12-2017

Developing Functionalized Peroxide Precursors for the Synthesis of Cyclic and Spirocyclic Ethers

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Diepenbrock, Anna J., "Developing Functionalized Peroxide Precursors for the Synthesis of Cyclic and Spirocyclic Ethers" (2017). *Student Research Projects, Dissertations, and Theses - Chemistry Department*. 88.
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DEVELOPING FUNCTIONALIZED PEROXIDE PRECURSORS FOR THE SYNTHESIS OF CYCLIC AND SPIROCYCLIC ETHERS

by

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A THESIS

Presented to the Faculty of

The Graduate College at the University of Nebraska

In Partial Fulfillment of Requirements

For the Degree of Master of Science

Major: Chemistry

Under the Supervision of Professor Patrick H. Dussault

Lincoln, Nebraska

December, 2017

DEVELOPING FUNCTIONALIZED PEROXIDE PRECURSORS FOR THE SYNTHESIS OF CYCLIC AND SPIROCYCLIC ETHERS

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University of Nebraska, 2017

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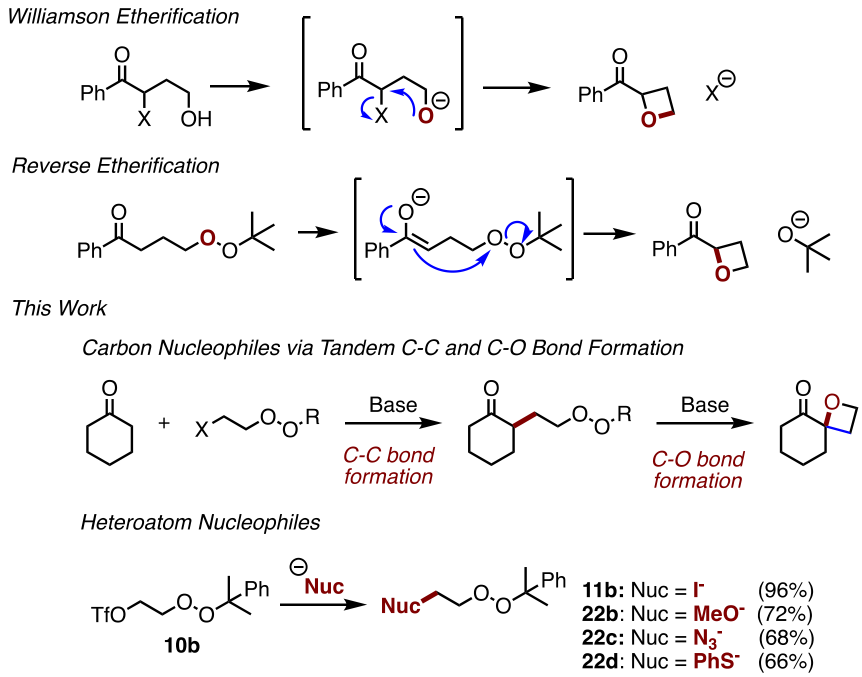
There is increasing interest in the development of methods for the synthesis of oxetanes and spirocyclic oxetanes, a class of molecules of interest to chemists as they synthesize libraries of possible drug target scaffolds with tunable physiochemical and biological properties.[1,2] Although most ethers are prepared through reaction of nucleophilic oxygen with electrophilic carbon, this work explores new reagents and routes for the synthesis of spirocyclic oxetanes based upon an application of "umpolung" or polarity reversal involving attack of nucleophilic carbon on the electrophilic oxygen of a peroxide (Scheme 1). In this work, a 2-carbon peroxide synthon for reverse etherification has been developed and tested with several nucleophilic substrate.



Scheme 1. Approach to Spirocyclic Oxetanes Utilizing Peroxide Containing Reagents.

ACKNOWLEDGEMENTS

I would like to thank, Dr. Dussault for his guidance and help during the last few years that I have been at the University of Nebraska. I would also like to thank my family for their support and encouragement, even while living on the other side of the world.

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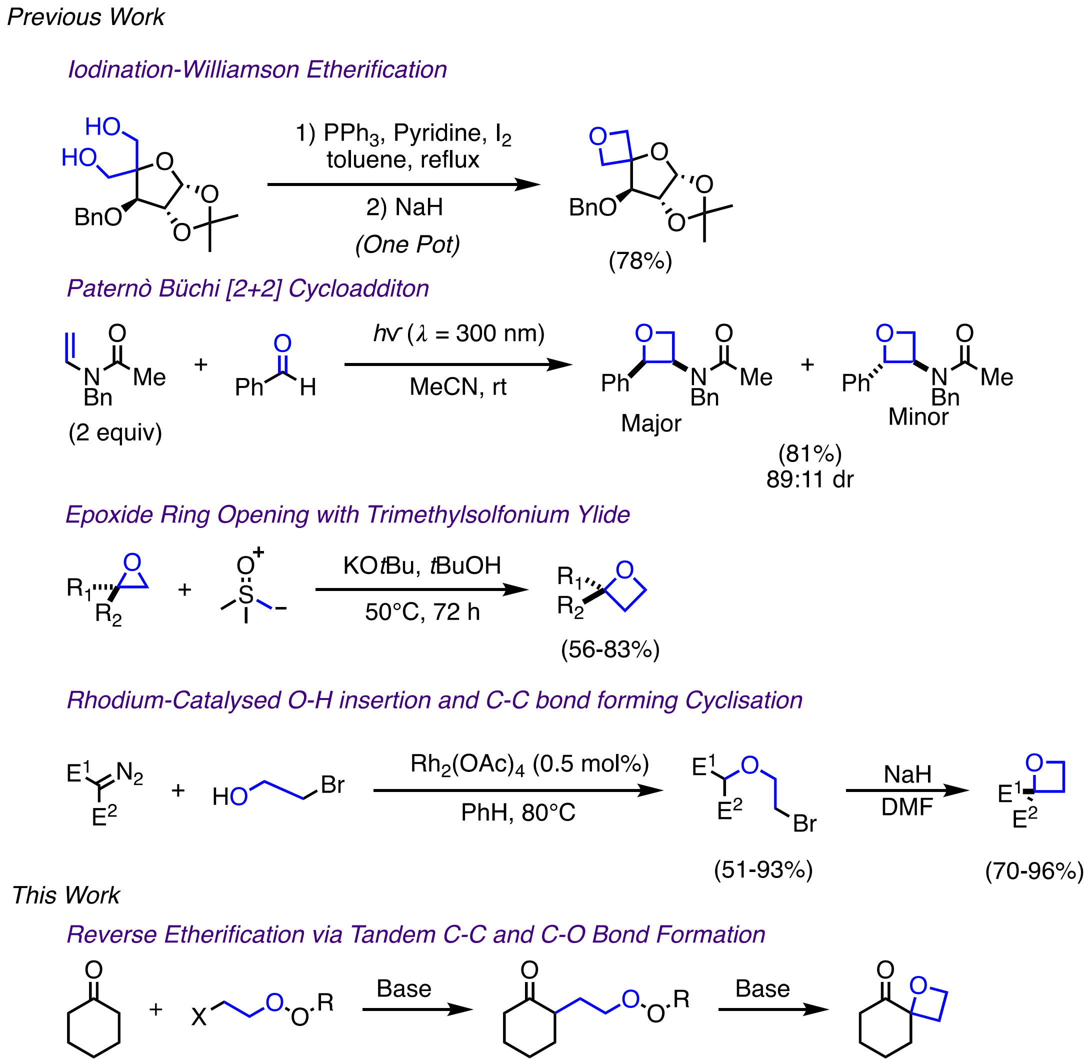
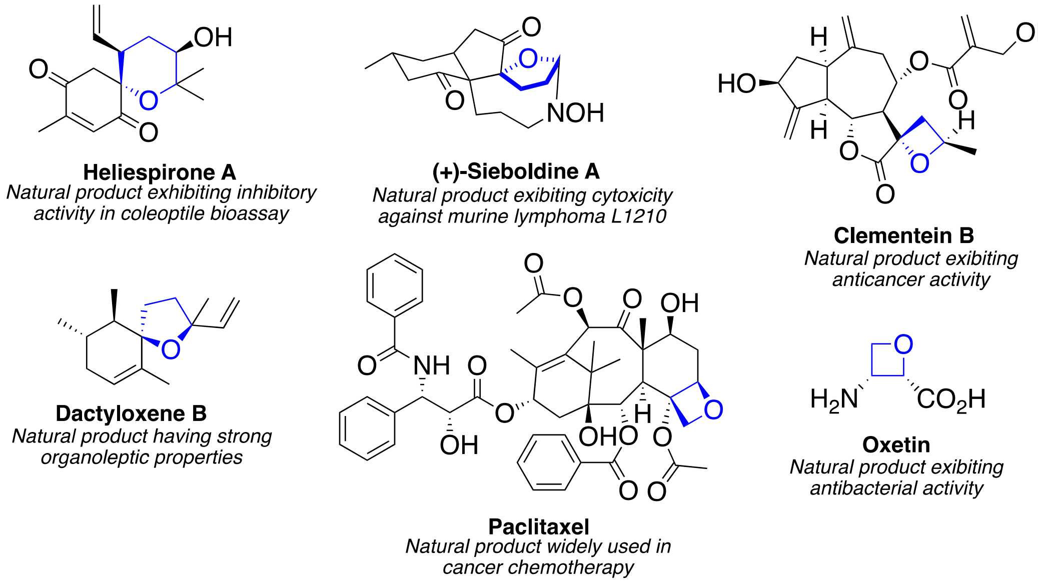
Introduction. *The Utility and Synthesis of Cyclic Ethers.*

In this work, new methods for the synthesis of ethers, specifically spirocyclic ethers will be explored. Common etherification strategies include the Williamson ether synthesis involving nucleophilic attack of oxygen on an electrophile (usually C-I, C-Br, C-OTf, etc), Paterno Büchi [2+2] photocycloaddition, epoxide ring opening with trimethylsolfonium ylide, rhodium-catalyzed O-H insertion and C-C bond forming cyclization (Scheme 2).[1] Oxetanes are an important functionality that is currently being used by pharmaceutical chemists as a new mode of introducing a way to tune lipophilicity, solubility, and metabolic stability of drugs.[1]



Scheme 2: Example of Approaches to the Synthesis of Oxetanes[3,4,5,6]

The synthesis of spirocyclic ethers has been applied to the synthesis of several natural products, as well as prodrug compounds (Scheme 3).[7,8] In particular, Clementein B and Oxetin both contain spirocyclic oxetanes, a class of cyclic ethers, in which both ends of the cyclic ether are bonded to the same carbon center.



Scheme 3. Examples of Natural Products Containing Cyclic Ethers[8,7,9,10,11,12]

In addition to their presence in natural products, cyclic oxetanes have also attracted interest for their unique physiochemical properties. For instance, a 3,3-disubstitued oxetane behaves similarly to a *gem*-dimethyl group with the oxetane being more polar and a better hydrogen bond acceptor than a *gem*-dimethyl group, considered to be a very similar to a carbonyl.[1] Several studies have explored the pharmacokinetics and biological properties of exchanging a carbonyl for an oxetane, and the results have shown an increase in lipophilicity and solubility.[1,11] With these attractive new ways to modify and tune a compound's properties, medicinal chemists need strategies for easily installing oxetanes as they develop libraries of compounds to screen. Multistep syntheses of oxetanes make it difficult to use similar moieties in preparing chemical libraries for screening.[11]

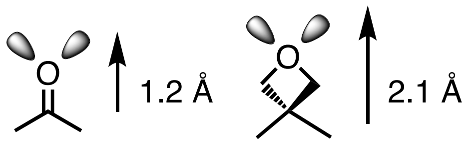
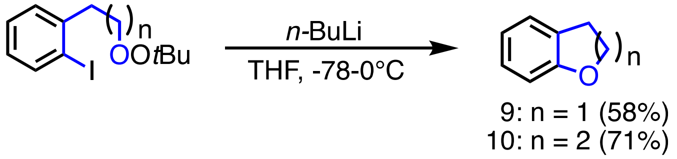


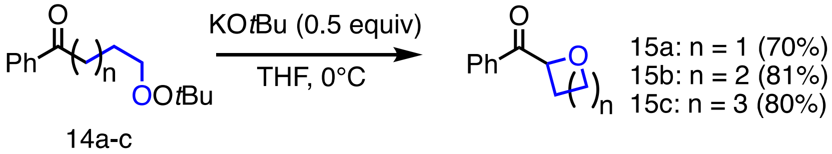
Figure 1. Length compared to carbonyls[11]

Our group recently reported a new method for synthesis of 5- and 6-membered spirocyclic ethers based on intramolecular carbanion attack of a carbanion on a peroxide electrophile. This method could be applied to the synthesis of a 4-, 5- and 6-membered spirocyclic ethers via a preformed peroxide precursor. The precursor could be assembled in advance of the key C-O bond forming process or, in some cases, could be assembled in advance.[13] Ben Puffer explored forming cyclic ethers by intramolecular C-O bond formation via an organolithium carbanion attack of the neighboring peroxide (Scheme 4a).[13] Another previous group member, Dr. Willand-Charnley investigated the use of stabilized enolates instead of organolithium carbanions to form the C-O bond for the 4-, 5-, and 6- membered cyclic ether (Scheme 4b). Dr. Willand-Charnley was also able to demonstrate the effectiveness of a modular peroxide precursor that would go through tandem C-C and then C-O bond formation under mild conditions to successfully form the 5- and 6- membered spirocyclic ethers (Scheme 4c).

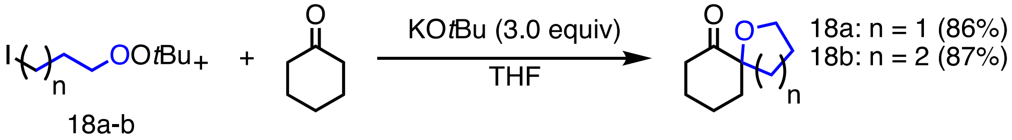
a) *Intramolecular C-O Formation via Oranolithium Carbanion*



b) *Intramolecular C-O Formation via Enolate Anions*

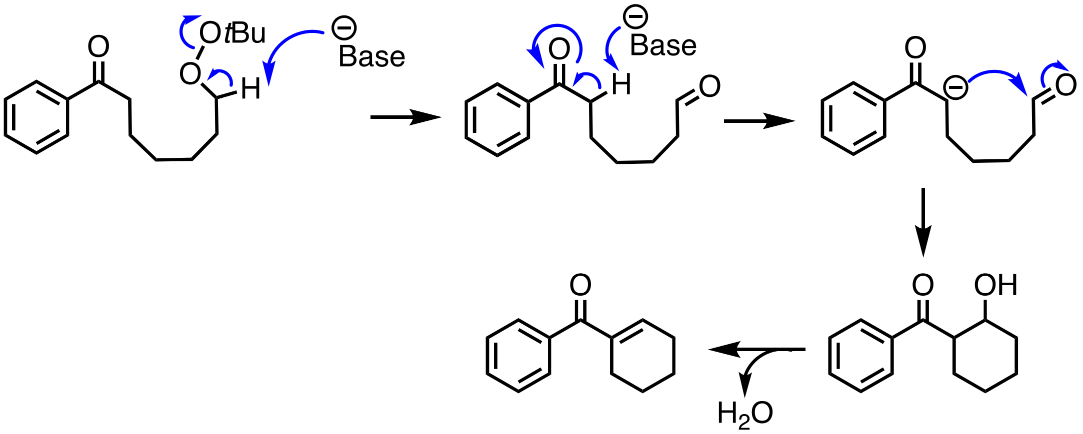


c) *Tandem C-C and C-O Bond Formation*



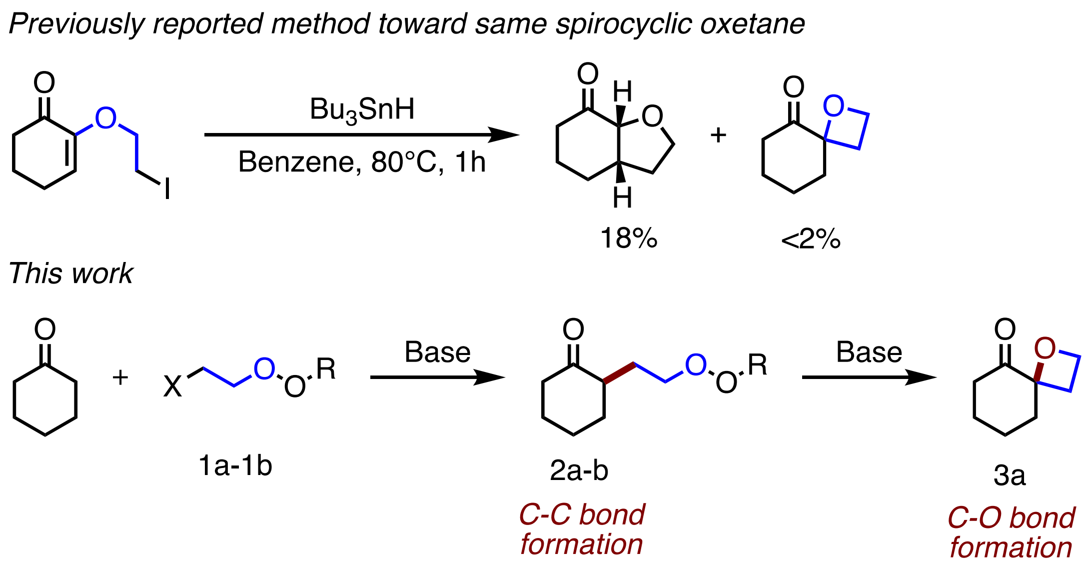
Scheme 4. Examples of C-O bond formation by intramolecular attack of peroxide[13]

This work explores routes toward spirocyclic oxetanes based on a class of reagents containing both a C- and O- electophile and capable of sequential formation of the C-C and C-O bonds of an oxetane (Scheme 6). Dr. Willand-Charnley synthesized these reagents for both the 5- and 6- membered spirocycle precursors, but observed that for 7-membered spirocycle precursor on the phenyl ketone framework, the iodoketone rapidly eliminated to the aldehyde via Kornblum fragmentation, which then underwent Aldol Condensation to form the major product (Scheme 5).[14,15]



Scheme 5. Byproduct from 7-membered ring closer[15]

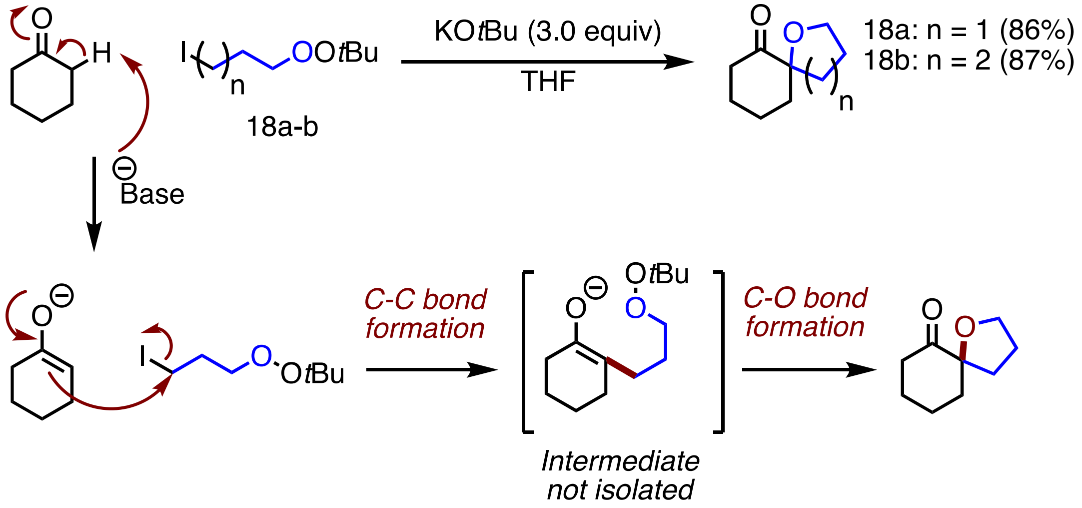
Strategies involving previous work has shown that this pattern of reactivity, utilizing the electrophilicity of the week O-O bond (32 kcal/mol), can provide an alternative strategy to ether synthesis, where a carbanion nucleophile can attack the electrophilic oxygen in the peroxide and form a cyclic ether in relatively few steps.[13] Utilizing intramolecular carbanion attack of an electrophilic peroxide oxygen as a way to access spirocyclic oxetanes under mild condition (Scheme 6).



Scheme 6. Previous work by Ponaras et al[16] and this work.

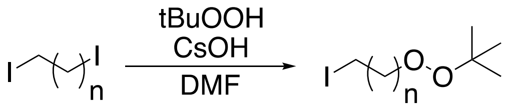
In the examples in Scheme 4, the tandem C-C and C-O bond formation was done in a one pot reaction to achieve rapid alkylation followed by cyclization, but in this research, we proceed by a stepwise alkylation followed by cyclization to optimize conditions for the alkylation conditions.

This work will focus on the C-C bond forming capability of peroxide precursors onto ketone substrates, as a way to make modular reagents that are capable of installing spirocyclic oxetanes by tandem C-C and C-O bond formation. The 5- and the 6-membered precursor to the spirocyclic ether have already been explored, but the peroxide precursor for the 4-membered ring had yet to be developed, prior to this work. The synthesis of a 4-membered ring peroxide precursor, referred to as the 2-peroxy-1-alkane precursor, will be explored in Chapter I, followed by the utility of the 2-peroxy-1-alkane precursor for C-C bond formation will be described in Chapter 2.



Scheme 7. Tandem C-C and C-O Bond Formation with Peroxide Precursors.

As previous work has shown, the 5- and 6- membered cyclic ether precursors have proven to be efficient modular reagents for forming spirocyclic ethers with stabilized carbanion.[13] The 4-membered cyclic ether precursor of this class of peroxide containing bis-electrophiles has yet to be explored. The previous peroxide precursors were synthesized by mono-alkylation of 1,*n*-diodoalkanes (Table 1).

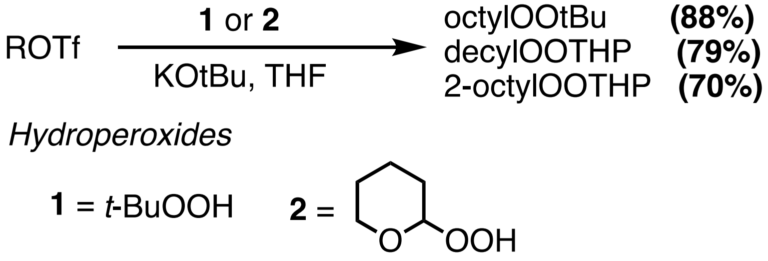


n	Yield	Ref.
4	64%	13
3	72%	13
2	70%[a]	13
1	Not attempted	

[a]Had difficulty reproducing

Table 1. Previous Method Toward the Bis-electrophile Peroxide Precursors of Different Chain Lengths.[13]

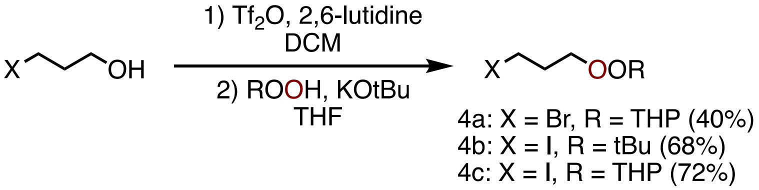
Synthesis of both the 5-carbon (n=4) and the 4-carbon (n=3) chain was efficient and high yielding, whereas the synthesis of the 3-carbon (n=2) chain proved to be high yielding, but was less reproducible and lead to substantial amounts of dialkylated product. Because of the lack of selectivity between mono- and di-alkylated products, a new route to these peroxide precursors was developed based on peroxide synthesis method developed by Dr. Kyasa. In his work, he demonstrated that primary triflates could be easily displaced by a peroxy anion, under mildly basic conditions (Scheme 8)



Scheme 8. Base Promoted Alkylation of Primary Triflates with Hydroperoxides.[17]

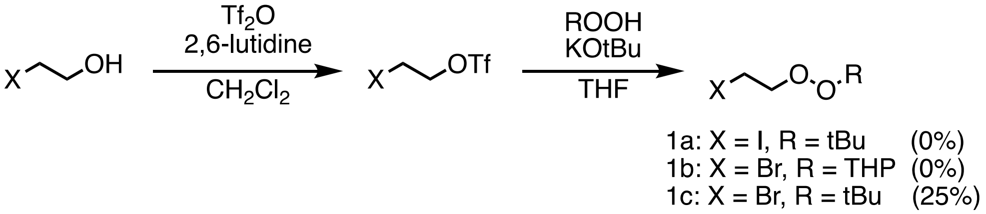
This methodology was utilized to synthesize several 3-carbon and 4-carbon chain peroxide precursors, illustrated for the 3-carbon systems in Scheme 9. However, as detailed below, the approach proved to be problematic for the synthesis of the 2-carbon reagent.

Results/Discussion. *Synthesis of a 2-peroxy-1-alkane precursor*



Scheme 9. Synthetic Route Utilizing Triflate Displacement to Access 4a-4c Peroxide Precursors.

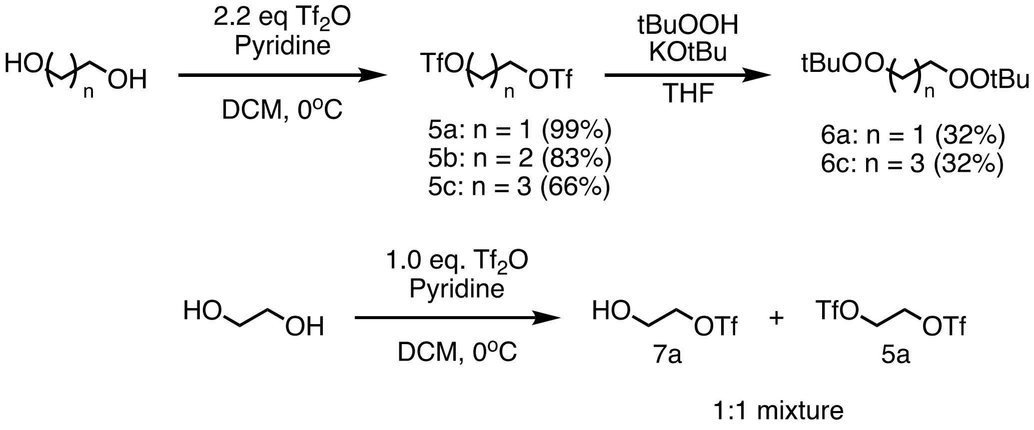
The synthesis of **4a-4c**, via based-catalyzed alkylation of a triflate using *t*-butyl hydroperoxide and tetrahydropyranyl hydroperoxie (THP) proved to be reproducible and high yielding (Scheme 9). This method was then applied to the synthesis of a 2-peroxy-1-alkane precursor, but was not as successful.



Scheme 10. Synthetic Route Utilizing Triflate Displacement to Access 1a-1c

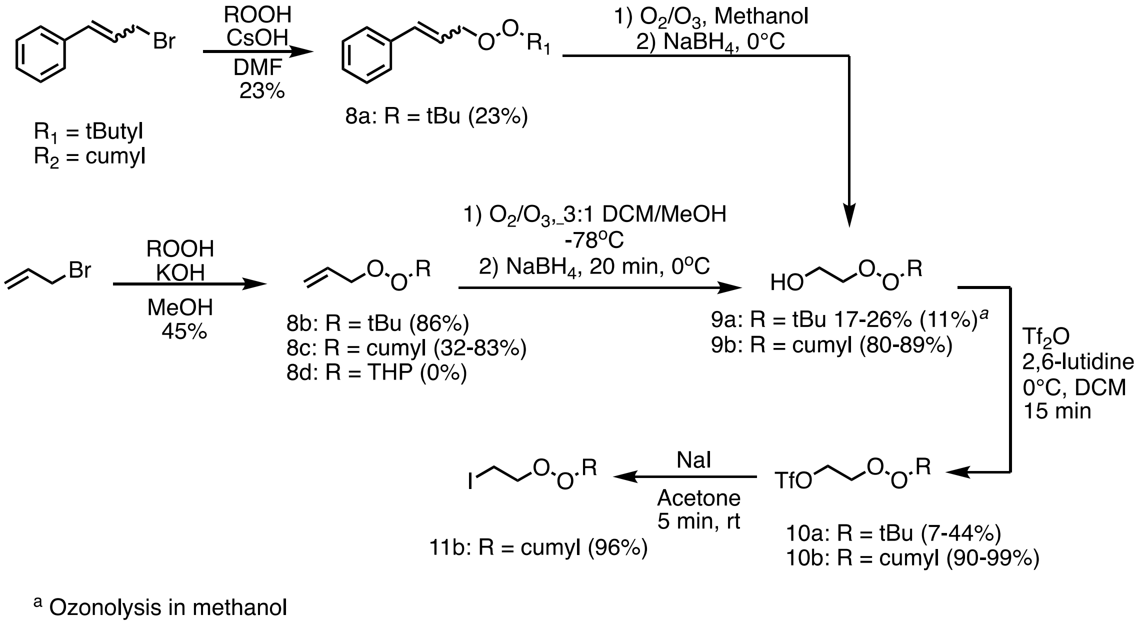
Starting with the 1-iodoethanol and using the same method as described earlier, did not furnish the corresponding product. The yield of this reaction was always low (>5%) and products rapidly decomposed under light or room temperature. These products were readily volatile and proved difficult to handle. Only in the case of the corresponding bromide, **1c,** was the monoperoxide isolated (25%) as a species which could be characterized before decomposing.

Our group's earlier failure to obtain the oxetane from reactions of a 2-peroxy-1-alkane (Scheme 7) could have resulted from the failure of either the initial C-C formation or the subsequent C-O bond forming steps (Scheme 7). Given the efficiency of the oxetane formation observed from preformed peroxyketones (Scheme 4b), it appeared likely that the failure reflected a C-C bond forming reaction that was slow enough to enable peroxide fragmentation to become dominant. Our proposed answer to this problem was to pursue a much more reactive C-electrophile. Therefore, we wanted to develop a much more reactive electrophile and design a peroxide precursor with a triflate electrophile for initical C-C bond forming alkylation.



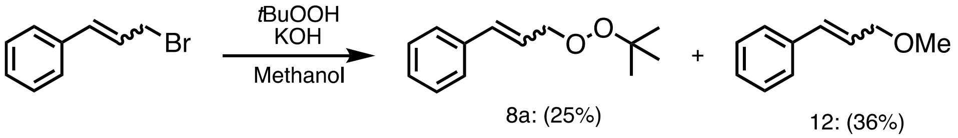
Scheme 11. Attempted Synthetic Route Utilizing Triflate Displacement of Bistriflates to Access Peroxide Precursors.

In this approach outlined above (Scheme 11), we converted several diols to bistriflate and then attempted to do monosubstitution with *t*-Butyl hydroperoxide. Instead of monoalkylation of **(5a)** and **(5c)**, only dialkylation was observed, giving diperoxides **(6a)** and **(6c).** It was observed that while trying to synthesize the bistriflate **(5a)** with only 1 equivalent of Tf_2O, the monosubstituted triflate was also observed **(7a)** in a 1:1 mixture of products. Isolation of **(7a)** proved to be difficult because both **(5a)** and **(7a)** are unstable and decompose at room temperature and during silica column chromatography. Unlike the 1,n-diodoalkanes (Table 1), the bistriflates did not yield monoalkylated peroxide products and were too reactive toward dialkylation with *t*-Butyl peroxide leading to diperoxides **(6a)** and **(6c)**. Since the bistriflate only affords diperoxides as the major product, another route toward a 2-peroxy-1-alkane precursor was explored.



Scheme 12. Synthetic Route to 2-peroxy-1-alkane precursor

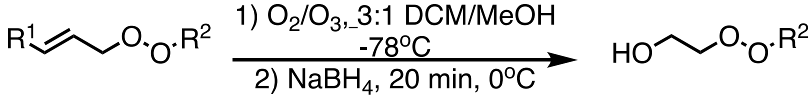
The final synthesis of the 2-peroxy-1-alkane precursor was achieved by synthesis of the **(10b)** with allyl bromide and cumyl hydroperoxide in a modified method originally published by Mosher et al.[18] After ozonolysis of **(8c)** and subsequent reduction with sodium borohydride**, (9b)** was obtained in excellent yields and was then easily converted to the primary triflate, which was then converted to the primary iodide by a substitution reaction. Several alkenes were synthesized as a precursor for ozonolysis, but **(8c)** proved to be the most easily accessible substrate.



