Supporting Information

Journal of Organic Chemistry

Access to enantiopure α-hydrazino acids for *N*-amino peptide synthesis

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Department of Chemistry, University of South Florida

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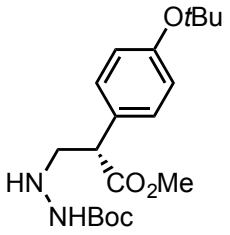
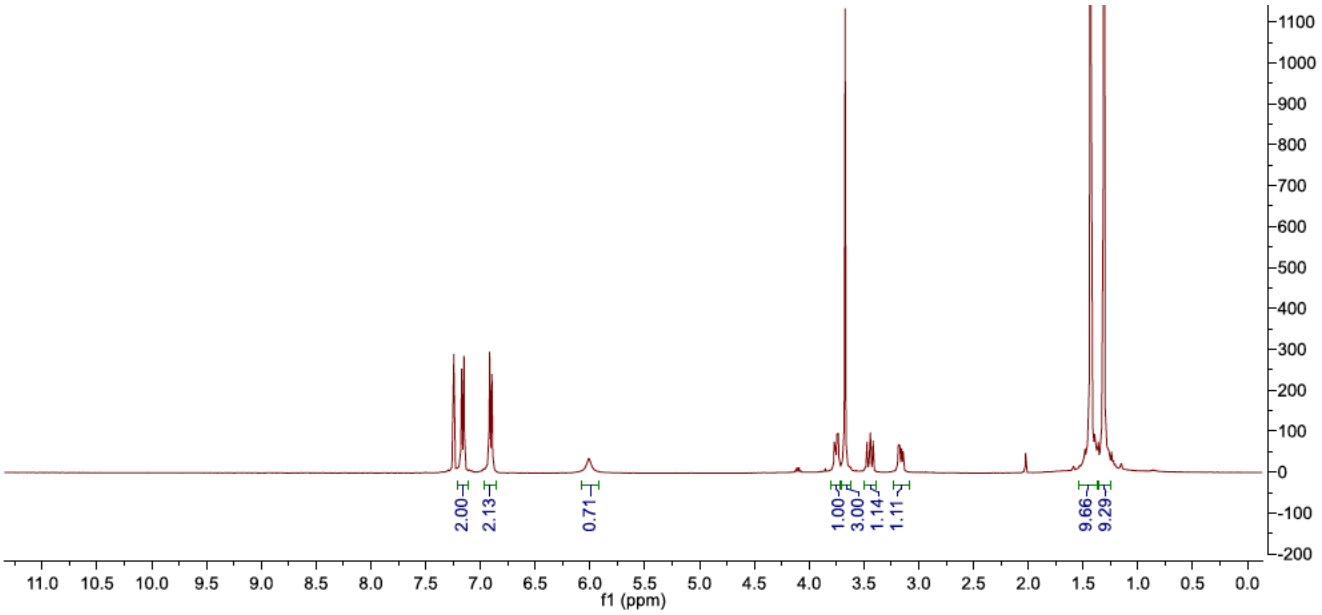
^{1}H AND ^{13}C NMR SPECTRA

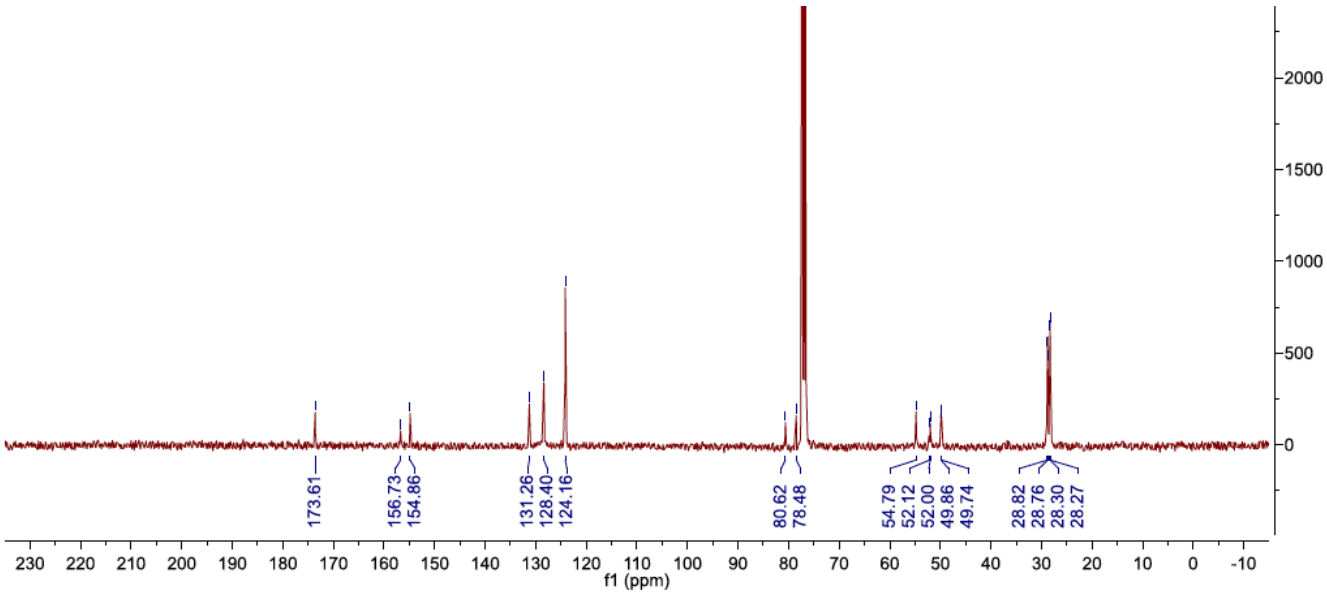


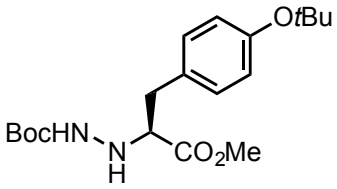
(2)

^{1}H NMR 400 MHz ($CDCl_3$)



^{13}C NMR 101 MHz ($CDCl_3$)





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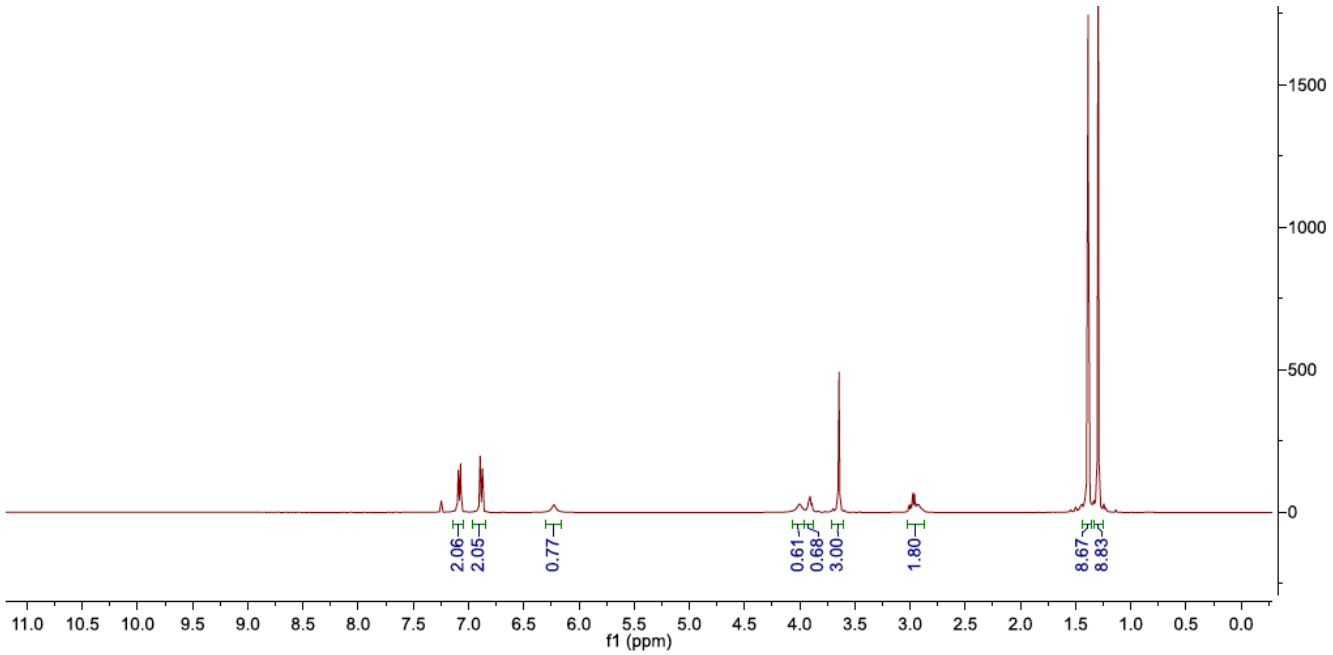
^{1}H NMR 400 MHz ($CDCl_3$)



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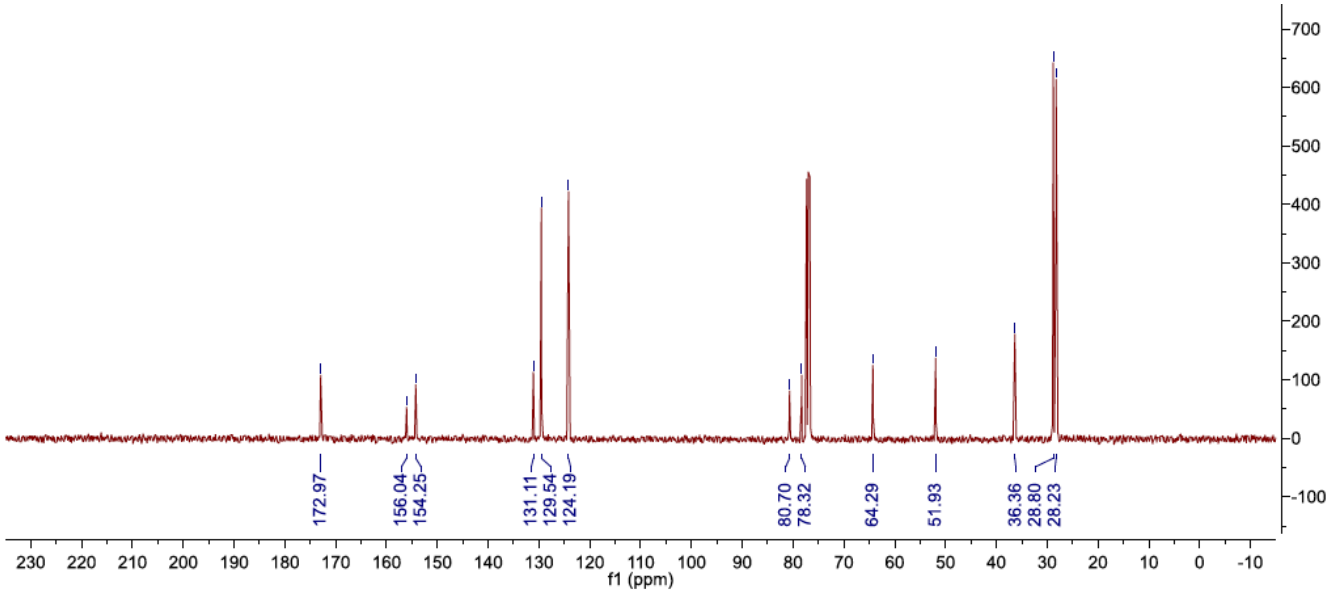

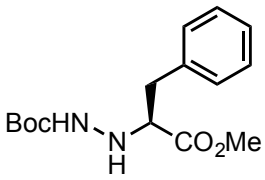

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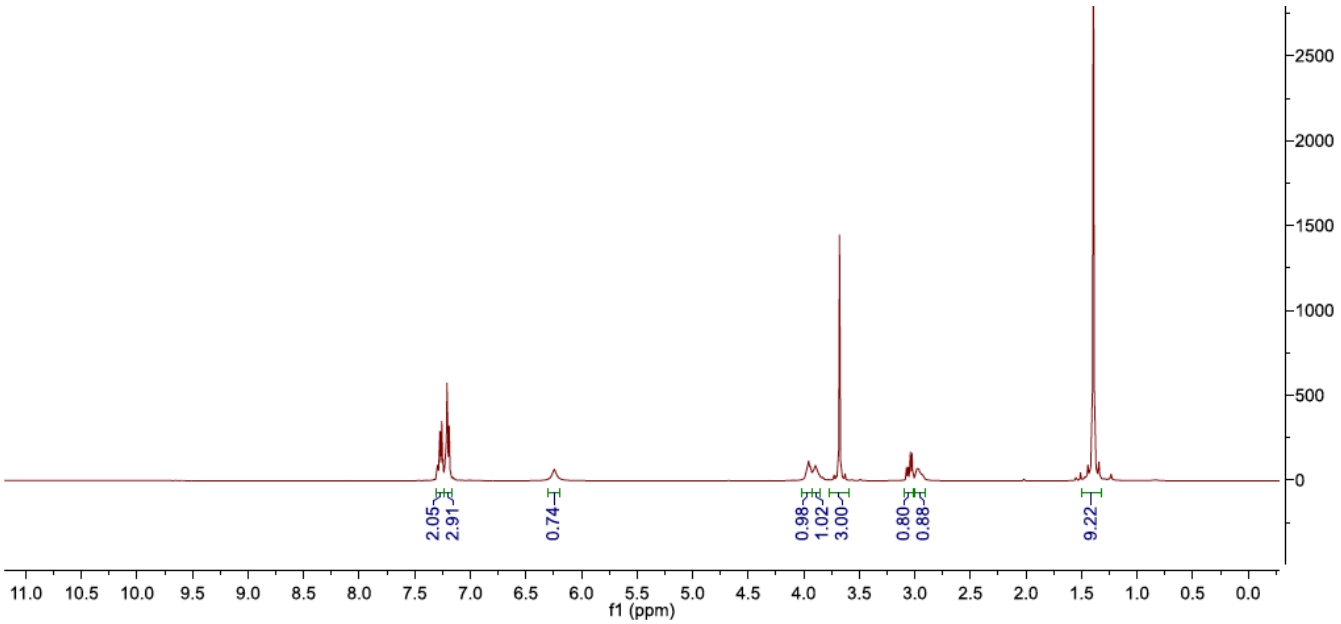

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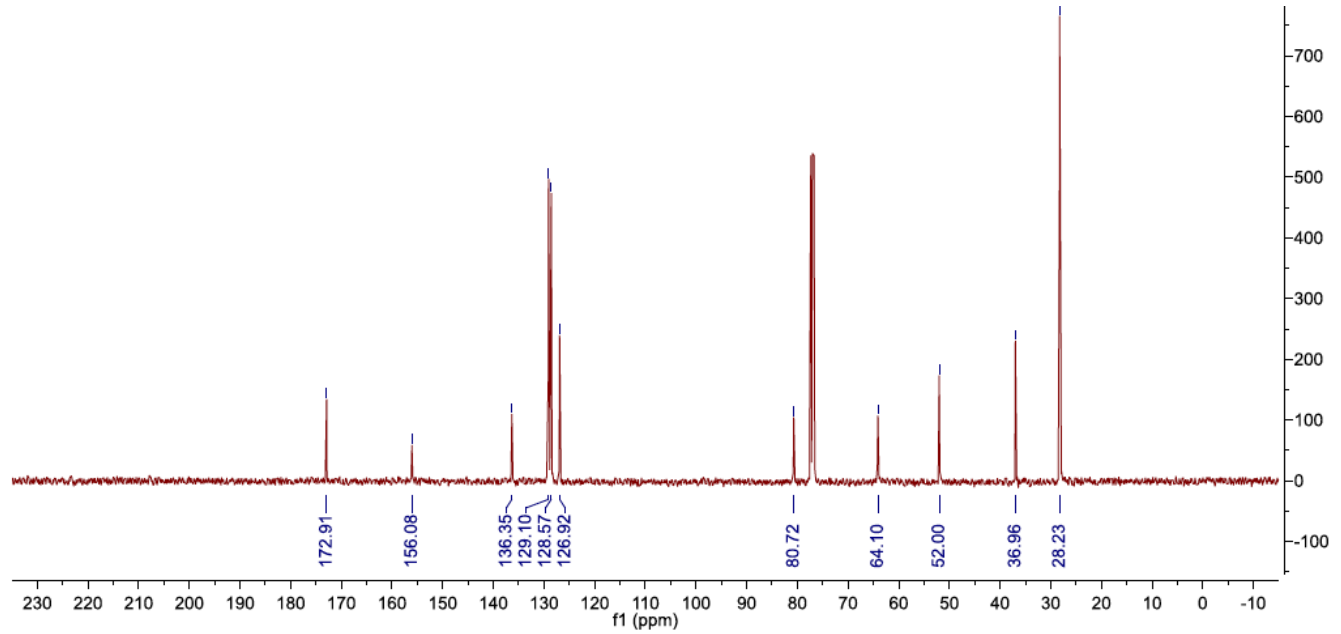

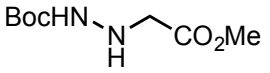

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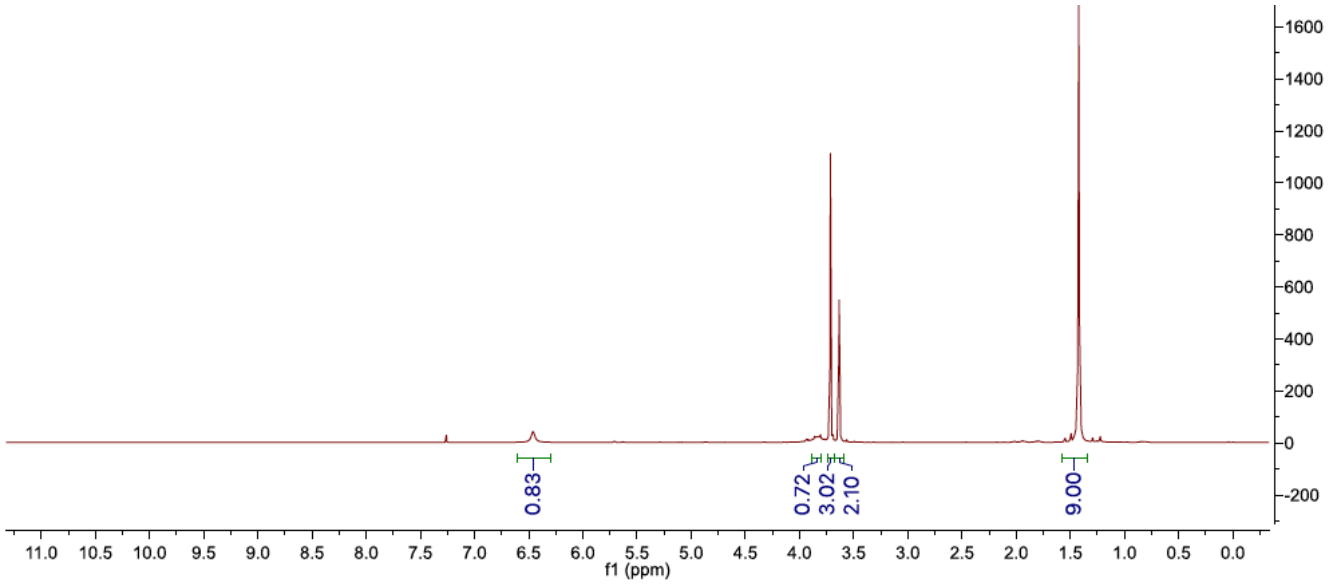
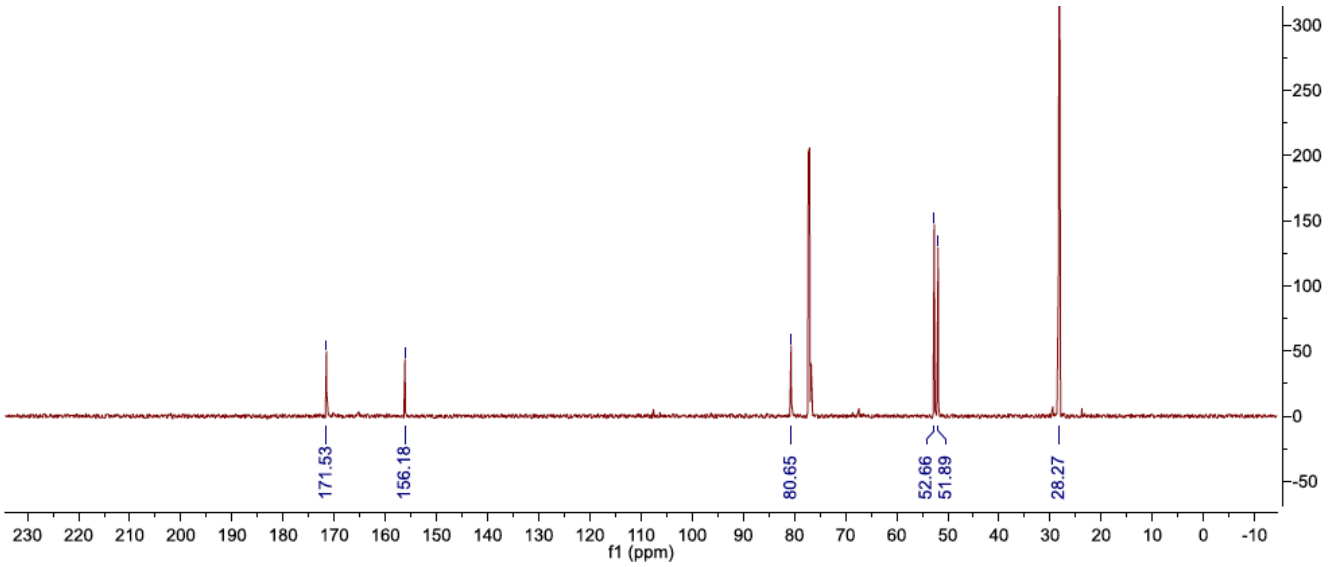
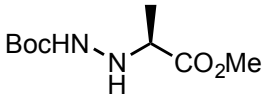


^{13}C NMR 126 MHz ($CDCl_3$)





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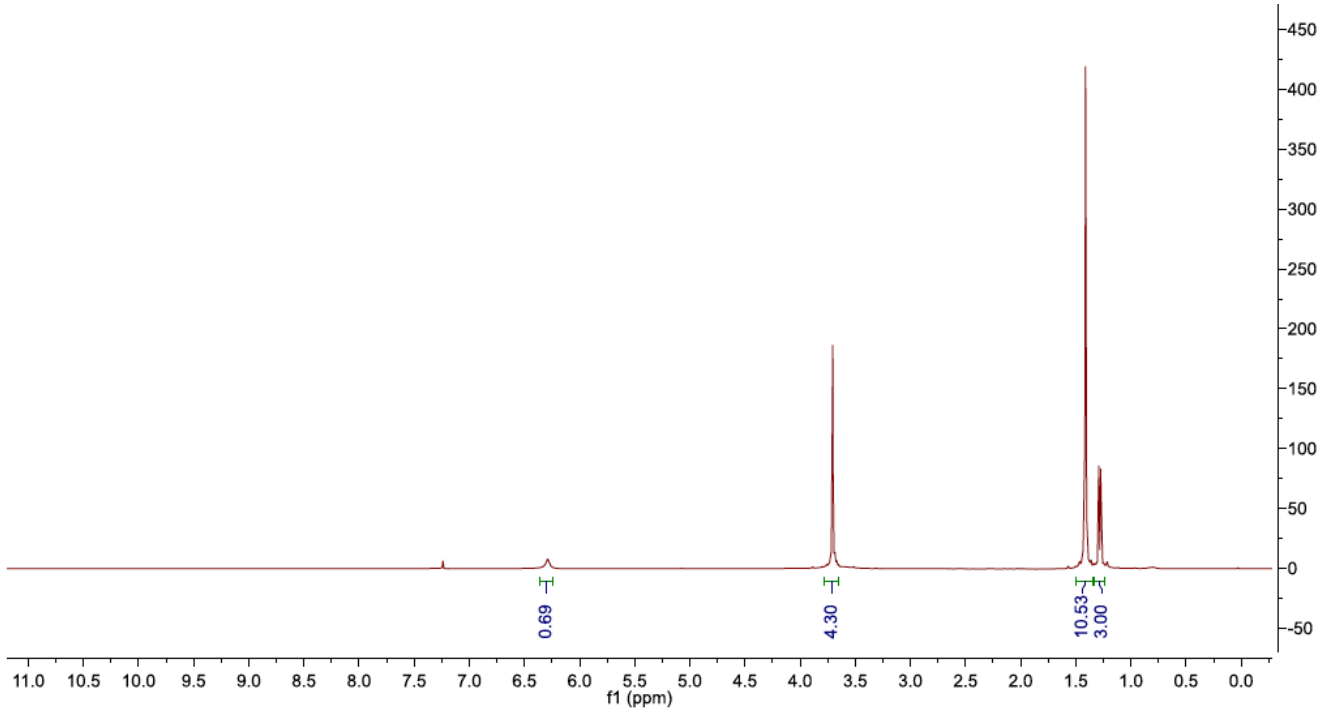

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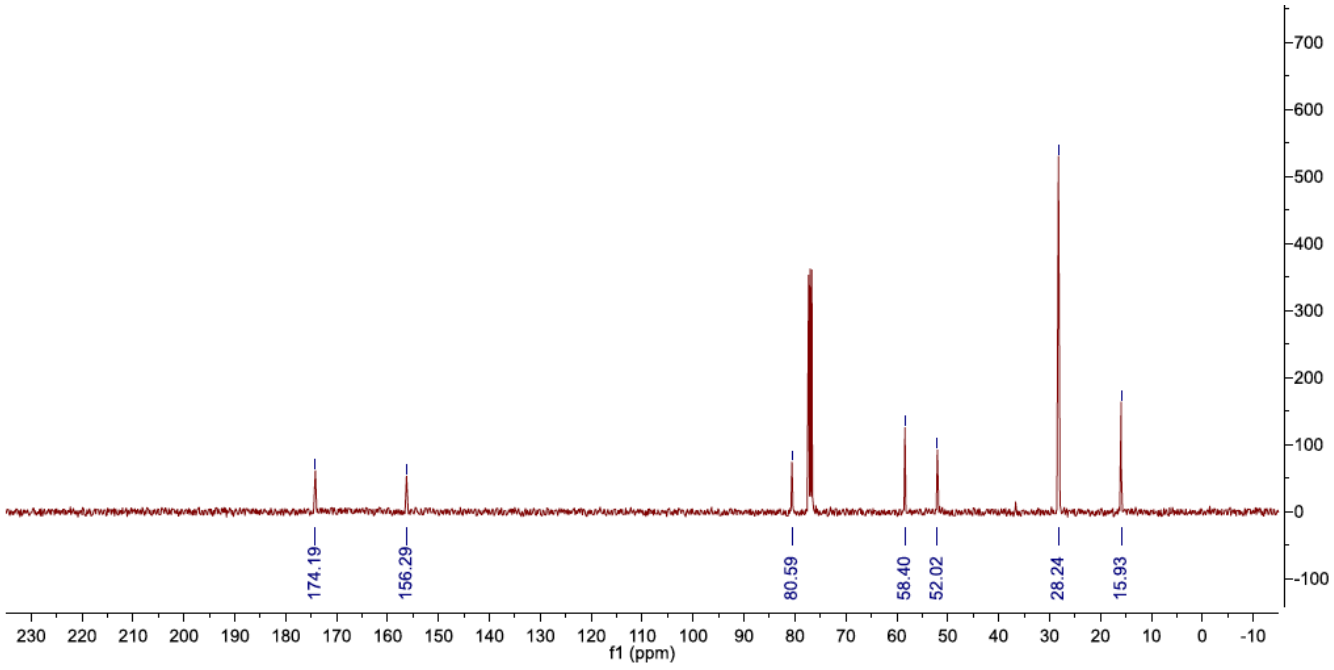

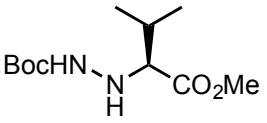

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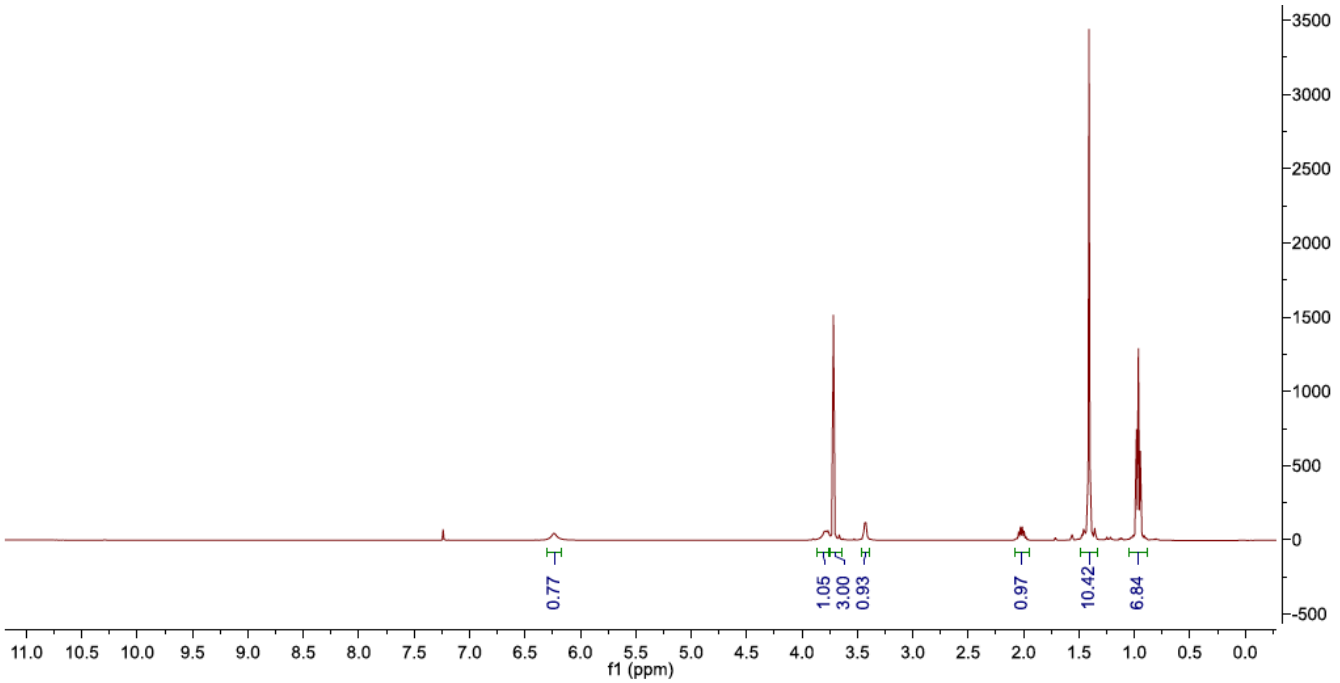

