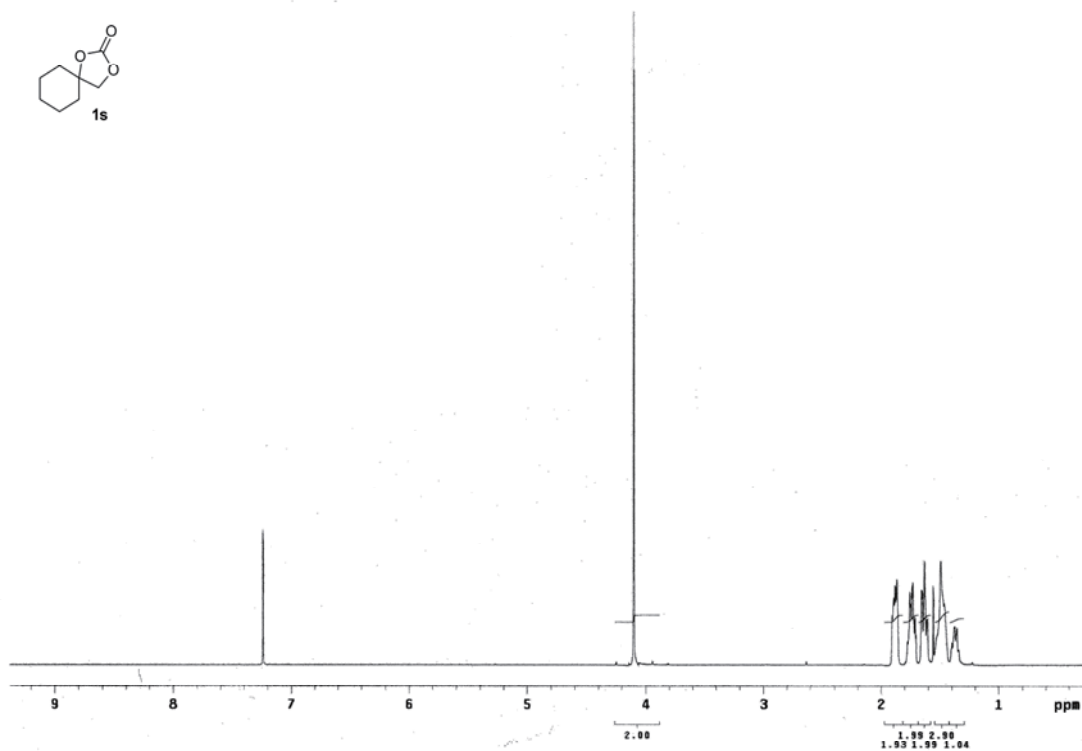
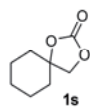
011013_Cyclohexyl
Pulse Sequence: s2pu1



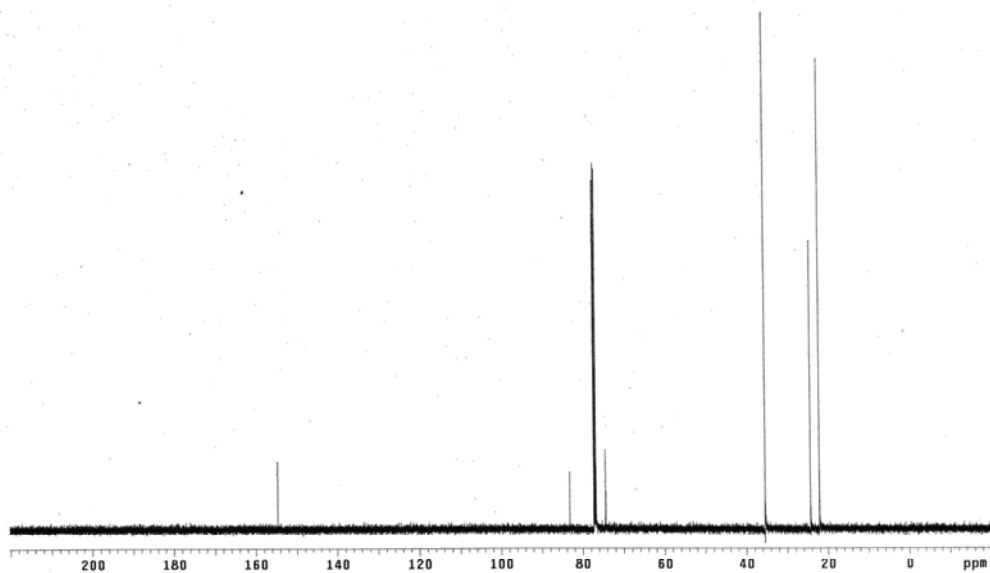
STANDARD CARBON PARAMETER
Pulse Sequence: s2pu1

