

Asymmetric Synthesis of Multifunctionalized 2,3-Benzodiazepines by a One-pot N-Heterocyclic Carbene/Chiral Palladium Sequential Catalysis

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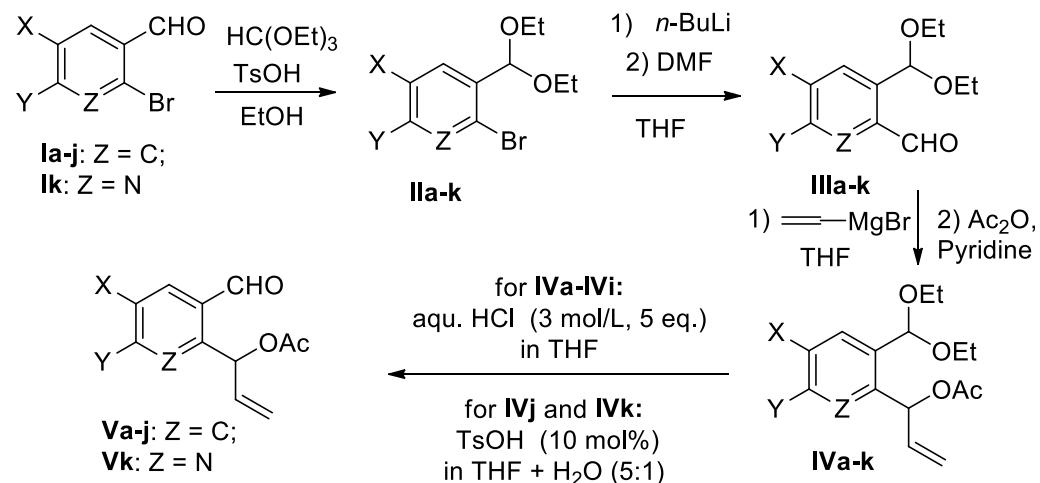
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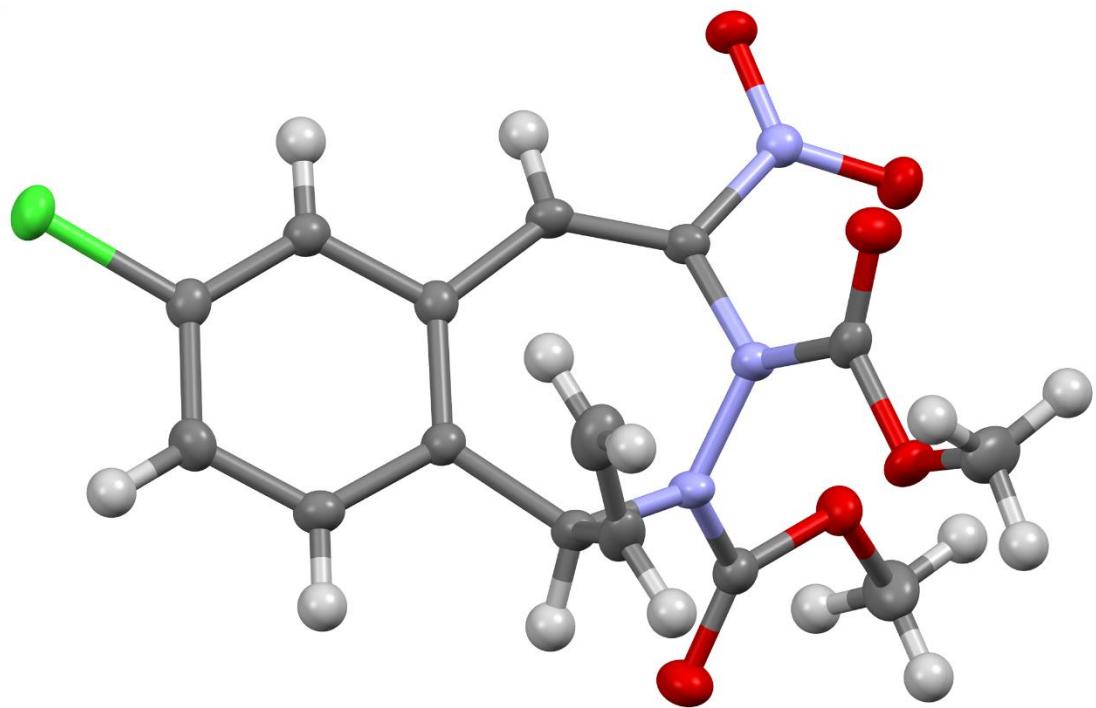
<b>1. Reaction scheme and results for the preparation of 1-(<i>o</i>-formylaryl)allyl acetates .....</b>	<b>pS2</b>
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**Preparation of 1-(2-Formylaryl)allyl acetates **Va-Vk**.**

**Table S1. Preparation of 1-(2-Formylaryl)allyl acetates **Va-Vk**.**



<b>I</b> (10 mmol): X, Y	Yield			
	<b>II</b>	<b>III</b>	<b>IV</b>	<b>V</b>
<b>Ia-j, IIa-j, IIIa-j, IVa-j and Va-j: </b> Z = C. <b>Ik, IIk, IIIk, IVk and Vb-k: </b> Z = N				
<b>Ia</b> , X = Y = H	<b>IIa</b> , 95%, 2.46 g	<b>IIIa</b> , 92%, 1.80 g	<b>IVa</b> , 84%, 2.01 g	<b>Va</b> , 85%, 1.26 g
<b>Ib</b> , X = OMe, Y = H	<b>IIb</b> , 91%, 2.85 g	<b>IIIb</b> , 98%, 2.31 g	<b>IVb</b> , 86%, 2.54 g	<b>Vb</b> , 70%, 1.37 g
<b>Ic</b> , X = Me, Y = H	<b>IIc</b> , 96%, 2.59 g	<b>IIIc</b> , 84%, 1.77 g	<b>IVc</b> , 90%, 2.08 g	<b>Vc</b> , 85%, 1.33 g
<b>Id</b> , X = Cl, Y = H	<b>IId</b> , 95%, 2.76 g	<b>IIId</b> , 88%, 2.01 g	<b>IVd</b> , 95%, 2.46 g	<b>Vd</b> , 72%, 1.37 g
<b>Ie</b> , X = CF <sub>3</sub> , Y = H	<b>IIe</b> , 91%, 2.93 g	<b>IIIe</b> , 82%, 2.04 g	<b>IVe</b> , 89%, 2.30 g	<b>Ve</b> , 80%, 1.45 g
<b>If</b> , X = H, Y = OMe	<b>IIf</b> , 93%, 2.69 g	<b>IIIf</b> , 85%, 1.88 g	<b>IVf</b> , 90%, 2.17 g	<b>Vf</b> , 70%, 1.16 g
<b> Ig</b> , X = H, Y = Me	<b>IIg</b> , 99%, 2.70 g	<b>IIIg</b> , 85%, 1.87 g	<b>IVg</b> , 88%, 2.13 g	<b>Vg</b> , 77%, 1.25 g
<b>Ih</b> , X = H, Y = Cl	<b>IIh</b> , 99%, 2.91 g	<b>IIIh</b> , 84%, 2.02 g	<b>IVh</b> , 89%, 2.30 g	<b>Vh</b> , 84%, 1.48 g
<b>Ii</b> , X = H, Y = CF <sub>3</sub>	<b>IIi</b> , 91%, 2.97 g	<b>IIIi</b> , 82%, 2.08 g	<b>IVi</b> , 92%, 2.10 g	<b>Vi</b> , 74%, 1.40 g
<b>Ij</b> , X, Y = OCH <sub>2</sub> O	<b>IIj</b> , 99%, 3 g	<b>IIIj</b> , 95%, 2.37 g	<b>IVj</b> , 90%, 2.74 g	<b>Vj</b> , 75%, 1.59 g
<b>Ik</b> , X = Y = H,	<b>IIk</b> , 97%, 2.51 g	<b>IIIk</b> , 91%, 1.84 g	<b>IVk</b> , 88%, 2.15 g	<b>Vk</b> , 73%, 1.15 g



**Figure S1.** X-ray molecular structure of product **5d**. The ellipsoid contour probability level is 50%.

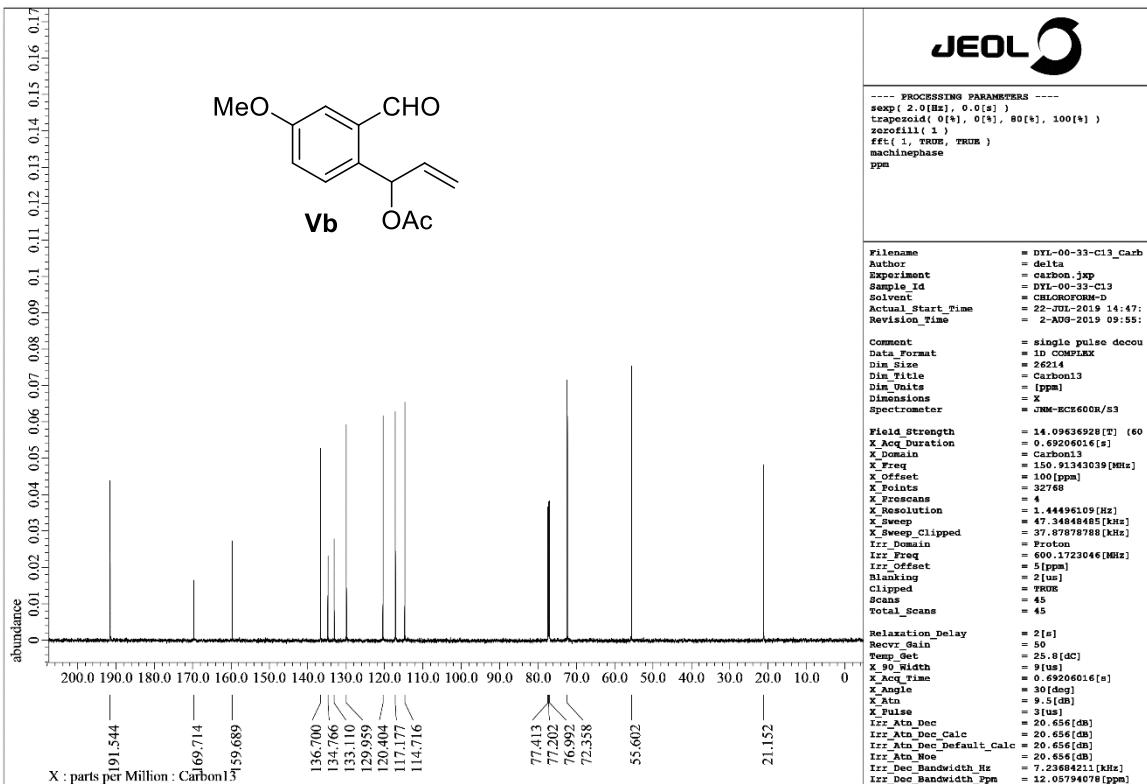
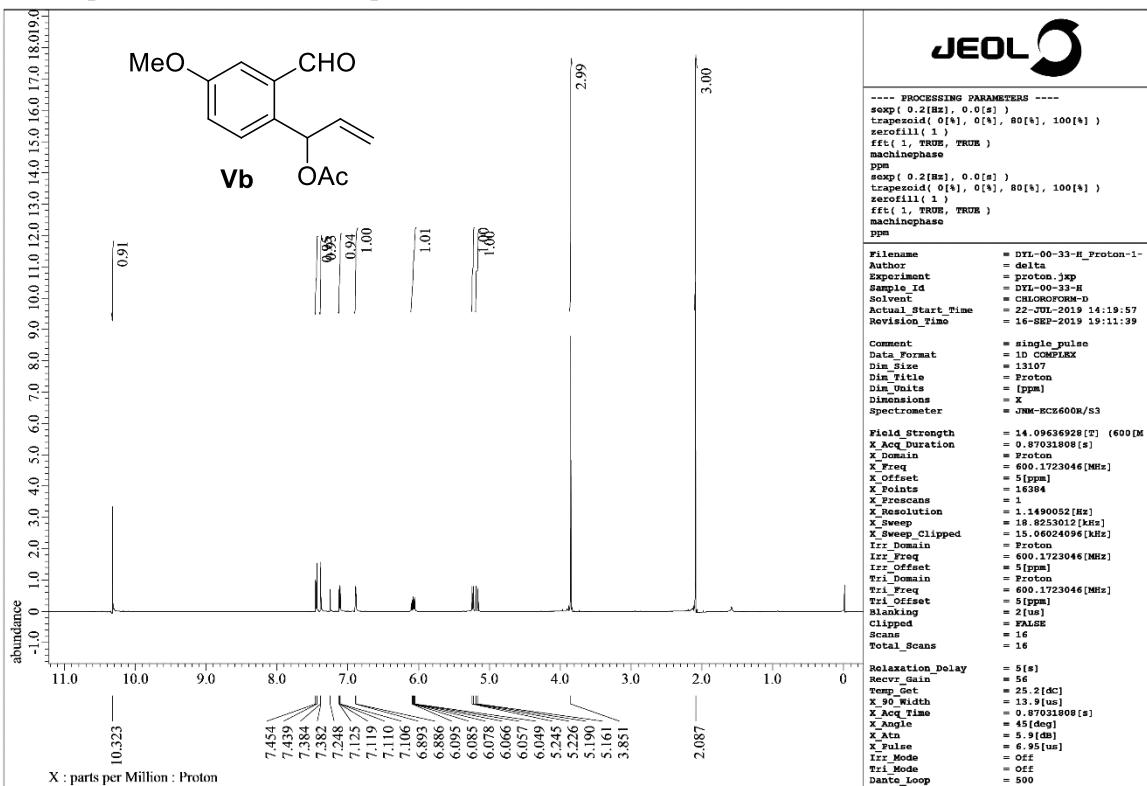
**Crystal data and structure refinements for products 5d.**

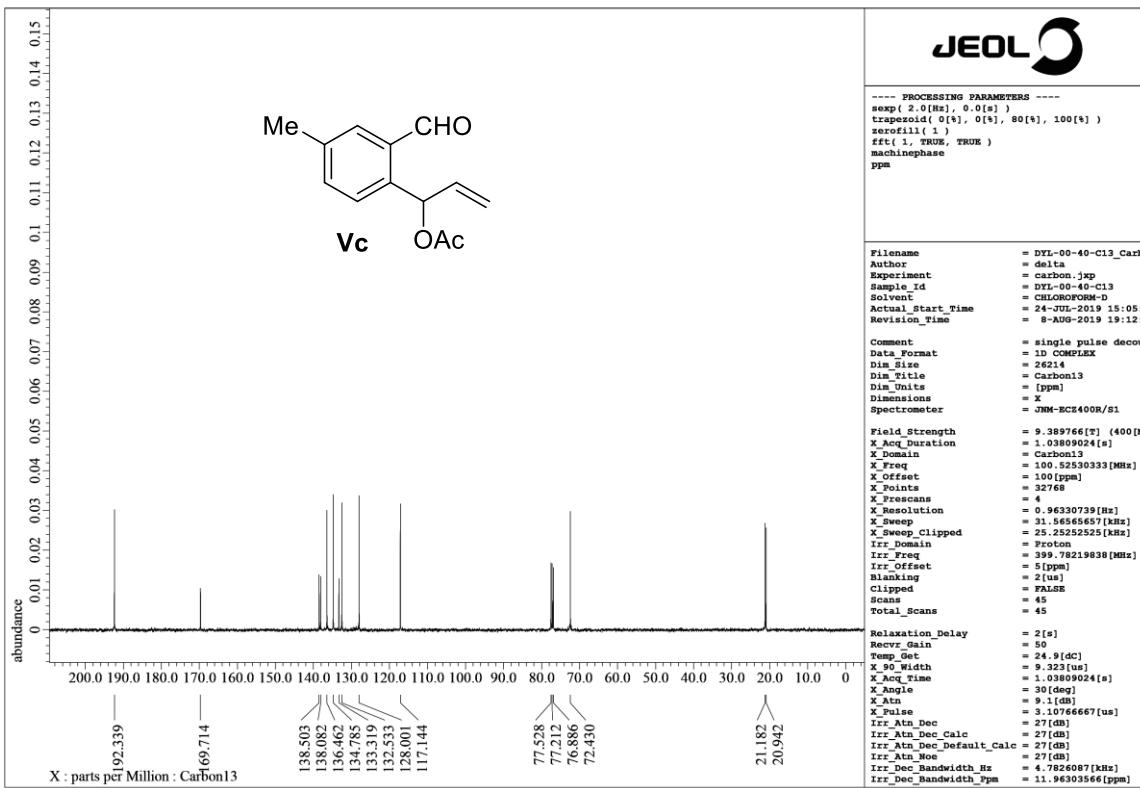
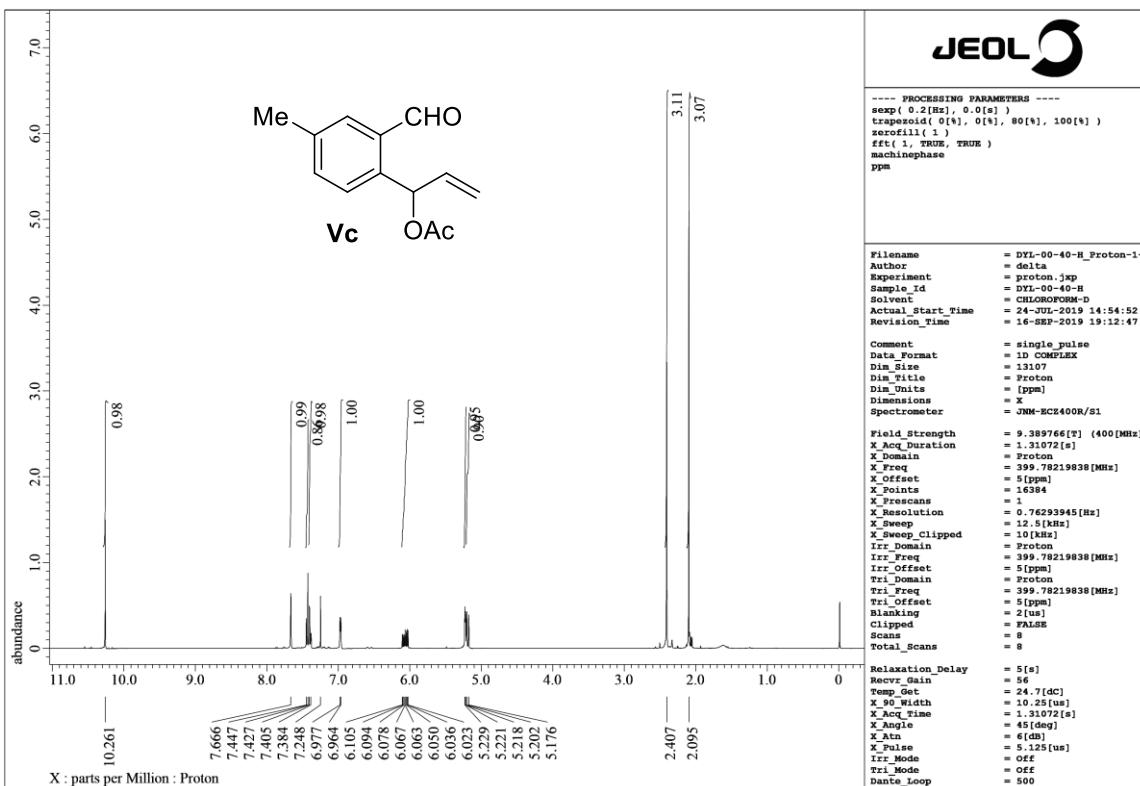
Crystals of compound **5d** were obtained by slow evaporation of a solution containing **5d** in the mixture of ethyl acetate and *n*-hexane. Single-crystal X-ray diffraction intensity data of the compound **5d** was collected on a 'XtaLAB Synergy R, DW system, HyPix' diffractometer equipped with graphite monochromatized CuK $\alpha$  ( $\lambda = 1.54184 \text{ \AA}$ ) at 100 K. The structure was solved by the program ShelXT (Sheldrick, 2015) and refined with the program ShelXL (Sheldrick, 2015). The crystal data and structure refinement results for compound **5d** are listed in the Table S1.

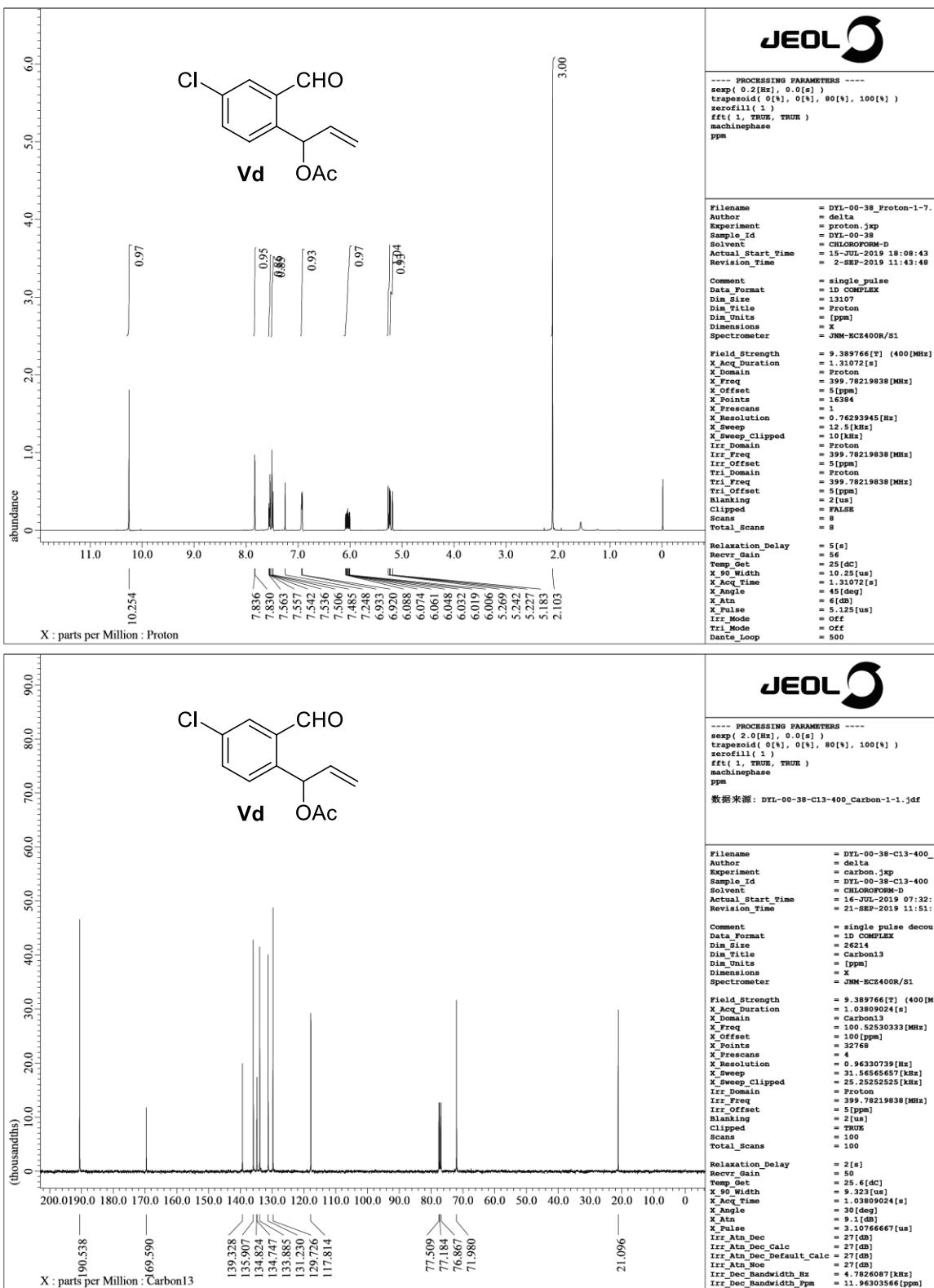
**Table S3.** Crystal data and structure refinement for **5d**.

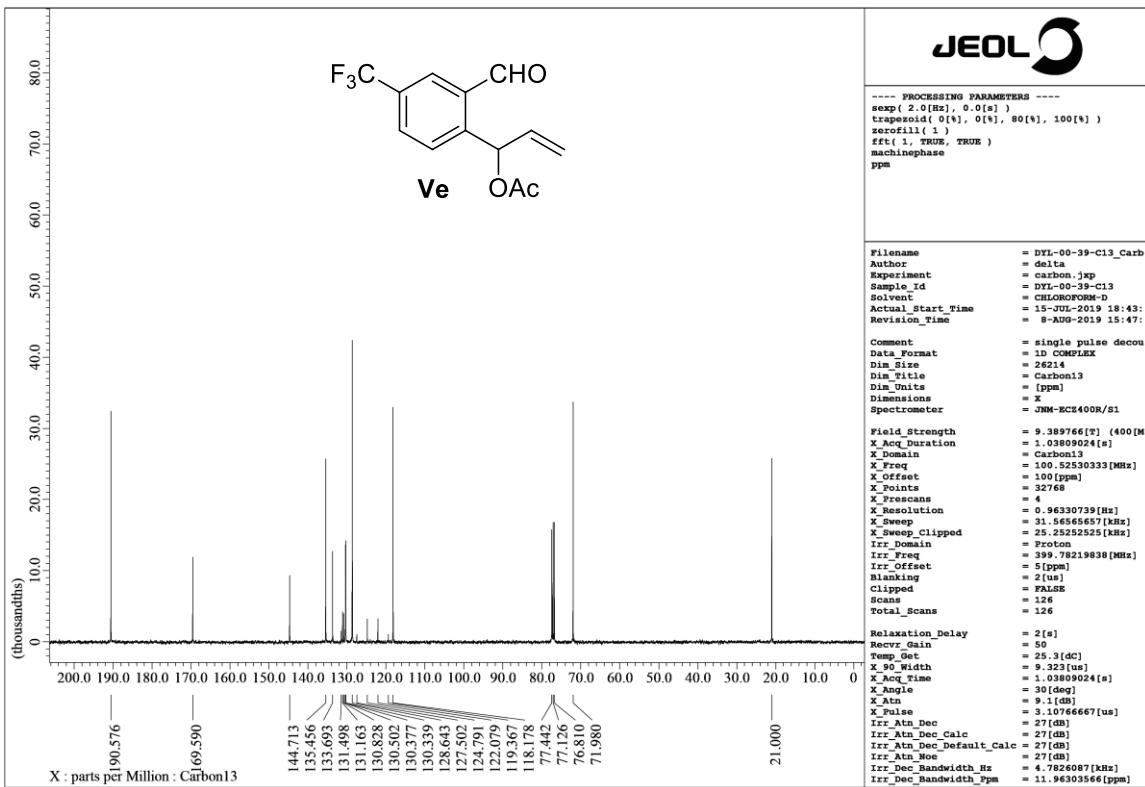
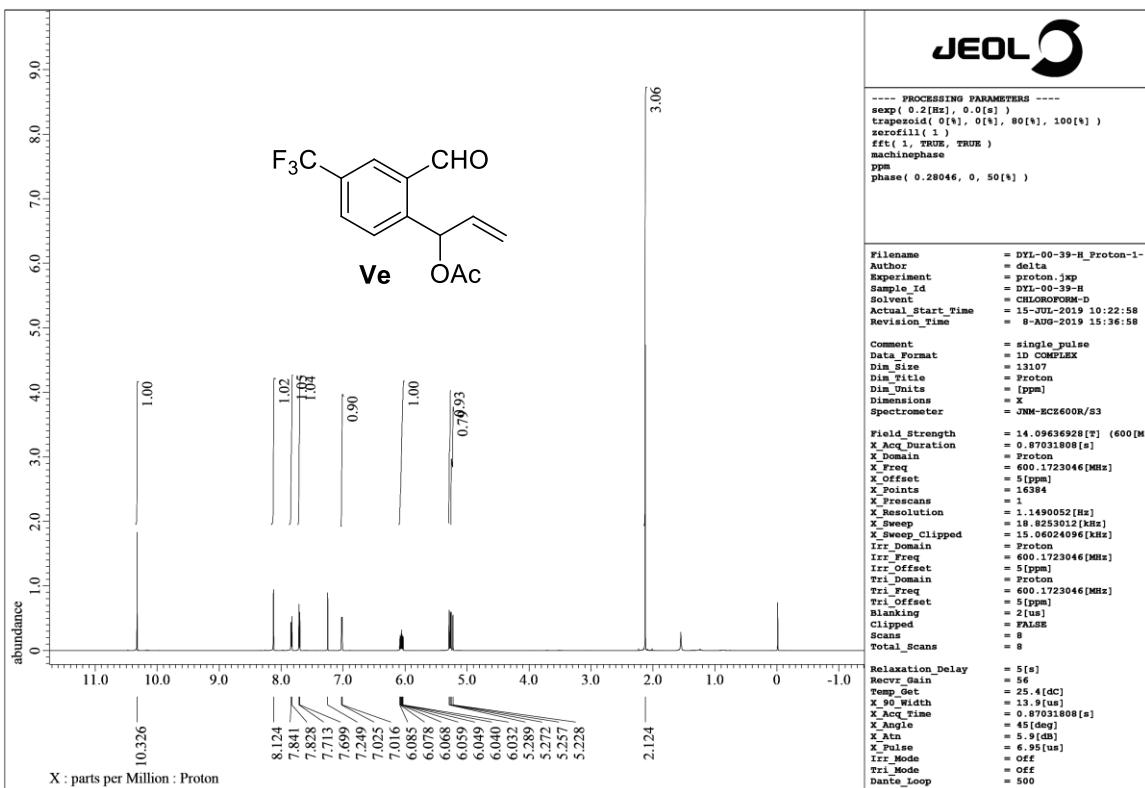
Identification code	20190605d
Empirical formula	C <sub>15</sub> H <sub>14</sub> ClN <sub>3</sub> O <sub>6</sub>
Formula weight	367.74
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
a/ $\text{\AA}$	8.35980(10)
b/ $\text{\AA}$	11.94590(10)
c/ $\text{\AA}$	32.5899(4)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	3254.60(6)
Z	8
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	1.501
$\mu/\text{mm}^{-1}$	2.443
F(000)	1520.0
Crystal size/mm <sup>3</sup>	0.2 × 0.15 × 0.1
Radiation	CuK $\alpha$ ( $\lambda = 1.54184 \text{ \AA}$ )
2 $\Theta$ range for data collection/°	5.424 to 150.686
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 13, -40 ≤ l ≤ 38
Reflections collected	15719
Independent reflections	6356 [ $R_{\text{int}} = 0.0365$ , $R_{\text{sigma}} = 0.0370$ ]
Data/restraints/parameters	6356/0/455
Goodness-of-fit on F <sup>2</sup>	1.099
Final R indexes [I ≥ 2 $\sigma$ (I)]	$R_1 = 0.0315$ , $wR_2 = 0.0770$
Final R indexes [all data]	$R_1 = 0.0367$ , $wR_2 = 0.0834$
Largest diff. peak/hole / e $\text{\AA}^{-3}$	0.30/-0.30
Flack parameter	-0.005(5)

