

Supporting Information

for:

Unified mild reaction conditions for C2-selective Pd-catalysed tryptophan arylation, including tryptophan-containing peptides

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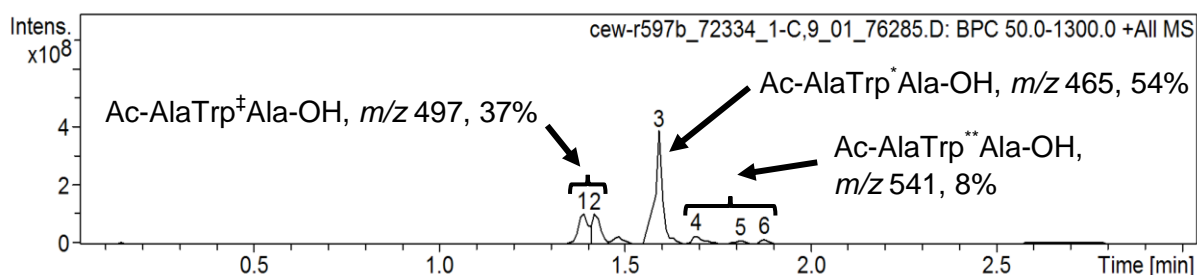
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1. Peptide Arylation HPLC Data

HPLC data for arylated peptides **4** and **6** are given in our preliminary communication on this work.¹

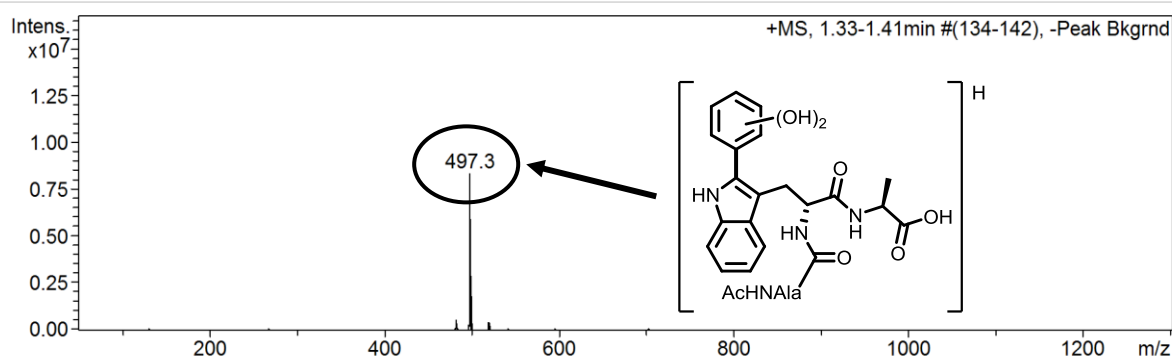
Arylated product of Ac-AlaTrpAla-OH **7**, **8**

HPLC-ESI-MS chromatogram (BPC) of the crude reaction material from **Method A** (arylated tryptophan donated Trp⁺, diarylated tryptophans donated Trp^{**}, dihydroxylated byproducts donated Trp[†]).

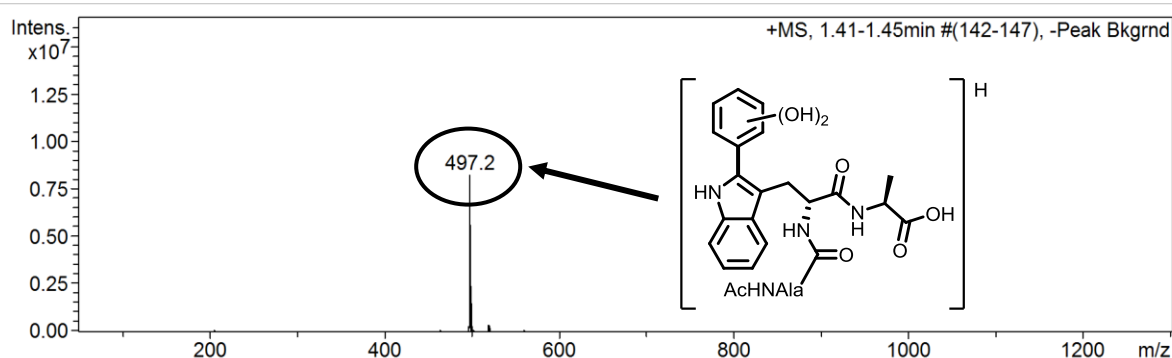


ESI-MS of the crude reaction material.

Cmpd 1, 1.39 min

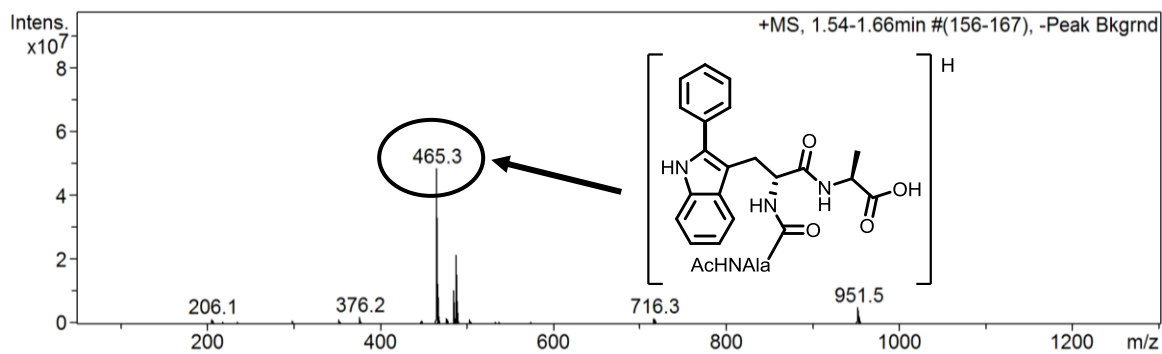


Cmpd 2, 1.42 min

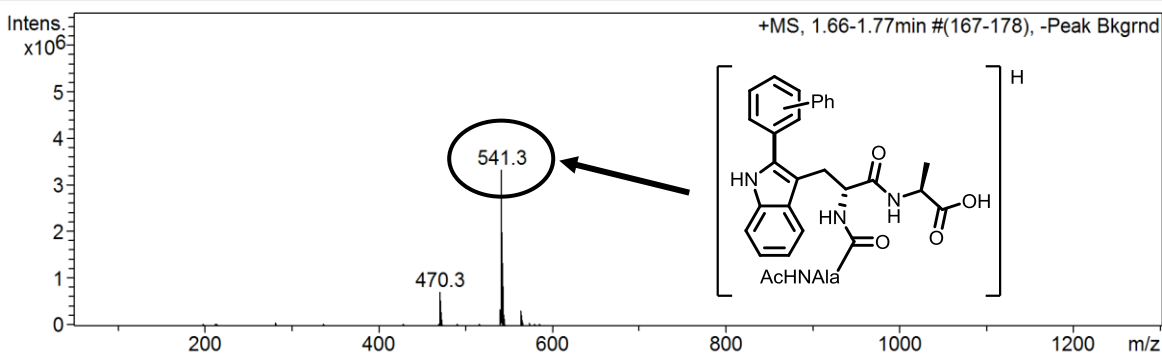


1 T. J. Williams, A. J. Reay, A. C. Whitwood and I. J. S. Fairlamb, *Chem. Commun.*, 2014, **50**, 3052.

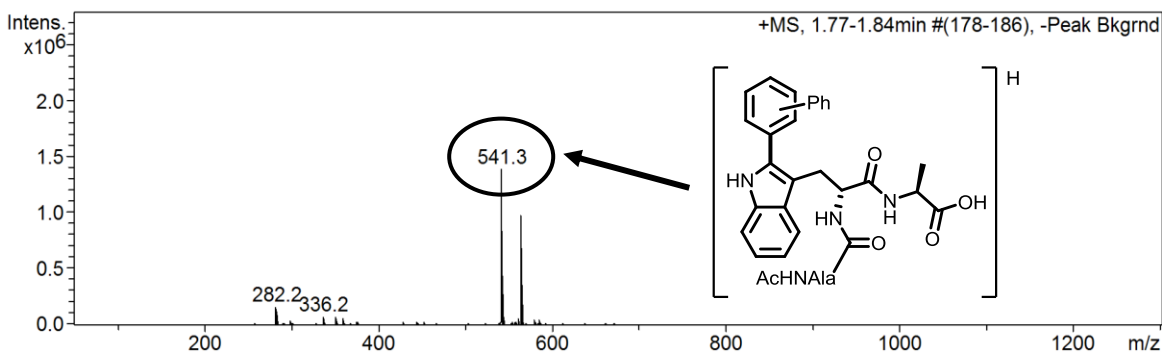
Cmpd 3, 1.59 min



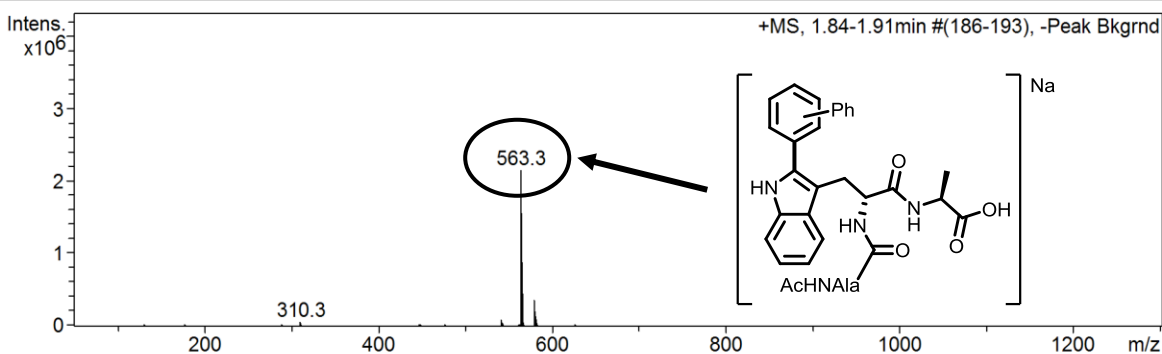
Cmpd 4, 1.69 min



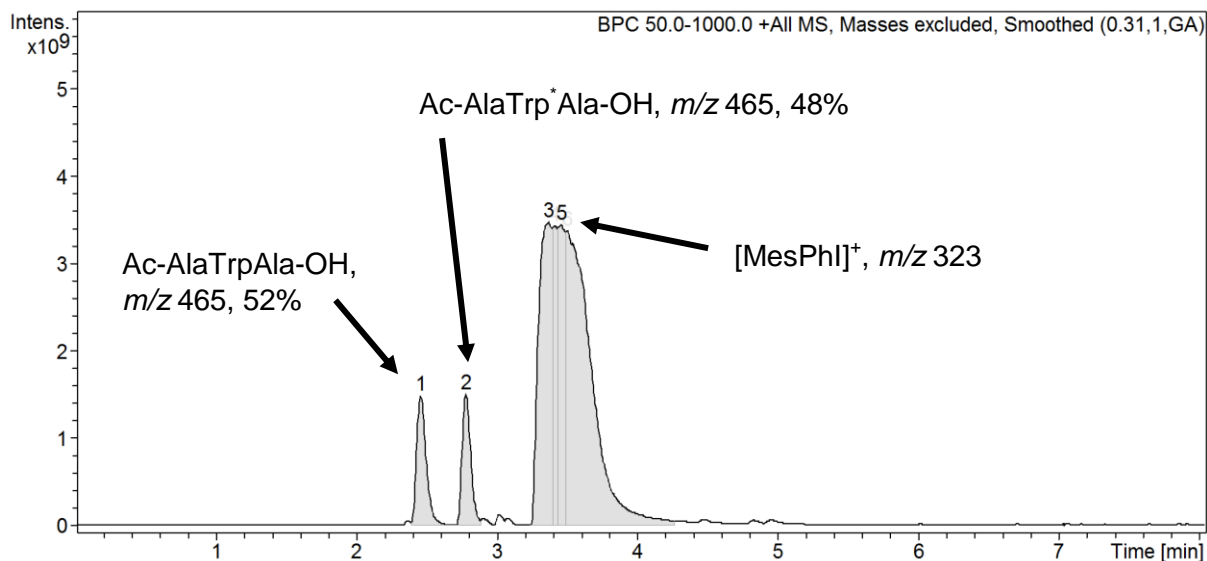
Cmpd 5, 1.81 min



Cmpd 6, 1.87 min

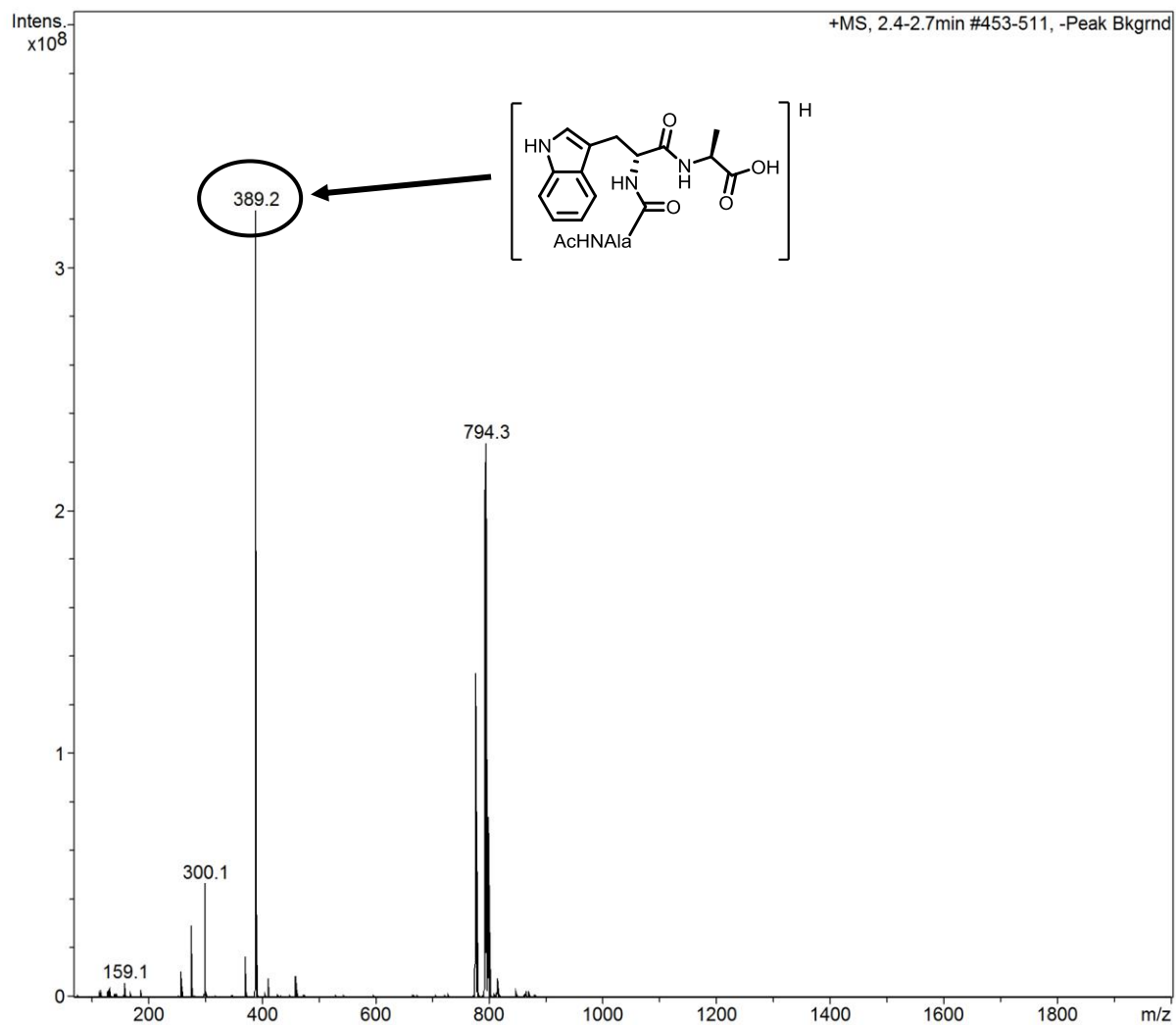


HPLC-ESI-MS chromatogram (BPC) of the crude reaction material from **Method B** (arylated tryptophan donated Trp*, starting material donated Trp).

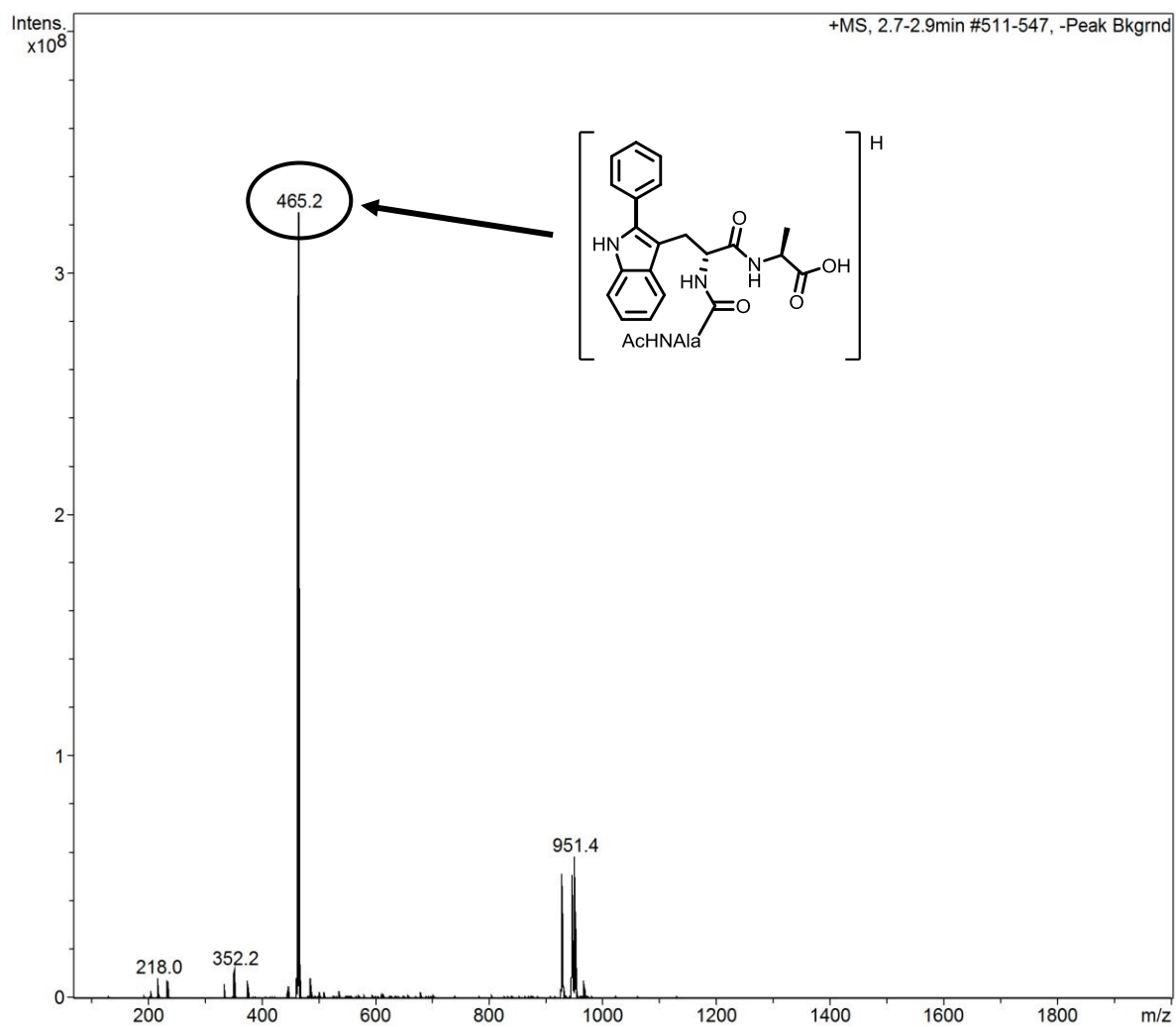


ESI-MS of the crude reaction material.

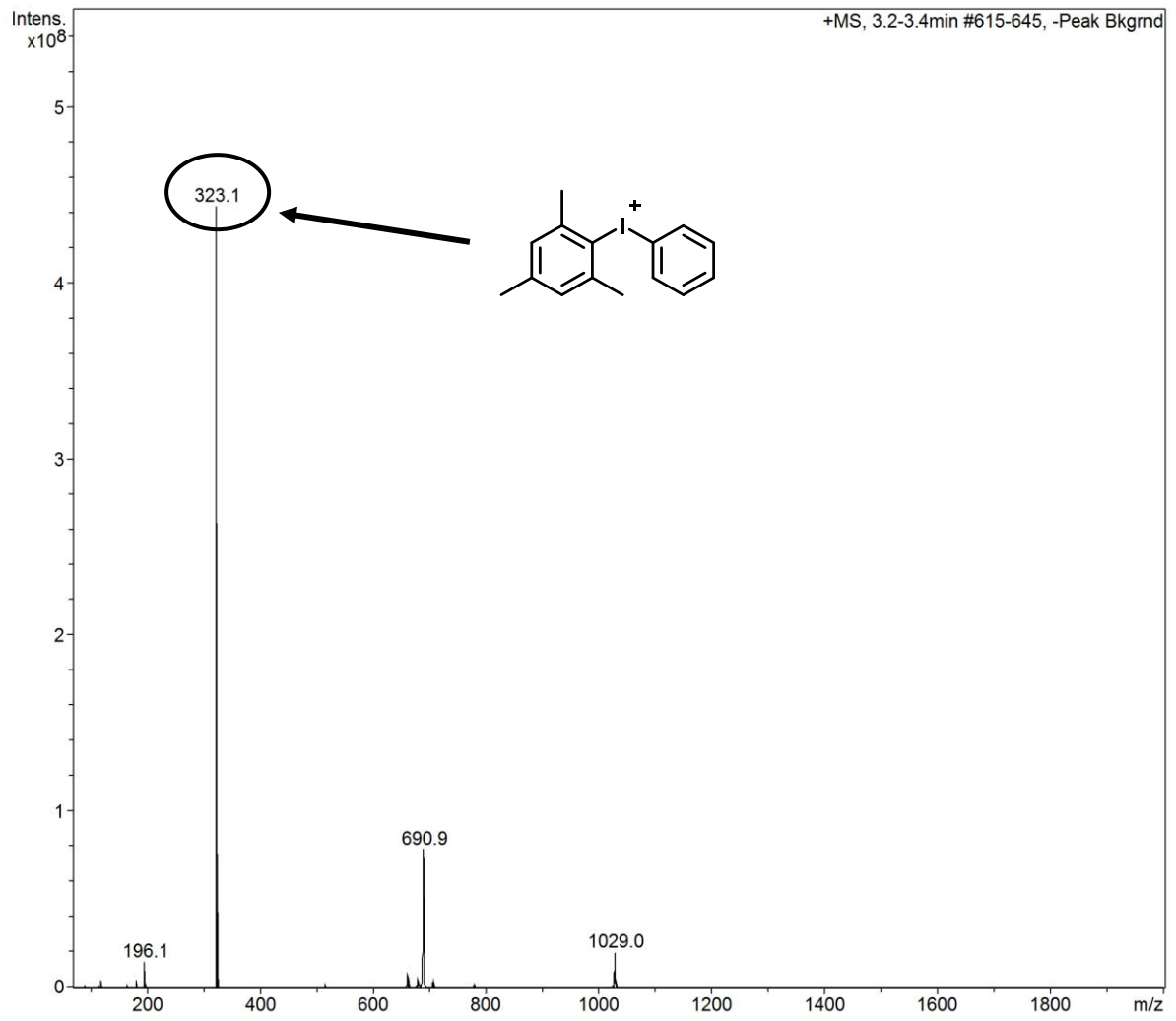
Cmpd 1, 2.5 min



Cmpd 2, 2.8 min

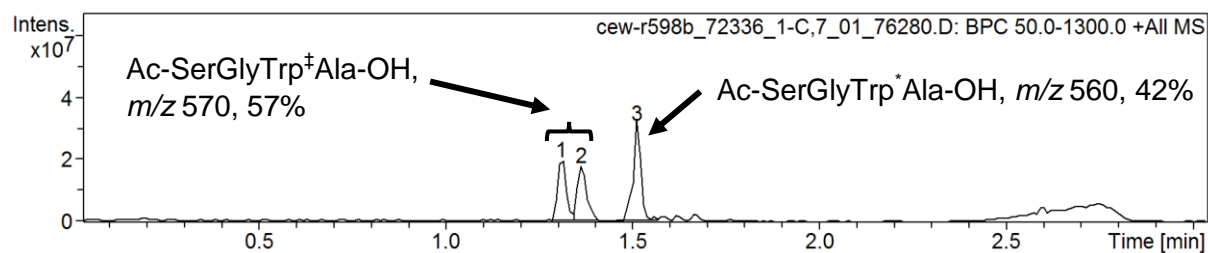


Cmpd 3, 3.4 min



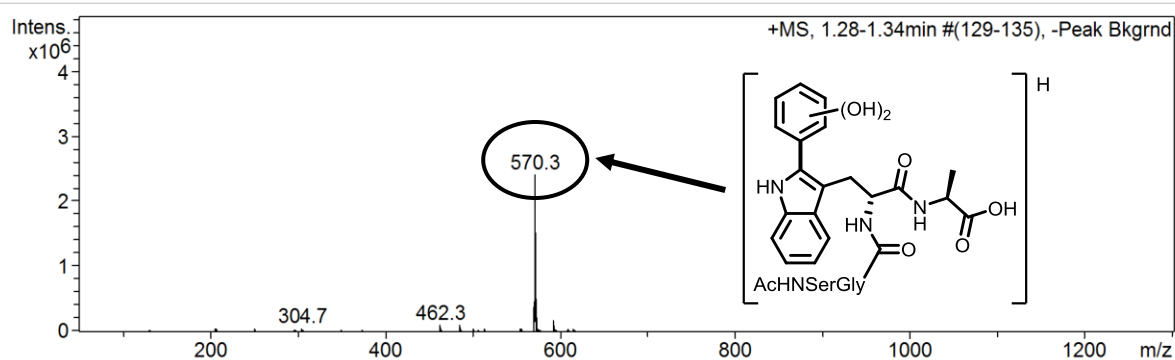
Arylated product of Ac-SerGlyTrp⁺Ala-OH 9, 10.

HPLC-ESI-MS chromatogram (BPC) of the crude reaction material from **Method A** (arylated tryptophan donated Trp⁺, dihydroxylated byproducts donated Trp⁺).

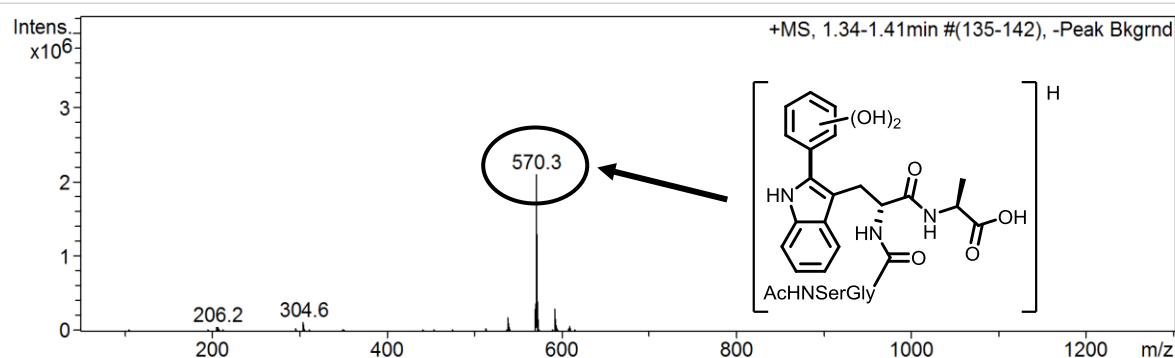


ESI-MS of the crude reaction material.

