

Supporting Information

Enantioselective Synthesis of β -Fluoro Amines via β -Amino α -Fluoro Nitroalkanes and a Traceless Activating Group Strategy

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| | |
|---------------------------------------------------------------------------------|----|
| Figure 1. ^1H NMR (400 MHz, CDCl_3) of 2..... | 3 |
| Figure 2. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 2 | 4 |
| Figure 3. ^1H NMR (600 MHz, CDCl_3) of 3..... | 5 |
| Figure 4. ^{13}C NMR/DEPT135 (150MHz, CDCl_3) of 3 | 6 |
| Figure 5. ^1H NMR (400 MHz, CDCl_3) of 7a..... | 7 |
| Figure 6. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 7a..... | 8 |
| Figure 7. ^1H NMR (400 MHz, CDCl_3) of 7b..... | 9 |
| Figure 8. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 7b | 10 |
| Figure 9. ^1H NMR (400 MHz, CDCl_3) of 7c..... | 11 |
| Figure 10. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 7c..... | 12 |
| Figure 11. ^1H NMR (400 MHz, CDCl_3) of 7d..... | 13 |
| Figure 12. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 7d | 14 |
| Figure 13. ^1H NMR (400 MHz, CDCl_3) of 7e..... | 15 |
| Figure 14. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 7e..... | 16 |
| Figure 15. ^1H NMR (400 MHz, CDCl_3) of 7f | 17 |
| Figure 16. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 7f | 18 |
| Figure 17. ^1H NMR (400 MHz, CDCl_3) of 7g..... | 19 |
| Figure 18. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 7g | 20 |
| Figure 19. ^1H NMR (600 MHz, CDCl_3) of 7h..... | 21 |
| Figure 20. ^{13}C NMR/DEPT135 (150 MHz, CDCl_3) of 7h | 22 |
| Figure 21. ^1H NMR (600 MHz, CDCl_3) of 7i..... | 23 |
| Figure 22. ^{13}C NMR/DEPT135 (150 MHz, CDCl_3) of 7i | 24 |
| Figure 23. ^1H NMR (600 MHz, CDCl_3) of 7j..... | 24 |
| Figure 24. ^{13}C NMR/DEPT135 (150 MHz, CDCl_3) of 7j | 26 |
| Figure 25. ^1H NMR (600 MHz, MeOD) of <i>cis</i> -8 | 27 |
| Figure 26. ^{13}C NMR/DEPT135 (150 MHz, MeOD) of <i>cis</i> -8 | 28 |
| Figure 27. ^1H NMR (400 MHz, MeOD) of <i>trans</i> -8..... | 29 |
| Figure 28. ^{13}C NMR/DEPT135 (100 MHz, MeOD) of <i>trans</i> -8 | 30 |
| Figure 29. ^1H NMR (400 MHz, CDCl_3) of 9..... | 31 |
| Figure 30. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 9 | 32 |
| Figure 31. ^1H NMR (400 MHz, CDCl_3) of 10..... | 33 |
| Figure 32. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 10 | 34 |
| Figure 33. ^1H NMR (400 MHz, CDCl_3) of 11..... | 35 |
| Figure 34. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of 11 | 36 |
| Figure 35. ^1H NMR (600 MHz, CDCl_3) of S1 | 37 |
| Figure 36. ^{13}C NMR/DEPT135 (150 MHz, CDCl_3) of S1 | 38 |

| | |
|--------------------------------------------------------------------------------|----|
| Figure 37. ^1H NMR (400 MHz, CDCl_3) of S2 | 39 |
| Figure 38. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of S2 | 40 |
| Figure 39. ^1H NMR (400 MHz, CDCl_3) of S3 | 41 |
| Figure 40. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of S3 | 42 |
| Figure 41. ^1H NMR (400 MHz, MeOD) of S4 | 43 |
| Figure 42. ^{13}C NMR/DEPT135 (100 MHz, MeOD) of S4..... | 44 |
| Figure 43. HPLC trace of 3..... | 45 |
| Figure 44. HPLC trace of 7a..... | 46 |
| Figure 45. HPLC trace of 7b..... | 47 |
| Figure 46. HPLC trace of 7c..... | 48 |
| Figure 47. HPLC trace of 7d..... | 49 |
| Figure 48. HPLC trace of 7e..... | 50 |
| Figure 49. HPLC trace of 7f + <i>ent</i> -7f. | 51 |
| Figure 50. HPLC trace of 7g..... | 52 |
| Figure 51. HPLC trace of 7h..... | 53 |
| Figure 52. HPLC trace of 7i. | 54 |
| Figure 53. HPLC trace of 7j. | 55 |
| Figure 54. HPLC trace of 10..... | 56 |