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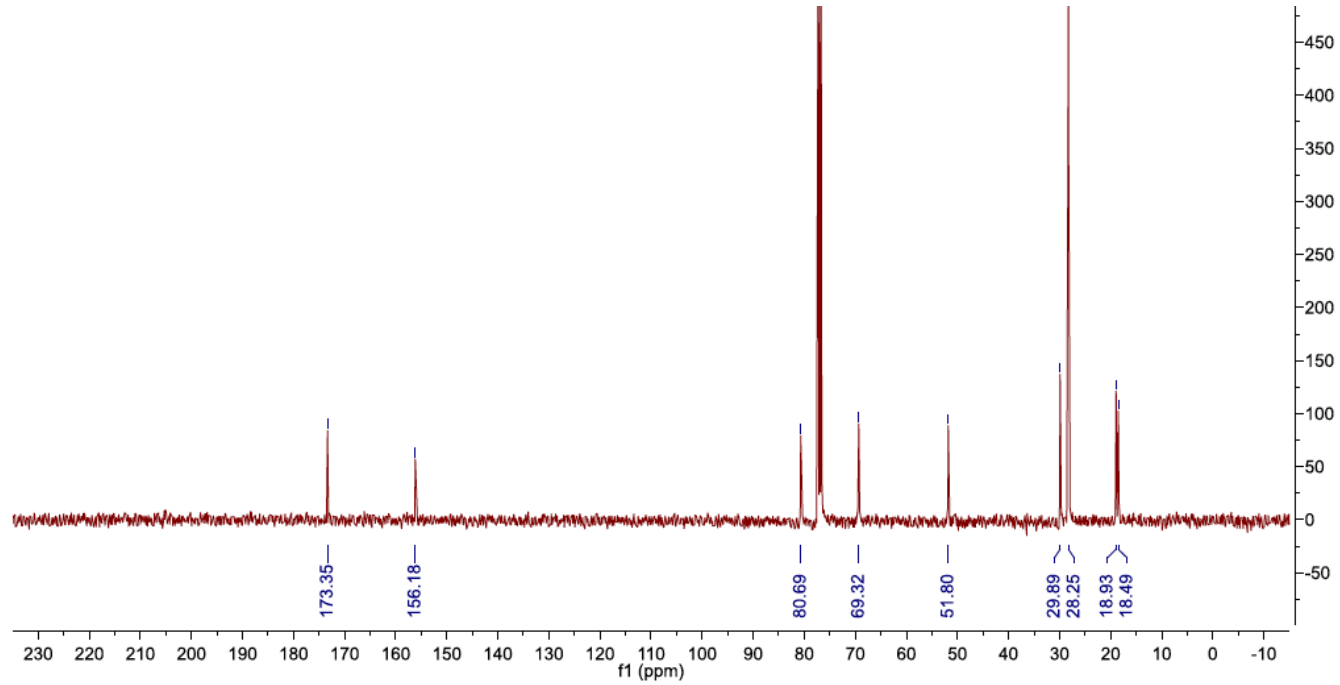

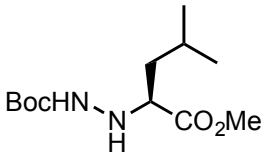

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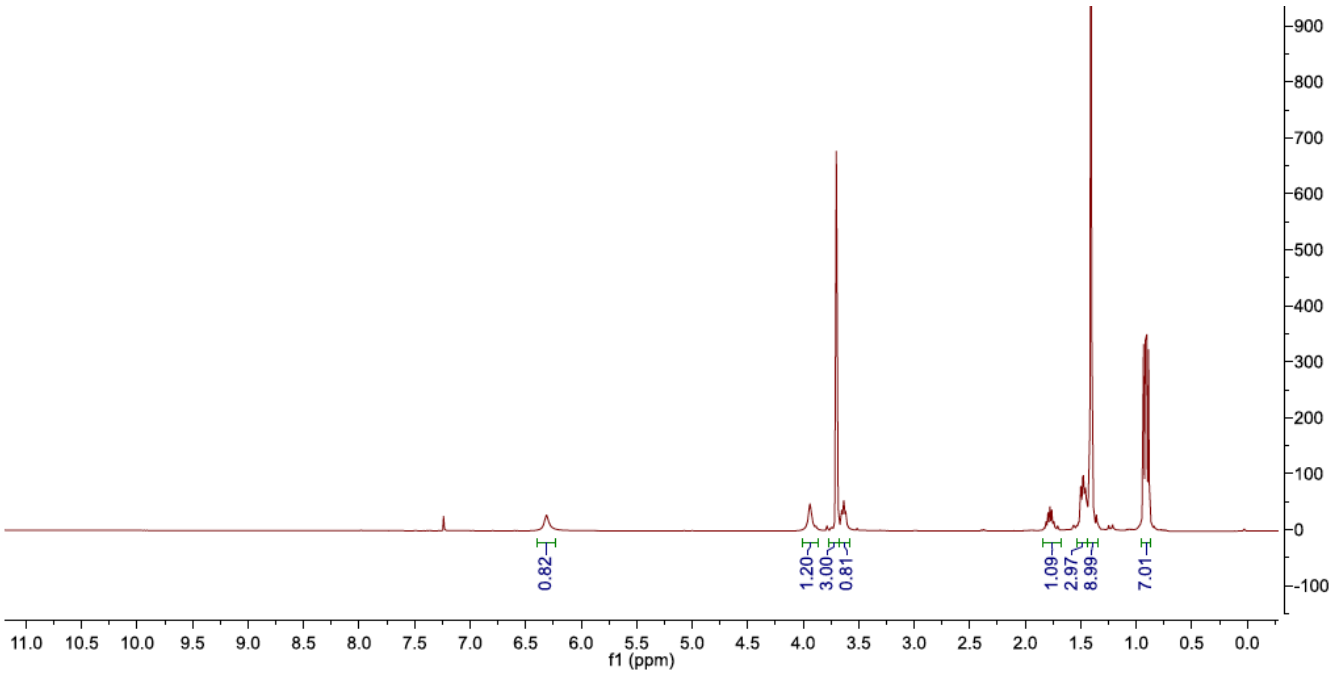

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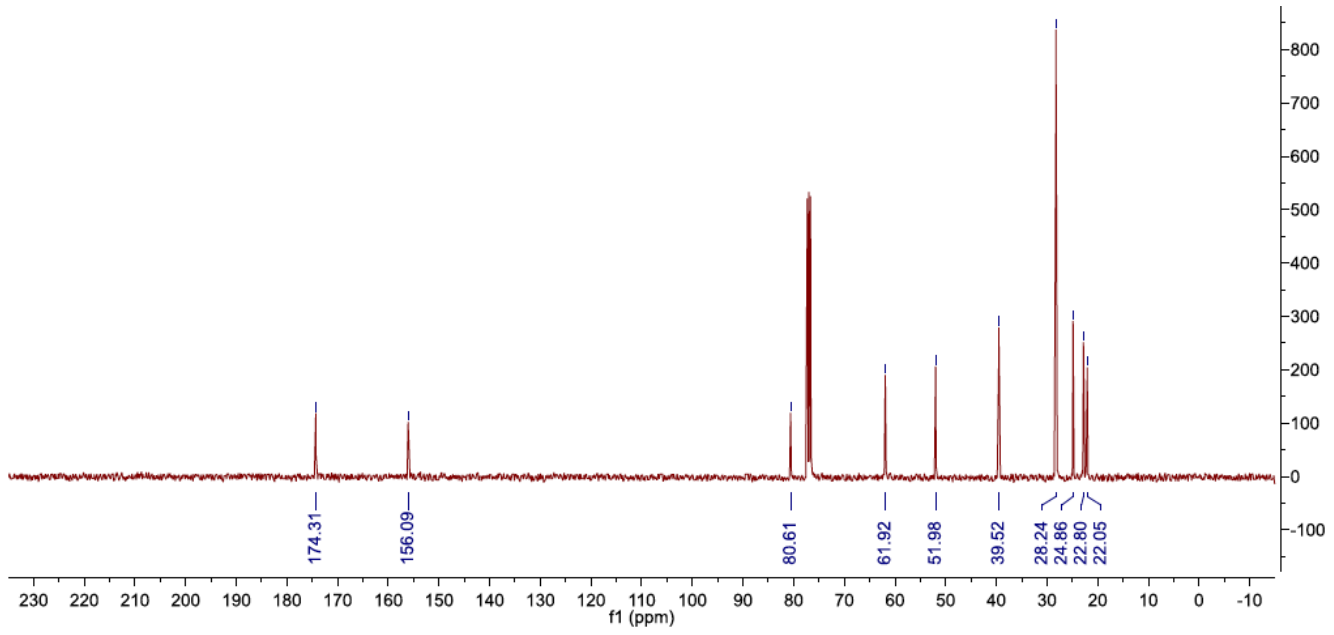

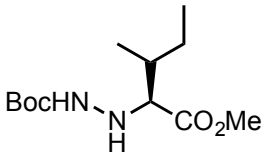

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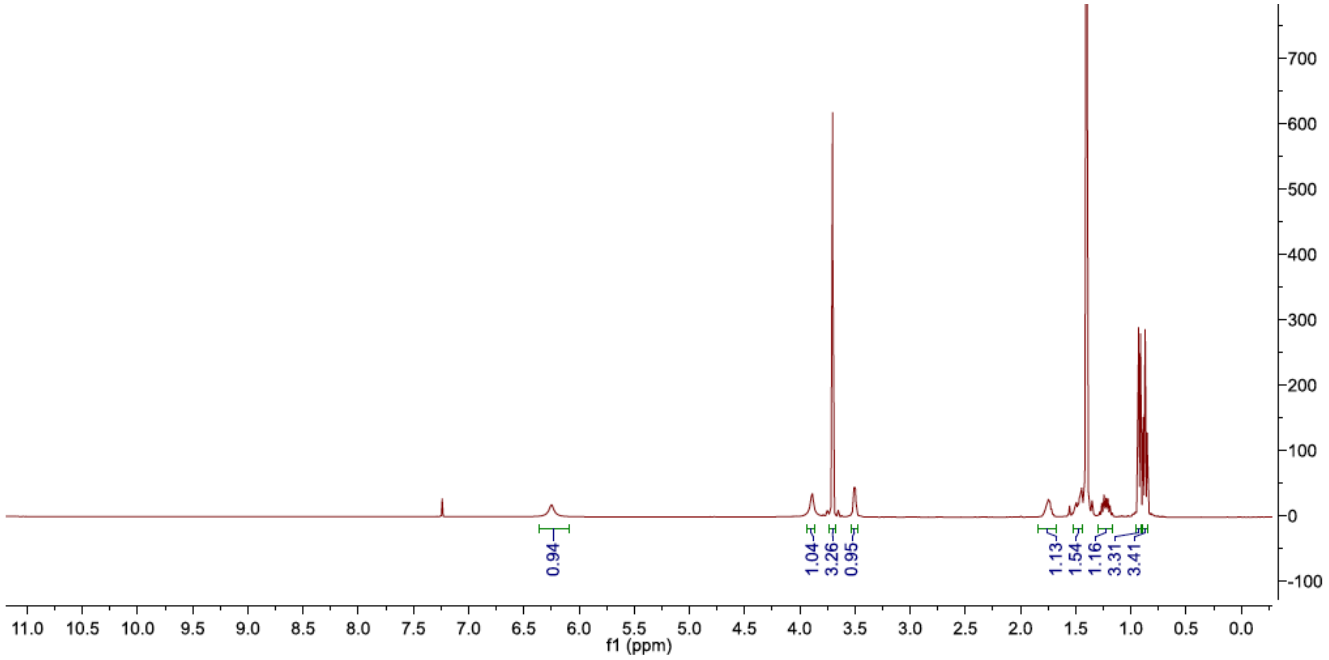

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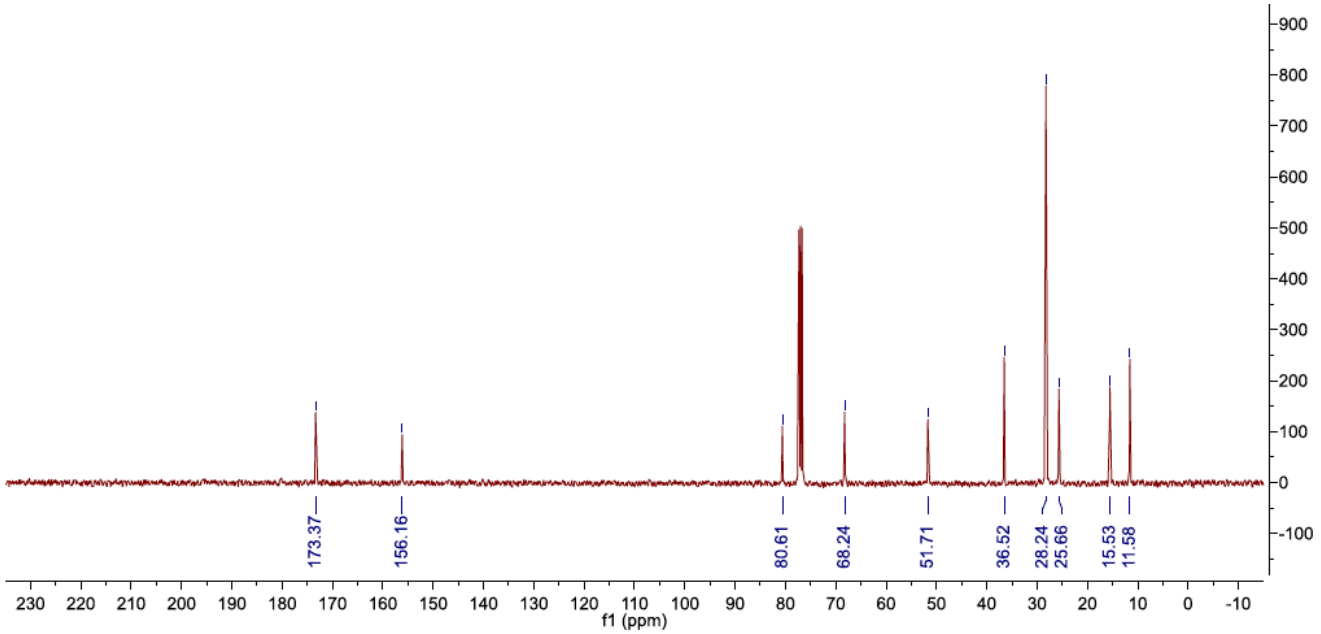

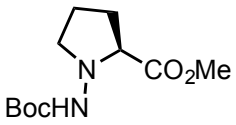

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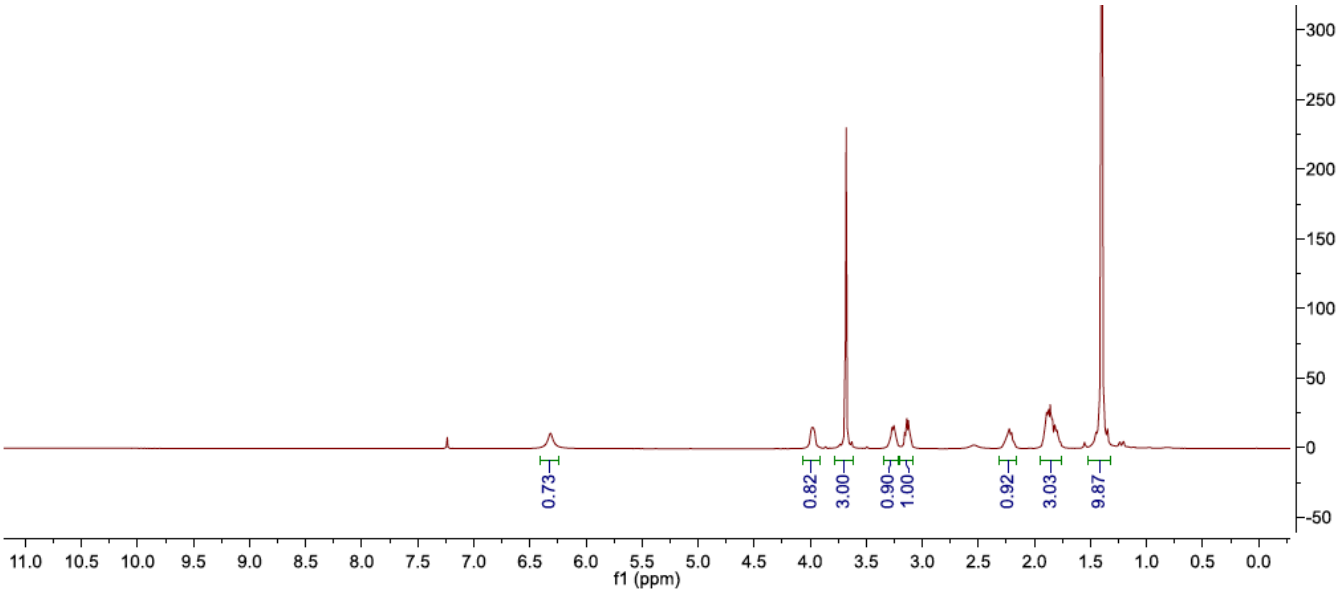

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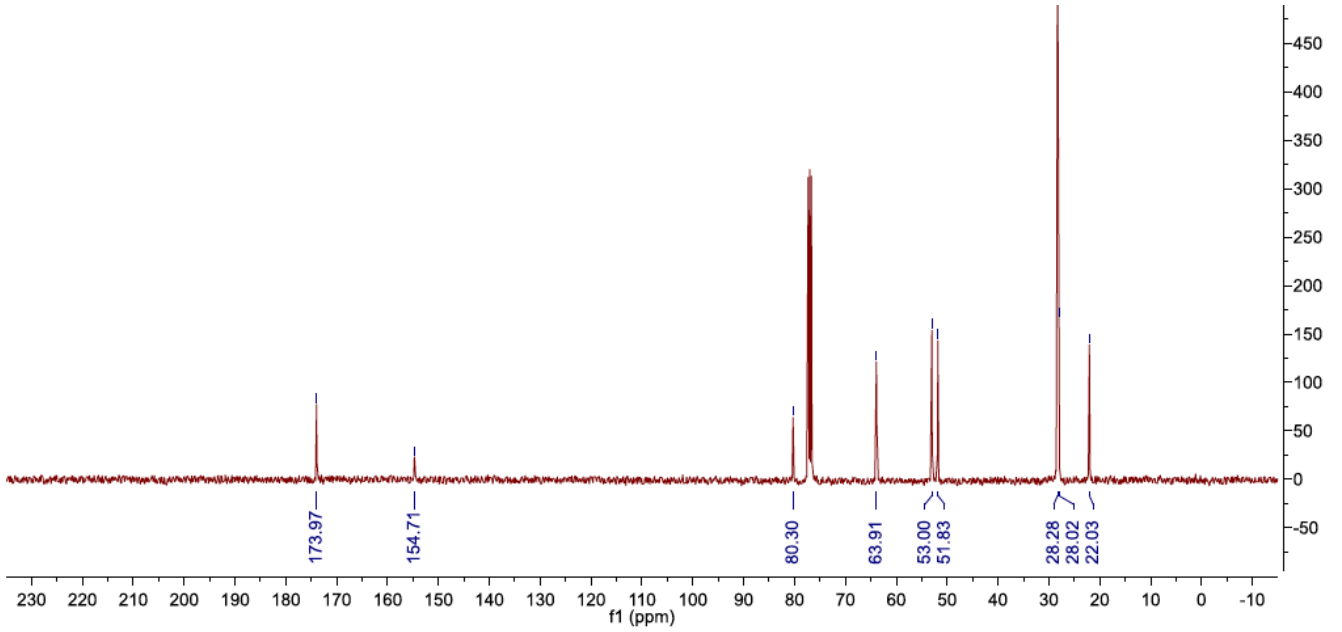

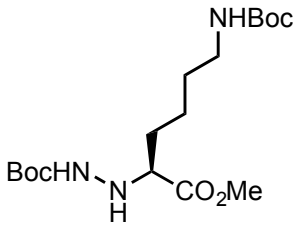

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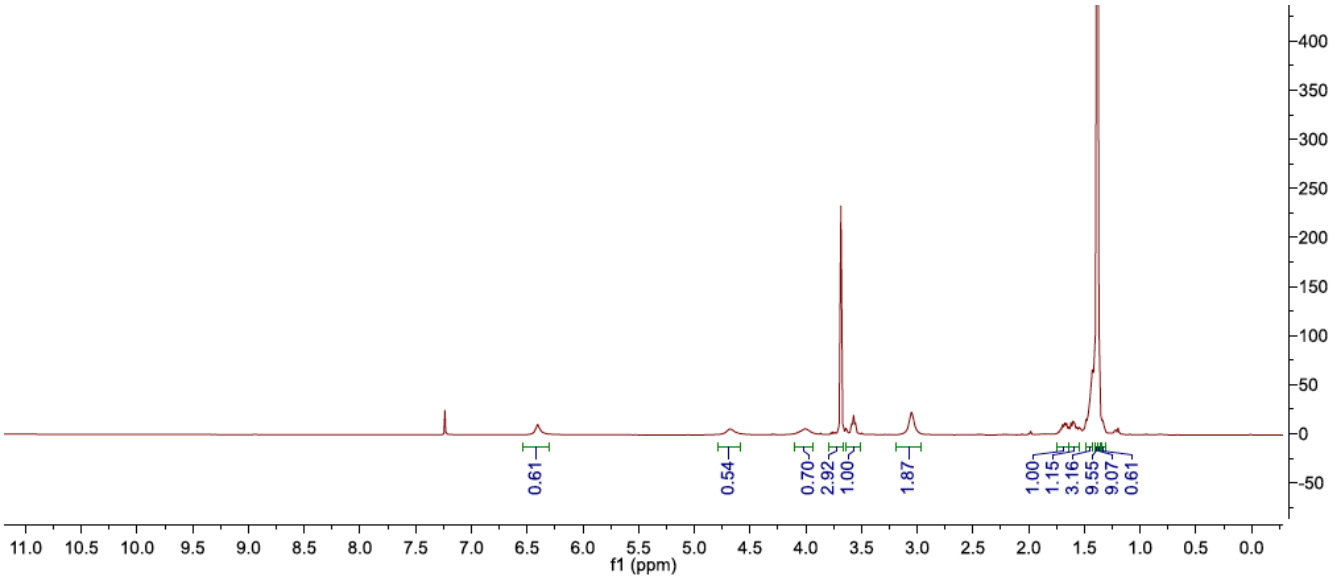
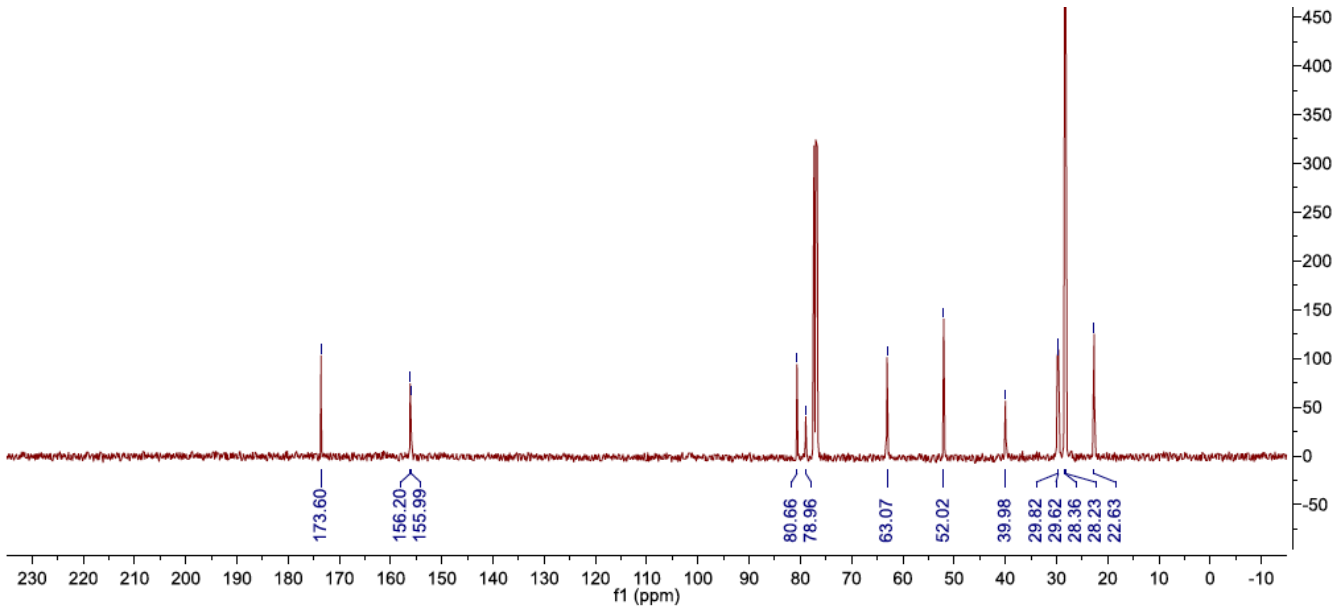
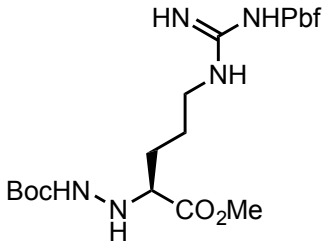
^{1}H NMR 400 MHz ($CDCl_3$)



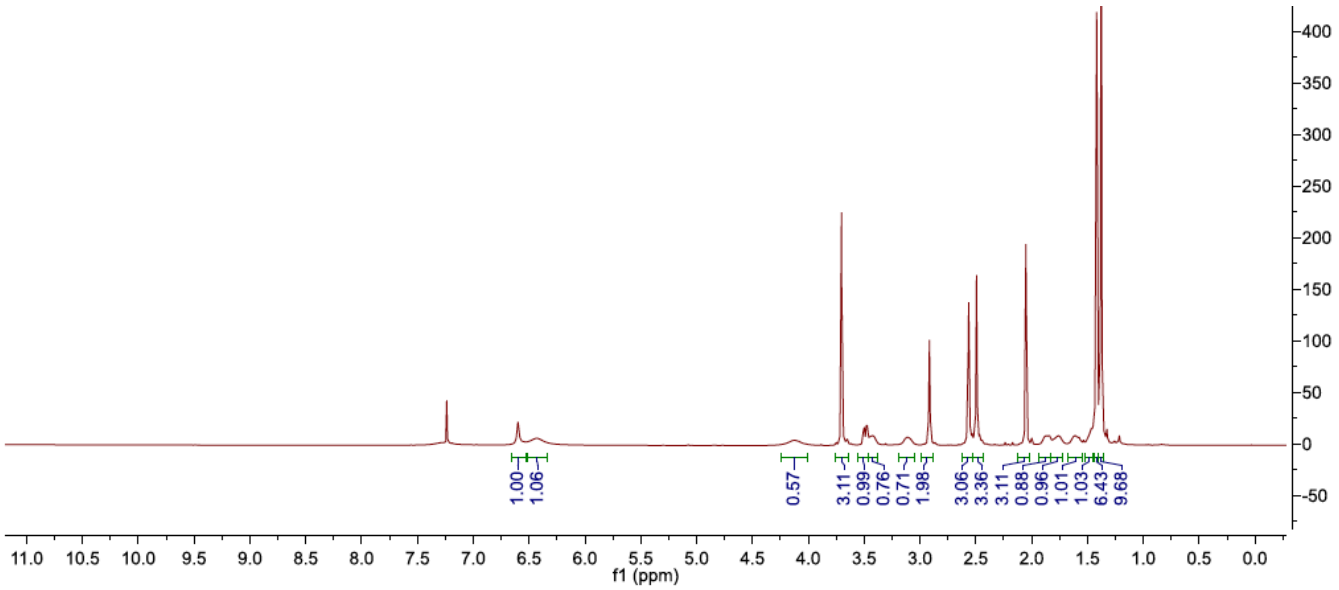
^{13}C NMR 101 MHz ($CDCl_3$)





(4j)

^{1}H NMR 400 MHz ($CDCl_3$)