Scheme 13. Synthesis of Alkene Precursor **8a**

While trying to synthesize an alkene precursor for a 2-peroxy-1-alkane precursor with *tert*-butyl hydroperoxide in potassium hydroxide in methanol, it was observed that the formation of the methyl ether **(12)** was a competing reaction in the synthesis of **(8a).** This could have been observed simply because the reaction was run in methanol. However, given the relative pKa values of hydroperoxides vs. alcohols, the hydroperoxyanion should have been the predominant deprotonated species. Thus, the results may actually suggest that methoxide is a considerably better nucleophile than the peroxyanion. Alkoxide was a stronger nucleophile when competing with the tert-butyl peroxy anion. This led to both **(8a)** and the methyl ether, **(12)**. Because of the competing reaction with the solvent, the reaction with cinnamyl bromide was done with a polar protic solvent, DMF which solvates the cesium cation and leads to a more dissociated anion. These conditions did not furnish a better yield of **(8a)**, so a different strategy was employed (Scheme 12).

The reaction between allyl bromide and *tert*butyl hydroperoxide, proved to be a more high yielding route, but the volatility of the product **(8b)** made isolation difficult, therefore cumyl hydroperoxide was used in place of the *tert*-butyl peroxide so that the product would be less volatile and were also more easily monitored by TLC. Ozonolysis of the **(8b)**, was low yielding and the product isolation difficult, so ozonolysis conditions were optimized (Table 2).



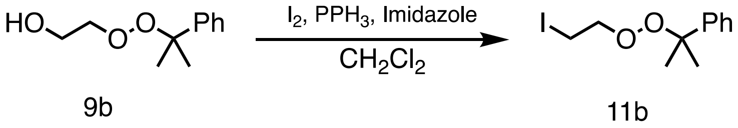
substrate	R^1	R^2	Solvent	Product	Yield of corresponding alcohol
8a	Ph	*t*Butyl	MeOH	**9a**	Only isolated benzyl alcohol byproduct
8b	H	*t*Butyl	MeOH	**9a**	26%
8c	H	Cumyl	DCM:MeOH 3:1	**9b**	84%
8c	H	Cumyl	MeOH	**9b**	>1%

Table 2. Ozonolysis of Alkene Precursors **8a-8c**

Ozonolysis was done with different methanol and methylene chloride combinations. In only methanol, **(8c)** was only isolated in less than 1%, but when the solvent system was a methylene chloride to methanol (3:1) mixture, the corresponding alcohol after reduction was achieved in an 84% yield. Since the **(8c)** yielded the highest yield of the alcohol after ozonolysis and subsequent reduction, this substrate was chosen as a good precursor to use while testing peroxide reactivity for reverse etherification.

The product **(9b)**, was easily converted to the triflate derivative, following a typical triflate procedure (Scheme 12).[17] The alcohol **(9b)** was also converted to the primary iodide by a modified Appel reaction to yield (**11b)** in moderate yield. It was also observed that temperature had a significant effect on this reaction; at 0°C less than 1% of **(11b)** was isolated, whereas at -41°C the reaction proceeded to **(11b)** in 56% yield.

Even though the reaction did proceed at -41°C, these results were not reproducible and thus the method was not a suitable approach to the **(11b)** 2-peroxy-1-alkane precursor.



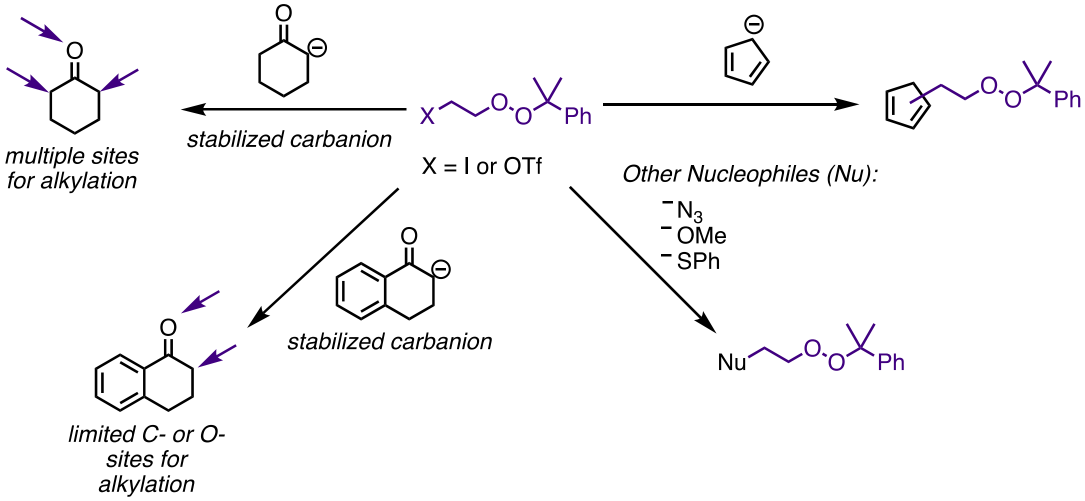
Temperature	% Yield of iodide
0°C	>1%
-41°C	56%

Table 3. Iodination of **9b** to Access the Peroxide Precursor **11b.**

Since the modified Appel reaction condition of **(9b)** proved problematic for reproducibility, the primary iodide was obtained by a simple substitution reaction on **(10b)** with sodium iodide exchange with sodium iodide. The downside to this, is that is requires an extra step in the synthesis of the primary iodide since the triflate has to be installed prior to the substitution reaction with iodide.

In conclusion, we have developed a robust synthetic route to two different 2-peroxy-1-alkane precursors (Scheme 12). With both a primary triflate **(10b)** and a primary iodide **(11b)** 2-peroxy-1-alkane precursors, we are now able to test the utility of these precursors for the synthesis of spirocyclic oxetanes by tandem C-C and C-O bond formation.

Chapter 2. *Introduction to the Utility of Peroxide Synthons*



Scheme 14. Substrates to explore C-C bond forming with **10b** and **11b**.

There are many different factors that affect selectivity in the reaction of nucleophiles and electrophiles. One well-known factor is the “hardness” or “softness” of the nucleophile and electrophile. Here is an overview of Pearson’s Hard Soft Acids Bases (HSAB) principle as it relates to alkylations of stabilized carbanion with triflate and iodide electrophiles and the preference for O-alkylation versus C-alkylation. “Hard” Lewis acids are less polarizable, small atomic radius, whereas “soft” Lewis bases are considered highly polarizable and low effective nuclear charge.[19] The HSAB principle says that hard acids prefer hard bases and soft acids prefer soft bases. In the table below, are some selected Lewis acids and bases and their classification according to the HSAB principle (Table 4).

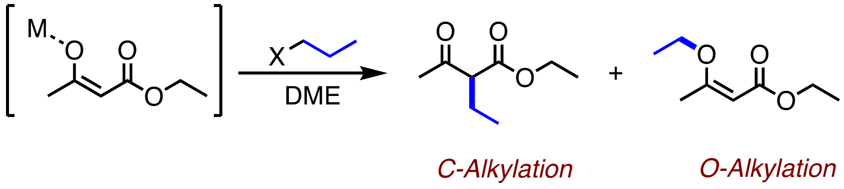
Lewis acids		
Hard	Borderline	Soft
H^+, Li^+, Na^+, K^+, RSO_2^+, $ROSO_2^+$, SO_3, RCO^+, NC^+	SO_2, NO^+, R_3C^+	RS^+, RSe^+, I^+, Br^+, ICN, O, Cl, Br, I, N
Lewis Bases		
Hard	Borderline	Soft

HO^-, F^-, $CH_3CO_2^-$, SO_4^{2-}, ROH, $RO^=$, RNH_2	N_3^-, N_2, Cl^-, Br^-, NO_2^-, SO_3^{2-}	R_2S, RSH, RS^-, I^-, SCN^-, $S_2O_3^{-2}$, CN^-, RNC, CO, R^-

Table 4. Classification of Several Lewis Acids and Lewis Bases.[19]

Enolate anions are ambident nucleophiles, containing both a hard oxygen and a soft carbon end. Because of this, alkylations with enolates can lead to a ratio of both O-alkylation and C-alkylation products, with the ratio often strongly dependent on the relative softness of the electrophile.[19] Alkylations under thermodynamic conditions, can lead to a mixture of highly substituted products.

The ratios of C-alkylation to O-alkyation are dependent on orbital overlap of the electrophile and nucleophile and also on how well the solvent solvates the counter ion. Table 5 outlines the general trends in reactivity with varying electrophiles, trending from soft (iodide) to hard (tosylate) and their C/O ratio dependent on various counterions and their added stability to the stabilized carbanion. In a tight transition state, lithium typical bound more tightly to the enolate, whereas cesium provides a more loosely coordinated enolate species. Because sulfonates are considered to be a “hard” electrophile, we expect that alkylation with triflate peroxides would lead to an increased fraction of O-alkyated products based on the orbital matching of the HSAB principle.



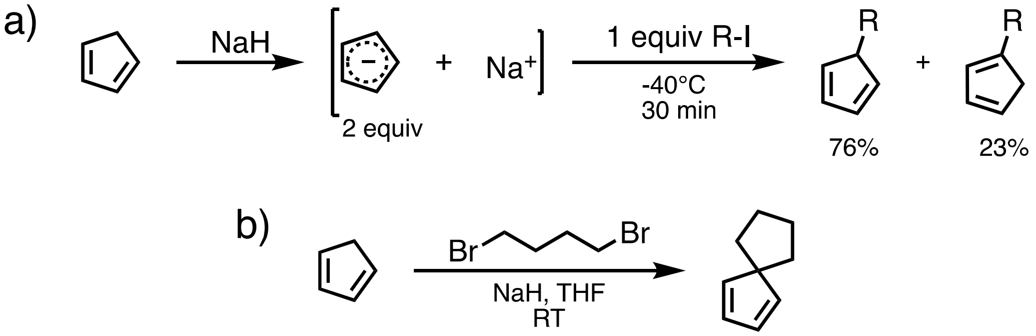
	C/O Ratio of Alkylation			
RX	Li	Na	K	Cs
CH_3CH_2I	>100	>100	>100	4.3
CH_3CH_2Br	70-75	60	41	10.3

$(CH_3CH_2O)_2SO$	3.8	14		
$CH_3CH_2OSO_2CF_3$	3.6	3.8		
$CH_3CH_2OSO_3CH_3$	2.4	8.6		
CH_3CH_2OTs	2.2-1.7	6-8.5	4.7	1.7

Table 5. C- versus O-Alkylation with Several Nucleophiles.[20]

Background on Cyclopentadiene Alkylations

We were also interested in exploring the reaction of our peroxide electrophiles with cyclpentadienes. According to literature examples, primary alkyl iodides, will alkylate onto cyclopentadiene in high yields, with the less substituted alkene isomer being the more favorable. According to Nokami et al, both isomers are able to be observed after the reaction is quenched, but that when left at room temperature for several hours, the isomers equilibrate to the more substituted isomer (Scheme 15a).[21]

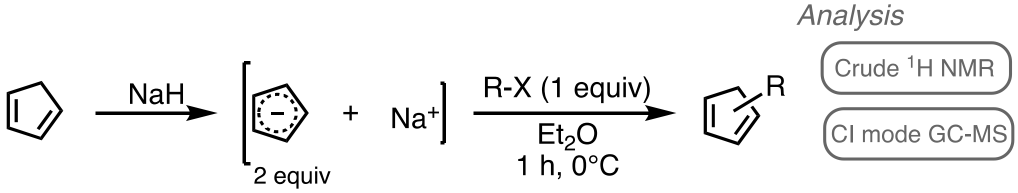


Scheme 15. Literature Alkylations with Cyclopentadiene[21,22]

It is also reported that alkylation can occur twice and that use of 1,*n*-dihalide (Scheme 15b), electrophiles leads to spirocyclic cyclopentadiene products. We used this reaction, along with monoalkylation by a primary alkyl iodide, as control reactions to verify the presence of the cyclopentadienyl anion in our studies.

With the 2-peroxy-1-alkane precursors **(10b)** and **(11b),** we now proceed to explore the reactivity of this new reagent. After the success shown by precursors for the 5- and 6-membered ring precursor, we expect 2-peroxy-1-alkane precursors **(10b)** and **(11b** to behave similarly. We proceeded by using similar alkylation conditions previously reported by Dussault et al.[13] Then a different ketone substrate, α-tetralone was explored as a good substrate to identify the C- and O-alkylation ratios. Following the these alkylations with stabilized enolates, we explored cylopentadiene alkylations. All of these alkylations were difficult and lead to a many byproducts, including some cases, self-reaction of the ketone.

Results/Discussion.



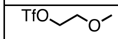
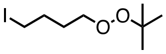
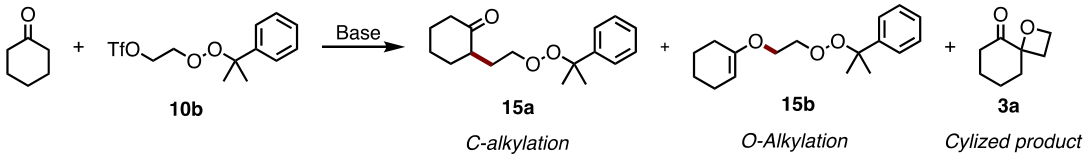
RX	Conditions	SM MW.	GC MS (CI with CH_4) major peaks	m/z	Rel. Int. %	Analysis	Crude NMR
11b	2 equiv CpNa	MW. 306	Peak #2	119 $[M+H]^{\bullet+}$	100	protonated cumyl alcohol with neutral loss of H_2O	^{1}H NMR shows SM peroxide as ~95%
			Peak #4	119 $[M+H]^{\bullet+}$ 135 $[M+H]^{\bullet+}$	100 70	Protonated SM intact peroxide with fragmentation of peroxide O-O	
10b		MW. 328	Peak #1	87 237	100 10		^{1}H NMR shows SM peroxide, diethyl ether, several other unidentified peaks
			Peak #2	119 $[M+H]^{\bullet+}$	100		
			Peak #3	159 $[M+CH_4]^{\bullet+}$ 119 236	100 42 24		
 **13a**		MW. 208	Peak #1	156 176 $[M+H]^{\bullet+}$ 204 216	100 80 20 5	α-cleavage of methyl ether to yield protonated allyl triflate ion	^{1}H NMR too messy to identify
			Peak #4	240 106 280	100 50 5		
 **14**		MW. 272	Peak #1	73 $[OC(CH)_3]^{\bullet+}$ 57 $[C(CH)_3]^{\bullet+}$ 18	100 84 10	t-Butyl oxide fragment ion	^{1}H NMR shows SM peroxide as ~95%
			Peak #2	57 $[C(CH)_3]^{\bullet+}$ 73	100 48	t-Butyl fragment ion	
1,4-diiodotbutane	1 equiv CpNa	MW. 309	Peak #1	183 55	100 52		
10b		MW. 328	Peak #1	119 $[M+H]^{\bullet+}$ 121	100 16		^{1}H NMR too messy to identify
13a		MW. 208	No peaks in GC				^{1}H NMR alkene signal too small to identify
1-iodoheptane		MW. 266	Peak #1	57 $[C_4H_9]^{\bullet+}$ 225	100 3	Stable fragment from alkane	^{1}H NMR alkene signal too small to identify
			Peak #2	67 163 205 $[cp+C_7H_{15}+C_3H_6]^{\bullet+}$	100 95 5	Dialkylated cp with loss of 57 neutral	
14		MW. 272	Peak #1	73 $[OC(CH)_3]^{\bullet+}$ 57 $[C(CH)_3]^{\bullet+}$ 183	100 90 10		^{1}H NMR alkene signal too small to identify
			Peak #2	73 $[OC(CH)_3]^{\bullet+}$ 57 $[C(CH)_3]^{\bullet+}$ 211	100 52 5		

Table 4. Alkylations with Cyclopentadiene and Analysis by GC-MS and crude ^{1}H NMR.

We explored cyclopentadienyl anion as a way to test the reactivity of both **(10b)** and **(11b)**. Based on the results from the alkylations with cyclopentadienyl anion, we are unable at this time to conclude whether alkylation of either occurred with **(10b)** and **(11b)** and then fragmented in the injector port of the GC-MS or if the peroxide precursor decomposed under basic conditions before alkylation took place.

Future directions to improve the experiments with cyclopentadienyl anion, would be to change the counter ion to thallium, which is a stable intermediate. Experiments run under electron ionization lead to excessive fragmentation which made interpretation of the crude reaction mixtures impossible. Fragmentation could have also occurred at the inlet to the GC, which would show no in tack peroxides present, whereas TLC and crude NMR spectroscopy showed still showed remaining peroxide starting materials in many cases.



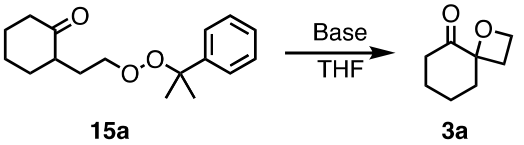
Rxn #	Base	Solvent	Time	% C-Alkylation product **15a**	% O-Alkylation product **15b**	% Cyclized product **3a**	% cumyl alcohol	% recovered SM peroxide **10b**
1	LDA	THF	17 h	6	1			
2	KOtBu	THF	17 h	0	0			
3	LDA	THF	20 min	14	1			13
4	LDA	Hexane	40 min	20	4			
5	LDA	Et_2O	20 min	32	10			9
6	LDA^a	THF	20 min	>1		>1		

7	LDA	Hexane	45 min	20	4	5	23	6

ᵃ3.0 equivalents of LDA. All (%) yields are isolated yields

Table 5. Alkylation Results of Cyclohexanone with **10b**.

It was concluded, that even though some mono-alkylation occurred, it was minor and therefore it was necessary to explore another substrate that limited the possible side reactions. Since cyclohexanone has the possibility of alkylating multiple times in the presence of excess base, that leads to several possible byproducts, as well as fragmentation products, we explored alpha-tetralone as a stabilized carbanion.

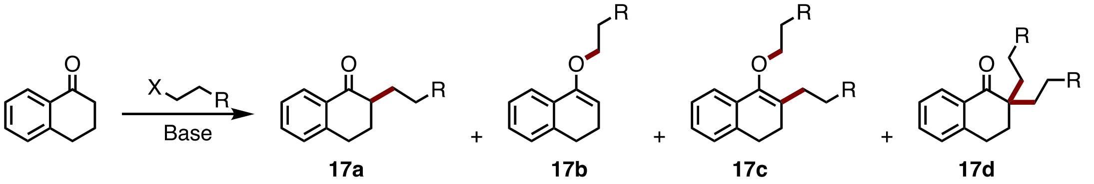


Base	Time	% Yield
KOtBu	20 min	0%
KH	20 min	0%
NaH	20 min	0%

Table 6. Cyclization Results from **15a**.

We therefore began to explore alkylations with alpha-tetralone, which is also forms a stabilized carbanion, but only has two possible reaction sites; limiting the reaction possibilities to either O- or C- alkylation under basic conditions. The alkylations with alpha-tetralone proved to be very revealing about the nature of the peroxy triflate and peroxy iodide synthons. Under basic conditions, the major products recovered were α-tetralone and cumyl alcohol. The large amounts of cumyl alcohol recovered suggested

Kornblum fragmentation was occurring faster than alkylation of our electrophile.

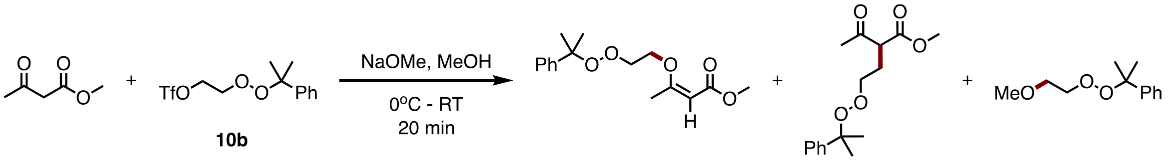


			Conditions		isolated % yield						
Entry	X	R	Base	Reaction Time	**17a**	**17b**	**17c**	**17d**	Recovered α-tetralone	Recovered alkylating agent	Cumyl alcohol
1	I	$OOC(CH_3)_2C_6H_5$	NaH^{c}	4 h 50 min					46	4^{a}	40
2			LDA^{c}	4 h 50 min					32	35	28
3			KOtBu^{c}	4 h 50 min	2^{a}				46	0	41
4	OTf	$OOC(CH_3)_2C_6H_5$	KOtBu^{d}	2 h					58	0	27
5			LDA^{d}	18 h							84
6	OTf	OCH_3	KOtBu^{d}	2 h	21	18	10		7	0	
7			LDA^{d}	18 h	17	>1	20^{b}		29	0	
8	I	$(CH_2)_4CH_3$	LDA^{d}	18 h	>1				69	51	
9			NaH^{c}	4 h 59 min				1	71	0	
10	I	$OOC(CH_3)_2C_6H_5$	NaH	16 h 50 min					46	4	40
11			LDA	16 h 50 min					32	35	28
12			KOtBu	16 h 50 min					46	8	52
13	OTf	$OOC(CH_3)_2C_6H_5$	KOtBu	2 h					58	0	27
14			LDA	18 h						0	84

[a] sample still contains impurities, [b] aldol product, [c] Solvent was THF, [d] Solvent was Et_2O because primary triflates in THF can lead to polymerization byproducts

Table 6. Alkylation Results of α-tetralone with **10b.**

Since α-tetralone proved to be a problematic substrate, we began to explore whether or not the 2-carbon synthon preferred O-alkylation or C-alkylation.[20] Previous research has shown that depending on the electrophile, whether hard or soft, it will ether alkylate to the carbon or oxygen or the stabilized enolate.



10b

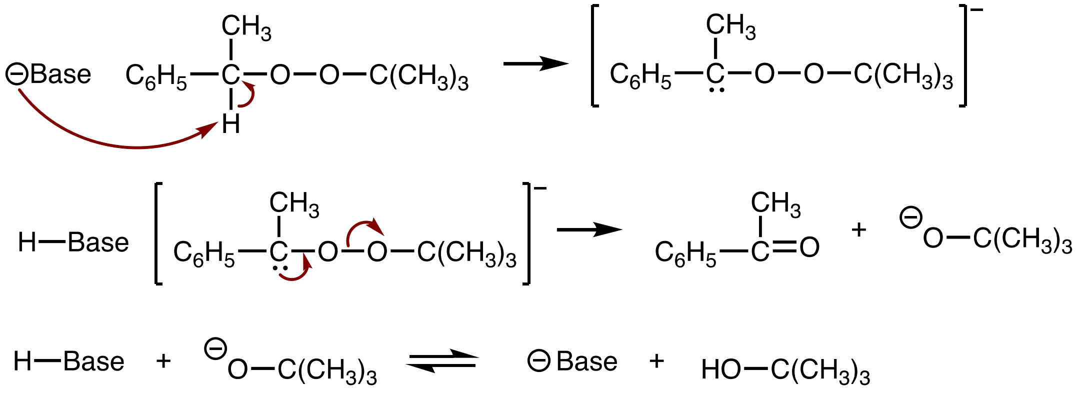
18a (4%) **18b** (9%) **18c** (18%)

Scheme 16. Alkylation with Methyl Acetoacte and **10b**.

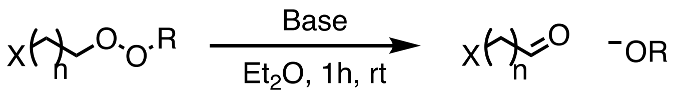
Although O-alkylation should be preferred according to the HSAB principle, alkylation with methyl acetoacetate with sodium hydroxide in methanol, shows that in general, both O-alkylation and C-alkylation are not the favored process. In the case above, the methyl ether formed as a byproduct of the methoxide present is the major product. It appears that since **18a** and **18b** are the major products, the alkylation with **10b** is considerably slower than the displacement of triflate by the methoxide to form **18c** as a competing product. This brings up a question about the stability and reactivity of the 2-peroxy-1-alkane precursor in the presence of carbon and oxygen nucleophiles.

Here in, we report attempted alkylations with both the iodo and triflate of the 2-peroxy-1-alkane precursor **(10b)** and **(11b)** on various carbon substrates; substrates that vary in carbanion stabilization. With this scope of reactions, we conclude that the two-carbon precursor is too sensitive to Kornblum fragmentation under the alkylation conditions (Scheme 17). Prior to alkylation, the base present is cannibalizing the peroxide substrate, which halts any alkylation and also any chance at future spirocyliziation on the substrate. The 5- and 6- membered ring precursors are significantly more stable to the alkylation system then the 2-peroxy-1-alkane precursor, which undergoes Kornblum fragmentation with a variety of bases (Table 7).

Base Catalyzed Decompositon of Dialkyl Peroxide



Scheme 17. Mechanism of Base Catalyzed Decomposition of Dialkyl Peroxides.[14]

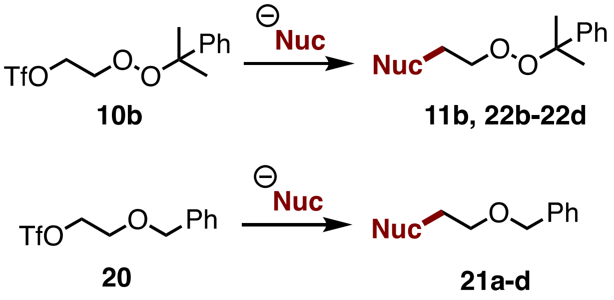


Entry	X	n	R	substituent	Base	%Recovered Starting Material	%Alcohol from fragmentation
1	OTf	1	-OOC$(CH_3)_2C_6H_5$	**10b**	KH	67%	37%
2					KO*t*Bu	13%[a]	83%
3					LDA	15%	55%
4	Br	2	-OOC$(CH_3)_3$	**19**	KH	82%	-
5					KO*t*Bu	28%[b]	-
6					LDA	72%	-
7	I	3	-OOC$(CH_3)_3$	**14**	KH	27%	-
8					KO*t*Bu	60%	-
9					LDA	68%	-

[a]No peroxide observed by TLC after 5 minutes for KOtBu/Et_2O conditions, [b]aldehyde seen not isolated, only observed by H NMR

Table 7. Base Catalyzed Decompostion of Dialkyl Peroxides **10b, 19, 14**.

Our final experiments used several classic heteromatic S_N2 nucleophiles (iodide, methoxide, azide, and thiolate) to probe the reactivity of our 2-peroxy-1-alkane precursor **(11b)** vs. a model substrate **(20)**, which lacked the peroxide (Table 8). In the reactions with these selected nucleophiles, the 2-peroxy-1-alkane precursor **(11b)** proved to be equally reactive toward nucleophilic attack, demonstrating that the presence of nearby peroxide did not inhibit S_N2 nucleophilic attack to any greater degree than an ether oxygen as seen in the model substrate **(20)**.



Substrate	Nucleophile	Product	% Yield of Substitution Reaction
10b	I^-	**11b**	96%
20	I^-	**21a**	85%
10b	MeO^-	**22b**	72%
20	MeO^-	**21b**	
10b	N_3^-	**22c**	68%
20	N_3^-	**21c**	59%
10b	PhS^-	**22d**	66%

20	PhS^-	**21d**	97%

Table 8. Nucleophilic Substitution Reactions with **10b** and Model Triflate Compound **20**.

In conclusion, the 2-peroxy-1-alkane precursor proved to have limited use for oxetane synthesis based upon tandem C-C and C-O bond formation. The 2-peroxy-1-alkane precursor proved highly sensitive to base-promoted (Kornblum)[14] fragmentation, even under relatively mild, conditions and the undesired fragmentation appears to be more rapid than the C-C bond formation required as a first step in the oxetane synthesis. In contrast, the 1,2-peroxide triflate efficiently C-alkylates a variety of heteroatom nucleophiles, suggesting that this substrate could prove a useful reagent for modular introduction of peroxide analogs of glymes.

Future work on this project should explore uses of this 2-peroxy-1-alkane precursor as a modular reagent for introduction of peroxides to form peroxide analogs of glymes. Although base-catalyzed fragmentation proved to be a significant problem for the 2-peroxy-1-alkane precursor **(10b)** and **(11b),** it would be interesting to explore the reactivity of a similar 2-peroxy-1-alkane precursor that blocks the basic site and prevents fragmentation. Once the fragmentation pathway is blocked, it is possible that a 2-peroxy-1-alkane precursor could undergo sequential C-C and C-O bond formation, leading to the spirocyclic oxetane.

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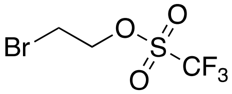
EXPERIMENTAL SECTION

General Experimental. Reagents and solvents were used as supplied commercially, except for DCM and THF, which were distilled from CaH_2 and Na/Ph_2CO, respectively. Reagents supplied as solutions were dispensed based upon manufacturer-supplied concentrations. Reactions were conducted under an atmosphere of N_2 except where noted. Unless otherwise noted, reactions were performed in glassware that was flame dried and evacuated and backfilled with nitrogen. Thin-layer chromatography (TLC) was performed on 0.25 mm hard-layer silica G plates visualized with a UV lamp or by staining: 1% ceric sulfate and 10% ammonium molybdate in 10% H_2SO_4 (general stain, after heating); 3% vanillin in 3% H_2SO_4 in EtOH (general stain, after heating); or a 1% N,N′-dimethyl-p- phenylenediamine in 1:20:100 acetic acid/water/methanol (specific for peroxides). Flash column chromatography was performed on 230-400μM silica gel. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were acquired in $CDCl_3$ on a Bruker Advance 400 MHz or a Bruker 300 MHz. ^1H spectra are reported as chemical shift (multiplicity, number of protons, J couplings in Hz). IR spectra were recorded as neat films on a ZrSe crystal; selected absorbances are reported wavenumbers (cm^{-1}). Abbreviations: hexane = Hex; EA = ethyl acetate; THF = tetrahydrofuran; THP = tetrahydropyranyl; DMF = dimethylformamide; Tf_2O = trifluoromethanesulfonic anhydride; KOtBu = potassium *tert*-butoxide; KOH = potassium hydroxide.

t-Butyl Hydroperoxide [75-91-2], 5.5 M in decane, was used as purchased from Sigma Aldrich.

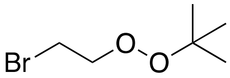
Cumene Hydroperoxide [80-15-9], 80% solution was purchased from Sigma Aldrich.