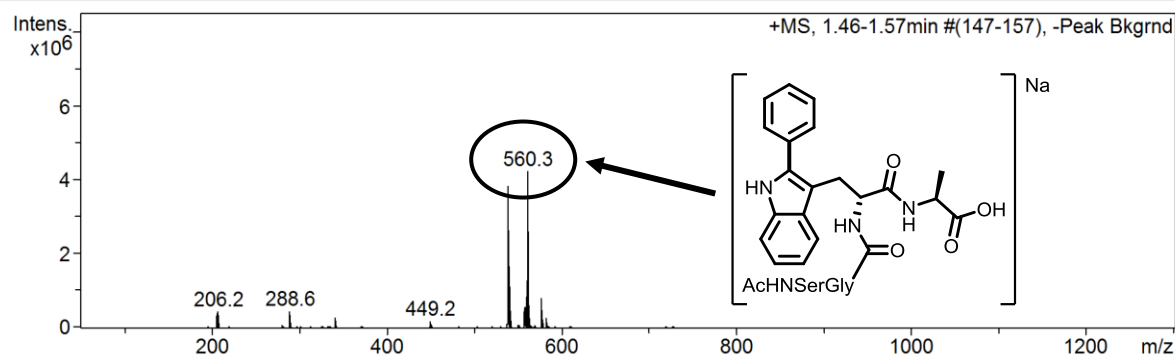
Cmpd 1, 1.31 min



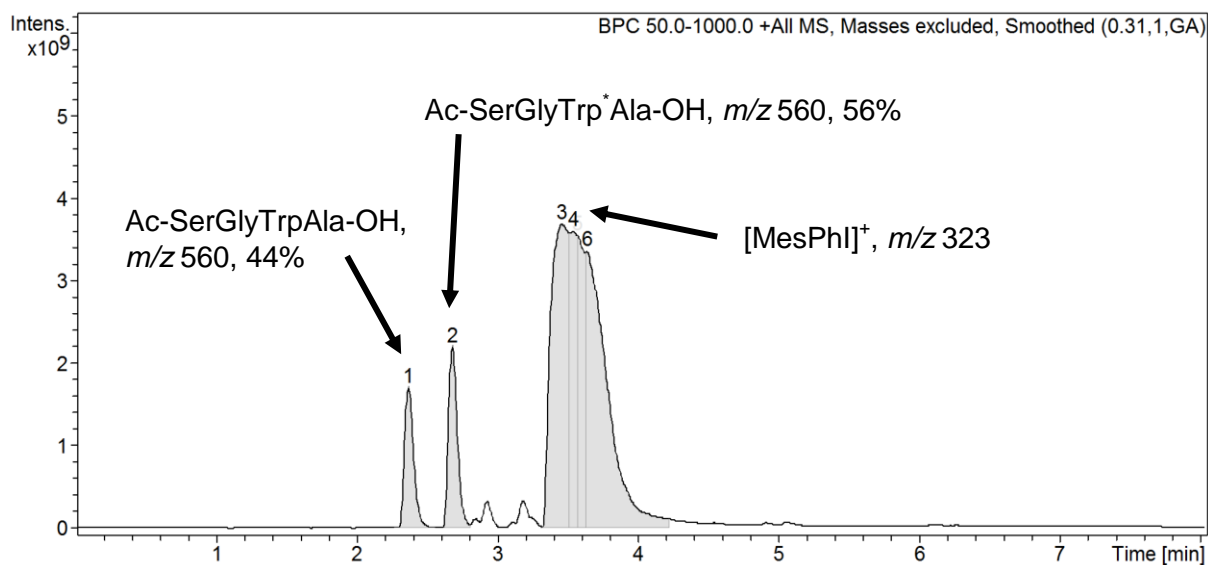
Cmpd 2, 1.36 min



Cmpd 3, 1.51 min

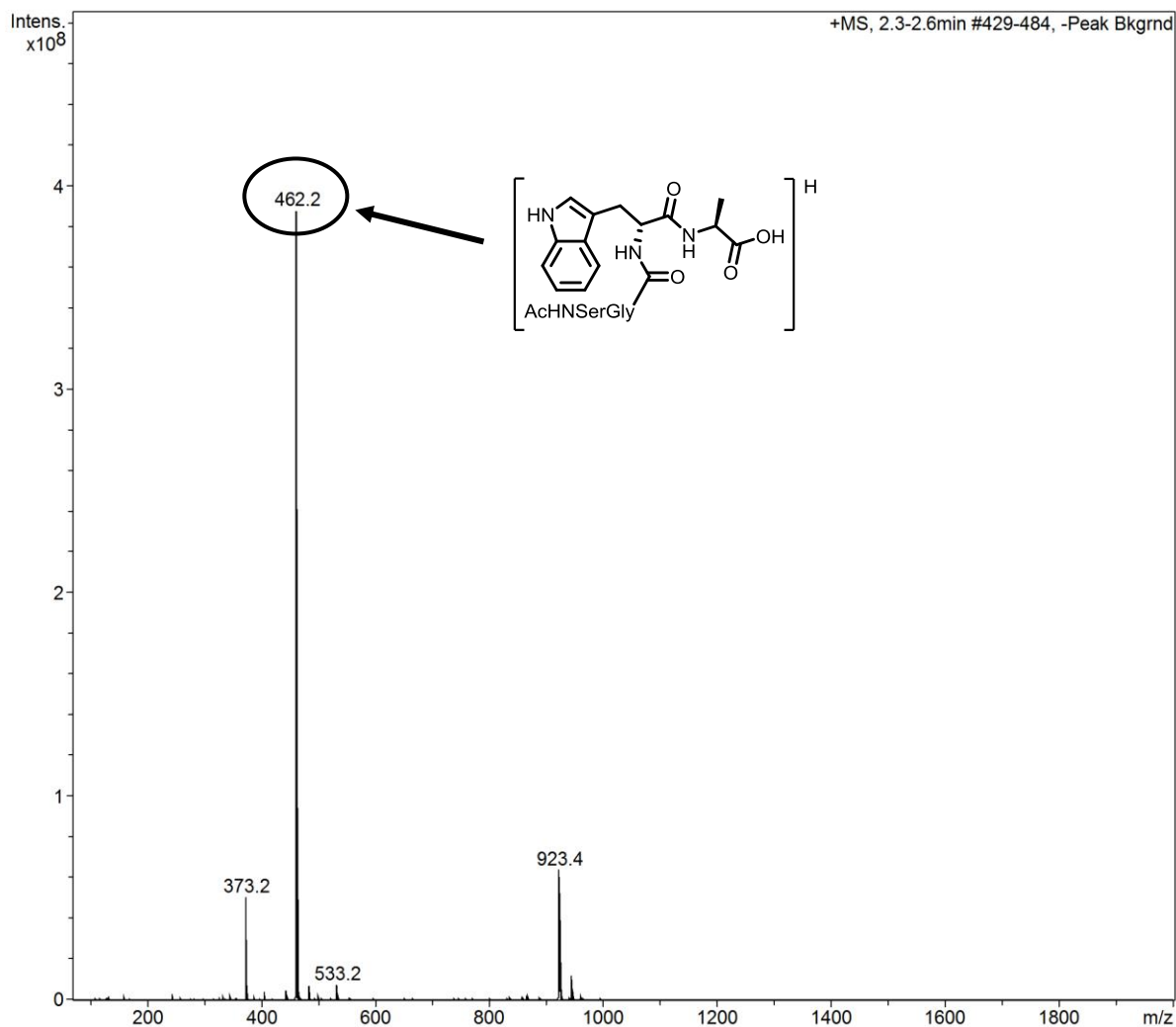


HPLC-ESI-MS chromatogram (BPC) of the crude reaction material from **Method B** (arylated tryptophan donated Trp*, starting material donated Trp).

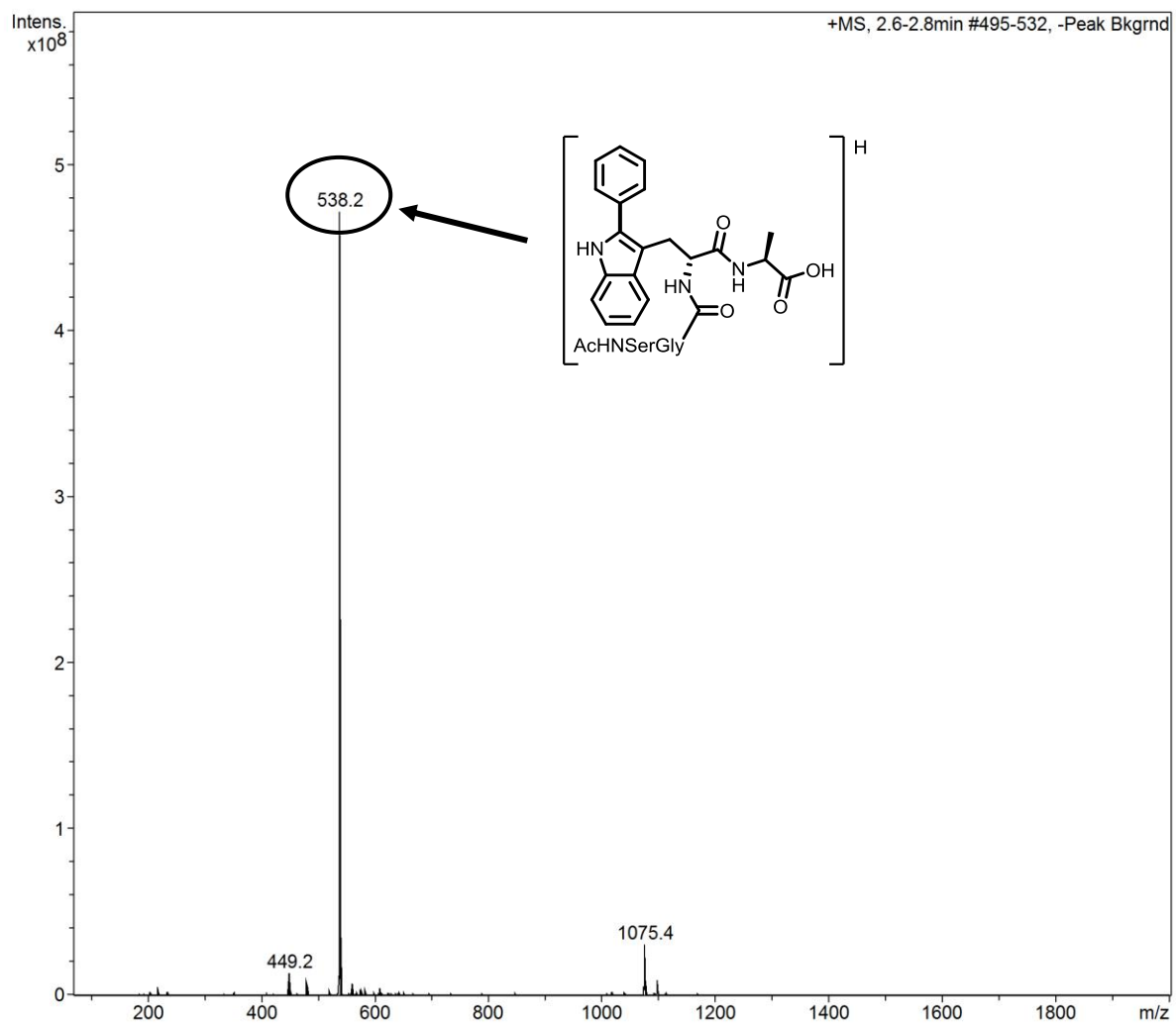


ESI-MS of the crude reaction material.

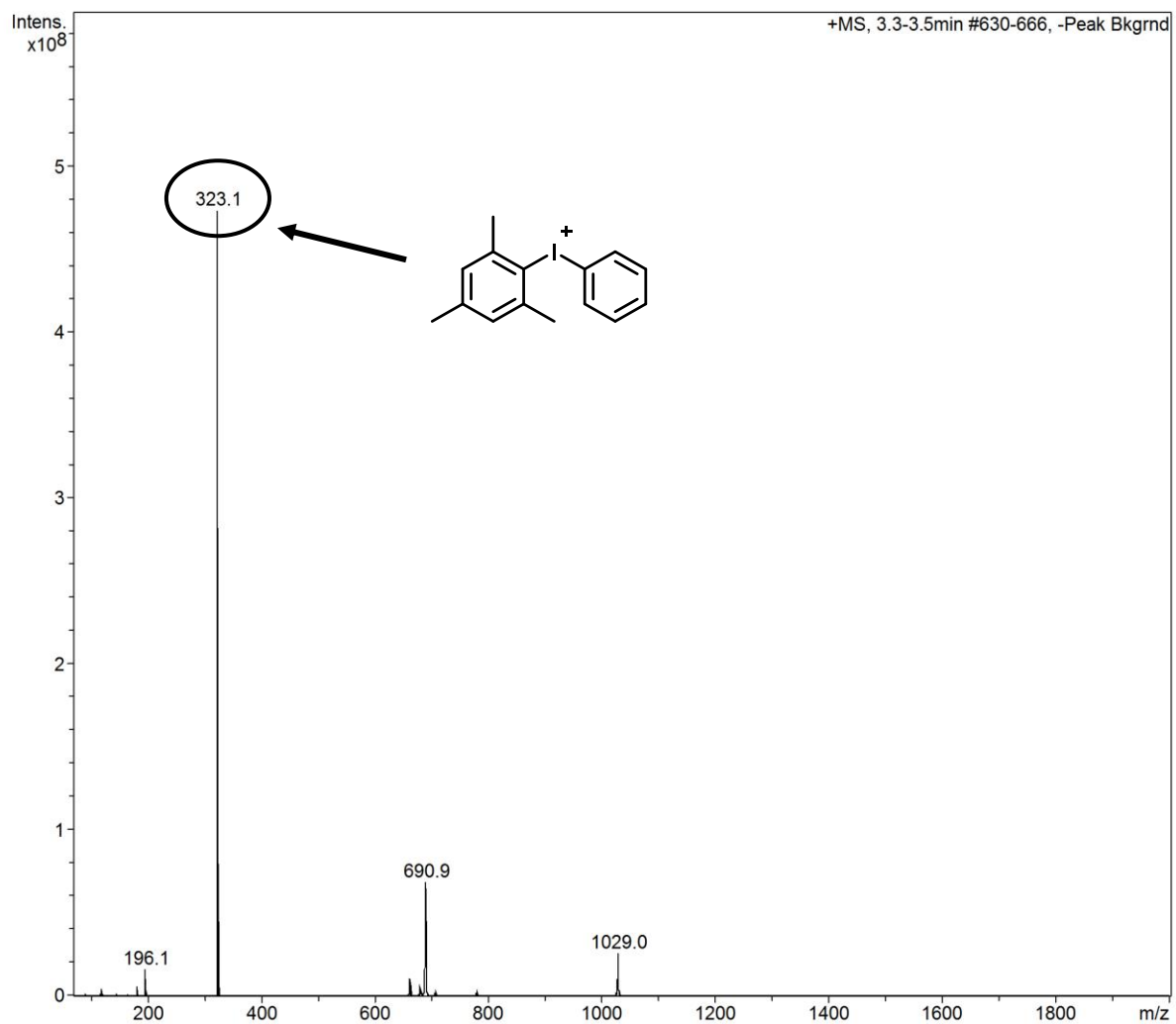
Cmpd 1, 2.4 min



Cmpd 2, 2.7 min

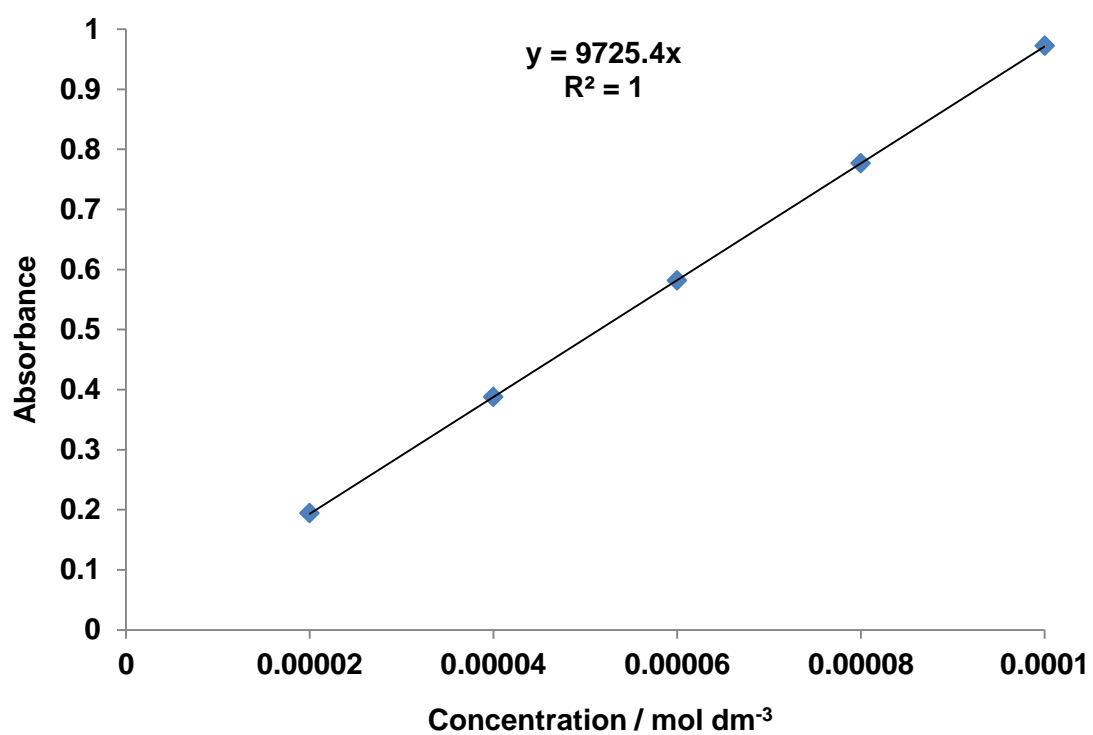
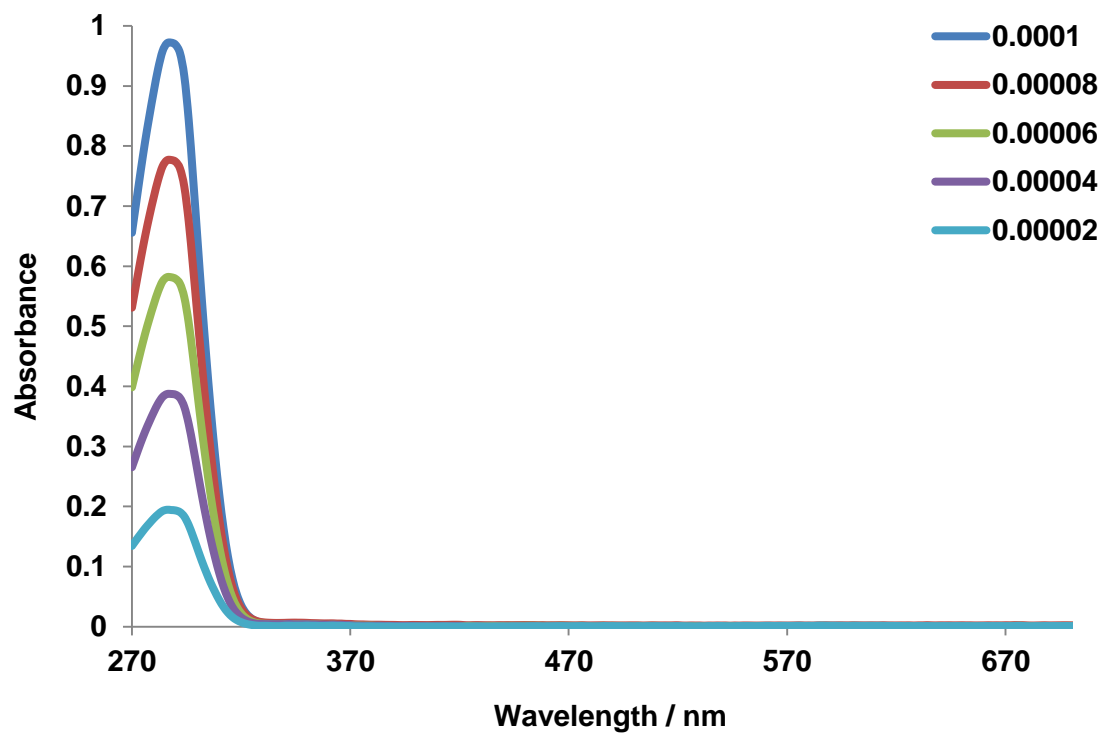


Cmpd 3, 3.5 min

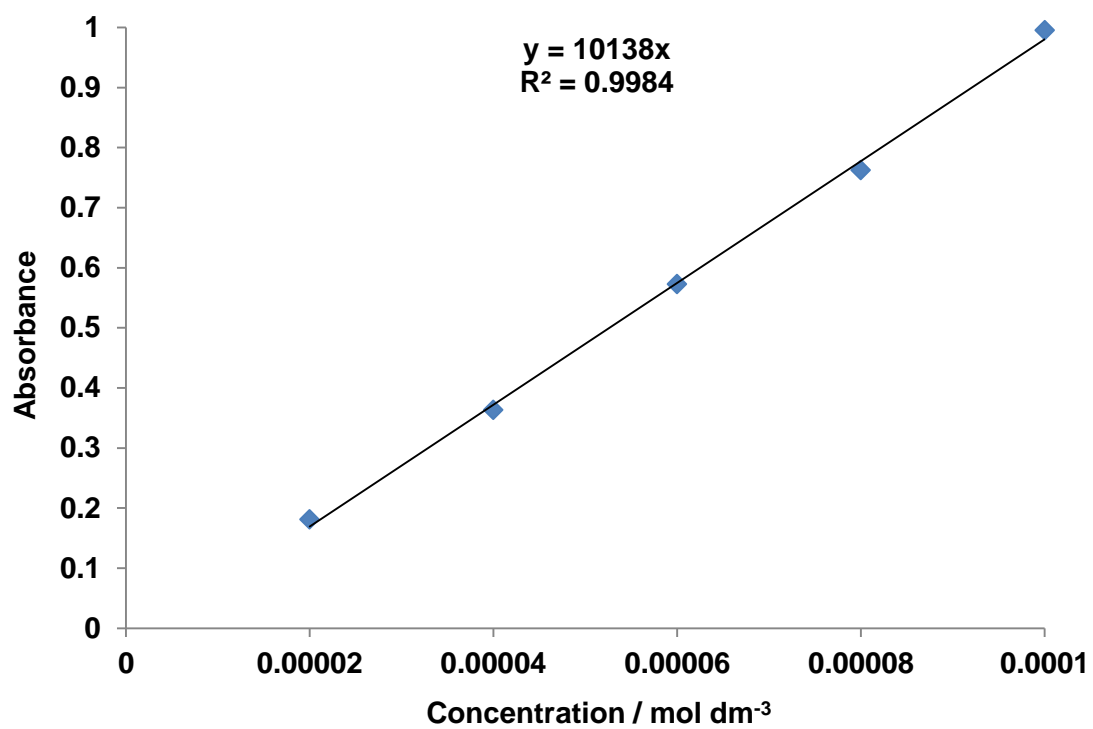
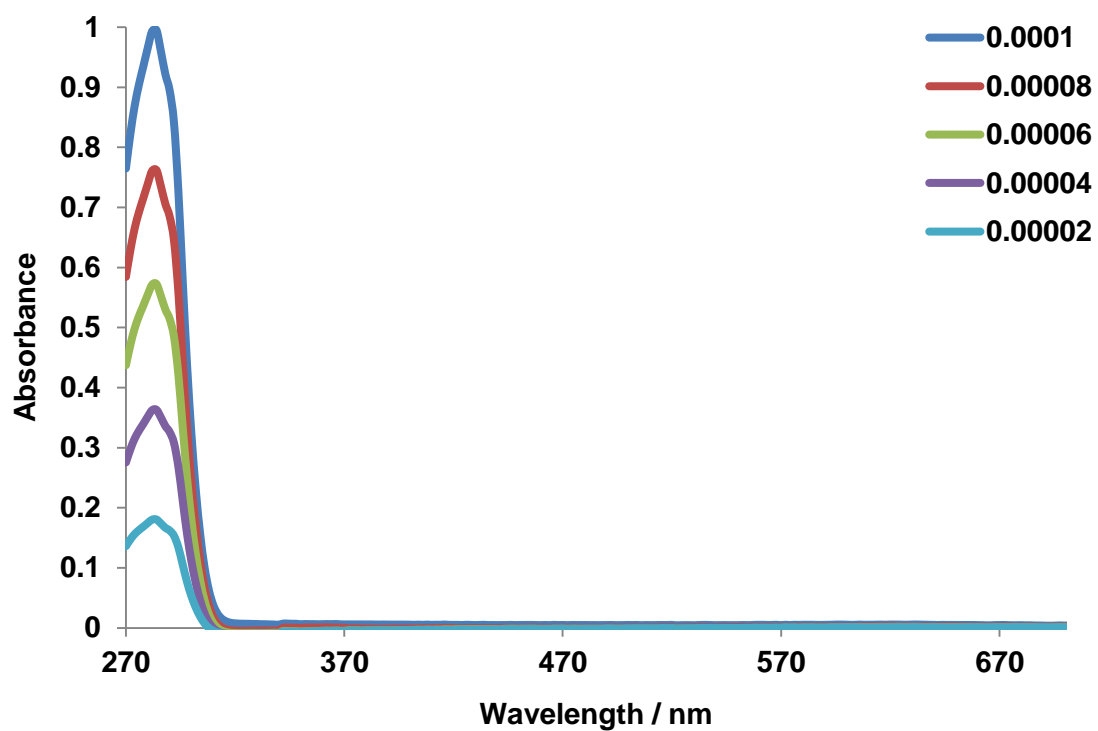


2. UV-Visible Spectroscopic Data

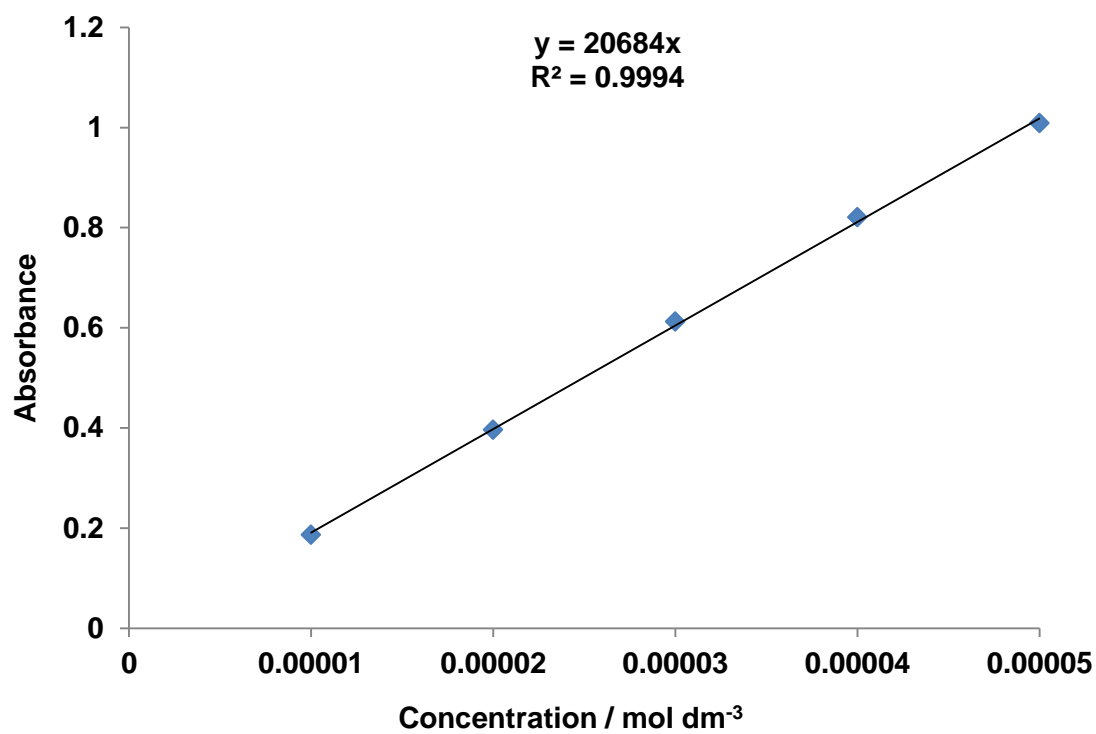
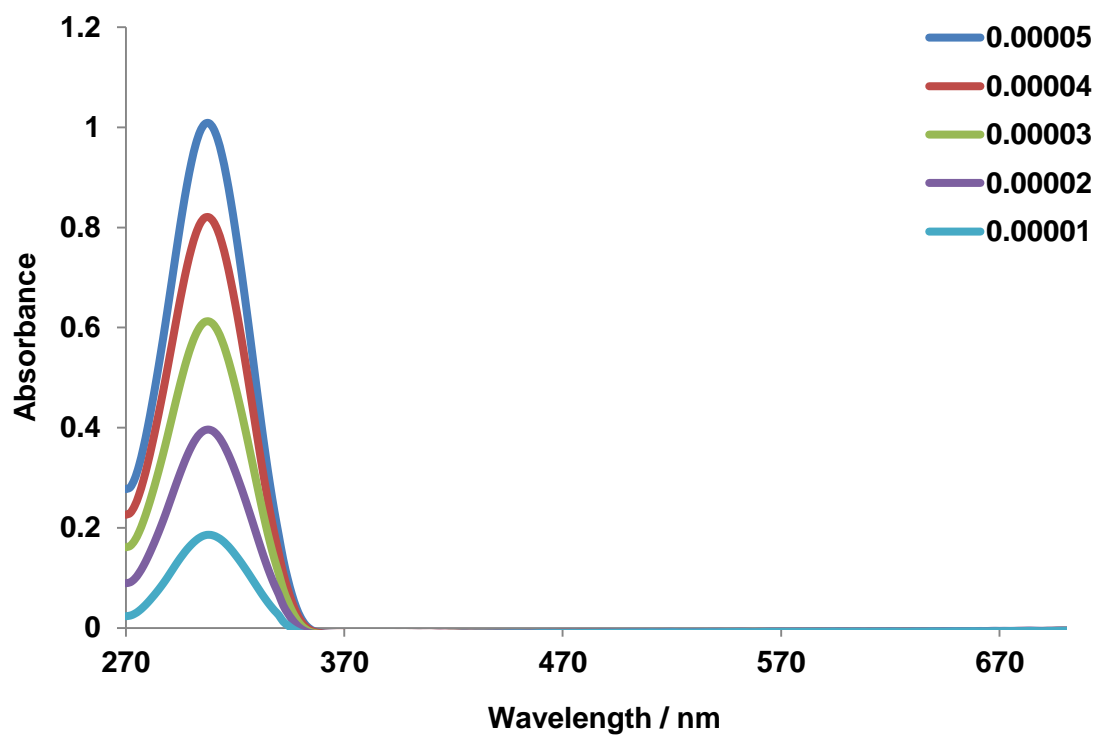
UV-visible spectroscopic analysis of **12b** (concentration range in legend, mol dm⁻³)



