Supporting Information for:

Redox Mediators in Visible Light Photocatalysis: Photocatalytic Radical Thiol-Ene Additions

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I. Bond Dissociation Energy Calculations

Homolytic N–H bond dissociation energies (BDEs) of anilines in Table 2 were calculated by subtracting the enthalpy at T = 298.15 K of the neutral molecules (closed shell) from the sum of the enthalpies of the nitrogen-centered radical (open shell) and that of the hydrogen atom as described by da Silva and coworkers.[1] Geometry optimizations for closed shell molecules were performed at B3LYP/6-311++G(3df,3pd) level of theory[2], radical species were optimized using unrestricted UB3LYP/6-311++G(3df,3pd) level of theory. The nature of each stationary point was evaluated by looking at harmonic vibrational frequencies and all structures were found to be at local minima. Following optimization, a single-point energy was calculated using the same level of theory and basis set; a restricted open-shell formalism ROB3LYP/6-311++G(3df,3pd) level of theory was used to generate enthalpies of radical species. All calculations were performed using Gaussian 03[3] and WebMO[4] software packages.

Table S1. Calculated enthalpy data for anilines.

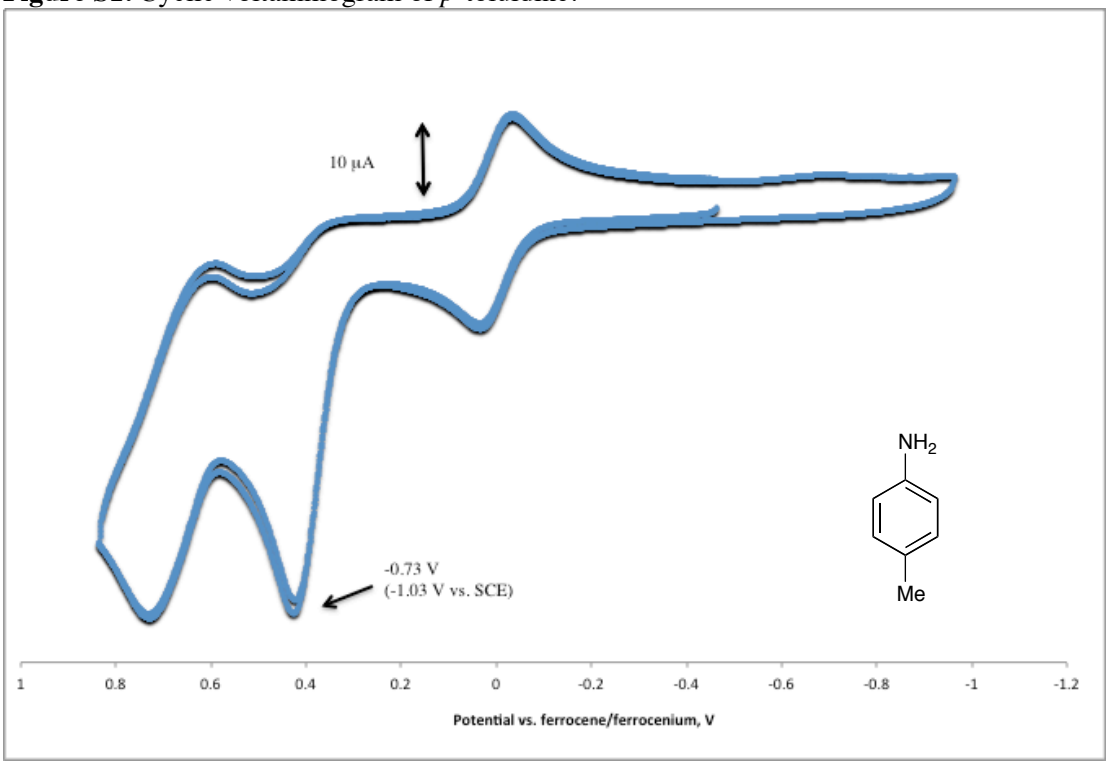
entry	substrate	H[a] closed shell (Hartree)	H[a] open shell (Hartree)	N–H BDE[b] (Hartree)	N-H BDE (kJ/mol)
1	1,4-phenylenediamine	-342.945497	-342.314049	0.130605	82.49
2	p-aminophenol	-362.831541	-362.196597	0.131551	84.69
3	p-anisidine	-402.114419	-401.479572	0.132987	84.63
4	1,2,3,4-tetrahydroquinoline	-404.287491	-403.654607	0.13495	83.39
5	p-toluidine	-326.887056	-326.248522	0.135047	86.94
6	N-methylaniline	-326.874556	-326.238078	0.136581	85.65
7	aniline	-287.586777	-286.945827	0.138637	88.45
8	diphenylamine	-518.620248	-517.989746	0.14075	81.90
9	4-bromoaniline	-2861.141086	-2860.500439	0.141053	88.26
10	4-nitroaniline	-492.164711	-491.517224	0.143551	92.55
11	1,2,3,4-tetrahydroisoquinoline	-404.276973	-403.633525	0.14759	90.02
12	4-aminopyridine	-303.644316	-302.995171	0.149248	93.59

[a]H = enthalpy. [b]Calculations were performed by including the computed enthalpy value of a hydrogen atom as H = -0.499897 Hartree.

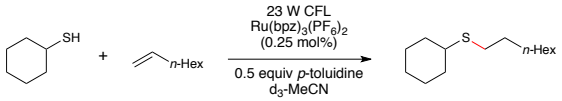
II. Cyclic Voltammetry

Oxidation potentials of the anilines in Table 2 were measured using cyclic voltammetry. Cyclic voltammetry measurements were performed with 0.015 mmol of substrate, 1.5 mmol of Bu_4NPF_6 as the supporting electrolyte in 15 mL of dry acetonitrile. The working electrode was a glassy carbon disk and a platinum wire was used for the counter electrode. A non-aqueous $Ag/AgNO_3$ electrode served as the reference electrode. A ferrocene/ferrocenium couple was employed as an internal standard and the measured potentials were subsequently corrected to a SCE reference. The first oxidation wave was used as the reported value in all cases. A representative example of the oxidation waves is shown in Figure S1.

Figure S1. Cyclic voltammogram of *p*-toluidine.



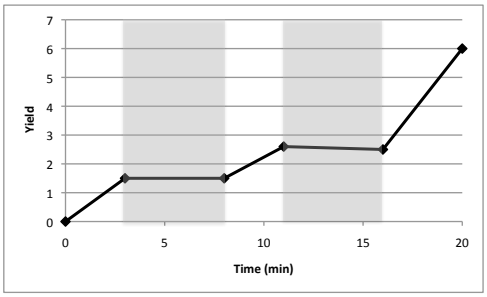
III. Dependence of Thiol-Ene Additions on Constant Irradiation



Into a 2 dram vial equipped with a stirbar were added 130 µL (0.828 mmol) octene, 41 µL (0.335 mmol) cyclohexanethiol, 17.9 mg (0.167 mmol) *p*-toluidine, 1.1 mg (1.0 µmol) $Ru(bpz)_3(PF_6)_2$, 0.67 mL acetonitrile-d_3, and trimethylsilylbenzene as internal standard. The vial was sealed with a Teflon cap and stirred in front of a 23 W CFL lightbulb for 16 min. Between 3–8 min and 11–16 min, light was excluded from the reaction by wrapping the vial with aluminum foil. The progress of the reaction was monitored by ^{1}H NMR at 3, 8, 11, and 16 min. These data, summarized in Figure S2 below, indicate that the progress of the reaction occurs only upon constant irradiation, verifying the photocatalytic nature of the reaction.

