Supporting information

for

Synthesis and functional evaluation of proteinogenic amino acid-derived synthetic cannabinoid

receptor agonists related to MPP-5F-PICA, MMB-5F-PICA, and MDMB-5F-PICA

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Figure S1. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)glycinate (GLY-5F-PICA, **16**).
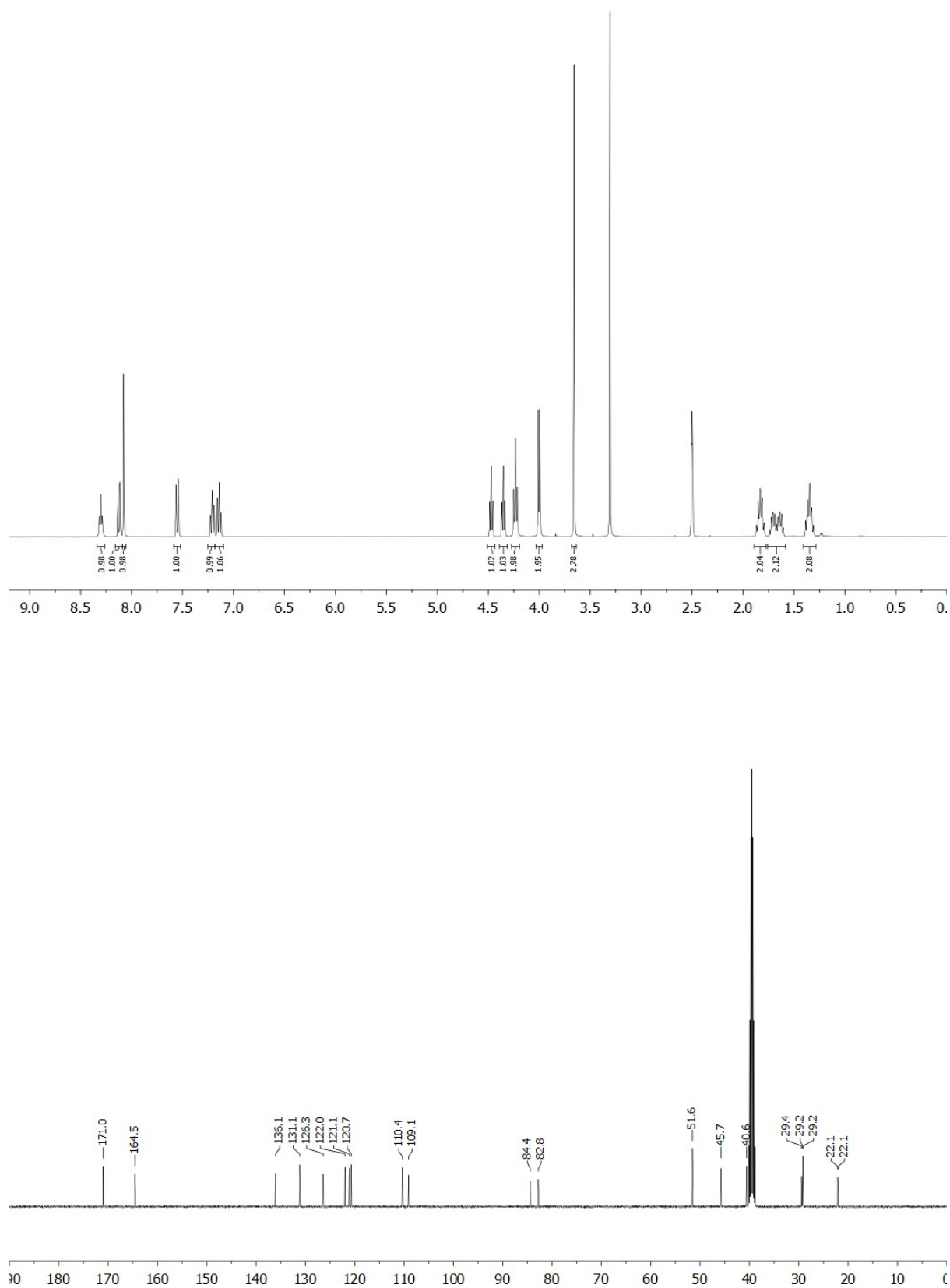
Figure S2. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-alaninate (*S*-ALA-5F-PICA, **17**).
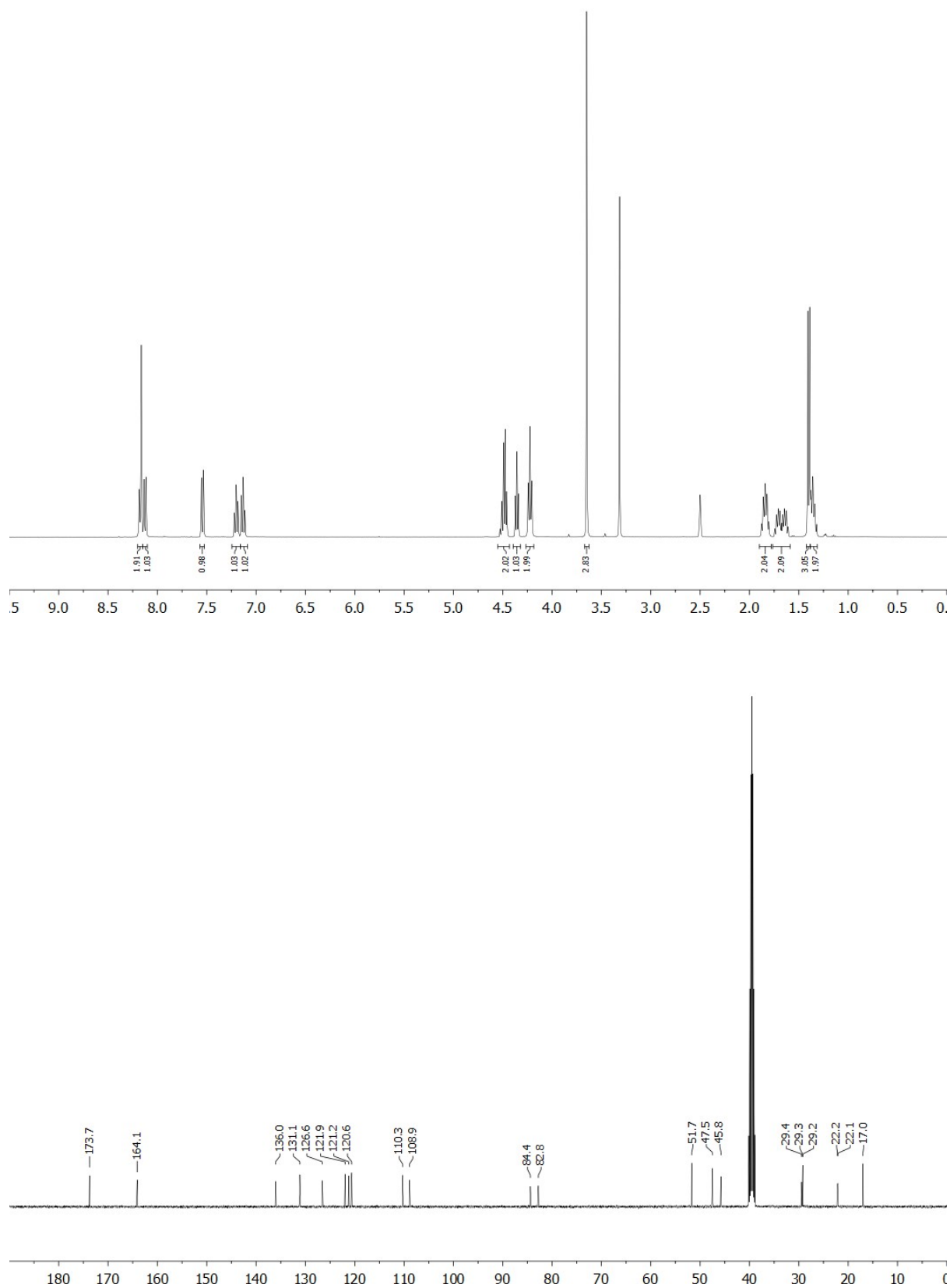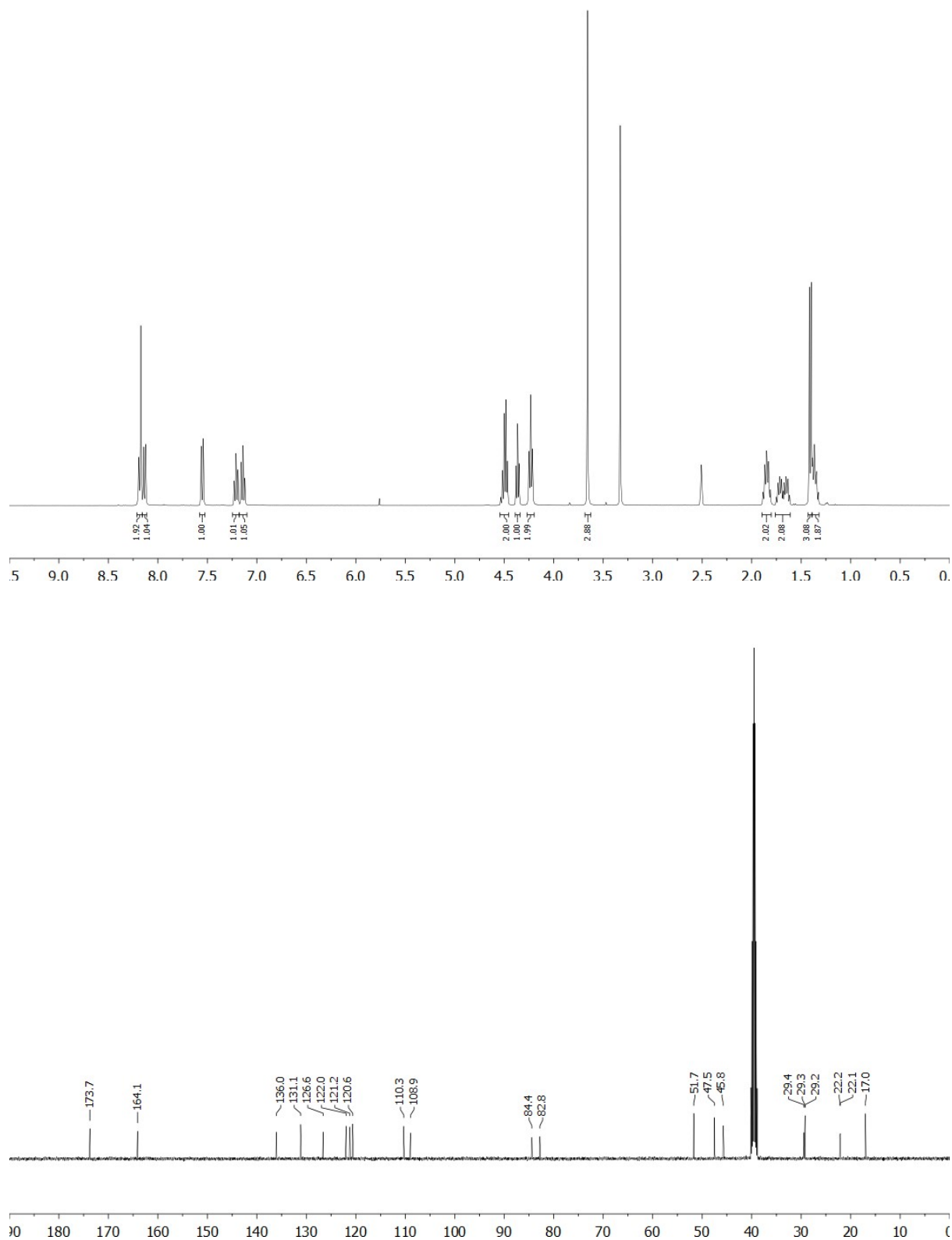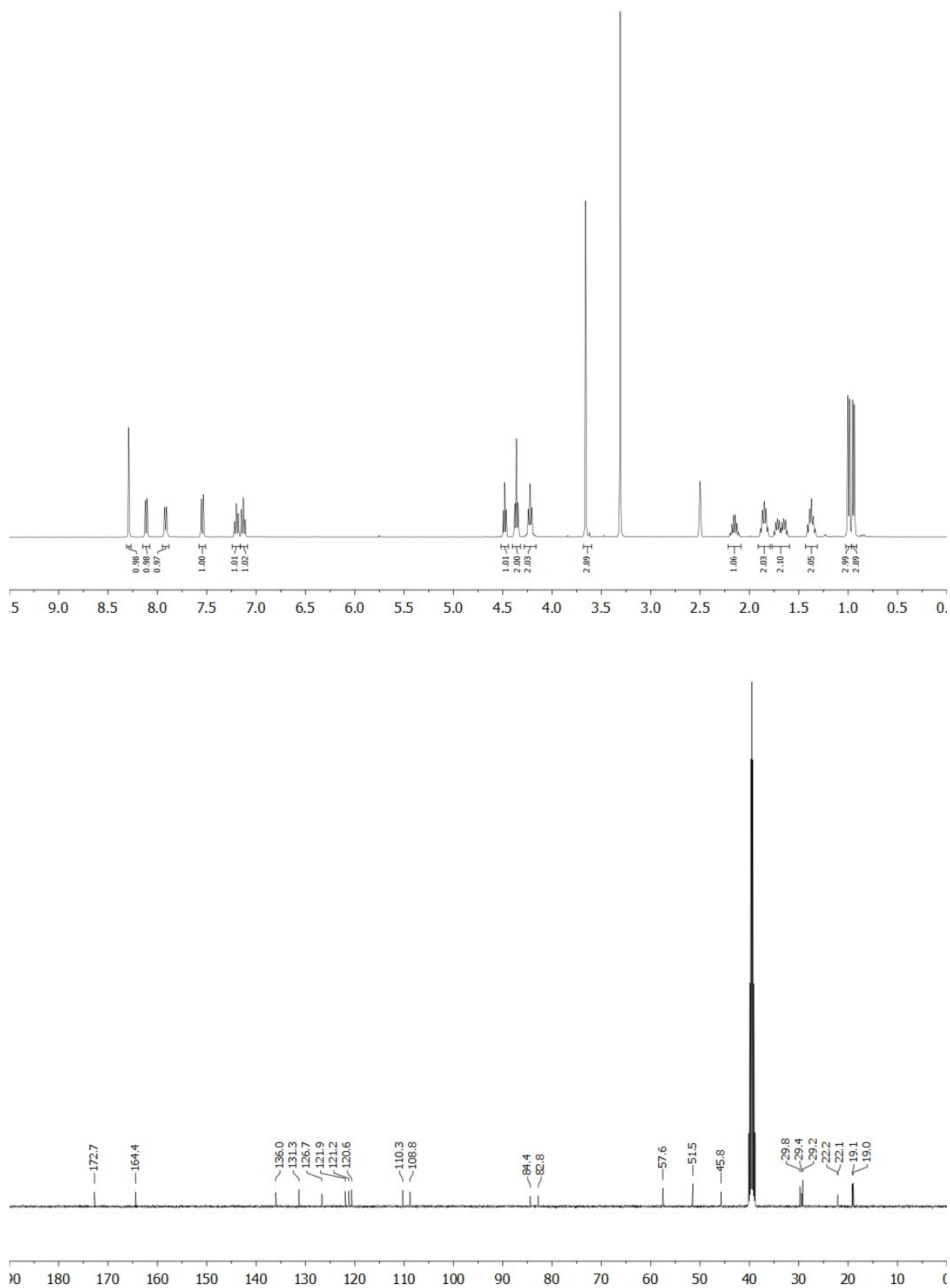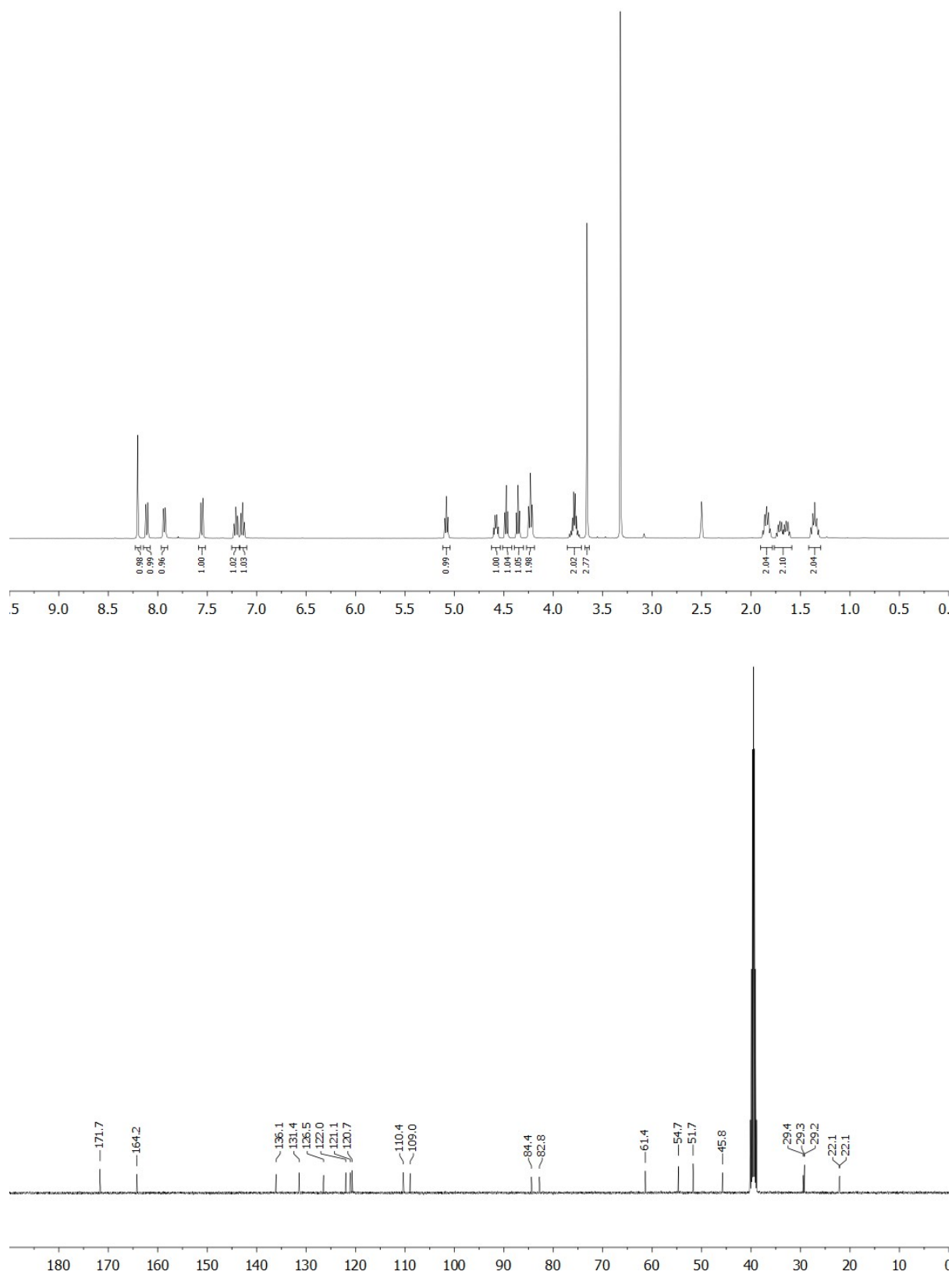
Figure S3. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1H-indole-3-carbonyl)-R-alaninate (R-ALA-5F-PICA, **18**).

Figure S4. ¹H and ¹³C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-valinate (*R*-MMB-5F-PICA, **20**).

Figure S5. ¹H and ¹³C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-serinate (*S*-SER-5F-PICA, **21**).
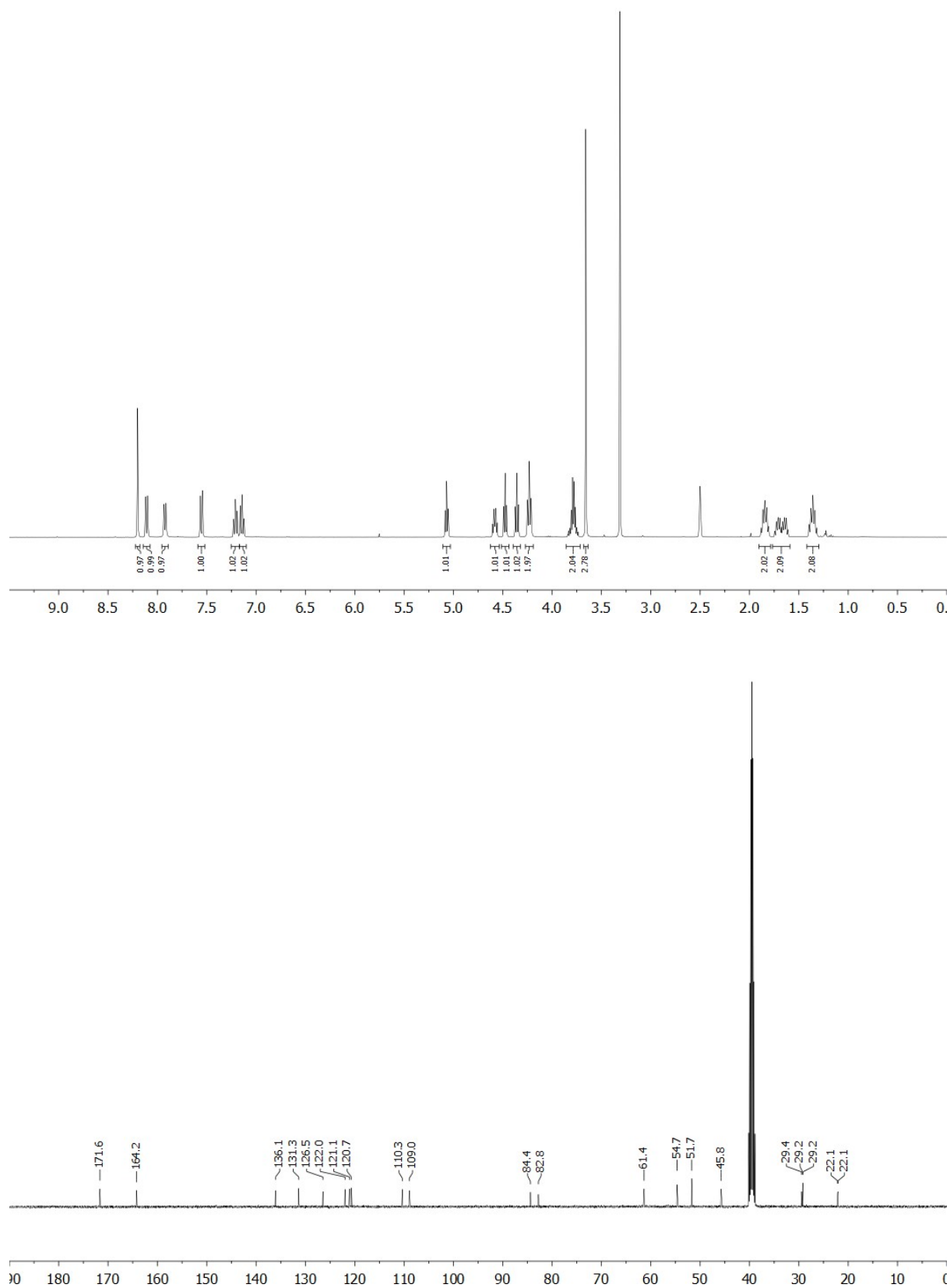
Figure S6. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1H-indole-3-carbonyl)-R-serinate (R-SER-5F-PICA, **22**).

Figure S7. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-2*S*,3*R*-threoninate (2*S*,3*R*-THR-5F-PICA, **23**).
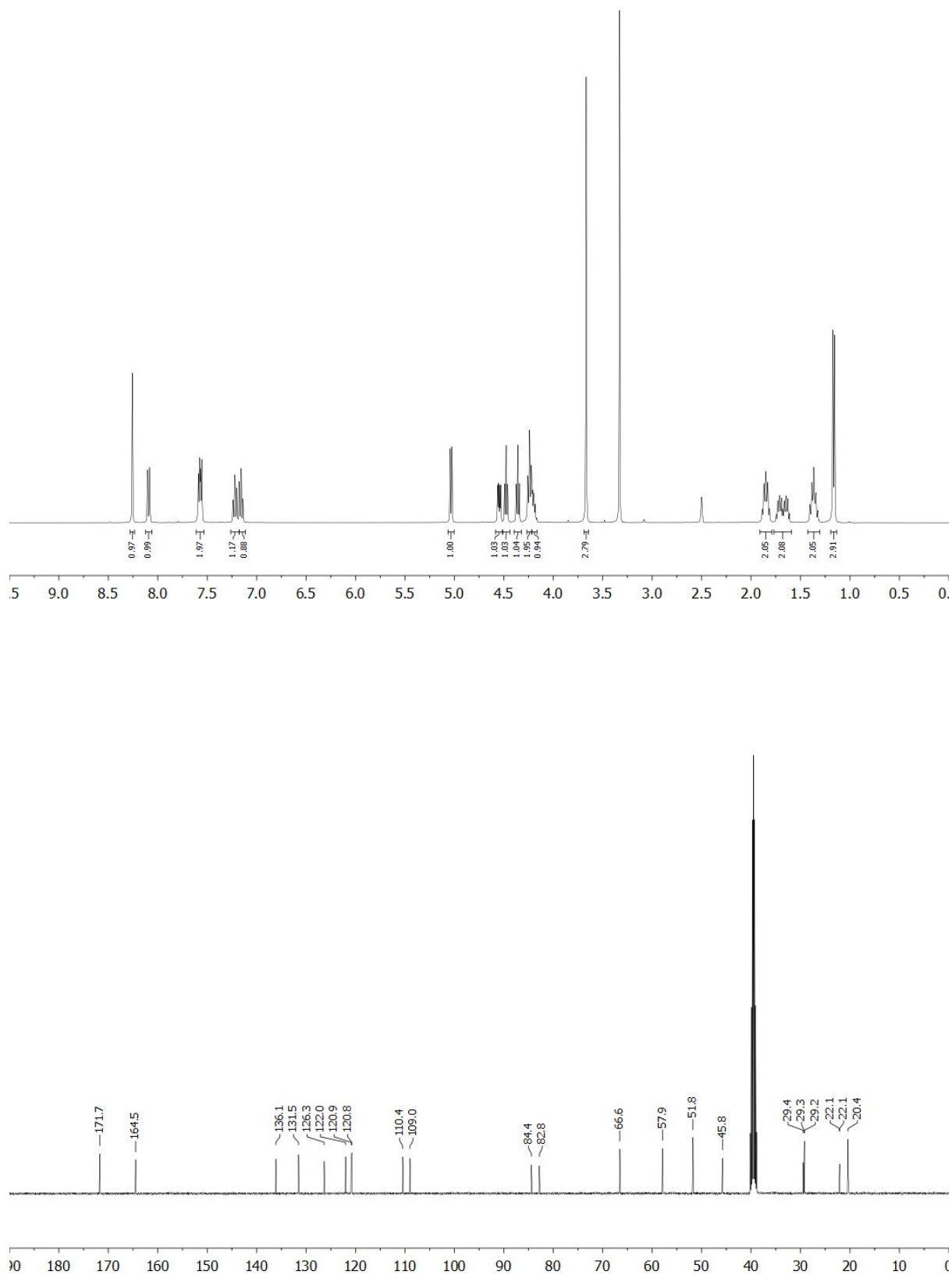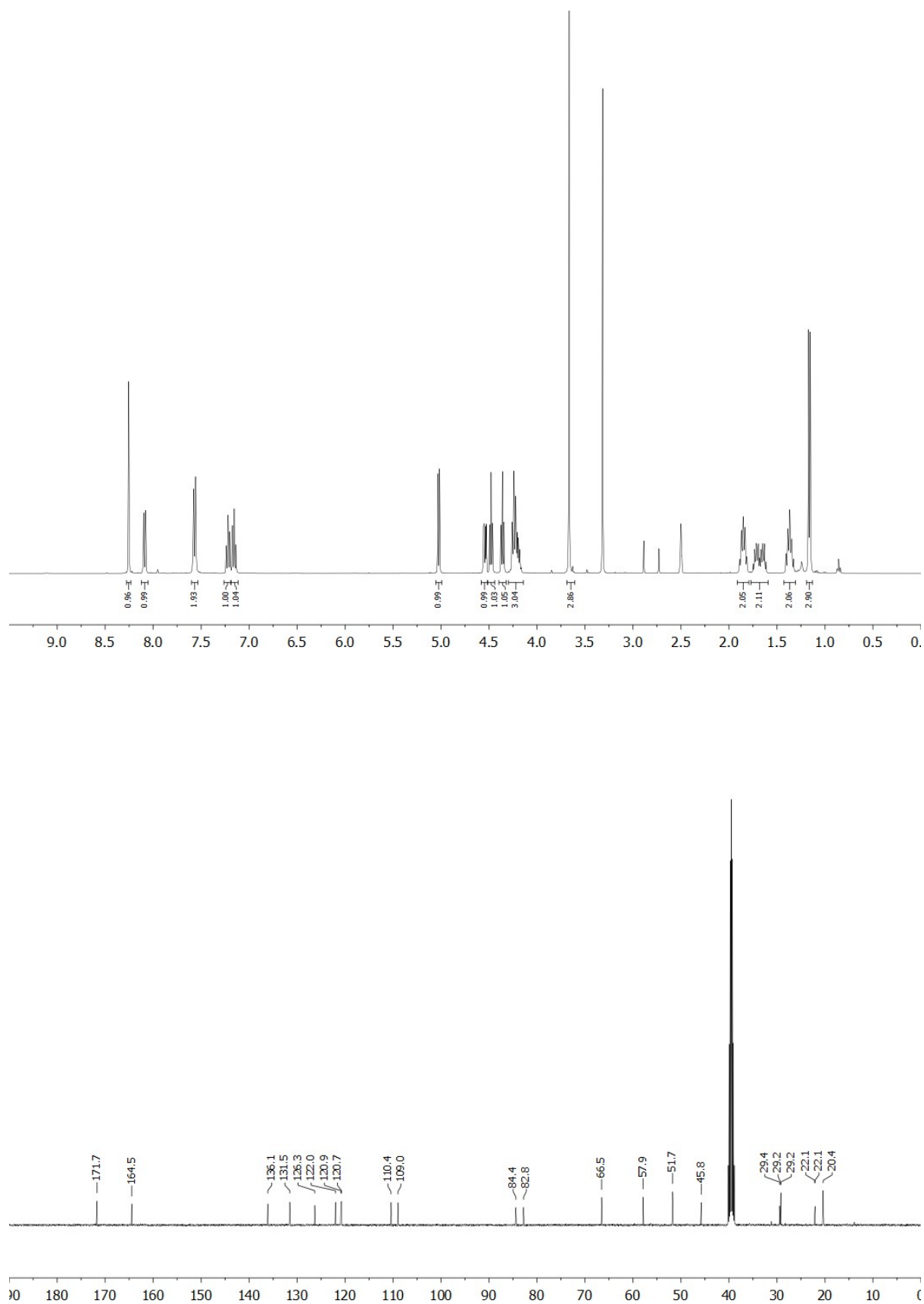
Figure S8. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1H-indole-3-carbonyl)-2R,3S-threoninate (2R,3S-THR-5F-PICA, **24**).

Figure S9. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-prolinate (*S*-PRO-5F-PICA, **25**).
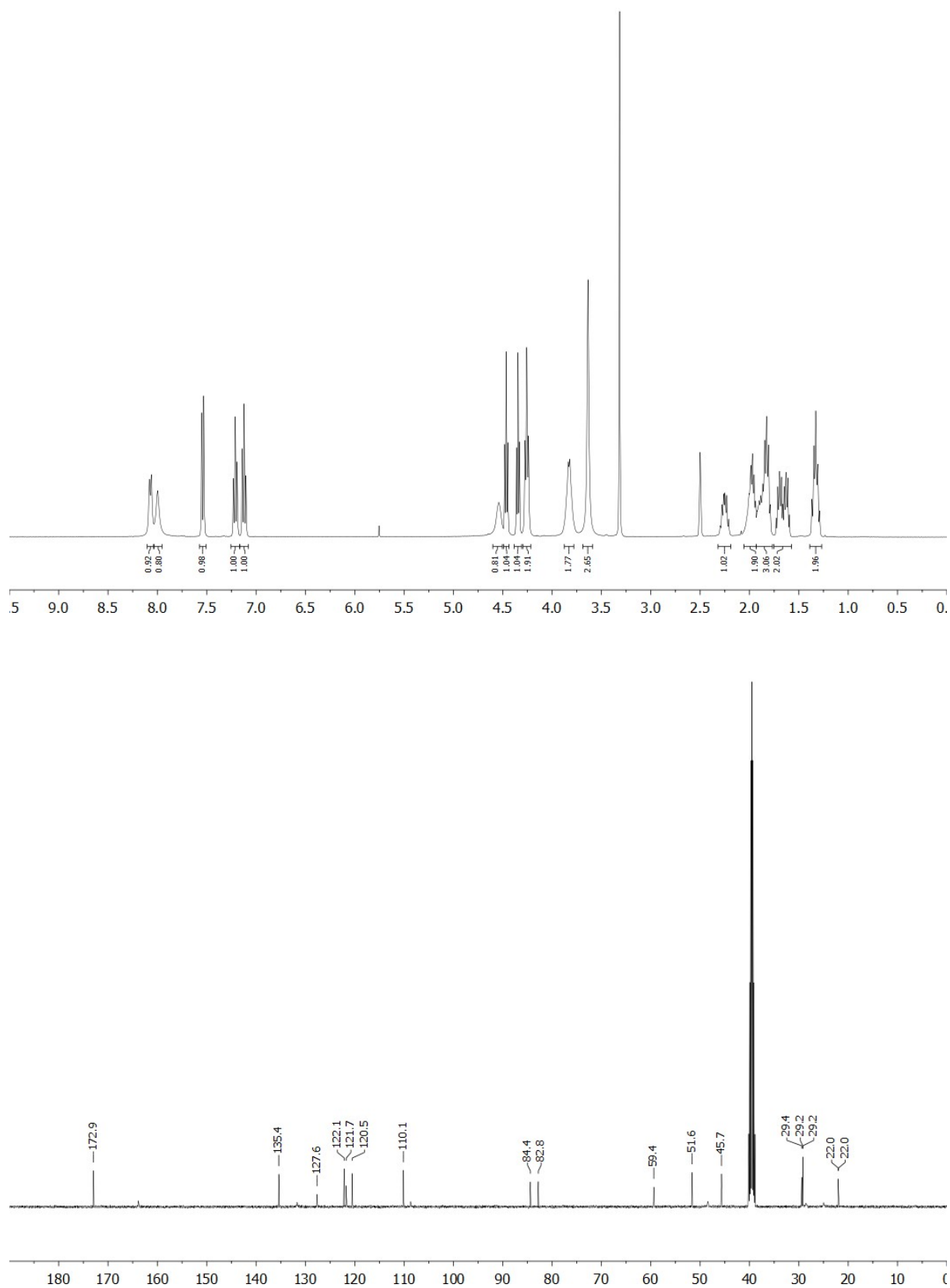
Figure S10. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-prolinate (*R*-PRO-5F-PICA, **26**).
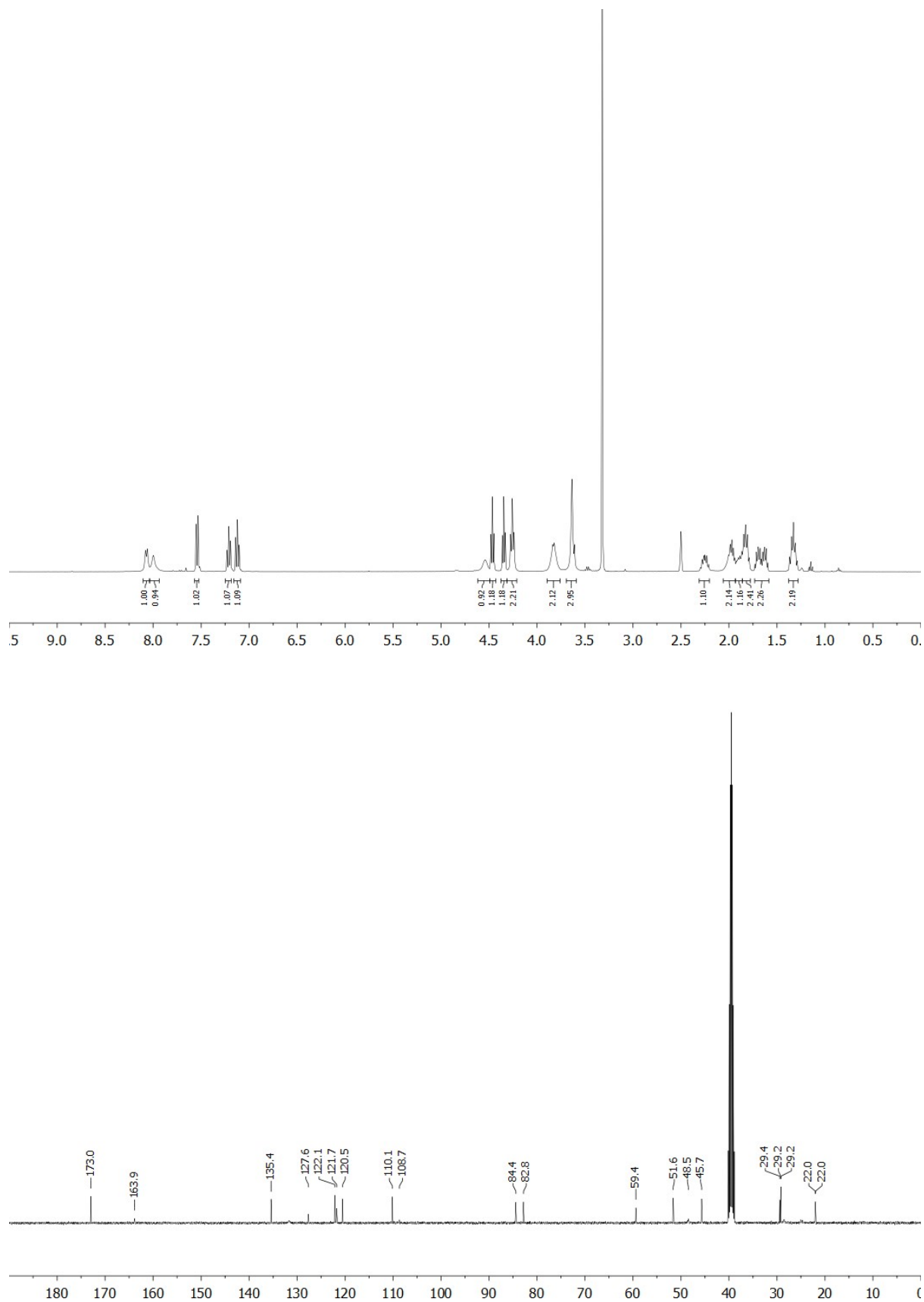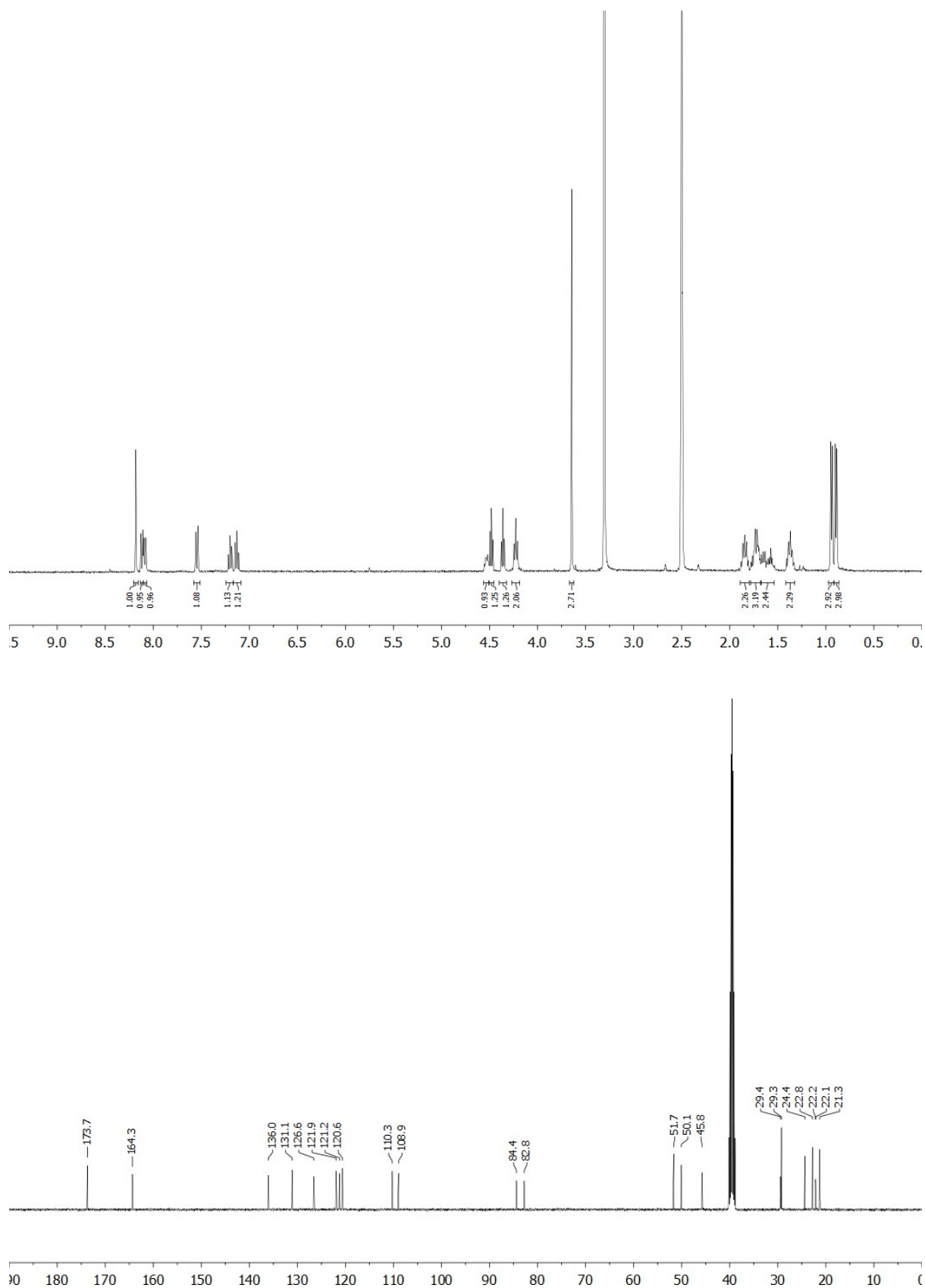
Figure S11. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1H-indole-3-carbonyl)-S-leucinate (S-LEU-5F-PICA, **27**).