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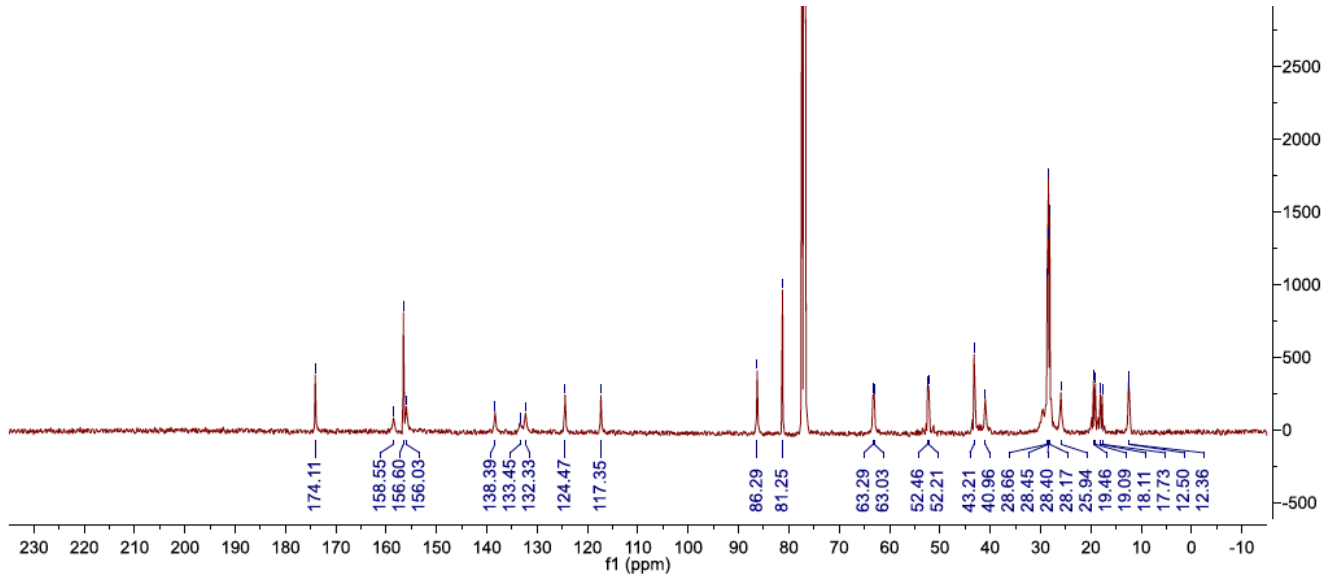

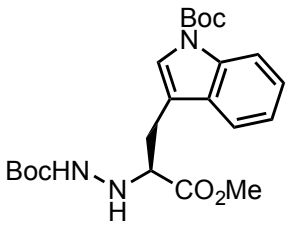

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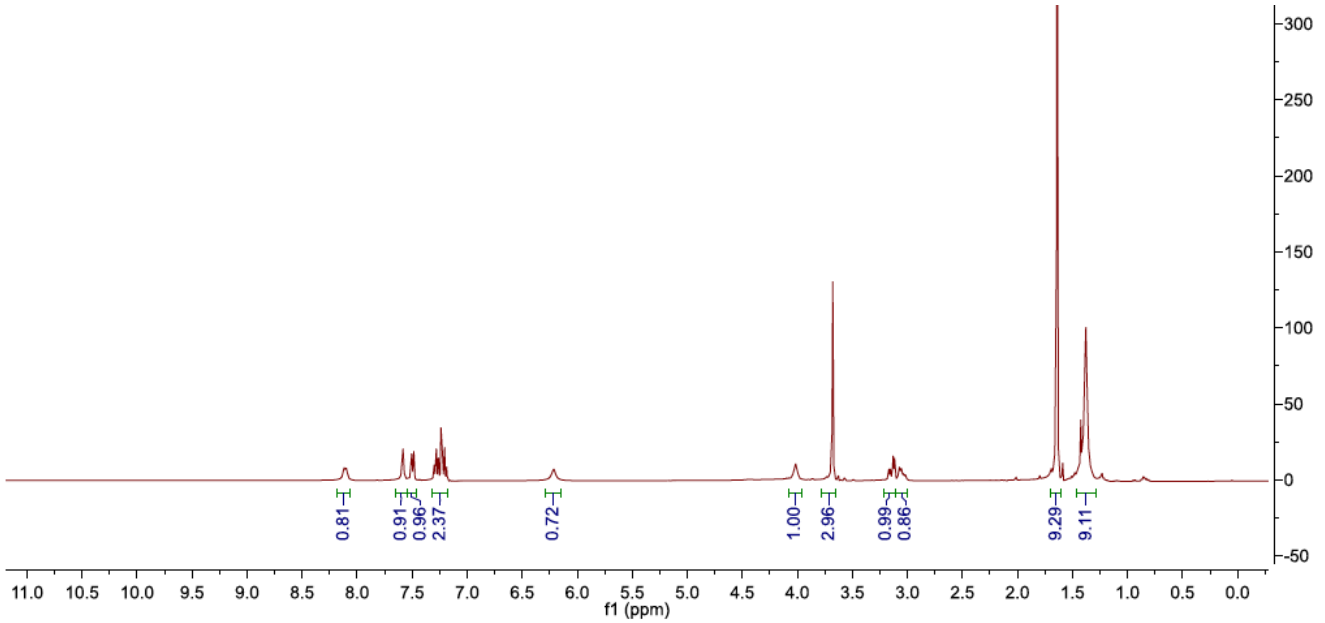
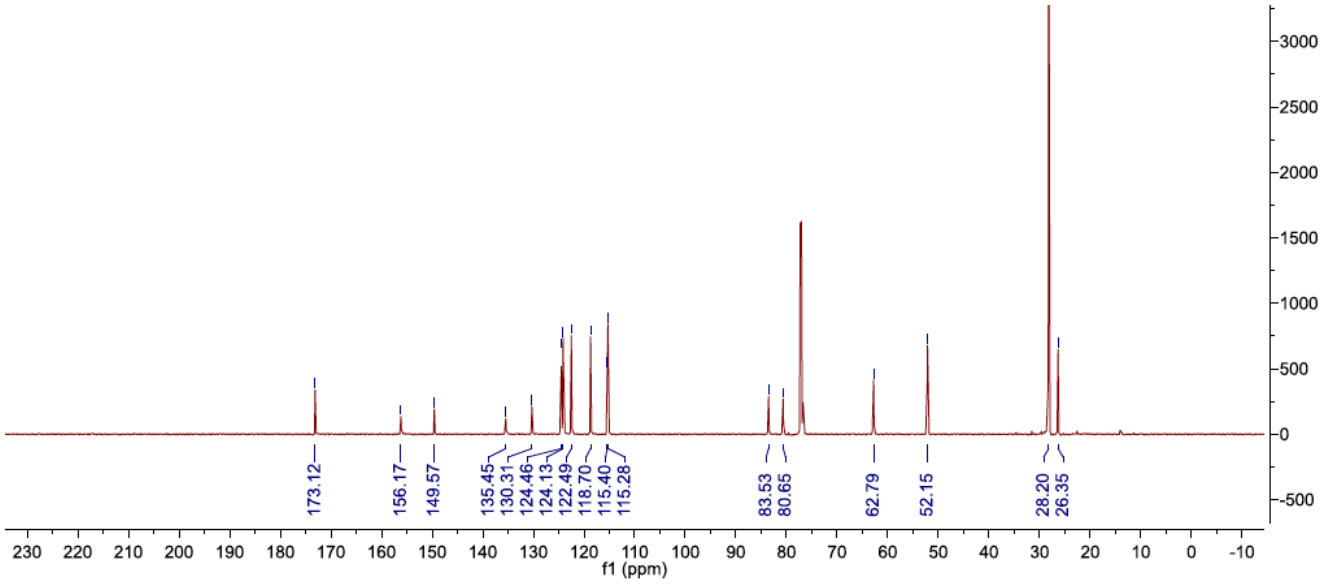
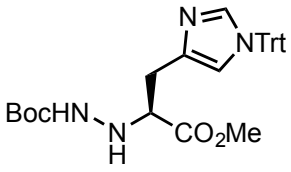


^{13}C NMR 126 MHz ($CDCl_3$)





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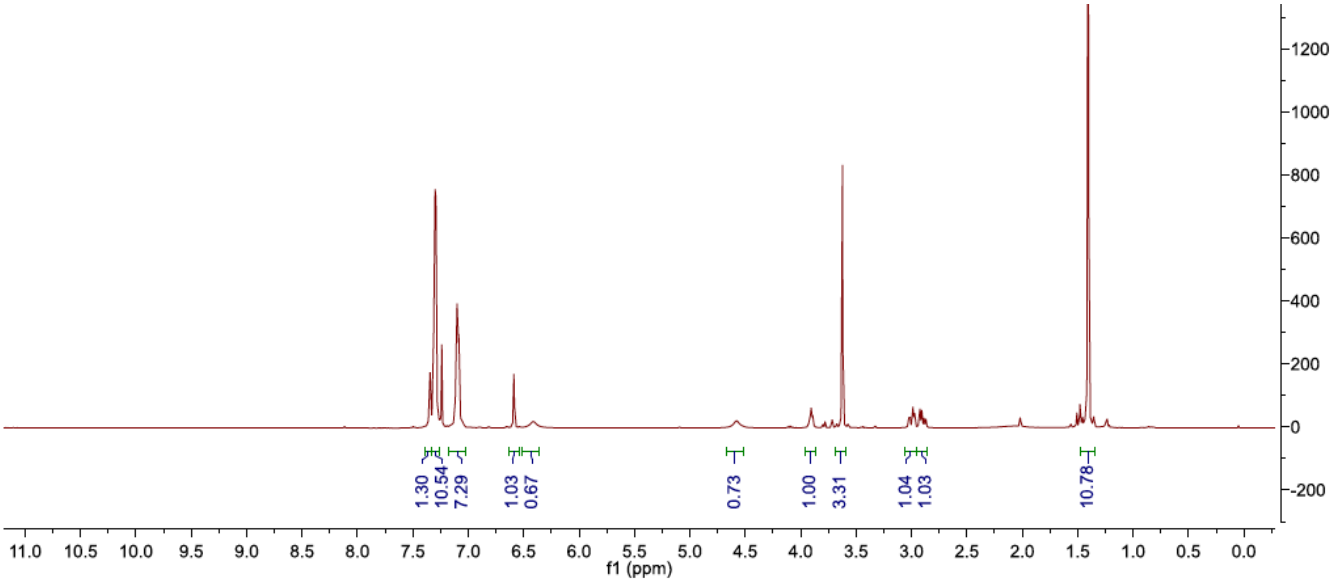
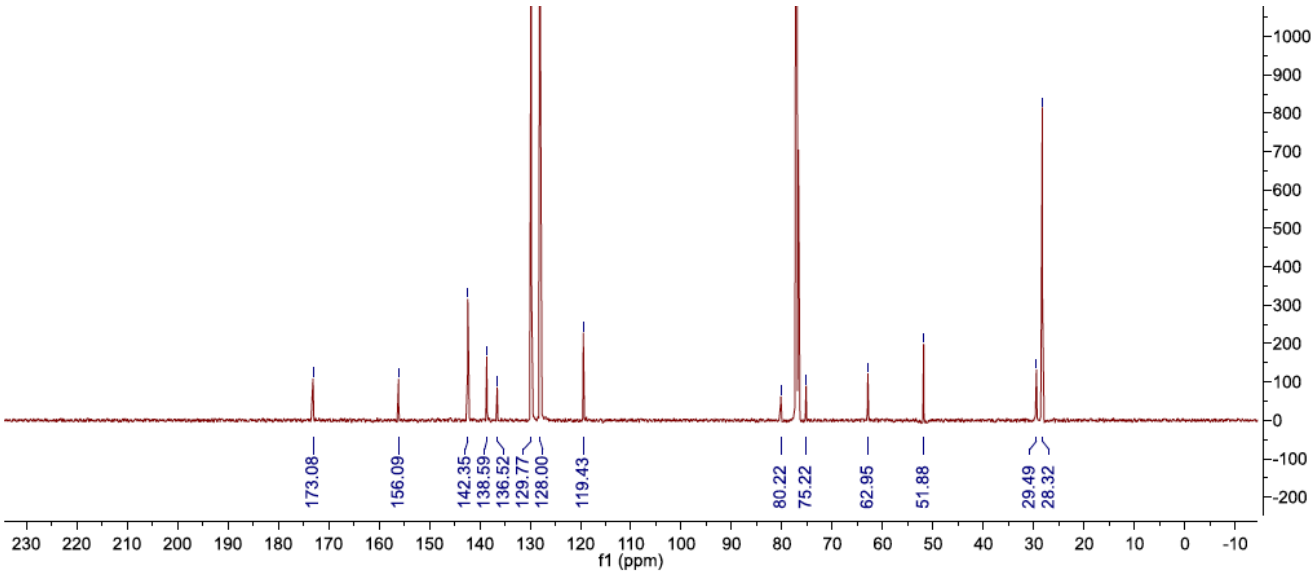
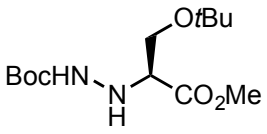
^{1}H NMR 400 MHz ($CDCl_3$)



^{13}C NMR 126 MHz ($CDCl_3$)





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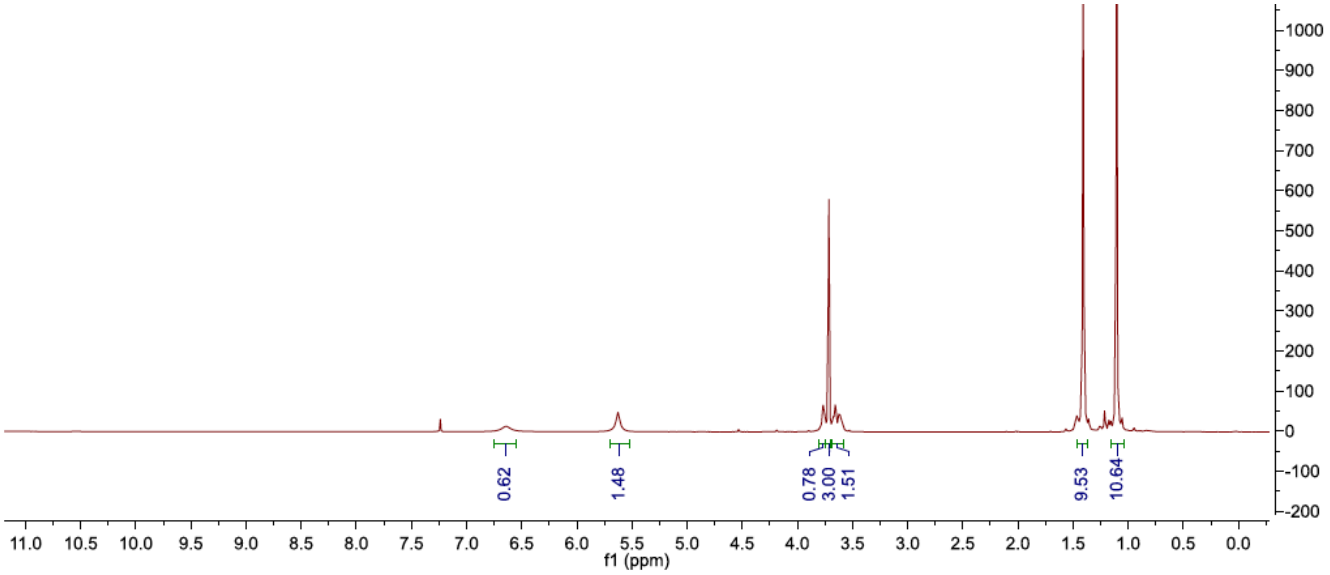

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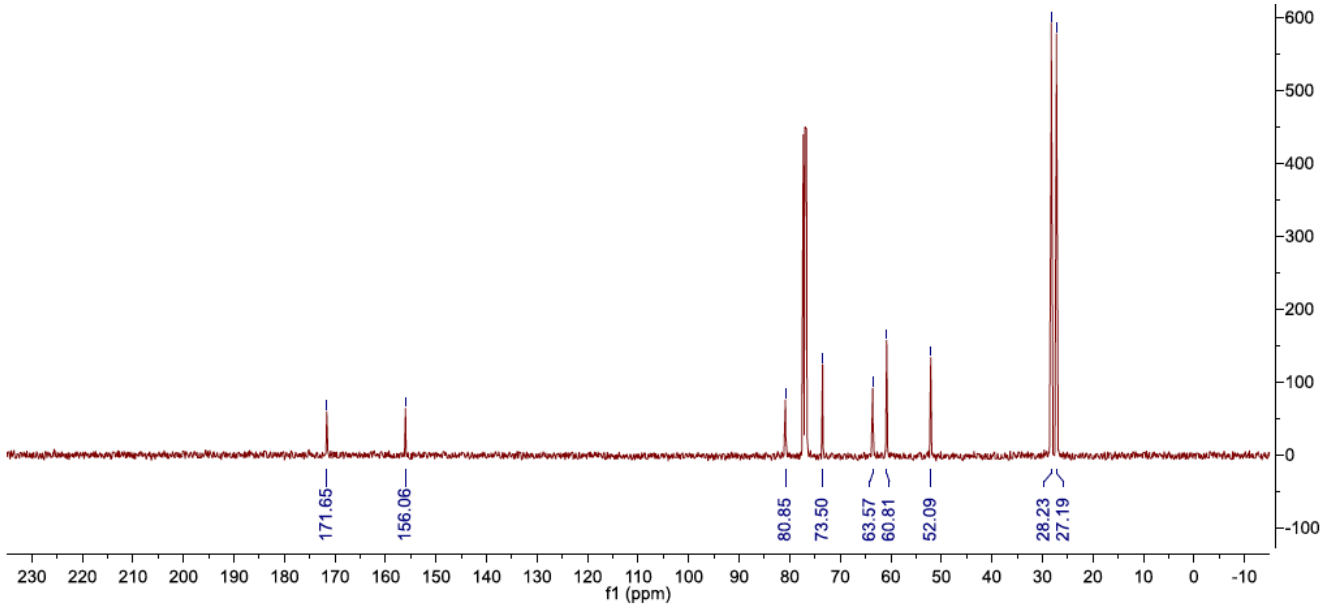

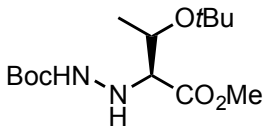

(4n)

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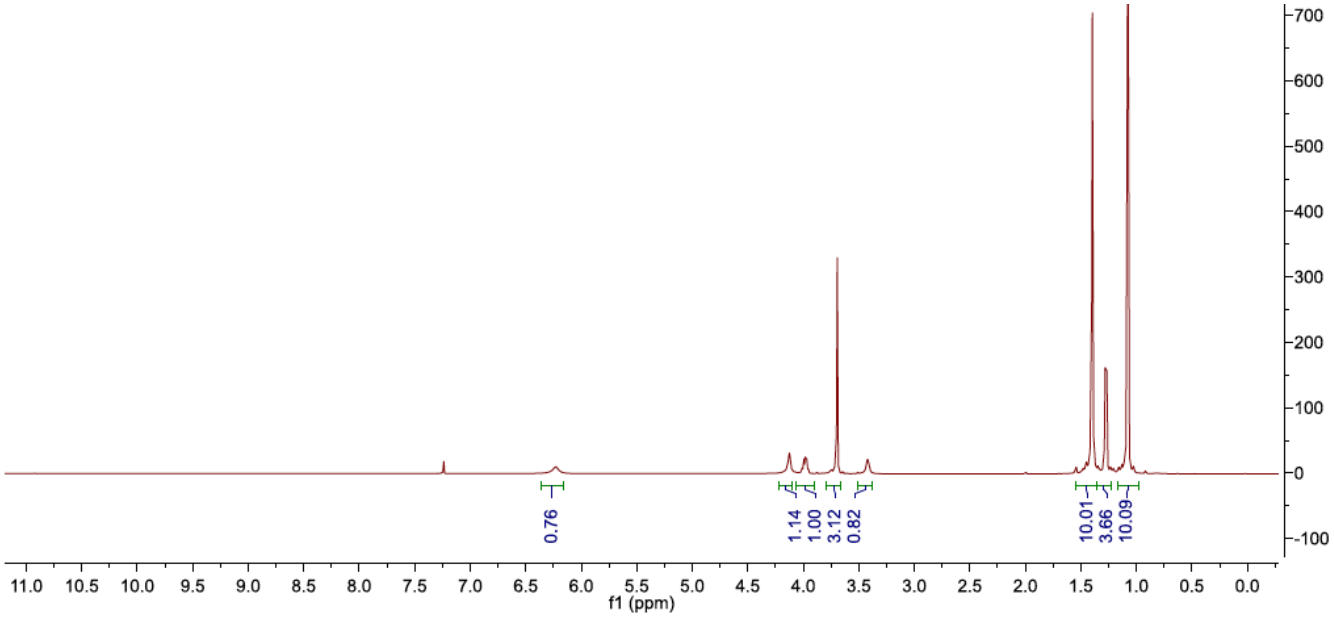

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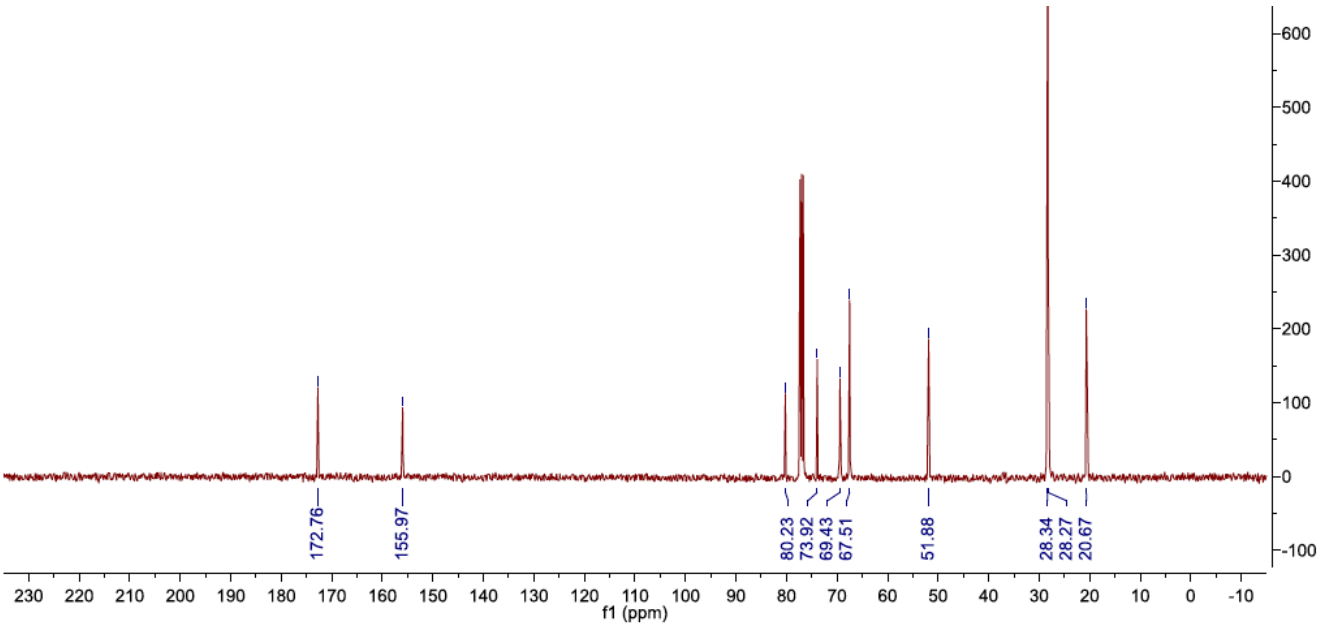

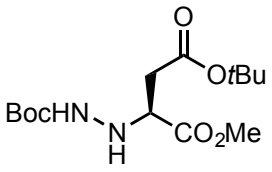

(4o)

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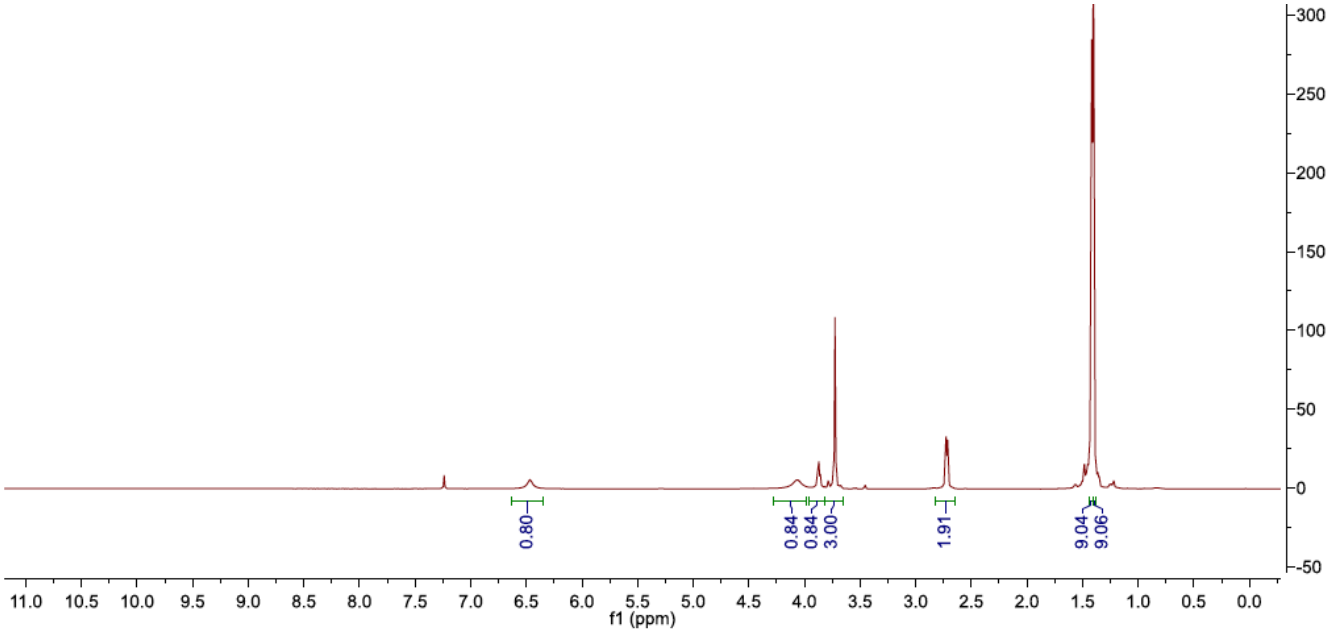
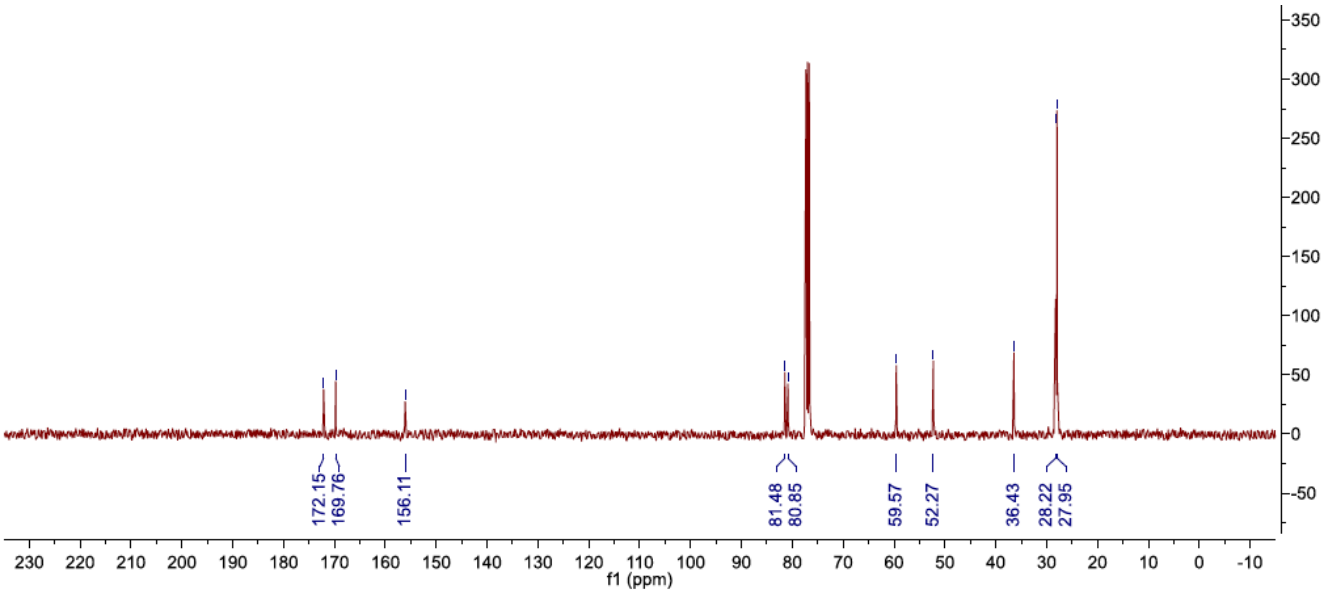
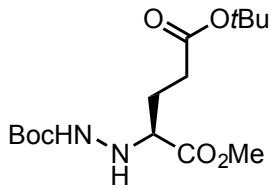


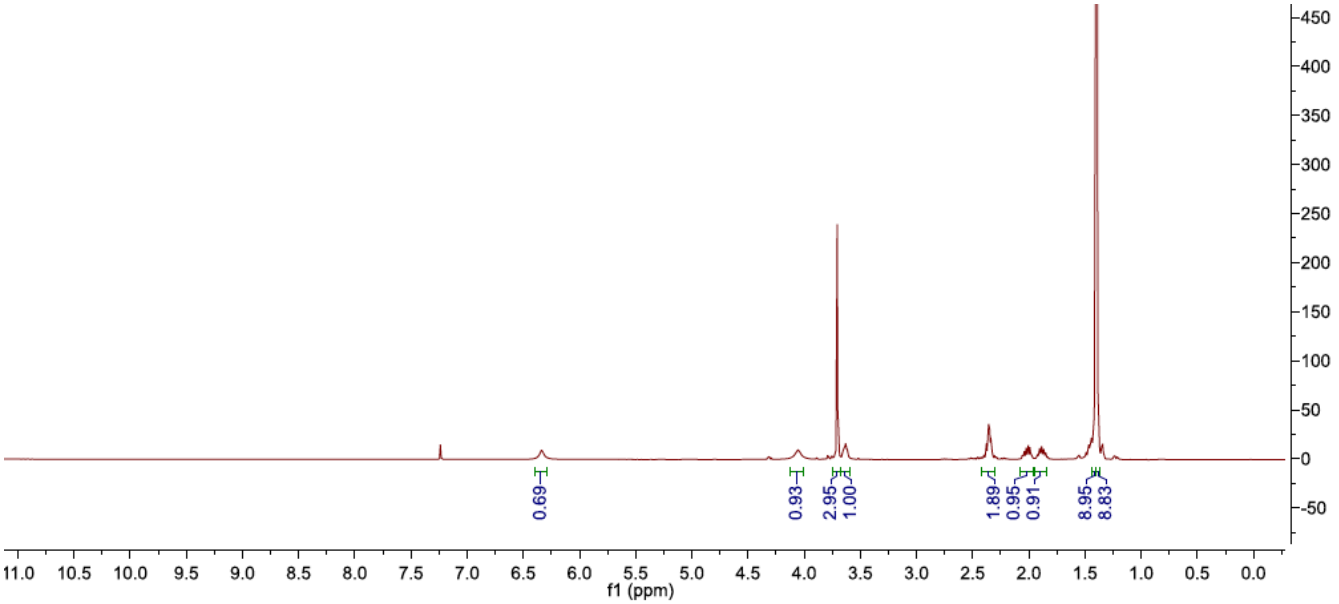
^{13}C NMR 126 MHz ($CDCl_3$)





