

Supporting Information

Michael Addition/Pericyclization/Rearrangement- A Multicomponent Strategy for the Synthesis of Substituted Resorcinols

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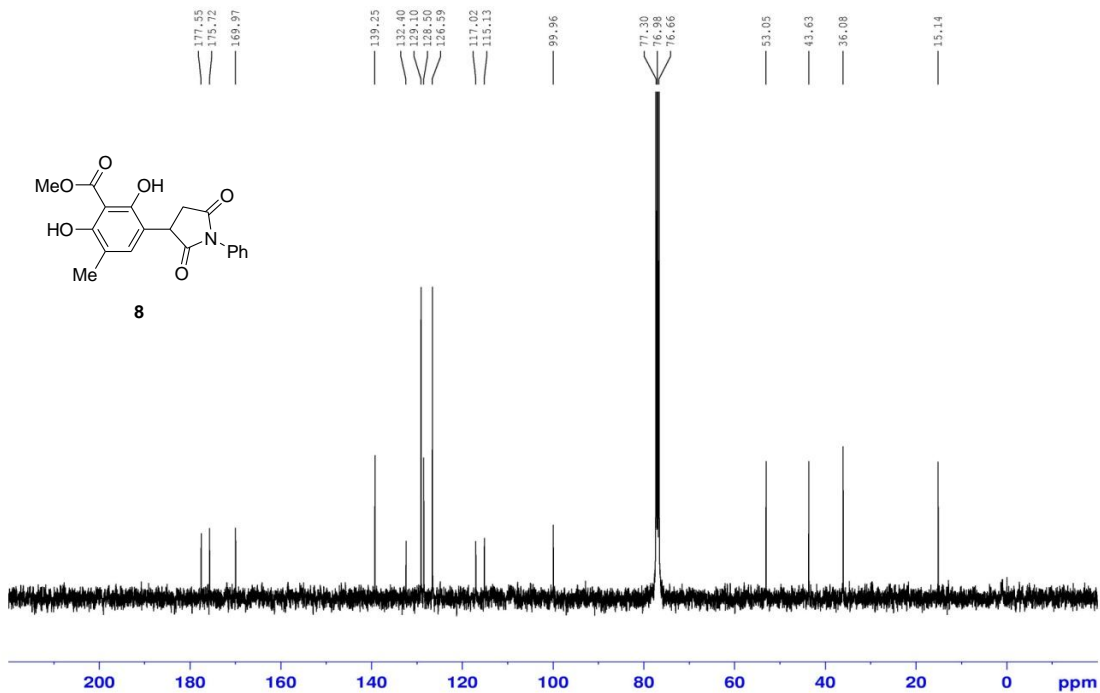
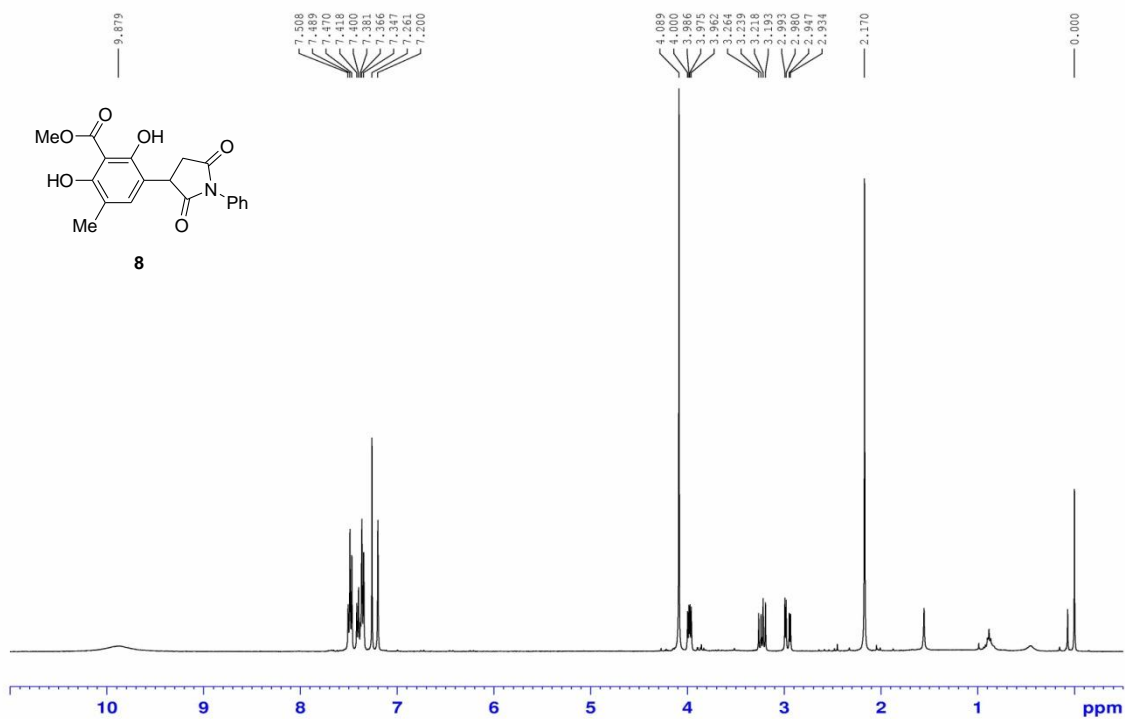
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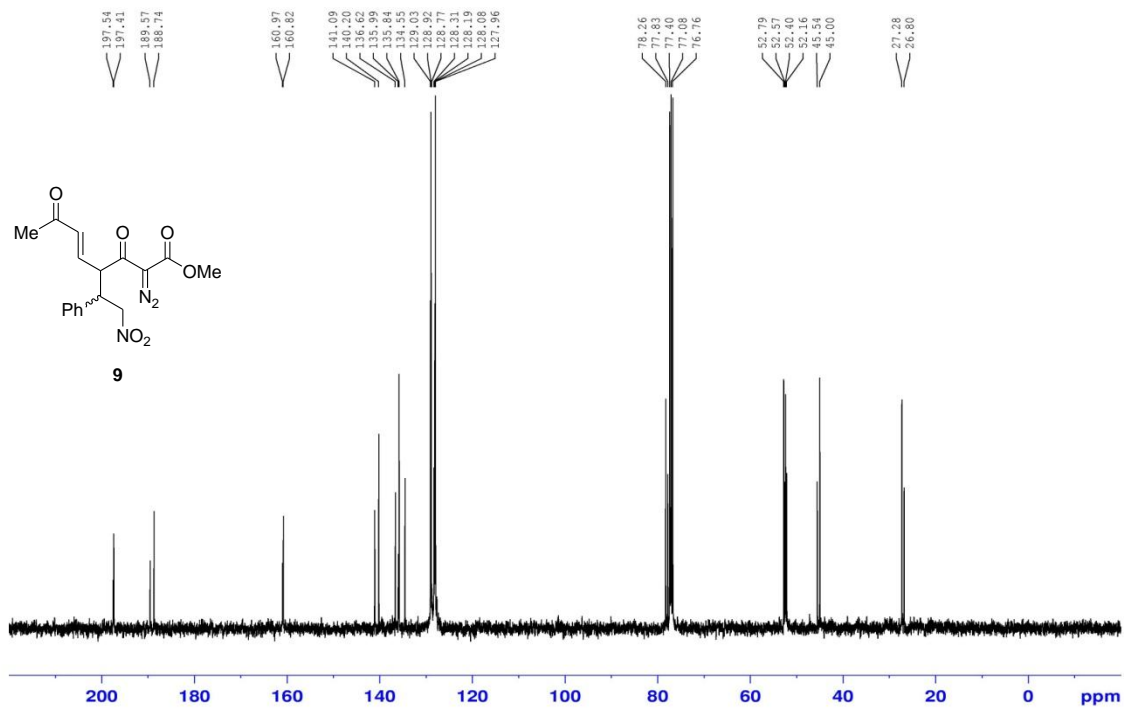
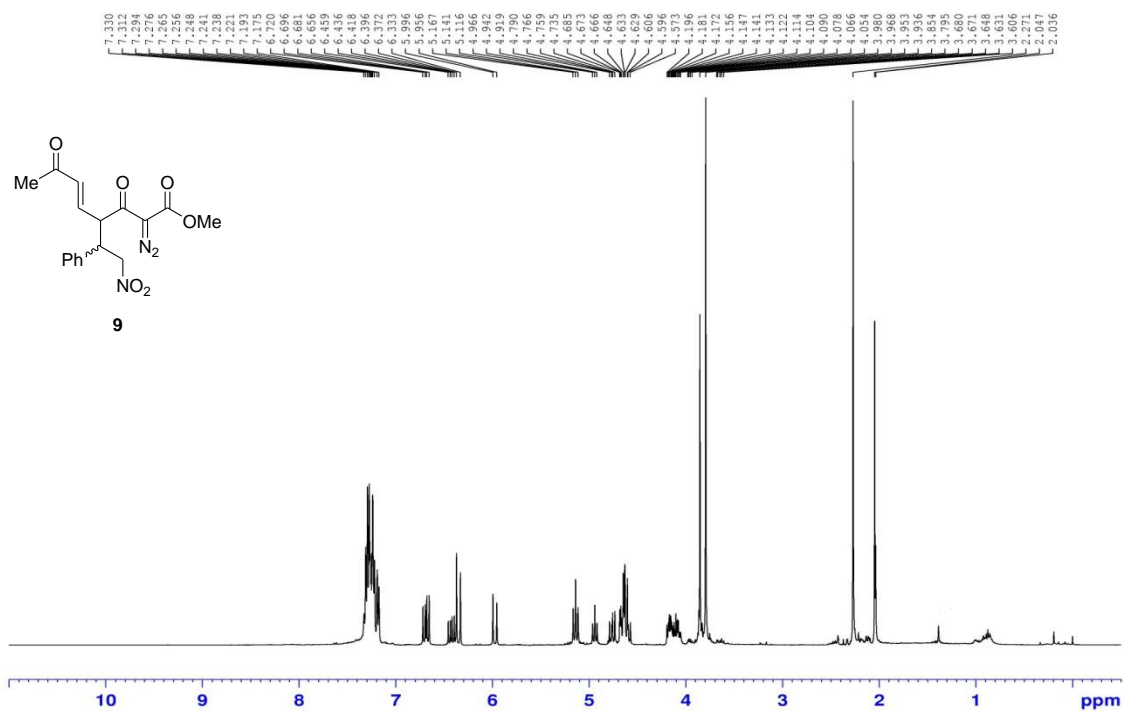
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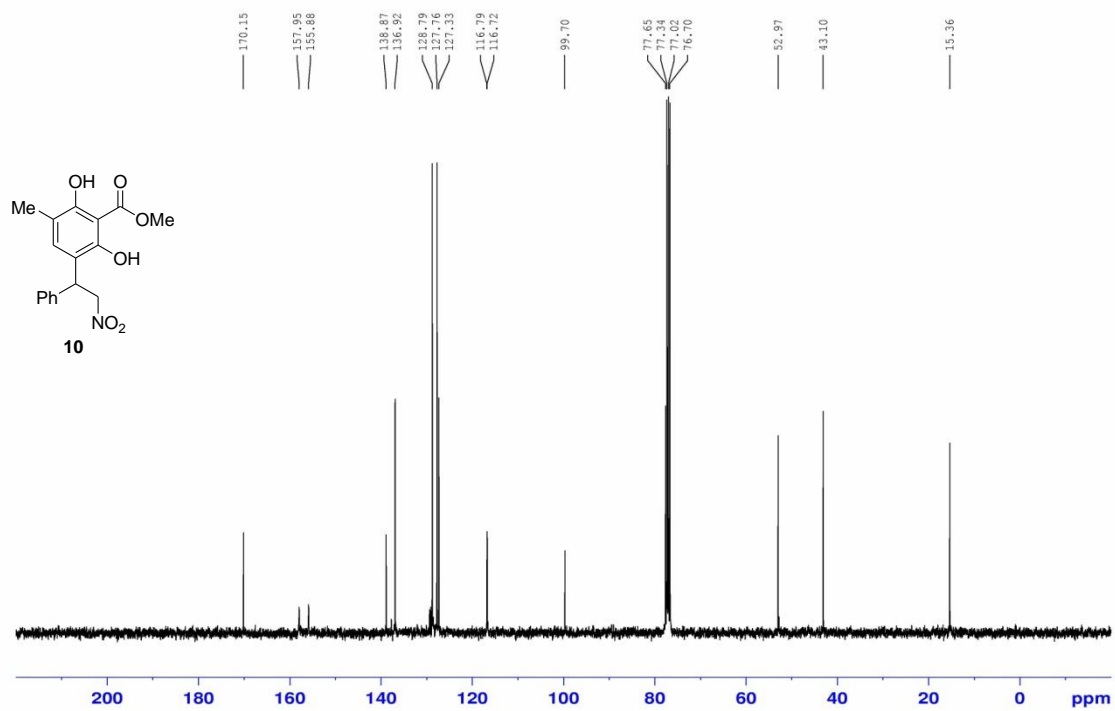
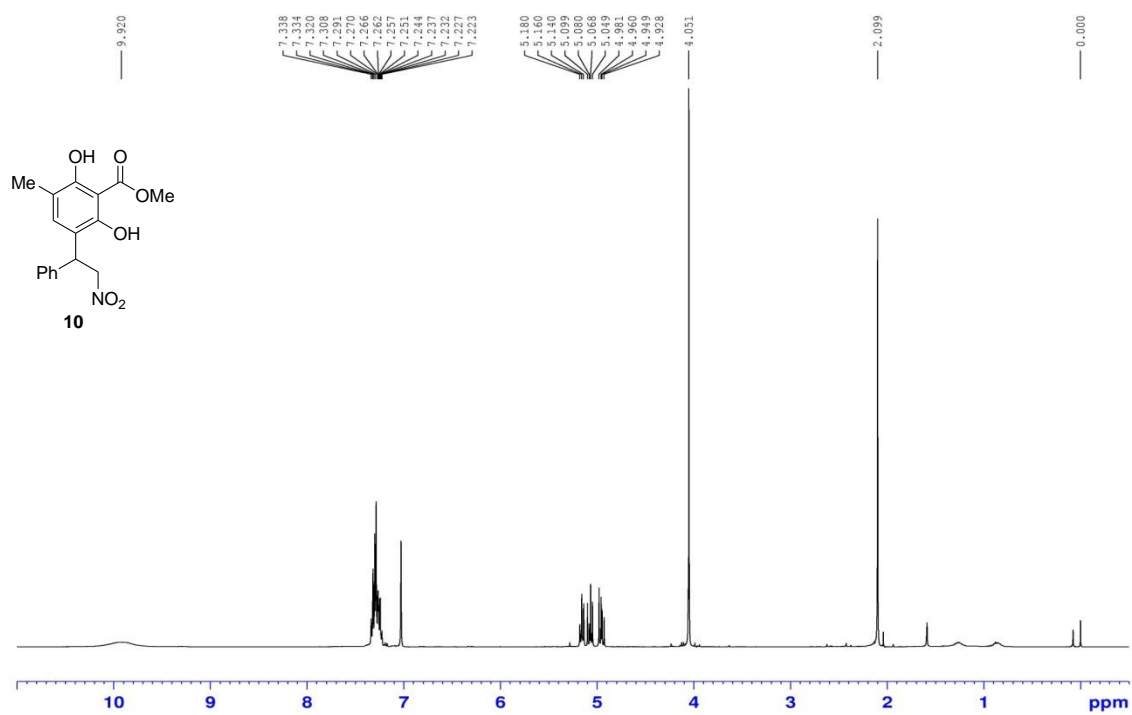
Table of Contents

