

Supplementary Materials

Peptide-Alkoxyamine Drugs: An Innovative Approach to Fight Schistosomiasis: “Digging Their Graves with Their Forks”

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- ⁷ INSERM, 146 rue Leo Saignat, CEDEX, 33076 Bordeaux, France
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- * Correspondence: g.audran@univ-amu.fr (G.A.); philippe.mellet@rmsb.u-bordeaux.fr (P.M.); boissier@univ-perp.fr (J.B.); sylvain.marque@univ-amu.fr (S.R.A.M.)

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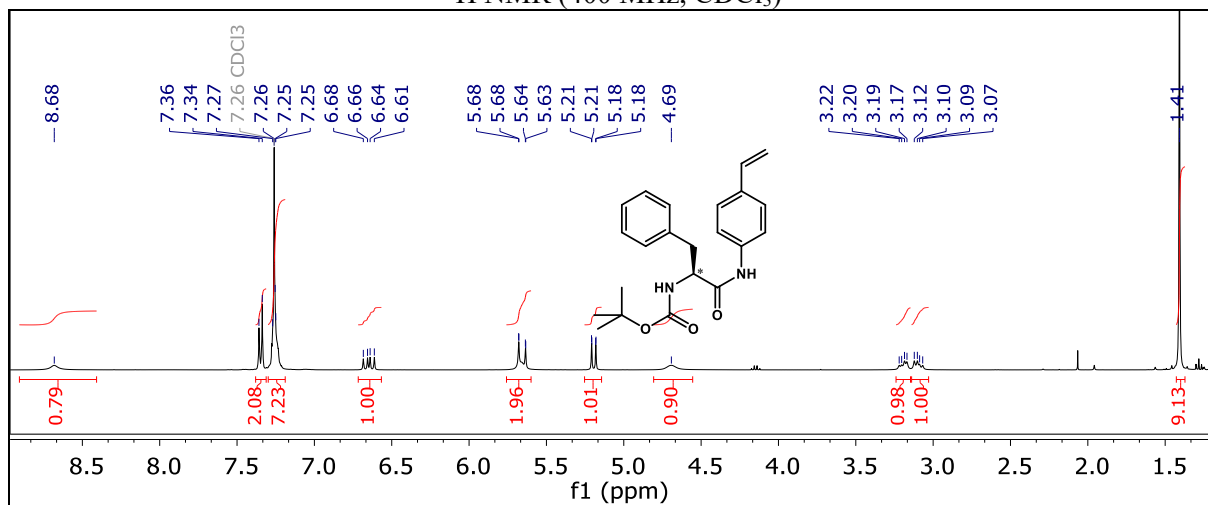
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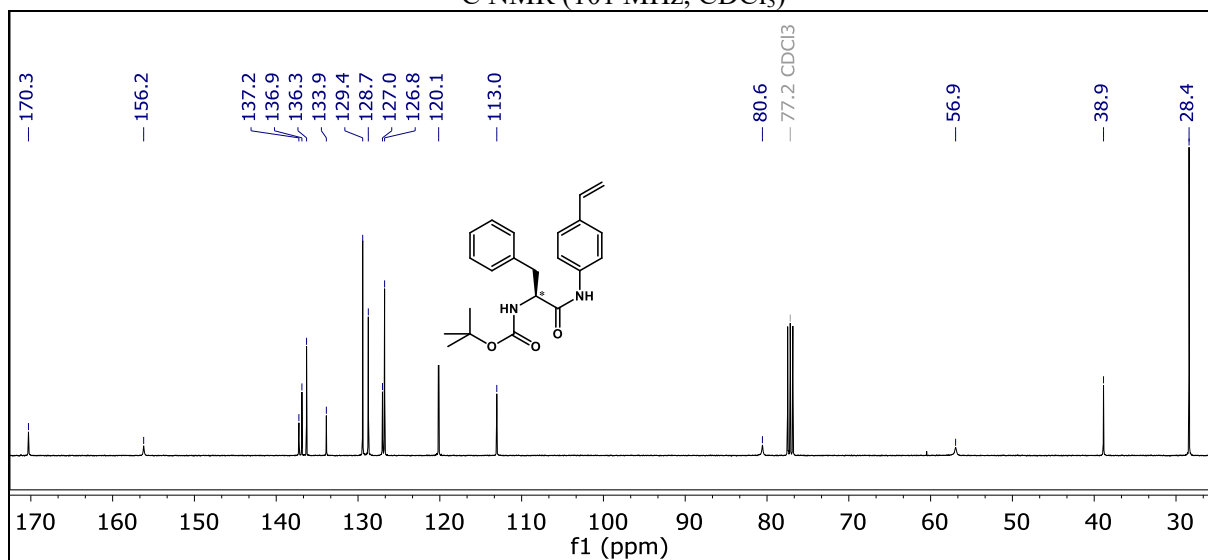
tert-butyl (S)-((1-oxo-3-phenyl-1-((4-vinylphenyl)amino)propan-2-yl)carbamate

(P3L)

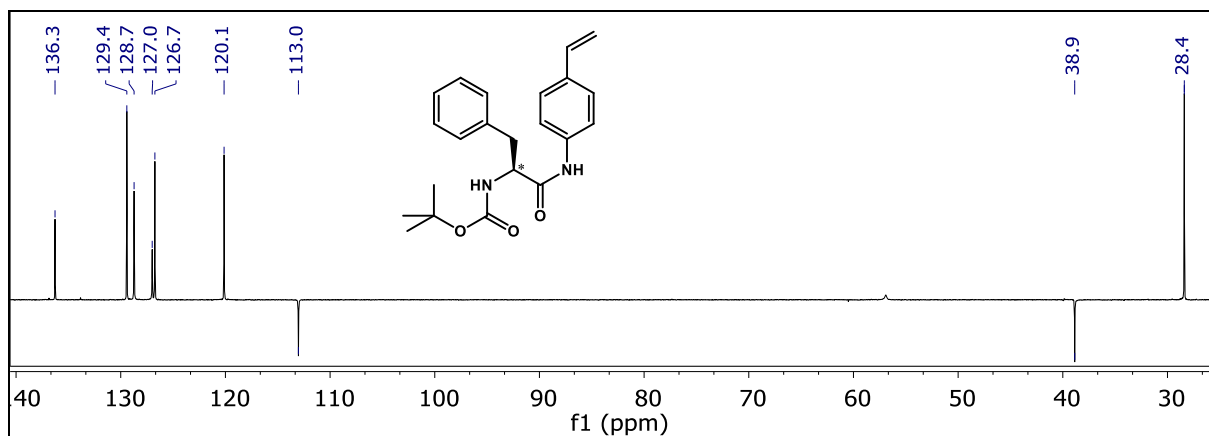
^1H NMR (400 MHz, CDCl_3)



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



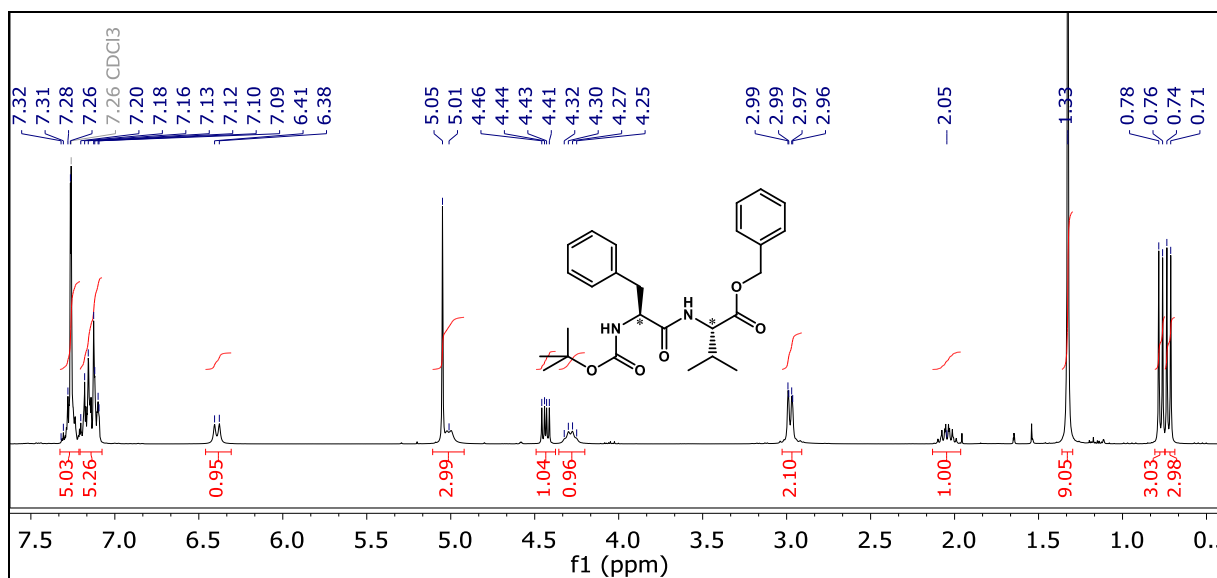
DEPT 135 (101 MHz, CDCl_3)



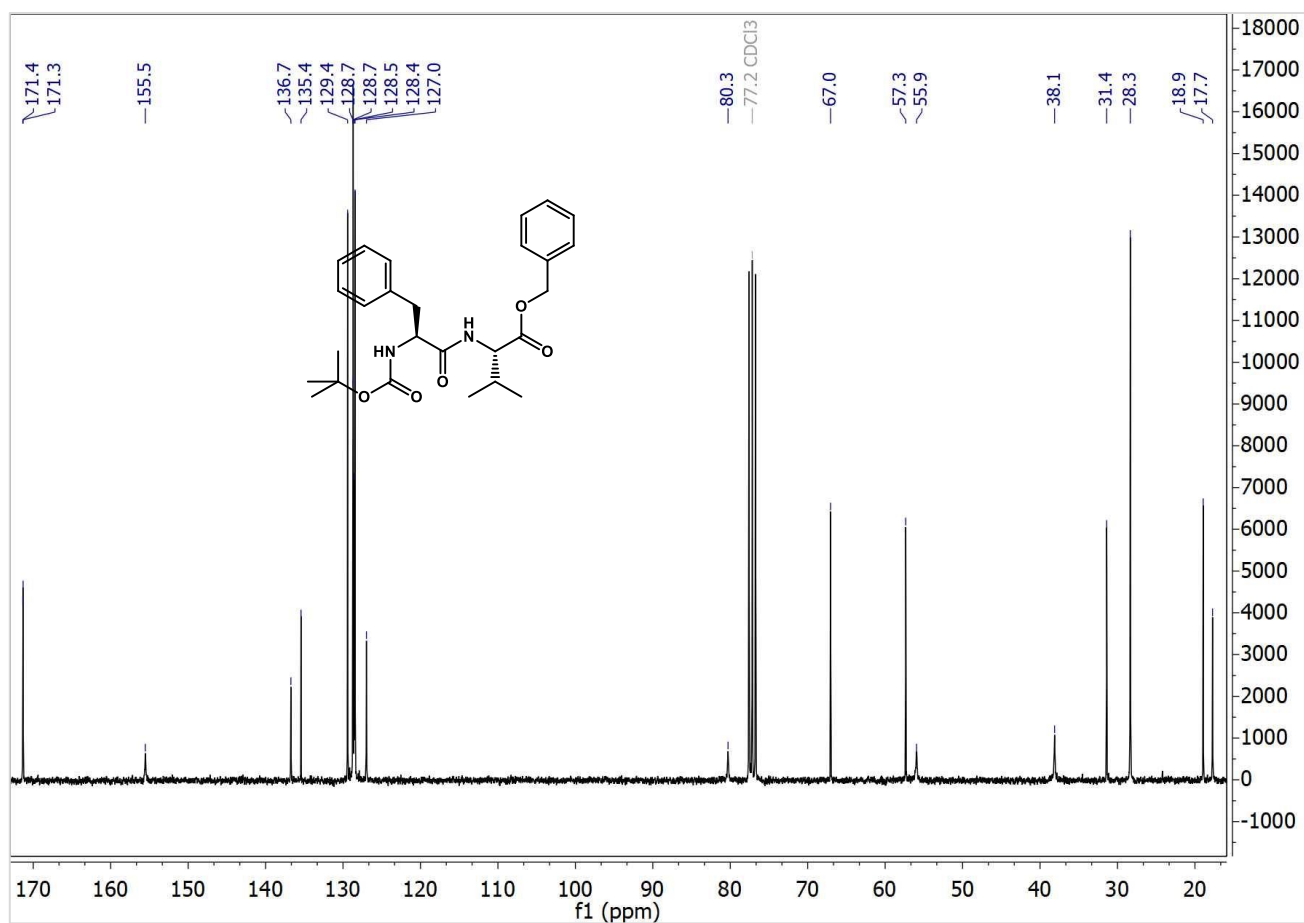
benzyl (tert-butoxycarbonyl)-L-phenylalanyl-L-valinate

(P4L)

¹H NMR (300 MHz, CDCl₃)



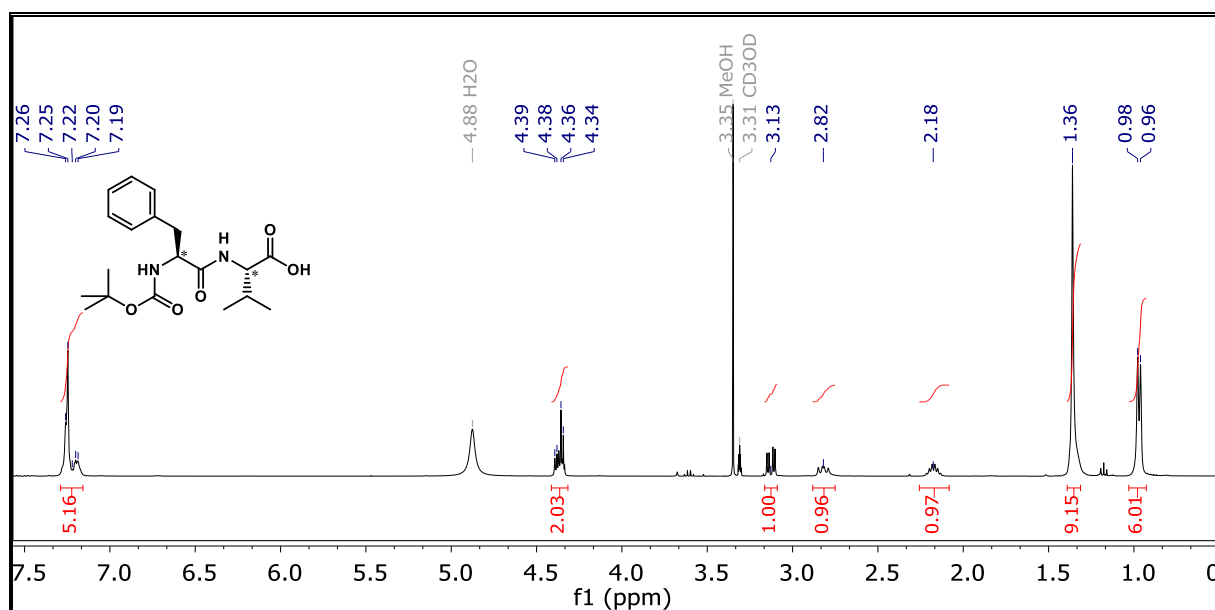
¹³C NMR (75 MHz, CDCl₃)



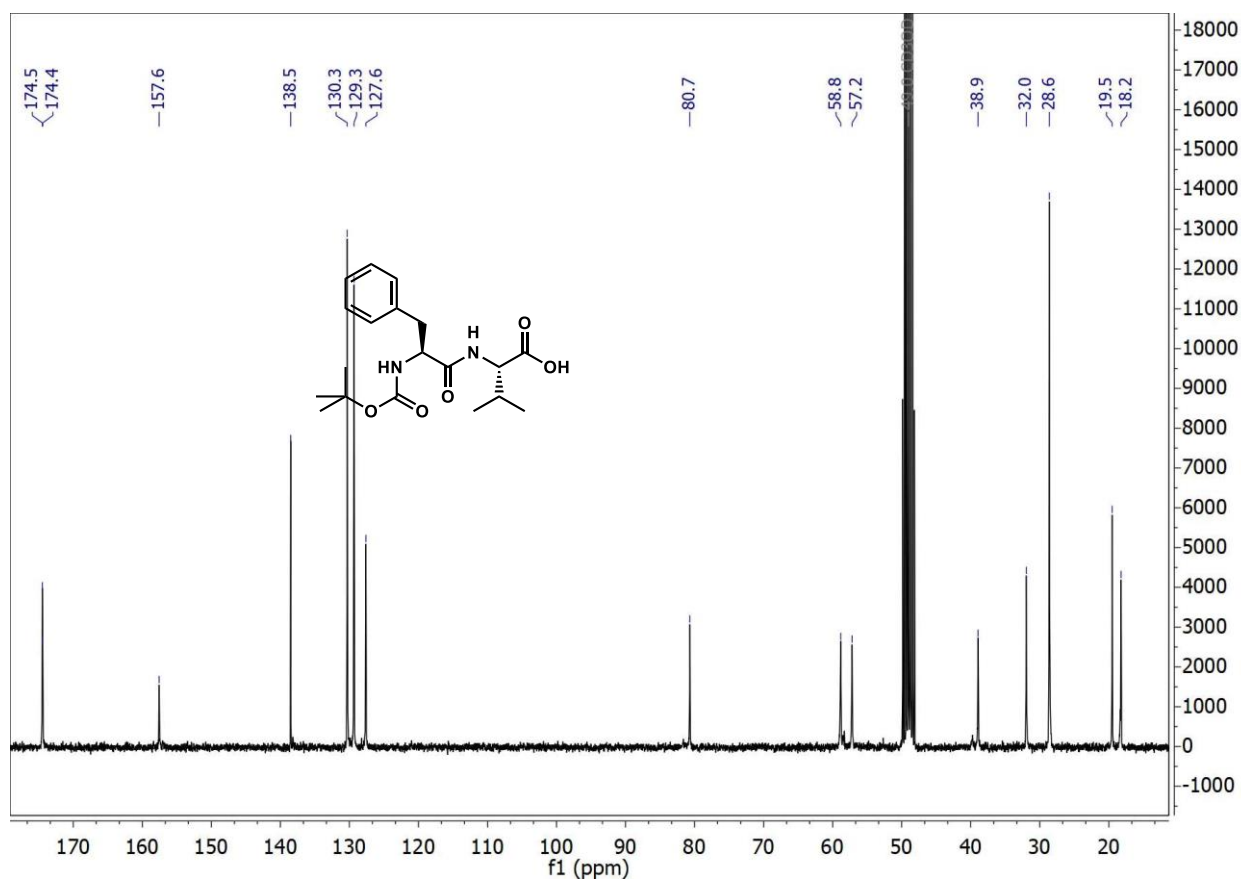
(tert-butoxycarbonyl)-L-phenylalanyl-L-valine

(P5L)

¹H NMR (400 MHz, MeOD)



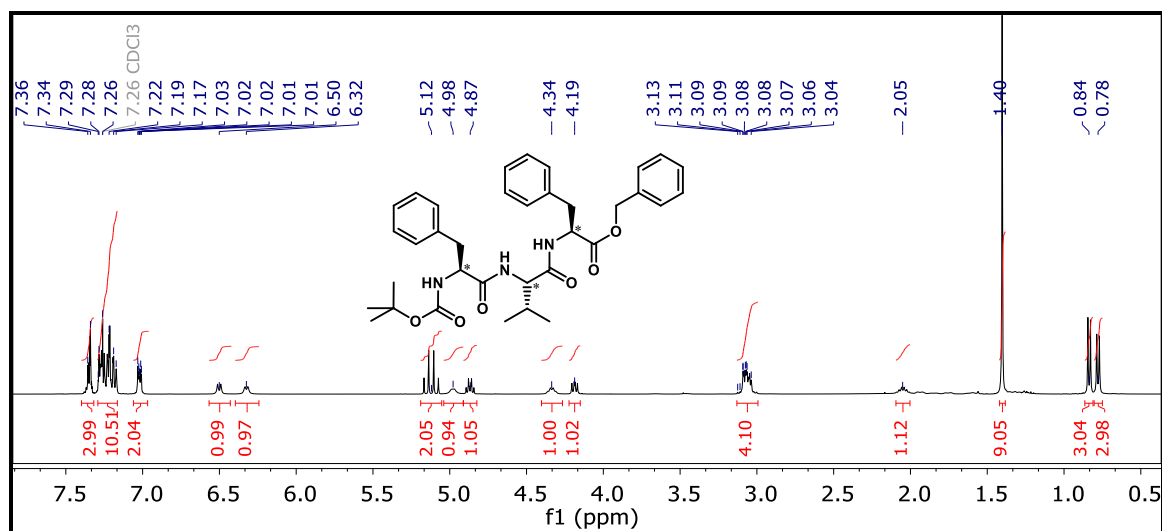
^{13}C NMR (75 MHz, MeOD)



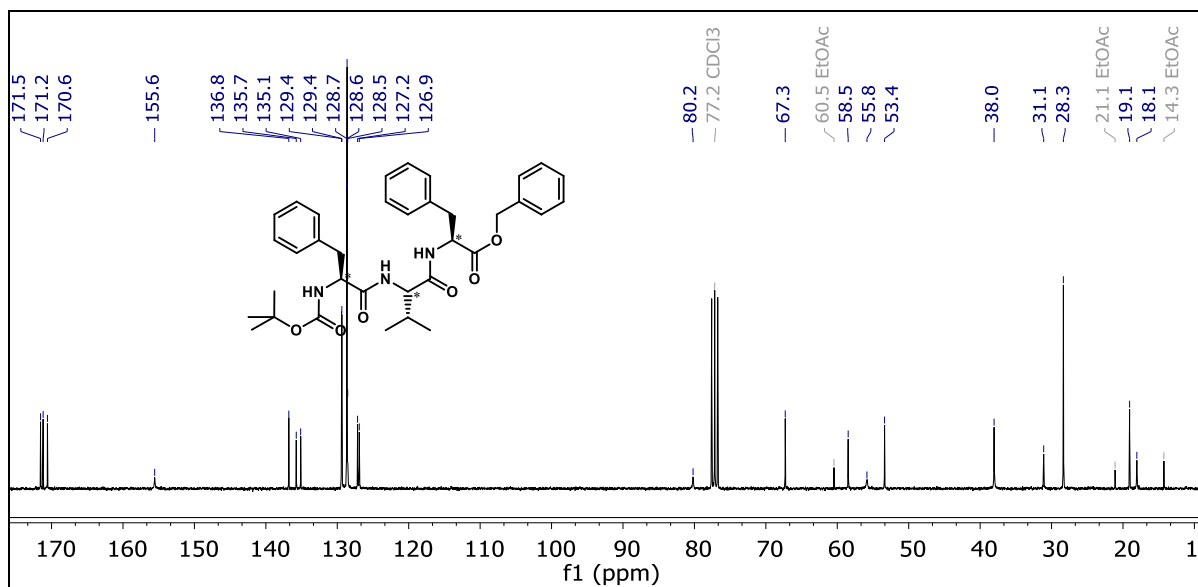
benzyl (tert-butoxycarbonyl)-L-phenylalanyl-L-valyl-L-phenylalaninate

(P6L)

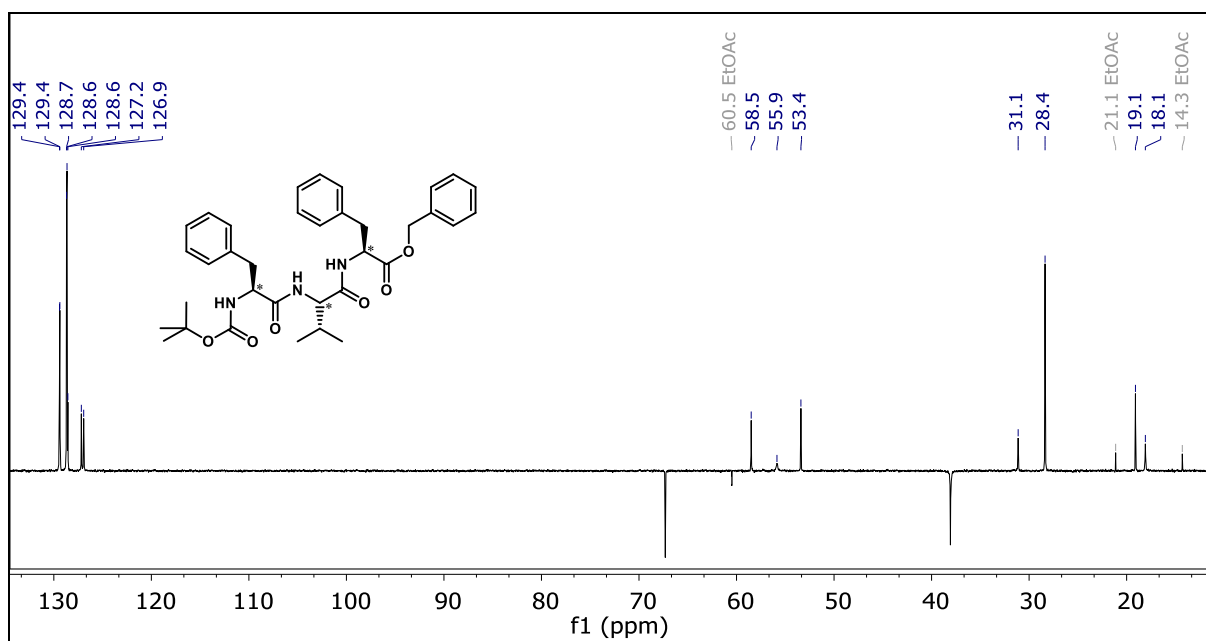
^1H NMR (400 MHz, CDCl_3)



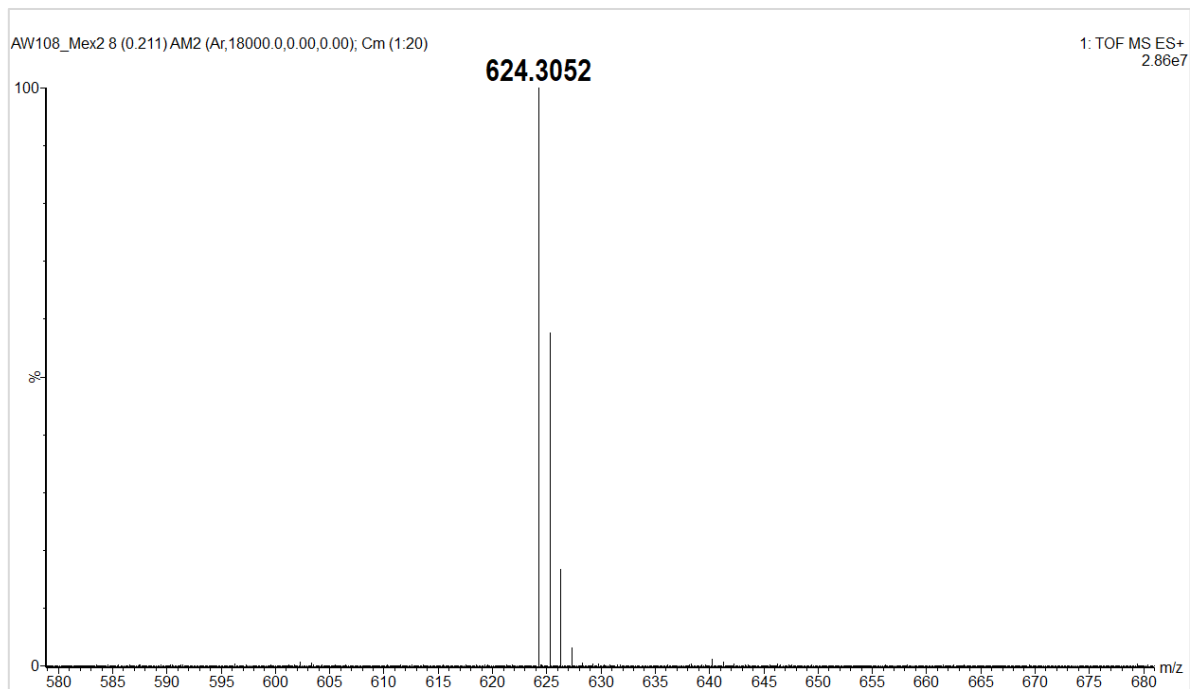
^{13}C NMR (75 MHz, CDCl_3)



DEPT 135 (75 MHz, CDCl₃)



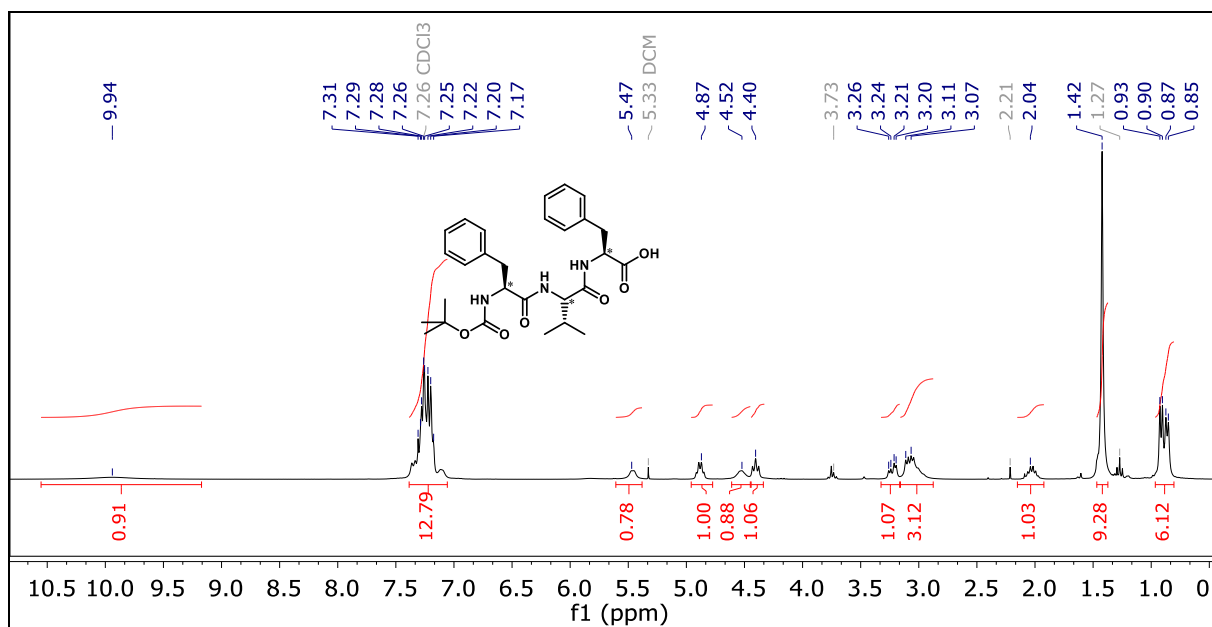
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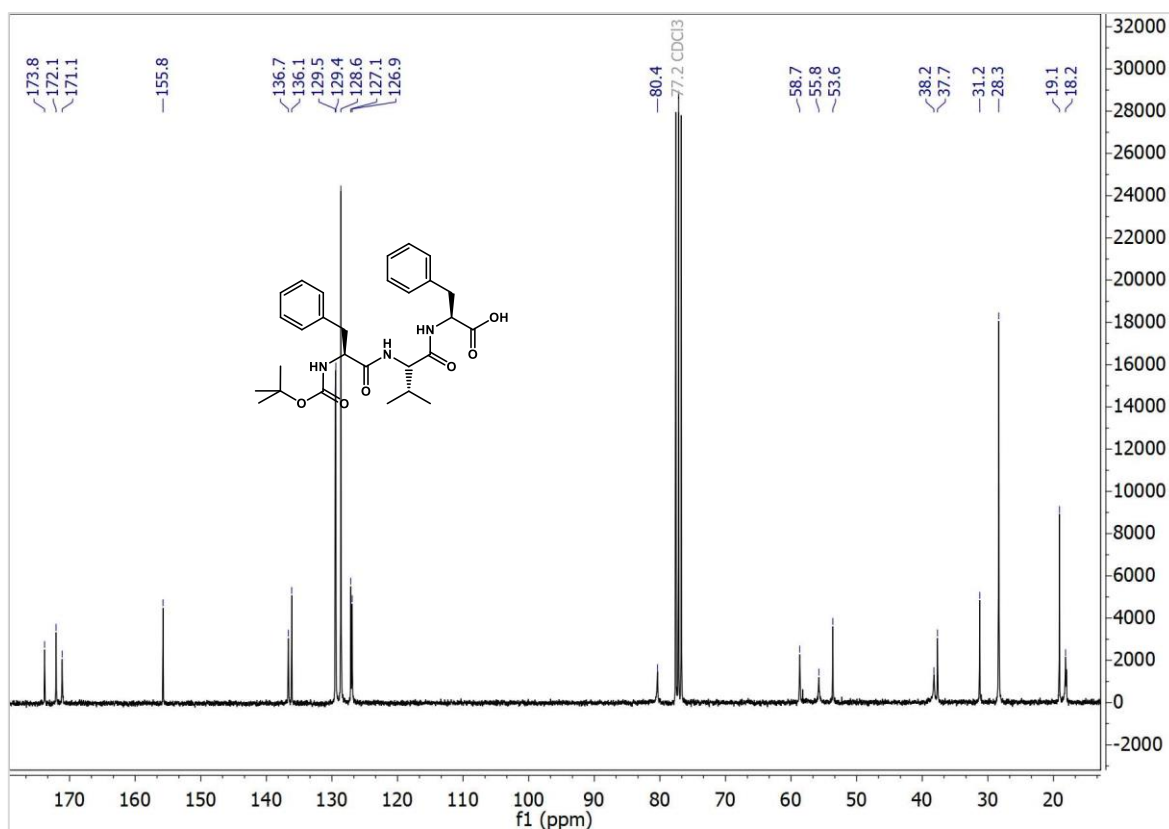
(tert-butoxycarbonyl)-L-phenylalanyl-L-valyl-L-phenylalanine

(P7L)

^1H NMR (300 MHz, CDCl_3)



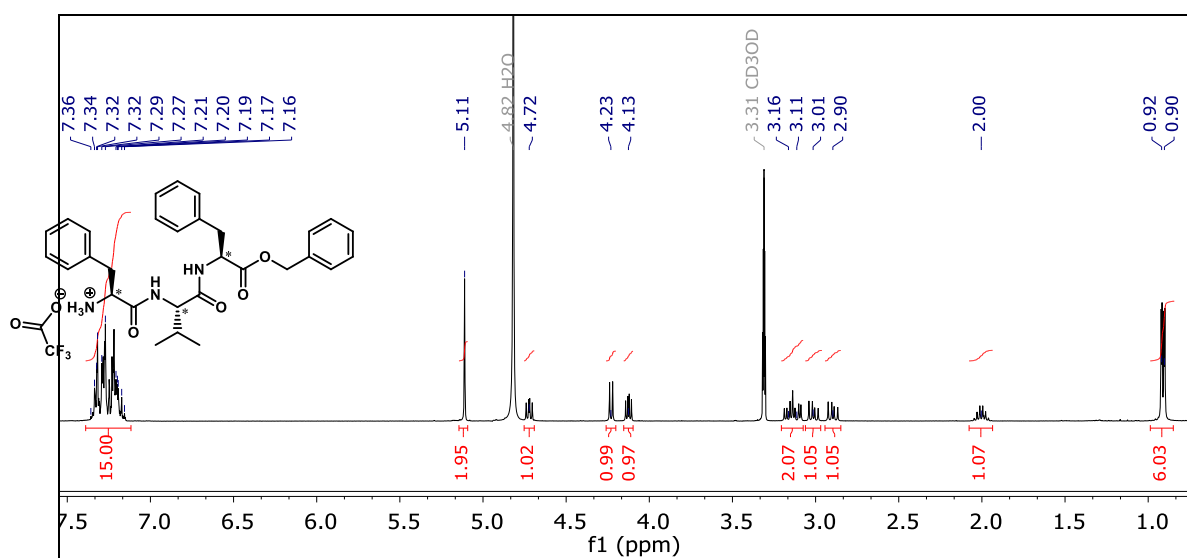
^{13}C NMR (75 MHz, CDCl_3)



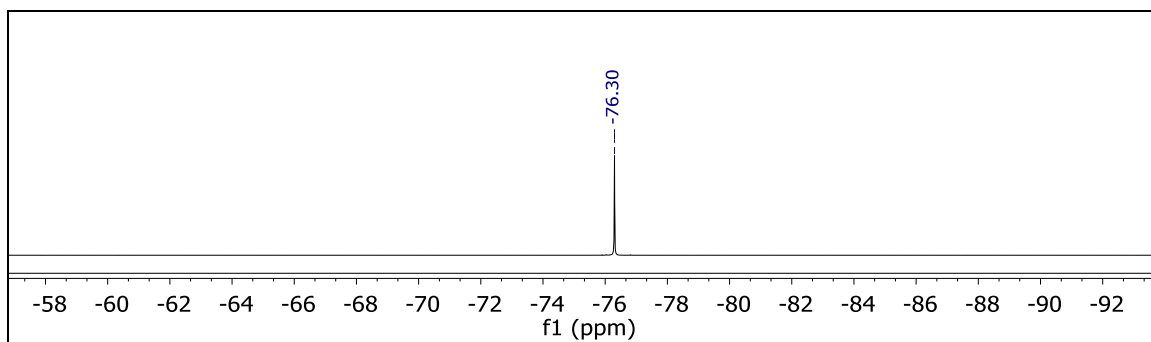
(S)-1-(((S)-1-(((S)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate

(P8L)

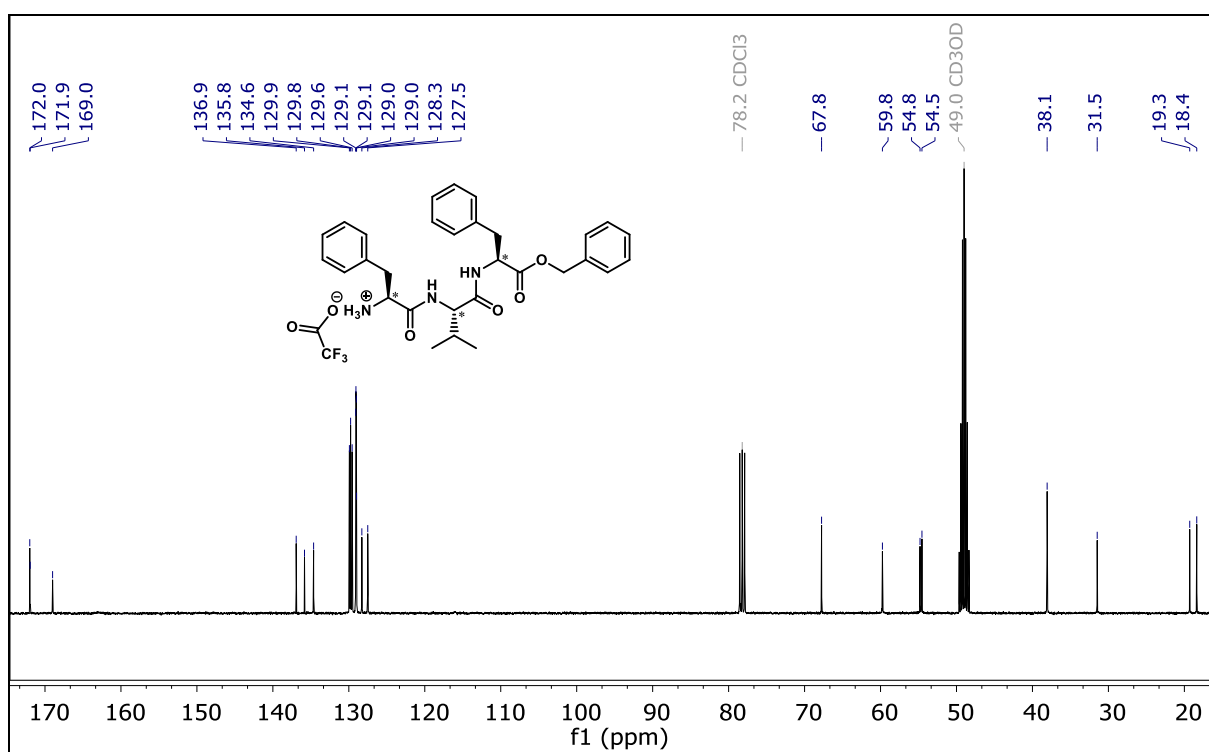
¹H NMR (400 MHz, MeOD)



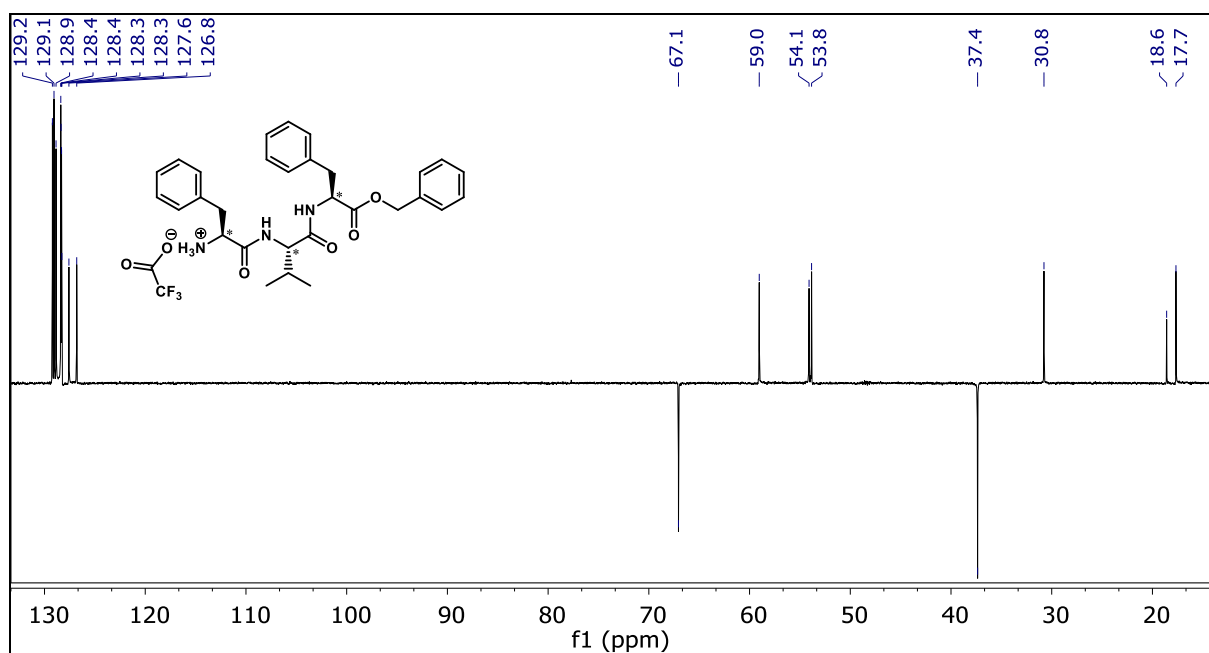
¹⁹F NMR (376 MHz, MeOD)



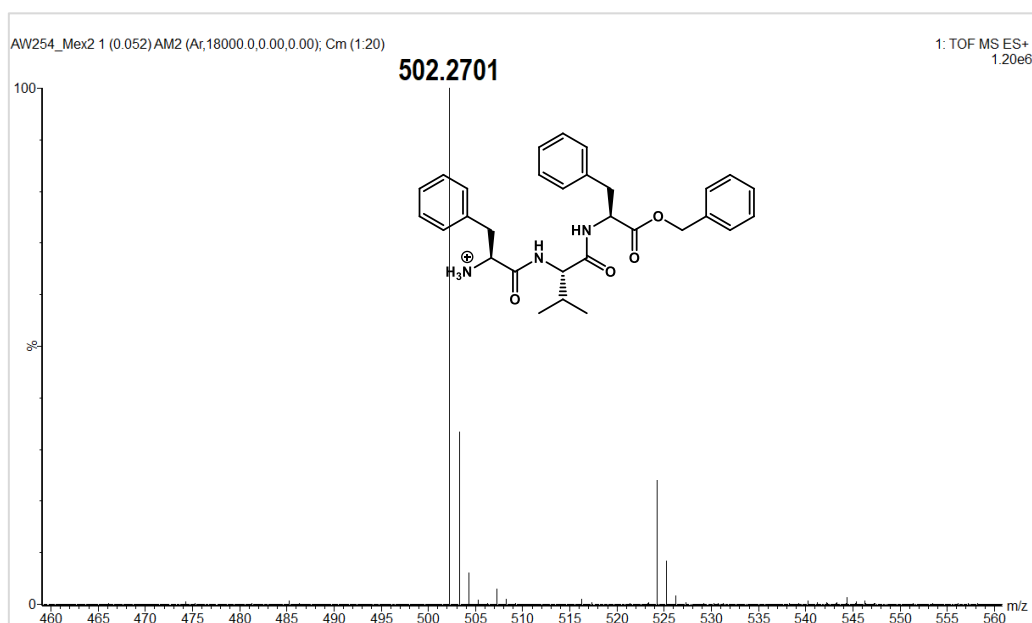
¹³C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



DEPT 135 (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))

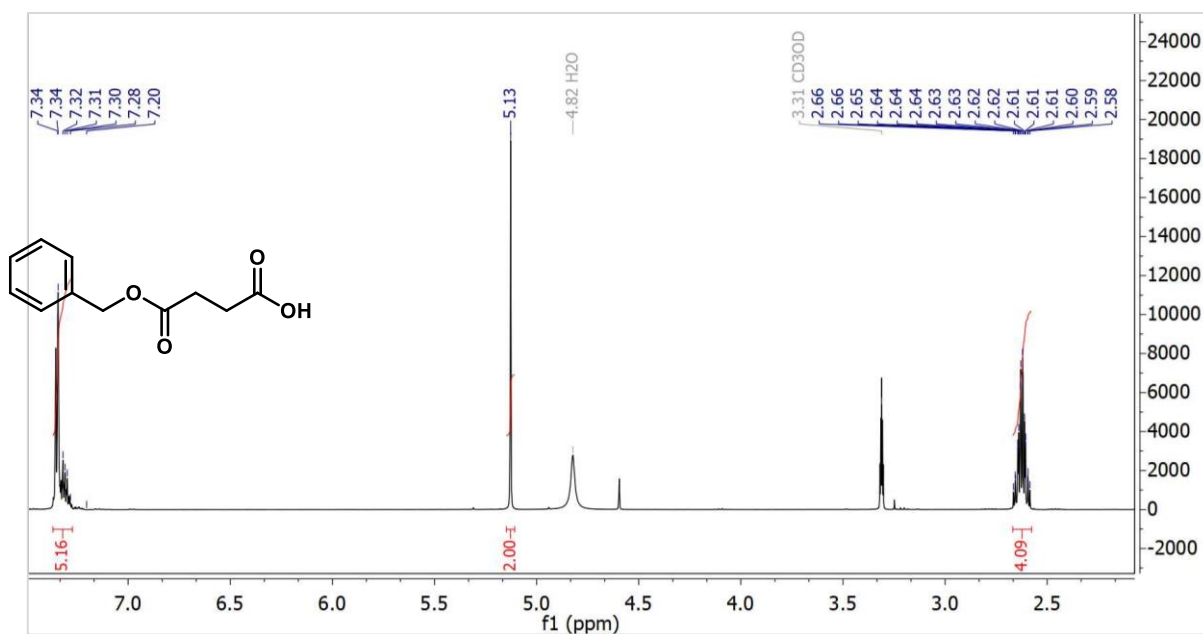


HMRS (ESI)



4-(benzyloxy)-4-oxobutanoic acid

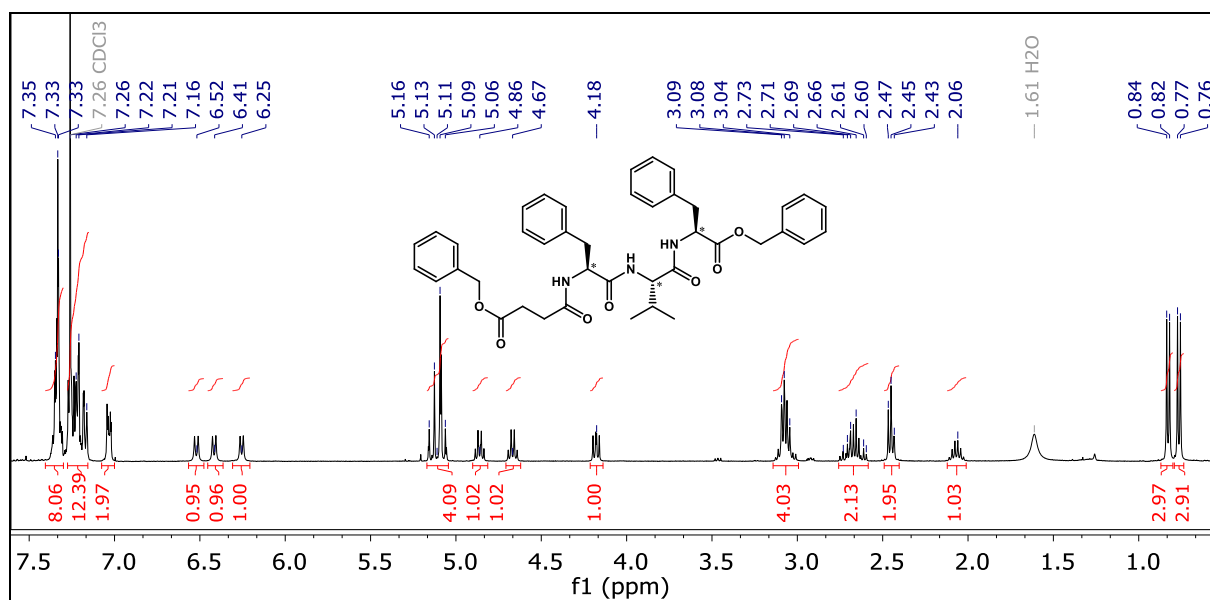
¹H NMR (400 MHz, MeOD)



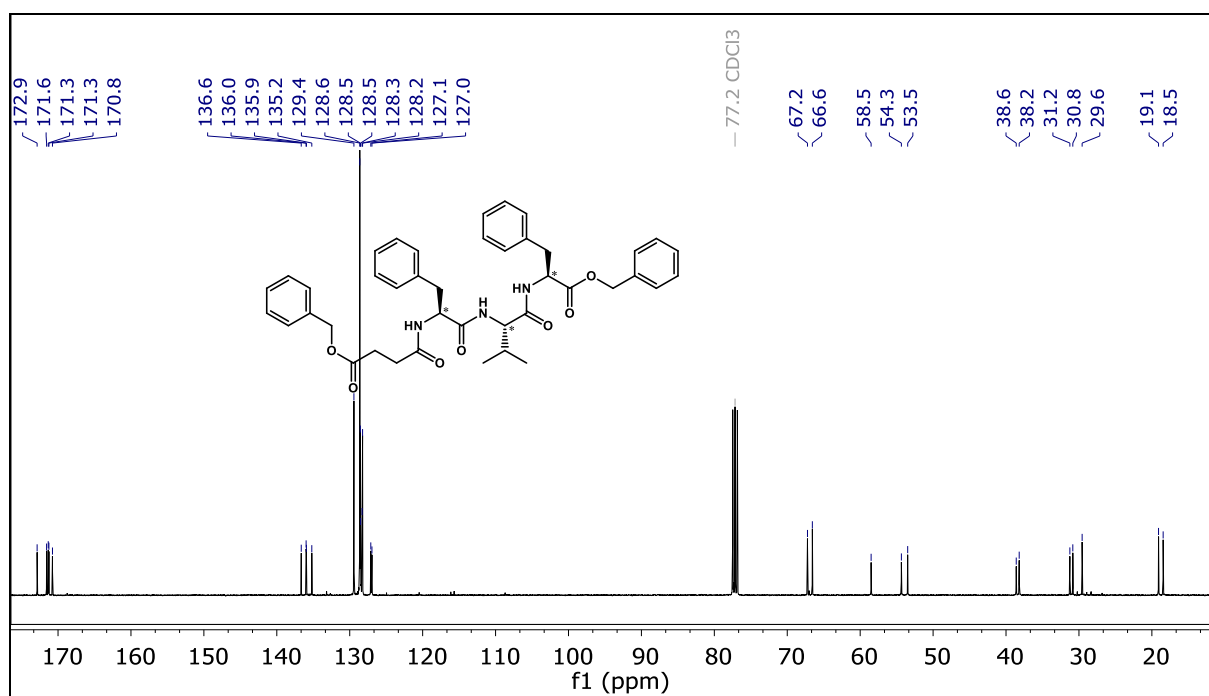
benzyl 4-(((S)-1-(((S)-1-(((S)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoate

(P9L)

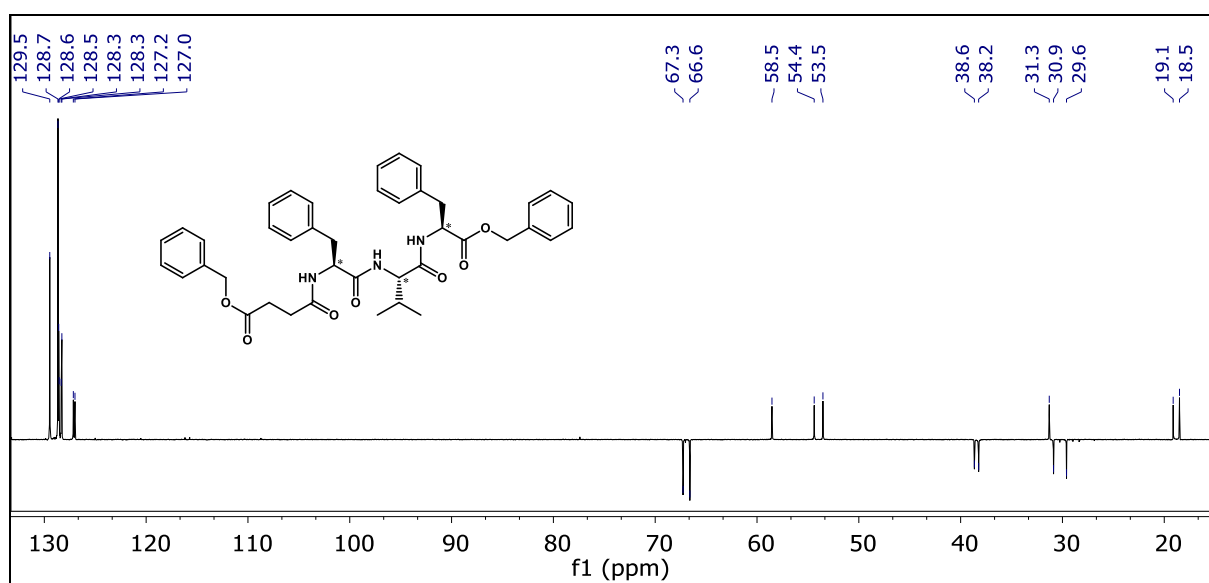
¹H NMR (400 MHz, CDCl₃)



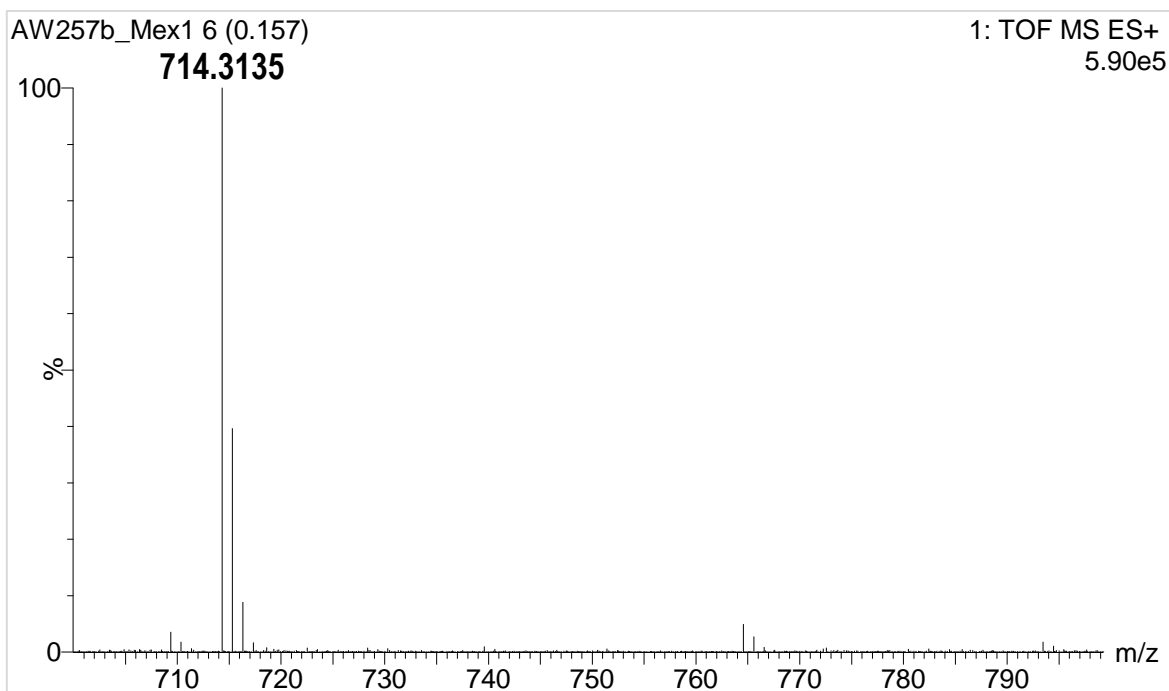
¹³C NMR (101 MHz, CDCl₃)



DEPT 135 (101 MHz, CDCl₃)

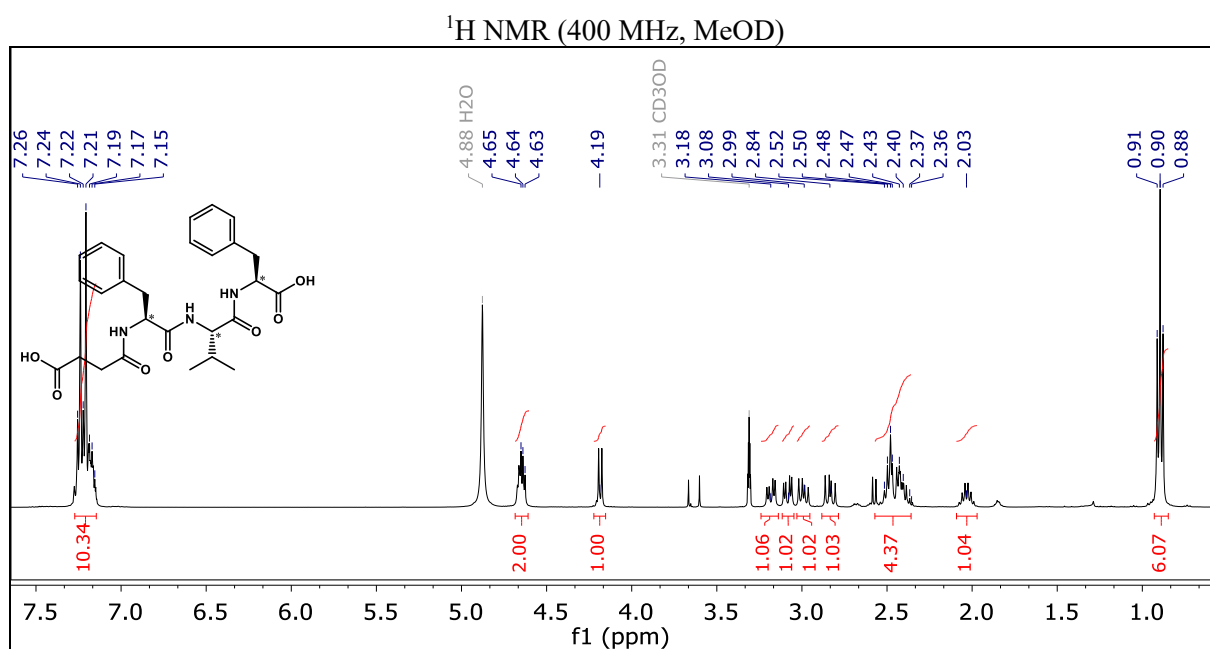


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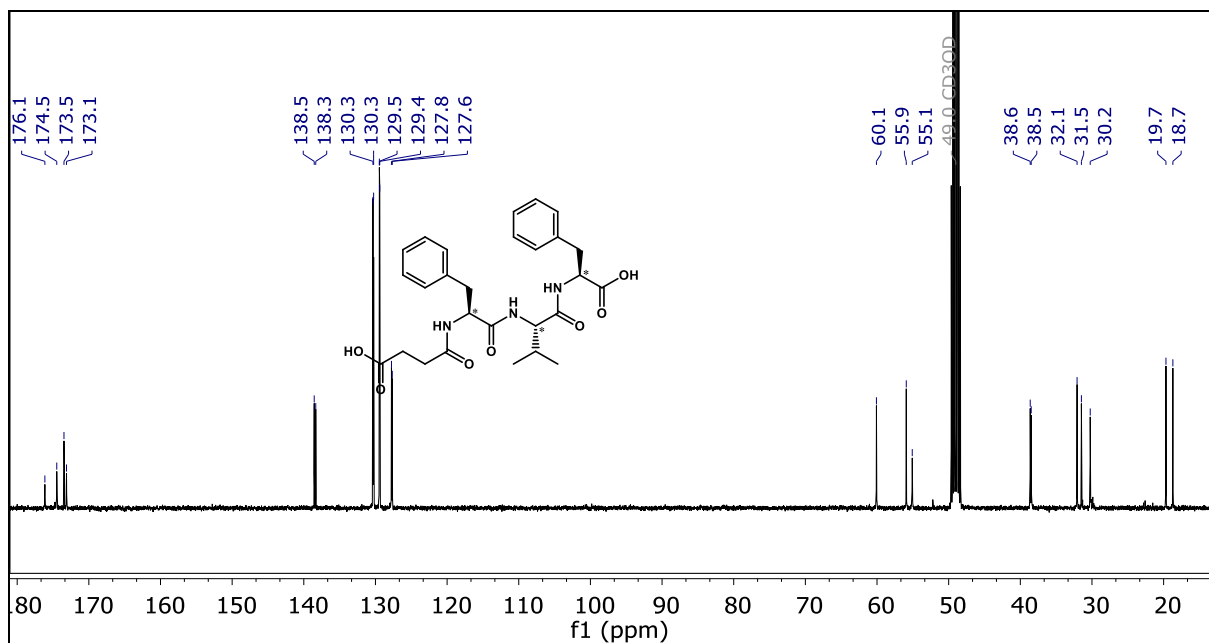


4-(((S)-1-(((S)-1-(((S)-1-carboxy-2-phenylethyl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoic acid