Figure S12. ¹H and ¹³C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-leucinate (*R*-LEU-5F-PICA, **28**).
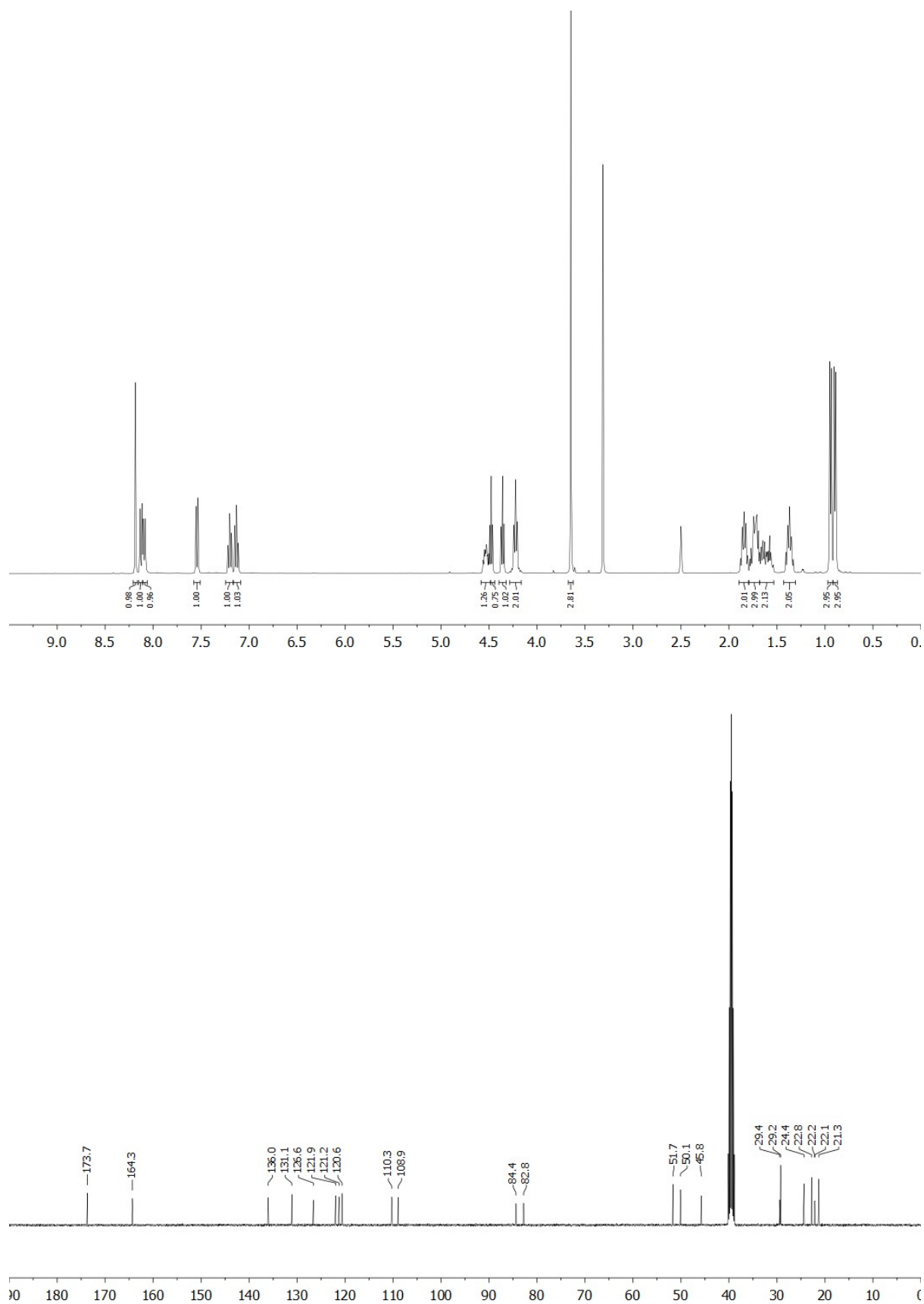
Figure S13. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-isoleucinate (*S*-ILE-5F-PICA, **29**).
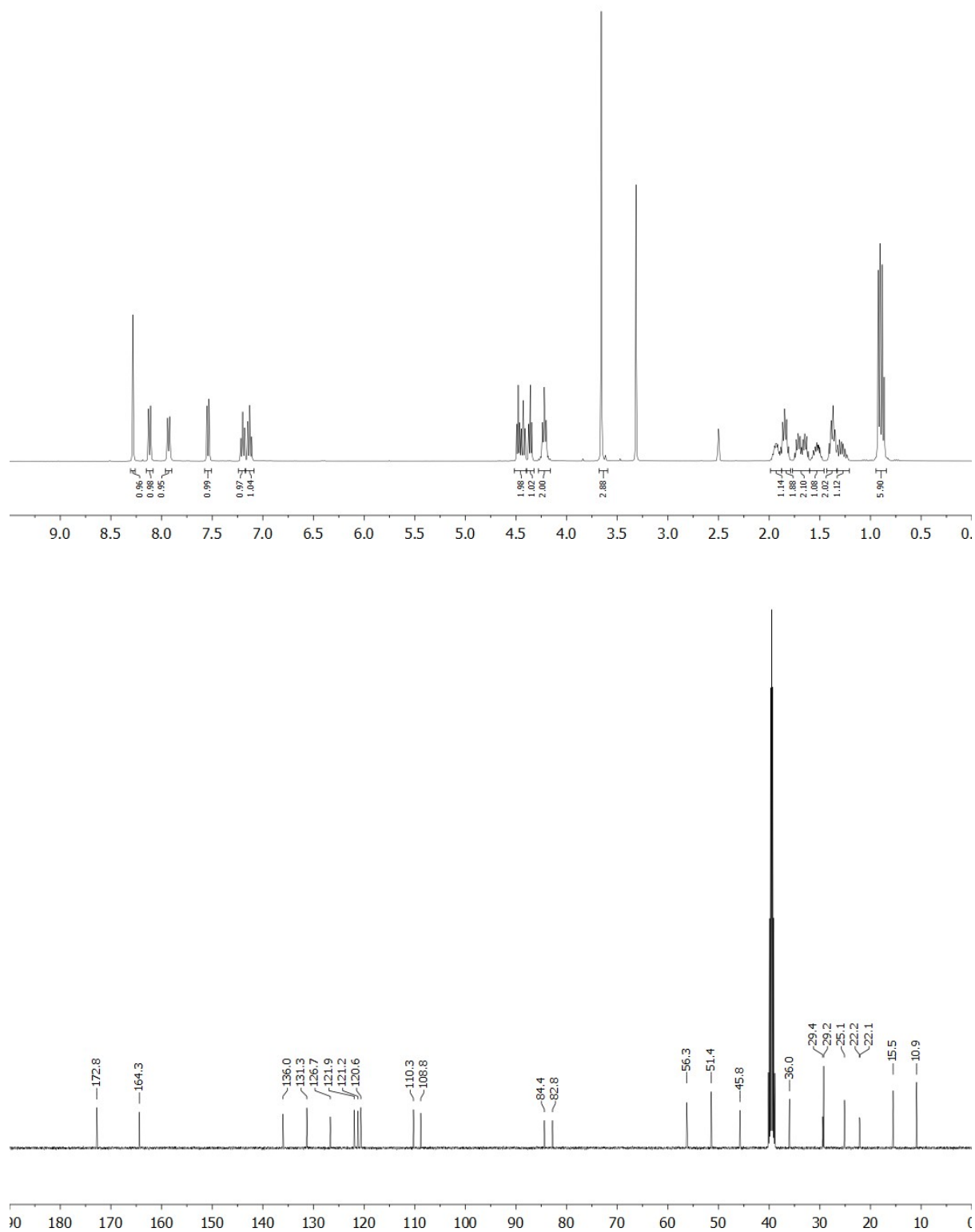
Figure S14. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-isoleucinate (*R*-ILE-5F-PICA, **30**).
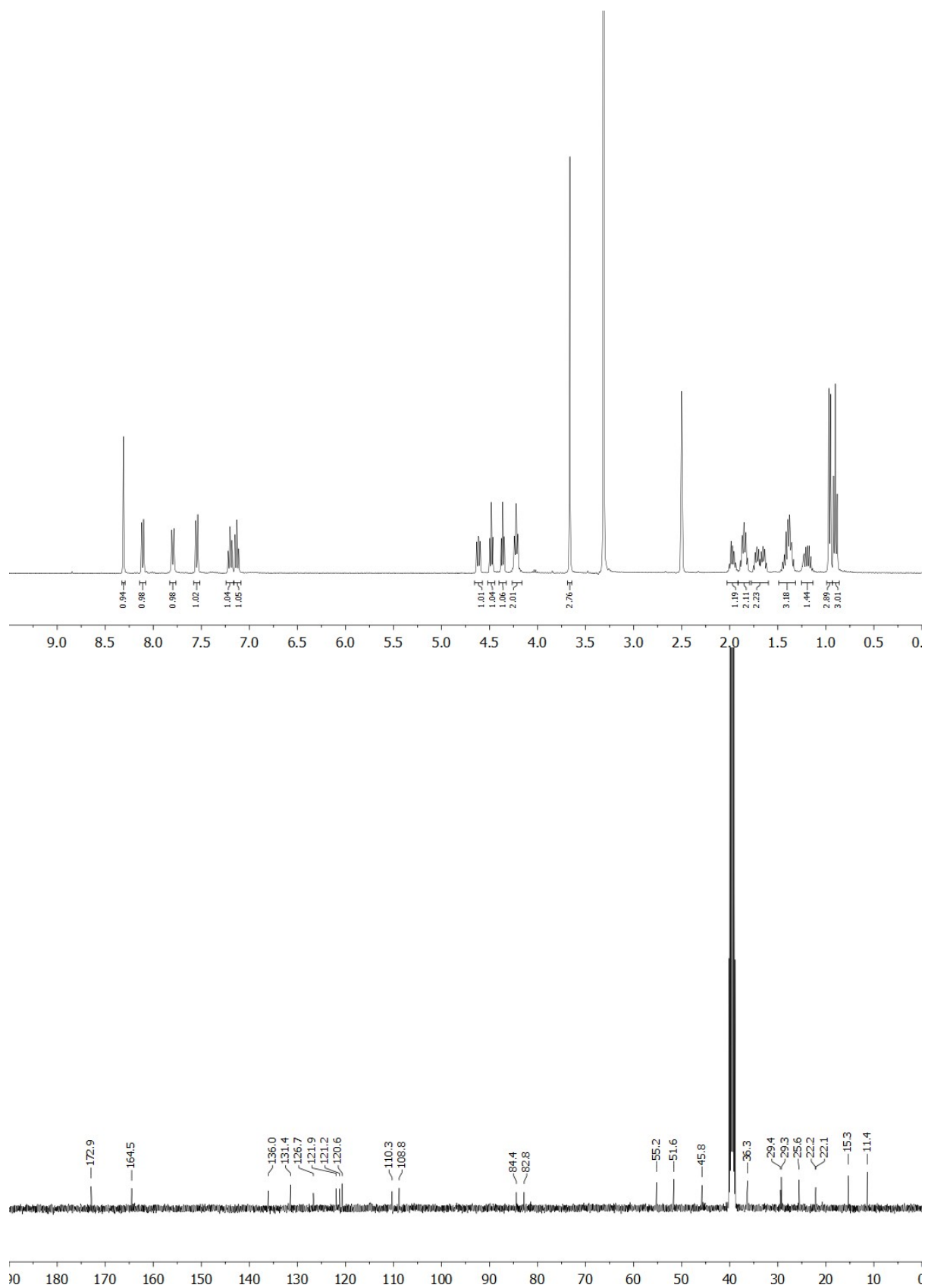
Figure S15. ¹H and ¹³C NMR spectra for methyl (*R*)-2-(1-(5-fluoropentyl)-1*H*-indole-3-carboxamido)-3,3-dimethylbutanoate (*R*-MDMB-5F-PICA, **32**).
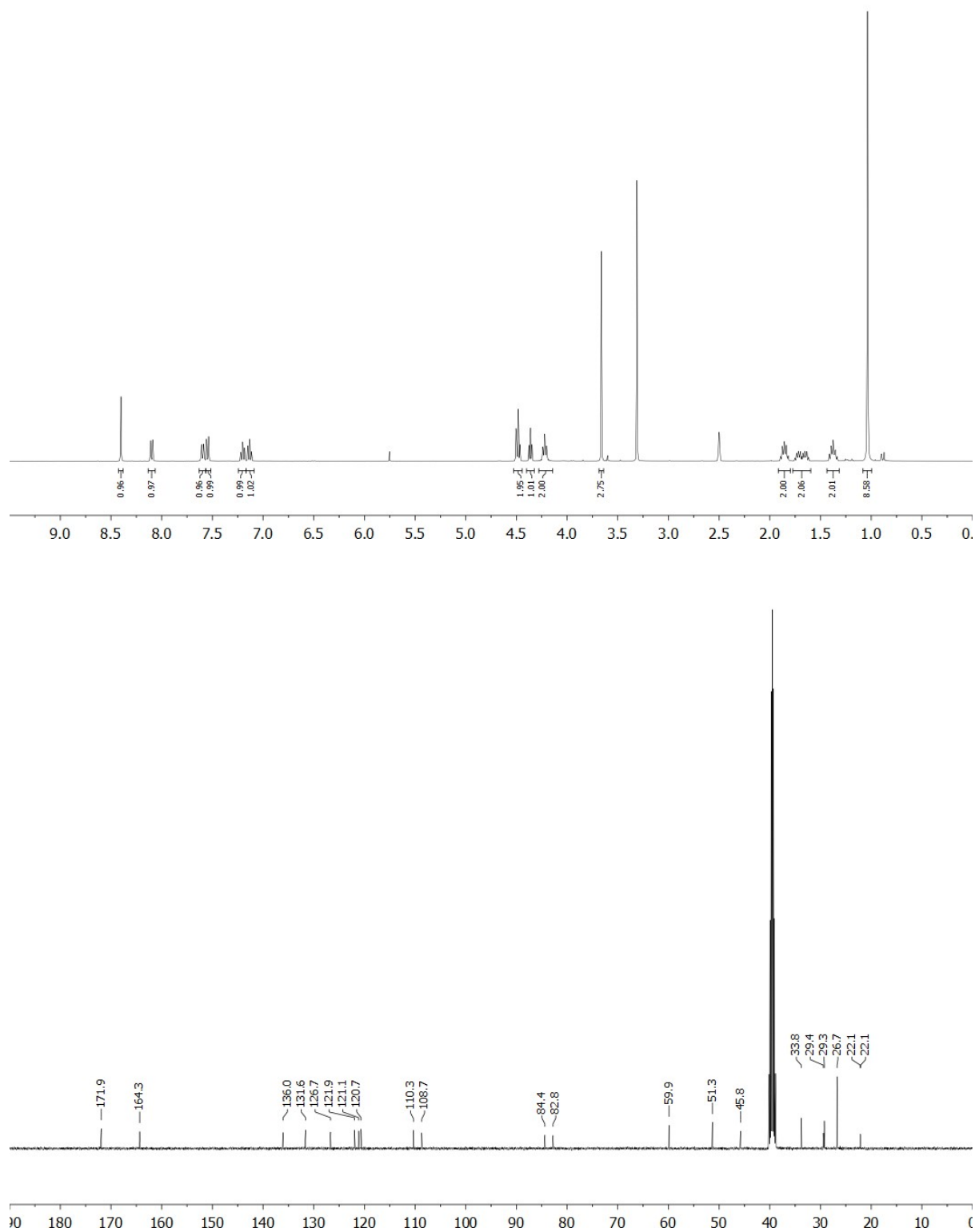
Figure S16. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1H-indole-3-carbonyl)-R-phenylalaninate (R-MPP-5F-PICA, **34**).
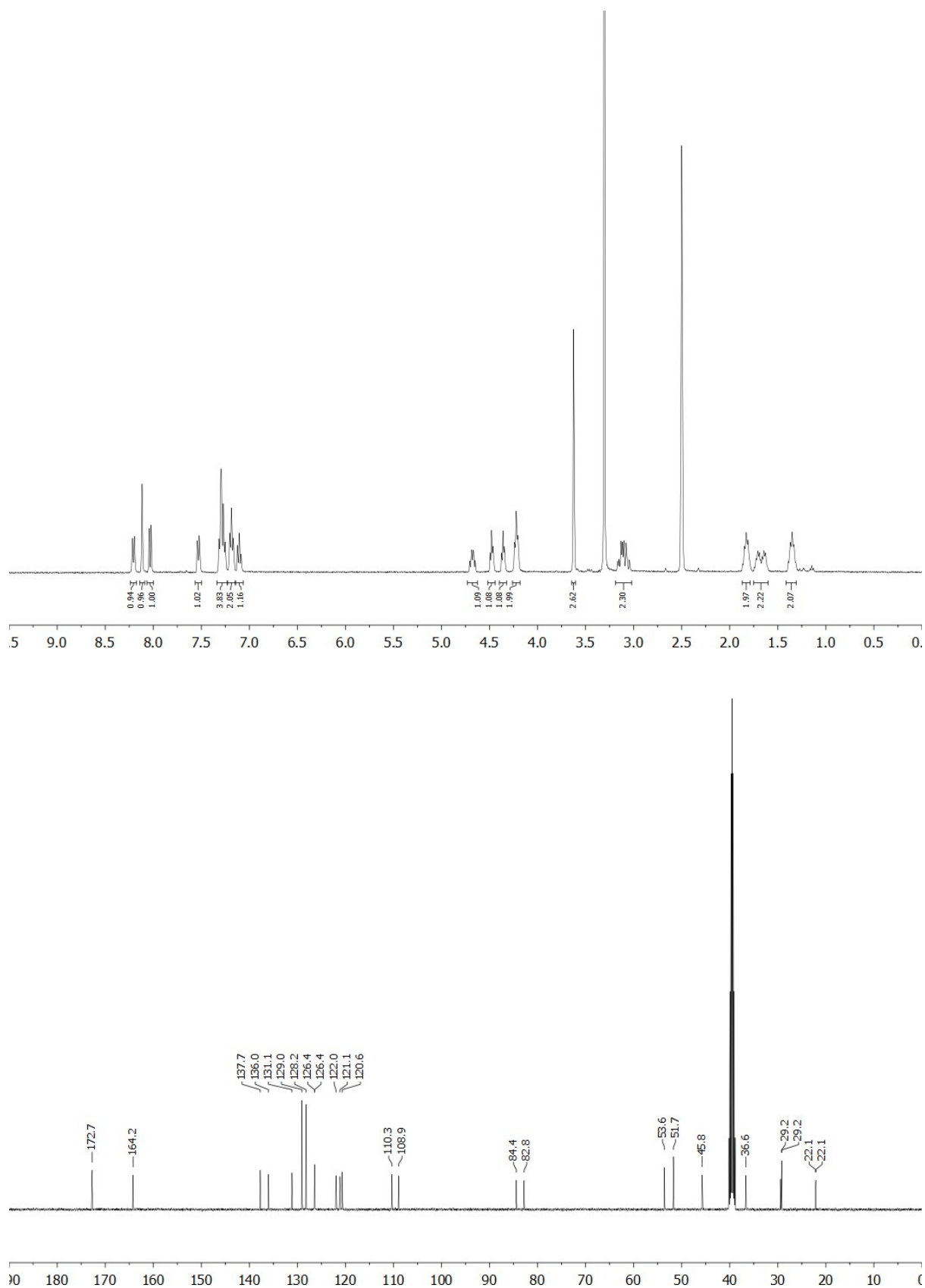
Figure S17. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-tyrosinate (*S*-TYR-5F-PICA, **35**).
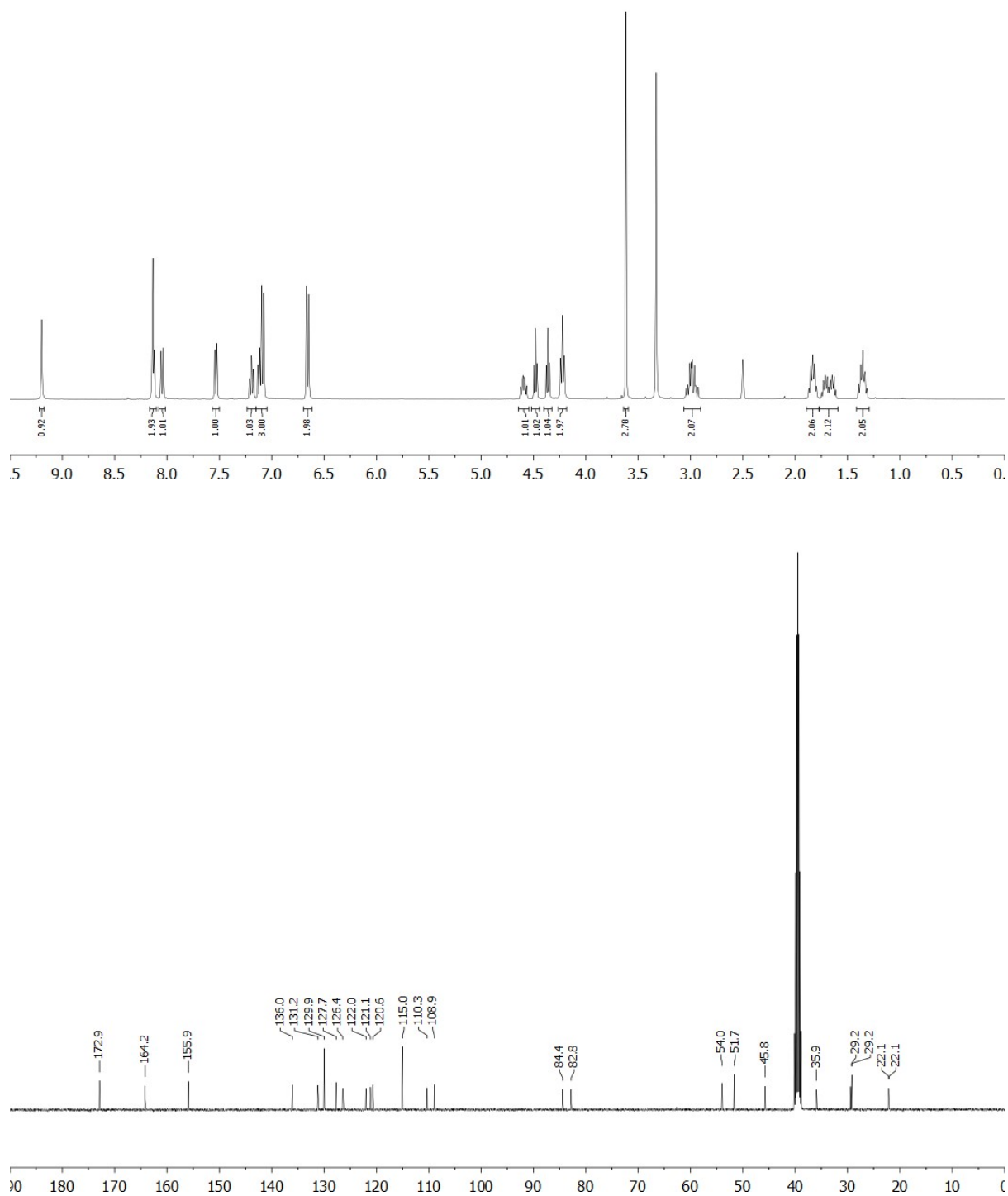
Figure S18. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-tyrosinate (*R*-TYR-5F-PICA, **36**).
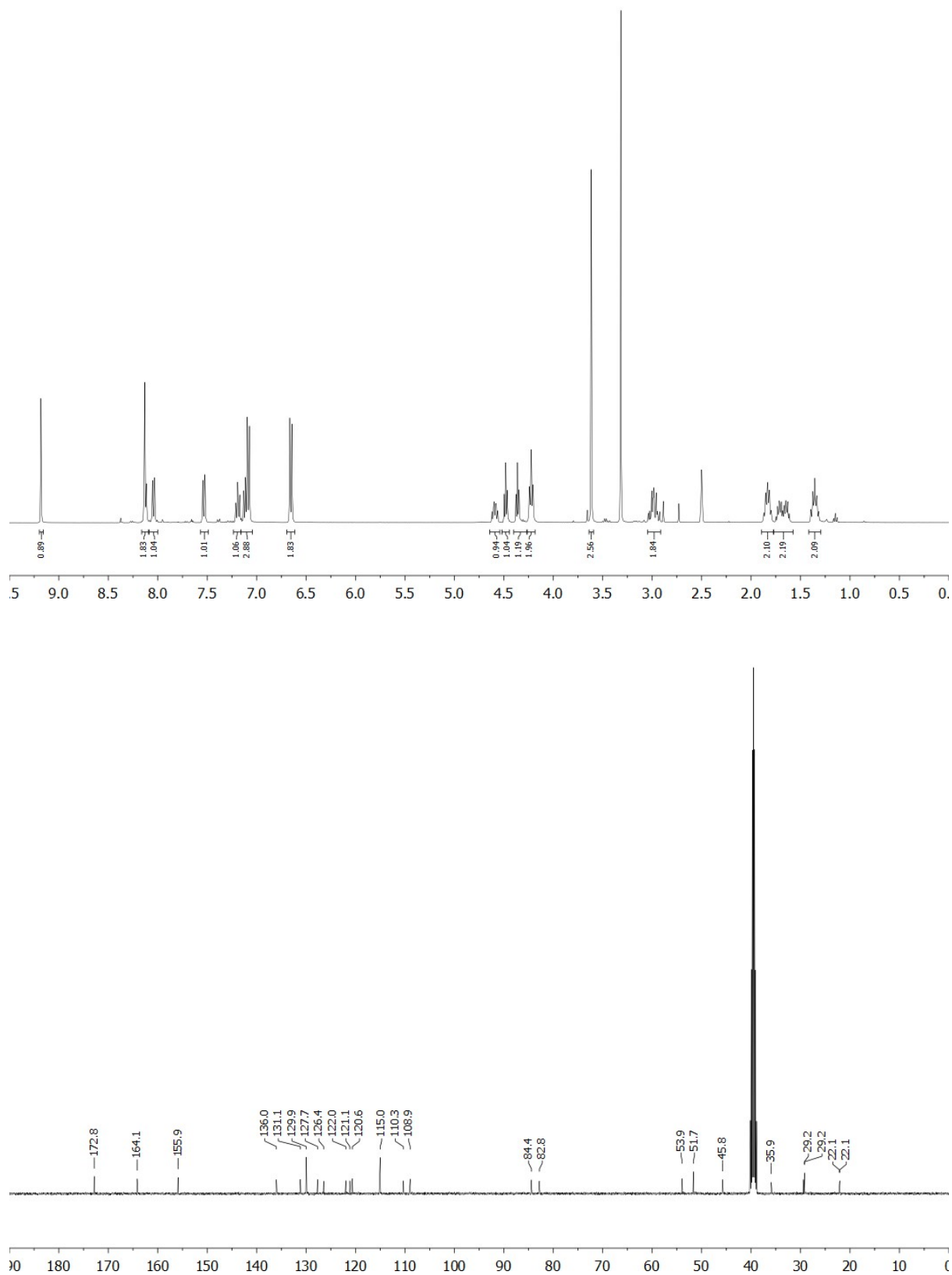
Figure S19. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-tryptophanate (*S*-TRP-5F-PICA, **37**).
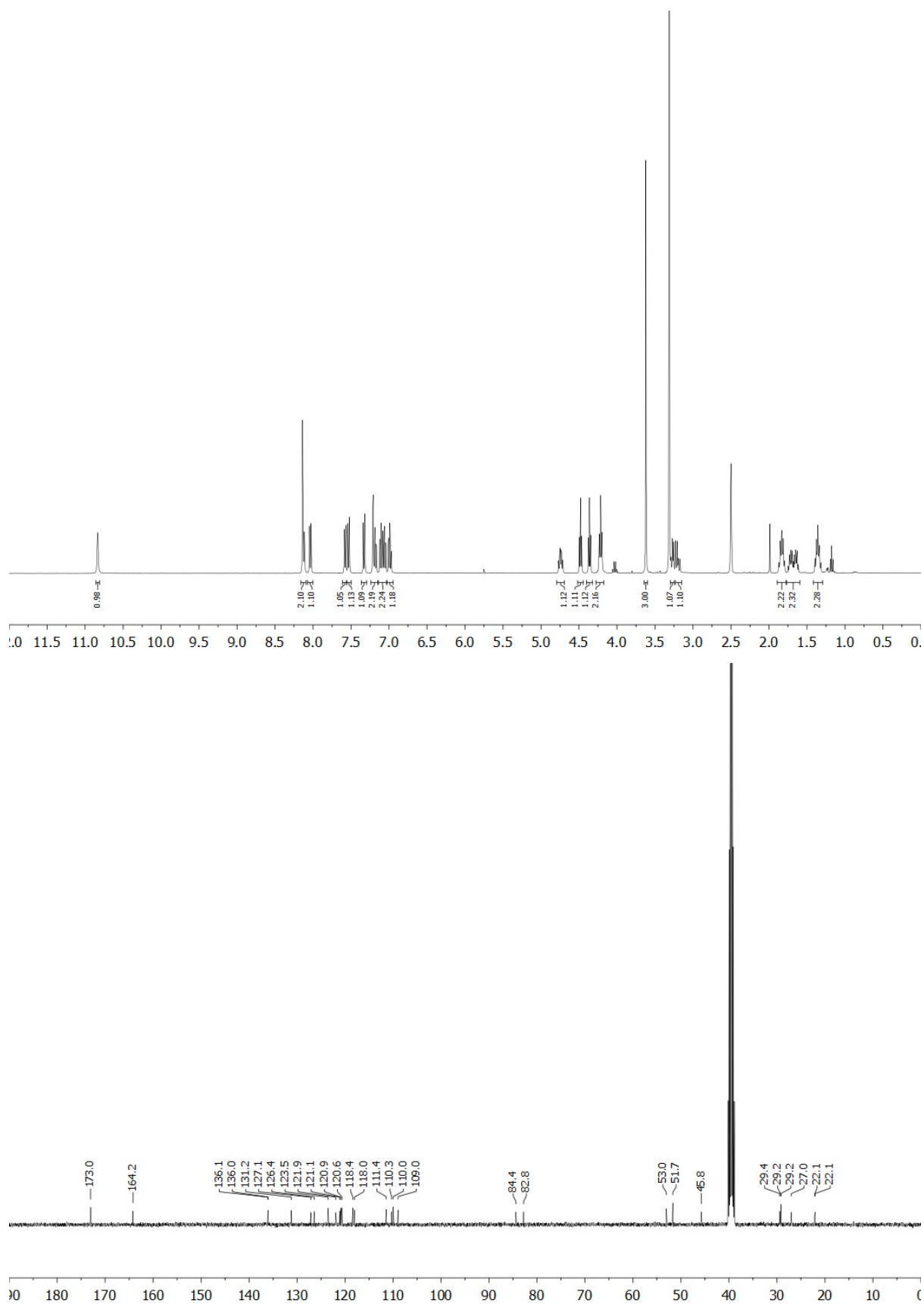
Figure S20. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-tryptophanate (*R*-TRP-5F-PICA, **38**).
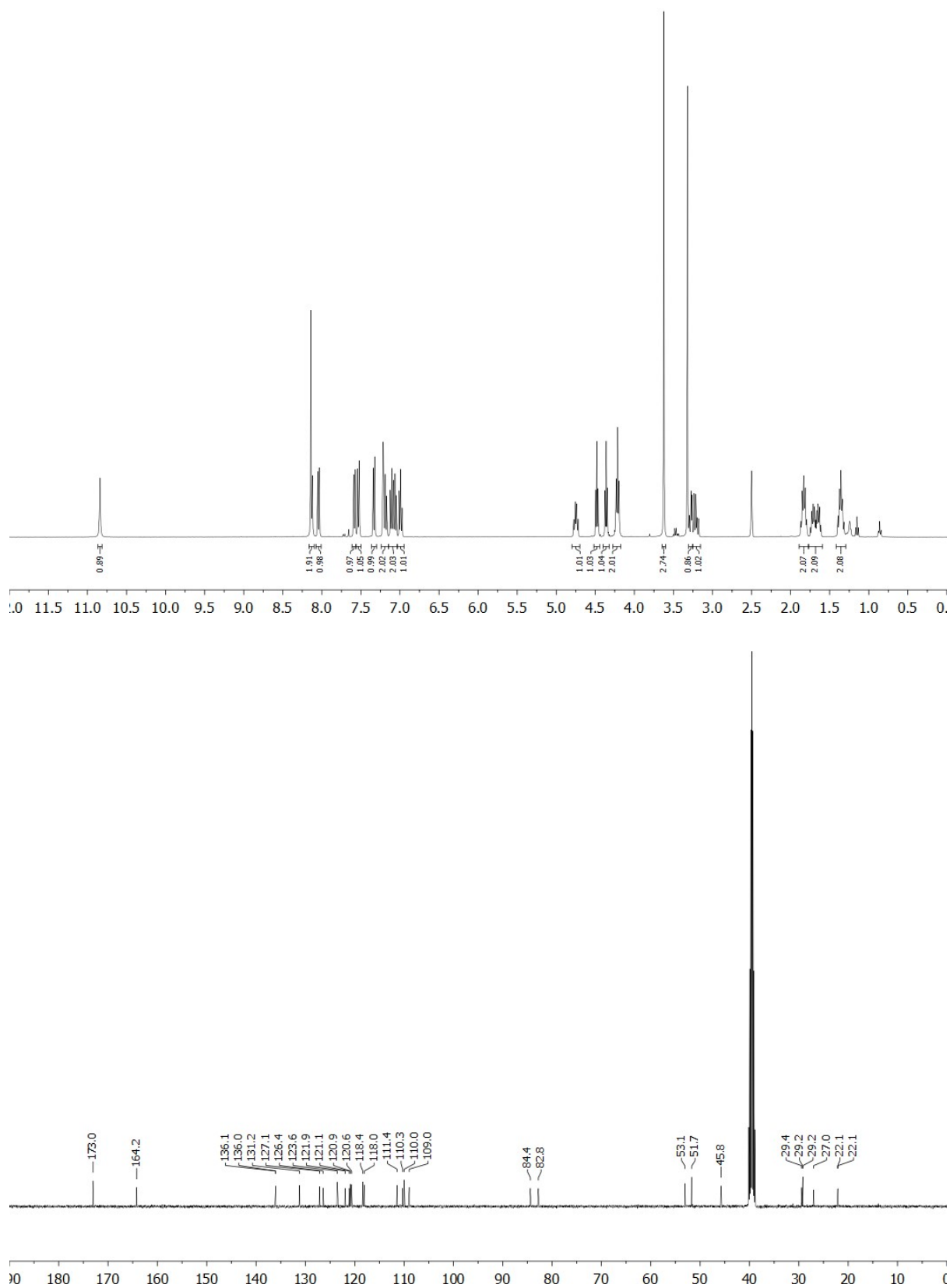
Figure S21. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-lysinate (*S*-LYS-5F-PICA **39**).
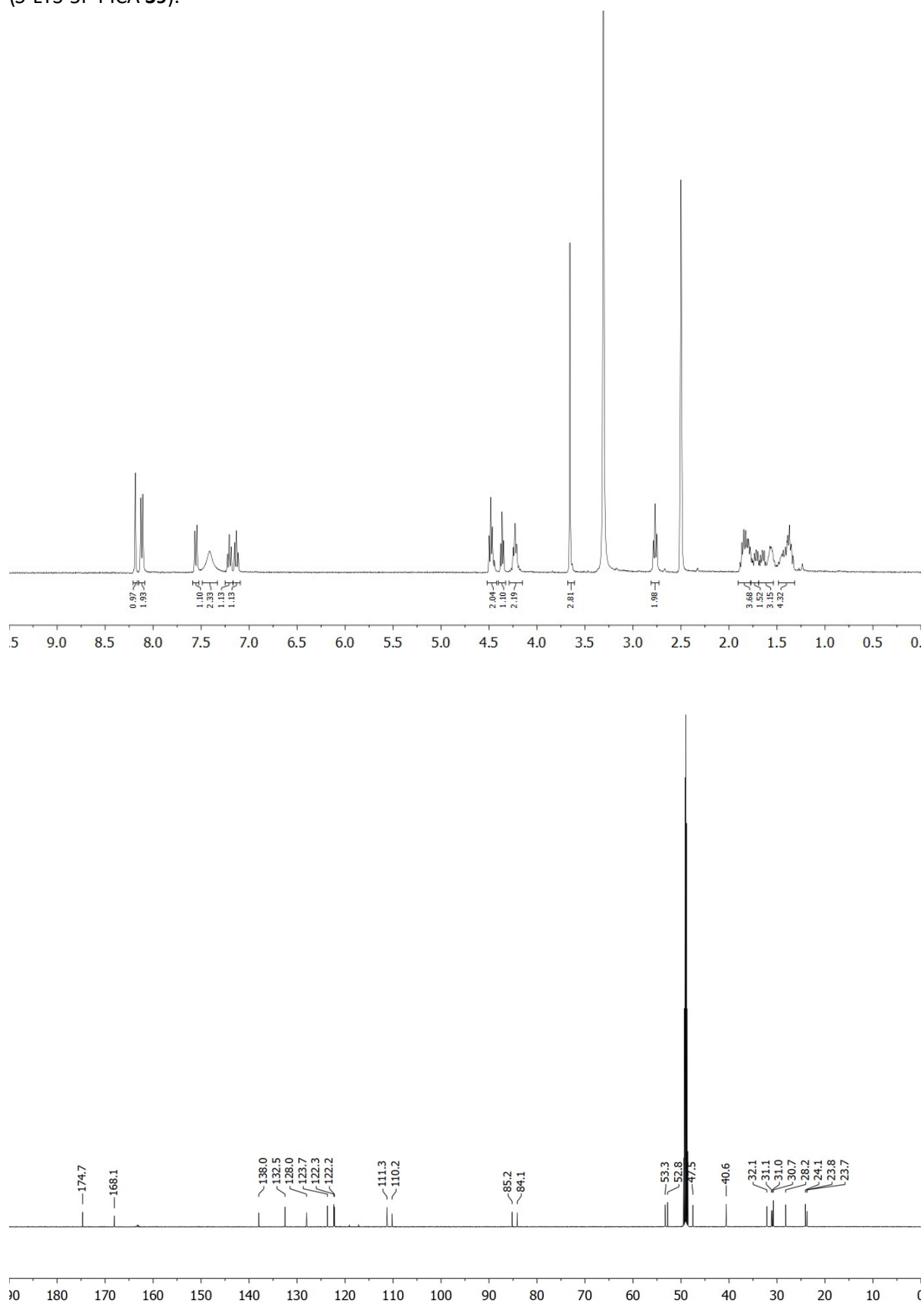
Figure S22. ^{1}H and ^{13}C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-lysinate (*R*-LYS-5F-PICA, **40**).
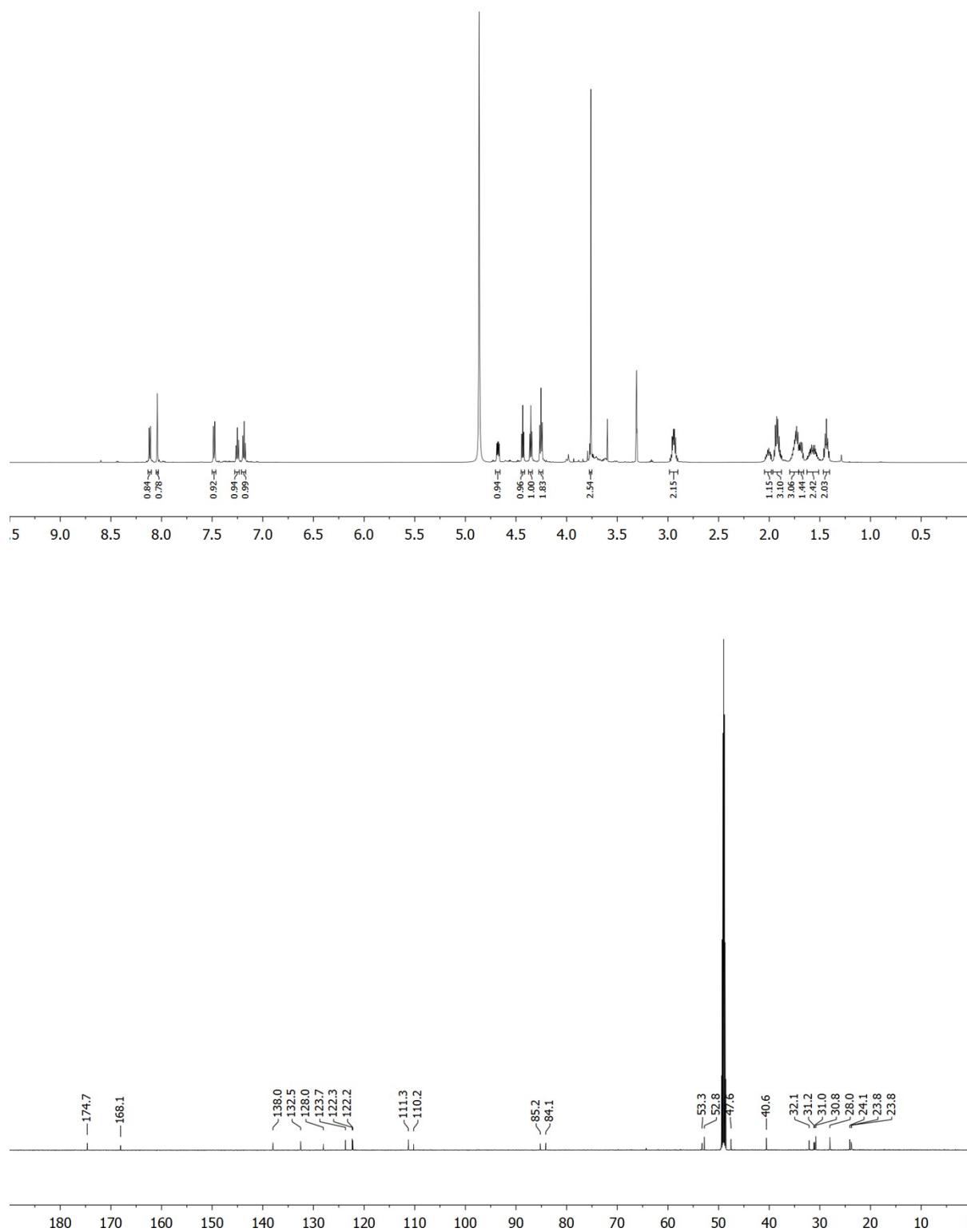
Figure S23. ¹H and ¹³C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-methioninate (*S*-MET-5F-PICA, **41**).
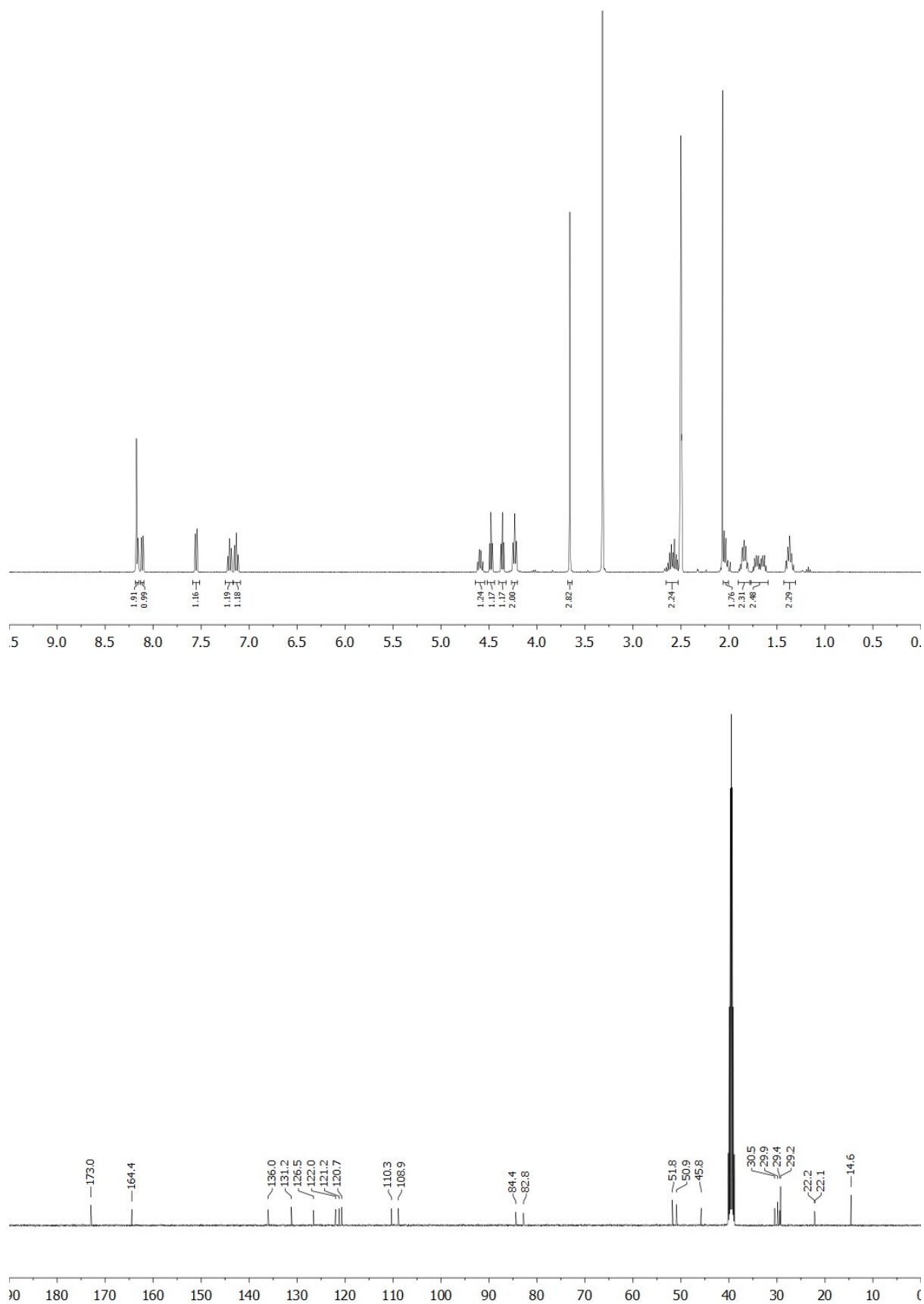
Figure S24. ¹H and ¹³C NMR spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-methioninate (*R*-MET-5F-PICA, **42**).
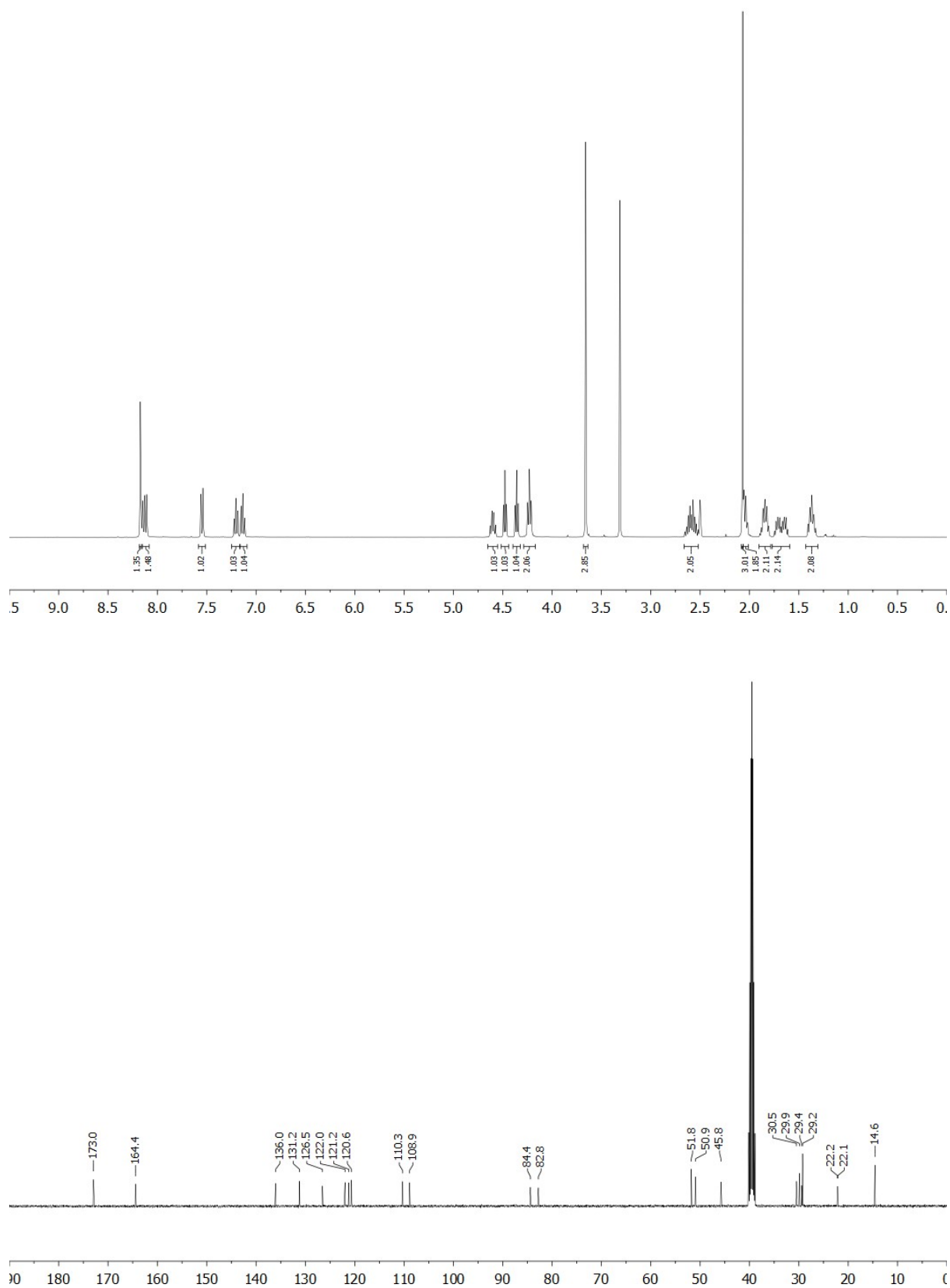
Figure S25. ^{1}H and ^{13}C NMR spectra for methyl (*S*)-5-amino-2-(1-(5-fluoropentyl)-1*H*-indole-3-carboxamido)-5-oxopentanoate (*S*-GLN-5F-PICA, **43**).