Figure 1. ^1H NMR (400 MHz, CDCl_3) of **2**

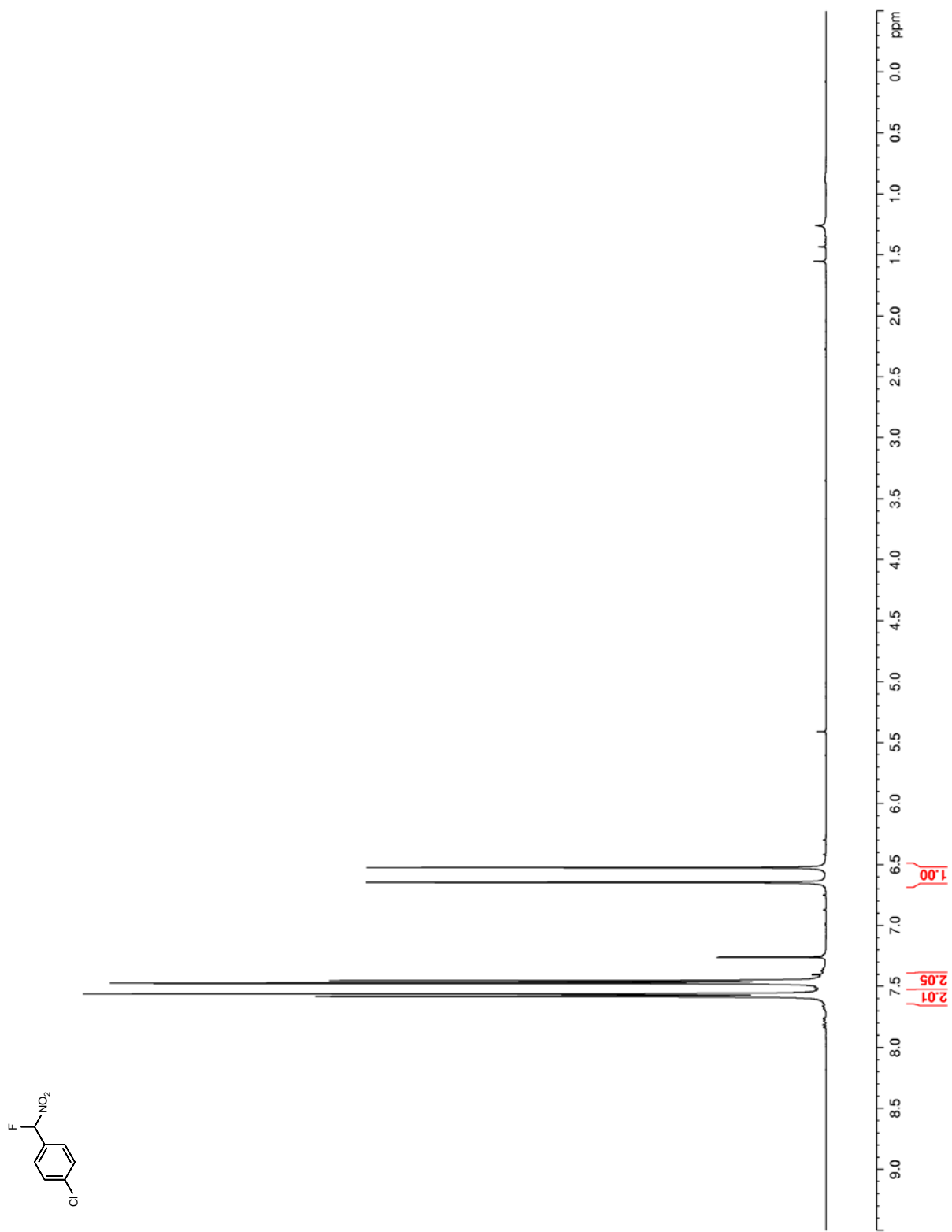


Figure 2. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **2**

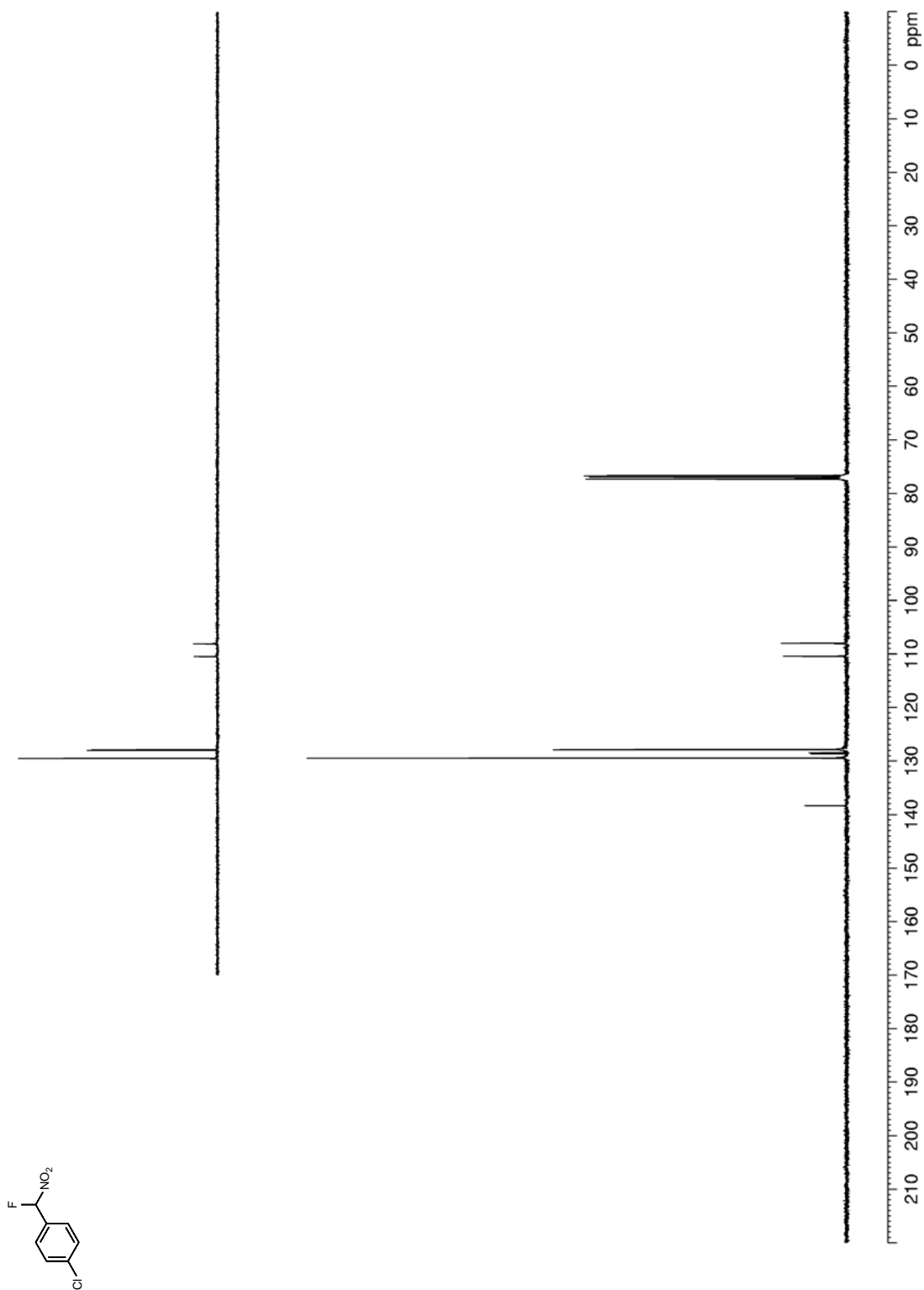


Figure 3. ^1H NMR (600 MHz, CDCl_3) of **3**

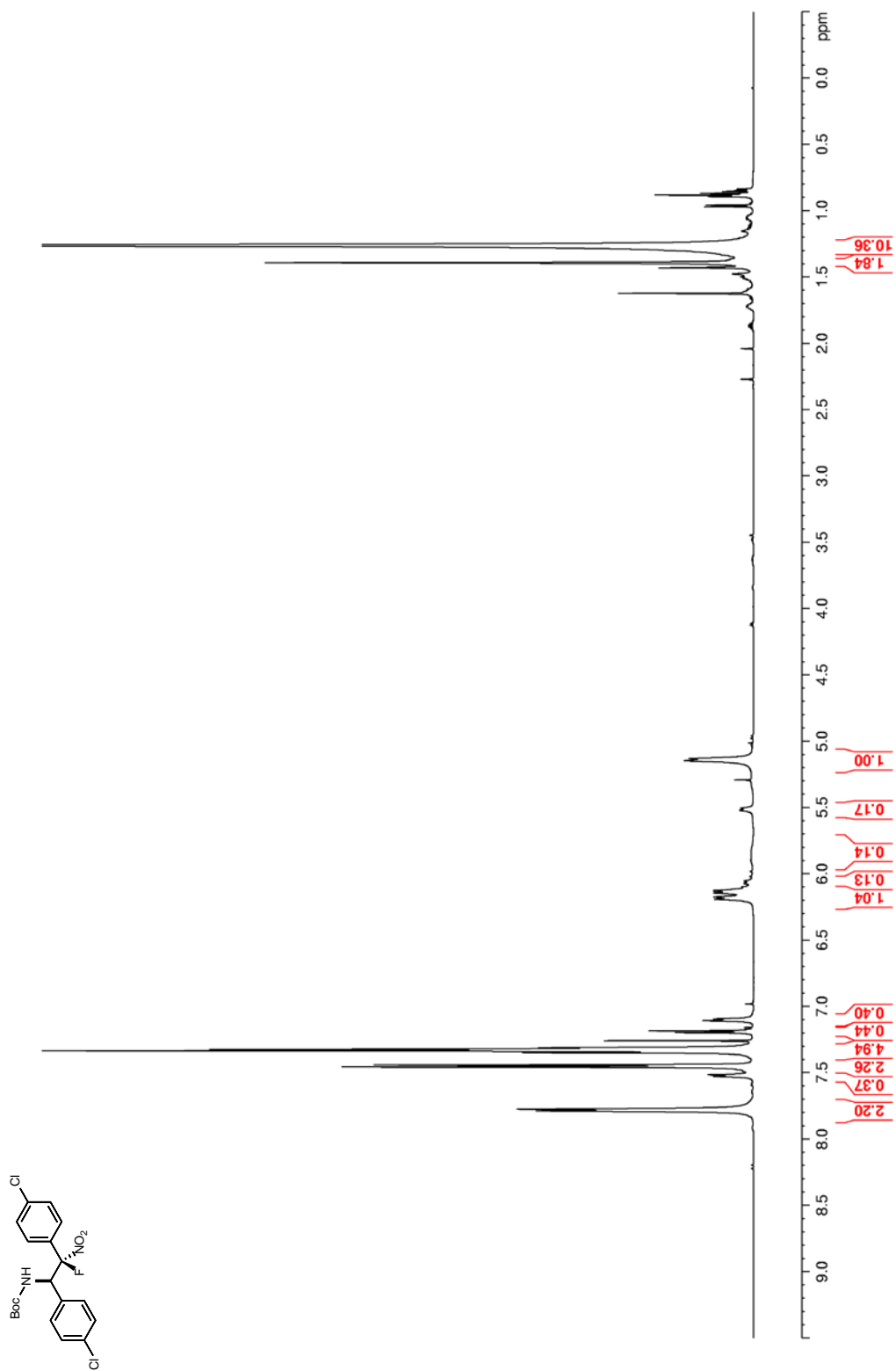


Figure 4. ^{13}C NMR/DEPT135 (150MHz, CDCl_3) of **3**

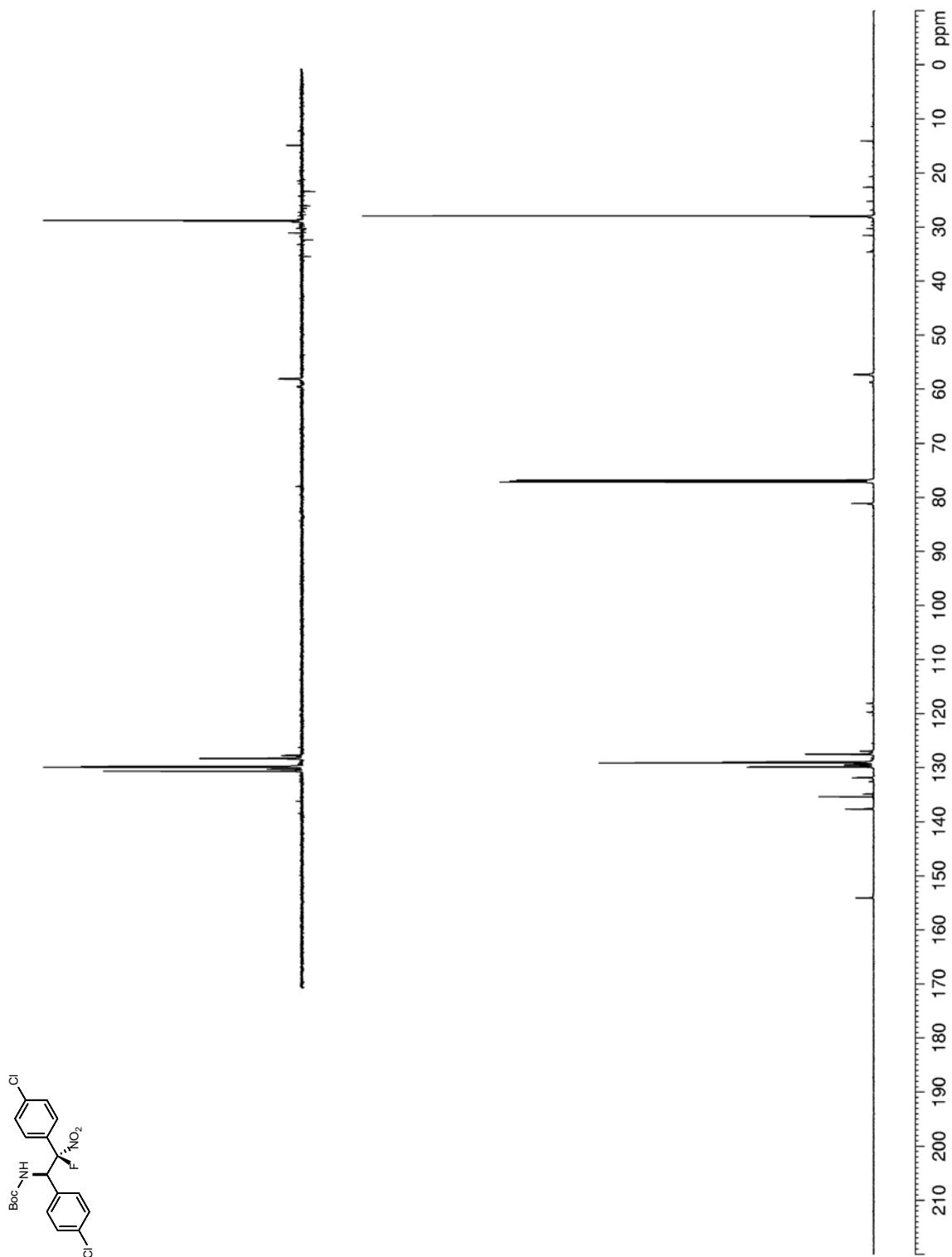


Figure 5. ^1H NMR (400 MHz, CDCl_3) of **7a**

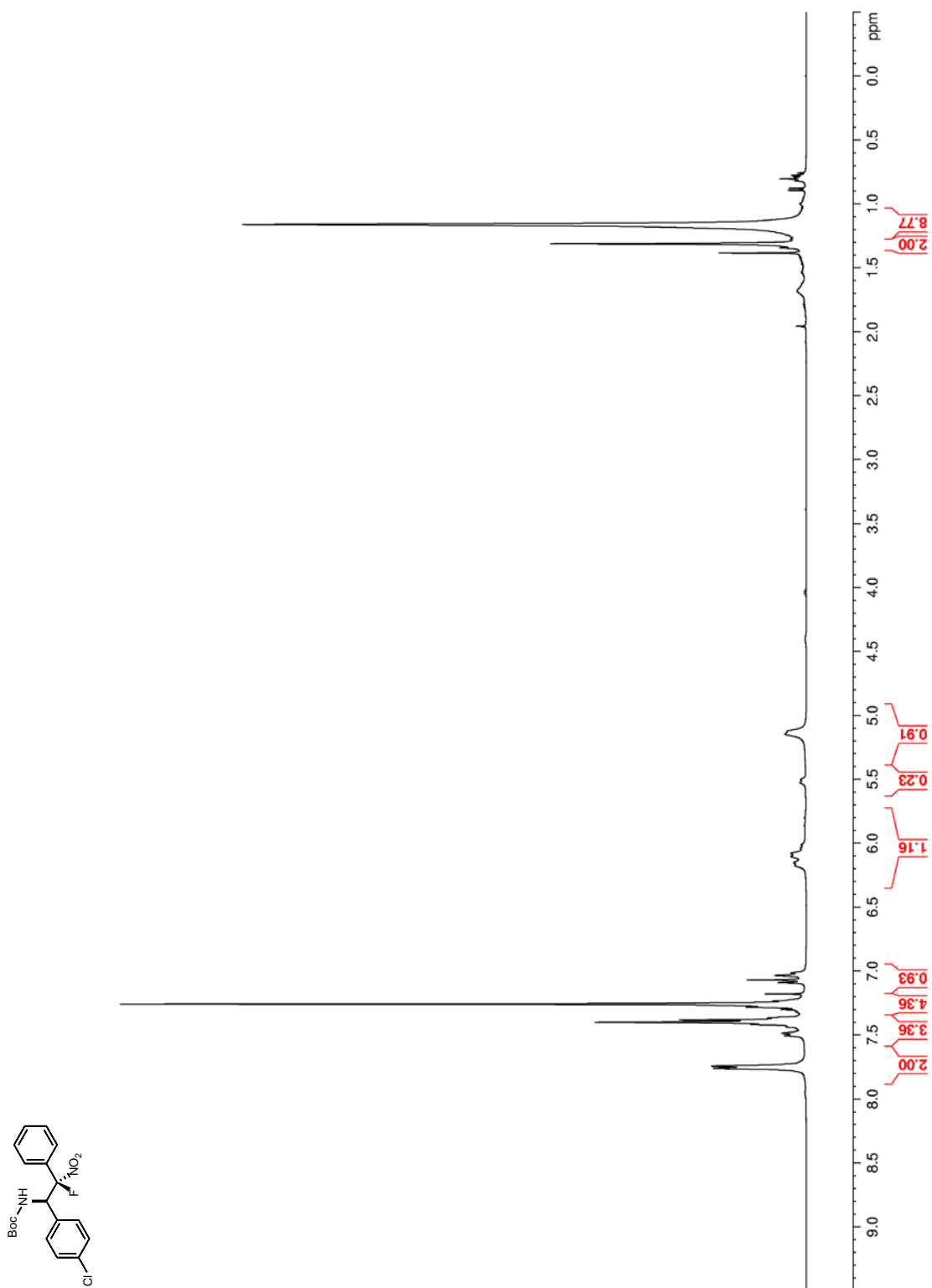


