#### **Supplementary Information**

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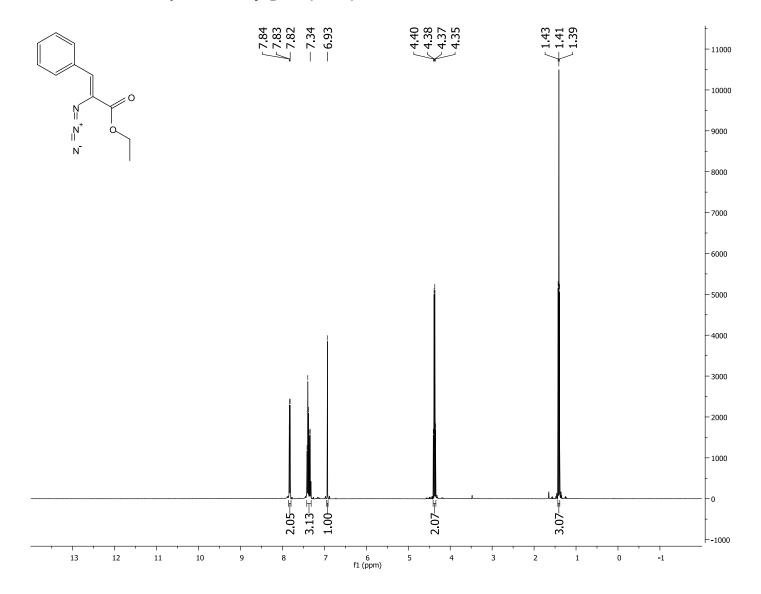
#### Experimental.

Nuclear magnetic resonance spectra were measured on a 400 MHz Varian (1-D measurements) and a Bruker AVIII HD 500 MHz (2-D measurements); chloroform-d was used as the solvent except where noted otherwise. Mass spectrometry measurements were performed by electron impact (EI) on a Micromass (Waters) Autospec M. Differential scanning calorimetry experiments were performed on a TA Instruments Q20 in hermetic pan/lid; samples were heated at a rate of 10°C/minute.

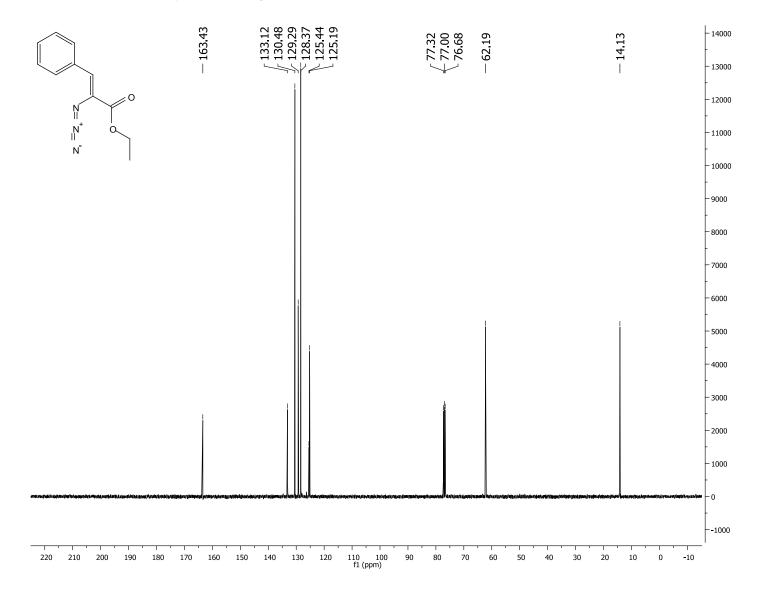
#### **Section 1:**

## <sup>1</sup>H, <sup>13</sup>C, and <sup>1</sup>H-<sup>13</sup>C-coupled NMR spectroscopies of ethyl α-azido-β-arylacrylates (2a-2j)

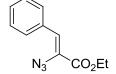
#### <sup>1</sup>H NMR: (Z)-Ethyl α-azido-β-phenylacrylate (2a)

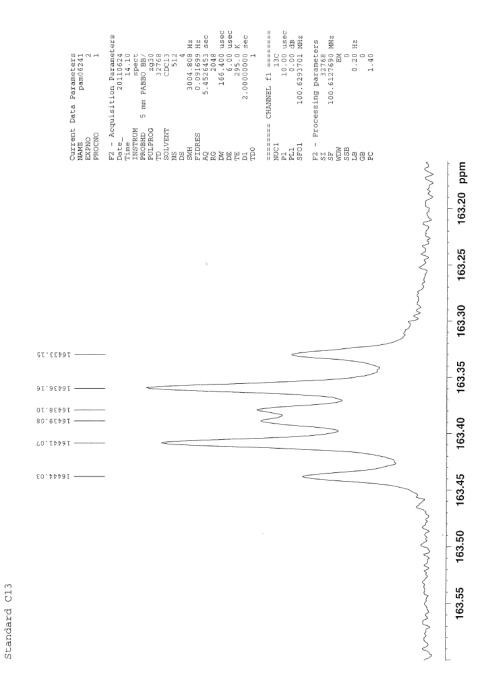


## $^{13}$ C NMR: (Z)-Ethyl α-azido-β-phenylacrylate (2a)

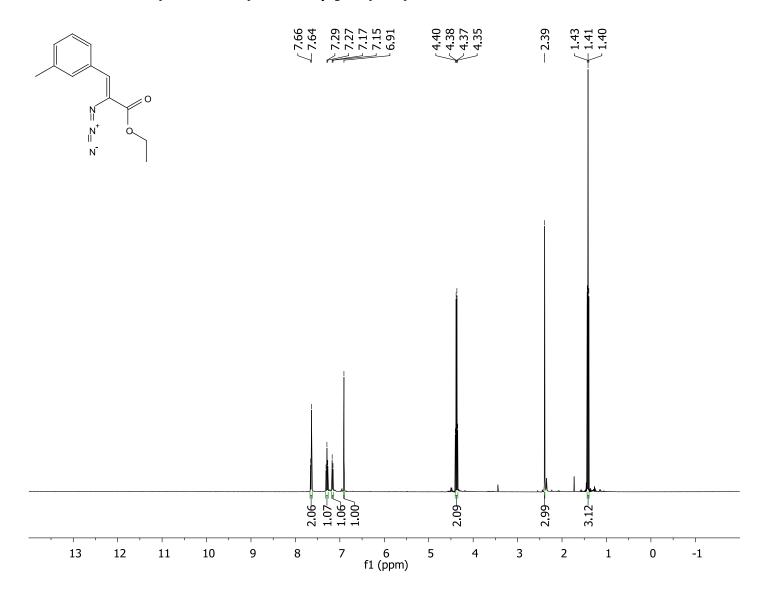


#### $^{3}J_{C,H}$ of $^{1}H-^{13}C$ Coupled NMR: (Z)-Ethyl $\alpha$ -azido- $\beta$ -phenylacrylate (2a)

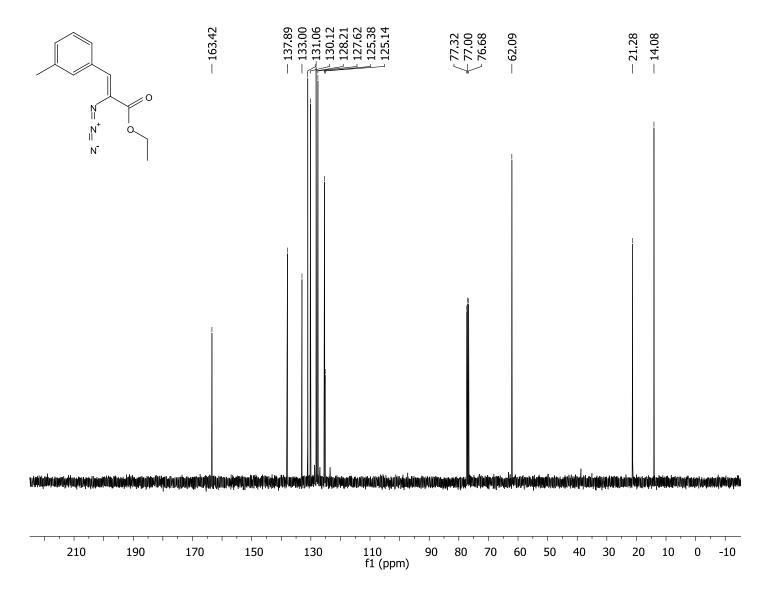




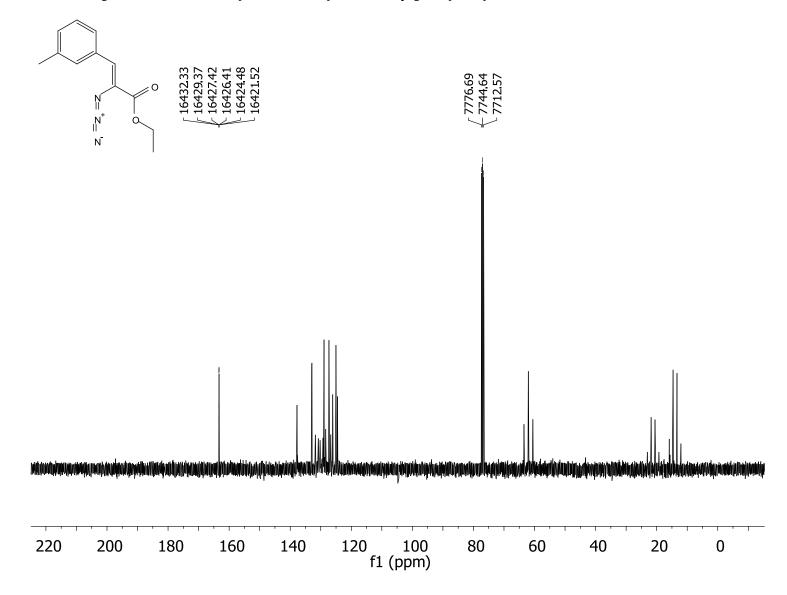
#### <sup>1</sup>H NMR: (Z)-Ethyl *meta*-methyl-α-azido-β-phenylacrylate (2b)



