Supporting Information for

A Survey of Enoldiazo Nucleophilicity in Selective C-C Bond Forming Reactions for the Synthesis of Natural Product-Like Frameworks

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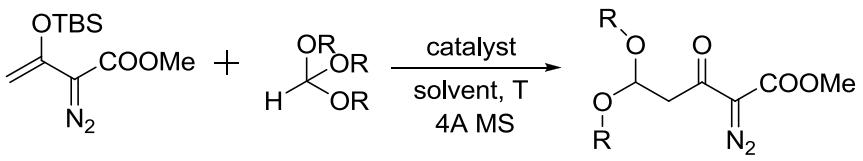
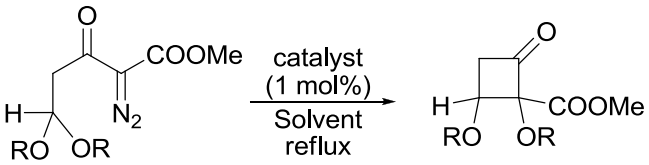
Table 1 Optimization of Reaction Conditions. [a]



Entry	R	Catalyst (mol%)	Solvent	Temperature (℃)	Yield [b] (%)
1	Me	$Zn(OTf)_2$ (0.5)	DCM	r.t.	65
2	Me	$La(OTf)_3$ (1.0)	DCM	r.t.	trace
3	Me	$Yb(OTf)_3$ (1.0)	DCM	r.t.	16
4	Me	$Sn(OTf)_2$ (1.0)	DCM	r.t.	16
5	Et	$Zn(OTf)_2$ (0.5)	DCM	r.t.	62
6	*i*-Pr	$Zn(OTf)_2$ (0.5)	DCM	r.t.	56
7	*i*-Pr	$Zn(OTf)_2$ (0.5)	MeCN	r.t.	66
8	*i*-Pr	$Zn(OTf)_2$ (1.0)	MeCN	r.t.	75
9	*i*-Pr	$Sc(OTf)_3$ (1.0)	MeCN	r.t.	88
10	*i*-Pr	$Sc(OTf)_3$ (1.0)	MeCN	40	60
11	*i*-Pr	$Sc(OTf)_3$ (1.0)	MeCN	60	44
12	*i*-Pr	$Sc(OTf)_3$ (0.5)	MeCN	r.t.	84

a Reaction conditions: a mixture of enoldiazoacetate (1.2 equiv.), orthoformate (1.0 equiv.), molecular sieve (100 mg/mmol) and catalyst (0.5-1.0 mol%) in freshly distilled solvent (0.5M) was stirred at the specified temperature for 16 hours. *b* Yield was determined by ^{1}H NMR spectroscopic analysis using naphthalene as the internal standard.

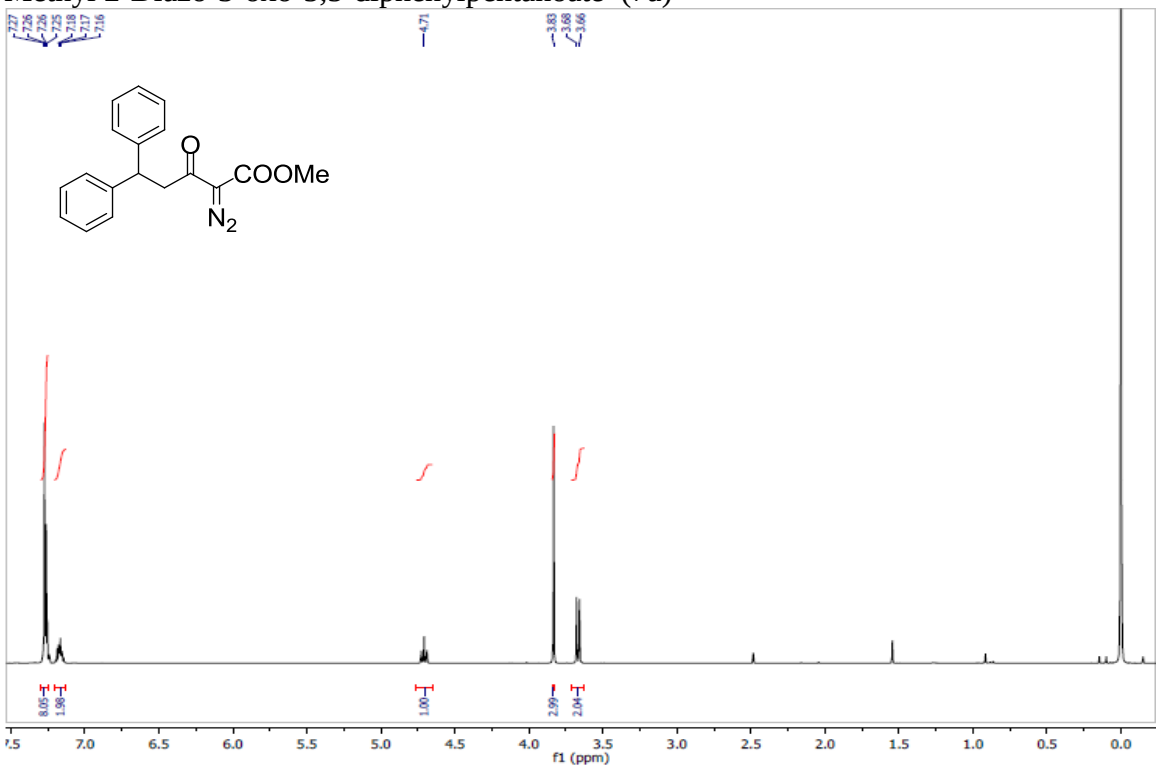
Table 2 Intramolecular Reactions of δ,δ-Dialkoxy-β-keto-α-diazoesters Catalyzed by Dirhodium Catalysts [a]

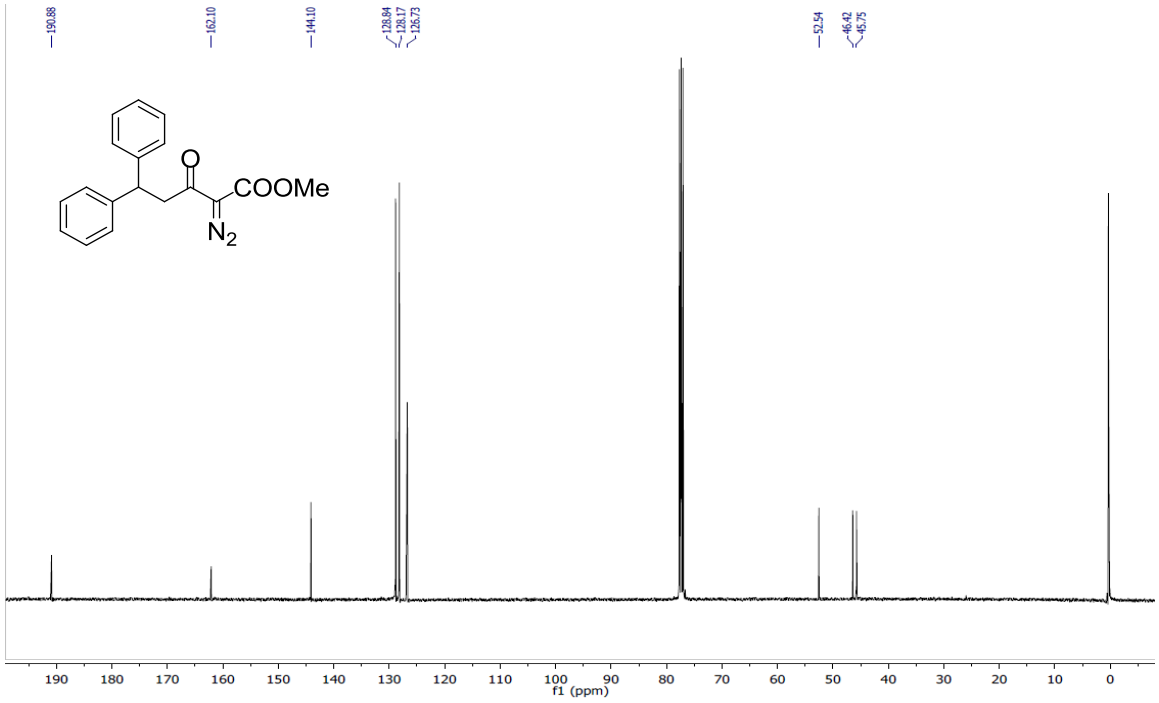


Entry	R	Catalyst (mol%)	Solvent	Yield [b] (%)	dr. [c]
1	Me	$Rh_2(OAc)_4$ (1.0)	DCM	80	75:25
2	Me	$Rh_2(pfb)_4$ (1.0)	DCM	46	58:42
3	Me	$Rh_2(OOCCPh_3)_4$ (1.0)	DCM	73	70:30
4	Me	$Rh_2(cap)_4$ (1.0)	DCM	trace	-
5	Me	$Rh_2(cap)_4$ (1.0)	DCE	28	70:30
6	Et	$Rh_2(OAc)_4$ (1.0)	DCM	75	72:28
7	*i*-Pr	$Rh_2(OAc)_4$ (1.0)	DCM	72	53:47

a Reaction conditions: a solution of diazoester (0.5 mmol) in 2 mL of anhydrous CH_2Cl_2 was added *via* syringe pump over 2 h to a refluxing solution catalyst (1 mol%) in 1 mL of anhydrous solvent. *b* Isolated yield after column chromatography. *c* Diastereoselectivities were determined by ^1H NMR spectral analysis.

Methyl 2-Diazo-3-oxo-5,5-diphenylpentanoate (7a)





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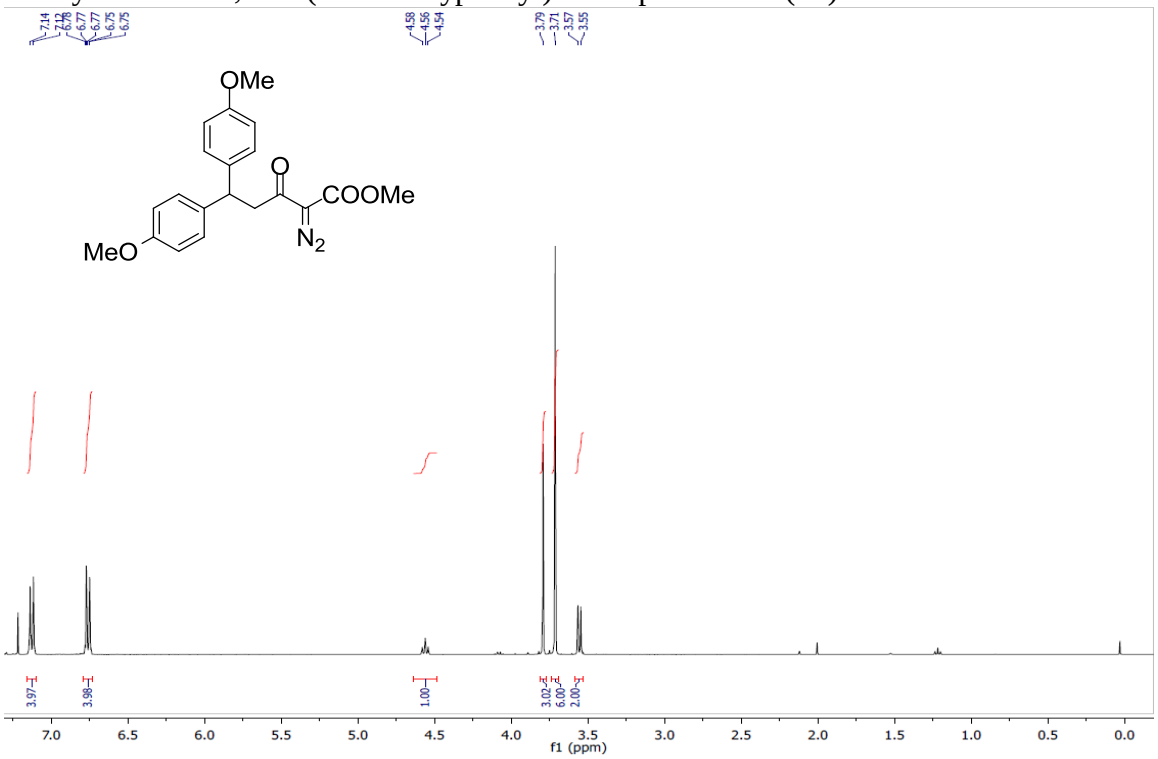
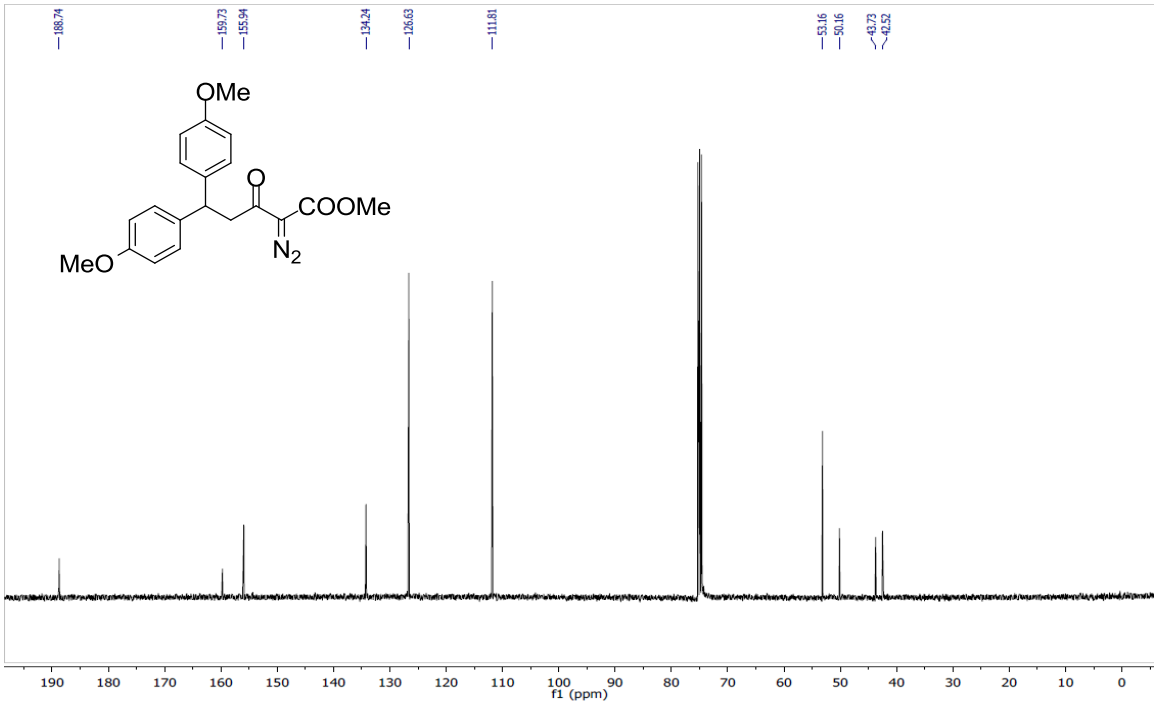
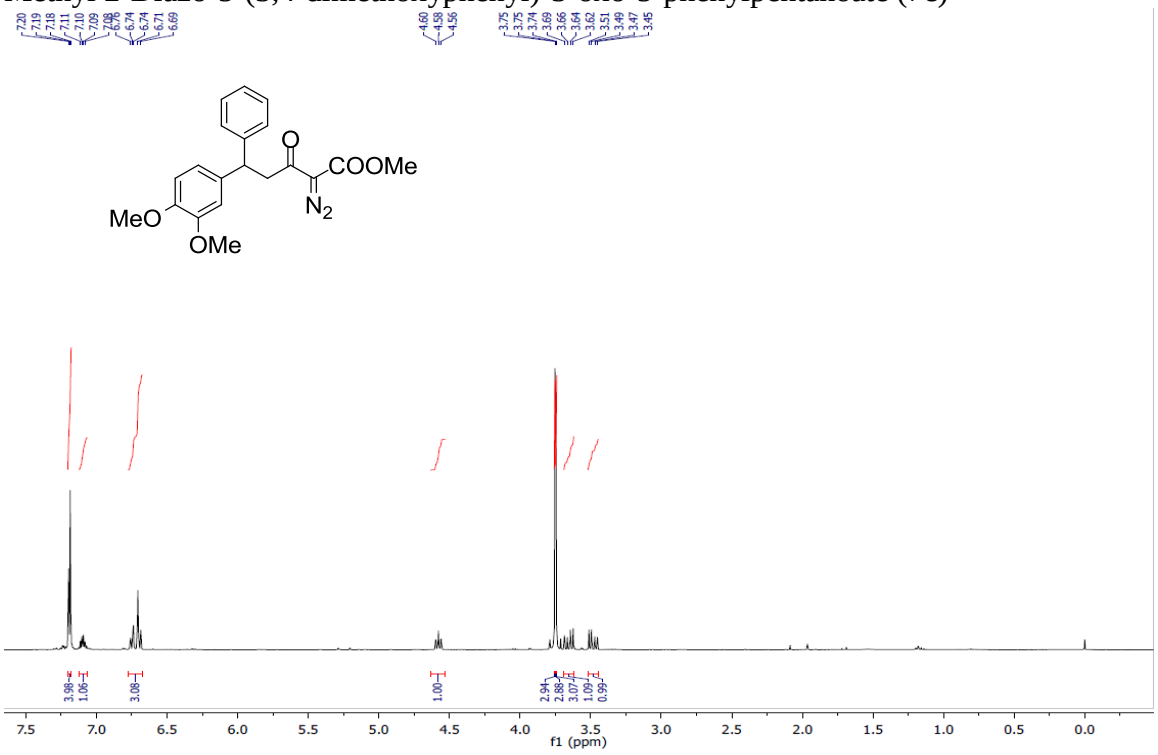
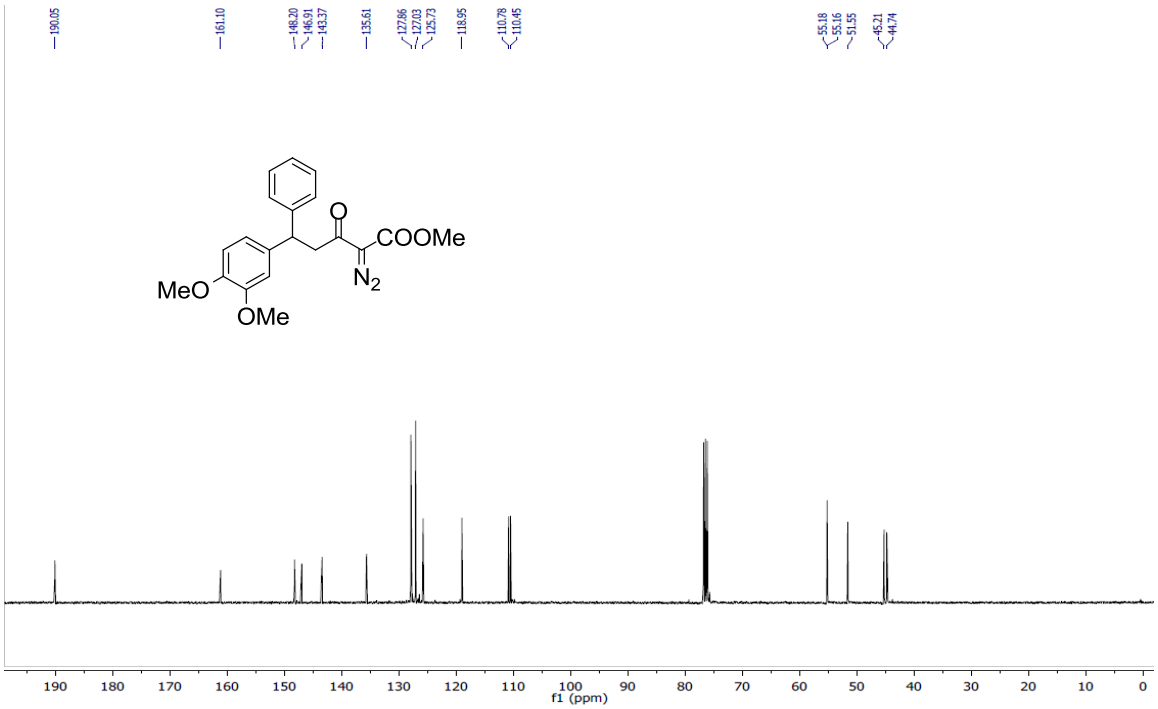