Figure 6. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **7a**

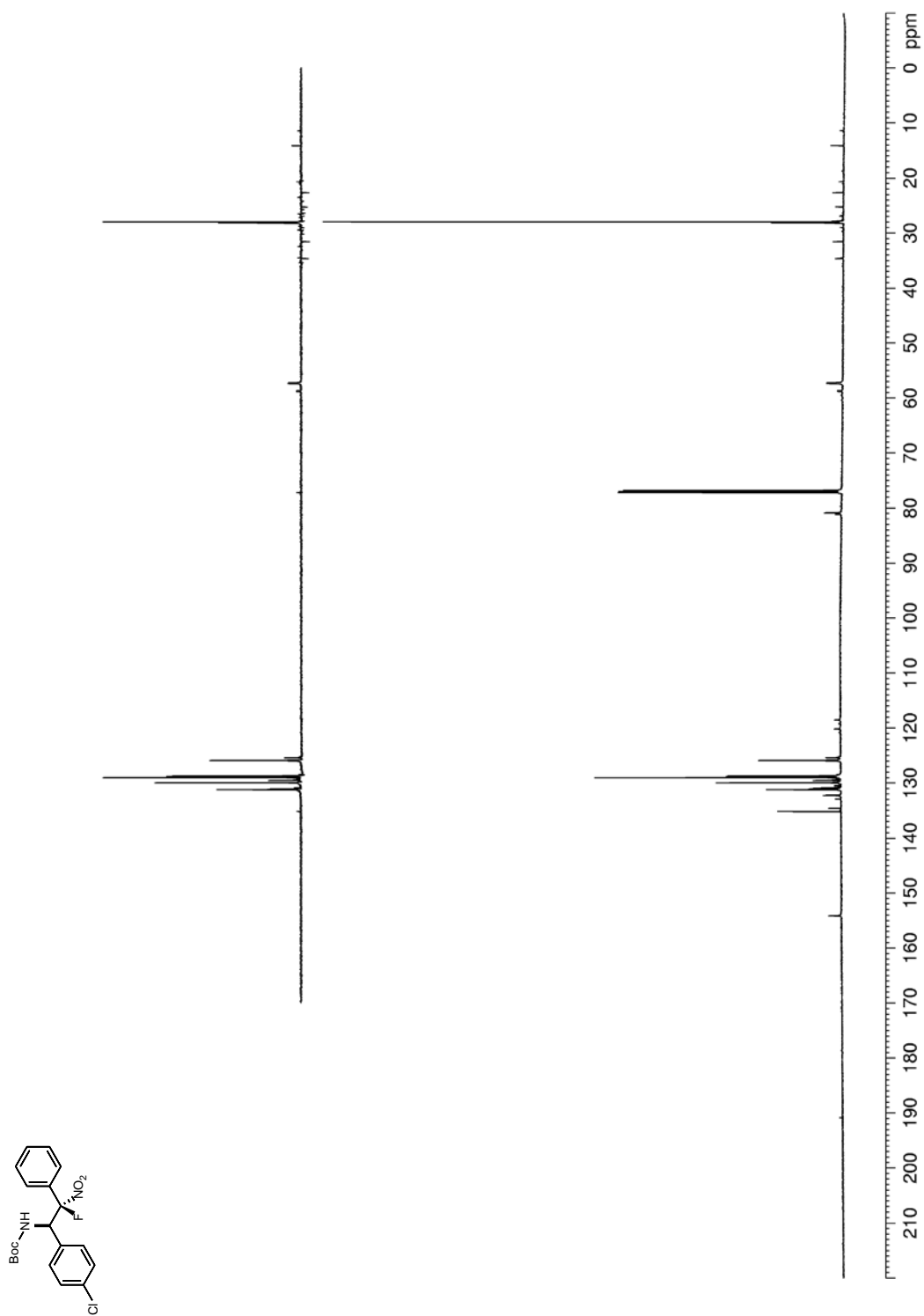


Figure 7. ^1H NMR (400 MHz, CDCl_3) of **7b**

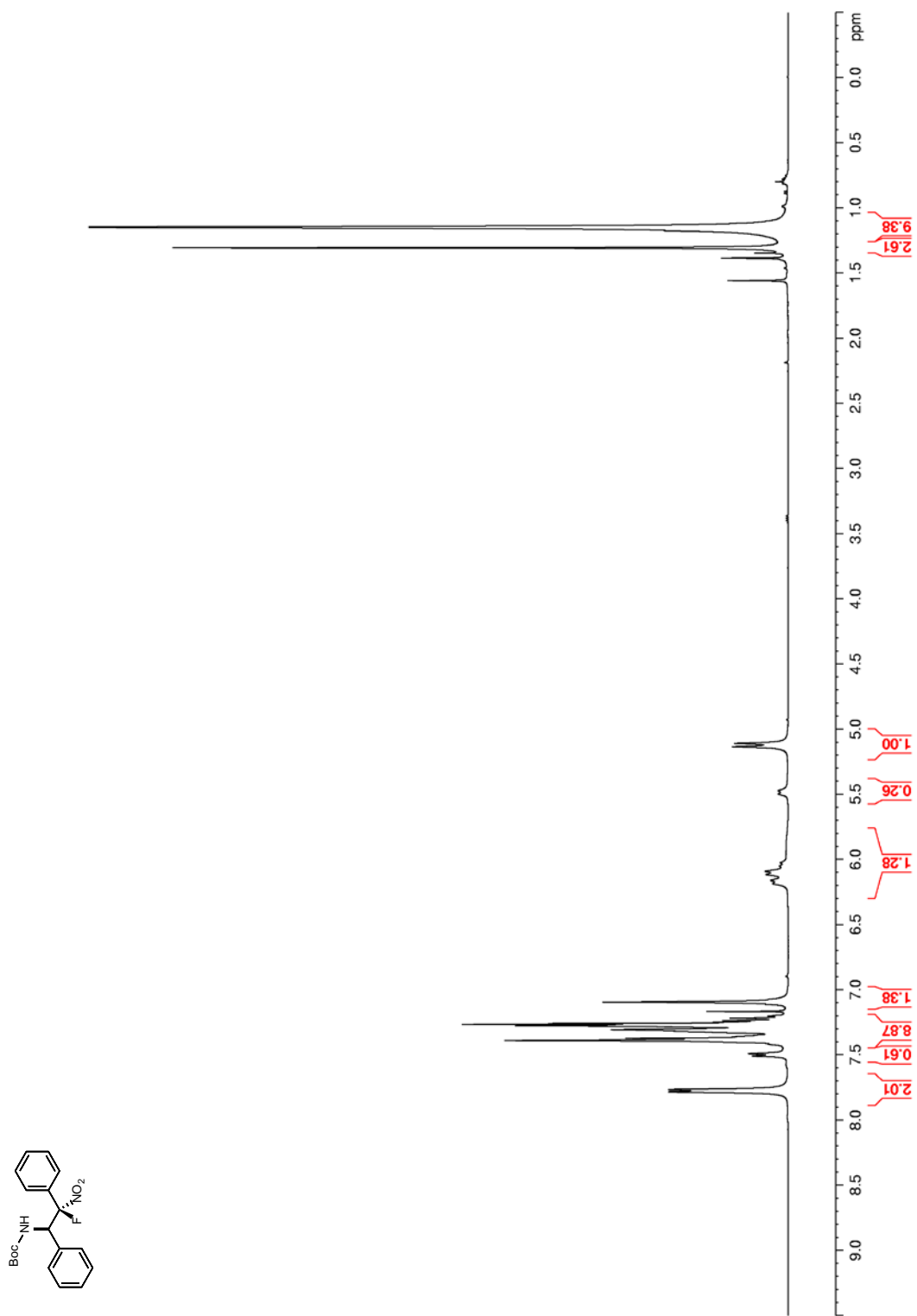


Figure 8. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **7b**

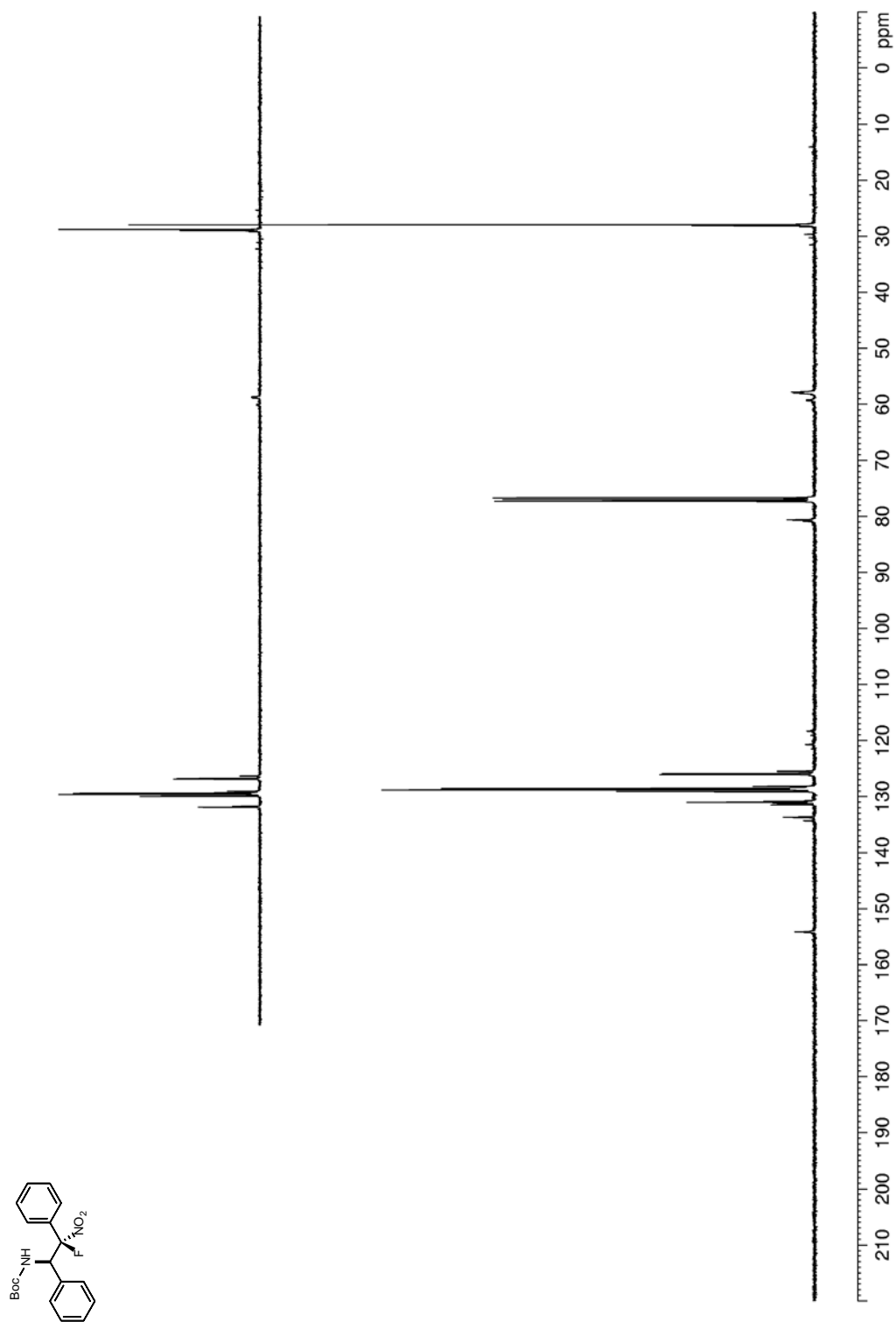


Figure 9. ^1H NMR (400 MHz, CDCl_3) of **7c**

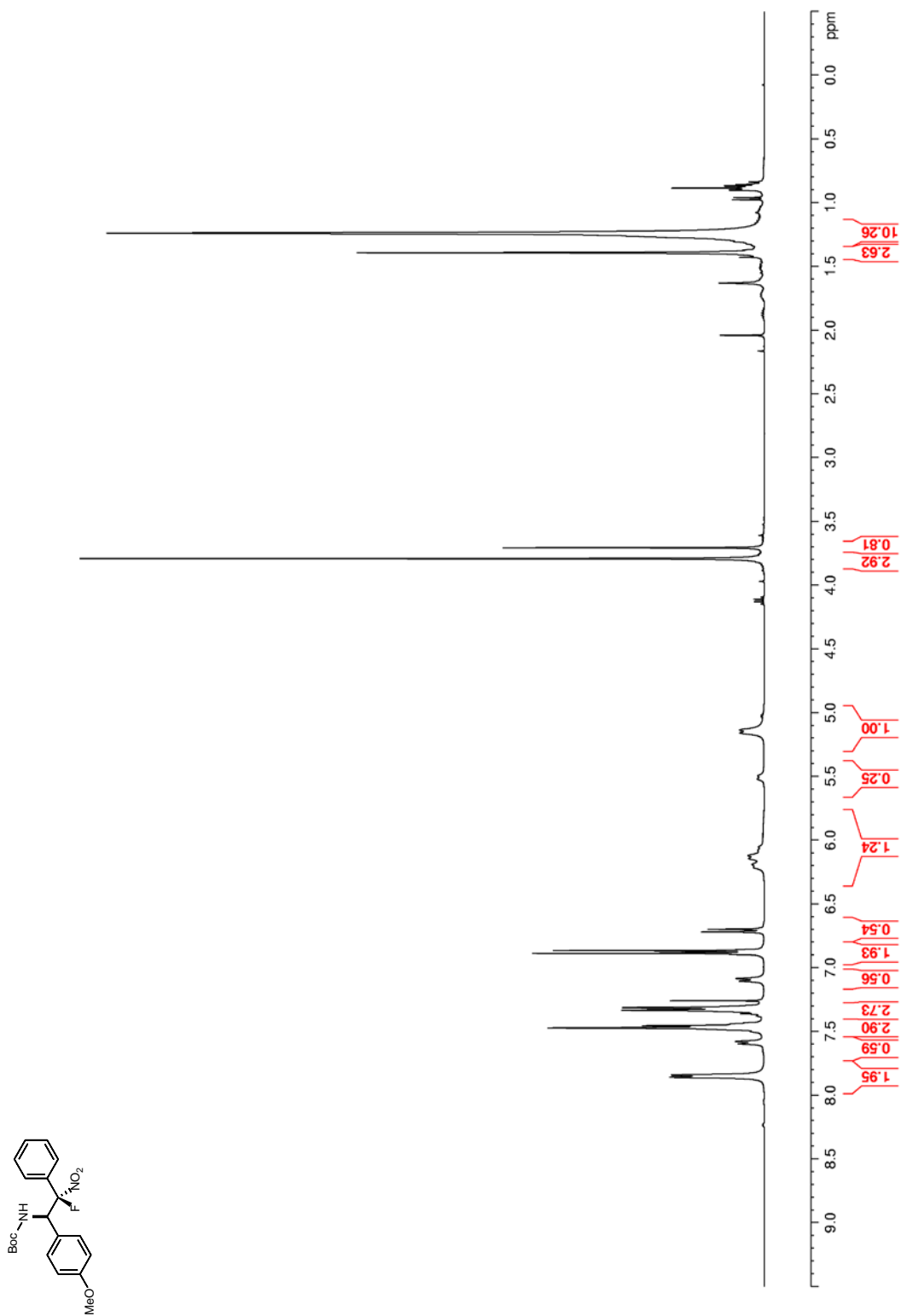


Figure 10. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **7c**

