The synthesis of carbon-substituted furoxans via radical-mediated pathway and further transformation to various nitrogen-containing functional groups

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Doctoral Dissertation

The synthesis of carbon-substituted furoxans via radical-mediated pathway and further transformation to various nitrogen-containing functional groups

ラジカル機構による炭素置換フロキサンの合成と含窒素化合物への変換反応

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Abbreviations

Acac	acetylacetonate
AcOH	acetic acid
AIBN	azodiisobutyronitrile
Ar	aryl
BPO	dibenzoyl peroxide
Cacld	calculated
DART	direct analysis in real time
DCE	dichloroethane
DCM	dichloromethane
DMF	*N*, *N*-dimethylformamide
DMSO	dimethyl sulfoxide
DTBP	di-tertbutyl peroxide
Equiv	equivalent
ESI	electrospray ionization
Et_3B	triethylborane
Et_3N	triethylamine
ET	energy transfer
EtOAc	ethyl acetate
EtOH	ethanol
FI	field ionization
HAT	hydrogen atom transfer
HRMS	high resolution mass spectrometry
IR	infra-red
MeCN	acetonitrile
MeOH	methanol
Mp	melting point
N.D.	not detected
NHC	*N*-heterocyclic carbine
NMP	*N*-methyl-2-pyrrolidone
NMR	nuclear magnetic resonance
NO	nitric oxide
o	ortho
OAc	acetate
PEG	polyethylene glycol
Ph	phenyl
PTC	phase transfer catalysts
PTLC	preparative thin layer chromatography
TBAB	tetrabutylammonium bromide
TBPB	t-butyl peroxybenzoate
t-BuOK	tert-butoxide
THF	tetrahydrofuran
TLC	thin layer chromatography

Abstract

Heterocyclic system is an important component of novel functional molecules in pharmaceuticals and agrichemicals. Furoxan (1,2,5-oxadiazole-2-oxide) is one such this heterocyclic system. It was originally synthesized by Kekulé in the late of 19th century, but the structure was not immediately identified due to the undeveloped technology at that time. Based on many arguments, furoxan was identified as a five-membered structure with three heteroatoms in which one of the nitrogen atoms is attached with an exo-ring oxygen atom. The different functional groups are substituted at 3- and 4-positions, which build the library of furoxan derivatives and exhibit different biological activities.

Furoxan has weak aromaticity and is prone to ring-opening under some strong reaction agents. It is also the reason for the slow development of direct construction of C−C bonds on the furoxan ring. Previously, our group reported carbon radical produced from aliphatic carboxylic acid and addition to 3-sulfonylfuroxan which brings the new synthesis strategy of furoxan molecules.

Although C−H bond is a week polar bond because of small electronegativity difference, many methods for activating C−H bond have been gradually developed. One common method is transition-metal catalysis, which cleaves C−H bonds and affords carbon-metal intermediates to form C−C bonds. Radical mediated HAT process is also a commonly used activation method. Our research focuses on developing a method to construct a C−C bond on furoxan through a simple radical process which utilizes different radical precursors, and C−H bond is one of our targets. Firstly, C−H bond containing compounds form carbon radicals under the action of oxidant, and the furoxan ring is introduced to realize “furoxanization” of C−H bond. Subsequently, the furoxan products are converted into many different nitrogen-containing functional groups in 1 or 2 steps, which is difficult to realize by other methods. This strategy was named “build-and-scrap” in which C−H functional group transforms to other functional group in few steps.

At the same time, we found that most aryl substituents on furoxan ring had been constructed before the ring formation. Until now, only two articles have reported the direct formation of aryl substituents on furoxan, but the scope has not been tested. Following the success of previous studies, we pay our attention to introduce an aryl substituent to furoxan via radical-mediated pathway. Here, potassium aryl trifluoroborates are served as convenient aryl radical precursors, which are easy to prepare and have a wide substrate scope. Although the optimal conditions did not achieve high yield, this method was concise and many substituted aryl groups were successfully introduced into furoxan.

Our work is devoted to providing a convenient method for the direct introduction of carbon substituents on furoxan ring. Afterwards, the furoxan products realize the transformation to other functional groups or derivatization to other furoxan compounds.

Key words: Furoxan; Radical reaction; C−C bond forming; “build and scrap” strategy

Acknowledgements

As time goes by, I have lived in Japan for 3 years and Ph.D. life is coming to an end. Here, I would like to gratitude the people who always help and support me. On this occasion of the accomplishment of the thesis, I hope to express appreciation to the supervisor, lab colleagues, parents and friends who have accompanied me around.

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And also, I owe my thanks to my wonderful lab colleagues, who tolerate my language barrier and make me feel warm and comfortable. We share and communicate different cultures, which promotes our relationship forward together. During this period, they give me a great amount of help, it is really enjoyable to learn and live with them.

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I'm glad to study at Kobe University, and the useful knowledge what I have learned will accompany me through my whole life. Although I feel still deficient, life is a continuous learning process. Let's grow up together in the future.

I: Introduction

1.1 An introduction of furoxan

Furoxans (1,2,5-oxadiazole 2-oxides), the research target of which was first synthesized by Kekulé in 1850s and has been around for more than 160 years (Figure 1, **1**).[1] Due to the undeveloped technology, furoxan structure could not be confirmed at the beginning, many possible formulas of furoxan had been proposed by researchers at that time (Figure 1).[2] Among them, Wieland[3,4] first proposed the correct structure **1** (although he supported the bicyclic structure **3** for a while), and after 60 years it was finally proofed by NMR and X-ray.

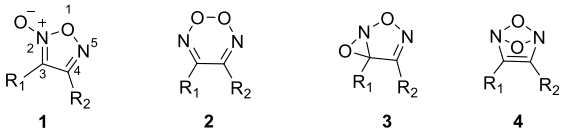
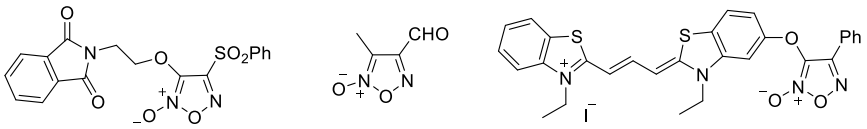


Figure 1: Proposed structures of furoxan.

A five-membered cycle and one exo-ring oxygen atom constitute a special kind of heterocycle that sets them different from other azoles. It is not difficult to find that a potential nitro group (NO_2) or two nitroso groups (NO) are contained in the furoxan skeleton and most of their special properties are based on these groups. An important feature is thermal isomerization and easy to occur, where the ring-outside oxygen atom moves to another nitrogen atom probably through ring-opening process. The sensitivity of this property depends on the substituents of furoxan.

For researchers, the potential application value of furoxans is another attractive research focus. Some furoxan derivatives are regarded as potential drug candidates, such as in the therapy of sickle cell anaemia (Figure 2, **5**), diabetic neuropathy (Figure 2, **6**) and Alzheimer's disease (Figure 2, **7**), etc.[5,6] The pharmacological activity of furoxans is primarily on account of their ability to release NO (a signaling molecule to improve blood circulation in the body and versatile regulator of cell metabolism that instructs the body to perform certain important functions).[7–12] Thus, structures containing a furoxan moiety can be considered as

pharmaceutical candidates and applied as potential NO donors.

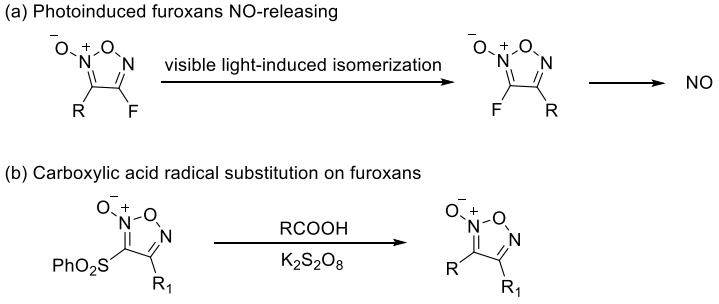


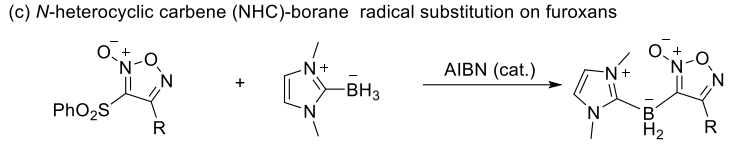
5 6 7

Figure 2: Some drug candidates contain furoxan ring.

Furoxans which reported with biological activity mostly are those substituted by one or two carbon functional groups.[11–13] However, due to the electron-deficient property, ring-opening side reaction may occur when nucleophilic substitution reaction takes place on furoxan. Therefore, the most common method for synthesizing carbon-substituted furoxans is to construct the corresponding carbon substituents before the furoxan ring formation, but obviously this is a cumbersome step. As a replacement, the direct construction of the desired carbon substituents after the ring formation becomes an attractive strategy that appears to be more concise than previous method.

Based on these unique properties, our group generates a great interest in developing furoxan. For example, developed photosensitive furoxans, which support the NO release in the absence of thiol cofactor (Scheme 1a),[14] a methodology in which carboxylic acids were used as carbon radical donors and added to 3-sulfonylfuroxan to obtain carbon-substituted furoxans (Scheme 1b),[15] *N*-heterocyclic carbene (NHC)-borane reacted with 3-sulfonylfuroxans via radical process (Scheme 1c),[16] etc.





Scheme 1: Some previous reports of our group.

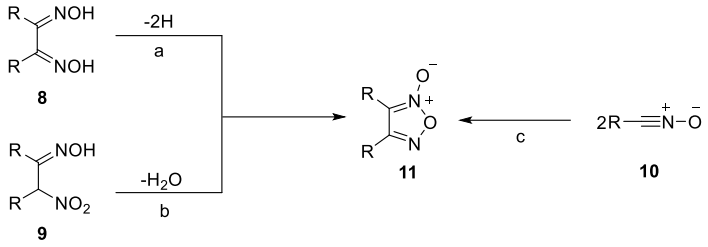
1.2 Research of furoxan

Furoxan is a series of structures that are generally stable under air and moisture. It is easy for them to isolate and store, and these characteristics make them considered as potential chemical compounds.[6,17] Up to now, furoxan participated applications are very limited because they are affected by ring-opening. The great interest of furoxan over the past few decades has mainly come from the ability of some of these derivatives to release nitric oxide, which is a special property that different from other heteroaromatics.

1.2.1 The synthesis of furoxan

The earliest furoxan was produced from metal fulminates[2] by Kekulé and used many years to determine the structure. So far, many methods for synthesizing furoxan have been developed, the most commonly useful methods[17] of which are shown in Scheme 2: (a) the oxidative cyclization of 1,2-dioxime **8**,[18] the furoxan is generated by oxidation of dioxime under various oxidants, the mechanism of most cases is via dinitrosoolefin intermediate. (b) the dehydration of α-nitroketoxime **9**,[19] since it is not clear whether the two oxygens of the furoxan are all donated by the nitro group, the mechanism of this method remains questionable. (c) the dimerization of nitrile oxide **10**,[20] it was first reported by Werner and obtained symmetrically substituted furoxans via heating the nitrile oxide. It is also possible for unsymmetrically

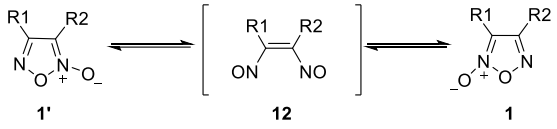
substituted furoxans to be formed from mixed nitrile oxides. It is worth noting that, most nitrile oxides are highly reactive and difficult to separate and store.



Scheme 2: Common methods for synthesizing furoxan.

1.2.2 Thermal and photochemical isomerization of furoxan

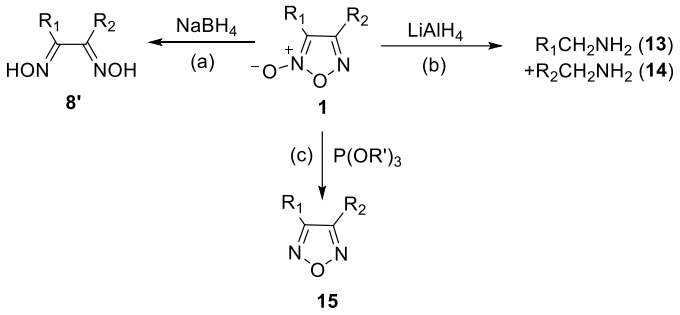
An important property of furoxan is isomerization, for example, isomeric furoxans **1** and **1'** are a pair of isomerization products ($\mathbf{1} \rightleftharpoons \mathbf{1}'$). One proposed mechanism of this process is the generation of dinitroso olefin intermediate **12**, which was first proposed by Hammick *et al* (Scheme 3).[21] Heat and light[22] are possible conditions to induce the rearrangement $\mathbf{1} \rightleftharpoons \mathbf{1}'$. However, the rate of this reaction depends on the substituents of furoxan ring.



Scheme 3: Isomerization of furoxan.

1.2.3 Reduction of furoxan

Furoxan can be reduced under various conditions.[23] Here we briefly illustrate the reaction conditions. Furoxan can be reduced to dioxime **8'** via hydrogenation by metal catalyst, although sometimes it will cause C−C bond or N−O bond cleavage. The reduction will occur with complex hydrides, under sodium borohydride ($NaBH_4$), dioxime **8'** is generated (Scheme 4a).[24] When using the more powerful reducing reagent lithium aluminum hydride ($LiAlH_4$), the C−C bond of the furoxan ring will cleave and corresponding amines **13, 14** are generated (Scheme 4b).[25,26] Tervalent phosphorus compounds are good candidates for furoxan deoxygenation to form the corresponding furazan **15**, which benefits from a strong P−O bond (Scheme 4c).[27] Dioxime and furazan are the common reduction products from furoxan. In addition to the reagents mentioned above, dissolving metals such as Zinc and acetic acid,[28,29] tin and hydrochloric acid[30,31] are also general reagents.



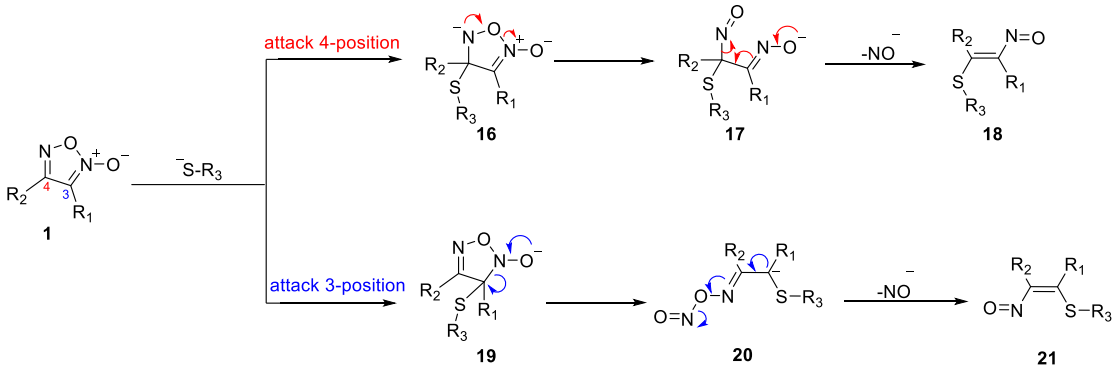
Scheme 4: Reduction conditions of furoxan.

1.2.4 Nitric oxide release from furoxan

NO is widely distributed in various tissues in the human body, especially in nerve tissue. It is a new type of biological messenger molecule, which was selected as a star molecule. NO is a very unstable biological radical with small molecule and simple structure, which takes part in various biological functions. For example, it controls vascular tone, platelet inhibition, enzyme regulation, and immune regulation.[32]

Furoxan derivatives are considered as potential NO donors, which can activate soluble

guanylate cyclase with the participation of thiol.[12,33,34] The proposed mechanism for the release of nitric oxide in the presence of thiol compounds is considered as the thiolate anion attacks the furoxan and leads the furoxan ring opening (Scheme 5). Furoxan has two possible positions that may be attacked by thiol, although 4-position exhibits more electrophilic, the 3-position is still attacked by strong nucleophiles. Therefore, there are two proposed mechanisms for NO release. When the 4-position is attacked by a thiolate anion, intermediate **16** is generated and a nitrogen anion is formed, then electrons transfer to another nitrogen cation leading to ring-opening intermediate **17**, followed by oxygen electrons transfer, one equivalent of NO release. The other is that thiolate anion attacks the 3-position to generate intermediate **19**, and then electrons from oxygen are transferred to 3-carbon to form carbon anion intermediate **20**, and quickly transfer leads to one equivalent of NO release.

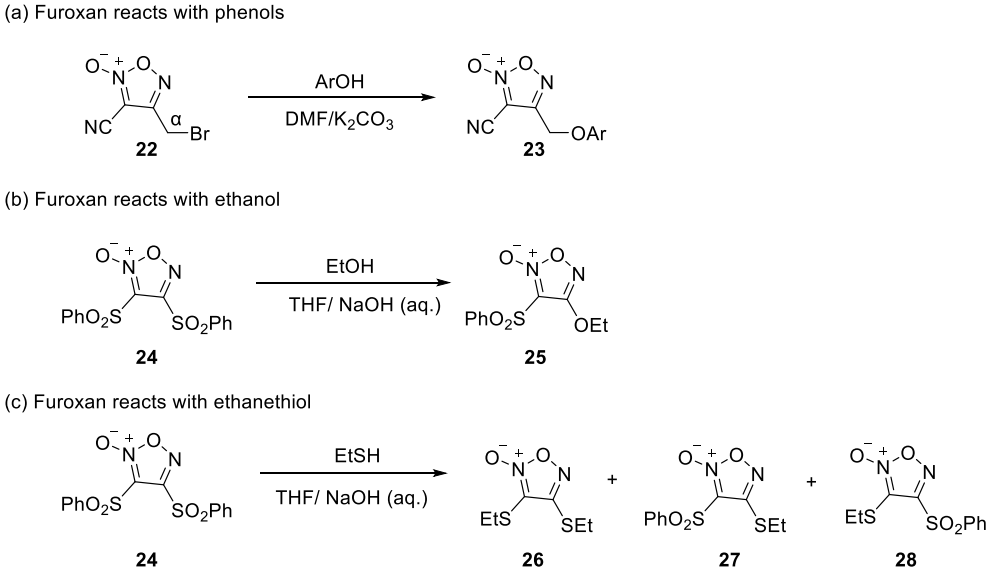


Scheme 5: Proposed NO releasing mechanisms of furoxan under the effect of thiol.

1.2.5 Nucleophilic substitution with furoxan

Furoxan derivatives can be prepared through nucleophilic substitution, but tend to ring-opening under the action of strong nucleophiles. Here we introduce some nucleophilic substitution reactions in which the furoxan reacts with a nucleophile and the furoxan ring remains (Scheme 6).[35–37] The oxygen anion formed under basic condition attacks the α-position of 4-carbon (**22)** due to the existence of a good leaving group (Scheme 6a). It is

same with Scheme 6b, except that it occurs directly on the furoxan ring. Scheme 6c, due to the strong nucleophilicity of sulfur, nucleophilic substitution occurs at both 3- and 4-positions, forming monosubstituted **27** and **28**, disubstituted **26**.

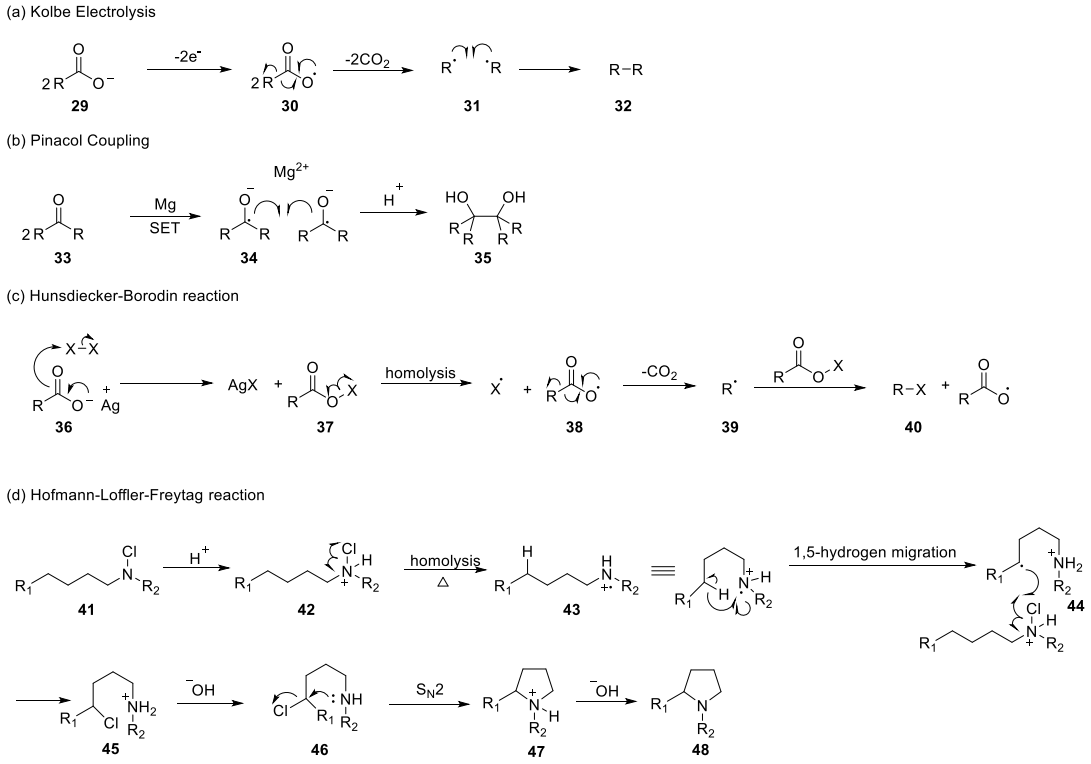


Scheme 6: Nucleophilic substitution reactions of furoxan.

1.3 Radical reaction

There are many types of organic chemical reactions, and radical reaction is one of them. It is widely used in the synthesis of various drug molecules, active intermediates and macromolecular polymers. Many useful radical reactions have been developed at a very early stage. For example, Kolbe Electrolysis[38] (Scheme 7a) realizes coupling by electrolytic decarboxylation to form radical **31**; Pinacol Coupling[39] (Scheme 7b) radical anion intermediate **34** is generated by single electron transfer (SET) of carbonyl group and subsequent radical coupling; Hunsdiecker-Borodin reaction[40] (Scheme 7c) the carboxylate anion **36** attacks halogen to form an O−X bond **37**, because of the low bond dissociation energy of O−X bond, it is easy to homolytic cleavage, the acyloxy radical **38** is

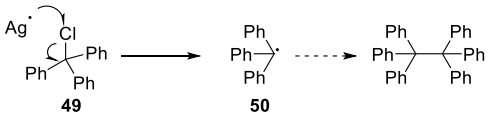
decarboxylated and the generated alkyl radical **39** coupled with halogen radical. Hofmann-Loffer-Freytag reaction[41] (Scheme 7d) under heating condition, the N−Cl bond of protonated *N*-haloamine **42** is homogenized, and the generated nitrogen radical cation **43** undergoes intramolecular 1,5-hydrogen migration to generate the corresponding carbon radical **44**, which is then coupled with the halogen radical, the formed halogenated amine intermediate **45** undergoes further intramolecular nucleophilic substitution, and then under the action of a base, a cyclic amine product **48** is obtained. However, due to the limitations of cognition at that time, the research value of radical reaction was not found. Therefore, in the subsequent development of organic chemistry, the development of radical reactions was relatively slow.



Scheme 7: Some useful radical reactions in the early stage.

Until 1900, chemist Gomberg began to recognize this strange species and speculated the existence of the triphenyl radical **50** through the reaction between triphenylchloromethane and Ag metal (Scheme 8).[42] Although Gomberg's prediction of dimerization product was incorrect,

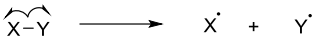
his bold guess about the triphenyl radical became one of the greatest achievements in the history of organic chemistry. After that, the concept of radical has been continuously supplemented and improved. The homolytic process is achieved when the bond is broken and the shared electrons are equally distributed to the two atoms that form the bond. The result of homolysis is the generation of radicals.



Scheme 8: Radical discovered from Gomberg's reaction.

1.3.1 The generation of radical

Radical reactions must involve radicals participating in the reaction. The radicals are usually produced by the homolytic cleavage of a bond into two parts, which contain unpaired electrons (Scheme 9). There are many ways to generate radicals, such as the redox reaction, light, electrolysis and heat. Although most radicals have a short lifetime, they are highly reactive.

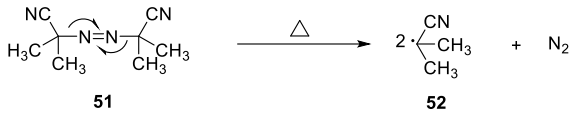


Scheme 9: Homolytic cleavage of bond.

1.3.1.1 Thermal initiation

Homolytic cleavage of general covalent bonds requires high energy. Certainly, for some covalent bonds with low bond dissociation energy, it is easy to undergo homolysis at a temperature slightly higher than room temperature. These compounds which have weak σ bonds are important initiators in chemical reactions. For example, organic peroxides and azo

compounds which contain weak O−O bond and C−N bond are often used as initiators of radical reaction. Here, we use azobisisobutyronitrile (AIBN) **51** as an example, which decomposes into two molecules of isobutyronitrile radical **52** and nitrogen gas at 66 ℃ (Scheme 10).

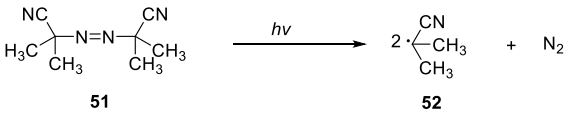


51 **52**

Scheme 10: Thermal initiation of AIBN.

1.3.1.2 Photoinitiation

Except heating, light is another energy source for homolytic cleavage of bonds. When some molecules receive energy from light, their weak bonds are homogenized into radicals. AIBN **51** can also form isobutyronitrile radical **52** as it absorbs light, resulting in an unstable *cis*-configuration (Scheme 11).



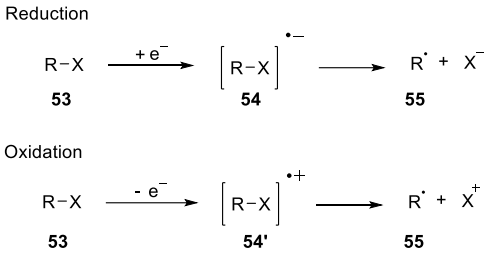
51 **52**

Scheme 11: Photoinitiation of AIBN.

1.3.1.3 Redox reaction

Single electron redox reaction is another common method to form radicals. It is usually achieved by intermolecular electron transfer (Scheme 12). During the reduction process, an electron is obtained to generate a radical anion intermediate **54**, which is quickly decomposed

to radical **55** and an anion. During the oxidation process, an electron is lost and a radical cation intermediate **54'** is formed, which is quickly decomposed to radical **55** and a cation. The well known name reaction Birch reduction is a good example of a reduction process.



Scheme 12: Redox reaction form radical.

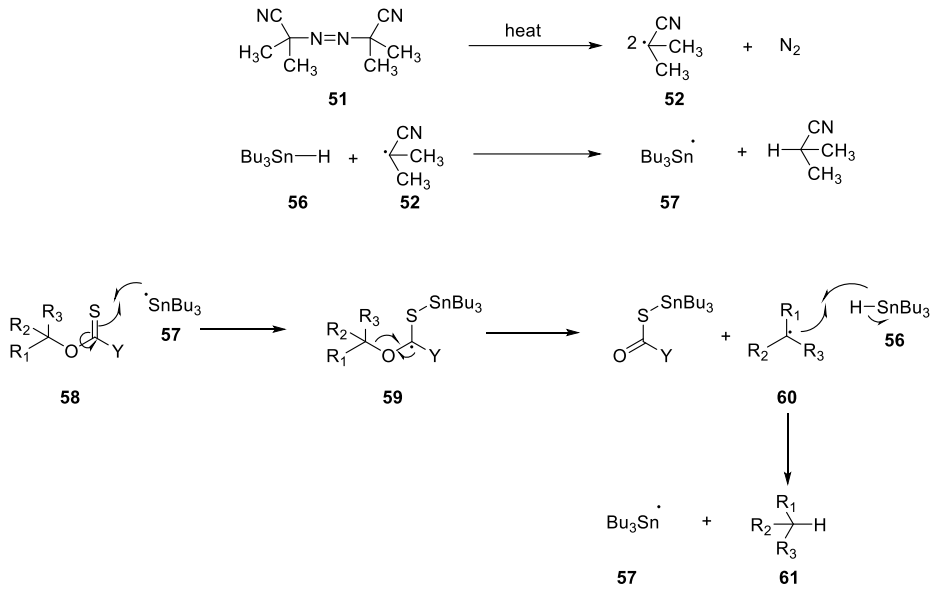
1.3.2 Radical initiators

Radical reaction is an important and widely used organic chemical reaction. In radical reaction, unpaired electrons tend to form new bonds, which are highly reactive. In order to make the most use of this reaction, researchers continue to optimize the conditions under which it occurs. In chemical use, it is impossible to employ high temperature to induce homolytic cleavage of bonds. The disadvantages come from high energy more than advantages. Thus, radical initiators become good partners for radical reaction that proceed under mild conditions. The properties of such initiators are generally relatively stable, easy to store, and contain weak bonds.

1.3.2.1 Azo compound

Azo compounds are commonly used radical initiators, and AIBN is one of these initiators. As mentioned before, AIBN **51** can be decomposed into two molecules of isobutyronitrile radical **52** and one molecule of nitrogen gas (N_2) under light or heating condition (Scheme 10 and 11). Subsequently, radical reaction is initiated. Such as Barton-McCombie radical deoxygenation

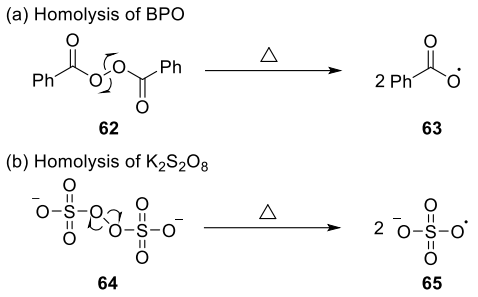
reaction (Scheme 13),[43] alcohol is converted to thiocarbonyl intermediate followed by radical cleavage to give the dehydroxylated product. The reaction is initiated by tributyltin radical **57** which formed from isobutyronitrile radical **52** and tributyltin hydride **56**, the tributyltin radical **57** abstracts sulfur from **58** and forms strong S−Sn bond, the intermediate **59** is decomposed to an alkyl radical **60**, then the hydrogen radical is abstracted from tributyltin hydride **56** to realize the reaction cycle.



Scheme 13: Barton-McCombie deoxygenation reaction is initiated by AIBN.

1.3.2.2 Peroxide

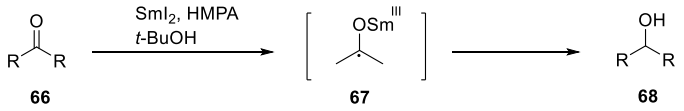
Peroxides which contain O−O bond also have a long history as radical initiators. They are easily homolyzed into two radicals due to the existence of weak O−O bond. It can be divided into inorganic peroxide and organic peroxide. Here we use organic peroxide dibenzoyl peroxide (BPO) **62** (Scheme 14a) and inorganic peroxide potassium persulfate ($K_2S_2O_8$) **64** (Scheme 14b) as examples which are homogenized under heating condition.



Scheme 14: Homolysis of BPO and $K_2S_2O_8$.

1.3.2.3 Organic metal and inorganic metal compound

In this kind, tributyltin hydride **56** (Bu_3SnH) and samarium(II) iodide (SmI_2) are popular radical initiators. The reason why Bu_3SnH can be used as an initiator is due to the existence of weak Sn−H bond. In many cases, the tin radical is used to abstract halogens, especially iodine and bromine, and form strong Sn−Hal bond. Kagan's reagent (SmI_2) acts as a single electron transfer reagent in many reactions.[44] Its earliest application in organic chemistry was the reduction of aldehydes and ketones (Scheme 15).



Scheme 15: Radical reaction is initiated by SmI_2.

1.3.2.4 Photocatalyst

Photocatalysts play an important role in organic photochemistry. The most common photocatalysts are mainly divided into two categories: transition metal complex

photocatalysts (such as Figure 3a)[45] and metal-free organic photocatalysts (such as Figure 3b).[46] These photocatalysts generally contain highly conjugated systems and unsaturated bonds, but also have different characteristics, such as including simple aromatic conjugated groups, neutral and charged systems, and transition metal complexes that can be modified by ligands.

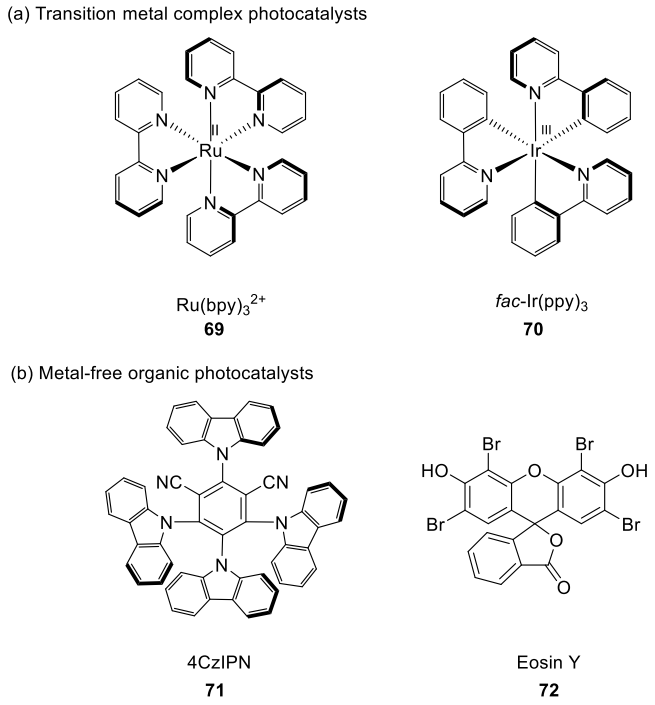


Figure 3: Different types of photocatalysts.

At present, there are three main proposed mechanisms of these photocatalysts in photoreactions, single electron transfer (SET), hydrogen atom abstraction and energy transfer (ET).[45] Here we briefly introduce the SET process (Figure 4), in which visible-light activates the transition metal and induces organic photocatalyst to excited states, leading to its strong redox property which can rapidly donate an electron to the electron-deficient acceptor A, or accept an electron from the electron-rich donor D. The catalytic cycle includes two reaction paths: oxidation process and reduction process, and the products produced include radical cation ($D^{\bullet+}$) and radical anion ($A^{\bullet-}$).

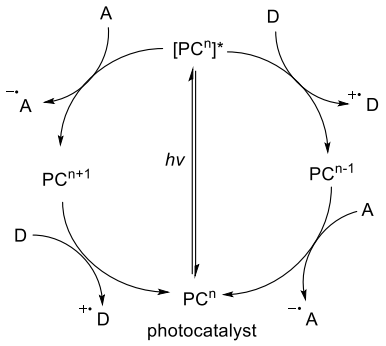
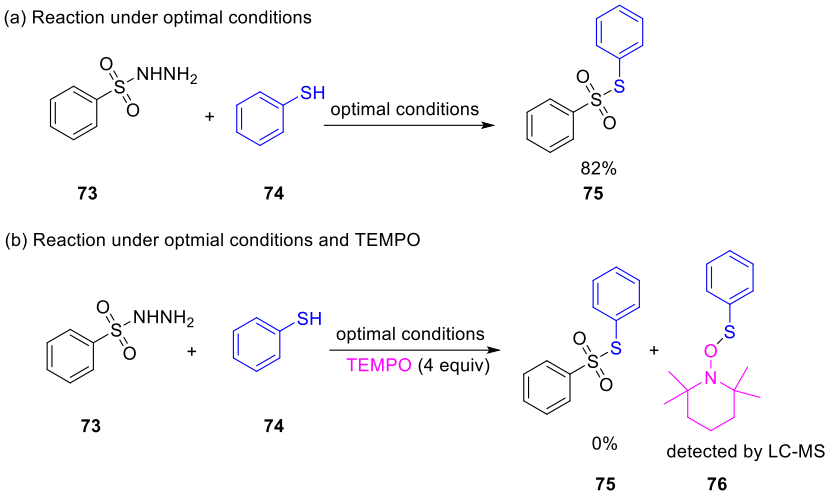


Figure 4: Radical generation enabled by photoredox process.

1.3.3 The verification of radical process

Last but not least is to verify the existence of radicals and confirm the radical structures. It is well known that radicals are highly reactive intermediates, therefore how to detect and trap them. So far, radical trapping reaction, radical clock reaction and electron paramagnetic resonance (EPR) detection are three common methods for radical detection. Here, we briefly describe the popular radical trapping reaction, under the action of an oxidant, thiol **74** gives a thiyl radical, which further reacts with **73** under optimal conditions (Scheme 16a).[47] However, in Scheme 16b, the addition of famous trapping agent TEMPO (2,2,6,6-tetramethylpiperidine oxide) traps the generated thiyl radical and inhibits the reaction under the previous conditions. This control experiment is designed to provide a basis for the existence of thiyl radical in the proposed mechanism.

Radicals tend to accept or lose an electron to form stable species. Therefore, in order to trap radicals, a "stabilization first and detection later" strategy was established, adding a radical scavenger which can rapidly extract radicals and form stable species, while the main reaction is inhibited. In some cases, the trapped products can be detected and isolated for further confirmation.



Scheme 16: Radical trapping reaction.

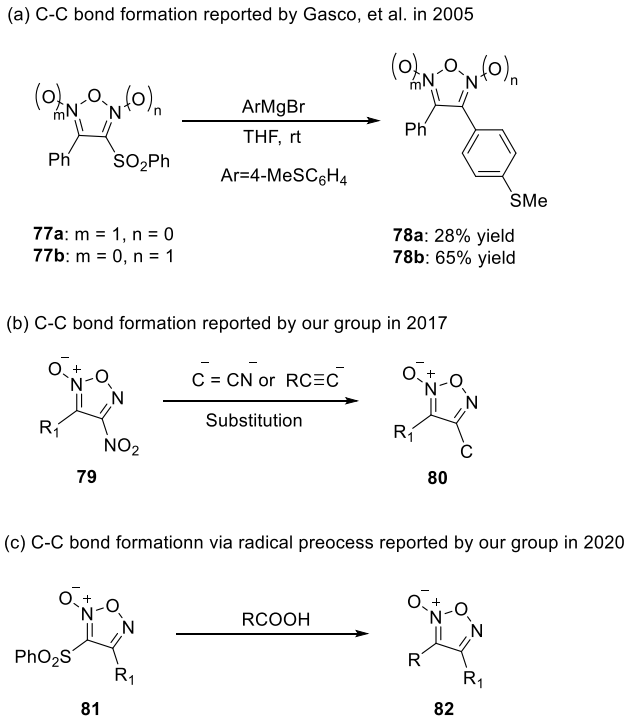
1.4 Summary of consideration

NO release is a special ability of furoxans under certain conditions that makes them become potential drug molecule candidates and attracts the attention of researchers. However, as mentioned before, the ring-opening disadvantages of furoxan under many conditions lead to the stagnation of its development.

Conventionally, various carbon-substituents of furoxan are established before the ring formation (e.g., dioxime, nitrile oxide). Therefore, this method requires the synthesis of carbon-substituted precursors in advance which makes the synthesis of furoxan derivatives inconvenient. In 2005, Gasco et al. first reported the method of direct C−C bond construction, which was also the first arylation of furoxan.[13a] In this publication, they used 3- and 4-(phenylsulfonyl)furoxans **77b** and **77a** to react with a aryl Grignard reagent respectively, and afforded an aromatic substituted furoxan **78b** and **78a** (Scheme 17a). However, the substrate scope of this method without further tested. In 2017, our group also developed a direct formation method of C−C bonds on furoxan ring (Scheme 17b),[48,49] 4-nitrofuroxans **79** reacted with alkynyl lithium and cyanating reagents to give the alkynyl furoxans and cyanide furoxans. In these reactions, the furoxan didn't open the ring due to the use of soft

nucleophiles.

In 2020, our group developed a radical reaction at the 3-position of furoxan, that is, the carbon radical which formed from the carboxylic acid, added to 3-sulfonylfuroxans **81** (Scheme 17c).[15] Based on previous reports in which a sulfonyl group was employed as a radical leaving group,[50–56] we used sulfonyl substituted furoxan as starting furoxan. To our delight, the radical reaction performed and the addition occurred at 3-position. At the same time, the special regioselectivity attract our attention, which is different from nucleophilic substitution.[17c,17d,37]



Scheme 17: The synthesis of carbon-substituted furoxan.

To account for the special regioselectivity, density functional theory (DFT) calculation was employed to calculate the radical process (Figure 5).[15] Furoxan **RT1** and simple radical **RT2** were used as starting species, the energy gap between addition intermediates **3-INT**, **4-INT** is about 15 kcal/mol, indicating that the reaction tended to occurr at 3-position. In spin density analysis, the delocalization of **3-TS1** is distributed in 2-position nitrogen and 1′-position

oxygen atoms. However, **4-TS1** is only at the 5-position nitrogen atom. Meanwhile, for the intermediate **3-INT**, the resonance form is a stable nitroxyl radical (Figure 5, **16**), which further explains that the radical addition occurs at 3-position.

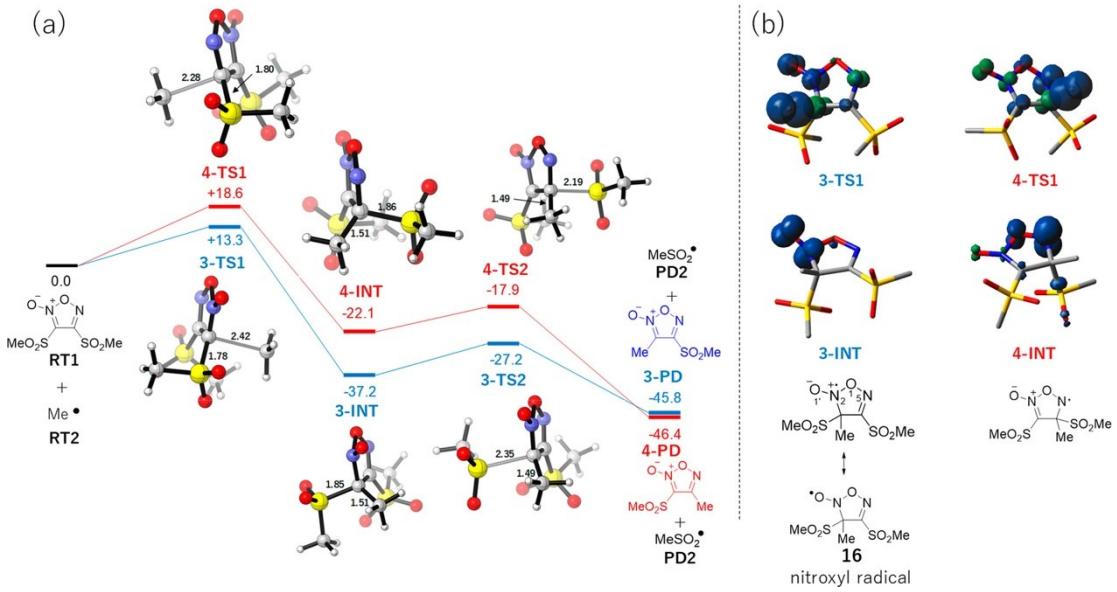


Figure 5: (a) DFT calculations of addition and elimination process of furoxan **RT1** and methyl radical **RT2**. (b) Spin density analysis.

This reaction tolerates various substituted carboxylic acids and affords suitable yield of 3-alkylfuroxans. It is a convenient method to introduce carbon substituents to furoxan under mild conditions.

Based on these backgrounds, radical reaction is a newly developed method with good regioselectivity, which insteads of nucleophilic substitution to form C−C bond on furoxan ring and avoids harsh conditions leading to the ring-opening. It is a more convenient strategy that is dedicated to build a library of furoxan derivatives and provides a broader scope for the screening of biologically active structures. However, only carboxylic acids have been developed as radical partner. Therefore, our research aim is to discover the radical donors and realize the diversity of furoxan.

II: Study toward radical reaction on furoxan

2.1 C−H furoxanization

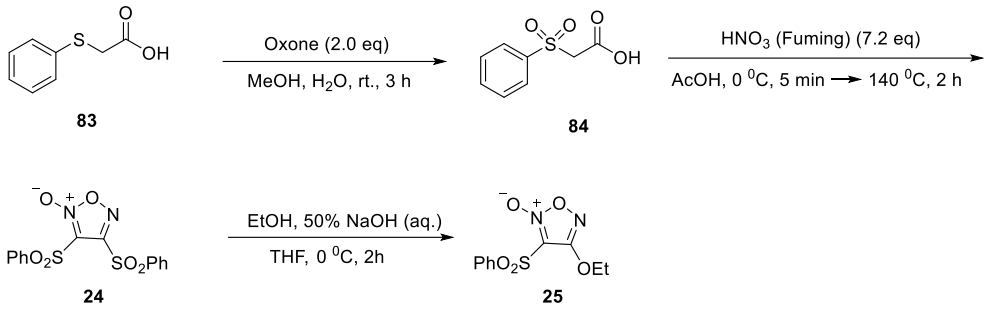
The C−H bonds are considered as inactive functional groups, but the advantages of high atom utilization and easy availability make them a reliable source for providing complex molecules. During recent decades, various C−H functionalization approaches have been developed.[57] Among them, one common method is transition-metal-catalyzed. In this method, the resulting carbon-metal species replaces the original C−H bond and is used as a reactive intermediate in the subsequent coupling reaction.[58] The formation of carbon radicals is another useful C−H bonds activation method. HAT also known as hydrogen atom abstraction, is a chemical reaction in which hydrogen radical is abstracted by a reactive radical species.[59] Here is the general equation (Scheme 18). There are many factors that affect the hydrogen atom abstraction efficiency, such as bond dissociation energy, polarity and geometric effects. It shows a mode for directly functionalization of unreactive C-H bonds.

Scheme 18: General equation for HAT.

2.1.1 Optimization of the radical reaction

First, we need to select an appropriate furoxan as the radical acceptor to react with carbon radical formed from the C−H bond to realize the "furoxanization" of the C−H bond. According to previous reports, a sulfonyl moiety installed at 3-position of furoxan performed as a leaving group in the radical reaction.[15] Therefore, in order to develop the radical reaction of furoxan, 3-sulfonyl substituted furoxan is required. Here, 4-ethoxy substituted furoxan **25** and 4-phenylsulfonyl substituted furoxan **24** were selected as starting furoxans. Their synthesis was according to previously reported methods (Scheme 19).[60,61] In these several steps, 2-(phenylsulfanyl)acetic acid **83** is firstly oxidized by Oxone and converted to

2-(phenylsulfonyl)acetic acid **84**, the fuming HNO_3 is then used to form (proposed) $PhSO_2CN^+O^-$ intermediate which dimerized immediately to 3,4-bis(phenylsulfonyl)furoxan **24**. To obtain another 4-ethoxy substituted furoxan **25**, a further step was employed. Using a simple nucleophilic substitution reaction, the ethoxy anion attacks the 4-position of **24**, where electron density is lower than 3-position because of the exo-ring oxygen atom.



Scheme 19: Synthesis of 3-phenylsulfonyl substituted furoxans.

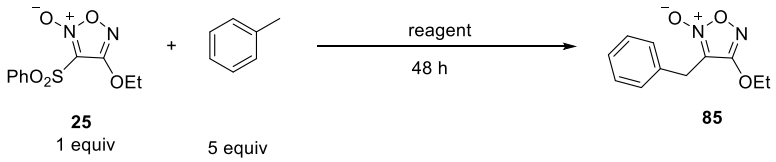
2.1.1.1 Using toluene as radical precursor

4-Ethoxy-3-(phenylsulfonyl)furoxan **25** was initially chosen as the starting furoxan, which is less hindrance than 3,4-bis(phenylsulfonyl)furoxan **24**. Due to the stability of benzyl radical, the C−H bond of benzyl group was selected as carbon radical source. Subsequently, the conditions of C−H furoxanization were optimized (Table 1). Under 70 ℃ oil bath, 1 equiv furoxan **25** and 5 equiv toluene were reacted in CH_3CN/H_2O (1/1) with 1.5 equiv potassium persulfate ($K_2S_2O_8$) as a radical initiator to obtain the desired product 3-Benzyl-4-ethoxyfuroxan **85**, and the yield was 70% (entry 1). When a catalytic amount of $K_2S_2O_8$ (0.2 equiv) was used, no desired product was produced (entry 2), indicating that no reaction cycle is involved in the reaction. When lowering the reaction temperature, the yield decreased significantly (entries 3 and 4). In this case, it is possible that temperature affected the rate and ability of the radical initiator to generate corresponding radicals. Other radical initiators including TBHP, DTBP, BPO and AIBN were tested but were ineffective for the reaction (entries 5−9). The solvent is one of the important factors affecting the reaction, and

the results revealed that CH_3CN/H_2O (1/1) system is the suitable solvent (entries 10−13).

Finally, in order to verify the participation of radicals, radical scavenger was used to trap them which formed during the reaction. Entry 14, a well-known radical scavenger TEMPO, was performed to inhibit the reaction and no product was obtained under the optimal conditions, which suggested that it is via a radical process.

Table 1: Screening the radical reaction (furoxan and toluene)



25
1 equiv

5 equiv

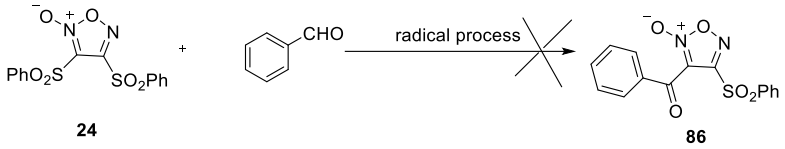
85

Entry	Solvent	Reagent (equiv)	Temp (℃)	Yield of **85** (%)[a]
1	CH_3CN/H_2O (1/1)	$K_2S_2O_8$ (1.5)	70	70 (69)[b]
2	CH_3CN/H_2O (1/1)	$K_2S_2O_8$ (0.2)	70	0
3	CH_3CN/H_2O (1/1)	$K_2S_2O_8$ (1.5)	50	63
4	CH_3CN/H_2O (1/1)	$K_2S_2O_8$ (1.5)	23	0
5	CH_3CN/H_2O (1/1)	TBHP (1.5)	70	0
6	CH_3CN/H_2O (1/1)	DTBP (1.5)	70	0
7	CH_3CN/H_2O (1/1)	BPO (1.5)	70	8
8	CH_3CN/H_2O (1/1)	AIBN (1.5)	70	5
9	CH_3CN/H_2O (1/1)	AIBN (0.2)	70	0
10	CH_3CN	$K_2S_2O_8$ (1.5)	70	0
11	H_2O	$K_2S_2O_8$ (1.5)	70	52
12	DMSO	$K_2S_2O_8$ (1.5)	70	6
13	$DMSO/H_2O$ (1/1)	$K_2S_2O_8$ (1.5)	70	7
14	CH_3CN/H_2O (1/1)	$K_2S_2O_8$ (1.5) TEMPO (3.0)	70	0

[a] Determined by ^1H NMR analysis using durene as an internal standard. [b] Isolated yield.

2.1.1.2 Using benzaldehyde as radical precursor

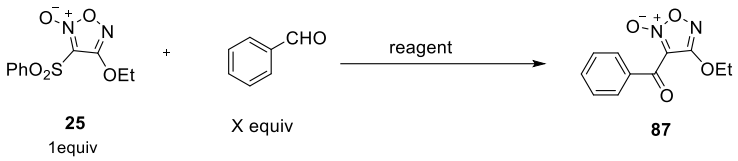
Next, following the success of toluene, other C−H bond sources attracted our attention. And benzaldehyde became the next research target. We investigated benzaldehyde as the carbon radical donor and reacted with furoxan **24** firstly (Scheme 20). However, no desired product **86** was obtained and both starting materials remained. The result may be due to the instability of the carbonyl radical, leading to other side reactions rather than radical substitution reaction. Meanwhile, it is possible that the steric hindrance of furoxan substituents affects the addition of carbonyl radical to furoxan.



Scheme 20: Radical reaction of benzaldehyde and 3,4-bis(phenylsulfonyl)furoxan **24**.

In order to achieve the reaction, we first considered the steric hindrance at 4-position of furoxan. Subsequently, continued to optimize the radical conditions of benzaldehyde and 4-ethoxy substituted furoxan **25** (Table 2). To our delight, 3 equiv benzaldehyde reacted with 1 equiv furoxan **25** in the presence of the same oxidant ($K_2S_2O_8$) in CH_3CN/H_2O system under 80 ℃ for 17 h to afford desired furoxan **87** in 57% yield (entry 1). This result proved that our hypothesis is correct and that the substituent at 4-position plays an important role in radical addition process of 3-position. The high temperature radical initiator DTBP caused side reactions and affected the yield (entry 2). Next, various radical initiators including AIBN, TBHP, BPO, $(NH_4)_2S_2O_8$, TBPB and CH_3CO_3H were examined but all failed to improve the yield (entries 3−8). In this reaction, H_2O is the necessary solvent to dissolve $K_2S_2O_8$, therefore DMSO was attempted to instead of CH_3CN (entry 9). Unfortunately, this solvent system was ineffective for the reaction.

Table 2: Screening the radical reaction (furoxan and benzaldehyde)



25 1equiv + X equiv → **87**

Entry	X (equiv)	Reagent (equiv)	Solvent	Temp (℃)	Time (h)	Yield of **87** (%)[a]
1	3	$K_2S_2O_8$ (1.5)	CH_3CN/H_2O (1/1)	80	17	57 (55)[b]
2	5	DTBP (2.5)	PhCl	115	20	40
3	2	AIBN (1.7)	CH_3CN	80	24	0
4	4	TBHP (4)	CH_3CN	90	17	42[b]
5	4	BPO (4)	CH_3CN	80	17	38
6	4	$(NH_4)_2S_2O_8$ (1.5)	CH_3CN/H_2O (1/1)	70	17	29
7	4	TBPB (4)	CH_3CN	80	20	35[b]
8	4	CH_3CO_3H (4)	CH_3CN	100	32	5
9	3	$K_2S_2O_8$ (1.5)	$DMSO/H_2O$ (1/1)	80	17	11

[a] Determined by ^1H NMR analysis using durene as an internal standard. [b] Isolated yield.

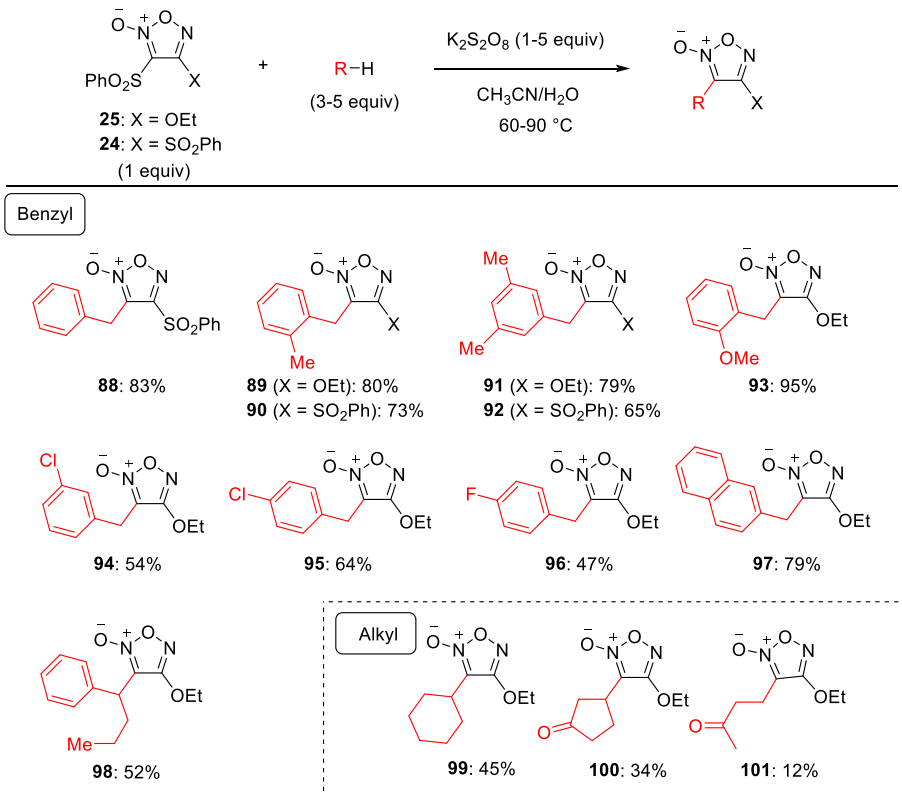
2.1.2 Substrate scope for C−H bond furoxanization

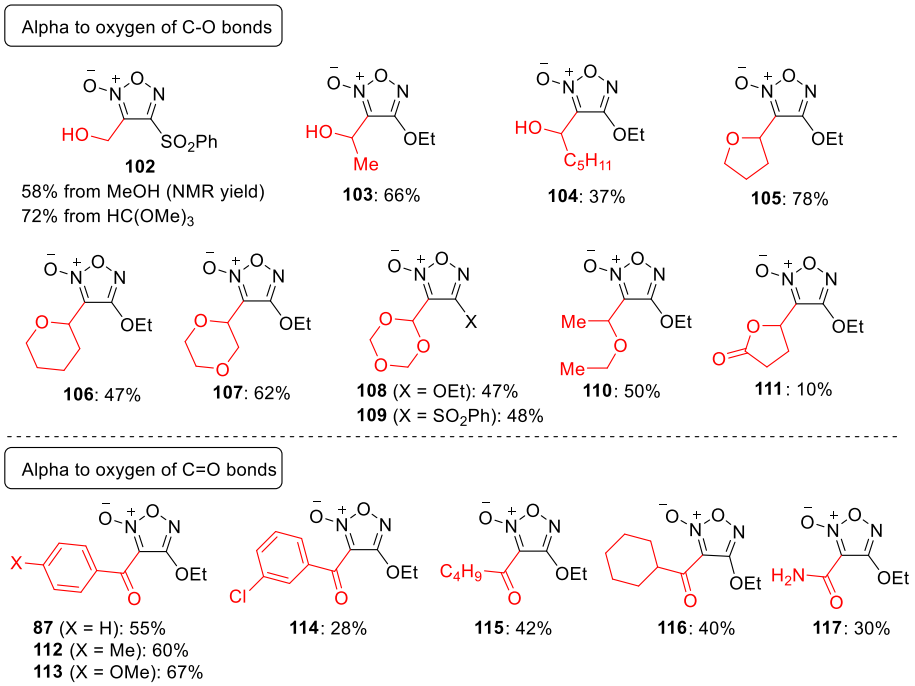
With the optimized conditions in hand, we examined the substrate scope of toluene and aldehyde, other C−H bond sources were also participated (Table 3). Meanwhile, in addition to furoxan **25**, disulfonyl furoxan **24** was also involved as a radical acceptor. As well as furoxan **25**, most carbon radicals tolerated the disulfonyl furoxan **24** and obtained desired furoxan successfully.

The results are shown below (Table 3), methylbenzene derivatives substituted with electron

donating groups were afforded in good yields (**89**–**93**) due to the stability of carbon-centered radicals. Correspondingly, these derivatives substituted with electron withdrawing groups were obtained in slightly lower yields (**94**–**96**). Long alkyl chain substituted derivative also performed the reaction at the benzylic position (**98**). Other C–H bonds with nonbenzylic group, including cyclohexane, cyclopentanone and butan-2-one were also examined and all introduced a furoxan ring successfully (**99**–**101**). Notably, the carbon radicals of ketones are generated at *β*-position instead of *α*-position (**100** and **101**). Next, alcohols and ethers were also involved in the substrate scope (**102**–**111**), the C-H bond which is α position of the oxygen atom underwent furoxanization under the optimized conditions. Subsequently, aromatic and aliphatic aldehydes were employed to obtain the corresponding carbonylated furoxans (**87**, **112**–**116**), the results were same as methylbenzene derivatives, in which electron-donating groups benefitted the yield. Formamide was also attempted to react with furoxan and gave the desired furoxan **117** in moderate yield.

Table 3: Substrate scope for C-H bond furoxanization





In addition, a gram-scale reaction was performed under optimized conditions to obtain the furoxan **93** in 92% yield. This result indicates that this method can be used to synthesize biologically active furoxans.

In the process of expanding the scope of substrates, some substrates provided no or lower yield of desired products are summarized in Figure 6. When the C−H bond was combined with some electron deficient groups (Figure 6a), most of the starting material remained. Perhaps, due to the radical polarity mismatch, they are difficult to realize HAT process. This is a possible reason for the reaction selectivity of cyclopentanone and butan-2-one, the hydrogen attached to the *β*-position of carbonyl groups is activated instead of the *α*-position (**100** and **101** in Table 2). Several heteroaromatics were also tested (Figure 6b), although they are electron rich substrates, the desired products were not obtained and they were consumed in large quantities. It is probably that they decomposed or the formed intermediates decomposed in the presence of the oxidizing agent which is used in this reaction. Secondary alcohol, which form the corresponding radical but failed to add to furoxan attributed to its hindrance making it difficult to access the starting furoxan (Figure 6c).

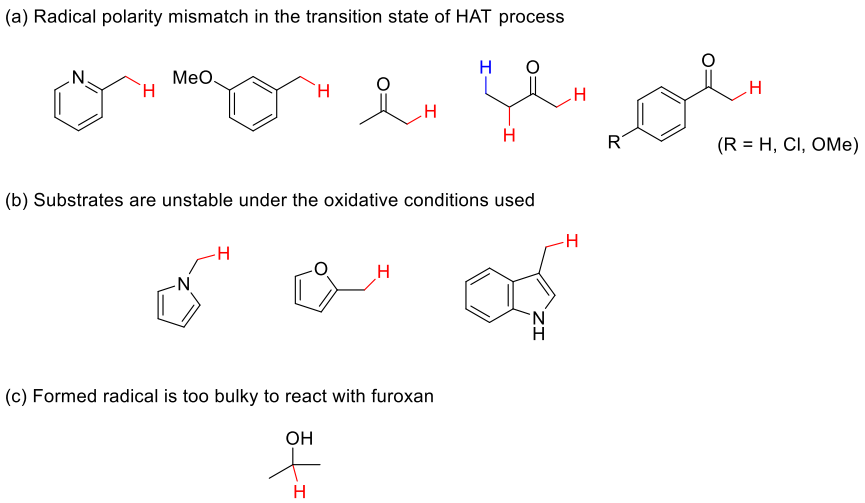


Figure 6: Substrates which provide no or lower yield of target product.

2.1.3 The proposed mechanism of C−H furoxanization

Next, according to the previous report,[15] the proposed mechanism of C−H bond furoxanization is described (Figure 7). Firstly, peroxide $K_2S_2O_8$ is used as radical initiator to form sulfate radical anions **65** under heating condition.[62] The hydrogen atom of substrate **118** is extracted in the presence of sulfate radical anion **65** and affords carbon radical **119**[63] which then reacts with the 3-sulfonylfuroxan **120** to form adduct intermediate **121**. The addition occurs at 3-position instead of 4-position due to the stability of this intermediate which shows delocalize over N and O atoms. Meanwhile, **121** has a resonance form **122** which is same as TEMPO and is considered as a stable radical (Figure 5). Finally, arylsulfonyl radical is used as leaving group to obtain the desired product **123**. During the optimization process, catalytic amount of $K_2S_2O_8$ is employed and desired furoxan is not obtained, suggesting that the leaving group arylsulfonyl radical can not undergo the HAT process directly from another corresponding C−H substrate molecule (**118)** (Table 1, entry 2).

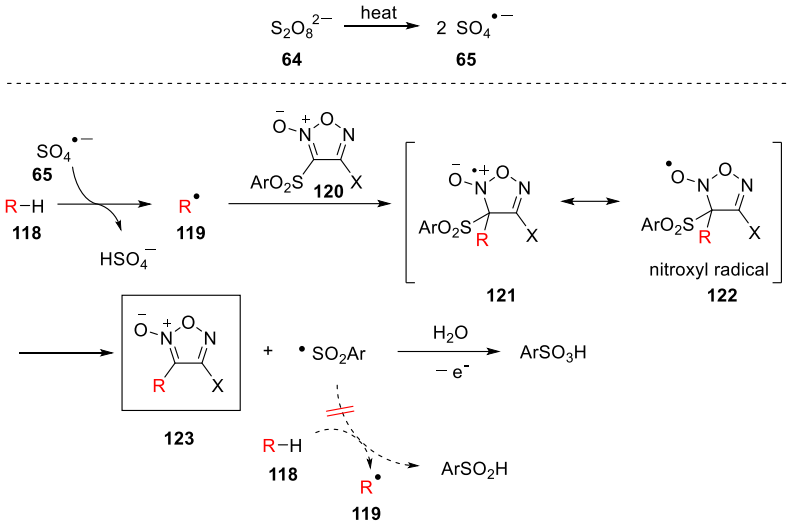
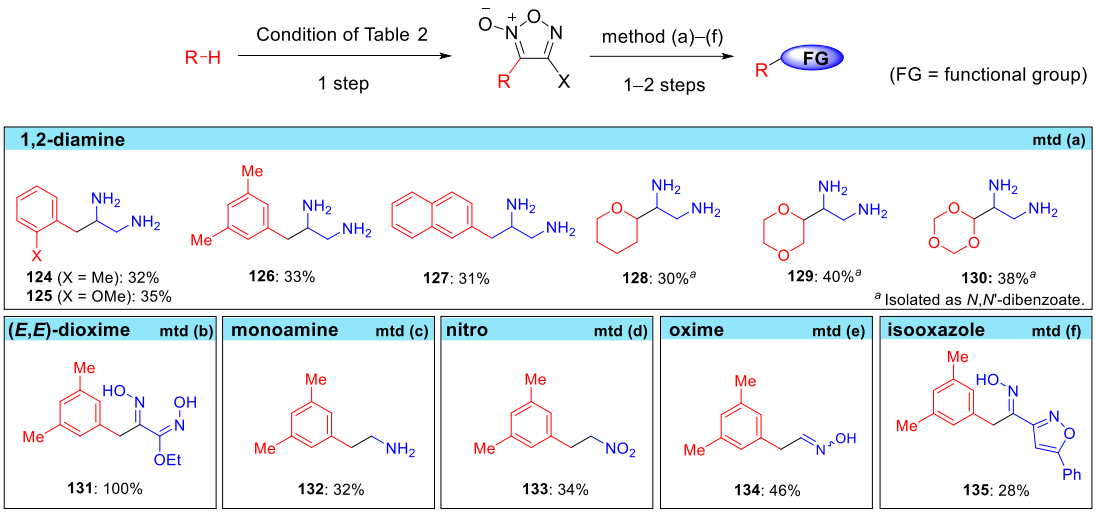


Figure 7: Proposed mechanism of C−H furoxanization.

2.1.4 Transformation of furoxan product

Under the optimized conditions, we introduced a furoxan ring into the C−H bond successfully and then worked on the functionalization of furoxan product.

As introduced before, furoxans have weekly aromatic and electron-deficient properties, and are prone to ring opening under some strong nucleophiles and reducing agents.2 Based on this property, we next converted the resulting furoxans into other functional groups, which is the final step of “build-and-scrap” strategy (Figure 8). Here, we employed different conditions to obtain structures containing diamine, dioxime, amine, nitro, oxime or isoxazole directly from resulting furoxans. Notably, it is difficult to obtain these nitrogen containing functional groups from C−H bond in several steps. In a word, this “build-and-scrap” strategy achieves both furoxanization and functionalization of the C−H bonds.



Method (mtd): (a) Pd/C (2–5 mol%), H_2 (1 atm), MeOH, 23 °C; $LiAlH_4$ (5 equiv), THF, 0 °C; (b) Pd/C (2 mol%), H_2 (1 atm), MeOH, 23 °C; (c) $LiAlH_4$ (5 equiv), THF, 23 °C; (d) Bu_3SnH (2 equiv), benzene, 40 °C; (e) Bu_3SnH (5 equiv), benzene, 40 °C; (f) phenylacetylene (3 equiv), DMF, 130 °C.

Figure 8: Transformation of furoxan rings into nitrogen containing functional groups.

2.1.4.1 Furoxan transform to dioxime

The most common synthesis method of oximes is through the reaction of aldehydes or ketones with hydroxylamine and they are participated in many important reactions. Here, another method was used to obtain dioxime **131** by hydrogenation of the starting furoxan **91**.[64] The proposed mechanism is described below (Figure 9). The reaction was carried out under hydrogen atmosphere, hydrogen was adsorbed on palladium and then furoxan was reduced to dioxime **131** in 100% yield without any purification.

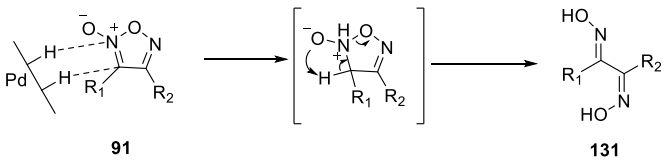


Figure 9: Proposed mechanism of dioxime.