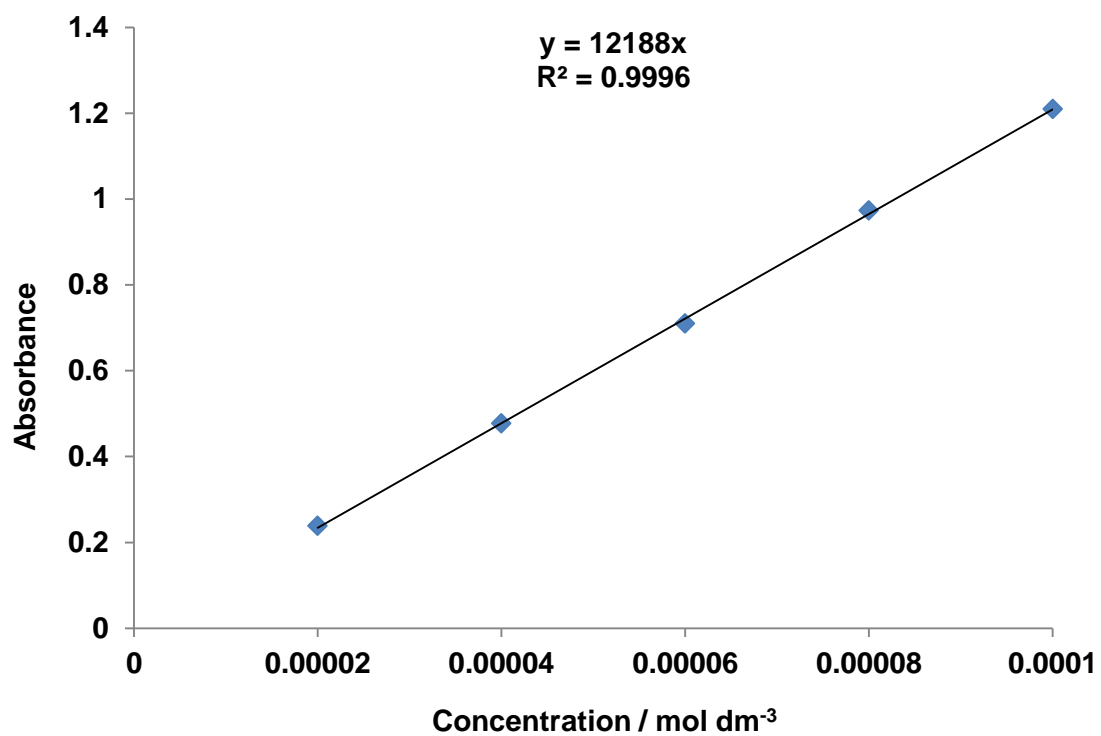
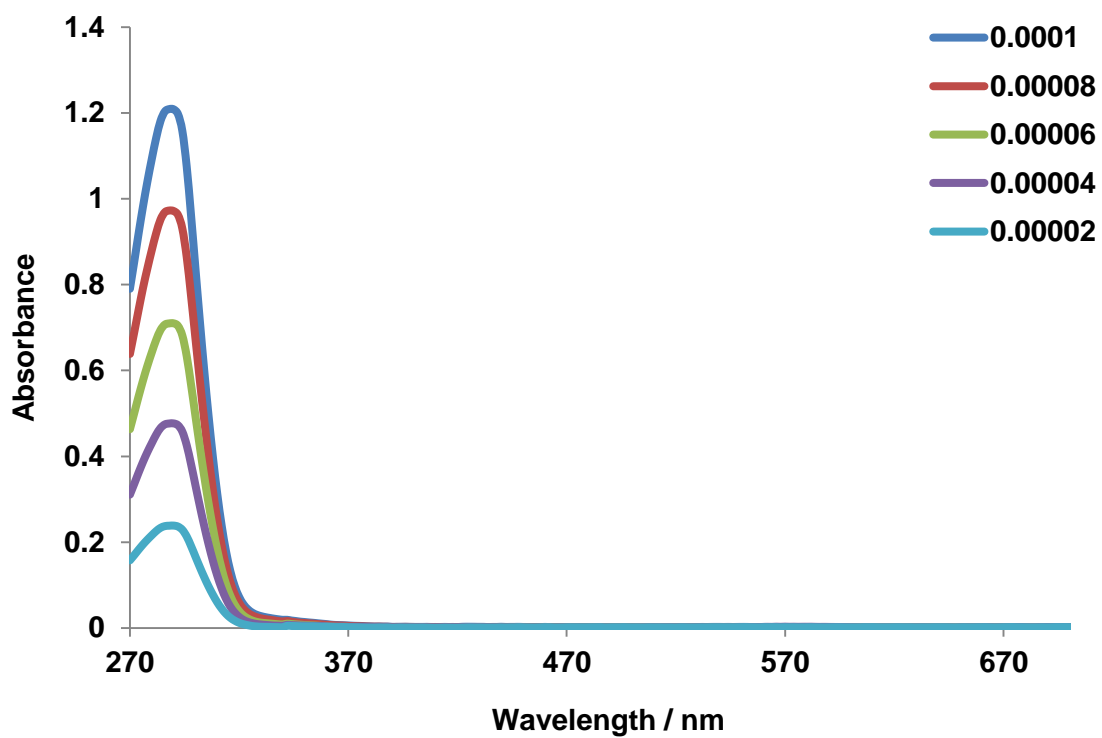
UV-visible spectroscopic analysis of **13** (concentration range in legend, mol dm⁻³)



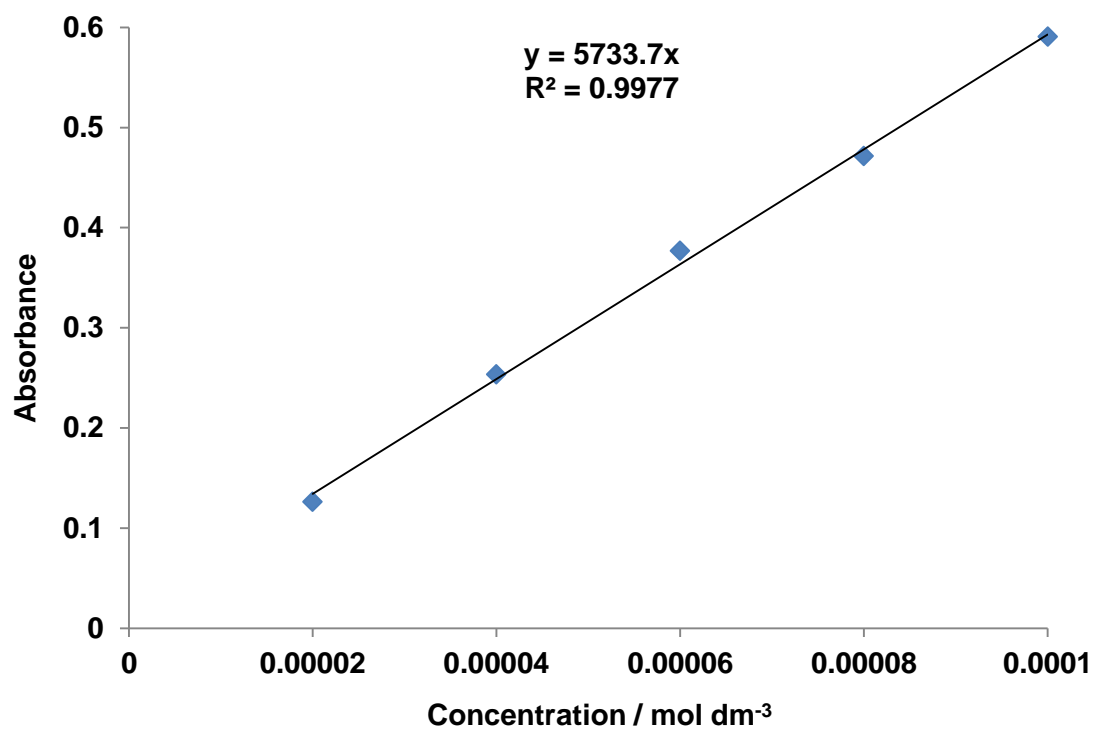
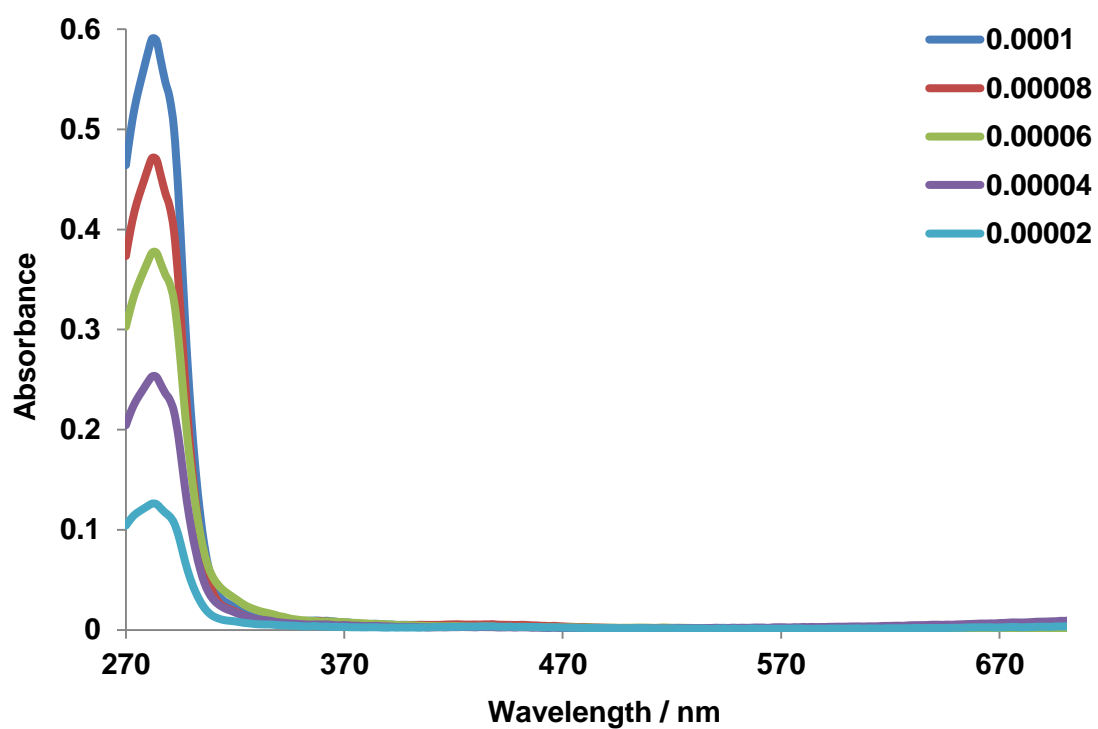
UV-visible spectroscopic analysis of **14a** (concentration range in legend, mol dm⁻³)



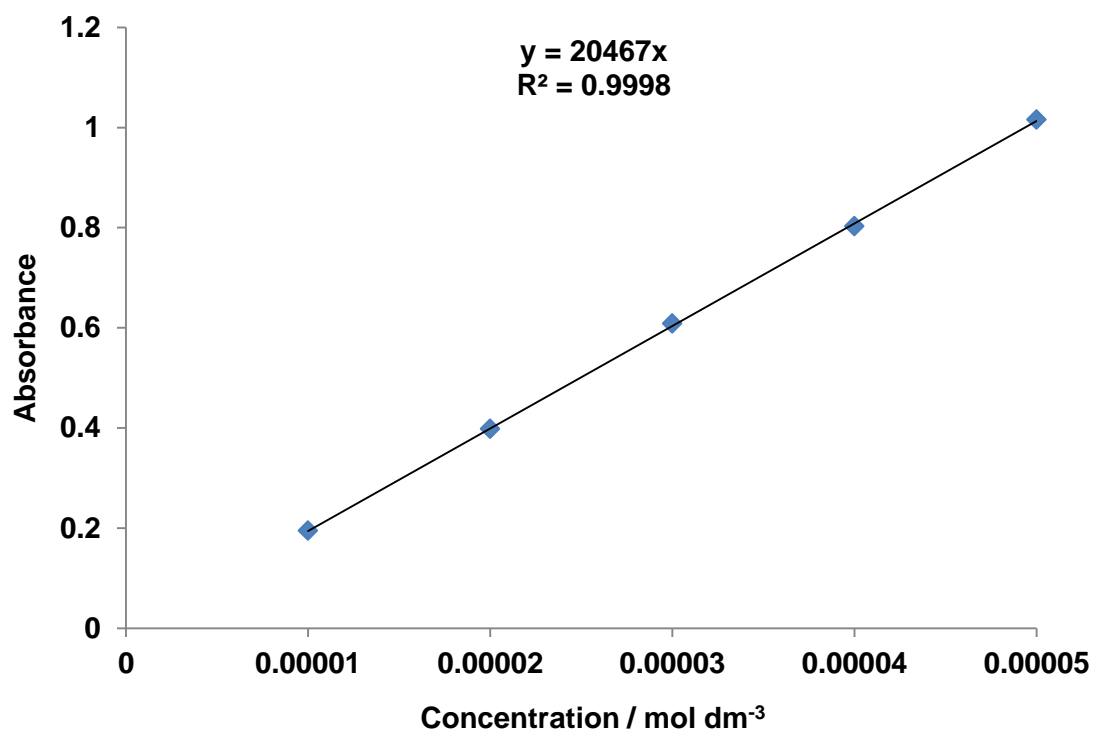
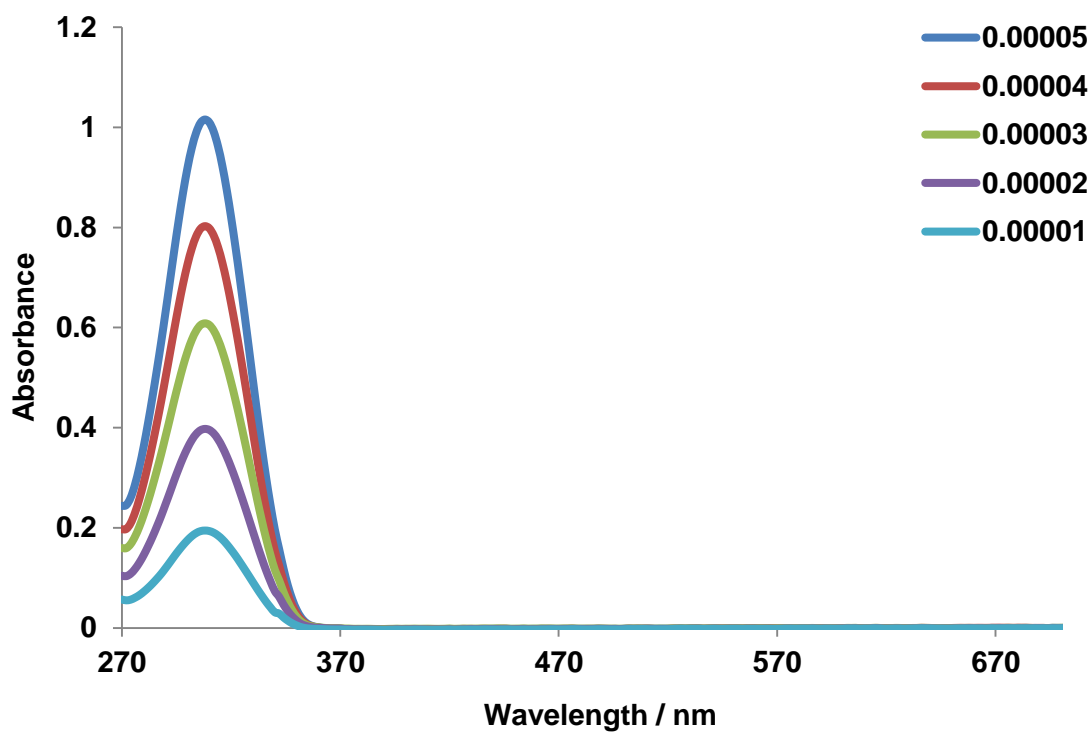
UV-visible spectroscopic analysis of **14b** (concentration range in legend, mol dm⁻³)



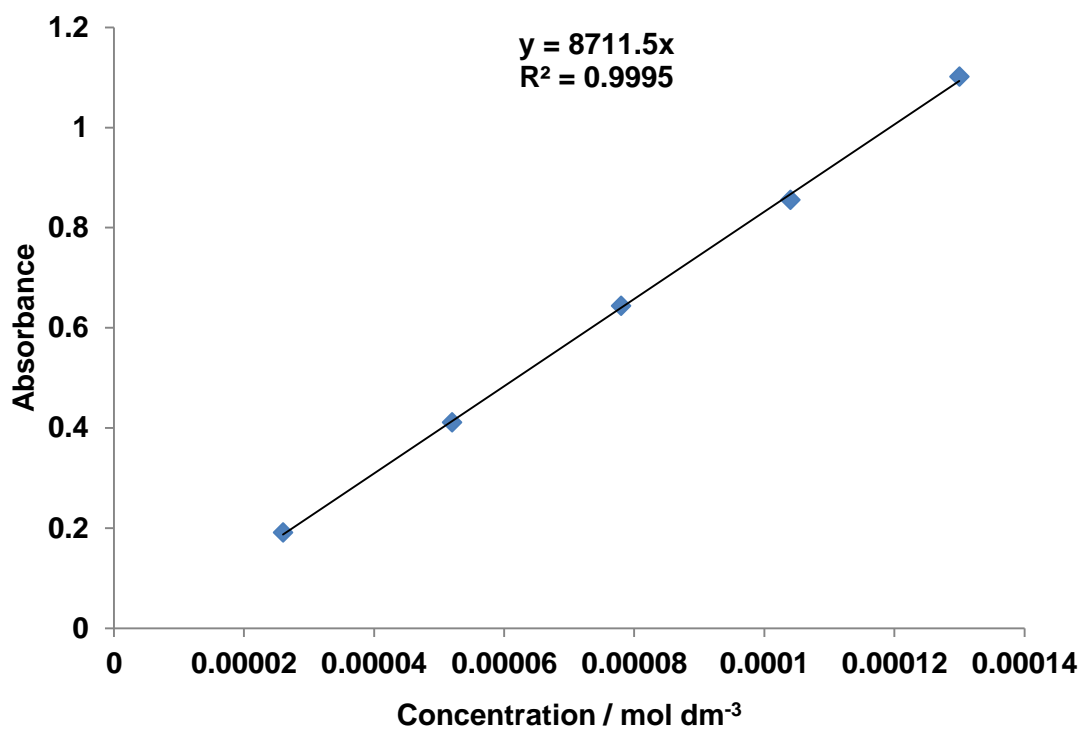
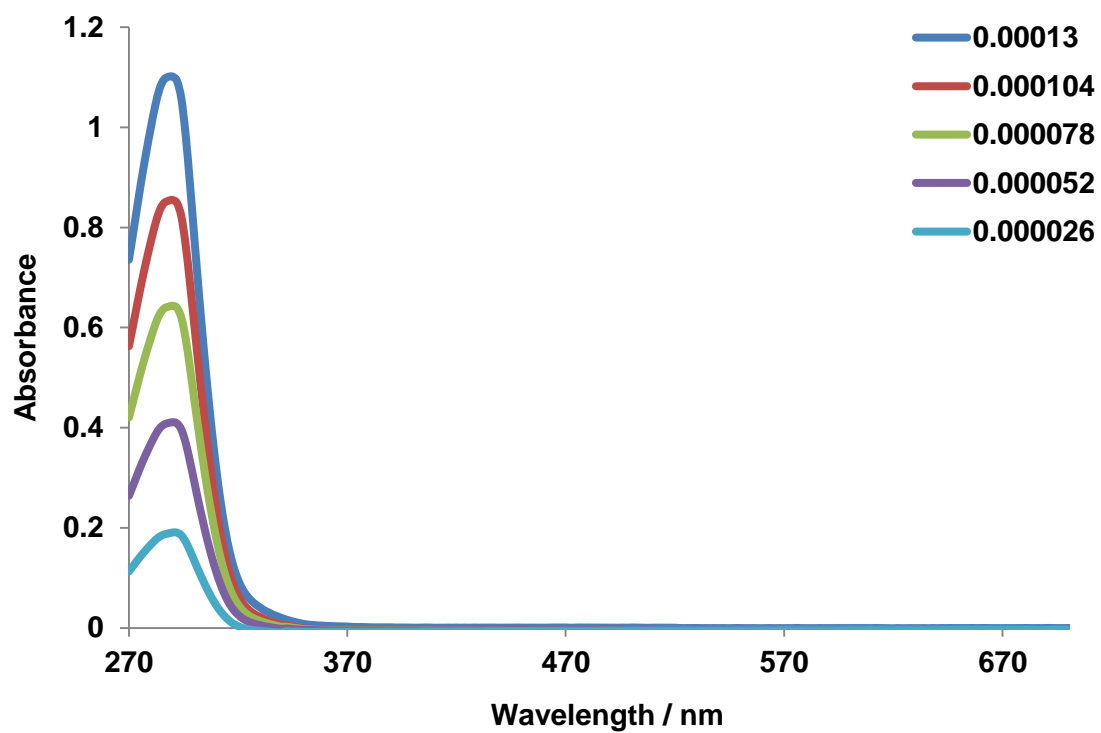
UV-visible spectroscopic analysis of **15** (concentration range in legend, mol dm⁻³)



UV-visible spectroscopic analysis of **16a** (concentration range in legend, mol dm⁻³)



UV-visible spectroscopic analysis of **16b** (concentration range in legend, mol dm⁻³)

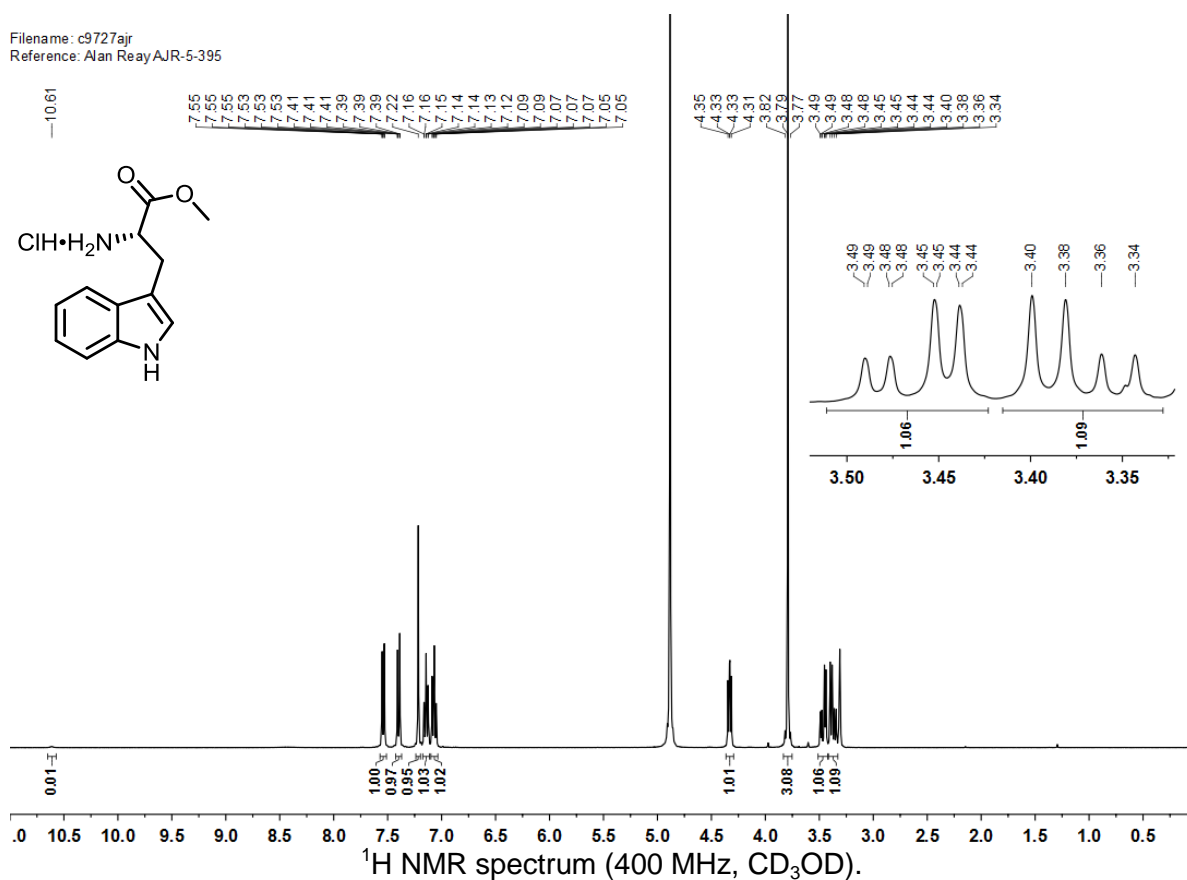


3. NMR spectroscopic data

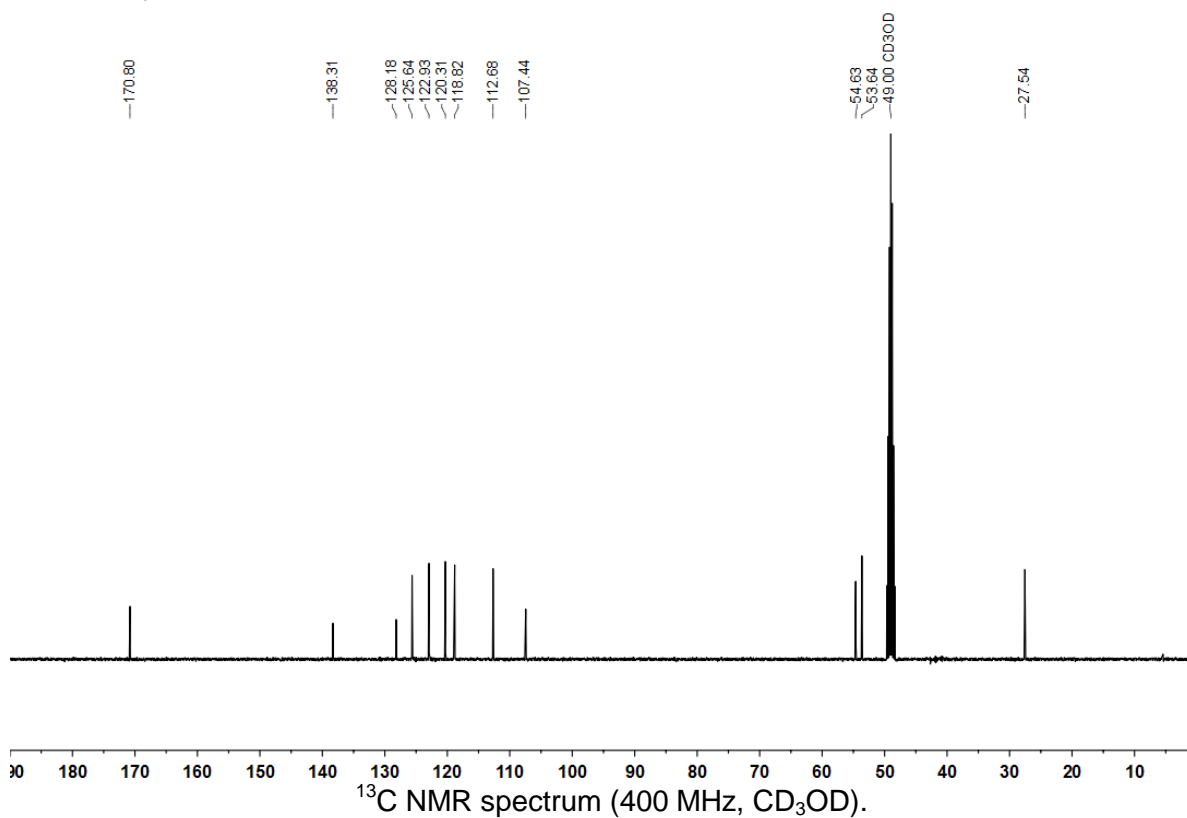
NMR spectra for compounds **2b**, **2e**, **3**, **4** and 2-Acetamidoacetic acid are given in our preliminary communication on this work.¹