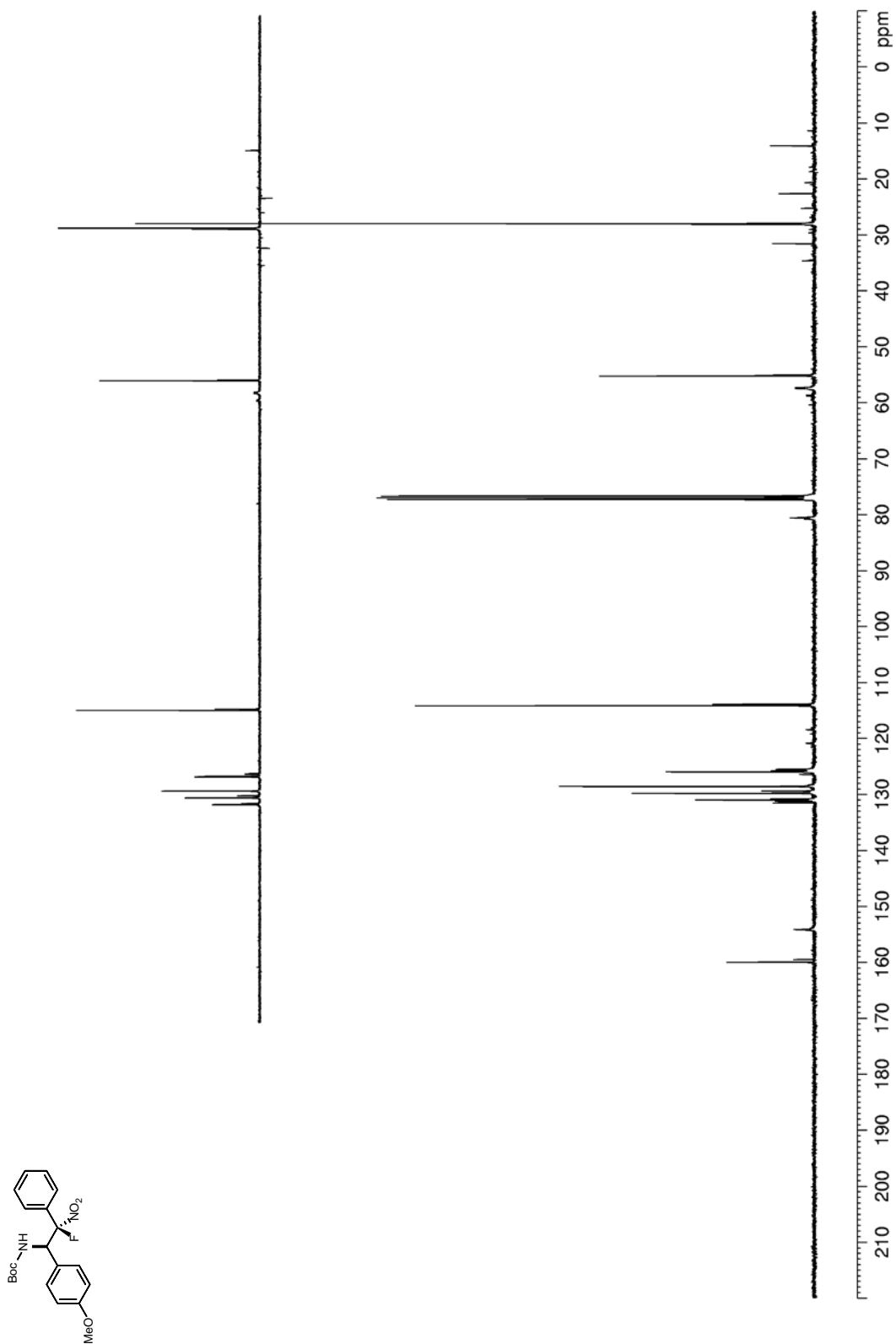


Figure 11. ^1H NMR (400 MHz, CDCl_3) of **7d**

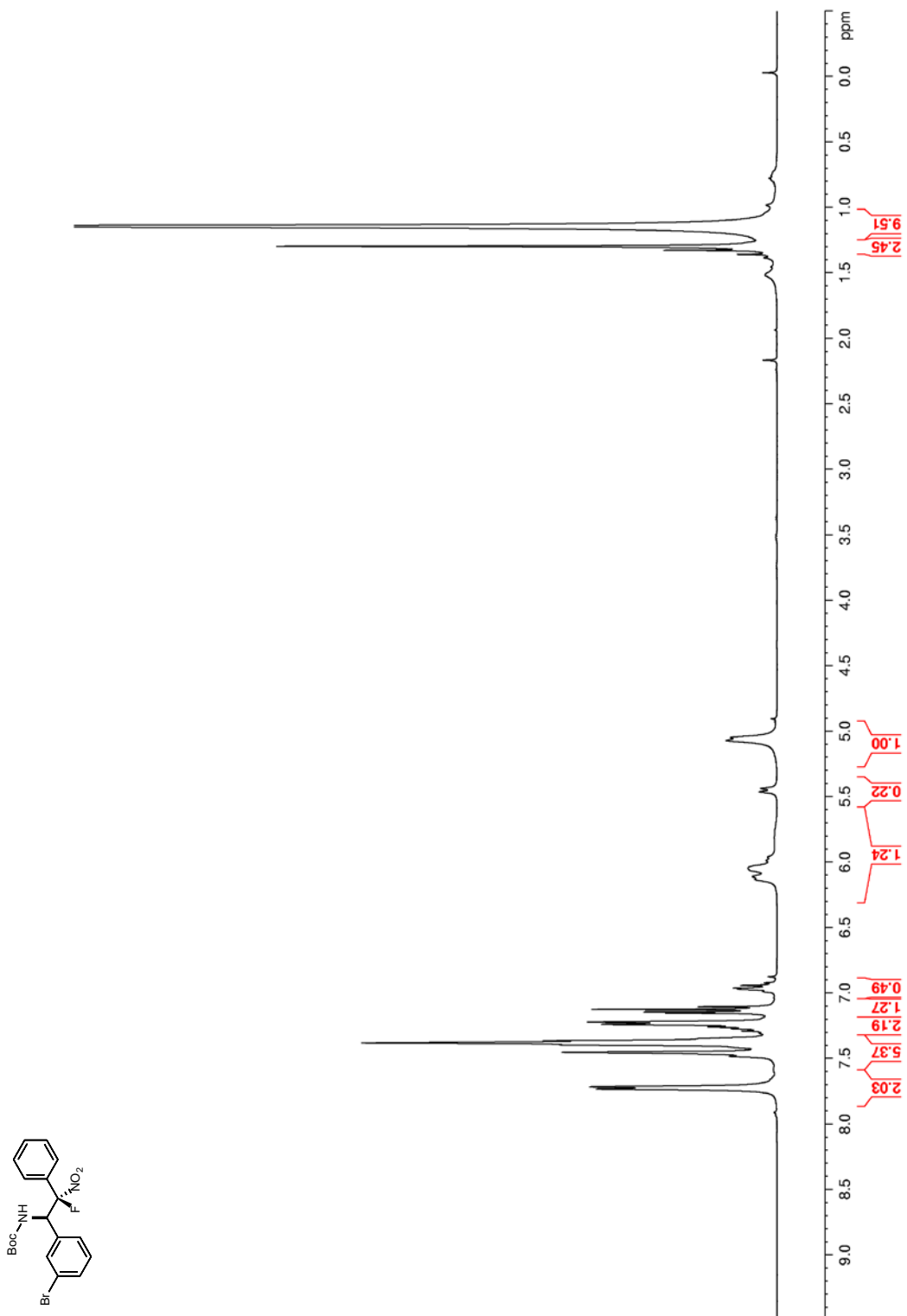


Figure 12. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **7d**

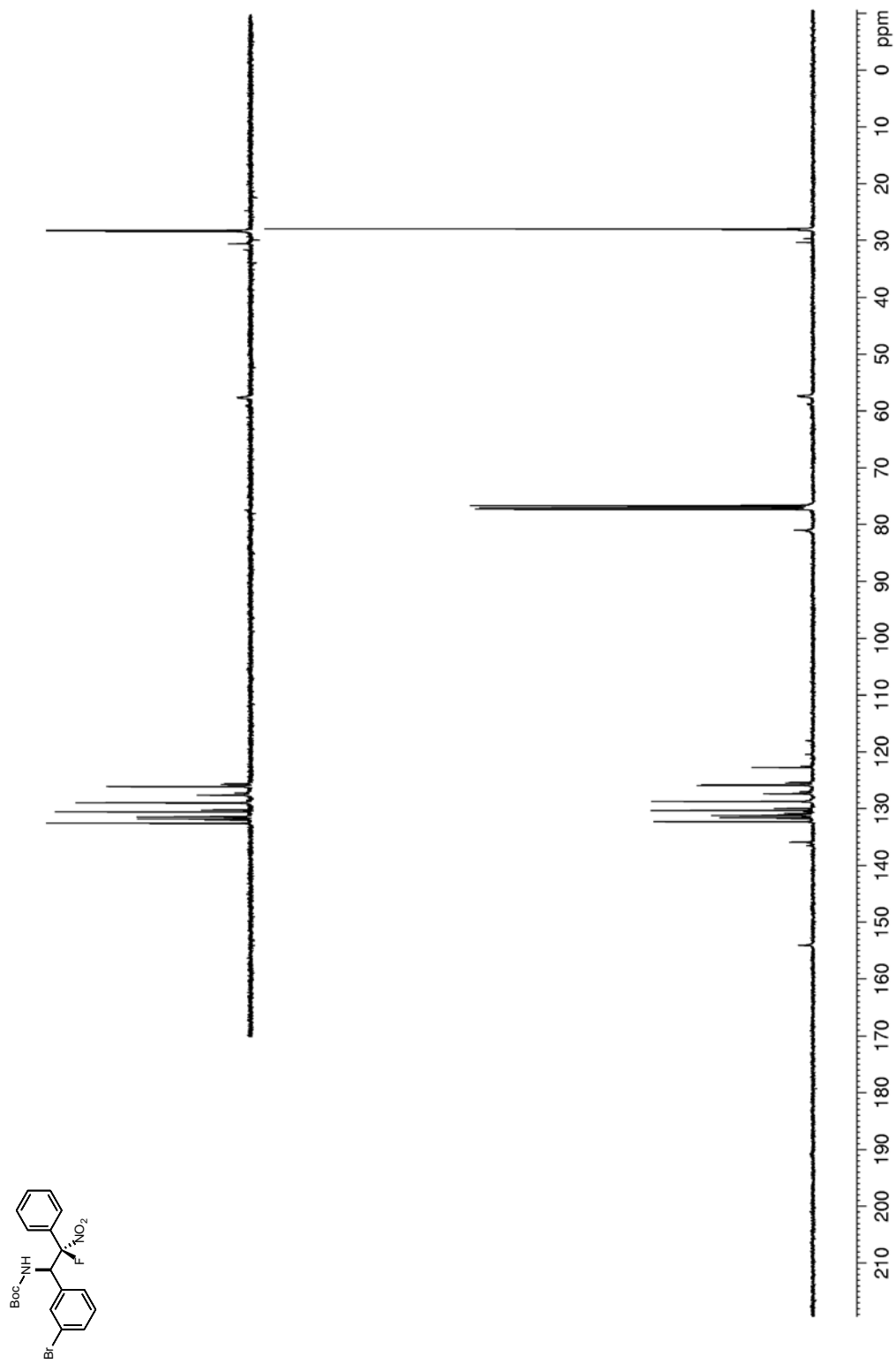


Figure 13. ^1H NMR (400 MHz, CDCl_3) of **7e**

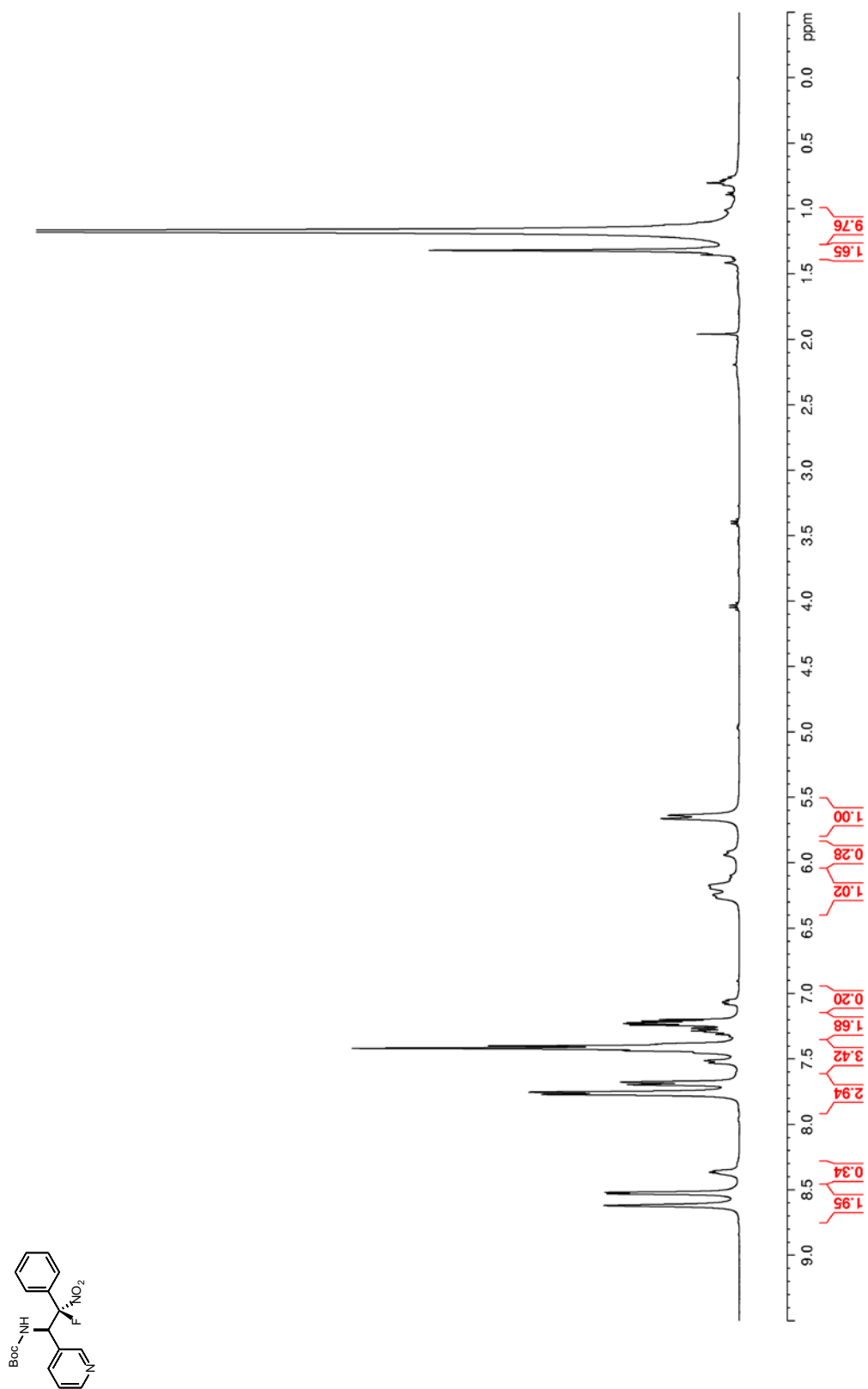


Figure 14. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **7e**

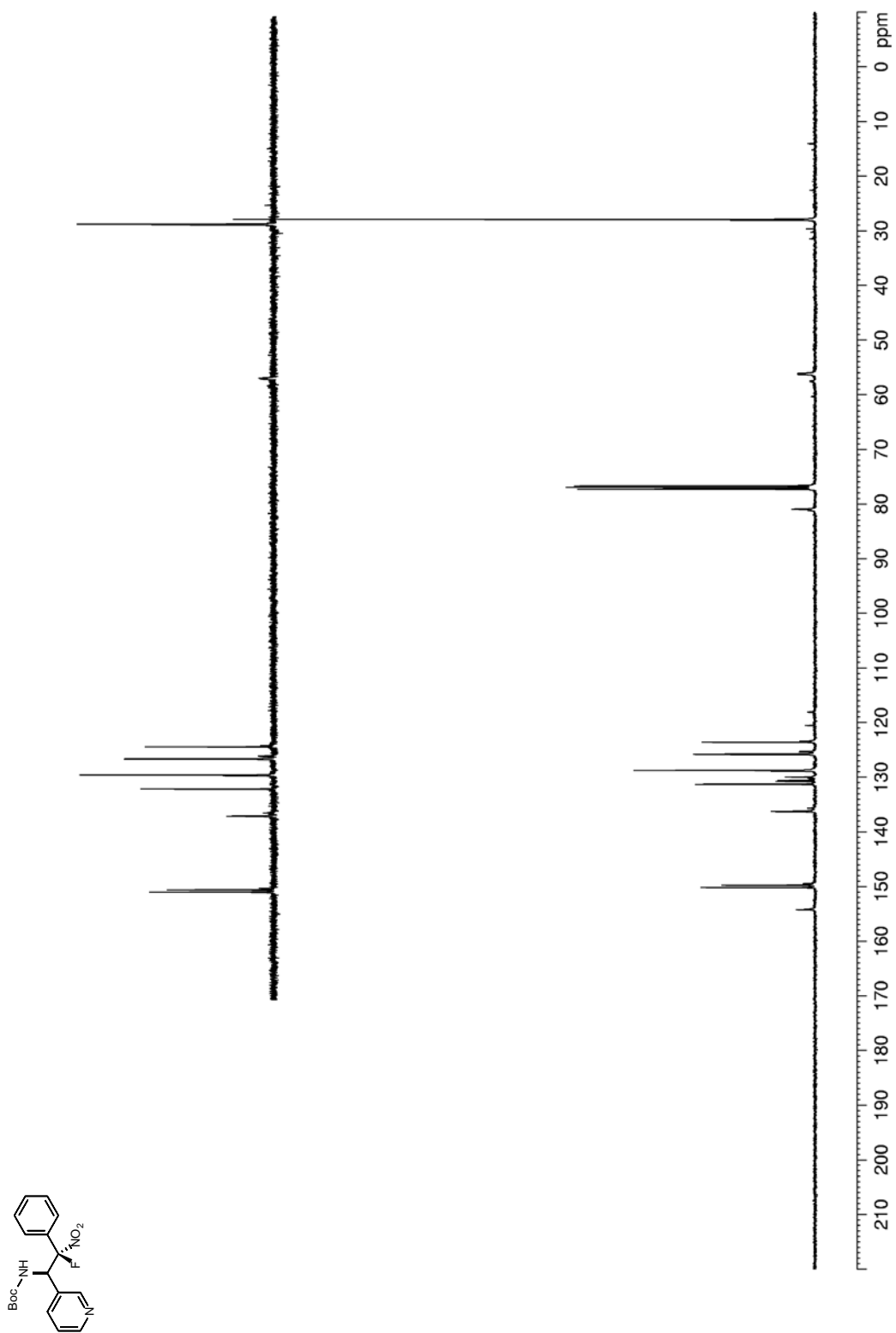


Figure 15. ^1H NMR (400 MHz, CDCl_3) of 7f