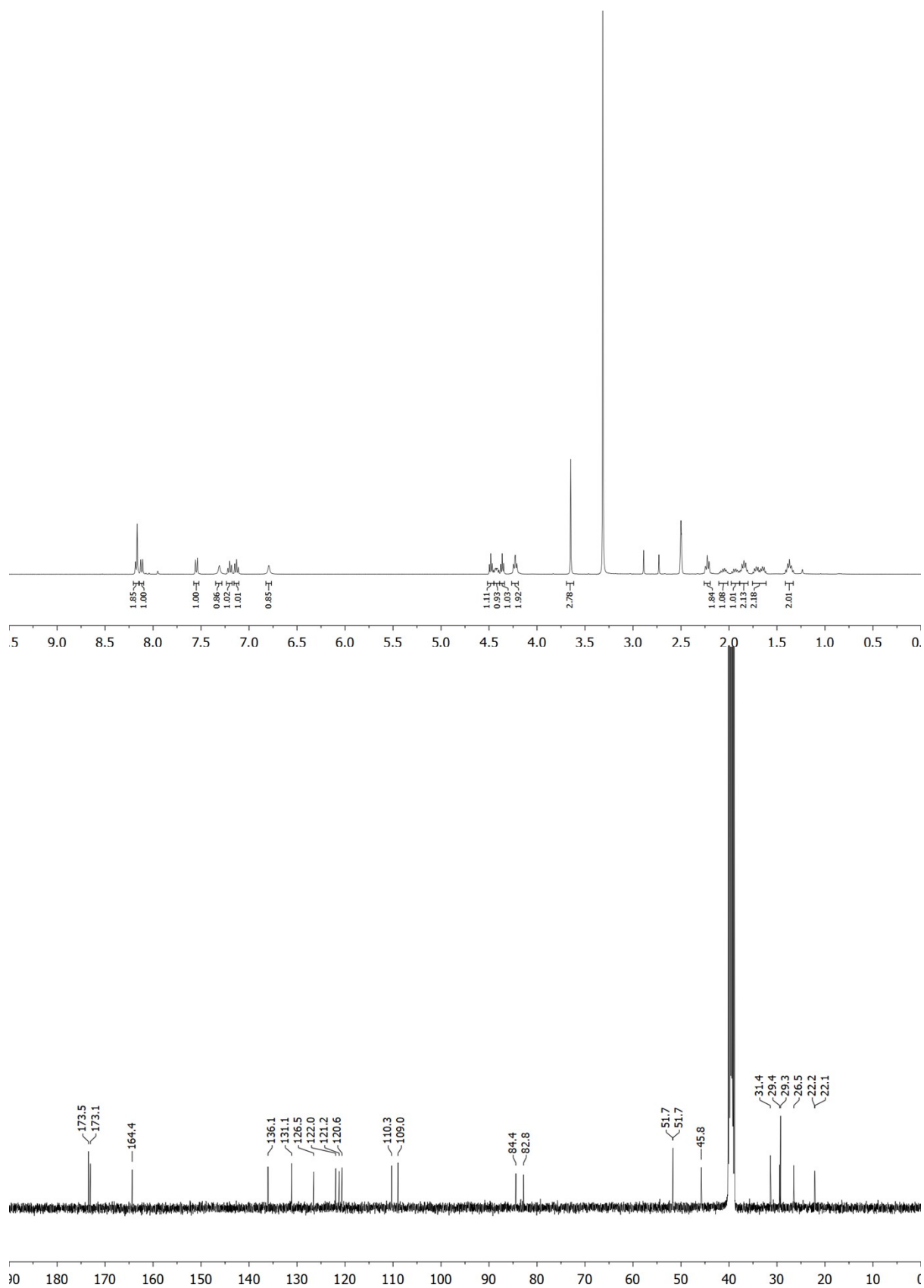**Figure S26.** ^{1}H and ^{13}C NMR spectra for methyl (*R*)-5-amino-2-(1-(5-fluoropentyl)-1*H*-indole-3-carboxamido)-5-oxopentanoate (*R*-GLN-5F-PICA, **44**).

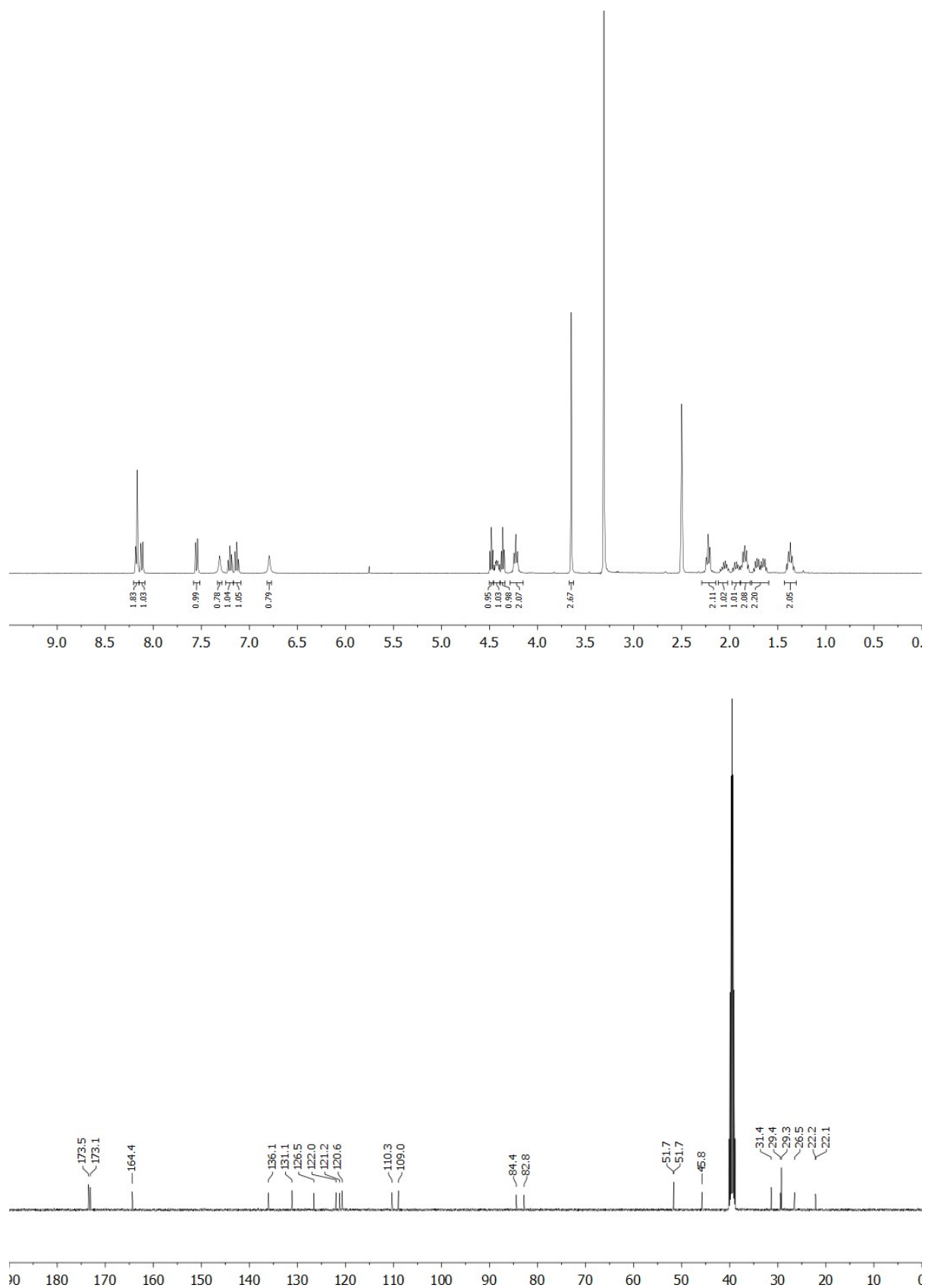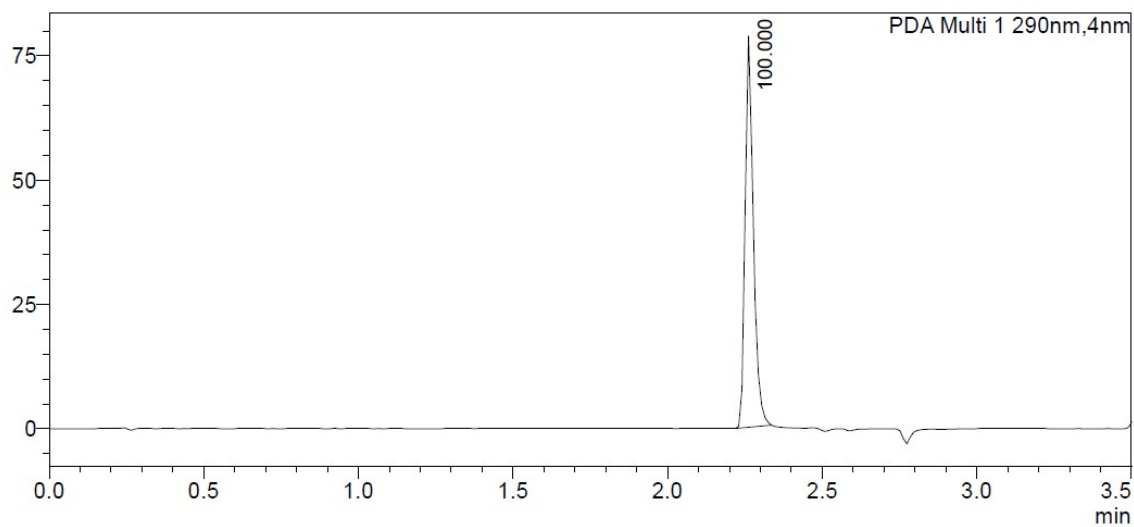**Figure S27.** LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)glycinate (GLY-5F-PICA, **16**).

UV Chromatogram

mAU

PDA Multi 1 290nm,4nm

100.000

MS Spectra

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MassPeaks:7 Mode: Positive
Spectrum Mode:Single 2.258(431) Base Peak:321.1(16593862)
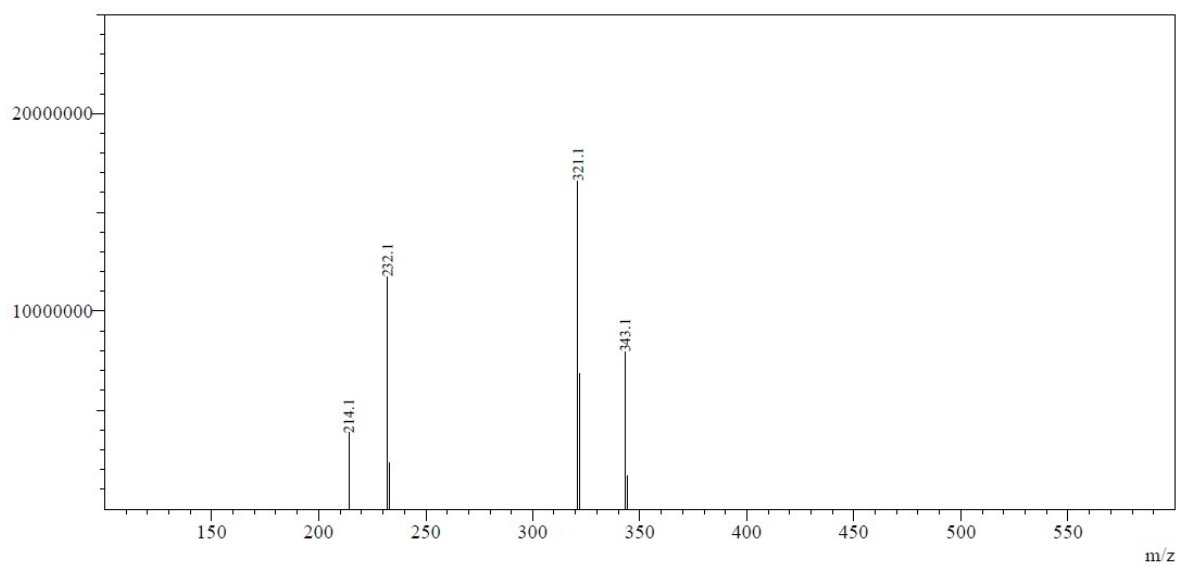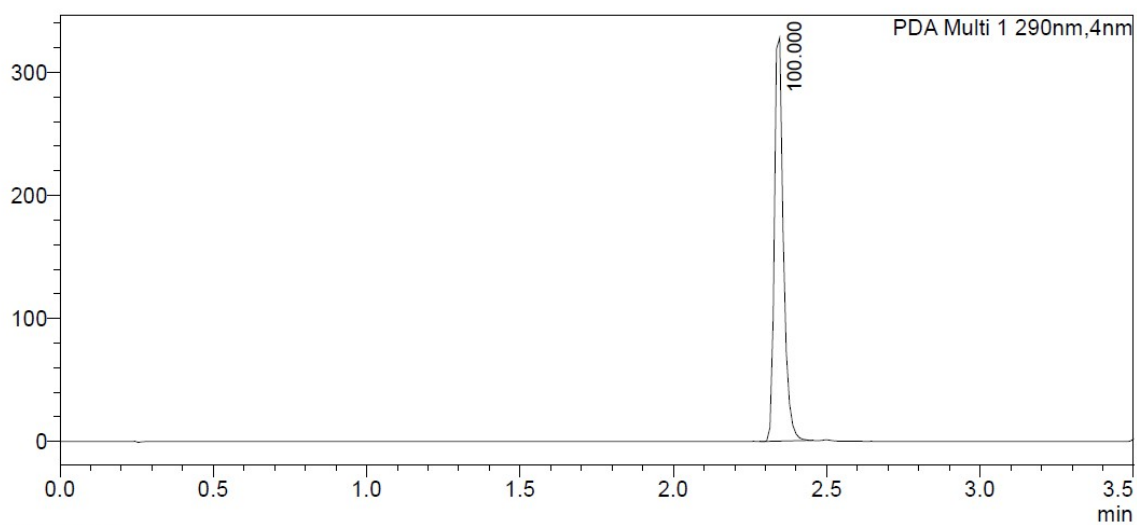BG Mode:None Segment 1 - Event 1

214.1
232.1
321.1
343.1

Figure S28. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-alaninate (*S*-ALA-5F-PICA, **17**).

UV Chromatogram

mAU

PDA Multi 1 290nm,4nm

100.000

MS Spectra

Line#:1　R.Time:----(Scan#:----)
MassPeaks:10　Mode: Positive
Spectrum Mode:Averaged 2.342-2.363(447-451)　Base Peak:232.0(16038082)
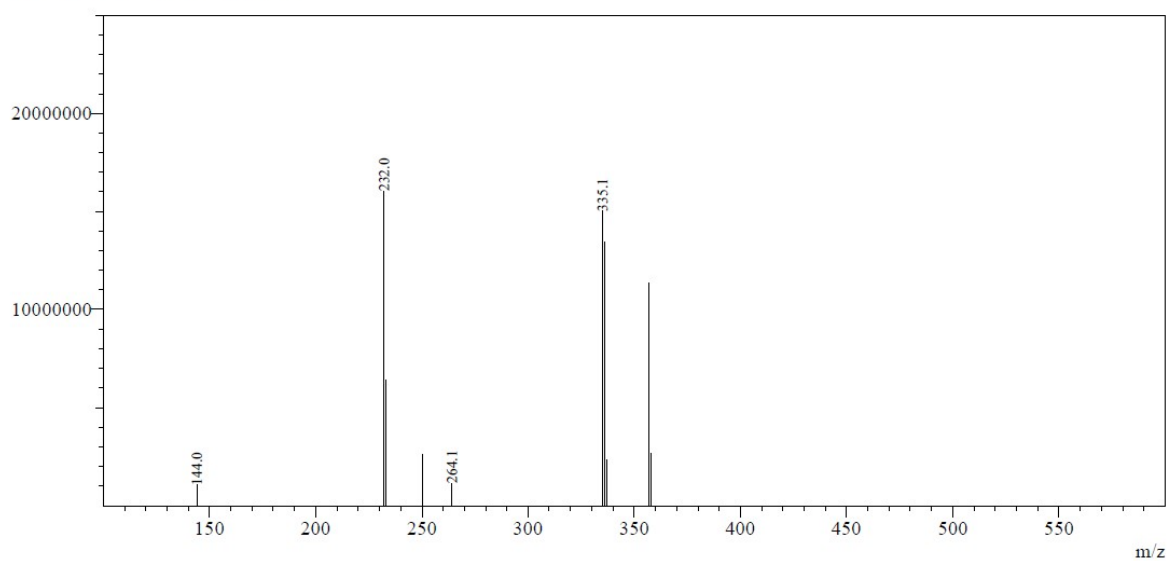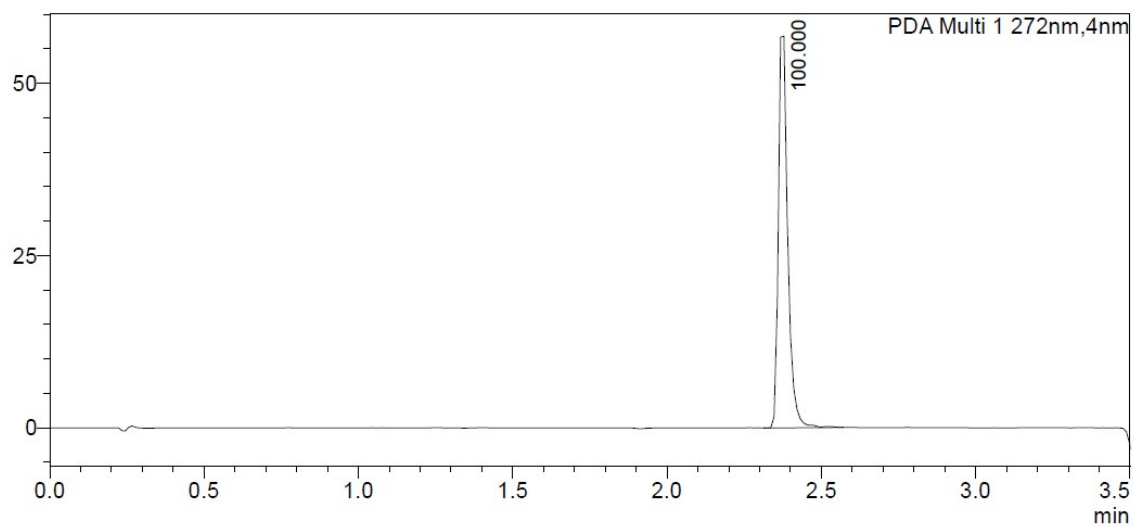BG Mode:Calc　Segment 1 - Event 1

144.0　232.0　264.1　335.1

m/z

Figure S29. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-alaninate (*R*-ALA-5F-PICA, **18**).

UV Chromatogram

mAU

PDA Multi 1 272nm,4nm

100.000

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:6   Mode: Positive
Spectrum Mode:Averaged 2.321-2.478(443-473)   Base Peak:335.1(9189262)
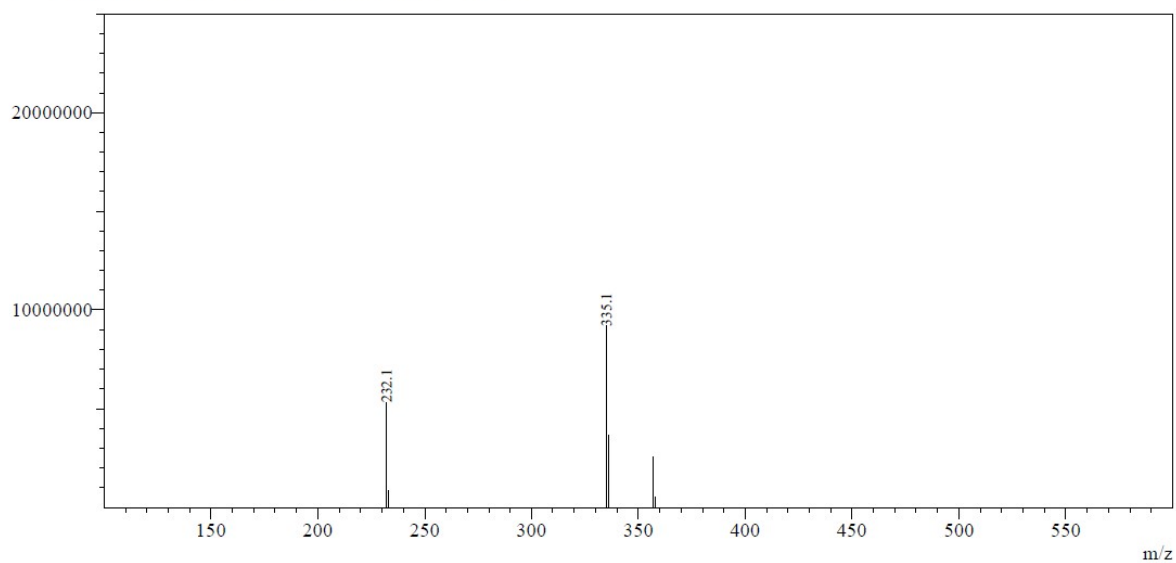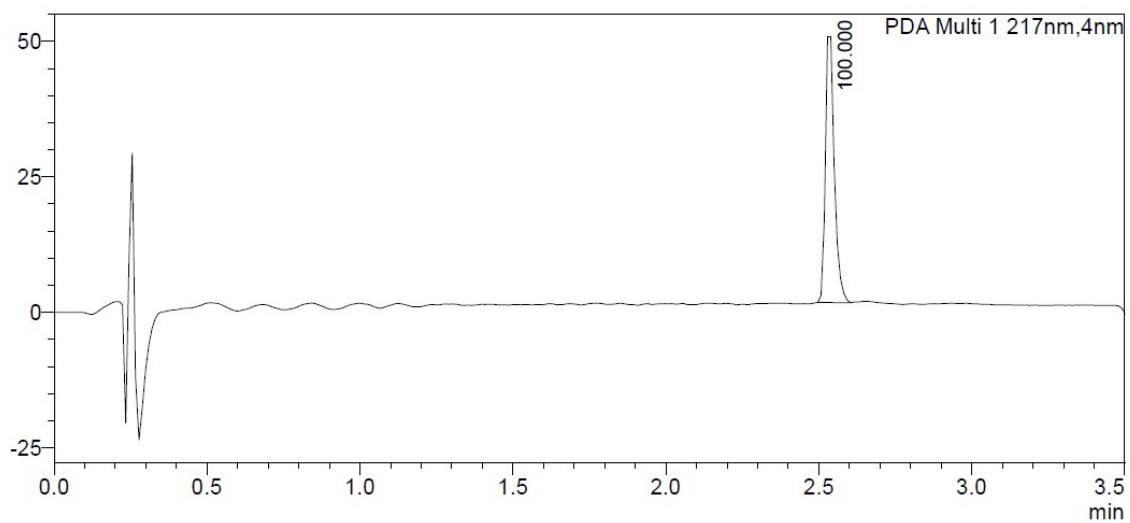BG Mode:Averaged 1.418-1.691(271-323) Segment 1 - Event 1

Figure S30. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-valinate (*R*-MMB-5F-PICA, **20**).