2-Tetrahydropyranyl (THP) Hydroperoxide [4676-84-0] was synthesized following a known procedure.[17]



2-bromoethyl trifluoromethanesulfonate

2-Bromoethyl trifluoromethanesulfonate [103935-47-3] was prepared (0.0422 g, 16%) was prepared by an adapted procedure.[23] 2-Bromoethanol (0.1249 g, 1.0 mmol) was added to 2,6-lutidine (2.1 mmol, 0.2250 g) and stirred at 0°C. Trifluoromethanesulfonic anhydride (2.2 mmol, 0.36 mL) was added dropwise and the reaction was then stirred for 30 min before being quenched with 10% EA/Hex (~2 mL). Was passed through a short silica plug and removed solvent under reduced pressure and temperature (water bath at 10°C), followed by distillation with Kügelrohr at 6 mmHg at 60°C to obtain a clear colorless liquid, with the following spectral details; ^{1}H NMR (400 MHz): 4.76 (t, 2H, J = 6.75 Hz), 3.62 (t, 2H, J = 6.0 Hz); R_f = 0.62 (20% EA/Hex). Spectral details matched previously reported.[23]

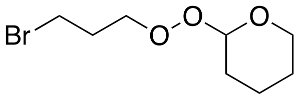


2-((2-bromoethyl)peroxy)-2-methylpropane

2-((2-Bromoethyl)peroxy)-2-methylpropane (1c) [56345-26-7] was prepared (0.1468 g, 25%) by adding pyridine (3.0 mmol, 0.24 mL) to THF (0.23 M, 13.0 mL), followed by dropwise addition of Tf_2O for 10 minutes at 0°C, which turned the clear colorless solution opaque white. 2-bromoethanol (3.0 mmol, 0.3749 g) was added to THF (1.5 M, 2 mL) dropwise to the reaction; after 30 minutes the solution mixture was a slight brown color and then was stirred for another 30 minutes before quenching with water. The mixture was extracted with two portions of diethyl ether (2x20 mL) and then the combined organic layers were dried over sodium sulfate. The resulting solution was concentrated on a rotary evaporator at reduced temperature (10°C at 200 mmHg) to give a clear yellow oil of crude bromotriflate. KOtBu (3.0 mmol, 0.4039 g) and tBuOOH (3.0 mmol, 0.54 mL of 5.5 M solution in decane) with THF (1.5 M, 2 mL) were added sequentially to THF (0.3 M, 10 mL) and cooled to 0°C. Crude triflate was then added with THF (1.0 M, 3 mL) dropwise to the mixture of KOtBu/tBuOOH over a period of 5 minutes. The reaction was stirred for 21 hours before being quenched with water. The mixture was extracted twice with diethyl ether (2x30 mL) and then the combined organic layers were dried over sodium sulfate. The resulting solution was concentrated on a rotary evaporator and purified with silica chromatography using 10% EA/Hex to furnish a clear colorless, sweet smelling liquid in with the following spectral details; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (t, 2H, J = 6.4 Hz), 3.57 (t, 2H, J = 6.4), 1.27 (s, 9H); ^{13}CNMR (400 MHz, $CDCl_3$) δ 80.8 (C), 74.5 (C, 2H), 28.7 (C, 2H), 26.4 (3C, 6H); IR (neat) 2977, 2931, 1363, 1195 cm^{-1}; R_f = 0.69 (20% EA/Hex). Spectral details previously reported show a similar coupling of the expected product and since previously report spectra was collect in CCl_4 on a ^{1}H NMR (60 MHz) it shows the expected downfield shifts.[24]

Procedure for dialkyl peroxides via Alkylation with triflate: **2-((3-Bromopropyl)peroxy)tetrahydro-2*H*-pyran** and **2-((3-Iodopropyl)peroxy)tetrahydro-2*H*-pyran.**

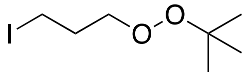
A solution of alcohol (3.0 mmol, 1.0 equiv) in CH_2Cl_2 (0.3 M, 9 mL) was cooled to 0°C, and Tf_2O (6.3 mmol, 2.1 equiv) and 2-6-lutidine (6.0 mmol, 2.2 equiv) were sequentially added. The reaction was allowed to stir for 20 minutes at 0°C before being diluted with cold hexane (25 mL). The solution was then washed with 0.1 M aq. $KHSO_4$ (10 mL) and then the combined organic layers were dried over sodium sulfate. The solution was then concentrated on a rotary evaporator (200 mmHg, 10°C bath) to yield a light brown oil of crude triflate residue, which was stored in a -20°C freezer, while a solution of alkyl hydroperoxide (3.0 mmol, 1.0 equiv) and THF (0.2 M, 20 mL) solution was prepared and cooled to 0°C. KOtBu (3.0 mmol, 1.0 equiv) was added to the solution, which was stirred stir for several minutes to achieve dissolution before adding triflate (described initially). Reaction was stirred at 0°C for 15 minutes before being quenched with water (5 mL). The mixture was extracted with three portions of 10% EA/Hex and then the combined organic layers were dried over sodium sulfate. The resulting solution was concentrated on rotary evaporator and purified with silica chromatography using 10% EA/Hex.



2-((3-bromopropyl)peroxy)tetrahydro-2*H*-pyran

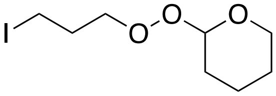
2-((3-Bromopropyl)peroxy)tetrahydro-2*H*-pyran (4a) was prepared (0.0832 g, 43%) by a procedure adapted from Kyasa et al[25]. Using the ***Procedure for dialkyl THP peroxides via Alkylation with triflate*** (above), 3-bromo-1-propanol (0.417 g, 3.0 mmol) was reacted with Tf_2O (3.17 mL, 6.3 mmol) and 2,6-lutitdine (2.1217 g, 6.6 mmol) to furnish crude bromopropyl triflate, which was then reacted with THP hydroperoxide (0.3543 g, 3.0 mmol) and KOtBu (0.3366 g, 3.0 mmol) to furnish a colorless oil ^1H NMR (400 MHz,

$CDCl_3$) δ 5.15 (m, 1H), 4.25 (t, 2H, J = 5.8 Hz), 4.02 (m, 1H), 3.65 (m, 1H), 3.54 (m, 3H), 2.24 (td, 2H, J = 6.1, 2.8 Hz,), 1.75-1.58 (overlapping peaks, 5H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 101.0 (C, 1H), 72.9 (C, 2H), 62.8 (C, 2H), 31.4 (C, 2H), 30.1 (C, 2H), 27.9 (C, 2H), 25.2 (C, 2H), 19.8 (C, 2H); IR (neat): 2869, 1724, 1440, 1104 cm^{-1}; R_f = 0.63 (20% EA/Hex).



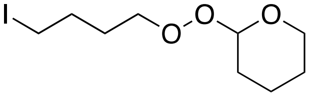
1-(*tert*-butylperoxy)-3-iodopropane

1-(*tert*-Butylperoxy)-3-iodopropane (4b) [101860-37-1] was prepared (0.6994 g, 68%) by first dissolving 1-iodopropanol (4.0 mmol, 0.7439 g) in CH_2Cl_2 (1.25 M, 5 mL) and cooled at 0°C, while adding Tf_2O (8.4 mmol, 2.3699 g) dropwise for 10 minutes. Then 2,6-lutidine (8.8 mmol, 0.9430 g) was added and stirred for 20 minutes before diluting with cold hexane (10 mL) and 0.1 M $KHSO_4$ (5 mL). Extract with a second portion of cold hexane and then dried over sodium sulfate. Solvent was removed solvent on rotary evaporator at reduced temperature (10°C). In a new flask, combine tBuOOH (4.0 mmol, 0.73 mL of 5.5 M solution in decane) was combined with THF (0.1 M, 10 mL) and stirred at 0°C. Then KOtBu (4.8 mmol, 0.5386 g) was added and stirred until dissolved. Combine THF (0.1 M, 10 mL) and triflate intermediate and then added to tBuOOH/THF solution and stirred for 4 hours before quenching dropwise with water. The mixture was extracted with three portions of EA (3x50mL) and the combined organic layers were dried over sodium sulfate. Remove solvent on rotary evaporator and residue was purified by chromatography with 10% EA/Hex. A clear oil was isolated in 68% with R_f = 0.77 (20% EA/Hex). Spectral details matched those previously reported[13,26]



2-((3-iodopropyl)peroxy)tetrahydro-2*H*-pyran

2-((3-Iodopropyl)peroxy)tetrahydro-2*H*-pyran (4c) was prepared (0.8252 g, 72%) by a procedure adapted from Kyasa et al[25]. Using the ***Procedure for dialkyl THP peroxides via Alkylation with triflate*** (above), 3-iodo-1-propanol (0.7439 g, 4.0 mmol) was reacted with Tf_2O (1.41 mL, 8.4 mmol) and 2,6-lutitdine (0.9430 g, 8.8 mmol) to furnish crude iodopropyl triflate, which was then reacted with THP hydroperoxide (0.4725 g, 4.0 mmol) and KOtBu (0.4488 g, 4.0 mmol) to furnish a colorless oil with the following spectral details; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (m, 1H), 4.17 (t, 2H, J = 5.8 Hz), 4.00 (m, 1H), 3.64 (m, 1H), 3.29 (t, 2H, J = 6.8 Hz), 2.19 (quint, 2H, J = 6.4 Hz), 1.74-1.56 (overlapping peaks, 4H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 101.0 (C, 1H), 74.8 (C, 2H), 62.8 (C, 2H), 32.0 (C, 2H), 27.9 (C, 2H), 25.2 (C, 2H), 19.8 (C, 2H), 2.5 (C, 2H); IR (neat) 2940, 2869, 1439, 1351 cm^{-1}; R_f = 0.35 (10% EA/Hex).



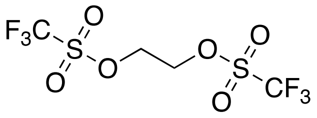
2-((4-iodobutyl)peroxy)tetrahydro-2*H*-pyran

2-((4-Iodobutyl)peroxy)tetrahydro-2*H*-pyran was prepared (0.3881 g, 43%) by an adaptation of an existing procedure[27]. Cesium hydroxide (0.4497 g, 3.0 mmol) was added to a flame dried flask in a glove bag under nitrogen atmosphere. DMF (5.3 mL, 0.56 M) was added to the cesium hydroxide and stirred at 0°C for 2 hours to achieve dissolution. The THP hydroperoxide (0.4252 g, 3.6 mmol) was added, followed by 1,4-diiodobutane (0.9295 g, 3.0 mmol) in DMF (2.0 mL, 1.0M). The reaction was stirred for

15 hours at 25°C and then quenched with water (~1.0mL). The aqueous layer was extracted with EA (12x10 mL) and the combined organic layers were dried over sodium sulfate. The solvent was removed on roto evaporator and then chromatographed with a 5-10% EA/Hex gradient to obtain a clear colorless oil with the following spectral details; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (m, 1H), 4.14 (t, 2H, J = 6.2 Hz), 4.01 (tt, 1 H, J = 8.3, 3.1 Hz), 3.65 (m, 1H), 3.24 (t, 2H, J = 6.9 Hz), 1.95 (quint, 2H, J = 6.9 Hz), 1.76 (m, 4H), 1.58 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 101.1 (C, 1H), 74.0 (C, 2H), 62.7 (C, 2H), 30.1 (C, 2H), 29.0 (C, 2H), 28.0 (C, 2H), 25.2 (C, 2H), 19.8 (C, 2H); IR: 2940, 2869, 1724, 1440, 1104 cm^{-1}; R_f = 0.47 (20% EA/Hex).

General Bistriflate Method.

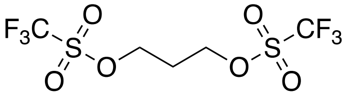
Tf_2O (7.5 mmol) was added dropwise to CH_2Cl_2 (0.1 M, 5 mL) and cooled to 0°C. In a separate vial, pyridine (5.0 mmol) and diol (5.0 mmol) were combined. The pyridine/diol mixture was then added dropwise to Tf_2O solution over a period of 20 minutes. The reaction was stirred for 10 minutes before being quenched with water. The mixture was extracted with three portions of EA and then the combined organic layers were dried over sodium sulfate. The resulting solution was concentrated on a rotary evaporator to furnish a waxy grey solid.



ethane-1,2-diyl bis(trifluoromethanesulfonate)

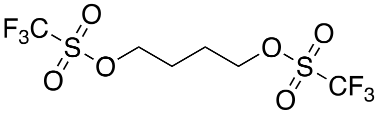
Ethane-1,2-diyl bis(trifluoromethanesulfonate) (5a) [18928-34-2] was prepared (1.7721 g, 99%) with the ***General Bistriflate Method*** (above), ethylene glycol (0.3103 g, 5.0

mmol) was reacted with Tf_2O (1.84 mL, 11.0 mmol) and pyridine (0.80 mL, 10.5 mmol) to furnish a bright purple waxy solid with spectral details; ^1H NMR (300 MHz, $CDCl_3$) δ 4.79 (s, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 71.5 (2C, 4H); ^{19}F NMR (400 MHz, $CDCl_3$) δ -74.2 (2C, 6F). Spectral details matched those previously reported.[28,29]



propane-1,3-diyl bis(trifluoromethanesulfonate)

Propane-1,3-diyl bis(trifluoromethanesulfonate) (5b) [63256-90-6] was prepared (1.4149 g, 83%) using the ***General Bistriflate Method*** (above), 1,3-propanediol (0.3805 g, 5.0 mmol) was reacted with Tf_2O (1.84 mL, 11.0 mmol) and pyridine (0.80 mL, 10.5 mmol) to furnish a pink/brown waxy solid with the following spectral details; ^1H NMR (300 MHz, $CDCl_3$) δ 4.69 (t, 4H, J = 5.8), 2.38 (quint, 2H, J = 5.8 Hz); ^{13}C NMR (300 MHz, $CDCl_3$) δ 71.3 (2C, 4H), 29.3 (C, 2H); ^{19}F NMR (300 MHz, $CDCl_3$) δ -74.4 (6F); IR (neat) 3440, 2986, 1714, 1410, 1195, 1138 cm^{-1}. Spectral details matched those previously reported.[29]



butane-1,4-diyl bis(trifluoromethanesulfonate)

Butane-1,4-diyl bis(trifluoromethanesulfonate) (5c) [18934-34-4] was prepared (3.2489 g, 91%) with the ***General Bistriflate Method*** (above), 1,4-butanediol (0.9012 g, 10.0 mmol) was reacted with Tf_2O (1.61 mL, 20.0 mmol) and pyridine (3.52 mL, 21.0 mmol) to furnish a purple/brown waxy solid with the following spectral details; ^1H NMR (400 MHz, $CDCl_3$) δ 4.61 (s, 4H), 2.03 (quint, 4H, J = 2.5 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ 75.8

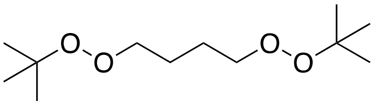
(2C, 4H), 25.4 (2C, 4H); ^{19}F NMR (400 MHz, CDCl$_3$) δ -74.6 (C, 3F); IR (neat) 3450, 2990, 2952, 2345, 1639, 1406 cm^{-1}; R$_f$ = 0.47 (20% EA/Hex). Spectral details matched those previously reported.[30]

***Bis tert-Butyl Peroxide Method A**:*

tBuOOH (0.18 mL, 1.0 mmol, of 5.5 M solution in decane) was added to THF (0.1 M, 10 mL) and cooled to 0°C, followed by addition to KOtBu (0.1122 g, 1.0 mmol) and stirred until dissolution was achieved. Butane-1,4-diol bis(trifluoromethanesulfonate) (0.3542 g, 1.0 mmol) was added to the mixture and stirred for 2 hours and 15 minutes before being quenched dropwise with water. The mixture was extracted with three portions of 10% EA/Hex (3x30 mL) and then the combined organic layers were dried over sodium sulfate. The resulting solution was concentrated on a rotary evaporator and purified with silica chromatography using 5%-10% EA/Hex solvent gradient to obtain a clear colorless oil (0.0748 g, 32%).

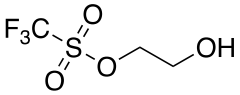
***Bis tert-Butyl Peroxide Method B**.*

tBuOOH (0.36 mL, 2.5 mmol, of 5.5 M solution in decane) was added to THF (0.1 M, 25 mL) and cooled to 0°C, followed by addition to KOtBu (0.2524 g, 2.5 mmol) until dissolution was achieved. Butane-1,4-diyl bis(trifluoromethanesulfonate) (0.8855 g, 2.5 mmol) was added and stirred for 20 minutes before being quenched dropwise with water. The mixture was extracted with three portions of EA (3x30 mL). The resulting solution was concentrated on the rotary evaporator and purified by silica chromatography using a 5%-10% EA/Hex solvent gradient to obtain a clear colorless oil (0.1985 g, 34%).



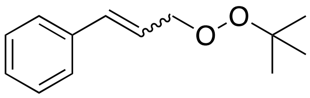
1,4-bis(*tert*-butylperoxy)butane

1,4-bis(*tert*-Butylperoxy)butane (6a) [1071-33-6] was synthesized using ***Bis tert-butyl peroxide method A*** and ***Bis tert-butyl peroxide method B*** as a clear colorless oil with the following spectral details; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.97 (t, 4H, J = 5.4 Hz), 1.69 (quint, 4H, J = 2.9 Hz), 1.25, (s, 18H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 80.2 (2C), 74.7 (2C, 4H), 26.4 (6C, 18H), 24.8 (2C, 4H); IR (neat) 2977, 2926, 2872, 1458, 1384, 1361, 1195 cm^{-1}; R$_f$ = 0.78 (20% EA/Hex).



2-hydroxyethyl trifluoromethanesulfonate

2-Hydroxyethyl trifluoromethanesulfonate (7a) [108286-01-7] was prepared (0.2263 g, 23%) using the ***Triflate Method,*** by reaction of ethylene glycol (0.3103 g, 5.0 mmol), pyridine (0.40 mL, 5.0 mmol) and Tf$_2$O (0.84 mL, 5.0 mmol). Residue was purified by silica chromatography with 100% DCM, followed by elution with 2% Methanol/DCM to furnish a viscous clear colorless oil with the following spectral details; ^{1}H NMR (300 MHz, CDCl$_3$) δ 4.63 (t, 2H, J = 3.9 Hz), 3.99 (t, 2H, J = 3.9 Hz), 2.47 (s, 1H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 77.6 (C), 71.5 (C, 2H), 60.4 (C, 2H); ^{19}F NMR (300 MHz, CDCl$_3$) δ -74.5 (3F); R$_f$ = 0.12 (100% CH$_2$Cl$_2$).



(3-(*tert*-butylperoxy)prop-1-en-1-yl)benzene

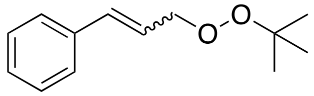
(3-(*tert*-Butylperoxy)prop-1-en-1-yl)benzene (8a) [101267-46-3] was prepared (0.2978 g, 48%) by addition of tBuOOH (3.0 mmol, 0.65 mL of a 5.5 M in decane solution) followed by cinnamyl bromide (3.0 mmol, 0.44 mL) to methanol (7.5 M, 0.4 mL) and stir at 0°C for 10 minutes. In a separate via, KOH (3.0 mmol, 0.1683 g) was added to methanol (2.5 M, 1.2 mL) and stirred until dissolution was achieved. KOH/methanol solution was added dropwise for 20 minutes to flask containing tBuOOH and cinnamyl bromide and then stirred for 2 days at 25°C and then quenched with acidified water (pH 3). The mixture was extracted with three portions of EA and then the combined organic layers were dried over sodium sulfate. The resulting solution was concentrated on rotary evaporator and purified with 5% EA/Hex to afford a clear colorless oil (0.3069 g, 25%) of **(8a)** and (0.3214 g, 36%) of **(3-Methoxyprop-1-en-1-yl)benzene**.

(3-(*tert*-Butylperoxy)prop-1-en-1-yl)benzene (8a) [101267-46-3]**.** Clear colorless oi; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.45 (d, 2H, J = 7.5 Hz), 7.36 (t, 2H, J = 7.2 Hz), 7.3-7.2 (overlapping peaks, 1 H), 6.66 (d, 1H, J = 15.9 Hz), 6.35 (dt, 1H, J = 16.0, 6.3 Hz), 1.28 (s, 9H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 133.8 (C), 128.5 (C, 1H), 128.3 (2C, 2H), 127.8 (2C, 2H), 126.4 (1C, 1H), 124.1 (C, 1H), 80.1 (C), 75.6 (C, 2H), 26.0 (3C, 9H); R$_f$ = 0.69 (20% EA/Hex). Spectral details matched those previously reported.[31]

HRMS submitted: calcd for 2-49F2 is $C_{13}H_{18}O_2$

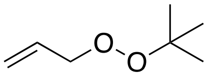
(3-Methoxyprop-1-en-1-yl)benzene (12) [16277-67-1]. Clear colorless oil; ^{1}H NMR (400 MHz), CDCl$_3$) δ 7.40 (d, 2H, J = 7.5 Hz), 7.32 (t, 2H, J = 7.3 Hz), 7.23 (t, 1H, J = 7.1 Hz), 6.60

(d, 1H, J = 16.1 Hz), 6.29 (td, 1H, J = 15.9, 5.8 Hz), 4.06 (d, 2H, J = 6.0 Hz), 3.35 (s, 3H); R_f = 0.58 (20% EA/Hex). Spectral details matched those previously reported.[32]



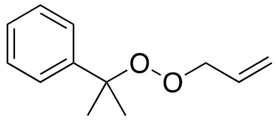
(3-(*tert*-butylperoxy)prop-1-en-1-yl)benzene

(3-(*tert*-Butylperoxy)prop-1-en-1-yl)benzene (8a) [101267-46-3] (0.1921 g, 23%) was prepared by an adapted procedure[27]. Cesium hydroxide (0.7195 g, 4.8 mmol) was added to a flame dried flask in a glove bag under nitrogen atmosphere. DMF (20 mL, 0.2 M) was added to the cesium hydroxide and stirred at 0°C for 20 minutes until dissolved. tBuOOH (0.72 mL, 4.0 mmol, of 5.5 M in decane) was added, followed by cinnamyl bromide (0.7882 g, 4.0 mmol) in DMF (10 mL, 0.4 M) and stirred for 10 minutes at 0°C before being quenched with water (5mL) and then diluted with EA (20 mL) and washed with aq. brine (150 mL) to remove DMF. The mixture was extracted with two portions of EA (2x20mL) and then combined organic layers were dried over sodium sulfate. The resulting solution was concentrated on rotary evaporator and purified with silica chromatography using 5% diethyl ether/Hex to furnish a clear colorless oil, with a faint cinnamon odor. Spectral details matched those previously reported.[31]



3-(*tert*-butylperoxy)prop-1-ene

3-(*tert*-Butylperoxy)prop-1-ene (8b) [39972-78-6] was prepared (1.1220 g, 86%) by an adaption of an existing procedure by Mosher et al.[18] tBuOOH (10 mmol, 1.80 mL of 5.5 M in decane) was added to a flask, followed by allyl bromide (10 mmol, 0.86 mL) and methanol (9.0 M, 1.1 mL) and then stirred at -5°C for a period of 10 minutes. In a separate vial, KOH (12 mmol, 0.6732 g) was added to methanol (2.9 M, 4.1 mL) and stirred until dissolution was achieved. The mixture was then added to a flask containing tBuOOH and allylbromide and stirred for a period of 20 minutes before being quenching with acidified water (pH 3) after 4 hours. The mixture was then extracted with two portions of pentane (2x30 mL) and the combined organic layers were dried over sodium sulfate. The resulting solution was concentrated on a rotary evaporator at reduced temperature (10°C and 200 mmHg) to furnish a clear colorless liquid with a strong burnt rubber/pentane odor (1.1220 g, 86%) ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (ddd, 1H, J = 6.1, 10.3, 12.2 Hz), 5.31 (dq, 1H, J = 17.3, 1.4 Hz), 5.20 (d, 1H, J = 10.3 Hz), 4.44 (dt, 2H, J = 6.1, 1.1 Hz), 1.26 (s, 9H); R_f = 0.78 (20% EA/Hex). Previously reported spectra by Baj et al does not match expected vinyl splitting, clearly shown by the spectra reported here.[33]

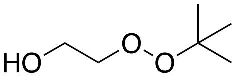


1-Methyl-1-phenylethyl 2-propen-1-yl peroxide

1-Methyl-1-phenylethyl 2-propen-1-yl peroxide (8c) [61808-93-3] was prepared (0.6093 g, 83%) by addition of Cumyl hydroperoxide (1.2175 g, 8 mmol) to the flask, followed by allyl bromide (0.9678 g, 8 mmol) with methanol (8.0 M, 1.0 mL) and cooled to -5°C (ice/brine bath). In a separate flame dried vial, KOH (0.4936 g, 8 mmol) and methanol (3.2 mL) were combined and stirred until dissolution was achieved. The mixture of potassium hydroxide and methanol was added dropwise to the flask containing the peroxide and allyl bromide. The reaction was warmed to room temperature and stirred for 18 hours before dropwise addition of acidified water (aq. HCl pH 3) while cooling at 0°C. The organic layer was separated and the aqueous layer was washed with three portions (3x25 mL) of hexane. The combined organic layers were dried over sodium sulfate and then concentrated with a rotary evaporator. The residue was purified by silica chromatography with 10% EA/Hex to furnish clear colorless oil with a slight burnt rubber odor with the following spectral details; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, 2H, J = 7.7 Hz), 7.36 (t, 2H, J = 7.7 Hz), 7.30-7.25 (overlapping peaks, 1H), 5.93 (dq, 1H, J = 17.2, 6.0 Hz), 5.25 (2H, J_{trans} = 10.6, J_{cis} = 18.9 Hz), 4.42 (d, 2H, J = 5.9 Hz), 1.62 (s, 6H), ^{13}C NMR (400 MHz, $CDCl_3$) δ 145.4 (C), 133.2 (C, 1H) 128.1 (2C, 2H), 127.2 (C, 1H), 125.6 (2C, 2H), 118.9 (C, 2H), 83.0 (C), 76.2 (1C, 2H), 26.6 (2C, 6H), R_f = 0.73 (20% EA/Hex). Spectral details previously reported.[33]

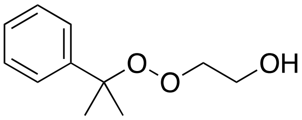
Triflate Method.

The alcohol (1.0 equiv) was added to CH_2Cl (0.1 M) and cooled to 0°C, before pyridine (2.2 equiv) and Tf_2O (2.1 equiv) were added sequentially. The reaction was warmed to 25°C and then stirred for 15-20 minutes before being quenched dropwise with water. The mixture was extracted with three portions of Hex and then the combined organic layers were dried over sodium sulfate. The solution was concentrated on a rotary evaporator to furnish a residue which was diluted with Hex and washed with three portions (3x10 mL) of 0.1M H_2SO_4. The combined organic layers were dried over sodium sulfate and then concentrated on a rotary evaporator to furnish triflate product without further purification.



2-(*tert*-butylperoxy)ethan-1-ol

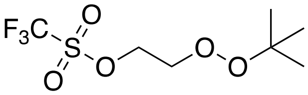
2-(*tert*-Butylperoxy)ethan-1-ol (9a) [15476-85-4] was prepared (0.0693 g, 26%) by addition of **3-(*tert*-butylperoxy)prop-1-ene** (0.2603 g, 2.0 mmol) to methanol (0.2 M, 10 mL) and cooled to -41°C (dry ice/acetonitrile bath). Was stirred while a stream of O_3/O_2 was introduced through a glass pipet directly over the surface for 3 min, or until TLC showed no more starting material. Solution was warmed solution to 0°C and then sodium borohydride (0.3026 g, 8.0 mmol) was added slowly over 20 minutes. Reaction was quenched dropwise with water after 30 minutes and then the mixture was washed with one portion of pentane. Product was extracted product from pentane wash with 50% methanol/water (20 mL), followed by extraction with five portions (5x10 mL) of EA. The combined EA/Methanol organic layers were combined and then dried over sodium sulfate. The solvent was removed on a rotary evaporator to furnish a viscous clear colorless oil with the following spectral details; ^1H NMR (300 MHz, $CDCl_3$) δ 4.08 (m, 2H), 3.84 (m, 2H), 2.09 (t, 1H, J = 5.5 Hz), 1.27 (s, 9H), R_f = 0.23 (20% EA/Hex). To obtain a ^1H NMR spectrum in $CDCl_3$, product, D_2O was added to the sample to clearly see coupling of the alcohol proton. Spectral details match those previously reported.[34]



2-[(1-methyl-1-phenylethyl)dioxy]-ethanol

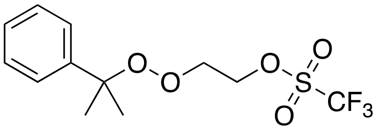
2-[(1-Methyl-1-phenylethyl)dioxy]-ethanol (9b) [54635-44-8] was prepared (0.3300g, 84%) by addition of **(8c)** (2.3956 g, 12.4 mmol) to a 3:1 mixture of CH_2Cl_2 (0.3 M, 45.0

mL) and methanol (0.8 M, 15.0 mL) and cooled to -78°C (dry ice/acetone bath). Stir while a stream of O_3/O_2 was introduced through a glass pipet directly over the surface for 30 min, or until TLC showed no more starting material. Solution was warmed solution to 0°C and then sodium borohydride (0.9419 g, 24.9 mmol) was added slowly over 20 minutes. Reaction was quenched dropwise with water after 30 minutes. The mixture was extracted with three portions of EA and the combined organic layers were dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue was purified by silica chromatography with a 5-20% solvent gradient to furnish a clear colorless oid with the following spectral details; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, 2H, J = 8.1 Hz), 7.38 (t, 2H, J = 7.4 Hz), 7.30 (t, 1H, J = 7.0 Hz), 4.05 (dt, 2H, J = -2.1, 4.4), 3.79 (m, 2H), 1.87 (t, 1H, J = 6.4 Hz), 1.64 (s, 6H), HRMS submitted: calcd for 4-32F3 is $C_{11}H_{16}O_3$. Spectral details matched previously reported.[35,34,36]



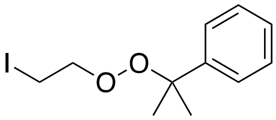
2-(*tert*-butylperoxy)ethyl trifluoromethanesulfonate

2-(*tert*-Butylperoxy)ethyl trifluoromethanesulfonate (10a) was prepared (0.0350 g 44) by following the ***General Triflate Method*** by the reaction of **2-(*tert*-Butylperoxy)ethan-1-ol** (0.0402 g, 3.0 mmol) with Tf_2O (0.06 mL, 3.6 mmol) and pyridine (0.02 mL, 3.0 mmol) to furnish a light brown oil with the following spectral details; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.72 (t, 2H, J = 4.3 Hz), 4.23 (t, 2H, J = 4.3 Hz), 1.26 (s, 9H), R_f = 0.61 (20% EA/Hex).



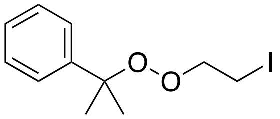
2-((2-phenylpropan-2-yl)peroxy)ethyl trifluoromethanesulfonate

2-((2-Phenylpropan-2-yl)peroxy)ethyl trifluoromethanesulfonate (10b) was prepared (0.6771 g, 90%) by *Triflate Method* by reaction of **(9b)** (0.6440 g, 3.5 mmol) with Tf_2O (1.29 mL, 7.7 mmol) and 2,6-lutidine (0.85 mL, 7.35 mmol) to furnish a light red/brown oil with the following spectral details; ^1H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, 2H, J = 7.2 Hz), 7.38 (t, 2H, J = 7.7 Hz), 7.30 (t, 1H, J = 6.6), 4.72 (t, 2H, J = 4.6 Hz), 4.21 (t, 2H, J = 4.6 Hz), 1.63 (s, 6H), ^{13}C NMR (400 MHz, $CDCl_3$) δ 144.6 (C, 1H), 128.2 (2C, 2H), 127.5 (2C, 2H), 125.5 (C), 83.7 (C) 73.4 (C, 2H), 71.7 (C, 2H), 26.4 (2C, 6H), ^{19}F NMR (400 MHz, $CDCl_3$) δ -74.6 (C, 3F), R_f = 0.53 (20% EA/Hex).



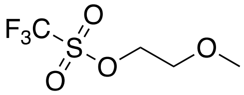
(2-((2-iodoethyl)peroxy)propan-2-yl)benzene

(2-((2-Iodoethyl)peroxy)propan-2-yl)benzene (11b) was prepared (0.5907 g, 96%) by mixing sodium iodide (1.4989 g, 10.0 mmol) in acetone (40.0 mL, 0.05 M) and then adding **2-((2-Phenylpropan-2-yl)peroxy)ethyl trifluoromethanesulfonate** (0.6566 g, 2.0 mmol) and stirring at 48°C for 30 minutes before adding water (~10 mL) and extracting with hexane (3x20 mL). The combined organic layers were dried over sodium sulfate and removed solvent on rotary evaporator to obtain a slightly yellow clear oil in 96%. ^1H (400 MHz, $CDCl_3$) δ 7.49 (d, 2H, J = 7.2 Hz), 7.37 (t, 2H, J = 7.8 Hz), 7.29 (t, 1H, J = 6.6), 4.16 (t, 2H, J = 7.2 Hz), 3.34 (t, 2H, J = 7.2 Hz), 1.63 (s, 6H).



(2-((2-iodoethyl)peroxy)propan-2-yl)benzene

(2-((2-Iodoethyl)peroxy)propan-2-yl)benzene (11b) was prepared (0.3319 g, 54%) by following a general Appel reaction conditions, where a round bottom flask was charged with DCM (20 mL, 0.1 M), followed by iodine (0.5583 g, 2.2mmol), followed by the slow addition of triphenylphospine (0.6294 g, 2.4mmol) and then the addition of imidazole (0.1633g, 2.4mmol) and stirred at -40°C (dry ice/acetonitrile bath). **2-[(1-Methyl-1-phenylethyl)dioxy]-ethanol** was then added dropwise and allowed to react for 5 minutes (no starting material by TLC) before being diluted with hexane (20 mL) and filtered through a silica plug. Residue was purified by silica chromotography with 10% EA/Hex to obtain slightly clear yellow oil in 54%.