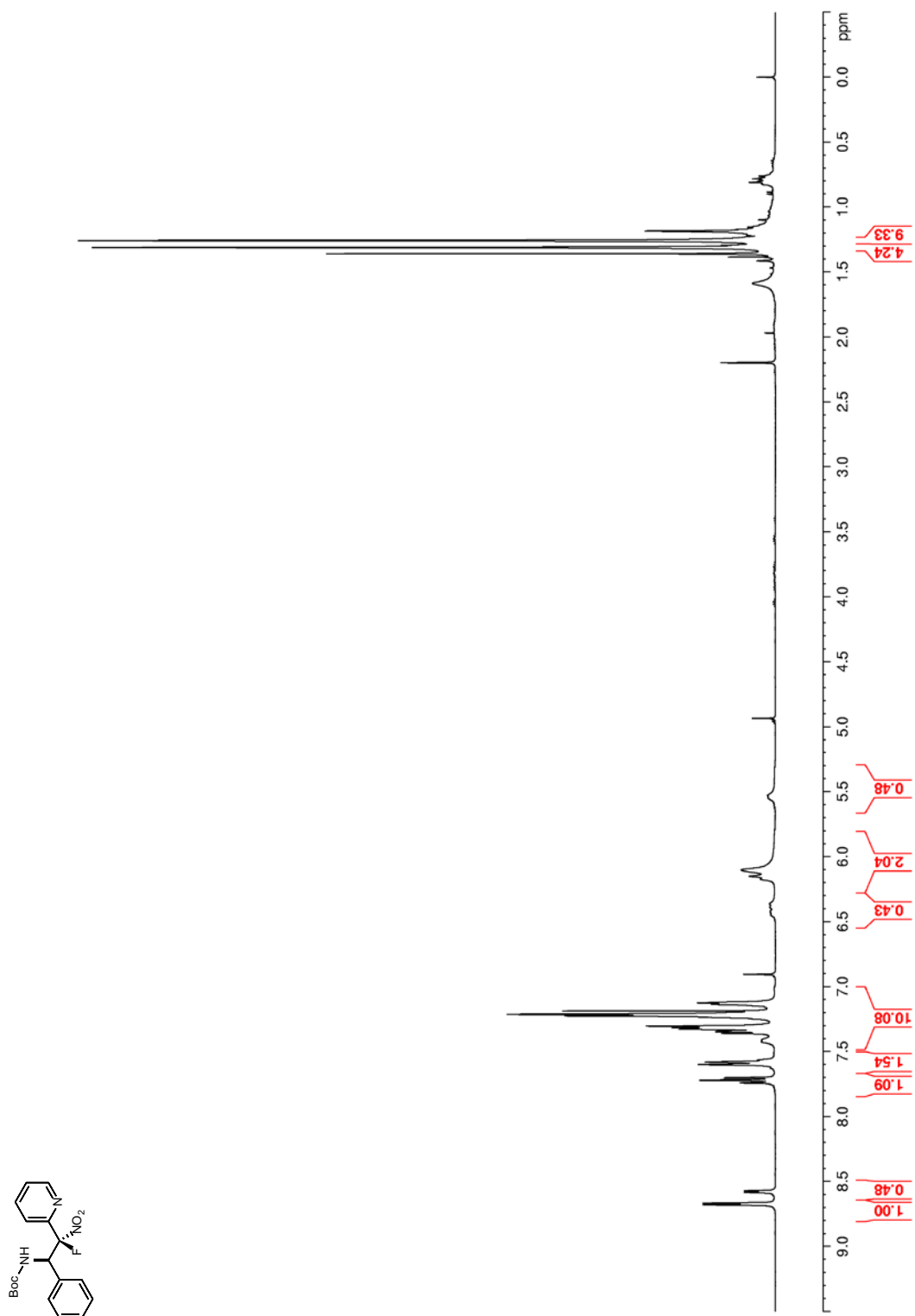


Figure 16. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **7f**

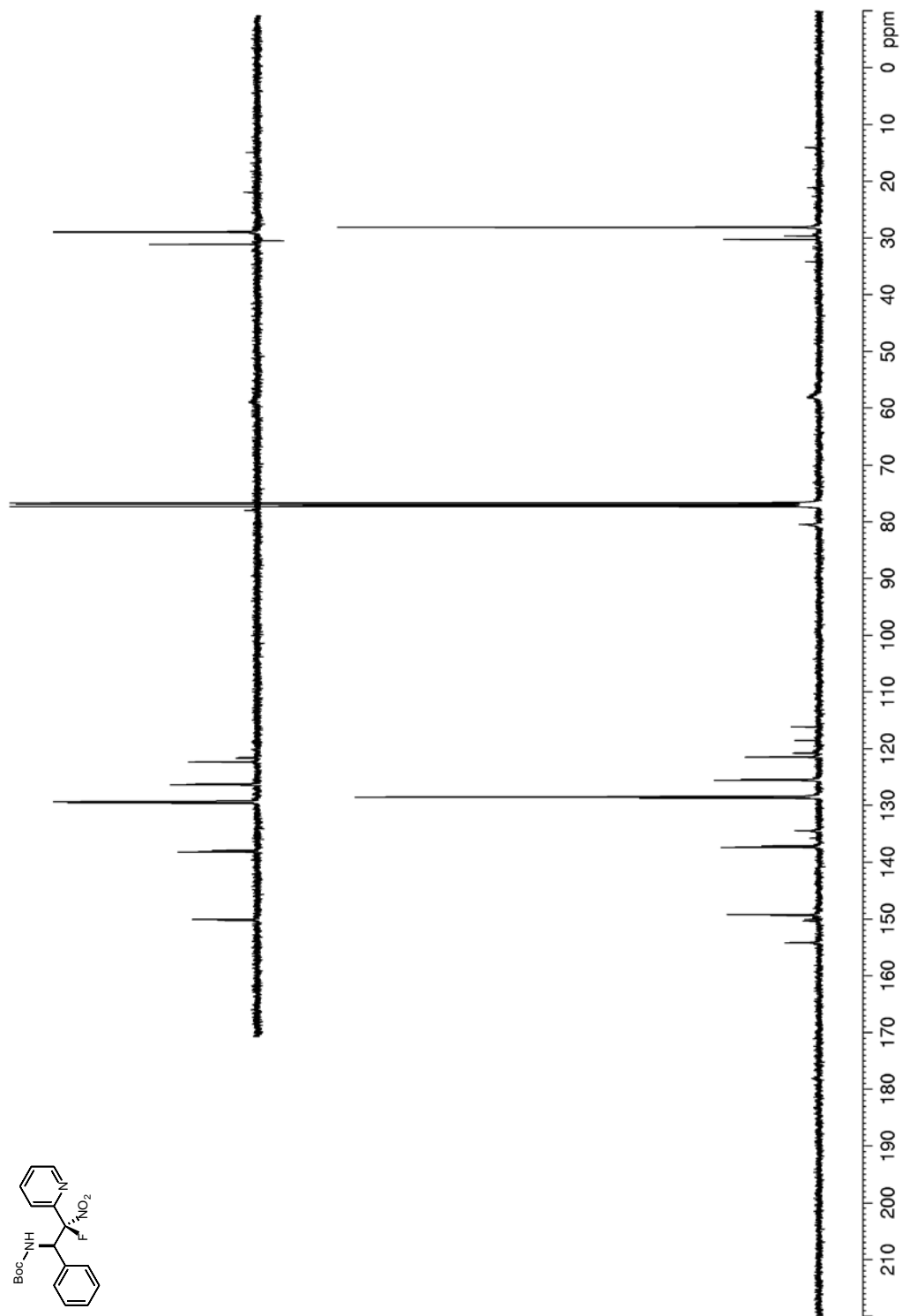


Figure 17. ^1H NMR (400 MHz, CDCl_3) of **7g**

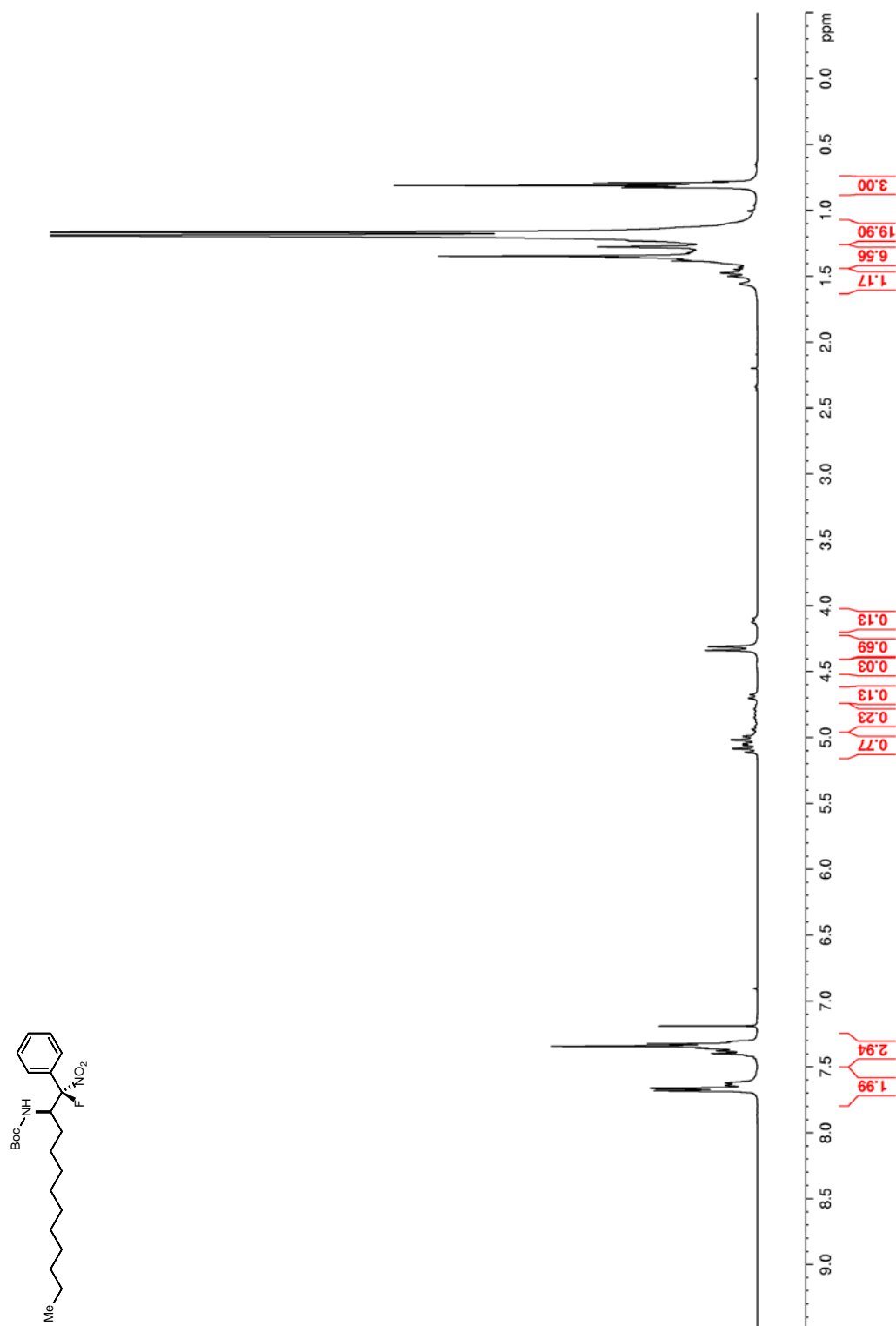


Figure 18. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **7g**

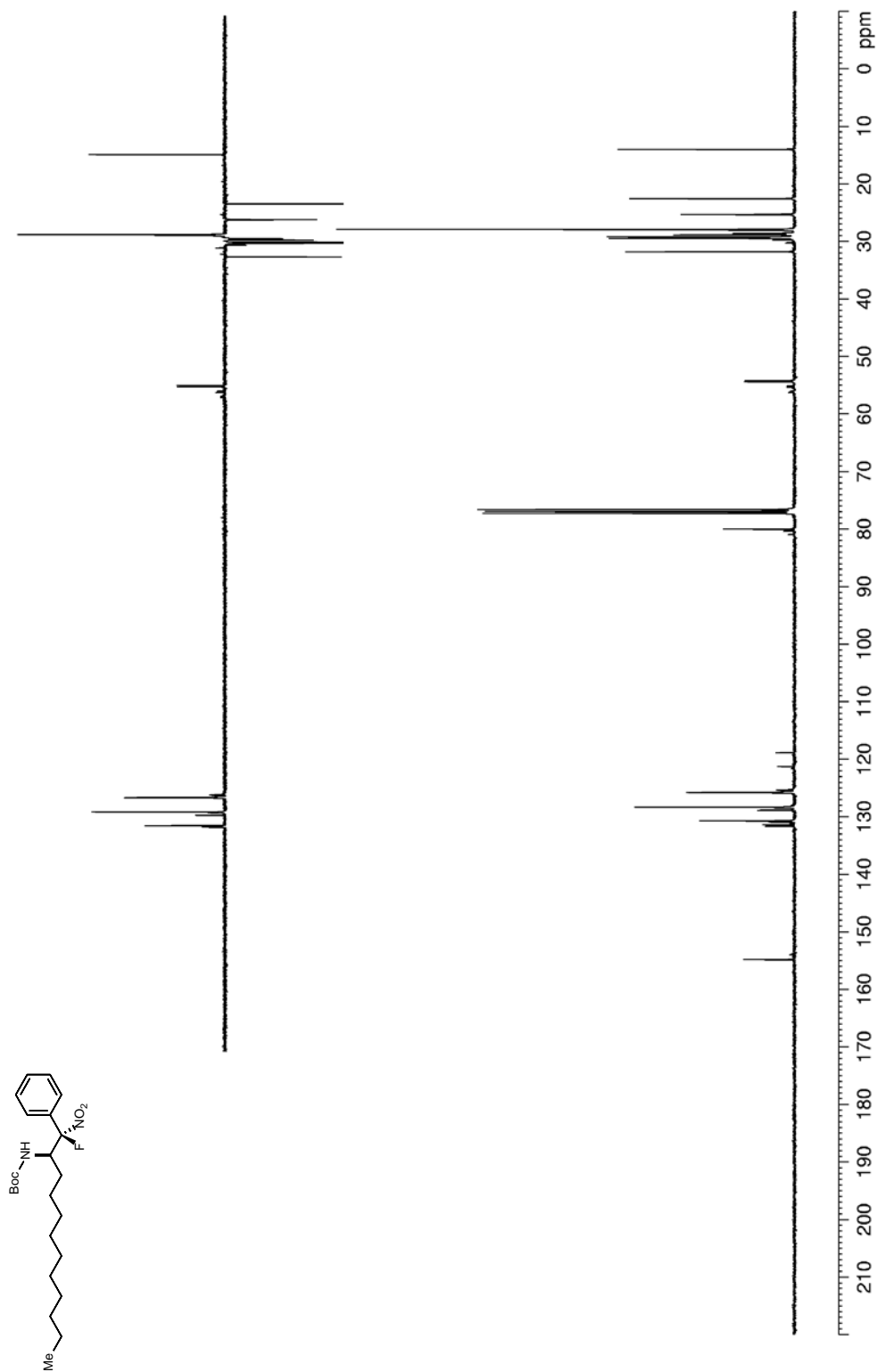


Figure 19. ^1H NMR (600 MHz, CDCl_3) of **7h**

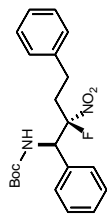
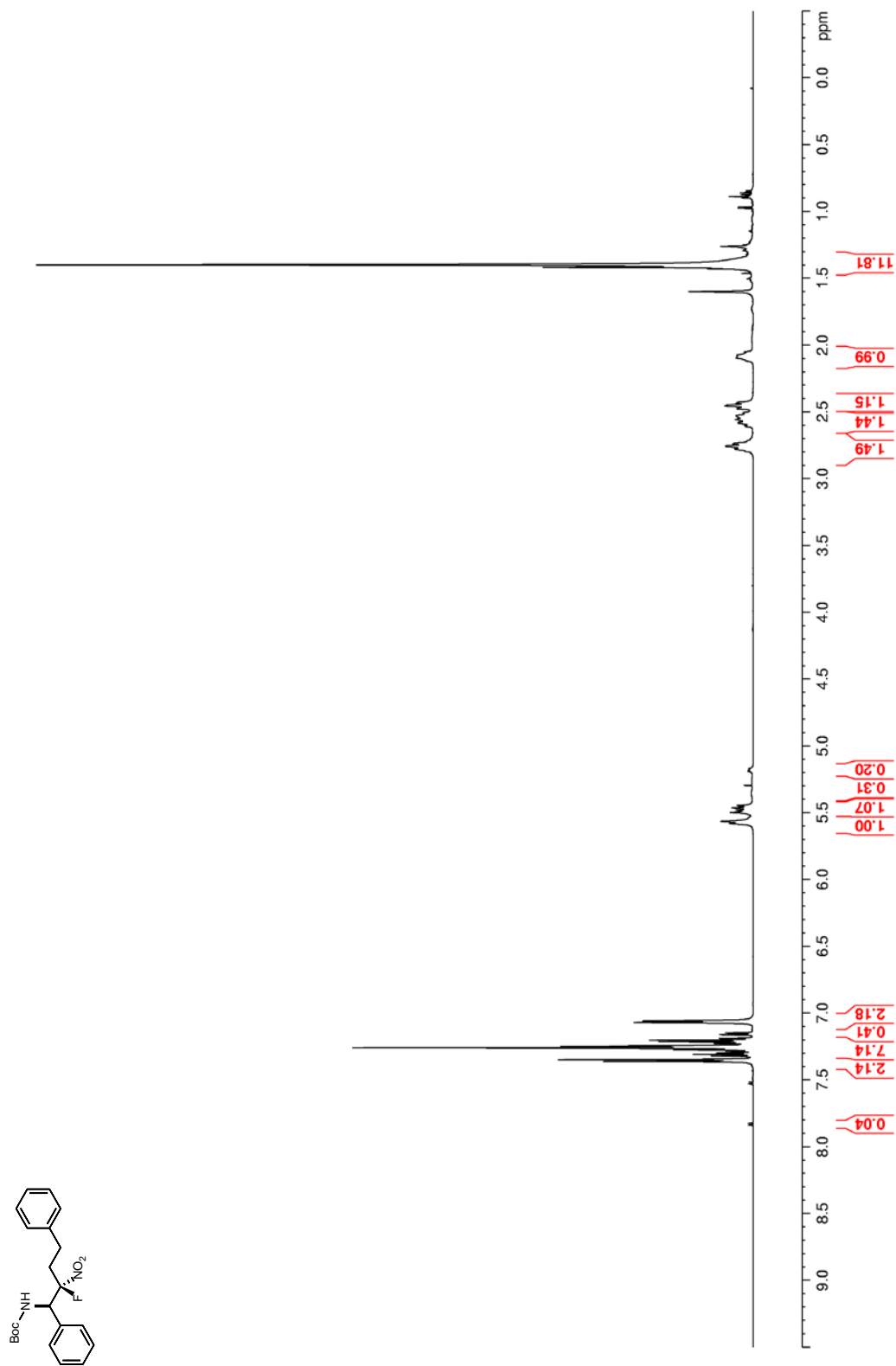


