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Generation of Nitroalkanes, Hydroximoyl Halides and Nitrile Oxides from the Reactions of β-Nitrostyrenes with Grignard or Organolithium Reagents

Ching-Fa Yao,* Kuo-Hsi Kao, Ju-Tsung Liu, Cheng-Ming Chu, Yeh Wang, Wen-Chang Chen, Yu-Mei Lin, Wen-Wei Lin, Ming-Chung Yan, Jing-Yuan Liu, Ming-Ching Chuang and Jin-Lien Shiue

Department of Chemistry, National Taiwan Normal University
88, Sec. 4, Tingchow Road, Taipei, Taiwan, 11718, R. O. C.

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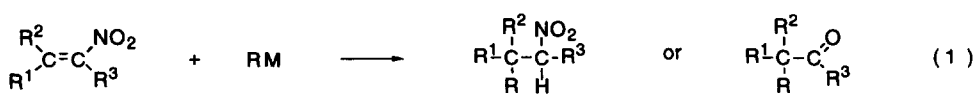
Abstract: The β-nitrostyrenes **1** or **2** react with Grignard or organolithium reagents in ether or THF solution to generate by 1,4-addition the intermediate nitronates **A**. When **A** is treated with dilute hydrochloric acid, high yields of the nitroalkanes **3** (and oximes **4**) or **5** are obtained. Hydroximoyl halides **6**, **8** or nitrile oxides **7** can be isolated when the intermediate **A** is slowly added to the ice cold concentrated hydrohalic acid. The same products **6** and/or **7** are observed if the nitronates, generated from the substrate **1a**, are added to 85% aqueous H_2SO_4 but only the hydrolyzed carboxylic acids **9** are generated when the β-nitrostyrenes **2** are reacted with Grignard reagents and worked up under the same condition. The nitrile oxides **7** can undergo 1,3-dipolar cycloaddition with alkenes or alkynes to generate 2-isoxazolines or isoxazoles. A one-pot synthesis of the [n,3,0] bicyclic (n = 3 or 4) compounds **23-27** by intramolecular nitrile oxide-olefin cycloadditions is reported.

Introduction

Conjugated nitroalkenes are useful intermediates in organic synthesis.[1] Due to the strong electron withdrawing property of the nitro group, nitro olefins can undergo Michael addition with organometallic reagents such as organolithium,[2] magnesium,[3] cadmium,[4] zinc,[5] aluminum[6] and copper[7] to generate nitroalkanes or carbonyl compounds (eq 1).



(1)

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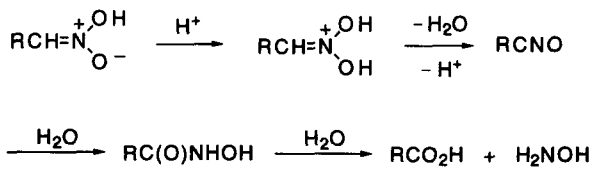
Reactions of nitro compounds, nitronate salts and nitronic esters with aqueous acid solution have been well studied. Nef found that primary or secondary nitro compounds can be hydrolyzed to aldehydes or ketones by treatment of their conjugated bases with sulfuric acid. For example, the reactions of β-nitrostyrenes with Grignard reagents in THF or diethyl ether followed by workup with dilute aqueous acid or concentrated sulfuric acid in methanol to generate nitroalkanes or aldehydes was reported by Wright in 1988.[3c]

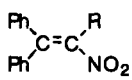
Primary nitro compounds also can be converted into carboxylic acids and hydroxylamine through the Meyer reaction when treated with concentrated sulfuric acid.[8] Carboxylic acids are formed from the hydrolysis of hydroxamic acids and hydroxamic acids are formed by the hydration of the nitrile oxides (Scheme I).[9]



Scheme I

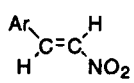
Nitrile oxides are important intermediates in organic synthesis. Several methods are reported in the literaure[10] for the *in situ* generation of nitrile oxides. Mukaiyama's[10a] dehydration of primary nitro compounds using phenyl isocyanate with a catalytic amount of triethylamine and Huisgen's[10b] base-induced dehydrohalogenation of hydroximoyl chlorides are the most frequently used routes to generate nitrile oxides. Although the utility of nitrile oxides in synthesis has been studied extensively, the synthesis of their precursors has received only limited attention. Usually hydroximoyl chlorides are prepared by chlorination of aldoximes. A number of chlorinating reagents such as chlorine,[11a] *tert*-butyl hypochlorite,[11b] nitrosyl chloride,[11c] *N*-chlorosuccinimide[11d] in DMF and HCl/DMF/oxone[11e] or $TiCl_4$[11f] have been reported to give good yields of the hydroximoyl chlorides without polyhalogenation.

After reviewing the literature reports, we thought that nitronate salts should be converted into different products when worked up under different conditions. We chose the β-nitrostyrenes **1** and **2**



1

a: R = H
b: R = Me
c: R = OPh



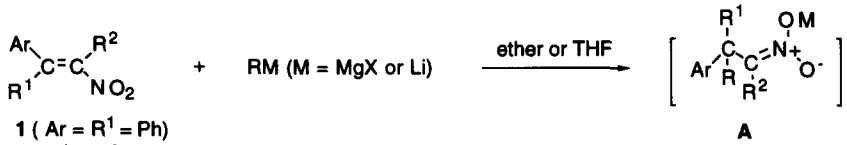
2

a: Ar = Ph
b: Ar = 2-thienyl
c: Ar = 2-furyl
d: Ar = 4-FC_6H_4
e: Ar = 4-$F_3COC_6H_4$
f: Ar = 4-$Et_2NC_6H_4$
g: Ar = 4-$MeOC_6H_4$
h: Ar = 1-naphthyl
i: Ar = 3-(*N*-phenyl)indolyl

as substrates to react with Grignard or organolithium reagents followed by workup under different concentrations of ice cold HX or H_2SO_4 aqueous solution. We found that alkylation and halogenation could occur in a one-pot reaction to give high yields of the hydroximoyl halides or nitrile oxides from the reactions of conjugated nitroalkenes with Grignard or organolithium reagents.[12]

Results and Discussion

The β–nitrostyrenes **1** or **2** were reacted with Grignard or organolithium reagents in ether or THF solution to generate the intermediate nitronates or *aci*-anions **A**. When the nitronates **A** were added to ice cold dilute (5%) hydrochloric acid, 22-100% of the nitroalkanes **3a-h** (and 30-55% of oximes **4a-e**) or 57-97% of **5a-n** were obtained (equation 2 and Table I).



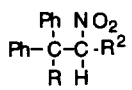
1 (Ar = R^1 = Ph)
2 (R^1 = R^2 = H)

A

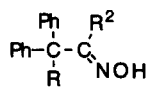
3 (Ar = R^1 = Ph)
5 (R^1 = R^2 = H)

4 (Ar = R^1 = Ph)

(2)



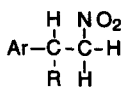
3



4

a: R = $PhCH_2$, R^2 = H
b: R = Me, R^2 = H
c: R = Pr, R^2 = H
d: R = *i*-Pr, R^2 = H
e: R = *t*-Bu, R^2 = H
f: R = Me, R^2 = OPh
g: R = Pr, R^2 = OPh
h: R = Bu, R^2 = H

a: R = R^2 = Me
b: R = Pr, R^2 = Me
c: R = $PhCH_2$, R^2 = OPh
d: R = Me, R^2 = OPh
e: R = *i*-Pr, R^2 = OPh



5

a: Ar = Ph, R = $PhCH_2$
b: Ar = Ph, R = Me
c: Ar = Ph, R = Pr
d: Ar = Ph, R = *i*-Pr
e: Ar = Ph, R = *t*-Bu
f: Ar = 2-thienyl, R = $PhCH_2$
g: Ar = 2-furyl, R = Pr
h: Ar = 4-FC_6H_4, R = Pr
i: Ar = 4-$F_3COC_6H_4$, R = *i*-Pr
j: Ar = 4-$Et_2NC_6H_4$, R = *t*-Bu
k: Ar = 4-$MeOC_6H_4$, R = $PhCH_2$
l: Ar = 1-naphthyl, R = Pr
m: Ar = 1-naphthyl, R = Me
n: Ar = 3-(*N*-Phenyl)indolyl, R = *t*-Bu

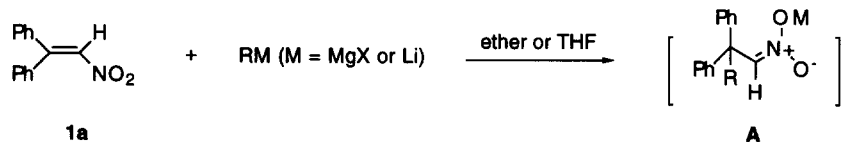
Table I. Reactions of β-nitrostyrenes with RMgX or RLi and workup with 5% hydrochloric acid

substrate	RMgX or RLi	product and yield (%)[a]					
		3	(%)	4	(%)	5	(%)
1a	$PhCH_2MgCl$	3a	(95)				
1a	CH_3MgI	3b	(98)				
1a	$CH_3CH_2CH_2MgBr$	3c	(98)				
1a	$(CH_3)_2CHMgBr$	3d	(60)				
1a	$(CH_3)_3CMgCl$	3e	(70)[b]				
1b	CH_3MgI			4a	(30)		
1b	$CH_3CH_2CH_2MgBr$			4b	(32)		
1c	$PhCH_2MgCl$			4c	(40)[c]		
1c	CH_3MgI	3f	(22)	4d	(55)[d]		
1c	$CH_3CH_2CH_2MgBr$	3g	(tr)				
1c	$(CH_3)_2CHMgBr$			4e	(tr)		
1a	CH_3Li	3b	(100)				
1a	$CH_3CH_2CH_2CH_2Li$	3h	(70)				
1a	$(CH_3)_2CHLi$	3d	(55)				
1a	$(CH_3)_3CLi$	3e	(46)				
2a	$PhCH_2MgCl$					5a	(70)
2a	CH_3MgI					5b	(77)
2a	$CH_3CH_2CH_2MgBr$					5c	(81)
2a	$(CH_3)_2CHMgBr$					5d	(64)
2a	$(CH_3)_3CMgCl$					5e	(80)
2b	$PhCH_2MgCl$					5f	(94)
2c	$CH_3CH_2CH_2MgBr$					5g	(82)
2d	$CH_3CH_2CH_2MgBr$					5h	(97)
2e	$(CH_3)_2CHMgBr$					5i	(95)
2f	$(CH_3)_3CMgCl$					5j	(91)
2g	$PhCH_2MgCl$					5k	(57)
2h	$CH_3CH_2CH_2MgBr$					5l	(86)
2h	CH_3MgI					5m	(78)
2i	$(CH_3)_3CMgCl$					5n	(62)

[a] NMR yields by using toluene or dibromomethane as an internal standard. [b] 10% of *aci* form.
[c] $E >> Z$. [d] $E : Z = 8 : 1$.

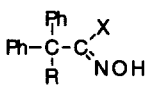
To compound **1b**, the presence of the phenyl and methyl groups increased the steric hindrance to the addition of the Grignard reagents and only low yields (30 and 32%) of oximes **4a** and **4b** were observed when CH_3MgI or $CH_3CH_2CH_2MgBr$ was used. Similar results were also observed when **1c** (R=OPh) reacted with $PhCH_2MgCl$ or CH_3MgI to generate 40% of **4c** or 55% of oxime **4d** (*E*- and *Z*-isomers) and 22% of **3f**. Only trace of product **3g** or **4e** was generated when $CH_3CH_2CH_2MgBr$ or $(CH_3)_2CHMgBr$, respectively, reacted with **1c**.

After obtaining high yields of the nitroalkanes **3a-h** and **5a-n** by using dilute acid aqueous solution, we also tried to add the nitronates **A** to the ice cold 85% sulfuric acid or concentrated aqueous HX (HCl 37%, HBr 48%, HI 57%) solutions to observe whether the reaction proceeded through the Nef mechanism or not. Surprisingly, 15-99% of hydroximoyl halides **6** and/or 20-95% of nitrile oxides **7** were generated when the intermediates **A**, generated from the substrate **1a**, were slowly added to either concentrated hydrohalic or 85% sulfuric acids (equation 3 and Table II).



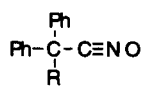
1a **A**

6 **7** (3)



6

a: R = $PhCH_2$, X = Cl
b: R = Pr, X = Br
c: R = *i*-Pr, X = Br
d: R = $PhCH_2$, X = Br
e: R = Me, X = Cl
f: R = Me, X = Br
g: R = Me, X = I
h: R = Pr, X = Cl
i: R = Pr, X = I
j: R = *i*-Pr, X = Cl
k: R = Bu, X = Cl
l: R = Bu, X = Br



7

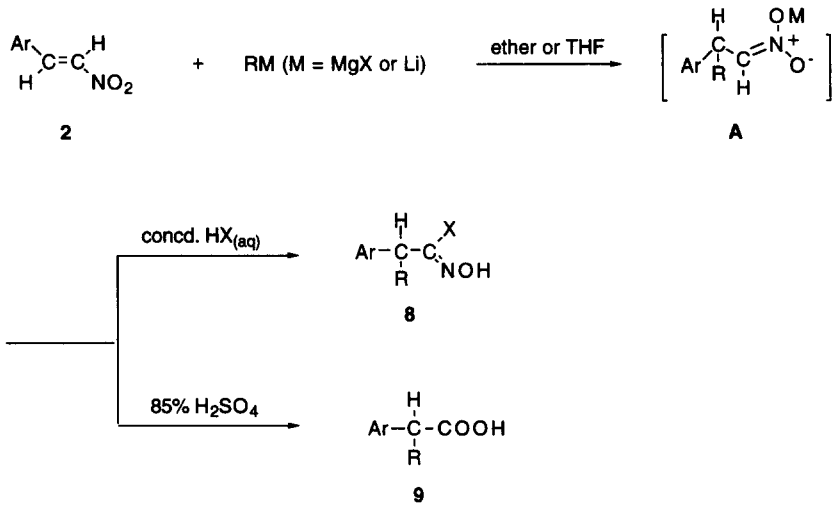
a: R = $PhCH_2$
b: R = Me
c: R = *i*-Pr
d: R = *t*-Bu
e: R = Pr
f: R = *c*-C_6H_{11}
g: R = Bu

Table II. Reactions of 1,1-diphenyl-2-nitroethylene (**1a**) with RMgX or RLi and workup with concentrated sulfuric or hydrohalic acids at 0 °C

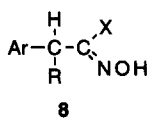
			product and yield (%)[a]			
substrate	RMgX or RLi	acid	**6**	(%)	**7**	(%)
1a	$PhCH_2MgCl$	H_2SO_4	**6a**	(95)		
1a	$PhCH_2MgCl$	H_2SO_4			**7a**	(95)[b]
1a	CH_3MgI	H_2SO_4			**7b**	(68)[c]
1a	$CH_3CH_2CH_2MgBr$	H_2SO_4	**6b**	(89)		
1a	$(CH_3)_2CHMgBr$	H_2SO_4	**6c**	(62)[d]	**7c**	(20)
1a	$(CH_3)_3CMgCl$	H_2SO_4			**7d**	(62)
1a	$PhCH_2MgCl$	HCl	**6a**	(94)		
1a	$PhCH_2MgBr$	HBr	**6d**	(95)		
1a	CH_3MgCl	HCl	**6e**	(82)		
1a	CH_3MgBr	HBr	**6f**	(85)		
1a	CH_3MgI	HI	**6g**	(95)		
1a	$CH_3CH_2CH_2MgCl$	HCl	**6h**	(96)		
1a	$CH_3CH_2CH_2MgBr$	HBr	**6b**	(93)		
1a	$CH_3CH_2CH_2MgI$	HI	**6i**	(15)[e]	**7e**	(70)
1a	$(CH_3)_2CHMgCl$	HCl	**6j**	(77)		
1a	$(CH_3)_2CHMgBr$	HBr	**6c**	(26)[d]	**7c**	(60)
1a	*c*-$C_6H_{11}MgBr$	HBr			**7f**	(70)
1a	$CH_3CH_2CH_2CH_2Li$	H_2SO_4			**7g**	(90)
1a	$(CH_3)_3CLi$	H_2SO_4			**7d**	(46)
1a	$(CH_3)_3CLi$	HCl			**7d**	(54)
1a	CH_3Li	HCl	**6e**	(73)		
1a	CH_3Li	HBr	**6f**	(99)		
1a	CH_3Li	HI	**6g**	(59)		
1a	$CH_3CH_2CH_2CH_2Li$	HCl	**6k**	(83)		
1a	$CH_3CH_2CH_2CH_2Li$	HBr	**6l**	(70)		
1a	$(CH_3)_2CHLi$	HCl	**6j**	(77)		
1a	$(CH_3)_2CHLi$	HCl			**7c**	(77)[f]

[a] NMR yields by using toluene or dibromomethane as an internal standard. [b] The CH_2Cl_2 solution was neutralized by $NaHCO_{3(aq)}$. [c] Furoxan. [d] Converted into nitrile oxide **7c** after flash column purification. [e] Converted into nitrile oxide **7e** after flash column purification. [f] The CH_2Cl_2 solution was neutralized by Et_3N.