2-methoxyethyl trifluoromethanesulfonate

2-Methoxyethyl trifluoromethanesulfonate (13a) [112981-50-7] was prepared(1.3910 g, 33%) by the *Triflate Method* by reaction of methoxy ethanol (1.518 g, 20.0 mmol) with Tf_2O (7.38 mL, 44.0 mmol) and 2,6-lutidine (4.87 mL, 42.0 mmol) to furnish a brown liquid which match the spectral details matched previously reported.[17]

General Ketone Alkylation Method

The base (1.0 equiv) was added to THF (0.1 M) and cooled to 0°C, before the ketone (1.0 equiv) was added and stirred for 15 minutes before the alkylating agent (1.0 equiv) was added. The mixture was stirred for 1 hour before being quenched dropwise with water.

The mixture was extracted with three portions of EA and the combined organic layers were dried over sodium sulfate. The solution was concentrated on a rotary evaporator to furnish a residue which was purified by silica chromatography.

NaH Alkylation with 11b. Alkylation was performed by the ***General Ketone Alkylation Method*** by reaction of α-tetralone (0.0584 g, 4.0 mmol) with NaH (0.0124 g, 5.2 mmol) in THF (0.1 M, 4.0 mL), followed by the addition of **(11b)** (0.1224 g, 4.0 mmol) and stirred for 4 hours and 50 minutes to furnish, following workup and silica chromatography, the following products: unreacted α-tetralone (0.0272 g, 46%), unreacted **(11b)** (0.0165 g, 4%), cumyl alcohol (0.0220 g, 40%).

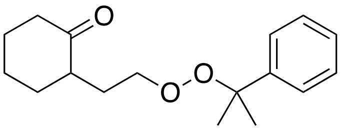
LDA Alkylation with 10b. Alkylation was performed by the ***General Ketone Alkylation Method*** by reaction of cyclohexanone (0.0981 g, 1.0 mmol) with newly prepared LDA (0.1071 g, 1.0 mmol) in THF (0.1 M, 10.0 mL), followed by the addition of **(10b)** (0.3283 g, 1.0 mmol) and stirred for 17 hours to furnish the following products after workup and silica chromatography: **(15a)** (0.0160 g, 6%) and **(15b)** (0.0017 g, 1%).

LDA Alkylation with 10b. Alkylation was performed by the ***General Ketone Alkylation Method*** by reaction of cyclohexanone (0.0981 g, 1.0 mmol) with newly prepared LDA (0.1071 g, 1.0 mmol) in THF (0.1 M, 10.0 mL), followed by the addition of **(10b)** (0.3283 g, 1.0 mmol) and stirred at -78 °C for 20 minutes to furnish the following products after workup and silica chromatography: unreacted **(10b)** (0.0426 g, 13%); **(15a)** (0.0377 g, 14%) and **(15b)** (0.0036 g, 1%).

LDA Alkylation with 10b. Alkylation was performed by the ***General Ketone Alkylation Method*** by reaction of cyclohexanone (0.0981 g, 1.0 mmol) with newly prepared LDA (0.1071 g, 1.0 mmol) in THF (0.1 M, 10.0 mL), followed by the addition of **(10b)** (0.3283 g, 1.0 mmol) and stirred at -78 °C for 20 minutes to furnish the following products after workup and silica chromatography: unreacted **(10b)** (0.0426 g, 13%); **(15a)** (0.0377 g, 14%) and **(15b)** (0.0036 g, 1%).

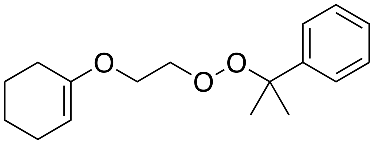
LDA Alkylation with 10b. Alkylation was performed by the ***General Ketone Alkylation Method*** by reaction of cyclohexanone (0.0490 g, 0.5 mmol) with newly prepared LDA (0.0589 g, 0.55 mmol) in Et_2O (0.1 M, 5.0 mL), followed by the addition of (**10b)** (0.1641 g, 0.5 mmol) and stirred at 0 °C for 20 minutes to furnish the following products after workup and silica chromatography: unreacted **(10b)** (0.0155 g, 9%); **(15a)** (0.0443 g, 32%) and **(15b)** (0.0149 g, 10%).

LDA Alkylation with 10b. Alkylation was performed by the ***General Ketone Alkylation Method*** by reaction of cyclohexanone (0.0981 g, 1.0 mmol) with newly prepared LDA (0.1071 g, 1.0 mmol) in THF (0.1 M, 10.0 mL), followed by the addition of **(10b)** (0.3283 g, 1.0 mmol) and stirred at 0 °C for 20 minutes to furnish the following products after workup and silica chromatography: unreacted **(10b)** (0.0092 g, 6%), **(15a)** (0.0283 g, 20%) and **(15b)** (0.0055 g, 4%).



2-(2-((2-phenylpropan-2-yl)peroxy)ethyl)cyclohexan-1-one

2-(2-((2-Phenylpropan-2-yl)peroxy)ethyl)cyclohexan-1-one (15a), a clear colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, 2H, J = 7.7 Hz), 7.36 (t, 2H, J = 7.7 Hz), 7.26-7.29 (m, 1H), 3.97 (m, 2H), 2.20-2.38 (m, 3H), 2.05 (m, 3H), 1.82 (m, 1H), 1.58-1.61 (overlapping peaks, 8H), 1.42 (dq, 1H, J = 14.1, 7.0), 1.28 (m, 1H); ^{13}C NMR (300 MHz, CDCl$_3$) δ 212.7 (C), 145.4 (C) 128.0 (2C, 2H), 127.0 (C), 125.5 (2C, 2H), 82.6 (C), 72.5 (C, 2H), 47.3 (C, 1H), 42.1 (C, 2H), 34.2 (C, 2H), 28.0 (C, 2H), 27.7 (C, 2H), 26.5 (C, 2H), 26.4 (C, 2H), 25.1 (2C, 6H); R$_f$ = 0.62 (20% EA/Hex).

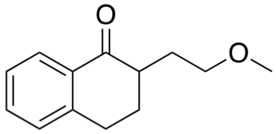


(2-((2-(cyclohex-1-en-1-yloxy)ethyl)peroxy)propan-2-yl)benzene

(2-((2-(Cyclohex-1-en-1-yloxy)ethyl)peroxy)propan-2-yl)benzene (15b), a clear colorless oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 (m, 2H), 7.35 (m, 2H), 7.27 (overlapping peak, 1H), 4.60 (s, 1H), 4.15 (m, 2H), 3.84 (m, 2H), 2.05 (s, 3H), 1.54-1.67 (overlapping peaks, 11H); ^{13}C NMR (400 MHz, CDCl$_3$) δ 128.2 (C, 1H), 128.1 (2C, 2H), 127.2 (C), 125.6 (2C, 2H), 94.1 (C, 1H), 83.1 (C), 73.4 (C, 2H), 63.4 (C, 2H), 29.8 (C, 2H), 27.8 (C, 2H), 26.5 (2C, 6H), 23.6 (C, 2H), 22.9 (C, 2H), 22.8 (C, 2H); R$_f$ = 0.94 (20% EA/Hex).

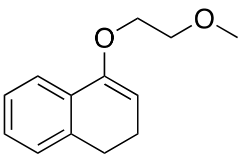
KOtBu Alkylation with 13a. Alkylation was performed by the ***General Ketone Alkylation Method*** by reaction of α-tetralone (0.1462 g, 1.0 mmol) with KOtBu (0.1122 g, 1.0 mmol) in Et$_2$O (0.1 M, 10 mL), followed by the addition of **(13a)** (0.2081 g, 1.0 mmol) and stirred for 2 hours to furnish, following workup and silica chromatography, the following products: unreacted α-tetralone (0.0102 g, 7%), **(17b)** (0.0370 g, 18%), **(17a)** (0.0429 g, 21%) and **(17c)** (0.0265 g, 10%). See spectral details below.

LDA Alkylation with 13a*.** Alkylation was performed by the ***General Ketone Alkylation Method by reaction of α-tetralone (0.1462 g, 1.0 mmol) with newly prepared LDA (0.1122 g, 1.0 mmol) in Et_2O (0.1 M, 10 mL), followed by the addition of **(13a)** (0.2081 g, 1.0 mmol) and stirred for 18 hours to furnish, following workup and silica chromatography, the following products: unreacted α-tetralone (0.0412 g, 28%); **(17b)** (0.0073 g, 1%); **(17a)** (0.0344 g, 17%) and **(17c)** (0.0157 g, 10%). See spectral details below.



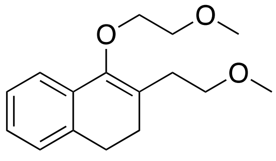
2-(2-methoxyethyl)-3,4-dihydronaphthalen-1(2*H*)-one

2-(2-Methoxyethyl)-3,4-dihydronaphthalen-1(2*H*)-one (17a) [1248366-17-7] colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, 1H, J = 7.8 Hz), 7.49 (m, 1H), 7.26-7.34 (overlapping peaks, 2H), 2.99 (t, 2H, J = 5.9 Hz), 2.68 (t, 2H, J = 6.3 Hz), (quint, 2H, J = 6.3 Hz); Rf = 0.51 (20% EA/Hex).



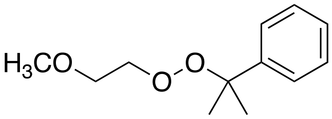
4-(2-methoxyethoxy)-1,2-dihydronaphthalene

4-(2-Methoxyethoxy)-1,2-dihydronaphthalene (17b) [619297-26-6] colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, 1H, J = 8.35 Hz), 7.12-7.38 (overlapping peaks, 3H), 5.01 (t, 1H, J = 4.7 Hz), 4.01 (t, 2H, J = 4.7 Hz), 3.80 (t, 2H, J = 4.7 Hz), 3.49 (s, 3H), 2.77 (t, 2H, J = 7.7 Hz), 2.36 (m, 2H) and; Rf = 0.71 (20% EA/Hex).



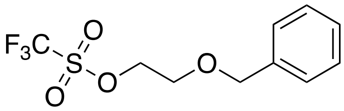
4-(2-methoxyethoxy)-3-(2-methoxyethyl)-1,2-dihydronaphthalene

4-(2-methoxyethoxy)-3-(2-methoxyethyl)-1,2-dihydronaphthalene (17c), a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, 1H, J = 7.1 Hz), 7.24 (m, 1H), 7.14 (m, 2H), 3.89 (m, 2H), 3.70 (m, 2H), 3.54 (t, 2H, J = 7.1 Hz), 3.47 (s, 3H), 3.37 (s, 3H), 2.76 (t, 2H, J = 7.8 Hz), 2.65 (t, 2H, J = 7.1 Hz), 2.33 (t, 2H, J = 7.8 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ 148.2 (C), 136.8 (C), 131.8(C), 127.2 (C, H), 126.7 (C, H), 126.4 (C, H), 123.0 (C, H), 121.1 (C), 71.9 (C, 2H), 71.2 (C, 2H), 70.9 (C, 2H), 59.1 (C, 3H), 58.6 (C, 3H), 30.6 (C, 2H), 28.1 (C, 2H), 27.0 (C, 2H); Rf = 0.3 (20% EA/Hex).



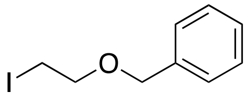
(2-((2-methoxyethyl)peroxy)propan-2-yl)benzene

(2-((2-Methoxyethyl)peroxy)propan-2-yl)benzene (18c) [308349-21-5] was prepared (0.0753 g, 72%) by adding **(10b)** (5 mmol, 0.1616 g) to methanol (4.9 mL, 0.1 M) and stir under nitrogen. Then a 30% w/w solution of sodium methoxide (5 mmol, 0.09 mL) was added and stirred at 25°C for 2 hours and 30 min before water was added dropwise to quench the reaction. Mixture was extracted with three portions of ethyl acetate (3 x 10 mL) and dry combined organic layers over sodium sulfate. Solvent was removed in rotary evaporator and residue was purified by silica chromatograph with 10% EA/Hex to obtain a clear colorless oil. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.50 (m, 2H), 7.36 (t, 2H, J = 7.0 Hz), 7.28 (m, 1H), 4.09 (t, 2H, J = 5.0 Hz), 3.59 (t, 2H, J = 5.0 Hz), 3.35 (s, 3H), 1.63 (s, 6H), ^{13}C NMR (400 MHz, CDCl$_3$) δ 145.3 (C), 128.1 (2C, 2H), 127.2 (C, 1H), 125.6 (2C, 2H), 83.1 (C), 74.3 (C, 2H), 69.9 (C, 2H), 59.0 (C, 3H), 26.5 (2C, 6H), R$_f$ = 0.63 (20% EA/Hex). Spectral details matched those previously reported.[37,38]



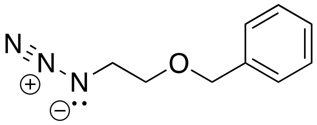
2-(benzyloxy)ethyl trifluoromethanesulfonate

2-(Benzyloxy)ethyl trifluoromethanesulfonate (20) [126694-13-1] was prepared (0.4590 g, 81%) using the ***General Triflate Procedure*** by reaction of 2-(benzyloxy)ethanol (0.3043 g, 2.0 mmol) and Tf$_2$O (0.73 mL, 4.4 mmol) and pyridine (0.48 mL, 4.2 mmol) to furnish a light yellow clear oil with the following spectral details; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 (m, 5H), 4.66 (t, 2H, J = 4.1 Hz), 4.61 (s, 2H), 3.79 (t, 2H, J = 4.1), ^{13}C NMR (400 MHz, CDCl$_3$) δ 137.2 (C), 128.6 (2C, 2H), 128.1 (C, 1H), 127.8 (2C, 2H), 75.5 (C, 2H), 73.5 (C, 2H), 67.1 (C, 2H), ^{19}F NMR (400 MHz CDCl$_3$) δ -74.6 (3F), R$_f$ = 0.48 (20% EA/Hex), which were previously reported in a patent.[39]



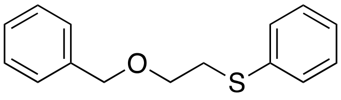
((2-iodoethoxy)methyl)benzene

((2-Iodoethoxy)methyl)benzene (21a) [54555-84-9] was prepared (0.1299 g, 99%) by adding sodium iodide (0.3747 g, 2.5 mmol) to acetone (10 mL, 0.05 M), followed by the addition of **(20)** (0.1421 g, 5 mmol). After stirring at 25°C for 10 minutes reaction was complete by TLC. Wash with water and extract twice with ethyl acetate (2x10 mL) and dry combined organic phases over sodium sulfate. Remove solvent on rotary evaporator to obtain a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28-7.42 (overlapping peaks, 5H), 4.60 (s, 2H), 3.76 (t, 2H, J = 6.8 Hz), 3.31 (t, 2H, J = 6.8 Hz), ^{13}C NMR (400 MHz, $CDCl_3$) δ 137.8 (C, 1H), 128.6 (2C, 2H), 127.9 (2C, 2H), 127.8 (C), 73.0 (C, 2H), 70.8 (C, 2H), 3.0 (C, 2H), R_f = 0.67 (20%EA/Hex). Spectral details matched previously reported.[40]



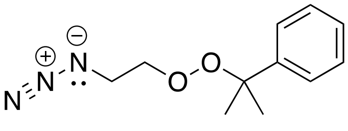
((2-azidoethoxy)methyl)benzene

((2-Azidoethoxy)methyl)benzene (21c) [66021-75-8] was prepared (0.0522 g, 59%) by adding sodium azide (0.1137g, 1.75 mmol) to DMF (0.6 mL, 0.3 M) and stirred at 0°C for 15 minutes. Then **(20)** (0.1421 g, 5 mmol) was added to the solution and stirred for 1 hour and 20 min before being diluted with hexane (~2 mL) and water (~1 mL). The mixture was extracted three times with hexane (3x10 mL) and then the combined organic layers were dried over sodium sulfate. Solvent was removed on a rotary evaporator and residue was purified by silica chromatography with 10% EA/Hex to obtain a clear colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (overlapping peaks, 5H), 4.61 (s, 2H), 3.68 (t, 2H, J = 5.2 Hz), 3.44 (t, 2H, J = 5.2 Hz), ^{13}C NMR (400 MHz, 137.8 (C, 1H), 128.5 (2C, 2H), 127.9 (2C, 2H), 127.7 (C), 73.4 (C, 2H), 68.9 (C, 2H), 50.9 (C, 2H), R_f = 0.58 (20% EA/Hex), HRMS submitted: calcd for 4-47F1 is $C_9H_{11}N_3O$. Spectral details matched previously reported.[41]



(2-(benzyloxy)ethyl)(phenyl)sulfane

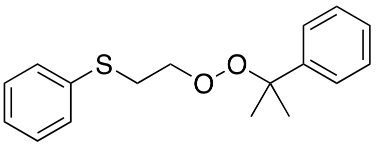
(2-(Benzyloxy)ethyl)(phenyl)sulfane (21d) [17414-04-9] was prepared (0.0196 g, 97%) by combining THF (2.0 mL, 2.5M), triethyl amine (0.07 mL, 0.5 mmol) and thiophenol (0.05 mL, 0.5 mmol) and then stirred before being added to a separate flask containing **(20)** (0.0976 g, 0.3 mmol) to THF (3.0 mL, 1.6 M). Reaction was allowed to go for 1 hour before quenching dropwise with water (~1.0 mL) and then extracting with diethyl ether (3x10 mL). The combined organic layers were dried over sodium sulfate and solvent was removed on rotary evaporator. Residue was purified by silica chromatography with 5% EA/Hex to obtain a clear colorless liquid with a strong thiol-like odor; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.37 (overlapping peaks, 10H), 4.55 (s, 2H), 3.69 (t, 2H, J = 7.0 Hz), 3.17 (t, 2H, J = 7.0 Hz), ^{13}C NMR (400 MHz, $CDCl_3$) δ 138.1 (C), 136.1 (C), 129.4 (2C, 2H), 129.0 (2C, 2H), 128.5 (2C, 2H), 127.8 (C, H), 126.2 (C, H), 73.1 (C, 2H), 68.8 (C, 2H), 33.4 (C, 2H), R_f = 0.58 (10% EA/Hex). Spectral details previously reported.[42]



(2-((2-azidoethyl)peroxy)propan-2-yl)benzene

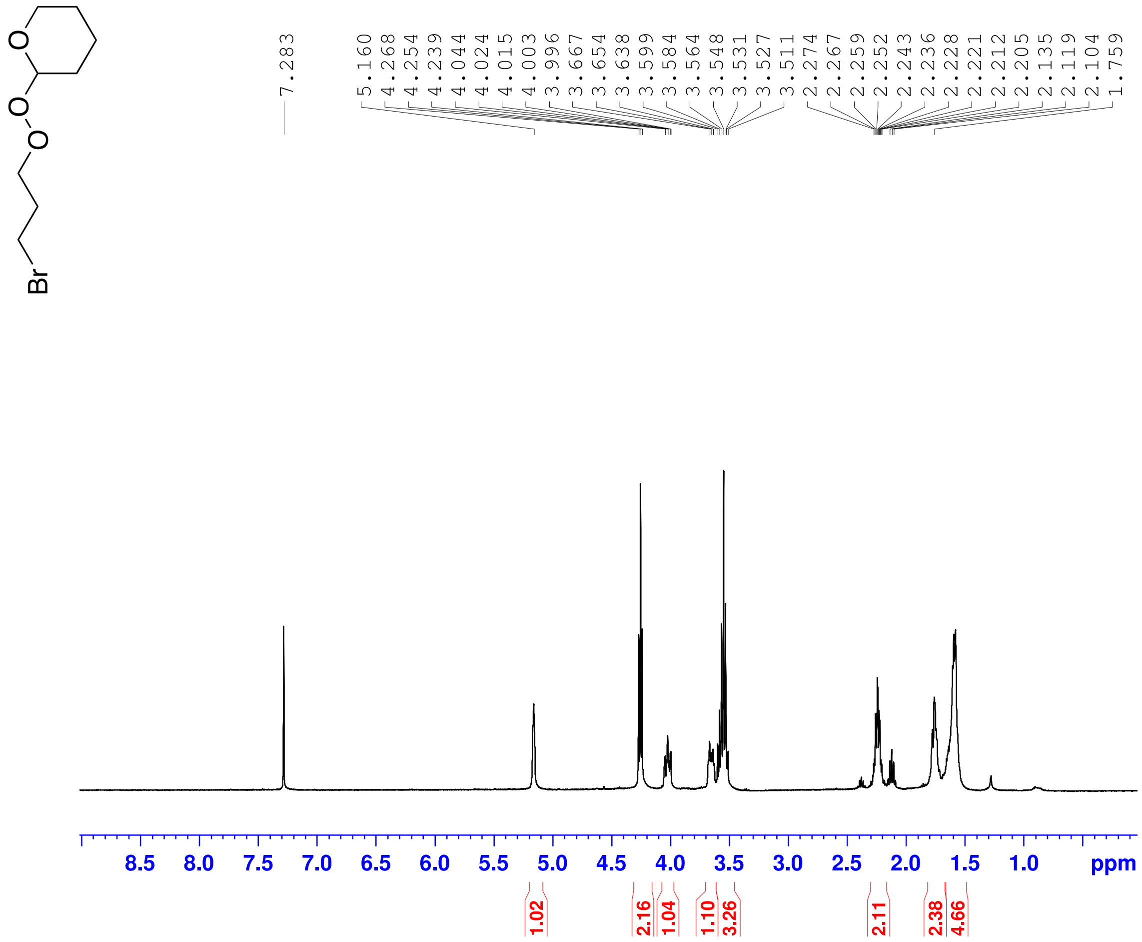
(2-((2-Azidoethyl)peroxy)propan-2-yl)benzene (22c) was prepared (0.075 g, 68%) by adding sodium azide (0.1137 g, 1.75 mmol) to DMF (0.6 mL, 0.3 M) and stirred at 0°C for

15 minutes. Then **(10b)** (0.1641 g, 5.0 mmol) was added to the solution and stirred for 1 hour and 20 min before diluting with hexane (~2 mL) and water (~1 mL). The mixture was extracted three times with hexane (3x10 mL) and then dry combined organic phases over sodium sulfate. Solvent was removed on rotary evaporator and the residue was purified by silica chromatography with 10% EA/Hex to obtain a clear colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, 2H, J = 3.9 Hz), 7.38 (t, 2H, J = 7.4 Hz), 7.29 (t, 1H, J = 6.5 Hz), 4.09 (t, 2H, J = 5.1 Hz), 3.46 (t, 2H, J = 5.1 Hz), 1.64 (s, 6H), ^{13}C NMR (400 MHz, $CDCl_3$) δ 145.0 (C), 128.2 (2C, 2H), 127.3 (C, 1H), 125.5 (2C, 2H), 83.4 (C, 2H), 73.5 (C, 2H), 49.1 (C, 2H), 26.5 (2C, 6H).



phenyl(2-((2-phenylpropan-2-yl)peroxy)ethyl)sulfane

Phenyl(2-((2-phenylpropan-2-yl)peroxy)ethyl)sulfane (22d) was a prepared (0.0946 g, 66%) by the method described above, with the exception that **(10b)** (0.1530 g, 0.5 mmol) which is a 1:1 equivalence with the thiophenol (0.05 mL, 0.5 mmol) and triethylamine (0.05 mL, 0.55 mmol).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, 2H, J = 7.4 Hz), 7.36 (t, 4H, J = 7.0 Hz), 7.28 (t, 4H, J = 7.0 Hz), 4.08 (t, 2H, J = 7.1 Hz), 3.18 (t, 2H, J = 7.2 Hz), 1.61 (s, 6H), ^{13}C NMR (400 MHz, $CDCl_3$) δ 145.1 (C), 135.8 (C), 129.3 (2C, 2H), 129.0 (2C, 2H), 128.2 (2C, 2H), 127.3 (C, 1H), 126.2 (C, 1H), 125.5 (2C, 2H), 83.2 (C, 2H), 73.5 (C, 2H), 31.3 (C, 2H), 26.6 (2C, 6H), R_f = 0.57 (10 EA/Hex)



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PROCNO                 1

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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                210.59
DW                62.400 usec
DE                 10.00 usec
TE                 298.2 K
D1          1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
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PC                  1.00
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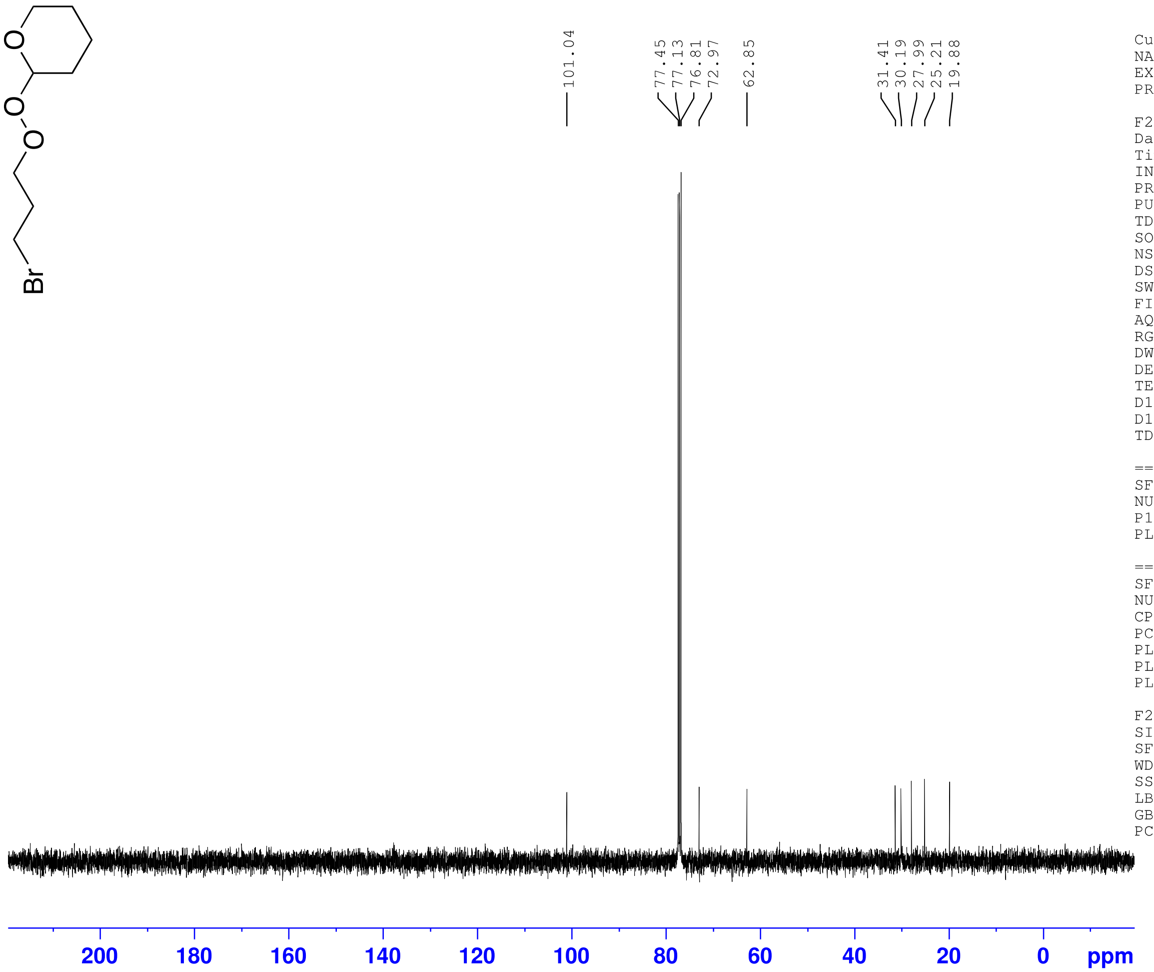

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Current Data Parameters
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EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
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Time               16.02
INSTRUM            spect
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PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                    58
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                210.59
DW                20.800 usec
DE                 10.00 usec
TE                 298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                  9.00 usec
PLW1         58.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         16.00000000 W
PLW12         0.28444001 W
PLW13         0.23040000 W

F2 - Processing parameters
SI                 32768
SF           100.6127578 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
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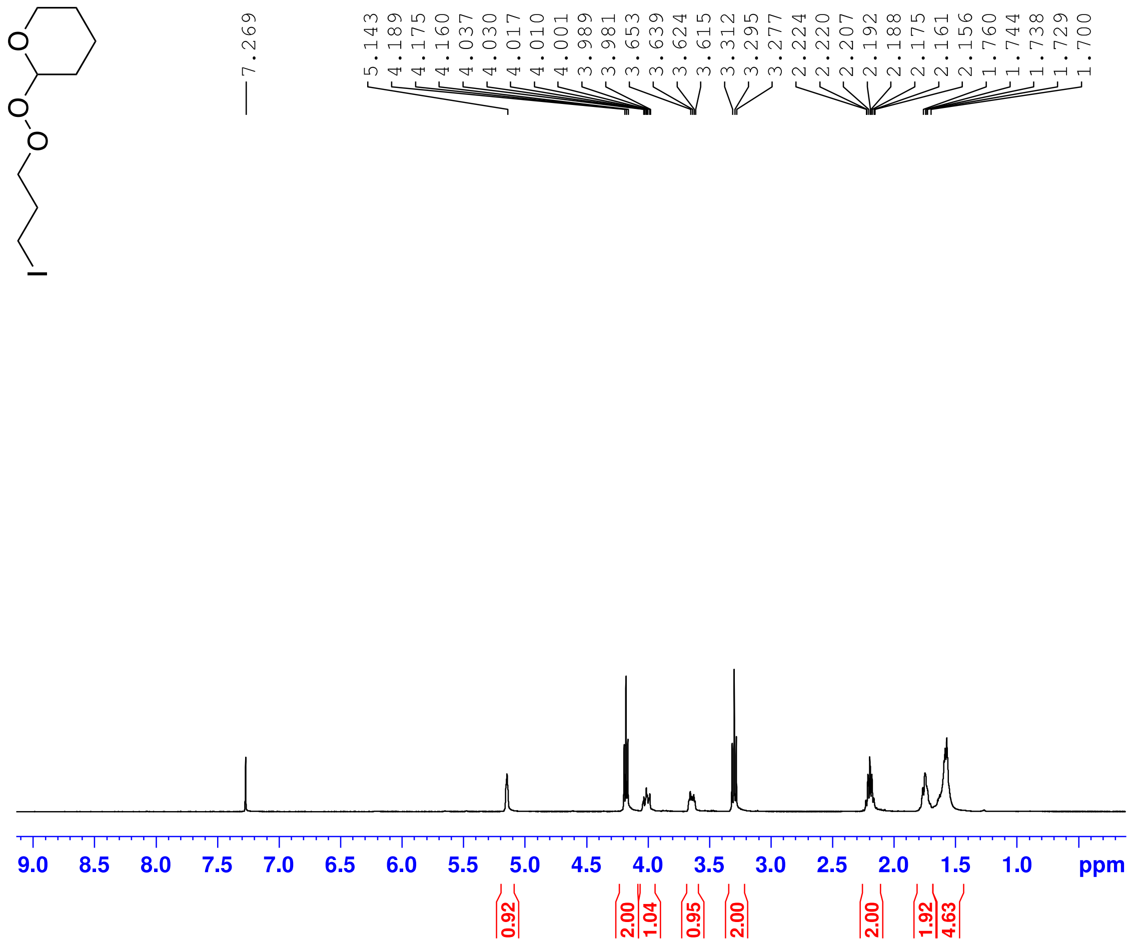