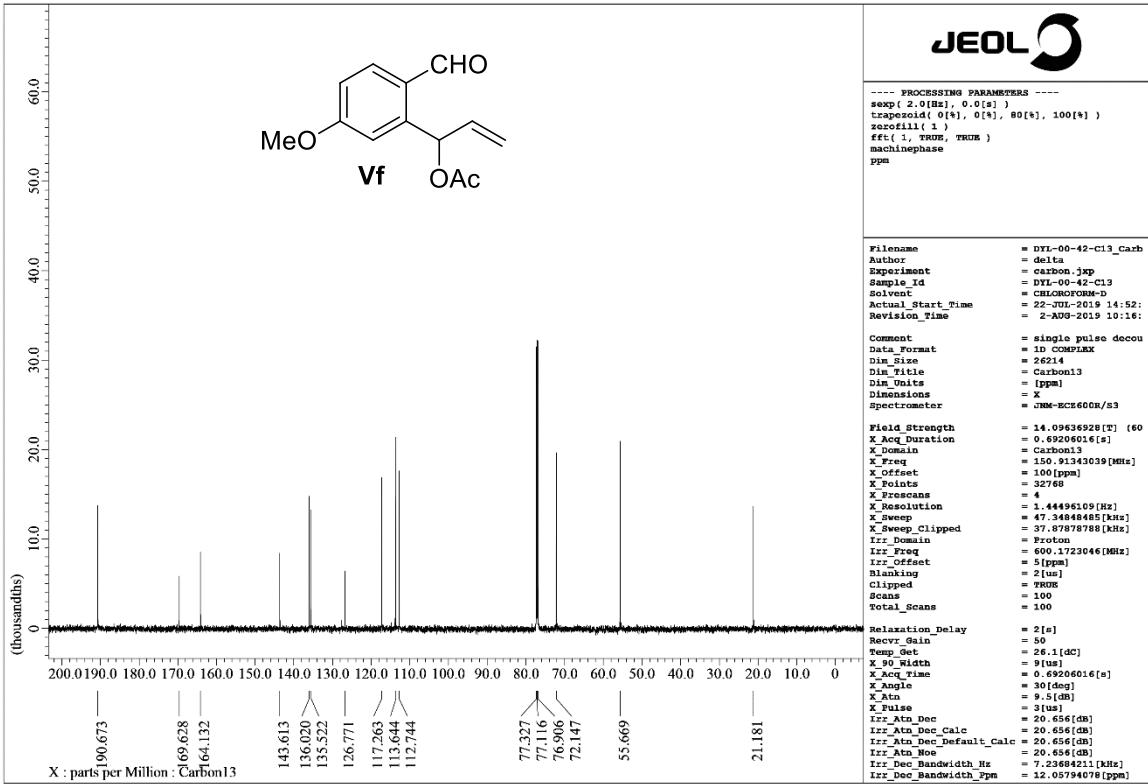
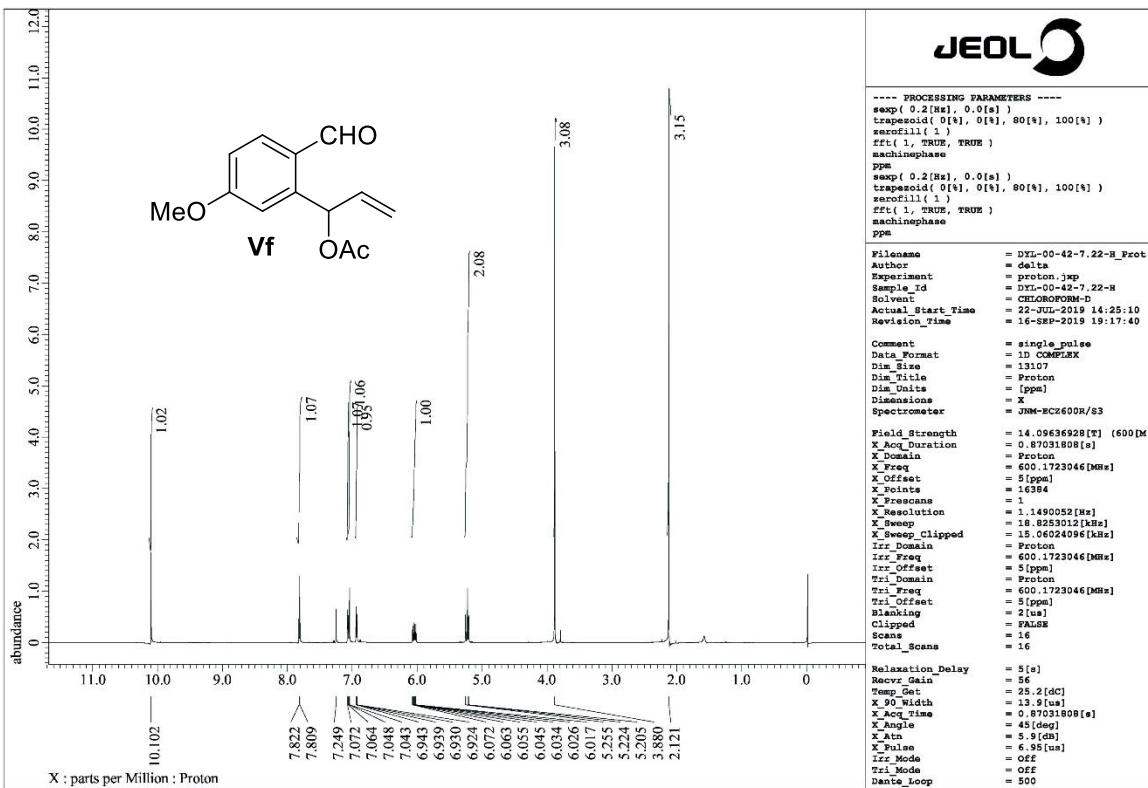
**NMR spectra of reactants and products.**

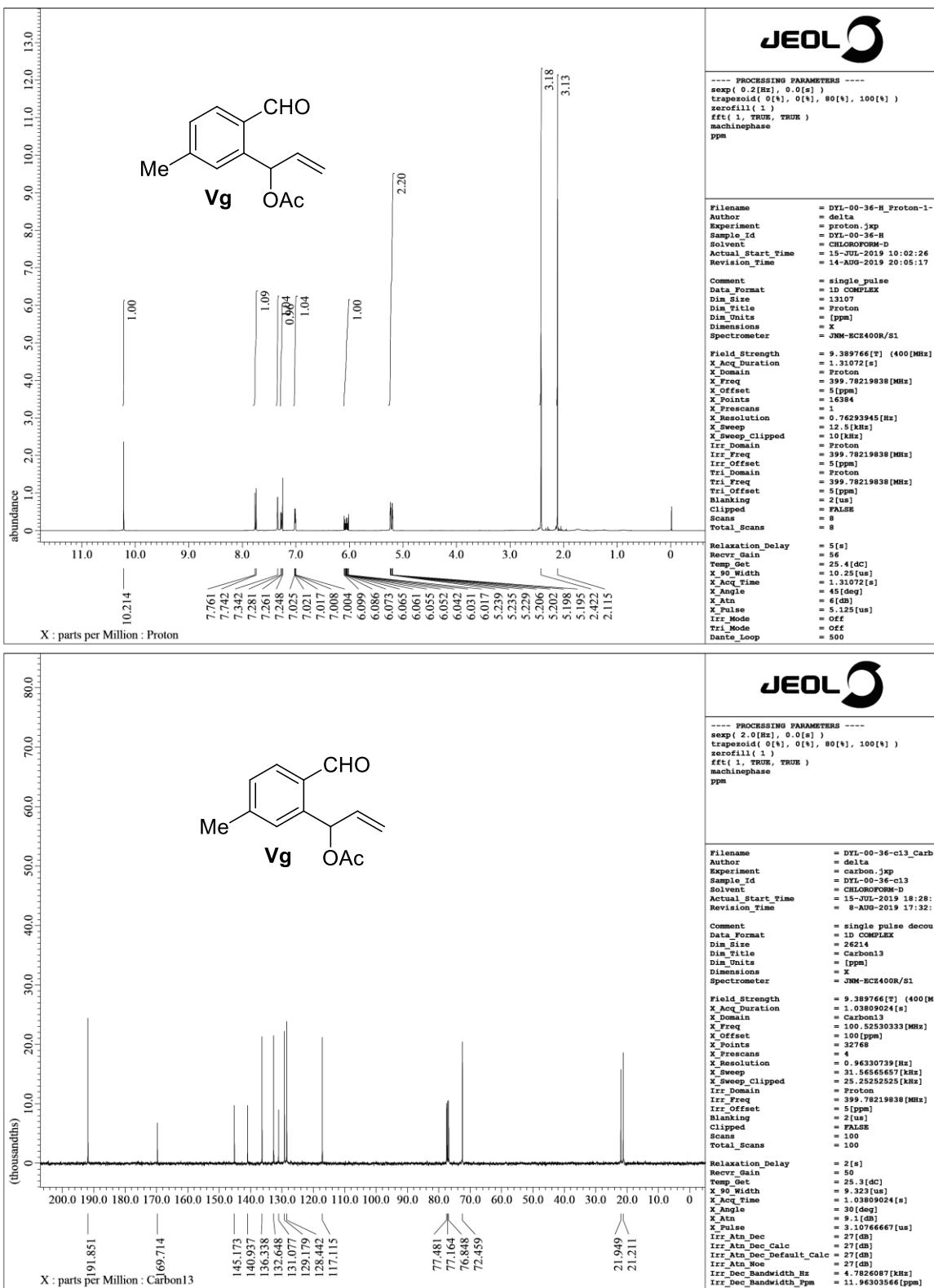


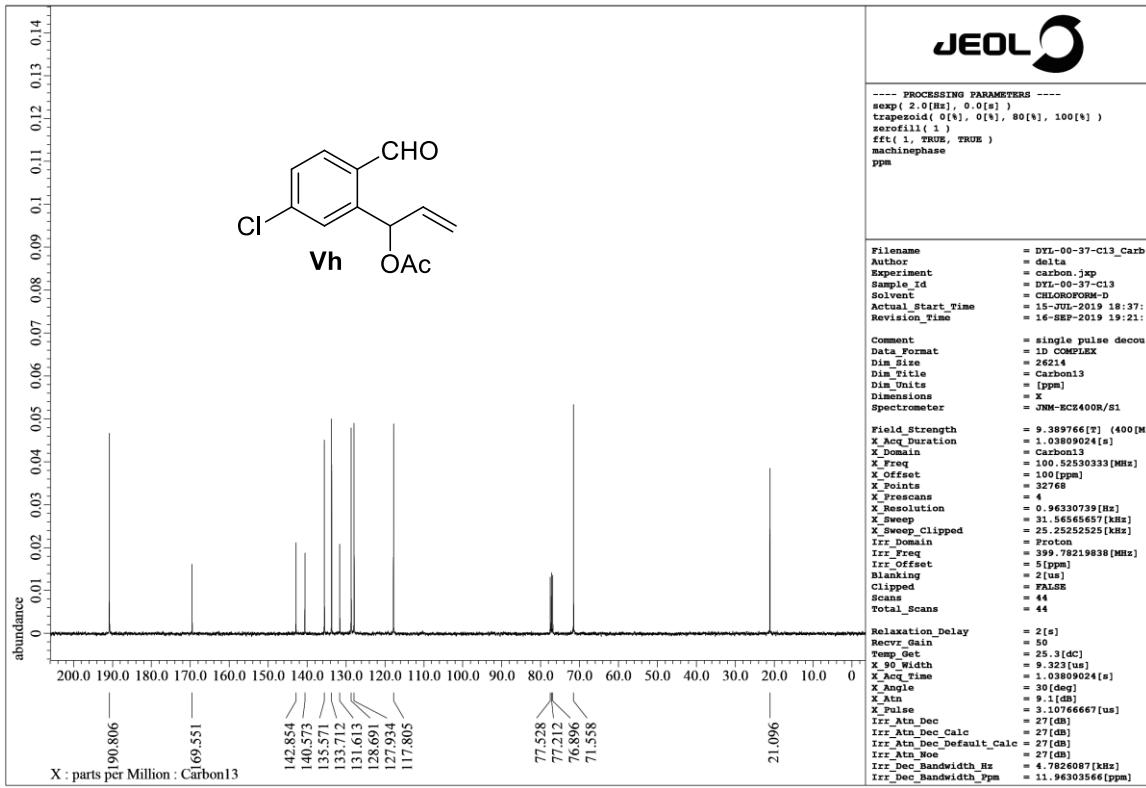
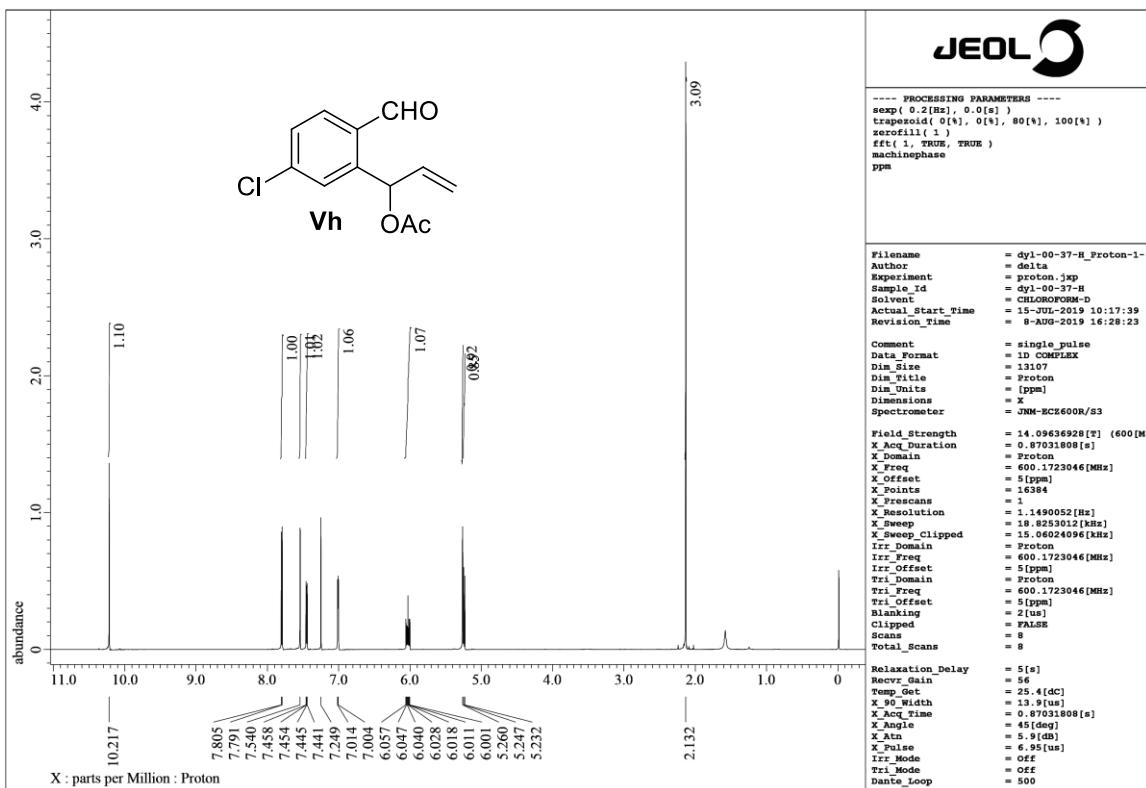


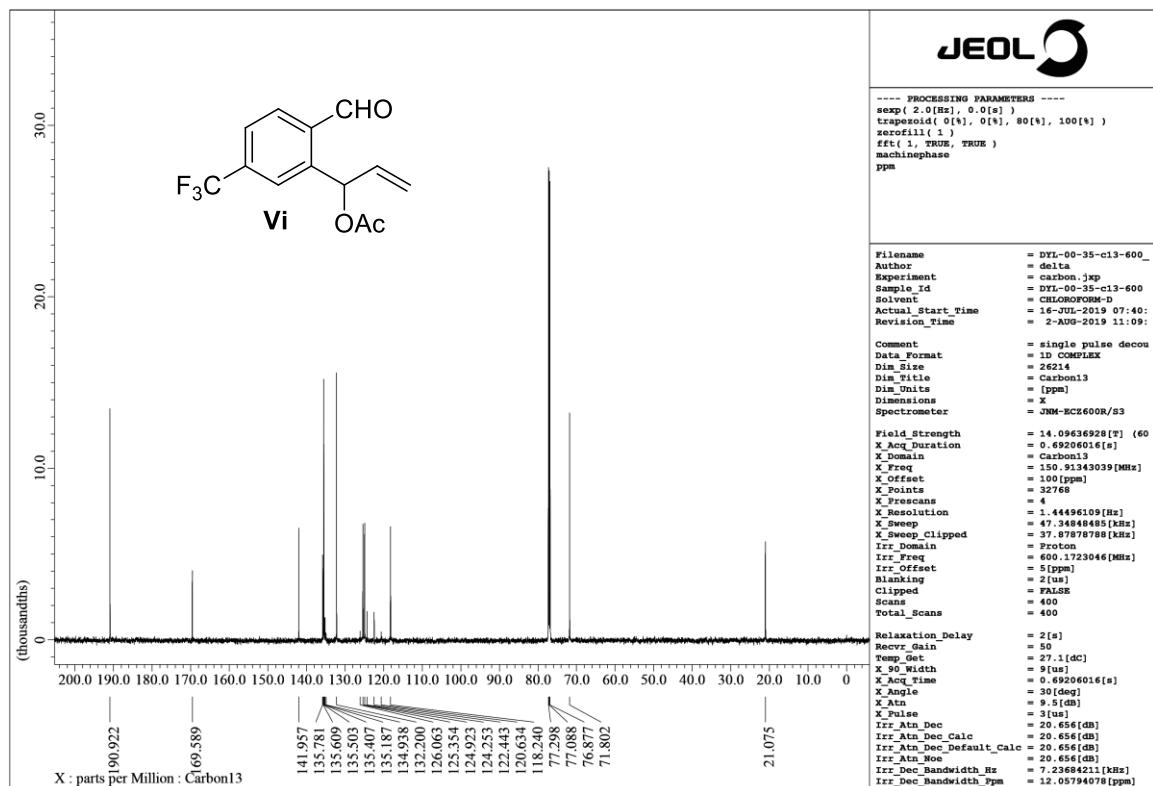
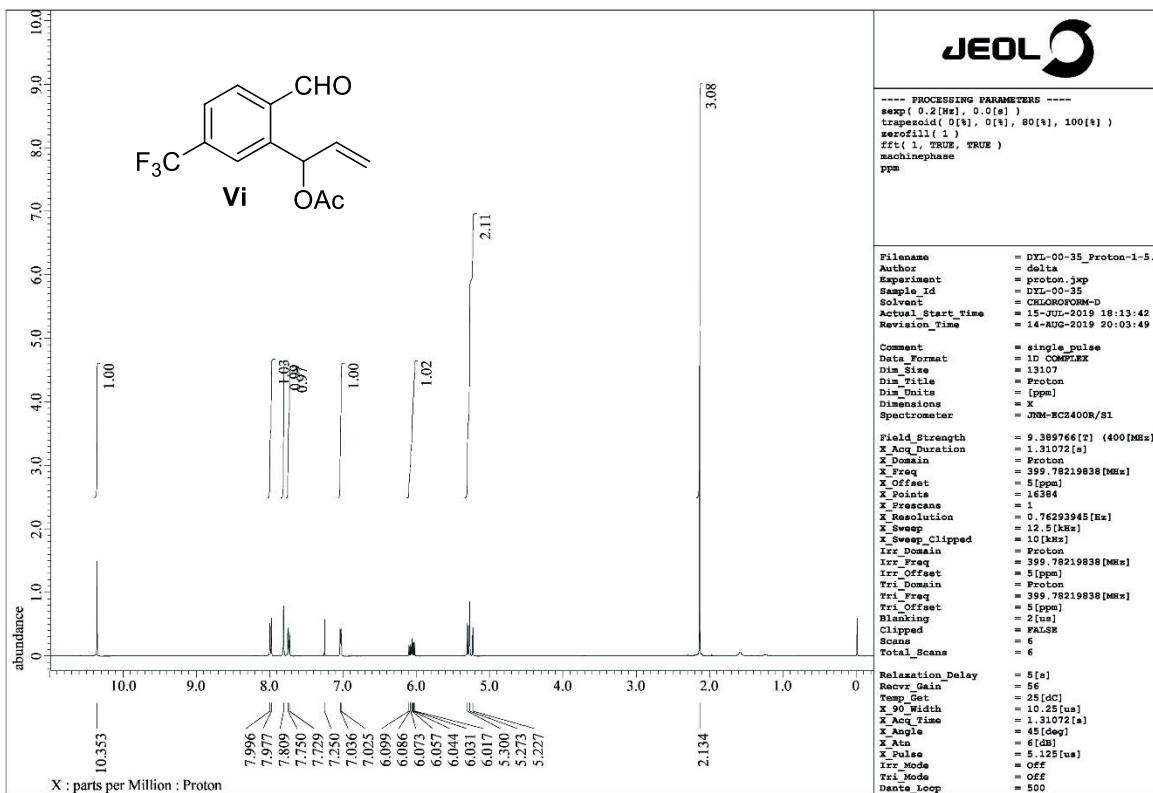


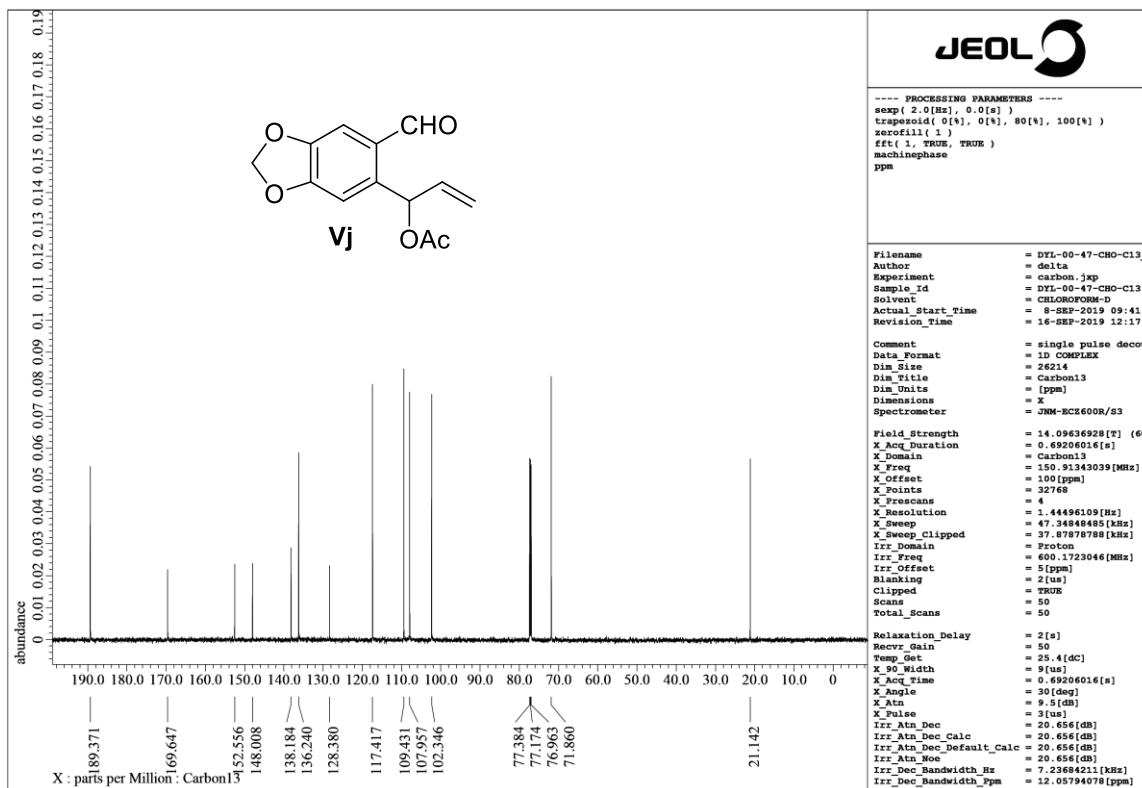
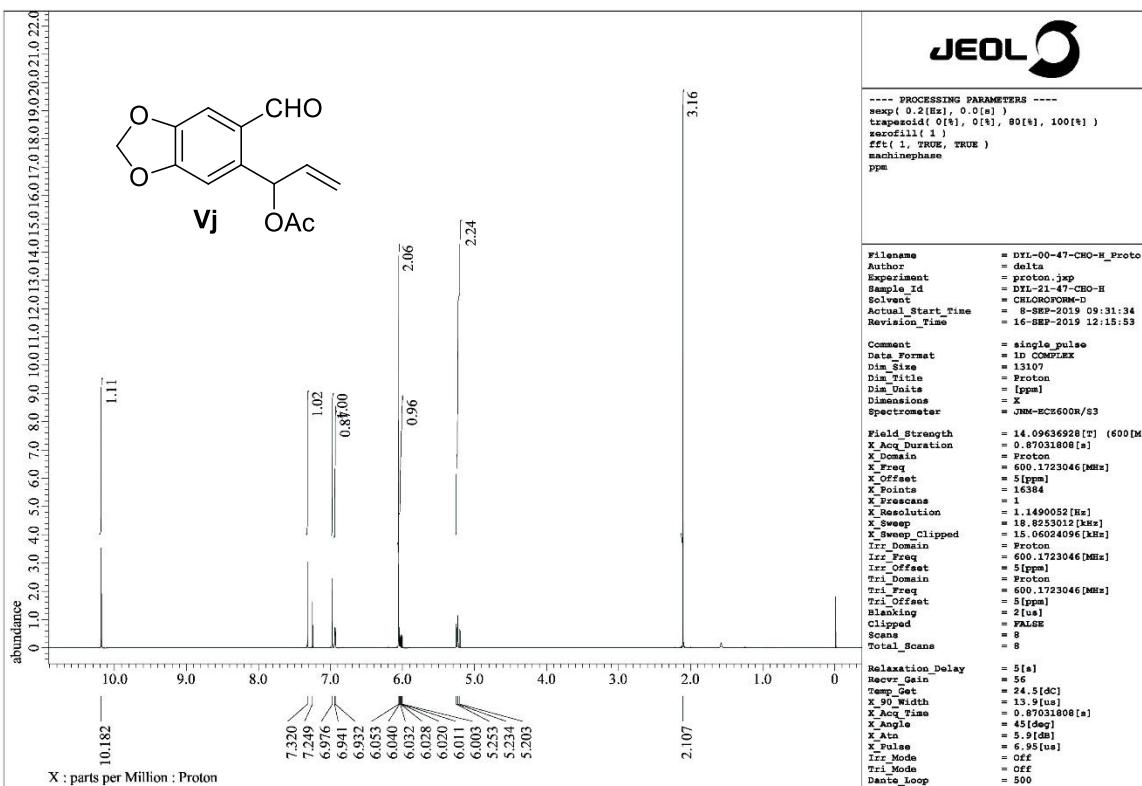


