SUPPORTING INFORMATION

Total Synthesis and Configurational Revision of Mozamide A – a Hydroxy-Brunsvicamide

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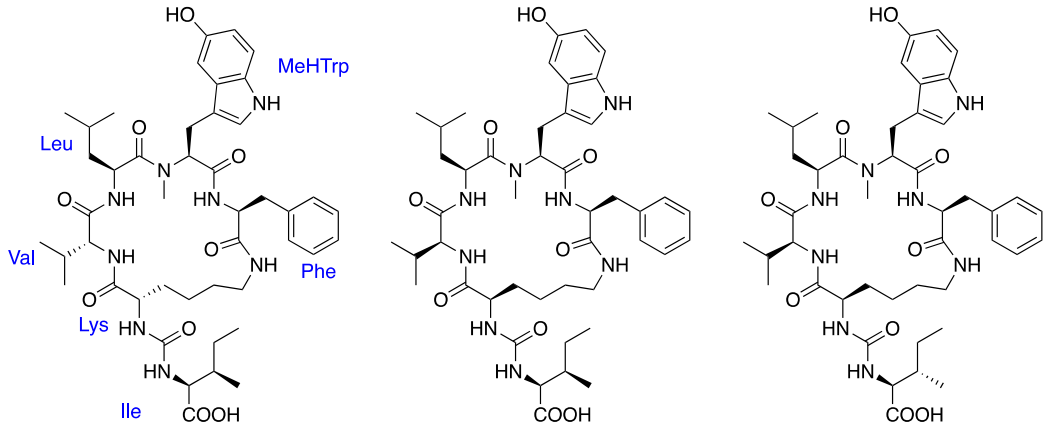
1. Comparison of synthetic 1a – c with natural 1

In order to compare the synthetic compounds with the natural product, the NMR data of **1a** – **c** was compared to that reported for natural **1**.[1] Tables 1 and 2 show the NMR frequencies for each proton and carbon (DMSO-d_6, 500/126 MHz, 298 K) for synthetic and natural **3**. Δδ values were calculated by Δδ = δ(**1x**) – δ(**1**).

Table S 1. **Comparison of** ^{1}H-NMR-data of **1a**, **1b** and **1c** with that reported for **1** (500 MHz, DMSO-d_6, δ in ppm).



3a **3b** **3c**

	1[1]	1a	Δδ (1 – 1a)	1b (L-*allo*-Ile)	Δδ (1 – 1b)	1c (L-Ile)	Δδ (1 – 1c)
MeHTrp α	4.64	4.52	0.12	4.52	0.12	4.68	-0.04
MeHTrp β1	2.72	2.65	0.07	2.72	0	2.73	-0.01
MeHTrp β2	3.04	3.23	-0.19	3.07	-0.03	3.08	-0.04
Indole 1	10.6	10.58	0.02	10.55	0.05	10.55	0.05
Indole 2	6.81	6.91	-0.1	6.81	0	6.81	0
Indole 4	6.84	6.79	0.05	6.84	0	6.84	0
Indole 6	6.58	6.57	0.01	6.58	0	6.58	0
Indole 7	7.1	7.1	0	7.09	0.01	7.09	0.01
Indole OH	8.5	8.59	-0.09	8.52	-0.02	8.53	-0.03
N-CH_3	1.85	2.37	-0.52	1.89	-0.04	1.9	-0.05
Leu α	4.24	4.35	-0.11	4.22	0.02	4.22	0.02
Leu β	-0.46	-0.47	0.01	-0.49	0.03	-0.49	0.03
Leu β2	0.9	1.01	-0.11	0.89	0.01	0.9	0
Leu γ	1.39	1.15	0.24	1.4	-0.01	1.41	-0.02
Leu δ1	0.22	0.09	0.13	0.24	-0.02	0.24	-0.02
Leu δ2	0.36	0.31	0.05	0.37	-0.01	0.37	-0.01
Leu NH	8.42	8.31	0.11	8.43	-0.01	8.43	-0.01
Val α	3.8	4.24	-0.44	3.78	0.02	3.78	0.02
Val β	1.86	2.15	-0.29	1.91	-0.05	1.91	-0.05
Val γ1	0.85	0.61	0.24	0.87	-0.02	0.87	-0.02
Val γ2	0.94	0.72	0.22	0.94	0	0.94	0
Val NH	6.73	7.03	-0.3	6.74	-0.01	6.8	-0.07

Lys α	3.84	4.03	-0.19	3.86	-0.02	3.86	-0.02
Lys β	1.58	1.65	-0.07	1.56	0.02	1.56	0.02
Lys γ	1.1	1.3	-0.2	1.12	-0.02	1.11	-0.01
Lys δ	1.4	1.47	-0.07	1.4	0	1.42	-0.02
Lys ε1	2.85	2.91	-0.06	2.87	-0.02	2.87	-0.02
Lys ε2	3.59	3.27	0.32	3.6	-0.01	3.6	-0.01
Lys α-NH	6.44	6.61	-0.17	6.51	-0.07	6.51	-0.07
Lys ε-NH	7.44	7.44	0	7.46	-0.02	7.45	-0.01
Phe α	4.58	4.6	-0.02	4.58	0	4.57	0.01
Phe β1	2.71	2.86	-0.15	2.74	-0.03	2.76	-0.05
Phe β2	3.37	3.16	0.21	3.42	-0.05	3.41	-0.04
Phe *o*	7.08	7.16	-0.08	7.08	0	7.08	0
Phe *m*	7.21	7.28	-0.07	7.23	-0.02	7.23	-0.02
Phe *p*	7.17	7.2	-0.03	7.17	0	7.17	0
Phe NH	8.79	7.84	0.95	8.81	-0.02	8.81	-0.02
Ile α	4.02	4.11	-0.09	4.15	-0.13	3.97	0.05
Ile β	1.72	1.78	-0.06	1.8	-0.08	1.71	0.01
Ile γ-CH_3	1.12	0.75	0.37	0.76	0.36	1.13	-0.01
Ile γ-CH_2-1	1.34	1.25	0.09	1.12	0.22	1.36	-0.02
Ile γ-CH_2-2	0.83	1.08	-0.25	1.27	-0.44	0.82	0.01
Ile δ-CH_3	0.82	0.81	0.01	0.84	-0.02	0.81	0.01
Ile NH	6.3	6.2	0.1	6.24	0.06	6.29	0.01

Table S 2. Comparison $^{13}C\{^1H\}$ NMR-data of **1a**, **1b** and **1c** with that reported for **1** (126 MHz, DMSO-d_6, δ in ppm).

	1[1]	**1a**	**Δδ (1 – 1a)**	**1b (L-*allo*-Ile)**	**Δδ (1 – 1b)**	**2c (L-Ile)**	**Δδ (1 – 1c)**
MeHTrp CO	169.9	169	0.9	169.9	0	169.9	0
MeHTrp α	60.7	61.4	-0.7	60.7	0	60.8	-0.1
MeHTrp β	22.3	23.6	-1.3	22.3	0	22.3	0
Indole 2	124.2	124.2	0	124.2	0	124.2	0
Indole 3	108.6	108.5	0.1	108.6	0	108.6	0
Indole 4	102.2	101.6	0.6	102.2	0	102.2	0
Indole 5	150.3	150.7	-0.4	150.4	-0.1	150.4	-0.1
Indole 6	111.3	111.5	-0.2	111.3	0	111.3	0
Indole 7	111.6	111.9	-0.3	111.6	0	111.6	0
Indole 3a	127.9	127.6	0.3	127.9	0	127.9	0
Indole 7a	130.4	130.6	-0.2	130.4	0	130.5	-0.1
N-CH_3	27.6	29	-1.4	27.6	0	27.6	0
Leu CO	172.2	172.6	-0.4	172.3	-0.1	172.2	0
Leu α	47.3	45.5	1.8	47.2	0.1	47.3	0
Leu β	37	39.1	-2.1	37.1	-0.1	37.1	-0.1
Leu γ	23.1	23	0.1	23.1	0	23.1	0
Leu δ1	19.5	19	0.5	19.5	0	19.5	0
Leu δ2	22.3	22.7	-0.4	22.6	-0.3	22.6	-0.3

Val CO	172.3	170.4	**1.9**	172.3	**0**	172.3	**0**
Val α	56.7	56.1	**0.6**	57.8	**-1.1**	57.8	**-1.1**
Val β	29.9	30.8	**-0.9**	30	**-0.1**	30	**-0.1**
Val γ1	18.8	16	**2.8**	18.9	**-0.1**	18.9	**-0.1**
Val γ2	18.9	19	**-0.1**	19	**-0.1**	19	**-0.1**
Lys CO	172	172.4	**-0.4**	172.1	**-0.1**	172	**0**
Lys α	56.7	53.3	**3.4**	54.4	**2.3**	54.5	**2.2**
Lys β	31.5	30.8	**0.7**	31.6	**-0.1**	31.6	**-0.1**
Lys γ	20.2	21.4	**-1.2**	20.2	**0**	20.2	**0**
Lys δ	28.3	27.7	**0.6**	28.4	**-0.1**	28.4	**-0.1**
Lys ε	39	38.6	**0.4**	38.4	**0.6**	38.4	**0.6**
Phe CO	170.1	170.3	**-0.2**	170.8	**-0.7**	170.8	**-0.7**
Phe α	54.4	54.4	**0**	54.5	**-0.1**	54.5	**-0.1**
Phe β	39	37.6	**1.4**	37.7	**1.3**	37.7	**1.3**
Phe *i*	138.4	137.7	**0.7**	138.4	**0**	138.4	**0**
Phe *o*	128.8	129.1	**-0.3**	128.9	**-0.1**	128.9	**-0.1**
Phe *m*	128.3	128.2	**0.1**	128.3	**0**	128.3	**0**
Phe *p*	126.1	126.3	**-0.2**	126.1	**0**	126.1	**0**
Urea CO	157.3	157.4	**-0.1**	157.6	**-0.3**	157.3	**0**
Ile CO	173.8	174.8	**-1**	174.5	**-0.7**	173.9	**-0.1**
Ile α	57.7	55.3	**2.4**	55.2	**2.5**	57.1	**0.6**
Ile β	37.7	37.1	**0.6**	36.7	**1**	36.9	**0.8**
Ile γ-CH_2	24.6	25.9	**-1.3**	26	**-1.4**	24.6	**0**
Ile δ-CH_3	11.5	11.8	**-0.3**	11.7	**-0.2**	11.5	**0**
Ile γ-CH_3	15.7	14.7	**1**	14.8	**0.9**	15.8	**-0.1**

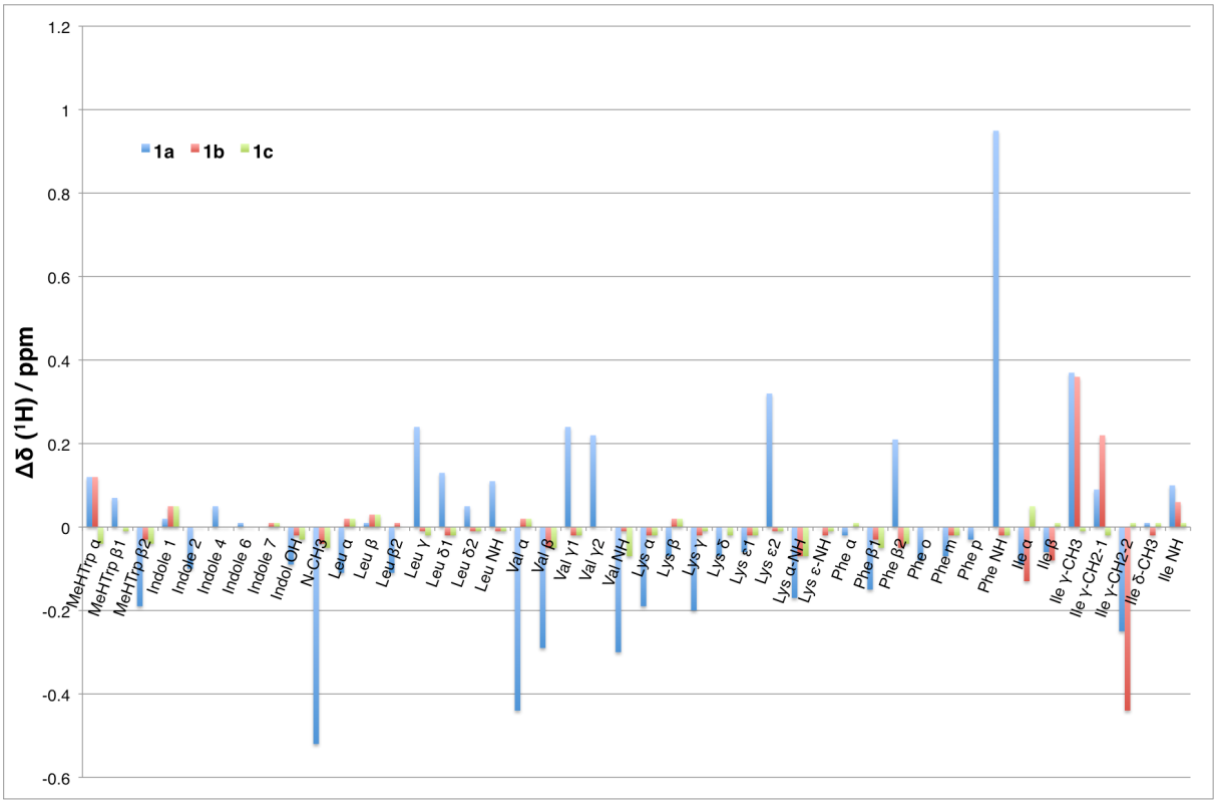


Figure S 1. Δδ(^{1}H) values of **1a** – **c** compared to **1**. (DMSO-d_6, 500 MHz, Δδ in ppm, MeHTrp: *N*-Methyl-5-hydroxytryptophan).

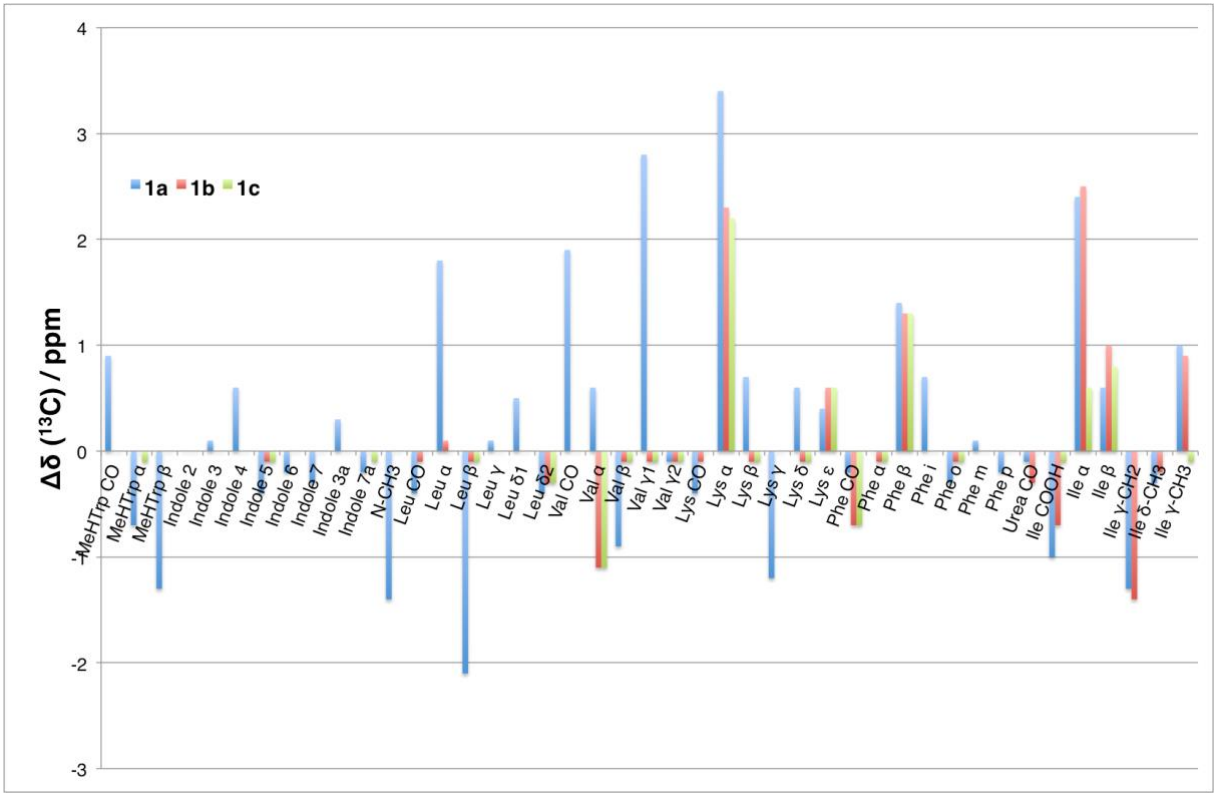


Figure S 2. Δδ(^{13}C) values of **1a** – **c** compared to **1**. (DMSO-d_6, 126 MHz, Δδ in ppm, MeHTrp: *N*-Methyl-5-hydroxytryptophan).

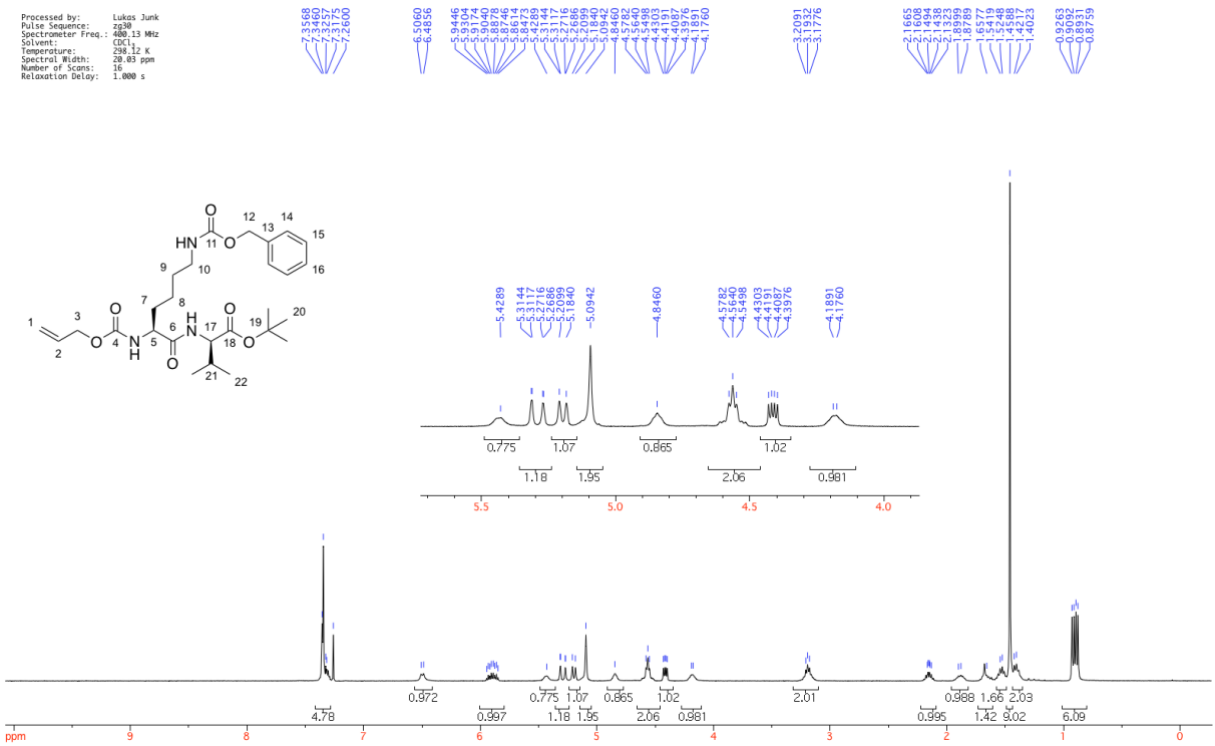
Figure S1 shows the Δδ values of **1a** (blue), **1b** (red) and **1c** (green) as a bar diagram. For **1a**, strong deviances can be found for almost every amino acid. In **1b** these deviances are very small except in the Ile part. **1c** shows a good accord to **1** in the whole ^{1}H-NMR-spectrum. We assume that **1a** takes on a different conformation compared to the natural product. Cyclic precursors **10a**, **11a** and **12a** also show two stable conformations in their NMR spectra. At 373 K, only signal broadening and no coalescence was observed for these molecules.
The spectral data of **1b** and **1c** only differ in the Ile-part. **1b** shows significant deviances ((Δδ (Ile-γ-CH_2-2)) = −0.44 ppm), whereas the deviances for **1c** are below 0.1 ppm in the whole spectrum.
The comparison of ^{13}C-NMR spectra (Figure S2) shows the same trends as observed for the ^{1}H-NMR spectra: **1a** shows strong deviances for almost every amino acid, **1b** and **1c** are quite similar, they only differ in the Isoleucin-units. **1c** shows the best accordance to the natural product. Several outliers (Val-α, Lys-α, Phe-CO and Phe-β) can be found. We cannot offer an explanation for these since no copies of ^{1}H and ^{13}C-NMR spectra of natural **1** are available. However, for Val-α and Lys-α the same value of δ = 56.7 ppm was reported, indicating possible copy-paste-errors.
Based on this analysis of NMR spectra we propose the natural strucutre of **1** to be that of **1c**.

2. References

[1] E. W. Schmidt, M. K. Harper, D. J. Faulkner, Mozamides A and B, cyclic peptides from a *Theonellid* sponge from Mozambique. *J. Nat. Prod.* **1997**, *60*, 779–782.

3. Copies of NMR-spectra

^{1}H-NMR of 4a



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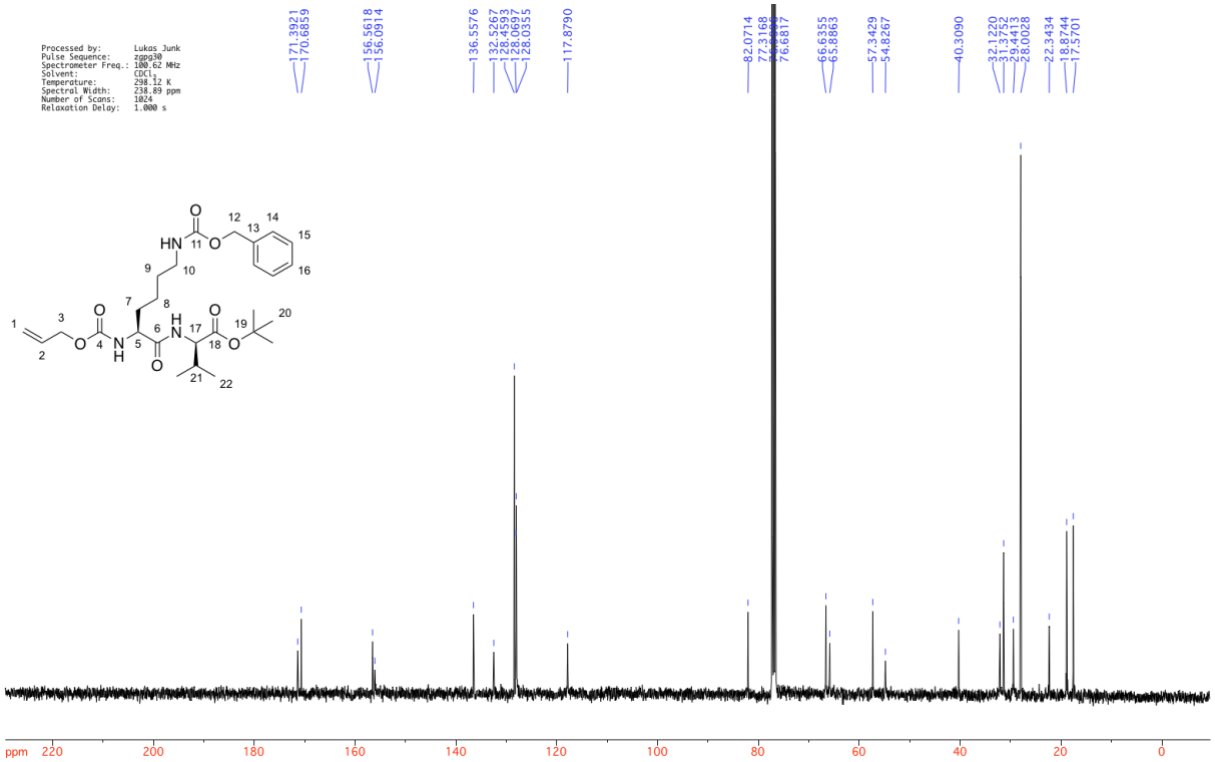