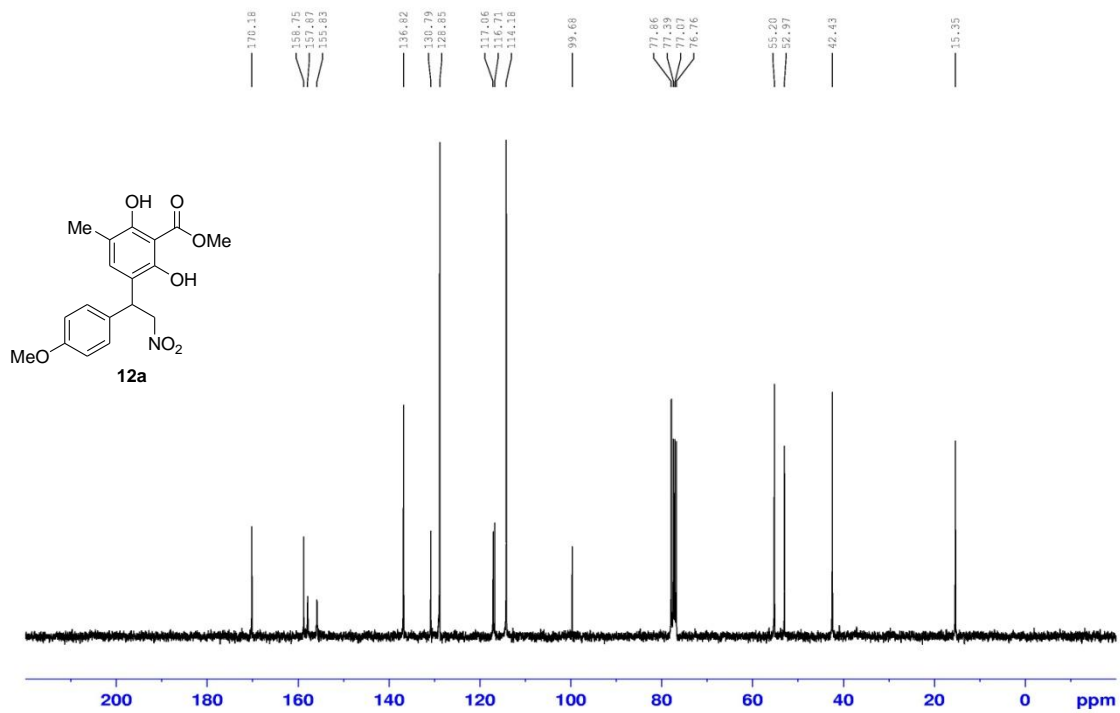
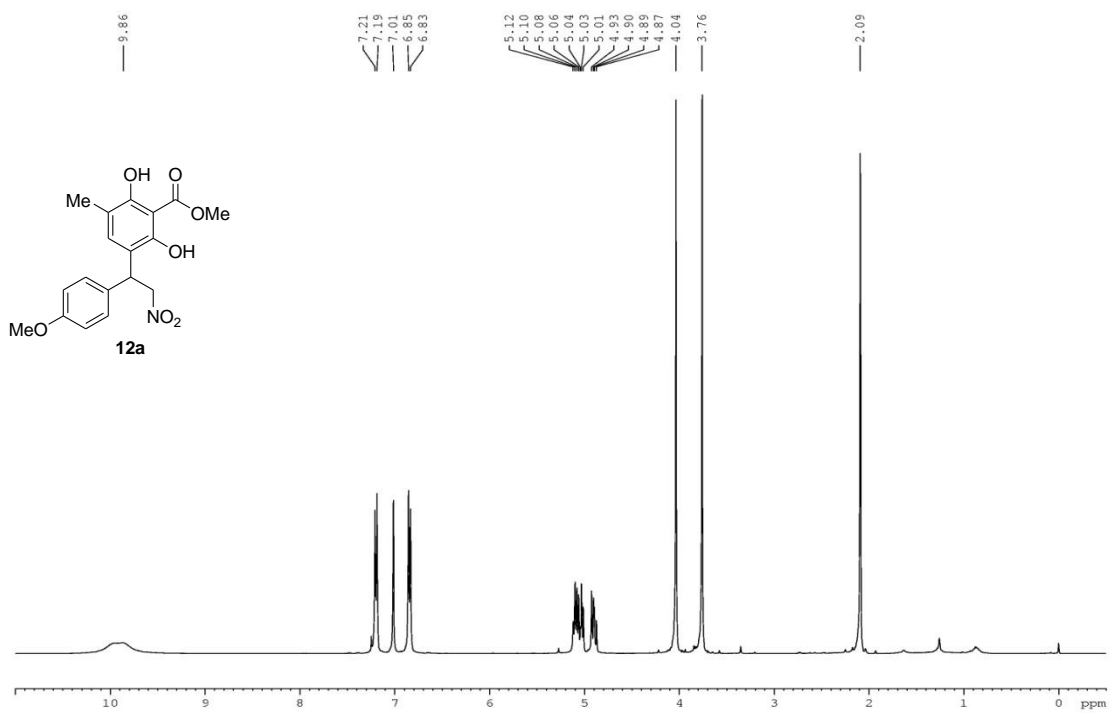
¹ H and ¹³ C Spectra of New Compounds.....	S-1
HMBC Experiment that elucidates the Structure of 13c	S-12
Proton NMR spectrum of 13b	S-14
Proton NMR spectrum of 13e	S-16
Structural characterization of 20 based on ¹ H NMR spectroscopy.....	S-17
Attempted Pericyclization/Rearrangement of 20	S-18