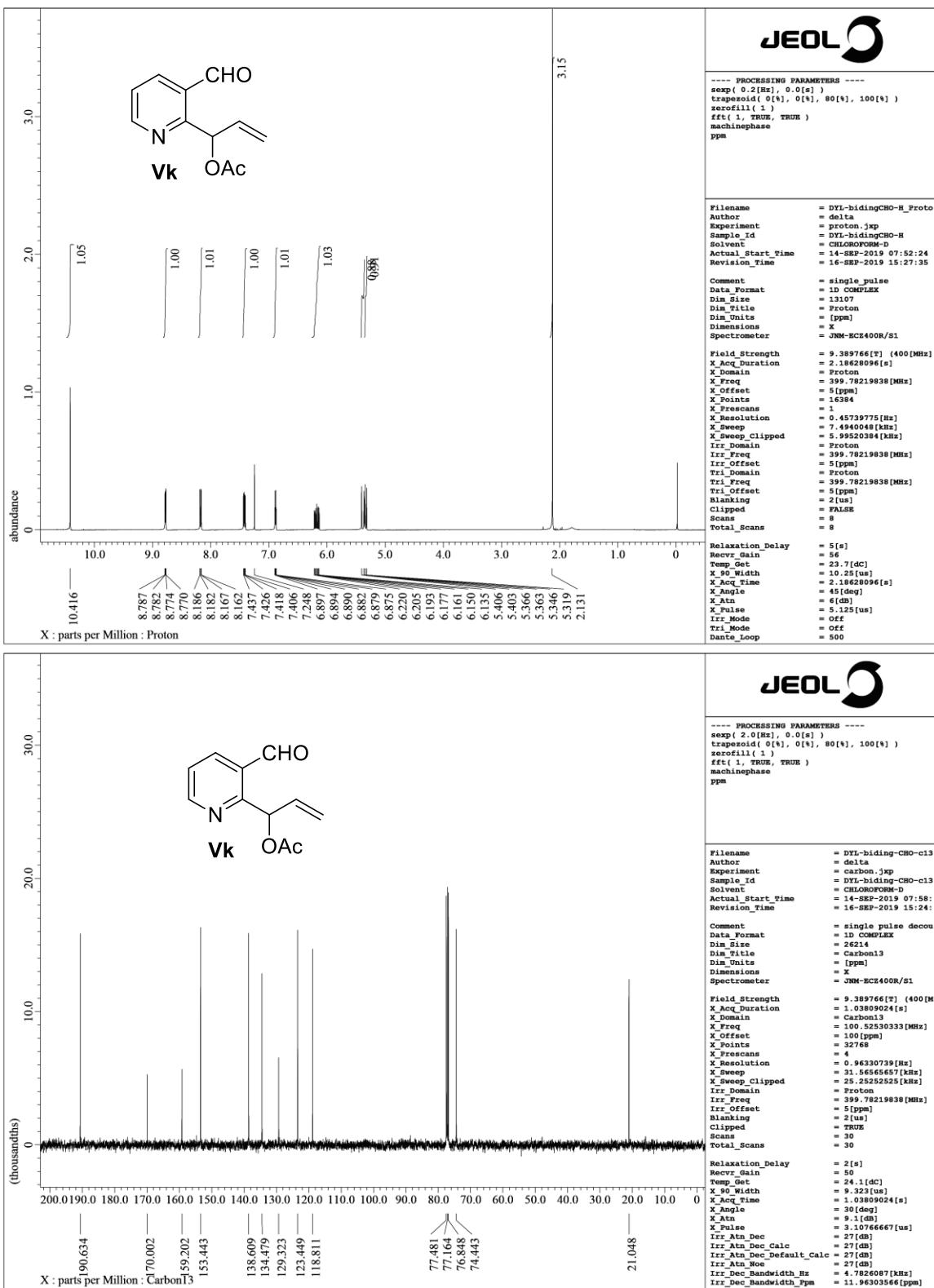


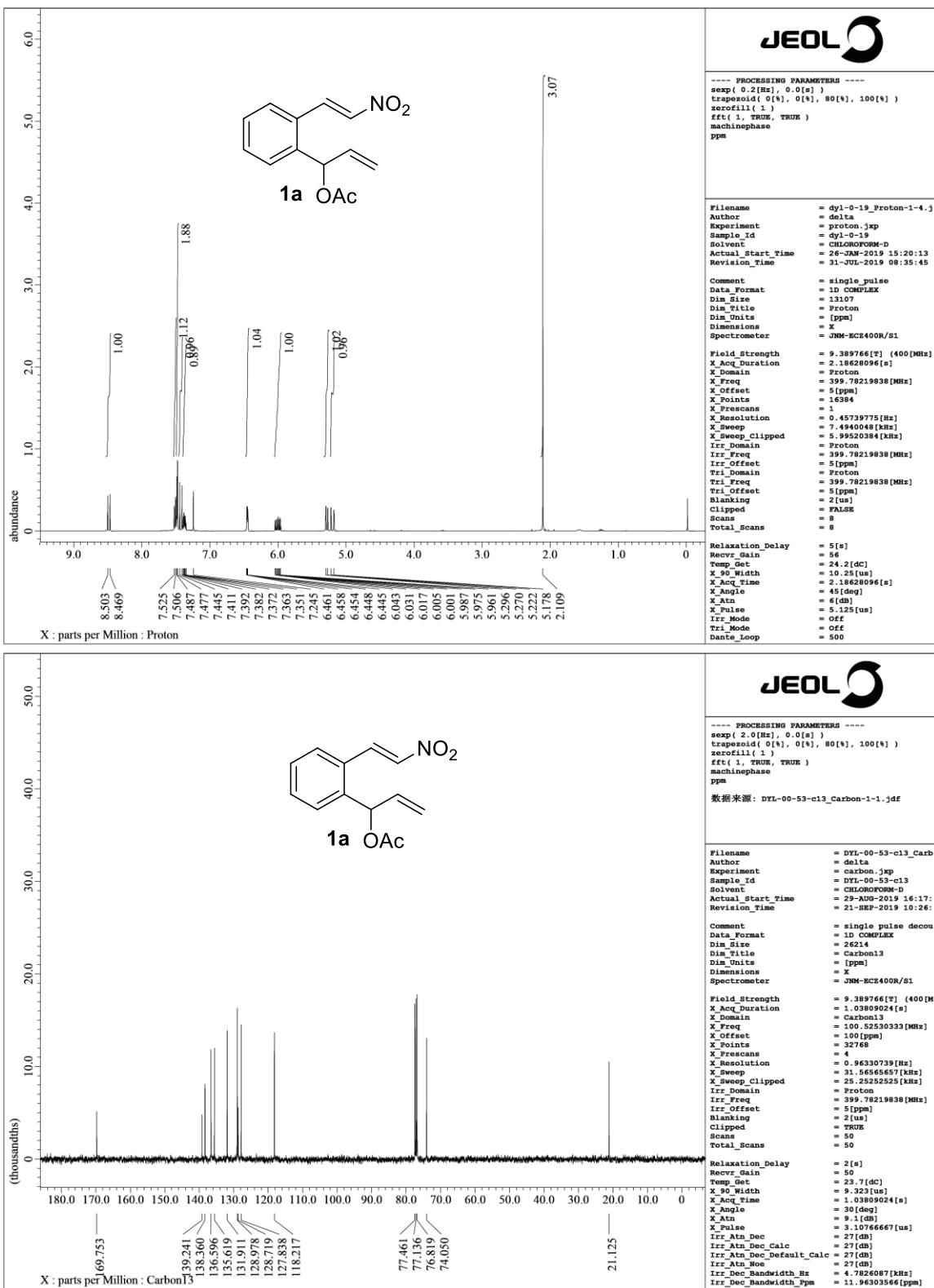


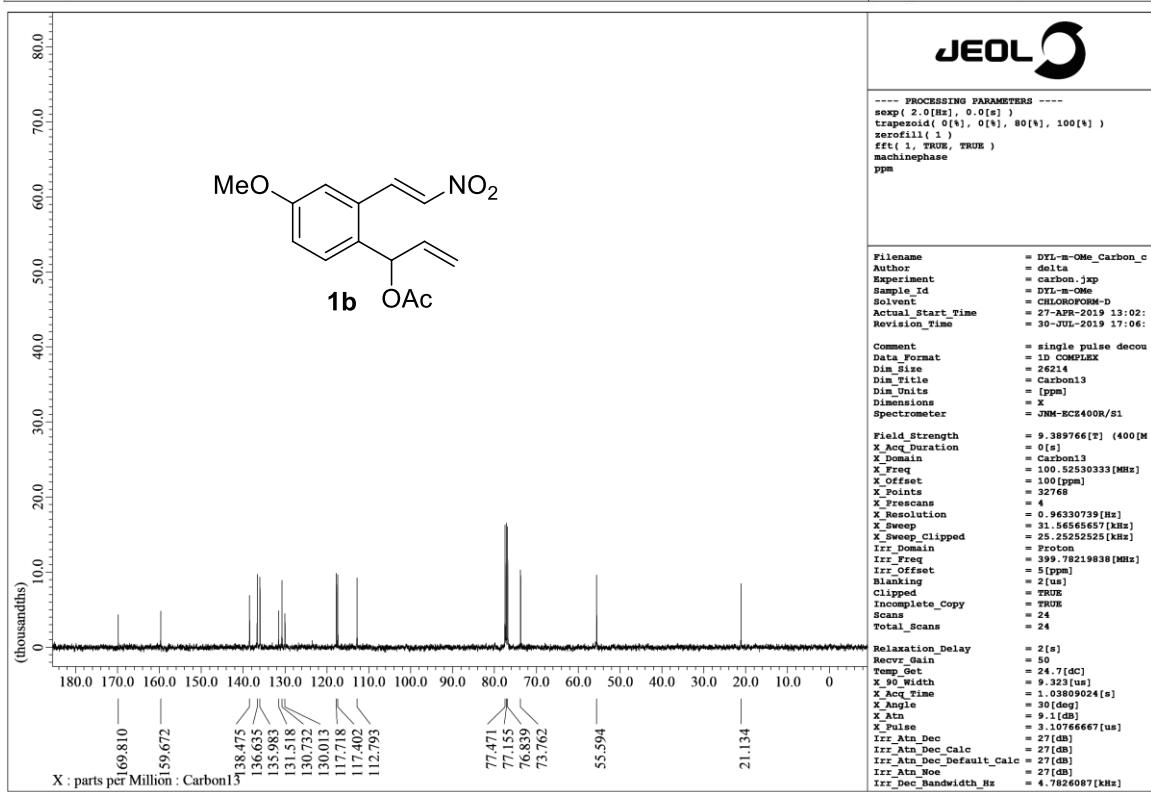
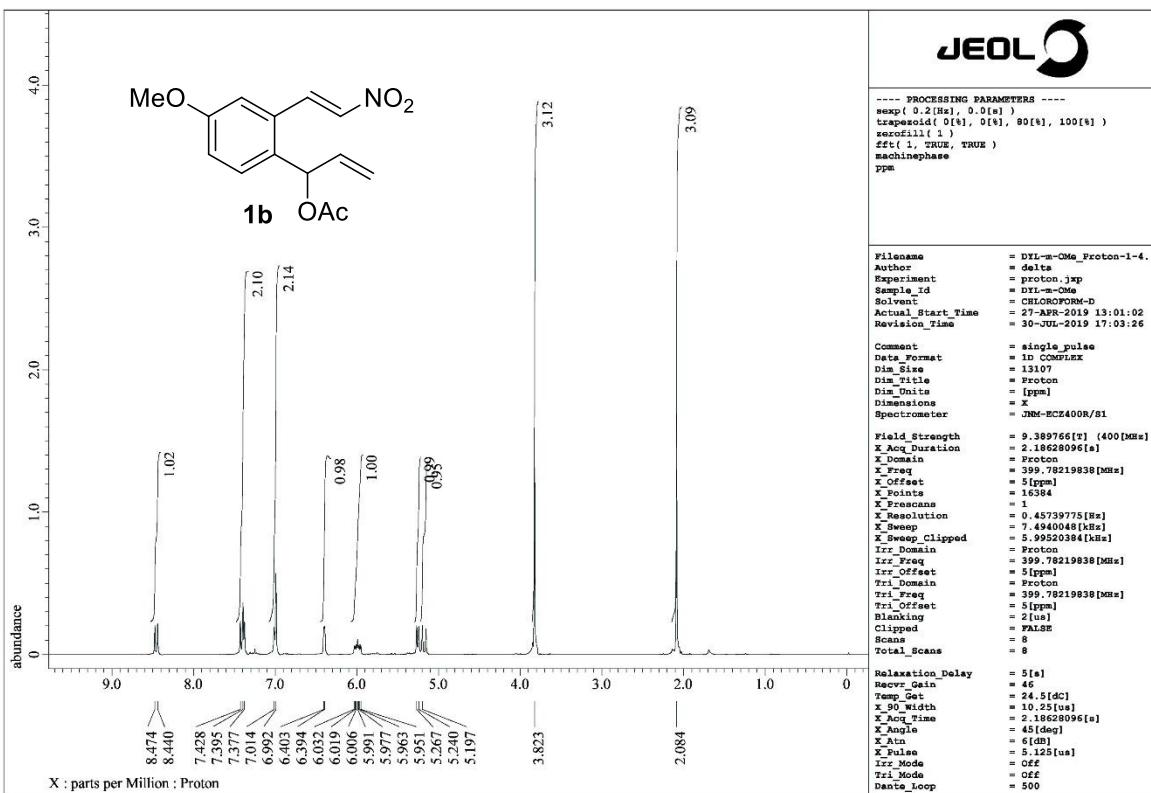


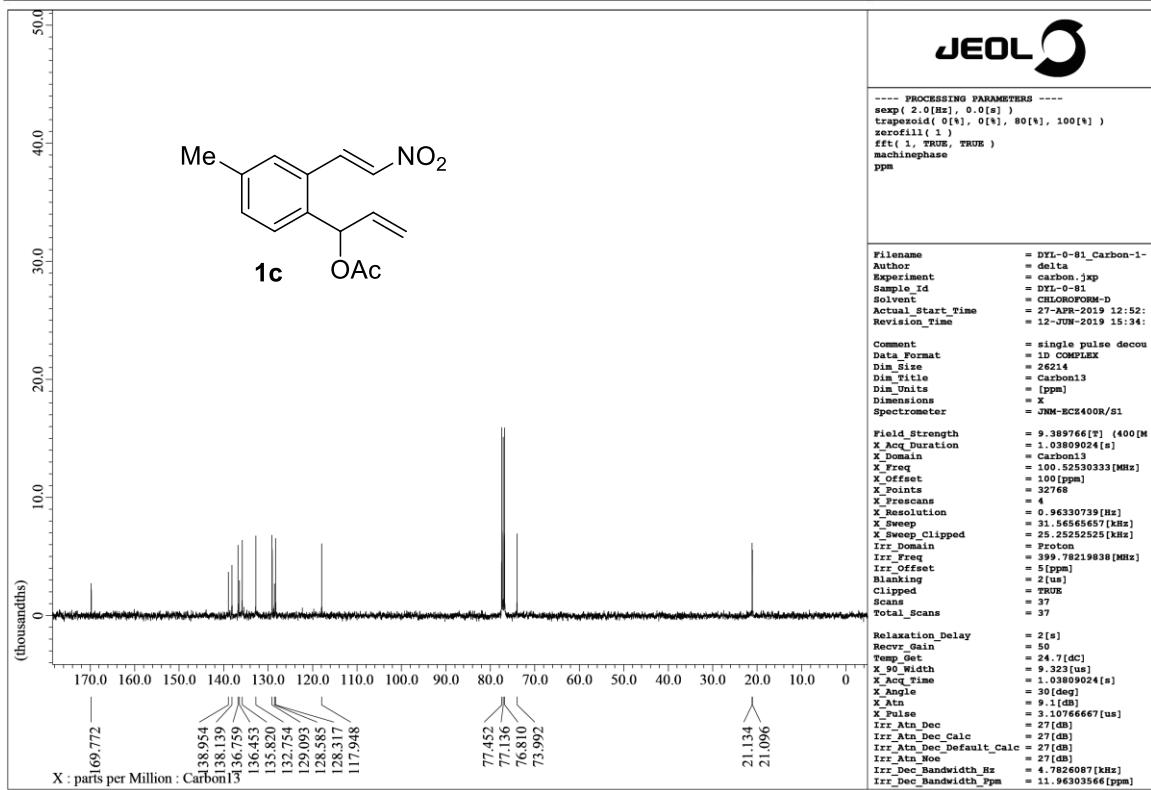
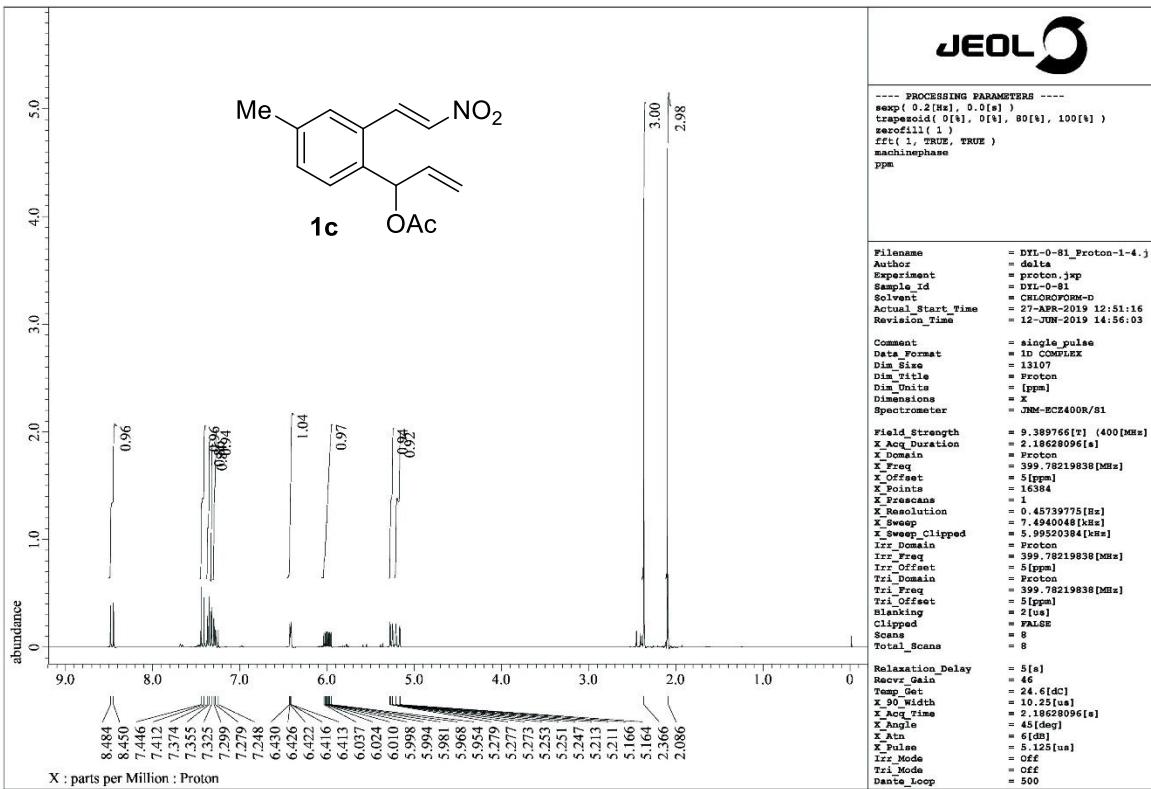


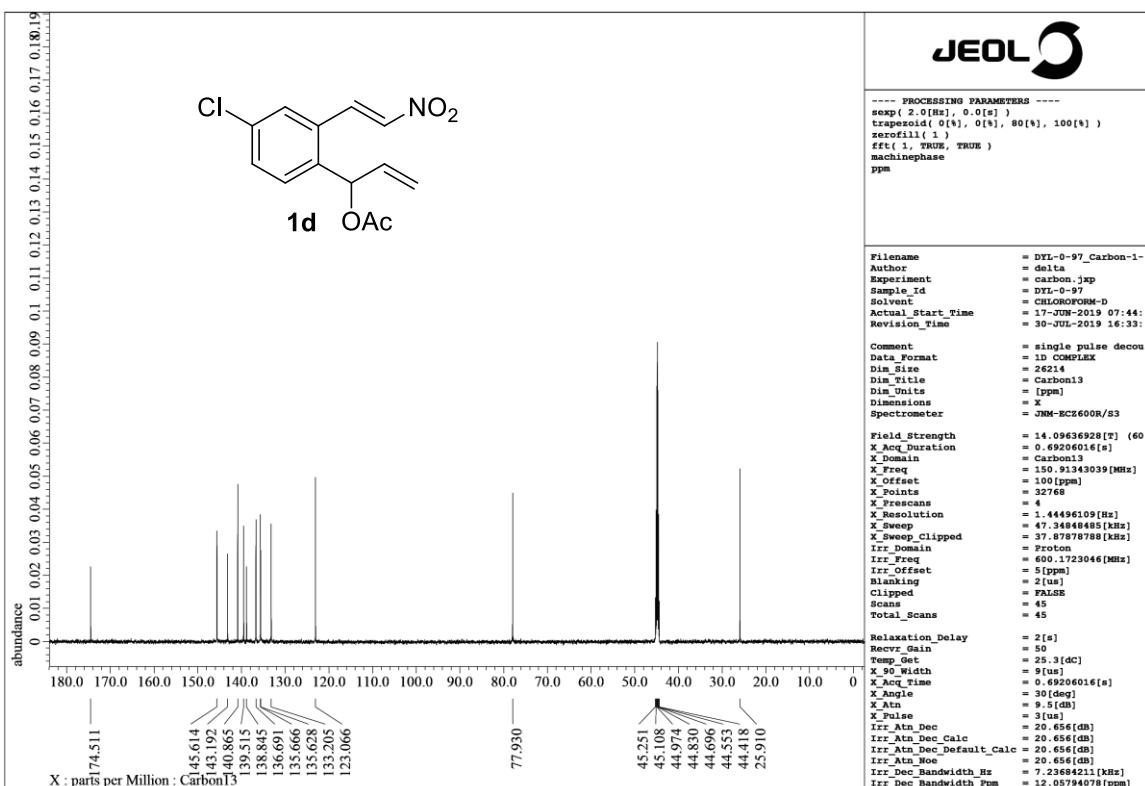
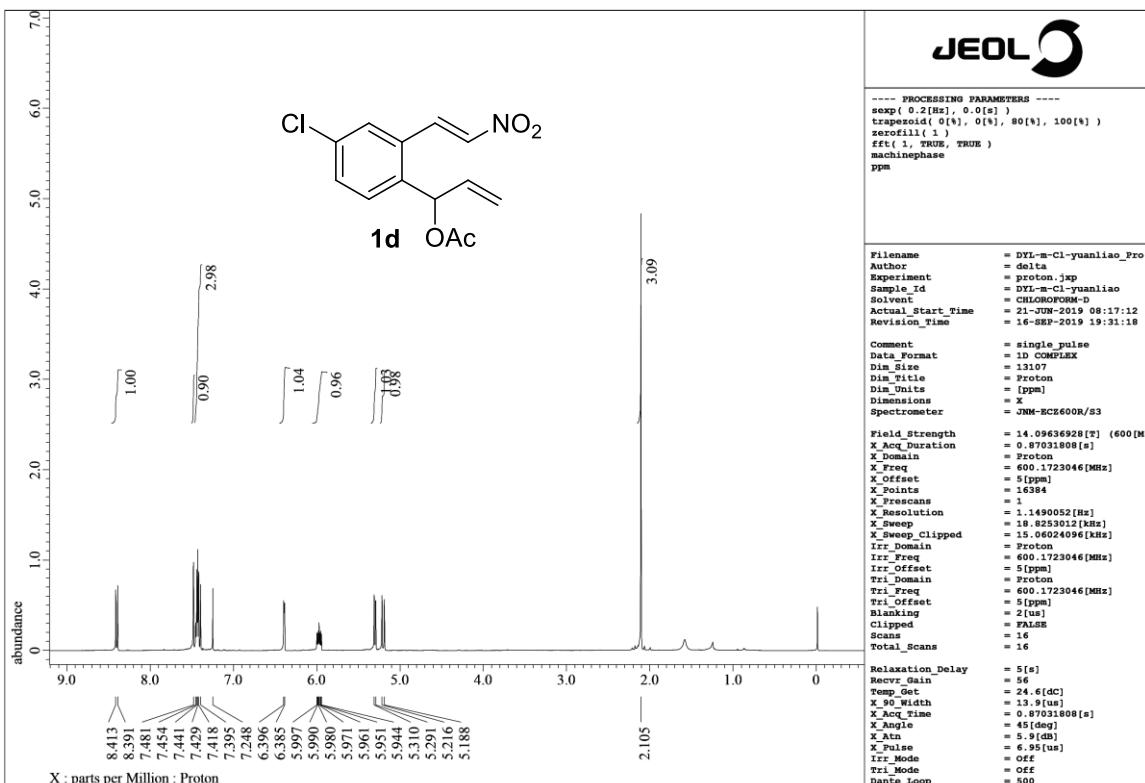