Figure 20. ^{13}C NMR/DEPT135 (150 MHz, CDCl_3) of **7h**

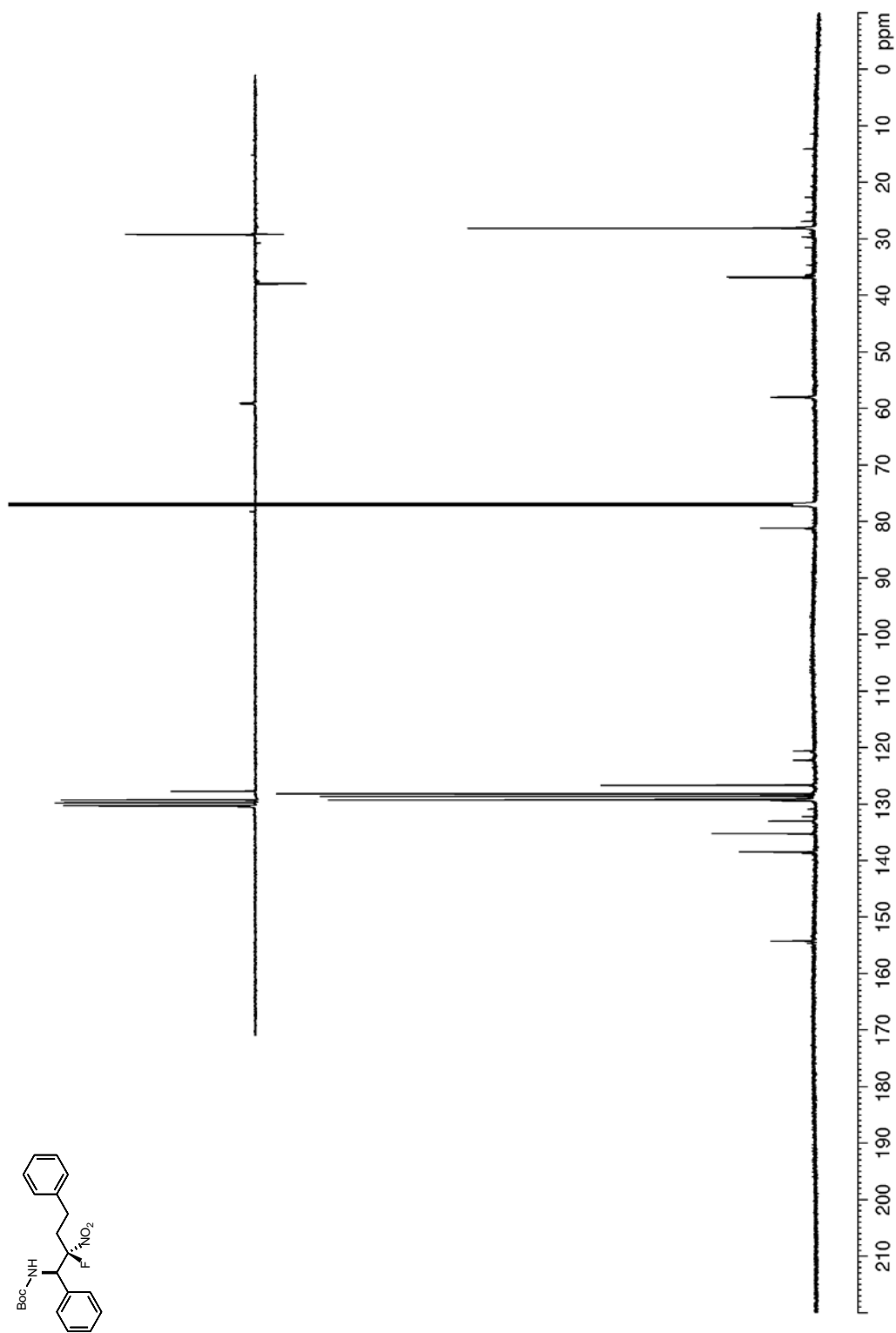


Figure 21. ^1H NMR (600 MHz, CDCl_3) of **7i**

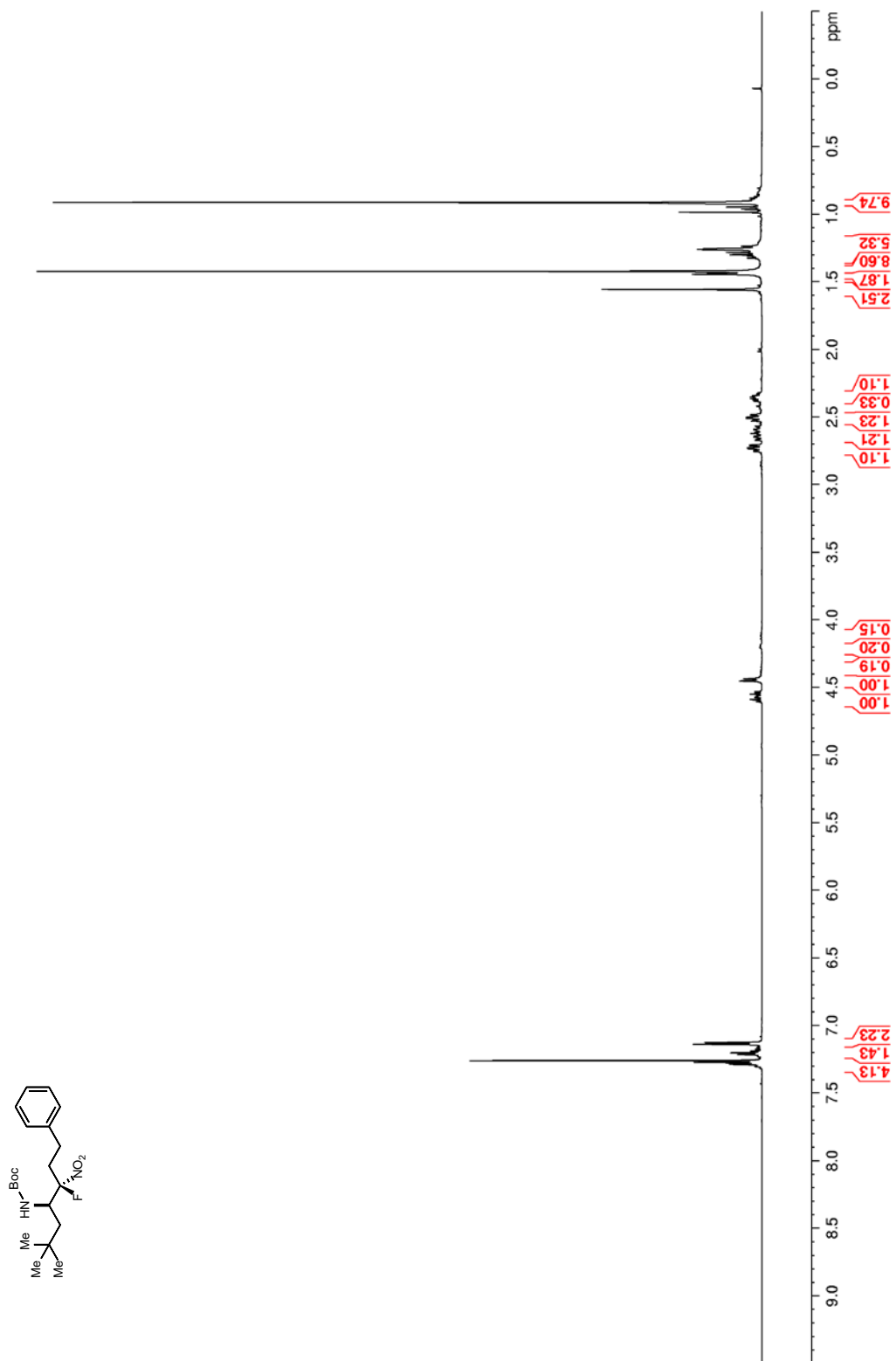


Figure 22. ^{13}C NMR/DEPT135 (150 MHz, CDCl_3) of **7i**

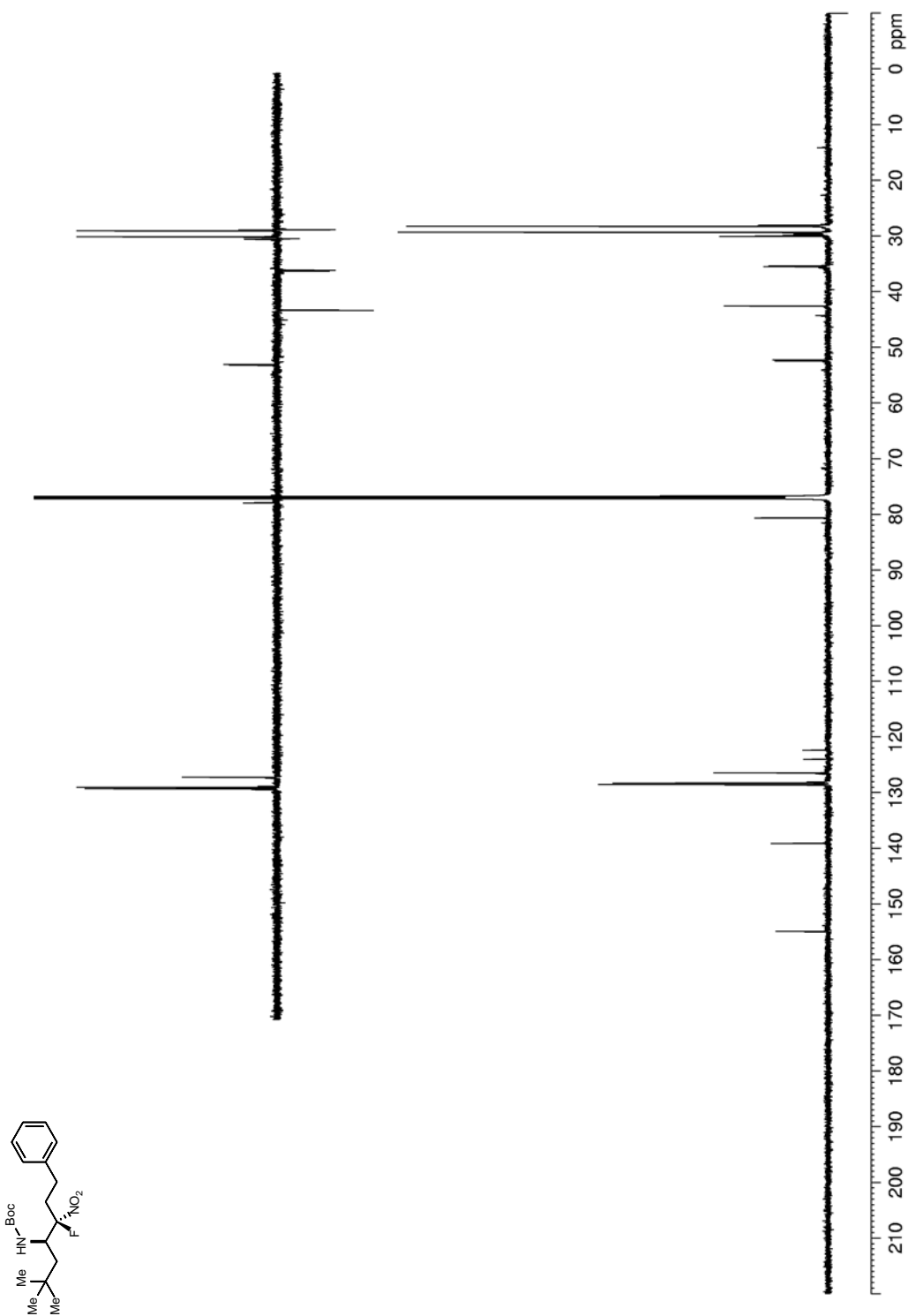


Figure 23. ^1H NMR (600 MHz, CDCl_3) of **7j**

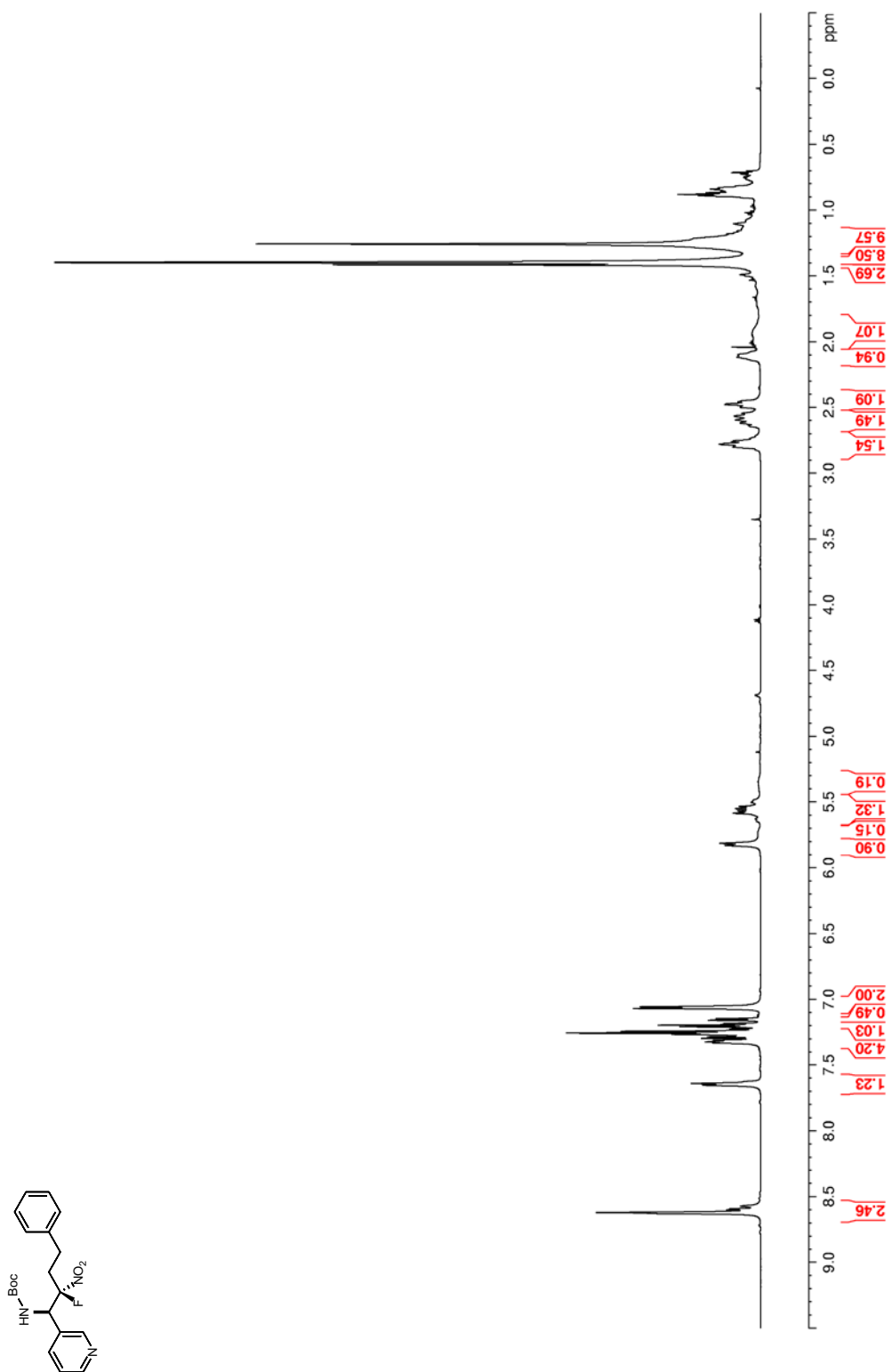


Figure 24. ^{13}C NMR/DEPT135 (150 MHz, CDCl_3) of **7j**

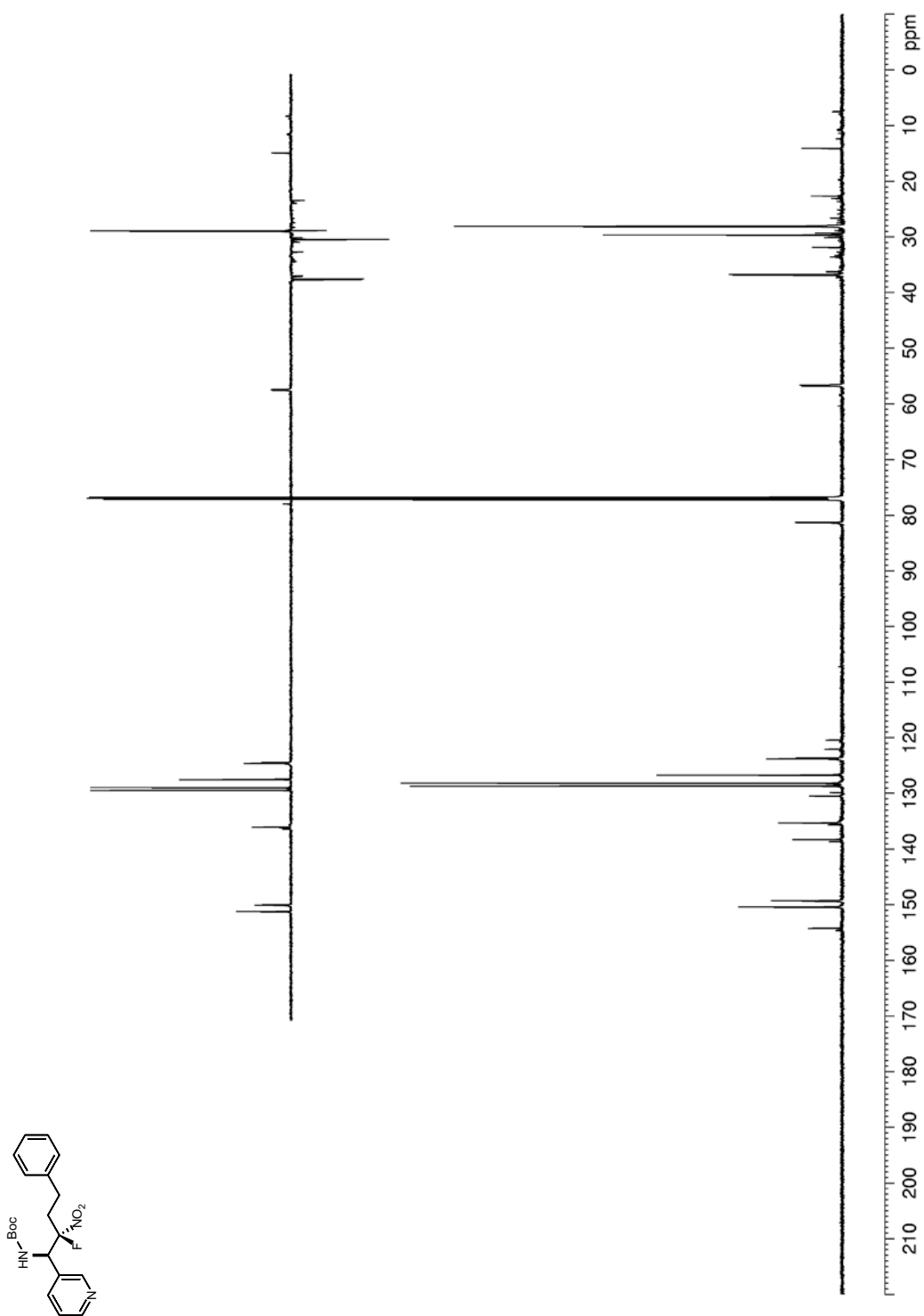