# $^{13}C$ NMR: (Z)-Ethyl $\textit{meta}\text{-methyl-}\alpha\text{-azido-}\beta\text{-phenylacrylate}$ (2b)

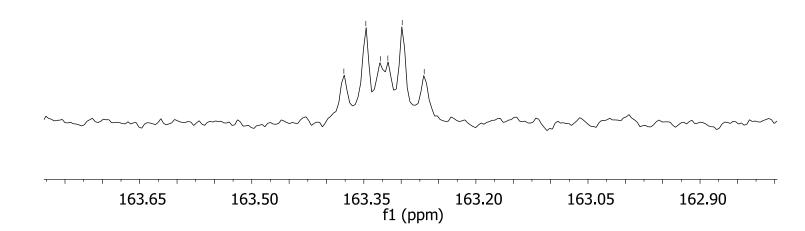


#### <sup>1</sup>H-<sup>13</sup>C Coupled NMR: (Z)-Ethyl *meta*-methyl-α-azido-β-phenylacrylate (2b)

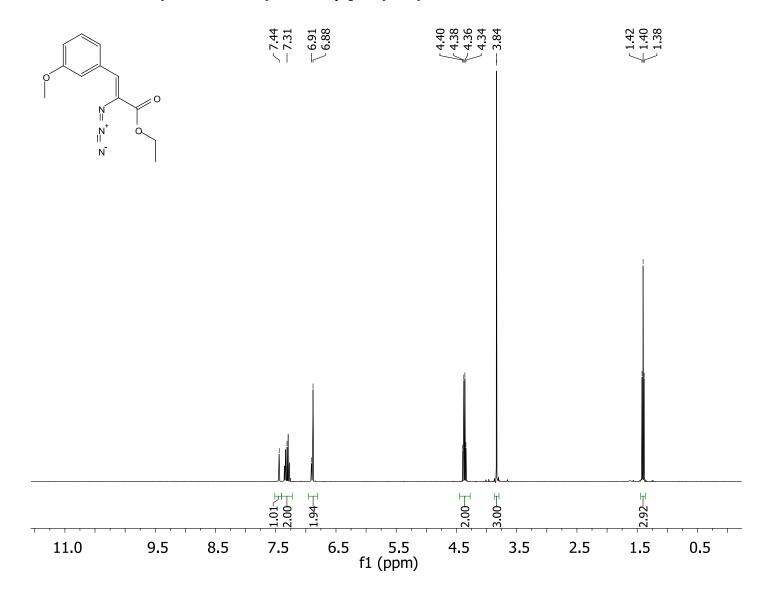


#### $^3J_{C,H}$ of $^1H$ - $^{13}C$ Coupled NMR: (Z)-Ethyl *meta*-methyl- $\alpha$ -azido- $\beta$ -phenylacrylate (2b)

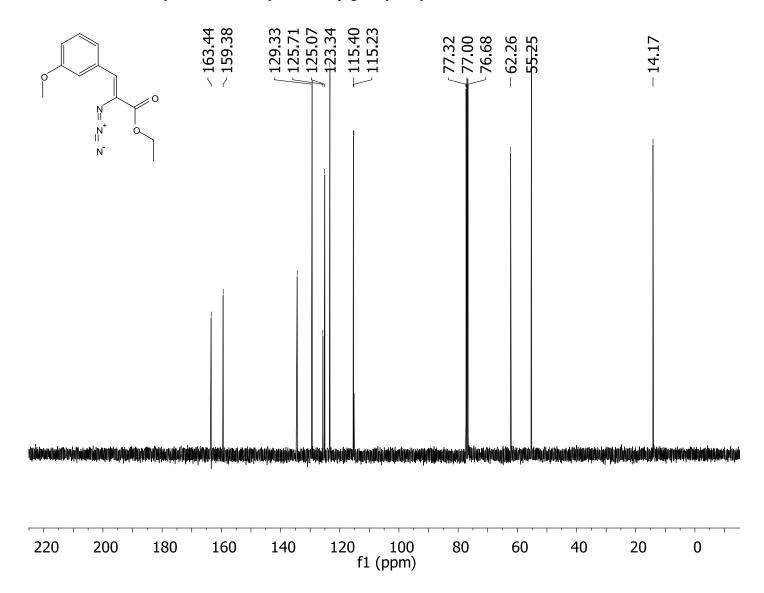




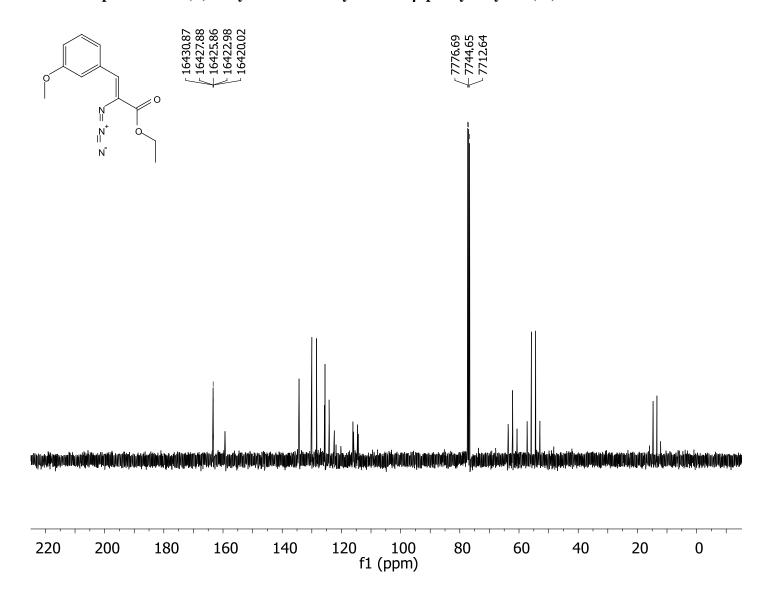
#### <sup>1</sup>H NMR: (Z)-Ethyl *meta*-methoxy-α-azido-β-phenylacrylate (2c)



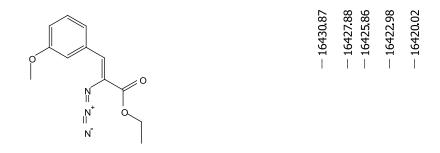
# $^{13}C$ NMR: (Z)-Ethyl $\textit{meta}\text{-methoxy-}\alpha\text{-azido-}\beta\text{-phenylacrylate}$ (2c)

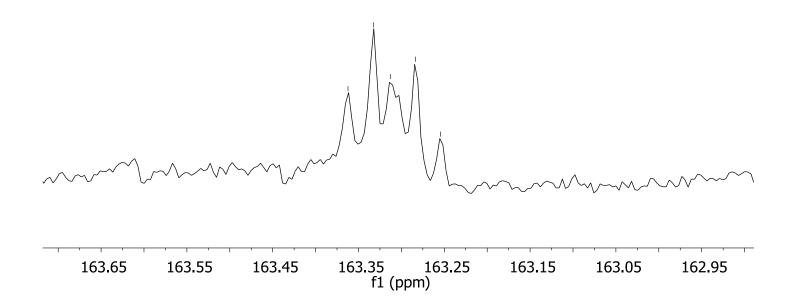


 $^{1}\text{H-}^{13}\text{C}$  Coupled NMR: (Z)-Ethyl *meta*-methoxy- $\alpha$ -azido- $\beta$ -phenylacrylate (2c)

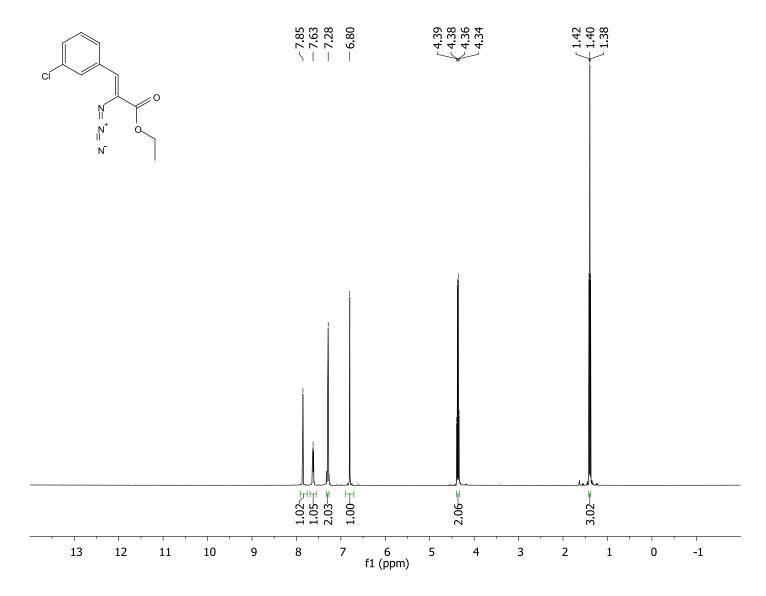


#### $^3J_{C,H}$ of $^1H$ - $^{13}C$ Coupled NMR: (Z)-Ethyl *meta*-methoxy- $\alpha$ -azido- $\beta$ -phenylacrylate (2c)

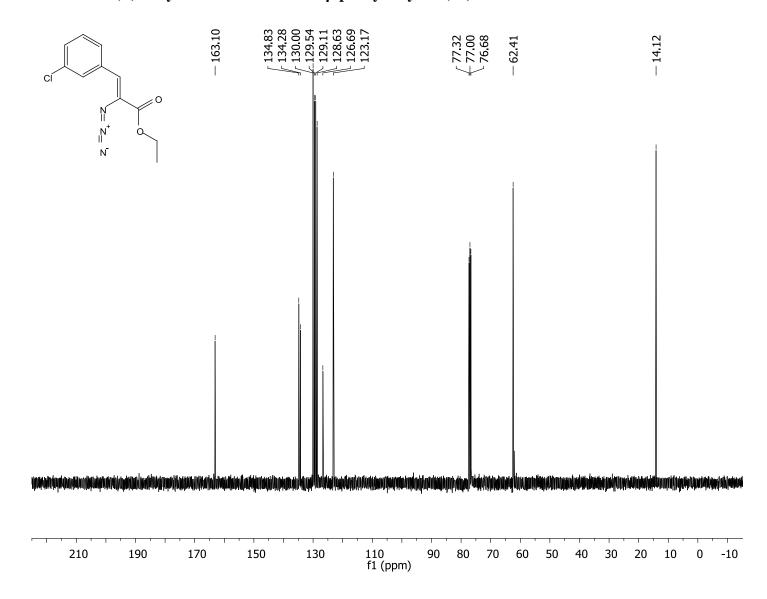


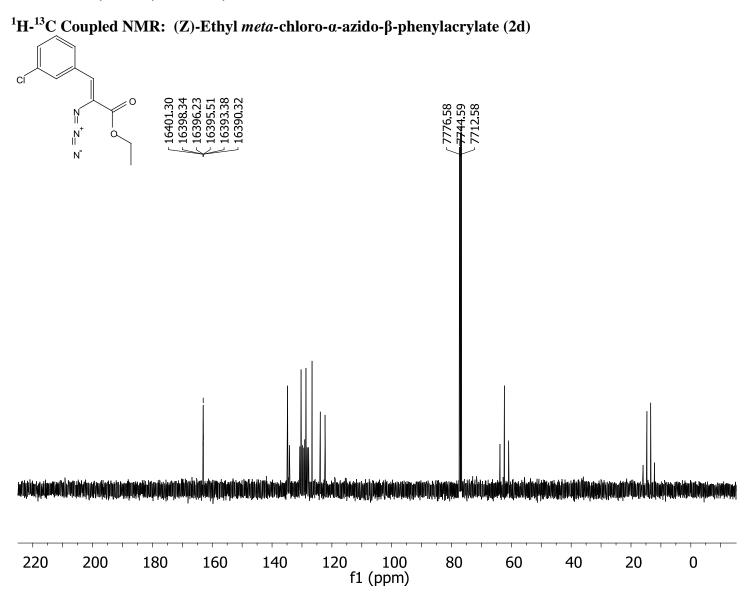


## $^{1}$ H NMR: (Z)-Ethyl *meta*-chloro-α-azido-β-phenylacrylate (2d)

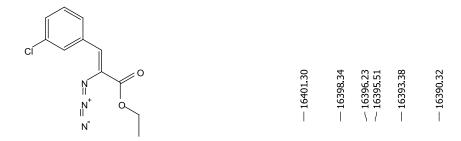


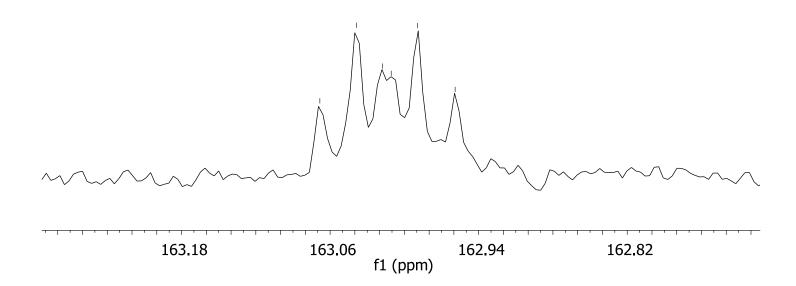
# $^{13}C$ NMR: (Z)-Ethyl meta-chloro- $\alpha$ -azido- $\beta$ -phenylacrylate (2d)