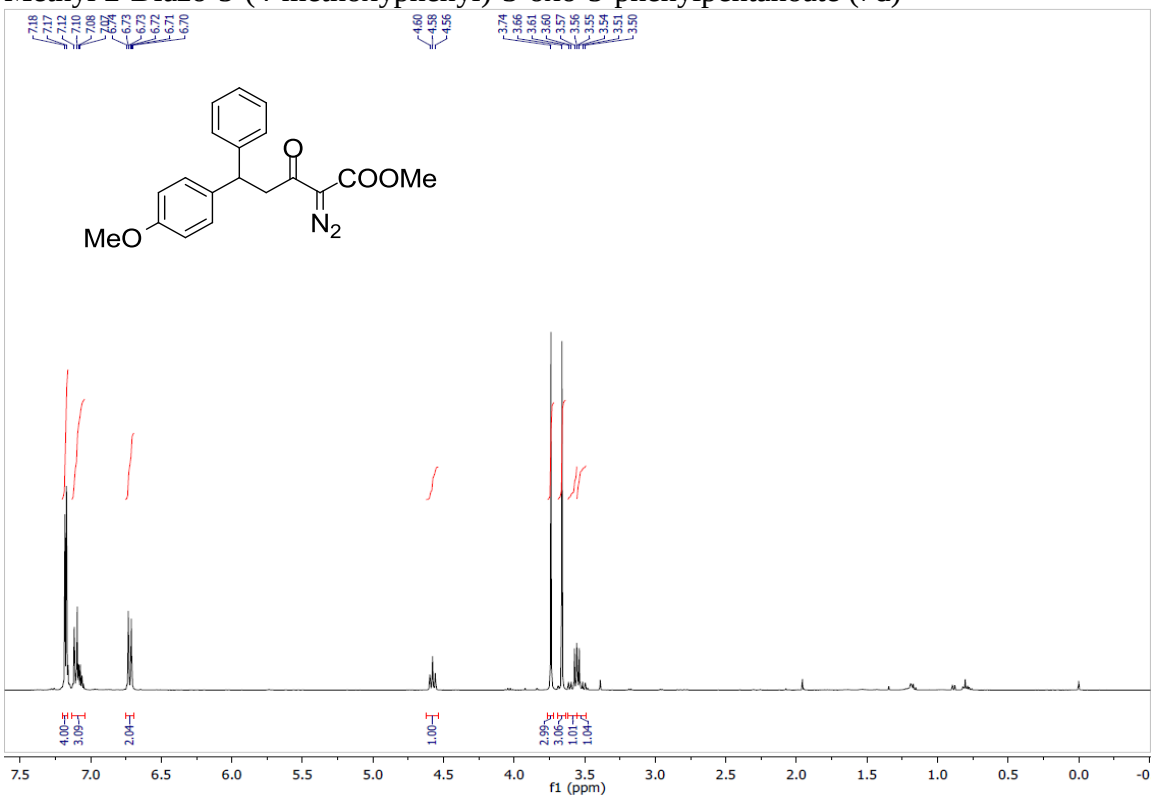


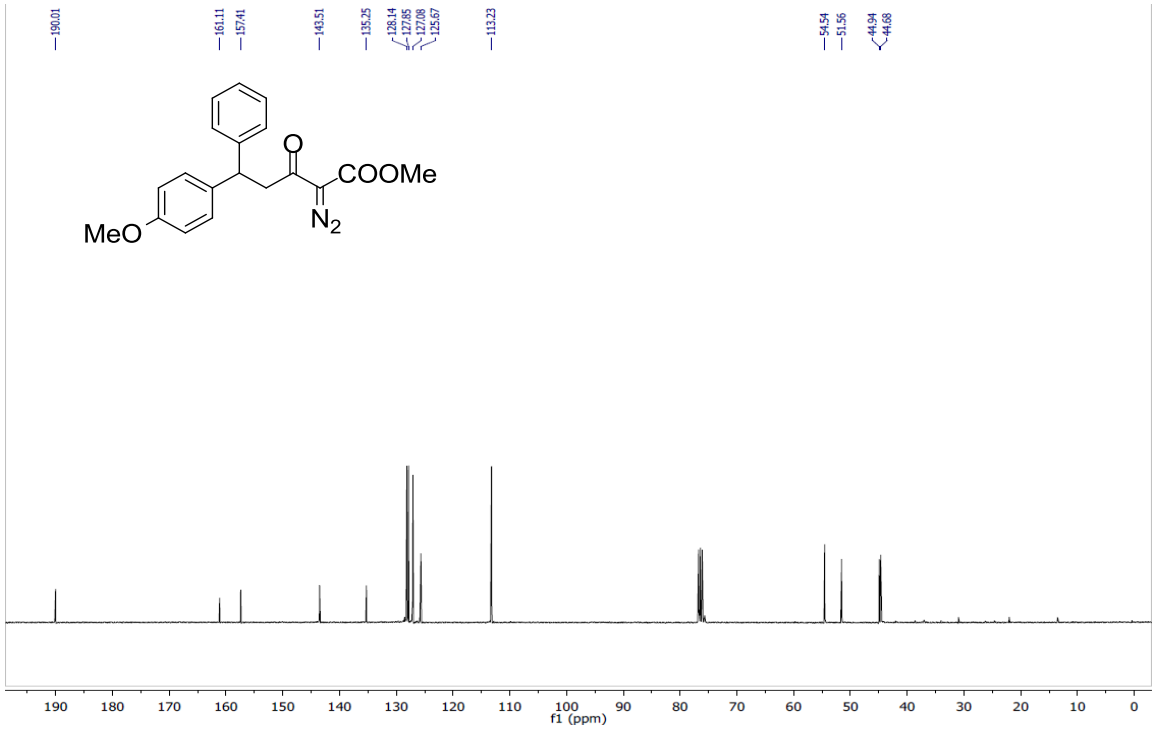
Methyl 2-Diazo-5-(3,4-dimethoxyphenyl)-3-oxo-5-phenylpentanoate (7c)





Methyl 2-Diazo-5-(4-methoxyphenyl)-3-oxo-5-phenylpentanoate (7d)





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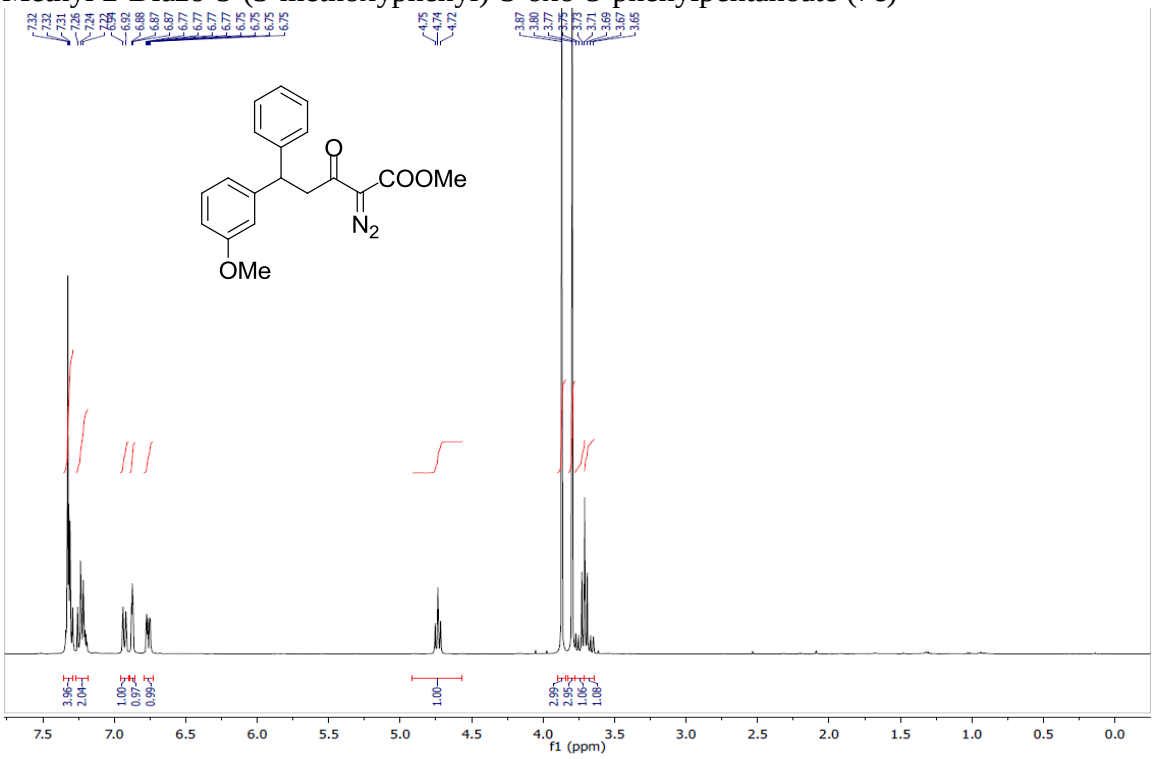

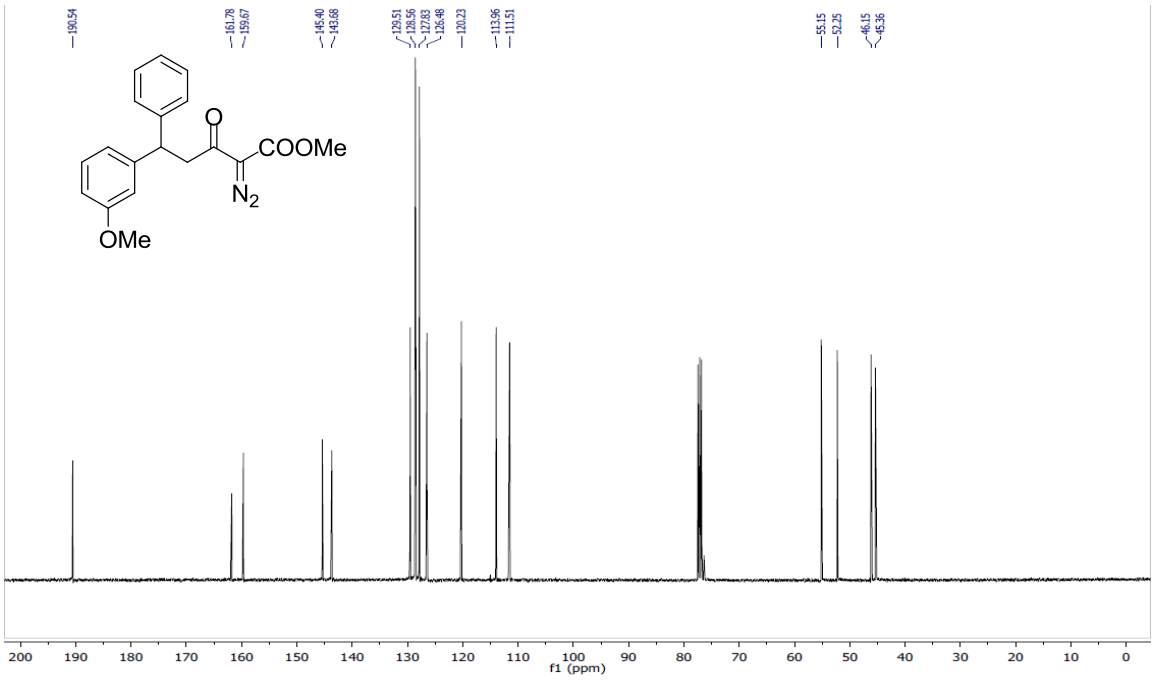

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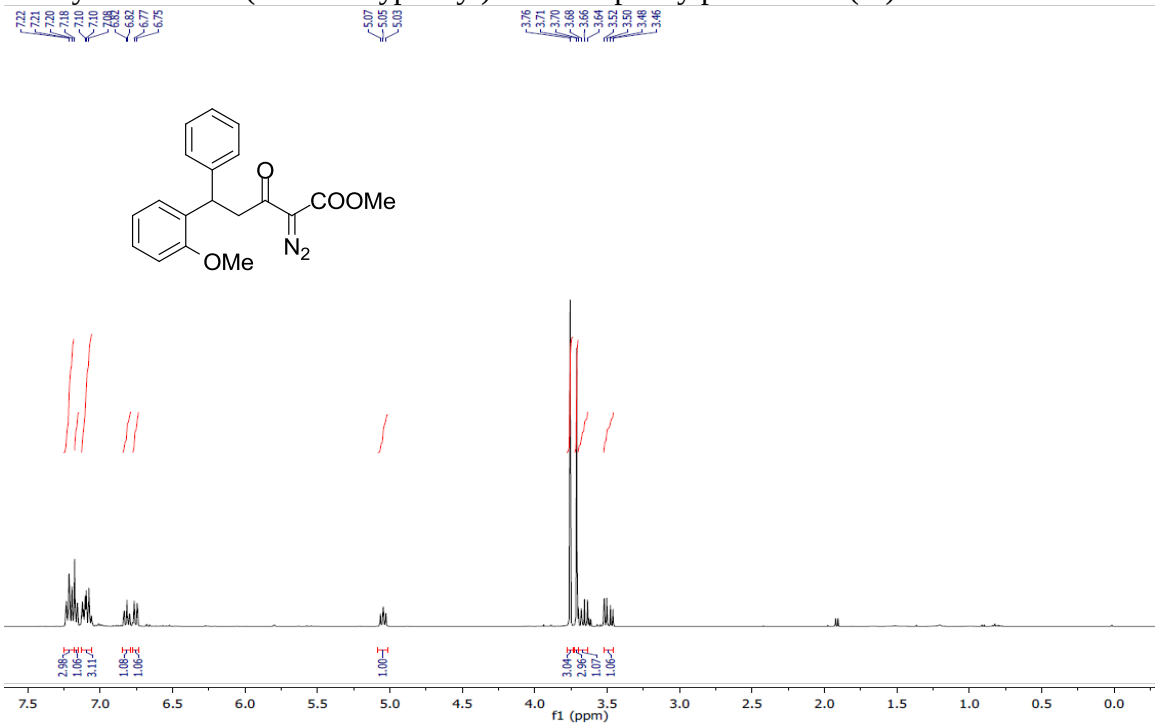