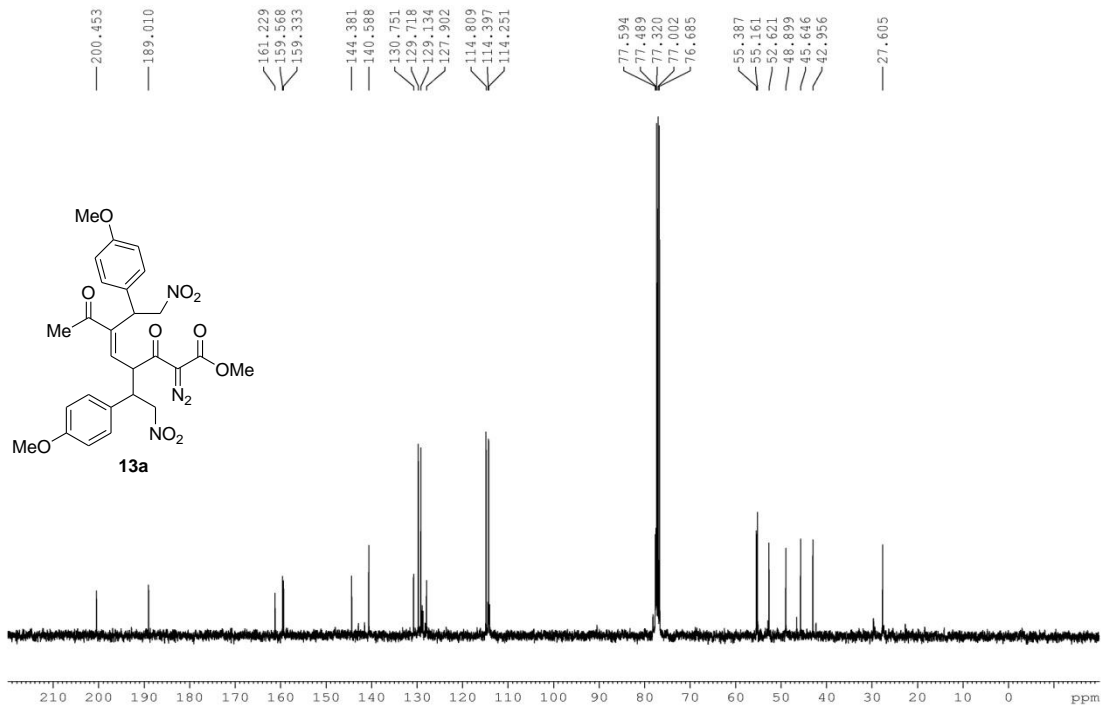
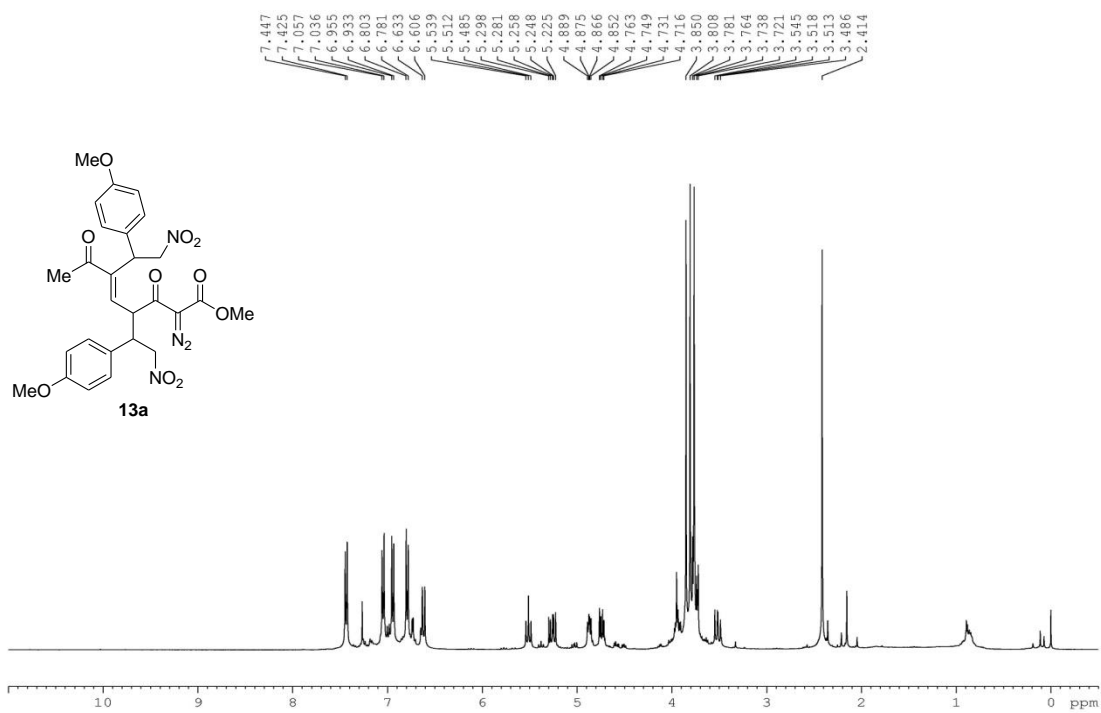
^1H and ^{13}C Spectra of New Compounds

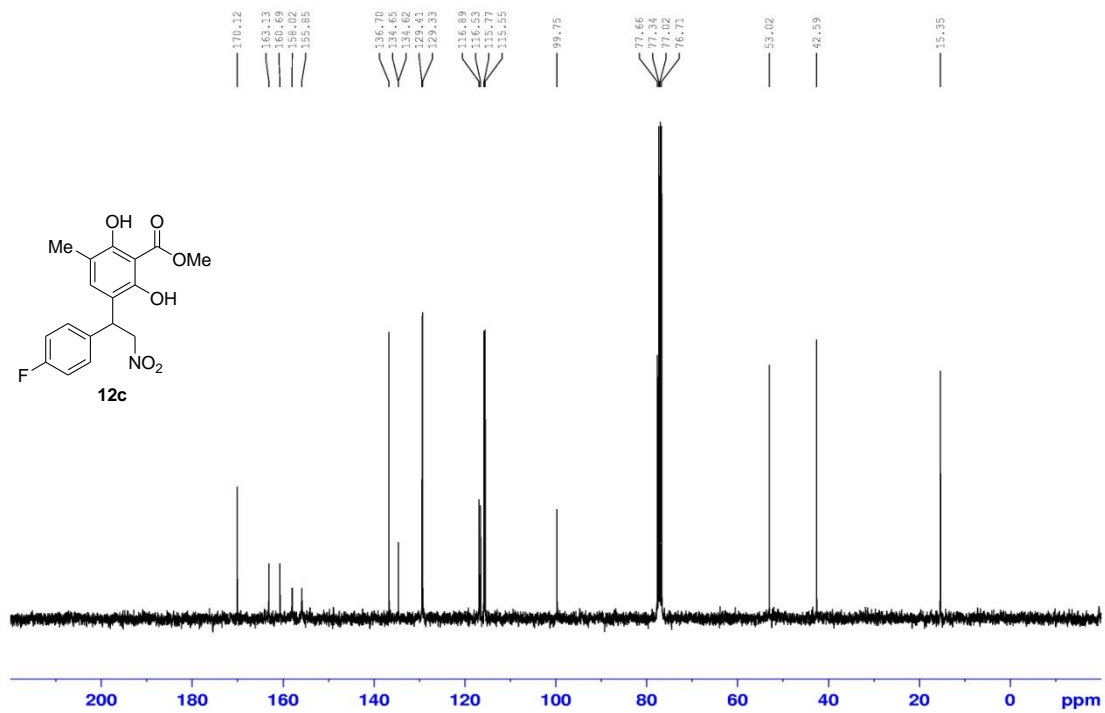
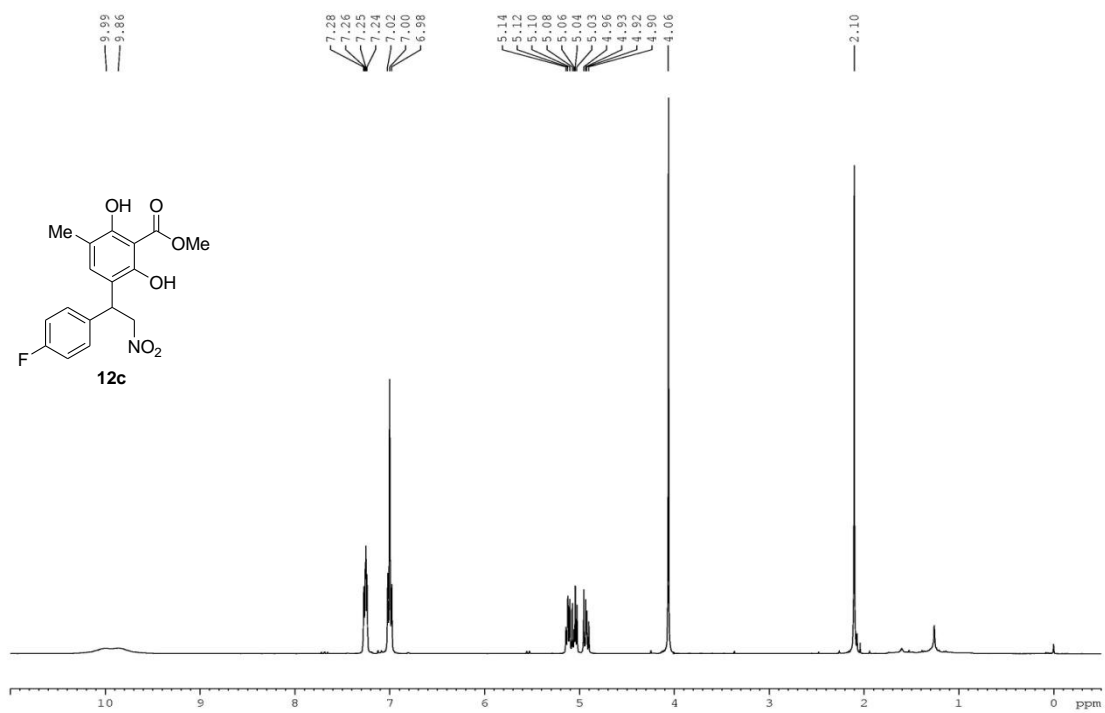