Figure S2. Dependence of Thiol-Ene Addition on Constant Irradiation

Time	Yield
0 min	0%
3 min	1.5%
8 min	1.5%
11 min	2.6%
16 min	2.5%
20 min	6%



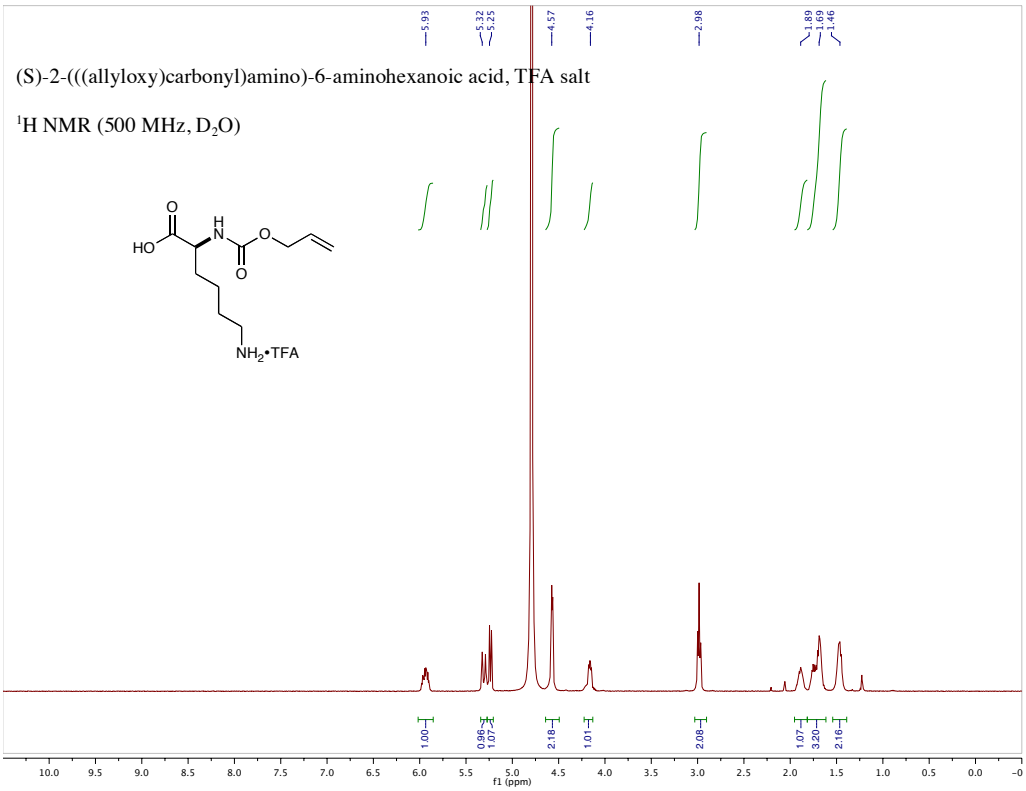
IV. References

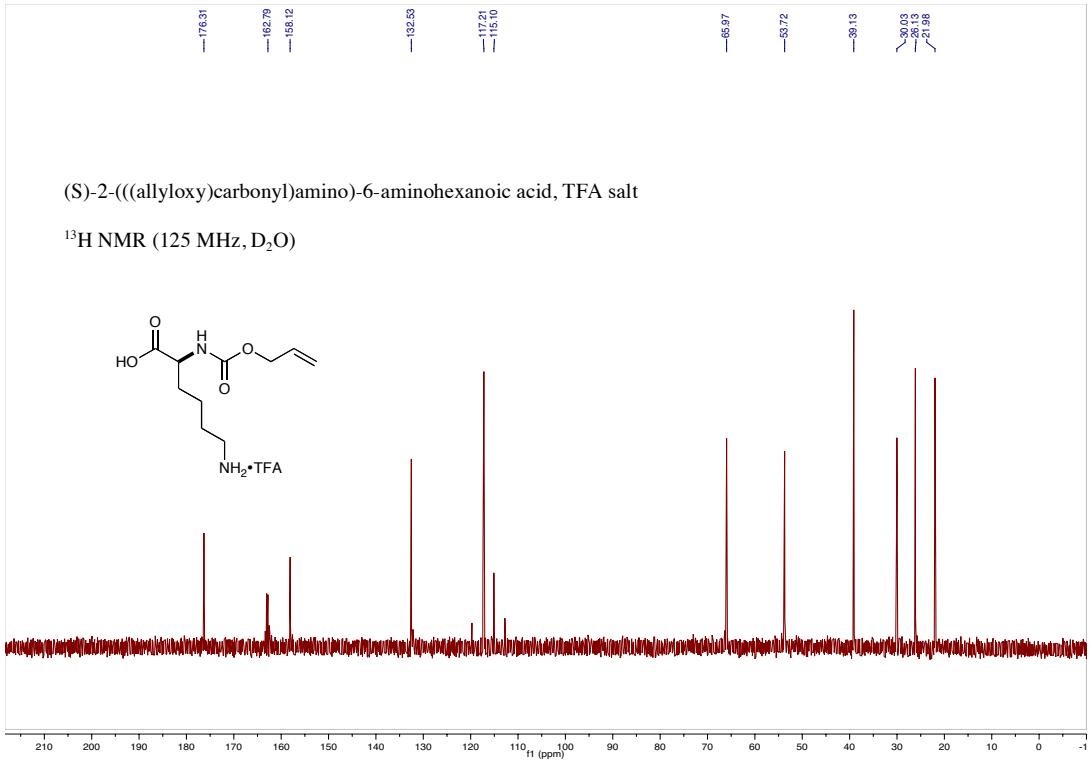
[1] Gomes, J. R. B.; Ribeiro da Silva, M. D. M. C.; Ribeiro da Silva, M. a. V. *J. Phys. Chem. A* **2004**, *108*, 2119–2130.

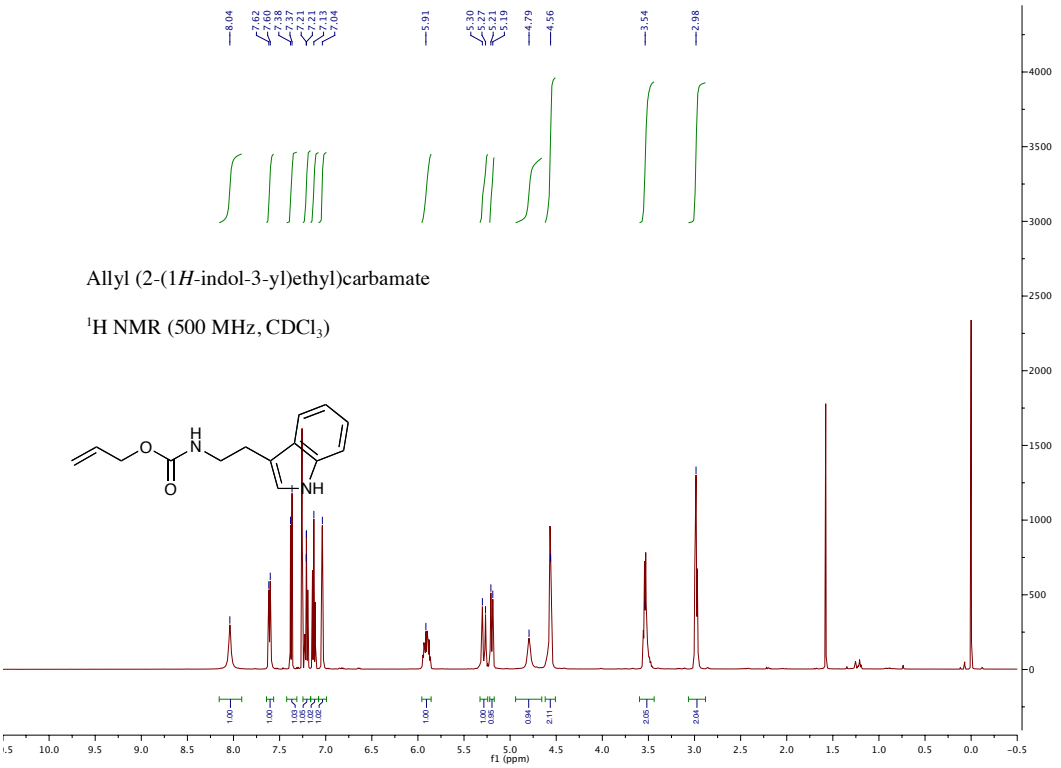
[2] As described in ref 1, the basis sets were obtained from the Extensible Computational Chemistry Environmental Basis Set Database, http://www.emsl.pnl.gov: 2080/forms/basisform.html Version 2/12/03.

[3] Gaussian 09, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson,G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2010.

[4] Schmidt, J.R., Polik, W.F. *WebMO Enterprise*, version 13.0, WebMO LLC: Holland, MI, USA, available from *http://www.webmo.net* (accessed March 2013).

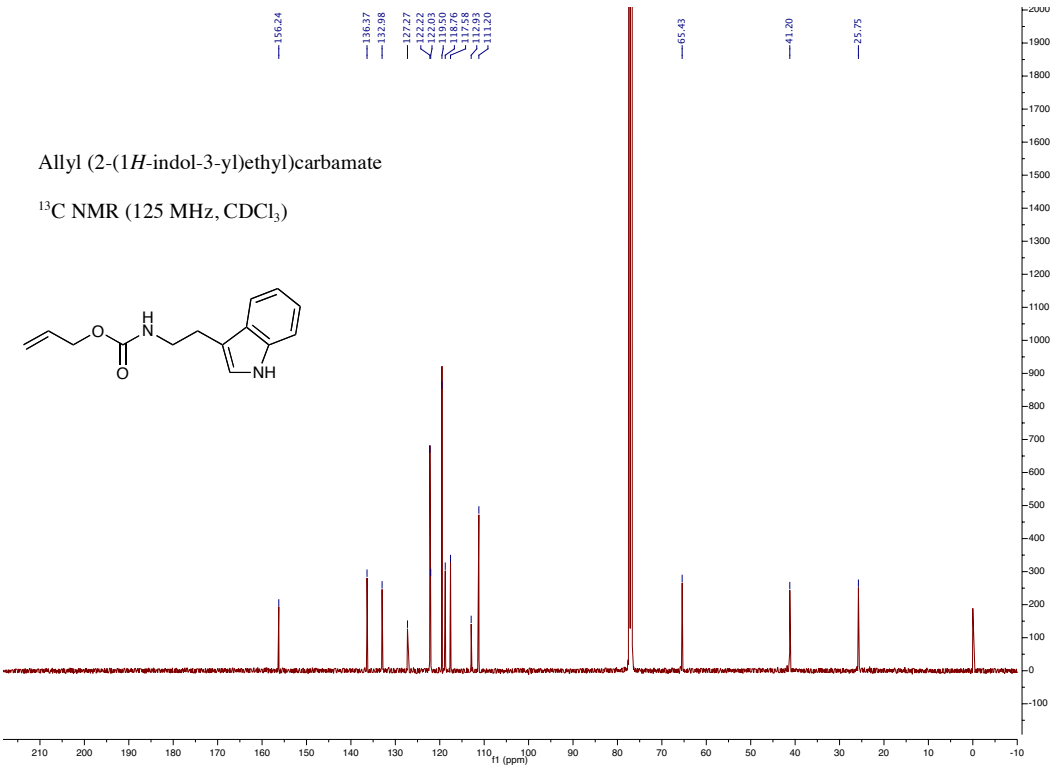

(S)-2-(((allyloxy)carbonyl)amino)-6-aminohexanoic acid, TFA salt
1H NMR (500 MHz, D2O)
HO
O
H
N
O
O
NH2•TFA
5.93
5.32
5.25
4.57
4.16
2.98
1.89
1.69
1.46
1.00
0.96
1.07
2.18
1.01
2.08
1.07
3.20
2.16
f1 (ppm)


(S)-2-(((allyloxy)carbonyl)amino)-6-aminohexanoic acid, TFA salt
13H NMR (125 MHz, D2O)
HO
O
H
N
O
O
NH2•TFA
176.31
162.79
158.12
132.53
117.21
115.10
65.97
53.72
39.13
30.03
26.33
21.98
f1 (ppm)