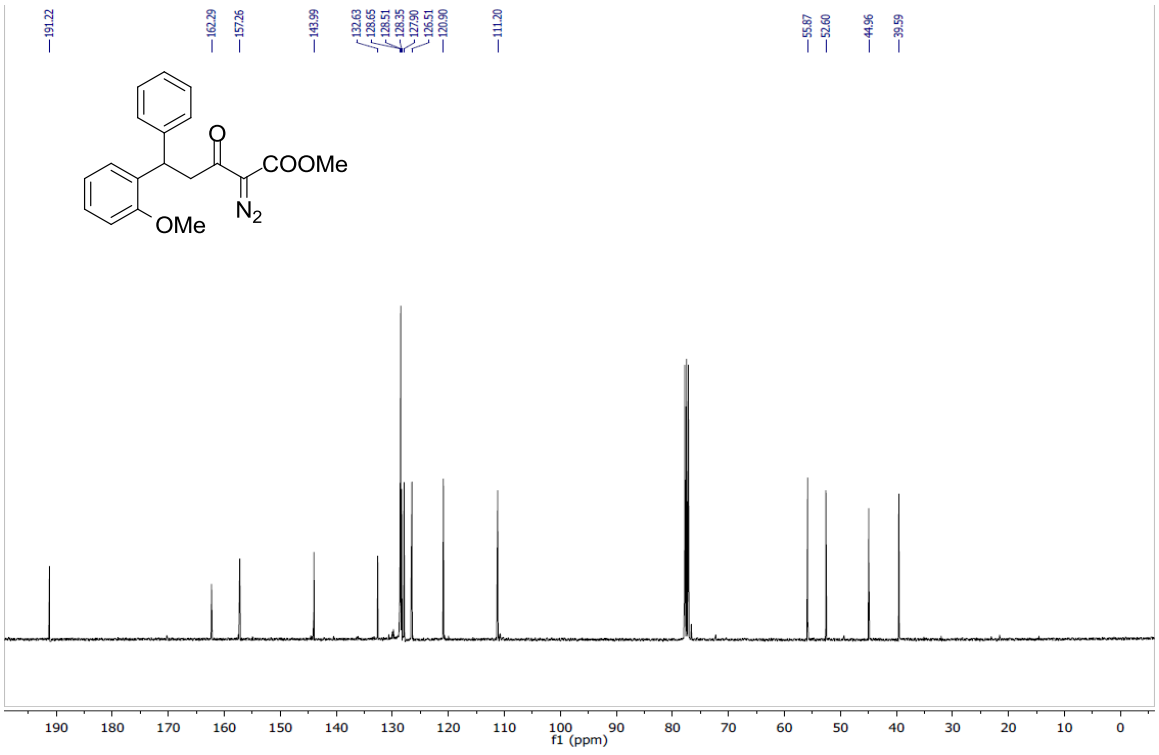

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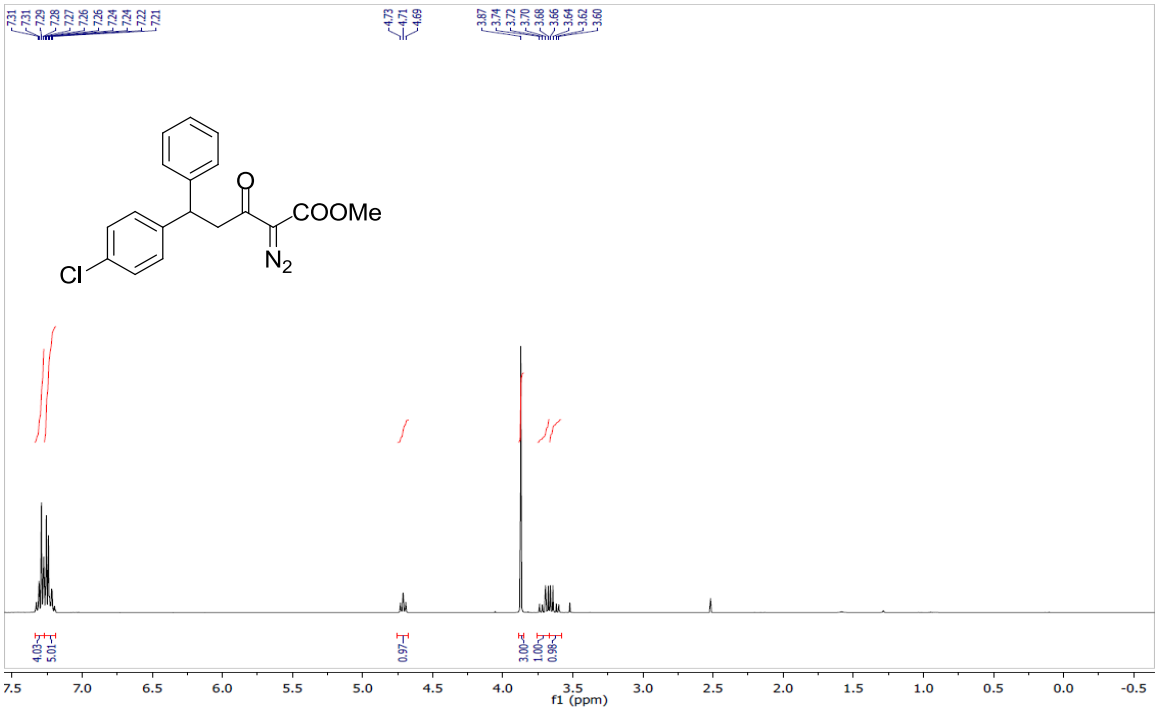
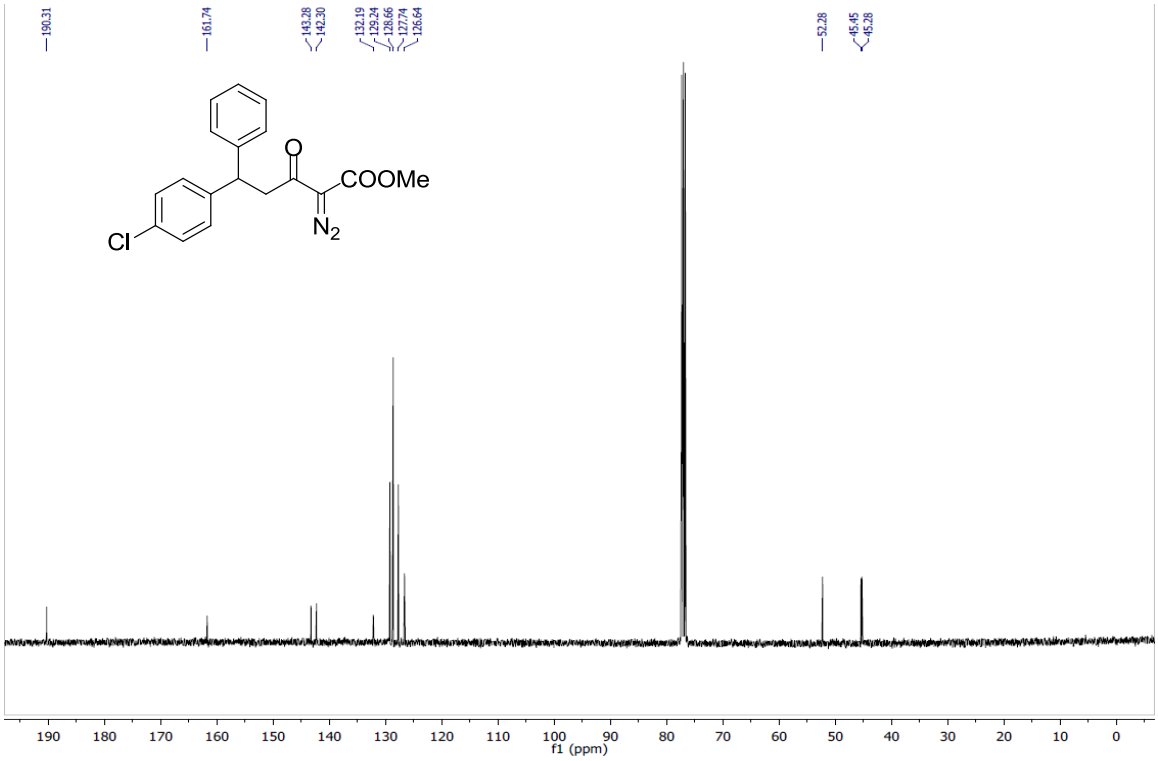
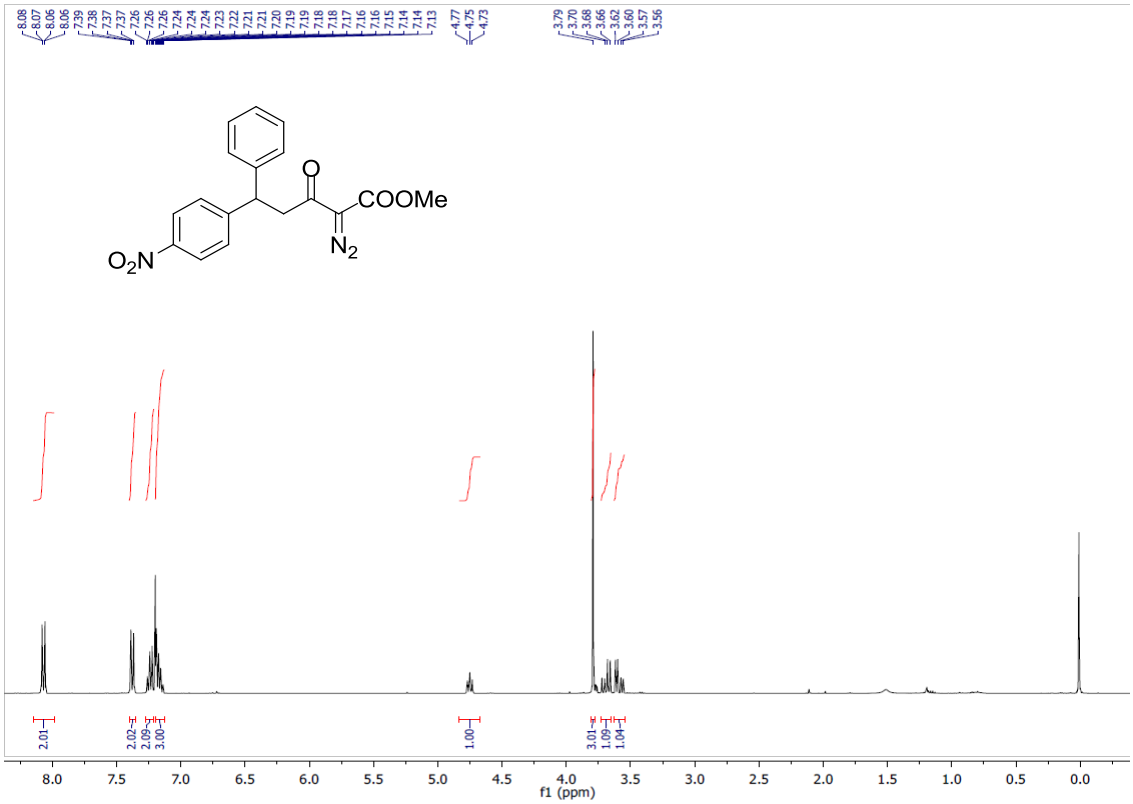
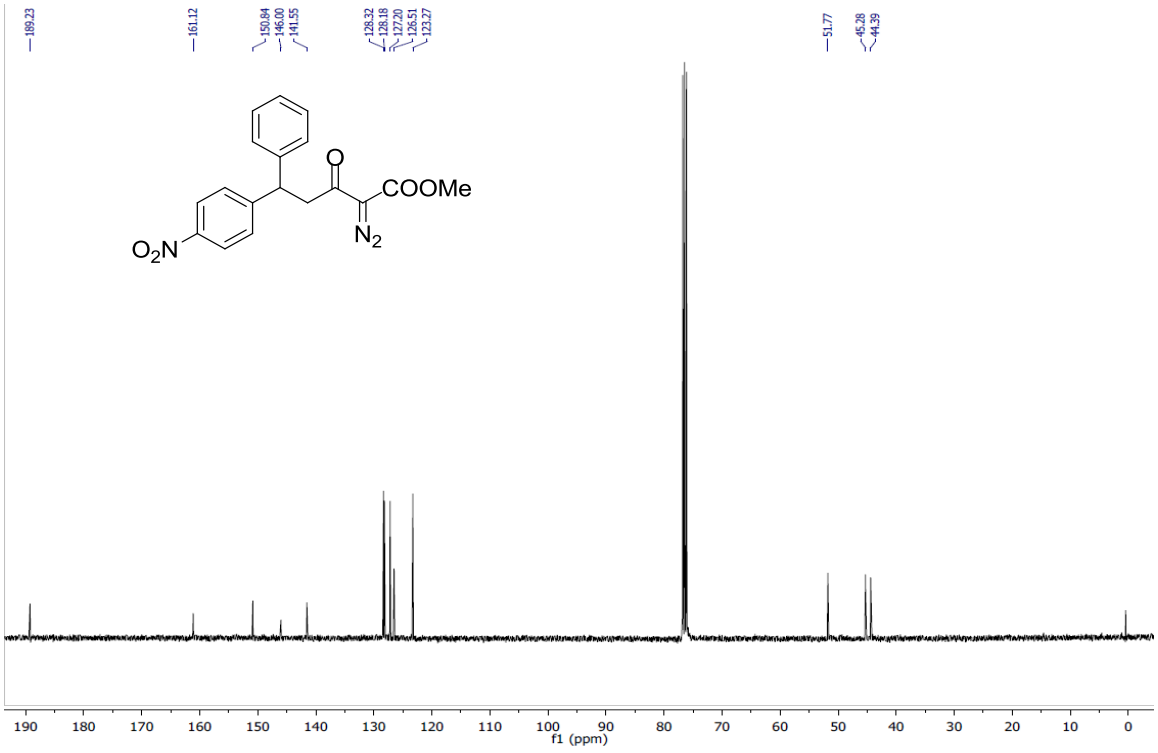


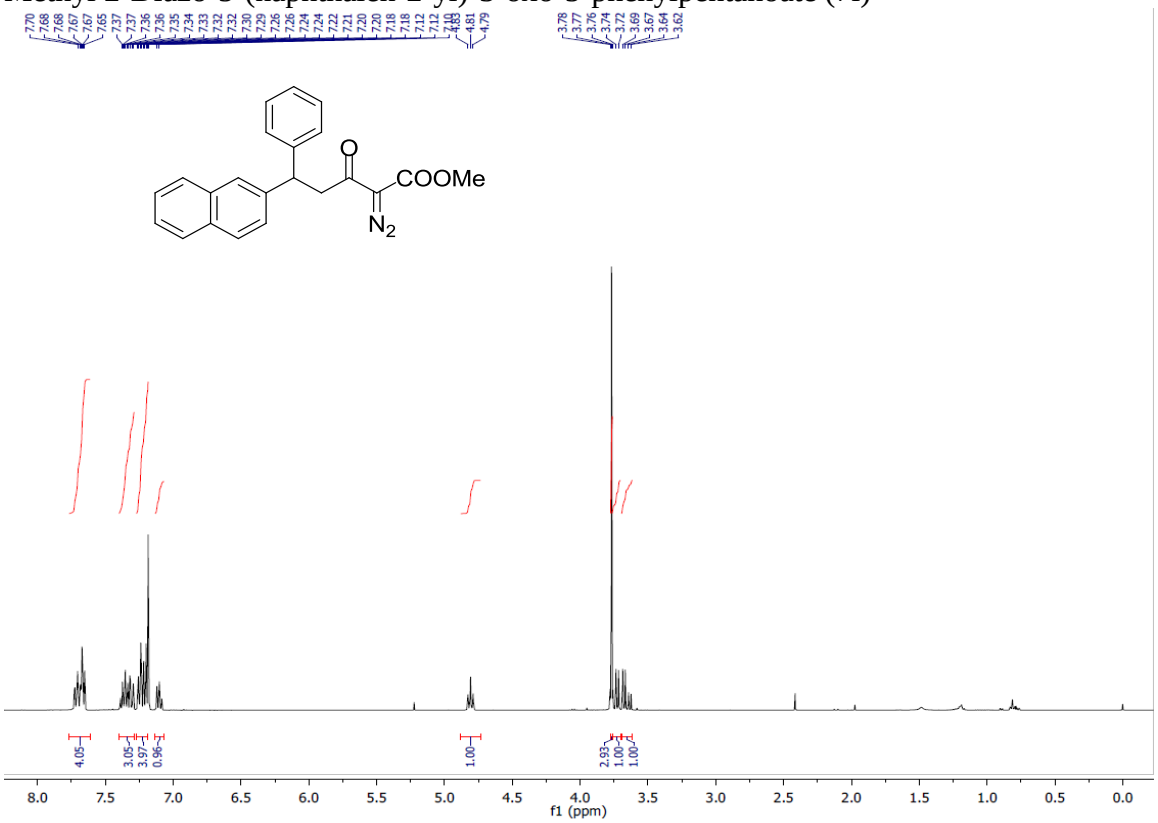


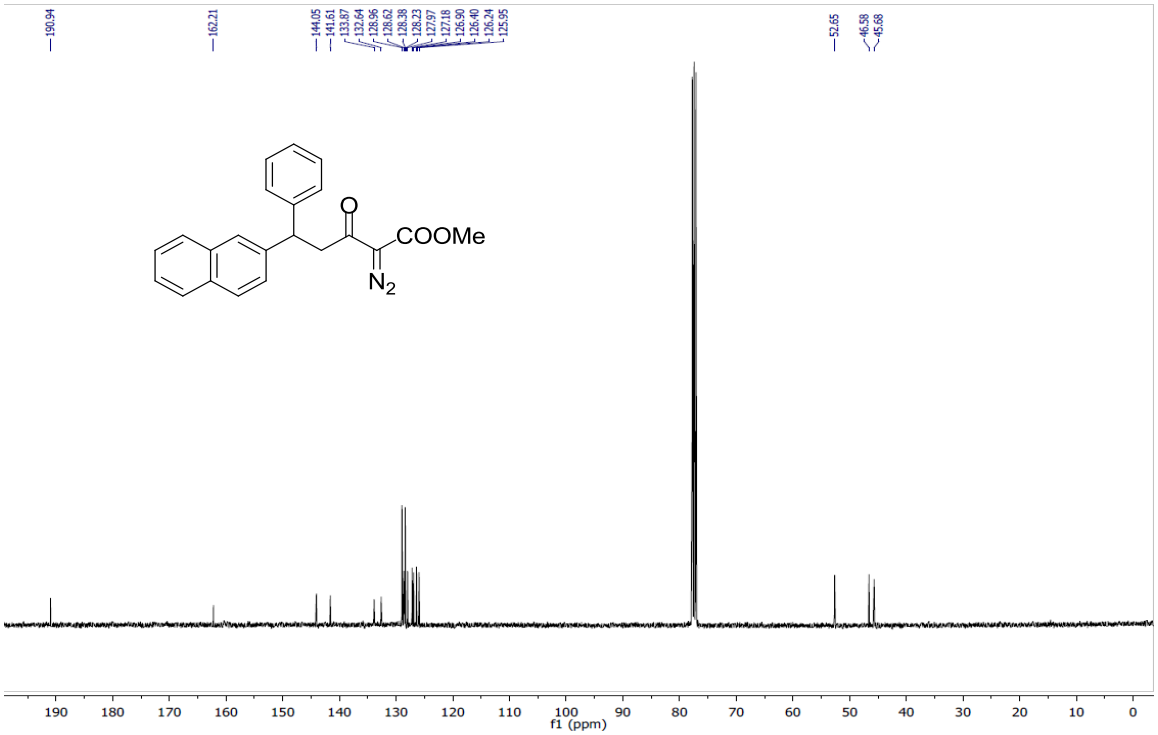
Methyl 2-Diazo-5-(4-nitrophenyl)-3-oxo-5-phenylpentanoate (7h)