Figure 25. ^1H NMR (600 MHz, MeOD) of *cis*-8

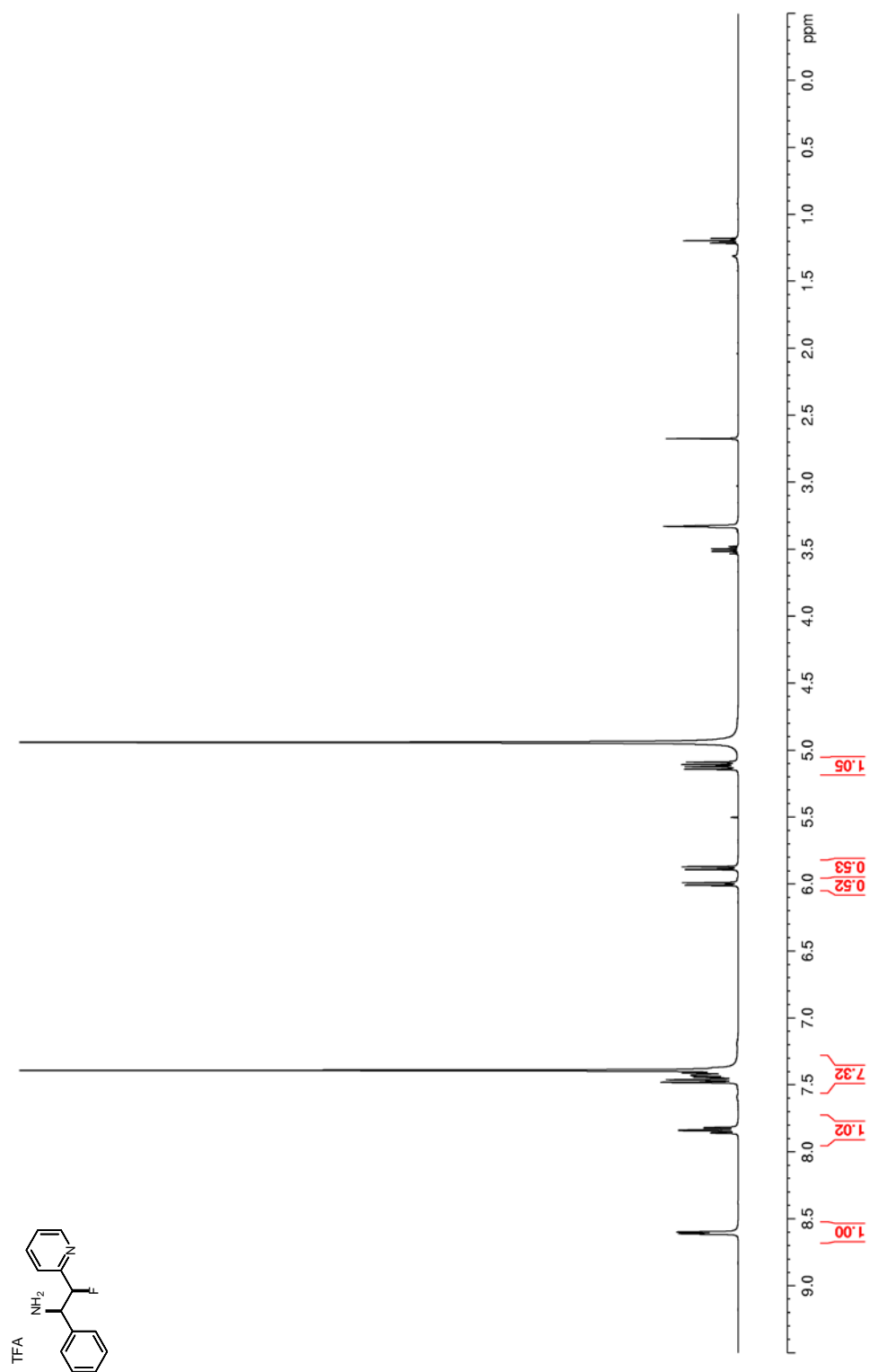


Figure 26. ^{13}C NMR/DEPT135 (150 MHz, MeOD) of *cis*-8

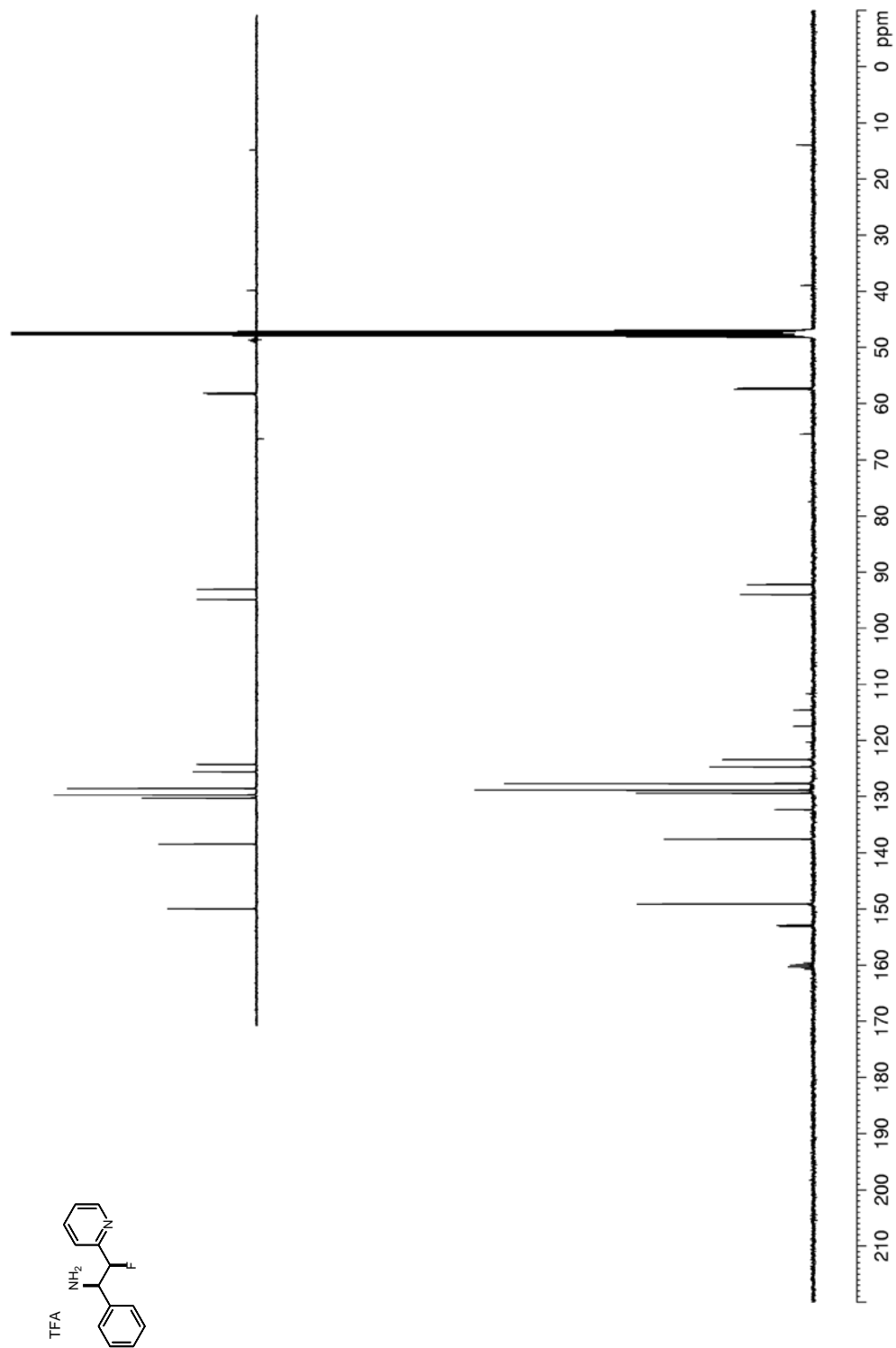


Figure 27. ^1H NMR (400 MHz, MeOD) of *trans*-8

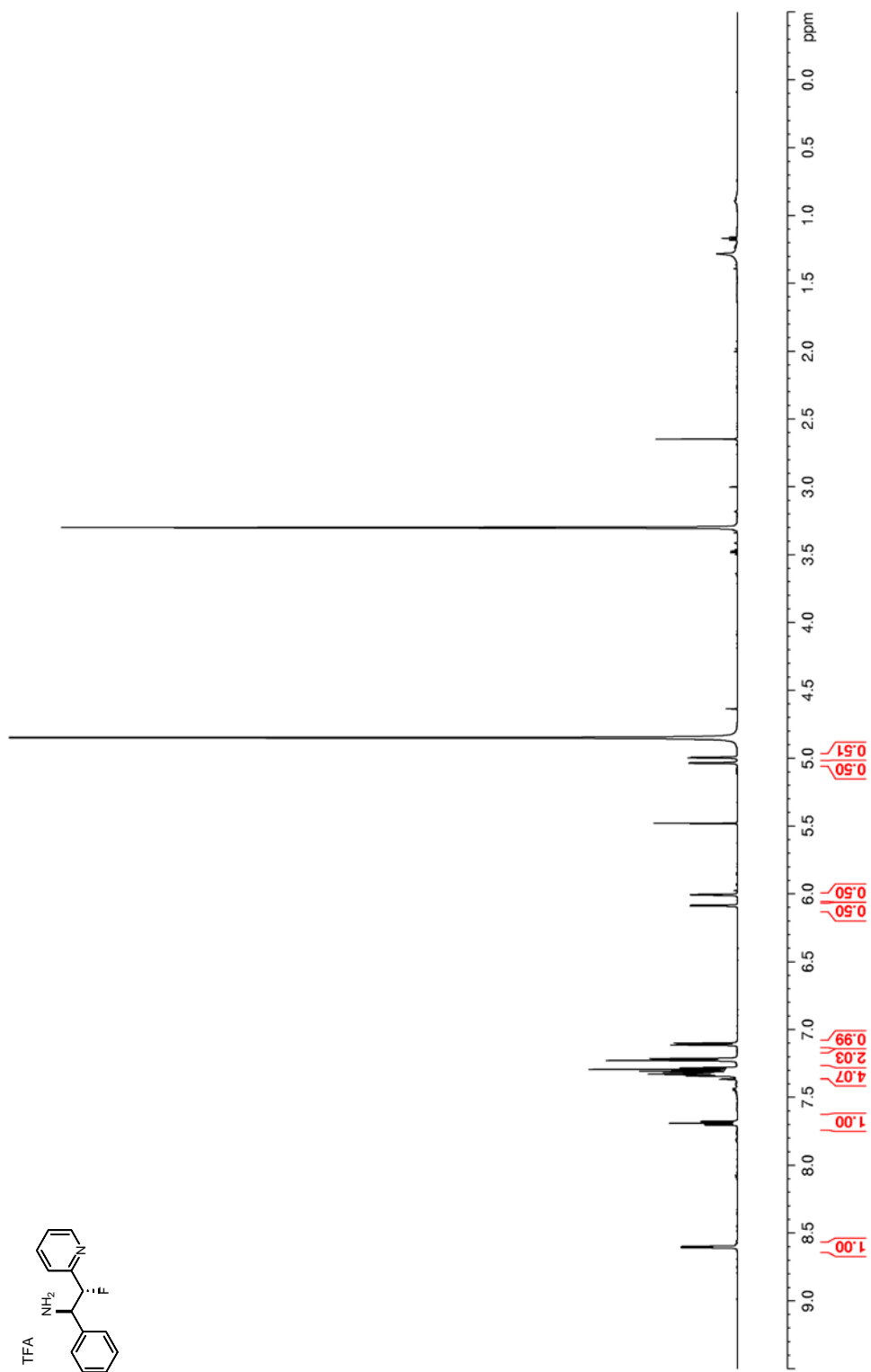


Figure 28. ^{13}C NMR/DEPT135 (100 MHz, MeOD) of *trans*-8

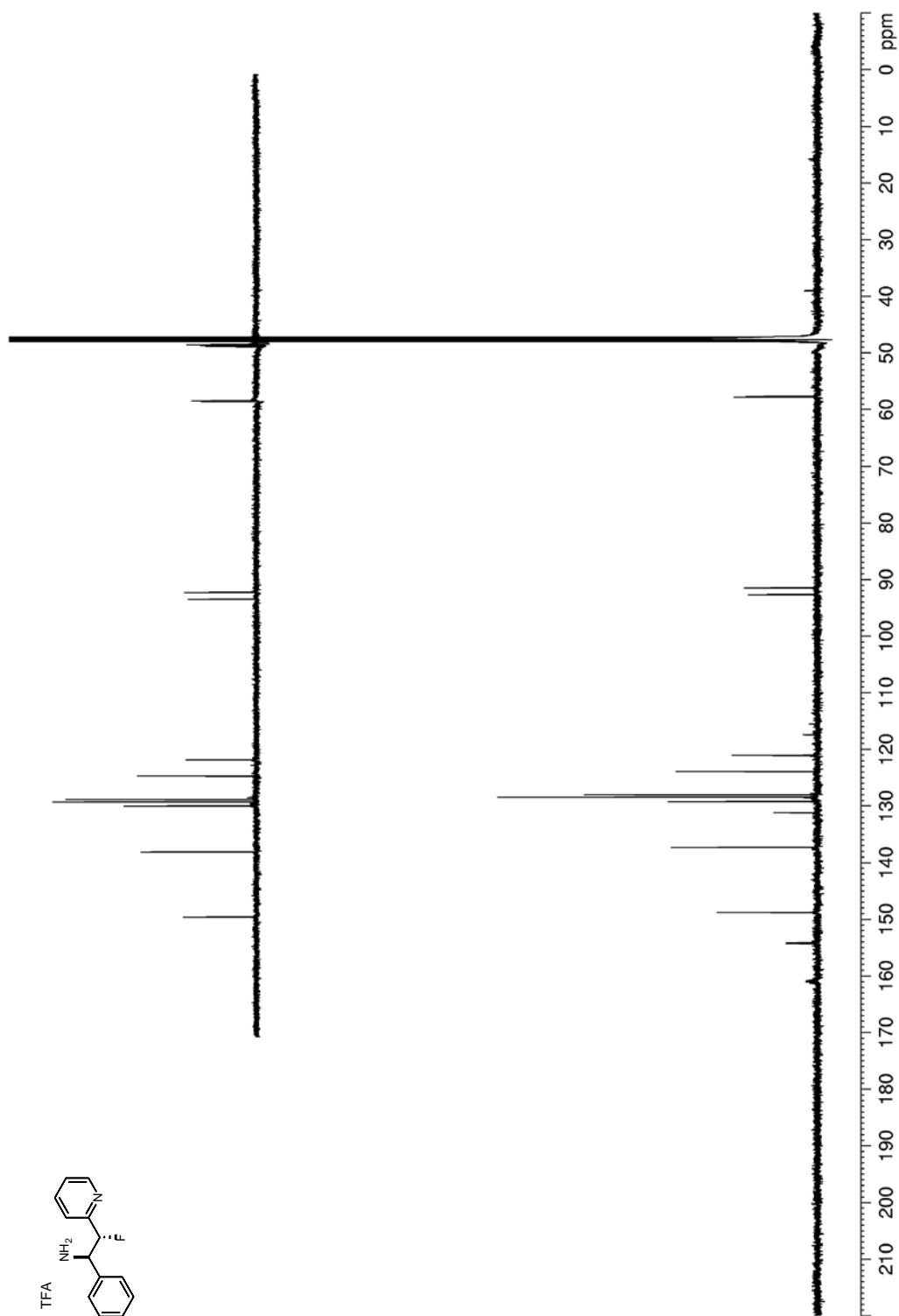


Figure 29. ^1H NMR (400 MHz, CDCl_3) of **9**

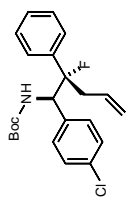
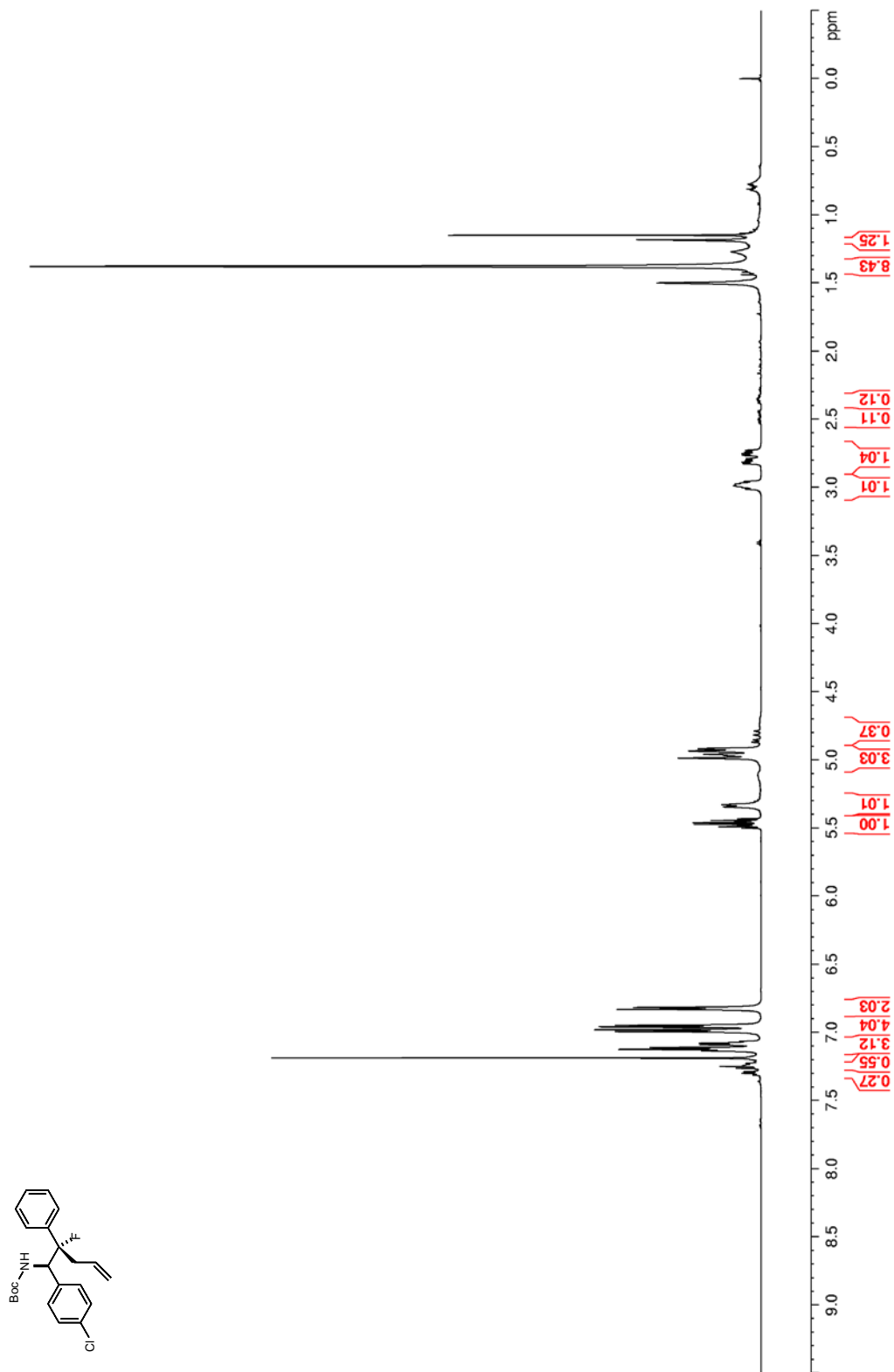