2.1.4.2 Furoxan transform to amine

The conversion of furoxan to amine is an important ring-opening application. There are many methods to synthesize monoamines, but few methods to construct two amine groups at the same time. An excess amount of lithium aluminum hydride ($LiAlH_4$) reduced the starting furoxan **92** to monoamine **132**.[65] The proposed mechanism is described below (Figure 10). The hydride ion from $LiAlH_4$ attacks 3-position of furoxan resulting in ring cleavage, forming the ion of nitro compound **136** and nitrile. As the reaction proceeded, **136** continued to be reduced to the primary amine **132** in 32% yield. Regarding the process of diamines (**124**−**130**), the corresponding dioximes were formed firstly and then reduced by $LiAlH_4$.

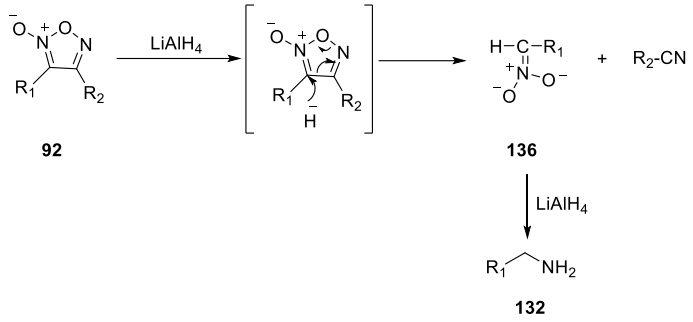


Figure 10: Proposed mechanism of monoamine.

To achieve this transformation of diamines, we encountered some problems during the reduction process. At the beginning, the reducing agent $LiAlH_4$ which was stored in our reagent cabinet was employed. Although H_2O/15% NaOH/H_2O (1/1/3) was used sequentially to consume excess $LiAlH_4$ and precipitate aluminum salts which were generated after quench, the desired diamine was not detected. This step was used to reduce the adsorption of diamines due to their large polarity. The reaction was repeated several times with the same results. Inadvertently, new $LiAlH_4$ was ordered and a possible diamine spot was found on thin-layer chromatography (TLC). It is possible that reducing ability of the old $LiAlH_4$ is weakened, resulting in the failure of the reaction. It was quenched by H_2O/15% NaOH/H_2O (1/1/3) and washed with room temperature tetrahydrofuran (THF). However, the possible diamine spot disappeared after the work-up. This is presumable that diamine absorbed on aluminum due to the large polarity. In order to solve this problem, the diamine appeared in the filtrate by washing with hot THF. In the final step, the diamine was separated by preparative thin-layer

chromatography (PTLC) on silica gel, but the diamine was absorbed again by silica gel. The mixture (diamine and silica gel) was washed by methanol and further concentrated, a small amount of dichloromethane (DCM) was added to the residue, and the diamine and insoluble silica gel were separated using a filter membrane. Ether derivatives do not contain fluorescent groups and are difficult to purify by PTLC. To address this inconvenience, we attempted to protect the amine group by a protecting group before purification (**128**−**130**).

2.1.4.3 Furoxan transform to nitro compound and oxime

Nitro compound **133** was formed by reduction of starting furoxan **92** with 2 equiv of tributyltin hydride. The proposed mechanism is described below (Figure 11a). The electrons of sulfonyl oxygen enter tin orbit to form O−Sn bond **137**, the hydrogen ion attacks and electrons transfer lead to the ring-opening intermediate **139**, the oxygen of nitro attacks tributyltin hydride to form intermediate **141**, and then a nitrile molecule is released to obtain nitro compound **133**. When the amount of tributyltin hydride was increased to 5 equiv, oxime **134** was obtained. This makes us suspect that the oxime is formed from the nitroalkane. The possible process is described in Figure 11b. The nitroalkane **133** continued to react with another molecule tributyltin hydride to afford oxime **134**.

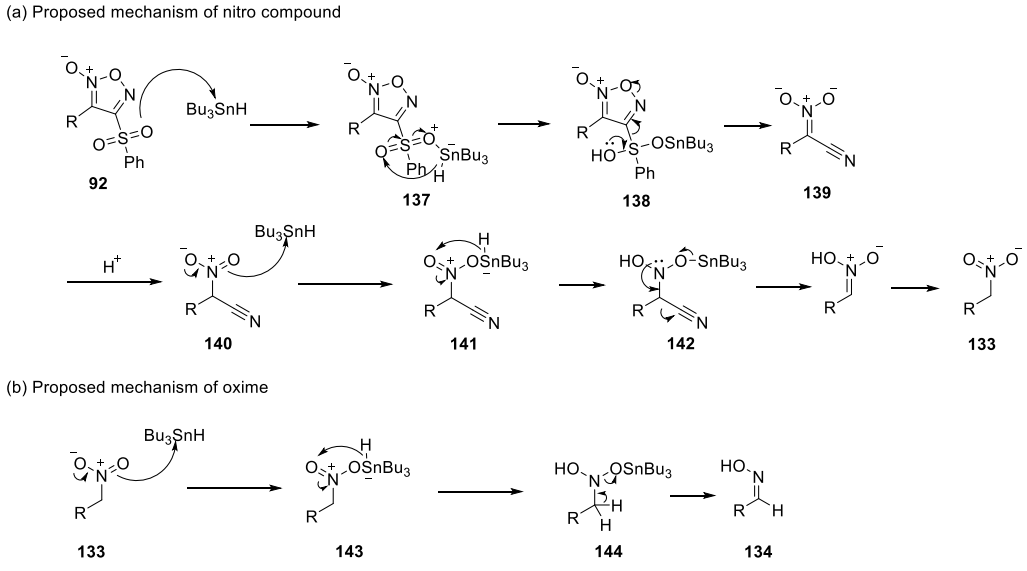


Figure 11: Proposed mechanism of nitro compound (a) and oxime (b).

Regarding the proposed mechanism, we initially suspected that the reaction was via a radical process, and tried to prove it with some control reactions. However, the expected radical product was not detected in addition to the desired functionalized product under the optimized conditions, proving that the reaction isn't via a radical process.

2.1.4.4 Furoxan transform to isoxazole

Isoxazole **135** was formed from starting furoxan **92** with 3 equiv phenylacetylene under heating and an oxime group was formed by ring-opening.[66] The proposed mechanism is described below (Figure 12). As previously mentioned, furoxan occurs isomerization under heating condition. In this reaction, furoxan **92** is ring-opened at 130 ℃ to give isomeric furoxan **92'**, which reacts with phenylacetylene to undergo 1,3-dipolar cycloaddition. The benzenesulfonyl group of bicyclic intermediate **145** is abstracted in the presence of DMF and ring-opened to give the isoxazole **135** with an oxime group.

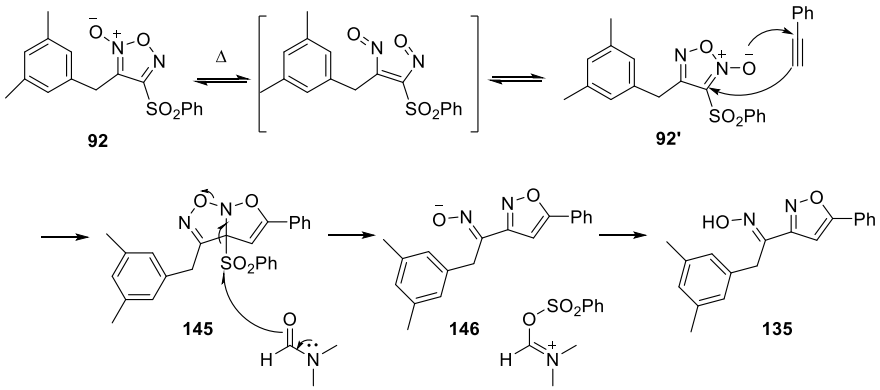


Figure 12: Proposed mechanism of isoxazole.

2.1.5 Conclusion

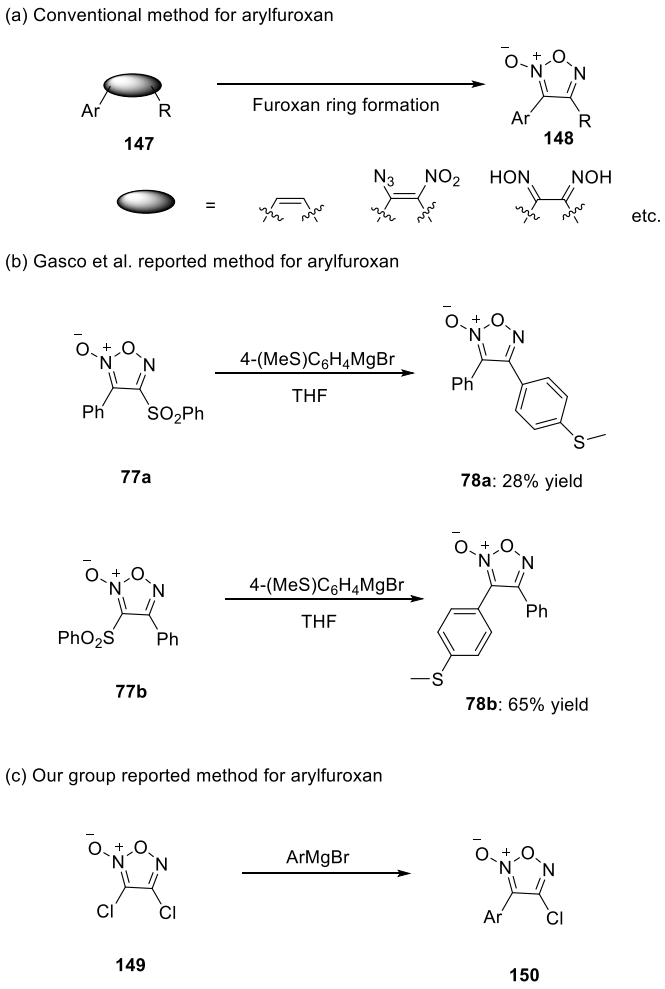
The research on furoxan has never stopped since its first synthesis. Our research is to develop a simple and efficient synthesis methodology for furoxan derivatives. As we know, carbon-substituted furoxans are difficult to synthesize directly from furoxans due to their special properties. Therefore, mild conditions are important to realize this conversion, and then radical-mediated C−C bond construction of furoxan exhibits a promising research. In this section, a simple C−H bond furoxanization method is achieved via a radical process. Afterwards, carbon-substituted furoxans were transferred to different nitrogen-containing functional groups, indicating that furoxan ring can be used as the source of nitrogen. In general, this method both achieves the carbon-substituted furoxans, and realizes functionalization of simple C−H bond into different nitrogen-containing functional groups through few synthesis steps. Meanwhile, this convenient protocol simplifies the synthesis of furoxans and promotes the study of active furoxans.

2.2 Arylation of furoxan

Furoxan, the special biological activities attract our attention and our group is also interested in expanding the furoxan-based chemical library. After the successful realization of C−H bond furoxanization, the value of radical reaction in the development of furoxan derivatives was further affirmed. Subsequently, other radical donors were required to achieve the diversity of furoxan, and direct arylation of furoxan attracted our attention.

As far as we know, they are two strategies for obtaining aryl-substituted furoxan. The most conventional method is to install the aryl group before the furoxan ring formation (Scheme 21a).[67] However, this method requires tedious synthesis of precursors with various aryl substituents, and for some unstable aryl derivatives, the preparation is difficult. Another strategy is to introduce the aryl group after the furoxan ring formation, which was first achieved by Gasco in 2005 (Scheme 21b).[13a] In his method, aryl substituted Grignard reagent was used to attack the the 3- or 4-position of furoxan (**77b**, **77a**) where a good leaving group

(sulfonyl group) was substituted. When nucleophilic substitution was conducted at the 4-position, the 28% yield indicated a low reaction efficiency (**78a**). However, 3-sulfonylfuroxan (**77b**) showed a different yield under the same conditions owing to the existence of exocyclic oxygen atom. It is possible that the Grignard reagent underwent a 1,3-addition to the $C{=}N^{+}{-}O^{-}$ part of furoxan and release the phenylsulfonyl (SO_2Ph) group. Nevertheless, the substrate scope had not been further developed. Recently in our group, the same procedure was used for dichlorofuroxan **149** to achieve aryl substituted furoxan (Scheme 21c).[68]



Scheme 21: Previous furoxan arylation methods.

Although direct arylation of furoxan has been developed, it is not a facile way due to the need to synthesize aryl substituted Grignard reagents. Therefore, a direct and convenient arylation method of furoxan remains an attractive research, and radical reaction is the method we

consider suitable. At the same time, it is also beneficial to develop the biologically active arylfuroxan derivatives.

2.2.1 Optimization of arylation conditions

Before optimization, which aryl radical precursor is suitable as model structure. We found that arylboronic acids are not only famous cross-coupling reagents in metal catalysis, but also commonly used as aryl radical precursors. Most arylboronic acids are known to be stable under air and water, and various substituted arylboronic acids are commercially available, helping to establish a broad substrate scope. Many literatures report that arylboronic acids are precursors of aryl radicals, which can be obtained under some oxidants, such as potassium permanganate ($KMnO_4$), manganese(III) acetate ($Mn(OAc)_3$), manganese(III) acetylacetonate ($Mn(acac)_3$), potassium persulfate ($K_2S_2O_8$) etc.[69] Guide by these studies, phenylboronic acid was initially used as the donor of phenyl radical, and we proceeded to construct C−C bonds on furoxans through a radical process.

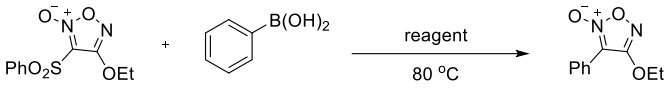
2.2.1.1 Using arylboronic acid as radical precursor

Our studies began by screening the conditions between furoxan **25** and phenylboronic acid (Table 4). Various oxidants including $KMnO_4$, $Mn(OAc)_3$, $Mn(OAc)_2$, $K_2S_2O_8$, $Mn(acac)_3$, *etc* were investigated (entries 1−9). When using $Mn(OAc)_3$ and $K_2S_2O_8$, the yields of radical substitution product **151** were 18% and 15% respectively (entries 2 and 3), slightly higher than other oxidants. After that, a further methodology was employed based on these two oxidants. Firstly, catalytic amount of Mn(II), Mn(III), Ag(I) and Pd(II) participated in oxidant $K_2S_2O_8$ were examined, and the yield of desired product **151** had no significant improvement (entries 10−13). Subsequently, different solvents such as DMF, DMSO, toluene, DCE, and

DCM were screened in the presence of $Mn(OAc)_3$, and MeCN was found to be a suitable solvent (entries 16−21). The reaction concentration and temperature were tested but had no beneficial effect (entries 22 and 25). Furthermore, increasing the amount of arylboronic acid and oxidant to 7 equiv and 10 equiv increased the yield to 36% and 40%, respectively (entries 23 and 24). The conditions of large quantities improved the yield slightly and were not considered as advantageous conditions.

The optimization results didn't meet our expectation, although large amount of oxidant and phenylboronic acid increased the yield to 40%, there was no advantage in substrate scope and large scale. During the screening process, large amount of starting furoxan remaining and phenylboronic acid consumption were found, and it was clear that most aryl radical didn't react with furoxan. It revealed that phenylboronic acid may not be a suitable aryl radical precursor for furoxan and forced us to consider other aryl radical donors.

Table 4: Optimization of arylation conditions (phenylboronic acid)



25
1equiv

X equiv

151

Entry	X (equiv)	Reagent (equiv)	Solvent	Time (h)	Yield of **151** (%)[a]
1	2	$KMnO_4$ (2)	MeCN	13	8[b]
2	2	$Mn(OAc)_3$ (2)	MeCN	15	18[b]
3	2	$K_2S_2O_8$ (2)	MeCN/H_2O (1/1)	16	15[b]
4	2	$Mn(acac)_3$ (2)	MeCN	18	10[b]
5	2	$Mn(OAc)_2$ (2)	MeCN	18	0
6	2	$Co(acac)_3$ (3)	MeCN	16	0
7	2	DTBP (3)	MeCN	16	trace
8	2	MnO_2 (3)	MeCN	60	7

9	2	$(NH_4)_2S_2O_8$ (2)	MeCN/H_2O (1/1)	15	trace
10	2	$K_2S_2O_8$ (2) $Mn(OAc)_3$ (0.2)	MeCN/H_2O (1/1)	18	21[b]
11	2	$K_2S_2O_8$ (2) $AgNO_3$ (0.2)	MeCN/H_2O (1/1)	18	14[b]
12	2	$K_2S_2O_8$ (2) $Mn(OAc)_2$ (0.2)	MeCN/H_2O (1/1)	18	19[b]
13	2	$K_2S_2O_8$ (2) $Pd(OAc)_2$(0.2)	MeCN/H_2O (1/1)	20	0
14	2	$K_2S_2O_8$ (2)	H_2O	18	14
15	14	$K_2S_2O_8$ (16)	MeCN/H_2O (1/1)	18	31
16	2	$Mn(OAc)_3$ (2)	toluene	18	trace
17	2	$Mn(OAc)_3$ (2)	DMF	18	0
18	2	$Mn(OAc)_3$ (2)	DMSO	18	16
19	2	$Mn(OAc)_3$ (2)	MeCN/H_2O (1/1)	18	trace
20	2	$Mn(OAc)_3$ (2)	DCE	18	16
21	2	$Mn(OAc)_3$ (2)	DCM	18	11[b]
22[c]	2	$Mn(OAc)_3$ (2)	MeCN	18	31
23	7	$Mn(OAc)_3$ (7)	MeCN	18	44(36)[b]
24	10	$Mn(OAc)_3$ (12)	MeCN	18	40[b]
25[d]	2	$Mn(OAc)_3$ (2)	MeCN	4	28

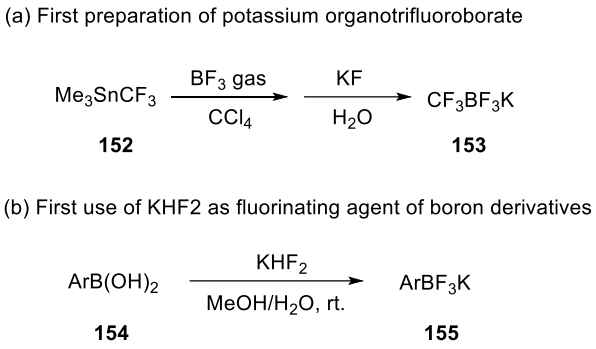
[a]Determined by ^1H NMR analysis using durene as an internal standard. [b]Isolated yield. [c]The concentration was 0.2 M. [d]The temperature was 100 ℃.

2.2.1.2 Using potassium aryltrifluoroborate as radical precursor

(Before this part, other aryl radical donors were investigated at the same time and the results are shown in **2.2.2**) Organoboranes have become popular reagents to form C−C bond undergoing transition-metal-catalysis after the discovery of Suzuki-Miyaura reaction.[70]

Potassium organotrifluoroborate is one of the organoboranes family members and is commonly used in cross-coupling reaction.[71] In 1960s, Chambers et al. first reported the synthesis of potassium organotrifluoroborate **153** from trifluoromethyltrimethyl stannane **152** with boron trifluoride gas and potassium fluoride (Scheme 22a).[72] These compounds were developed to replace some unstable organoboranes and are more stable than corresponding boronic acids since there are no empty p-orbital. As is the case with arylboronic acids, aryltrifluoroborates can also serve as precursors of radical species.[73] Based on these studies, it was decided to use aryltrifluoroborates as aryl radical donors.

Since most organotrifluoroborates are commercially unavailable, a simple synthetic method of them should be selected before the optimization. To date, the most commonly used synthesis method of potassium organotrifluoroborates was reported by Vedejs et al. in 1995.[74] This efficient method is shown in Scheme 22b, in which arylboronic acid **154** is directly converted to potassium aryltrifluoroborate **155** using potassium hydrogen difluoride (KHF_2) as the fluorination reagent. The improvement of the preparation method promotes the development of organotrifluoroborates in organic reactions.

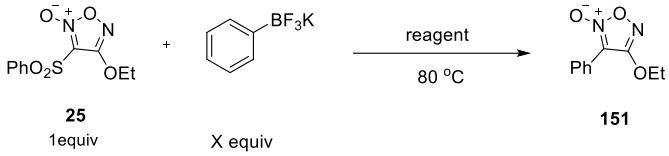


Scheme 22: The synthesis of potassium organotrifluoroborates.

We next investigated the arylation conditions between furoxan **25** and potassium phenyltrifluoroborate (Table 5). Referring to the results in Table 4, we mainly placed hope on $Mn(OAc)_3$ and $K_2S_2O_8$, although other oxidants were also involved in the screening (entries 1−5). When $K_2S_2O_8$ was used as the oxidant, the desired furoxan product **151** was gave in 46%

yield, which surprised us. A catalytic amount of $AgNO_3$ and $Mn(OAc)_3$ were used, but the yield was not improved (entries 6 and 7). Subsequently, different solvents were examined and the results revealed that MeCN/H_2O was the best solvent (entries 11−15). The ratio of MeCN and H_2O was further adjusted, and indicating that H_2O is an important solvent for dissolving $K_2S_2O_8$ in the reaction (entries 8−10). By increasing the amount of $PhBF_3K$ and $K_2S_2O_8$, the isolated yield was slightly increased to 44% (entries 16−18). At the same time, prolonging the reaction time also failed to improve it (entry 21). Finally, increasing the concentration and temperature had no improvement on the yield (entries 19 and 20). We observed that the starting furoxan **25** was remained in these cases and indicated that the consumption of $PhBF_3K$ and $K_2S_2O_8$. Considering the reaction efficiency and economy, the optimized reaction conditions included the following: furoxan **25** (1 equiv) with potassium phenyltrifluoroborate (3 equiv) in MeCN/H_2O (1/1) under 3 equive $K_2S_2O_8$ at 80 ℃ (entry 2).

Table 5: Optimization of arylation conditions (potassium phenyltrifluoroborate)



Entry	X (equiv)	Reagent (equiv)	Solvent	Time (h)	Yield of **151** (%)[a]
1	3	$Mn(OAc)_3$ (3)	MeCN	9	25
2	3	$K_2S_2O_8$ (3)	MeCN/H_2O (1/1)	4	46(38)[b]
3	3	Selectfluor (2) $AgNO_3$ (0.2)	MeCN/H_2O (1/1)	48	23
4	3	DTBP (3)	MeCN	16	trace
5	3	$(NH_4)_2S_2O_8$ (3)	DMSO	18	trace
6	3	$K_2S_2O_8$ (3) $AgNO_3$ (0.2)	MeCN/H_2O (1/1)	4	45

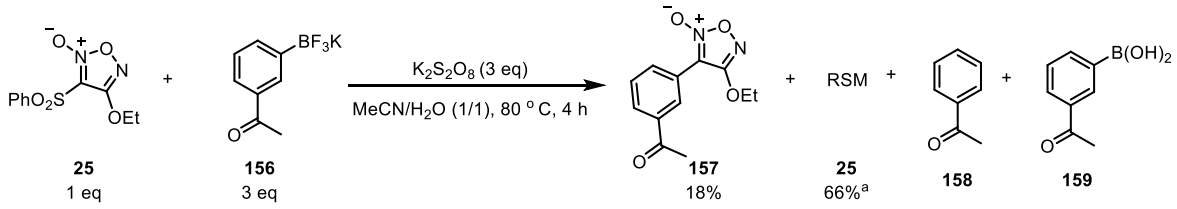
7	3	$K_2S_2O_8$ (3) $Mn(OAc)_3$ (0.2)	MeCN/H_2O (1/1)	4	42
8	3	$K_2S_2O_8$ (3)	MeCN/H_2O (2/1)	4	35
9	3	$K_2S_2O_8$ (3)	MeCN/H_2O (1/2)	4	44
10	3	$K_2S_2O_8$ (3)	MeCN/H_2O (1/5)	4	22
11	3	$K_2S_2O_8$ (3)	Acetone/H_2O (1/1)	4	22
12	3	$K_2S_2O_8$ (3)	NMP	4	0
13	3	$K_2S_2O_8$ (3)	DMF	4	0
14	3	$K_2S_2O_8$ (3)	DMSO	4	trace
15	3	$K_2S_2O_8$ (3)	MeCN	4	0
16	5	$K_2S_2O_8$ (5)	MeCN/H_2O (1/1)	4	51(44)[b]
17	3	$K_2S_2O_8$ (5)	MeCN/H_2O (1/1)	4	38
18	5	$K_2S_2O_8$ (3)	MeCN/H_2O (1/1)	4	45
19[c]	3	$K_2S_2O_8$ (3)	MeCN/H_2O (1/1)	4	40
20[d]	3	$K_2S_2O_8$ (3)	MeCN/H_2O (1/1)	4	42
21	3	$K_2S_2O_8$ (3)	MeCN/H_2O (1/1)	21	45

[a]Determined by ^{1}H NMR analysis using durene as an internal standard. [b]Isolated yield. [c]The temperature was 100 ℃. [d]The concentration was 0.2 M.

2.2.2 Several strategies for optimizing the reaction

This part is mainly about the strategies proposed to improve the yield. We tried our best efforts to promote the yield of the arylation reaction. Before we start, we illustrate the process with a reaction as an example (Scheme 23). In this arylation reaction, furoxan **25** was reacted with 4-acetylphenyltrifluoroborate **156** under the optimized conditions for 4 h. Most of the starting furoxan **25** was still remained except for the desired product **156** which was obtained in 18% yield. Meanwhile, by-products acetylphenyl **158** and acetylpheneylboronic acid **159** were detected, and trifluoroborate **156** was completely consumed. Therefore, reducing the

consumption of trifluoroborate becomes one of our solutions.



[a]Determined by ^1H NMR analysis using durene as an internal standard.

Scheme 23: An example reaction to illustrate the process.

We suspected that $PhBF_3K$ would convert to $PhB(OH)_2$ in the presence of H_2O and demonstrated this using NMR. In Figure 13, NMR spectrums show the different shift of $PhB(OH)_2$ and $PhBF_3K$ (Figure 13a, b). Afterwards, the water solution of $PhBF_3K$ was determined by NMR spectroscopy (Figure 13c), and the active hydrogen of $PhB(OH)_2$ was clearly observed at 7.9 ppm. We then speculated that $PhBF_3K$ undergoes hydrolysis in water. In 2012, Lennox et al. reported that potassium organotrifluoroborate (RBF_3K) hydrolyze to boronic acid in the presence of H_2O.[75]

Based on these discoveries, several strategies were set out to achieve further optimization. They are briefly described below: (a) other aryl radical precursors were performed to improve the utilization of aryl radical; (b) Phase transfer catalyst (PTC) was added to improve the heterogeneous reaction; (c) other oxidants that are soluble in organic solvents were investigated, avoiding the use of H_2O.

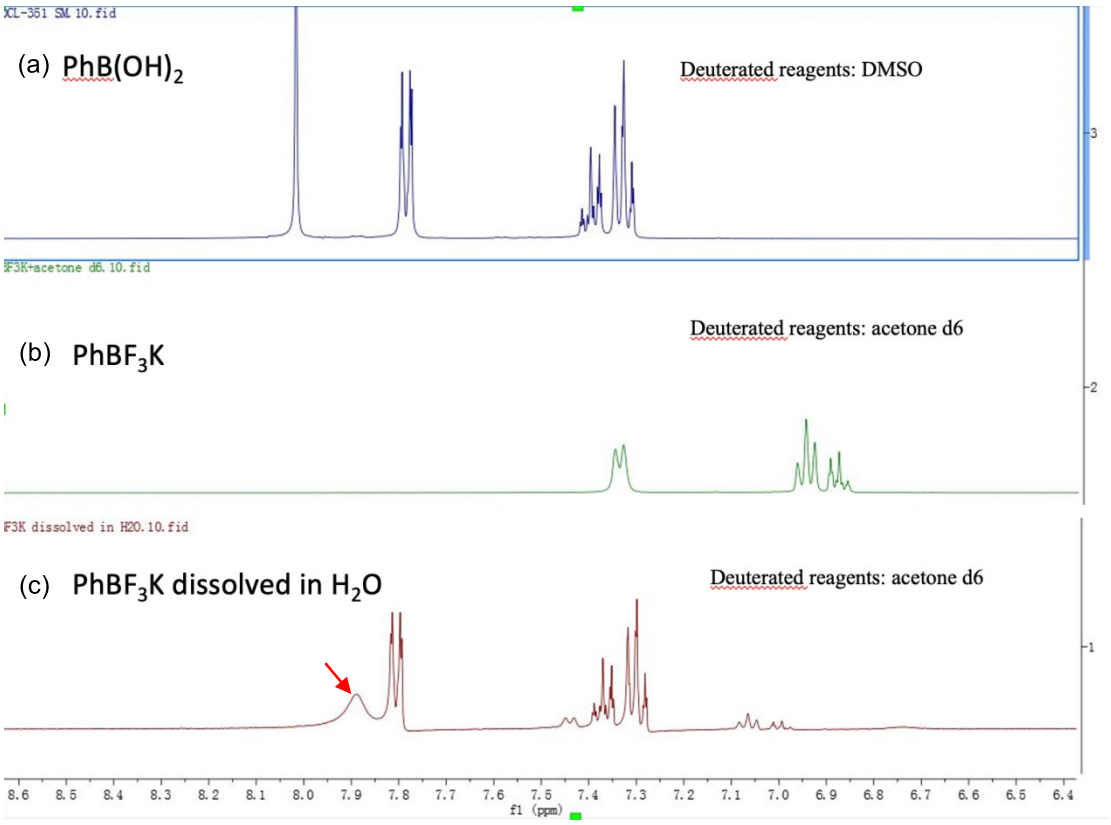
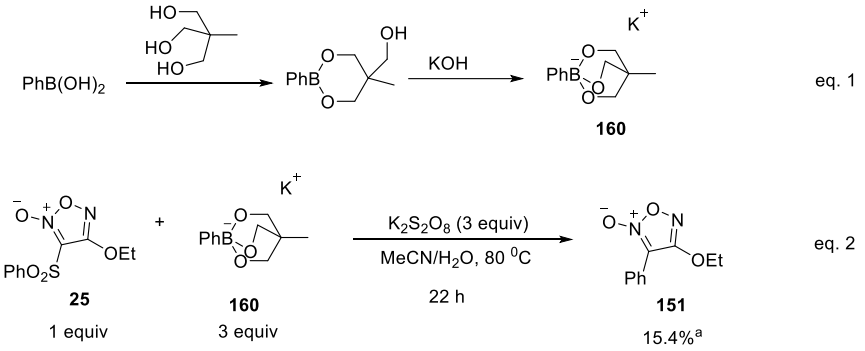


Figure 13: NMR spectrums explain the hydrolysis of $PhBF_3K$ in water.

2.2.2.1 Using other aryl radical precursors

Comparing the results between $PhB(OH)_2$ and $PhBF_3K$, the latter performed slightly better as a phenyl radical precursor. It is well known that, phenyl radical is active and prone to conduct side reactions, such as self-coupling. It is possible that the phenyl radical formed form $PhBF_3K$ is not as fast as that formed from $PhB(OH)_2$, thus extending the lifetime of phenyl radical. Based on this possibility, it is necessary to test similar borate of $PhBF_3K$ and then synthesize cyclic phenyltriolborate **160**, a bulky sterically hindered borate becomes the radical precursor, leading to the slow formation of phenyl radical (Scheme 24, eq. 1).[76] This cyclic triolborate is very stable even in water and is a useful boron agent that acts as a useful partner in organic reactions such as cross-coupling partner, but no publications report it as an aryl radical donor. Here, we investigated it (**160**) with furoxan **25** in the presence of $K_2S_2O_8$ (3

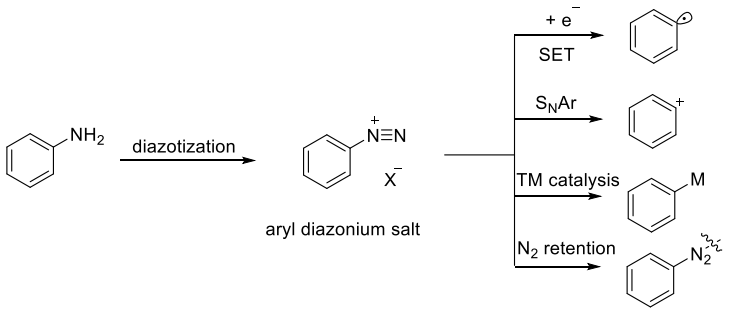
equiv) at 80 ℃ (Scheme 24, eq. 2). However, the result was unsatisfactory and the yield was lower than that of $PhBF_3K$. The possible reason is that the large steric hindrance makes it difficult to form aryl radical.



[a] Determined by ^1H NMR analysis using durene as an internal standard.

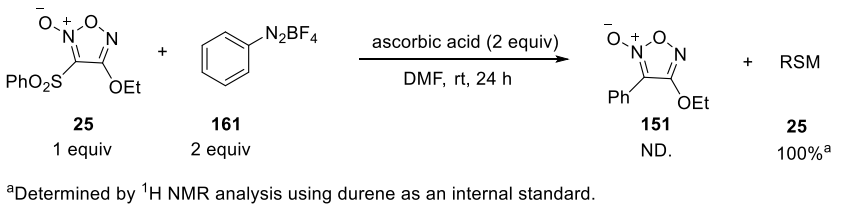
Scheme 24: Cyclic phenyltriolborate **160** wa**s** used as aryl radical precursor.

Subsequently, we turned our attention to other aryl radical donors. Aryldiazonium salt, a famous structure first reported by Griefs in 1858,[77] and many important named reactions have been discovered in the decades since.[78] Recently, with the development of photochemistry, the participation of aryldiazonium salt and visible-light in the formation of aromatic C−C bonds has been established. In general, the reactions involved in aryl diazonium salts mainly via the following reaction intermediates, through aryl radicals, aryl cations, aryl−metal species and diazo group remaining species (Scheme 25).[79] With the exception of the last type, the formation of other three intermediates is due to the electrophilicity of diazonium salts, which contain a good leaving group (N_2).

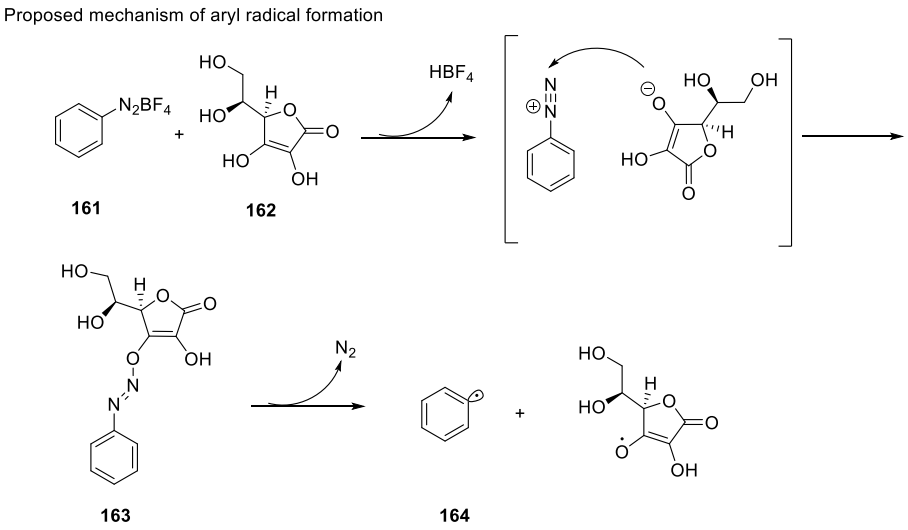


Scheme 25: Four main reaction types for aryl diazonium salts.

Subsequently, we tested aryldiazonium tetrafluoroborate **161** as an aryl radical precursor and reacted with furoxan 25 at room temperature (Scheme 26). The formation of aryl radical is described below,[80] under metal-free and light absenece conditions, the ascorbate anion reacts with aryldiazonium ion to form diazoether intermediate **163** through nucleophilic attack. This intermediate is then homolytic cleavage to release one molecular N_2 and form an aryl radical **164**. Unfortunately, the desired furoxan product **151** was not detected and 100% starting furoxan **25** was remained.



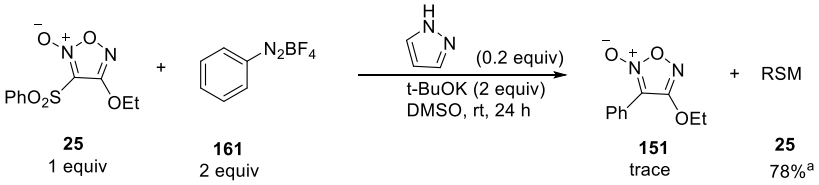
[a]Determined by ^{1}H NMR analysis using durene as an internal standard.



Scheme 26: Arylation between aryldiazonium salt **161** and furoxan **25** in the presence of ascorbic acid.

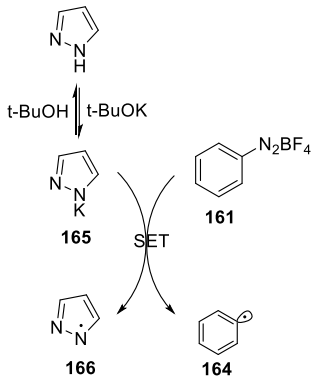
For aryldiazonium salts, another method was found to generate an aryl radical. We examined the aryldiazonium tetrafluoroborate **161**, which forms an aryl radical in the presence of base and pyrazole, and followed by reaction with furoxan 25 (Scheme 27). The aryl radical formation process is described below,[81] the additive pyrazole is deprotonated under potassium *tert*-butoxide (*t*-BuOK) to form an reactive intermediate **165**, which promotes the SET

process with aryldiazonium **161**. Consequently, the aryl radical **164** is formed and pyrazole radical **166** is obtained at the same time. However, only trace of furoxan product **151** was obtained, and 78% of starting furoxan **25** remained.



[a]Determined by ^{1}H NMR analysis using durene as an internal standard.

proposed mechanism



Scheme 27: Arylation between aryldiazonium salt **161** and furoxan **25** under base and pyrazole.

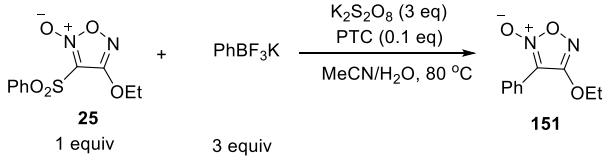
The conclusion of the reactions between aryldiazonium salt **161** and furoxan **25**, we attempted to investigate other aryl radical precursors. However, this combination was ineffective. Although we do not clear the reason, it is possible that the slow formation of aryl radical leads to the low concentration of aryl radical, and thus the inefficient reaction with furoxan.

2.2.2.2 Using phase transfer catalysts (PTC)

During the optimization process of furoxan **25** and $PhBF_3K$, we found that the reaction system is a heterogeneous system consisting of organic phase and aqueous phase. It is worth

noting that acetonitrile and water were miscible at the initial moment of the reaction, and the desired furoxan product was not appreciably increased after 4 h. Based on these experimental phenomena, we speculate that the generation of some inorganic salts affects the solubility of water in acetonitrile, resulting in a heterogeneous reaction. And the heterogeneous reaction system causes the inability of reactants to contact each other, resulting in the reaction stop halfway. One of the solutions to improve heterogeneous reactions is to use phase transfer catalyst (PTC), which can carry one reactant from one phase to another phase and then promote the reaction. Subsequently, we examined several types of phase transfer catalysts, such as crown ether, quaternary ammonium salt and polyethylene glycol (Table 6). However, these catalysts had no improvement on the yield. It is possible that the heterogeneous system is not the reason which leads to the reaction incompletely and moderate yield.

Table 6: Optimization of phase transfer catalyst (PTC)



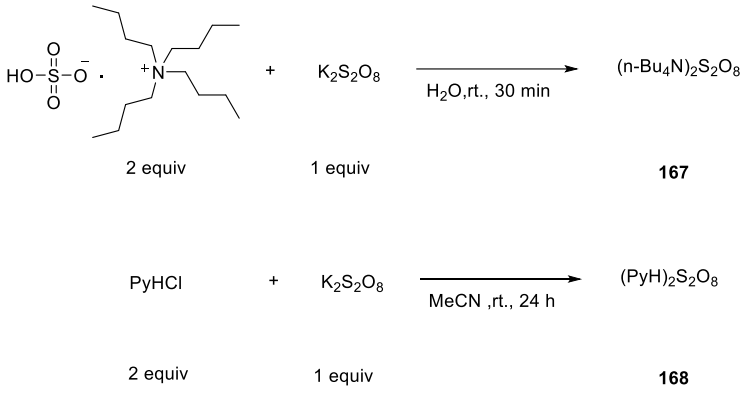
Entry	PTC	Time (h)	Yield of **151** (%)[a]
1	PEG 400	7	40
2	TBAB	7	40
3	β-cyclodextrin	24	38
4[b]	TBAB	20	0

[a] Determined by ^{1}H NMR analysis using durene as an internal standard. [b] DCM/H_2O (1/1) as solvent.

2.2.2.3 Using oxidant that are soluble in organic solvent

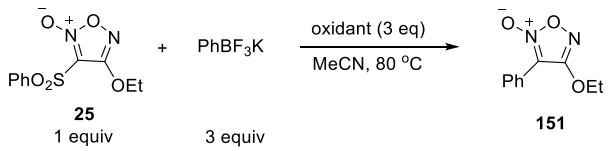
It was found that the conversion of $PhBF_3K$ into the relevant boronic acid is one of its consumption ways. This conversion is due to the hydrolysis of $PhBF_3K$ in water and implies that it is unstable in water. However, it should be noted that the efficient oxidant $K_2S_2O_8$ is

only soluble in water. In order to solve this problem, it is necessary to investigate other oxidants that are soluble in organic solvent. Subsequently, we synthesized two oxidants similar to $K_2S_2O_8$, tetrabutylammonium peroxydisulfate **167** and pyridinium peroxydisulfate **168** (Scheme 28), which were formed through ion exchange with $K_2S_2O_8$ and both were soluble in organic solvent.[82] Afterwards, we examined them instead of $K_2S_2O_8$ in the reaction of 3-sulfonylfuroxan **25** and $PhBF_3K$ (Table 7). As it was supposed, they were soluble in MeCN and no boronic acid was formed due to the absence of water. However, most of starting furoxan **25** was remained and the radical addition essentially did not occur. Although these oxidants are similar to $K_2S_2O_8$, they are not as effective as $K_2S_2O_8$, and most of them remained in crude product. It is possible that the poor ionization of these oxidants in MeCN resulted in the reaction unsuccessful.



Scheme 28: The synthesis of tetrabutylammonium peroxydisulfate **167** and pyridinium peroxydisulfate **168**

Table 7: Optimization of other oxidants



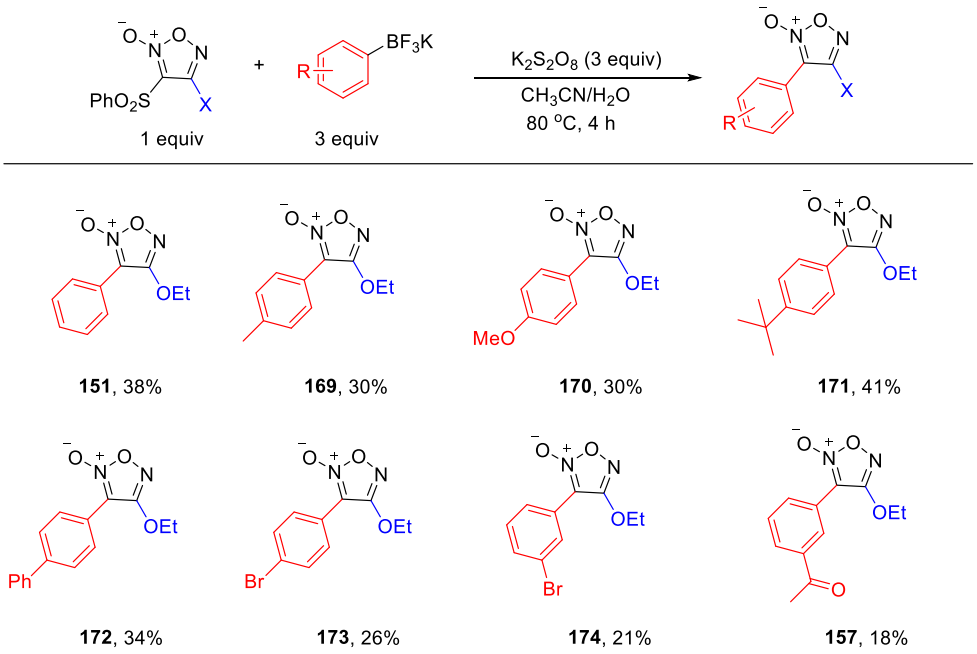
Entry	Oxidant	Time (h)	Yield of **151**[a] (%)	RSM **25** (%)[a]
1	$(n\text{-}Bu_4N)_2S_2O_8$	4	trace	80
2	$(PyH)_2S_2O_8$	4	trace	81

[a]Determined by ^1H NMR analysis using durene as an internal standard.

2.2.3 Substrate scope for arylation of furoxan

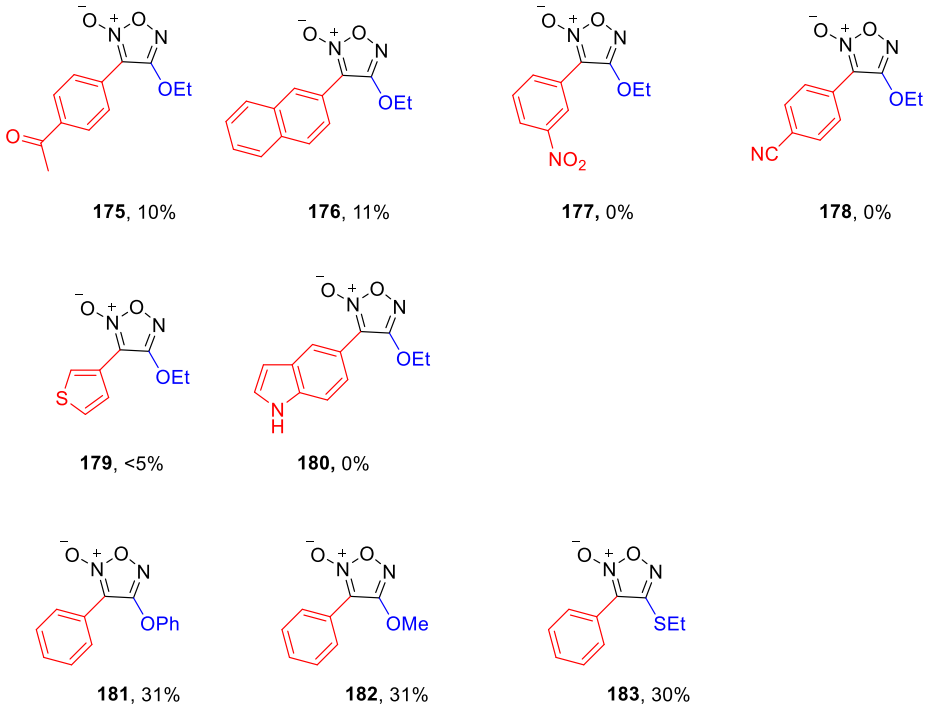
As a part of the research, we next examined the substrate scope under the optimized conditions (Table 8). The reaction tolerated electron-donating group (**169**−**171**) could give better yield than electron-withdrawing group (**173**−**175**). This result indicated that the stability of the aryl radical is a critical factor in the radical addition process. It should be noted that steric hindrance has a great influence on the reaction. Gratifying, the desired product was obtained using 2-naphthyl trifluoroborate (**176**). However, strong electron-withdrawing substituents (−NO_2, −CN) failed to obtain the desired product (**177** and **178**). Unfortunately, aromatic heterocycle trifluoroborate performed poorly (**179** and **180**), this may be due to instability under the oxidative conditions. As a part of the study, we next employed other substituents at the 4-position and obtained similar results (**181**−**183**).

Table 8: Substrate scope for arylation of furoxan



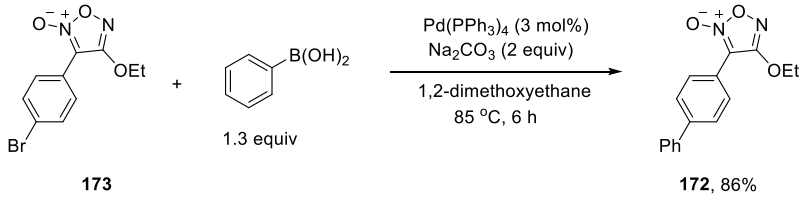
151, 38% **169**, 30% **170**, 30% **171**, 41%

172, 34% **173**, 26% **174**, 21% **157**, 18%



Meanwhile, a gram-scale arylation reaction was performed under optimized conditions, proving that it can be used to synthesize useful furoxans (**151**, 36% vs. 38%).

Derivatization of bromo-substituted arylfuroxan was employed (Scheme 29). The famous Suzuki coupling was performed, furoxan **173** tolerated the standard conditions and the coupling product **172** was achieved in 86% yield. The result indicates the utilization of aryl-substituted furoxan.



Scheme 29: Derivatization of furoxan product **173.**

2.2.4 The proposed mechanism of arylation of furoxan

The reaction process is same as previous reports and C−H furoxanization (Figure 7).[15] The phenyl radical **164** is formed from $PhBF_3K$ in the company of the radical anion **65**. Afterwards, the phenyl radical **164** is added to furoxan **25** and intermediate **184** is formed. Finally, an elimination step takes place and accompanied by the departure of the arylsulfonyl radical, while desired furoxan **151** is obtained.

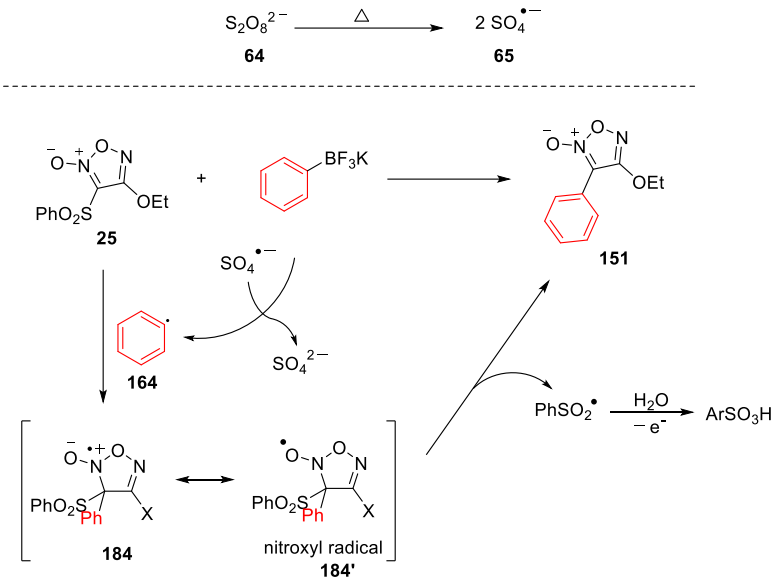


Figure 14: Proposed mechanism of arylation of furoxan.

2.2.5 Conclusion

Unfortunately, these proposed strategies didn't provide any improvement for the arylation of furoxan. What is the main reason for the moderate yield? We next computed the reaction process (Figure 14). Comparing the energy barriers for radical addition and elimination process between methyl radical and phenyl radical, there is no much difference in energy. This result may suggest that the different reactivity of these two radicals with furoxan is due to their stability.[83] The decomposition rate of phenyl radical is faster than reacting with furoxan, resulting in moderate yield of the radical reaction.

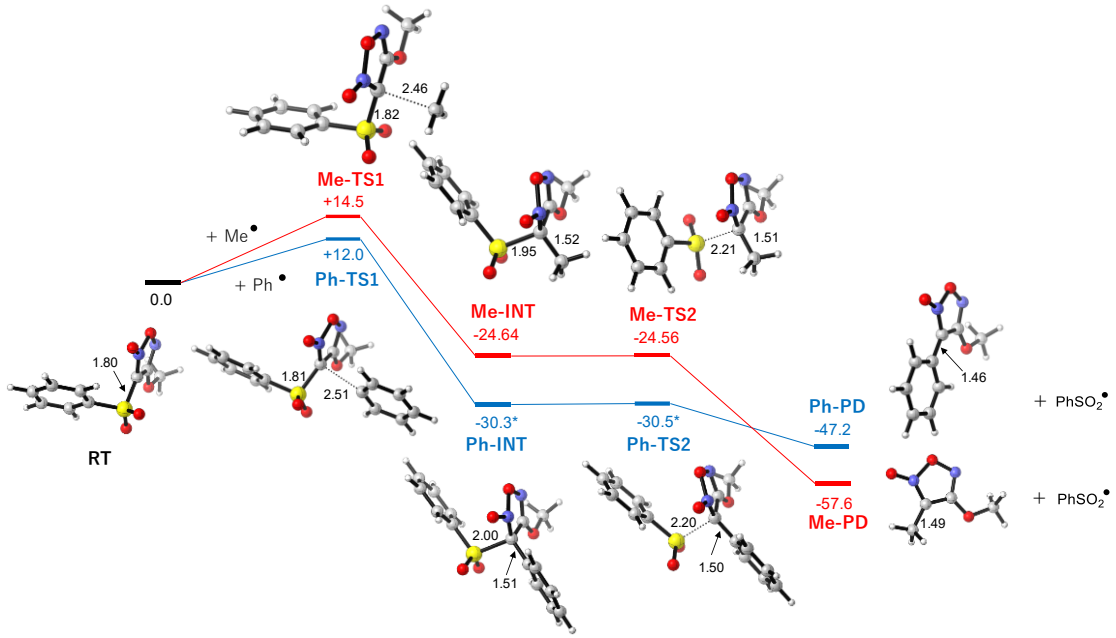


Figure 14: DFT calculations of addition and elimination process of furoxan **RT** with methyl radical and phenyl radical.

Ⅲ：Conclusion

Furoxans are considered as potential biologically active compounds due to their special cyclic structure. However, the special structure also leads to its electron-deficient character, making it unstable under some strong agents. Over the years, the research on furoxan has always been tepid attributed to this reason. Our research is to overcome this drawback and develop a facile synthetic method to obtain the furoxan derivatives under mild conditions.

First, simple C−H bonds were employed to introduce a furoxan and achieve carbon substitution on furoxan. The reaction was performed successfully under mild conditions via radical process due to the existence of exo-ring oxygen for dispersing electrons. As we expected, it tolerated a wide substrate scope and obtained suitable yields. Subsequently, the furoxan products were transformed to various nitrogen-containing functional groups, which also implied the transformation of C−H bond. This method not only obtains carbon substituted furoxans, but also realizes the functionalization of C−H bonds.

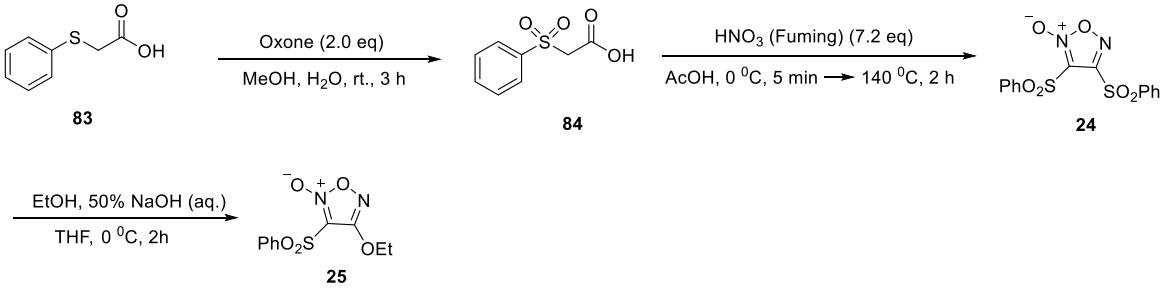
After the successful furoxanization of C−H bond, we pay our attention to introducing an aryl group into furoxan through radical process. It is a novel method for direct arylation of furoxan under mild conditions. Several aryl radical precursors were investigated and aryltrifluoroborates were found to be suitable aryl radical donors. During this optimization process, although some strategies were proposed to promote the reaction, no improvement was obtained for the yield. Afterwards, substrate scope for arylation was examined and this method can tolerate many substituted aryl groups. After comparing the calculated energy, we speculate that the moderate yield is due to the instability of the aryl radical. Nevertheless, this is a direct and simple arylation method for furoxan and aryl-substituted furoxans are obtained in moderate yield.

It was discovered that many bioactive furoxans are substituted with carbon groups, which indicated the importance of research on carbon group substitution reaction of furoxan. Our study mainly focuses on the establishment of C−C bonds on furoxan via a radical pathway that avoids the utilization of strong agents. This protocol is expected to facilitate the synthesis of furoxan derivatives and promote the research of these compounds.

Ⅳ：Experimental

Unless otherwise noted, all reactions were carried out in well cleaned glasswares with magnetic stirring. Operations were performed under an atmosphere of dry argon using Schlenk and vacuum techniques, unless otherwise noted. All starting materials were obtained from commercial sources or were synthesized using standard procedures. Melting points were measured on a Yanaco MP-500D and are not corrected. ^{1}H and $^{13}C\{^{1}H\}$NMR (400 and 100 MHz, respectively) were recorded on a Bruker Avance III HD 400 using TMS (0 ppm) and $CDCl_3$ (77.0 ppm) as an internal standard, respectively. The following abbreviations are used in connection with NMR; s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet and br = broad. Mass spectra were measured using a LTQ Orbitrap Elite (Thermo Fisher Scientific, Brehmen, Germany) with an electrospray ionization (ESI) ion source, a JEOL JMS-T100LP (DART method, ambient ionization) and an atmospheric pressure chemical ionization (APCI). Preparative column chromatography was performed using Kanto Chemical silica gel 60 N (spherical, neutral). Thin layer chromatography (TLC) was carried out on Merck 25 TLC silica gel 60 F_{254} aluminium sheets. Preparative TLC was carried out on home-made glass-based TLC plates (20×20 cm) using Wakogel B-5F (FUJIFILM).

Preparation of 4-ethoxy-3-(phenylsulfonyl)furoxan (25) and 3,4-bis(phenylsulfonyl)furoxan (24)



83 to **84**: To a solution of (phenylthio)acetic acid **83** (26 g, 1 equiv, 0.15 mol) in methanol (800 mL) was added oxone (190 g, 2 equiv, 0.31 mol) in H_2O (200 mL) at room temperature. The mixture was stirred for 4 h. Upon reaction completion, the solvents were removed with a rotary evaporator and then filtrated to remove white solid. Extracted four times with CH_2Cl_2, the organics were dried over Na_2SO_4, filtrated, and concentrated in vacuo to afford the

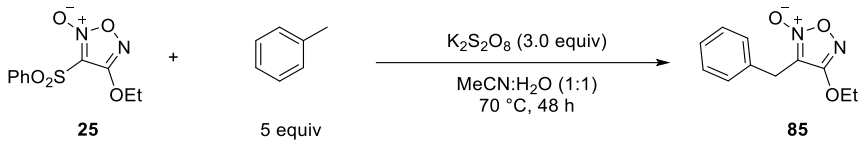
product (phenylsulfonyl)acetic acid **84** (30 g, 97%) which was used without further purification.

84 to **24**: Fuming nitric acid (48.3 mL, 7.5 equiv, 1.2 mol) was added dropwise to a suspension of (phenylsulfonyl)acetic acid **84** (30 g, 1 equiv, 0.15 mol) in acetic acid (100 mL) at 0 °C. The mixture was stirred at 0 °C for 10 minutes and refluxed at 140 °C for 5 h. The mixture was then cooled to room temperature and quenched with H_2O. Extracted four times with CH_2Cl_2 and then washed twice with $NaHCO_3$. The organics were dried over Na_2SO_4, filtrated, and concentrated in vacuo to afford the crude product. The crude product was purified by silica chromatography (5:1 Hexane/EtOAc) to obtain **3,4-bis(phenylsulfonyl)furoxan (24)** as a white solid (8.1 g, 31% yield). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ = 8.21−8.15 (m, 2H), 8.05−8.02 (m, 2H), 7.97−7.89 (m, 2H), 7.83−7.72 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $(CD_3)_2CO$) δ = 155.7, 137.3, 136.9, 136.2, 135.9, 130.0, 129.8, 129.6, 129.1, 115.8.

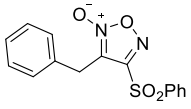
24 to 25: To a solution of 3,4-bis(phenylsulfonyl)furoxan **24** (3 g, 1 equiv, 8.2 mmol) in THF (30 mL) was added EtOH (814 μL, 1.7 equiv, 13.9 mmol), stirred at 0 ℃, 50% NaOH (602 μL, 1.4 equiv, 11.5 mmol) was added dropwise. The mixture was stirred at 0 ℃ for 3 h. Upon reaction completion, the solvents were removed with a rotary evaporator and obtained yellow solid. Extracted three times with EtOAc, the organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The crude residue was purified by silica chromatography (hexane-EtOAc (2:1)) to afford **4-Ethoxy-3-(phenylsulfonyl)furoxan** (**25**) (1.7 g, 77.5% yield). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ = 8.08 (dt, *J* = 8.4, 1.2 Hz, 2H), 7.8 9 (tt, *J* = 7.5, 1.2 Hz, 1H), 7.75 (tt, *J* = 7.4, 1.6 Hz, 2H), 4.52 (q, *J* = 7.0 Hz, 1H), 1.47 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 158.9, 138.1, 135.6, 129.6, 128.6, 110.5, 67.7, 14.2.

Experimental procedures for substrate scope in furoxanization of C-H bonds (Table 3 in the main text)

General procedure with product 85 as a representative example



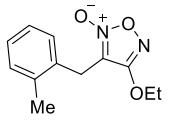
4-Ethoxy-3-(phenylsulfonyl)furoxan (**25**) (54.0 mg, 0.2 mmol, 1.0 equiv), toluene (0.106 mL, 1.0 mmol, 5.0 equiv), potassium peroxodisulfate (162.2 mg, 0.6 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (2.0 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 70 ℃ for 48 h. The reaction was extracted thrice with CH_2Cl_2, the organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The crude residue was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **85** (30.3 mg, 0.14 mmol, 69% yield). 3-Benzyl-4-ethoxyfuroxan (**85**) Colorless oil; IR (neat): 2984, 1621, 1549, 1484, 1453, 1420, 1392, 1360, 1296, 1240, 1113, 1022, 886, 841, 735, 695, 631, 567, 521 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.33–7.26 (m, 5H), 4.41 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 163.0, 134.0, 128.9, 128.7, 127.6, 108.7, 66.4, 27.7, 14.3. HRMS *m/z* (ESI) calcd for $C_{11}H_{12}N_2O_3$ $(M + Na)^+$ 243.0740, found 243.0760.



88

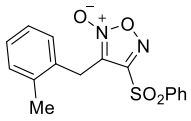
3-Benzyl-4-(phenylsulfonyl)furoxan (88) According to the general procedure, **24** (73.3 mg, 0.2 mmol, 1.0 equiv), toluene (0.11 mL, 1.0 mmol, 5.0 equiv), and potassium peroxodisulfate (270 mg, 1.0 mmol, 5.0 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 96 h. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **88** (52.4 mg, 0.17 mmol, 83% yield). White solid; Mp, 95.0–95.5 °C. IR (neat): 1605, 1580, 1497, 1461, 1455, 1446, 1426, 1349, 1290, 1199, 1181, 1160, 1088, 1043, 1028, 998, 857, 737, 757, 724, 698, 683, 643, 619, 609, 582, 569 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.89–7.87 (m, 2H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 2H), 7.29 (m, 5H), 4.14 (s,

2H). $^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$) δ = 158.7, 136.8, 135.5, 133.0, 129.7, 129.0, 129.0, 128.9, 127.9, 112.5, 28.2. HRMS *m/z* (DART) calcd for $C_{15}H_{13}N_2O_4S_1$ $(M+H)^+$ 317.0591, found 317.0596.



89

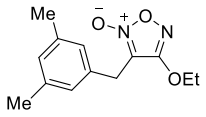
3-[(2-Methylphenyl)methyl]-4-ethoxyfuroxan (89). According to the general procedure, **25** (54.0 mg, 0.2 mmol, 1.0 equiv), *o*-xylene (0.12 mL, 1.0 mmol, 5.0 equiv), and potassium peroxodisulfate (162 mg, 0.6 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 70 ℃ for 48 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (10/1)) to afford **89** (37.6 mg, 0.16 mmol, 80% yield). Yellow solid; Mp, 33.6–34.0 ºC. IR (neat): 2985, 1622, 1551, 1471, 1393, 1361, 1309, 1236, 1135, 1116, 1091, 1020, 888, 848, 828, 743, 713, 702, 633, 597, 539, 517 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.21–7.11(m, 4H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 2H), 2.36 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 163.1, 136.4, 132.0, 130.6, 129.6, 127.7, 126.2, 108.4, 66.3, 25.4, 19.6, 14.3. HRMS *m/z* (ESI) calcd for $C_{12}H_{14}N_2O_3$ $(M + H)^+$ 235.1077, found 235.1066.



90

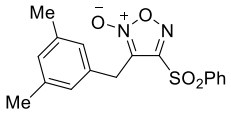
3-[(2-Methylphenyl)methyl]-4-(phenylsulfonyl)furoxan (90). According to the general procedure, **24** (366 mg, 1.0 mmol, 1.0 equiv), *o*-xylene (0.6 mL, 5.0 mmol, 5.0 equiv), and potassium peroxodisulfate (540 mg, 2.0 mmol, 2.0 equiv) were reacted in CH_3CN:H_2O (1:1) (15.0 mL) at 60 ℃ for 36 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (5/1)) to afford **90** (242 mg, 0.73 mmol, 73% yield). White solid; Mp, 87.5–88.4 ℃. IR (neat): 2922, 1608, 1582, 1493, 1448, 1417, 1349, 1312, 1291, 1204, 1181, 1160, 1088, 1053, 1028, 998, 849, 750, 740, 722, 685, 698, 653, 612, 581, 590, 547 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74–7.71 (m, 2H), 7.67–7.63 (m, 1H), 7.48–7.43 (m, 2H), 7.19–7.17(m, 2H), 7.03–6.98 (m, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 4.12 (s,

2H), 2.36 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$) δ = 159.0, 136.8, 136.6, 135.4, 131.1, 130.8, 129.6, 128.8, 128.2, 127.8, 126.4, 112.3, 25.7, 19.7. HRMS *m/z* (ESI) calcd for $C_{16}H_{14}N_2O_4SNa$ $(M + Na)^+$ 353.0567, found 353.0571.



91

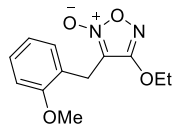
3-[(3,5-Dimethylphenyl)methyl]-4-ethoxyfuroxan (91). According to the general procedure, **25** (54.0 mg, 0.2 mmol, 1.0 equiv), mesitylene (0.14 mL, 1.0 mmol, 5.0 equiv), and potassium peroxodisulfate (162 mg, 0.6 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 70 ℃ for 48 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **91** (39.0 mg, 0.16 mmol, 79% yield). White solid; Mp, 56.2–56.7 ℃. IR (neat): 2916, 2848, 1616, 1548, 1482, 1418, 1394, 1378, 1361, 1299, 1281, 1243, 1106, 1024, 883, 850, 832, 782, 739, 689, 640, 610, 542, 513, 504 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.90 (s, 1H), 6.88 (s, 2H), 4.42 (q, *J* = 7.0 Hz, 2H), 3.72 (s, 2H), 2.28 (s, 6H), 1.45 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 163.1, 138.5, 133.8, 129.2, 126.4, 108.8, 66.3, 27.5, 21.2, 14.3. HRMS *m/z* (ESI) calcd for $C_{13}H_{16}N_2O_3$ $(M + H)^+$ 249.1234, found 249.1221.



92

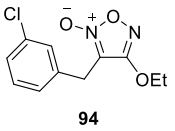
3-[(3,5-Dimethylphenyl)methyl]-4-(phenylsulfonyl)furoxan (92). According to the general procedure, **24** (800 mg, 2.2 mmol, 1.0 equiv), 1,3,5-trimethylbenzene (1.53 mL, 11.0 mmol, 5.0 equiv), and potassium peroxodisulfate (1.8 g, 6.6 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (40.0 mL) at 80 ℃ for 18 h. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc(10/1)) to afford **92** (490.6 mg, 1.42 mmol, 65% yield). Yellow solid; Mp, 94.8–96.2 ℃. IR (neat): 2917, 1602, 1459, 1446, 1420, 1346, 1156, 1088, 1043, 1031, 830, 733, 682, 598 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88–7.85 (m, 2H), 7.70 (tt, *J* = 1.2, 7.5 Hz, 1H), 7.55–7.51 (m, 2H), 6.90 (s, 1H), 6.81 (s, 2H), 4.06 (s, 2H), 2.24 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 158.8, 138.7, 137.2, 135.5, 132.9, 129.7,

129.6, 129.1, 126.7, 112.8, 28.2, 21.3. HRMS *m/z* (ESI) calcd for $C_{17}H_{16}N_2O_4SNa$ $(M + Na)^+$ 367.0723, found 367.0709.



