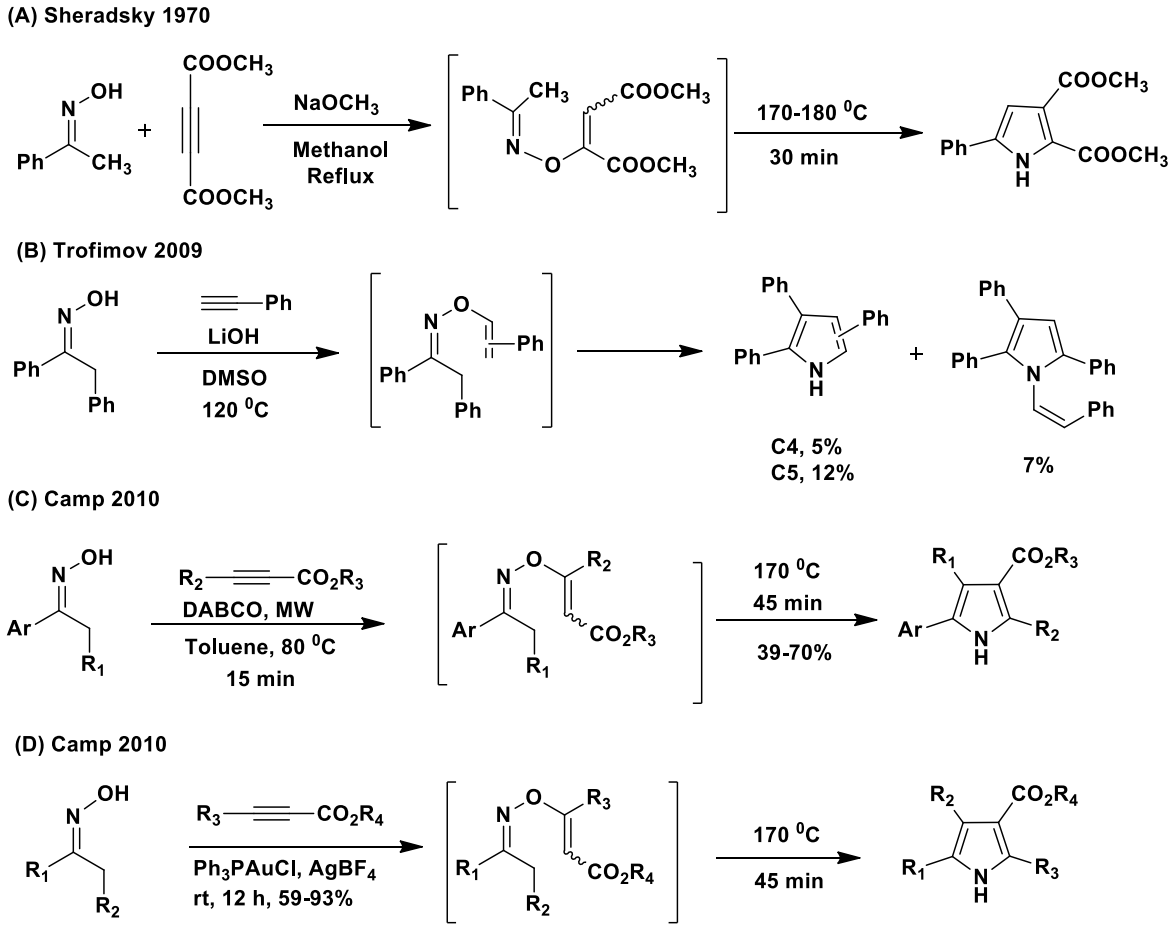
Chapter 2

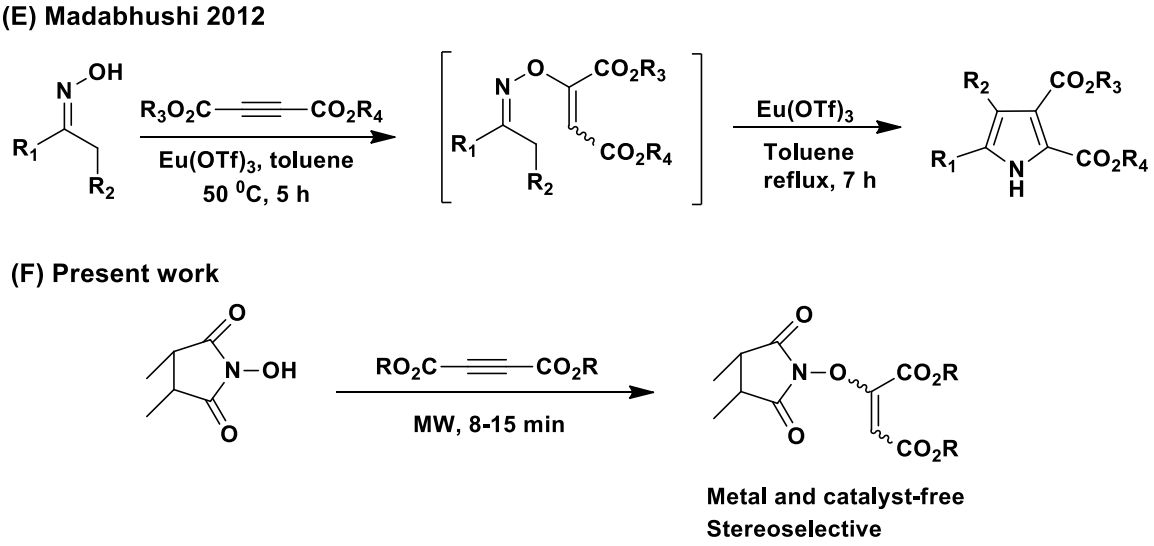
Microwave Induced Stereoselective Green Synthesis of *O*–Vinyl Oximes using Acetylenic Esters as Efficient Michael Acceptors: Some Remark on Synthesis and Stereochemistry

2.1 Introduction

O–Vinyl oximes are important building blocks for the synthesis of biologically active compounds and natural products such as pyrroles, oxazoles and isoxazoles (Gribble 1996, Abele et al. 2010, Rani et al. 2017). Syntheses of *O*–vinyl oximes were achieved by the nucleophilic addition of oximes to the alkynes using different catalysts. Most of the reactions were accomplished for the terminal alkynes, but there are limited examples with internal alkynes and always there are issues of selectivity because of formation of more than one product (Bolotin et al. 2017). The survey of literature reveals that preparation of *O*–vinyl oximes required harsh reaction conditions like strong base, high temperature, longer reaction time, poor yields and different catalysts. Sheradsky in 1970 synthesized pyrrole from the reaction of acetophenone oxime and diethyl acetylenedicarboxylate using strong base $NaOCH_3$ (Sheradsky 1970). Trofimov has reported the pyrrole synthesis by the reaction of oximes to alkynes under strongly basic conditions using LiOH, known as Trofimov reaction (Hyun et al. 2009, Trofimov et al. 2009). Different catalysts were used like DABCO (Ngwerume et al. 2010), PPh_3AuCl-$AgBF_4$ (Ngwerume et al. 2011), Ph_3AuCl–AgOTf (Ngwerume et al. 2013), $Eu(OTf)_3$ (Madabhushi et al. 2012) and PPh_3 (Yavari et al. 1997, Trofimov et al. 2010) for pyrrole synthesis via in situ formations of *O*–vinyl oximes.

In most of the cases isomeric mixtures obtained were used in the subsequent transformations (**Scheme 2.1**). *O*–vinyl oximes also undergo the different types of rearrangements like [1, 3] and [3, 3] sigmatropic rearrangements (Wang et al. 2010, Wang et al. 2011, Kontokosta et al. 2013), Wang et al. have reported an iridium-catalyzed isomerization reaction to convert *O*–allyl oximes to *O*–vinyl oximes (Wang et al. 2010).





Scheme 2.1: Synthesis of *O*–vinyl oximes which further rearrange to substituted pyrroles (**A-E**) except in the present work (**F**).

Restricted rotation and nonplanar conformation about N–N bond and the energy of activation $\Delta G^{\neq} \approx 20$ kcal/mol have been demonstrated in tetraacylhydrazine derivatives (**1**) through the magnetically asymmetrical cage moieties with the help of ^{1}H NMR in solution state (Korsch et al. 1966, Verma et al. 1972, Verma et al. 1973, Verma et al. 1974, Verma et al. 1976, Verma et al. 1978). X–ray crystallography established the stereochemistry of (**1**) in solid state where the *N'*–diacetyl fragment and the dicarboximide ring planes are almost perpendicular to each other (Wolska et al. 2003). Interaction of the lone electron pairs in the p-orbitals of the nitrogen atoms has been considered to be an important factor for the torsional barrier about N-N bond. While evaluating the effective bulk of lone pair of nitrogen in sp^2- state through conformational analysis about N-C bond it was observed that

the lone pair of pyridal nitrogen exihibit a strong repulsion from the benzene ring of the cage moiety and remains in *anti* orientation (**2**) (Allinger et al. 1967, Katritzky et al. 1968, Mahanti et al. 1982). Restricted rotation and nonplanar conformation about N**–**N bond and the isopropylideneamino moiety orthogonal to the succinimide plane with the lone pair in *anti*-orientation have been proposed on the basis of the shielding parameters of the methyl protons and VT NMR studies (**3**) (Srivastava et al. 1994). The stereochemistry of addition product obtained from the reaction of *N*–amino–3,4–(9',10'–dihydroanthracene–9',10'–diyl)succinimide and diethyl acetylenedicarboxylate shows the tautomeric structure (**4**), where the lone pair of nitrogen lies in *anti*–orientation to the cage while diethyl succinate moiety *syn* to the cage and orthogonal to the succinimidyl plane. The azomethine structure (**4b**) has been demonstrated with the help of ^{1}H, ^{13}C NMR and X–ray crystallography **(Figure 2.1)**. On acetylation, the product (**4**) was transformed into *N*–acetyl derivative which exhibits restricted rotation about N–N bond and a preferred conformation with *N*–acetyl in *syn*–orientation (Srivastava et al. 1994).

Tremendous amount of work has been reported on conformational analysis about N–N and N–C bonds but perusal of literature reveals that no work has been done about N–O bond in acyclic system. Herein, we wish to report the synthesis of *O*-vinyl oximes under

When the substituent is towards the cage it is referred as *syn* and when it is away from the cage it is referred as *anti*.

catalyst and metal-free conditions by conventional and microwave irradiation methods. Further an attempt has also been made to study the effectiveness of the cage moiety and sp^3-hybridized lone pairs of oxygen in controlling the conformational preferences about N–O bond and configuration of the synthesized *O*–vinyl oximes. Compounds (**I**–**V**) were synthesized from the reaction of *N*-hydroxy-3,4-(9',10'-dihydroanthracene-9',10'-diyl)succinimide (**6**), *N*-hydroxyphthalimide and dialkyl acetylenedicarboxylates (**Figure 2.2**) and their stereochemistry have been established through ^{1}H NMR, ^{13}C NMR and X–ray crystallography.

