Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

C-Terminally modified peptides via cleavage of the HMBA linker by *O*-, *N*- or *S*-nucleophiles

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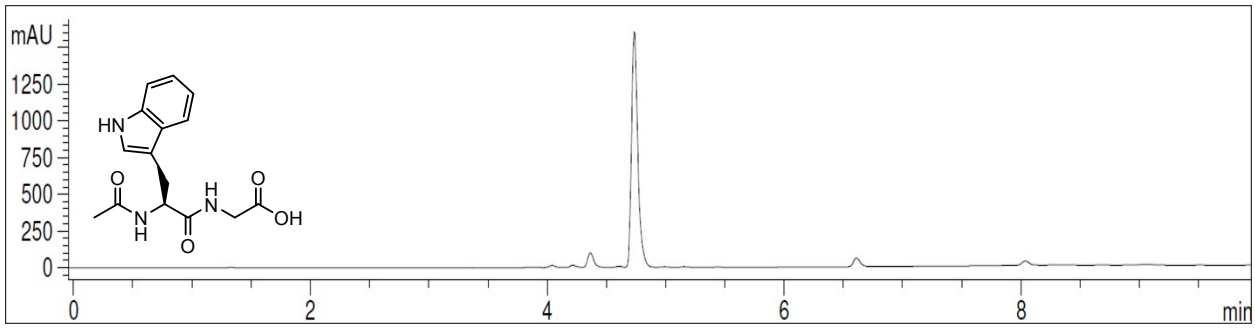
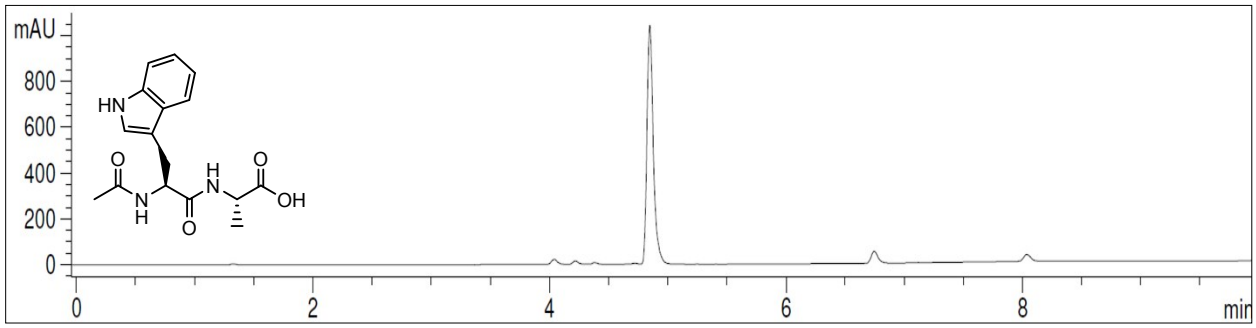
Contents:

HPLC chromatograms of crude reactions:

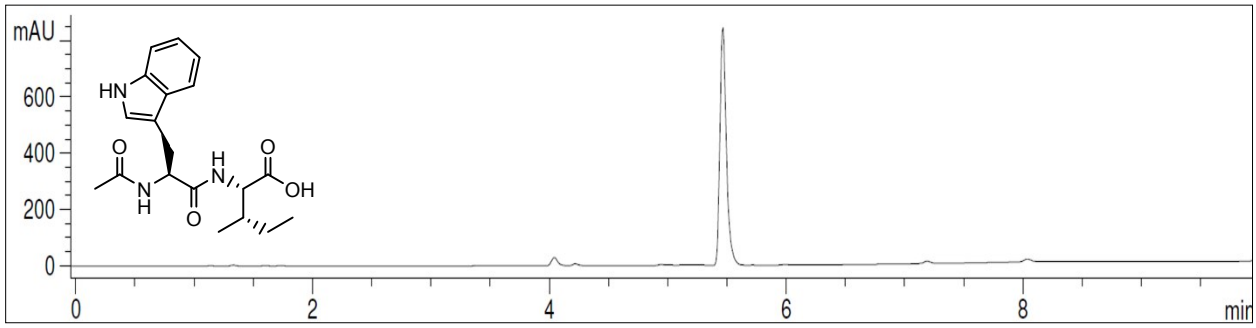
Ac-Trp-Gly-OH (**1**):



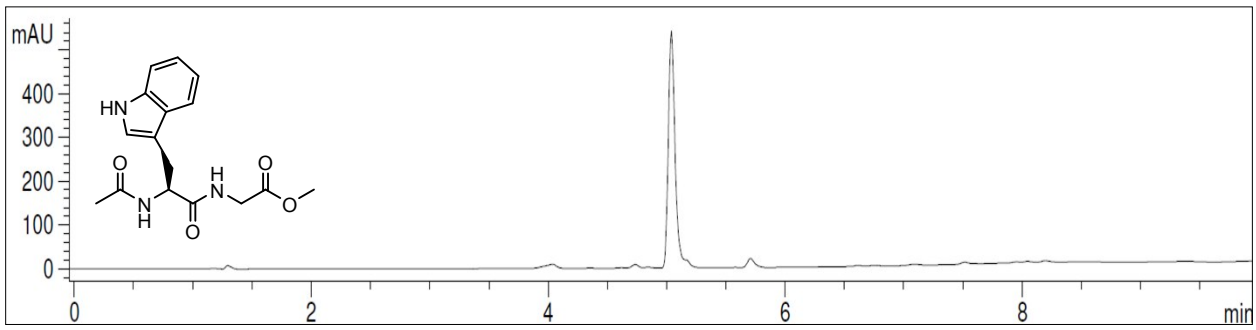
Ac-Trp-Ala-OH (**2**):



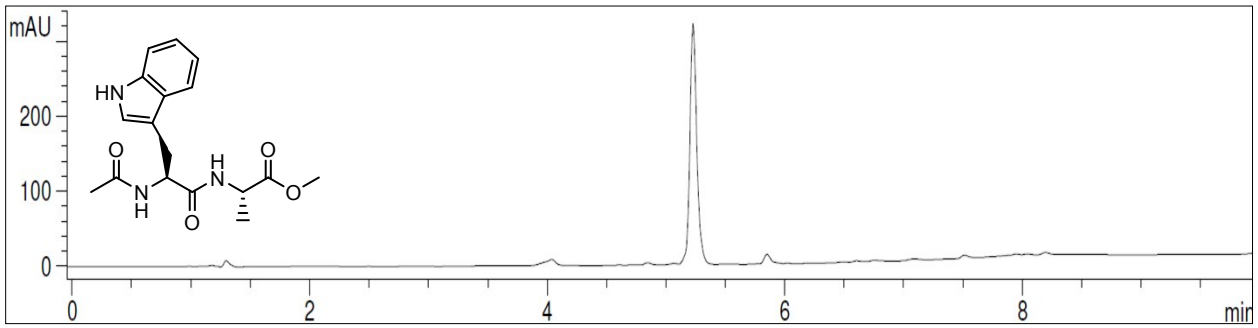
Ac-Trp-Ile-OH (**3**):



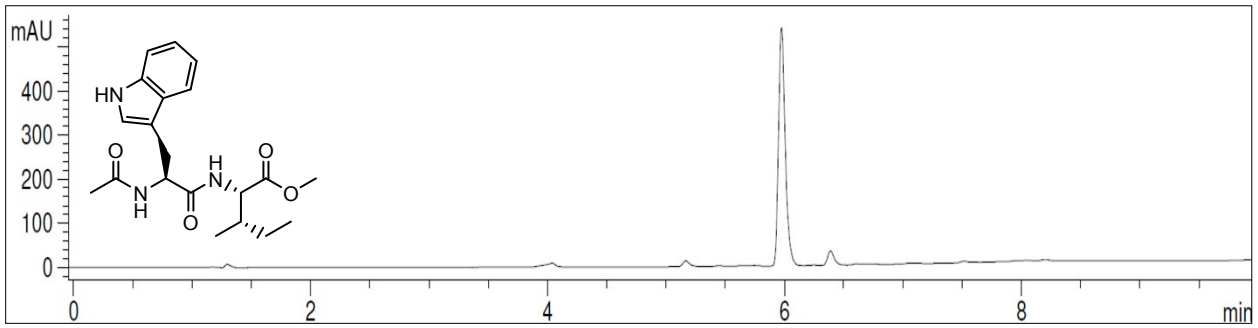
Ac-Trp-Gly-O-Me (**4**):



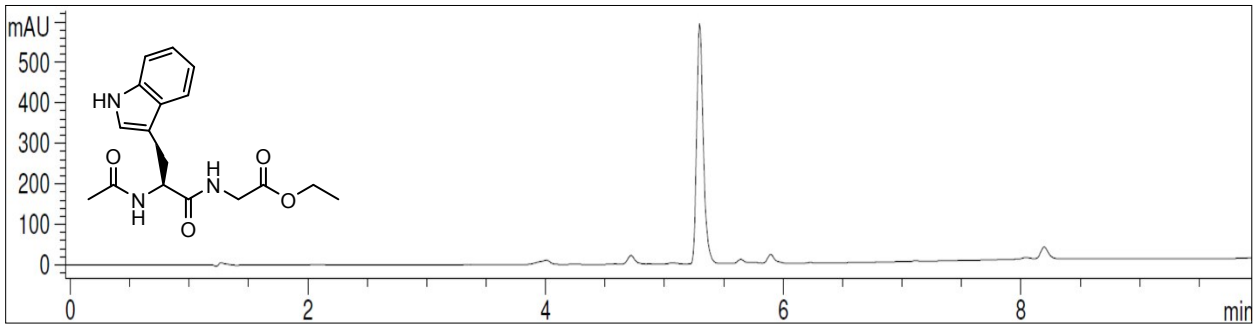
Ac-Trp-Ala-O-Me (**5**) :



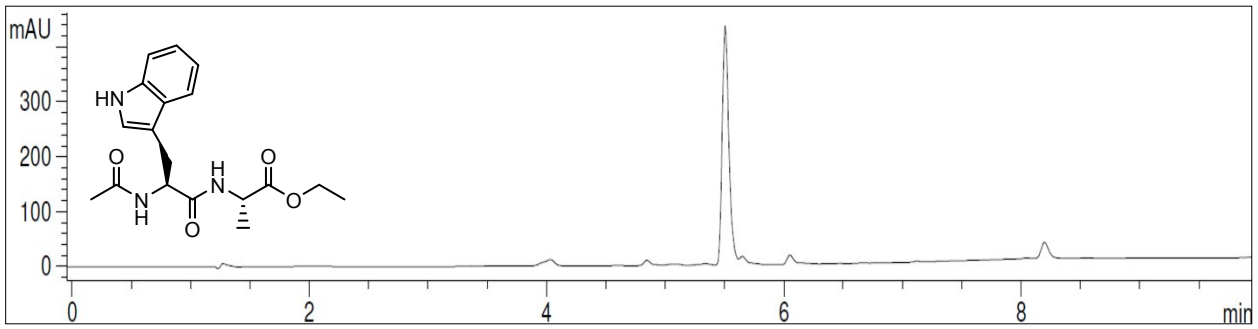
Ac-Trp-Ile-O-Me (**6**):



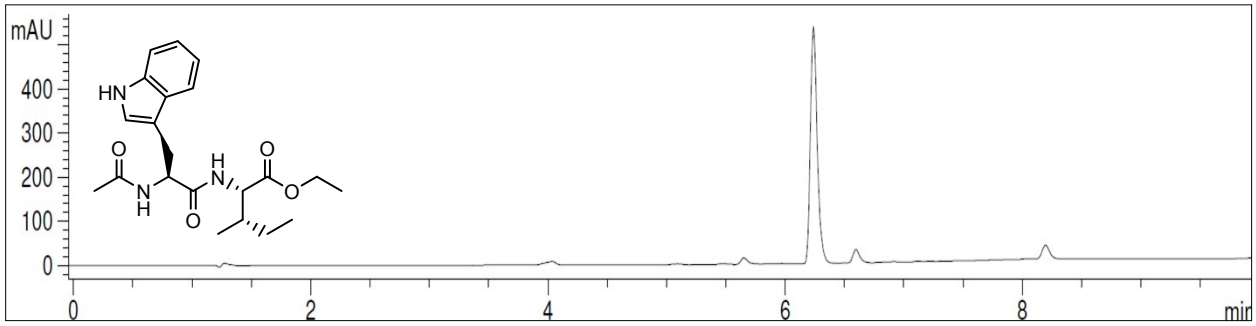
Ac-Trp-Gly-O-Et (**7**):



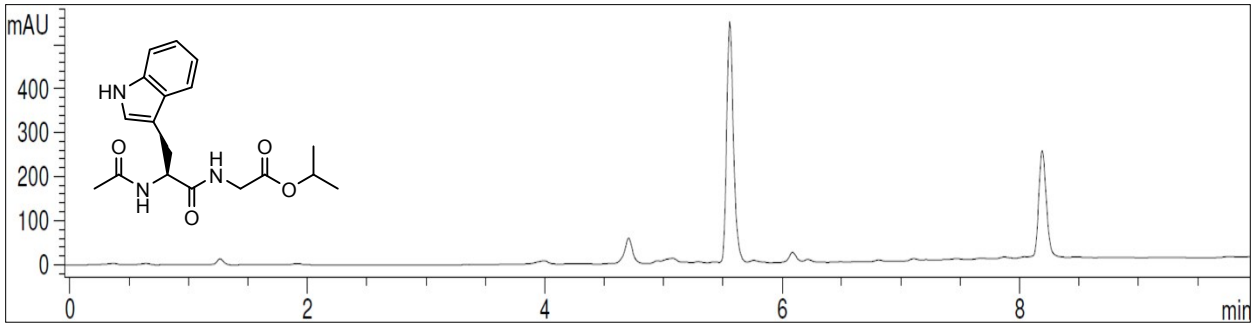
Ac-Trp-Ala-O-Et (**8**):



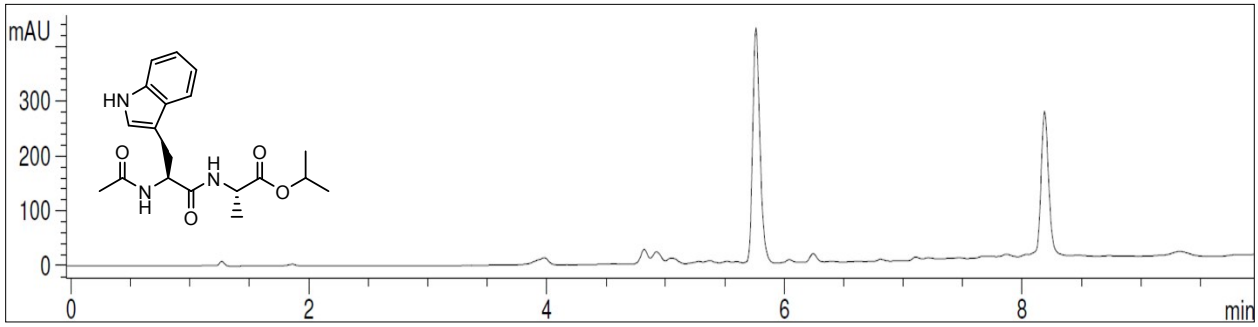
Ac-Trp-Ile-O-Et (**9**):



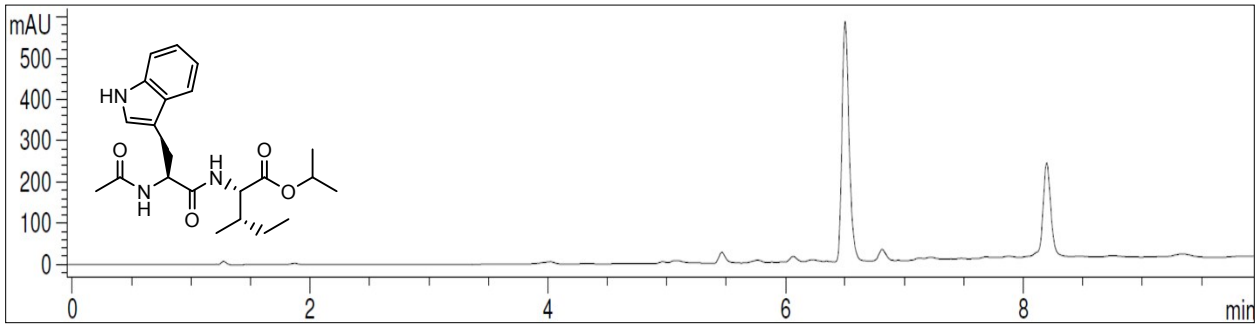
Ac-Trp-Gly-O-^{i}Pr (**10**):



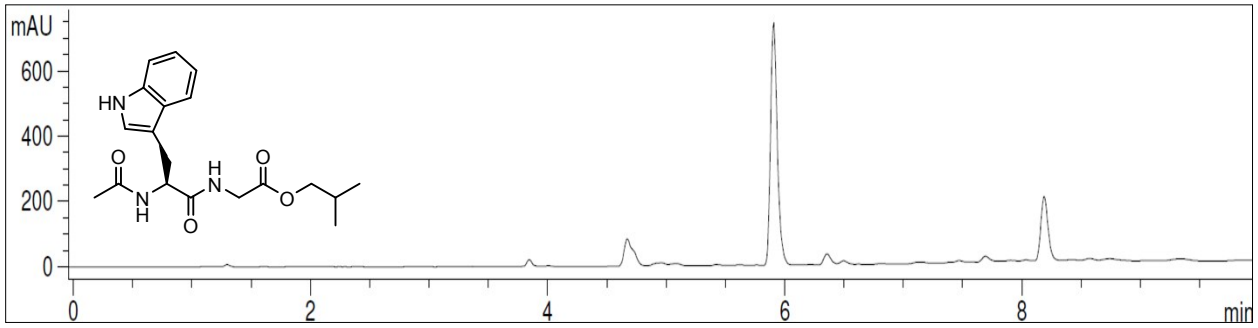
Ac-Trp-Ala-O-^{i}Pr (**11**):