When β-nitrostyrenes **2** were used as the substrates, only 16-93% of hydroximoyl halides **8** were generated after added the nitronates **A** to the concentrated aqueous hydrohalic acids. On the contrary, 21-63% of the hydrolyzed product carboxylic acids **9** were observed when the same intermediates **A** were treated with 85% H_2SO_4 (equation 4 and Table III).

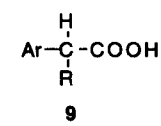


2 A 8 9 (4)



8

a: Ar = Ph, R = *i*-Pr, X = Cl
b: Ar = 2-thienyl, R = $PhCH_2$, X = Cl
c: Ar = 2-thienyl, R = Me, X = Cl
d: Ar = 2-thienyl, R = Pr, X = Cl
e: Ar = 2-thienyl, R = *i*-Pr, X = Cl
f: Ar = 2-thienyl, R = *t*-Bu, X = Cl
g: Ar = 2-furyl, R = *t*-Bu, X = Cl
h: Ar = 4-FC_6H_4, R = *t*-Bu, X = Cl
i: Ar = 4-$F_3COC_6H_4$, R = *i*-Pr, X = Br
j: Ar = 1-naphthyl, R = *i*-Pr, X = Cl
k: Ar = 3-(*N*-Phenyl)indolyl, R = *i*-Pr, X = Cl
l: Ar = Ph, R = Me, X = Cl
m: Ar = Ph, R = Bu, X = Cl
n: Ar = Ph, R = *t*-Bu, X = Cl
o: Ar = 2-thienyl, R = Bu, X = Cl
p: Ar = 2-furyl, R = Me, X = Cl
q: Ar = 4-FC_6H_4, R = Me, X = Cl
r: Ar = 4-FC_6H_4, R = Bu, X = Cl
s: Ar = 4-$F_3COC_6H_4$, R = Me, X = Cl
t: Ar = 4-$F_3COC_6H_4$, R = Bu, X = Cl



9

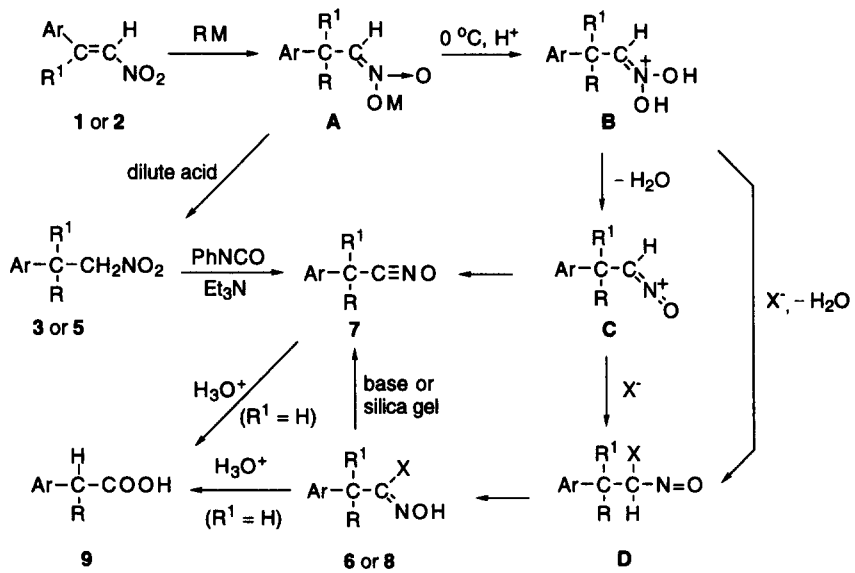
a: Ar = Ph, R = $PhCH_2$
b: Ar = Ph, R = Me
c: Ar = Ph, R = Pr
d: Ar = Ph, R = *i*-Pr
e: Ar = Ph, R = *t*-Bu
f: Ar = 4-FC_6H_4, R = Me
g: Ar = 4-$CF_3C_6H_4$, R = *i*-Pr
h: Ar = 1-naphthyl, R = $PhCH_2$
i: Ar = 1-naphthyl, R = *t*-Bu

Table III. Reactions of β-nitrostyrenes (2) with RMgX or RLi and workup with concentrated sulfuric or hydrohalic acids

			product and yield (%)[a]			
substrate	RMgX or RLi	HX	**8**	(%)	**9**	(%)
2a	$(CH_3)_2CHMgCl$	HCl	**8a**	(77)		
2b	$PhCH_2MgCl$	HCl	**8b**	(93)		
2b	CH_3MgCl	HCl	**8c**	(78)		
2b	$CH_3CH_2CH_2MgCl$	HCl	**8d**	(75)		
2b	$(CH_3)_2CHMgCl$	HCl	**8e**	(48)		
2b	$(CH_3)_3CMgCl$	HCl	**8f**	(56)		
2c	$(CH_3)_3CMgCl$	HCl	**8g**	(30)		
2d	$(CH_3)_3CMgCl$	HCl	**8h**	(56)		
2e	$(CH_3)_2CHMgBr$	HBr	**8i**	(75)		
2h	$(CH_3)_2CHMgCl$	HCl	**8j**	(50)		
2i	$(CH_3)_2CHMgCl$	HCl	**8k**	(36)		
2a	CH_3Li	HCl	**8l**	(90)		
2a	$CH_3CH_2CH_2CH_2Li$	HCl	**8m**	(65)		
2a	$(CH_3)_2CHLi$	HCl	**8a**	(44)		
2a	$(CH_3)_3CLi$	HCl	**8n**	(16)		
2b	$CH_3CH_2CH_2CH_2Li$	HCl	**8o**	(46)		
2c	CH_3Li	HCl	**8p**	(36)		
2d	CH_3Li	HCl	**8q**	(85)		
2d	$CH_3CH_2CH_2CH_2Li$	HCl	**8r**	(90)		
2e	CH_3Li	HCl	**8s**	(70)		
2e	$CH_3CH_2CH_2CH_2Li$	HCl	**8t**	(63)		
2a	$PhCH_2MgCl$	H_2SO_4			**9a**	(31)
2a	CH_3MgI	H_2SO_4			**9b**	(63)
2a	$CH_3CH_2CH_2MgBr$	H_2SO_4			**9c**	(60)
2a	$(CH_3)_2CHMgBr$	H_2SO_4			**9d**	(50)
2a	$(CH_3)_3CMgCl$	H_2SO_4			**9e**	(21)
2d	CH_3MgI	H_2SO_4			**9f**	(44)
2e	$(CH_3)_2CHMgBr$	H_2SO_4			**9g**	(28)
2h	$PhCH_2MgCl$	H_2SO_4			**9h**	(53)
2h	$(CH_3)_3CMgCl$	H_2SO_4			**9i**	(30)

[a] NMR yields by using toluene or dibromomethane as an internal standard.

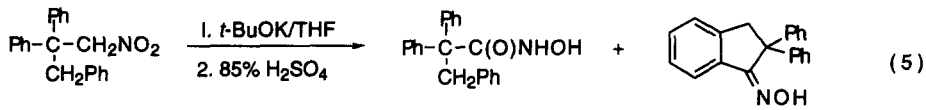
All these results indicate that the reaction proceed through the Meyer mechanism and not the Nef process. The generation of the different products can be attributed to the steric effect of the phenyl group of the starting material and the R groups of the Grignard or organolithium reagents and the presence of good trapping reagents in the form of halide ions. Usually two phenyl groups in the nitronates are bulky enough to block the water molecules to attack the hydroximoyl halides **6** or nitrile oxides **7**. On the other hand, intermediates **7** or **8** were directly hydrolyzed to carboxylic acids **9** in ice cold 85% sulfuric acid solution when substrates **2** were used. Hydroximoyl halides **6** or **8** are believed to be formed from the α-nitroso halides **D** because transient intense blue or green color were always observed when the nitronates **A** were slowly added to concentrated acids. α-Nitroso compounds **D** arise if the halides (from RMgX, MgX_2 and/or aqueous HX) trap the protonated nitronates **B** (analogous to water in the Nef reaction) or the nitroso cations **C**. The proposed reaction mechanism is shown as in Scheme II.



Scheme II

In addition to the steric effect in the starting material nitroalkenes and the Grignard or organolithium reagents, the nature of the halide ions was also important in determining the reaction products. It is known that the order of halide nucleophilicity is $I^- > Br^- > Cl^- > F^-$ in protic solvents. For the nitronates which were generated from the substrate **1a**, chloride, bromide or iodide ion trapped the intermediates readily to generate products **6e-g** when CH_3MgX or CH_3Li was used. When R was the benzylic, primary alkyl (propyl or butyl) or secondary alkyl (isopropyl) group, the chloride ion could trap all the reactive intermediates successfully (**6a**, **6h**, **6j** and **6k**) but the bromide ion gave significant trapping products only with the primary or benzylic group (**6b**, **6l** and **6d**) under the similar workup condition. For the *tert*-butylmagnesium chloride, cyclohexylmagnesium bromide or *tert*-butyllithium, only nitrile oxide **7d** or **7f** and no hydroximoyl chloride or bromide was isolated

due to the steric effect of the bulky *t*-Bu or *c*-C_6H_{11} groups. For substrates **2**, the chloride ion could trap all the reactive intermediates to generate the hydroximoyl chlorides (**8a-t**) no matter what kind of RMgX or RLi was used. These results indicated that the nucleophilicity of the halides, the steric effects of the substrates and RMgX or RLi reagents and the bond strength of the C-X in the hydroximoyl halides were important to the stability of the final products. This was the reason why **6g** could be isolated only when concentrated hydroiodic but not sulfuric acid was used during the reaction of the CH_3MgI or CH_3Li with compound **1a**. To prove the importance of the nature of the halide ion, we also deprotonated the nitroalkane **3a** $Ph_2C(CH_2Ph)CH_2NO_2$ with the strong base $(CH_3)_3COK$ in THF solution and then added the nitronate to 85% sulfuric acid. In addition to 5% of recovered **3a**, 38% of the hydroxamic acid **10** and 36% of the oxime **11** were isolated (eq 5). When the same intermediate nitronate was added to concentrated hydrochloric acid, 91% of **6a** was generated and 7% of **3a** was recovered. These results indicate that the intermediate **B** or **C** could be directly hydrolyzed to **10** and **11** in the absence of trapping reagent X^-.



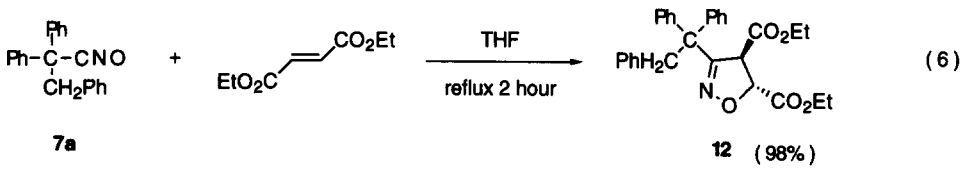
3a **10** **11** (5)

Grignard and organolithium reagents are reactive organometallic reagents. Usually, organolithium is more reactive than Grignard reagents. From tables I-III, we can find that methyl or butyl lithium sometimes can react with the β-nitrostyrenes as well as the Grignard reagents to generate high yields of products. To isopropyl or *tert*-butyl lithium, the yields of the products decrease dramatically due to their high reactivity and steric effect. Although there are many differences between Grignard and organolithium reagents, some advantages can be observed when organolithium reagents are used. For example, methyllithium or butyllithium can react with β-nitrostyrenes and workup with different kinds of concentrated hydrohalic acids to generate high yields of hydroximoyl halides efficiently but the preparation of some Grignard reagents such as CH_3MgCl, CH_3MgBr or BuMgCl is troublesome compare to methyllithium or butyllithium.

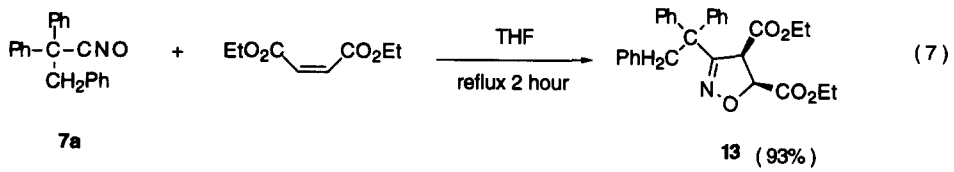
Hydroximoyl halides and nitrile oxides are important intermediates in organic synthesis. Comparing to the method of the dehydration of the primary nitro compounds (Mukaiyama-Hoshino method)[10a] or oxidation of the aldoximes[10b] to generate nitrile oxides, we have developed a new route for the synthesis of hydroximoyl halides **6** or nitrile oxides **7** from β-nitrostyrenes by reactions with Grignard or organolithium reagents. The advantages of this method are the following : (a) the starting materials β-nitrostyrenes are easily synthesized or are commerically available, (b) low cost of the hydrohalic acids, and (c) the workup procedures are simple and the products easily purified.

It is known that nitrile oxides can undergo 1,3-dipolar cycloaddition with olefins or acetylenes to generate 2-isoxazolines or isoxazoles respectively.[13] The nitrile oxide **7a** reacted with diethyl

fumarate or diethyl maleate to form the cyaloaddition products **12** or **13** in high yield (98 and 93%, respectively) and in a stereospecific manner (eq 6 and 7). The products **12** (35%) and **13** (60%) were also generated when compound **3a** was treated with $PhNCO/Et_3N$ (Mukaiyama-Hoshino method) in the presence of excess of the dipolarophiles.[10a] These results indicate that the use of the pure nitrile oxide **7a** is better than the use of the nitroalkane **3a** as a precursor to the nitrile oxide.