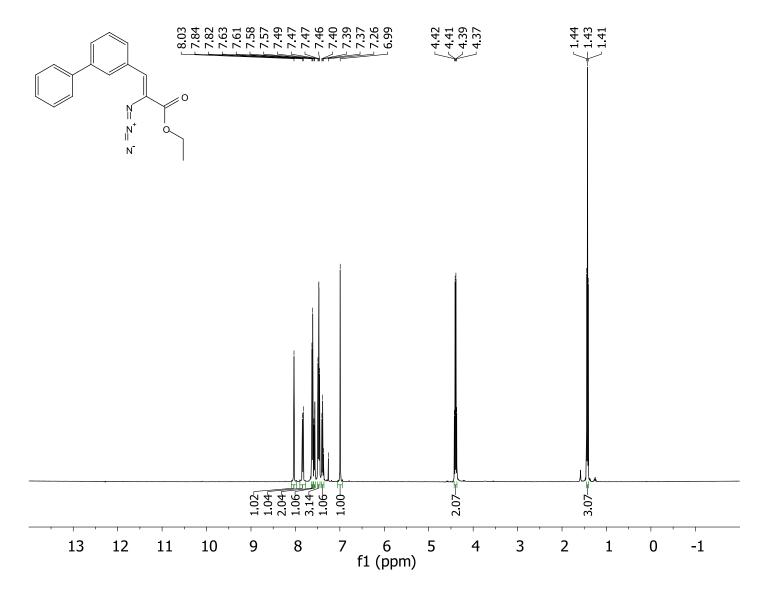


#### $^3J_{C,H}$ of $^1H$ - $^{13}C$ Coupled NMR: (Z)-Ethyl *meta*-chloro- $\alpha$ -azido- $\beta$ -phenylacrylate (2d)

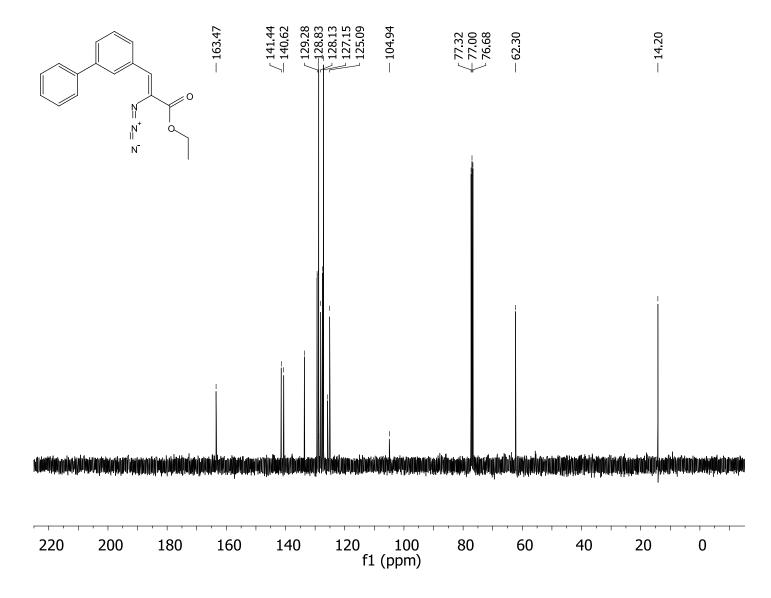




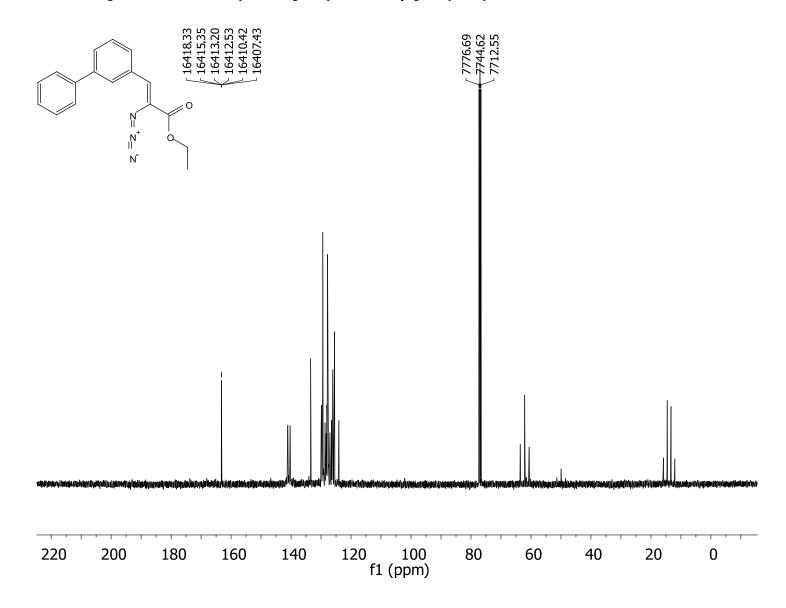
## <sup>1</sup>H NMR: Z)-Ethyl *meta*-phenyl-α-azido-β-phenylacrylate (2e)



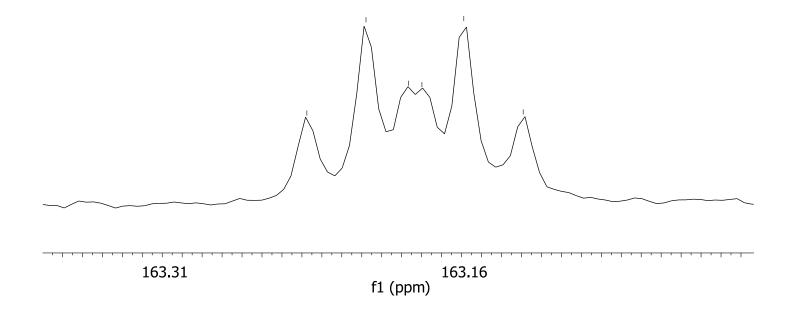
# $^{13}C$ NMR: Z)-Ethyl *meta*-phenyl- $\alpha$ -azido- $\beta$ -phenylacrylate (2e)



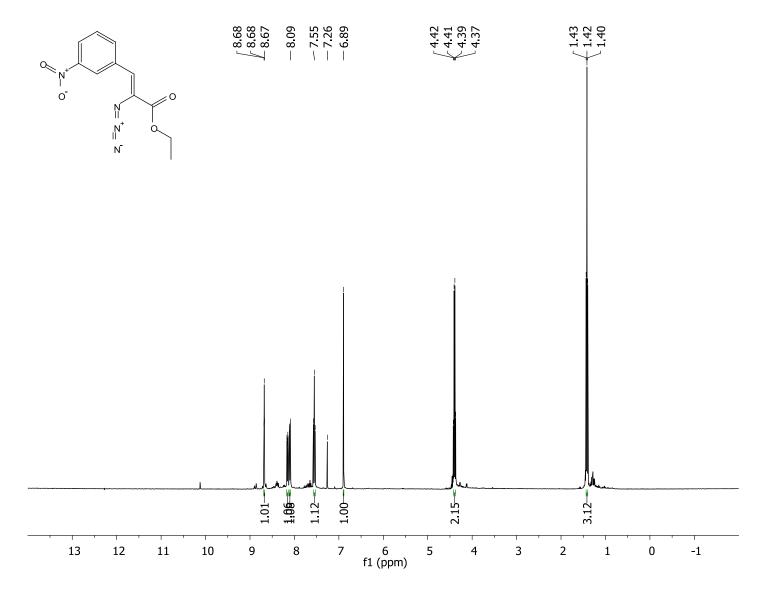
 $^{1}\text{H-}^{13}\text{C}$  Coupled NMR: Z)-Ethyl *meta*-phenyl- $\alpha$ -azido- $\beta$ -phenylacrylate (2e)



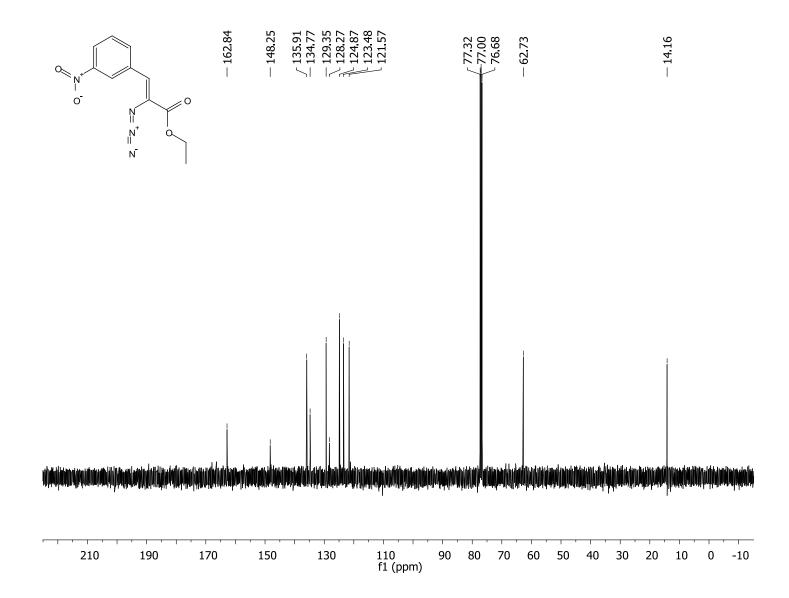
## $^3J_{C,H}$ of $^1H$ - $^{13}C$ Coupled NMR: Z)-Ethyl *meta*-phenyl- $\alpha$ -azido- $\beta$ -phenylacrylate (2e)