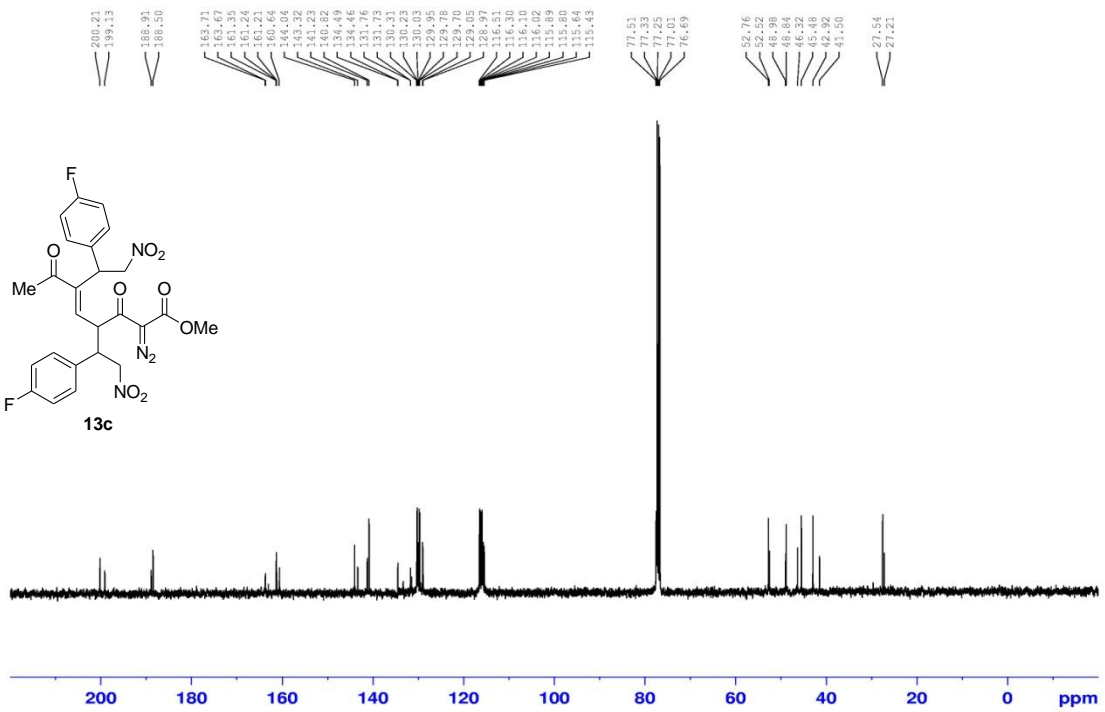
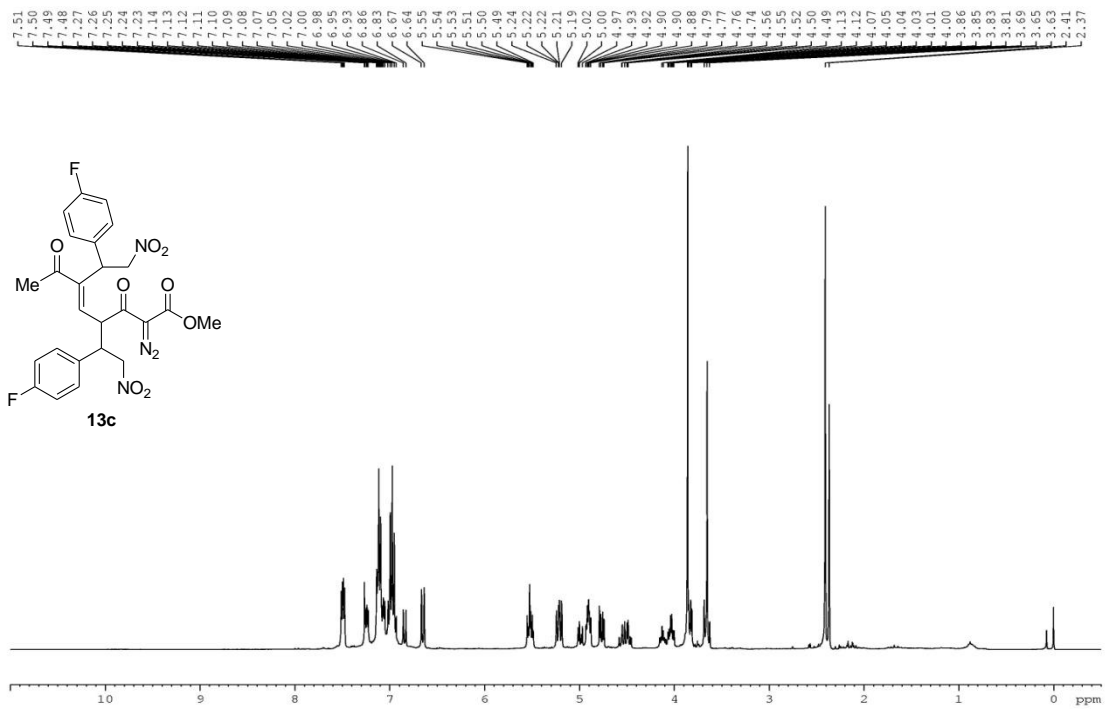


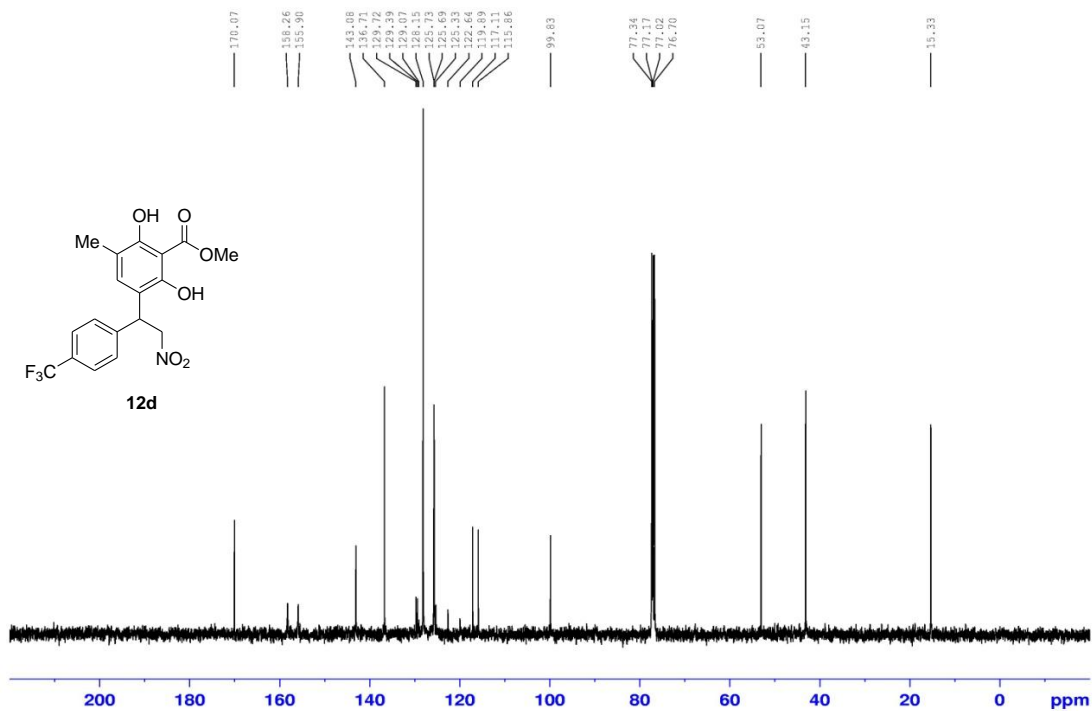
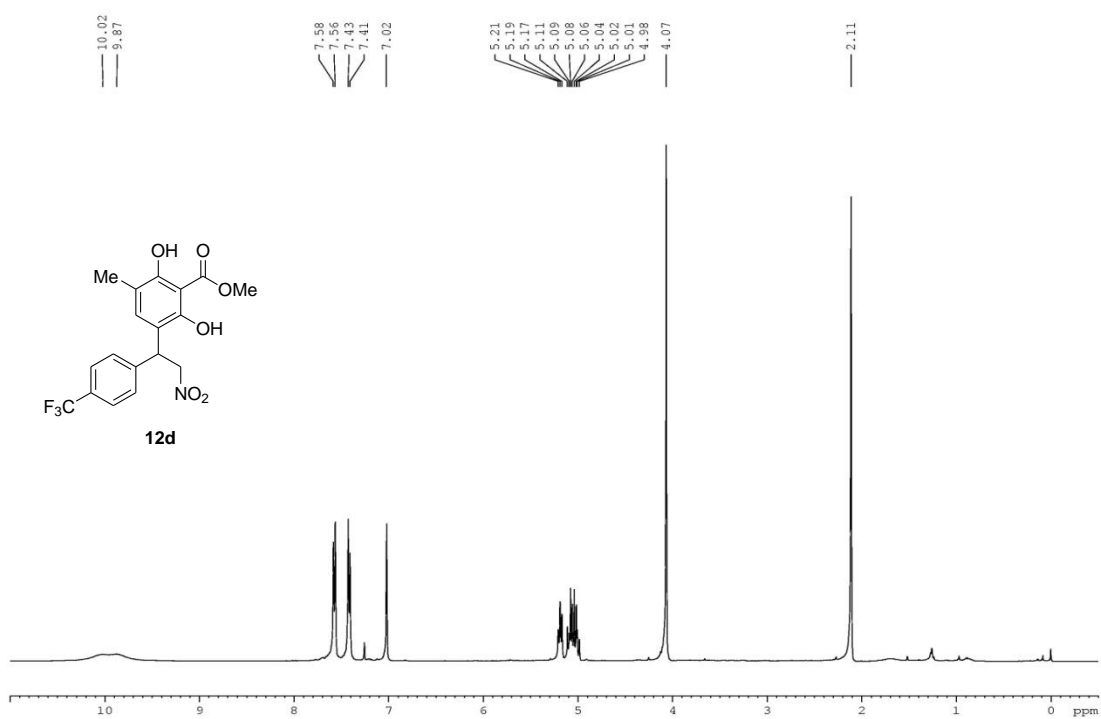