UV Chromatogram

mAU

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:5 Mode: Positive
Spectrum Mode:Averaged 2.531-2.552(483-487) Base Peak:385.2(12331779)
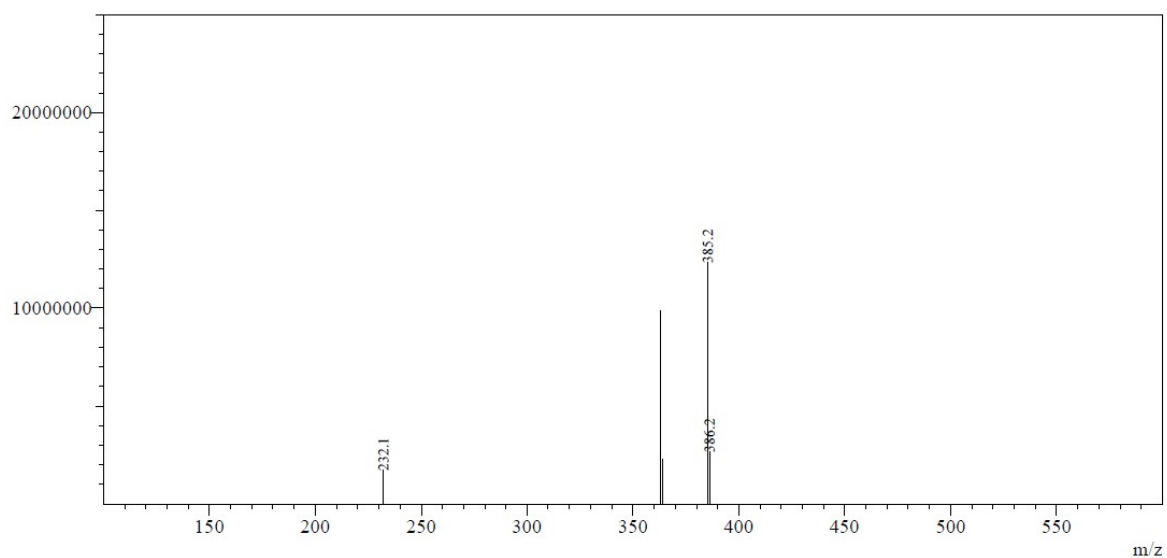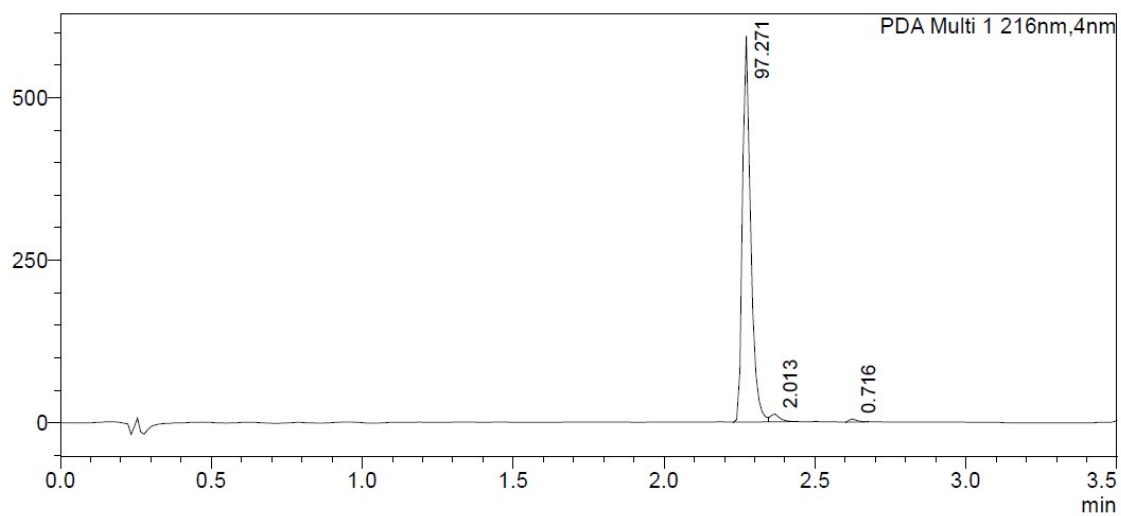BG Mode:Averaged 0.042-4.473(9-853) Segment 1 - Event 1

Figure S31. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-serinate (*S*-SER-5F-PICA, **21**).

UV Chromatogram

mAU

PDA Multi 1 216nm,4nm

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:8 Mode: Positive
Spectrum Mode:Averaged 2.258-2.300(431-439) Base Peak:373.1(15911108)
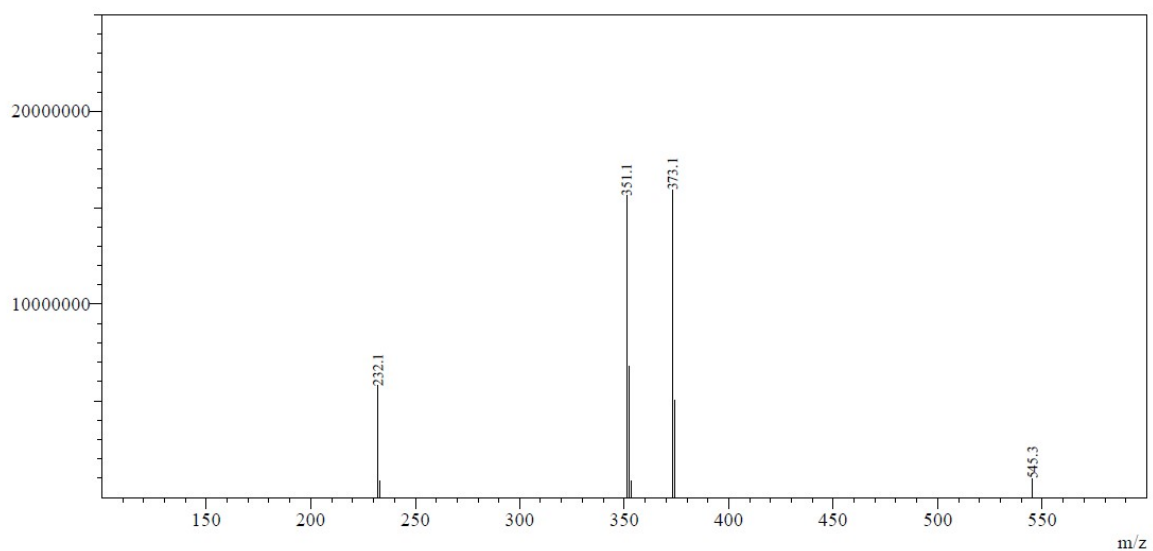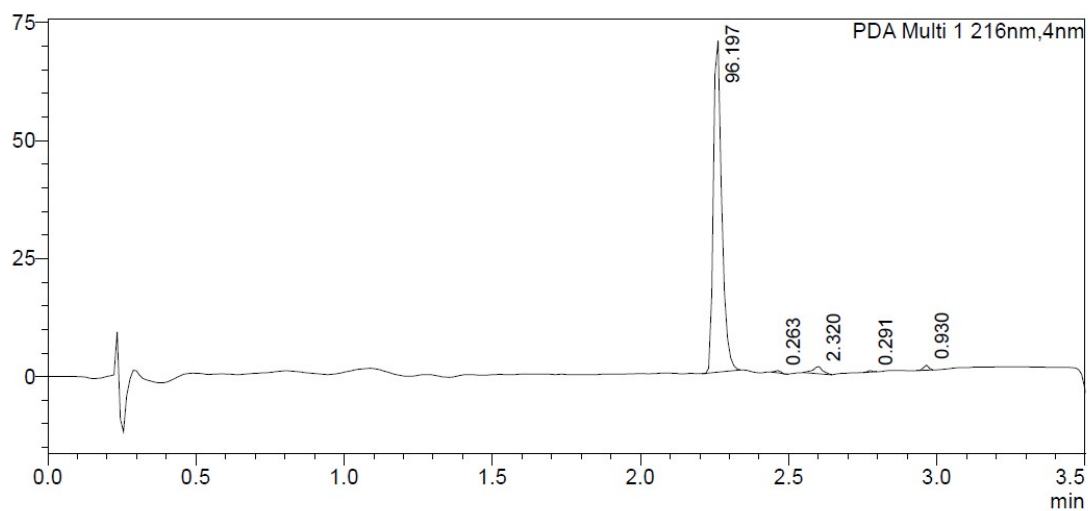BG Mode:Averaged 0.084-4.410(17-841) Segment 1 - Event 1

Figure S32. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-serinate (*R*-SER-5F-PICA, **22**).

UV Chromatogram

mAU

PDA Multi 1 216nm,4nm

96.197

0.263
2.320
0.291
0.930

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:5 Mode: Positive
Spectrum Mode:Averaged 2.258-2.300(431-439) Base Peak:373.1(7801970)
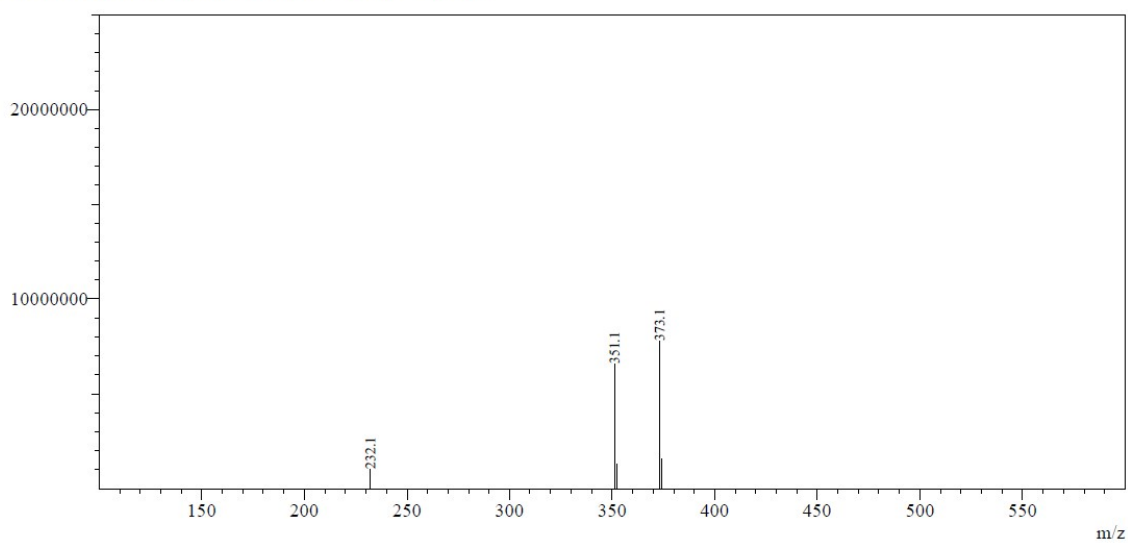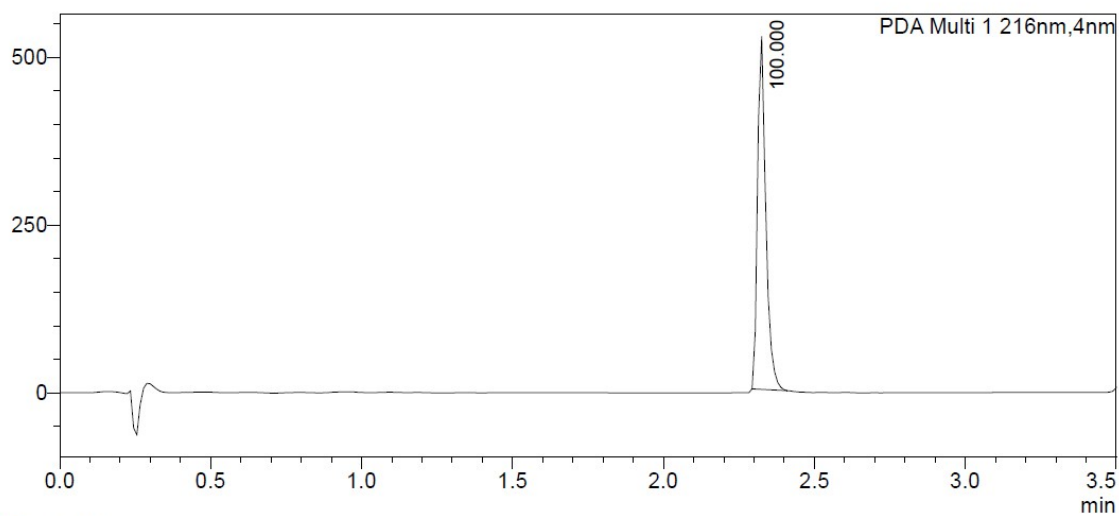BG Mode:Averaged 0.063-4.379(13-835) Segment 1 - Event 1

232.1

351.1

373.1

Figure S33. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-2*S*,3*R*-threoninate
(2*S*,3*R*-THR-5F-PICA, **23**).

UV Chromatogram

mAU

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:7 Mode: Positive
Spectrum Mode:Averaged 2.321-2.363(443-451) Base Peak:387.1(17479359)
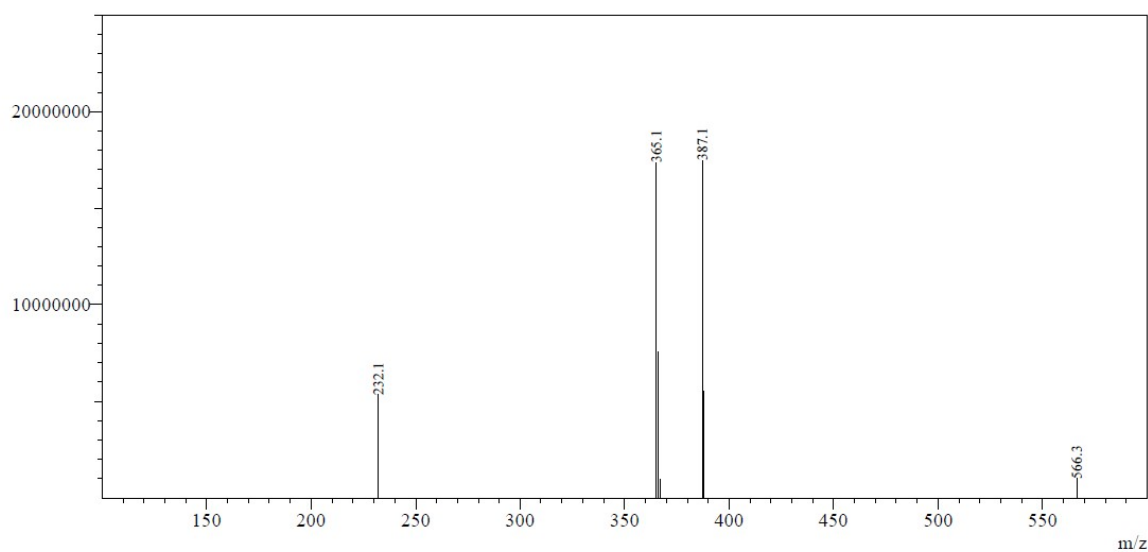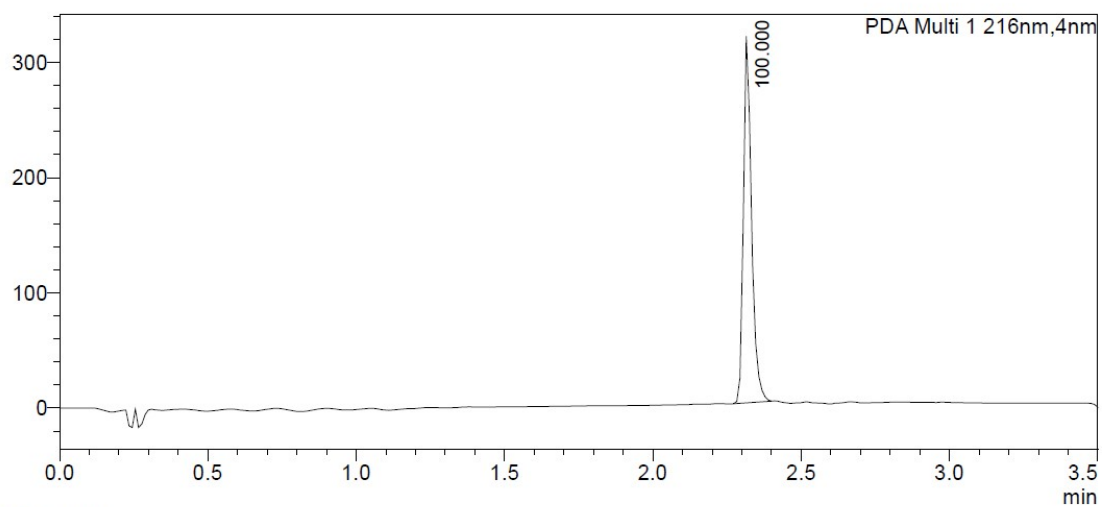BG Mode:Averaged 0.021-4.410(5-841) Segment 1 - Event 1

Figure S34. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-2*R*,3*S*-threoninate (2*R*,3*S*-THR-5F-PICA, **24**).

UV Chromatogram

mAU

PDA Multi 1 216nm,4nm

100.000

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:5   Mode: Positive
Spectrum Mode:Averaged 2.321-2.342(443-447)   Base Peak:365.1(17446089)
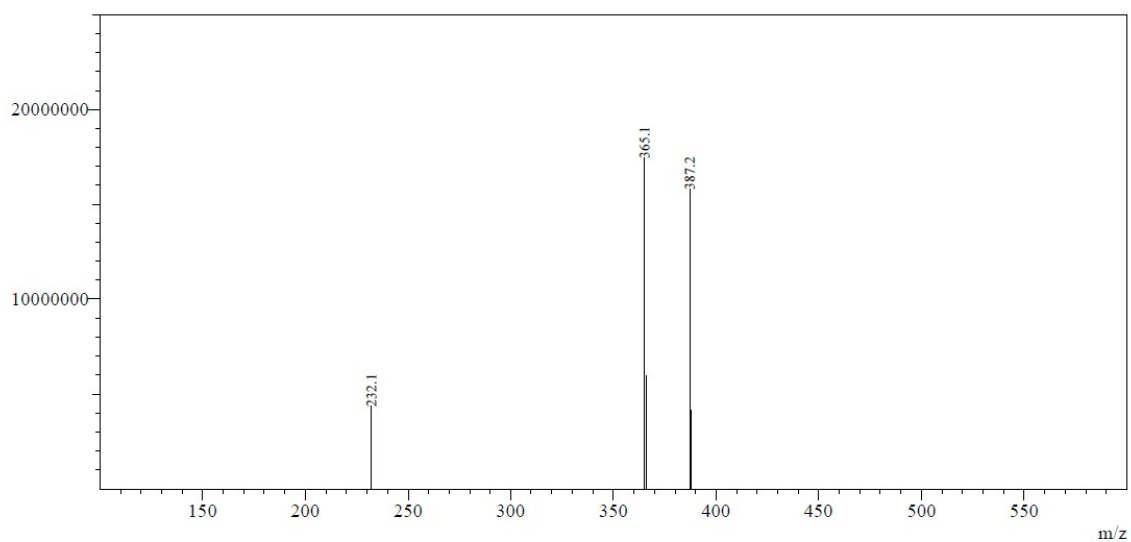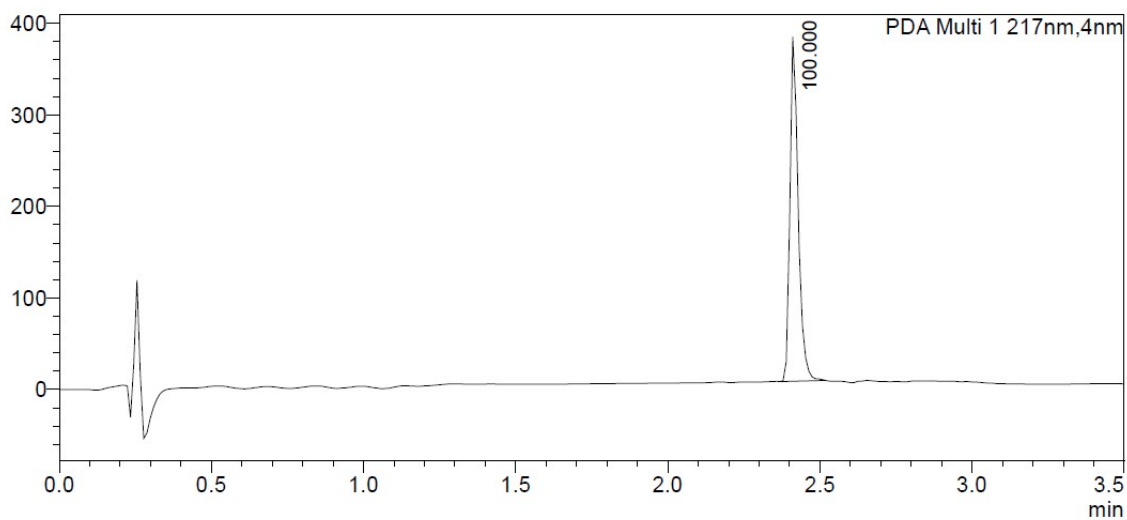BG Mode:Averaged 0.074-4.400(15-839) Segment 1 - Event 1

Figure S35. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-prolinate (*S*-PRO-5F-PICA, **25**).

UV Chromatogram

mAU

PDA Multi 1 217nm,4nm

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:6 Mode: Positive
Spectrum Mode:Averaged 2.415-2.436(461-465) Base Peak:361.1(19753459)
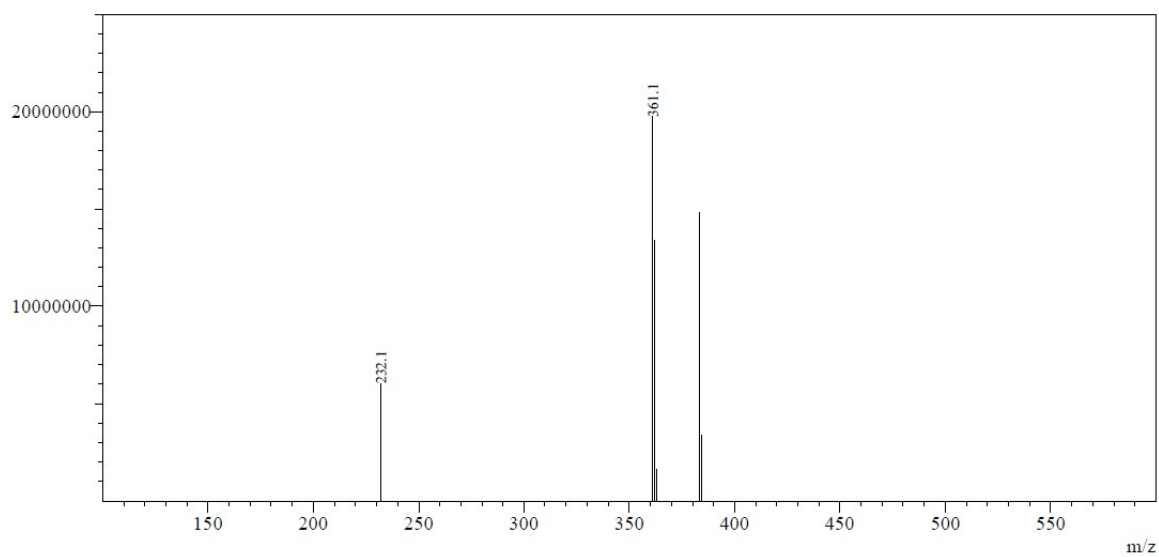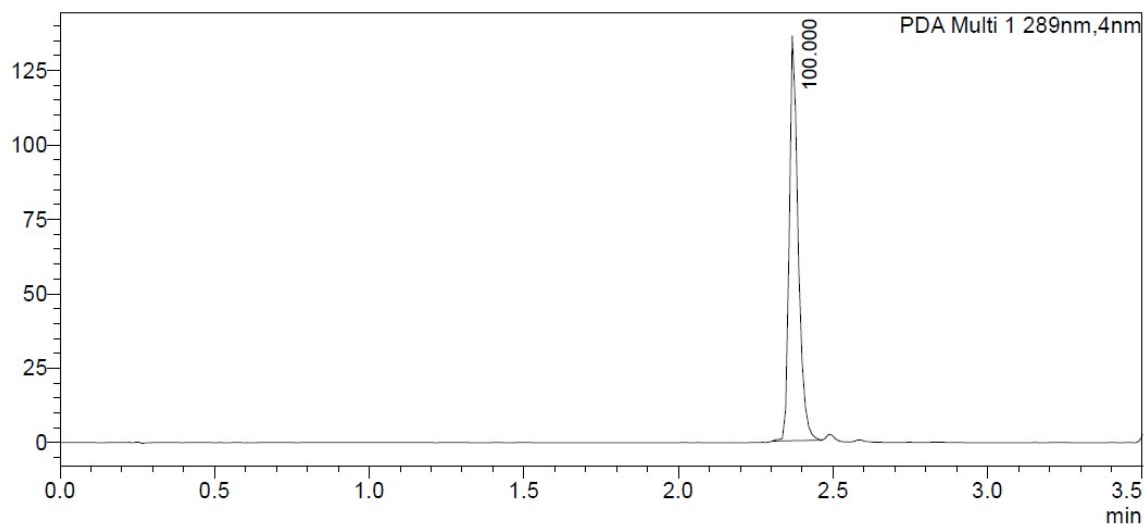BG Mode:Averaged 0.074-4.368(15-833) Segment 1 - Event 1

Figure S36. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-prolinate (*R*-PRO-5F-PICA, **26**).

UV Chromatogram

mAU

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:11   Mode: Positive
Spectrum Mode:Averaged 2.321-2.457(443-469)   Base Peak:361.1(12243786)
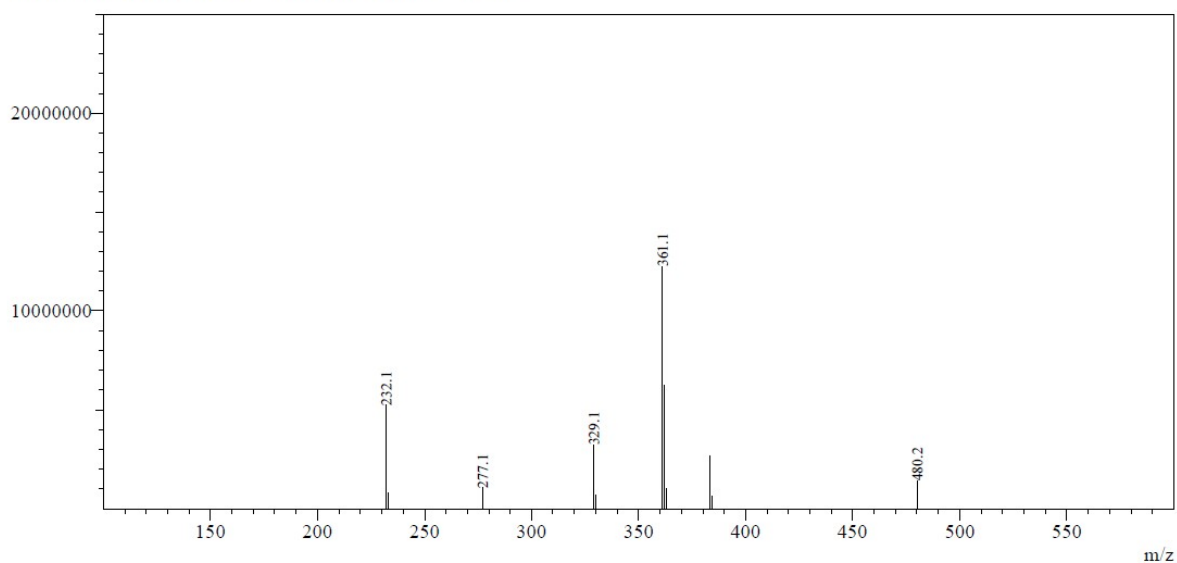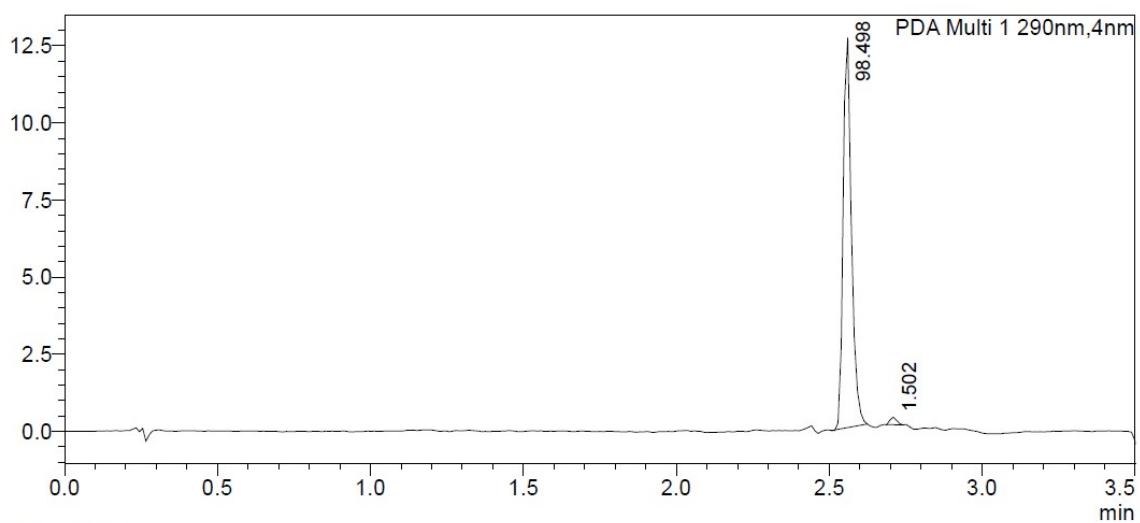BG Mode:Averaged 1.628-1.953(311-373) Segment 1 - Event 1

Figure S37. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-leucinate (*S*-LEU-5F-PICA, **27**).

UV Chromatogram

mAU

PDA Multi 1 290nm,4nm

98.498

1.502

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:5   Mode: Positive
Spectrum Mode:Averaged 2.510-2.615(479-499)   Base Peak:377.2(7753698)
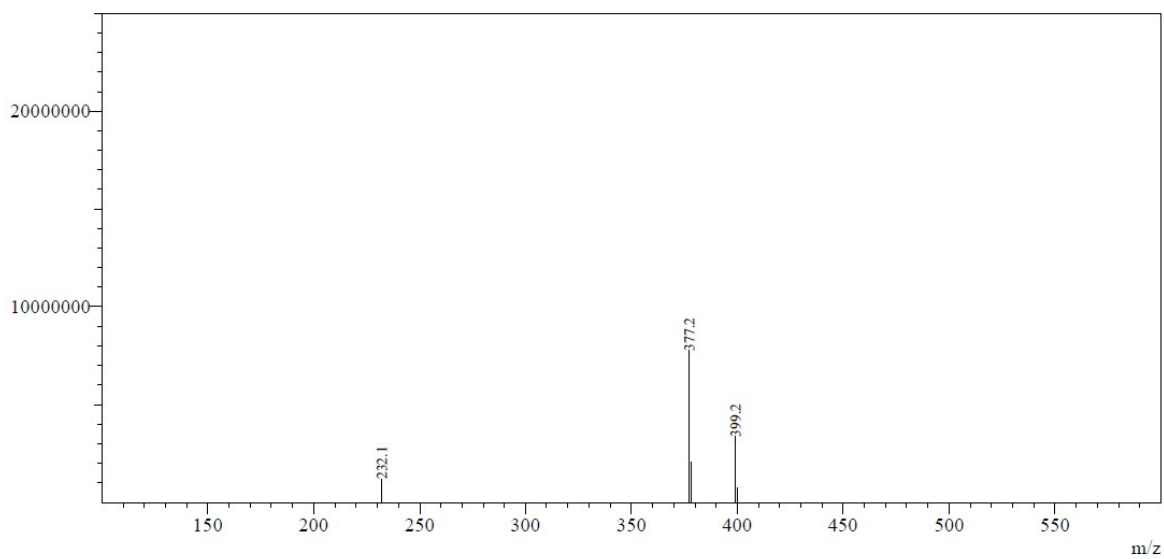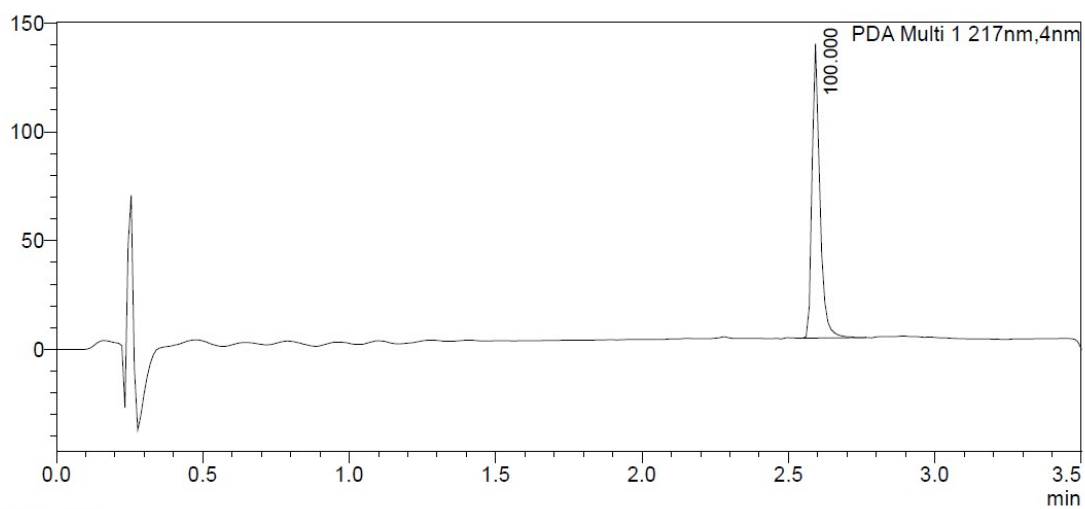BG Mode:Averaged 1.754-2.415(335-461) Segment 1 - Event 1

232.1

377.2

399.2

m/z

Figure S38. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-leucinate (*R*-LEU-5F-PICA, **28**).

UV Chromatogram

mAU

PDA Multi 1 217nm,4nm

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:6   Mode: Positive
Spectrum Mode:Averaged 2.552-2.667(487-509)   Base Peak:399.2(7725972)
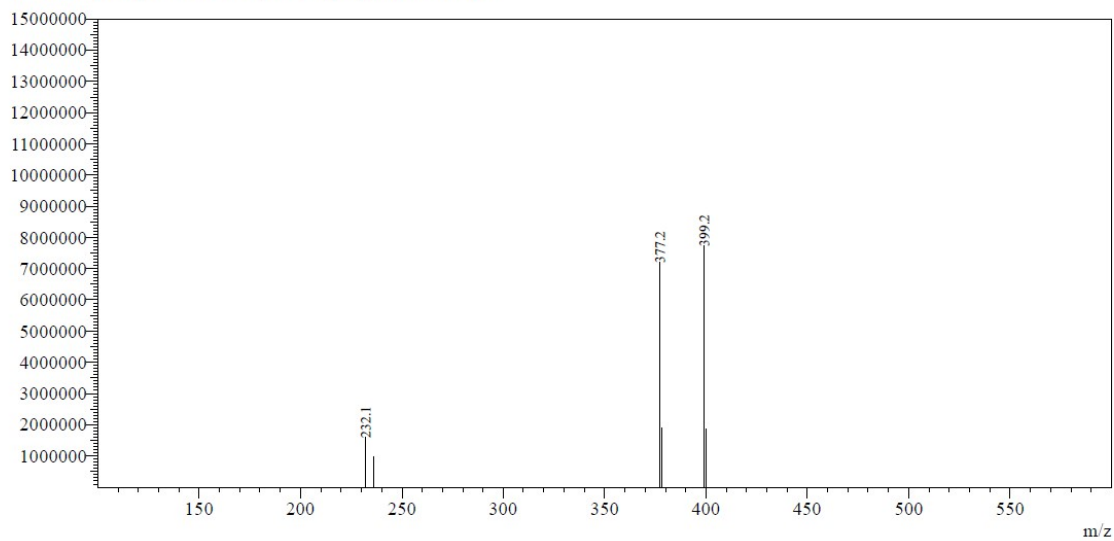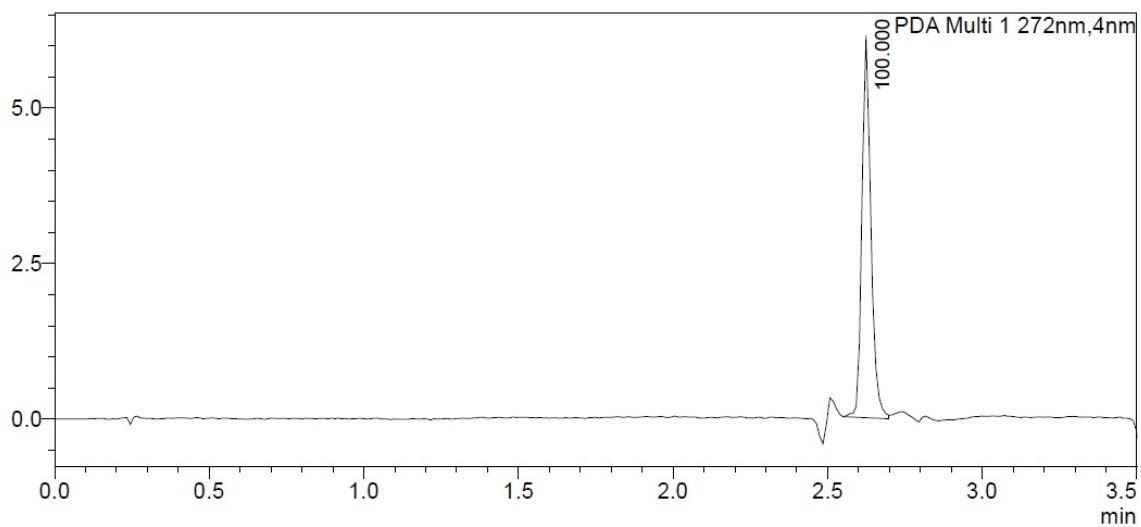BG Mode:Averaged 1.008-2.048(193-391) Segment 1 - Event 1

Figure S39. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-isoleucinate (*S*-ILE-5F-PICA, **29**).