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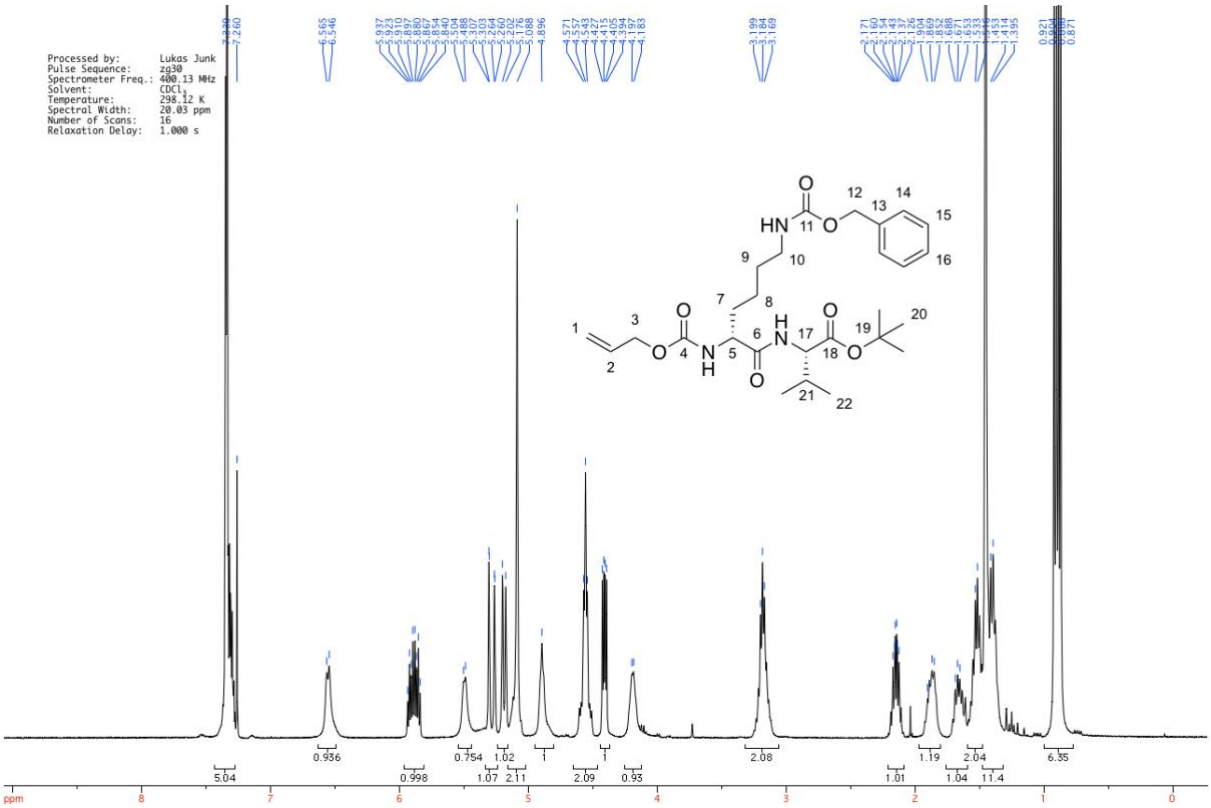

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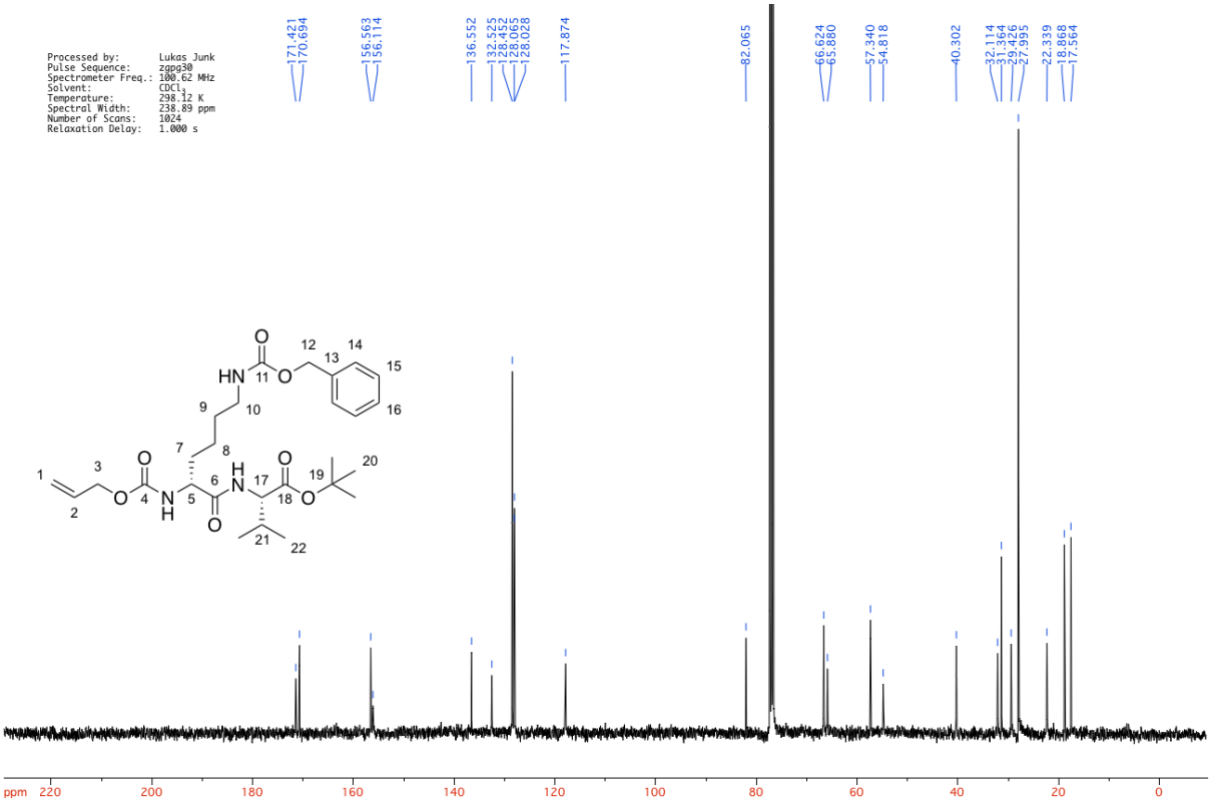

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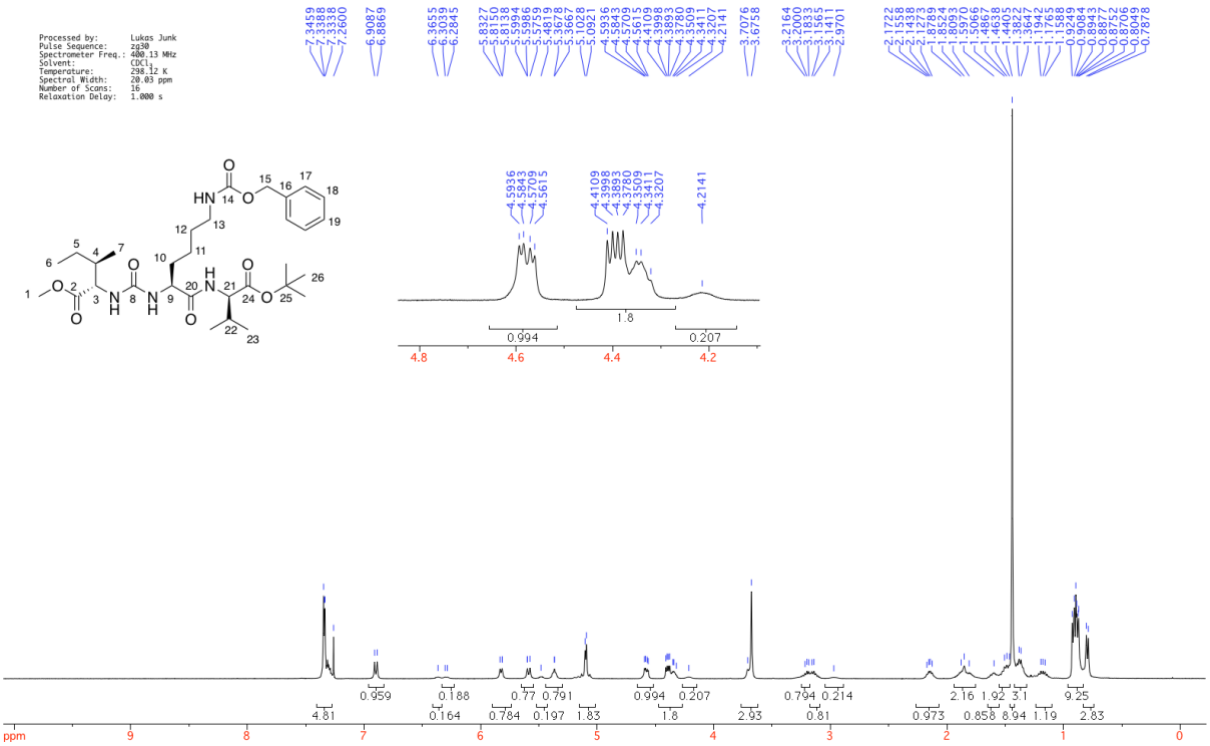

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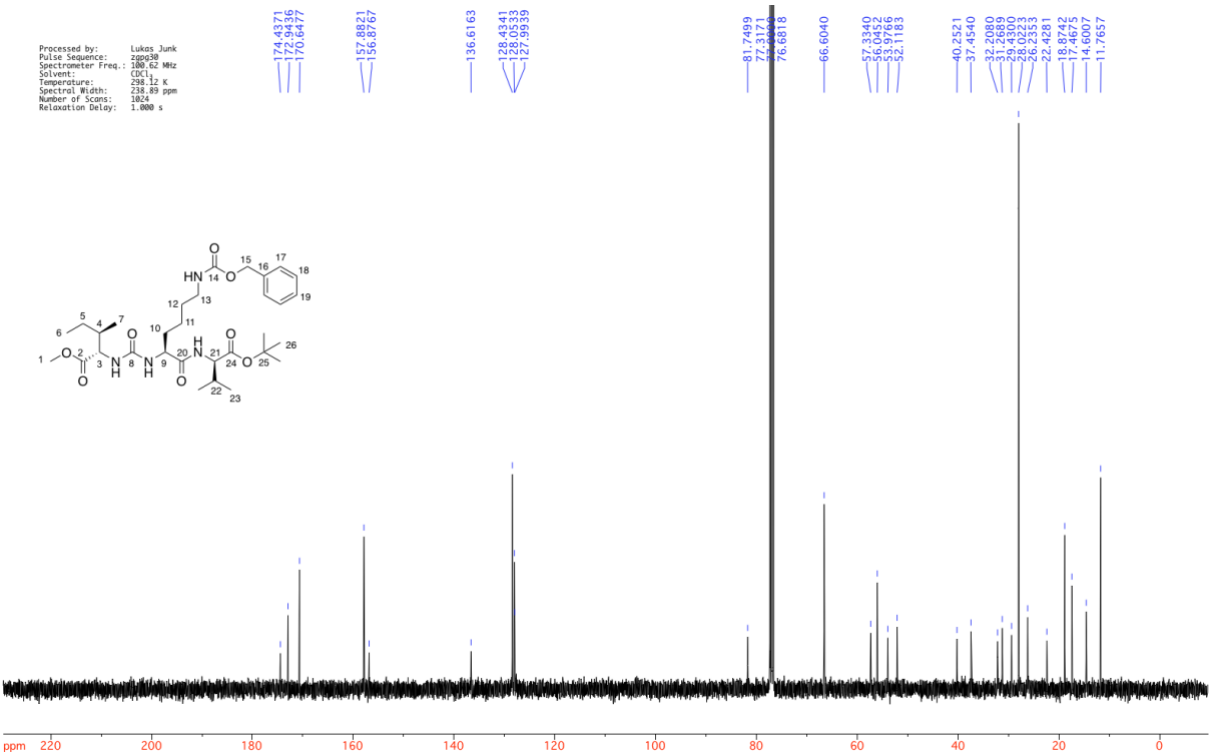

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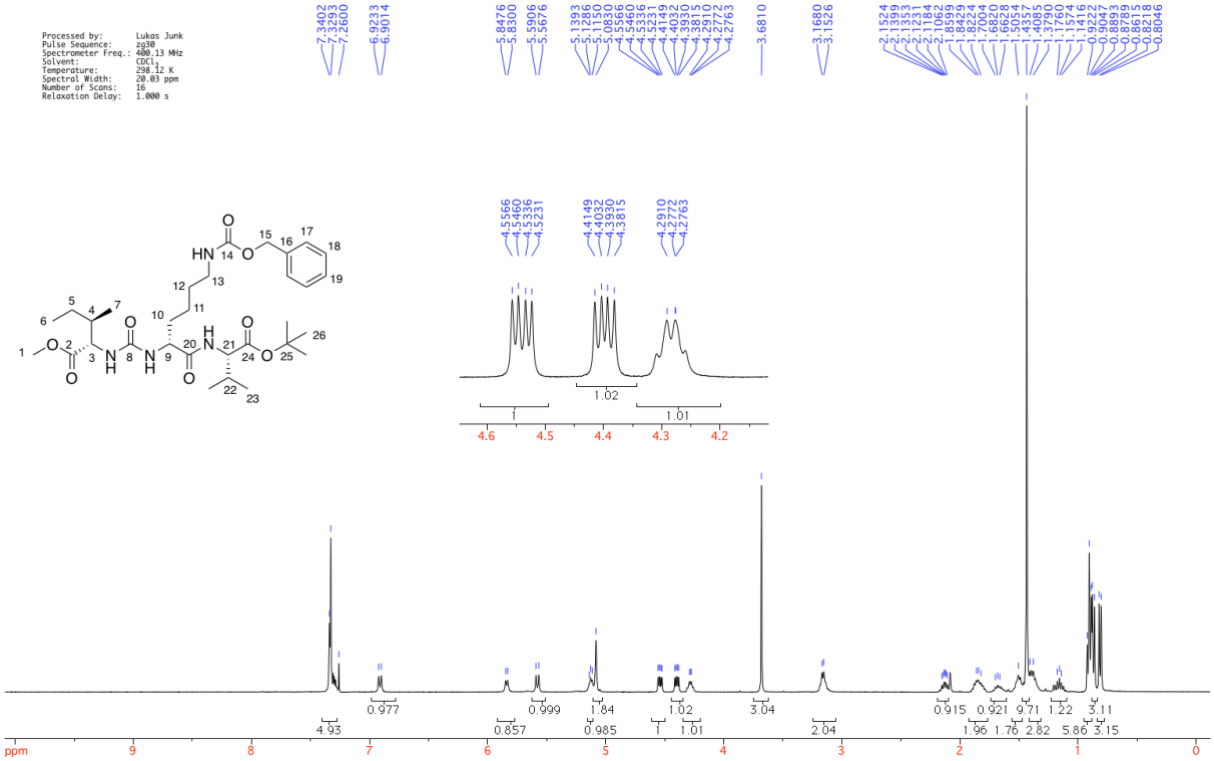

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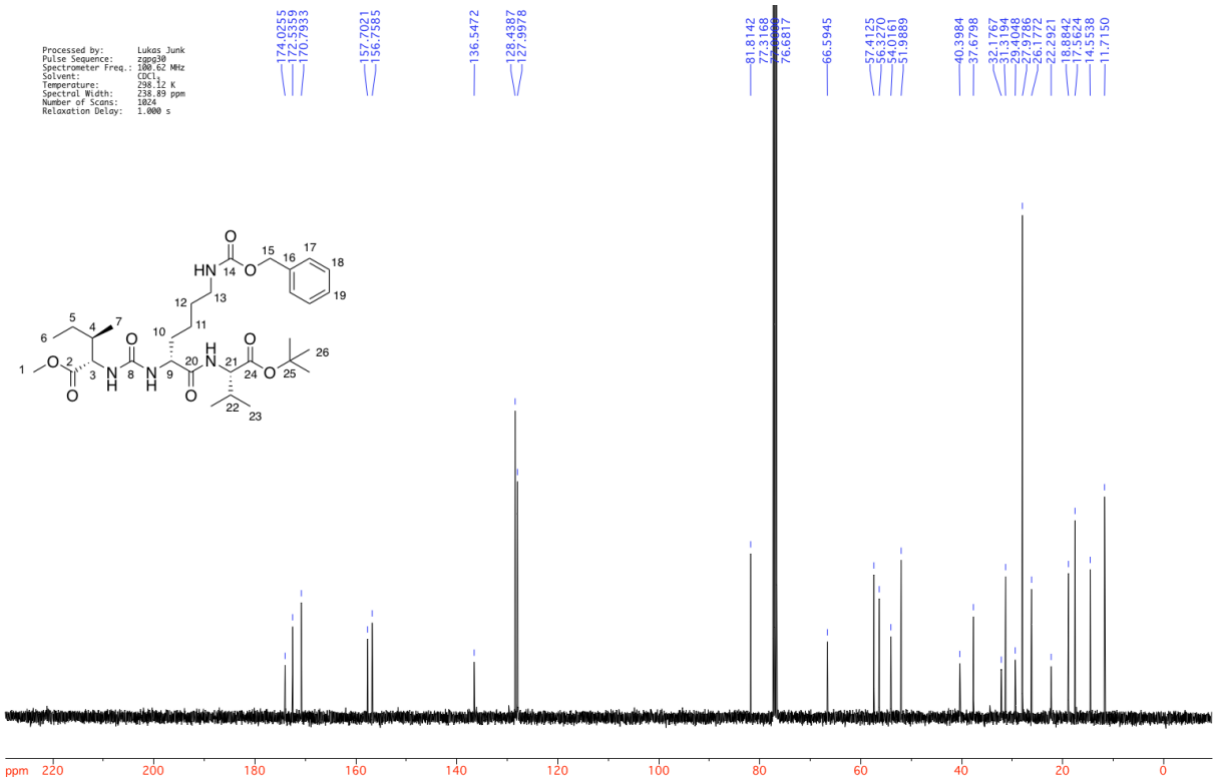

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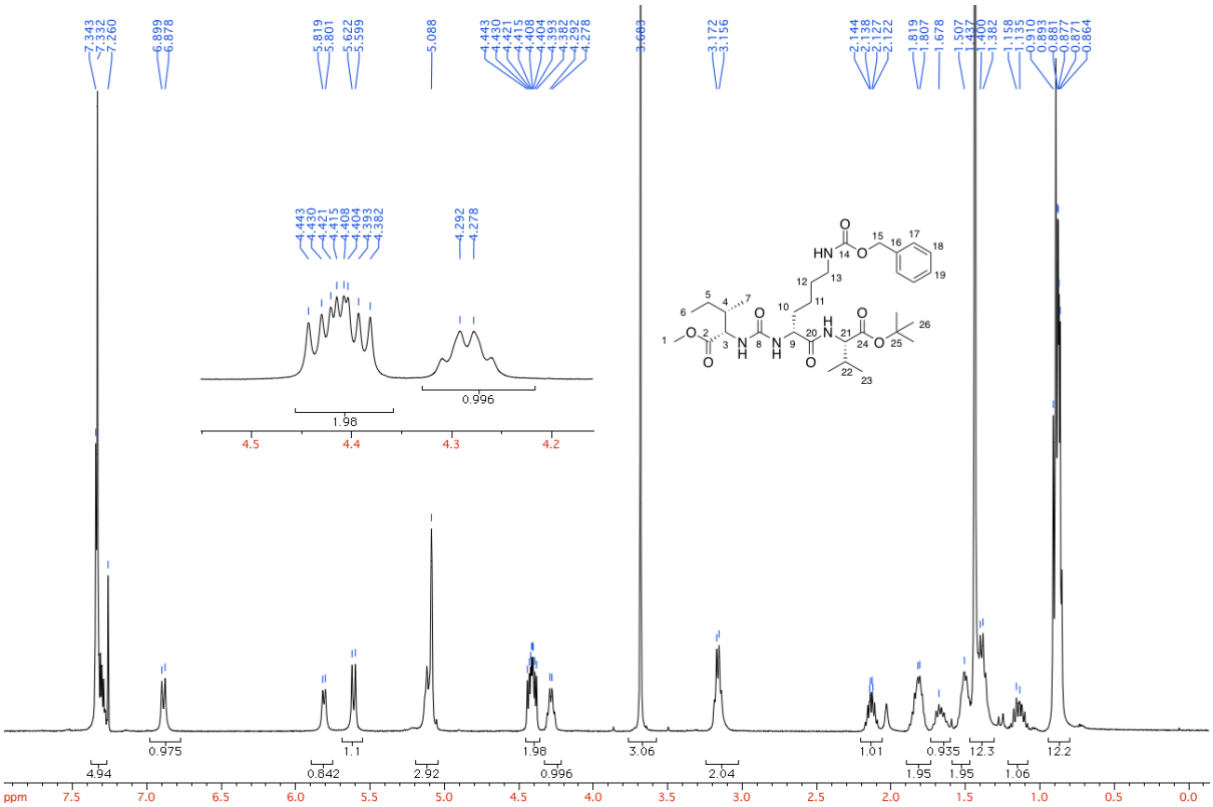

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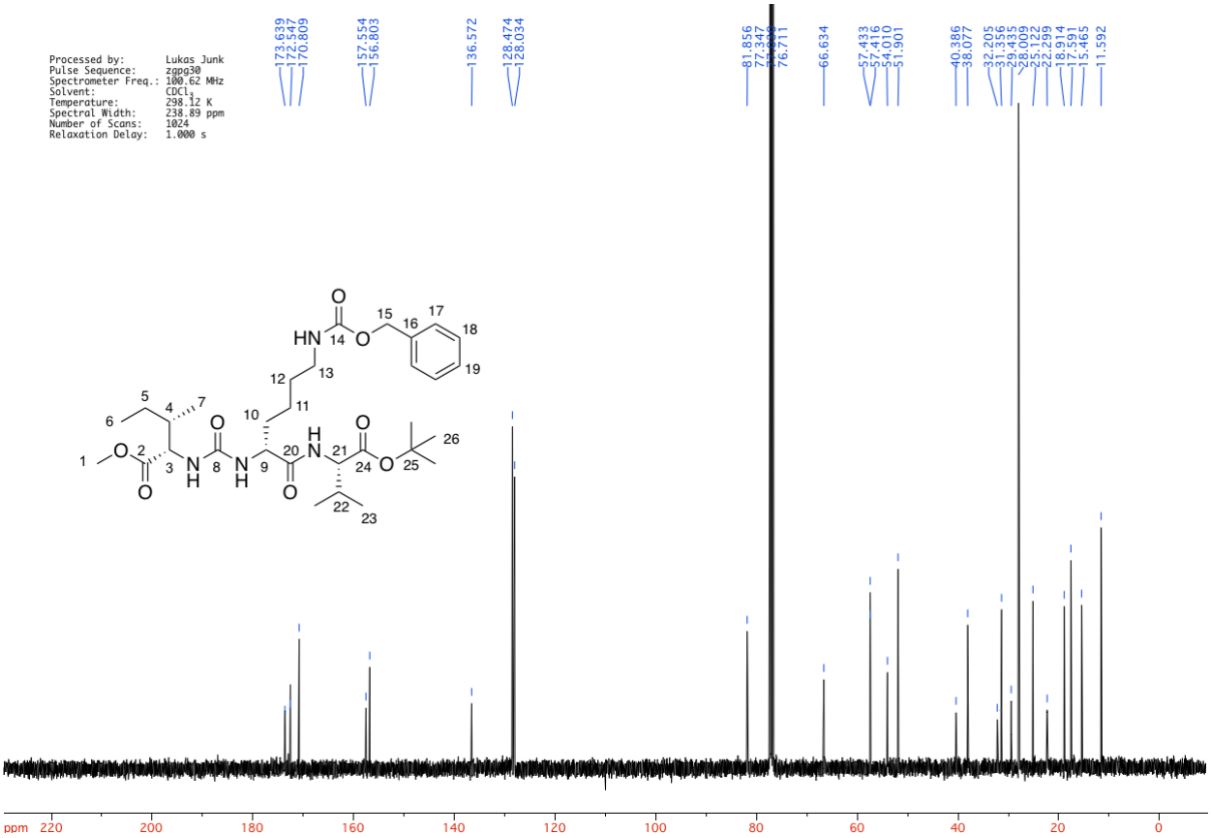

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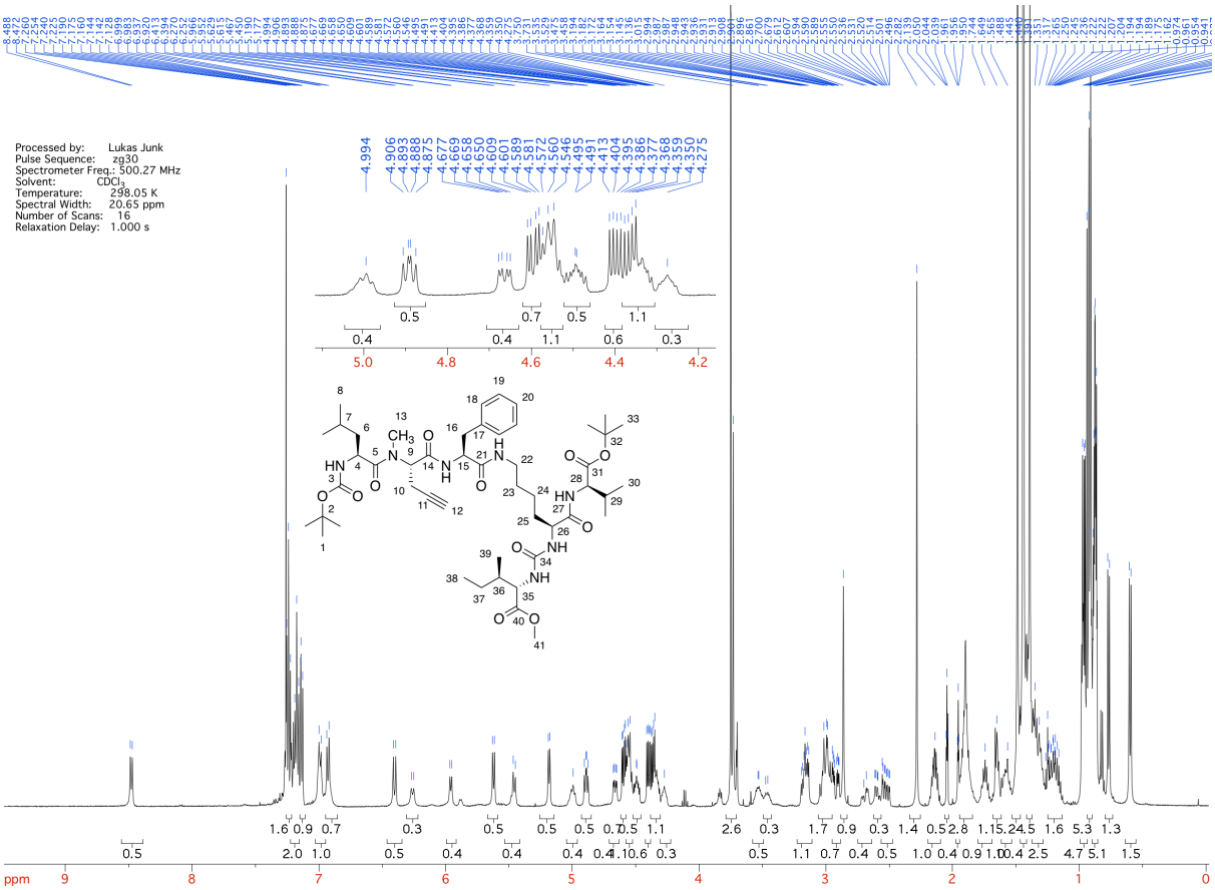