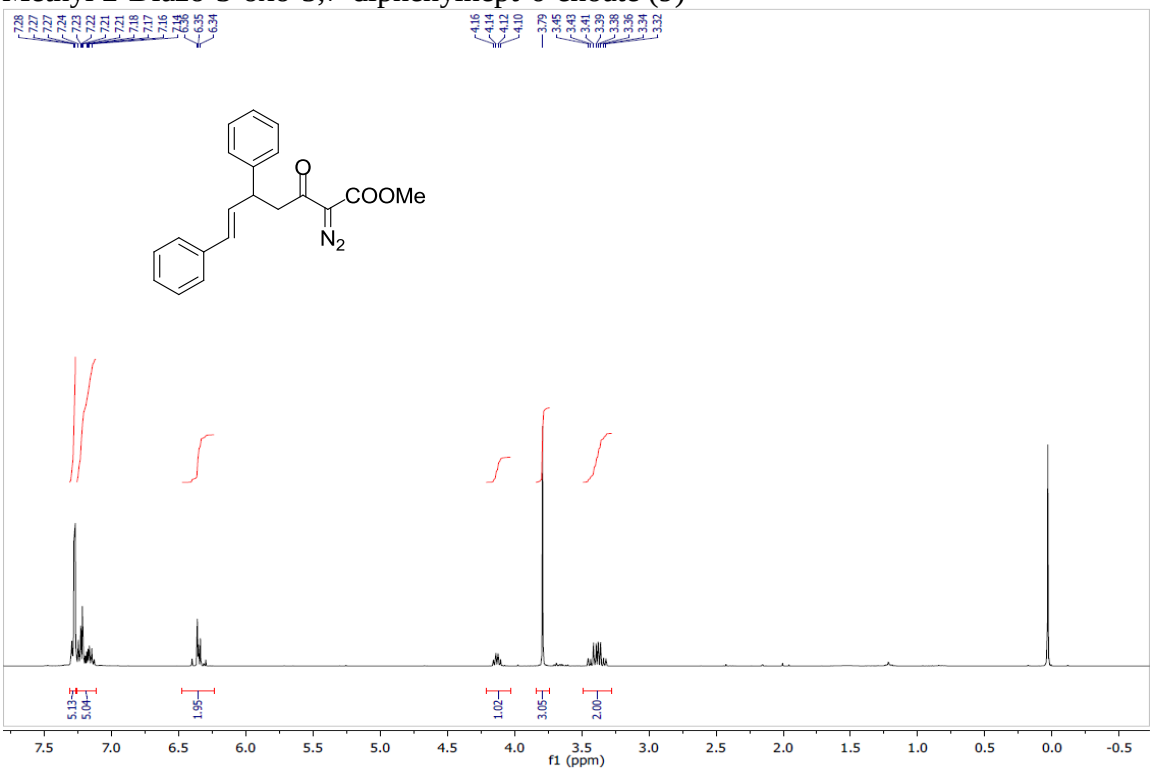


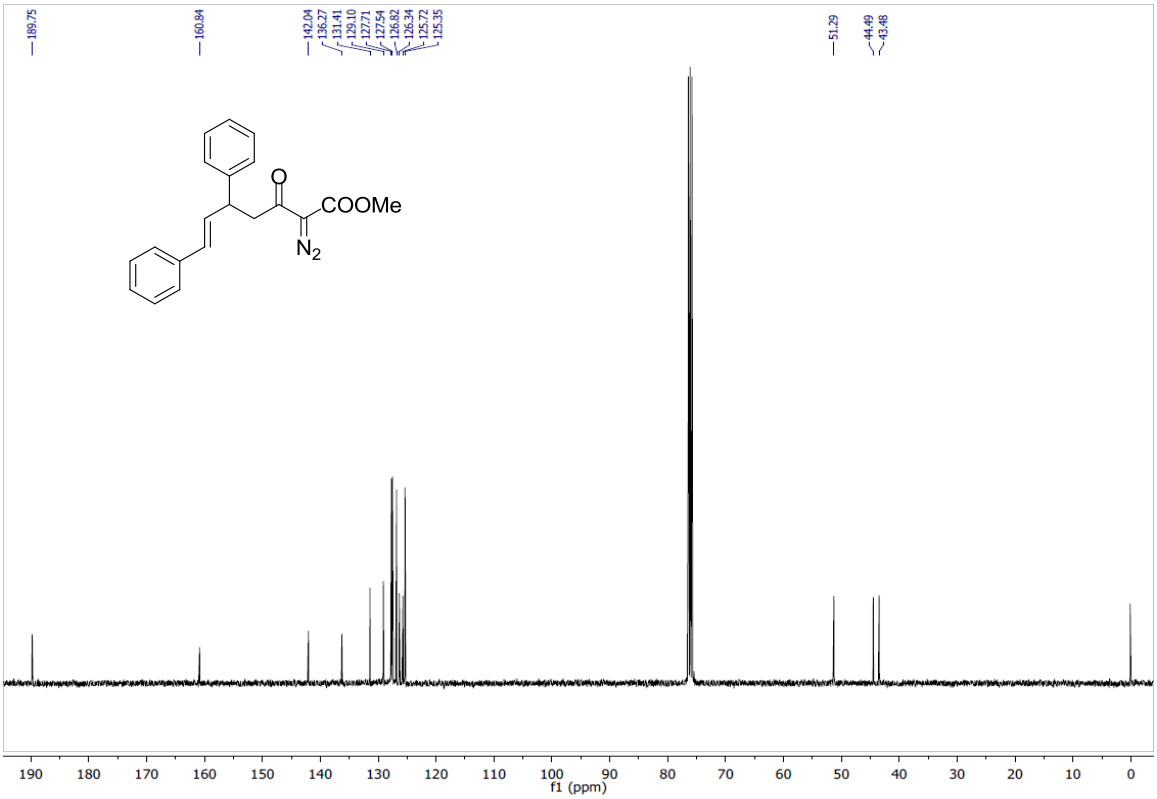
Methyl 2-Diazo-5-(naphthalen-2-yl)-3-oxo-5-phenylpentanoate (7i)



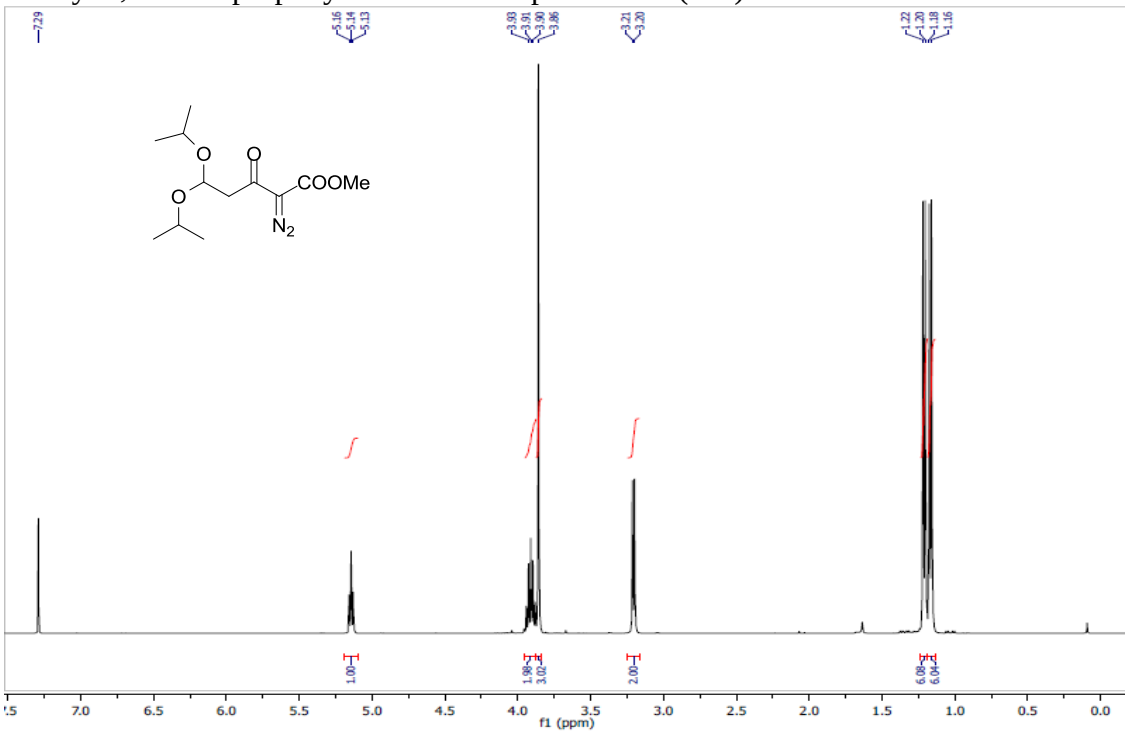


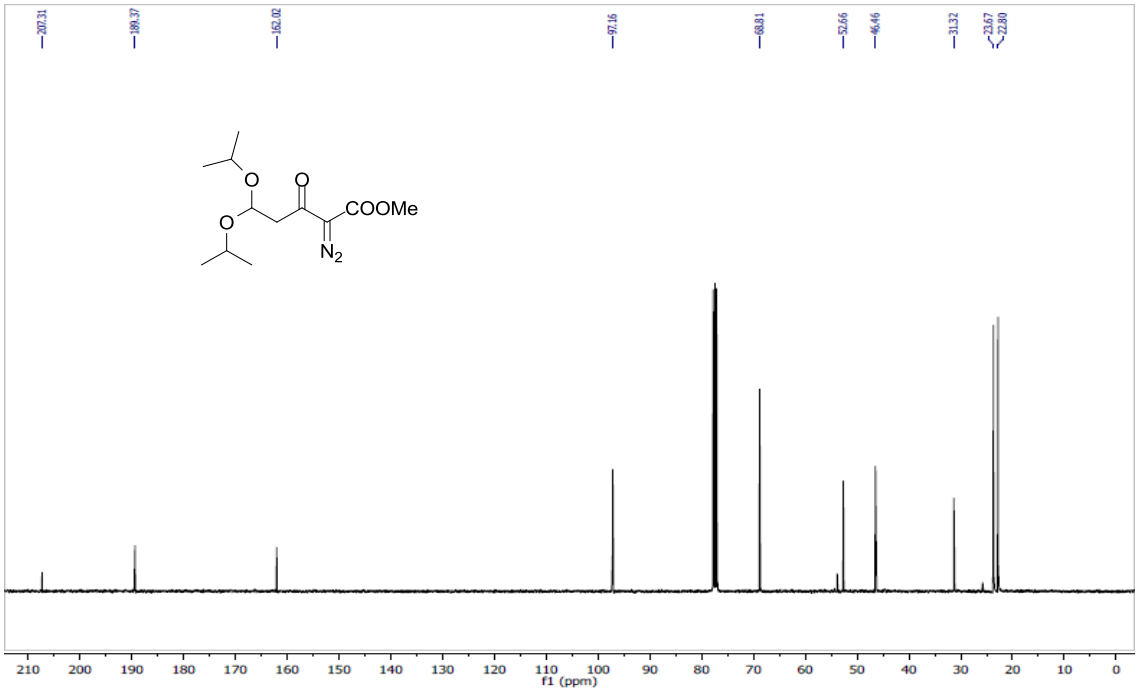
Methyl 2-Diazo-3-oxo-5,7-diphenylhept-6-enoate (9)



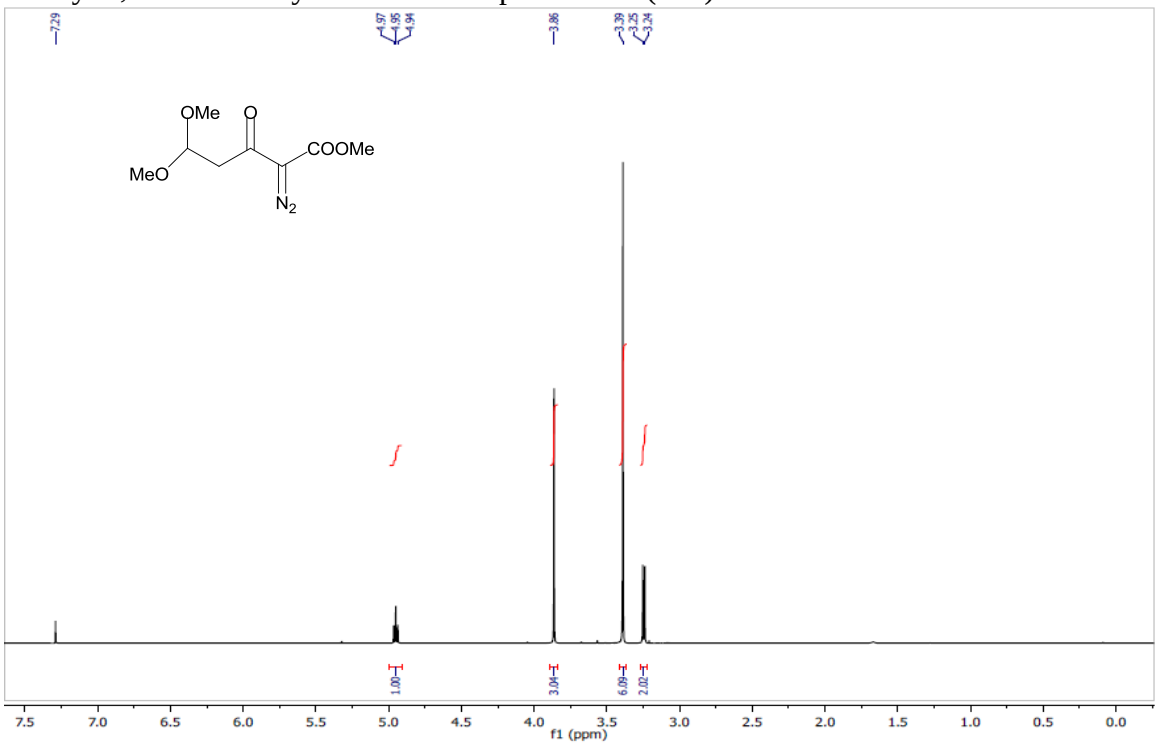


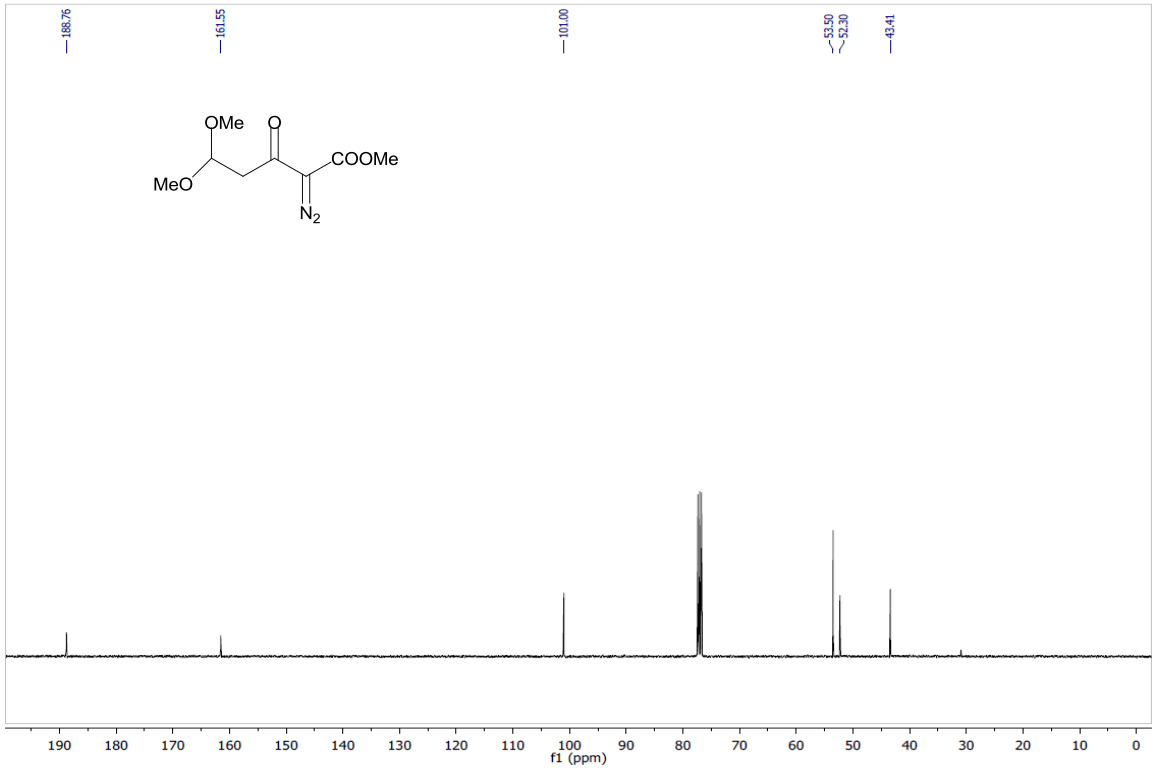
Methyl 5, 5-Diisopropoxy-3-oxo-2-diazopentanoate (11a)