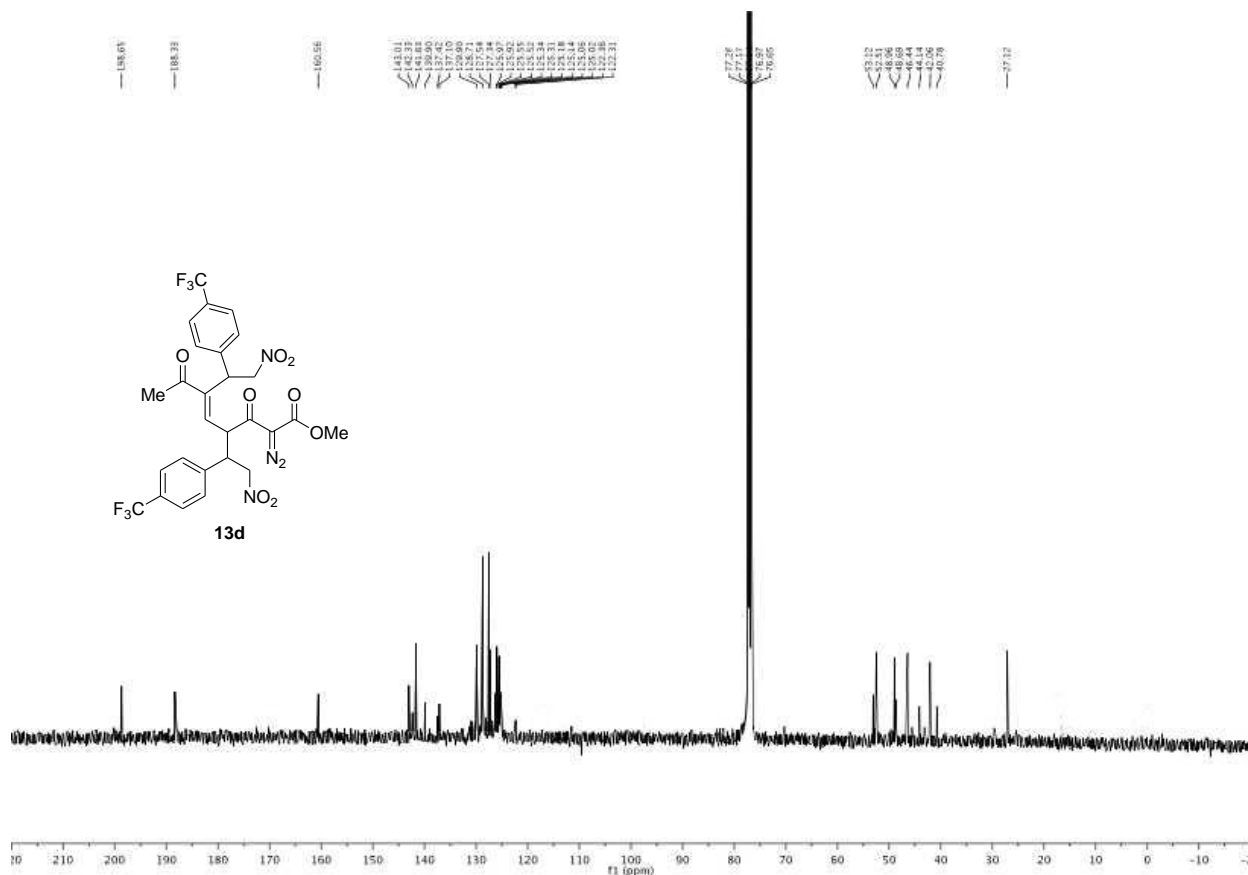
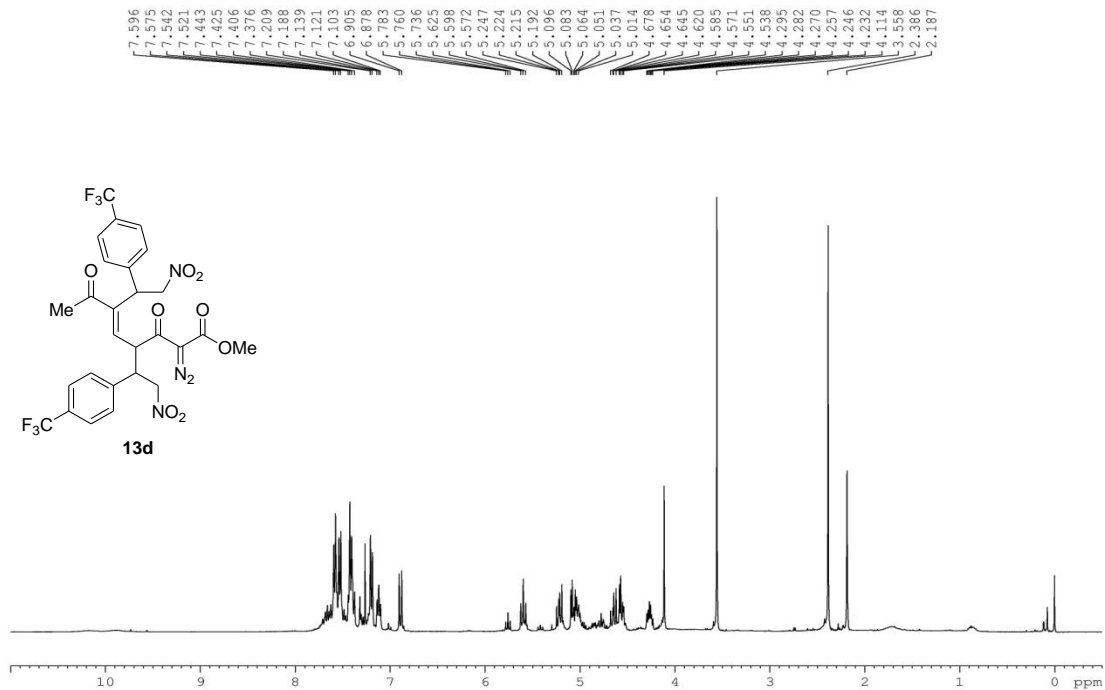