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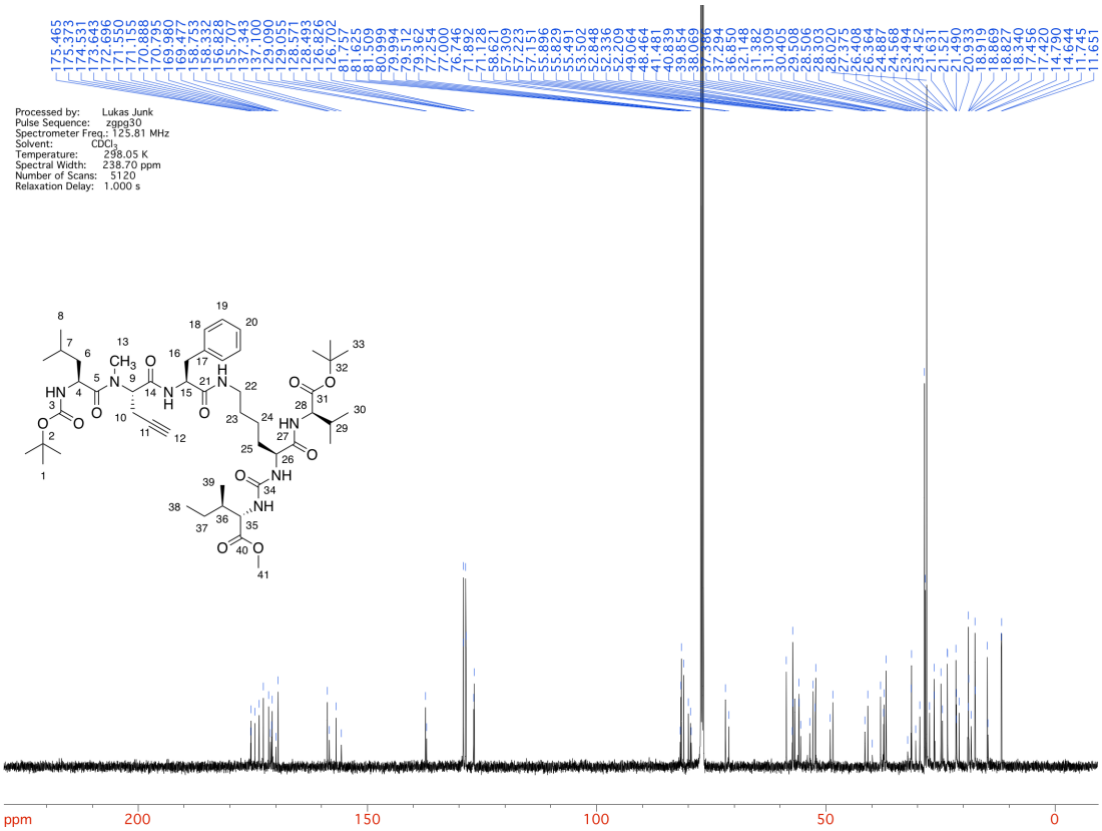

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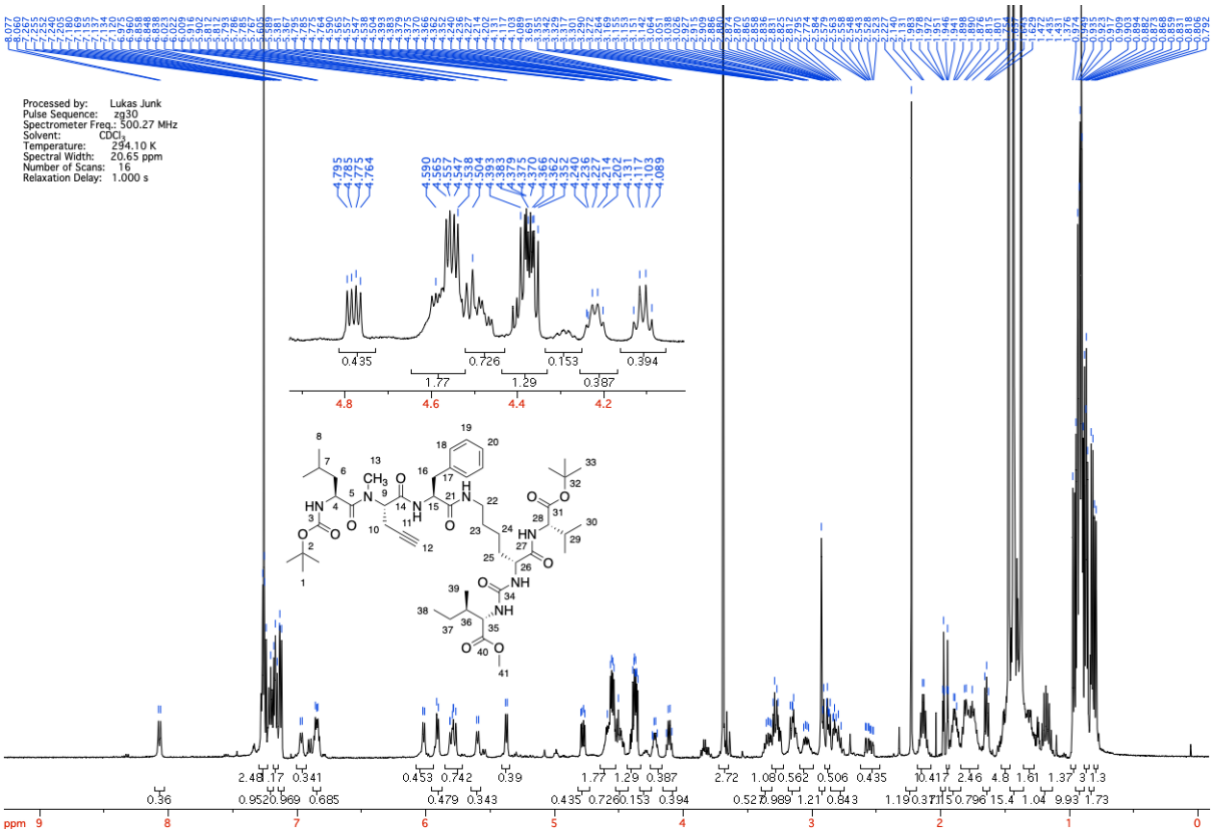

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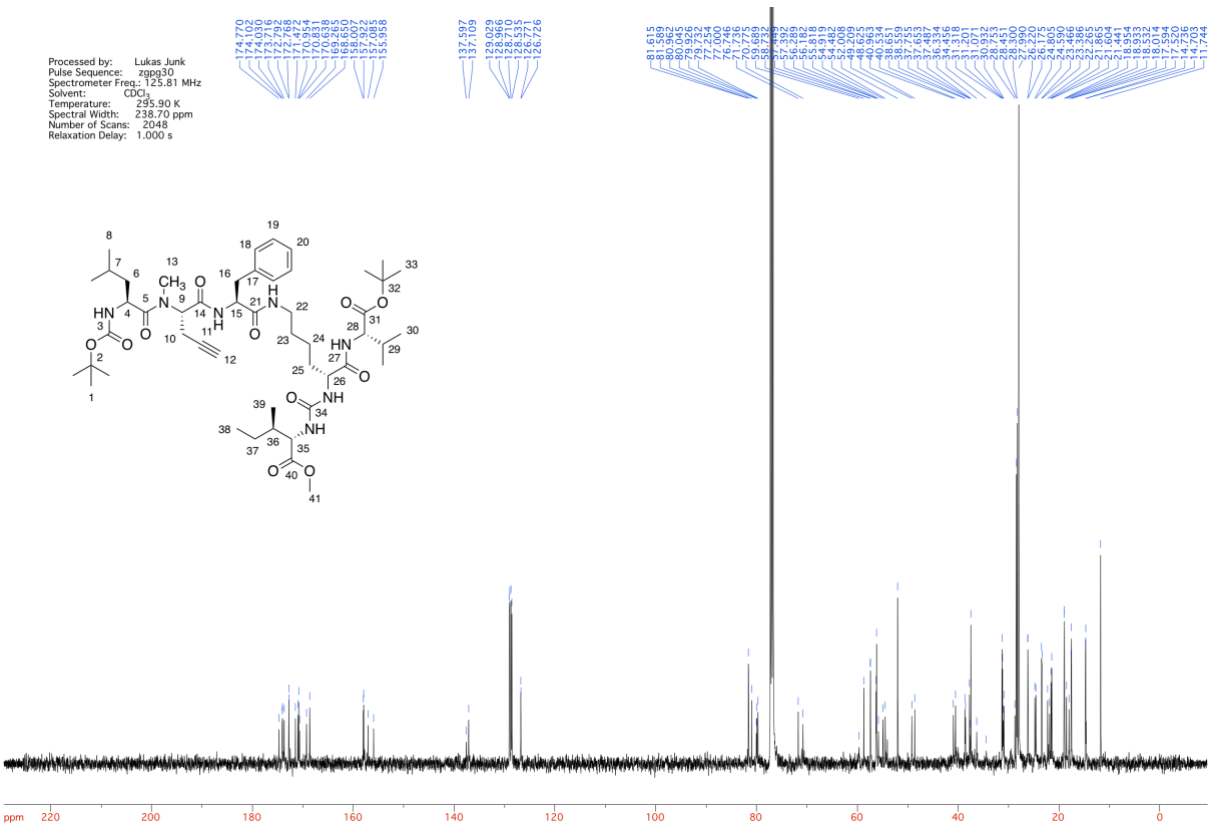

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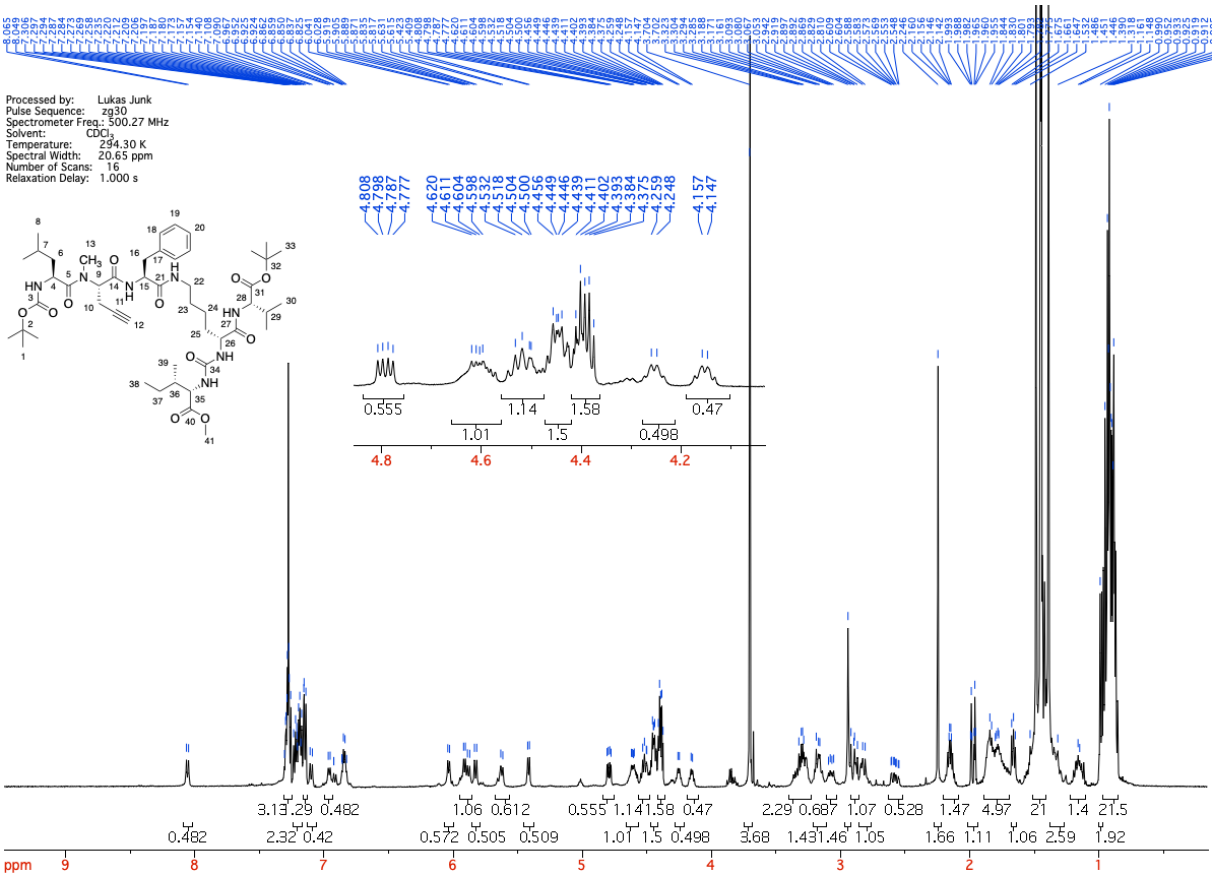

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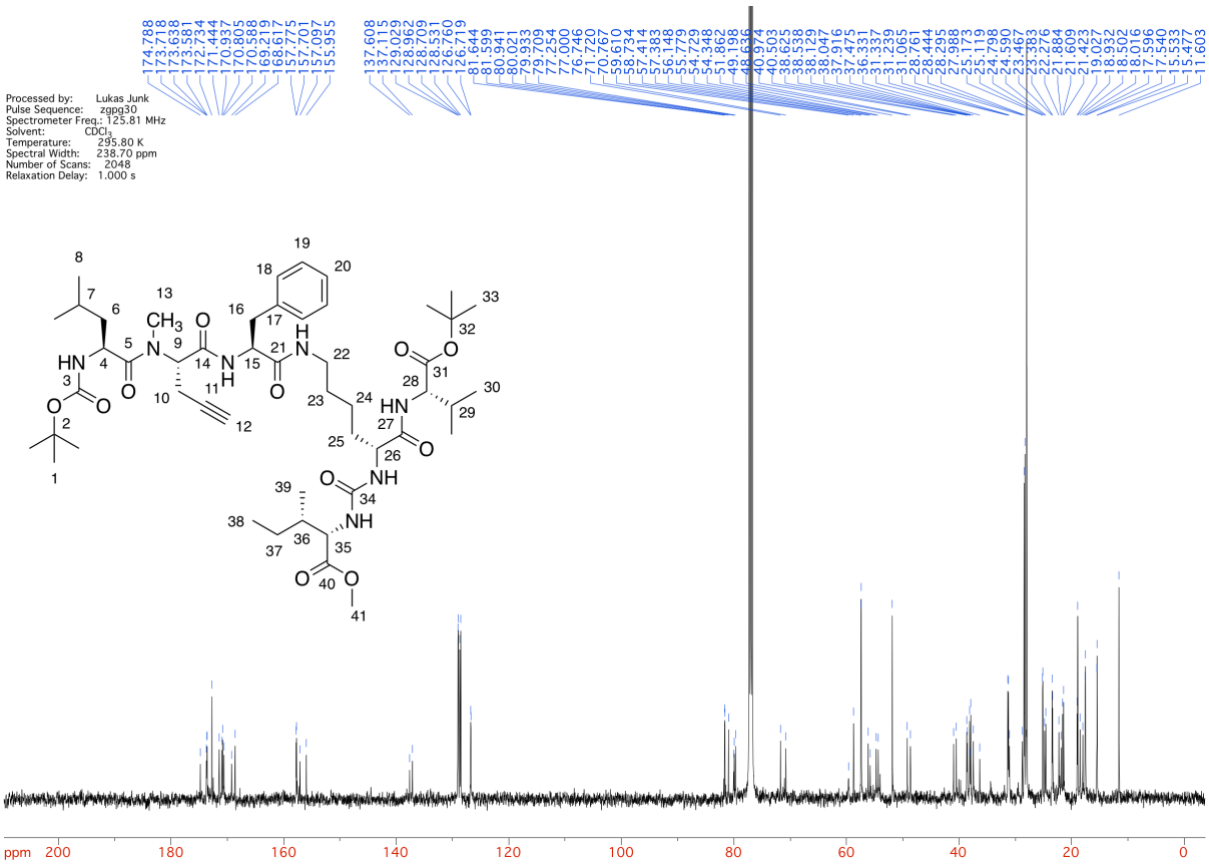

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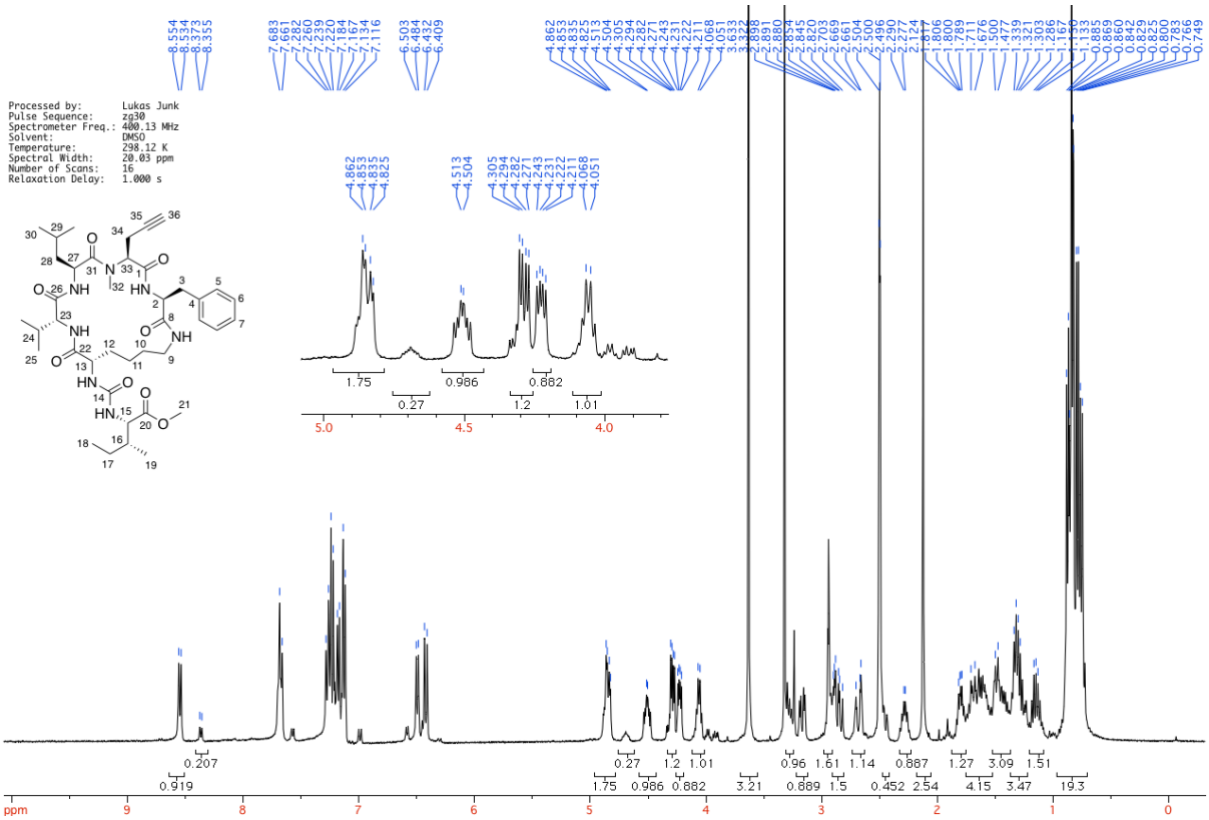

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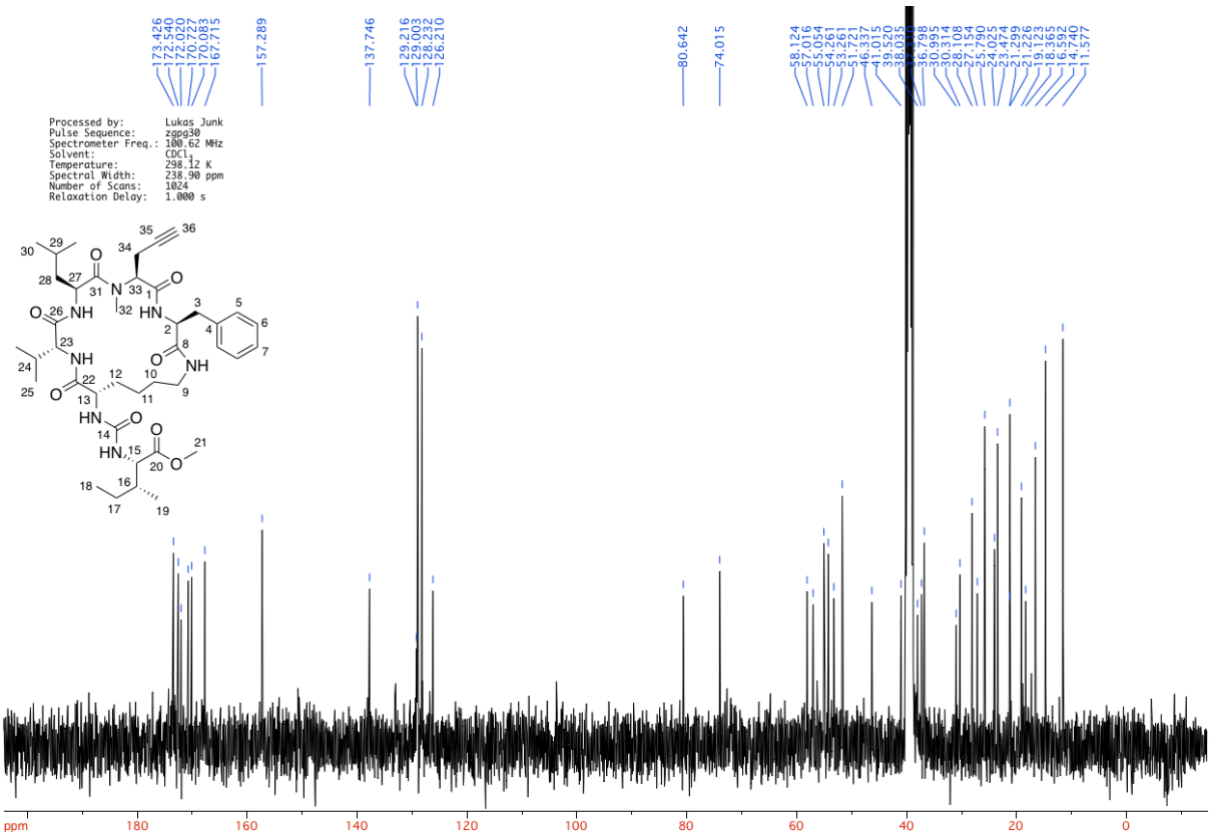

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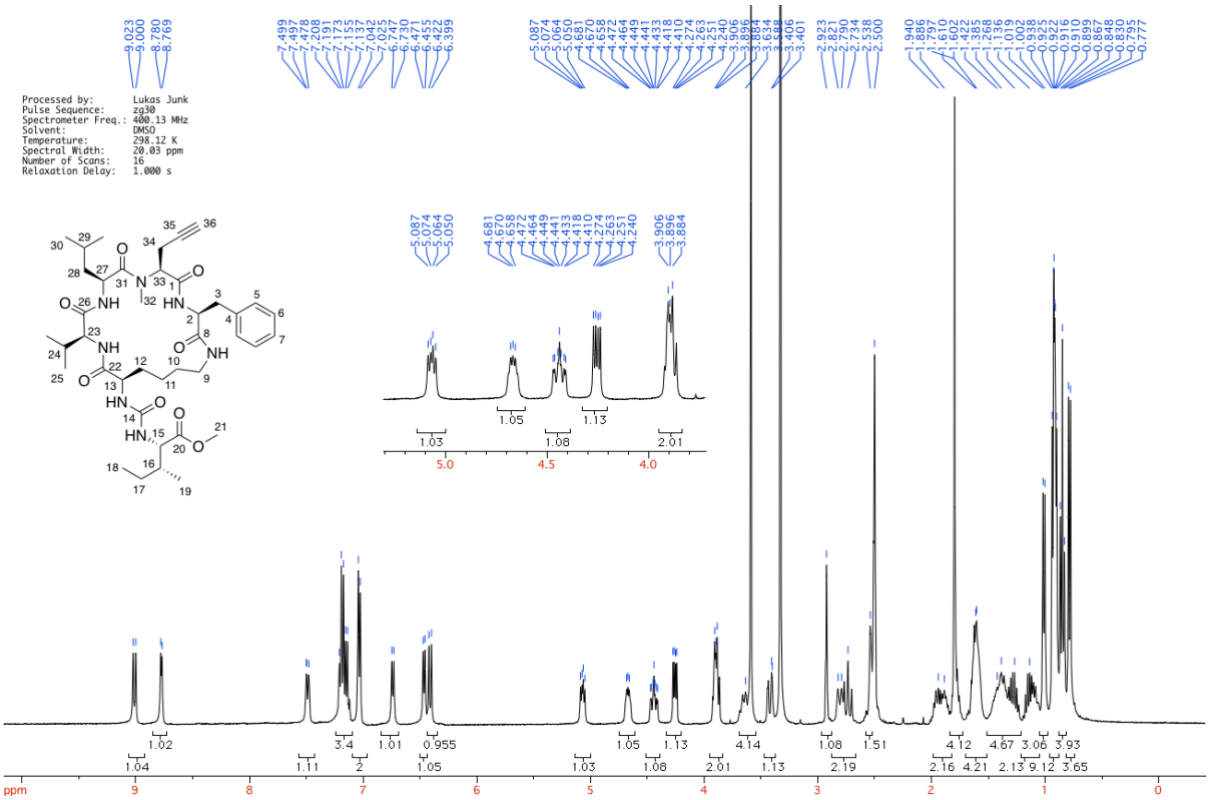