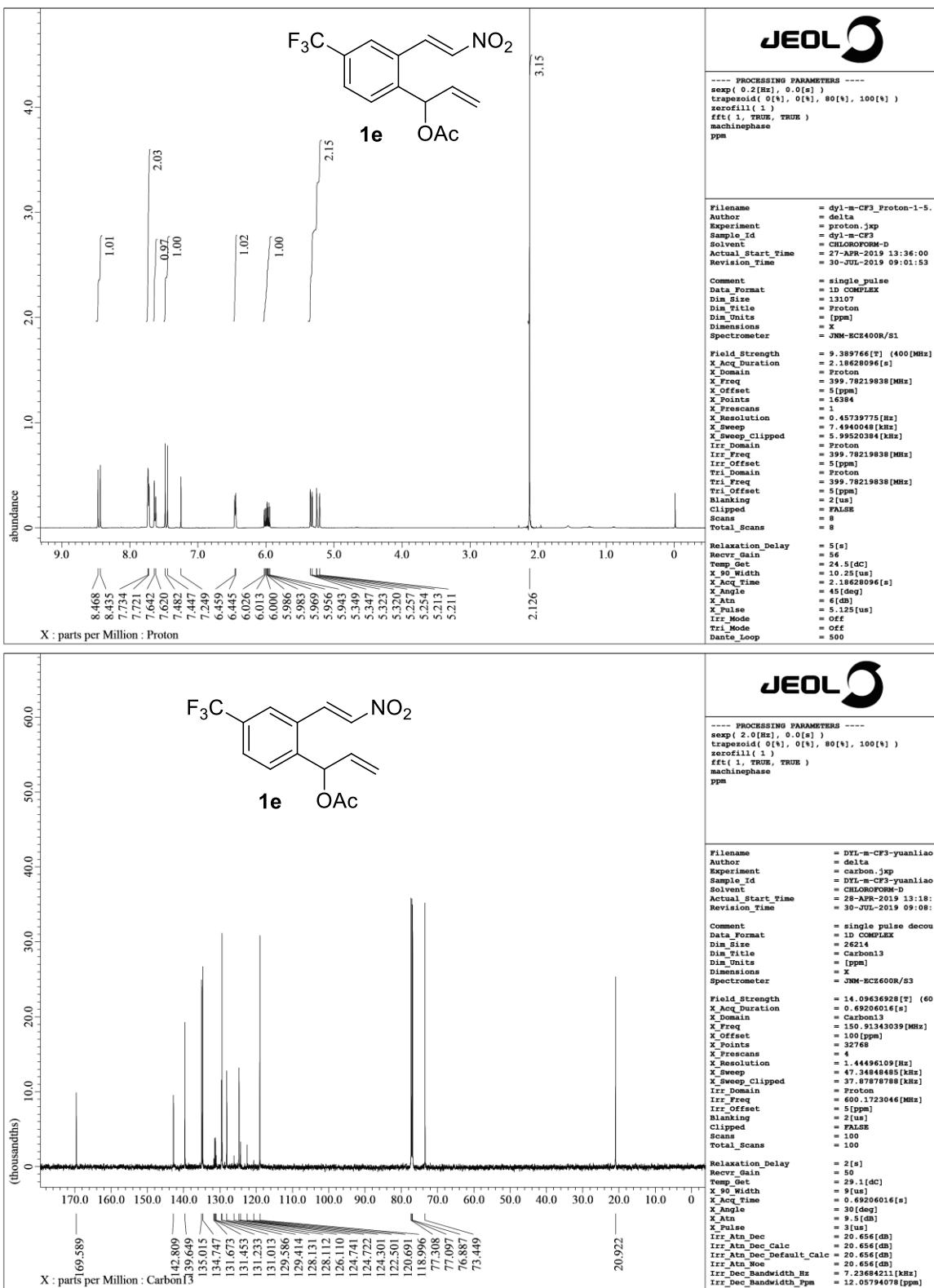


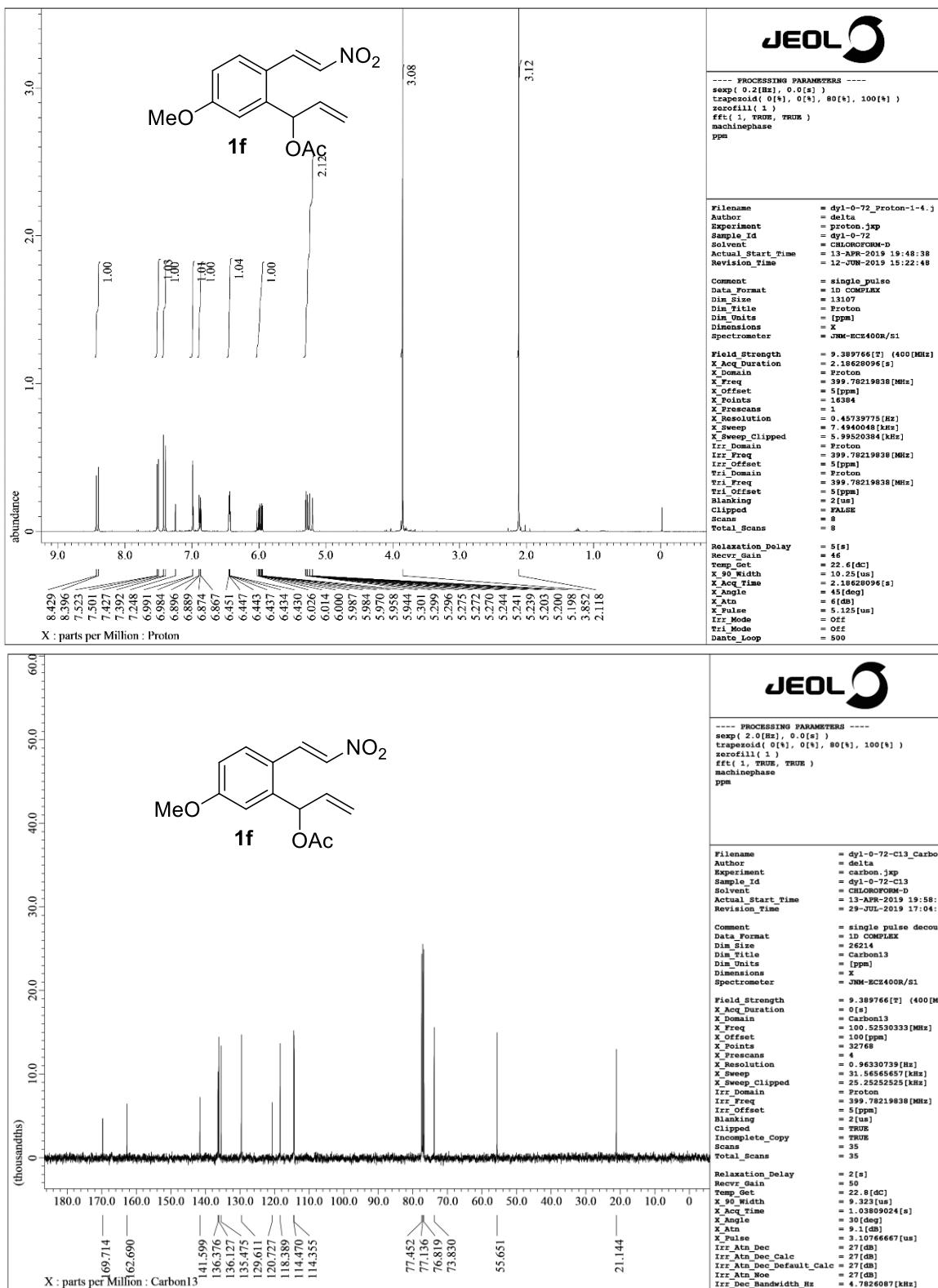


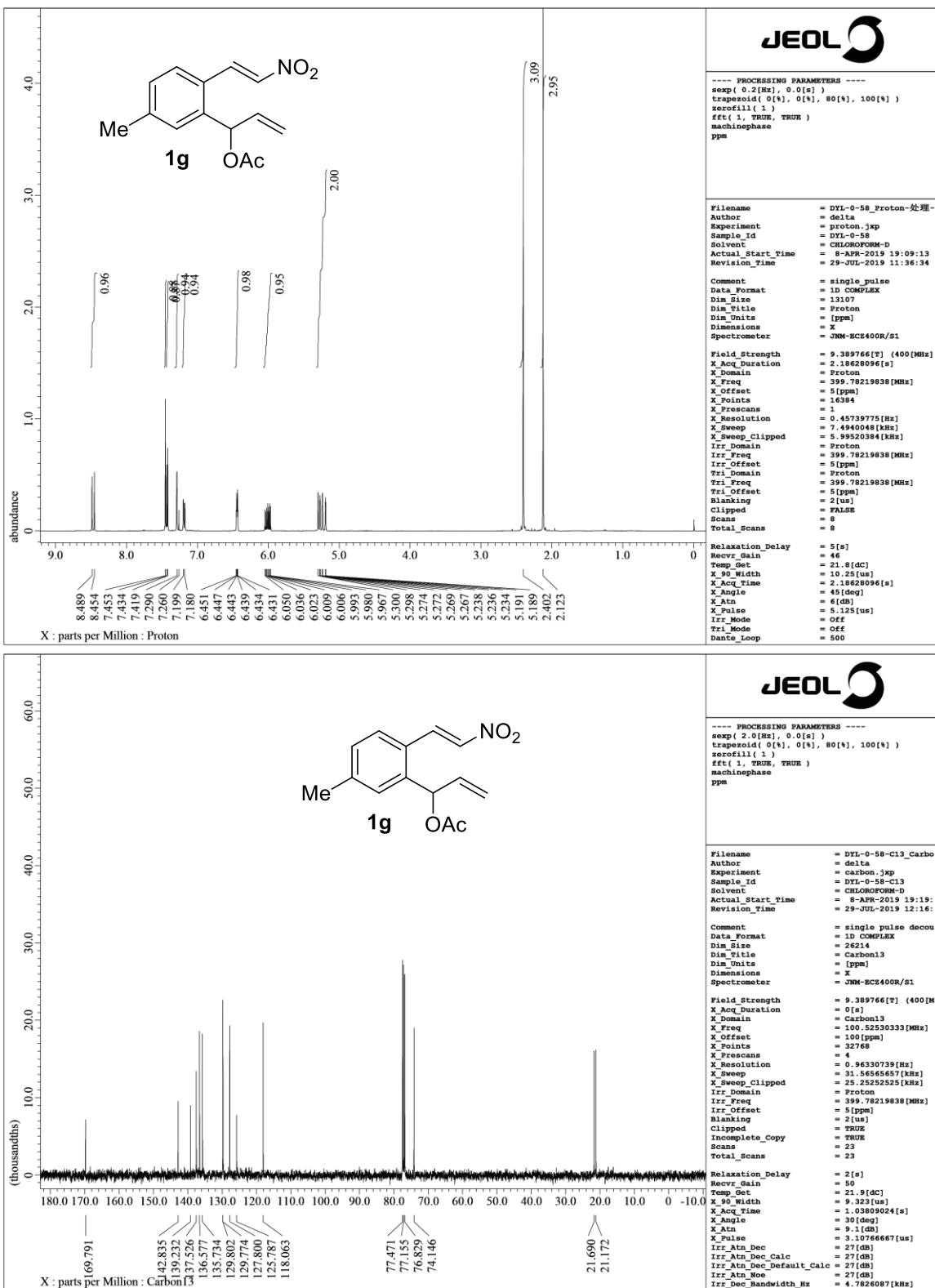


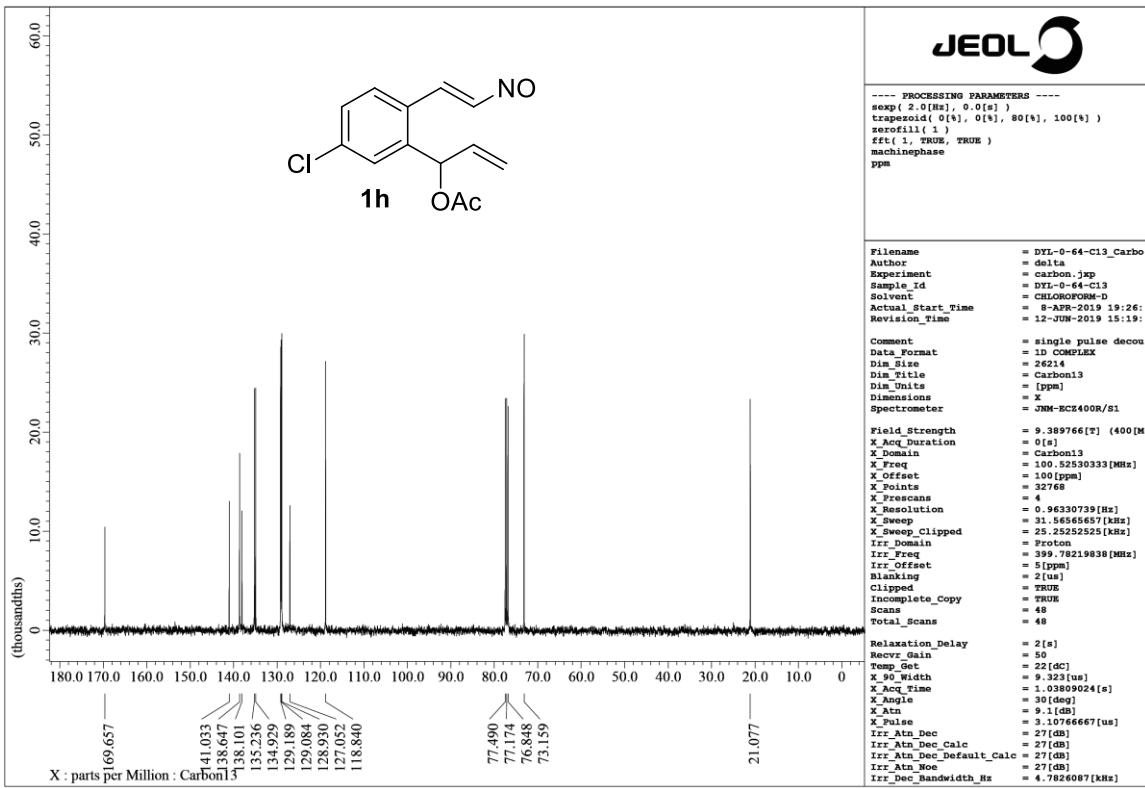
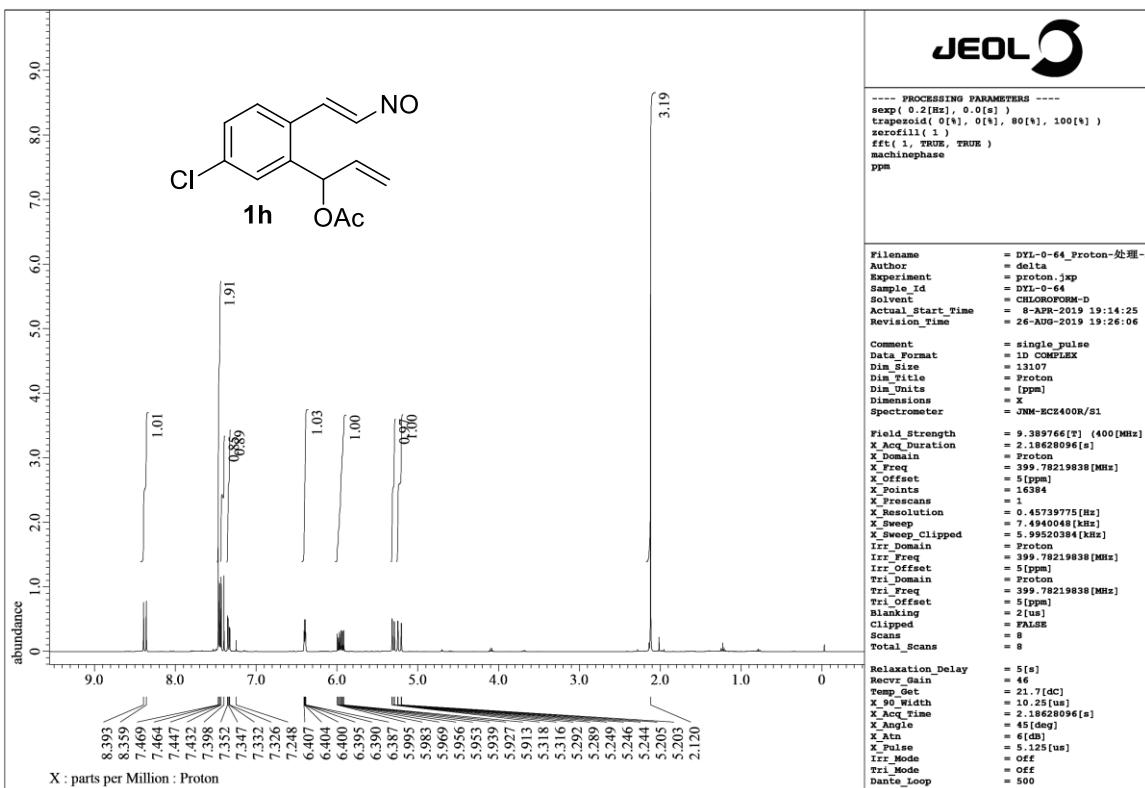


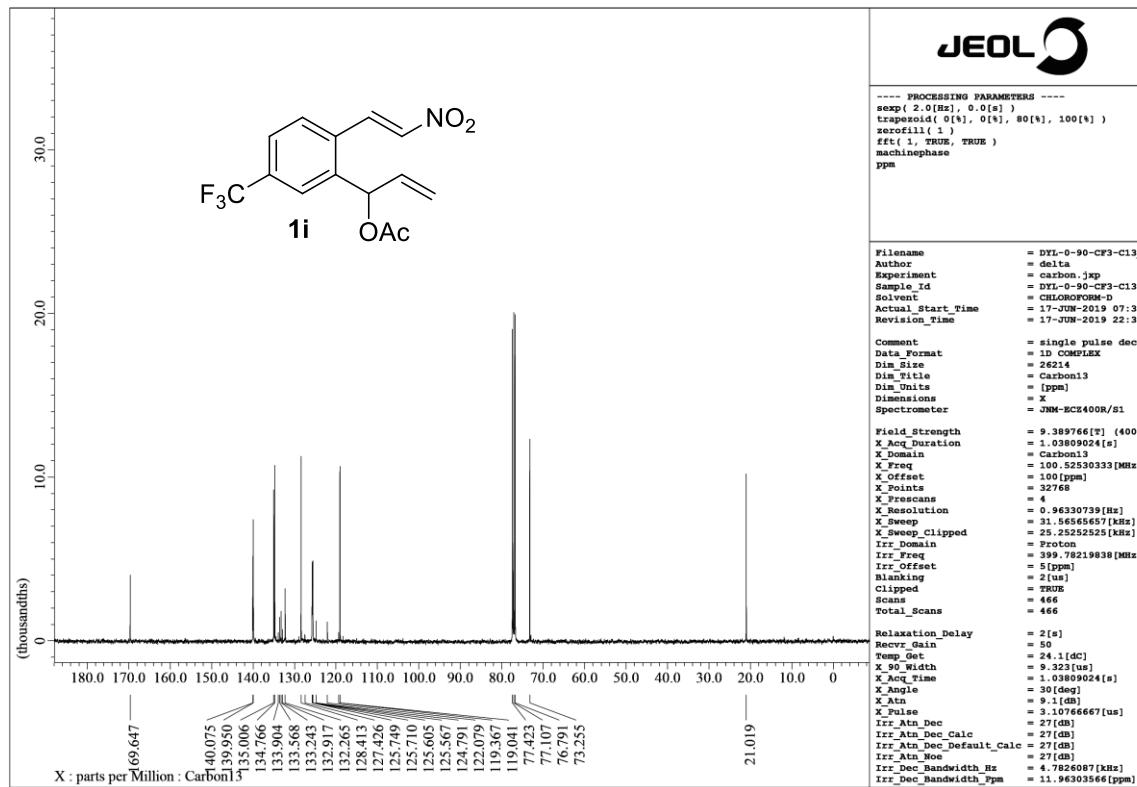
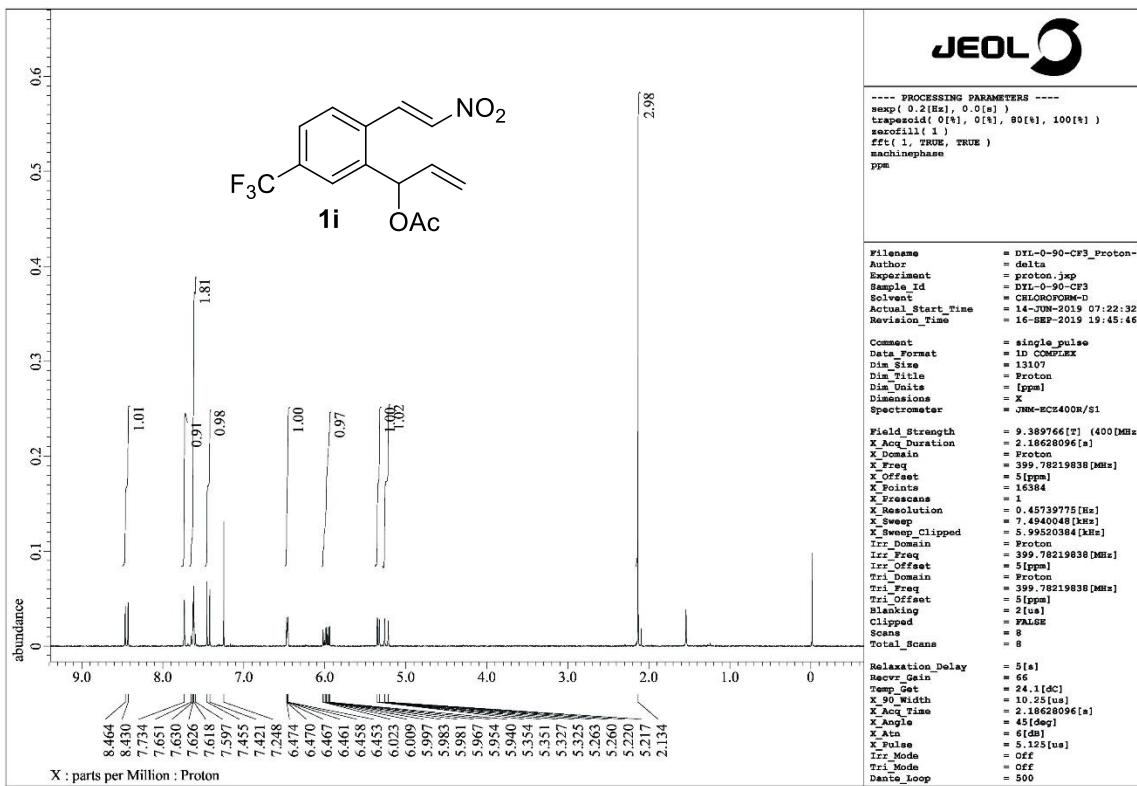


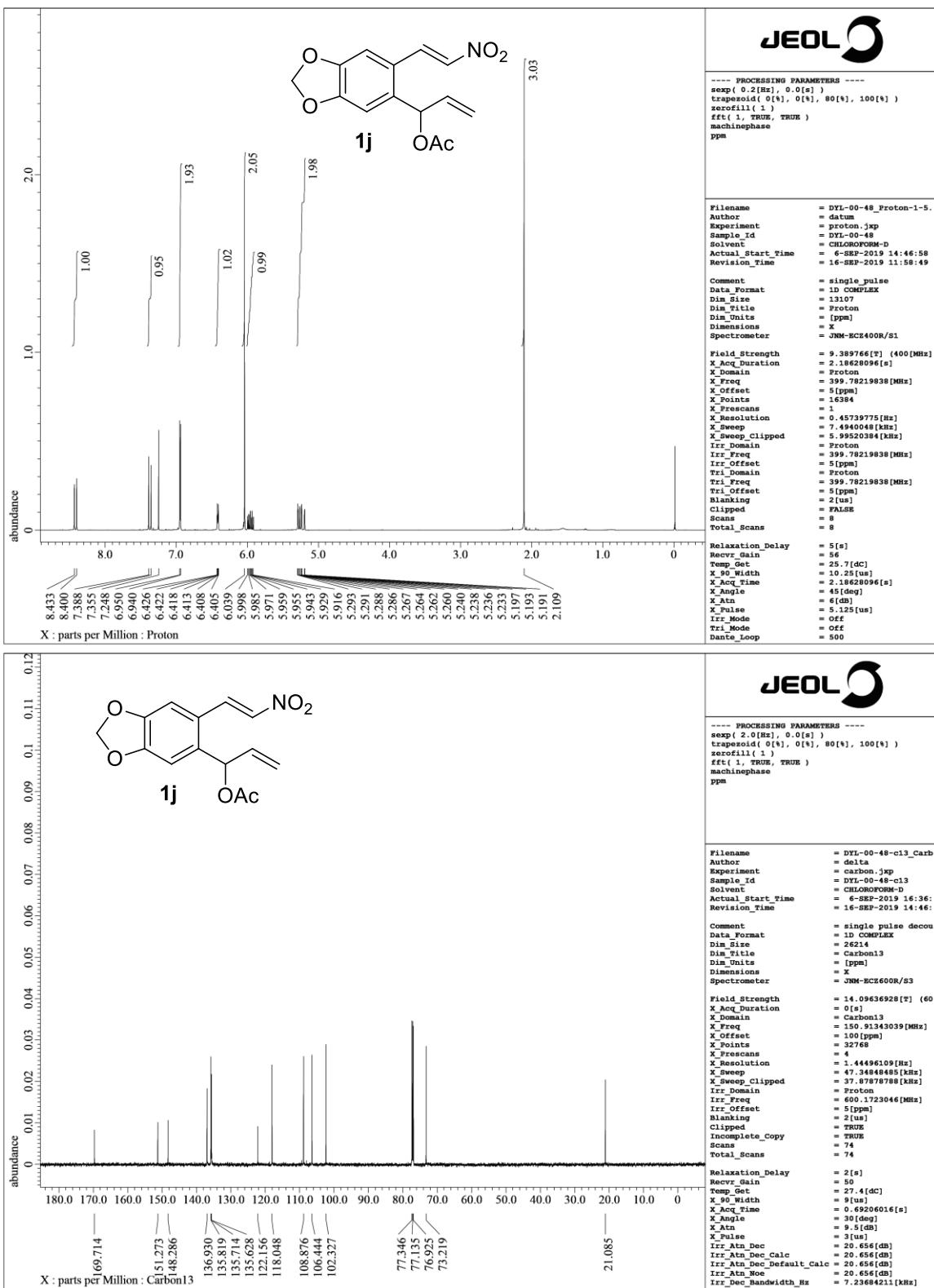


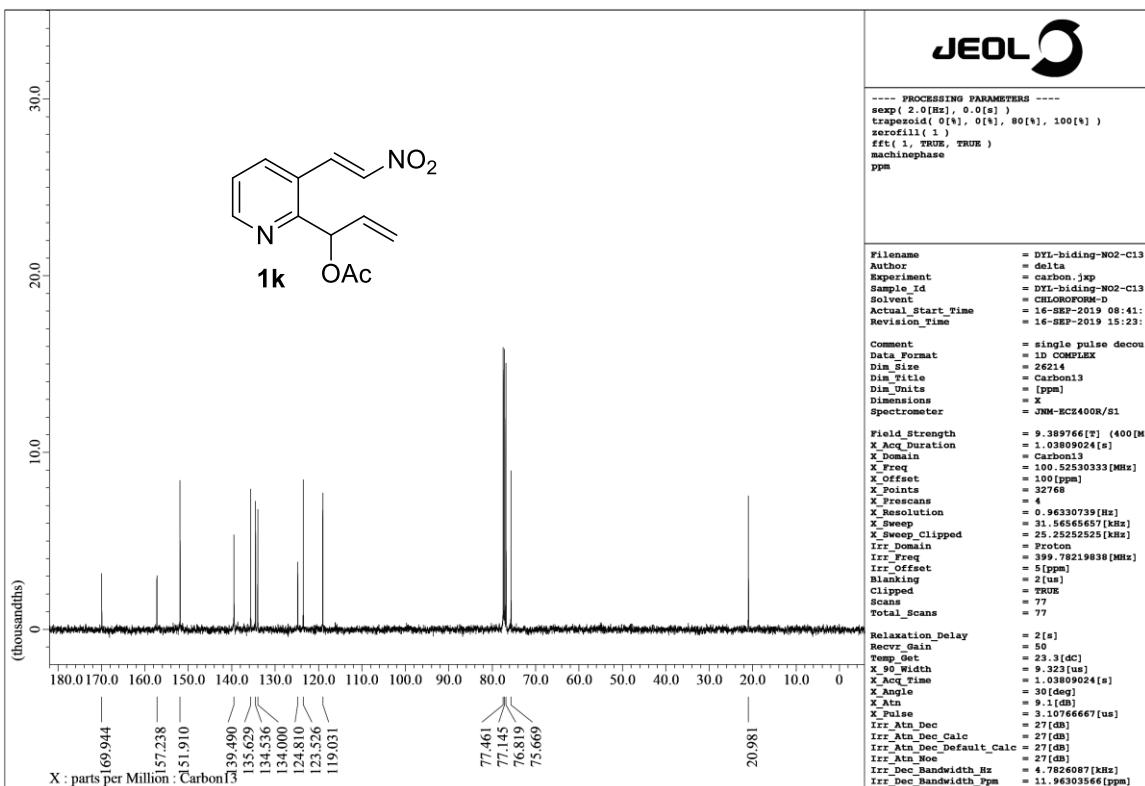
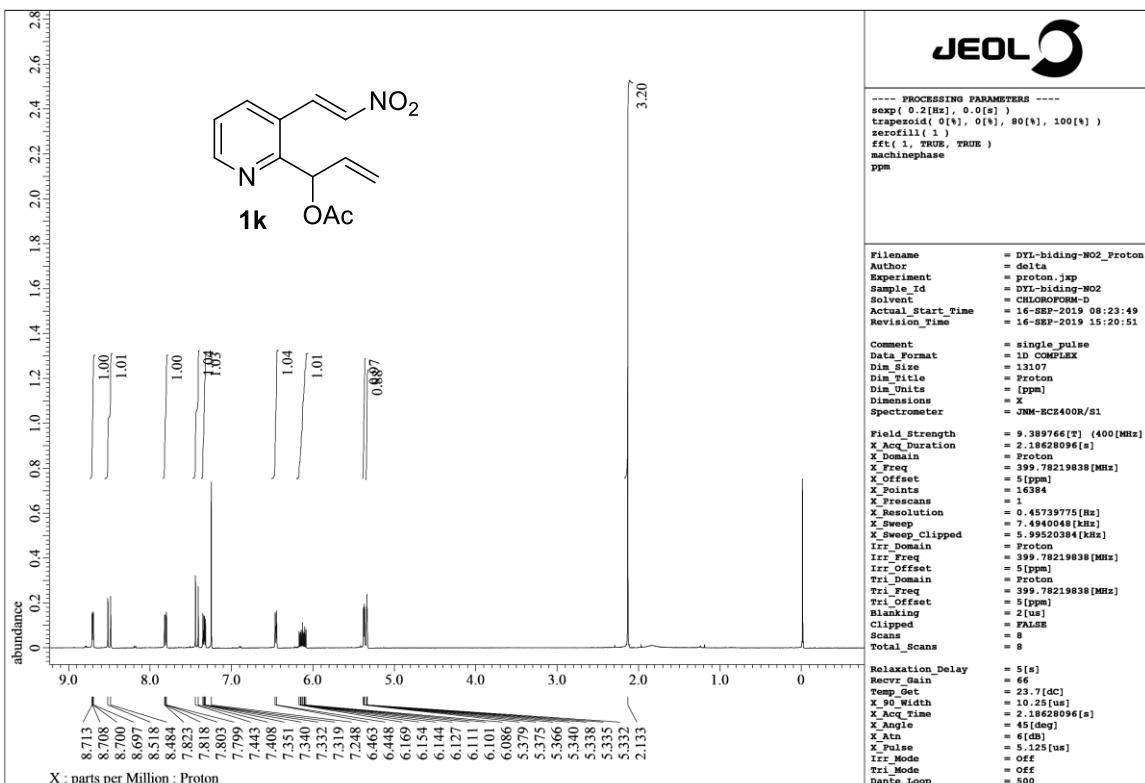