93

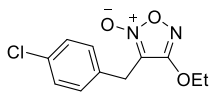
4-Ethoxy-3-[(2-methoxyphenyl)methyl]furoxan (93). According to the general procedure, **25** (54.0 mg, 0.2 mmol, 1.0 equiv), 2-methoxyltoluene (0.125 mL, 1.0 mmol, 5.0 equiv), and potassium peroxodisulfate (162 mg, 0.6 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 70 ℃ for 48 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **93** (47.6 mg, 0.19 mmol, 95% yield). Yellow solid; Mp, 51.3–51.9 ℃. IR (neat): 1629, 1550, 1455, 1439, 1424, 1389, 1293, 1248, 1133, 1114, 1098, 1020, 753, 709, 630 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.28–7.24 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 6.92–6.84 (m, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 3.80 (s, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 163.4, 157.3, 130.3, 128.9, 121.7, 120.4, 110.3, 108.4, 66.1, 55.3, 22.9, 14.3. HRMS *m/z* (ESI) calcd for $C_{12}H_{14}N_2O_4$ $(M + H)^+$ 251.1026, found 251.1013.



94

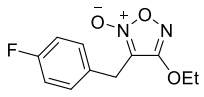
3-[(3-Chlorophenyl)methyl]-4-ethoxyfuroxan (94). According to the general procedure, **25** (81.0 mg, 0.3 mmol, 1.0 equiv), 3-chlorotoluene (0.18 mL, 1.5 mmol, 5.0 equiv), and potassium peroxodisulfate (243.3 mg, 0.9 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (3.0 mL) at 70 ℃ for 48 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **94** (41.4 mg, 0.16 mmol, 54% yield). Yellow oil. IR (neat): 2984, 1621, 1550, 1472, 1432, 1392, 1360, 1301, 1237, 1197, 1113, 1092, 1023, 864, 838, 773, 731, 682, 640 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.27–7.24 (m, 3H), 7.17–7.14 (m, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.9, 135.8, 134.6, 130.2, 128.8, 127.9, 126.9, 108.1, 66.5, 27.4, 14.3. HRMS *m/z* (ESI) calcd for $C_{11}H_{15}{}^{37}ClN_3O_3$ $(M + NH_4)^+$

274.0767, found 274.0753.



95

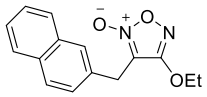
3-[(4-Chlorophenyl)methyl]-4-ethoxyfuroxan (95). According to the general procedure, **25** (45.0 mg, 0.17 mmol, 1.0 equiv), 4-chlorotoluene (0.1 mL, 0.83 mmol, 5.0 equiv), and potassium peroxodisulfate (135 mg, 0.5 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 70 ℃ for 48 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (10/1)) to afford **95** (26.0 mg, 0.1 mmol, 64% yield). Yellow solid; Mp, 29.7–30.1 ℃. IR (neat): 2989, 1616, 1550, 1542, 1481, 1466, 1408, 1388, 1358, 1288, 1236, 1122, 1094, 1022, 1013, 882, 835, 802, 782, 734, 712, 645, 622, 507 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.28 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.8, 133.6, 132.4, 130.1, 129.1, 108.3, 66.5, 27.1, 14.3. HRMS *m/z* (ESI) calcd for $C_{11}H_{15}{}^{37}ClN_3O_3$ $(M + NH_4)^+$ 274.0767, found 274.0752.



96

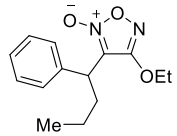
4-Ethoxy-3-[(4-fluorophenyl)methyl]furoxan (96). According to the general procedure, **25** (54.0 mg, 0.2 mmol, 1.0 equiv), 4-fluorotoluene (0.11 mL, 1.0 mmol, 5.0 equiv), and potassium peroxodisulfate (162.0 mg, 0.6 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 70 ℃ for 48 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **96** (22.5 mg, 0.09 mmol, 47% yield). Yellow oil. IR (neat): 2918, 1621, 1550, 1508, 1484, 1419, 1389, 1360, 1221, 1113, 1020, 844, 707, 622, 579, 565, 523, 508 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.25–7.23 (m, 2H), 7.00 (t, *J* = 8.7 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.2 (d, *J* = 244.7 Hz), 162.9, 130.3 (d, *J* = 8.1 Hz), 129.6 (d, *J* = 3.2 Hz), 115.8 (d, *J* = 21.4 Hz), 108.6, 66.5, 27.0, 14.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ = –113.0. HRMS *m/z* (ESI) calcd for $C_{11}H_{11}FN_2O_3$ $(M + H)^+$ 239.0826, found

239.0810.



97

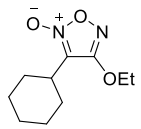
4-Ethoxy-3-[(naphthalen-2-yl)methyl]furoxan (97) According to the general procedure, **25** (54.0 mg, 0.2 mmol, 1.0 equiv), 2-methylnaphthalene (142.2 mg, 1.0 mmol, 5.0 equiv), and potassium peroxodisulfate (162.0 mg, 0.6 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 70 ℃ for 48 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **97** (42.8 mg, 0.16 mmol, 79% yield). Yellow oil. IR (neat): 1620, 1549, 1482, 1391, 1358, 1292, 1241, 1107, 1022, 785, 696, 566, 560, 554, 537, 531, 521, 516 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.83–7.79 (m, 3H), 7.73 (s, 1H), 7.51–7.45 (m, 2H), 7.39 (dd, *J* = 8.5, 1.7 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 163.1, 133.4, 132.6, 131.4, 128.7, 127.7, 127.4, 126.6, 126.4, 126.1, 108.7, 66.4, 27.9, 14.4. HRMS *m/z* (ESI) calcd for $C_{15}H_{14}N_2O_3$ $(M + H)^+$ 271.1077, found 271.1059.



98

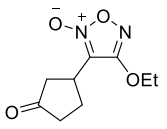
4-Ethoxy-3-(1-phenylbutyl)furoxan (98). According to the general procedure, **25** (54.0 mg, 0.2 mmol, 1.0 equiv), butylbenzene (0.16 mL, 1.0 mmol, 5.0 equiv), and potassium peroxodisulfate (162.0 mg, 0.6 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 70 ℃ for 48 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (10/1)) to afford **98** (27.2 mg, 0.1 mmol, 52% yield). Colorless oil. IR (neat): 2959, 2932, 2872, 1611, 1547, 1457, 1391, 1358, 1301, 1256, 1153, 1092, 1069, 1025, 880, 847, 754, 716, 696, 617, 606, 546, 507 cm^{-1}.^1H NMR (400 MHz, $CDCl_3$) δ = 7.36–7.24 (m, 5H), 4.43 (q, *J* = 7.0 Hz, 2H), 3.96–3.92 (m, 1H), 2.25–2.16 (m, 1H), 2.08–1.98 (m, 1H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.35–1.26 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.9, 139.0, 128.8, 127.8, 127.6, 111.0, 66.4, 40.2, 32.6, 20.9, 14.4, 13.7. HRMS *m/z* (ESI) calcd for $C_{14}H_{18}N_2O_3$ $(M + H)^+$ 263.1390, found

263.1377.



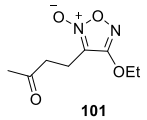
99

3-Cyclohexyl-4-ethoxyfuroxan (99). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), cyclohexane (0.16 mL, 1.5 mmol, 10.0 equiv), and potassium peroxodisulfate (120 mg, 0.45 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 100 °C for 30 min. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (6/1)) to afford **99** (14mg, 0.07 mmol, 45% yield). White solid; Mp, 79.6–80.3 ℃. IR (neat): 2981, 2935, 2851, 1616, 1544, 1480, 1443, 1395, 1362, 1338, 1271, 1250, 1171, 1122, 1027, 984, 883, 840, 810, 721, 674 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 4.41 (q, *J* = 7.1 Hz, 2H), 2.68 (tt, *J* = 11.8, 4.1 Hz, 1H), 1.86–1.64 (m, 7H), 1.47 (t, *J* = 7.1 Hz, 3H), 1.39–1.22 (m, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 163.1, 112.2, 66.2, 33.3, 27.6, 25.8, 25.4, 14.4. HRMS *m/z* (ESI) calcd for $C_{10}H_{17}N_2O_3$ $(M + H)^+$ 213.1234, found 213.1229.



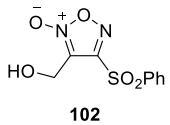
100

4-Ethoxy-3-(3-oxocyclopentyl)furoxan (100). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), cyclopentanone (66 μL, 0.75 mmol, 5.0 equiv), and potassium peroxodisulfate (100 mg, 0.38 mmol, 2.5equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **100** (10.7 mg, 0.05 mmol, 34% yield). White solid; Mp, 29.3–30.5 ℃. IR (neat): 1738, 1622, 1552, 1487, 1471, 1394, 1359, 1269, 1247, 1194, 1162, 1116, 1021, 899, 836, 686 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 4.44 (q, *J* = 7.1 Hz, 2H), 3.49–3.40 (m, 1H), 2.72–2.64 (m, 1H), 2.52–2.42 (m, 2H), 2.36–2.21 (m, 3H), 1.46 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 215.2, 162.7, 109.7, 66.9, 39.2, 37.9, 30.6, 25.4, 14.5. HRMS *m/z* (ESI) calcd for $C_9H_{13}N_2O_4$ $(M + H)^+$ 213.0870, found 213.0860.



101

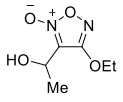
4-Ethoxy-3-(butanone)furoxan (101). According to the general procedure, **25** (62 mg, 0.23 mmol, 1.0 equiv), butanone (0.5 mL, 5.59 mmol, 24.3 equiv), and potassium peroxodisulfate (186 mg, 0.69 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (3.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **101** (5.7 mg, 0.03 mmol, 12.4% yield). Yellow oil. IR (neat): 1716, 1622, 1549, 1483, 1472, 1392, 1358, 1304, 1218, 1167, 1133, 1039, 1019, 836 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 4.43 (q, *J* = 7.1 Hz, 2H), 2.88−2.85 (m, 2H), 2.76−2.72 (m, 2H), 2.18 (s, 3H), 1.47 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 205.6, 163.0, 108.5, 66.4, 37.2, 29.6, 15.9, 14.3. HRMS *m/z* (ESI) calcd for $C_8H_{12}N_2O_4Na$ $(M + Na)^+$ 223.0689, found 223.0686.



102

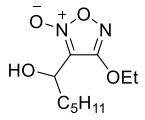
3-(Hydroxymethyl)-4-(phenylsulfonyl)furoxan (102). According to the general procedure, **24** (73.3 mg, 0.2 mmol, 1.0 equiv), methanol (121μL, 3.0 mmol, 15.0 equiv), and potassium peroxodisulfate (54.1 mg, 0.2 mmol, 1.0 equiv) were reacted in CH_3CN:H_2O (1:1) (3.0 mL) at 60 ℃ for 18 h. The yield of **102** was determined to be 58% by ^1H NMR spectroscopic analysis of the crude material with durene (15.8 mg) as an internal standard. **102** was also synthesized using trimethyl orthofomate as a reactant instead of methanol. According to the general procedure, **24** (73.3 mg, 0.2 mmol, 1.0 equiv), trimethyl orthoformate (109 μL, 1.0 mmol, 5.0 equiv), and potassium peroxodisulfate (54.1 mg, 0.2 mmol, 1.0 equiv) were reacted in CH_3CN:H_2O (1:1) (3.0 mL) at 60 ℃ for 6 h. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **102** (36.9 mg, 0.144 mmol, 72% yield). Colorless oil; IR (neat): 3342, 2923, 2848, 1716, 1602, 1581, 1447, 1358, 1345, 1310, 1294, 1181, 1162, 1092, 1053, 1041, 1020, 998, 946, 844, 759, 737, 723, 706, 683, 652, 631, 602, 582, 547, 528 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 7.9 Hz, 2H), 7.81 (t, *J* =

7.5 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 2H), 4.83 (d, *J* = 6.0 Hz, 2H), 2.94 (s, 1H). $^{13}C\{^{1}H\}$ NMR (100MHz, $CDCl_3$) δ = 158.6, 136.5, 136.0, 129.9, 129.1, 111.8, 53.2. HRMS *m/z* (DART) calcd for $C_9H_9N_2O_5S_1$ $(M+H)^+$ 257.0227, found 257.0243.



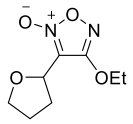
103

4-Ethoxy-3-(1-hydroxyethyl)furoxan (103). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), ethanol (0.2 mL, 3.4 mmol, 23 equiv), and potassium peroxodisulfate (100 mg, 0.38 mmol, 2.5 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 1 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **103** (17.0 mg, 0.10 mmol, 66% yield). Colorless oil; IR (neat): 3439, 2987, 1611, 1549, 1471, 1446, 1358, 1278, 1182, 1075, 1019, 990, 902, 881, 838, 727, 609 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.92–4.86 (m, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 2.80 (d, *J* = 6.9 Hz, 1H), 1.59 (d, *J* = 6.8 Hz, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.1, 111.2, 66.9, 60.9, 19.6, 14.5. HRMS *m/z* (ESI) calcd for $C_6H_{10}N_2O_4Na$ $(M + Na)^+$ 197.0533, found 197.0522.



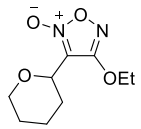
104

4-Ethoxy-3-(1-hydroxyhexyl)furoxan (104). According to the general procedure, **24** (40.0 mg, 0.15 mmol, 1.0 equiv), 1-hexanol (74 μL, 0.6 mmol, 4 equiv), and potassium peroxodisulfate (100 mg, 0.38 mmol, 2.5 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (CH_2Cl_2) to afford **104** (12.7 mg, 0.06 mmol, 37% yield). Colorless oil; IR (neat): 3449, 2956, 2930, 2860, 1613, 1549, 1469, 1391, 1358, 1159, 1022, 837, 726, 570 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.70 (q, *J* = 1.9 Hz, 1H), 4.45 (q, *J* = 7.0 Hz, 2H), 2.65 (d, *J* = 8.2 Hz, 1H), 1.95–1.82 (m, 2H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.32–1.31 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.2, 110.8, 66.9, 65.0, 33.7, 31.4, 24.9, 22.6, 14.5, 14.0. HRMS *m/z* (ESI) calcd for $C_{10}H_{19}N_2O_4$ $(M + H)^+$ 231.1339, found 231.1326.



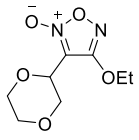
105

4-Ethoxy-3-(oxolan-2-yl)furoxan (105) According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), tetrahydrofuran (0.5 mL, 6.2 mmol, 41 equiv), and potassium peroxodisulfate (100 mg, 0.38 mmol, 2.5equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **105** (23.0mg, 0.11 mmol, 78% yield). Colorless oil; IR (neat): 2983, 1613, 1549, 1471, 1392, 1348, 1195, 1159, 1054, 1018, 921, 832, 618, 567 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 4.95 (t, *J* = 6.9 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.01–3.87 (m, 2H), 2.30–1.95 (m, 4H), 1.46 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.5, 109.7, 70.1, 69.8, 66.6, 28.6, 26.6, 14.5. HRMS *m/z* (ESI) calcd for $C_8H_{13}N_2O_4$ $(M + H)^+$ 201.0870, found 201.0862.



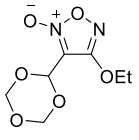
106

4-Ethoxy-3-(oxan-2-yl)furoxan (106). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), tetrahydropyran (143 μL, 1.5 mmol, 10 equiv), and potassium peroxodisulfate (100 mg, 0.38 mmol, 2.5 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (10/1)) to afford **106** (15 mg, 0.07 mmol, 47% yield). Colorless oil; IR (neat): 2987, 2943, 2857, 1617, 1547, 1497, 1472, 1375, 1353, 1303, 1206, 1180, 1158, 1102, 1081, 1041, 1019, 987, 912, 850, 814, 667, 560 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 4.47–4.39 (m, 3H), 4.08–4.04 (m, 1H), 3.55 (td, *J* = 11.6, 2.2 Hz, 1H), 2.16–2.06 (m, 1H), 1.98–1.94 (m, 1H), 1.73–1.54 (m, 4H), 1.48 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.7, 109.1, 70.1, 69.4, 66.7, 27.1, 25.3, 23.2, 14.4. HRMS *m/z* (ESI) calcd for $C_9H_{15}N_2O_4$ $(M + H)^+$ 215.1026, found 215.1018.



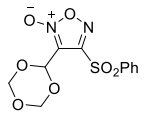
107

3-(1,4-Dioxan-2-yl)-3-ethoxyfuroxan (**107**). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), 1,4-dioxane (125 μL, 1.5 mmol, 10.0 equiv), and potassium peroxodisulfate (100 mg, 0.38 mmol, 2.5 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **107** (19.8 mg, 0.09 mmol, 62% yield). White solid; Mp, 66.3–68.5 ℃. IR (neat): 2870, 1751, 1609, 1547, 1487, 1471, 1388, 1261, 1169, 1116, 1085, 1016, 911, 856, 834, 728, 702, 582 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 4.70 (dd, *J* = 10.4, 2.8 Hz, 1H), 4.44 (q, *J* = 7.0 Hz 2H), 4.02 (t, *J* = 10.4 Hz, 1H), 3.91–3.69 (m, 5H), 1.48 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.5, 106.4, 68.1, 67.3, 66.9, 66.3, 66.1, 14.4. HRMS *m/z* (ESI) calcd for $C_8H_{13}N_2O_5$ $(M + H)^+$ 217.0819, found 217.0807.



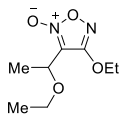
108

4-Ethoxy-3-(1,3,5-trioxane-2-yl)furoxan (108). According to the general procedure, **24** (40.0 mg, 0.15 mmol, 1.0 equiv), 1,3,5-trioxane (66.6 mg, 0.75 mmol, 5.0 equiv), and potassium peroxodisulfate (120 mg, 0.45 mmol, 3.0 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **108** (15 mg, 0.07 mmol, 47% yield). White solid; Mp, 64.9–65.7 ℃. IR (neat): 2996, 2891, 1624, 1567, 1502, 1391, 1183, 1088, 1071, 1025, 958, 940, 887, 841, 732, 690, 566 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 6.02 (s, 1H), 5.33 (d, *J* = 6.8 Hz, 2H), 5.22 (d, *J* = 6.9 Hz, 2H), 4.49 (q, *J* = 7.0 Hz, 2H), 1.51 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 161.7, 106.0, 93.7, 93.7, 67.0, 14.2. HRMS *m/z* (ESI) calcd for $C_7H_{10}N_2NaO_6$ $(M + Na)^+$ 241.0431, found 241.0429.



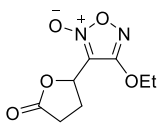
109

4-(Phenylsulfonyl)-3-(1,3,5-trioxane-2-yl)furoxan**(109)**. According to the general procedure, **24** (73.3 mg, 0.2 mmol, 1.0 equiv), 1,3,5-trioxane (90.1 mg, 1.0 mmol, 5.0 equiv), and potassium peroxodisulfate (54 mg, 1.0 mmol, 5.0 equiv) were reacted in CH_3CN:H_2O (1:1) (3.0 mL) at 60 ℃ for 24 h. The crude material was purified by column chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **109** (30.2 mg, 0.096 mmol, 48% yield). Colorless oil: IR (neat): 2923, 2853, 1731, 1620, 1448, 1353, 1261, 1194, 1163, 1112, 1084, 1066, 1051, 1023, 966, 950, 890, 800, 757, 725, 683, 639, 597, 550 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.11–8.09 (m, 2H), 7.81–7.76 (m, 1H), 7.65 (t, *J* = 7.9 Hz, 2H), 6.31 (s, 1H), 5.34 (d, *J* = 6.9 Hz, 2H), 5.25 (d, *J* = 7.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (100MHz, $CDCl_3$) δ = 157.4, 136.8, 135.7, 129.6, 129.1, 108.5, 93.5, 92.9. HRMS *m/z* (DART) calcd for $C_{11}H_{14}N_3O_7S_1$ $(M+NH_4)^+$ 332.0547, found 332.0572.



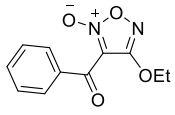
110

4-Ethoxy-3-(1-ethoxyethyl)furoxan (110). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), ethyl ether (0.5 mL, 4.8 mmol, 32 equiv), and potassium peroxodisulfate (100 mg, 0.38 mmol, 2.5equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **110** (15 mg, 0.07 mmol, 50% yield). Colorless oil. IR (neat): 2981, 2939, 2875, 1610, 1548, 1472, 1444, 1392, 1358, 1187, 1101, 1021, 987, 941, 852, 834, 725 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 4.56 (q, *J* = 6.8 Hz, 1H), 4.44 (q, *J* = 7.0 Hz, 2H), 3.53–3.40 (m, 2H), 1.54 (d, *J* = 6.8 Hz, 3H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.8, 109.5, 67.9, 66.6, 65.5, 17.7, 15.2, 14.5. HRMS *m/z* (ESI) calcd for $C_8H_{15}N_2O_4$ $(M + H)^+$ 203.1026, found 203.1017.



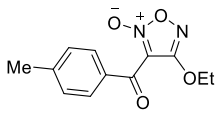
111

4-Ethoxy-3-(5-oxooxolan-2-yl)furoxan **(111)**. According to the general procedure, **25** (80.0 mg, 0.3 mmol, 1.0 equiv), γ-Butyrolactone (45.5 μL, 0.6 mmol, 2.0 equiv), and potassium peroxodisulfate (160 mg, 0.6 mmol, 2.0 equiv) were reacted in CH_3CN:H_2O (1:1) (4.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **111** (6.1 mg, 0.03 mmol, 10% yield). Colorless oil. IR (neat): 2920, 2850, 1783, 1616, 1553, 1493, 1471, 1350, 1150, 1018, 993, 835, 810, 724, 667 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 5.53–5.49 (m, 1H), 4.50–4.43 (m, 2H), 2.87–2.76 (m, 1H), 2.69–2.54 (m, 3H), 1.48 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 175.5, 161.9, 107.5, 69.5, 67.3, 27.7, 24.1, 14.4. HRMS *m/z* (ESI) calcd for $C_8H_{11}N_2O_5$ $(M + H)^+$ 215.0662, found 215.0652.



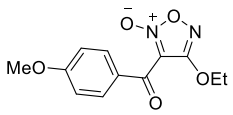
87

3-Benzoyl-4-ethoxyfuroxan (87). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), benzaldehyde (45 μL, 0.45 mmol, 3.0 equiv), and potassium peroxodisulfate (60 mg, 0.23 mmol, 1.5 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (10/1)) to afford **87** (19 mg, 0.08 mmol, 55% yield). Colorless oil. IR (neat): 2983, 1656, 1598, 1545, 1474, 1387, 1329, 1228, 1155, 1109, 1023, 1003, 904, 864, 836, 795, 724, 690, 655, 598 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.85–7.82 (m, 2H), 7.67 (tt, *J* = 1.2, 7.4 Hz, 1H), 7.54–7.50 (m, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 180.8, 161.3, 135.0, 134.5, 129.7, 128.9, 107.3, 67.3, 14.3. HRMS *m/z* (ESI) calcd for $C_{11}H_{11}N_2O_4$ $(M + H)^+$ 235.0713, found 235.0704.



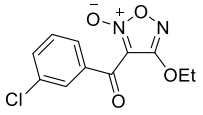
112

4-Ethoxy-3-(4-methylbenzoyl)furoxan (**112**). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), 4-methylbenzaldehyde (53 μL, 0.45 mmol, 3.0 equiv), and potassium peroxodisulfate (60 mg, 0.23 mmol, 1.5 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (10/1)) to afford **112** (22 mg, 0.09 mmol, 60% yield). Yellow solid; Mp, 45.2–46.7 ℃. IR (neat): 2995, 1671, 1598, 1550, 1463, 1395, 1358, 1327, 1231, 1164, 1020, 908, 872, 828, 792, 761, 735, 707, 613, 587 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.76–7.73 (m, 2H), 7.33–7.30 (m, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 2.46 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 180.2, 161.4, 146.5, 132.0, 130.0, 129.7, 107.3, 67.2, 22.1, 14.3. HRMS *m/z* (ESI) calcd for $C_{12}H_{13}N_2O_4$ $(M + H)^+$ 249.0870, found 249.0861.



113

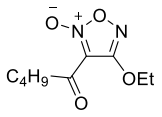
4-Ethoxy-3-(4-methoxybenzoyl)furoxan (113). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), 4-methoxybenzaldehyde (45 μL, 0.38 mmol, 2.5 equiv), and potassium peroxodisulfate (100 mg, 0.38 mmol, 2.5 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 18 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Benzene/CH_2Cl_2 (3/1)) to afford **113** (26 mg, 0.1 mmol, 67% yield). Yellow solid; Mp, 95.2–96.5 ℃. IR (neat): 1654, 1583, 1574, 1548, 1526, 1459, 1386, 1362, 1273, 1224, 1167, 1123, 1010, 928, 844, 769, 704, 614 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.85–7.81 (m, 2H), 7.00–6.96 (m, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 1.44 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 178.8, 165.4, 161.4, 132.5, 127.4, 114.3, 107.4, 67.2, 55.8, 14.3. HRMS *m/z* (ESI) calcd for $C_{12}H_{12}N_2O_5Na$ $(M + Na)^+$ 287.0638, found 287.0634.



114

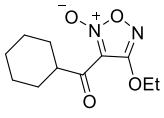
3-(3-Chlorobenzoyl)-4-ethoxyfuroxan (114). According to the general procedure, **25** (40.0

mg, 0.15 mmol, 1.0 equiv), 3-chlorobenzaldehyde (34 μL, 0.3 mmol, 2.0 equiv), and potassium peroxodisulfate (68 mg, 0.23 mmol, 1.7 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 18 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **114** (11 mg, 0.04 mmol, 28% yield). Yellow oil. IR (neat): 1677, 1594, 1573, 1527, 1486, 1463, 1443, 1419, 1394, 1357, 1326, 1221, 1159, 1025, 919, 874, 841, 804, 756, 729, 710, 689, 653 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.79 (t, *J* = 1.8 Hz, 1H), 7.69 (dt, *J* = 1.0, 7.8 Hz, 1H), 7.65–7.62 (m, 1H), 7.47 (t, *J* = 7.9 Hz, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 179.6, 161.0, 136.1, 135.2, 134.8, 130.2, 129.5, 127.8, 107.1, 67.4, 14.3. HRMS *m/z* (ESI) calcd for $C_{11}H_9N_2O_4ClNa$ $(M + Na)^+$ 291.0143, found 291.0139.



115

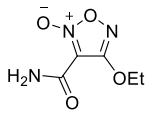
4-Ethoxy-3-pentanoylfuroxan (115). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), pentanal (32 μL, 0.3 mmol, 2.0 equiv), and potassium peroxodisulfate (68 mg, 0.23 mmol, 1.7 equiv) were reacted in CH_3CN:H_2O (1:1) (2.0 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (7/1)) to afford **115** (13.4 mg, 0.06 mmol, 42% yield). Colorless oil. IR (neat): 2960, 2935, 2874, 1705, 1595, 1531, 1464, 1389, 1356, 1331, 1174, 1017, 945, 878, 840, 675 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 4.51 (q, *J* = 7.1 Hz, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 1.81–1.68 (m, 2H), 1.52 (t, *J* = 7.1 Hz, 3H), 1.43–1.33 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 187.8, 161.3, 107.6, 67.3, 41.5, 25.2, 22.2, 14.4, 13.9. HRMS *m/z* (ESI) calcd for $C_9H_{14}N_2O_4Na$ $(M + Na)^+$ 237.0846, found 237.0835.



116

3-(Cyclohexanecarbonyl)-4--ethoxyfuroxan (116). According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), cyclohexane carboxaldehyde (54 μL, 0.45 mmol, 3.0 equiv), and potassium peroxodisulfate (100 mg, 0.38 mmol, 2.5 equiv) were reacted in CH_3CN:H_2O

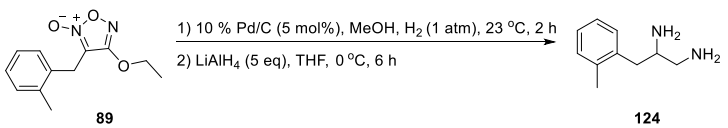
(1:1) (2.0 mL) at 80 ℃ for 1 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (6/1)) to afford **116** (14.1 mg, 0.06 mmol, 40% yield). Colorless oil. IR (neat): 2935, 2857, 1694, 1591, 1534, 1472, 1460, 1445, 1384, 1352, 1172, 1019, 963, 885, 830, 798, 678 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 4.52 (q, *J* = 7.0 Hz, 2H), 3.10–3.04 (m, 1H), 1.89–1.81 (m, 4H), 1.74–1.69 (m, 1H), 1.53 (t, *J* = 7.1 Hz, 3H), 1.45–1.18 (m, 5H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 189.6, 160.2, 105.9, 66.1, 47.1, 26.6, 24.6, 24.4, 13.3. HRMS *m/z* (ESI) calcd for $C_{11}H_{16}N_2O_4Na$ $(M + Na)^+$ 263.1002, found 263.1008.



117

3-(Carbamoyl)-4-ethoxyfuroxan (117). According to the general procedure, **25** (60.0 mg, 0.22 mmol, 1.0 equiv), formamide (27 μL, 0.66 mmol, 3.0 equiv), and potassium peroxodisulfate (150 mg, 0.55 mmol, 2.5equiv) were reacted in CH_3CN:H_2O (1:1) (2.4 mL) at 80 ℃ for 17 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (1/1)) to afford **117** (11.4 mg, 0.07 mmol, 30% yield). White solid; Mp, 86.3–87.9 ℃. IR (neat): 3435, 1705, 1685, 1558, 1542, 1485, 1391, 1352, 1169, 1112, 1017, 874, 848, 769, 644 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.38 (br, 1H), 6.09 (br, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 1.54 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 161.9, 155.6, 104.6, 67.8, 14.3. HRMS *m/z* (ESI) calcd for $C_5H_8N_3O_4$ $(M + H)^+$ 174.0509, found 174.0503.

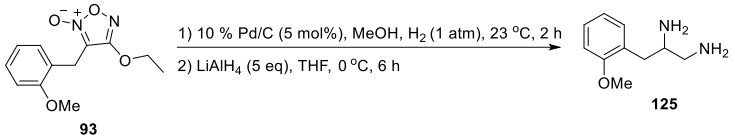
Experimental procedures for functionalization of R–H substrates via furoxan (Figure 8 in the main text)



89 **124**

3-(2-Methylphenyl)propane-1,2-diamine (124). Furoxan **89** (50 mg, 0.21 mmol, 1 equiv),

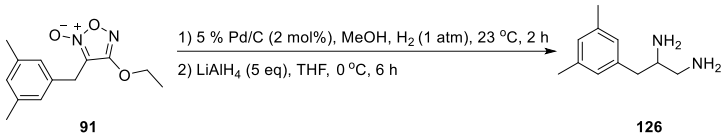
10% Pd/C (11.5 mg, 0.01 mmol, 0.05 equiv), and MeOH (2 mL) were added to a reaction vessel under argon. The atmosphere was exchanged to H_2 and kept using a balloon. The mixture was stirred at 23 ℃ for 2 h. The mixture was filtered through celite and concentrated in vacuo. To a suspension of $LiAlH_4$ (40.2 mg, 5 equiv) in anhydrous THF (4 mL) was added the crude material thus obtained at 0 ℃. The mixture was stirred for 6 h at 0 ℃, and the reaction was quenched by the subsequent addition of water (0.04 mL), 15% NaOH (0.04 mL), and water (0.12 mL). The mixture was filtered through celite, washed with hot THF and concentrated in vacuo. The crude residue was purified by preparative thin-layer chromatography on silica gel (CH_2Cl_2/MeOH (10/1) with 15% triethylamine) to afford **124** (11 mg, 0.07 mmol, 32% yield). Yellow oil; IR (neat): 3291, 2919, 1575, 1489, 1470, 1382, 1365, 1312, 1163, 1071, 820, 741, 728 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.17–7.11 (m, 4H), 3.00–2.94 (m, 1H), 2.84–2.76 (m, 2H), 2.60–2.48 (m, 2H), 2.33 (s, 3H), 1.56 (br, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 137.6, 136.5, 130.6, 130.1, 126.5, 126.1, 54.0, 48.5, 39.8, 19.7. HRMS *m/z* (ESI) calcd for $C_{10}H_{17}N_2$ $(M + H)^+$ 165.1386, found 165.1392.



93 125

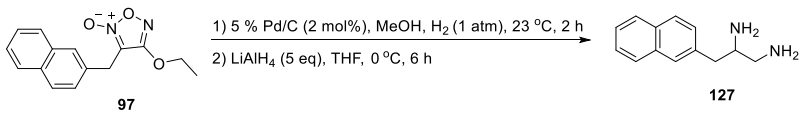
3-(2-Methoxyphenyl)propane-1,2-diamine (125). Furoxan **93** (80 mg, 0.32 mmol, 1 equiv), 10% Pd/C (17 mg, 0.02 mmol, 0.05 equiv), and MeOH (2 mL) were added to a reaction vessel under argon. The atmosphere was exchanged to H_2 and kept using a balloon. The mixture was stirred at 23 ℃ for 2 h. The mixture was filtered through celite and concentrated in vacuo. To a suspension of $LiAlH_4$ (60.3 mg, 5 equiv) in anhydrous THF (5 mL) was added the crude material thus obtained at 0 ℃. The mixture was stirred for 6 h at 0 ℃, and the reaction was quenched by the subsequent addition of water (0.06 mL), 15% NaOH (0.06 mL), and water (0.18 mL). The mixture was filtered through celite, washed with hot THF and concentrated in vacuo. The crude residue was purified by preparative thin-layer chromatography on silica gel (CH_2Cl_2/MeOH (10/1) with 15% triethylamine) to afford **125** (20 mg, 0.11 mmol, 35% yield). Yellow oil; IR (neat): 3356, 3277, 2917, 1598, 1584, 1492, 1463, 1438, 1240, 1049, 1026, 817, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.20 (td, *J* =

7.6, 1.7 Hz, 1H), 7.12 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.90–6.84 (m, 2H), 3.80 (s, 3H), 3.01–2.94 (m, 1H), 2.81–2.72 (m, 2H), 2.53 (d, *J* = 7.7 Hz, 1H), 2.49 (d, *J* = 7.6 Hz, 1H), 1.56 (br, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 157.8, 131.2, 127.7, 127.7, 120.5, 110.5, 55.3, 54.0, 48.3, 36.8. HRMS *m/z* (ESI) calcd for $C_{10}H_{17}N_2O$ $(M + H)^+$ 181.1335, found 181.1330.



91 126

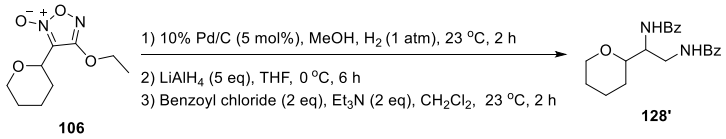
3-(3,5-Dimethylphenyl)propane-1,2-diamine (126). Furoxan **91** (50 mg, 0.2 mmol, 1.0 equiv), 5% Pd/C (8.6 mg, 0.004 mmol, 0.02 equiv), and MeOH (2 mL) were added to a reaction vessel under argon. The atmosphere was exchanged to H_2 and kept using a balloon. The mixture was stirred at 23 ℃ for 2 h. The mixture was filtered through celite and concentrated in vacuo. To a suspension of $LiAlH_4$ (38 mg, 5 equiv) in anhydrous THF (4 mL) was added the crude material thus obtained at 0 ℃. The mixture was stirred for 6 h at 0 ℃, and the reaction was quenched by the subsequent addition of water (0.04 mL), 15% NaOH (0.04 mL), and water (0.12 mL). The mixture was filtered through celite, washed with hot THF and concentrated in vacuo. The crude residue was purified by preparative thin-layer chromatography on silica gel (CH_2Cl_2/MeOH (10/1) with 15% triethylamine) to afford **126** (11.6 mg, 0.07 mmol, 33% yield). Colorless oil; IR (neat): 3276, 3011, 2195, 2851, 1604, 1462, 1375, 1036, 846, 706 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.86 (s, 1H), 6.81 (s, 2H), 2.99–2.92 (m, 1H), 2.80 (dd, *J* = 12.7, 4.1 Hz, 1H), 2.71 (dd, *J* = 13.3, 5.0 Hz, 1H), 2.58–2.51 (m, 1H), 2.43–2.38 (m, 1H), 2.29 (s, 6H), 1.72 (br, 4H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 139.1, 138.0, 127.9, 127.1, 55.1, 48.3, 42.2, 21.3. HRMS *m/z* (ESI) calcd for $C_{11}H_{18}N_2$ $(M + H)^+$ 179.1543, found 179.1540.



97 127

3-(Naphthalen-2-yl)propane-1,2-diamine (127). Furoxan **97** (60 mg, 0.22 mmol, 1.0 equiv), 5% Pd/C (9.45 mg, 0.004 mmol, 0.02 equiv), and MeOH (2 mL) were added to a reaction

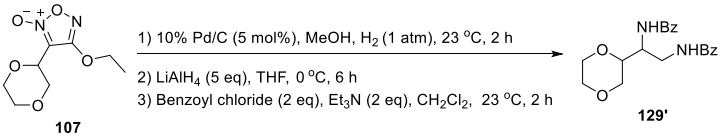
vessel under argon. The atmosphere was exchanged to H_2 and kept using a balloon. The mixture was stirred at 23 ℃ for 2 h. The mixture was filtered through celite and concentrated in vacuo. To a suspension of $LiAlH_4$ (42.2 mg, 5 equiv) in anhydrous THF (4 mL) was added the crude material thus obtained at 0 ℃. The mixture was stirred for 6 h at 0 ℃, and the reaction was quenched by the subsequent addition of water (0.04 mL), 15% NaOH (0.04 mL), and water (0.12 mL). The mixture was filtered through celite, washed with hot THF and concentrated in vacuo. The crude residue was purified by preparative thin-layer chromatography on silica gel (CH_2Cl_2/MeOH (10/1) with 15% triethylamine) to afford **127** (13.6 mg, 0.07 mmol, 31% yield). Yellow oil. IR (neat): 3357, 3272, 3049, 2915, 2848, 1598, 1506, 1442, 1364, 1270, 1124, 1017, 893, 856, 810, 747, 621 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.83–7.78 (m, 3H), 7.64 (s, 1H), 7.49–7.42 (m, 2H), 7.33 (dd, *J* = 8.4, 1.7 Hz, 1H), 3.10–3.04 (m, 1H), 2.95 (dd, *J* = 13.3, 4.9 Hz, 1H), 2.85 (dd, *J* = 12.6, 4.1 Hz, 1H), 2.68–2.57 (m, 2H), 1.55 (br, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 136.7, 133.5, 132.2, 128.2, 127.6, 127.6, 127.5, 126.1, 125.4, 55.0, 48.3, 42.5. HRMS *m/z* (ESI) calcd for $C_{13}H_{16}N_2$ $(M + H)^+$ 201.1386, found 201.1387.



106 128'

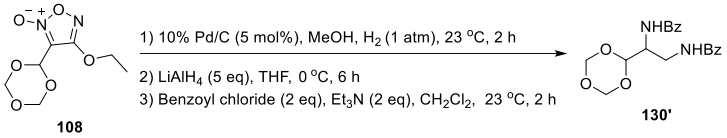
***N,N'*-Dibenzoyl 3-(oxan-2-yl)propane-1,2-diamine (128')**. Furoxan **106** (50 mg, 0.23 mmol, 1 equiv), 10% Pd/C (12.4 mg, 0.01 mmol, 0.05 equiv), and MeOH (2 mL) were added to a reaction vessel under argon. The atmosphere was exchanged to H_2 and kept using a balloon. The mixture was stirred at 23 ℃ for 2 h. The mixture was filtered through celite and concentrated in vacuo. To a suspension of $LiAlH_4$ (44 mg, 5 equiv) in anhydrous THF (4 mL) was added the crude material thus obtained at 0 ℃. The mixture was stirred for 6 h at 0 ℃, and the reaction was quenched by the subsequent addition of water (0.04 mL), 15% NaOH (0.04 mL), and water (0.12 mL). The mixture was filtered through celite, washed with hot THF and concentrated in vacuo. The obtained crude material containing diamine **128** was dissolved in 4 mL CH_2Cl_2, then benzoyl chloride (53 μL, 0.46 mmol, 2 equiv) and Et_3N (64 μL, 0.46 mmol, 2 equiv) were added into the solution. The mixture was stirred under argon at

23 ℃ for 2 h, after which the volatiles were removed under vacuum. The residue was purified by preparative thin-layer chromatography on silica gel (CH_2Cl_2/MeOH (20/1)) to afford **128'** (24.7 mg, 0.07 mmol, 30% yield). White solid; Mp, 150–151.7 ℃. IR (neat): 3322, 2937, 2848, 1633, 1578, 1538, 1491, 1295, 1206, 1089, 1047, 930, 895, 800, 692, 649 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.81–7.78 (m, 4H), 7.51–7.36 (m, 7H), 7.28 (s, 1H), 4.36–4.27 (m, 1H), 4.04 (d, *J* = 10.4 Hz, 1H), 3.89–3.38 (m, 4H), 1.90–1.43 (m, 6H). $^{13}C\{^1H\}$ NMR (100MHz, $CDCl_3$) δ = 168.6, 168.3, 134.3, 134.2, 131.7, 131.5, 128.7, 128.6, 127.2, 127.1, 79.2, 69.1, 53.5, 41.7, 28.6, 26.1, 23.3. HRMS *m/z* (ESI) calcd for $C_{21}H_{24}N_2O_3Na$ $(M + Na)^+$ 375.1679, found 375.1674.



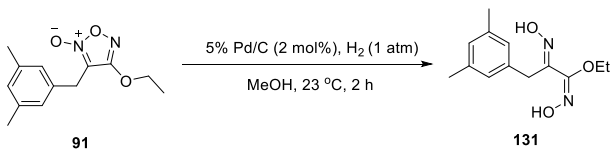
***N,N'*-Dibenzoyl 3-(1,4-dioxan-2-yl)propane-1,2-diamine (129').** Furoxan **107** (50 mg, 0.23 mmol, 1 equiv), 10% Pd/C (12.3 mg, 0.01 mmol, 0.05 equiv), and MeOH (2 mL) were added to a reaction vessel under argon. The atmosphere was exchanged to H_2 and kept using a balloon. The mixture was stirred at 23 ℃ for 2 h. The mixture was filtered through celite and concentrated in vacuo. To a suspension of $LiAlH_4$ (43.5 mg, 5 equiv) in anhydrous THF (4 mL) was added the crude material thus obtained at 0 ℃. The mixture was stirred for 6 h at 0 ℃, and the reaction was quenched by the subsequent addition of water (0.04 mL), 15% NaOH (0.04 mL), and water (0.12 mL). The mixture was filtered through celite, washed with hot THF and concentrated in vacuo. The obtained crude material containing diamine **129** was dissolved in 4 mL CH_2Cl_2, then benzoyl chloride (53 μL, 0.46 mmol, 2 equiv) and Et_3N (64 μL, 0.46 mmol, 2 equiv) were added into the solution. The mixture was stirred under argon at 23 ℃ for 2 h, after which the volatiles were removed under vacuum. The residue was purified by preparative thin-layer chromatography on silica gel (CH_2Cl_2/MeOH (20/1)) to afford **129'** (32.5 mg, 0.09 mmol, 40% yield). White solid; Mp, 181.5–183.2 ℃. IR (neat): 3876, 3315, 2850, 1633, 1539, 1490, 1354, 1296, 1125, 1092, 970, 899, 885, 691, 662 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 7.85–7.81 (m, 2H), 7.77–7.74 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.51–7.46 (m, 2H), 7.43–7.37 (m, 4H), 7.04 (t, *J* = 5.7 Hz, 1H), 4.38–4.31 (m, 1H),

3.89–3.81 (m, 3H), 3.74–3.67 (m, 4H), 3.65–3.55 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 169.5, 168.1, 133.9, 133.8, 131.9, 131.8, 128.7, 128.7, 127.3, 127.1, 76.6, 69.3, 67.2, 66.6, 51.3, 41.9. HRMS *m/z* (ESI) calcd for $C_{20}H_{22}N_2O_4Na$ $(M + Na)^+$ 377.1472, found 377.1469.



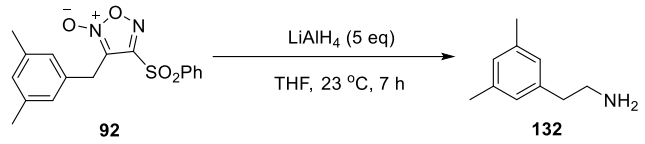
108 **130'**

***N,N'*-Dibenzoyl 3-(1,3,5-trioxan-2-yl)propane-1,2-diamine (130').** Furoxan **108** (50 mg, 0.23 mmol, 1 equiv), 10% Pd/C (12.2 mg, 0.01 mmol, 0.05 equiv), and MeOH (2 mL) were added to a reaction vessel under argon. The atmosphere was exchanged to H_2 and kept using a balloon. The mixture was stirred at 23 ℃ for 2 h. The mixture was filtered through celite and concentrated in vacuo. To a suspension of $LiAlH_4$ (43.2 mg, 5 equiv) in anhydrous THF (4 mL) was added the crude material thus obtained at 0 ℃. The mixture was stirred for 6 h at 0 ℃, and the reaction was quenched by the subsequent addition of water (0.04 mL), 15% NaOH (0.04 mL), and water (0.12 mL). The mixture was filtered through celite, washed with hot THF and concentrated in vacuo. The obtained crude material containing diamine **130** was dissolved in 4 mL CH_2Cl_2, then benzoyl chloride (53 μL, 0.46 mmol, 2 equiv) and Et_3N (64 μL, 0.46 mmol, 2 equiv) were added into the solution. The mixture was stirred under argon at 23 ℃ for 2 h, after which the volatiles were removed under vacuum. The residue was purified by preparative thin-layer chromatography on silica gel (CH_2Cl_2/MeOH (20/1)) to afford **130'** (31 mg, 0.09 mmol, 38% yield). White solid; Mp, 172.1–173.4 ℃. IR (neat): 3372, 3333, 2858, 1637, 1579, 1539, 1494, 1390, 1318, 1168, 1113, 1055, 1037, 989, 956, 691 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84–7.78 (m, 4H), 7.51–7.31 (m, 8H), 5.27 (d, *J* = 2.6 Hz, 1H), 5.22 (t, *J* = 5.4 Hz, 2H), 5.09–5.05 (m, 2H), 4.47–4.41 (m, 1H), 4.02–3.94 (m, 1H), 3.82–3.76 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 169.0, 168.5, 134.1, 133.7, 131.9, 131.7, 128.7, 128.6, 127.3, 127.2, 99.7, 93.3, 93.3, 53.4, 39.7. HRMS *m/z* (ESI) calcd for $C_{19}H_{20}N_2O_5Na$ $(M + Na)^+$ 379.1264, found 379.1261.



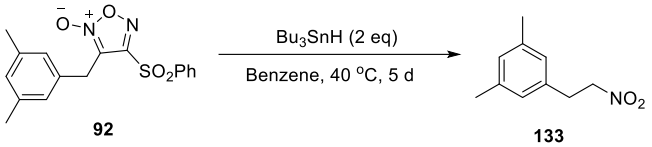
91 **131**

Ethyl3-(3,5-dimethylphenyl)-N-hydroxy-2-(hydroxyimino)propanimidate (131). Furoxan **91** (250 mg, 1.0 mmol, 1 equiv), 5% Pd/C (42.6 mg, 0.02 mmol, 0.02equiv), and MeOH (16 mL) were added to a reaction vessel under argon. The atmosphere was exchanged to H_2 and kept using a balloon. The mixture was stirred at 23 ℃ for 2 h. The mixture was filtered through celite and concentrated in vacuo to afford **131** (252 mg, 1.0 mmol, 100% yield). Brownish solid; Mp, 102.2–102.7 ℃. IR (neat): 3163, 3016, 2978, 2868, 1601, 1546, 1489, 1470, 1441, 1427, 1369, 1317, 1221, 1115, 1048, 992, 797, 686 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 9.86 (br, 1H), 7.64 (br, 1H), 6.89 (s, 2H), 6.86 (s, 1H), 4.03 (q, *J* = 7.0 Hz, 2H), 3.91 (s, 2H), 2.28 (s, 6H), 1.28 (t, *J* = 7.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 154.6, 152.4, 137.9, 135.1, 128.3, 126.9, 63.3, 30.8, 21.3, 14.2. HRMS *m/z* (ESI) calcd for $C_{13}H_{18}N_2O_3$ $(M + H)^+$ 251.1390, found 251.1390.



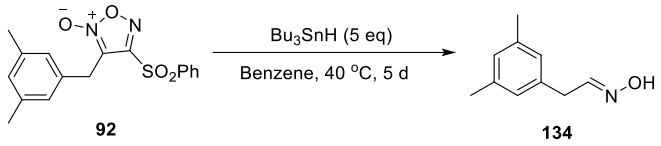
92 132

2-(3,5-Dimethylphenyl)ethan-1-amine (132). To a suspension of $LiAlH_4$ (44.1 mg, 1.16 mmol, 5.0 equiv) in anhydrous THF (4 mL) was added portionwise **92** (80 mg, 0.23 mmol, 1.0 equiv) at 0 ℃. The mixture was stirred for 7 h at 23 ℃ and the reaction was quenched by subsequent addition of water (0.04 mL), 15% NaOH (0.04mL), and water (0.12 mL). The mixture was filtered through celite, washed with hot THF and concentrated in vacuo. The crude residue was purified by preparative thin-layer chromatography on silica gel (CH_2Cl_2/MeOH (10/1) with 15 % triethylamine) to afford **132** (11 mg, 0.07 mmol, 32% yield). Yellow oil; IR (neat): 3309, 2917, 1606, 1575, 1476, 1447, 1380, 1321, 1306, 1034, 842, 822, 702, 668 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 6.86 (s, 1H), 6.82 (s, 2H), 2.95 (t, *J* = 6.9 Hz, 2H), 2.68 (t, *J* = 6.9 Hz, 2H), 2.30 (d, *J* = 0.7 Hz, 6H), 1.26 (br, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 139.8, 138.0, 127.9, 126.8, 43.7, 40.1, 21.4. HRMS *m/z* (ESI) calcd for $C_{10}H_{16}N$ $(M + H)^+$ 150.1277, found 150.1283.



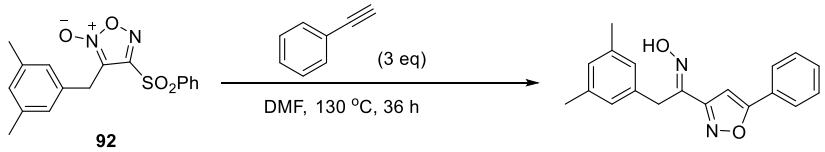
92 133

1,3-Dimethyl-5-(2-nitroethyl)benzene (133). Furoxan **92** (80 mg, 0.23 mmol, 1.0 equiv), tributyltin hydride (125 μL, 0.46 mmol, 2 equiv) and benzene (1.2 mL) were added to a reaction vessel. The mixture was stirred at 40 ℃ for 5 d. The solvents were removed with a rotary evaporator. The crude residue was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **133** (14 mg, 0.08 mmol, 34% yield). Yellow oil; IR (neat): 2919, 1607, 1548, 1431, 1377, 846, 695, 553 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.91 (s, 1H), 6.82 (s, 2H), 4.58 (t, *J* = 7.5 Hz, 2H), 3.24 (t, *J* = 7.5 Hz, 2H), 2.29 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 138.6, 135.5, 129.1, 126.4, 76.4, 33.4, 21.3. HRMS *m/z* (FI) calcd for $C_{10}H_{14}NO_2$ $(M)^+$ 179.0964, found 179.0943.



92 134

***N*-[2-(3,5-Dimethylphenyl)ethylidene]hydroxylamine (134).** Furoxan **92** (80 mg, 0.23 mmol, 1.0 equiv), tributyltin hydride (312 μL, 1.16 mmol, 5.0 equiv) and benzene (1.2 mL) were added to a reaction vessel. The mixture was stirred at 40 ℃ for 5 d. The solvents were removed with a rotary evaporator. The crude residue was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **134** (17.6 mg, 0.11 mmol, 46% yield). White solid; Mp, 82.1–83.5 ℃. IR (neat): 3150, 2916, 1605, 1454, 1407, 1329, 1260, 1056, 932, 844, 815, 695 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.32 (br, 1H), 6.82–6.76 (m, 4H), 3.60 (d, *J* = 5.3 Hz, 2H), 2.23 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 151.2, 138.4, 136.5, 128.3, 126.6, 31.5, 21.2. HRMS *m/z* (ESI) calcd for $C_{10}H_{14}NO$ $(M + H)^+$ 164.1070, found 164.1065.



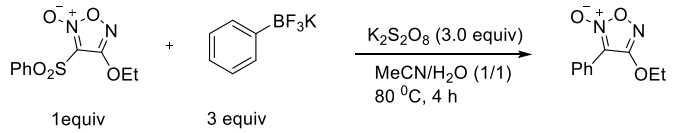
92 135

***N*-[2-(3,5-Dimethylphenyl)-1-(5-phenyl-1,2-oxazol-3-yl)-ethylidene]hydroxylamine (135).** Furoxan **92** (80 mg, 0.23 mmol, 1.0 equiv), phenylacetylene (77 μL, 0.70 mmol, 3.0 equiv) and DMF (4.0 mL) were added to a reaction vessel. The mixture was stirred under Ar at

130 °C for 36 h. Extracted thrice with EtOAc, washed five times with H_2O, the organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The crude residue was purified by preparative thin-layer chromatography on silica gel ($CHCl_3$) to afford **135** (20 mg, 0.07 mmol, 28% yield). Yellow solid; Mp, 149.2–151.7 ℃. IR (neat): 3174, 2917, 1602, 1574, 1434, 1247, 1101, 1009, 829, 898, 759, 682 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.48 (br, 1H), 7.78–7.74 (m, 2H), 7.47–7.42 (m, 3H), 7.03 (s, 2H), 6.83 (s, 1H), 6.79 (s, 1H), 4.20 (s, 2H), 2.26 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 170.2, 160.6, 151.7, 138.0, 135.9, 130.4, 129.0, 128.3, 127.2, 126.9, 125.9, 97.1, 31.0, 21.3. HRMS *m/z* (ESI) calcd for $C_{19}H_{18}N_2O_2Na$ $(M + Na)^+$ 329.1260, found 329.1253.

Experimental procedures for substrate scope in arylation of furoxan (Table 8 in the main text)

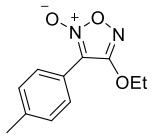
General procedure with product 151 as a representative example



1equiv 3 equiv

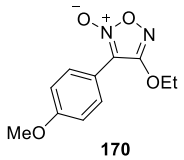
25 **151**

4-Ethoxy-3-(phenylsulfonyl)furoxan 25 (40.0 mg, 0.15 mmol, 1.0 equiv), $PhBF_3K$ (81.7 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The reaction was extracted thrice with EtOAc, the organic layer was dried over Na_2SO_4, filtrated, and concentrated in vacuo. The crude residue was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (20/1)) to afford **151** (11.6 mg, 38% yield). **4-Ethoxy-3-phenylfuroxan** (**151**), white solid; Mp, 75.4−76.3 ℃. IR (neat): 2914, 1590, 1550, 1497, 1436, 1391, 1358, 1320, 1161, 1114, 1069, 1022, 967, 877, 850, 766, 735, 690, 653, 571 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.16–8.14 (m, 2H), 7.53–7.47 (m, 3H), 4.57 (q, *J* = 7.1 Hz, 2H), 1.56 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.3, 130.4, 128.8, 126.2, 122.6, 107.6, 66.9, 14.5. HRMS *m/z* (APCI) calcd for $C_{10}H_{11}O_3N_2$ $(M + H)^+$ 207.0764, found 207.0763.



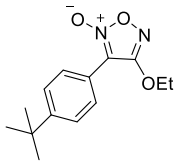
169

4-Ethoxy-3-(4-Methylphenyl)furoxan (169) According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), potassium 4-methylphenyl trifluoroborate (87.9 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (7/1)) to afford **169** (9.8 mg, 30% yield). White solid; Mp, 74.6−75.5 ℃. IR (neat): 2985, 1598, 1550, 1517, 1466, 1437, 1387, 1335, 1317, 1185, 1115, 1018, 968, 879, 844, 807, 733, 589 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.06–8.02 (m, 2H), 7.32–7.30 (m, 2H), 4.56 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.56 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.3, 140.9, 129.6, 126.1, 119.6, 107.8, 66.9, 21.6, 14.5. HRMS *m/z* (ESI) calcd for $C_{11}H_{12}O_3N_2Na$ $(M + Na)^+$ 243.0740, found 243.0741.



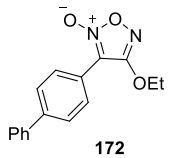
170

4-Ethoxy-3-(4-Methoxyphenyl)furoxan (170) According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), potassium 4-methoxyphenyltrifluoroborate (95.0 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (7/1)) to afford **170** (10.5 mg, 30% yield). White solid; Mp, 78.2−79.6 ℃. IR (neat): 2934, 1593, 1554, 1518, 1454, 1385, 1335, 1303, 1255, 1186, 1166, 1116, 1025, 964, 839, 811, 737, 594 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.15–8.11 (m, 2H), 7.04–7.00 (m, 2H), 4.56 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.56 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.3, 161.0, 127.9, 114.7, 114.3, 107.7, 66.9, 55.4, 14.5. HRMS *m/z* (ESI) calcd for $C_{11}H_{12}O_4N_2Na$ $(M + Na)^+$ 259.0689, found 259.0691.



171

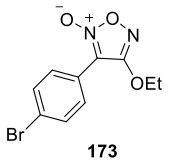
4-Ethoxy-3-(4-*t*-butylphenyl)furoxan (171) According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), potassium 4-*t*-butylphenyl trifluoroborate (106.6 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (7/1)) to afford **171** (15.8 mg, 41% yield). White solid; Mp, 32.4−33.6 ℃. IR (neat): 2963, 1602, 1549, 1464, 1385, 1337, 1321, 1171, 1126, 1111, 1018, 970, 879, 842, 833, 704, 567, 556 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.09−8.05 (m, 2H), 7.54−7.51 (m, 2H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.55 (t, *J* = 7.1 Hz, 3H), 1.34 (s, 9H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.3, 153.9, 126.0, 125.8, 119.6, 107.6, 66.8, 35.0, 31.1, 14.5. HRMS *m/z* (ESI) calcd for $C_{14}H_{18}O_3N_2Na$ $(M + Na)^+$ 285.1210, found 285.1212.



172

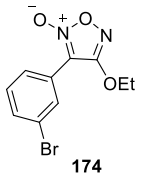
4-Ethoxy-3-(4-biphenyl)furoxan (172) According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), potassium 4-biphenyl trifluoroborate (115.5 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (7/1)) to afford **172** (14.0 mg, 34% yield). White solid; Mp, 104.5−105.3 ℃. IR (neat): 1598, 1545, 1466, 1387, 1355, 1333, 1319, 1169, 1118, 1020, 975, 876, 844, 763, 725, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.25–8.22 (m, 2H), 7.76–7.72 (m, 2H), 7.65–7.62 (m, 2H), 7.50–7.46 (m, 2H), 7.42–7.38 (m, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 1.59 (t, *J* = 7.1 Hz, 3H).$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.3, 143.0, 139.9, 129.0,

128.1, 127.4, 127.1, 126.6, 121.4, 107.6, 67.0, 14.5. HRMS *m/z* (ESI) calcd for $C_{16}H_{14}O_3N_2Na$ $(M + Na)^+$ 305.0897, found 305.0898.



173

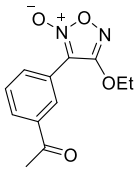
4-Ethoxy-3-(4-bromophenyl)furoxan (173) According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), potassium 4-bromophenyl trifluoroborate (116.8 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (7/1)) to afford **173** (10.8 mg, 26% yield). White solid; Mp, 78.6−79.4 ℃. IR (neat): 2980, 1599, 1563, 1551, 1499, 1467, 1387, 1335, 1305, 1166, 1114, 1072, 1018, 1008, 970, 878, 824, 761, 689 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.07–8.03 (m, 2H), 7.66–7.62 (m, 2H), 4.58 (q, *J* = 7.1 Hz, 2H), 1.57 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.0, 132.1, 127.5, 124.8, 121.5, 107.2, 67.1, 14.5. HRMS *m/z* (APCI) calcd for $C_{10}H_{10}O_3N_2Br$ $(M + H)^+$ 284.9869, found 284.9871.



174

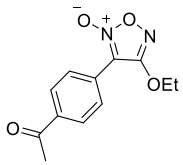
4-Ethoxy-3-(3-bromophenyl)furoxan (174) According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), potassium 3-bromophenyl trifluoroborate (116.8 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (7/1)) to afford **174** (9.0 mg, 21% yield). White solid; Mp, 75.2−76.4 ℃. IR (neat): 2920, 1596, 1556, 1543, 1489, 1381, 1358, 1336, 1165, 1114, 1075, 1022, 978, 896, 870, 856, 785, 692, 680, 646 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.32 (t, *J* = 1.8 Hz, 1H), 8.12–8.09 (m, 1H), 7.62–7.59 (m, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 1.58 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 161.9,

133.5, 130.3, 128.8, 124.6, 124.5, 123.0, 106.7, 67.2, 14.5. HRMS *m/z* (APCI) calcd for $C_{10}H_{10}O_3N_2Br$ $(M + H)^+$ 284.9869, found 284.9871.



157

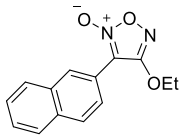
4-Ethoxy-3-(3-acetylphenyl)furoxan (157) According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), potassium 3-acetylphenyl trifluoroborate (100.3 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (7/1)) to afford **157** (6.6 mg, 18% yield). White solid; Mp, 74.3−75.6 ℃. IR (neat): 1691, 1597, 1554, 1502, 1421, 1390, 1358, 1331, 1254, 1168, 1119, 1016, 985, 860, 813, 721, 685, 649, 597, 553 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ = 8.76−8.75 (m, 1H), 8.38−8.35 (m, 1H), 8.07−8.05 (m, 1H), 7.65−7.61 (m, 1H), 4.60 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 1.59 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 197.2, 162.1, 137.5, 130.2, 129.8, 129.3, 126.2, 123.3, 107.1, 67.2, 26.6, 14.4. HRMS *m/z* (ESI) calcd for $C_{12}H_{12}O_4N_2Na$ $(M + Na)^+$ 271.0689, found 271.0691.



175

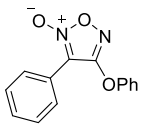
4-Ethoxy-3-(4-acetylphenyl)furoxan (175) According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), potassium 4-acetylphenyl trifluoroborate (100.3 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **175** (3.8 mg, 10% yield). White solid; Mp,

109.2−110.1 ℃. IR (neat): 2914, 1687, 1594, 1550, 1466, 1407, 1355, 1316, 1257, 1171, 1117, 1021, 958, 840, 716, 604, 591 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.29−8.26 (m, 2H), 8.09−8.06 (m, 2H), 4.60 (q, *J* = 7.1 Hz, 2H), 2.64 (s, 3H), 1.58 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 197.1, 162.0, 137.9, 128.6, 126.9, 126.2, 107.1, 67.2, 26.7, 14.4. HRMS *m/z* (APCI) calcd for $C_{12}H_{13}O_4N_2$ $(M + H)^+$ 249.0870, found 249.0871.



176

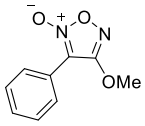
4-Ethoxy-3-(2-naphthyl)furoxan (176) According to the general procedure, **25** (40.0 mg, 0.15 mmol, 1.0 equiv), potassium 2-naphthylphenyl trifluoroborate (103.9 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (20/1)) to afford **176** (4.0 mg, 11% yield). White solid; Mp, 69.8−70.7 ℃. IR (neat): 2920, 1604, 1590, 1549, 1487, 1476, 1394, 1342, 1147, 1117, 1027, 899, 856, 813, 752, 736, 709, 581 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.73 (d, *J* = 0.8 Hz, 1H), 8.18 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.95−7.93 (m, 2H), 7.88−7.86 (m, 1H), 7.60−7.53 (m, 2H), 4.62 (q, *J* = 7.1 Hz, 2H), 1.61 (t, *J* = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.4, 133.8, 132.8, 128.9, 128.6, 127.7, 127.7, 126.9, 126.8, 122.4, 119.9, 107.9, 67.0, 14.5. HRMS *m/z* (ESI) calcd for $C_{14}H_{12}O_3N_2Na$ $(M + Na)^+$ 279.0740, found 279.0742.



181

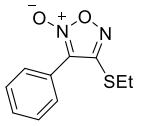
4-Phenoxy-3-phenylfuroxan (181) According to the general procedure, 4-Phenoxy-3-(phenylsulfonyl)furoxan[15] (47.0 mg, 0.15 mmol, 1.0 equiv), potassium phenyl trifluoroborate (81.6 mg, 0.44 mmol, 3.0 equiv), potassium peroxodisulfate (120.0 mg, 0.44 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.5 mL) were added to a flame-dried schlenk flask

under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **181** (11.5 mg, 31% yield). White solid; Mp, 107.5−108.6 ℃. IR (neat): 2917, 1604, 1542, 1483, 1467, 1429, 1335, 1318, 1191, 1066, 970, 842, 765, 723, 685, 648 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22−8.19 (m, 2H), 7.57−7.51 (m, 3H), 7.50−7.45 (m, 2H), 7.40−7.36 (m, 2H), 7.34−7.30 (m, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.0, 152.7, 130.7, 130.1, 129.0, 126.6, 126.4, 122.1, 120.1, 107.9. HRMS *m/z* (APCI) calcd for $C_{14}H_{11}O_3N_2$ $(M + H)^+$ 255.0764, found 255.0765.



182

4-Methoxy-3-phenylfuroxan (182) According to the general procedure, 4-Methoxy-3-(phenylsulfonyl)furoxan[15] (40.0 mg, 0.16 mmol, 1.0 equiv), potassium phenyl trifluoroborate (86.2 mg, 0.47 mmol, 3.0 equiv), potassium peroxodisulfate (126.6 mg, 0.47 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.6 mL) were added to a flame-dried schlenk flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (3/1)) to afford **182** (9.3 mg, 31% yield). White solid; Mp, 65.8−66.6 ℃. IR (neat): 2917, 1598, 1557, 1471, 1443, 1414, 1320, 1199, 1161, 1073, 999, 842, 766, 740, 690, 643 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14−8.11 (m, 2H), 7.53−7.45 (m, 3H), 4.22 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 162.9, 130.5, 128.8, 126.2, 122.4, 107.7, 57.5. HRMS *m/z* (APCI) calcd for $C_9H_9O_3N_2$ $(M + H)^+$ 193.0608, found 193.0608.



183

4-Ethylsulfanyl-3-phenylfuroxan (183) According to the general procedure, 4-Ethylsulfanyl-3-(phenylsulfonyl)furoxan[15] (30.0 mg, 0.10 mmol, 1.0 equiv), potassium phenyl trifluoroborate (57.6 mg, 0.31 mmol, 3.0 equiv), potassium peroxodisulfate (84.7 mg, 0.31 mmol, 3.0 equiv) and CH_3CN:H_2O (1:1) (1.0 mL) were added to a flame-dried schlenk

flask under argon. The mixture was stirred at 80 ℃ for 4 h. The crude material was purified by preparative thin-layer chromatography on silica gel (Hexane/EtOAc (8/1)) to afford **183** (7.0 mg, 30% yield). White solid; Mp, 32.4−33.3 ℃. IR (neat): 1573, 1503, 1437, 1393, 1247, 1121, 1100, 1024, 953, 823, 766, 726, 688, 666 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91−7.87 (m, 2H), 7.55−7.47 (m, 3H), 3.28 (q, *J* = 7.4 Hz, 2H), 1.49 (t, *J* = 7.4 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ = 154.4, 130.7, 129.0, 127.4, 122.5, 114.3, 25.6, 14.1. HRMS *m/z* (APCI) calcd for $C_{10}H_{11}O_2N_2S$ $(M + H)^+$ 223.0536, found 223.0536.

Procedure for the Suzuki coupling reaction[84]

The reaction was performed in a Schlenk flask. To a degassed solution of 4-Ethoxy-3-(4-bromophenyl)furoxan **173** (30 mg, 0.11 mmol, 1.0 equiv) in 1,2-dimethoxyethane (0.8 mL), $Pd(PPh_3)_4$ (3.6 mg, ca. 3 mol%) was added, and the mixture was stirred under argon for 40 min. Phenylboronic acid (16.7 mg, 0.14 mmol, 1.3 equiv) was added, and the mixture was degassed by pumping argon filling. Then a freshly prepared degassed solution of sodium carbonate (22.3 mg, 0.21 mmol, 2.0 equiv) in water (0.1 mL) was added, and the mixture was refluxed for 6 h, cooled, diluted with water, and extracted with EtOAc for three times. The combined extracts were dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by preparative thin-layer chromatography on silica gel (hexane/EtOAc (3/1)) to afford **172** (25.5 mg, 86% yield).