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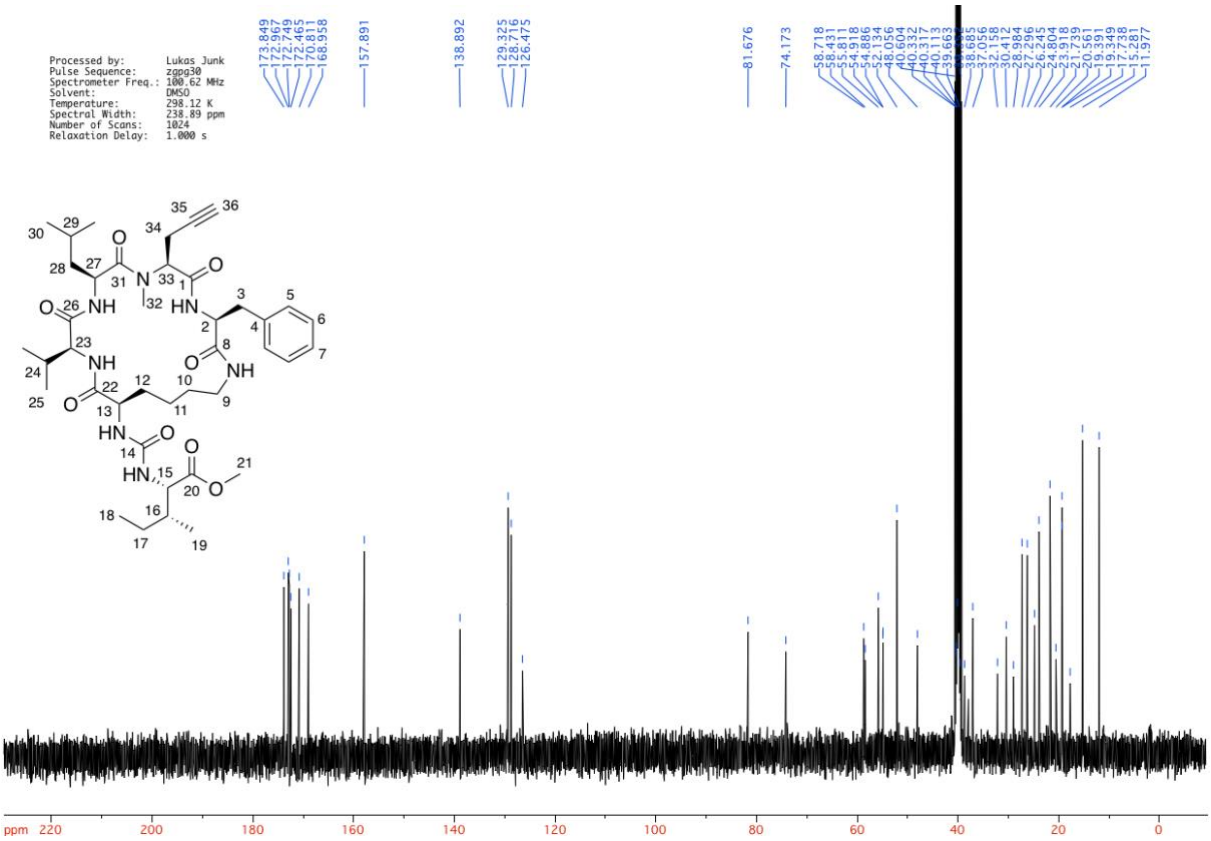

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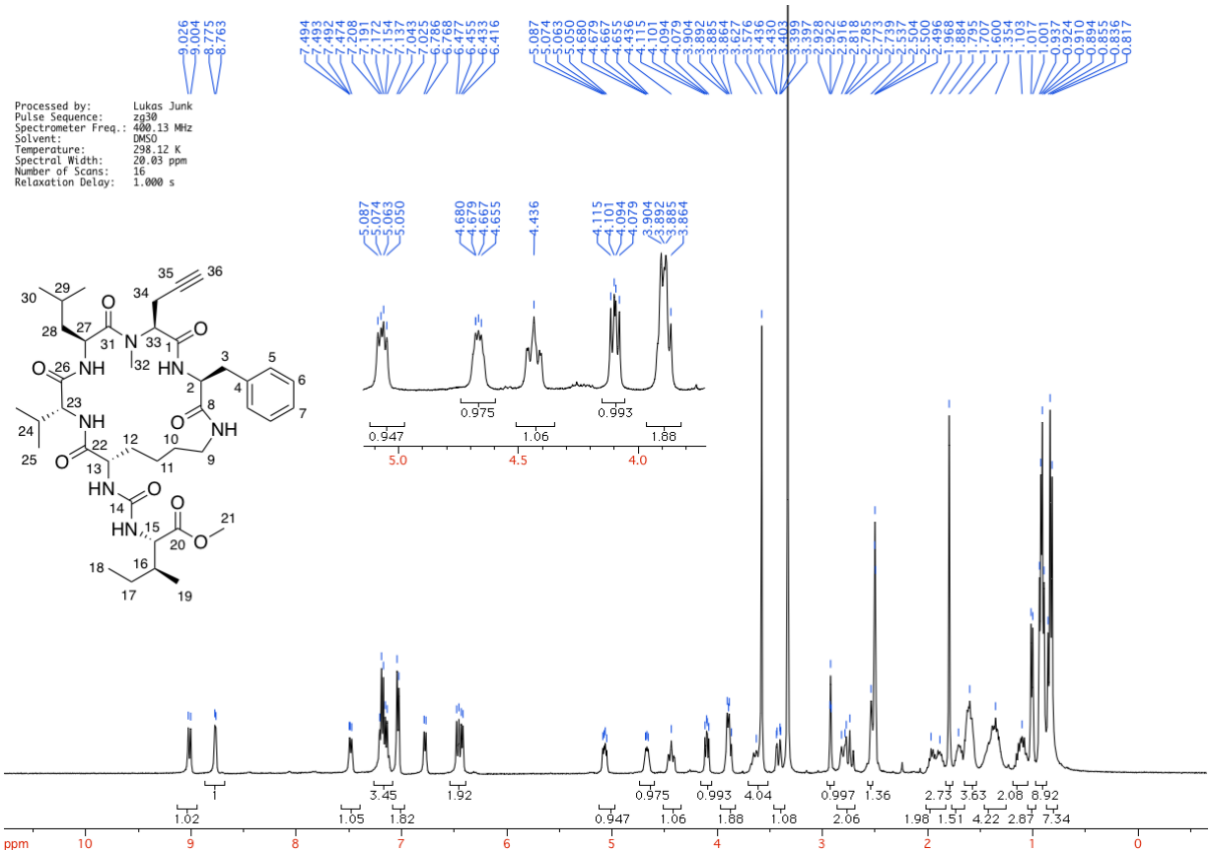

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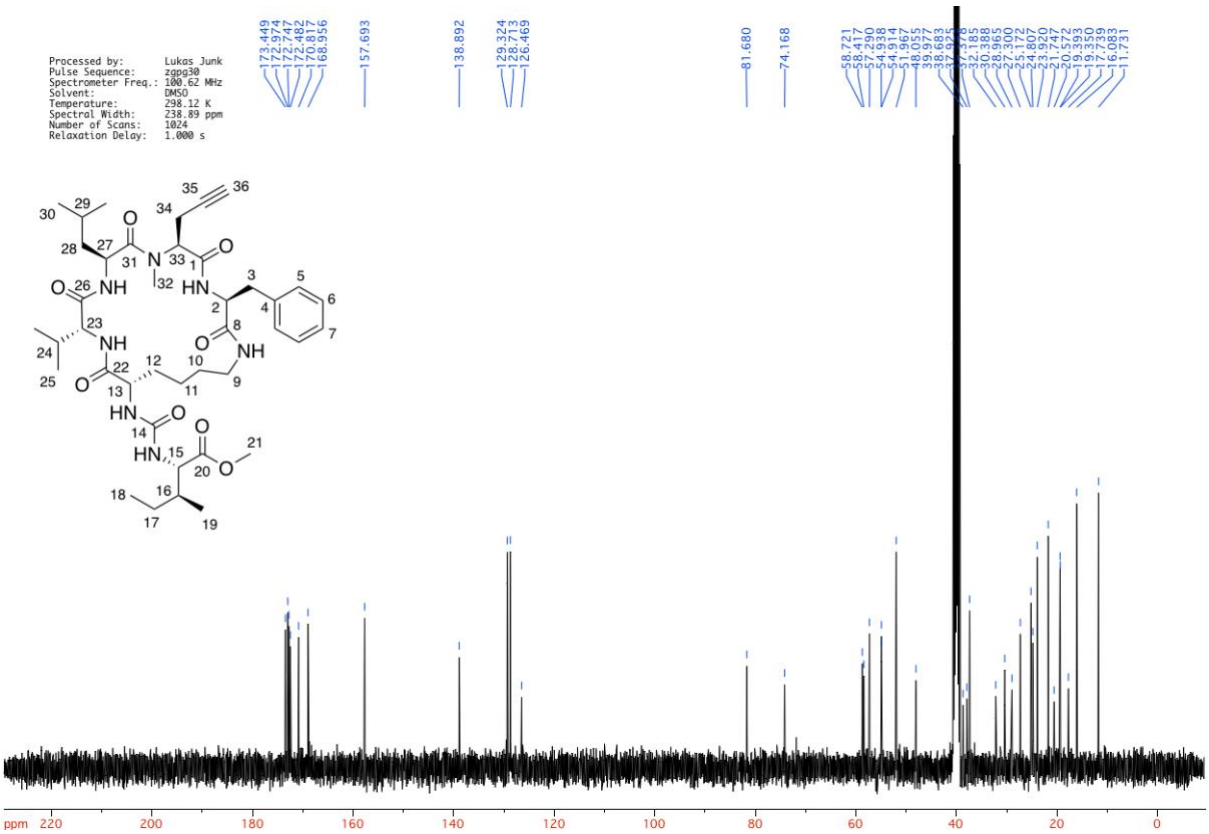

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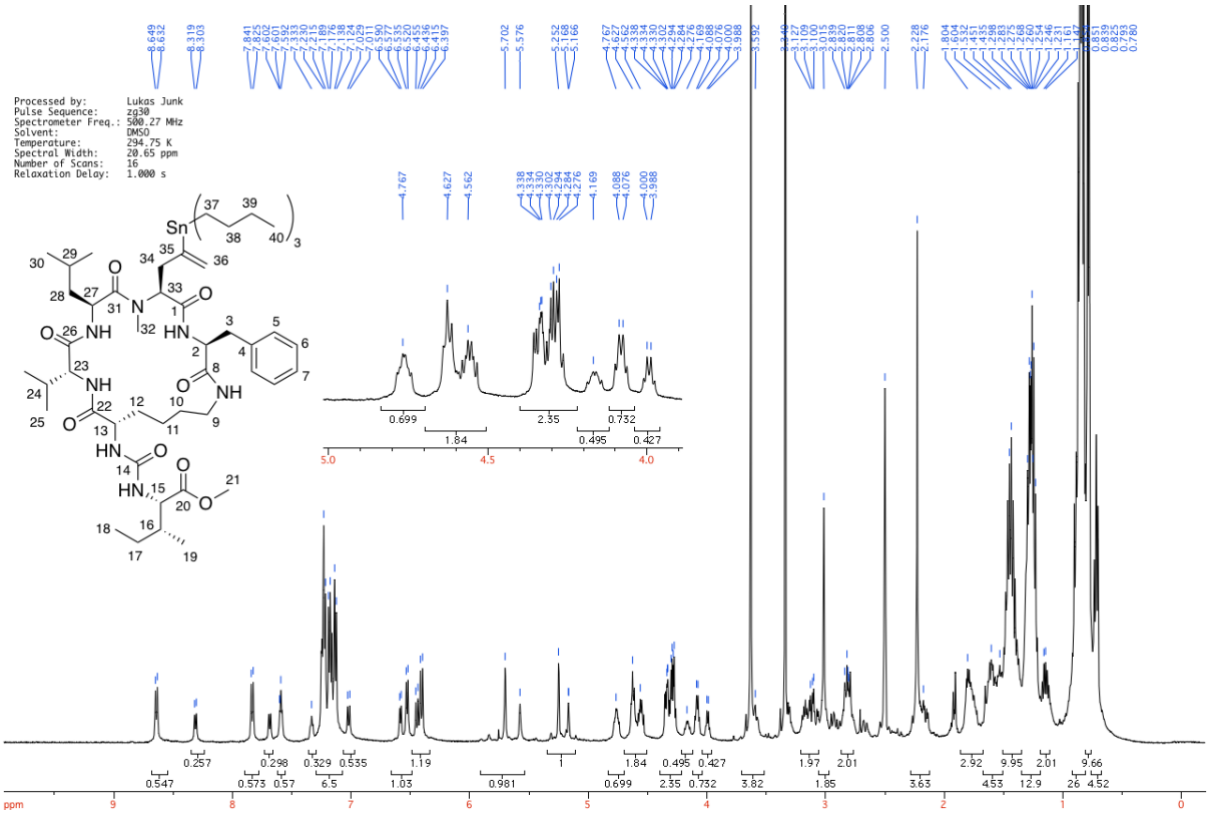
^{1}H-NMR of 9a



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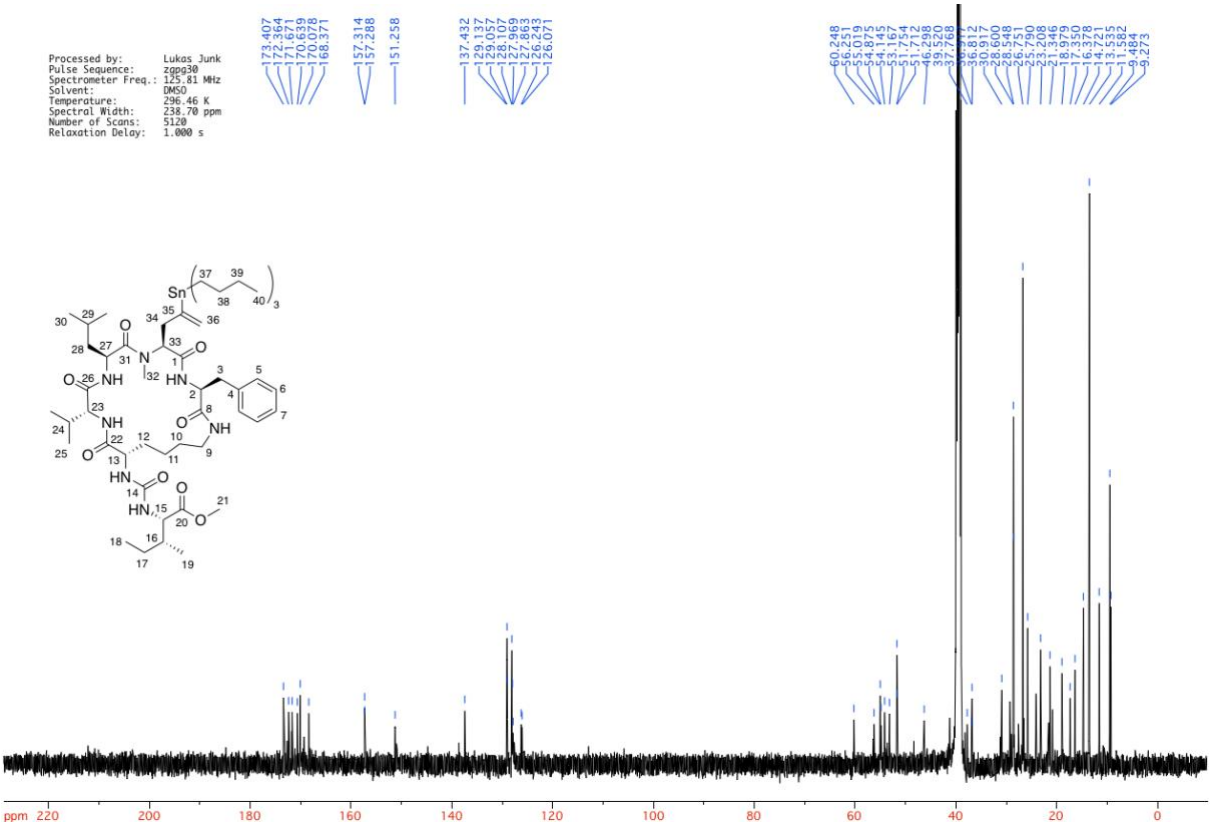

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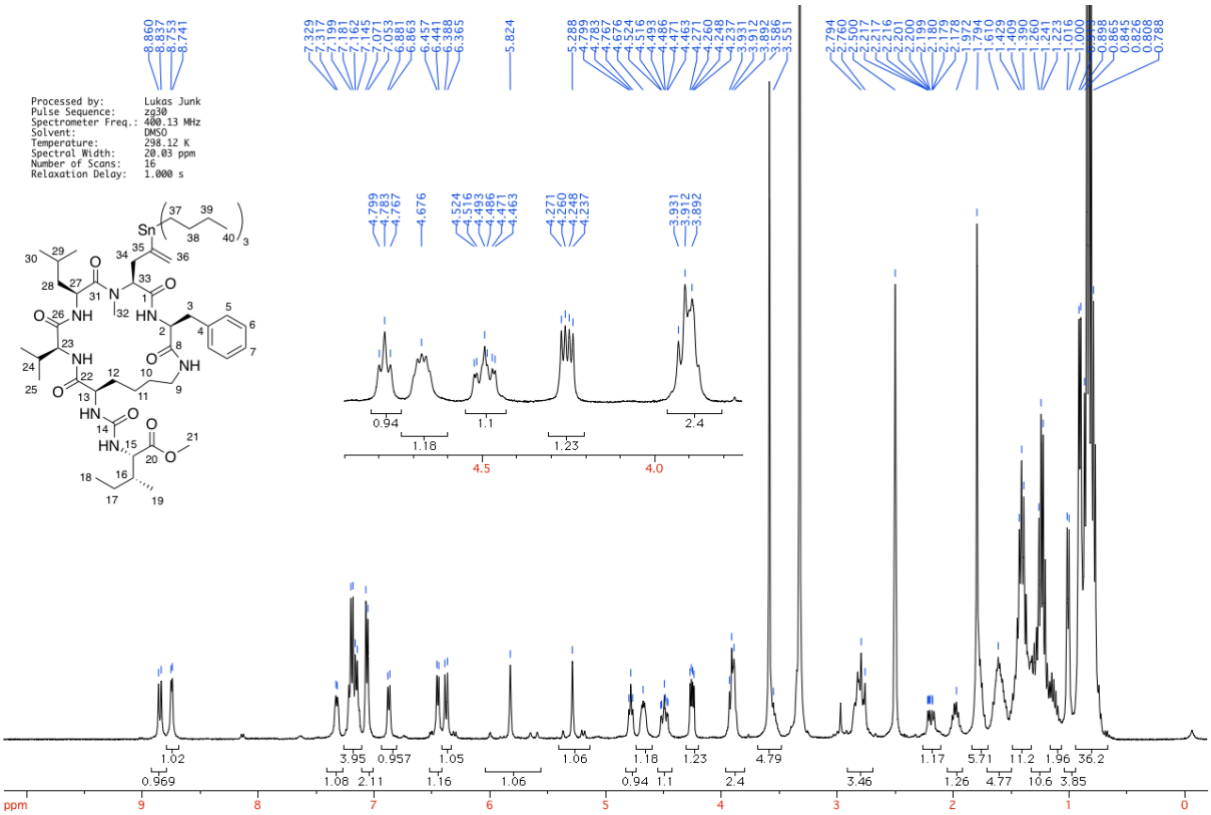
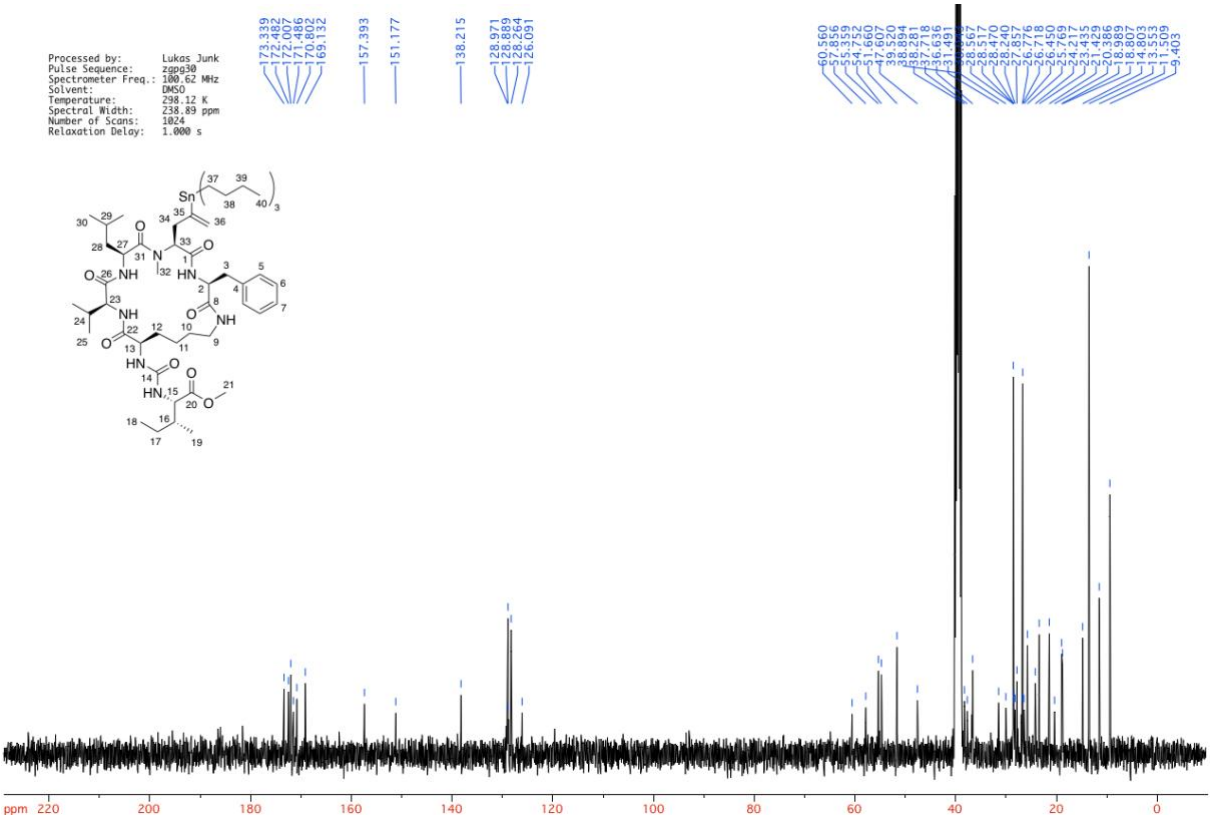
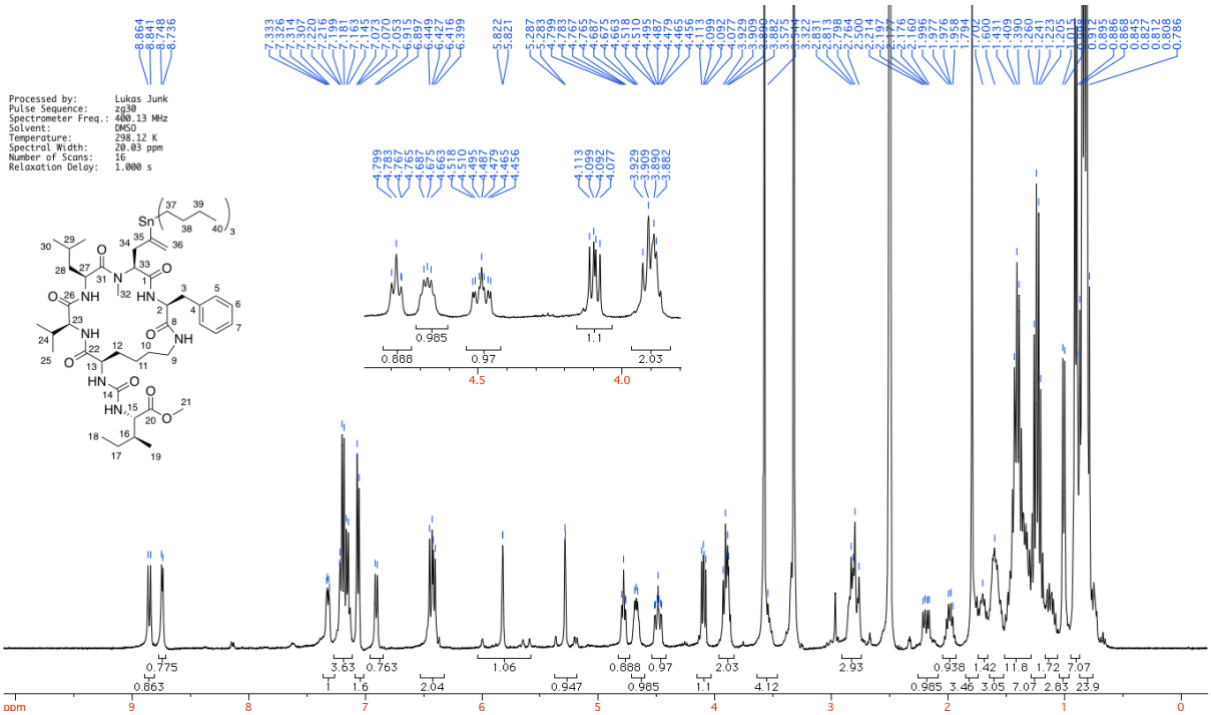