(4p)

^{1}H NMR 400 MHz ($CDCl_3$)



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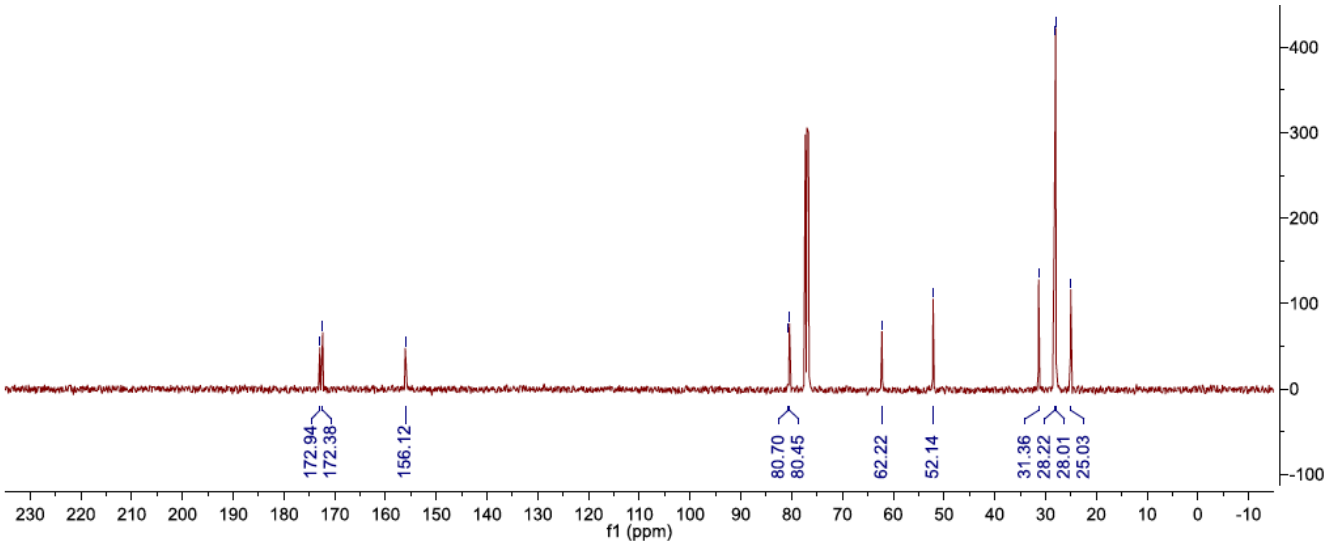

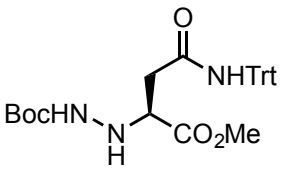

(4q)

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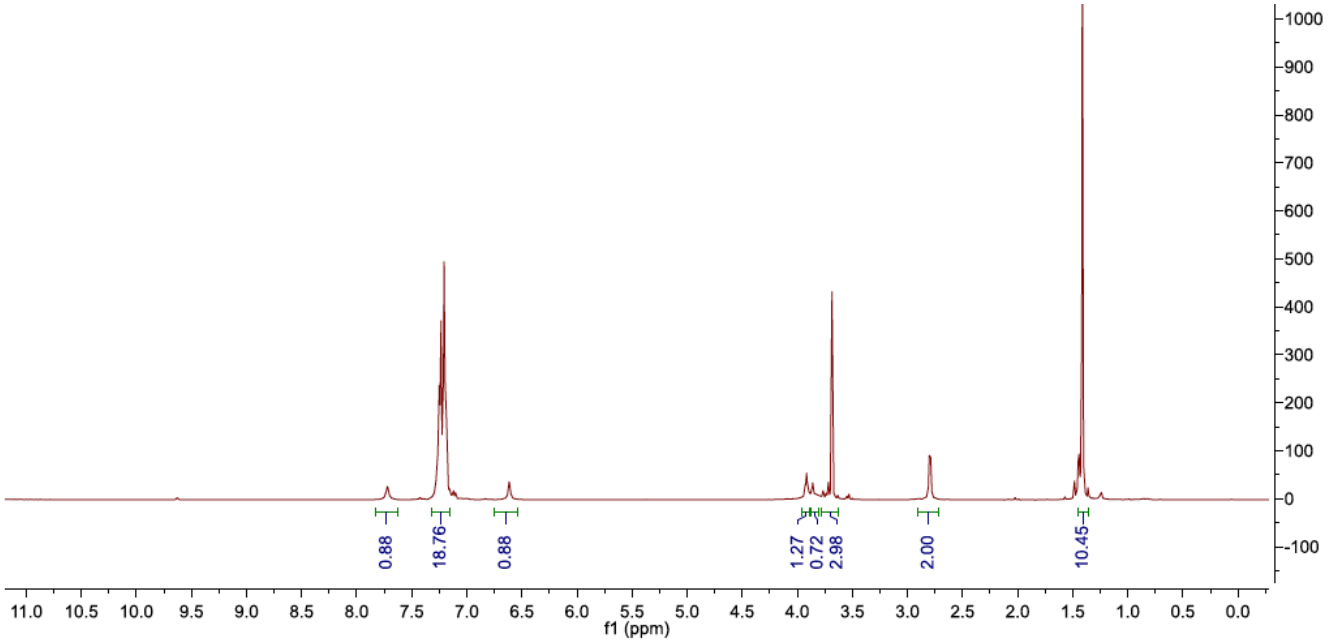

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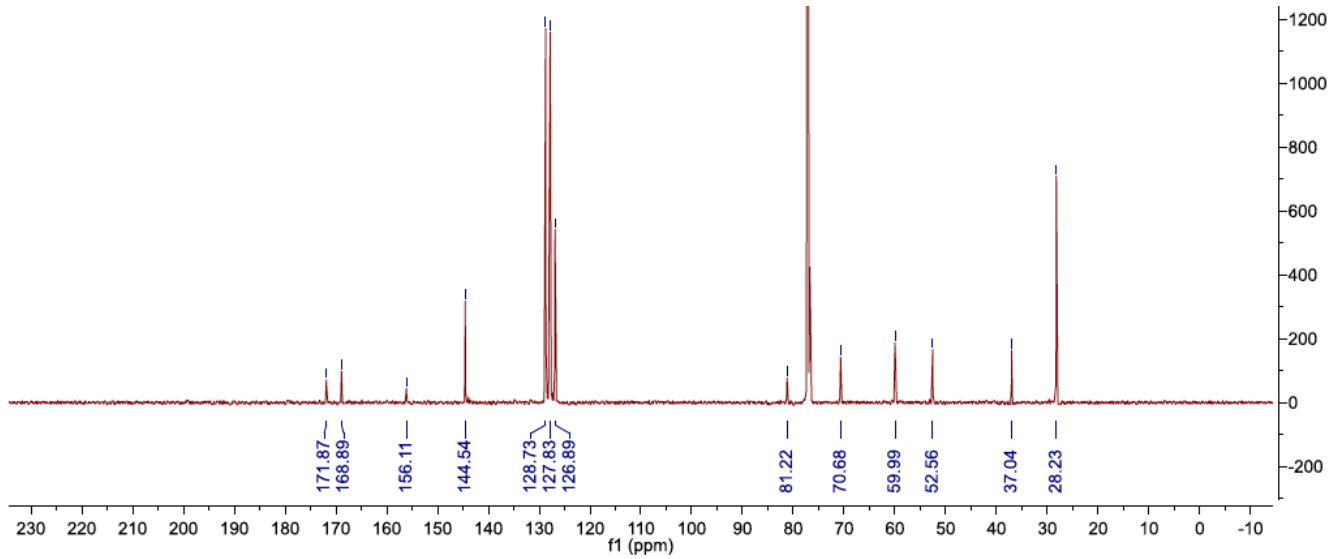
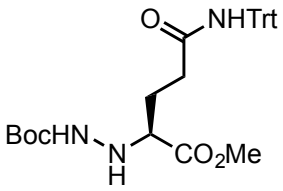
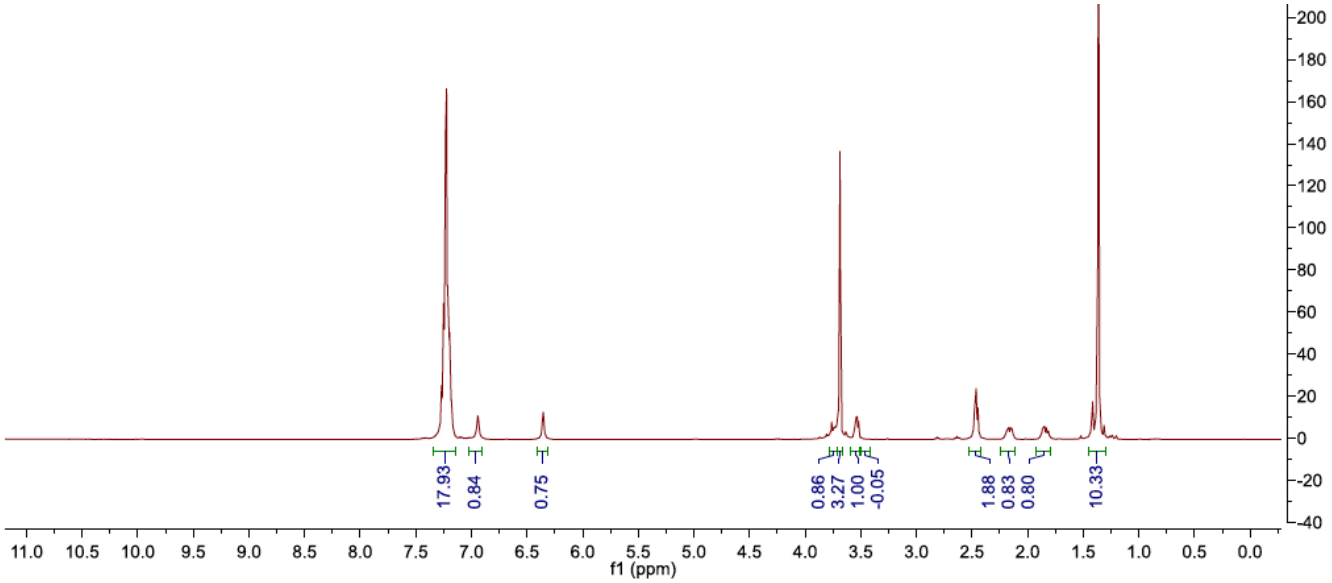


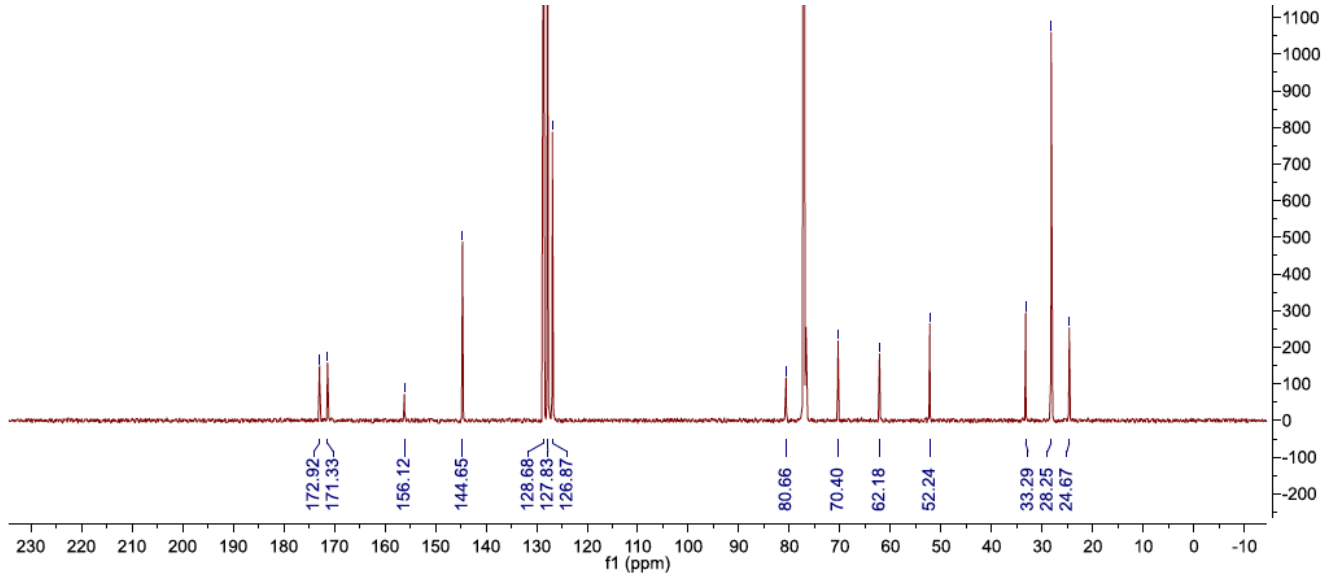


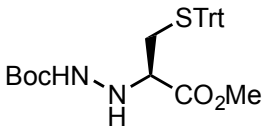
(4r)

^{1}H NMR 400 MHz ($CDCl_3$)



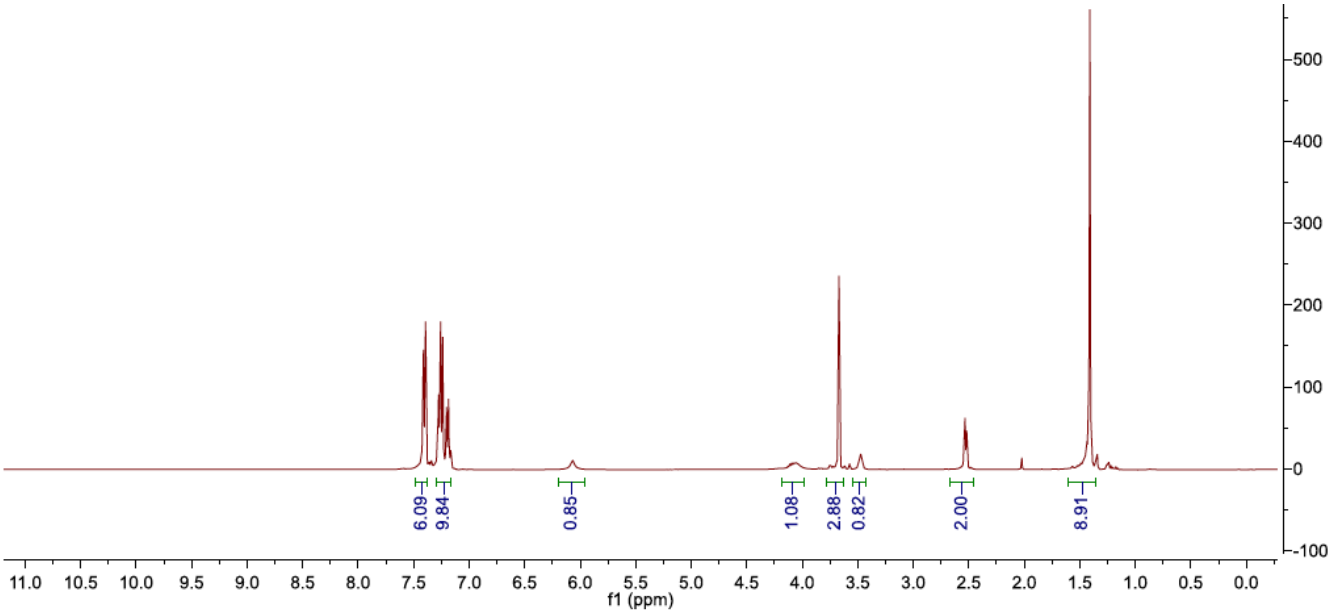
^{13}C NMR 126 MHz ($CDCl_3$)



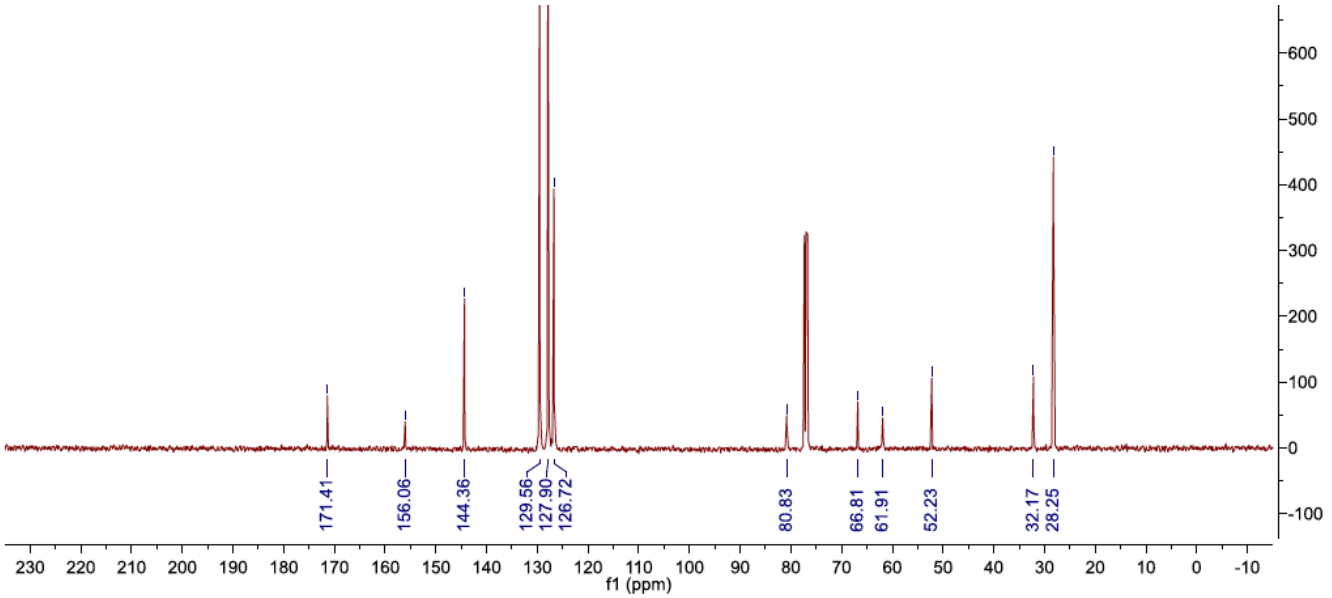


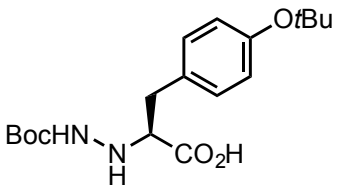
(4s)

^{1}H NMR 400 MHz ($CDCl_3$)



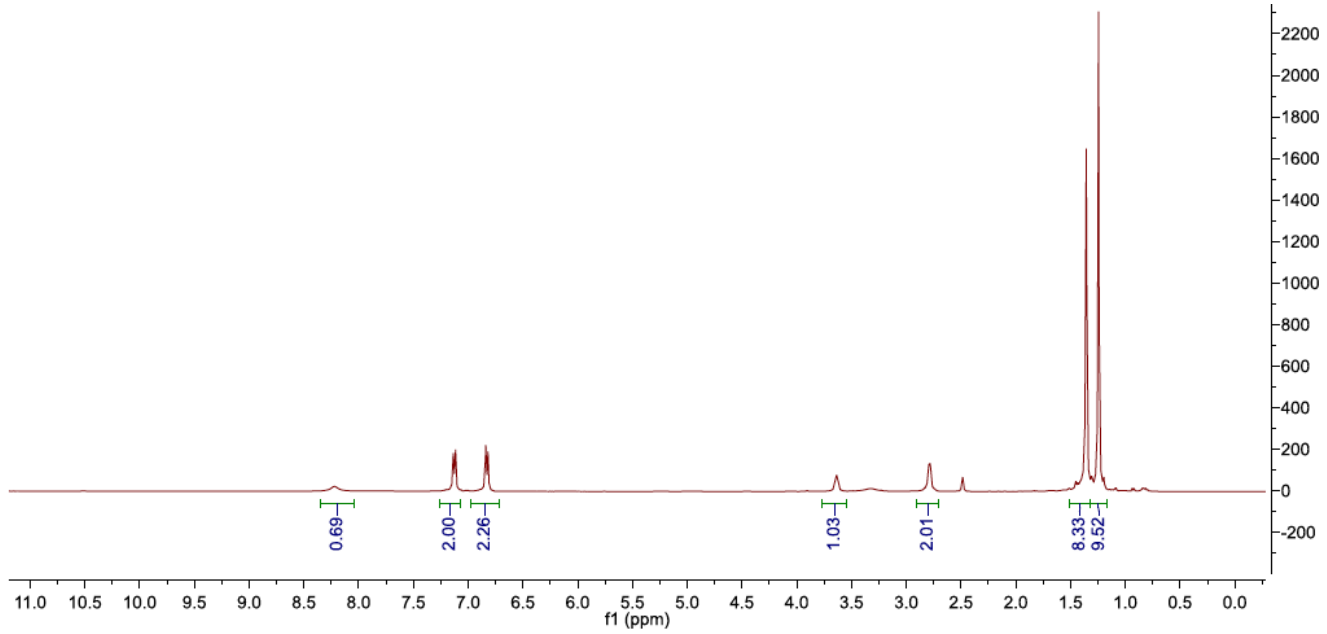
^{13}C NMR 101 MHz ($CDCl_3$)



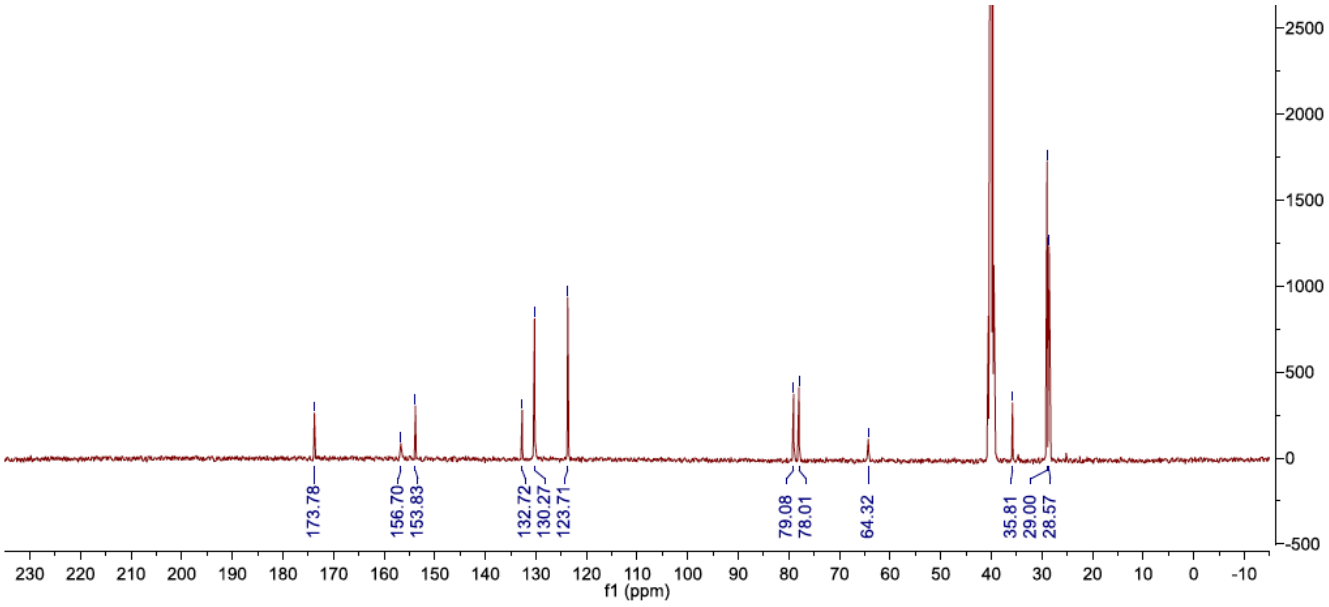


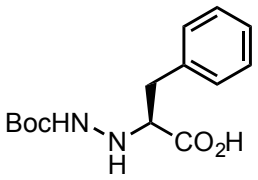
(6a)

^{1}H NMR 400 MHz (DMSO-d_6)



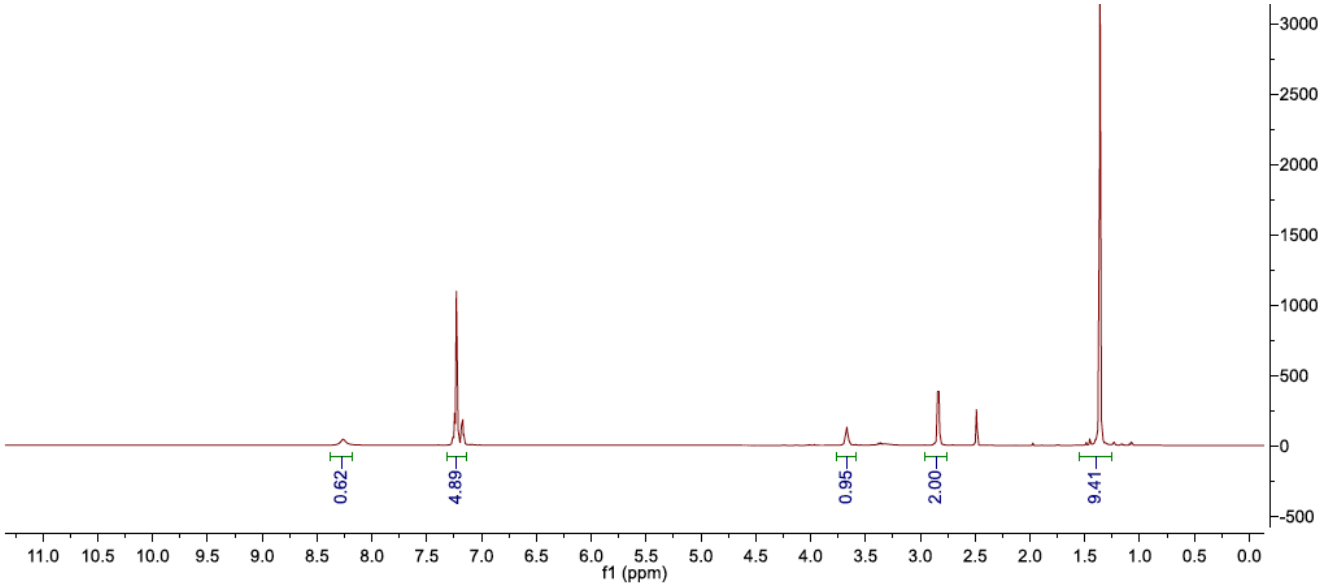
^{13}C NMR 101 MHz (DMSO-d_6)



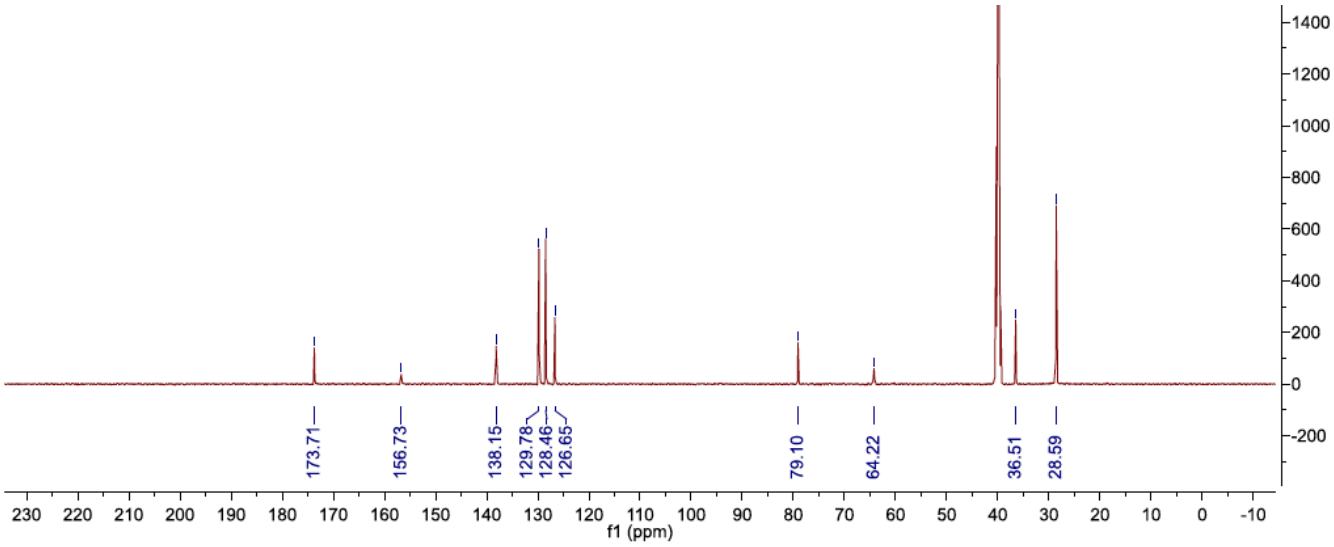


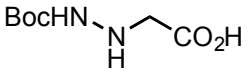
(6b)