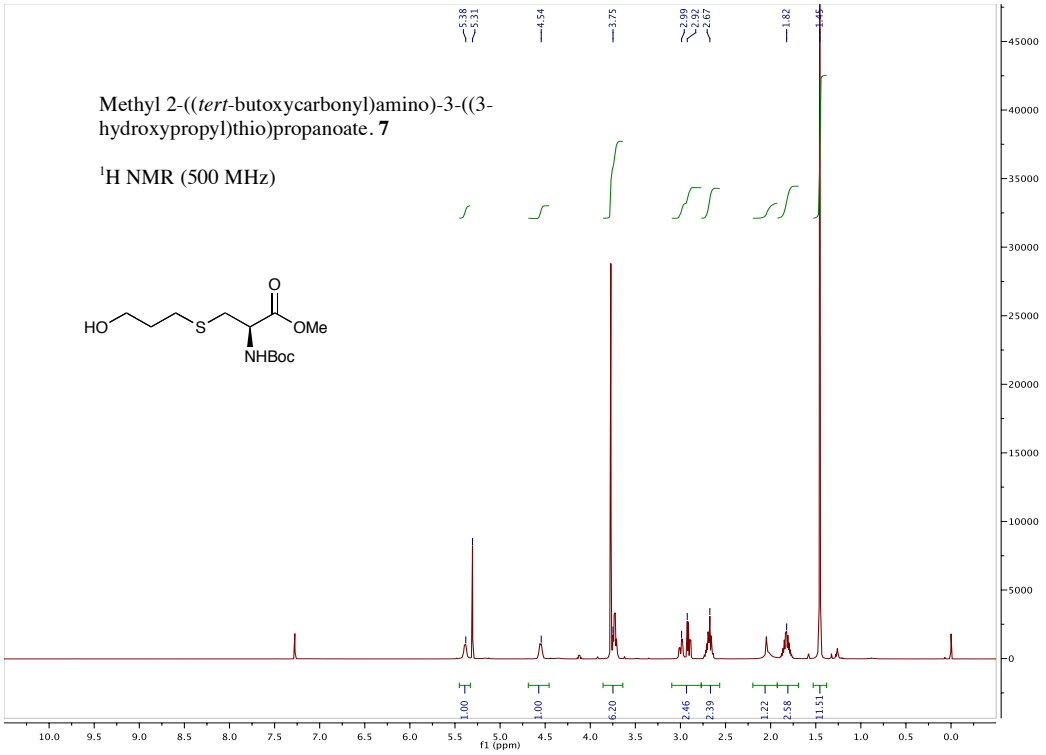
Allyl (2-(1*H*-indol-3-yl)ethyl)carbamate

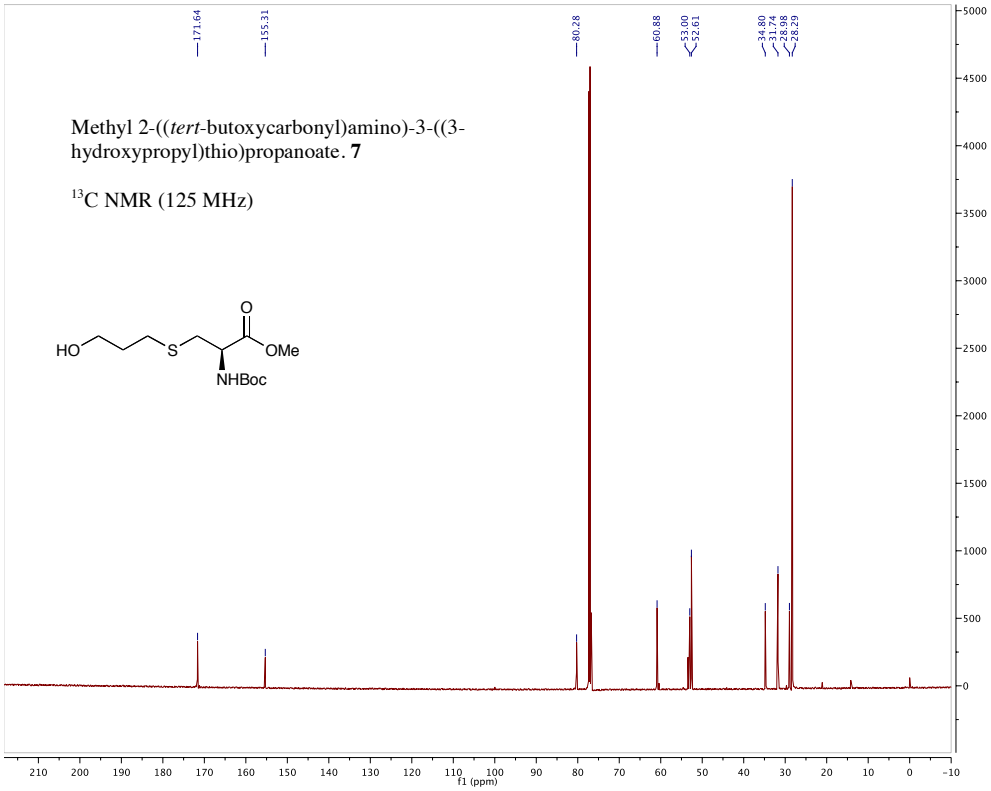
^{1}H NMR (500 MHz, $CDCl_3$)



Allyl (2-(1*H*-indol-3-yl)ethyl)carbamate

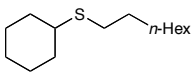
^{13}C NMR (125 MHz, $CDCl_3$)


Methyl 2-((tert-butoxycarbonyl)amino)-3-((3-hydroxypropyl)thio)propanoate. 7
1H NMR (500 MHz)
HO
S
O
OMe
NHBoc
5.38
5.31
4.54
3.75
2.99
2.93
2.67
1.82
1.45
1.00
1.00
6.20
2.46
2.39
1.22
2.58
11.51
f1 (ppm)


Methyl 2-((tert-butoxycarbonyl)amino)-3-((3-hydroxypropyl)thio)propanoate. 7
13C NMR (125 MHz)
HO
S
O
OMe
NHBoc
171.64
155.31
80.28
60.88
53.00
52.61
34.80
33.74
28.98
28.29
f1 (ppm)

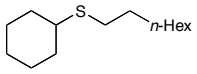
Cyclohexyl(octyl)sulfane (Table 3, **10**).

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



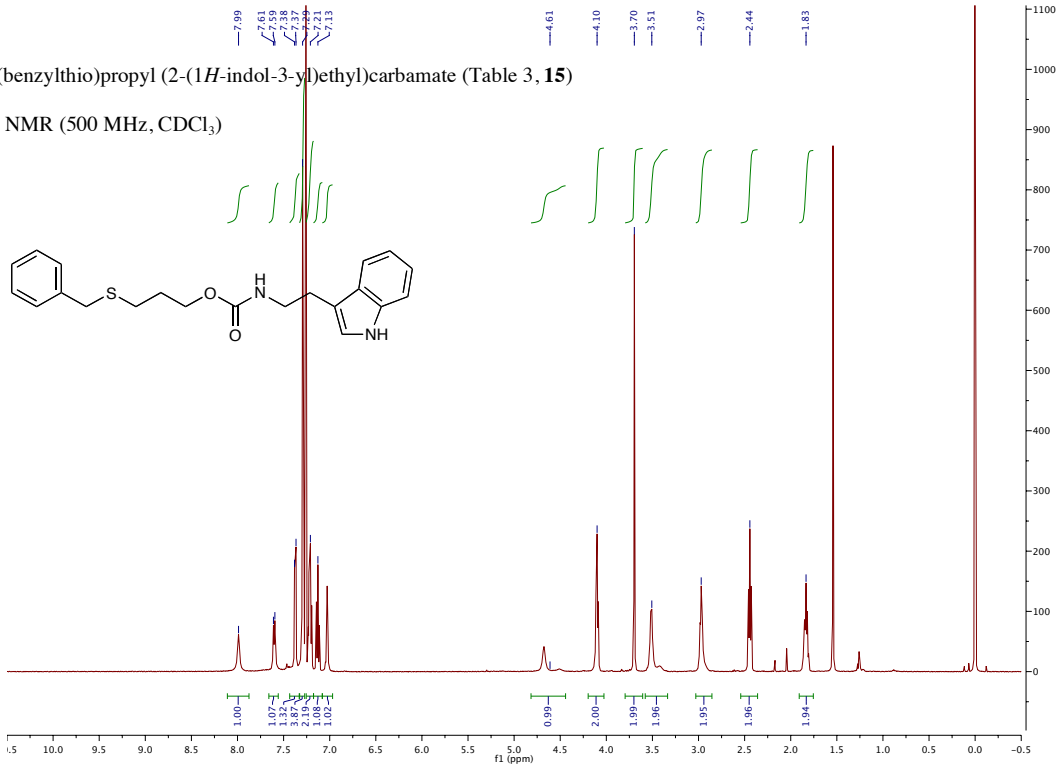
Cyclohexyl(octyl)sulfane (Table 3, **10**).