^{13}C-NMR of 9b



SUPPORTING INFORMATION

^{1}H-NMR of 9c



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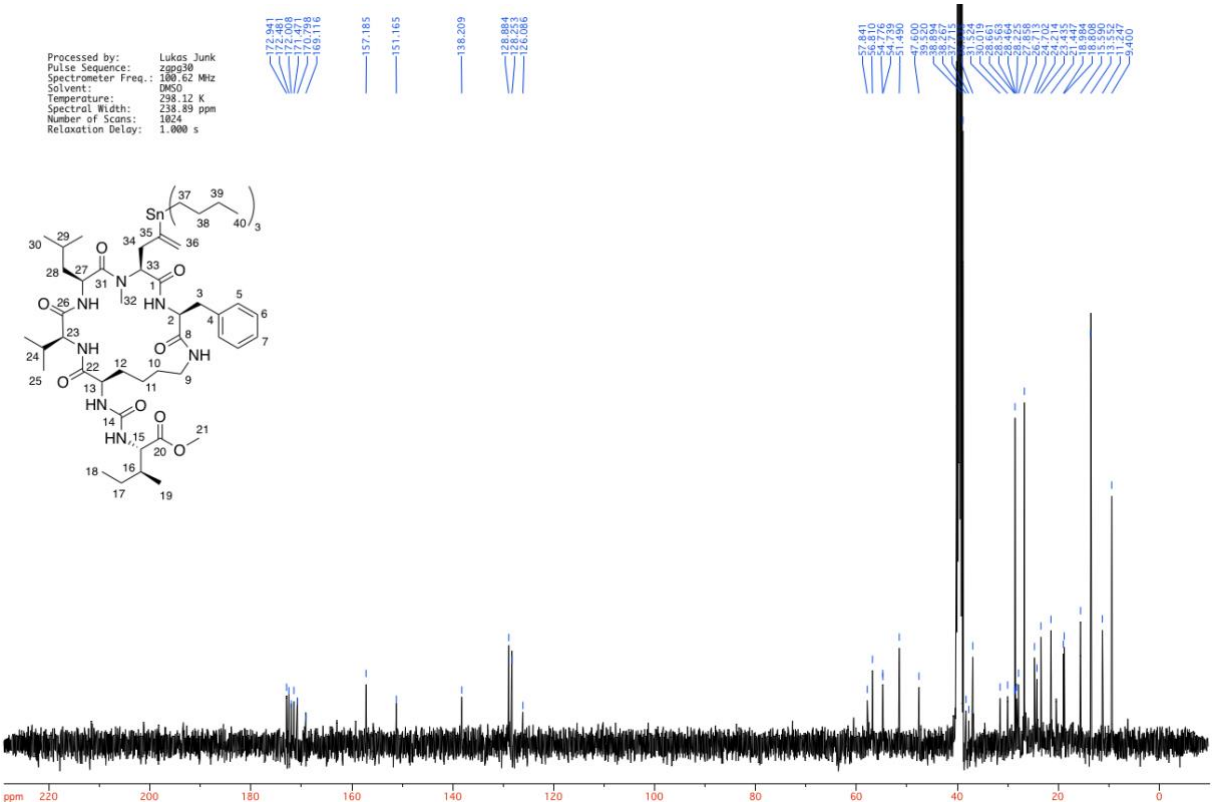
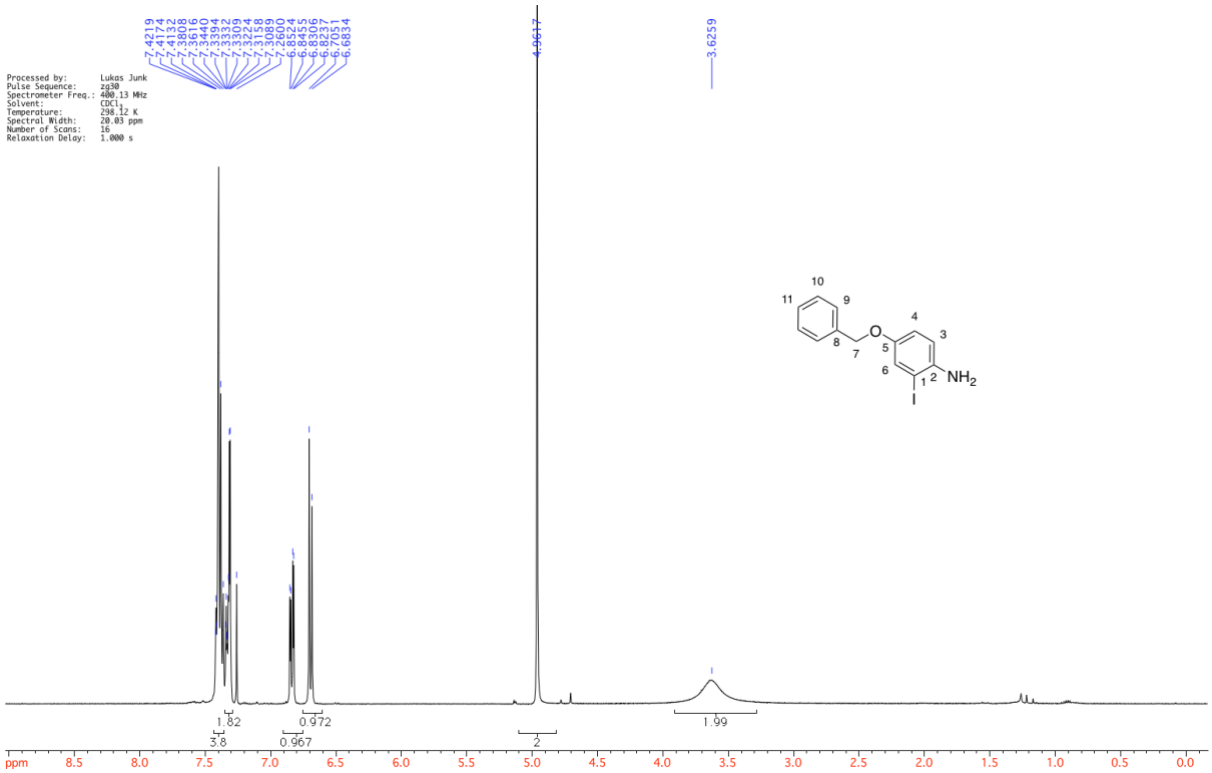


SUPPORTING INFORMATION

^{1}H-NMR of E



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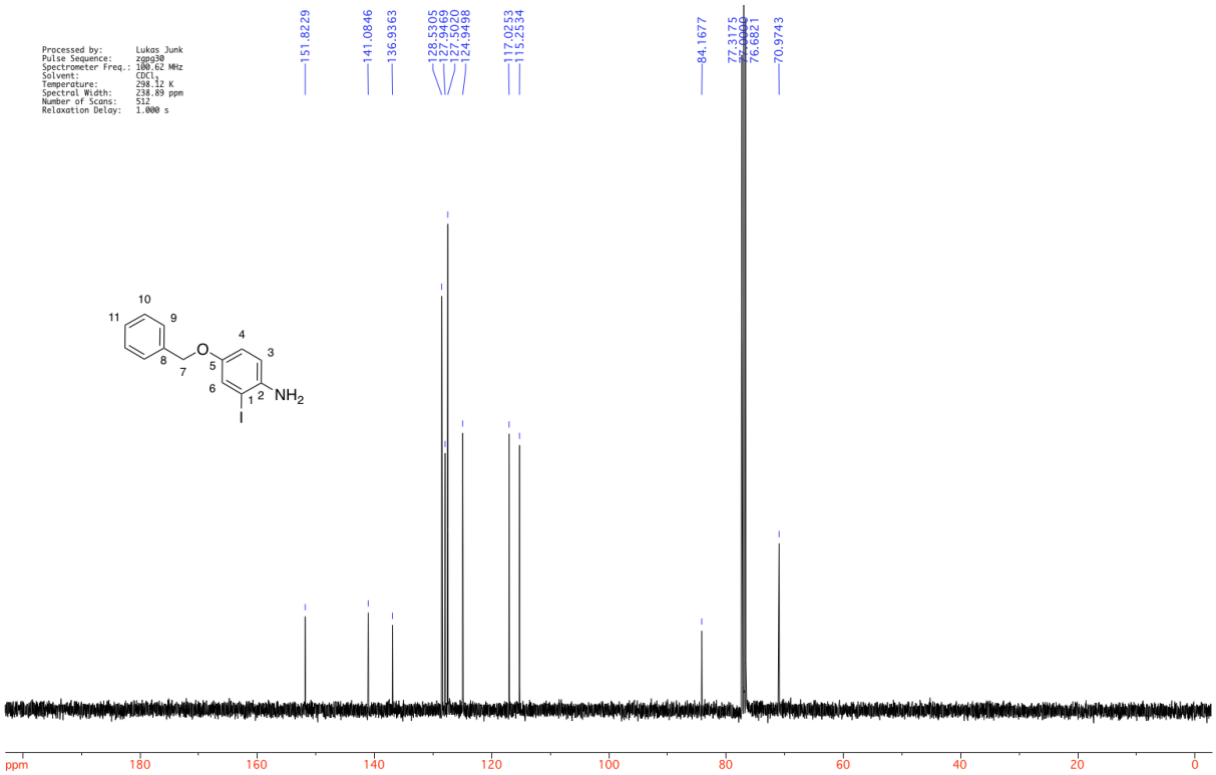

SUPPORTING INFORMATION

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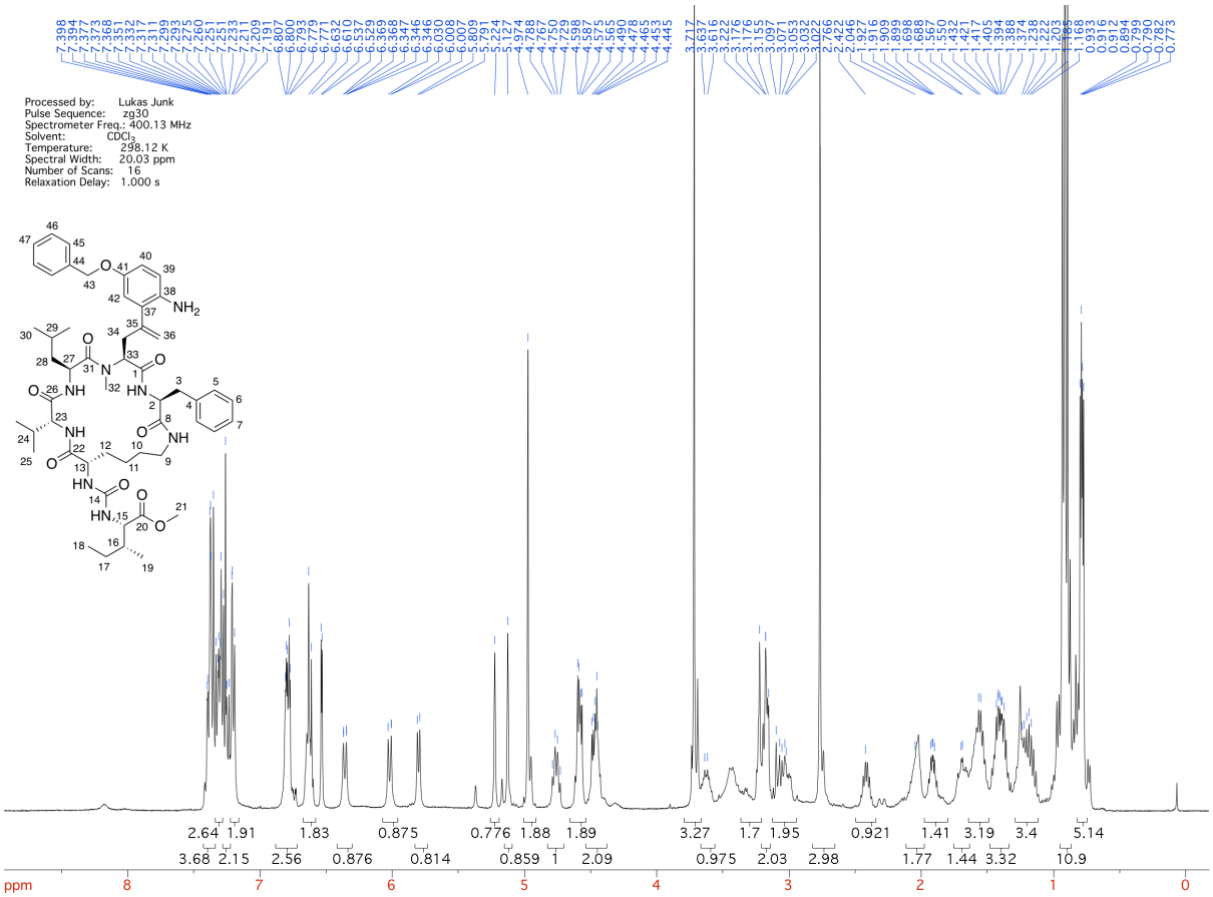

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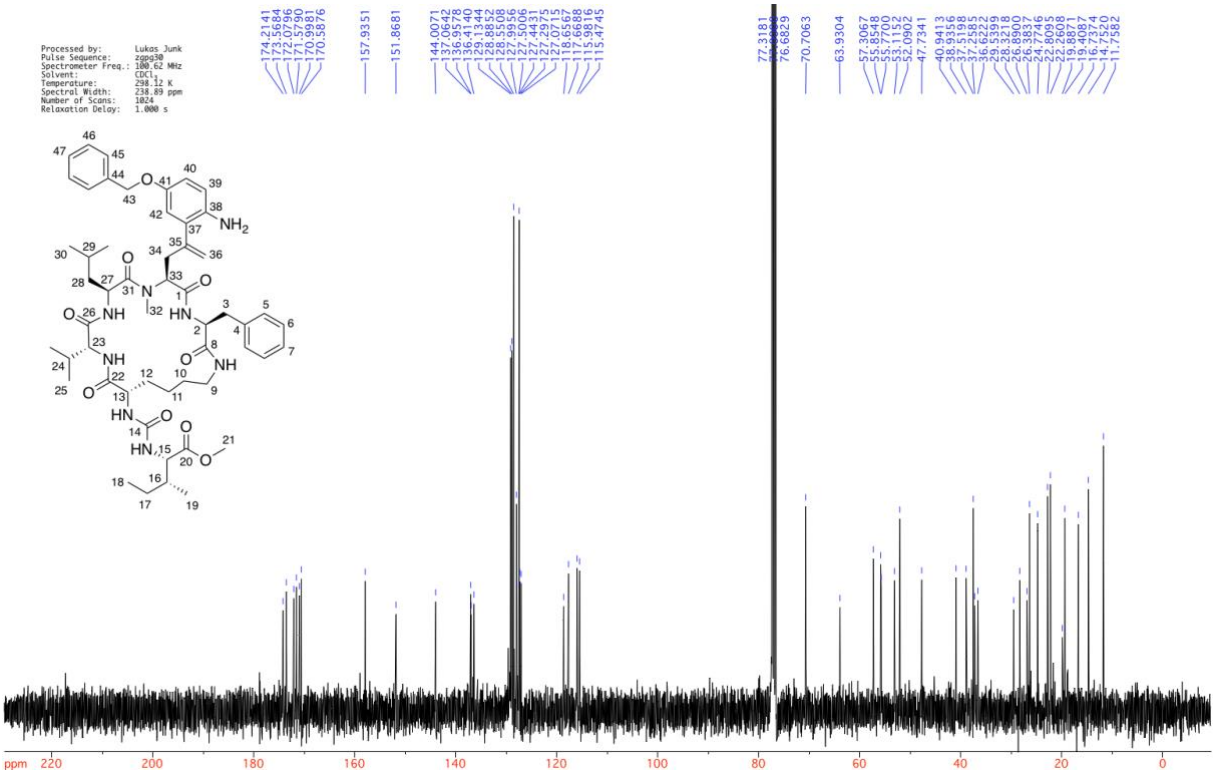

SUPPORTING INFORMATION

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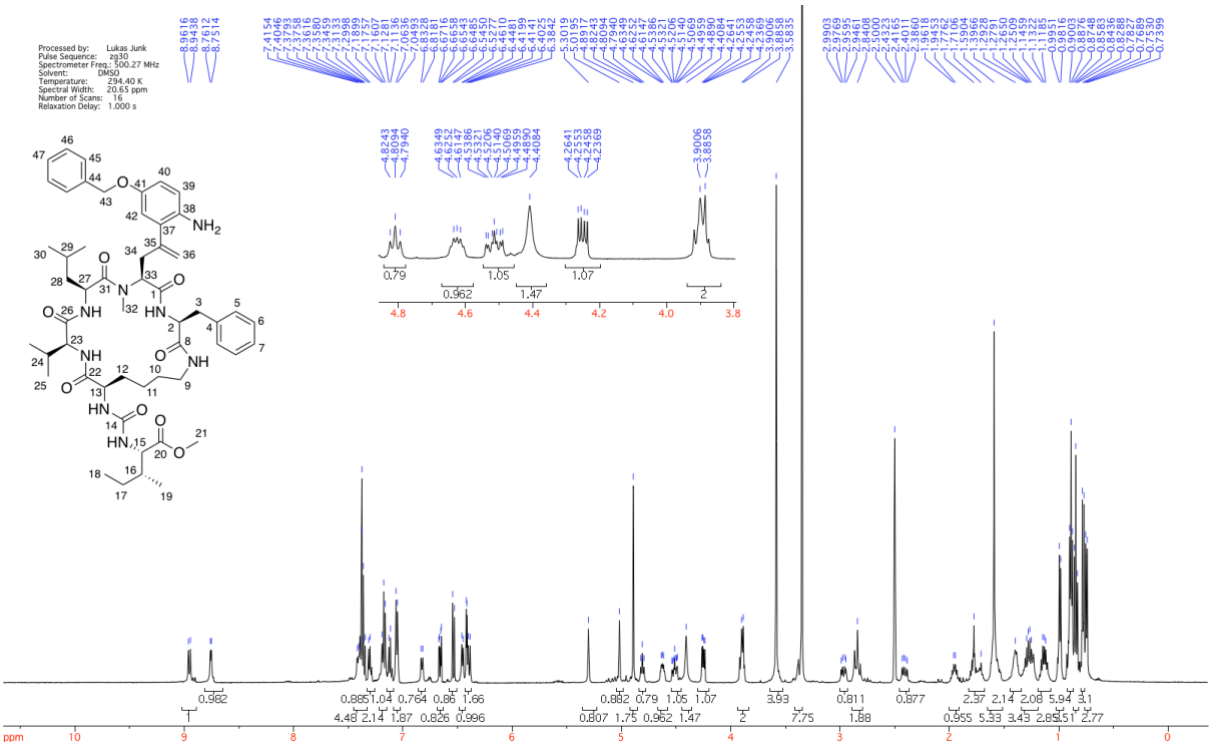

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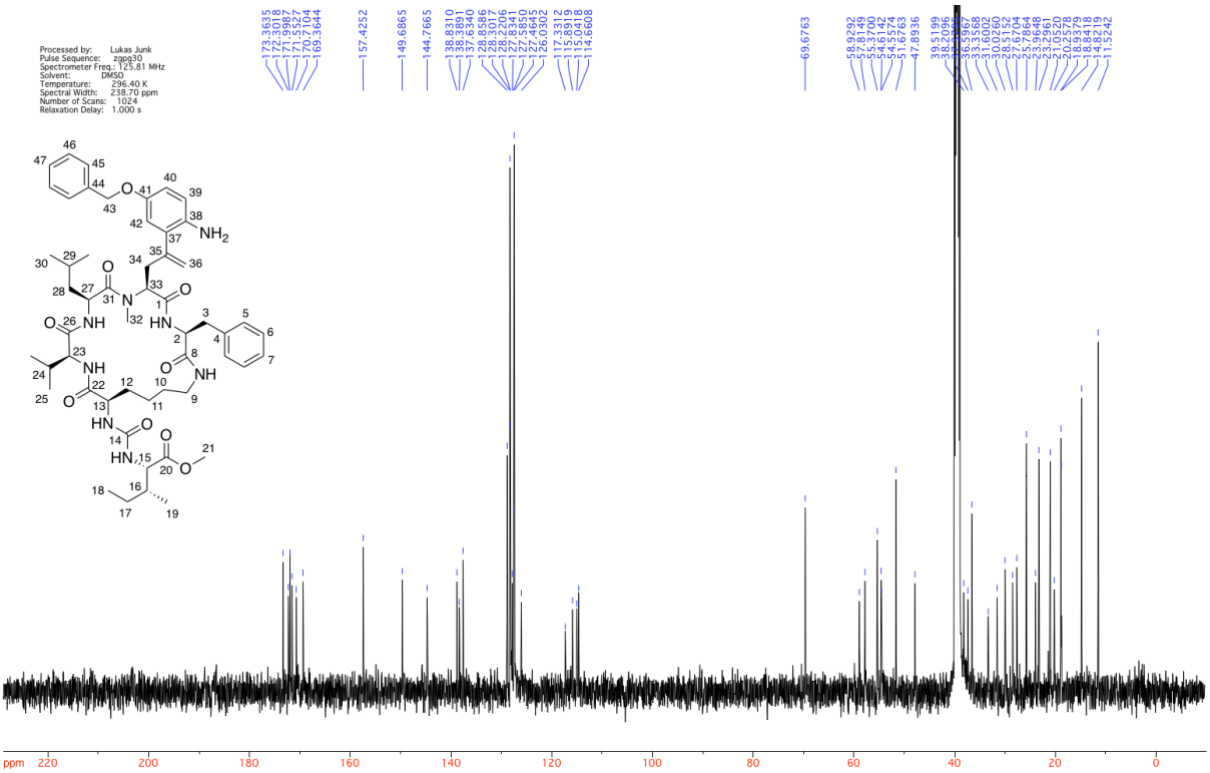

SUPPORTING INFORMATION

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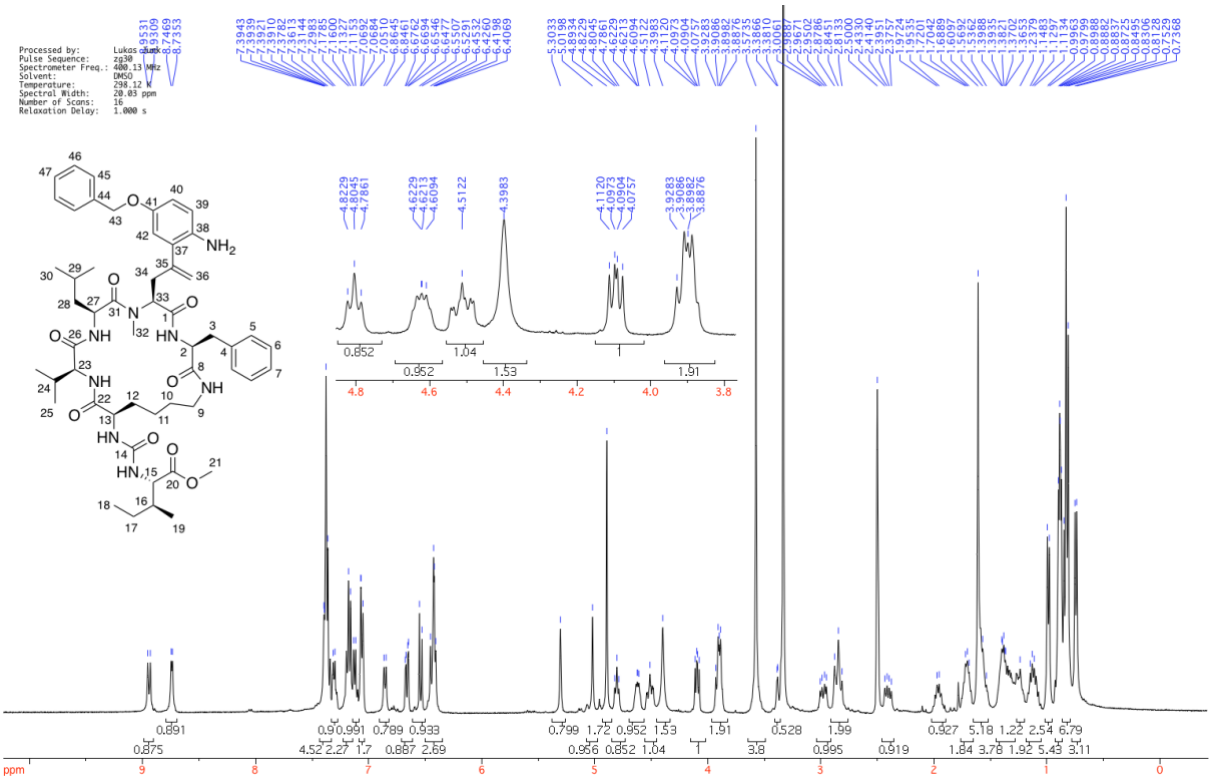