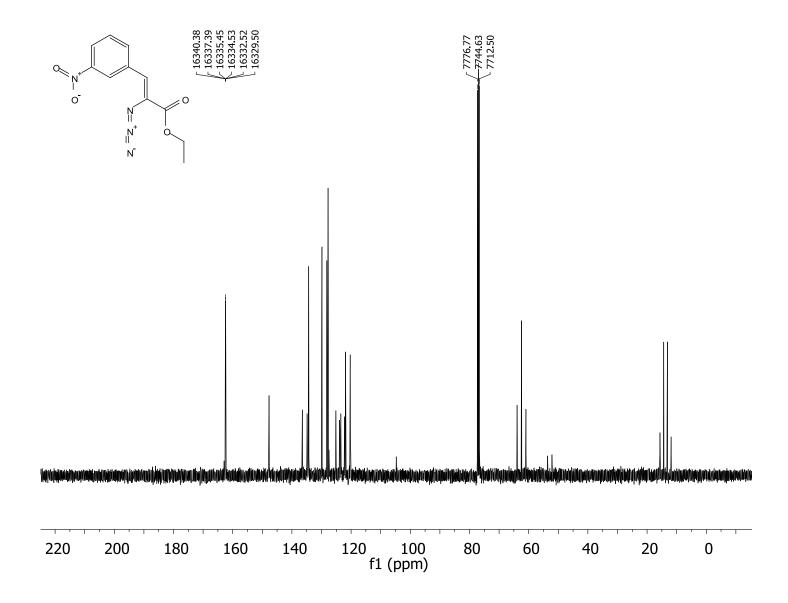
## <sup>1</sup>H NMR: (Z)-Ethyl *meta*-nitro-α-azido-β-phenylacrylate (2f)



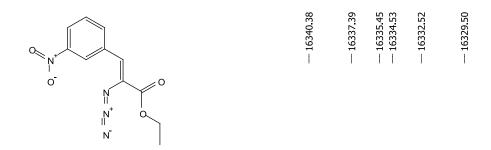
# $^{13}C$ NMR: (Z)-Ethyl meta-nitro- $\alpha$ -azido- $\beta$ -phenylacrylate (2f)

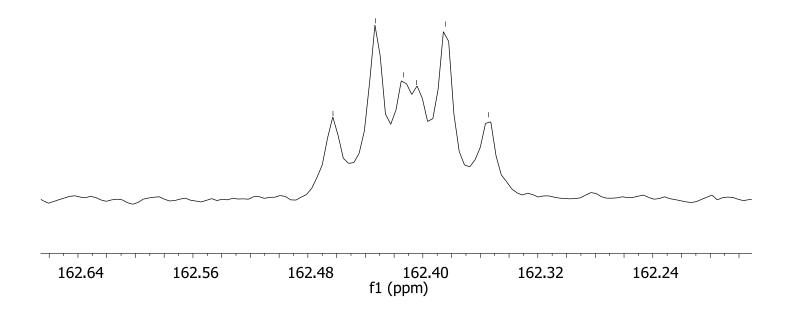


#### <sup>1</sup>H-<sup>13</sup>C Coupled NMR: (Z)-Ethyl *meta*-nitro-α-azido-β-phenylacrylate (2f)

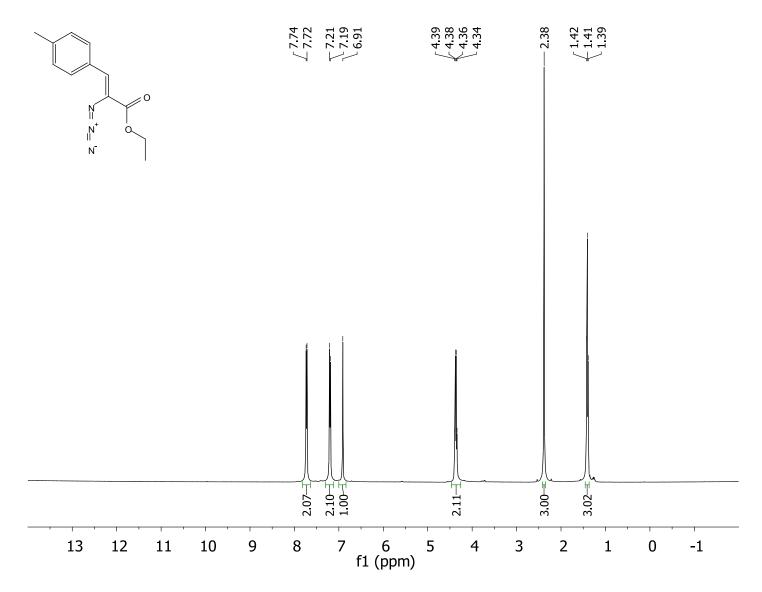


#### $^3J_{C,H}$ of $^1H$ - $^{13}C$ Coupled NMR: (Z)-Ethyl *meta*-nitro- $\alpha$ -azido- $\beta$ -phenylacrylate (2f)

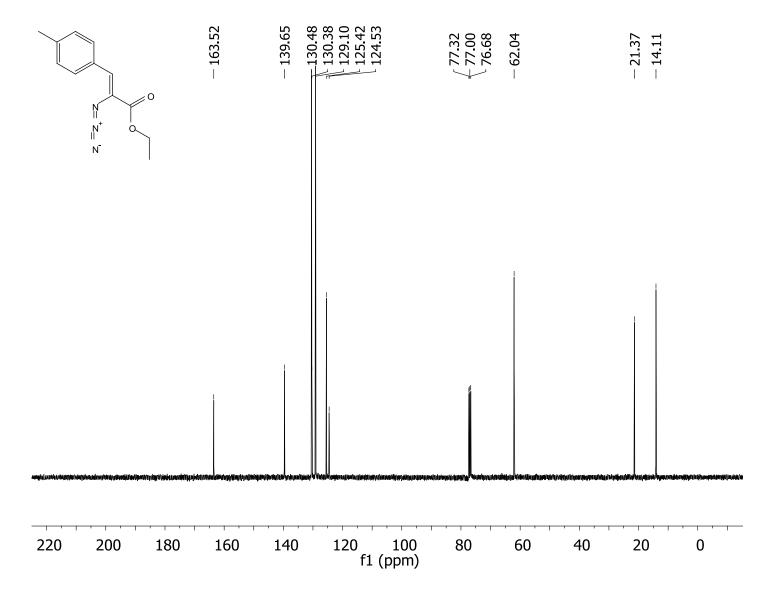




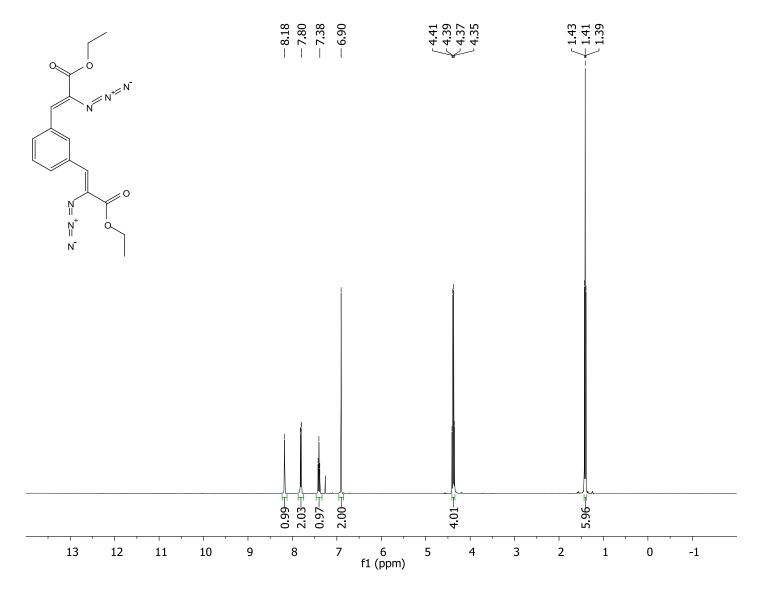
## $^{1}$ H NMR: (Z)-Ethyl *para*-methyl-α-azido-β-phenylacrylate (2g)



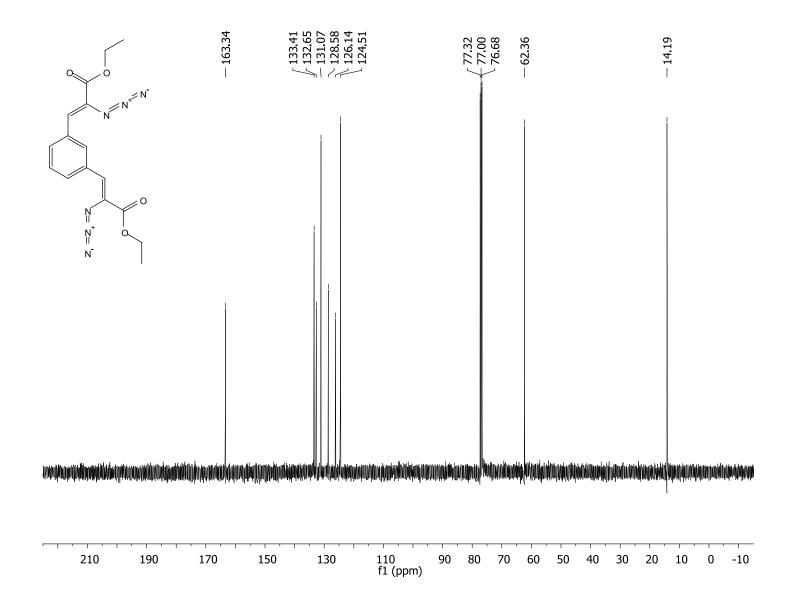
# $^{13}C$ NMR: (Z)-Ethyl $\it para$ -methyl- $\alpha$ -azido- $\beta$ -phenylacrylate (2g)



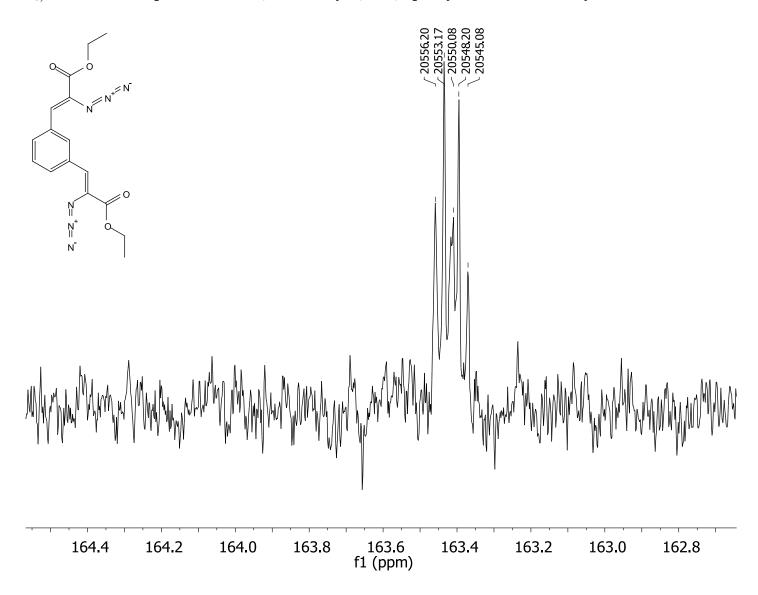
## $^{1}H$ NMR: (2Z,2'Z)-diethyl 3,3'-(1,3-phenylene)bis(2-azidoacrylate) (2h)