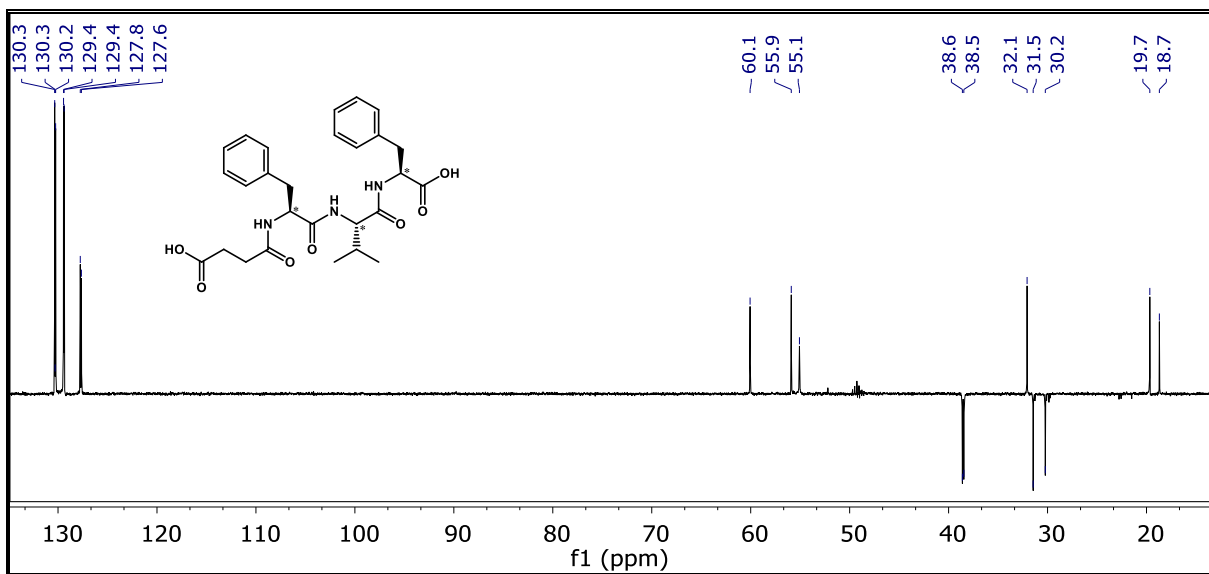
(P10L)



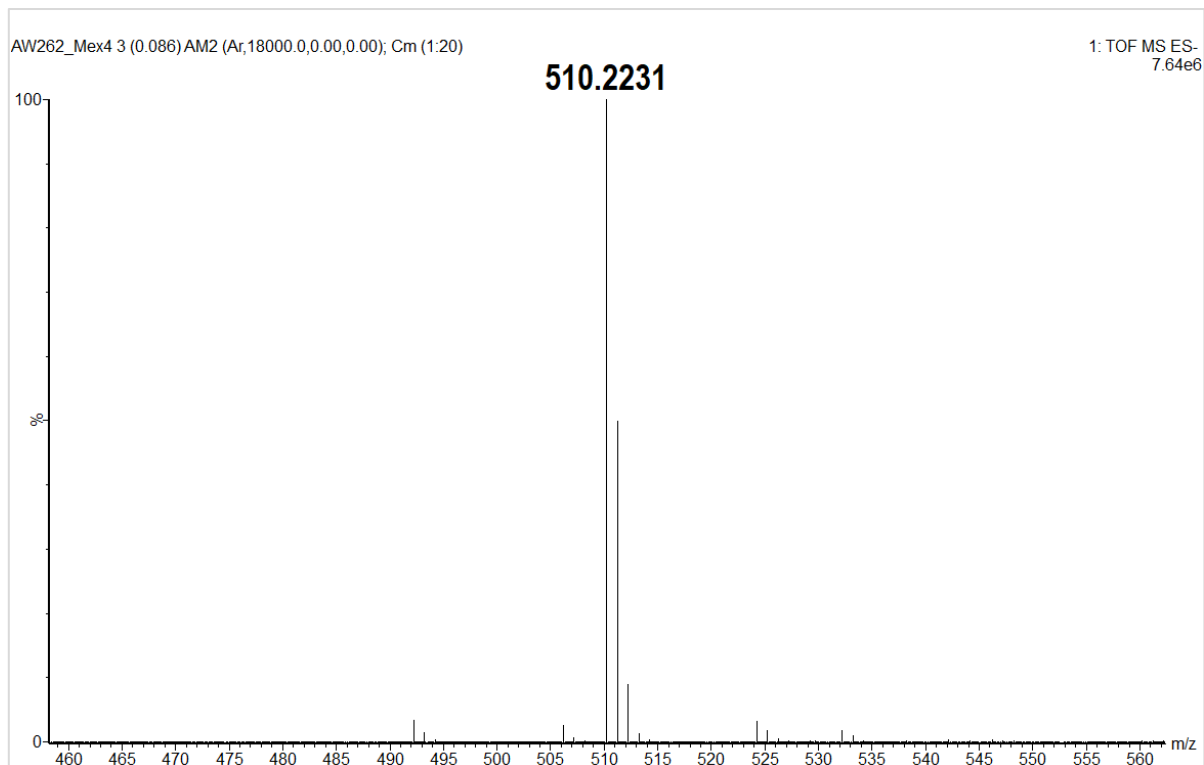
¹³C NMR (101 MHz, MeOD)



DEPT 135 (101 MHz, MeOD)



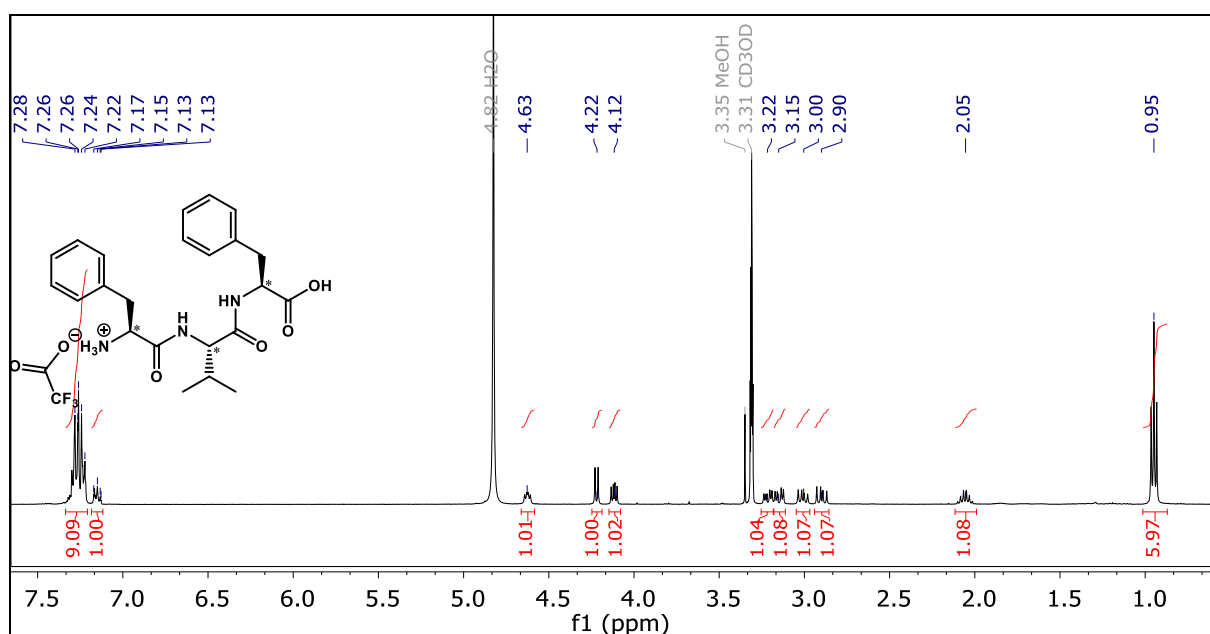
HRMS (ESI)



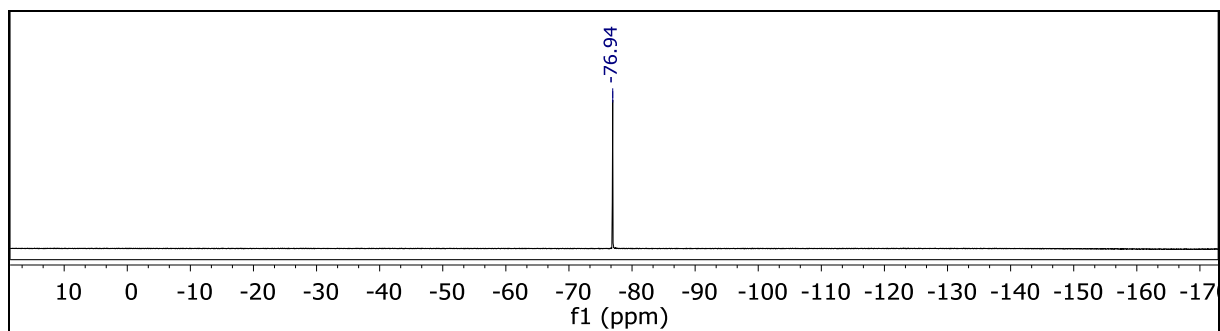
(S)-1-(((S)-1-(((S)-1-carboxy-2-phenylethyl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate

(P11L)

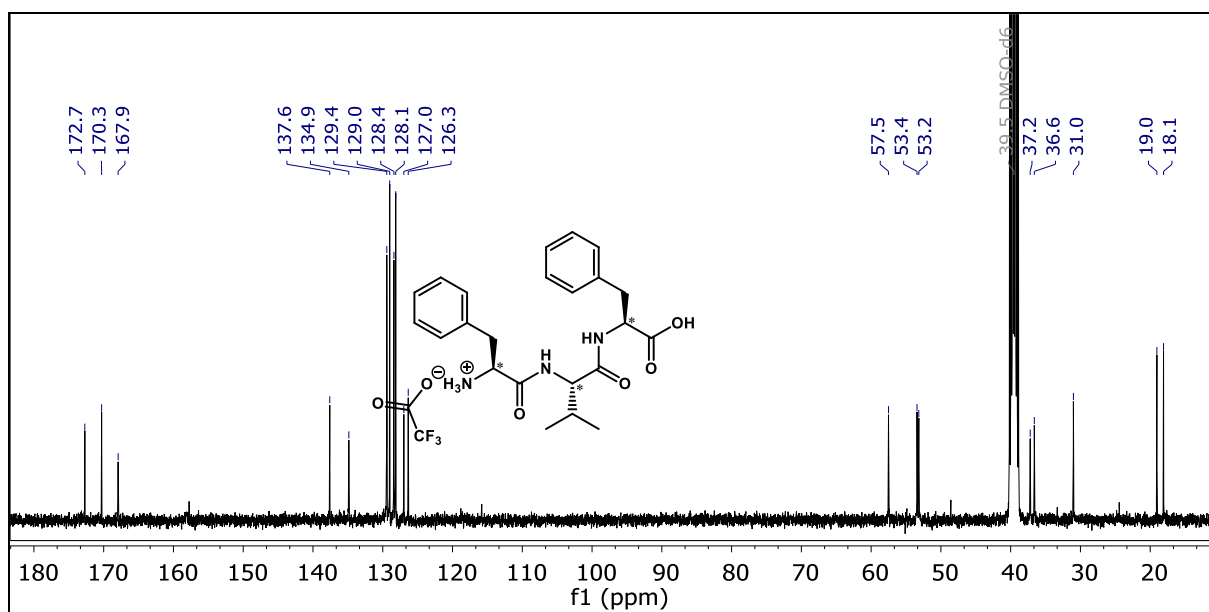
^1H NMR (400 MHz, MeOD)



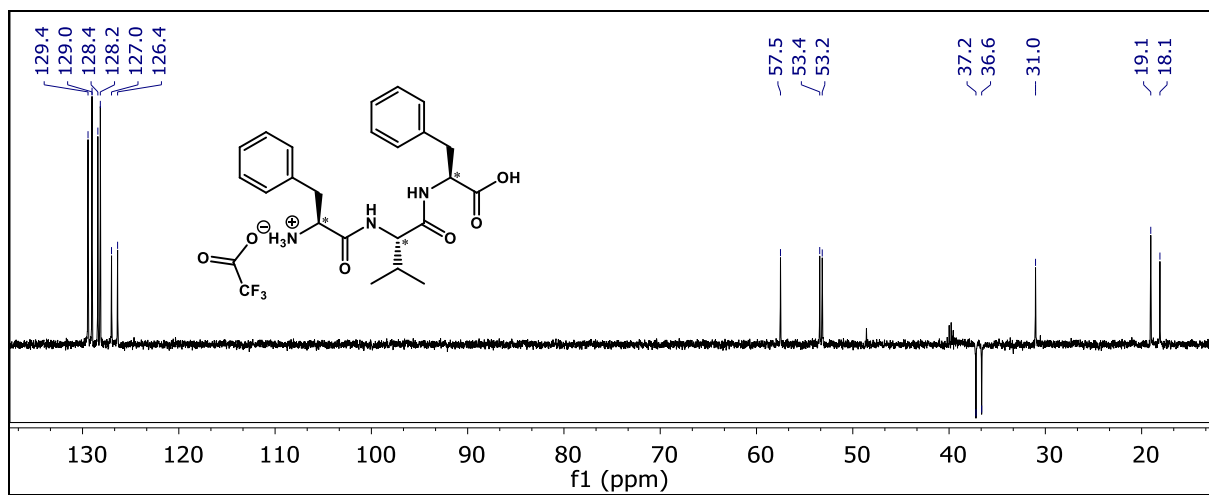
^{19}F NMR (376 MHz, MeOD)



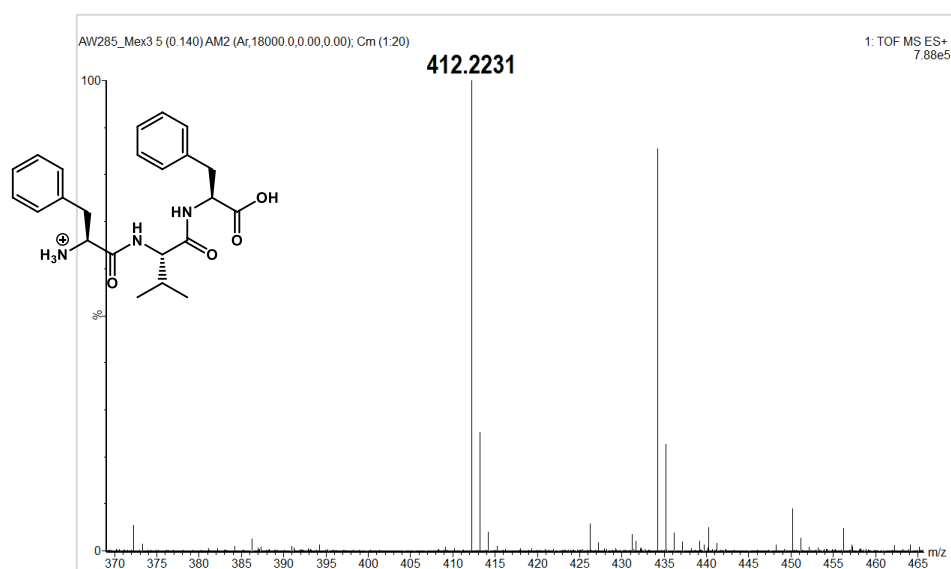
¹³C NMR (101 MHz, DMSO)



DEPT 135 (101 MHz, DMSO)



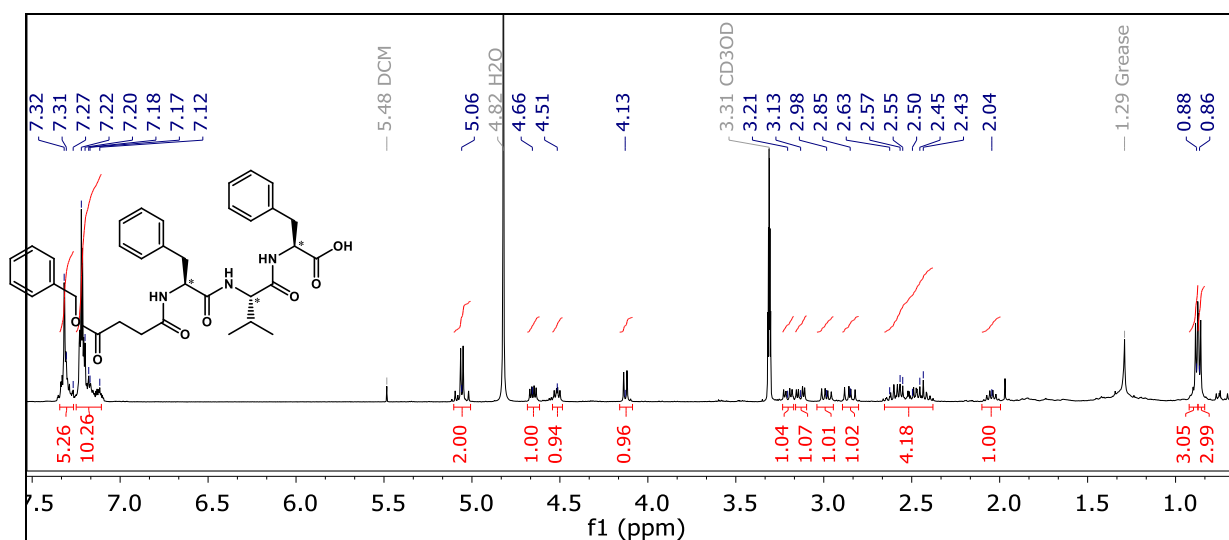
HRMS (ESI)



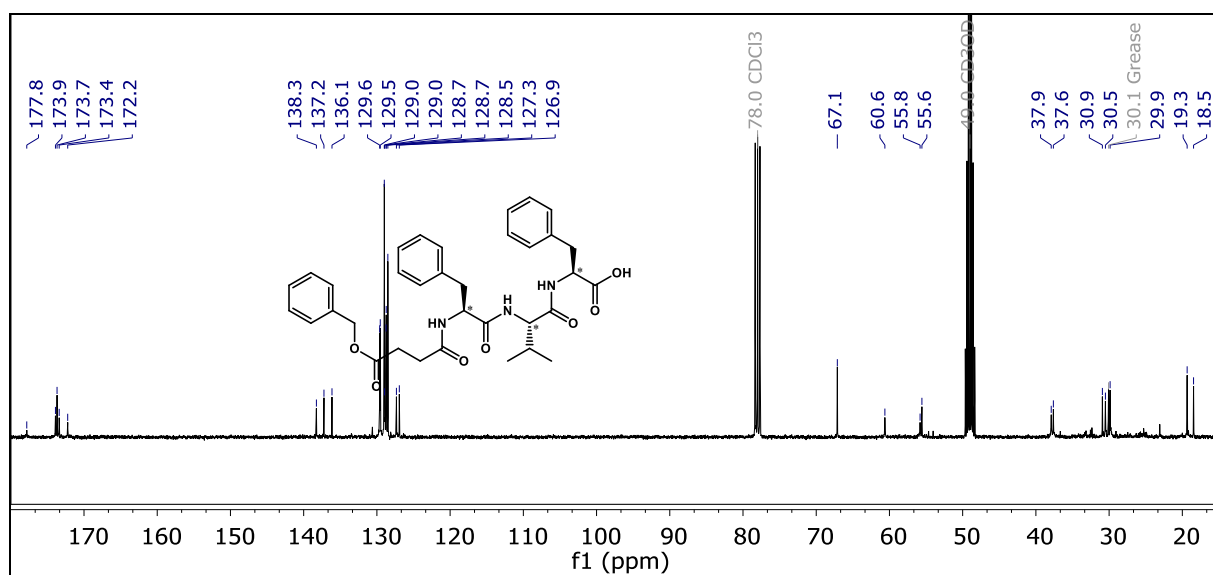
(4-(benzyloxy)-4-oxobutanoyl)-L-phenylalanyl-L-valyl-L-phenylalanine

(P12L)

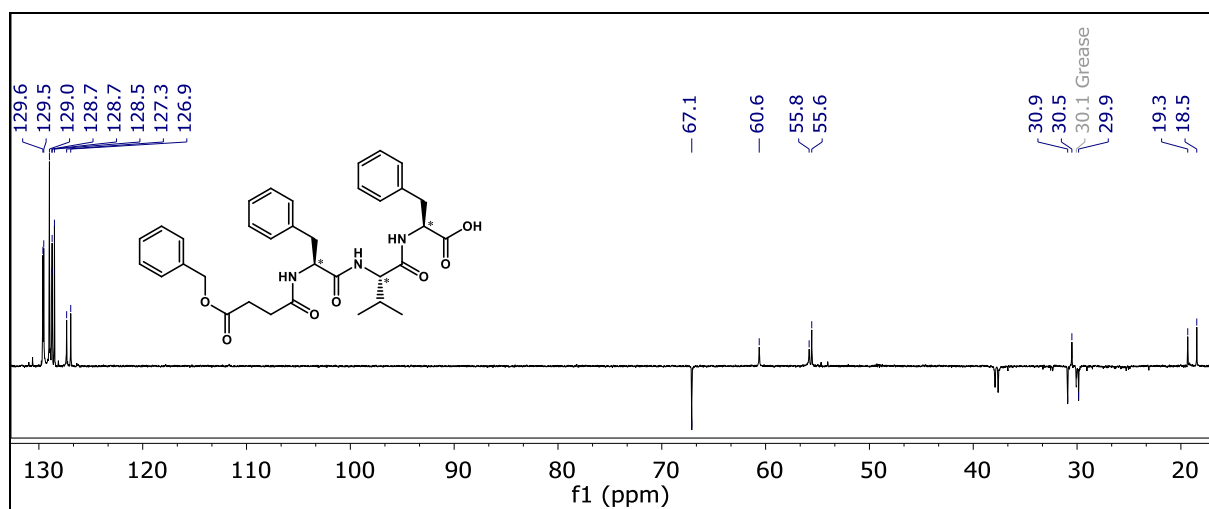
¹H NMR (400 MHz, MeOD)



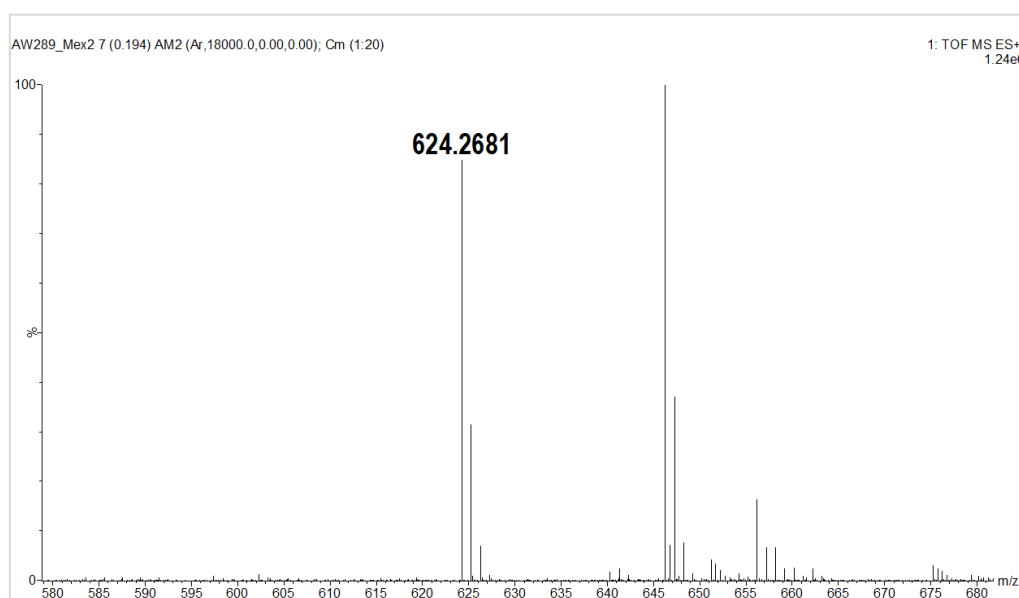
¹³C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



DEPT 135 (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



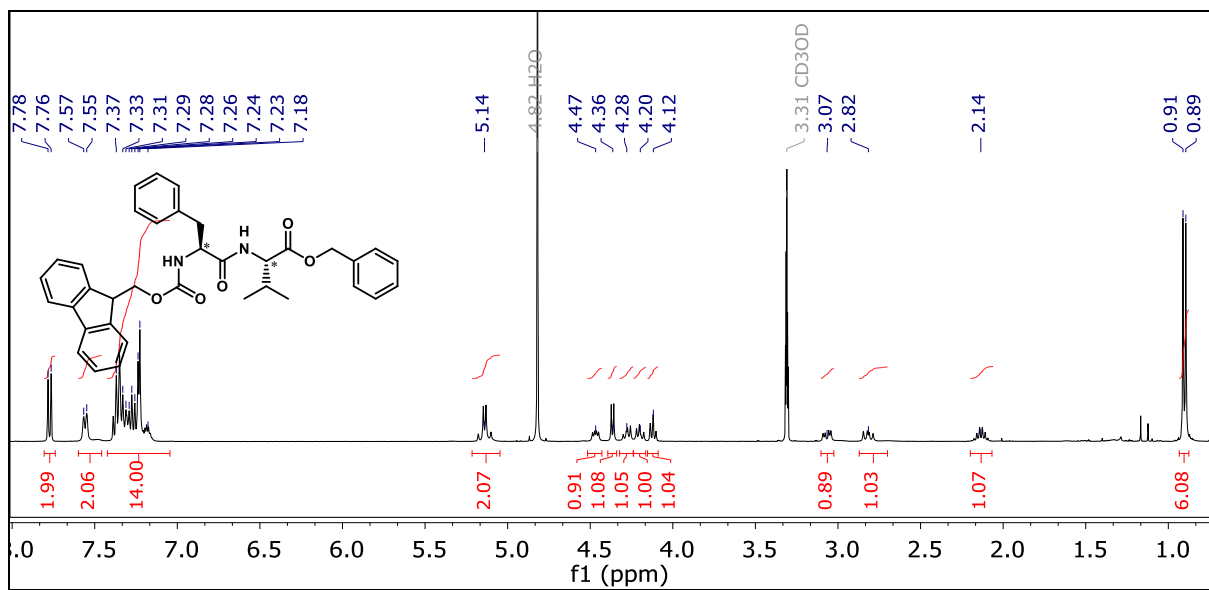
HRMS (ESI)



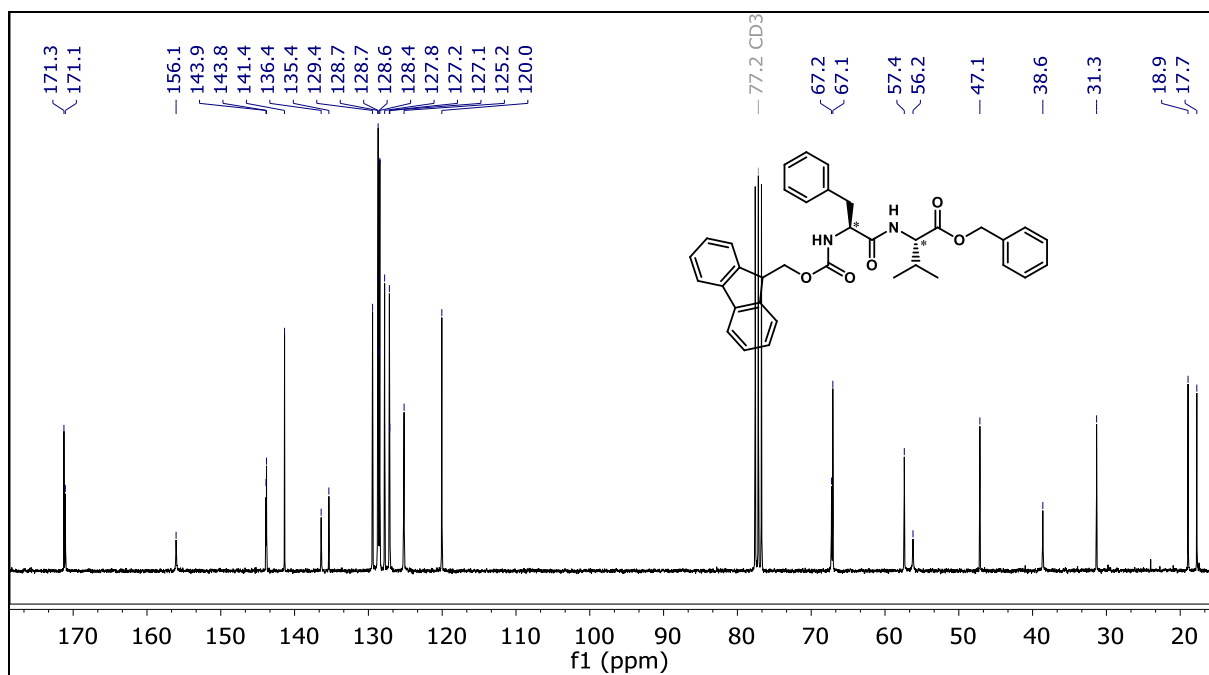
benzyl (((9H-fluoren-9-yl)methoxy)carbonyl)-L-phenylalanyl-L-valinate

(P14L)

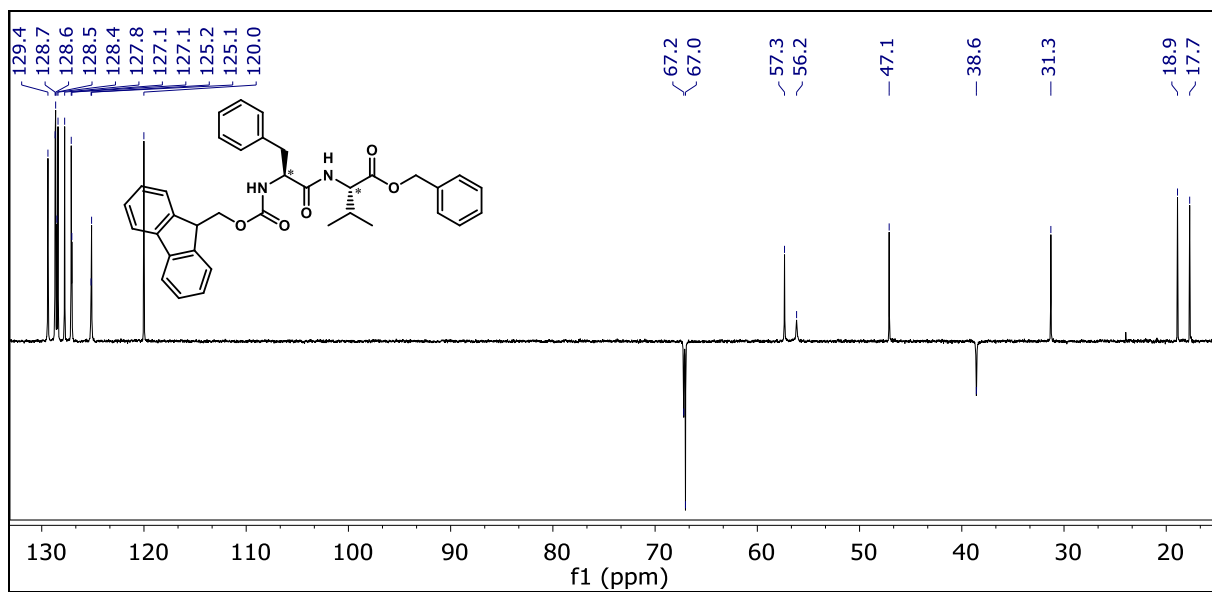
¹H NMR (400 MHz, MeOD)



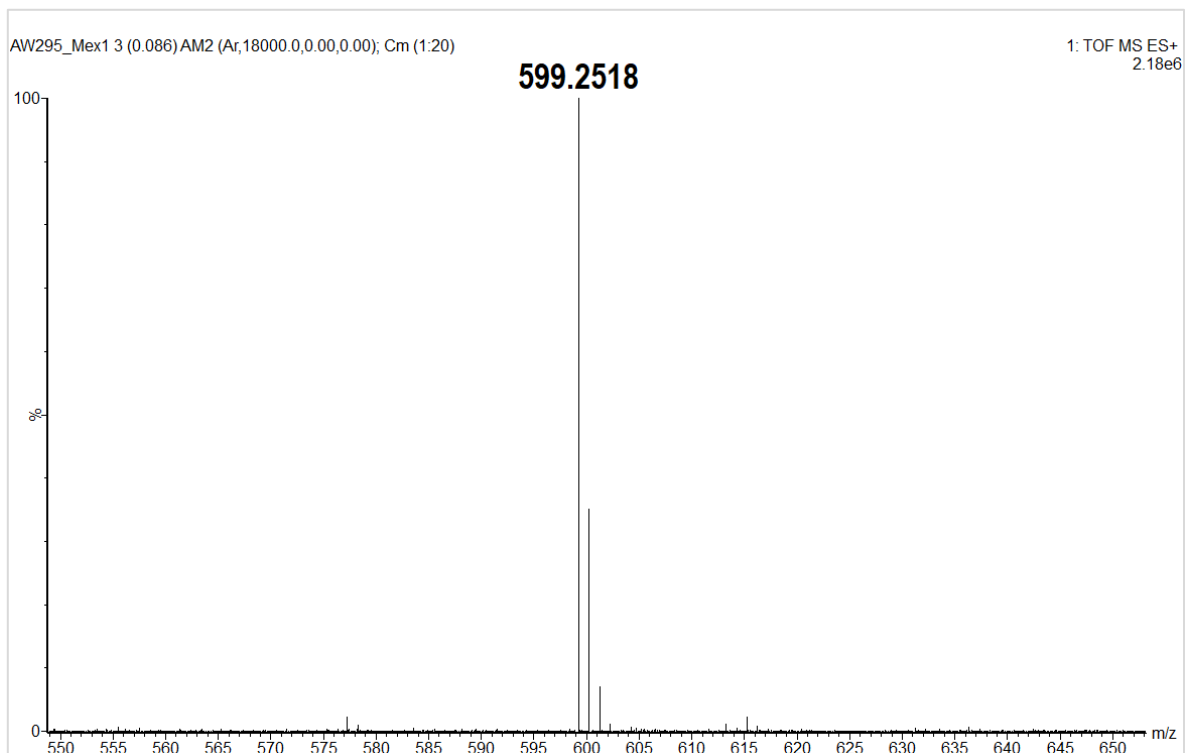
¹³C NMR (75 MHz, CDCl₃)



DEPT 135 (75 MHz, CDCl₃)



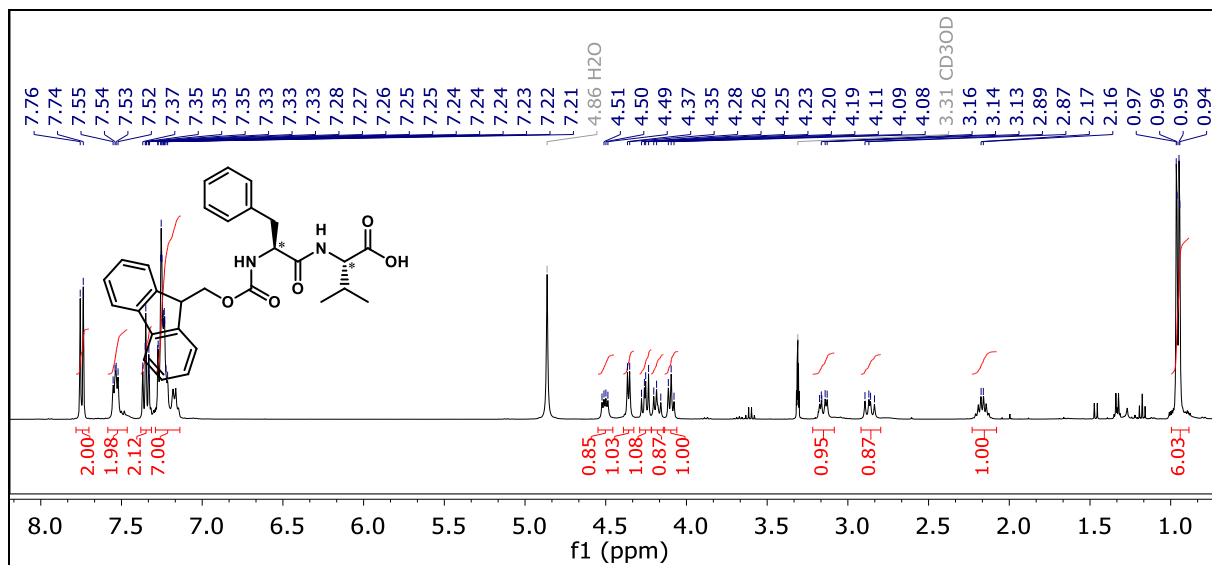
HMRS (ESI)



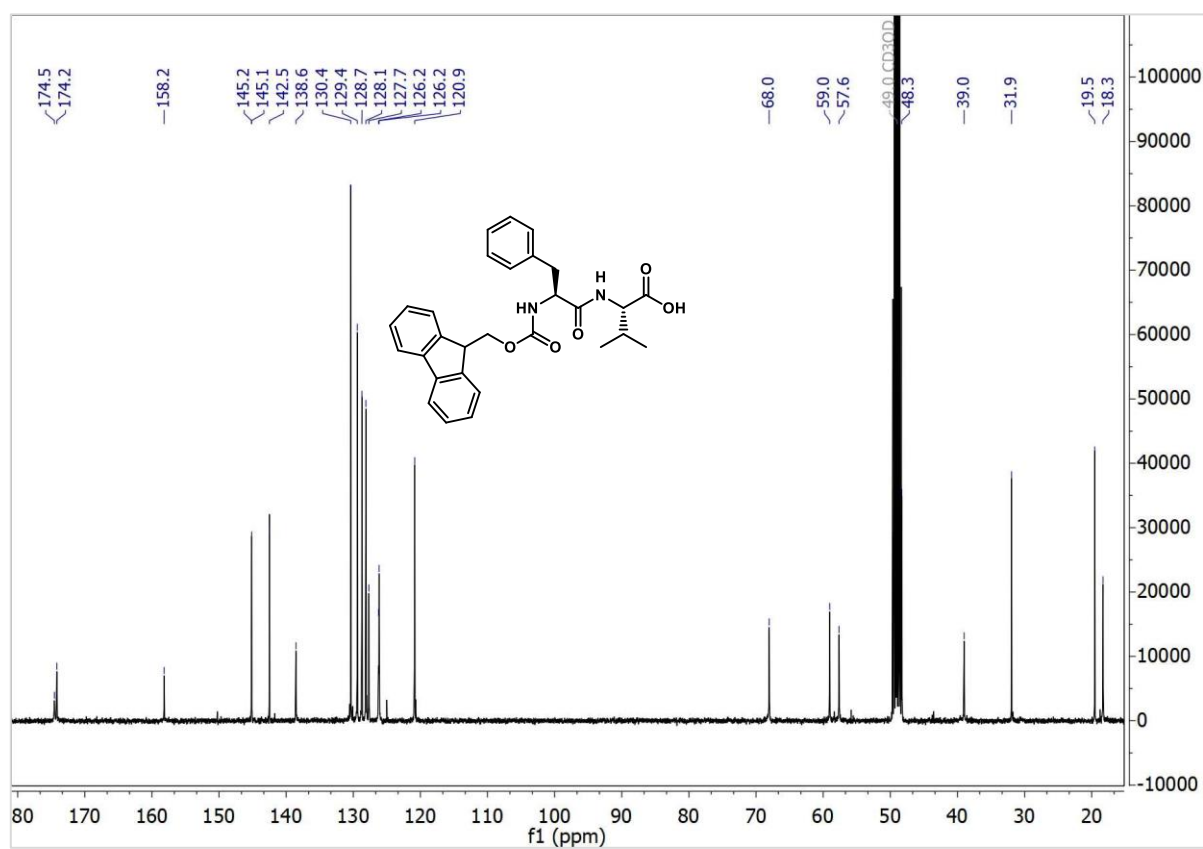
(((9H-fluoren-9-yl)methoxy)carbonyl)-L-phenylalanyl-L-valine

(P15L)

^1H NMR (400 MHz, MeOD)



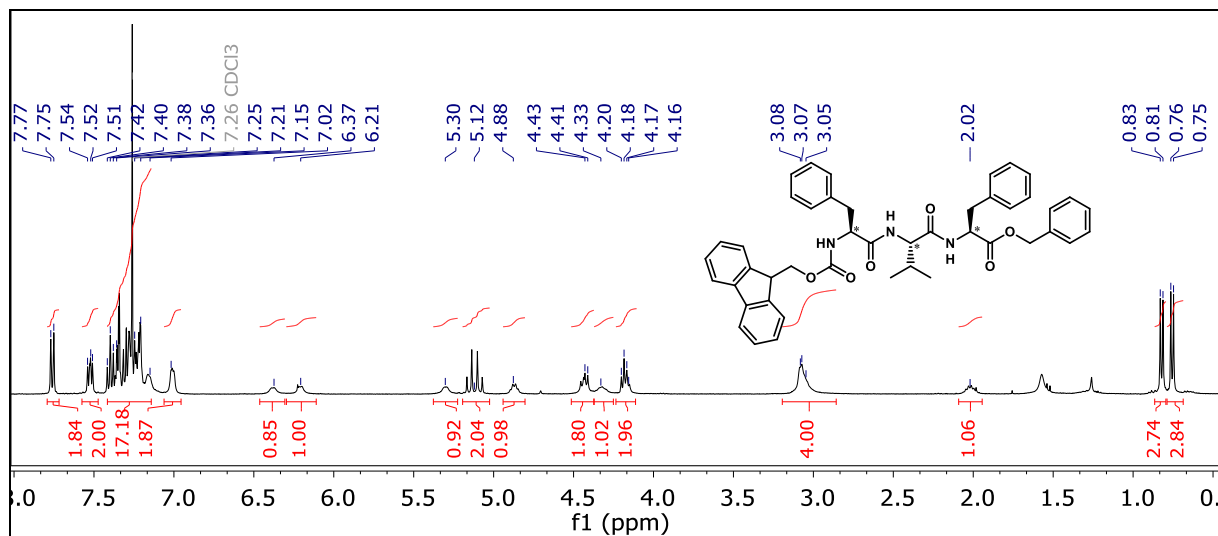
^{13}C NMR (101 MHz, MeOD)



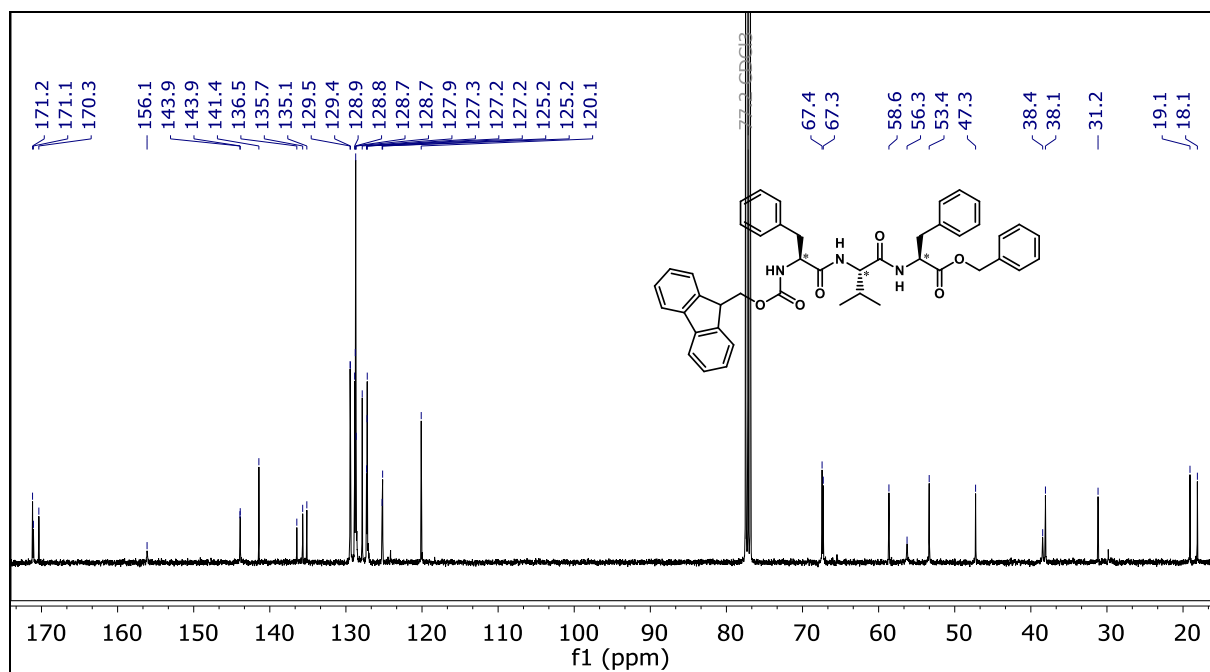
benzyl (((9H-fluoren-9-yl)methoxy)carbonyl)-L-phenylalanyl-L-valyl-L-phenylalaninate

(P16L)

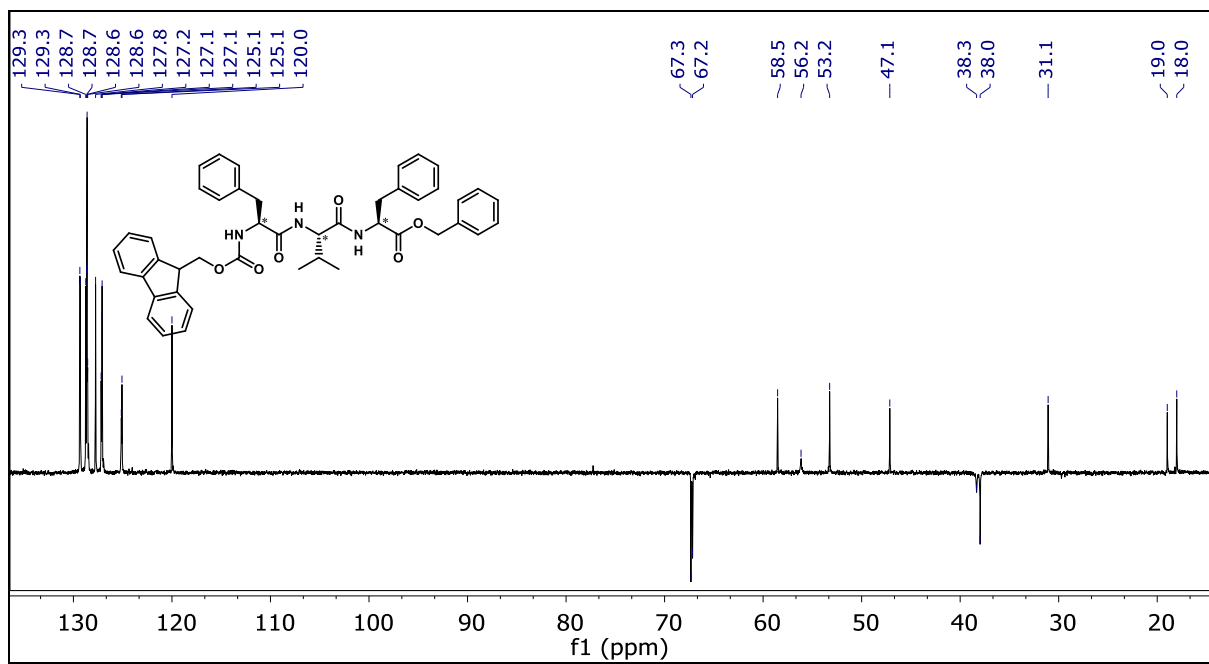
^1H NMR (400 MHz, CDCl_3)



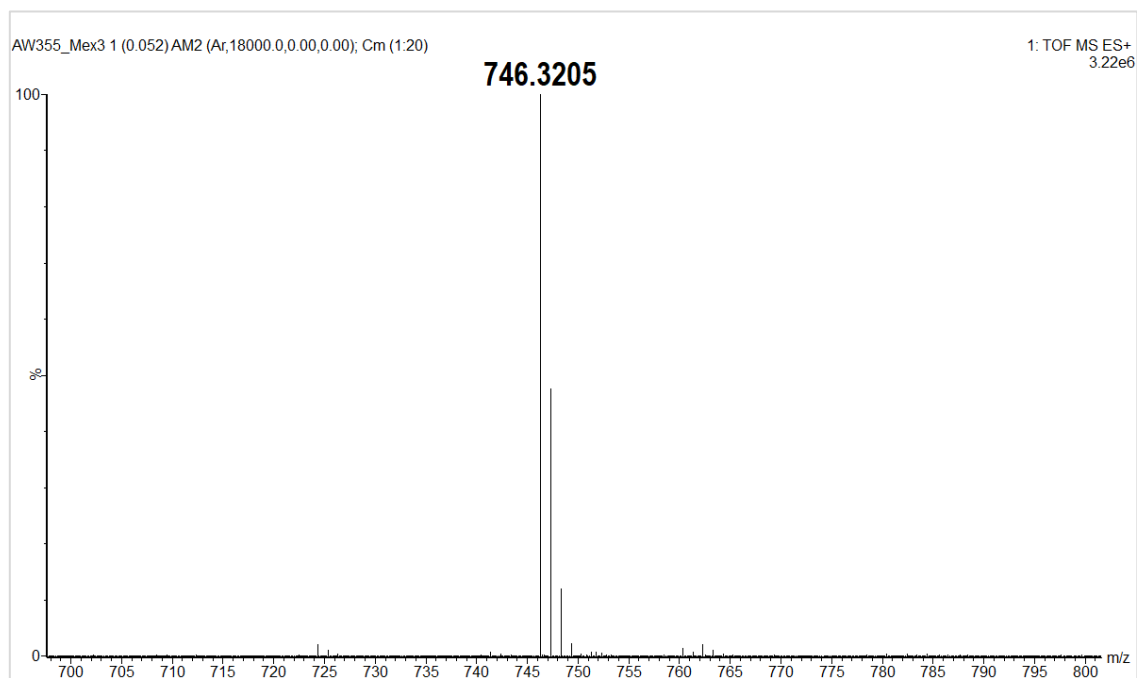
^{13}C NMR (101 MHz, CDCl_3)



DEPT 135 (101 MHz, CDCl_3)



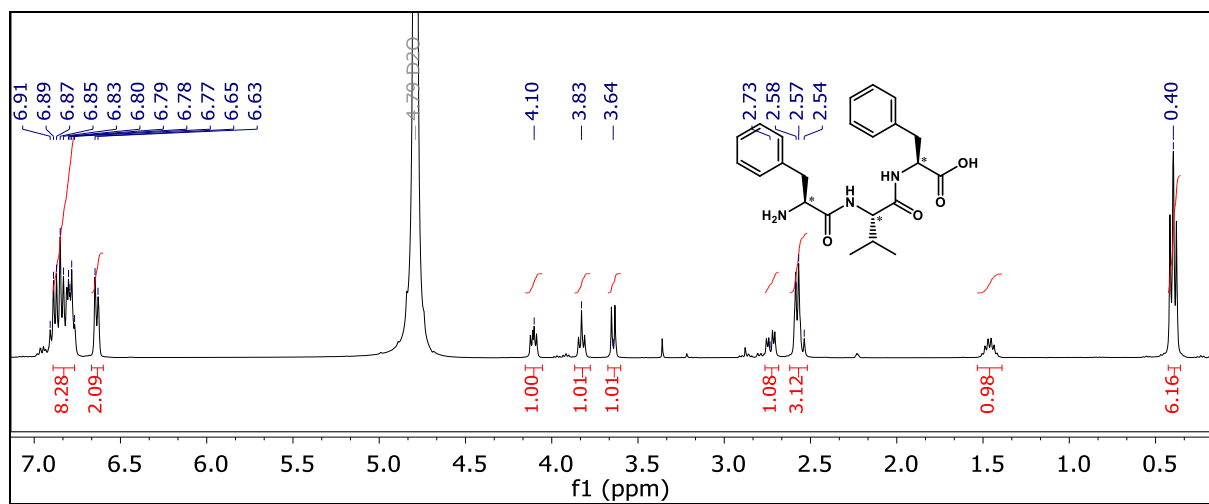
HRMS (ESI)



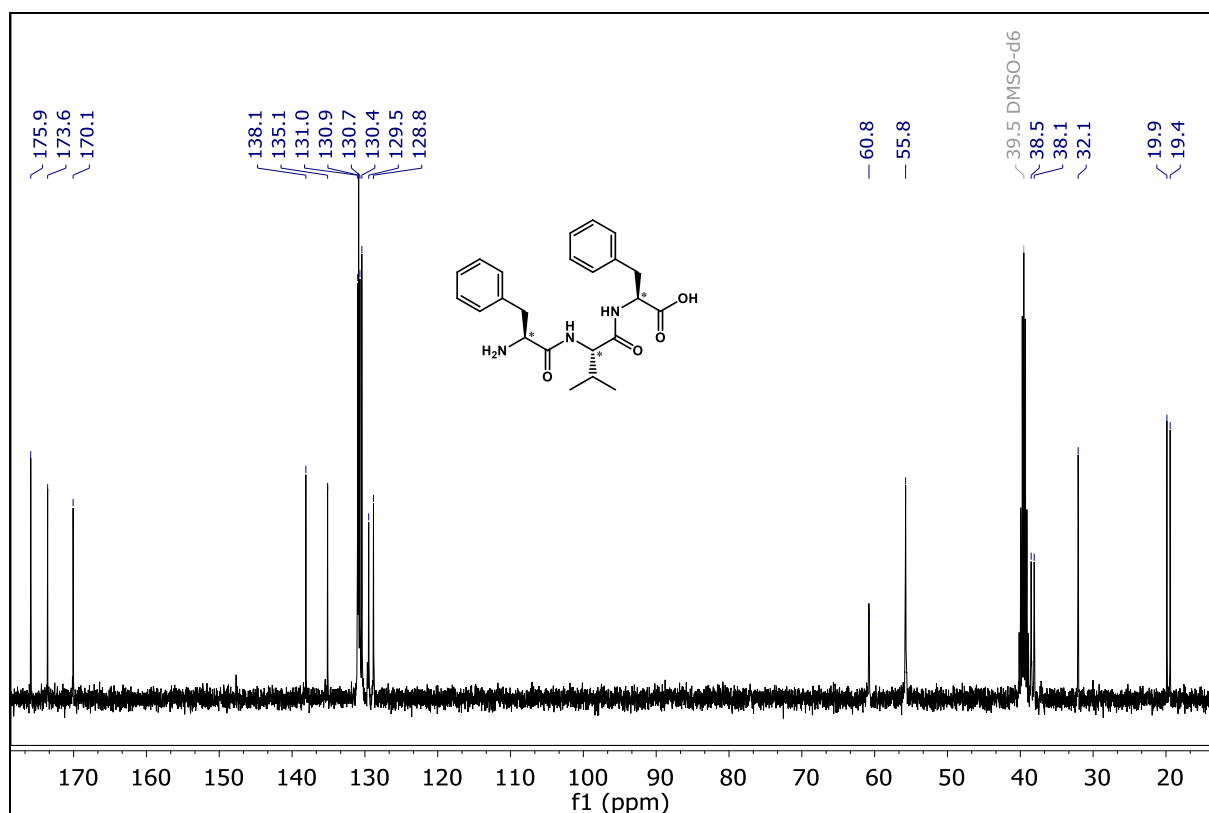
L-phenylalanyl-L-valyl-L-phenylalanine

(P18L)

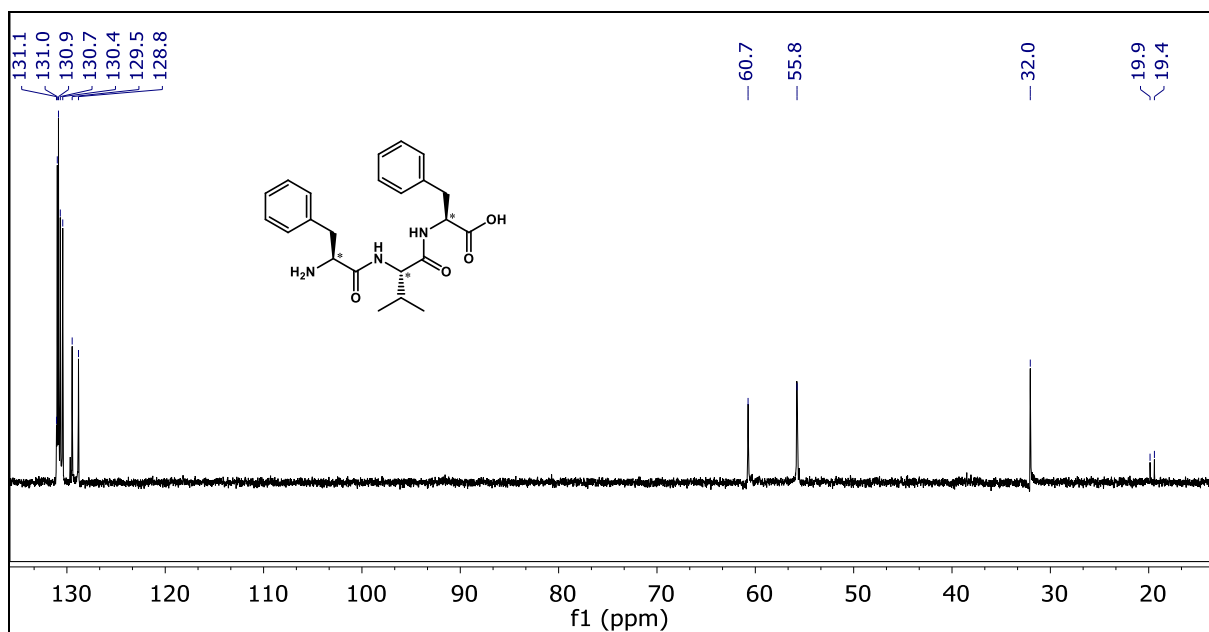
^1H NMR (400 MHz, D_2O)



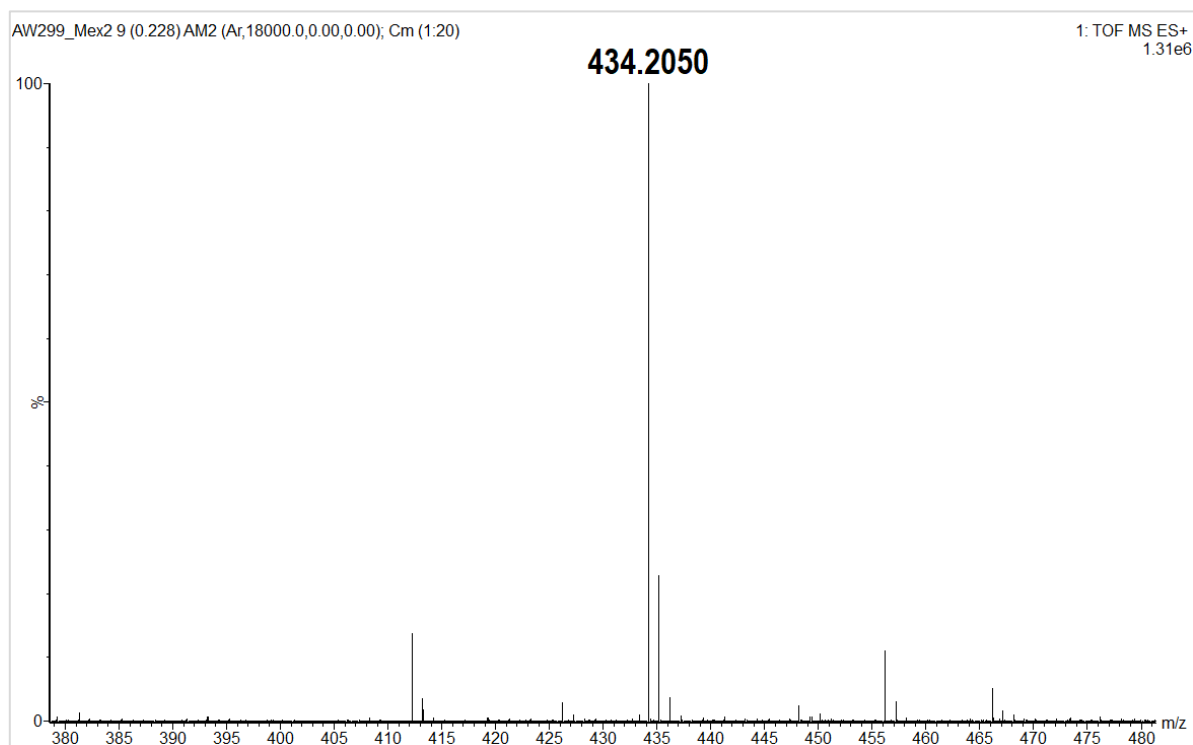
^{13}C NMR (101 MHz, D_2O -DMSO, 5% DCI)



DEPT 135 (101 MHz, D₂O-DMSO, 5% DCl)



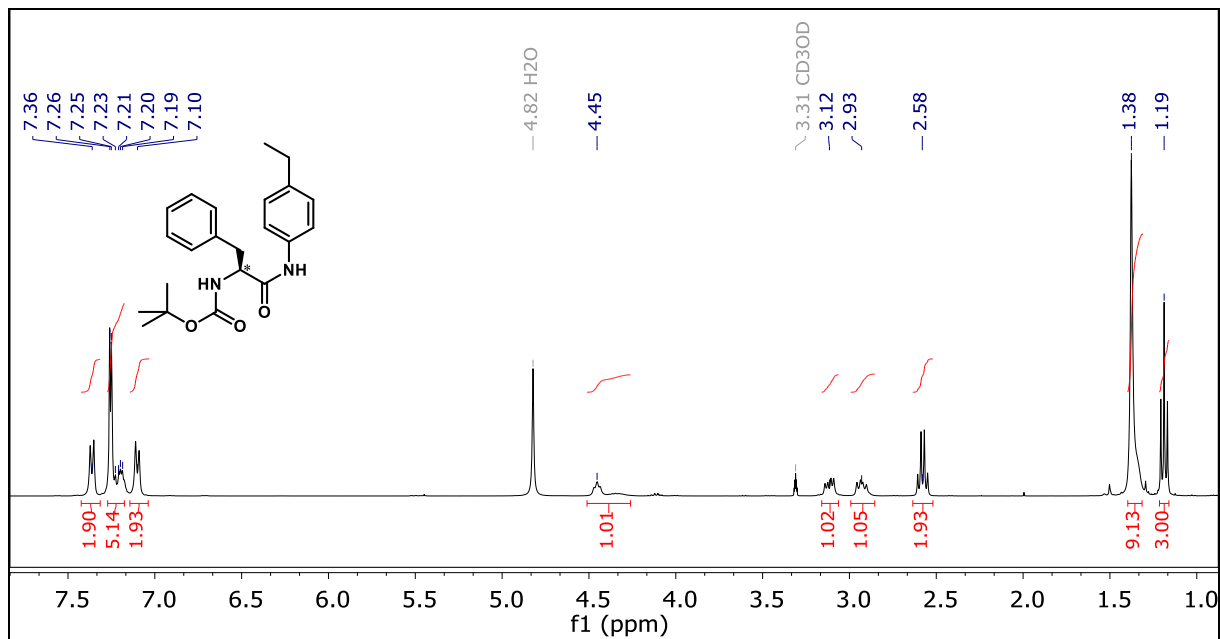
HMRS (ESI)