UV Chromatogram

mAU

PDA Multi 1 272nm,4nm

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:5 Mode: Positive
Spectrum Mode:Averaged 2.583-2.699(493-515) Base Peak:377.3(3964375)
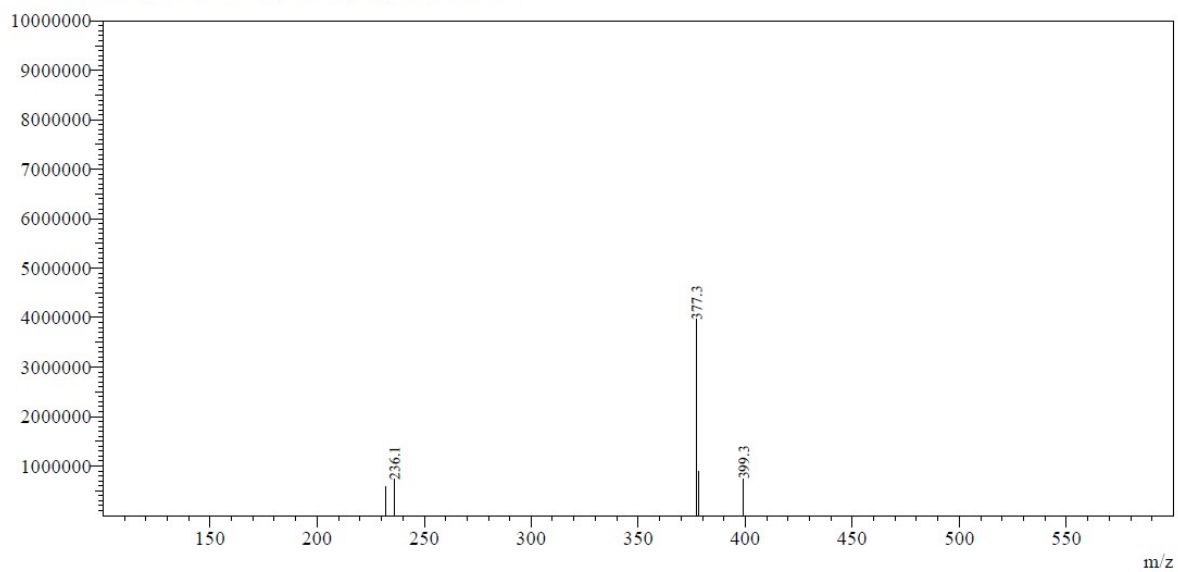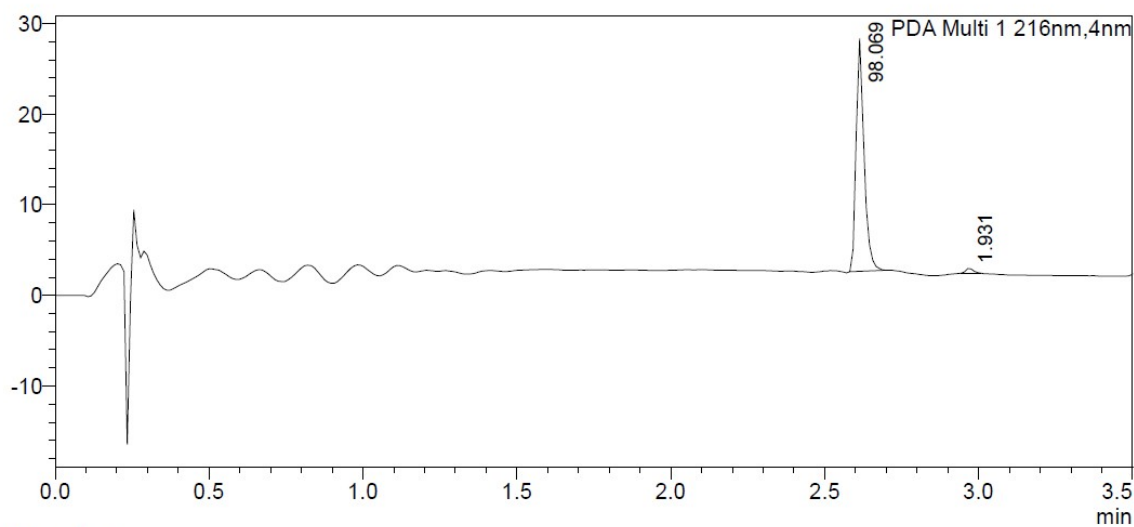BG Mode:Averaged 1.187-1.523(227-291) Segment 1 - Event 1

Figure S40. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-isoleucinate (*R*-ILE-5F-PICA, **30**).

UV Chromatogram

mAU

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:7 Mode: Positive
Spectrum Mode:Averaged 2.562-2.699(489-515) Base Peak:399.2(3173545)
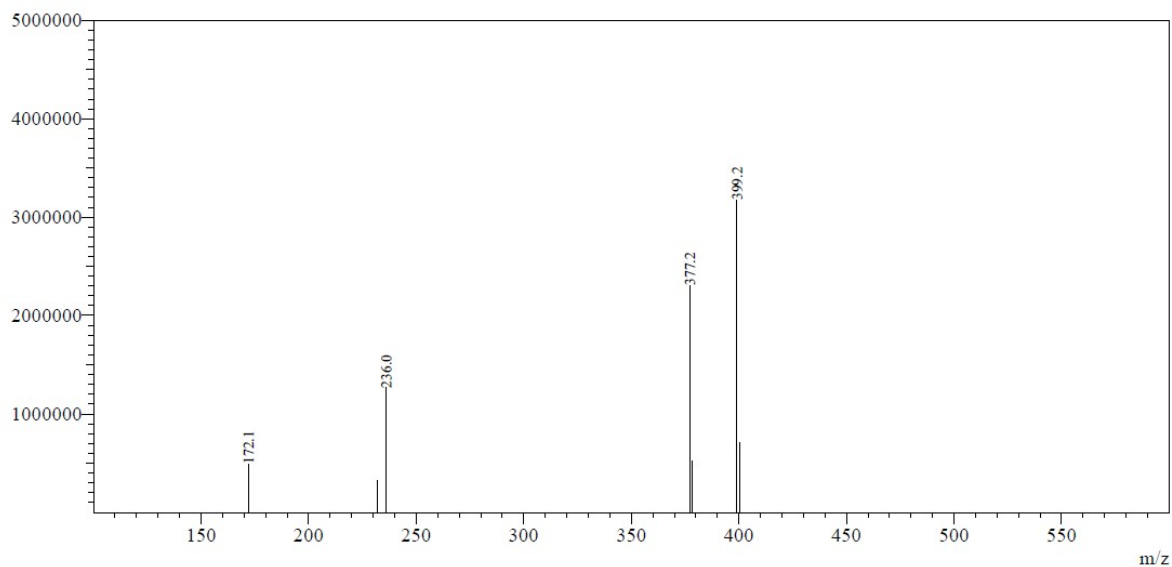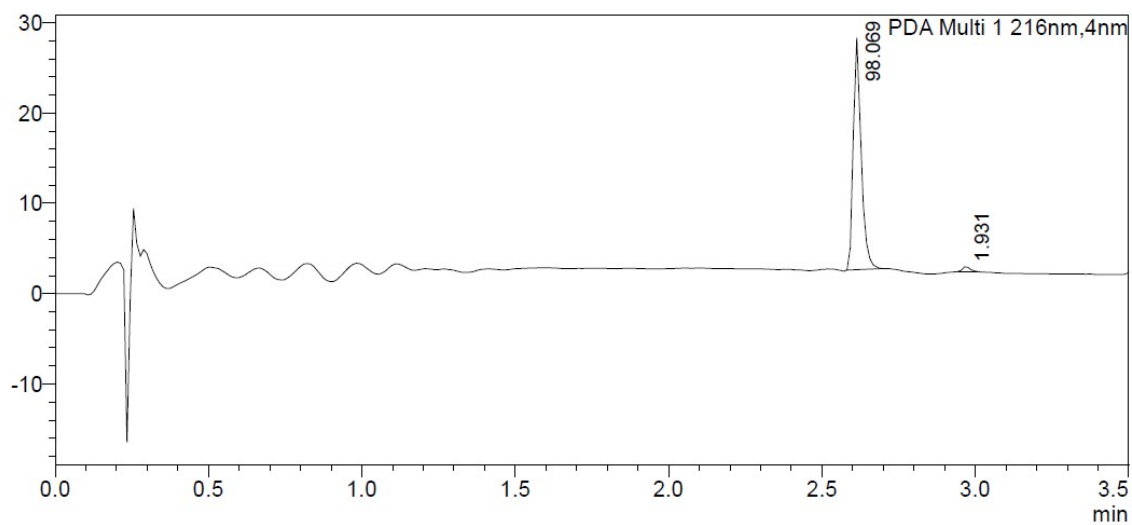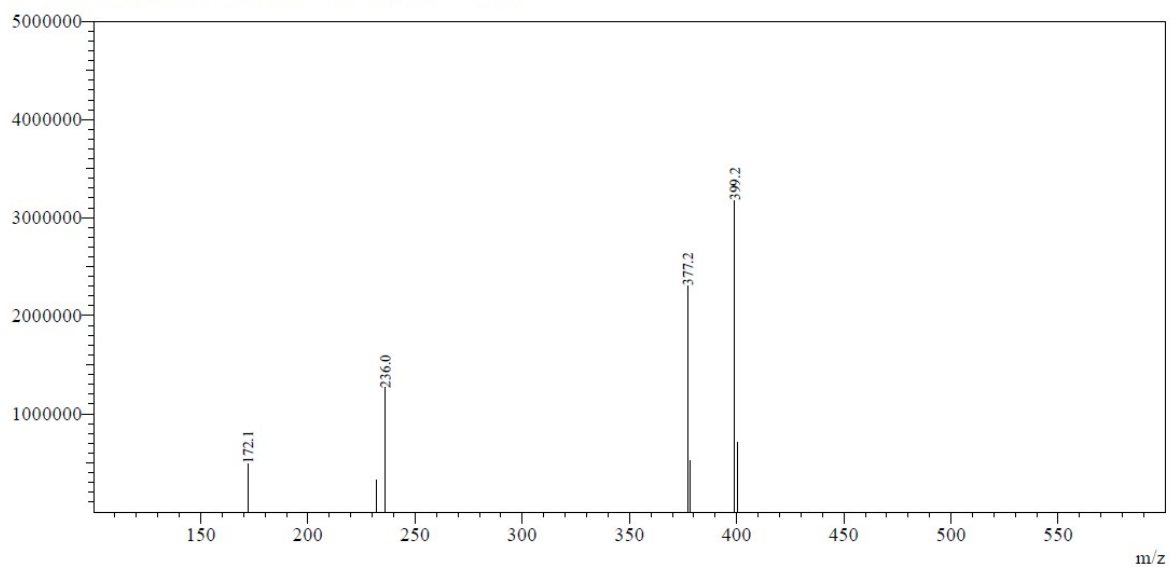BG Mode:Averaged 1.565-2.069(299-395) Segment 1 - Event 1

Figure S41. LCMS spectra for methyl (*R*)-2-(1-(5-fluoropentyl)-1*H*-indole-3-carboxamido)-3,3-dimethylbutanoate (*R*-MDMB-5F-PICA, **32**).

UV Chromatogram

mAU

PDA Multi 1 216nm,4nm

98.069

1.931

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:7 Mode: Positive
Spectrum Mode:Averaged 2.562-2.699(489-515) Base Peak:399.2(3173545)
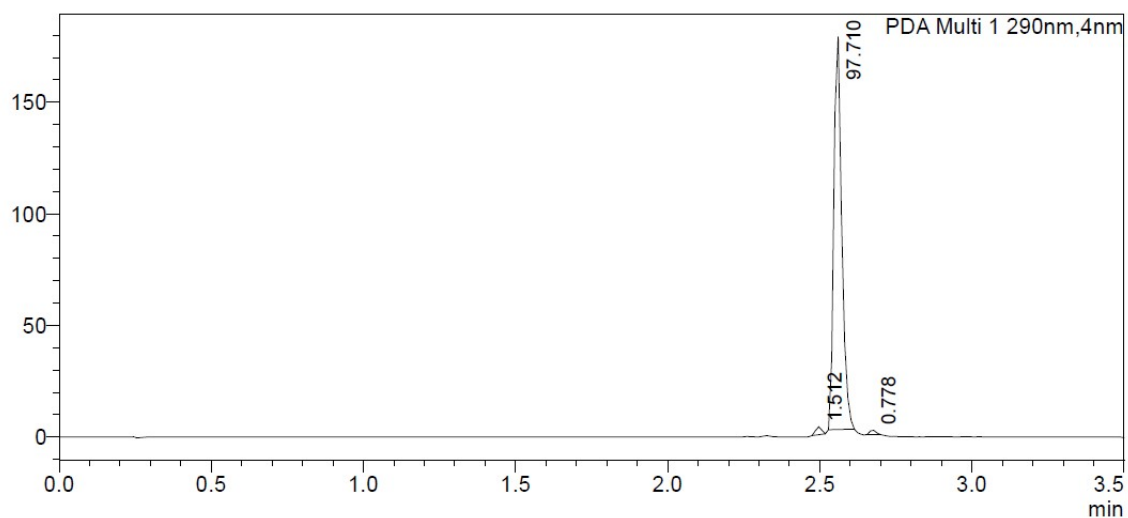BG Mode:Averaged 1.565-2.069(299-395) Segment 1 - Event 1

172.1

236.0

377.2

399.2

Figure S42. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-phenylalaninate (*R*-MPP-5F-PICA, **34**).

UV Chromatogram

mAU

PDA Multi 1 290nm,4nm

97.710

1.512

0.778

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:11 Mode: Positive
Spectrum Mode:Averaged 2.457-2.699(469-515) Base Peak:411.2(6718031)
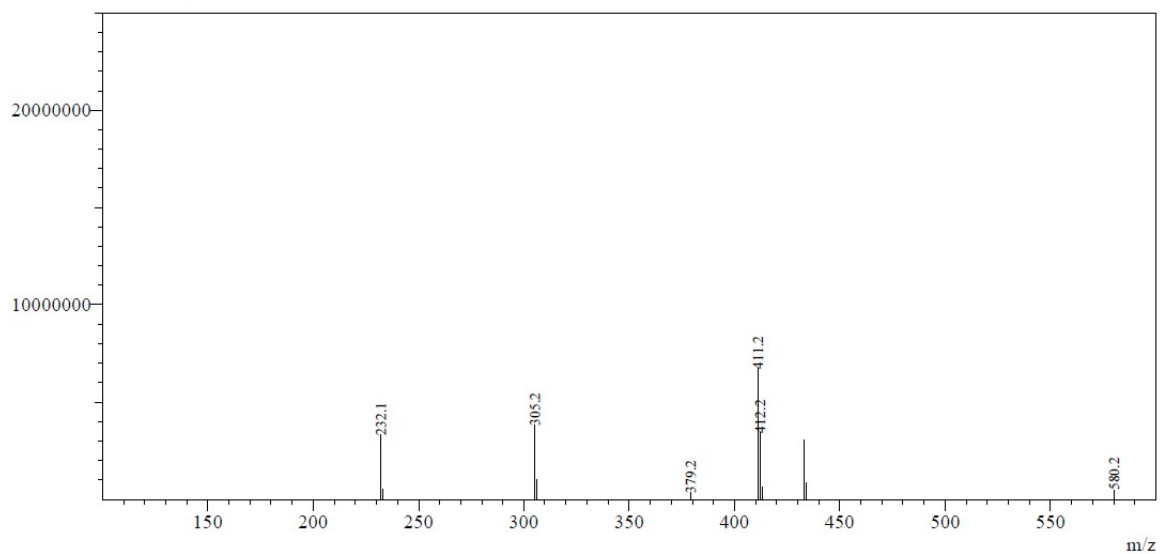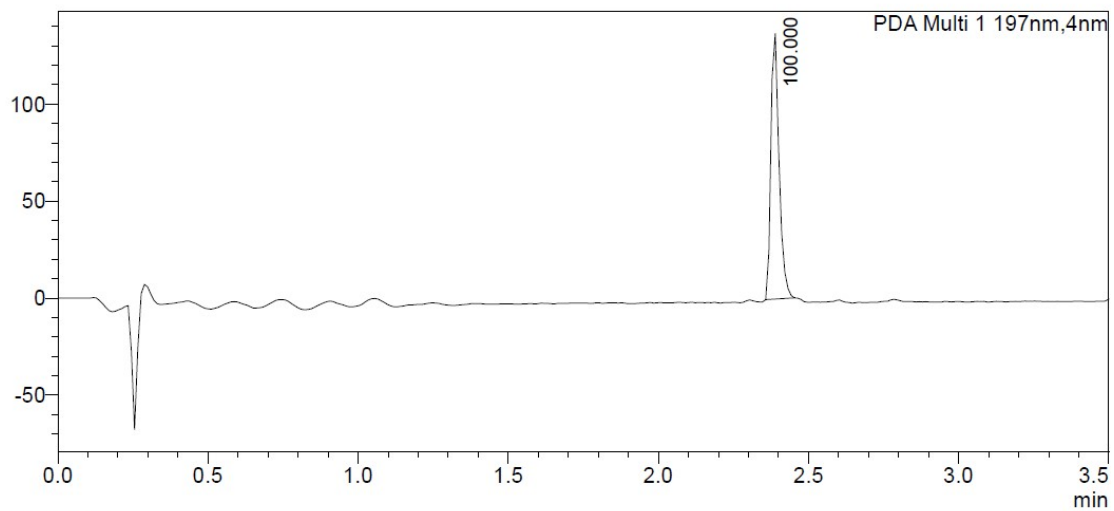BG Mode:Averaged 1.428-2.100(273-401) Segment 1 - Event 1

232.1
305.2
379.2
411.2
412.2
580.2

m/z

Figure S43. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-tyrosinate (*S*-TYR-5F-PICA, **35**).

UV Chromatogram

mAU

PDA Multi 1 197nm,4nm

100.000

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:5 Mode: Positive
Spectrum Mode:Averaged 2.394-2.415(457-461) Base Peak:427.2(10681895)
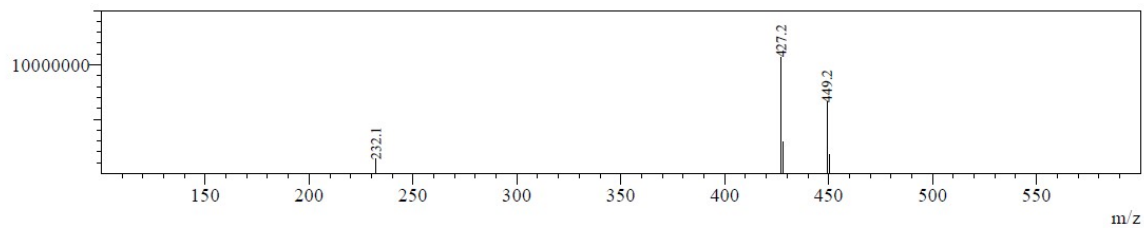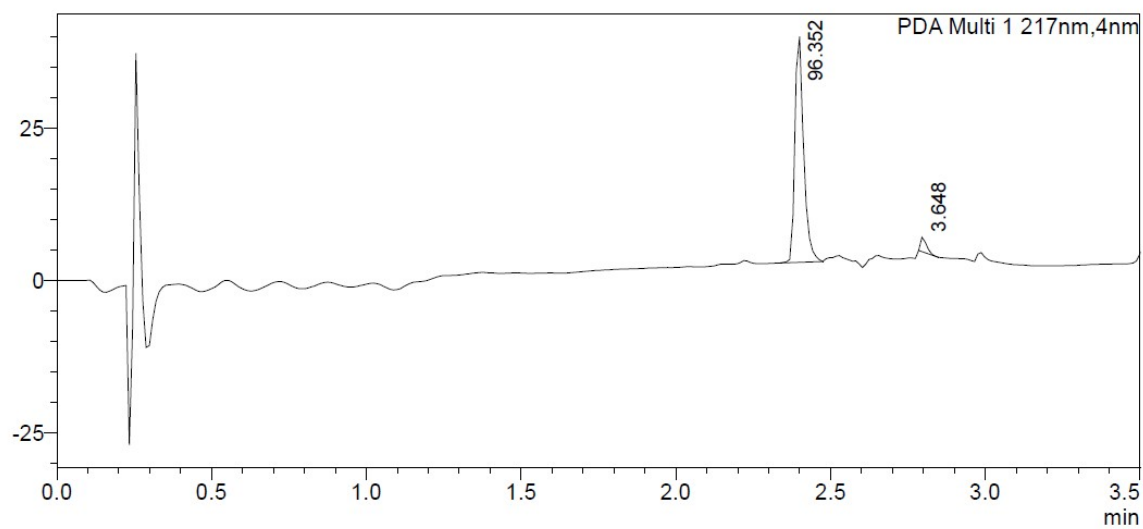BG Mode:Averaged 0.042-4.463(9-851) Segment 1 - Event 1

427.2

449.2

232.1

m/z

Figure S44. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-tyrosinate (*R*-TYR-5F-PICA, **36**).

UV Chromatogram

mAU

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:5 Mode: Positive
Spectrum Mode:Averaged 2.394-2.415(457-461) Base Peak:449.2(3579634)
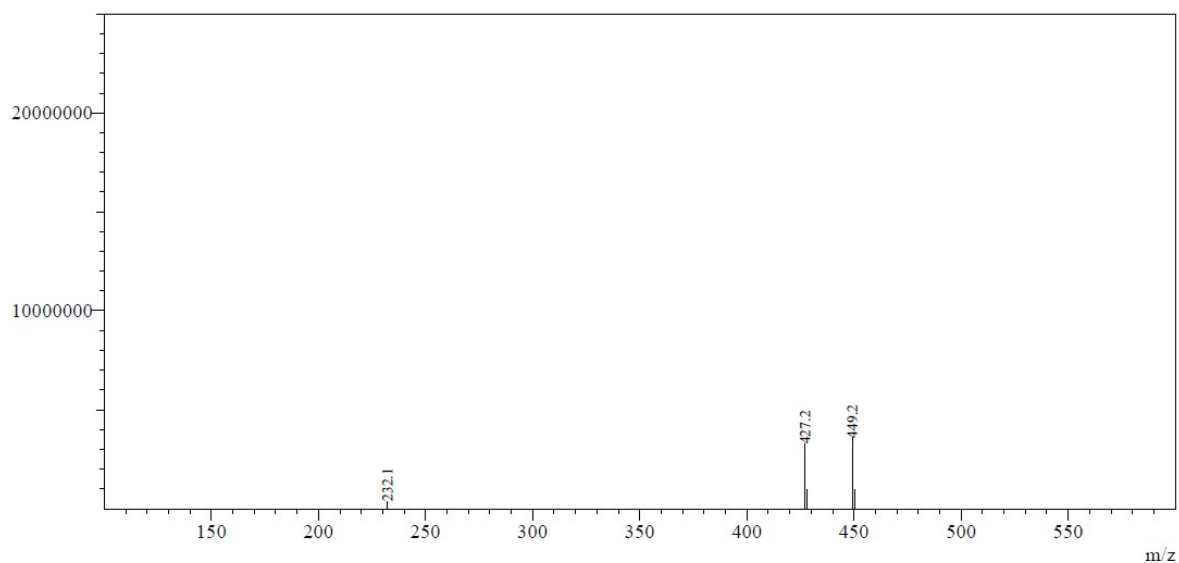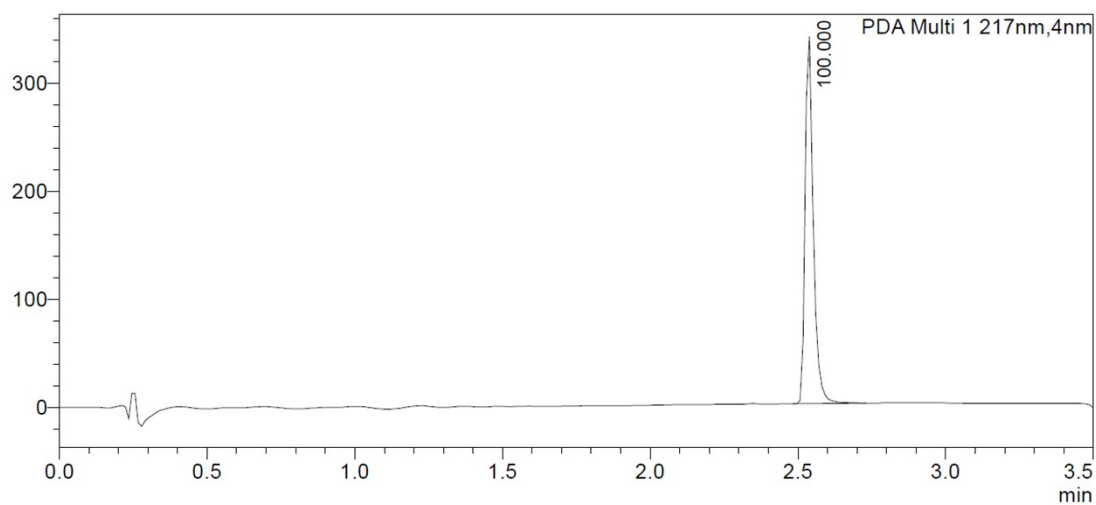BG Mode:Averaged 0.053-4.400(11-839) Segment 1 - Event 1

Figure S45. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-tryptophanate (*S*-TRP-5F-PICA, **37**).

UV Chromatogram

mAU

PDA Multi 1 217nm,4nm

100.000

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:6   Mode: Positive
Spectrum Mode:Averaged 2.541-2.552(485-487)   Base Peak:450.2(14490289)
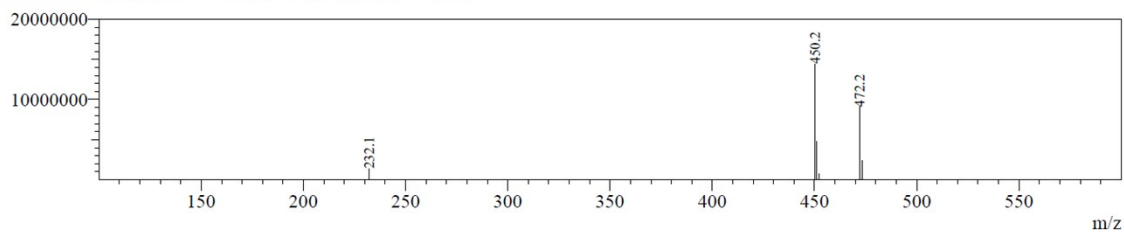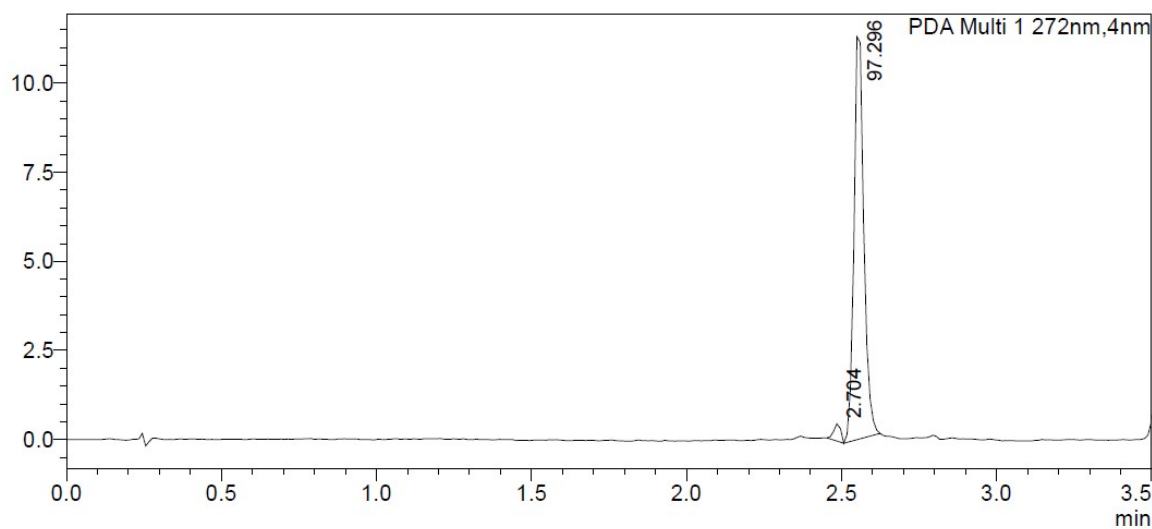BG Mode:Averaged 0.032-4.421(7-843) Segment 1 - Event 1

Figure S46. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-tryptophanate (*R*-TRP-5F-PICA, **38**).

UV Chromatogram

mAU

PDA Multi 1 272nm,4nm

97.296

2.704

min

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:8   Mode: Positive
Spectrum Mode:Averaged 2.478-2.636(473-503)   Base Peak:450.3(2020082)
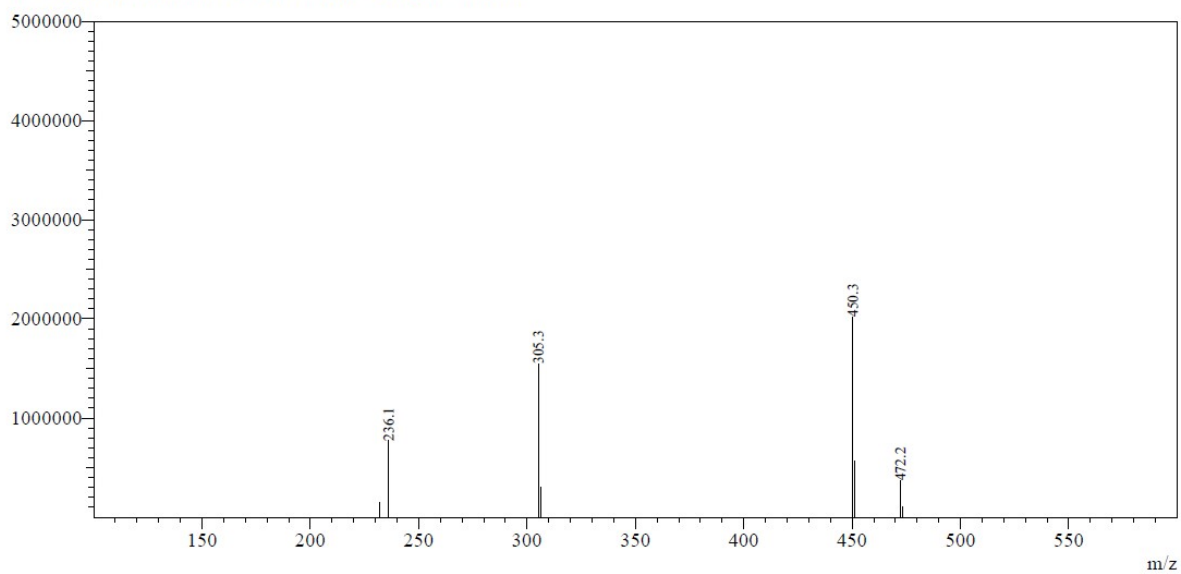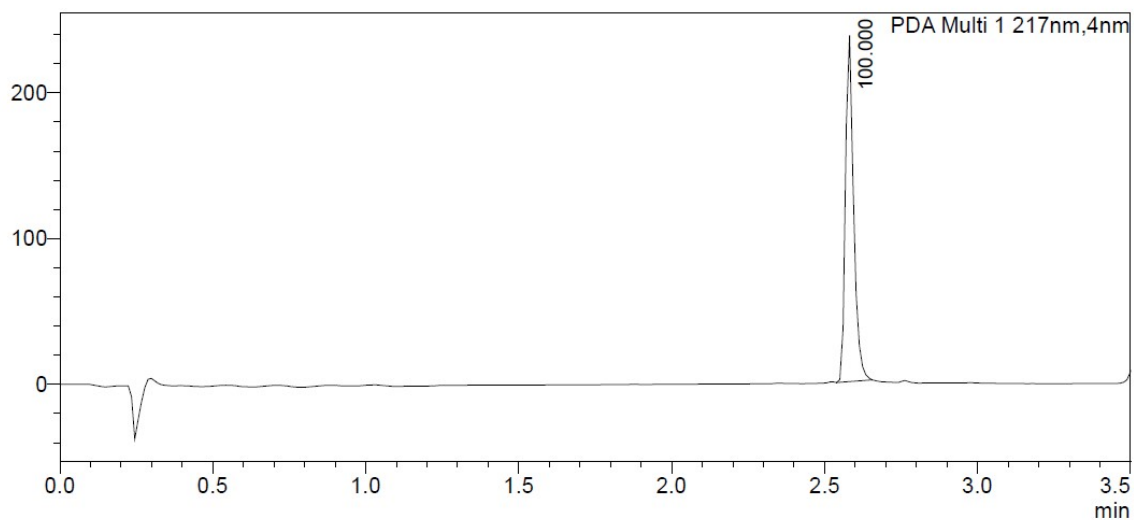BG Mode:Averaged 0.903-1.292(173-247) Segment 1 - Event 1

236.1

305.3

450.3

472.2

m/z

Figure S47. LCMS spectra for methyl N^6-(tert-butoxycarbonyl)-N^2-(1-(5-fluoropentyl)-1H-indole-3-carbonyl)-S-lysinate (**39a**)

UV Chromatogram

mAU

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:12   Mode: Positive
Spectrum Mode:Averaged 2.573-2.604(491-497)   Base Peak:514.2(14878315)
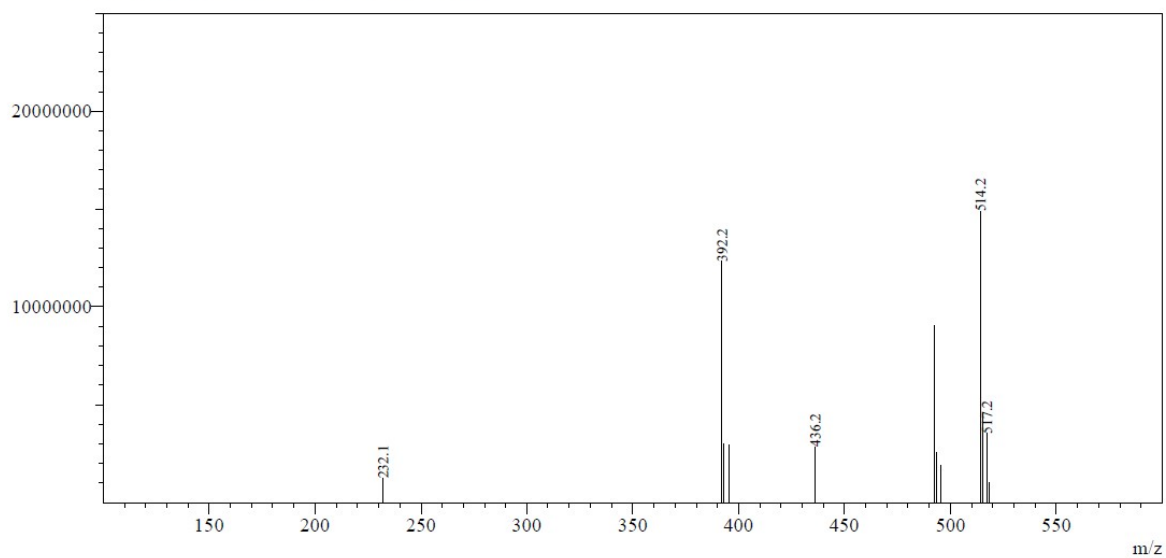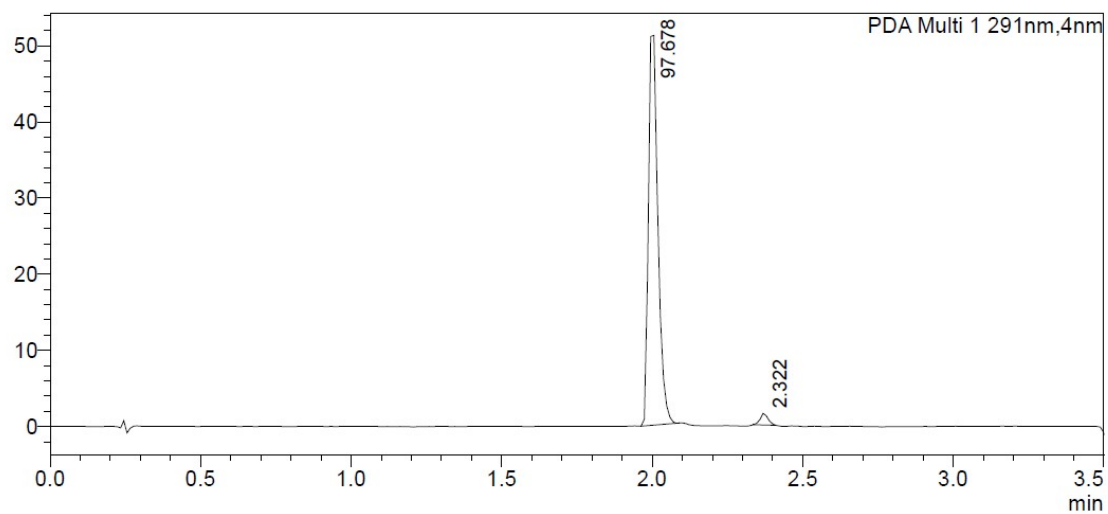BG Mode:Averaged 0.084-4.442(17-847) Segment 1 - Event 1

Figure S48. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-lysinate (*S*-LYS-5F-PICA **39**).

UV Chromatogram

mAU

PDA Multi 1 291nm,4nm

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:5 Mode: Positive
Spectrum Mode:Averaged 1.943-2.079(371-397) Base Peak:392.2(10334432)
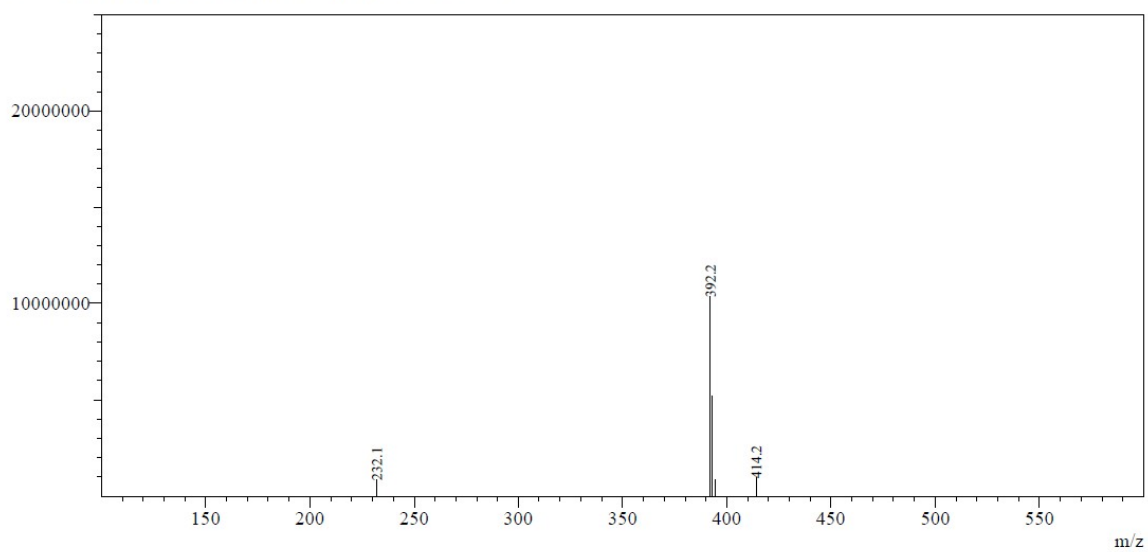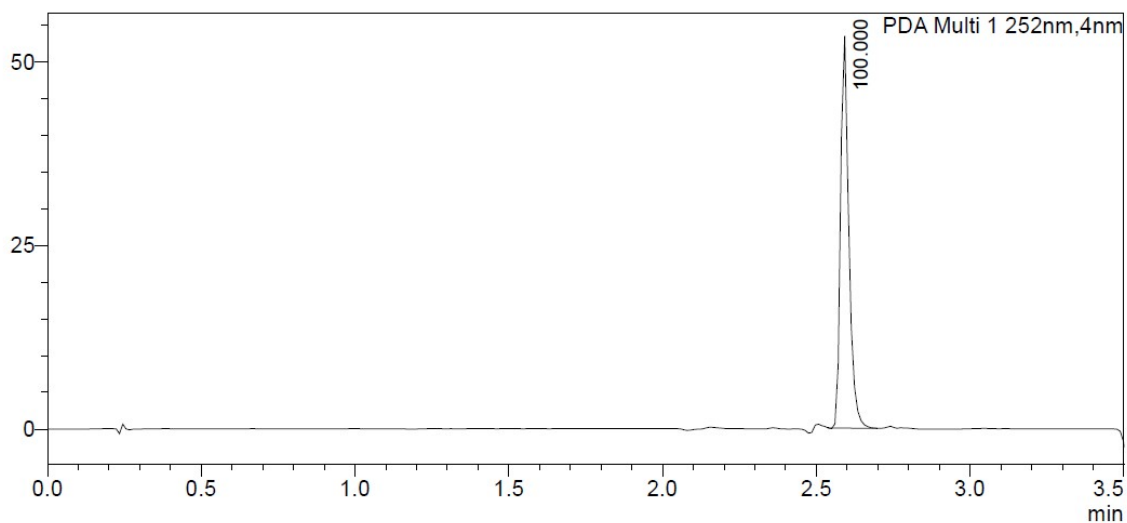BG Mode:Averaged 1.292-1.701(247-325) Segment 1 - Event 1

Figure S49. LCMS spectra for methyl N^6-(tert-butoxycarbonyl)-N^2-(1-(5-fluoropentyl)-1H-indole-3-carbonyl)-R-lysinate (**40a**).