^{1}H NMR 500 MHz (DMSO-d_6)



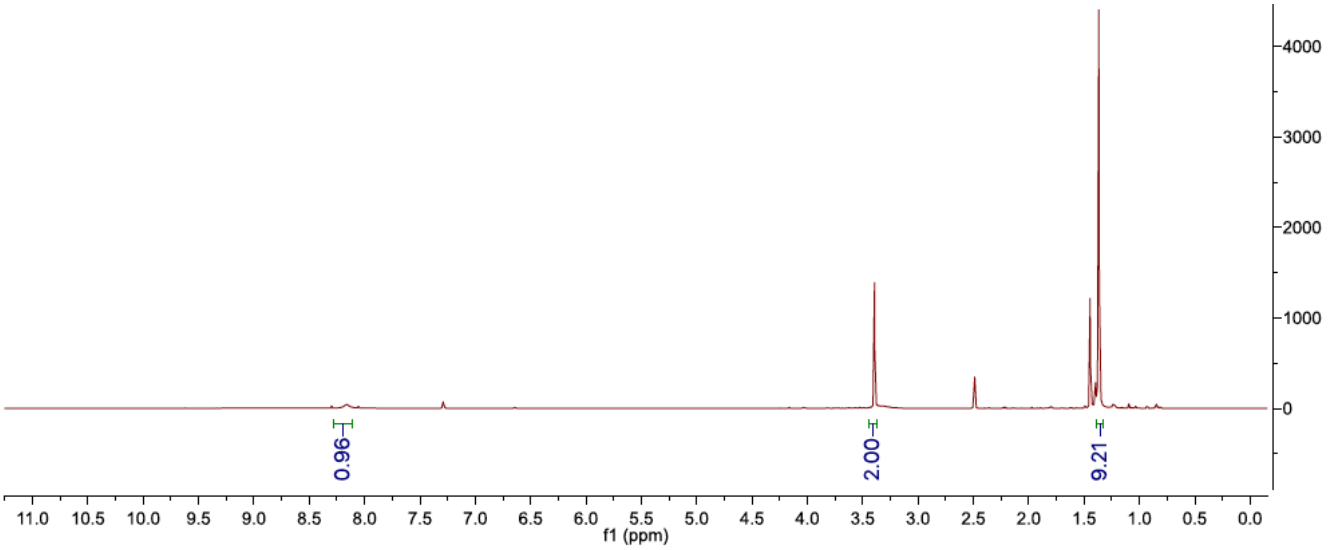
^{13}C NMR 126 MHz (DMSO-d_6)



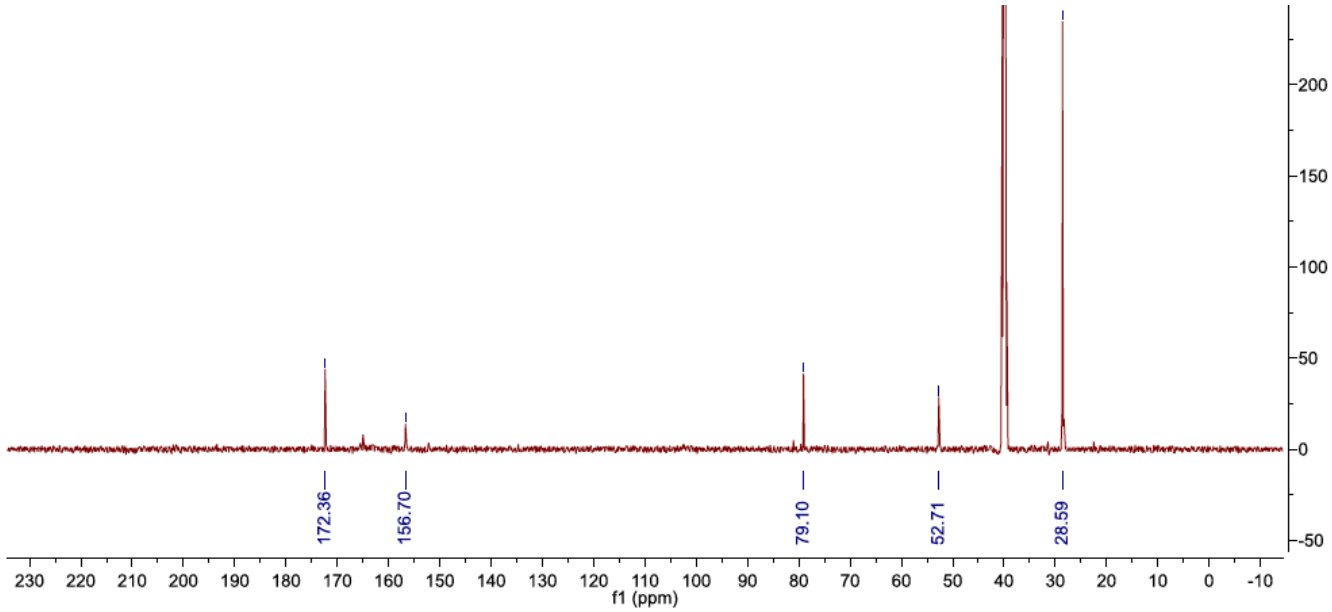


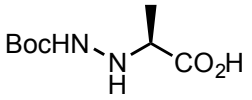
(6c)

^{1}H NMR 500 MHz ($CDCl_3$)



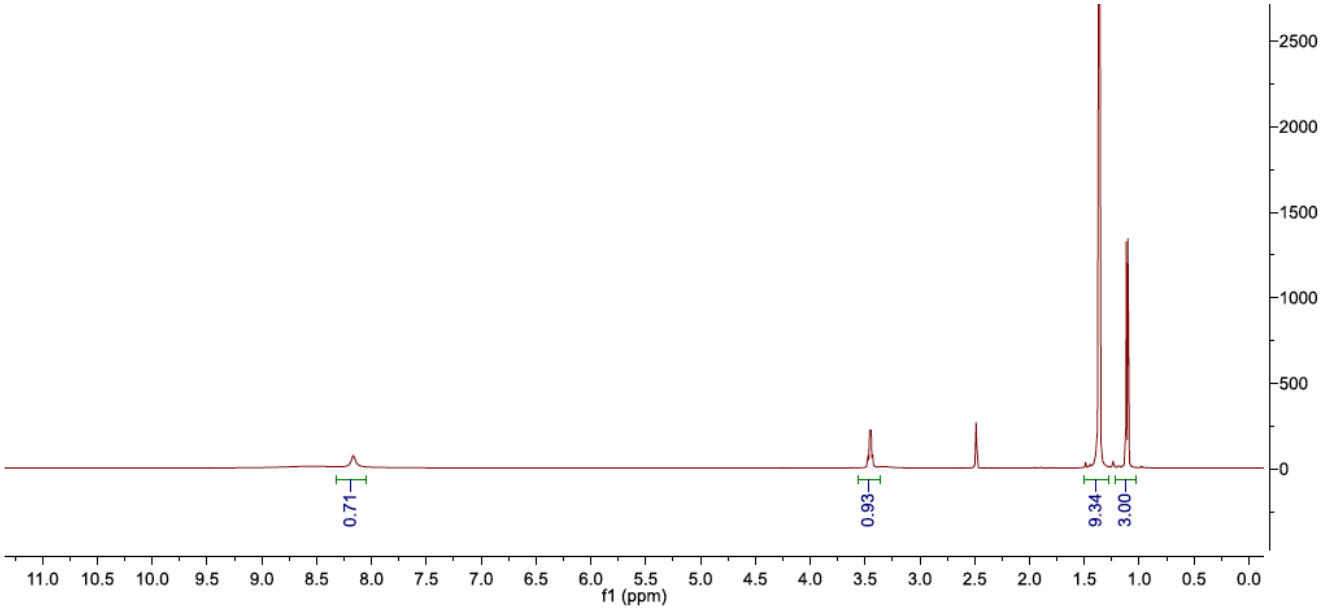
^{13}C NMR 126 MHz ($CDCl_3$)



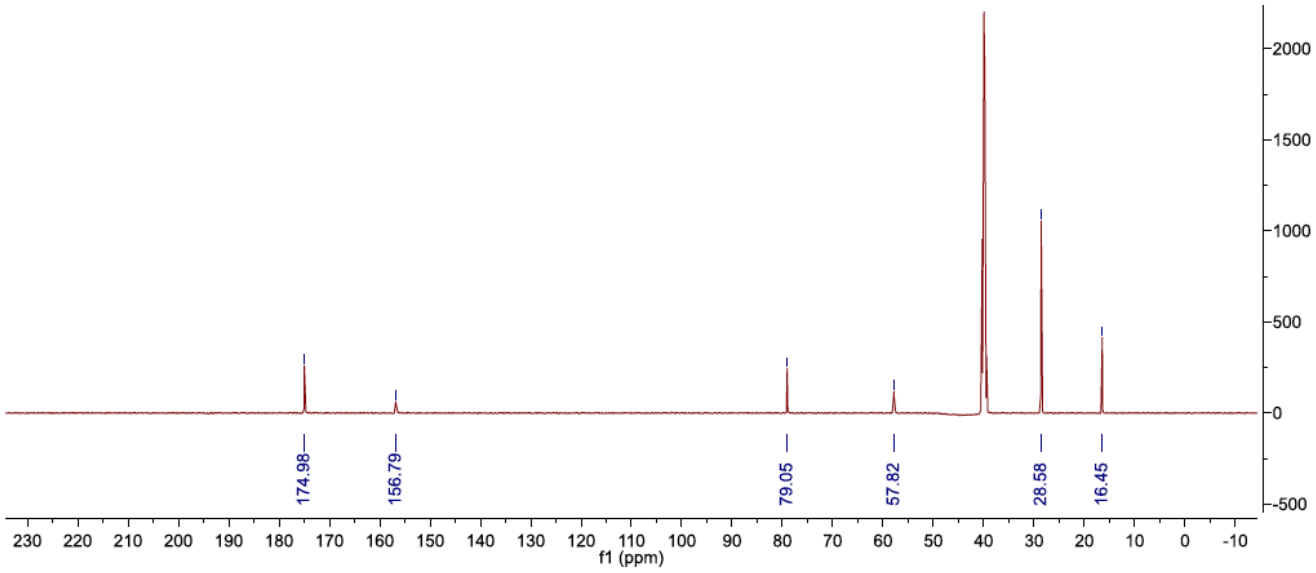


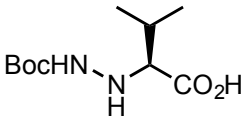
(6d)

^{1}H NMR 500 MHz (DMSO-d_6)



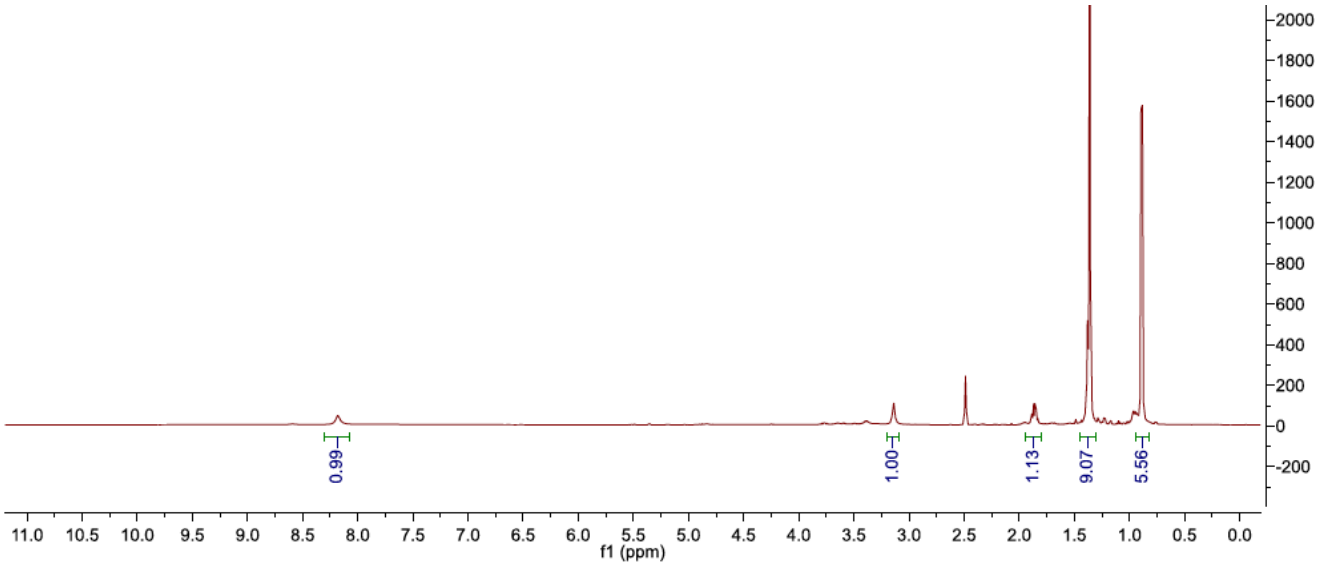
^{13}C NMR 126 MHz (DMSO-d_6)



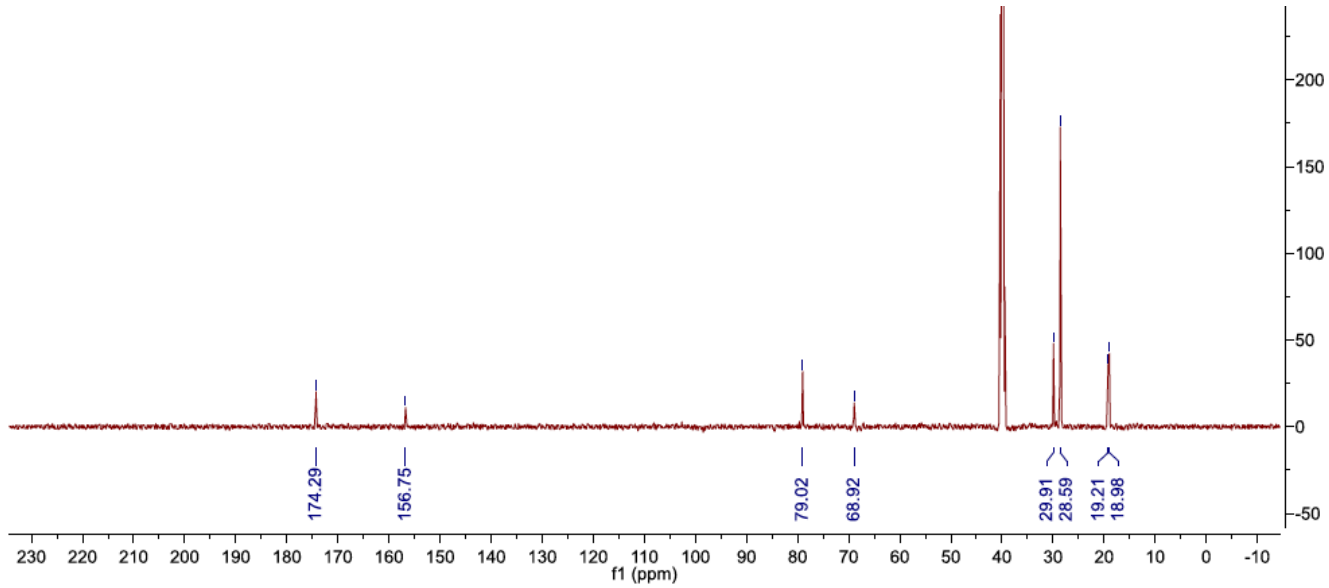


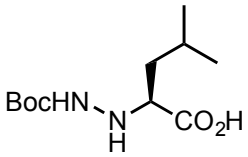
(6e)

^{1}H NMR 500 MHz (DMSO-d_6)



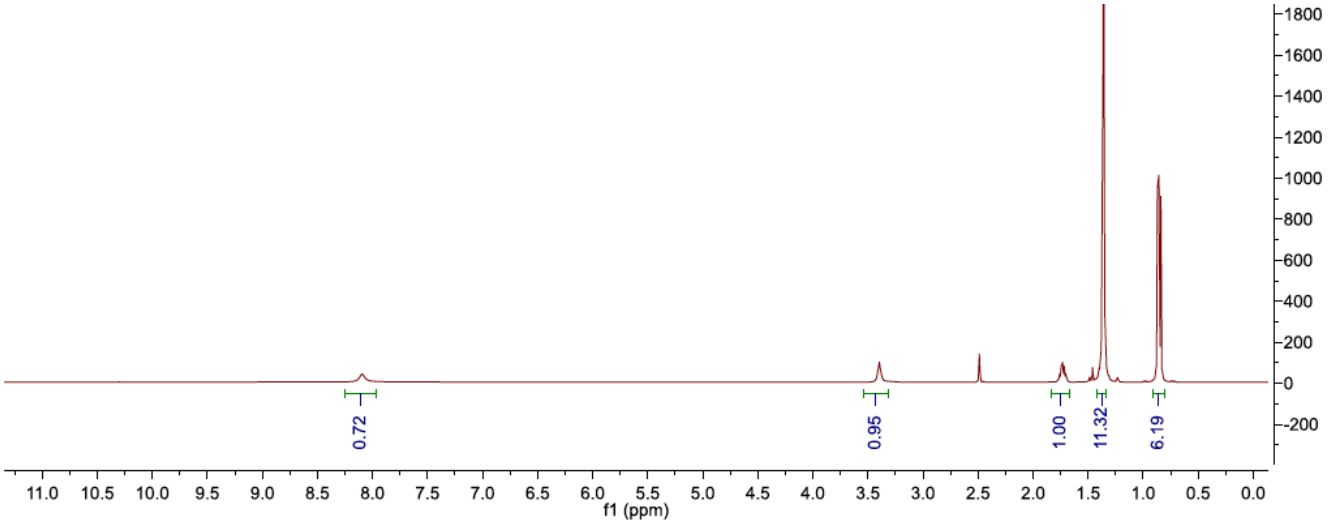
^{13}C NMR 126 MHz (DMSO-d_6)



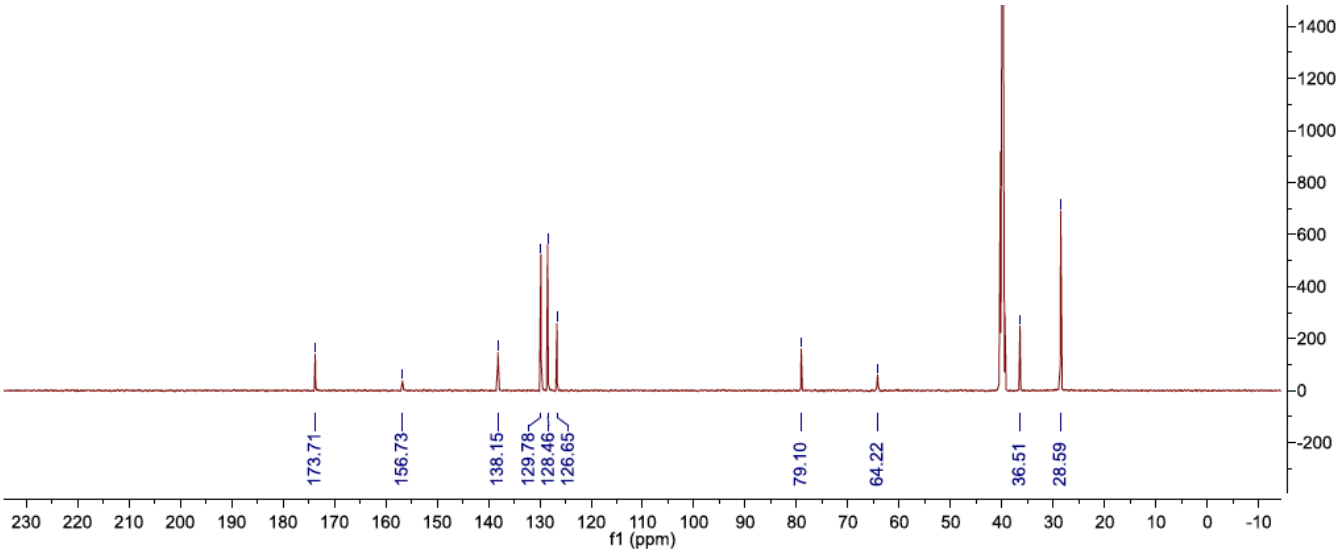


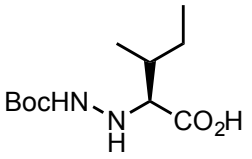
(6f)

^{1}H NMR 500 MHz (DMSO-d_6)



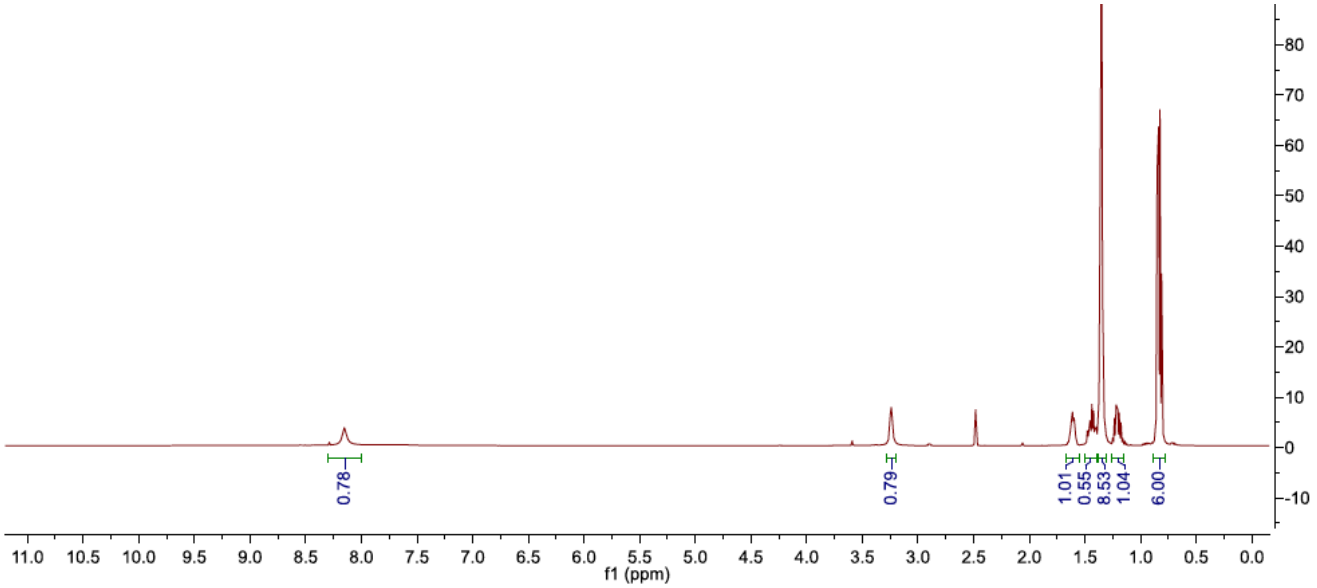
^{13}C NMR 126 MHz (DMSO-d_6)



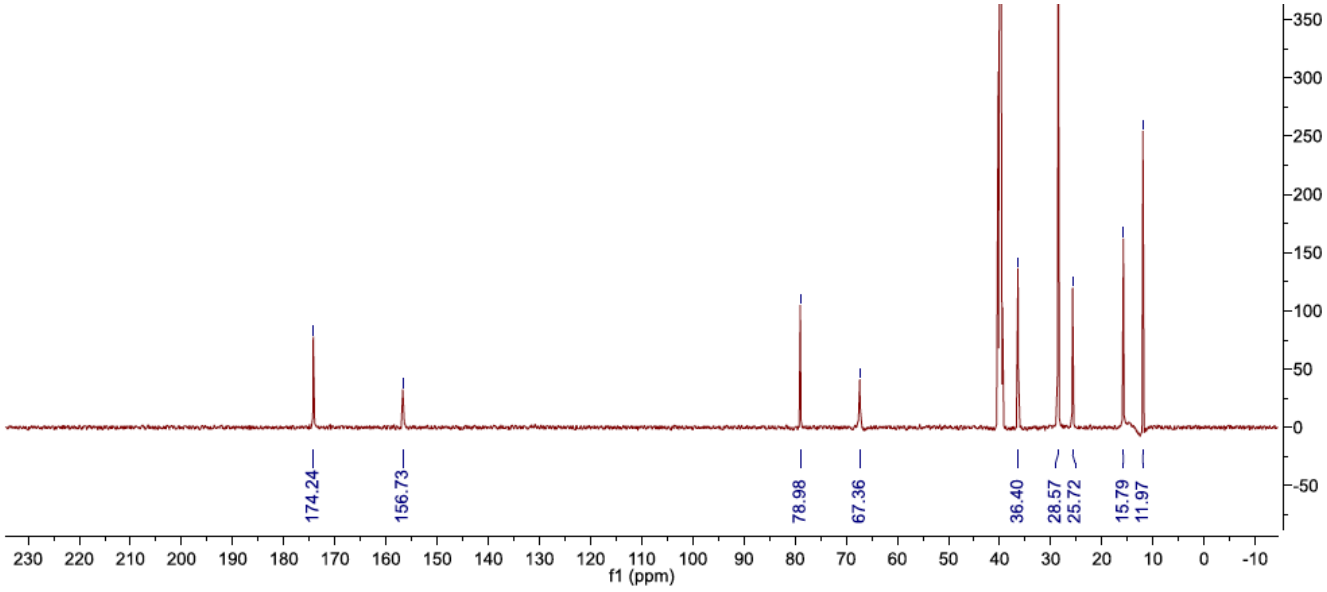


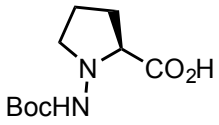
(6g)

^{1}H NMR 500 MHz (DMSO-d_6)



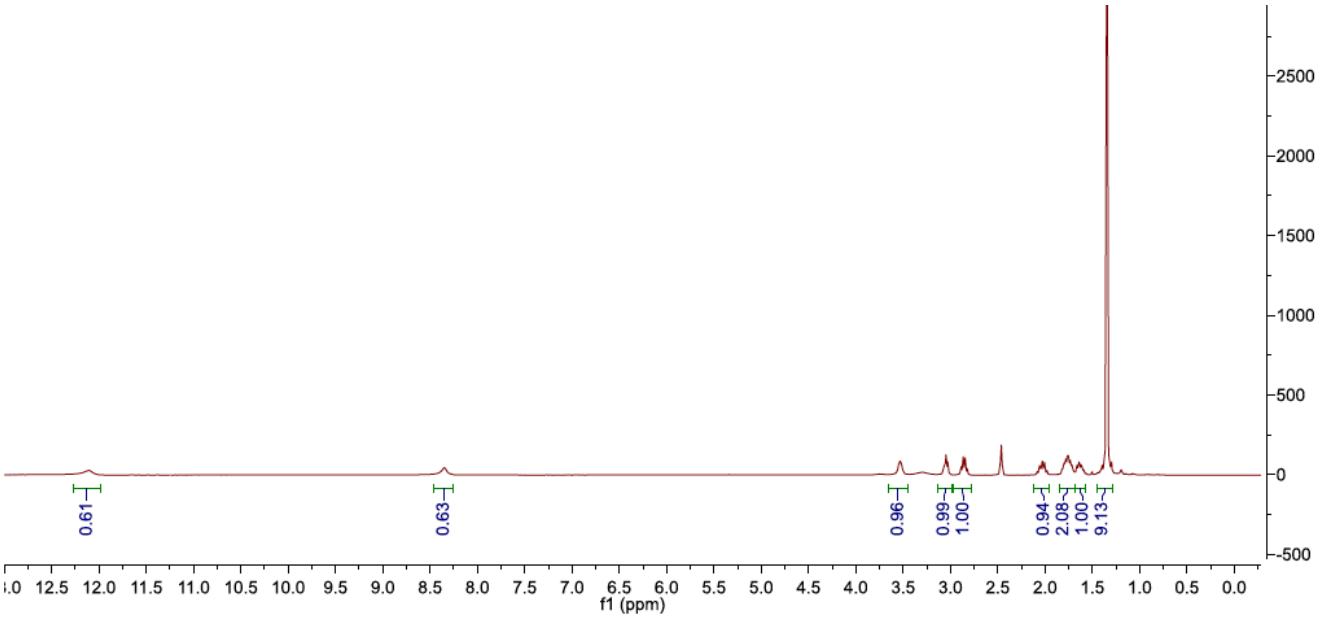
^{13}C NMR 126 MHz (DMSO-d_6)