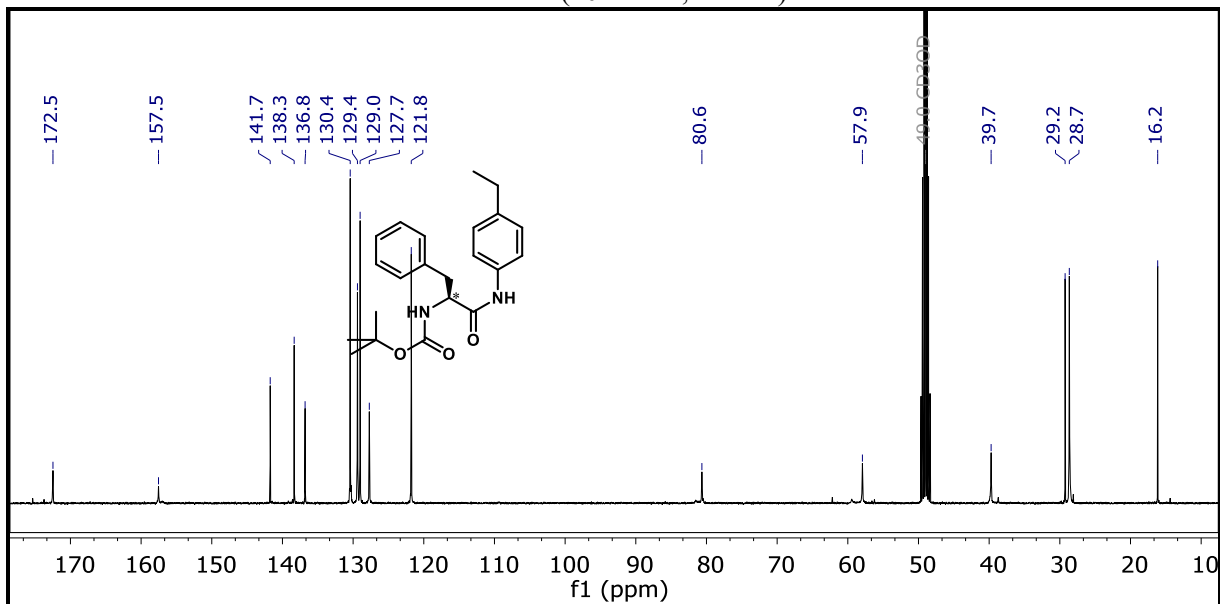
tert-butyl(S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate

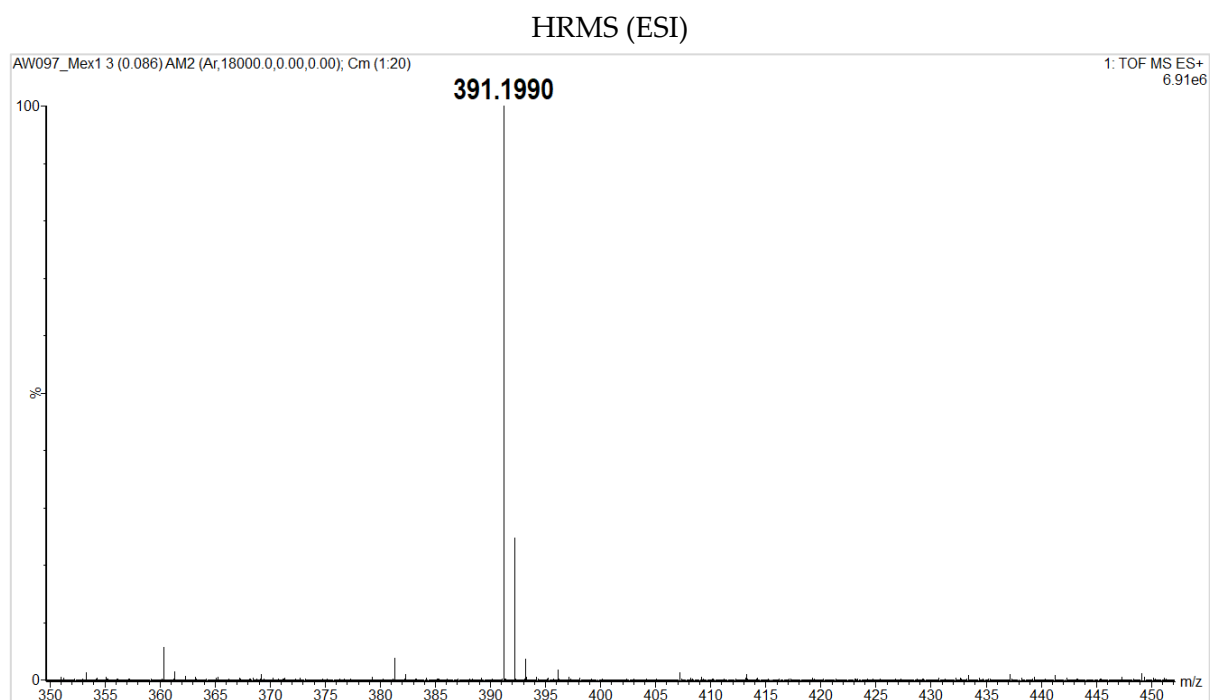
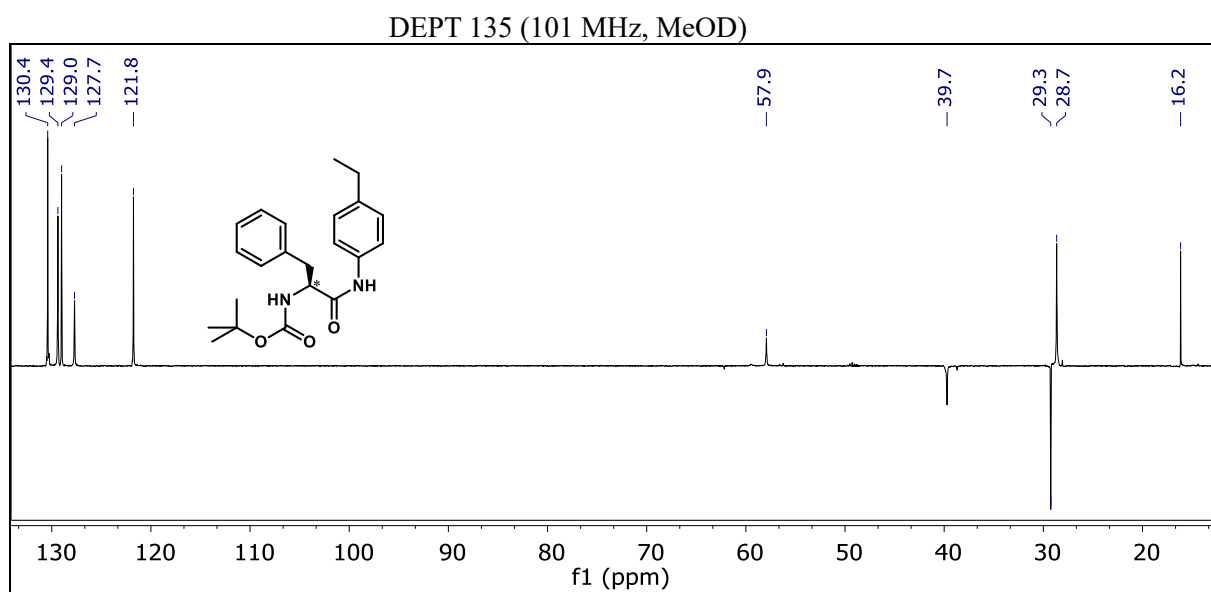
(P19L)

^1H NMR (400 MHz, MeOD)



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

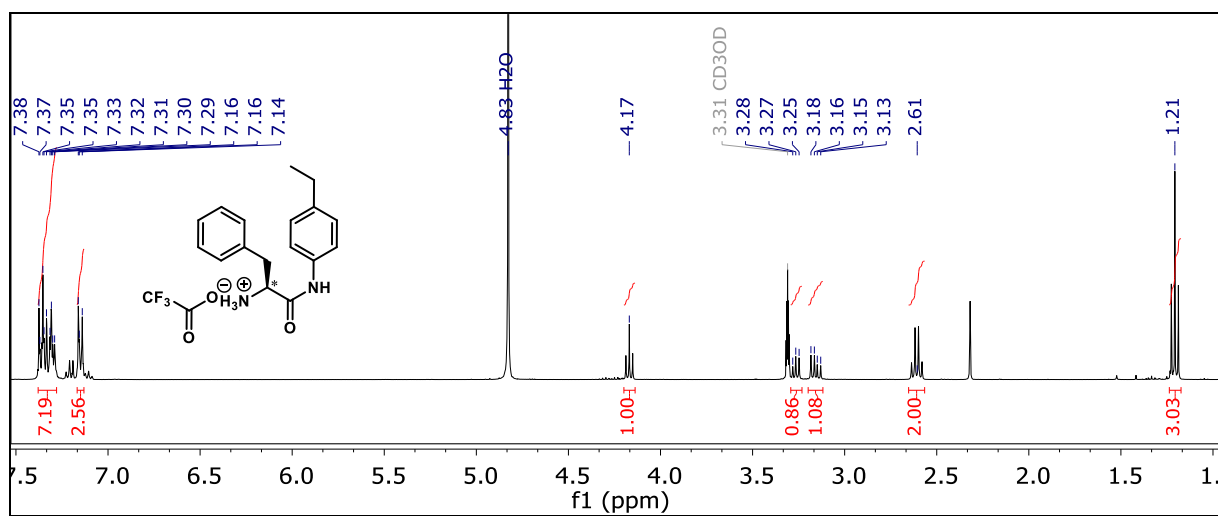




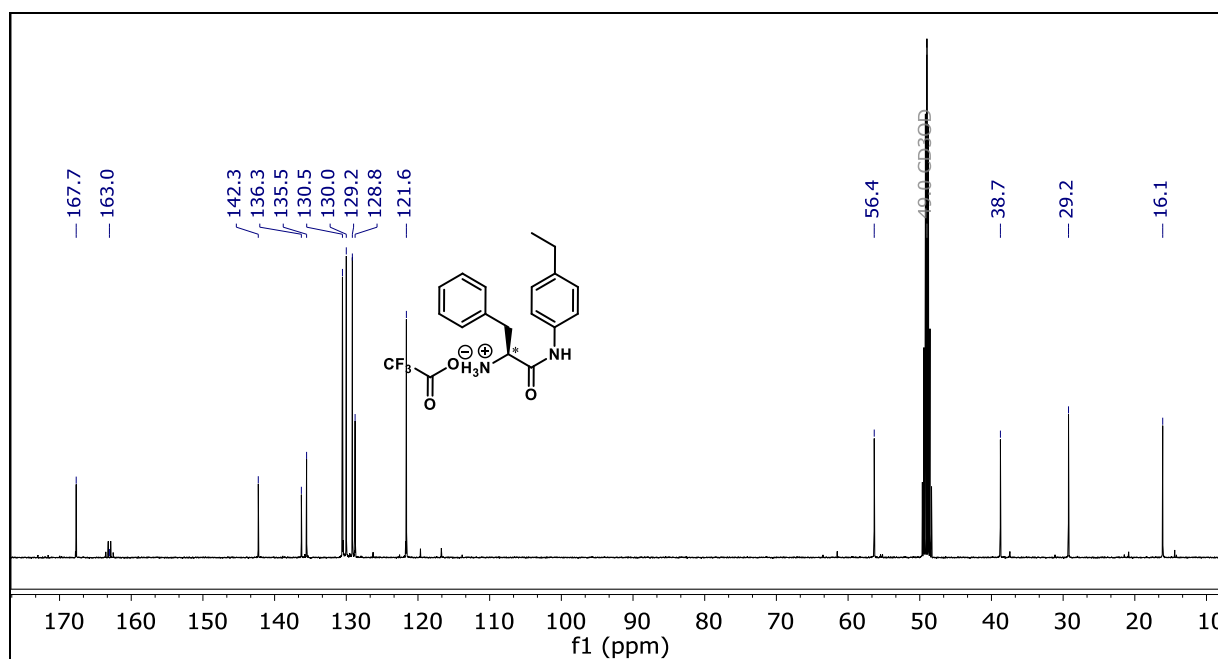
(S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate

(P20L)

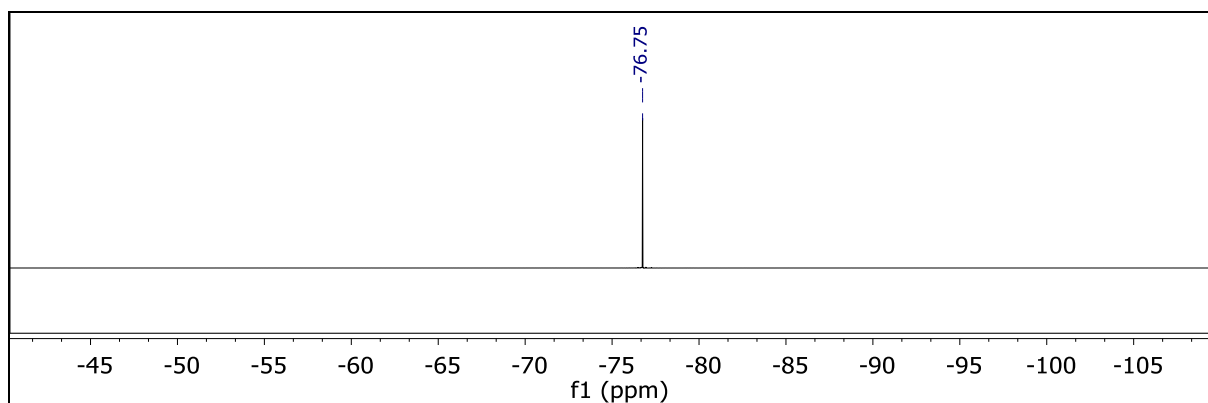
^1H NMR (400 MHz, MeOD)



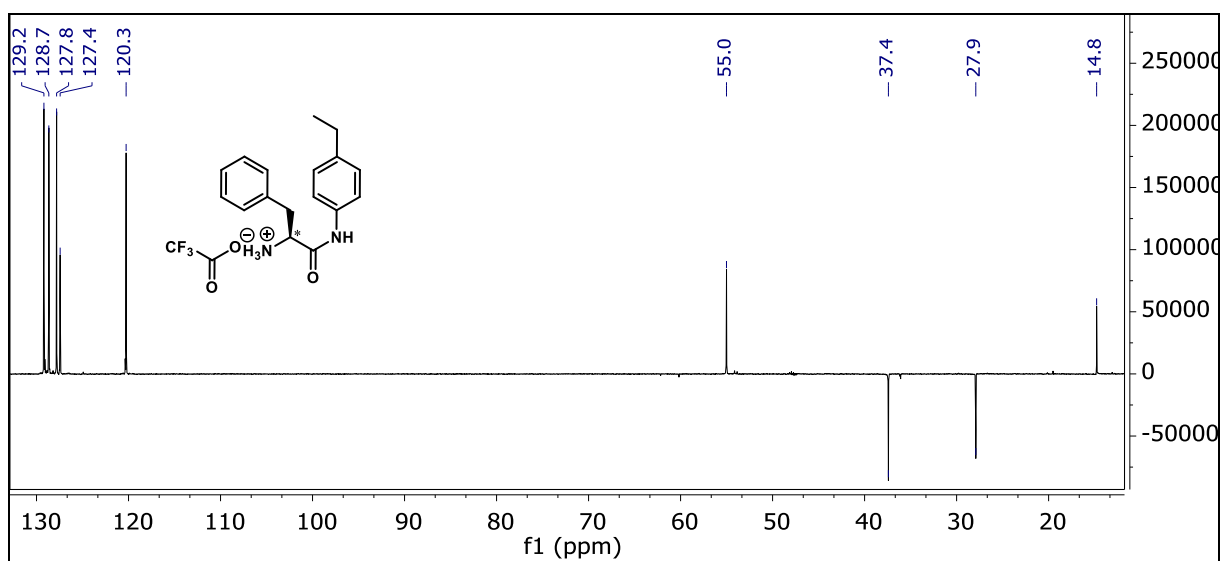
^{13}C NMR (101 MHz, MeOD)



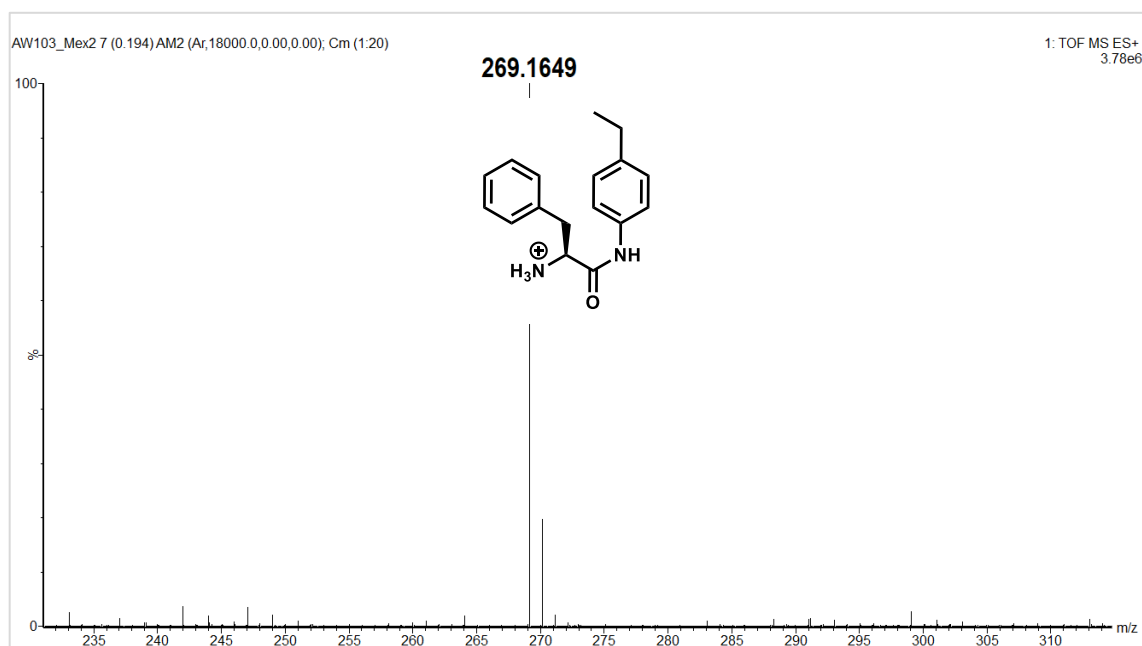
^{19}F NMR (376 MHz, MeOD)



DEPT 135 (101 MHz, MeOD)



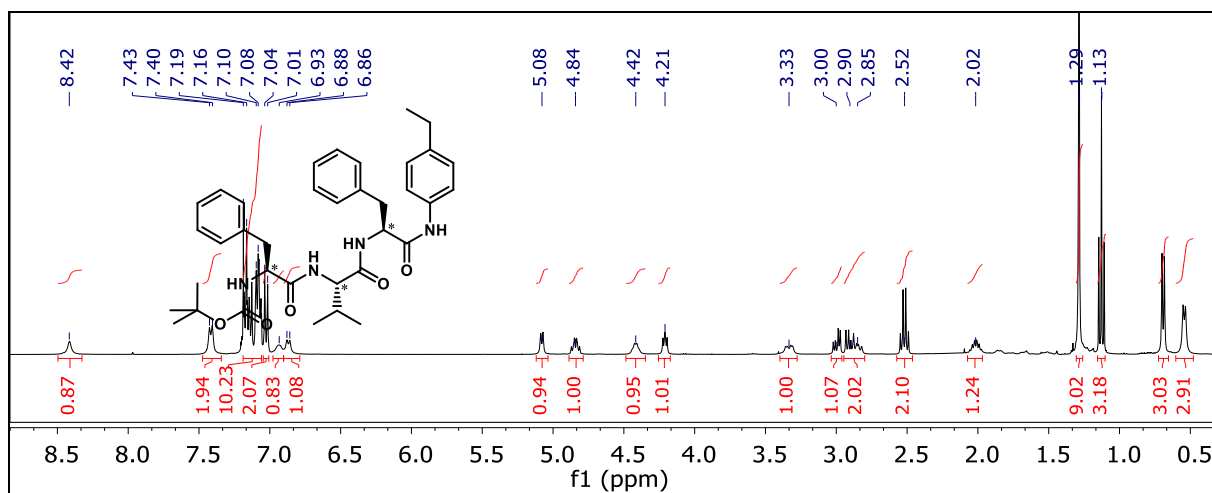
HRMS (ESI)



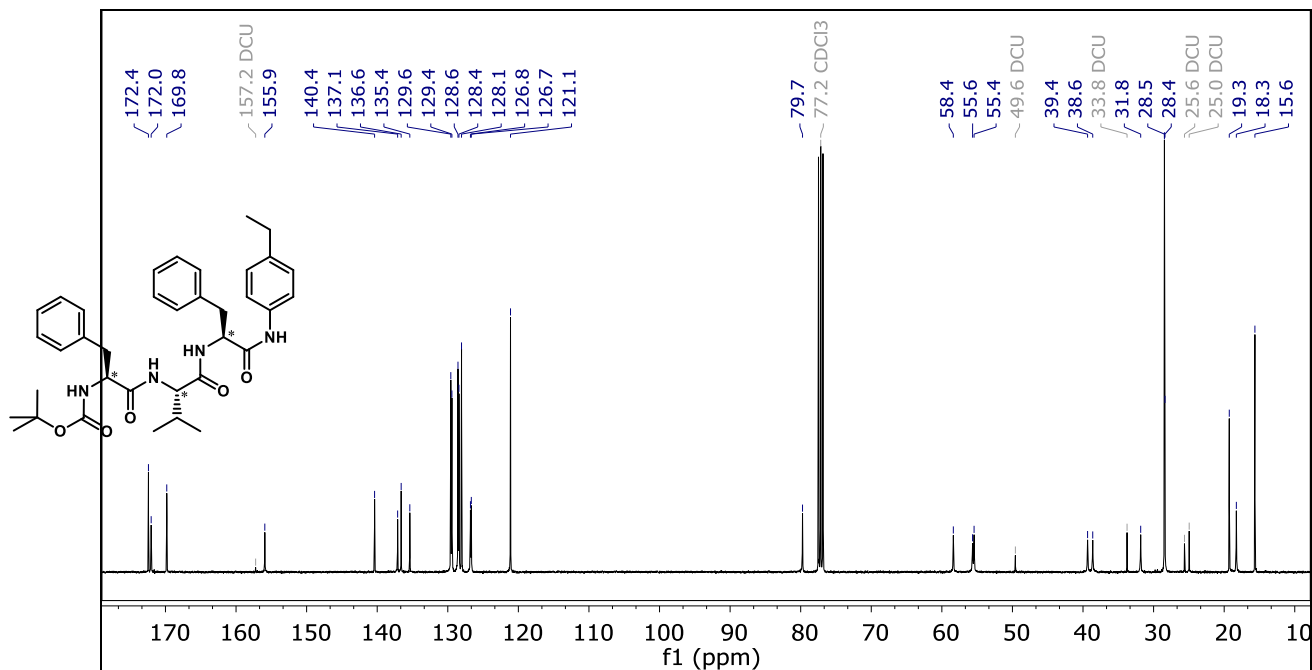
tert-butyl ((S)-1-(((S)-1-(((S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate

(P21L)

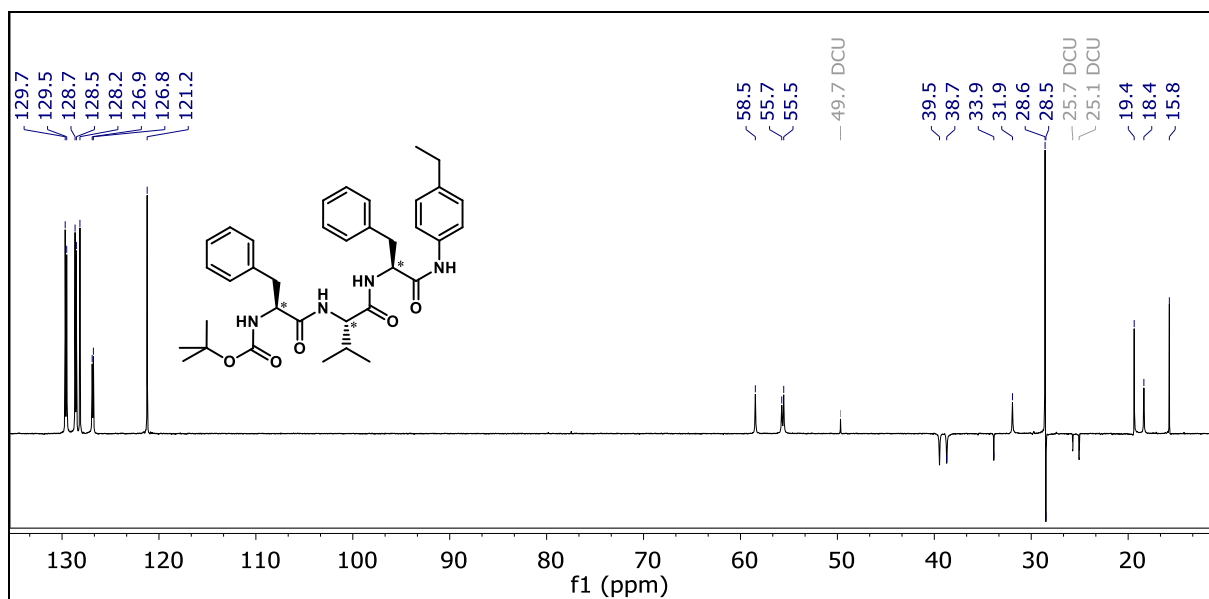
^1H NMR (400 MHz, CDCl_3)



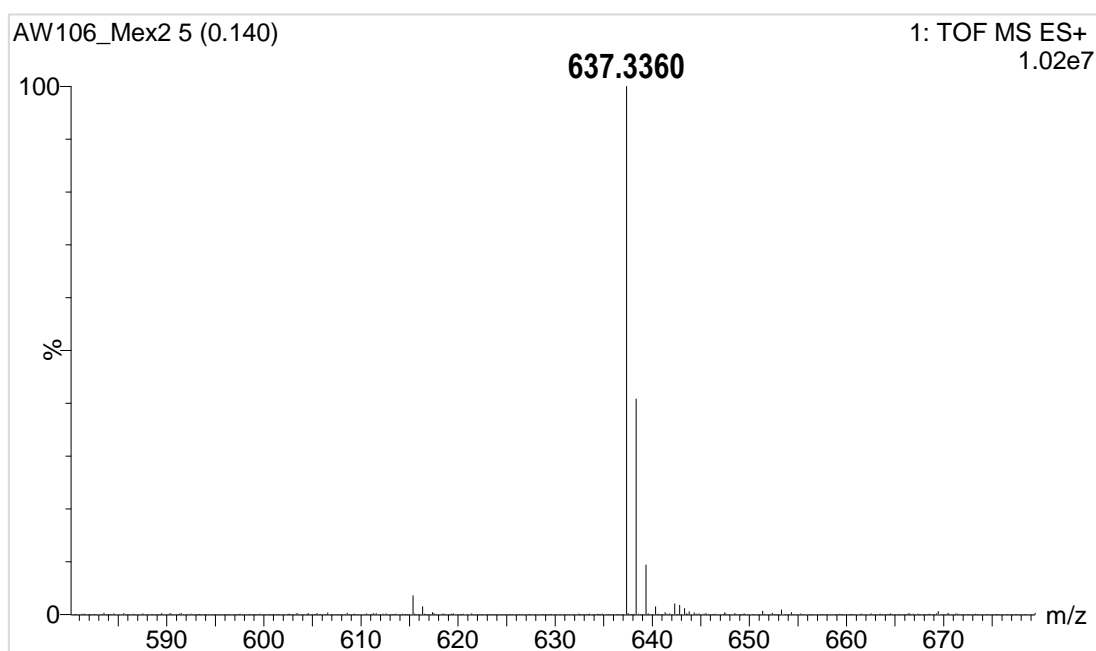
^{13}C NMR (101 MHz, CDCl_3)



DEPT 135 (101 MHz, CDCl₃)



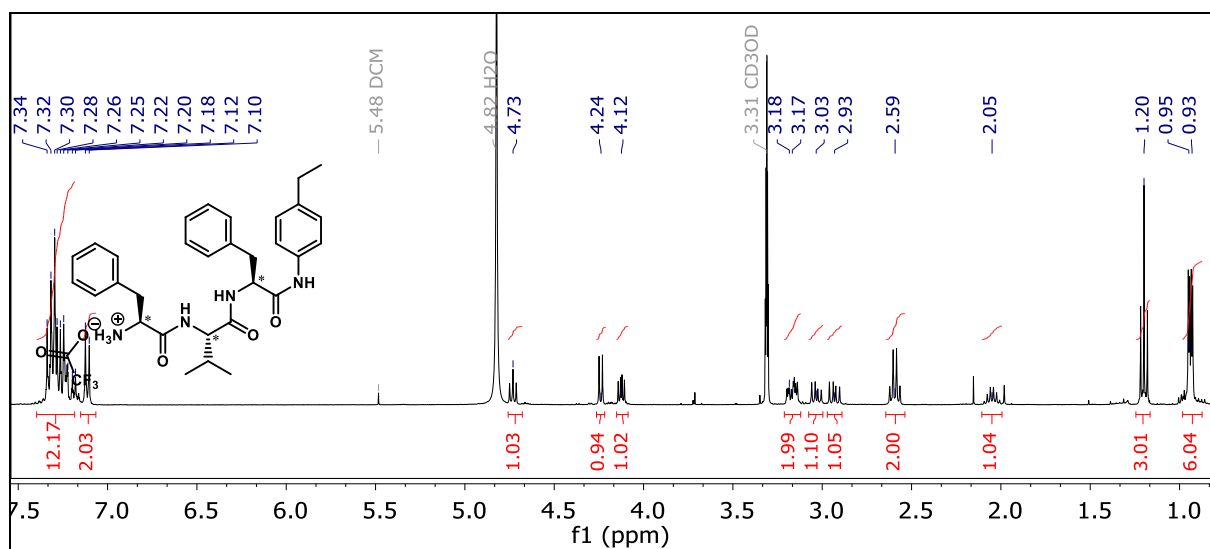
HRMS (ESI)



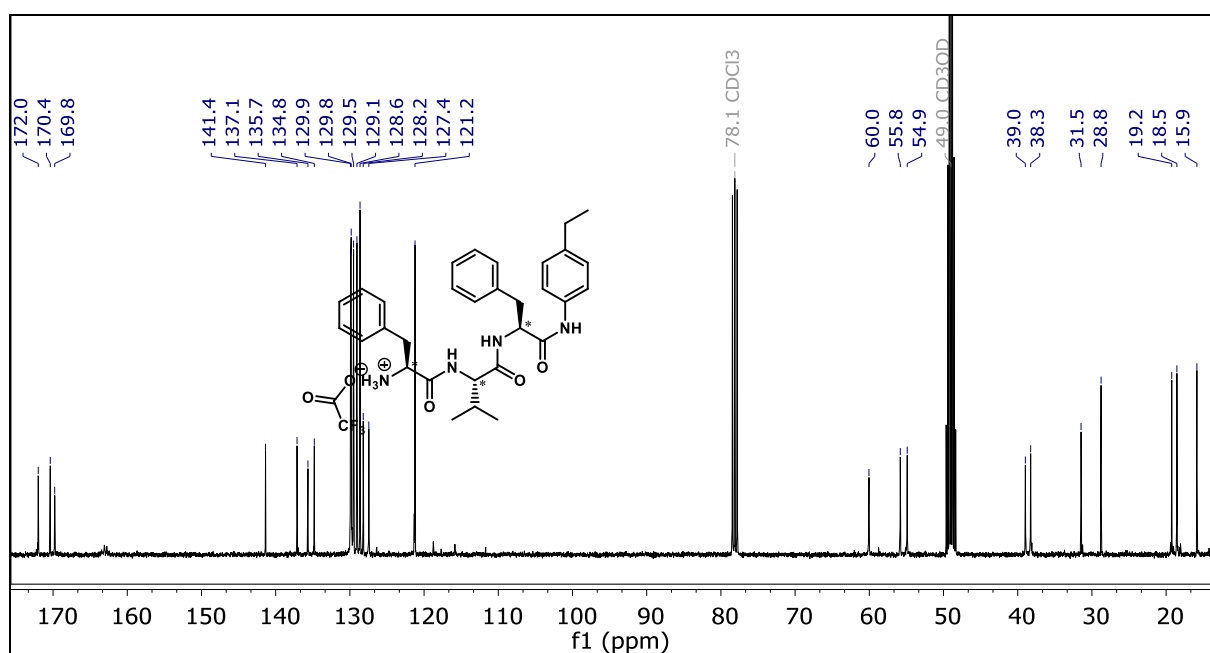
(S)-1-(((S)-1-(((S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate

(P22L)

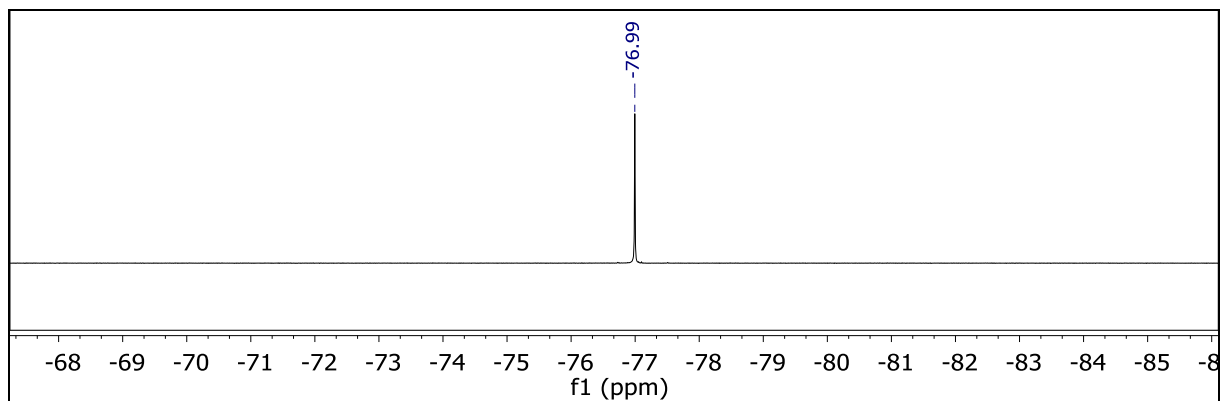
^1H NMR (400 MHz, MeOD)



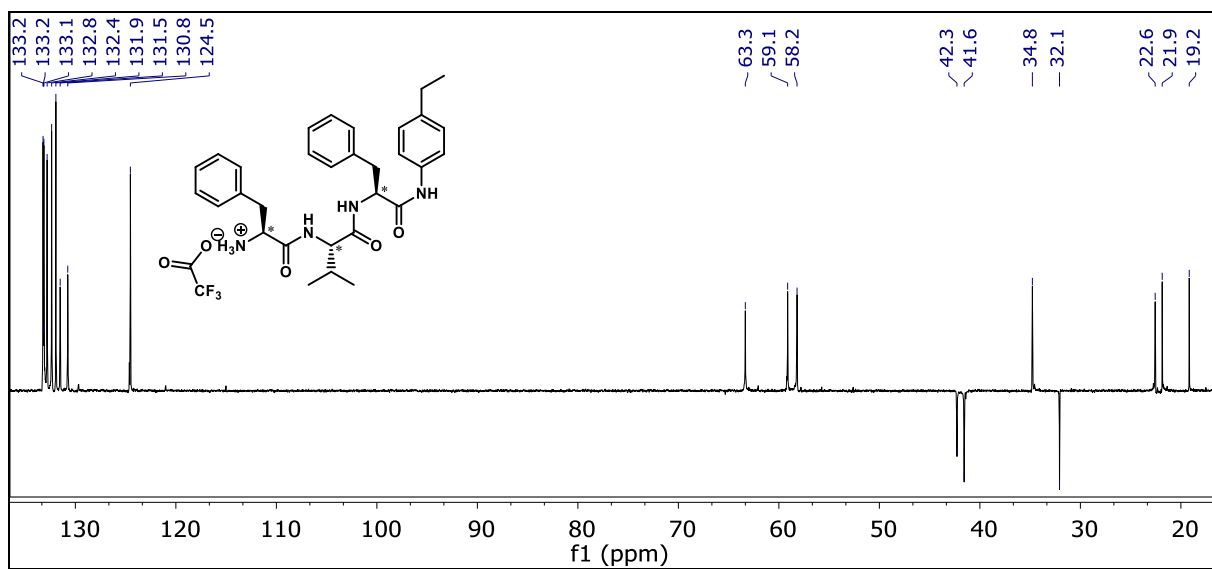
^{13}C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



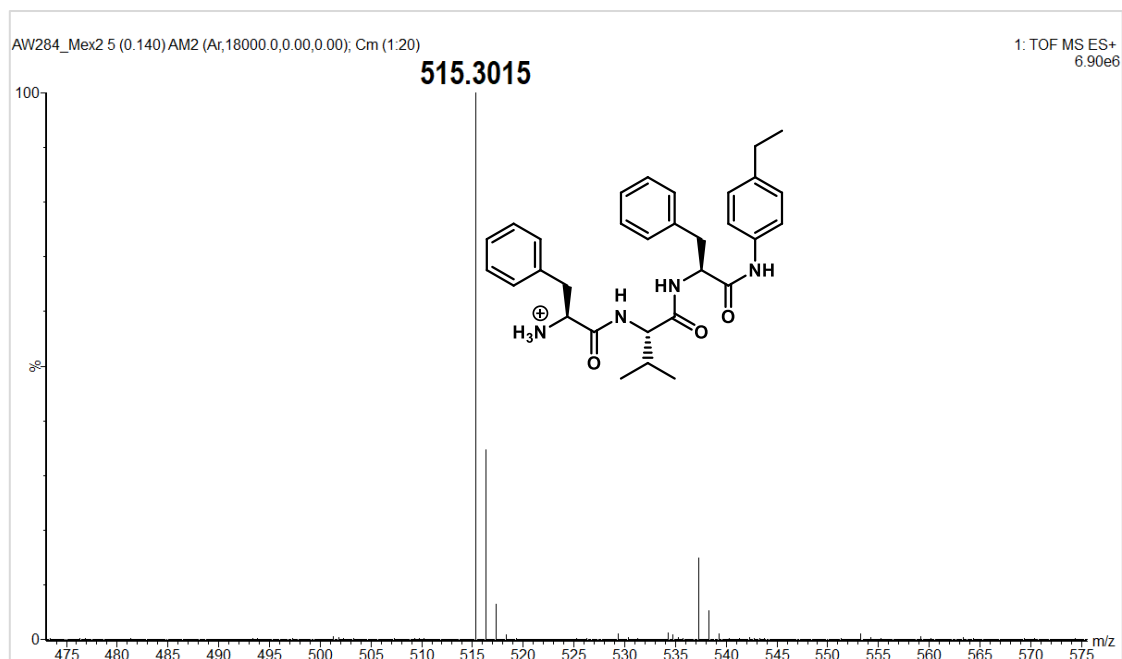
^{19}F NMR (376 MHz, MeOD)



DEPT 135 (101 MHz, MeOD- CDCl_3 (1 : 1 ; v : v))



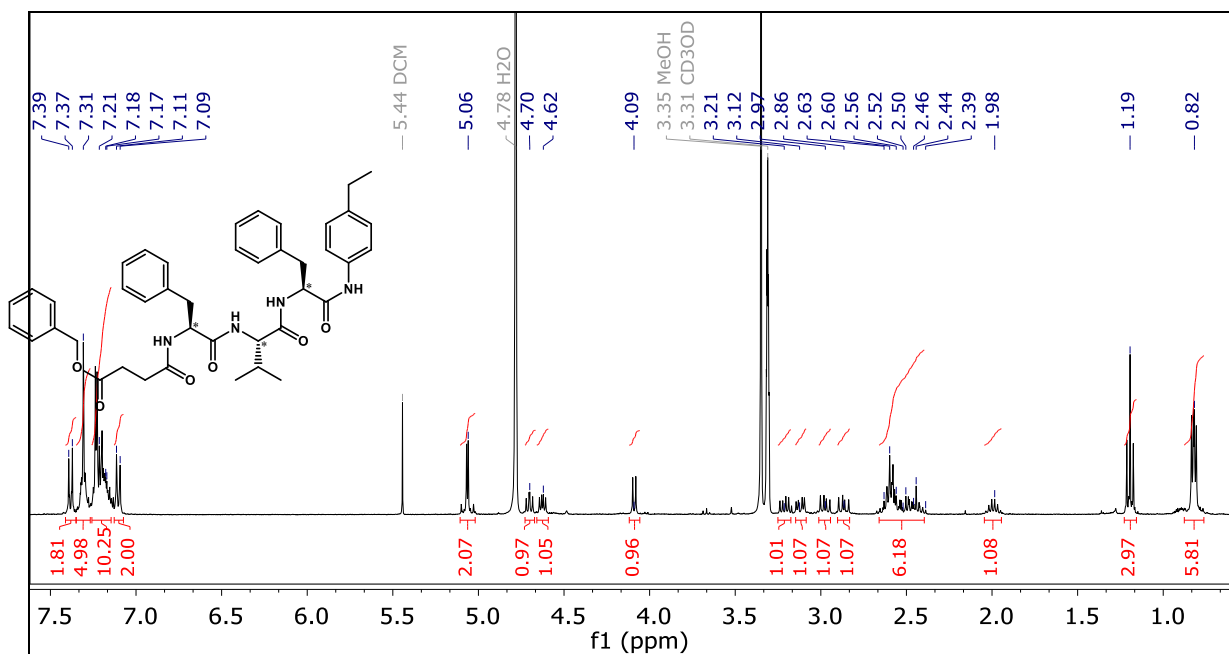
HRMS (ESI)



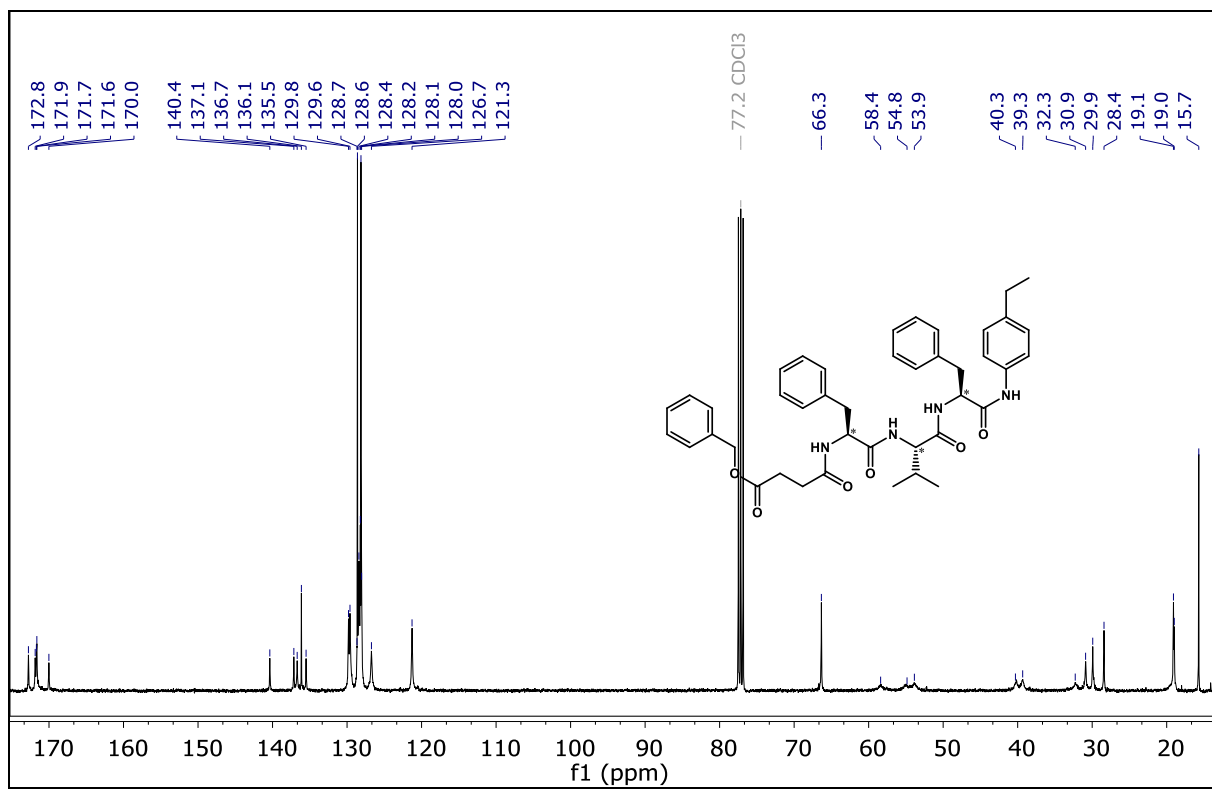
benzyl 4-(((S)-1-(((S)-1-(((S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino))-4-oxobutanoate

(P23L)

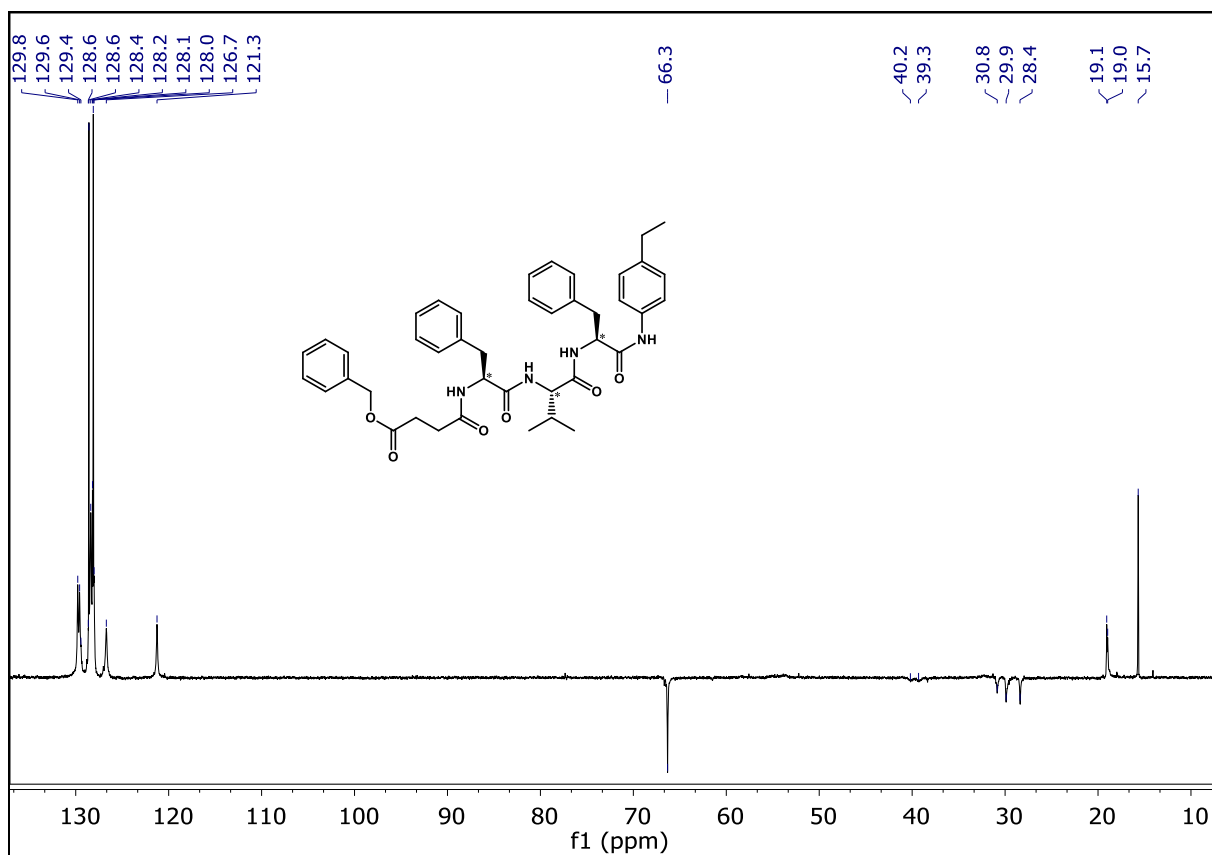
^1H NMR (400 MHz, MeOD)



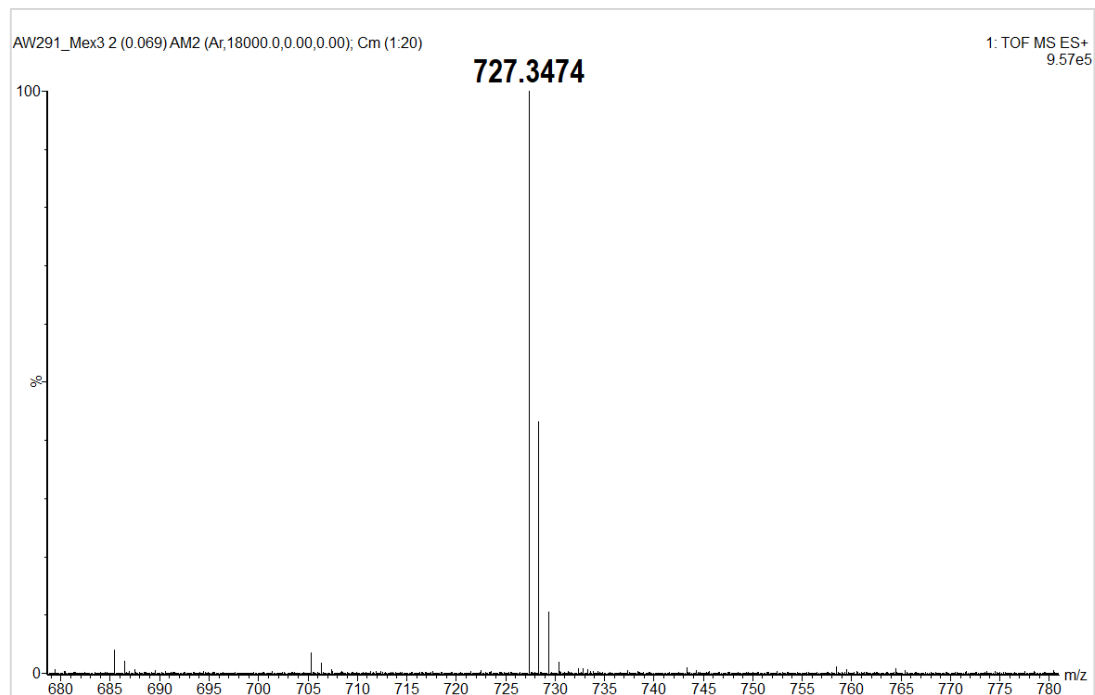
^{13}C NMR (101 MHz, CDCl₃)



DEPT 135 (101 MHz, CDCl₃)



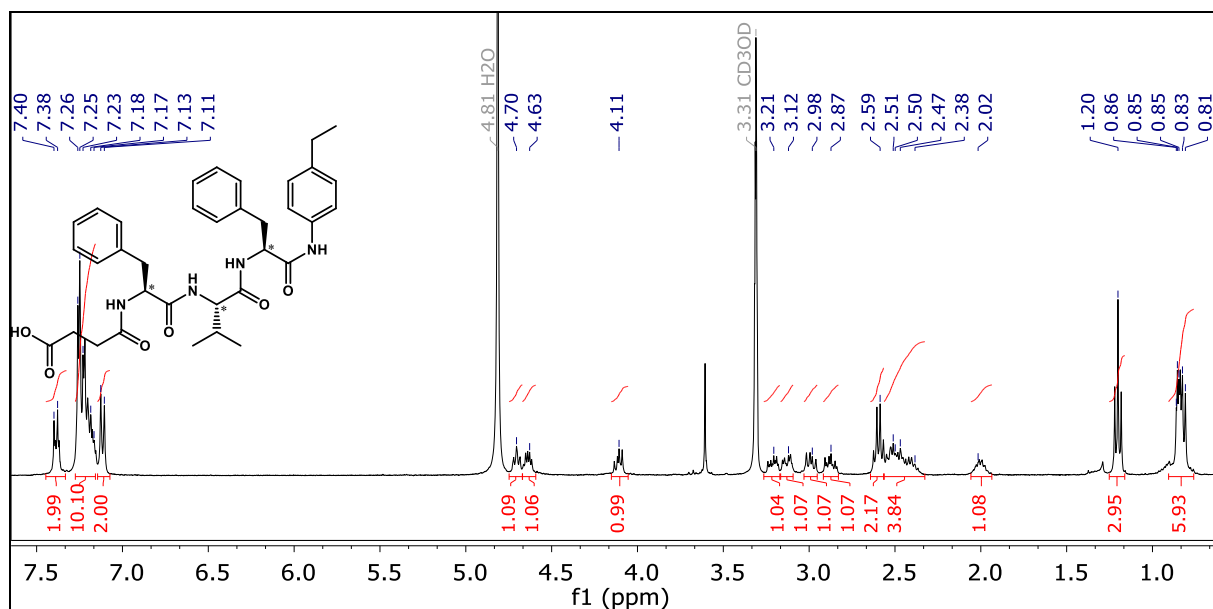
HRMS (ESI)



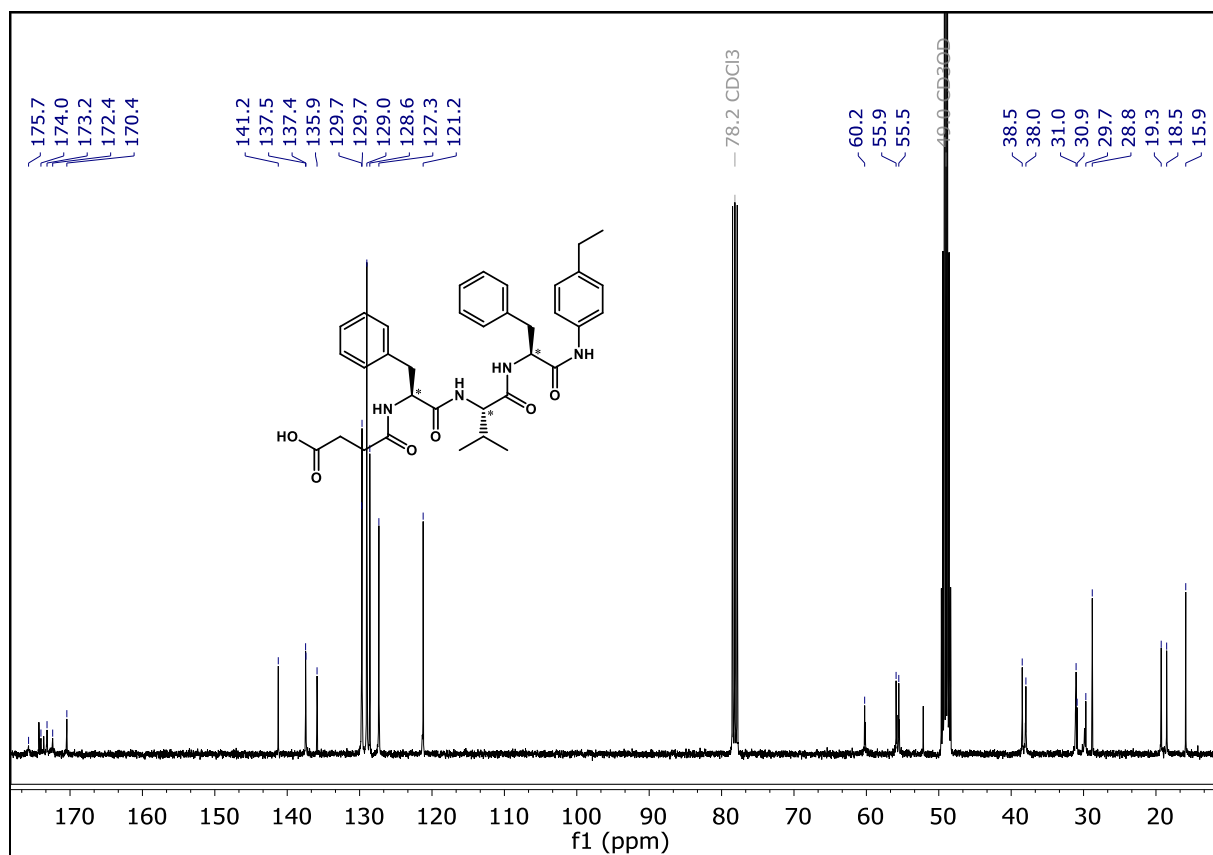
4-(((S)-1-(((S)-1-(((S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoic acid

(P24L)

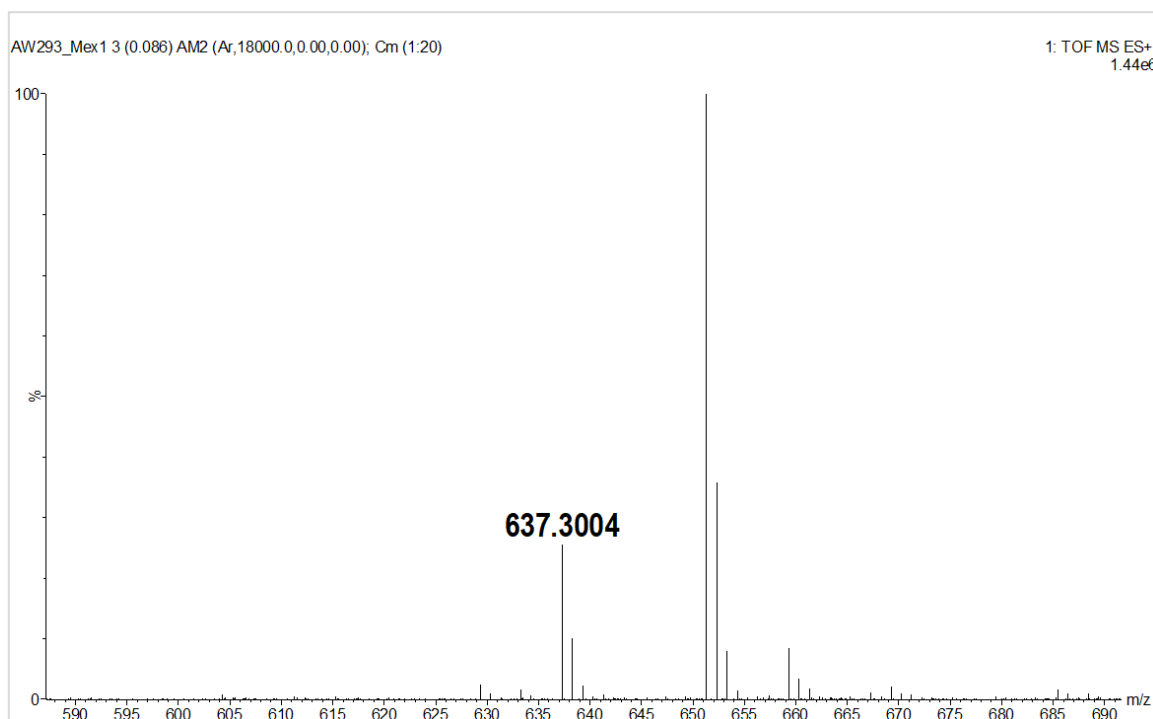
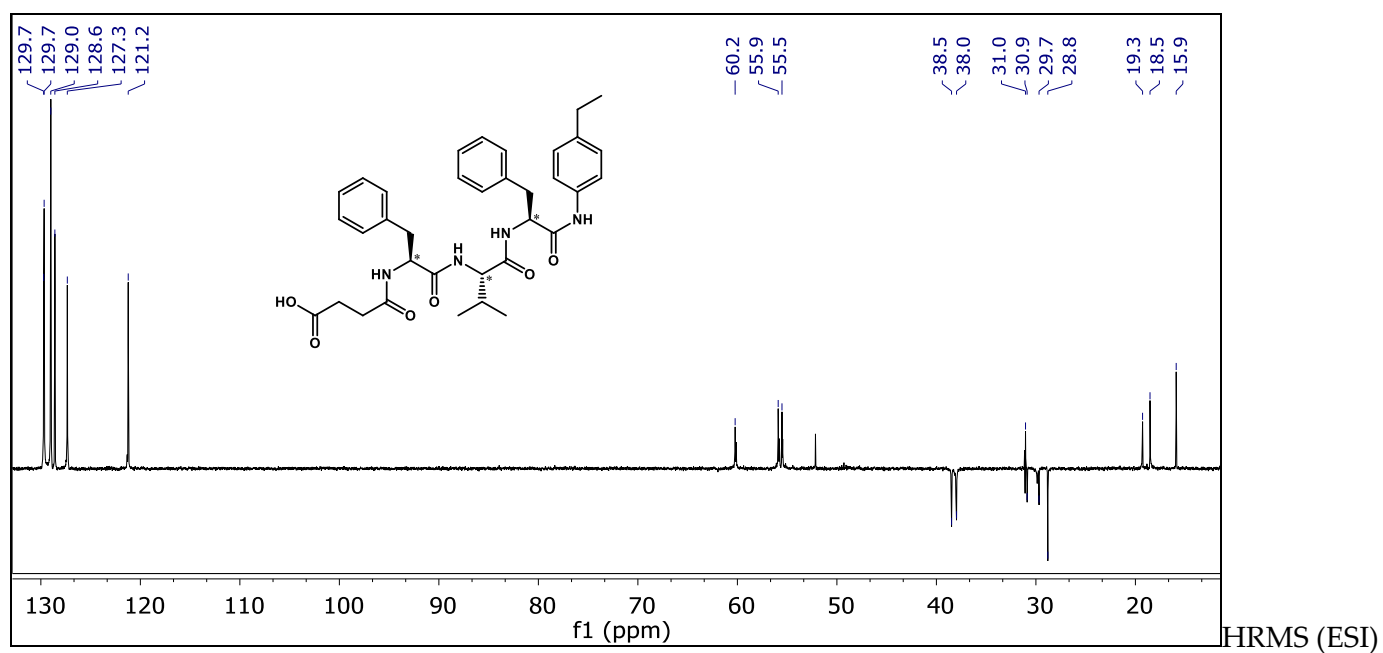
^1H NMR (400 MHz, MeOD)