Methyl (2S)-2-amino-3-(1H-indol-3-yl)propanoate hydrochloride

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Reference: Alan ReayAJR-5-395

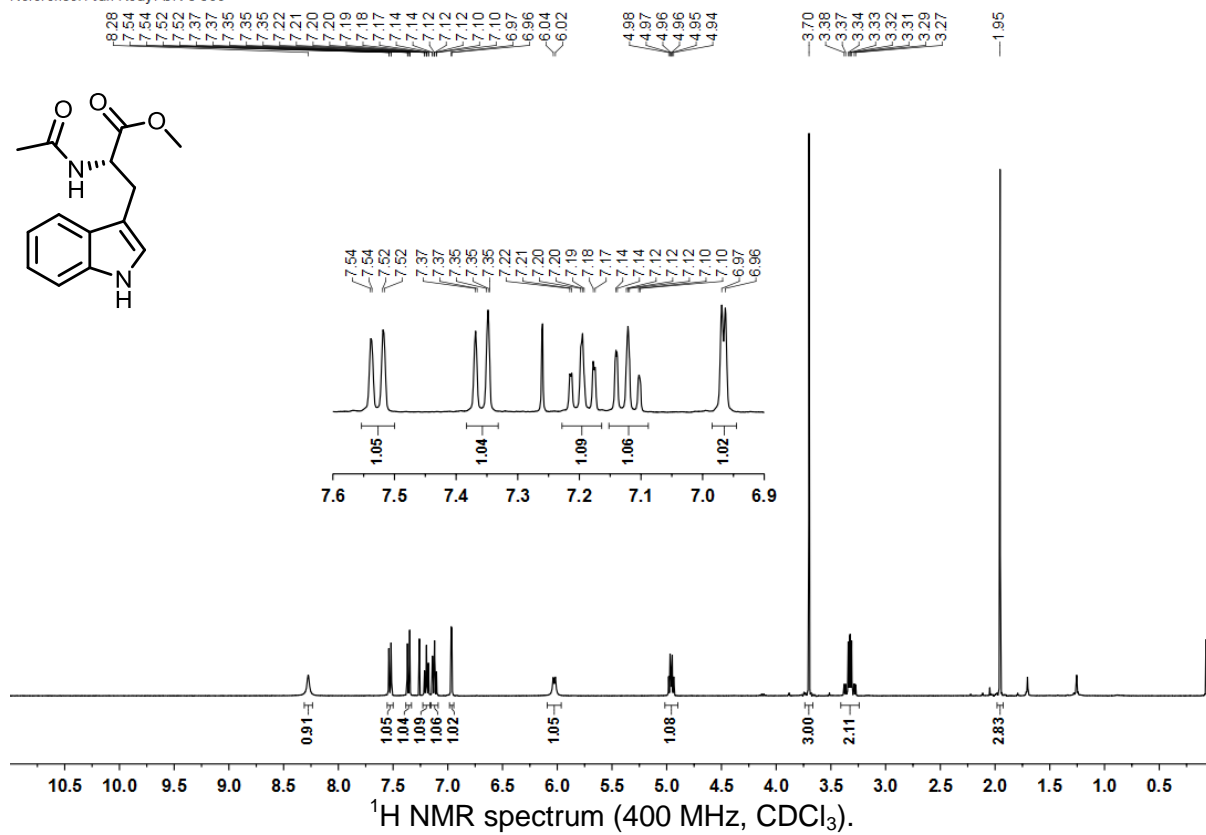


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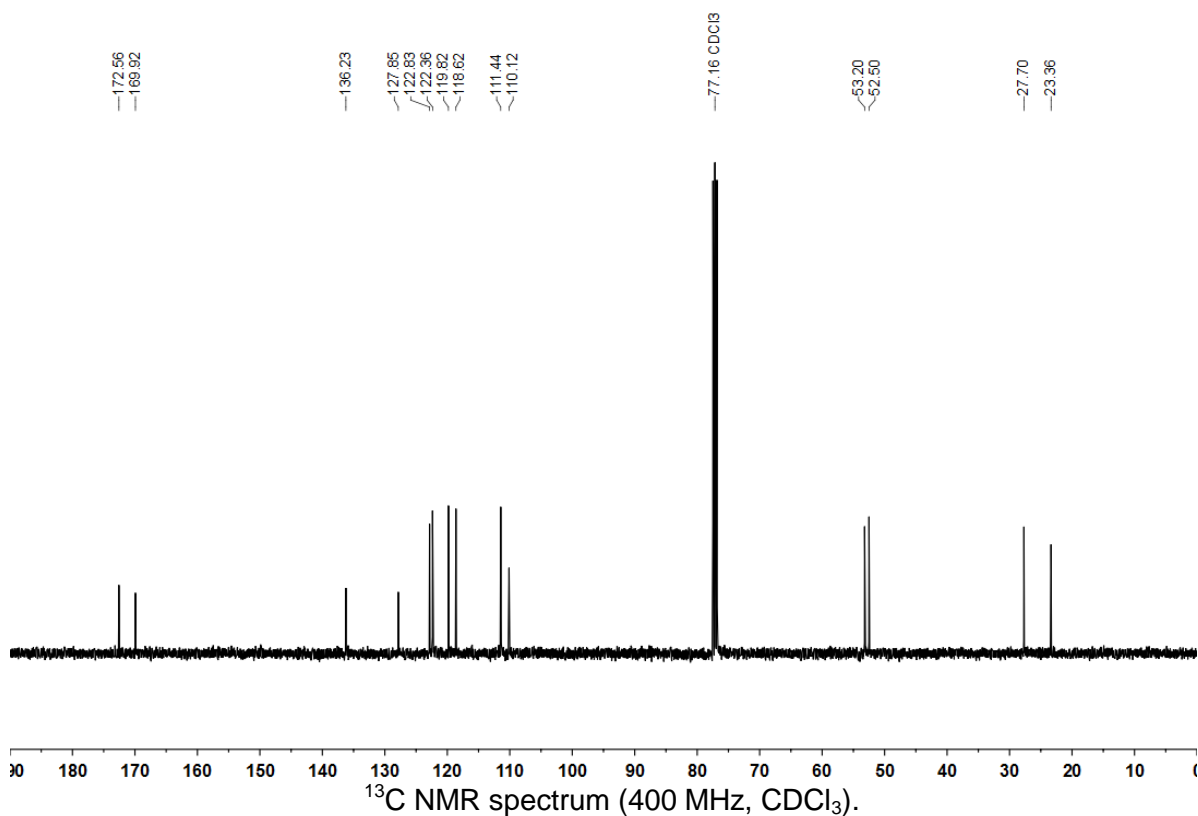


Methyl (2S)-2-acetamido-3-(1H-indol-3-yl)propanoate, **1a**

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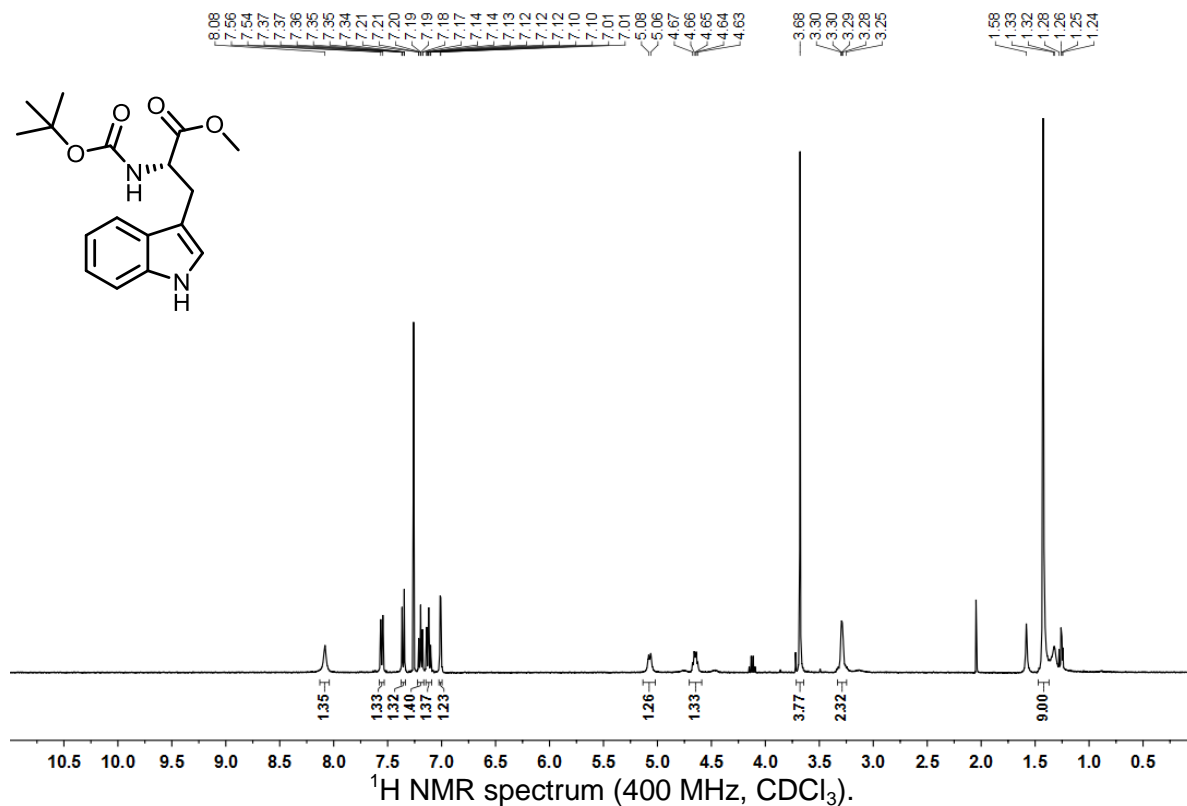


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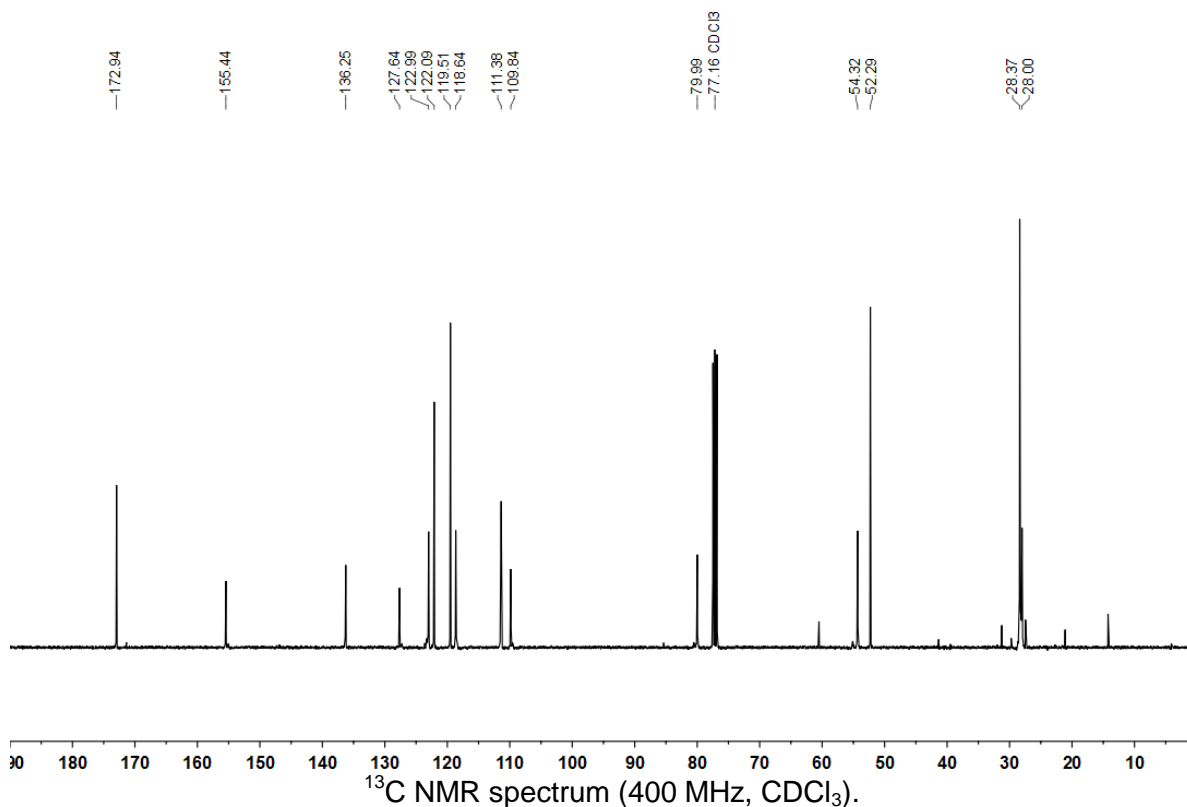


Methyl (2S)-2-[(*tert*-butoxy)carbonyl]amino}-3-(1*H*-indol-3-yl)propanoate, **1b**

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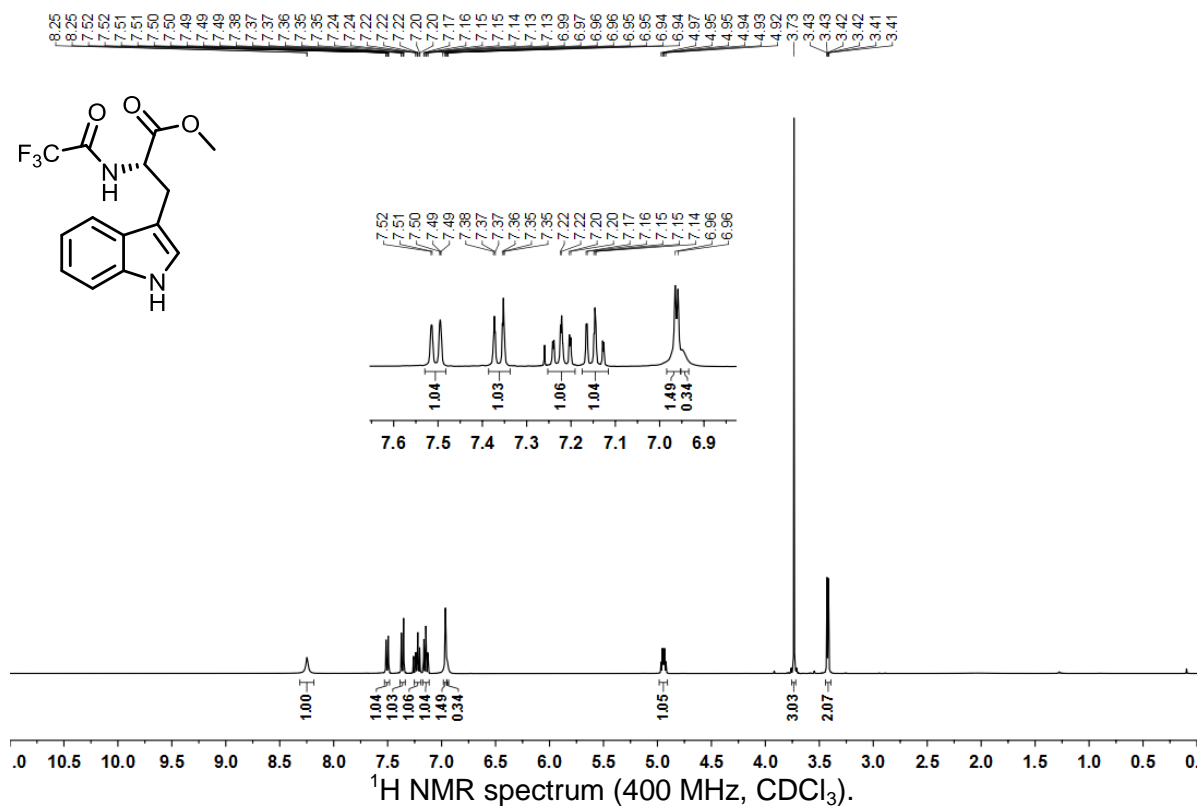


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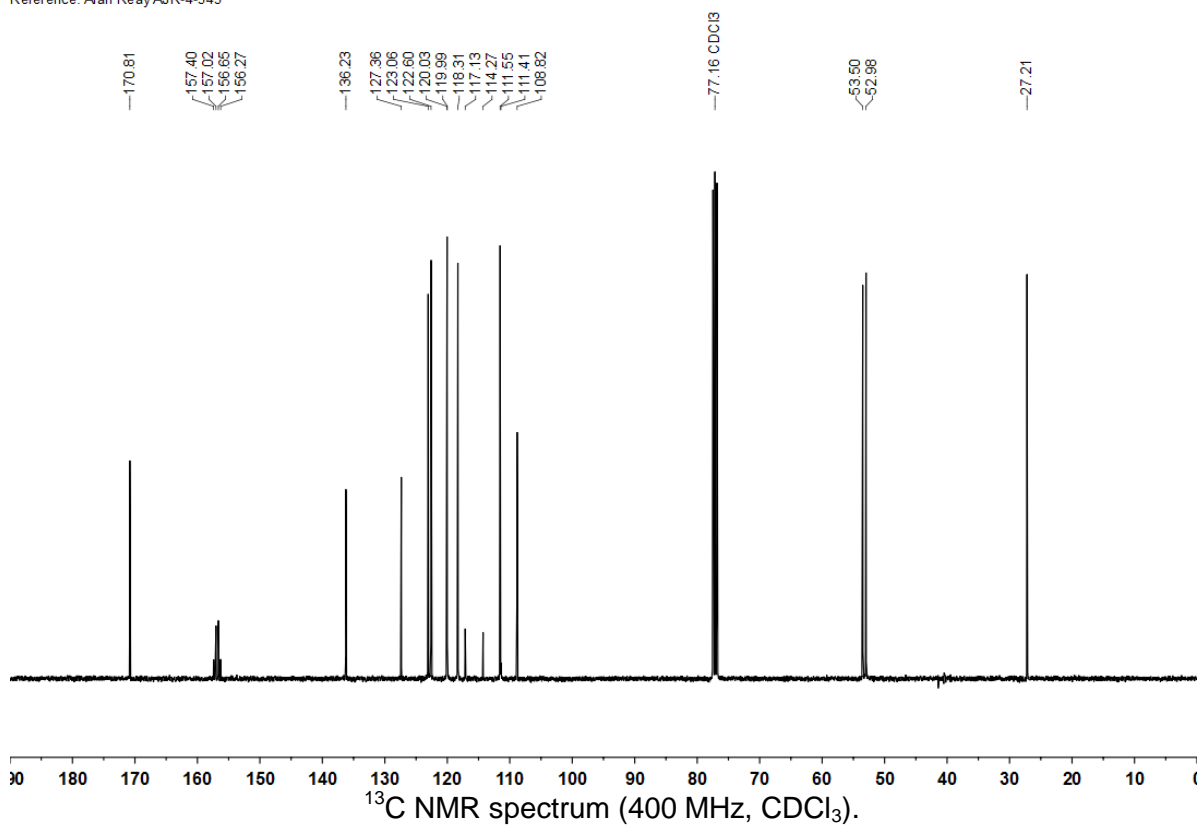


Methyl (2S)-3-(1H-indol-3-yl)-2-(trifluoroacetamido)propanoate, **1c**

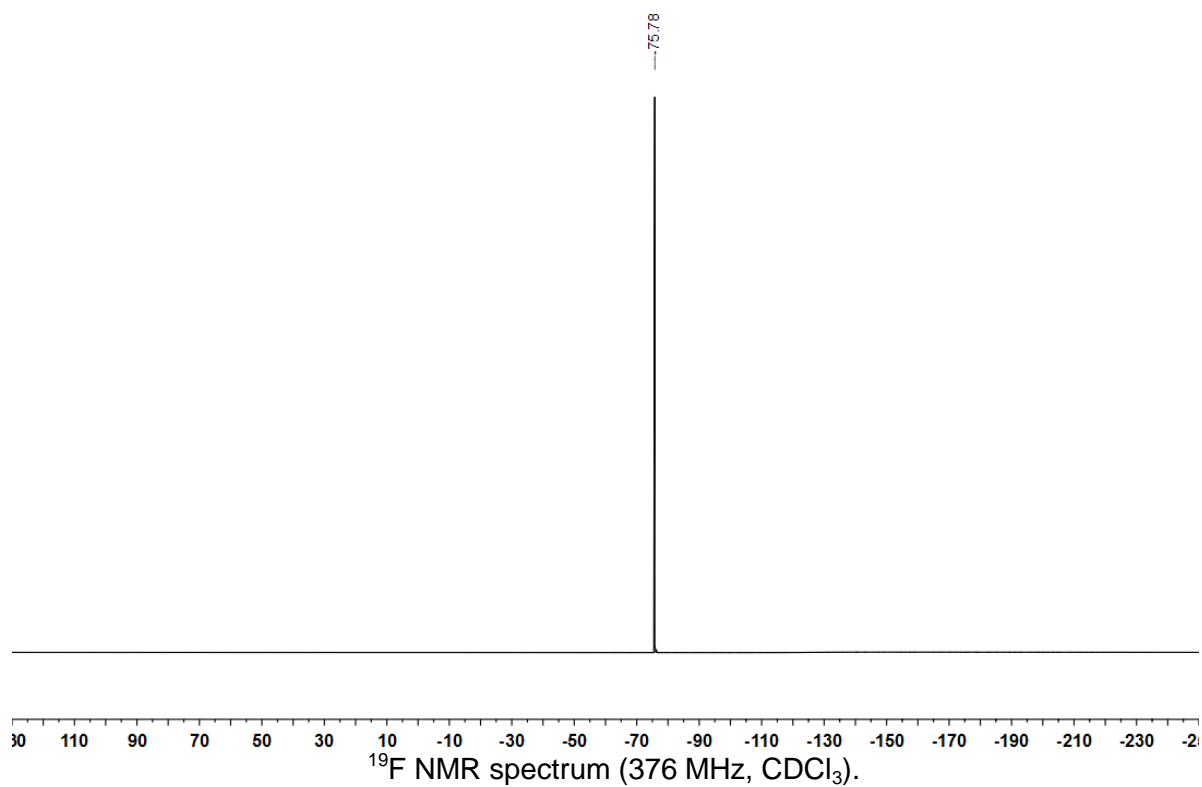
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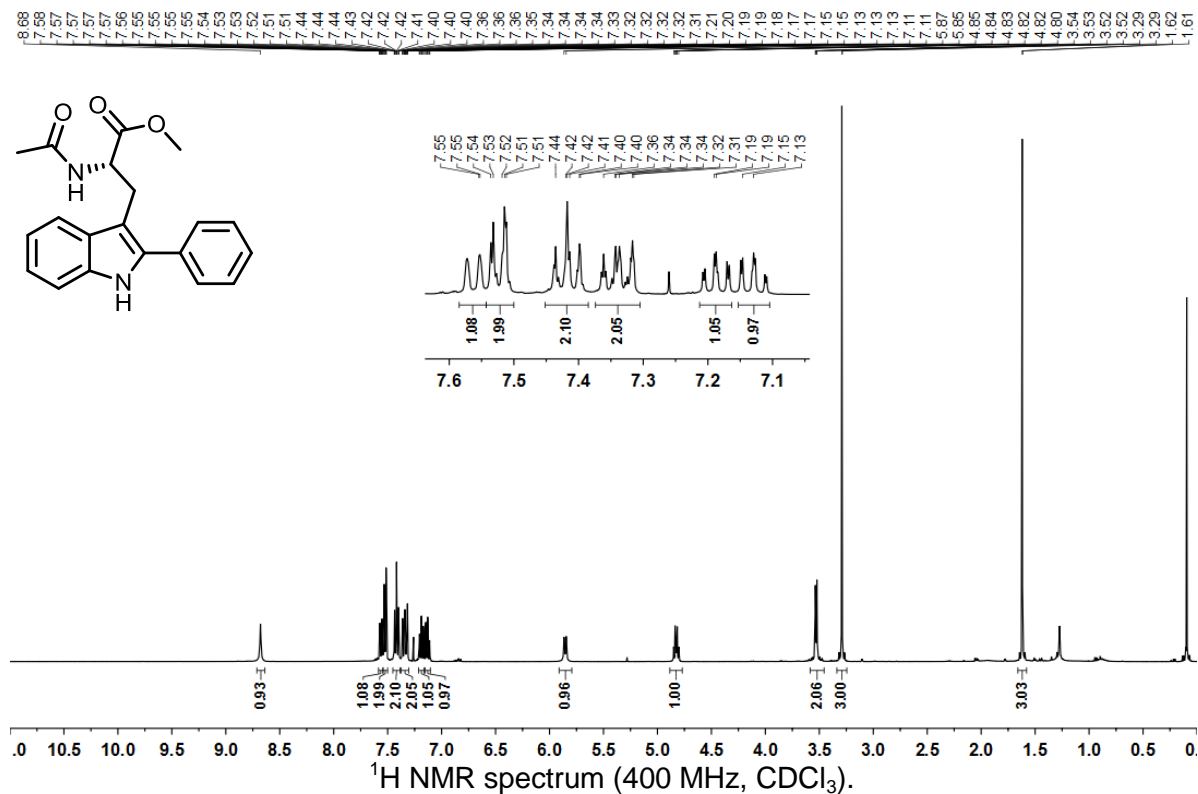


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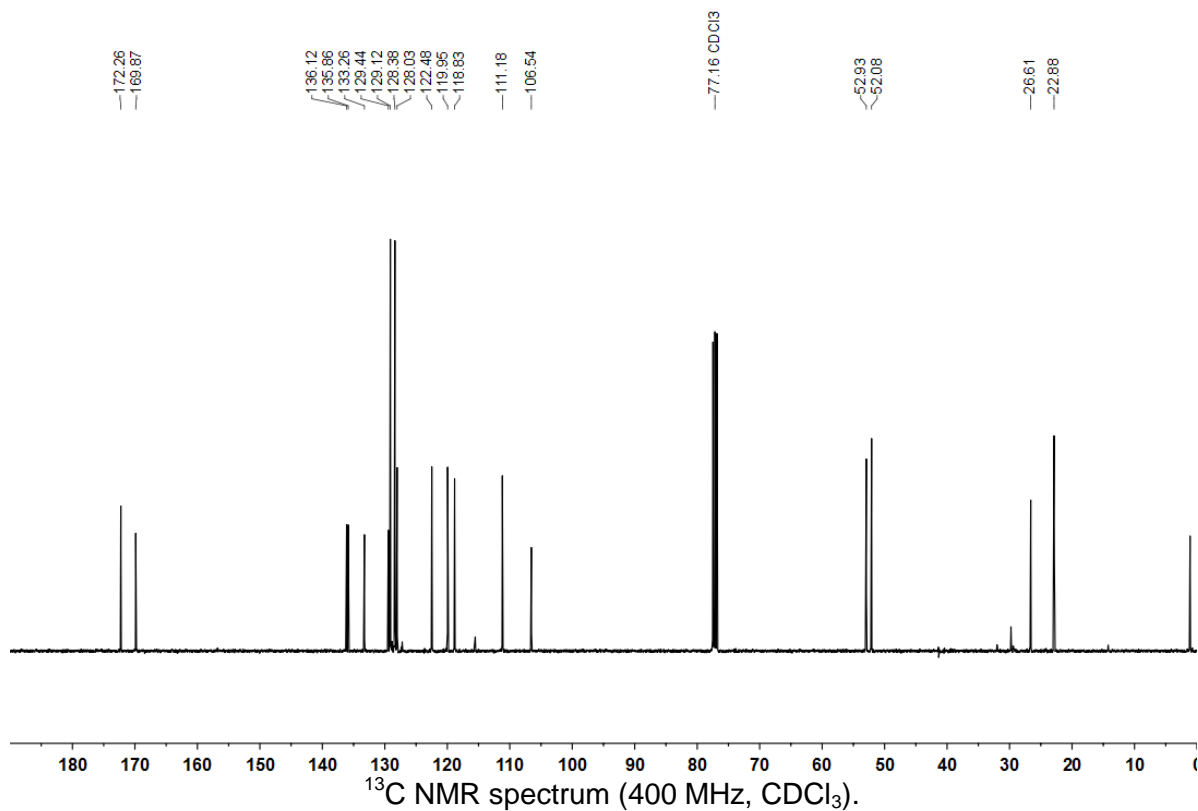