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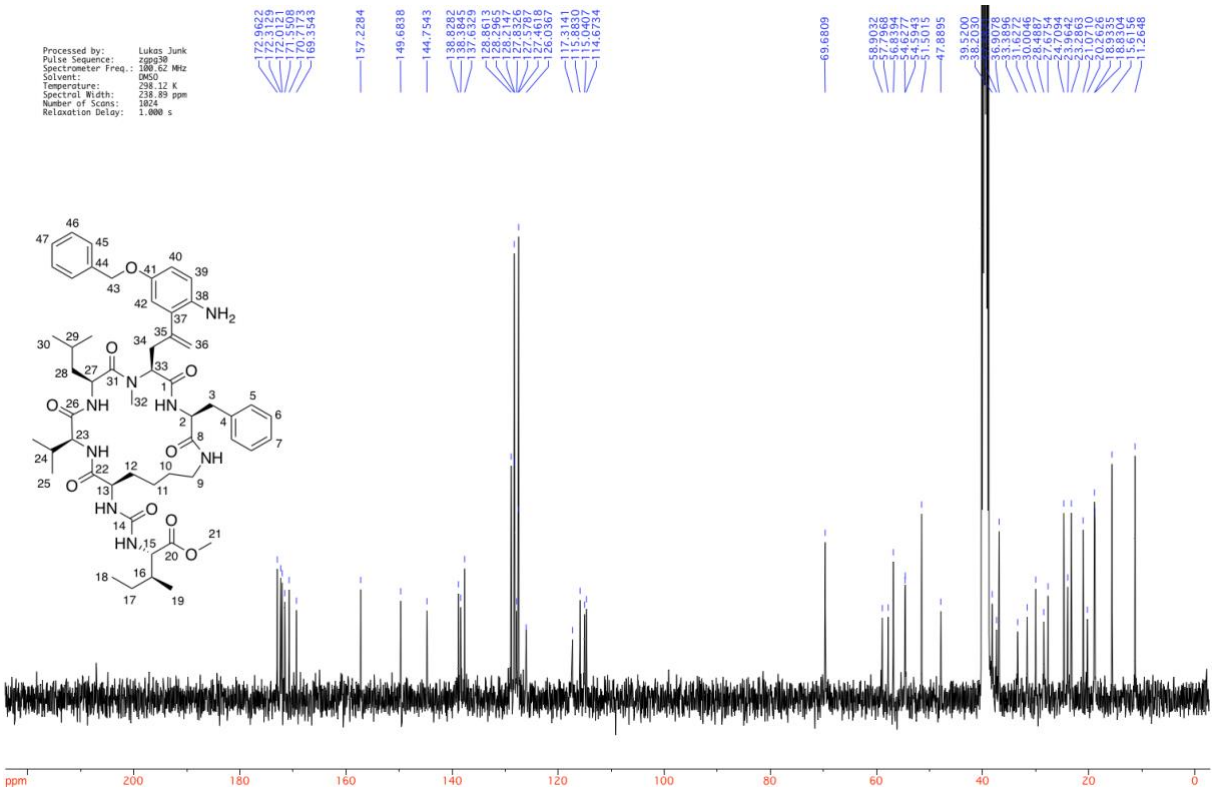

SUPPORTING INFORMATION

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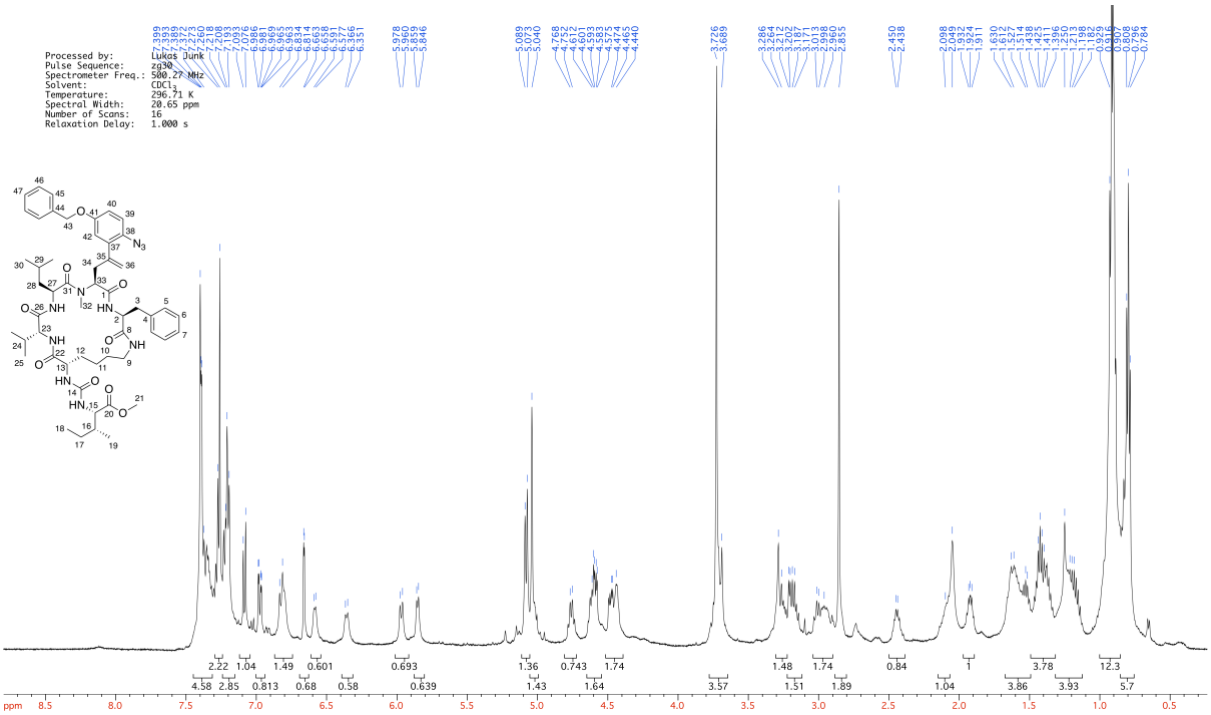

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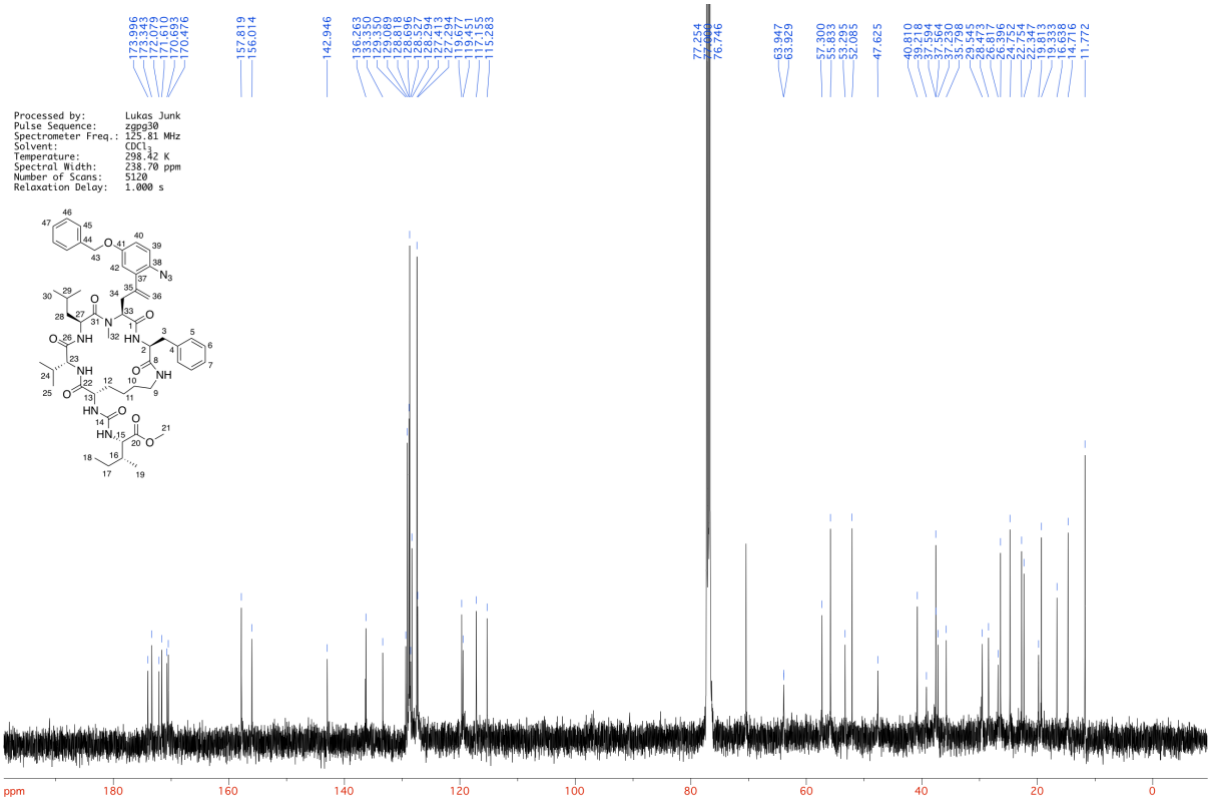

SUPPORTING INFORMATION

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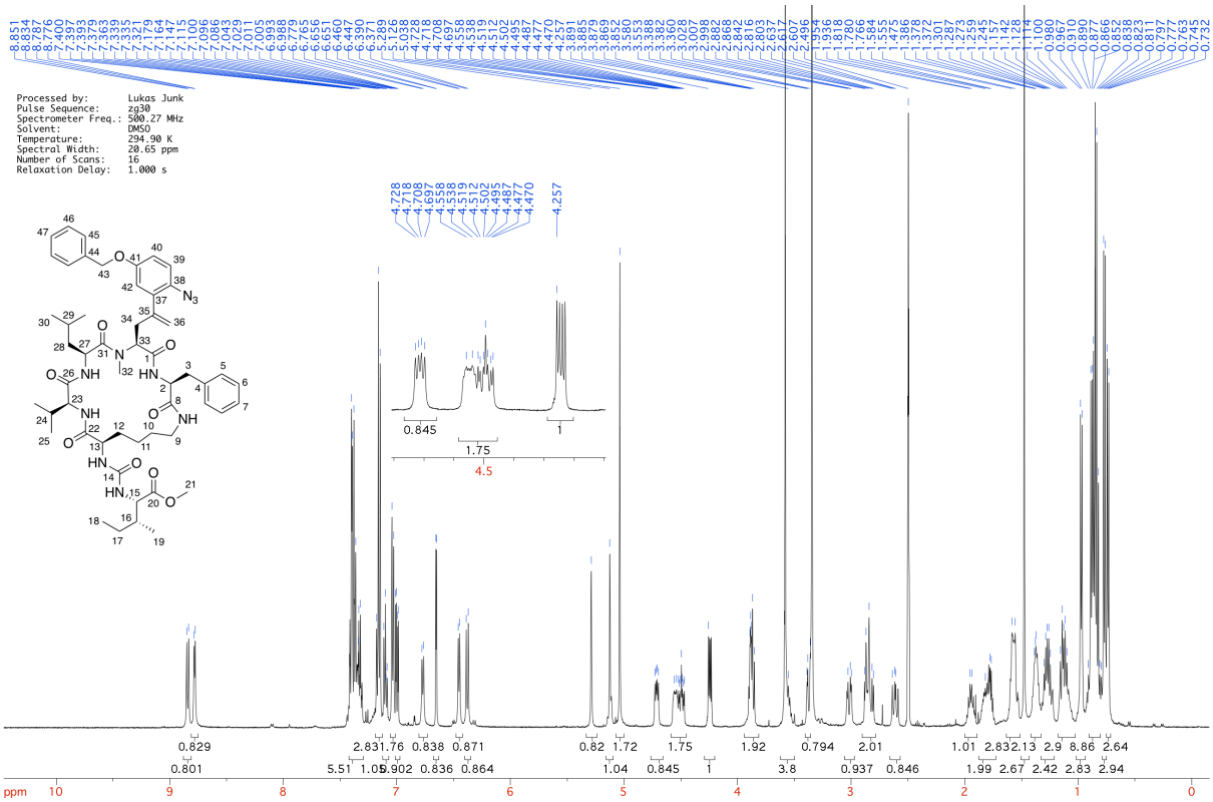

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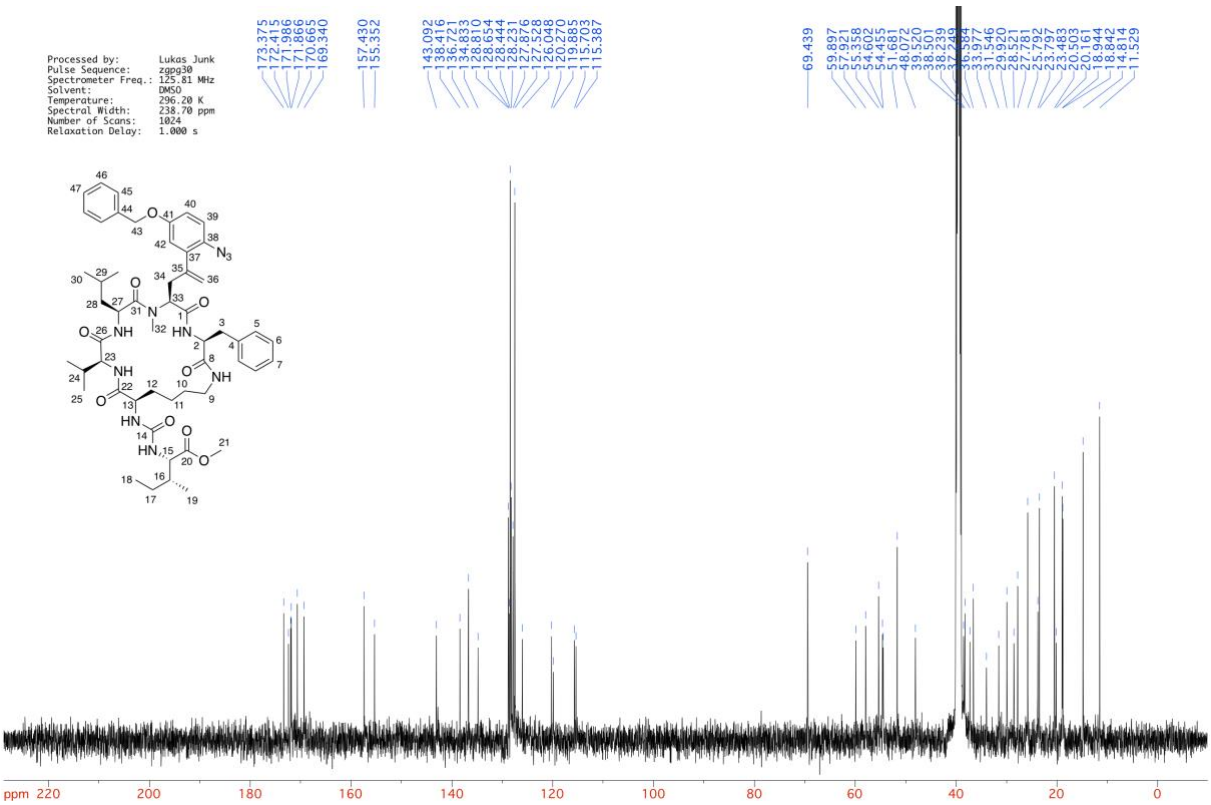
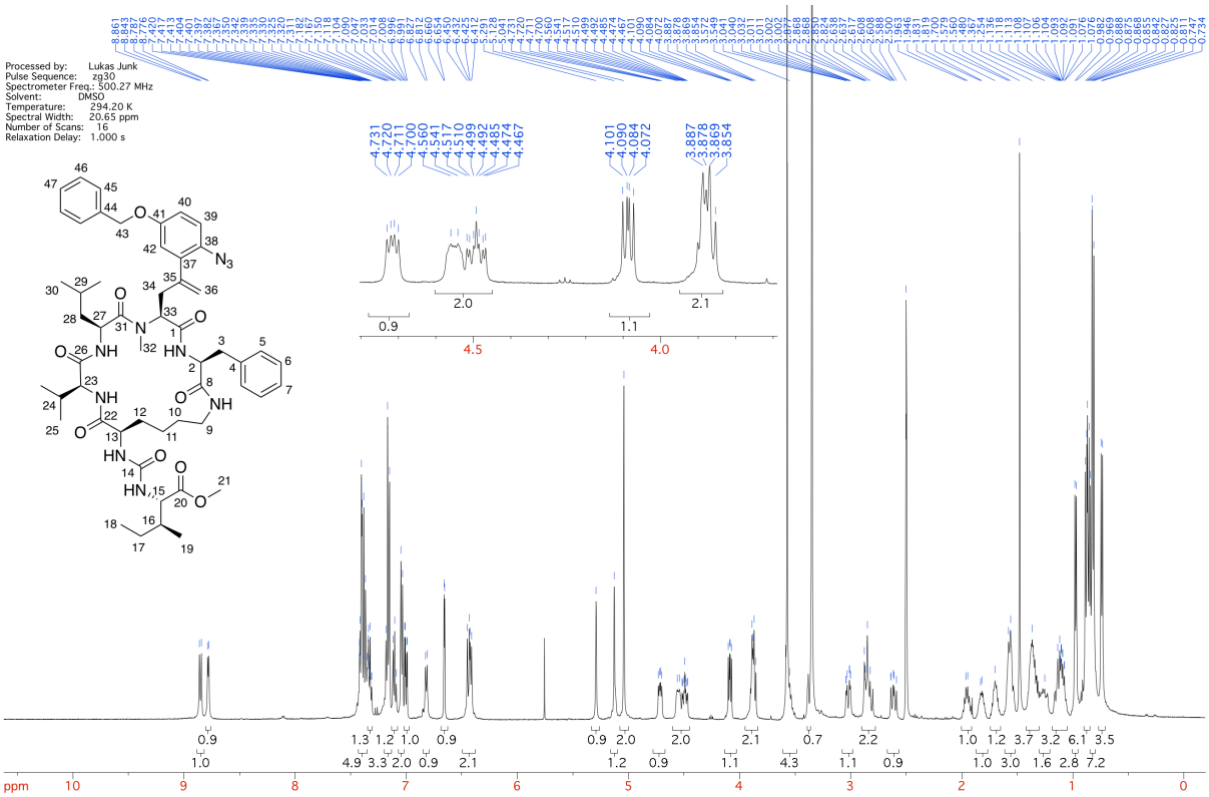


SUPPORTING INFORMATION

^{1}H-NMR of 11c



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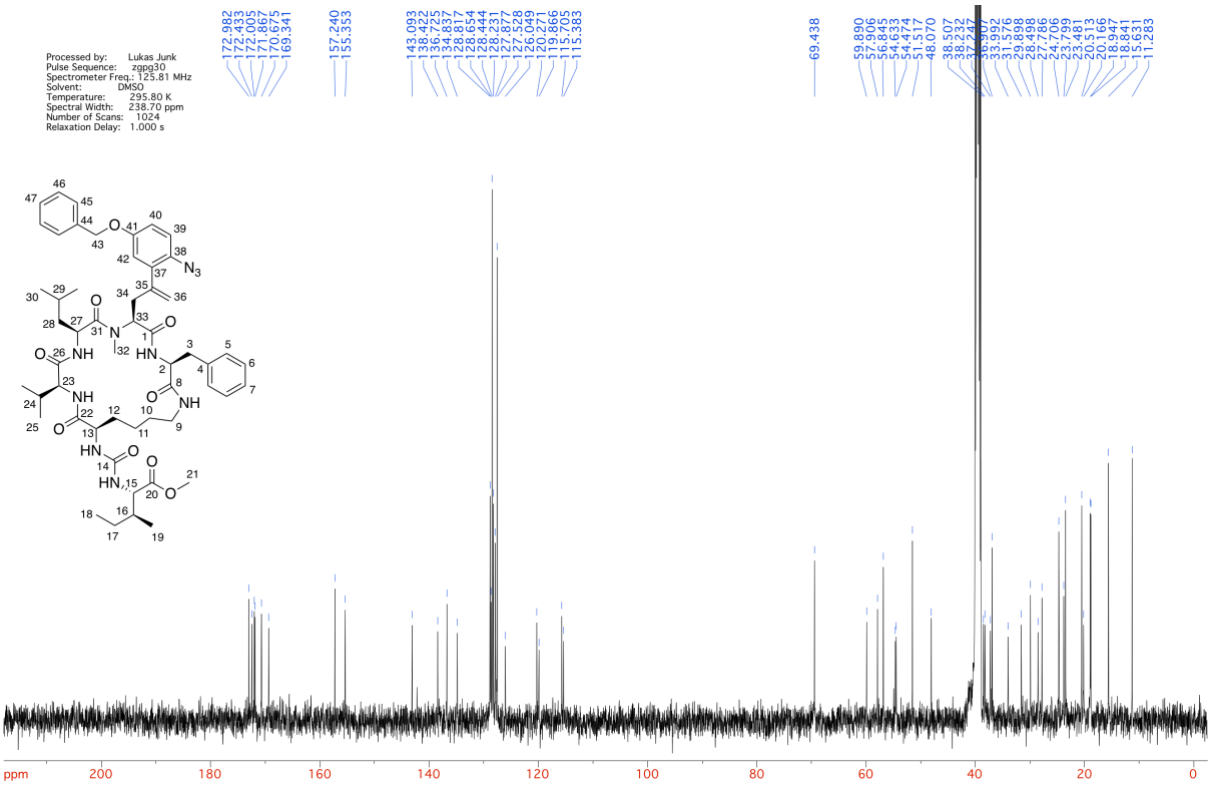
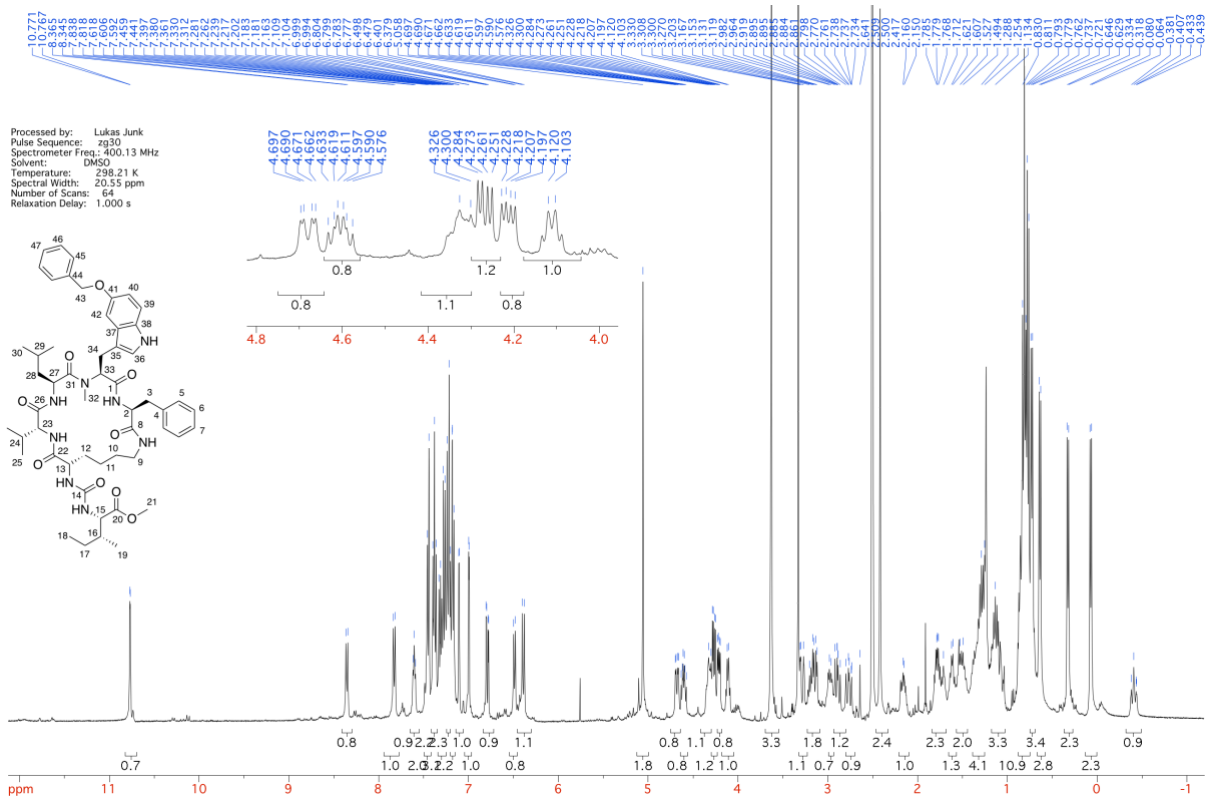


SUPPORTING INFORMATION

^{1}H-NMR of 12a



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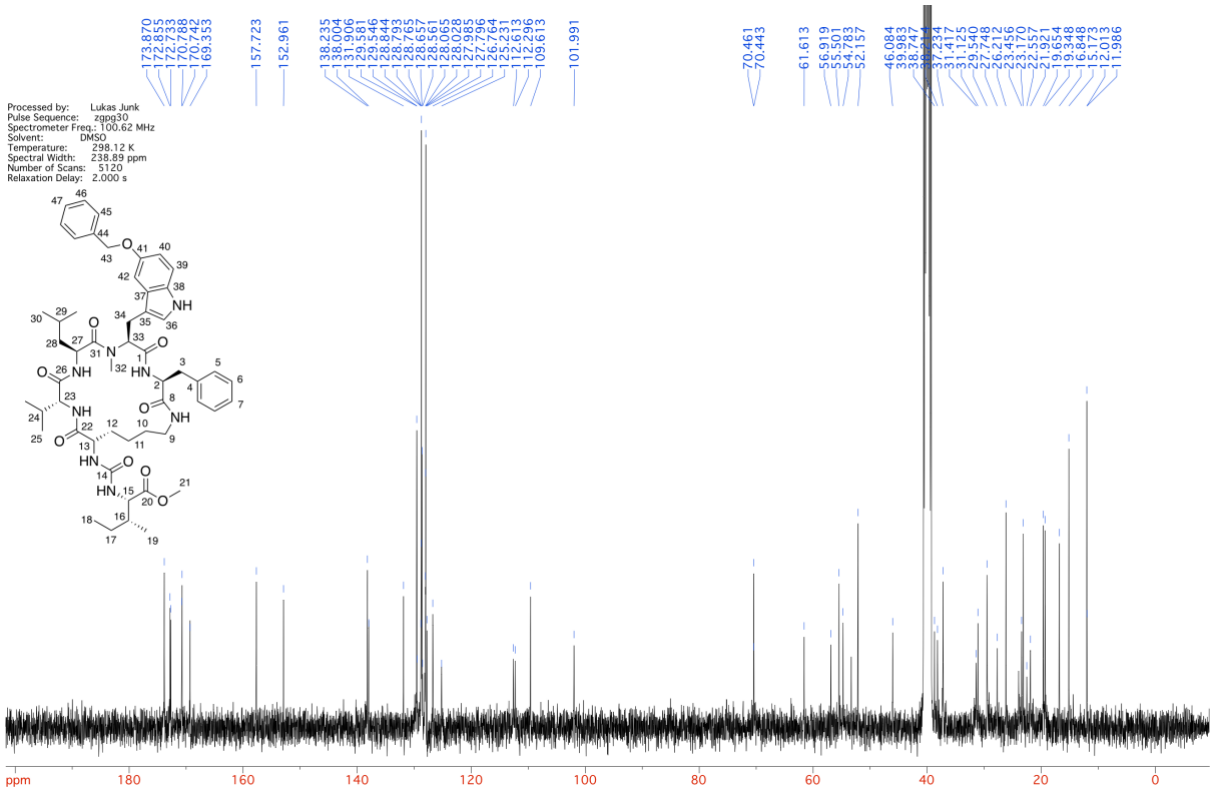