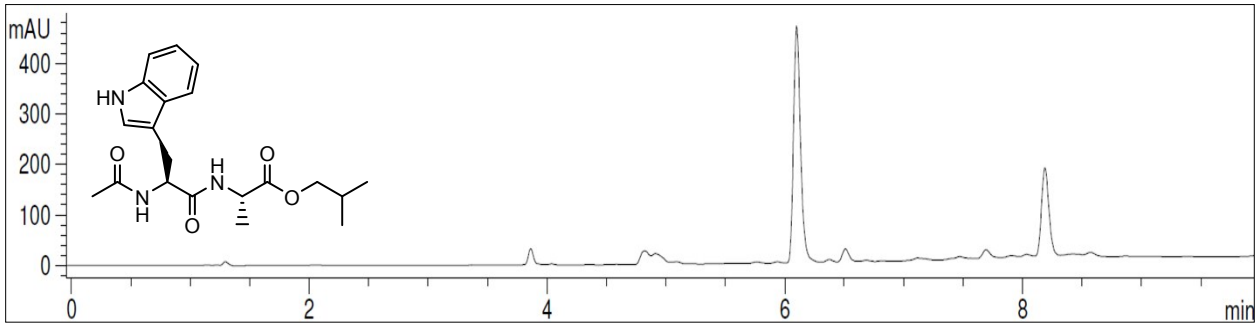
Ac-Trp-Ile-O-^{i}Pr (**12**):



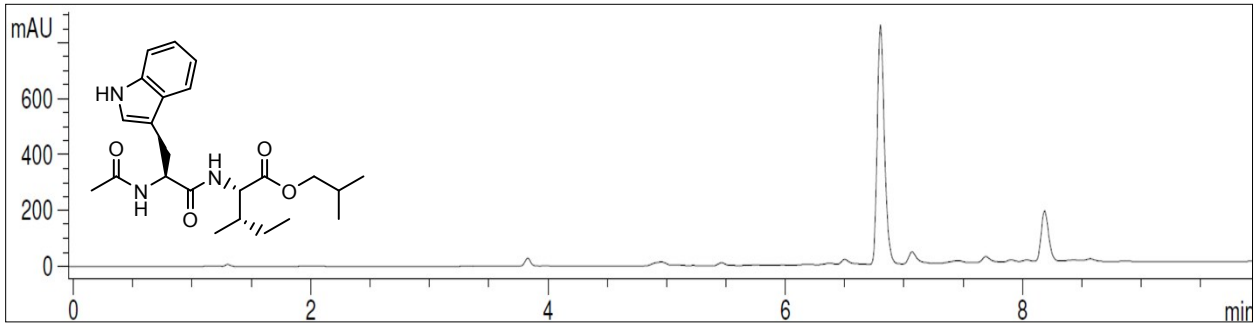
Ac-Trp-Gly-O-^{i}Bu (**13**):



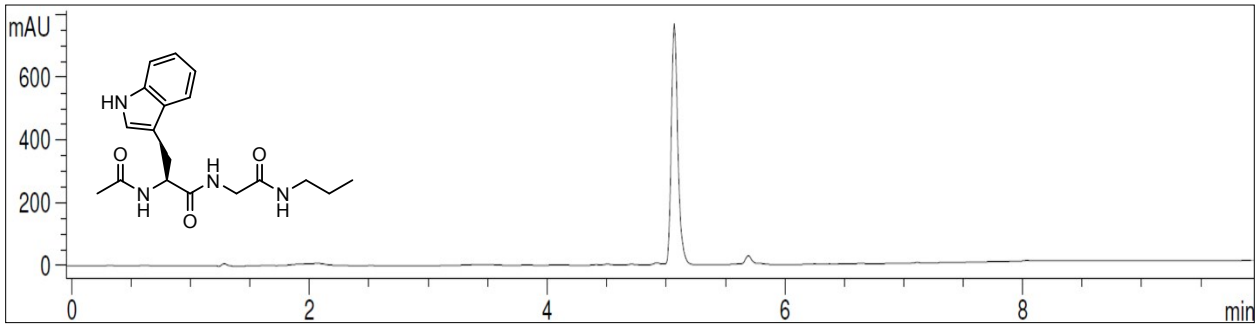
Ac-Trp-Ala-O-^{i}Bu (**14**):



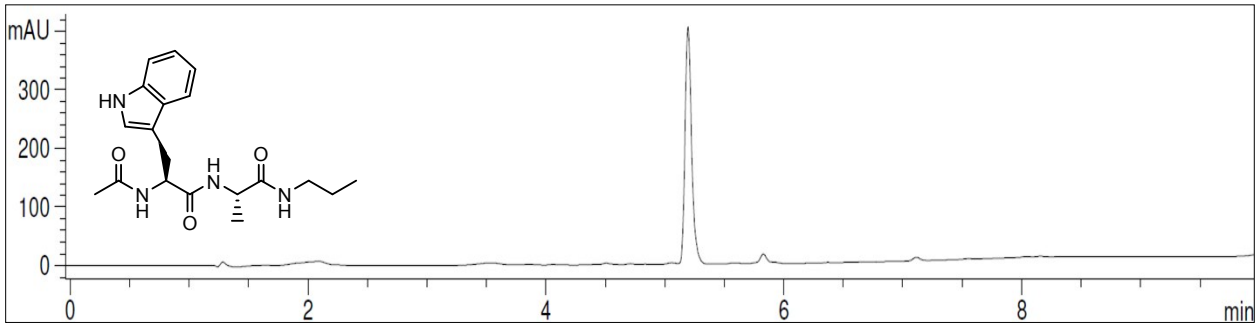
Ac-Trp-Ile-O-^{i}Bu (**15**):



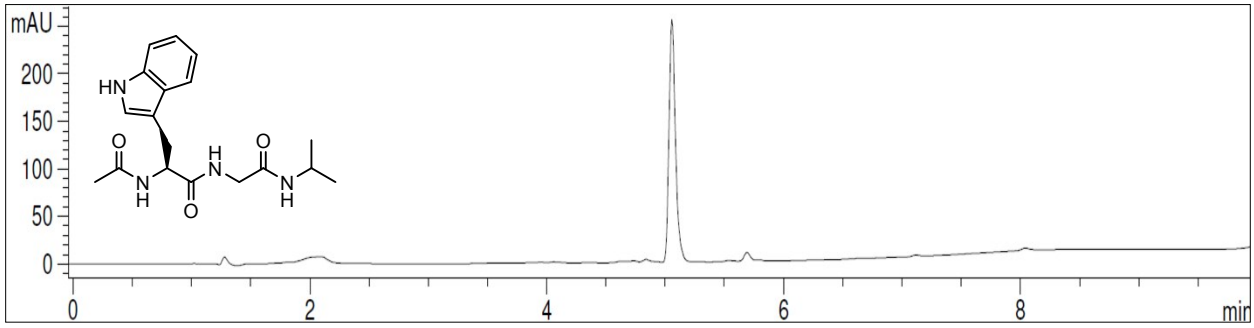
Ac-Trp-Gly-N-Pr (**19**):



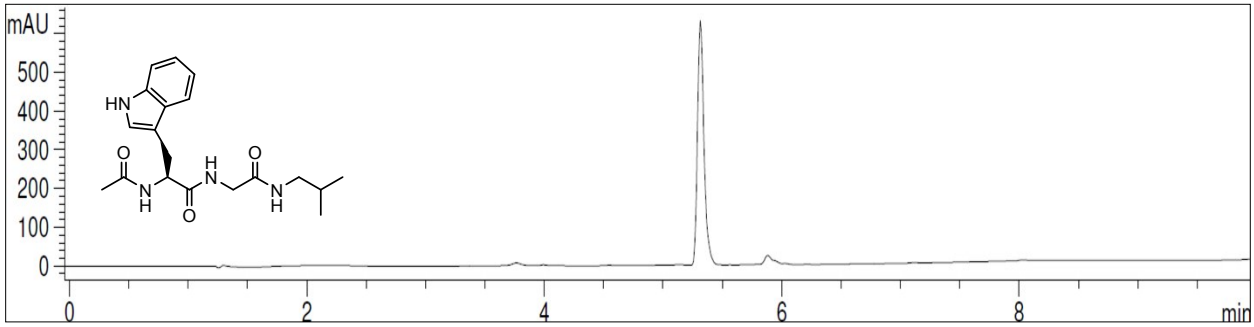
Ac-Trp-Ala-N-Pr (**20**):



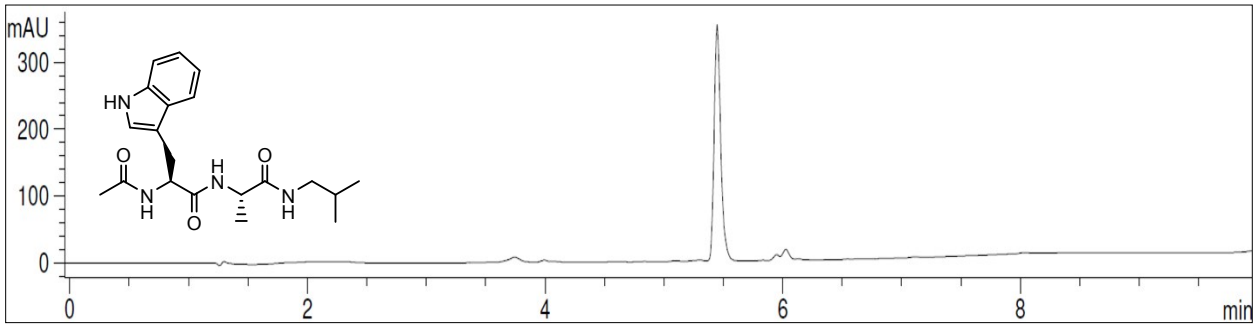
Ac-Trp-Gly-N-^{i}Pr (**22**):



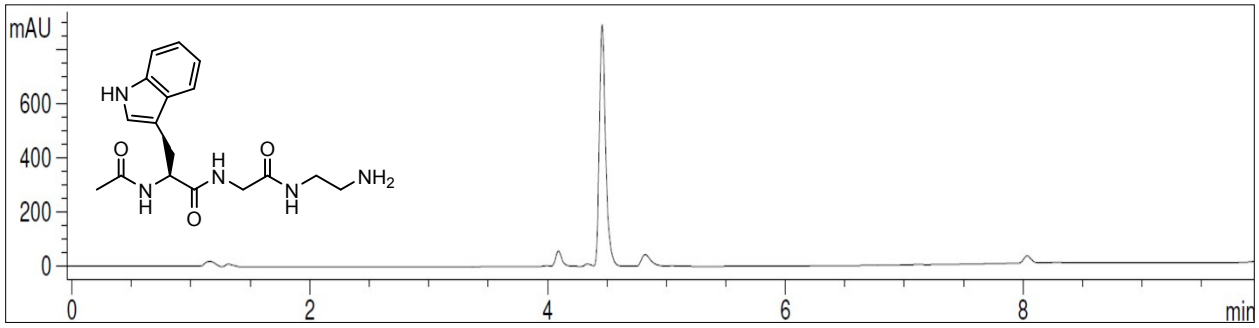
Ac-Trp-Gly-N-^{i}Bu (**25**):



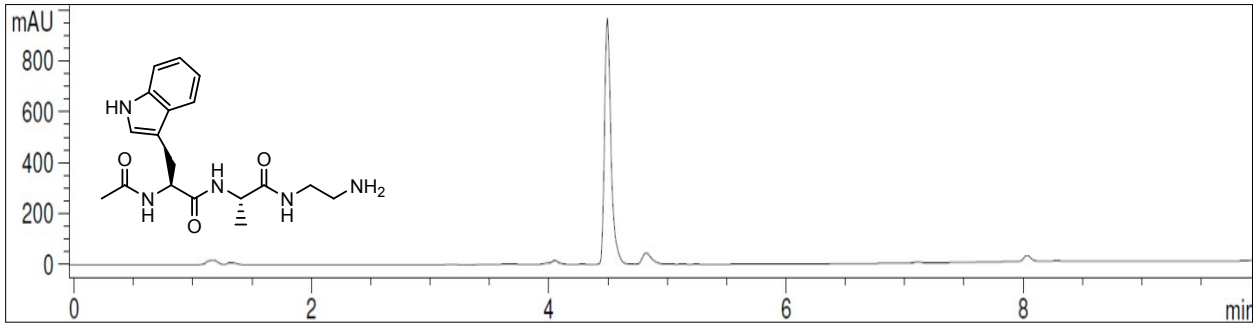
Ac-Trp-Ala-N-^{i}Bu (**26**):



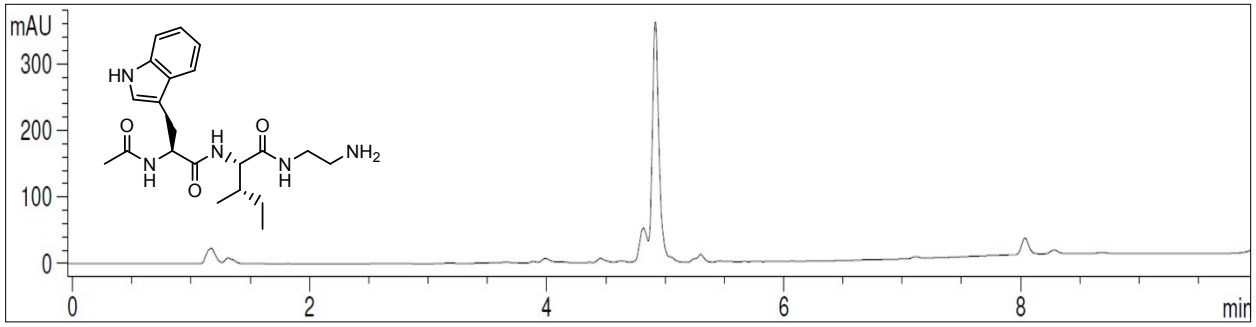
Ac-Trp-Gly-N-$CH_2CH_2NH_2$ (**28**):



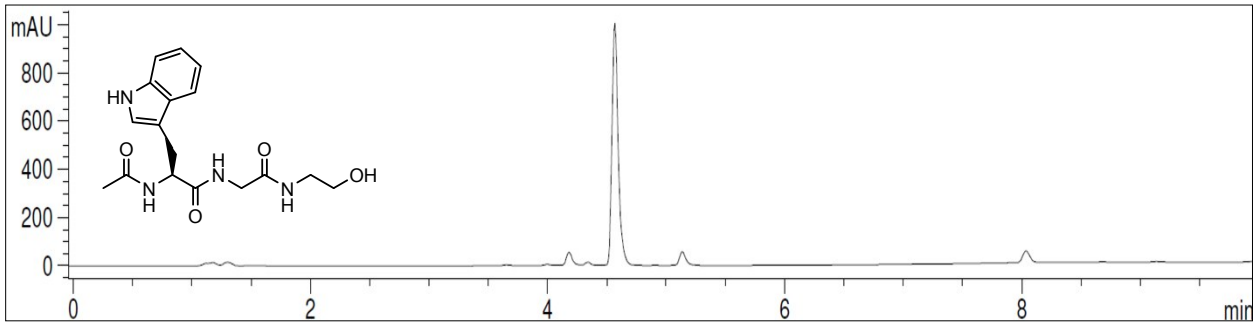
Ac-Trp-Ala-N-$CH_2CH_2NH_2$ (**29**):



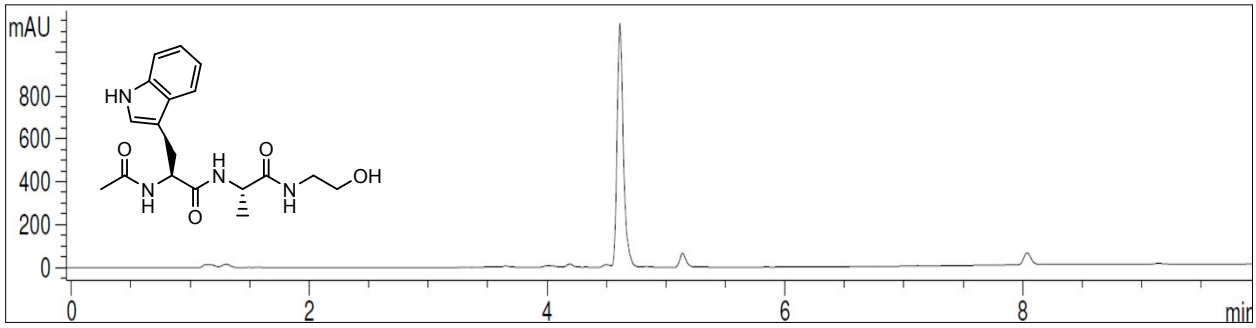
Ac-Trp-Ile-N-$CH_2CH_2NH_2$ (**30**):