Methyl (2S)-2-acetamido-3-(2-phenyl-1H-indol-3-yl)propanoate, **2a**

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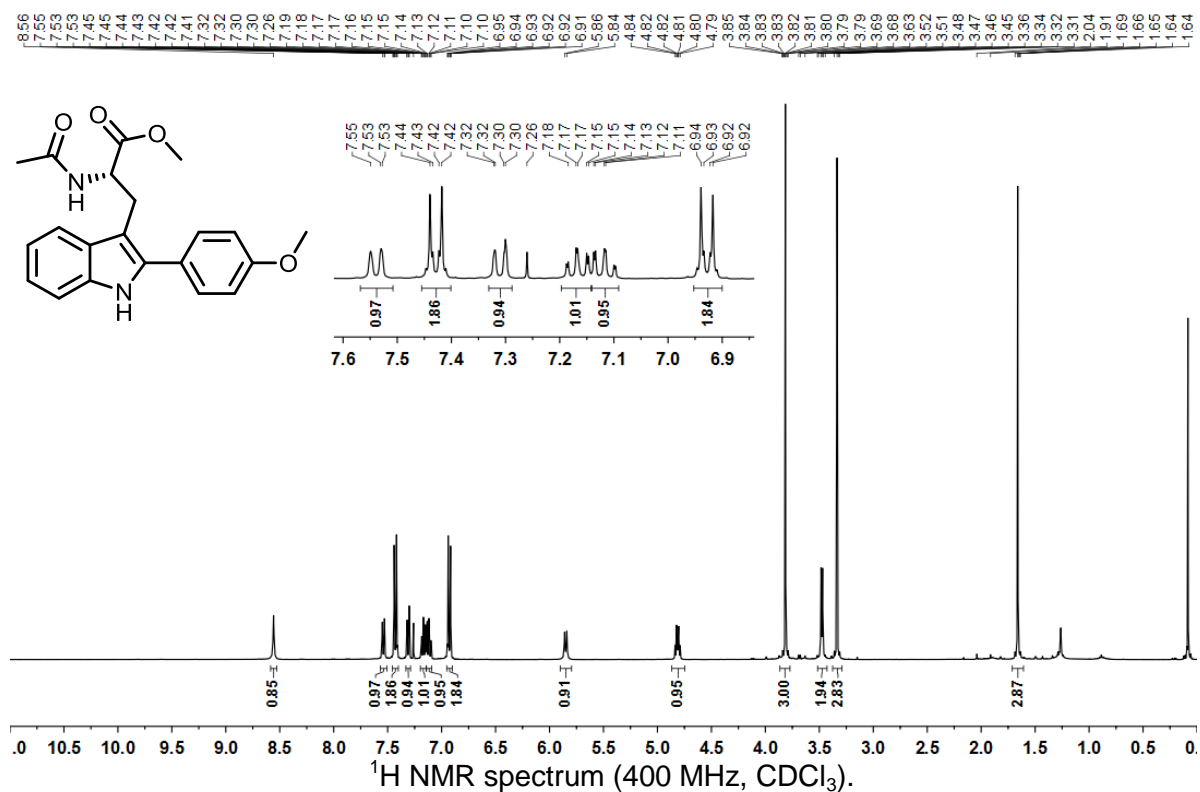


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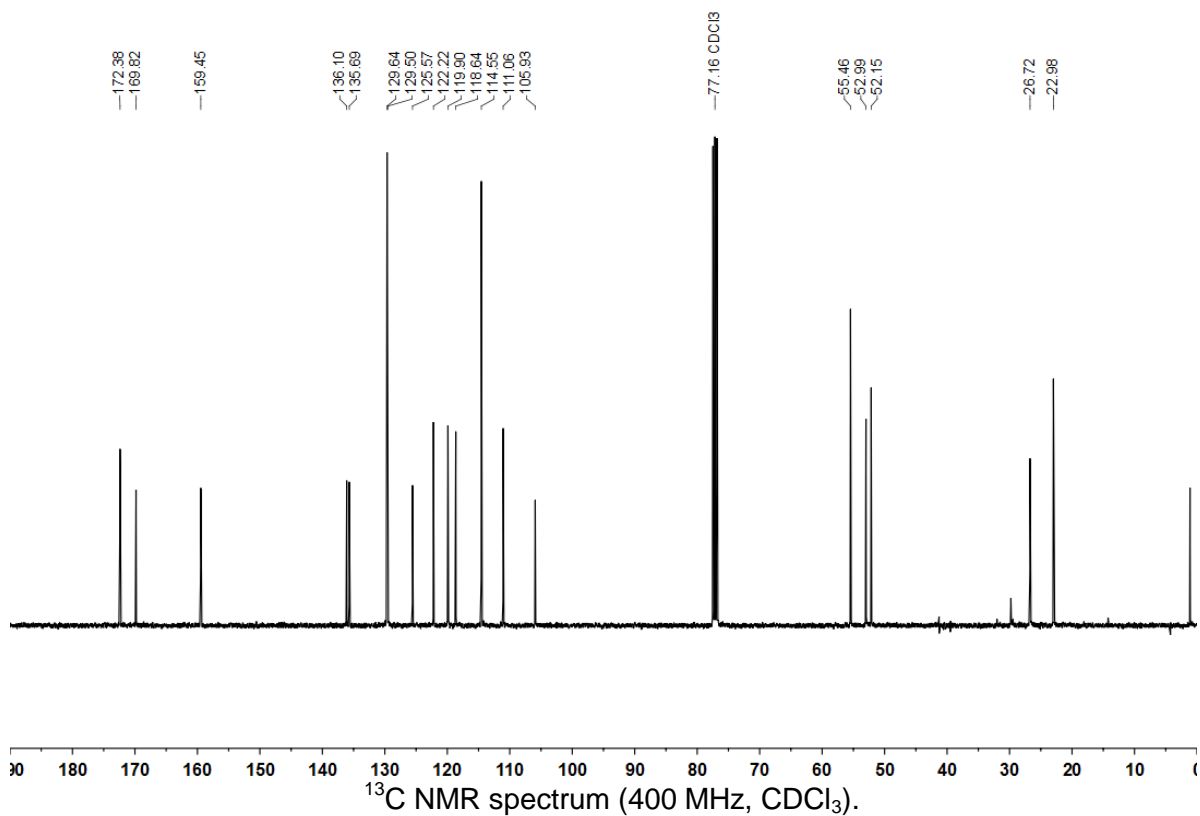


Methyl (2S)-2-acetamido-3-[2-(4-methoxyphenyl)-1H-indol-3-yl]propanoate, **2c**

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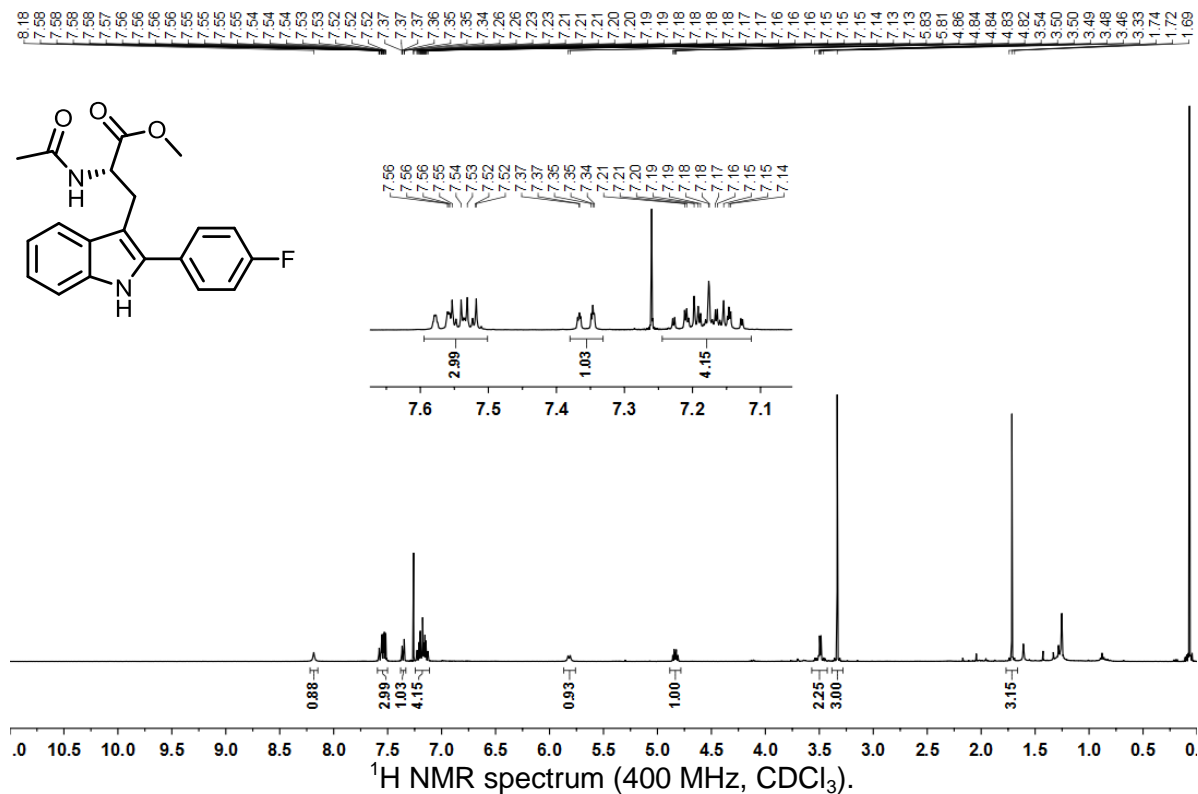


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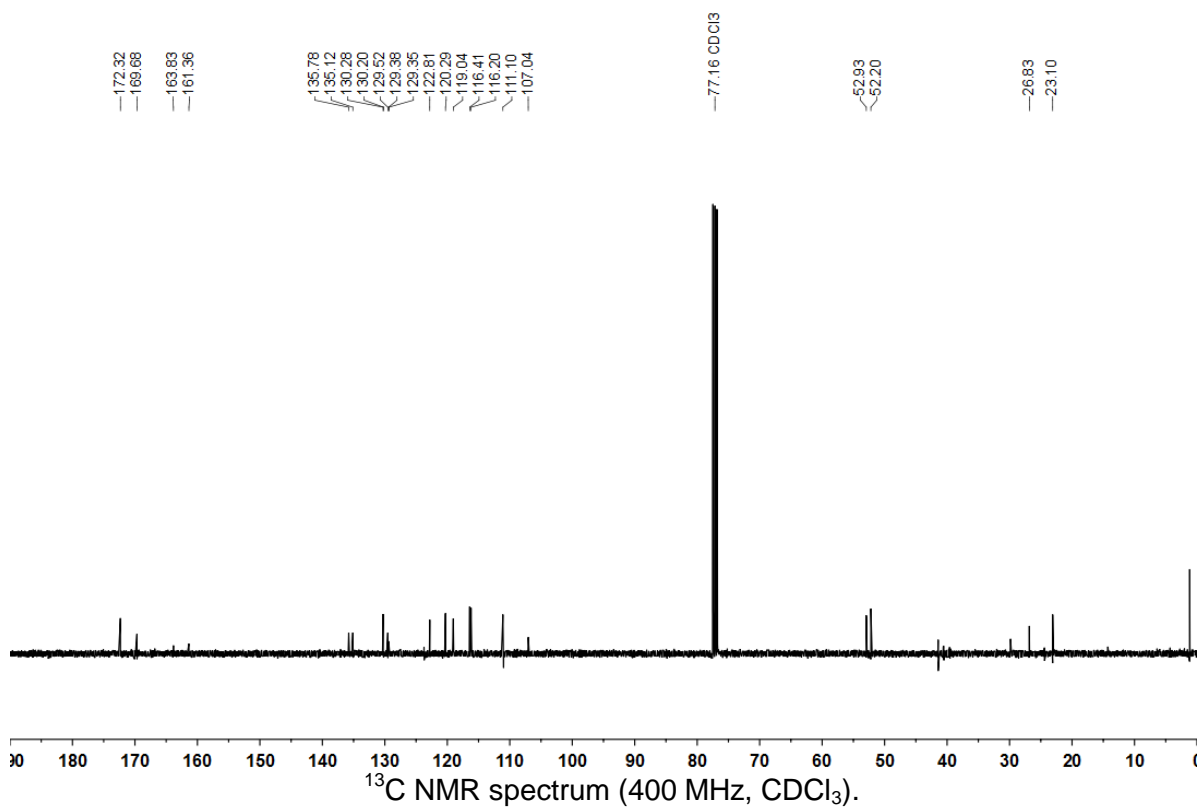


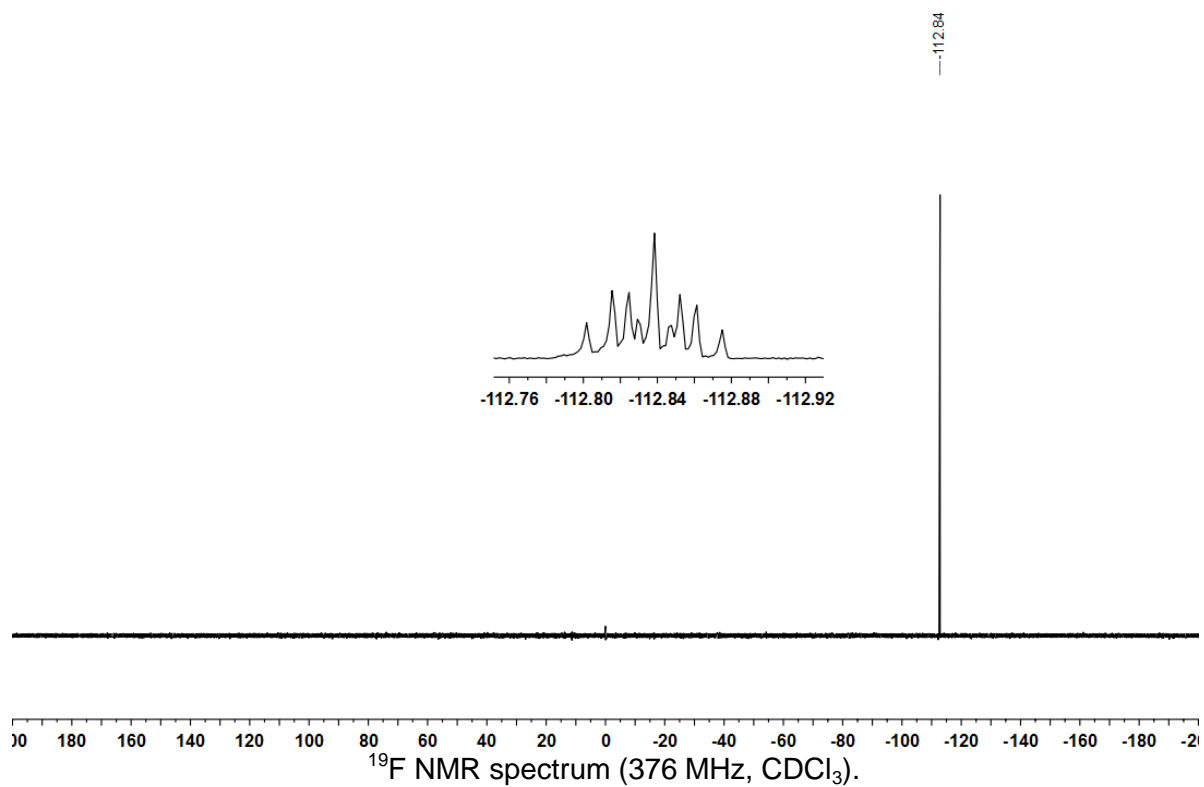
Methyl (2S)-3-[2-(4-fluorophenyl)-1H-indol-3-yl]-2-acetamidopropanoate, **2d**

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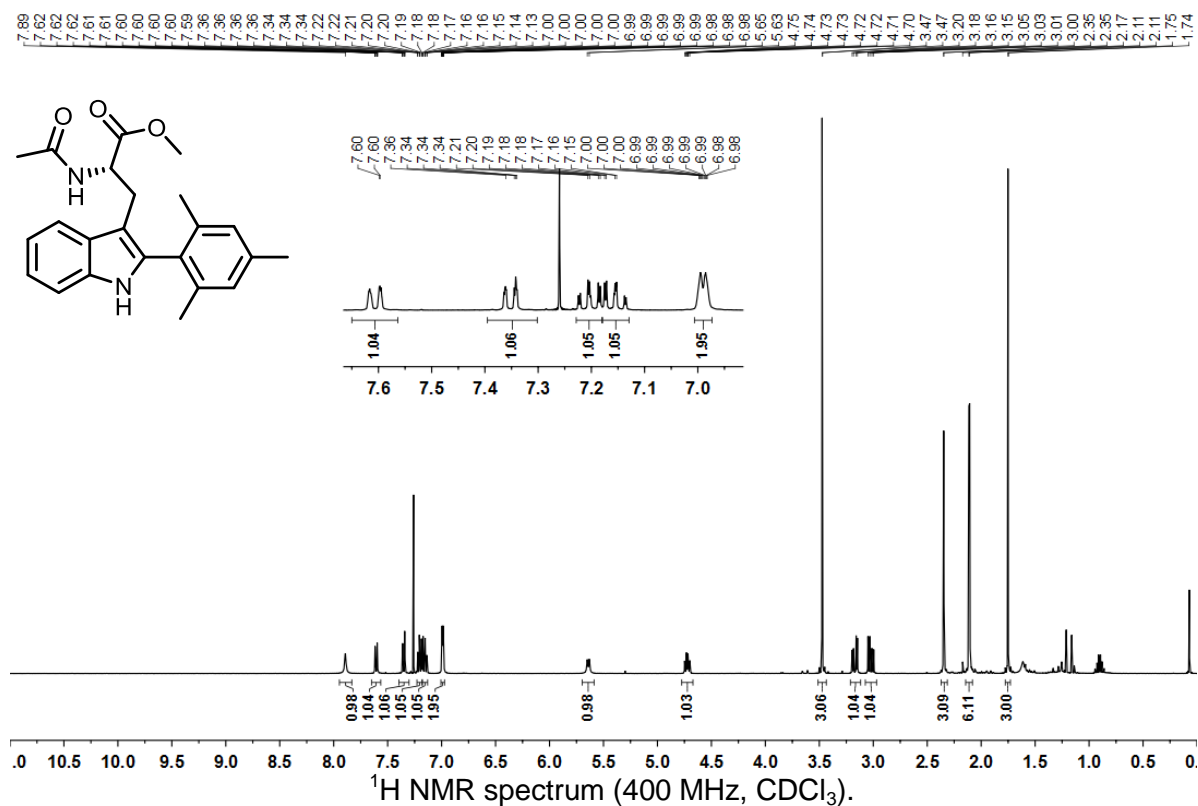
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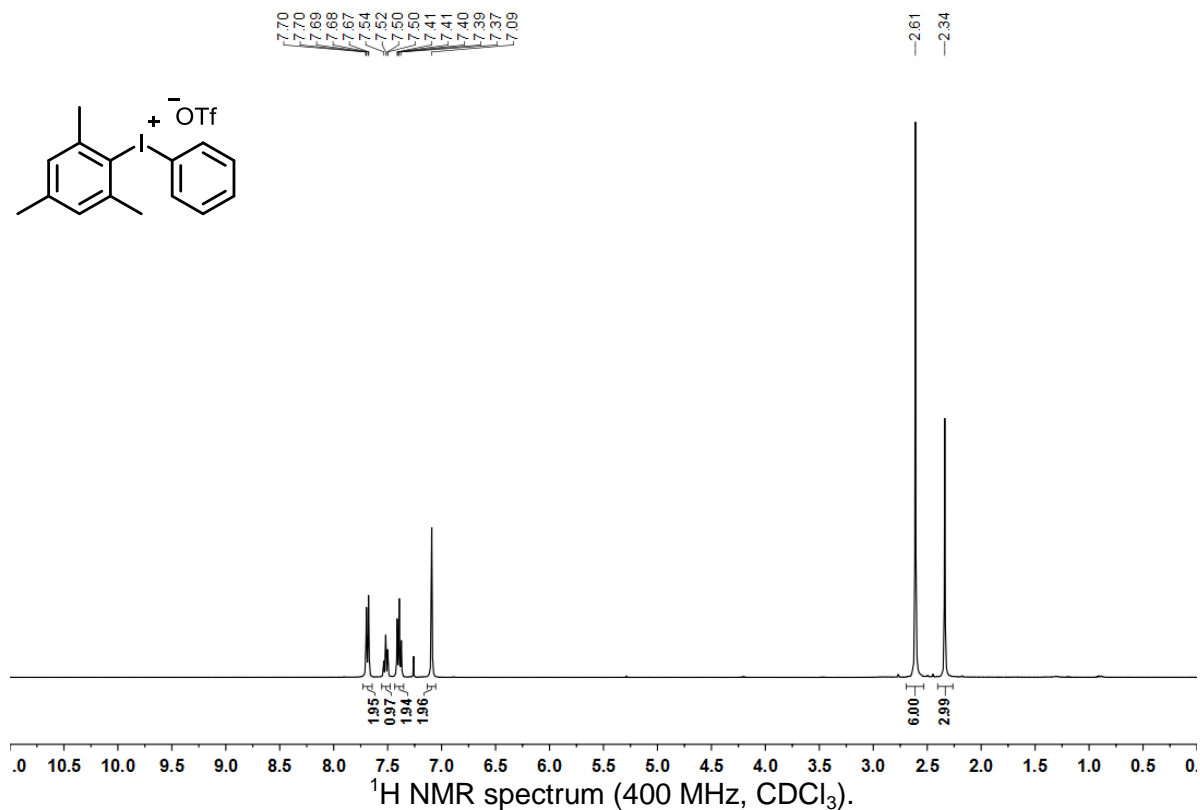
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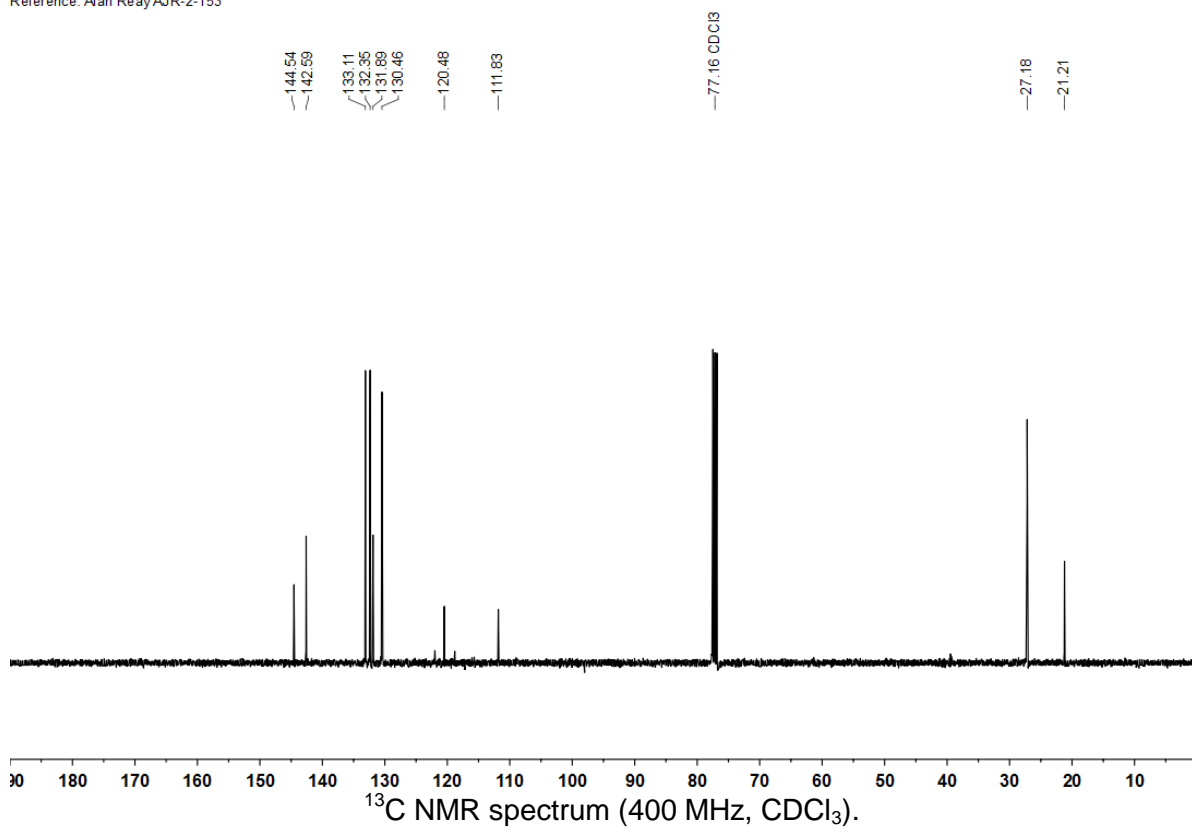


Phenyl(2,4,6-trimethylphenyl)iodonium trifluoromethanesulfonate, **11a**

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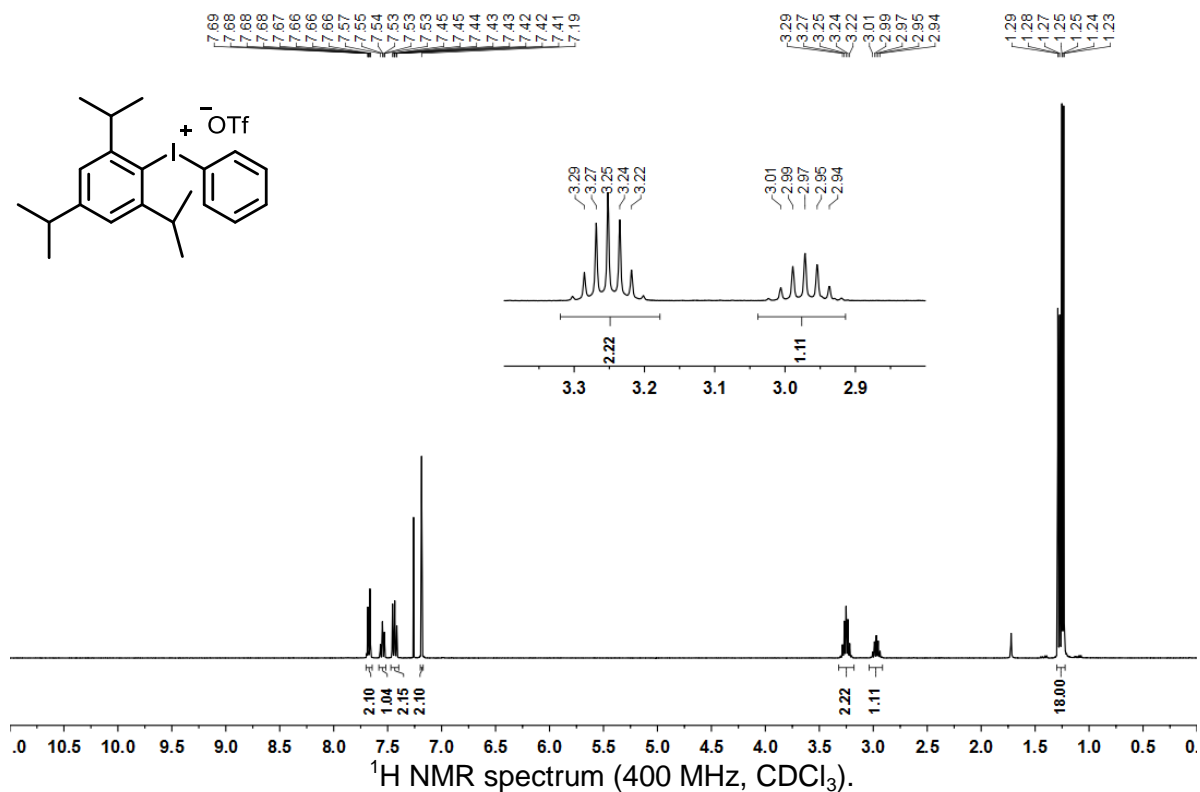