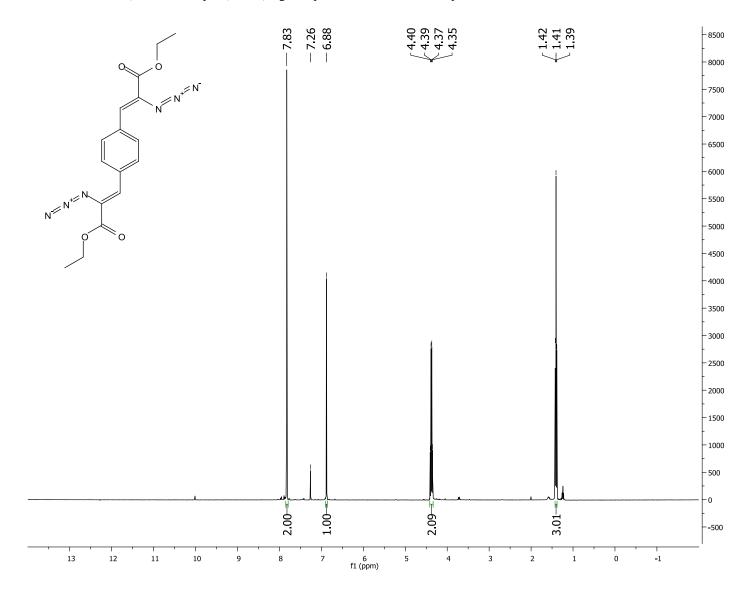
## $^{13}C\ NMR:\ (2Z,2'Z)\text{-diethyl }3,3'\text{-}(1,3\text{-phenylene}) bis(2\text{-azidoacrylate})\ (2h)$



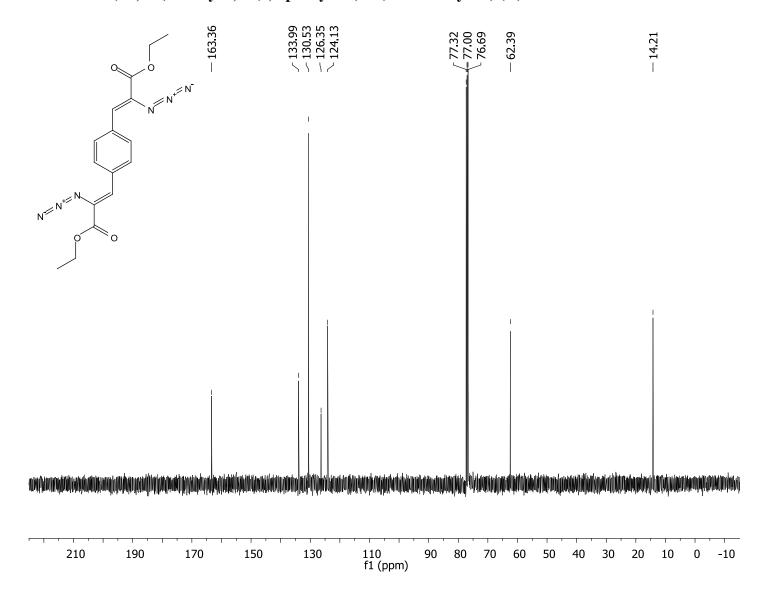
 $^3J_{C,H}\ of\ ^1H\text{-}^{13}C\ Coupled\ NMR:\ (2Z,2'Z)\text{-}diethyl\ 3,3'\text{-}(1,3\text{-}phenylene)bis(2-azidoacrylate)\ (2h)$ 



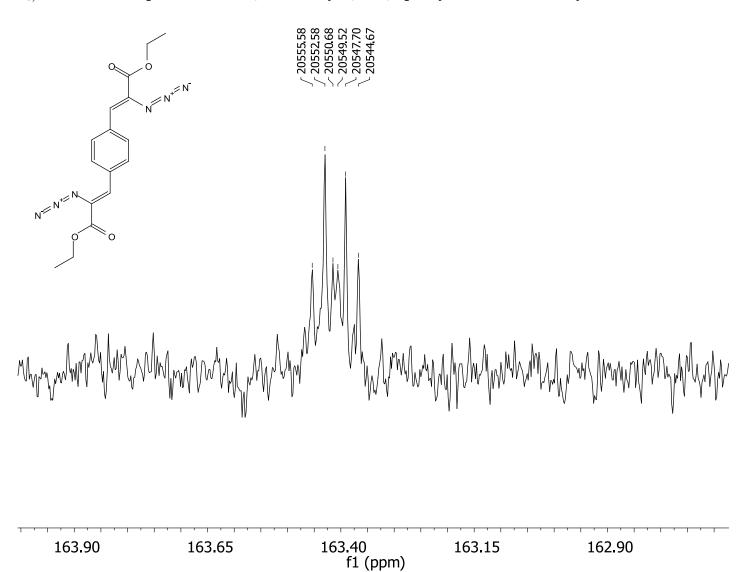
#### <sup>1</sup>H NMR: (2Z,2'Z)-diethyl 3,3'-(1,4-phenylene)bis(2-azidoacrylate) (2i)



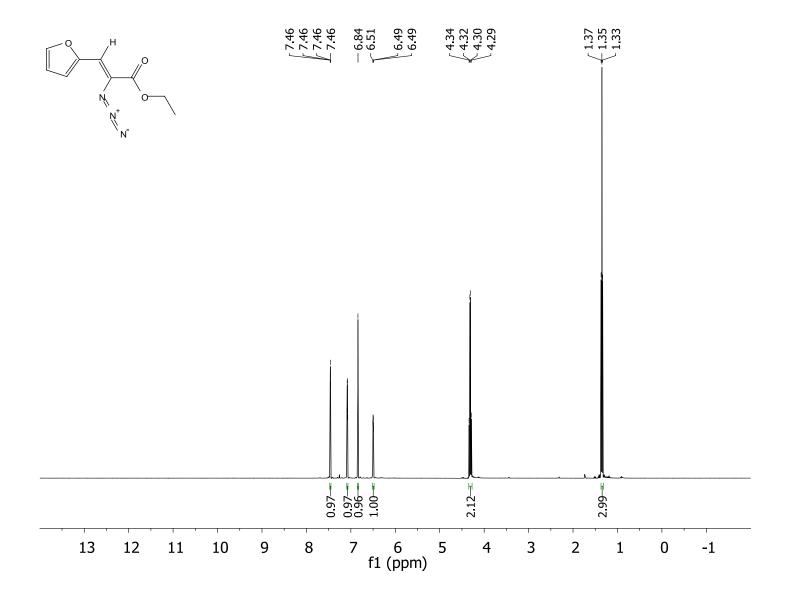
# $^{13}C\ NMR:\ (2Z,2'Z)\text{-diethyl }3,3'\text{-}(1,4\text{-phenylene}) bis(2\text{-azidoacrylate})\ (2i)$



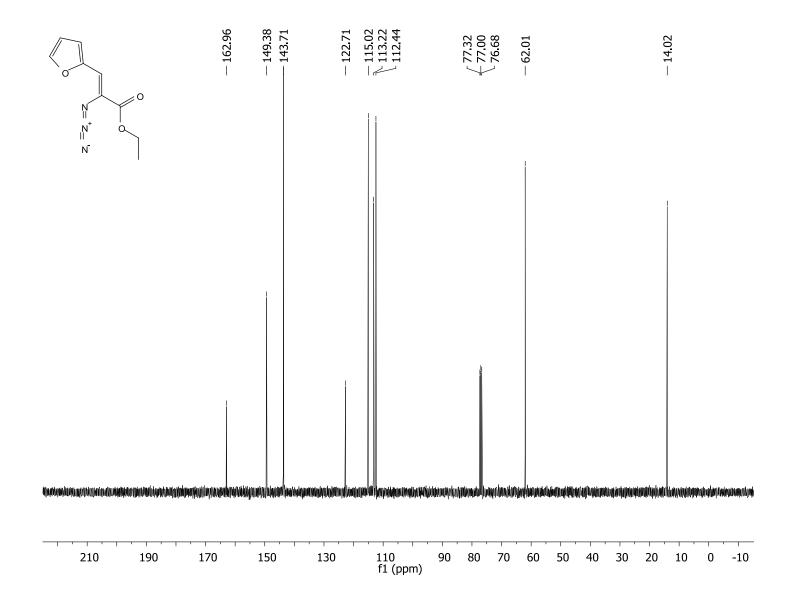
## $^3J_{C,H}\ of\ ^1H\text{-}^{13}C\ Coupled\ NMR:\ (2Z,2'Z)\text{-}diethyl\ 3,3'\text{-}(1,4\text{-}phenylene)bis(2\text{-}azidoacrylate)\ (2i)$



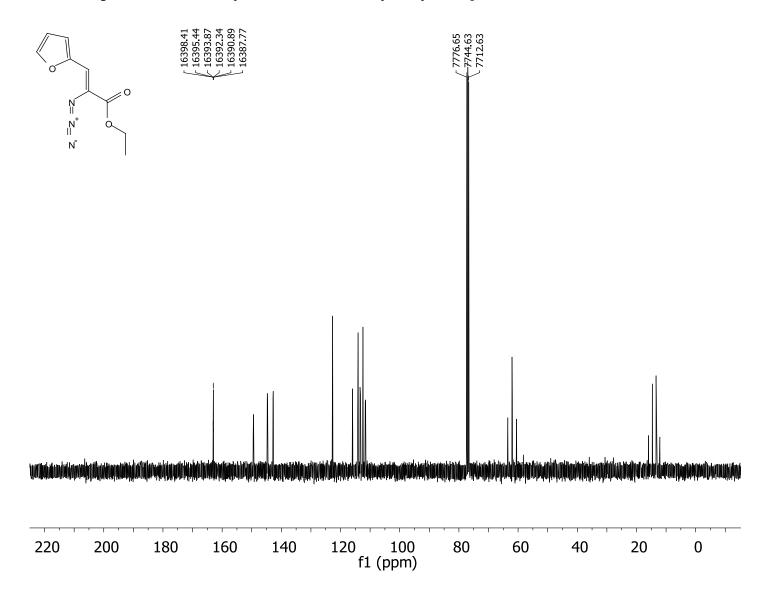
## <sup>1</sup>H NMR: (Z)-ethyl 2-azido-3-(furan-2-yl)acrylate (2j)



## $^{13}C\ NMR$ : (Z)-ethyl 2-azido-3-(furan-2-yl)acrylate (2j)

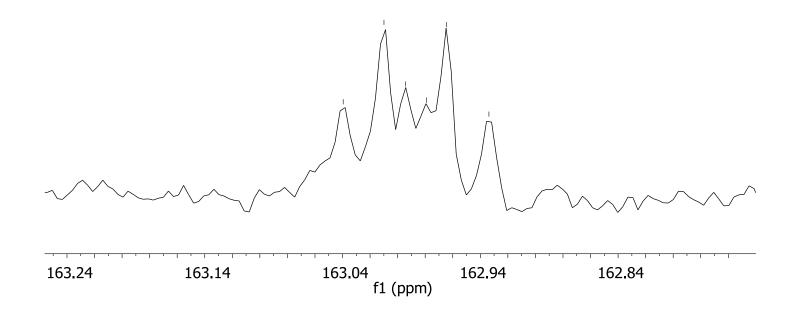


 $^{1}\text{H-}^{13}\text{C}$  Coupled NMR: (Z)-ethyl 2-azido-3-(furan-2-yl)acrylate (2j)