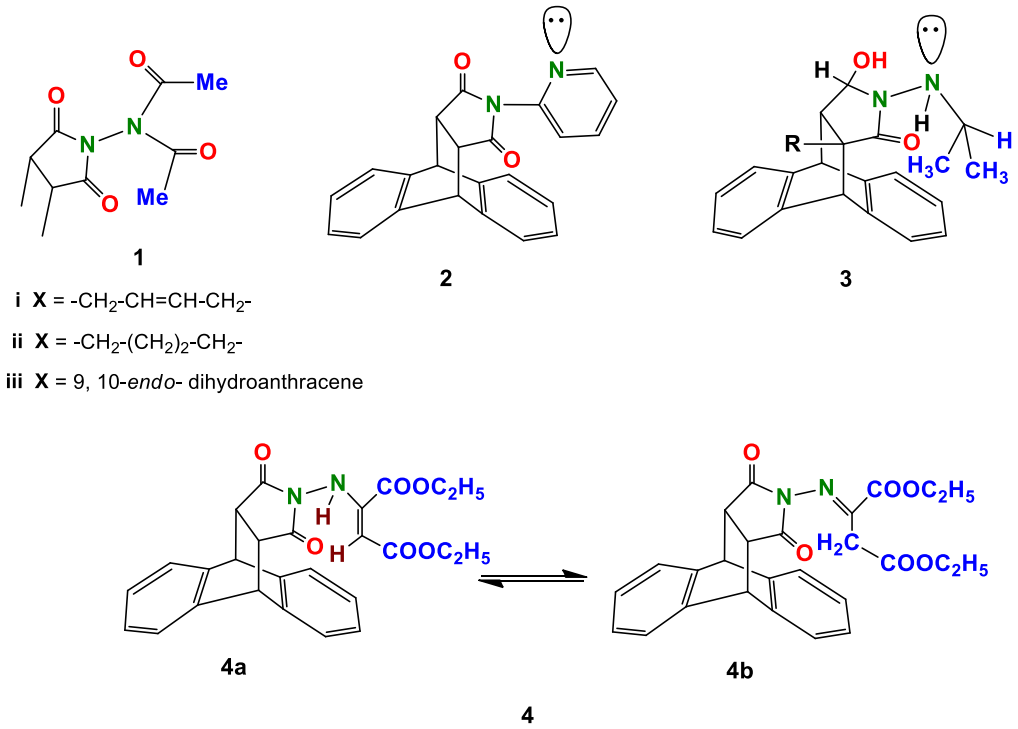


Figure 2.1: Restricted rotation and non-planer conformations about N–N and N–C bond (**1**-**4**).

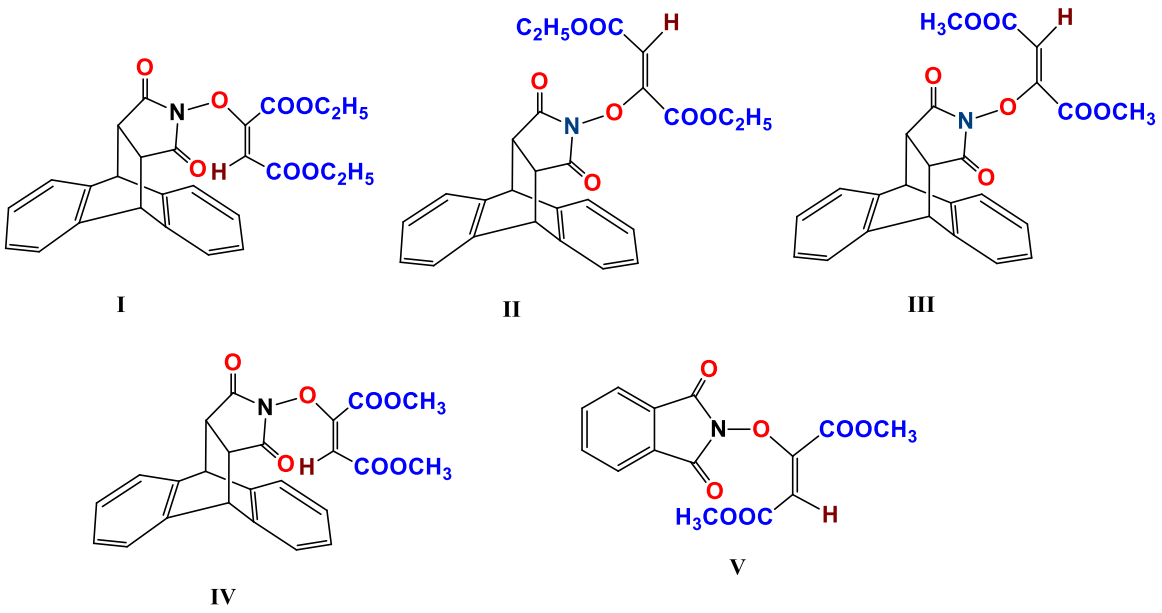
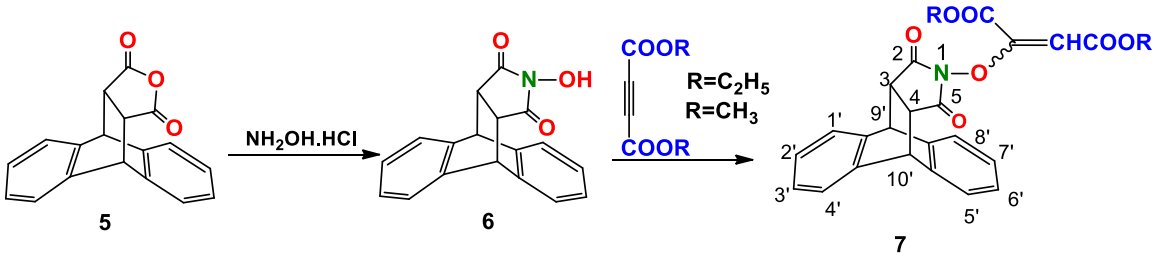


Figure 2.2: Synthesized *O*–vinyl oximes (**I**–**V**).

The systematic scheme for the synthesis of *O*–vinyl oximes **(6)** involves the synthesis of oxime of anthracene-maleic anhydride Diels-Alder adduct (**5**) followed by Michael addition of oxime with dialkyl acetylenedicarboxylates (**Scheme 2.2**).



Scheme 2.2: Synthesis of *N*-hydroxy compound (**7**) and its Michael addition with dialkyl acetylenedicarboxylates.

2.2 Results and Discussion

To optimize the reaction condition for the synthesis of *O*-vinyl oximes (**7**), oxime (**6**) and diethyl acetylenedicarboxylate were selected as model substrates. The reaction was carried out in ethanol at reflux under conventional heating method. The progress of reaction was monitored by TLC and the reaction was completed in 1.5 h. After completion of reaction solvent was evaporated under reduced pressure and the ^{1}H NMR spectrum of the crude product shows it is a mixture of two isomers in the ratio of 1:1. The two isomers were separated by fractional crystallization from ethanol. The fractions with melting point 202 ^{0}C which crystallized out first was assigned as compound (**I**) and the fractions of melting point 120 ^{0}C was recrystallized out later, as compound (**II**) and were in the ratio of 1:1.

To obtain products (**I**) and (**II**) stereoselectively the model reaction was performed in various polar and nonpolar solvents at their reflux temperature under conventional heating method. Among the polar solvents (like methanol, ethanol, acetonitrile), ethanol gave the best result of the desired product in 80% yield within 1.5 h with isomeric mixture of (**I**) and (**II**) in 1:1 ratio and in the case of non-polar solvents (like toluene and xylene) no product was obtained. Therefore, to observe the selectivity at lower temperature under conventional method an attempt has been made by varying the experimental temperature of the reaction in ethanol. The reaction was performed at 40 ^{0}C, 60 ^{0}C in ethanol for 3 h and it was observed that at 40 ^{0}C no product was obtained while at 60 ^{0}C only 30% product was

obtained and it is the mixture of isomers (**I**) and (**II**) in 1:1 ratio, no selectivity was observed in conventional method and the results are summarized in **Table 2.3**.

The ^{1}H NMR spectrum of compound (**I**) exhibits two overlapping triplets (6H) at δ 1.30, two quartets (2H each) at δ 4.14, 4.28 for ethyl ester protons, a singlet (2H) at δ 3.28 for 3 & 4–H, a singlet (1H) at δ 3.47 for vinylic proton, a singlet at 4.86 (2H) for 9'& 10'-H and multiplet (8H) at 7.19-7.21 & 7.36-7.40 for aromatic protons. The absence of duplicity and the appearance of shielded signal (1H) at δ 3.47 for vinylic proton and magnetic equivalence of 3 & 4 protons shows restricted rotation and preferred nonplanar conformation about N–O bond and the *O*–vinyl group is orthogonal to the succinimidyl plane with the lone pairs of oxygen in *anti*-orientation to the cage. The highly shielded signal for the vinylic proton (Δδ = 2.98) indicates it is under the influence of anisotropic effect of the cage benzo ring, this implies *O*–vinyl moiety is *syn* to the cage benzo ring and both the ethyl ester groups are *cis* to each other (E-configuration), it is also in agreement with its electronic interactions with the cage. There are two possible geometries (**7a**) and (**7b**) in case of *syn*-orientation of the *O*–vinyl oxime (**Figure 2.3**), in configuration (**7b)** i.e. trans (E) one of the ethyl ester group must be highly shielded due to its strong interaction with cage benzo ring. Absences of such shielding of ethyl ester group and presence of highly shielded signal of vinyl proton geometry (**7a**) i.e. cis (Z) for the compound (I). has been proposed. ^{13}C NMR of the compound (**I**) exhibits a (CH, vinylic) resonance at

δ 99.95, slightly shielded position because of the aromatic ring current further supports the proposed geometry (**7a**).

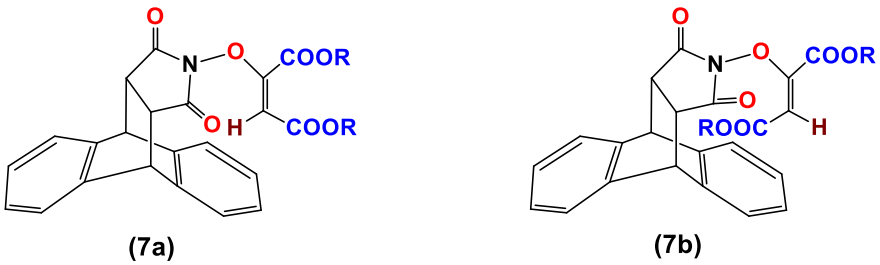


Figure 2.3: Two possible geometries of *syn*-isomer of (**7**).

Therefore, an attempt has been made to synthesize compound (**I**) stereoselectively, the model reaction was performed with 2-3 drops of DMF under microwave irradiation at 300 W, 100 ^{0}C and the progress of reaction was monitored by TLC, the reaction was completed in 10 minutes. After completion of reaction, the reaction mixture was cooled to room temperature and diluted with methanol. The solid product thus obtained in 93% yield has melting point 202 ^{0}C and its ^{1}H NMR shows the presence of single isomer and it is same as compound (**I**) obtained by conventional method.

2.2.1 X-ray crystallographic data of compound (I)

The X-ray crystallographic data of compound (**I**) shows that the exo-cyclic oxygen is in sp^{3}–hybridized [C(19)–O(3)–N(1)=114.54^{0}] with lone pairs of oxygen in *anti*-orientation to the cage and also both the ethyl ester groups are *cis* to each

other i.e. E-configuration which is in full agreement with the findings in solution state. The X–ray crystal structure of compound (**I**) is shown in **Figure 2.4**.

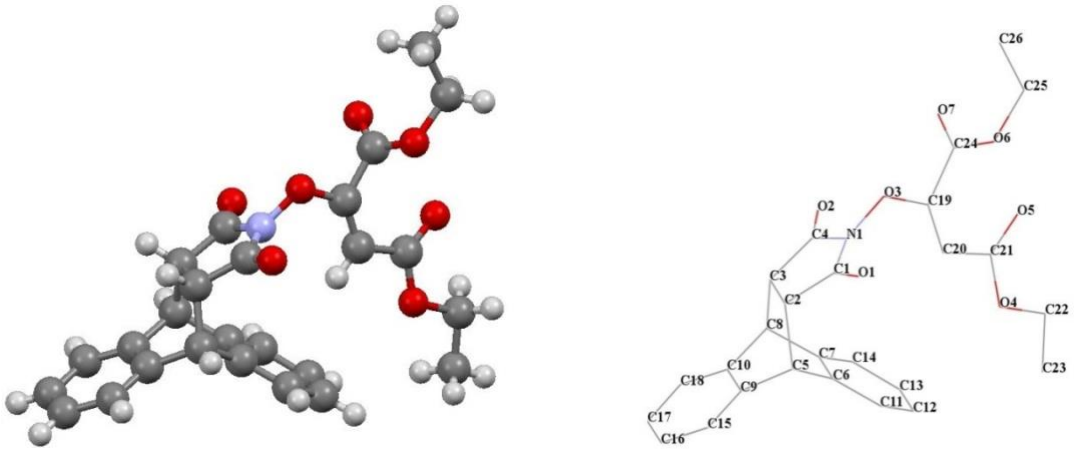


Figure 2.4: Single crystal XRD structure of compound (**I**).