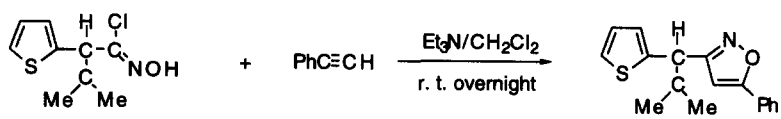


7a **12** (98%) (6)

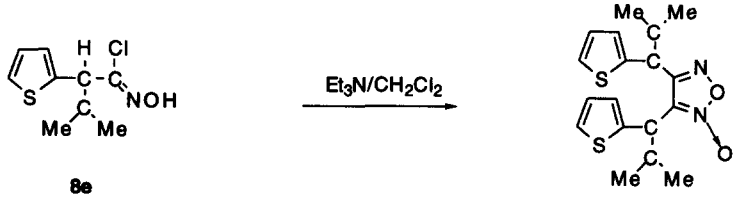


7a **13** (93%) (7)

Nitrile oxides are readily formed upon treatment of hydroximoyl halides with base such as Et_3N. Usually nitrile oxides are unstable and easy to dimerize to form furoxans in the absence of a dipolarophile. For example, 92% of **14** was formed when compound **8e** was reacted with phenylacetylene in the presence of Et_3N (eq 8) and almost a quantative of the furoxan **15** was formed in the absence of the trapping reagents (eq 9).

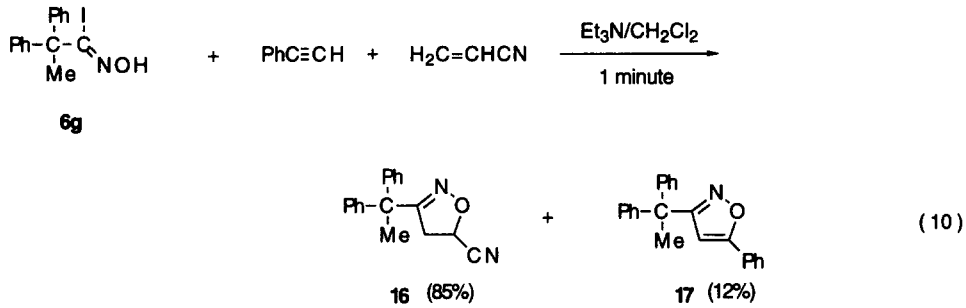


8e **14** (92%) (8)



8e **15** (100%) (9)

It has been reported that acetylenes are less reactive than the corresponding olefins in 1,3-dipolar additions.[13] When a few drops of triethylamine was added to the solution of **6g** in the presence of an excess of a 1:1 mixture of acrylnitrile and phenylacetylene, reaction occurred very quickly (1 min). After evaporating the solvent, the mixture was purified to yield 85% of the 2-isoxazoline **16** and 12% of the isoxazole **17** (eq 10). This result is consistent with the explanation that although an increase in aromaticity will decrease the energy of the transition state, the transition state appears early on the reaction coordinate and is reactant like.

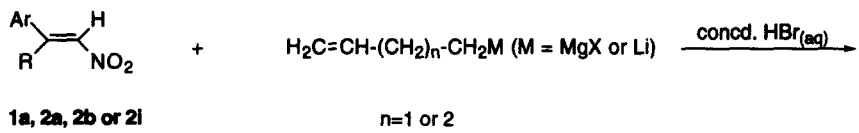


(10)

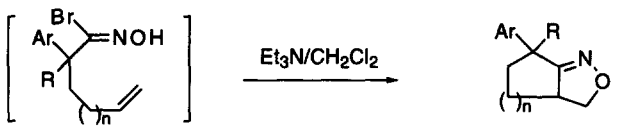
1,3-Dipolar cycloaddition has been proved to be useful in organic synthesis,[14] including intramolecular nitrile oxide-olefin cycloadditions (INOC).[15,16] After obtaining high yields of hydroximoyl halides **6** and **8** or nitrile oxides **7**, we then tried to apply this method to synthesize [n, 3, 0] bicyclic compounds (n= 3 or 4) by reaction of the β-nitrostyrenes with the proper alkenyl Grignard or organolithium reagents. High yields of **23-26** (85-95%) were generated when substrates **1a**, **2a** or **2b** reacted with 3-butene-1-magnesium bromide or 4-pentene-1-magnesium bromide, respectively, under the one-pot condition. Same compounds **24-26** (60-90%) also could be synthesized when 1-lithio-4-pentene was used to react with **1a**, **2a** or **2b**, respectively. Compounds **25** or **26** also could be synthesized quantitatively by reaction of **20** or **21**, which was isolated from the reaction intermediate directly, with Et_3N in CH_2Cl_2 solution. The *cis/trans* ratio of the products **25** was 4.5/1 and 1/1 for compound **26** based on the NMR analysis. Only 33% of **27** was isolated when **2i** reacted with 3-butene-1-magnesium bromide under the one-pot condition. All the results are shown as equation 11.

Conclusion

In summary, we had developed a general and high-yielding route for the synthesis of nitrile oxides **7** or hydroximoyl halides **6** and **8**. We had demonstrated the utility of this method by the synthesis of [n, 3, 0] bicyclic compounds **23-27**. Further applications using other nitroalkenes and organometallic reagents are being investigated.



1a, 2a, 2b or 2i n=1 or 2



(11)

18: Ar = R = Ph, n=1

19: Ar = R = Ph, n=2

isolated:

20: Ar = Ph, R= H, n=2, 95%

21: Ar = 2-thienyl, R= H, n=2, 93%

22: Ar = *N*-phenyl-3-indolyl, R= H, n=1

23: Ar = R = Ph, n=1, M = MgBr, 95%

24: Ar = R = Ph, n=2, M = MgBr, 92%; M = Li, 90%

25: Ar = Ph, R= H, n=2, M = MgBr, 88%; M = Li, 60%

26: Ar = 2-thienyl, R= H, n=2, M = MgBr, 85%; M = Li, 60%

27: Ar = *N*-phenyl-3-indolyl, R= H, n=1, M = MgBr, 33%

Experimental Section

1. General. Diethyl ether and tetrahydrofuran (THF) were dried by being refluxed over sodium wire until the blue color of benzophenone ketyl persisted, and it was then distilled into a dry receiver under nitrogen. The methyllithium, butyllithium, *tert*-butyllithium, magnesium turnings (98%), HCl (37%), HBr (48%), HI (57%), H_2SO_4 (98%), triethylamine, 4-bromo-1-butene, 5-bromo-1-pentene, *trans*-β-nitrostyrene (**2a**), *trans*-2-(2-nitrovinyl)thiophene (**2b**), *trans*-4-fluoro-β-nitrostyrene (**2d**), *trans*-β-nitro-4-(trifluoromethoxy)styrene (**2e**), *trans*-4-methoxy-β-nitrostyrene (**2g**), 3-(2-nitrovinyl)-1-phenylindole (**2i**), were purchased from Aldrich Chemical Co. The following starting materials were prepared according to the literature: isopropyllithium,[17a] 1-lithio-4-pentene,[17b] α-phenyl-β-nitrostyrene (**1a**),[18] β-methyl-β-nitro-α-phenylstyrene (**1b**),[18] β-nitro-β-phenoxy-α-phenylstyrene (**1c**),[19] *trans*-2-(2-nitrovinyl)furan (**2c**),[20] β-nitro-4-(dimethylamino)styrene (**2f**),[21] 1-(2-nitrovinyl)-naphthalene (**2h**).[22] ^1H and ^{13}C-NMR spectra were recorded with a Varian Gemini 200 or JEOL EX-400 instrument. Chemical shift were given in ppm from Me_4Si in $CDCl_3$ solution. Mass spectra were obtained with Jeol JMS-D300 and high resolution mass spectra were obtained by a Jeol JMS-HX110 spectrometer. Elemental analysis were performed by a Perkin-Elemer 2400 instrument. All melting points were determined on a MEL-TEMP II melting point appartus and were uncorrected. Infared spectra were recorded in the FT mode by a Jasco IR-700 spectrometer.

2. General Procedure for the Preparation of Nitroalkanes 3a-h, and 5a-n or Oximes 4a-e (equation 2 and Table I).

(a) Grignard reagents method: The preparation of **3a** from **1a** will serve to illustrate the general procedure utilized. 1,1-Diphenyl-2-nitroethene **1a** (2 mmol) in 20 mL dry ether or THF was added to 10 mmol of benzylmagnesium chloride in 30 mL of ether or THF at -20 °C. Within 10 min, the solution was added to ice cold 5% aqueous HCl solution and stirred 30 min. The solution was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and the solvent was evaporated to give the product **3a**. The yield (95%) was based on NMR by using toluene or dibromomethane as an internal standard. The residue was purified by flash column chromatography on silica gel using hexane-ethyl acetate as eluent to obtain the pure product **3a**.

(b) Organolithium reagents method: The preparation of **3h** from **1a** will serve to illustrate the general procedure utilized. 1,1-Diphenyl-2-nitroethene **1a** (2 mmol) in 20 mL dry ether or THF was added to 10 mmol of n-butyllithium (in hexane) at -78 °C. The solution was added to ice cold 5% aqueous HCl solution and stirred 30 min after the starting material was disappeared by checking the solution with TLC plates. The solution was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and the solvent was evaporated to give the product **3h**. The yield (95%) was based on NMR by using toluene or dibromomethane as an internal standard. The residue was purified by flash column chromatography on silica gel using hexane-ethyl acetate as eluent to obtain the pure product **3h**.

1-Nitro-2,2,3-triphenylpropane (3a): mp 160-161 °C. ^{1}H NMR ($CDCl_3$): 7.27-7.00 (m, 13H), 6.70 (d, 2H, *J* =7.81), 5.02 (s, 2H), 3.74 (s, 2H). ^{13}C NMR ($CDCl_3$): 143.68, 136.00, 131.00, 128.24, 127.91, 127.77, 127.16, 126.74, 80.90, 51.43, 42.56. MS *m/z* (relative intensity) 317 (M^+, tr), 180 (100), 165 (13), 91 (16). Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.49; H, 6.27; N, 4.67.

1-Nitro-2,2-diphenylpropane (3b): ^{1}H NMR ($CDCl_3$): 7.33-7.15 (m, 10H), 5.10 (s, 2H), 1.96 (s, 3H). ^{13}C NMR ($CDCl_3$): 144.52, 128.44, 127.00, 126.91, 85.03, 47.26, 26.73. MS *m/z* (relative intensity) 241 (M^+, 98), 195 (100), 181 (81), 165 (28), 117 (41), 91 (33), 77 (7). Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.81. Found: C, 74.88; H, 6.30; N, 5.67.

1-Nitro-2,2-diphenylpentane (3c): ^{1}H NMR ($CDCl_3$): 7.40-7.02 (m, 10H), 5.07 (s, 2H), 2.26-2.22 (m, 2H), 1.12-1.02 (m, 2H), 0.84 (t, 3H, *J* = 6.83). ^{13}C NMR ($CDCl_3$): 144.03, 128.28, 127.46, 126.89, 82.65, 50.63, 38.96, 17.36, 14.33. MS *m/z* (relative intensity) 269 (M^+, 39), 226 (50), 180 (100), 165 (23), 91 (17), 77 (2). HRMS calcd for $C_{17}H_{19}NO_2$ 269.1416, found 269.1420.

3-Methyl-1-nitro-2,2-diphenylbutane (3d): ^{1}H NMR ($CDCl_3$): 7.46-7.11 (m, 10H), 5.14 (s, 2H), 3.15 (sept, 1H, *J* = 6.35), 0.95 (d, 6H, *J* = 6.35). ^{13}C NMR ($CDCl_3$): 140.28, 129.41, 127.66, 127.13, 83.69, 55.51, 29.23, 18.35. MS *m/z* (relative intensity) 269 (M^+, 4), 226 (24), 180 (100), 165 (25), 91 (12), 77 (4). Anal. Calcd for $C_{17}H_{19}NO_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 75.87; H, 7.10; N, 5.08.

3,3-Dimethyl-1-nitro-2,2-diphenylbutane (3e1): mp 94-95 °C. ^{1}H NMR ($CDCl_3$): 7.36-7.26 (m, 10H), 5.29 (s, 2H), 1.16 (s, 9H). ^{13}C NMR ($CDCl_3$): 141.50, 130.64, 127.04, 126.74, 81.55, 58.71, 38.63, 29.16. MS *m/z* (relative intensity) 283 (M^+, tr), 223 (3), 180 (100), 165 (13), 91 (4), 57 (28). Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.42; N, 4.94. Found: C, 76.07; H, 7.23; N, 5.31.

3,3-Dimethyl-*aci*-1-nitro-2,2-diphenylbutane (3e2): ^{1}H NMR ($CDCl_3$): 8.21 (s, 1H), 7.50-7.25 (m, 10H), 1.53 (s, 9H). ^{13}C NMR ($CDCl_3$): 144.34, 138.38, 128.41, 127.49, 125.98, 70.62, 58.71, 27.86. MS *m/z* (relative intensity) 283 (M^+, tr), 223 (3), 180 (100), 165 (13), 91 (4), 57 (28). Anal. Calcd for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.42; N, 4.94. Found: C, 76.32; H, 7.53; N, 4.87.

1-Nitro-1-phenoxy-2,2-diphenylpropane (3f): mp 113-114 °C. ^{1}H NMR ($CDCl_3$): 7.40-6.95 (m, 15H), 6.56 (s, 1H), 2.04 (s, 3H). ^{13}C NMR ($CDCl_3$): 155.29, 143.97, 143.20, 130.13, 128.35, 128.24, 127.90, 127.82, 127.37, 127.04, 124.24, 115.64, 111.71, 51.42, 22.87. MS *m/z* (relative intensity) 333 (M^+, tr), 287 (100), 209 (34), 194 (66), 179 (59), 165 (22), 115 (42), 103 (15), 77 (14). HRMS calcd for $C_{21}H_{19}NO_3$ 333.1349, found 333.1348.

1-Nitro-1-phenoxy-2,2-diphenylpentane (3g): mp 91-93 °C. ^{1}H NMR ($CDCl_3$): 7.35-6.94 (m, 15H), 6.61 (s, 1H), 2.43-2.25 (m, 2H), 1.40-1.26 (m, 1H), 1.11-0.96 (m, 1H), 0.90 (t, 3H, J = 7.32). ^{13}C NMR ($CDCl_3$): 155.51, 142.76, 140.53, 130.05, 129.85, 128.54, 128.02, 127.57, 127.46, 126.87, 124.11, 115.52, 110.34, 55.11, 39.18, 17.99, 14.53. MS *m/z* (relative intensity) 361 (M^+, tr), 315 (100), 222 (26), 209 (56), 183 (70), 178 (52), 165 (30), 91 (72), 77 (15). HRMS calcd for $C_{23}H_{23}NO_3$ 361.1694, found 361.1678.

1-Nitro-2,2-diphenylhexane (3h): ^{1}H NMR ($CDCl_3$): 7.29-7.28 (m, 10H), 5.12 (s, 2H), 2.35-2.30 (m, 2H), 1.35-1.26 (m, 2H), 1.12-1.06 (m, 2H), 0.84 (t, 3H, J = 7.32). ^{13}C NMR ($CDCl_3$): 144.02, 128.23, 127.42, 126.84, 82.58, 50.46, 36.36, 26.05, 22.87, 13.80. MS *m/z* (relative intensity) 283 (M^+, 27), 237 (3), 226 (51), 180 (100), 77 (4). HRMS calcd for $C_{18}H_{21}NO_2$ 283.1573, found 283.1589.

3,3-Diphenyl-2-butanone Oxime (4a): mp 152 °C. ^{1}H NMR ($CDCl_3$): 8.76 (s br, 1H), 7.32-7.18 (m, 10H), 1.91 (s, 3H), 1.77 (s, 3H). ^{13}C NMR ($CDCl_3$) 162.35, 145.01, 128.37, 128.06, 126.48, 54.54, 27.33, 13.45. MS *m/z* (relative intensity) 239 (M^+, 48), 222 (100), 165 (32), 103 (26), 77 (20). Anal. Calcd for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 80.10; H, 7.28; N, 6.25.