SUPPORTING INFORMATION

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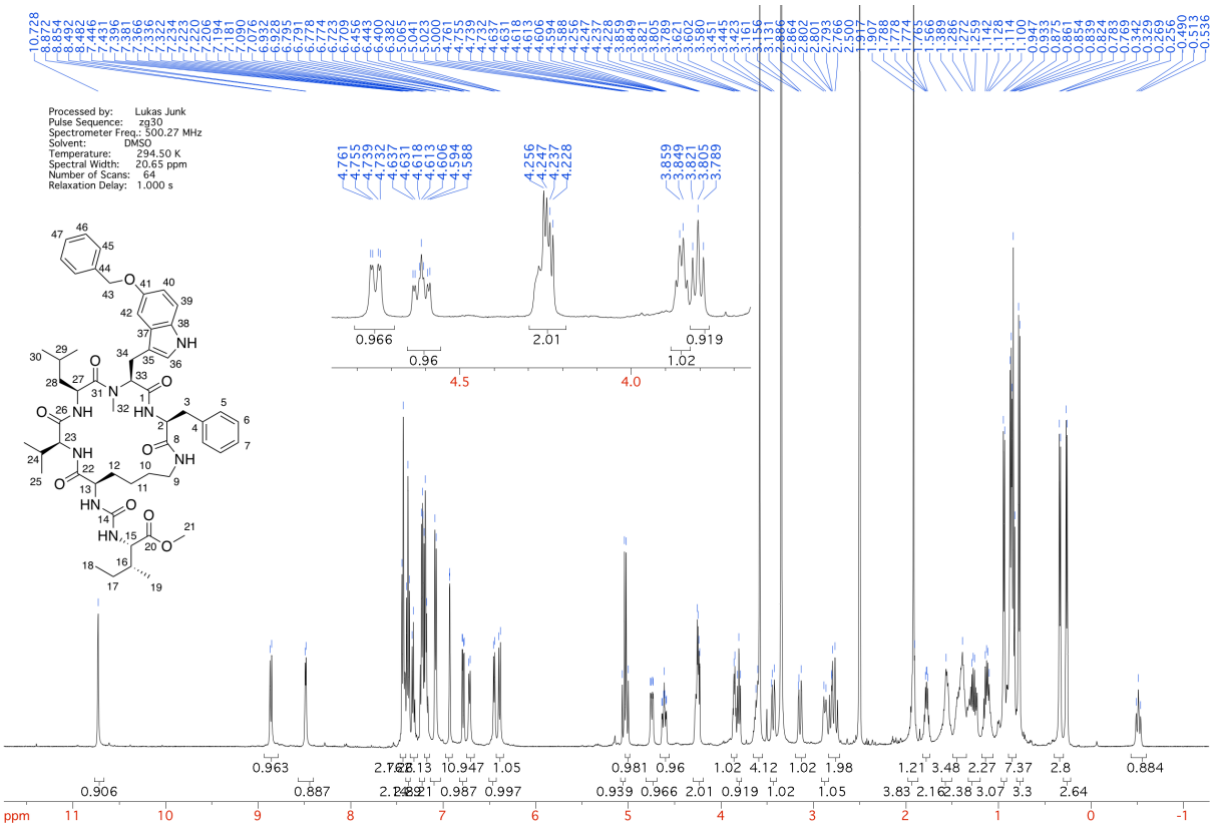

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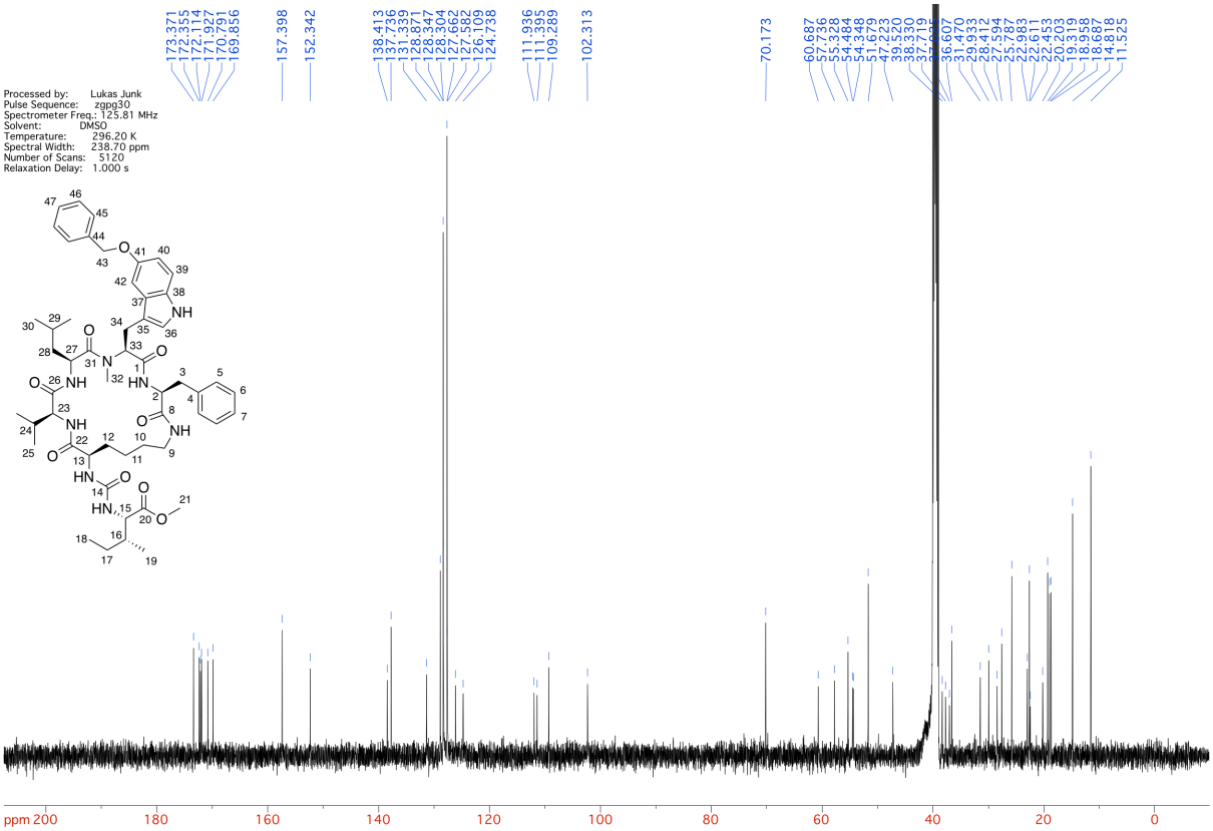
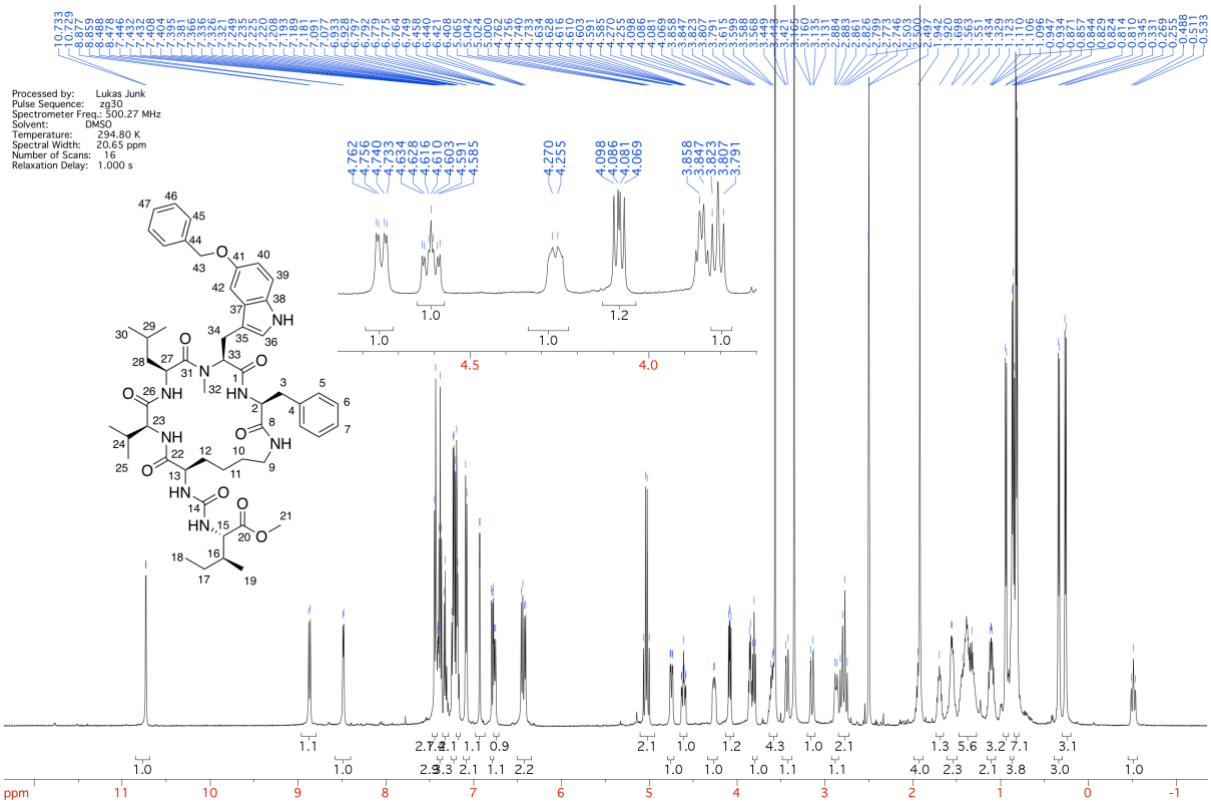


SUPPORTING INFORMATION

^{1}H-NMR of 12c



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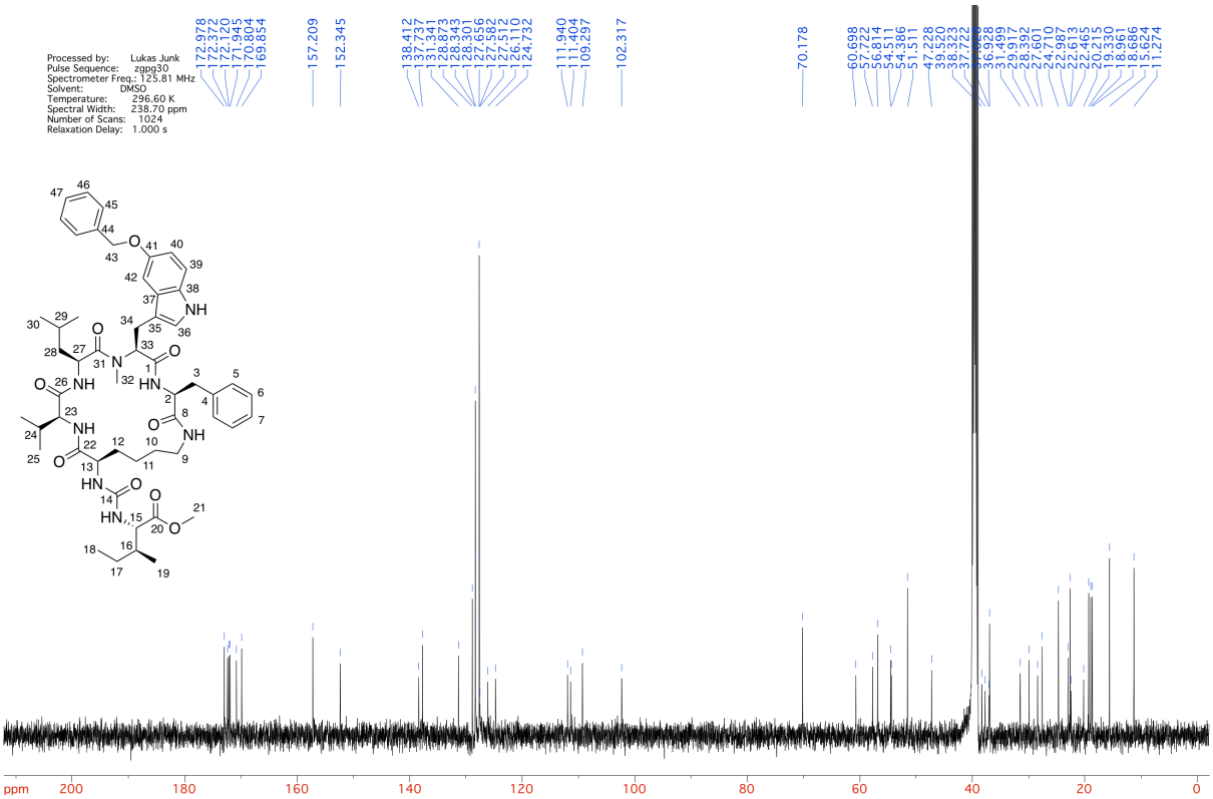

SUPPORTING INFORMATION

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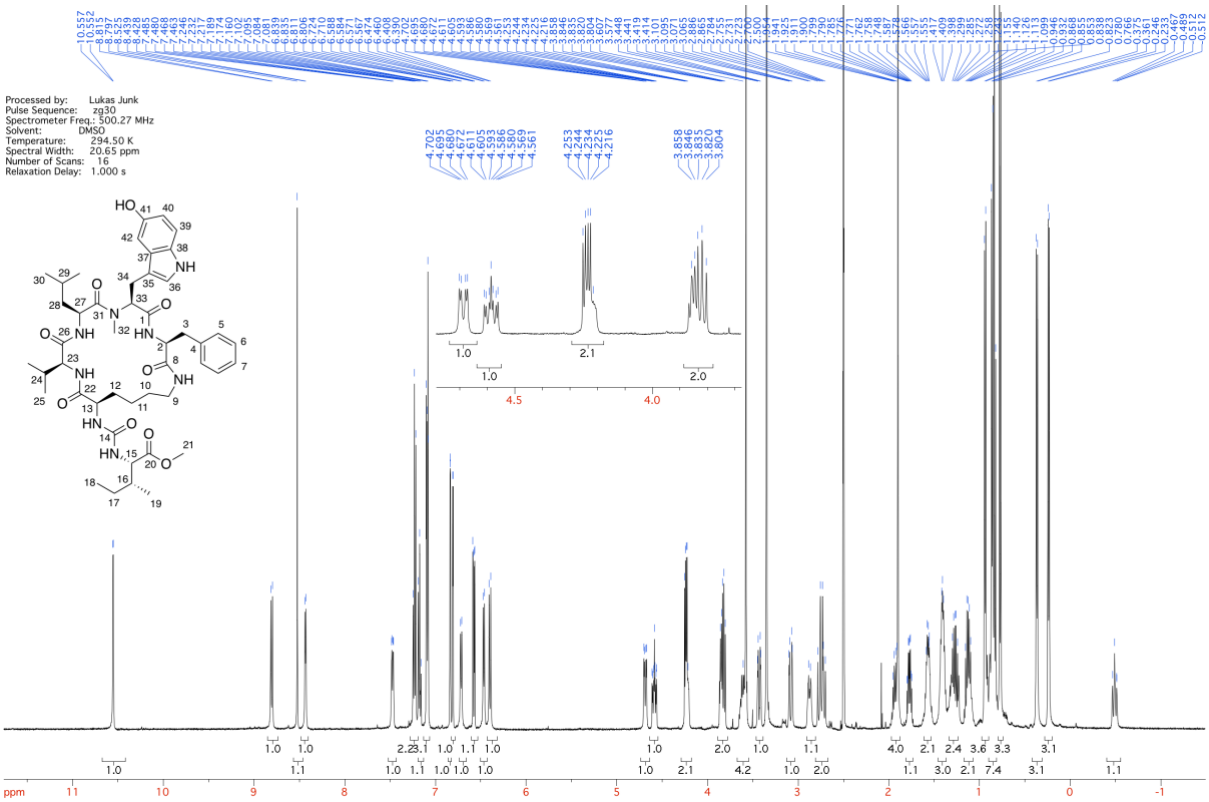

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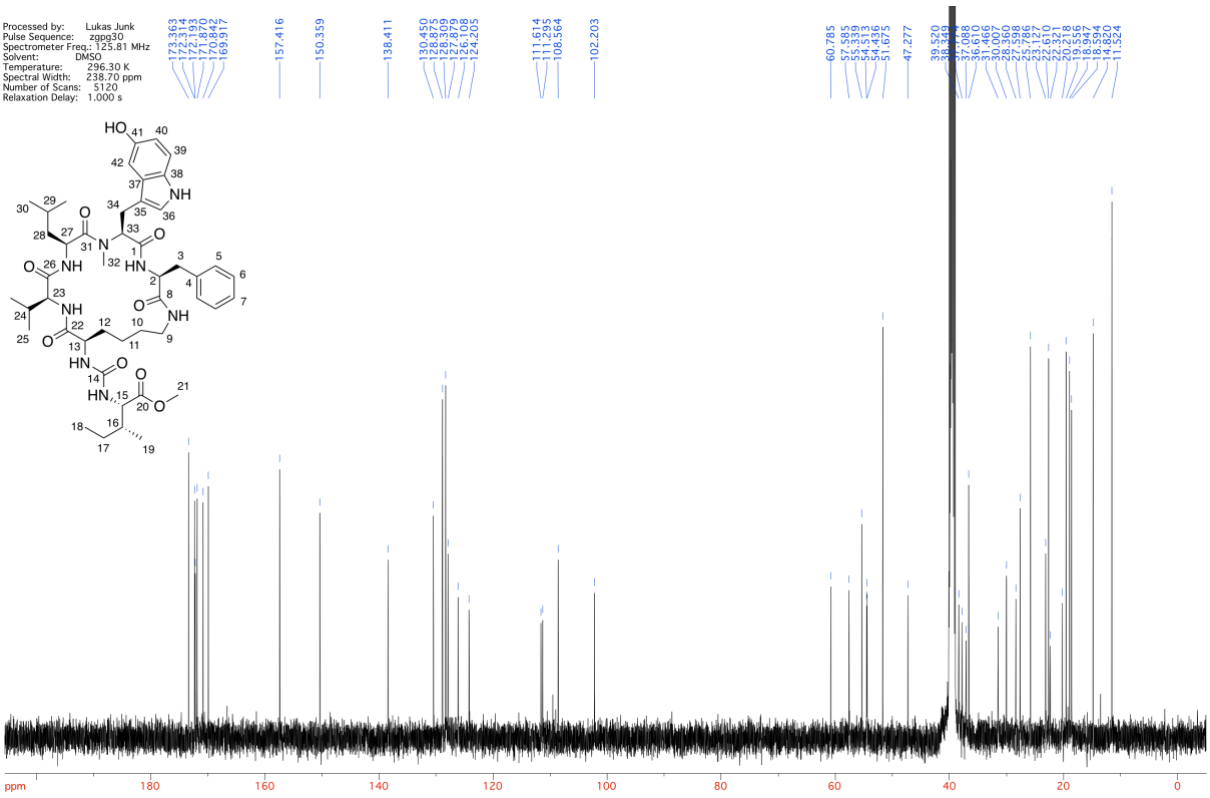

SUPPORTING INFORMATION

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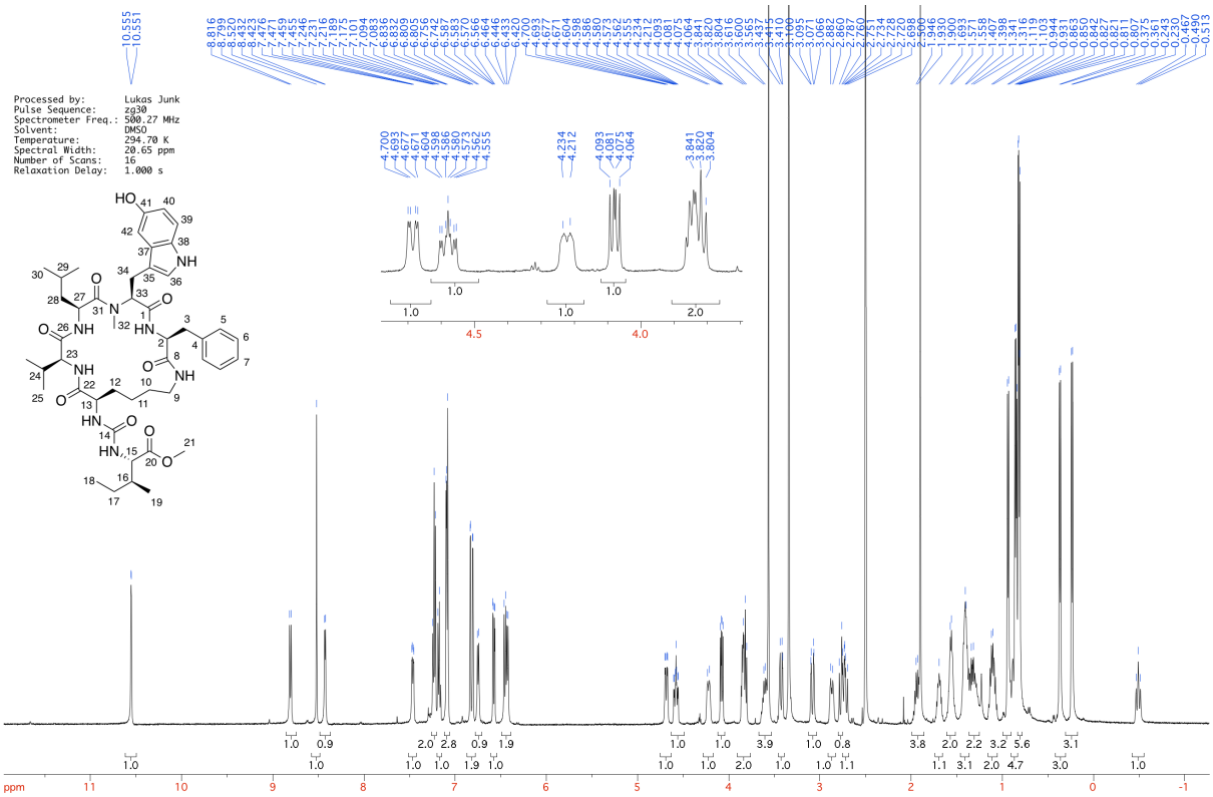

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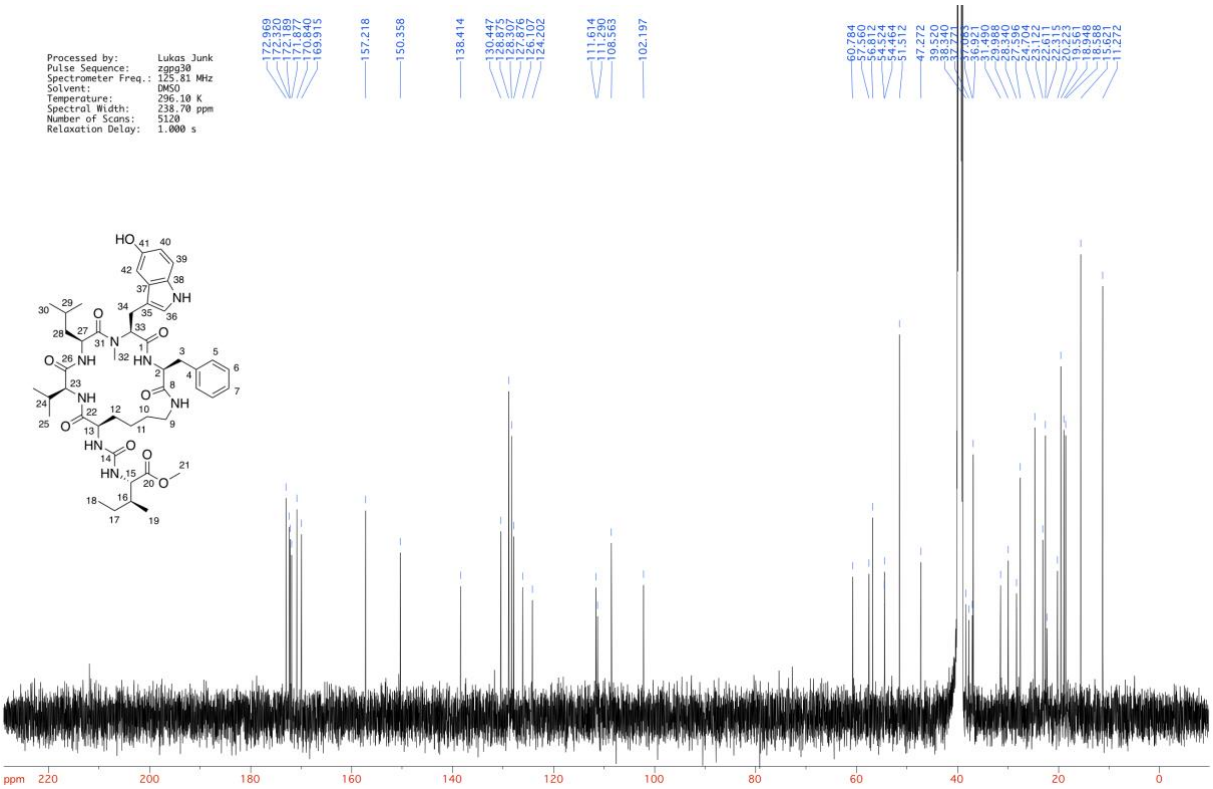