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EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
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PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                126.38
DW                62.400 usec
DE                 10.00 usec
TE                 298.2 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                 12.00 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300055 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
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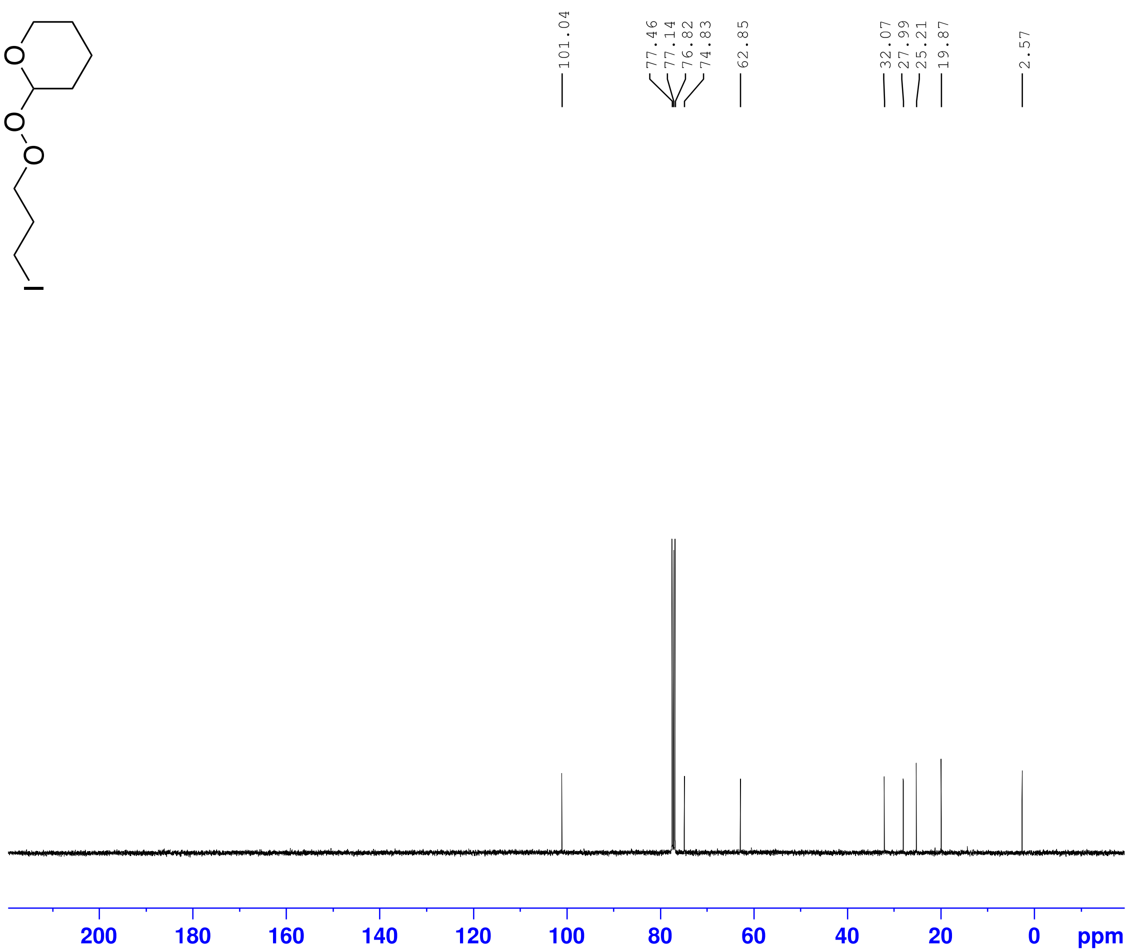

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EXPNO                 2
PROCNO                1

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PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  175
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                10.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228293 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        16.00000000 W
PLW12        0.28444001 W
PLW13        0.14307000 W

F2 - Processing parameters
SI                32768
SF          100.6127578 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
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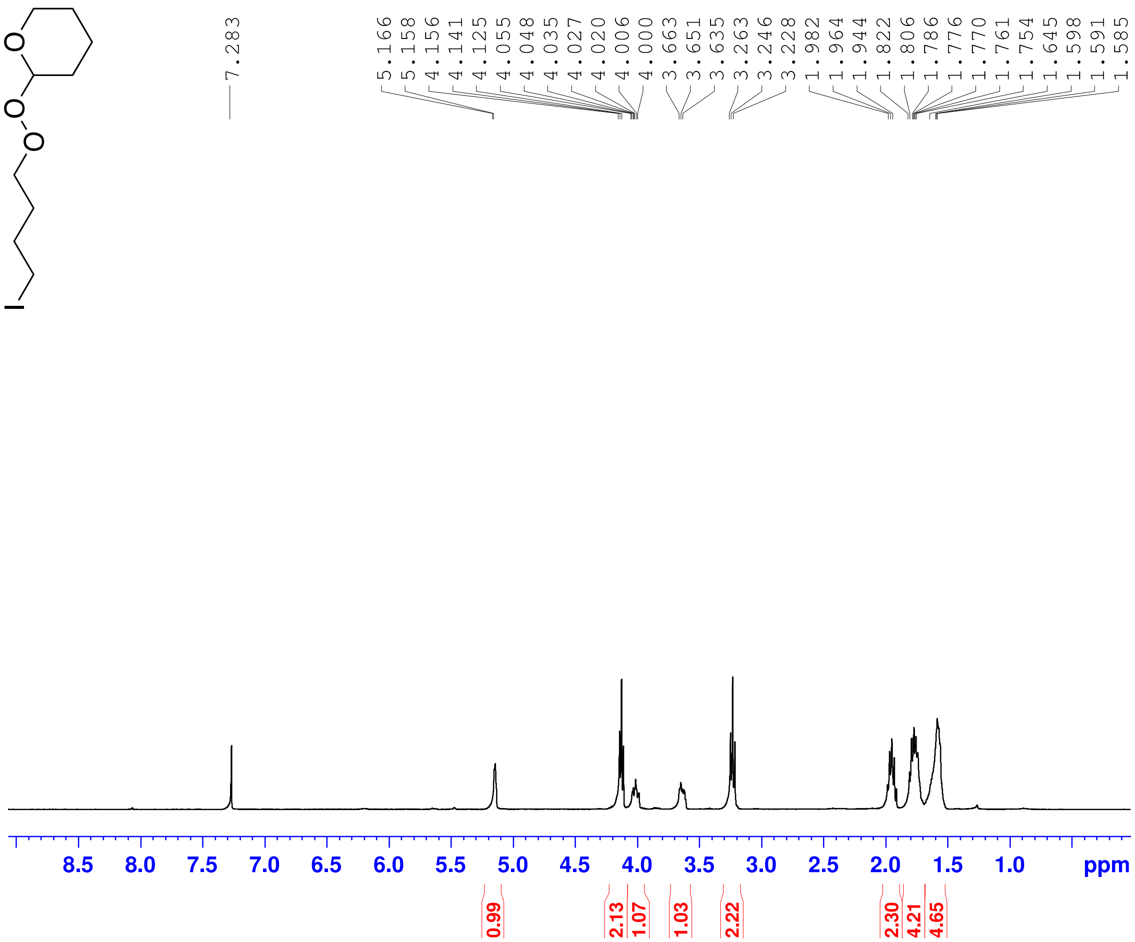

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PROCNO                  1

F2 - Acquisition Parameters
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INSTRUM             spect
PROBHD   5 mm PABBO BB/
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ              4.0894465 sec
RG                 210.59
DW                 62.400 usec
DE                  10.00 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                  12.00 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                  65536
SF           400.1300058 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
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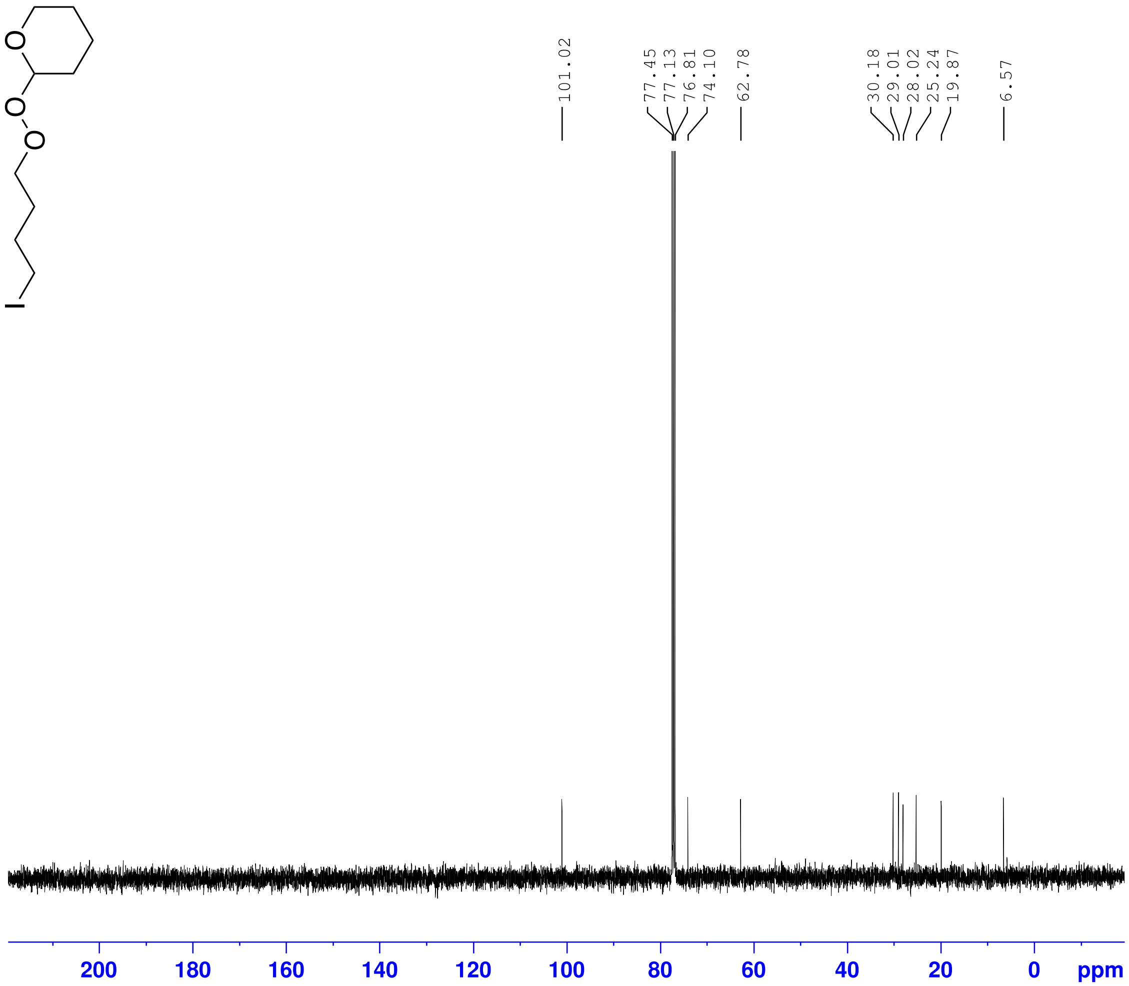

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Current Data Parameters
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EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
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Time              12.41
INSTRUM           spect
PROBHD   5 mm PABBO BB/
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   88
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                10.00 usec
TE                298.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        100.6228293 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W

======== CHANNEL f2 ========
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        16.00000000 W
PLW12        0.28444001 W
PLW13        0.23040000 W

F2 - Processing parameters
SI                32768
SF          100.6127578 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
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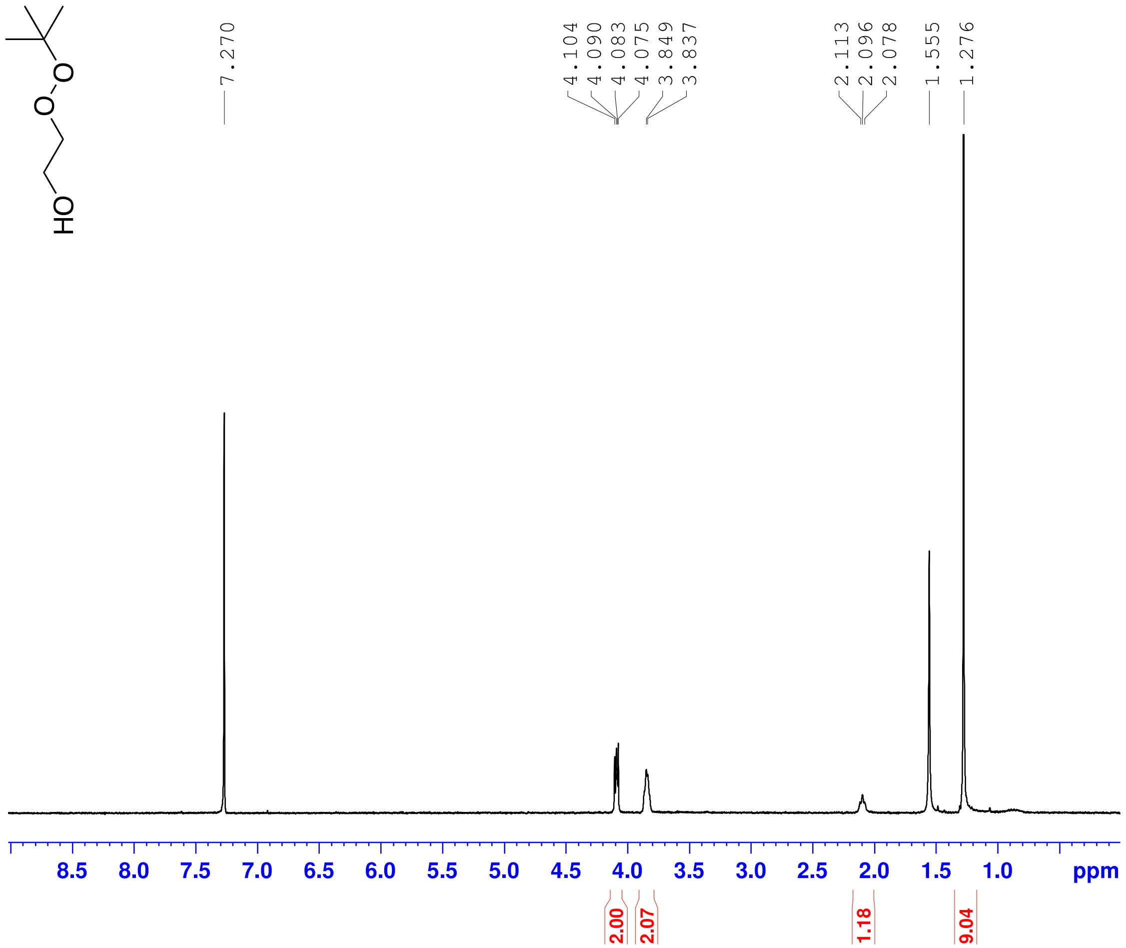

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Current Data Parameters
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EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161007
Time               10.14
INSTRUM            spect
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.091699 Hz
AQ             5.4525952 sec
RG                   406
DW                83.200 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         300.1318534 MHz
NUC1                  1H
P1                 15.00 usec
PLW1          6.55999994 W

F2 - Processing parameters
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SF           300.1300042 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
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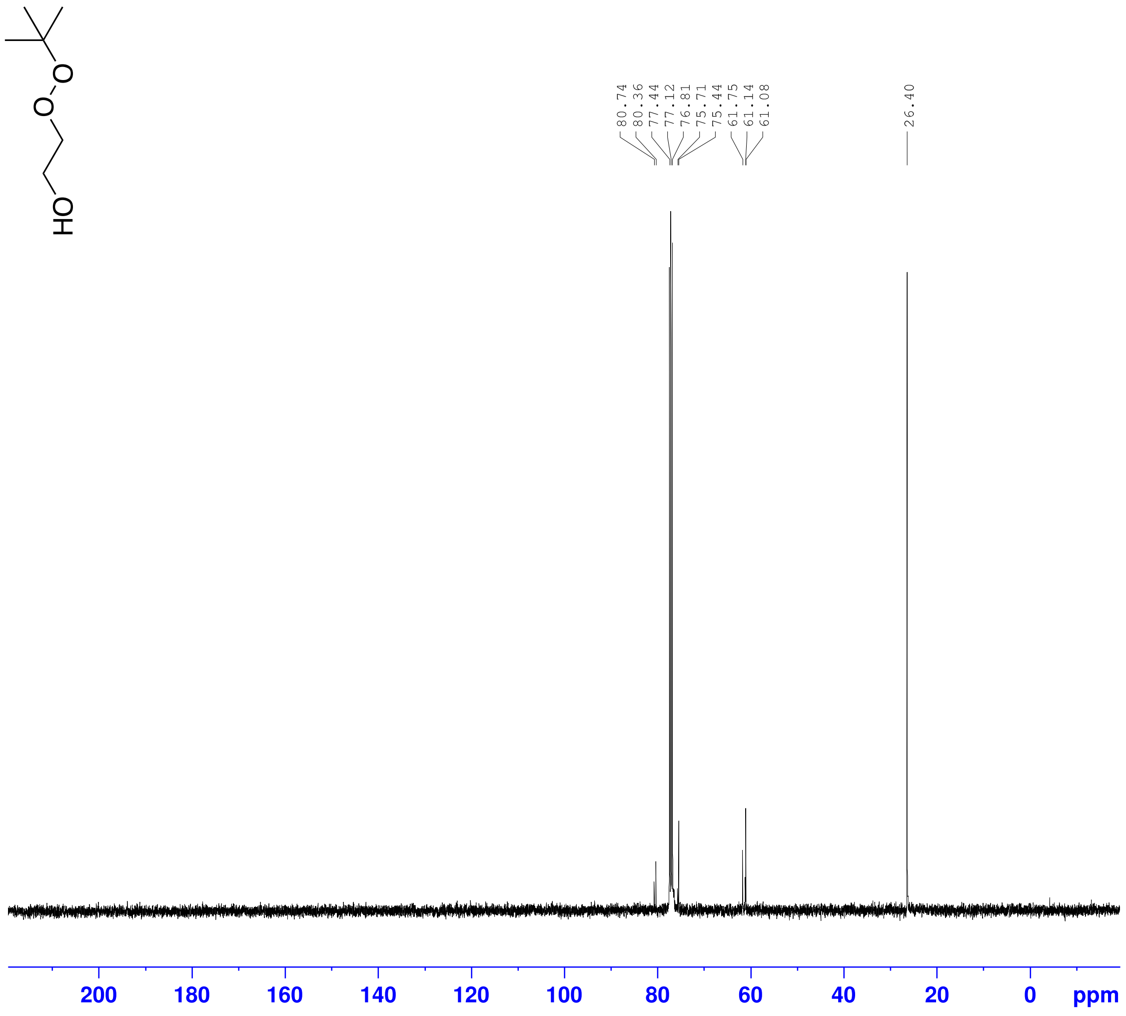

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Current Data Parameters
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EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161005
Time               17.57
INSTRUM            spect
PROBHD    5 mm PABBO BB/
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   345
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ             1.3631488 sec
RG                210.59
DW                20.800 usec
DE                 10.00 usec
TE                 298.2 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         100.6228293 MHz
NUC1                 13C
P1                  9.00 usec
PLW1         58.00000000 W

======== CHANNEL f2 ========
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         16.00000000 W
PLW12         0.28444001 W
PLW13         0.23040000 W

F2 - Processing parameters
SI                 32768
SF           100.6127578 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
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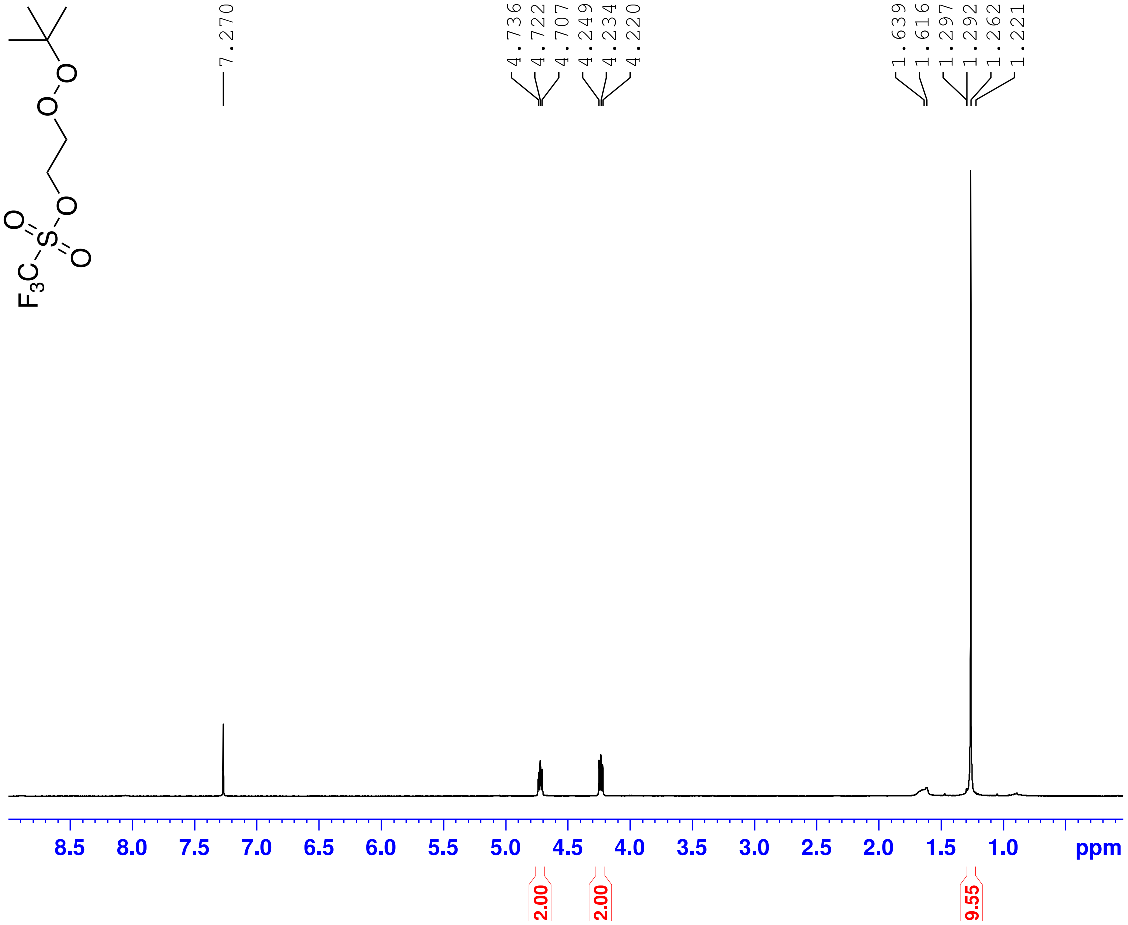

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Current Data Parameters
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EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20161020
Time                21.13
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6009.615 Hz
FIDRES           0.091699 Hz
AQ              5.4525952 sec
RG                    512
DW                 83.200 usec
DE                   6.50 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1          300.1318534 MHz
NUC1                   1H
P1                  15.00 usec
PLW1           6.55999994 W

F2 - Processing parameters
SI                  65536
SF            300.1300043 MHz
WDW                    EM
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LB                   0.30 Hz
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PC                   1.00
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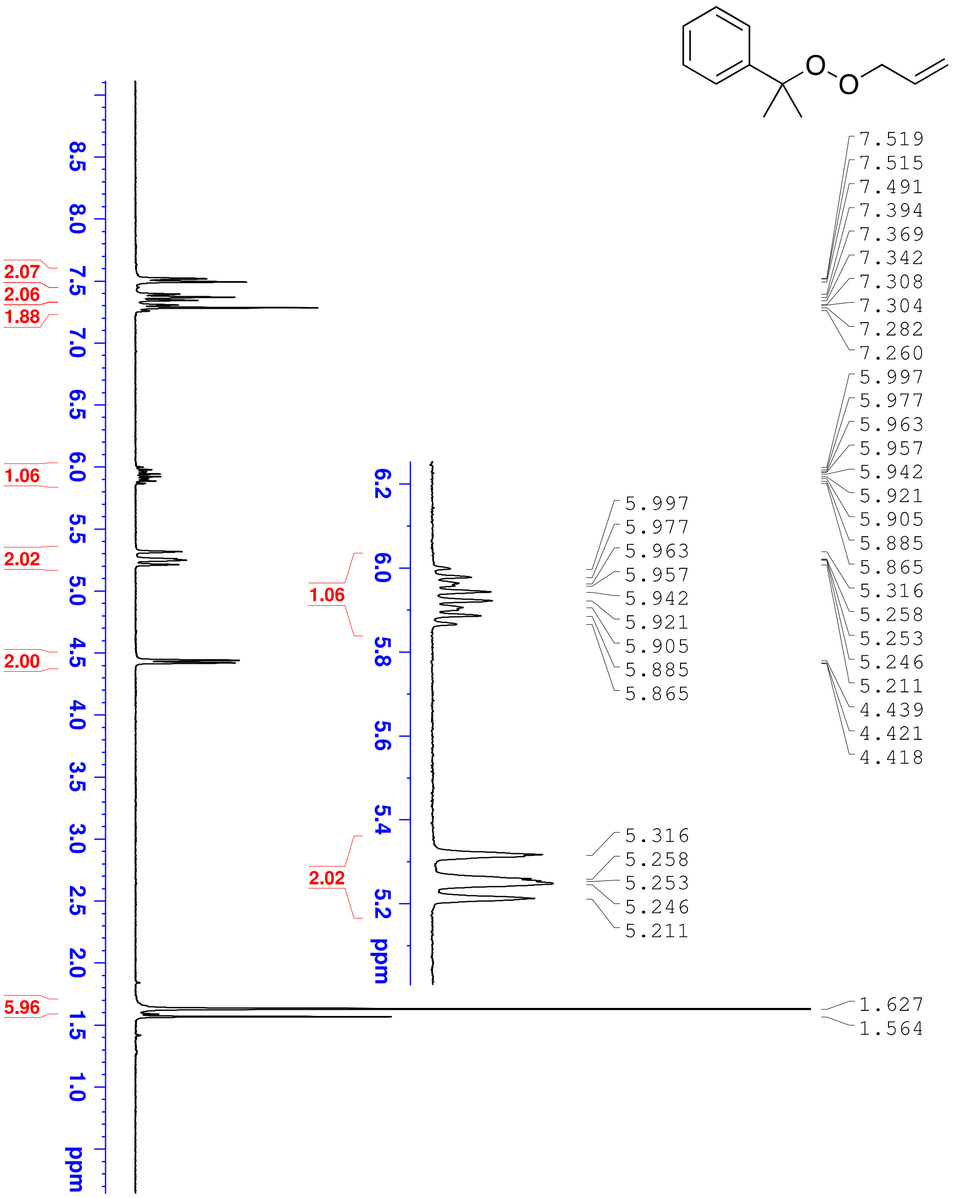

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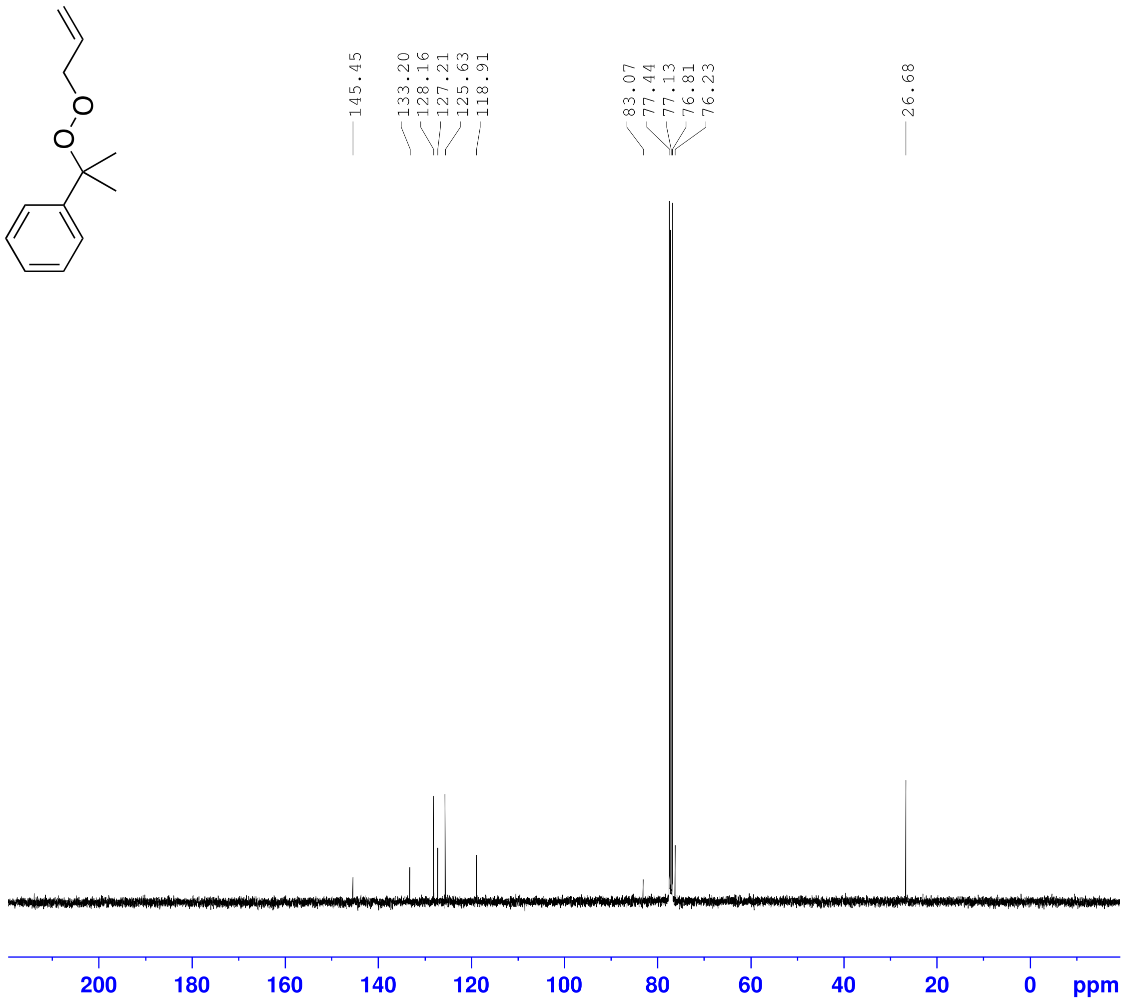
Current Data Parameters
NAME          AJD-4-30F1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170814
Time               12.23 h
INSTRUM            spect
PROBHD   Z104275_0302 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             5.4525952 sec
RG                   645
DW                83.200 usec
DE                  6.50 usec
TE                 298.1 K
D1            1.00000000 sec
TD0                    1
SFO1         300.1318534 MHz
NUC1                  1H
P1                 12.00 usec
PLW1          6.55999994 W

F2 - Processing parameters
SI                 65536
SF           300.1300000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



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Current Data Parameters
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EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
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Time              16.49 h
INSTRUM           spect
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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  239
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                10.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228293 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        16.00000000 W
PLW12        0.28444001 W
PLW13        0.14307000 W

F2 - Processing parameters
SI                32768
SF          100.6127578 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
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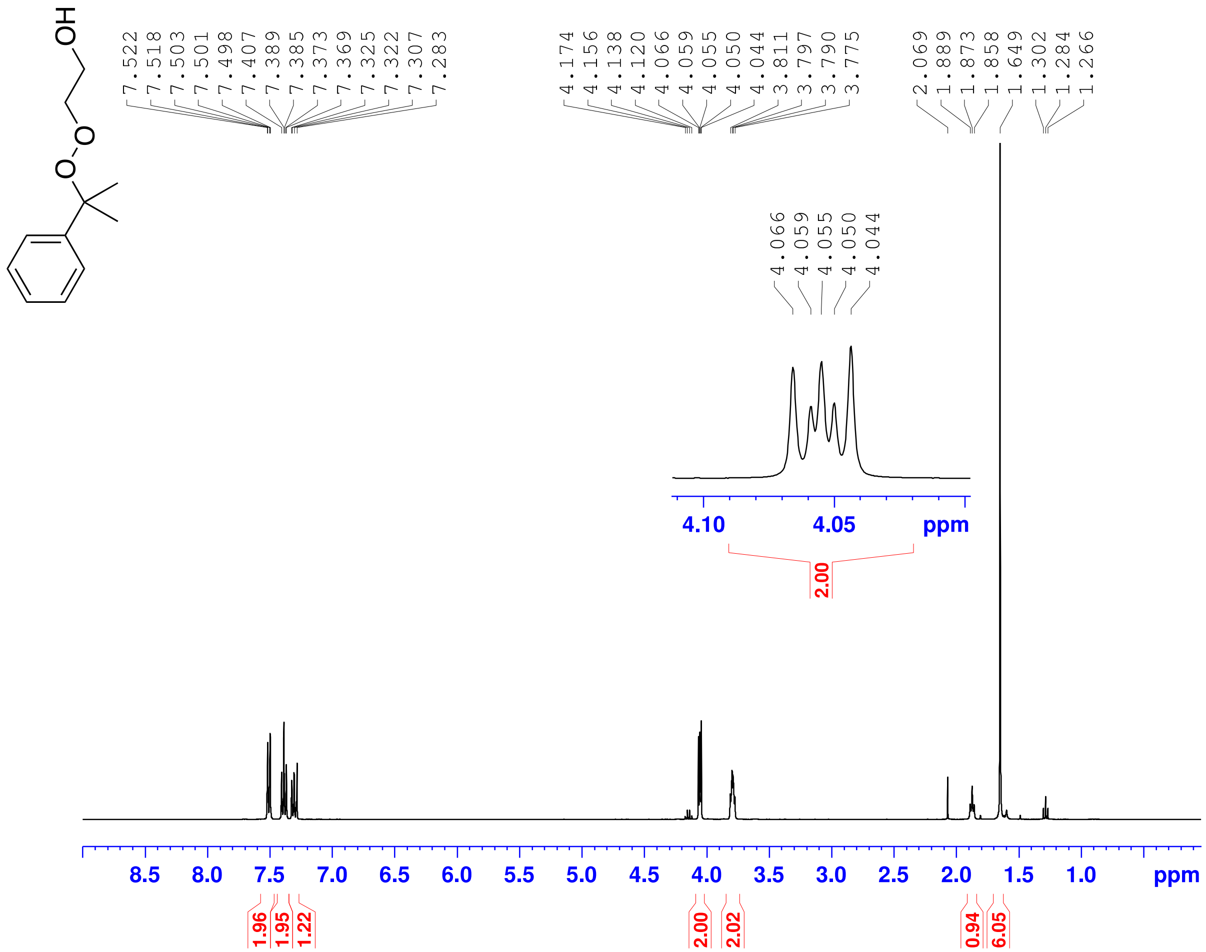