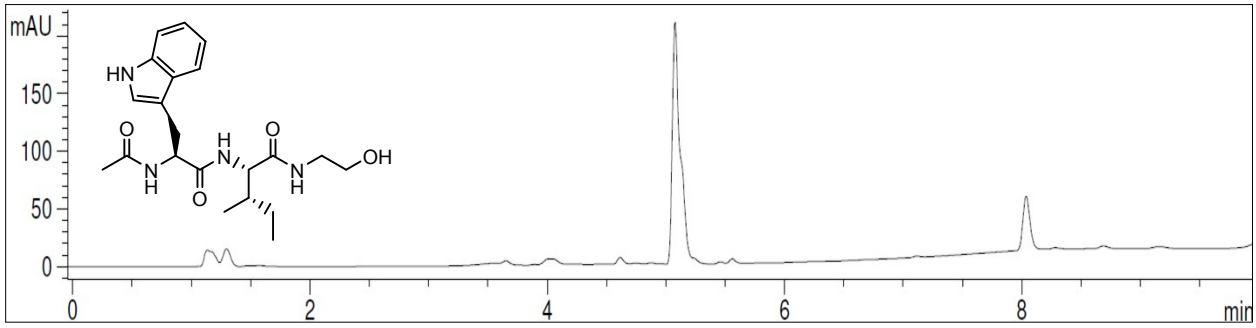
Ac-Trp-Gly-N-CH_2CH_2OH (**31**):



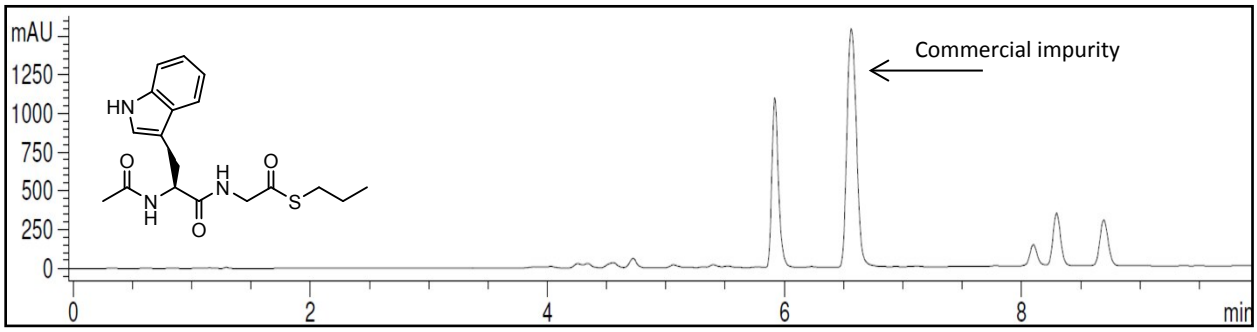
Ac-Trp-Ala-N-CH_2CH_2OH (**32**):



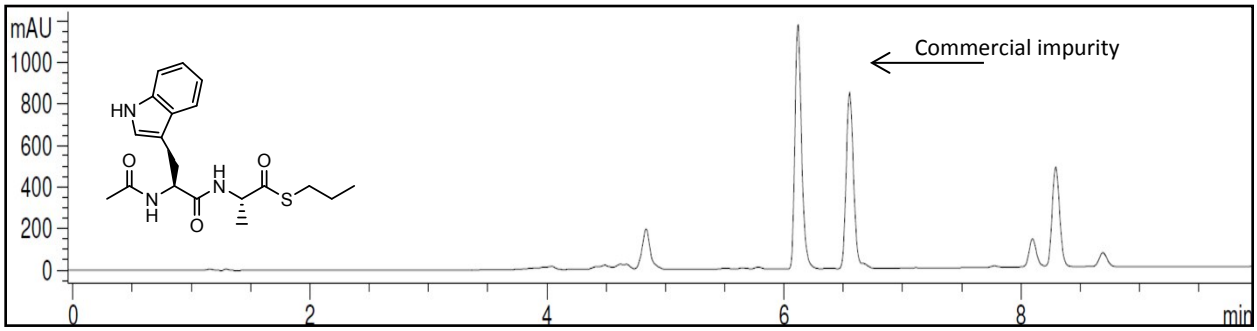
Ac-Trp-Ile-N-CH_2CH_2OH (**33**):



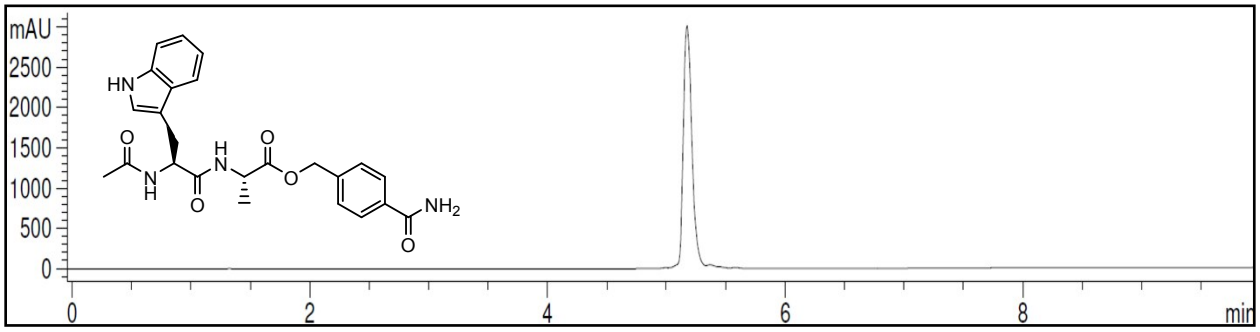
Ac-Trp-Gly-S-Pr (**34**):



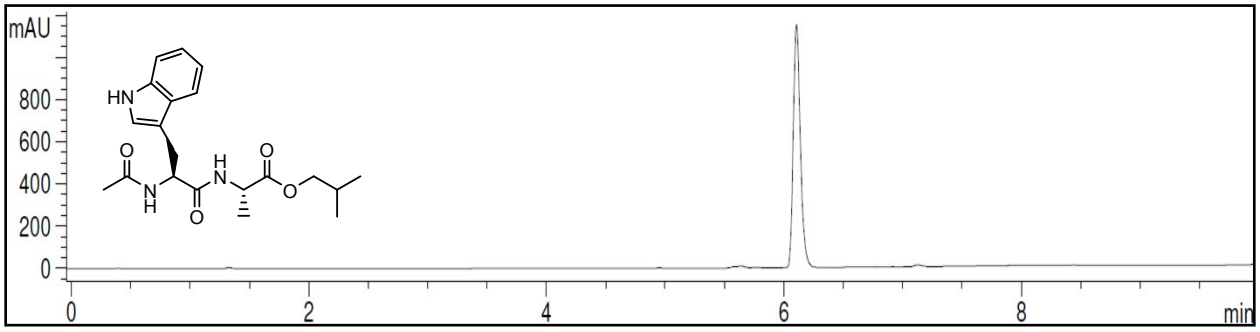
Ac-Trp-Ala-S-Pr (**35**):



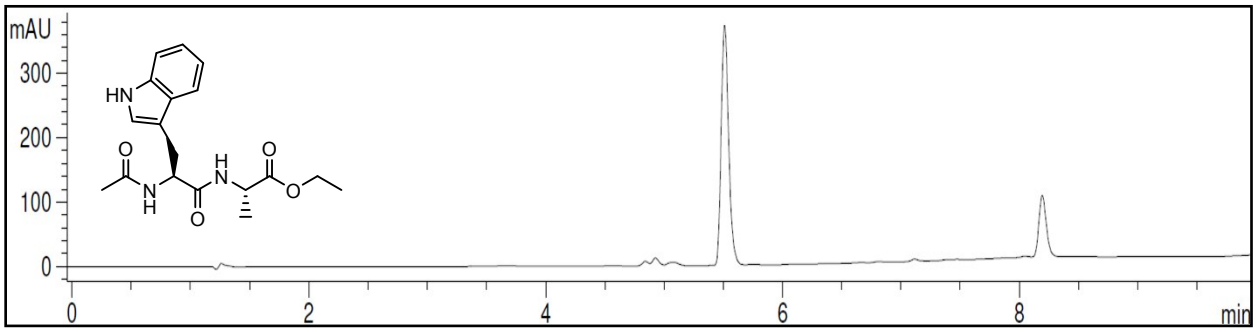
4-carbamoylbenzyl ester (**4**):



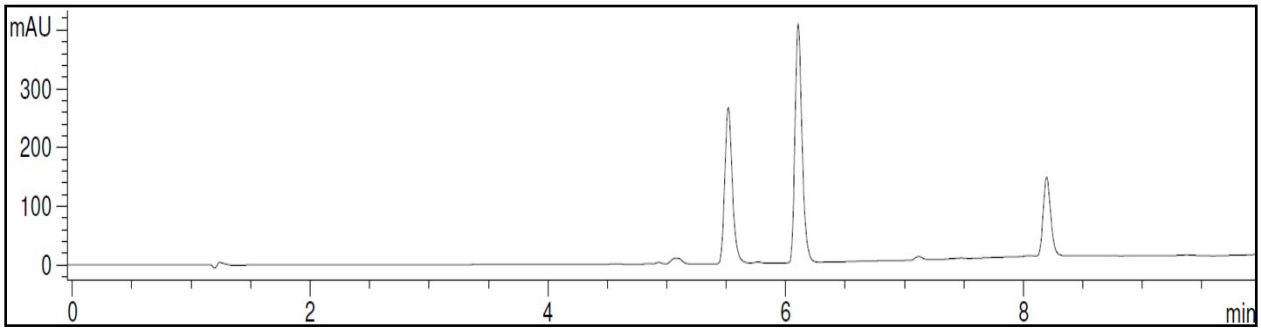
isobutyl ester (**5**):



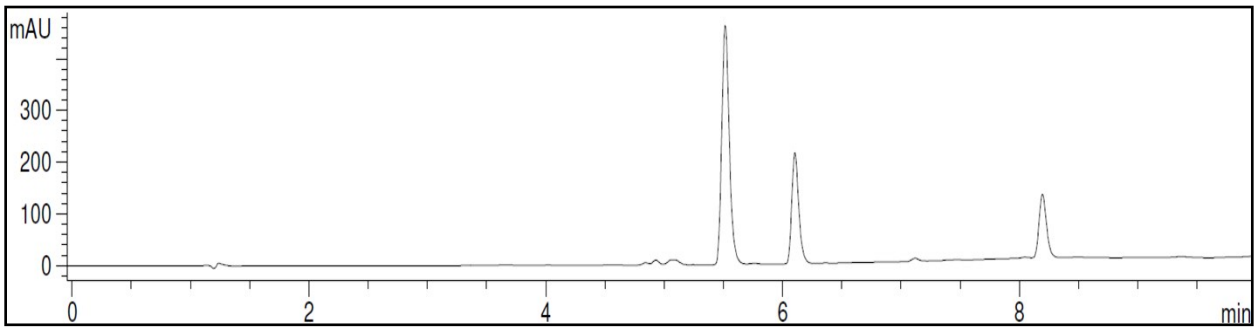
Ethyl ester (**6**):



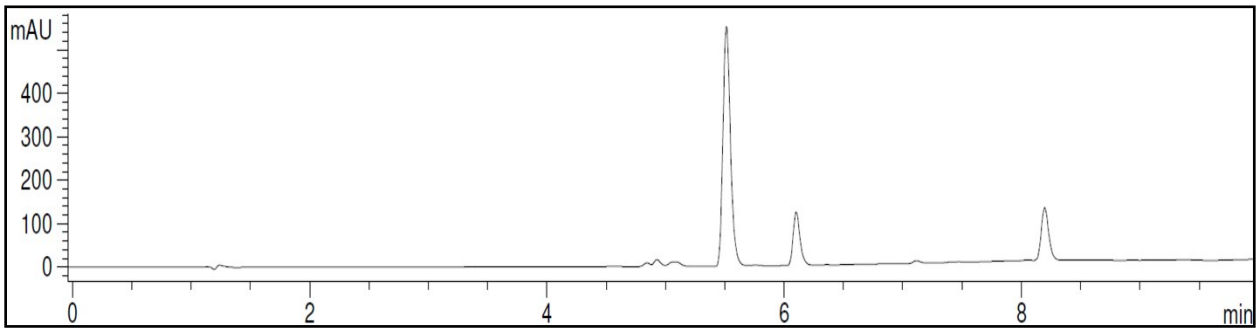
isobutyl ester after 2min (**5a**):



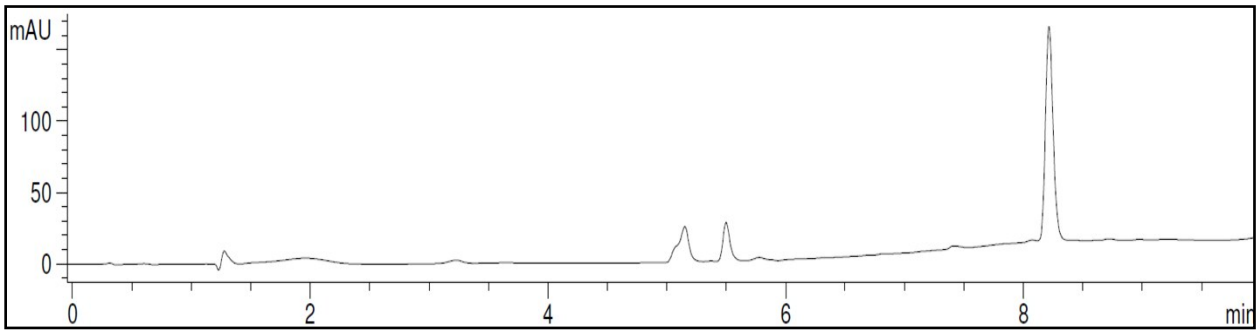
isobutyl ester after 5min (**5b**):



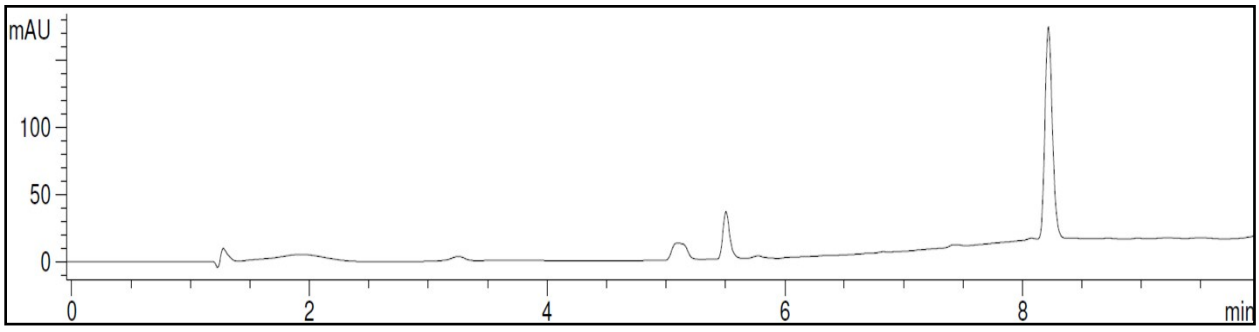
isobutyl ester after 10min (**5c**):



4-carbamoylbenzyl ester after 15 seconds (**4a**):

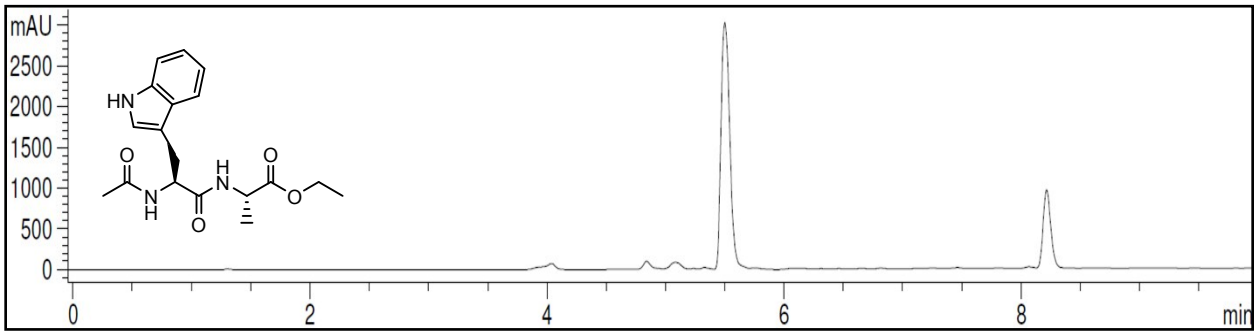


4-carbamoylbenzyl ester after 30 seconds (**4b**):

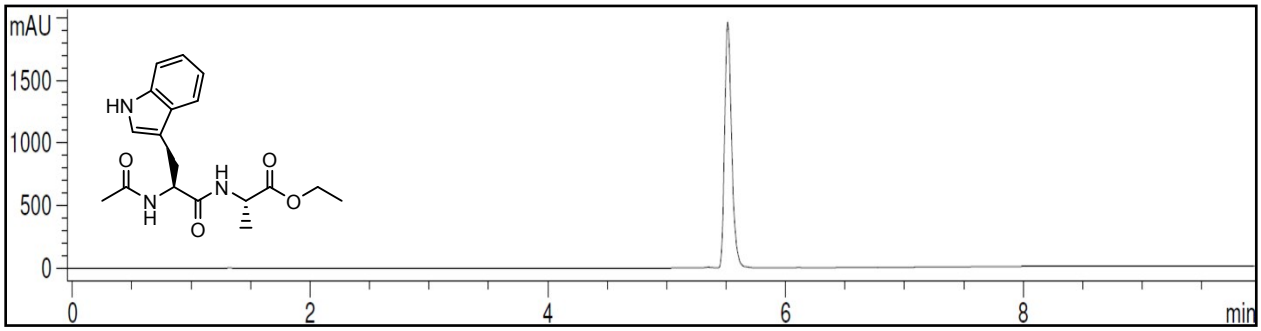


Preparative amount reactions.