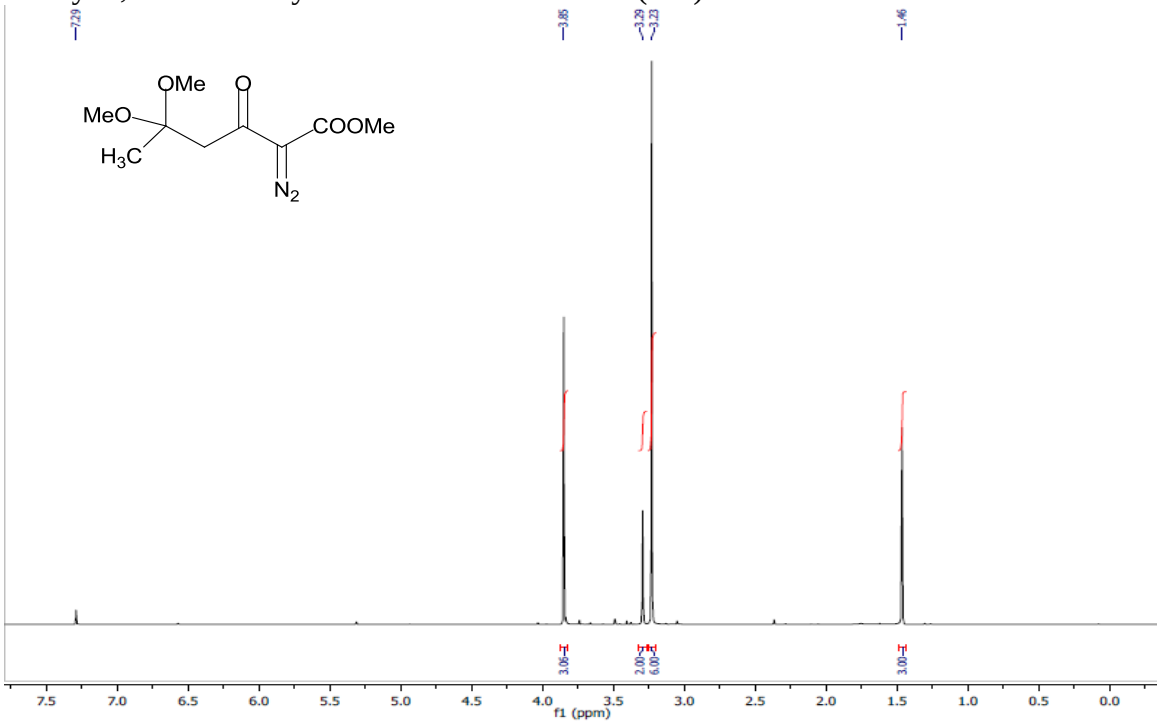


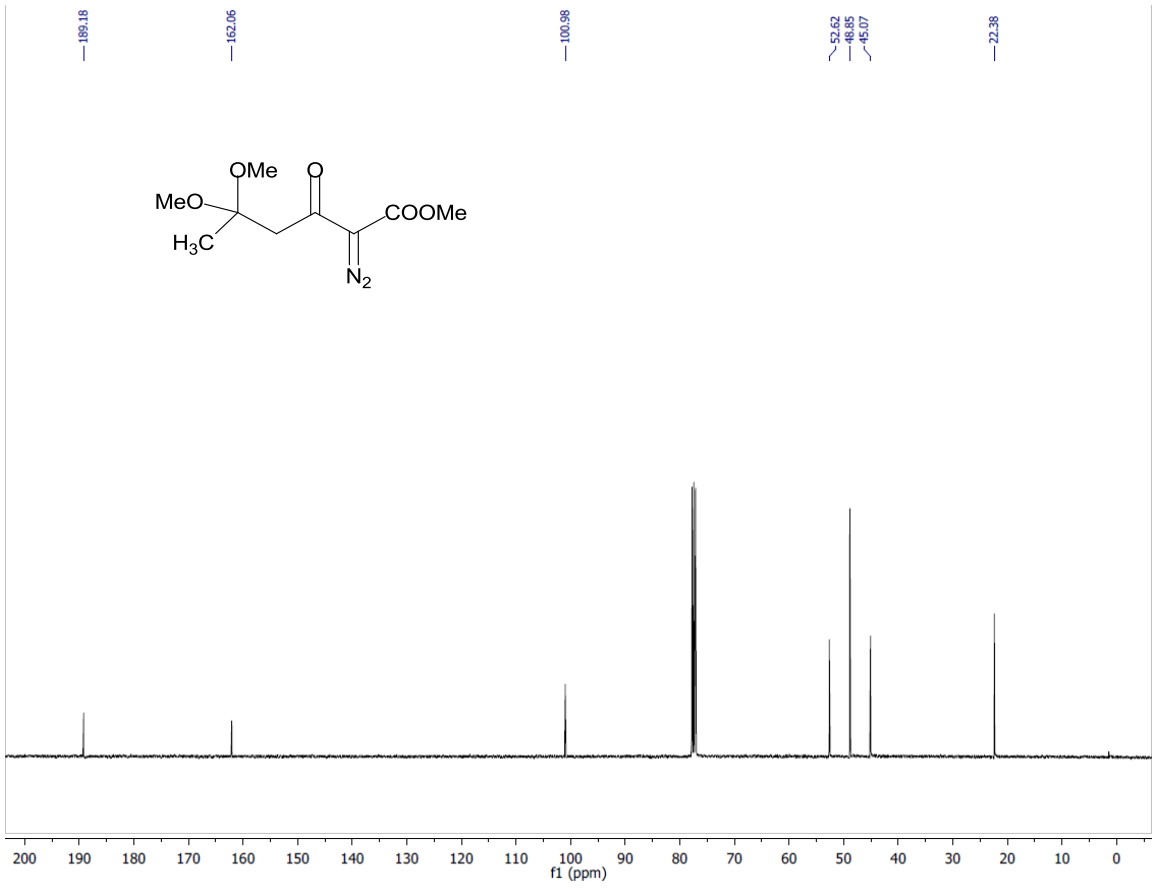
Methyl 5, 5-Dimethoxy-3-oxo-2-diazopentanoate (11b)



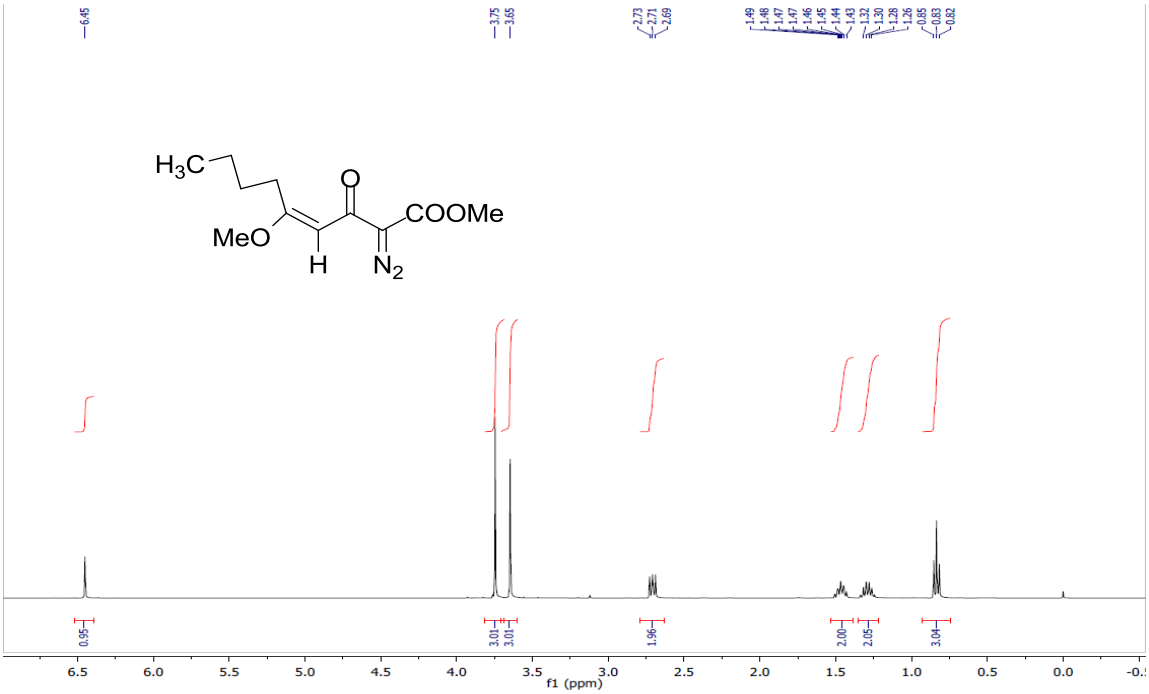


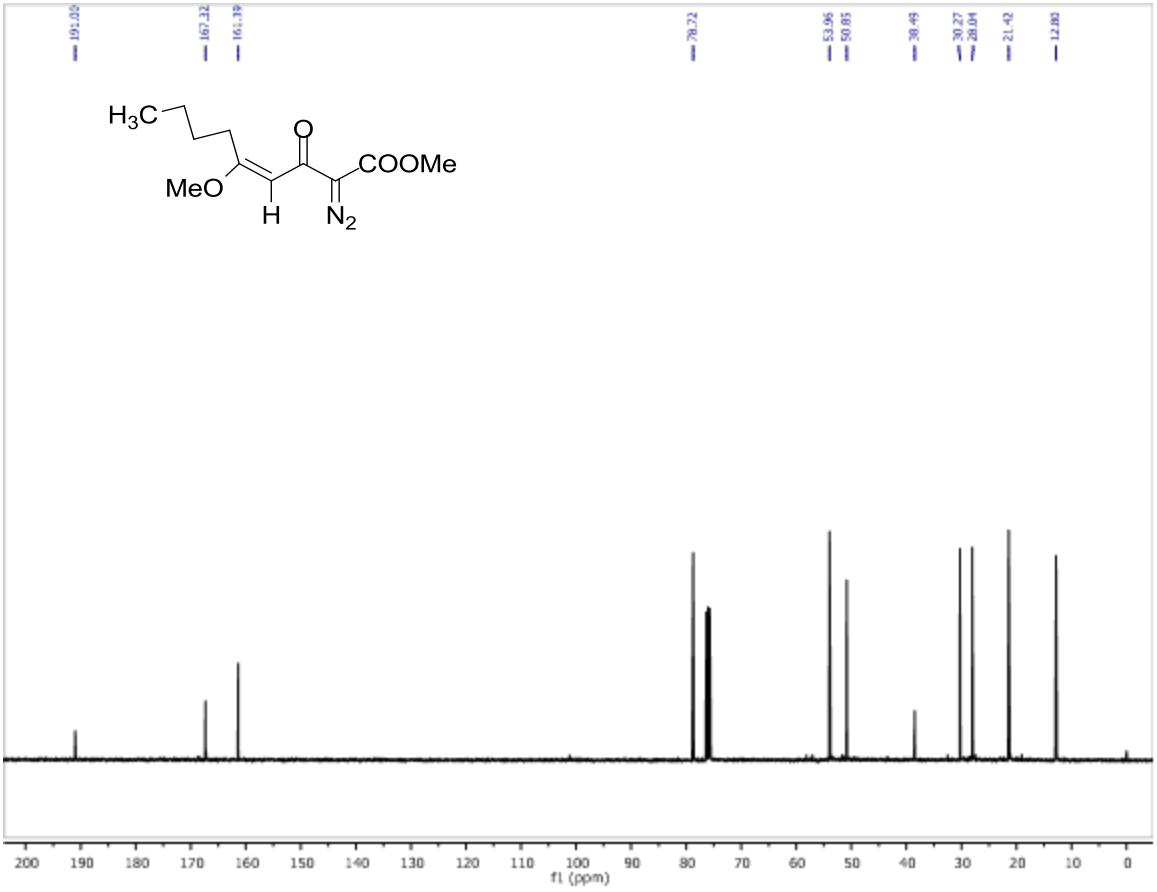
Methyl 5, 5-Dimethoxy-3-oxo-2-diazohexanoate (11c)



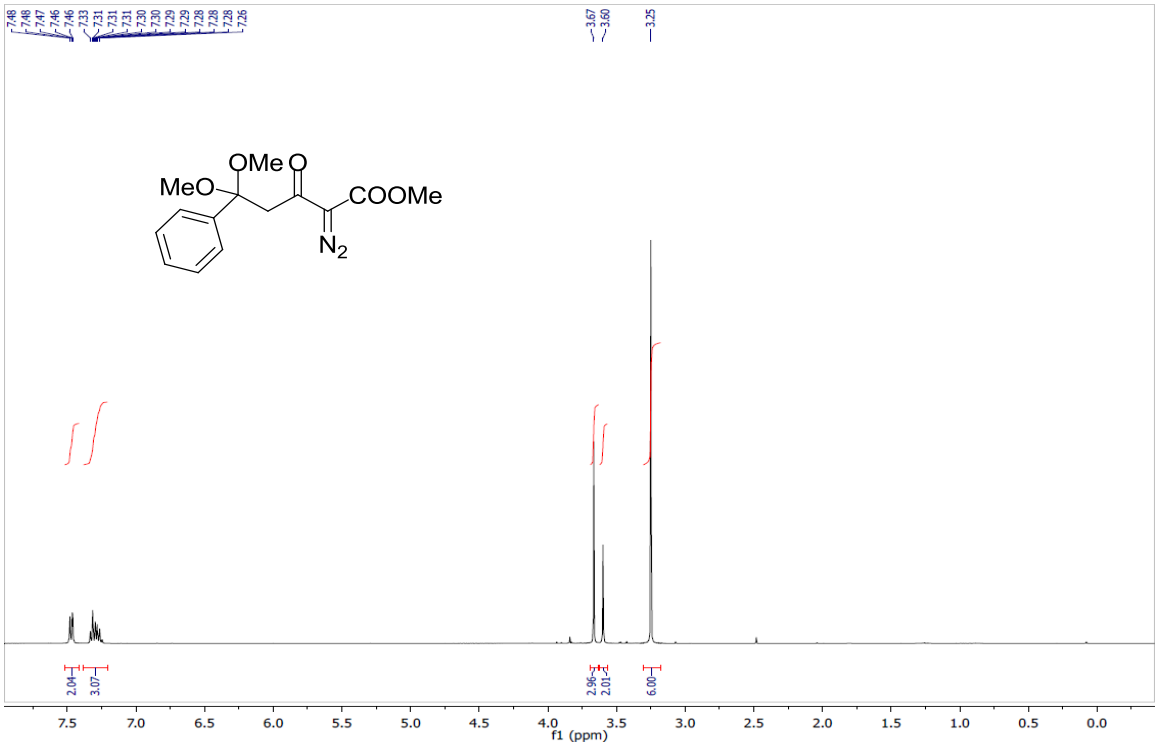


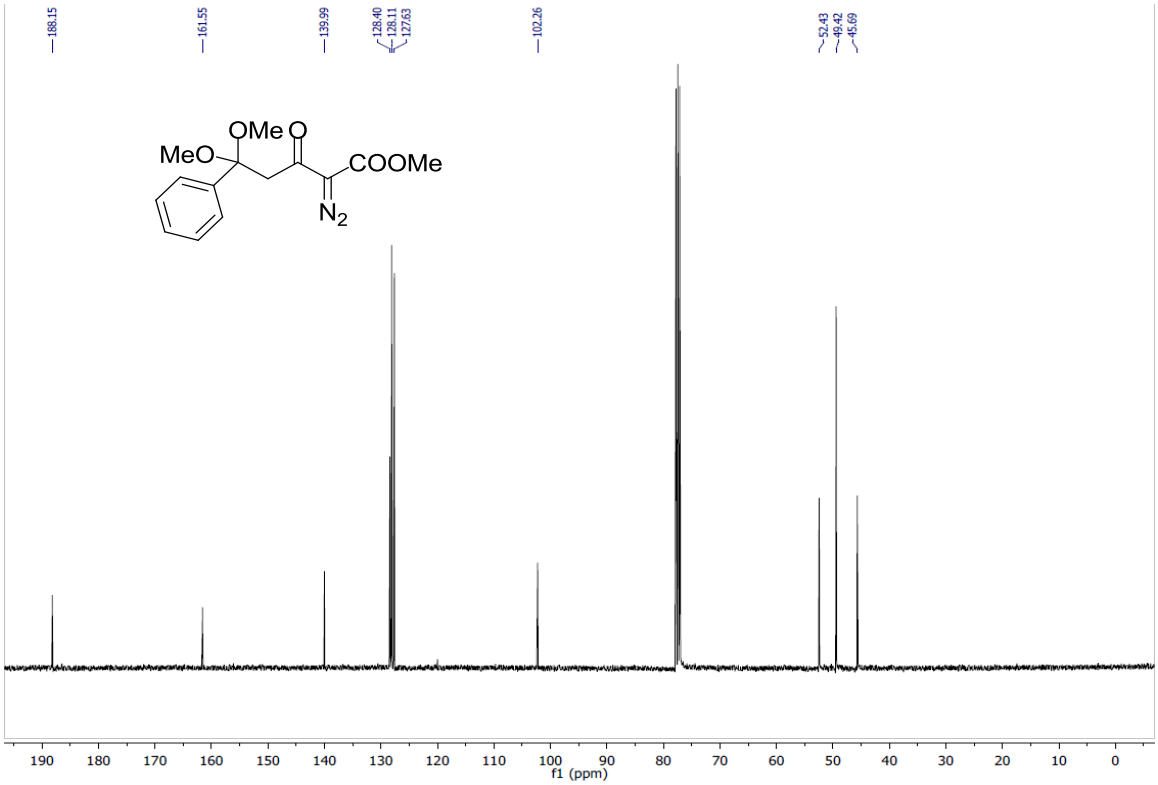
Methyl *(E)*-2-Diazo-5-methoxy-3-oxonon-4-enoate (11d)