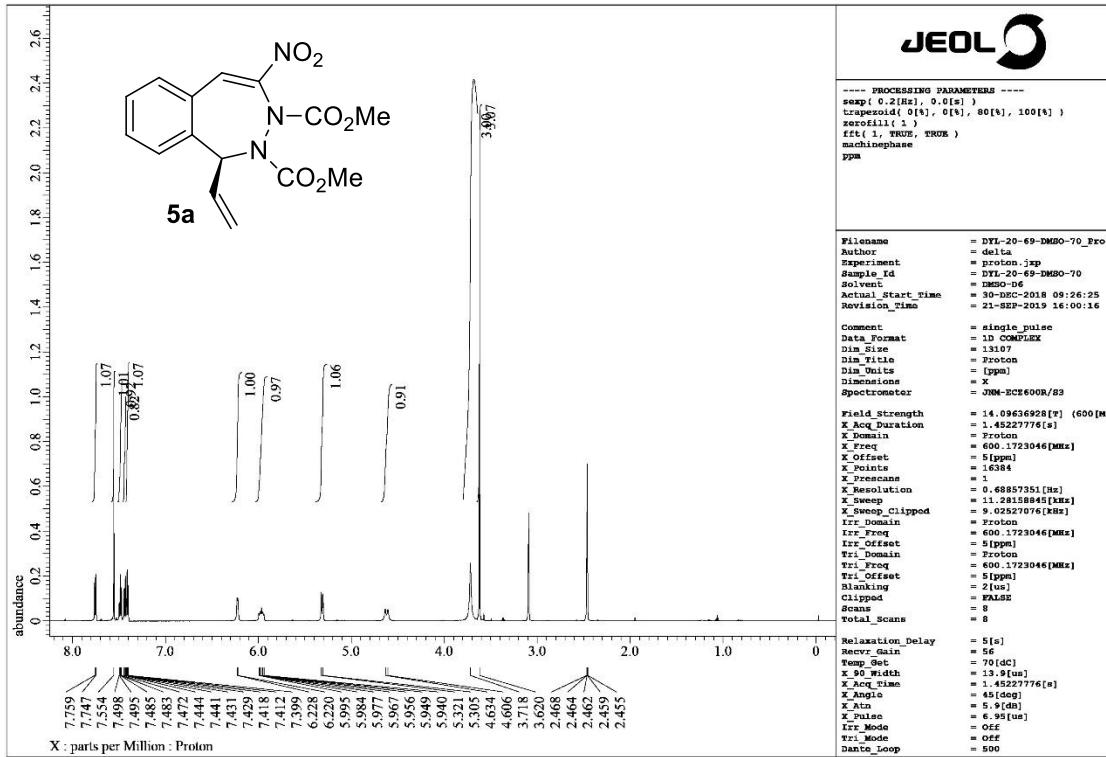




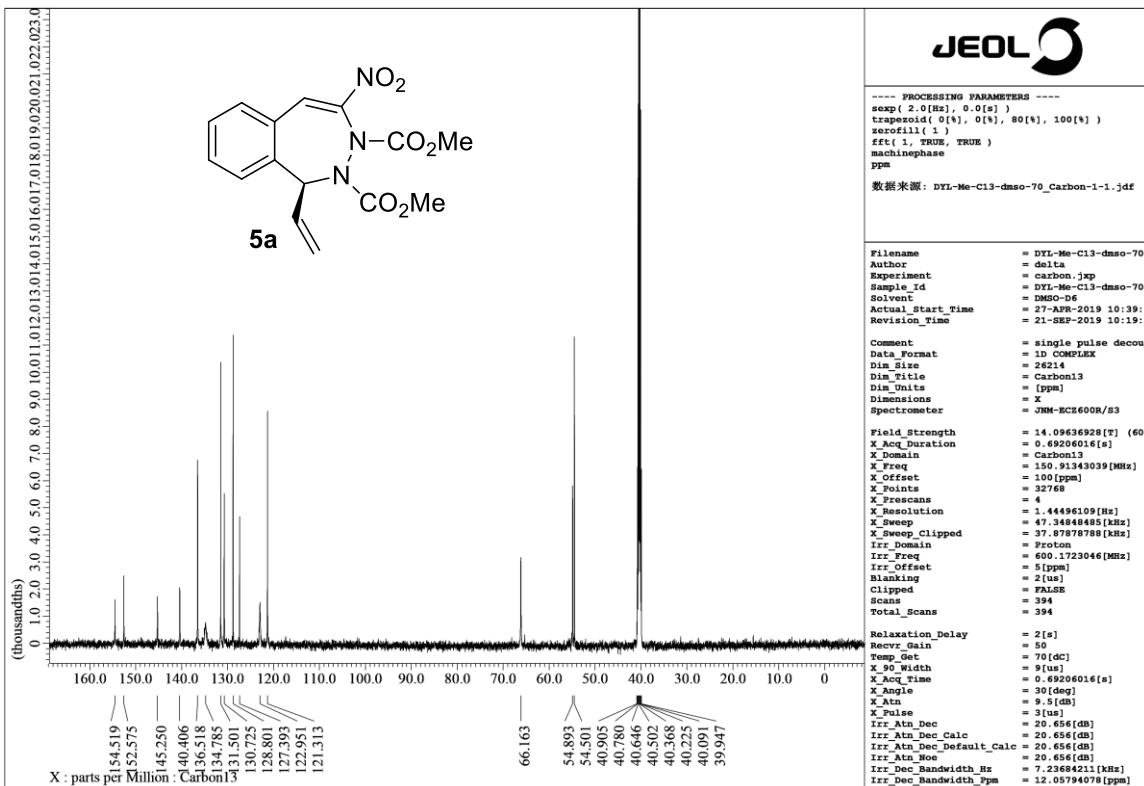


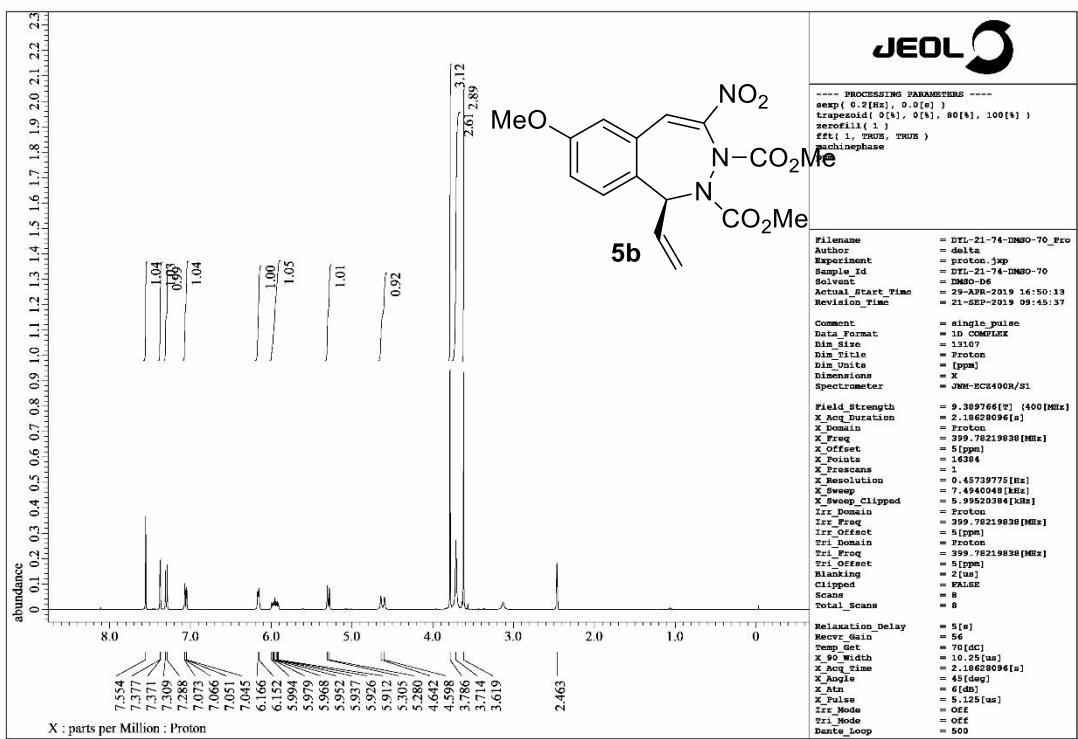




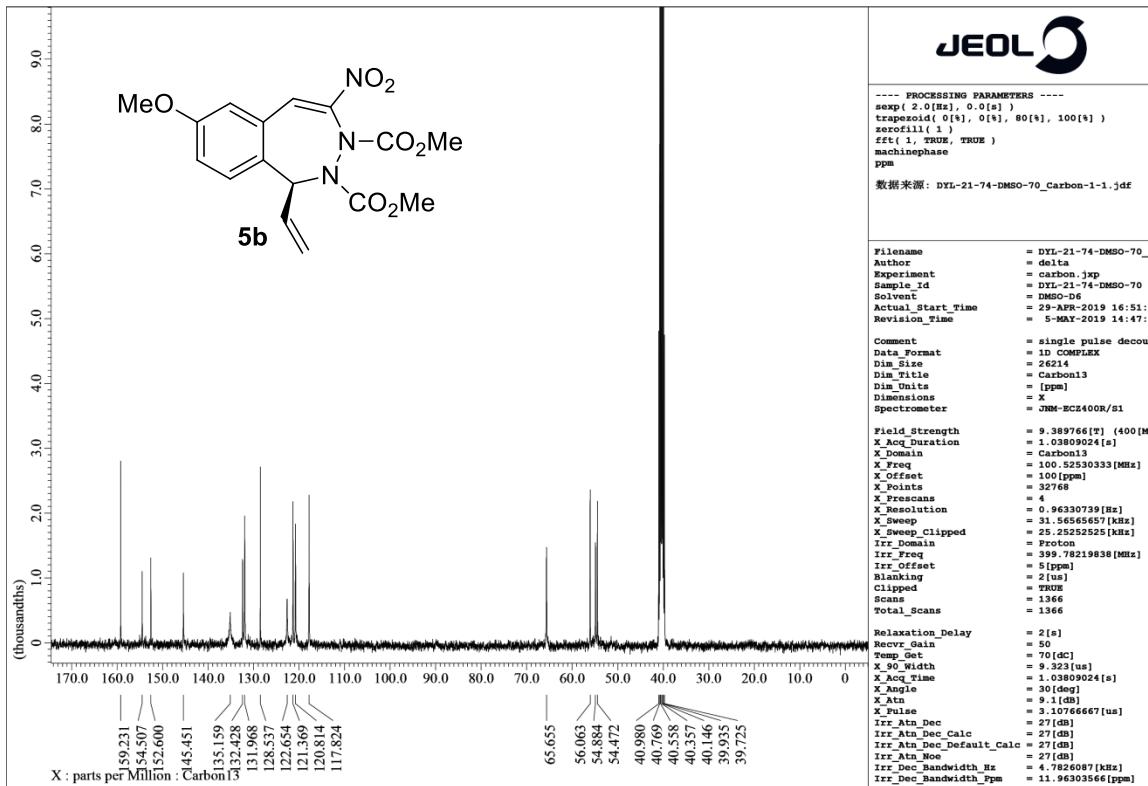


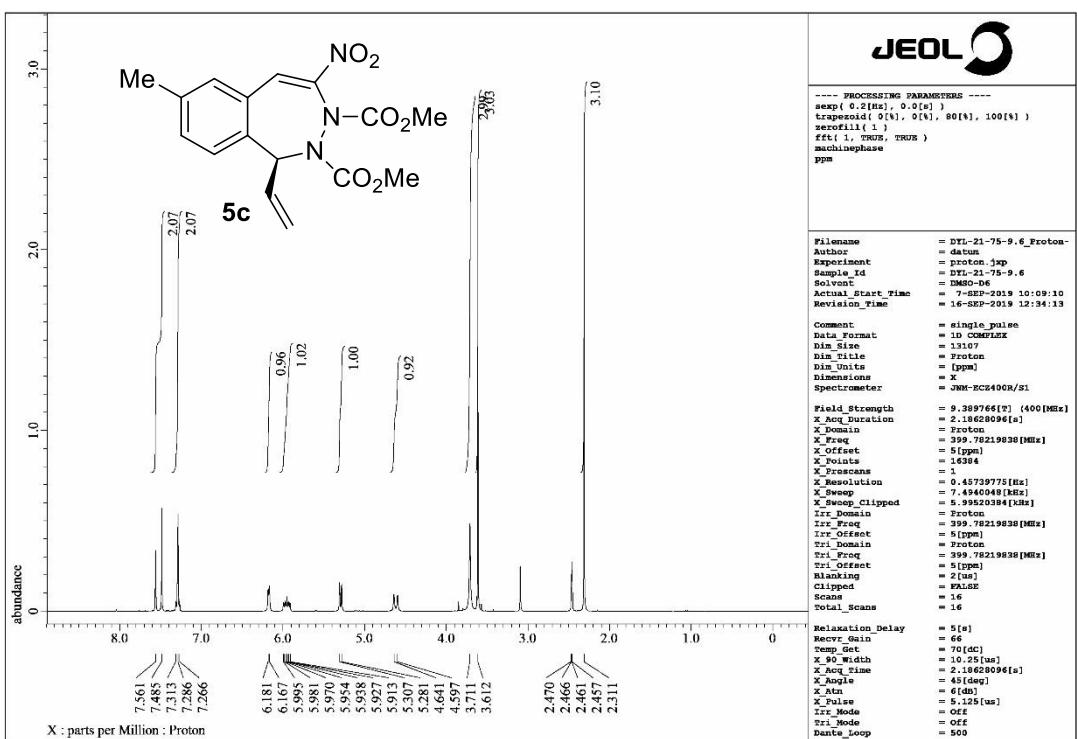
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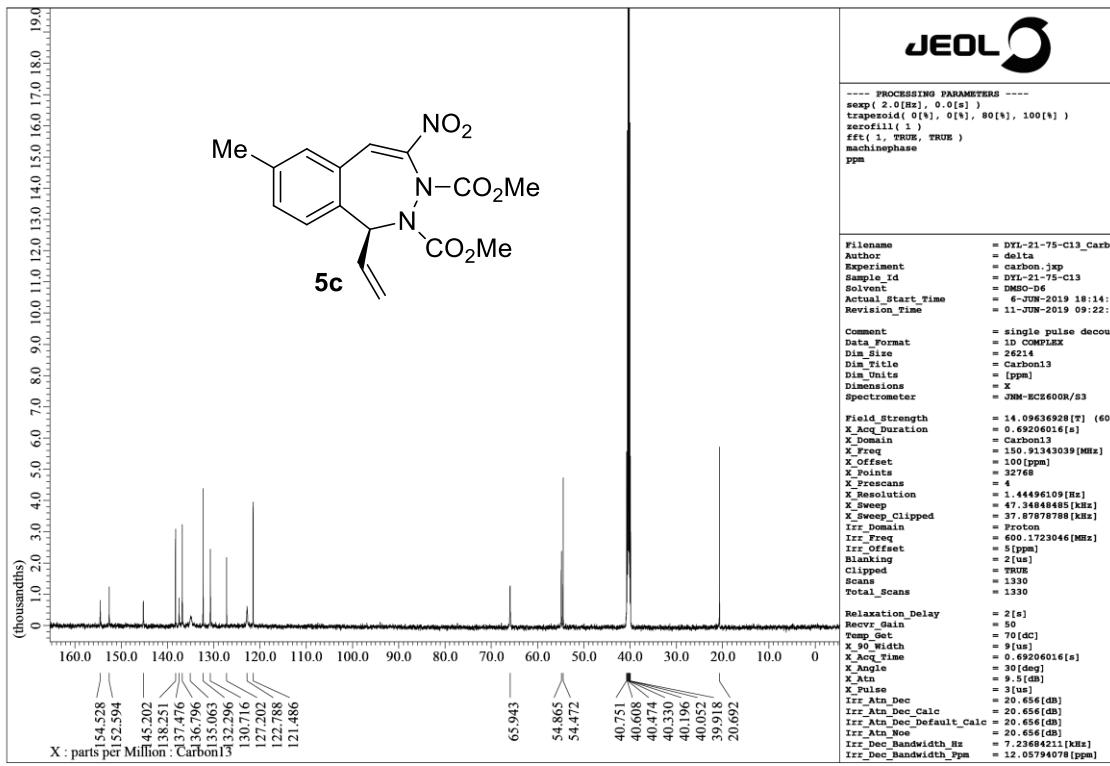


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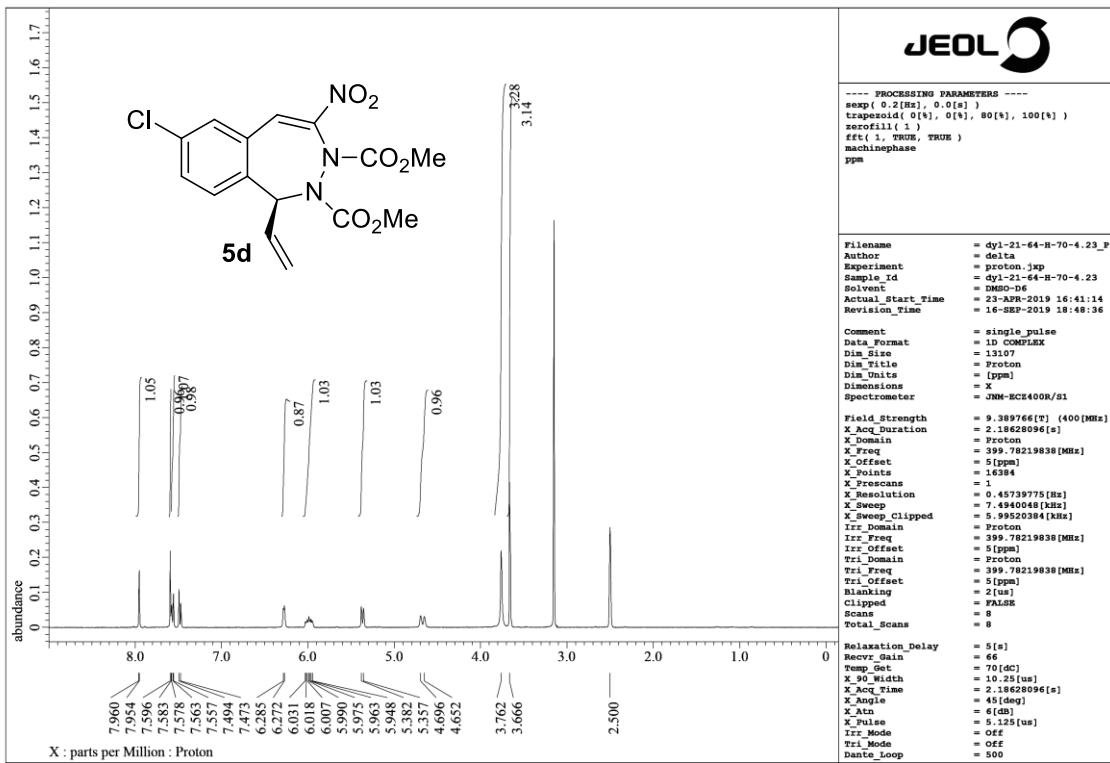




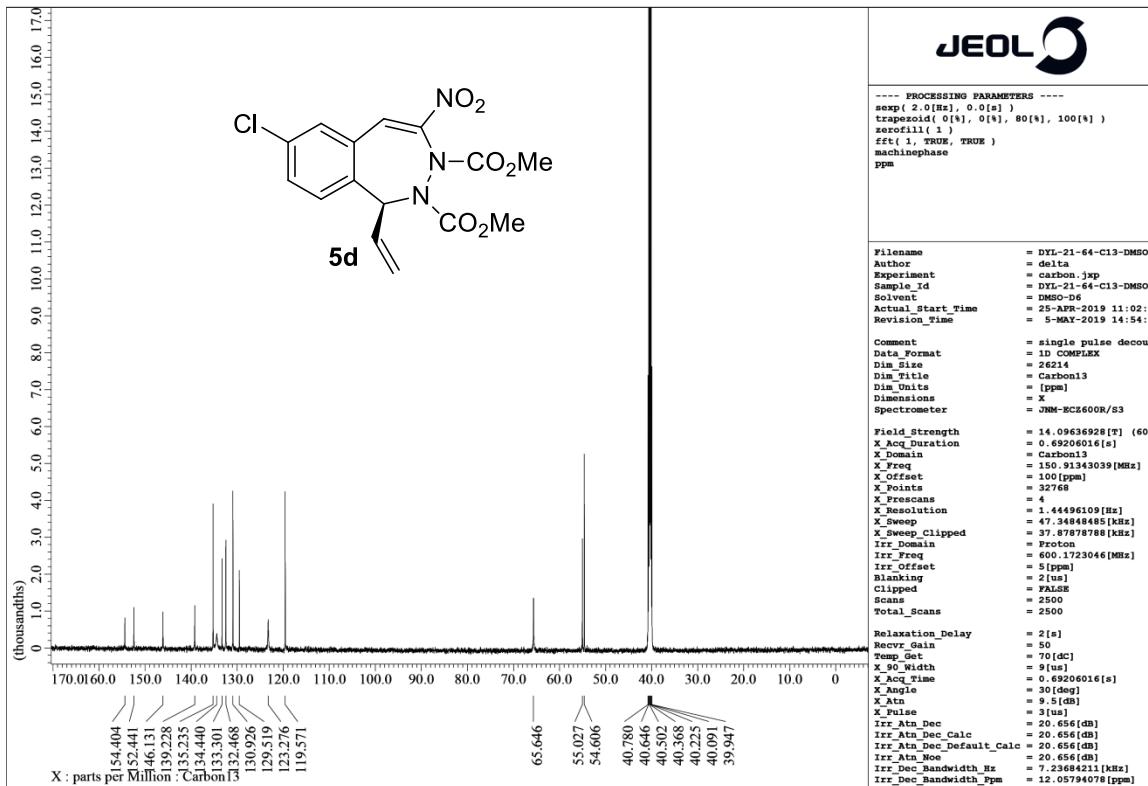
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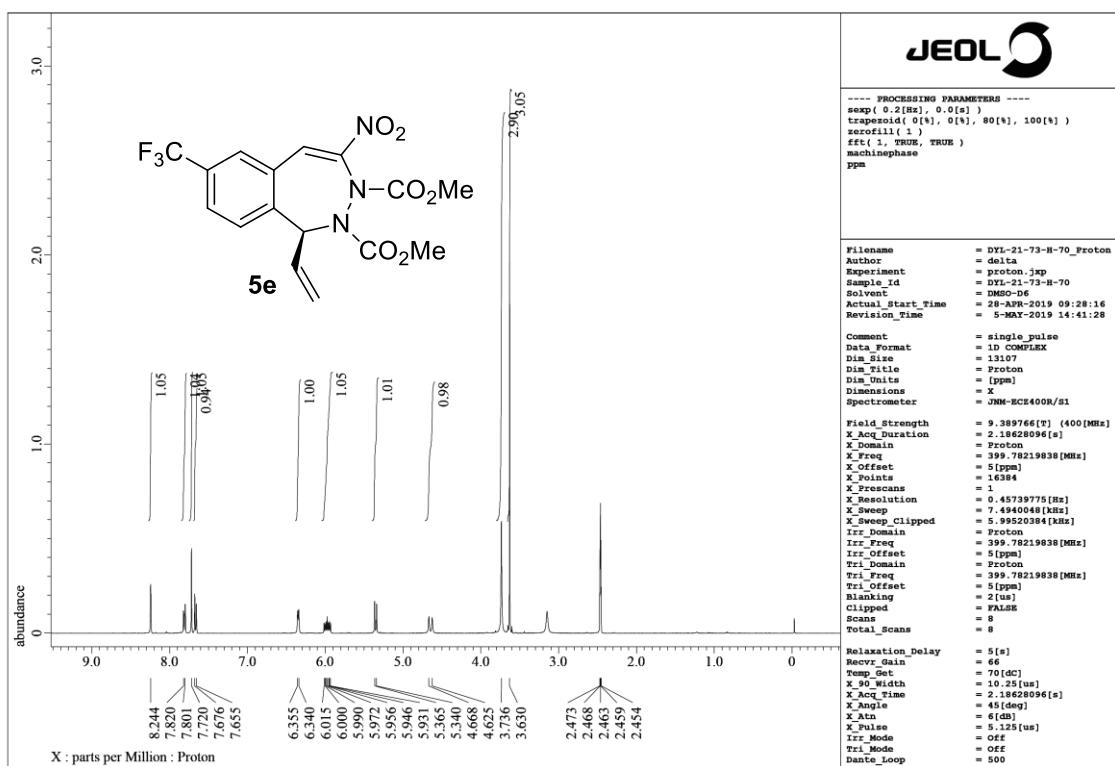


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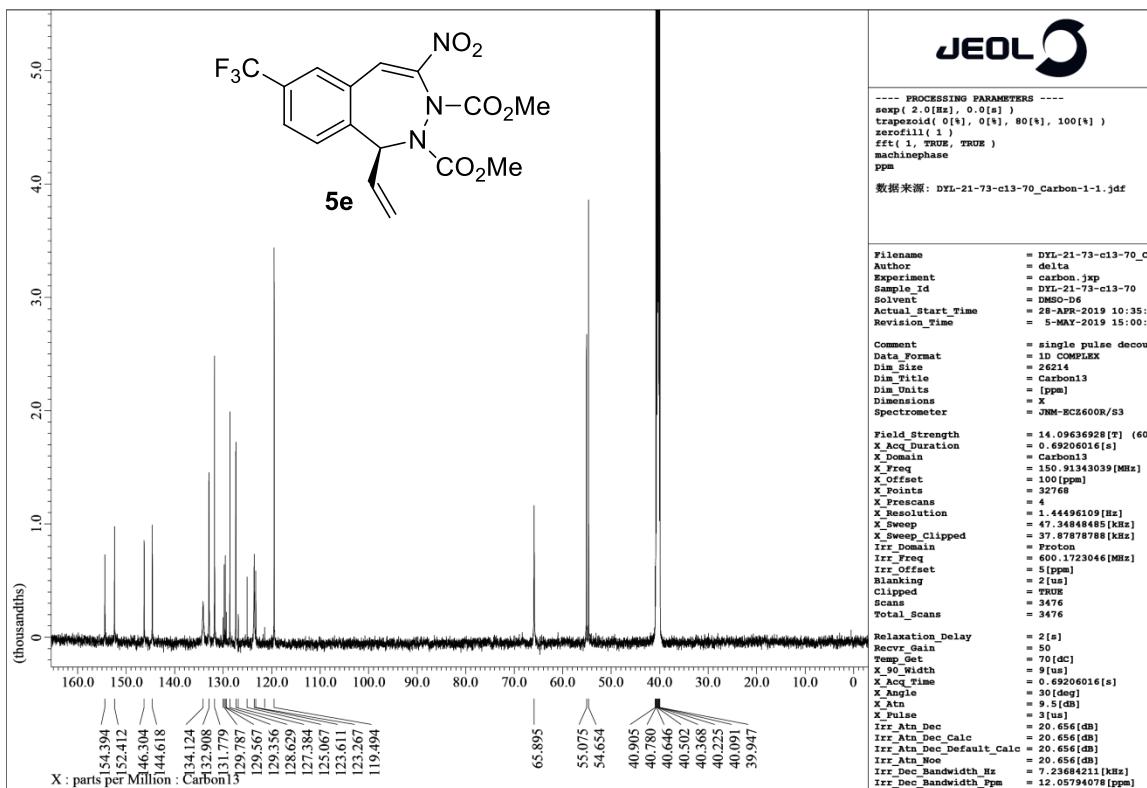


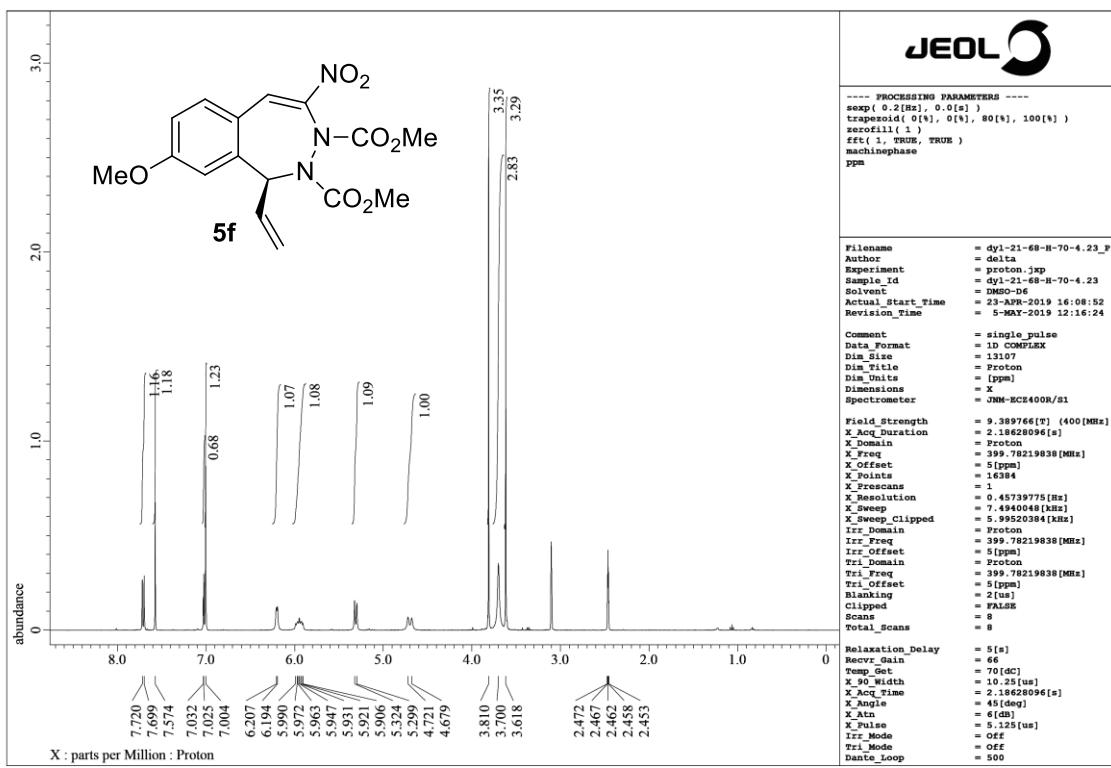
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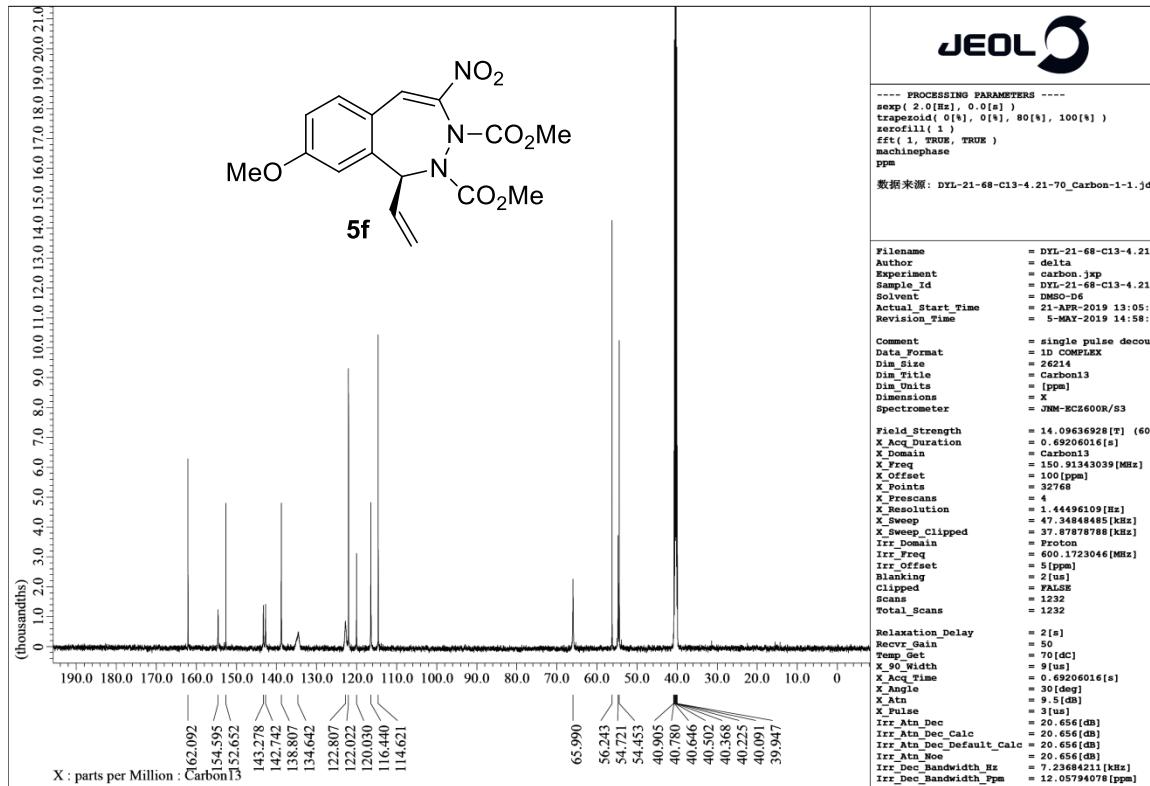


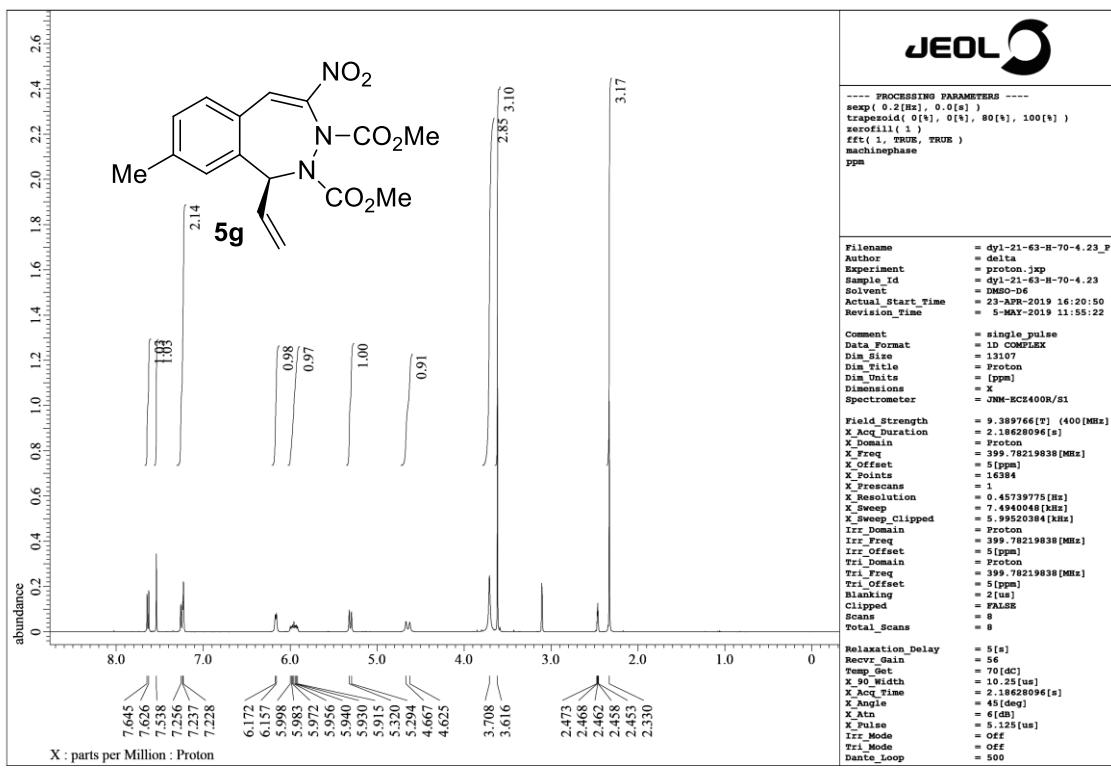
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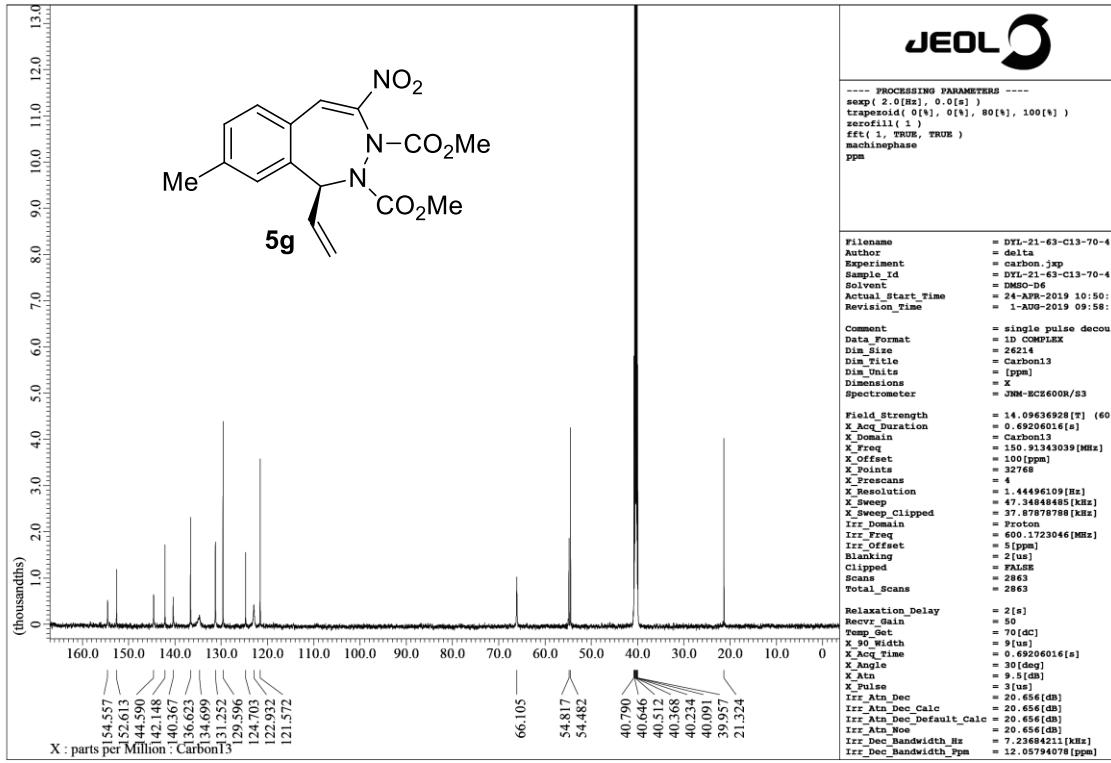