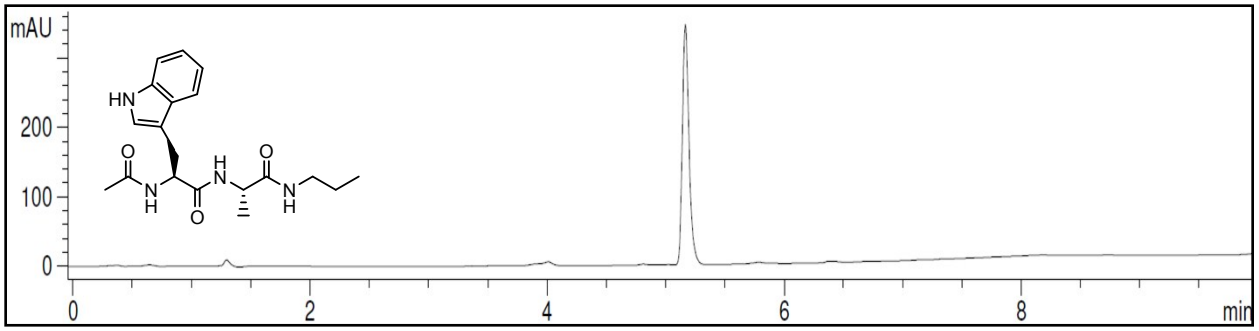
Ac-Trp-Ala-O-Et (**11**) Crude



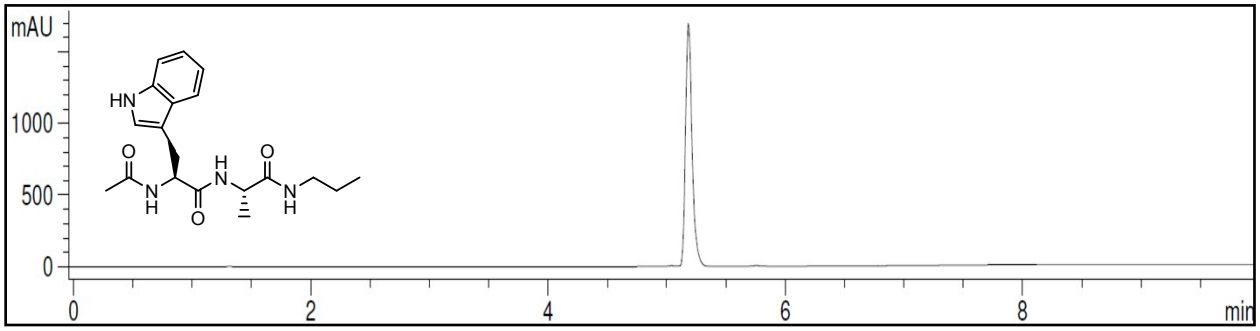
Ac-Trp-Ala-O-Et (**11**) Purified



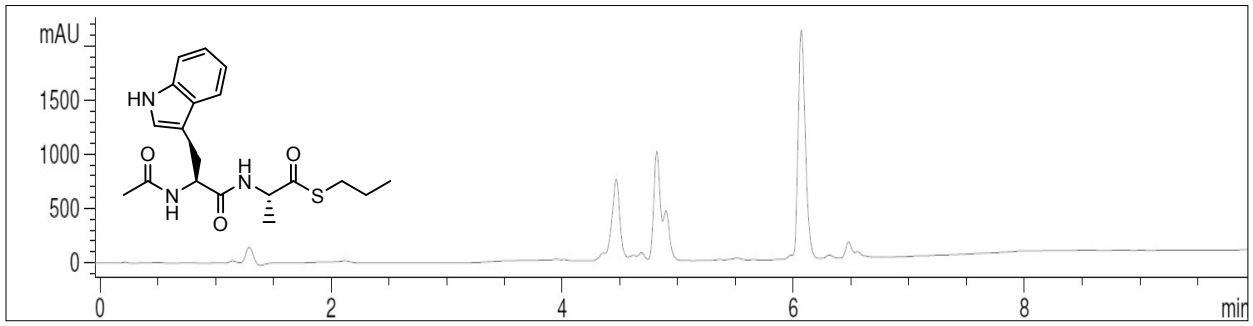
Ac-Trp-Ala-N-Pr (**20**) Crude



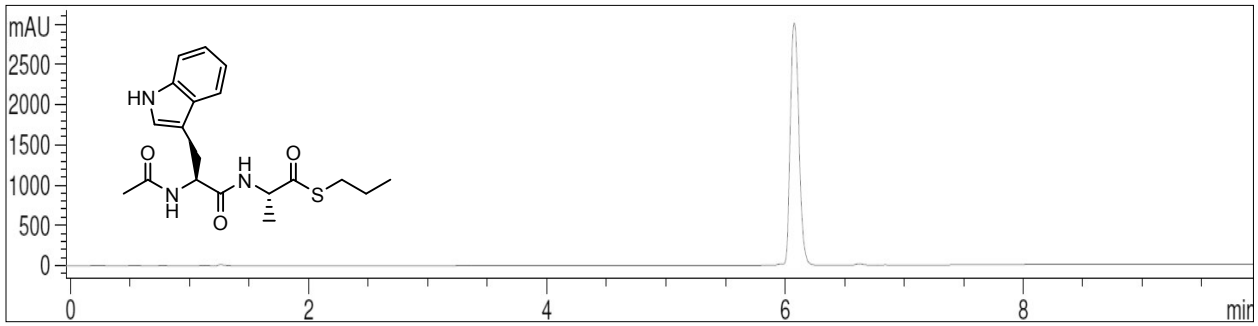
Ac-Trp-Ala-N-Pr (**20**) Purified



Ac-Trp-Ala-S-Pr (**35**) Crude



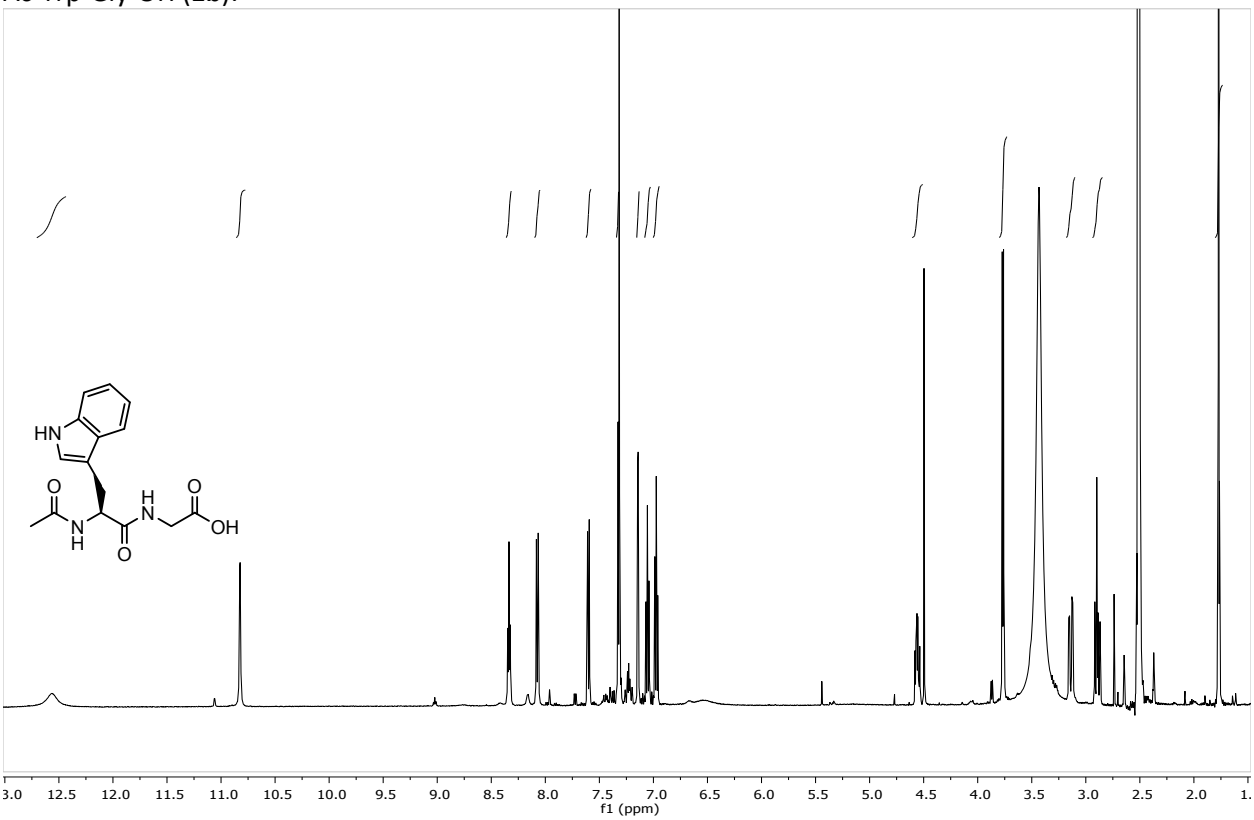
Ac-Trp-Ala-S-Pr (**35**) Purified



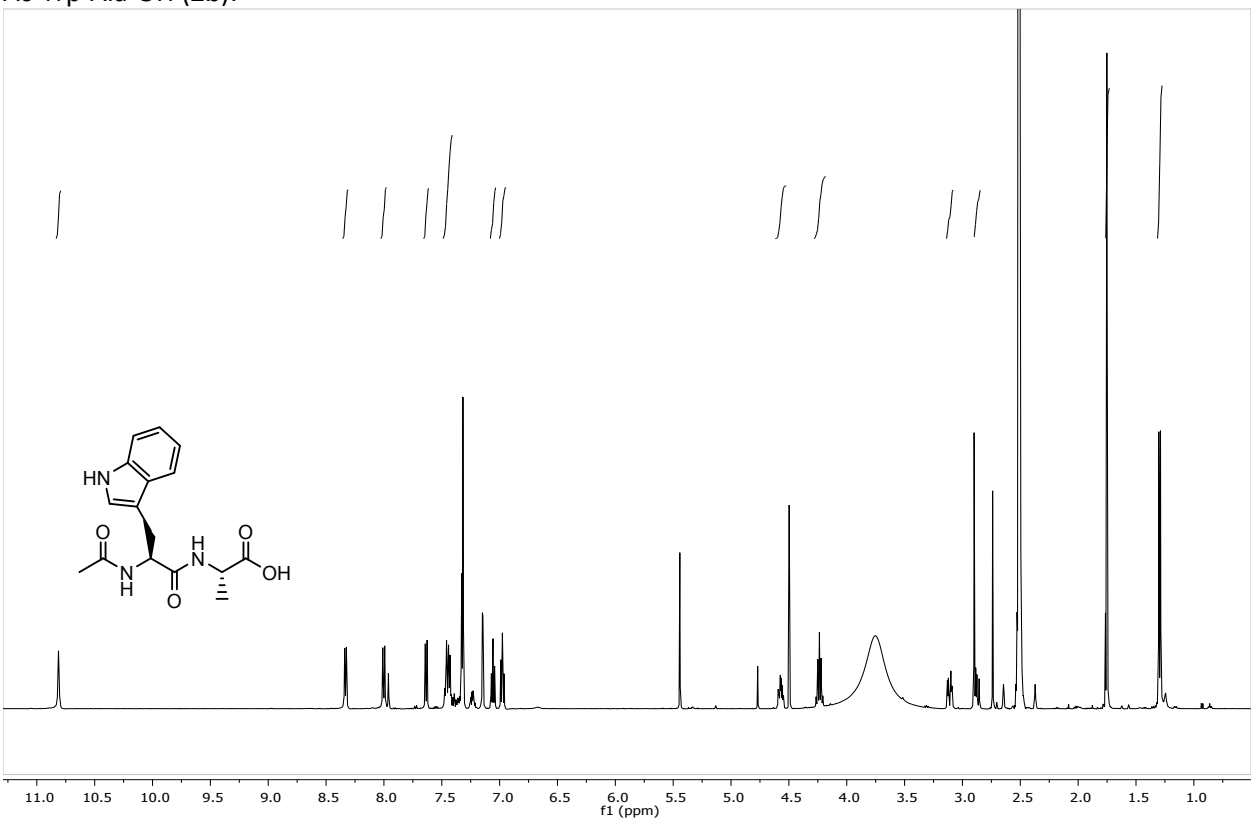
HRMS data of all compounds:

	Compound Nr.	Calc. Mass. [M+H$^+$]	Found mass.
Ac-Trp-Gly-OH	1b	304.1292	304.1299
Ac-Trp-Ala-OH	2b	318.1448	318.1457
Ac-Trp-Ile-OH	3b	360.1918	360.1925
Ac-Trp-Gly-O-Me	4	318.1448	318.1454
Ac-Trp-Ala-O-Me	5	332.1605	332.1610
Ac-Trp-Ile-O-Me	6	374.2074	374.2078
Ac-Trp-Gly-O-Et	7	332.1605	332.1621
Ac-Trp-Ala-O-Et	8	346.1761	346.1783
Ac-Trp-Ile-O-Et	9	388.2231	388.2249
Ac-Trp-Gly-O-isoPr	10	346.1761	346.1780
Ac-Trp-Ala-O-isoPr	11	260.1918	360.1933
Ac-Trp-Ile-O-isoPr	12	402.2387	402.2400
Ac-Trp-Gly-O-isoBu	13	360.1918	360.2075
Ac-Trp-Ala-O-isoBu	14	374.2074	374.2079
Ac-Trp-Ile-O-isoBu	15	416.2544	416.2562
Ac-Trp-Gly-N-Pr	19	345.1921	345.1921
Ac-Trp-Ala-N-Pr	20	359.2078	359.2078
Ac-Trp-Gly-N-isoPr	22	345.1921	345.1921
Ac-Trp-Gly-N-isoBu	25	359.2078	359.2077
Ac-Trp-Ala-N-isoBu	26	373.2234	373.2234
Ac-Trp-Gly-$NCH_2CH_2NH_2$	28	346.1874	346.1876
Ac-Trp-Ala-$NCH_2CH_2NH_2$	29	360.2030	360.2032
Ac-Trp-Ile-$NCH_2CH_2NH_2$	30	402.2500	402.2503
Ac-Trp-Gly-NCH_2CH_2OH	31	347.1714	347.1716
Ac-Trp-Ala- NCH_2CH_2OH	32	361.1870	361.1872
Ac-Trp-Ile- NCH_2CH_2OH	33	403.2340	403.2340
Ac-Trp-Gly-S-Pr	34	362.4675	362.4663
Ac-Trp-Ala-S-Pr	35	376.1689	376.1660
Ac-Trp-Ala-O-isoBu	16	374.2074	374.2097
Ac-Trp-Ala-O-HMBA	17	451.1976	451.1980

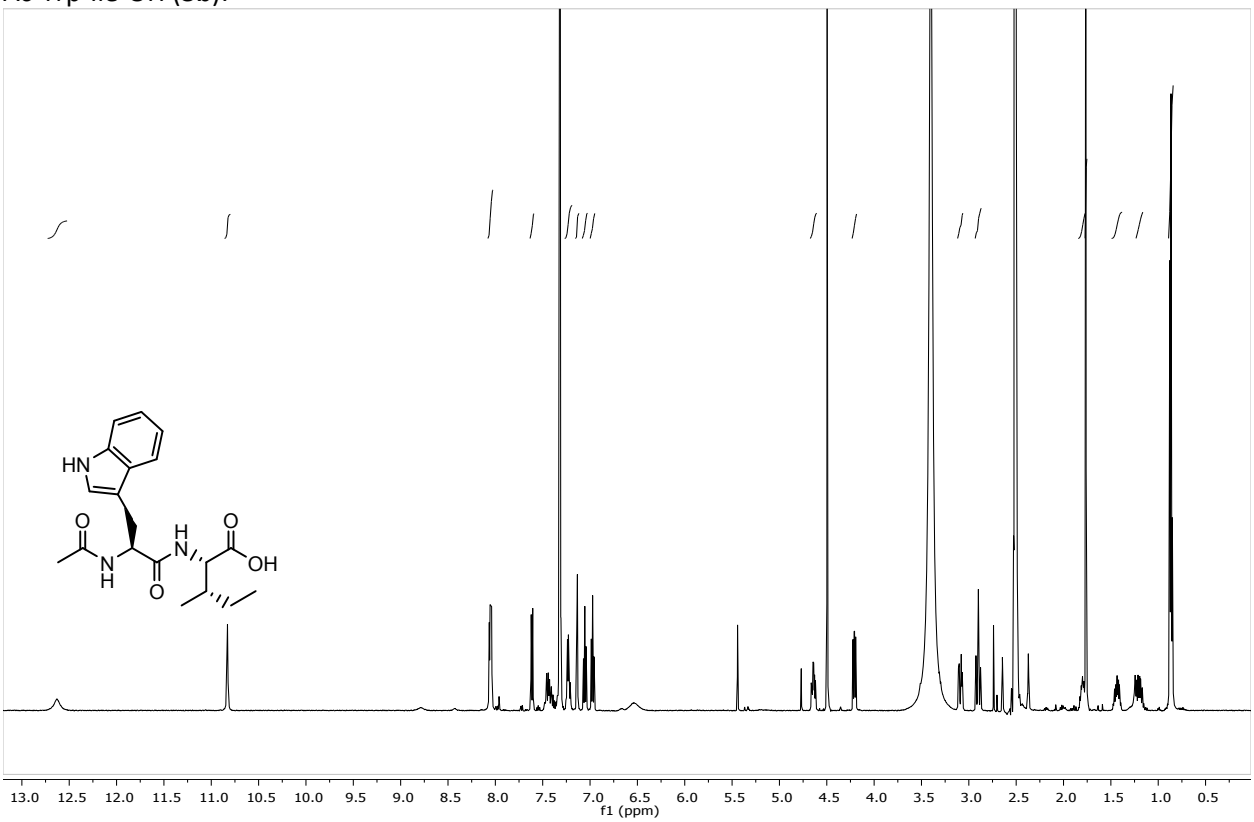
Ac-Trp-Gly-OH (**1b**):