^{13}C NMR (125 MHz, $CDCl_3$)



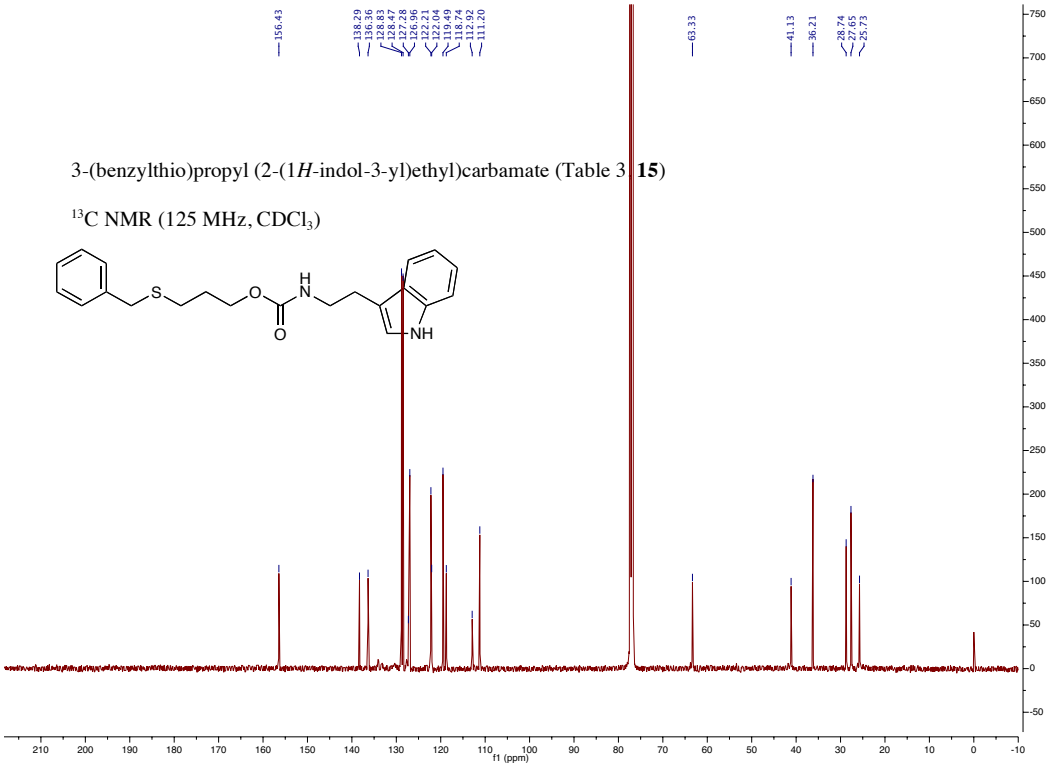
3-(benzylthio)propyl (2-(1*H*-indol-3-yl)ethyl)carbamate (Table 3, **15**)

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



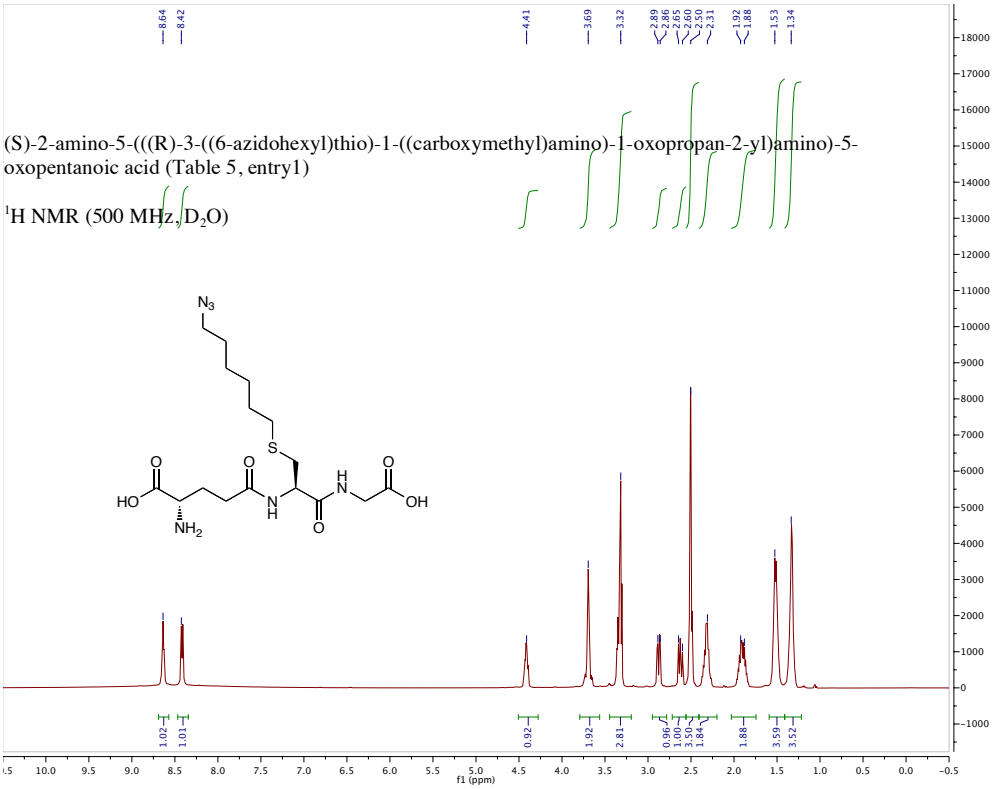
3-(benzylthio)propyl (2-(1*H*-indol-3-yl)ethyl)carbamate (Table 3, **15**)

^{13}C NMR (125 MHz, $CDCl_3$)



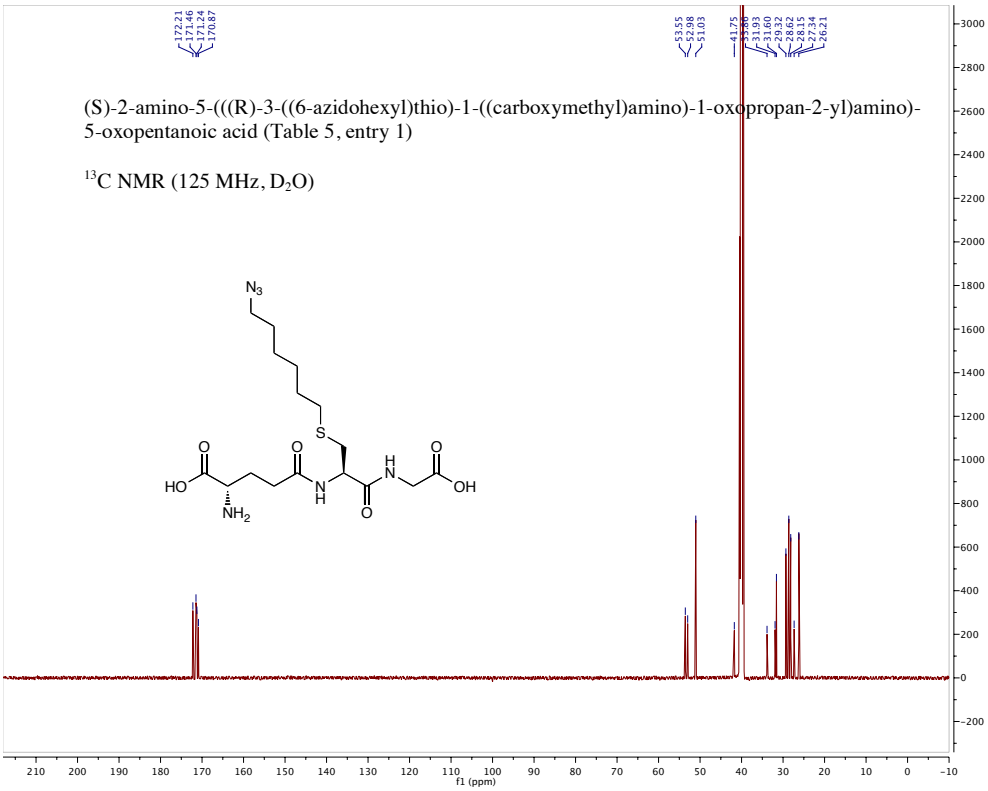
(S)-2-amino-5-(((R)-3-((6-azidohexyl)thio)-1-((carboxymethyl)amino)-1-oxopropan-2-yl)amino)-5-oxopentanoic acid (Table 5, entry1)

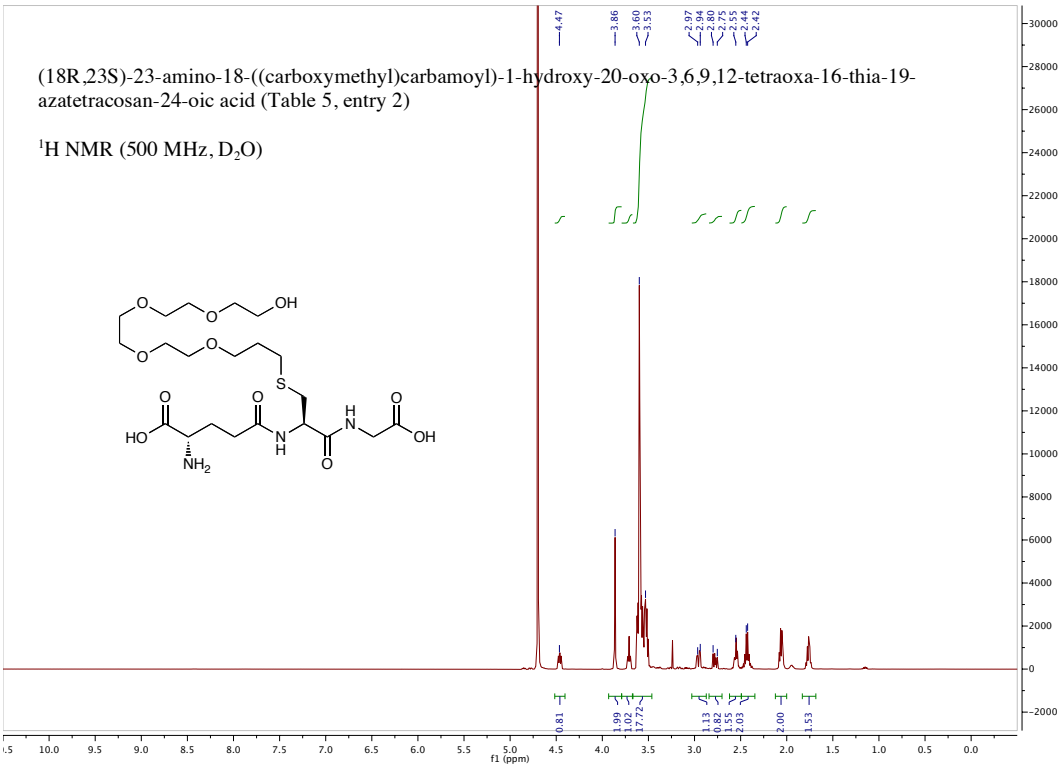
^{1}H NMR (500 MHz, D_2O)