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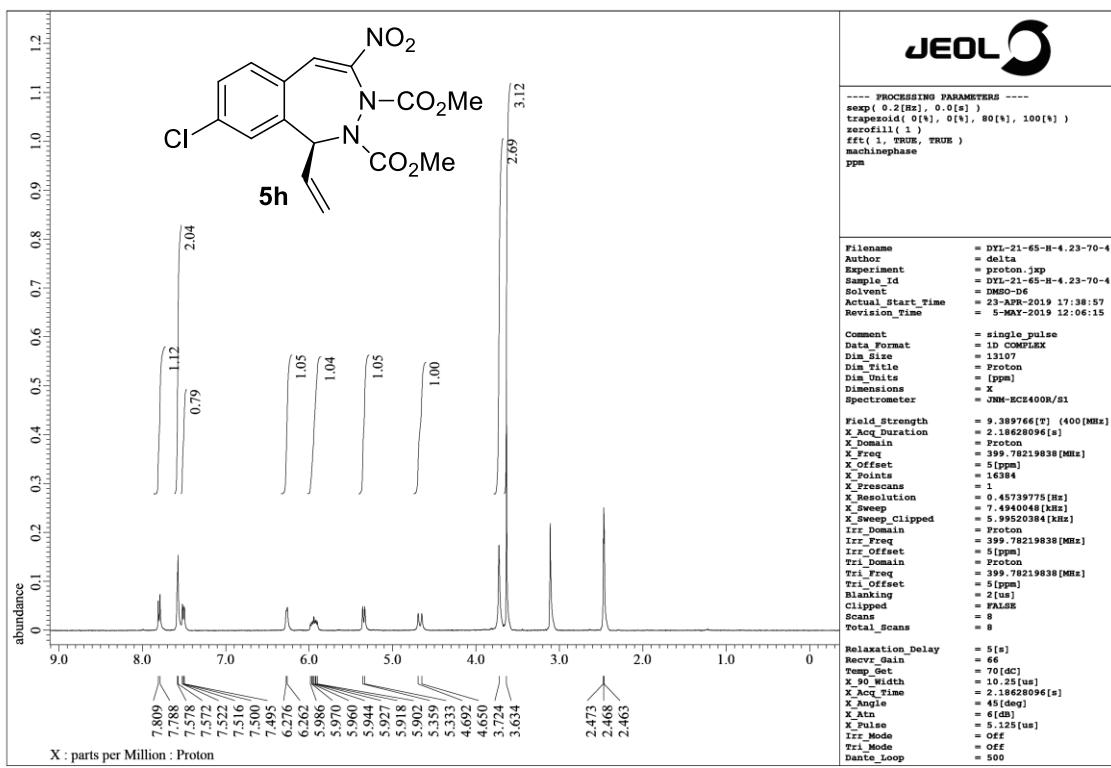




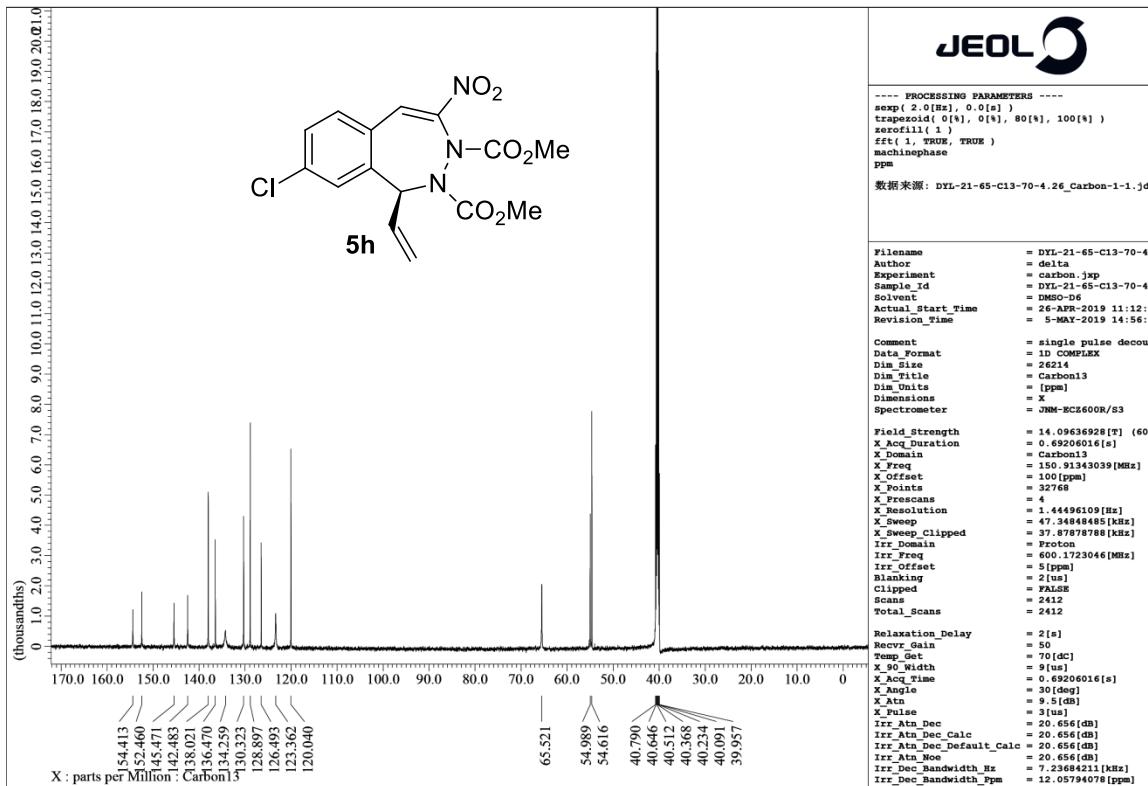
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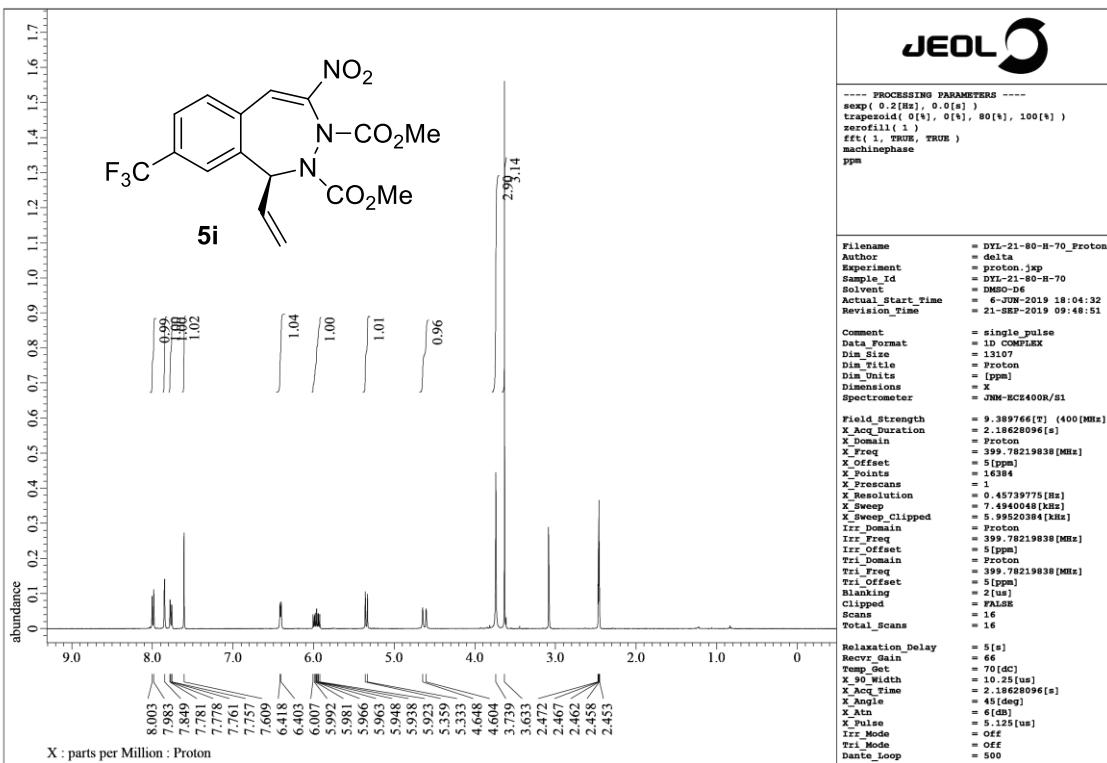


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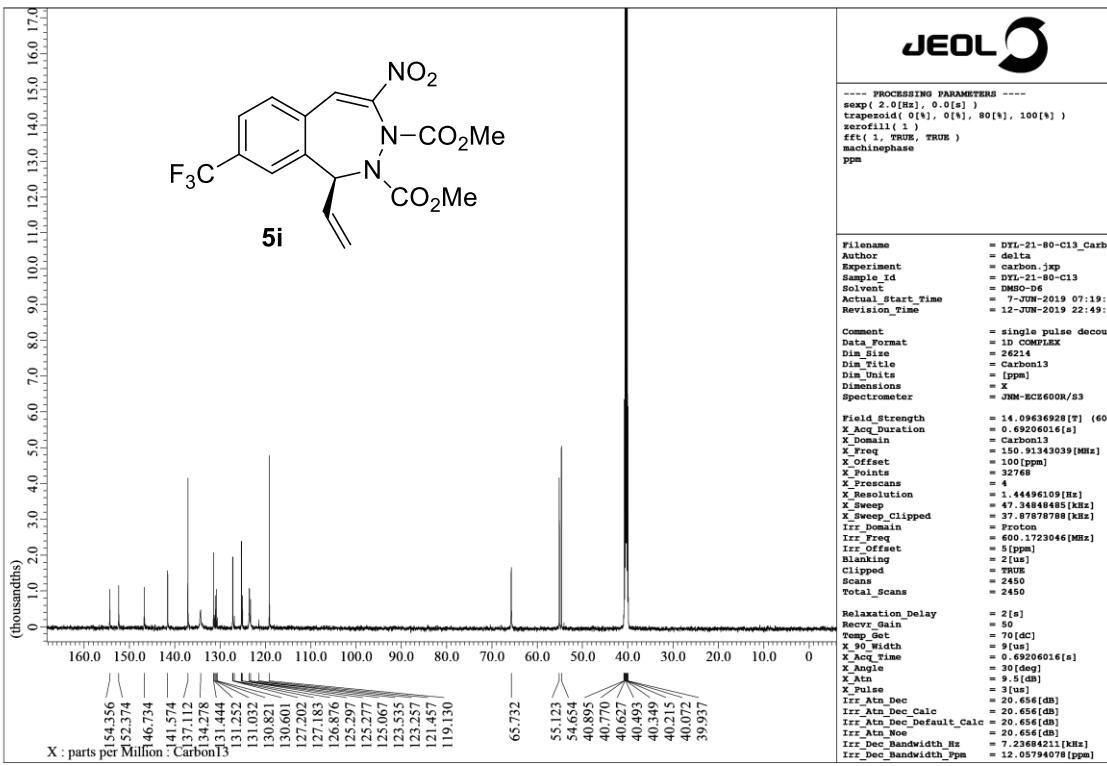


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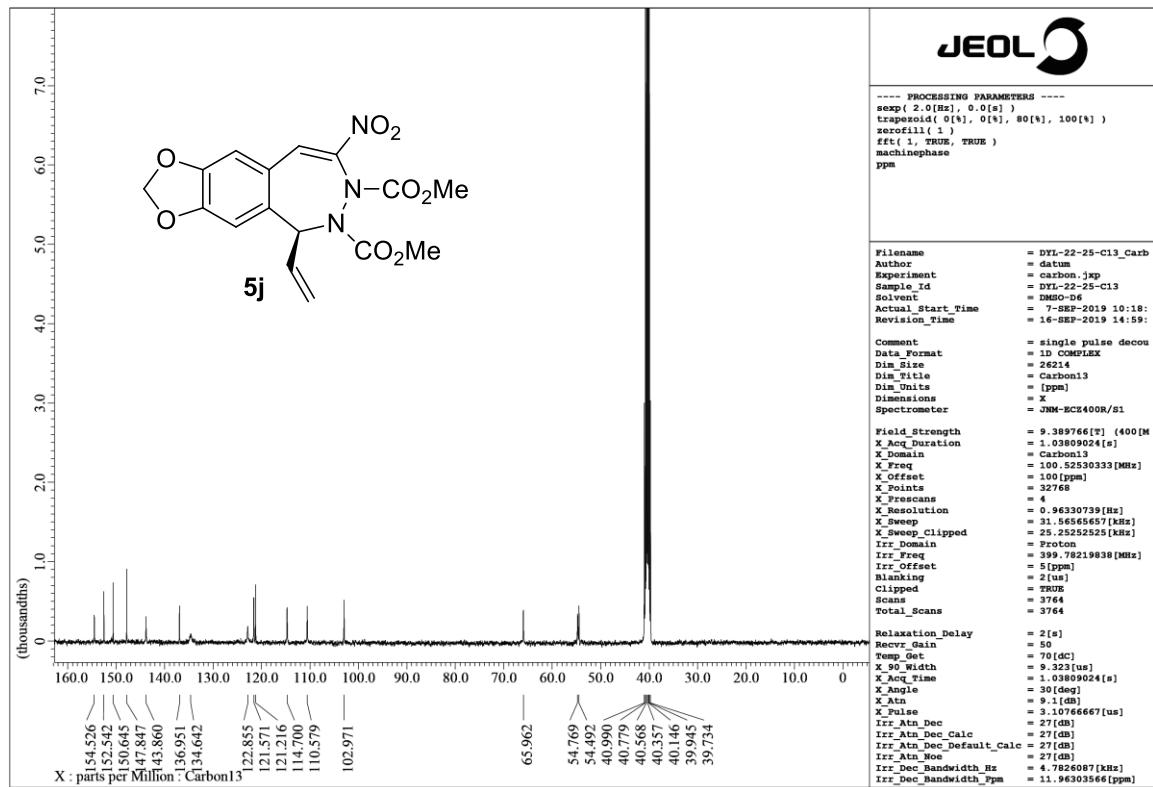
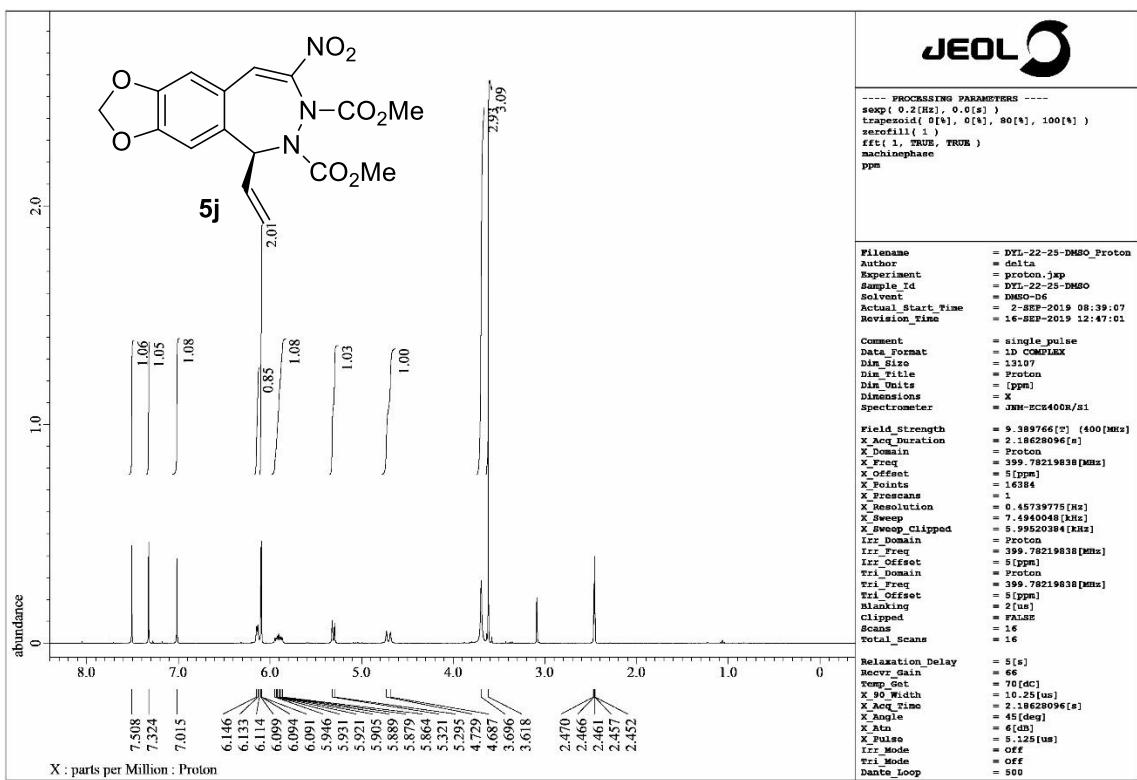


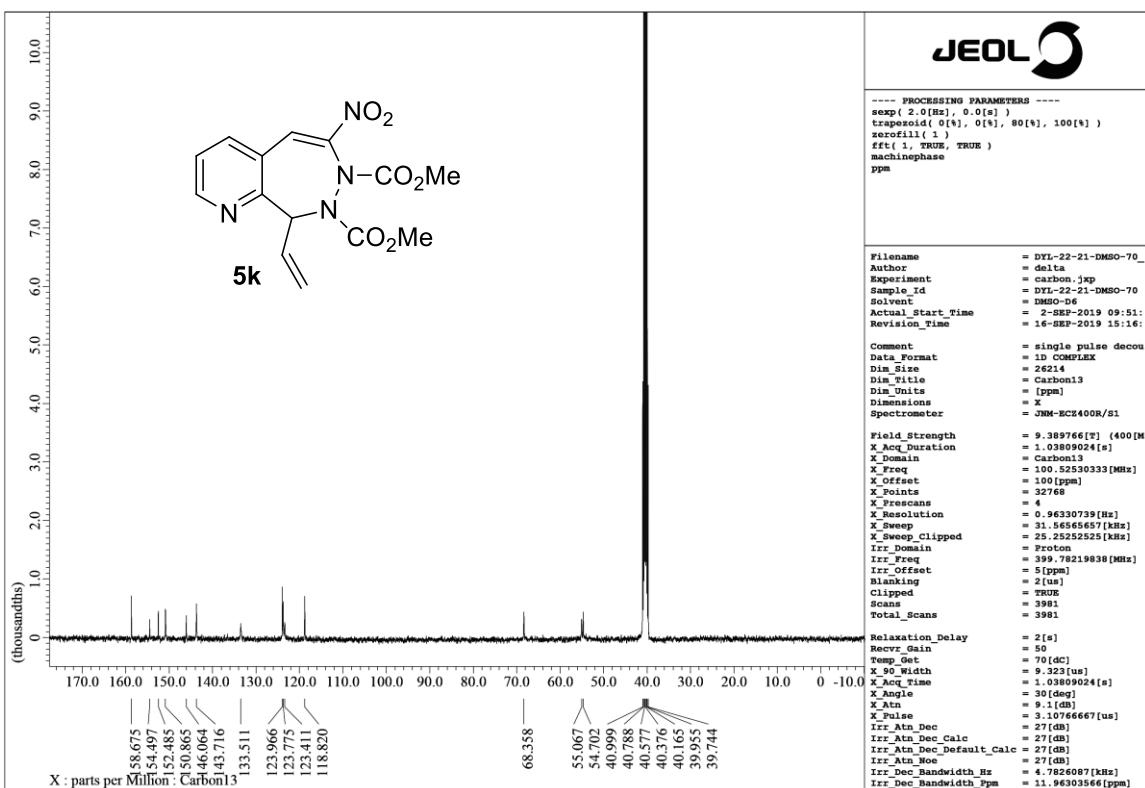
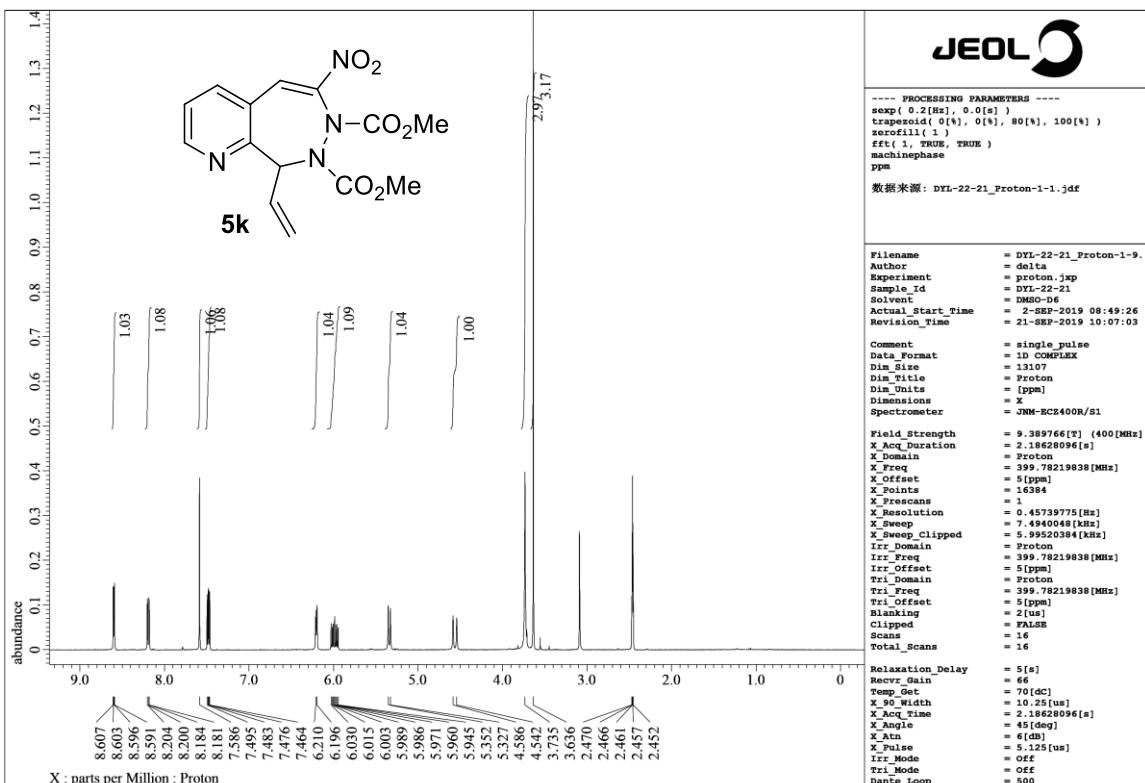


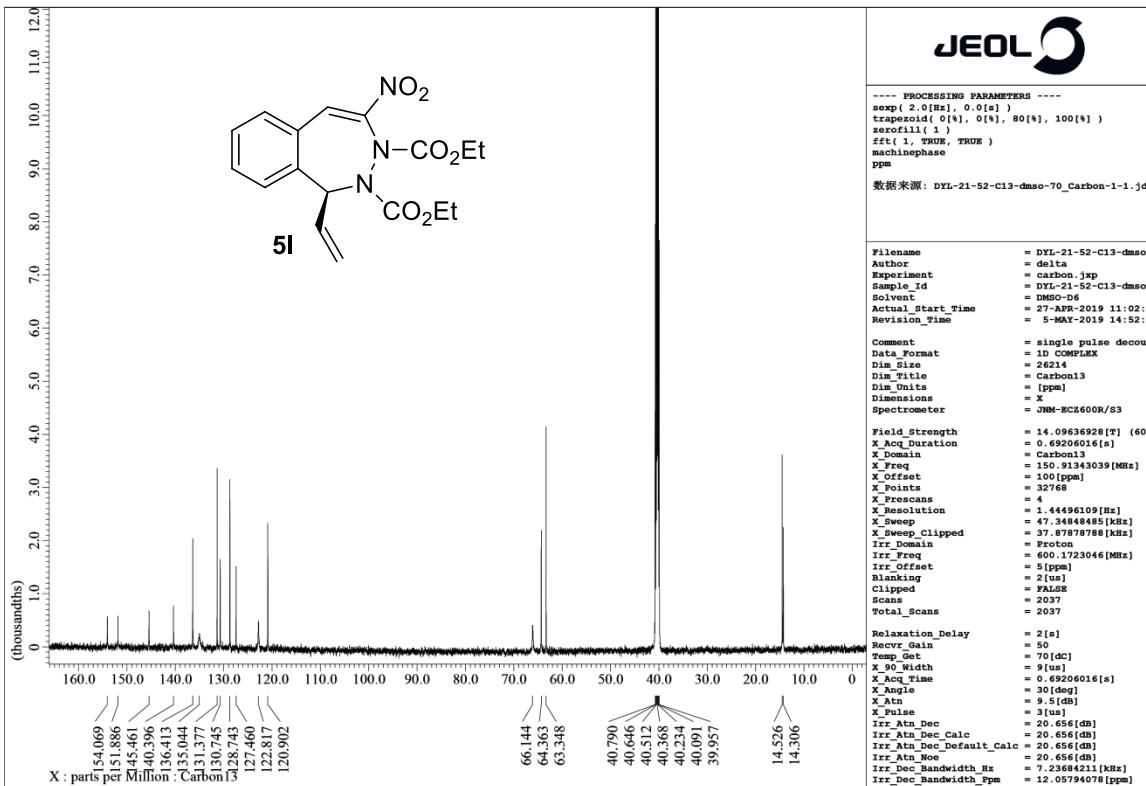
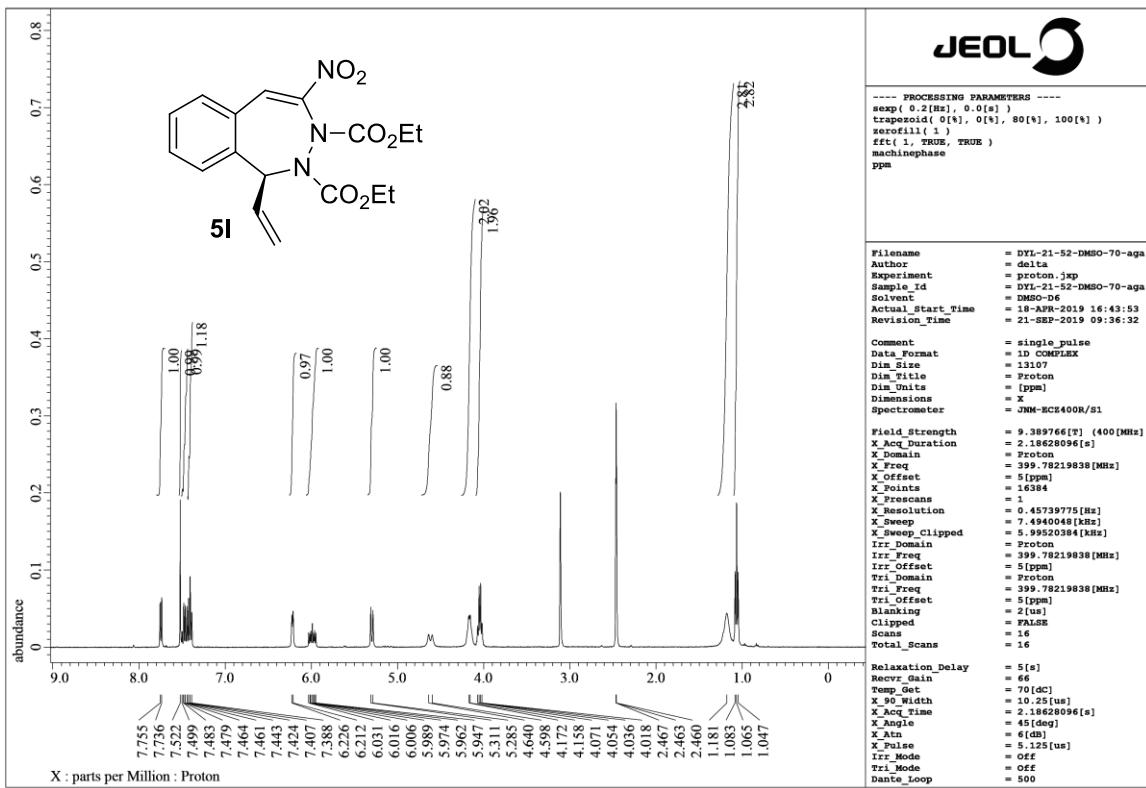
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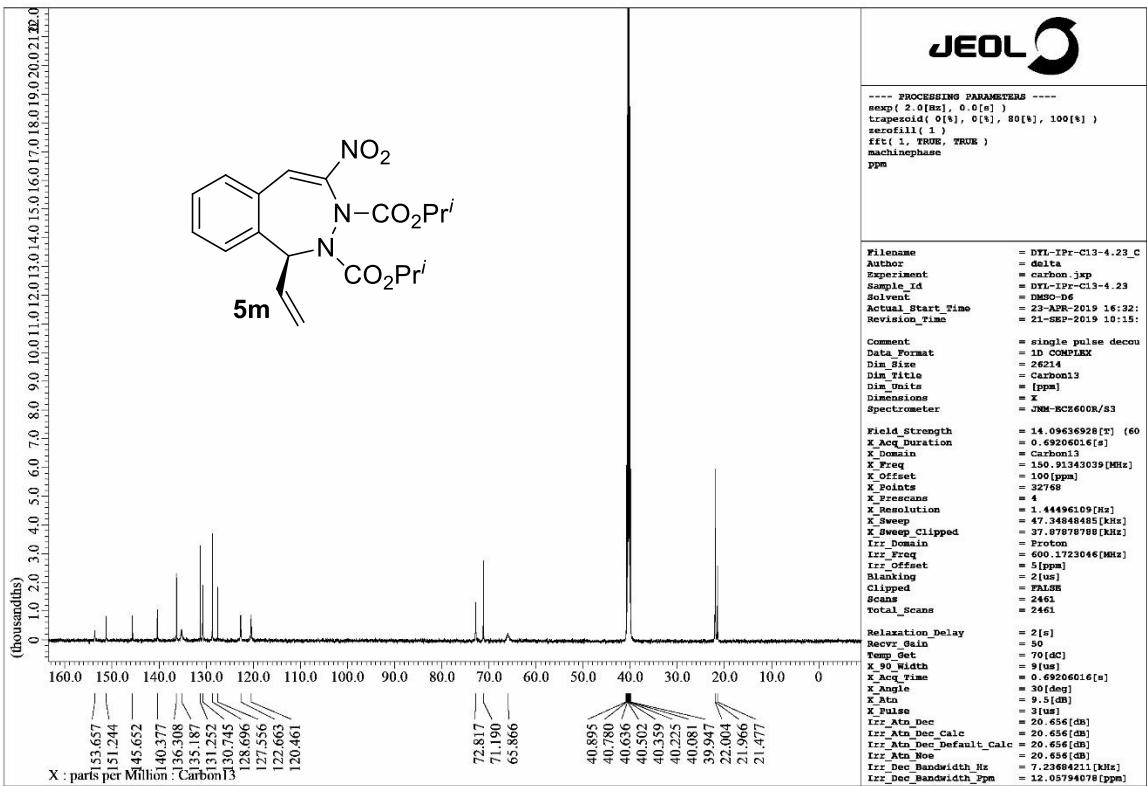
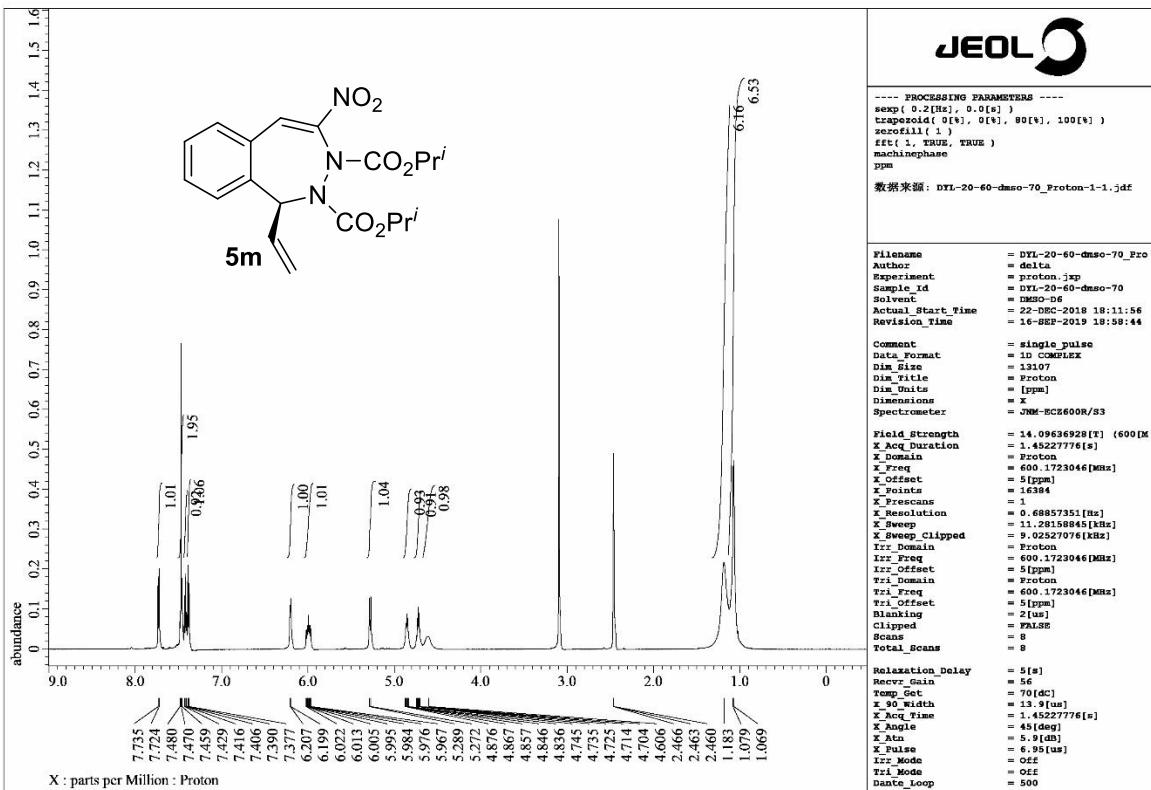