 $^3J_{C,H}$  of  $^1H$ - $^{13}C$  Coupled NMR: (Z)-ethyl 2-azido-3-(furan-2-yl)acrylate (2j)



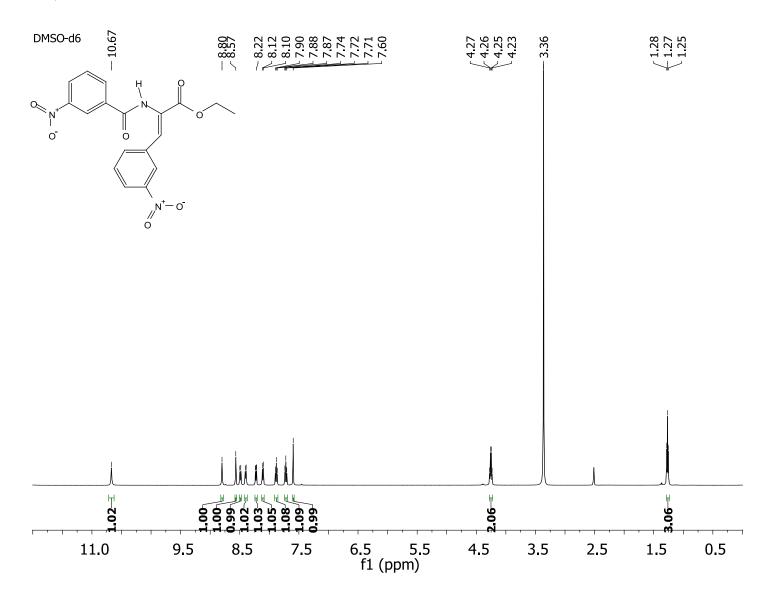


# **Section 2:**

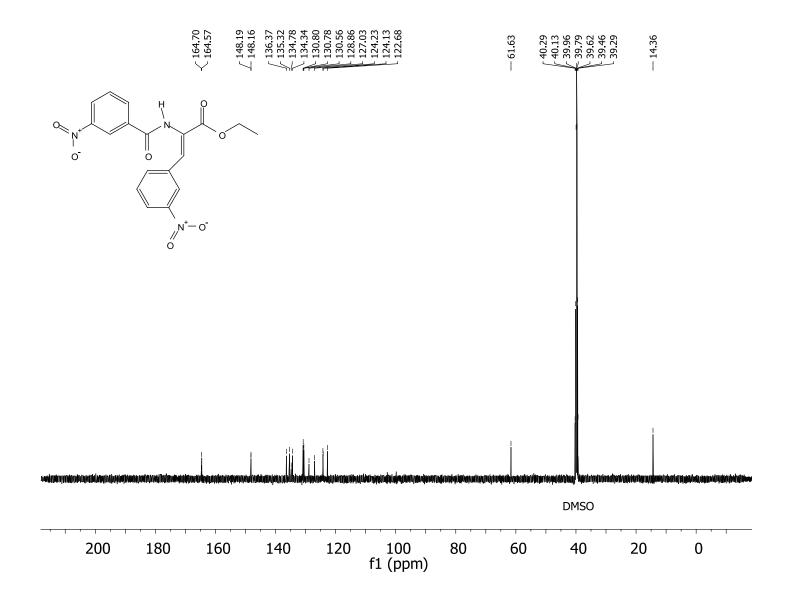
### NMR and Mass Spectroscopy of

## $\underline{(Z)\text{-}ethyl\ 2\text{-}(3\text{-}nitrobenzamido)\text{-}3\text{-}(3\text{-}nitrophenyl)}acrylate$

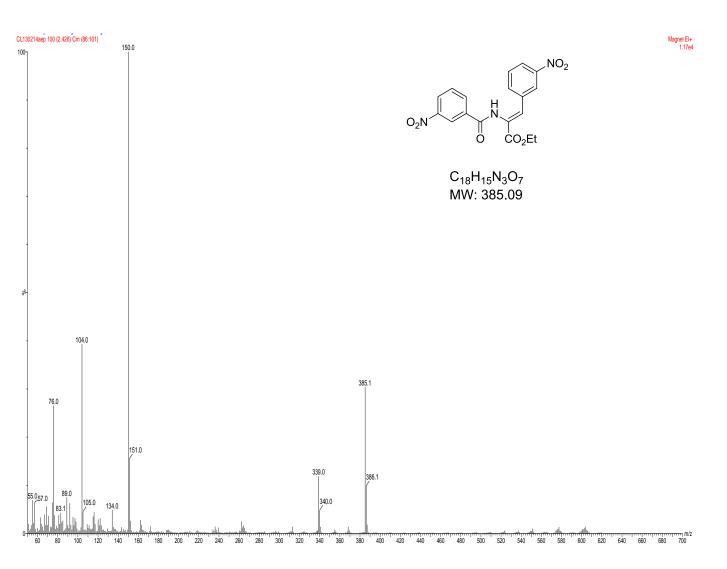
## <sup>1</sup>H NMR



## <sup>13</sup>C NMR: (Z)-ethyl 2-(3-nitrobenzamido)-3-(3-nitrophenyl)acrylate



#### Mass Spectroscopy (EI+): (Z)-ethyl 2-(3-nitrobenzamido)-3-(3-nitrophenyl)acrylate

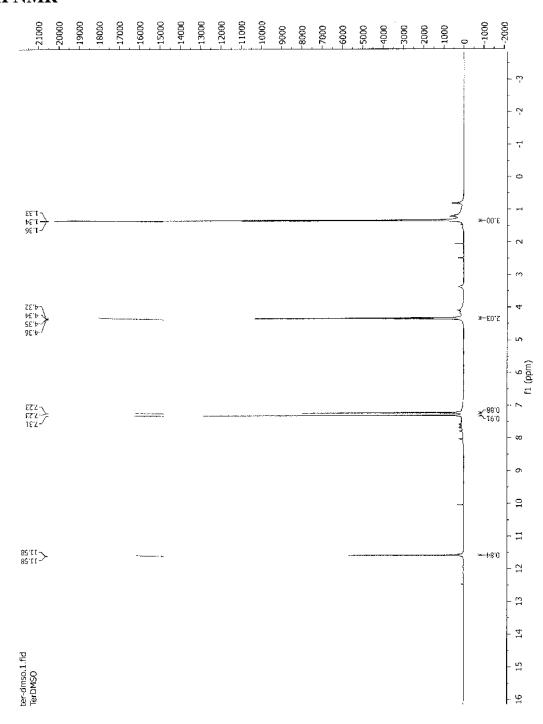


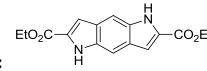
## **Section 3:**

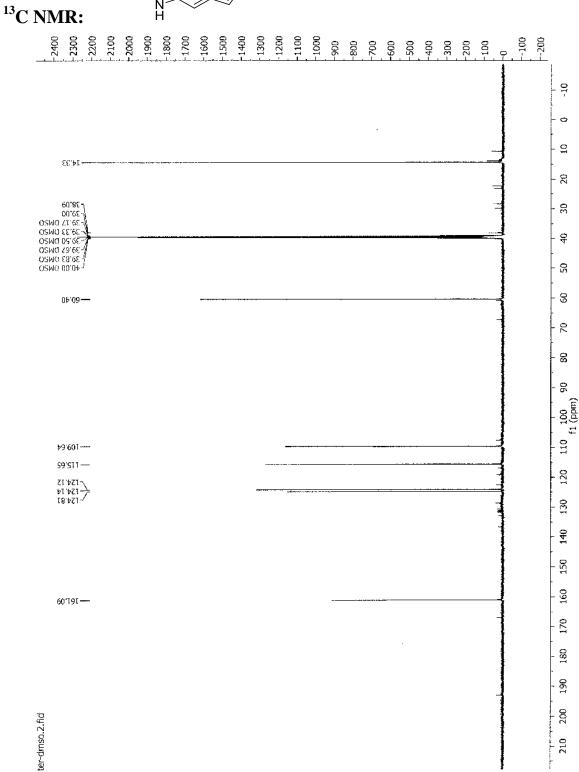
#### NMR (1-D and 2-D) of diethyl 1,6-dihydropyrrolo[2,3-e]indole-2,7-dicarboxylate, 3j