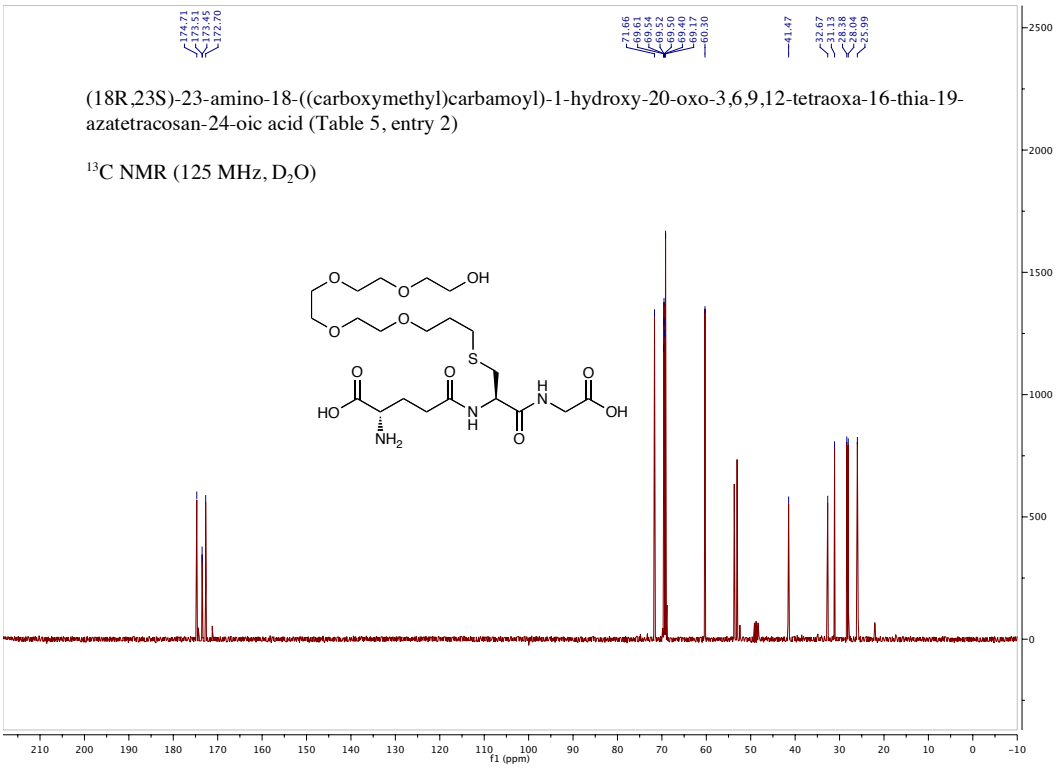


(S)-2-amino-5-(((R)-3-((6-azidohexyl)thio)-1-((carboxymethyl)amino)-1-oxopropan-2-yl)amino)-5-oxopentanoic acid (Table 5, entry 1)

^{13}C NMR (125 MHz, D_2O)

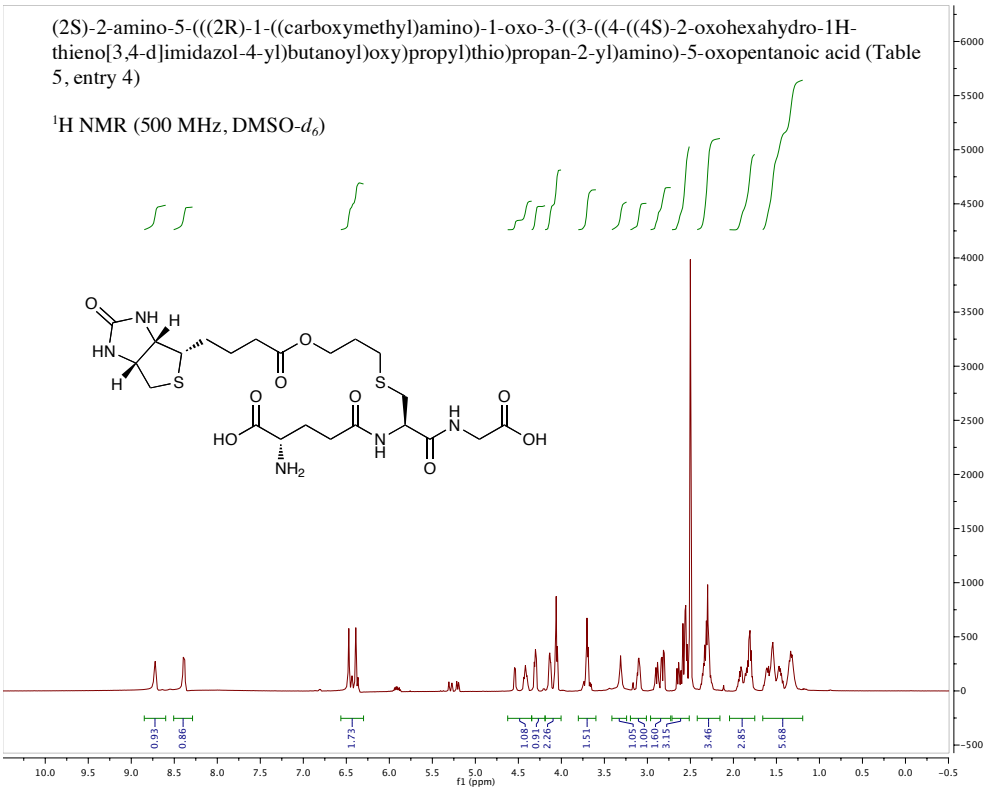



(18R,23S)-23-amino-18-((carboxymethyl)carbamoyl)-1-hydroxy-20-oxo-3,6,9,12-tetraoxa-16-thia-19-azatetracosan-24-oic acid (Table 5, entry 2)
^{1}H NMR (500 MHz, D_2O)
4.47
3.86
3.60
3.53
2.97
2.94
2.80
2.75
2.55
2.44
2.42
0.81
1.99
1.02
17.24
1.13
0.82
1.55
2.03
2.00
1.53
f1 (ppm)


(18R,23S)-23-amino-18-((carboxymethyl)carbamoyl)-1-hydroxy-20-oxo-3,6,9,12-tetraoxa-16-thia-19-azatetracosan-24-oic acid (Table 5, entry 2)
^{13}C NMR (125 MHz, D_2O)
174.71
173.51
173.45
172.70
71.66
69.61
69.54
69.52
69.50
69.40
69.17
60.30
41.47
32.67
31.13
28.38
28.04
25.99
f1 (ppm)

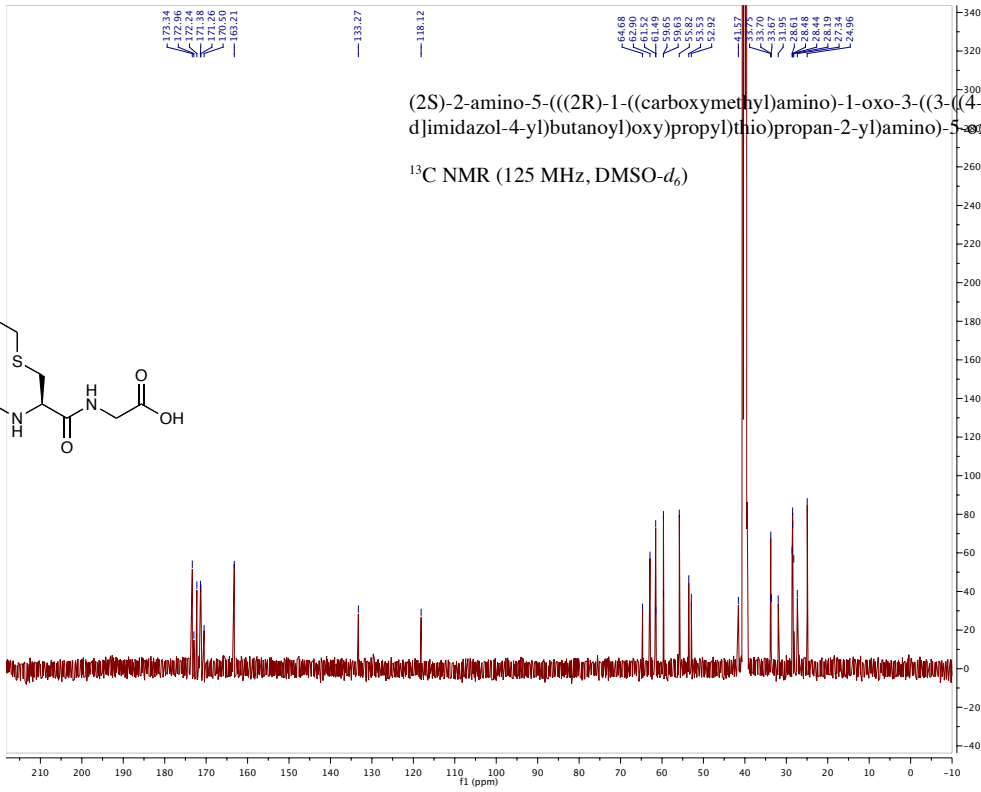
(2S)-2-amino-5-(((2R)-1-((carboxymethyl)amino)-1-oxo-3-((3-((4-((4S)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)butanoyl)oxy)propyl)thio)propan-2-yl)amino)-5-oxopentanoic acid (Table 5, entry 4)