Details of X-ray analysis of compound (I)

1. The lone pairs of electron of oxygen are pointing away from the ring system (*anti*-orientation).

2. The product is recrystallized from ethanol, m.f. $C_{26}H_{23}NO_7$ in space group $P_{21/c}$ with unit cell parameters a = 9.13353(14) Å, b = 9.21245(13) Å, c = 27.1668(4) Å, β = 94.6623(14)°, V = 2278.31(6) $Å^3$, D_{calc}= 1.345 Mg/m^3, λ= 1.54184, μ = 0.817 mm^{-1}, F (000) = 968. Final R = 0.0396, R_w = 0.1059, maximum 2θ = 67.49°, crystal size = (0.34 x 0.14 x 0.13 mm^3).

Table 2.1: Bond lengths and bond angles in compound (**I**)

Bond lengths [Å]		**Bond angles [°]**	
N(1)-C(1)	1.3907(19)	C(1)-N(1)-O(3)	121.67(11)
N(1)-O(3)	1.3935(15)	C(1)-N(1)-C(4)	116.32(11)
N(1)-C(4)	1.3940(19)	O(3)-N(1)-C(4)	120.14(11)
O(2)-C(4)	1.2043(18)	C(19)-O(3)-N(1)	114.54(10)
O(1)-C(1)	1.2014(18)	C(21)-O(4)-C(22)	116.24(12)
O(3)-C(19)	1.3788(17)	C(24)-O(6)-C(25)	115.30(12)
O(4)-C(21)	1.3366(18)	O(1)-C(1)-N(1)	124.28(13)
O(4)-C(22)	1.4543(19)	O(1)-C(1)-C(2)	129.92(13)
O(5)-C(21)	1.2092(18)	N(1)-C(1)-C(2)	105.79(11)
O(6)-C(24)	1.3268(18)	C(1)-C(2)-C(3)	105.97(11)
O(6)-C(25)	1.4669(19)	C(1)-C(2)-C(5)	112.87(11)
O(7)-C(24)	1.1983(18)	C(3)-C(2)-C(5)	109.29(11)
C(1)-C(2)	1.5101(19)	C(4)-C(3)-C(2)	105.54(11)
C(2)-C(3)	1.5465(18)	C(4)-C(3)-C(8)	111.56(11)
C(2)-C(5)	1.5631(19)	C(2)-C(3)-C(8)	110.26(11)
C(3)-C(4)	1.5046(19)	O(2)-C(4)-N(1)	123.86(13)
C(3)-C(8)	1.5620(19)	O(2)-C(4)-C(3)	129.84(13)
C(5)-C(6)	1.513(2)	N(1)-C(4)-C(3)	106.27(11)
C(5)-C(9)	1.5171(19)	C(6)-C(5)-C(9)	108.06(11)
C(6)-C(11)	1.391(2)	C(6)-C(5)-C(2)	106.93(11)
C(6)-C(7)	1.399(2)	C(9)-C(5)-C(2)	104.62(11)
C(7)-C(14)	1.387(2)	C(11)-C(6)-C(7)	120.00(14)
C(7)-C(8)	1.5137(19)	C(11)-C(6)-C(5)	126.21(14)
C(8)-C(10)	1.515(2)	C(7)-C(6)-C(5)	113.78(12)
C(9)-C(15)	1.384(2)	C(14)-C(7)-C(6)	120.52(14)
C(9)-C(10)	1.400(2)	C(14)-C(7)-C(8)	126.34(14)
C(10)-C(18)	1.386(2)	C(6)-C(7)-C(8)	113.12(12)

C(11)-C(12)	1.392(2)	C(7)-C(8)-C(10)	108.01(12)
C(12)-C(13)	1.383(3)	C(7)-C(8)-C(3)	106.46(11)
C(13)-C(14)	1.393(2)	C(10)-C(8)-C(3)	105.23(11)
C(15)-C(16)	1.391(2)	C(15)-C(9)-C(10)	120.21(13)
C(16)-C(17)	1.389(2)	C(15)-C(9)-C(5)	126.23(13)
C(17)-C(18)	1.393(2)	C(10)-C(9)-C(5)	113.54(12)
C(19)-C(20)	1.326(2)	C(18)-C(10)-C(9)	120.33(14)
C(19)-C(24)	1.512(2)	C(18)-C(10)-C(8)	126.36(13)
C(20)-C(21)	1.471(2)	C(9)-C(10)-C(8)	113.25(12)
C(22)-C(23)	1.505(2)	C(6)-C(11)-C(12)	119.24(15)
C(25)-C(26)	1.483(3)	C(13)-C(12)-C(11)	120.55(14)
		C(12)-C(13)-C(14)	120.62(15)
		C(7)-C(14)-C(13)	119.06(15)
		C(9)-C(15)-C(16)	119.43(14)
		C(17)-C(16)-C(15)	120.42(14)
		C(16)-C(17)-C(18)	120.34(14)
		C(10)-C(18)-C(17)	119.26(14)
		C(20)-C(19)-O(3)	126.97(13)
		C(20)-C(19)-C(24)	126.26(13)
		O(3)-C(19)-C(24)	106.63(11)
		C(19)-C(20)-C(21)	120.13(13)
		O(5)-C(21)-O(4)	123.88(14)
		O(5)-C(21)-C(20)	125.27(14)
		O(4)-C(21)-C(20)	110.85(12)
		O(4)-C(22)-C(23)	107.13(13)
		O(7)-C(24)-O(6)	126.96(14)
		O(7)-C(24)-C(19)	121.27(13)
		O(6)-C(24)-C(19)	111.75(12)
		O(6)-C(25)-C(26)	110.52(17)

The ^{1}H NMR spectrum of compound (**II**) exhibits dt (6H) at δ 1.20 and 1.26 for CH_3 and dq (4H) at δ 4.10 and 4.18 for the CH_2 for the two ethyl ester protons, a singlet (2H) at δ 3.23 for 3 & 4 protons, a singlet (2H) at 4.81 for 9' & 10' protons and a singlet (1H) at δ 6.25 for vinylic proton along with other normal resonances. Appearance of vinylic proton at δ 6.25 as a singlet of 1H at normal position suggests that it is not under the influence of the cage moiety and the magnetic equivalence of the 3 & 4 protons suggests restricted rotation and nonplanar conformation about N–O bond and the *O*–vinyl group is orthogonal to the succinimidyl plane with the lone pairs of oxygen in *syn*-orientation and *O*–vinyl group is in *anti*-orientation to the cage. There are two possible geometry of the *anti*-orientation of compound **7**; (**7c**) and (**7d**) (**Figure 2.5**). On the basis of the shielding parameters of the vinylic proton and that of ethyl ester protons geometry (**7c**) for the compound (**II**) has been proposed where both the ethyl ester groups are *trans* to each other (Z-configuration). ^{13}C NMR of the compound (**II**) exhibits (1 CH, vinylic) resonance at δ 110.38, normal chemical shift suggests that it is not under the influence of the aromatic ring current and it further supports the proposed geometry (**7c**).

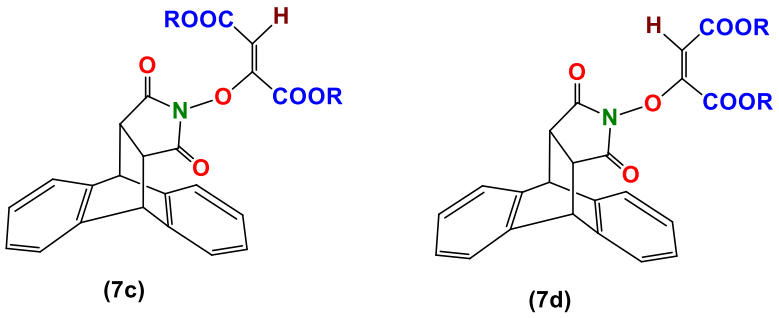


Figure 2.5: Two possible geometries of *trans*-isomer of (**7**).

To synthesize compound (**II**) stereoselectively, the reaction of oxime (**6**) with diethyl acetylenedicarboxylates was performed under microwave irradiations at different experimental conditions 400 W – 700 W. When the reaction was carried out at 400 W, 100 ^{0}C it gave a mixture of compound (**I**) and (**II**) 5:1 ratio in 10 minutes and at 500 W, 100 ^{0}C, mixture of isomer (**I**) and (**II**) in the ratio 3:1. Then the reaction was performed at 600 W, 100 ^{0}C in 15 minutes surprisingly it gave compound (**II**) stereoselectively in 95% yield. The melting point of the product (**II**) is 120 ^{0}C and its NMR spectrum is same as the isomer obtained under conventional method.

The two isomers *syn* (**I**) and *anti* (**II**) in the ratio of 1:1 suggest that the effective bulk of electron lone pairs of oxygen in sp^3-hybridized state and *O*–vinyl ethyl ester are of comparable in controlling the conformation about N-O bond.

The model compound (**V**) was prepared for the comparative study to see the effect of magnetically asymmetric cage moiety in controlling the stereochemistry of the molecule. The ^{1}H NMR spectrum of (**V**) exhibits two singlets (6H) at δ 3.71 & 3.83 for two methyl ester groups, a singlet (1H) at δ 6.43 for vinylic proton together with other normal resonances. Appearance of vinylic proton at normal position and duplicity in methyl ester protons shows Z-configuration for the compound (**V**) (Islami et al. 2004, Ramazani et al. 2009, Zhou et al. 2013).

When *N*-hydroxyl-3,4-(9',10'-dihydroanthracene-9',10'-diyl)succinimide (**6**) was treated with dimethyl acetylenedicarboxylate by conventional method in ethanol, it shows two spots on TLC. ^{1}H NMR spectrum of the crude product exhibits the presence of two isomers in 1:2 ratio and were separated by fractional crystallization. The first few fractions, m.p. 195 ^{0}C was assigned as compound (**III**) and the other fraction, m.p. 226 ^{0}C as compound (**IV**) and the adducts (**III**) and (**IV**) were in 1:2 ratio. ^{1}H NMR spectrum of compound (**III**) exhibits a singlet (2H) at δ 3.24 for 3, 4–H, two sharp singlets at δ 3.65 and 3.73 (6H) for two methyl ester protons and a singlet at δ 6.27 (1H) for vinylic proton along with other normal resonances. Presence of vinylic proton chemical shift at δ 6.27 as singlet of (1H) suggests it is uninfluenced by the cage moiety and the magnetic equivalence of the 3 & 4 protons suggests restricted rotation and nonplanar conformation about N–O bond with the lone pairs of oxygen in *syn*-orientation. On the basis of the chemical shifts of the vinylic and methyl ester protons geometry (**7c**) for the compound (**III**) has been proposed where both the methyl ester groups are *trans* to each other (Z-configuration). ^{13}C NMR of the compound exhibits a vinylic carbon resonance at δ 109.88, normal chemical shift suggests that it is uninfluenced by the anisotropic effect of the cage benzo ring and further supports the proposed geometry (**7c**) as for compound (**II**). Stereoselectively product (**III**) was synthesized under microwave irradiation at 600 W, 100 ^{0}C for 10 minutes.