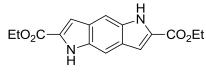
$$EtO_2C$$
 $N$ 
 $H$ 
 $CO_2Et$ 

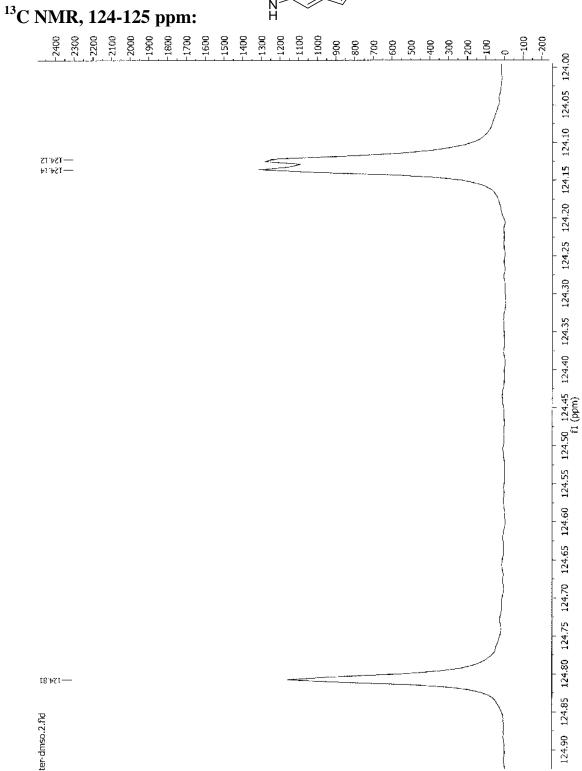
# <sup>1</sup>H NMR

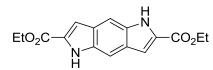


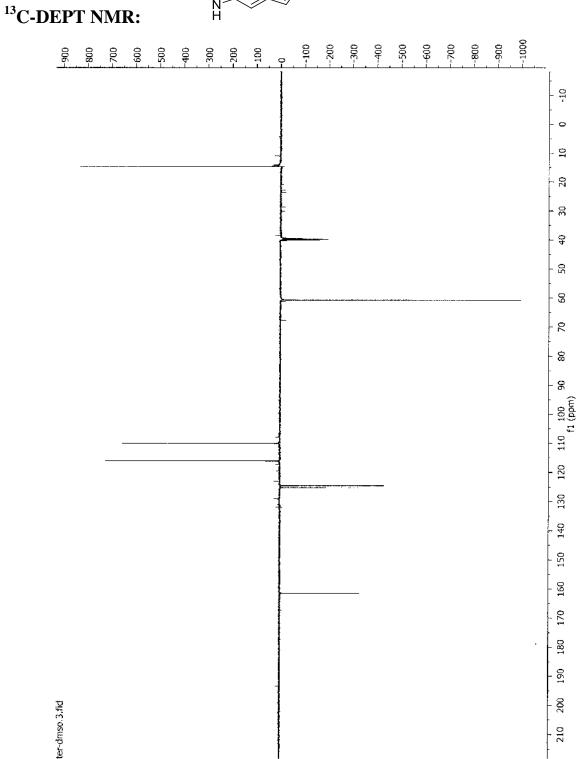


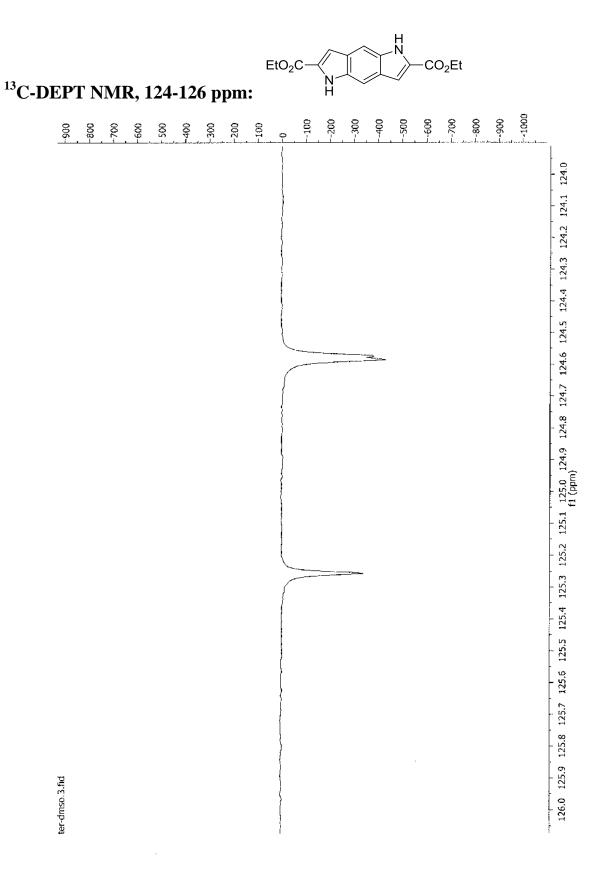




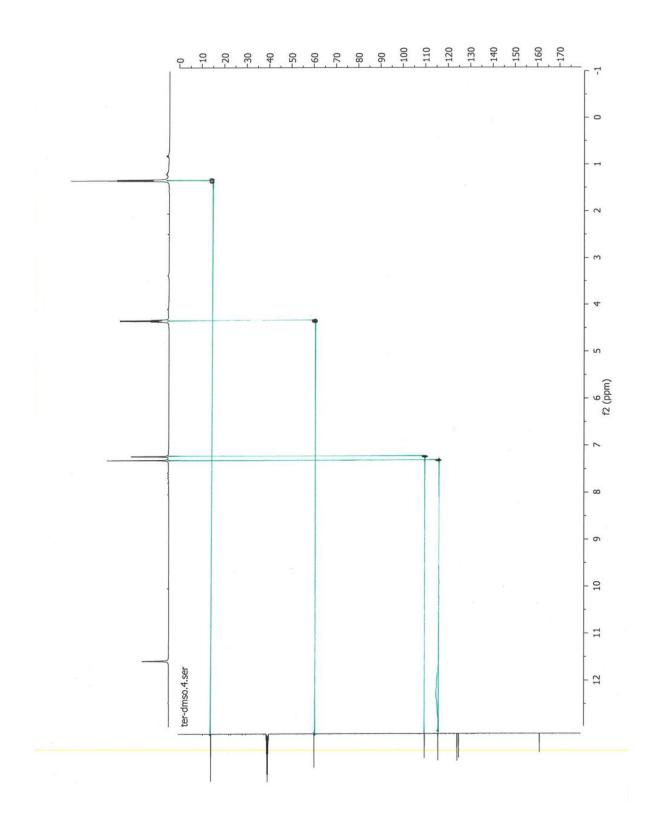


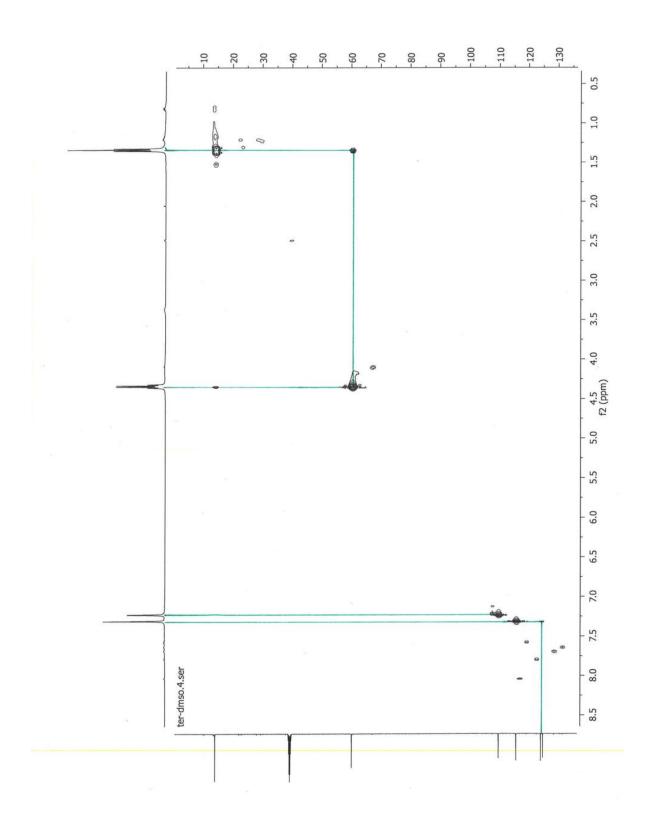


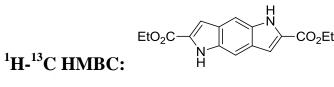


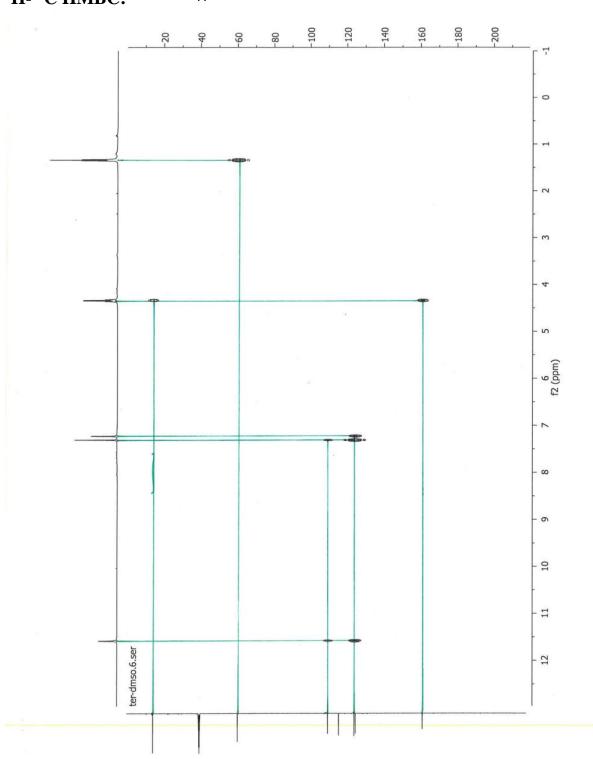


<sup>1</sup>H-
$$^{13}$$
C HMQC: EtO<sub>2</sub>C  $\stackrel{\text{H}}{\longrightarrow}$  CO<sub>2</sub>Et



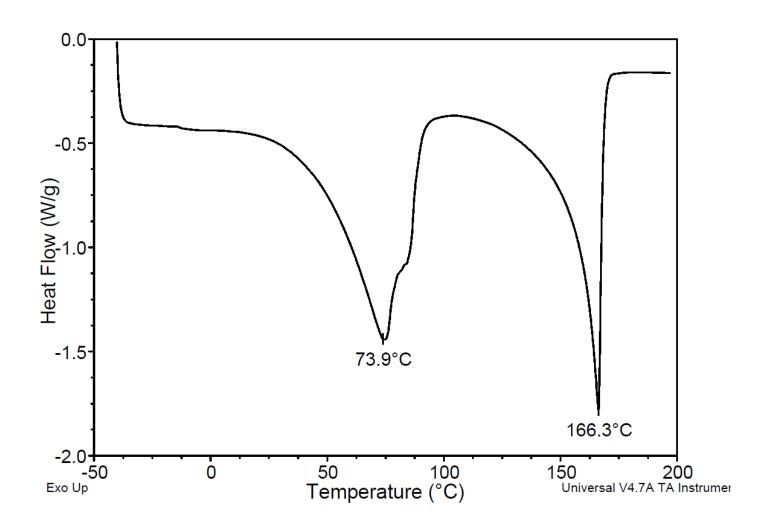




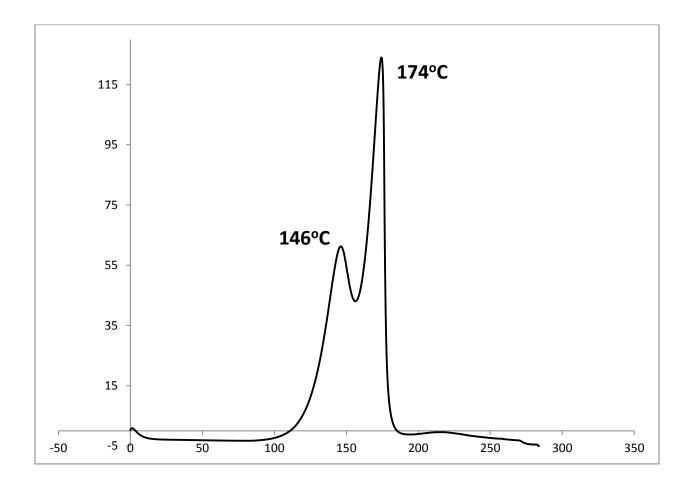


**Section 4:** 

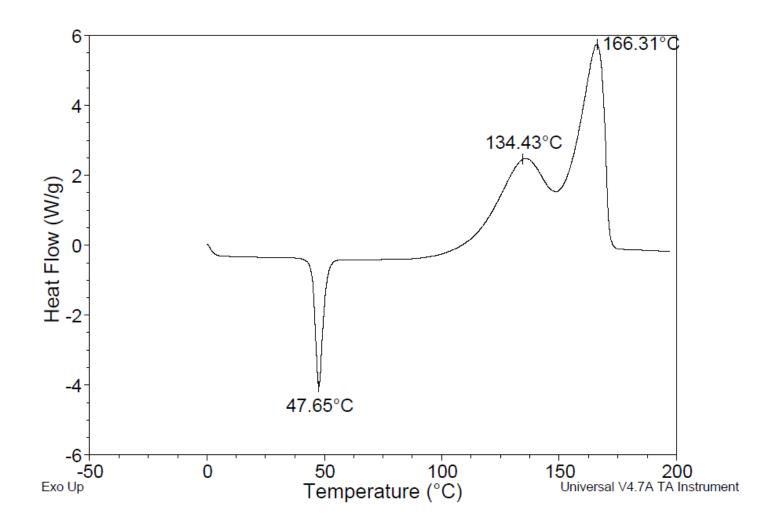
# <u>Differential Scanning Calorimetry of ethyl azidoacetate (1) and ethyl α-azido-β-arylacrylates</u> (2a-2j)