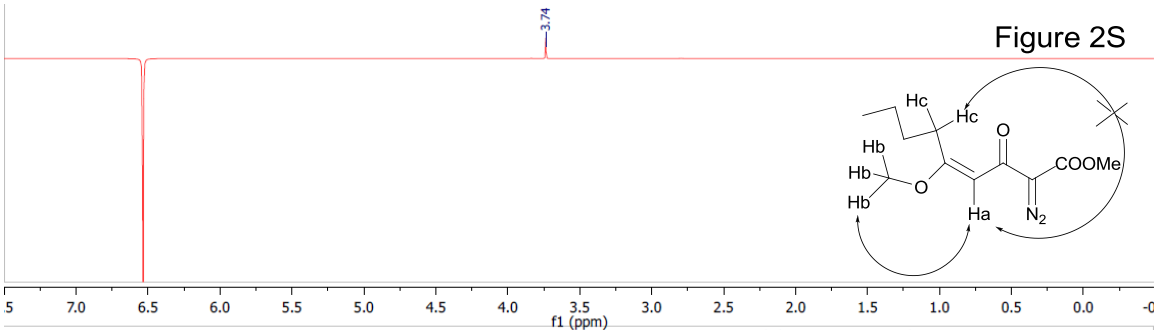


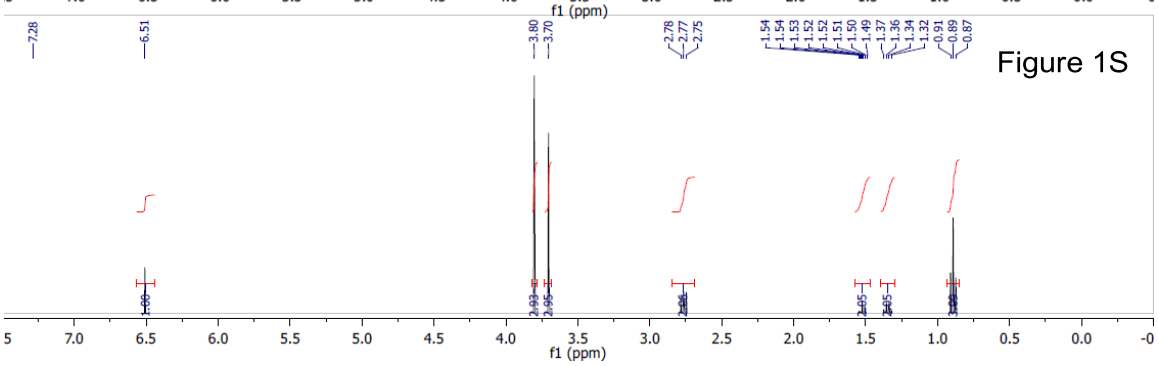
Methyl 2-Diazo-5,5-dimethoxy-3-oxo-5-phenylpentanoate (11e)





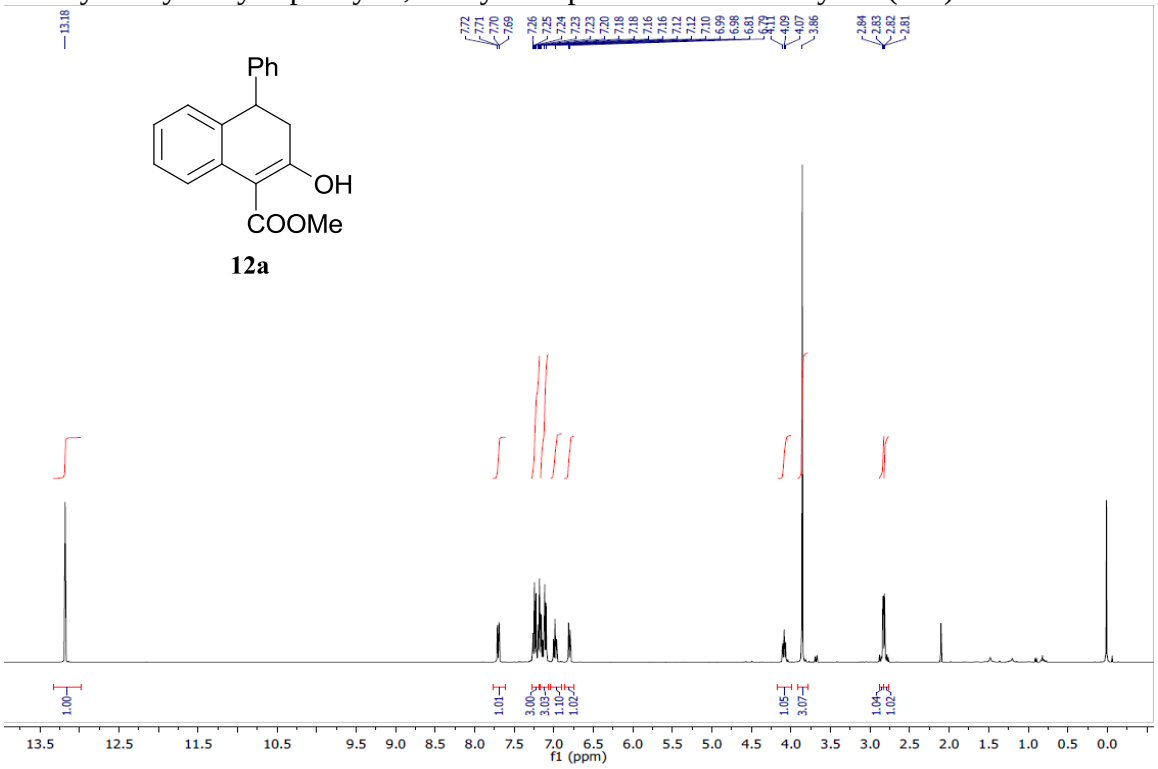
1D NOE study of the product 11d:

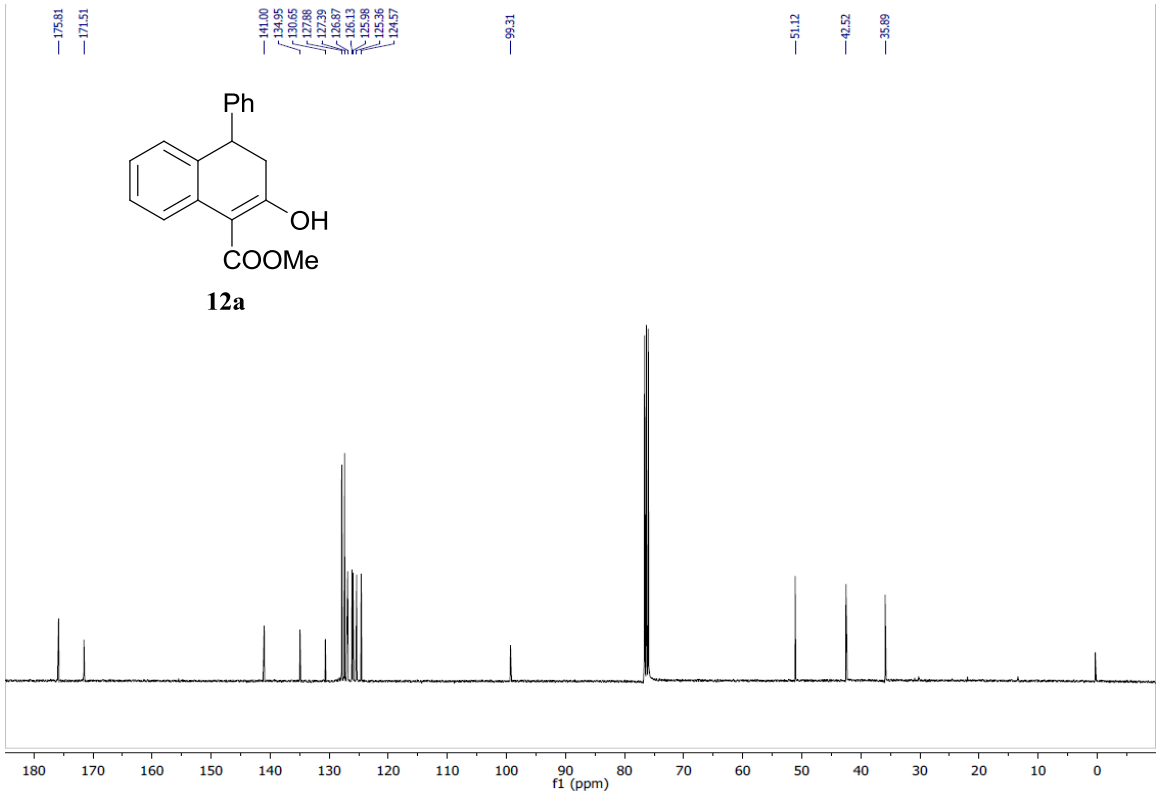




The configuration of **11d** was determined by a 1D NOE study (Figure 1S). When proton Ha was activated (Figure 2S), a clear correlation was observed between Ha and Hb but no correlation with Hc. Based on the above spectral data, product **11d** is assigned to have the (*E*)-configuration.

Methyl 2-Hydroxy-4-phenyl-3,4-dihydronaphthalene-1-carboxylate (12a)





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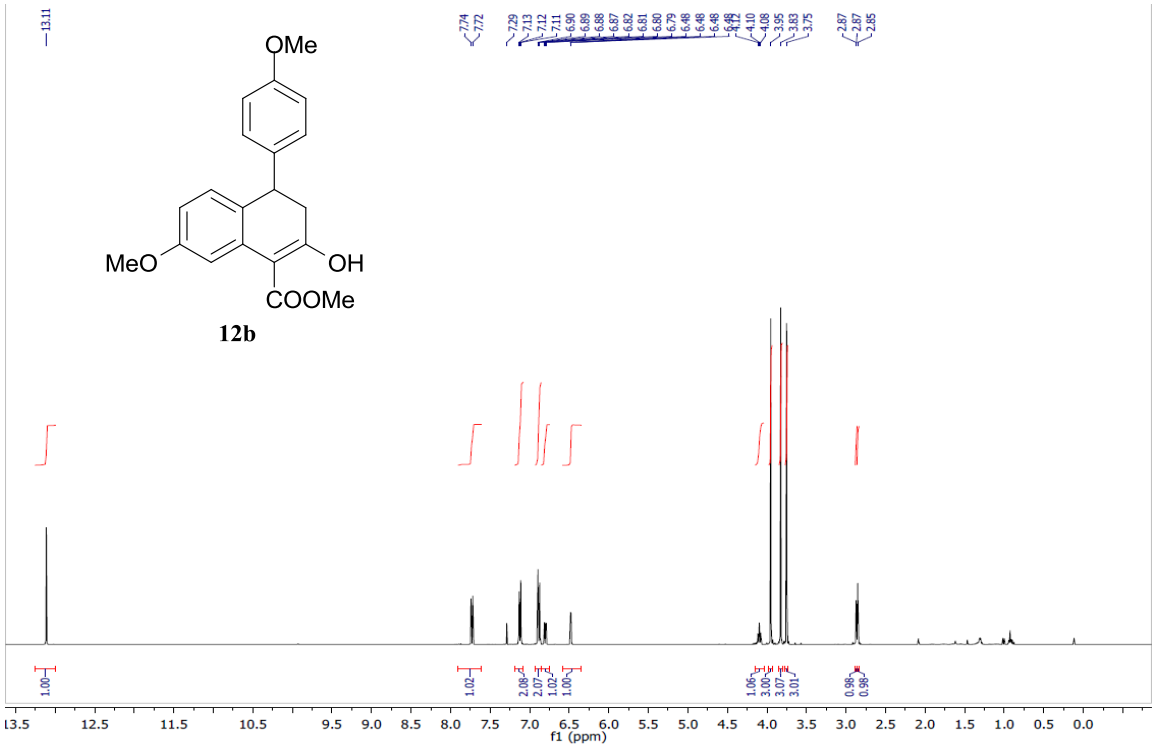
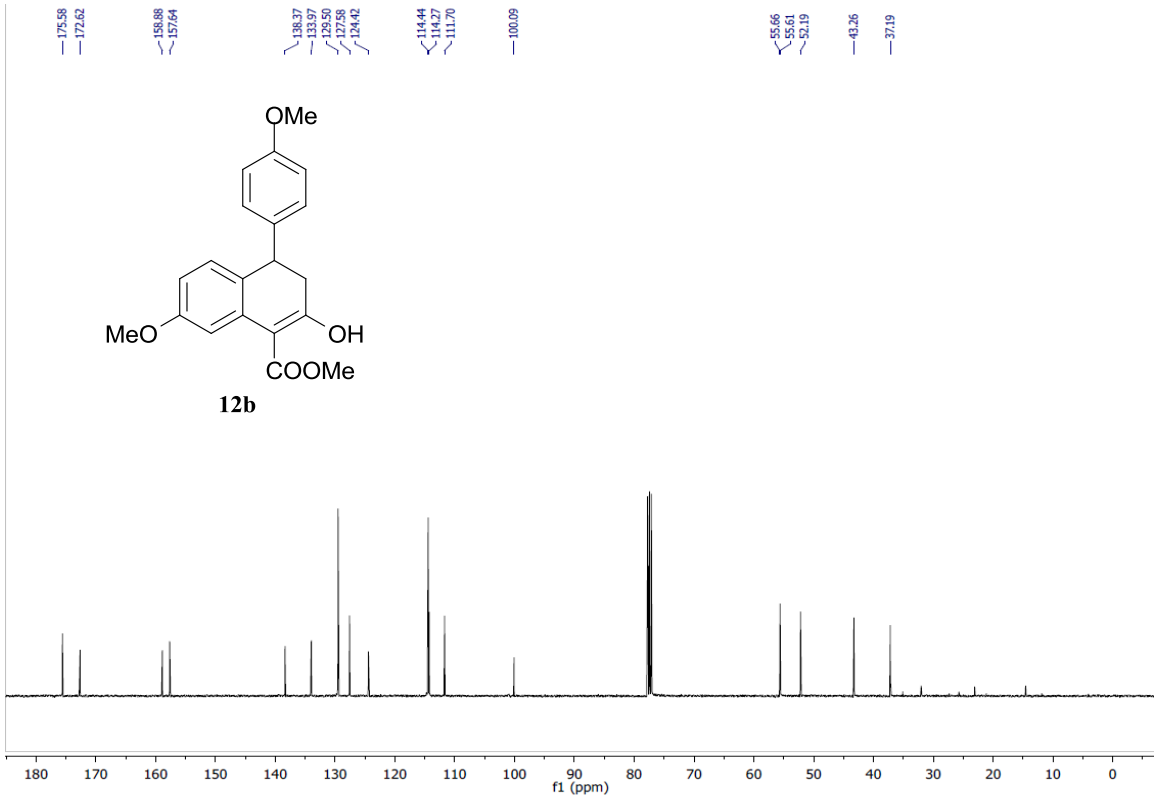
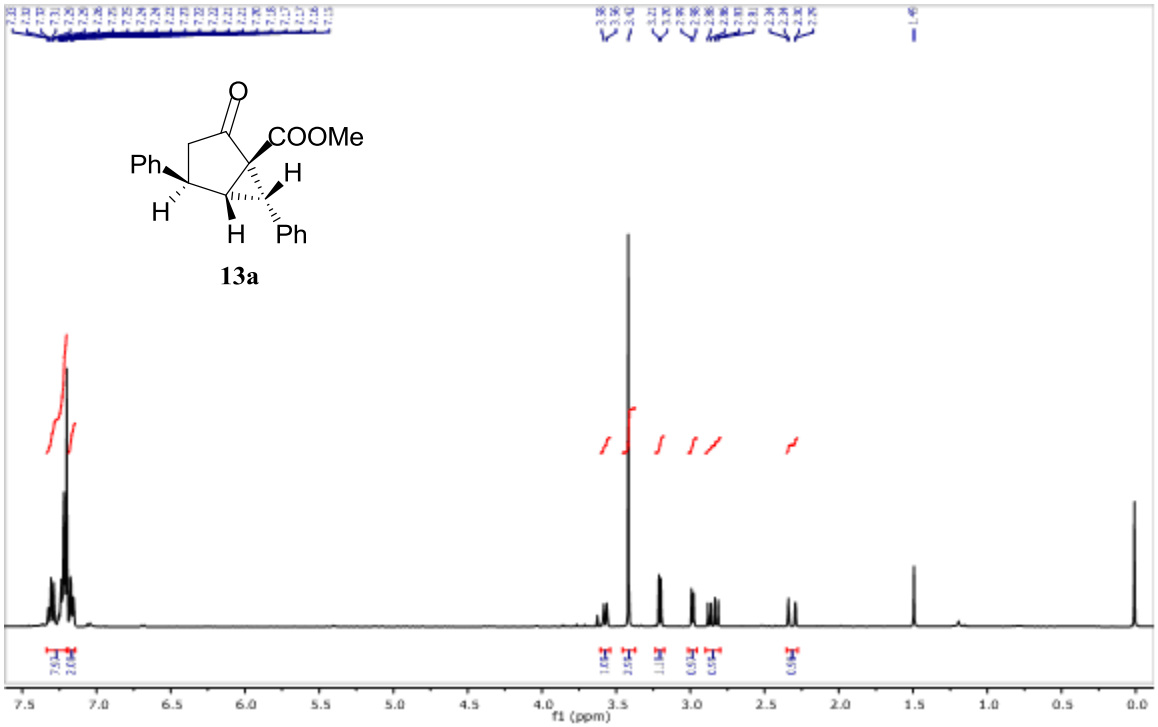
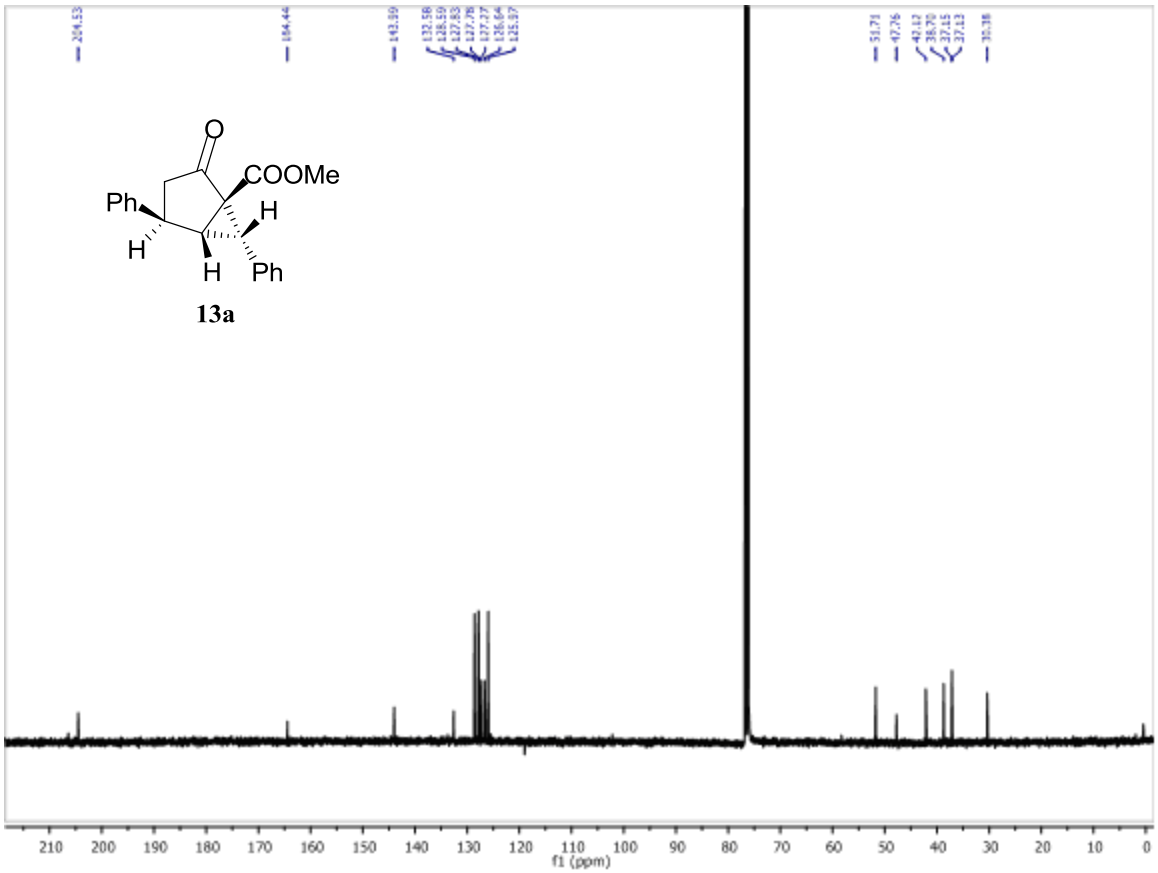
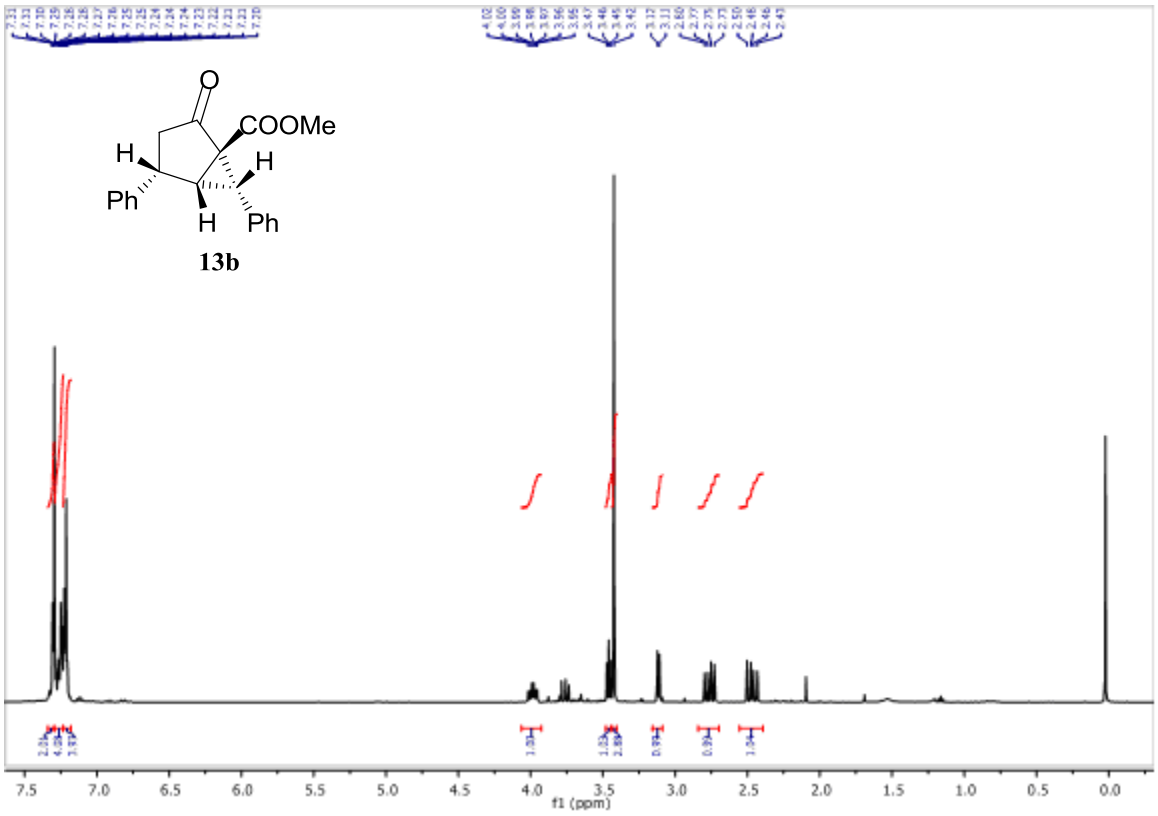