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Appendix I: list of publication

1. Furoxan Incorporation into C−H Bonds Enabling Nitrogen Containing Functional Group Installation into the Same.

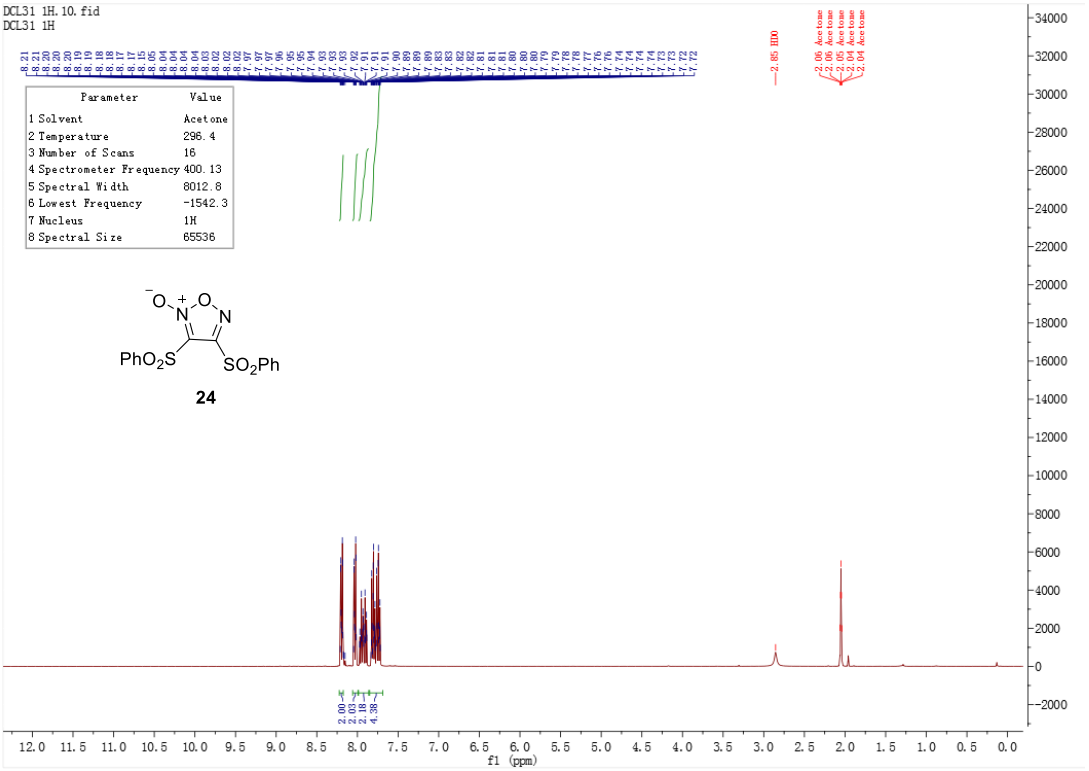
   Dong, C.; Zhao, X.; Katsuragi, Y.; Kim, H.; Hayashi, M.; Matsubara, R. *J. Org. Chem.* **2021**, *86*, 15807−15817.

2. Directarylation of Furoxan Using Potassium Aryltrifluoroborates.

   Dong, C.; Hayashi, M.; Matsubara, R. *Tetrahedron* (submitted)

Appendix II: ^{1}H and ^{13}C spectra of published compounds and arylation substrate scope

1. Furoxan Incorporation into C−H Bonds Enabling Nitrogen Containing Functional Group Installation into the Same.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DCL31 1H
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7 Nucleus 1H
8 Spectral Size 65536
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SO2Ph
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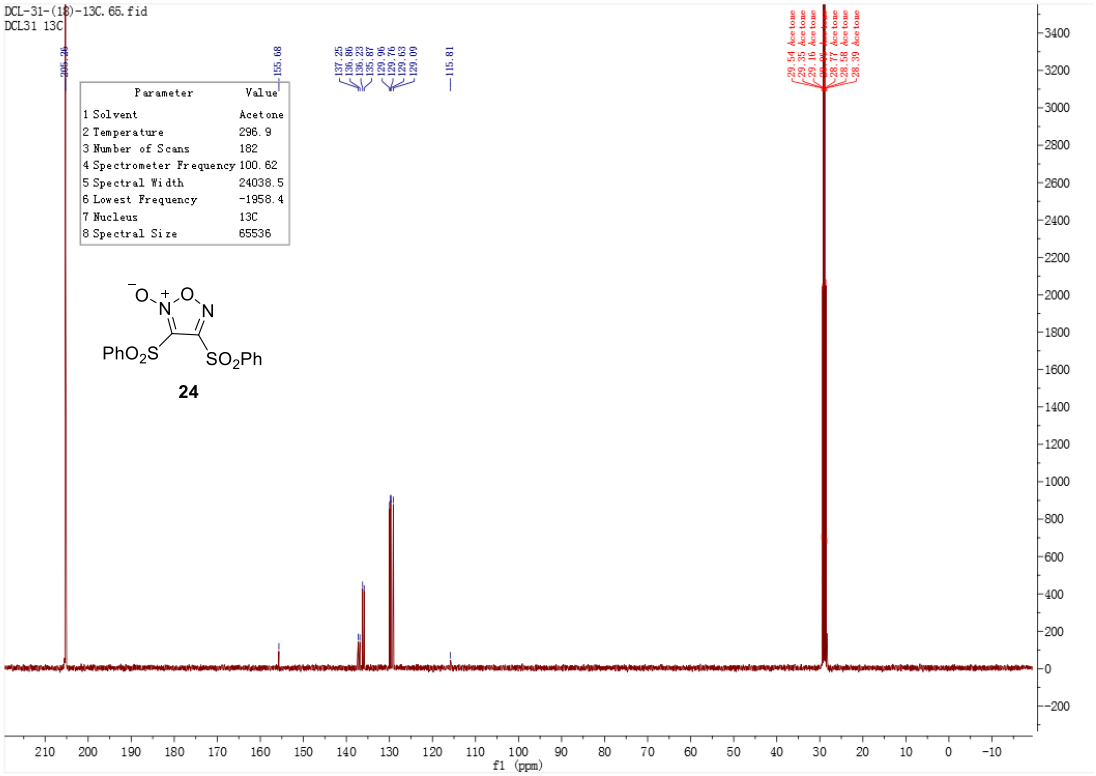
f1 (ppm)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DCL31 13C
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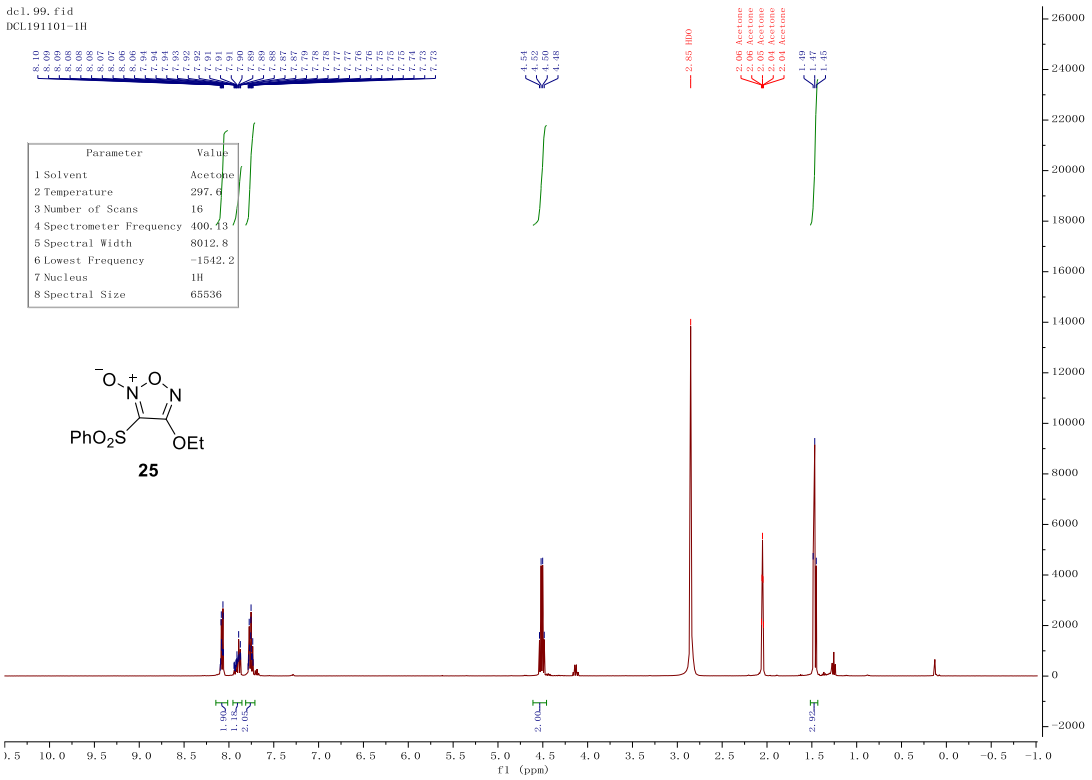
f1 (ppm)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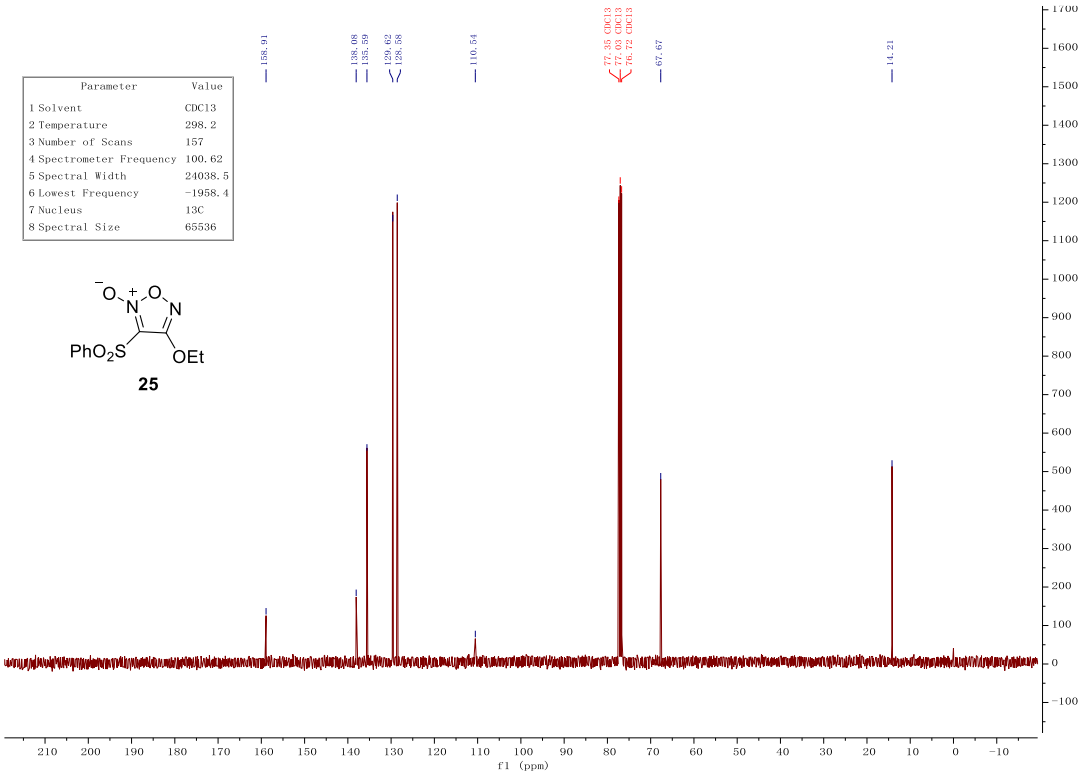
f1 (ppm)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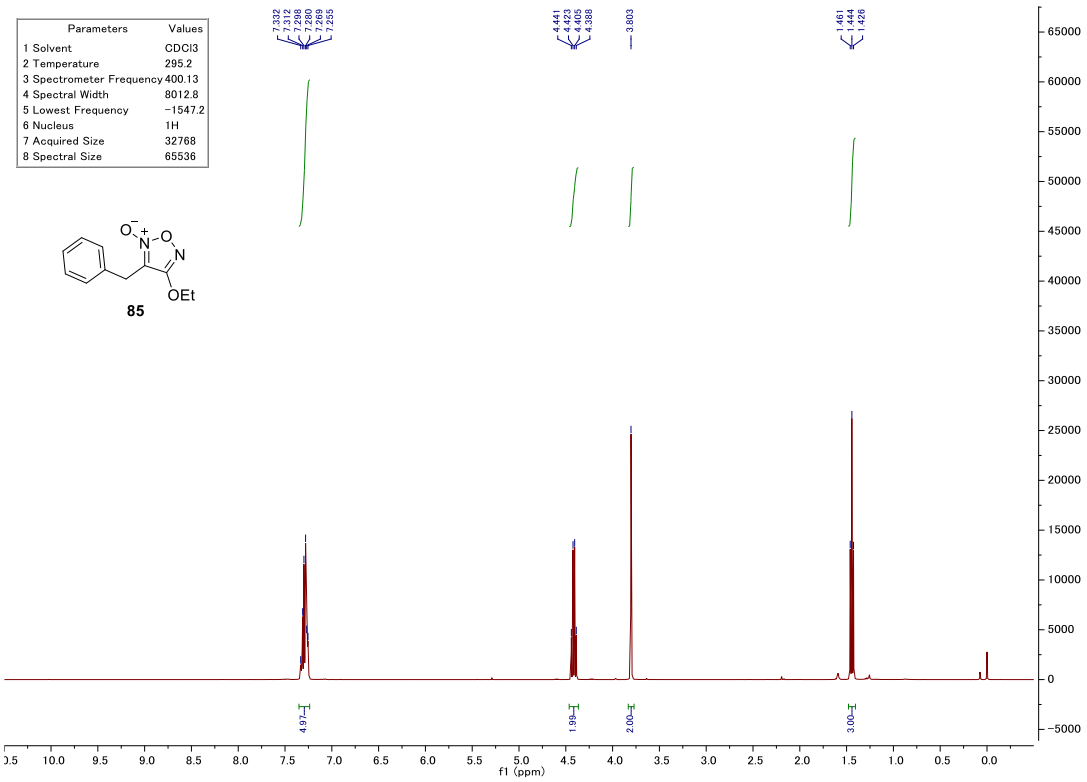
PhO2S
OEt
25
f1 (ppm)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5 Lowest Frequency −1547.2
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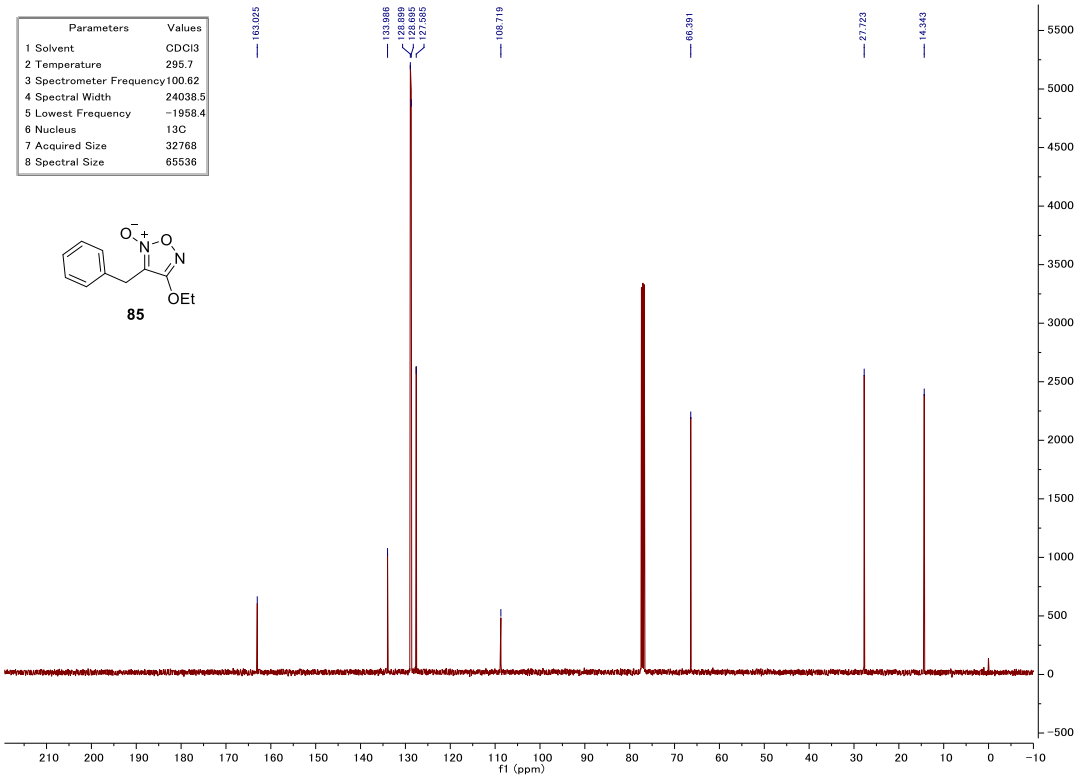
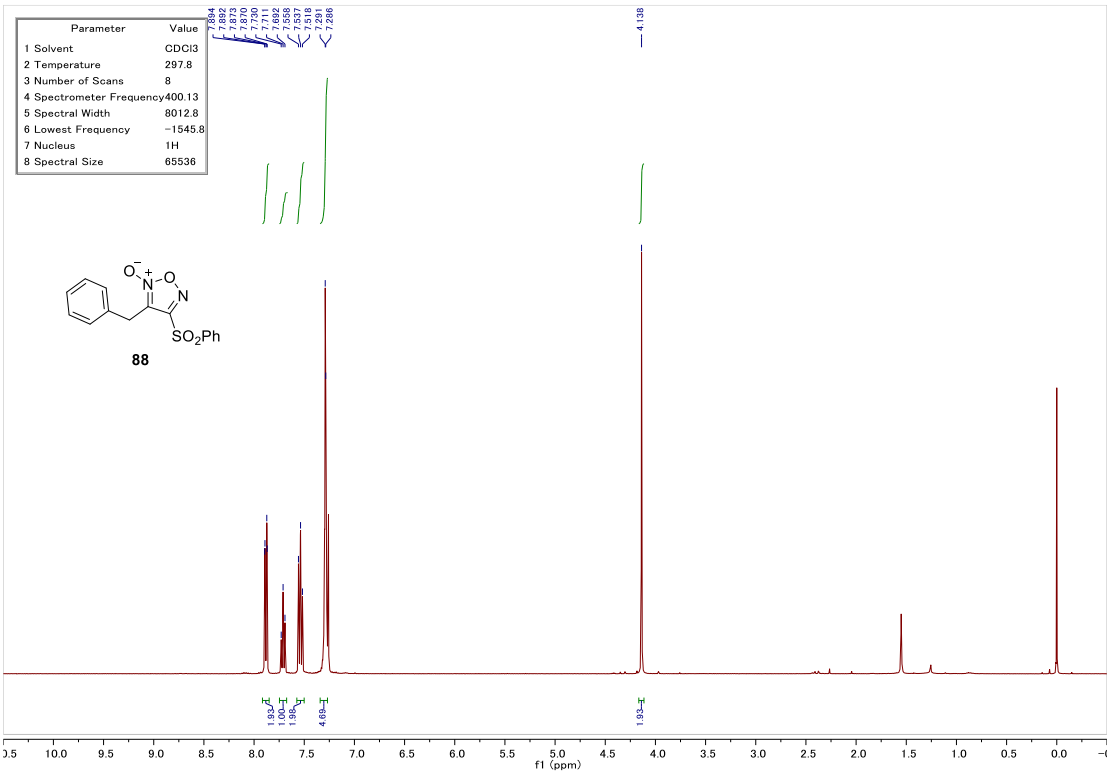
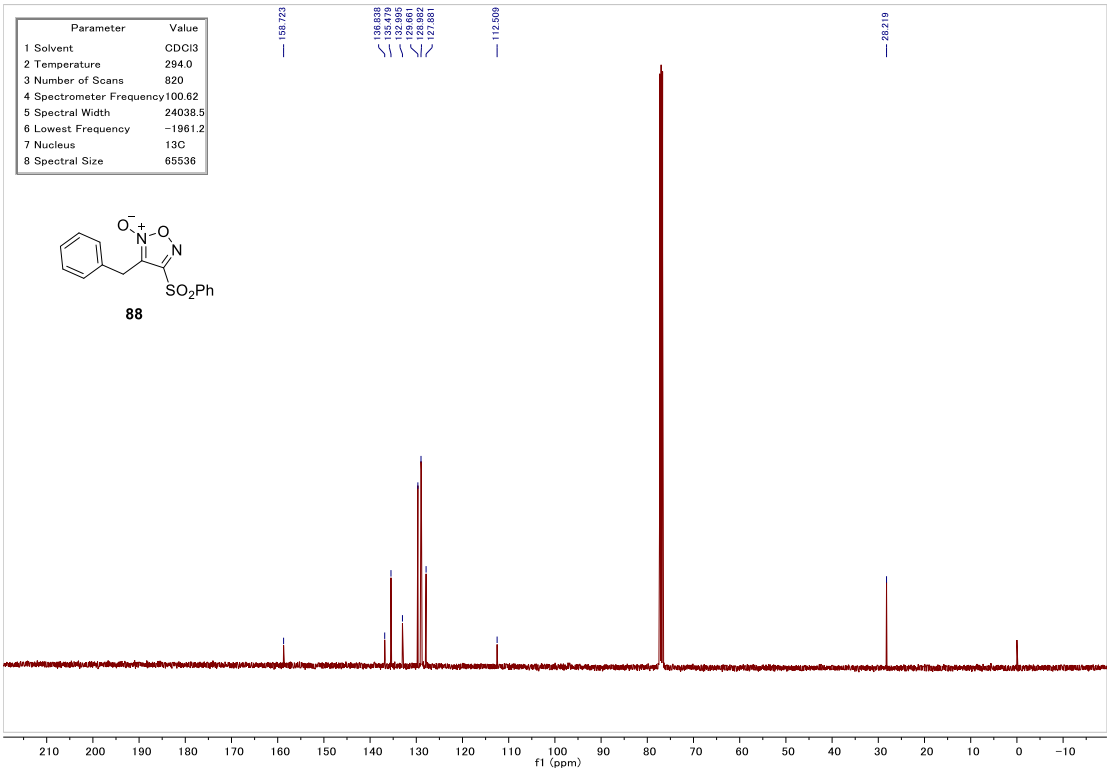
7.312
7.298
7.290
7.269
7.255
4.441
4.423
4.405
4.388
3.803
1.461
1.444
1.426
4.97
1.99
2.00
3.00
f1 (ppm)
85


Parameters Values
1 Solvent CDCl3
2 Temperature 295.7
3 Spectrometer Frequency 100.62
4 Spectral Width 24038.5
5 Lowest Frequency −1958.4
6 Nucleus 13C
7 Acquired Size 32768
8 Spectral Size 65536
163.025
133.986
128.899
128.695
127.585
108.719
66.391
27.723
14.343
f1 (ppm)
85

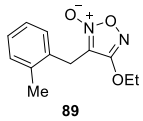

Parameter Value
1 Solvent CDCl3
2 Temperature 297.8
3 Number of Scans 8
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.8
7 Nucleus 1H
8 Spectral Size 65536
7.894
7.892
7.873
7.870
7.730
7.711
7.692
7.558
7.537
7.518
7.286
4.138
1.93
1.00
1.96
4.69
1.93
f1 (ppm)

88


Parameter Value
1 Solvent CDCl3
2 Temperature 294.0
3 Number of Scans 820
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1961.2
7 Nucleus 13C
8 Spectral Size 65536
158.723
136.838
134.479
132.995
129.661
128.982
127.581
112.509
28.219
f1 (ppm)

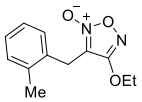
88

Parameter	Value
1 Solvent	CDCl3
2 Temperature	299.8
3 Number of Scans	16
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	−1550.0
7 Nucleus	1H
8 Acquired Size	32768
9 Spectral Size	65536

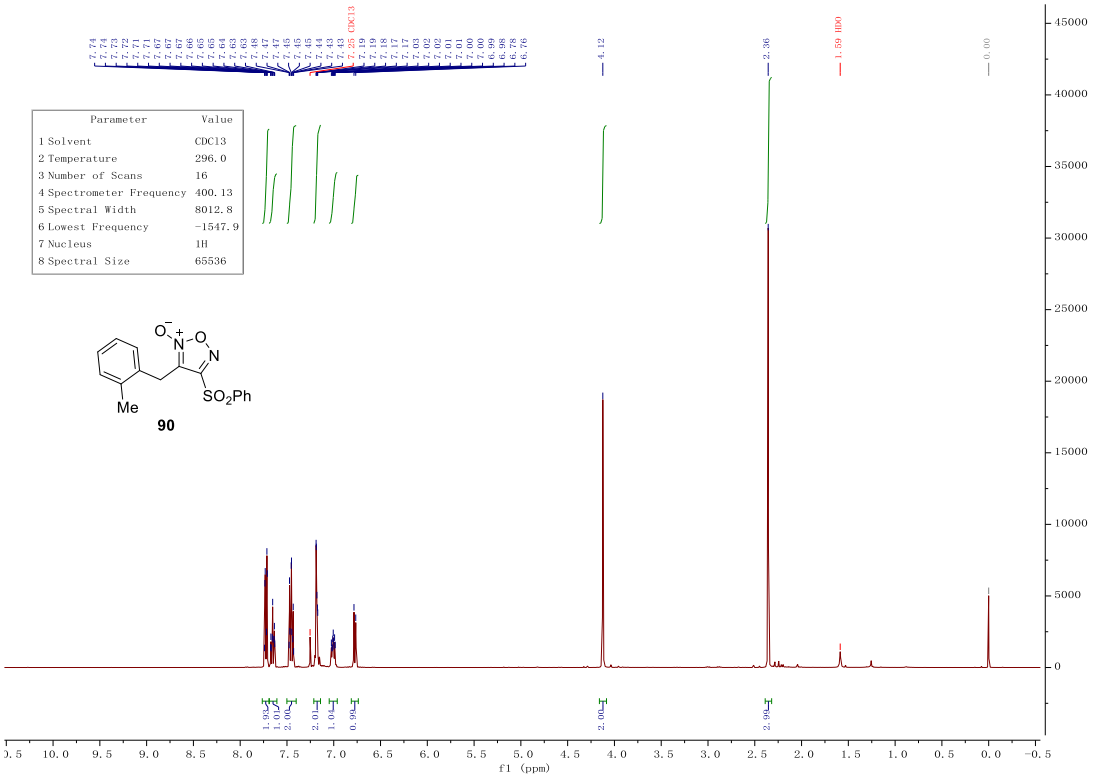


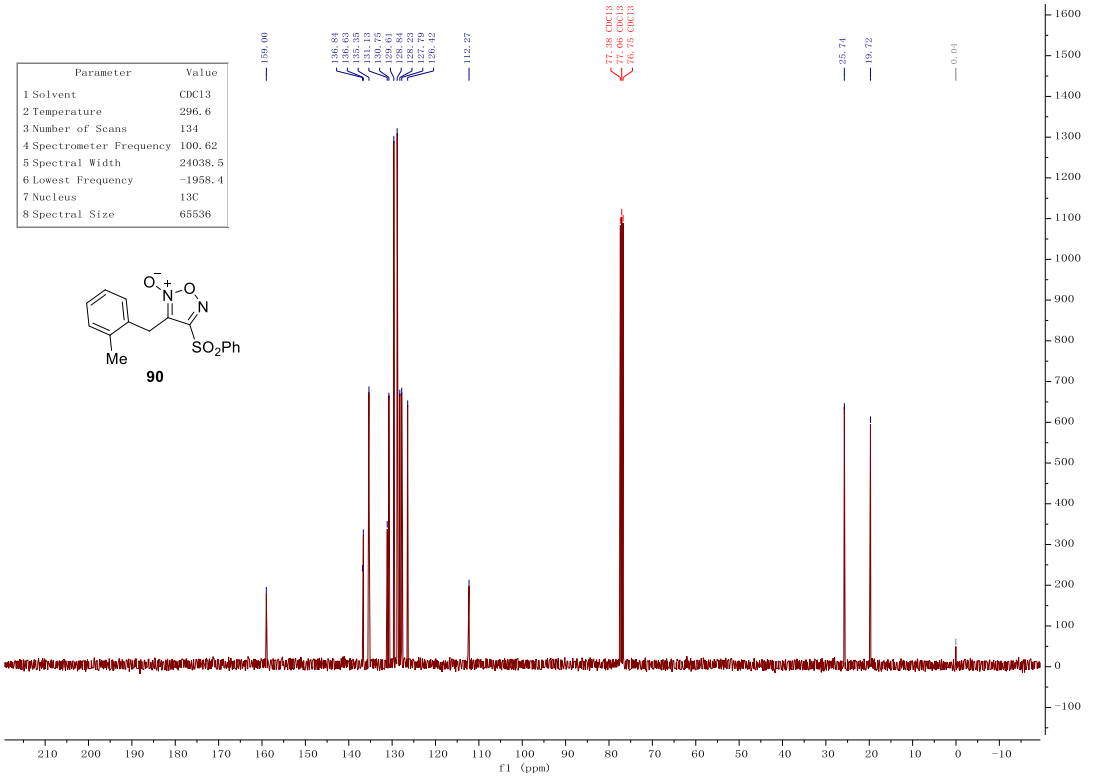
89

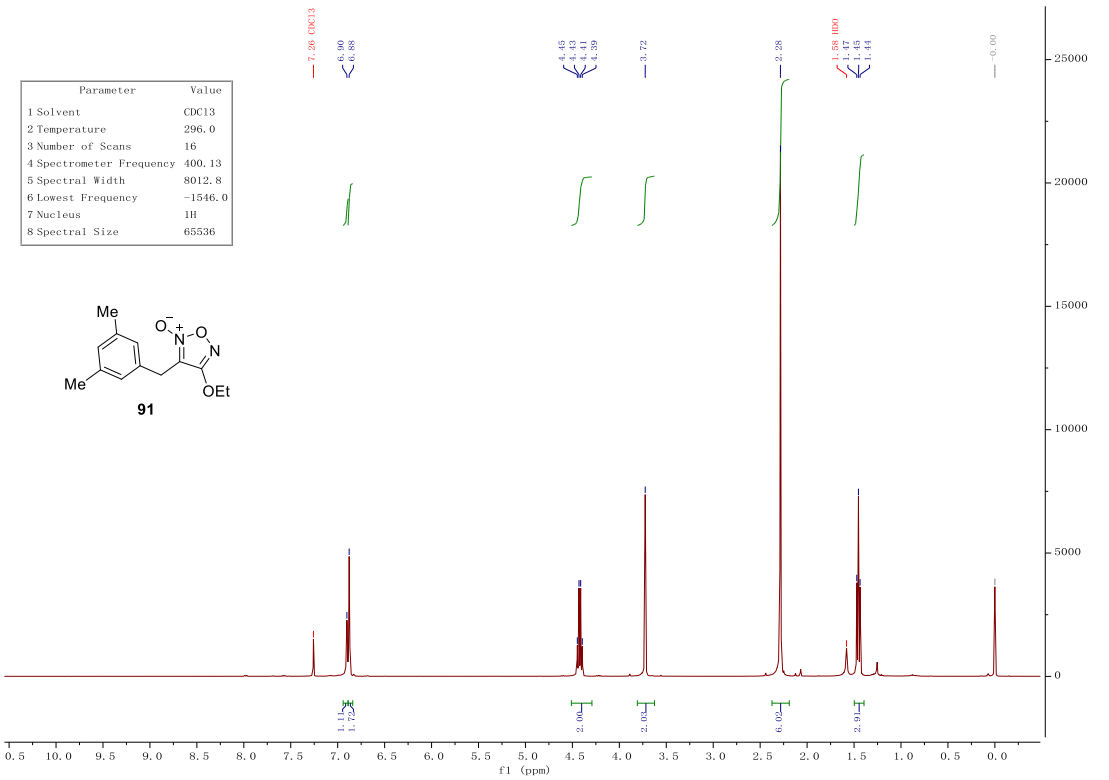
Parameter	Value
1 Solvent	CDCl3
2 Temperature	300.2
3 Number of Scans	91
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	−1958.4
7 Nucleus	13C
8 Acquired Size	32768
9 Spectral Size	65536

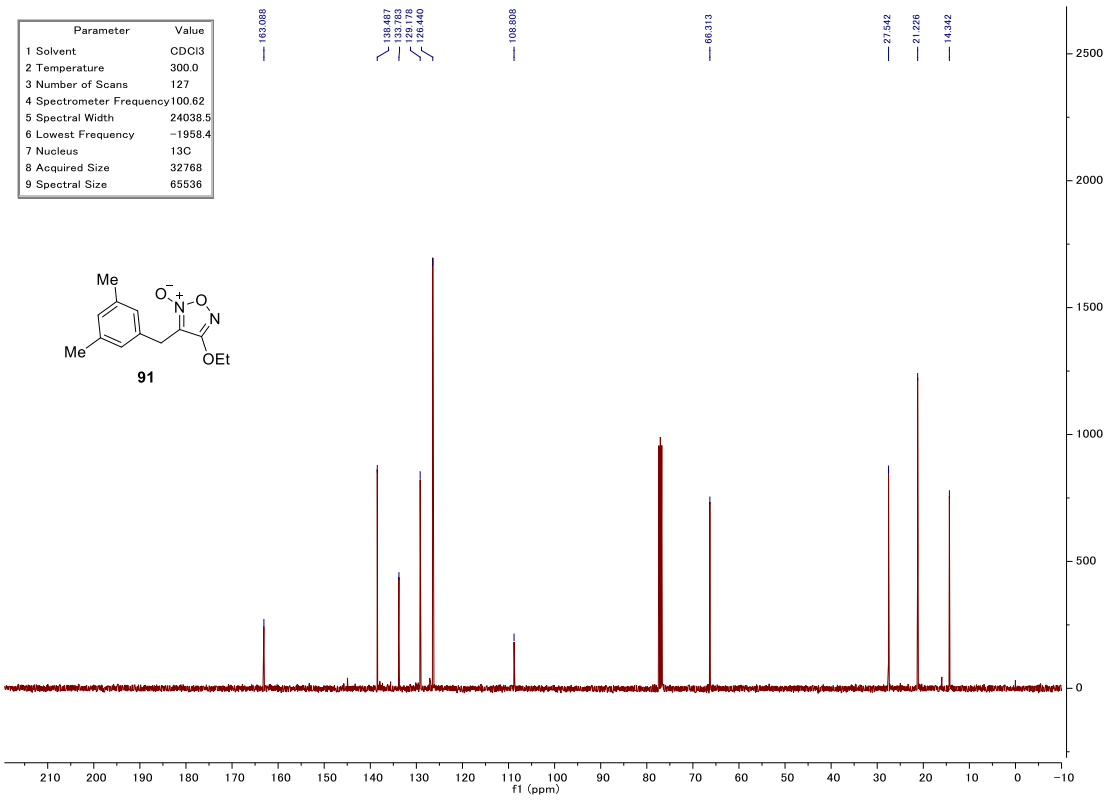


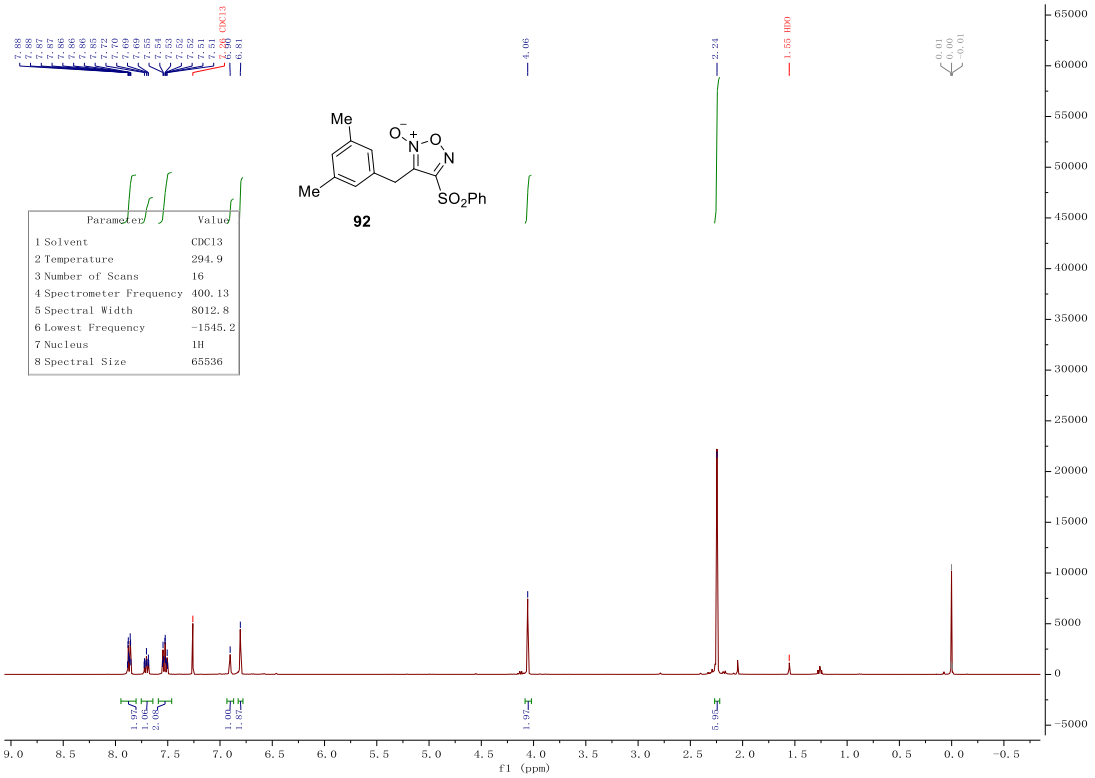
89

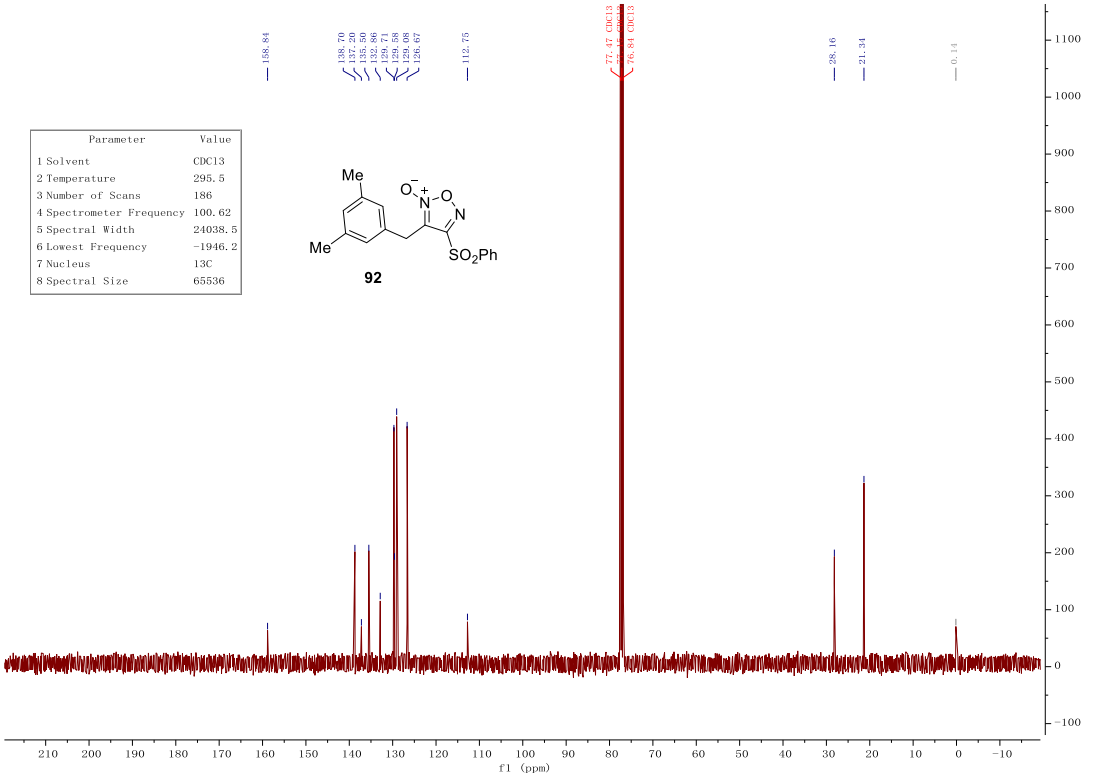

Parameter Value
1 Solvent CDCl3
2 Temperature 296.0
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1547.9
7 Nucleus 1H
8 Spectral Size 65536
Me
SO2Ph
90
f1 (ppm)

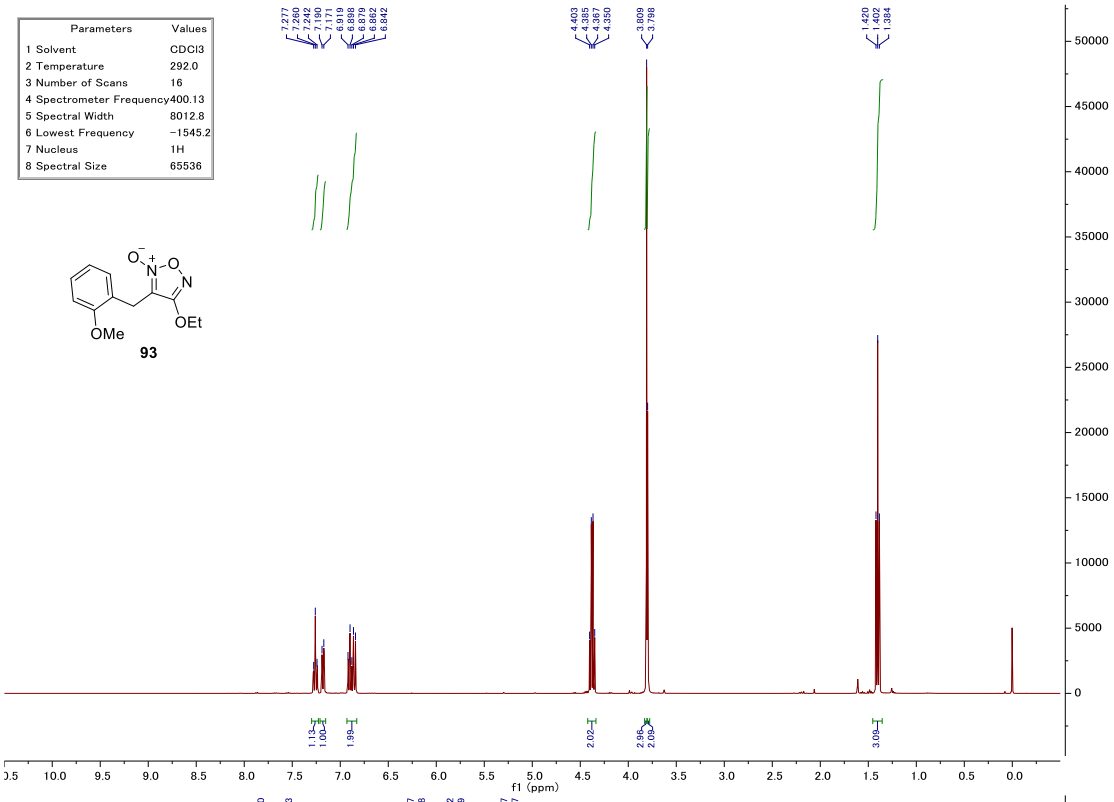

Parameter Value
1 Solvent CDCl3
2 Temperature 296.6
3 Number of Scans 134
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
Me
SO2Ph
90
f1 (ppm)

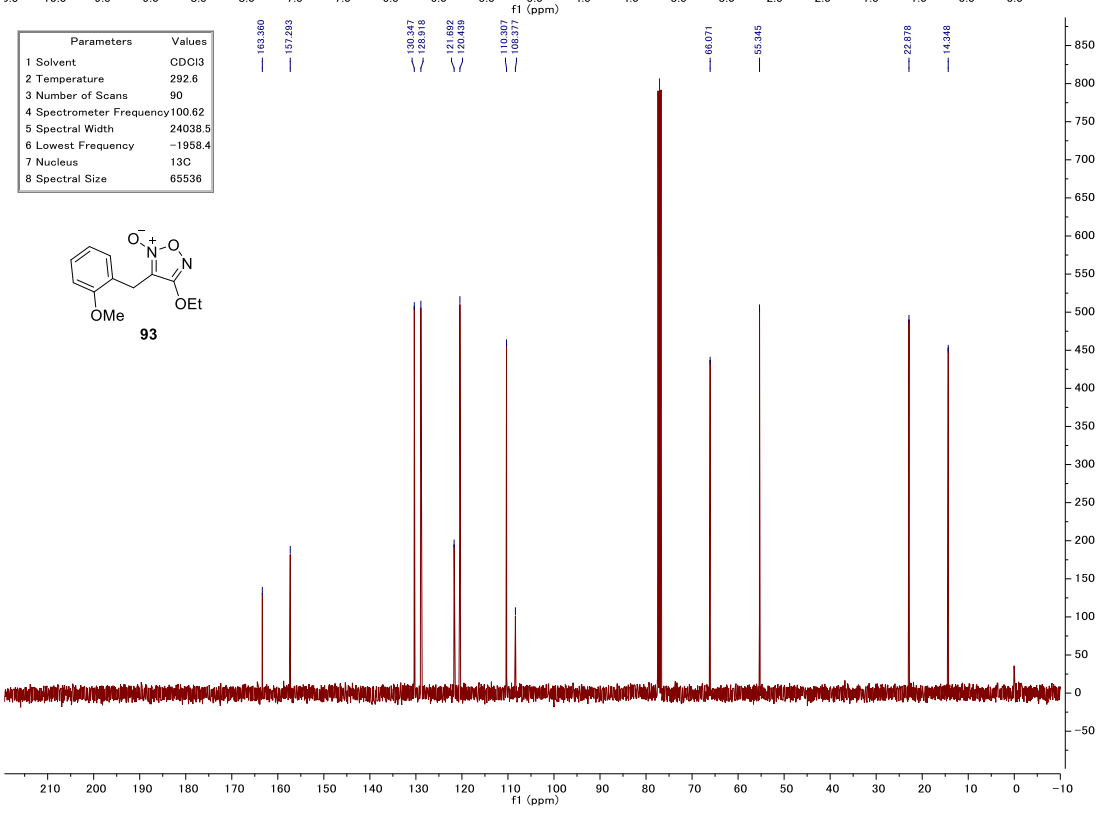

Parameter Value
1 Solvent CDCl3
2 Temperature 296.0
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1546.0
7 Nucleus 1H
8 Spectral Size 65536
7.26 CDCl3
6.90
6.88
4.45
4.43
4.41
4.39
3.72
2.28
1.58 H2O
1.47
1.45
1.44
0.00
Me
Me
OEt
91
f1 (ppm)

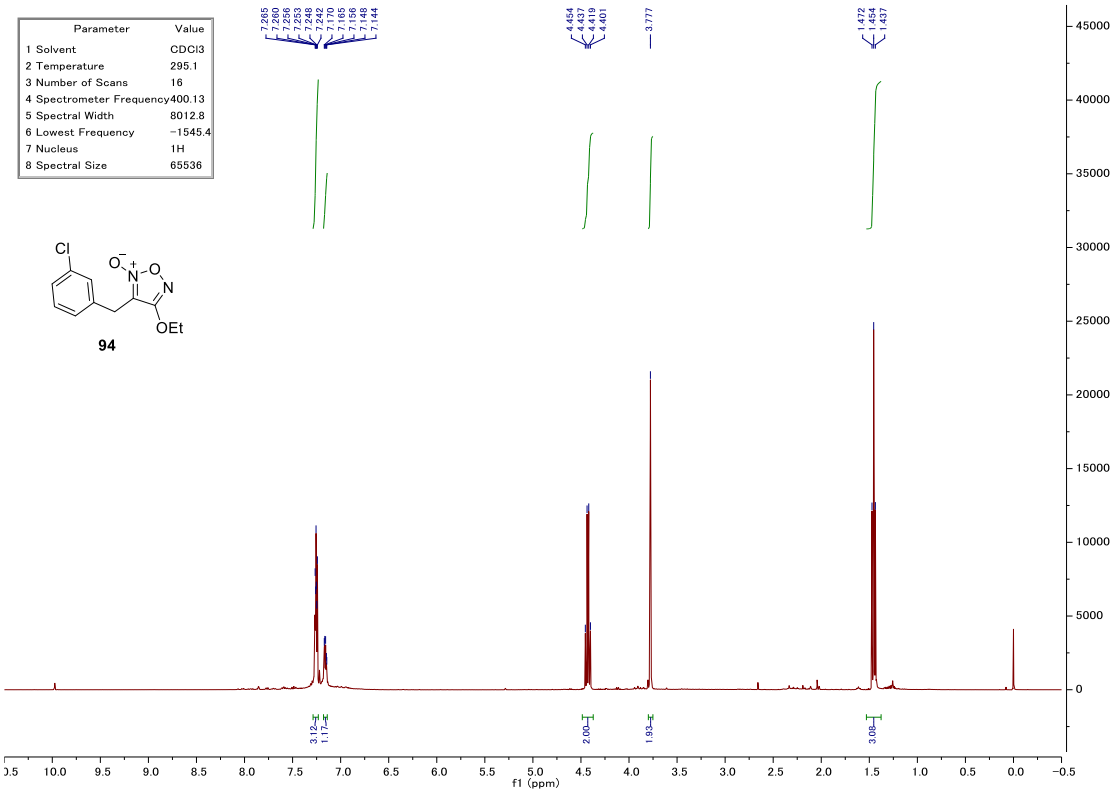

Parameter Value
1 Solvent CDCl3
2 Temperature 300.0
3 Number of Scans 127
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Acquired Size 32768
9 Spectral Size 65536
163.088
138.487
133.783
129.178
128.440
108.808
66.313
27.542
21.226
14.342
Me
Me
OEt
91
f1 (ppm)


Me
Me
SO2Ph
92
Parameter Value
1 Solvent CDCl3
2 Temperature 294.9
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.2
7 Nucleus 1H
8 Spectral Size 65536
f1 (ppm)


Me
Me
SO2Ph
92
Parameter Value
1 Solvent CDCl3
2 Temperature 295.5
3 Number of Scans 186
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1946.2
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

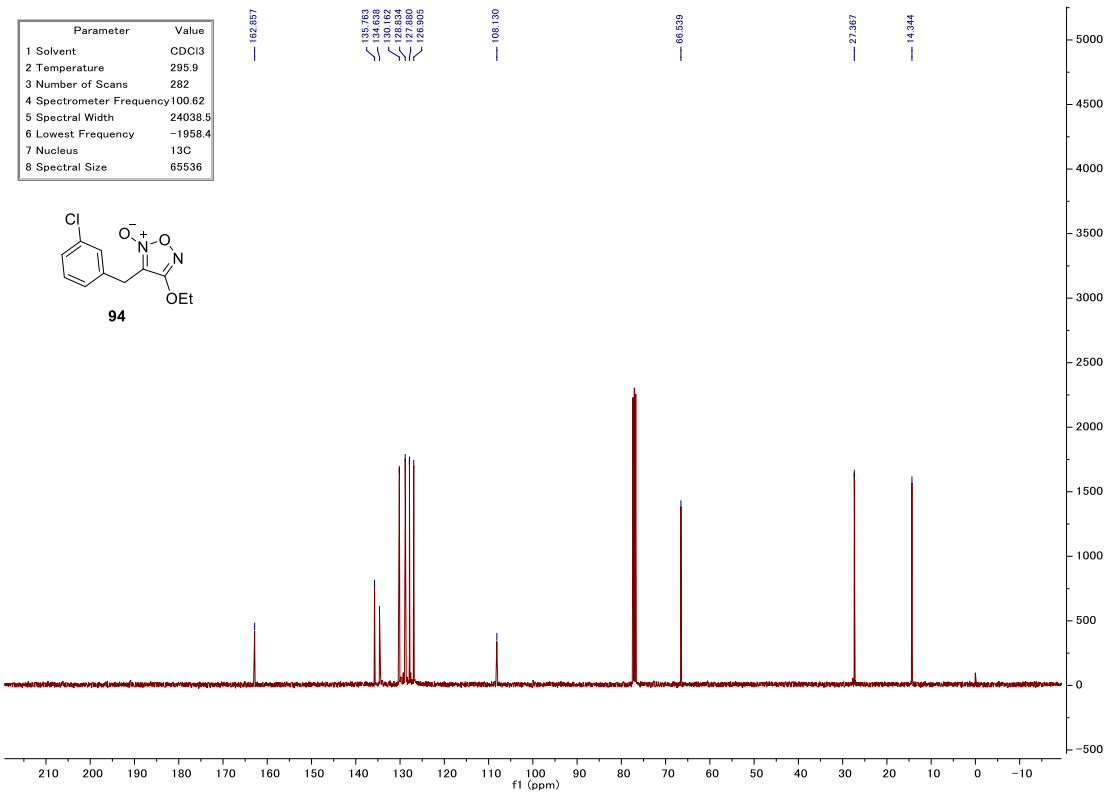

Parameters Values
1 Solvent CDCl3
2 Temperature 292.0
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.2
7 Nucleus 1H
8 Spectral Size 65536
7.277
7.260
7.242
7.190
7.171
6.919
6.898
6.879
6.882
6.842
4.403
4.385
4.367
4.350
3.809
3.798
1.420
1.402
1.384
OMe
OEt
93
f1 (ppm)


Parameters Values
1 Solvent CDCl3
2 Temperature 292.6
3 Number of Scans 90
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
163.360
157.293
130.347
129.918
121.692
120.439
110.307
108.377
66.071
55.345
22.878
14.348
OMe
OEt
93
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 295.1
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.4
7 Nucleus 1H
8 Spectral Size 65536
7.265
7.260
7.256
7.253
7.246
7.242
7.170
7.165
7.156
7.148
7.144
4.454
4.437
4.419
4.401
3.777
1.472
1.454
1.437
3.12
1.17
2.00
1.93
3.08
f1 (ppm)

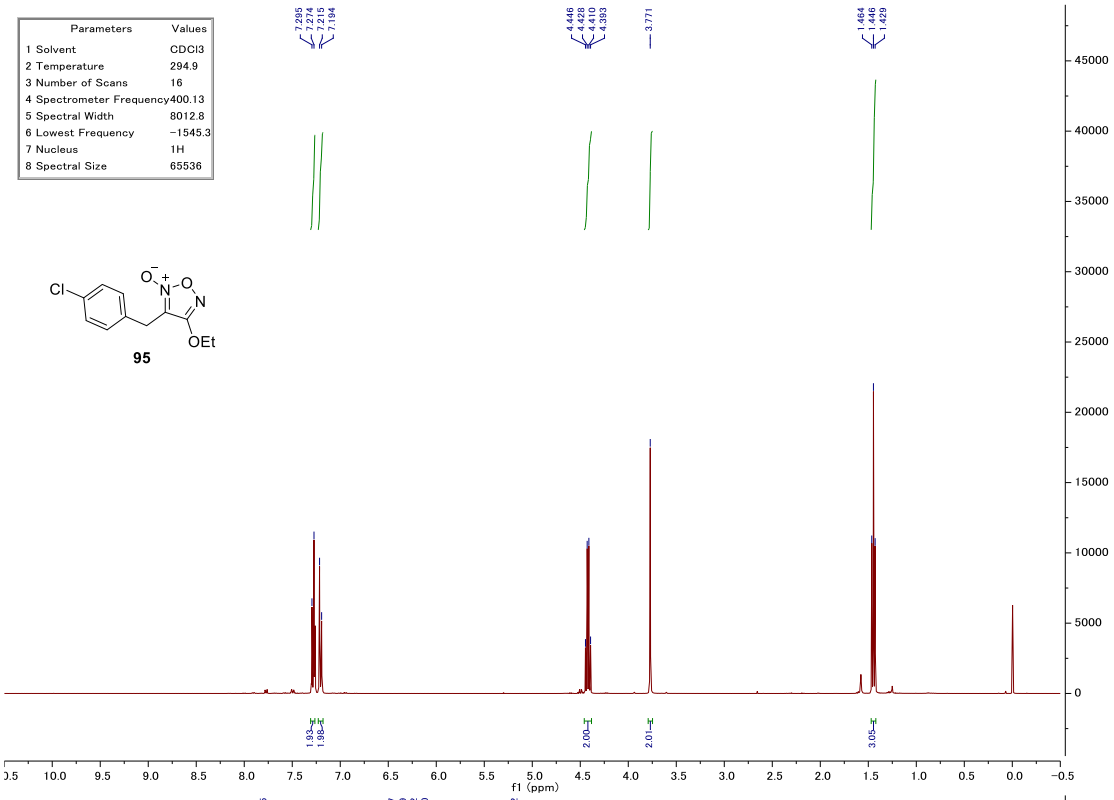
Cl
OEt

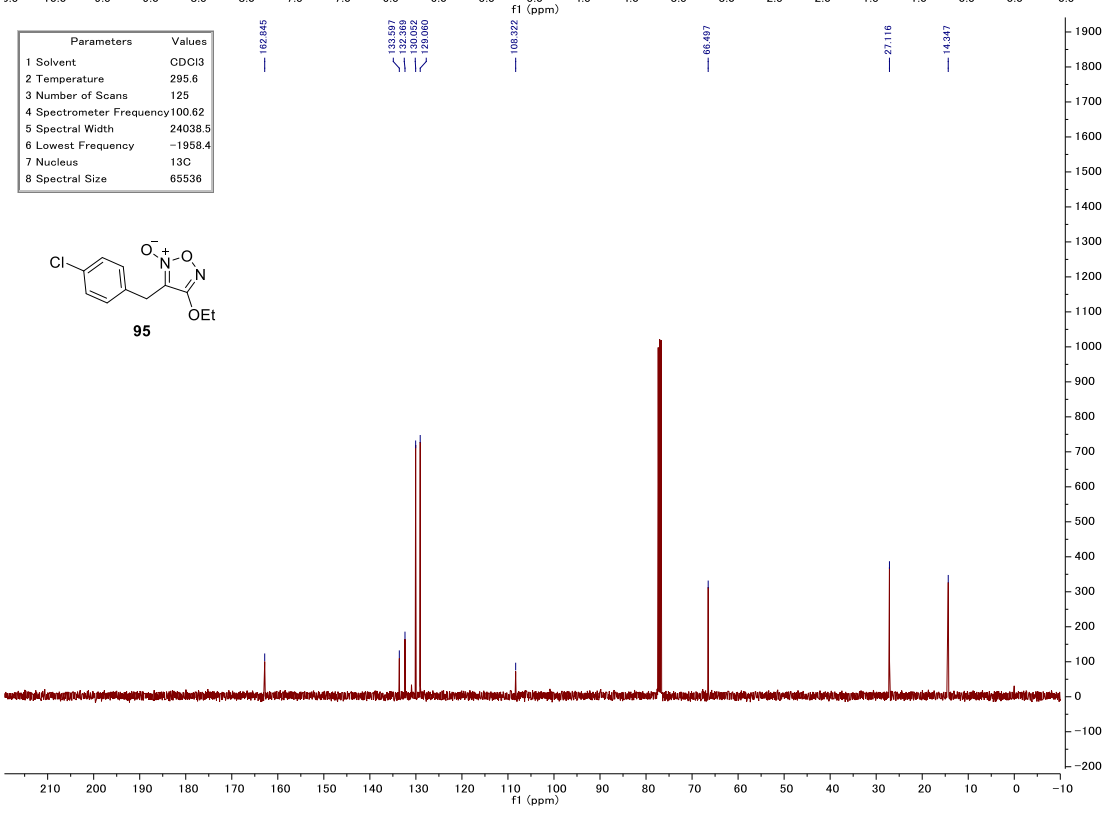
94

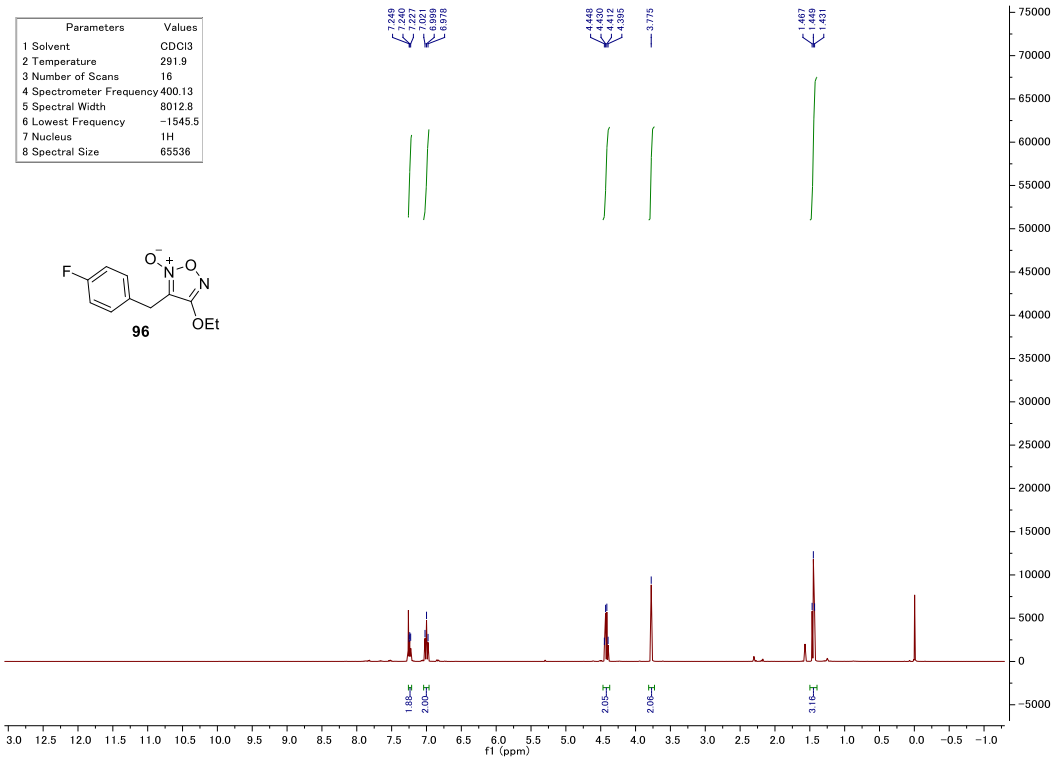

Parameter Value
1 Solvent CDCl3
2 Temperature 295.9
3 Number of Scans 282
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
162.857
135.763
134.638
130.162
128.834
127.880
126.905
108.130
66.539
27.367
14.344
f1 (ppm)

Cl
OEt

94

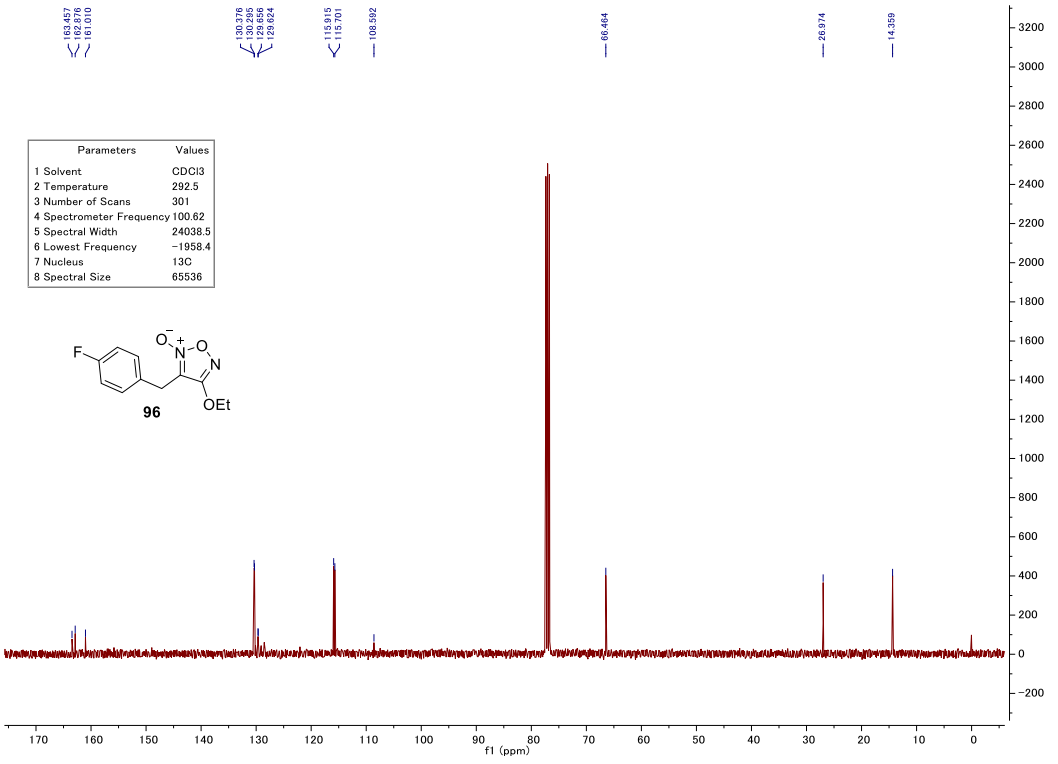

Parameters Values
1 Solvent CDCl3
2 Temperature 294.9
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.3
7 Nucleus 1H
8 Spectral Size 65536
7.295
7.274
7.215
7.194
4.446
4.428
4.410
4.393
3.771
1.464
1.446
1.429
Cl
O
N
O
N
OEt
95
1.93
1.98
2.00
2.01
3.05
f1 (ppm)


Parameters Values
1 Solvent CDCl3
2 Temperature 295.6
3 Number of Scans 125
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
162.845
133.597
132.369
130.052
129.060
108.322
66.497
27.116
14.347
Cl
O
N
O
N
OEt
95
f1 (ppm)


Parameters Values
1 Solvent CDCl3
2 Temperature 291.9
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1545.5
7 Nucleus 1H
8 Spectral Size 65536
7.249
7.240
7.227
7.001
6.999
6.978
4.448
4.430
4.412
4.395
3.775
1.467
1.449
1.431
1.88
2.00
2.05
2.06
3.16
f1 (ppm)

F
O
N
O
N
OEt

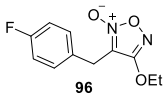
96


63.457
162.876
161.010
130.376
130.295
129.656
129.624
115.915
115.701
108.592
66.464
26.974
14.359
Parameters Values
1 Solvent CDCl3
2 Temperature 292.5
3 Number of Scans 301
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
f1 (ppm)