2.2.2 X-ray crystallographic data of compound (III)

The X–Ray crystallography of the compound (**III**) has demonstrated that the exocyclic oxygen is sp^3–hybridized (C(19)–O(3)–N(1) bond angle = 113.85^0), lone pairs of oxygen is in *syn*-orientation and dimethyl vinyl moiety is in *anti*-orientation to the cage moiety and the methyl ester groups are in *trans*-geometry (Z-configuration). The X–ray crystal structure of the compound (**III**) is shown in **Figure 2.6**.

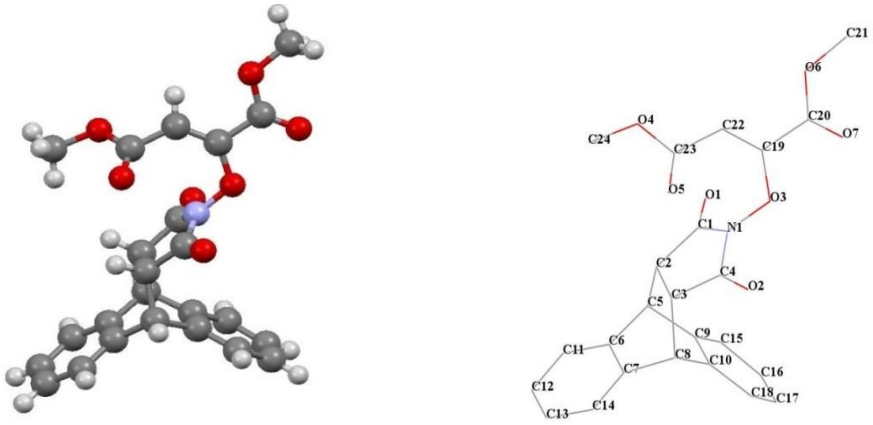


Figure 2.6: Crystal structure of compound (**III**).

Details of the X–Ray Analysis of compound (III)

1. The lone pairs of electrons of oxygen are pointing towards the ring system (*syn*-orientation).
2. The product is recrystallized from ethanol, m.f. $C_{24}H_{19}NO_7$ in the space group P–1 with unit cell parameters a = 8.1160(3) Å, b = 11.3300(5) Å, c = 11.9749(5) Å,

β = 99.660(4)°, V = 992.76(7)Å^3 , D_{calc}= 1.450 Mg/m^3, λ = 1.54184, μ = 0.901mm^{-1}, F (000) = 452. Final R = 0.0368, R_w = 0.0933, maximum 2θ = 67.50°, crystal size = (0.33 x 0.24 x 0.18 mm^3).

Table 2.2: Bond lengths and bond angles in compound (**III**)

Bond lengths [Å]		**Bond angles [°]**	
N(1)-O(3)	1.3886(14)	O(3)-N(1)-C(4)	120.57(11)
N(1)-C(4)	1.3953(18)	O(3)-N(1)-C(1)	121.11(11)
N(1)-C(1)	1.3964(18)	C(4)-N(1)-C(1)	116.09(11)
O(1)-C(1)	1.2022(17)	C(19)-O(3)-N(1)	113.85(10)
O(2)-C(4)	1.2025(17)	C(23)-O(4)-C(24)	116.15(12)
O(3)-C(19)	1.3818(17)	C(20)-O(6)-C(21)	115.62(12)
O(4)-C(23)	1.3206(18)	O(1)-C(1)-N(1)	124.05(13)
O(4)-C(24)	1.4526(18)	O(1)-C(1)-C(2)	130.79(13)
O(5)-C(23)	1.2022(18)	N(1)-C(1)-C(2)	105.14(11)
O(6)-C(20)	1.3275(18)	C(1)-C(2)-C(3)	105.51(10)
O(6)-C(21)	1.4505(18)	C(1)-C(2)-C(5)	113.91(11)
O(7)-C(20)	1.1966(19)	C(3)-C(2)-C(5)	109.71(10)
C(1)-C(2)	1.5164(18)	C(4)-C(3)-C(2)	105.67(10)
C(2)-C(3)	1.5549(18)	C(4)-C(3)-C(8)	112.71(11)
C(2)-C(5)	1.5563(18)	C(2)-C(3)-C(8)	109.74(10)
C(3)-C(4)	1.5109(18)	O(2)-C(4)-N(1)	124.87(13)
C(3)-C(8)	1.5562(18)	O(2)-C(4)-C(3)	129.73(13)
C(5)-C(9)	1.5159(18)	N(1)-C(4)-C(3)	105.39(11)
C(5)-C(6)	1.5181(18)	C(9)-C(5)-C(6)	106.85(10)
C(6)-C(11)	1.3859(19)	C(9)-C(5)-C(2)	107.45(10)
C(6)-C(7)	1.3994(19)	C(6)-C(5)-C(2)	105.50(10)
C(7)-C(14)	1.3881(19)	C(11)-C(6)-C(7)	120.03(13)
C(7)-C(8)	1.5204(18)	C(11)-C(6)-C(5)	126.48(13)
C(8)-C(10)	1.5146(18)	C(7)-C(6)-C(5)	113.49(11)

C(9)-C(15)	1.3847(19)	C(14)-C(7)-C(6)	120.44(13)
C(9)-C(10)	1.4004(19)	C(14)-C(7)-C(8)	126.25(12)
C(10)-C(18)	1.3874(19)	C(6)-C(7)-C(8)	113.30(11)
C(11)-C(12)	1.395(2)	C(10)-C(8)-C(7)	107.14(11)
C(12)-C(13)	1.382(2)	C(10)-C(8)-C(3)	107.83(10)
C(13)-C(14)	1.393(2)	C(7)-C(8)-C(3)	104.74(10)
C(15)-C(16)	1.391(2)	C(15)-C(9)-C(10)	120.50(12)
C(16)-C(17)	1.385(2)	C(15)-C(9)-C(5)	126.04(12)
C(17)-C(18)	1.391(2)	C(10)-C(9)-C(5)	113.35(11)
C(19)-C(22)	1.328(2)	C(18)-C(10)-C(9)	120.04(13)
C(19)-C(20)	1.5090(19)	C(18)-C(10)-C(8)	126.30(12)
C(22)-C(23)	1.488(2)	C(9)-C(10)-C(8)	113.53(11)
		C(6)-C(11)-C(12)	119.53(13)
		C(13)-C(12)-C(11)	120.24(13)
		C(12)-C(13)-C(14)	120.70(13)
		C(7)-C(14)-C(13)	119.07(14)
		C(9)-C(15)-C(16)	119.10(13)
		C(17)-C(16)-C(15)	120.56(13)
		C(16)-C(17)-C(18)	120.47(13)
		C(10)-C(18)-C(17)	119.25(13)
		C(22)-C(19)-O(3)	130.24(13)
		C(22)-C(19)-C(20)	122.84(13)
		O(3)-C(19)-C(20)	106.88(11)
		O(7)-C(20)-O(6)	125.99(13)
		O(7)-C(20)-C(19)	123.19(13)
		O(6)-C(20)-C(19)	110.83(12)
		C(19)-C(22)-C(23)	130.18(13)
		O(5)-C(23)-O(4)	123.91(14)
		O(5)-C(23)-C(22)	125.92(13)
		O(4)-C(23)-C(22)	110.12(12)

The ^{1}H NMR spectrum of compound (**IV**) exhibits a singlet (2H) at δ 3.28 for 3 & 4-H, a sharp singlet (1H) at δ 3.51 for vinylic proton and two sharp singlets (6H) at δ 3.70 and 3.83 for methoxy protons. The shielding parameter and the splitting pattern of the vinylic proton suggests restricted rotation and preferred nonplanar conformation about N–O bond, with lone pairs of oxygen in *anti*-orientation to the cage benzo ring. Equivalence of the 3, 4-H suggests that *O*–vinyl moiety is orthogonal to the succinimide plane. The highly shielded signal of the vinylic proton suggests it is under the influence of anisotropic effect of the cage benzo ring and methyl ester groups are *cis* to each other (E-configuration). ^{13}C NMR of the compound (**IV**) exhibits a (1 CH, vinyl) resonance at δ 100.23, shielded position because of the aromatic ring current and geometry (**7a**) has also been proposed for the compound (**IV**) as for the compound (**I**). The compound (**IV**) was synthesized stereoselectively under microwave irradiation at 300 W, 100 ^{0}C in 8 minutes.

The two isomers *anti* (**III**) and *syn* (**IV**) are in the ratio of 1:2 suggest that the effective bulk of lone pairs of oxygen in sp^{3}-hybridized state is more than *O*–vinyl methyl ester in controlling the conformation about N-O bond and it may be due to the smaller size of methyl ester group. The appearance of higher population of *syn*-isomer (towards the cage) implies that it is of lower energy than the *anti*-conformation (away from the cage) that might be the reason, at lower microwave

power *syn*-isomer while at higher microwave power *anti*-isomer were stereoselectively obtained.

A complete optimization of reaction conditions and the selectivity pattern of the *syn* and *anti*-isomers at different microwave parameters have been summarized in **Table 2.3**. The results in **Table 2.3** show that microwave irradiation provides selectivity at appropriate microwave parameters and stereoselectively both the isomers were synthesized. The selectivity (chemo-, regio- and stereoselectivity) under microwave irradiation is due to controlled and uniform heating as compared to the conventional method. The selectivity under microwave irradiation is mainly achieved by selecting appropriate microwave power, temperature, time, solvent or by using kinetic vs. thermodynamic control. The effect of microwave irradiation on organic transformations are not merely due to thermal effect but it is the combination of both thermal and non-thermal effects i.e., overheating, hot spots and selective heating, due to thermal effects and non-thermal effects create the highly polarizing field, in addition to effects on the mobility and diffusion that may increase the probabilities of effective contacts. The higher temperature was possibly achieved under MW heating, resulting in different selectivity, especially under higher MW power conditions (de la Hoz, Diaz-Ortiz et al. 2005, Hu, Wang et al. 2007, Jiaxi Xu 2007, Li and Xu 2016, Li and Xu 2017, Li and Xu 2017).

Table 2.3: Reaction of anthracene-maleic anhydride oxime (4) with DEAD* and DMAD* under conventional[a] and microwave irradiations[b]

S. No.	Micheal Acceptor	Reaction Condition	Temperature (^{0}C)	Time	Yield (%)[c]	Isomeric ratio of adducts
1	DEAD[a]	Heating	40	3 h	NR	--
2	DEAD[a]	Heating	60	3 h	30	(I):(II):: (1:1)
3	DEAD[a]	Reflux	80	1.5 h	80	(I):(II):: (1:1)
4	DMAD[a]	Reflux	80	3 h	88	(III):(IV):: (1:2)
5	**DEAD[b]**	**300 W**	**100**	**10 min**	**93**	**(I) *syn* only**
7	DEAD[b]	400 W	100	10 min	91	(I):(II):: 5:1
8	DEAD[b]	500 W	100	10 min	94	(I):(II):: 3:1
9	**DEAD[b]**	**600 W**	**100**	**15 min**	**95**	**(II) *anti* only**
10	**DMAD[b]**	**300 W**	**100**	**8 min**	**96**	**(IV) *syn* only**
11	DMAD[b]	400 W	100	10 min	93	(III):(IV)::1:1
12	DMAD[b]	500 W	100	10 min	94	(III):(IV)::4:1
13	**DMAD[b]**	**600 W**	**100**	**10 min**	**92**	**(III) *anti* only**

*DEAD-Diethyl acetylenedicarboxylate; DMAD-Dimethyl acetylenedicarboxylate. **Reaction Conditions:** [a] An equimolar amount of *N*-hydroxy-3,4-(9',10'-dihydroanthracene-9',10'-diyl)succinimide (**6**) and dialkyl acetylenedicarboxylate in ethanol. [b] Equimolar amount of *N*-hydroxy compound (**6**) and dialkyl acetylenedicarboxylate and 2-3 drops of DMF was irradiated under microwave. [c] Isolated yield.