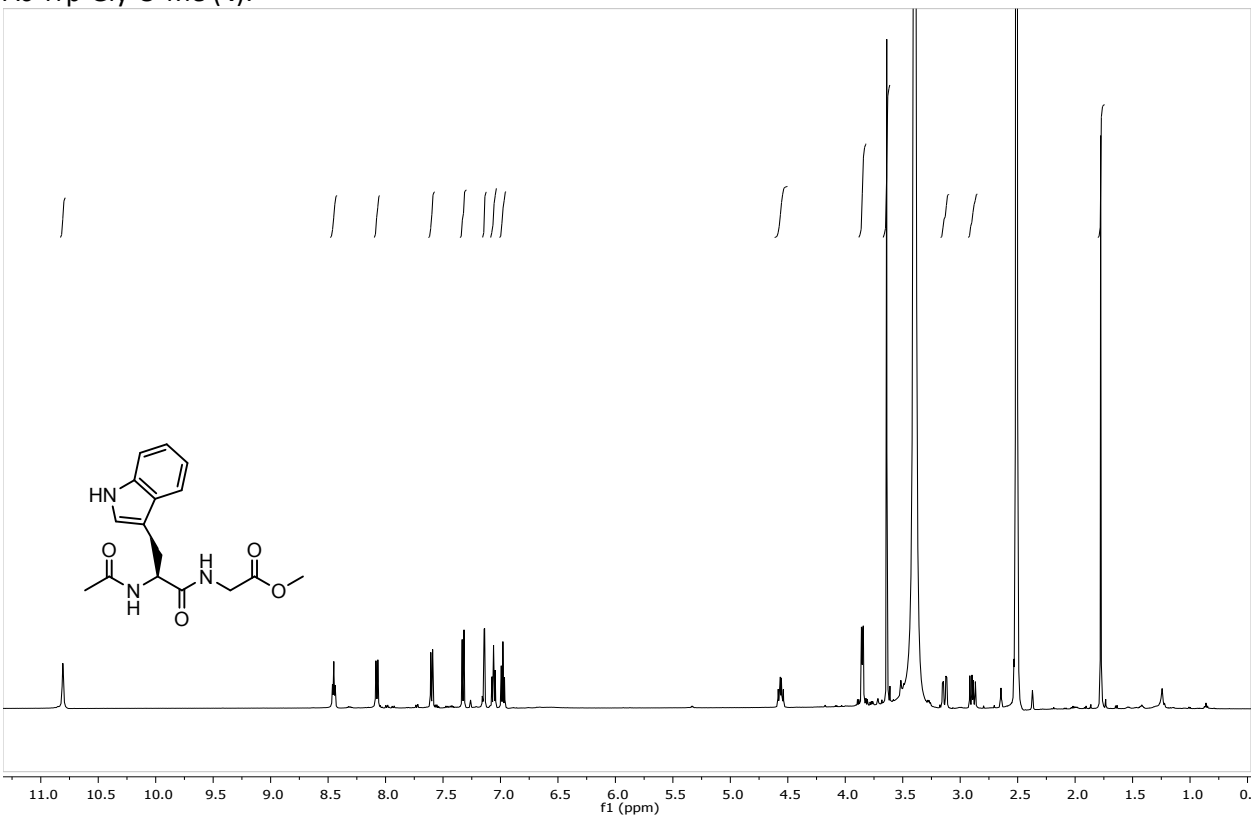
Ac-Trp-Ala-OH (**2b**):



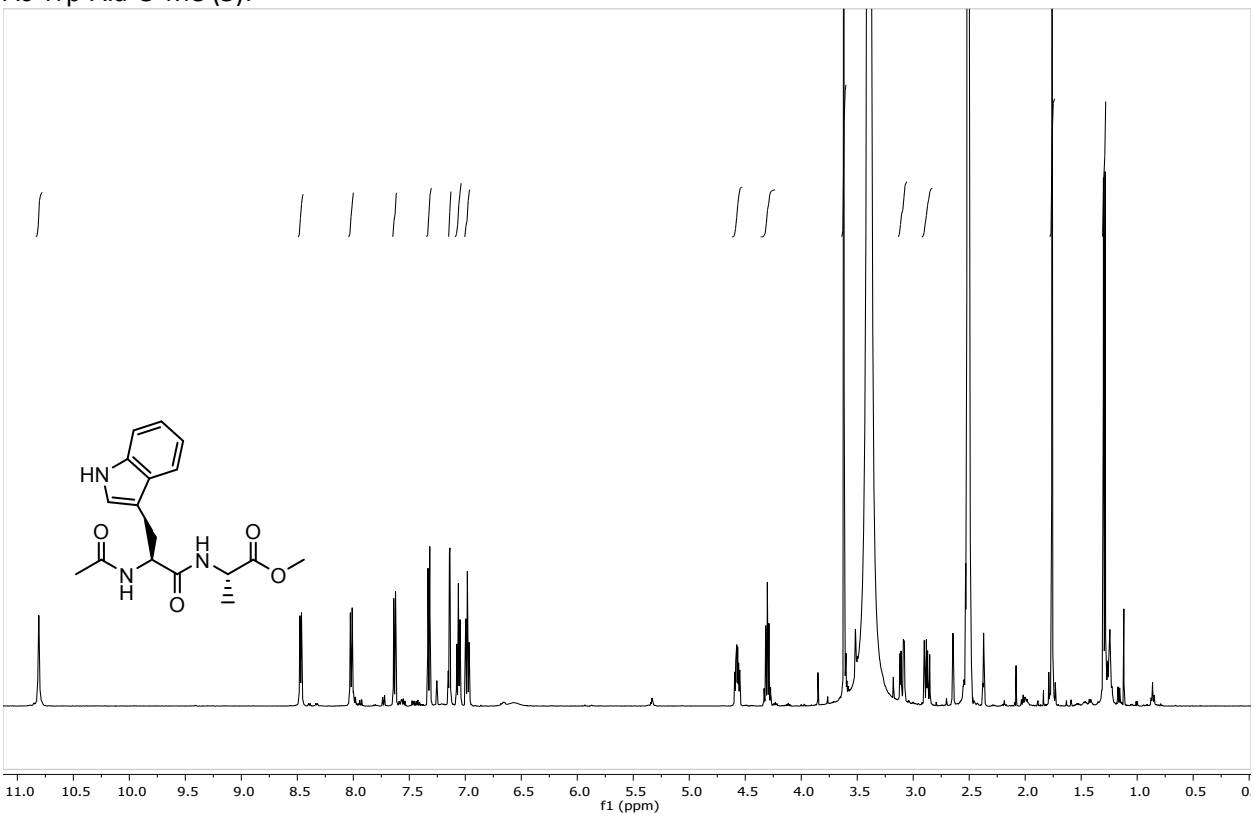
Ac-Trp-Ile-OH (**3b**):



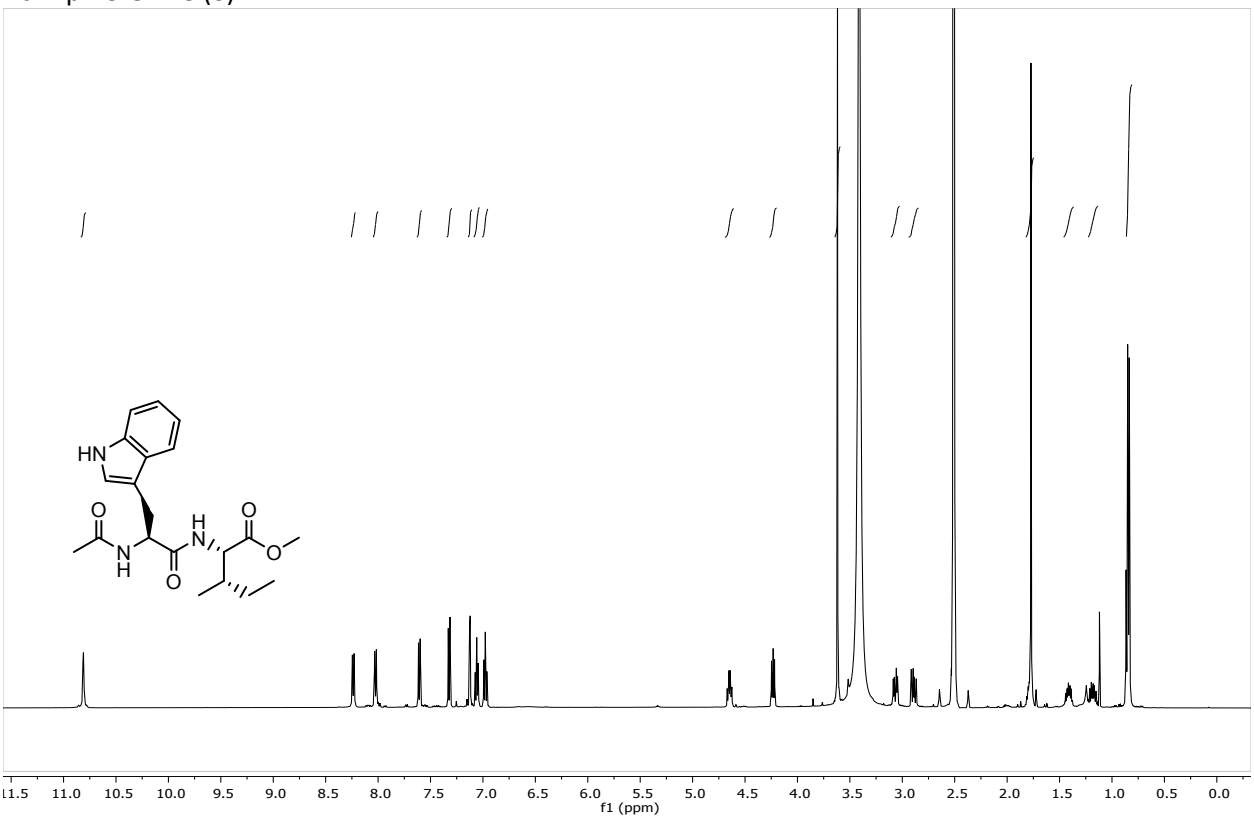
Ac-Trp-Gly-O-Me (**4**):



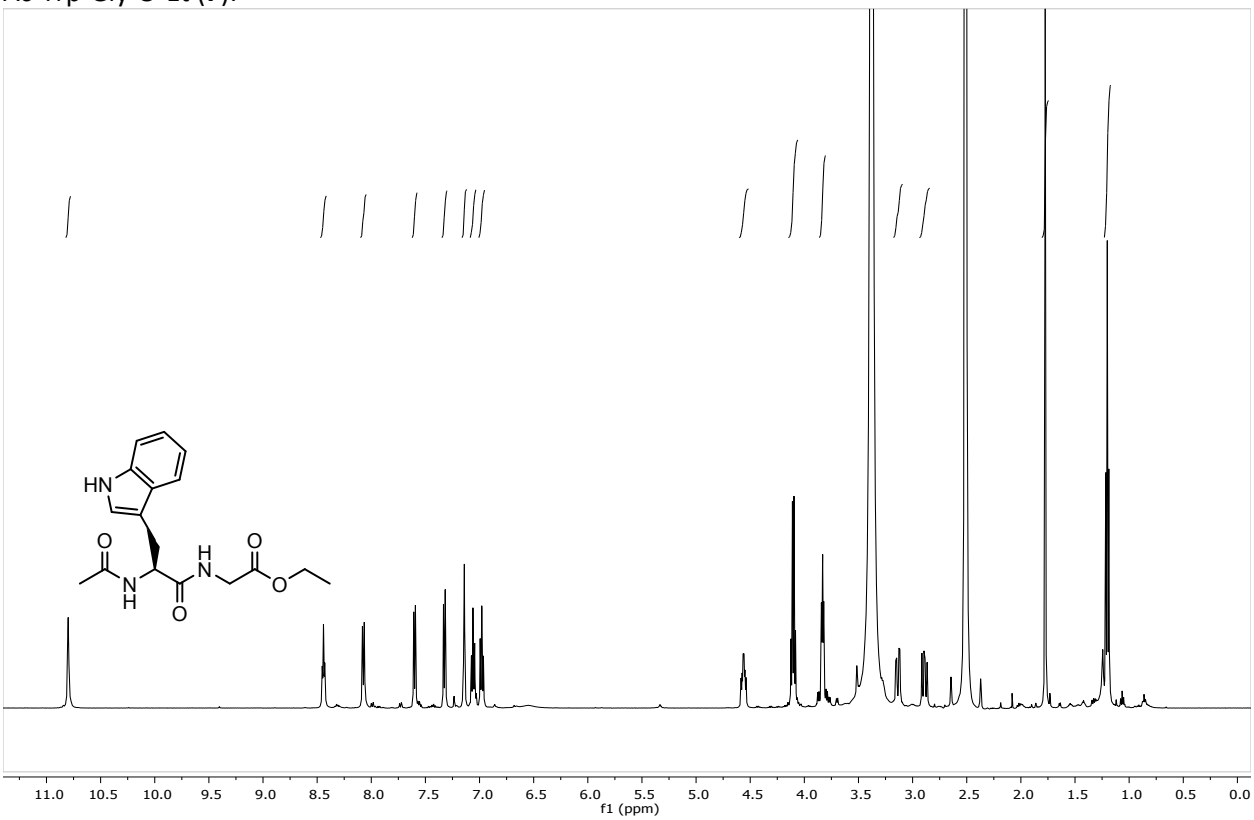
Ac-Trp-Ala-O-Me (**5**):



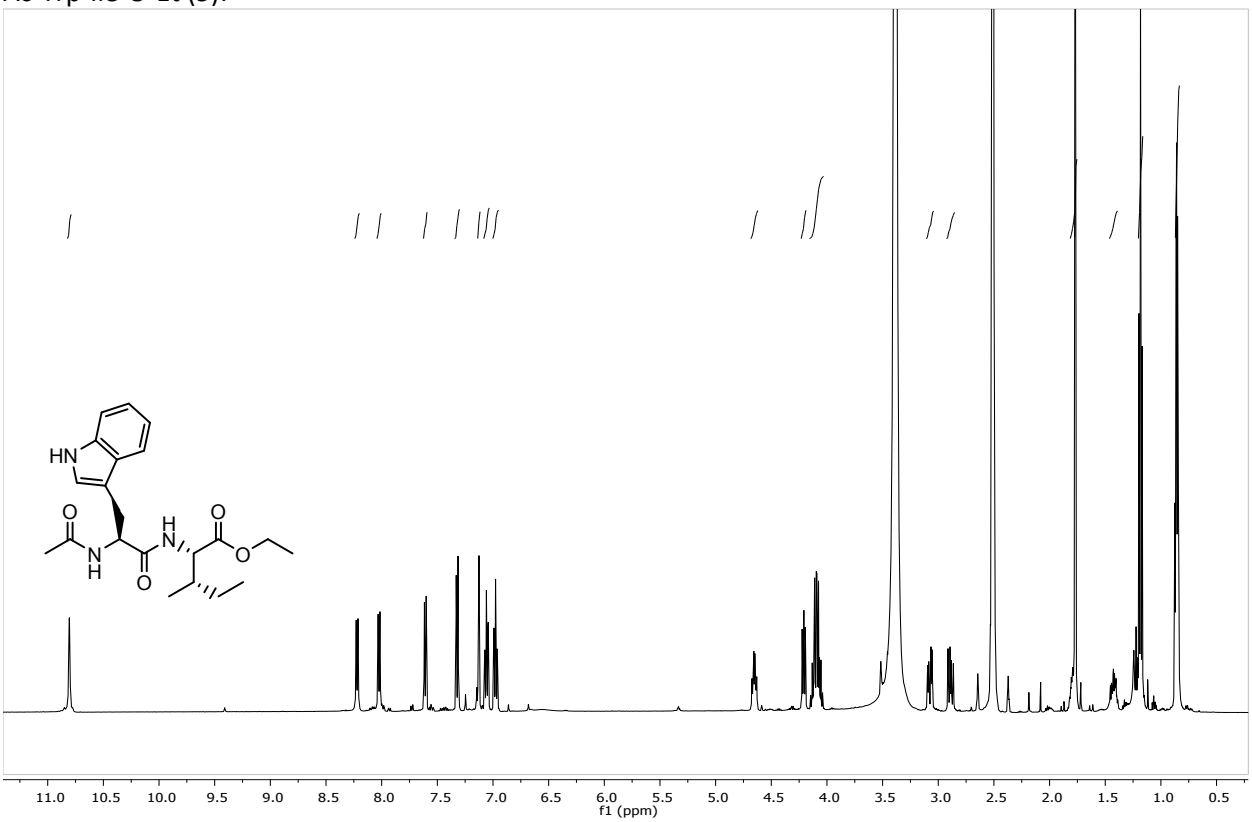
Ac-Trp-Ile-O-Me (**6**):