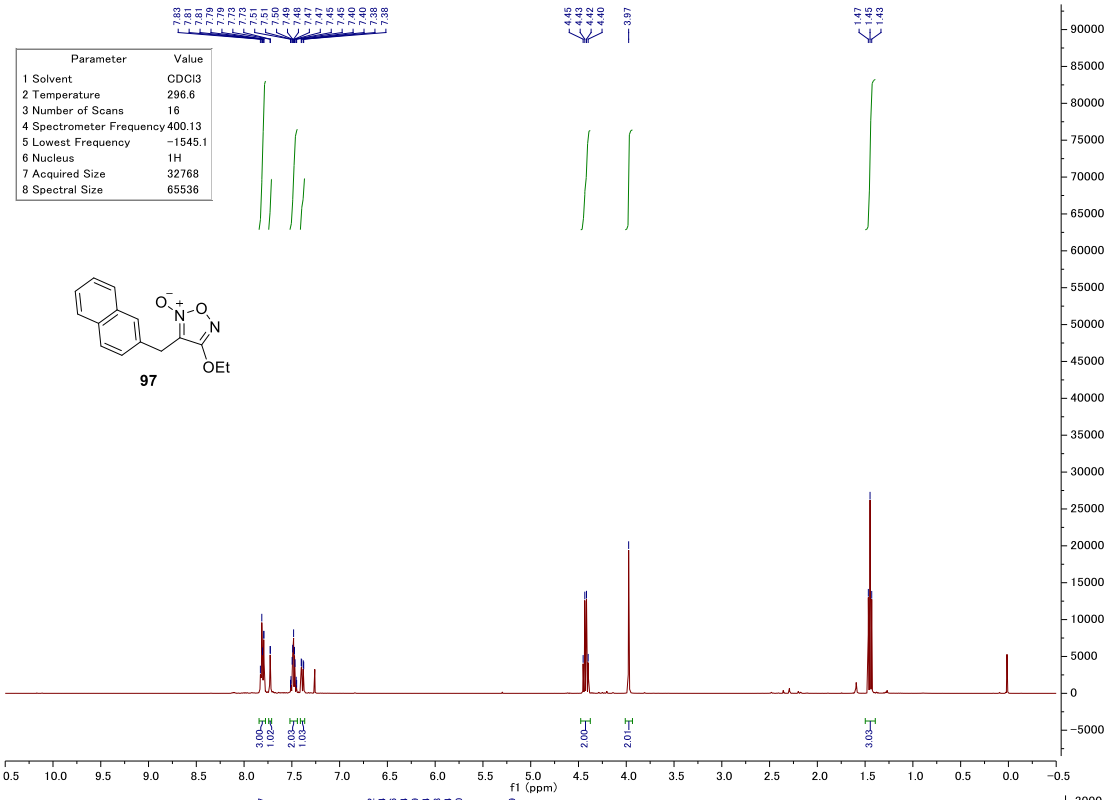
F
O
N
O
N
OEt

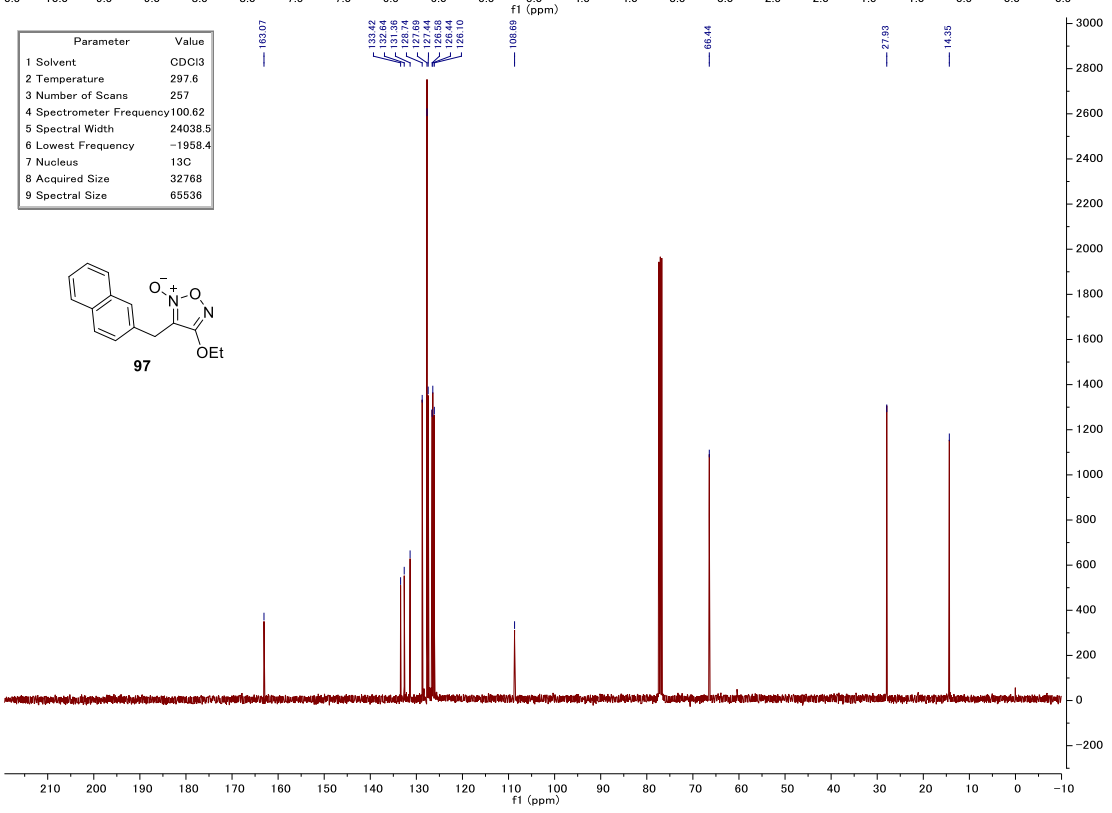
96

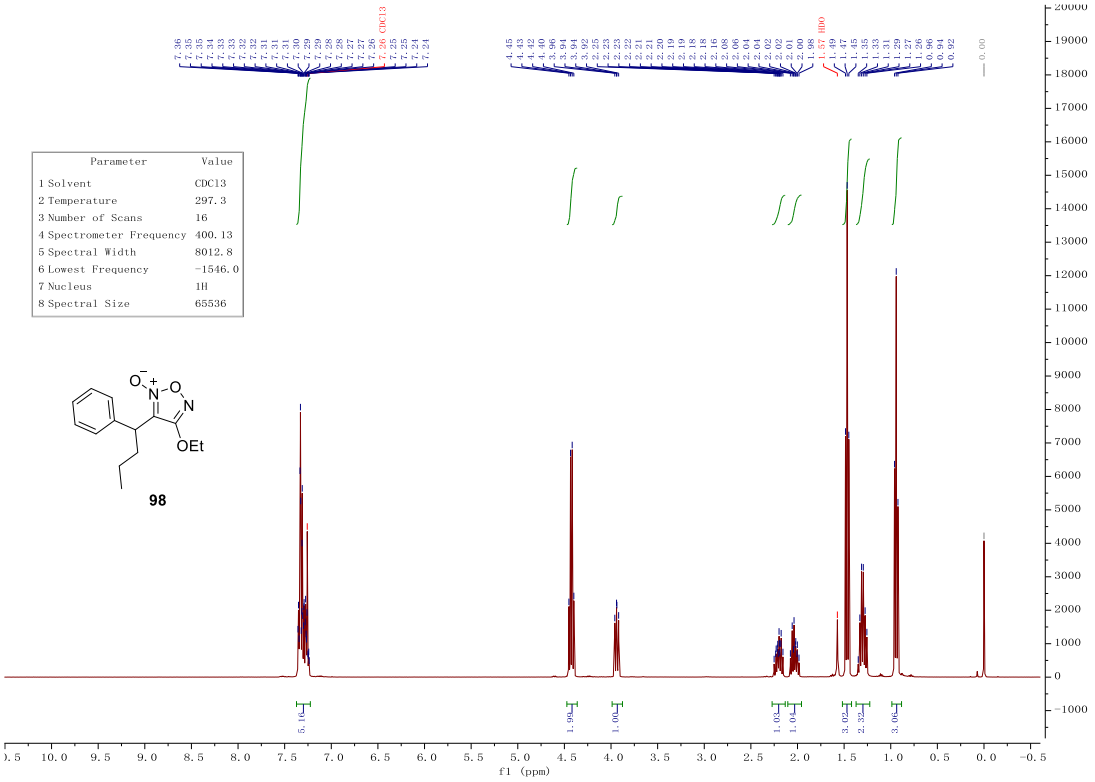
Parameter	Value
1 Solvent	CDCl3
2 Temperature	288.4
3 Number of Scans	16
4 Spectrometer Frequency	376.50
5 Spectral Width	300000.0
6 Lowest Frequency	−187039.3
7 Nucleus	19F
8 Spectral Size	65536

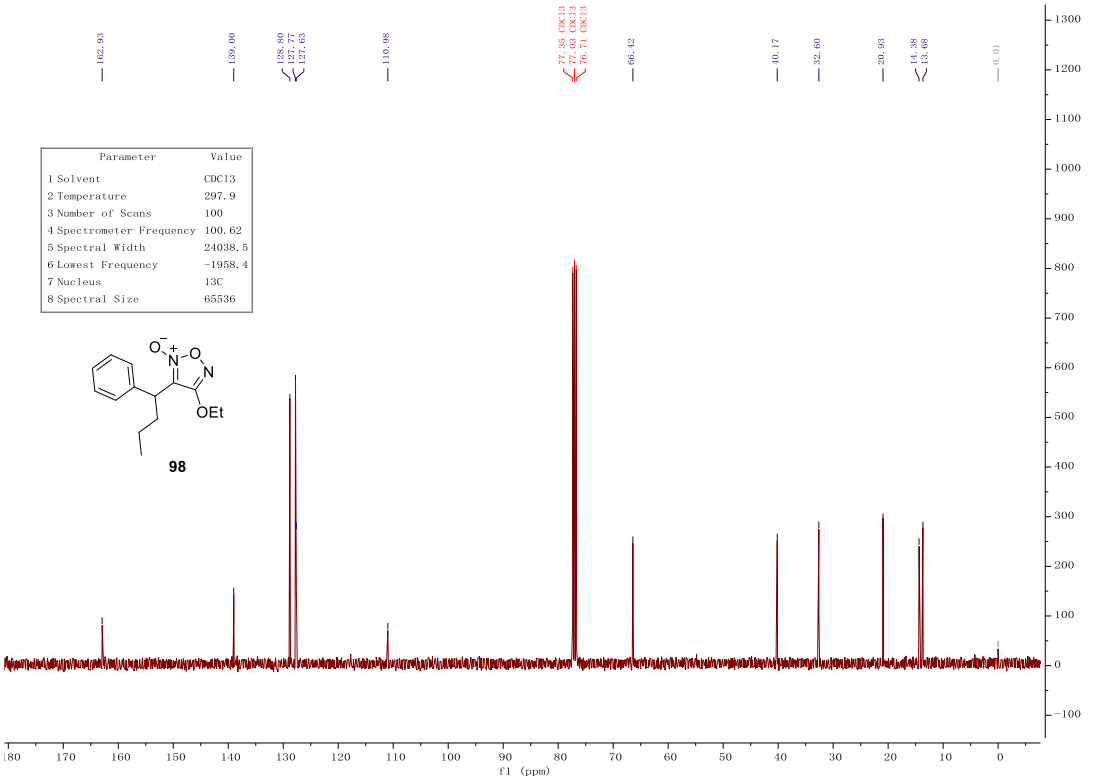


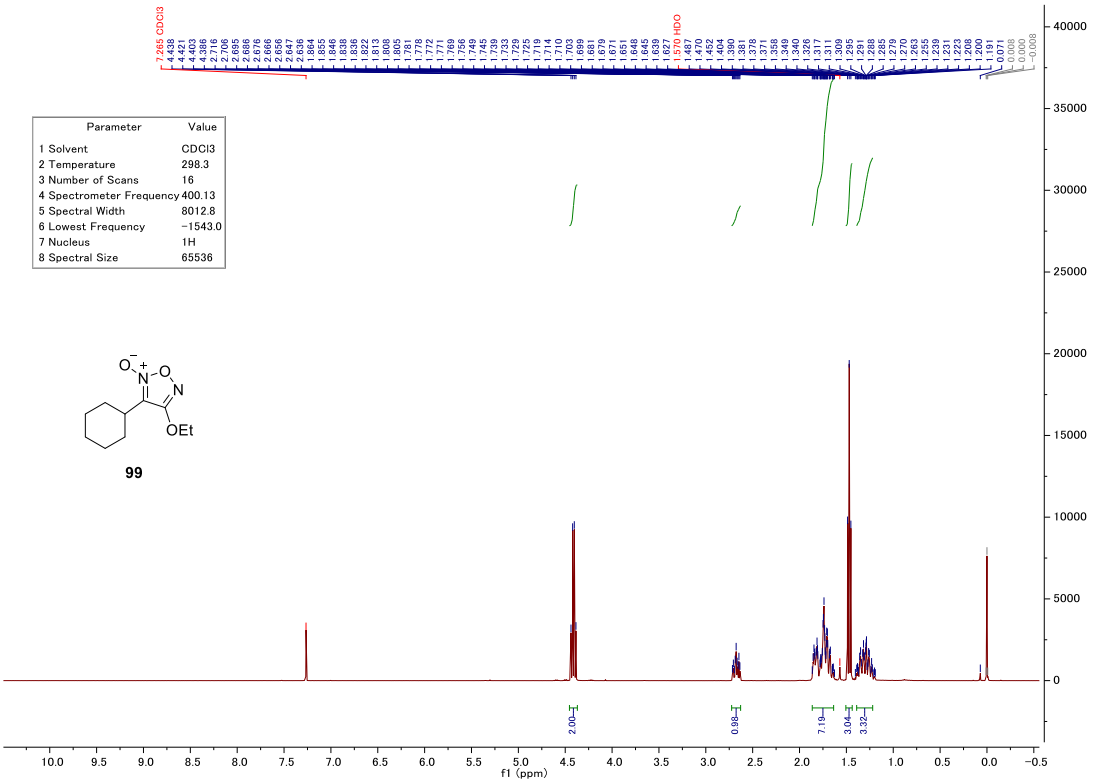
96

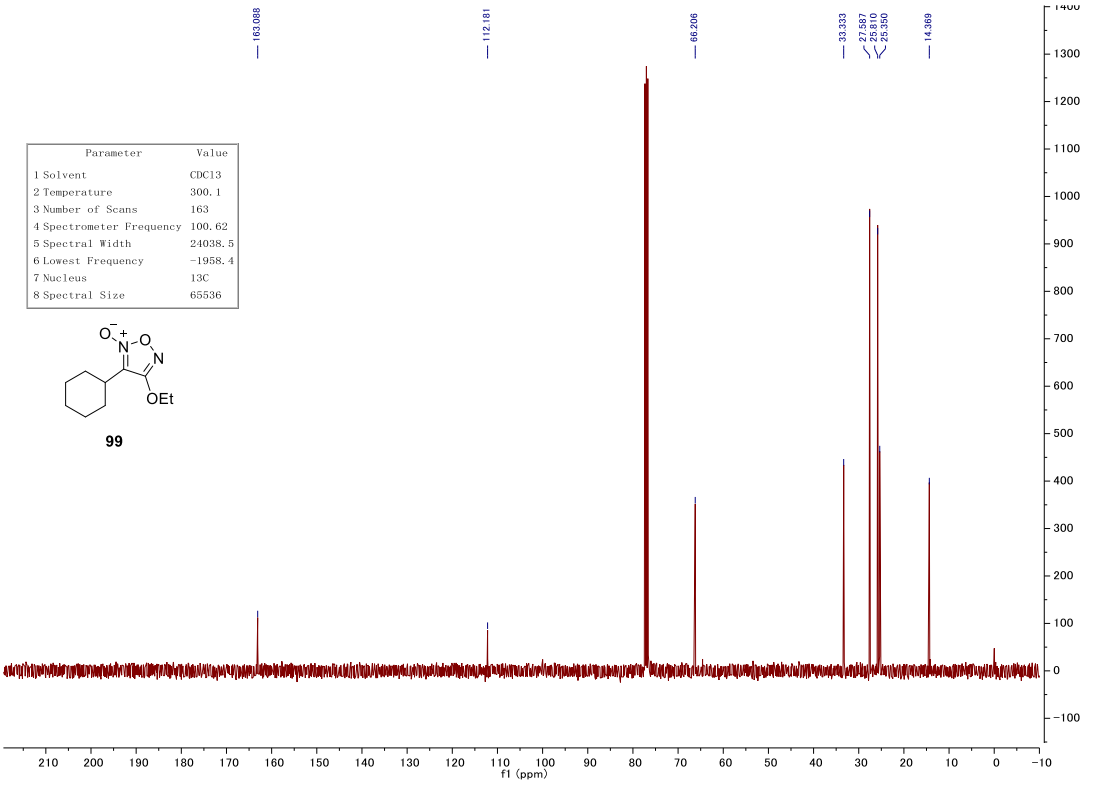

7.83
7.81
7.81
7.79
7.79
7.73
7.73
7.51
7.51
7.50
7.49
7.48
7.47
7.47
7.45
7.45
7.40
7.40
7.38
7.38
4.45
4.43
4.42
4.40
3.97
1.47
1.45
1.43
Parameter Value
1 Solvent CDCl3
2 Temperature 296.6
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Lowest Frequency −1545.1
6 Nucleus 1H
7 Acquired Size 32768
8 Spectral Size 65536
97
3.00
1.02
2.03
1.03
2.00
2.01
3.03
f1 (ppm)

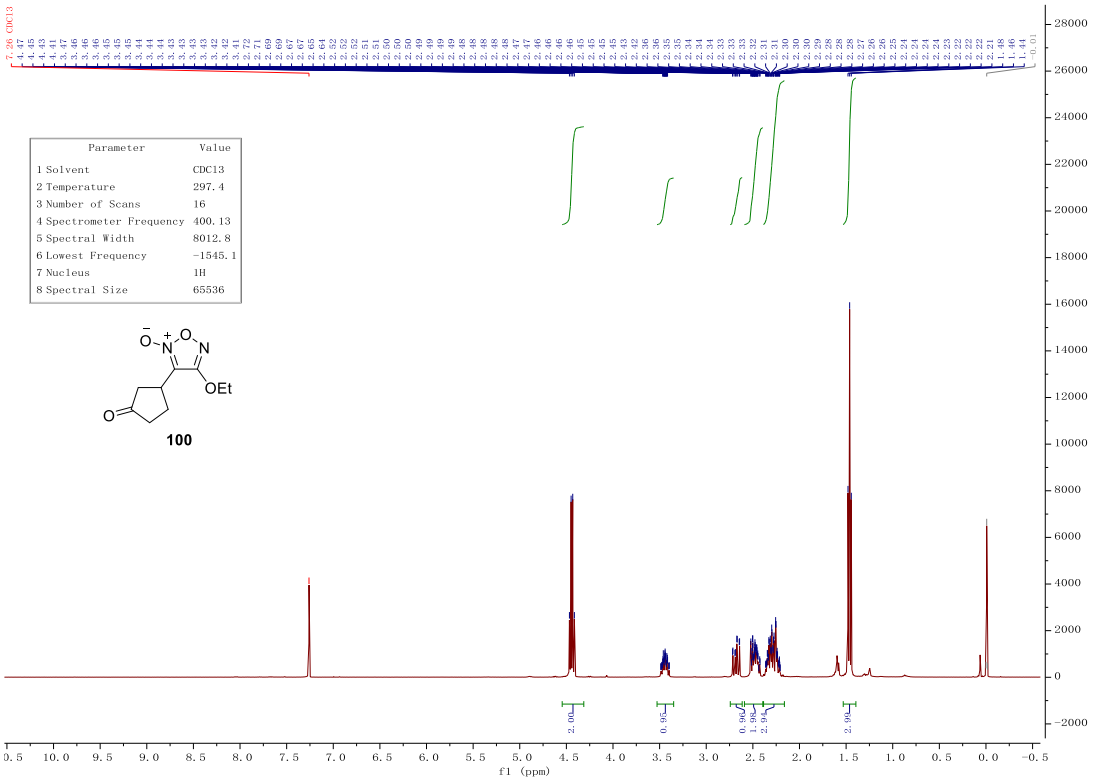

163.07
133.42
132.64
131.36
128.74
127.69
127.44
126.38
126.44
126.10
108.69
66.44
27.93
14.35
Parameter Value
1 Solvent CDCl3
2 Temperature 297.6
3 Number of Scans 257
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Acquired Size 32768
9 Spectral Size 65536
97
f1 (ppm)

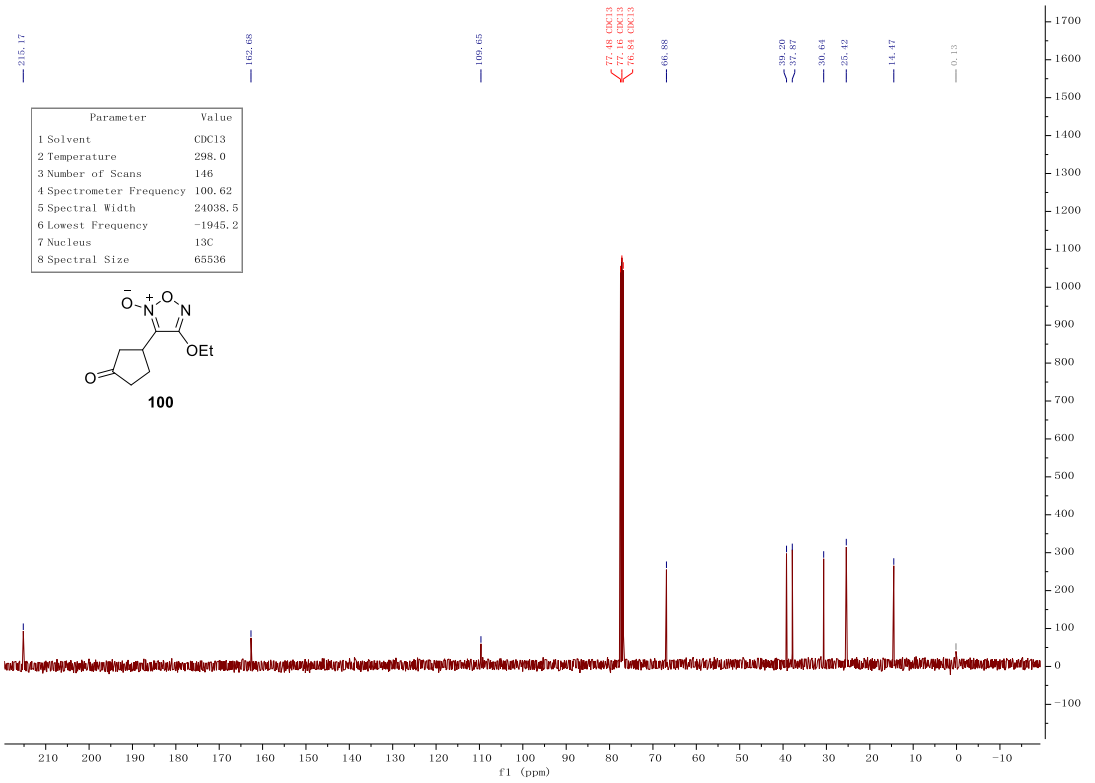

Parameter Value
1 Solvent CDCl3
2 Temperature 297.3
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1546.0
7 Nucleus 1H
8 Spectral Size 65536
OEt
98
f1 (ppm)

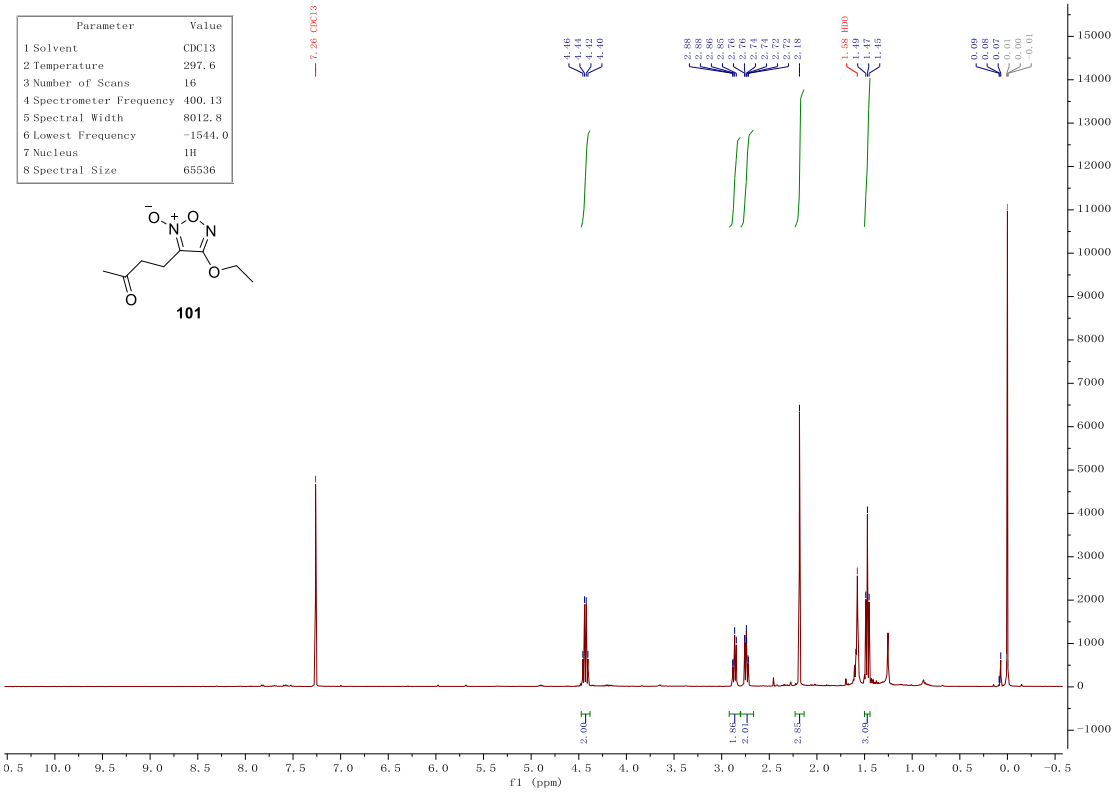

Parameter Value
1 Solvent CDCl3
2 Temperature 297.9
3 Number of Scans 100
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
OEt
98
f1 (ppm)

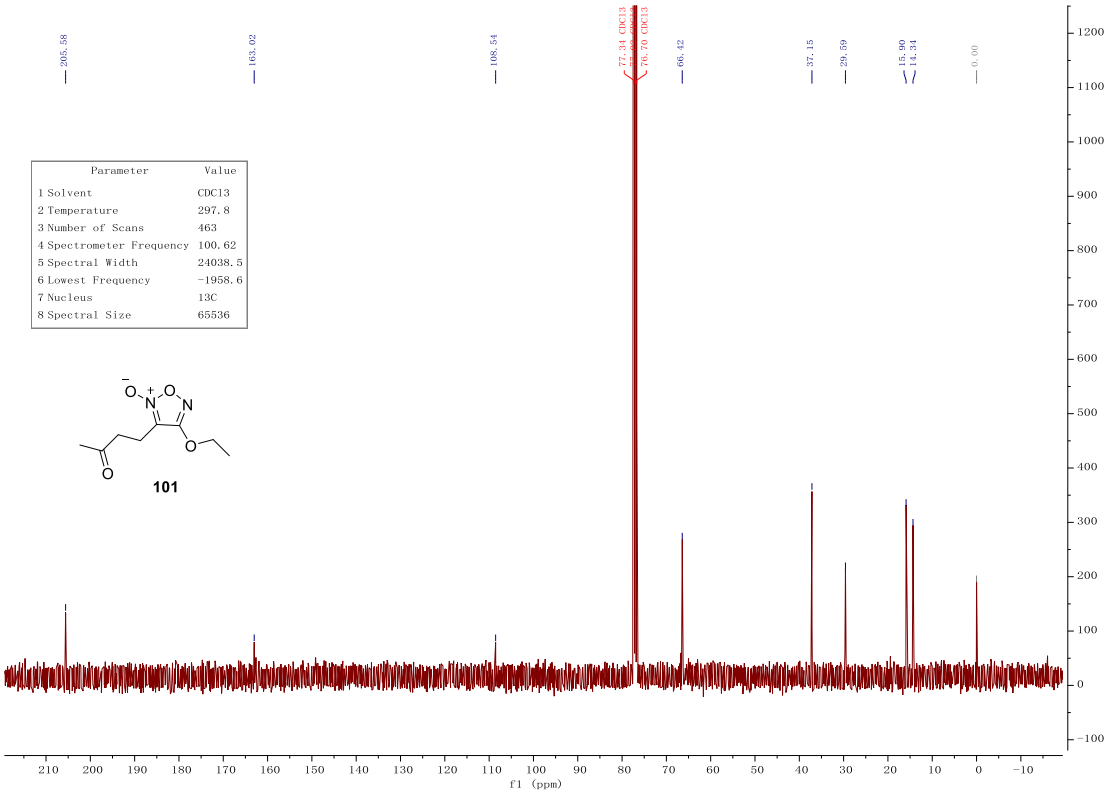

7.285 CDCl3
1.570 HDO
Parameter Value
1 Solvent CDCl3
2 Temperature 298.3
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1543.0
7 Nucleus 1H
8 Spectral Size 65536
OEt
99
2.00
0.98
7.19
3.04
3.32
f1 (ppm)

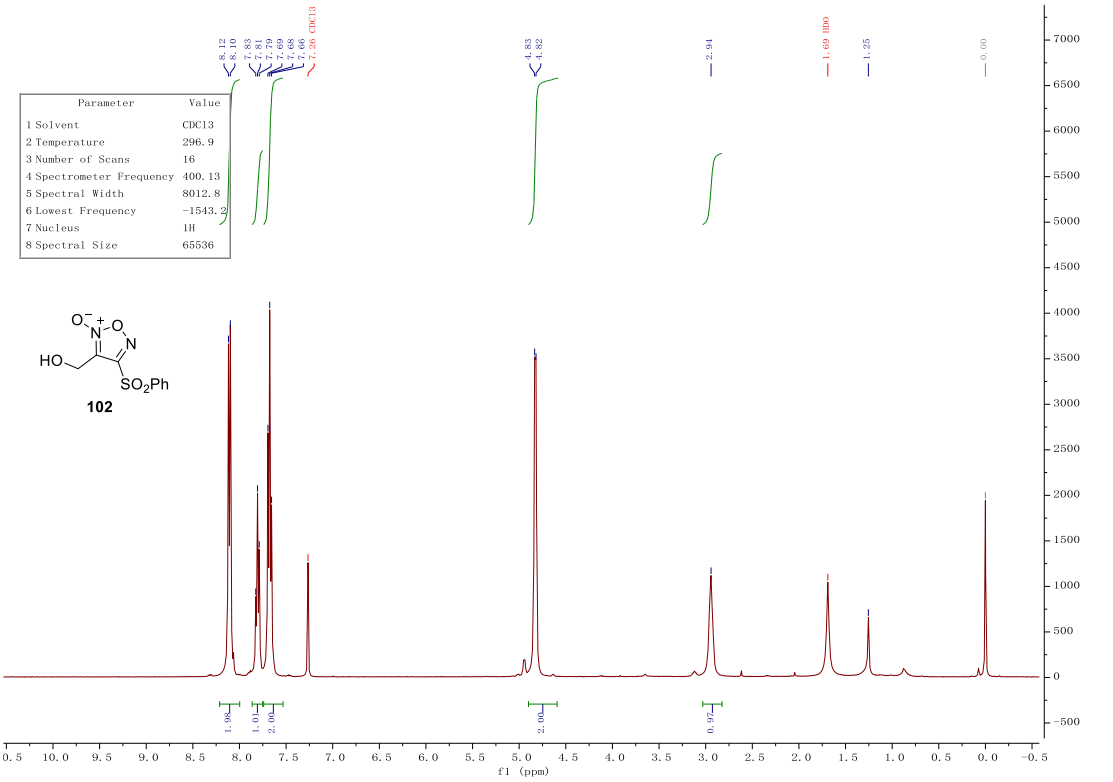

163.088
112.181
66.206
33.333
27.587
25.810
25.350
14.369
Parameter Value
1 Solvent CDCl3
2 Temperature 300.1
3 Number of Scans 163
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
OEt
99
f1 (ppm)

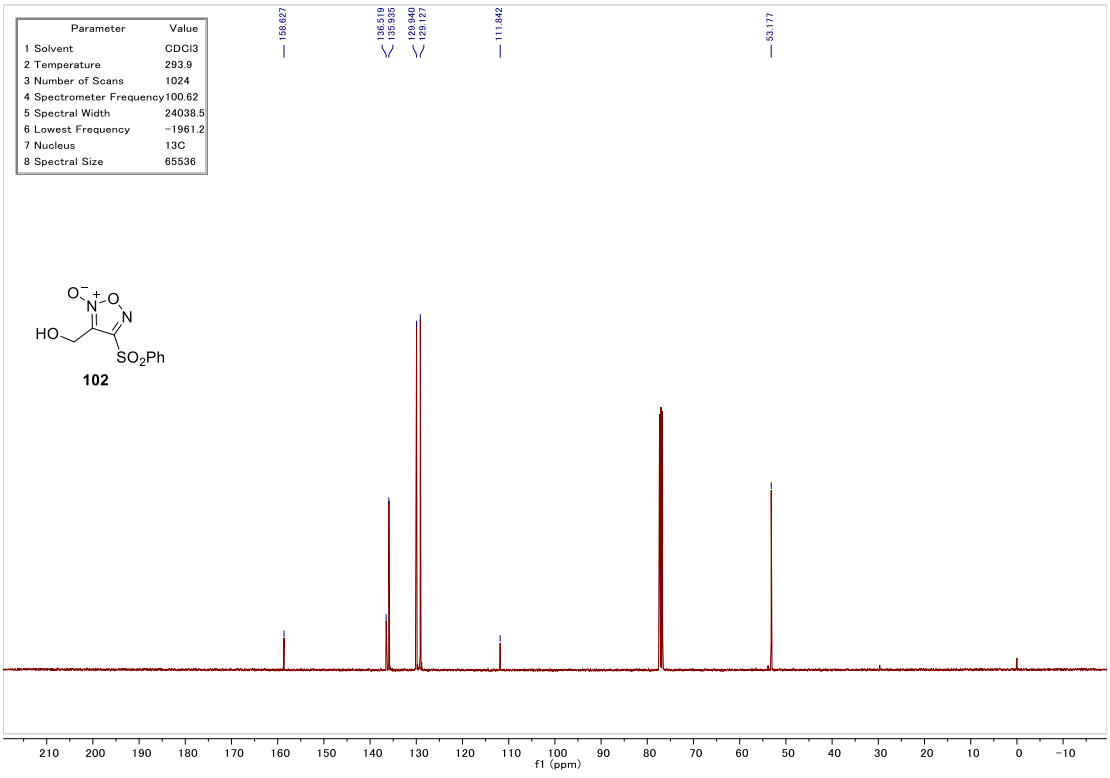

Parameter Value
1 Solvent CDCl3
2 Temperature 297.4
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.1
7 Nucleus 1H
8 Spectral Size 65536
OEt
100
f1 (ppm)

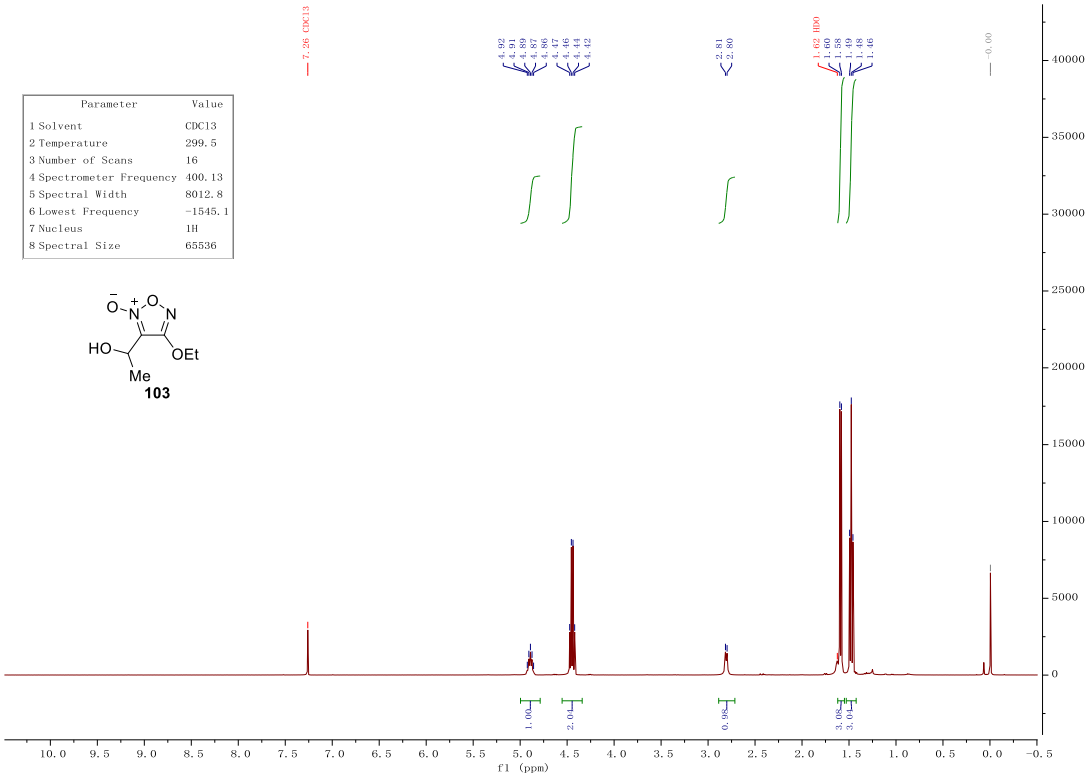

Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Number of Scans 146
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1945.2
7 Nucleus 13C
8 Spectral Size 65536
OEt
100
f1 (ppm)

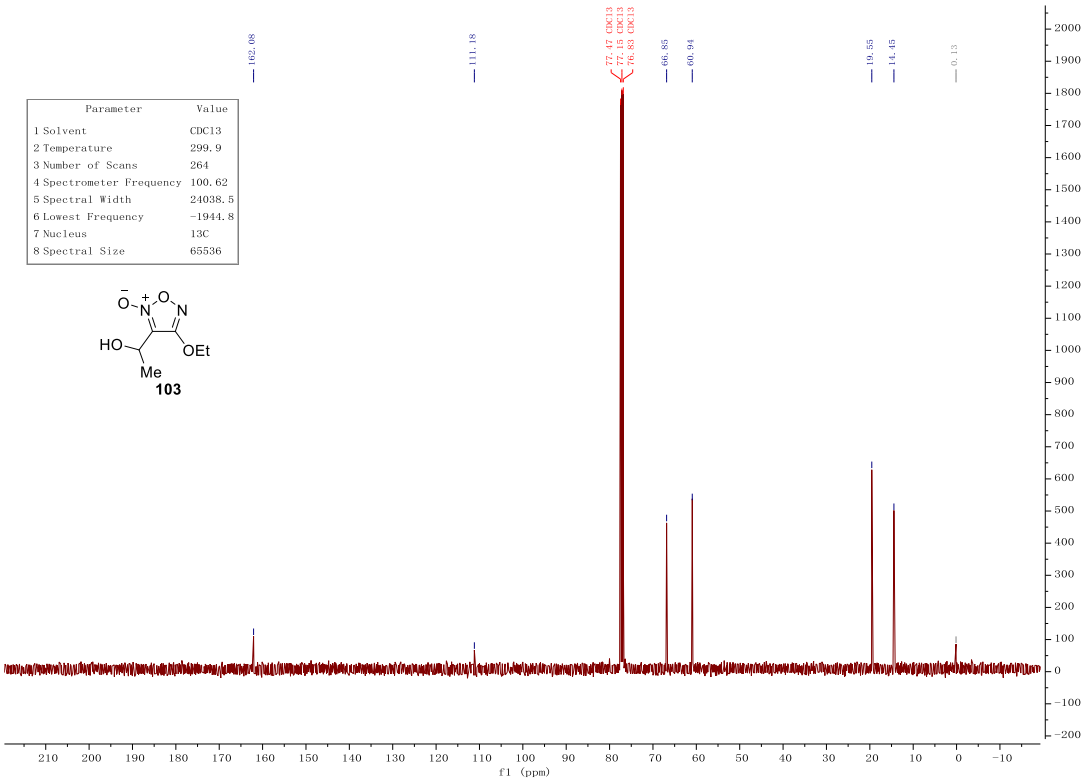

Parameter Value
1 Solvent CDCl3
2 Temperature 297.6
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1544.0
7 Nucleus 1H
8 Spectral Size 65536
101
f1 (ppm)

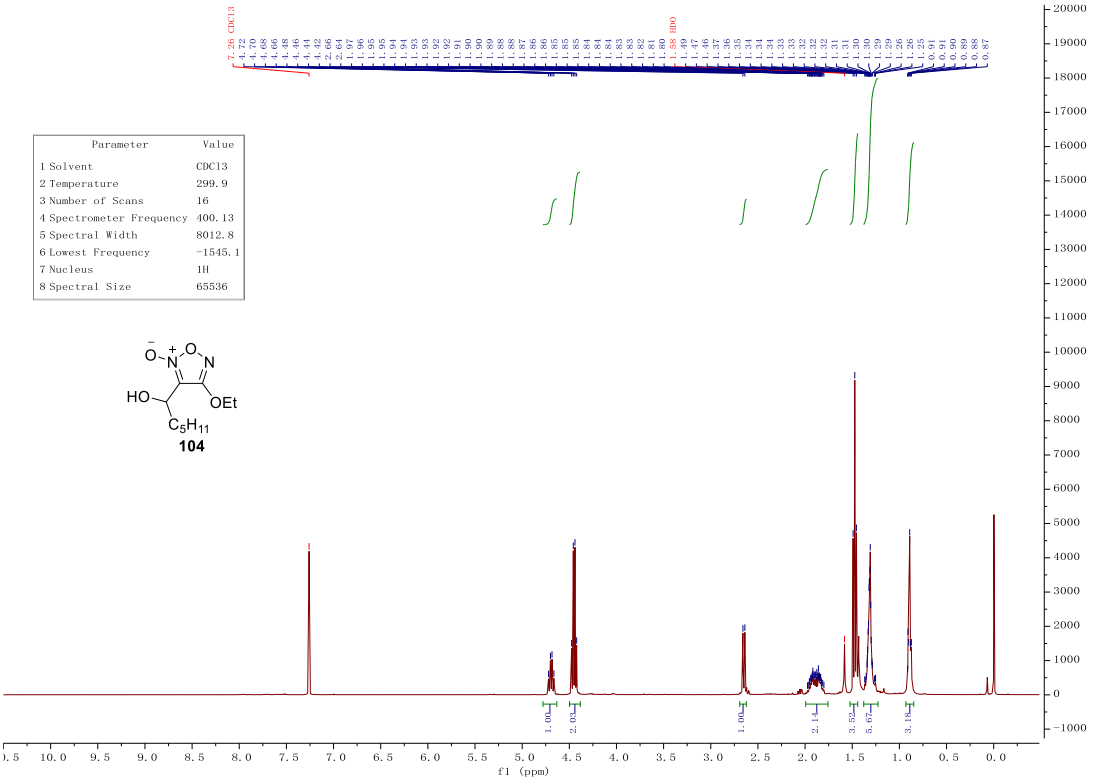

Parameter Value
1 Solvent CDCl3
2 Temperature 297.8
3 Number of Scans 463
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.6
7 Nucleus 13C
8 Spectral Size 65536
101
f1 (ppm)

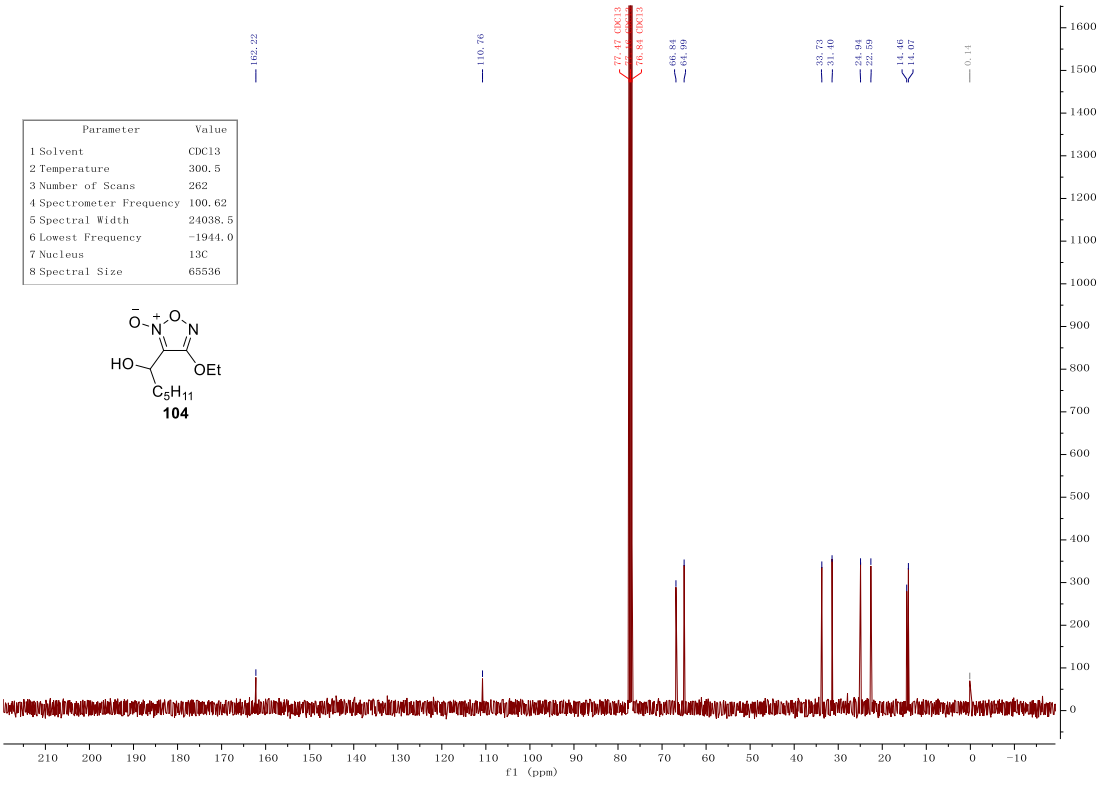

Parameter Value
1 Solvent CDCl3
2 Temperature 296.9
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1543.2
7 Nucleus 1H
8 Spectral Size 65536
8.12
8.10
7.83
7.81
7.79
7.69
7.68
7.66
7.26 CDCl3
4.83
4.82
2.94
1.69 H2O
1.25
0.00
HO
SO2Ph
102
1.98
1.01
2.00
2.00
0.97
f1 (ppm)

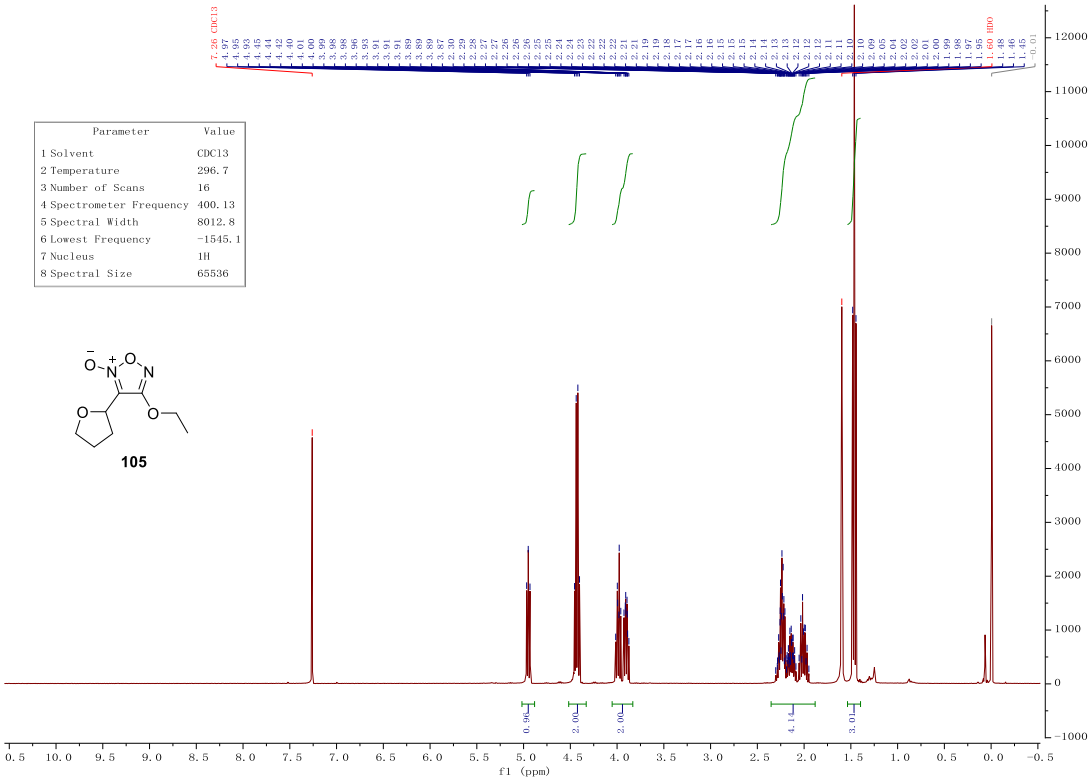

Parameter Value
1 Solvent CDCl3
2 Temperature 293.9
3 Number of Scans 1024
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1961.2
7 Nucleus 13C
8 Spectral Size 65536
158.627
136.519
135.935
129.940
129.127
111.842
53.177
HO
SO2Ph
102
f1 (ppm)

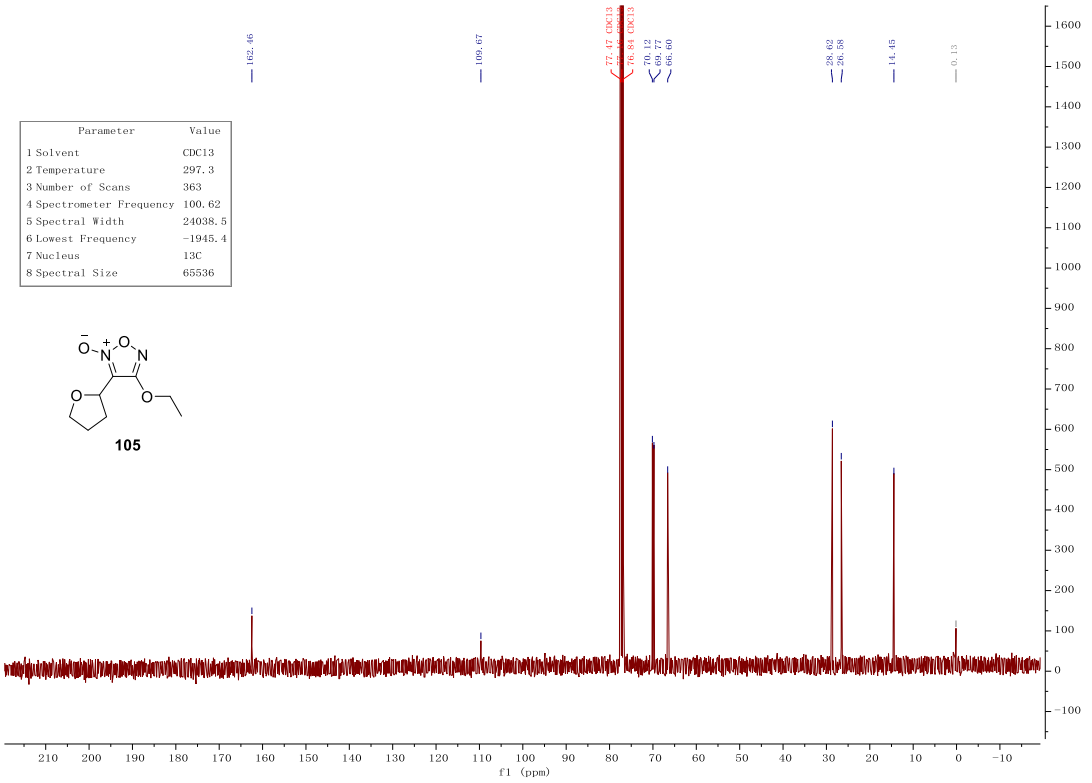

Parameter Value
1 Solvent CDCl3
2 Temperature 299.5
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.1
7 Nucleus 1H
8 Spectral Size 65536
HO
OEt
Me
103
7.26 CDCl3
4.92
4.91
4.89
4.87
4.86
4.47
4.46
4.44
4.42
2.81
2.80
1.62 H2O
1.60
1.58
1.49
1.48
1.46
0.00
1.00
2.04
0.98
3.08
3.04
f1 (ppm)

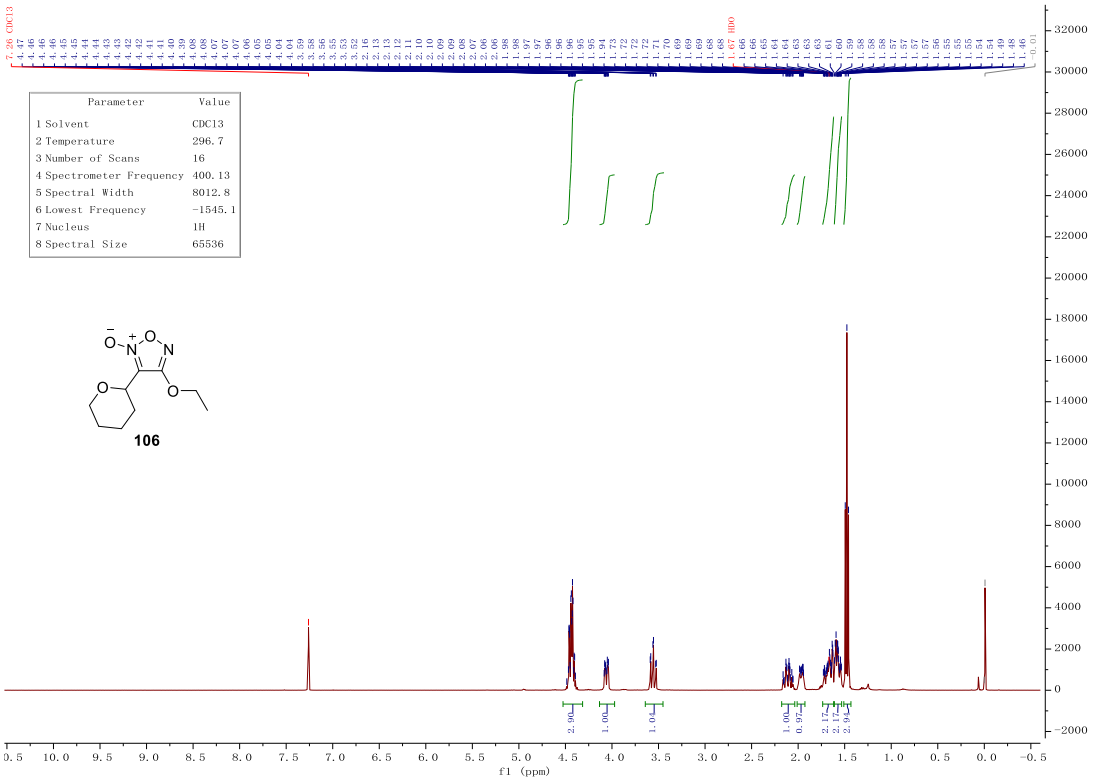

Parameter Value
1 Solvent CDCl3
2 Temperature 299.9
3 Number of Scans 264
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1944.8
7 Nucleus 13C
8 Spectral Size 65536
HO
OEt
Me
103
162.08
111.18
77.47 CDCl3
77.15 CDCl3
76.83 CDCl3
66.85
60.94
19.55
14.45
0.13
f1 (ppm)

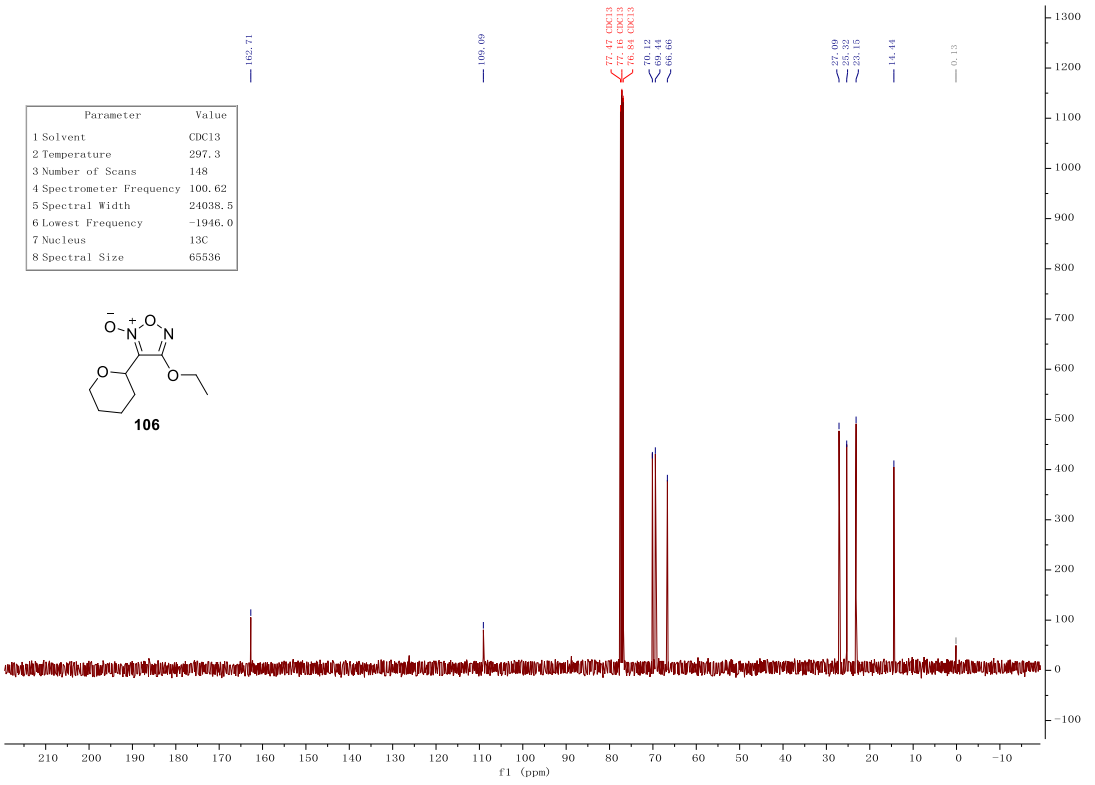

Parameter Value
1 Solvent CDCl3
2 Temperature 299.9
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.1
7 Nucleus 1H
8 Spectral Size 65536
HO
OEt
C5H11
104
f1 (ppm)

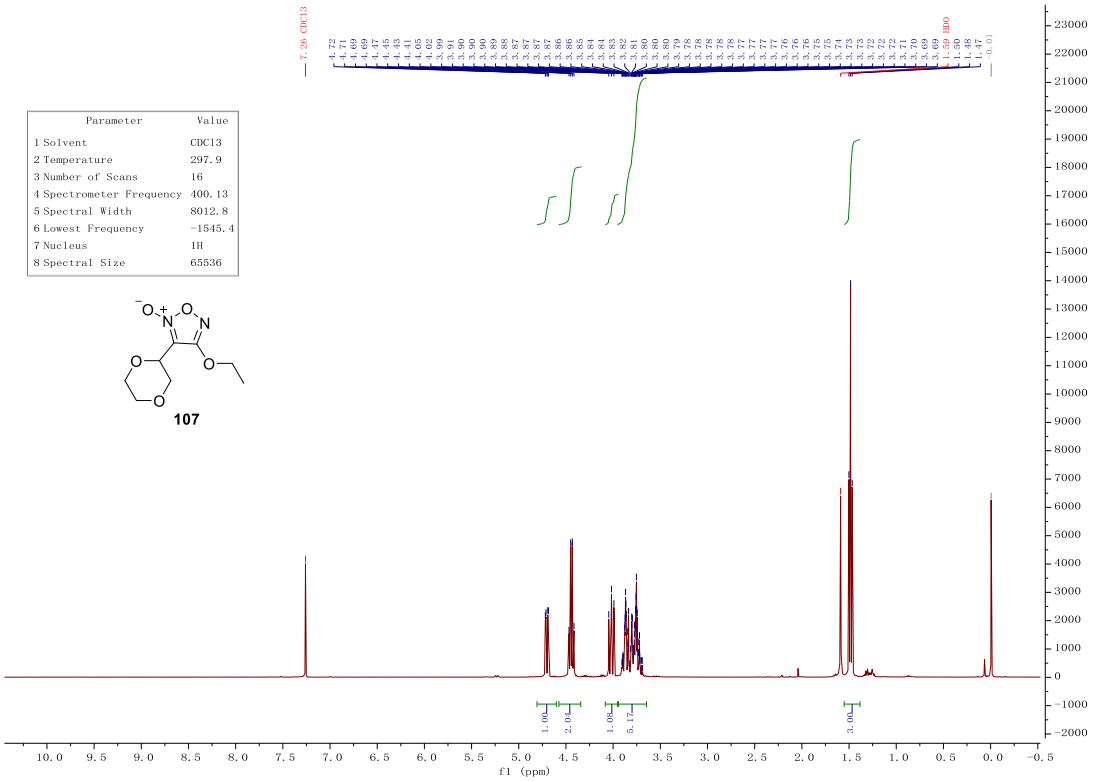

Parameter Value
1 Solvent CDCl3
2 Temperature 300.5
3 Number of Scans 262
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1944.0
7 Nucleus 13C
8 Spectral Size 65536
HO
OEt
C5H11
104
f1 (ppm)

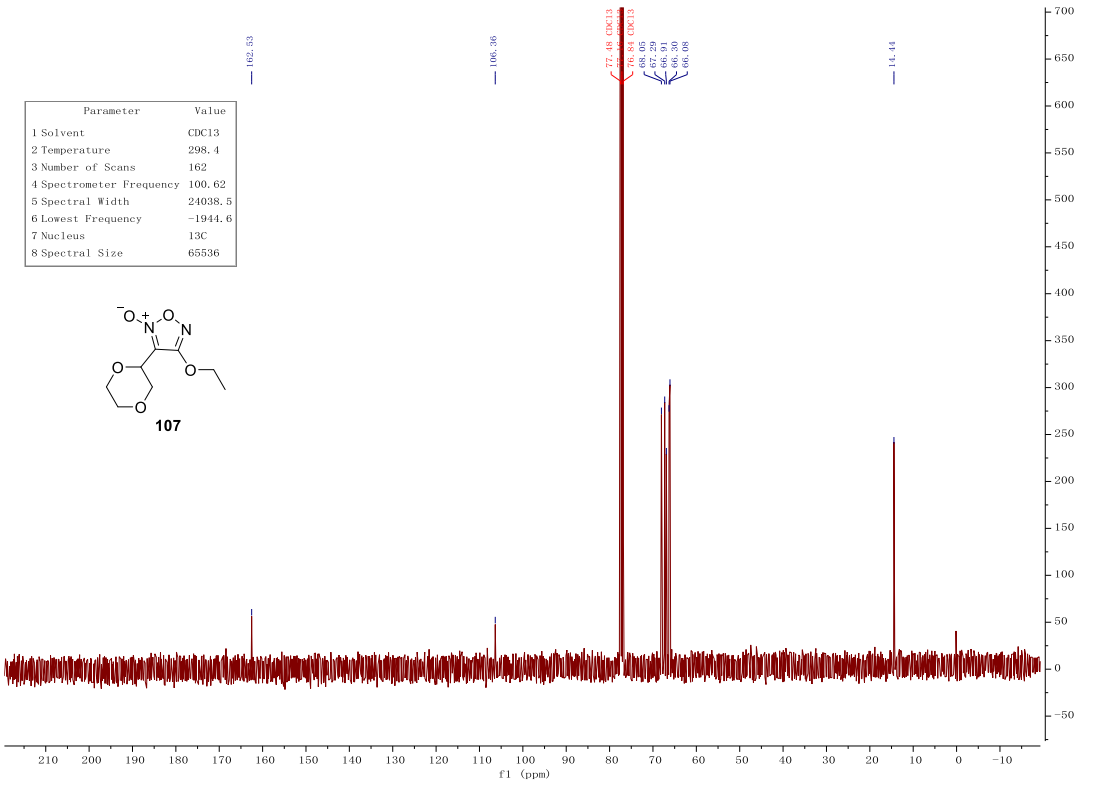

Parameter Value
1 Solvent CDCl3
2 Temperature 296.7
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.1
7 Nucleus 1H
8 Spectral Size 65536
105
f1 (ppm)

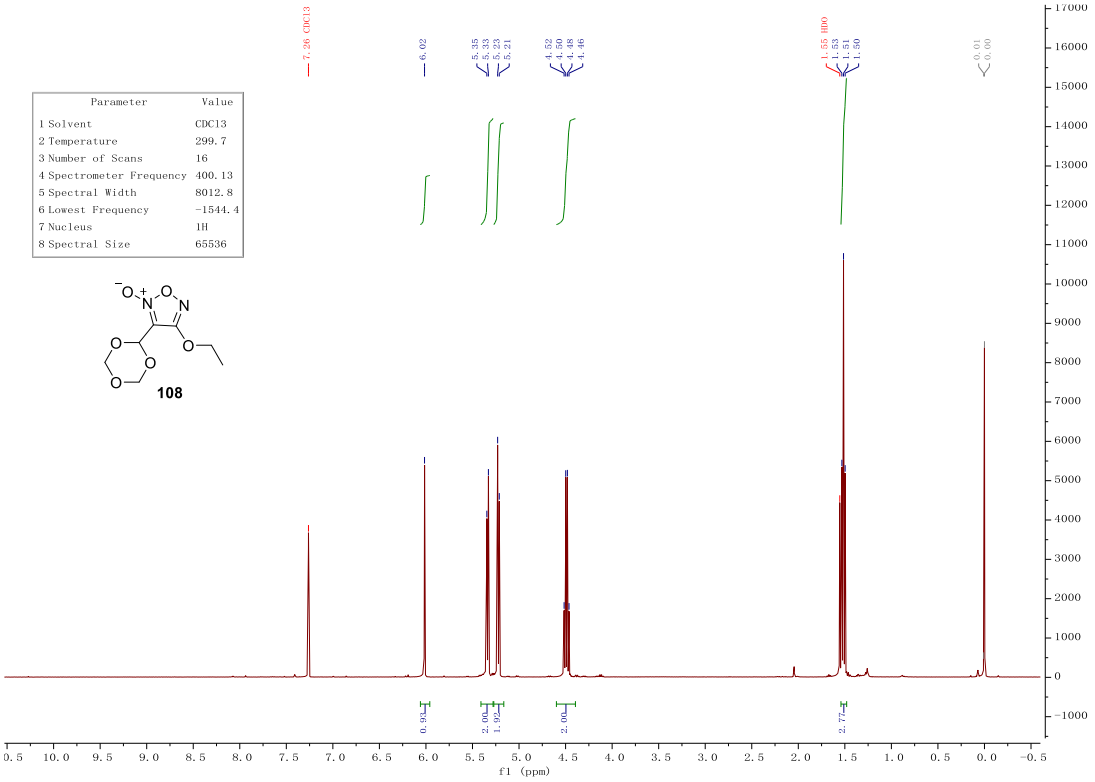

Parameter Value
1 Solvent CDCl3
2 Temperature 297.3
3 Number of Scans 363
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1945.4
7 Nucleus 13C
8 Spectral Size 65536
105
f1 (ppm)

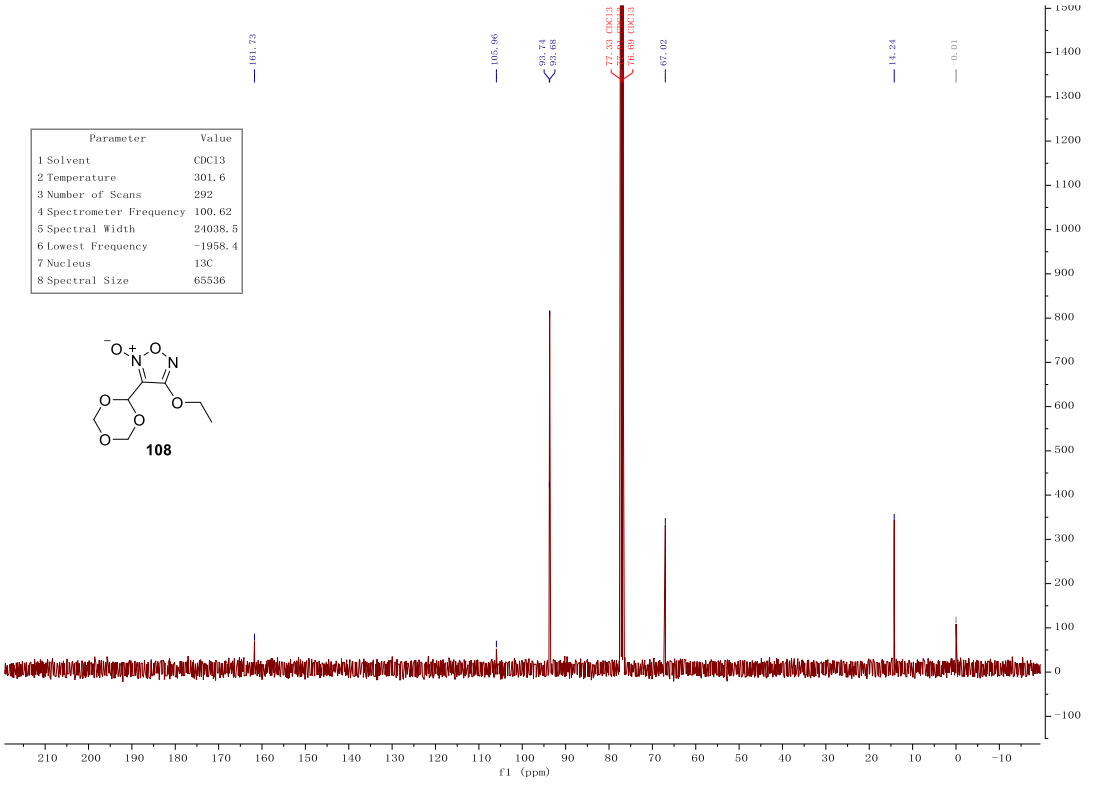

Parameter Value
1 Solvent CDCl3
2 Temperature 296.7
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.1
7 Nucleus 1H
8 Spectral Size 65536
106
f1 (ppm)

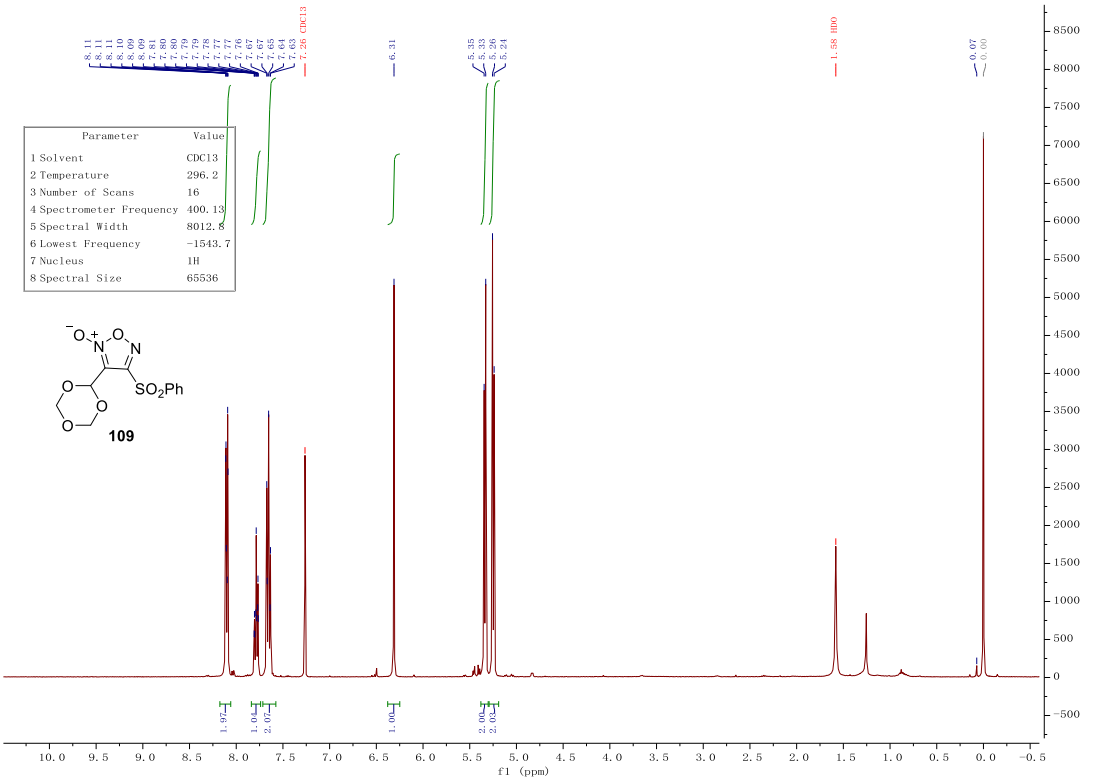

Parameter Value
1 Solvent CDCl3
2 Temperature 297.3
3 Number of Scans 148
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1946.0
7 Nucleus 13C
8 Spectral Size 65536
106
f1 (ppm)