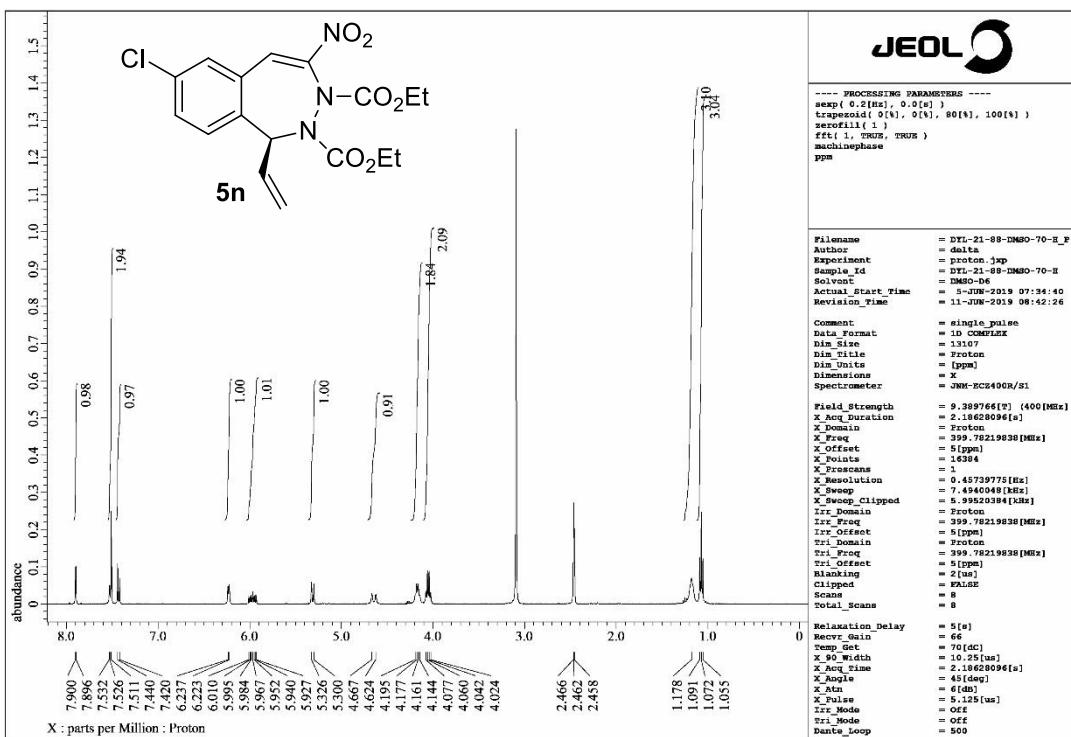
You created this PDF from an application that is not licensed to print to novaPDF printer (<http://www.novapdf.com>)



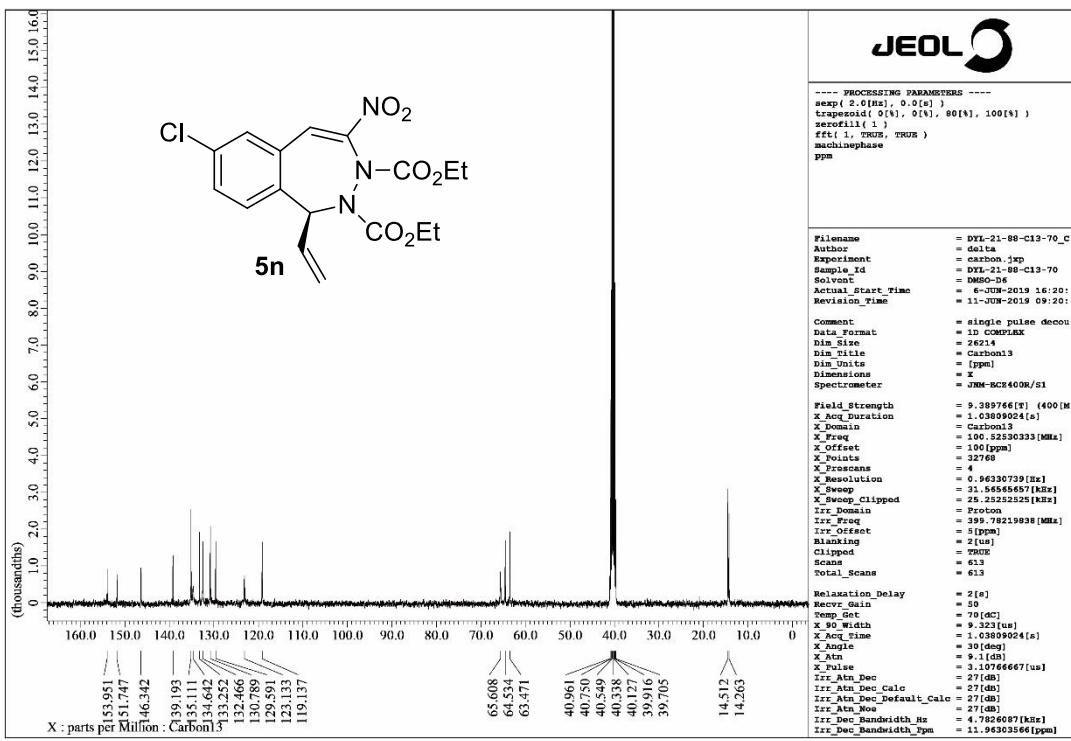




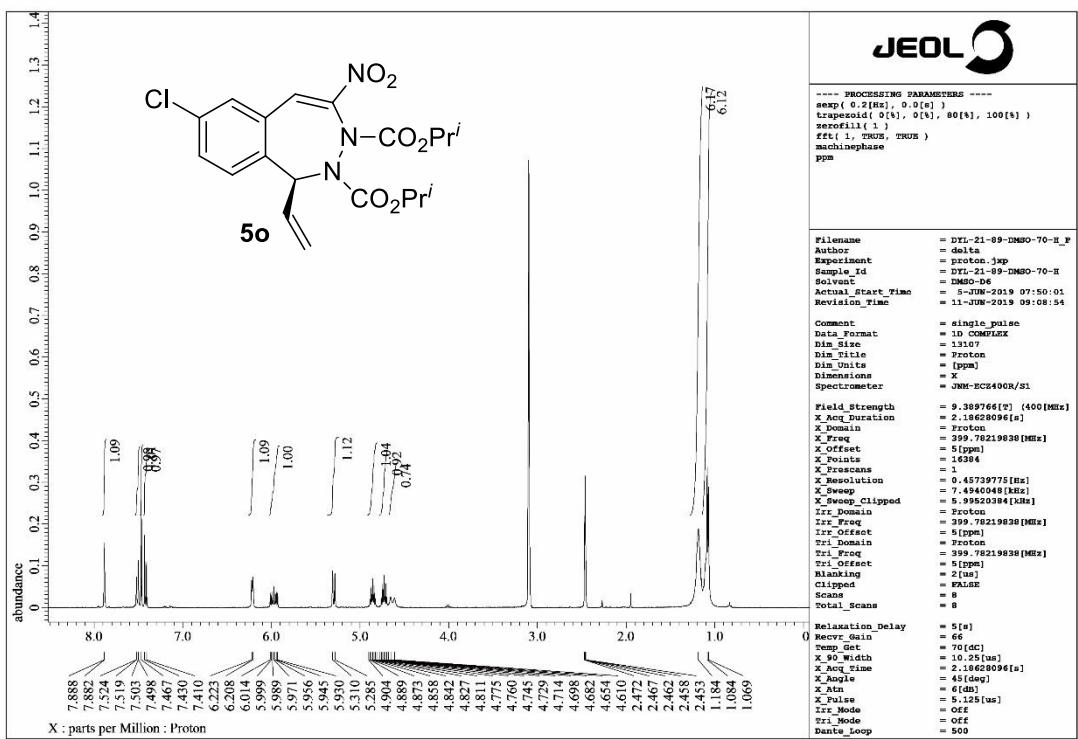




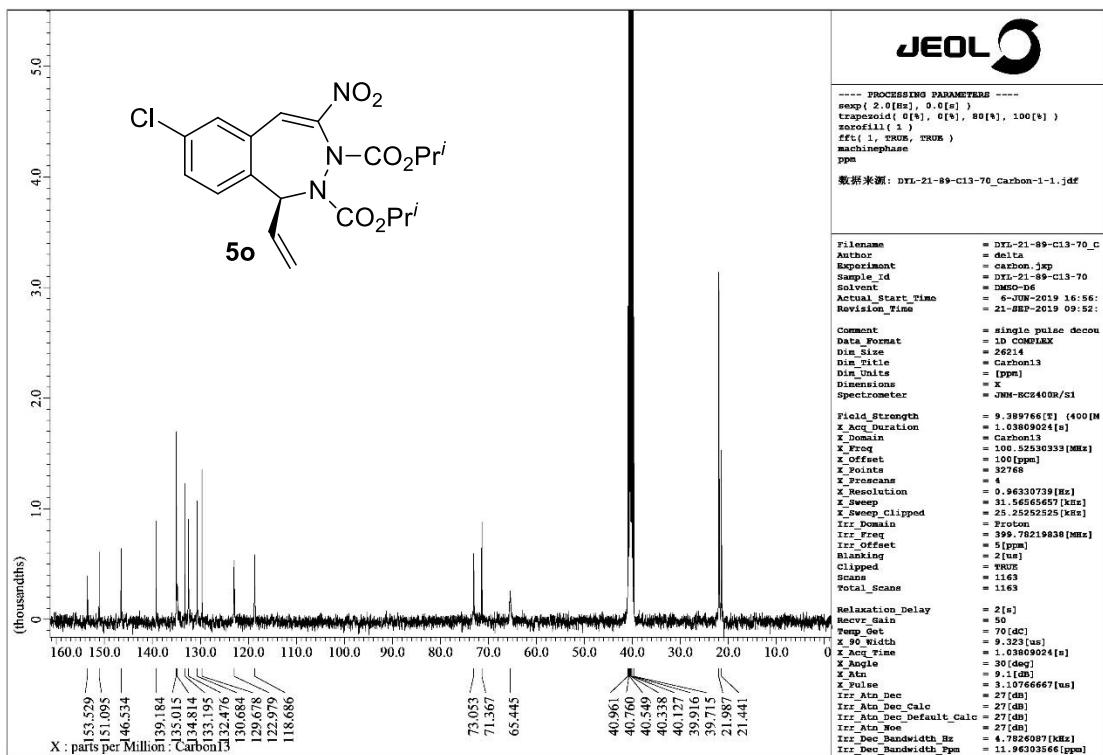
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You created this PDF from an application that is not licensed to print to novaPDF printer (<http://www.novapdf.com>)

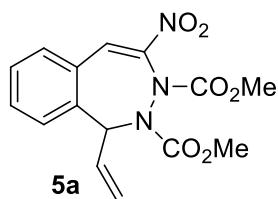


You created this PDF from an application that is not licensed to print to novaPDF printer (<http://www.novapdf.com>)



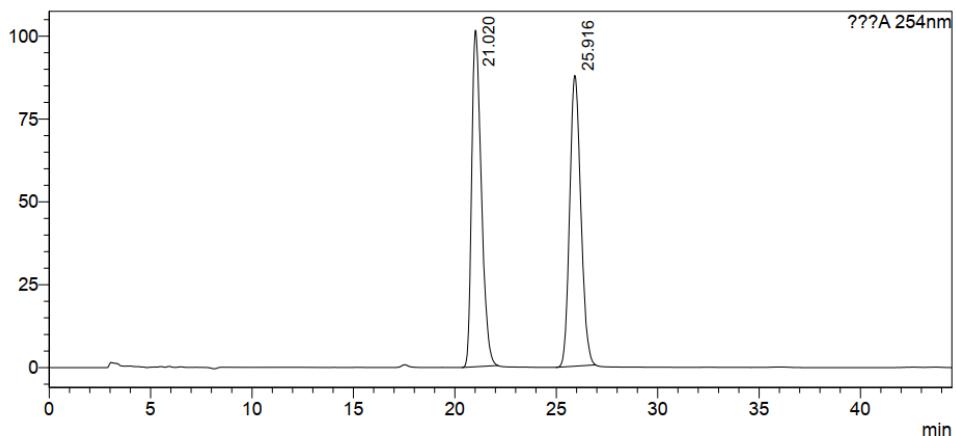
You created this PDF from an application that is not licensed to print to novaPDF printer (<http://www.novapdf.com>)

### HPLC spectra of products 5.



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 88:12 er.

mV

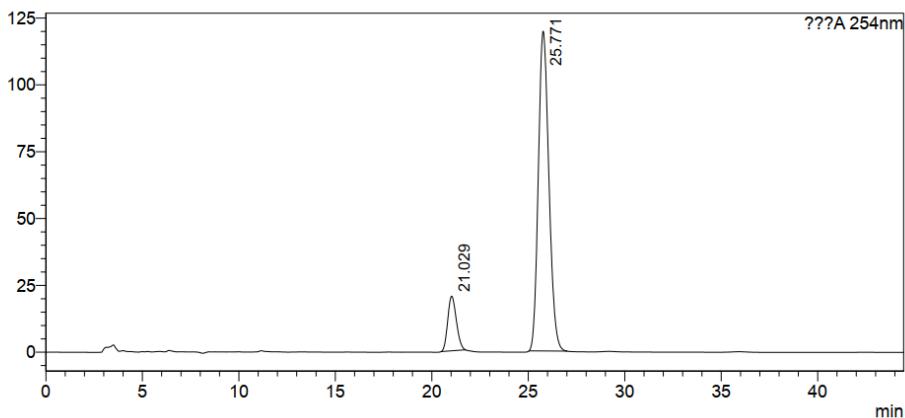


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	21.020	50.049	53.652
2	25.916	49.951	46.348
Total		100.000	100.000

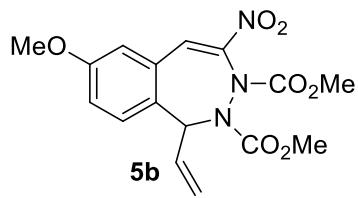
mV



<Peak Table>

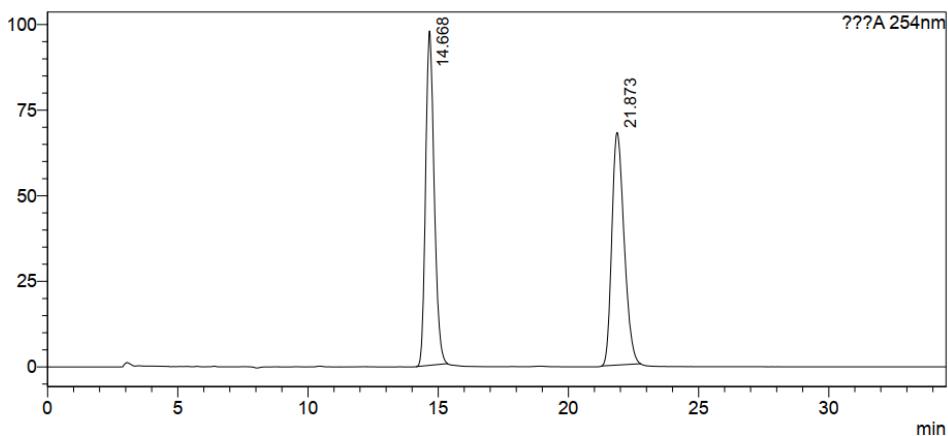
???A 254nm

Peak#	Ret. Time	Area%	Height%
1	21.029	12.190	14.583
2	25.771	87.810	85.417
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 92:8 er.

mV

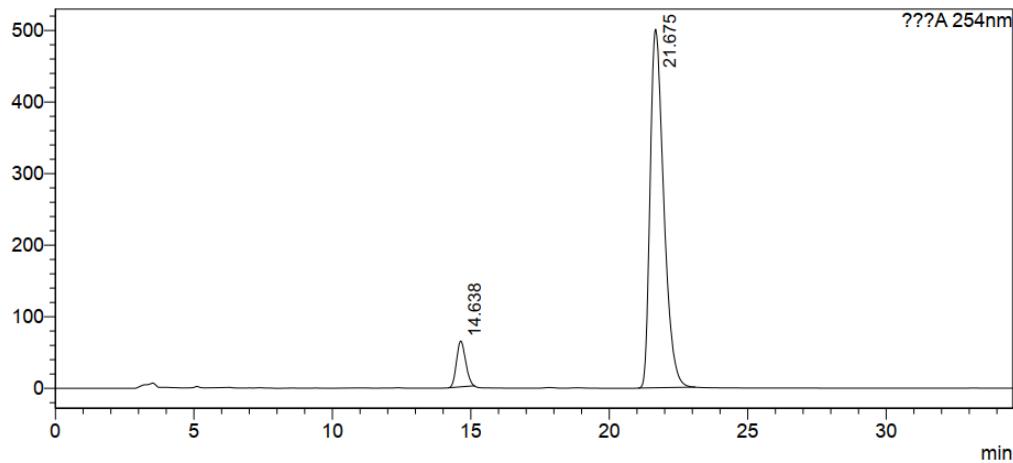


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	14.668	50.217	58.985
2	21.873	49.783	41.015
Total		100.000	100.000

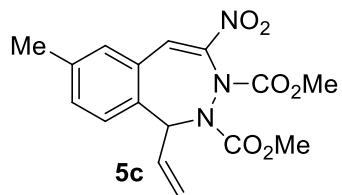
mV



**<Peak Table>**

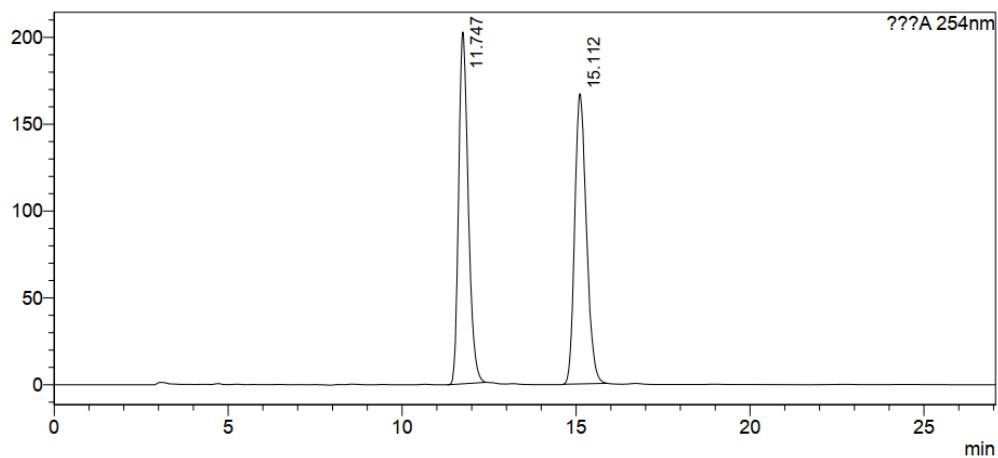
???A 254nm

Peak#	Ret. Time	Area%	Height%
1	14.638	7.844	11.314
2	21.675	92.156	88.686
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 85:15 er.

mV

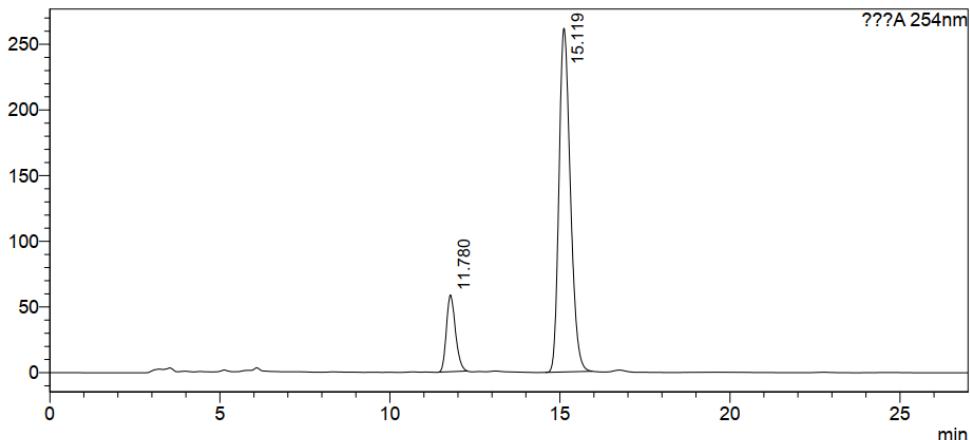


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	11.747	49.849	54.802
2	15.112	50.151	45.198
Total		100.000	100.000

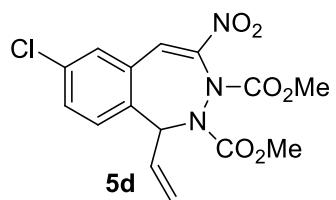
mV



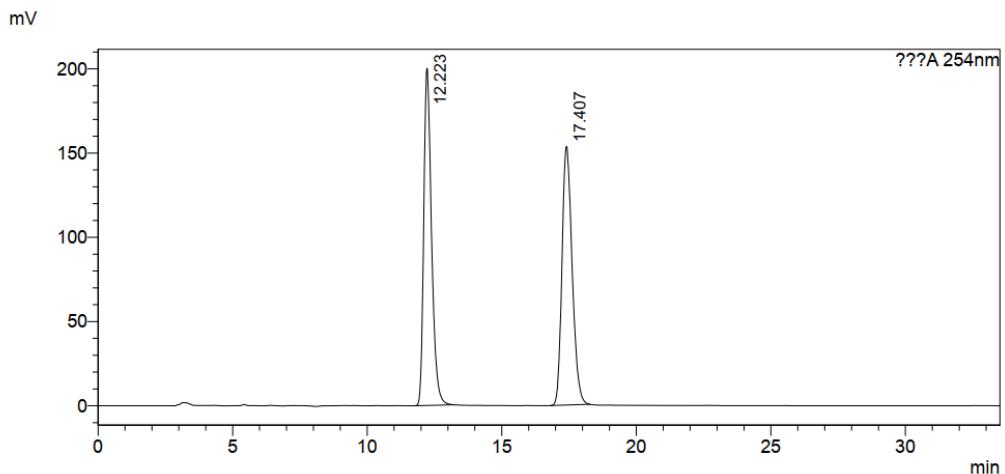
**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	11.780	15.077	18.256
2	15.119	84.923	81.744
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 94:6 er.

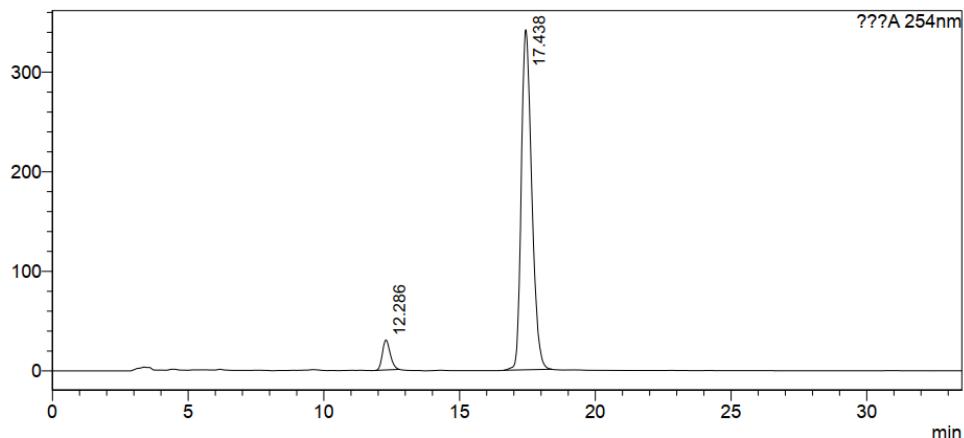


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	12.223	50.041	56.597
2	17.407	49.959	43.403
Total		100.000	100.000

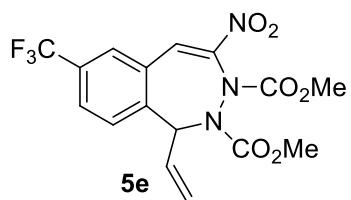
mV



**<Peak Table>**

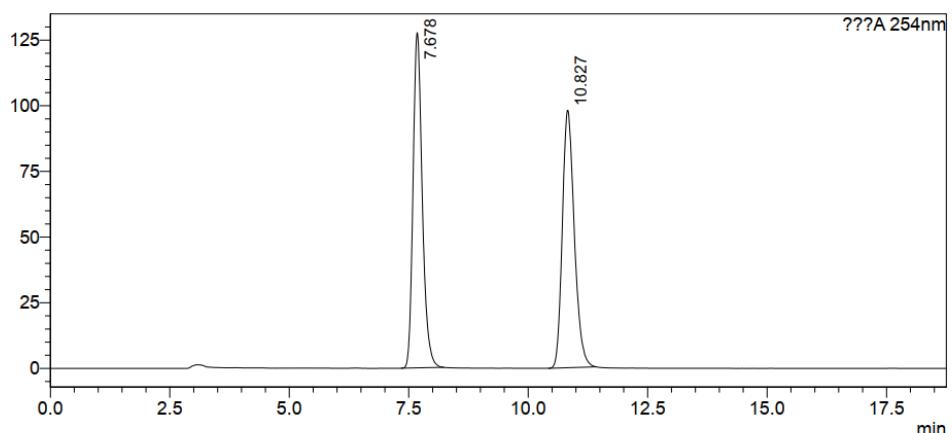
???A 254nm

Peak#	Ret. Time	Area%	Height%
1	12.286	6.195	8.099
2	17.438	93.805	91.901
Total		100.000	100.000



AD-H column, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 95:5 er.

my

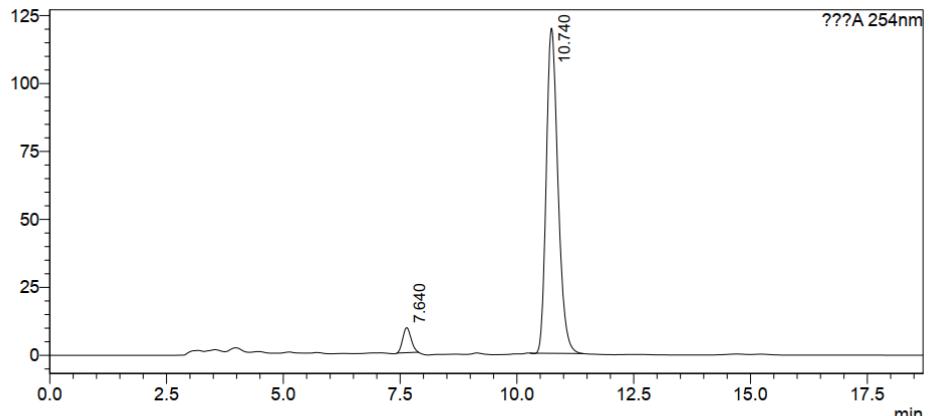


## <Peak Table>

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	7.678	50.012	56.552
2	10.827	49.988	43.448
Total		100.000	100.000

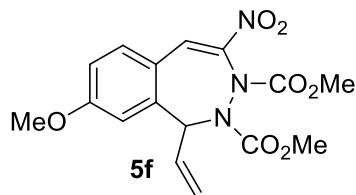
mV



## <Peak Table>

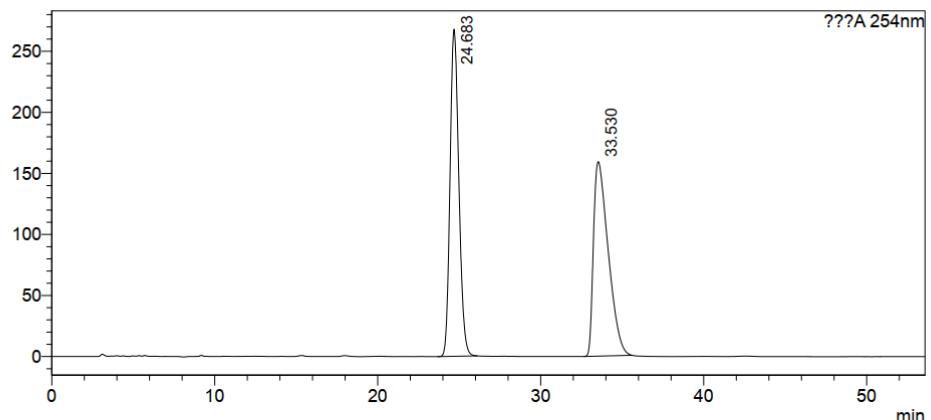
?? A 254nm

Peak#	Ret. Time	Area%	Height%
1	7.640	5.184	7.145
2	10.740	94.816	92.855
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 92:8 er.