3,3-Diphenyl-2-hexanone Oxime (4b): mp 117-118 °C. ^{1}H NMR ($CDCl_3$): 7.33-7.22 (m, 10H), 2.32-2.28 (m, 2H), 1.72 (s, 3H), 1.07-0.99 (m, 2H), 0.84 (t, 3H, J = 7.33). ^{13}C NMR ($CDCl_3$) 161.55, 143.13, 129.25, 127.88, 126.41, 58.91, 40.79, 18.53, 14.53, 13.69. MS *m/z* (relative intensity) 267 (M^+, 50), 250 (100), 238 (21), 208 (28), 164 (26). Anal. Calcd for $C_{18}H_{21}NO$: C, 80.86; H, 7.92; N, 5.24. Found: C, 80.43; H, 7.91; N, 5.36.

2,2,3-Triphenyl-propanohydroximoyl Phenoxide (4c): mp 182-183 °C. ^{1}H NMR ($CDCl_3$): 8.43 (s br, 1H), 7.36-6.97 (m, 18H), 6.74 (dd, 2H, *J* = 7.81, 7.32), 3.81 (s, 2H). ^{13}C NMR ($CDCl_3$): 172.54, 159.53, 141.10, 137.09, 131.30, 129.43, 129.36, 128.33, 127.55, 127.48, 126.30, 122.89, 112.99, 62.08, 44.37. MS *m/z* (relative intensity) 393 (M^+, 3), 302 (44), 257 (100), 208 (79), 179 (84), 165 (75), 91 (88), 77 (20). Anal. Calcd for $C_{27}H_{23}NO_2$: C, 82.42; H, 5.89; N, 3.56. Found: C, 82.13; H, 5.88; N, 3.45.

***Z*-2,2-Diphenylpropanohydroximoyl Phenoxide (4d):** mp 137-138 °C. ^{1}H NMR ($CDCl_3$): 8.23 (s br, 1H), 7.39-6.93 (m, 15H), 2.07 (s, 3H). ^{13}C NMR ($CDCl_3$): 173.41, 159.48, 143.68, 129.47, 128.76, 128.02, 127.42, 123.03, 113.10, 55.70, 27.15. MS *m/z* (relative intensity) 317 (M^+, 17), 224 (7), 181 (100), 165 (22), 103 (8), 77 (2). HRMS calcd for $C_{21}H_{19}NO_2$ 317.1412, found 317.1410. Anal. Calcd: C, 79.46; H, 6.04; N, 4.42. Found: C, 78.73; H, 6.04; N, 4.40.

***E*-2,2-Diphenylpropanohydroximoyl Phenoxide (4d):** mp 148-149 °C. ^{1}H NMR ($CDCl_3$): 7.38-7.21 (m, 10H), 7.11 (t, 2H, *J* = 8.30), 6.91 (t, 1H, *J* = 7.32), 6.61 (d, 2H, *J* = 8.30), 1.96 (s, 3H). ^{13}C NMR ($CDCl_3$) 156.99, 155.53, 144.36, 128.81, 128.39, 128.02, 126.80, 122.21, 115.57, 53.67, 26.80. MS *m/z* (relative intensity) 317 (M^+, 100), 300 (5), 224 (4), 207 (99), 181 (70), 165 (37), 103 (18), 94 (28), 77 (13). HRMS calcd for $C_{21}H_{19}NO_2$ 317.1412, found 317.1416.

3-Methyl-2,2-diphenylbutanohydroximoyl Phenoxide (4e): mp 159-160 °C. ^{1}H NMR ($CDCl_3$): 8.42 (s br, 1H), 7.57-7.23 (m, 10H), 7.14 (t, 2H, *J* = 7.32), 6.94 (t, 1H, *J* = 7.32), 6.63 (d, 2H, *J* = 7.81), 3.39 (hep, 1H, *J* = 6.84), 0.87 (d, 6H, *J* = 6.84). ^{13}C NMR ($CDCl_3$): 172.81, 159.68, 139.91, 130.05, 129.30, 128.10, 127.26, 122.72, 112.84, 64.45, 31.72, 18.88. MS *m/z* (relative intensity) 345 (M^+, 3), 302 (3), 209 (100), 165 (27), 131 (26), 105 (29), 91 (30), 77 (3). HRMS calcd for $C_{22}H_{23}NO_2$ 345.1729, found 345.1733.

1-Nitro-2,3-diphenylpropane (5a):[23] ^{1}H NMR ($CDCl_3$): 7.30-7.05 (m, 10H), 4.60 (dd, 1H, *J* = 11.23, 5.86), 4.55 (dd, 1H, *J* = 11.23, 6.83), 3.73 (quint, 1H, *J* = 7.81), 3.01 (dd, 1H, *J* = 13.67, 7.81), 2.94 (dd, 1H, *J* = 13.67, 7.81). ^{13}C NMR ($CDCl_3$): 139.05, 137.75, 128.99, 128.79, 128.52, 127.60, 127.44, 126.73, 79.49, 45.91, 39.93. Anal. Calcd for $C_{15}H_{15}NO_2$: C, 74.67; H, 6.27; N, 5.80. Found: C, 74.77; H, 6.36; N, 5.75.

1-Nitro-2-phenylpropane (5b):[24, 25] ^{1}H NMR ($CDCl_3$): 7.34-7.20 (m, 5H), 4.53 (dd, 1H, *J* = 12.20, 7.33), 4.46 (dd, 1H, *J* = 12.20, 8.30), 3.64-3.58 (m, 1H), 1.36 (d, 3H, *J* = 6.84). ^{13}C NMR ($CDCl_3$): 140.86, 128.94, 127.53, 126.87, 81.81, 38.61, 18.70. HRMS calcd for $C_9H_{11}NO_2$ 165.0790, found 165.0790. Anal. Calcd for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.15; H, 6.72; N, 8.18.

1-Nitro-2-phenylpentane (5c):[25] ^{1}H NMR ($CDCl_3$): 7.45-7.26 (m, 5H), 4.54 (dd, 1H, *J* = 10.49, 7.32), 4.50 (dd, 1H, *J* = 10.49, 7.32), 3.78-3.76 (m, 1H), 1.60-1.55 (m, 2H), 1.30-1.29 (m, 2H), 1.25 (t, 3H, *J* = 7.32). ^{13}C NMR ($CDCl_3$): 144.55, 133.86, 132.25, 85.96, 49.11,

40.11, 25.06, 18.73. Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.65; H, 7.84; N, 7.16.

3-Methyl-1-nitro-2-phenylbutane (5d): ^{1}H NMR ($CDCl_3$): 7.28-7.07 (m, 5H), 4.69 (dd, 1H, *J* = 12.46, 5.86), 4.58 (dd, 1H, *J* = 12.46, 9.77), 3.20-3.14 (m, 1H), 1.92-1.87 (m, 1H), 0.95 (d, 3H, *J* = 6.35), 0.75 (d, 3H, *J* = 6.84). ^{13}C NMR ($CDCl_3$): 138.63, 128.50, 128.06, 127.35, 78.99, 50.96, 31.26, 20.53, 20.16. MS *m/z* (relative intensity) 193 (M^+, 4), 146 (100), 131 (34), 104 (97), 91 (39), 77 (6). HRMS calcd for $C_{11}H_{15}NO_2$ 193.1103, found 193.1099. Anal. Calcd: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.99; H, 7.77; N, 7.11.

3,3-Dimethyl-1-nitro-2-phenylbutane (5e): mp 64-65 °C. ^{1}H NMR ($CDCl_3$): 7.32-7.17 (m, 5H), 4.84 (dd, 1H, *J* = 12.69, 5.61), 4.80 (dd, 1H, *J* = 12.69, 4.88), 3.67 (dd, 1H, *J* = 5.61, 4.88), 0.95 (s, 9H). ^{13}C NMR ($CDCl_3$): 137.53, 129.03, 128.12, 127.38, 77.31, 54.29, 33.66, 27.99. MS *m/z* (relative intensity) 207 (M^+, 6), 145 (12), 104 (100), 77 (5), 57 (61). HRMS calcd for $C_{11}H_{15}NO_2$ 193.1103, found 193.1099. Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.76; H, 8.35; N, 6.76.

1-Nitro-3-phenyl-2-(2-thienyl)propane (5f): ^{1}H NMR ($CDCl_3$): 7.30-6.80 (m, 8H), 4.57 (d, 2H, *J* = 7.32), 4.40 (quint, 1H, *J* = 7.32), 3.09 (dd, 1H, *J* = 13.92, 7.32), 3.01 (dd, 1H, *J* = 13.92, 7.32). ^{13}C NMR ($CDCl_3$): 141.96, 137.35, 128.96, 128.63, 126.98, 125,45, 124.53, 79.98, 41.27, 40.79. MS *m/z* (relative intensity) 247 (6), 200 (71), 110 (87), 91 (100). Anal. Calcd for $C_{13}H_{13}NO_2S$: C, 63.14; H, 5.30; N, 5.66. Found: C, 63.48; H, 5.42; N, 5.68.

2-(2-Furyl)-1-nitropentane (5g): mp 64-65 °C. ^{1}H NMR ($CDCl_3$): 7.35 (d, 1H, *J* = 1.95), 6.30 (dd, 1H, *J* = 2.93, 1.95), 6.14 (d, 1H, *J* = 2.93), 4.65 (dd, 1H, *J* = 12.21, 7.82), 4.52 (dd, 1H, *J* = 12.21, 6.84), 3.63-3.58 (m, 1H), 1.76-1.69 (m, 1H), 1.64-1.55 (m, 1H), 1.32-1.31 (m, 2H), 0.92 (t, 3H, *J* = 7.32). ^{13}C NMR ($CDCl_3$): 152.58, 142.09, 110.19, 107.16, 78.52, 37.68, 33.02, 19.96, 13.65. Anal. Calcd for $C_9H_{13}NO_3$: C, 59.00; H, 7.15; N, 7.65. Found: C, 59.04; H, 7.23; N, 7.50.

2-(4-fluorophenyl)-1-nitropentane (5h): ^{1}H NMR ($CDCl_3$): 7.17-6.98 (m, 4H), 4.55 (dd, 1H, *J* = 12.20, 7.33), 4.48 (dd, 1H, *J* = 12.20, 8.30), 3.49-3.41 (m, 1H), 1.66-1.59 (m, 2H), 1.24-1.15 (m, 2H), 0.89 (t, 3H, *J* = 7.32). ^{13}C NMR ($CDCl_3$): 161.98 (d, *J*= 244.5), 135.19, 128.97 (d, *J*= 7.4), 115.68 (d, *J*= 22.0), 80.86, 43.33, 35.08, 19.94, 13.58. MS *m/z* (relative intensity) 211 (M^+, 15), 164 (64), 149 (37), 136 (100), 122 (36), 109 (41). Anal. Calcd for $C_{11}H_{14}NO_2F$: C, 62.55; H, 6.68; N, 6.63. Found: C, 62.55; H, 6.84; N, 6.94.

3-Methyl-1-nitro-2-(4-trifluoromethoxyphenyl)butane (5i): ^{1}H NMR ($CDCl_3$): 7.20-7.15 (m, 4H), 4.75 (dd, 1H, *J* = 12.21, 5.37), 4.61 (dd, 1H, *J* = 12.70, 10.26), 3.27-3.24 (m, 1H), 1.94-1.91 (m, 1H), 0.99 (d, 3H, *J* = 6.84), 0.78 (d, 3H, *J* = 6.84). ^{13}C NMR ($CDCl_3$): 148.45, 137.37, 129.41, 120.98, 120.36 (q, *J*= 257.4), 78.81, 50.39, 31.34, 20.40, 20.12. MS *m/z* (relative intensity) 193 (4), 146 (100), 131 (34), 104 (97), 91 (39), 77 (6). HRMS calcd for $C_{11}H_{15}NO_2$ 193.1103, found 193.1099. Anal. Calcd for $C_{12}H_{14}NO_3F_3$: C, 52.20; H, 5.37; N, 4.79. Found: C, 52.15; H, 5.29; N, 4.87.

3,3-Dimethyl-1-nitro-2-[4-(*N*,*N*-diethylamino)phenyl]butane (5j): mp 67 °C. ^{1}H NMR ($CDCl_3$): 6.99 (d, 2H, *J* = 8.78), 6.97 (d, 2H, *J* = 8.78), 4.77-4.74 (m, 2H), 3.34 (q, 4H, *J* = 7.33), 3.22 (dd, 1H, *J* = 9.77, 6.35), 1.16 (t, 6H, *J* = 7.33), 0.93 (s, 9H). ^{13}C NMR ($CDCl_3$): 147.04, 129.85, 123.84, 111.22, 77.44, 53.52, 44.16, 33.88, 27.99, 12.61. MS *m/z* (relative intensity) 278 (M^+, 43), 263 (4), 175 (100), 160 (31), 57 (7). Anal. Calcd for $C_{19}H_{24}N_2O_2$: C, 69.03; H, 9.41; N, 10.06. Found: C, 69.26; H, 9.52; N, 10.07.

1-Nitro-3-phenyl-2-(4-methoxyphenyl)propane (5k): ^{1}H NMR ($CDCl_3$): 7.26-6.81 (m, 9H), 4.56 (d, 2H, *J* = 7.81), 3.70 (s, 3H), 3.73-3.67 (m, 1H), 2.96 (dd, 1H, *J* = 12.70, 7.81), 2.93 (dd, 1H, *J* = 12.70, 7.32). ^{13}C NMR ($CDCl_3$): 158.95, 137.92, 130.95, 129.03, 128.50, 125.33, 126.71, 114.20, 79.84, 55.18, 45.23, 40.04. MS *m/z* (relative intensity) 271 (M^+, 6), 200 (71), 110 (87), 91 (100). Anal. Calcd $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16. Found: C, 69.95; H, 6.17; N, 5.47.

2-(1-Naphthyl)-1-nitropentane (5l): ^{1}H NMR ($CDCl_3$): 8.03-7.16 (m, 7H), 4.46-4.44 (m, 2H), 4.34-4.22 (m, 1H), 1.66-1.64 (m, 2H), 1.09-1.03 (m, 2H), 0.67 (t, 3H, *J* = 7.32). ^{13}C NMR ($CDCl_3$): 135.45, 133.95, 131.61, 129.01, 127.80, 126.43, 125.68, 125.37, 123.42, 80.34, 37.52, 35.01, 20.05, 13.76. MS *m/z* (relative intensity) 243 (M^+, 85), 196 (24), 167 (43), 153 (69), 141 (100), 115 (28). HRMS calcd for $C_{15}H_{17}NO_2$: 243.1259, found 243.1269. Anal. Calcd: C, 74.05; H, 7.04; N, 5.76. Found: C, 73.25; H, 7.13; N, 5.77.

2-(1-Naphthyl)-1-nitropropane (5m): ^{1}H NMR ($CDCl_3$): 8.10-7.28 (m, 7H), 4.64-4.41 (m, 1H), 4.45-4.38 (m, 2H), 1.43 (d, 3H, *J* = 6.35). ^{13}C NMR ($CDCl_3$): 136.49, 133.88, 130.75, 129.08, 127.93, 126.60, 125.77, 125.30, 122.87, 122.08, 81.11, 32.94, 18.13. MS *m/z* (relative intensity) 215 (M^+, 85), 169 (89), 153 (81),141 (100), 128 (31), 115 (30). Anal. Calcd for $C_{13}H_{13}NO_2$: C, 72.54; H, 6.09; N, 6.51. Found: C, 72.28; H, 6.28; N, 6.31.