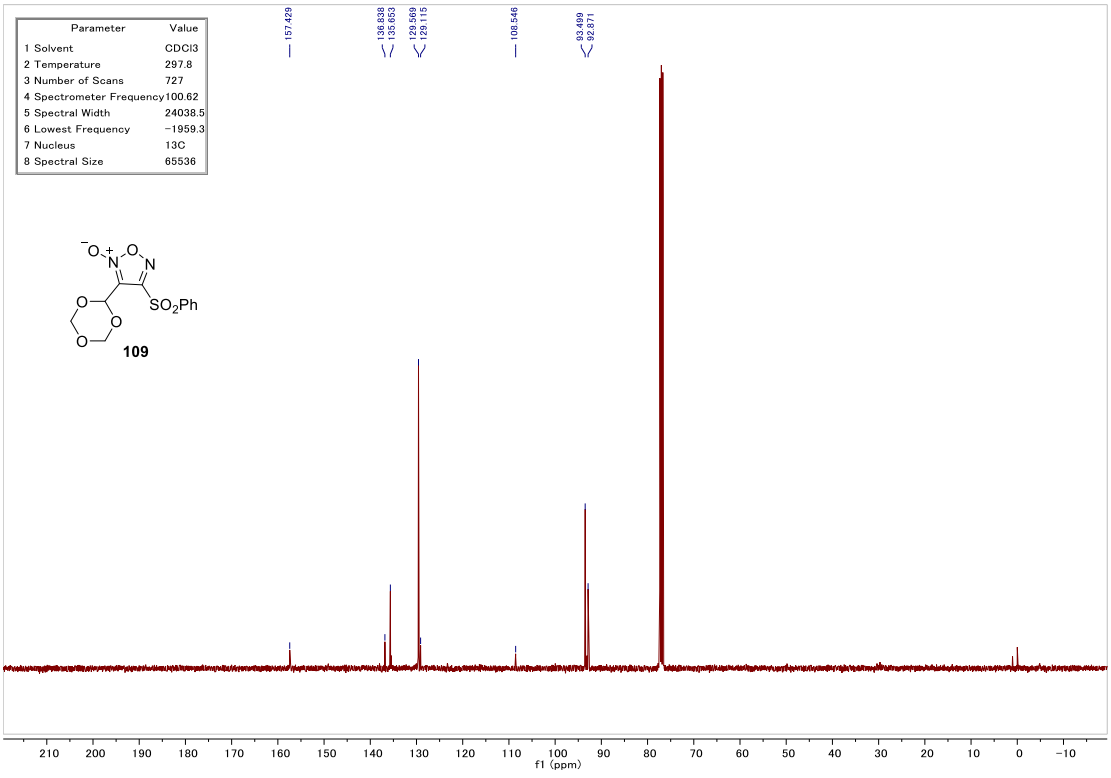

Parameter Value
1 Solvent CDCl3
2 Temperature 297.9
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.4
7 Nucleus 1H
8 Spectral Size 65536
107
f1 (ppm)

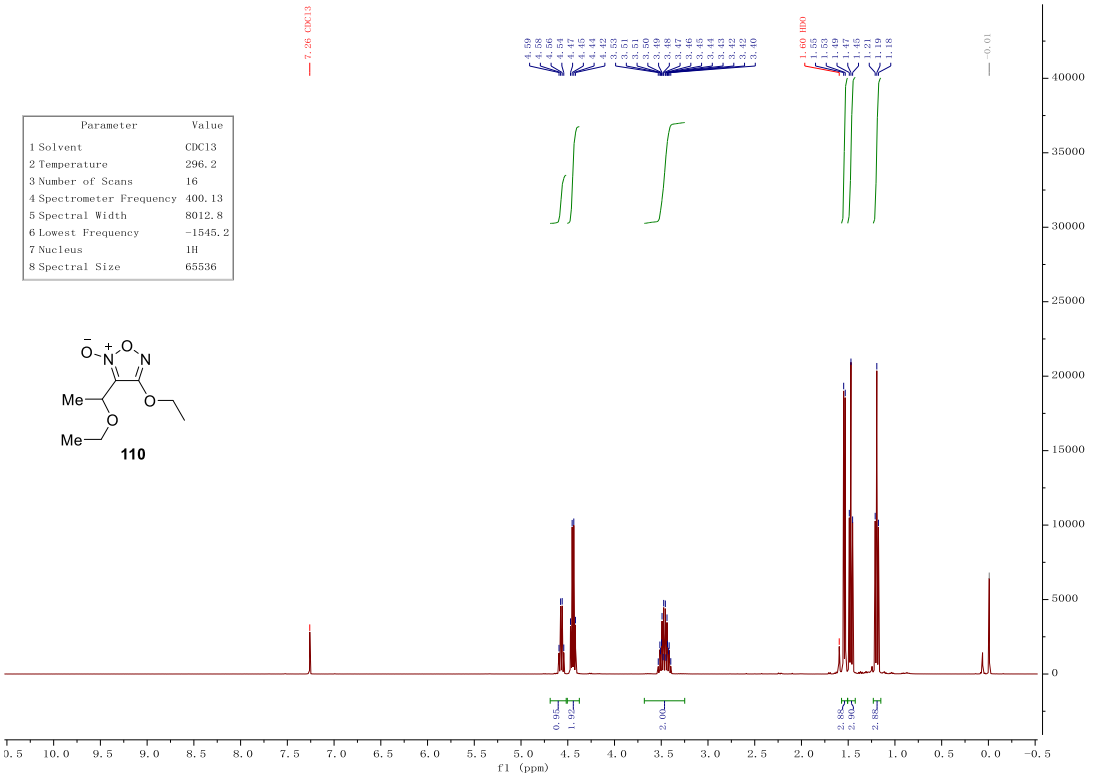

Parameter Value
1 Solvent CDCl3
2 Temperature 298.4
3 Number of Scans 162
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1944.6
7 Nucleus 13C
8 Spectral Size 65536
107
f1 (ppm)


7.26 CDCl3
6.02
5.35
5.33
5.23
5.21
4.52
4.50
4.48
4.46
1.55 H2O
1.53
1.51
1.50
0.01
0.00
Parameter Value
1 Solvent CDCl3
2 Temperature 299.7
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1544.4
7 Nucleus 1H
8 Spectral Size 65536
108
0.93
2.00
1.92
2.00
2.77
f1 (ppm)


161.73
105.96
93.74
93.68
77.33 CDCl3
77.01
76.69 CDCl3
67.02
14.24
-0.01
Parameter Value
1 Solvent CDCl3
2 Temperature 301.6
3 Number of Scans 292
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
108
f1 (ppm)

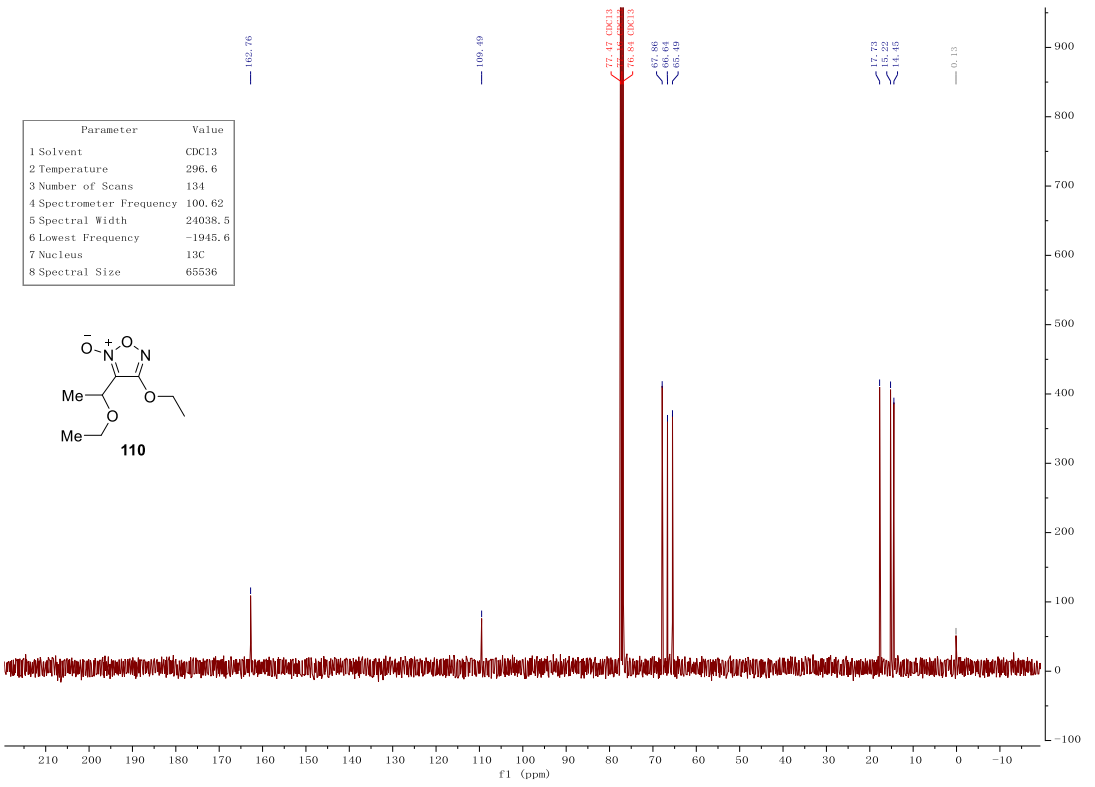

Parameter Value
1 Solvent CDCl3
2 Temperature 296.2
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1543.7
7 Nucleus 1H
8 Spectral Size 65536
SO2Ph
109
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 297.8
3 Number of Scans 727
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1959.3
7 Nucleus 13C
8 Spectral Size 65536
SO2Ph
109
f1 (ppm)



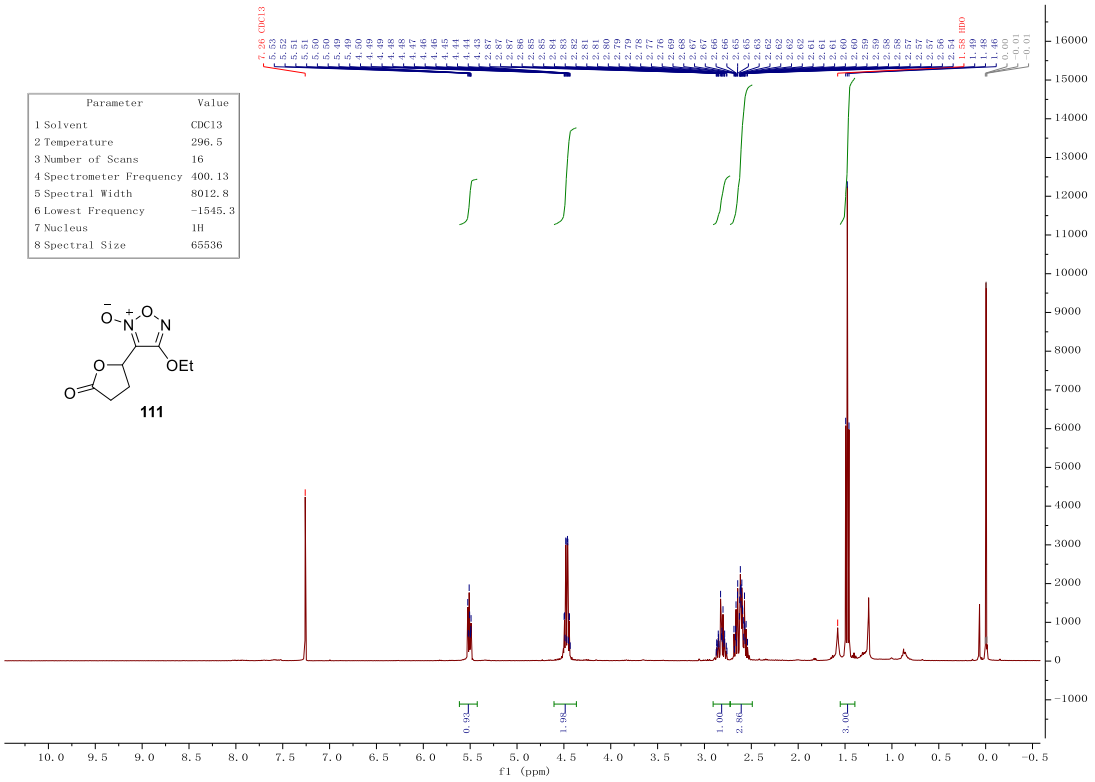
Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.2
3 Number of Scans	16
4 Spectrometer Frequency	400.13
5 Spectral Width	8012.8
6 Lowest Frequency	-1545.2
7 Nucleus	1H
8 Spectral Size	65536

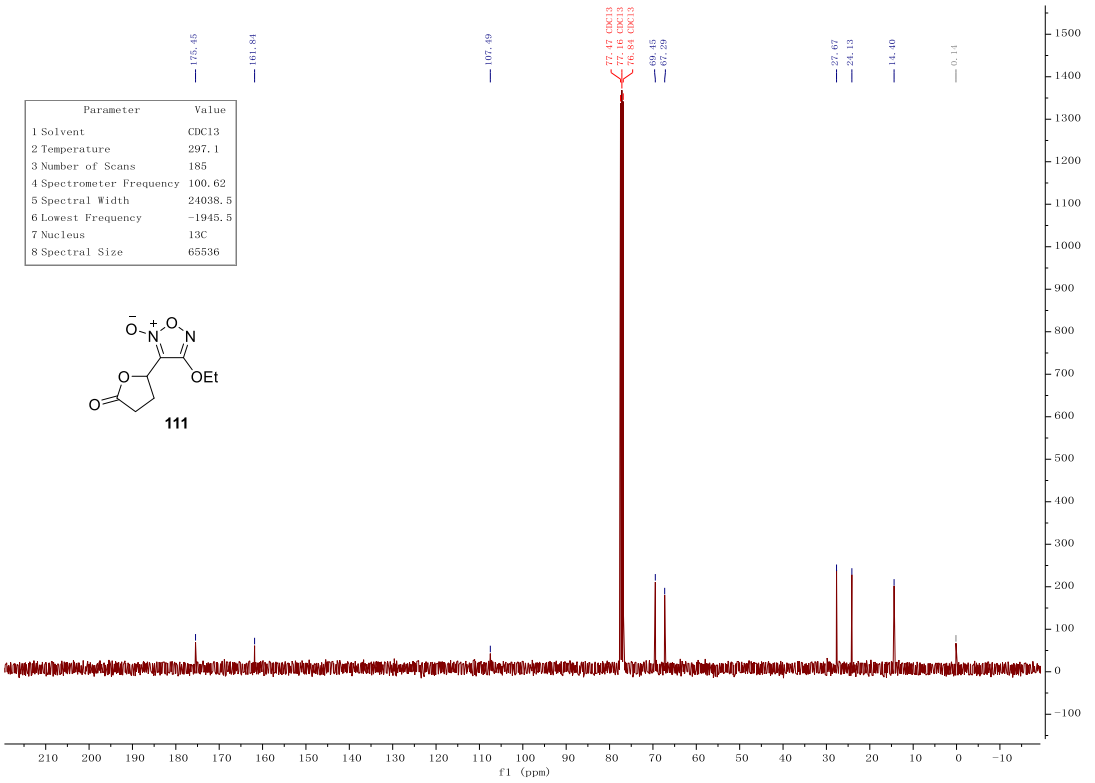
110

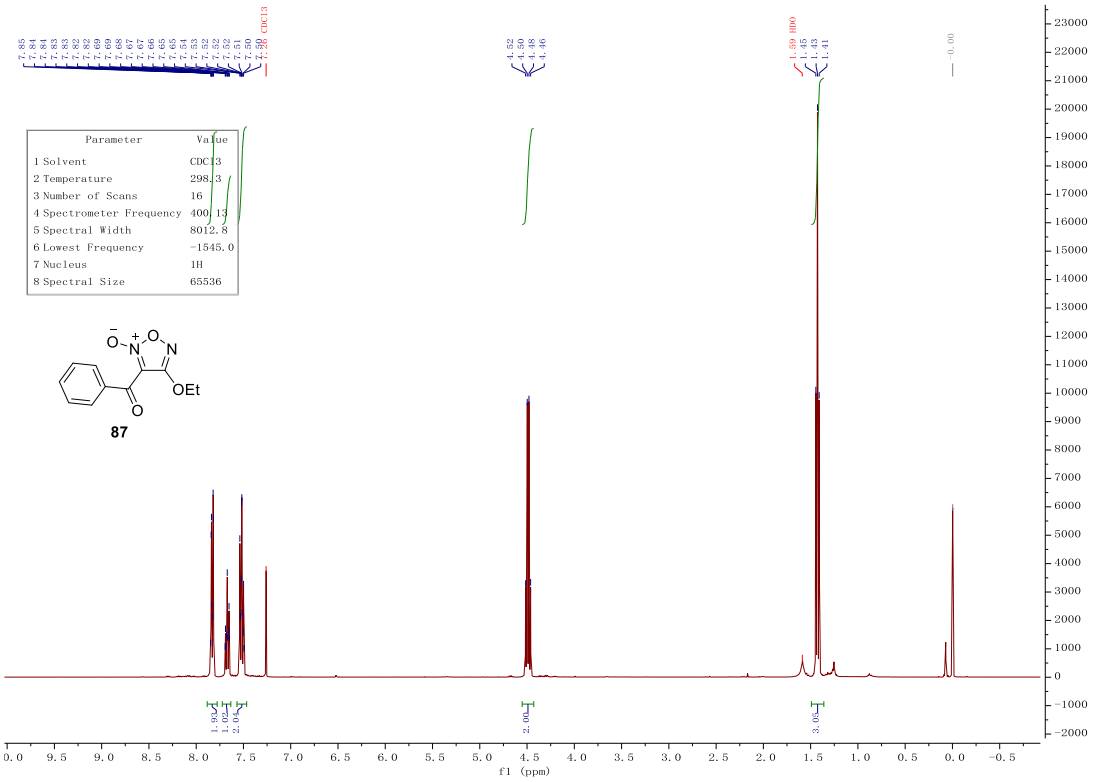


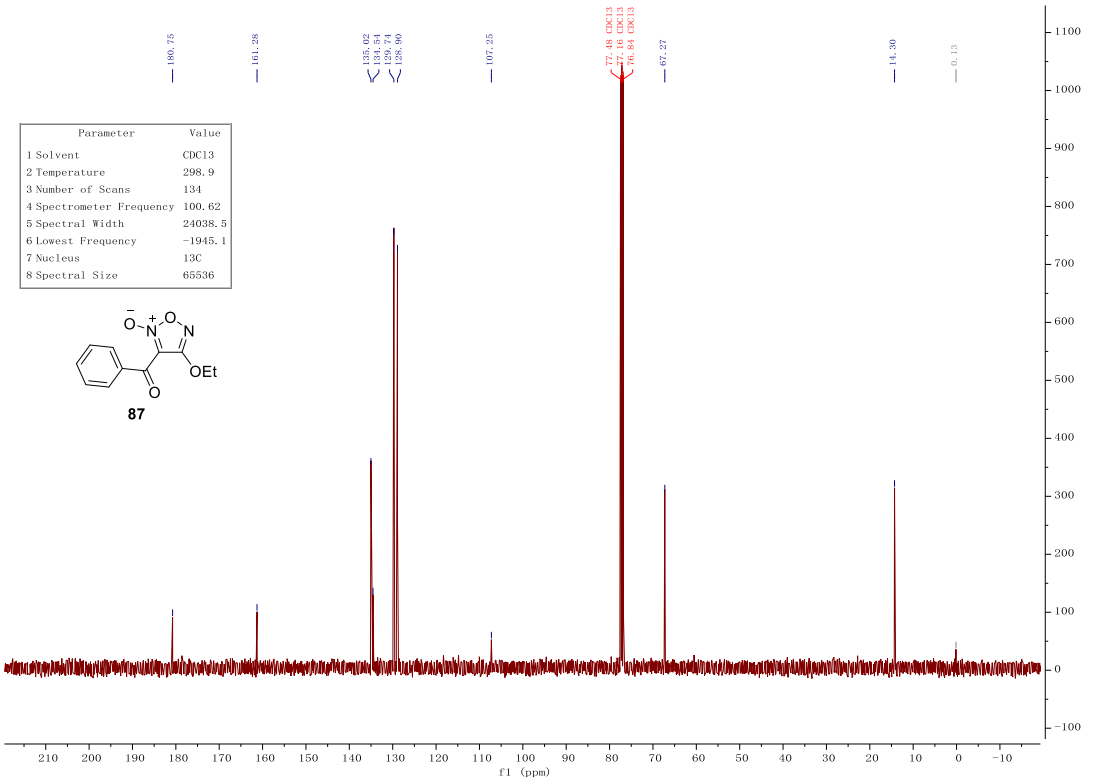
Parameter	Value
1 Solvent	CDCl3
2 Temperature	296.6
3 Number of Scans	134
4 Spectrometer Frequency	100.62
5 Spectral Width	24038.5
6 Lowest Frequency	-1945.6
7 Nucleus	13C
8 Spectral Size	65536

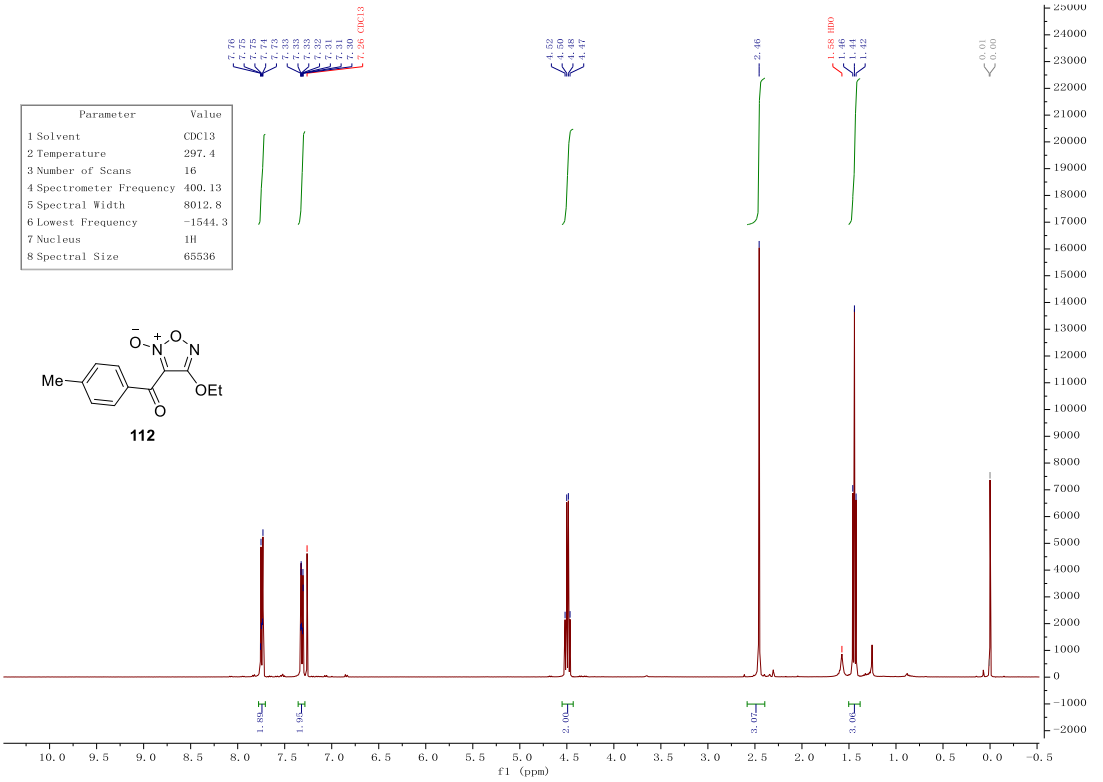
110

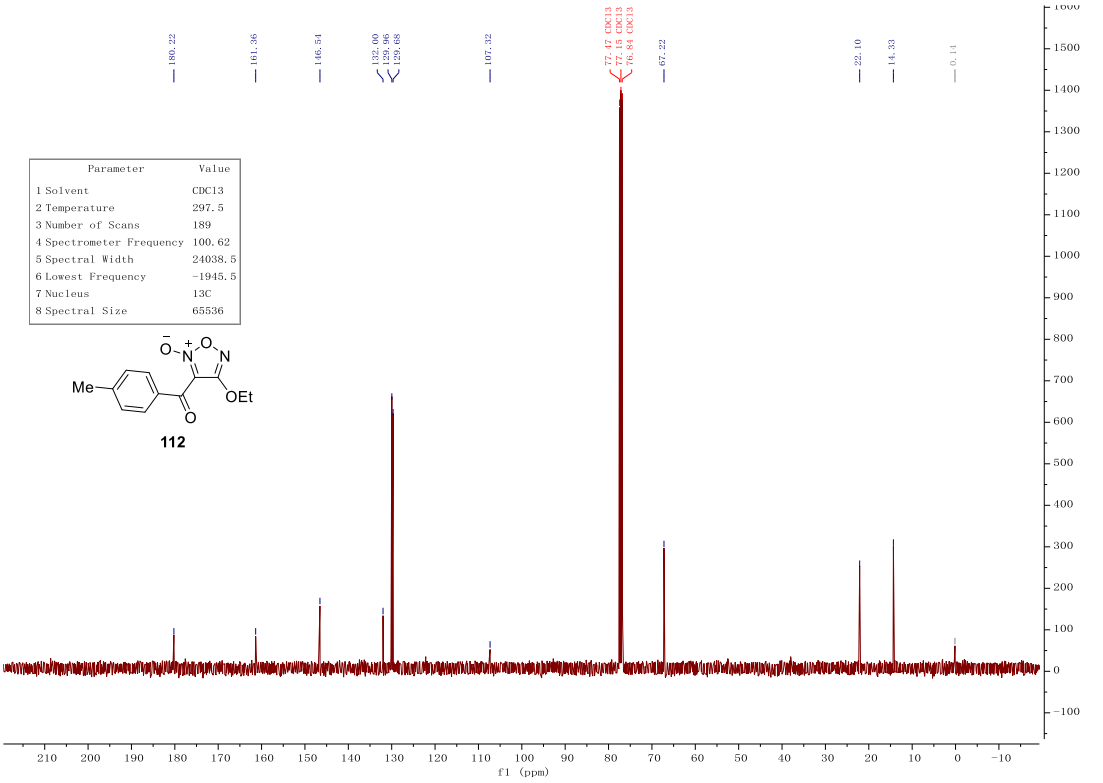

Parameter Value
1 Solvent CDCl3
2 Temperature 296.5
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.3
7 Nucleus 1H
8 Spectral Size 65536
OEt
111
f1 (ppm)

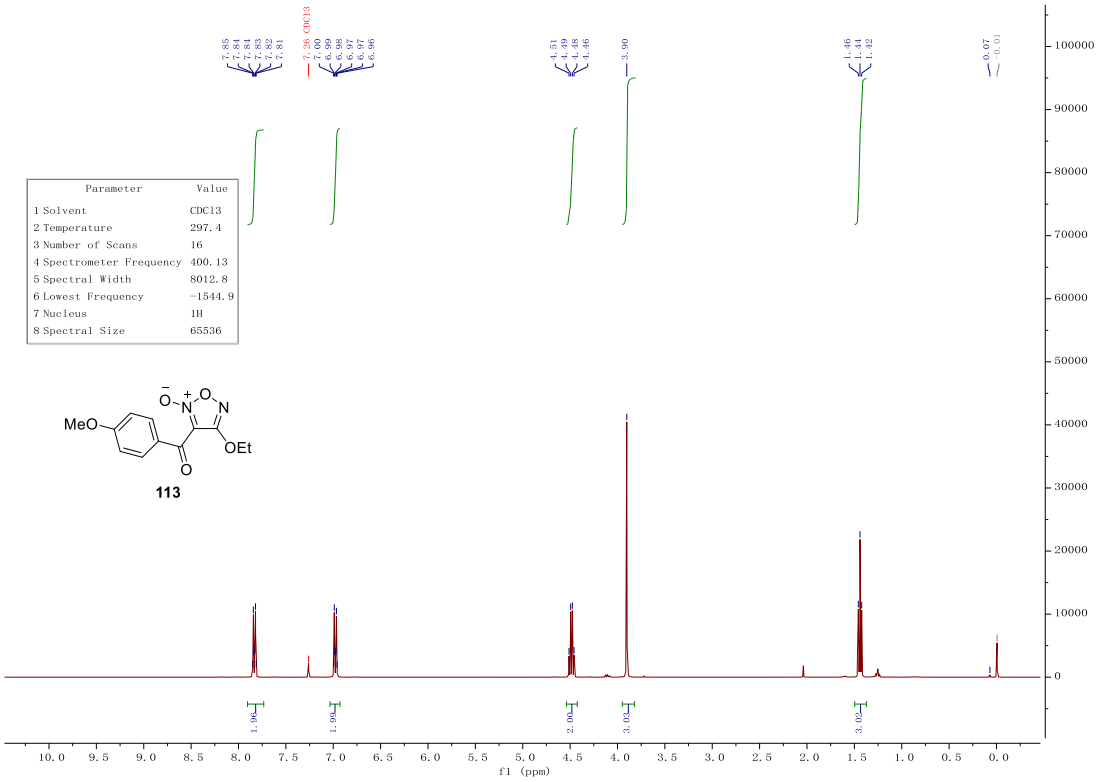

Parameter Value
1 Solvent CDCl3
2 Temperature 297.1
3 Number of Scans 185
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1945.5
7 Nucleus 13C
8 Spectral Size 65536
OEt
111
f1 (ppm)

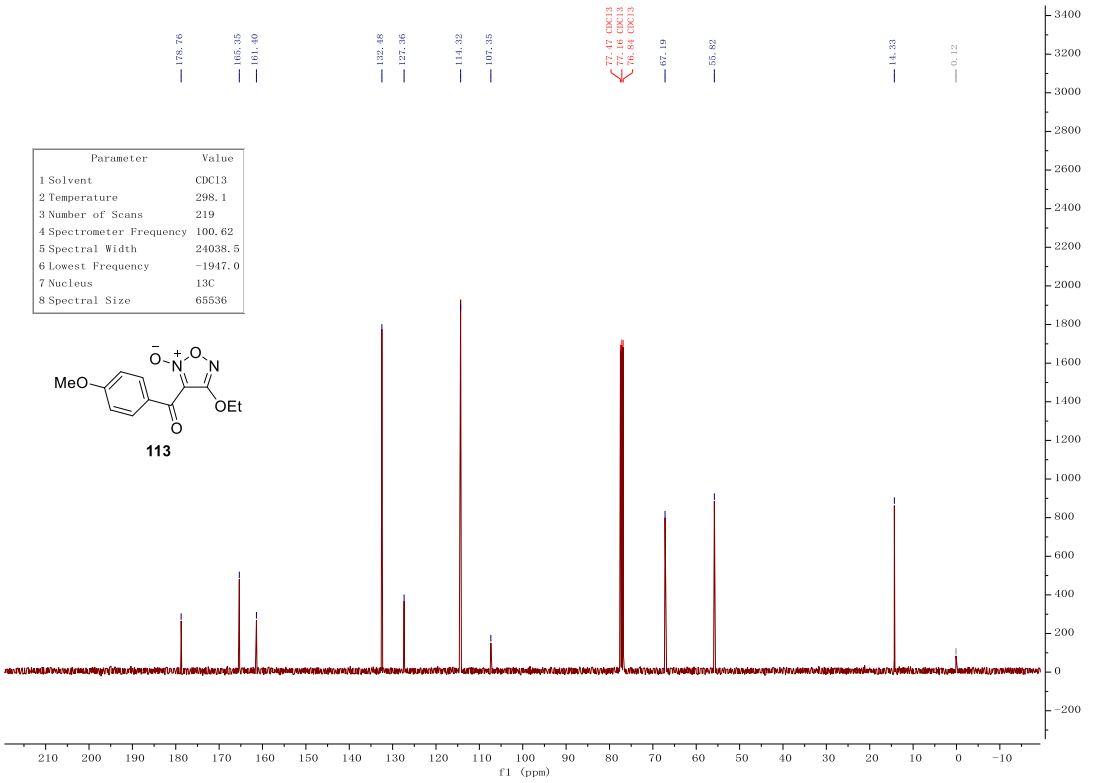

Parameter Value
1 Solvent CDCl3
2 Temperature 298.3
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.0
7 Nucleus 1H
8 Spectral Size 65536
OEt
87
f1 (ppm)

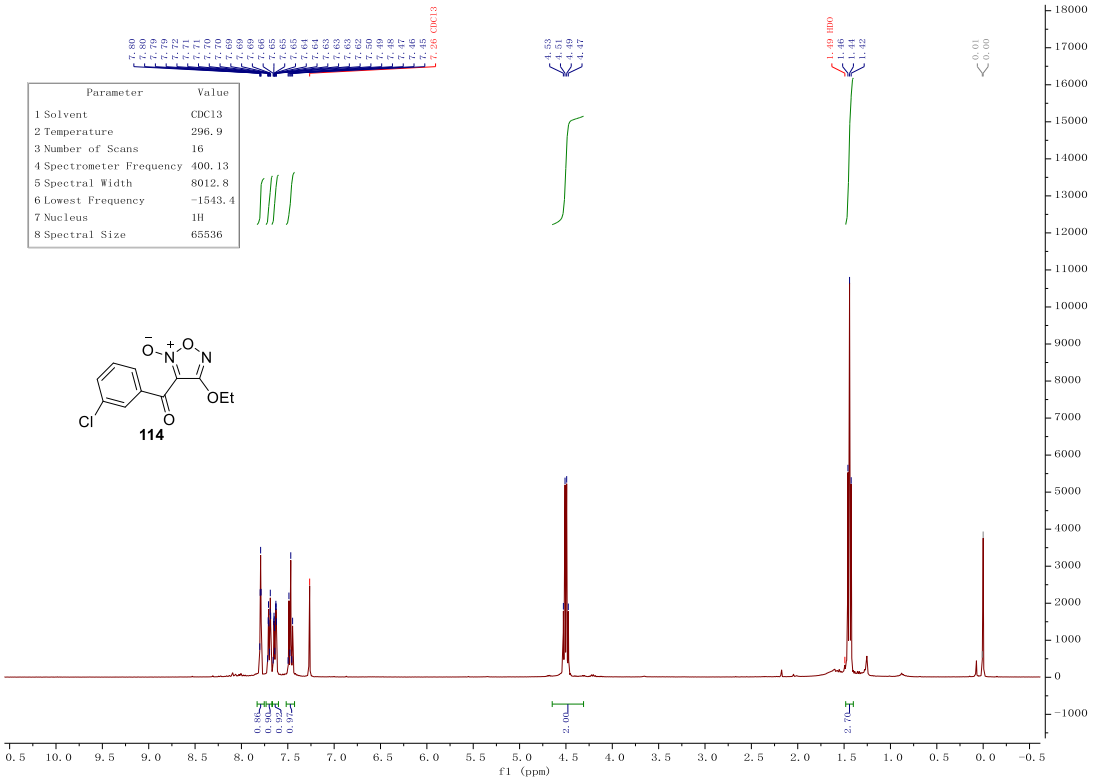

Parameter Value
1 Solvent CDCl3
2 Temperature 298.9
3 Number of Scans 134
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1945.1
7 Nucleus 13C
8 Spectral Size 65536
OEt
87
f1 (ppm)

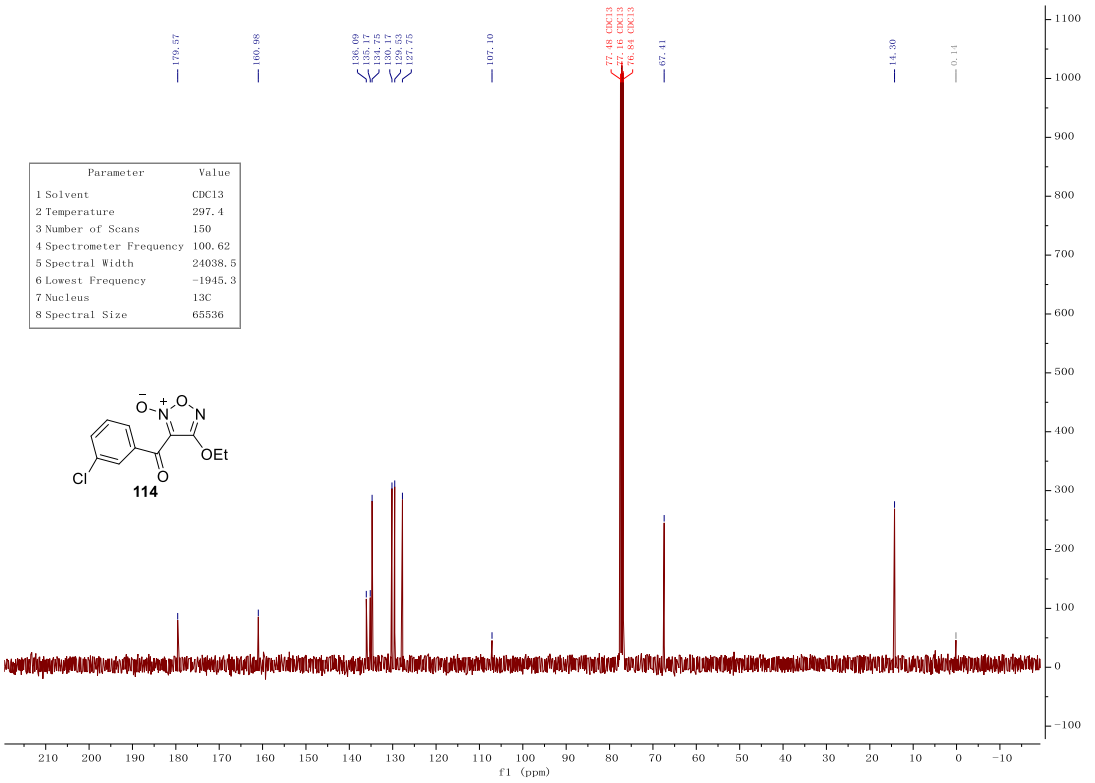

Parameter Value
1 Solvent CDCl3
2 Temperature 297.4
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1544.3
7 Nucleus 1H
8 Spectral Size 65536
Me
OEt
O
112
f1 (ppm)

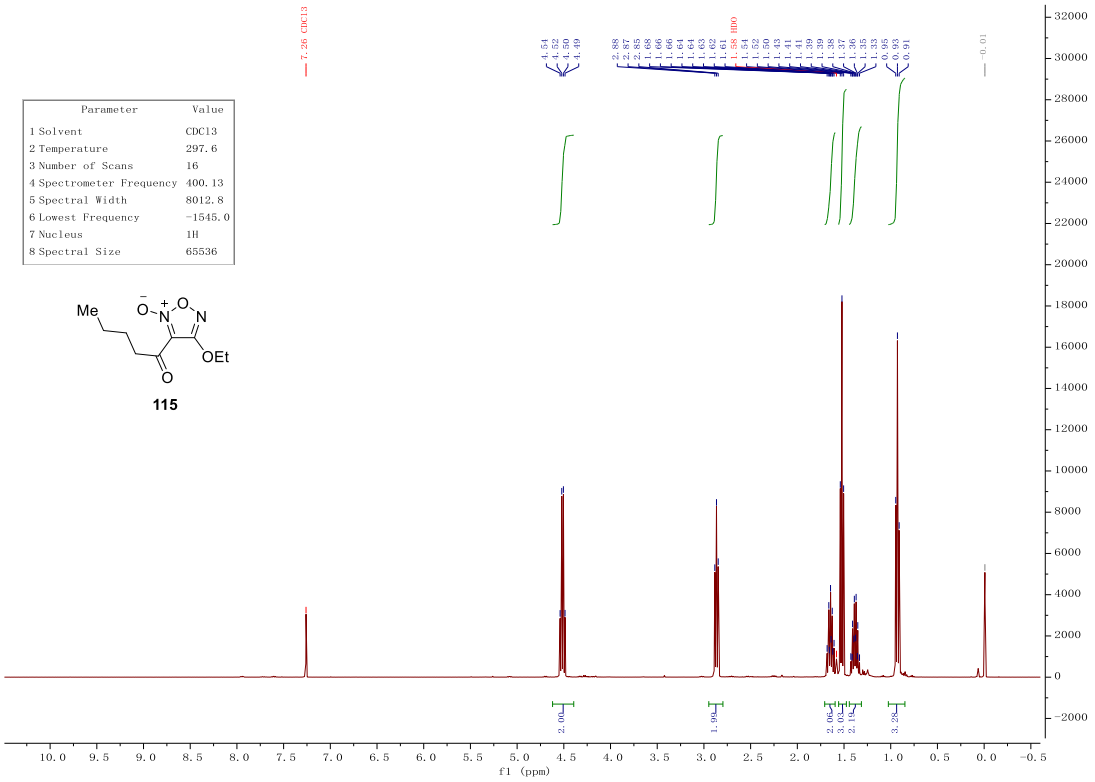

Parameter Value
1 Solvent CDCl3
2 Temperature 297.5
3 Number of Scans 189
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1945.5
7 Nucleus 13C
8 Spectral Size 65536
Me
OEt
O
112
f1 (ppm)

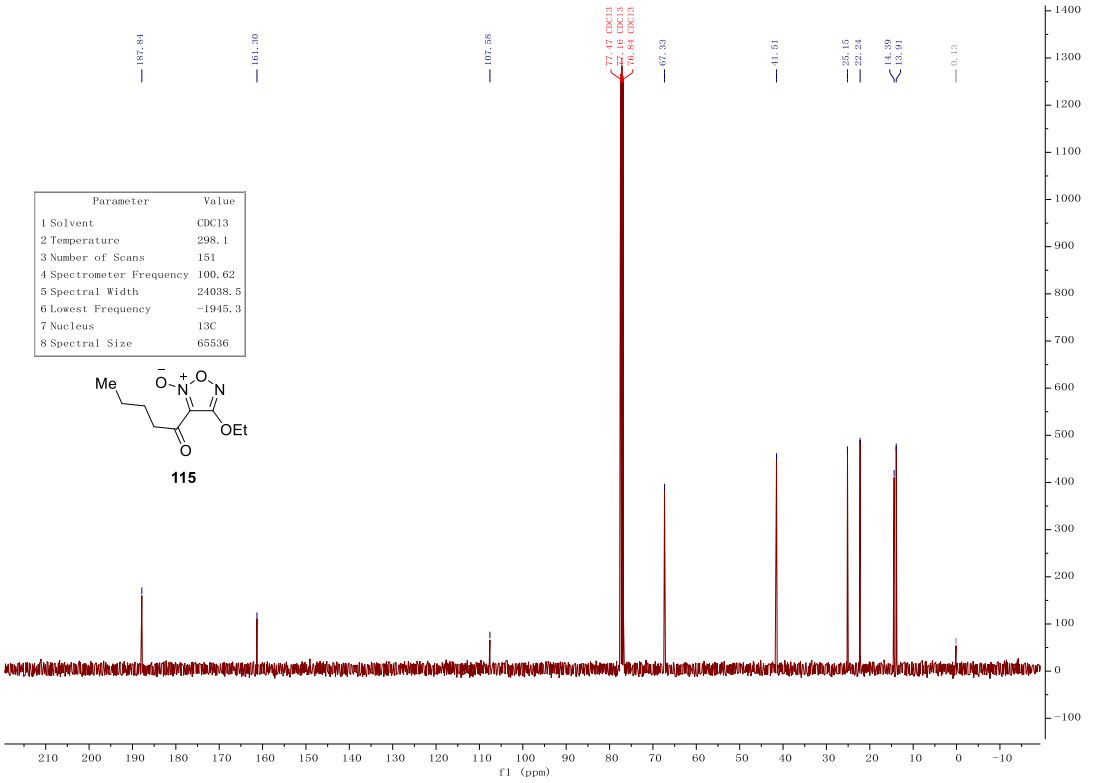

7.85
7.84
7.84
7.83
7.82
7.81
7.26 CDCl3
7.00
6.99
6.98
6.97
6.96
4.51
4.49
4.48
4.46
3.90
1.46
1.44
1.42
0.07
0.01
Parameter Value
1 Solvent CDCl3
2 Temperature 297.4
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1544.9
7 Nucleus 1H
8 Spectral Size 65536
MeO
OEt
113
1.96
1.99
2.00
3.03
3.02
f1 (ppm)

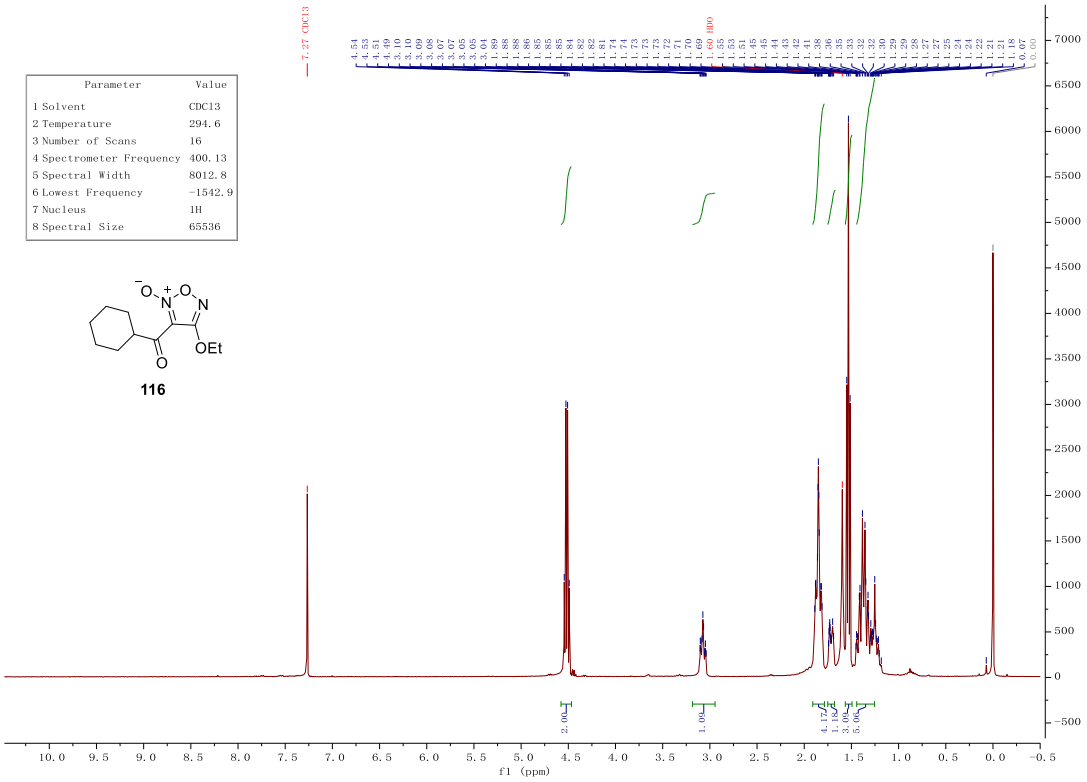

178.76
165.35
161.40
132.48
127.36
114.32
107.35
77.47 CDCl3
77.16 CDCl3
76.84 CDCl3
67.19
55.82
14.33
0.12
Parameter Value
1 Solvent CDCl3
2 Temperature 298.1
3 Number of Scans 219
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1947.0
7 Nucleus 13C
8 Spectral Size 65536
MeO
OEt
113
f1 (ppm)

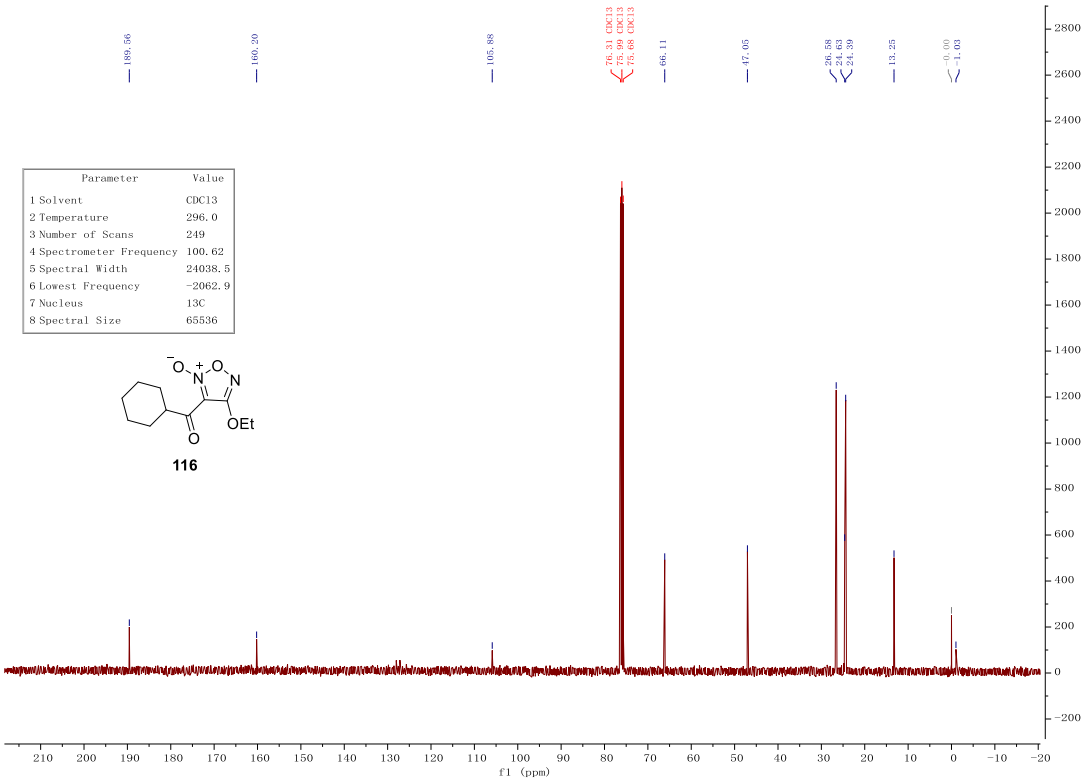

Parameter Value
1 Solvent CDC13
2 Temperature 296.9
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1543.4
7 Nucleus 1H
8 Spectral Size 65536
114
f1 (ppm)

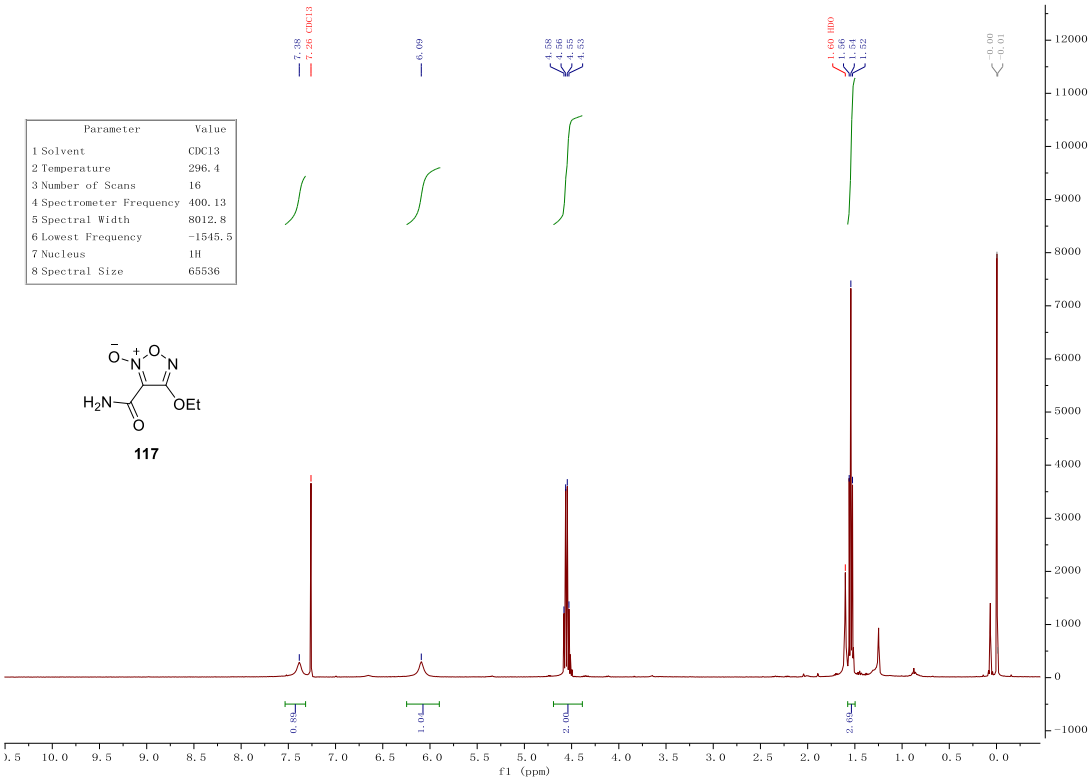

Parameter Value
1 Solvent CDC13
2 Temperature 297.4
3 Number of Scans 150
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1945.3
7 Nucleus 13C
8 Spectral Size 65536
114
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 297.6
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.0
7 Nucleus 1H
8 Spectral Size 65536
Me
OEt
O
115
f1 (ppm)

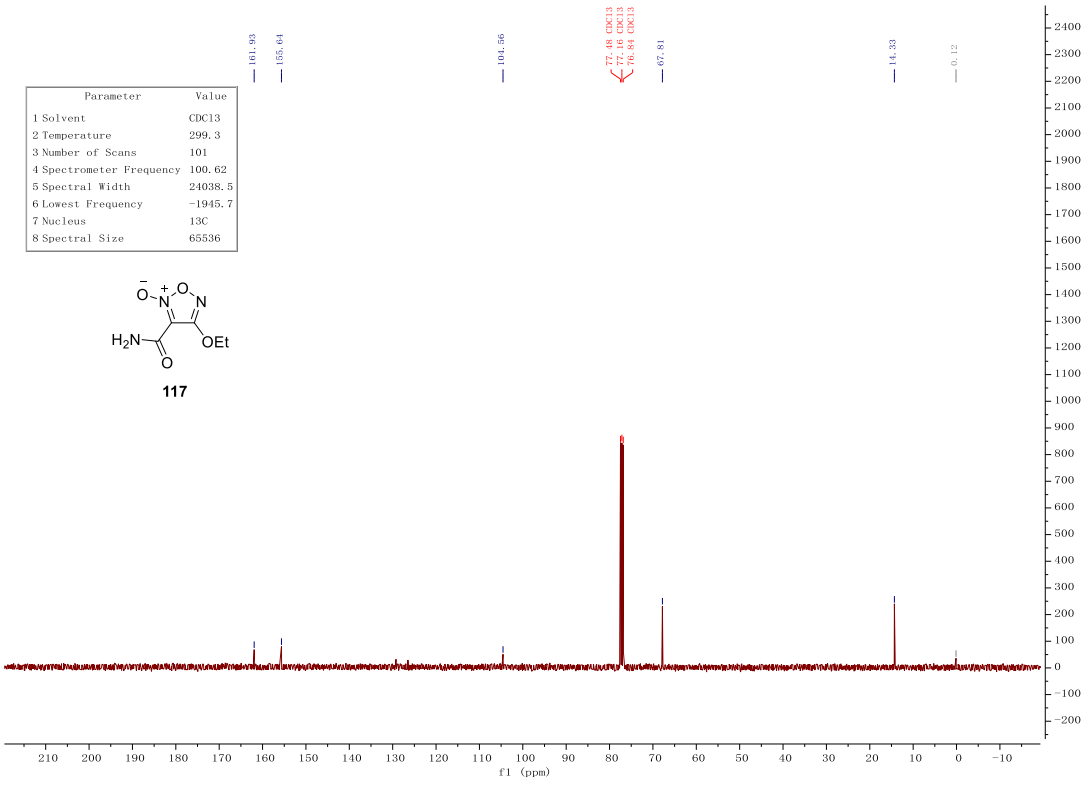

Parameter Value
1 Solvent CDCl3
2 Temperature 298.1
3 Number of Scans 151
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1945.3
7 Nucleus 13C
8 Spectral Size 65536
Me
OEt
O
115
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 294.6
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1542.9
7 Nucleus 1H
8 Spectral Size 65536
OEt
O
116
f1 (ppm)

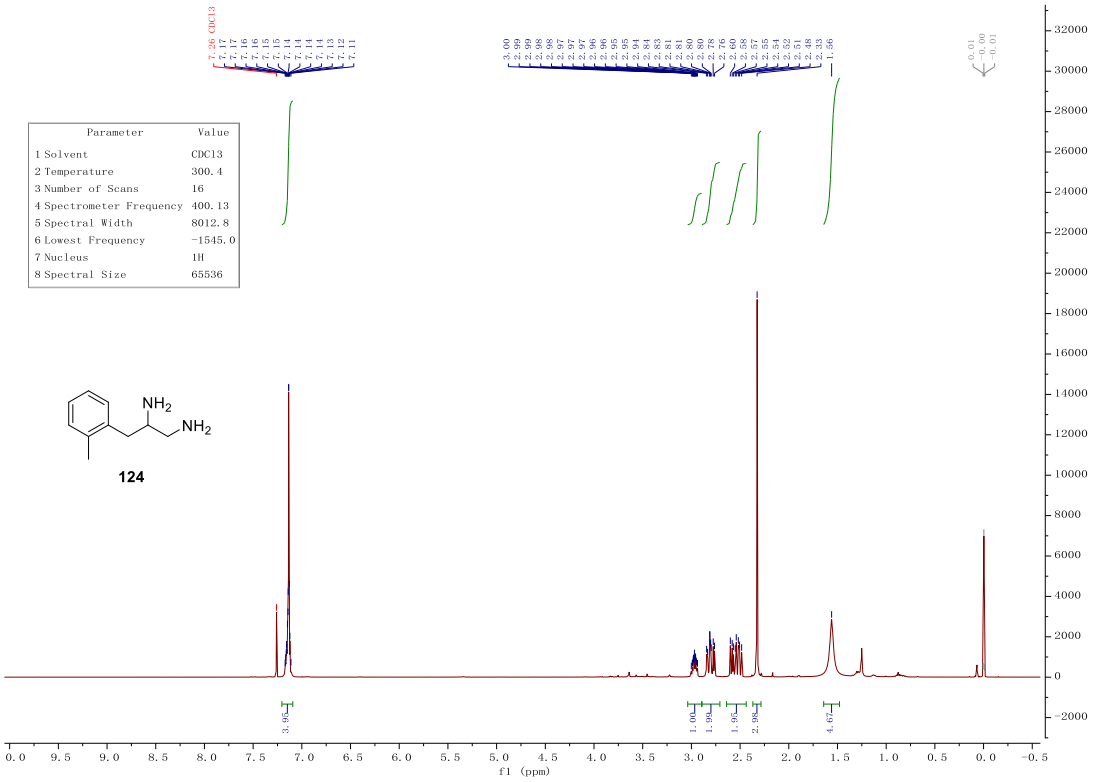

Parameter Value
1 Solvent CDCl3
2 Temperature 296.0
3 Number of Scans 249
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -2062.9
7 Nucleus 13C
8 Spectral Size 65536
OEt
O
116
f1 (ppm)

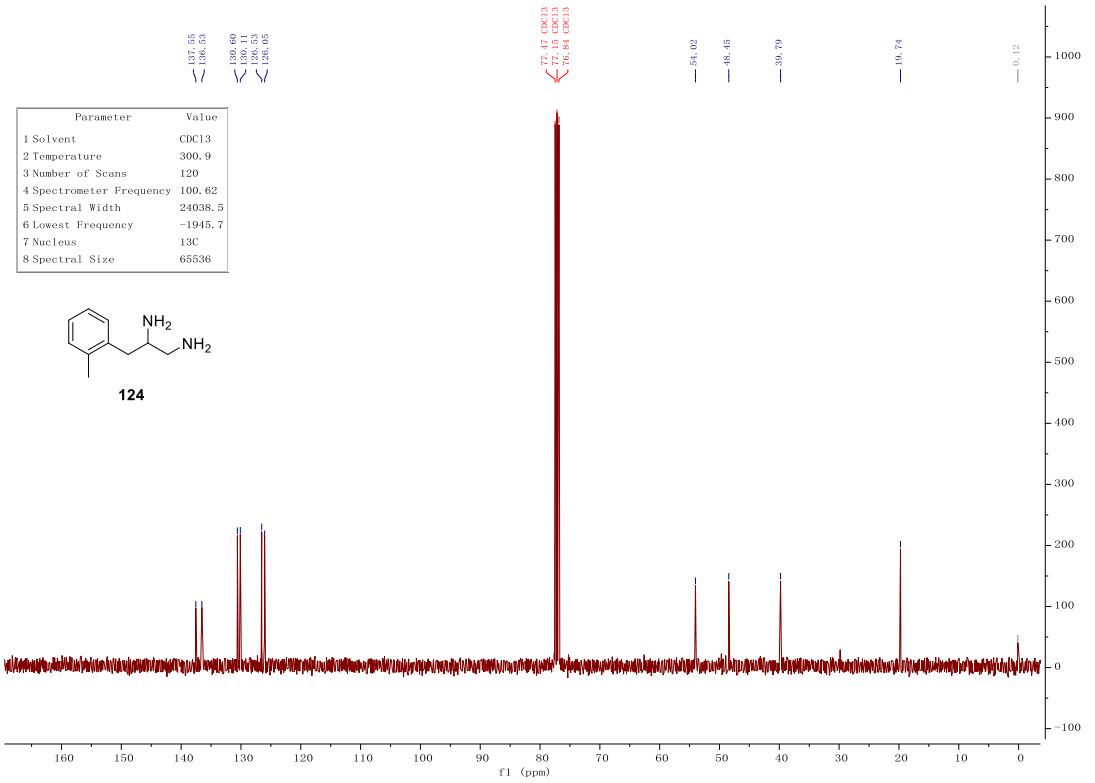

Parameter Value
1 Solvent CDCl3
2 Temperature 296.4
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.5
7 Nucleus 1H
8 Spectral Size 65536
7.38
7.26 CDCl3
6.09
4.58
4.56
4.55
4.53
1.60 HDO
1.56
1.54
1.52
0.00
-0.01
0.84
1.04
2.00
2.69
f1 (ppm)

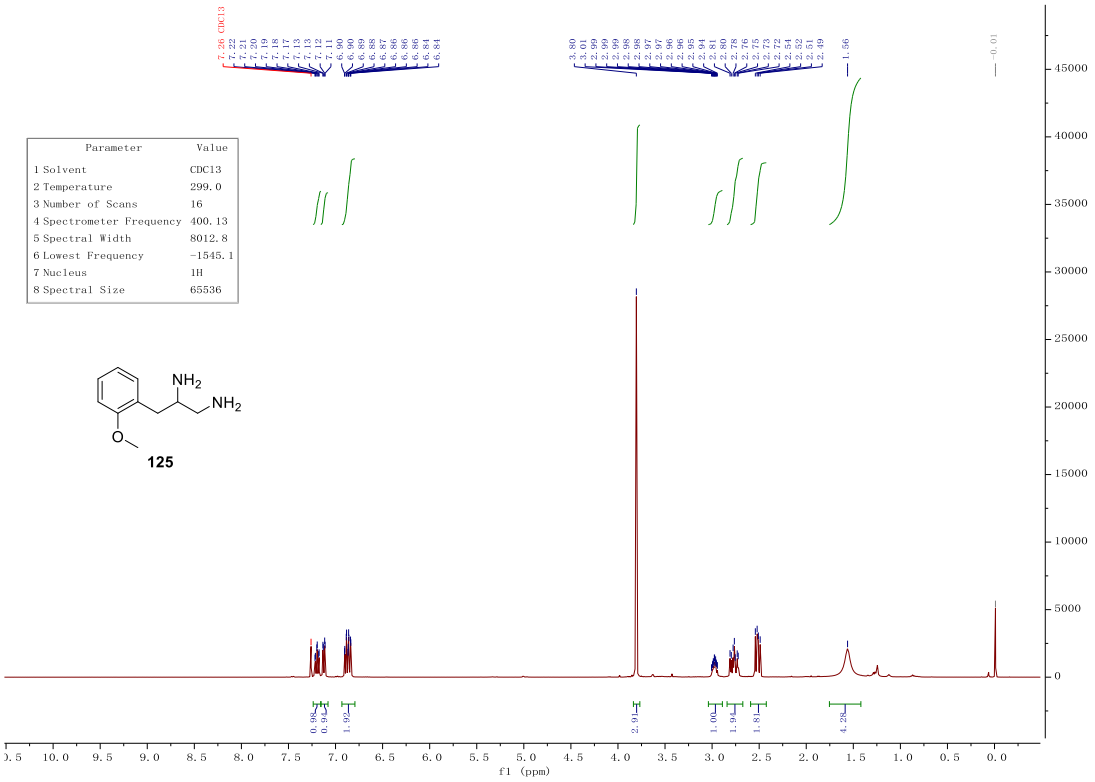
117

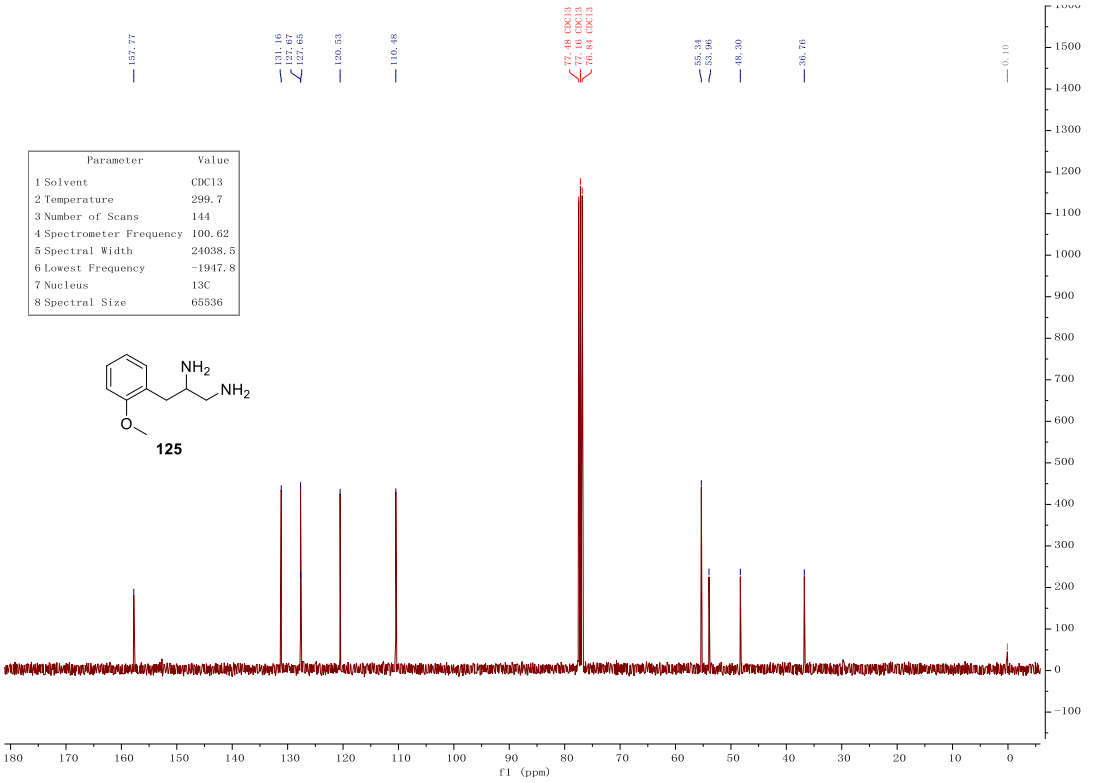

Parameter Value
1 Solvent CDCl3
2 Temperature 299.3
3 Number of Scans 101
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1945.7
7 Nucleus 13C
8 Spectral Size 65536
161.93
155.64
104.56
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
67.81
14.33
0.12
f1 (ppm)