UV Chromatogram

mAU

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:11   Mode: Positive
Spectrum Mode:Averaged 2.510-2.657(479-507)   Base Peak:392.2(8125304)
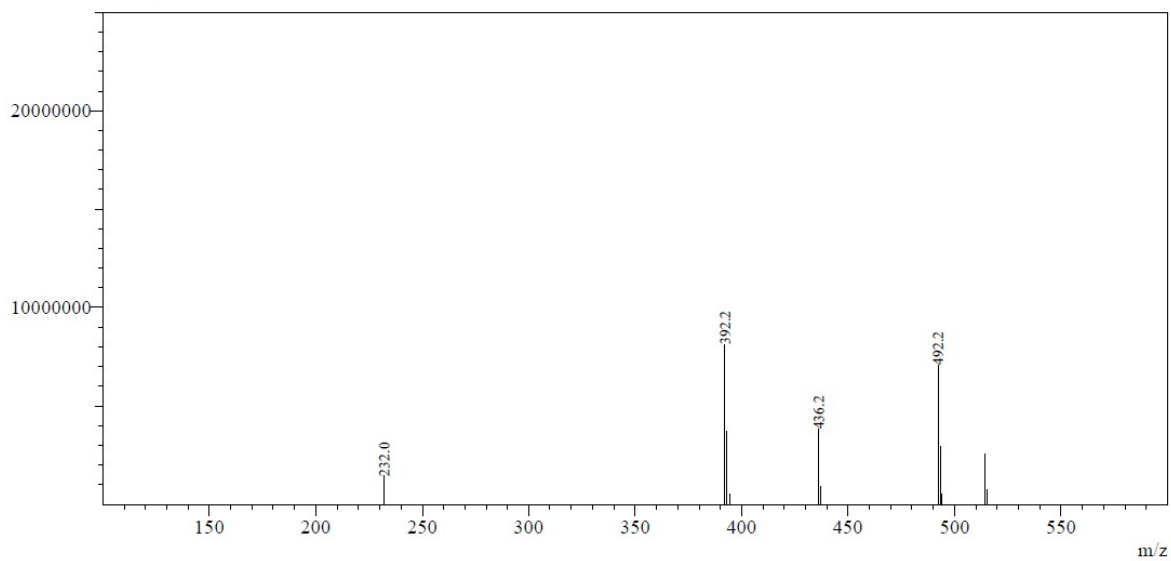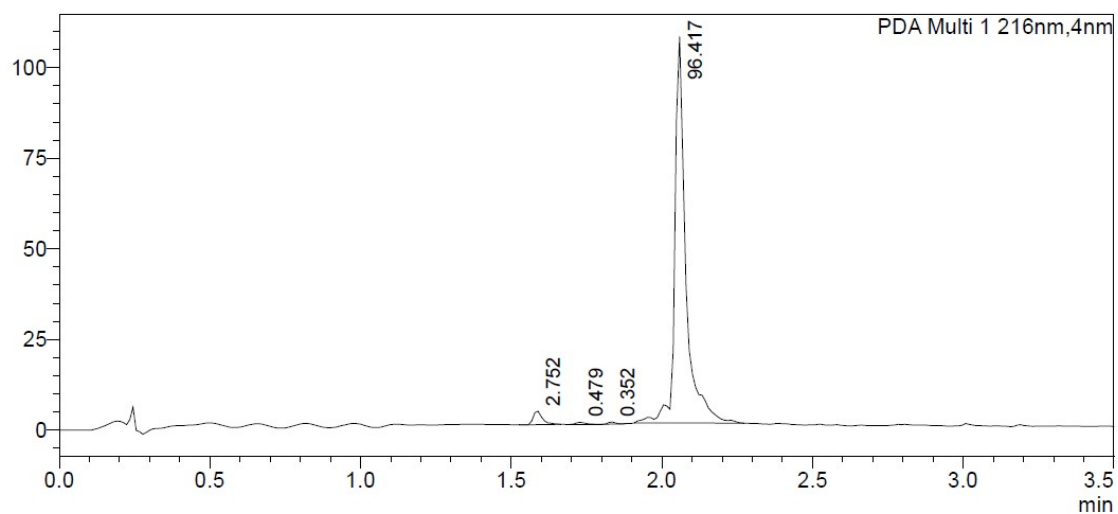BG Mode:Averaged 1.649-2.237(315-427) Segment 1 - Event 1

Figure S50. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-lysinate (*R*-LYS-5F-PICA, **40**).

UV Chromatogram

mAU

PDA Multi 1 216nm,4nm

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:4 Mode: Positive
Spectrum Mode:Averaged 2.048-2.079(391-397) Base Peak:392.3(17143219)
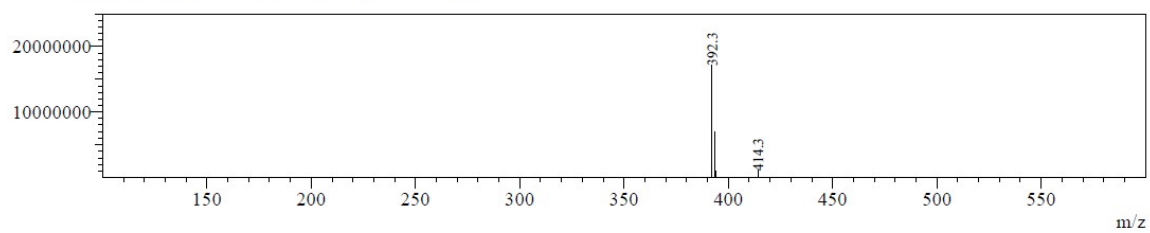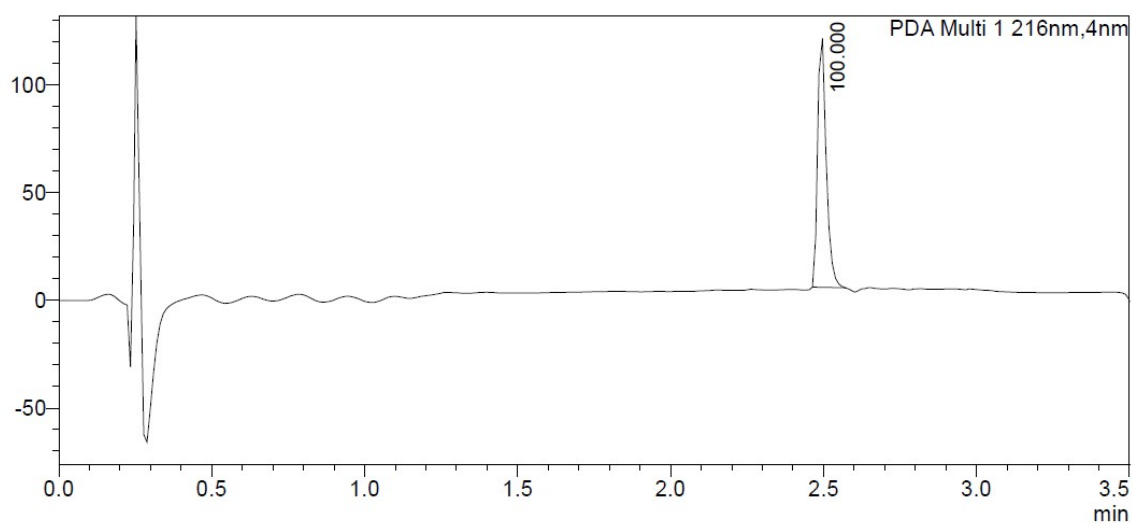BG Mode:Averaged 0.021-4.484(5-855) Segment 1 - Event 1

Figure S51. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-methioninate (*S*-MET-5F-PICA, **41**).

UV Chromatogram

mAU

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:7 Mode: Positive
Spectrum Mode:Averaged 2.489-2.510(475-479) Base Peak:395.2(13450163)
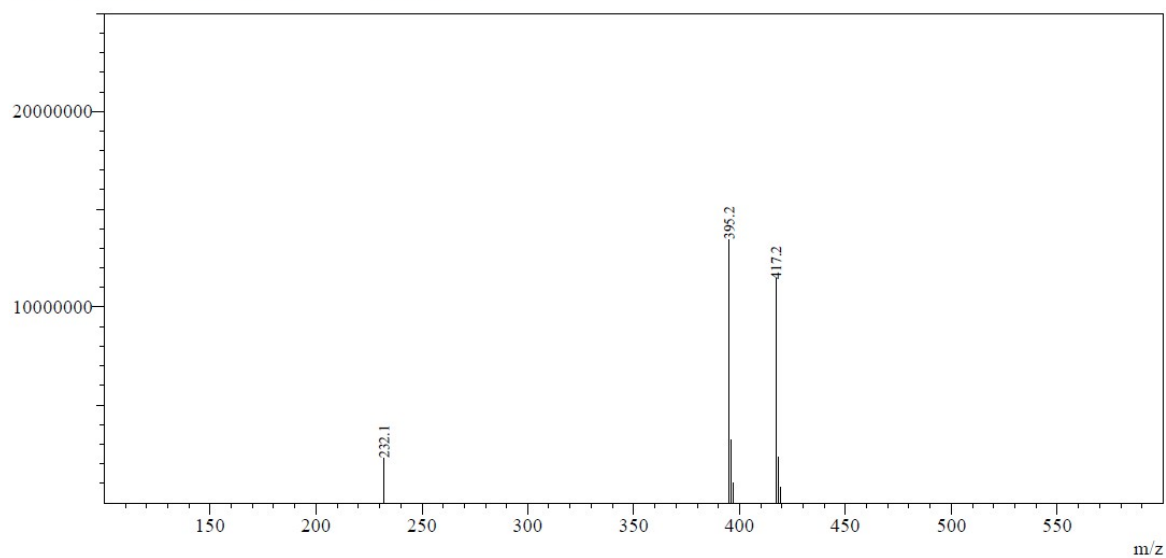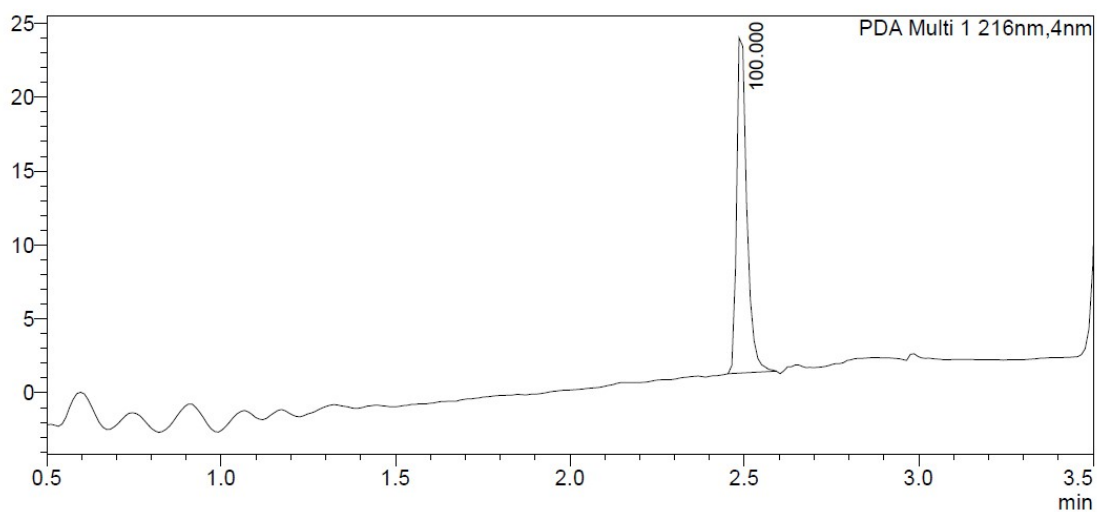BG Mode:Averaged 0.053-4.358(11-831) Segment 1 - Event 1

Figure S52. LCMS spectra for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-methioninate (*R*-MET-5F-PICA, **42**).

UV Chromatogram

mAU

PDA Multi 1 216nm,4nm

100.000

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:8 Mode: Positive
Spectrum Mode:Averaged 2.489-2.531(475-483) Base Peak:417.1(4811180)
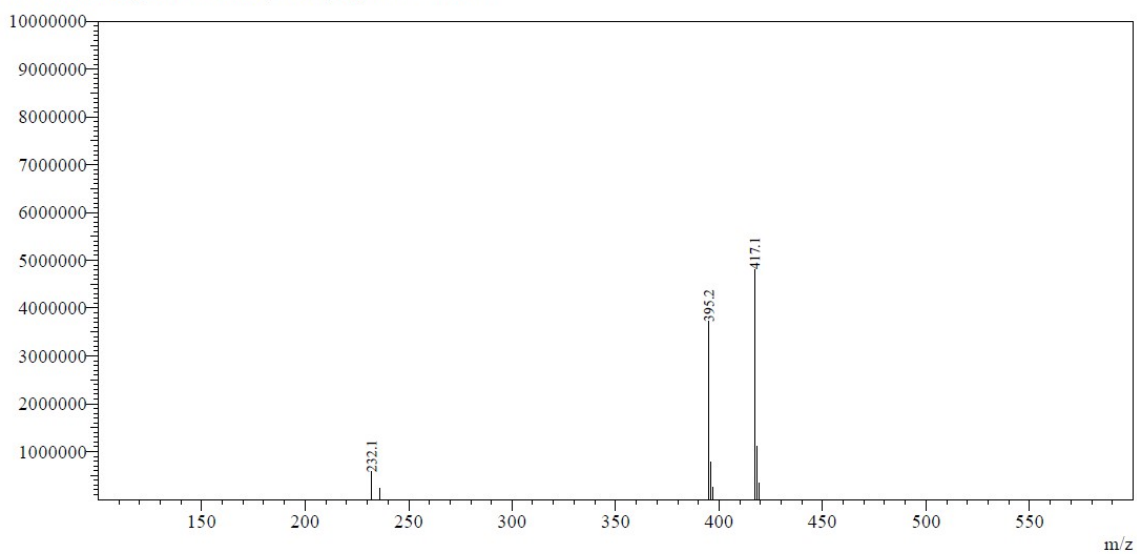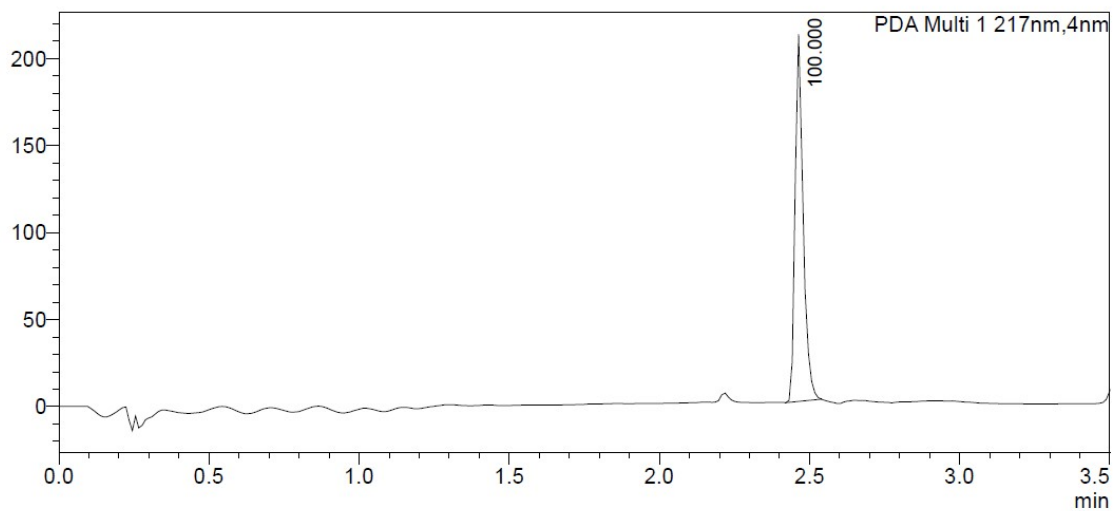BG Mode:Averaged 0.105-4.358(21-831) Segment 1 - Event 1

232.1

395.2

417.1

m/z

Figure S53. LCMS spectra for *tert*-butyl (S)-5-amino-2-(1-(5-fluoropentyl)-1*H*-indole-3-carboxamido)-5-oxopentanoate (**43a**)

UV Chromatogram

mAU

PDA Multi 1 217nm,4nm

100.000

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:8 Mode: Positive
Spectrum Mode:Averaged 2.457-2.499(469-477) Base Peak:434.2(13542104)
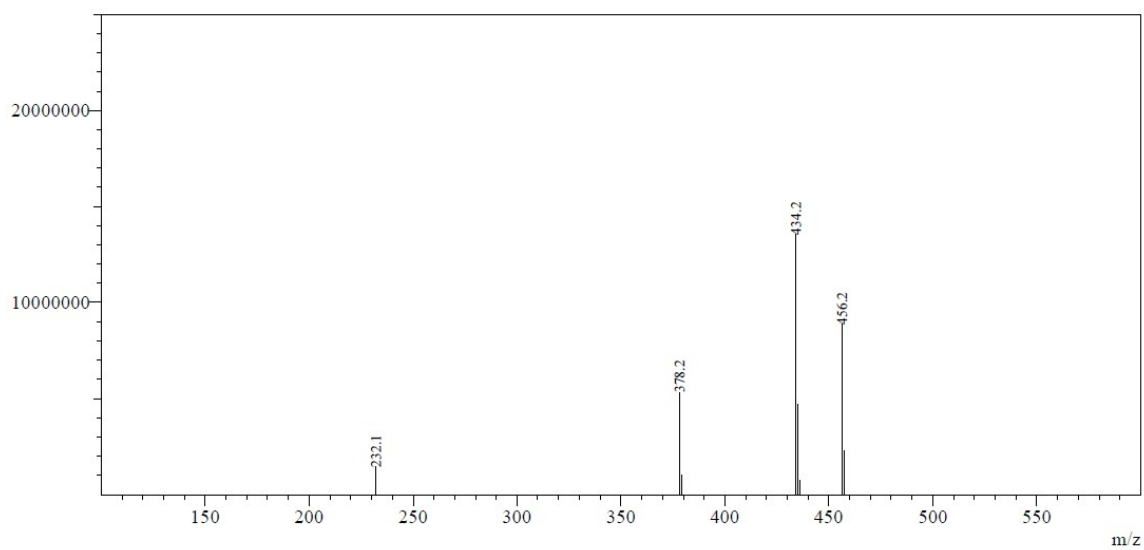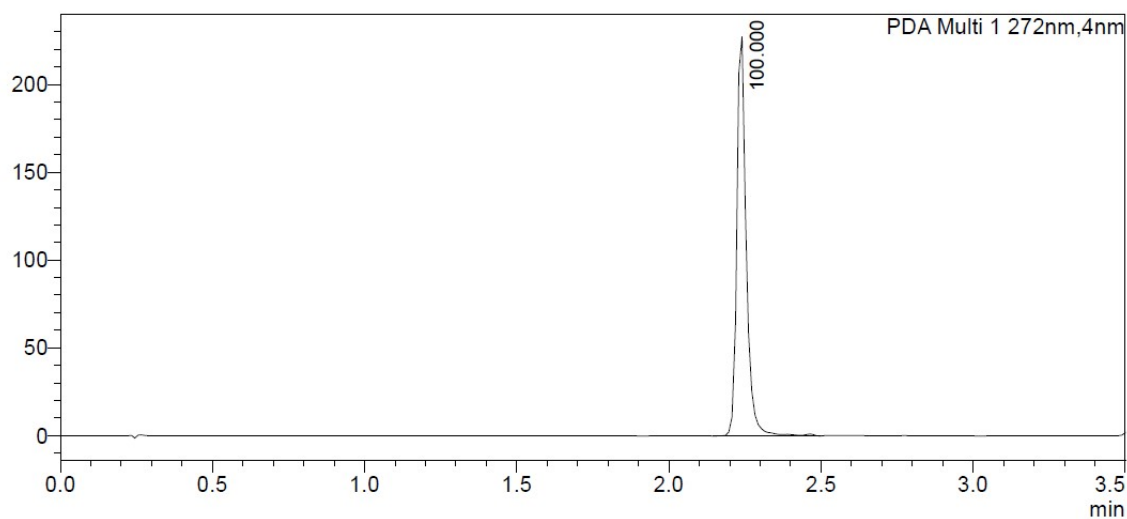BG Mode:Averaged 0.074-4.400(15-839) Segment 1 - Event 1

Figure S54. LCMS spectra for methyl (S)-5-amino-2-(1-(5-fluoropentyl)-1*H*-indole-3-carboxamido)-5-oxopentanoate (*S*-GLN-5F-PICA, **43**).

UV Chromatogram

mAU

PDA Multi 1 272nm,4nm

100.000

MS Spectra

Line#:1 R.Time:----(Scan#:----)
MassPeaks:7 Mode: Positive
Spectrum Mode:Averaged 2.184-2.405(417-459) Base Peak:392.2(9788160)
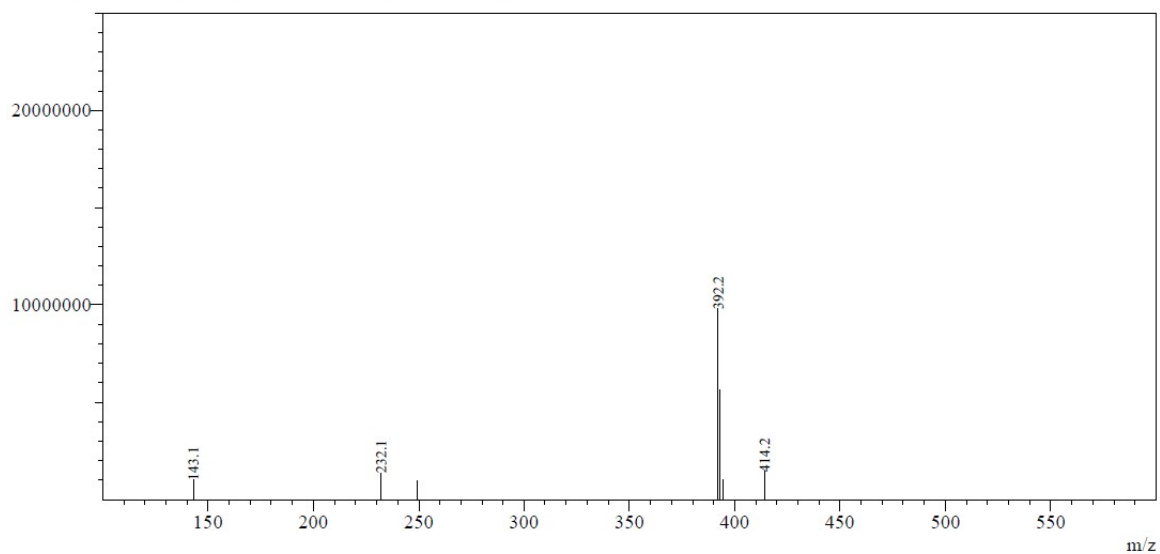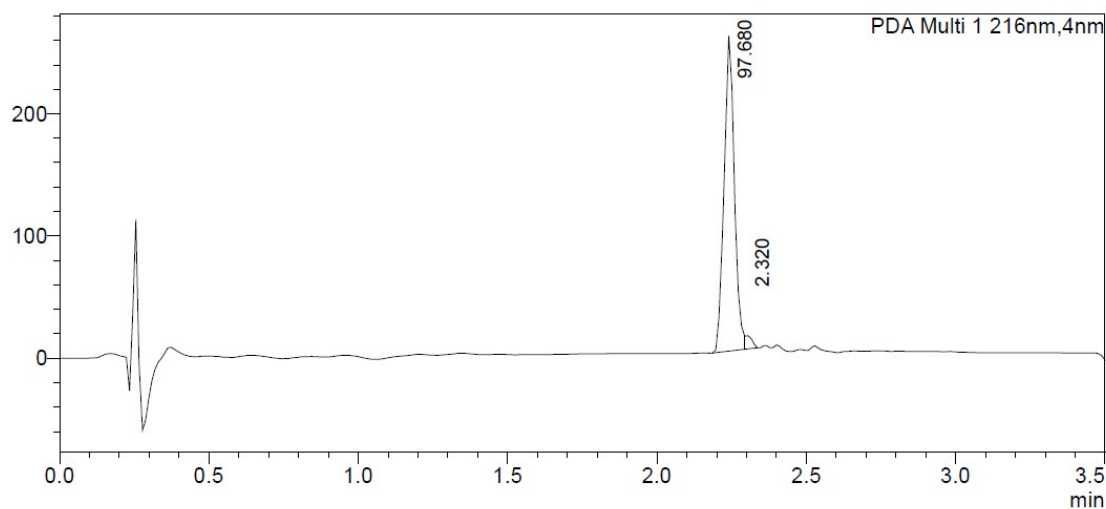BG Mode:Averaged 1.008-1.775(193-339) Segment 1 - Event 1

Figure S55. LCMS spectra for methyl (R)-5-amino-2-(1-(5-fluoropentyl)-1*H*-indole-3-carboxamido)-5-oxopentanoate (*R*-GLN-5F-PICA, **44**).

UV Chromatogram

mAU

PDA Multi 1 216nm,4nm

MS Spectra

Line#:1   R.Time:----(Scan#:----)
MassPeaks:10   Mode: Positive
Spectrum Mode:Averaged 2.226-2.268(425-433)   Base Peak:392.2(12070248)
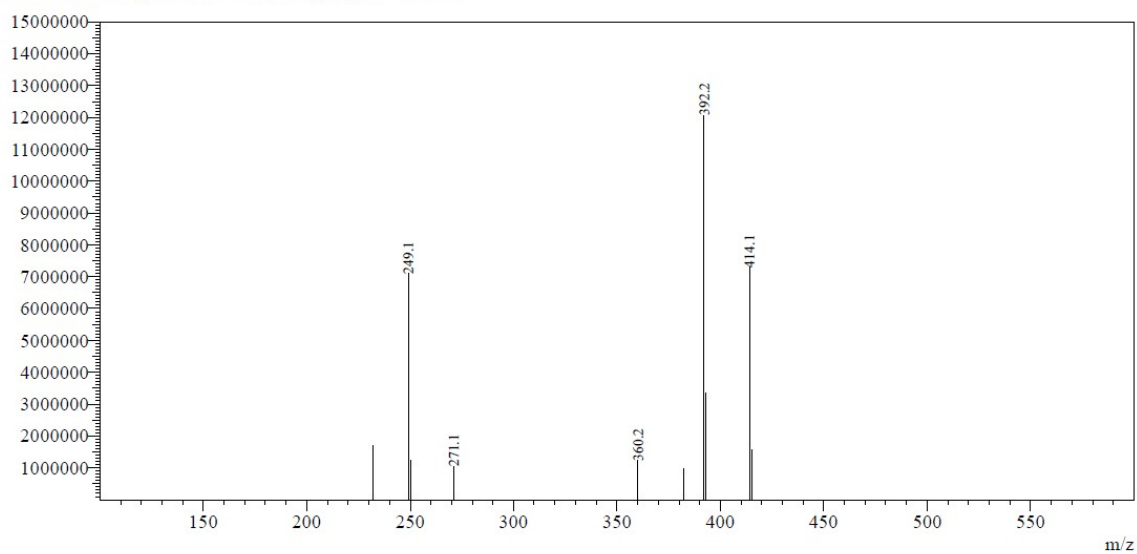BG Mode:Averaged 0.000-4.421(1-843) Segment 1 - Event 1

Figure S56. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)glycinate (GLY-5F-PICA, **16**).

Figure S57. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-alaninate (*S*-ALA-5F-PICA, **17**).

Figure S58. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*D*-alaninate (*R*-ALA-5F-PICA, **18**).
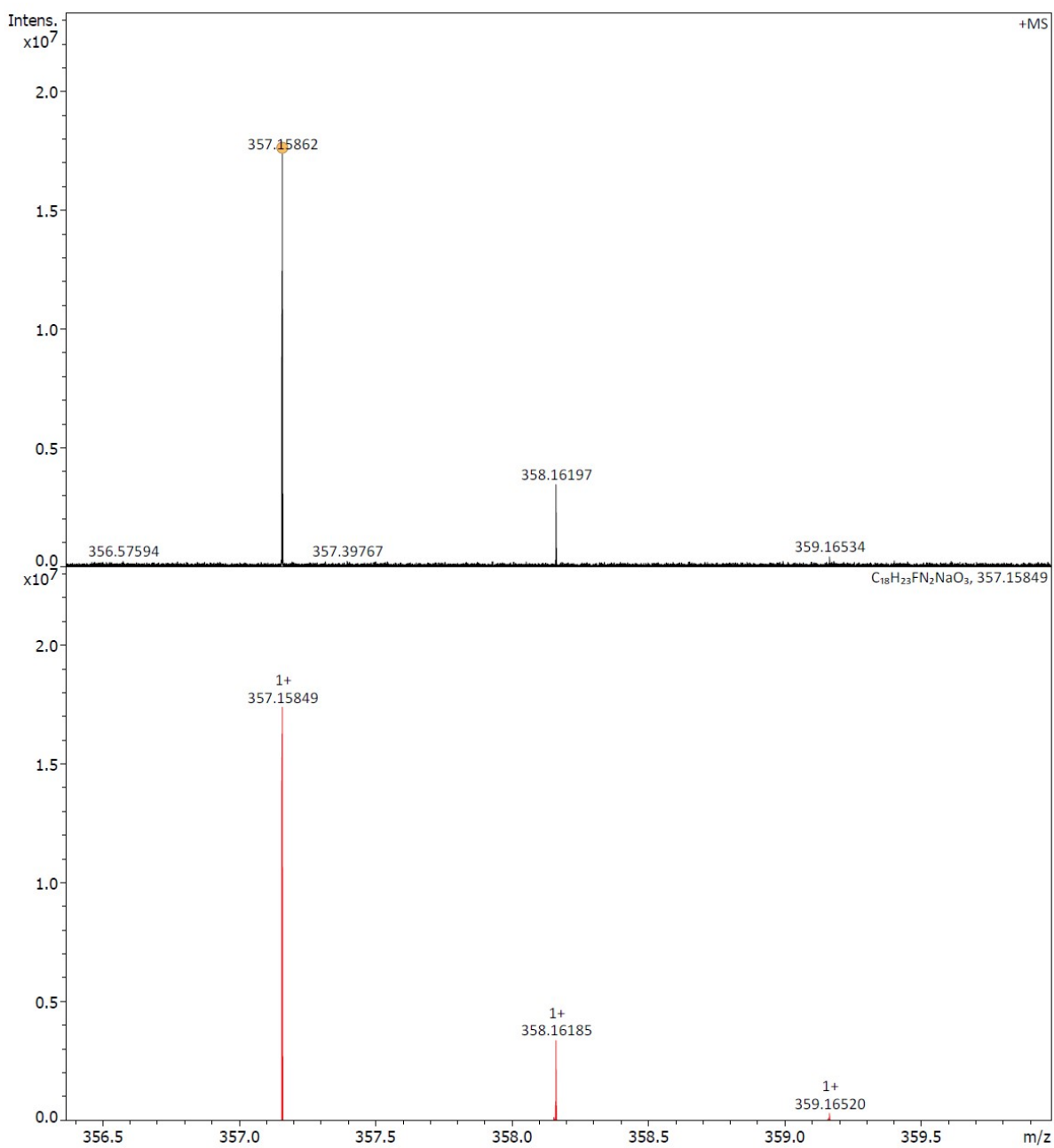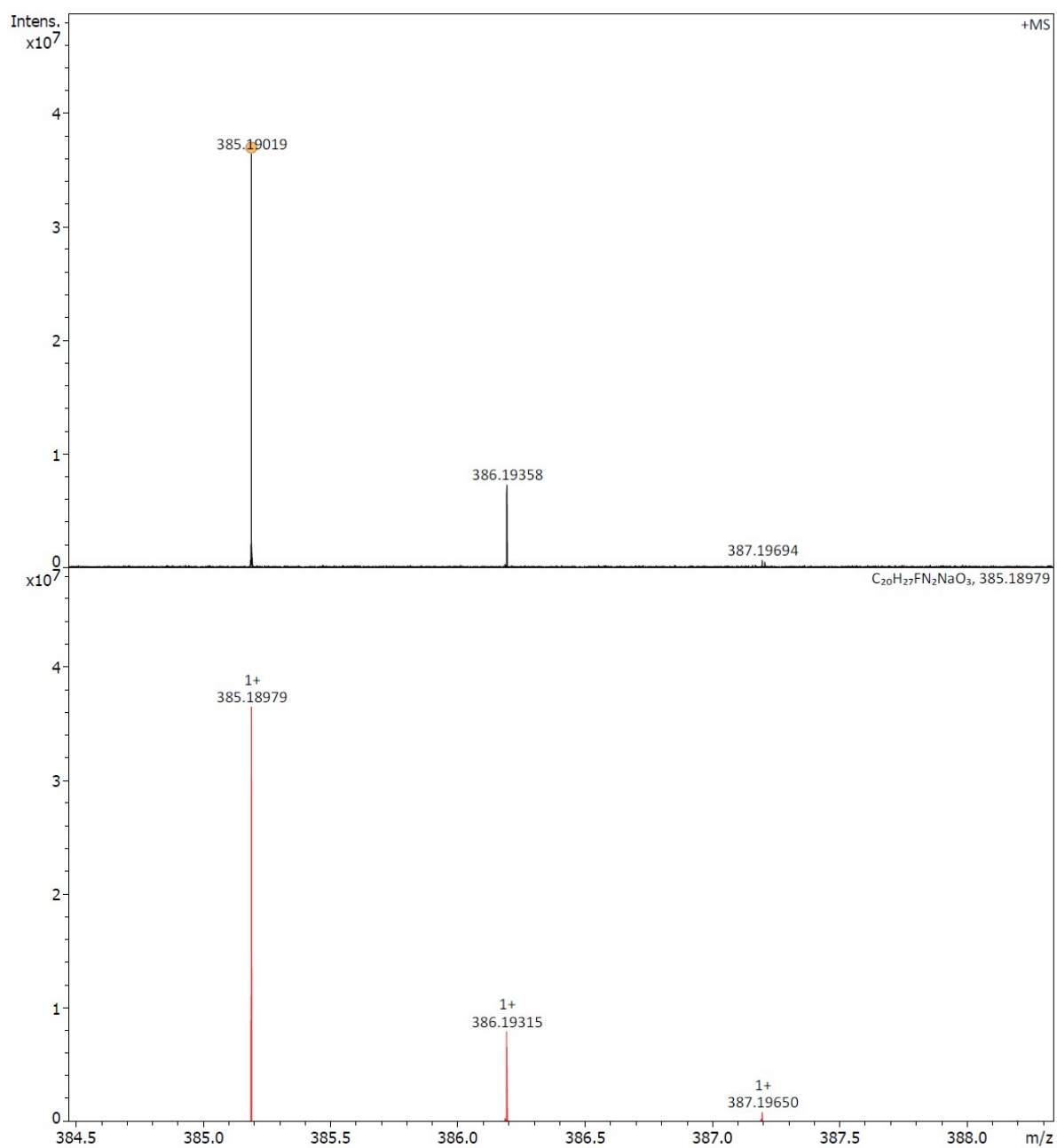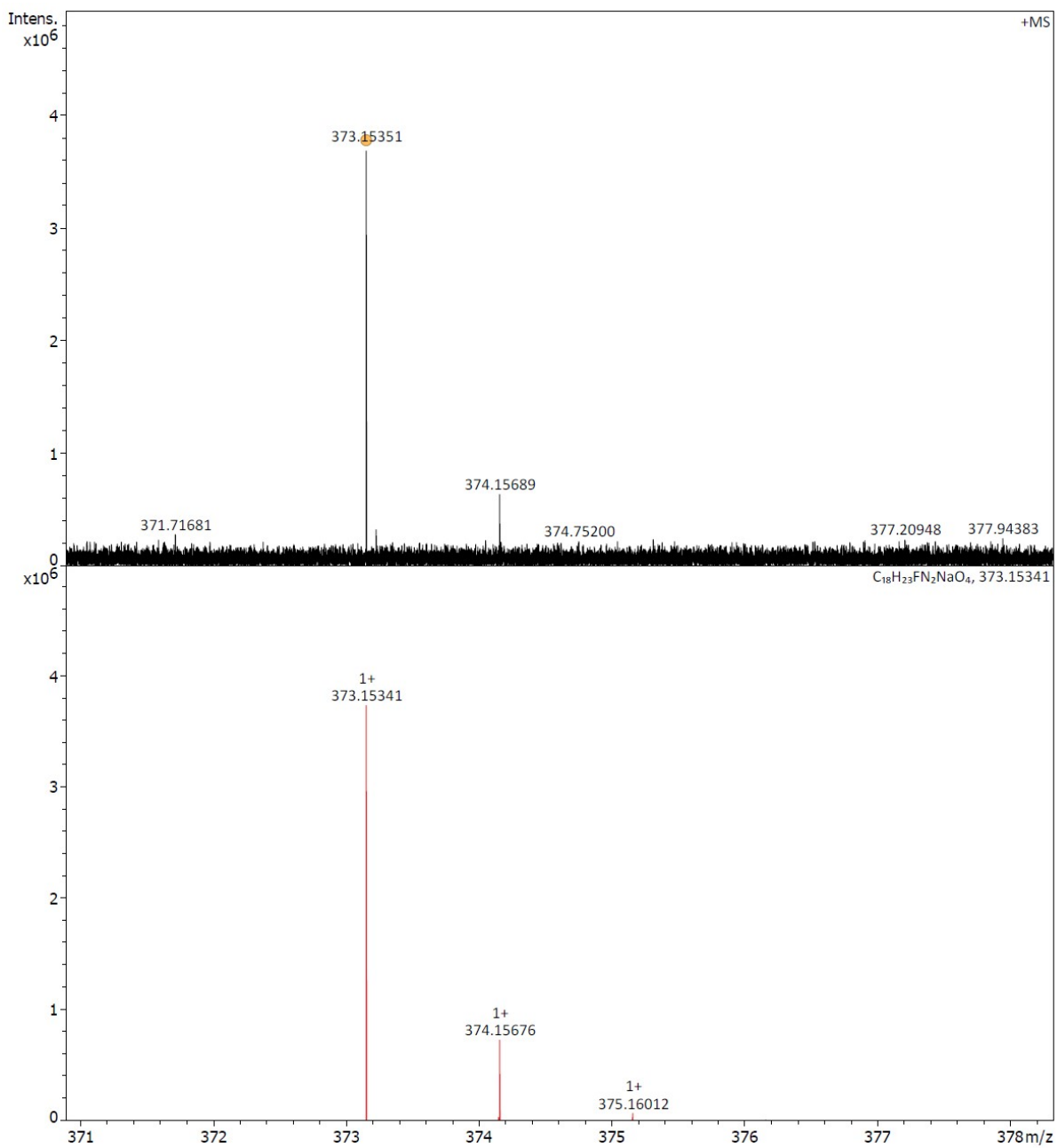
Figure S59. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-valinate (*R*-MMB-5F-PICA, **20**).