^{13}C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



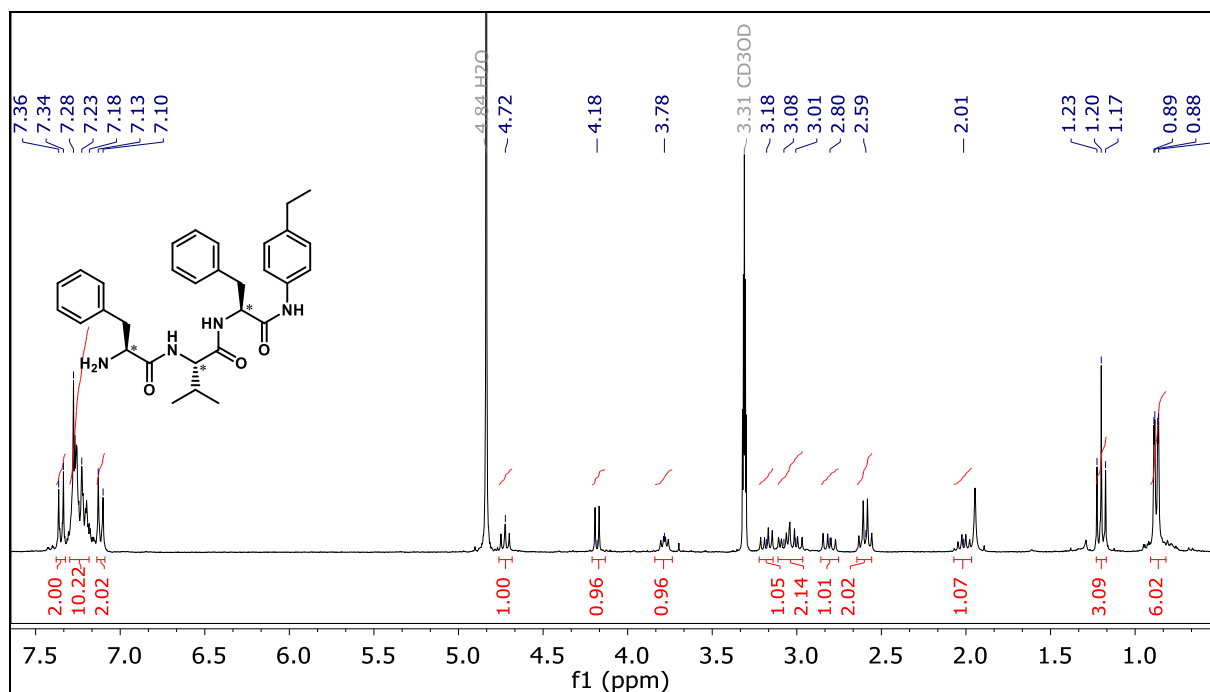
DEPT 135 (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



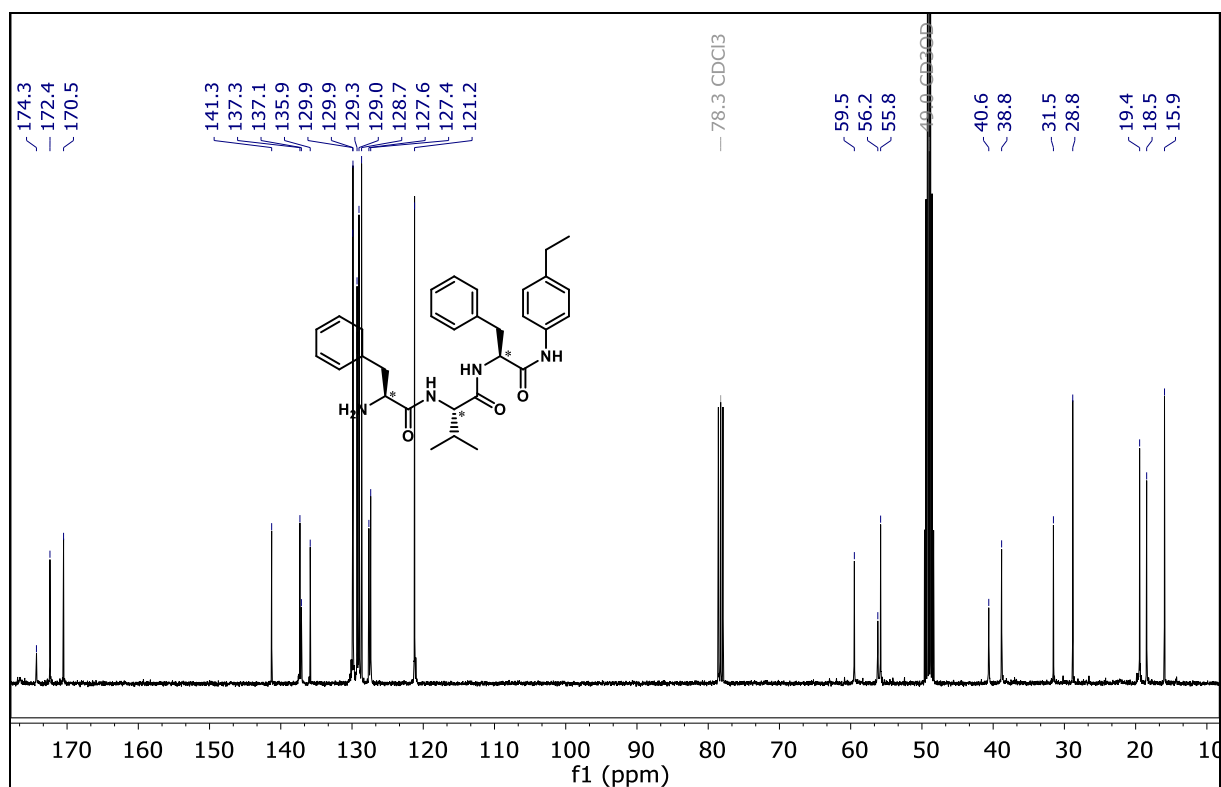
(S)-2-((S)-2-amino-3-phenylpropanamido)-N-((S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)-3-methylbutanamide

(P25L)

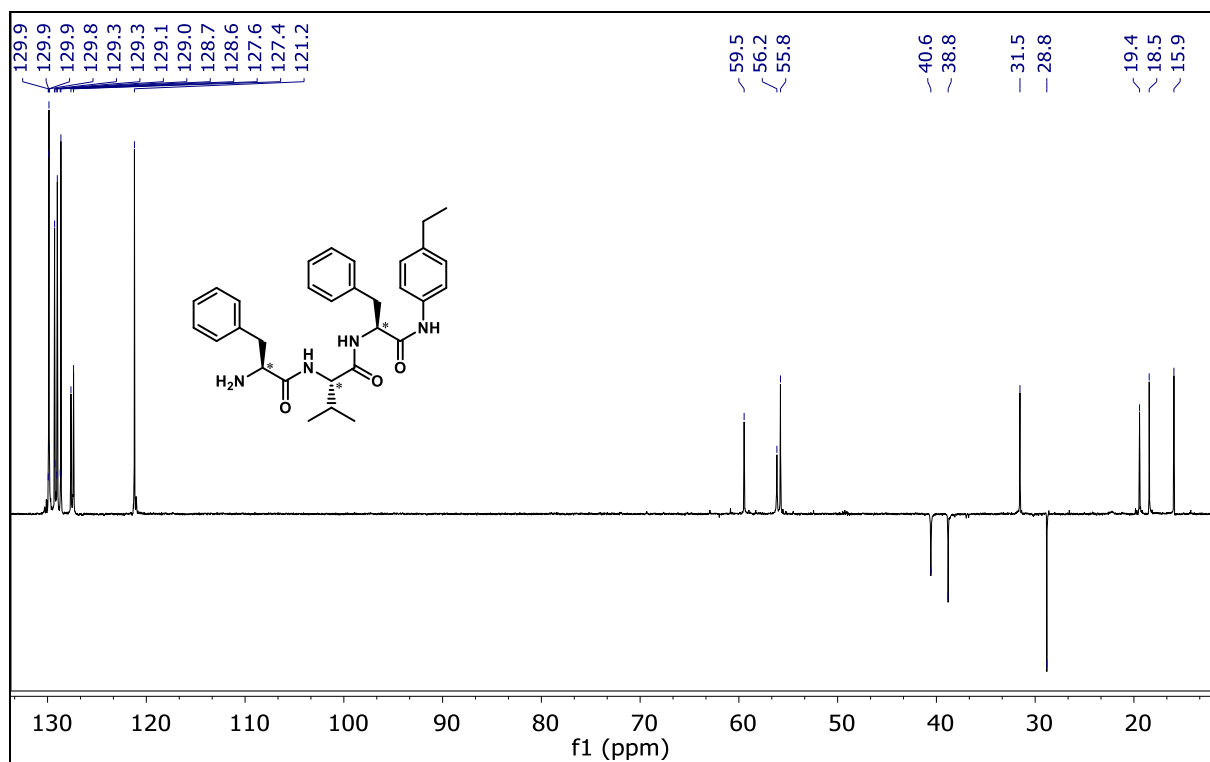
^1H NMR (300 MHz, MeOD)



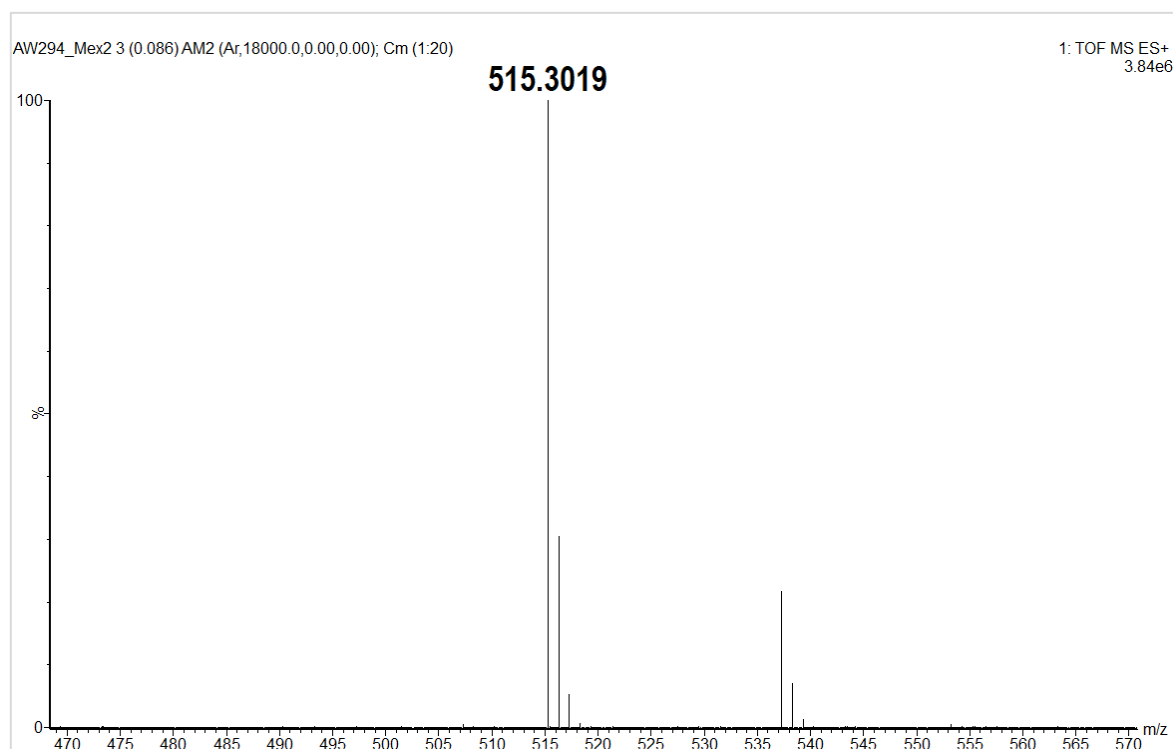
^{13}C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



DEPT 135 (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



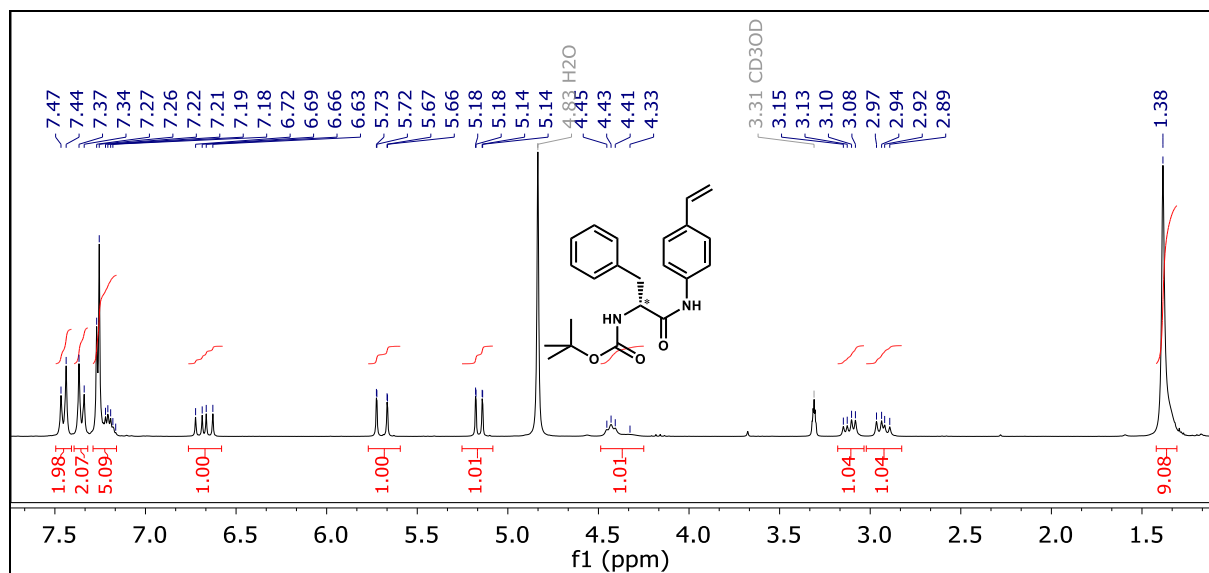
HRMS (ESI)



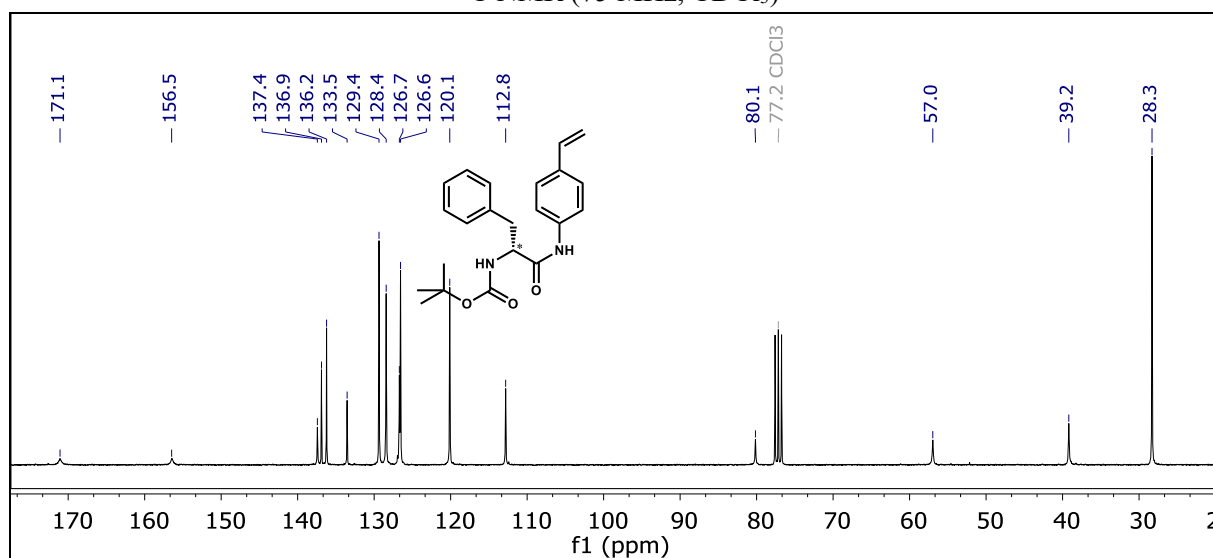
tert-butyl (R)-(1-oxo-3-phenyl-1-((4-vinylphenyl)amino)propan-2-yl)carbamate

(P3D)

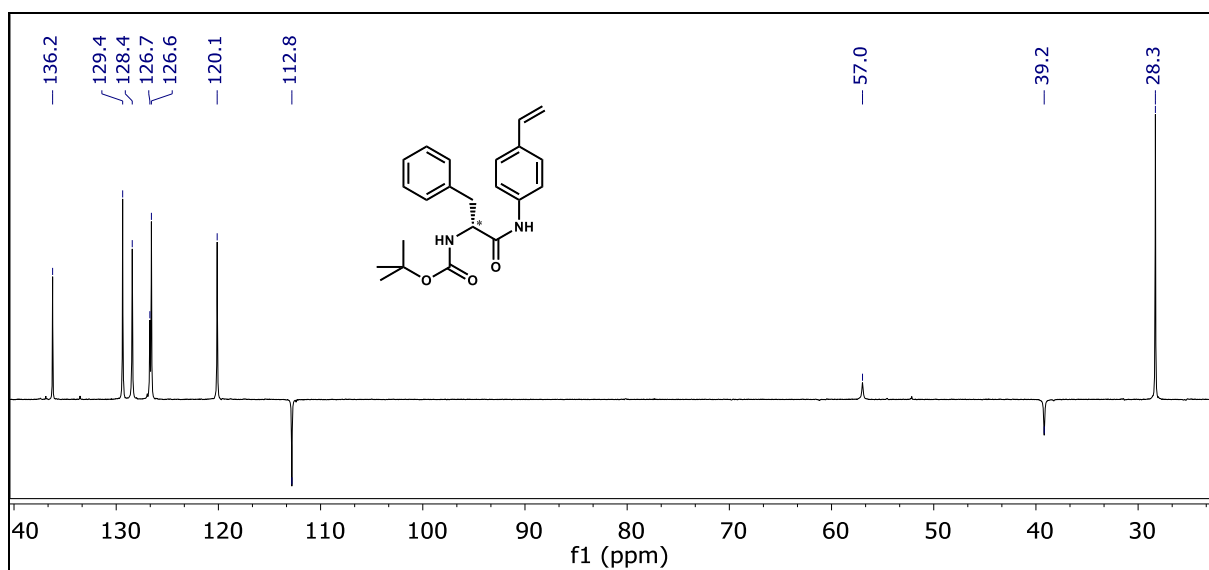
^1H NMR (300 MHz, MeOD)



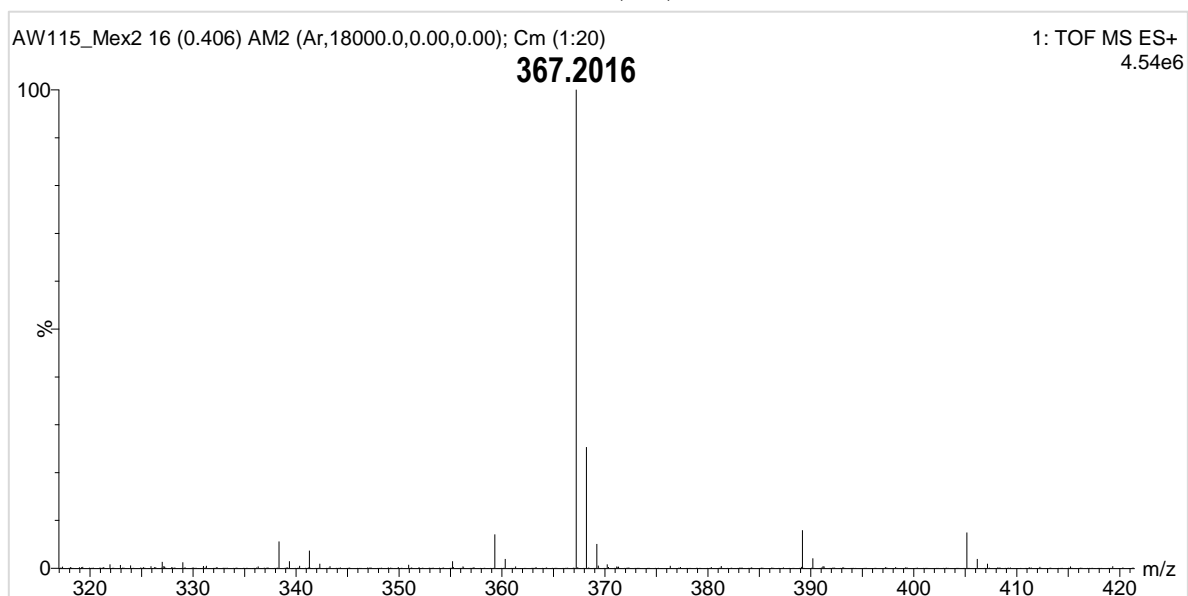
^{13}C NMR (75 MHz, CDCl_3)



DEPT 135 (75 MHz, CDCl_3)



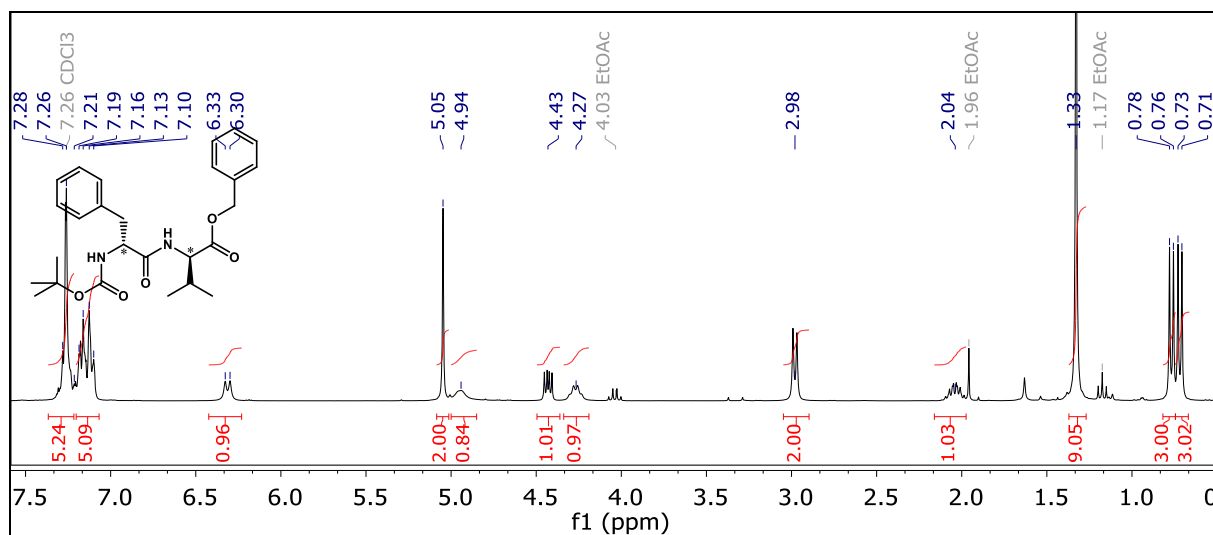
HRMS (ESI)



benzyl (tert-butoxycarbonyl)-D-phenylalanyl-D-valinate

(P4D)

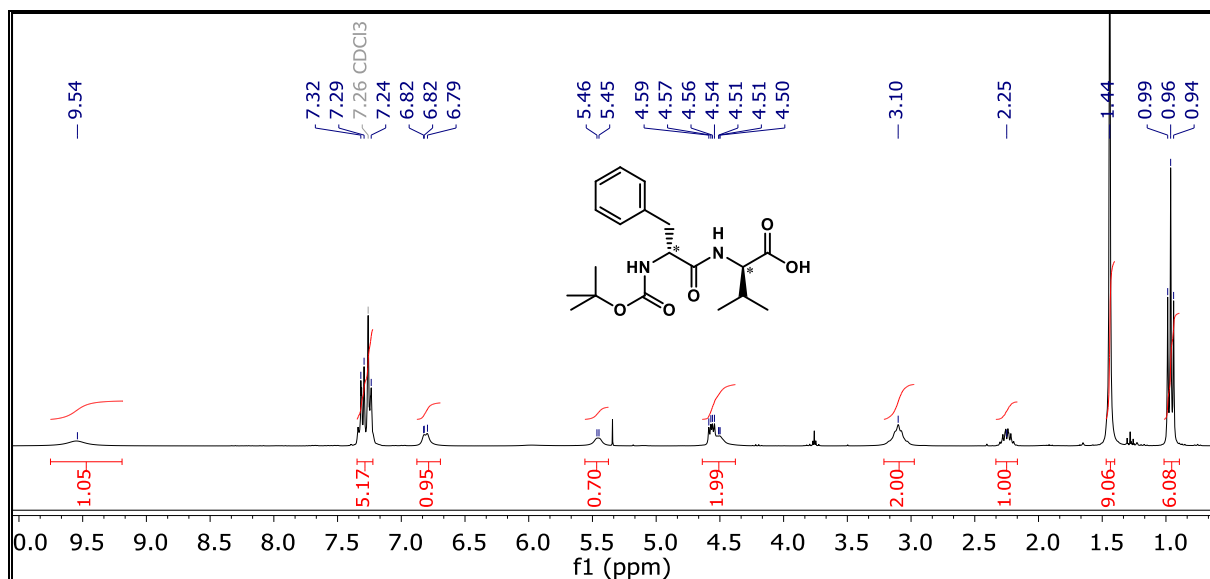
^1H NMR (300 MHz, CDCl_3)



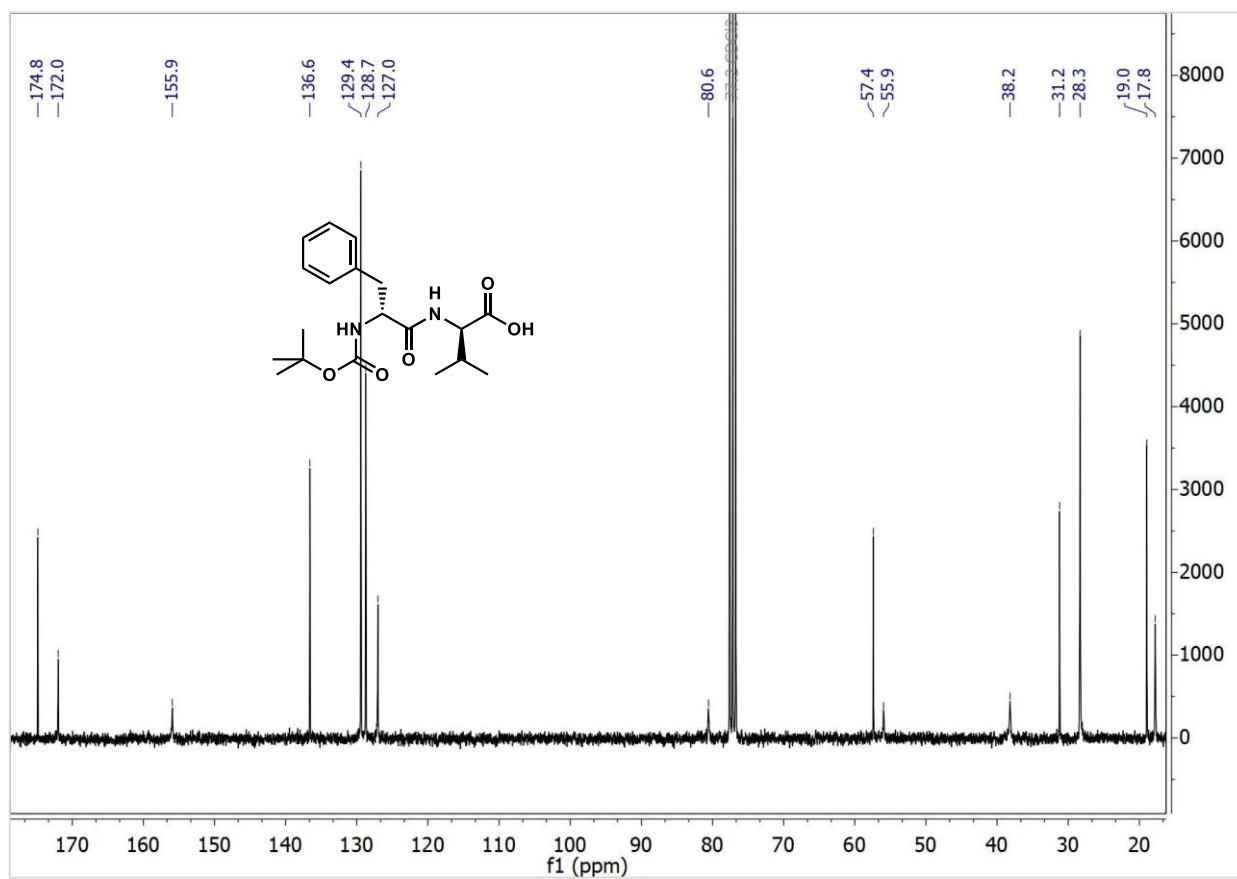
(tert-butoxycarbonyl)-D-phenylalanyl-D-valine

(P5D)

^1H NMR (300 MHz, CDCl_3)



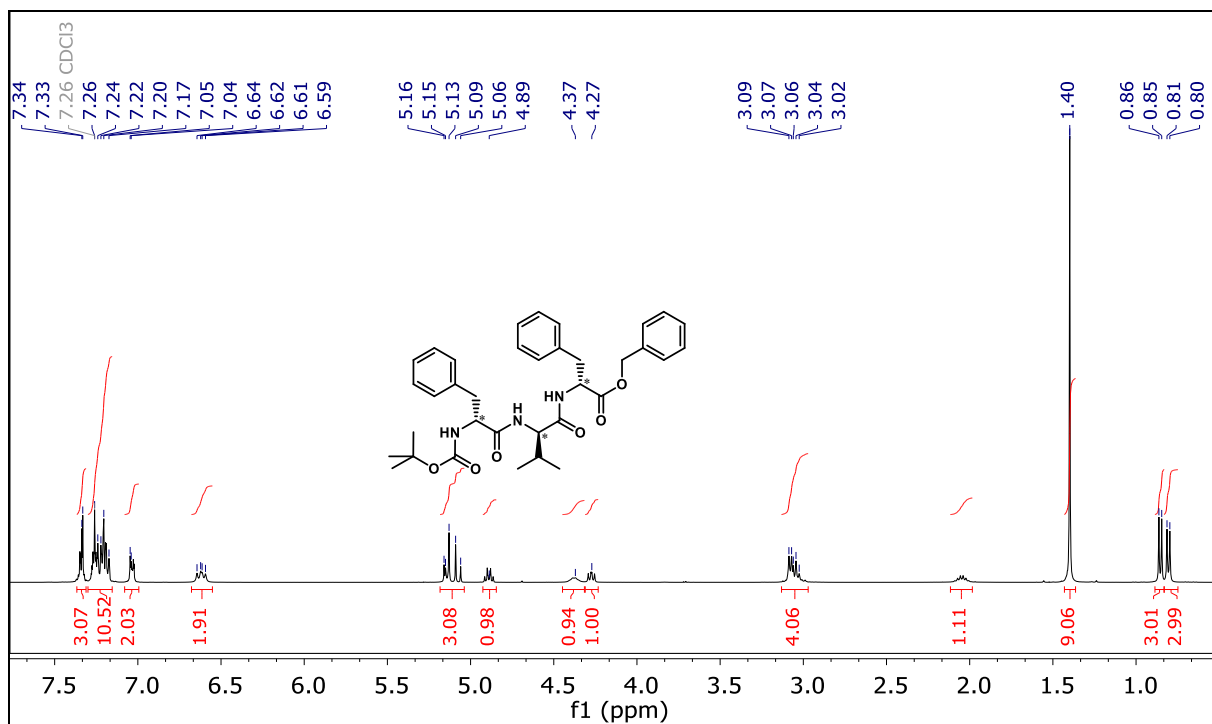
^{13}C NMR (75 MHz, CDCl_3)



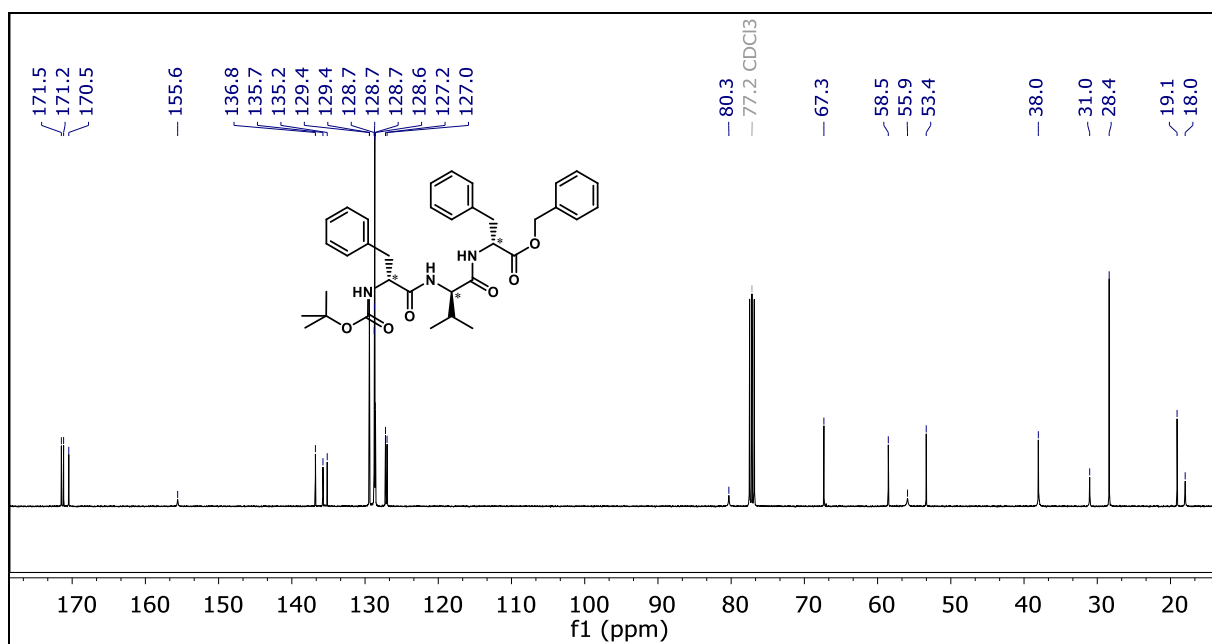
benzyl (tert-butoxycarbonyl)-D-phenylalanyl-D-valyl-D-phenylalaninate

(P6D)

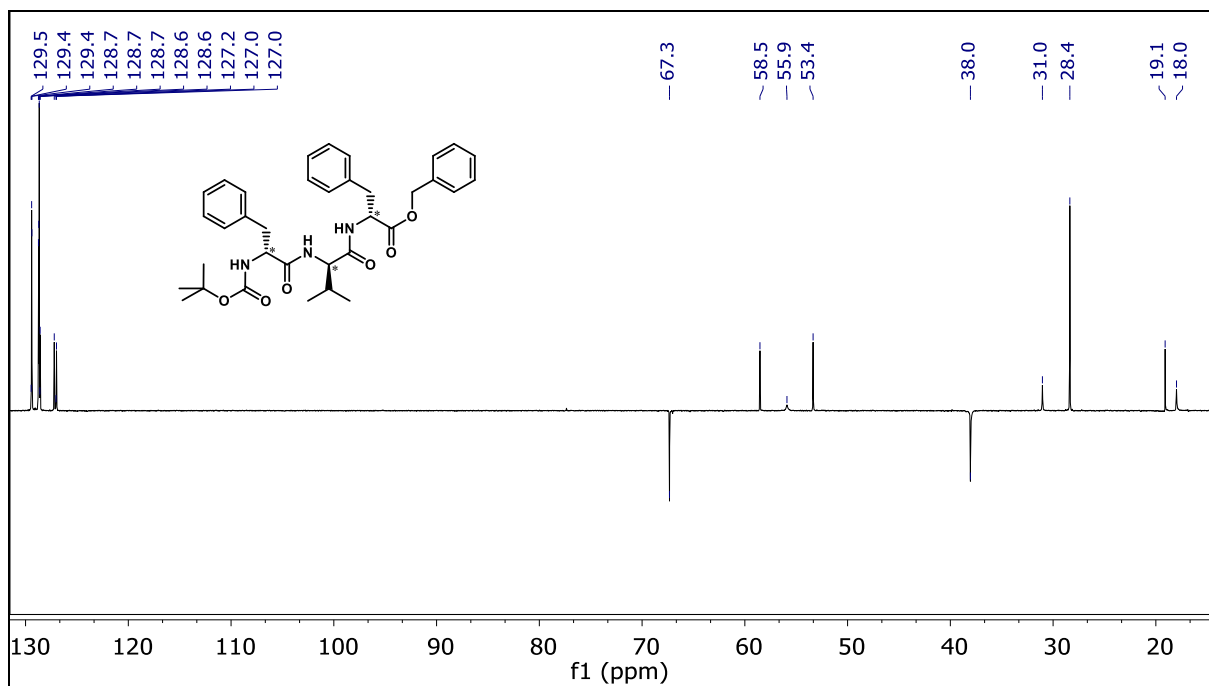
^1H NMR (400 MHz, CDCl_3)



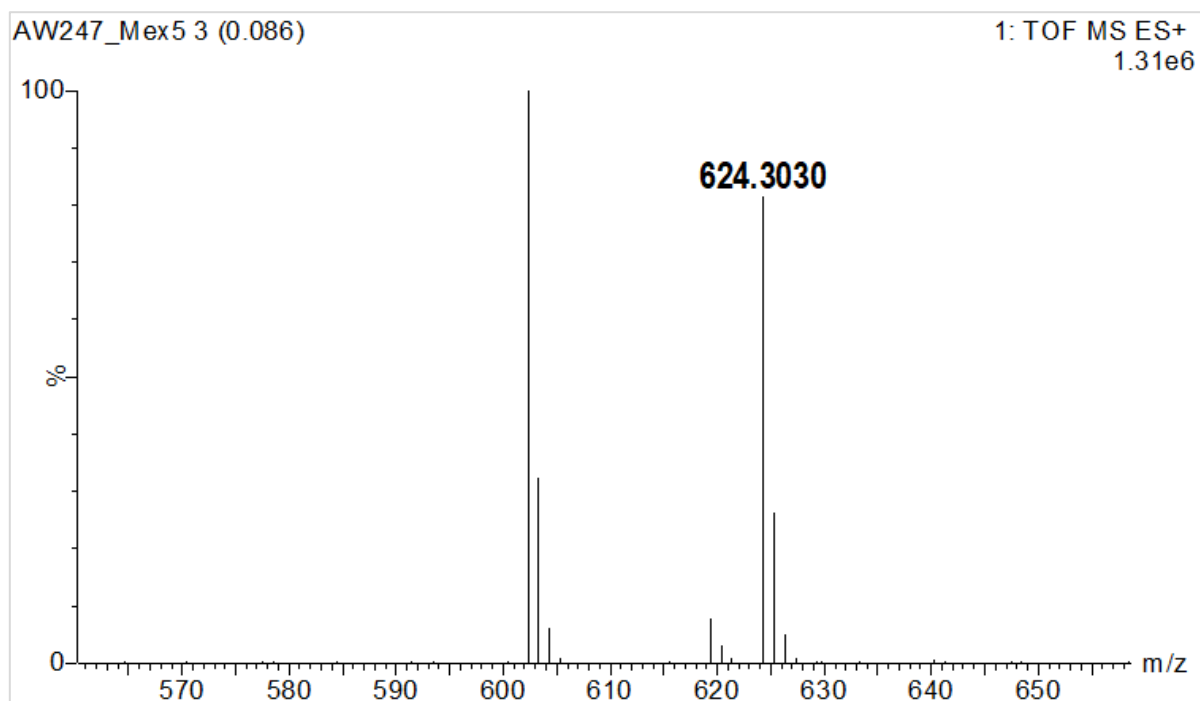
¹³C NMR (101 MHz, CDCl₃)



DEPT 135 (101 MHz, CDCl₃)



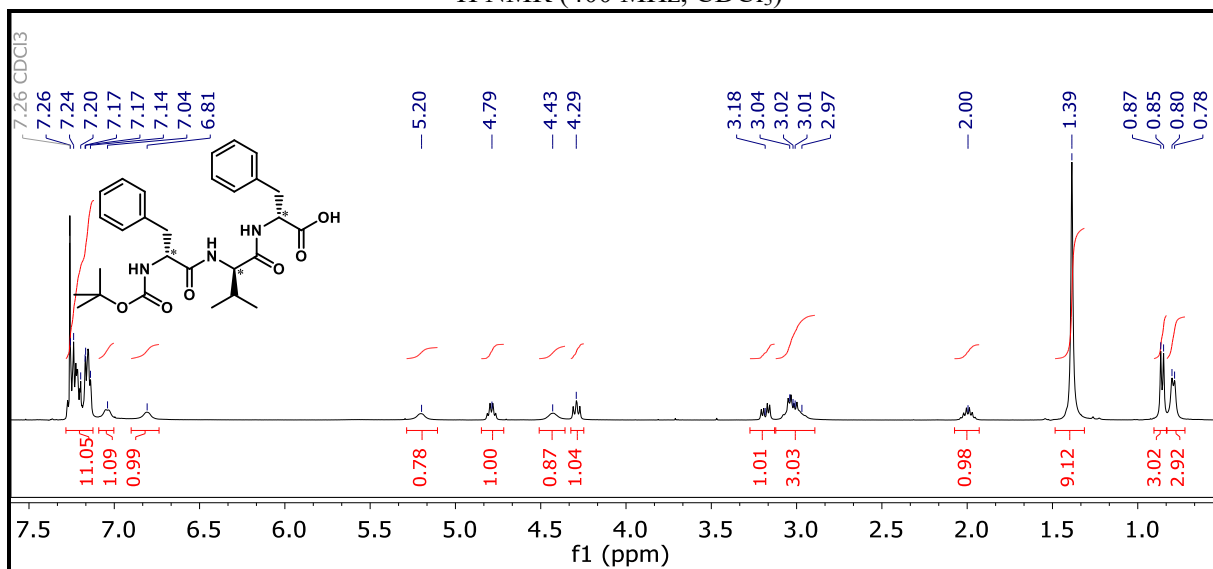
HRMS (ESI)



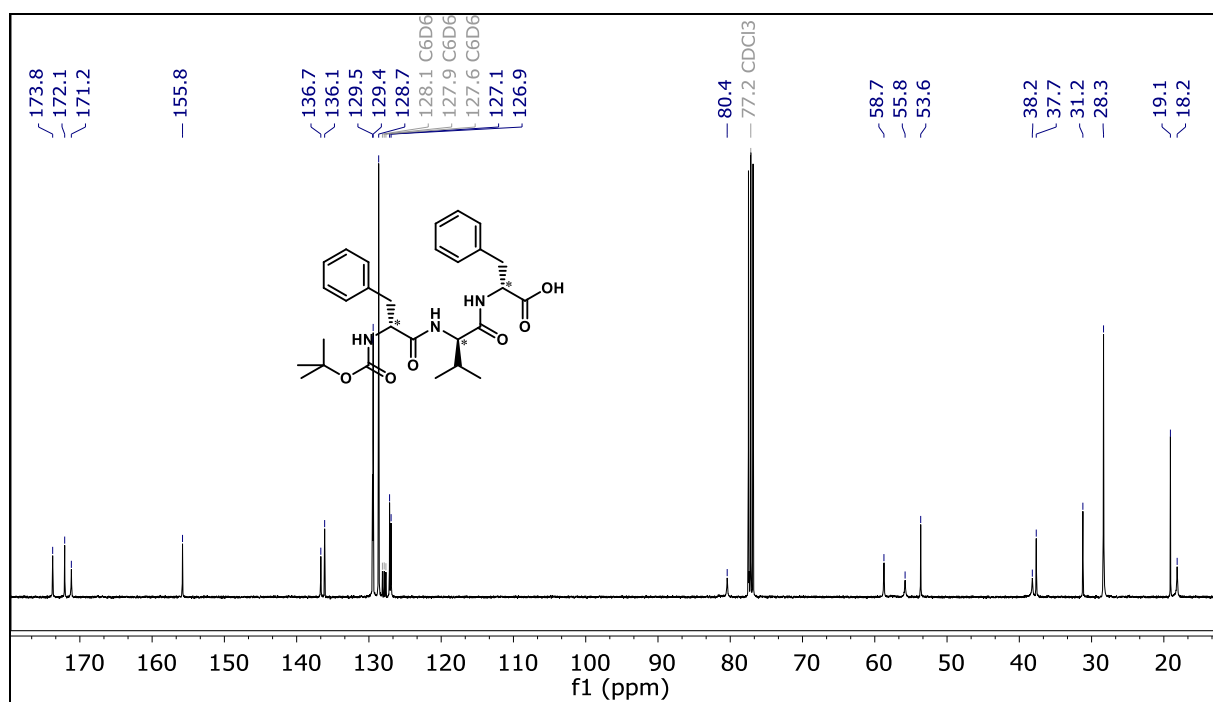
(tert-butoxycarbonyl)-D-phenylalanyl-D-valyl-D-phenylalanine

(P7D)

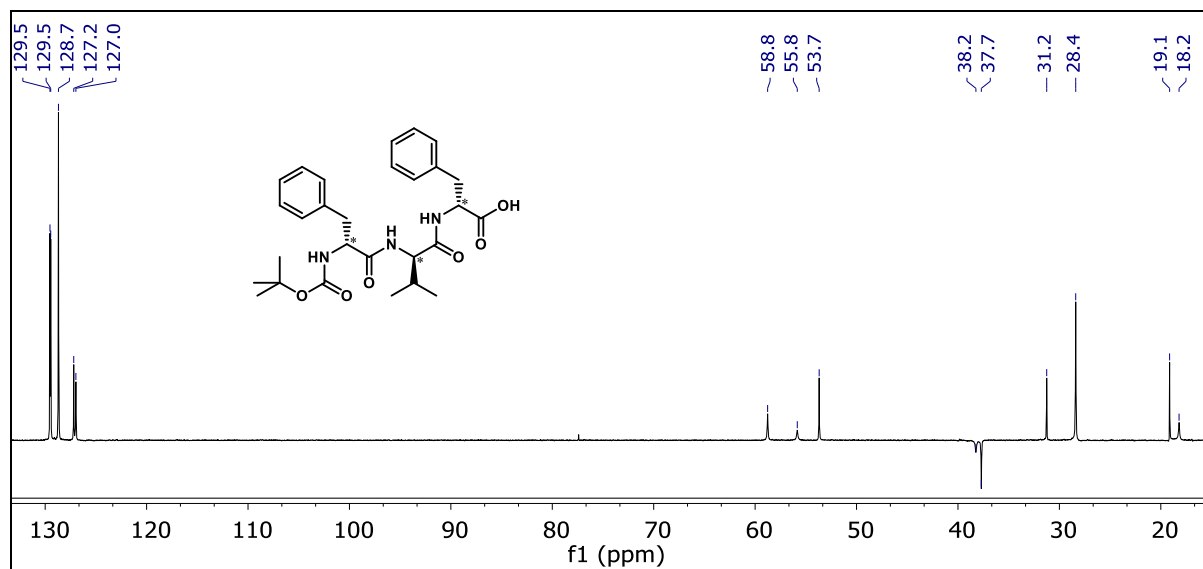
^1H NMR (400 MHz, CDCl_3)



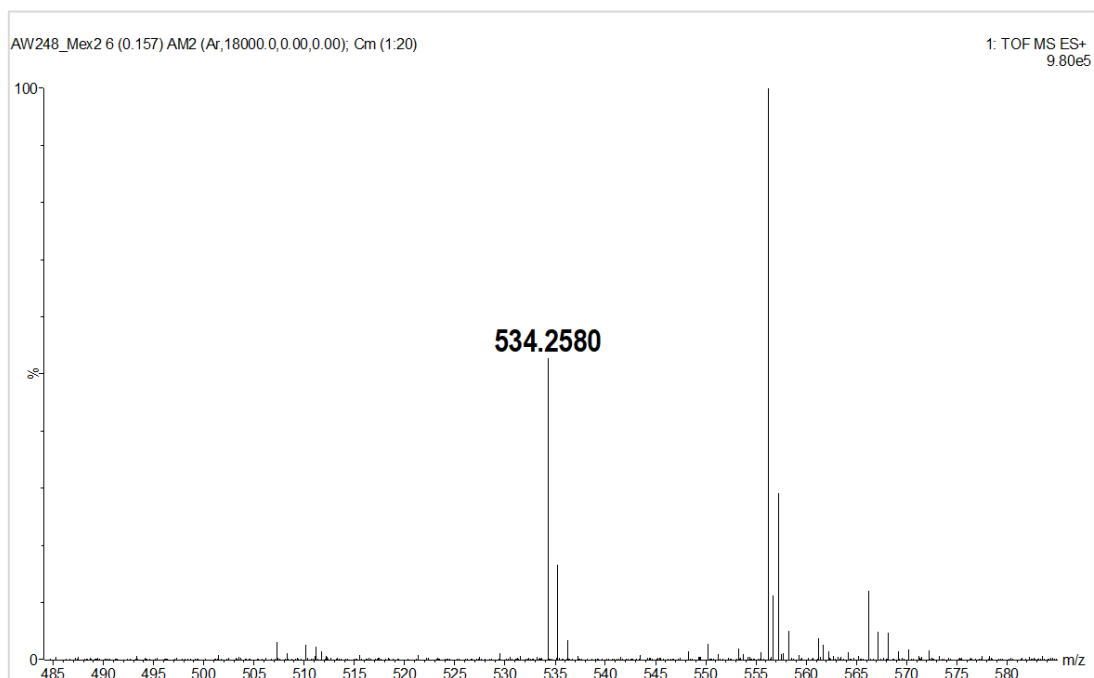
^{13}C NMR (101 MHz, CDCl_3)



DEPT 135 (101 MHz, CDCl₃)



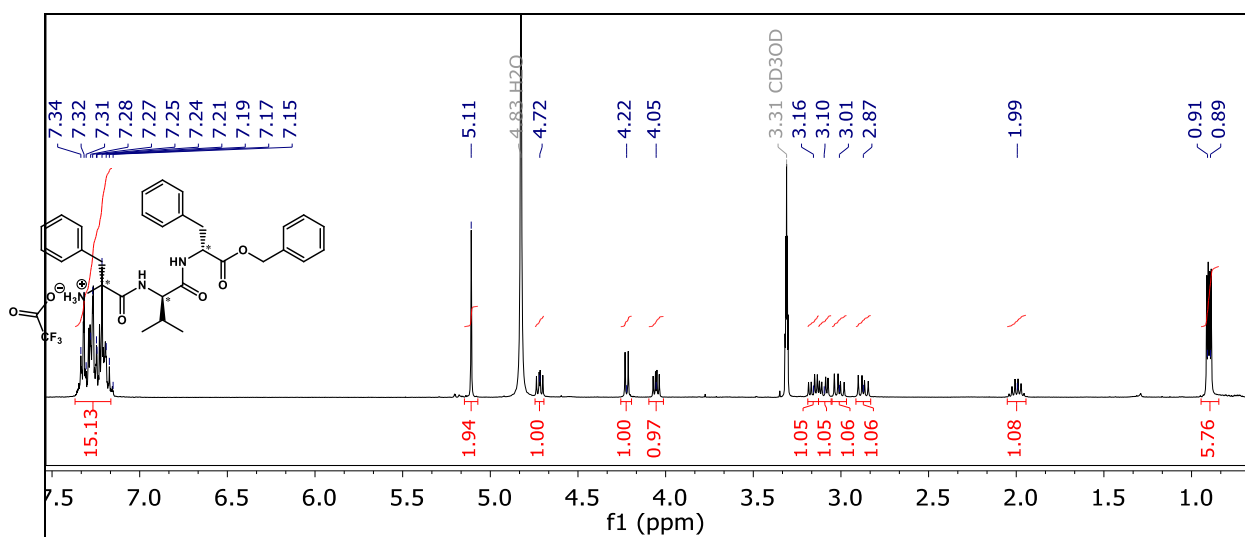
HRMS (ESI)



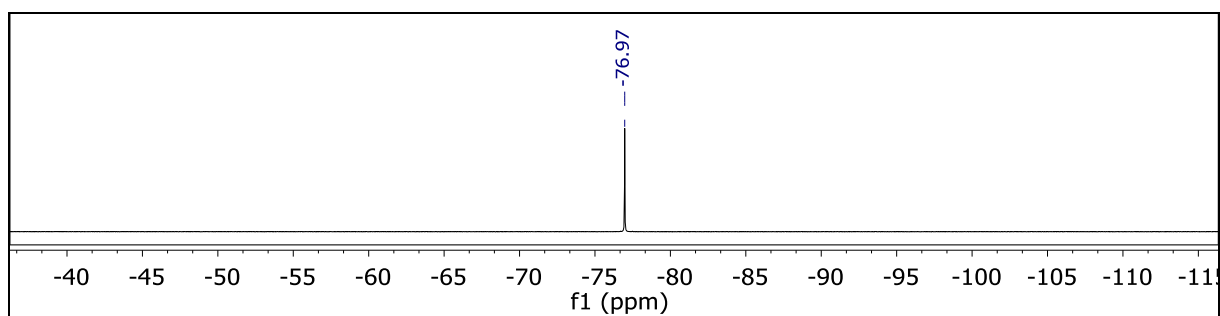
(R)-1-(((R)-1-(((R)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate

(P8D)

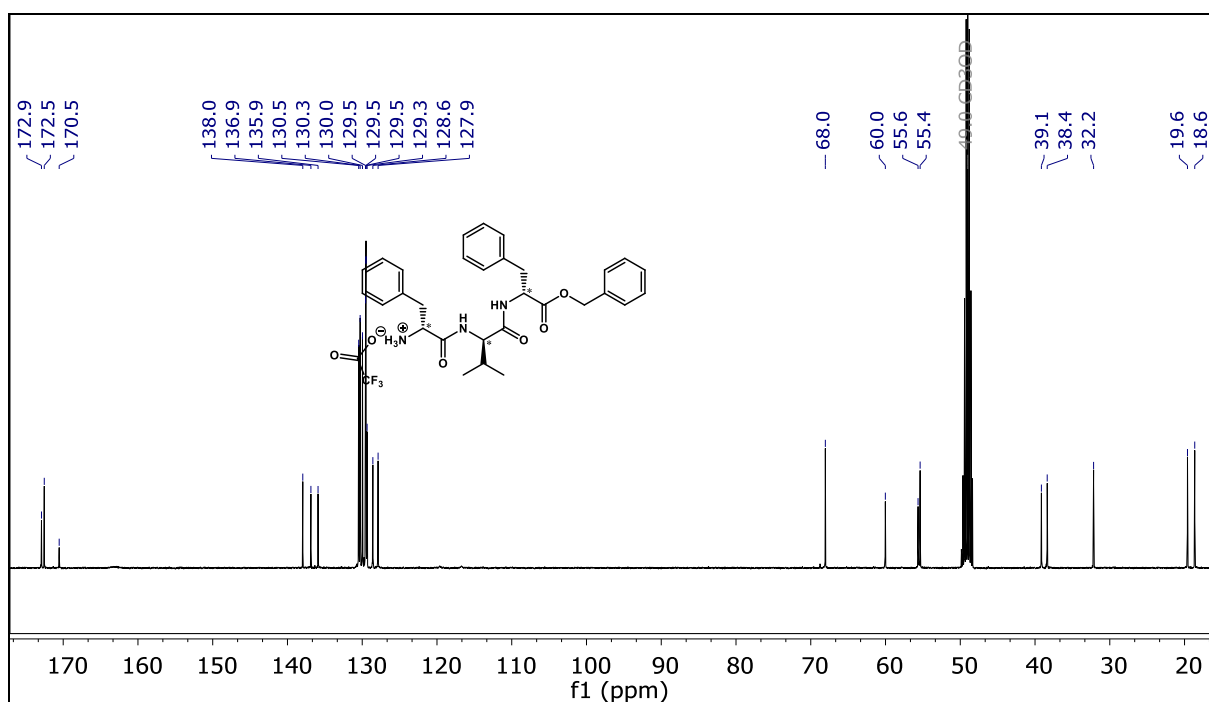
^1H NMR (400 MHz, MeOD)



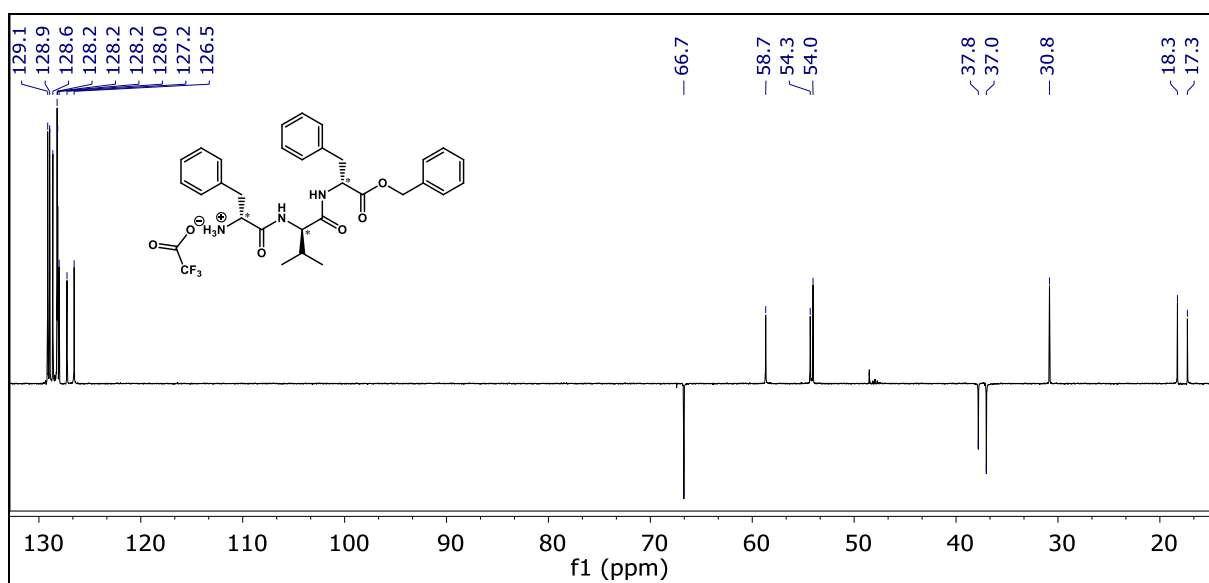
^{19}F NMR (376 MHz, MeOD)



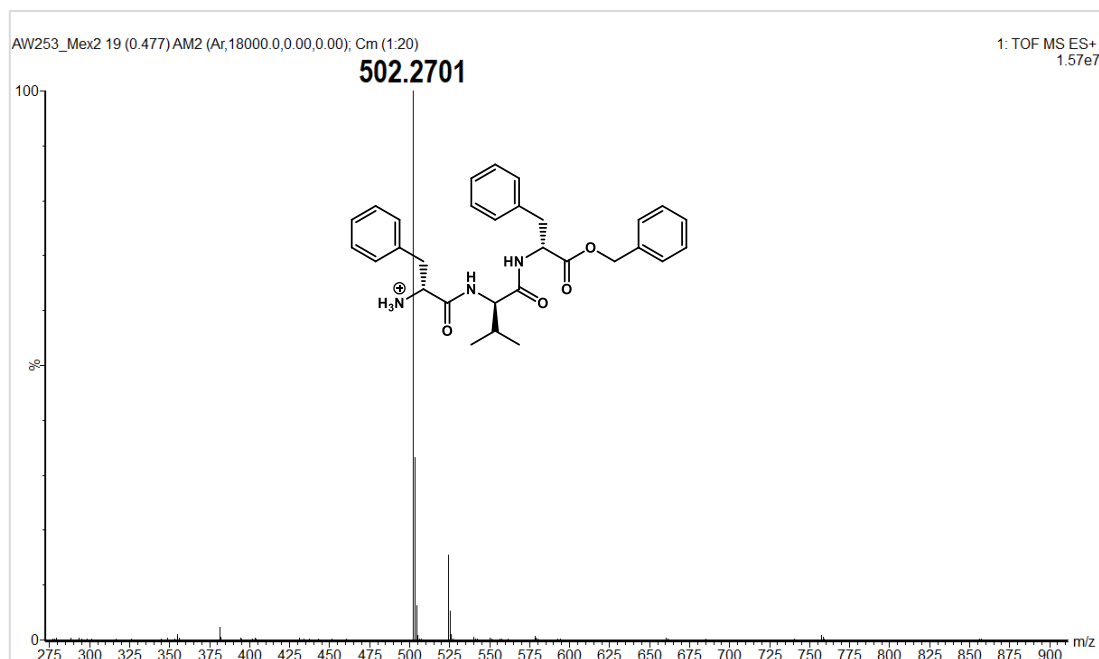
^{13}C NMR (101 MHz, MeOD)



DEPT 135 (101 MHz, MeOD)



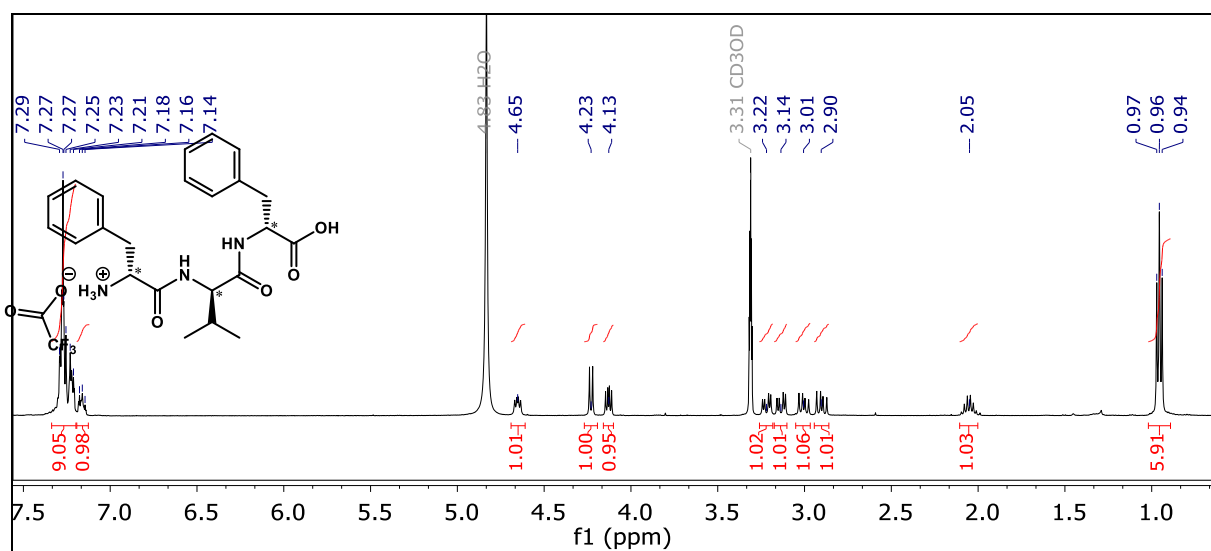
HMRS (ESI)