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



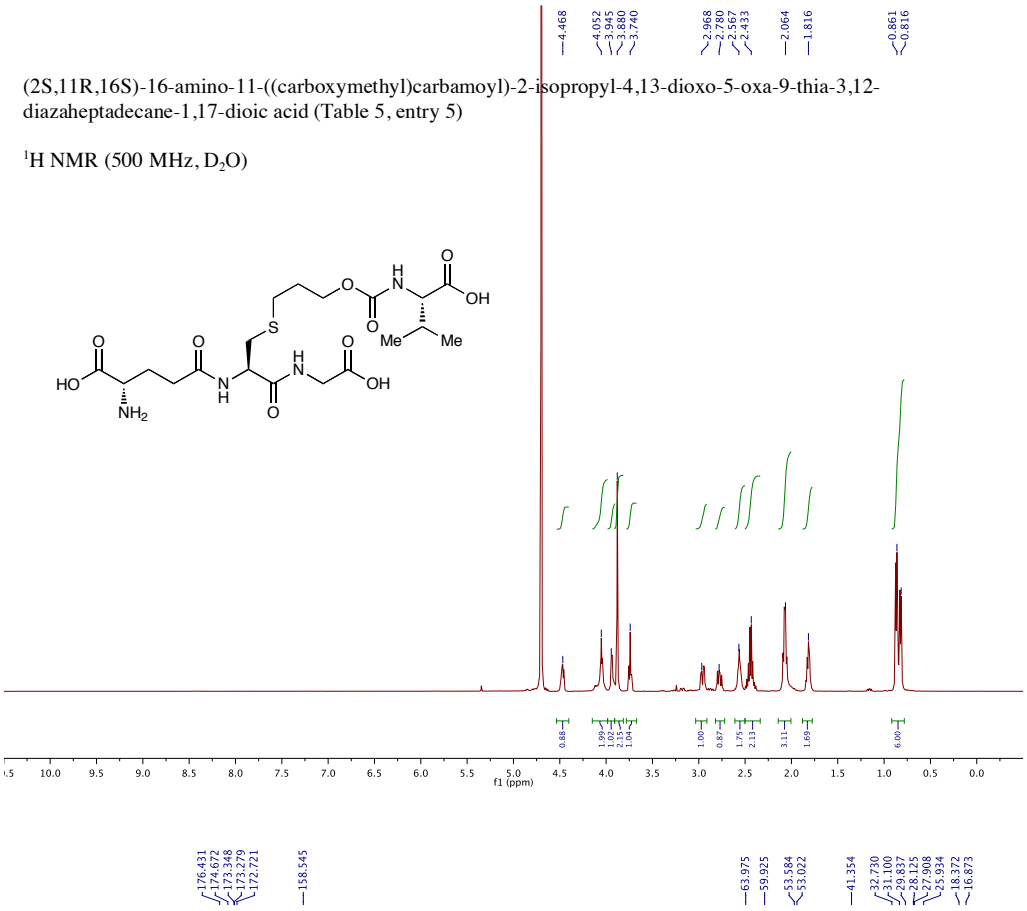
(2S)-2-amino-5-(((2R)-1-((carboxymethyl)amino)-1-oxo-3-((3-((4-((4S)-2-oxohexahydro-1H-thieno[3,4-d]imidazol-4-yl)butanoyl)oxy)propyl)thio)propan-2-yl)amino)-5-oxopentanoic acid (Table 5, entry 4)

^{13}C NMR (125 MHz, DMSO-d_6)



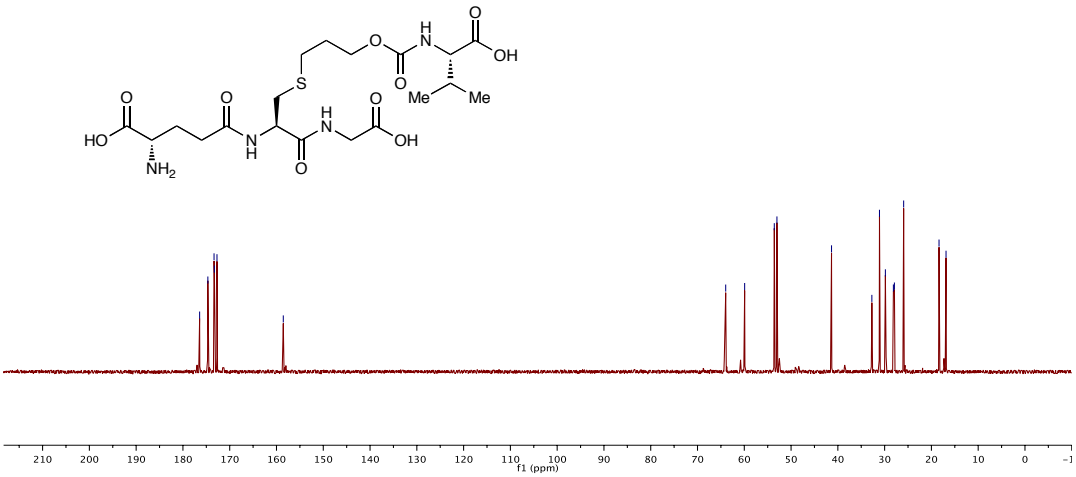
(2S,11R,16S)-16-amino-11-((carboxymethyl)carbamoyl)-2-isopropyl-4,13-dioxo-5-oxa-9-thia-3,12-diazaheptadecane-1,17-dioic acid (Table 5, entry 5)

^{1}H NMR (500 MHz, D_2O)



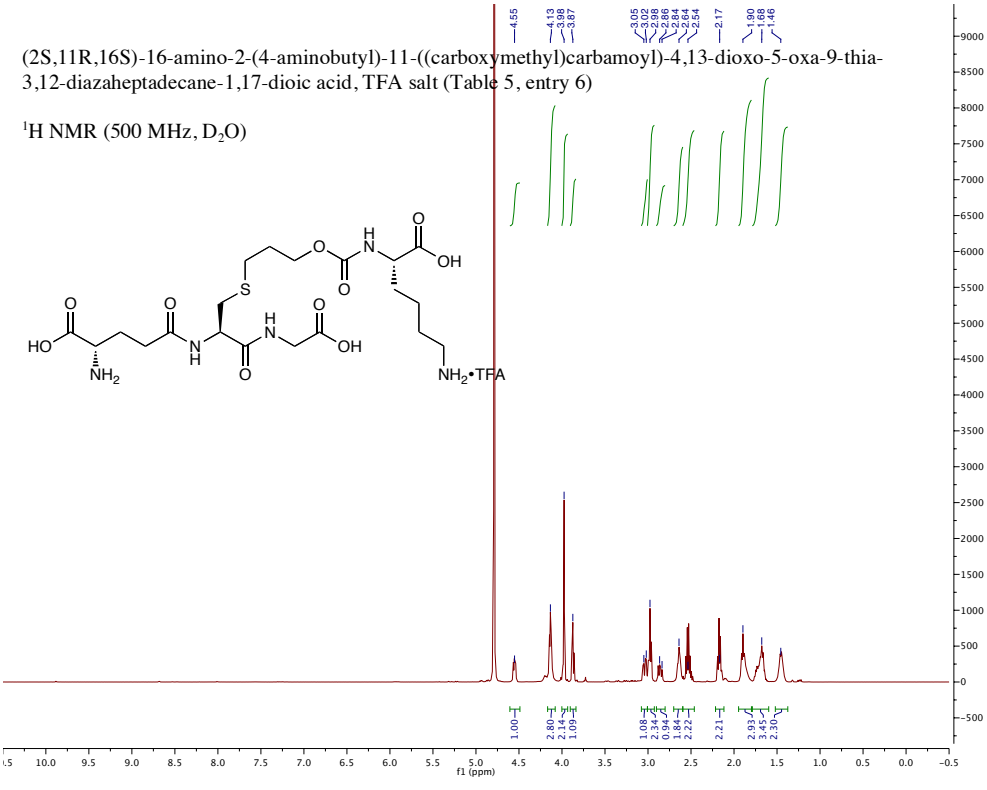
(2S,11R,16S)-16-amino-11-((carboxymethyl)carbamoyl)-2-isopropyl-4,13-dioxo-5-oxa-9-thia-3,12-diazaheptadecane-1,17-dioic acid (Table 4-5, entry 5)

^{13}C NMR (125 MHz, D_2O)



(2S,11R,16S)-16-amino-2-(4-aminobutyl)-11-((carboxymethyl)carbamoyl)-4,13-dioxo-5-oxa-9-thia-3,12-diazaheptadecane-1,17-dioic acid, TFA salt (Table 5, entry 6)

^{1}H NMR (500 MHz, D_2O)