1-Nitro-2-(*N*-phenyl-3-indolyl)-3,3-dimethylbutane (5n): mp 138-140 °C. ^{1}H NMR ($CDCl_3$): 7.67-7.15 (m, 10H), 4.88 (dd, 1H, *J* = 12.21, 4.88), 4.80 (t, 1H, *J* = 12.21), 3.86 (dd, 1H, *J* = 12.21, 4.88), 1.05 (s, 9H). ^{13}C NMR ($CDCl_3$) 139.49, 135.70, 129.74, 129.60, 126.51, 125.57, 124.38, 122.57, 120.27, 119.67, 113.96, 110.45, 77.95, 45.36, 34.39, 28.08. MS *m/z* (relative intensity) 322 (M^+, 21), 265 (10), 219 (100), 115 (2), 57 (11). Anal. Calcd for $C_{20}H_{22}N_2O_2$: C, 74.51; H, 6.88, N, 8.69. Found: C, 74.61; H, 6.90; N, 8.72.

3. General Procedure for the Preparation of Hydroximoyl Halides 6a-l and 8a-t or Nitrile Oxides 7a-g by Using of the Concentrated Aqueous HX (equations 3, 4 and Tables II, III).

(a) Grignard reagents method: The preparation of **6a** from **1a** will serve to illustrate the general procedure utilized. 1,1-Diphenyl-2-nitroethene **1a** (2 mmol) in 10 mL dry ether or THF was added to 10 mmol of benzylmagnesium chloride in 30 mL of ether or THF at -20 °C. Within 10 min, the solution was slowly added to the ice cold concentrated hydrochloric acid. A blue or green

color was always observed during the addition. After stirring 30 min, the solution was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated to give the hydroximoyl chloride or the nitrile oxide. The yield (95%) was based on NMR by using toluene or dibromomethane as an internal standard. The residue was purified by flash column chromatography on silica gel using hexane-ethyl acetate as eluent to obtain the pure product **6a**.

(b) Organolithium reagents method: The preparation of **8l** from **2a** will serve to illustrate the general procedure utilized. trans β-Nitrostyrene **2a** (2 mmol) in 10 mL dry ether or THF was added to 10 mmol of methyllithium (in diethyl ether) at -78 °C. Within 5 min, the solution was slowly added to the ice cold concentrated hydrochloric acid. A blue or green color was always observed during the addition. After stirring 30 min, the solution was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated to give the hydroximoyl chloride. The yield (90%) was based on NMR by using toluene or dibromomethane as an internal standard. The residue was purified by flash column chromatography on silica gel using hexane-ethyl acetate as eluent to obtain the pure product **8l**.

2,2,3-Triphenylpropanohydroximoyl Chloride (6a): mp 167-169 °C. ^{1}H NMR ($CDCl_3$): 7.66 (s br, 1H), 7.26-6.99 (m, 13H), 6.68 (d, 2H, J = 7.32), 3.79 (s, 2H). ^{13}C NMR ($CDCl_3$): 146.34, 140.97, 136.91, 131.13, 130.05, 129.89, 127.59, 127.39, 127.11, 126.36, 62.19, 45.07. MS *m/z* (relative intensity) 337 ($(M+2)^+$, tr), 335 (M^+, tr), 300 (100), 282 (62), 257 (21), 222 (11), 208 (19), 178 (7), 165 (3), 131 (26), 105 (2), 91 (8). Anal. Calcd for $C_{21}H_{18}NOCl$: C, 75.11; H, 5.40; N, 4.17. Found: C, 75.05; H, 5.38; N, 4.02.

2,2-Diphenylpentanohydroximoyl Bromide (6b): mp 115-116 °C. ^{1}H NMR ($CDCl_3$): 7.90 (s br, 1H), 7.35-7.24 (m, 10H), 2.49-2.41 (m, 2H), 1.65-1.21 (m, 2H), 0.87 (t, 3H, J = 6.96). ^{13}C NMR ($CDCl_3$): 142.47, 142.15, 129.55, 127.85, 126.97, 61.37, 42.43, 18.49, 14.33. MS *m/z* (relative intensity) 333 ($(M+2)^+$, 23), 331 ((M^+, 24), 252 (20), 235 (50), 208 (100), 192 (48), 178 (94), 165 (70), 143 (41), 117 (47), 91 (45), 77 (10). Anal. Calcd for $C_{17}H_{18}NOBr$: C, 61.47; H, 5.46; N, 4.23. Found: C, 61.82; H, 5.34; N, 4.06.

3-Methyl-2,2-diphenylbutanohydroximoyl Bromide (6c): This compound underwent dehydrobromination to generate nitrile oxide **7c** during the flash column chromatography and only trace peak of 331 was observed in GCMS. The crude ^{1}H-NMR contained two peaks at (δ) 3.4 (sept, J = 6.6) and 0.81 (d, J = 6.6) which were believed to belong to this compound.

2,2,3-Triphenylpropanohydroximoyl Bromide (6d): mp 156-158 °C. ^{1}H NMR ($CDCl_3$): 7.89 (s br, 1H), 7.25-6.99 (m, 13H), 6.67 (d, 2H, J = 7.32), 3.82 (s, 2H); ^{13}C NMR ($CDCl_3$): 142.02, 141.07, 137.08, 131.19, 130.19, 127.59, 127.41, 127.14, 126.41, 63.23, 45.79. MS *m/z* (relative intensity) 381 ($(M+2)^+$, tr), 379 (M^+, tr), 282 (11), 208 (65), 192 (100), 178 (59), 165 (28), 152 (8), 91 (26). HRMS calcd for $C_{21}H_{18}NOBr$ 381.0552, found 381.0528; calcd 379.0572, found 379.0609. Anal. Calcd: C, 66.33; H, 4.77; N, 3.68. Found: C, 66.33; H, 4.70; N, 3.48.

2,2-Diphenylpropanohydroximoyl Chloride (6e): mp 136 °C. ^{1}H NMR ($CDCl_3$): 8.26 (s br, 1H), 7.40-7.17 (m, 10H), 2.09 (s, 3H). ^{13}C NMR ($CDCl_3$): 147.86, 143.71, 128.33,

128.20, 127.14, 56.11, 28.07. MS *m/z* (relative intensity) 261 ($(M+2)^+$, 12), 259 (M^+, 41), 244 (16), 242 (49), 222 (61), 193 (100), 178 (18), 165 (77), 139 (74), 115 (97), 103 (46), 91 (24), 77 (40). Anal. Calcd for $C_{15}H_{14}NOCl$: C, 69.36; H, 5.43; N, 5.39. Found: C, 69.62; H, 5.62; N, 5.28.

2,2-Diphenylpropanohydroximoyl Bromide (6f): mp 145 °C. ^1H NMR ($CDCl_3$) 8.43 (s br, 1H), 7.38-7.20 (m, 10H), 2.09 (s, 3H). ^{13}C NMR ($CDCl_3$): 143.85, 142.76, 128.47, 128.13, 127.07, 57.03, 29.07. MS *m/z* (relative intensity) 305 ($(M+2)^+$, 11), 303 (M^+, 11), 224 (4), 222 (7), 207 (50), 193 (100), 178 (66), 165 (45), 115 (92), 77 (21). Anal. Calcd for $C_{15}H_{14}NOBr$: C, 59.23; H, 4.64; N, 4.60. Found: C, 59.70; H, 4.75; N, 4.37.

2,2-Diphenylpropanohydroximoyl Iodide (6g): mp 173-174 °C. ^1H NMR ($CDCl_3$): 8.33 (s br, 1H), 7.34-7.21 (m, 10H), 2.09 (s, 3H). ^{13}C NMR ($CDCl_3$): 143.81, 133.51, 128.72, 128.06, 127.02, 57.78, 30.48. MS *m/z* (relative intensity) 351 (M^+, 1), 224 (100), 193 (98), 178 (63), 165 (50), 115 (56), 77 (12). Anal. Calcd for $C_{15}H_{14}NOI$: C, 51.30; H, 4.02; N, 3.99. Found: C, 51.52; H, 3.99; N, 3.81.

2,2-Diphenylpentanohydroximoyl Chloride (6h): mp 136 °C. ^1H NMR ($CDCl_3$): 7.70 (s br, 1H), 7.37-7.25 (m, 10H), 2.44-2.40 (m, 2H), 1.13-1.08 (m, 2H), 0.87 (t, 3H, J = 7.32). ^{13}C NMR ($CDCl_3$): 147.01, 141.94, 129.30, 127.82, 126.95, 60.45, 41.63, 18.44, 14.40. MS *m/z* (relative intensity) 289 ($(M+2)^+$, 18), 287 (M^+, 59), 272 (15), 270 (43), 246 (15), 244 (47), 208 (100), 178 (66), 165 (83), 143 (23), 117 (24), 91 (25), 77 (12). Anal. Calcd for $C_{17}H_{18}NOCl$: C, 70.95; H, 6.30; N, 4.87. Found: C, 71.05; H, 6.26; N, 5.07.

2,2-Diphenylpentanohydroximoyl Iodide (6i): This compound was quite unstable and converted into nitrile oxide after column purification. Only trace peak of 379 was observed in MS which was believed to belong to the molecular weight of this compound.

3-Methyl-2,2-diphenylbutanohydroximoyl Chloride (6j): mp 136 °C. ^1H NMR ($CDCl_3$): 7.97 (s br, 1H), 7.46-7.23 (m, 10H), 3.36 (sept, 1H, J = 6.83), 0.81 (d, 6H, J = 6.83). ^{13}C NMR ($CDCl_3$): 147.18, 139.29, 130.77, 127.33, 126.98, 65.01, 31.81, 18.89. MS *m/z* (relative intensity) 289 ($(M+2)^+$, 10), 287 (M^+, 31), 246 (28), 244 (97), 228 (33), 208 (100), 192 (93), 178 (49), 165 (85), 152 (12), 115 (9), 105 (8), 77 (5). HRMS calcd for $C_{17}H_{18}NOCl$ 287.1077, found 287.1101. Anal. Calcd: C, 70.95; H, 6.30 N, 4.87. Found: C, 70.76; H, 6.31; N, 4.64.

2,2-Diphenylhexanohydroximoyl Chloride (6k): mp 124 °C. ^1H NMR ($CDCl_3$): 7.64 (s br, 1H), 7.31 (s, 10H), 2.49-2.41 (m, 2H), 1.34-1.20 (m, 2H), 1.14-0.99 (m, 2H), 0.82 (t, 3H, J = 7.32). ^{13}C NMR ($CDCl_3$): 147.02, 142.08, 129.40, 127.88, 126.98, 60.39, 39.21, 27.16, 23.06, 13.83. MS *m/z* (relative intensity) 303 ($(M+2)^+$, 4), 301 (M^+, 12), 244 (12), 223 (15), 178 (19), 77 (40), 57 (14). HRMS calcd for $C_{18}H_{20}NOCl$ 303.1204, found 303.1203; calcd 301.1233, found 301,1251. Anal. Calcd: C, 71.63; H, 6.67 N, 4.64. Found: C, 71.31; H, 6.53; N, 4.57.

2,2-Diphenylhexanohydroximoyl Bromide (6l): mp 115 °C. ^1H NMR ($CDCl_3$): 7.96 (s

br, 1H), 7.32 (s, 10H), 2.51-2.43 (m, 2H), 1.34-1.20 (m, 2H), 1.15-1.03 (m, 2H), 0.82 (t, 3H, J = 7.20). ^{13}C NMR ($CDCl_3$): 142.55, 142.16, 129.57, 127.85, 126.96, 61.31, 39.99, 27.25, 23.05, 13.83. MS *m/z* (relative intensity) 347 ($(M+2)^+$, 7), 345 (M^+, 7), 266 (23), 249 (18), 223 (16), 131 (100), 77 (15), 57 (3). HRMS calcd for $C_{18}H_{20}NOBr$ 347.0708, found 347.0713; calcd 345.0728, found 345.0703.

2,2,3-Triphenylpropanenitrile Oxide (7a): mp 155-156 °C. ^{1}H NMR ($CDCl_3$): 7.35-7.17 (m, 13H), 6.81 (d, 2H, J = 7.32), 3.70 (s, 2H). ^{13}C NMR ($CDCl_3$): 141.39, 135.03, 130.26, 128.65, 128.08, 127.88, 127.27, 54.43, 46.72. MS *m/z* (relative intensity) 299 (M^+, tr), 282 (10), 257 (21), 208 (42), 178 (46), 165 (26), 91 (12). IR (cm^{-1}): 2924, 2286, 1491, 1450, 702; UV (nm) 259. Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N,4.68. Found: C, 84.44; H, 5.98; N, 4.83.

Di(1,1-diphenylethyl)furoxan (7b): mp 190-191 °C. ^{1}H NMR ($CDCl_3$): 7.31-6.89 (m, 20H), 1.94 (s, 3H), 1.37 (s, 3H). ^{13}C NMR ($CDCl_3$): 163.30, 143.62, 143.50, 128.28, 127.26, 126.96, 121.64, 51.25, 48.84, 30.73, 30.07. MS *m/z* (relative intensity) 446 (M^+, tr), 353 (3), 275 (5), 181 (100), 165 (11), 103 (8), 77 (3). Anal. Calcd for $C_{30}H_{26}N_2O_2$: C, 80.69; H, 5.87; N, 6.27. Found: C, 80.10; H, 5.91; N, 5.98.

3-Methyl-2,2-diphenylbutanenitrile Oxide (7c): mp 64 °C. ^{1}H NMR ($CDCl_3$): 7.44-7.24 (m, 10H), 2.98 (sept, 1H, J = 6.35), 1.07 (d, 6H, J = 6.35). ^{13}C NMR ($CDCl_3$): 141.25, 128.72, 127.42, 126.56, 60.58, 35.96, 19.30. MS *m/z* (relative intensity) 251 (M^+, 5), 234 (6), 221 (28), 208 (74), 192 (100), 178 (56), 165 (47), 77 (5). HRMS calcd for $C_{17}H_{17}NO$ 251.1314, found 251.1310. Anal. Calcd: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.24; H, 6.71; N, 5.95.

3,3-Dimethyl-2,2-diphenylbutanenitrile Oxide (7d): mp 108-110 °C. ^{1}H NMR ($CDCl_3$): 7.41-7.26 (m, 10H), 1.29 (s, 9H). ^{13}C NMR ($CDCl_3$): 140.62, 129.40, 127.95, 127.37, 62.37, 39.69, 28.50. MS *m/z* (relative intensity) 266 ($(M+1)^+$, tr), 235 (1), 208 (2), 192 (100), 165 (26), 152 (4), 91 (2), 77 (1), 57 (10). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.25; H, 7.16; N, 5.60.

2,2-Diphenylpentanenitrile Oxide (7e): mp 73-74 °C. ^{1}H NMR ($CDCl_3$): 7.36-7.25 (m, 10H), 2.38-2.34 (m, 2H), 1.41-1.36 (m, 2H), 0.96 (t, 3H, J= 7.33). ^{13}C NMR ($CDCl_3$): 141.78, 128.77, 127.71, 126.78, 53.23, 42.91, 19.30, 13.91. MS *m/z* (relative intensity) 251 (M^+, 8), 221 (21), 208 (96), 178 (100), 165 (35), 143 (53), 117 (70), 105 (16), 91 (53), 77 (7). Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.09; H, 6.90; N, 5.50.

Cyclohexyldiphenylethanenitrile Oxide (7f): mp 115 °C. ^{1}H NMR ($CDCl_3$): 7.41-7.19 (m, 10H), 2.56-1.24 (m, 11H). ^{13}C NMR ($CDCl_3$): 140.99, 128.86, 127.51, 126.76, 59.71, 45.63, 29.48, 26.25, 25.90. MS *m/z* (relative intensity) 291 (M^+, 3), 274 (8), 192 (100), 178 (21), 165 (69), 91 (8), 77 (4). Anal. Calcd for $C_{20}H_{21}NO$: C, 82.44; H, 7.26; N, 4.81. Found: C, 82.12; H, 7.23; N, 4.74.