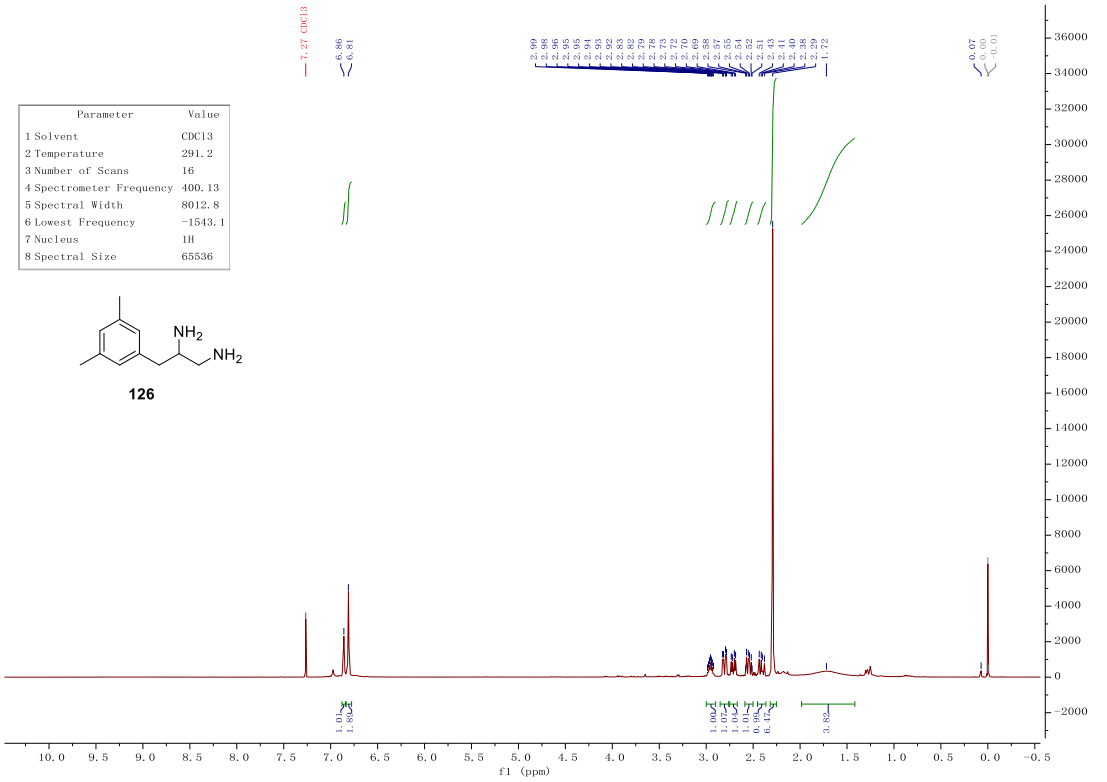
117

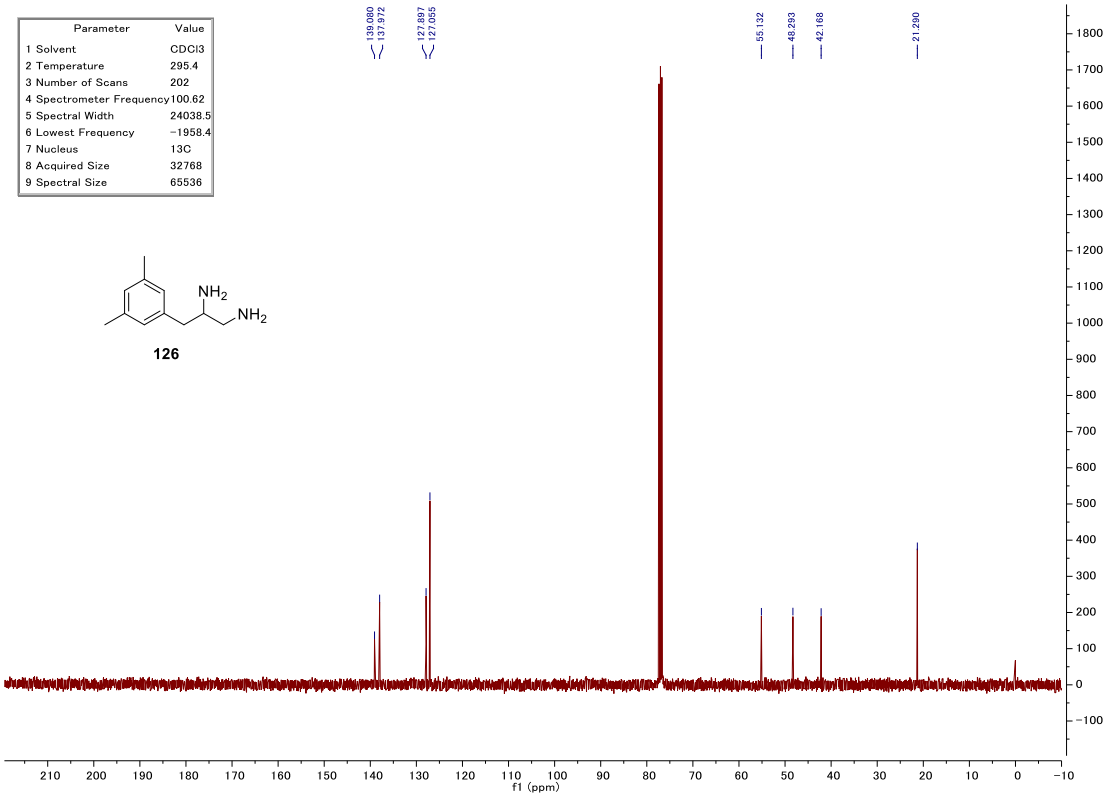

Parameter Value
1 Solvent CDCl3
2 Temperature 300.4
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.0
7 Nucleus 1H
8 Spectral Size 65536
NH2
NH2
124
f1 (ppm)

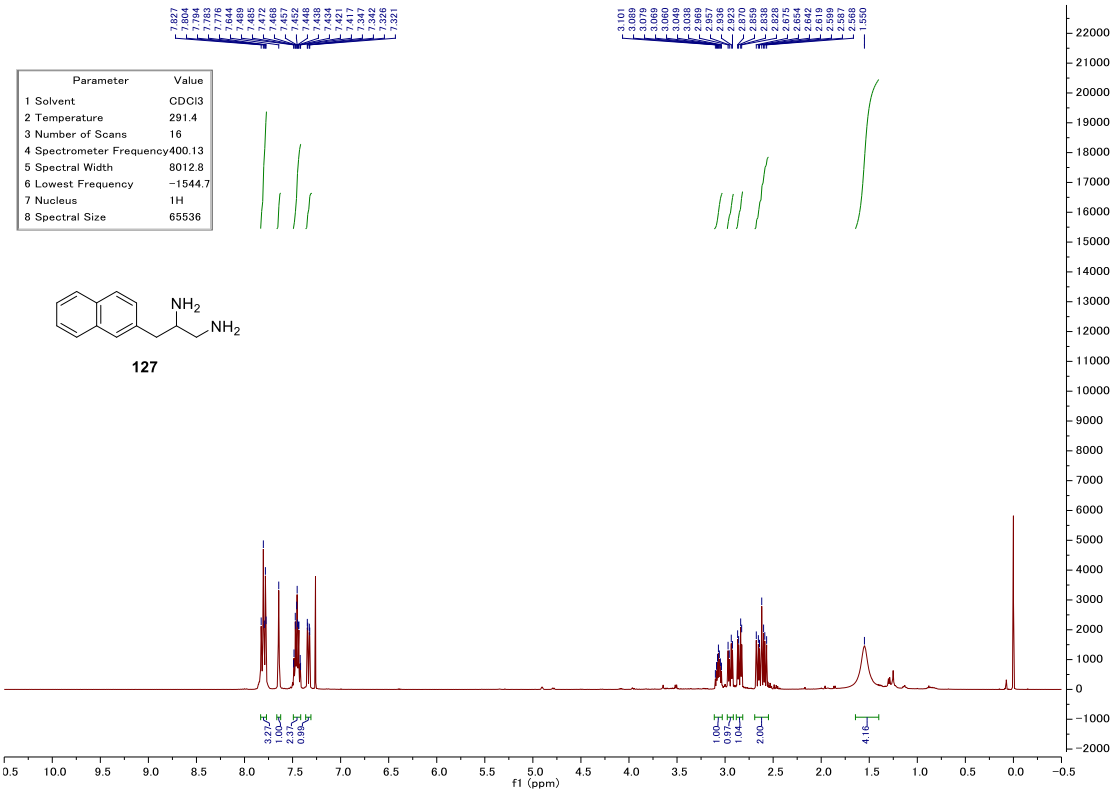

Parameter Value
1 Solvent CDCl3
2 Temperature 300.9
3 Number of Scans 120
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1945.7
7 Nucleus 13C
8 Spectral Size 65536
NH2
NH2
124
f1 (ppm)

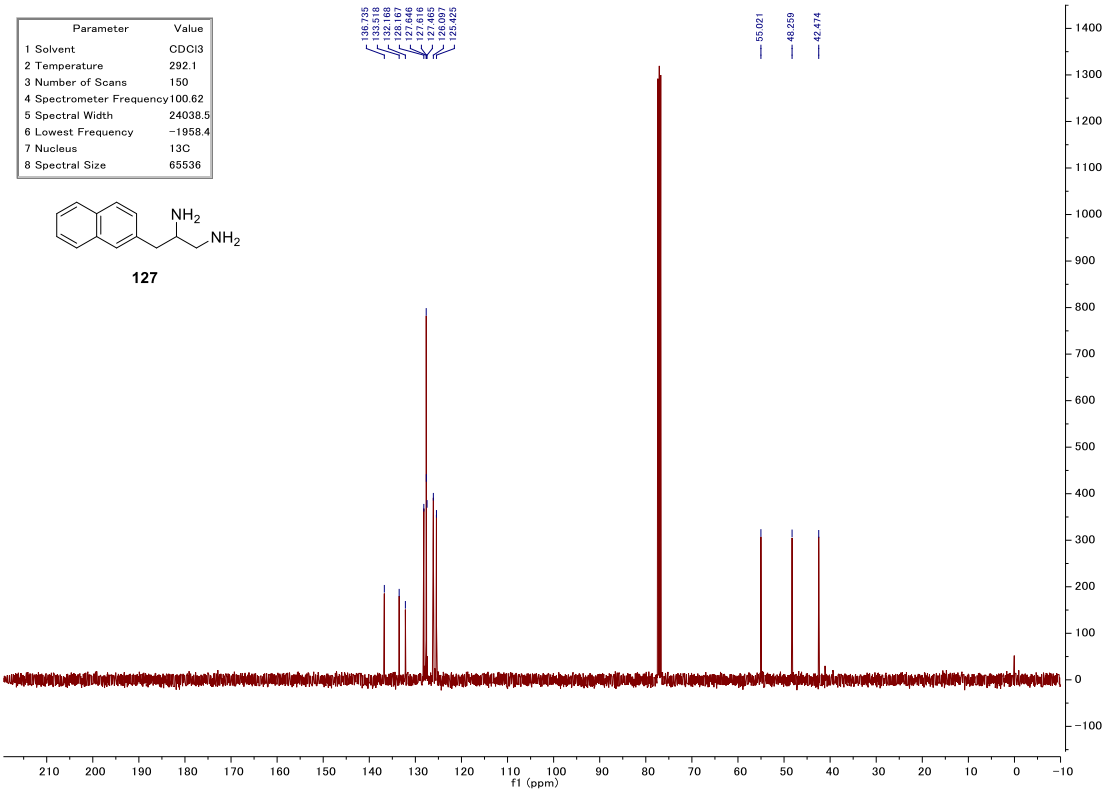

Parameter Value
1 Solvent CDCl3
2 Temperature 299.0
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.1
7 Nucleus 1H
8 Spectral Size 65536
NH2
NH2
O
125
f1 (ppm)

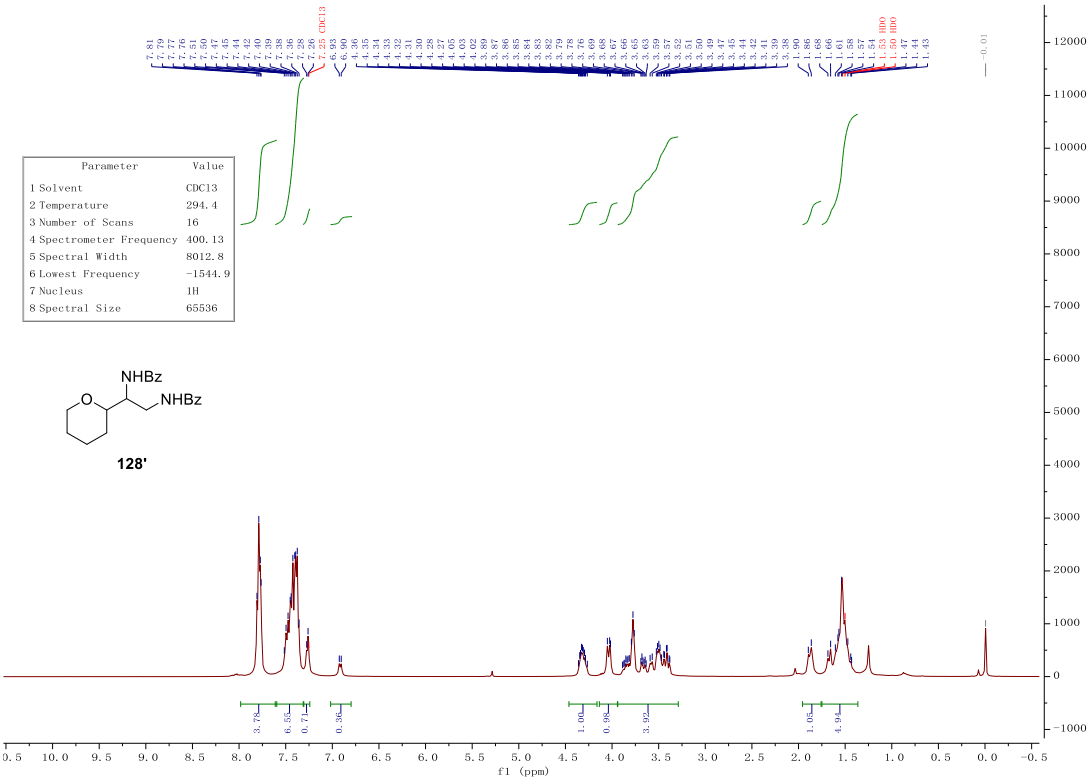

Parameter Value
1 Solvent CDCl3
2 Temperature 299.7
3 Number of Scans 144
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1947.8
7 Nucleus 13C
8 Spectral Size 65536
NH2
NH2
O
125
f1 (ppm)

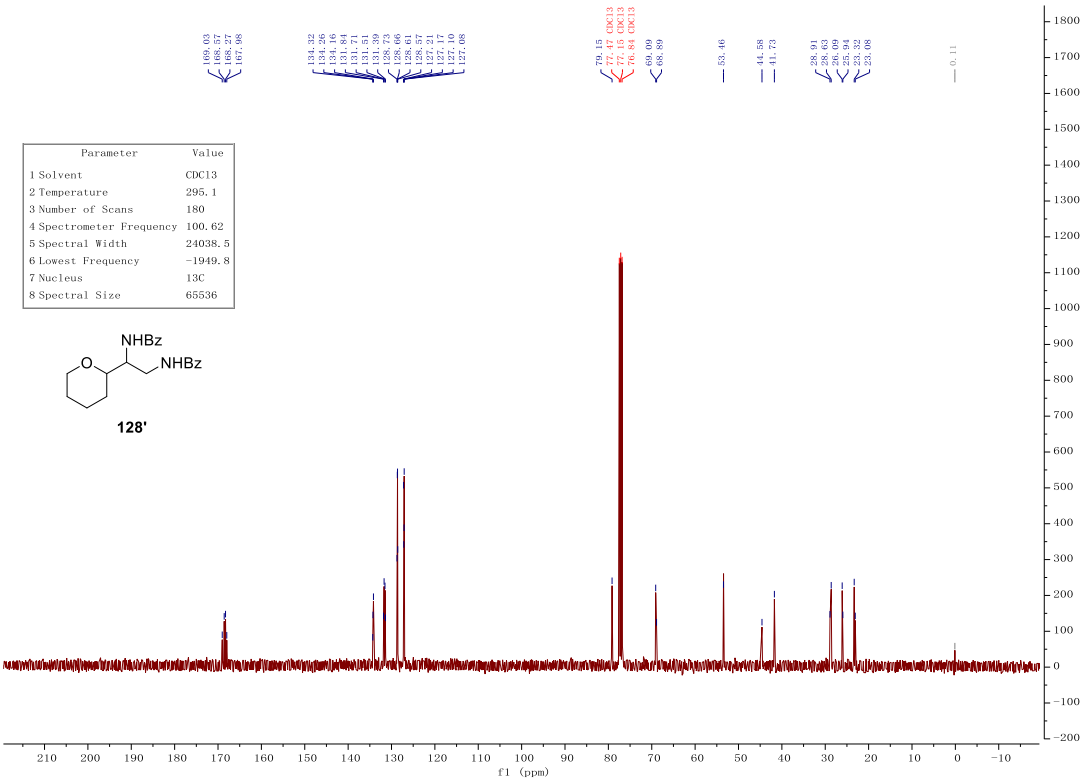

Parameter Value
1 Solvent CDCl3
2 Temperature 291.2
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1543.1
7 Nucleus 1H
8 Spectral Size 65536
NH2
NH2
126
f1 (ppm)

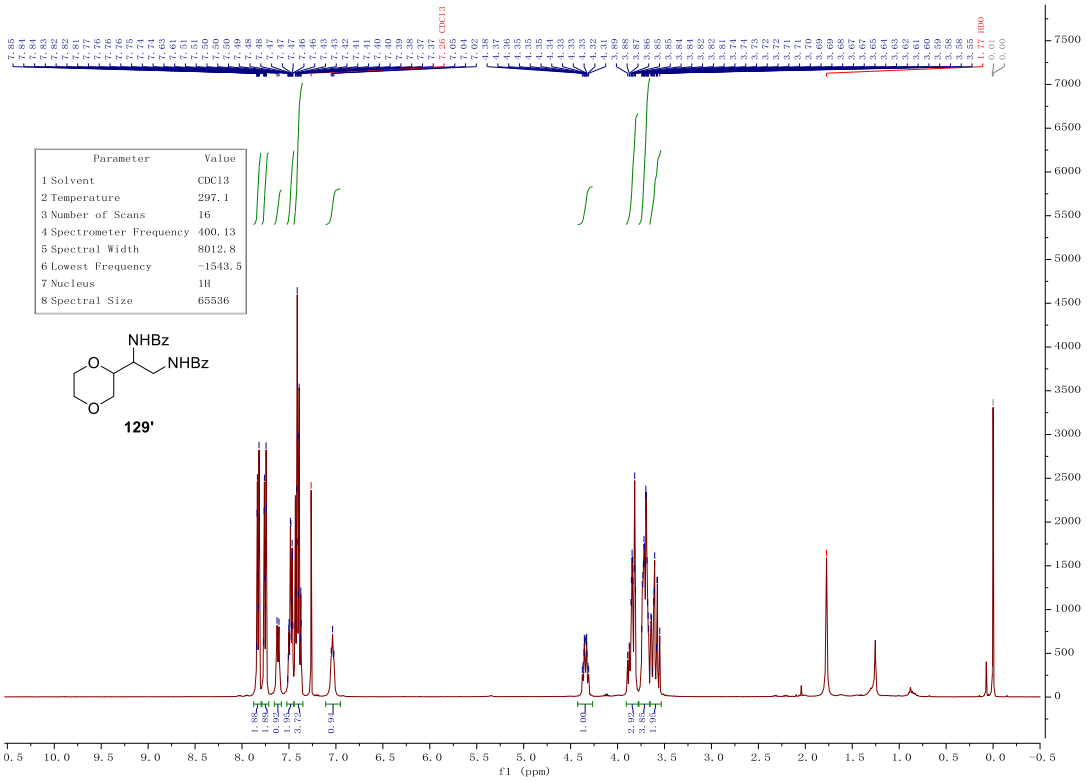

Parameter Value
1 Solvent CDCl3
2 Temperature 295.4
3 Number of Scans 202
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Acquired Size 32768
9 Spectral Size 65536
NH2
NH2
126
f1 (ppm)

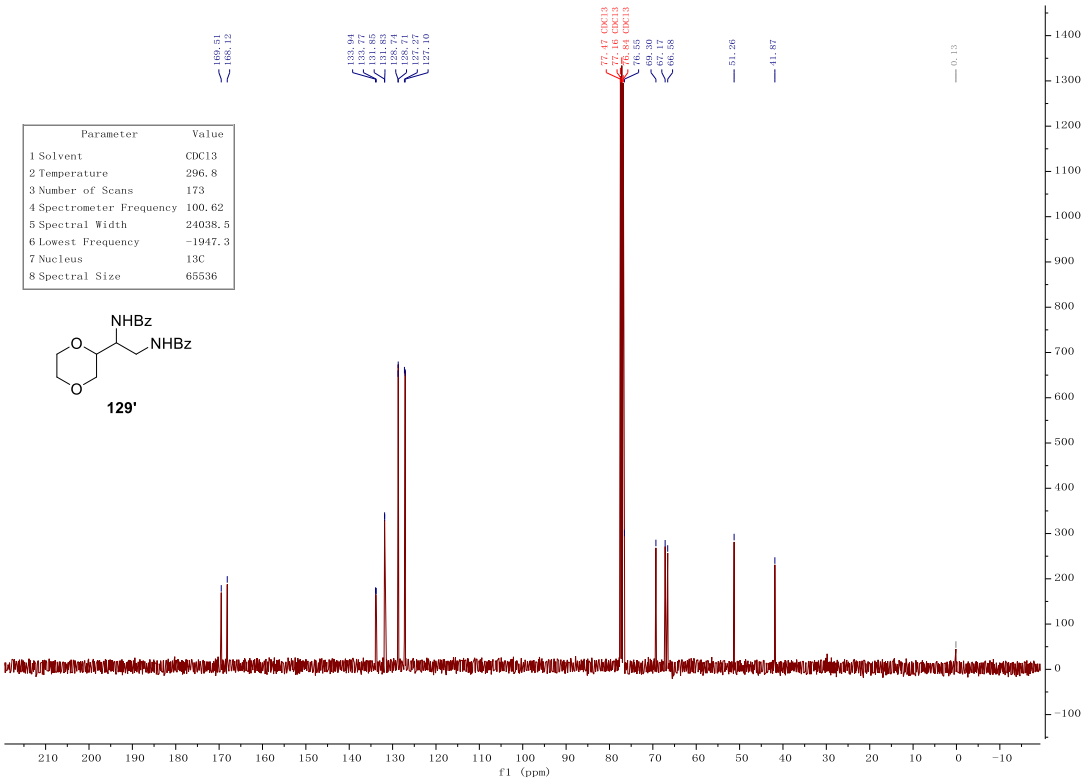

7.827
7.804
7.784
7.783
7.776
7.644
7.489
7.485
7.472
7.468
7.457
7.452
7.446
7.438
7.434
7.421
7.417
7.347
7.342
7.326
7.321
3.101
3.089
3.079
3.069
3.060
3.049
3.038
2.969
2.957
2.936
2.923
2.870
2.859
2.838
2.828
2.675
2.654
2.642
2.619
2.599
2.587
2.568
1.550
Parameter Value
1 Solvent CDCl3
2 Temperature 291.4
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1544.7
7 Nucleus 1H
8 Spectral Size 65536
NH2
NH2
127
3.22
1.00
2.37
0.99
1.00
0.97
1.04
2.00
4.16
f1 (ppm)

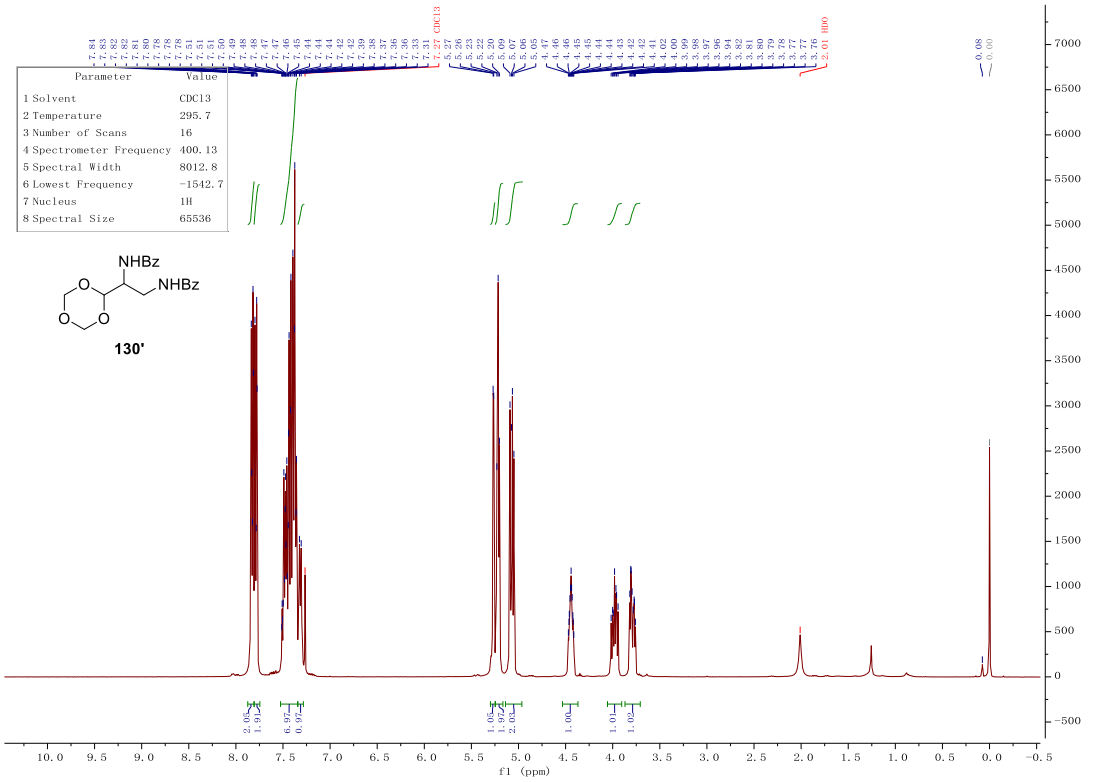

136.735
133.518
132.168
128.167
127.646
127.515
127.485
126.097
125.425
55.021
48.259
42.474
Parameter Value
1 Solvent CDCl3
2 Temperature 292.1
3 Number of Scans 150
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Spectral Size 65536
NH2
NH2
127
f1 (ppm)

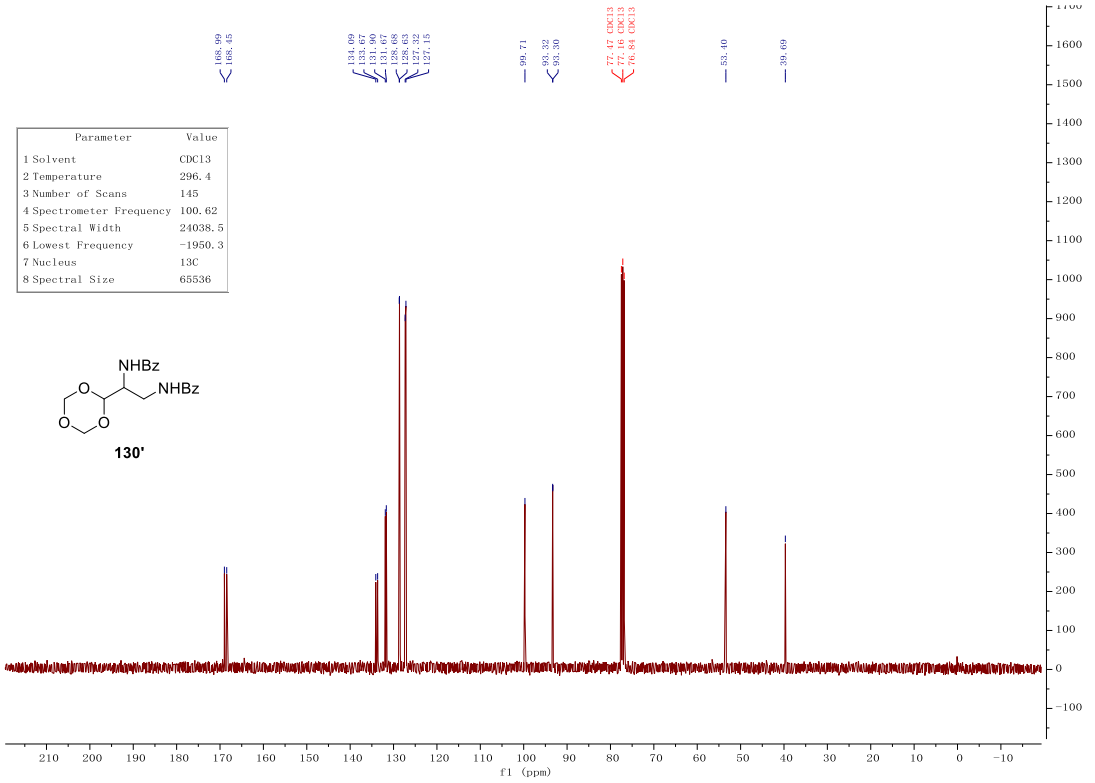

Parameter Value
1 Solvent CDCl3
2 Temperature 294.4
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1544.9
7 Nucleus 1H
8 Spectral Size 65536
NHBz
NHBz
O
128'
f1 (ppm)

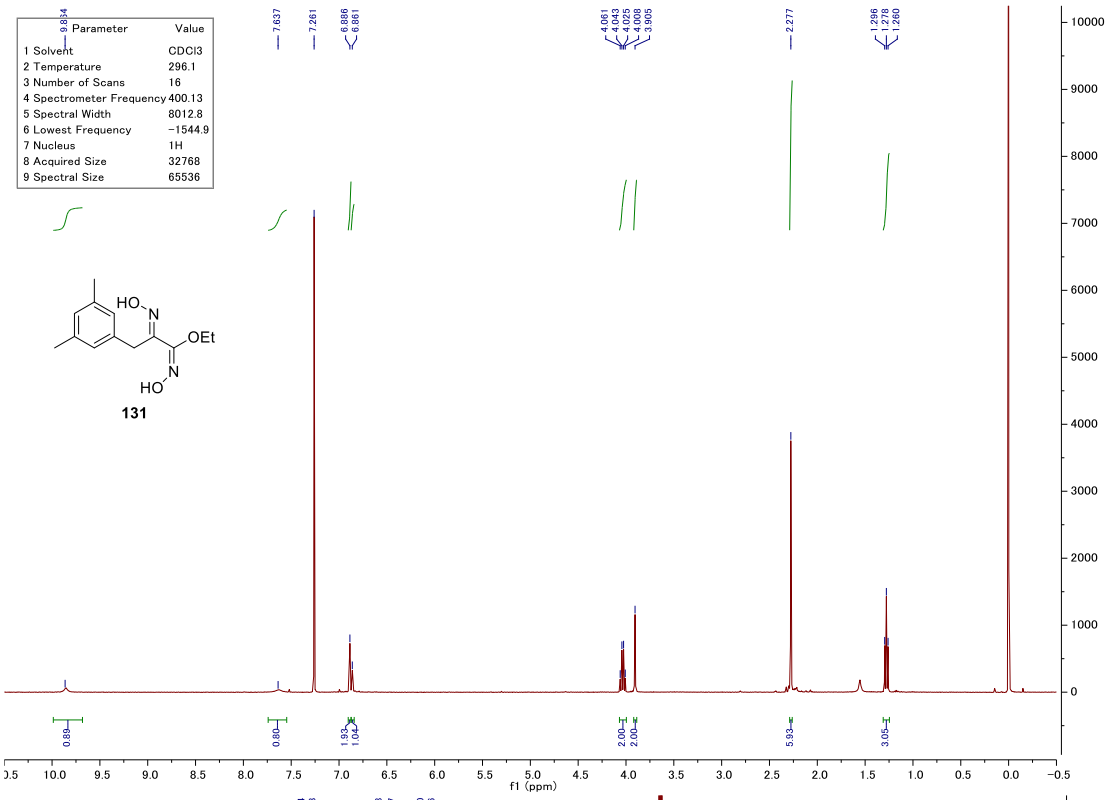

Parameter Value
1 Solvent CDCl3
2 Temperature 295.1
3 Number of Scans 180
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1949.8
7 Nucleus 13C
8 Spectral Size 65536
NHBz
NHBz
O
128'
f1 (ppm)

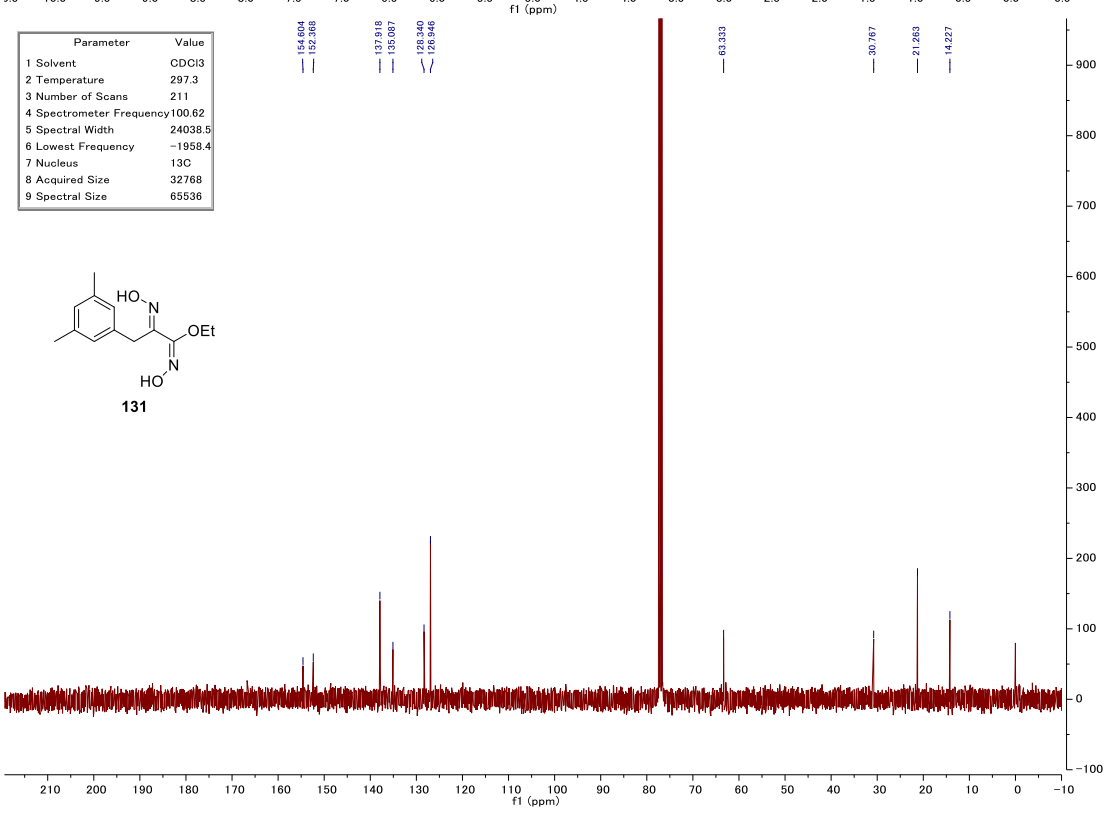

Parameter Value
1 Solvent CDCl3
2 Temperature 297.1
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1543.5
7 Nucleus 1H
8 Spectral Size 65536
NHBz
NHBz
O
O
129'
f1 (ppm)

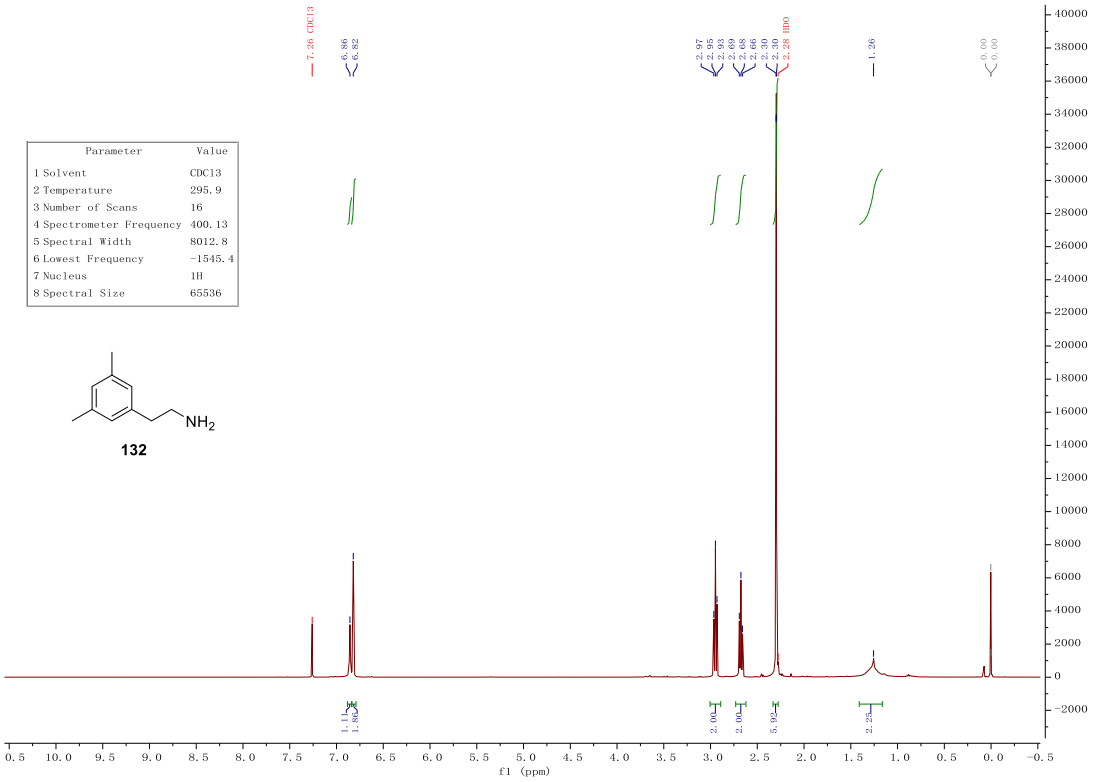

Parameter Value
1 Solvent CDCl3
2 Temperature 296.8
3 Number of Scans 173
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1947.3
7 Nucleus 13C
8 Spectral Size 65536
NHBz
NHBz
O
O
129'
f1 (ppm)

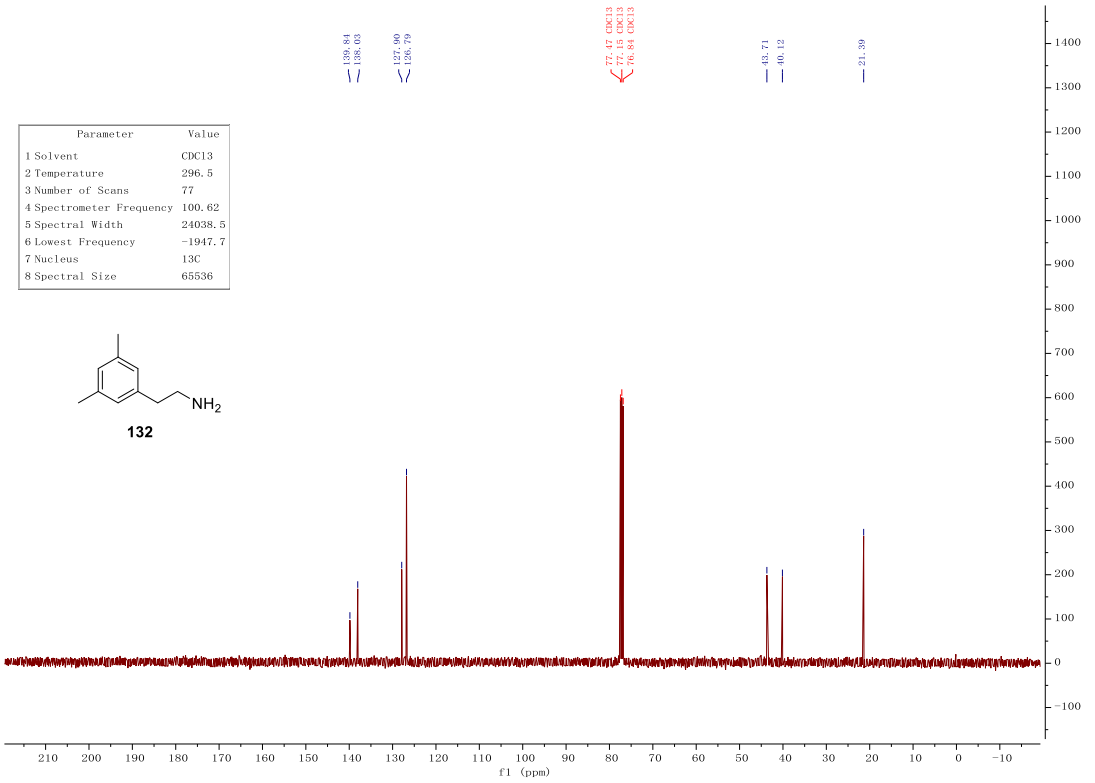

Parameter Value
1 Solvent CDCl3
2 Temperature 295.7
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1542.7
7 Nucleus 1H
8 Spectral Size 65536
NHBz
NHBz
130'
f1 (ppm)

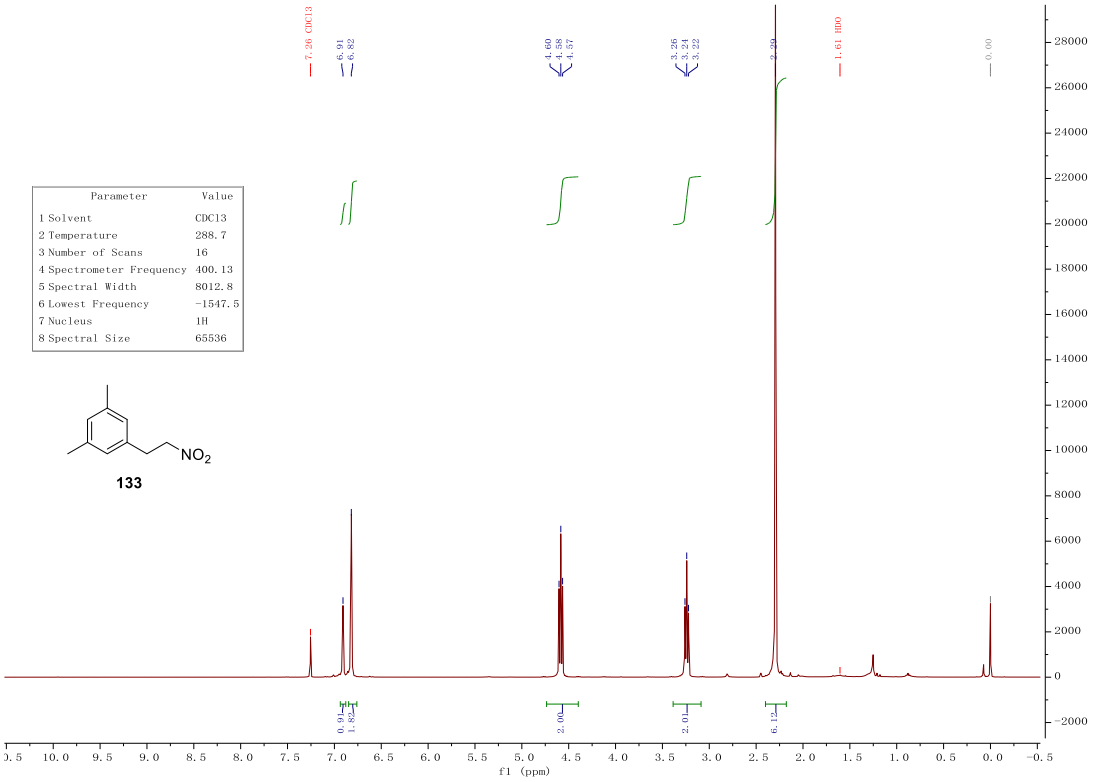

Parameter Value
1 Solvent CDCl3
2 Temperature 296.4
3 Number of Scans 145
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1950.3
7 Nucleus 13C
8 Spectral Size 65536
NHBz
NHBz
130'
f1 (ppm)

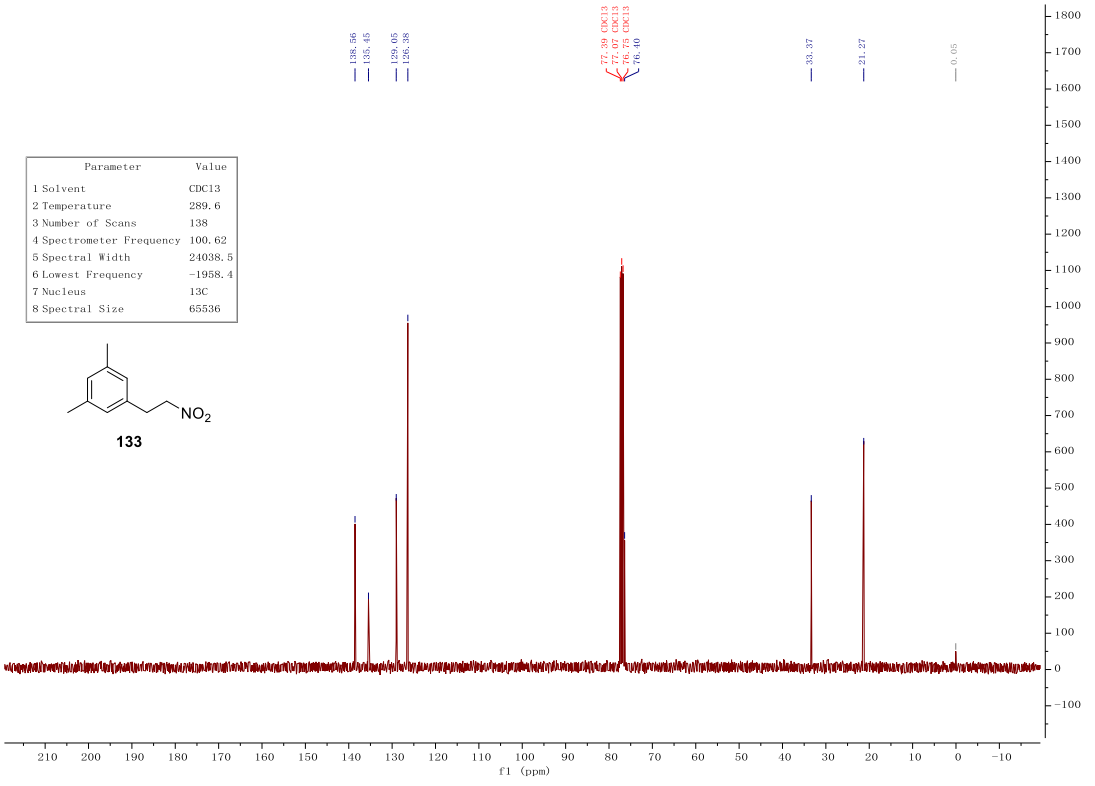

Parameter Value
1 Solvent CDCl3
2 Temperature 296.1
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency −1544.9
7 Nucleus 1H
8 Acquired Size 32768
9 Spectral Size 65536
9.934
7.637
7.261
6.886
6.861
4.061
4.043
4.025
4.008
3.905
2.277
1.296
1.278
1.260
HO
N
OEt
N
HO
131
0.89
0.80
1.93
1.04
2.00
2.00
5.93
3.05
f1 (ppm)

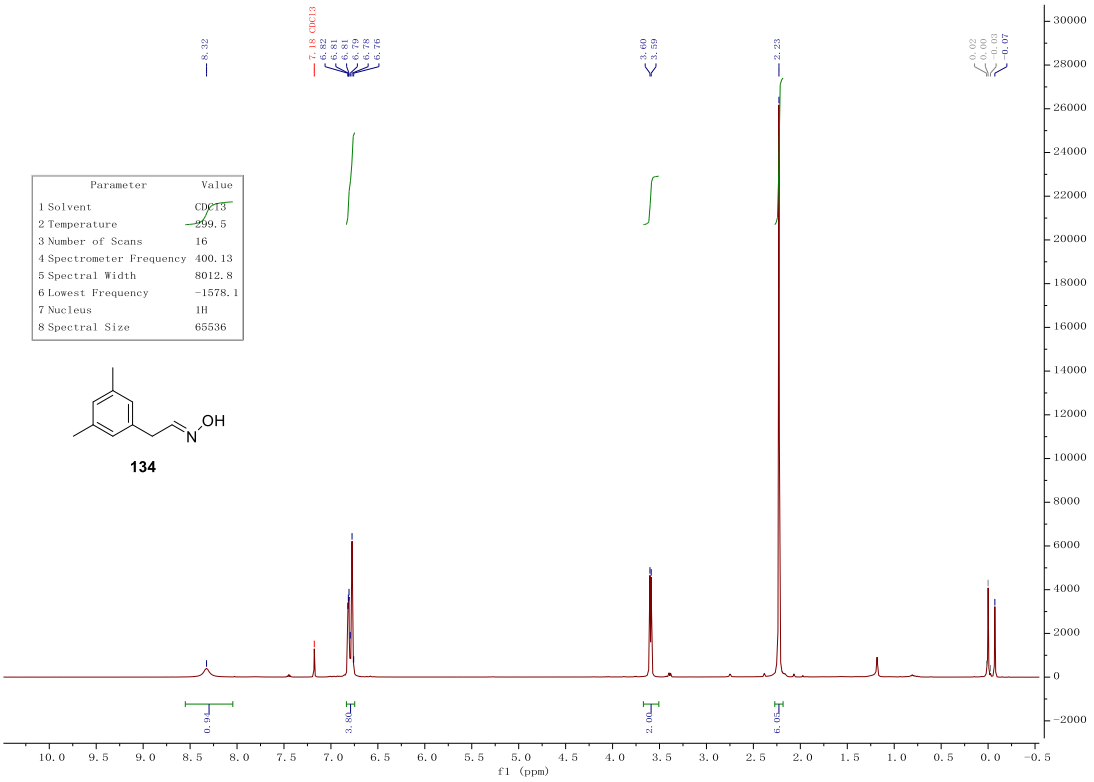

Parameter Value
1 Solvent CDCl3
2 Temperature 297.3
3 Number of Scans 211
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency −1958.4
7 Nucleus 13C
8 Acquired Size 32768
9 Spectral Size 65536
154.604
152.368
137.918
135.087
128.340
126.946
63.333
30.767
21.263
14.227
HO
N
OEt
N
HO
131
f1 (ppm)

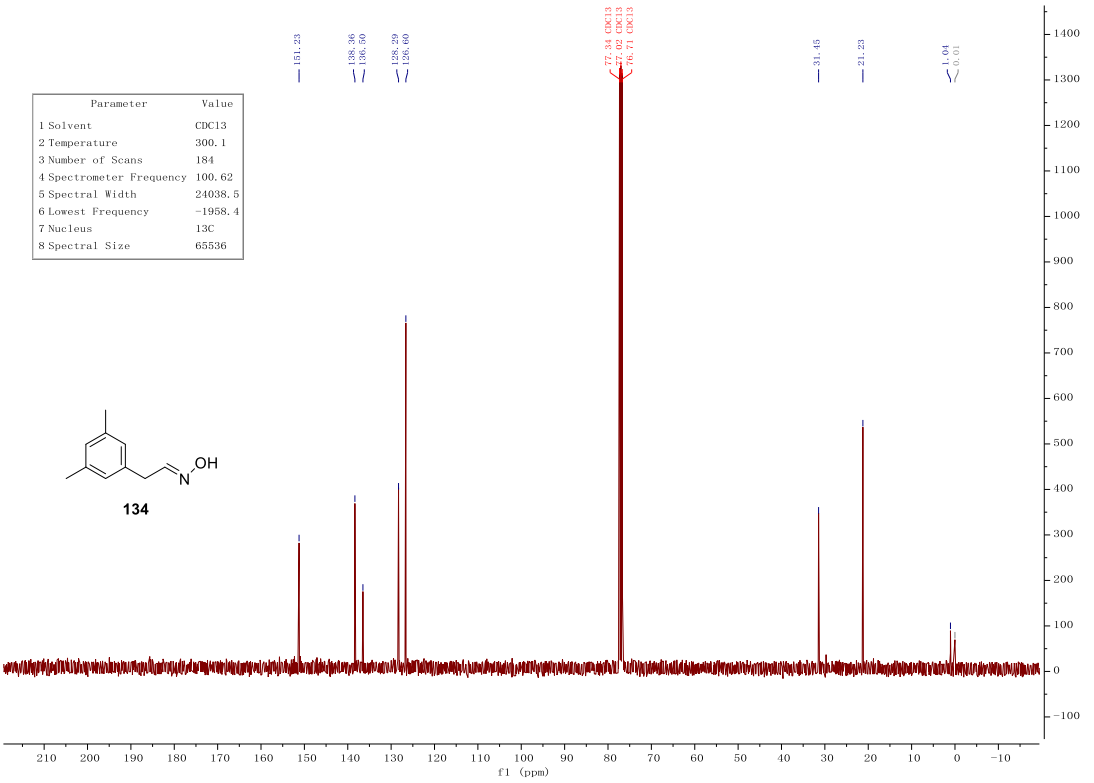

7.26 CDCl3
6.86
6.82
2.97
2.95
2.93
2.69
2.68
2.66
2.30
2.28 HDO
1.26
0.00
0.00
Parameter Value
1 Solvent CDCl3
2 Temperature 295.9
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.4
7 Nucleus 1H
8 Spectral Size 65536
NH2
132
1.11
1.86
2.00
2.00
5.92
2.25
f1 (ppm)

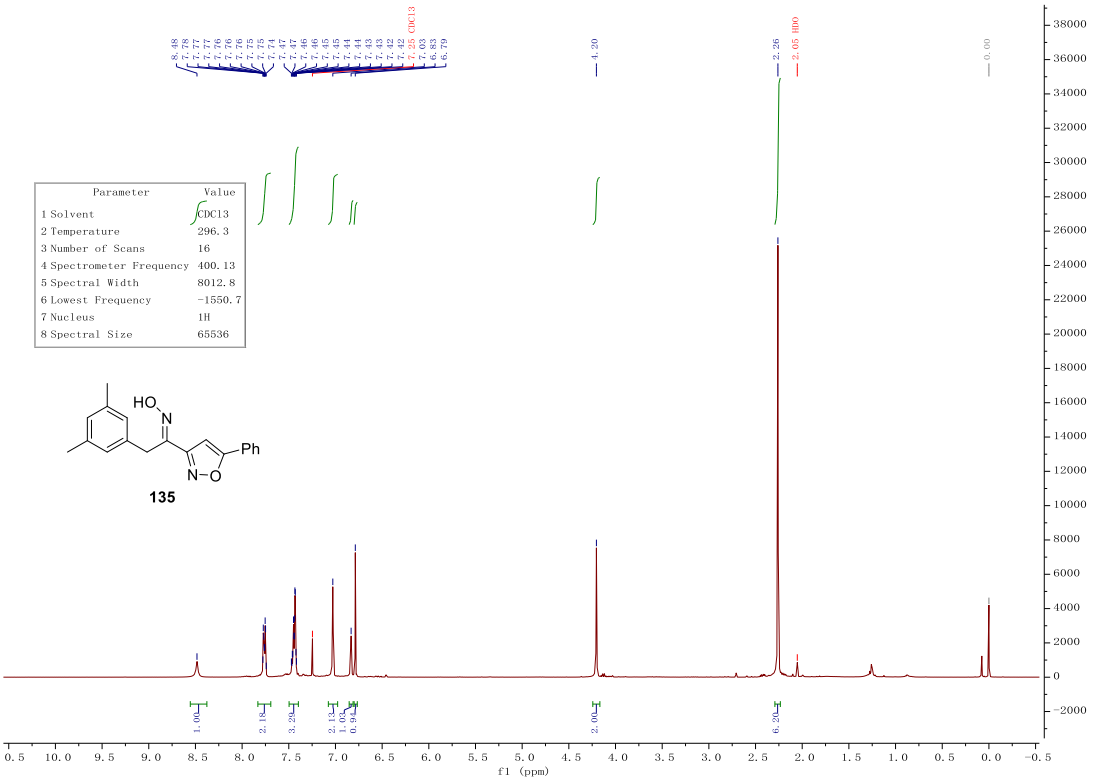

139.84
138.03
127.90
126.79
77.47 CDCl3
77.15 CDCl3
76.84 CDCl3
43.71
40.12
21.39
Parameter Value
1 Solvent CDCl3
2 Temperature 296.5
3 Number of Scans 77
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1947.7
7 Nucleus 13C
8 Spectral Size 65536
NH2
132
f1 (ppm)

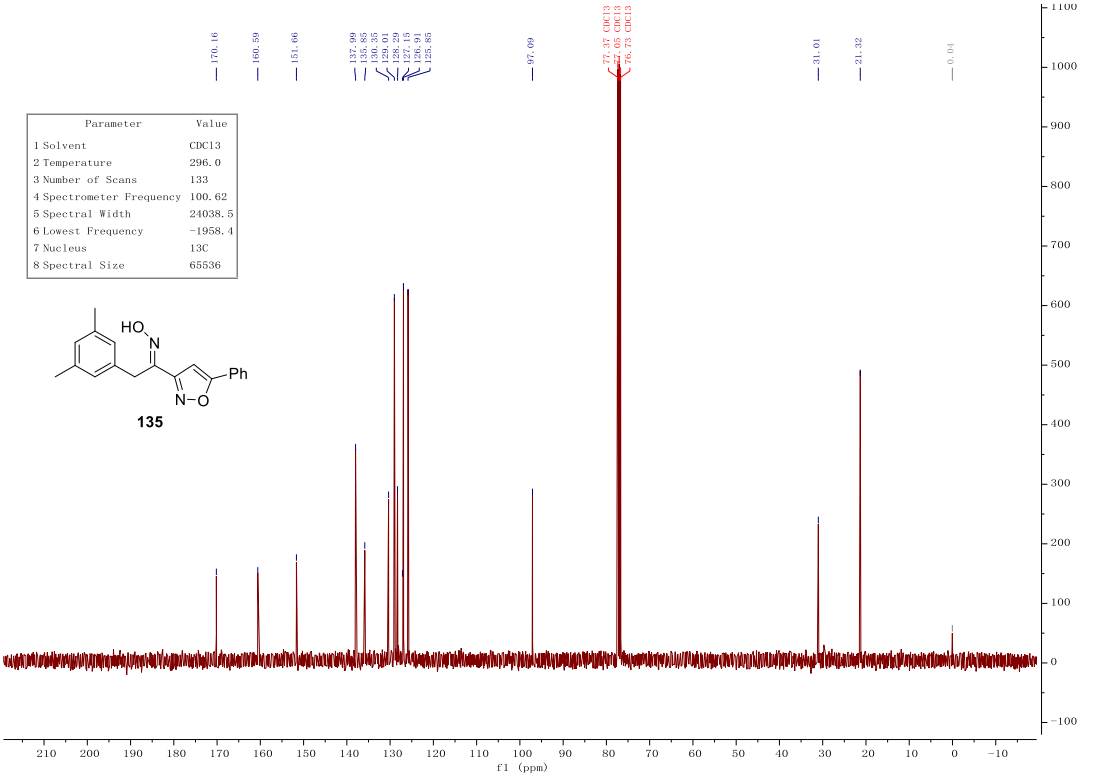

7.26 CDCl3
6.91
6.82
4.60
4.58
4.57
3.26
3.24
3.22
2.29
1.61 HDO
0.00
Parameter Value
1 Solvent CDCl3
2 Temperature 288.7
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1547.5
7 Nucleus 1H
8 Spectral Size 65536
NO2
133
0.91
1.82
2.00
2.01
6.12
f1 (ppm)


138.56
135.45
129.05
126.38
77.39 CDCl3
77.07 CDCl3
76.75 CDCl3
76.40
33.37
21.27
0.05
Parameter Value
1 Solvent CDCl3
2 Temperature 289.6
3 Number of Scans 138
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
NO2
133
f1 (ppm)

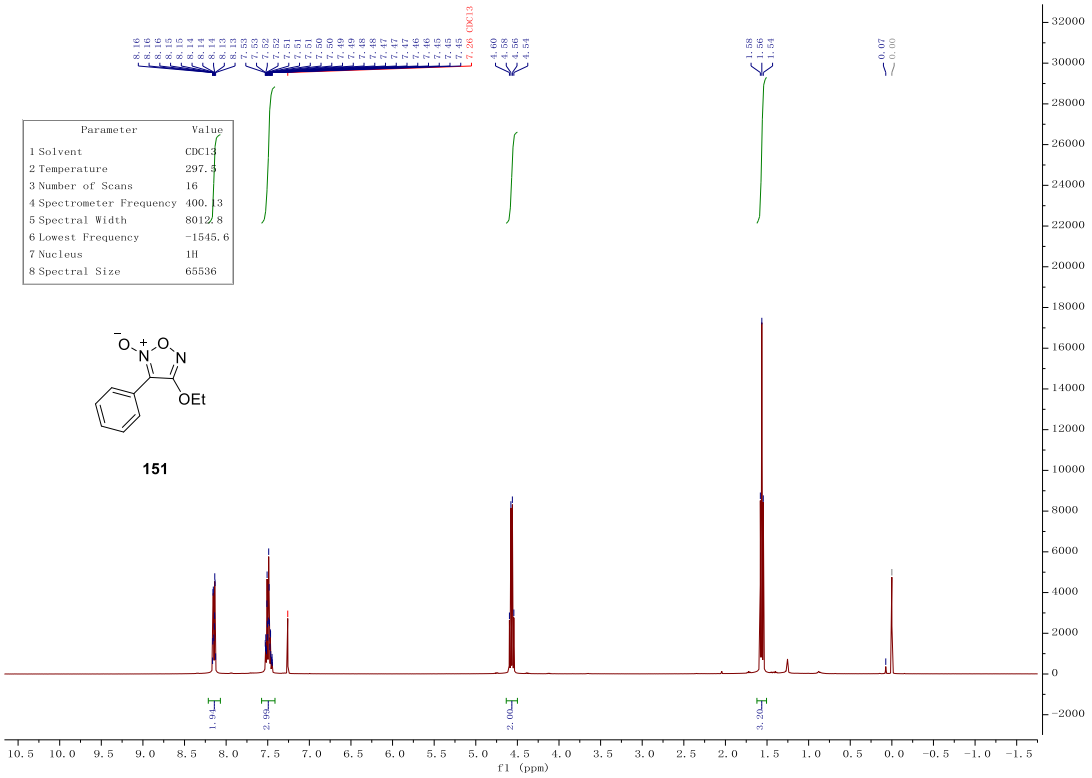

8.32
7.18 CDCl3
6.82
6.81
6.79
6.78
6.76
3.60
3.59
2.23
0.02
0.00
-0.03
0.07
Parameter Value
1 Solvent CDCl3
2 Temperature 299.5
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1578.1
7 Nucleus 1H
8 Spectral Size 65536
OH
N
134
0.94
3.80
2.00
6.05
f1 (ppm)

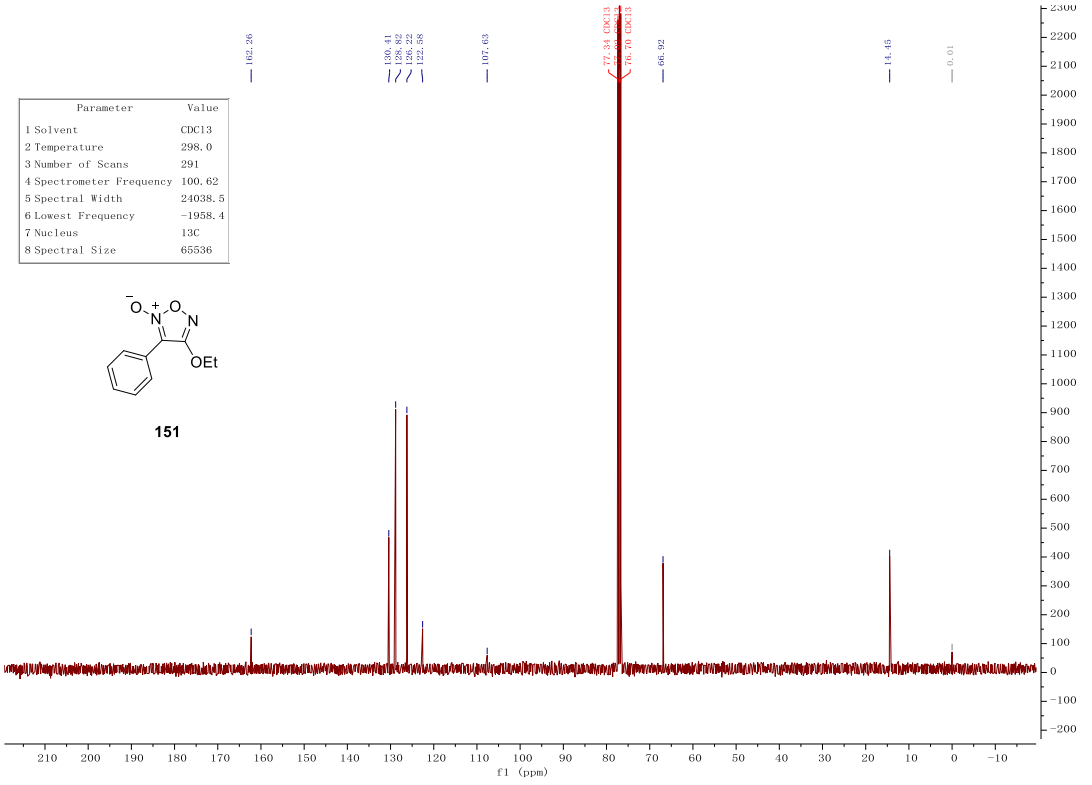

151.23
138.36
136.59
128.29
126.60
77.34 CDCl3
77.02 CDCl3
76.71 CDCl3
31.43
21.23
1.04
0.01
Parameter Value
1 Solvent CDCl3
2 Temperature 300.1
3 Number of Scans 184
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
OH
N
134
f1 (ppm)

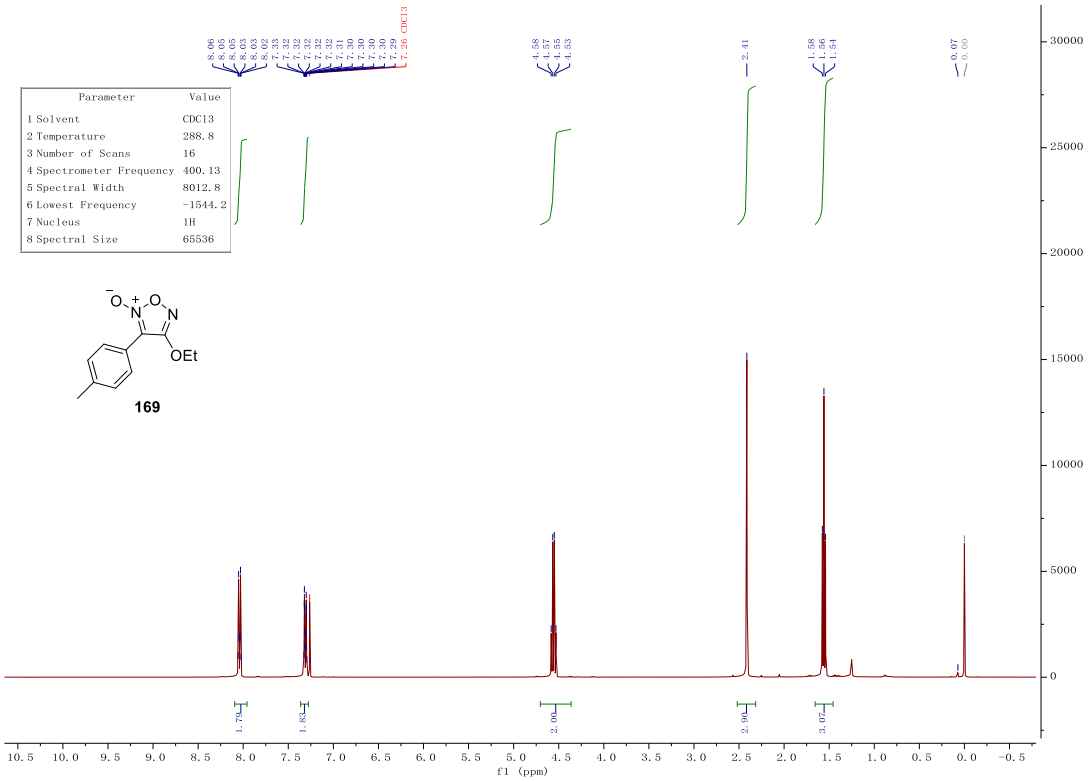

8.48
7.78
7.77
7.77
7.76
7.76
7.75
7.75
7.74
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.25 CDCl3
6.93
6.85
6.79
4.20
2.26
2.05 H2O
0.00
Parameter Value
1 Solvent CDCl3
2 Temperature 296.3
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1550.7
7 Nucleus 1H
8 Spectral Size 65536
HO
N
Ph
N–O
135
1.00
2.18
3.29
2.13
1.03
0.94
2.00
6.26
f1 (ppm)

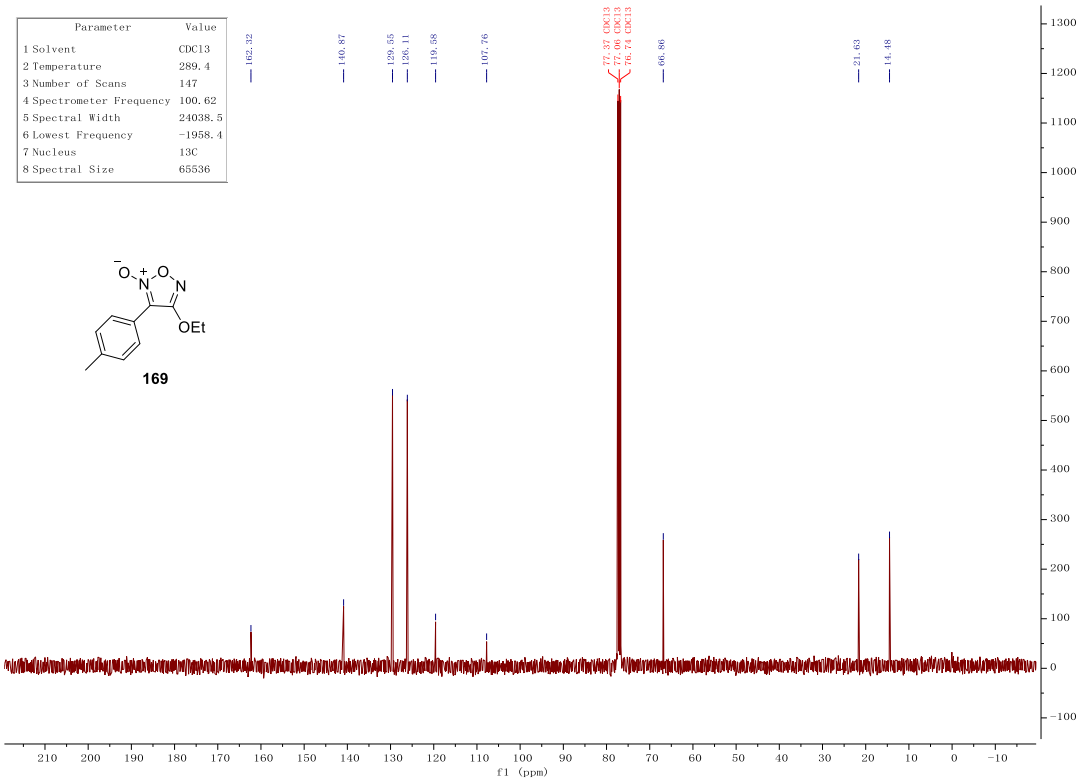

170.16
160.59
151.66
137.99
135.55
130.35
129.01
128.29
127.15
126.91
125.85
97.09
77.37 CDCl3
77.05 CDCl3
76.73 CDCl3
31.01
21.32
0.04
Parameter Value
1 Solvent CDCl3
2 Temperature 296.0
3 Number of Scans 133
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
HO
N
Ph
N–O
135
f1 (ppm)

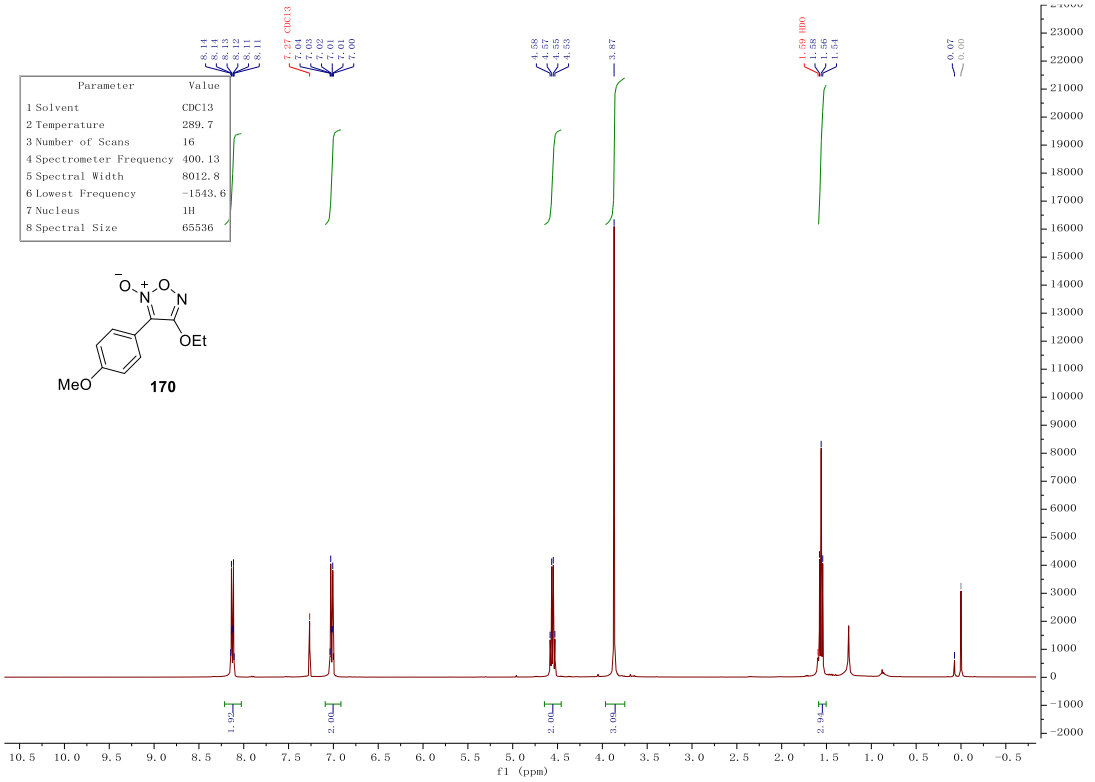
2. Directarylation of Furoxan Using Potassium Aryltrifluoroborates.