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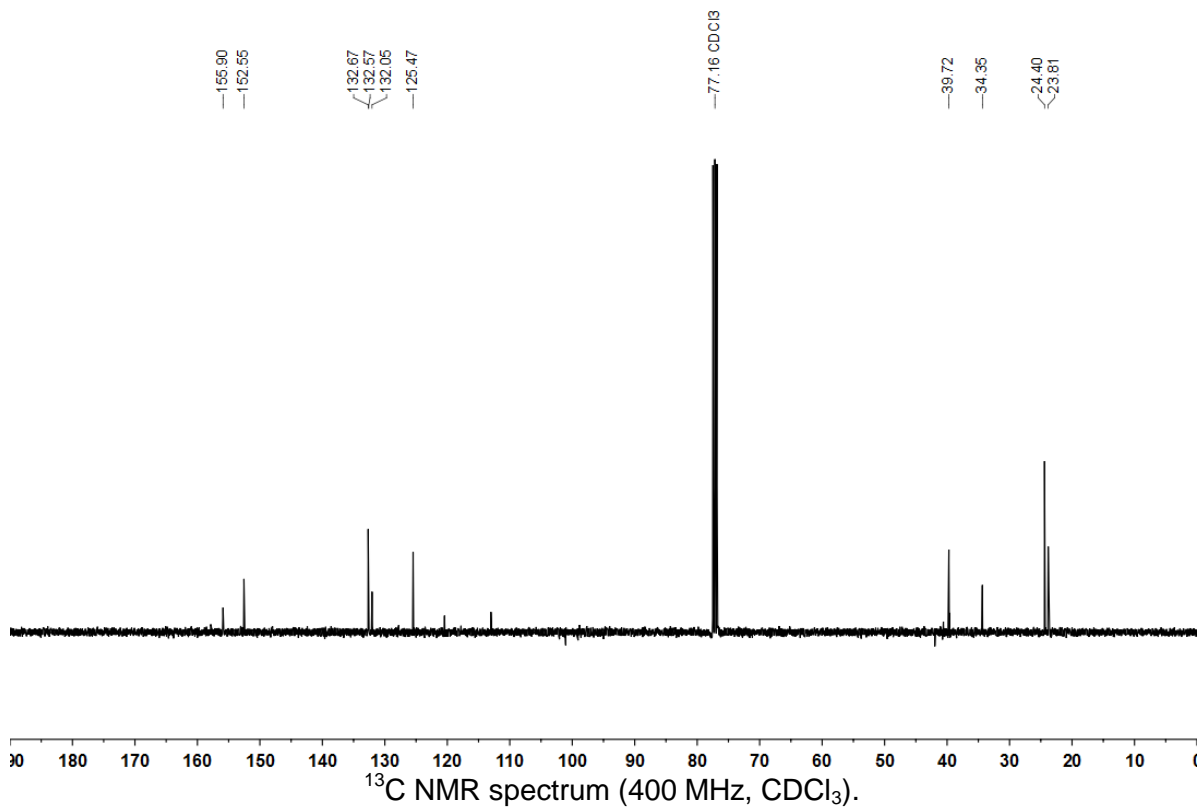


Phenyl(2,4,6-triisopropylphenyl)iodonium trifluoromethanesulfonate, **11b**

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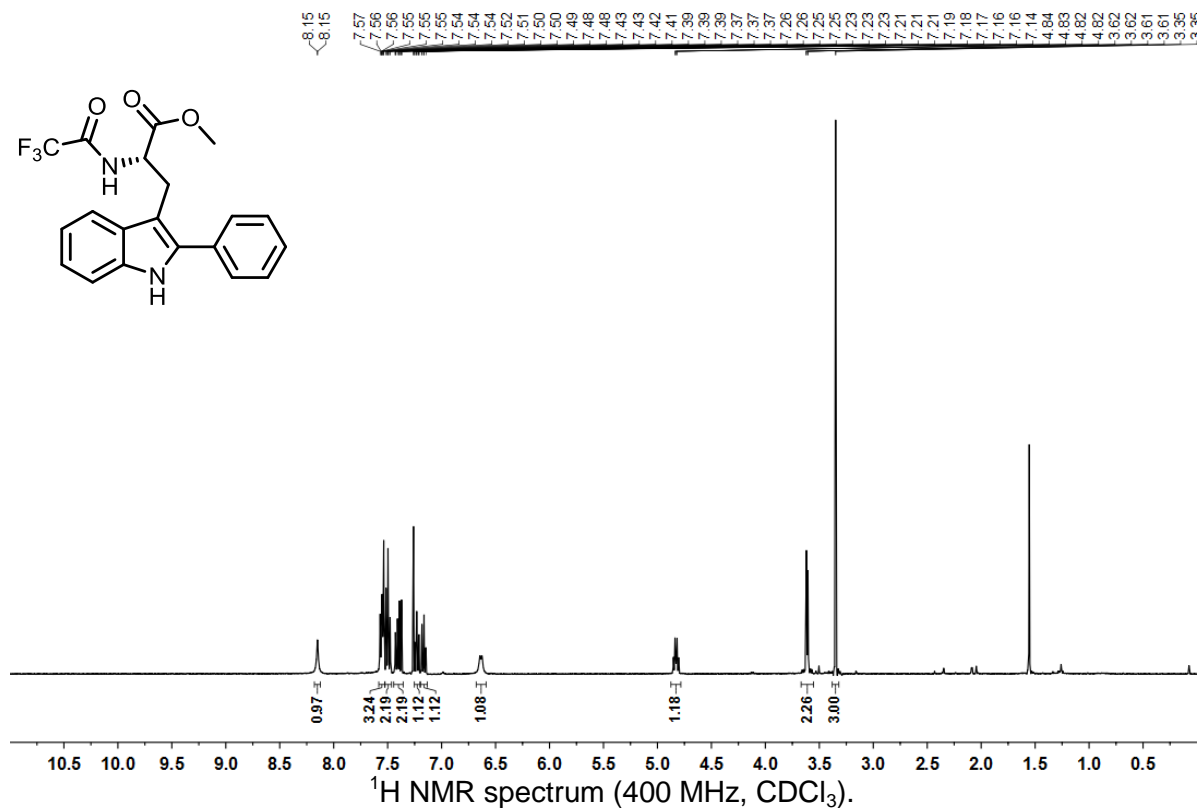


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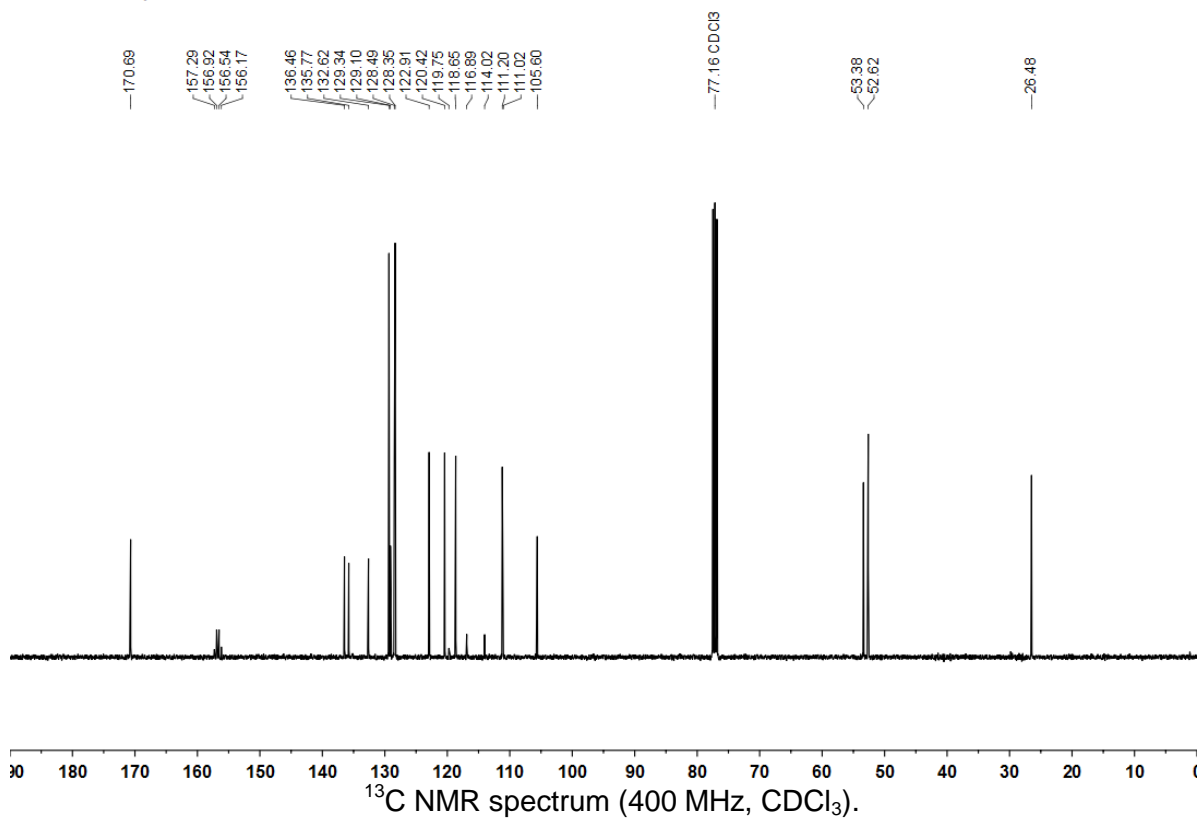


Methyl (2S)-3-(2-phenyl-1H-indol-3-yl)-2-(trifluoroacetamido)propanoate, **12a**

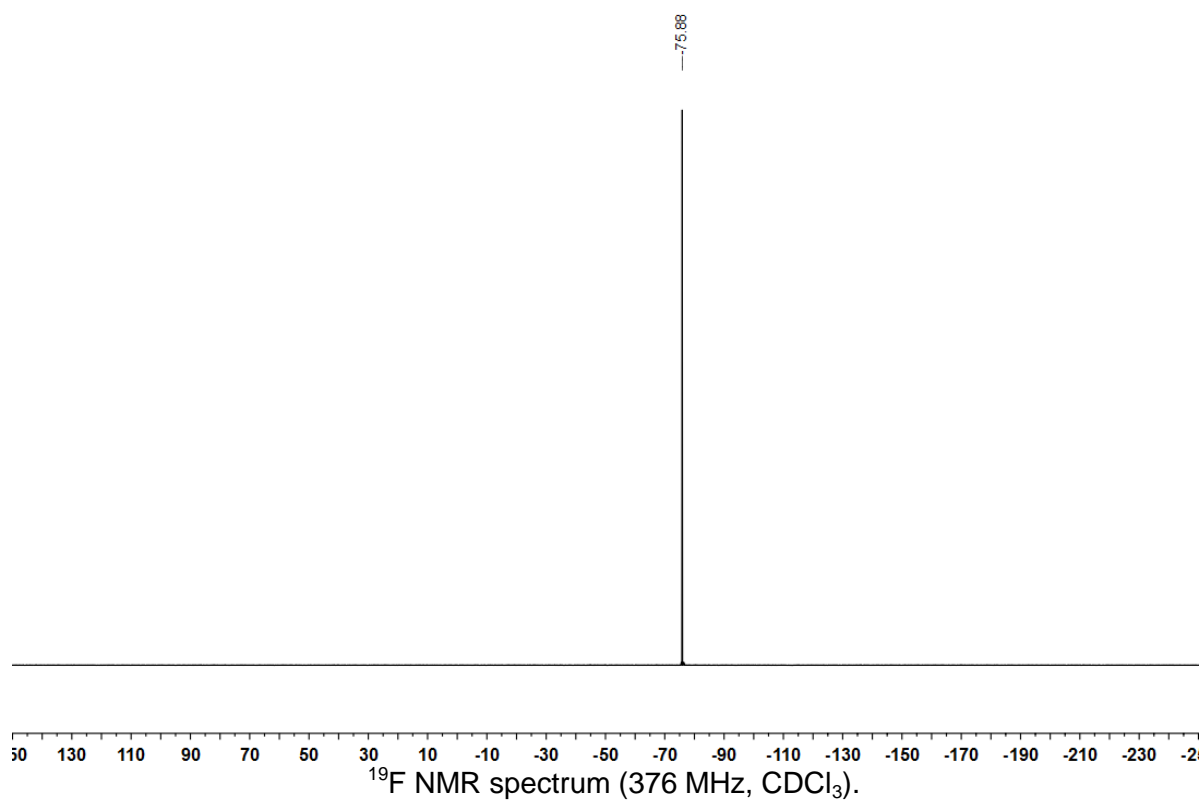
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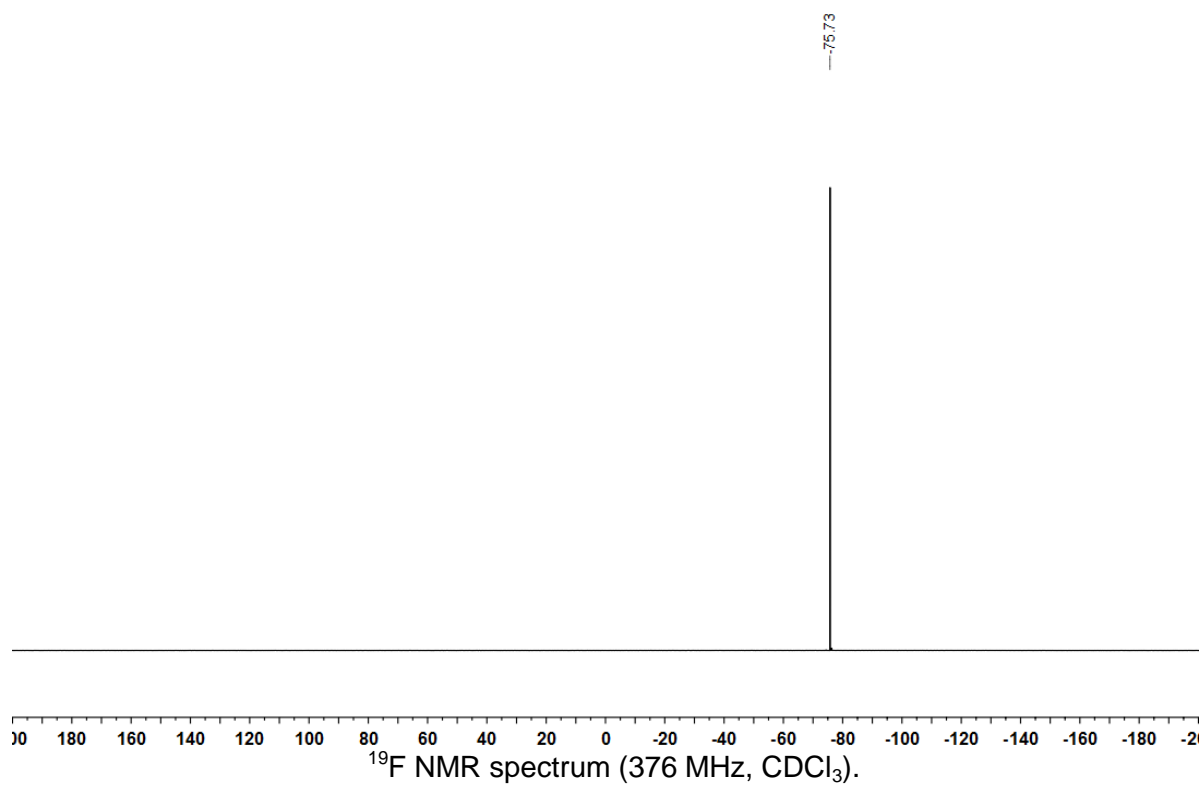
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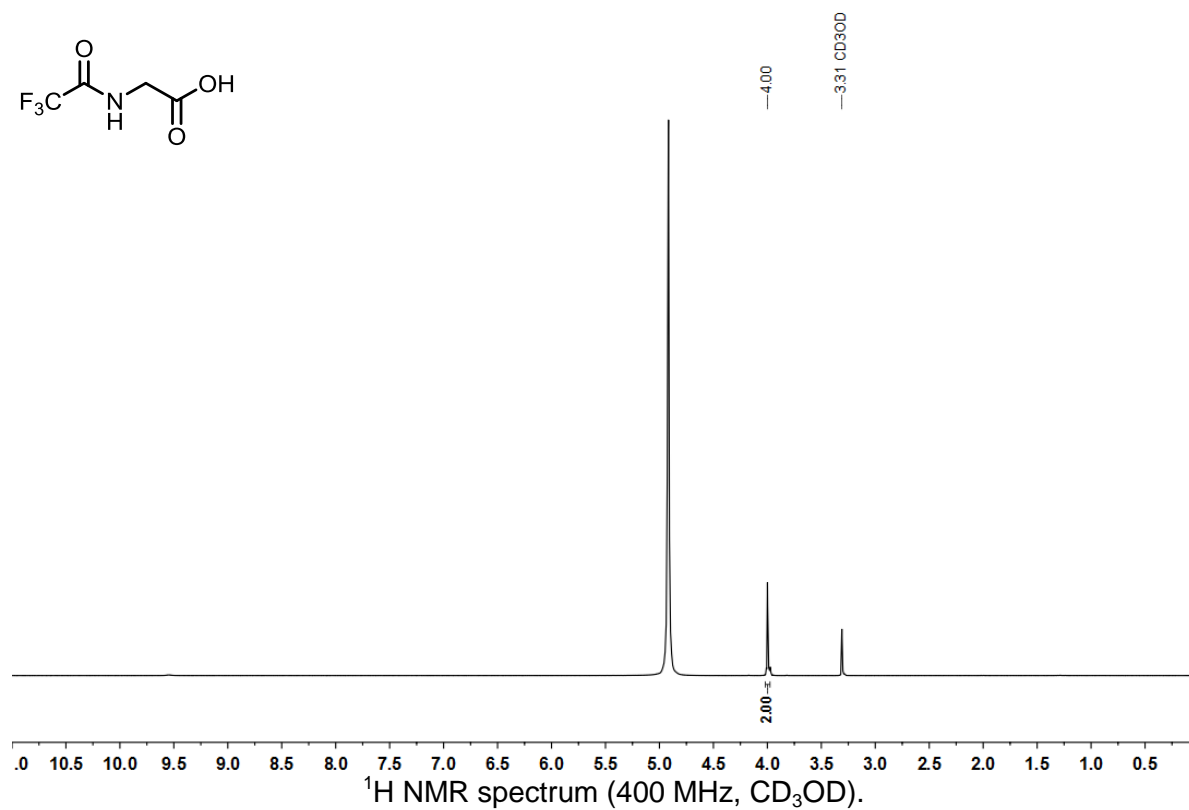
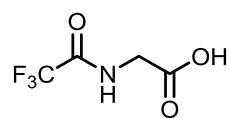


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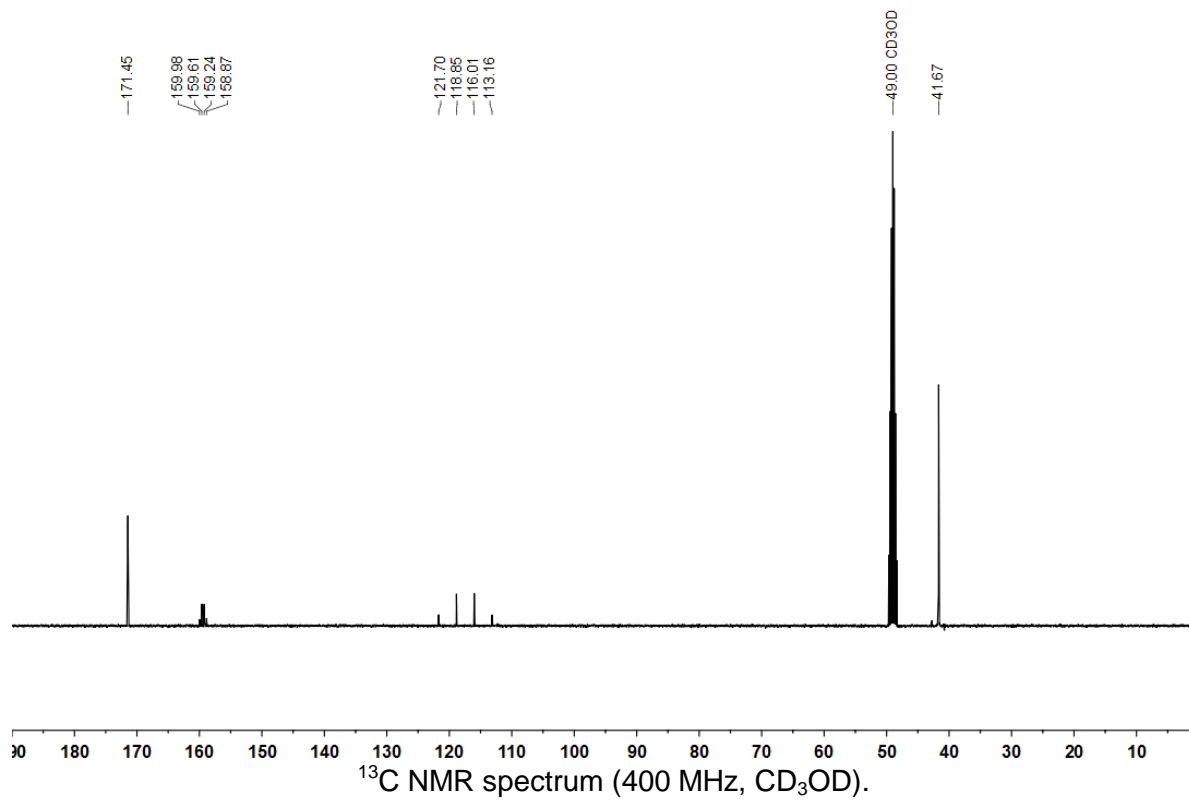


2-(Trifluoroacetamido)acetic acid

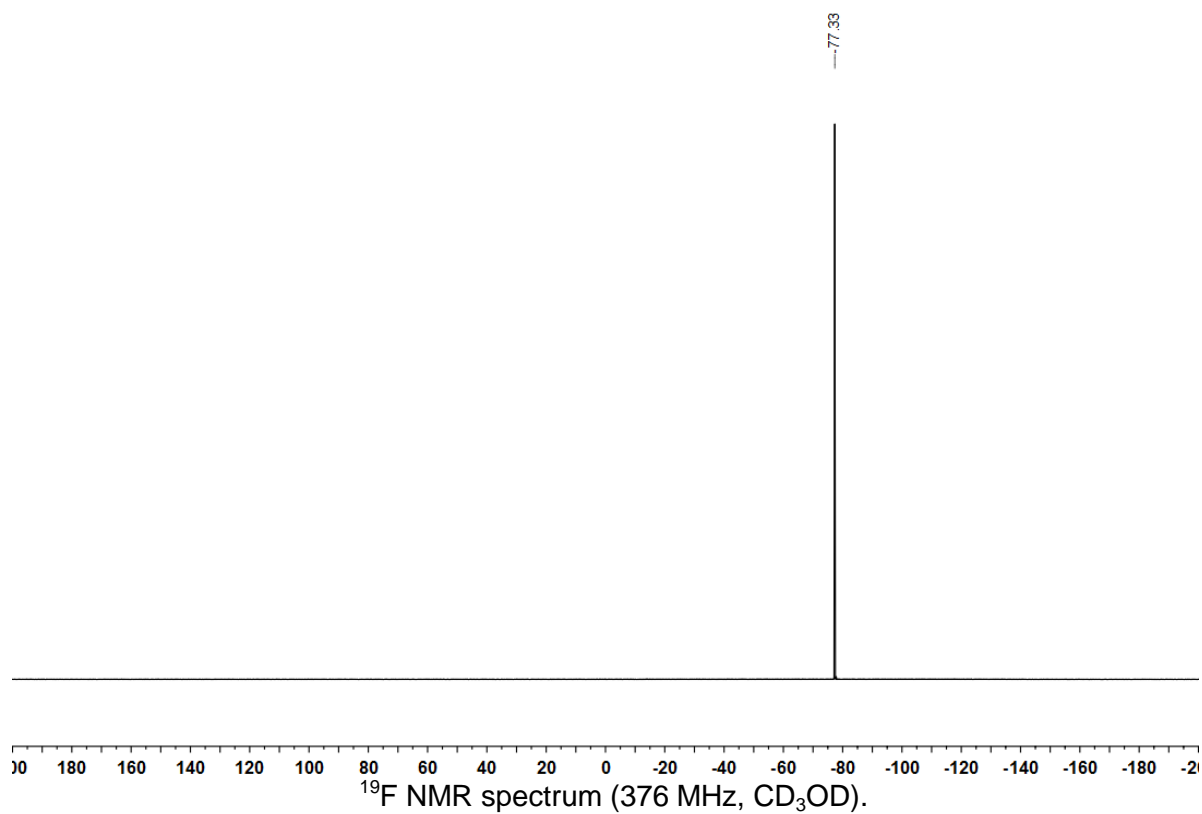
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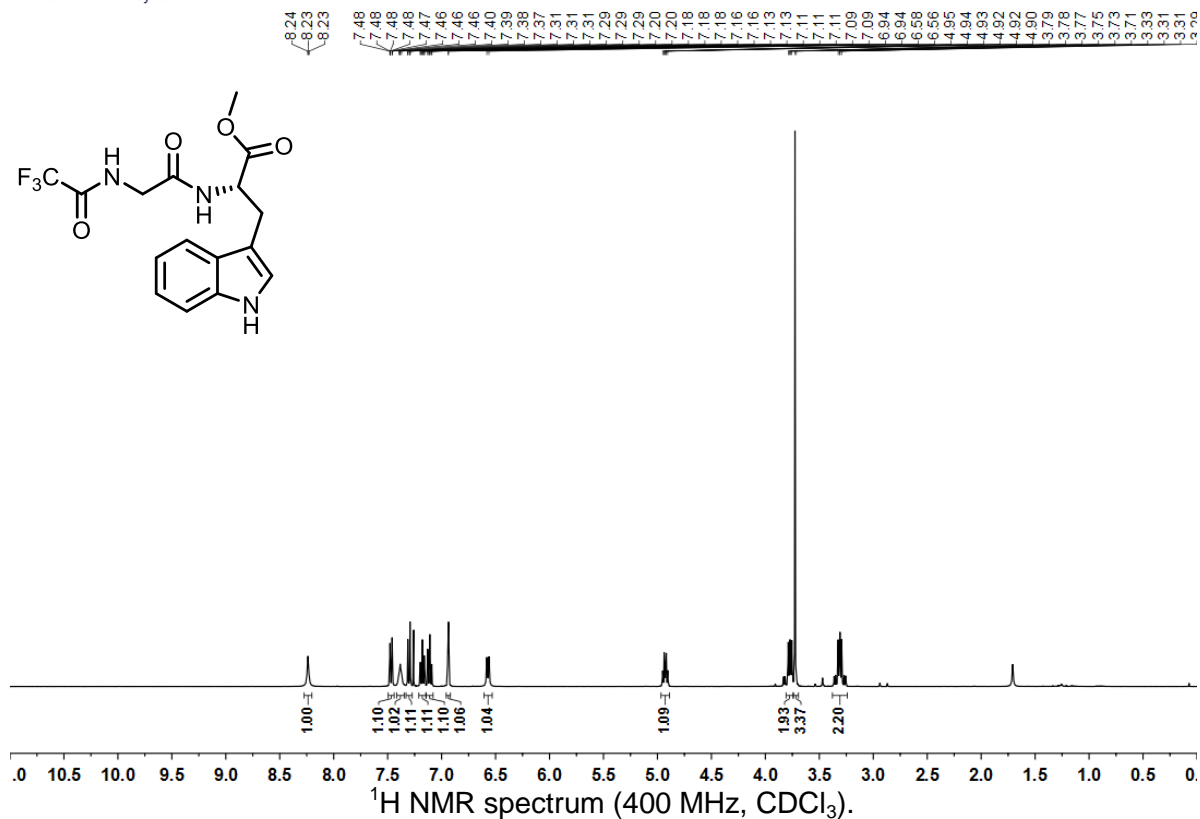


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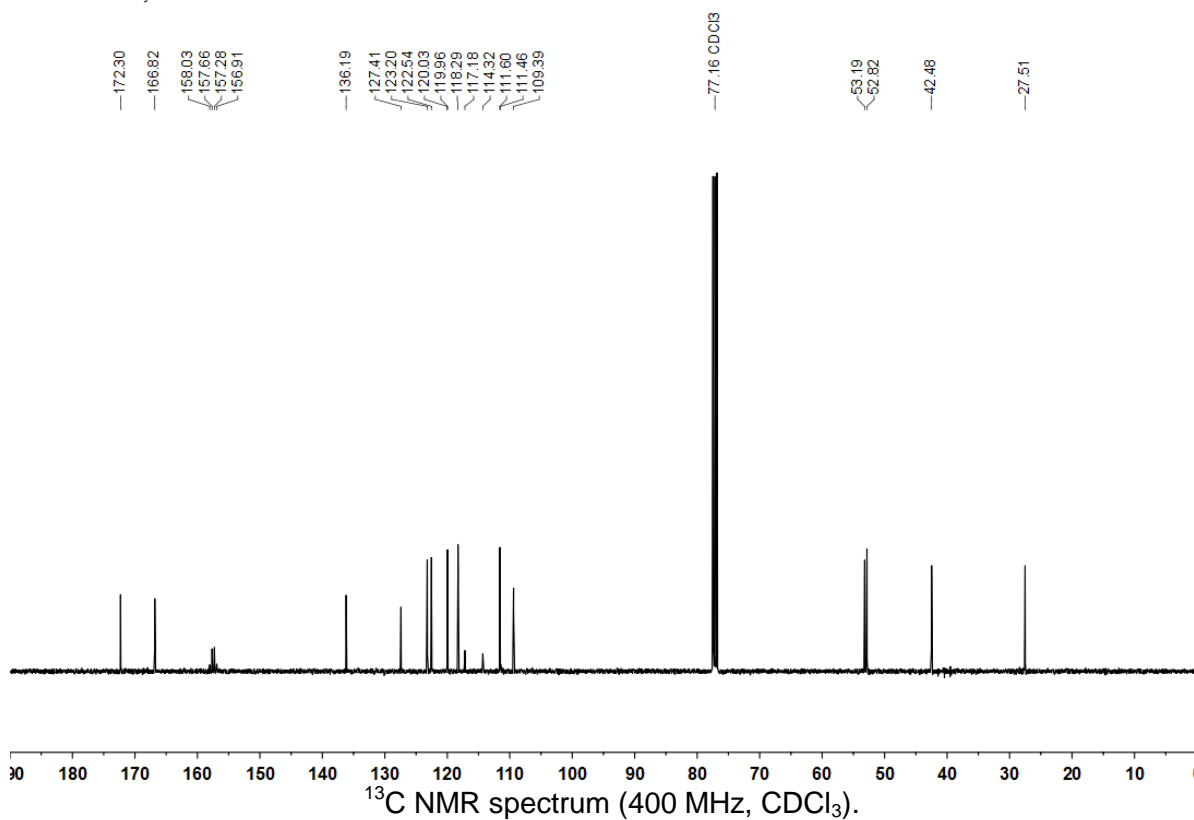