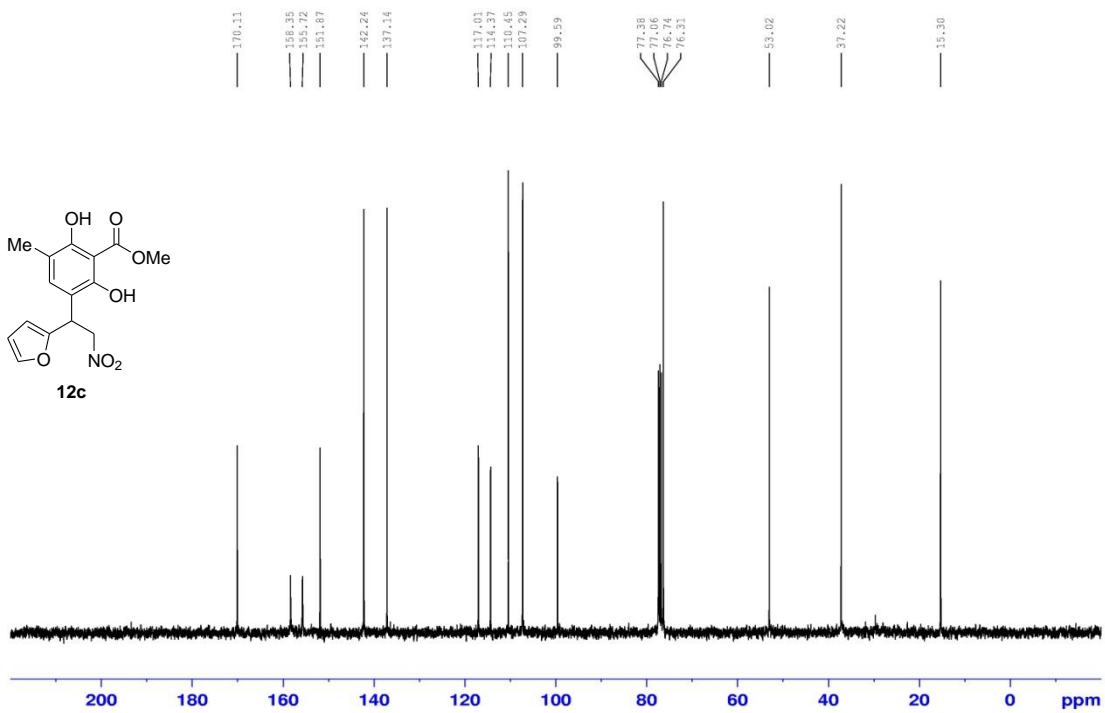
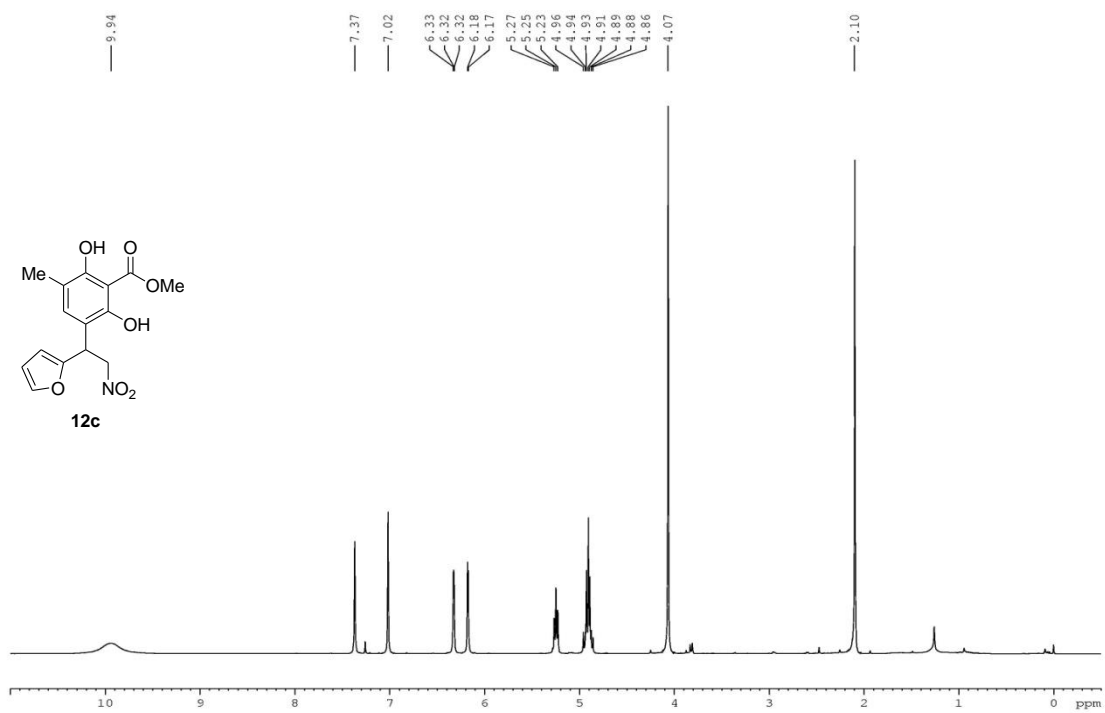








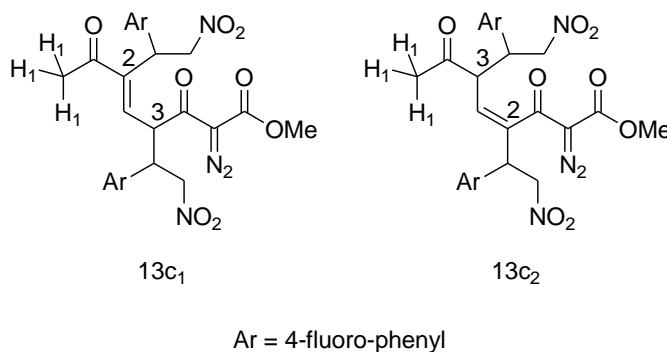




HMBC experiments that support the structure of methyl 3,7-dioxo-4,6-[1-(4-fluorophenyl)-2-nitroethyl]-2-diazoct-5-enoate (**13c**)

Compound **13c** could have two possible structures (Figure 1, **13c₁** and **13c₂**) which are difficult to differentiate by ¹H and ¹³C NMR. Therefore a HMBC experiment was performed on this compound to illuminate its structure. With structure **13c₁**, one would expect to see correlation between **H₁** and alkene carbon **C₂** through a 3 bond coupling. By comparison, there should be no coupling between these two signals in structure **13c₂** since they would be 5 bonds between these two atoms. Meanwhile, there should be no correlation between **H₁** and alkyl carbon **C₃** with structure **13c₁** but it should be visible if the structure is **13c₂**

Figure 1. Two Possible Isomers of **13c** with Different Position for the Alkene Double Bond.



The result is depicted in Figure 2 and an enlargement of the key region is shown in Figure 2. It can be seen from this experimental result that other than the carbonyl carbon at 200 ppm, **H₁** is coupled with the alkene carbon **C₂** at 140.8 ppm (possibly the other alkene carbon at 144.0 ppm as well) but not to the alkyl carbon **C₃** which appears in the range between 42.9 ppm and 52.7 ppm. What is more, since the same correlation is shown for both isomers, it suggests that these two isomers are diastereomers rather than isomers caused by different positions of the double bond in the molecule. Based on these results from the HMBC experiments, we believe that methyl 3,7-dioxo-4,6-[1-(4-fluorophenyl)-2-nitroethyl]-2-diazoct-5-enoate has the structure depicted by **13c₁**, rather than by **13c₂**.

Figure 2. HMBC Spectrum of methyl 3,7-dioxo-4,6-[1-(4-fluorophenyl)-2-nitroethyl]-2-diazo-oct-5-enoate (**13c**).