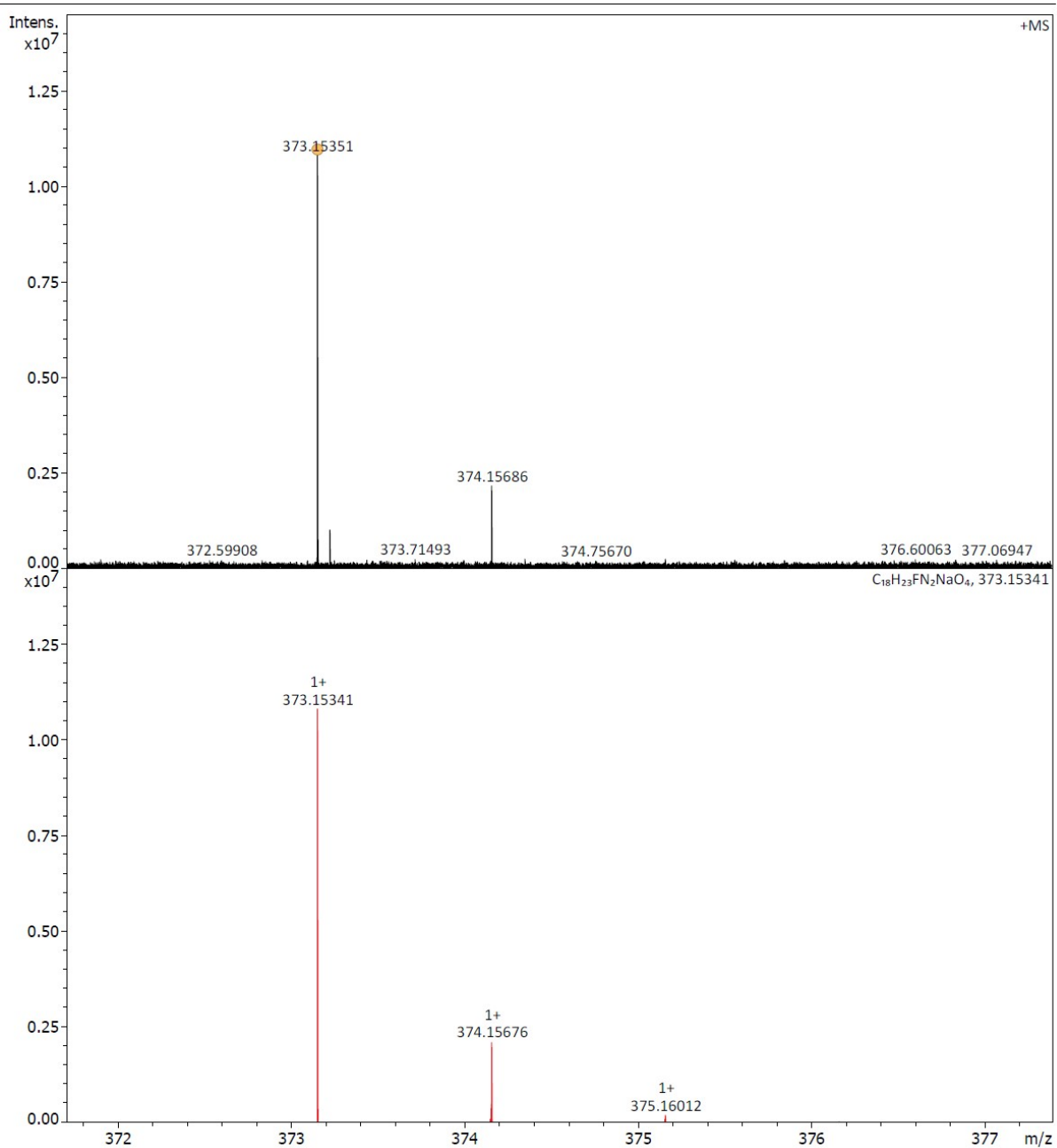**Figure S60.** HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-serinate (*S*-SER-5F-PICA, **21**).
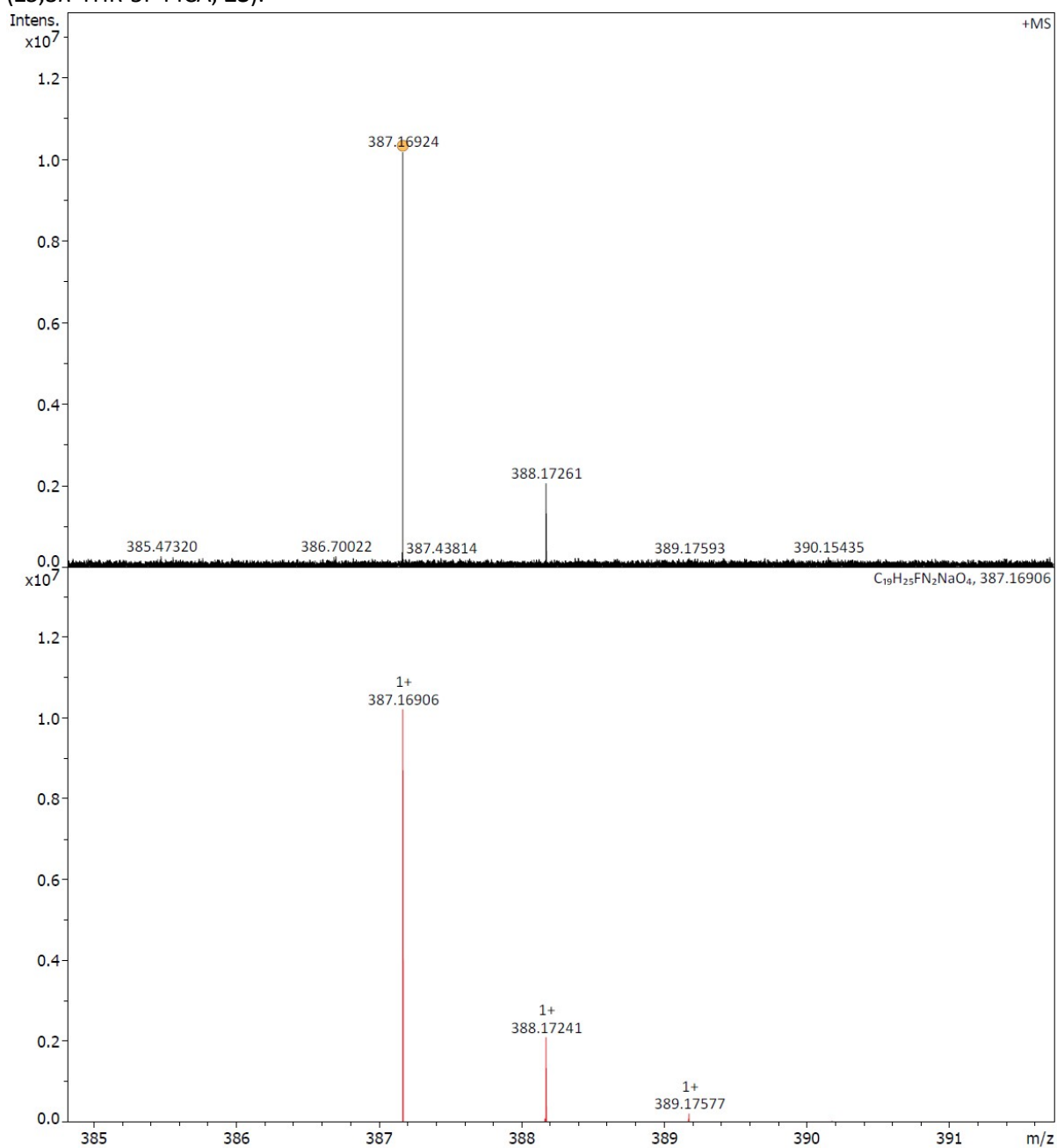
Figure S61. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-serinate (*R*-SER-5F-PICA, **22**).

Figure S62. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-2*S*,3*R*-threoninate (2*S*,3*R*-THR-5F-PICA, **23**).

Figure S63. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-2*R*,3*S*-threoninate (2*R*,3*S*-THR-5F-PICA, **24**).
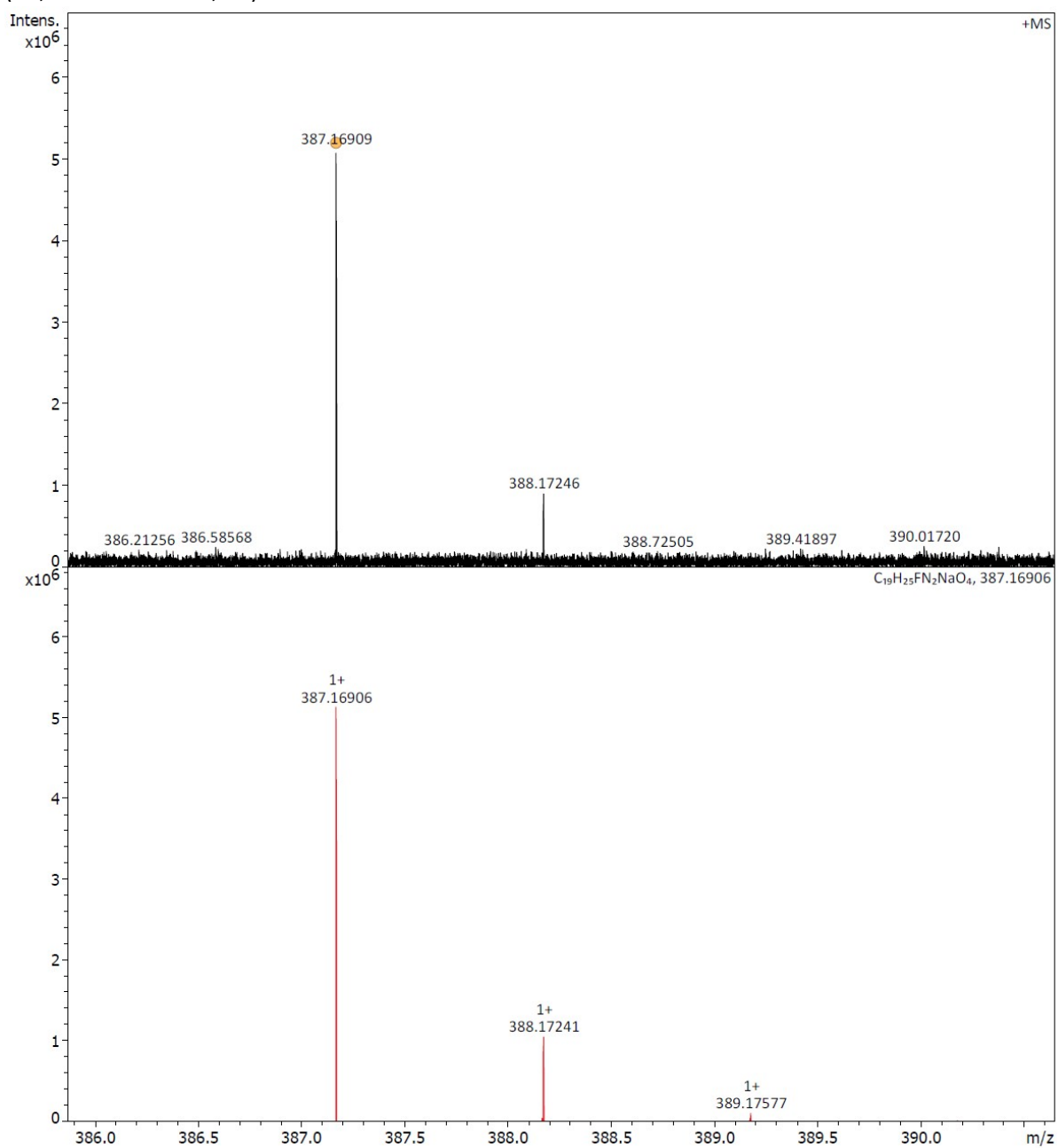
Figure S64. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-prolinate (*S*-PRO-5F-PICA, **25**).
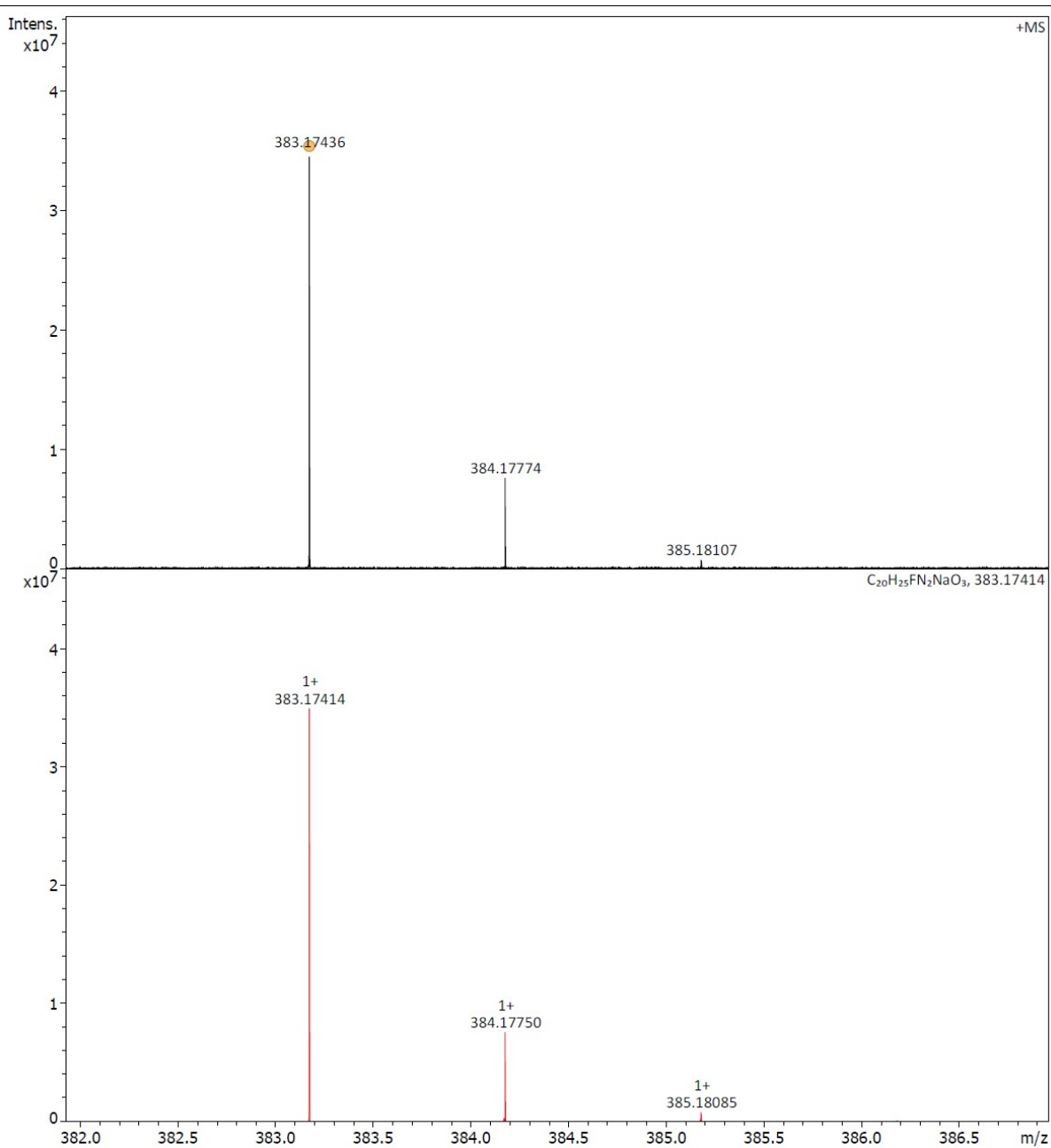
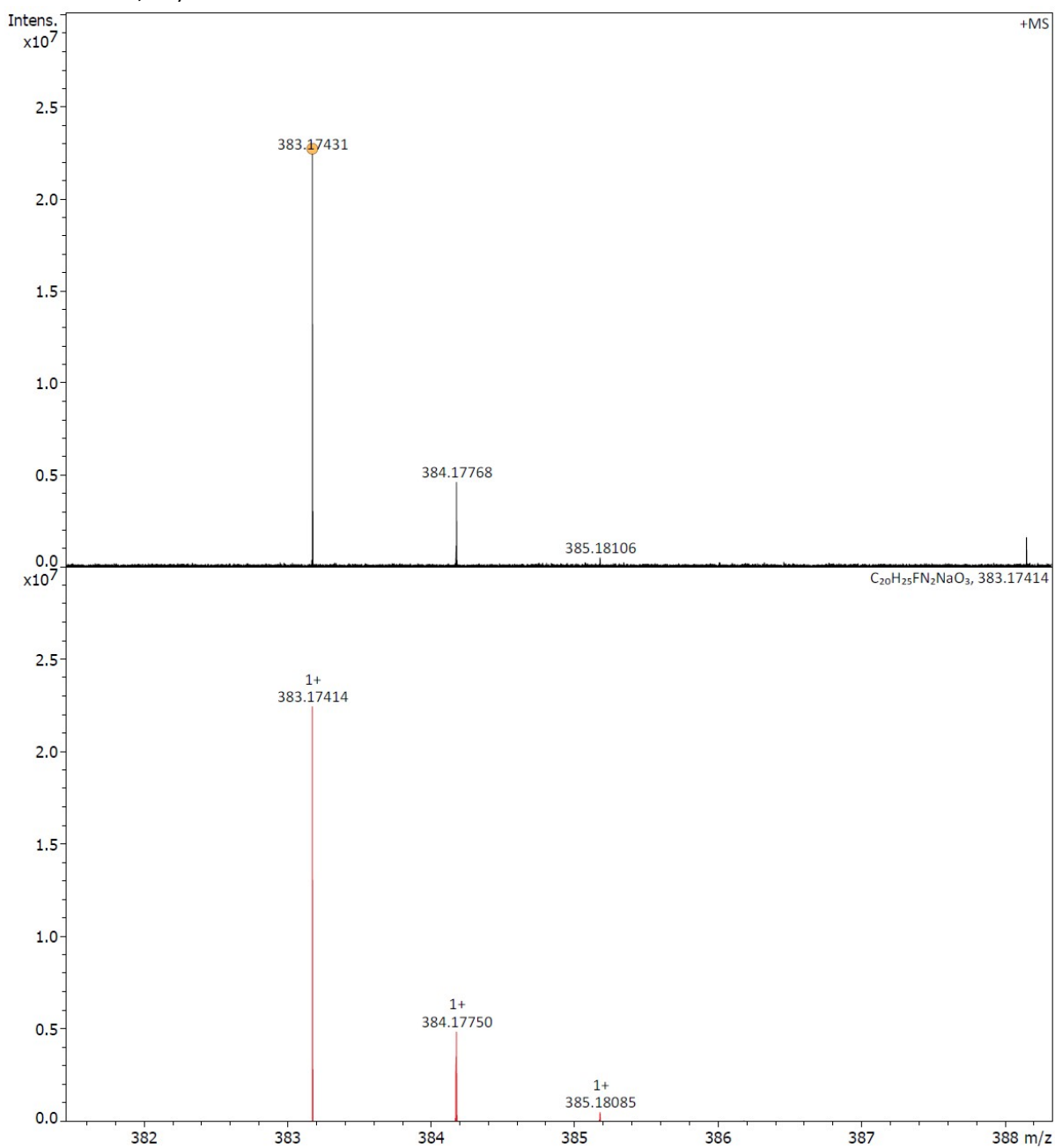**Figure S65.** HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-prolinate (*R*-PRO-5F-PICA, **26**).