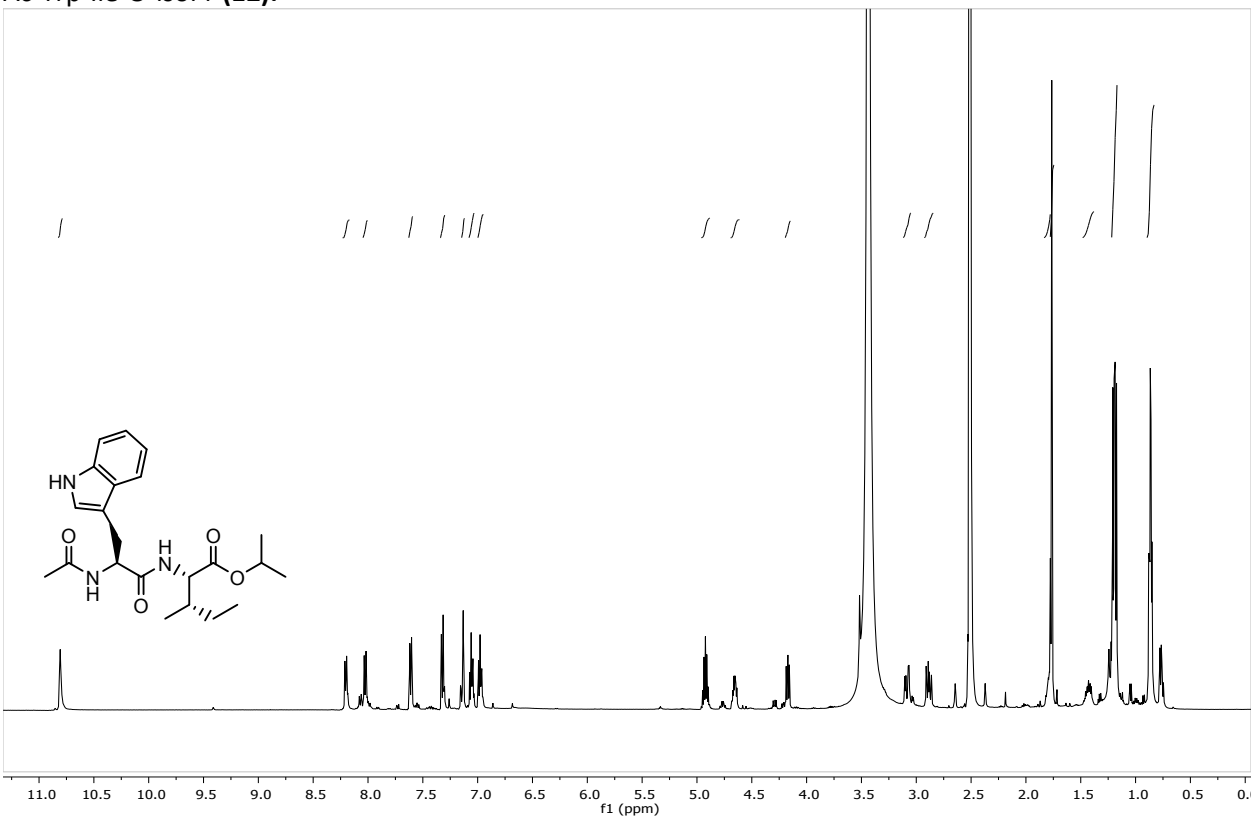
Ac-Trp-Gly-O-Et (**7**):



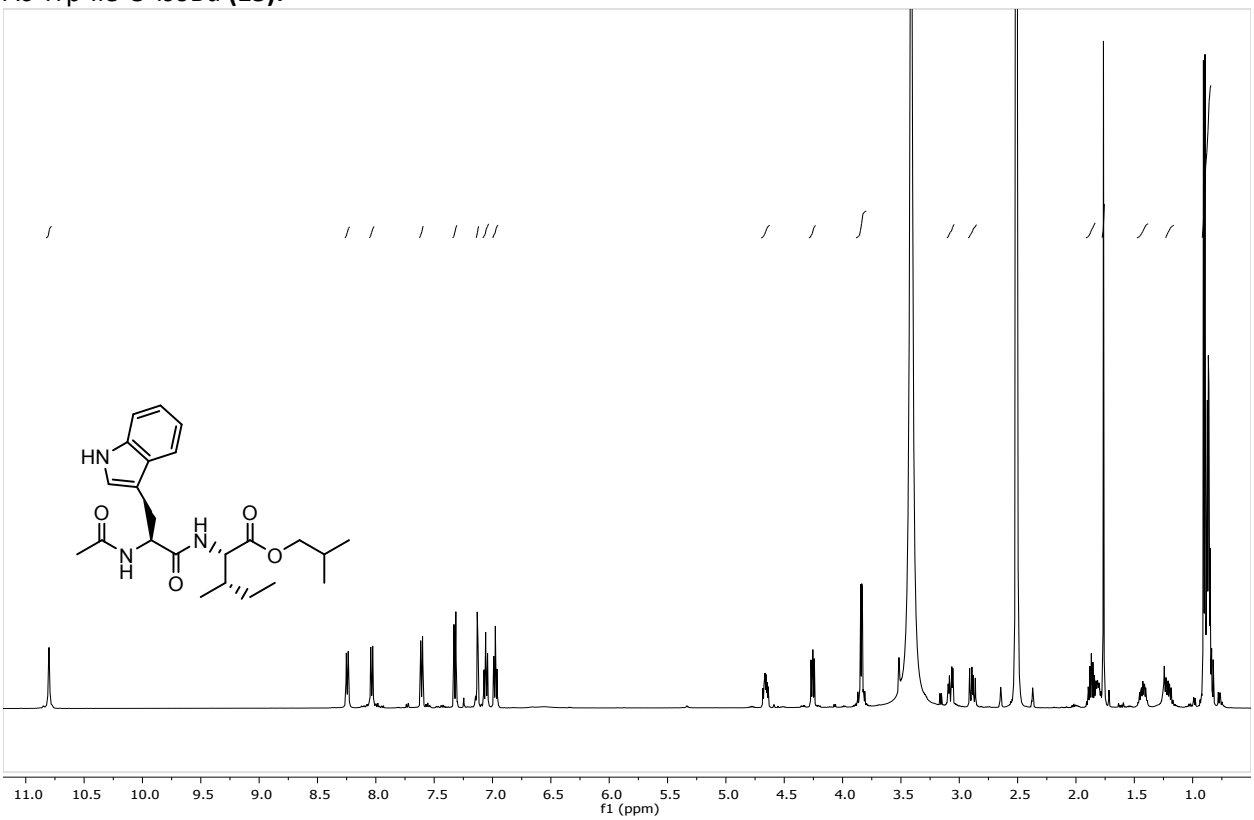
Ac-Trp-Ile-O-Et (**9**):