2,2-Diphenylhexanenitrile Oxide (7g): ^{1}H NMR ($CDCl_3$): 7.37-7.23 (m, 10H), 2.42-2.34 (m, 2H), 1.38-1.26 (m, 4H), 0.88 (t, 3H, *J*= 6.40). ^{13}C NMR ($CDCl_3$): 141.80, 128.78, 127.71, 126.78, 53.15, 40.47, 27.92, 22.49, 13.70. MS *m/z* (relative intensity) 265 (M^+, 4), 223 (6), 208 (62), 178 (52), 165 (26), 131 (100), 115 (16), 91 (26), 77 (5). HRMS calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1471.

3-Methyl-2-phenylbutanohydroximoyl Chloride (8a): mp 136 °C. ^{1}H NMR ($CDCl_3$): 7.31-7.24 (m, 5H), 3.39 (d, 1H, *J*= 10.74), 2.50-2.41 (m, 1H), 1.06 (d, 3H, *J*= 6.84), 0.76 (d, 3H, *J* = 6.84). ^{13}C NMR ($CDCl_3$): 144.61, 138.22, 128.77, 128.56, 127.49, 60.27, 29.89, 21.06, 20.45. MS *m/z* (relative intensity) 213 ($(M+2)^+$, 21), 211 (M^+, 69), 169 (55), 125 (49), 115 (100), 91 (33), 77 (11). HRMS calcd for $C_{11}H_{14}NOCl$ 211.0764, found 211.0765.

3-Phenyl-2-(2-thienyl)propanohydroximoyl Chloride (8b): ^{1}H NMR ($CDCl_3$): 8.20 (s br, 1H), 7.25-6.94 (m, 8H), 4.42 (dd, 1H, *J*= 8.79, 6.84), 3.39 (dd, 1H, *J*= 13.68, 8.79), 3.22 (dd, 1H, *J*= 13.68, 6.84). ^{13}C NMR ($CDCl_3$): 143.04, 141.21, 137.72, 128.80, 128.41, 126.76, 126.71, 125.94, 124.92, 49.17, 39.77. MS *m/z* (relative intensity) 267 ($(M+2)^+$, 10), 265 (M^+, 27), 212 (11), 174 (74), 138 (24), 122 (28), 91 (100), 77 (4). HRMS calcd for $C_{13}H_{12}NOSCl$ 265.0328, found 265.0328.

2-(2-Thienyl)propanohydroximoyl Chloride (8c): ^{1}H NMR ($CDCl_3$): 8.50 (s br, 1H), 7.22 (d, 1H, *J* = 3.0), 6.99-6.96 (m, 2H), 4.27 (q, 1H, *J* = 7.20), 1.64 (d, 3H, *J* = 7.20). ^{13}C NMR ($CDCl_3$): 144.95, 143.21, 126.85, 125.28, 124.75, 41.78, 19.38. MS *m/z* (relative intensity) 191 ($(M+2)^+$, 27), 189 (M^+, 71), 175 (11), 173 (35), 143 (50), 136 (24), 111 (100), 77 (12). HRMS calcd for C_7H_8NOSCl 189.0015, found 189.0007.

2-(2-Thienyl)pentanohydroximoyl Chloride (8d): ^{1}H NMR ($CDCl_3$): 7.20 (d, 1H, *J*= 3.91), 6.96 (dd, 1H, *J* = 3.91, 3.21), 6.93 (d, 1H, *J*= 3.21), 4.45 (dd, 1H, *J*= 8.30, 6.83), 2.08 (m, 1H), 1.90 (m, 1H), 1.35 (m, 2H), 0.92 (t, 3H, *J* = 7.33). ^{13}C NMR ($CDCl_3$): 143.40, 142.27, 126.67, 125.46, 124.57, 46.81, 35.52, 20.31, 13.60. MS *m/z* (relative intensity) 219 ($(M+2)^+$, 18), 217 (M^+, 46), 175 (35), 173 (100), 138 (19), 131 (22), 122 (26), 97 (34). HRMS calcd for $C_9H_{12}NOSCl$ 217.0328, found 217.0330.

3-Methyl-2-(2-thienyl)butanohydroximoyl Chloride (8e): ^{1}H NMR ($CDCl_3$): 8.32 (br s, 1H), 7.13 (d, 1H, *J*= 3.47), 6.90 (dd, 1H, *J*= 3.47, 3.42), 6.87 (d, 1H, *J*= 3.42), 3.65 (d, 1H, *J* = 10.25), 2.34-2.22 (m, 1H), 0.96 (d, 3H, *J* = 6.34), 0.81 (d, 3H, *J* = 6.34). ^{13}C NMR ($CDCl_3$): 143.96, 140.94, 126.62, 126.33, 124.85, 54.99, 31.97, 20.90, 20.42. MS *m/z* (relative intensity) 219 ($(M+2)^+$, 19), 217 (M^+, 54), 176 (35), 174 (100), 158 (39), 131 (58), 122 (84), 83 (33). HRMS calcd for $C_9H_{12}NOSCl$ 217.0328, found 217.0318.

3,3-Dimethyl-2-(2-thienyl)butanohydroximoyl Chloride (8f): ^{1}H NMR ($CDCl_3$): 7.82 (s br, 1H), 7.21 (d, 1H, *J*= 3.91), 7.01 (dd, 1H, *J*= 3.91, 3.42), 6.96 (d, 1H, *J*= 3.42), 4.01 (s, 1H), 1.09 (s, 9H). ^{13}C NMR ($CDCl_3$): 142.34, 138.54, 127.91, 126.21, 124.93, 58.97, 35.56,

28.30. MS *m/z* (relative intensity) 233 ((M+2)$^+$, 3), 231 (M$^+$, 8), 177 (24), 175 (59), 158 (54), 122 (100), 57 (79). HRMS calcd for $C_{10}H_{14}NOSCl$ 231.0485, found 231.0482.

2-(2-Furyl)-3,3-dimethylbutanohydroximoyl Chloride (8g): ^{1}H NMR ($CDCl_3$): 7.75 (s br, 1H), 7.36 (dd, 1H, *J* = 1.80, 1.00), 6.34 (dd, 1H, *J* = 3.40, 1.80), 6.26 (dd, 1H, *J* = 1.80, 1.00), 3.82 (s, 1H), 1.06 (s, 9H). ^{13}C NMR ($CDCl_3$): 151.28, 141.51, 139.33, 110.18, 108.82, 55.70, 35.45, 28.17. MS *m/z* (relative intensity) 215 ((M+2)$^+$, tr), 213 (M$^+$, tr), 182 (4), 158 (83), 142 (31), 123 (13), 106 (10), 91 (7), 77 (9), 57 (100). HRMS calcd for $C_{10}H_{14}NO_2Cl$ 217.0683, found 217.0681;.calcd 215.0713, found 215.0717.

3,3-Dimethyl-2-(4-fluorophenyl)butanohydroximoyl Chloride (8h): ^{1}H NMR ($CDCl_3$): 8.25 (s br, 1H), 7.31-6.97 (m, 4H), 3.58 (s, 1H), 1.03 (s, 9H). ^{13}C NMR ($CDCl_3$): 162.11 (d, *J* = 246.3), 141.23, 132.65, 131.61 (d, *J* = 7.3), 114.70 (d, *J* = 20.2), 64.29, 35.56, 28.13. MS *m/z* (relative intensity) 245 (M$^+$, tr), 189 (15), 187 (35), 165 (20), 151 (27), 134 (79), 123 (50), 109 (43), 95 (21), 57 (100). HRMS calcd for $C_{12}H_{15}NOFCl$ 245.0797, found 245.0804.

3-Methyl-2-(4-trifluoromethoxyphenyl)butanohydroximoyl Bromide (8i): ^{1}H NMR ($CDCl_3$): 8.87 (s br, 1H), 7.34 (d, 2H, *J* = 8.78), 7.15 (d, 2H, *J* = 8.78), 3.48 (d, 1H, *J* = 10.75), 2.44 (m, 1H), 1.06 (d, 3H, *J* = 6.35), 0.77 (d, 3H, *J* = 6.35). ^{13}C NMR ($CDCl_3$) 148.54, 138.52, 136.82, 130.20, 130.17, 120.84, 120.44 (q, *J* = 257.4), 61.13, 30.70, 21.08, 20.34. MS *m/z* (relative intensity) 341 ((M+2)$^+$, 5), 339 (M$^+$, 6), 299 (24), 217 (41), 200 (100), 175 (38), 115 (10), 69 (18). HRMS calcd for $C_{12}H_{13}NO_2F_3Br$ 341.0061, found 341.0040; calcd 339.0082, found 339.0082.

3-Methyl-2-(1-naphthyl)butanohydroximoyl Chloride (8j): ^{1}H NMR ($CDCl_3$): 8.27 (s br, 1H), 8.24-7.44 (m, 7H), 4.37 (d, 1H, *J* = 10.60), 2.66 (m, 1H), 1.18 (d, 3H, *J* = 6.40), 0.80 (d, 3H, *J* = 6.40). ^{13}C NMR ($CDCl_3$): 144.32, 134.06, 133.45, 132.42, 129.03, 128.10, 126.39, 125.82, 125.55, 125.31, 123.03, 53.77, 30.19, 21.30, 20.38. MS *m/z* (relative intensity) 263 ((M+2)$^+$, 22), 261 (M$^+$, 71), 220 (16), 218 (50), 204 (11), 202 (37), 183 (54), 166 (100), 152 (65), 139 (27), 127 (11), 115 (8). HRMS calcd for $C_{15}H_{16}NOCl$ 261.0921, found 261.0911.

2-(*N*-Phenyl-3-indolyl)-3-methylbutanohydroximoyl Chloride (8k): ^{1}H NMR ($CDCl_3$): 7.75-7.12 (m, 11H), 3.87 (d, 1H, *J* = 10.60), 2.55 (m, 1H), 1.12 (d, 3H, *J* = 6.60), 0.98 (d, 3H, *J* = 6.60). ^{13}C NMR ($CDCl_3$): 144.52, 139.68, 135.91, 129.64, 128.71, 126.51, 126.44, 124.39, 122.65, 120.31, 119.41, 113.97, 110.59, 50.85, 30.39, 21.17, 20.76. MS *m/z* (relative intensity) 328 ((M+2)$^+$, 5), 326 (M$^+$, 16), 290 (17), 285 (11), 283 (37), 260 (37), 247 (100), 231 (15), 204 (9), 165 (4), 77 (10). HRMS calcd for $C_{19}H_{19}N_2OCl$ 326.1185, found 326.1184.

2-Phenylpropanohydroximoyl Chloride (8l): ^{1}H NMR ($CDCl_3$): 8.85 (s br, 1H), 7.28 (s, 5H), 3.96 (q, 1H, *J* = 7.00), 1.54 (d, 3H, *J* = 7.00). ^{13}C NMR ($CDCl_3$): 145.18, 139.95, 128.50, 127.38, 127.26, 46.57, 18.50. MS *m/z* (relative intensity) 185 ((M+2)$^+$, 30), 183 (M$^+$, 92), 149 (11), 105 (100), 77 (26). HRMS calcd for $C_9H_{10}NOCl$ 185.0421, found 185.0420; calcd

183.0451, found 183.0453.

2-Phenylhexanohydroximoyl Chloride (8m): ^{1}H NMR ($CDCl_3$): 8.71 (s br, 1H), 7.34-7.23 (m, 5H), 3.79 (t, 1H, J = 7.60), 2.21-2.03 (m, 1H), 1.95-1.76 (m, 1H), 1.41-1.20 (m, 4H), 0.87 (t, 3H, J = 6.80). ^{13}C NMR ($CDCl_3$): 145.07, 138.99, 128.61, 128.07, 127.48, 52.24, 31.89, 29.27, 22.48, 13.75. MS *m/z* (relative intensity) 227 ($(M+2)^+$, 6), 225 (M^+, 20), 190 (52), 169 (93), 148 (2), 91 (100), 77 (27), 57 (15). HRMS calcd for $C_{12}H_{16}NOCl$ 227.0891, found 227.0881; calcd 225.0921, found 225.0930.

3,3-Dimethyl-2-phenylbutanohydroximoyl Chloride (8n): this product contained trace nitrile oxide after flash column purification and ^{1}H NMR ($CDCl_3$): 8.90 (s br, 1H), 7.34-7.15 (m, 5H), 3.60 (s, 1H), 1.10 (s, 9H). ^{13}C NMR ($CDCl_3$): 141.52, 136.80, 130.02, 127.71, 127.11, 64.69, 35.36, 28.19. MS *m/z* (relative intensity) 227 ($(M+2)^+$, tr), 226 (16), 225 (M^+, tr), 190 (100), 169 (32), 147 (57), 57 (19). HRMS calcd for $C_{12}H_{16}NOCl$ 225.0921, found 225.0921.

2-(2-Thienyl)hexanohydroximoyl Chloride (8o): ^{1}H NMR ($CDCl_3$): 8.85 (s br, 1H), 7.21 (dd, 1H, J = 3.80, 2.40), 6.96 (d, 1H, J = 3.80), 6.93 (d, 1H, J = 2.40), 4.45 (dd, 1H, J = 8.40, 6.80), 2.20-1.87 (m, 2H), 1.36-1.26 (m, 4H), 0.89 (t, 3H, J = 6.80). ^{13}C NMR ($CDCl_3$): 144.14, 142.11, 126.69, 125.52, 124.62, 47.10, 33.18, 29.20, 22.21, 13.80. MS *m/z* (relative intensity) 233 ($(M+2)^+$, 14), 231 (M^+, 39), 196 (4), 174 (100), 57 (4). HRMS calcd for $C_{10}H_{14}NOSCl$ 233.0455, found 233.0449; calcd 231.0485, found 231.0488.

2-(2-Furyl)propanohydroximoyl Chloride (8p): ^{1}H NMR ($CDCl_3$): 8.16 (s br, 1H), 7.37 (dd, 1H, J = 1.80, 0.80), 6.35 (dd, 1H, J = 3.20, 1.80), 6.22 (dd, 1H, J = 3.20, 0.80), 4.08 (q, 1H, J = 7.00), 1.56 (d, 3H, J = 7.00). ^{13}C NMR ($CDCl_3$): 153.07, 143.11, 142.22, 110.38, 106.86, 40.35, 16.15. MS *m/z* (relative intensity) 175 ($(M+2)^+$, 29), 173 (M^+, 75), 158 (34), 138 (11), 120 (43), 95 (100), 77 (7), 55 (4). HRMS calcd for $C_7H_8NO_2Cl$ 175.0214, found 175.0215; calcd 173.0243, found 173.0241.

2-(4-Fluorophenyl)propanohydroximoyl Chloride (8q): ^{1}H NMR ($CDCl_3$): 9.90 (s br, 1H), 7.24 (dd, 2H, J = 8.40, 5.40), 6.99 (dd, 2H, J = 8.40, 5.40), 3.96 (q, 1H, J = 7.00), 1.53 (d, 3H, J = 7.00). ^{13}C NMR ($CDCl_3$): 162.02 (d, J = 246.6), 144.97, 135.80 (d, J = 3.0), 129.11 (d, J = 8.0), 115.39 (d, J = 21.8), 45.77, 18.47. MS *m/z* (relative intensity) 203 ($(M+2)^+$, 13), 201 (M^+, 41), 166 (6), 148 (39), 122 (100).