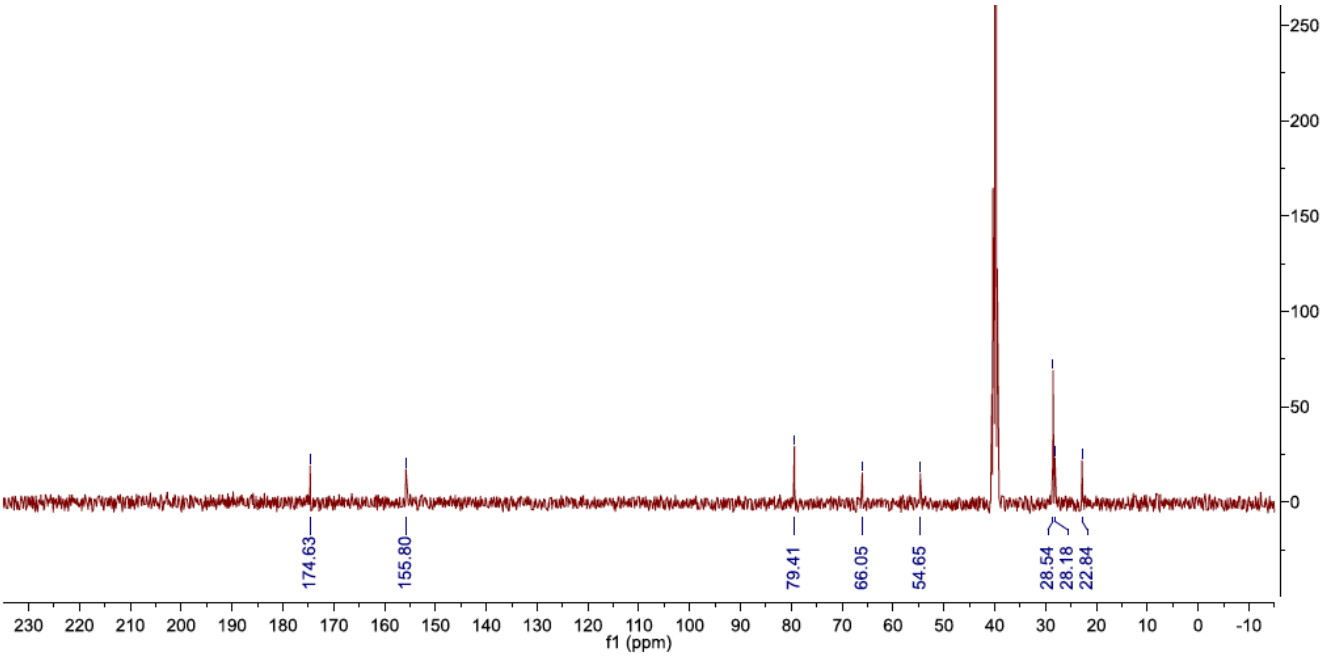


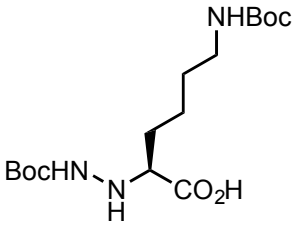
(6h)

^{1}H NMR 400 MHz (DMSO-d_6)



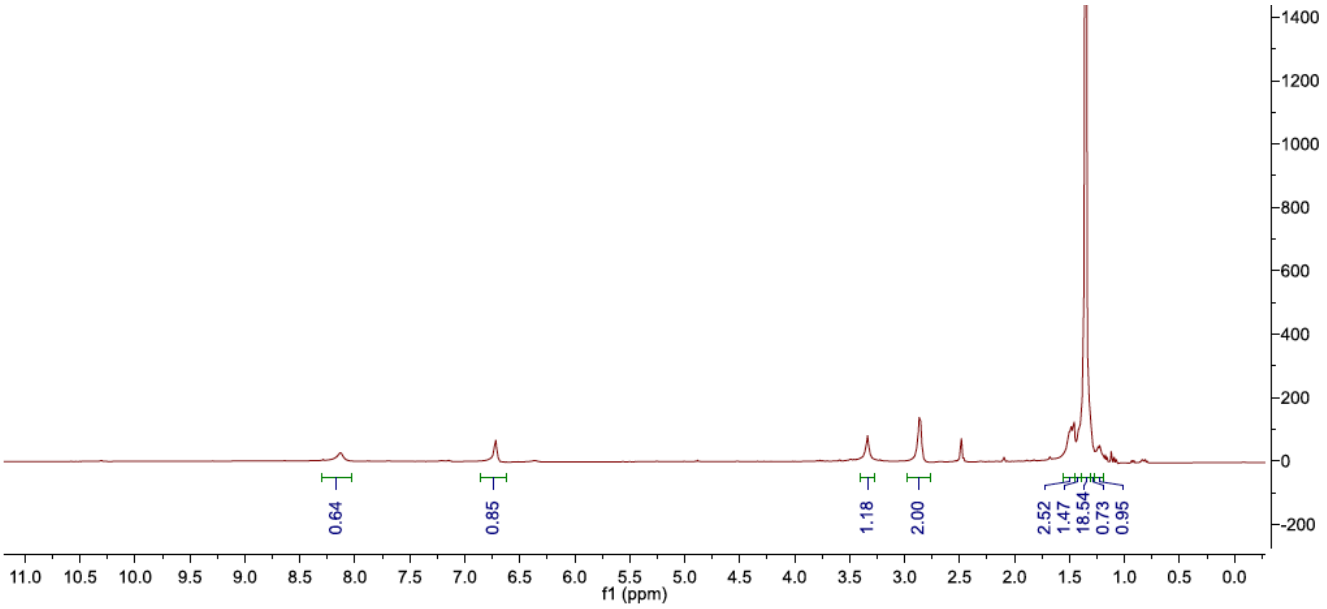
^{13}C NMR 101 MHz (DMSO-d_6)



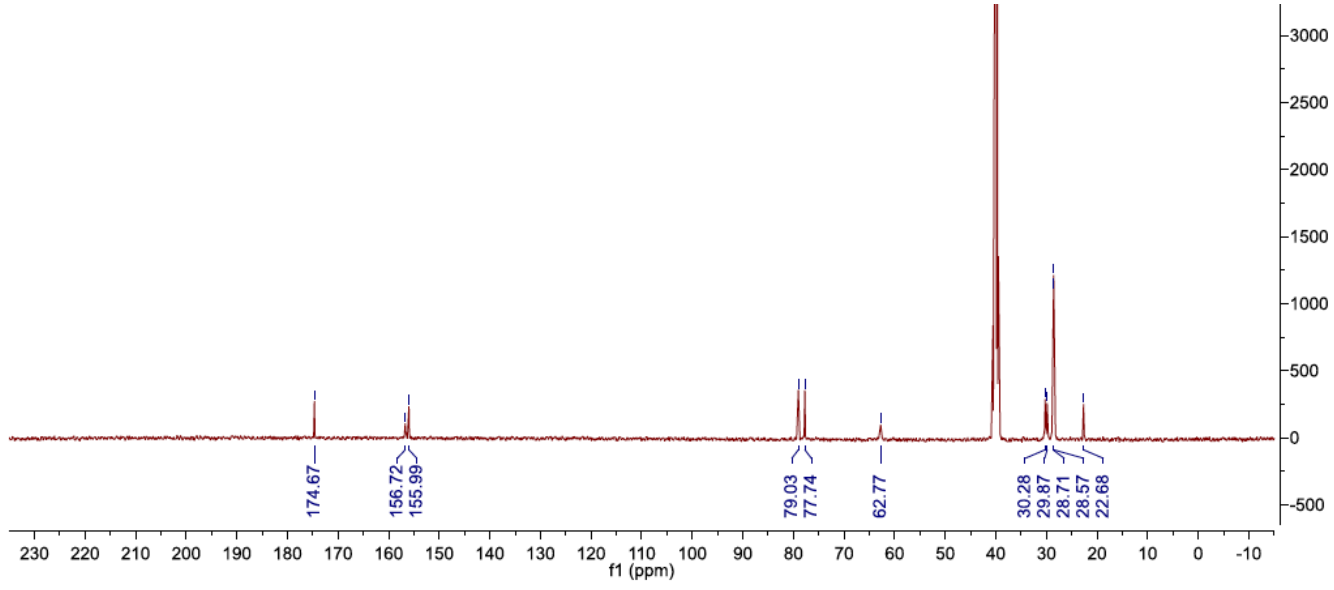


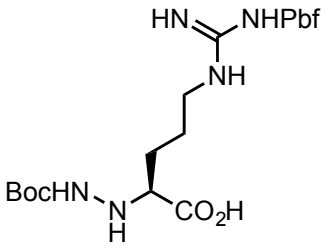
(6i)

^{1}H NMR 400 MHz (DMSO-d_6)



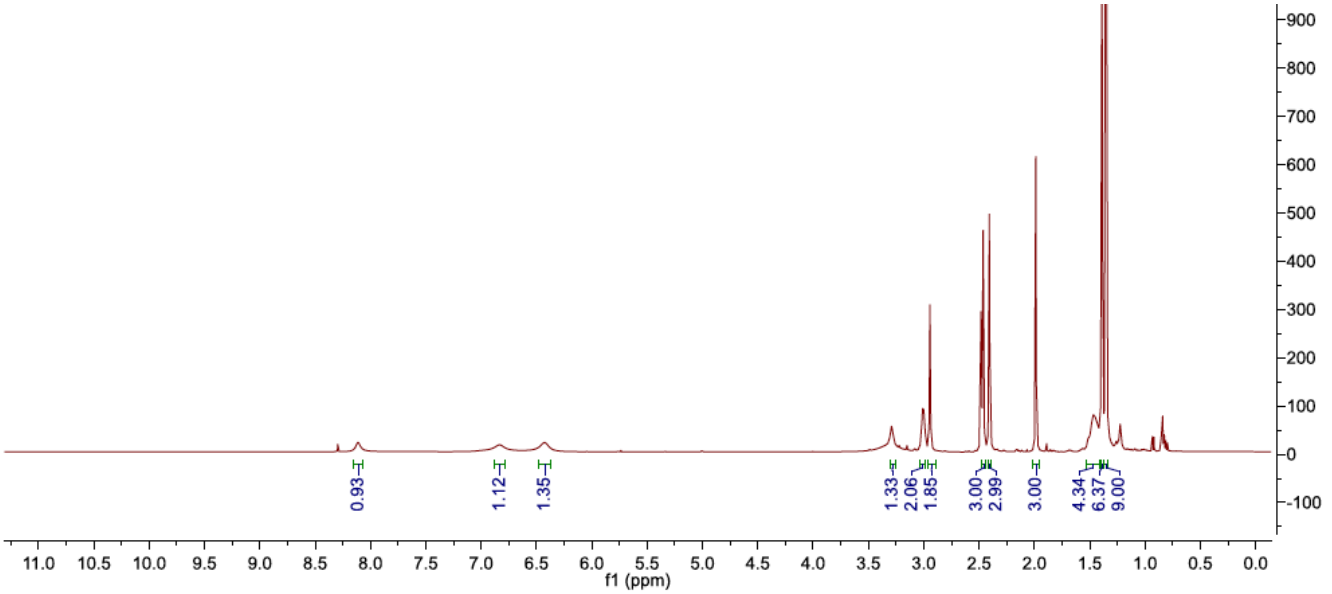
^{13}C NMR 101 MHz (DMSO-d_6)



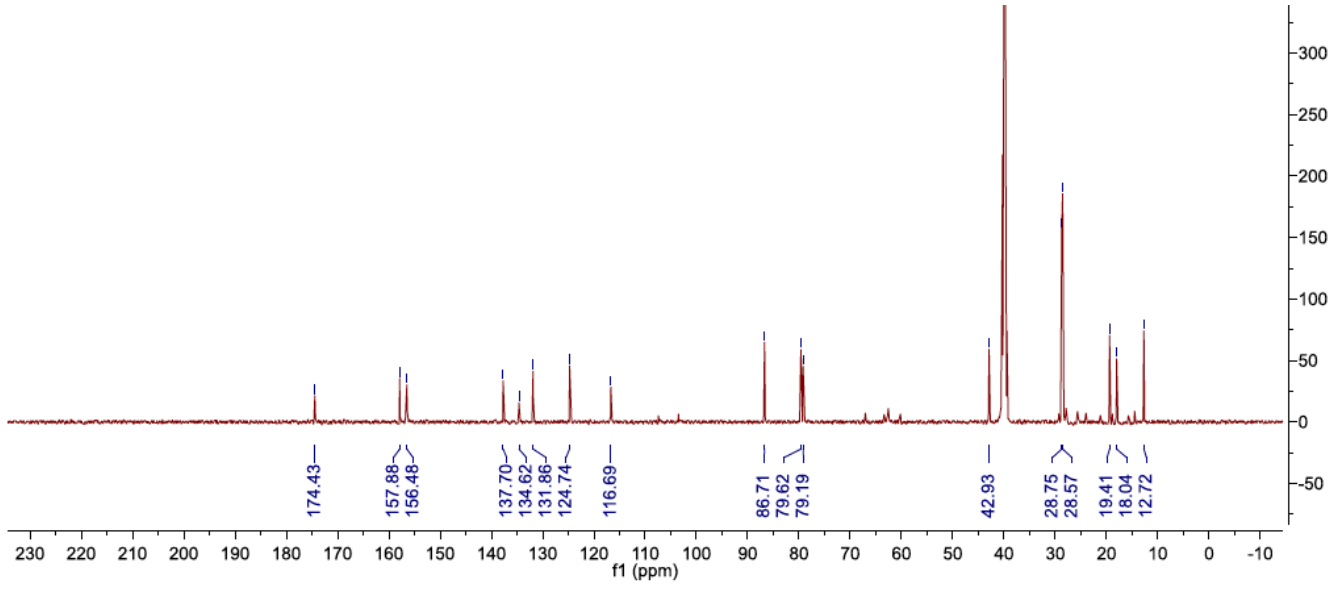


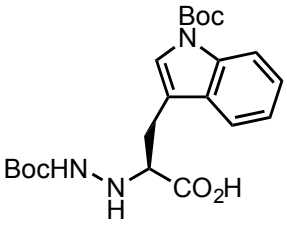
(6j)

^{1}H NMR 500 MHz (DMSO-d_6)



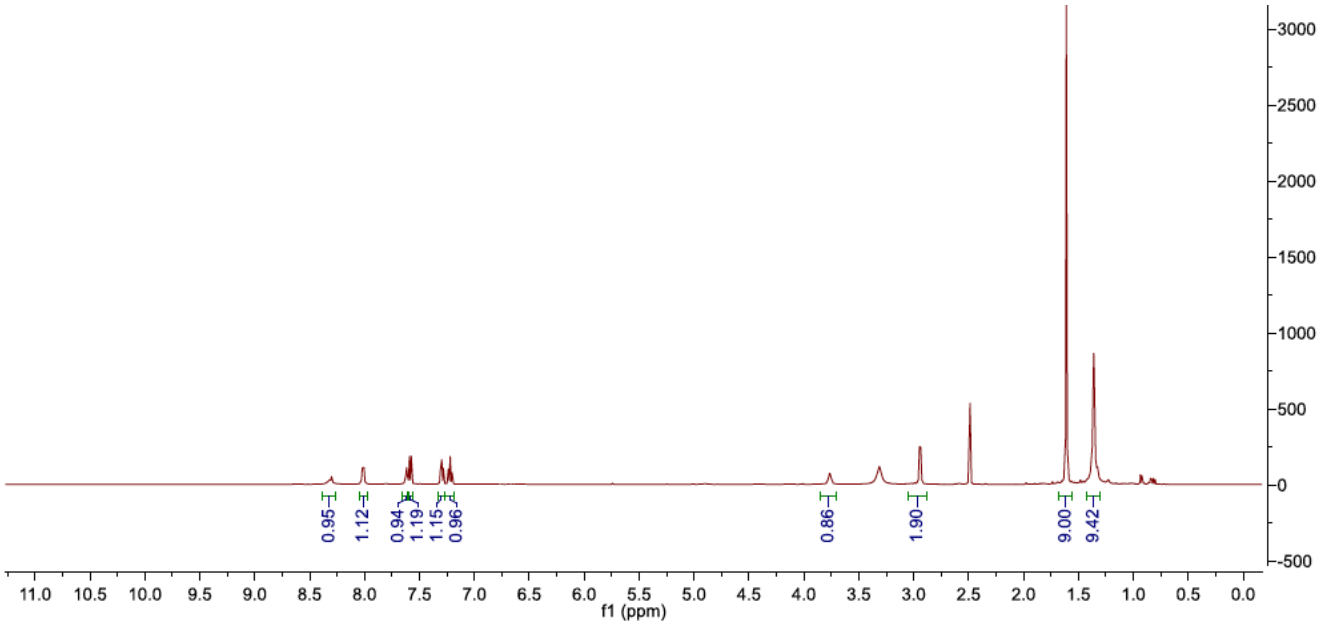
^{13}C NMR 126 MHz (DMSO-d_6)



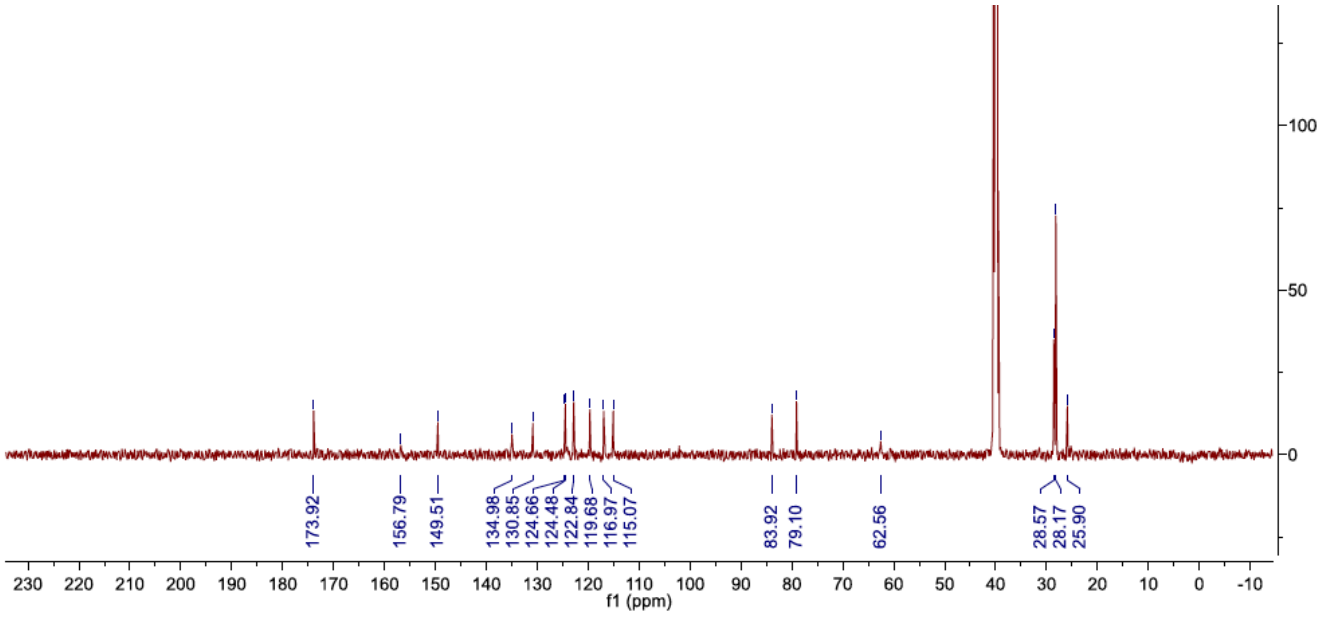


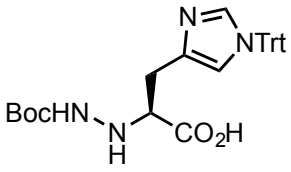
(6k)

^{1}H NMR 500 MHz (DMSO-d_6)



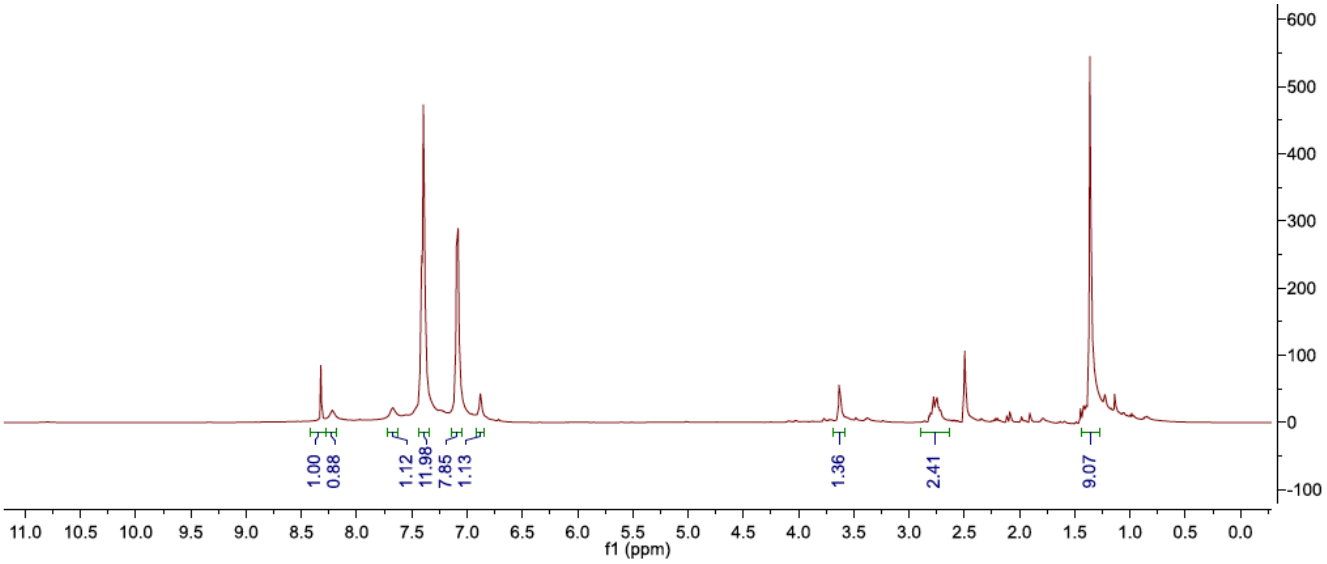
^{13}C NMR 126 MHz (DMSO-d_6)



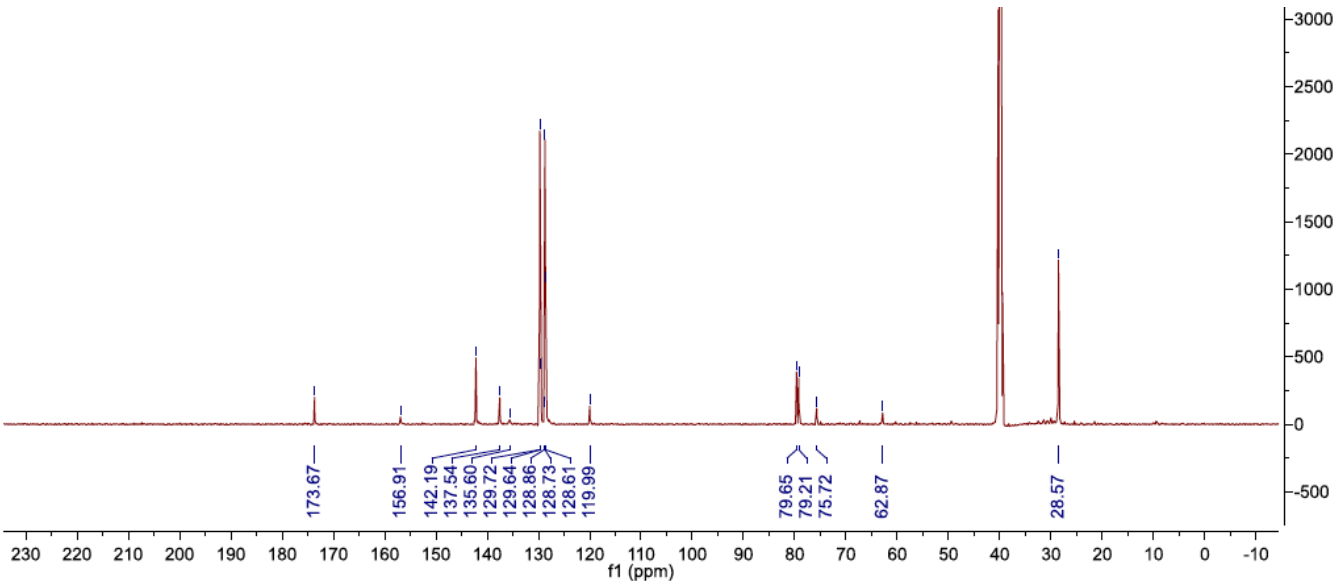


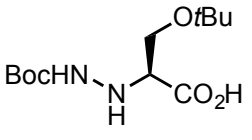
(6l)

^{1}H NMR 500 MHz (DMSO-d_6)



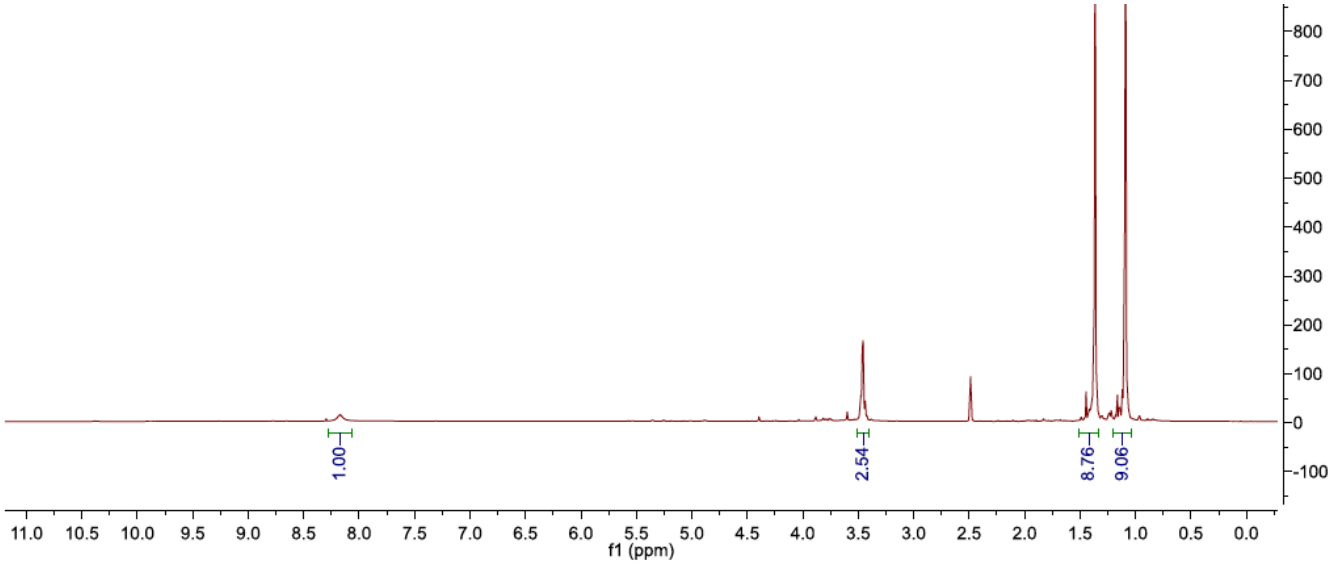
^{13}C NMR 126 MHz (DMSO-d_6)



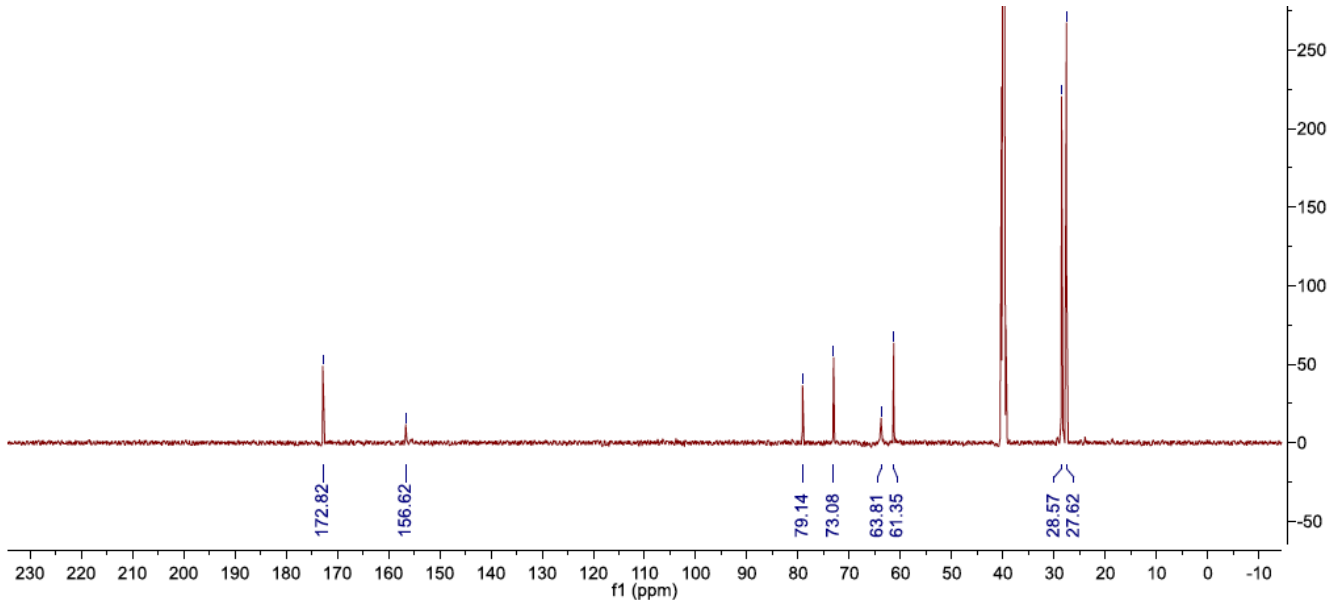


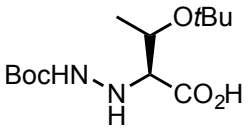
(6m)

^{1}H NMR 500 MHz (DMSO-d_6)