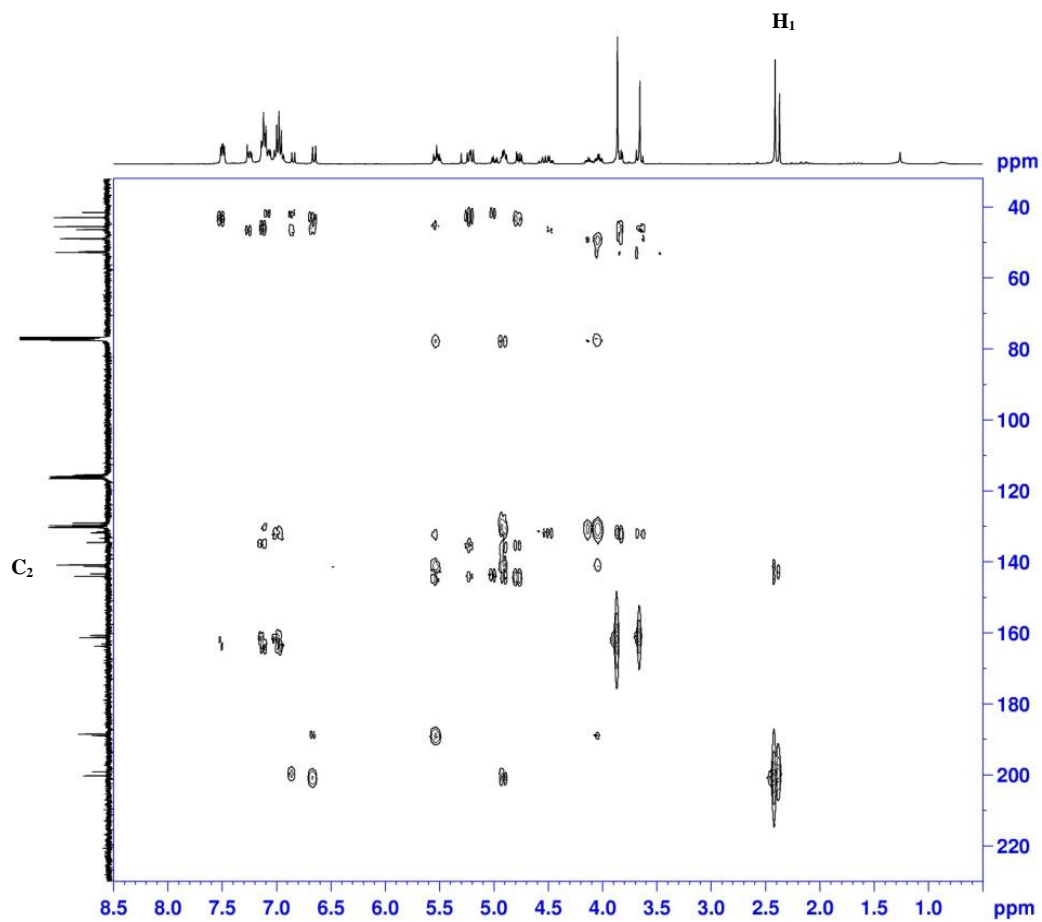
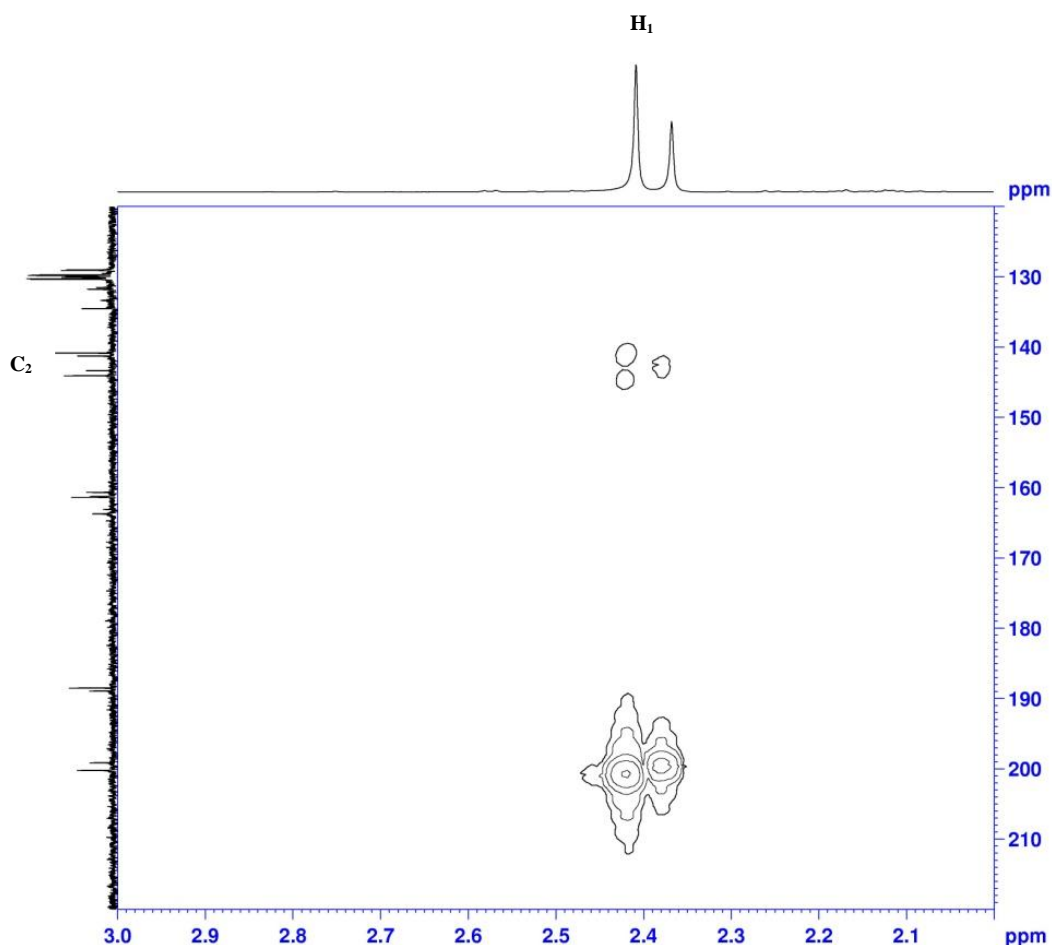
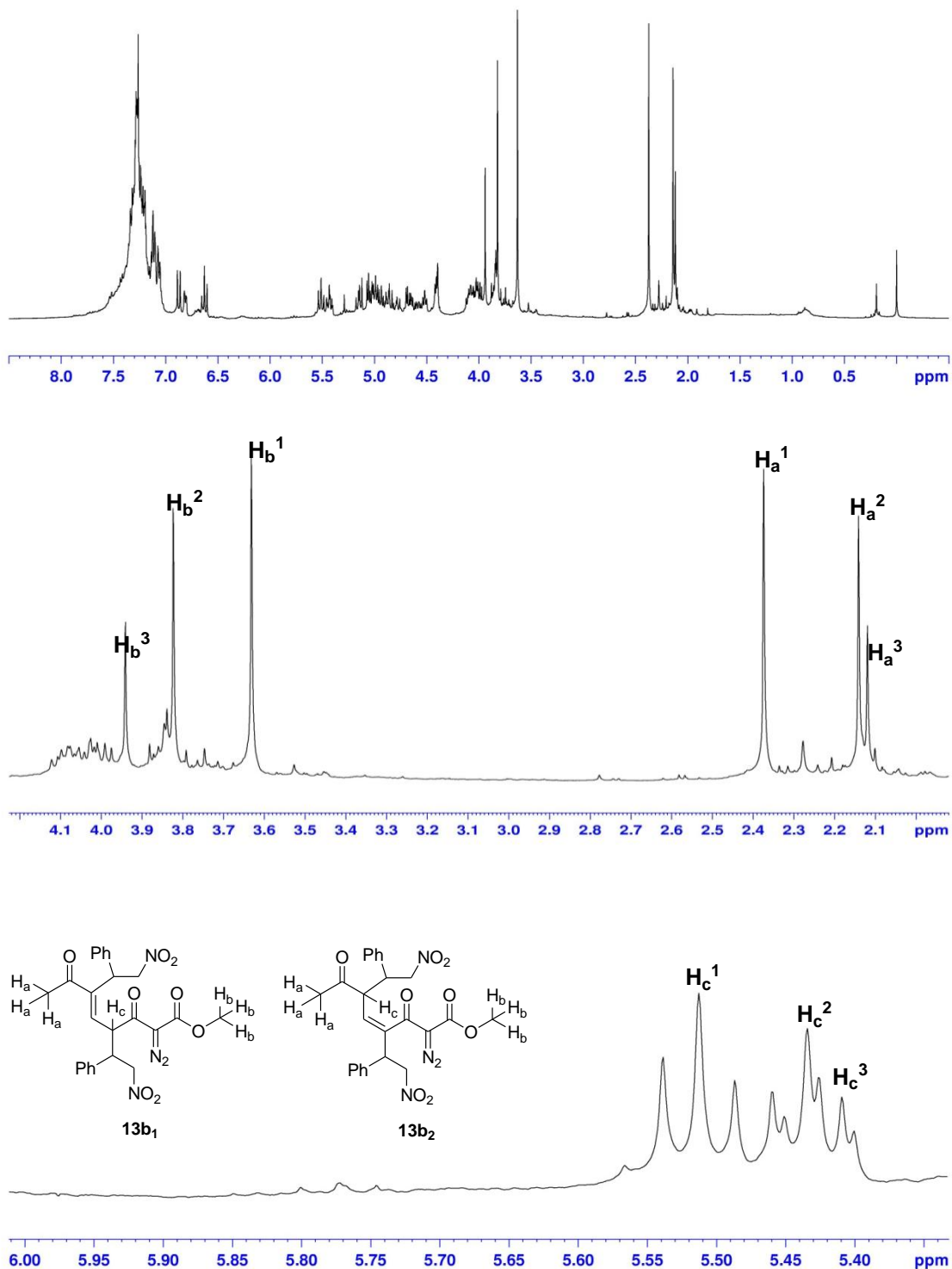


Figure 3. Expanded HMBC spectrum of methyl 3,7-dioxo-4,6-[1-(4-fluorophenyl)-2-nitroethyl]-2-diazoct-5-enoate (**13c**) at the key region.



Proton NMR spectrum of methyl 3,7-dioxo-4,6-(1-phenyl-2-nitroethyl)-2-diazoct-5-enoate (13b). Compound **13b** was isolated as a mixture of three detectable isomers that could not be further separated by column chromatography. The three isomers could be identified by three sets of **H_a**, **H_b** and **H_c**. The ¹H NMR spectra, with key regions expanded (Figure 4), are shown below. These isomers could be diastereomers or regioisomers caused by the migration of the double bond (**13b₁** and **13b₂**)

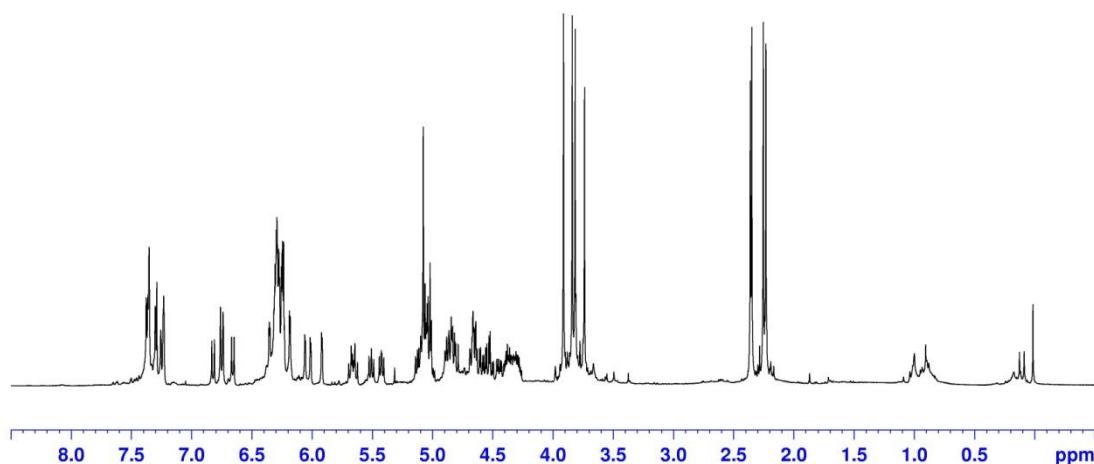
Figure 4. Proton NMR Spectrum of methyl 3,7-dioxo-4,6-(1-phenyl-2-nitroethyl)-2-diazooct-5-enoate (13b) Indicating Multiple Isomers.