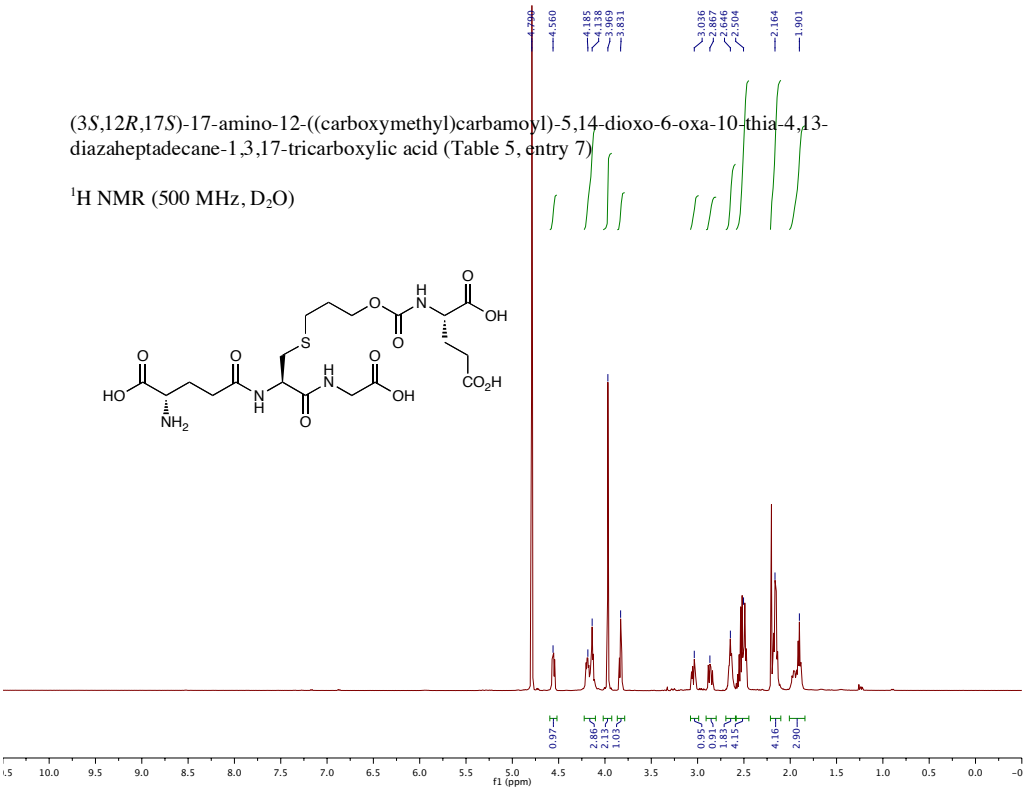


(2S,11R,16S)-16-amino-2-(4-aminobutyl)-11-((carboxymethyl)carbamoyl)-4,13-dioxo-5-oxa-9-thia-3,12-diazaheptadecane-1,17-dioic acid, TFA salt (Table 5, entry 6)

^{13}C NMR (125 MHz, D_2O)

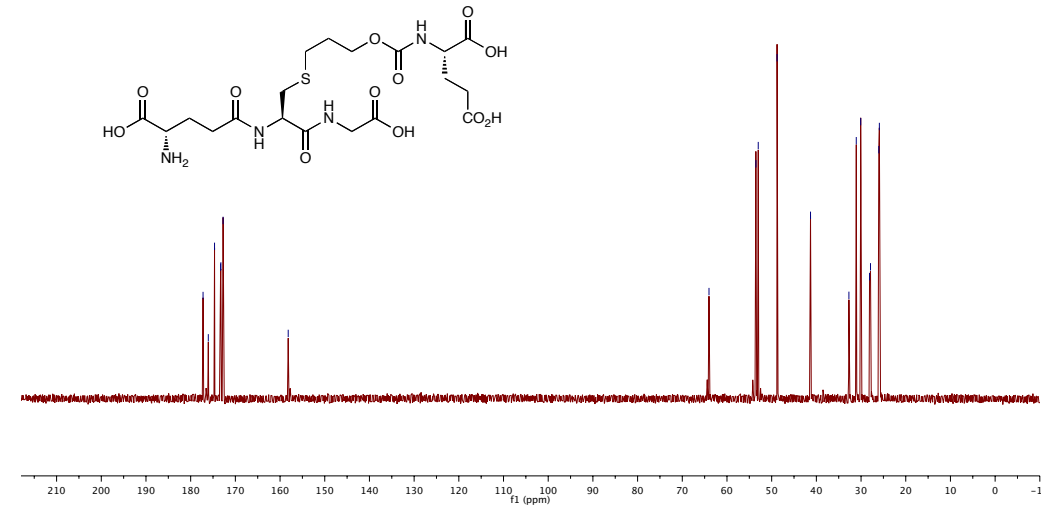
(3*S*,12*R*,17*S*)-17-amino-12-((carboxymethyl)carbamoyl)-5,14-dioxo-6-oxa-10-thia-4,13-diazaheptadecane-1,3,17-tricarboxylic acid (Table 5, entry 7)

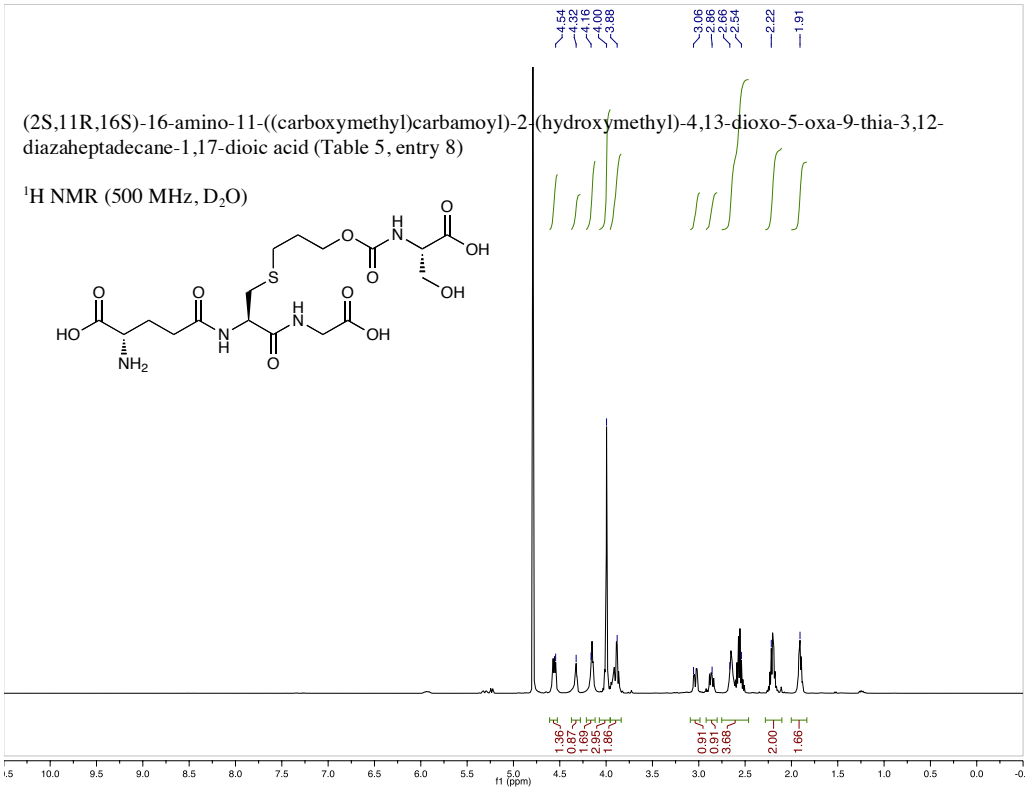
^{1}H NMR (500 MHz, D_2O)



(3*S*,12*R*,17*S*)-17-amino-12-((carboxymethyl)carbamoyl)-5,14-dioxo-6-oxa-10-thia-4,13-diazaheptadecane-1,3,17-tricarboxylic acid (Table 5, entry 7)

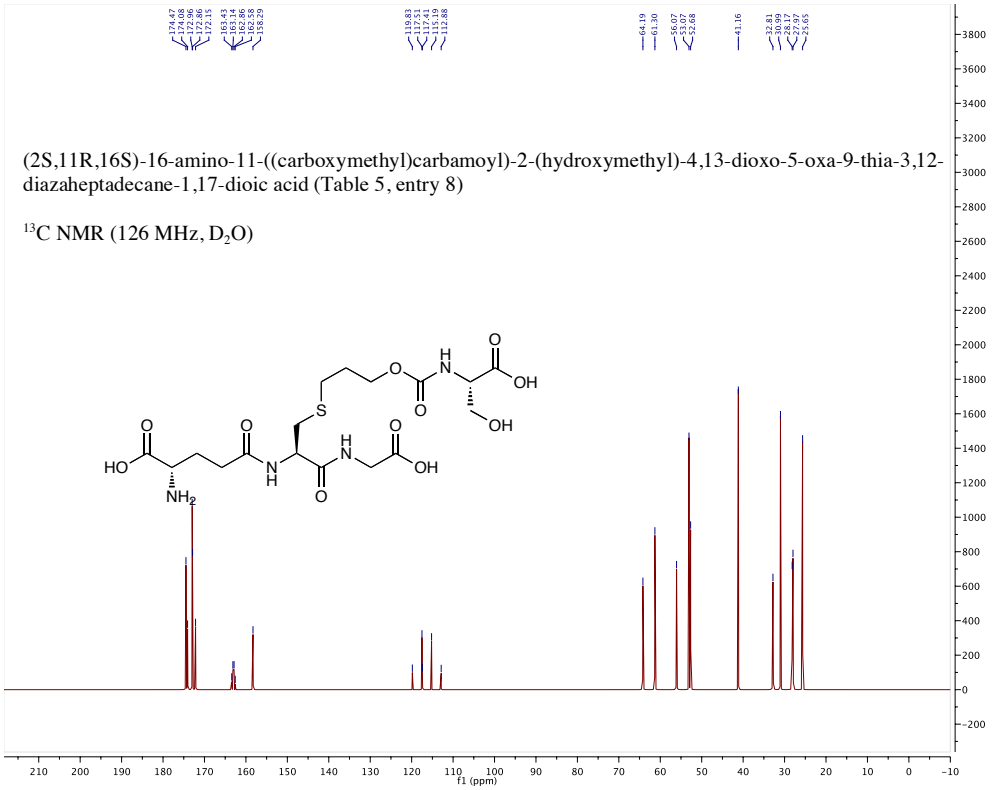
^{13}C NMR (125 MHz, D_2O)