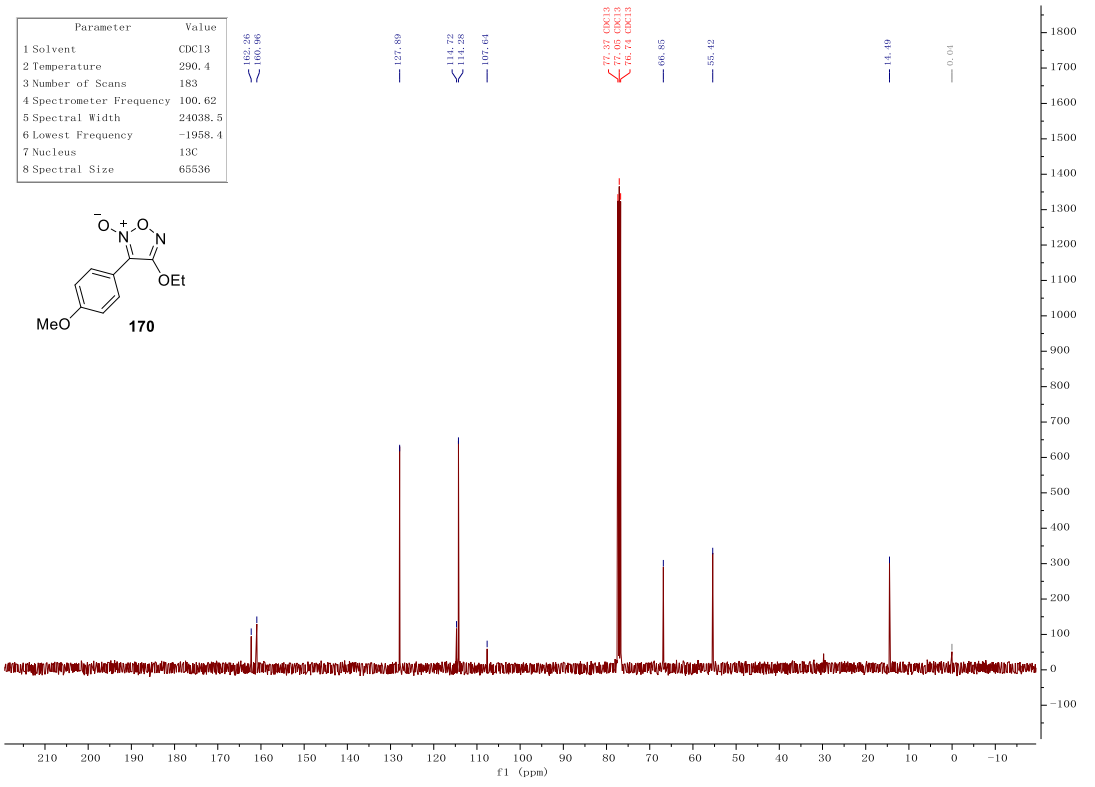

8.16
8.16
8.16
8.15
8.15
8.14
8.14
8.13
8.13
7.53
7.52
7.52
7.51
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.46
7.46
7.45
7.45
7.45
7.26 CDCl3
4.60
4.58
4.56
4.54
1.58
1.56
1.54
0.07
0.00
Parameter Value
1 Solvent CDCl3
2 Temperature 297.5
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.6
7 Nucleus 1H
8 Spectral Size 65536
O
N
O
N
OEt
151
1.94
2.99
2.00
3.20
f1 (ppm)

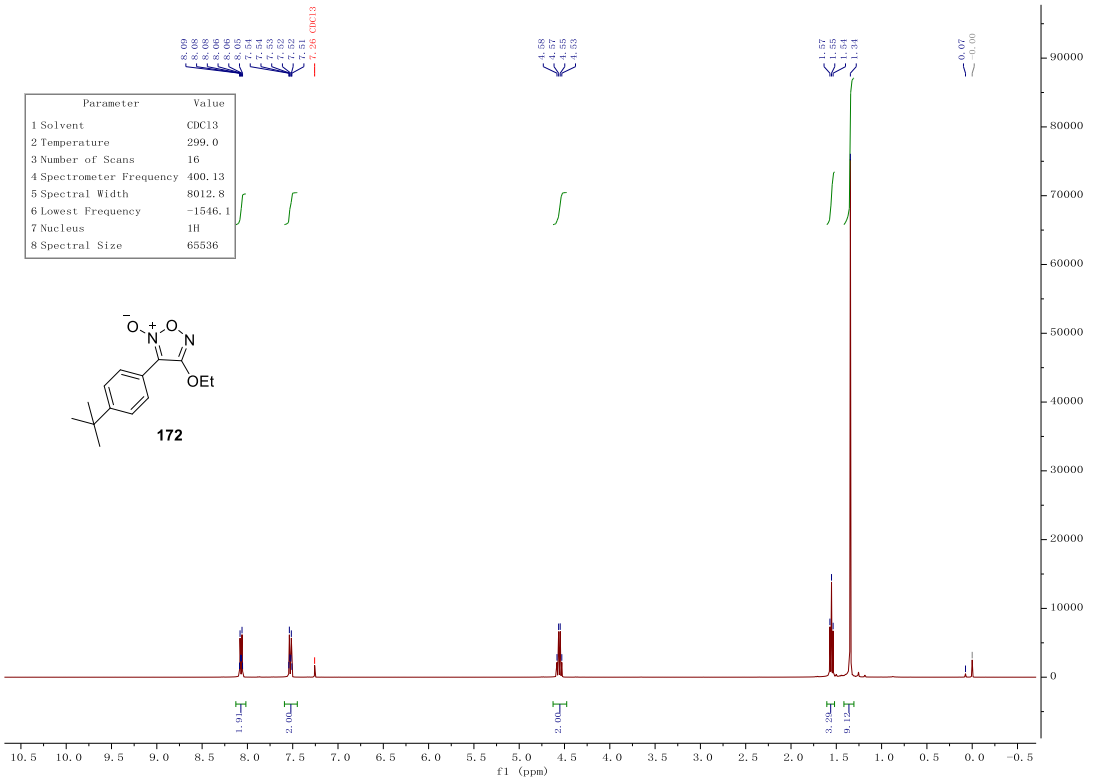

162.26
130.41
128.82
126.22
122.38
107.63
77.34 CDCl3
77.02 CDCl3
76.70 CDCl3
66.92
14.43
0.01
Parameter Value
1 Solvent CDCl3
2 Temperature 298.0
3 Number of Scans 291
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
O
N
O
N
OEt
151
f1 (ppm)

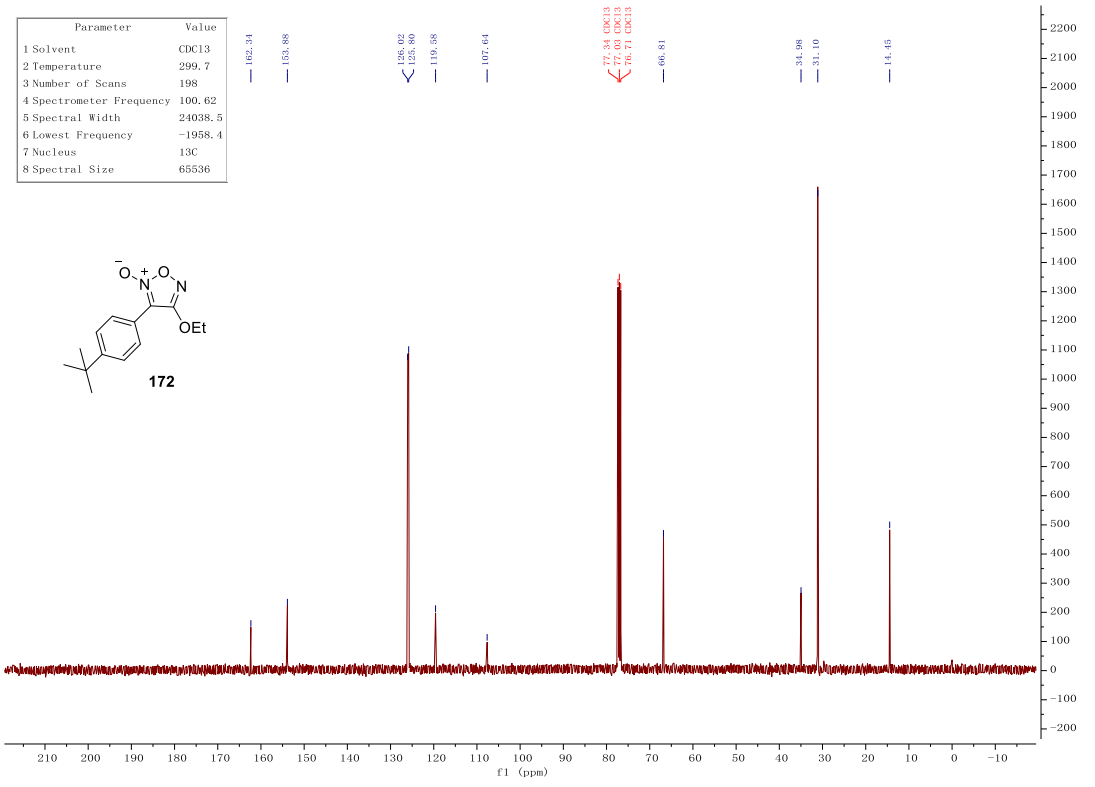

8.06
8.05
8.05
8.03
8.03
8.02
7.33
7.32
7.32
7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.26 CDCl3
4.58
4.57
4.55
4.53
2.41
1.58
1.56
1.54
0.07
0.00
Parameter Value
1 Solvent CDCl3
2 Temperature 288.8
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1544.2
7 Nucleus 1H
8 Spectral Size 65536
OEt
169
1.79
1.85
2.00
2.90
3.07
f1 (ppm)

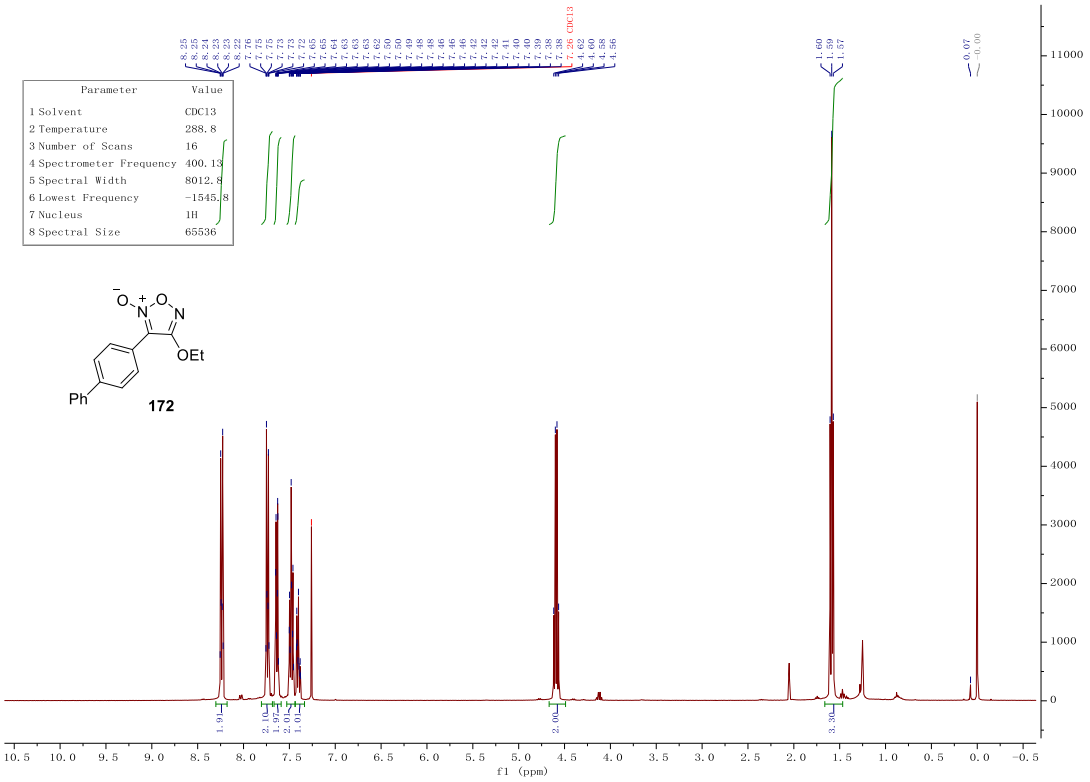

Parameter Value
1 Solvent CDCl3
2 Temperature 289.4
3 Number of Scans 147
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
162.32
140.87
129.55
126.11
119.58
107.76
77.37 CDCl3
77.00 CDCl3
76.74 CDCl3
66.86
21.63
14.48
OEt
169
f1 (ppm)

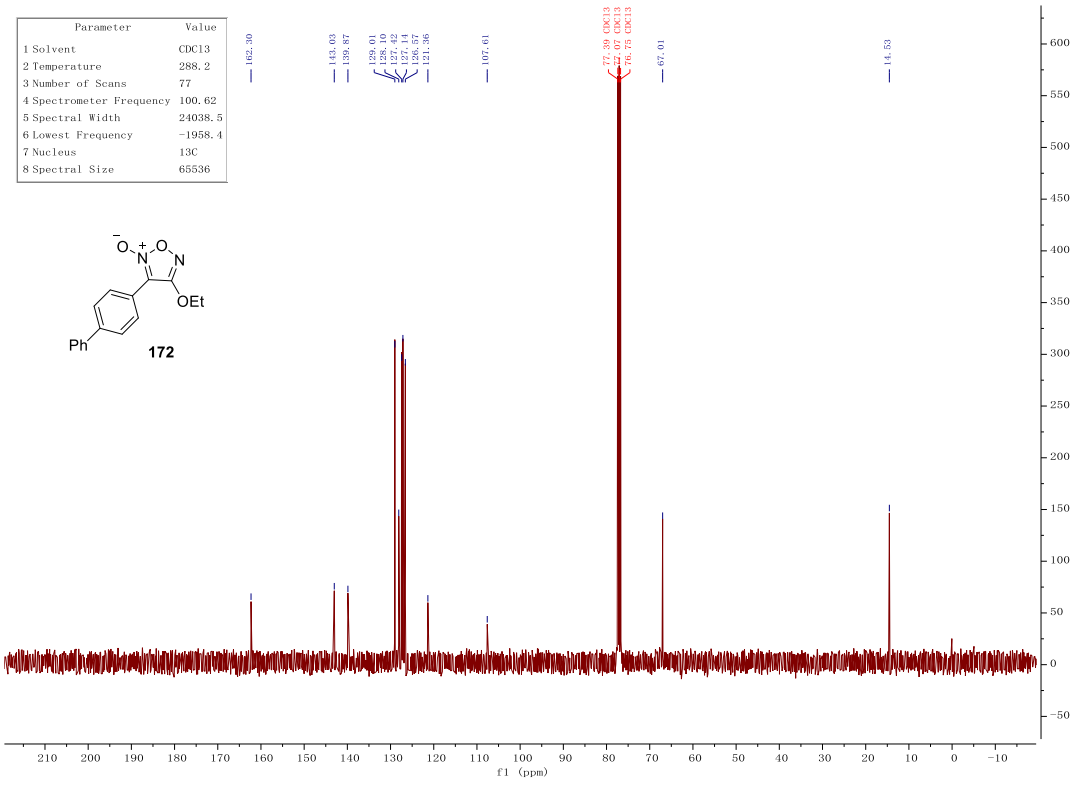

Parameter Value
1 Solvent CDCl3
2 Temperature 289.7
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1543.6
7 Nucleus 1H
8 Spectral Size 65536
MeO
OEt
170
f1 (ppm)

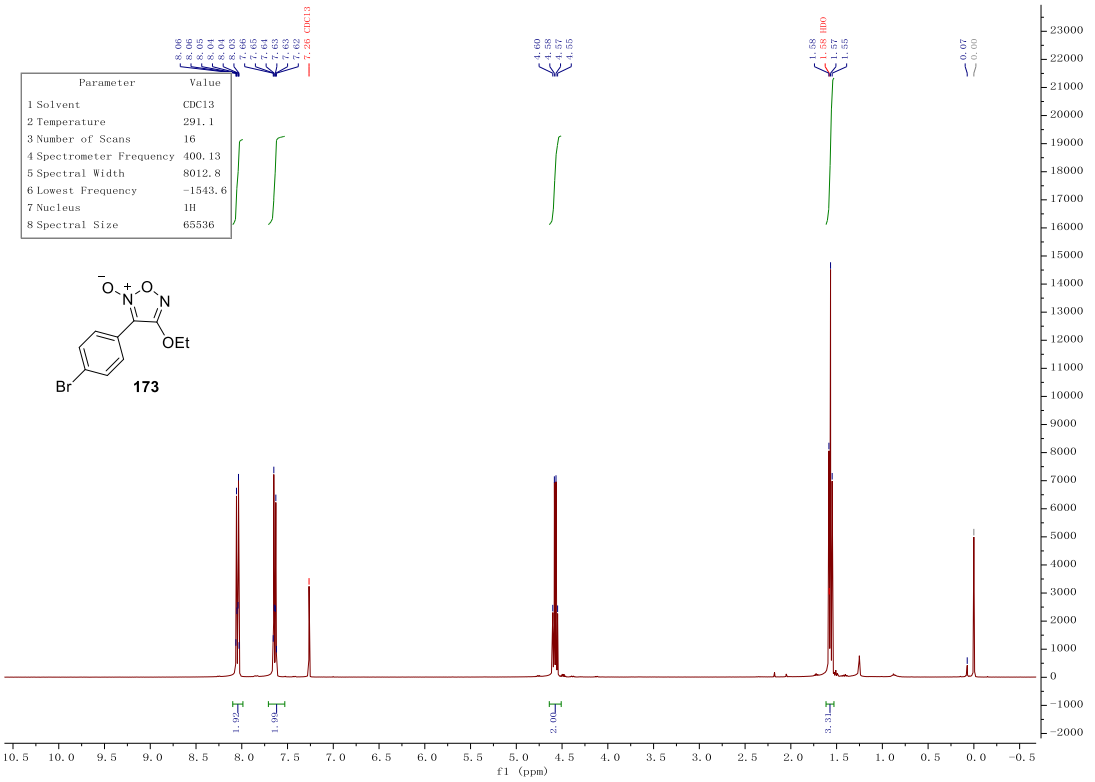

Parameter Value
1 Solvent CDCl3
2 Temperature 290.4
3 Number of Scans 183
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
MeO
OEt
170
f1 (ppm)

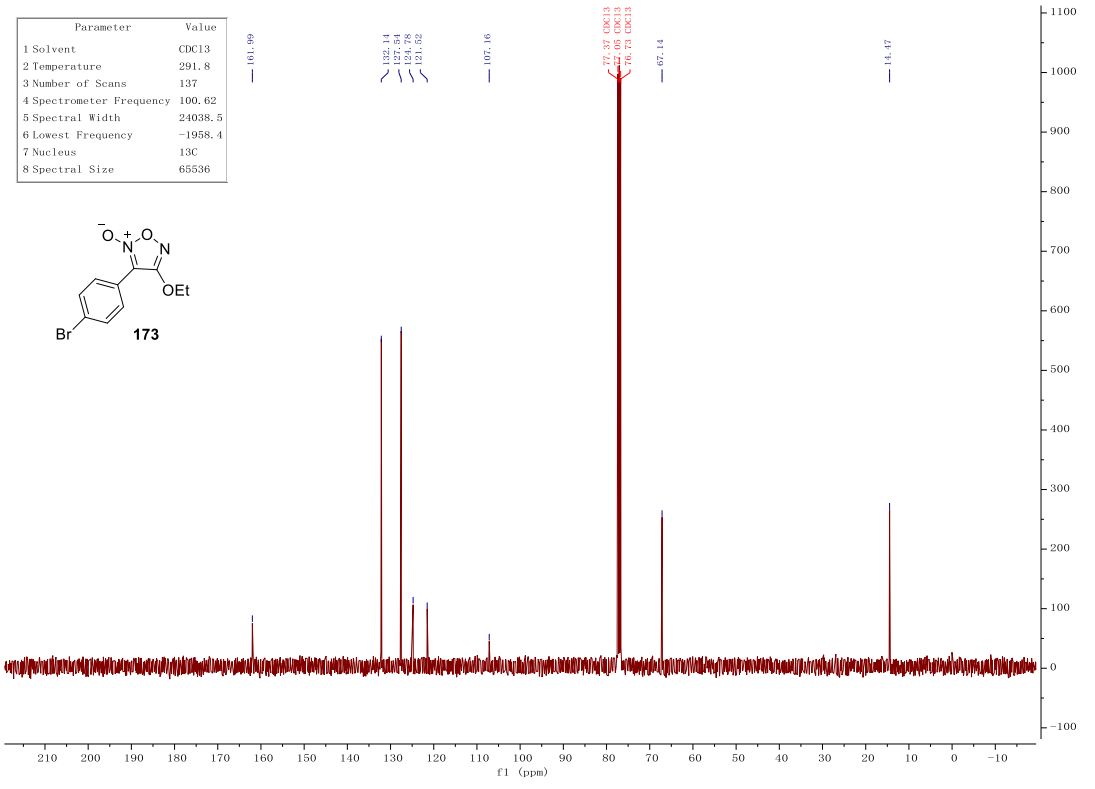

8.09
8.08
8.08
8.06
8.06
7.54
7.54
7.53
7.52
7.52
7.51
7.26 CDCl3
4.58
4.57
4.55
4.55
4.53
1.57
1.55
1.54
1.54
0.07
0.00
Parameter Value
1 Solvent CDCl3
2 Temperature 299.0
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1546.1
7 Nucleus 1H
8 Spectral Size 65536
OEt
172
1.91
2.00
2.00
3.29
9.12
f1 (ppm)

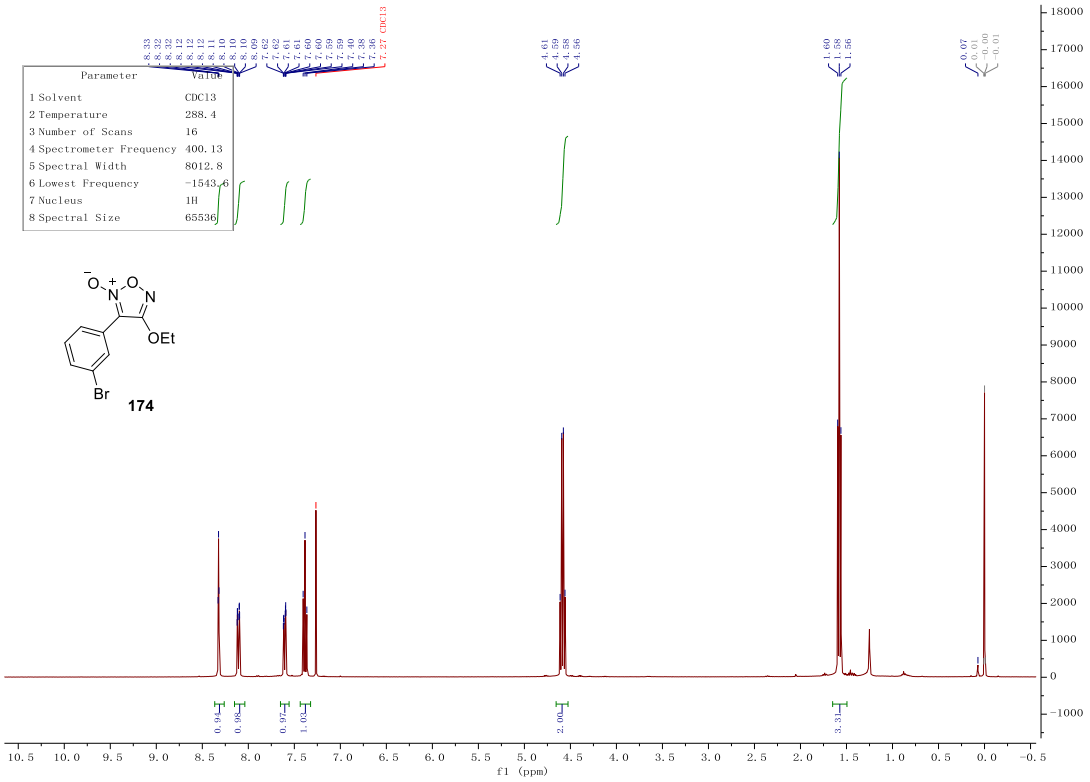

Parameter Value
1 Solvent CDCl3
2 Temperature 299.7
3 Number of Scans 198
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
162.34
153.88
126.02
125.80
119.58
107.64
77.34 CDCl3
77.00 CDCl3
76.71 CDCl3
66.81
34.98
31.10
14.43
OEt
172
f1 (ppm)

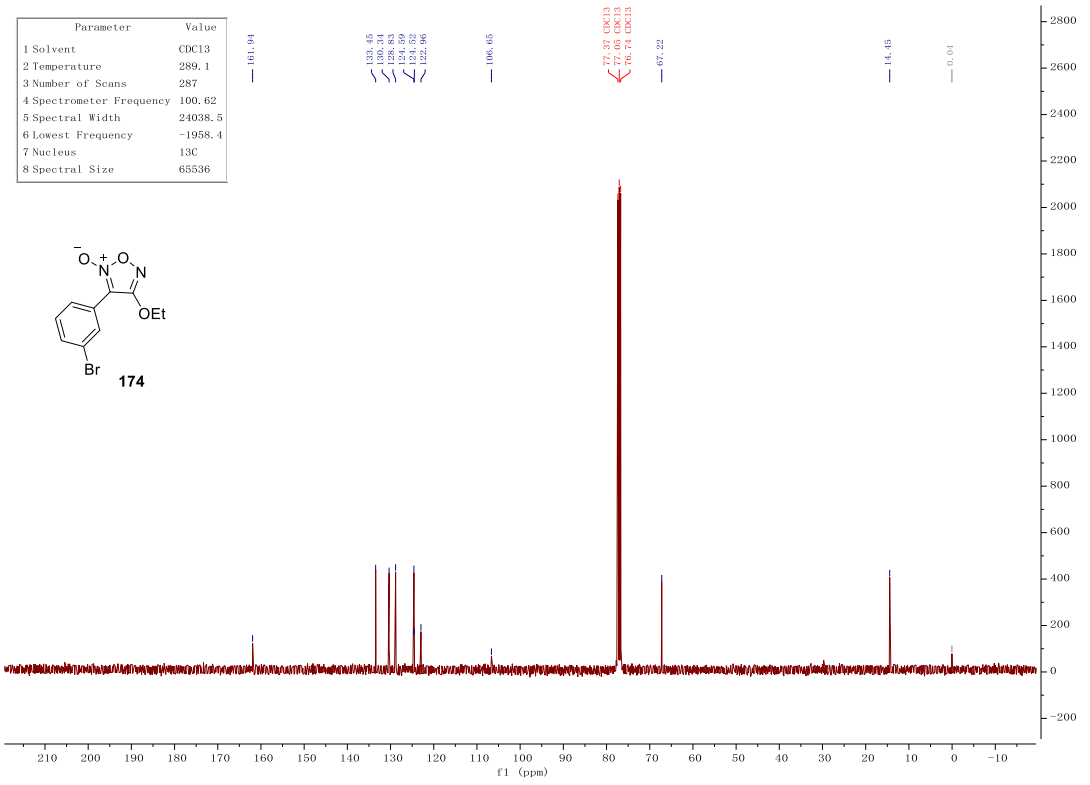

Parameter Value
1 Solvent CDCl3
2 Temperature 288.8
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.8
7 Nucleus 1H
8 Spectral Size 65536
OEt
Ph
172
f1 (ppm)

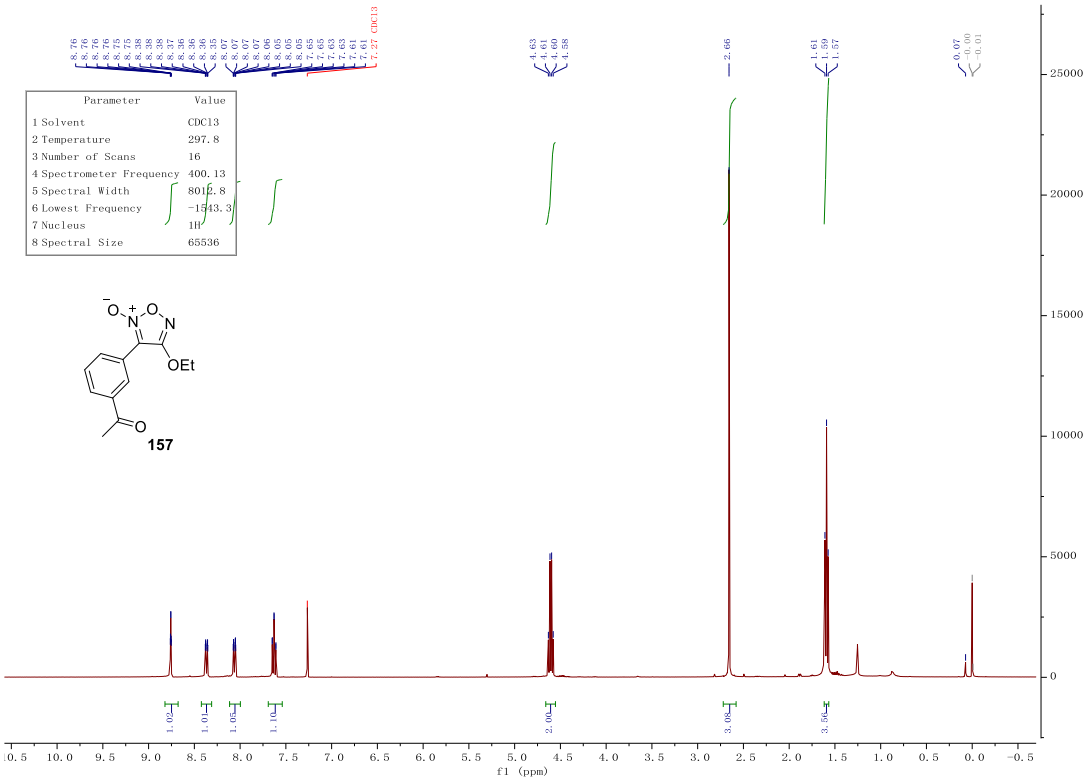

Parameter Value
1 Solvent CDCl3
2 Temperature 288.2
3 Number of Scans 77
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
OEt
Ph
172
f1 (ppm)

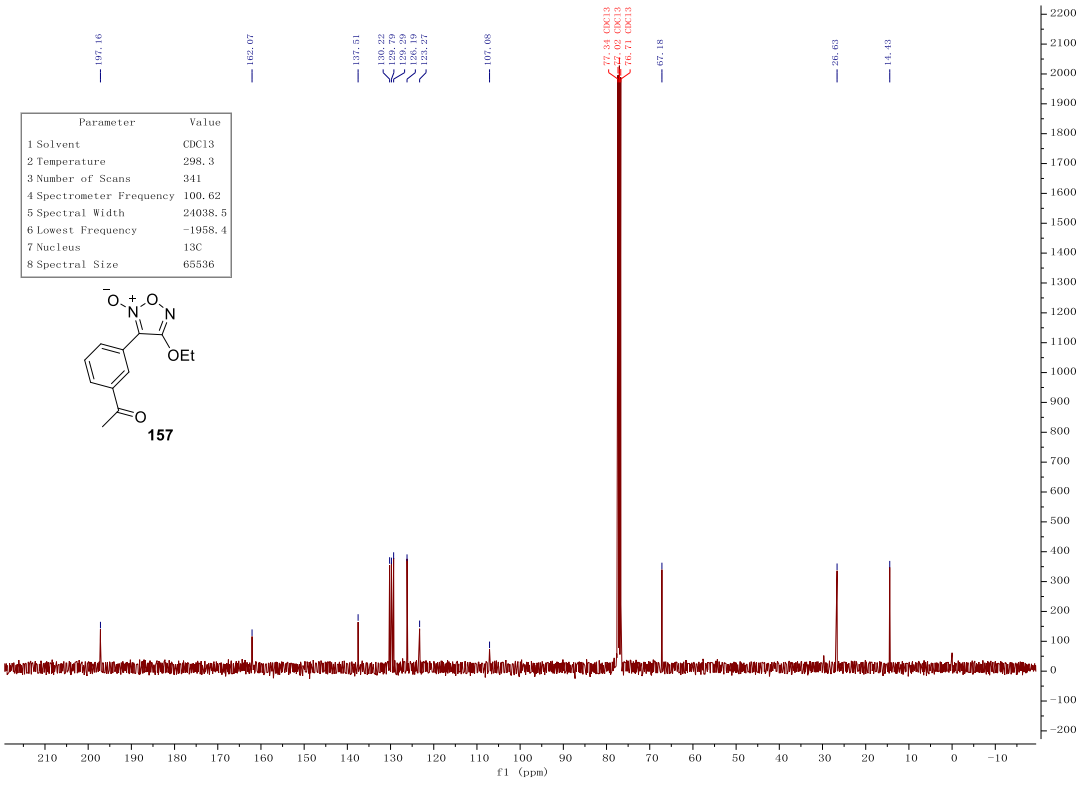

8.06
8.06
8.05
8.05
8.04
8.04
8.03
7.66
7.65
7.64
7.63
7.63
7.62
7.26 CDCl3
4.60
4.58
4.57
4.55
1.58
1.58 H2O
1.57
1.55
0.07
0.00
Parameter Value
1 Solvent CDCl3
2 Temperature 291.1
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1543.6
7 Nucleus 1H
8 Spectral Size 65536
OEt
Br
173
1.92
1.90
2.00
3.31
f1 (ppm)

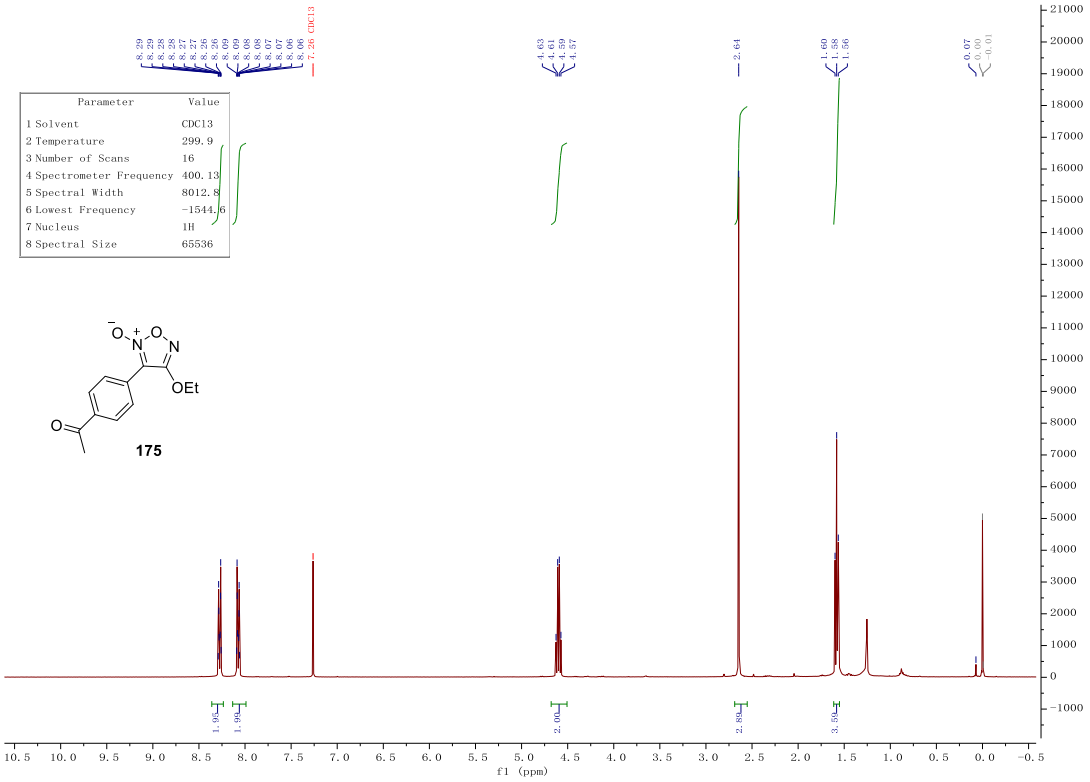

Parameter Value
1 Solvent CDCl3
2 Temperature 291.8
3 Number of Scans 137
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
161.99
132.14
127.54
126.78
121.52
107.16
77.47 CDCl3
77.05 CDCl3
76.73 CDCl3
67.14
14.47
OEt
Br
173
f1 (ppm)

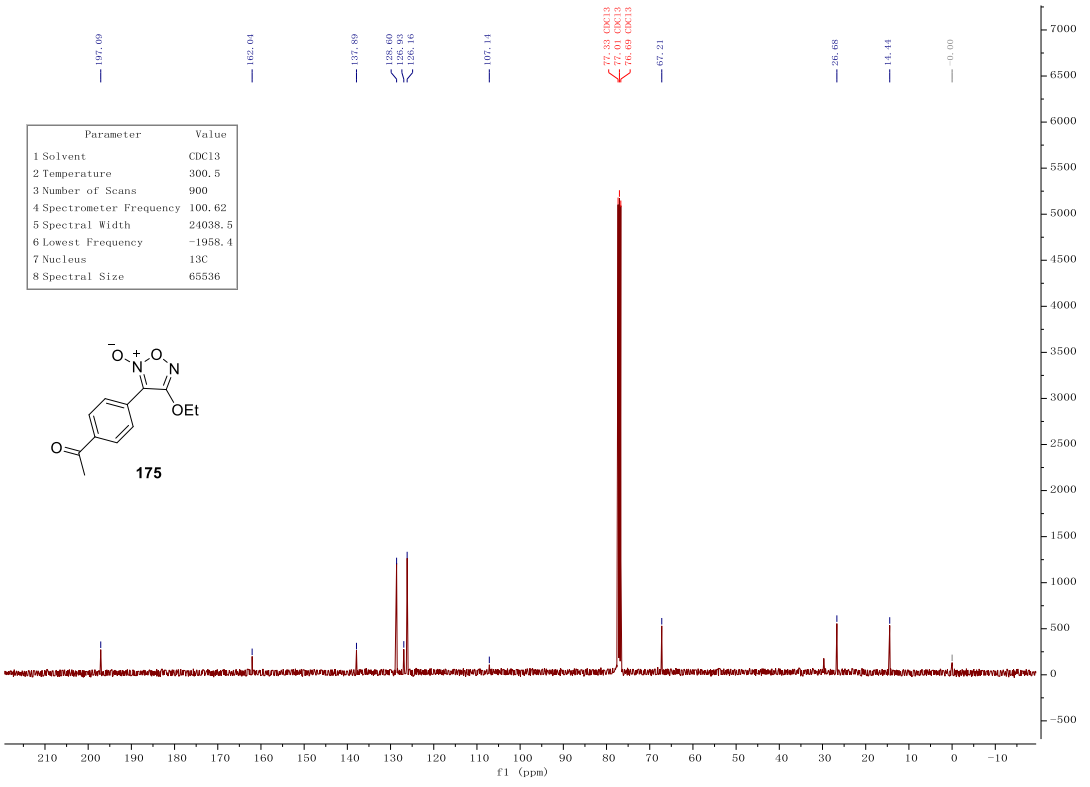

Parameter Value
1 Solvent CDCl3
2 Temperature 288.4
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1543.6
7 Nucleus 1H
8 Spectral Size 65536
OEt
Br
174
f1 (ppm)

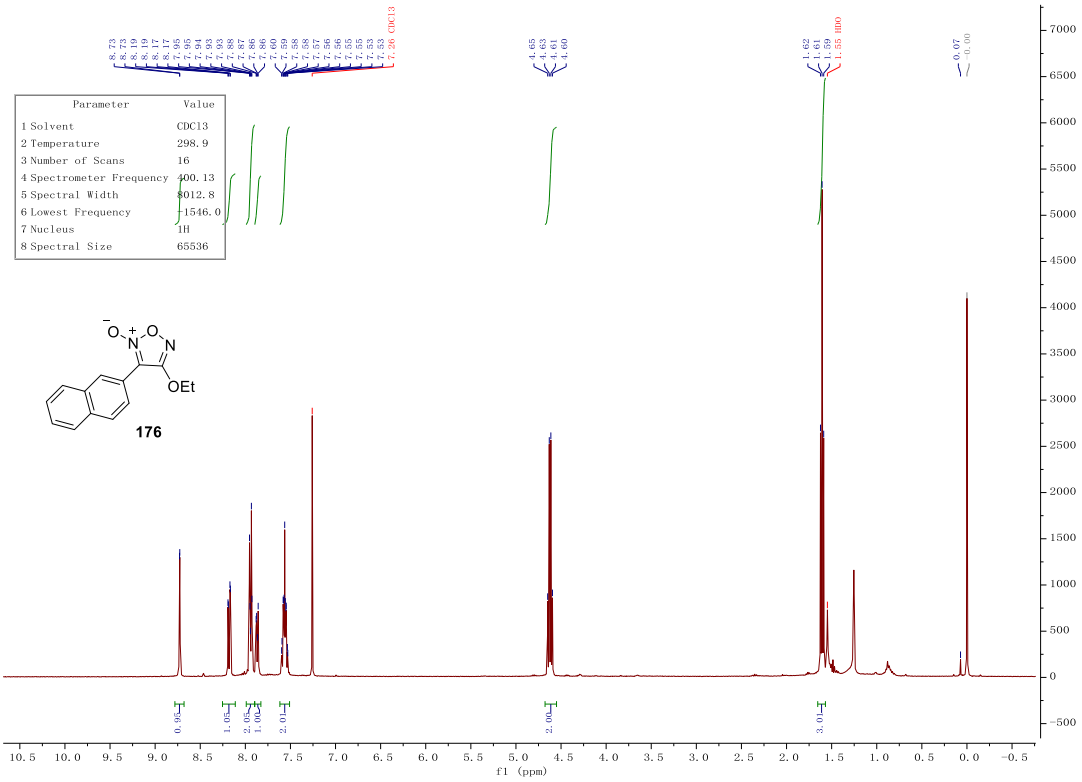

Parameter Value
1 Solvent CDCl3
2 Temperature 289.1
3 Number of Scans 287
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
OEt
Br
174
f1 (ppm)

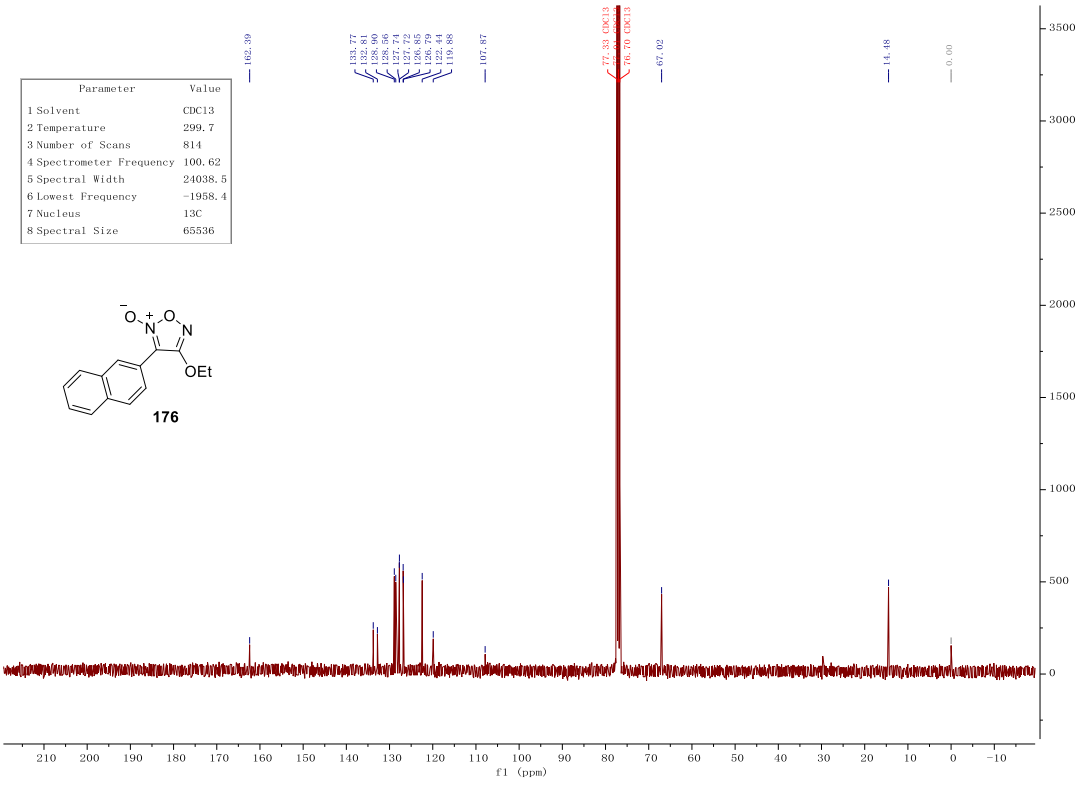

Parameter Value
1 Solvent CDCl3
2 Temperature 297.8
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1543.3
7 Nucleus 1H
8 Spectral Size 65536
157
f1 (ppm)

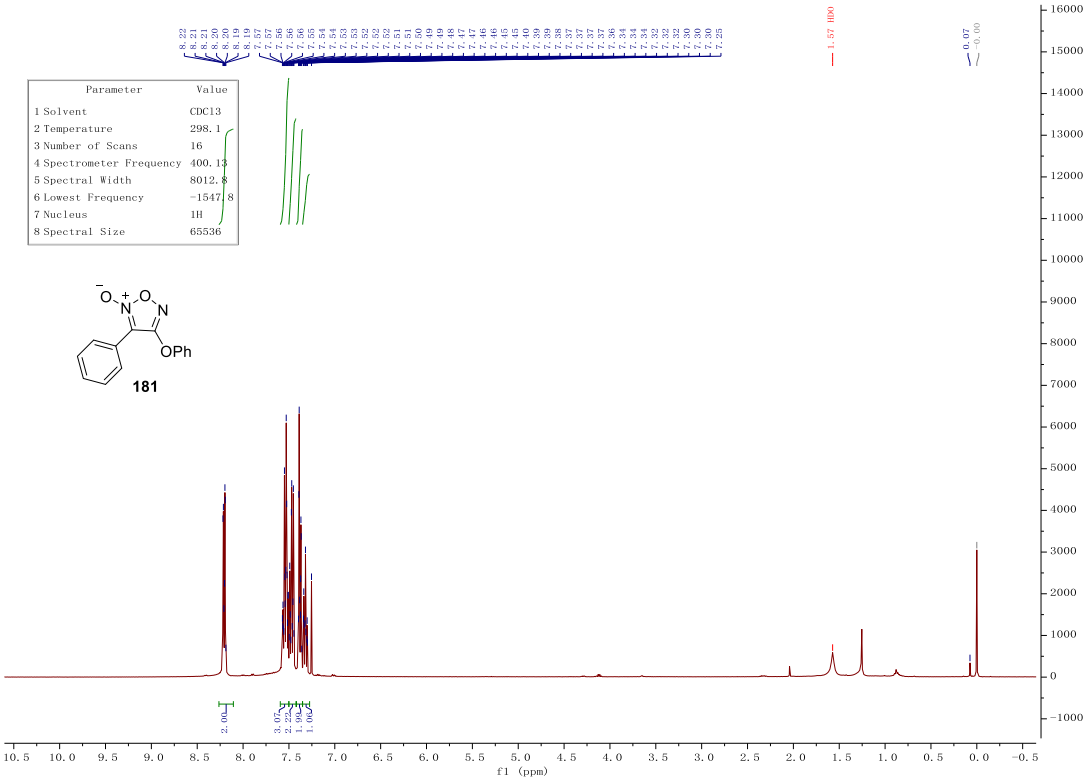

Parameter Value
1 Solvent CDCl3
2 Temperature 298.3
3 Number of Scans 341
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
157
f1 (ppm)

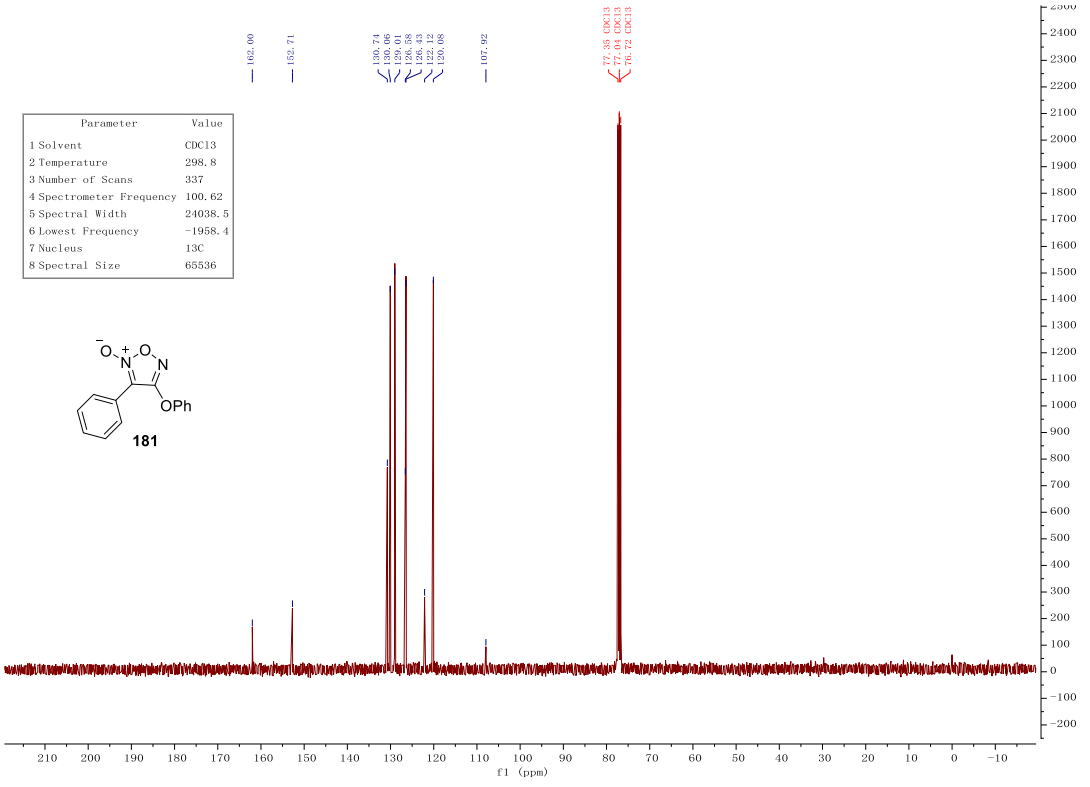

8.29
8.28
8.27
8.26
8.09
8.08
8.07
8.06
7.26 CDCl3
4.63
4.61
4.59
4.57
2.64
1.60
1.58
1.56
0.07
0.00
-0.01
Parameter Value
1 Solvent CDCl3
2 Temperature 299.9
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1544.6
7 Nucleus 1H
8 Spectral Size 65536
OEt
175
1.93
1.99
2.00
2.89
3.59
f1 (ppm)

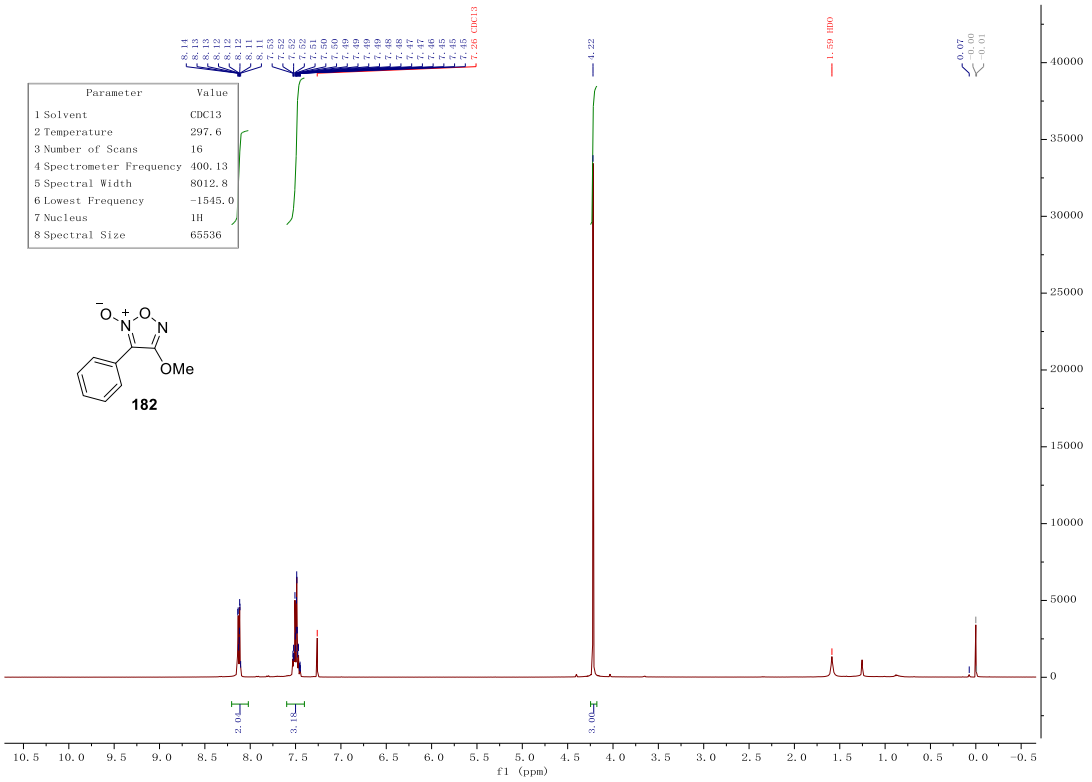

197.09
162.04
137.89
128.60
126.93
126.16
107.14
77.33 CDCl3
77.01 CDCl3
76.69 CDCl3
67.21
26.68
14.44
0.00
Parameter Value
1 Solvent CDCl3
2 Temperature 300.5
3 Number of Scans 900
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
OEt
175
f1 (ppm)

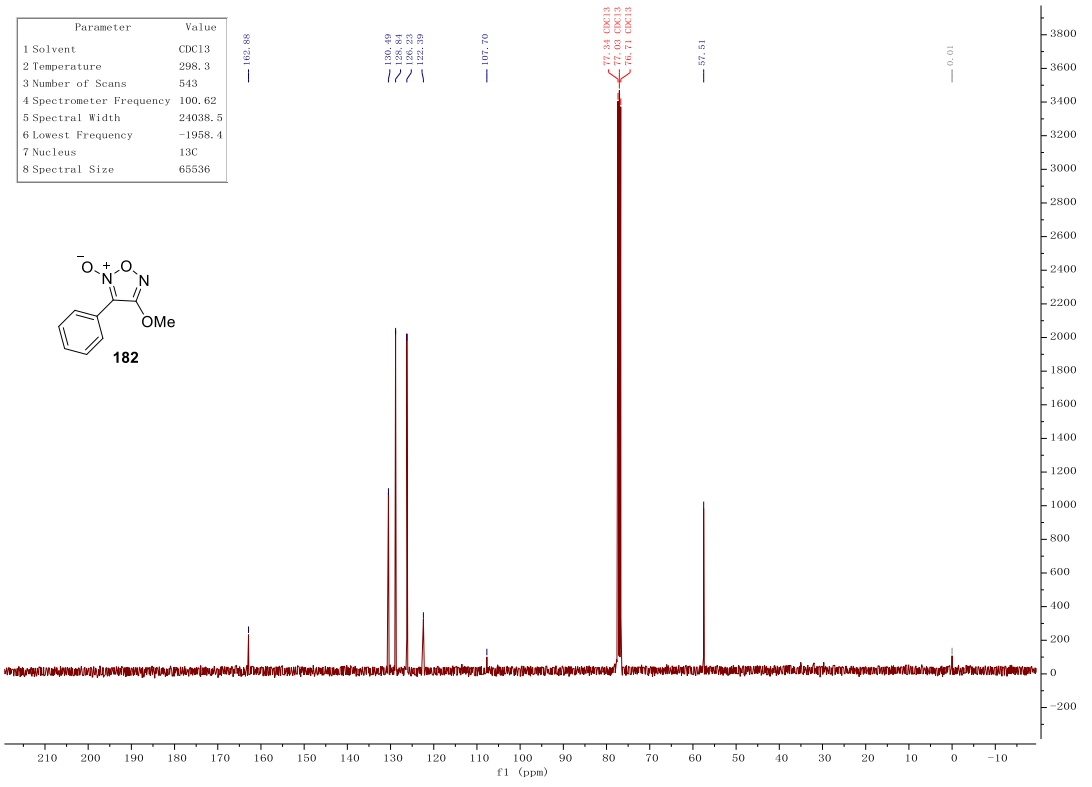

Parameter Value
1 Solvent CDCl3
2 Temperature 298.9
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1546.0
7 Nucleus 1H
8 Spectral Size 65536
OEt
176
f1 (ppm)

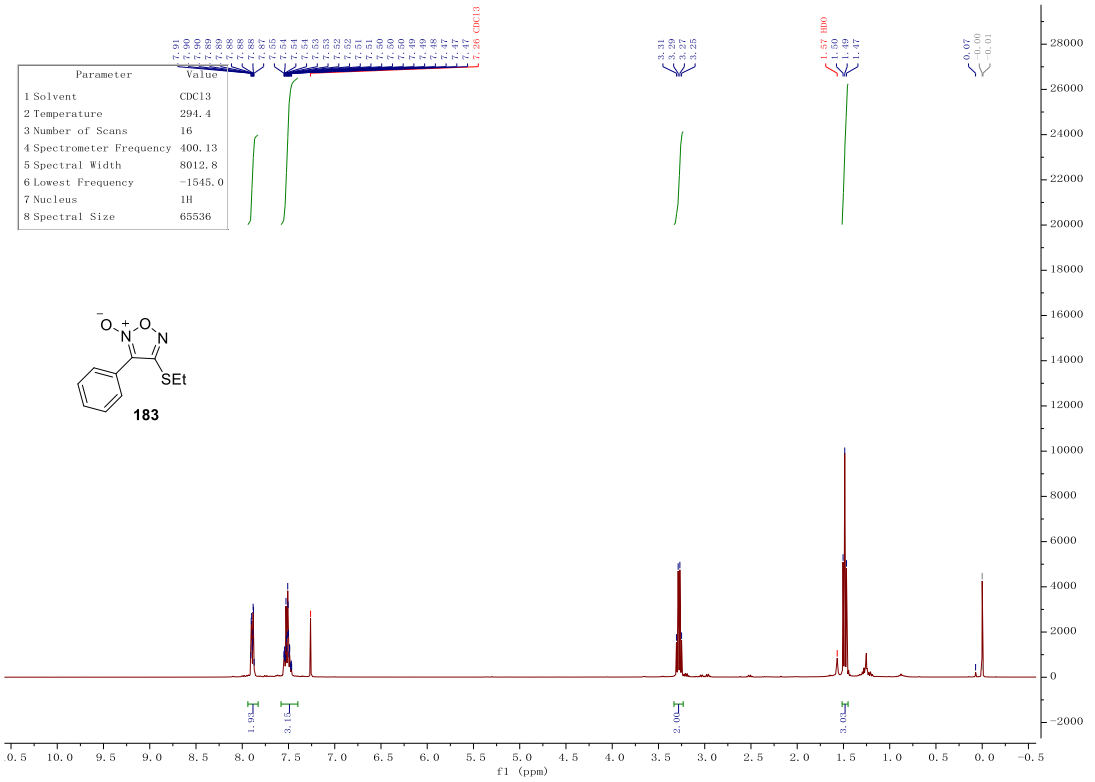

Parameter Value
1 Solvent CDCl3
2 Temperature 299.7
3 Number of Scans 814
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
OEt
176
f1 (ppm)

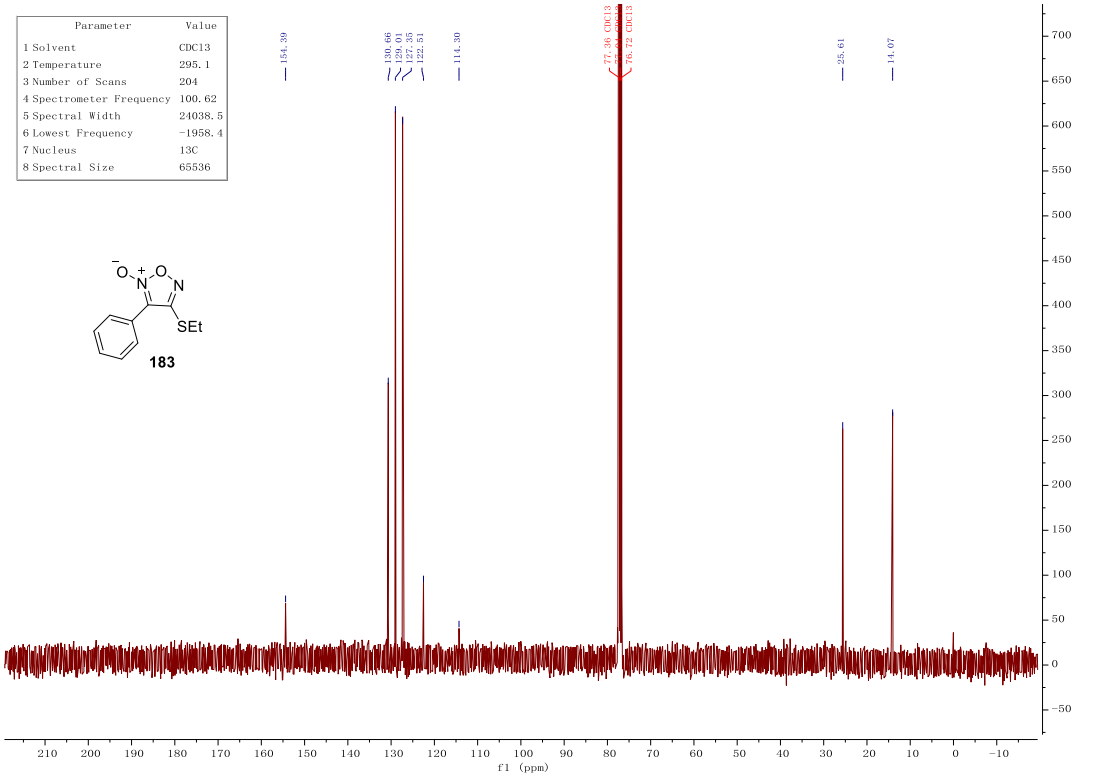

Parameter Value
1 Solvent CDCl3
2 Temperature 298.1
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1547.8
7 Nucleus 1H
8 Spectral Size 65536
OPh
181
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 298.8
3 Number of Scans 337
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
OPh
181
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 297.6
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.0
7 Nucleus 1H
8 Spectral Size 65536
8.14
8.13
8.13
8.12
8.12
8.12
8.11
8.11
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.49
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.45
7.26 CDCl3
4.22
1.59 H2O
0.07
0.00
-0.01
2.04
3.18
3.00
OMe
182
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 298.3
3 Number of Scans 543
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
163.88
130.49
128.84
126.23
122.39
107.70
77.34 CDCl3
77.00 CDCl3
76.71 CDCl3
57.51
0.01
OMe
182
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 294.4
3 Number of Scans 16
4 Spectrometer Frequency 400.13
5 Spectral Width 8012.8
6 Lowest Frequency -1545.0
7 Nucleus 1H
8 Spectral Size 65536
SEt
183
f1 (ppm)


Parameter Value
1 Solvent CDCl3
2 Temperature 295.1
3 Number of Scans 204
4 Spectrometer Frequency 100.62
5 Spectral Width 24038.5
6 Lowest Frequency -1958.4
7 Nucleus 13C
8 Spectral Size 65536
SEt
183
f1 (ppm)