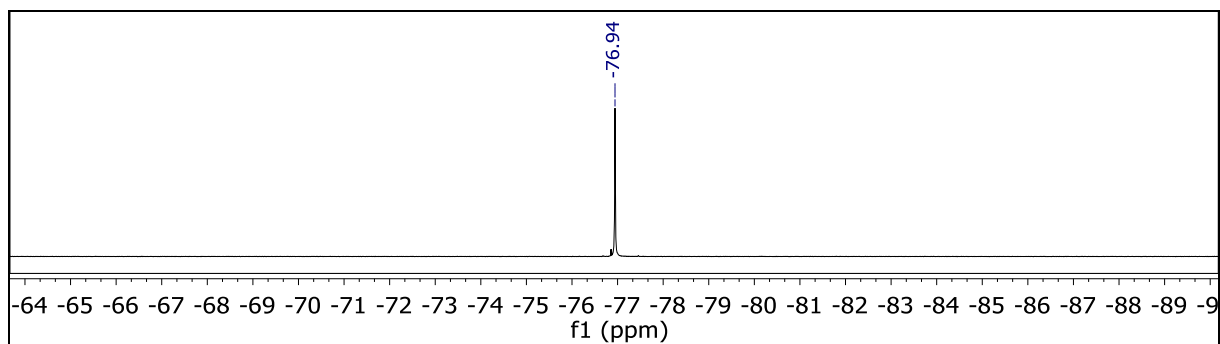
(R)-1-(((R)-1-(((R)-1-carboxy-2-phenylethyl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate

(P11D)

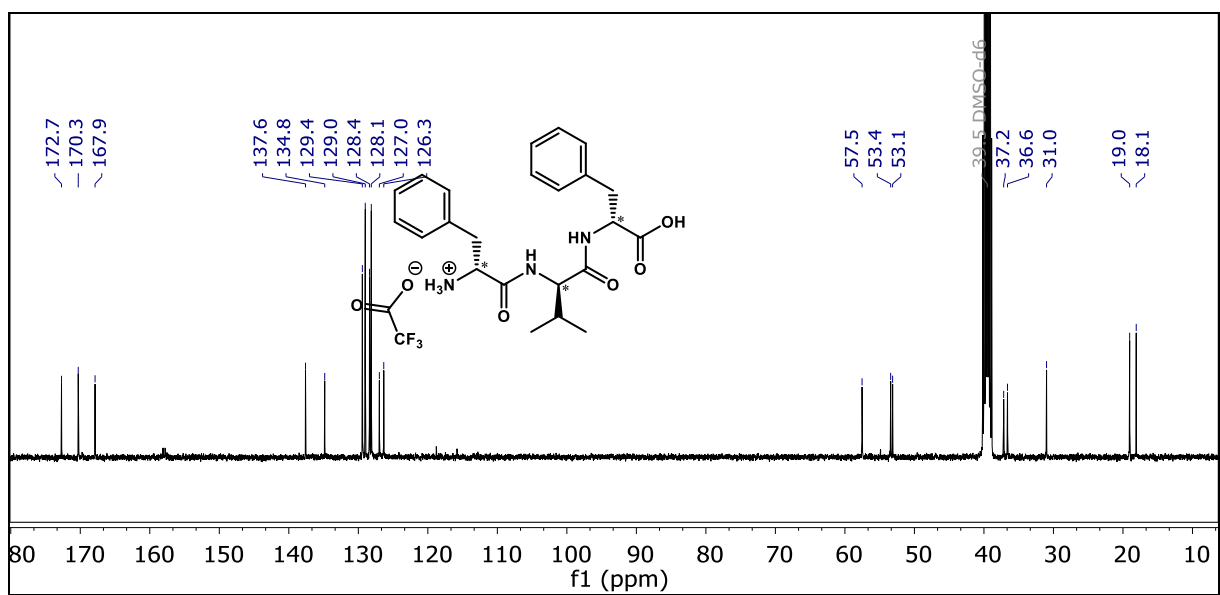
^1H NMR (400 MHz, MeOD)



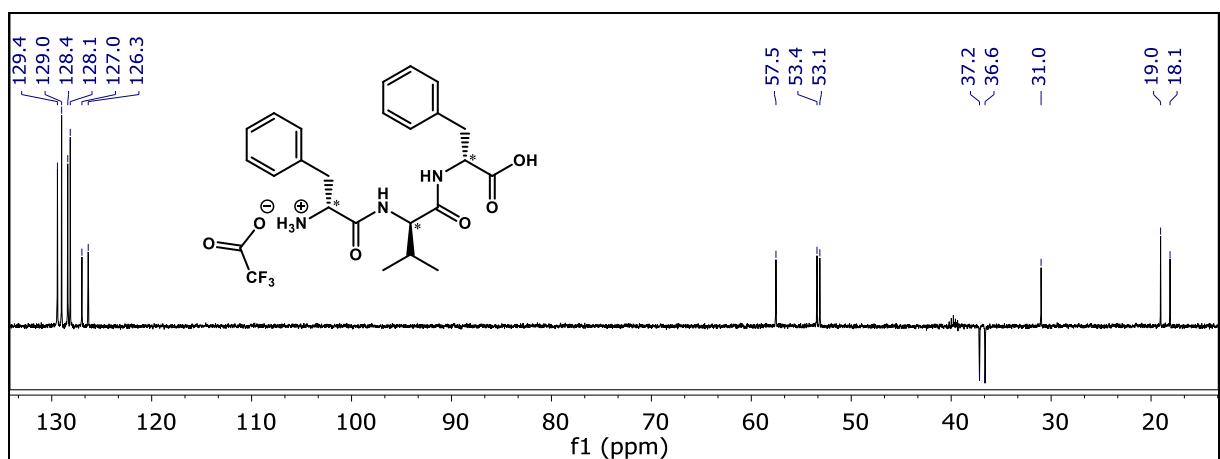
^{19}F NMR (376 MHz, MeOD)



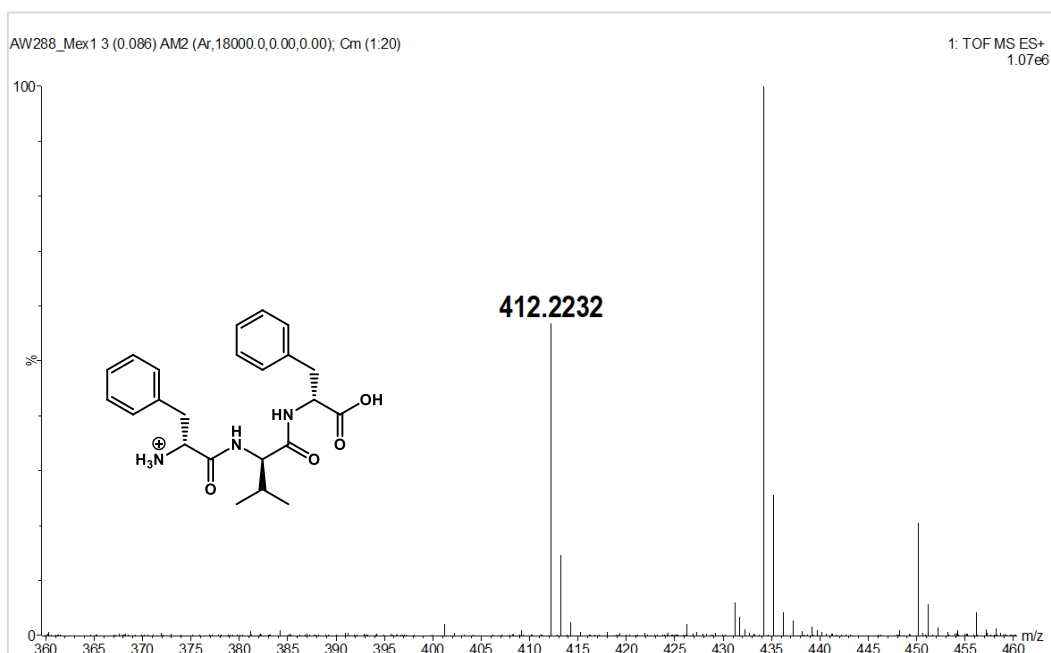
¹³C NMR (101 MHz, DMSO)



DEPT 135 (101 MHz, DMSO)

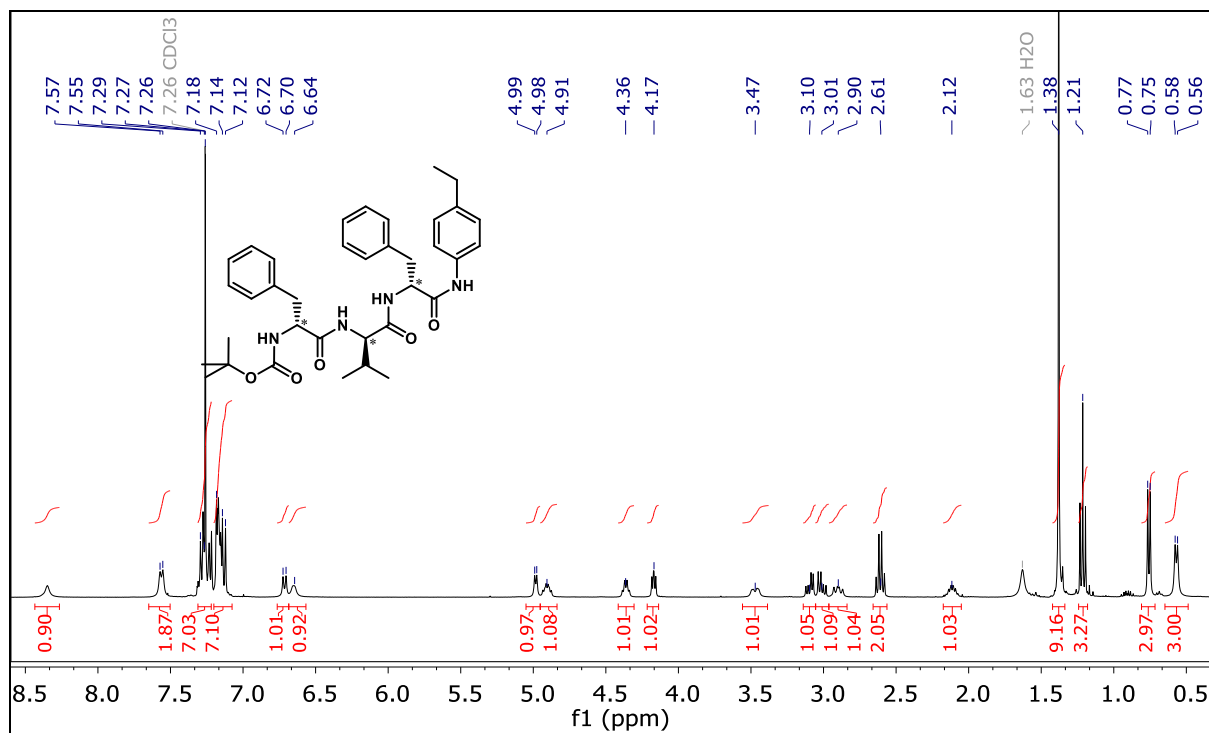


HRMS (ESI)

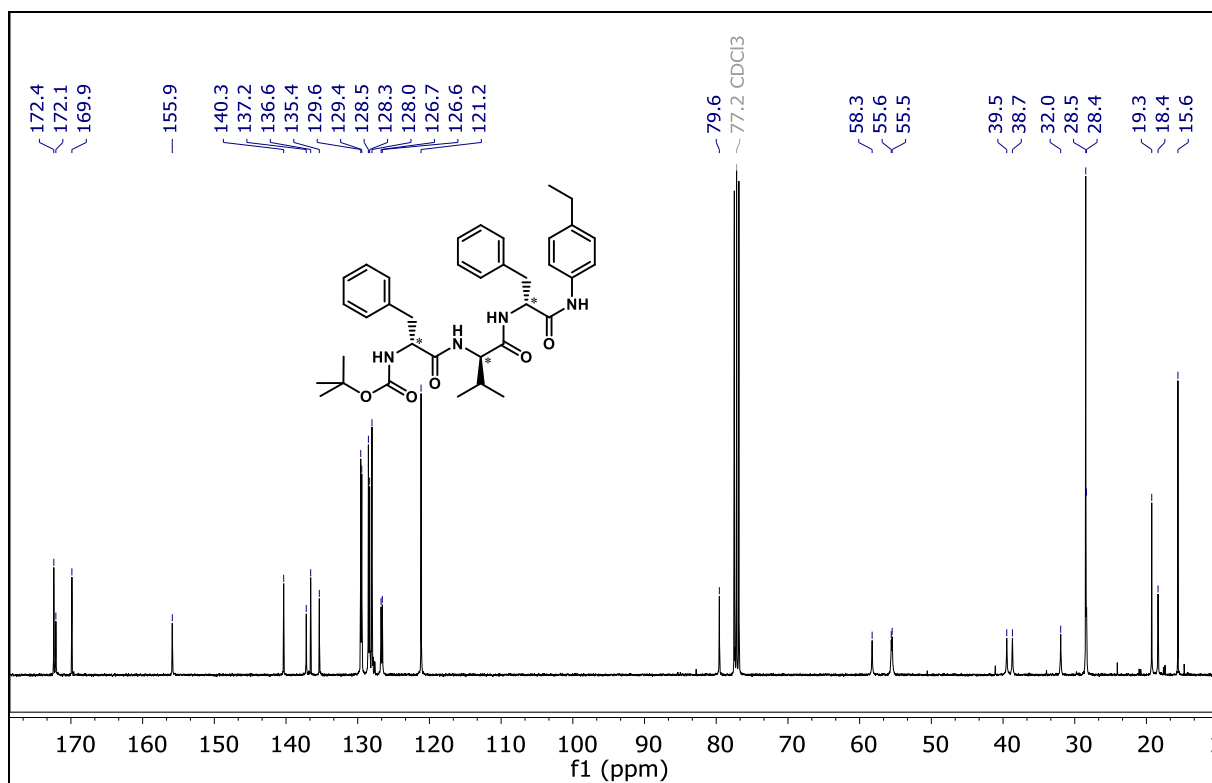


tert-butyl ((R)-1-(((R)-1-(((R)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate

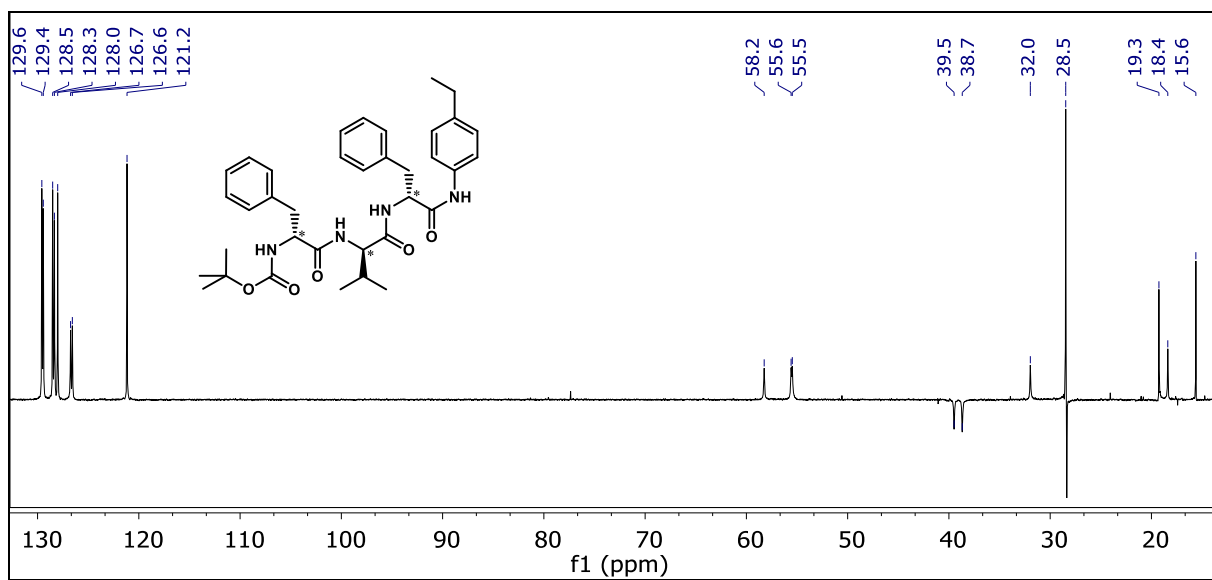
(P21D)

¹H NMR (400 MHz, CDCl₃)

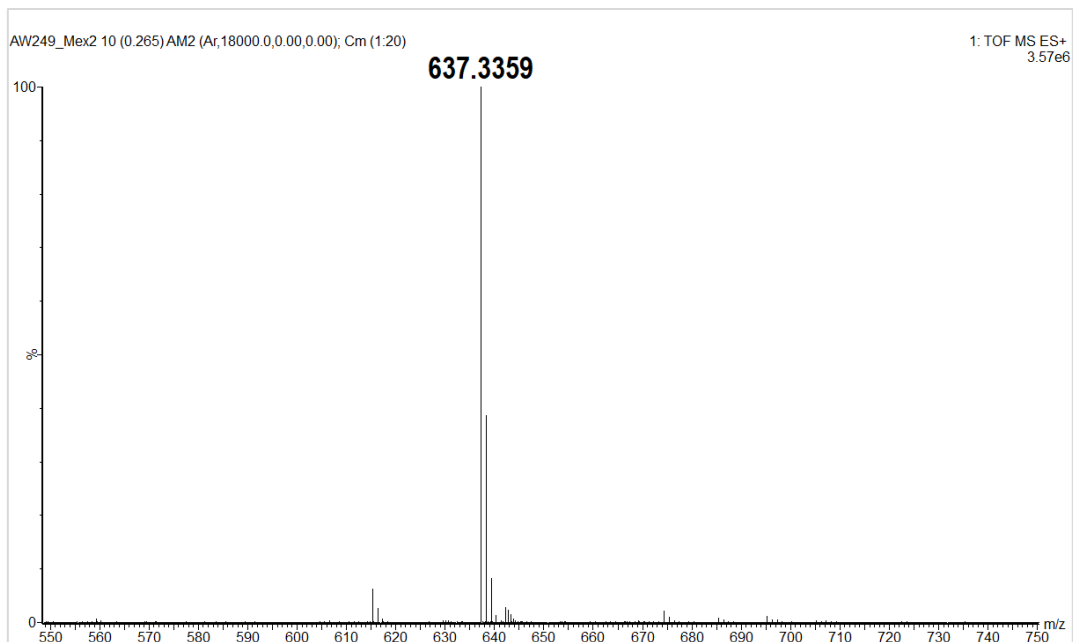
¹³C NMR (101 MHz, CDCl₃)



DEPT 135 (101 MHz, CDCl₃)



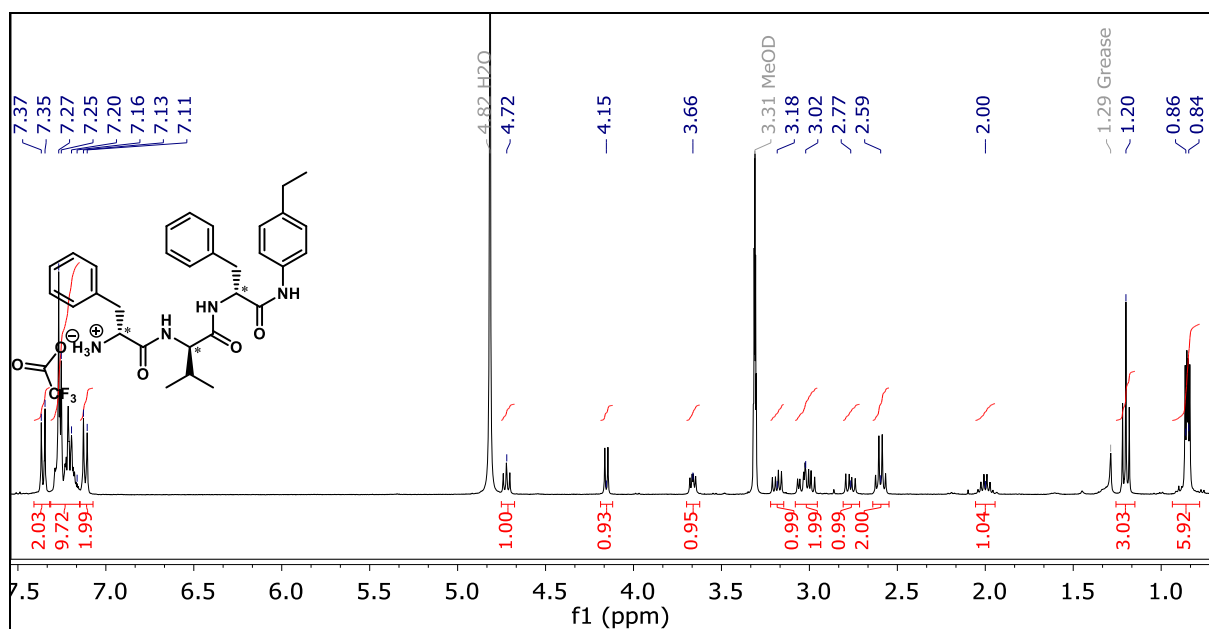
HRMS (ESI)



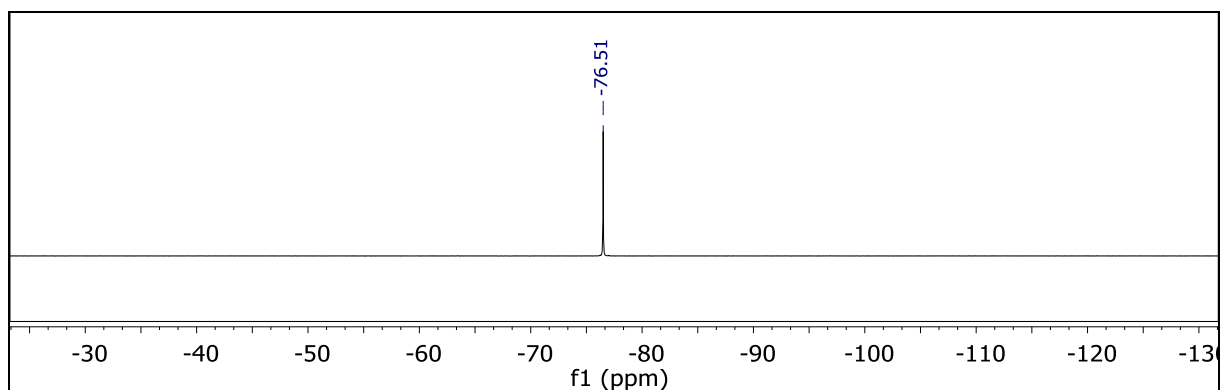
(R)-1-(((R)-1-(((R)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate

(P22D)

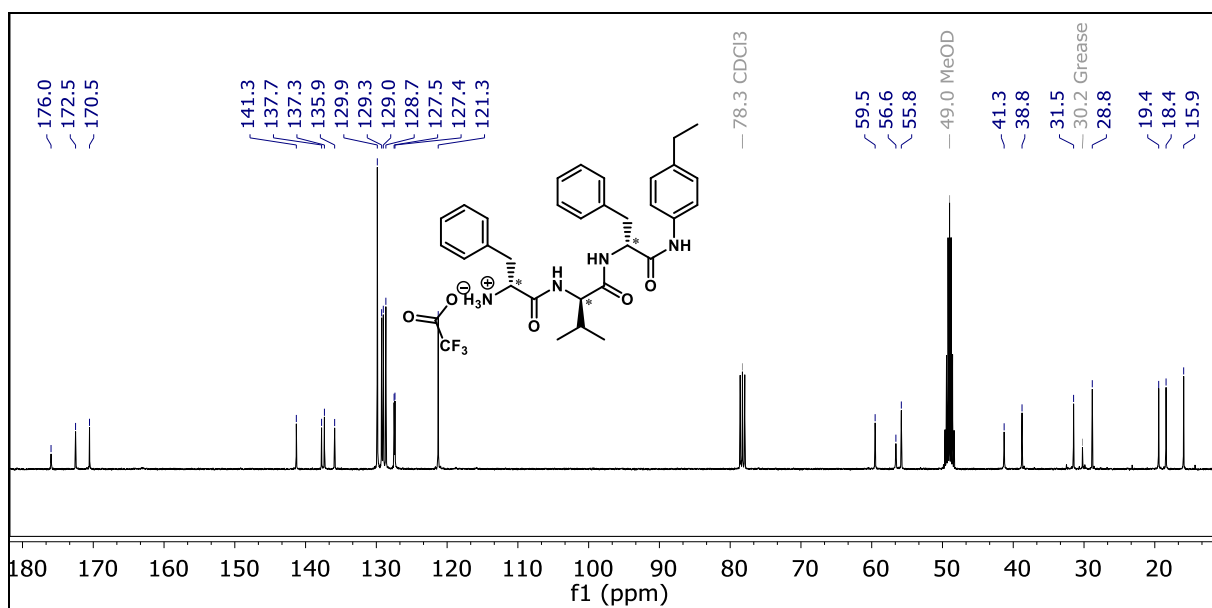
^1H NMR (400 MHz, MeOD)



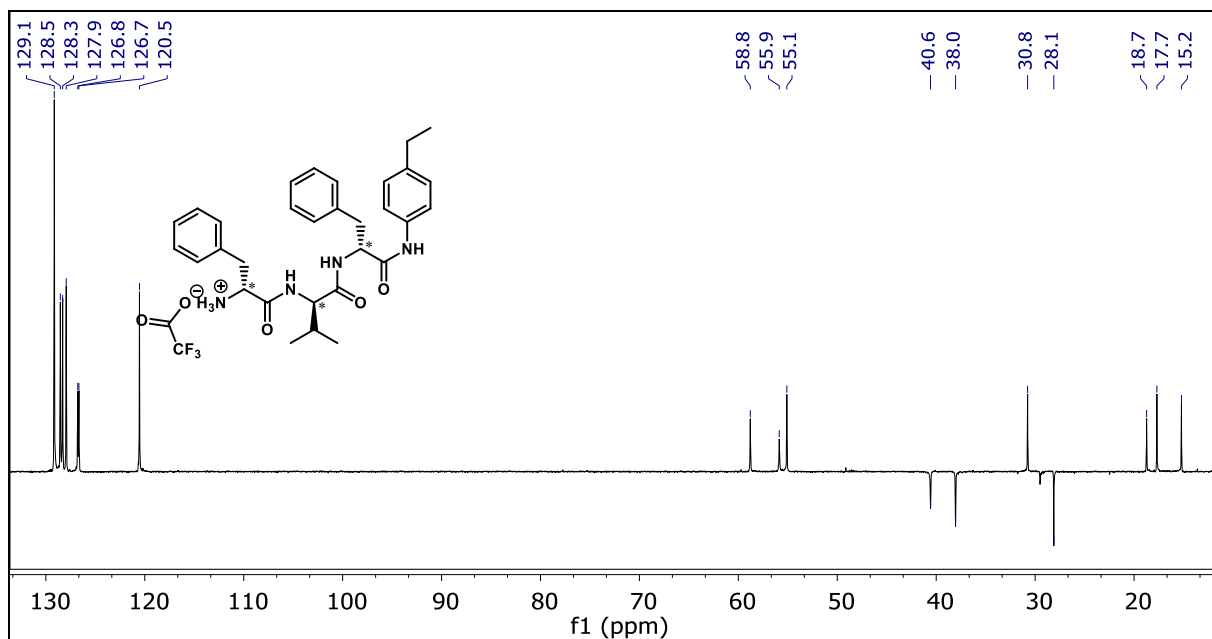
^{19}F NMR (376 MHz, MeOD)



^{13}C NMR (101 MHz, MeOD- CDCl_3 (1 : 1 ; v : v))

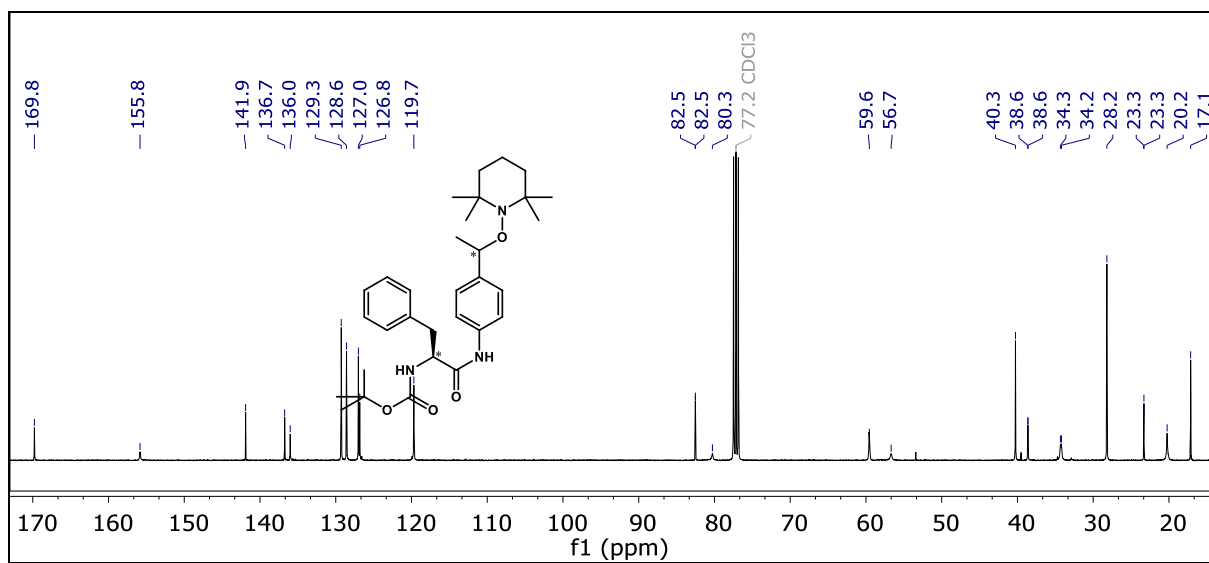


DEPT 135 (101 MHz, MeOD- CDCl_3 (1 : 1 ; v : v))

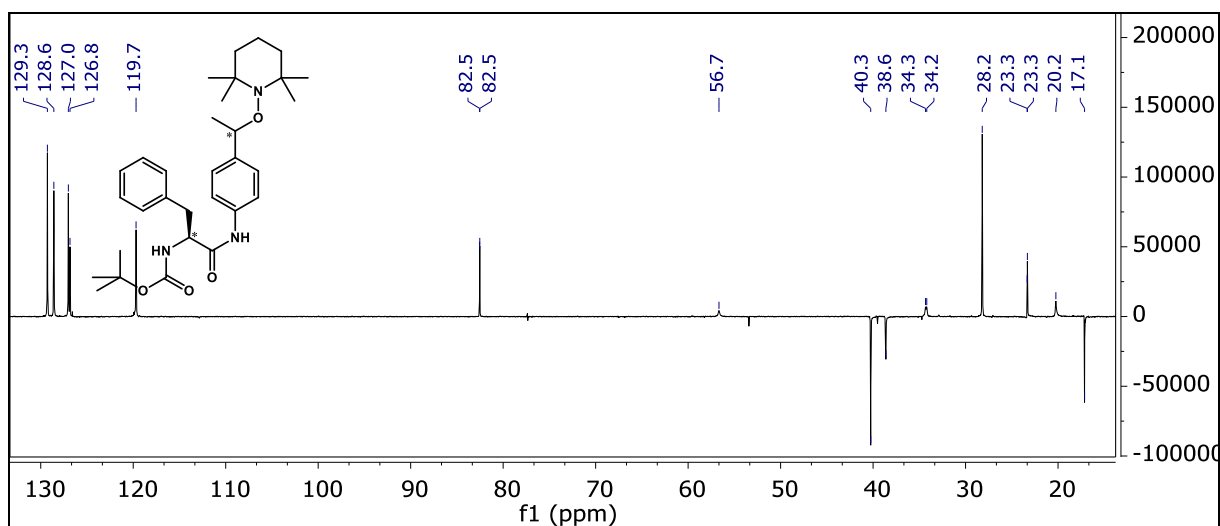


HRMS (ESI)

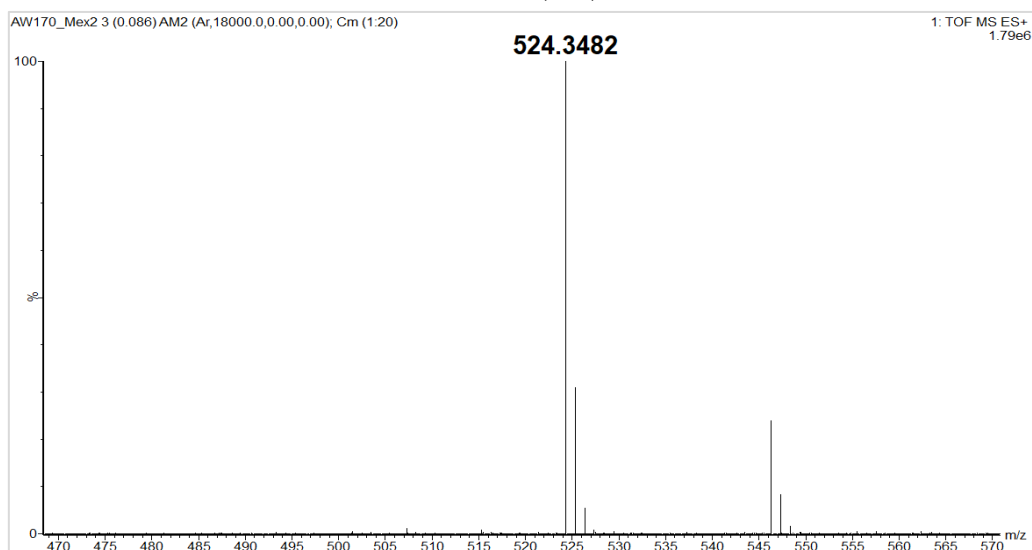
^{13}C NMR (101 MHz, CDCl_3)



DEPT 135 (101 MHz, CDCl_3)



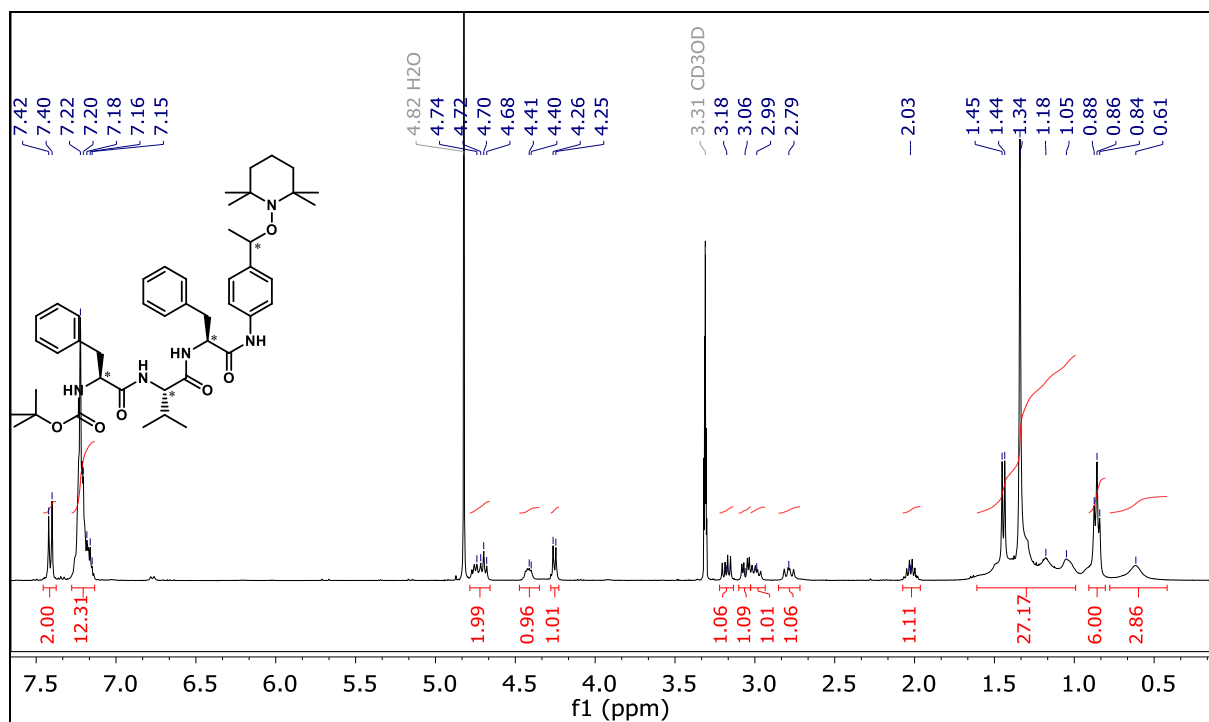
HRMS (ESI)



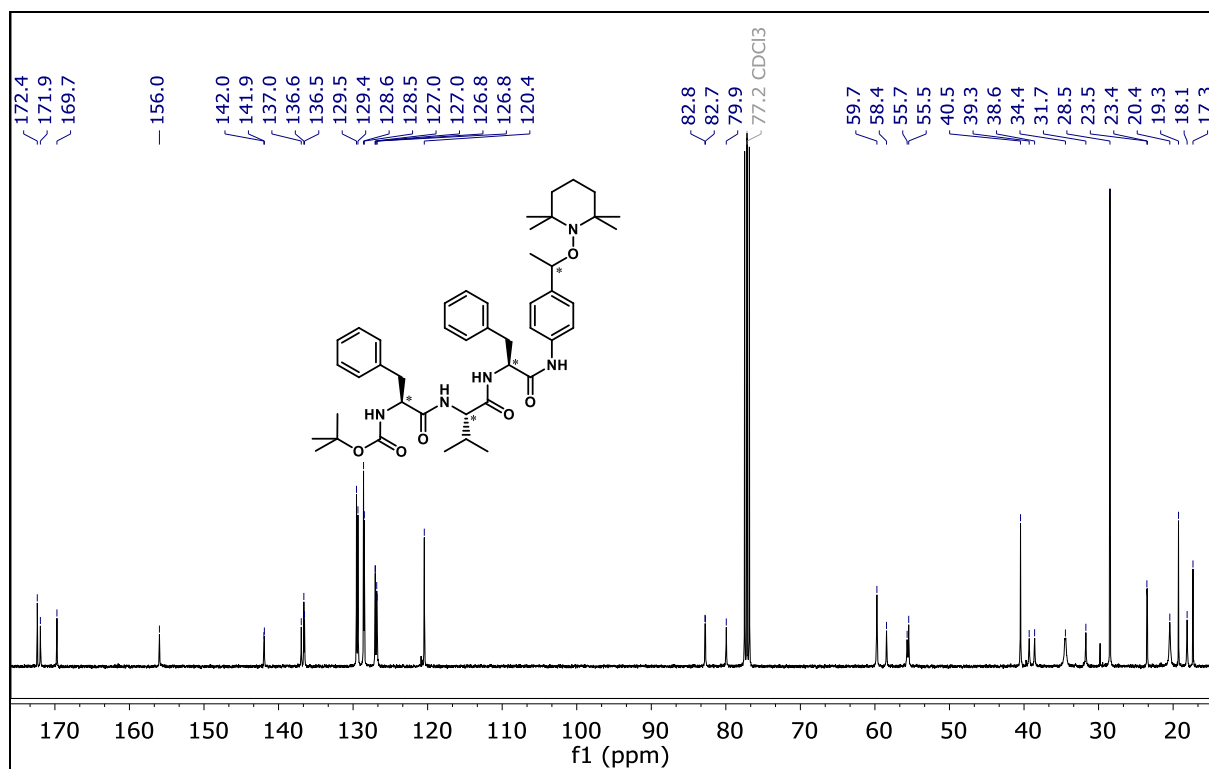
tert-butyl ((2S)-1-(((2S)-3-methyl-1-oxo-1-(((2S)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate

(A3L)

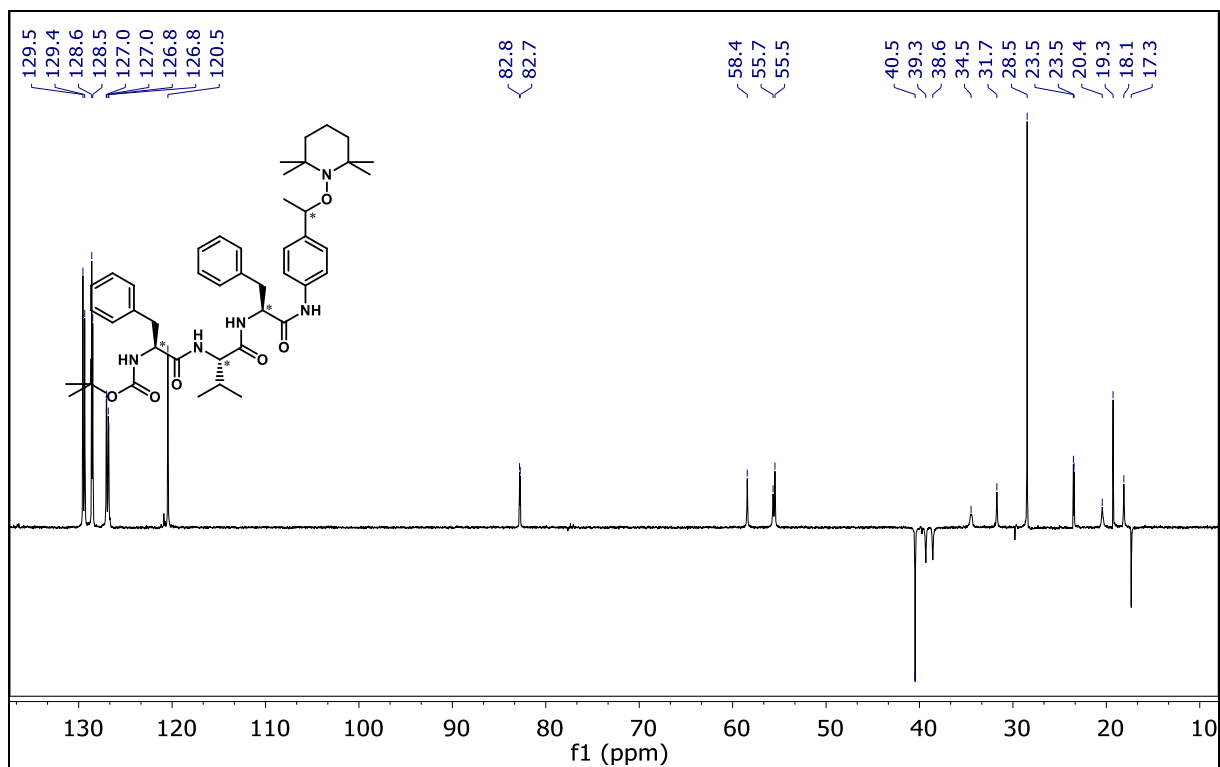
^1H NMR (300 MHz, MeOD)



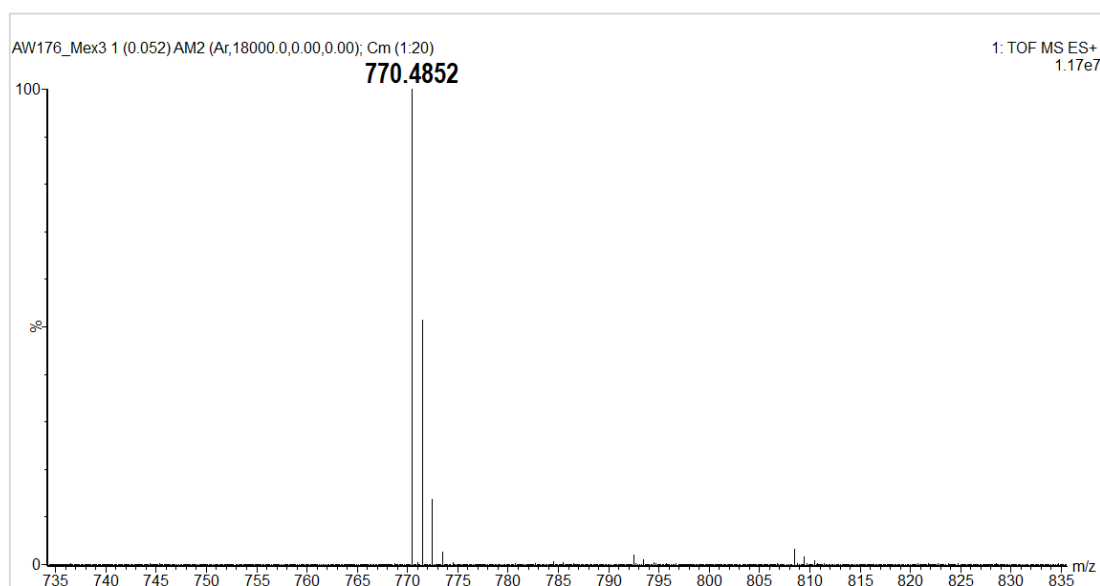
^{13}C NMR (101 MHz, CDCl₃)



DEPT 135 (101 MHz, CDCl₃)



HRMS (ESI)



(A4L)

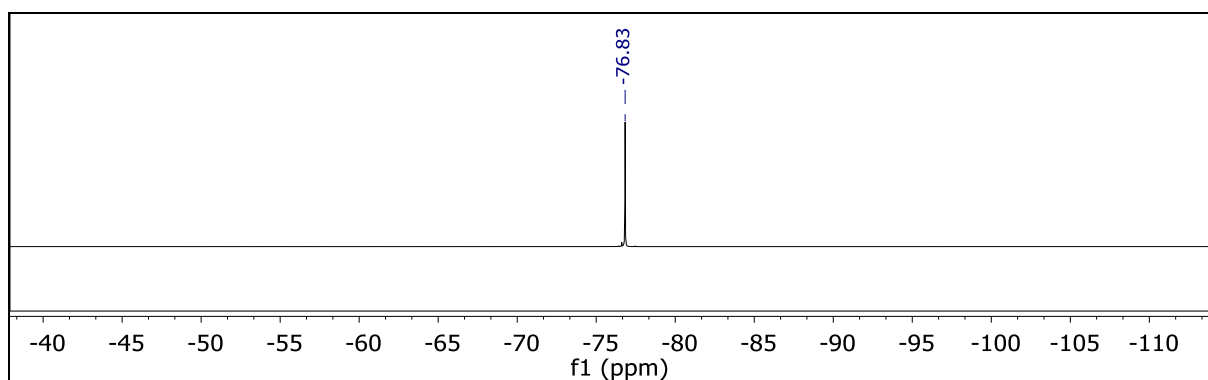
Chemical structure of compound 1: CC(C)[C@H](NC(=O)N[C@@H](Cc1ccccc1)C(=O)N[C@@H](Cc2ccc(NC(=O)N[C@@H](Cc3ccccc3)C(=O)N[C@@H](Cc4ccccc4)C(=O)N[C@@H](Cc5ccccc5)C(=O)N[C@@H](Cc6ccccc6)C(=O)N[C@@H](Cc7ccccc7)C(=O)N[C@@H](Cc8ccccc8)C(=O)N[C@@H](Cc9ccccc9)C(=O)N[C@@H](Cc10ccccc10)C(=O)N[C@@H](Cc11ccccc11)C(=O)N[C@@H](Cc12ccccc12)C(=O)N[C@@H](Cc13ccccc13)C(=O)N[C@@H](Cc14ccccc14)C(=O)N[C@@H](Cc15ccccc15)C(=O)N[C@@H](Cc16ccccc16)C(=O)N[C@@H](Cc17ccccc17)C(=O)N[C@@H](Cc18ccccc18)C(=O)N[C@@H](Cc19ccccc19)C(=O)N[C@@H](Cc20ccccc20)C(=O)N[C@@H](Cc21ccccc21)C(=O)N[C@@H](Cc22ccccc22)C(=O)N[C@@H](Cc23ccccc23)C(=O)N[C@@H](Cc24ccccc24)C(=O)N[C@@H](Cc25ccccc25)C(=O)N[C@@H](Cc26ccccc26)C(=O)N[C@@H](Cc27ccccc27)C(=O)N[C@@H](Cc28ccccc28)C(=O)N[C@@H](Cc29ccccc29)C(=O)N[C@@H](Cc30ccccc30)C(=O)N[C@@H](Cc31ccccc31)C(=O)N[C@@H](Cc32ccccc32)C(=O)N[C@@H](Cc33ccccc33)C(=O)N[C@@H](Cc34ccccc34)C(=O)N[C@@H](Cc35ccccc35)C(=O)N[C@@H](Cc36ccccc36)C(=O)N[C@@H](Cc37ccccc37)C(=O)N[C@@H](Cc38ccccc38)C(=O)N[C@@H](Cc39ccccc39)C(=O)N[C@@H](Cc40ccccc40)C(=O)N[C@@H](Cc41ccccc41)C(=O)N[C@@H](Cc42ccccc42)C(=O)N[C@@H](Cc43ccccc43)C(=O)N[C@@H](Cc44ccccc44)C(=O)N[C@@H](Cc45ccccc45)C(=O)N[C@@H](Cc46ccccc46)C(=O)N[C@@H](Cc47ccccc47)C(=O)N[C@@H](Cc48ccccc48)C(=O)N[C@@H](Cc49ccccc49)C(=O)N[C@@H](Cc50ccccc50)C(=O)N[C@@H](Cc51ccccc51)C(=O)N[C@@H](Cc52ccccc52)C(=O)N[C@@H](Cc53ccccc53)C(=O)N[C@@H](Cc54ccccc54)C(=O)N[C@@H](Cc55ccccc55)C(=O)N[C@@H](Cc56ccccc56)C(=O)N[C@@H](Cc57ccccc57)C(=O)N[C@@H](Cc58ccccc58)C(=O)N[C@@H](Cc59ccccc59)C(=O)N[C@@H](Cc60ccccc60)C(=O)N[C@@H](Cc61ccccc61)C(=O)N[C@@H](Cc62ccccc62)C(=O)N[C@@H](Cc63ccccc63)C(=O)N[C@@H](Cc64ccccc64)C(=O)N[C@@H](Cc65ccccc65)C(=O)N[C@@H](Cc66ccccc66)C(=O)N[C@@H](Cc67ccccc67)C(=O)N[C@@H](Cc68ccccc68)C(=O)N[C@@H](Cc69ccccc69)C(=O)N[C@@H](Cc70ccccc70)C(=O)N[C@@H](Cc71ccccc71)C(=O)N[C@@H](Cc72ccccc72)C(=O)N[C@@H](Cc73ccccc73)C(=O)N[C@@H](Cc74ccccc74)C(=O)N[C@@H](Cc75ccccc75)C(=O)N[C@@H](Cc76ccccc76)C(=O)N[C@@H](Cc77ccccc77)C(=O)N[C@@H](Cc78ccccc78)C(=O)N[C@@H](Cc79ccccc79)C(=O)N[C@@H](Cc80ccccc80)C(=O)N[C@@H](Cc81ccccc81)C(=O)N[C@@H](Cc82ccccc82)C(=O)N[C@@H](Cc83ccccc83)C(=O)N[C@@H](Cc84ccccc84)C(=O)N[C@@H](Cc85ccccc85)C(=O)N[C@@H](Cc86ccccc86)C(=O)N[C@@H](Cc87ccccc87)C(=O)N[C@@H](Cc88ccccc88)C(=O)N[C@@H](Cc89ccccc89)C(=O)N[C@@H](Cc90ccccc90)C(=O)N[C@@H](Cc91ccccc91)C(=O)N[C@@H](Cc92ccccc92)C(=O)N[C@@H](Cc93ccccc93)C(=O)N[C@@H](Cc94ccccc94)C(=O)N[C@@H](Cc95ccccc95)C(=O)N[C@@H](Cc96ccccc96)C(=O)N[C@@H](Cc97ccccc97)C(=O)N[C@@H](Cc98ccccc98)C(=O)N[C@@H](Cc99ccccc99)C(=O)N[C@@H](Cc100ccccc100)C(=O)N[C@@H](Cc101ccccc101)C(=O)N[C@@H](Cc102ccccc102)C(=O)N[C@@H](Cc103ccccc103)C(=O)N[C@@H](Cc104ccccc104)C(=O)N[C@@H](Cc105ccccc105)C(=O)N[C@@H](Cc106ccccc106)C(=O)N[C@@H](Cc107ccccc107)C(=O)N[C@@H](Cc108ccccc108)C(=O)N[C@@H](Cc109ccccc109)C(=O)N[C@@H](Cc110ccccc110)C(=O)N[C@@H](Cc111ccccc111)C(=O)N[C@@H](Cc112ccccc112)C(=O)N[C@@H](Cc113ccccc113)C(=O)N[C@@H](Cc114ccccc114)C(=O)N[C@@H](Cc115ccccc115)C(=O)N[C@@H](Cc116ccccc116)C(=O)N[C@@H](Cc117ccccc117)C(=O)N[C@@H](Cc118ccccc118)C(=O)N[C@@H](Cc119ccccc119)C(=O)N[C@@H](Cc120ccccc120)C(=O)N[C@@H](Cc121ccccc121)C(=O)N[C@@H](Cc122ccccc122)C(=O)N[C@@H](Cc123ccccc123)C(=O)N[C@@H](Cc124ccccc124)C(=O)N[C@@H](Cc125ccccc125)C(=O)N[C@@H](Cc126ccccc126)C(=O)N[C@@H](Cc127ccccc127)C(=O)N[C@@H](Cc128ccccc128)C(=O)N[C@@H](Cc129ccccc129)C(=O)N[C@@H](Cc130ccccc130)C(=O)N[C@@H](Cc131ccccc131)C(=O)N[C@@H](Cc132ccccc132)C(=O)N[C@@H](Cc133ccccc133)C(=O)N[C@@H](Cc134ccccc134)C(=O)N[C@@H](Cc135ccccc135)C(=O)N[C@@H](Cc136ccccc136)C(=O)N[C@@H](Cc137ccccc137)C(=O)N[C@@H](Cc138ccccc138)C(=O)N[C@@H](Cc139ccccc139)C(=O)N[C@@H](Cc140ccccc140)C(=O)N[C@@H](Cc141ccccc141)C(=O)N[C@@H](Cc142ccccc142)C(=O)N[C@@H](Cc143ccccc143)C(=O)N[C@@H](Cc144ccccc144)C(=O)N[C@@H](Cc145ccccc145)C(=O)N[C@@H](Cc146ccccc146)C(=O)N[C@@H](Cc147ccccc147)C(=O)N[C@@H](Cc148ccccc148)C(=O)N[C@@H](Cc149ccccc149)C(=O)N[C@@H](Cc150ccccc150)C(=O)N[C@@H](Cc151ccccc151)C(=O)N[C@@H](Cc152ccccc152)C(=O)N[C@@H](Cc153ccccc153)C(=O)N[C@@H](Cc154ccccc154)C(=O)N[C@@H](Cc155ccccc155)C(=O)N[C@@H](Cc156ccccc156)C(=O)N[C@@H](Cc157ccccc157)C(=O)N[C@@H](Cc158ccccc158)C(=O)N[C@@H](Cc159ccccc159)C(=O)N[C@@H](Cc160ccccc160)C(=O)N[C@@H](Cc161ccccc161)C(=O)N[C@@H](Cc162ccccc162)C(=O)N[C@@H](Cc163ccccc163)C(=O)N[C@@H](Cc164ccccc164)C(=O)N[C@@H](Cc165ccccc165)C(=O)N[C@@H](Cc166ccccc166)C(=O)N[C@@H](Cc167ccccc167)C(=O)N[C@@H](Cc168ccccc168)C(=O)N[C@@H](Cc169ccccc169)C(=O)N[C@@H](Cc170ccccc170)C(=O)N[C@@H](Cc171ccccc171)C(=O)N[C@@H](Cc172ccccc172)C(=O)N[C@@H](Cc173ccccc173)C(=O)N[C@@H](Cc174ccccc174)C(=O)N[C@@H](Cc175ccccc175)C(=O)N[C@@H](Cc176ccccc176)C(=O)N[C@@H](Cc177ccccc177)C(=O)N[C@@H](Cc178ccccc178)C(=O)N[C@@H](Cc179ccccc179)C(=O)N[C@@H](Cc180ccccc180)C(=O)N[C@@H](Cc181ccccc181)C(=O)N[C@@H](Cc182ccccc182)C(=O)N[C@@H](Cc183ccccc183)C(=O)N[C@@H](Cc184ccccc184)C(=O)N[C@@H](Cc185ccccc185)C(=O)N[C@@H](Cc186ccccc186)C(=O)N[C@@H](Cc187ccccc187)C(=O)N[C@@H](Cc188ccccc188)C(=O)N[C@@H](Cc189ccccc189)C(=O)N[C@@H](Cc190ccccc190)C(=O)N[C@@H](Cc191ccccc191)C(=O)N[C@@H](Cc192ccccc192)C(=O)N[C@@H](Cc193ccccc193)C(=O)N[C@@H](Cc194ccccc194)C(=O)N[C@@H](Cc195ccccc195)C(=O)N[C@@H](Cc196ccccc196)C(=O)N[C@@H](Cc197ccccc197)C(=O)N[C@@H](Cc198ccccc198)C(=O)N[C@@H](Cc199ccccc199)C(=O)N[C@@H](Cc200ccccc200)C(=O)N[C@@H](Cc201ccccc201)C(=O)N[C@@H](Cc202ccccc202)C(=O)N[C@@H](Cc203ccccc203)C(=O)N[C@@H](Cc204ccccc204)C(=O)N[C@@H](Cc205cc

Chemical structure of compound 10 is shown above the spectrum. The structure is a complex molecule with a central amide bond, a trifluoromethyl group, a phenyl ring, and a piperidine ring. The piperidine ring is labeled with '84.0' and '84.6'.