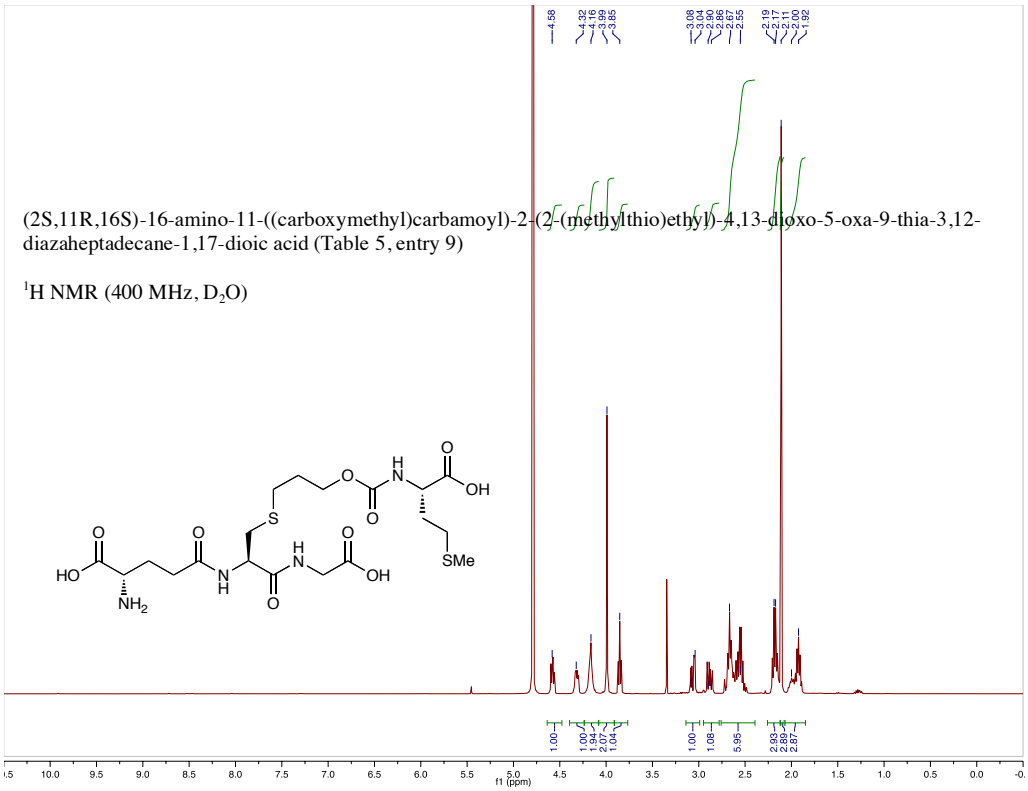
(2S,11R,16S)-16-amino-11-((carboxymethyl)carbamoyl)-2-(hydroxymethyl)-4,13-dioxo-5-oxa-9-thia-3,12-diazaheptadecane-1,17-dioic acid (Table 5, entry 8)

^{1}H NMR (500 MHz, D_2O)



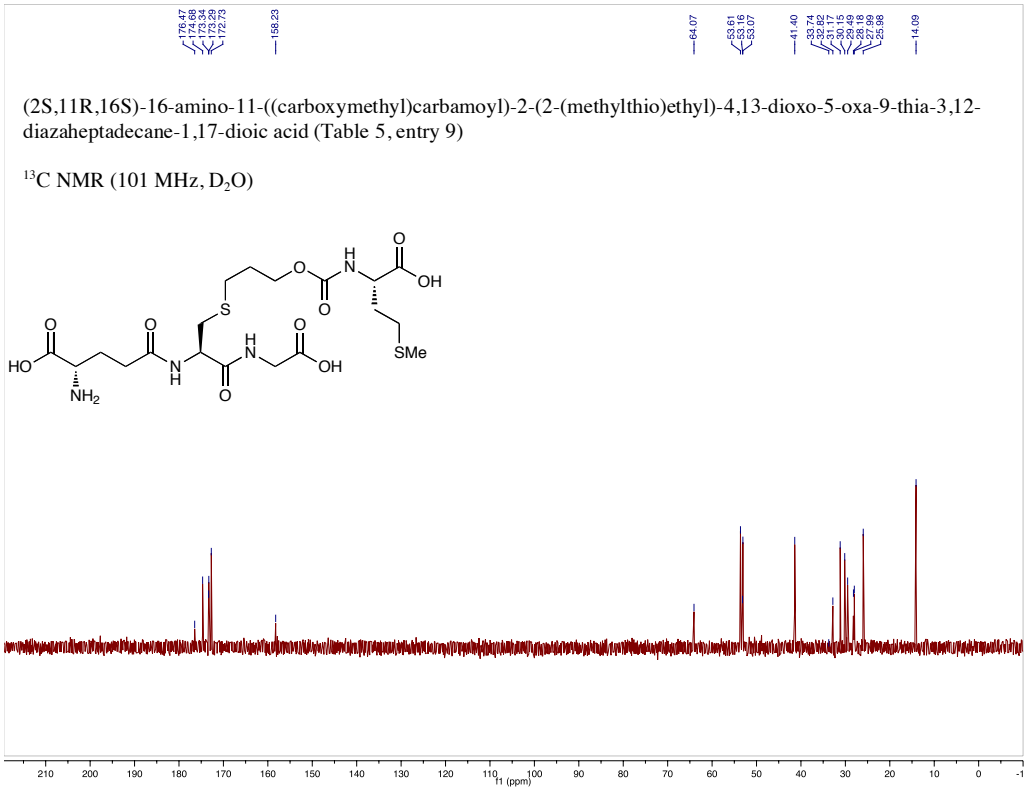
(2S,11R,16S)-16-amino-11-((carboxymethyl)carbamoyl)-2-(hydroxymethyl)-4,13-dioxo-5-oxa-9-thia-3,12-diazaheptadecane-1,17-dioic acid (Table 5, entry 8)

^{13}C NMR (126 MHz, D_2O)



(2S,11R,16S)-16-amino-11-((carboxymethyl)carbamoyl)-2-(2-(methylthio)ethyl)-4,13-dioxo-5-oxa-9-thia-3,12-diazaheptadecane-1,17-dioic acid (Table 5, entry 9)

^{1}H NMR (400 MHz, D_2O)

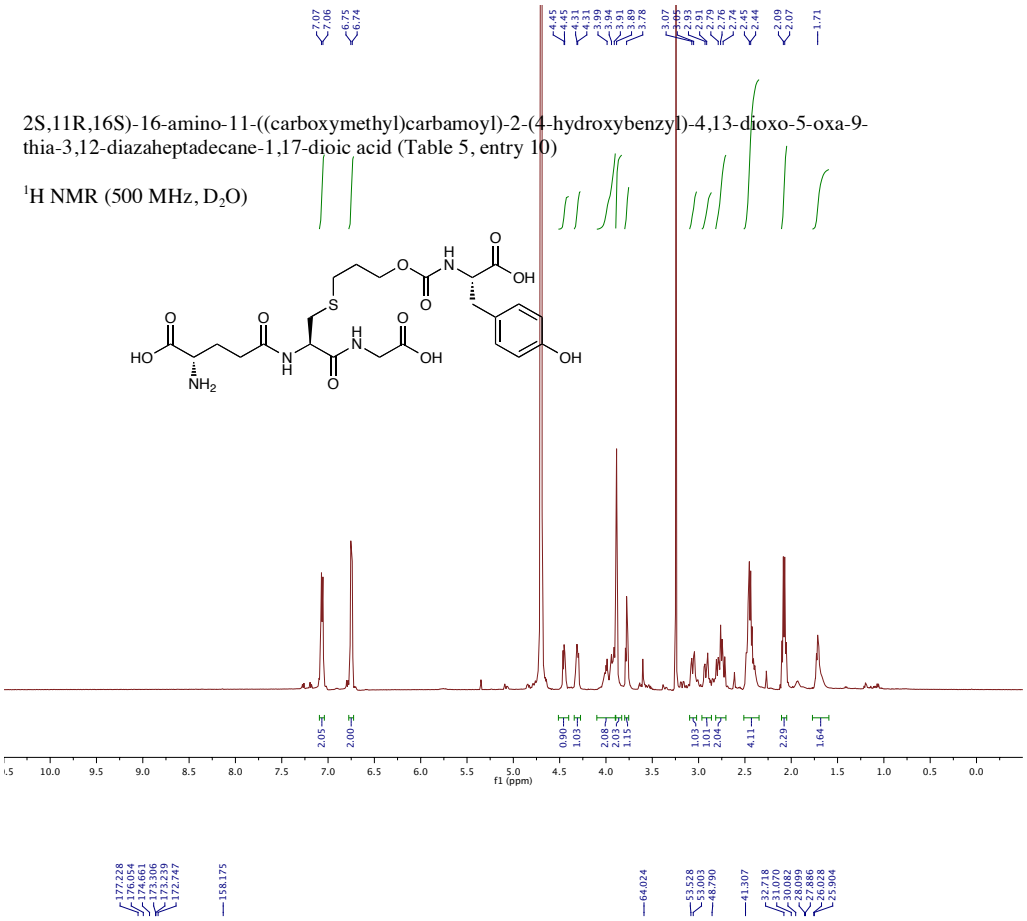


(2S,11R,16S)-16-amino-11-((carboxymethyl)carbamoyl)-2-(2-(methylthio)ethyl)-4,13-dioxo-5-oxa-9-thia-3,12-diazaheptadecane-1,17-dioic acid (Table 5, entry 9)

^{13}C NMR (101 MHz, D_2O)

2S,11R,16S)-16-amino-11-((carboxymethyl)carbamoyl)-2-(4-hydroxybenzyl)-4,13-dioxo-5-oxa-9-thia-3,12-diazaheptadecane-1,17-dioic acid (Table 5, entry 10)

^{1}H NMR (500 MHz, D_2O)



2S,11R,16S)-16-amino-11-((carboxymethyl)carbamoyl)-2-(4-hydroxybenzyl)-4,13-dioxo-5-oxa-9-thia-3,12-diazaheptadecane-1,17-dioic acid (Table 5, entry 10)

^{13}C NMR (125 MHz, D_2O)