Methyl (2S)-3-(1H-indol-3-yl)-2-[2-(trifluoroacetamido)acetamido]propanoate, **13**

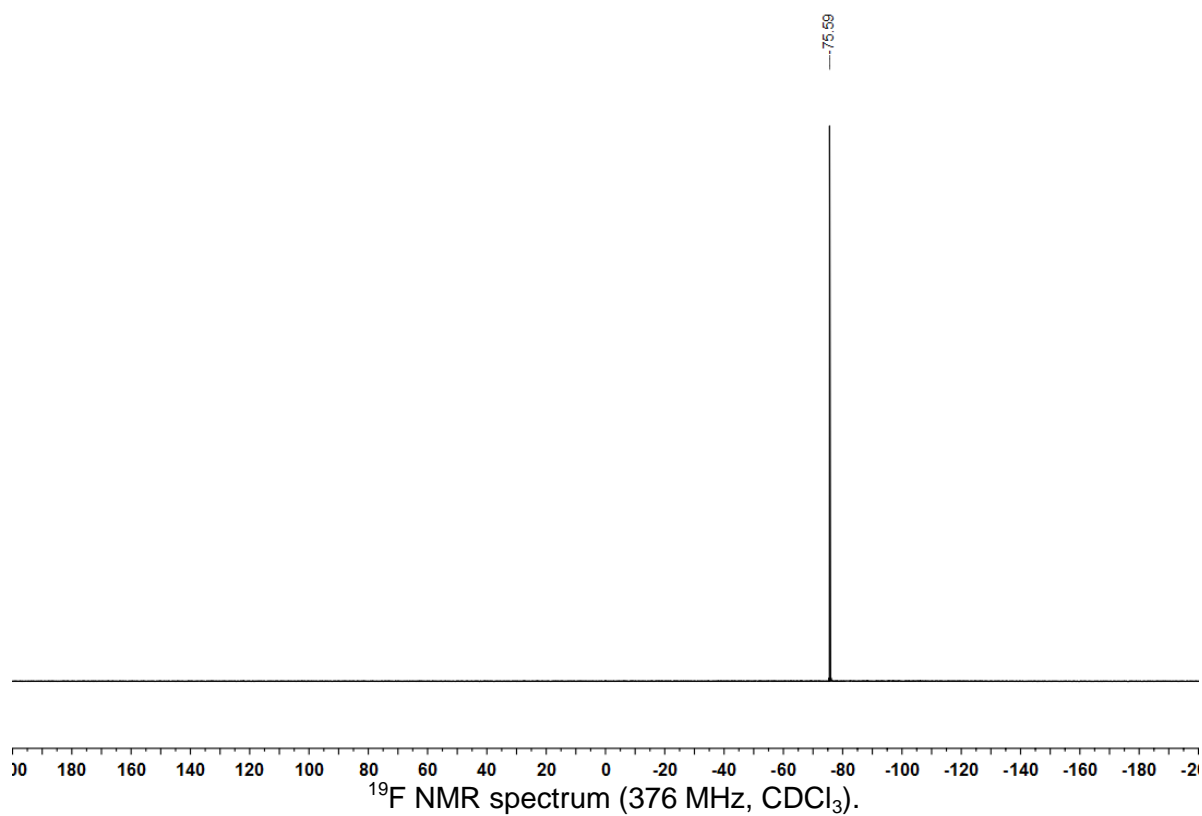
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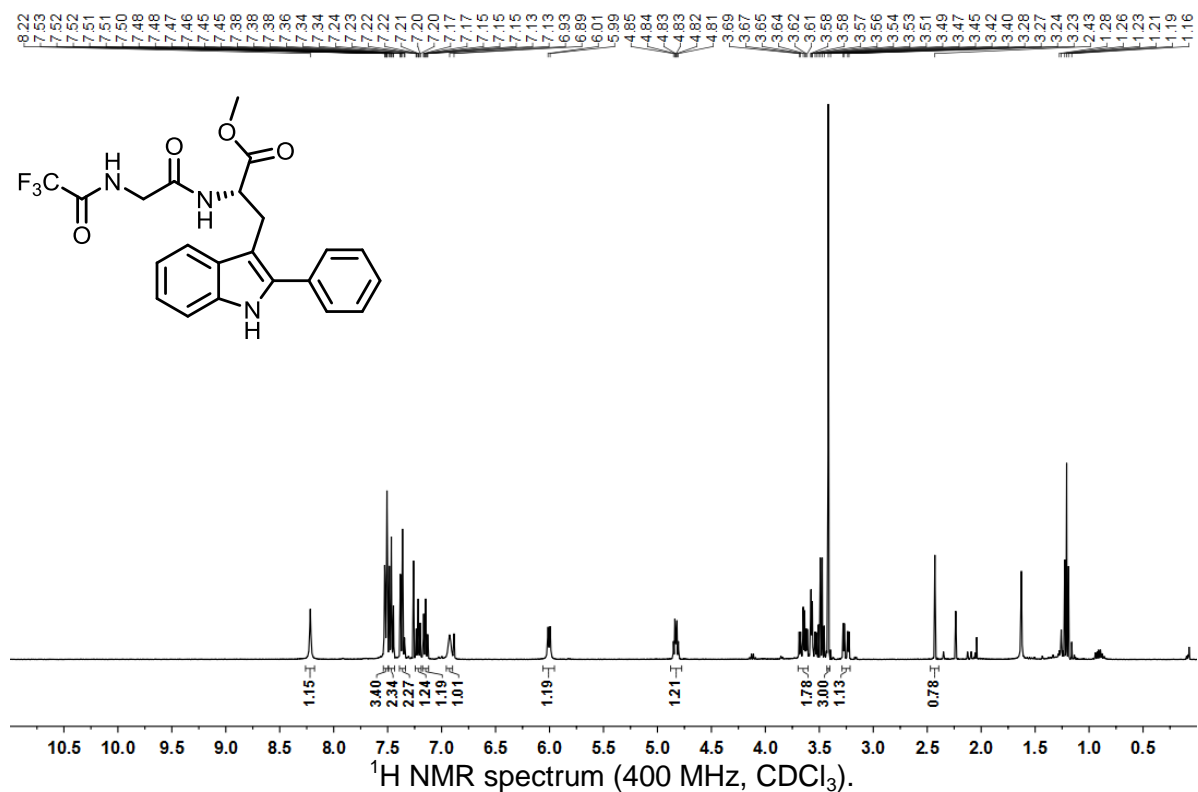


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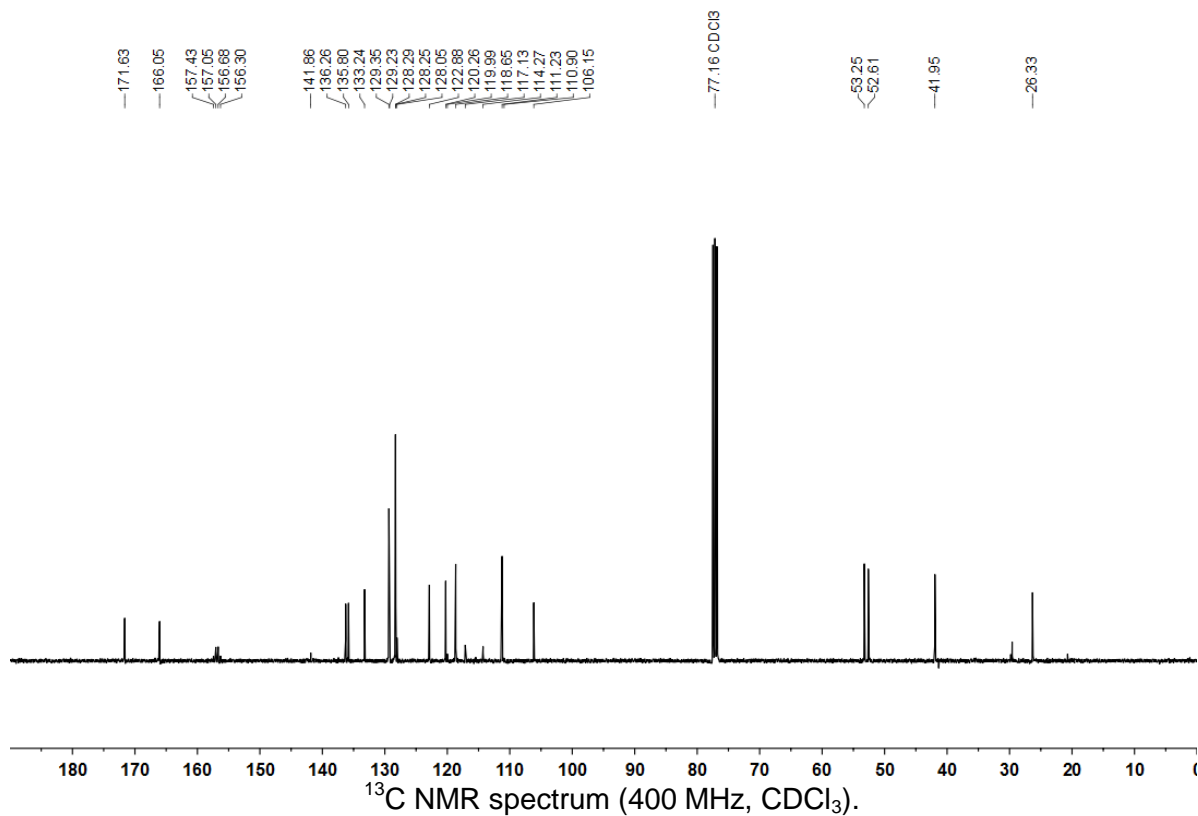


Methyl (2S)-3-(2-phenyl-1H-indol-3-yl)-2-[2-(trifluoroacetamido)acetamido]propanoate, **14a**

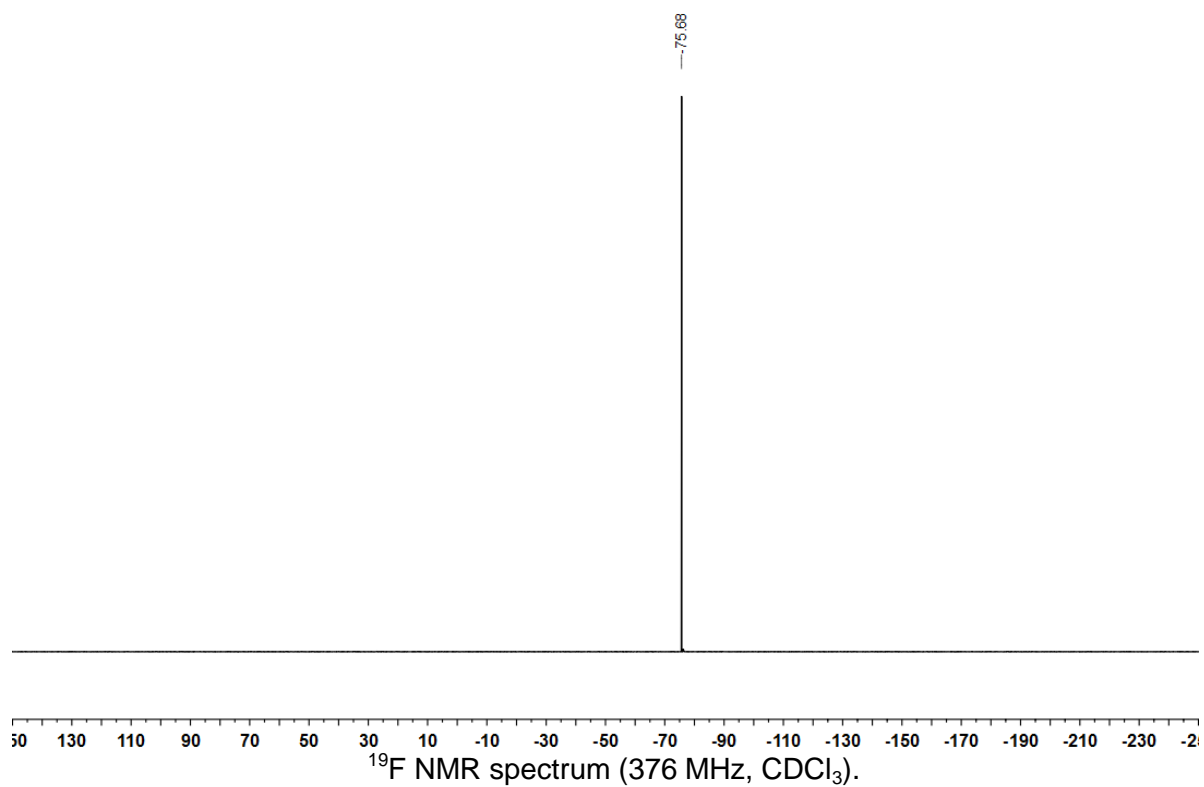
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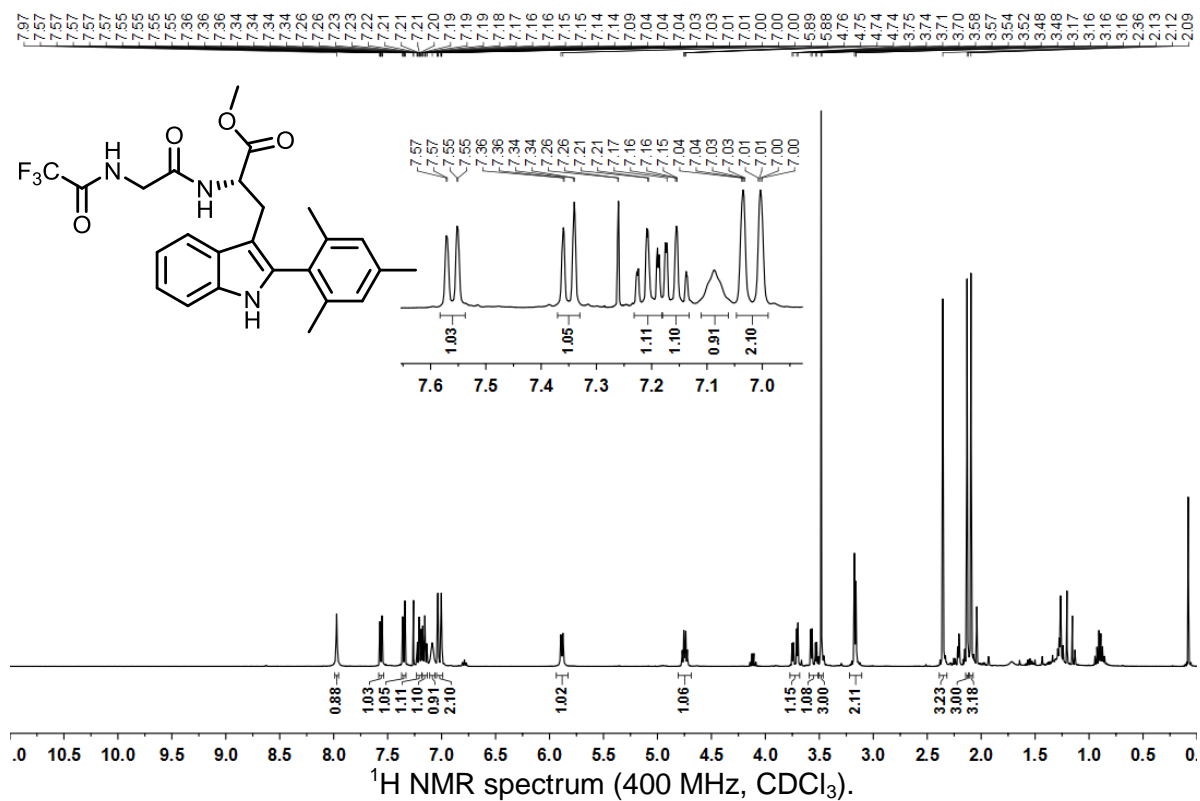


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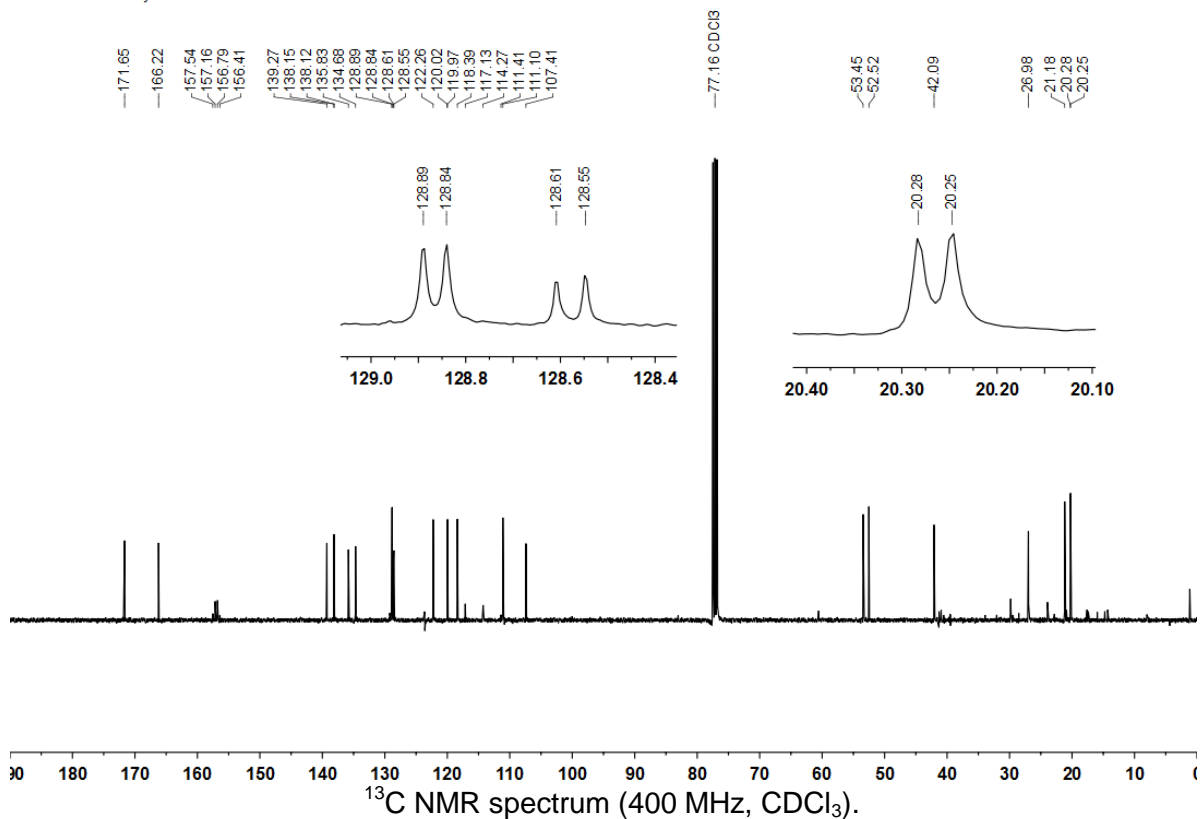


Methyl (2S)-2-[2-(trifluoroacetamido)acetamido]-3-[2-(2,4,6-trimethylphenyl)-1H-indol-3-yl]propanoate, **14b**

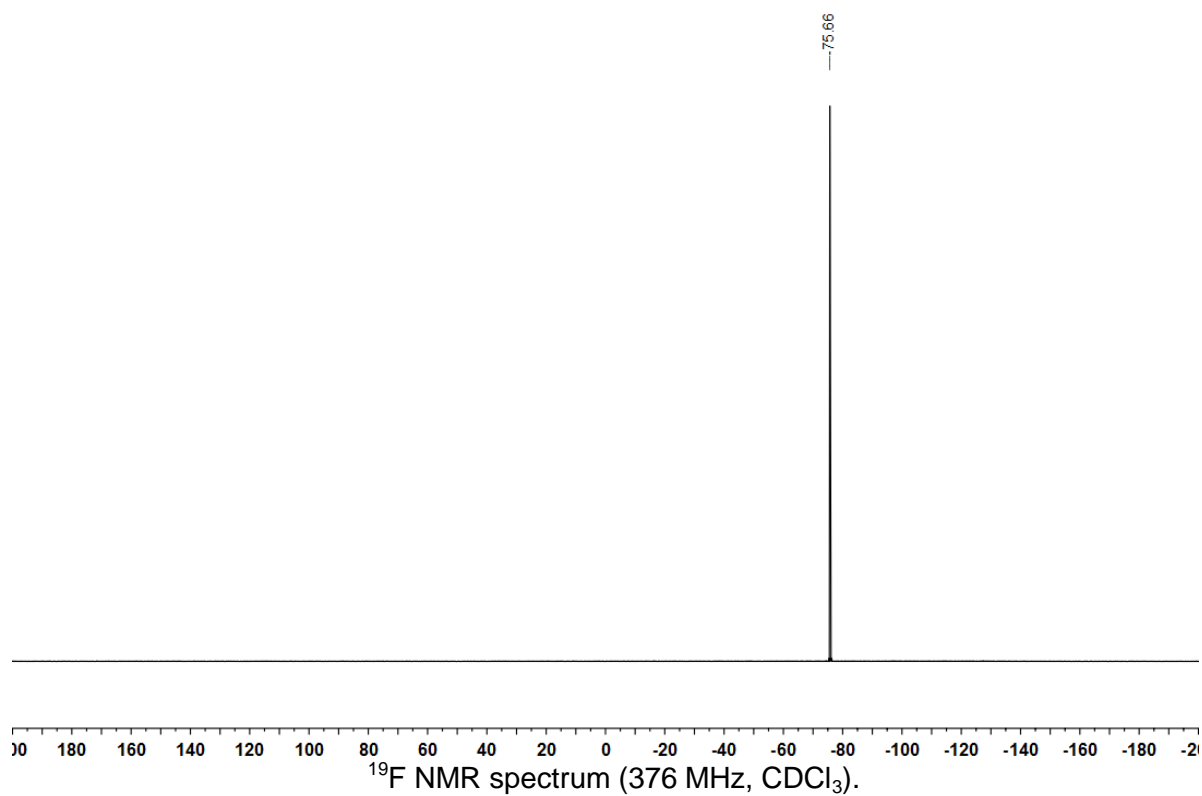
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Filename: d0838ajr
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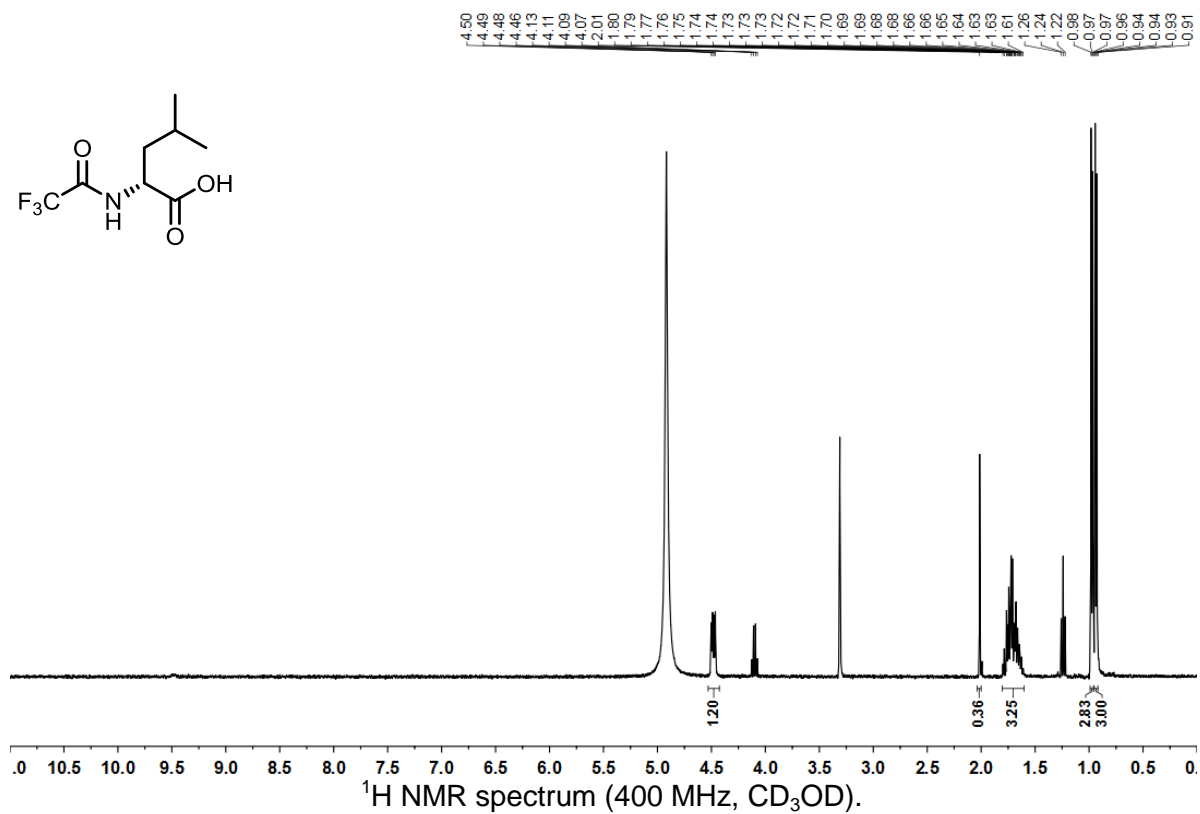


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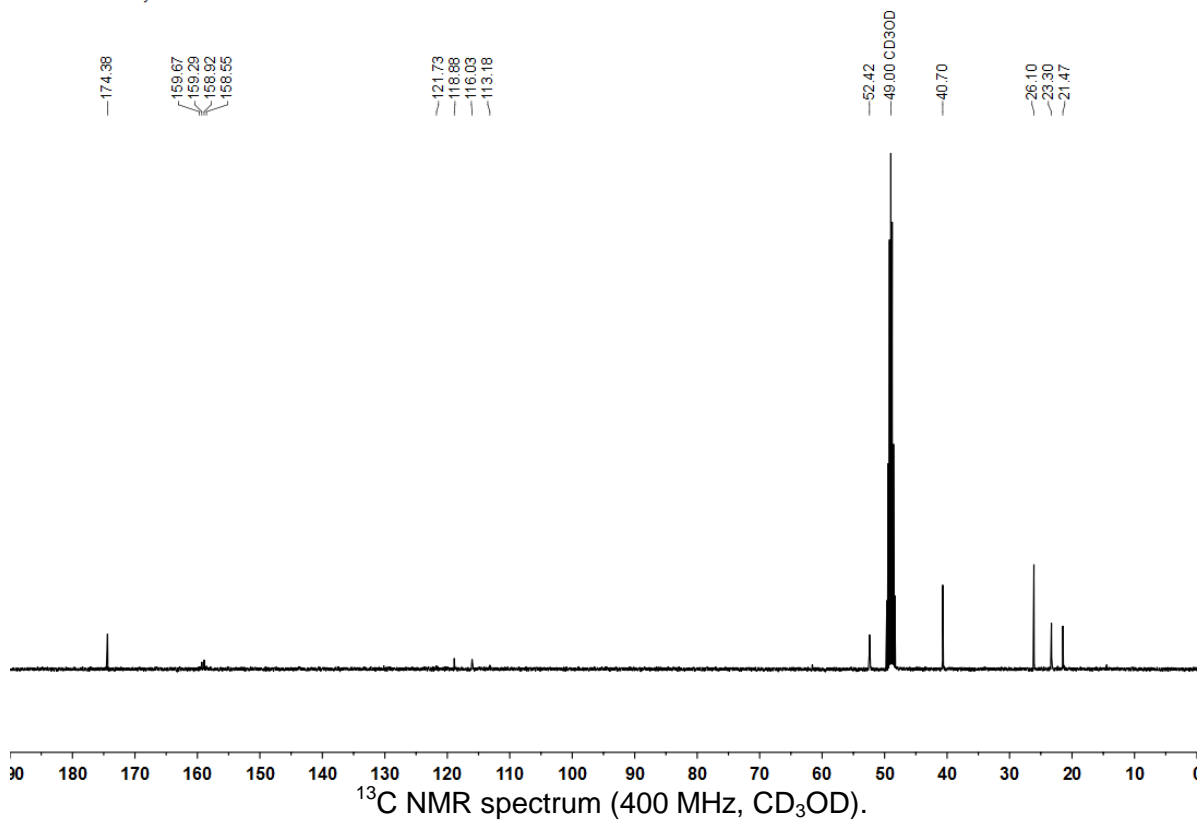