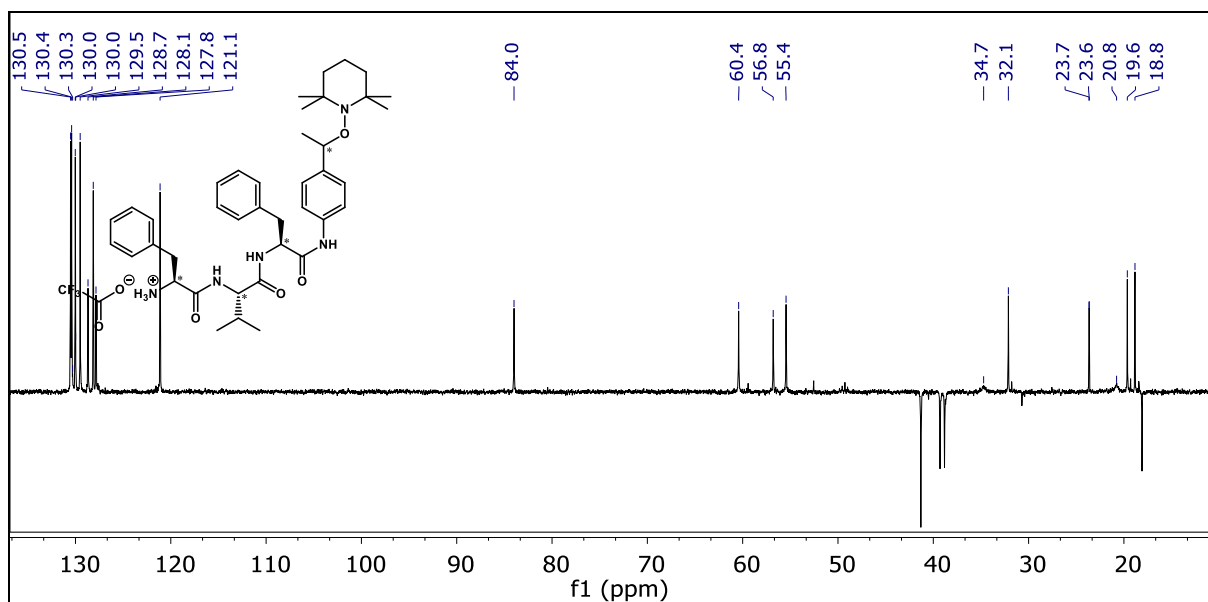
¹³C NMR peaks (ppm):

- 172.9
- 171.4
- 170.2
- 143.0
- 138.1
- 138.0
- 135.6
- 130.5
- 130.4
- 130.0
- 129.5
- 128.7
- 128.1
- 127.9
- 121.1
- 84.0
- 84.6
- 60.9
- 60.4
- 56.8
- 55.5
- 49.0 CD3OD
- 41.3
- 39.3
- 38.8
- 34.7
- 32.1
- 23.7
- 20.8
- 19.6
- 18.8
- 18.1

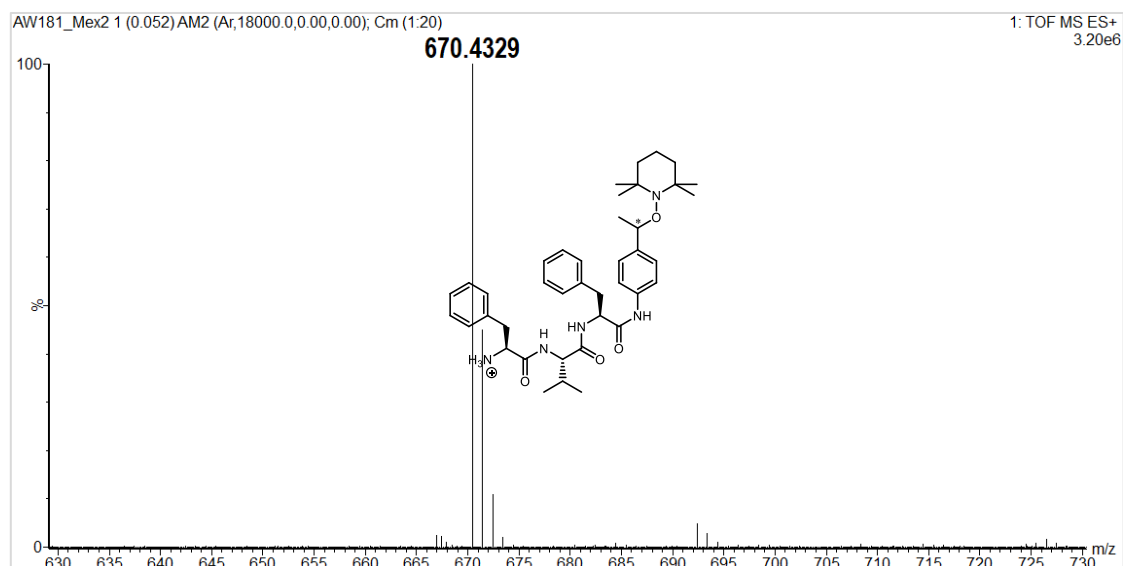
^{19}F NMR (376 MHz, MeOD)



DEPT 135 (75 MHz, MeOD)



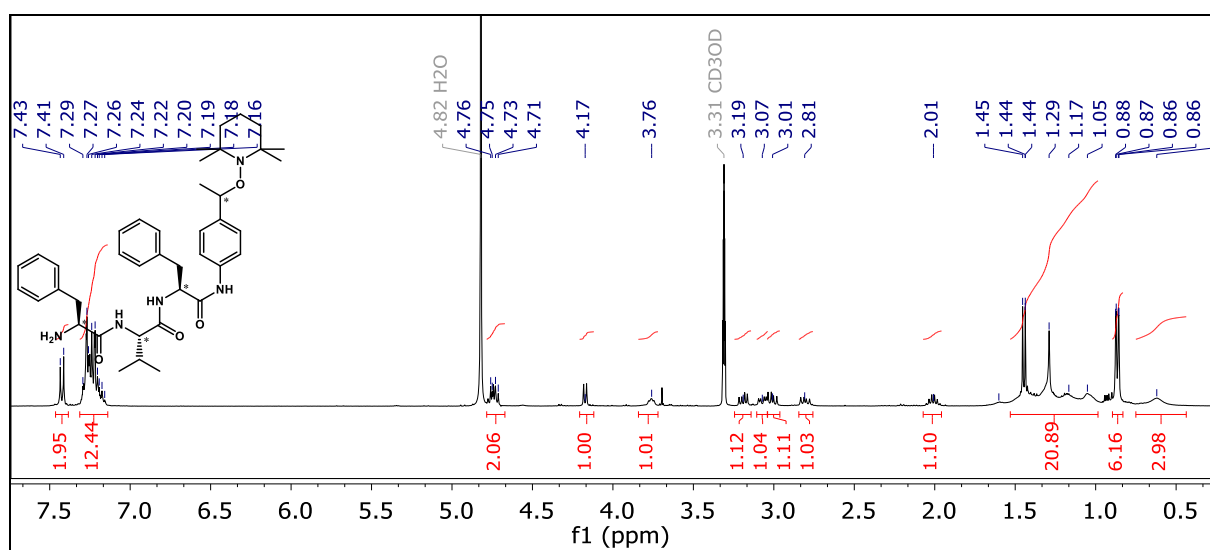
HRMS (ESI)



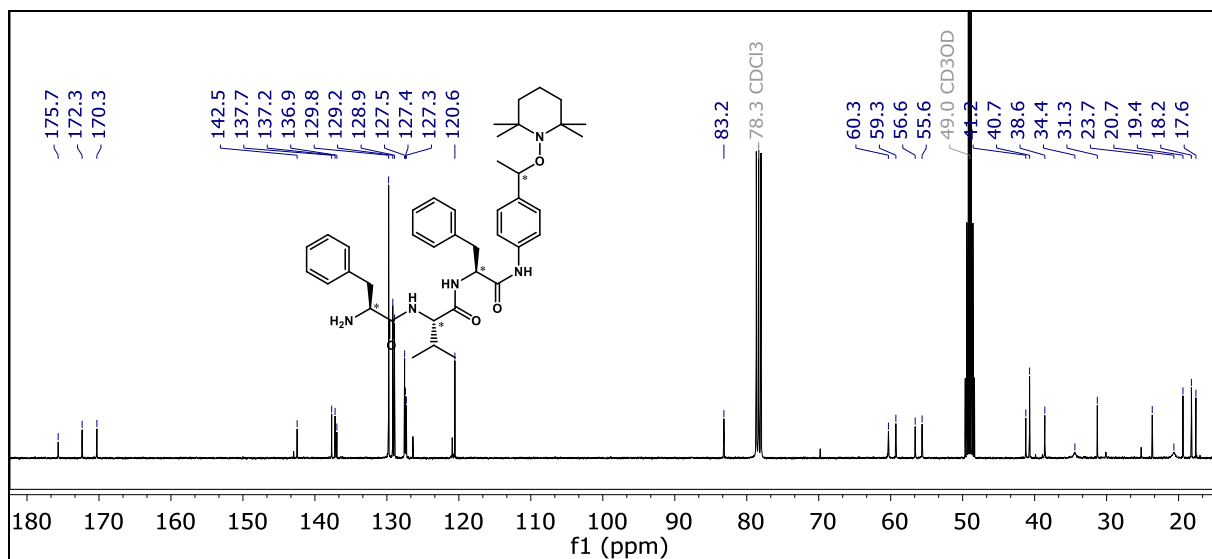
(2S)-2-((S)-2-amino-3-phenylpropanamido)-3-methyl-N-((2S)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)butanamide

(A5L)

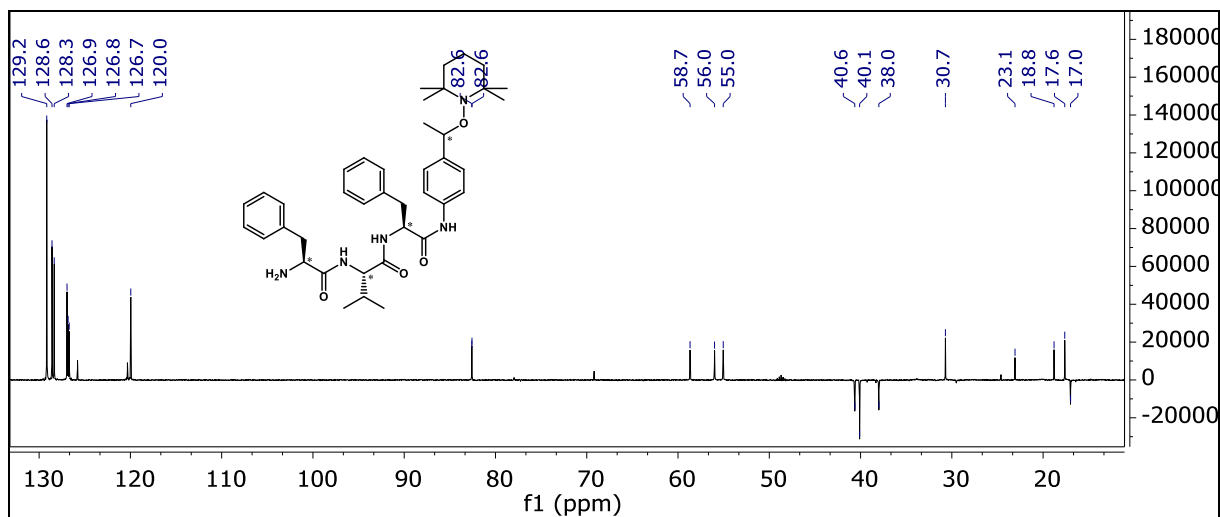
^1H NMR (400 MHz, MeOD)



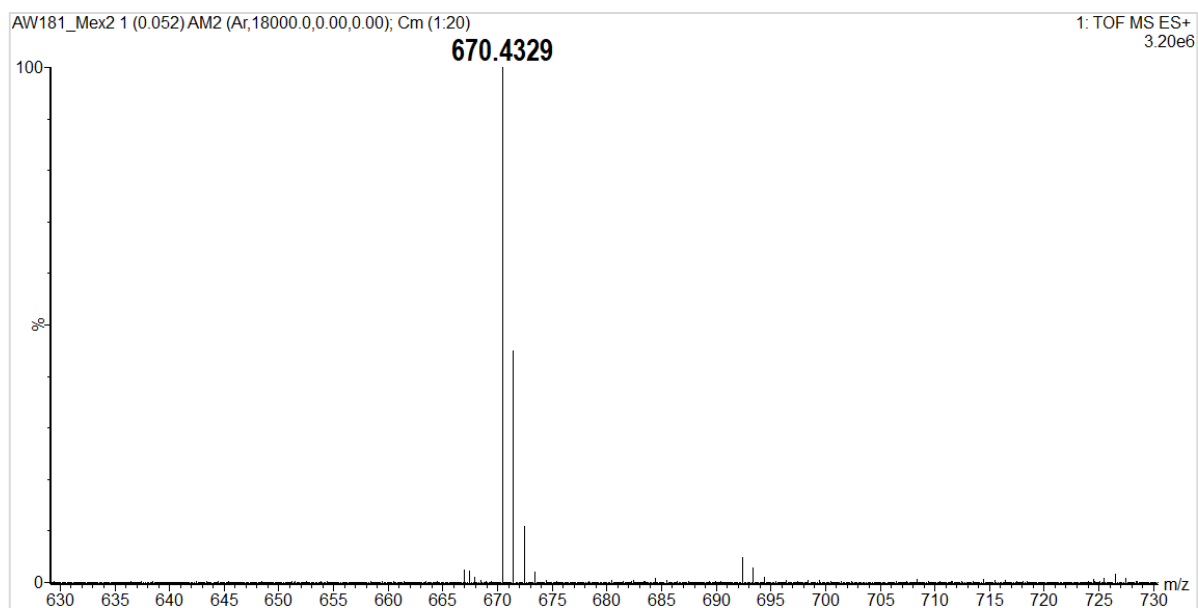
^{13}C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



DEPT 135 (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



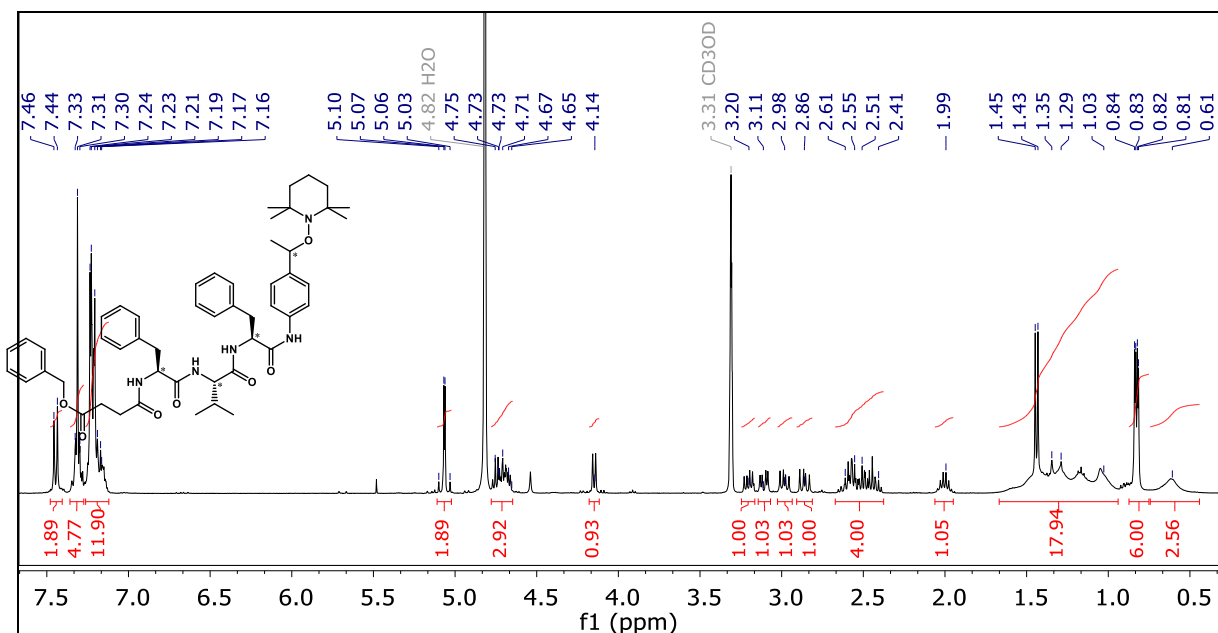
HRMS (ESI)



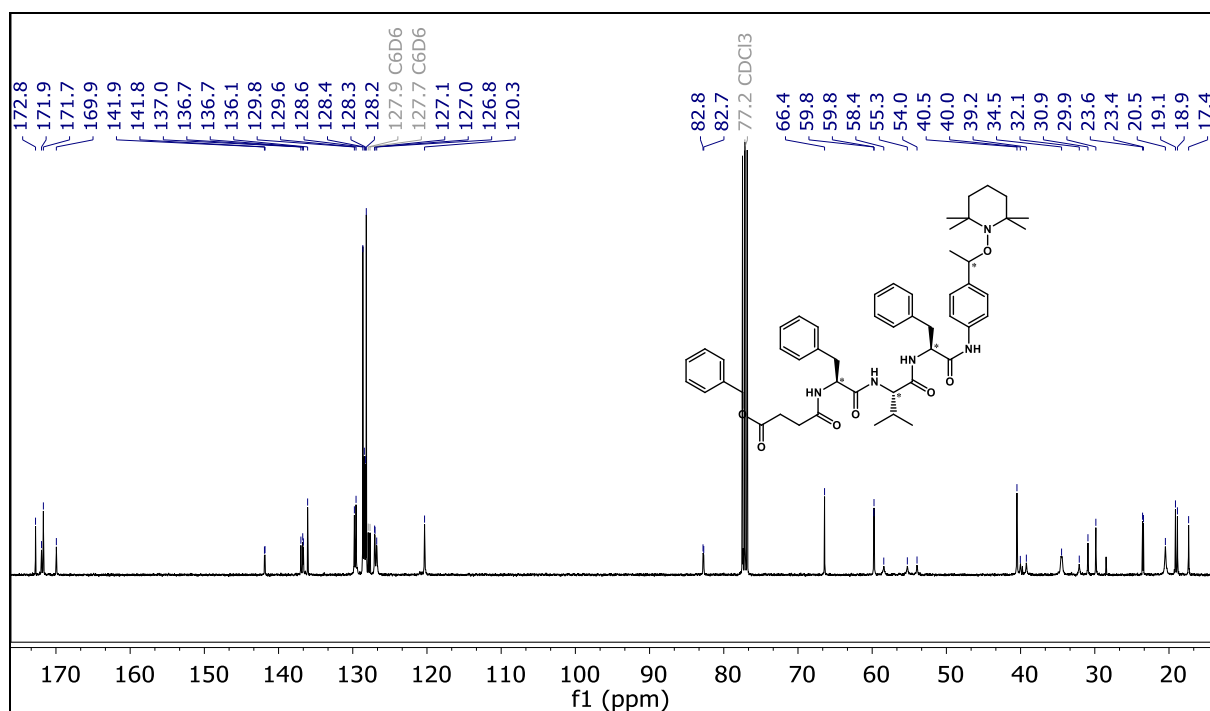
benzyl 4-(((2S)-1-(((2S)-3-methyl-1-oxo-1-(((2S)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoate

(A6L)

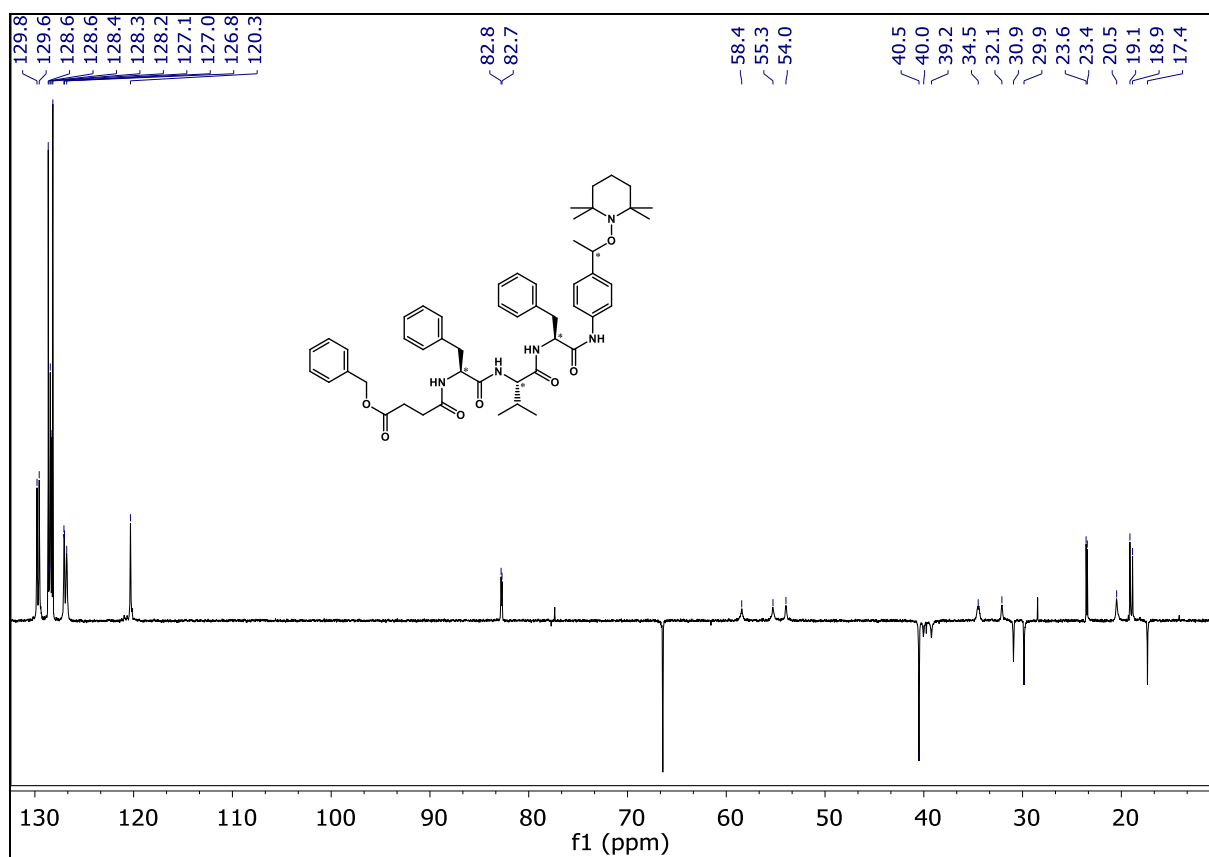
^1H NMR (400 MHz, MeOD)



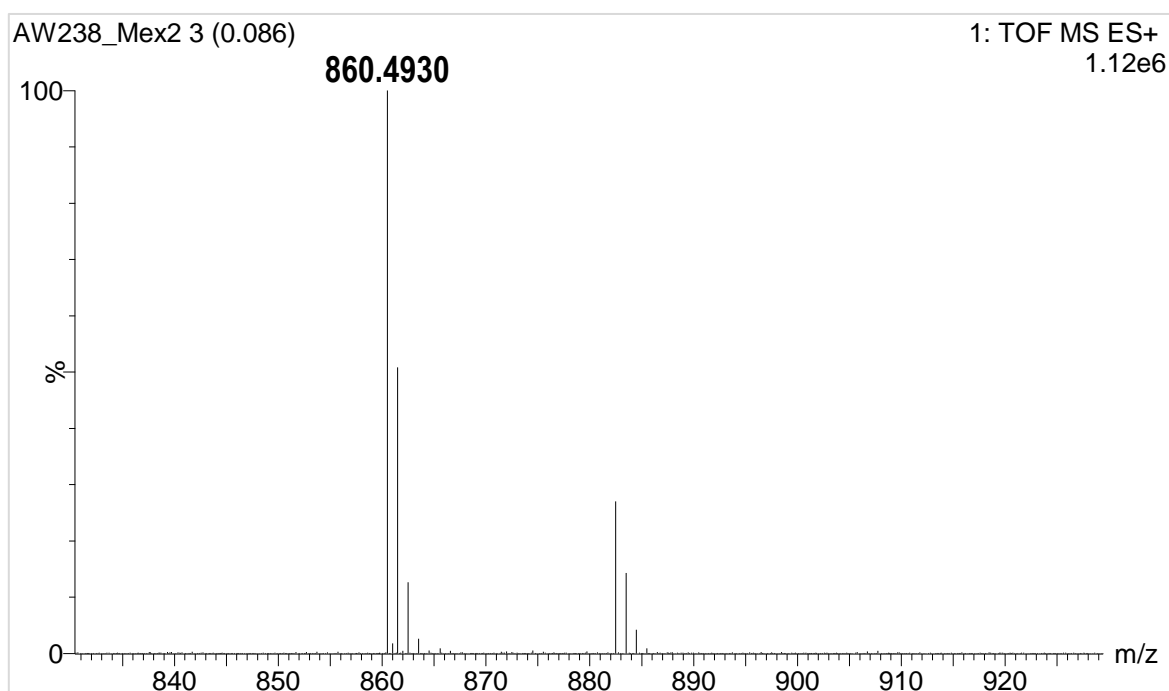
^{13}C NMR (101 MHz, CDCl₃ / C₆D₆ : 19 : 1)



DEPT 135 (101 MHz, CDCl₃ / C₆D₆ : 19 : 1)

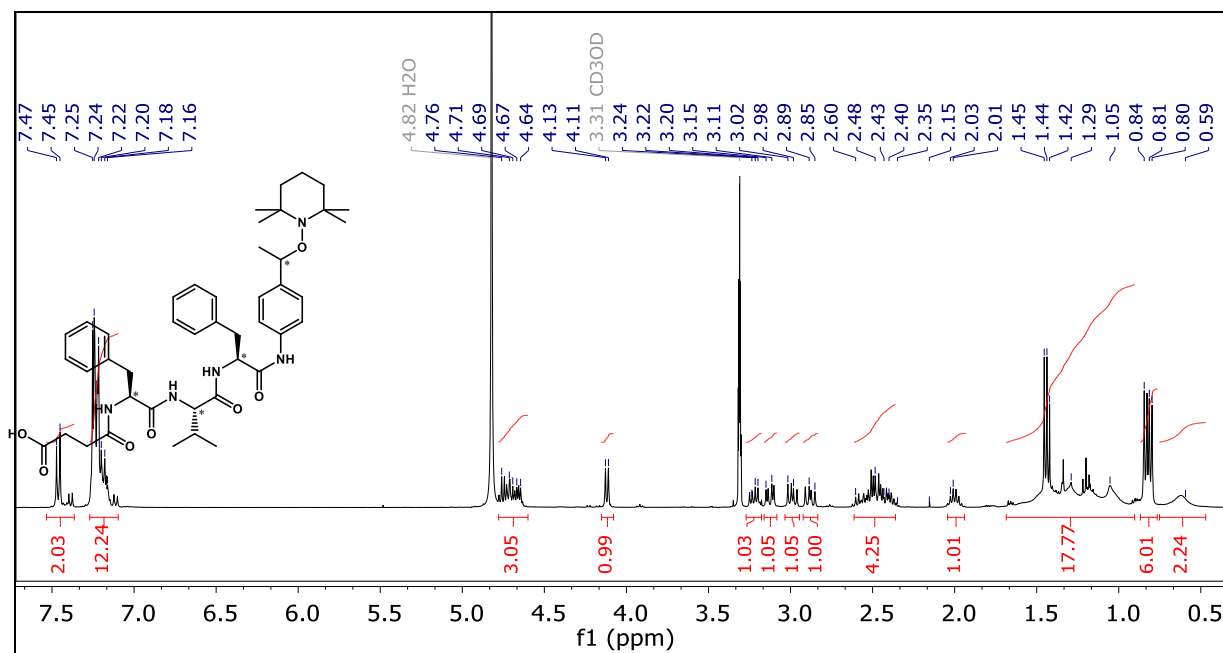


HRMS (ESI)

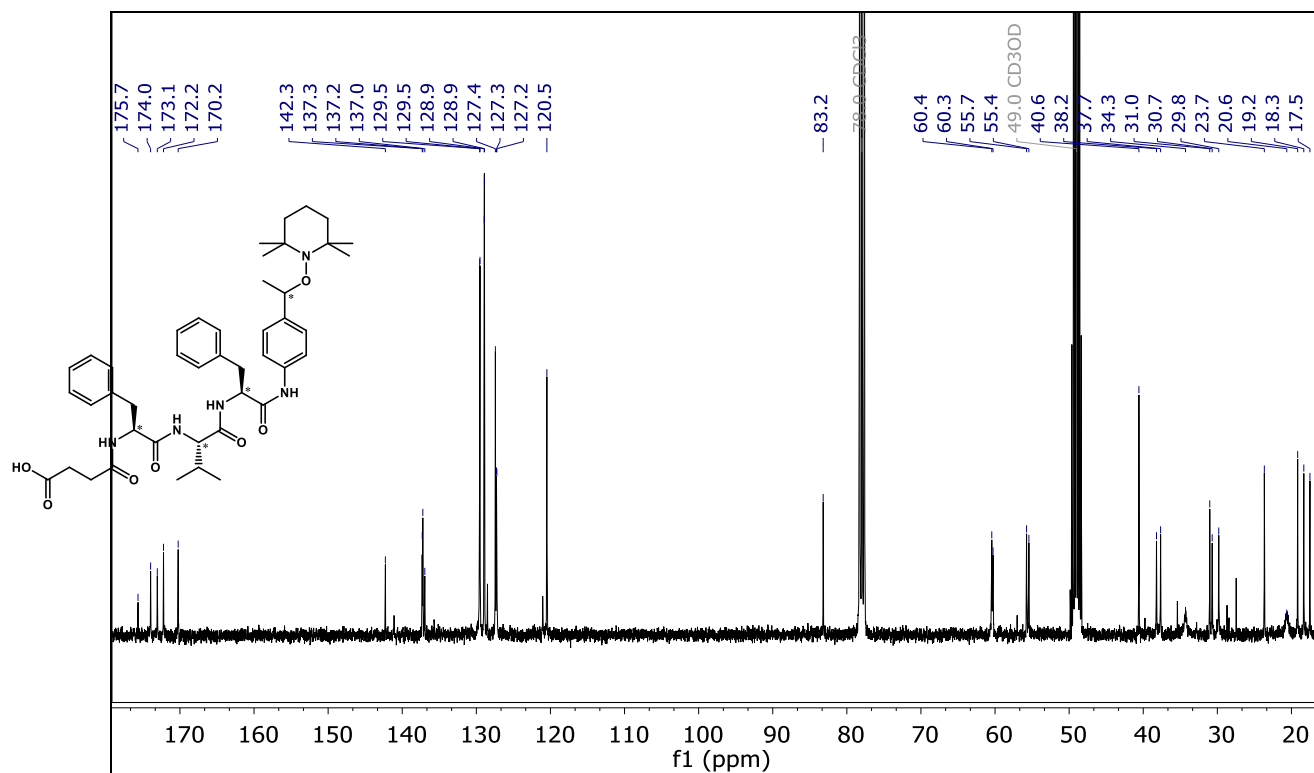


4-(((2S)-1-(((2S)-3-methyl-1-oxo-1-(((2S)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoic acid

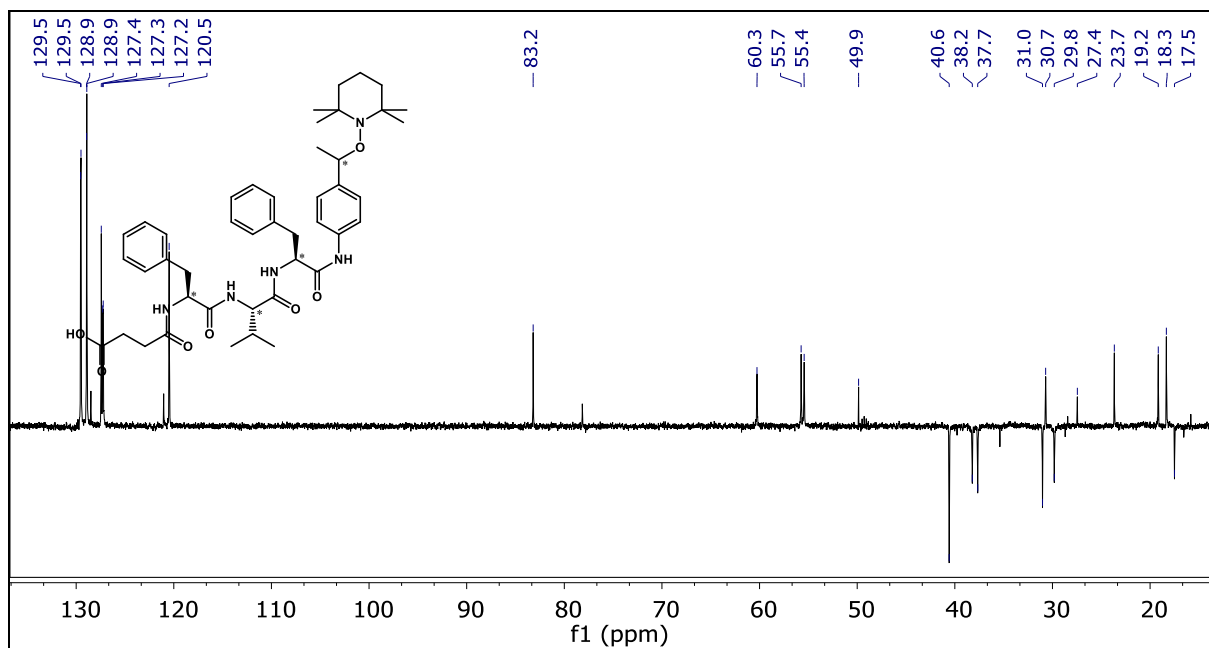
(A7L)
¹H NMR (400 MHz, MeOD)



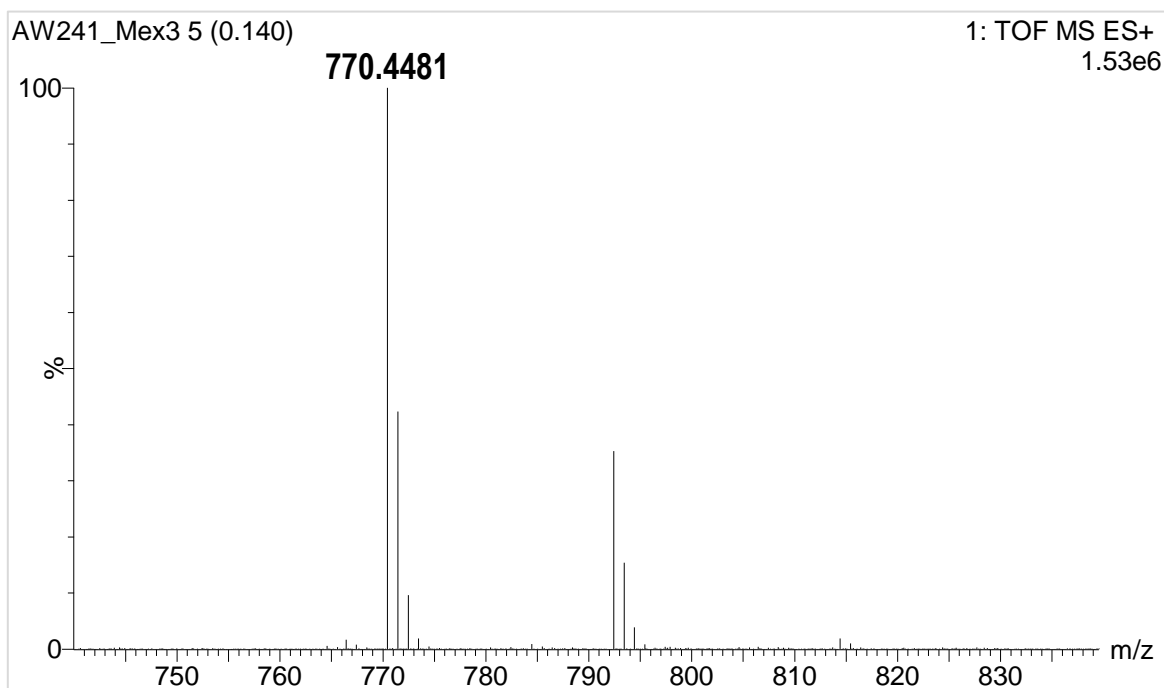
¹³C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



DEPT 135 (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v))



HRMS (ESI)

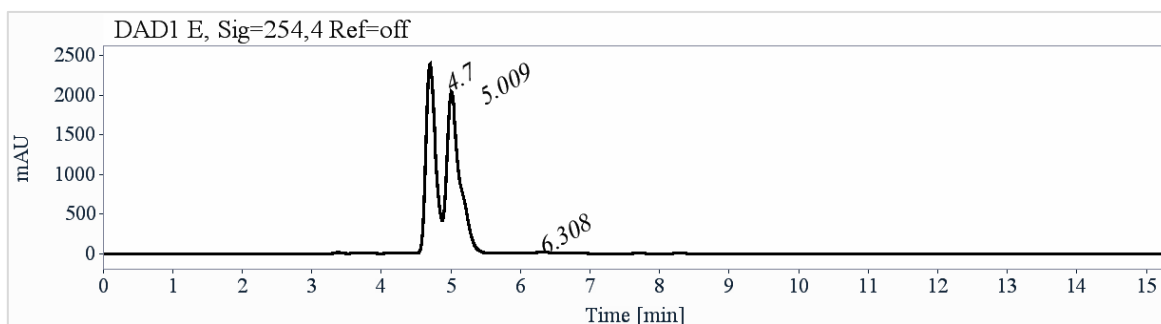


tert-butyl ((2R)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)carbamate

(A1D)

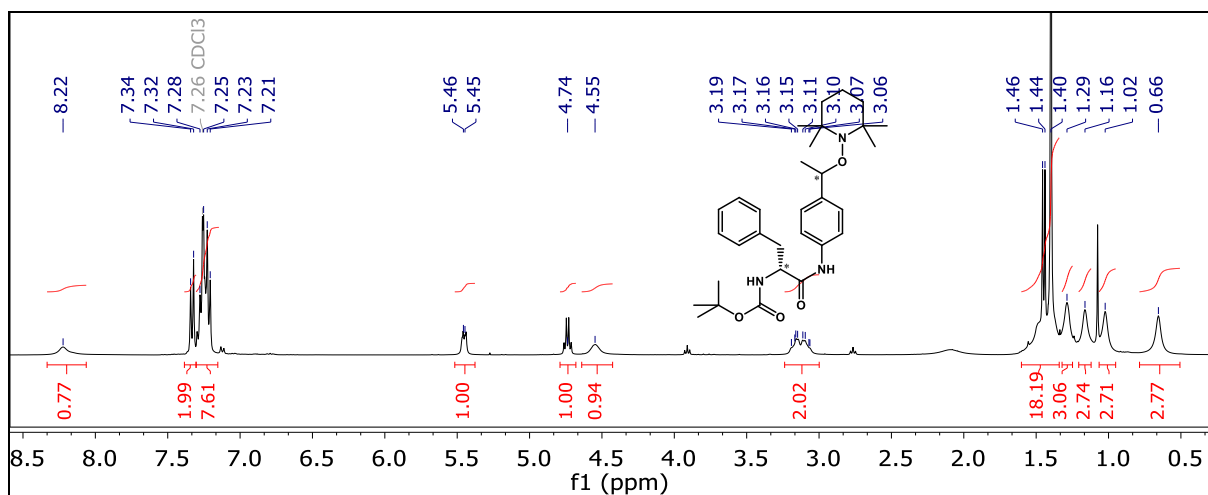
Chiral HPLC report

Heptane/ethanol/dichloromethane (80/10/10), 1 mL/min

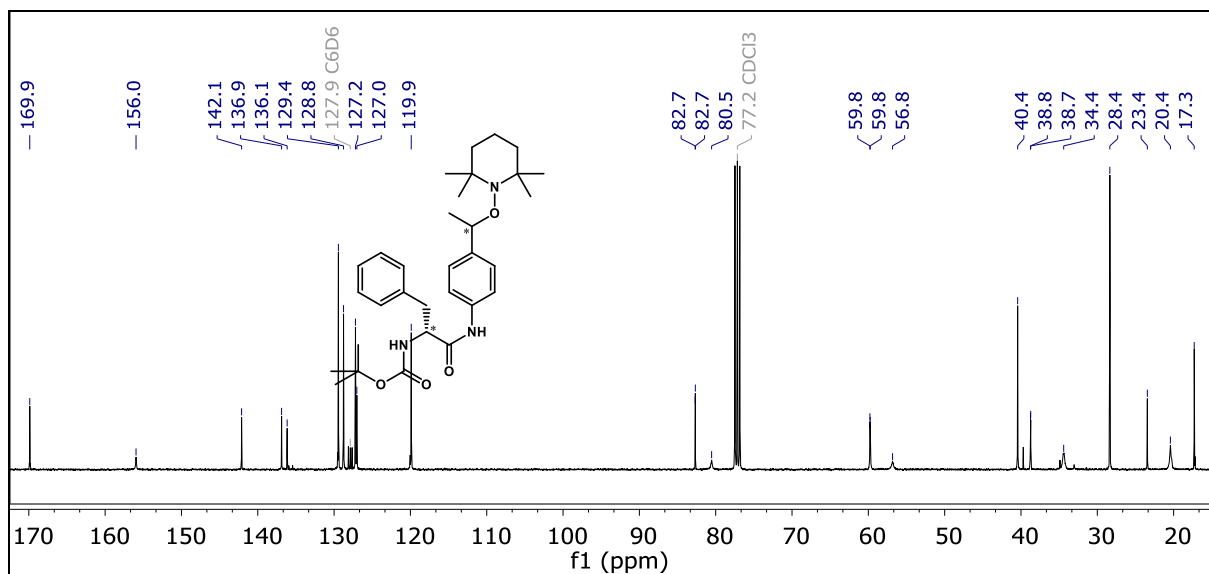


Diastereomers have retention times too close (around 5 min). their separation is difficult.

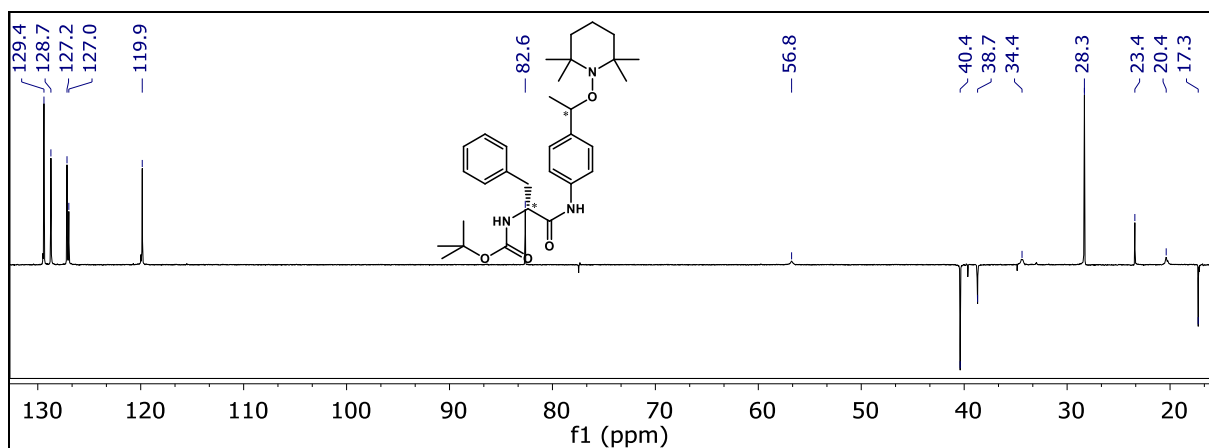
^1H NMR (400 MHz, CDCl_3)



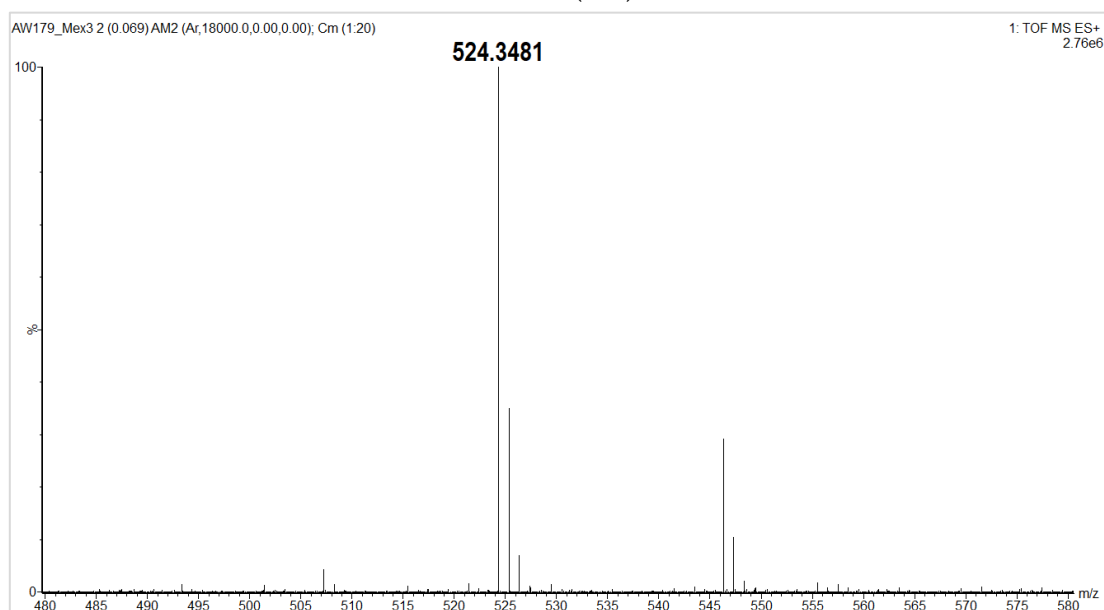
^{13}C NMR (101 MHz, CDCl_3)



DEPT 135 (101 MHz, CDCl₃)



HRMS (ESI)

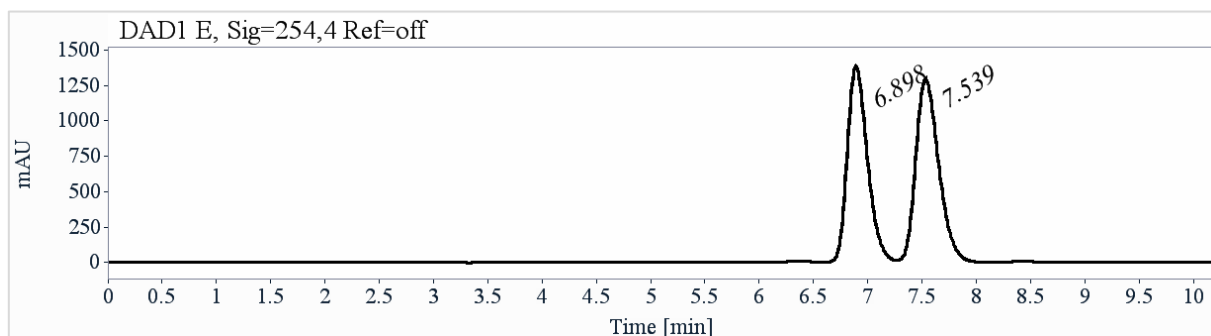


tert-butyl ((2R)-1-(((2R)-3-methyl-1-oxo-1-(((2R)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate

(A3D)

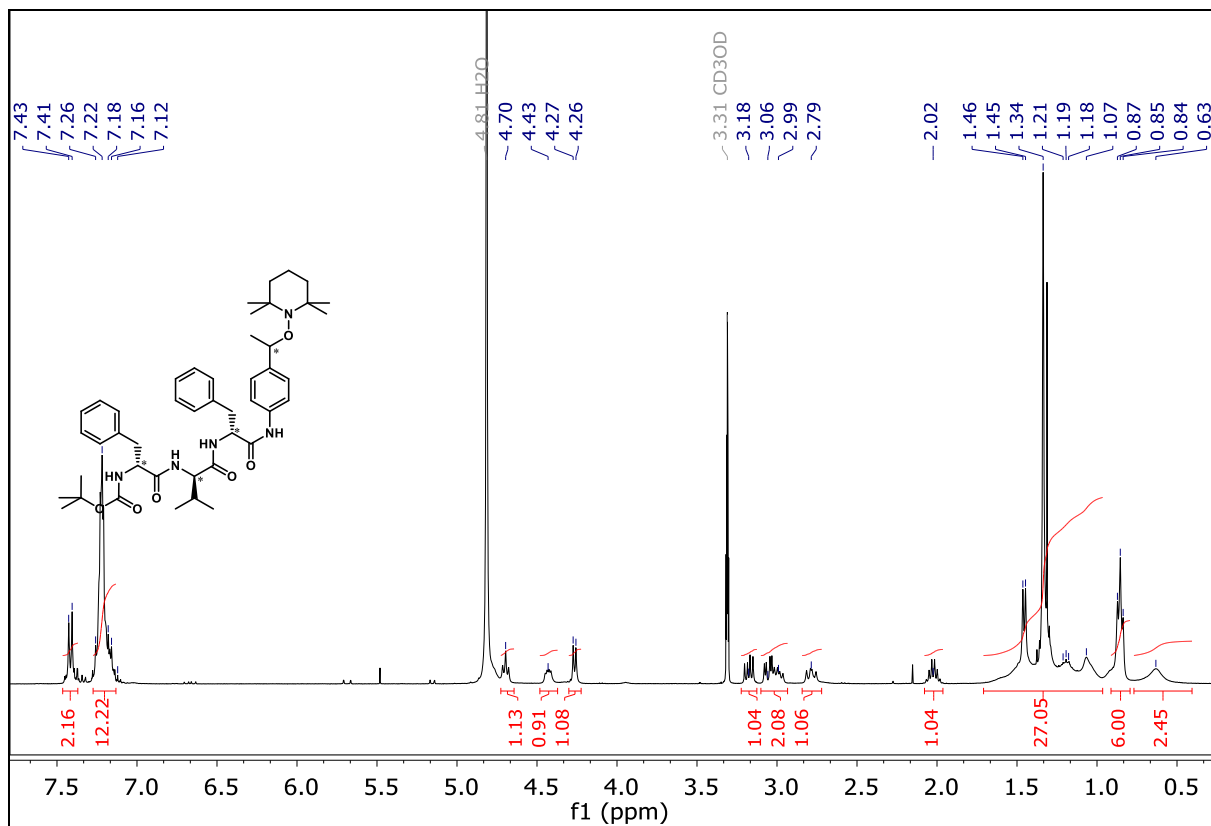
Chiral HPLC report

Heptane/Ethanol/dichloromethane (60/20/20), 1 mL/min

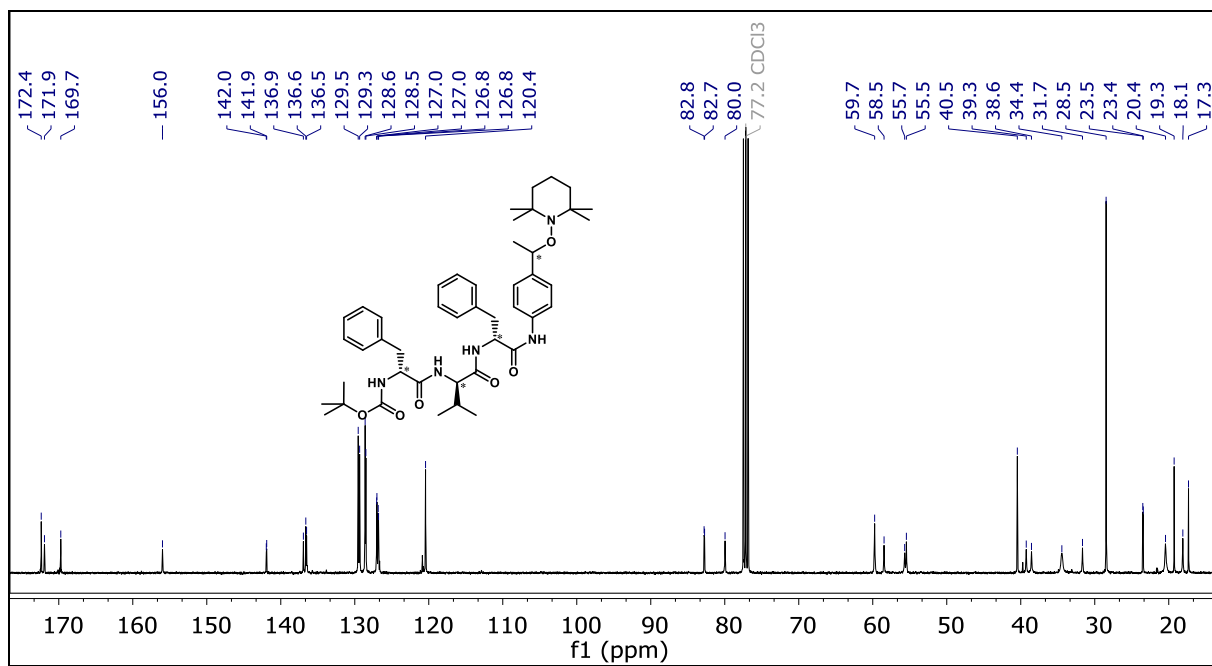


Diastereomers have retention times too close (around 7 min).

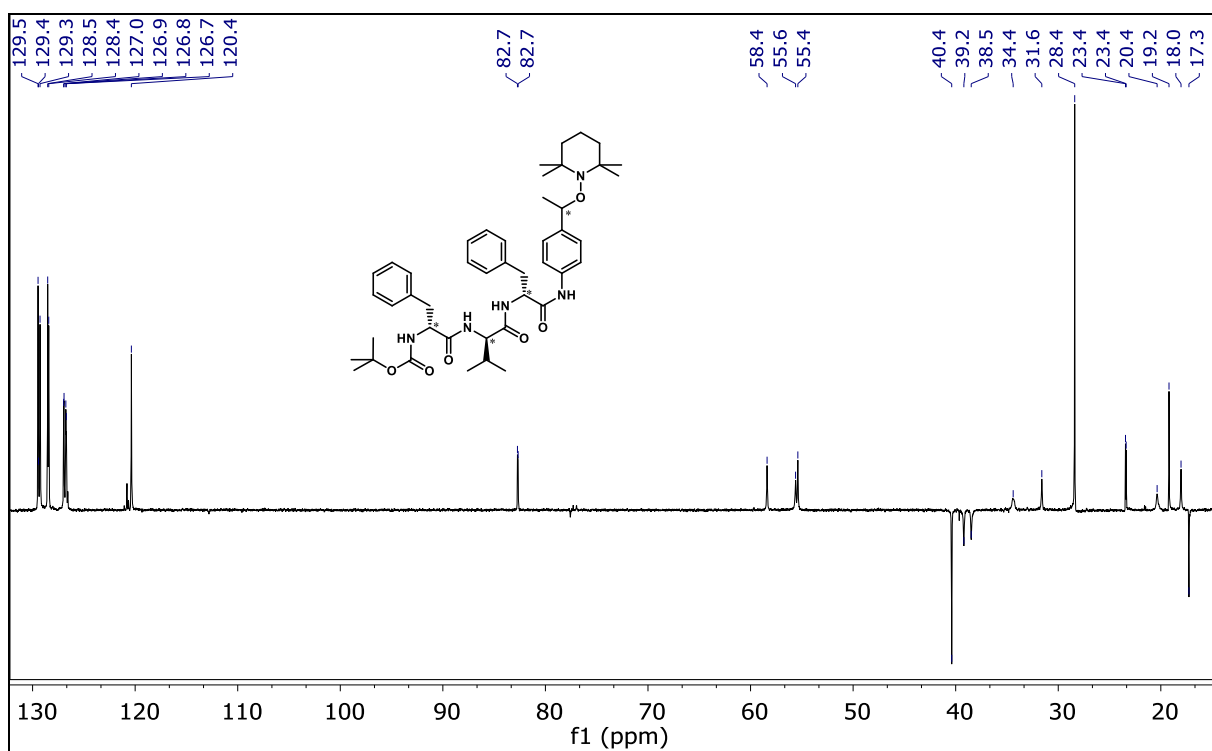
¹H NMR (400 MHz, MeOD)



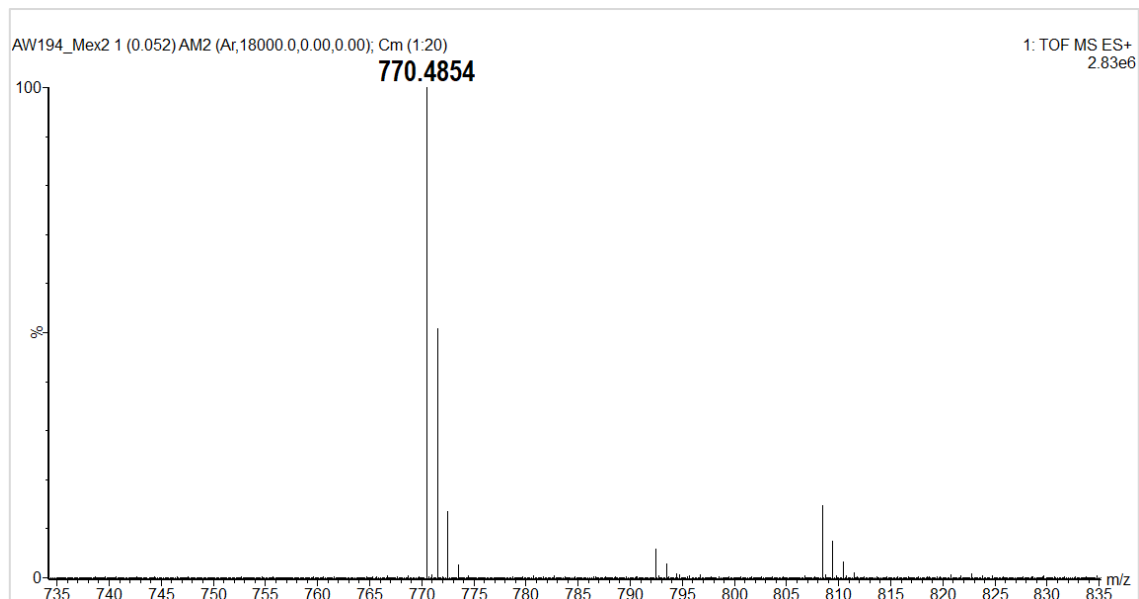
¹³C NMR (101 MHz, CDCl₃)



DEPT 135 (101 MHz, CDCl₃)



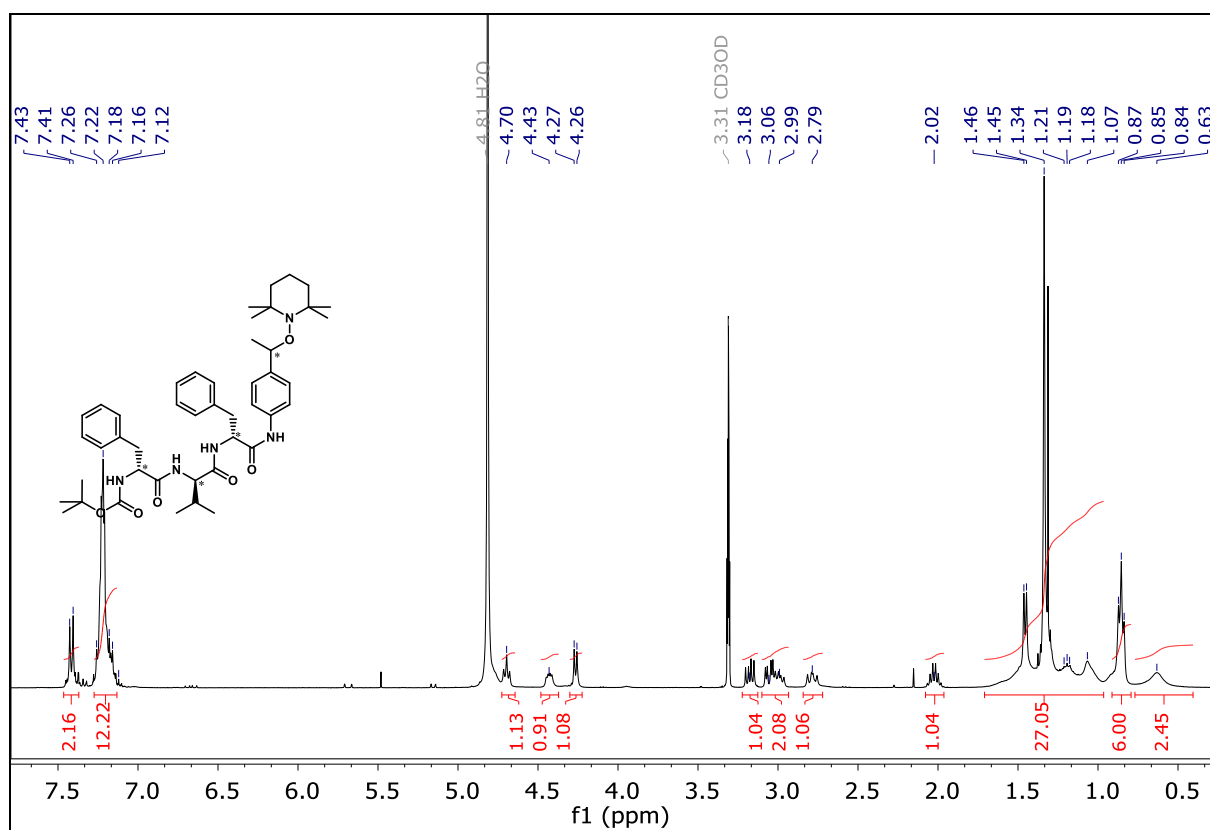
HRMS (ESI)



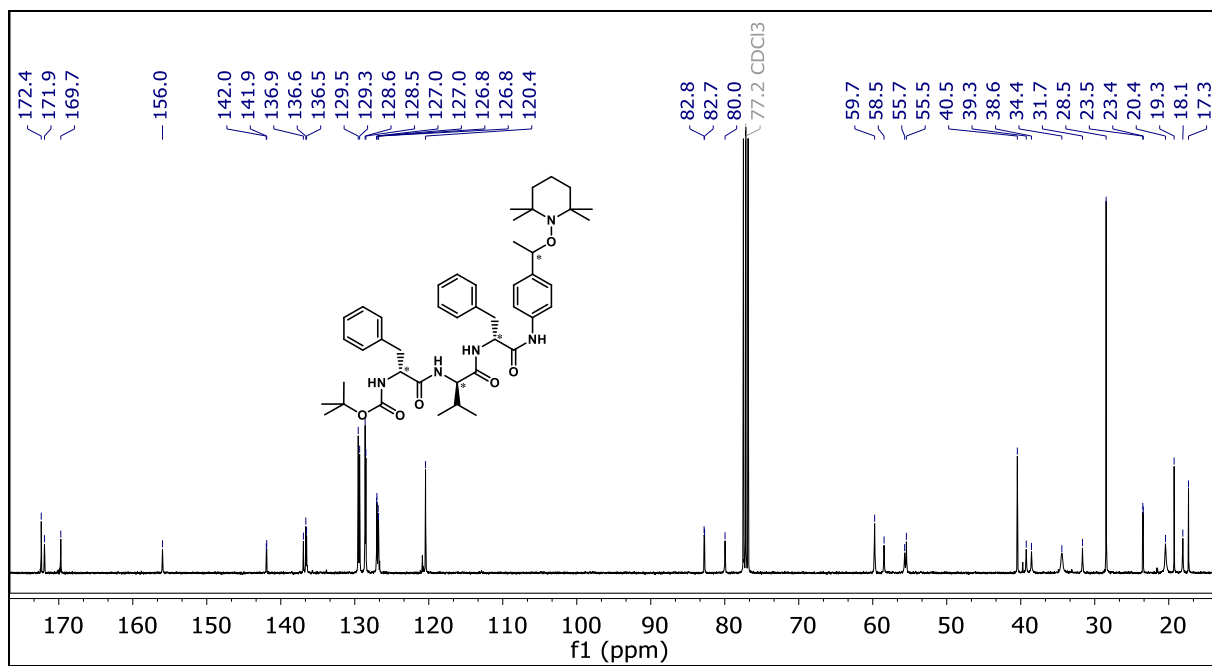
(2R)-1-(((2R)-3-methyl-1-oxo-1-(((2R)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium
trifluoroacetate

(A4D)

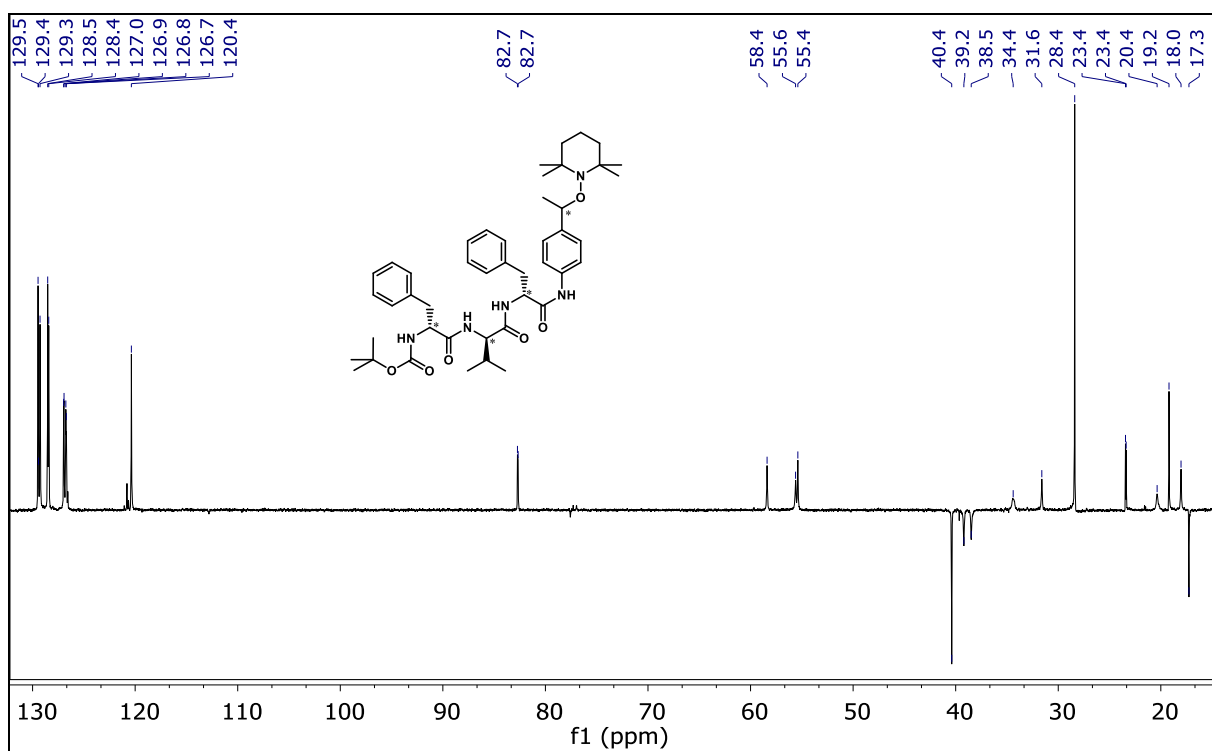
^1H NMR (400 MHz, MeOD)