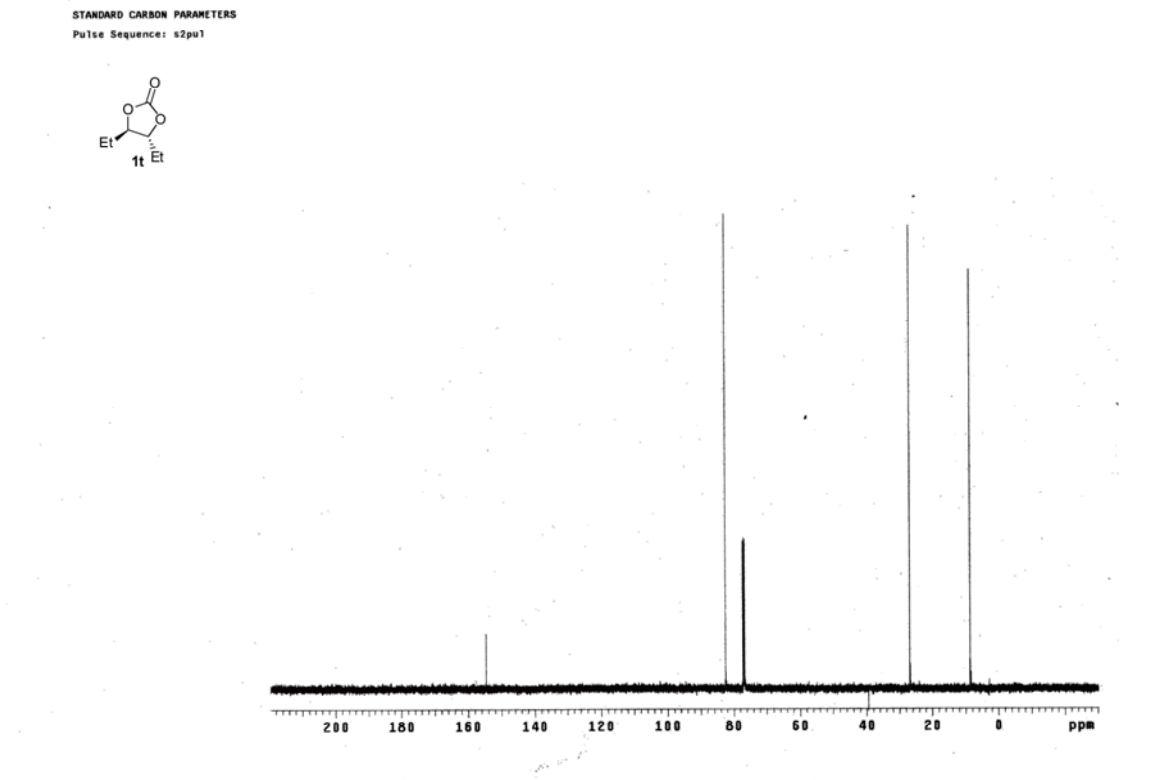
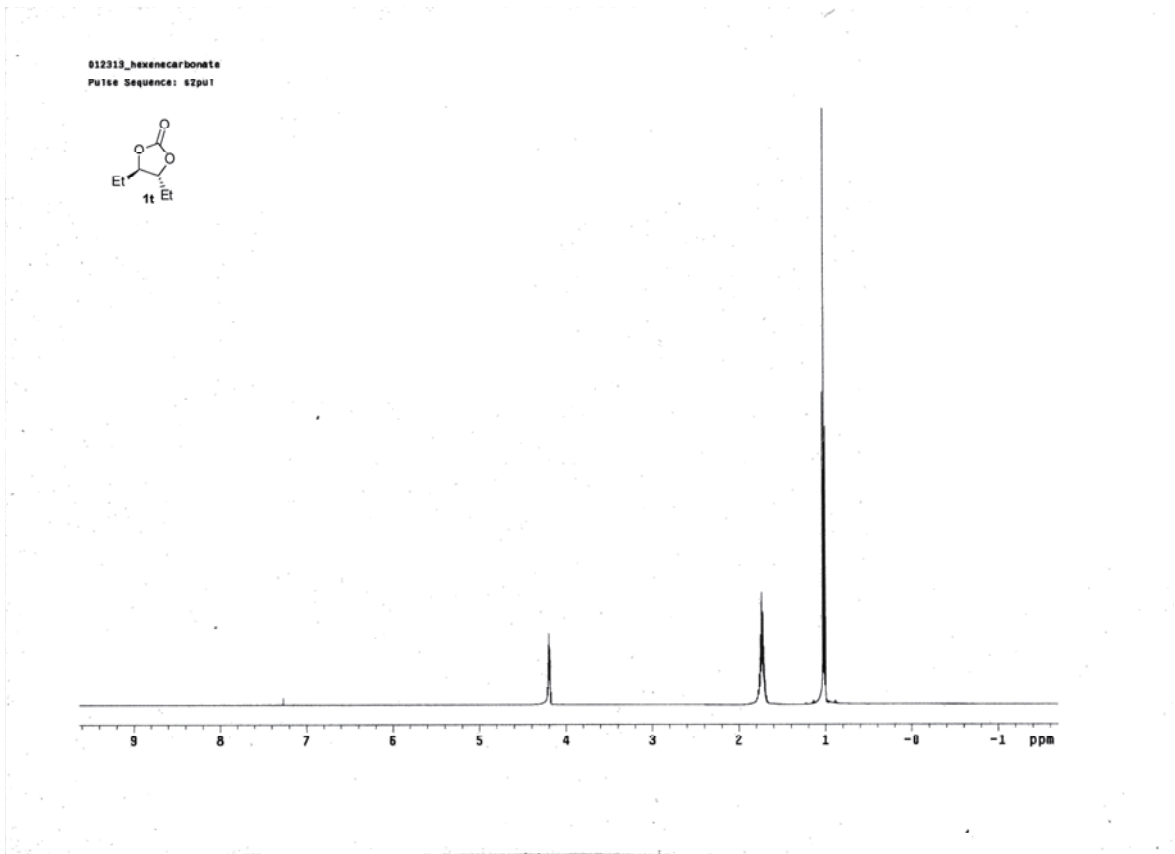