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Current Data Parameters
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EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
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Time                  16.25 h
INSTRUM               spect
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PULPROG                zg30
TD                    65536
SOLVENT               CDCl3
NS                       16
DS                        2
SWH                8012.820 Hz
FIDRES             0.244532 Hz
AQ                4.0894465 sec
RG                   142.43
DW                   62.400 usec
DE                    10.00 usec
TE                    298.1 K
D1               1.00000000 sec
TD0                       1
SFO1            400.1324708 MHz
NUC1                     1H
P1                    13.00 usec
PLW1            16.00000000 W

F2 - Processing parameters
SI                    65536
SF              400.1300000 MHz
WDW                      EM
SSB      0
LB                     0.30 Hz
GB       0
PC                     1.00
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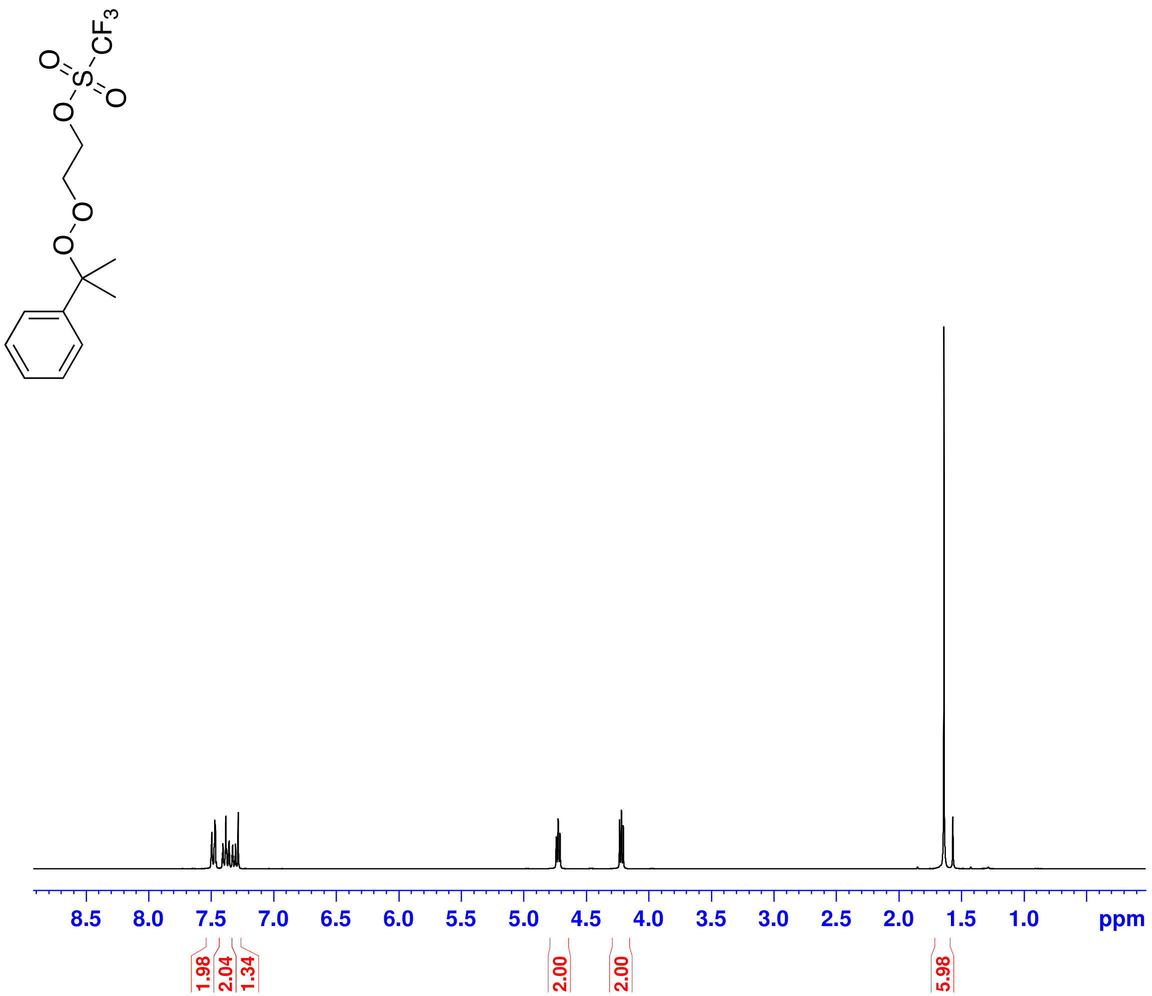

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Current Data Parameters
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EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
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Time                16.06 h
INSTRUM             spect
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              6009.615 Hz
FIDRES           0.183399 Hz
AQ              5.4525952 sec
RG                    512
DW                 83.200 usec
DE                   6.50 usec
TE                  298.1 K
D1             1.00000000 sec
TD0                     1
SFO1          300.1318534 MHz
NUC1                   1H
P1                  12.00 usec
PLW1           6.55999994 W

F2 - Processing parameters
SI                  65536
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WDW                    EM
SSB      0
LB                   0.30 Hz
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PC                   1.00
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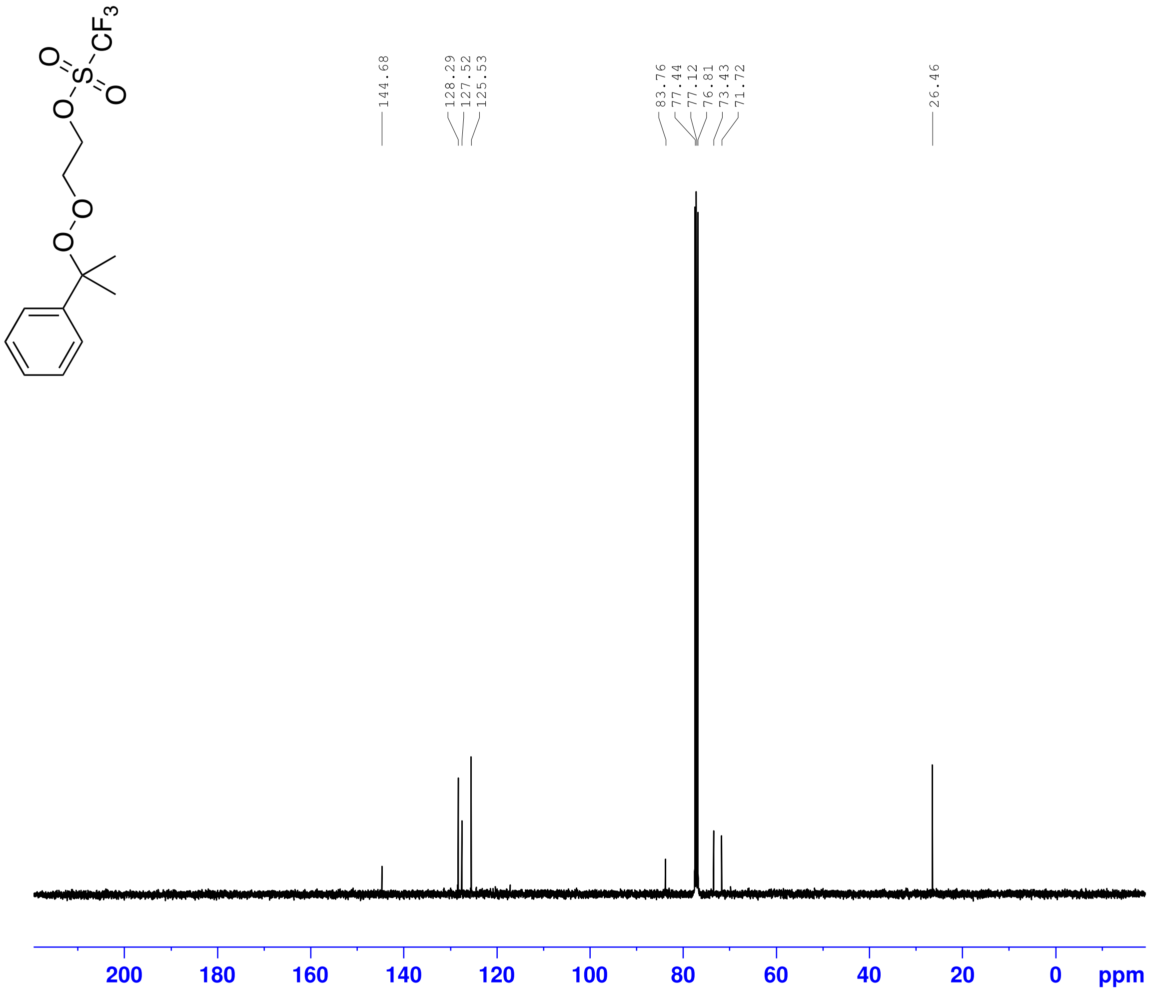

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Current Data Parameters
NAME      AJD-3-62check
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20170522
Time              10.34 h
INSTRUM           spect
PROBHD   Z108618_0594 (
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 365
DS                   4
SWH          24038.461 Hz
FIDRES        0.733596 Hz
AQ           1.3631488 sec
RG              210.59
DW              20.800 usec
DE               10.00 usec
TE               298.2 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1
SFO1       100.6228293 MHz
NUC1               13C
P1                9.00 usec
PLW1       58.00000000 W
SFO2       400.1316005 MHz
NUC2                1H
CPDPRG[2       waltz16
PCPD2            90.00 usec
PLW2       16.00000000 W
PLW12       0.28444001 W
PLW13       0.14307000 W

F2 - Processing parameters
SI               32768
SF         100.6127578 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```
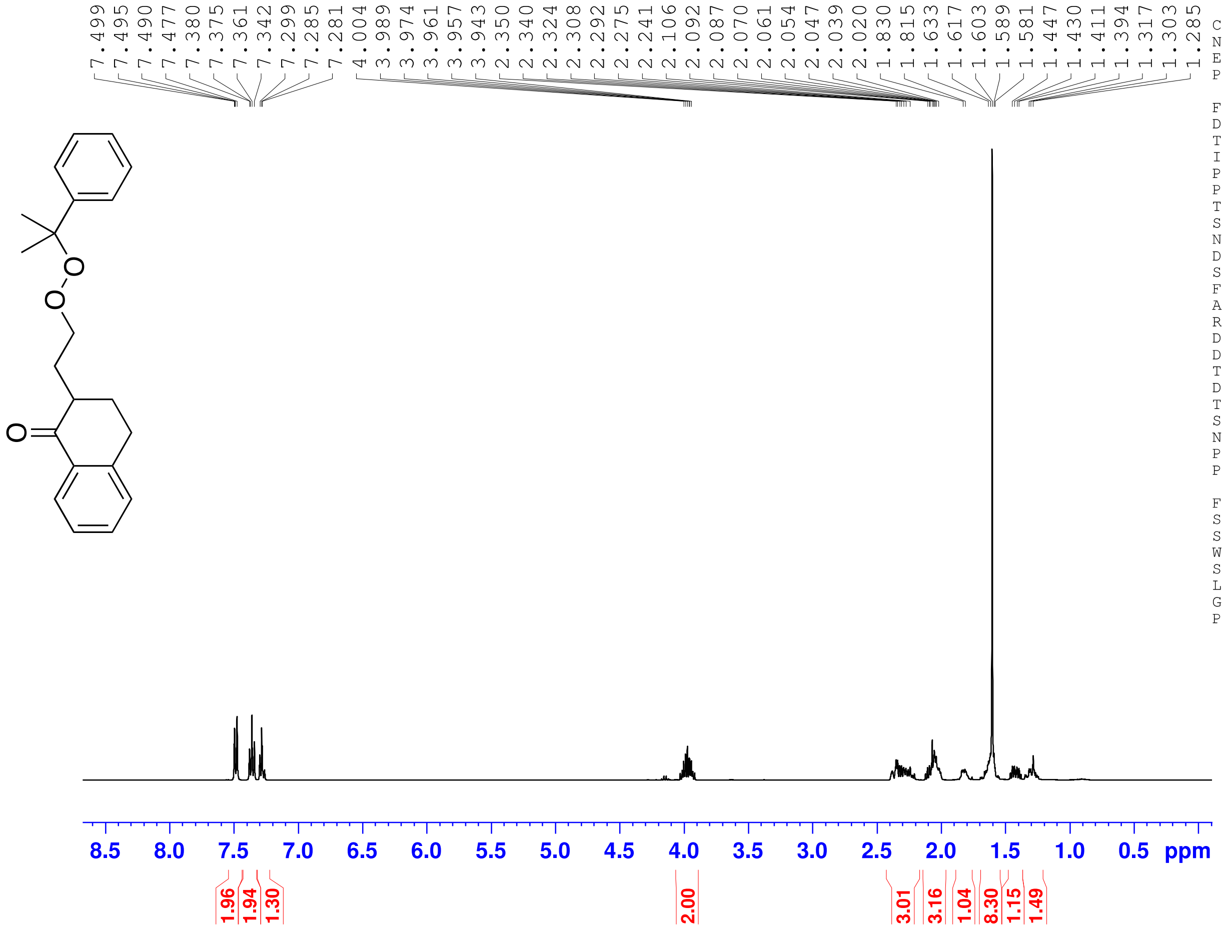
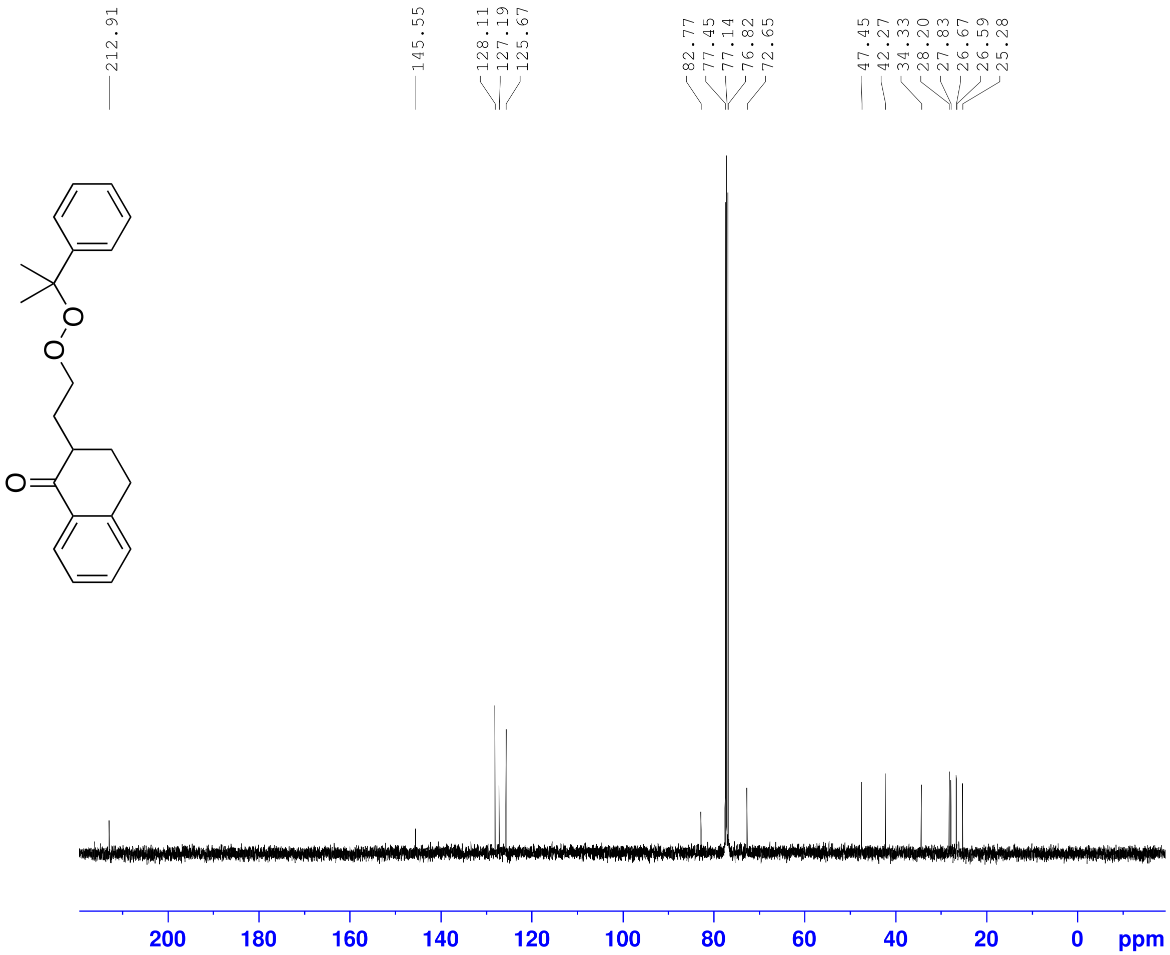
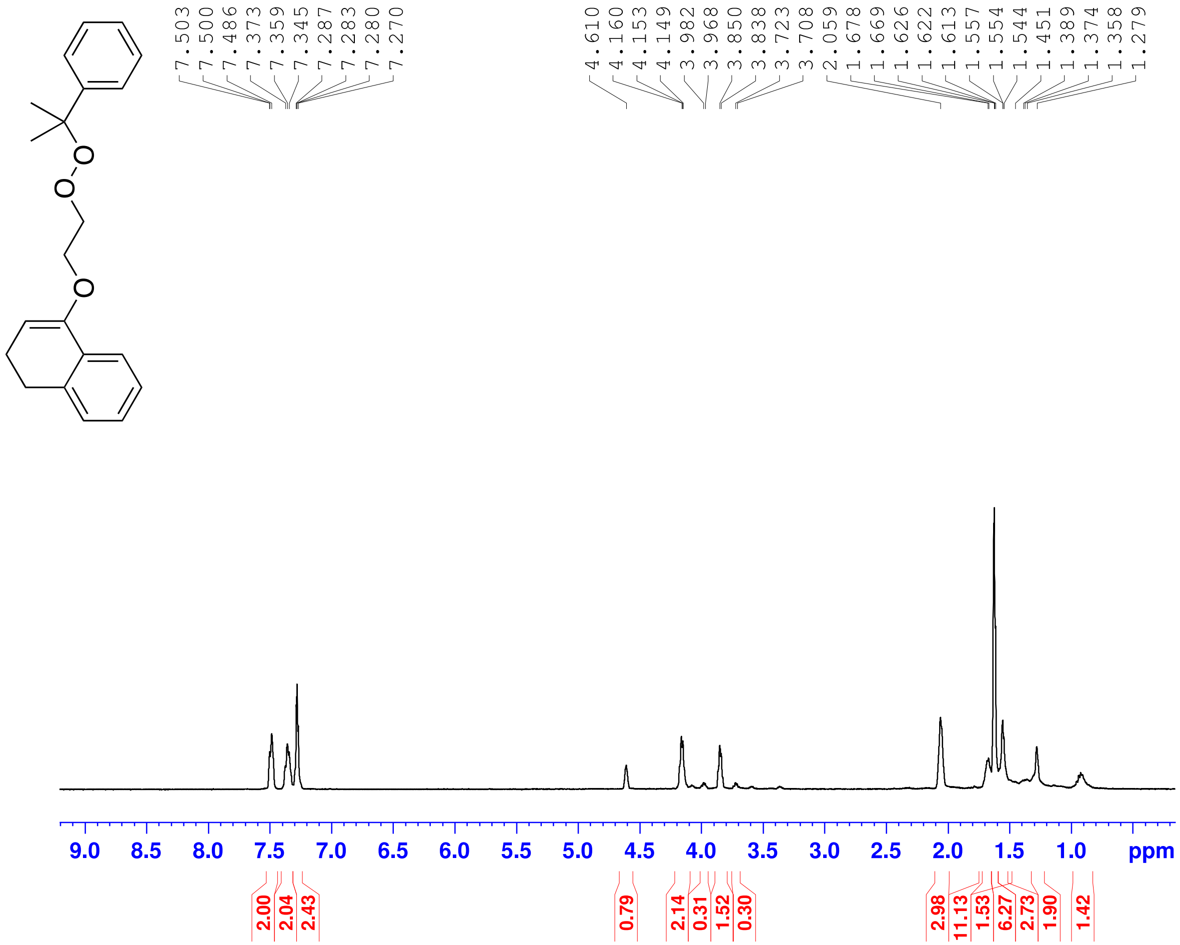



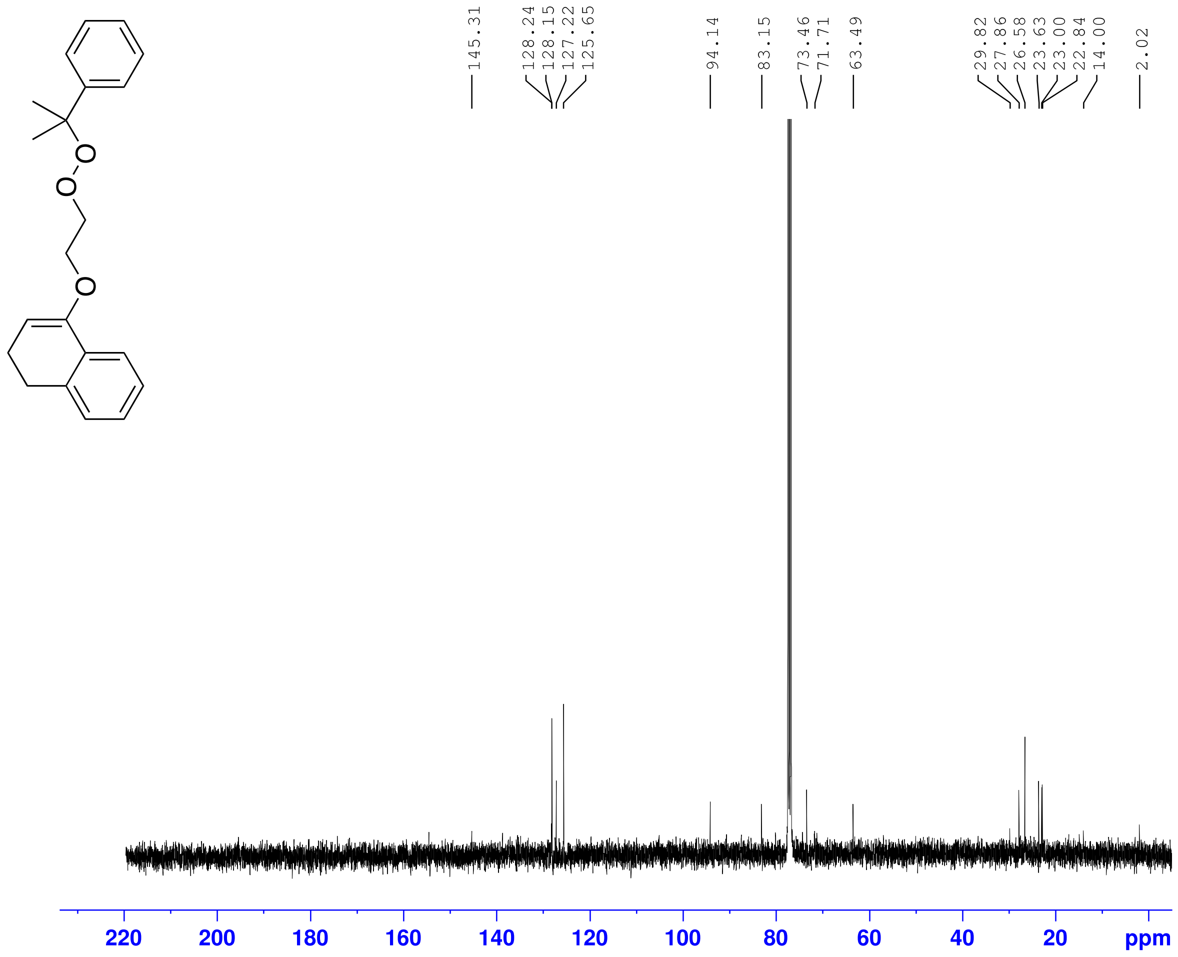
```
Current Data Parameters
NAME          AJD-3-49F4
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170202
Time               15.51 h
INSTRUM            spect
PROBHD   Z108618_0594 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ             4.0894465 sec
RG                142.43
DW                62.400 usec
DE                 10.00 usec
TE                 298.0 K
D1          1.00000000 sec
TD0                    1
SFO1         400.1324708 MHz
NUC1                  1H
P1                 13.00 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



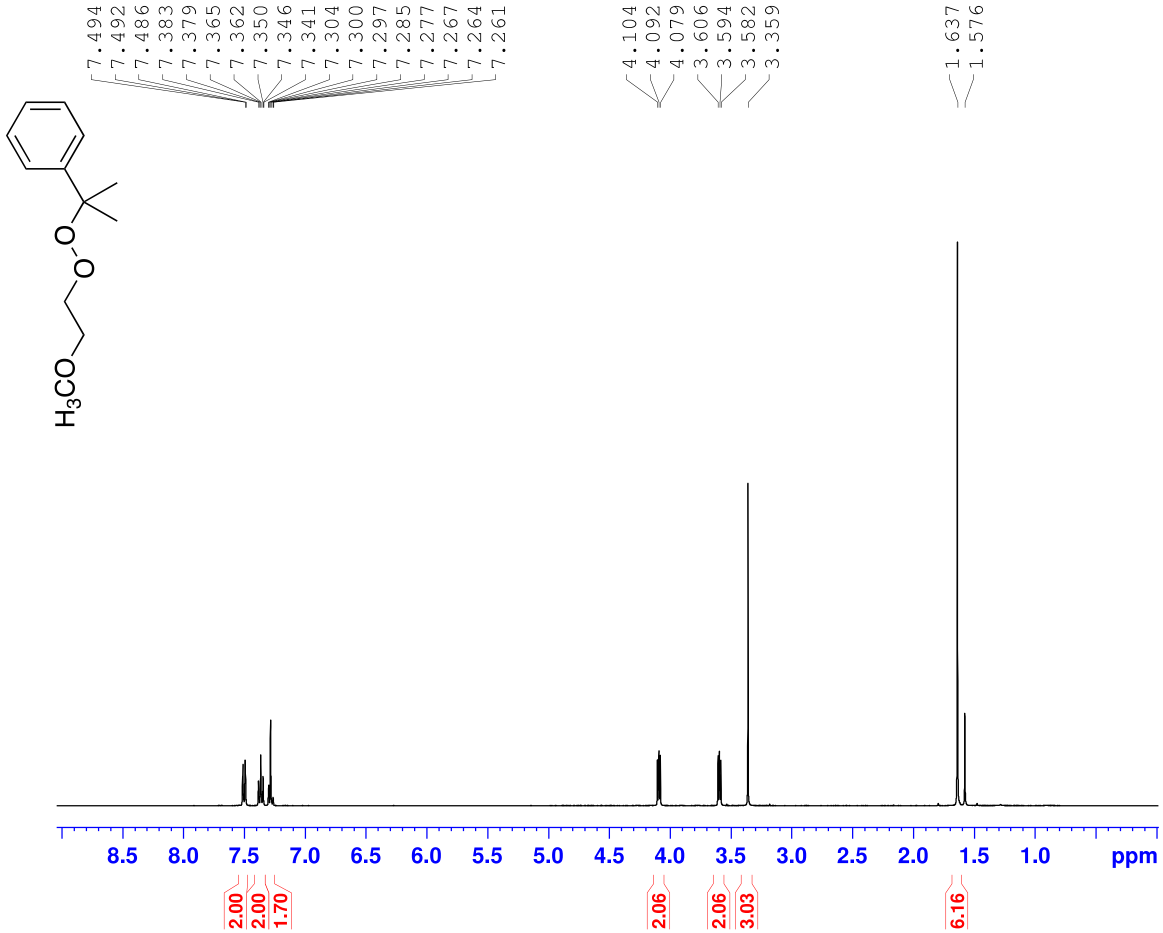
```
Current Data Parameters
NAME     AJD-3-49F4checkA
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_          20170920
Time              20.07 h
INSTRUM           spect
PROBHD   Z108618_0594 (
PULPROG         zgpg30
TD               65536
SOLVENT          CDCl3
NS                 144
DS                   4
SWH          24038.461 Hz
FIDRES        0.733596 Hz
AQ           1.3631488 sec
RG              210.59
DW              20.800 usec
DE               10.00 usec
TE               298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0                  1
SFO1       100.6228293 MHz
NUC1               13C
P1                9.00 usec
PLW1       58.00000000 W
SFO2       400.1316005 MHz
NUC2                1H
CPDPRG[2        waltz16
PCPD2            90.00 usec
PLW2       16.00000000 W
PLW12       0.28444001 W
PLW13       0.14307000 W

F2 - Processing parameters
SI               32768
SF         100.6127578 MHz
WDW                 EM
SSB      0
LB                1.00 Hz
GB       0
PC                1.40
```



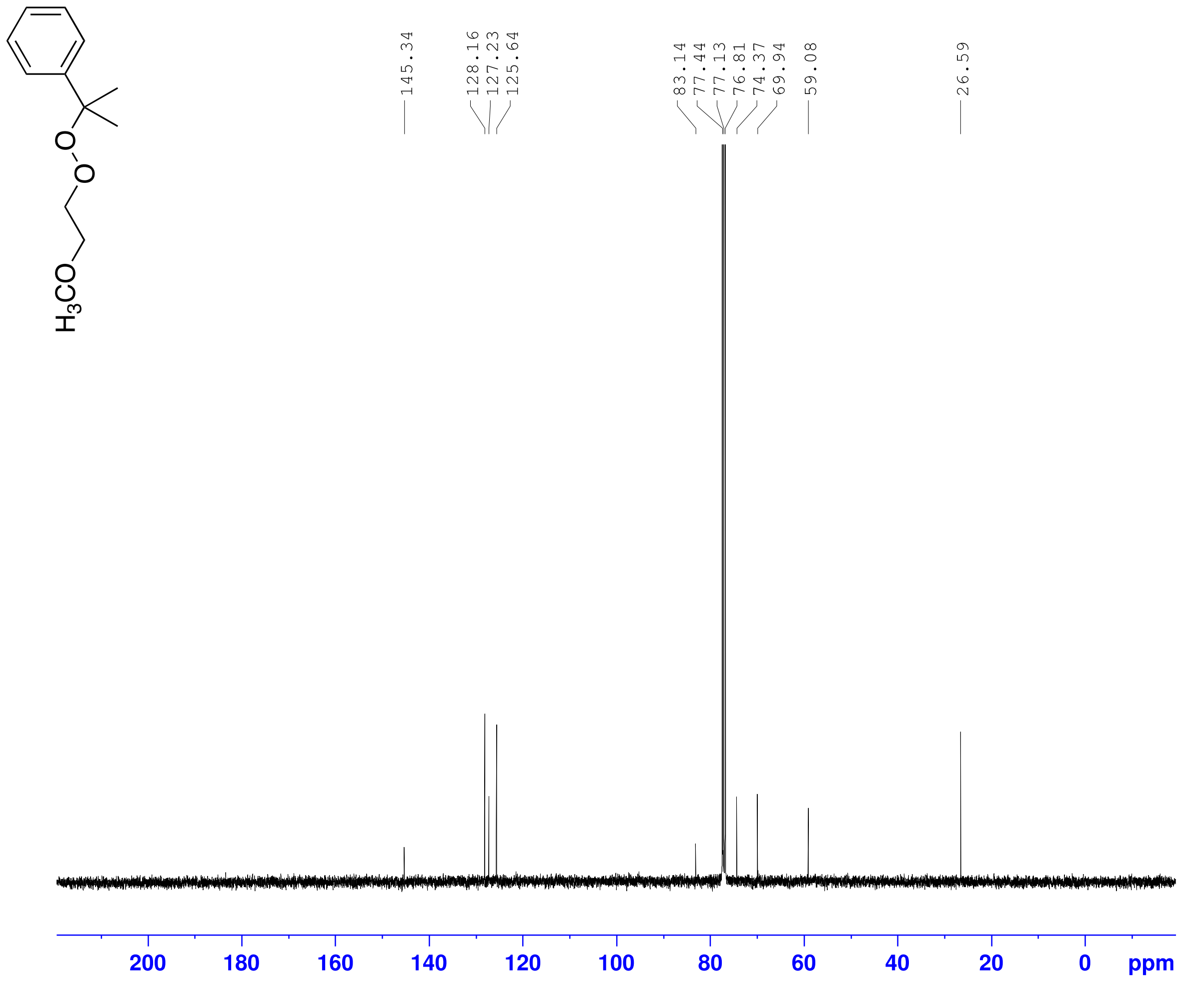
```
Current Data Parameters
NAME          AJD-3-39F2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20161216
Time                8.57
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.122266 Hz
AQ             4.0894465 sec
RG                210.59
DW                62.400 usec
DE                 10.00 usec
TE                 298.1 K
D1            1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                  1H
P1                 13.00 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