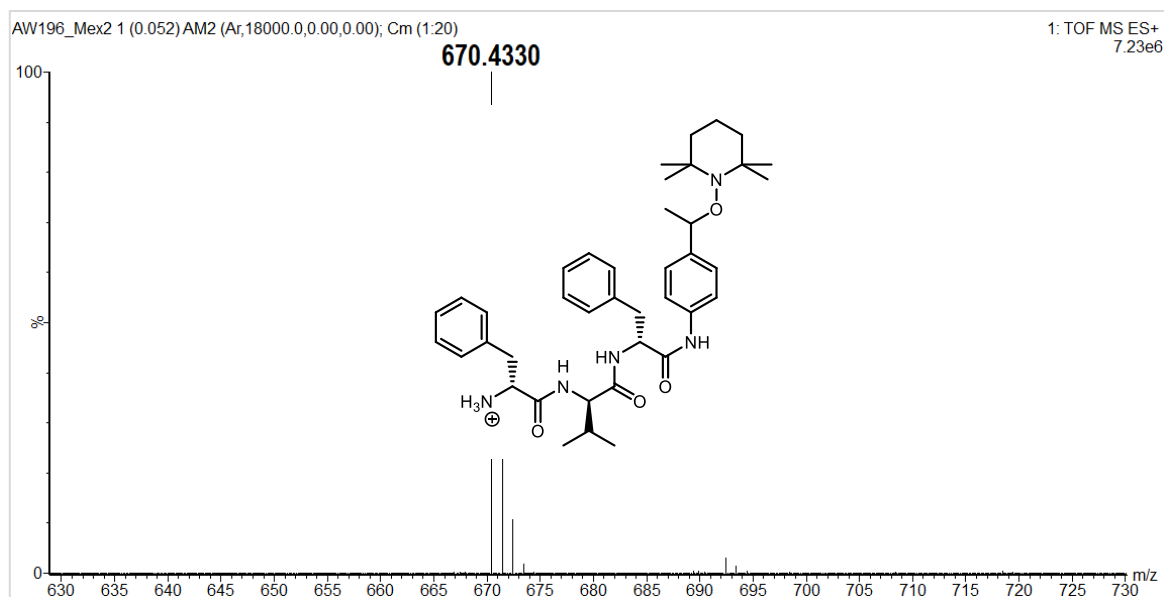
^{13}C NMR (101 MHz, CDCl₃)



DEPT 135 (101 MHz, CDCl₃)



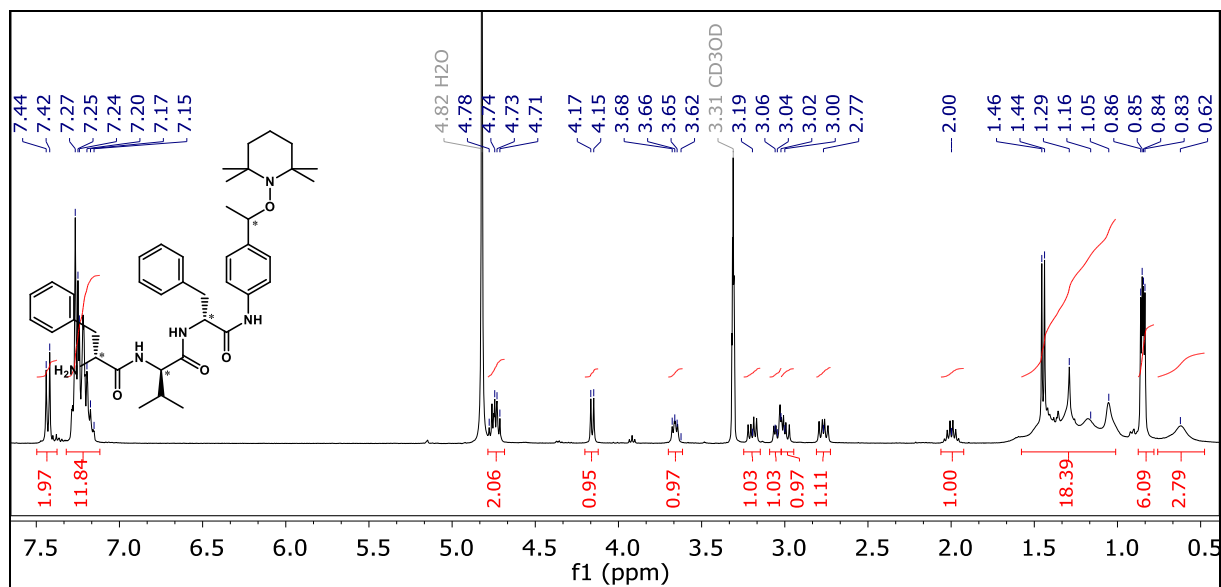
HRMS (ESI)



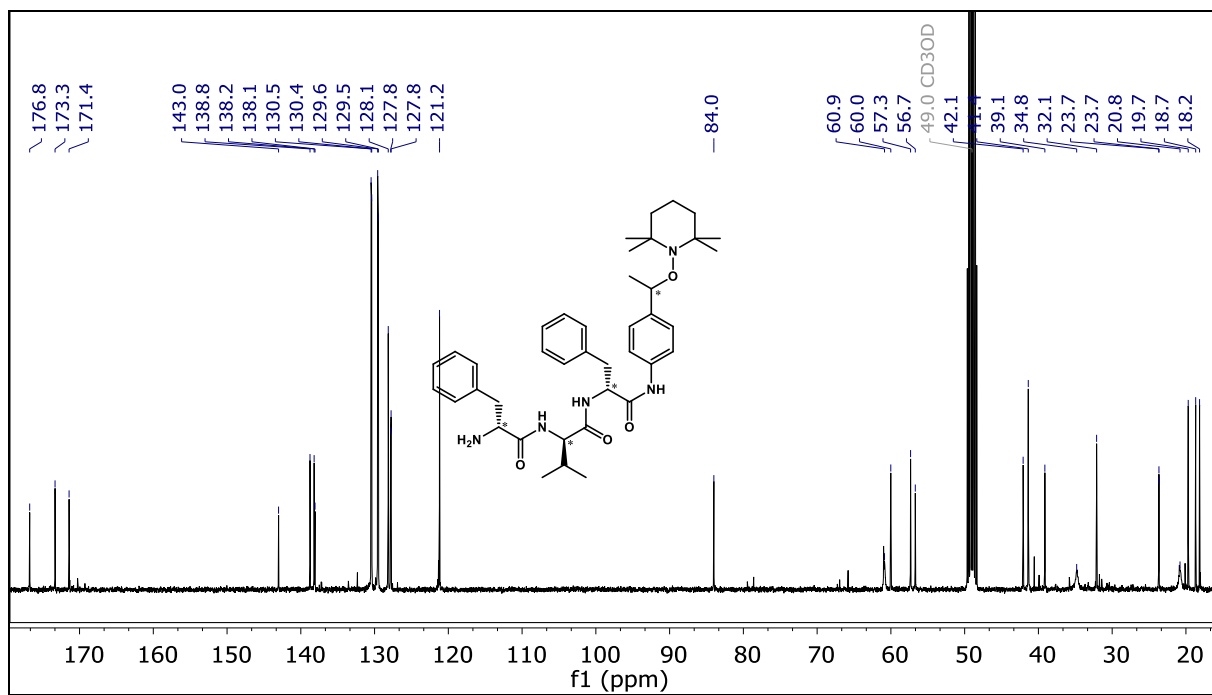
(2R)-2-((R)-2-amino-3-phenylpropanamido)-3-methyl-N-((2R)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)butanamide

(A5D)

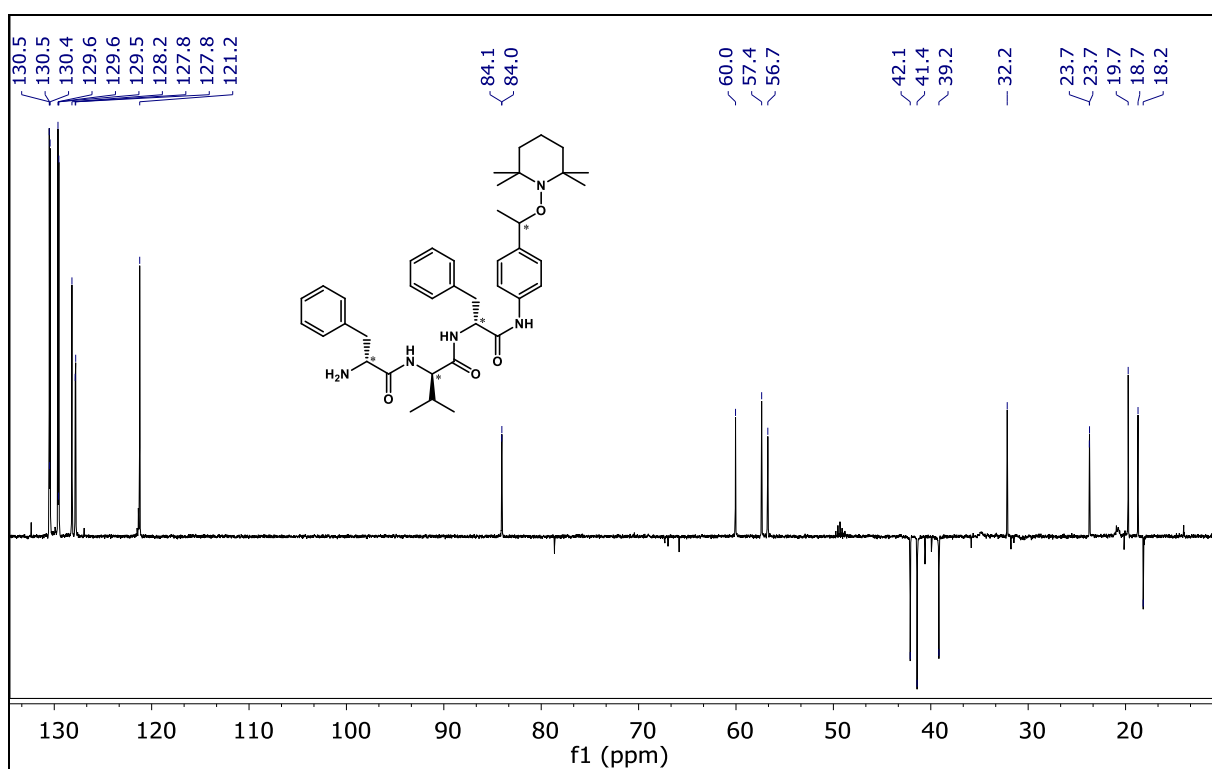
^1H NMR (400 MHz, MeOD)



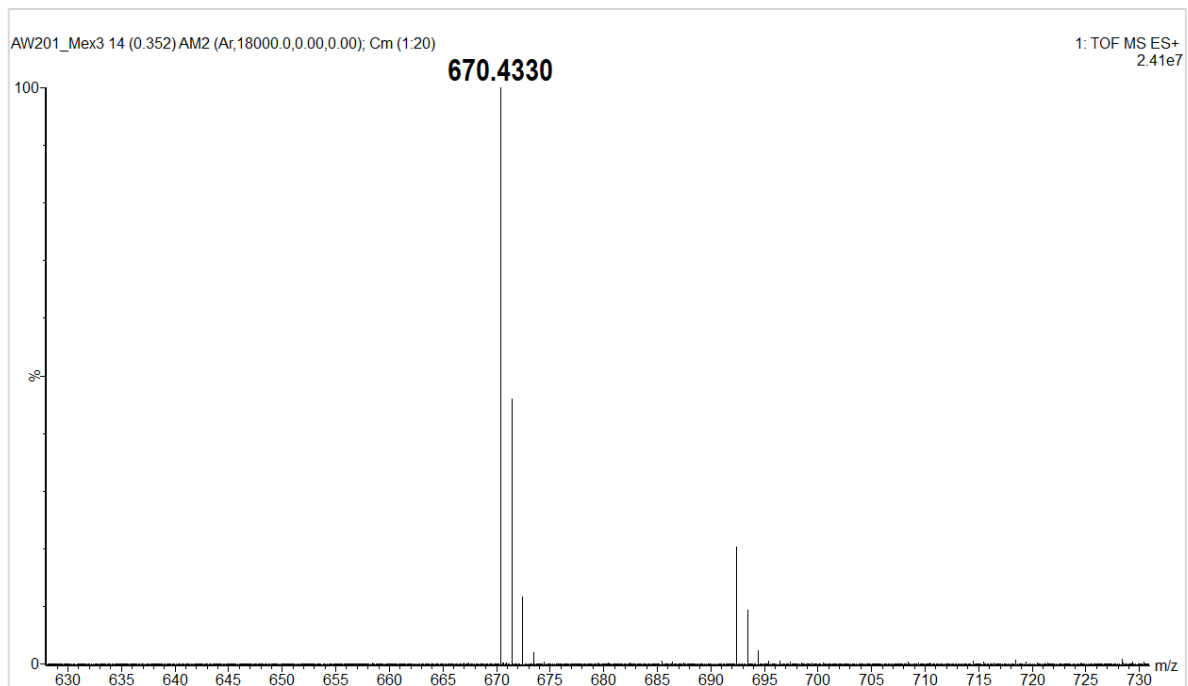
^{13}C NMR (101 MHz, MeOD)



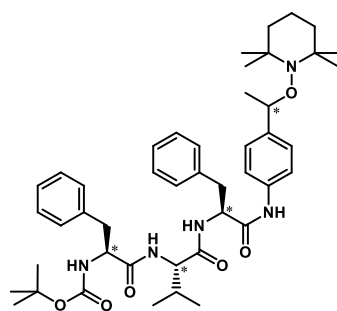
DEPT 135 (101 MHz, MeOD)



HRMS (ESI)



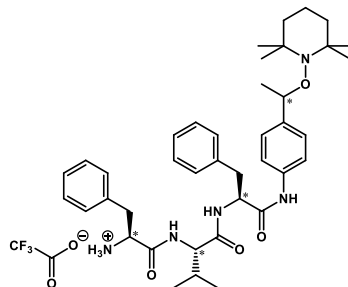
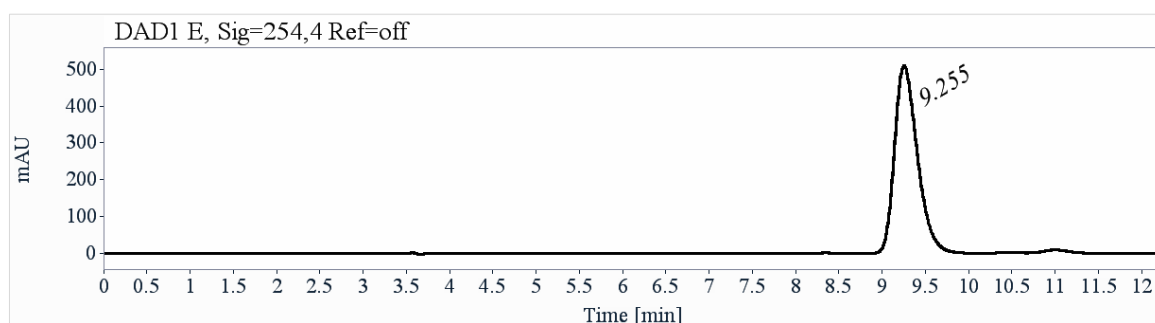
HPLC of hybrid-alkoxyamines



A3L

Chiral HPLC report

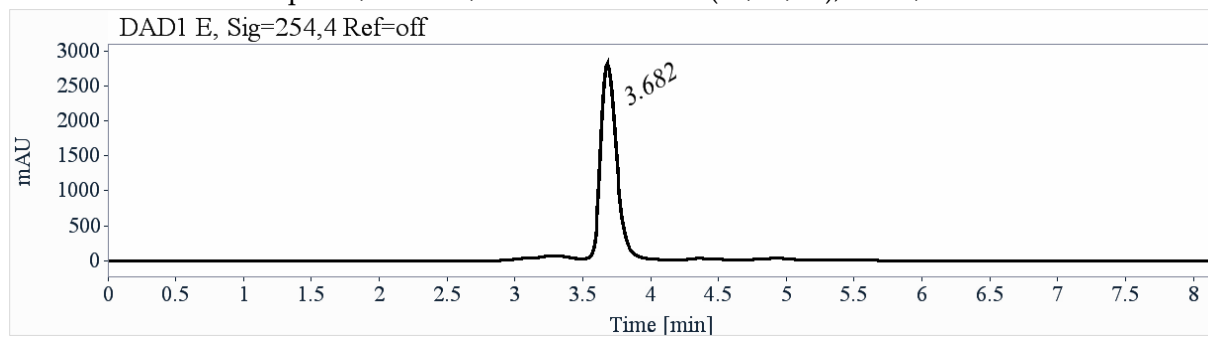
Heptane/ethanol/dichloromethane (80/10/10), 1 mL/min

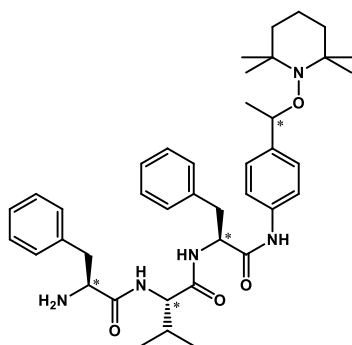


A4L

Chiral HPLC report

Heptane/Ethanol/dichloromethane (60/20/20), 1 mL/min

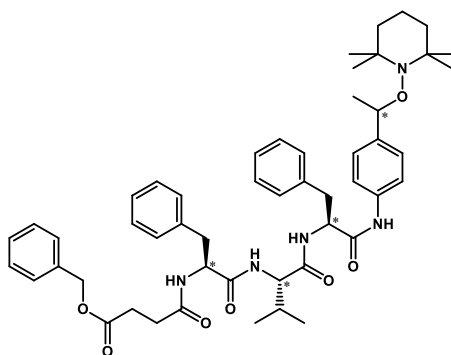
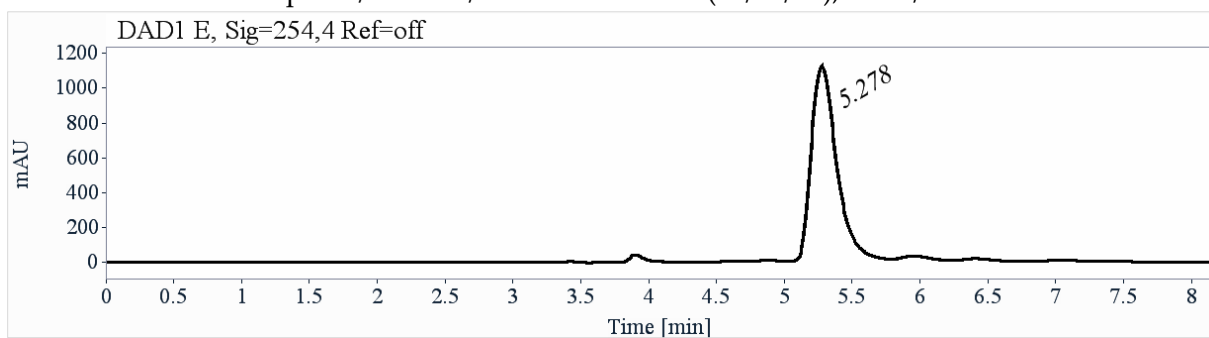




A5L

Chiral HPLC report

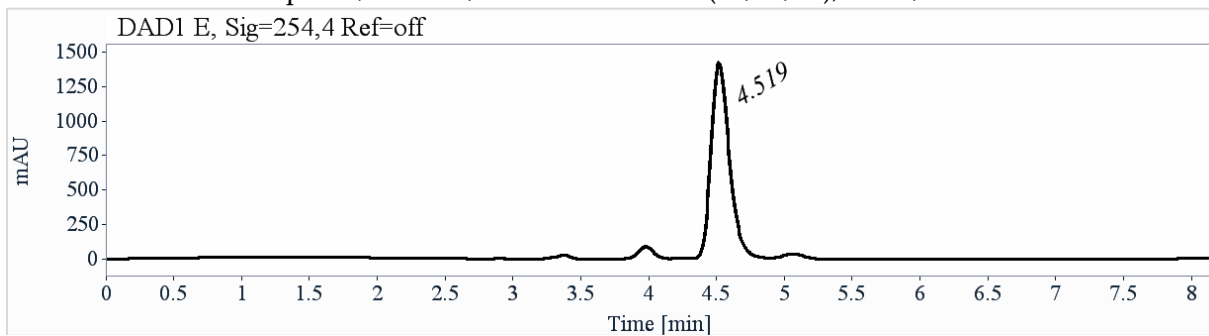
Heptane/Ethanol/dichloromethane (60/20/20), 1 mL/min

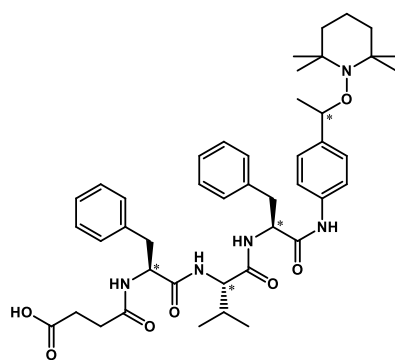


A6L

Chiral HPLC report

Heptane/Ethanol/dichloromethane (60/20/20), 1 mL/min

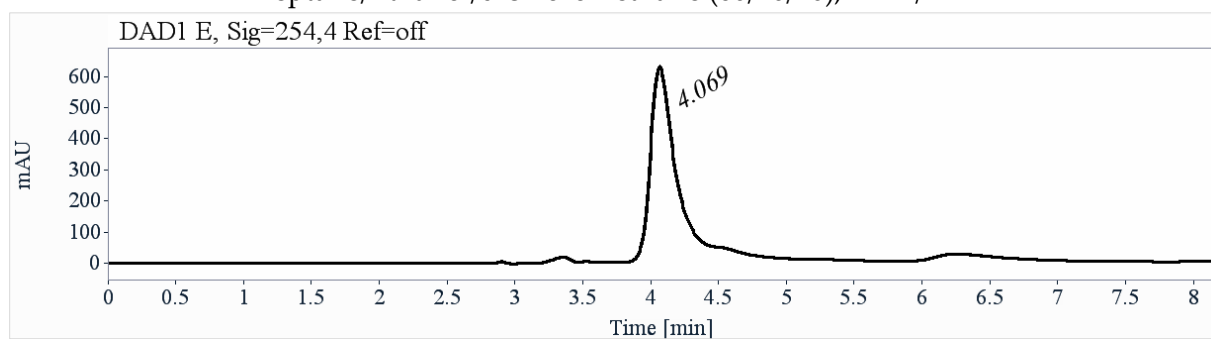




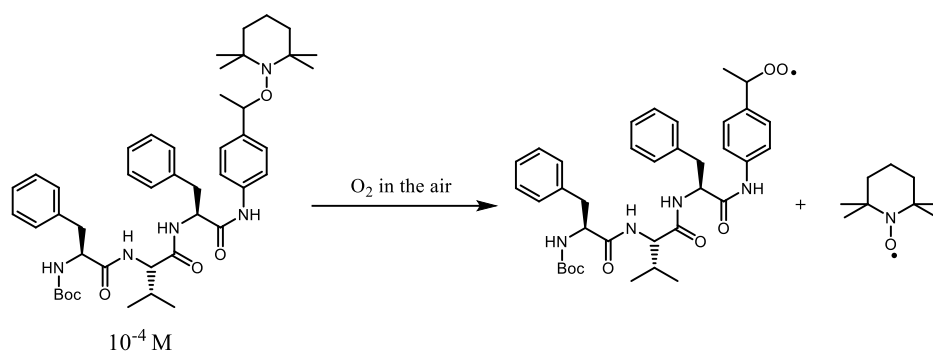
A7L

Chiral HPLC report

Heptane/Ethanol/dichloromethane (60/20/20), 1 mL/min



Kinetics and homolysis constants of alkoxyamines A3L



Solvent : tBuPh, temperature : 125°C , $k_d = 8.4 \times 10^{-4} \text{ s}^{-1}$.

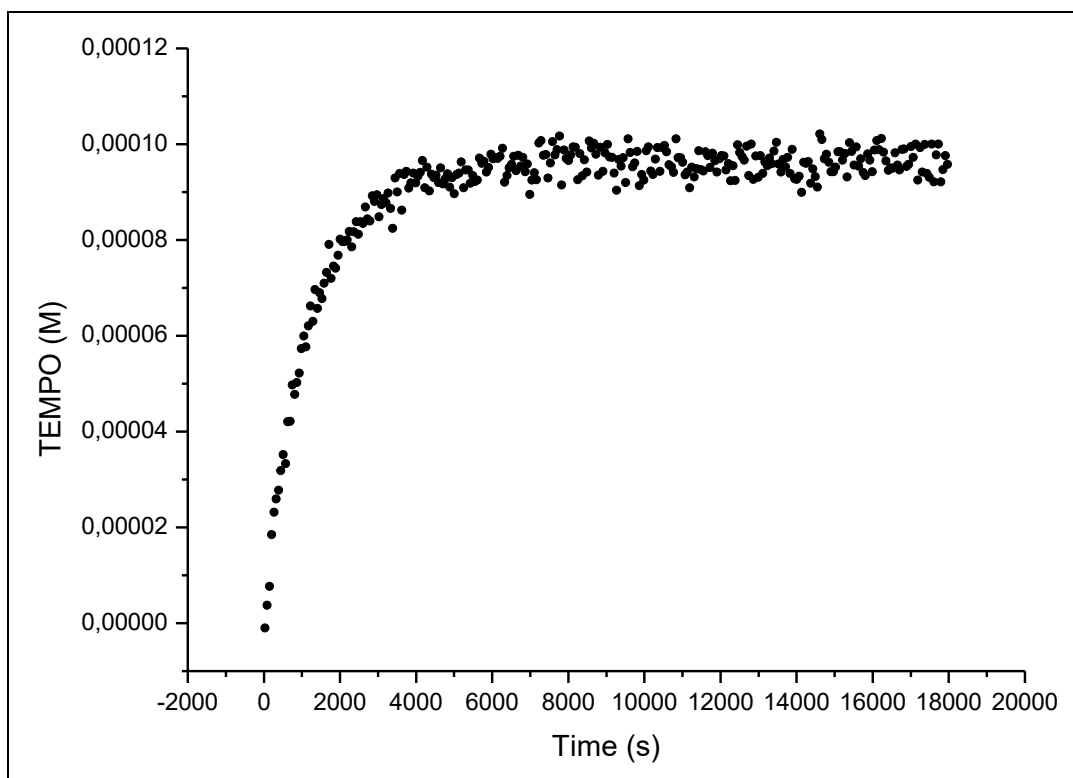


Table S1. Doses of alkoxyamines provided to *Schistosoma* at 37 °C, time to reach the death of half of the population of worms, time to kill all parasites, and their cytotoxicity on Vero cells (CC₅₀ in μ M).

	Dose at 100 μ g/ml ^a		CC ₅₀ (μ M) ^b
P6L	NA	NA	> 50
P8L	7	24	> 50
P9L	3	5	> 50
A3D	NA	NA	> 50
A4D	<u>2</u>	<u>7</u>	2.6 \pm 0.3 ^c
A5D	<u>1</u>	<u>4</u>	2.2 \pm 0.3
P6D	4	24	3.2
P8D	1	1	> 50
P21D	5	24	> 50
P22D	4	24	11

^a. NA: No Activity. Concentrations span from 100 to 200 μ M for alkoxyamines, and from 200 to 400 μ M for peptides. ^b Cytotoxicity values correspond to the mean of 2 to 7 independant experiments ^c Correspond to the mean of 7 independant experiments. ^d data from reference [Sun, Q.; Mao, R.; Wang, D.; Hu, C.; Zheng, Y.; Sun, D. The cytotoxicity study of praziquantel enantiomers. *Drug Des. Dev. Ther.* **2016**, *10*, 2061–2068].

Table S2 : Biological Testing: Raw Data.

molecule	[C] μ g/mL	0	1	2	3	4	5	6	7	8	24	48	72
P21L	100	27	27	27	27	27	27	27	27	27	-	-	-
	10	29	29	29	29	29	29	29	29	29	-	-	-
P6L	100	30	30	30	30	30	30	30	30	30	-	-	-
	10	27	27	27	27	27	27	27	27	27	-	-	-
P7L	100	43	43	43	43	43	43	43	43	43	-	-	-
	10	28	28	28	28	28	28	28	28	28	-	-	-
A3L	100	39	39	39	39	39	39	39	38	38	38	38	38
	10	42	42	42	42	42	42	42	42	42	42	42	42
A4L	100	35	19	17	14	7	7	7	4	4	0	0	0
	10	26	26	26	26	26	26	26	26	26	26	26	26
A3D	100	30	30	30	30	30	30	30	28	28	28	28	28
	10	28	28	28	28	28	28	28	28	28	28	28	28
A4D	100	32	29	17	10	3	3	3	0	0	0	0	0
	10	27	27	27	27	27	27	27	27	27	27	27	27
A5L	100	31	31	15	10	2	2	2	0	0	0	0	0
	10	29	29	29	29	29	29	29	29	29	29	29	29
A5D	100	29	13	4	2	0	0	0	0	0	0	0	0
	10	33	33	33	33	33	33	33	33	30	30	30	30
P7D	100	26	26	26	26	26	26	26	26	26	26	26	26
	10	21	21	21	21	21	21	21	21	21	21	21	21
P11L	100	26	26	26	26	26	26	26	26	26	26	26	26
	10	28	28	28	28	28	28	28	28	28	28	28	28

P11D	100	22	22	22	22	22	22	22	22	22	22	22	22
	10	19	19	19	19	19	19	19	19	19	19	19	19
P12L	100	37	37	37	37	37	37	37	37	37	6	0	0
	10	24	24	24	24	24	24	24	24	24	24	24	24
P22L	100	35	35	35	35	35	35	35	35	35	29	14	0
	10	29	29	29	29	29	29	29	29	29	29	29	29
P23L	100	25	25	25	25	25	25	25	25	25	25	25	25
	10	20	20	20	20	20	20	20	20	20	20	20	20
P24L	100	29	29	29	29	29	29	29	29	29	29	29	29
	10	26	26	26	26	26	26	26	26	26	26	26	26
P25L	100	21	21	21	21	21	21	21	21	21	21	21	21
	10	24	24	24	24	24	24	24	24	24	24	24	24
P18L	100	19	19	19	19	19	19	19	19	19	19	19	19
	10	27	27	27	27	27	27	27	27	27	27	27	27
PZQ	10	22	0	0	0	0	0	0	0	0	0	0	0
Controle		27	27	27	27	27	27	27	27	27	27	27	27

Molécule	[C] µg/mL	T0	1 H	2 H	3 H	4 H	5 H	6 H	7 H	8 H	24 H	48 H	72 H
A6L	100	25	25	25	25	25	25	25	25	25	13	0	0
	10	23	23	23	23	23	23	23	23	23	12	0	0
A7L	100	29	29	29	29	29	29	29	29	29	12	0	0
	10	24	24	24	24	24	24	24	24	24	24	24	24
P21D	100	42	42	42	42	42	23	23	6	6	0	0	0
	10	32	32	32	32	32	32	32	32	32	32	32	32
P22D	100	36	36	36	36	13	13	5	1	1	0	0	0
	10	29	29	29	29	29	29	29	29	29	22	8	0
P6D	100	26	26	26	26	15	8	8	5	5	0	0	0
	10	11	11	11	11	11	11	11	11	11	11	11	11
P8D	100	18	0	0	0	0	0	0	0	0	0	0	0
	10	25	25	25	25	25	25	25	25	25	0	0	0
P8L	100	26	24	24	24	24	24	17	8	8	0	0	0
	10	24	24	24	24	24	24	24	24	24	24	24	24
P9L	100	25	25	25	7	7	0	0	0	0	0	0	0
	10	26	26	26	26	26	26	26	26	26	26	26	26
P10L	100	28	28	28	28	28	28	4	4	4	0	0	0
	10	19	19	19	19	19	19	19	19	19	19	19	19
TFA	100	25	25	25	25	25	19	19	3	3	0	0	0
	10	20	20	20	20	20	20	20	20	20	20	20	20
Contrôle		39	39	39	39	39	39	39	39	39	39	39	39
		36	36	36	36	36	36	36	36	36	36	36	36
PZQ	100	17	0	0	0	0	0	0	0	0	0	0	0
	10	29	0	0	0	0	0	0	0	0	0	0	0

tert-butyl (S)-(1-oxo-3-phenyl-1-((4-vinylphenyl)amino)propan-2-yl)carbamate P3L. ^1H NMR (400 MHz, CDCl_3) δ 8.57 (s, $1\text{H}_{(9)}$), 7.23 (Broad AB, d, $J = 8.6$ Hz, $2\text{H}_{(1, 5)}$), 7.29 – 7.19 (m, $7\text{H}_{(2, 4, 15-19)}$), 6.53 (dd, $J = 17.6, 10.9$ Hz, $1\text{H}_{(7)}$), 5.71 – 5.60 (overlapped signals : d, $J = 17.5$ Hz, $1\text{H}_{(8)}$ and s, $1\text{H}_{(20)}$), 5.08 (d, $J = 10.8$, $1\text{H}_{(8)}$), 4.58 (m, $1\text{H}_{(12)}$), 3.08 (dd, $J = 13.7, 6.4$ Hz, $1\text{H}_{(13)}$), 2.98 (dd, $J = 13.8, 8.0$ Hz, $1\text{H}_{(13)}$), 1.29 (s, $9\text{H}_{(25-27)}$). ^{13}C NMR (101 MHz, CDCl_3) δ 170.3 ($\text{C}_{(10)}$), 156.2 ($\text{C}_{(21)}$), 137.2 ($\text{C}_{(3)}$), 136.9 ($\text{C}_{(14)}$), 136.3 ($\text{C}_{(7)}$), 133.9 ($\text{C}_{(6)}$), 129.4 ($2\text{CH}_{(16, 18)}$), 128.7 ($2\text{CH}_{(1, 5)}$), 127.0 ($\text{CH}_{(17)}$), 126.7 ($2\text{CH}_{(15, 19)}$), 120.1 ($2\text{CH}_{(2-4)}$), 113.0 ($\text{CH}_{(28)}$), 80.6 ($\text{C}_{(24)}$), 56.9 ($\text{CH}_{(12)}$), 38.9 ($\text{CH}_{(213)}$), 28.4 ($3\text{CH}_{(25-27)}$). HRMS (ESI) : m/z calc for $\text{C}_{22}\text{H}_{27}\text{N}_2\text{O}_3^+$: 367.2016 $[\text{M}+\text{H}]^+$; found : 367.2015.

Benzyl (tert-butoxycarbonyl)-L-phenylalanyl-L-valinate P4L. ^1H NMR (300 MHz, CDCl_3) δ 7.33 – 7.22 (m, $5\text{H}_{(1-5)}$), 7.21 – 7.07 (m, $5\text{H}_{(21-25)}$), 6.39 (d, $J = 8.6$ Hz, $1\text{H}_{(12)}$), 5.15 – 5.03 (overlapped signals : $3\text{H}_{(7, 26)}$), 4.44 (dd, $J = 8.6, 4.9$ Hz, $1\text{H}_{(10)}$), 4.29 (q, $J = 7.4$ Hz, $1\text{H}_{(18)}$), 2.98 (m, $2\text{H}_{(19)}$), 2.04 (pd, $J = 6.9, 4.9$ Hz, $1\text{H}_{(13)}$), 1.33 (s, $9\text{H}_{(31-33)}$), 0.77 (d, $J = 6.9$ Hz, $3\text{H}_{(14)}$), 0.72 (d, $J = 6.9$ Hz, $3\text{H}_{(15)}$). ^{13}C NMR (75 MHz, CDCl_3) δ 171.3 ($\text{C}_{(9)}$), 171.3 ($\text{C}_{(16)}$), 155.5 ($\text{C}_{(27)}$), 136.7 ($\text{C}_{(20)}$), 135.4 ($\text{C}_{(6)}$), 129.4 ($2\text{CH}_{(22, 24)}$), 128.7 ($2\text{CH}_{(2, 4)}$), 128.7 ($2\text{CH}_{(1, 5)}$), 128.5 ($\text{CH}_{(3)}$), 128.4 ($2\text{CH}_{(21, 25)}$), 127.0 ($\text{CH}_{(23)}$), 80.3 ($\text{C}_{(30)}$), 67.0 ($\text{CH}_{(27)}$), 57.3 ($\text{CH}_{(10)}$), 55.9 ($\text{CH}_{(18)}$), 38.1 ($\text{CH}_{(219)}$), 31.4 ($\text{CH}_{(13)}$), 28.3 ($3\text{CH}_{(31-33)}$), 18.9 ($\text{CH}_{(314)}$), 17.7 ($\text{CH}_{(314)}$).

(Tert-butoxycarbonyl)-L-phenylalanyl-L-valine P5L. Using GP6 with P4L (12.00 g, 26.417 mmol, 1.0 eq) affords P5L as a white solid (9.62 g, quantitative yield) as described in literature [1]. ^1H NMR (400 MHz, MeOD) δ 7.36 – 7.09 (m, $5\text{H}_{(9-13)}$), 4.52 – 4.16 (overlapped signals : m, $2\text{H}_{(2, 14)}$), 3.13 (dd, $J = 13.9, 5.0$ Hz, $1\text{H}_{(4)}$), 2.82 (dd, $J = 13.9, 9.5$ Hz, $1\text{H}_{(4)}$), 2.17 (h, $J = 6.7$ Hz, $1\text{H}_{(16)}$), 1.36 (s, $9\text{H}_{(24-26)}$), 1.05 – 0.93 (overlapped signals : m, $6\text{H}_{(17, 18)}$). ^{13}C NMR (75 MHz, MeOD) δ 174.5 ($\text{C}_{(15)}$), 174.4 ($\text{C}_{(3)}$), 157.6 ($\text{C}_{(7)}$), 138.5 ($\text{C}_{(8)}$), 130.3 ($2\text{CH}_{(10, 12)}$), 129.3 ($2\text{CH}_{(9, 13)}$), 127.6 ($\text{CH}_{(11)}$), 80.7 ($\text{C}_{(23)}$), 58.8 ($\text{CH}_{(14)}$), 57.2 ($\text{CH}_{(2)}$), 38.9 ($\text{CH}_{(24)}$), 31.9 ($\text{CH}_{(16)}$), 28.6 ($3\text{CH}_{(24-26)}$), 19.5 ($\text{CH}_{(17)}$), 18.2 ($\text{CH}_{(18)}$).

Benzyl (tert-butoxycarbonyl)-L-phenylalanyl-L-valyl-L-phenylalaninate P6L. ^1H NMR (400 MHz, CDCl_3) δ 7.35 (m, $3\text{H}_{(41-43)}$), 7.30 – 7.15 (m, $10\text{H}_{(9-13, 34-38)}$), 7.02 (m, $2\text{H}_{(40, 44)}$), 6.50 (d, $J = 8.5$ Hz, $1\text{H}_{(6)}$), 6.32 (d, $J = 8.0$ Hz, $1\text{H}_{(17)}$), 5.12 (q, $J = 12.1$ Hz, $2\text{H}_{(11)}$), 4.98 (m, $1\text{H}_{(24)}$), 4.86 (dt, $J = 8.0, 6.1$ Hz, $1\text{H}_{(5)}$), 4.34 (q, $J = 6.5$ Hz, $1\text{H}_{(22)}$), 4.18 (dd, $J = 8.5, 6.1$ Hz, $1\text{H}_{(15)}$), 3.07 (ddd, $J = 13.0, 6.6, 3.4$ Hz, $4\text{H}_{(7, 25)}$), 2.04 (dq, $J = 6.7$ Hz, $1\text{H}_{(18)}$), 1.40 (s, $9\text{H}_{(31-33)}$), 0.84 (d, $J = 6.7$ Hz, $3\text{H}_{(20)}$), 0.77 (d, $J = 6.8$ Hz, $3\text{H}_{(19)}$). ^{13}C NMR (75 MHz, CDCl_3) δ 171.5 ($\text{C}_{(3)}$), 171.2 ($\text{C}_{(21)}$), 170.6 ($\text{C}_{(14)}$), 155.6 ($\text{C}_{(27)}$), 136.8 ($\text{CH}_{(26)}$), 135.7 ($\text{C}_{(39)}$), 135.1 ($\text{C}_{(8)}$), 129.4 ($2\text{CH}_{(35, 37)}$), 129.4 ($2\text{CH}_{(10, 12)}$), 128.7 ($4\text{CH}_{(34, 38, 41, 43)}$), 128.6 ($4\text{CH}_{(9, 13, 40, 44)}$), 128.6 ($\text{CH}_{(42)}$), 127.2 ($\text{CH}_{(36)}$), 126.9 ($\text{CH}_{(11)}$), 80.2 ($\text{C}_{(30)}$), 67.3 ($\text{CH}_{(21)}$), 58.5 ($\text{CH}_{(15)}$), 55.9 ($\text{CH}_{(5)}$), 53.4 ($\text{CH}_{(22)}$), 38.1 ($2\text{CH}_{(2, 25)}$), 31.1 ($\text{CH}_{(18)}$), 28.3 ($3\text{CH}_{(31-33)}$), 19.1 ($\text{CH}_{(20)}$), 18.1 ($\text{CH}_{(19)}$). HRMS (ESI) : m/z calc for $\text{C}_{35}\text{H}_{43}\text{N}_3\text{O}_6\text{Na}^+$: 624.3044 $[\text{M}+\text{Na}]^+$; found : 624.3052.

(Tert-butoxycarbonyl)-L-phenylalanyl-L-valyl-L-phenylalanine P7L. ^1H NMR (300 MHz, CDCl_3) δ 9.94 (s, $1\text{H}_{(11)}$), 7.61 – 6.92 (m, $12\text{H}_{(5, 16, 8-12, 33-37)}$), 5.46 (d, $J = 7.9$ Hz, $1\text{H}_{(23)}$), 4.88 (q, $J = 6.6$ Hz, $1\text{H}_{(4)}$), 4.53 (m, $1\text{H}_{(21)}$), 4.40 (t, $J = 8.1$ Hz, $1\text{H}_{(14)}$), 3.23 (dd, $J = 14.0, 5.6$ Hz, $1\text{H}_{(24)}$), 3.13 – 2.90 (overlapped signals : m, $3\text{H}_{(6, 24)}$), 2.03 (h, $J = 6.8$ Hz, $1\text{H}_{(17)}$), 1.42 (s, $9\text{H}_{(30-32)}$), 0.89 (overlapped signals : 2d, $J = 6.6$ Hz, $6\text{H}_{(18, 19)}$). ^{13}C NMR (75 MHz, CDCl_3) δ 173.8 ($\text{C}_{(2)}$), 172.1 ($\text{C}_{(13)}$), 171.1 ($\text{C}_{(20)}$), 155.8 ($\text{C}_{(26)}$), 136.6 ($\text{C}_{(25)}$), 136.1 ($\text{C}_{(7)}$), 129.5 ($2\text{CH}_{(34, 36)}$), 129.4 ($2\text{CH}_{(9, 11)}$), 128.6 ($4\text{CH}_{(33, 37, 8, 12)}$), 127.1 ($\text{CH}_{(35)}$), 126.9 ($\text{CH}_{(10)}$), 80.4 ($\text{C}_{(29)}$), 58.7 ($\text{CH}_{(14)}$), 55.8 ($\text{CH}_{(4)}$), 53.6 ($\text{CH}_{(21)}$), 38.2 ($\text{CH}_{(26)}$), 37.7 ($\text{CH}_{(24)}$), 31.2 ($\text{CH}_{(17)}$), 28.3 ($3\text{CH}_{(30-32)}$), 19.1 ($\text{CH}_{(18)}$), 18.1 ($\text{CH}_{(19)}$). HRMS (ESI) : m/z calc for $\text{C}_{28}\text{H}_{37}\text{N}_3\text{O}_6\text{Na}^+$: 534.2575 $[\text{M}+\text{Na}]^+$; found : 534.2580.

(S)-1-(((S)-1-(((S)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate P8L. ^1H NMR (400 MHz, MeOD) δ 7.39 – 7.12 (m, $15\text{H}_{(2-6, 16-20, 34-38)}$), 5.11 (s, $2\text{H}_{(8)}$), 4.72 (dd, $J = 8.4, 6.1$ Hz, $1\text{H}_{(12)}$), 4.23 (d, $J = 7.3$ Hz, $1\text{H}_{(22)}$), 4.12 (dd, $J = 8.7, 5.4$ Hz, $1\text{H}_{(29)}$), 3.20 – 3.07 (Overlapped signals : ddd, $J = 19.9, 14.1, 5.7$ Hz, $2\text{H}_{(14, 32)}$), 3.01 (dd, $J = 13.9, 8.4$ Hz, $1\text{H}_{(14)}$), 2.90 (dd, $J = 14.4, 8.6$ Hz, $1\text{H}_{(32)}$), 2.00 (h, $J = 6.8$ Hz, $1\text{H}_{(25)}$), 0.91 (overlapped signals : 2d, $J = 6.8$ Hz, $6\text{H}_{(26, 27)}$). ^{13}C NMR (101 MHz, MeOD- CDCl_3 (1 : 1 ; v : v)) δ 172.0 ($\text{C}_{(10)}$), 171.9 ($\text{C}_{(21)}$), 169.0 ($\text{C}_{(28)}$), 136.9 ($\text{C}_{(32)}$), 135.8 ($\text{C}_{(7)}$), 134.6 ($\text{C}_{(15)}$), 129.9 ($2\text{CH}_{(35, 37)}$), 129.8 ($2\text{CH}_{(17, 19)}$), 129.6 ($2\text{CH}_{(3, 5)}$), 129.1 ($2\text{CH}_{(2, 6)}$), 129.1 ($2\text{CH}_{(34, 38)}$), 129.0 ($2\text{CH}_{(16, 20)}$), 129.0 ($\text{CH}_{(4)}$), 128.3 ($\text{CH}_{(35)}$), 127.5 ($\text{CH}_{(18)}$), 67.8 ($\text{CH}_{(28)}$), 59.7 ($\text{CH}_{(22)}$), 54.8 ($\text{CH}_{(29)}$), 54.5 ($\text{CH}_{(12)}$), 38.1 ($2\text{CH}_{(214, 32)}$), 31.5 ($\text{CH}_{(25)}$), 19.3 ($\text{CH}_{(26)}$), 18.4 ($\text{CH}_{(27)}$). ^{19}F NMR (376 MHz, MeOD) δ -76.30. HRMS (ESI) : m/z calc for cation $\text{C}_{30}\text{H}_{36}\text{N}_3\text{O}_4^+$: 502.2700 ; found : 502.2701. m/z calc for anion $\text{C}_2\text{F}_3\text{O}_2^-$: 112.9856 ; found : 112.9860.

Benzyl 4-(((S)-1-(((S)-1-(((S)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoate P9L. ^1H NMR (400 MHz, CDCl_3) δ 7.41 – 7.30 (m, $8\text{H}_{(47-51, 34-36)}$), 7.28 – 7.15 (m, $10\text{H}_{(8-12, 26-30)}$), 7.08 – 7.00 (m, $2\text{H}_{(33, 37)}$), 6.52 (d, $J = 8.4$ Hz, $1\text{H}_{(16)}$), 6.42 (d, $J = 7.9$ Hz, $1\text{H}_{(5)}$), 6.26 (d, $J = 7.5$ Hz, $1\text{H}_{(23)}$), 5.19 – 5.05 (overlapped signals : m, $4\text{H}_{(31, 45)}$), 4.86 (dt, $J = 7.9, 6.2$ Hz, $1\text{H}_{(4)}$), 4.67 (q, $J = 6.9$ Hz, $1\text{H}_{(21)}$), 4.18 (dd, $J = 8.5, 6.3$ Hz, $1\text{H}_{(14)}$), 3.14 – 3.00 (overlapped signals : m, $4\text{H}_{(6, 24)}$), 2.76 – 2.55 (m, $2\text{H}_{(41)}$), 2.50 – 2.38 (m, $2\text{H}_{(39)}$), 2.07 (h, $J = 6.7$ Hz, $1\text{H}_{(17)}$), 0.83 (d, $J = 6.8$ Hz, $3\text{H}_{(18)}$), 0.76 (d, $J = 6.8$ Hz, $3\text{H}_{(19)}$). ^{13}C NMR (101 MHz, CDCl_3) δ 172.9 ($\text{C}_{(38)}$), 171.6 ($\text{C}_{(2)}$), 171.3

(C₄₂), 171.2 (C₁₃), 170.8 (C₂₀), 136.6 (C₂₅), 136.0 (C₄₆), 135.9 (C₃₂), 135.2 (C₇), 129.4 (4CH_{27, 29, 9, 11}), 128.6 (8CH_{26, 30, 8, 12, 34, 36, 48, 50}), 128.5 (2CH_{33, 37}), 128.5 (CH₃₅), 128.3 (CH₄₉), 128.2 (2CH_{47, 51}), 127.1 (CH₂₈), 126.9 (CH₁₀), 67.2 (CH₂₃₁), 66.6 (CH₂₄₅), 58.5 (CH₁₄), 54.3 (CH₂₁), 53.5 (CH₄), 38.6 (CH₂₂₄), 38.2 (CH₂₆), 31.2 (CH₁₇), 30.8 (CH₂₄₁), 29.6 (CH₂₃₉), 19.1 (CH₃₁₈), 18.4 (CH₃₁₉). HRMS (ESI) : m/z calc for C₄₁H₄₅N₃O₇Na⁺ : 714.3150 [M+Na]⁺ ; found : 714.3135.

4-(((S)-1-(((S)-1-(((S)-1-carboxy-2-phenylethyl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoic acid P10L. ¹H NMR (400 MHz, MeOD) δ 7.31 – 7.04 (m, 10H_{8-12, 26-30}), 4.71 – 4.51 (overlapped signals : m, 2H_{4, 21}), 4.18 (d, J = 7.5 Hz, 1H₁₄), 3.18 (dd, J = 14.0, 5.3 Hz, 1H₄), 3.08 (dd, J = 14.1, 5.0 Hz, 1H₂₄), 2.99 (dd, J = 13.9, 8.4 Hz, 1H₄), 2.83 (dd, J = 14.1, 9.5 Hz, 1H₂₄), 2.60 – 2.34 (m, 4H_{32, 34}), 2.03 (h, J = 6.9 Hz, 1H₁₇), 0.90 (overlapped signals : t, J = 6.9 Hz, 6H_{18, 19}). ¹³C NMR (101 MHz, MeOD) δ 176.1 (C₃₅), 174.4 (2C_{2, 31}), 173.5 (C₁₃), 173.1 (C₂₀), 138.5 (C₂₅), 138.3 (C₇), 130.3 (2CH_{27, 29}), 130.2 (2CH_{9, 11}), 129.5 (2CH_{26, 30}), 129.4 (2CH_{8, 12}), 127.8 (CH₂₈), 127.6 (CH₁₀), 60.1 (CH₁₄), 55.9 (CH₄), 55.1 (CH₂₁), 38.6 (CH₂₆), 38.5 (CH₂₂₄), 32.1 (CH₁₇), 31.5 (CH₂₃₄), 30.2 (CH₂₃₂), 19.7 (CH₃₁₈), 18.7 (CH₃₁₉). HRMS (ESI) : m/z calc for C₂₇H₃₂N₃O₇ : 510.2246 [M-H]⁻ ; found : 510.2231.

(S)-1-(((S)-1-(((S)-1-carboxy-2-phenylethyl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate P11L. ¹H NMR (400 MHz, MeOD) δ 7.34 – 7.10 (m, 10H_{8-12, 26-30}), 4.63 (dd, J = 8.2, 5.1 Hz, 1H₄), 4.22 (d, J = 7.3 Hz, 1H₁₄), 4.12 (dd, J = 8.9, 5.1 Hz, 1H₂₁), 3.21 (dd, J = 13.9, 5.0 Hz, 1H₆), 3.15 (dd, J = 14.3, 5.1 Hz, 1H₂₄), 3.01 (dd, J = 13.9, 8.2 Hz, 1H₆), 2.90 (dd, J = 14.4, 9.0 Hz, 1H₂₄), 2.06 (h, J = 6.8 Hz, 1H₁₇), 0.95 (overlapped signals : t, J = 6.6 Hz, 6H_{18, 19}). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 172.7 (C₂), 170.3 (C₁₃), 167.9 (C₂₀), 137.6 (C₇), 134.9 (C₂₅), 129.4 (2CH_{9, 11}), 129.0 (2CH_{27, 29}), 128.4 (2CH_{8, 12}), 128.1 (2CH_{26, 30}), 127.0 (CH₁₀), 126.3 (CH₂₈), 57.5 (CH₁₄), 53.4 (CH₄), 53.2 (CH₂₁), 37.2 (CH₂₆), 36.6 (CH₂₂₄), 31.0 (CH₁₇), 19.0 (CH₃₁₈), 18.1 (CH₃₁₉). ¹⁹F NMR (376 MHz, MeOD) δ -76.94. HRMS (ESI) : m/z calc for cation C₃₁H₃₉N₄O₃⁺ : 412.2231 ; found : 412.2231. m/z calc for anion C₂F₃O₂⁻ : 112.9856 ; found : 112.9856.

(4-(benzyloxy)-4-oxobutanoyl)-L-phenylalanyl-L-valyl-L-phenylalanine P12L. ¹H NMR (400 MHz, MeOD) δ 7.41 – 7.27 (m, 5H₄₀₋₄₄), 7.25 – 7.07 (m, 10H_{8-12, 26-30}), 5.12 – 4.93 (m, 2H₃₈), 4.65 (dd, J = 9.8, 4.7 Hz, 1H₂₁), 4.52 (dd, J = 7.9, 5.1 Hz, 1H₄), 4.13 (d, J = 7.5 Hz, 1H₁₄), 3.20 (dd, J = 14.0, 5.1 Hz, 1H₆), 3.13 (dd, J = 14.2, 4.8 Hz, 1H₂₄), 2.98 (dd, J = 13.9, 7.9 Hz, 1H₆), 2.85 (dd, J = 14.2, 9.8 Hz, 1H₂₄), 2.72 – 2.29 (m, 4H_{32, 34}), 2.05 (h, J = 6.8 Hz, 1H₁₇), 0.88 (d, J = 6.8 Hz, 3H₁₈), 0.86 (d, J = 6.8 Hz, 3H₁₉). ¹³C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v)) δ 177.8 (C₂), 173.9 (C₃₁), 173.7 (C₃₅), 173.4 (C₁₃), 172.2 (C₂₀), 138.3 (C₇), 137.2 (C₂₅), 136.1 (C₃₉), 129.6 (2CH_{27, 29}), 129.5 (2CH_{9, 11}), 129.0 (4CH_{40, 41, 43, 44}), 128.9 (2CH_{8, 12}), 128.8 (2CH_{40, 44}), 128.5 (CH₄₂), 127.3 (CH₂₈), 126.9 (CH₁₀), 67.1 (CH₂₃₈), 60.6 (CH₁₄), 55.8 (CH₄), 55.6 (CH₂₁), 37.9 (CH₂₆), 37.6 (CH₂₄), 30.9 (CH₂₃₄), 30.5 (CH₁₇), 29.9 (CH₂₃₂), 19.3 (CH₃₁₈), 18.5 (CH₃₁₉). HRMS (ESI) : m/z calc for C₃₄H₃₉N₃O₇Na⁺ : 624.2680 [M+Na]⁺ ; found : 624.2681.

Benzyl (((9H-fluoren-9-yl)methoxy)carbonyl)-L-phenylalanyl-L-valinate P14L. ¹H NMR (400 MHz, MeOD) δ 7.77 (d, J = 7.6 Hz, 2H_{32, 33}), 7.56 (broad d, J = 6.9 Hz, 2H_{29, 36}), 7.42 – 7.12 (m, 14H_{30, 31, 34, 35, 9-13, 39-43}), 5.20 – 5.09 (m, 2H₃₇), 4.47 (dd, J = 9.5, 5.2 Hz, 1H₂), 4.37 (d, J = 6.1 Hz, 1H₁₄), 4.28 (dd, J = 10.3, 7.2 Hz, 1H₂₃), 4.20 (dd, J = 10.3, 7.2 Hz, 1H₂₃), 4.12 (t, J = 7.1 Hz, 1H₂₄), 3.07 (dd, J = 13.9, 5.2 Hz, 1H₄), 2.82 (dd, J = 13.8, 9.6 Hz, 1H₄), 2.13 (h, J = 6.7 Hz, 1H₁₆), 0.90 (d, J = 6.8 Hz, 6H_{17, 19}). ¹³C NMR (75 MHz, CDCl₃) δ 171.2 (C₁₅), 171.1 (C₃), 156.1 (C₇), 143.9 (C₂₅), 143.8 (C₂₈), 141.4 (2C_{26, 27}), 136.4 (C₈), 135.3 (C₃₈), 129.4 (2CH_{10, 12}), 128.8 (2CH_{9, 13}), 128.7 (2CH_{40, 42}), 128.5 (CH₄₁), 128.4 (2CH_{39, 43}), 127.8 (2CH_{31, 34}), 127.2 (2CH_{32, 33}), 127.1 (CH₁₁), 125.2 (2CH_{30, 35}), 120.0 (2CH_{29, 36}), 67.2 (CH₂₃₇), 67.1 (CH₂₂₃), 57.4 (CH₁₄), 56.2 (CH₂), 47.1 (CH₂₄), 38.6 (CH₂₄), 31.3 (CH₁₆), 18.9 (CH₃₁₇), 17.7 (CH₃₁₈). HRMS (ESI) : m/z calc for C₃₆H₃₆N₂O₅Na⁺ : 599.2516 [M+Na]⁺ ; found : 599.2518.

(((9H-fluoren-9-yl)methoxy)carbonyl)-L-phenylalanyl-L-valine P15L. ¹H NMR (400 MHz, MeOD) δ 7.77 (d, J = 7.5 Hz, 2H_{32, 33}), 7.56 (dd, J = 7.6, 4.3 Hz, 2H_{29, 36}), 7.41 – 7.15 (m, 7H_{30, 31, 34, 35, 9-13}), 4.48 (dd, J = 9.7, 5.0 Hz, 1H₂), 4.34 (d, J = 5.6 Hz, 1H₁₄), 4.28 (dd, J = 10.4, 7.2 Hz, 1H₂₃), 4.21 (dd, J = 10.5, 7.0 Hz, 1H₂₃), 4.13 (t, J = 7.0 Hz, 1H₂₄), 3.15 (dd, J = 14.0, 5.0 Hz, 1H₄), 2.86 (dd, J = 13.9, 9.7 Hz, 1H₄), 2.17 (dq, J = 13.8, 6.7 Hz, 1H₁₆), 0.96 (overlapped signals : 2d, J = 6.9 Hz, 6H_{17, 18}). ¹³C NMR (101 MHz, MeOD) δ 174.5 (C₁₅), 174.2 (C₃), 158.2 (C₇), 145.2 (C₂₅), 145.1 (C₂₈), 142.5 (2C_{26, 27}), 138.5 (C₈), 130.4 (2CH_{10, 12}), 129.4 (2CH_{9, 13}), 128.7 (2CH_{31, 34}), 128.1 (2CH_{32, 33}), 127.7 (CH₁₁), 126.2 (CH₃₀), 126.2 (2CH₃₅), 120.8 (2CH_{29, 36}), 68.0 (CH₂₂₃), 59.0 (CH₁₄), 57.6 (CH₂), 48.3 (CH₂₄), 39.0 (CH₂₄), 31.9 (CH₁₆), 19.5 (CH₃₁₇), 18.3 (CH₃₁₈).

Benzyl (((9H-fluoren-9-yl)methoxy)carbonyl)-L-phenylalanyl-L-valyl-L-phenylalaninate P16L. ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.70 (m, 2H_{43, 44}), 7.58 – 7.48 (m, 2H_{40, 47}), 7.44 – 7.11 (m, 17H_{9-13, 25-29, 41, 42, 45, 46, 51-53}), 7.05 – 6.95 (m, 2H_{50, 54}), 6.38 (m, 1H₅), 6.25 – 6.13 (m, 1H₁₉), 5.30 (m, 1H₁₁), 5.19 – 5.03 (m, 2H₄₈), 4.94 – 4.81 (m, H₂₁), 4.43 (overlapped signals : dd, J = 10.6, 7.0 Hz, 2H_{14, 35}), 4.32 (m, 1H₂), 4.18 (m, 2H₃₄), 3.06 (m, 4H_{4, 23}), 2.01 (m, 1H₁₆), 0.82 (d, J = 6.8

Hz, 3H₍₁₇₎), 0.76 (d, J = 6.8 Hz, 3H₍₁₈₎). ¹³C NMR (101 MHz, CDCl₃) δ 171.2 (C₍₂₁₎), 171.1 (C₍₁₅₎), 170.3 (C₍₃₎), 156.1 (C₍₇₎), 143.9 (C₍₃₆₎), 143.8 (C₍₃₉₎), 141.4 (2C_(37, 38)), 136.4 (C₍₈₎), 135.7 (C_(C₍₂₄₎)), 135.1 (C₍₄₉₎), 129.4 (2CH_(10, 12)), 129.4 (2CH_(26, 28)), 128.9 (2CH_(9, 13)), 128.8 (2CH_(25, 29)), 128.7 (4CH_(50, 51, 53, 54)), 128.6 (CH₍₅₂₎), 127.9 (2CH_(42, 45)), 127.3 (CH₍₁₁₎), 127.2 (CH₍₂₇₎), 127.2 (2CH_(43, 44)), 125.2 (CH₍₄₁₎), 125.2 (CH₍₄₆₎), 120.1 (2CH_(40, 47)), 67.4 (CH₍₂₄₈₎), 67.3 (CH₍₂₃₄₎), 58.6 (CH₍₁₄₎), 56.3 (CH₍₂₎), 53.4 (CH₍₂₁₎), 47.3 (CH₍₃₅₎), 38.4 (CH₍₂₄₎), 38.1 (CH₍₂₃₎), 31.2 (CH₍₁₆₎), 19.1 (CH₍₃₁₇₎), 18.1 (CH₍₃₁₈₎). HRMS (ESI) : m/z calc for C₄₅H₄₅N₃O₆Na⁺ : 746.3201 [M+Na]⁺ ; found : 746.3205.