031213_32spcheck
Pulse Sequence: zgpg1

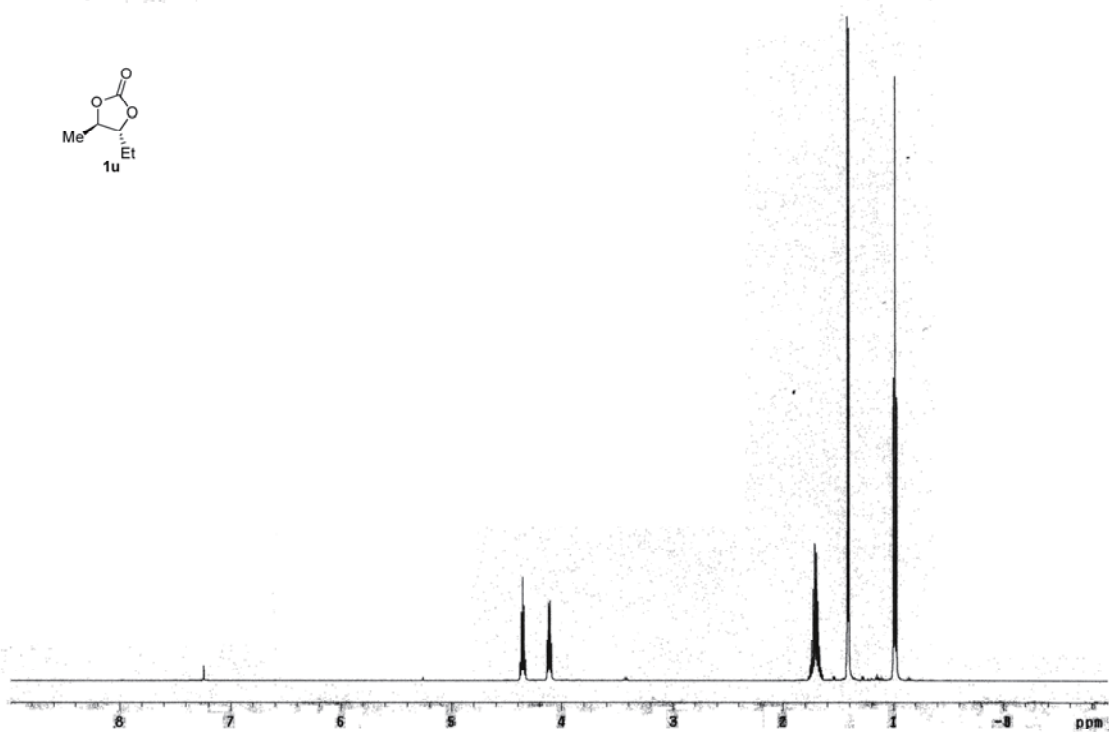
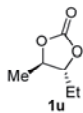


STANDARD CARBON PARAMETERS





STANDARD PROTON PARAMETERS
Pulse Sequence: s2pu1



STANDARD CARBON PARAMETERS
Pulse Sequence: s2pu1