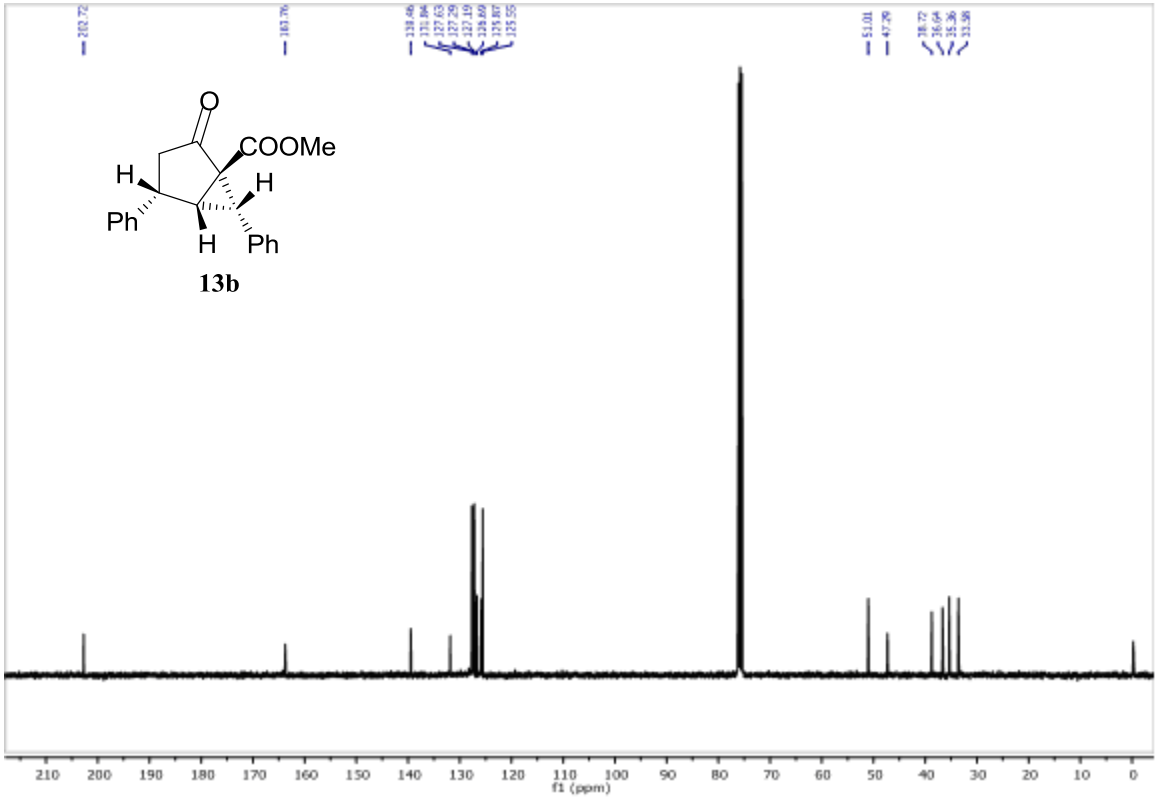


Methyl 2-Oxo-4,6-diphenylbicyclo[3.1.0]hexane-1-carboxylate (13a and b)

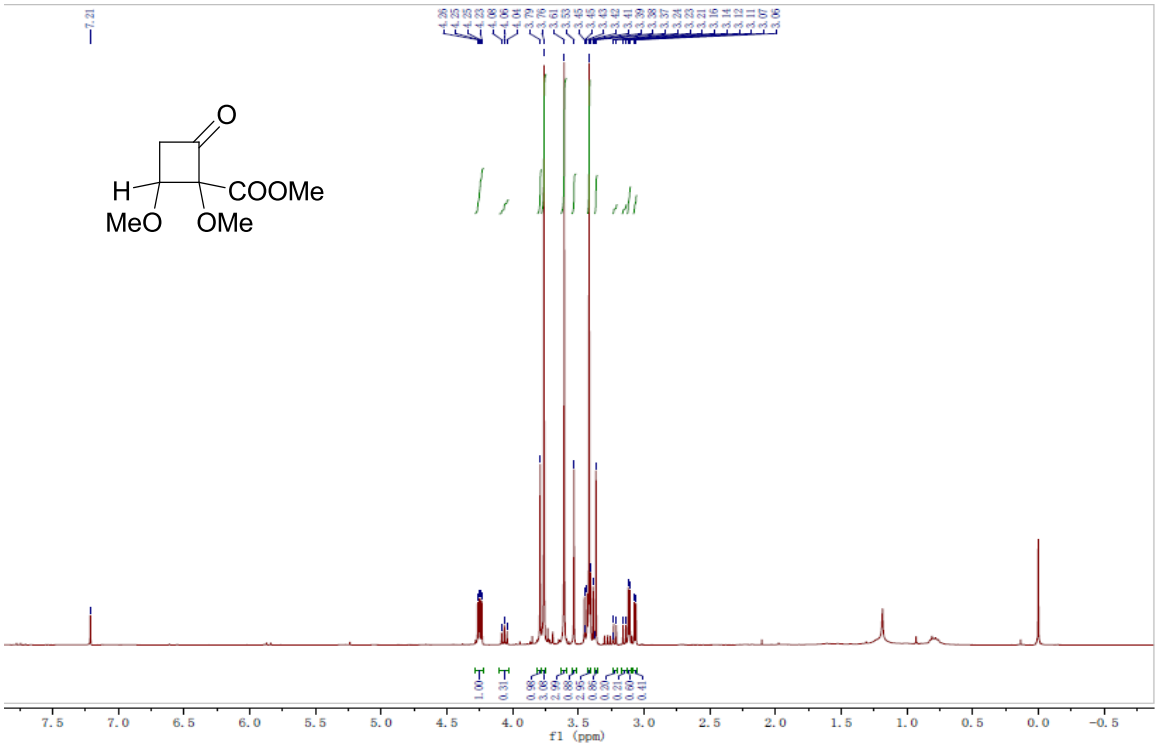


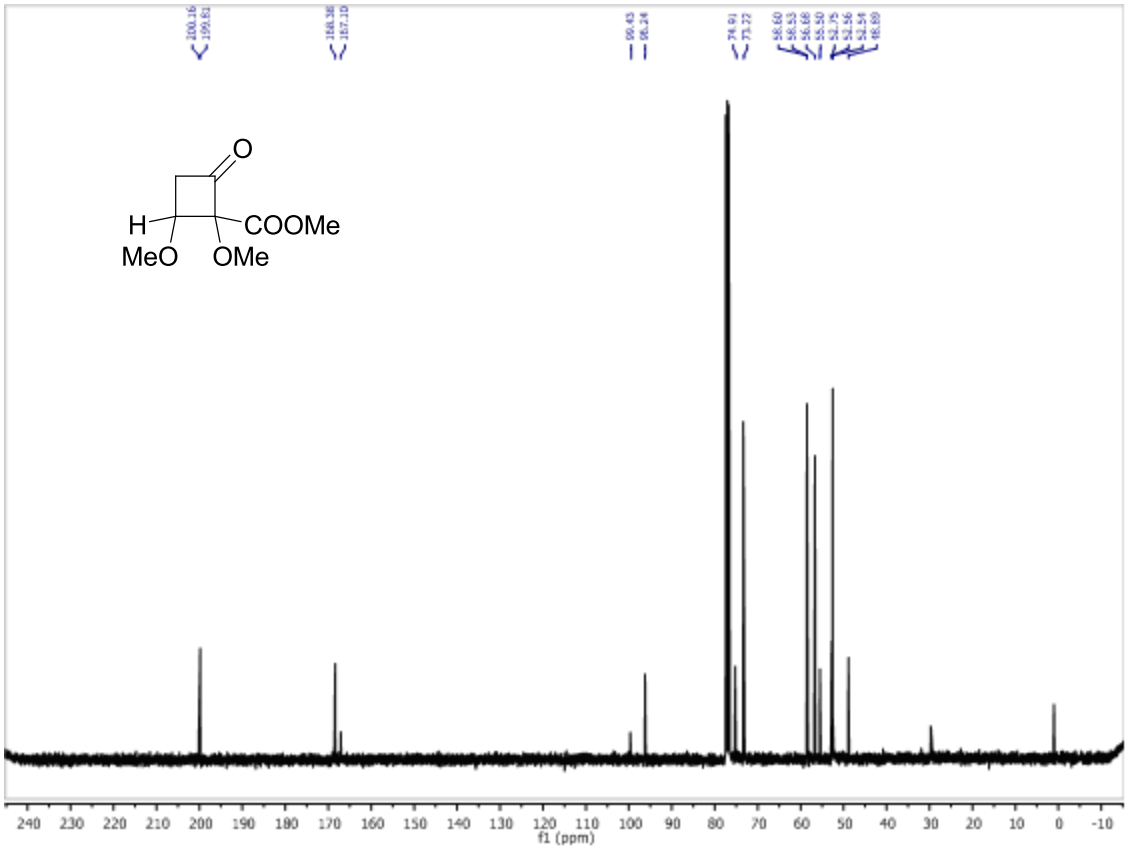



O
COOMe
H
Ph
H
H
Ph
13b
f1 (ppm)

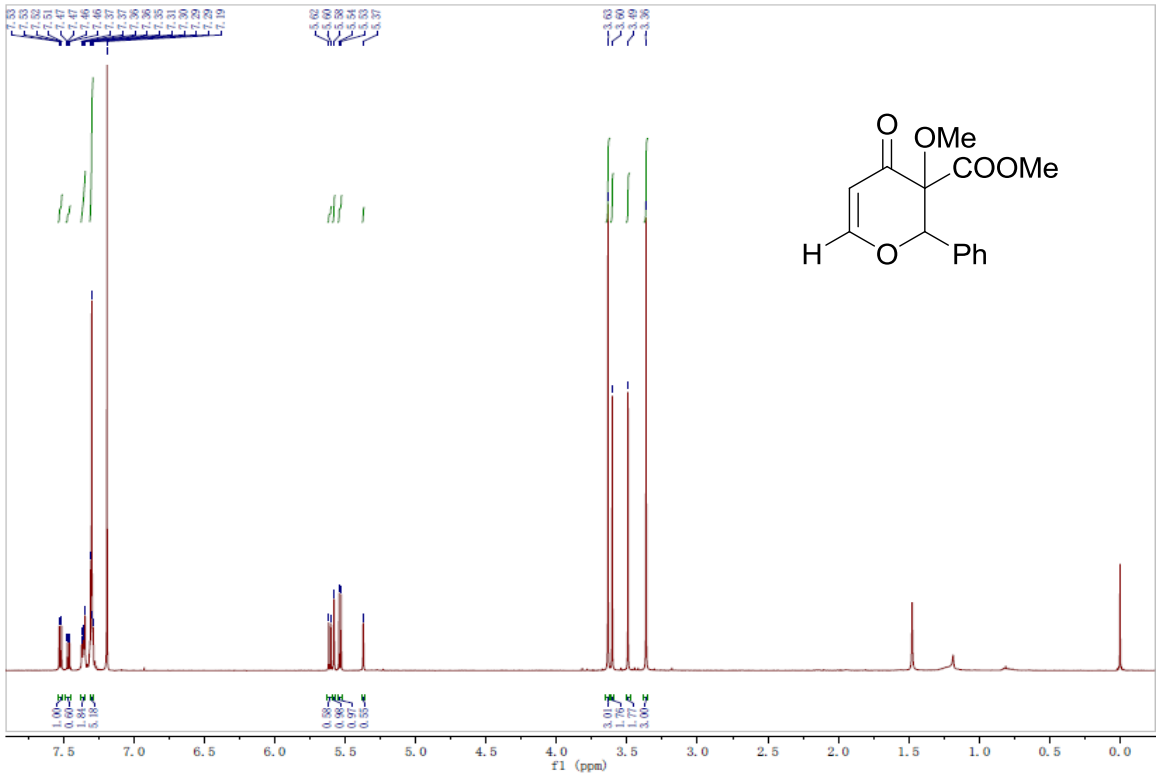

O
COOMe
H
Ph
H
H
Ph
13b
f1 (ppm)