2-(4-Fluorophenyl)hexanohydroximoyl Chloride (8r): ^{1}H NMR ($CDCl_3$): 8.93 (s br, 1H), 7.26 (dd, 2H, J = 8.30, 5.40), 7.01 (dd, 2H, J = 8.30, 5.40), 3.78 (t, 1H, J = 7.60), 2.14-2.04 (m, 1H), 1.88-1.79 (m, 1H), 1.36-1.19 (m, 4H), 0.87 (d, 3H, J = 7.10). ^{13}C NMR ($CDCl_3$): 162.09 (d, J = 246.3), 144.89, 134.60 (d, J = 3.7), 129.54 (d, J = 7.4), 115.42 (d, J = 20.2), 51.43, 31.99, 29.25, 22.30, 13.78. MS *m/z* (relative intensity) 245 ($(M+2)^+$, 4), 243 (M^+, 12), 208 (18), 187 (31), 170 (31), 150 (33), 135 (43), 109 (100), 57 (12). HRMS calcd for $C_{12}H_{15}NOFCl$ 245.0797, found 245.0812; calcd 243.0826, found 243.0816.

2-(4-Trifluoromethoxylphenyl)propanohydroximoyl Chloride (8s): ^{1}H NMR ($CDCl_3$): 8.50 (s br, 1H), 7.32 (d, 2H, J = 8.60), 7.18 (d, 2H, J = 8.60), 3.99 (q, 1H, J = 7.00), 1.57 (d, 3H, J = 7.00). ^{13}C NMR ($CDCl_3$): 148.58 (q, J = 1.9), 145.10, 138.79, 129.02, 121.17, 120.48 (d, J = 258.2), 46.14, 18.56. MS *m/z* (relative intensity) 269 ($(M+2)^+$, 12), 267 (M^+, 44), 233 (18), 214 (34), 189 (100), 78 (2), 69 (18). HRMS calcd for $C_{10}H_9NO_2F_3Cl$ 269.0244, found 269.0268; calcd 267.0274, found 267.0288.

2-(4-Trifluoromethoxylphenyl)hexanohydroximoyl Chloride (8t): ^{1}H NMR ($CDCl_3$): 8.55 (s br, 1H), 7.33 (d, 2H, J = 8.20), 7.18 (d, 2H, J = 8.20), 3.80 (t, 1H, J = 7.60), 2.20-2.02 (m, 1H), 2.20-2.02 (m, 1H), 1.93-1.79 (m, 1H), 1.40-1.20 (m, 4H), 0.88 (t, 3H, J = 6.80). ^{13}C NMR ($CDCl_3$): 148.60 (q, J = 1.5), 144.36, 137.75, 129.46, 121.17, 120.47 (d, J = 258.0), 51.58, 31.96, 29.22, 22.26, 13.71. MS *m/z* (relative intensity) 311 ($(M+2)^+$, 4), 309 (M^+, 14), 274 (23), 252 (44), 224 (6), 175 (100), 85 (3), 57 (12). HRMS calcd for $C_{13}H_{15}NO_2F_3Cl$ 311.0714, found 311.0688; calcd 309.0743, found 309.0736.

4. General Procedure for the Preparation of Carboxylic Acids 9a-i by Using of 85% Sulfuric Acid (equation 4 and Table III). The preparation of **9a** from **2a** will serve to illustrate the general procedure utilized. β-Nitrostyrene **2a** (2 mmol) in 10 mL dry ether or THF was added to 10 mmol of benzylmagnesium chloride in 30 mL of ether or THF at -20 °C. Within 10 min, the solution was added to ice cold concd (85%) sulfuric acid and the solution was stirred 30 min. The solution was extracted with CH_2Cl_2, dried over $MgSO_4$, filtered and concentrated to give the product **9a**. The yield (31%) was based on NMR by using toluene or dibromomethane as an internal standard. The residue was purified by flash column chromatography on silica gel using hexane-ethyl acetate as eluent to obtain pure product. When substrate **1a** was used, the isolated products were hydroximoyl halides **6a-c** and/or nitrile oxides **7a-d** under the same workup procedures.

2,3-Diphenylpropionic Acid (9a): mp 77-78 °C. ^{1}H NMR ($CDCl_3$): 7.19-7.07 (m, 10H), 3.84 (dd, 1H, J = 8.30, 7.32), 3.39 (dd, 1H, J = 13.68, 8.30), 3.01 (dd, 1H, J = 13.68, 7.32). ^{13}C NMR ($CDCl_3$): 178.79, 138.65, 128.88, 128.68, 128.35, 128.06, 127.60, 126.43, 53.28, 39.20. MS *m/z* (relative intensity) 226 (M^+, 33), 178 (3), 165 (3), 118 (6), 91 (100), 77 (6). HRMS calcd for $C_{15}H_{14}O_2$ 226.0944, found 226.1006.

2-Phenylpropionic Acid (9b): mp 62 °C. ^{1}H NMR ($CDCl_3$): 11.98 (s br, 1H), 7.27-7.15 (m, 5H), 3.69(q, 1H, J = 7.32), 1.44 (d, 3H, J = 7.32). ^{13}C NMR ($CDCl_3$): 181.03, 139.52, 128.42, 127.59, 127.34, 45.15, 17.76. MS *m/z* (relative intensity) 150 (M^+, 67), 178 (3), 105 (100), 77 (32). HRMS calcd for $C_9H_{10}O_2$ 150.0861, found 150.0675.

2-Phenylpentionic Acid (9c): mp 77 °C. ^{1}H NMR ($CDCl_3$): 7.34-7.22 (m, 5H), 3.57(t, 1H, J = 7.82), 2.02-1.76 (m, 2H), 1.32-1.25 (m, 2H), 0.93 (t, 3H, J = 7.32). ^{13}C NMR ($CDCl_3$) 180.62, 138.52, 128.61, 127.38, 51.34, 35.14, 20.64, 13.74. MS *m/z* (relative intensity) 178 (M^+, 31), 136 (54), 118 (11), 91 (100), 77 (9). HRMS calcd for $C_{11}H_{14}O_2$ 178.0994, found

178.0987.

3-Methyl-2-phenylbutionic acid (9d): mp 85 °C. ^{1}H NMR ($CDCl_3$): 7.33-7.23 (m, 5H), 3.11(d, 1H, *J* = 10.25), 2.32-2.28 (m, 1H), 1.06 (d, 3H, *J* = 6.35), 0.68 (d, 3H, *J* = 6.35). ^{13}C NMR ($CDCl_3$): 180.22, 137.81, 128.57, 128.48, 127.38, 60.10, 31.52, 21.42, 20.09. MS *m/z* (relative intensity) 178 (M^+, 59), 136 (100), 118 (35), 91 (31), 77 (3). HRMS calcd for $C_{11}H_{14}O_2$ 178.0994, found 178.0989.

3,3-Dimethyl-2-phenylbutionic Acid (9e): mp 98 °C. ^{1}H NMR ($CDCl_3$): 7.41-7.26 (m, 5H), 2.91(s, 1H), 0.98 (s, 9H). ^{13}C NMR ($CDCl_3$): 171.51, 135.96, 129.83, 127.86, 127.26, 59.33, 34.74, 27.95. MS *m/z* (relative intensity) 192 (M^+, 2), 175 (14), 151 (100), 147 (69), 134 (44), 105 (59), 91 (58), 77 (7), 57 (16). HRMS calcd for $C_{12}H_{16}O_2$ 192.2600, found 192.2604.

2-(4-Fluorophenyl)propionic Acid (9f): ^{1}H NMR ($CDCl_3$): 7.30-7.01 (m, 4H), 3.74 (q, 1H, *J* = 7.32), 0.98 (d, 3H, *J* = 7.32). ^{13}C NMR ($CDCl_3$): 180.58, 162.08 (d, *J* = 246.3), 135.36, 129.16 (d, *J* = 7.4), 115.48 (d, *J* = 22.1), 44.56, 18.17. MS *m/z* (relative intensity) 168 (98), 123 (100), 103 (91), 77 (28). HRMS calcd for $C_9H_9O_2F$ 168.0587, found 168.0579.

3-Methyl-2-(4-trifluoromethoxyphenyl)butionic Acid (9g): ^{1}H NMR ($CDCl_3$): 7.37-7.15 (m, 4H), 3.15(d, 1H, *J* = 10.25), 2.31-2.27 (m, 1H), 1.07 (d, 3H, *J* = 6.84), 0.70 (d, 3H, *J* = 6.84). ^{13}C NMR ($CDCl_3$): 179.47, 145.28, 136.31, 129.93, 120.95, 120.22 (q, *J*= 257.4), 59.19, 31.79, 21.33, 20.03. MS *m/z* (relative intensity) 262 (M^+, 56), 220 (100), 202 (39), 175 (88), 77 (19). HRMS calcd for $C_{12}H_{13}O_3F_3$ 262.0817, found 262.0812.

2-(1-Naphthyl)-3-phenylpropionic Acid (9h): ^{1}H NMR ($CDCl_3$): 8.11-7.15 (m, 12H), 4.68 (dd, 1H, *J* = 8.79, 5.86), 3.59 (dd, 1H, *J* = 13.92, 8.79), 3.45 (dd, 1H, *J* = 13.92, 5.86). ^{13}C NMR ($CDCl_3$): 179.40, 139.02, 134.28, 133.99, 131.33, 128.99, 128.80, 128.43, 128.21, 126.49, 125.70, 125.45, 125.19, 122.96, 48.65, 38.82. MS *m/z* (relative intensity) 276 (M^+, 100), 185 (97), 157 (19), 129 (33), 91 (76). HRMS calcd for $C_{19}H_{16}O_2$ 276.1150, found 276.1149.

3,3-Dimethyl-2-(1-naphthyl)butionic Acid (9i): ^{1}H NMR ($CDCl_3$): 8.19-7.26 (m, 7H), 4.54(d, 1H), 1.08 (s, 9H). ^{13}C NMR ($CDCl_3$): 177.97, 133.97, 132.83, 131.97, 129.08, 128.01, 127.13, 126.18, 125.32, 124.80, 123.51, 52.99, 35.42, 28.13. MS *m/z* (relative intensity) 242 (M^+, 28), 186 (100), 168 (36), 141 (41), 115 (7), 57 (20). HRMS calcd for $C_{12}H_{18}O_2$ 242.1307, found 242.1303.

5. General Procedure for the Preparation of Compounds 10 and 11 (equation 5). To a sitrred solution of the nitroalkane **3a** (2 mmol) in THF 20 mL, cooled to 0 °C, was added potassium *tert*-butoxide (3 mmol) in THF 20 mL. After stirring 30 min, the solution was slowly added to 85% aqueous H_2SO_4 and stirred 30 min. The solution was extracted with CH_2Cl_2 and washed with brine, dried over $MgSO_4$ and the solvent was evaporated then the residue was purified by flash column chromatography on silica gel using hexane/ethyl acetate as eluent to obtain pure

compounds **10** (38%), **11** (36%) and 5% of unreacted starting material **3a**. When the same nitronate was added to the concd HCl aqueous and workup as previously described to obtain 91% of **6a** and 7% of unreacted starting material **3a**.

α,α,β-Triphenylpropanohydroxamic Acid (10): mp 110-111 °C. ^{1}H NMR ($CDCl_3$): 8.44 (s, 1H), 8.21 (s, 1H), 7.25-7.03 (m, 13H), 6.79 (d, 2H, *J* = 7.33), 3.74 (s, 2H). ^{13}C NMR ($CDCl_3$): 172.06, 141.15, 137.13, 131.13, 129.27, 128.19, 127.61, 127.42, 126.41, 60.76, 44.12. MS *m/z* (relative intensity) 317 (M^+, 71), 285 (9), 257 (35), 226 (79), 198 (98), 178 (67), 165 (100), 91 (74), 77 (23). IR (cm^{-1}) 3283, 1638. Anal. Calcd for $C_{21}H_{19}NO_2$: C, 79.47; H, 6.03; N, 4.41. Found: C, 79.21; H, 6.16; N, 4.32.

2,2-Diphenyl-1-indanone Oxime (11): mp 186-187 °C. ^{1}H NMR ($CDCl_3$): 8.56 (s, 1H), 8.34 (d, 2H, *J* = 7.32), 7.39-6.97 (m, 12H), 3.89 (s, 2H). ^{13}C NMR ($CDCl_3$): 163.70, 145.91, 145.01, 132.96, 131.28, 129.78, 128.50, 128.08, 127.26, 126.45, 124.77, 59.13, 48.31. MS *m/z* (relative intensity) 299 (M^+, 15), 282 (100), 265 (11), 204 (40), 165 (15), 140 (4), 77 (3). Anal. Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.72; N, 4.68. Found: C, 83.86; H, 5.76; N, 4.65.

6. General Procedure for the Preparation of the 2-Isoxazoline by Reaction of Nitrile Oxide with a Dipolarophile (equations 6 and 7). Nitrile oxide **7a** (1 mmol) and diethyl fumarate or diethyl maleate (3 mmol) in 20 mL THF reflux 2 hours then evaporated the solvent to obtain oily mixture. The residue was purified by flash column chromatography on silica gel using hexane/ethyl acetate as eluent to obtain pure product **12** (95%) or **13** (93%).

***trans*-4,5-Diethyl 3-(1,1,2-triphenylethyl)-2-isoxazoline-4,5-dicarboxylate (12):** ^{1}H NMR ($CDCl_3$): 7.36-6.55 (m, 15H), 5.19 (d, 1H, *J* = 4.39), 4.18 (q, 2H, *J* = 7.32), 3.91 (d, 1H, *J* = 4.39), 3.89 (d, 1H, *J* = 13.67), 3.81 (d, 1H, *J* = 13.67), 3.62-3.58 (m, 1H), 3.46-3.42 (m, 1H), 1.24 (t, 3H, *J* = 7.32), 0.92 (t, 3H, *J* = 7.32). ^{13}C NMR ($CDCl_3$): 168.88, 167.65, 159.28, 140.17, 139.53, 136.89, 131.21, 129.76, 129.63, 127.99, 127.59, 127.33, 127.20, 127.11, 126.12, 82.25, 62.11, 61.84, 58.05, 56.37, 45.67, 14.03, 13.36. MS (isobutane) *m/z* (relative intensity) 471 (M^+, 24), 380 (14), 278 (24), 204 (100), 165 (30), 91 (20), 77 (3). CIMS *m/z* 472 ($M+1^+$). HRMS calcd for $C_{29}H_{29}NO_5$ 471.2045, found 471.2026. Anal. Calcd: C, 73.87; H, 6.20; N, 2.97. Found: C, 73.24; H, 6.30; N, 2.83.

***cis*-4,5-Diethyl 3-(1,1,2-triphenylethyl)-2-isoxazoline-4,5-dicarboxylate (13):** ^{1}H NMR ($CDCl_3$): 7.33-6.56 (m, 15H), 5.10 (d, 1H, *J* = 10.26), 4.19 (q, 2H, *J* = 6.84), 3.91 (d, 1H, *J* = 10.26), 3.88 (d, 1H, *J* = 13.67), 3.79 (d, 1H, *J* = 13.67), 3.52-3.45 (m, 2H), 1.25 (t, 3H, *J* = 6.84), 0.94 (t, 3H, *J* = 6.84). ^{13}C NMR ($CDCl_3$): 166.96, 166.41, 160.94, 140.33, 139.34, 136.82, 131.28, 129.94, 129.60, 128.12, 127.60, 127.42, 127.28, 127.22, 126.14, 82.10, 61.91, 61.57, 56.90, 56.61, 45.36, 13.98, 13.41. MS *m/z* (relative intensity) 471 (M^+, 20), 380 (22), 307 (11), 278 (53), 233 (15), 204 (100), 165 (28), 91 (24), 77 (2). HRMS calcd for $C_{29}H_{29}NO_5$ 471.2045, found 471.2039.

7. General Procedure for the Preparation of the 2-Isoxaxoline by Reaction of Nitroalkane 3a with Dipolarophile and PhNCO/Et_3N (Mukaiyama-Hoshino Method). To 20 mL of dry THF containing 2.2 mmol of phenyl isocyanate and 3 mmol of diethyl fumarate or diethyl maleate was added to a solution of 1 mmol nitroalkane **3a** and 20 drops of triethylamine in 20 mL of dry THF. After stirring the solution for 30 min, it was reflux 2 hours, cooled and filtered. The solvent was evaporated and the residue was purified by flash column chromatography on silica gel using hexane/ethyl acetate as eluent to obtain pure product **12** (35%) or **13** (60%) and all the spectral data were consistent with those previously reported.