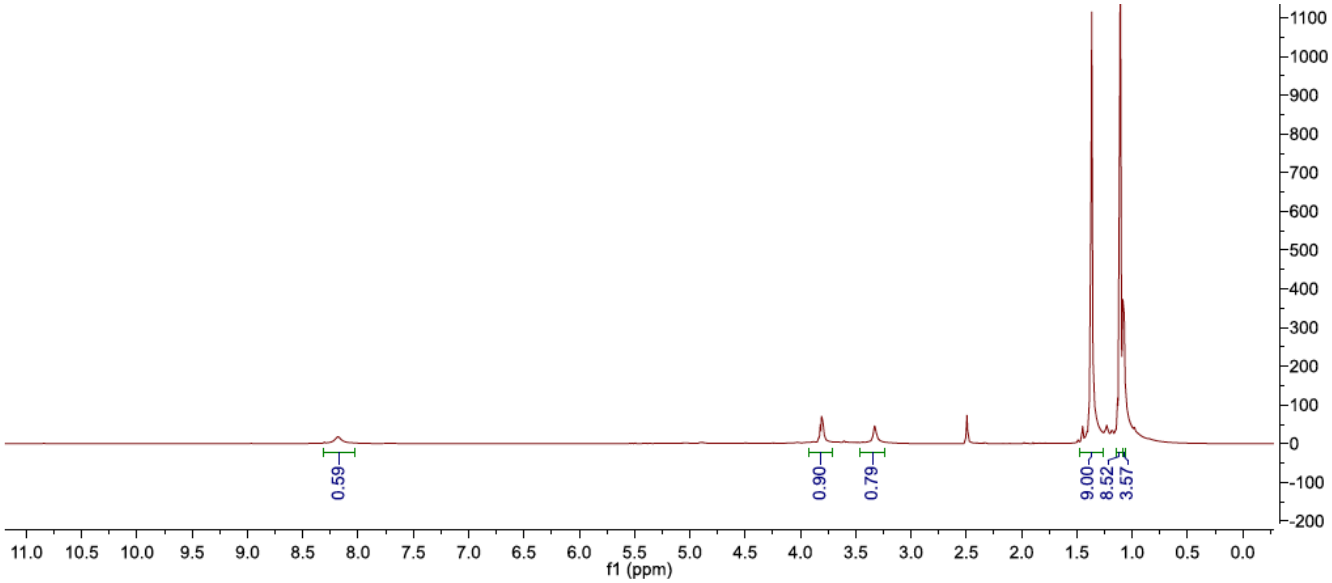
^{13}C NMR 126 MHz (DMSO-d_6)



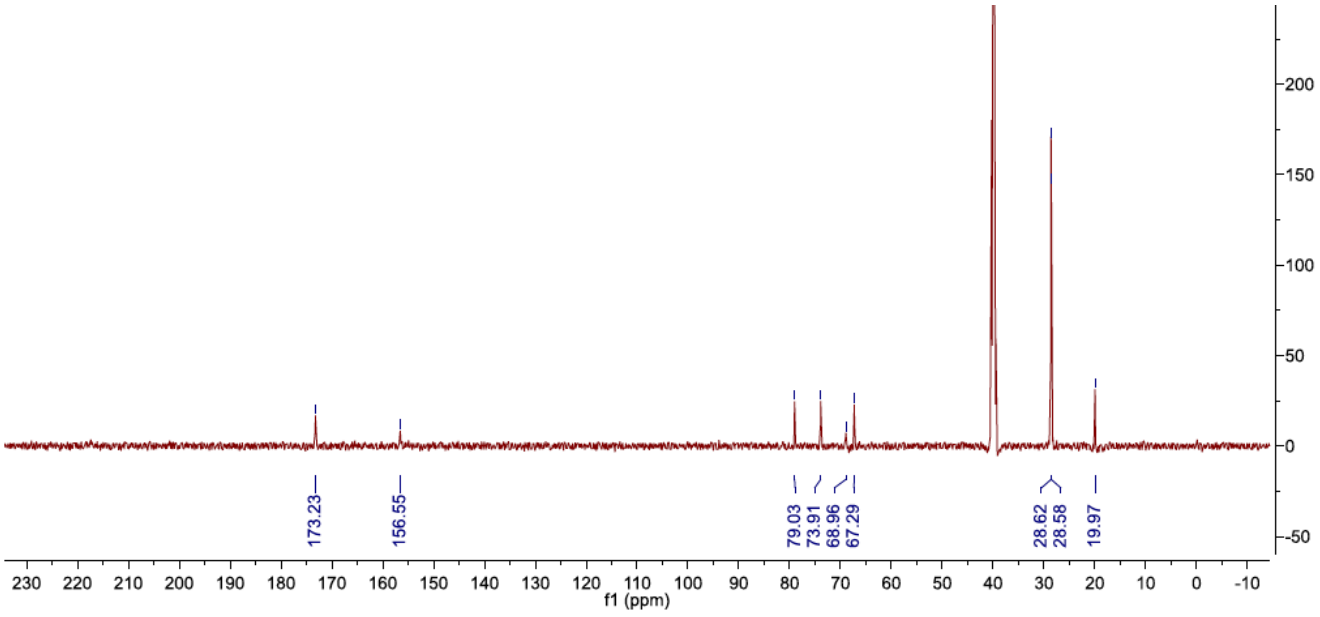


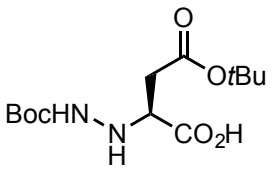
(6n)

^{1}H NMR 500 MHz (DMSO-d_6)



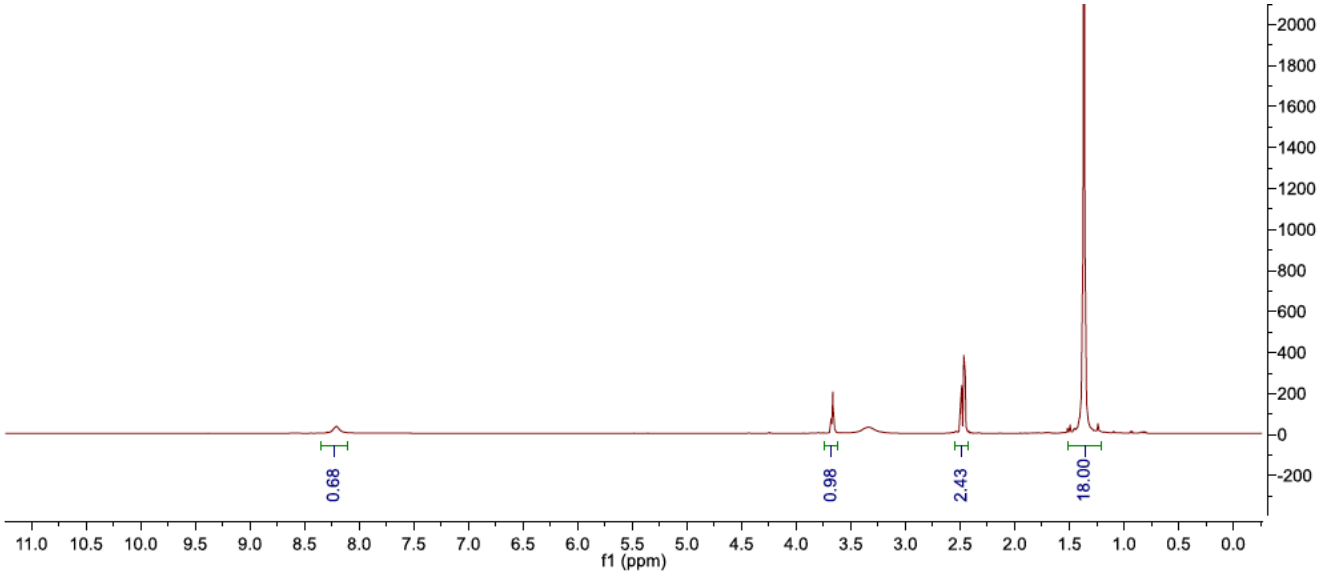
^{13}C NMR 126 MHz (DMSO-d_6)



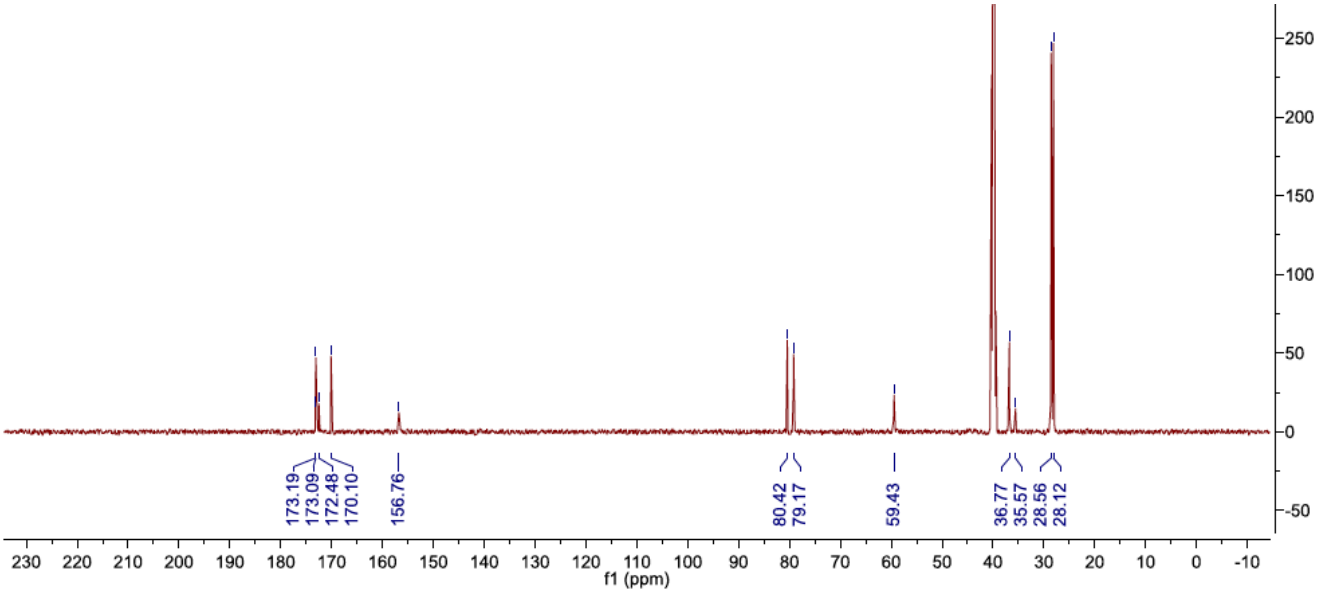


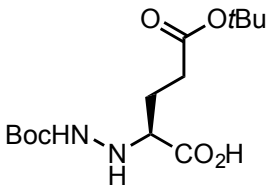
(6o)

^{1}H NMR 500 MHz (DMSO-d_6)



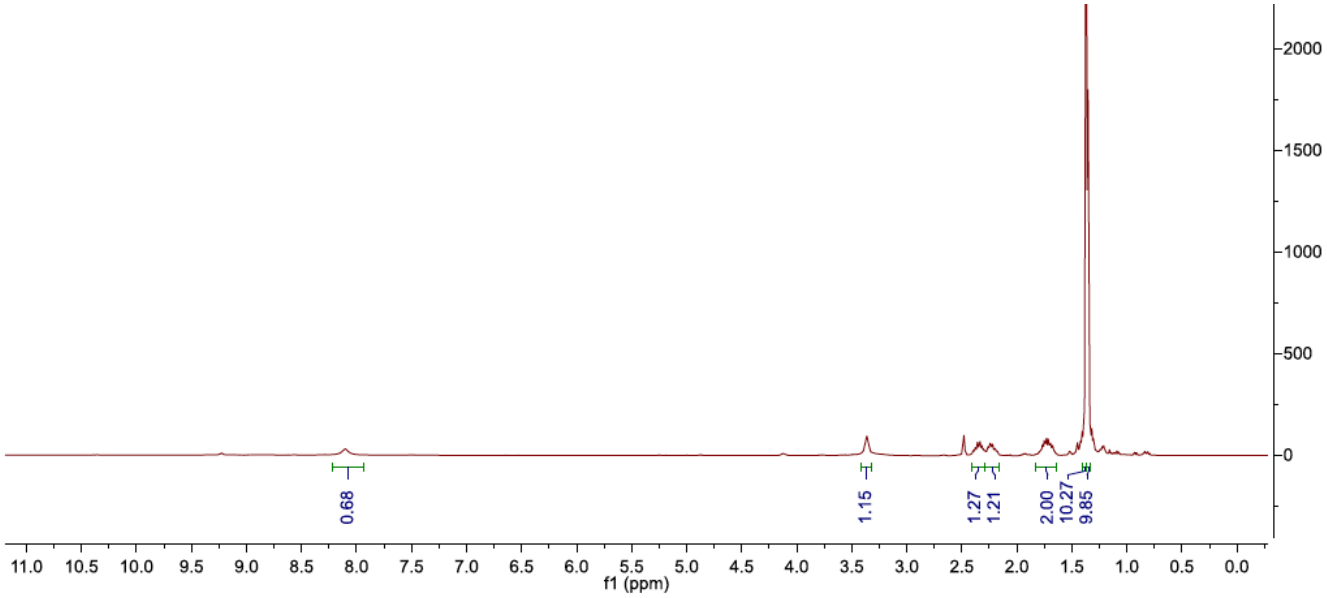
^{13}C NMR 126 MHz (DMSO-d_6)



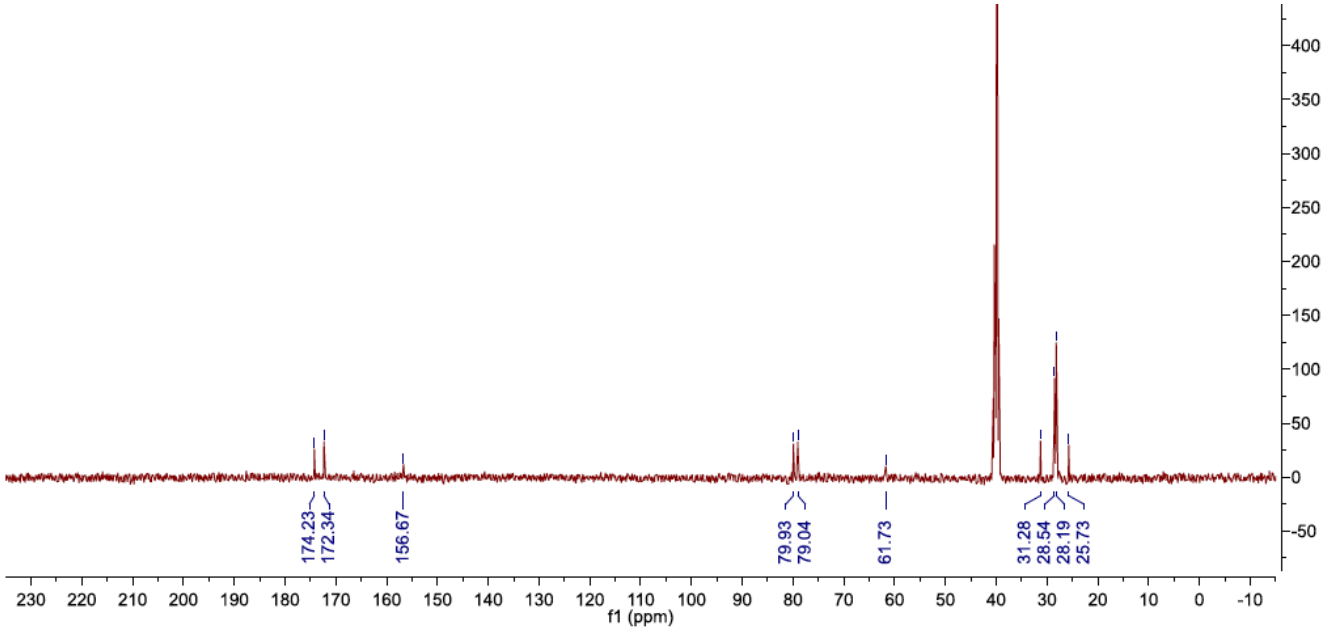


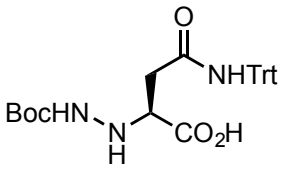
(6p)

^{1}H NMR 400 MHz ($CDCl_3$)



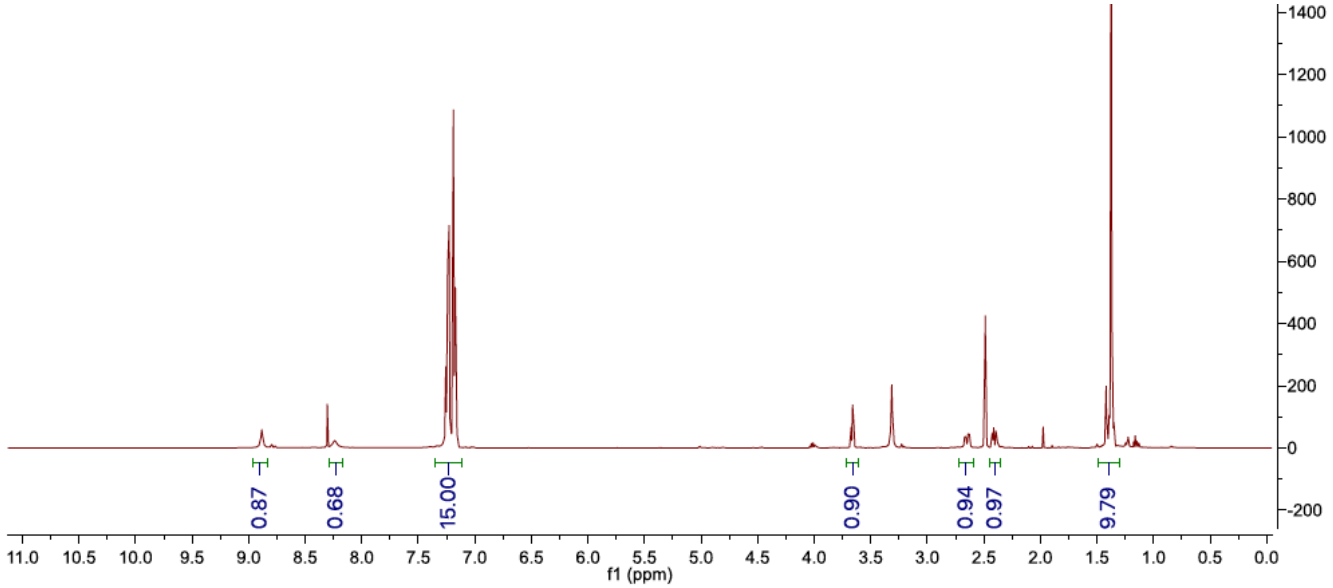
^{13}C NMR 101 MHz ($CDCl_3$)



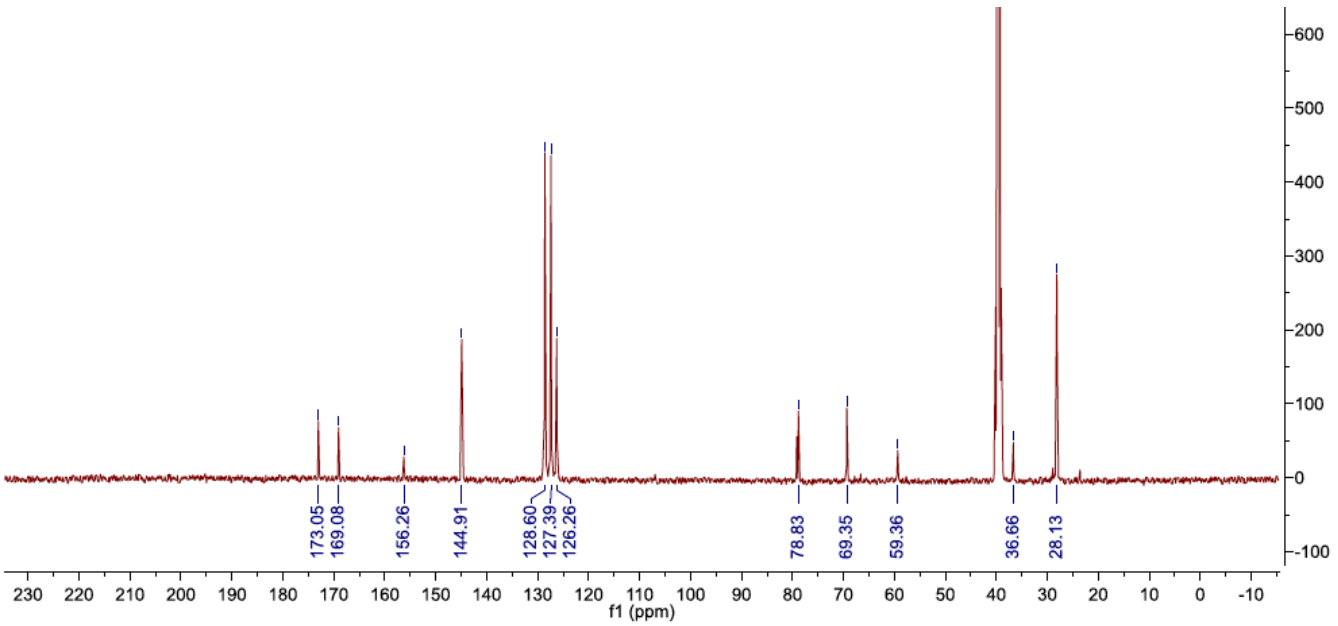


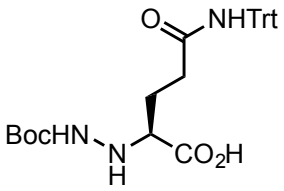
(6q)

^{1}H NMR 500 MHz (DMSO-d_6)



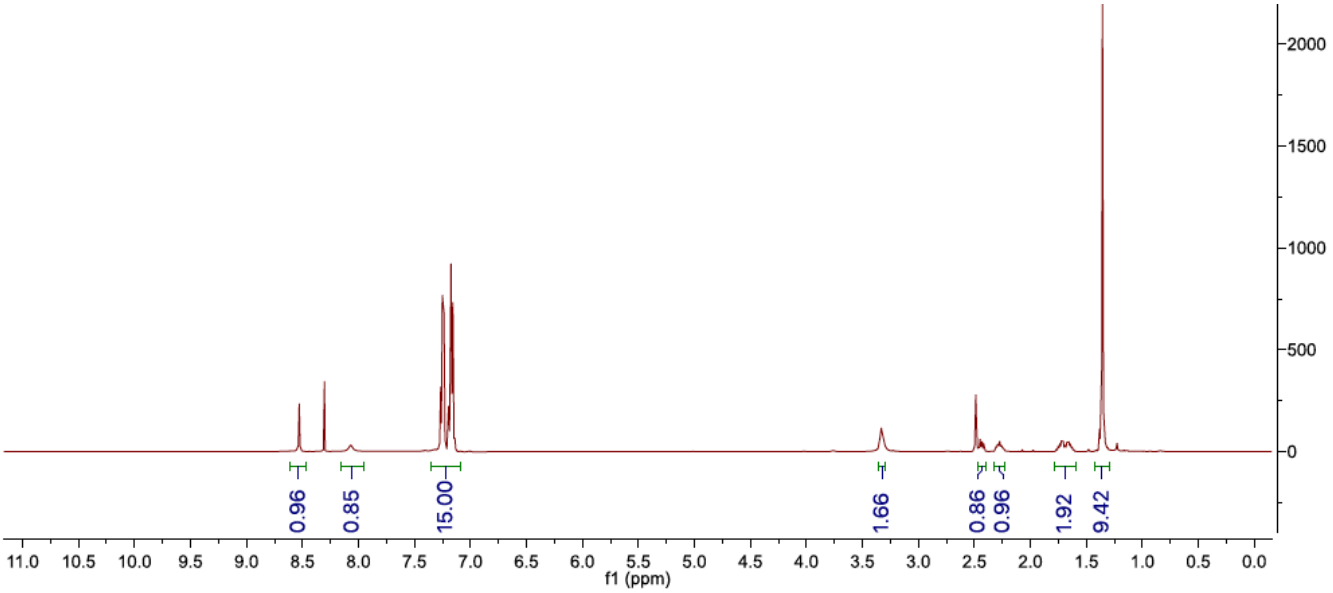
^{13}C NMR 101 MHz (DMSO-d_6)



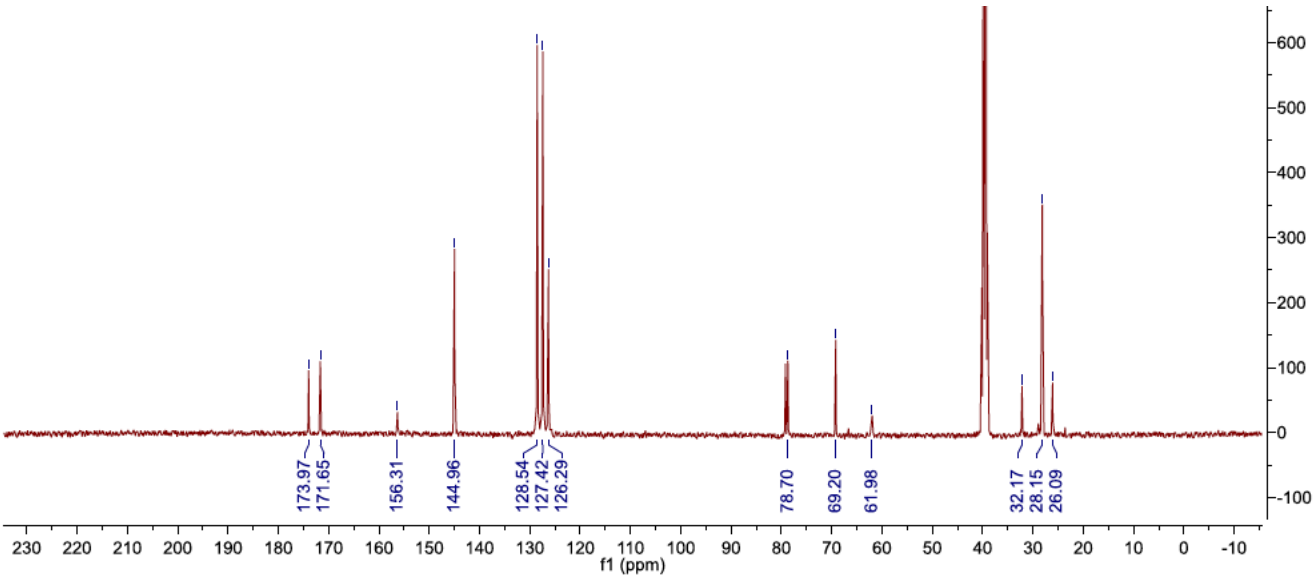


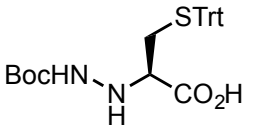
(6r)

^{1}H NMR 500 MHz (DMSO-d_6)



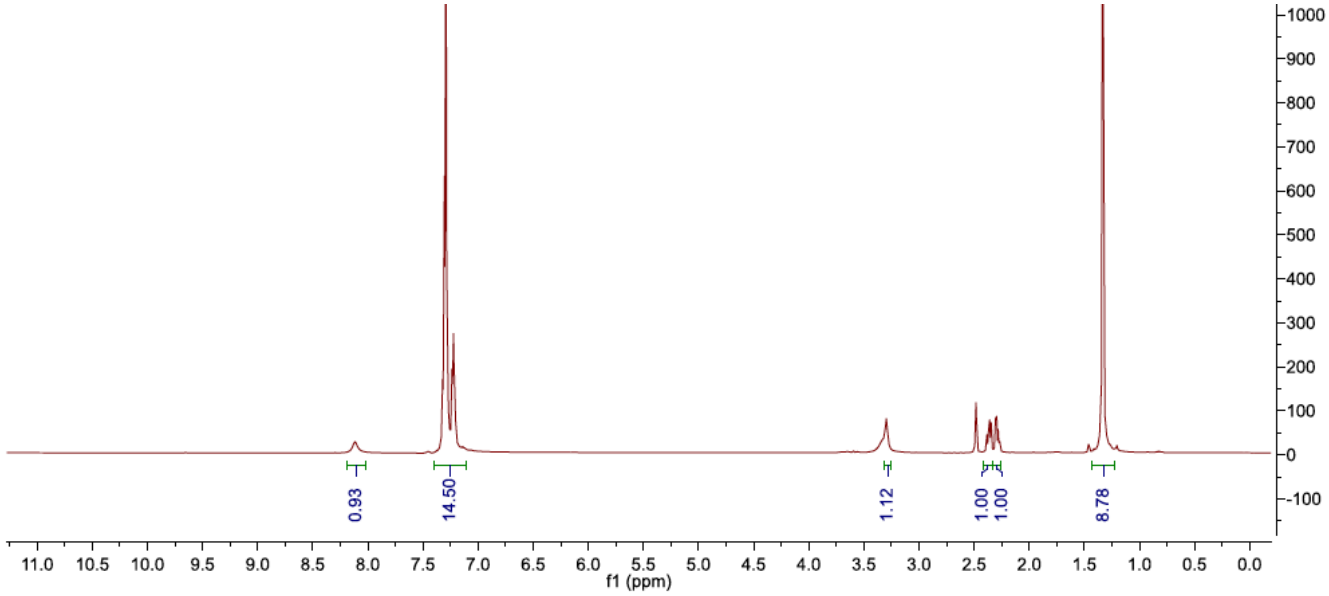
^{13}C NMR 101 MHz (DMSO-d_6)