2.3 Experimental section

***N*-hydroxy-3,4-(9',10'-dihydroanthracene-9',10'-diyl)succinimide (6):**

(a) Conventional method:

To an equimolar amount of 3,4-(9',10'-dihydroanthracene-9',10'-diyl)succinic anhydride (**6**) and hydroxylamine hydrochloride in ethanol catalytic amount of pyridine was added, and the reaction mixture was refluxed for 3 h. The progress of reaction was monitored with TLC and after completion of reaction; reaction mixture was allowed to cool at room temperature. The solid product thus obtained was filtered out and recrystallized from ethanol.

(b) Microwave irradiation method:

An equimolar amount of 3,4-(9',10'-dihydroanthracene-9',10'-diyl)succinic anhydride (**6**) and hydroxylamine hydrochloride in ethanol with catalytic amount of pyridine was irradiated under MW power of 300 W at 80 ^{0}C for 5 min. After completion of reaction, reaction mixture was cooled to the room temperature and poured into ice cold water. The solid mass thus obtained was filtered and recrystallized from ethanol.

White solid; yield 95%; m.p. 278 ^{0}C; **IR** (KBr) ν (cm^{-1}): 3564, 1742, 1707, 1648, 1626, 1533, 1516, 1461; **^{1}H NMR** (500 MHz, DMSO-d_6) δ (ppm): 3.18 (s, 2 H, 3 & 4-H), 4.75 (s, 2 H, 9' & 10'-H), 7.11 – 7.16 (m, 4 H, ArH), 7.23 – 7.24 (m, 2 H, ArH), 7.44 – 7.46 (m, 2 H, ArH), 10.57 (s, 1 H, D_2O exchangeable); **^{13}C NMR** (126 MHz, DMSO-d_6) δ (ppm): 43.32 (3 & 4-C), 44.27 (9' & 10'-C), 124.37, 124.89, 126.49, 126.81, 139.14, 141.88 (aromatic carbons), 172.21(imide carbons). Elemental analysis: (Found: C, 74.18; H, 4.52. Calc. for $C_{18}H_{13}NO_3$: C, 74.22; H, 4.50%).

2.3.1 General procedure for synthesis of product (I-V)

(a) Conventional method

An equimolar amount of *N*-hydroxy-3,4-(9',10'-dihydroanthracene-9',10'-diyl)succinimide (**7**) and dialkyl acetylenedicarboxylate in ethanol was refluxed for corresponding time and progress of reaction was monitored by TLC. After completion of reaction, reaction mixture was cooled to the room temperature. The solid product thus obtained was recrystallized from ethanol and separated by fractional crystallization.

(b) Microwave method

An equimolar amount of *N*-hydroxy-3,4-(9',10'-dihydroanthracene-9',10'-diyl) succinimide (**7**) and dialkyl acetylenedicarboxylate and 2-3 drops of DMF was taken in irradiated under appropriate microwave conditions. After the completion of reaction (TLC), the reaction mixture was cooled to the room temperature and diluted with methanol. The solid product thus obtained was filtered and recrystallized from ethanol.

***O*-(*syn*-Diethylmaleate)-3,4-(9',10'-dihydroanthracene-9',10'-diyl)succinimide (I):** White solid; yield 93%; m.p. 202 ^{0}C; **IR** (KBr) ν (cm^{-1}): 2908, 2258, 1792, 1735, 1654, 1466, 1035; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 1.30 (m, 6 H, 2 -CH_3), 3.28 (s, 2 H, 3 & 4-H), 3.47 (s, 1 H, vinylic H), 4.14 & 4.28 (dq, 4 H, 2 -OCH_2), 4.86 (s, 2 H, 9'& 10'-H), 7.19-7.21 (m, 4 H, ArH), 7.36-7.40 (m, 4 H, ArH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 13.89 & 14.19 (2 -CH_3), 44.30 (3 & 4-C), 45.06 (9' & 10'-C), 61.15 & 62.84 (-OCH_2), 99.95 (CH, vinylic), 124.49, 125.53, 127.27, 128.22, 138.50 & 140.90 (aromatic carbons), 154.60 (1 C, vinylic), 159.60, 163.97 & 168.75 (two imide carbons and two ester carbons). Elemental analysis: (Found: C, 67.63; H, 4.97. Calc. for $C_{26}H_{23}NO_7$: C, 67.67; H, 5.02%).

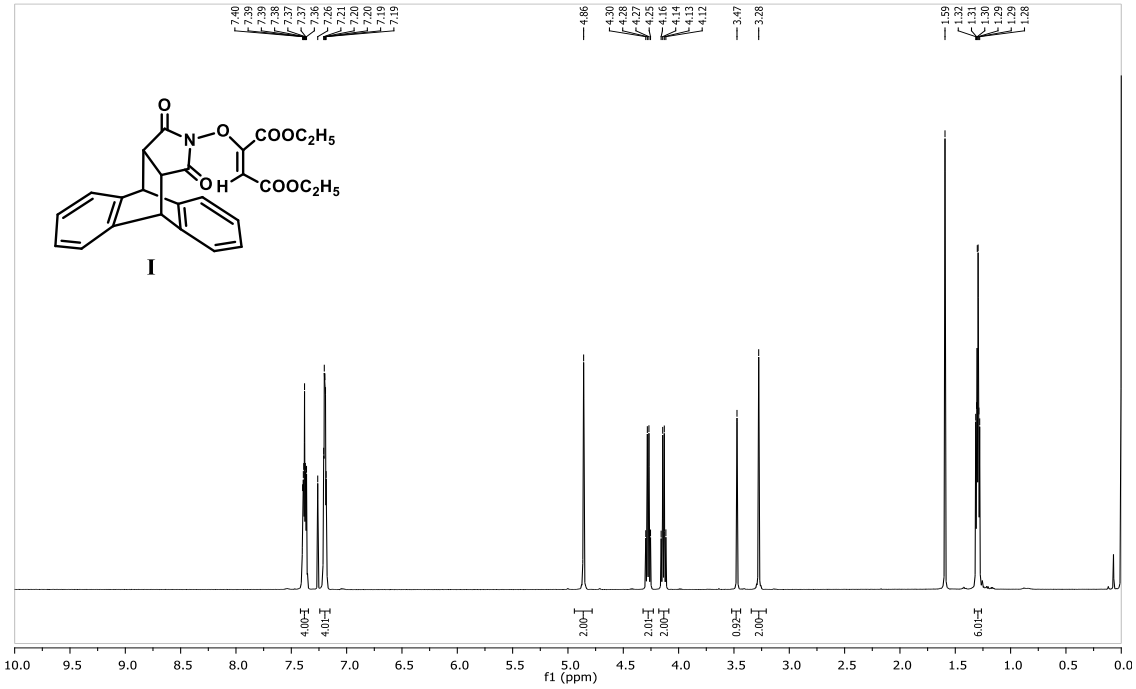
***O*-(*anti*-Diethylfumarate)-3,4-(9',10'-dihydroanthracene-9',10'-diyl)succinimide (II):** White solid; yield 95%; m.p. 120 ^{0}C; **IR** (KBr) ν (cm^{-1}): 3060, 2981, 2363, 2326, 1794, 1729, 1700, 1653, 1541, 1459, 1353, 1265, 1200, 1094, 1024; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 1.20 & 1.26 (dt, 6 H, 2 -CH_3), 3.23 (s, 2 H, 3 & 4-H), 4.10 & 4.18 (dq, 4 H, 2 -OCH_2), 4.81 (s, 2 H, 9'& 10'-H), 6.25 (s, 1 H, vinylic H), 7.15-7.19 (m, 4 H, ArH), 7.30 (dd, 2 H, ArH), 7.37 (m, 2 H, ArH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 14.02 & 14.16 (2 -CH_3), 44.13 (3 & 4-C), 44.98 (9' & 10'-C), 61.44 & 62.86 (-OCH_2), 110.38 (CH, vinylic), 124.41, 125.24, 127.05, 127.47, 138.37 & 141.33 (aromatic carbons), 149.51 (1C, vinylic), 159.67, 162.74 & 169.41 (two imide carbons and two ester carbons). Elemental analysis: (Found: C, 67.59; H, 4.97. Calc. for $C_{26}H_{23}NO_7$: C, 67.67; H, 5.02%).

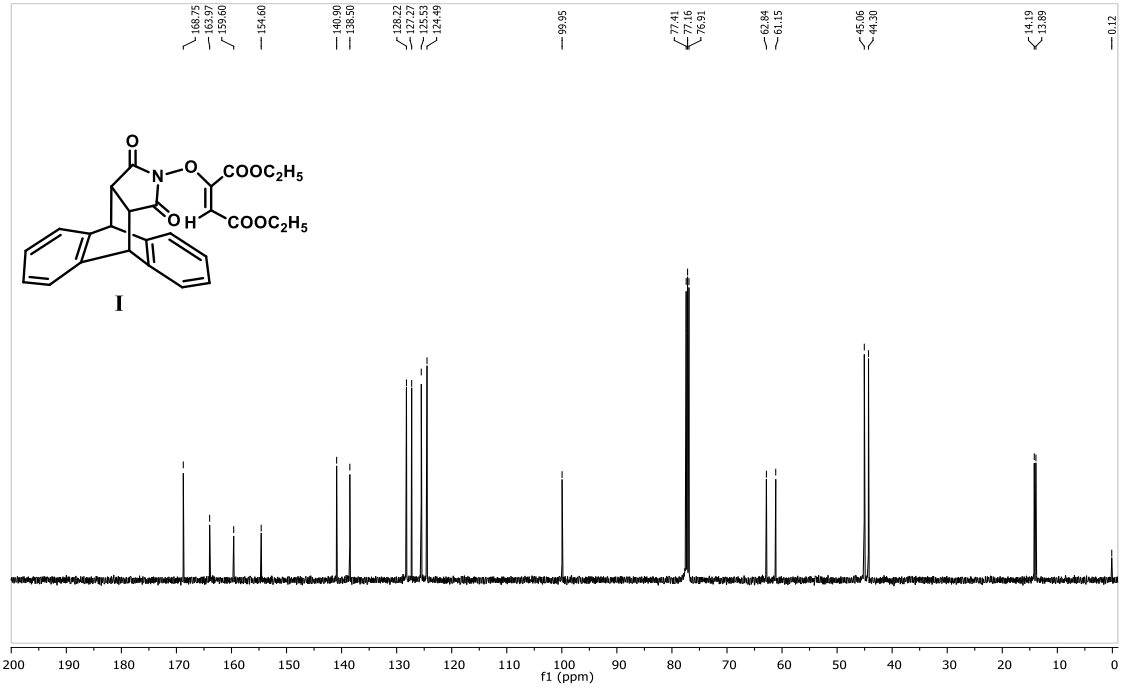
***O*-(*anti*-Dimethylfumarate)-3,4-(9',10'-dihydroanthracene-9',10'-diyl)succinimide (III):** White solid; yield 92%; m.p. 195 ^{0}C; **IR** (KBr) ν (cm^{-1}): 3074, 3010, 2957, 1793, 1731, 1655, 1458, 1435, 1023; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 3.24 (s, 2 H, 3 & 4-H), 3.65 & 3.73 (ds, 6 H, 2 -OCH_3), 4.80 (s, 2 H, 9' & 10'-H), 6.27 (s, 1 H, vinylic H), 7.16 – 7.19 (m, 4 H, ArH), 7.30 – 7.31 (m, 2 H, ArH), 7.37 – 7.38 (m, 2 H, ArH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 44.20 (3 & 4-C), 45.01 (9'& 10'-C), 52.37 & 53.47 (-OCH_3), 109.88 (CH, vinylic), 124.41, 125.25, 127.07, 127.49, 138.39 & 141.32 (aromatic carbons), 149.48 (1 C, vinylic), 160.12, 163.06, 169.37 (two imide carbons and two ester carbons). Elemental analysis: (Found: C, 66.44; H, 4.39. Calc. for $C_{24}H_{19}NO_7$: C, 66.51; H, 4.42%).