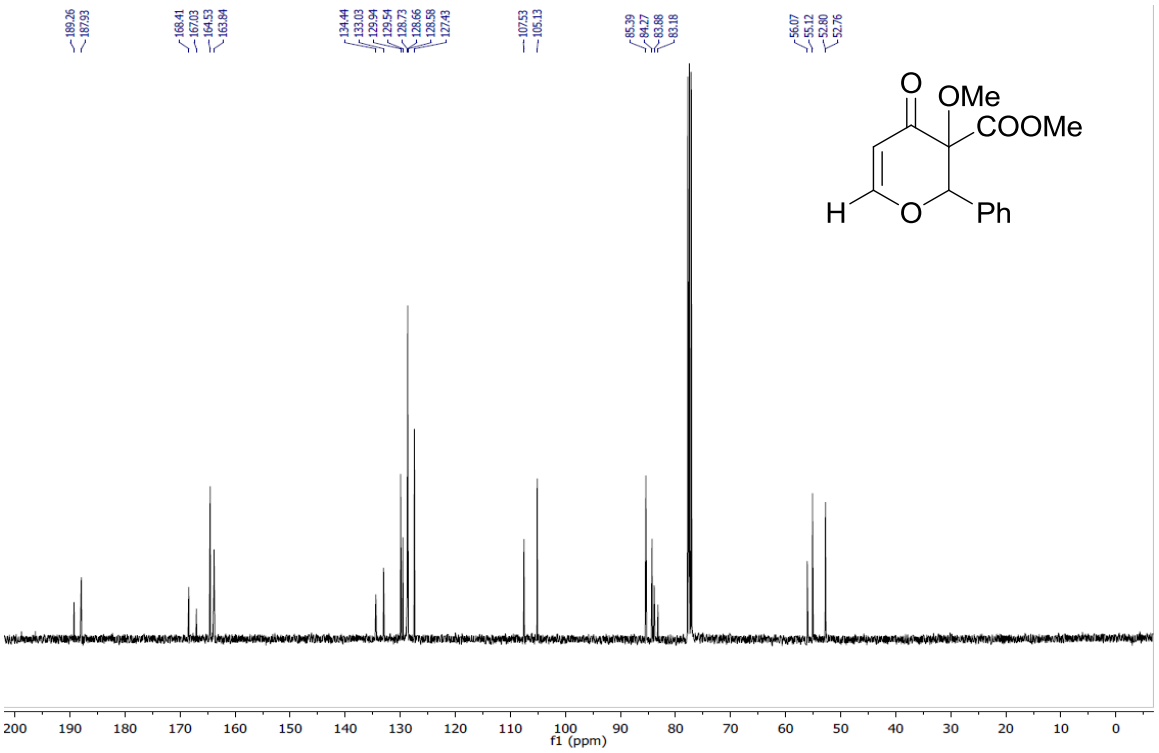
1, 2-Dimethoxy-4-oxocyclobutanecarboxylate (14)



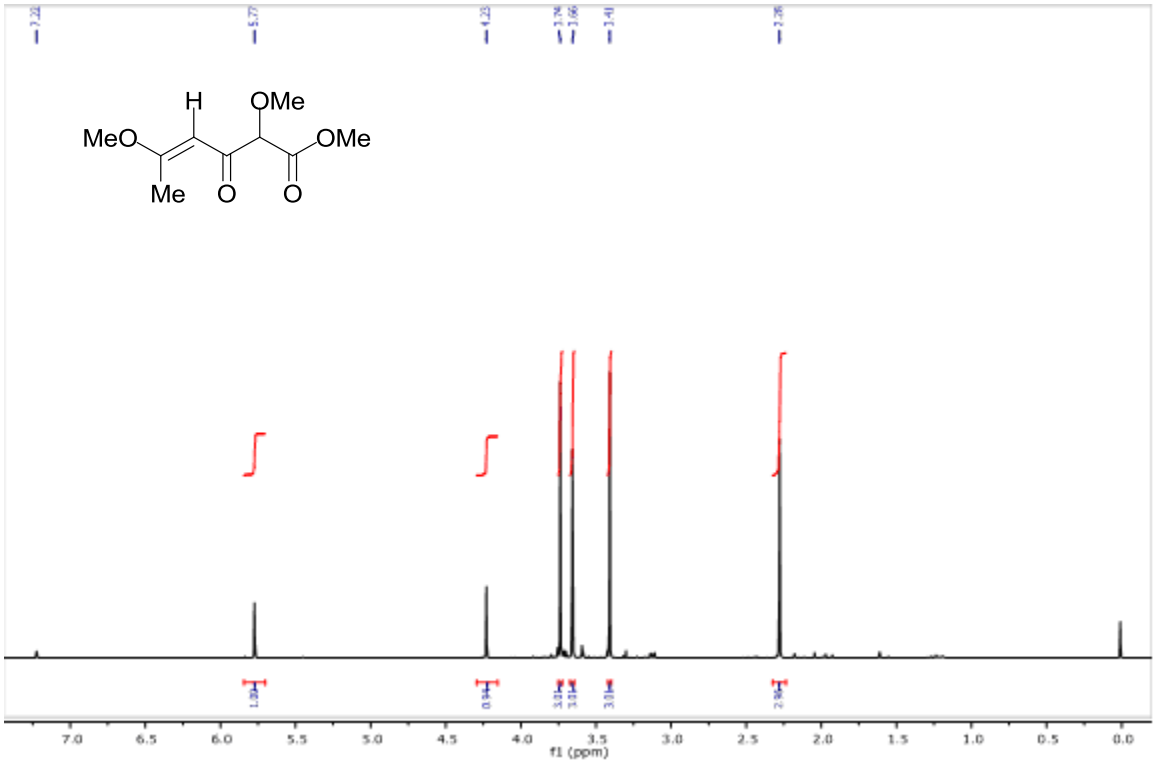


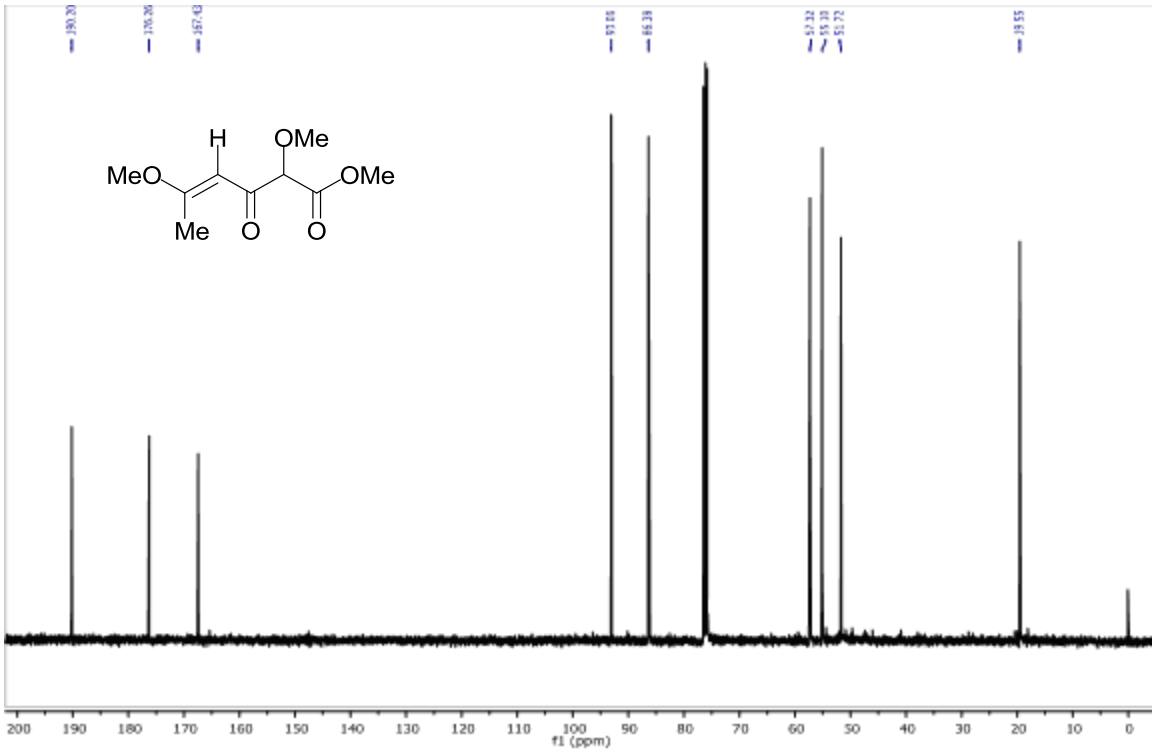
Methyl 3,4-Dihydro-3-methoxy-4-oxo-2-phenyl-2H-pyran-3-carboxylate (15)



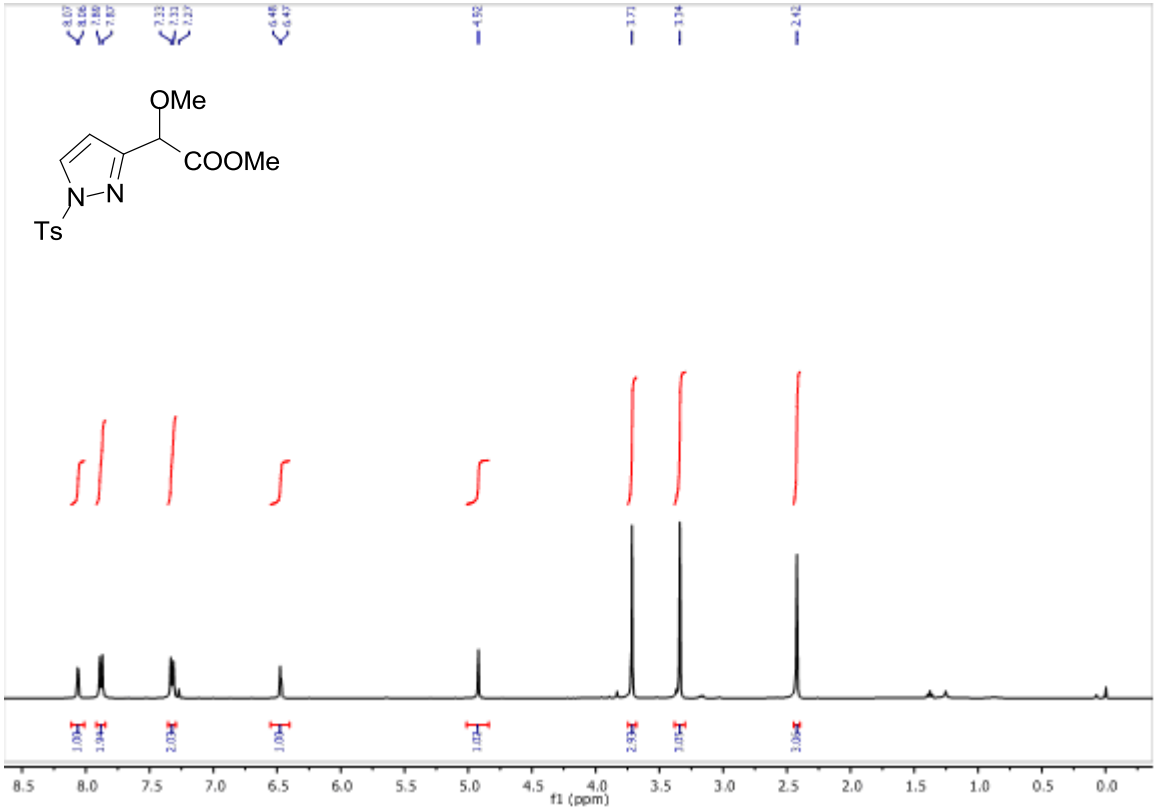


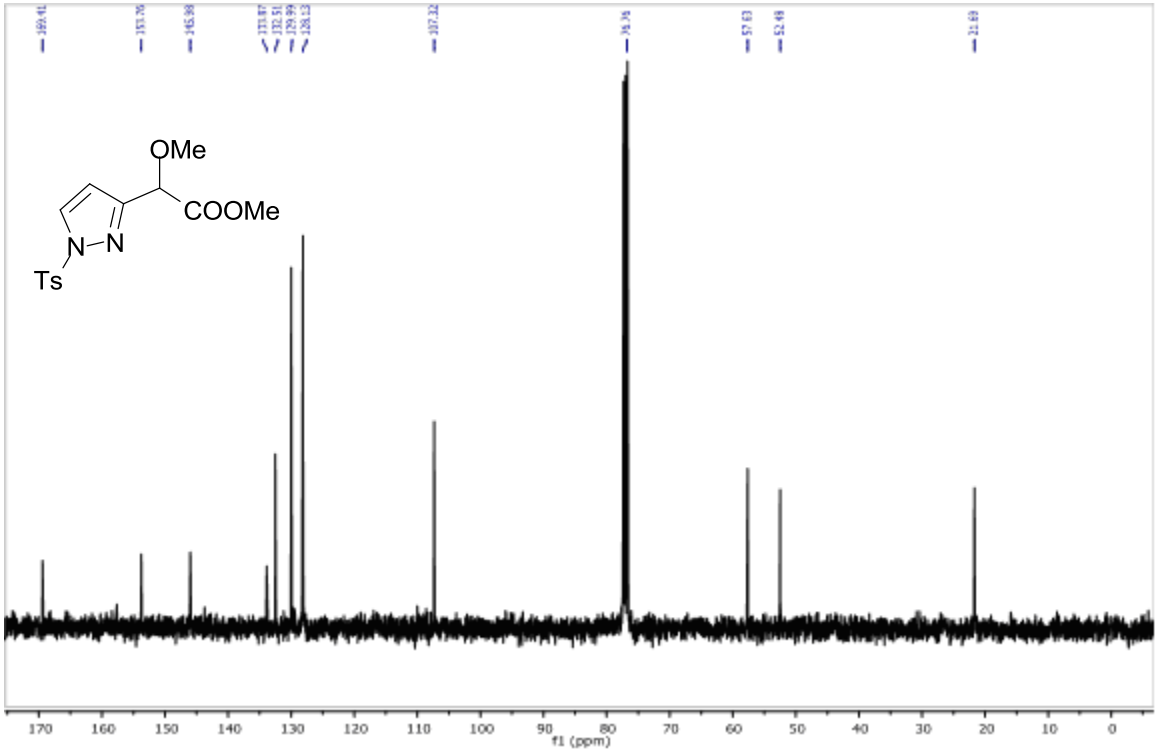
Methyl *(E)*-2,5-Dimethoxy-3-oxohex-4-enoate (17)



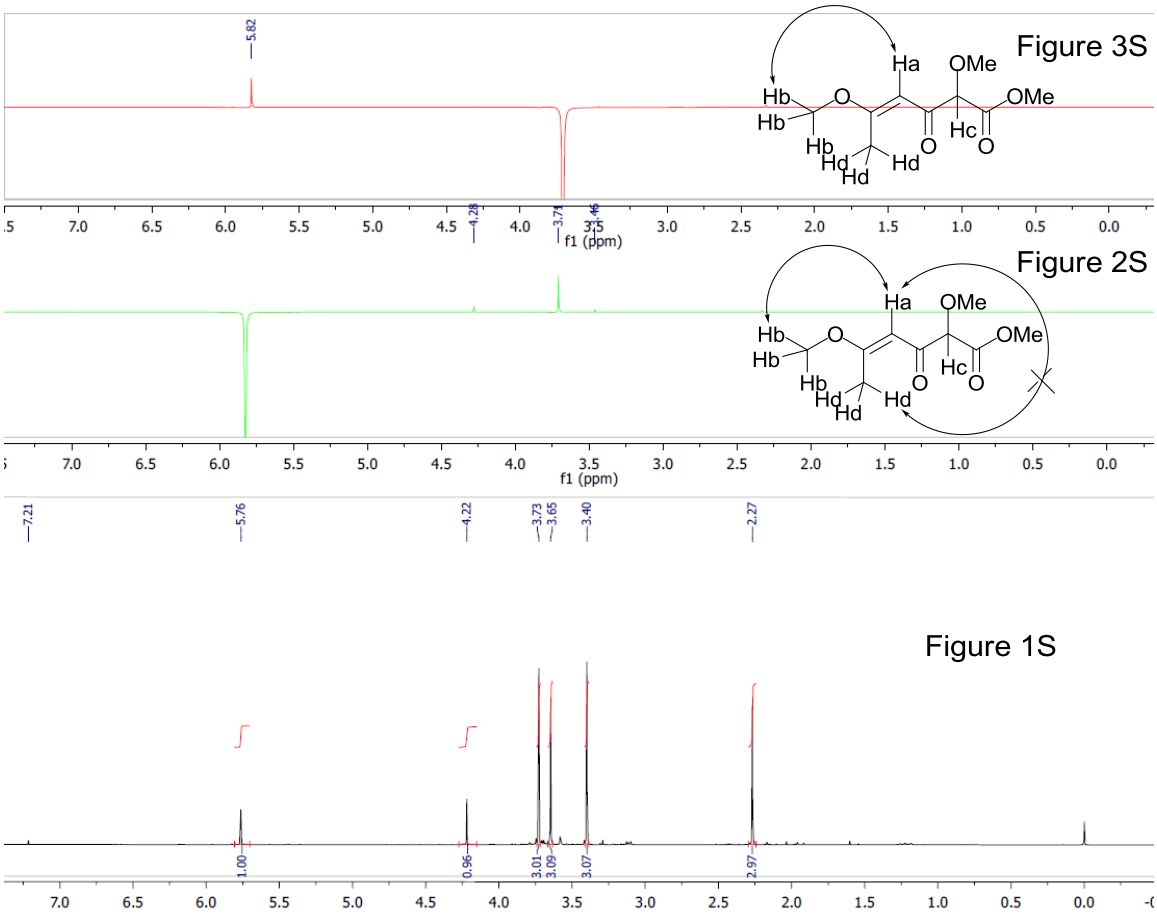


Methyl 2-Methoxy-2-(1-tosyl-1*H*-pyrazol-3-yl) acetate (18)





1D NOE study of the product 17:



The configuration of **17** was determined by a 1D NOE study (Figure 1S). Activation of proton Ha (Figure 2S) of **17** gave a correlation with Hb and a very weak correlation with Hc, but no correlation with Hd. Again, when proton Hb was activated (Figure 3S), a clear correlation was observed between Ha and Hb. Based on the above spectral data, product **17** is assigned to have the (*E*)-configuration.