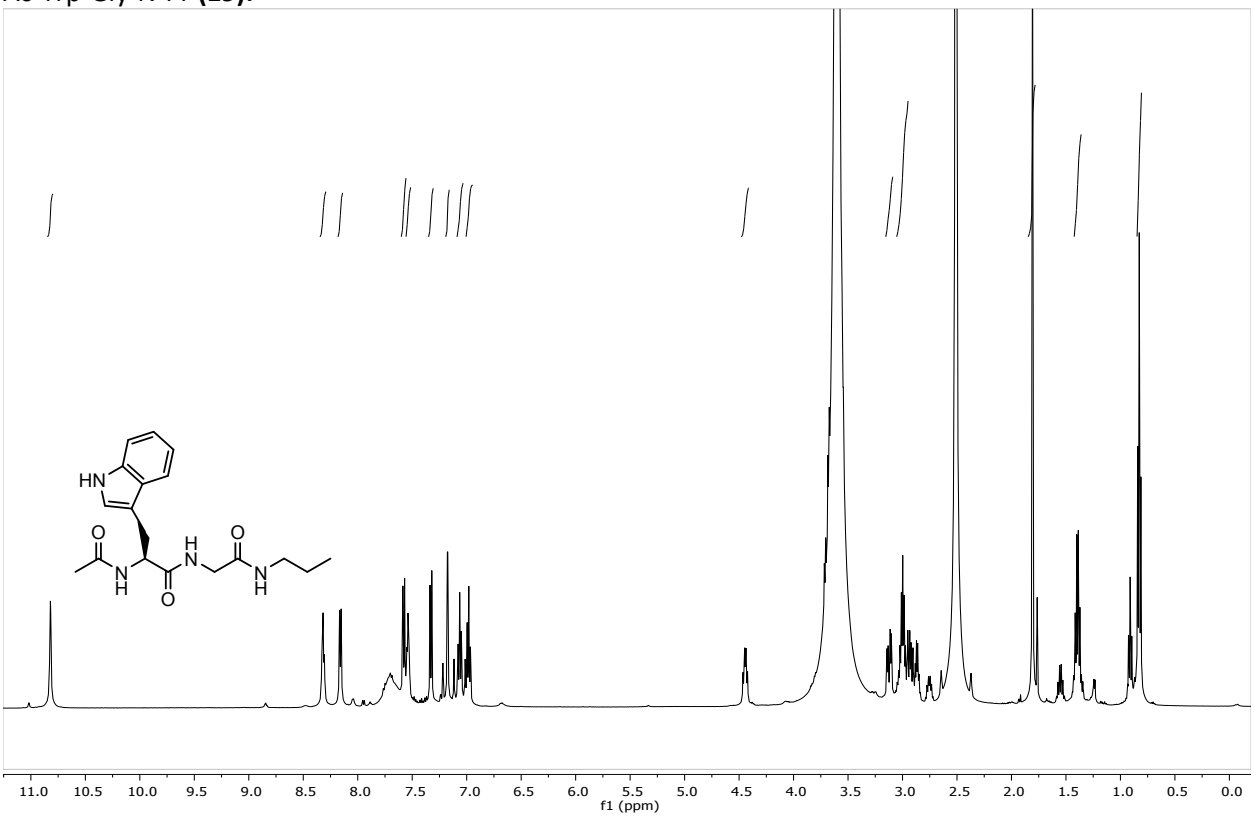
Ac-Trp-Ile-O-isoPr **(12):**



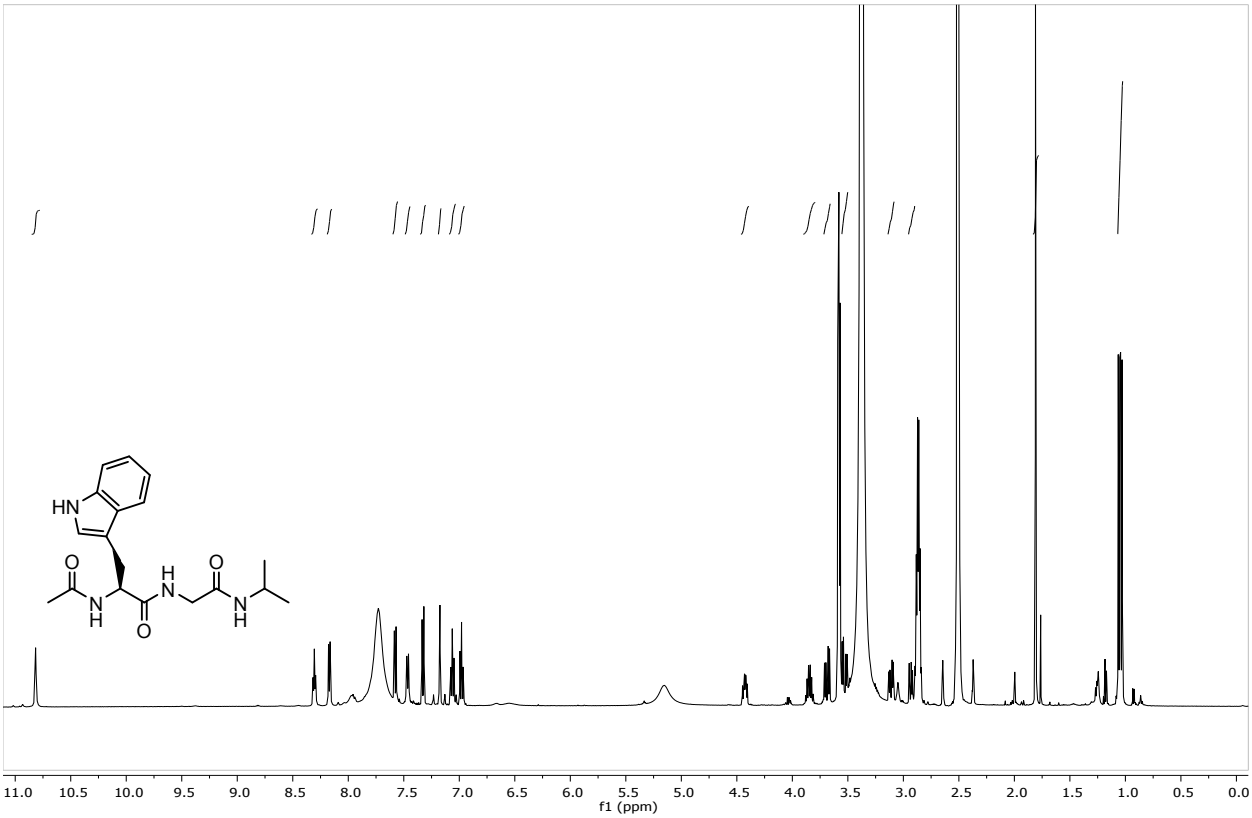
Ac-Trp-Ile-O-isoBu **(15):**



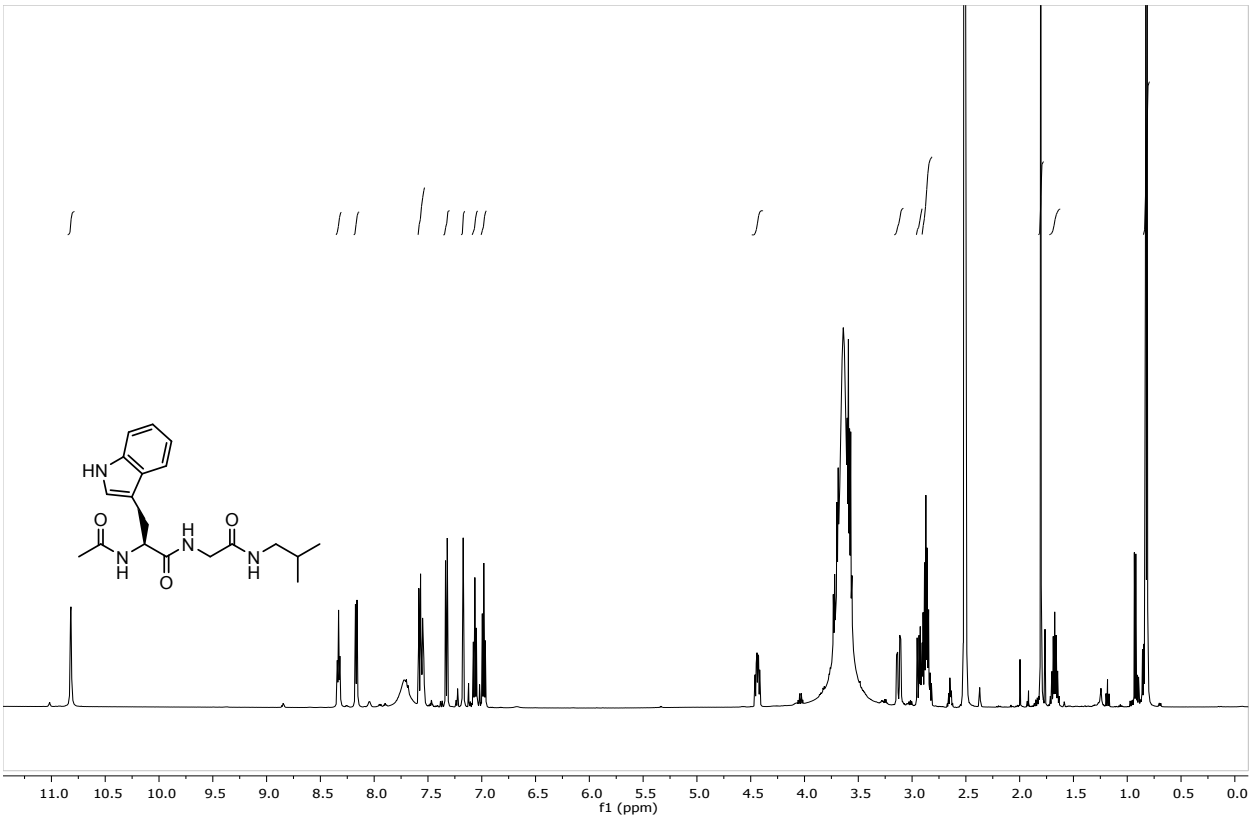
Ac-Trp-Gly-N-Pr **(19):**



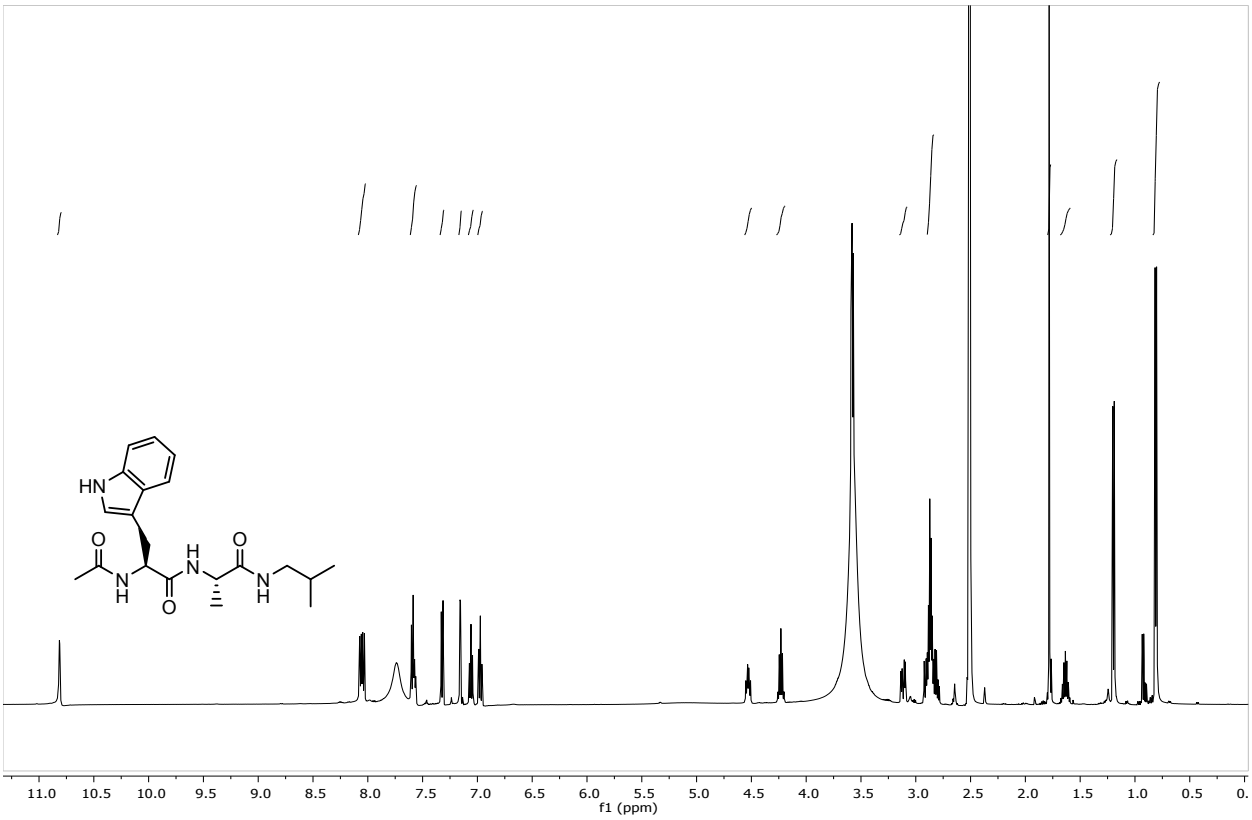
Ac-Trp-Gly-N-isoPr **(22):**



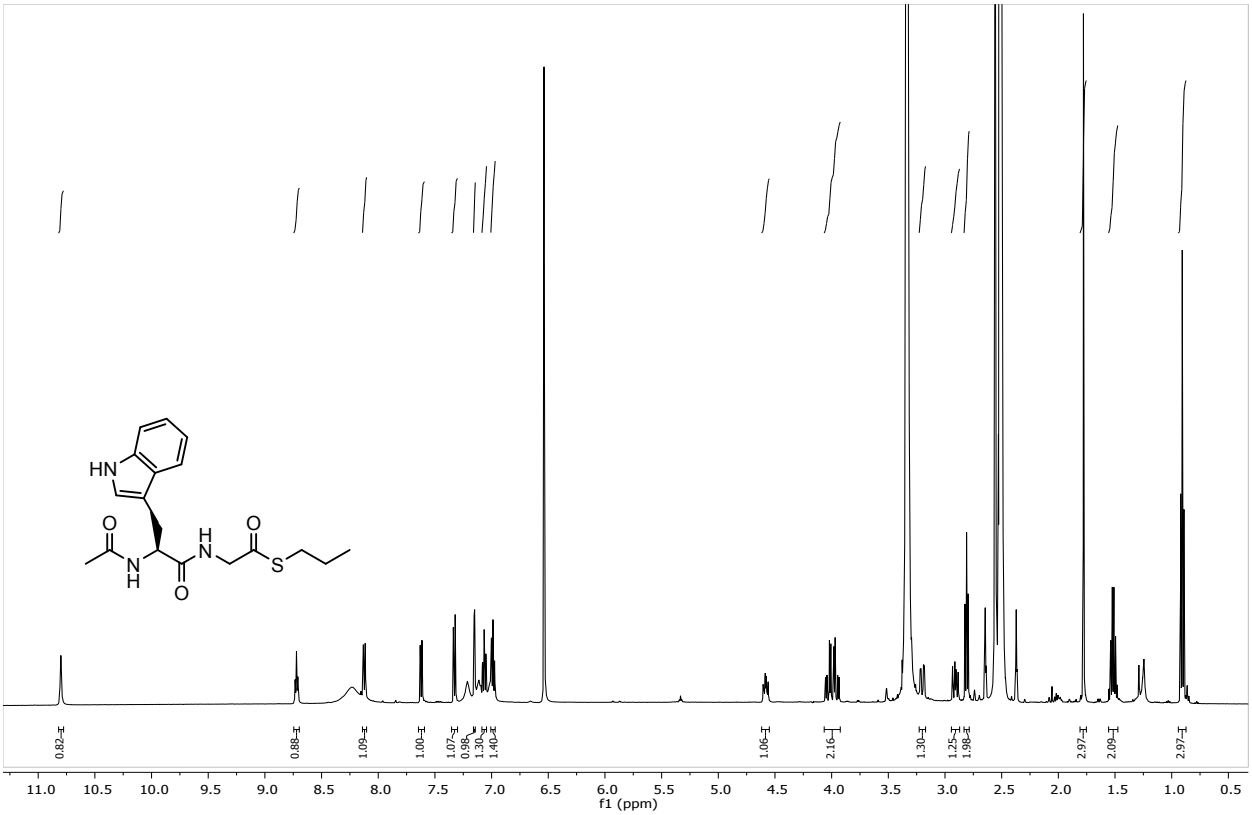
Ac-Trp-Gly-N-isoBu **(25):**



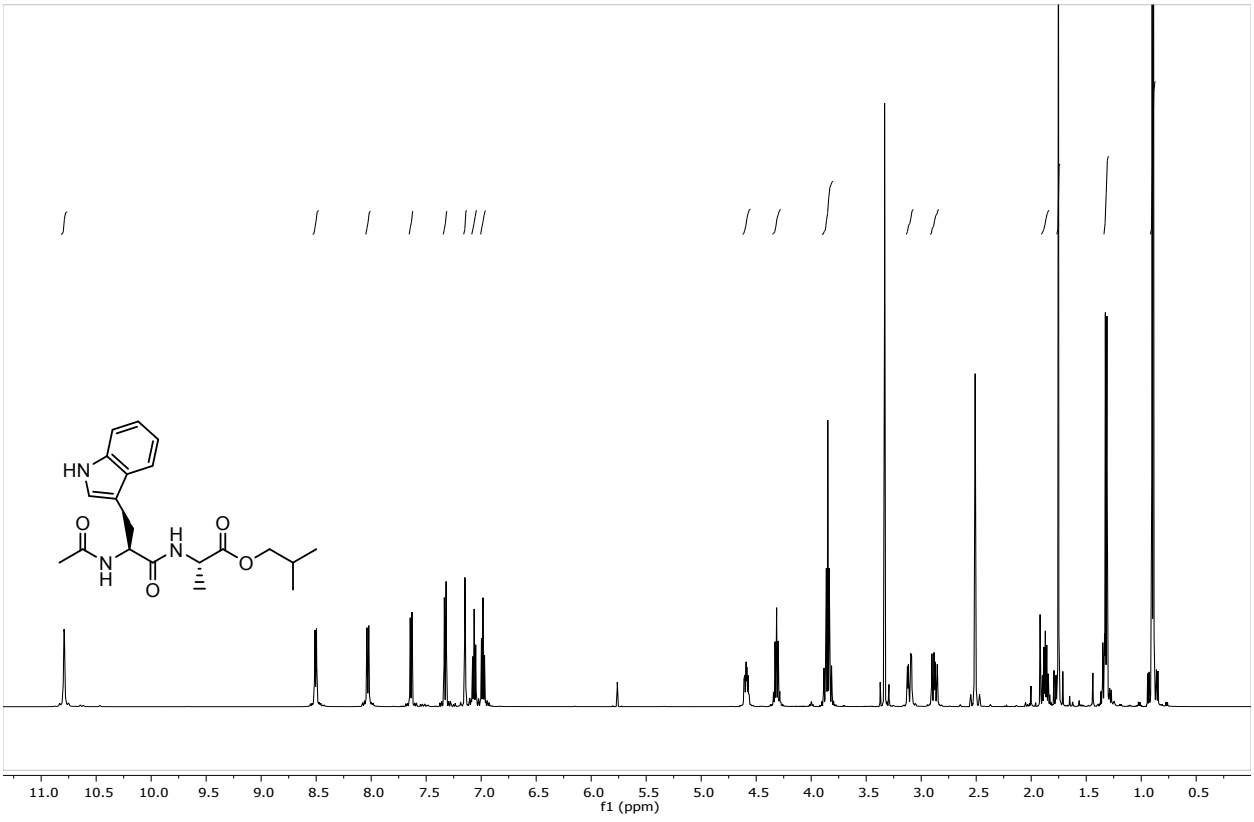
Ac-Trp-Ala-N-isoBu **(26):**



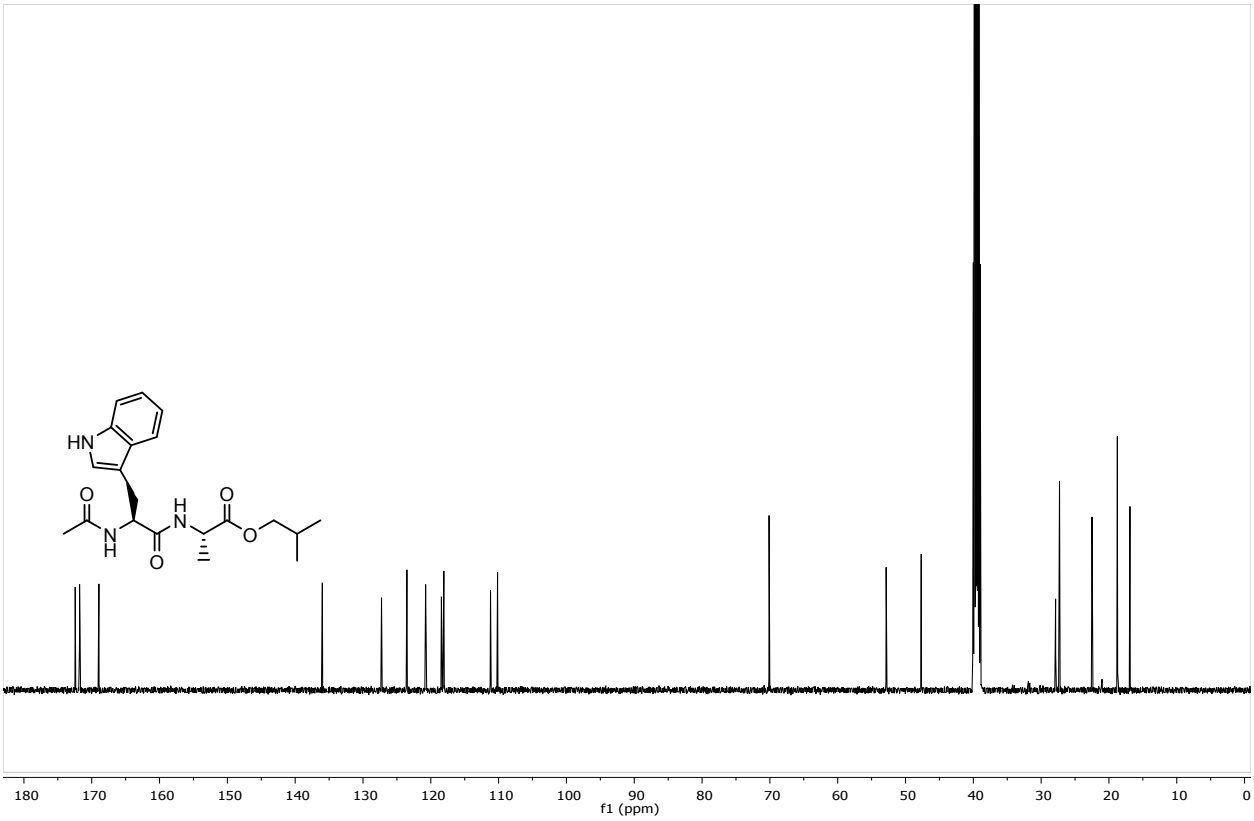
Ac-Trp-Gly-S-Pr **(34):**



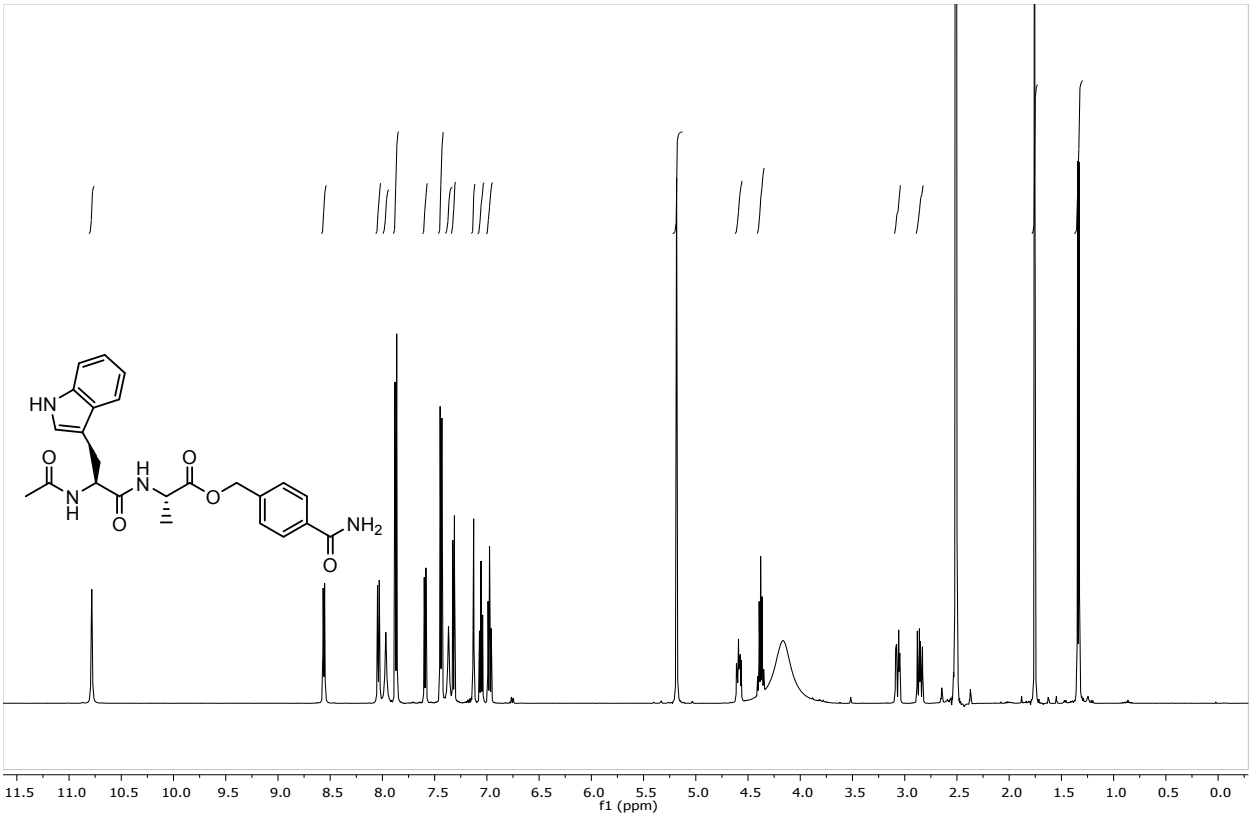
Ac-Trp-Ala-O-isoBu (**14**):



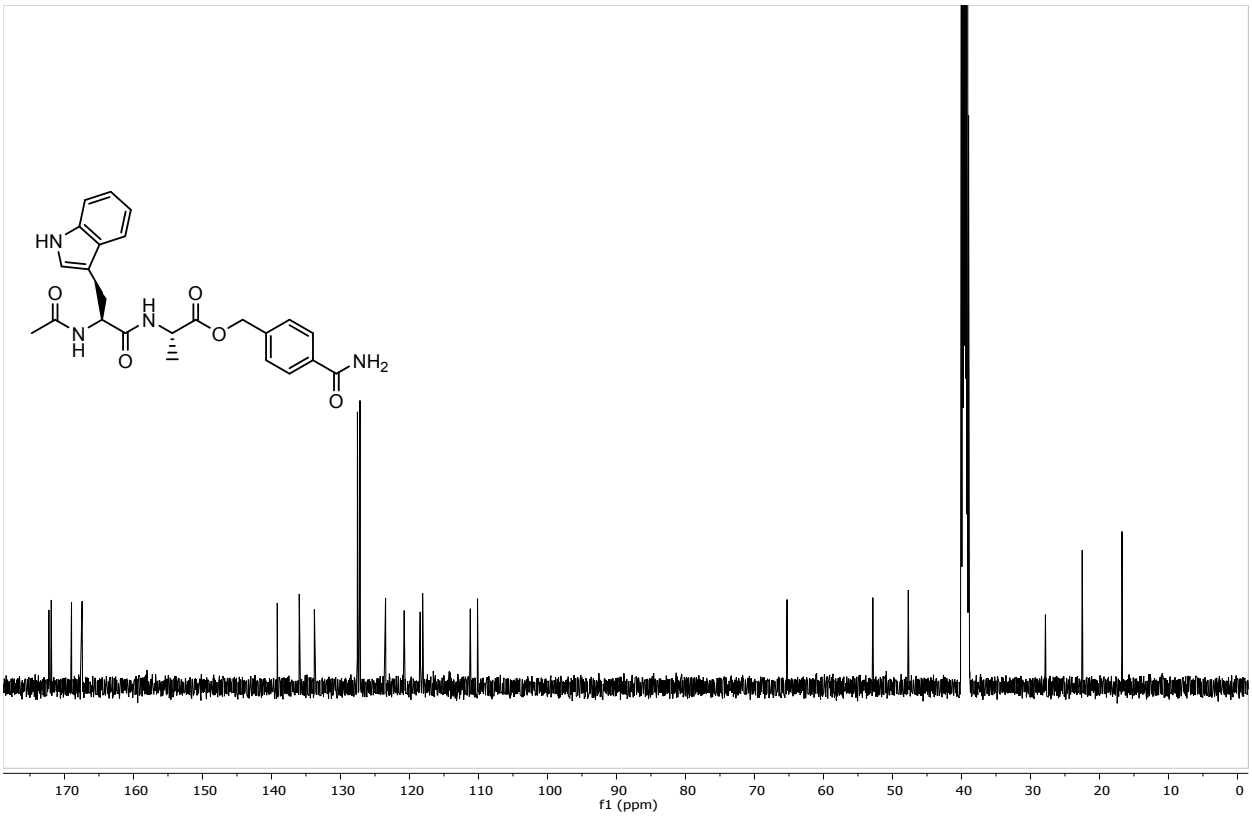
Ac-Trp-Ala-O-isoBu (**14**):