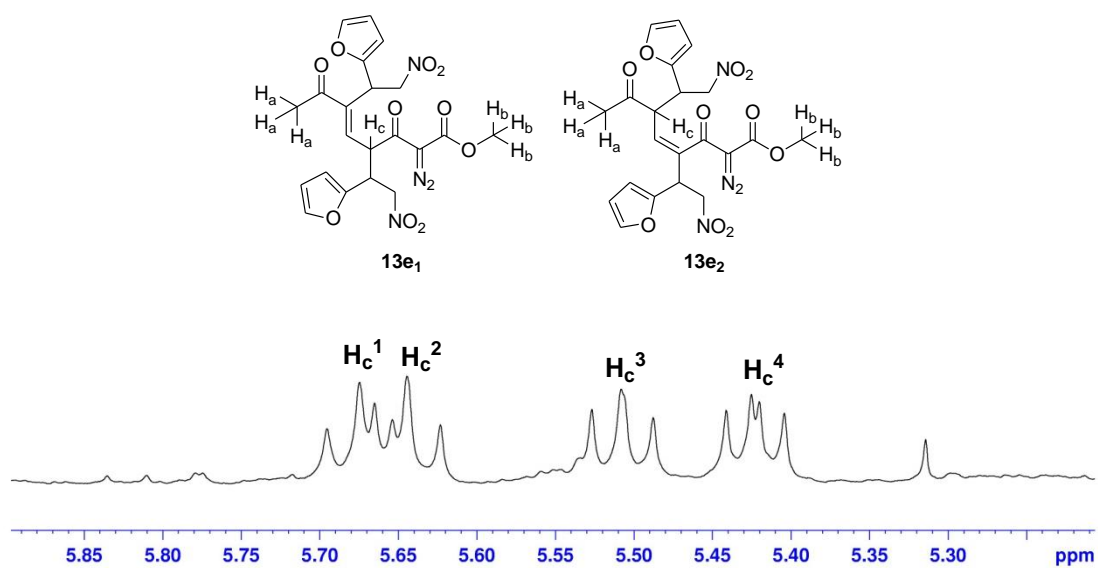
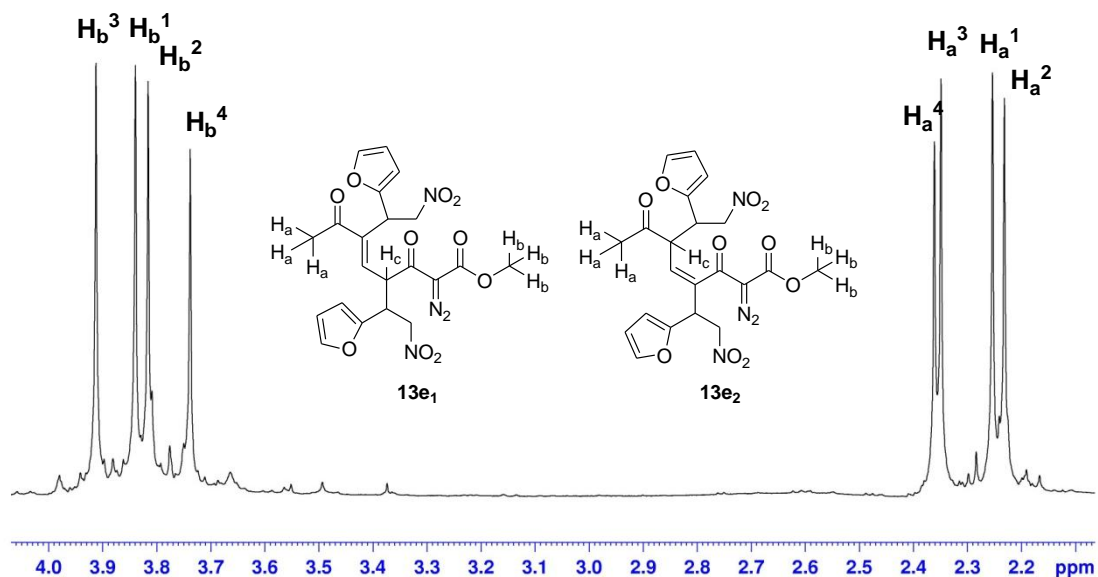


Proton NMR spectrum of methyl 3,7-dioxo-4,6-[1-(1-furyl)-2-nitroethyl]-2-diazoct-5-enoate (13e)

Compound **13e** was isolated as a mixture of four isomers in about equal amounts that could not be further separated by column chromatography. The four isomers could be identified by four sets of **H_a**, **H_b** and **H_c**. The ¹H NMR spectra including enlarged key regions are shown in Figure 5. These isomers could be diastereomers or regioisomers caused by the migration of the double bond (**13e₁** and **13e₂**)

Figure 5. Proton NMR Spectrum of Methyl 3,7-Dioxo-4,6-(1-(1-furyl)-2-nitroethyl)-2-diazo-oct-5-enoate (13e) Indicating Multiple Isomers.



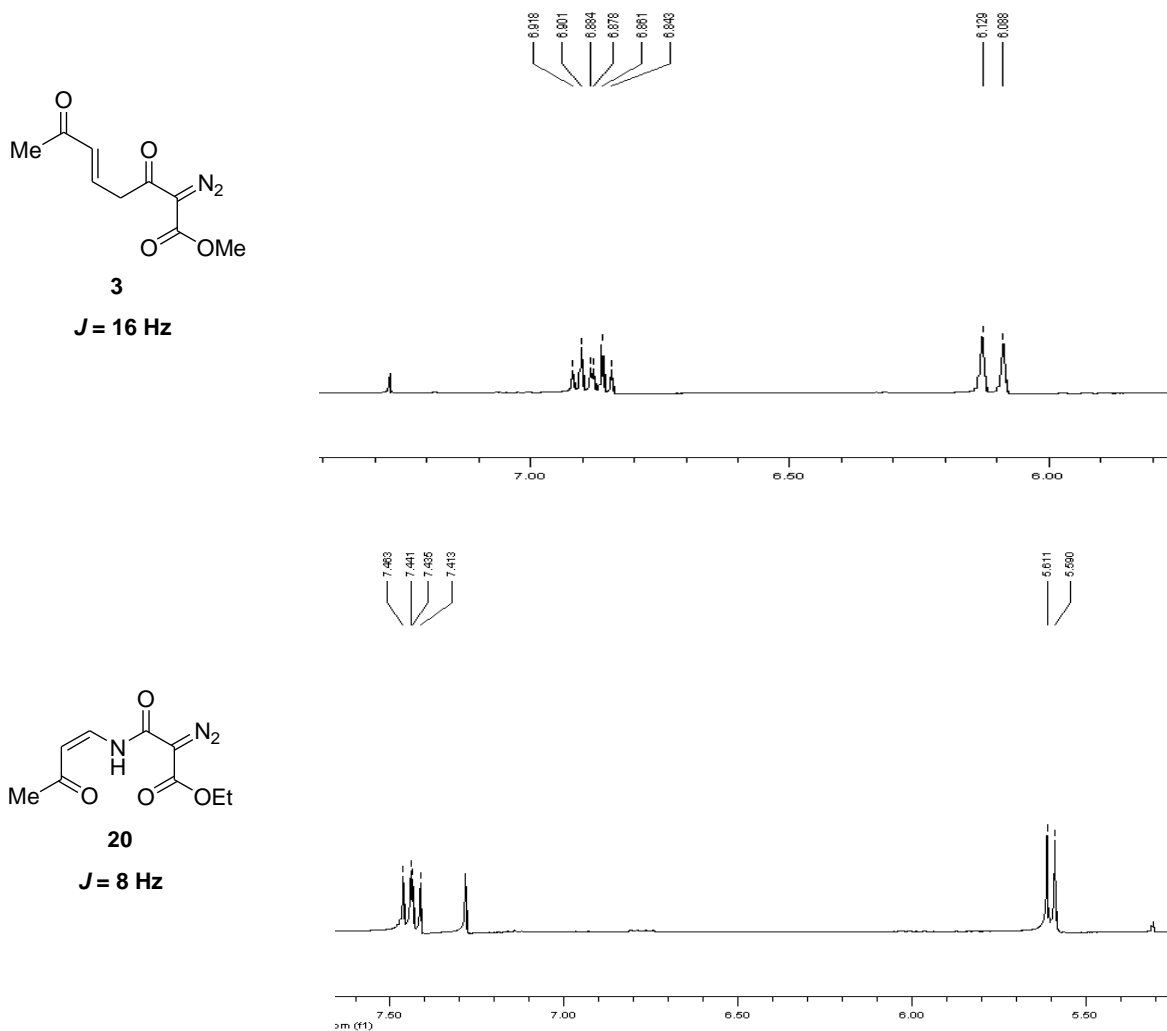


Structural characterization of ethyl (*Z*)-3,7-dioxo-2-diazo-oct-5-enoate (**20**)

Enlarged key regions of the ^1H NMR spectra of diazoester **20** and diazoester **3** are shown in Figure 6. A coupling constant of 8 Hz between the two vinyl protons indicating a *cis* geometry of the alkene double bond was observed in compound **20**. By contrast, a 16 Hz coupling

constant between the vinyl protons was observed in the ^1H NMR spectrum of compound **3** which predicts the *trans* geometry.

Figure 6. Comparison of coupling constants for the two vinylic protons in methyl 3,7-dioxo-2-diazo-(*E*)-oct-5-enoate (**3**) and ethyl (*Z*)-3,7-dioxo-2-diazo-oct-5-enoate (**20**).

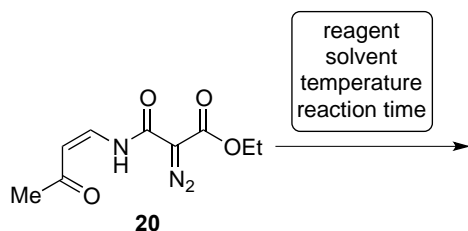


Attempted pericyclization/rearrangement of ethyl 3,7-dioxo-2-diazo-oct-5-enoate (**20**)

Reaction conditions evaluated for promoting pericyclization/rearrangement of diazoester **20** are summarized in Table 1. Triethylamine (Entry 1), DBU (Entry 2), sodium hydride (Entry 3) sodium methoxide (Entry 4) were used. However, essentially no reaction occurred, and the

starting material remained in the reaction solution even after long reaction times (16 hours overnight). Under acidic conditions (Entry 5-Entry 7), the trans isomer of diazoester **20** was formed in various ratios to the cis isomer, but no other product could be identified in the reaction mixture according to ¹H NMR of the reaction mixture.

Table 1. Various conditions to promote pericyclization/rearrangement of ethyl (Z)-3,7-dioxo-2-diazo-oct-5-enoate (**20**).



Entry	reagent	solvent	temperature	reaction time	result	<i>cis:trans</i>
1	2 eq Et ₃ N	DCM	40°C	2 h	NR	-
2	2 eq DBU	DCM	40°C	16 h	NR	-
3	0.5 eq NaH	THF	rt	16 h	NR	-
4	0.5 eq CH ₃ ONa	CH ₃ OH	rt	16 h	NR	-
5	2 eq CF ₃ COOH	DCM	40°C	2 h	isomerization	79:21
6	0.5 eq 1 N HCl	THF	rt	16 h	isomerization	83:17
7	0.5 eq <i>p</i> -TsOH	DCM	40°C	16 h	isomerization	72:28