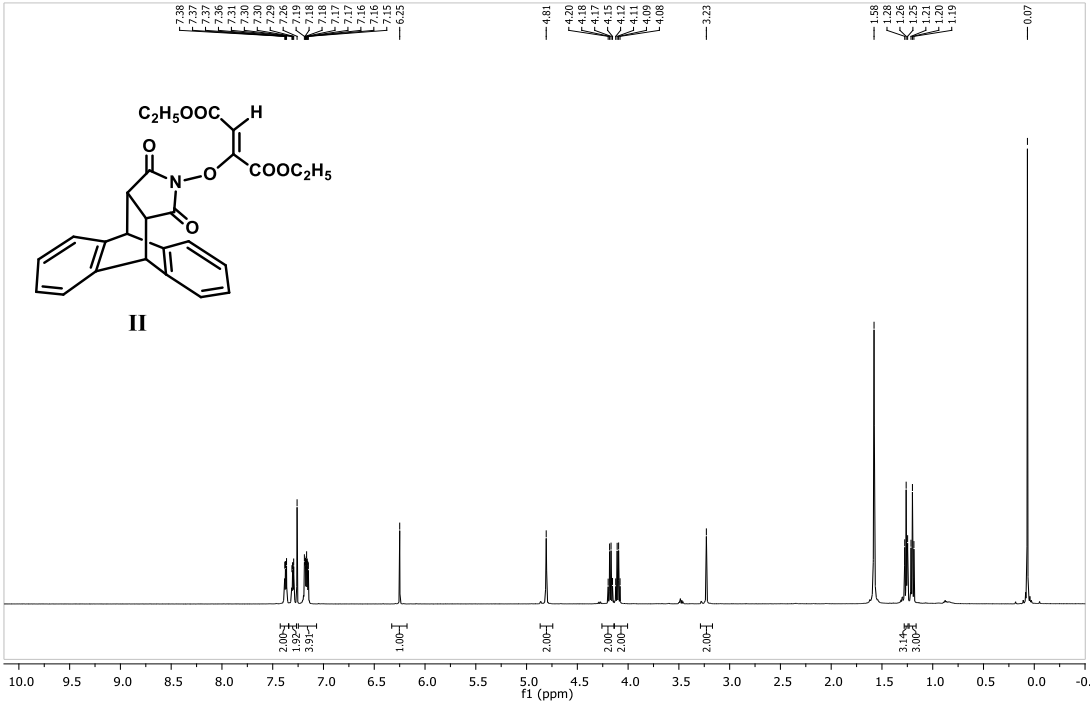
***O*-(*syn*-Dimethylmaleate)-3,4-(9',10'-dihydroanthracene-9',10'-diyl) succinimide (IV):** White solid, yield 96%; m.p. 226 ^{0}C; **IR** (KBr) ν (cm^{-1}): 2958, 1794, 1731, 1654, 1549, 1454, 1056, 1022; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 3.28 (s, 2 H, 3 & 4-H), 3.51 (s, 1 H, vinylic H), 3.70 & 3.83 (ds, 6 H, 2 -OCH_3), 4.86 (s, 2 H, 9' & 10'-H), 7.18 – 7.21 (m, 4 H, ArH), 7.36 – 7.40 (m, 4 H, ArH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 44.31 (3 & 4-C), 45.08 (9', 10'-C), 52.17 & 53.43 (2 -OCH_3), 100.23 (CH, vinylic), 124.51, 125.58, 127.33, 128.19, 138.51 & 140.87 (aromatic carbons), 154.37 (1 C, vinylic), 160.01, 164.43 & 168.71 (two imide carbons and two ester carbons. Elemental analysis: (Found: C, 66.57; H, 4.48. Calc. for $C_{24}H_{19}NO_7$: C, 66.51; H, 4.42%).

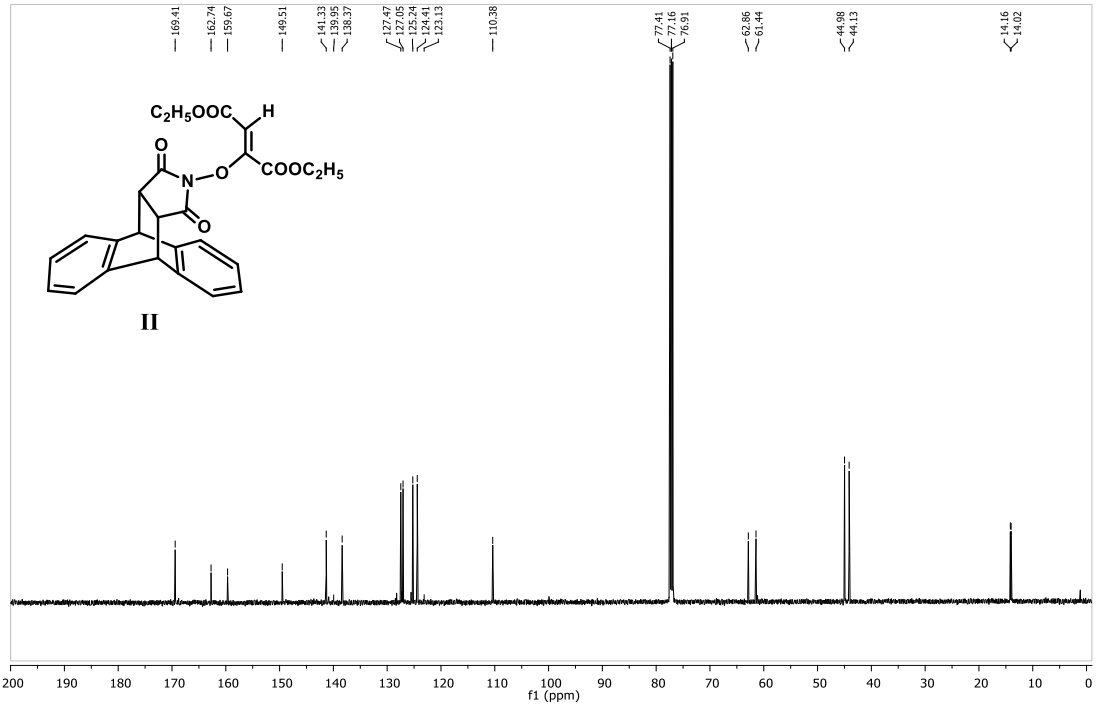
***O*-(Dimethylmaleate)phthalimide (V):** White solid; yield 90%; m.p. 123 ^{0}C; **IR** (KBr) ν (cm^{-1}): 3084, 1792, 1734, 1700, 1623, 1465, 1428, 1012; **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm): 3.71 & 3.83 (ds, 6 H, 2 -OCH_3), 6.43 (s, 1 H, vinylic H), 7.79 (s, 2 H, ArH), 7.88 (s, 2 H, ArH); **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm): 52.39 & 53.51 (2 -OCH_3), 111.21 (CH, vinylic), 124.10, 128.86 & 134.98 (aromatic carbons), 150.58 (1 C, vinylic), 160.62, 161.87, 163.18 (two imide carbons and two ester carbons). Elemental analysis: (Found: C, 55.12; H, 3.59. Calc. for $C_{14}H_{11}NO_7$: C, 55.09; H, 3.63%).

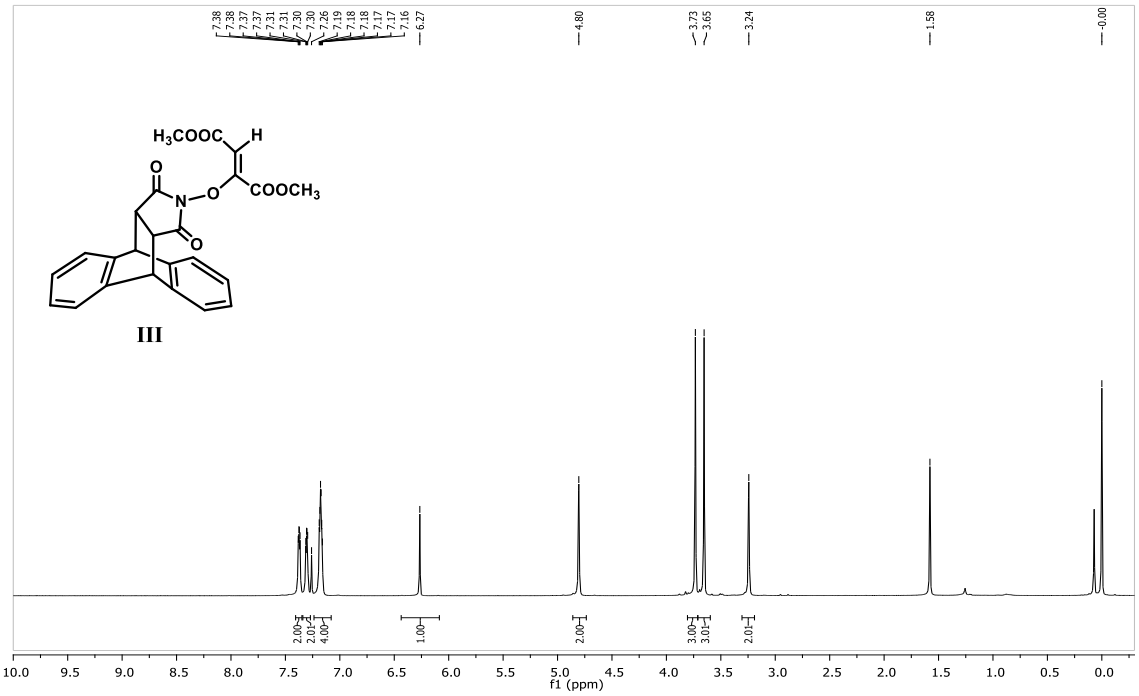
2.4 Spectral data of synthesized products (I-V)



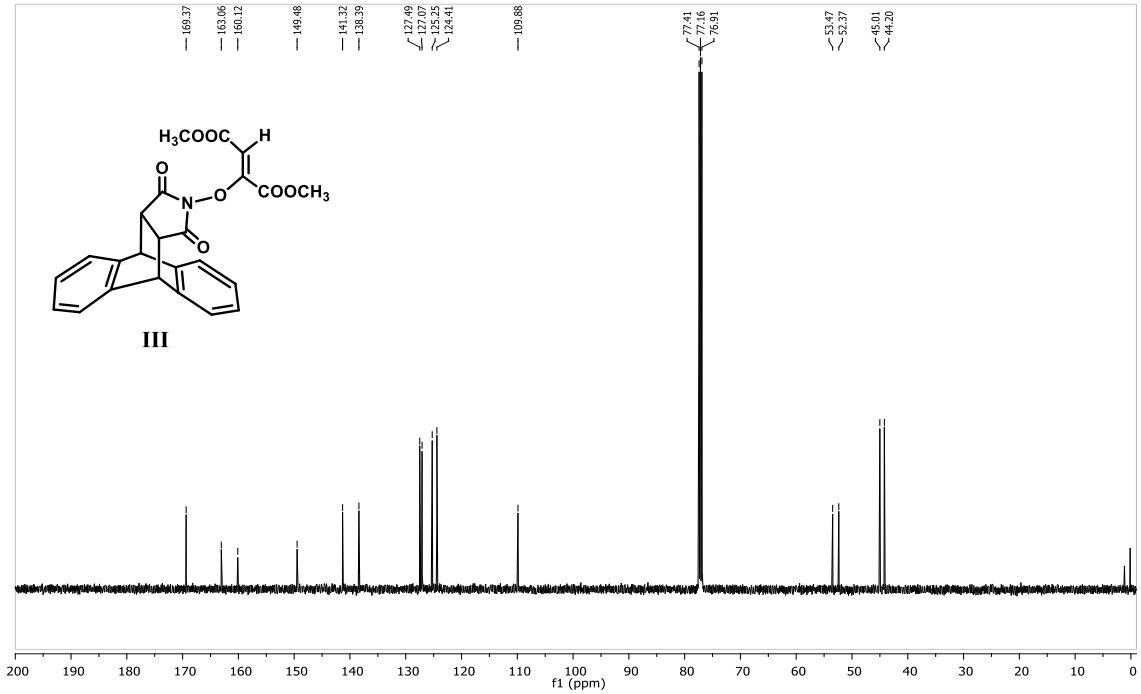



7.38
7.37
7.37
7.36
7.31
7.30
7.30
7.29
7.26
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.15
6.25
4.81
4.20
4.18
4.17
4.15
4.12
4.11
4.09
4.08
3.23
1.58
1.28
1.26
1.25
1.21
1.20
1.19
0.07
C2H5OOC
H
O
N
O
COOC2H5
O
II
2.00
1.92
3.91
1.00
2.00
2.00
2.00
2.00
3.14
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