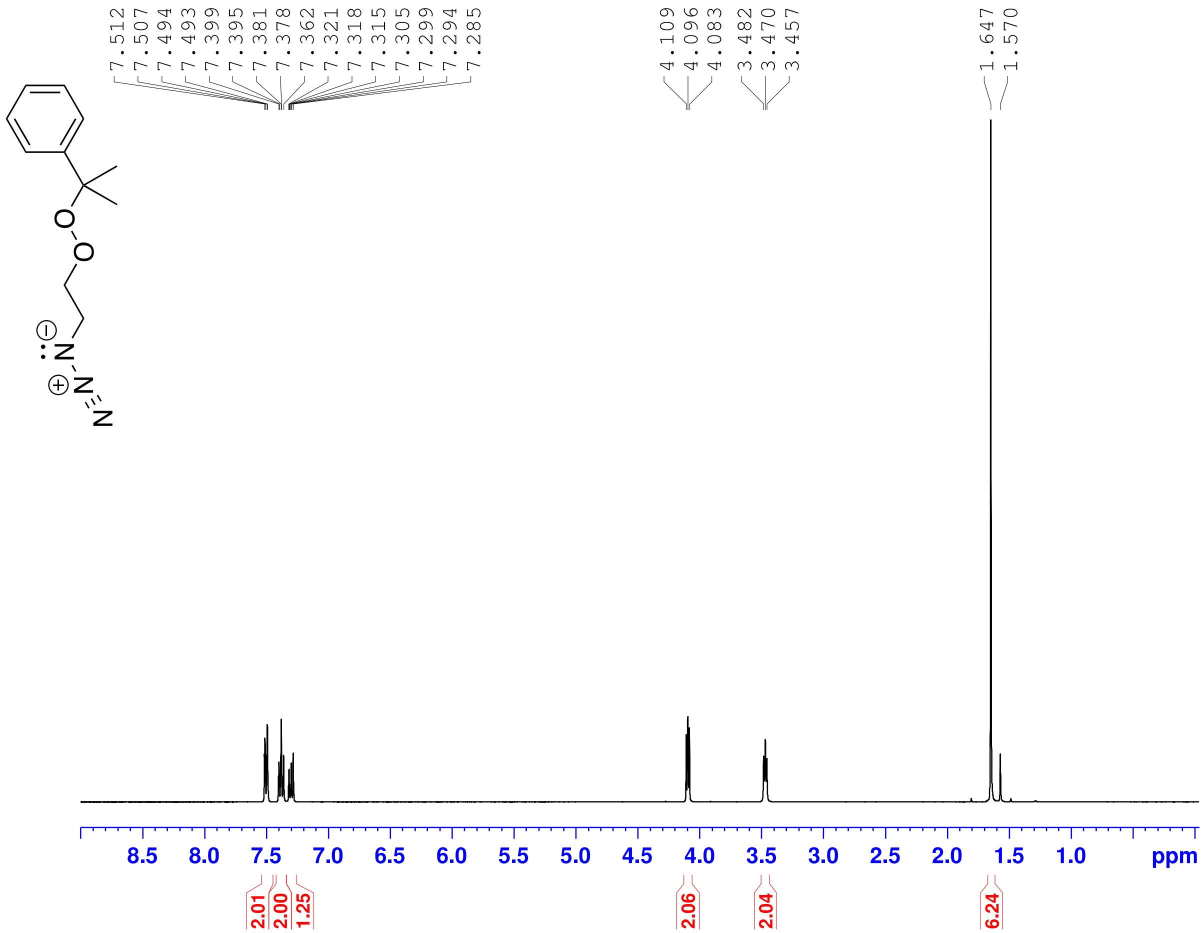
```
Current Data Parameters
NAME      AJD-3-39F2checkB
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170920
Time                 22.01 h
INSTRUM              spect
PROBHD   Z108618_0594 (
PULPROG            zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    1024
DS                       4
SWH              24038.461 Hz
FIDRES            0.733596 Hz
AQ               1.3631488 sec
RG                  210.59
DW                  20.800 usec
DE                   10.00 usec
TE                   298.1 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                      1
SFO1           100.6228293 MHz
NUC1                   13C
P1                    9.00 usec
PLW1           58.00000000 W
SFO2           400.1316005 MHz
NUC2                    1H
CPDPRG[2           waltz16
PCPD2                90.00 usec
PLW2           16.00000000 W
PLW12           0.28444001 W
PLW13           0.14307000 W

F2 - Processing parameters
SI                   32768
SF             100.6127578 MHz
WDW                     EM
SSB      0
LB                    1.00 Hz
GB       0
PC                    1.40
```



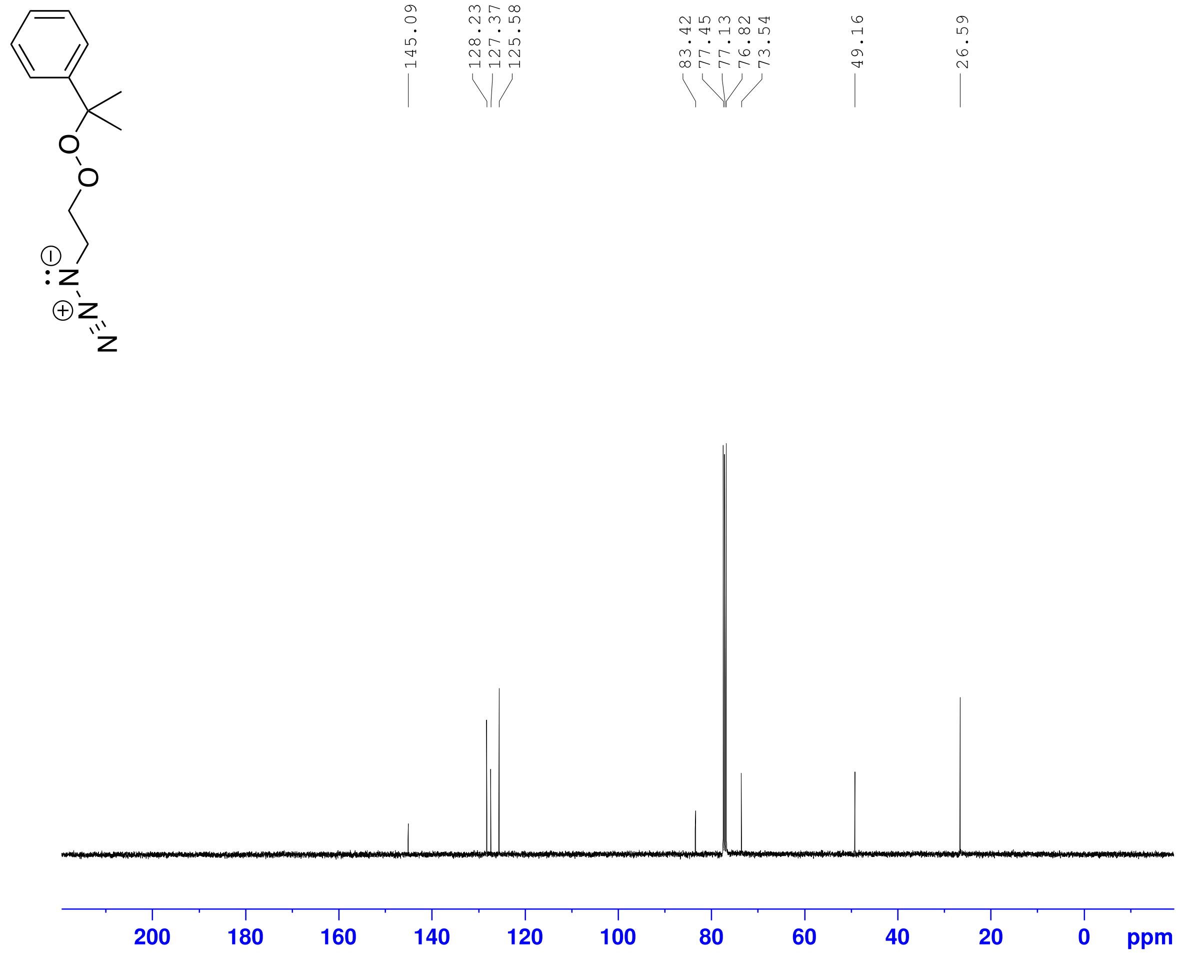
```
Current Data Parameters
NAME          AJD-4-42F1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_          20170810
Time              10.07 h
INSTRUM           spect
PROBHD   Z108618_0594 (
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                   16
DS                    2
SWH            8012.820 Hz
FIDRES         0.244532 Hz
AQ            4.0894465 sec
RG               210.59
DW               62.400 usec
DE                10.00 usec
TE                298.0 K
D1           1.00000000 sec
TD0                   1
SFO1        400.1324708 MHz
NUC1                 1H
P1                13.00 usec
PLW1        16.00000000 W

F2 - Processing parameters
SI                65536
SF          400.1300000 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
GB       0
PC                 1.00
```



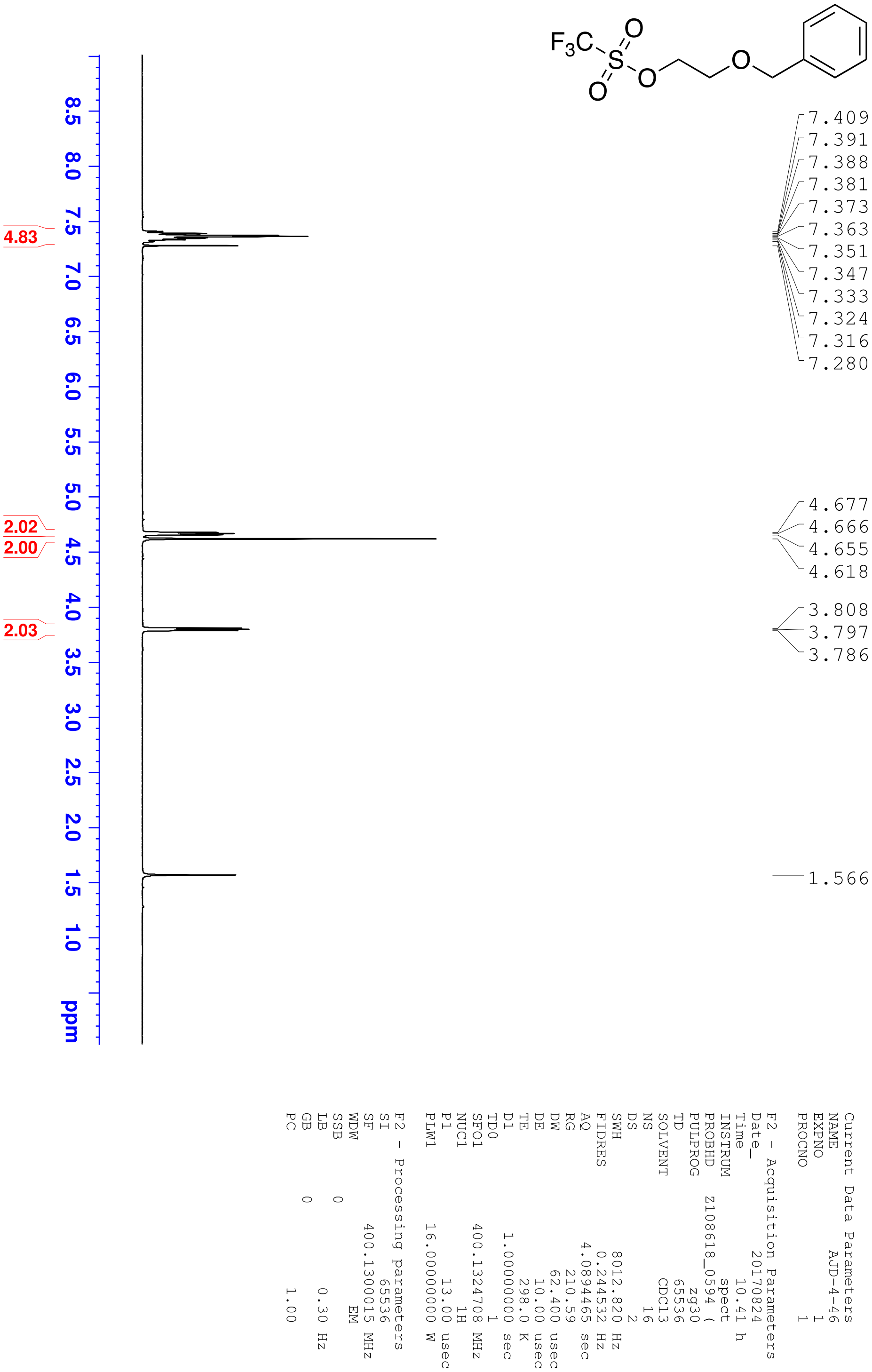
```
Current Data Parameters
NAME          AJD-4-42F1
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170810
Time               11.09 h
INSTRUM            spect
PROBHD   Z108618_0594 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  522
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                10.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228293 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        16.00000000 W
PLW12        0.28444001 W
PLW13        0.14307000 W

F2 - Processing parameters
SI                32768
SF          100.6127578 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```

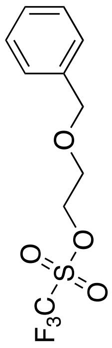


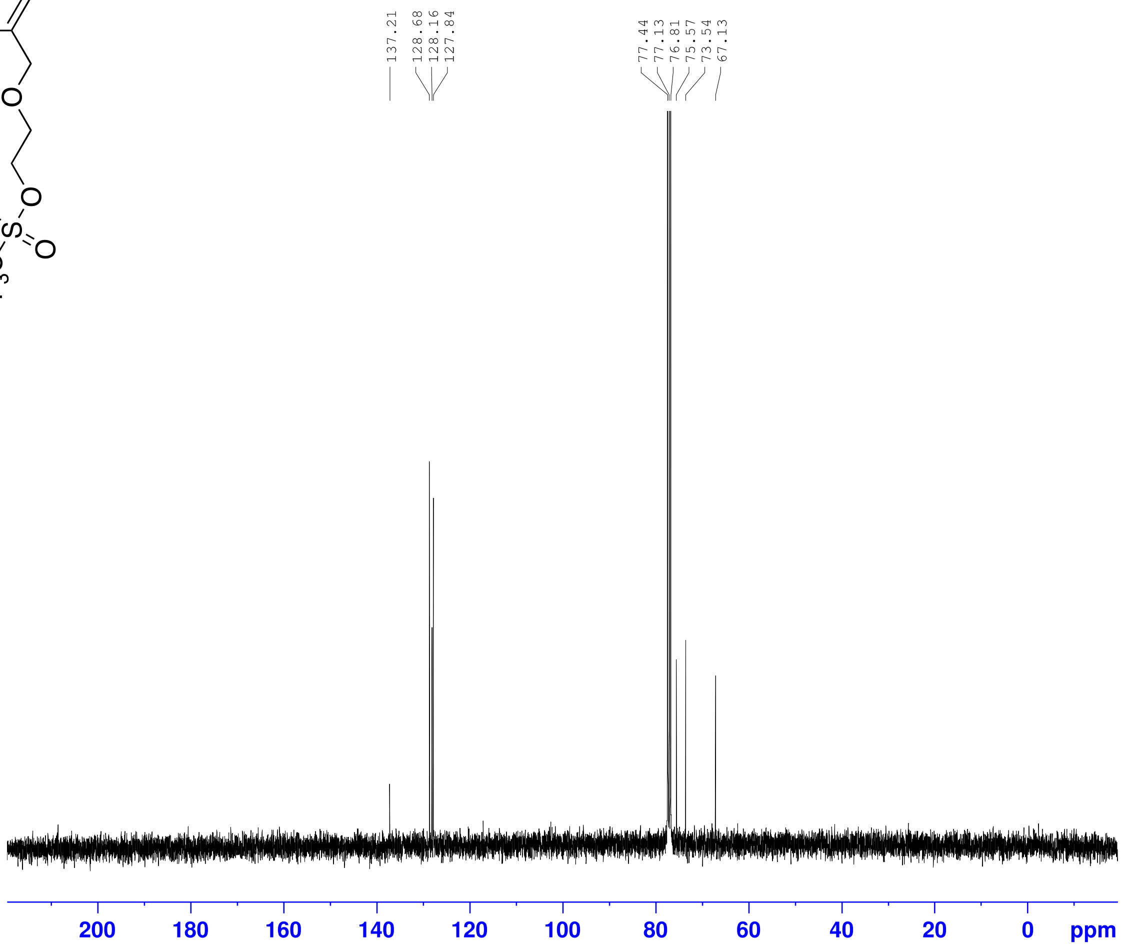
```
Current Data Parameters
NAME          AJD-4-45F1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170824
Time               11.11 h
INSTRUM            spect
PROBHD   Z108618_0594 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ             4.0894465 sec
RG                164.14
DW                62.400 usec
DE                 10.00 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1
SFO1         400.1324708 MHz
NUC1                  1H
P1                 13.00 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



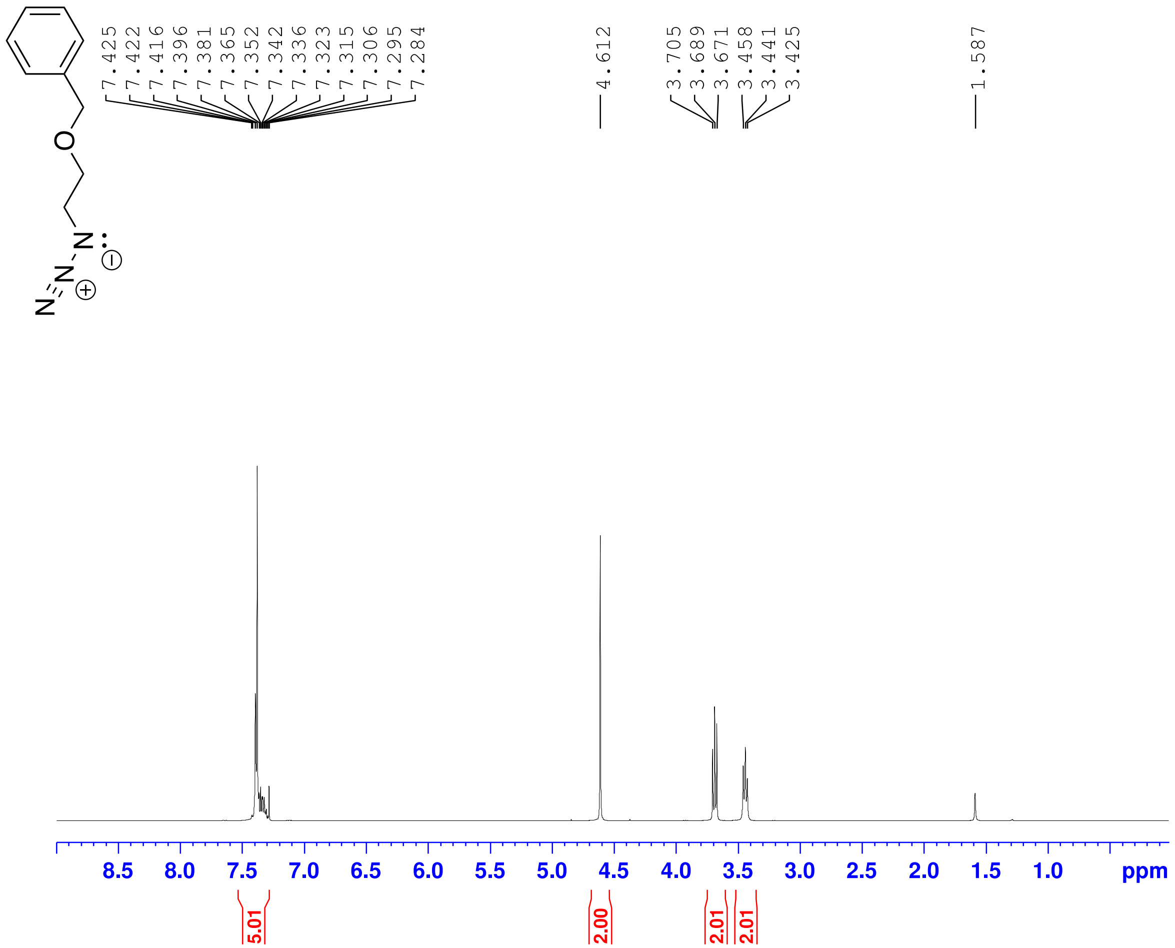
```
Current Data Parameters
NAME     AJD-4-45F1-carbon
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_          20170824
Time              12.07 h
INSTRUM           spect
PROBHD   Z108618_0594 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  304
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                10.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228293 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        16.00000000 W
PLW12        0.28444001 W
PLW13        0.14307000 W

F2 - Processing parameters
SI                32768
SF          100.6127578 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```


F_3C
S
O
O
O
O
7.409
7.391
7.388
7.381
7.373
7.363
7.351
7.347
7.333
7.324
7.316
7.280
4.677
4.666
4.655
4.618
3.808
3.797
3.786
1.566
4.83
2.02
2.00
2.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
Current Data Parameters
NAME AJD-4-46
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20170824
Time 10.41 h
INSTRUM spect
PROBHD Z108618_0594 (
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 4.0894465 sec
RG 210.59
DW 62.400 usec
DE 10.00 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
SFO1 400.1324708 MHz
NUC1 1H
P1 13.00 usec
PLW1 16.00000000 W
F2 - Processing parameters
SI 65536
SF 400.1300015 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

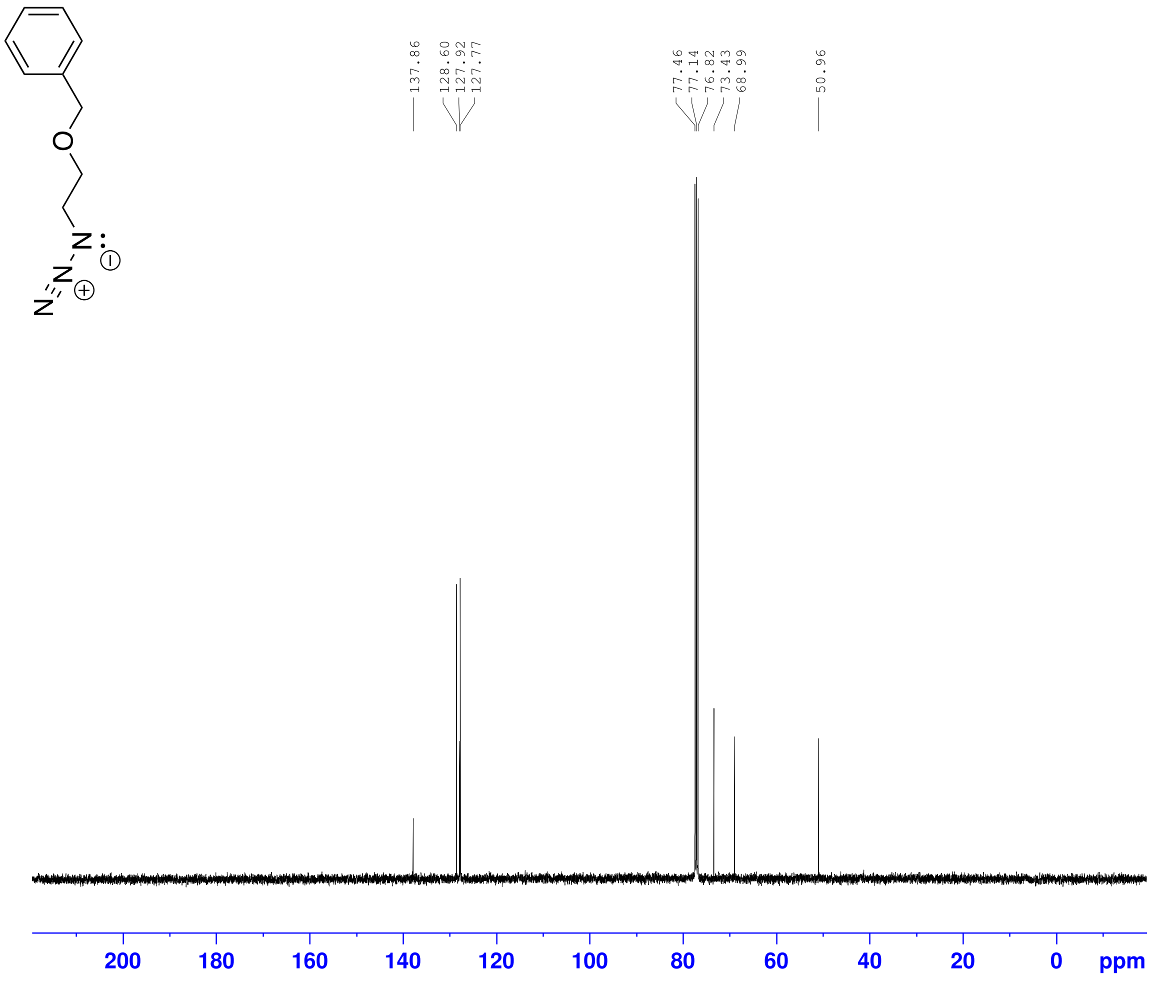




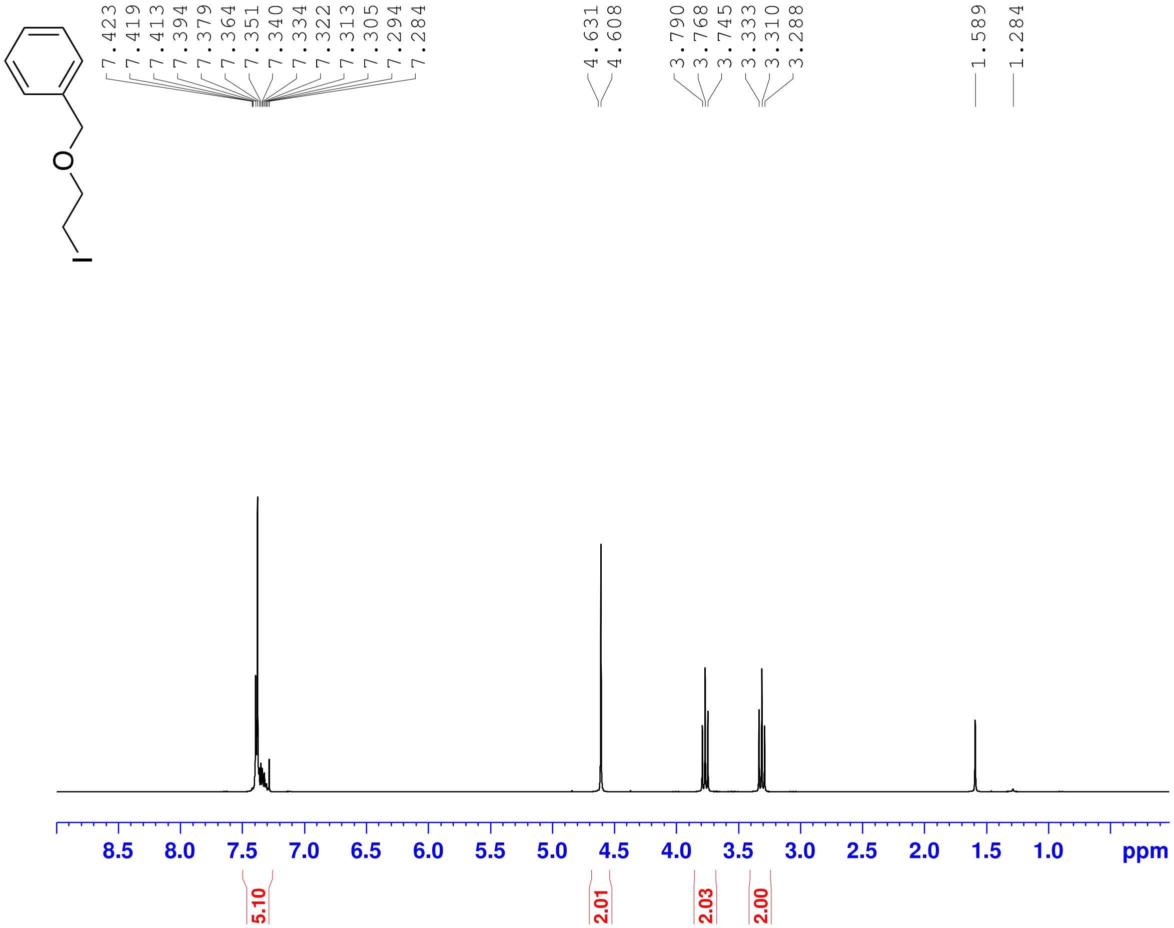
```
Current Data Parameters
NAME           AJD-4-46
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20170824
Time              11.06 h
INSTRUM           spect
PROBHD   Z108618_0594 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  300
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                10.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228293 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        16.00000000 W
PLW12        0.28444001 W
PLW13        0.14307000 W

F2 - Processing parameters
SI                32768
SF          100.6127578 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