(2R)-4-Methyl-2-(trifluoroacetamido)pentanoic acid

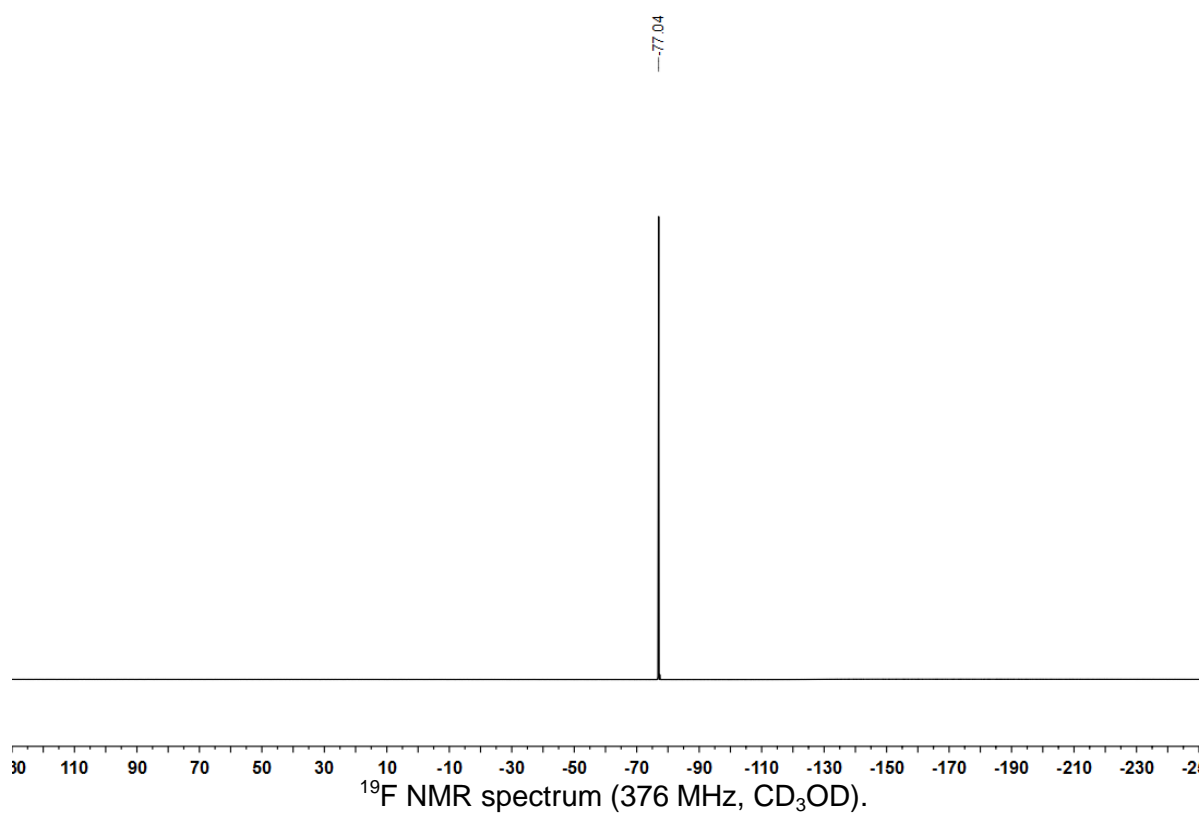
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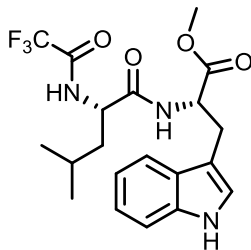
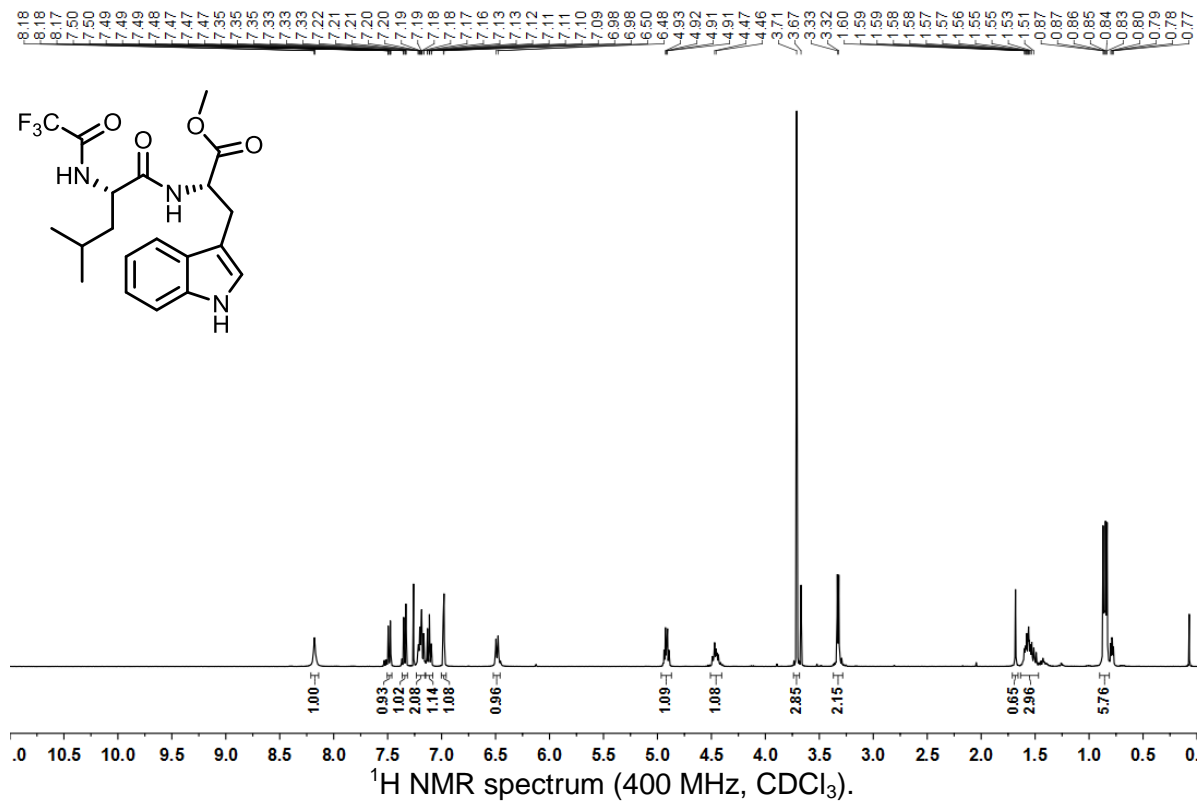


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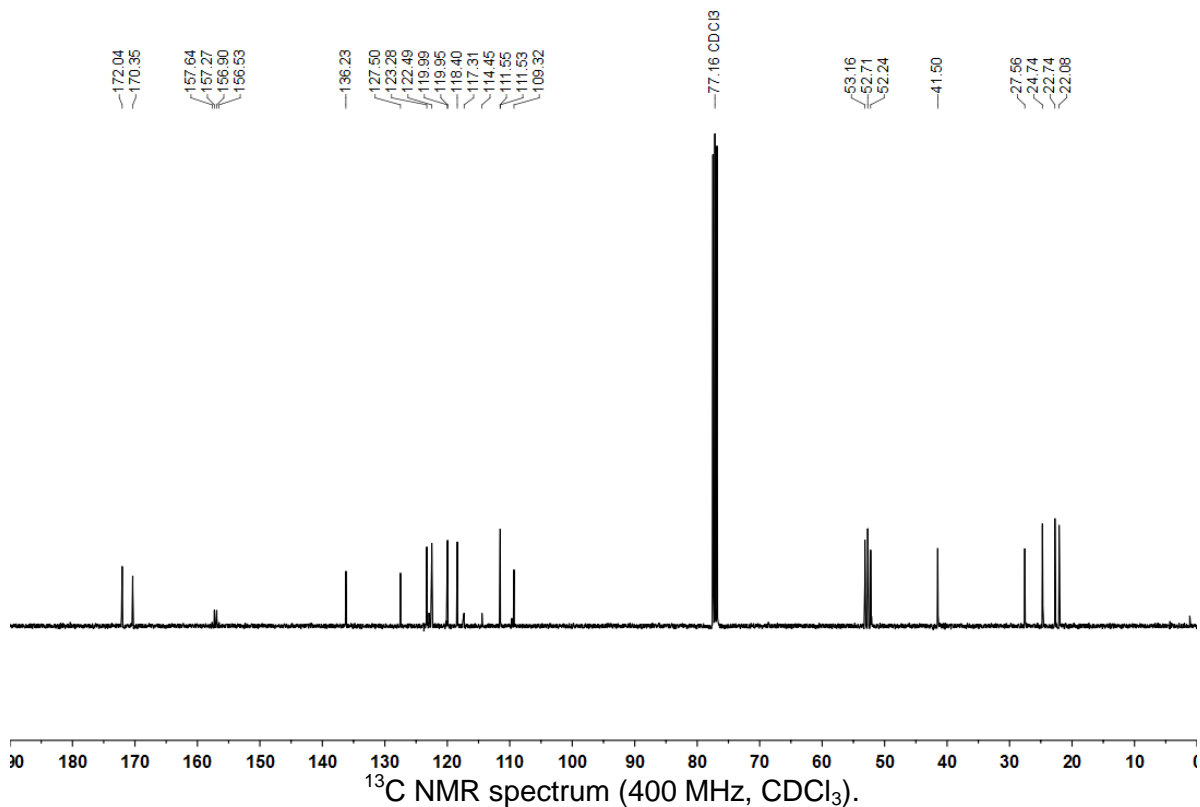


Methyl (2S)-3-(1H-indol-3-yl)-2-[(2R)-4-methyl-2-trifluoroacetamido]pentanamido]propanoate, **15**

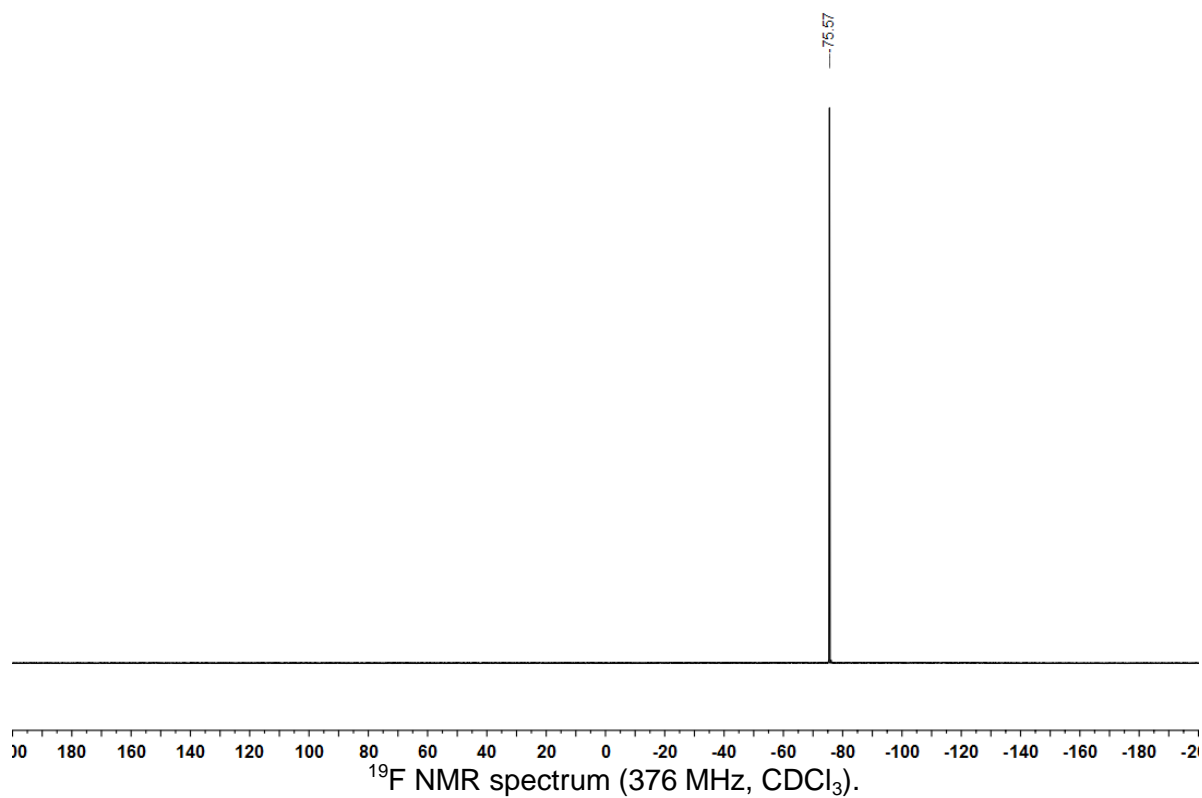
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Filename: c7166ajr
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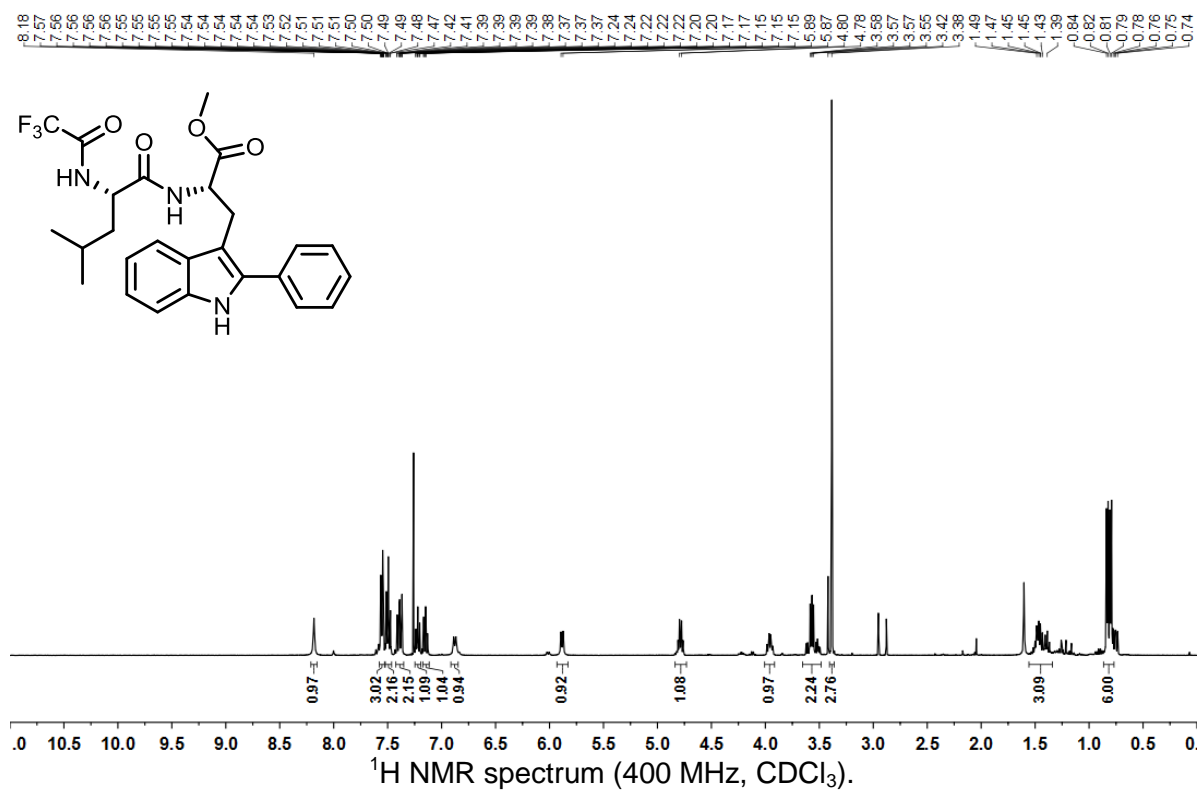


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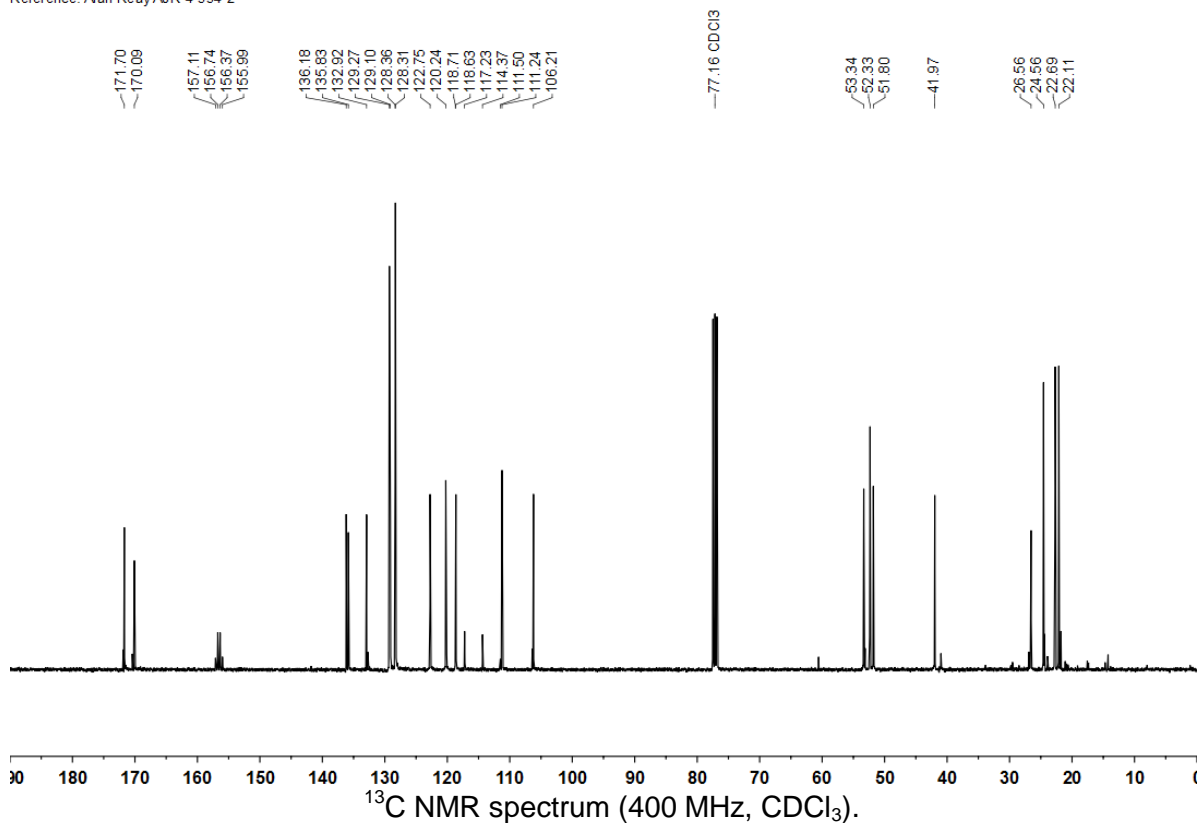


Methyl (2S)-2-[(2R)-4-methyl-2-(trifluoroacetamido)pentanamido]-3-(2-phenyl-1H-indol-3-yl)propanoate, **16a**

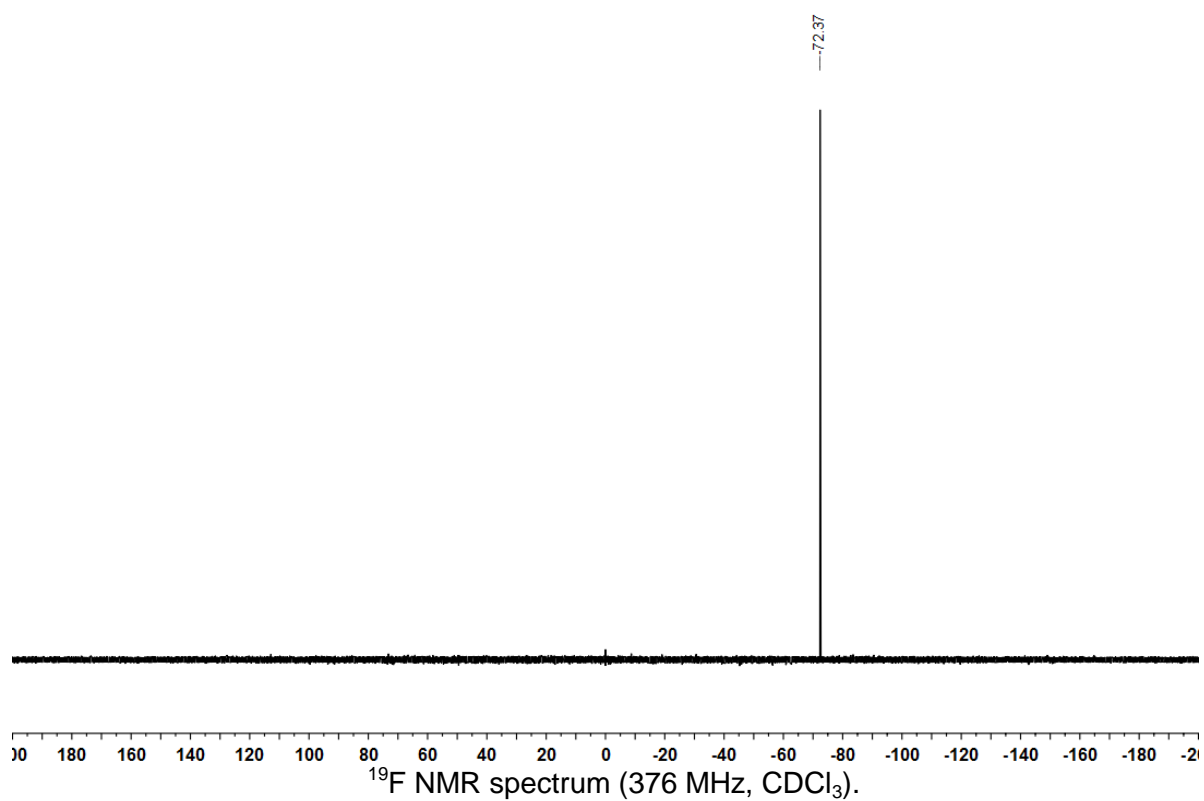
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Filename: c6993ajr
Reference: Alan Reay AJR-4-354-2

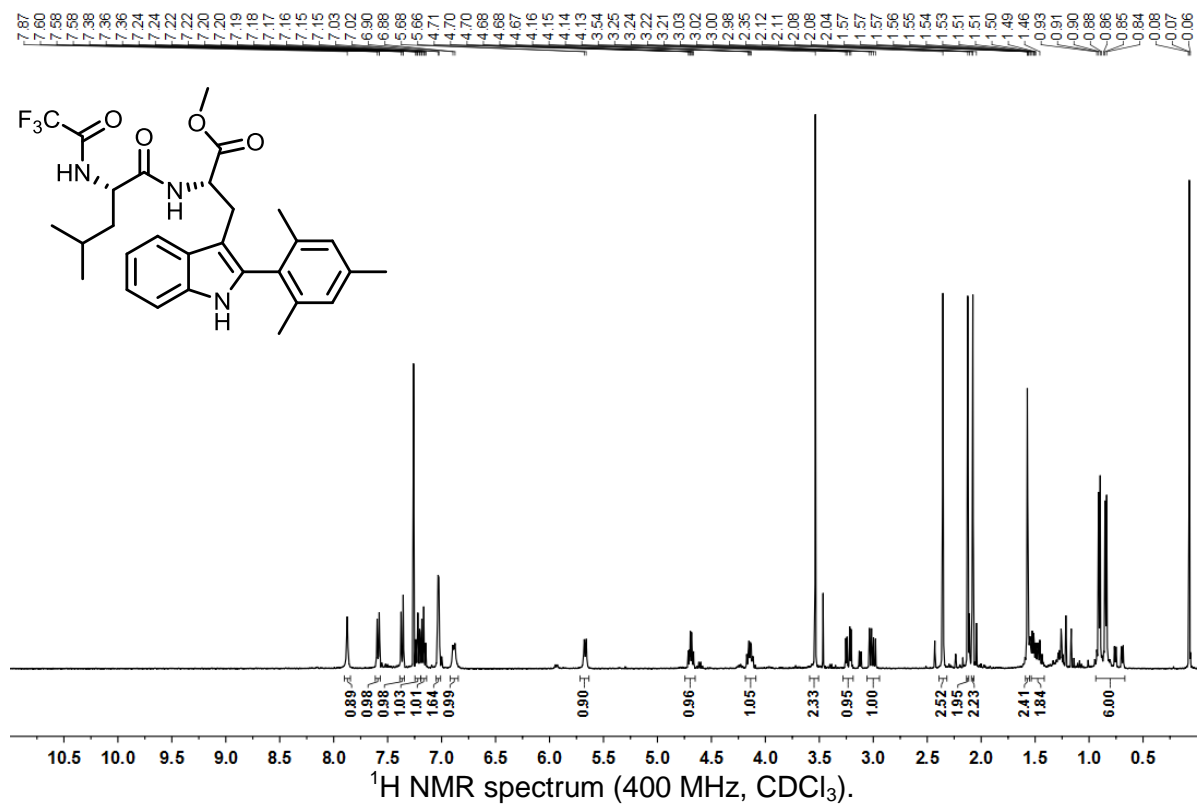


Filename: c4774ajr
Reference: Alan ReayAJR-4-348-2

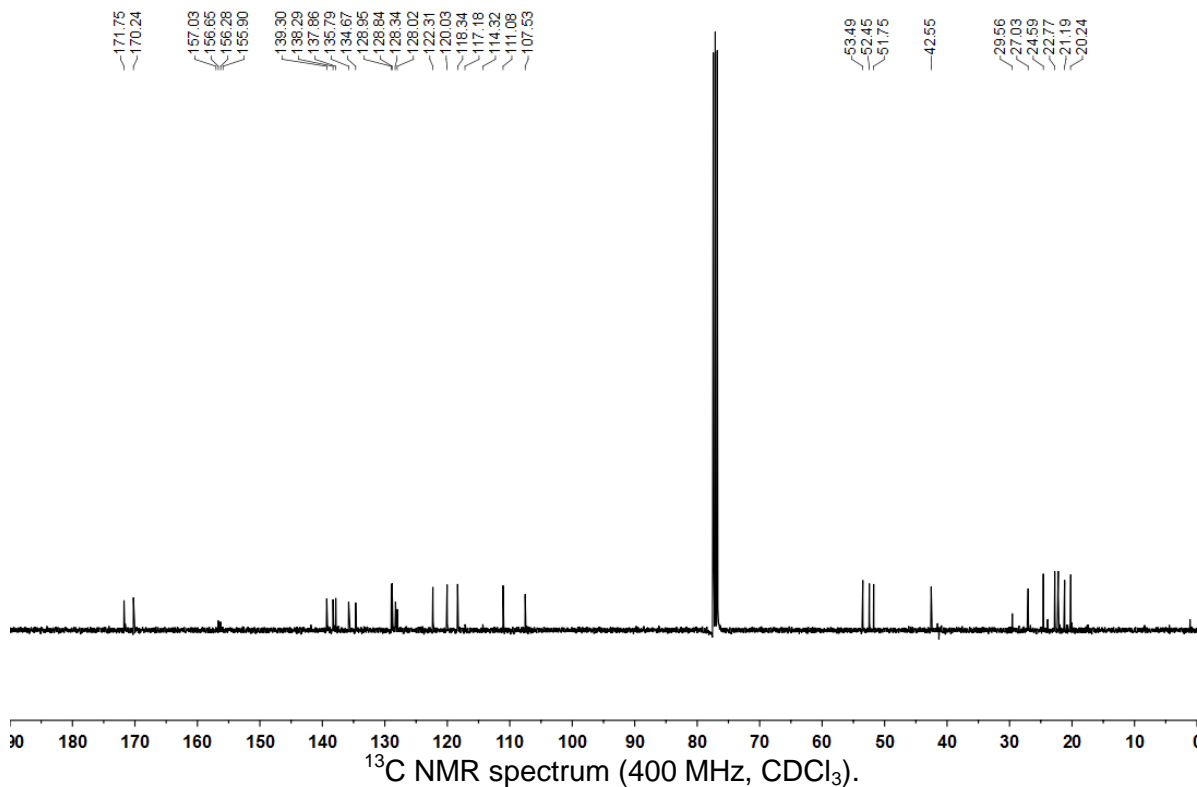


Methyl (2S)-2-[(2R)-4-methyl-2-(trifluoroacetamido)pentanamido]-3-[2-(2,4,6-trimethylphenyl)-1H-indol-3-yl]propanoate, **16b**

Filename: m8656ajr
Reference: Alan Reay AJR-4-348-1



Filename: c6992ajr
Reference: Alan Reay AJR-4-354-1



Filename: m8656ajr
Reference: Alan ReayAJR-4-348-1