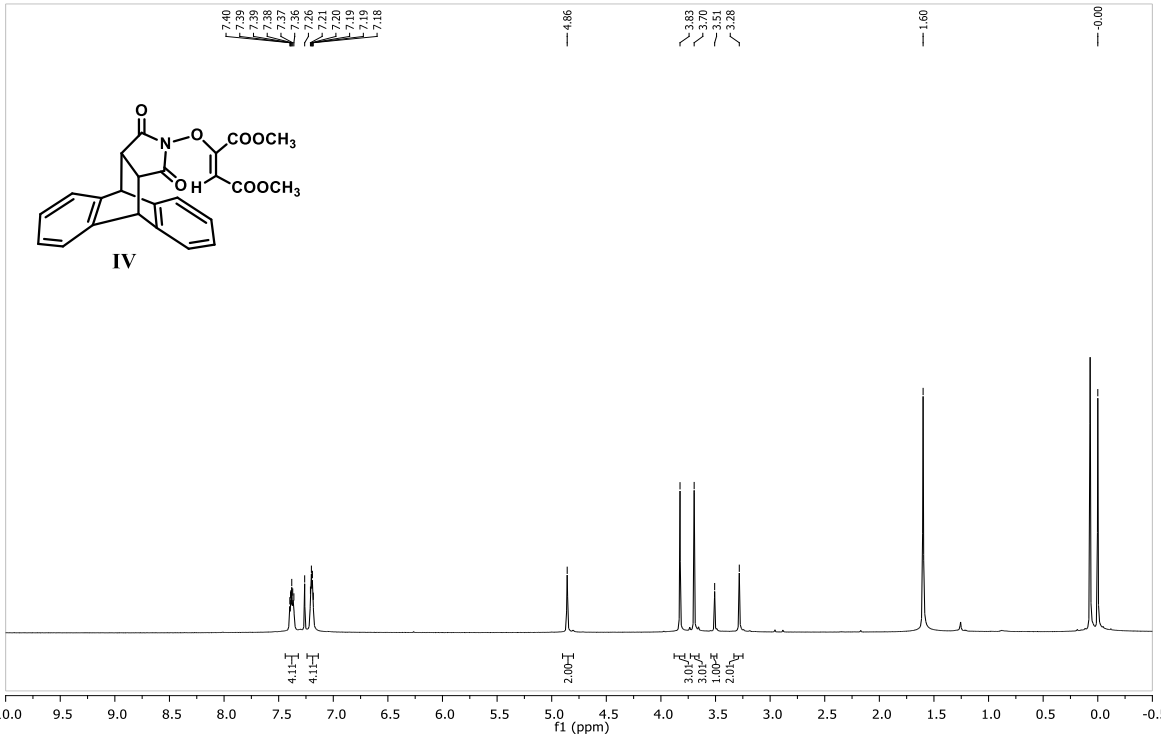

169.41
162.74
159.67
149.51
141.33
139.95
138.37
127.47
127.05
125.24
124.41
123.13
110.38
77.41
77.16
76.91
62.86
61.44
44.98
44.13
14.16
14.02
C2H5OOC
H
O
N
O
COOC2H5
O
II
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.38
7.38
7.37
7.37
7.31
7.31
7.30
7.30
7.26
7.19
7.18
7.18
7.17
7.17
7.16
6.27
4.80
3.73
3.65
3.24
1.58
0.00
H3COOC
H
O
N
O
COOCH3
O
2.00
2.01
4.00
1.00
2.00
3.00
3.01
2.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

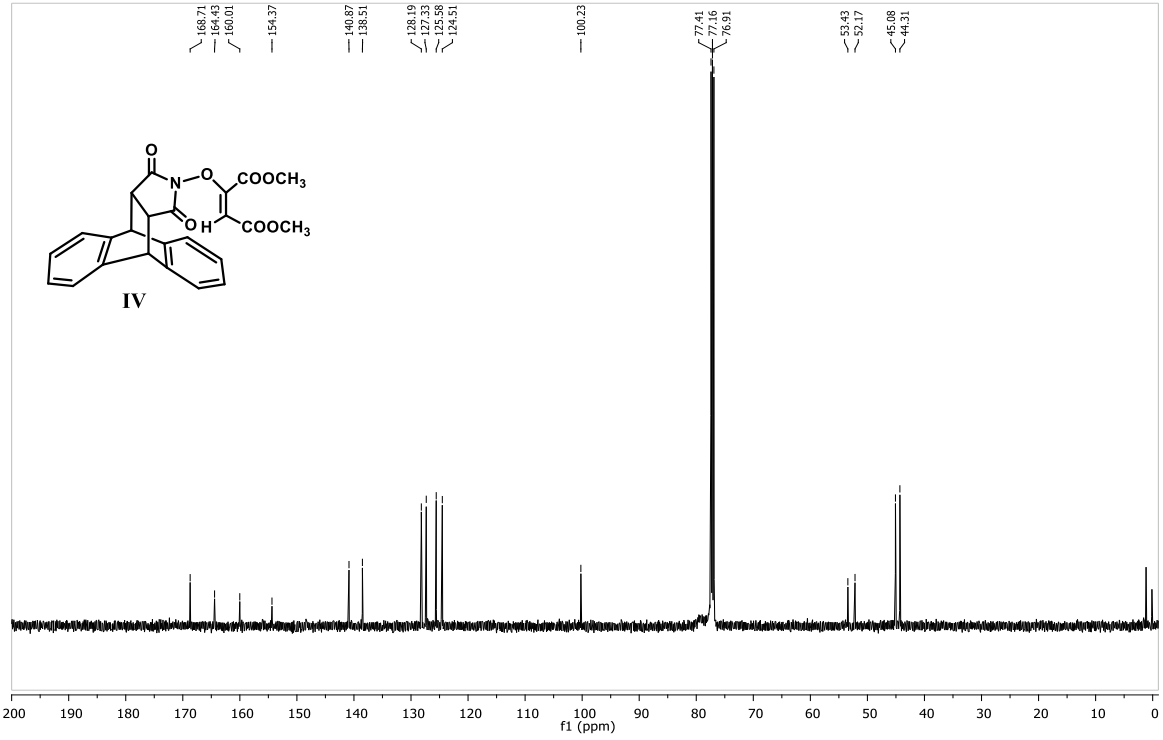
III


169.37
163.06
160.12
149.48
141.32
138.39
127.49
127.07
125.25
124.41
109.88
77.41
77.16
76.91
53.47
52.37
45.01
44.20
H3COOC
H
O
N
O
COOCH3
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

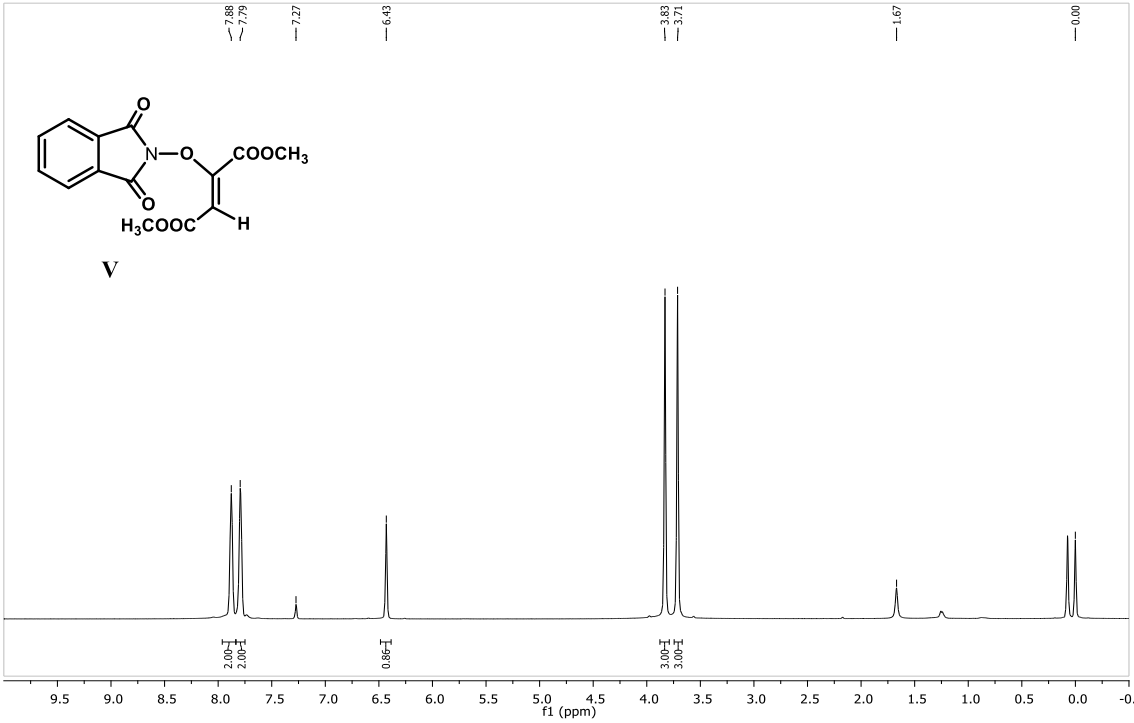
III


7.40
7.39
7.39
7.38
7.37
7.36
7.26
7.21
7.20
7.19
7.19
7.18
4.86
3.83
3.70
3.51
3.28
1.60
0.00
COOCH3
COOCH3
O
N
O
O
H
4.11
4.11
2.00
3.01
3.01
1.00
2.01
f1 (ppm)