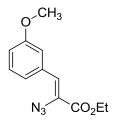
#### (Z)-Ethyl $\alpha$ -azido- $\beta$ -phenylacrylate (2a)

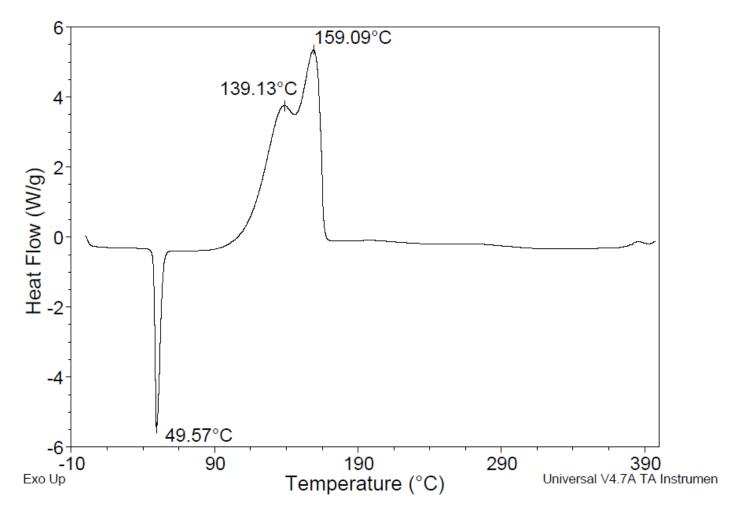


#### (Z)-Ethyl meta-methyl- $\alpha$ -azido- $\beta$ -phenylacrylate (2b)

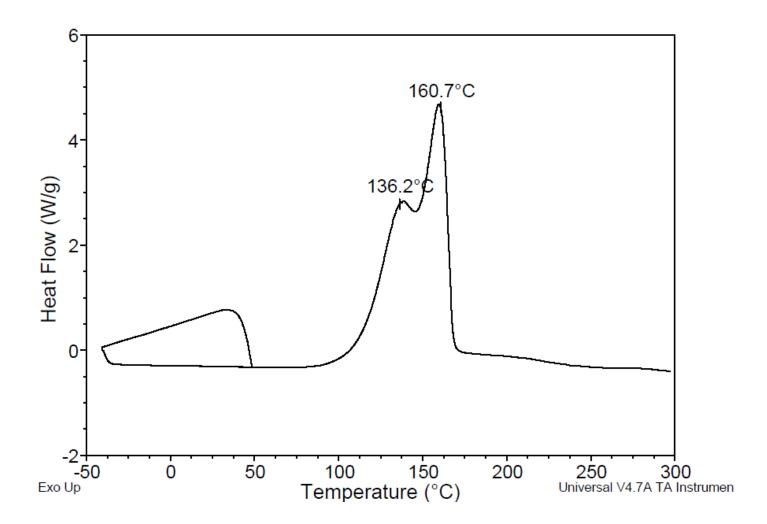


#### (Z)-Ethyl meta-methoxy- $\alpha$ -azido- $\beta$ -phenylacrylate (2c)

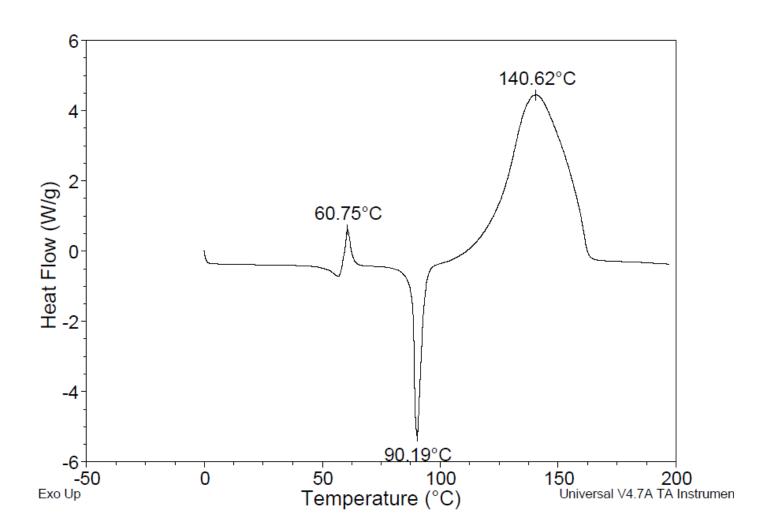




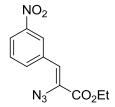
#### (Z)-Ethyl meta-chloro- $\alpha$ -azido- $\beta$ -phenylacrylate (2d)

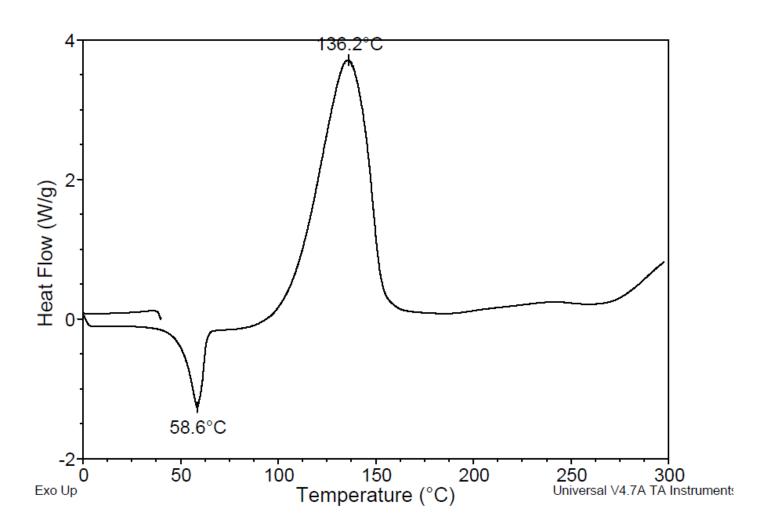


#### (Z)-Ethyl meta-phenyl- $\alpha$ -azido- $\beta$ -phenylacrylate (2e)

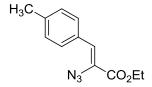


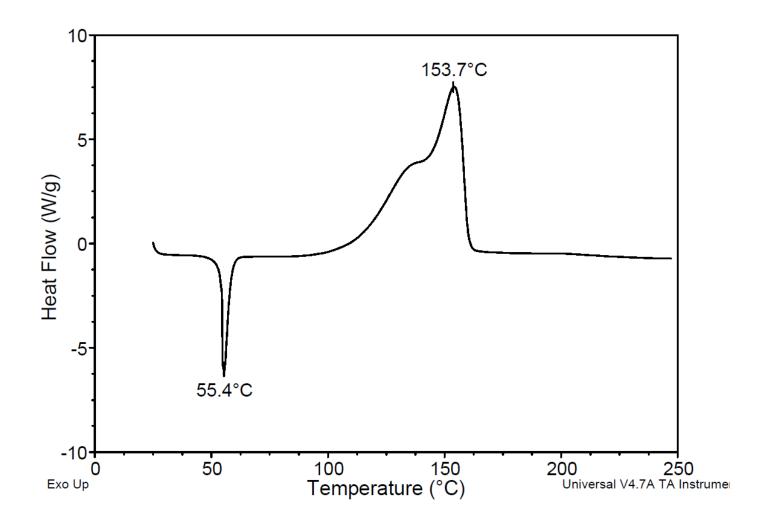
#### (Z)-Ethyl meta-nitro- $\alpha$ -azido- $\beta$ -phenylacrylate (2f)



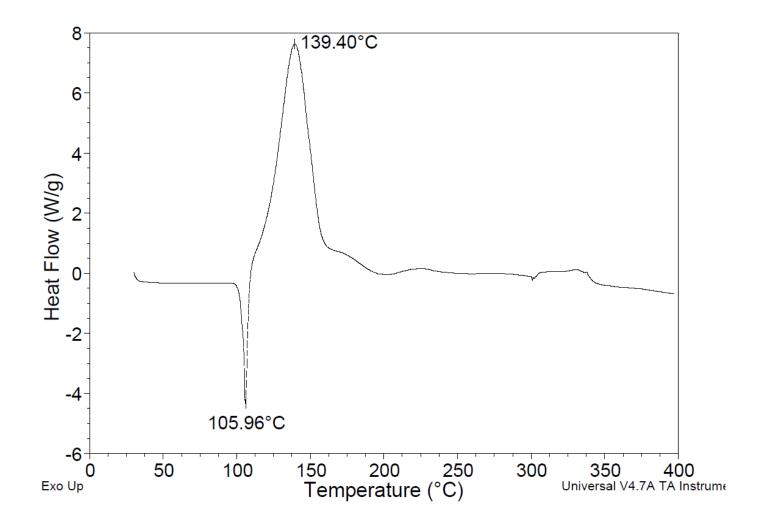


#### (Z)-Ethyl para-methyl- $\alpha$ -azido- $\beta$ -phenylacrylate (2g)



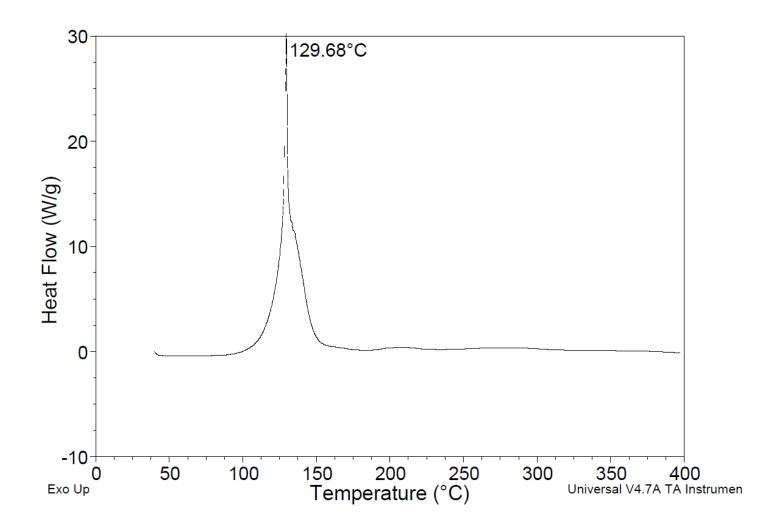


#### (2Z,2'Z)-diethyl 3,3'-(1,3-phenylene)bis(2-azidoacrylate) (2h)



#### (2Z,2'Z)-diethyl 3,3'-(1,4-phenylene)bis(2-azidoacrylate) (2i)

$$N_3$$
  $N_3$   $N_3$ 



#### (Z)-ethyl 2-azido-3-(furan-2-yl)acrylate (2j)