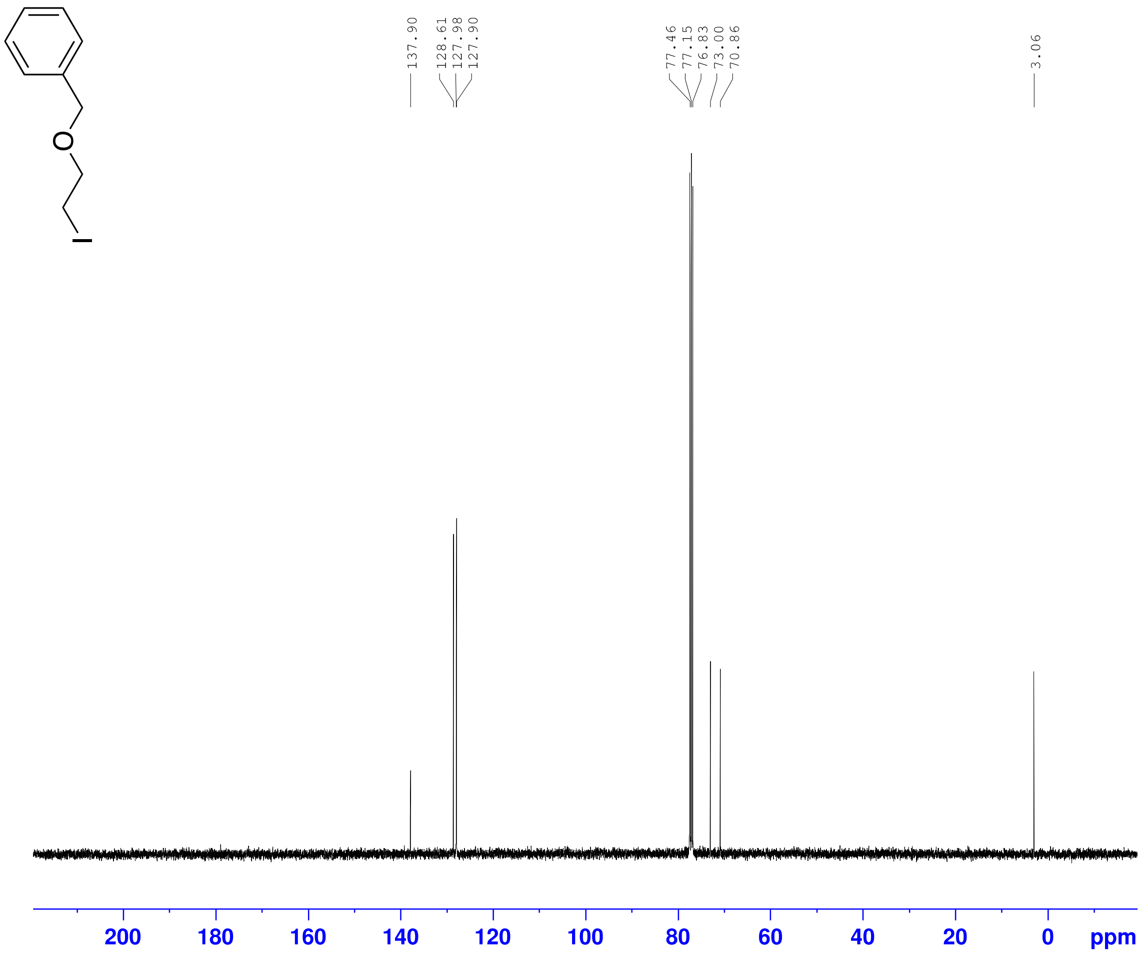
```
Current Data Parameters
NAME          AJD-4-47F1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170825
Time               10.43 h
INSTRUM            spect
PROBHD   Z104275_0302 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6009.615 Hz
FIDRES          0.183399 Hz
AQ             5.4525952 sec
RG                   228
DW                83.200 usec
DE                  6.50 usec
TE                 298.1 K
D1            1.00000000 sec
TD0                    1
SFO1         300.1318534 MHz
NUC1                  1H
P1                 12.00 usec
PLW1          6.55999994 W

F2 - Processing parameters
SI                 65536
SF           300.1300000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



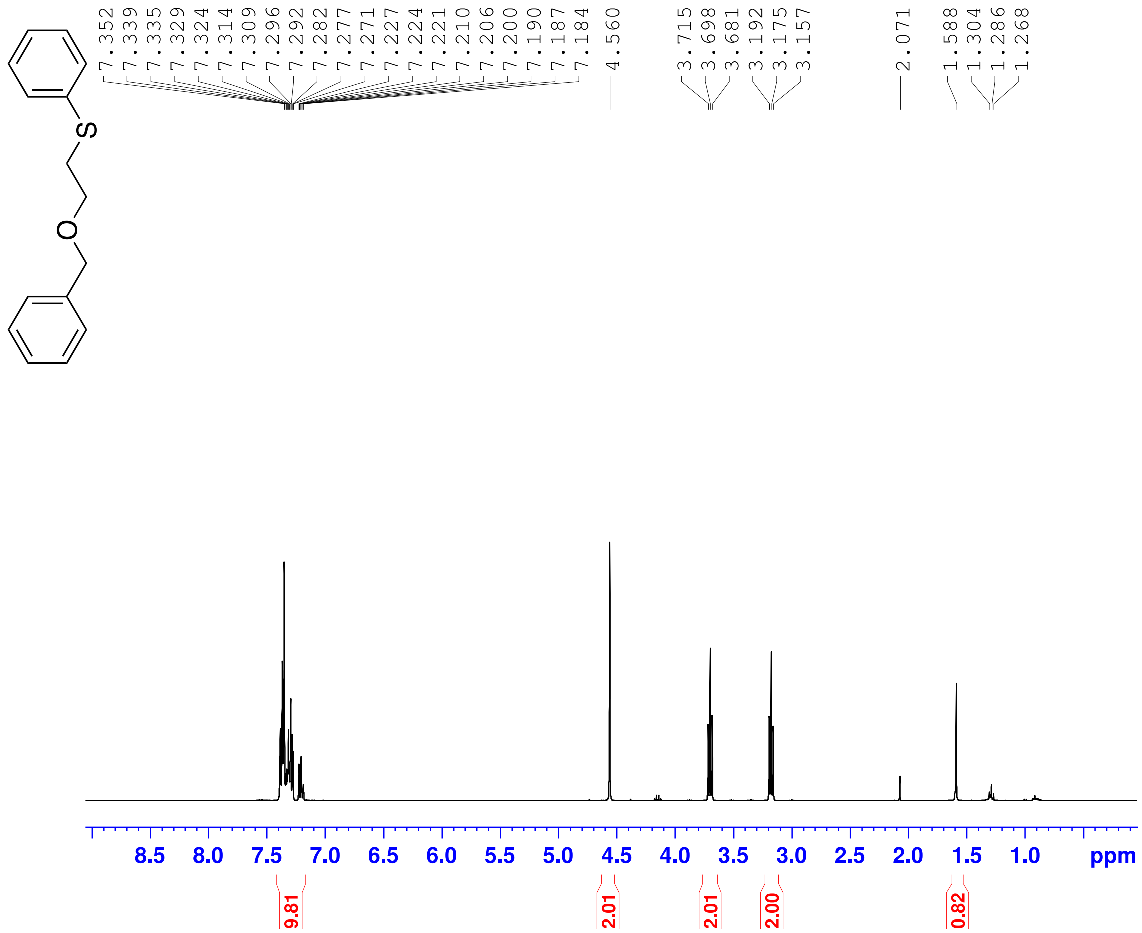
```
Current Data Parameters
NAME     AJD-4-47F1-carbon
EXPNO                   2
PROCNO                  1

F2 - Acquisition Parameters
Date_          20170904
Time              14.17 h
INSTRUM           spect
PROBHD   Z108618_0594 (
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                  200
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                10.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228293 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        16.00000000 W
PLW12        0.28444001 W
PLW13        0.14307000 W

F2 - Processing parameters
SI                32768
SF          100.6127578 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



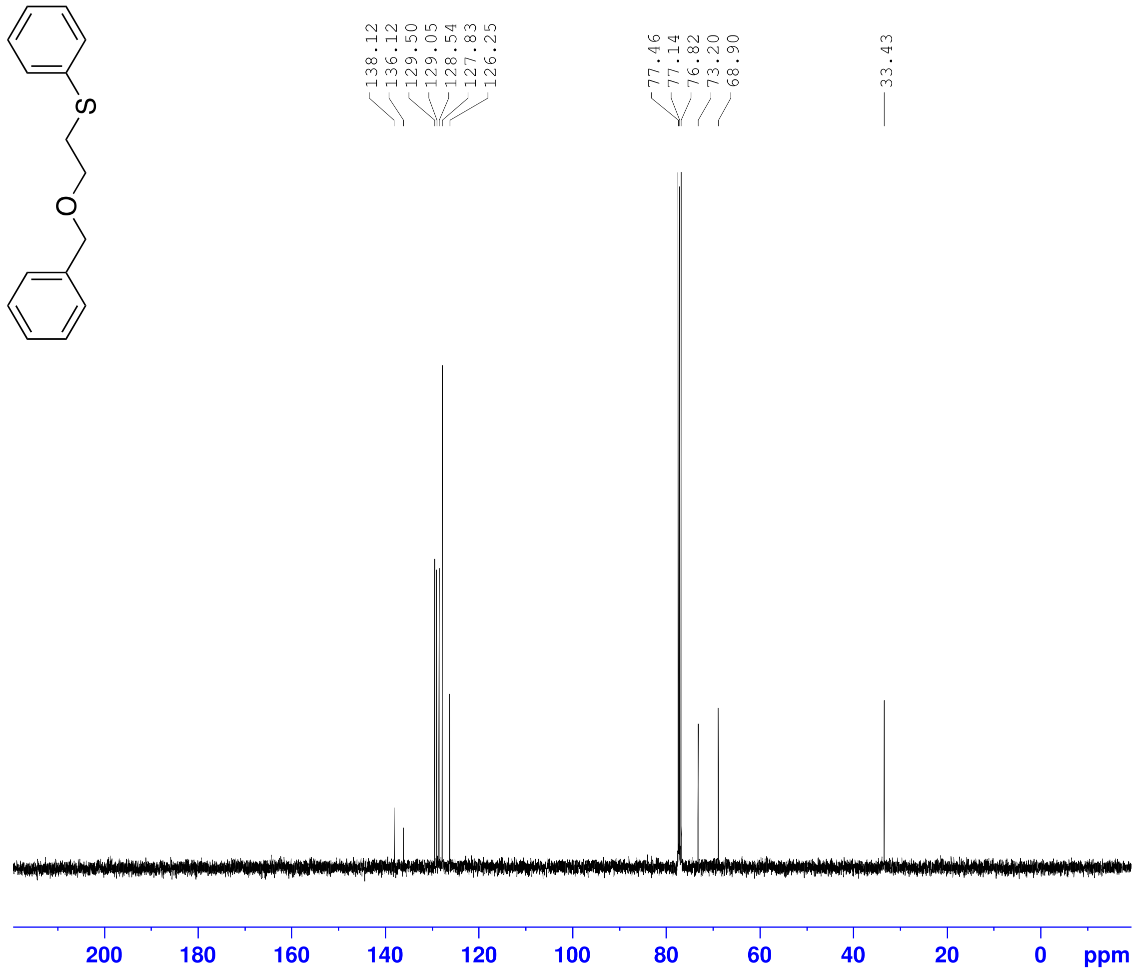
```
Current Data Parameters
NAME              AJD-4-49
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170901
Time                 10.04 h
INSTRUM              spect
PROBHD   Z104275_0302 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               6009.615 Hz
FIDRES            0.183399 Hz
AQ               5.4525952 sec
RG                     256
DW                  83.200 usec
DE                    6.50 usec
TE                   298.1 K
D1              1.00000000 sec
TD0                      1
SFO1           300.1318534 MHz
NUC1                    1H
P1                   12.00 usec
PLW1            6.55999994 W

F2 - Processing parameters
SI                   65536
SF             300.1300000 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```



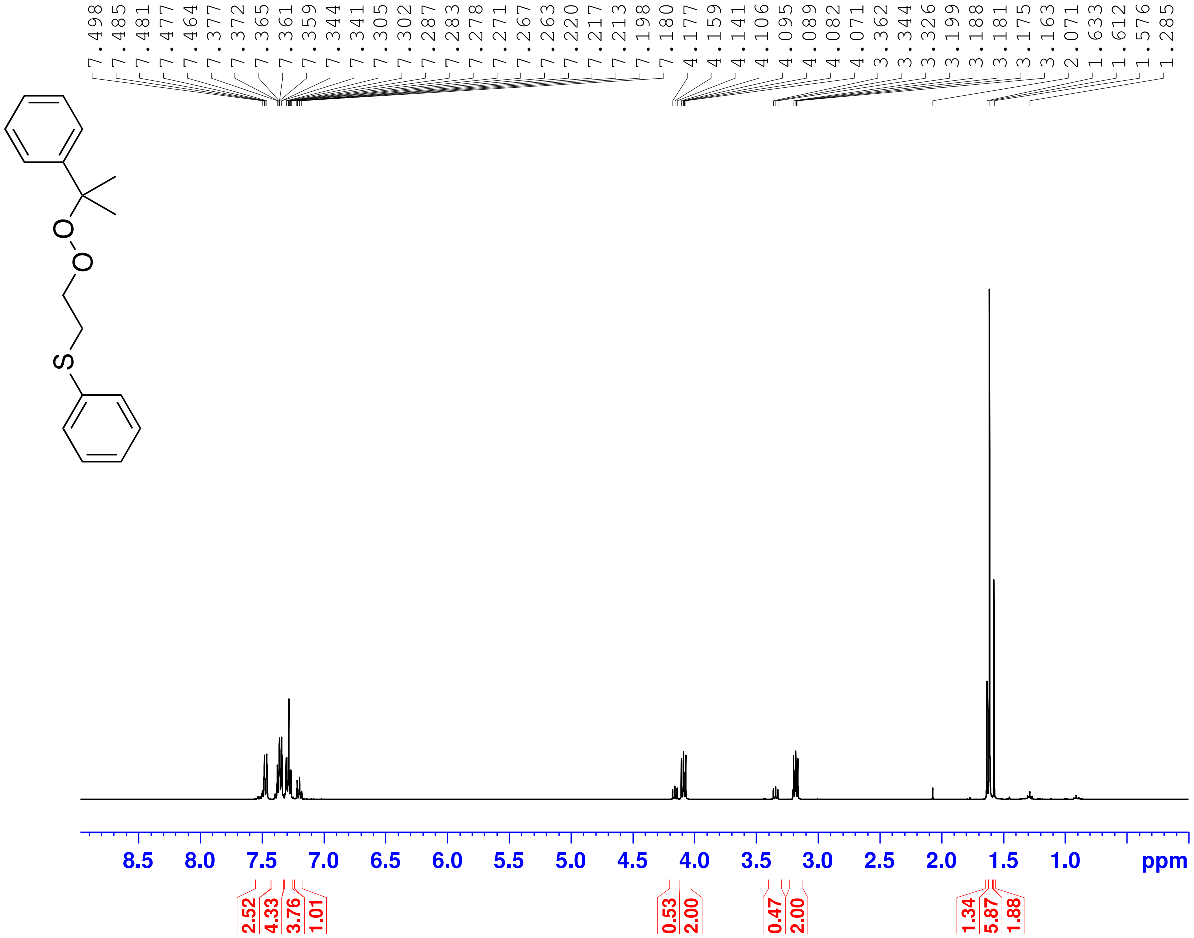
```
Current Data Parameters
NAME     AJD-4-49-carbon
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170904
Time               14.33 h
INSTRUM            spect
PROBHD   Z108618_0594 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   204
DS                     4
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ             1.3631488 sec
RG                210.59
DW                20.800 usec
DE                 10.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         100.6228293 MHz
NUC1                 13C
P1                  9.00 usec
PLW1         58.00000000 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         16.00000000 W
PLW12         0.28444001 W
PLW13         0.14307000 W

F2 - Processing parameters
SI                 32768
SF           100.6127578 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



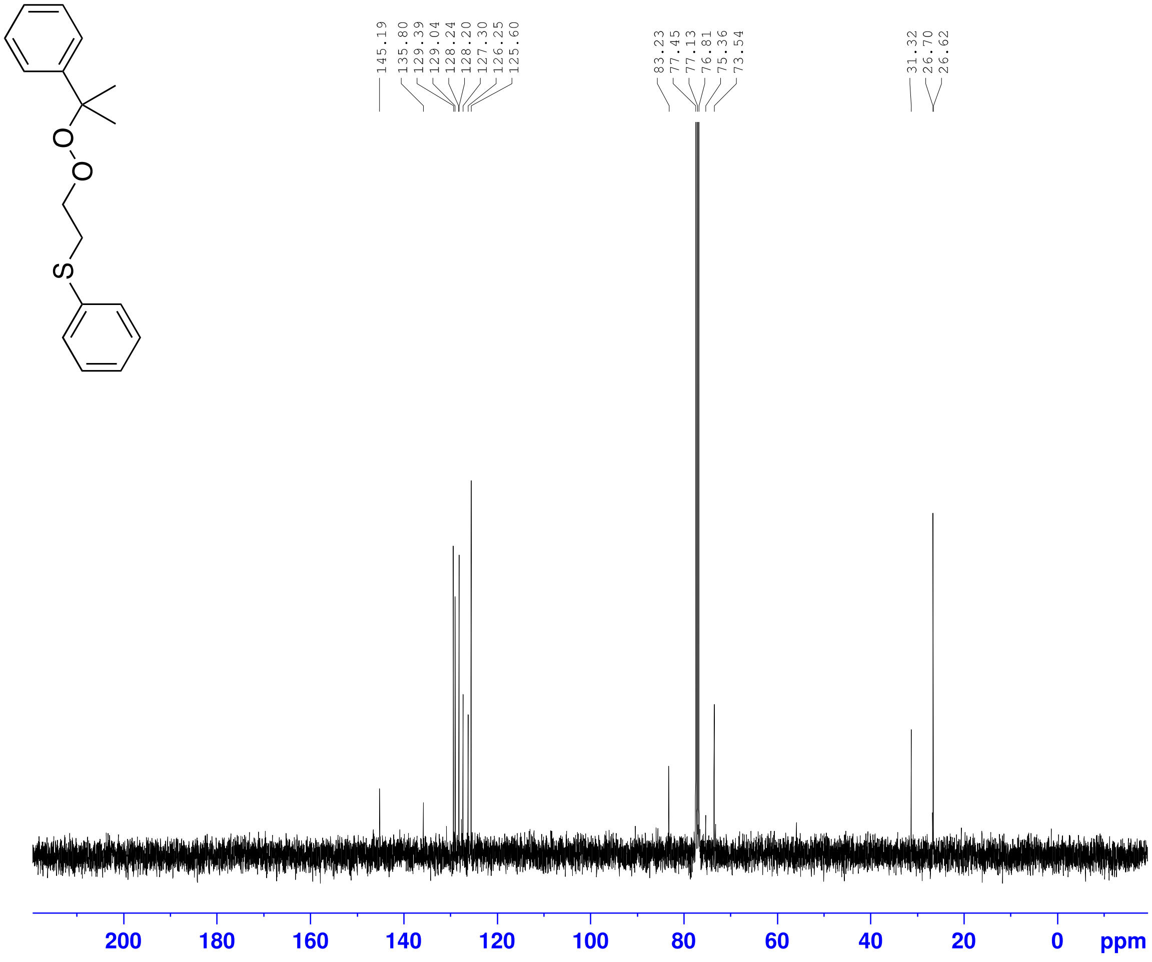
```
Current Data Parameters
NAME           AJD-4-58F2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_            20170912
Time                14.05 h
INSTRUM             spect
PROBHD   Z108618_0594 (
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.244532 Hz
AQ              4.0894465 sec
RG                 142.43
DW                 62.400 usec
DE                  10.00 usec
TE                  298.0 K
D1             1.00000000 sec
TD0                     1
SFO1          400.1324708 MHz
NUC1                   1H
P1                  13.00 usec
PLW1          16.00000000 W

F2 - Processing parameters
SI                  65536
SF            400.1300000 MHz
WDW                    EM
SSB      0
LB                   0.30 Hz
GB       0
PC                   1.00
```



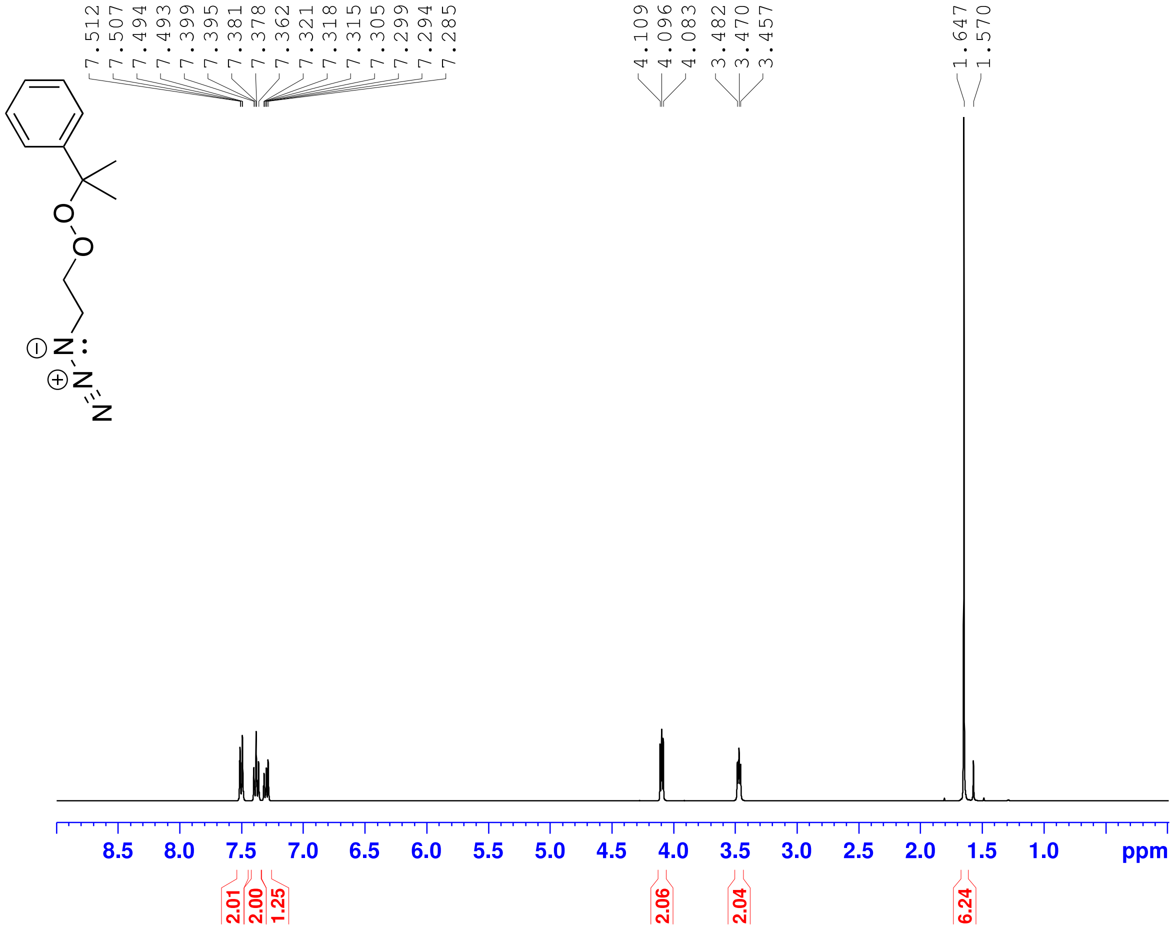
```
Current Data Parameters
NAME          AJD-4-58F2
EXPNO                  2
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170912
Time               14.15 h
INSTRUM            spect
PROBHD   Z108618_0594 (
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   150
DS                     4
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ             1.3631488 sec
RG                210.59
DW                20.800 usec
DE                 10.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         100.6228293 MHz
NUC1                 13C
P1                  9.00 usec
PLW1         58.00000000 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         16.00000000 W
PLW12         0.28444001 W
PLW13         0.14307000 W

F2 - Processing parameters
SI                 32768
SF           100.6127578 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



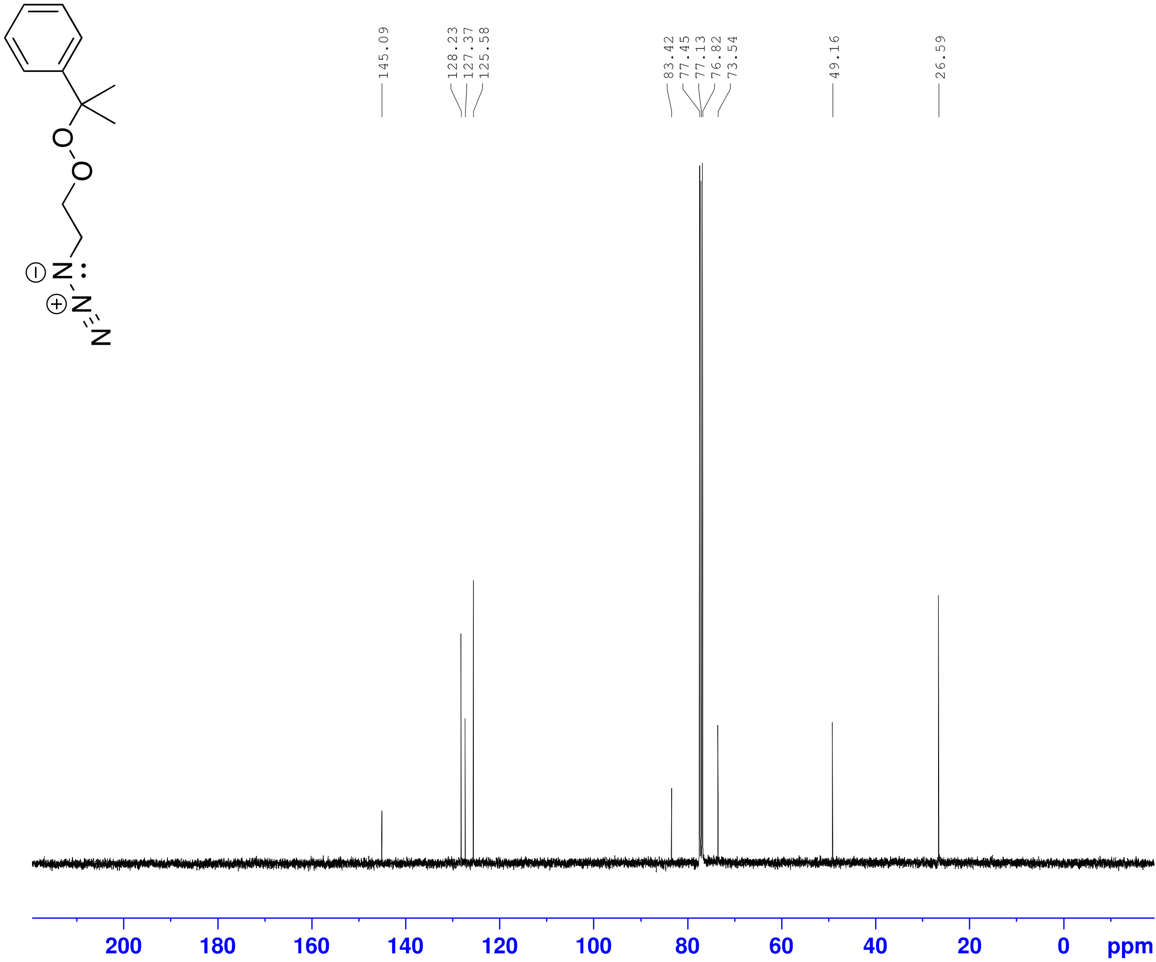
```
Current Data Parameters
NAME          AJD-4-57F2
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170912
Time               14.21 h
INSTRUM            spect
PROBHD   Z108618_0594 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ             4.0894465 sec
RG                187.87
DW                62.400 usec
DE                 10.00 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1
SFO1         400.1324708 MHz
NUC1                  1H
P1                 13.00 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



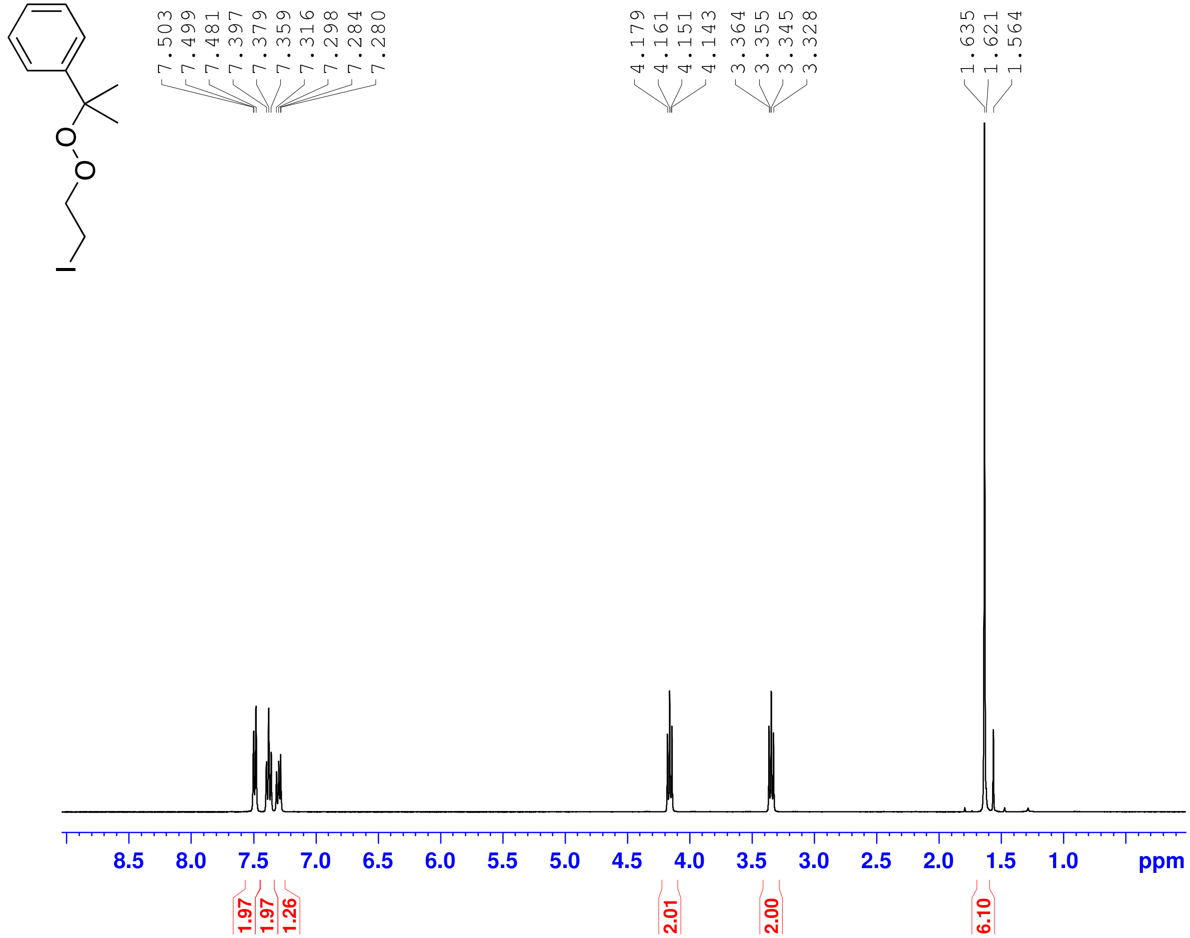
```
Current Data Parameters
NAME         AJD-4-57F2
EXPNO                 2
PROCNO                1

F2 - Acquisition Parameters
Date_          20170912
Time              14.30 h
INSTRUM           spect
PROBHD   Z108618_0594 (
PULPROG         zgpg30
TD                65536
SOLVENT           CDCl3
NS                  132
DS                    4
SWH           24038.461 Hz
FIDRES         0.733596 Hz
AQ            1.3631488 sec
RG               210.59
DW               20.800 usec
DE                10.00 usec
TE                298.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
SFO1        100.6228293 MHz
NUC1                13C
P1                 9.00 usec
PLW1        58.00000000 W
SFO2        400.1316005 MHz
NUC2                 1H
CPDPRG[2        waltz16
PCPD2             90.00 usec
PLW2        16.00000000 W
PLW12        0.28444001 W
PLW13        0.14307000 W

F2 - Processing parameters
SI                32768
SF          100.6127578 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
GB       0
PC                 1.40
```



```
Current Data Parameters
NAME          AJD-4-45F1
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20170824
Time               11.11 h
INSTRUM            spect
PROBHD   Z108618_0594 (
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES          0.244532 Hz
AQ             4.0894465 sec
RG                164.14
DW                62.400 usec
DE                 10.00 usec
TE                 298.0 K
D1            1.00000000 sec
TD0                    1
SFO1         400.1324708 MHz
NUC1                  1H
P1                 13.00 usec
PLW1         16.00000000 W

F2 - Processing parameters
SI                 65536
SF           400.1300000 MHz
WDW                   EM
SSB      0
LB                  0.30 Hz
GB       0
PC                  1.00
```



```
Current Data Parameters
NAME     AJD-4-45F1-carbon
EXPNO                    2
PROCNO                   1

F2 - Acquisition Parameters
Date_           20170824
Time               12.07 h
INSTRUM            spect
PROBHD   Z108618_0594 (
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   304
DS                     4
SWH            24038.461 Hz
FIDRES          0.733596 Hz
AQ             1.3631488 sec
RG                210.59
DW                20.800 usec
DE                 10.00 usec
TE                 298.0 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                    1
SFO1         100.6228293 MHz
NUC1                 13C
P1                  9.00 usec
PLW1         58.00000000 W
SFO2         400.1316005 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              90.00 usec
PLW2         16.00000000 W
PLW12         0.28444001 W
PLW13         0.14307000 W

F2 - Processing parameters
SI                 32768
SF           100.6127578 MHz
WDW                   EM
SSB      0
LB                  1.00 Hz
GB       0
PC                  1.40
```



```
Current Data Parameters
NAME              AJD-4-34
EXPNO                    1
PROCNO                   1

F2 - Acquisition Parameters
Date_             20170727
Time                 13.07 h
INSTRUM              spect
PROBHD    Z108618_0594 (
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      16
DS                       2
SWH               8012.820 Hz
FIDRES            0.244532 Hz
AQ               4.0894465 sec
RG                  164.14
DW                  62.400 usec
DE                   10.00 usec
TE                   298.2 K
D1              1.00000000 sec
TD0                      1
SFO1           400.1324708 MHz
NUC1                    1H
P1                   13.00 usec
PLW1           16.00000000 W

F2 - Processing parameters
SI                   65536
SF             400.1300000 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```