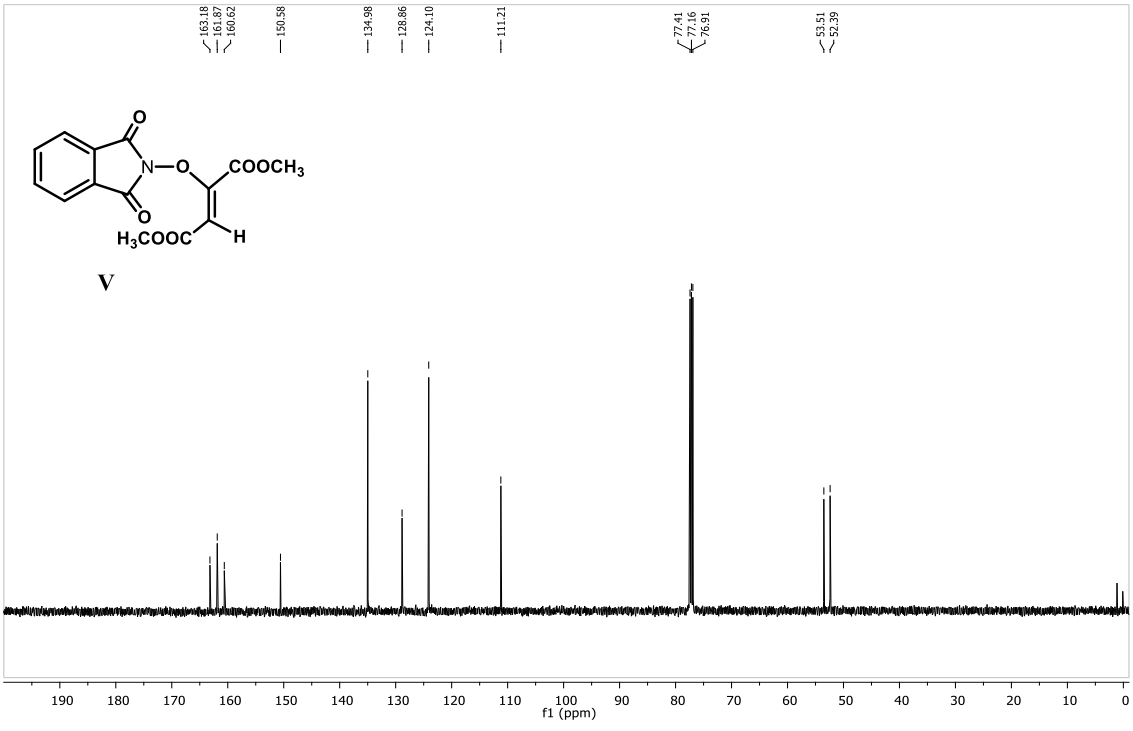
IV


168.71
164.43
160.01
154.37
140.87
138.51
128.19
127.33
125.58
124.51
100.23
77.41
77.16
76.91
53.43
52.17
45.08
44.31
COOCH3
COOCH3
O
N
O
O
H
f1 (ppm)

IV


7.88
7.79
7.27
6.43
3.83
3.71
1.67
0.00
O
N—O
COOCH3
O
H3COOC
H
2.00
2.00
0.86
3.00
3.00
f1 (ppm)

V


163.18
161.87
160.62
150.58
134.98
128.86
124.10
111.21
77.41
77.16
76.91
53.51
52.39
O
N—O
COOCH3
O
H3COOC
H
f1 (ppm)

V

2.5 References

Abele, E. and E. Lukevics, "Synthesis of heterocycles from oximes," *Patai's Chemistry of Functional Groups* (2010).

Allinger, N. L., J. A. Hirsch and M. A. Miller, "The “size” of the lone pair on nitrogen," *Tetrahedron Letters*, **8** (1967) 3729-3734.

Bolotin, D. S., N. A. Bokach, M. Y. Demakova and V. Y. Kukushkin, "Metal-Involving Synthesis and Reactions of Oximes," *Chemical reviews*, **117** (2017) 13039-13122.

de la Hoz, A., A. Diaz-Ortiz and A. Moreno, "Microwaves in organic synthesis. Thermal and non-thermal microwave effects" *Chemical Society Reviews*, **34** (2005) 164-178.

Gribble, G. W., "Pyrroles and their benzo derivatives: applications," *Comprehensive heterocyclic chemistry II*, **2** (1996) 207-257.

Hu, L., Y. Wang, B. Li, D.-M. Du and J. Xu, "Diastereoselectivity in the Staudinger reaction: a useful probe for investigation of nonthermal microwave effects" *Tetrahedron*, 63 (2007) 9387-9392.

Hyun, H. and B. A. Trofimov, "Reaction of acetophenone and benzylphenylketone oximes with phenylacetylene: a route to di-and triphenylpyrroles," *ARKIVOC*, **4** (2009) 14-20.

Islami, M. R., J. Abedini-Torghabeh, S. J. Fatemi, Z. Hassani and A. Amiry, "An efficient and novel protocol for the synthesis of pyrazolo [5, 1-a] isoindole derivatives," *Synlett*, **2004** (2004) 1707-1710.

Jiaxi Xu, "Selectivity of Microwave and Organic Chemical Reactions" *Progress in Chemistry*, **19** (2007) 700-712.

Katritzky, A., P. Kennewell and M. Snarey, "Steric requirements of sp2-hybridised lone electron pairs. Part II. The conformations of 2-(pyridylmethylene)-benzofuran-3 (2 H)-one," *Journal of the Chemical Society B: Physical Organic*, (1968) 554-556.

Kontokosta, D., D. S. Mueller, H.-Y. Wang and L. L. Anderson, "Preparation of α-imino aldehydes by [1, 3]-rearrangements of O-alkenyl oximes," *Organic Letters*, **15** (2013) 4830-4833.

Korsch, B. and N. Riggs, "Restricted rotation about N-N single bonds. The conformation of tetrahydropyridazine rings," *Tetrahedron Letters*, **7** (1966) 5897-5903.

Li, X. and J. Xu, "Determination on temperature gradient of different polar reactants in reaction mixture under microwave irradiation with molecular probe" *Tetrahedron*, **72** (2016) 5515-5520.

Li, X. and J. Xu, "Effects of the Microwave Power on the Microwave-assisted Esterification" *Current Microwave Chemistry*, **4** (2017) 158-162.

Li, X. and J. Xu, "Identification of Microwave Selective Heating Effort in an Intermolecular Reaction with Hammett Linear Relationship as a Molecular Level Probe" *Current Microwave Chemistry*, **4** (2017) 339-346.

Madabhushi, S., V. S. Vangipuram, K. K. R. Mallu, N. Chinthala and C. R. Beeram, "Europium (III) Triflate-Catalyzed Trofimov Synthesis of Polyfunctionalized Pyrroles," *Advanced Synthesis & Catalysis*, **354** (2012) 1413-1416.

Mahanti, S. and S. M. Verma, "Steric requirements of sp^2-hybridised lone electron pair: A PMR study of restricted rotation about pyridyl C-N bond," *Indian Journal of Chemistry Section B: Organic including Medicinal*, **21** (1982) 1098-1101.

Ngwerume, S. and J. E. Camp, "Synthesis of highly substituted pyrroles via nucleophilic catalysis," *The Journal of organic chemistry,* **75** (2010) 6271-6274.

Ngwerume, S. and J. E. Camp, "Gold-catalysed rearrangement of *O*-vinyl oximes for the synthesis of highly substituted pyrroles," *Chemical Communications,* **47** (2011) 1857-1859.

Ngwerume, S., W. Lewis and J. E. Camp, "Development of a gold-multifaceted catalysis approach to the synthesis of highly substituted pyrroles: mechanistic insights via huisgen cycloaddition studies," *The Journal of organic chemistry,* **78** (2013) 920-934.

Ramazani, A., S. Salmanpour and A. Souldozi, "(N-Isocyanimino) triphenylphosphorane-Catalyzed Stereoselective O-Vinylation of *N*-Hydroxyimides," *Phosphorus, Sulfur, and Silicon,* **185** (2009) 97-102.

Rani, V., V. Abbot, Y. Kapoor, D. Konar and K. Kumar, "Recent synthetic and medicinal perspectives of pyrroles: An overview," *Journal of Pharmaceutical Chemistry & Chemical Science,* **1** (2017) 17-32.

Sheradsky, T., "The rearrangement of o-vinyloximes a new synthesis of substituted pyrroles," *Tetrahedron Letters,* **11**(1970) 25-26.

Trofimov, B. A., T. E. Glotova, M. Y. Dvorko, U. Igor'A, E. Y. Schmidt and I. M. Al'bina, "Triphenylphosphine as an effective catalyst for ketoximes addition to acylacetylenes: regio-and stereospecific synthesis of (E)-(O)-2-(acyl) vinylketoximes," *Tetrahedron,* **66** (2010) 7527-7532.

Srivastava, A., V. Srivastava, S. M. Verma and V. Pattabhi, "Stereochemistry of the addition product of N-aminosuccinimide moiety to an acetylenic ester," *Bulletin of the Chemical Society of Japan,* **67** (1994) 1386-1389.

Srivastava, A., V. Srivastava, S. M. Verma and E. Subramanian, "Restricted Inversion of Pyramidal Nitrogen through π-Electronic Interaction in an Acyclic System," *The Journal of Organic Chemistry,* **59** (1994) 3560-3563.

Trofimov, B. A., E. Y. Schmidt, A. I. Mikhaleva, C. Pozo-Gonzalo, J. A. Pomposo, M. Salsamendi, N. I. Protzuk, N. V. Zorina, A. V. Afonin and A. V. Vashchenko, "Synthesis of 2-(Selenophen-2-yl) pyrroles and Their Electropolymerization to Electrochromic Nanofilms," *Chemistry-A European Journal,* **15** (2009) 6435-6445.

Verma, S. and C. K. Rao, "Conformational analysis about the N-N′ bond by NMR spectroscopy: N′-derivatives of N-amino [2.2. 1] Bicyclo-5-heptene-2, 3-endodicarboximide," *Tetrahedron,* **28** (1972) 5029-5036.

Verma, S., O. S. Rao and C. K. Rao, "A novel pmr technique for the determination of the configuration of diels-alder adducts of maleic anhydride: model compounds with naphthalene derivatives," *Tetrahedron Letters,* **14** (1973) 1639-1642.

Verma, S., O. S. Rao and K. Sinha, "Conformational Analysis About N–N Bond by NMR Spectroscopy: N-Sulphonyl Derivatives of N-Aminoimides of Anthracene-Citraconic Anhydride and Naphthalene-Maleic Anhydride Adducts," *Bulletin of the Chemical Society of Japan,* **47** (1974) 2311-2314.

Verma, S. and R. Singh, "Assignment of configurations to adducts of 2-substituted anthracene with maleic anhydride by NMR spectroscopy," *Australian Journal of Chemistry,* **29** (1976) 1215-1222.

Verma, S. M. and A. K. Singh, "Structural Assignment by NMR Analyses of N-(Diacylamino) imide Derivatives. Diels-Alder Adducts of 2, 3-Dimethylnaphthalene and 6, 6-Diphenylfulvene with Maleic Anhydride," *Bulletin of the Chemical Society of Japan,* **51** (1978) 516-519.

Wang, H.-Y., D. S. Mueller, R. M. Sachwani, R. Kapadia, H. N. Londino and L. L. Anderson, "Regioselective synthesis of 2, 3, 4-or 2, 3, 5-trisubstituted pyrroles via [3, 3] or [1, 3] rearrangements of O-vinyl oximes," *The Journal of organic chemistry*,**76** (2011) 3203-3221.

Wang, H.-Y., D. S. Mueller, R. M. Sachwani, H. N. Londino and L. L. Anderson, "Carbon-Carbon Bond Formation and Pyrrole Synthesis via the [3, 3] Sigmatropic Rearrangement of O-Vinyl Oxime Ethers," *Organic letters,* **12** (2010) 2290-2293.

Wolska, I. and E. Hejchman, "2-(N, N-Diacetamido)-3a, 4, 9, 9a-tetrahydro-4, 9-[1′, 2′] benzeno-1H-benzo [f] isoindole-1, 3 (2H)-dione," *Acta Crystallographica Section E: Structure Reports Online,* **59** (2003) o2007-o2009.

Yavari, I. and A. Ramazani, "Triphenylphosphine catalyzed stereoselective synthesis of O-vinyloximes," *Synthetic communications,* **27** (1997) 1449-1454.

Zhou, Q. F., X. P. Chu, F. F. Ge, Y. Wang and T. Lu, "Phosphine-Catalyzed [3+ 2] Annulation of Electron-Deficient Alkynes with N-Hydroxyphthalimide: Synthesis of 3a-Hydroxyisoxazolo [3, 2-a] isoindol-8 (3aH)-ones," *Advanced Synthesis & Catalysis,* **355** (2013) 2787-2792.