mV

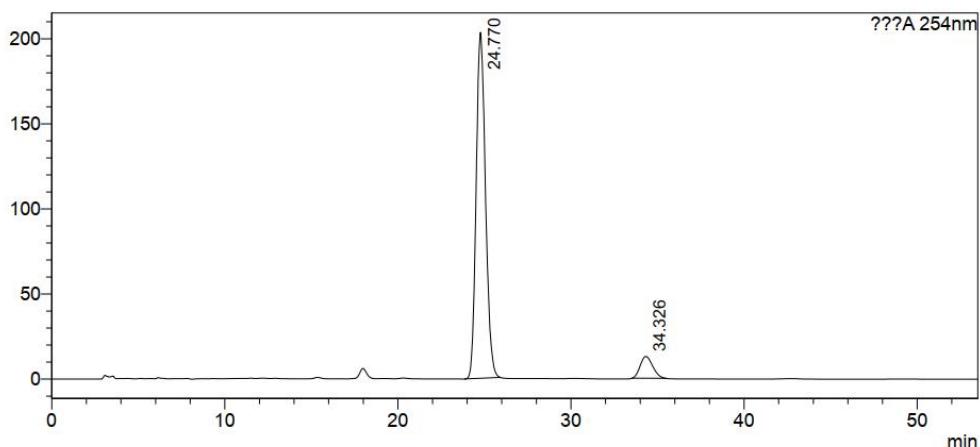


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	24.683	50.194	62.709
2	33.530	49.806	37.291
Total		100.000	100.000

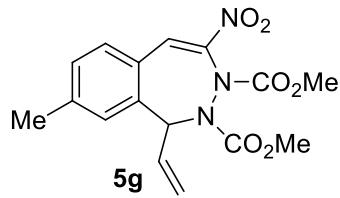
mV



**<Peak Table>**

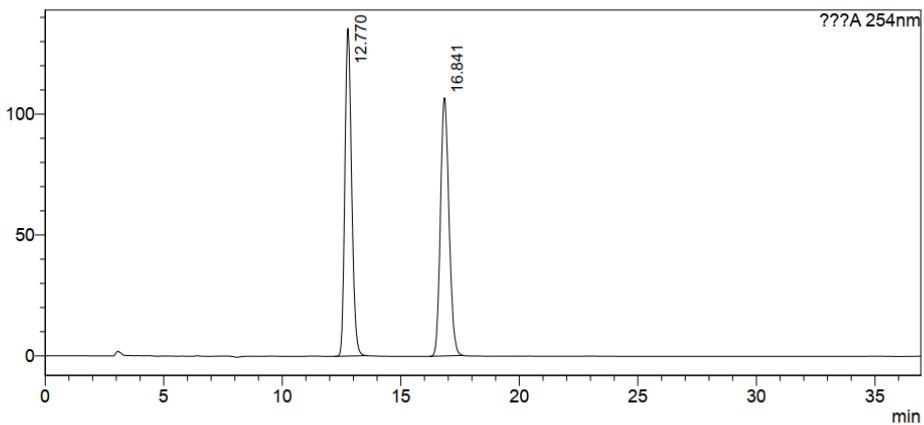
???A 254nm

Peak#	Ret. Time	Area%	Height%
1	24.770	92.215	94.070
2	34.326	7.785	5.930
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 87:13 er.

mV

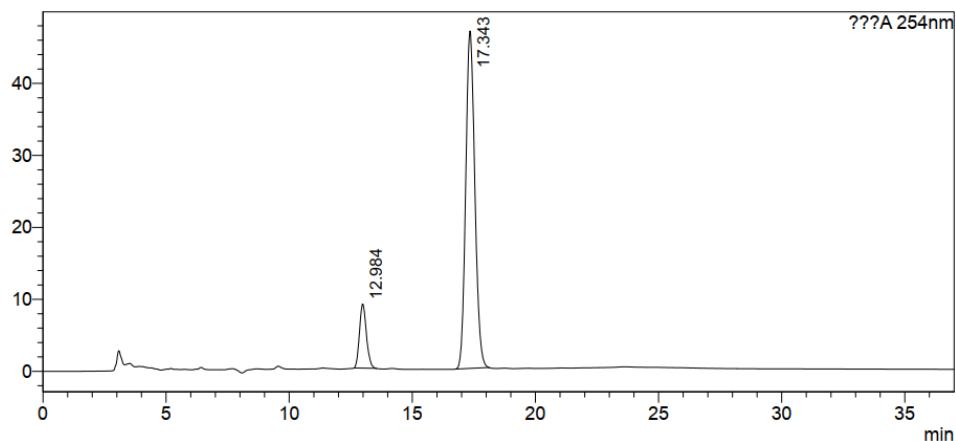


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	12.770	50.050	55.928
2	16.841	49.950	44.072
Total		100.000	100.000

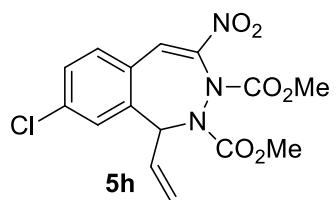
mV



**<Peak Table>**

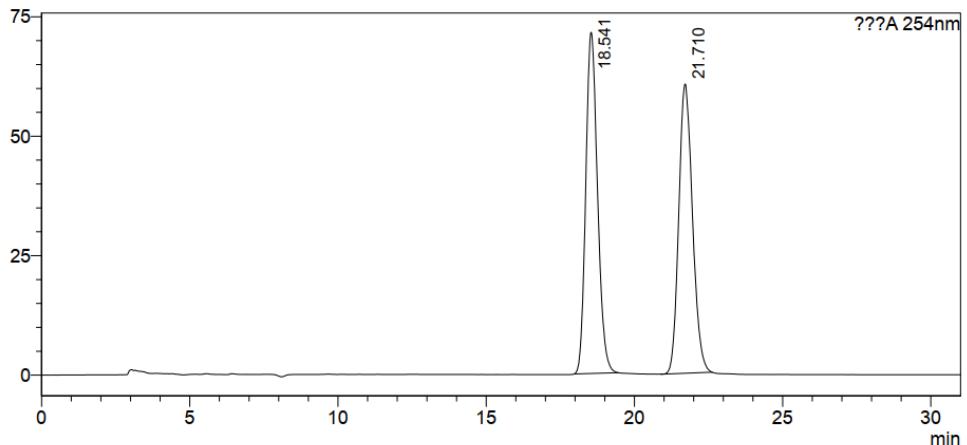
???A 254nm

Peak#	Ret. Time	Area%	Height%
1	12.984	12.635	15.952
2	17.343	87.365	84.048
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 90:10 er.

mV

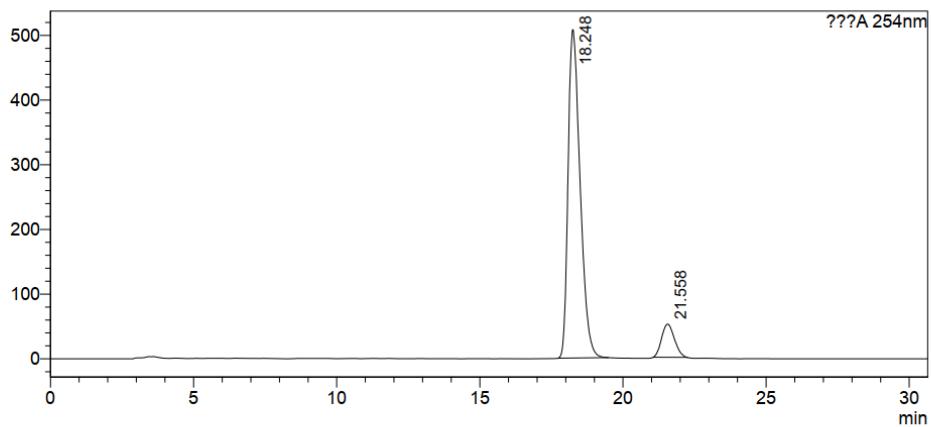


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	18.541	50.165	54.118
2	21.710	49.835	45.882
Total		100.000	100.000

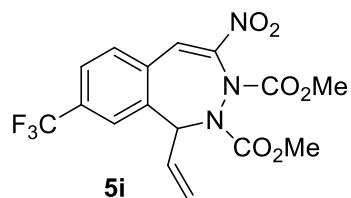
mV



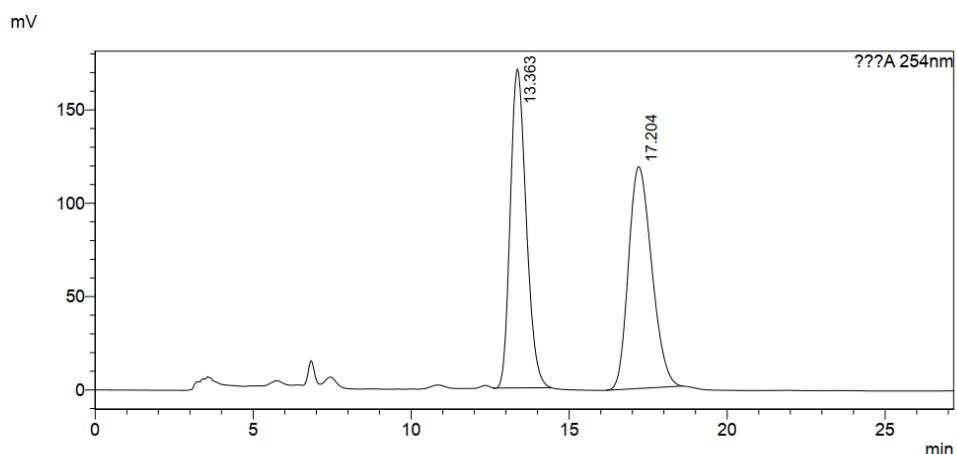
**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	18.248	90.292	90.814
2	21.558	9.708	9.186
Total		100.000	100.000



AS-H column, 95 : 5 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 90:10 er.



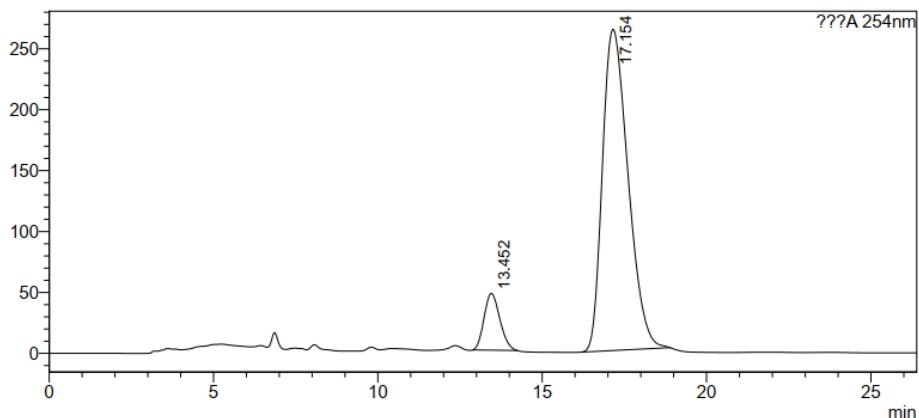
## <Peak Table>

?? A 254nm

Peak#	Ret. Time	Area%	Height%
1	13.363	49.579	58.972
2	17.204	50.421	41.028
Total		100.000	100.000

## <Chromatogram>

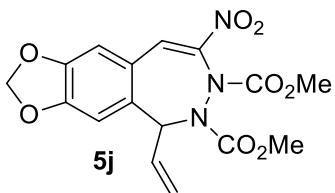
mV



## <Peak Table>

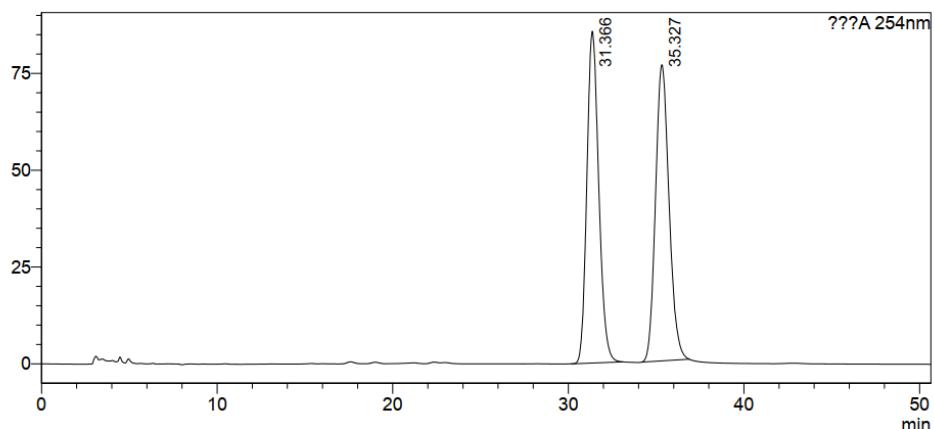
???

Peak#	Ret. Time	Area%	Height%
1	13.452	9.808	15.007
2	17.154	90.192	84.993
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 89:11 er.

mV

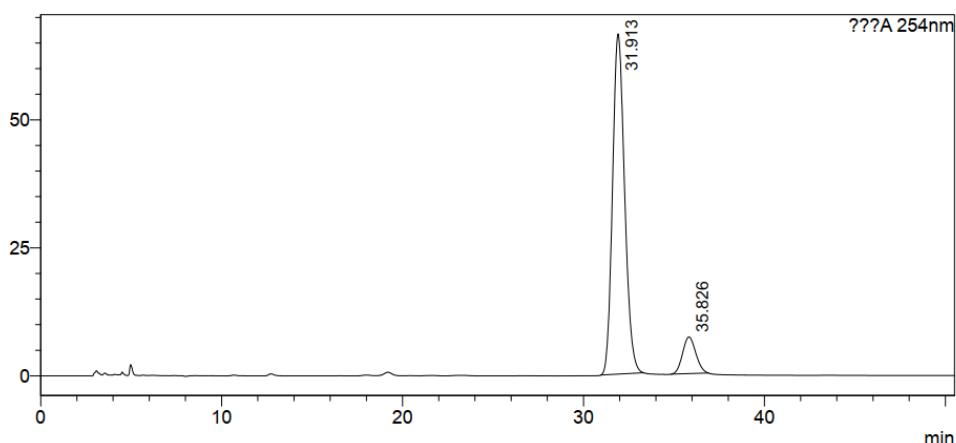


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	31.366	49.600	52.837
2	35.327	50.400	47.163
Total		100.000	100.000

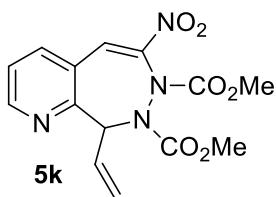
mV



**<Peak Table>**

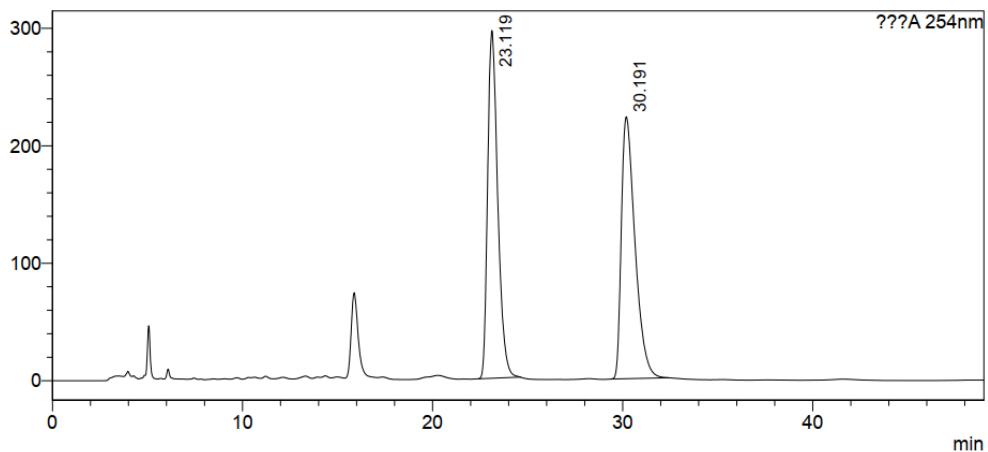
???A 254nm

Peak#	Ret. Time	Area%	Height%
1	31.913	89.468	90.278
2	35.826	10.532	9.722
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 77:23 er.

mV

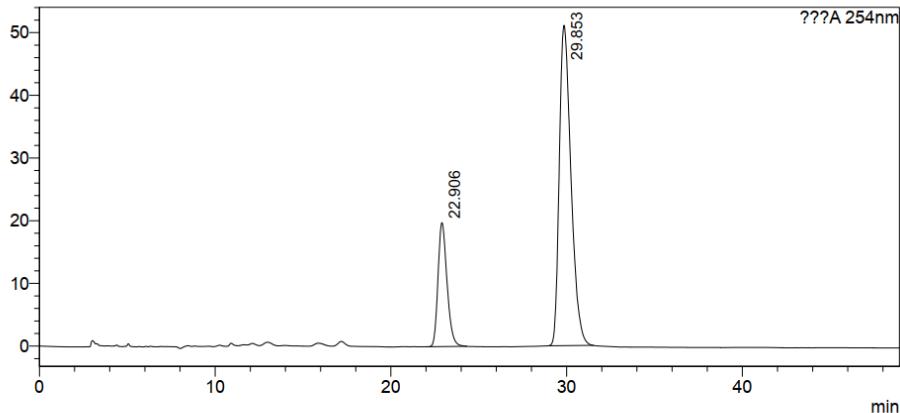


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	23.119	49.567	57.043
2	30.191	50.433	42.957
Total		100.000	100.000

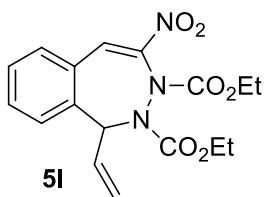
mV



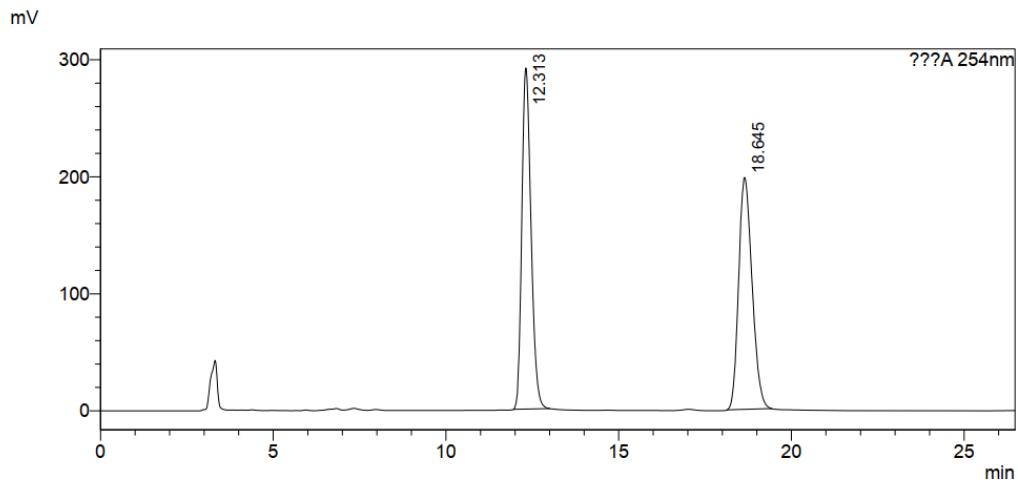
**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	22.906	22.988	27.895
2	29.853	77.012	72.105
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 86:14 er.

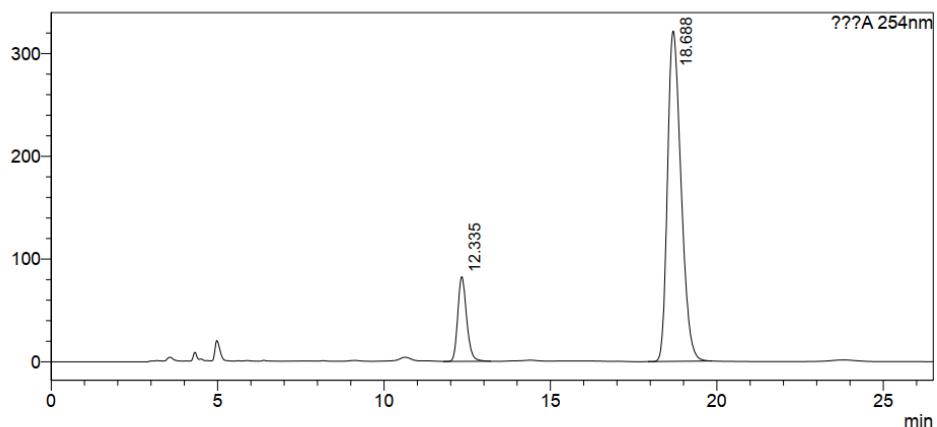


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	12.313	50.226	59.523
2	18.645	49.774	40.477
Total		100.000	100.000

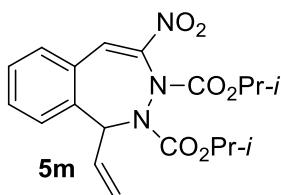
mV



**<Peak Table>**

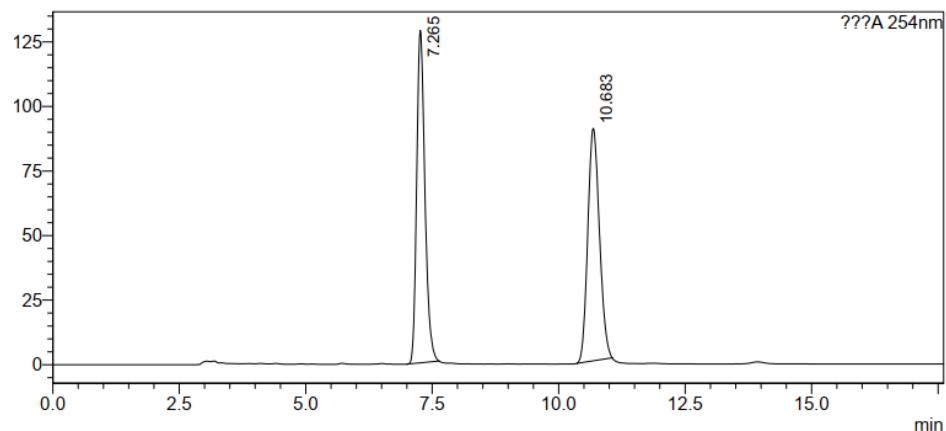
???A 254nm

Peak#	Ret. Time	Area%	Height%
1	12.335	14.389	20.394
2	18.688	85.611	79.606
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 78:22 er.

mV

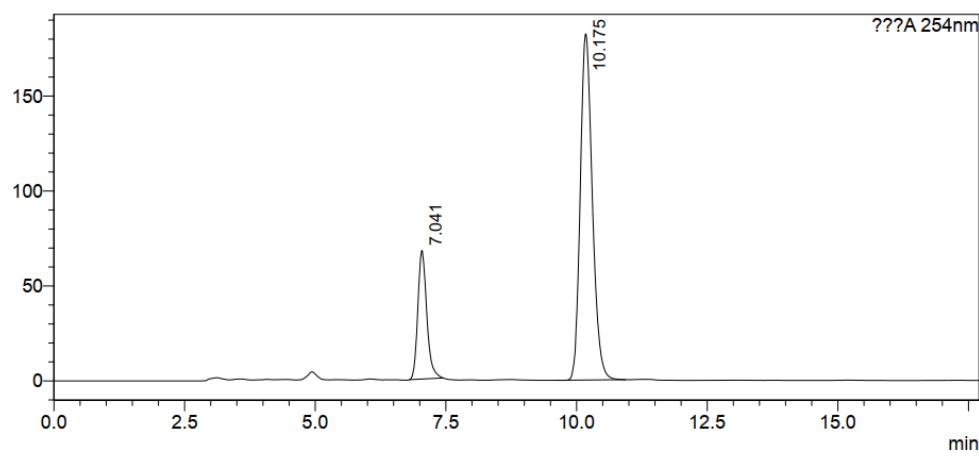


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	7.265	50.126	58.837
2	10.683	49.874	41.163
Total		100.000	100.000

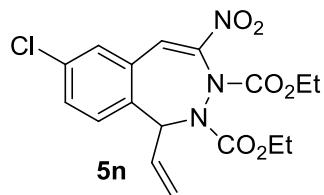
mV



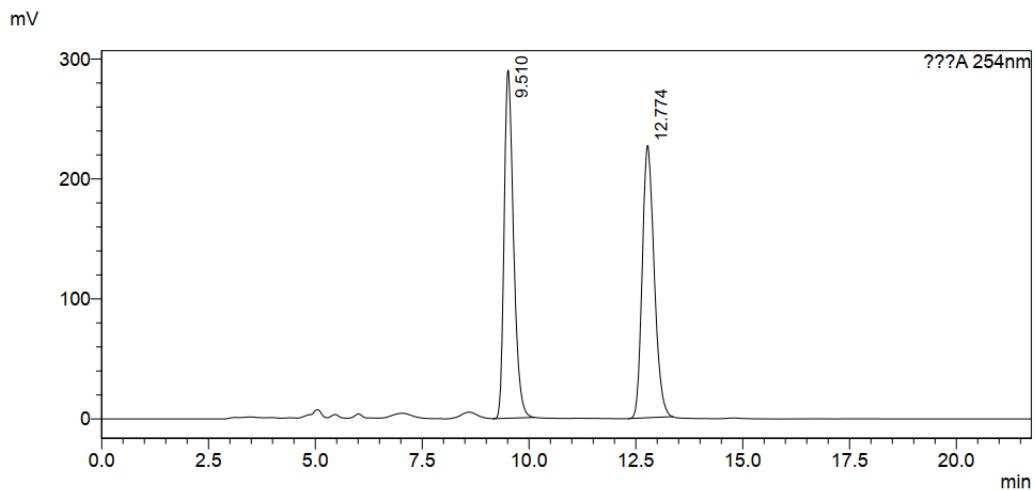
**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	7.041	21.534	27.065
2	10.175	78.466	72.935
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 88:12 er.

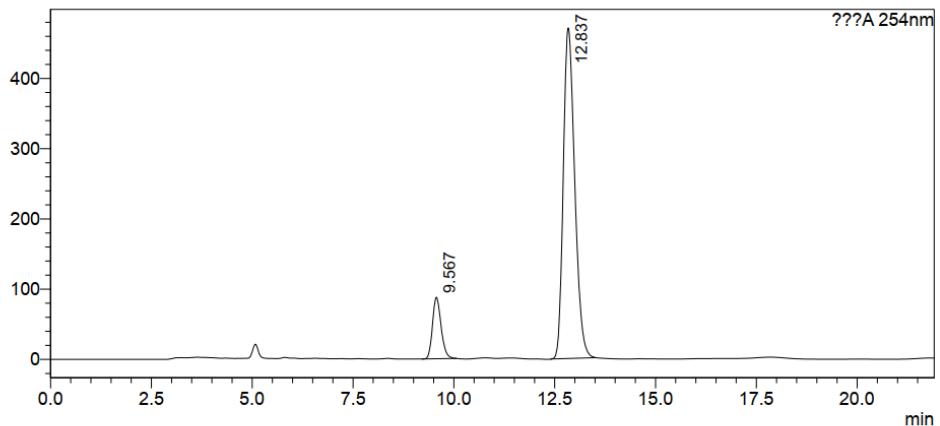


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	9.510	50.151	56.104
2	12.774	49.849	43.896
Total		100.000	100.000

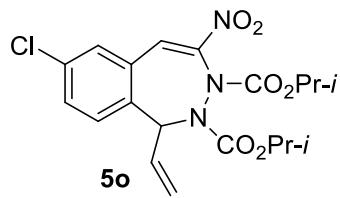
mV



**<Peak Table>**

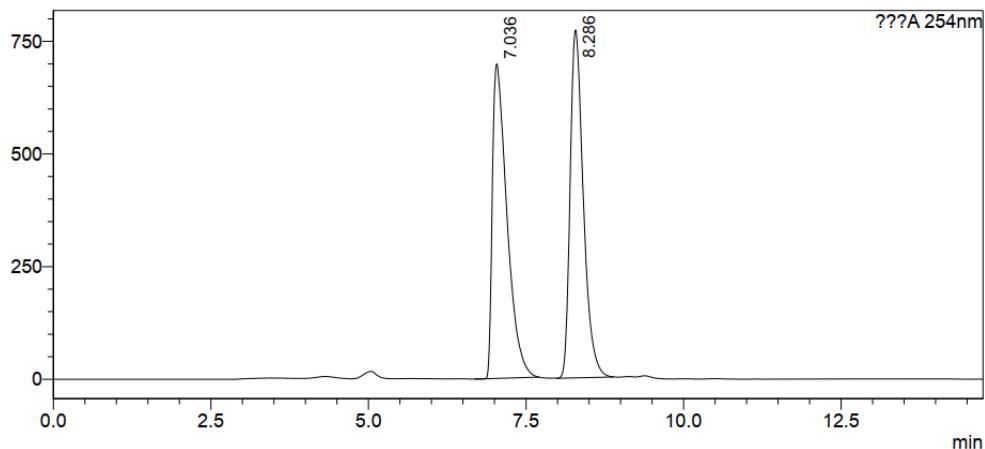
???A 254nm

Peak#	Ret. Time	Area%	Height%
1	9.567	12.262	15.682
2	12.837	87.738	84.318
Total		100.000	100.000



AD-H colum, 90 : 10 hexane : IPA, flow rate 1 mL/min, 254 nm, 25 °C, 85:15 er.

mV

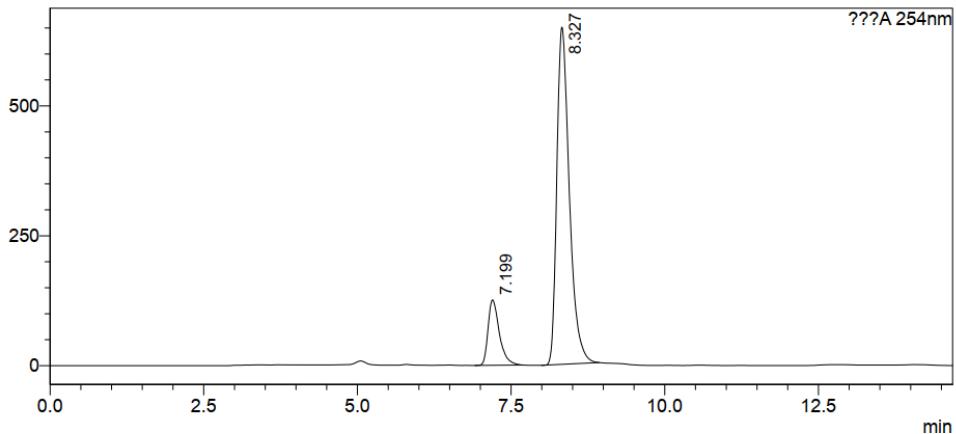


**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	7.036	50.000	47.479
2	8.286	50.000	52.521
Total		100.000	100.000

mV



**<Peak Table>**

???A 254nm

Peak#	Ret. Time	Area%	Height%
1	7.199	14.872	16.247
2	8.327	85.128	83.753
Total		100.000	100.000