SUPPORTING INFORMATION

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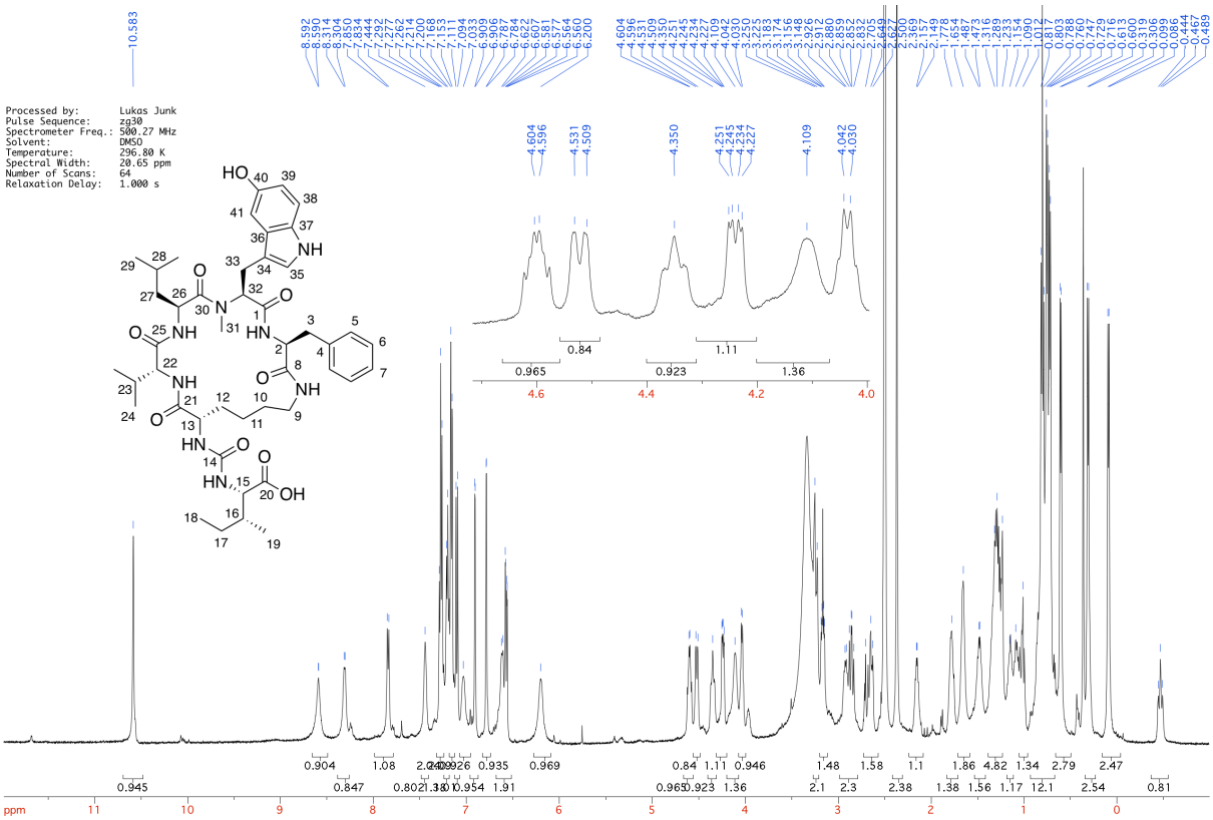

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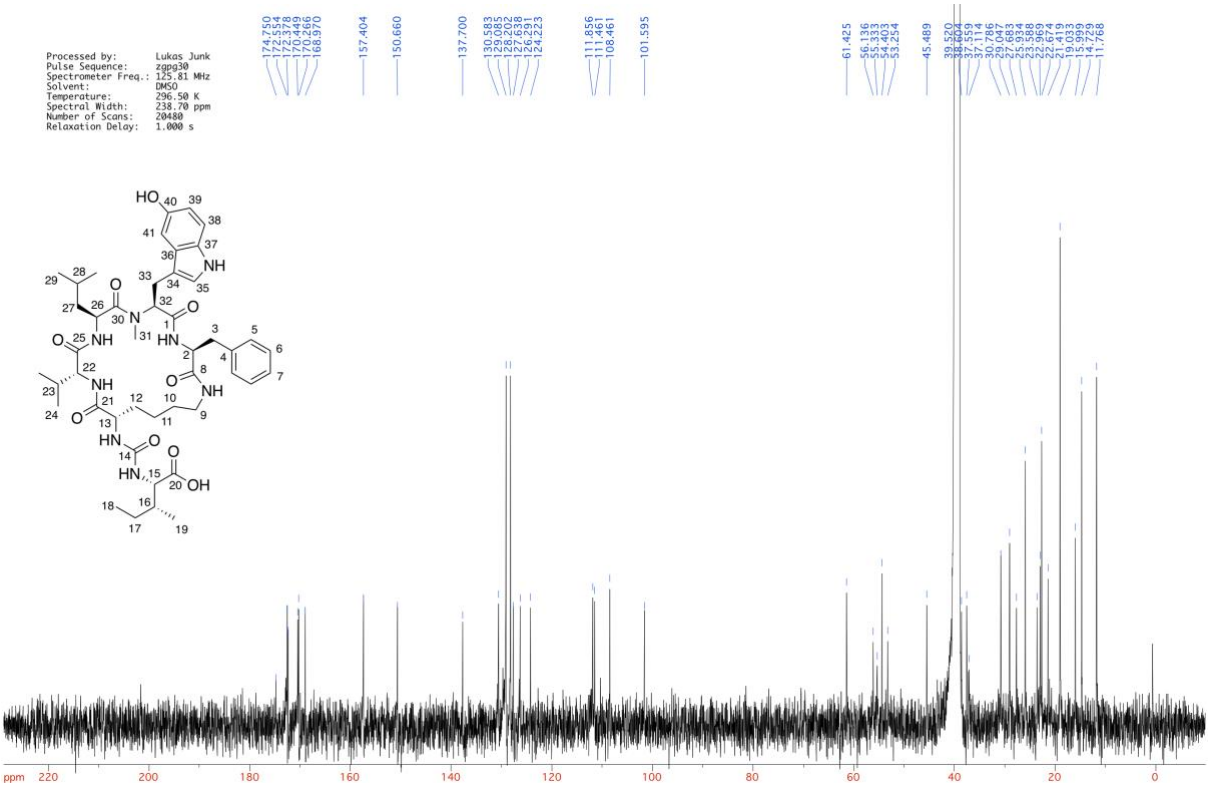

SUPPORTING INFORMATION

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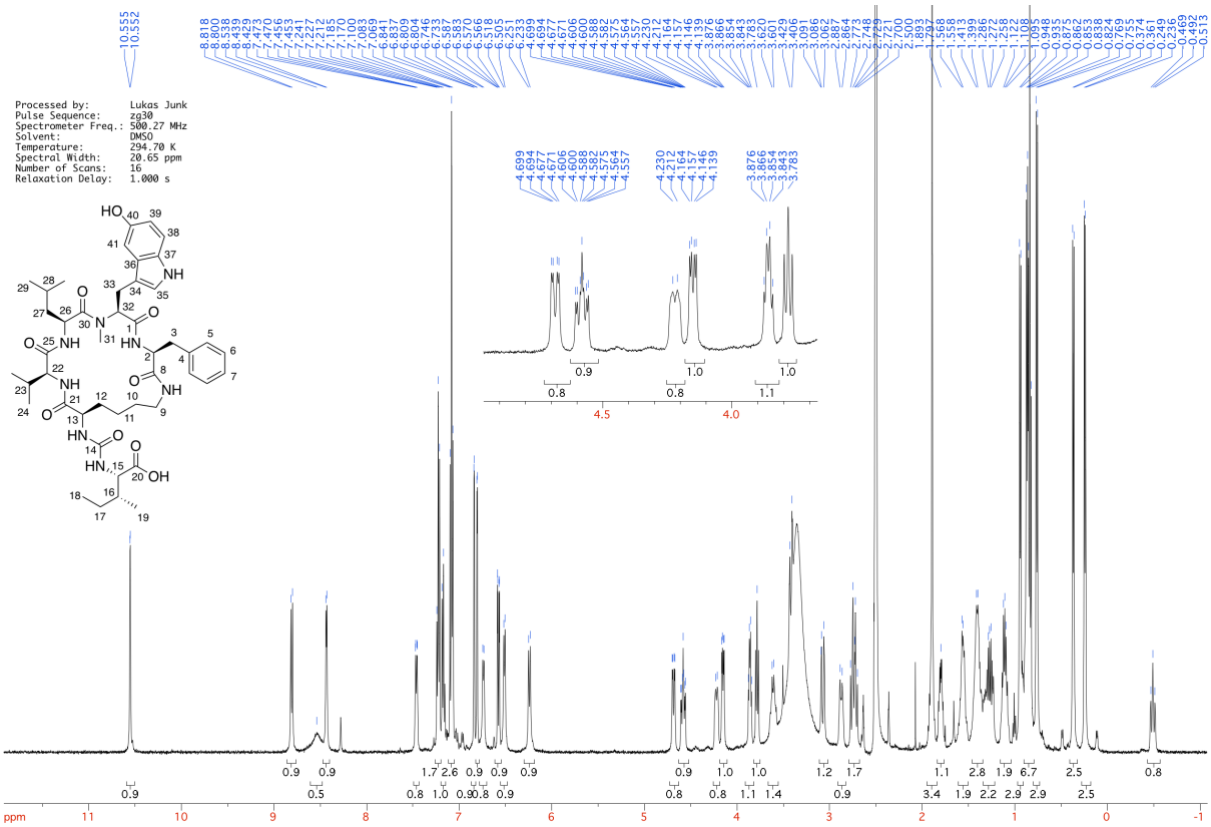

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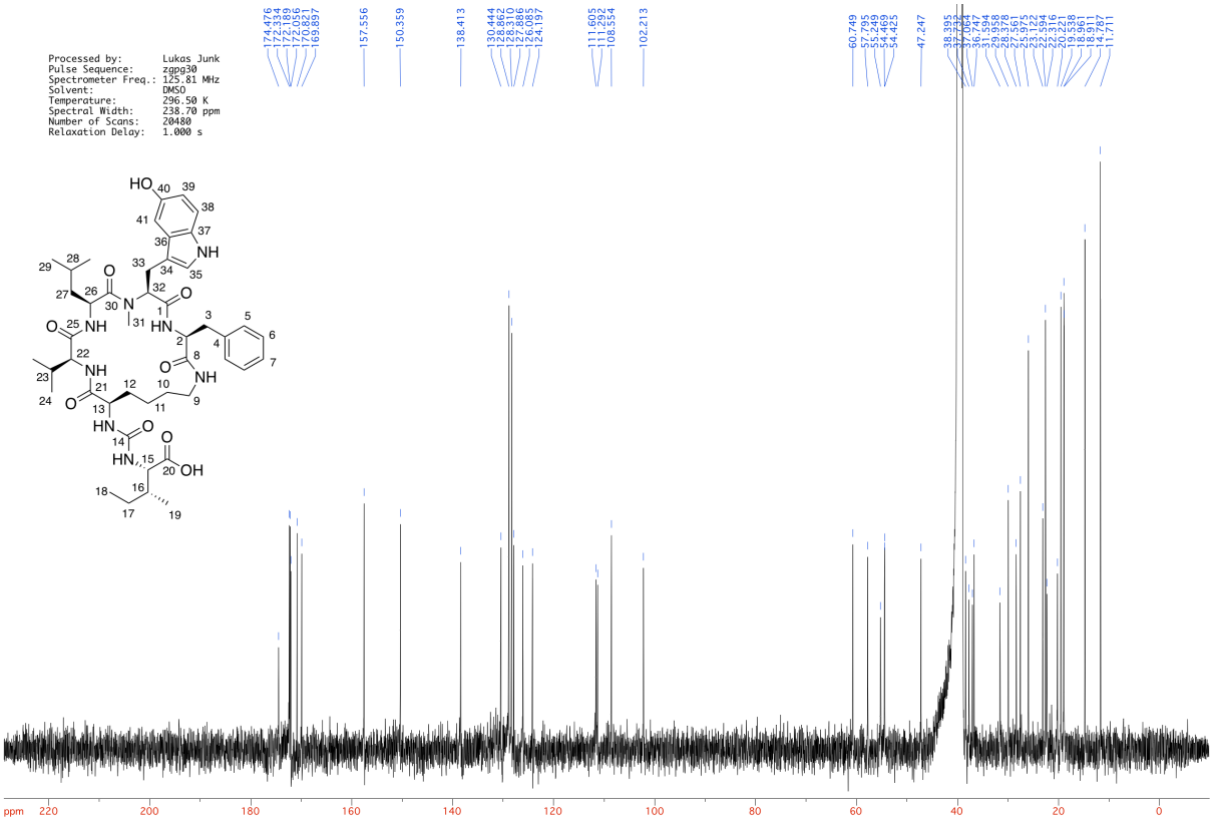

SUPPORTING INFORMATION

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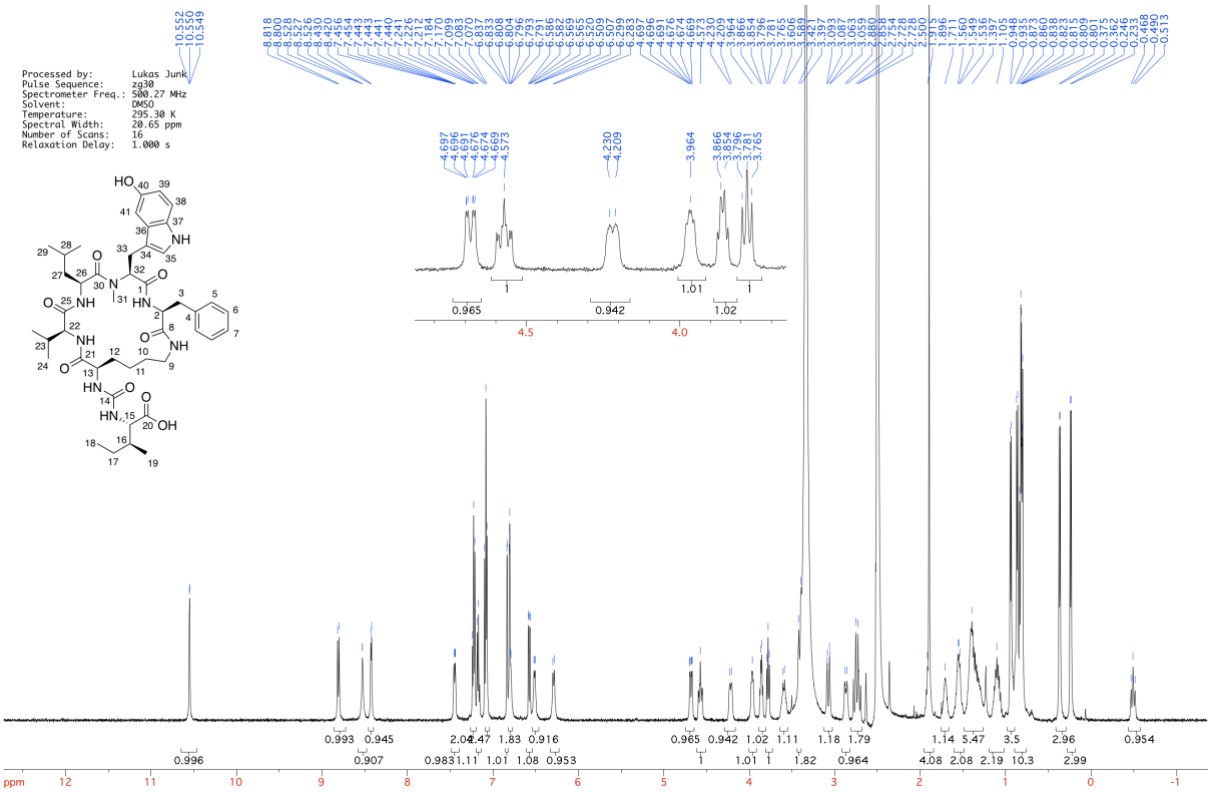

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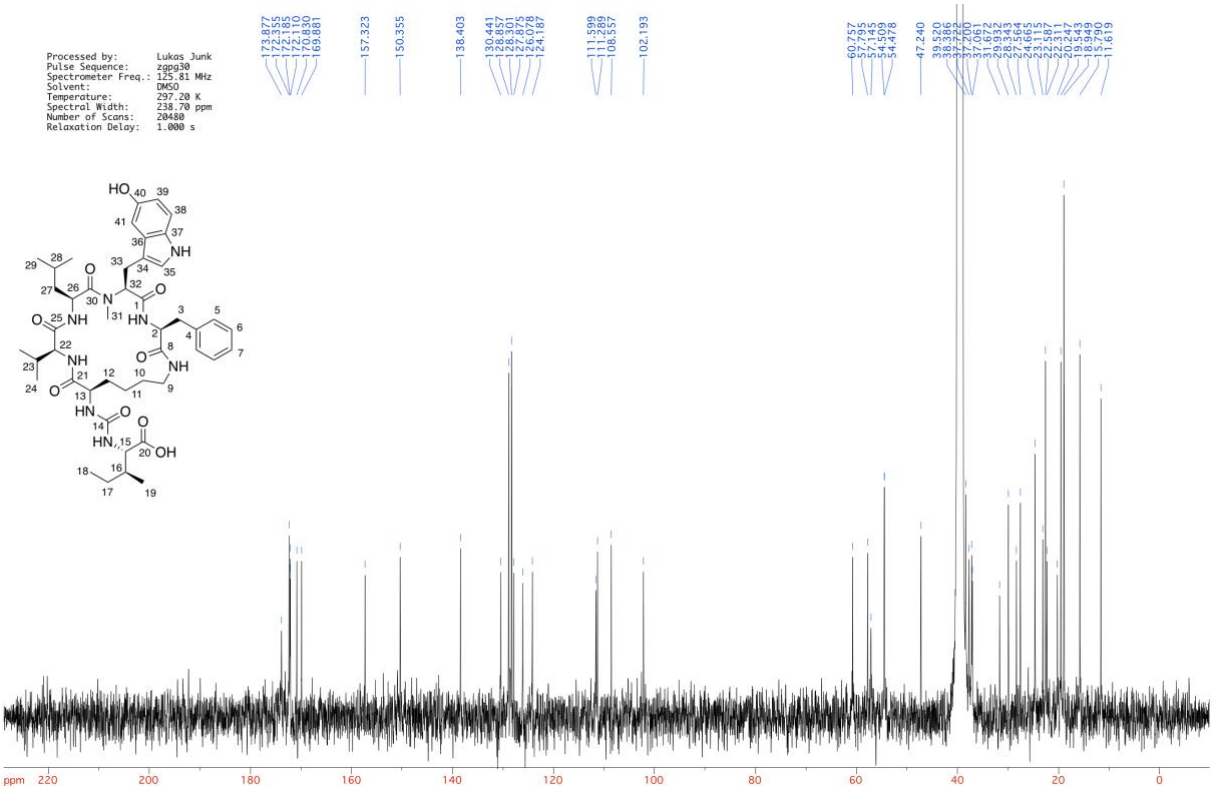
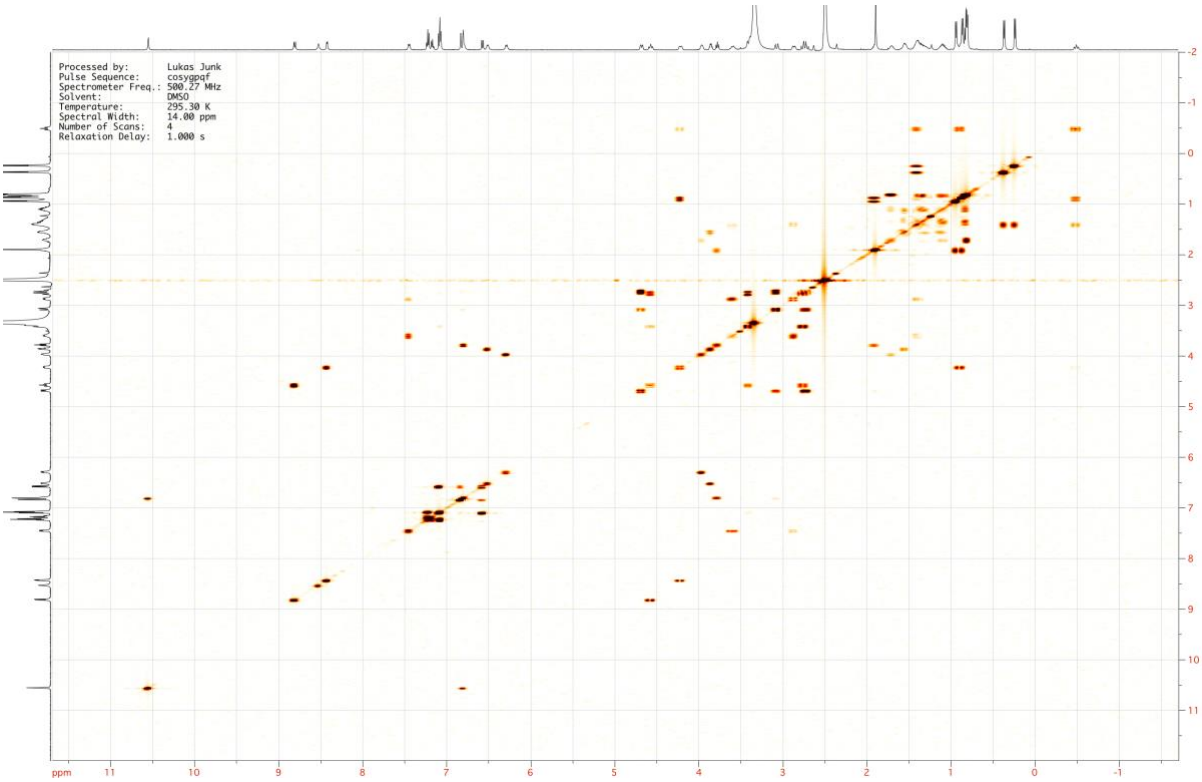


^{1}H-^{1}H-COSY-NMR of 1c



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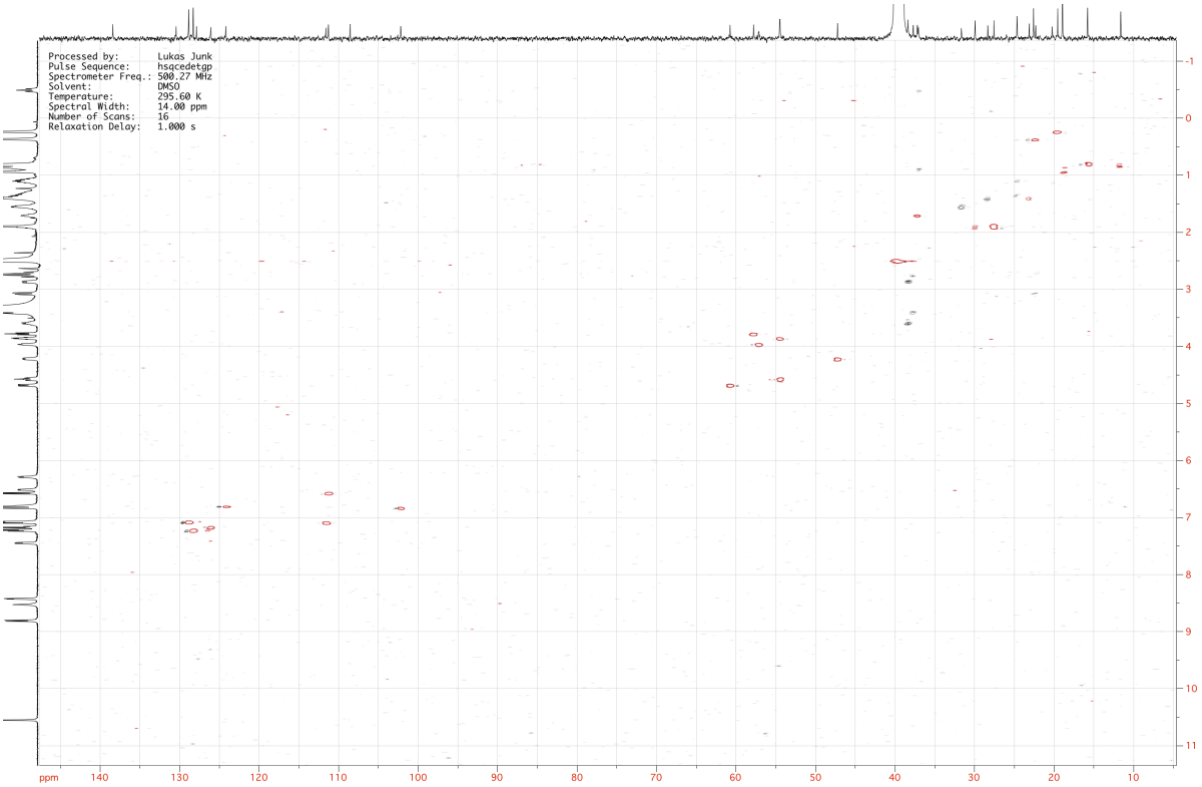

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