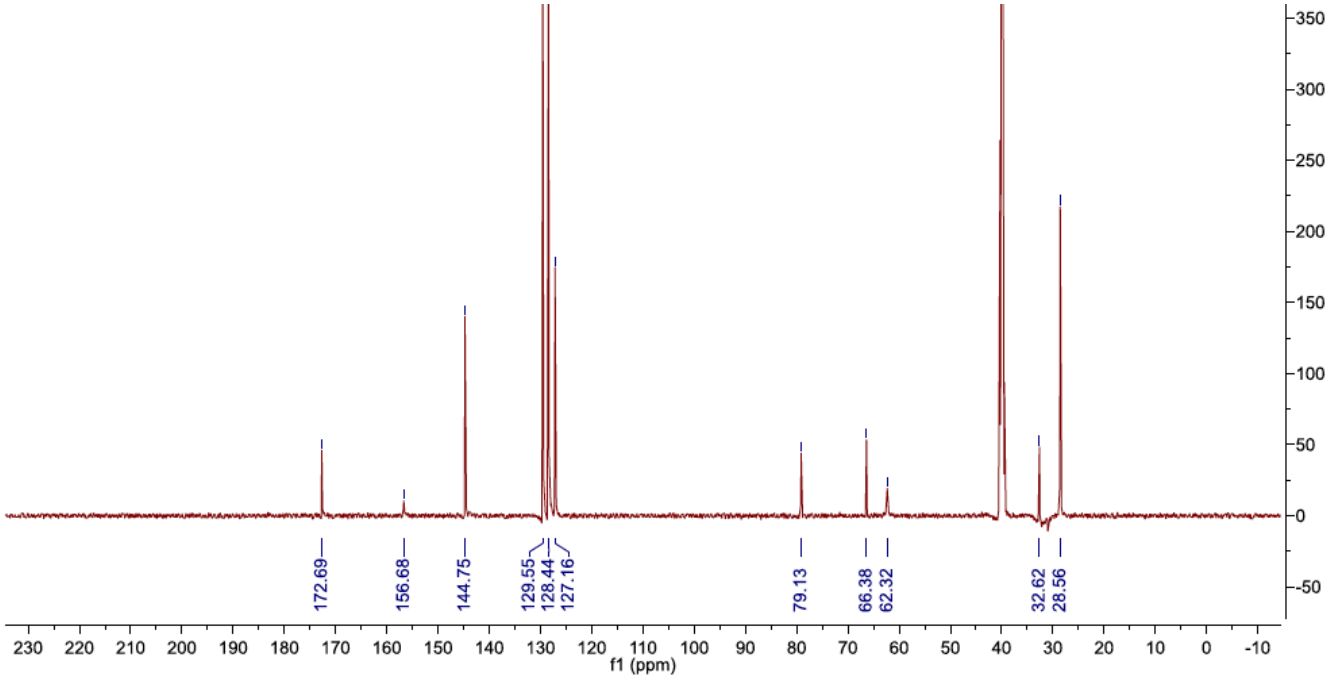


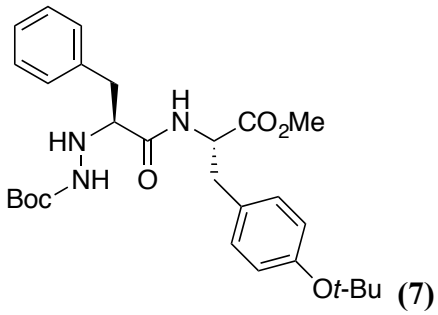
(6s)

^{1}H NMR 500 MHz (DMSO-d_6)



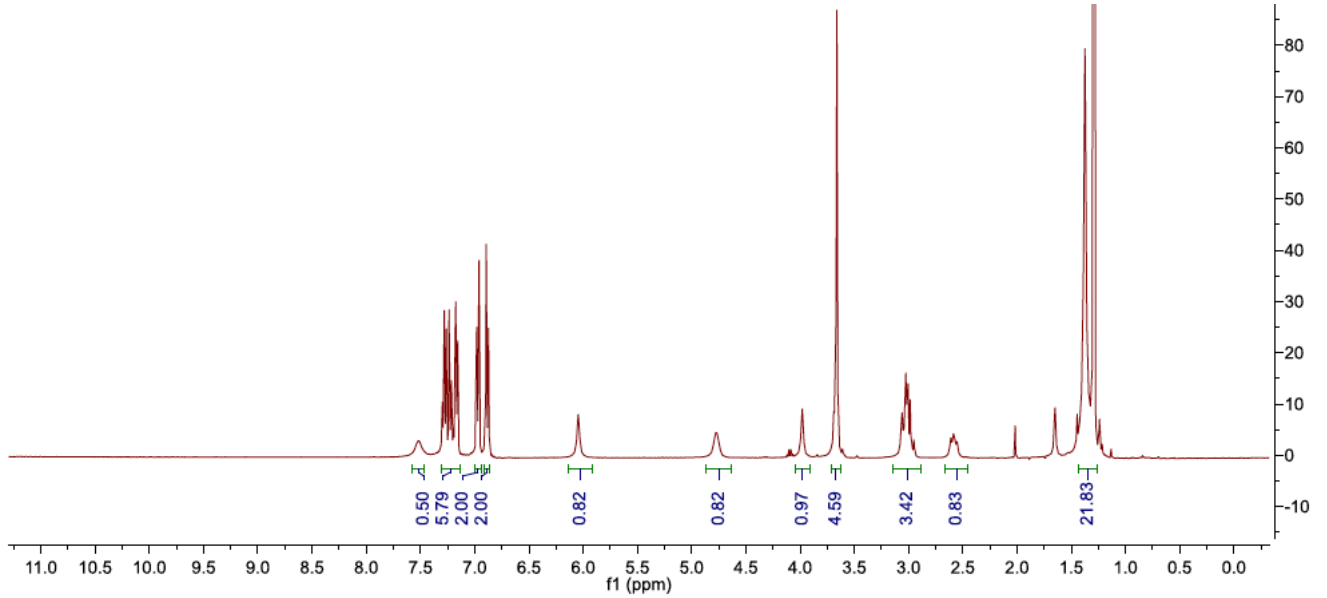
^{13}C NMR 126 MHz (DMSO-d_6)



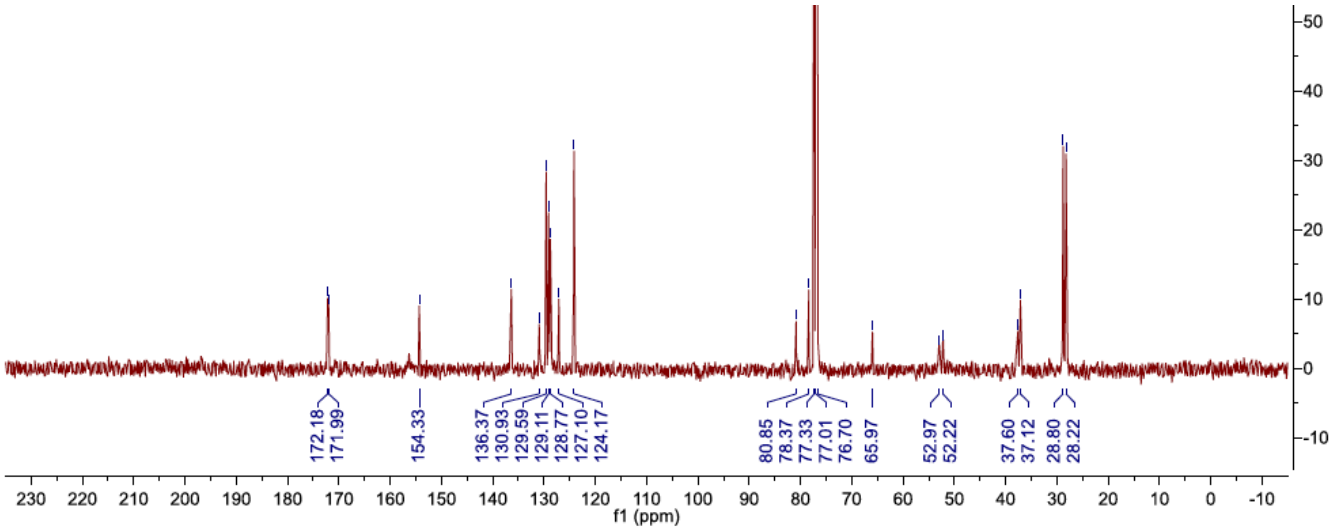


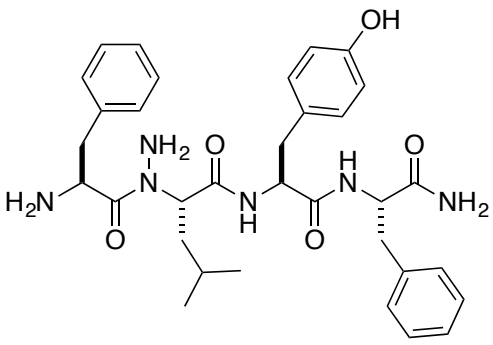
(7)

^{1}H NMR 400 MHz ($CDCl_3$)



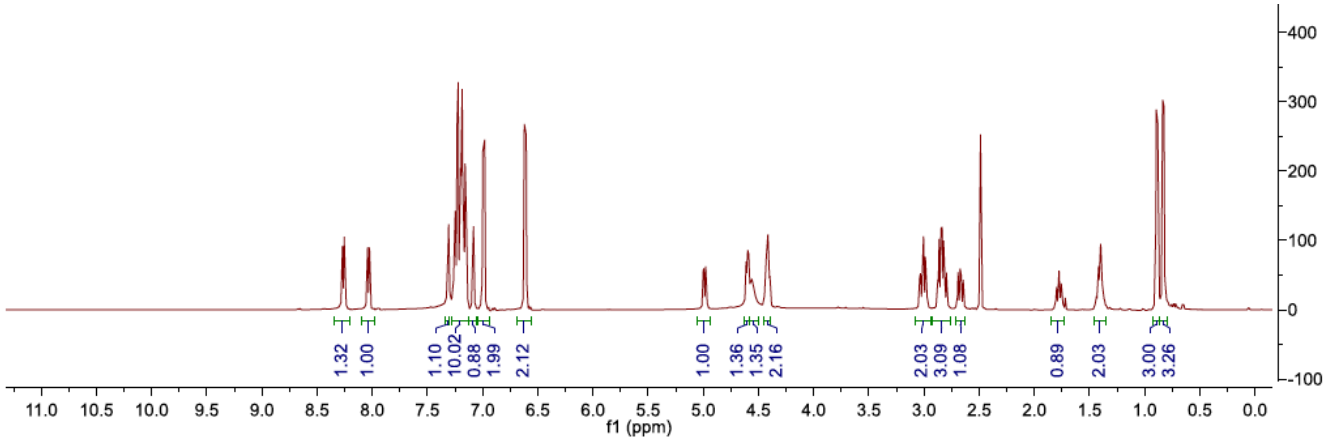
^{13}C NMR 101 MHz ($CDCl_3$)



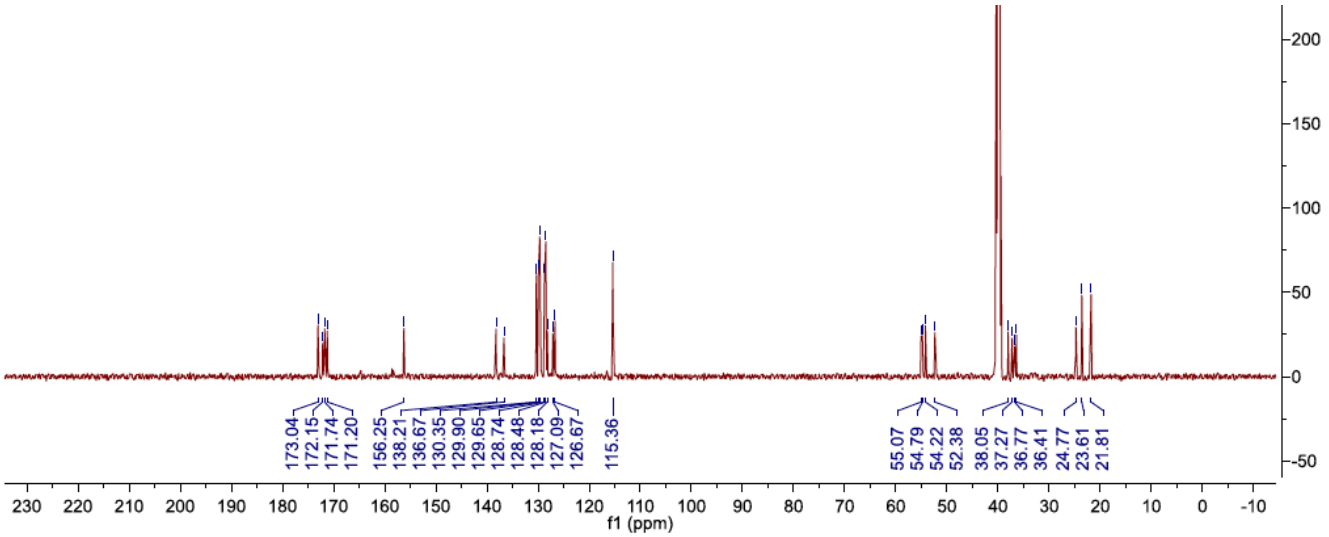


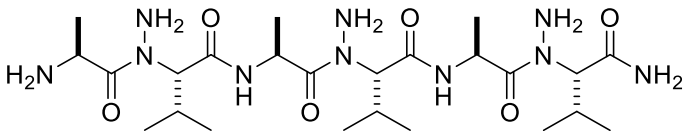
(11)

^{1}H NMR 500 MHz (DMSO-*d*6)



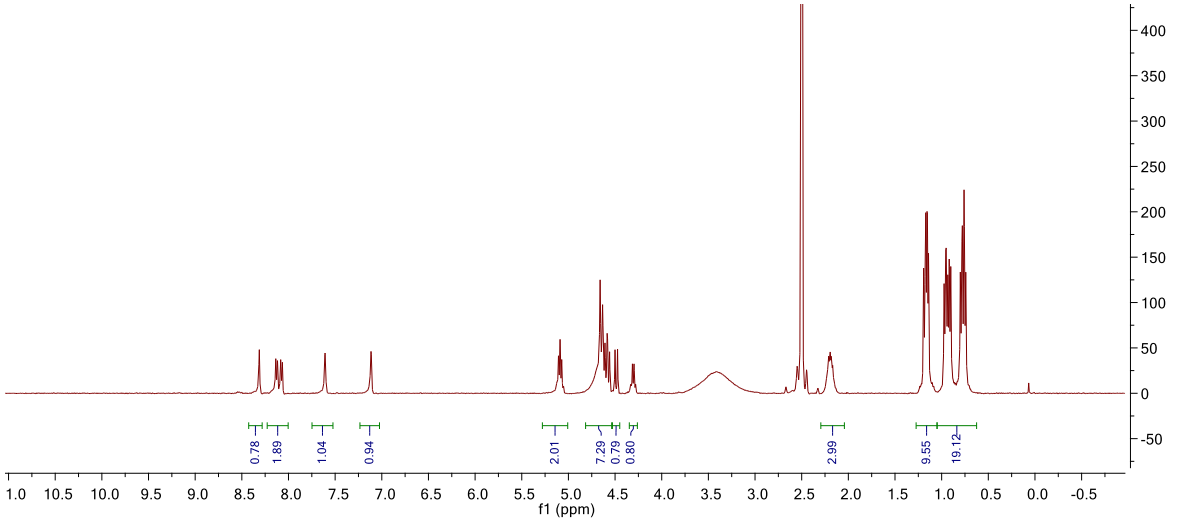
^{13}C NMR 126 MHz (DMSO-*d*6)



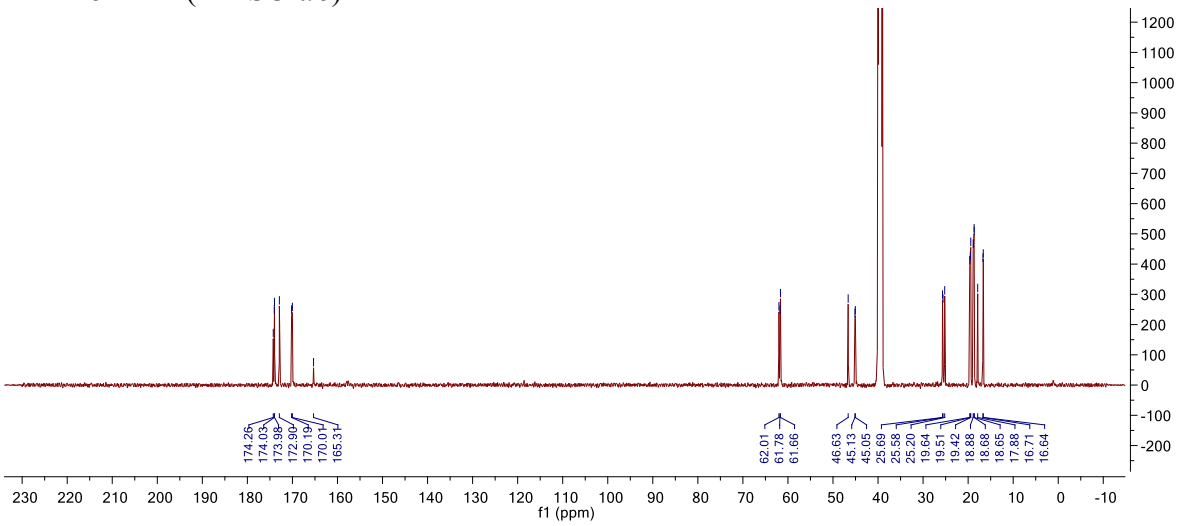


(**13**)

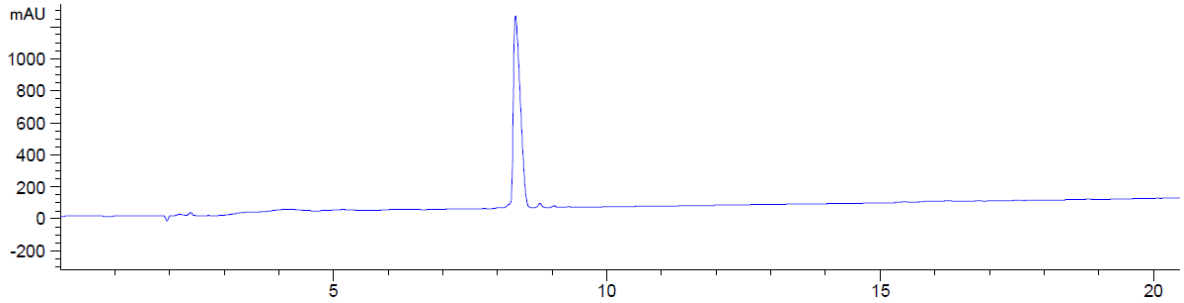
^{1}H NMR 500 MHz (DMSO-*d*6)

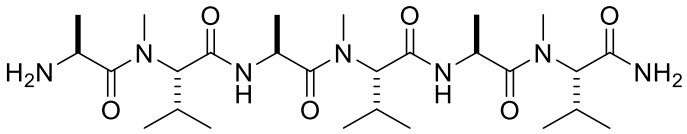


^{13}C NMR 126 MHz (DMSO-*d*6)



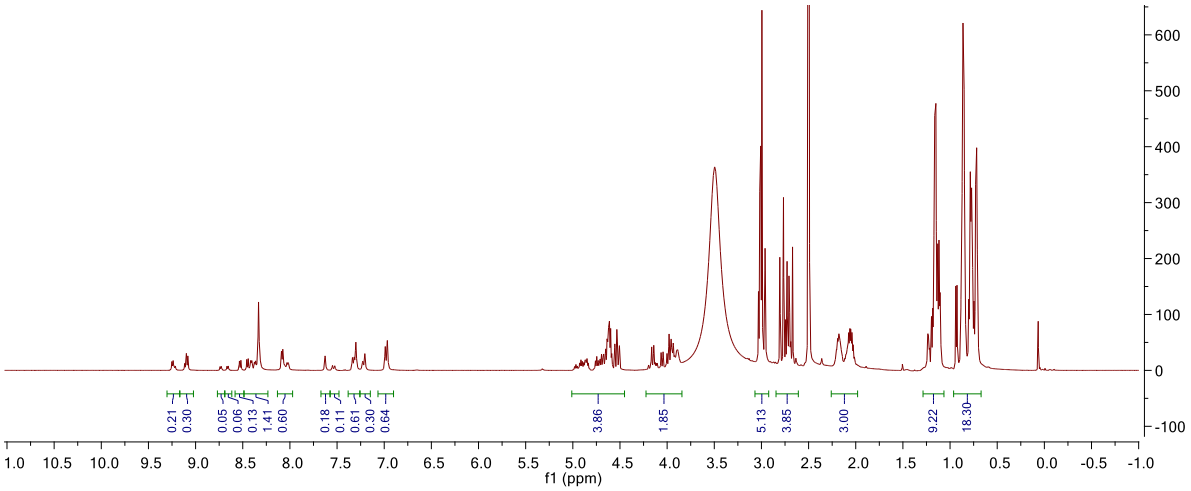
RP-HPLC (C_{12} column, 0-30% MeCN in 0.1M aq. HCO_2H linear gradient)



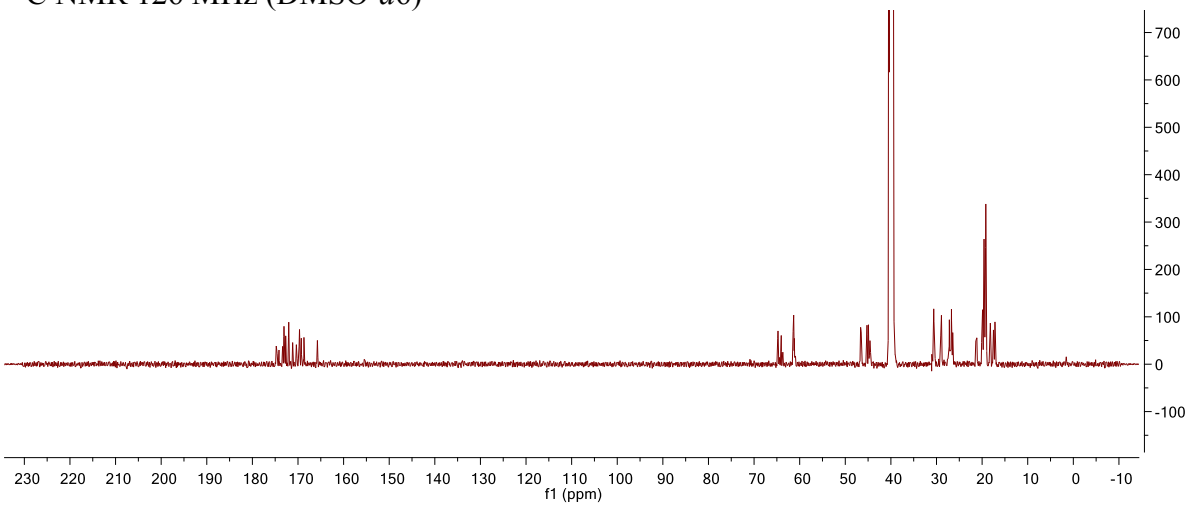


(**14**)

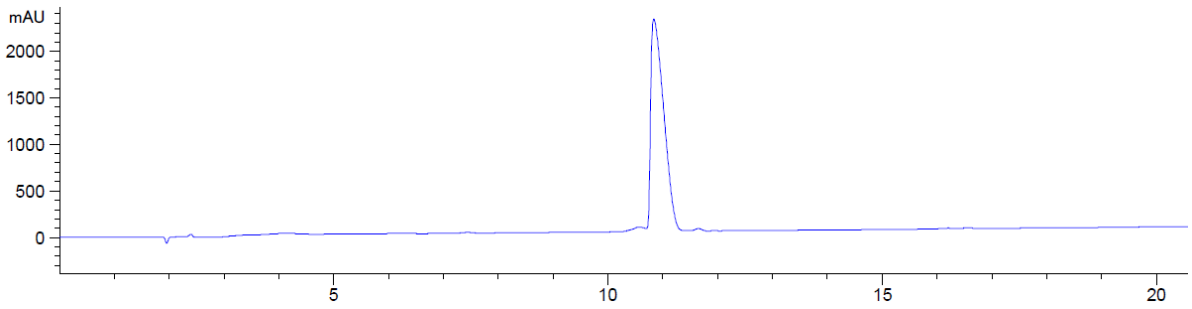
^{1}H NMR 500 MHz (DMSO-*d*6)



^{13}C NMR 126 MHz (DMSO-*d*6)



RP-HPLC (C_{12} column, 0-30% MeCN in 0.1M aq. HCO_2H linear gradient)



X-RAY DIFFRACTION FOR COMPOUND 2

The X-ray diffraction data for compound **2** were measured on Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu K_α INCOATEC ImuS micro-focus source (λ = 1.54178 Å). Indexing was performed using *APEX3* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01 [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX3 [1]. Structures were solved using SHELXS-97 (direct methods) and refined using SHELXL-2014 [4-6] (full-matrix least-squares on F^2) through OLEX2 interface program [7]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of –CH, -CH_3, groups were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2[1.5]Ueq(-CH,-CH3]). Hydrogen atoms of –NH- groups were found from difference Fourier map and were refined with distance restraint and Uiso(H)=1.5[-N-].

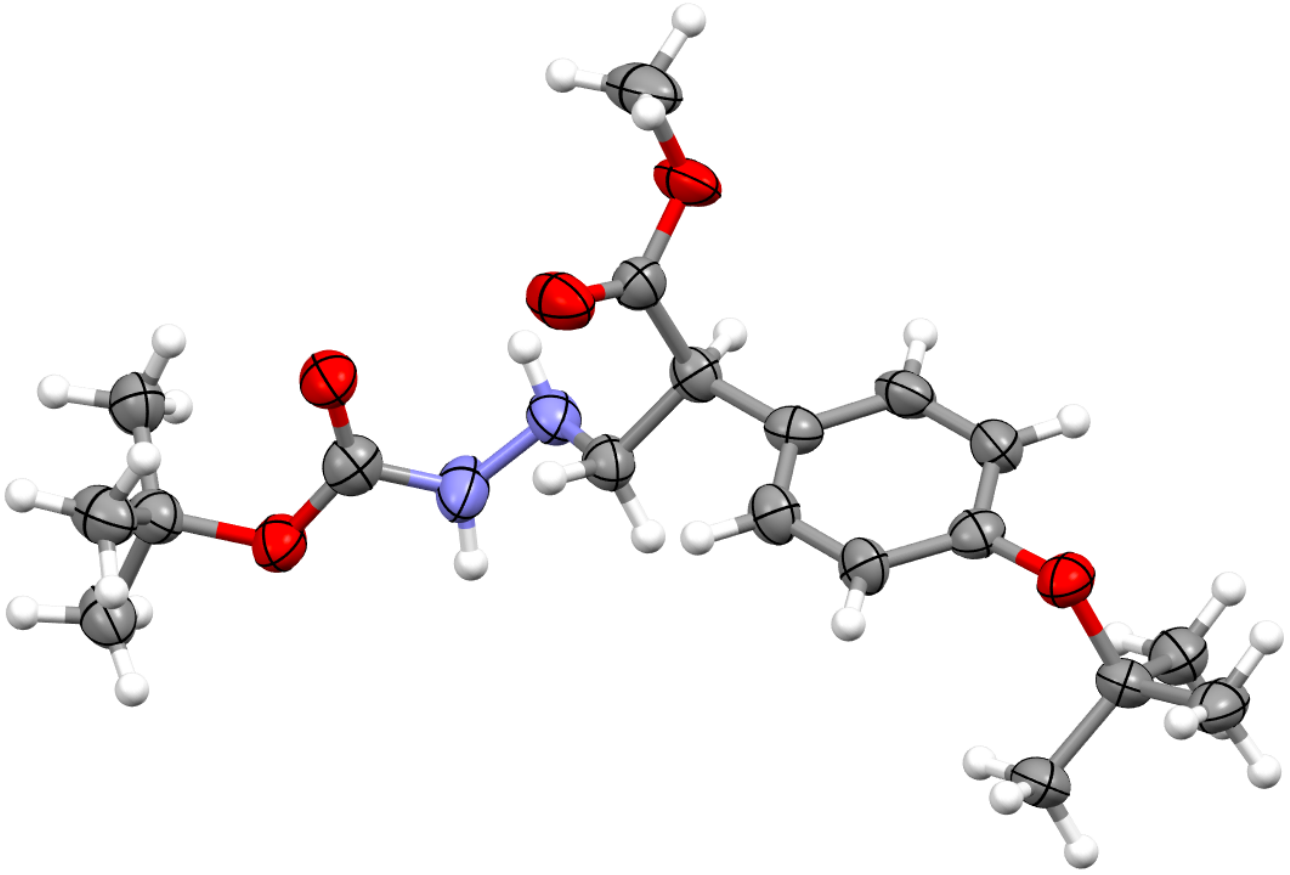


Figure 1. Thermal ellipsoid plot of the X-ray diffraction structure of **2** (ellipsoid contours shown at 50% probability level with hydrogens fixed as 0.25 Å spheres).

Crystal data and structure refinement for 2	
Identification code	BK_01_017_0m
Empirical formula	$C_{19}H_{30}N_2O_5$
Formula weight	366.45
Temperature/K	99.99
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	6.0244(4)
b/Å	16.4432(10)
c/Å	20.5214(13)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2032.9(2)
Z	4
ρ_{calc}g/cm^3	1.197
μ/mm^{-1}	0.707
F(000)	792.0
Crystal size/mm^3	0.12 × 0.03 × 0.01
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.888 to 133.204
Index ranges	$-5 \leq h \leq 6$, $-19 \leq k \leq 19$, $-24 \leq l \leq 24$
Reflections collected	8097
Independent reflections	3421 [R_{int} = 0.0685, R_{sigma} = 0.0868]
Data/restraints/parameters	3421/2/248
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0704, wR_2 = 0.1644
Final R indexes [all data]	R_1 = 0.1085, wR_2 = 0.1892
Largest diff. peak/hole / e Å^{-3}	0.23/-0.26
Flack parameter	-0.1(4)

[1] Bruker (2016). *APEX3* (Version 2015.9). Bruker AXS Inc., Madison, Wisconsin, USA.
[2] Bruker (2016) SAINT V8.35A. Data Reduction Software.
[3] Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction.* University of Gottingen, Germany.
[4] Sheldrick, G.M. (1997) SHELXL-97. Program for the Refinement of Crystal
[5] Sheldrick, G.M. (1990) Acta Cryst. A46, 467-473
[6] Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.
[7] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341