L-phenylalanyl-L-valyl-L-phenylalanine P18L. ¹H NMR (400 MHz, D₂O-DMSO-*d*₆, 5% DCl) δ 6.96 – 6.71 (m, 8H_(8, 9, 11, 12, 26, 27, 29, 30)), 6.68 – 6.50 (m, 2H_(10, 28)), 4.11 (dd, J = 9.0, 5.3 Hz, 1H₍₄₎), 3.83 (t, J = 7.1 Hz, 1H₍₂₁₎), 3.64 (d, J = 8.0 Hz, 1H₍₁₄₎), 2.73 (dd, J = 14.0, 5.3 Hz, 1H₍₆₎), 2.67 – 2.33 (m, 3H_(6, 24)), 1.46 (h, J = 6.8 Hz, 1H₍₁₇₎), 0.40 (overlapped signals : dd, J = 6.8 Hz, 6H_(18, 19)). ¹³C NMR (101 MHz, D₂O-DMSO-*d*₆, 5% DCl) δ 175.9 (C₍₄₎), 173.6 (C₍₂₁₎), 170.1 (C₍₁₃₎), 138.1 (C₍₇₎), 135.1 (C₍₂₅₎), 131.0 (2CH_(9, 11)), 130.9 (2CH_(27, 29)), 130.7 (2CH_(8, 12)), 130.4 (2CH_(26, 30)), 129.5 (CH₍₁₀₎), 128.8 (CH₍₂₈₎), 60.8 (CH₍₄₎), 55.7 (CH₍₂₁₎), 38.5 (CH₍₂₆₎), 38.1 (CH₍₂₄₎), 32.0 (CH₍₁₇₎), 19.9 (CH₍₃₁₈₎), 19.4 (CH₍₃₁₉₎). HRMS (ESI) : m/z calc for C₂₃H₂₉N₃O₄Na⁺ : 434.2050 [M+Na]⁺ ; found : 434.2050.

tert-butyl (S)-(1-oxo-3-phenyl-1-((4-vinylphenyl)amino)propan-2-yl)carbamate P19L. ¹H NMR (400 MHz, MeOD) δ 7.36 (Broad AB, d, J = 8.0 Hz, 2H_(2, 4)), 7.29 – 7.15 (m, 5H₍₂₂₋₂₆₎), 7.10 (Broad AB, d, J = 8.0 Hz, 2H_(1, 5)), 4.50 – 4.24 (m, 1H₍₁₁₎), 3.12 (dd, J = 13.7, 6.4 Hz, 1H₍₁₂₎), 2.93 (dd, J = 13.7, 8.3 Hz, 1H₍₁₂₎), 2.58 (q, J = 7.6 Hz, 2H₍₇₎), 1.38 (s, 9H₍₁₉₋₂₁₎), 1.19 (t, J = 7.6 Hz, 3H₍₂₇₎). ¹³C NMR (101 MHz, MeOD) δ 172.4 (C₍₉₎), 157.5 (C₍₁₅₎), 141.7 (C₍₆₎), 138.3 (C₍₁₃₎), 136.8 (C₍₃₎), 130.4 (2CH_(23, 25)), 129.4 (2CH_(1, 5)), 129.0 (2CH_(22, 26)), 127.7 (CH₍₂₄₎), 121.7 (2CH_(2, 4)), 80.6 (C₍₁₈₎), 57.9 (CH₍₁₁₎), 39.7 (CH₍₂₁₂₎), 29.2 (CH₍₂₇₎), 28.6 (3CH₍₃₁₉₋₂₁₎), 16.1 (CH₍₃₂₇₎). HRMS (ESI) : m/z calc for C₂₂H₂₈N₂O₃Na⁺ : 391.1992 [M+Na]⁺ ; found : 391.1990.

(S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate P20L: ¹H NMR (400 MHz, MeOD) δ 7.39 – 7.28 (m, 7H_(2, 4, 14-18)), 7.16 – 7.13 (m, 2H_(1, 5)), 4.17 (t, J = 7.4 Hz, 1H₍₁₁₎), 3.27 (dd, J = 13.8, 7.2 Hz, 1H₍₁₂₎), 3.16 (dd, J = 13.8, 7.5 Hz, 1H₍₁₂₎), 2.61 (q, J = 7.6 Hz, 2H₍₇₎), 1.21 (t, J = 7.6 Hz, 3H₍₂₀₎). ¹³C NMR (101 MHz, MeOD) δ 167.7 (C₍₉₎), 163.0 (q, J_{C-F} = 34.6 Hz, CF₃), 142.3 (C₍₆₎), 136.3 (C₍₁₃₎), 135.5 (C₍₃₎), 130.5 (2CH_(15, 17)), 130.0 (2CH_(1, 5)), 129.1 (2CH_(14, 18)), 128.8 (CH₍₁₆₎), 121.6 (2CH_(2, 4)), 56.3 (CH₍₁₁₎), 38.7 (CH₍₂₁₂₎), 29.2 (CH₍₂₇₎), 16.1 (CH₍₃₂₀₎). ¹⁹F NMR (376 MHz, MeOD) δ -76.75. HRMS (ESI) : m/z calc for cation C₁₇H₂₁N₂O⁺ : 269.1648 ; found : 269.1649. m/z calc for anion C₂F₃O₂⁻ : 112.9856 ; found : 112.9856.

tert-butyl ((S)-1-(((S)-1-(((S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate P21L. ¹H NMR (400 MHz, CDCl₃) δ 8.41 (s, 1H₍₉₎), 7.42 (broad, AB, d, J = 8.0 Hz, 2H_(2, 4)), 7.20 – 7.05 (m, 10H_(16-20, 41-45)), 7.02 (AB, d, J = 8.1 Hz, 2H_(1, 5)), 6.94 (s, 1H₍₁₃₎), 6.87 (d, J = 8.3 Hz, 1H₍₂₄₎), 5.08 (d, J = 6.5 Hz, 1H₍₃₁₎), 4.84 (td, J = 8.6, 8.6, 6.0 Hz, 1H₍₁₂₎), 4.42 (q, J = 6.7 Hz, 1H₍₂₉₎), 4.21 (dd, J = 7.0, 5.2 Hz, 1H₍₂₂₎), 3.33 (dd, J = 14.5, 5.7 Hz, 1H₍₃₂₎), 3.00 (dd, J = 13.9, 5.7 Hz, 1H₍₁₄₎), 2.95 – 2.80 (overlapped signals, 2dd, 2H_(14, 32)), 2.52 (q, J = 7.6 Hz, 2H₍₇₎), 2.02 (dq, J = 13.7, 6.7 Hz, 1H₍₂₅₎), 1.29 (s, 9H₍₃₈₋₄₀₎), 1.13 (t, J = 7.6 Hz, 3H₍₄₆₎), 0.69 (d, J = 6.8 Hz, 3H₍₂₇₎), 0.54 (d, J = 6.8 Hz, 3H₍₂₆₎). ¹³C NMR (101 MHz, CDCl₃) δ 172.4 (C₍₁₀₎), 172.0 (C₍₂₁₎), 169.8 (C₍₂₈₎), 155.9 (C₍₃₄₎), 140.4 (C₍₆₎), 137.1 (C₍₃₃₎), 136.6 (C₍₁₅₎), 135.4 (C₍₃₎), 129.6 (2CH_(42, 44)), 129.4 (2CH_(17, 19)), 128.6 (2CH_(41, 45)), 128.4 (2CH_(16, 20)), 128.1 (2CH_(1, 5)), 126.8 (CH₍₄₃₎), 126.7 (CH₍₁₈₎), 121.1 (2CH_(2, 4)), 79.7 (C₍₃₇₎), 58.4 (CH₍₂₂₎), 55.7 (CH₍₁₂₎), 55.4 (CH₍₂₉₎), 39.4 (CH₍₂₁₄₎), 38.6 (CH₍₂₃₂₎), 31.8 (CH₍₂₅₎), 28.5 (3CH₍₃₈₋₄₀₎), 28.4 (CH₍₂₇₎), 19.3 (CH₍₃₂₇₎), 18.3 (CH₍₃₂₆₎), 15.7 (CH₍₃₄₆₎). HRMS (ESI) : m/z calc for C₃₆H₄₆N₄O₅Na⁺ : 637.3360 [M+Na]⁺ ; found : 637.3360.

(S)-1-(((S)-1-(((S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate P22L. ¹H NMR (400 MHz, MeOD) δ 7.39 – 7.17 (m, 12H_(16-20, 34-38, 2, 4)), 7.11 (Broad AB, d, J = 8.5 Hz, 2H_(1, 5)), 4.73 (dd, J = 7.8, 7.0 Hz, 1H₍₁₂₎), 4.24 (d, J = 7.5 Hz, 1H₍₂₂₎), 4.12 (dd, J = 8.6, 5.4 Hz, 1H₍₂₉₎), 3.21 – 3.13 (overlapped signals : ddd, J = 13.7, 6.2, 3.4 Hz, 2H_(32, 14)), 3.03 (dd, J = 13.7, 7.8 Hz, 1H₍₁₄₎), 2.93 (dd, J = 14.3, 8.6 Hz, 1H₍₃₂₎), 2.59 (q, J = 7.6 Hz, 2H₍₇₎), 2.05 (dq, J = 13.8, 6.9 Hz, 1H₍₂₅₎), 1.20 (t, J = 7.6 Hz, 3H₍₈₎), 0.94 (Overlapped signals : 2d, J = 6.8 Hz, 6H_(26, 27)). ¹³C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v)) δ 172.0 (C₍₁₀₎), 170.4 (C₍₂₁₎), 169.8 (C₍₂₈₎), 141.4 (C₍₆₎), 137.1 (C₍₃₃₎), 135.6 (C₍₃₎), 134.8 (C₍₁₅₎), 129.9 (2CH_(35, 37)), 129.8 (2CH_(17, 19)), 129.5 (2CH_(1, 5)), 129.0 (2CH_(34, 38)), 128.6 (2CH_(16, 20)), 128.2 (CH₍₃₆₎), 127.4 (CH₍₁₈₎), 121.2 (2CH_(2, 4)), 60.0 (CH₍₂₂₎), 55.8 (CH₍₂₉₎), 54.9 (CH₍₁₂₎), 39.0 (CH₍₂₃₂₎), 38.3 (CH₍₂₁₄₎), 31.5 (CH₍₂₅₎), 28.8 (CH₍₇₎), 19.2 (CH₍₃₂₆₎), 18.5 (CH₍₃₂₇₎), 15.8 (CH₍₃₈₎). ¹⁹F NMR (376 MHz, MeOD) δ -76.99. HRMS (ESI) : m/z calc for cation C₃₁H₃₉N₄O₃⁺ : 515.3017 ; found : 515.3015. m/z calc for anion C₂F₃O₂⁻ : 112.9856 ; found : 112.9858.

Benzyl 4-(((S)-1-(((S)-1-(((S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoate P23L. ¹H NMR (400 MHz, MeOD) δ 7.43 – 7.35 (Broad AB, J = 8.5 Hz, 2H_(2, 4)), 7.35 – 7.27 (m, 5H₍₄₈₋₅₂₎), 7.27 – 7.14 (m, 10H_(15-19, 33-37)), 7.10 (Broad AB, J = 8.5 Hz, 2H_(1, 5)), 5.12 – 5.00 (m, 2H₍₄₆₎),

4.70 (dd, $J = 8.3, 6.7$ Hz, $1H_{(11)}$), 4.63 (dd, $J = 9.2, 5.2$ Hz, $1H_{(28)}$), 4.09 (d, $J = 7.2$ Hz, $1H_{(21)}$), 3.21 (dd, $J = 13.8, 6.7$ Hz, $1H_{(13)}$), 3.12 (dd, $J = 14.2, 5.3$ Hz, $1H_{(46)}$), 2.97 (dd, $J = 13.8, 8.3$ Hz, $1H_{(13)}$), 2.87 (dd, $J = 14.1, 9.2$ Hz, $1H_{(31)}$), 2.70 – 2.36 (overlapped signals : m, $6H_{(7, 40, 42)}$), 1.99 (h, $J = 6.9$ Hz, $1H_{(24)}$), 1.19 (t, $J = 7.6$ Hz, $3H_{(38)}$), 0.83 (d, $J = 6.8$ Hz, $3H_{(25)}$), 0.81 (d, $J = 6.8$ Hz, $3H_{(26)}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8 ($C_{(39)}$), 171.8 ($C_{(9)}$), 171.7 ($C_{(43)}$), 171.6 ($C_{(20)}$), 170.0 ($C_{(27)}$), 140.4 ($C_{(6)}$), 137.1 ($C_{(32)}$), 136.7 ($C_{(14)}$), 136.1 ($C_{(47)}$), 135.5 ($C_{(3)}$), 129.8 ($2CH_{(34, 36)}$), 129.6 ($2CH_{(16, 18)}$), 128.8 – 128.0 (overlapped signals : $11CH_{(48-52, 33, 35, 37, 15, 17, 19)}$), 126.7 ($2CH_{(1, 5)}$), 121.3 ($2CH_{(2, 4)}$), 66.3 ($CH_{(246)}$), 58.4 ($CH_{(21)}$), 54.8 ($CH_{(11)}$), 53.9 ($CH_{(28)}$), 40.3 ($CH_{(213)}$), 39.3 ($CH_{(231)}$), 32.3 ($CH_{(24)}$), 30.9 ($CH_{(242)}$), 29.9 ($CH_{(240)}$), 28.4 ($CH_{(27)}$), 19.1 ($CH_{(325)}$), 19.0 ($CH_{(326)}$), 15.7 ($CH_{(38)}$). HRMS (ESI) : m/z calc for $C_{42}H_{48}N_4O_6Na^+$: 727.3466 $[M+Na]^+$; found : 727.3474.

4-(((S)-1-(((S)-1-(((S)-1-carboxy-2-phenylethyl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoic acid **P24L**. 1H NMR (400 MHz, MeOD) δ 7.31 – 7.04 (m, $10H_{(8-12, 26-30)}$), 4.71 – 4.51 (overlapped signals : m, $2H_{(4, 21)}$), 4.18 (d, $J = 7.5$ Hz, $1H_{(14)}$), 3.18 (dd, $J = 14.0, 5.3$ Hz, $1H_{(4)}$), 3.08 (dd, $J = 14.1, 5.0$ Hz, $1H_{(24)}$), 2.99 (dd, $J = 13.9, 8.4$ Hz, $1H_{(4)}$), 2.83 (dd, $J = 14.1, 9.5$ Hz, $1H_{(24)}$), 2.60 – 2.34 (m, $4H_{(32, 34)}$), 2.03 (h, $J = 6.9$ Hz, $1H_{(17)}$), 0.90 (overlapped signals : t, $J = 6.9$ Hz, $6H_{(18, 19)}$). ^{13}C NMR (101 MHz, MeOD) δ 176.1 ($C_{(35)}$), 174.4 ($2C_{(2, 31)}$), 173.5 ($C_{(13)}$), 173.1 ($C_{(20)}$), 138.5 ($C_{(25)}$), 138.3 ($C_{(7)}$), 130.3 ($2CH_{(27, 29)}$), 130.2 ($2CH_{(9, 11)}$), 129.5 ($2CH_{(26, 30)}$), 129.4 ($2CH_{(8, 12)}$), 127.8 ($CH_{(28)}$), 127.6 ($CH_{(10)}$), 60.1 ($CH_{(14)}$), 55.9 ($CH_{(4)}$), 55.1 ($CH_{(21)}$), 38.6 ($CH_{(26)}$), 38.5 ($CH_{(24)}$), 32.1 ($CH_{(17)}$), 31.5 ($CH_{(34)}$), 30.2 ($CH_{(32)}$), 19.7 ($CH_{(318)}$), 18.7 ($CH_{(319)}$). HRMS (ESI) : m/z calc for $C_{27}H_{32}N_3O_7$: 510.2246 $[M-H]^-$; found : 510.2231.

(S)-2-((S)-2-amino-3-phenylpropanamido)-N-((S)-1-((4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)-3-methylbutanamide **P25L**. 1H NMR (300 MHz, MeOD) δ 7.35 (Broad AB d, $J = 8.5$ Hz, $2H_{(2, 4)}$), 7.32 – 7.15 (m, $10H_{(15-19, 33-37)}$), 7.12 (Broad AB d, $J = 8.5$ Hz, $2H_{(1, 5)}$), 4.72 (dd, $J = 8.0, 6.9$ Hz, $1H_{(11)}$), 4.18 (d, $J = 7.2$ Hz, $1H_{(21)}$), 3.78 (dd, $J = 8.2, 5.1$ Hz, $1H_{(28)}$), 3.18 (dd, $J = 13.6, 6.9$ Hz, $1H_{(13)}$), 3.12 – 2.96 (m, $2H_{(31)}$), 2.81 (dd, $J = 13.8, 8.2$ Hz, $1H_{(13)}$), 2.60 (q, $J = 7.6$ Hz, $2H_{(7)}$), 2.02 (h, $J = 6.8$ Hz, $1H_{(24)}$), 1.20 (t, $J = 7.6$ Hz, $3H_{(38)}$), 0.87 (overlapped signals : 2d, $J = 6.8$ Hz, $6H_{(25, 26)}$). ^{13}C NMR (101 MHz, MeOD- $CDCl_3$ (1 : 1 ; v : v)) δ 174.3 ($C_{(27)}$), 172.4 ($C_{(9)}$), 170.5 ($C_{(20)}$), 141.3 ($C_{(6)}$), 137.3 ($C_{(32)}$), 137.1 ($C_{(14)}$), 135.9 ($C_{(3)}$), 129.9 ($2CH_{(34, 36)}$), 129.9 ($2CH_{(16, 18)}$), 129.3 ($2CH_{(33, 37)}$), 129.0 ($2CH_{(1, 5)}$), 128.7 ($2CH_{(15, 19)}$), 127.6 ($CH_{(35)}$), 127.4 ($CH_{(17)}$), 121.2 ($2CH_{(2, 4)}$), 59.5 ($CH_{(21)}$), 56.2 ($CH_{(28)}$), 55.8 ($CH_{(11)}$), 40.6 ($CH_{(231)}$), 38.8 ($CH_{(213)}$), 31.5 ($CH_{(24)}$), 28.8 ($CH_{(27)}$), 19.4 ($CH_{(325)}$), 18.4 ($CH_{(326)}$), 15.9 ($CH_{(38)}$). HRMS (ESI) : m/z calc for $C_{40}H_{56}N_5O_4^+$: 515.3017 $[M+H]^+$; found : 515.3019.

tert-butyl (R)-(1-oxo-3-phenyl-1-((4-vinylphenyl)amino)propan-2-yl)carbamate **P3D**. 1H NMR (300 MHz, MeOD) δ 7.45 (Broad AB, d, $J = 8.6$ Hz, $2H_{(1, 5)}$), 7.35 (Broad AB, d, $J = 8.6$ Hz, $2H_{(2, 4)}$), 7.29 – 7.16 (m, $5H_{(15-19)}$), 6.68 (dd, $J = 17.6, 11.0$ Hz, $1H_{(7)}$), 5.70 (dd, $J = 18.38, 17.6$ Hz, $1H_{(8)}$), 5.16 (dd, $J = 11.70, 10.9$ Hz, $1H_{(8)}$), 4.43 (m, $1H_{(12)}$), 3.11 (dd, $J = 13.6, 6.4$ Hz, $1H_{(13)}$), 2.93 (dd, $J = 13.5, 8.4$ Hz, $1H_{(13)}$), 1.38 (s, $9H_{(25-27)}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1 ($C_{(10)}$), 156.5 ($C_{(21)}$), 137.4 ($C_{(3)}$), 136.9 ($C_{(14)}$), 136.2 ($CH_{(7)}$), 133.5 ($C_{(6)}$), 129.4 ($2CH_{(16, 18)}$), 128.4 ($2CH_{(1, 5)}$), 126.7 ($CH_{(17)}$), 126.5 ($2CH_{(15, 19)}$), 120.1 ($2CH_{(2-4)}$), 112.8 ($CH_{(8)}$), 80.1 ($C_{(24)}$), 57.0 ($CH_{(12)}$), 39.2 ($CH_{(213)}$), 28.3 ($3CH_{(25-27)}$). HRMS (ESI) : m/z calc for $C_{22}H_{27}N_2O_3^+$: 367.2016 $[M+H]^+$; found : 367.2016.

Benzyl (tert-butoxycarbonyl)-D-phenylalanyl-D-valinate **P4D**. 1H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.19 (m, $5H_{(1-5)}$), 7.19 – 7.04 (m, $5H_{(21-25)}$), 6.31 (d, $J = 8.6$ Hz, $1H_{(12)}$), 5.05 (s, $2H_{(7)}$), 4.92 (m, $1H_{(26)}$), 4.43 (dd, $J = 8.6, 4.9$ Hz, $1H_{(10)}$), 4.27 (q, $J = 7.3$ Hz, $1H_{(18)}$), 2.98 (d, $J = 6.9$ Hz, $2H_{(19)}$), 2.18 – 1.97 (m, $1H_{(13)}$), 1.33 (s, $9H_{(31-33)}$), 0.77 (d, $J = 6.9$ Hz, $3H_{(14)}$), 0.72 (d, $J = 6.9$ Hz, $3H_{(15)}$).

(Tert-butoxycarbonyl)-D-phenylalanyl-D-valine **P5D**. 1H NMR (300 MHz, $CDCl_3$) δ 9.55 (s, $1H_{(19)}$), 7.37 – 7.11 (m, $5H_{(9-13)}$), 6.87 – 6.69 (m, $1H_{(5)}$), 5.58 – 5.38 (m, $1H_{(11)}$), 4.62 – 4.41 (overlapped signals : m, $2H_{(2, 14)}$), 3.20 – 2.99 (m, $2H_{(4)}$), 2.25 (h, $J = 6.9$ Hz, $1H_{(16)}$), 1.44 (s, $9H_{(24-26)}$), 0.96 (overlapped signals, t, $J = 7.0$ Hz, $6H_{(17, 18)}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8 ($C_{(15)}$), 172.0 ($C_{(3)}$), 155.9 ($C_{(7)}$), 136.6 ($C_{(8)}$), 129.4 ($2CH_{(10, 12)}$), 128.7 ($2CH_{(9, 13)}$), 127.0 ($CH_{(11)}$), 80.6 ($C_{(23)}$), 57.4 ($CH_{(14)}$), 55.9 ($CH_{(2)}$), 38.2 ($CH_{(24)}$), 31.2 ($CH_{(16)}$), 28.3 ($3CH_{(24-26)}$), 19.0 ($CH_{(317)}$), 17.8 ($CH_{(318)}$).

Benzyl (tert-butoxycarbonyl)-D-phenylalanyl-D-valyl-D-phenylalaninate **P6D**. 1H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, $3H_{(41, 43)}$), 7.29 – 7.15 (m, $10H_{(8-13, 34-38)}$), 7.08 – 7.00 (m, $2H_{(40-44)}$), 6.62 (overlapped signals : 2d, $J = 9.0, 8.3$ Hz, $2H_{(6, 17)}$), 5.19 – 5.04 (overlapped signals : , $3H_{(24, 1)}$), 4.89 (dt, $J = 8.0, 6.2$ Hz, $1H_{(5)}$), 4.38 (d, $J = 7.3$ Hz, $1H_{(22)}$), 4.27 (dd, $J = 8.6, 6.4$ Hz, $1H_{(15)}$), 3.14 – 2.97 (m, $4H_{(7, 25)}$), 2.05 (h, $J = 6.7$ Hz, $1H_{(18)}$), 1.40 (s, $9H_{(31-33)}$), 0.85 (d, $J = 6.8$ Hz, $3H_{(19)}$), 0.81 (d, $J = 6.8$ Hz, $3H_{(20)}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5 ($C_{(3)}$), 171.2 ($C_{(14)}$), 170.1 ($C_{(21)}$), 155.6 ($C_{(27)}$), 136.8 ($CH_{(26)}$), 135.7 ($CH_{(39)}$), 135.2 ($CH_{(8)}$), 129.4 ($2CH_{(35, 37)}$), 129.4 ($2CH_{(10, 12)}$), 128.8 ($2CH_{(34, 38)}$), 128.7 ($2CH_{(9, 13)}$), 128.6 ($4CH_{(40, 41, 43, 45)}$), 128.6 ($CH_{(42)}$), 127.2 ($CH_{(36)}$), 127.0 ($2CH_{(11)}$), 80.3 ($C_{(30)}$), 67.3 ($CH_{(21)}$), 58.5 ($CH_{(15)}$), 55.9 ($CH_{(5)}$), 53.4 ($CH_{(22)}$), 38.0 ($2CH_{(27, 25)}$), 31.0 ($CH_{(18)}$), 28.4 ($3CH_{(31-33)}$), 19.1 ($CH_{(319)}$), 18.0 ($CH_{(320)}$). HRMS (ESI) : m/z calc for $C_{35}H_{43}N_3O_6Na^+$: 624.3044 $[M+Na]^+$; found : 624.3052.

(*Tert*-butoxycarbonyl)-*D*-phenylalanyl-*D*-valyl-*D*-phenylalanine ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.11 (m, 10H_[8-12, 26-30]), 7.04 (d, J = 8.7 Hz, 1H_[16]), 6.81 (broad s, 1H_[5]), 5.20 (s, 1H_[23]), 4.79 (q, J = 6.7 Hz, 1H_[4]), 4.43 (broad s, 1H_[21]), 4.29 (dd, J = 8.8, 6.9 Hz, 1H_[14]), 3.18 (dd, J = 14.0, 5.7 Hz, 1H_[24]), 3.10 – 2.90 (overlapped signals : m, 3H_[24, 6]), 2.00 (h, J = 6.8 Hz, 1H_[17]), 1.39 (s, 9H_[35-37]), 0.86 (d, J = 6.7 Hz, 3H_[19]), 0.79 (d, J = 6.7 Hz, 3H_[18]). ¹³C NMR (101 MHz, CDCl₃) δ 173.8 (C_[2]), 172.1 (C_[13]), 171.2 (C_[20]), 155.8 (C_[31]), 136.7 (C_[25]), 136.1 (C_[7]), 129.5 (2CH_[27, 29]), 129.4 (2CH_[9, 11]), 128.6 (4CH_[26, 30, 8, 12]), 127.1 (CH_[28]), 126.9 (CH_[10]), 80.4 (C_[34]), 58.7 (CH_[14]), 55.8 (CH_[4]), 53.6 (CH_[21]), 38.2 (CH₂[24]), 37.7 (CH₂[6]), 31.2 (CH_[17]), 28.3 (3CH₃[35-37]), 19.1 (CH₃[19]), 18.2 (CH₃[18]). HRMS (ESI) : m/z calc for C₂₈H₃₇N₃O₆Na⁺ : 534.2575 [M+Na]⁺ ; found : 534.2580

(*R*)-1-(((*R*)-1-(((*R*)-1-(benzyloxy)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate **P8D**. ¹H NMR (400 MHz, MeOD) δ 7.37 – 7.15 (m, 15H_[2-6, 16-20, 34-38]), 5.11 (s, 2H_[8]), 4.72 (dd, J = 8.4, 6.1 Hz, 1H_[12]), 4.22 (d, J = 7.2 Hz, 1H_[22]), 4.05 (dd, J = 8.6, 5.3 Hz, 1H_[29]), 3.16 (dd, J = 13.9, 6.1 Hz, 1H_[14]), 3.10 (dd, J = 14.2, 5.3 Hz, 1H_[32]), 3.01 (dd, J = 13.9, 8.4 Hz, 1H_[14]), 2.87 (dd, J = 14.3, 8.6 Hz, 1H_[32]), 2.00 (dq, J = 13.8, 6.9 Hz, 1H_[25]), 0.90 (overlapped signals : 2d, J = 6.8 Hz, 6H_[26, 27]). ¹³C NMR (101 MHz, MeOD) δ 172.9 (C_[10]), 172.5 (C_[21]), 170.5 (C_[28]), 137.9 (C_[32]), 136.9 (C_[7]), 135.9 (C_[15]), 130.5 (2CH_[35, 37]), 130.3 (2CH_[17, 19]), 130.0 (2CH_[3, 5]), 129.5 (2CH_[34, 38]), 129.5 (2CH_[2, 6]), 129.4 (2CH_[16, 20]), 129.3 (CH_[4]), 128.6 (CH_[36]), 127.9 (CH_[18]), 68.0 (CH₂[8]), 60.0 (CH_[22]), 55.6 (CH_[29]), 55.4 (CH_[12]), 39.1 (CH₂[32]), 38.4 (CH_[25]), 32.1 (CH₂[8]), 19.6 (CH_[26]), 18.6 (CH₂[27]). ¹⁹F NMR (376 MHz, MeOD) δ -76.97. HRMS (ESI) : m/z calc for cation C₃₀H₃₆N₃O₄⁺ : 502.2700 ; found : 502.2701. m/z calc for anion C₂F₃O₂⁻ : 112.9856 ; found : 112.9856.

(*R*)-1-(((*R*)-1-(((*R*)-1-carboxy-2-phenylethyl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate **P11D**. ¹H NMR (400 MHz, MeOD) δ 7.33 – 7.07 (m, 10H_[16-20, 34-38]), 4.65 (dd, J = 8.5, 5.0 Hz, 1H_[12]), 4.23 (d, J = 7.4 Hz, 1H_[22]), 4.13 (dd, J = 8.8, 5.2 Hz, 1H_[29]), 3.22 (dd, J = 14.0, 5.0 Hz, 1H_[14]), 3.13 (dd, J = 14.4, 5.2 Hz, 1H_[32]), 3.00 (dd, J = 14.0, 8.5 Hz, 1H_[14]), 2.90 (dd, J = 14.4, 8.8 Hz, 1H_[32]), 2.05 (h, J = 6.8 Hz, 1H_[25]), 0.96 (overlapped signals : 2d, J = 6.8 Hz, 6H_[26, 27]). ¹³C NMR (101 MHz, DMSO) δ 172.7 (C_[10]), 170.3 (C_[21]), 167.9 (C_[28]), 137.6 (C_[15]), 134.8 (C_[32]), 129.4 (2CH_[17, 19]), 129.0 (2CH_[35, 37]), 128.4 (2CH_[16, 20]), 128.1 (2CH_[34, 38]), 127.0 (CH_[18]), 126.3 (CH_[36]), 57.5 (CH_[22]), 53.4 (CH_[12]), 53.1 (CH_[29]), 37.2 (CH₂[14]), 36.6 (CH₂[32]), 31.0 (CH_[25]), 19.0 (CH₃[26]), 18.1 (CH₃[27]). ¹⁹F NMR (376 MHz, MeOD) δ -76.94. HRMS (ESI) : m/z calc for cation C₃₁H₃₉N₄O₃⁺ : 412.2231 ; found : 412.2232. m/z calc for anion C₂F₃O₂⁻ : 112.9856 ; found : 112.9859.

Tert-butyl ((*R*)-1-(((*R*)-1-(((*R*)-1-(4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate **P21D**. ¹H NMR (400 MHz, CDCl₃) δ 8.35 (s, 1H_[9]), 7.56 (Broad d, J = 7.9 Hz, 2H_[2, 4]), 7.33 – 7.20 (m, 5H_[16-20]), 7.20 – 7.06 (m, 7H_[1, 5, 41-45]), 6.71 (d, J = 8.3 Hz, 1H_[13]), 6.65 (s, 1H_[24]), 4.98 (d, J = 5.8 Hz, 1H_[31]), 4.90 (td, J = 8.7, 5.7 Hz, 1H_[12]), 4.36 (q, J = 6.4 Hz, 1H_[29]), 4.17 (dd, J = 6.4, 4.7 Hz, 1H_[22]), 3.47 (Broad d, J = 14.2 Hz, 1H_[32]), 3.10 (dd, J = 14.0, 6.1 Hz, 1H_[14]), 3.01 (dd, J = 14.0, 7.3 Hz, 1H_[14]), 2.90 (dd, J = 14.6, 9.6 Hz, 1H_[32]), 2.61 (q, J = 7.6 Hz, 2H_[7]), 2.11 (ddd, J = 13.8, 9.4, 5.9 Hz, 1H_[25]), 1.38 (s, 9H_[38-40]), 1.21 (t, J = 7.6 Hz, 3H_[46]), 0.76 (d, J = 6.9 Hz, 3H_[26]), 0.57 (d, J = 6.9 Hz, 3H_[27]). ¹³C NMR (101 MHz, CDCl₃) δ 172.4 (C_[10]), 172.1 (C_[21]), 169.9 (C_[28]), 155.9 (C_[34]), 140.3 (C_[6]), 137.2 (C_[33]), 136.6 (C_[15]), 135.3 (C_[3]), 129.6 (2CH_[42, 44]), 129.4 (2CH_[17, 19]), 128.5 (2CH_[41, 45]), 128.3 (2CH_[16, 20]), 128.0 (2CH_[1, 5]), 126.7 (CH_[43]), 126.6 (CH_[18]), 121.2 (2CH_[2, 4]), 79.6 (C_[37]), 58.3 (CH_[22]), 55.6 (CH_[12]), 55.5 (CH_[29]), 39.5 (CH₂[14]), 38.7 (CH₂[32]), 32.0 (CH_[25]), 28.5 (CH₃[38-40]), 28.4 (CH₂[7]), 19.3 (CH₃[26]), 18.4 (CH₃[27]), 15.6 (CH₃[46]). HRMS (ESI) : m/z calc for C₃₆H₄₆N₄O₅Na⁺ : 637.3360 [M+Na]⁺ ; found : 637.3359.

(*R*)-1-(((*R*)-1-(((*R*)-1-(4-ethylphenyl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-3-methyl-1-oxobutan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate **P22D**. ¹H NMR (400 MHz, MeOD) δ 7.36 (Broad AB, d, J = 8.5 Hz, 2H_[2, 4]), 7.31 – 7.15 (m, 10H_[16-20, 34-38]), 7.12 (d, J = 8.5 Hz, 2H_[1, 5]), 4.72 (dd, J = 8.1, 6.9 Hz, 1H_[12]), 4.15 (d, J = 7.1 Hz, 1H_[22]), 3.66 (dd, J = 8.0, 5.1 Hz, 1H_[29]), 3.18 (dd, J = 13.7, 6.9 Hz, 1H_[14]), 3.08 – 2.95 (overlapped signals : dd, J = 13.7, 5.0 Hz, 1H_[32], dd, J = 13.5, 7.9 Hz, 1H_[32]), 2.77 (dd, J = 13.6, 8.0 Hz, 1H_[14]), 2.60 (q, J = 7.6 Hz, 2H_[7]), 2.00 (h, J = 6.8 Hz, 1H_[25]), 1.20 (t, J = 7.6 Hz, 3H_[8]), 0.85 (overlapped signals : 2d, J = 6.8 Hz, 6H_[26, 27]). ¹³C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v)) δ 176.0 (C_[10]), 172.5 (C_[21]), 170.5 (C_[28]), 141.3 (C_[6]), 137.7 (C_[33]), 137.3 (C_[15]), 135.9 (C_[3]), 129.9 (4CH_[17, 19, 35, 37]), 129.2 (2CH_[1, 5]), 129.0 (2CH_[34, 38]), 128.7 (2CH_[16, 20]), 127.5 (CH_[36]), 127.4 (CH_[18]), 121.3 (2CH_[2, 4]), 59.5 (CH_[22]), 56.6 (CH_[29]), 55.8 (CH_[12]), 41.3 (CH₂[32]), 38.8 (CH₂[14]), 31.5 (CH_[25]), 28.8 (CH₂[7]), 19.4 (CH₃[26]), 18.4 (CH₃[27]), 15.9 (CH₃[8]). ¹⁹F NMR (376 MHz, MeOD) δ -76.51. HRMS (ESI) : m/z calc for cation C₃₁H₃₉N₄O₃⁺ : 515.3017 ; found : 515.3017. m/z calc for anion C₂F₃O₂⁻ : 112.9856 ; found : 112.9856.

tert-butyl ((2*S*)-1-oxo-3-phenyl-1-((4-(1-(2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)carbamate **A1L**. ¹H NMR (400 MHz, CDCl₃) δ 8.34 (s, 1H_[9]) 7.33 (Broad AB, d, J = 8.1 Hz, 2H_[2, 4]), 7.30 – 7.22 (m, 5H_[15-19]), 7.20

(Broad AB, d, $J = 8.2$ Hz, $2H_{[1, 5]}$), 5.54 (m, $1H_{[20]}$), 4.73 (q, $J = 6.6$ Hz, $1H_{[7]}$), 4.65 – 4.55 (m, $1H_{[12]}$), 3.23 – 3.02 (m, $2_{[13]}$), 1.60 – 1.33 (overlapped signals : m, $6H_{[32, 35, 38]}$, d, $J = 6.6$ Hz, $3H_{[28]}$, s, $9H_{[25-27]}$), 1.29 (s, $3H_{[33]}$), 1.16 (s, $3H_{[36]}$), 1.02 (s, $3H_{[34]}$), 0.65 (s, $3H_{[37]}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8 ($C_{[10]}$), 155.8 ($C_{[21]}$), 141.9 ($C_{[3]}$), 136.7 ($C_{[14]}$), 136.0 ($C_{[6]}$), 129.3 ($2CH_{[16, 18]}$), 128.6 ($2CH_{[1, 5]}$), 127.0 ($2CH_{[15, 19]}$), 126.8 ($CH_{[17]}$), 119.7 ($2CH_{[2, 4]}$), 82.5 ($CH_{[7]}$), 80.3 ($C_{[24]}$), 59.5 ($C_{[30, 31]}$), 56.7 ($CH_{[12]}$), 40.3 ($2CH_{[32, 35]}$), 38.6 ($CH_{[2[13]]}$), 34.3 ($CH_{[3[33]]}$), 34.3 ($CH_{[3[36]]}$), 28.2 ($3CH_{[3[25-27]]}$), 23.3 ($CH_{[3[28]]}$), 20.2 ($2CH_{[3[34, 37]]}$), 17.1 ($CH_{[2[38]]}$). HRMS (ESI) : m/z calc for $C_{31}H_{46}N_3O_4^+$: 524.3483 $[M+H]^+$; found : 524.3482

(2*S*)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-aminium trifluoroacetate **A2L**. By using GP3 with **A1L** (0.86 g, 1.643 mmol, 1.0 eq) afforded **A2L** as a white solid (0.71 g, 81 %). The product was directly used in the coupling reaction without characterization.

tert-butyl ((2*S*)-1-(((2*S*)-3-methyl-1-oxo-1-(((2*S*)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate **A3L**. 1H NMR (300 MHz, MeOD) δ 7.44 – 7.39 (m, $2H_{[2, 4]}$), 7.30 – 7.12 (m, $12H_{[1, 5, 16-20, 41-45]}$), 4.79 – 4.66 (overlapped signals, m, $2H_{[7, 12]}$), 4.42 (dd, $J = 9.9, 5.0$ Hz, $1H_{[29]}$), 4.25 (d, $J = 7.1$ Hz, $1H_{[22]}$), 3.18 (dd, $J = 13.6, 7.1$ Hz, $1H_{[14]}$), 3.06 (dd, $J = 14.0, 5.1$ Hz, $1H_{[32]}$), 2.99 (dd, $J = 13.7, 8.0$ Hz, $1H_{[14]}$), 2.79 (dd, $J = 13.7, 9.4$ Hz, $1H_{[32]}$), 2.03 (dq, $J = 6.8$ Hz, $1H_{[25]}$), 1.60 – 0.97 (overlapped signals : m, $15H_{[50-54, 56]}$, d, $J = 6.7$ Hz, $3H_{[46]}$, s, $9H_{[38-40]}$), 0.90 – 0.80 (overlapped signals, m, $6H_{[26, 27]}$), 0.61 (s, $3H_{[55]}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4 ($C_{[10]}$), 172.0 ($C_{[21]}$), 169.7 ($C_{[28]}$), 156.0 ($C_{[34]}$), 142.0 ($C_{[3]}$, dia 1), 141.9 ($C_{[3]}$, dia 2), 136.9 ($C_{[33]}$), 136.6 ($C_{[15]}$), 136.5 ($C_{[6]}$), 129.5 ($2CH_{[42, 44]}$), 129.3 ($2CH_{[17, 19]}$), 128.6 ($2CH_{[41, 45]}$), 128.5 ($2CH_{[16, 20]}$), 127.1 ($CH_{[43]}$), 127.0 ($CH_{[18]}$), 126.8 ($CH_{[11]}$), 126.7 ($CH_{[5]}$), 120.4 ($2CH_{[2, 4]}$), 82.8 ($CH_{[7]}$, dia 1), 82.7 ($CH_{[43]}$, dia 2), 79.9 ($C_{[37]}$), 59.7 ($2C_{[48, 49]}$), 58.4 ($CH_{[22]}$), 55.7 ($CH_{[12]}$), 55.5 ($CH_{[29]}$), 40.5 ($2CH_{[51, 53]}$), 39.3 ($CH_{[2[32]]}$), 38.6 ($CH_{[2[14]]}$), 34.4 ($2CH_{[3[50, 52]]}$), 31.7 ($CH_{[25]}$), 28.5 ($3CH_{[3[38-40]]}$), 23.5 ($CH_{[3[46]]}$, dia 1), 23.4 ($CH_{[3[46]]}$, dia 2), 20.4 ($2CH_{[3[54, 55]]}$), 19.3 ($CH_{[3[26]]}$), 18.1 ($CH_{[3[27]]}$), 17.3 ($CH_{[2[56]]}$). HRMS (ESI) : m/z calc for $C_{45}H_{64}N_5O_6^+$: 770.4851 $[M+H]^+$; found : 770.4852.

(2*S*)-1-(((2*S*)-3-methyl-1-oxo-1-(((2*S*)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate **A4L**. 1H NMR (300 MHz, MeOD) δ 7.41 (Broad AB, d, $J = 8.5$ Hz, $2H_{[2, 4]}$), 7.36 – 7.09 (m, $12H_{[1, 5, 16-20, 34-38]}$), 4.76 (overlapped signal : t, $J = 7.4$ Hz, $1H_{[12]}$ q, $J = 6.6$ Hz, $1H_{[7]}$), 4.30 (d, $J = 7.6$ Hz, $1H_{[22]}$), 4.20 (dd, $J = 8.4, 5.4$ Hz, $1H_{[29]}$), 3.24 – 3.10 (m, $2H_{[14, 32]}$), 3.03 (dd, $J = 13.7, 8.0$ Hz, $1H_{[14]}$), 2.93 (dd, $J = 14.3, 8.5$ Hz, $1H_{[32]}$), 2.03 (dq, $J = 12.4, J = 6.1$ Hz, $1H_{[25]}$), 1.62 – 1.00 (overlapped signals : m, $6H_{[44, 46, 49]}$, d, $J = 6.6$ Hz, $3H_{[39]}$, m, $9H_{[43, 45, 47]}$), 0.95 – 0.85 (Overlapped signals: d, $J = 6.6$ Hz, $3H_{[27]}$, d, $J = 6.6$ Hz, $3H_{[26]}$), 0.62 (s, $3H_{[48]}$). ^{13}C NMR (75 MHz, MeOD) δ 172.9 ($C_{[10]}$), 171.4 ($C_{[21]}$), 170.2 ($C_{[28]}$), 143.0 ($C_{[3]}$), 138.1 ($C_{[33]}$), 138.0 ($C_{[15]}$), 135.6 ($C_{[6]}$), 130.5 ($2CH_{[35, 37]}$), 130.4 ($2CH_{[17, 19]}$), 130.0 ($2CH_{[34, 38]}$), 129.5 ($2CH_{[16, 20]}$), 128.7 ($CH_{[36]}$), 128.1 ($2CH_{[1, 5]}$), 127.9 ($CH_{[18]}$), 121.1 ($2CH_{[2, 4]}$), 84.0 ($CH_{[7]}$), 60.9 ($2C_{[41, 42]}$), 60.4 ($CH_{[22]}$), 56.8 ($CH_{[29]}$), 55.5 ($CH_{[12]}$), 41.3 ($2CH_{[44, 46]}$), 39.3 ($CH_{[2[32]]}$), 38.8 ($CH_{[2[14]]}$), 34.7 ($2CH_{[3[43, 45]]}$), 32.1 ($CH_{[25]}$), 23.7 ($CH_{[3[39]]}$), 20.8 ($2CH_{[3[47, 48]]}$), 19.6 ($CH_{[3[27]]}$), 18.5 ($CH_{[3[26]]}$), 18.1 ($CH_{[2[49]]}$). ^{19}F NMR (376 MHz, MeOD) δ -76.83. HRMS (ESI) : m/z calc for cation $C_{40}H_{56}N_5O_4^+$: 670.4327 ; found : 670.4329. m/z calc for anion $C_2F_3O_2^-$: 112.9856 ; found : 112.9857.

(2*S*)-2-((*S*)-2-amino-3-phenylpropanamido)-3-methyl-N-((2*S*)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)butanamide **A5L**. 1H NMR (400 MHz, MeOD) δ 7.42 (broad AB d, $J = 8.5$ Hz, $2H_{[2, 4]}$), 7.32 – 7.12 (m, $12H_{[1, 5, 16-20, 34-38]}$), 4.78 – 4.67 (overlapped signals : m, $2H_{[12, 7]}$), 4.17 (d, $J = 7.2$ Hz, $1H_{[22]}$), 3.77 (m, $1H_{[29]}$), 3.19 (dd, $J = 13.6, 6.9$ Hz, $1H_{[32]}$), 3.07 (dd, $J = 13.8, 5.1$ Hz, $1H_{[32]}$), 3.01 (dd, $J = 13.7, 8.2$ Hz, $1H_{[14]}$), 2.81 (dd, $J = 13.8, 8.2$ Hz, $1H_{[14]}$), 2.01 (h, $J = 6.8$ Hz, $1H_{[25]}$), 1.69 – 0.98 (overlapped signals : m, $6H_{[44, 46, 49]}$, d, $J = 6.6$ Hz, $3H_{[39]}$, s, $3H_{[43]}$, s, $3H_{[45]}$, s, $3H_{[47]}$), 0.89 – 0.84 (overlapped signals : d, $J = 6.7$ Hz, $3H_{[27]}$, d, $J = 6.6$ Hz, $3H_{[26]}$), 0.62 (s, $3H_{[48]}$). ^{13}C NMR (101 MHz, MeOD- $CDCl_3$ (1 : 1 ; v : v)) δ 175.7 ($C_{[28]}$), 172.3 ($C_{[10]}$), 170.3 ($C_{[21]}$), 142.5 ($C_{[3]}$), 137.7 ($C_{[33]}$), 137.2 ($C_{[15]}$), 136.9 ($C_{[6]}$), 129.8 ($4CH_{[17, 19, 35, 37]}$), 129.2 ($2CH_{[34, 38]}$), 128.9 ($2CH_{[16, 20]}$), 127.5 ($2CH_{[1, 5]}$), 127.4 ($CH_{[36]}$), 127.3 ($2CH_{[18]}$), 120.5 ($2CH_{[2, 4]}$), 83.2 ($CH_{[7]}$), 60.3 ($2C_{[41, 42]}$), 59.3 ($CH_{[22]}$), 56.6 ($CH_{[29]}$), 55.6 ($CH_{[12]}$), 41.2 ($CH_{[2[32]]}$), 40.7 ($2CH_{[2[44, 46]]}$), 38.6 ($CH_{[2[14]]}$), 34.4 ($2CH_{[3[43, 45]]}$), 31.3 ($CH_{[25]}$), 23.7 ($CH_{[3[39]]}$), 20.7 ($2CH_{[3[47, 48]]}$), 19.4 ($CH_{[3[26]]}$), 18.2 ($CH_{[3[27]]}$), 17.6 ($CH_{[2[49]]}$). HRMS (ESI) : m/z calc for $C_{40}H_{56}N_5O_4^+$: 670.4327 $[M+H]^+$; found : 670.4329.

Benzyl 4-(((2*S*)-1-(((2*S*)-3-methyl-1-oxo-1-(((2*S*)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoate **A6L**. 1H NMR (400 MHz, MeOD) δ 7.45 (broad AB, d, $J = 8.5$ Hz, $2H_{[2, 4]}$), 7.36 – 7.27 (m, $5H_{[59-63]}$), 7.26 – 7.12 (m, $12H_{[1, 5, 16-20, 34-38]}$), 5.12 – 5.01 (m, $2H_{[57]}$), 4.79 – 4.64 (overlapped signals : m, $3H_{[7, 12, 29]}$), 4.15 (d, $J = 7.1$ Hz, $1H_{[22]}$), 3.20 (dd, $J = 13.7, 6.8$ Hz, $1H_{[14]}$), 3.11 (dd, $J = 14.1, 5.2$ Hz, $1H_{[32]}$), 2.98 (dd, $J = 13.7, 8.2$ Hz, $1H_{[14]}$), 2.86 (dd, $J = 14.1, 9.4$ Hz, $1H_{[32]}$), 2.67 – 2.37 (m, $4H_{[51, 53]}$), 2.00 (h, $J = 6.8$ Hz, $1H_{[25]}$), 1.70 – 0.93 (overlapped signals : $6H_{[44, 46, 49]}$, d, $J = 6.7$ Hz, $3H_{[39]}$, three broad s, $9H_{[45, 47, 48]}$), 0.83 (overlapped signals : 2d, $J = 6.8$ Hz, $6H_{[26, 27]}$), 0.62 (s, $3H_{[43]}$). ^{13}C NMR (101 MHz, $CDCl_3$ /

C₆D₆ : 19 : 1) δ 172.7 (C_[50]), 171.9 (C_[10]), 171.7 (2C_[21, 54]), 169.9 (C_[28]), 141.9 (C_[3], dia 1), 141.8 (C_[3], dia 2), 137.0 (C_[33]), 136.8 (C_[58]), 136.7 (C_[15]), 136.1 (C_[6]), 129.8 (2CH_[35, 37]), 129.6 (2CH_[17, 19]), 128.6 (2CH_[60, 62]), 128.4 (4CH_[16, 20, 34, 38]), 128.3 (CH_[61]), 128.2 (2CH_[59, 63]), 127.1 (CH_[36]), 127.0 (CH_[18]), 126.8 (2CH_[1, 5]), 120.3 (2CH_[2, 4]), 82.8 (CH_[7], dia 1), 82.7 (CH_[7], dia 2), 66.4 (CH_{2[57]}), 59.8 (C_[41]), 59.7 (C_[42]), 58.4 (CH_[22]), 55.3 (CH_[12]), 54.0 (CH_[29]), 40.5 (2CH_{2[44, 46]}), 40.0 (CH_{2[14]}), 39.2 (CH_{2[32]}), 34.5 (2CH_{3[43, 45]}), 32.1 (CH_[25]), 30.9 (CH_{2[53]}), 29.8 (CH_{2[51]}), 23.6 (CH_{3[39]}, dia 1), 23.4 (CH_{3[39]}, dia 2), 20.5 (2CH_{3[47, 48]}), 19.1 (CH_{3[26]}), 18.9 (CH_{3[27]}), 17.4 (CH_{2[49]}). HRMS (ESI) : m/z calc for C₅₁H₆₆N₅O₇⁺ : 860.4957 [M+H]⁺ ; found : 860.4930.

4-(((2S)-1-(((2S)-3-methyl-1-oxo-1-(((2S)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoic acid **A7L**. ¹H NMR (400 MHz, MeOD) δ 7.52 – 7.41 (m, 2H_[2, 4]), 7.28 – 7.05 (overlapped signals : m, 12H_[1, 5, 16-20, 34-38]), 4.79 – 4.59 (overlapped signals : m, 3H_[7, 14, 32]), 4.12 (d, J = 7.3 Hz, 1H_[22]), 3.22 (dd, J = 13.7, 6.6 Hz, 1H_[14]), 3.13 (dd, J = 14.1, 5.1 Hz, 1H_[32]), 2.99 (dd, J = 13.7, 8.4 Hz, 1H_[14]), 2.88 (dd, J = 14.1, 9.4 Hz, 1H_[32]), 2.63 – 2.31 (m, 4H_[51, 53]), 2.00 (h, J = 6.8 Hz, 1H_[25]), 1.68 – 0.90 (overlapped signals : m, 6H_[44, 46, 49], d, J = 6.8 Hz, 3H_[39], 3broads s, 9H_[43, 47, 48]), 0.84 (d, J = 6.7 Hz, 3H_[26]), 0.81 (d, J = 6.8 Hz, 3H_[27]), 0.62 (s, 3H_[45]). ¹³C NMR (101 MHz, MeOD-CDCl₃ (1 : 1 ; v : v)) δ 175.7 (C_[54]), 174.0 (C_[50]), 173.0 (C_[10]), 172.2 (C_[21]), 170.2 (C_[28]), 142.3 (C_[3]), 137.3 (C_[33]), 137.2 (C_[15]), 136.9 (C_[6]), 129.5 (2CH_[35, 37]), 129.5 (2CH_[17, 19]), 129.0 (4CH_[16, 20, 34, 38]), 127.4 (2CH_[1, 5]), 127.3 (CH_[36]), 127.2 (CH_[18]), 120.5 (2CH_[2, 4]), 83.2 (CH_[7]), 60.4 (2C_[41, 42]), 60.3 (CH_[22]), 55.7 (CH_[12]), 55.4 (CH_[29]), 40.6 (2CH_{2[44, 46]}), 38.2 (CH_{2[14]}), 37.7 (CH_{2[32]}), 34.3 (2CH_{3[43, 45]}), 31.0 (CH_[53]), 30.7 (CH_{2[25]}), 29.8 (CH_{2[51]}), 23.7 (CH_{3[39]}), 20.6 (2CH_{3[47, 48]}), 19.2 (CH_{3[26]}), 18.3 (CH_{3[27]}), 17.5 (CH_{2[49]}). HRMS (ESI) : m/z calc for C₄₄H₆₀N₅O₇⁺ : 770.4487 [M+H]⁺ ; found : 770.4481.

tert-butyl ((2R)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)carbamate **A1D**. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (s, 1H_[9]), 7.33 (Broad AB, d, J = 8.3 Hz, 2H_[2, 4]), 7.29 – 7.19 (m, 7H_[1, 5, 15-19]), 5.44 (m, 1H_[20]), 4.73 (q, J = 6.6 Hz, 1H_[7]), 4.53 (s, 1H_[12]), 3.21 – 3.01 (m, 2H_[13]), 1.59 – 1.34 (overlapped signals : m, 6H_[32, 35, 38], d, J = 6.6 Hz, 3H_[28], s, 9H_[25-27]), 1.29 (s, 3H_[33]), 1.15 (s, 2H_[36]), 1.03 (s, 3H_[34]), 0.65 (s, 3H_[37]). ¹³C NMR (101 MHz, CDCl₃) δ 169.9 (C_[10]), 155.9 (C_[21]), 142.1 (C_[3]), 136.9 (C_[14]), 136.1 (C_[6]), 129.4 (2CH_[16, 18]), 128.8 (2CH_[1, 5]), 127.2 (2CH_[15, 19]), 127.0 (CH_[17]), 119.9 (2CH_[2, 4]), 82.7 (CH_[7]), 80.5 (C_[24]), 59.8 (C_[30, 31]), 56.8 (CH_[12]), 40.4 (2CH_{2[32, 35]}), 38.7 (CH_{2[13]}), 34.4 (2CH_{3[33, 36]}), 28.4 (3CH_{3[25-27]}), 23.5 (CH_{3[28]}), 20.4 (2CH_{3[34, 37]}), 17.3 (CH_{2[38]}). Triplet at 127.9 ppm is solvent C₆D₆. HRMS (ESI) : m/z calc for C₃₁H₄₆N₃O₄⁺ : 524.3483 [M+H]⁺ ; found: 524.3481.

(2R)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-aminium trifluoroacetate **A2D**. By using GP3 with **A1D** (1.50 g, 2.866 mmol, 1.0 eq) afforded **A2D** as a white solid (1.33 g, yield: 86 %). The product was used in coupling reaction without characterization.

tert-butyl ((2R)-1-(((2R)-3-methyl-1-oxo-1-(((2R)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-yl)carbamate **A3D**. ¹H NMR (400 MHz, MeOD) δ 7.42 (Broad, AB, d, J = 8.6 Hz, 2H_[2, 4]), 7.30 – 7.12 (m, 12H_[1, 5, 16-20, 41-45]), 4.80 (overlapped signal : water and q, 1H_[7]), 4.69 (t, J = 7.5 Hz, 1H_[12]), 4.42 (dd, J = 10.0, 4.6 Hz, 1H_[29]), 4.25 (d, J = 7.0 Hz, 1H_[22]), 3.18 (dd, J = 13.7, 7.2 Hz, 1H_[14]), 3.06 (dd, J = 13.9, 4.9 Hz, 1H_[32]), 2.99 (dd, J = 13.6, 7.9 Hz, 1H_[14]), 2.79 (dd, J = 14.2, 10.0 Hz, 1H_[32]), 2.02 (dq, J = 6.8 Hz, 1H_[25]), 1.51 – 1.00 (overlapped signals : m, 6H_[51, 53, 56], d, J = 6.7 Hz, 3H_[46], s, 9H_[38-40] and s, 3H_[52], s, 3H_[50], s, 3H_[54]), 0.89 – 0.81 (overlapped signals : 2d, J = 6.9 Hz, 6H_[26, 27]), 0.61 (s, 3H_[55]). ¹³C NMR (101 MHz, CDCl₃) δ 172.4 (C_[10]), 171.9 (C_[21]), 169.7 (C_[28]), 156.0 (C_[34]), 142.0 (C_[3]), 137.0 (C_[33]), 136.6 (C_[15]), 136.5 (C_[6]), 129.5 (2CH_[42, 44]), 129.3 (2CH_[17, 19]), 128.6 (2CH_[41, 45]), 128.5 (2CH_[16, 20]), 127.1 (CH_[43]), 127.0 (CH_[18]), 126.9 (CH_[1]), 126.8 (CH_[5]), 120.4 (2CH_[2, 4]), 82.8 (CH_[7]), 80.0 (C_[37]), 59.8 (2C_[48, 49]), 58.5 (CH_[22]), 55.7 (CH_[12]), 55.4 (CH_[29]), 40.5 (2CH_{2[51, 53]}), 39.3 (CH_{2[32]}), 38.5 (CH_{2[14]}), 34.4 (2CH_{3[50, 52]}), 31.6 (CH_[25]), 28.5 (3CH_{3[38-40]}), 23.5 (CH_{3[46]}), 20.4 (2CH_{3[54, 55]}), 19.3 (CH_[26]), 18.1 (CH_[27]), 17.3 (CH_{2[56]}). HRMS (ESI) : m/z calc for C₄₅H₆₄N₅O₆⁺ : 770.4851 [M+H]⁺ ; found : 770.4854

(2R)-1-(((2R)-3-methyl-1-oxo-1-(((2R)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)amino)butan-2-yl)amino)-1-oxo-3-phenylpropan-2-aminium trifluoroacetate **A4D**. ¹H NMR (400 MHz, MeOD) δ 7.48 – 7.41 (m, 2H_[2, 4]), 7.34 – 7.14 (m, 12H_[1, 5, 16-20, 34-38]), 4.99 – 4.89 (m, 1H_[7]), 4.74 (dd, J = 7.9, 7.0 Hz, 1H_[112]), 4.25 (d, J = 7.5 Hz, 1H_[22]), 4.16 (dd, J = 8.5, 5.4 Hz, 1H_[29]), 3.18 (ddd, J = 14.5, 6.2, 4.2 Hz, 2H_[32]), 3.04 (dd, J = 13.7, 7.9 Hz, 1H_[14]), 2.95 (dd, J = 14.3, 8.6 Hz, 1H_[14]), 2.05 (dq, J = 13.1, 6.5 Hz, 1H_[25]), 1.77 – 1.45 (overlapped signals : m, 6H_[44, 46, 49], d, J = 6.6 Hz, 3H_[39]), 1.38 (s, 3H_[43]), 1.29 (s, 3H_[45]), 1.13 (s, 3H_[47]), 0.98 – 0.92 (overlapped signals : d, J = 6.7 Hz, 3H_[27], d, J = 6.7 Hz, 3H_[26]), 0.71 (s, 3H_[48]). ¹³C NMR (75 MHz, MeOD) δ 172.8 (C_[10]), 171.5 (C_[28]), 169.7 (C_[21]), 141.3 (C_[3]), 138.6 (C_[33]), 138.0 (C_[15]), 135.3 (C_[6]), 130.5 (2CH_[35, 37]), 130.4 (2CH_[17, 19]), 130.0 (2CH_[34, 38]), 129.5 (2CH_[16, 20]), 128.7 (CH_[36]), 128.2 (2CH_[1, 5]), 127.8 (CH_[18]), 121.2 (2CH_[2, 4]), 85.1 (CH_[7]), 64.2 (2C_[41, 42]), 60.4 (CH_[22]), 56.8

(CH_{29}), 55.3 (CH_{12}), 40.3 (2CH_{2{44, 46}}), 39.7 (CH_{2{32}}), 38.6 (CH_{2{14}}), 33.1 (2CH_{3{43, 45}}), 32.1 (CH_{25}), 23.6 (CH_{3{39}}), 20.8 (2CH_{3{47, 48}}), 19.7 (CH_{3{27}}), 18.9 (CH_{3{26}}), 17.5 (CH_{2{49}}). ¹⁹F NMR (376 MHz, MeOD) δ -76.96. HRMS (ESI) : m/z calc for cation C₄₀H₅₆N₅O₄⁺ : 670.4327 ; found : 670.4330. m/z calc for anion C₂F₃O₂⁻ : 112.9856 ; found : 112.9856.

(2R)-2-((R)-2-amino-3-phenylpropanamido)-3-methyl-N-((2R)-1-oxo-3-phenyl-1-((4-(1-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethyl)phenyl)amino)propan-2-yl)butanamide **A5D**. ¹H NMR (400 MHz, MeOD) δ 7.43 (broad AB, d, J = 8.5 Hz, 2H_{2, 4}), 7.32 – 7.14 (m, 12H_{1, 5, 16-20, 34-38}), 4.78 – 4.68 (overlapped signals : m, 2H_{12, 71}), 4.16 (d, J = 7.1 Hz, 1H_{22}), 3.66 (dd, J = 8.0, 5.1 Hz, 1H_{29}), 3.20 (dd, J = 13.7, 6.8 Hz, 1H_{14}), 3.09 – 2.94 (m, 2H_{32}), 2.77 (dd, J = 13.6, 8.1 Hz, 1H_{14}), 2.00 (h, J = 6.8 Hz, 1H_{25}), 1.62 – 0.93 (overlapped signals : m 6H_{44, 46, 49}, d, J = 6.6 Hz, 3H_{39}, three Broad s, 9H_{43, 47, 48}), 0.85 (overlapped signals : 2d, J = 6.8 Hz, 6H_{26, 27}), 0.62 (s, 3H_{45}). ¹³C NMR (101 MHz, MeOD) δ 176.7 (C_{28}), 173.3 (C_{10}), 171.4 (C_{21}), 143.0 (C_{3}), 138.7 (C_{33}), 138.2 (C_{15}), 138.1 (C_{6}), 130.5 (2CH_{35, 37}), 130.4 (2CH_{17, 19}), 129.6 (2CH_{34, 38}), 129.5 (2CH_{16, 20}), 128.1 (2CH_{1, 5}), 127.8 (CH_{36}), 127.8 (CH_{18}), 121.2 (2CH_{2, 4}), 84.0 (CH_{71}), 60.9 (2C_{41, 42}), 60.0 (CH_{22}), 57.3 (CH_{29}), 56.7 (CH_{12}), 42.1 (CH_{2{32}}), 41.4 (2CH_{2{44, 46}}), 39.1 (CH_{2{14}}), 34.8 (2CH_{3{43, 45}}), 32.1 (CH_{25}), 23.7 (CH_{3{39}}), 20.8 (2CH_{3{47, 48}}), 19.7 (CH_{3{26}}), 18.7 (CH_{3{27}}), 18.1 (CH_{2{49}}). HRMS (ESI) : m/z calc for C₄₀H₅₆N₅O₄⁺ : 670.4327 [M+H]⁺ ; found : 670.4330.

4-(Benzyloxy)-4-oxobutanoic acid. ¹H NMR (400 MHz, MeOD) δ 7.51 – 7.15 (m, 5H_{3-7}), 5.13 (s, 2H_{11}), 2.75 – 2.46 (m, 4H_{10, 12}).