Ac-Trp-Ala-O-HMBA (**16**):

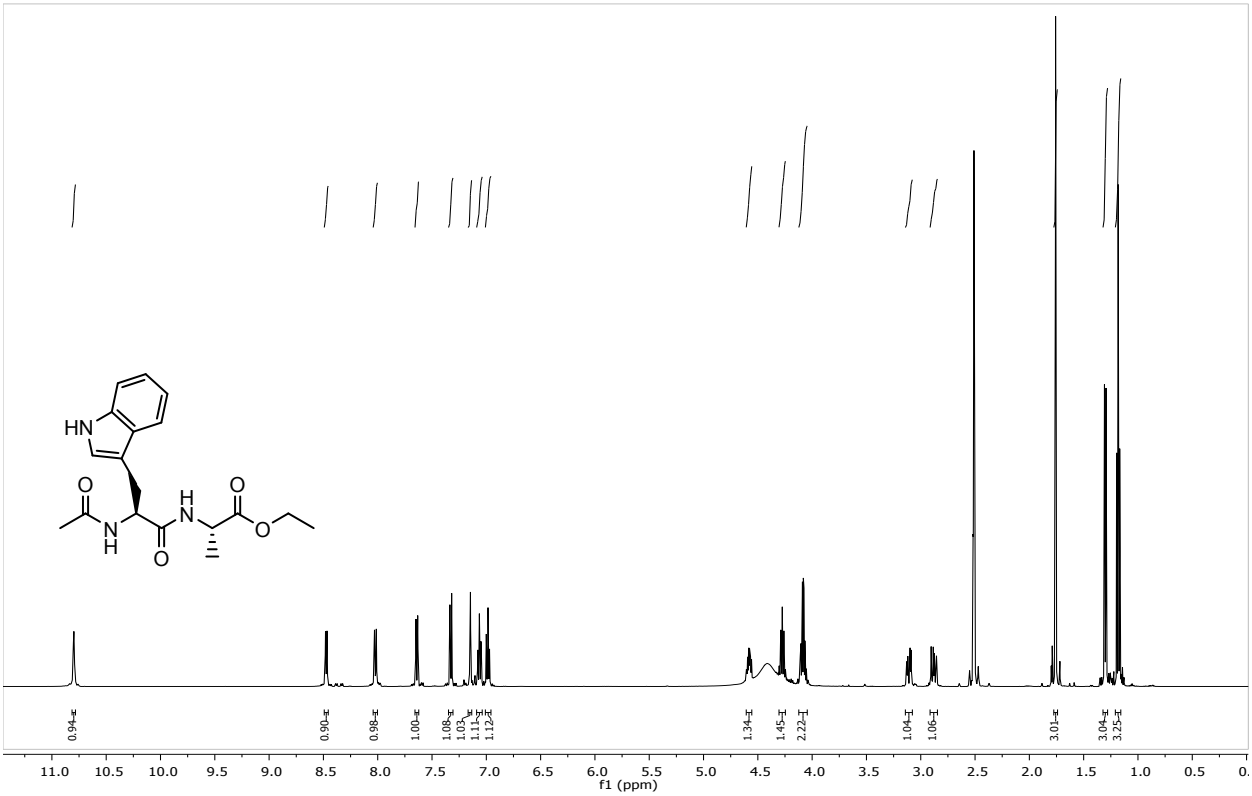


Ac-Trp-Ala-O-HMBA (**16**):

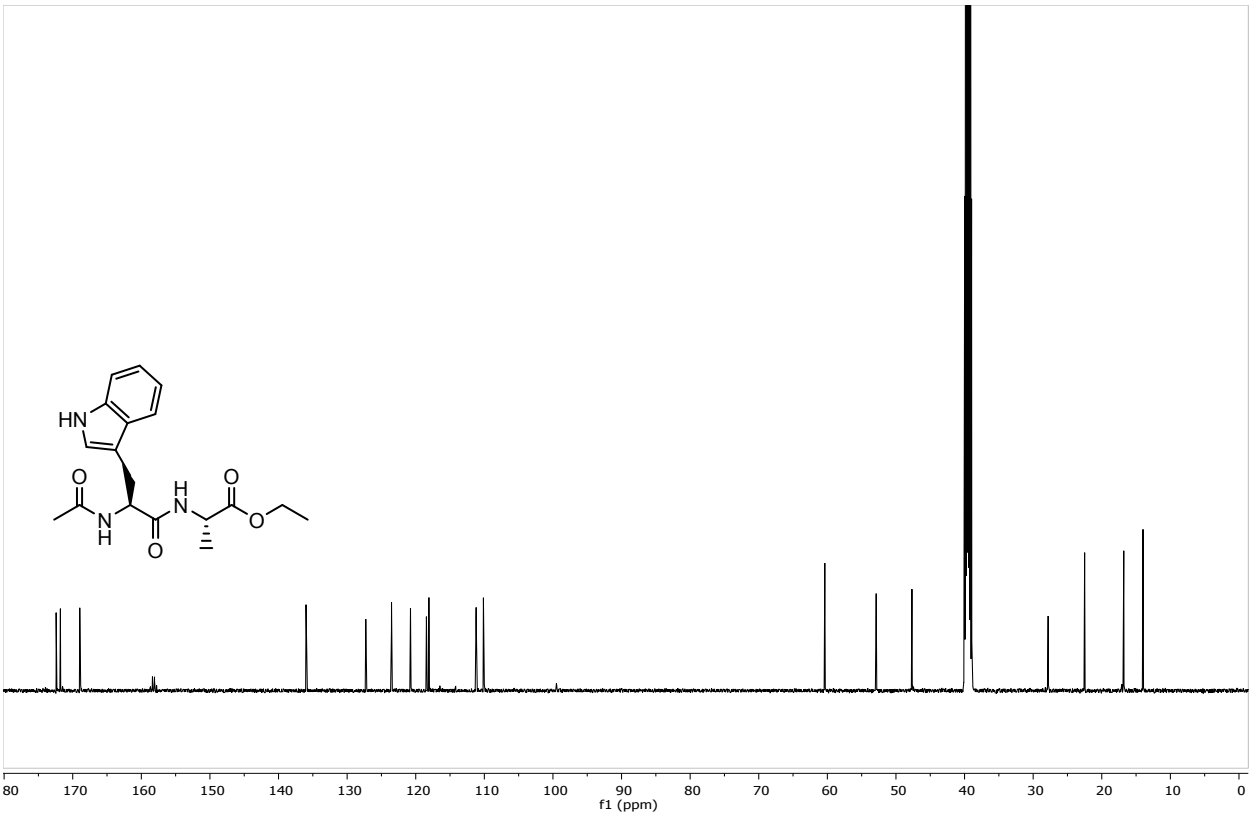


Preparative amount reactions.

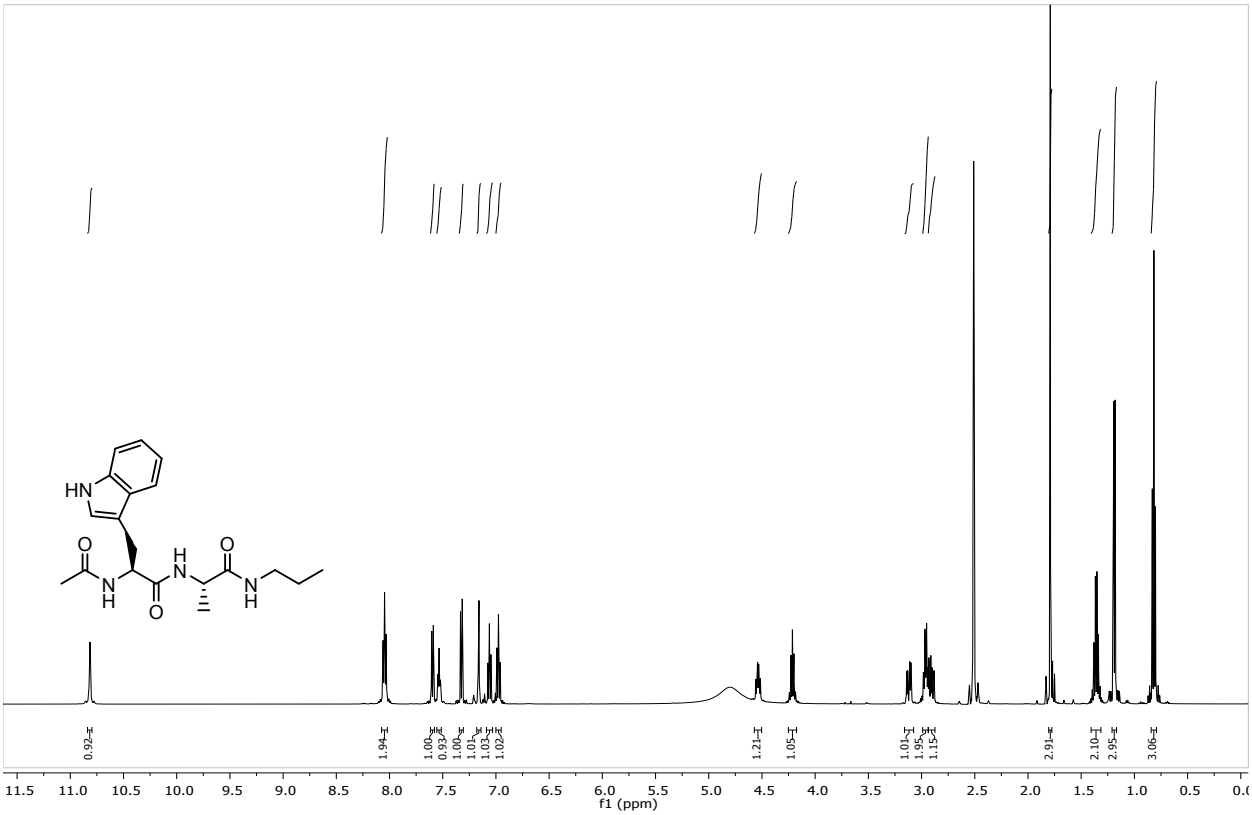
Ac-Trp-Ala-O-Et (**8**): Purified



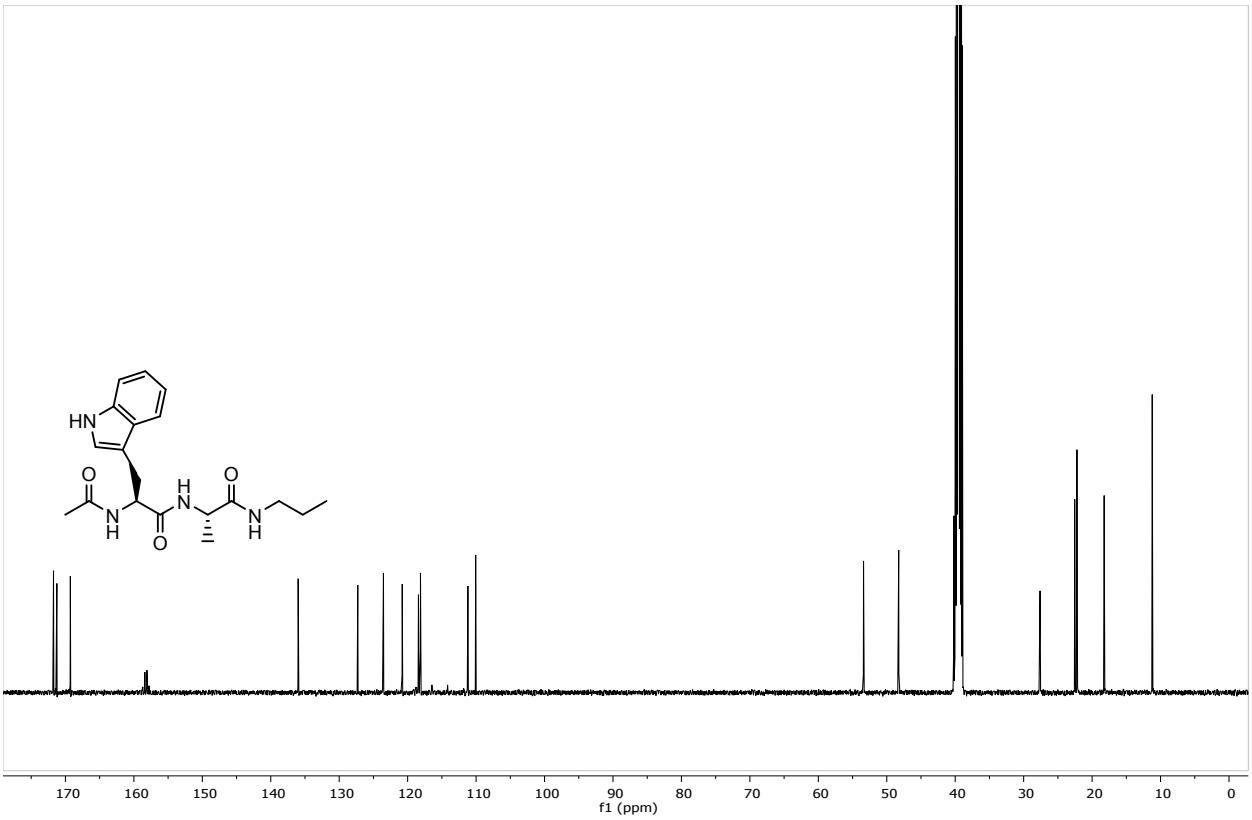
Ac-Trp-Ala-O-Et (**8**): Purified



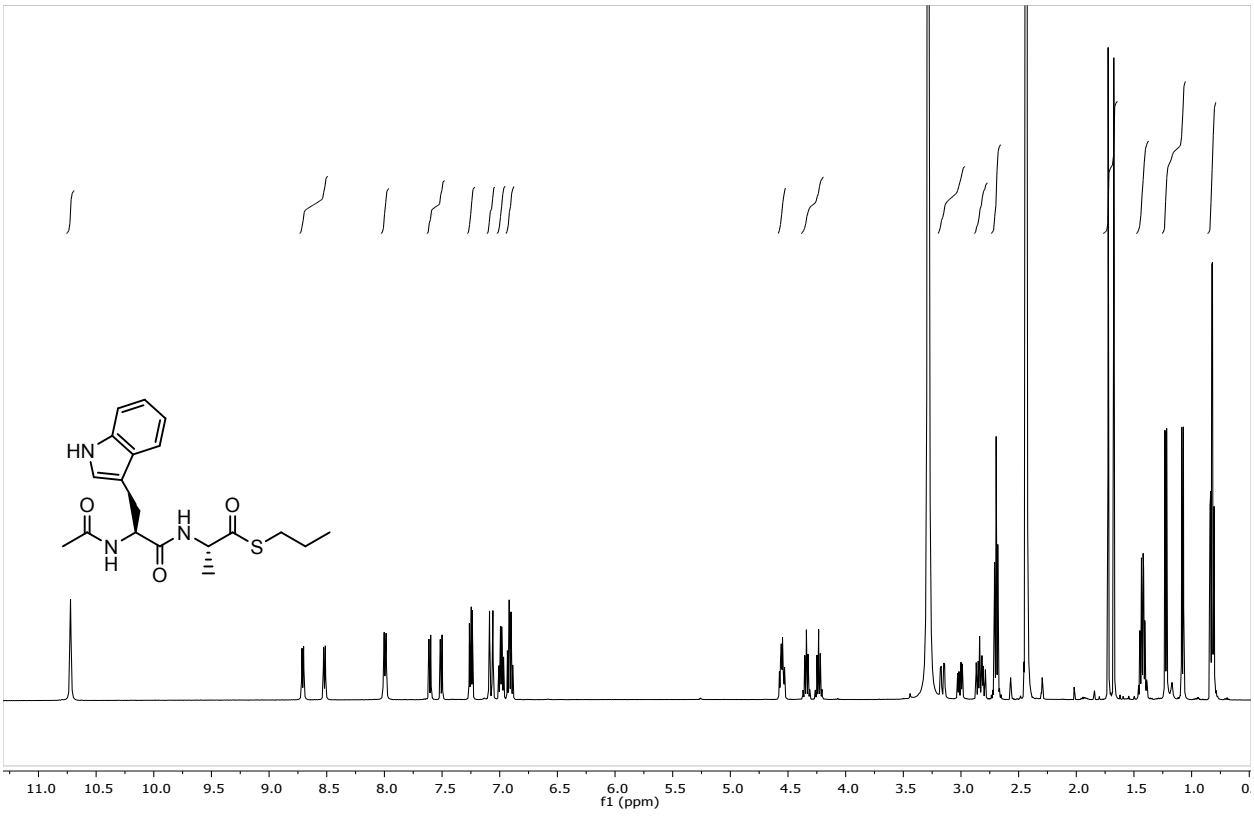
Ac-Trp-Ala-N-Pr (**20**): Purified



Ac-Trp-Ala-N-Pr (**20**): Purified



Ac-Trp-Ala-S-Pr (**35**): Purified



Ac-Trp-Ala-S-Pr (**35**): Purified