8. General Procedure for the Preparation of the Isoxazole 14 or Furoxan 15 by Reaction of Hydroximoyl Chloride 8e with or without Phenylacetylene in the Presence of Triethylamine (equations 8 and 9). Triethyl amine 3 mmol in 20 mL CH_2Cl_2 was slowly added to the the 20 mL CH_2Cl_2 solution which contained hydroximoyl chloride **8e** (1 mmol) and phenylacetylene (10 mmol) and the solution was stirred overnight then the solvent was evaporated to obtain oily mixture. The residue was purified by flash column chromatography on silica gel using hexane/ethyl acetate as eluent to obtain pure product **14** (92%). Almost quantative yield of **15** was generated when hydroximoyl chloride **8e** was treated with triethyl amine only.

3-(2-methyl-1-(2-thienyl)propyl)-5-phenylisoxazole (14): mp 88 °C ^1H NMR ($CDCl_3$): 7.78-6.90 (m, 8H), 6.48 (s, 1H), 4.19 (d, 1H, J = 9.53), 2.45-2.27 (m, 1H), 1.00 (d, 3H, J = 7.33), 0.94 (t, 3H, J = 6.84). ^{13}C NMR ($CDCl_3$): 169.79, 166.17, 144.44, 130.11, 128.94, 127.59, 126.69, 125.83, 125.62, 124.16, 98.51, 46.47, 33.86, 20.98. MS *m/z* (relative intensity) 283 (M^+, 41), 240 (100), 211 (27), 178 (5), 136 (33), 105 (33), 97 (15), 77 (22). HRMS calcd for $C_{17}H_{17}NOS$ 283.1031, found 283.1040. Anal. Calcd for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94. Found: C, 71.29; H, 5.96; N, 5.02.

Di(2-methyl-1-(2-thienyl)propyl)furoxan (15): mp 117 °C ^1H NMR ($CDCl_3$): 7.26-6.83 (m, 6H), 3.85 (d, 1H, J = 9.27), 3.71 (d, 1H, J = 11.23), 3.87-2.63 (m, 1H), 2.62-2.51 (m, 1H), 0.98-0.84 (m, 9H), 0.71 (d, 3H, J = 6.84). ^{13}C NMR ($CDCl_3$): 158.93, 141.14, 139.44, 127.02, 126.67, 126.60, 126.25, 125.19, 124.77, 116.69, 45.78, 43.15, 32.63, 29.67, 21.46, 21.30, 20.93, 20.73. MS *m/z* (relative intensity) 362 (M^+, 9), 345 (11), 319 (14), 277 (5), 235 (6), 139 (100), 111 (16), 97 (69), 77 (6). Anal. Calcd for $C_{18}H_{22}N_2O_2S$: C, 59.64; H, 6.12; N, 7.73. Found: C, 59.72; H, 6.11; N, 7.58.

9. General Procedure for the Preparation of the 2-Isoxazoline and Isoxazole by Reaction of Hydroximoyl Iodide 6g with Phenylacetylene and Acrylnitrile in the Presence of Triethylamine (equation 10). Triethyl amine 3 mmol in 20 mL CH_2Cl_2 was quickly added to the the 20 mL CH_2Cl_2 solution which contained hydroximoyl iodide **6g** (1 mmol), phenylacetylene (10 mmol) and acrylnitrile (10 mmol) and the solution was stirred 1 min then the solvent was evaporated to obtain oily mixture. The residue was purified by flash column chromatography on silical gel using hexane/ethyl acetate as eluent to obtain pure product **16** (85%) and **17** (12%).

5-Cyano-3-(1,1-diphenylethyl)-2-isoxazoline (16): mp 120 °C. ^{1}H NMR ($CDCl_3$): 7.38-7.20 (m, 10H), 5.18 (dd, 1H, J = 9.71, 6.22), 3.20 (dd, 1H, J = 17.22, 6.22), 3.14 (dd, 1H, J = 17.22, 9.71), 2.02 (s, 3H). ^{13}C NMR ($CDCl_3$): 163.69, 144.17, 143.13, 128.65, 128.57, 127.91, 127.59, 127.42, 127.27, 117.22, 66.43, 49.95, 42.31, 28.03. MS *m/z* (relative intensity) 276 (M^+, 5), 261 (16), 220 (71), 165 (79), 118 (100), 77 (33). Anal. Calcd for $C_{18}H_{16}N_2O$: C, 78.24; H, 5.84; N, 10.14. Found: C, 77.91; H, 5.82; N, 9.85.

3-(1,1-Diphenylethyl)-5-phenylisoxazole (17): mp 105 °C. ^{1}H NMR ($CDCl_3$): 7.73-7.68 (m, 2H), 7.40-7.21 (m, 13H), 6.25 (s, 1H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$): 170.60, 169.43, 146.60, 130.01, 128.87, 128.21, 128.07, 127.51, 126.67, 125.75, 100.35, 48.89, 28.40. MS *m/z* (relative intensity) 325 (M^+, 100), 310 (23), 220 (12), 195 (38), 182 (8), 105 (9). HRMS calcd for $C_{25}H_{19}NO$ 325.1466, found 325.1456. Anal. Calcd for $C_{23}H_{19}NO$: C, 84.89; H, 5.88; N, 4.30. Found: C, 84.91; H, 5.68; N, 4.30.

10. General Procedure for the Synthesis of the [n,3,0] Bicyclic (n = 3 or 4) Compounds under the One-Pot Conditions (equations 11). β-Nitrostyrene **2a** 1.0 mmol in 20 mL dry THF or diethyl ether was slowly added to the 4-pentene-1-magnesium bromide 1.2 mmol in 20 mL THF or diethyl ether solution at -20 °C. After stirring 30 min, the solution was slowly added to 50 mL of ice cold concd hydrobromic acid and stirred 30 min. The solution was extracted with CH_2Cl_2 and washed with brine then few drops of Et_3N were added to the mixture to obtain the final product [4,3,0] bicyclic compound. After the solvent was evaporated, the crude NMR analysis found that the oily mixture contained two major components and the total yield was 88% and the ratio of the *cis/trans* was 4.5/1. Flash column chromatography was used to obtain the pure products **25**. The intermediate **20** also could be isolated after the solvent CH_2Cl_2 was evaporated in the absence of the Et_3N and the mixture was purified by the flash column chromatography. Similar procedures were repeated when 1-lithio-4-pentene was used to react with β-Nitrostyrene **1a**, **2a**, and **2b**, respectively.

2-Phenyl-6-heptenohydroximoyl Bromide (20): ^{1}H NMR ($CDCl_3$): 8.90(s, 1H), 7.42-7.20 (m, 5H), 5.81-5.71 (m, 1H), 5.03-4.94 (m, 2H), 3.86 (t, 1H, J = 9.53), 2.18-1.78 (m, 4H), 1.50-1.26 (m, 2H). ^{13}C NMR ($CDCl_3$): 139.02, 138.56, 138.14, 128.54, 128.12, 127.40, 114.89, 53.96, 33.33, 32.38, 26.42. MS *m/z* (relative intensity) 283 ($(M+2)^+$, 2), 281 (M^+, 3), 202 (60), 185 (24), 170 (37), 143 (33), 117 (61), 102 (37), 91 (100), 77 (23). HRMS calcd for $C_{13}H_{13}NOBr$ 283.0395, found 283.0416; calcd 281.0415, found 281.0414.

2-(2-Thienyl)-6-heptenohydroximoyl Bromide (21): ^{1}H NMR ($CDCl_3$): 8.35 (s, 1H), 7.23 (d, 1H, J = 3.42), 6.97 (dd, 1H, J = 3.42, 2.64), 6.95 (d, 1H, J = 2.64), 5.81-5.74 (m, 1H), 5.05-4.96 (m, 2H), 4.15 (dd, 1H, J = 6.84, 6.35), 2.22-1.84 (m, 4H), 1.52-1.36 (m, 2H). ^{13}C NMR ($CDCl_3$): 142.38, 138.03, 137.81, 126.73, 125.65, 124.70, 115.02, 48.56, 33.46, 33.18, 26.67. MS *m/z* (relative intensity) 289 ($(M+2)^+$, 5), 287 (M^+, 5), 272 (7), 270 (7), 256 (7), 254 (8), 220 (13), 218 (14), 208 (55), 177 (29), 149 (38), 138 (85), 123 (65), 108 (26), 97 (100).

HRMS calcd for $C_{11}H_{14}NOSBr$ 286.9980, found 287.0002.

3a,4,5-Trihydro-6,6-diphenyl-3*H*-cyclopenta[c]isoxazole (23): mp 87 °C. ^{1}H NMR ($CDCl_3$): 7.40-7.12 (m, 10H), 4.69-4.53 (m, 1H), 4.00-3.78 (m, 2H), 3.11-2.88 (m, 2H), 2.18-2.01 (m, 1H), 1.85-1.67 (m, 1H). ^{13}C NMR ($CDCl_3$): 174.63, 144.22, 143.66, 128.86, 128.27, 127.61, 127.26, 127.03, 126.64, 75.45, 53.89, 53.67, 43.95, 25.27. MS *m/z* (relative intensity) 263 (M^+, 5), 233 (100), 206 (19), 178 (37), 165 (67), 130 (25), 115 (33), 105 (16), 91 (14), 77 (16). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 81.97; H, 6.49; N, 5.25.

3,3a,4,5,6-Pentahydro-7,7-diphenylcyclohexa[c]isoxazole (24): mp 117-118 °C. ^{1}H NMR ($CDCl_3$): 7.43-7.06 (m 10H), 4.57 (dd, 1H, *J* = 10.62, 7.88), 3.90 (dd, 1H, *J* = 10.44, 7.85), 3.32-3.22 (m, 1H), 2.83-2.76 (m, 1H), 2.38-2.22 (m, 1H), 2.11-2.01 (m, 1H), 1.85-1.68 (m, 1H), 1.62-1.45 (m, 2H). ^{13}C NMR ($CDCl_3$): 174.63, 144.22, 143.66, 128.86, 128.27, 127.61, 127.26, 127.03, 126.64, 75.45, 53.89, 53.67, 43.95, 25.27. MS *m/z* (relative intensity) 277 (M^+, 12), 247 (100), 219 (63), 179 (33), 165 (68), 144 (76), 115 (34), 103 (18), 91 (20), 77 (13). HRMS calcd for $C_{19}H_{19}NO$ 277.1467, found 277.1476. Anal. Calcd: C, 82.28; H, 6.91; N, 5.05. Found: C, 82.72; H, 6.73; N, 4.79.

***cis*-3,3a,4,5,6,7-Hexahydro-7-phenylcyclohexa[c]isoxazole (25):**[16b] mp 78 °C. ^{1}H NMR ($CDCl_3$): 7.38-7.21 (m, 5H), 4.55 (dd, 1H, *J* = 10.54, 7.87), 3.90 (dd, 1H, *J*= 10.34, 7.88), 3.51 (dd, 1H, *J*= 12.30, 4.94), 3.39-3.20 (m, 1H), 2.27-1.41 (m, 6H). ^{13}C NMR ($CDCl_3$): 162.46, 139.73, 128.43, 128.34, 127.16, 73.63, 49.14, 44.58, 34.59, 32.16, 24.82. MS *m/z* (relative intensity) 201 (M^+, 61), 170 (100), 143 (53), 115 (20), 103 (21), 91 (28). HRMS calcd for $C_{13}H_{15}NO$ 201.1279, found 201.1270. Anal. Calcd: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.02; H, 7.36; N, 7.29.

***trans*-3,3a,4,5,6,7-Hexahydro-7-phenylcyclohexa[c]isoxazole (25):**[16b] ^{1}H NMR ($CDCl_3$): 7.40-7.20 (m, 5H), 4.50 (dd, 1H, *J*= 10.40, 8.00), 4.25 (d, 1H, *J*= 6.80), 3.87 (dd, 1H, *J*= 9.40, 8.00), 3.21 (qd, 1H, *J*= 10.40, 6.20), 2.58 (m, 1H), 2.14-1.38 (m, 5H). ^{13}C NMR ($CDCl_3$): 161.39, 138.74, 128.71, 127.27, 126.64, 73.66, 45.88, 37.74, 32.74, 29.86, 20.06. MS *m/z* (relative intensity) 202 ($(M+1)^+$, 100), 201 (M^+, 69), 171 (60), 170 (52) 143 (29), 115 (14), 103 (9), 91 (23).

***cis*-3,3a,4,5,6,7-Hexahydro-7-(2-thienyl)cyclohexa[c]isoxazole (26):** ^{1}H NMR ($CDCl_3$): 7.21 (dd, 1H, *J*= 5.00, 1.60), 7.03-6.95 (m, 2H), 4.55 (dd, 1H, *J*= 10.44, 7.87), 3.92-3.83 (m, 2H), 3.37-3.18 (m, 1H), 2.37-1.43 (m, 6H). ^{13}C NMR ($CDCl_3$): 161.38, 138.74, 128.71, 127.27, 126.64, 73.66, 45.88, 37.74, 32.74, 29.86, 20.06. MS *m/z* (relative intensity) 207 (M^+, 100), 176 (48), 149 (37), 135 (21), 109 (15), 97 (28). HRMS calcd for $C_{11}H_{13}NOS$ 207.0718, found 207.0717.

***trans*-3,3a,4,5,6,7-Hexahydro-7-(2-thienyl)cyclohexa[c]isoxazole (26):** ^{1}H NMR ($CDCl_3$): 7.21 (dd, 1H, *J*= 5.00, 1.20), 6.96 (dd, 1H, *J*= 5.00, 3.60), 6.85 (dd, 1H, *J*= 3.60, 1.20), 4.54 (dd, 1H, *J*= 10.60, 8.40), 4.40 (d, 1H, *J*= 5.20), 3.86 (dd, 1H, *J*= 9.60, 8.40), 3.35

(qd, *J*= 10.20, 6.20, 1H), 2.46-1.20 (m, 6H). ^{13}C NMR ($CDCl_3$): 160.40, 143.38, 127.05, 124.91, 124.26, 73.69, 45.23, 34.94, 32.32, 32.14, 20.04. MS *m/z* (relative intensity) 207 (M^+, 100), 176 (49), 150 (69), 149 (55), 135 (28), 122 (18), 109 (21), 97 (54). HRMS calcd for $C_{11}H_{13}NOS$ 207.0718, found 207.0727.

***cis*-3a,4,5,6-Tetrahydro-6-(*N*-phenyl-3-indolyl)-3*H*-cyclopenta[c]-isoxazole (27):** ^1H NMR ($CDCl_3$): 7.67-7.16 (m, 10H), 4.72-4.50 (m, 1H), 4.35 (dd, 1H, *J*= 10.20, 6.20), 4.06-3.87 (m, 2H), 2.95-2.75 (m, 1H), 2.51-2.34 (m, 1H), 2.25-2.06 (m, 1H), 1.80-1.65 (m, 1H). ^{13}C NMR ($CDCl_3$): 173.00, 139.65, 136.65, 129.52, 128.13, 126.29, 125.88, 124.28, 122.62, 120.06, 119.30, 115.36, 110.73, 75.26, 54.93, 37.13, 32.02, 26.11. MS *m/z* (relative intensity) 302 (M^+, 100), 273 (35), 244 (18), 232 (37), 219 (65), 206 (18), 165 (14), 115 (39), 77 (29). HRMS calcd for $C_{20}H_{18}N_2O$ 302.1419, found 302.1409.

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