Figure S66. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-leucinate (*S*-LEU-5F-PICA, **27**).
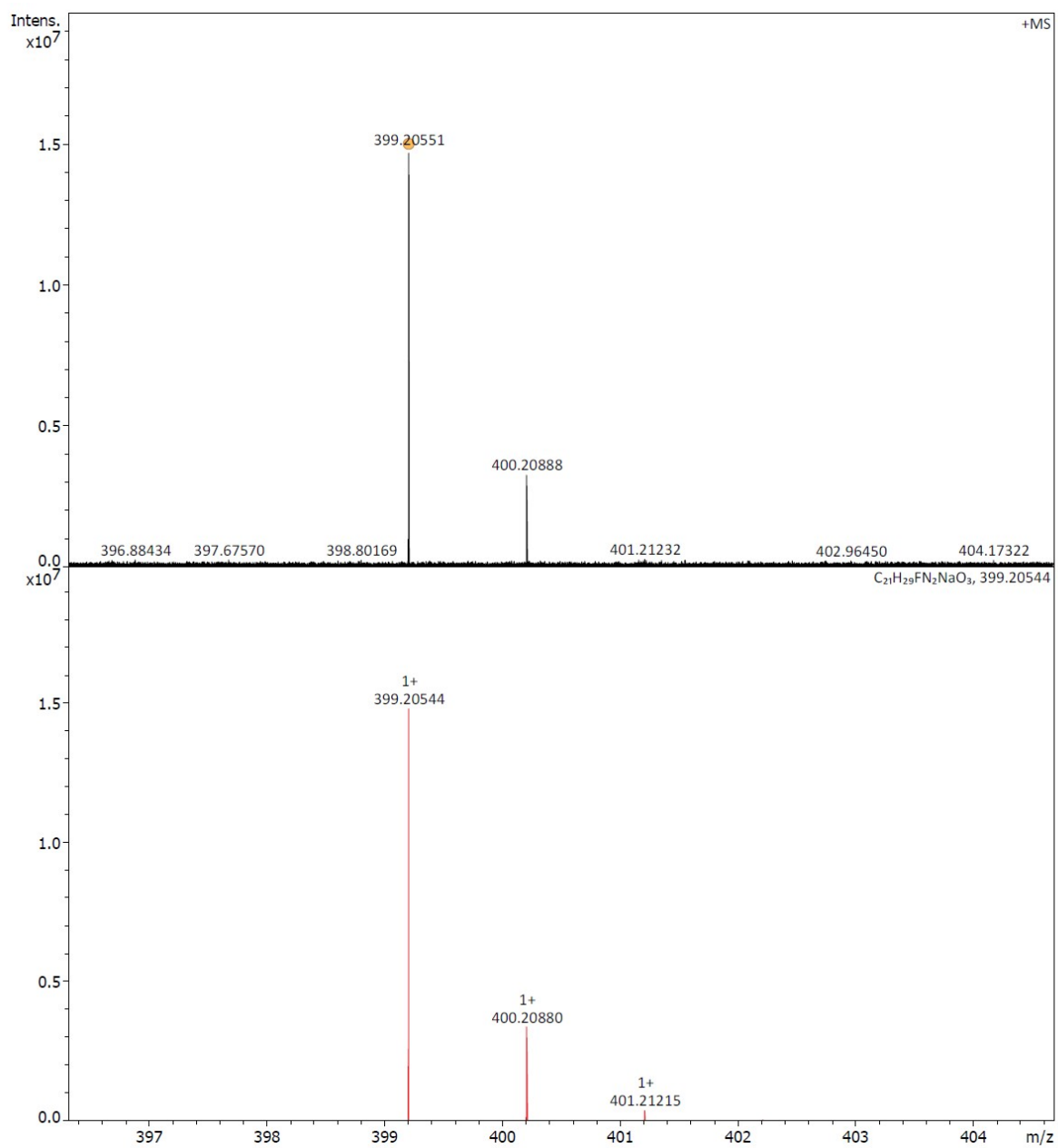
Figure S67. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-leucinate (*R*-LEU-5F-PICA, **28**).
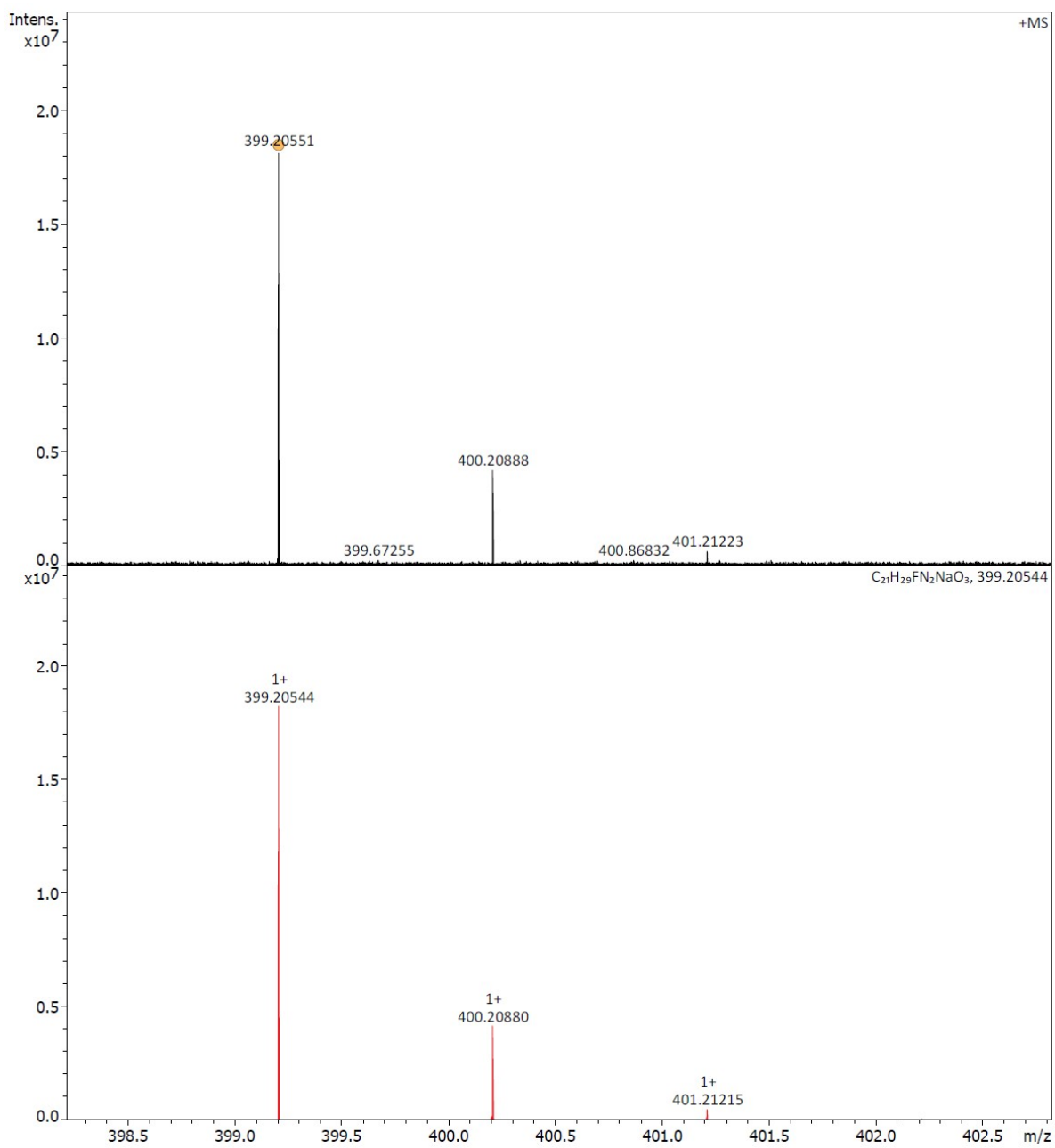
Figure S68. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-isoleucinate (*S*-ILE-5F-PICA, **29**).
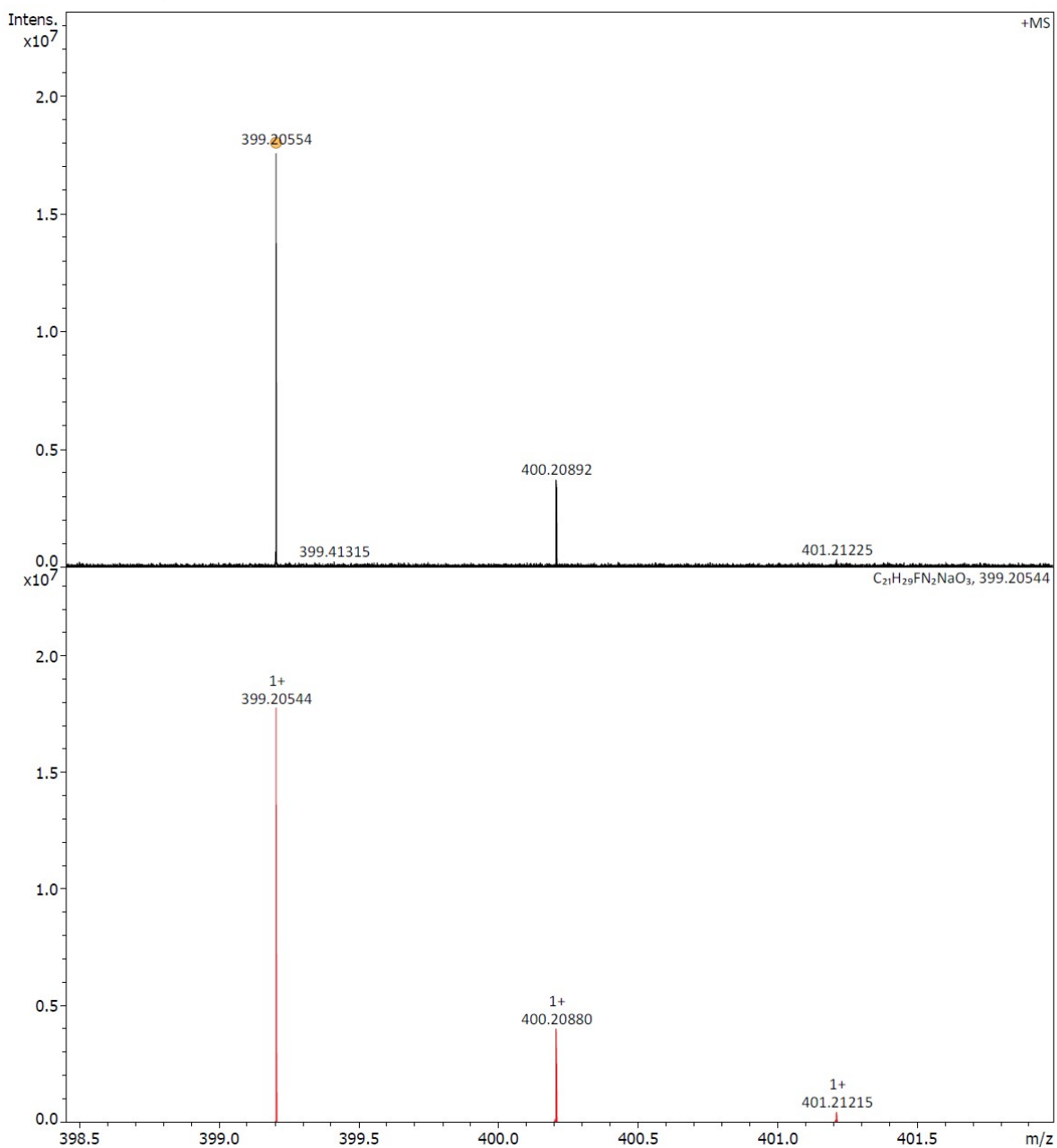
Figure S69. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-isoleucinate (*R*-ILE-5F-PICA, **30**).
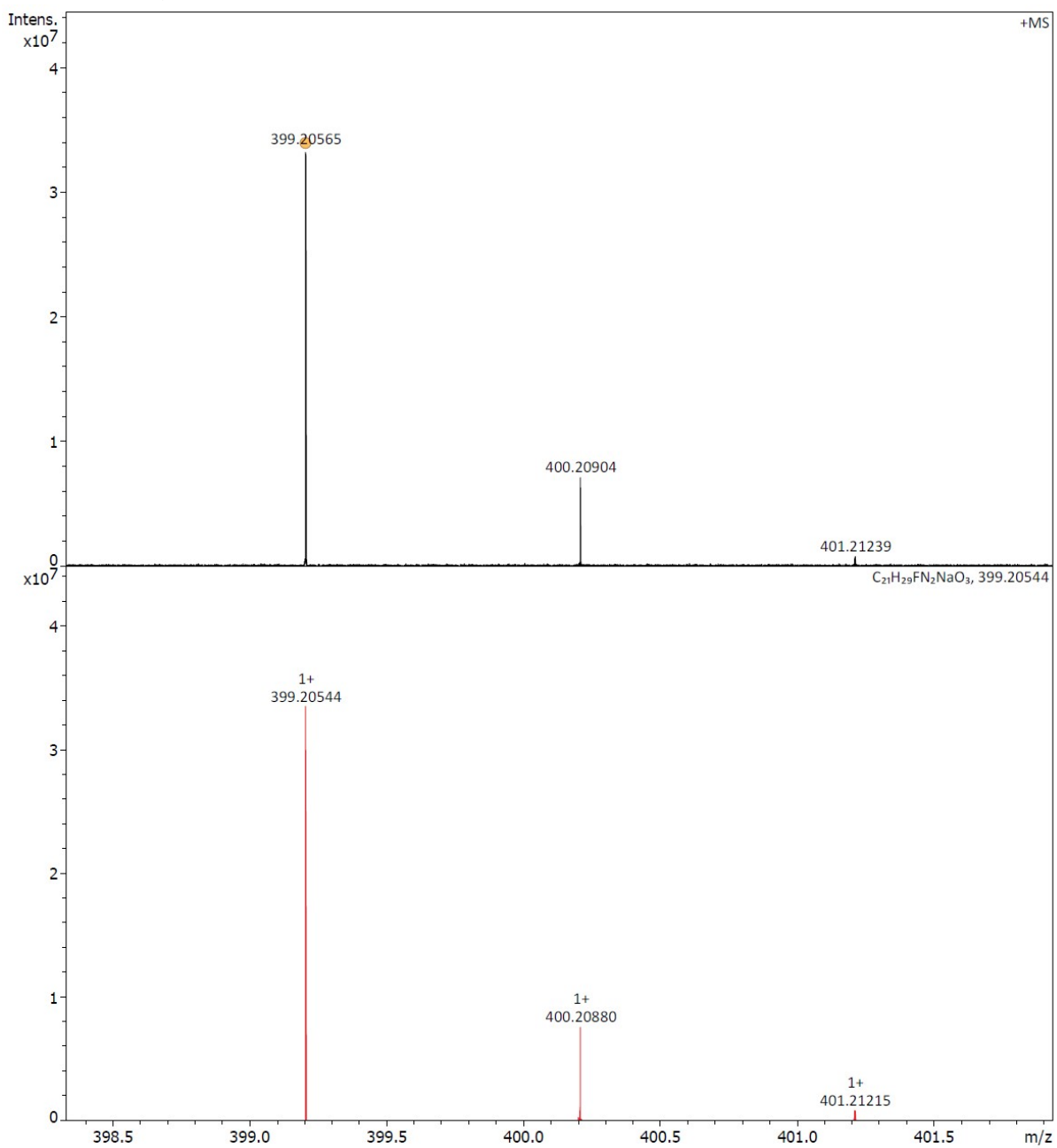
Figure S70. HRMS spectrum for methyl (*R*)-2-(1-(5-fluoropentyl)-1*H*-indole-3-carboxamido)-3,3-dimethylbutanoate (*R*-MDMB-5F-PICA, **32**).
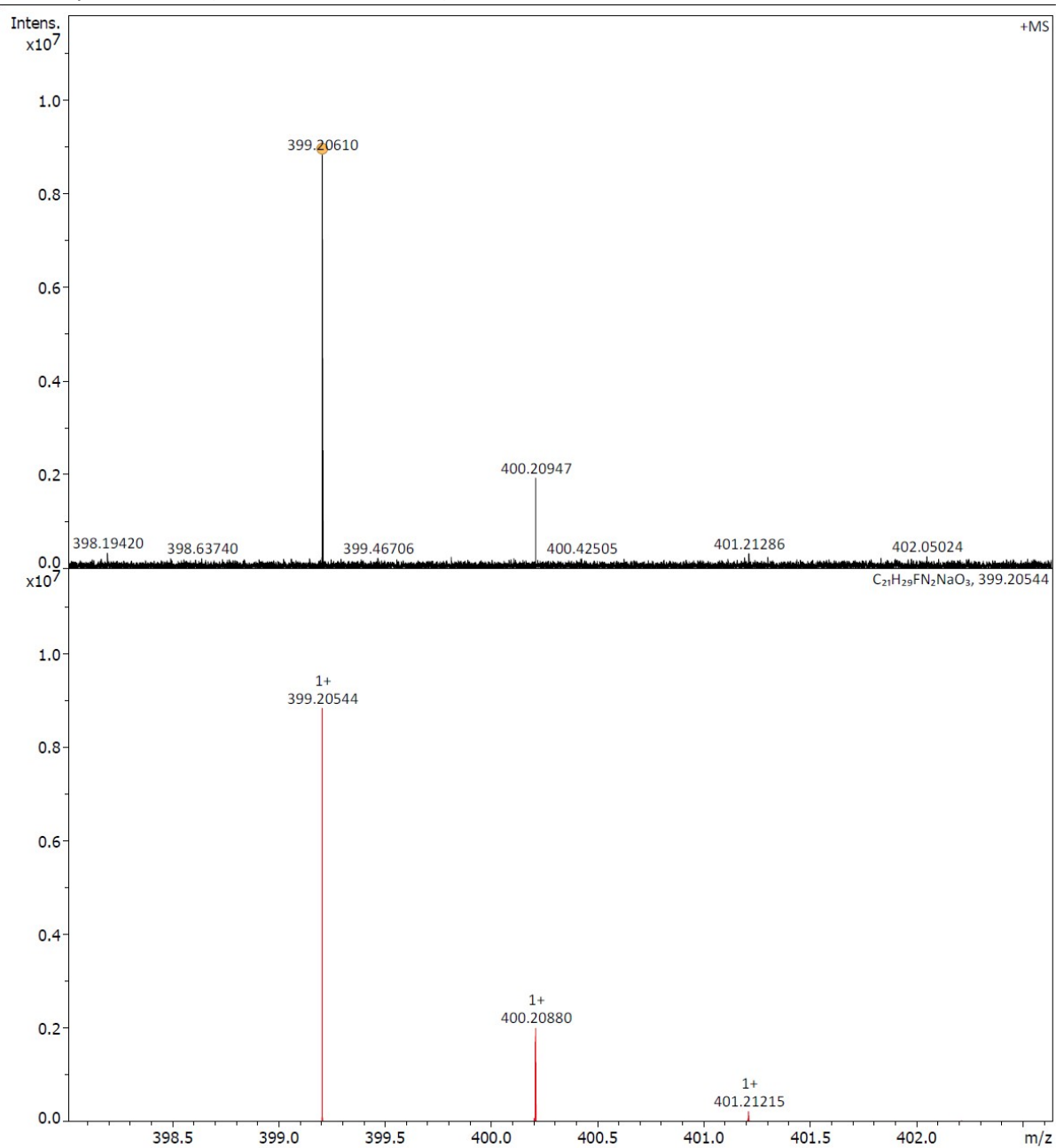
Figure S71. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-phenylalaninate (*R*-MPP-5F-PICA, **34**).
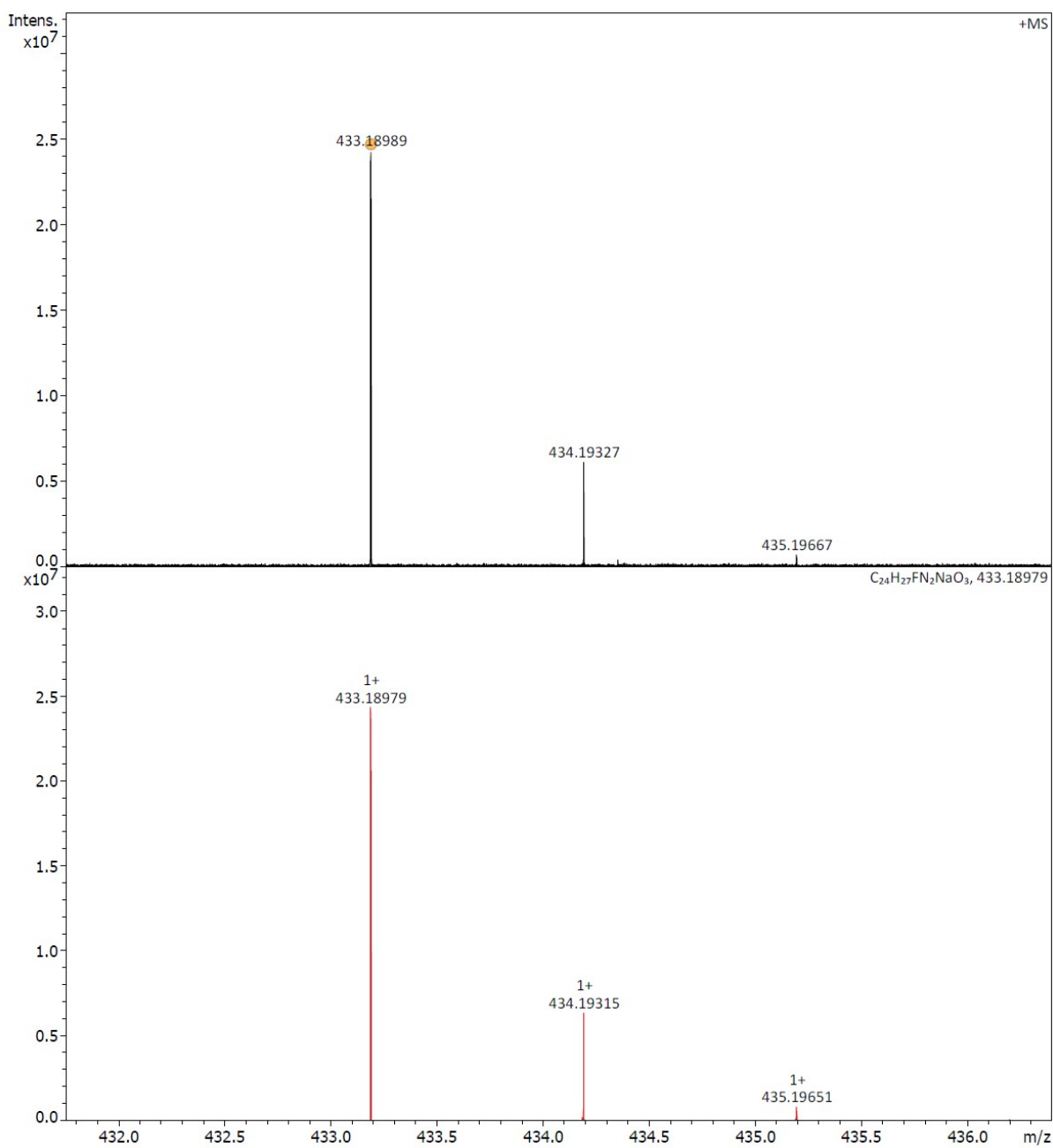
Figure S72. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-tyrosinate (*S*-TYR-5F-PICA, **35**).
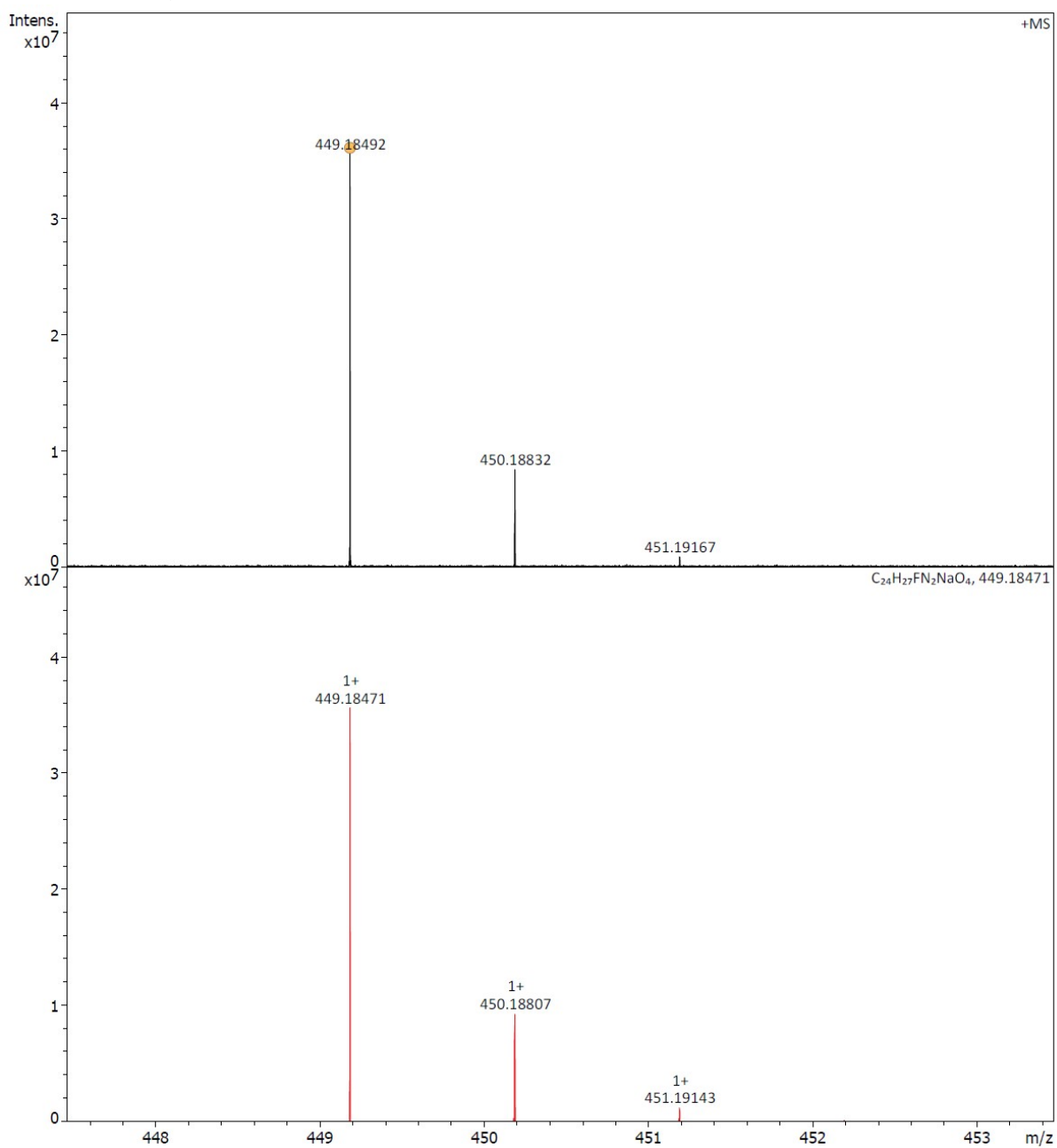
Figure S73. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-tyrosinate (*R*-TYR-5F-PICA, **36**).
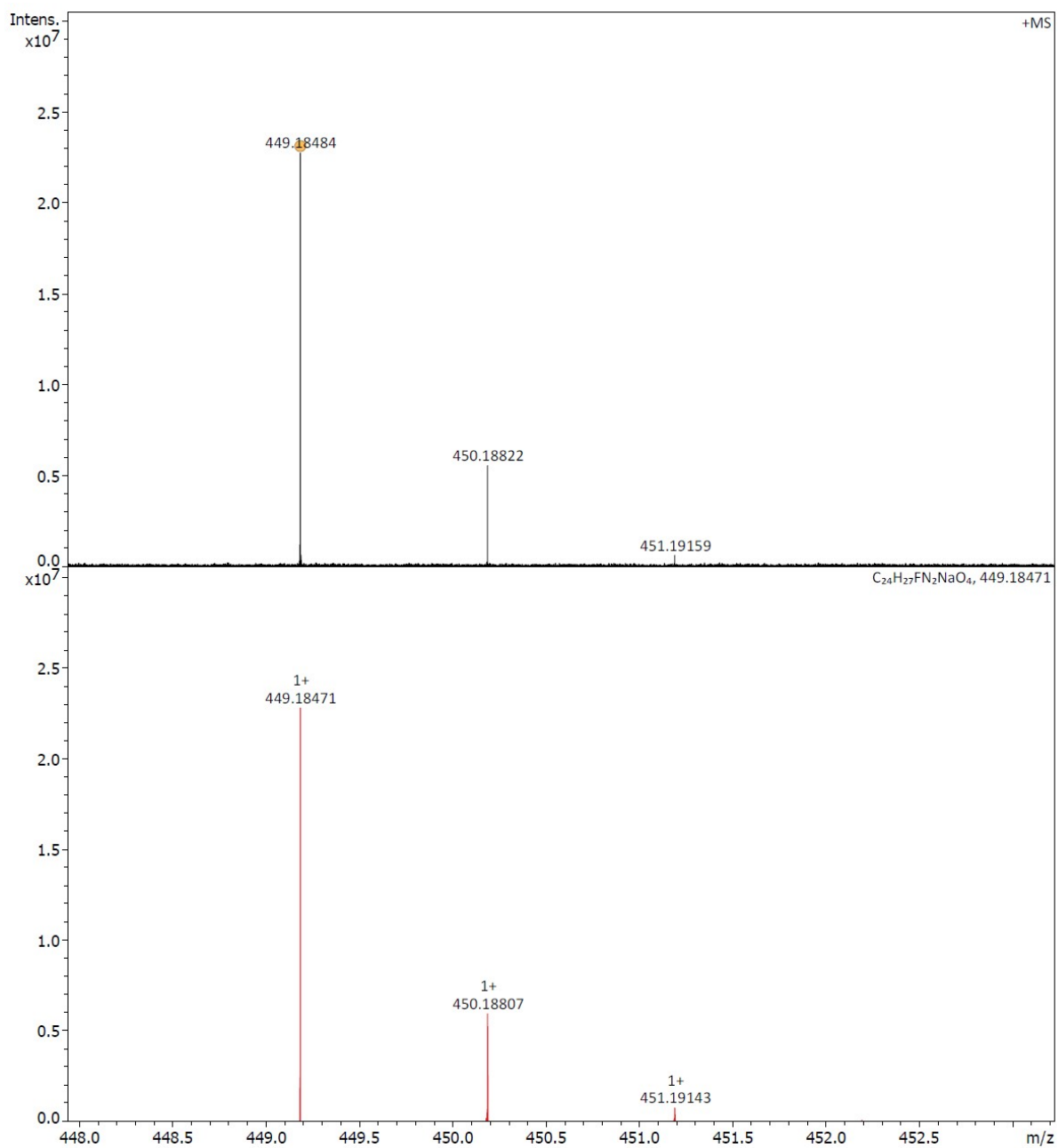
Figure S74. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-tryptophanate (*S*-TRP-5F-PICA, **37**).
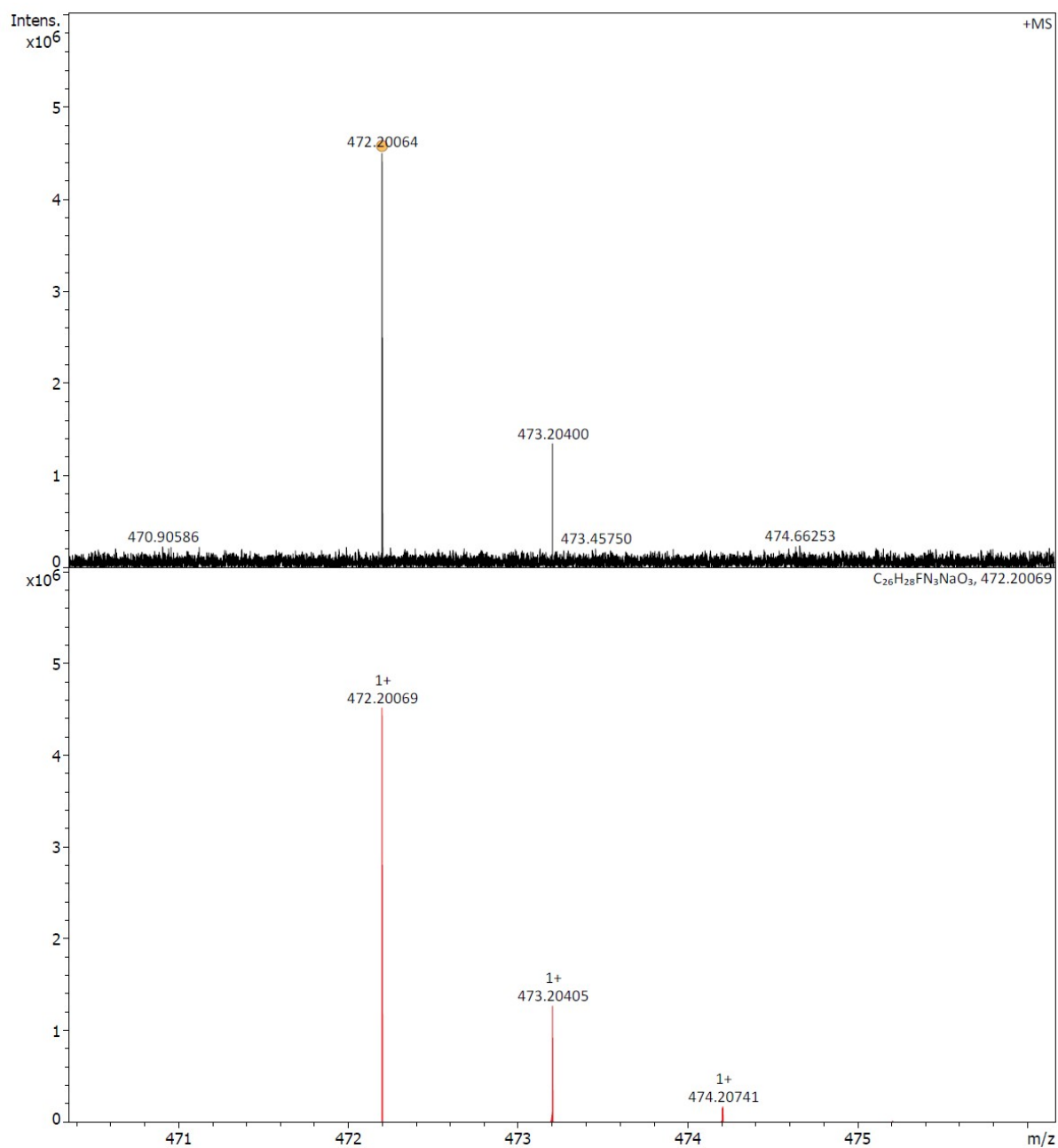
Figure S75. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-tryptophanate (*R*-TRP-5F-PICA, **38**).
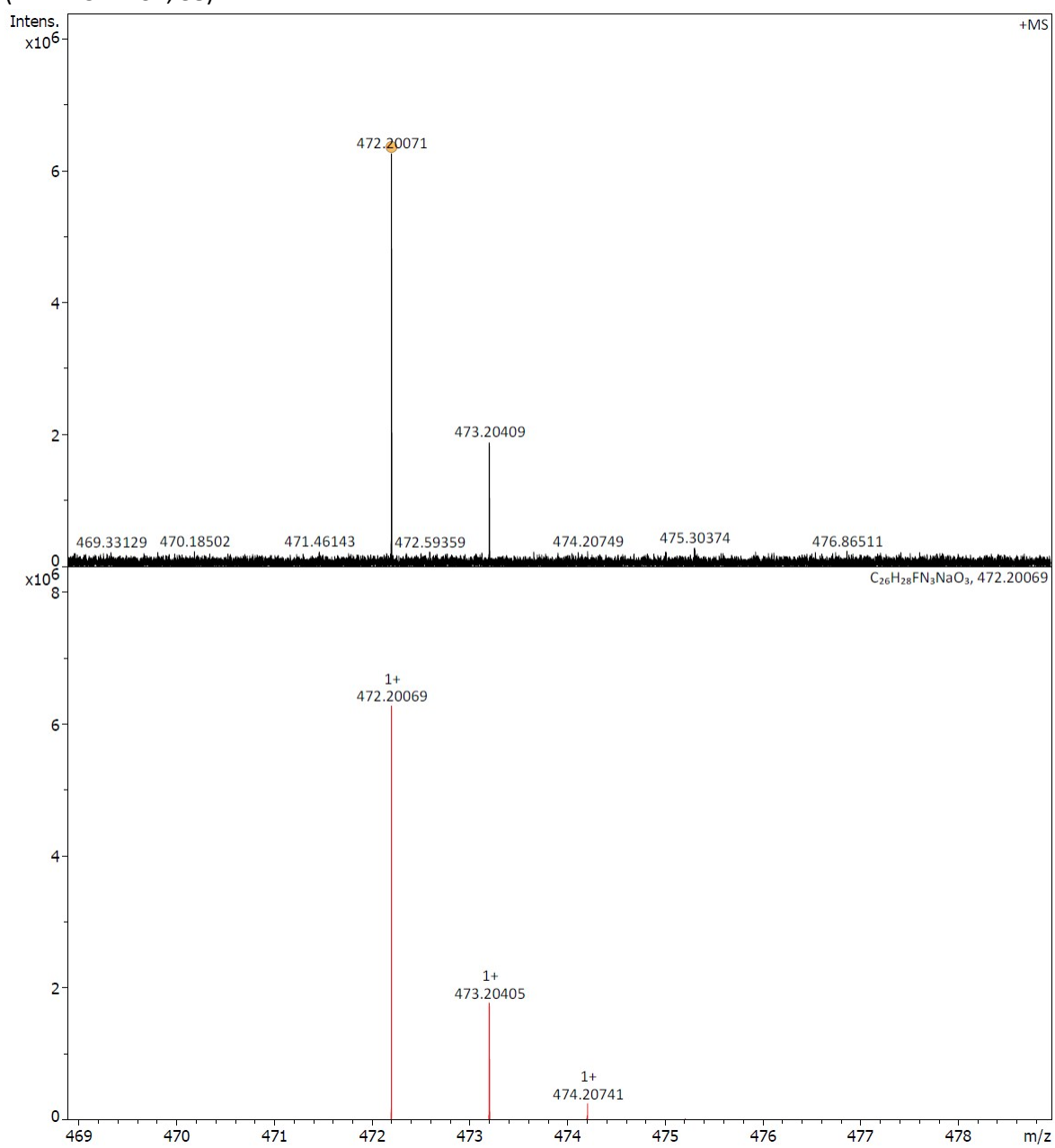
Figure S76. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-lysinate (*S*-LYS-5F-PICA **39**).
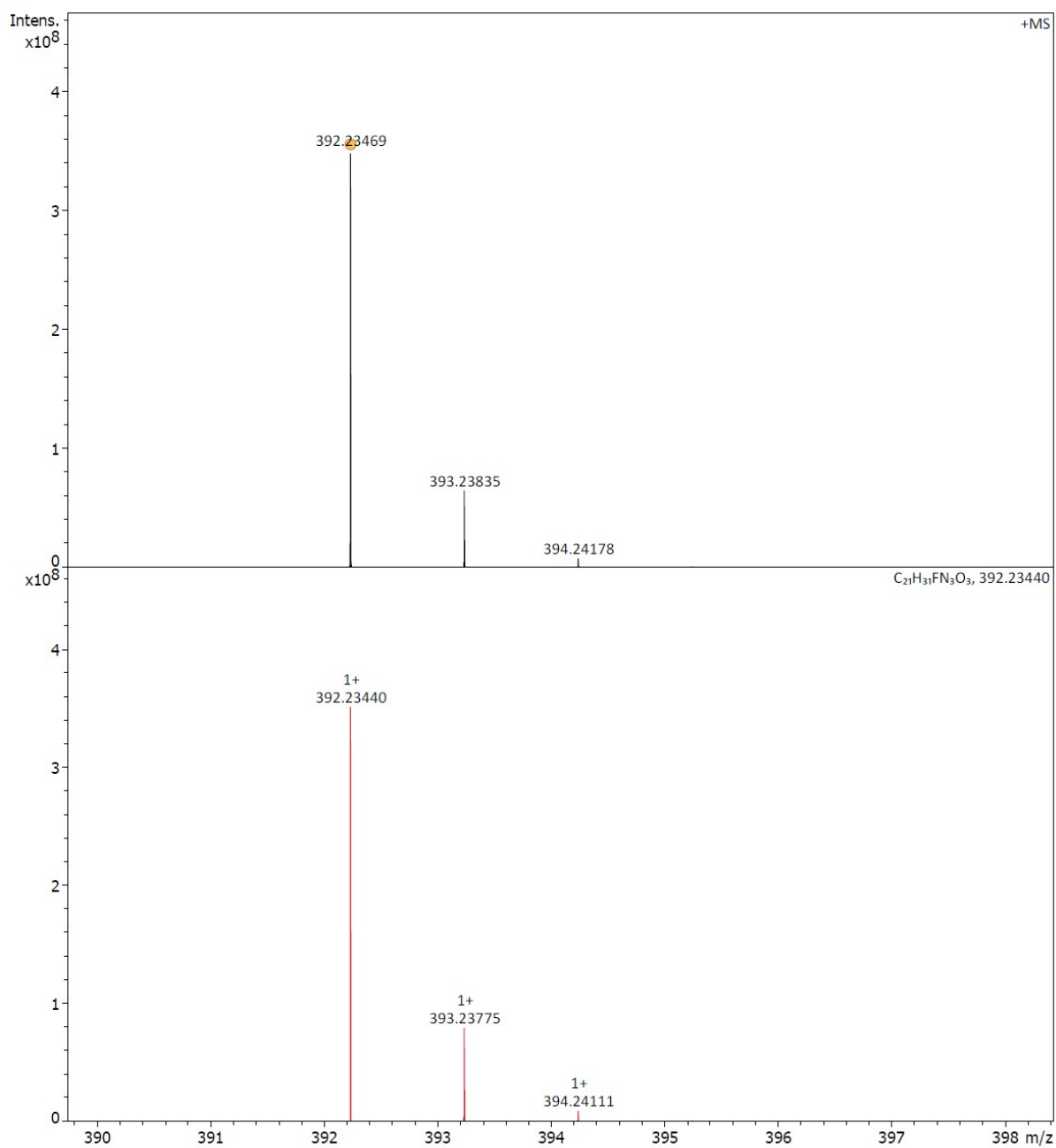
Figure S77. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-lysinate (*R*-LYS-5F-PICA, **40**).
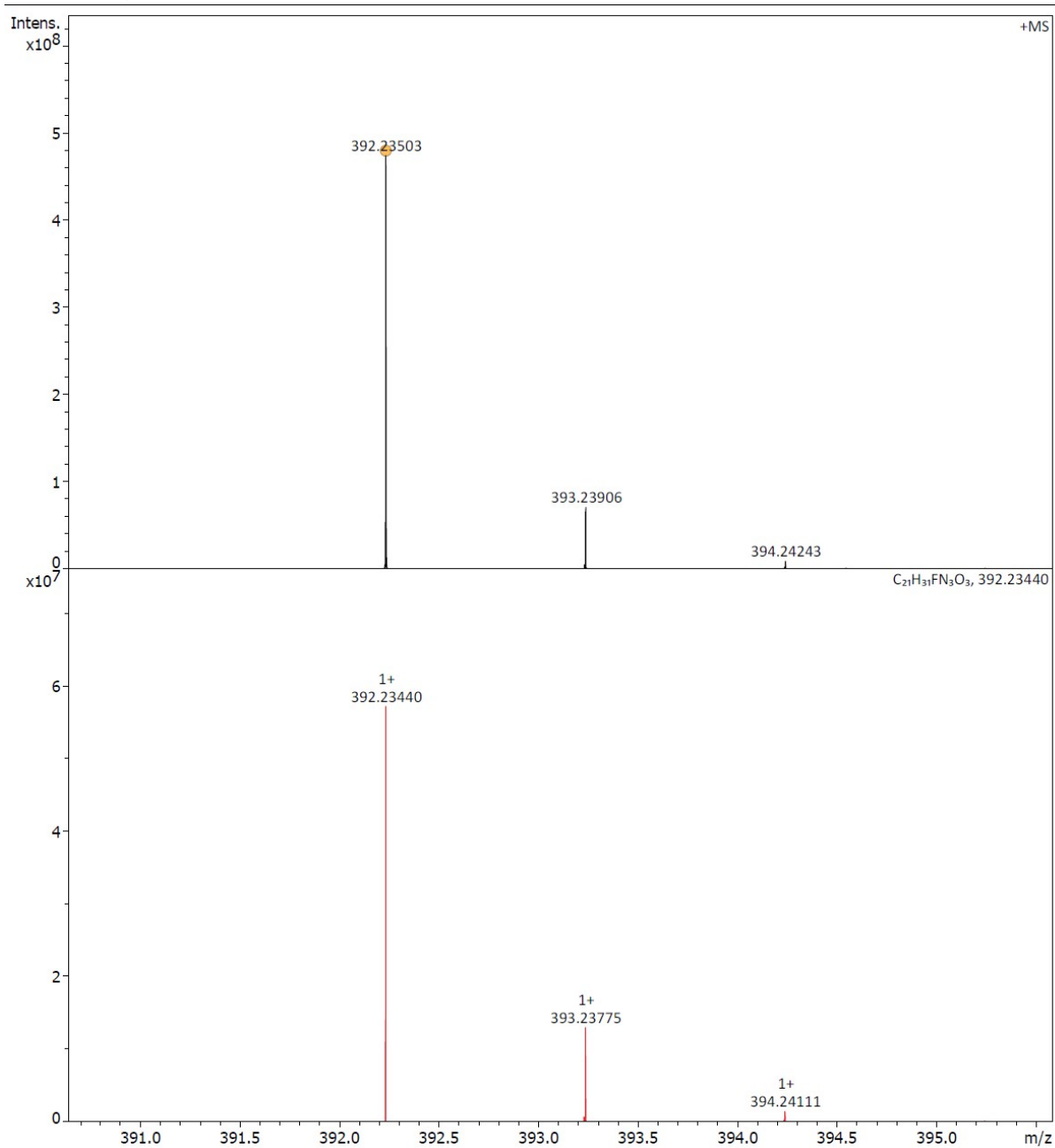
Figure S78. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*S*-methioninate (*S*-MET-5F-PICA, **41**).
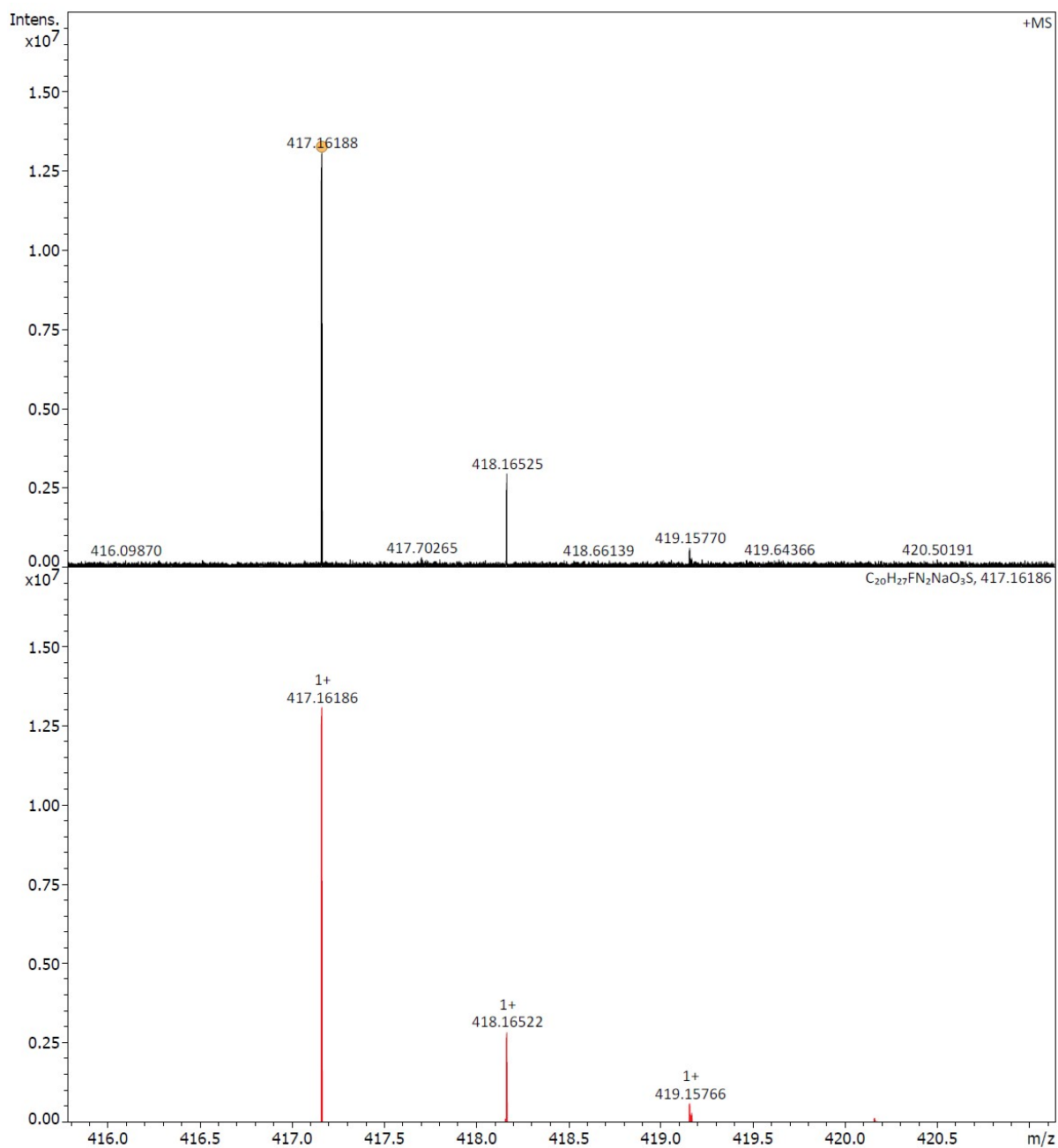
Figure S79. HRMS spectrum for methyl (1-(5-fluoropentyl)-1*H*-indole-3-carbonyl)-*R*-methioninate (*R*-MET-5F-PICA, **42**).
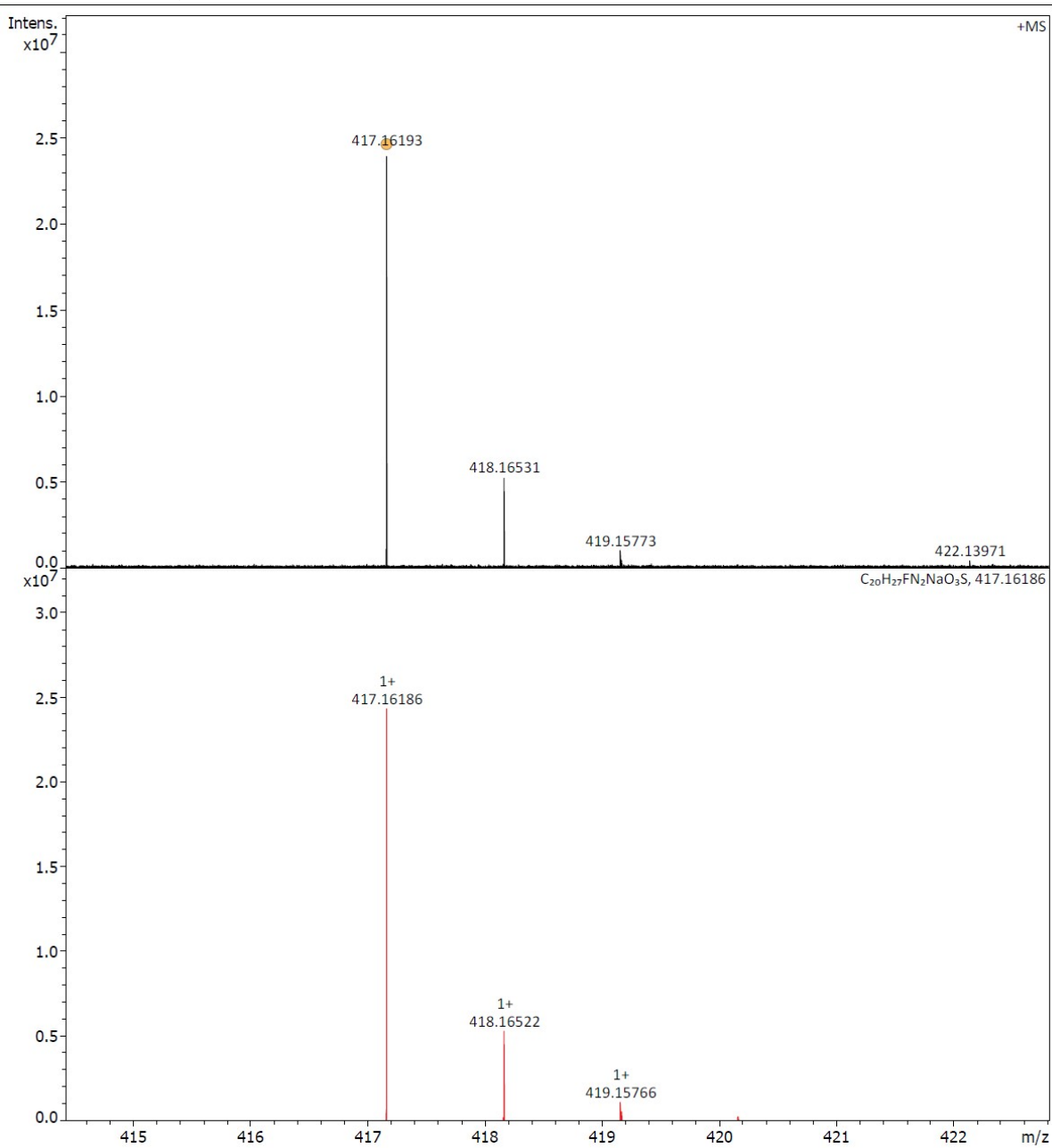
Figure S80. HRMS spectrum for methyl (S)-5-amino-2-(1-(5-fluoropentyl)-1*H*-indole-3-carboxamido)-5-oxopentanoate (*S*-GLN-5F-PICA, **43**).
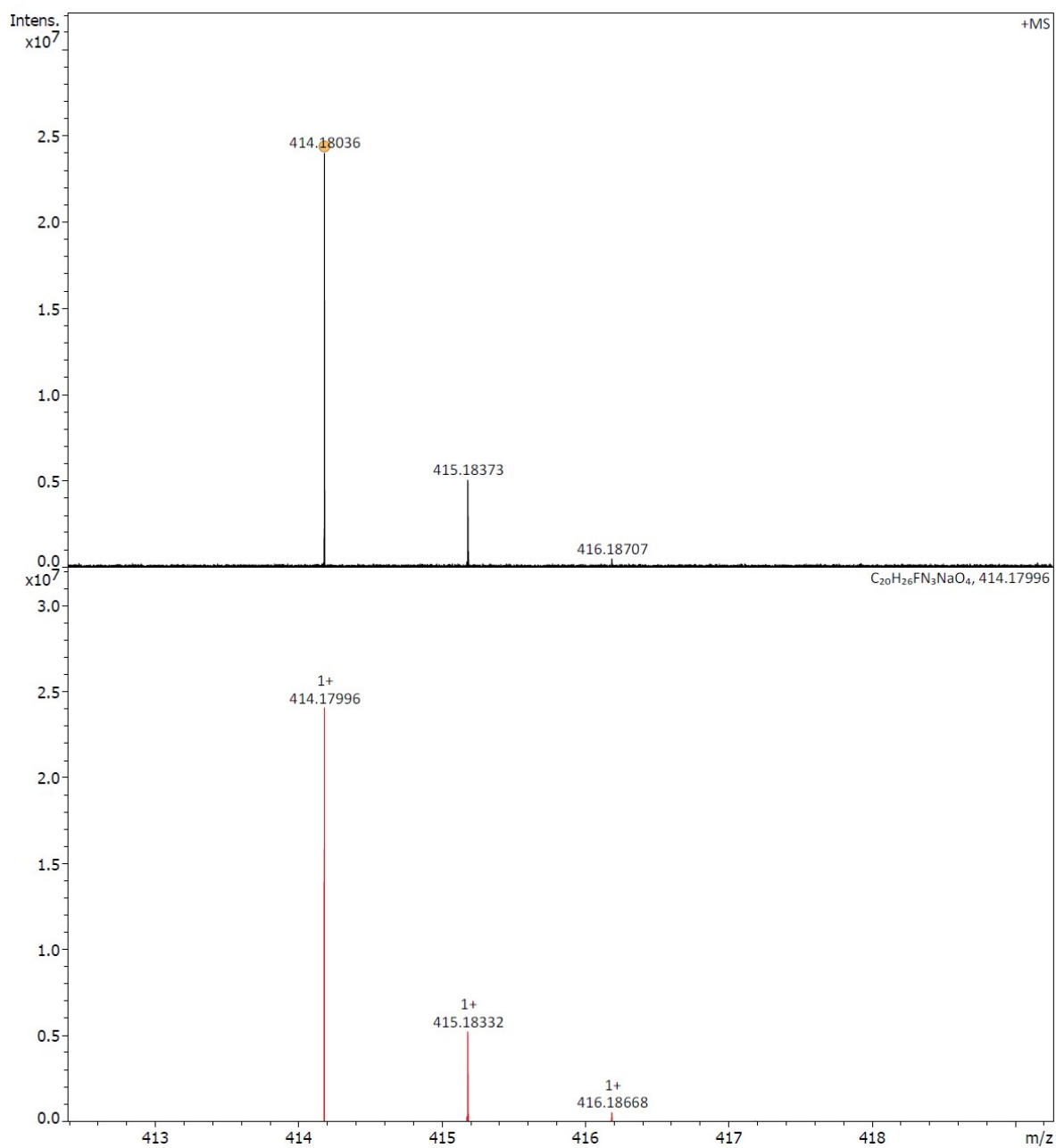
Figure S81. HRMS spectrum for methyl (R)-5-amino-2-(1-(5-fluoropentyl)-1*H*-indole-3-carboxamido)-5-oxopentanoate (*R*-GLN-5F-PICA, **44**).