Figure 30. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **9**

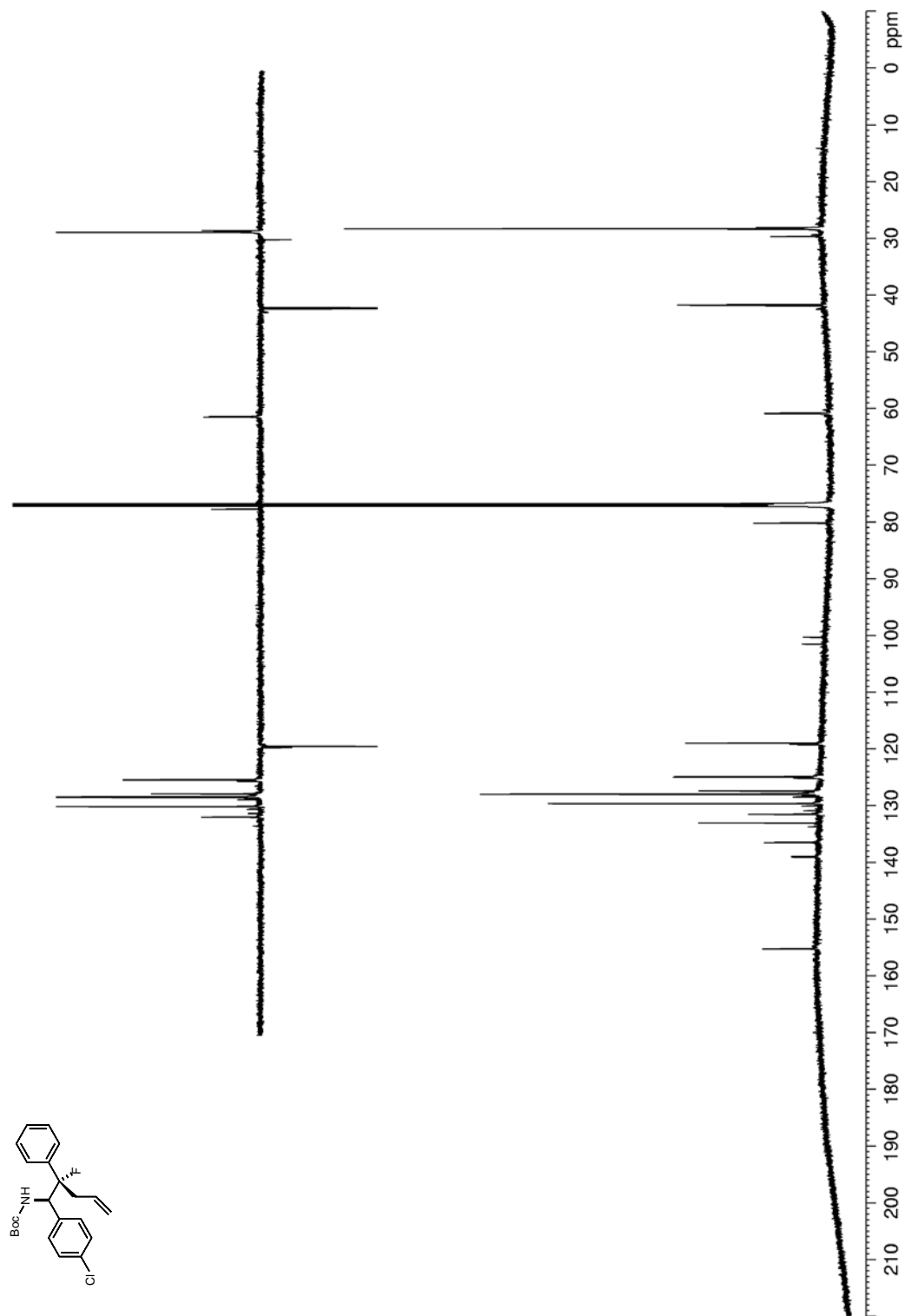


Figure 31. ^1H NMR (400 MHz, CDCl_3) of **10**

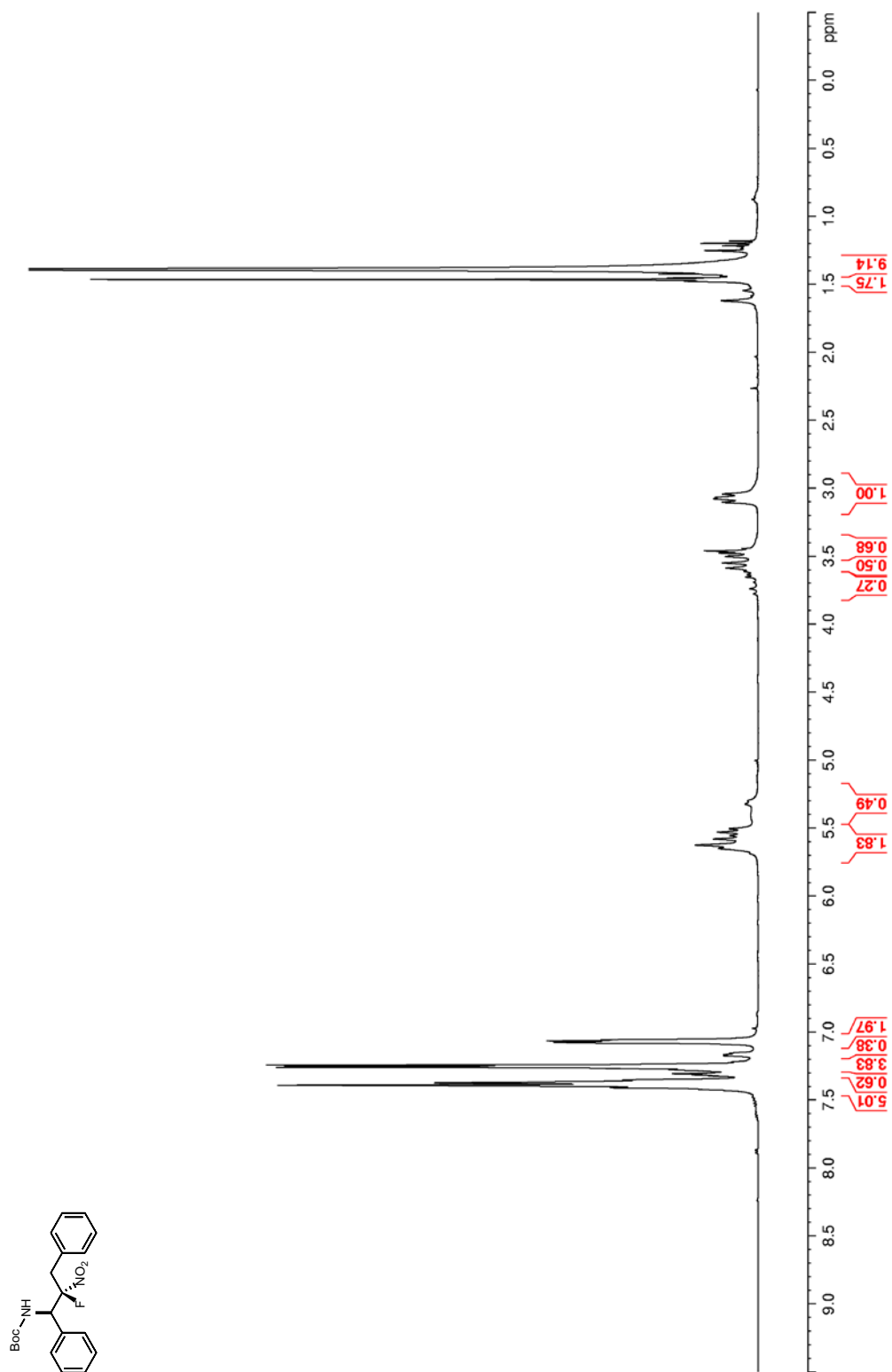


Figure 32. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **10**

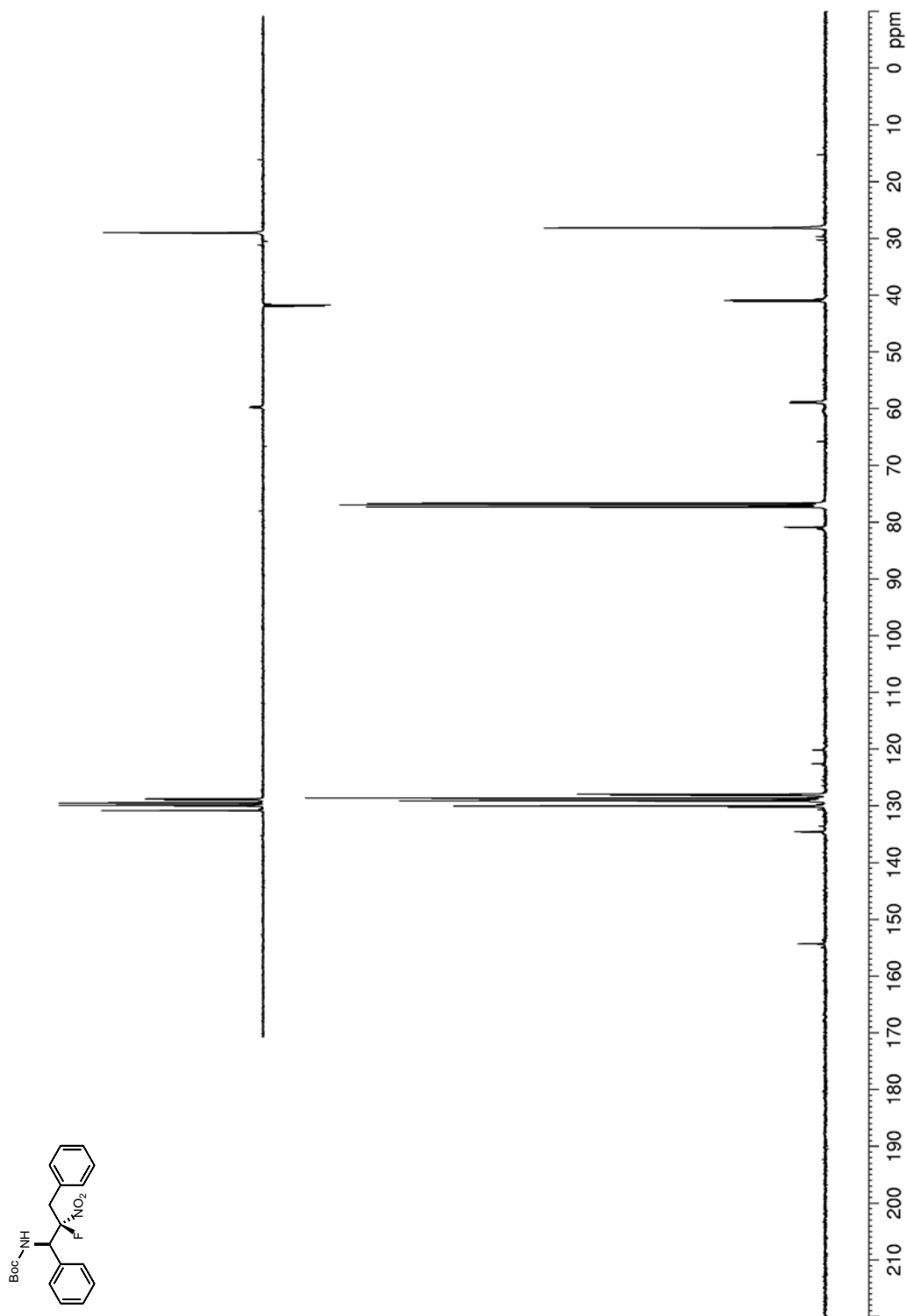


Figure 33. ^1H NMR (400 MHz, CDCl_3) of **11**

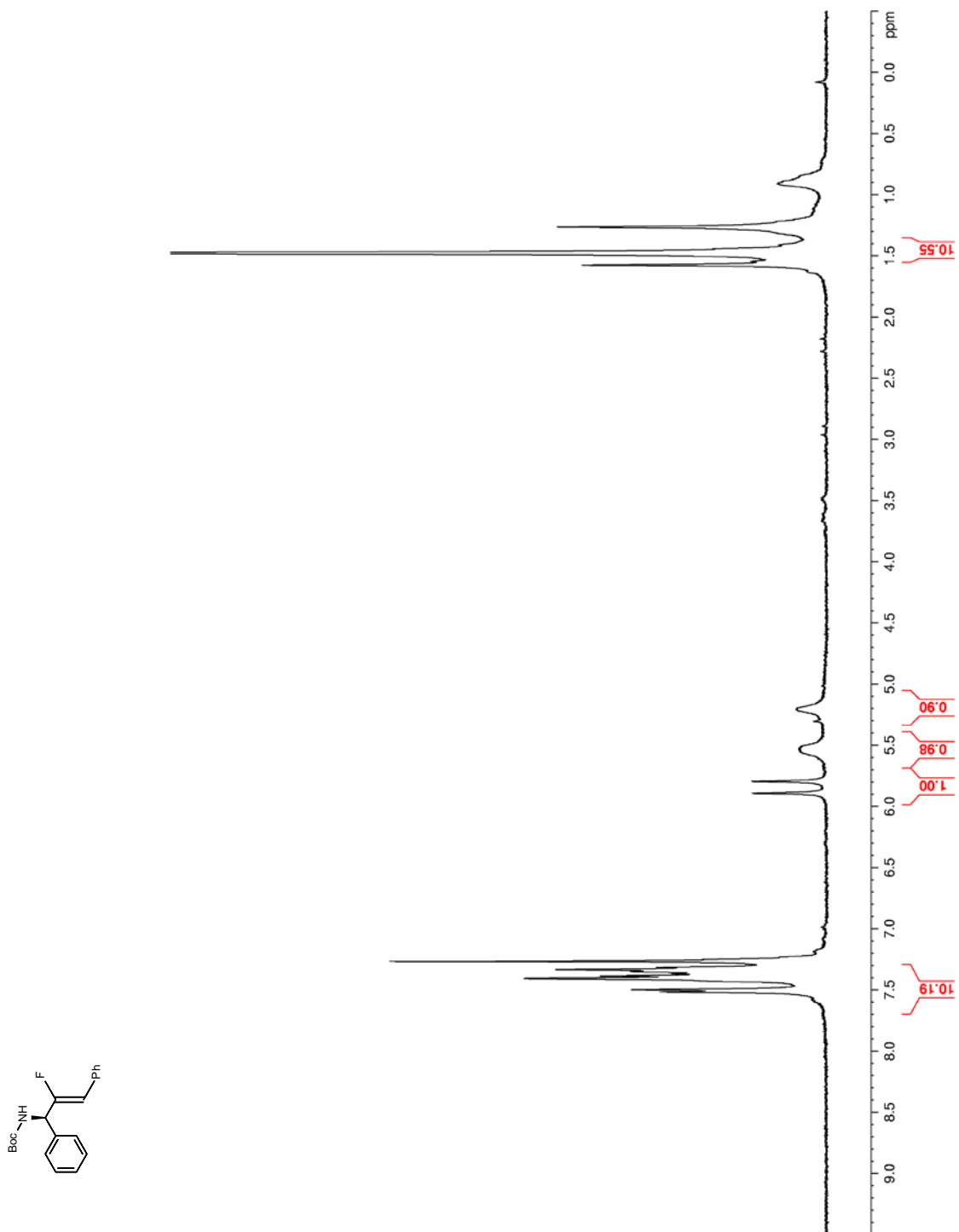


Figure 34. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **11**

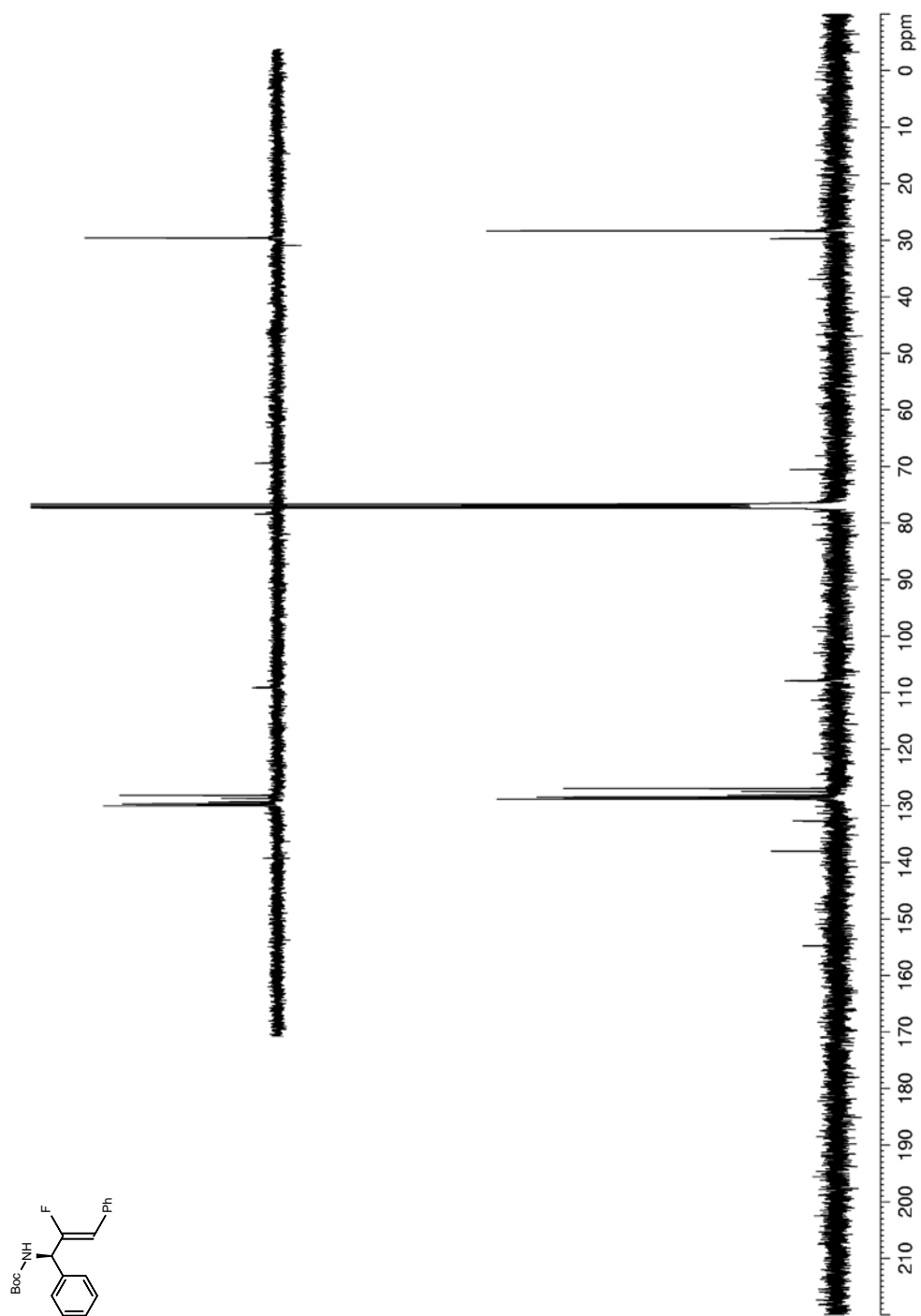


Figure 35. ^1H NMR (600 MHz, CDCl_3) of **S1**

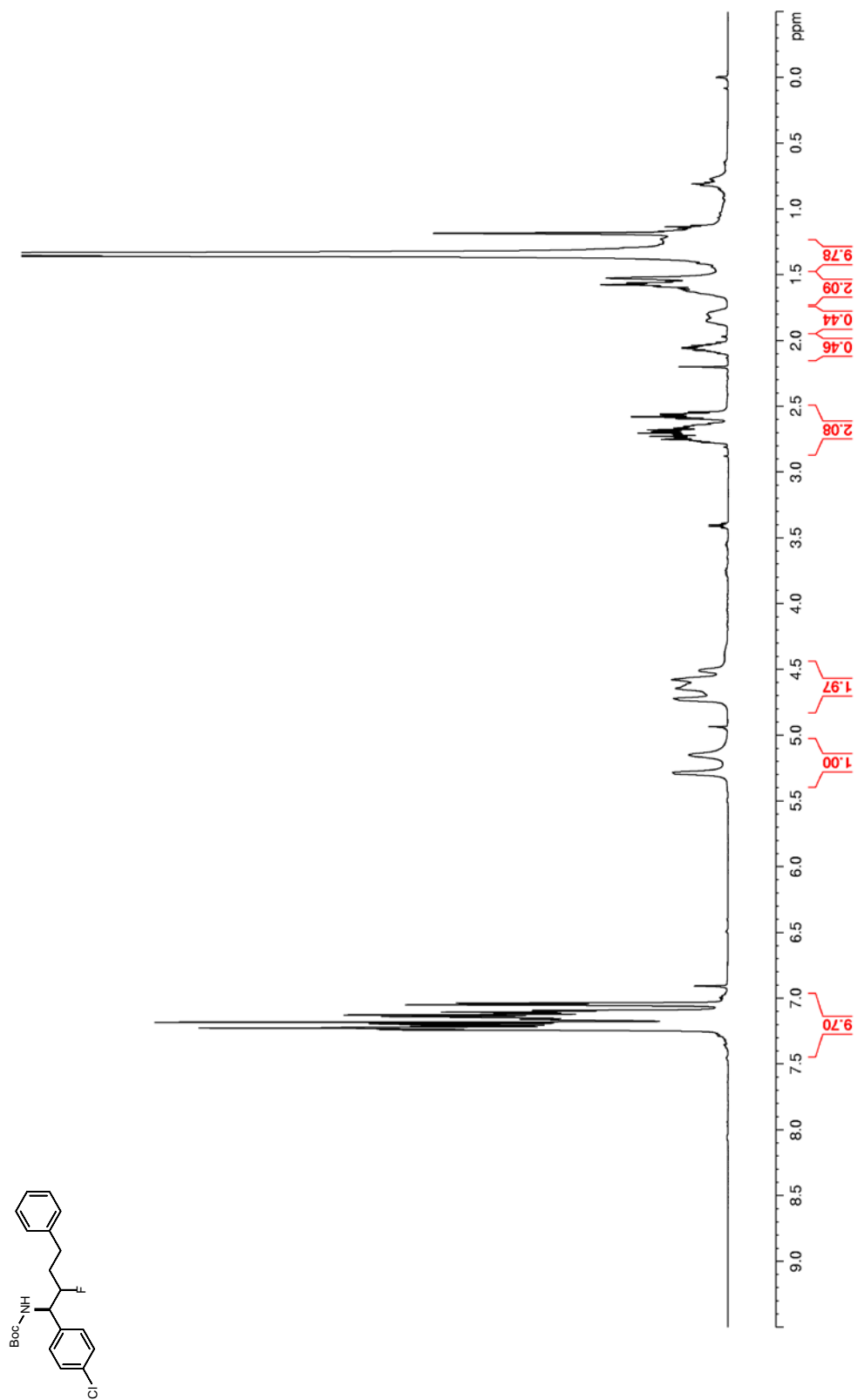


Figure 36. ^{13}C NMR/DEPT135 (150 MHz, CDCl_3) of **S1**

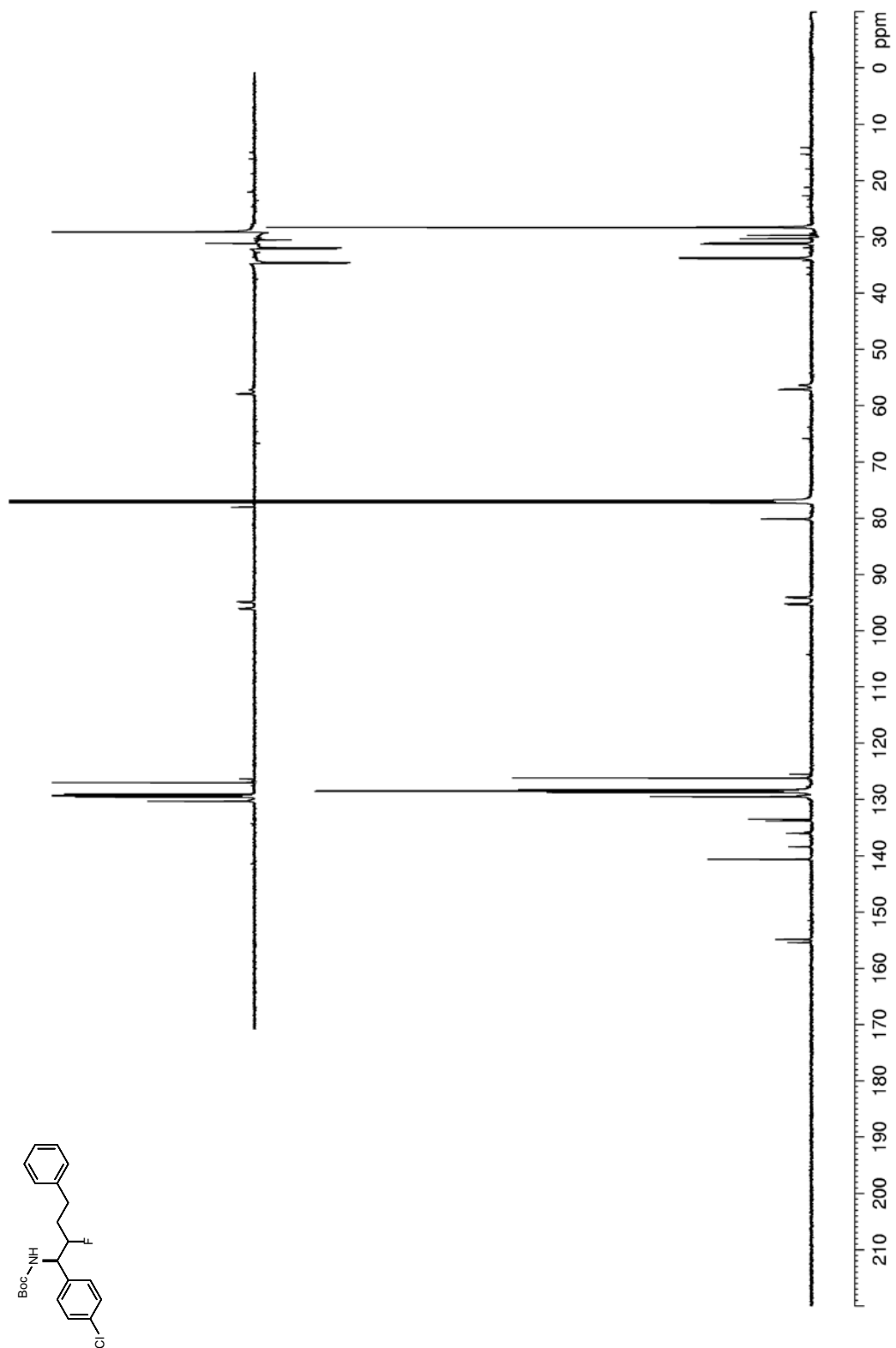


Figure 37. ^1H NMR (400 MHz, CDCl_3) of **S2**

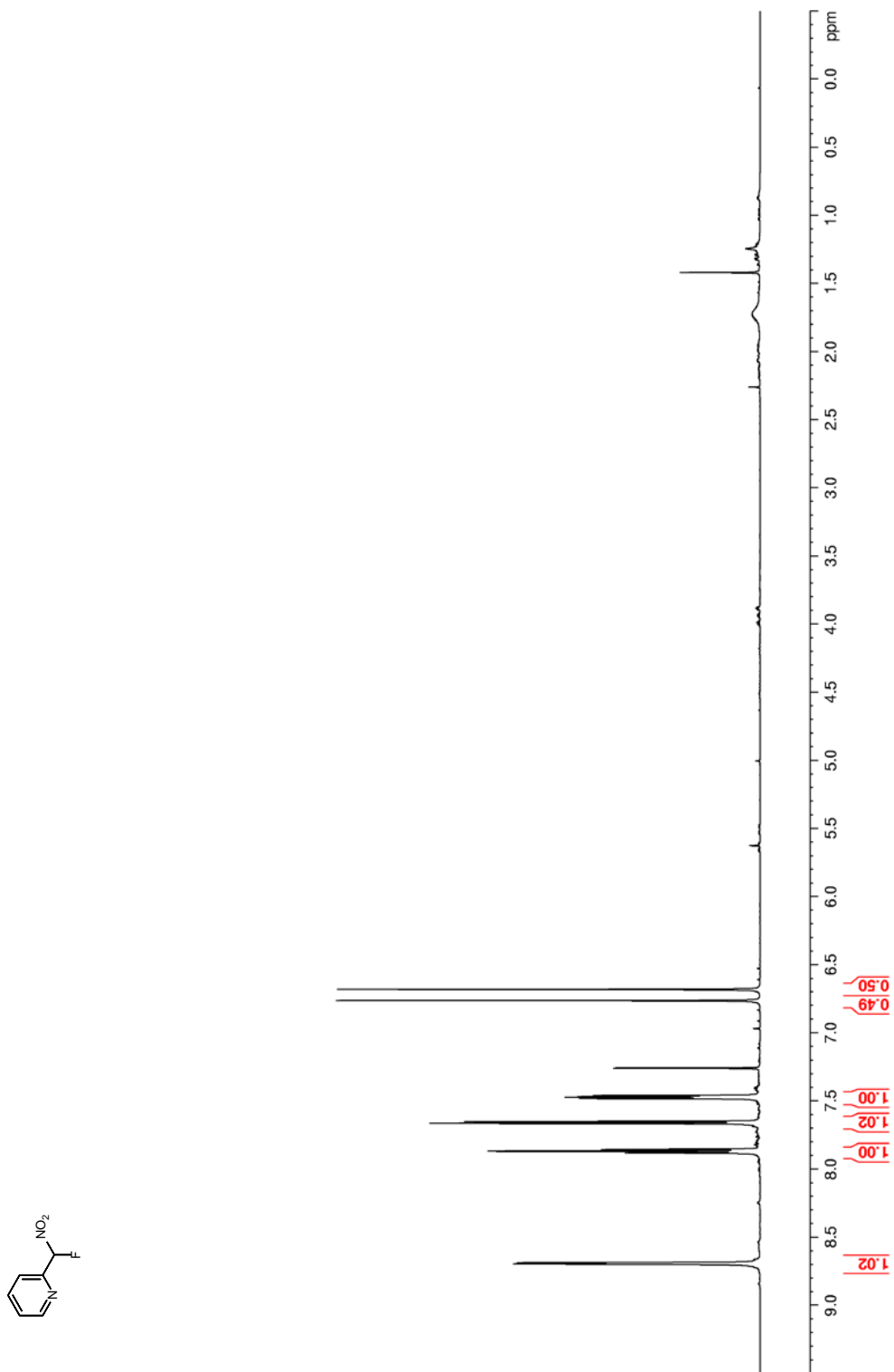


Figure 38. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **S2**

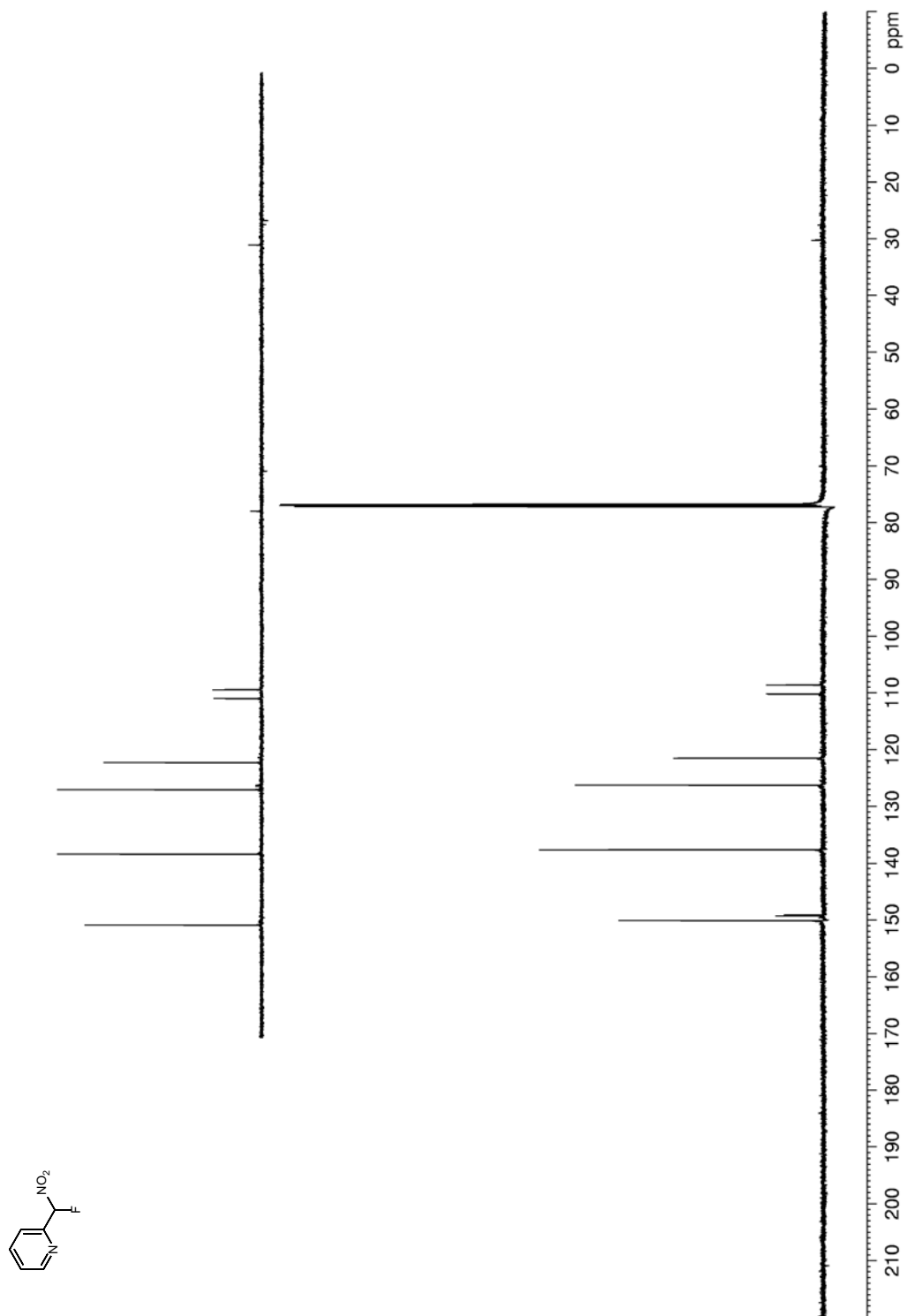


Figure 39. ^1H NMR (400 MHz, CDCl_3) of S3

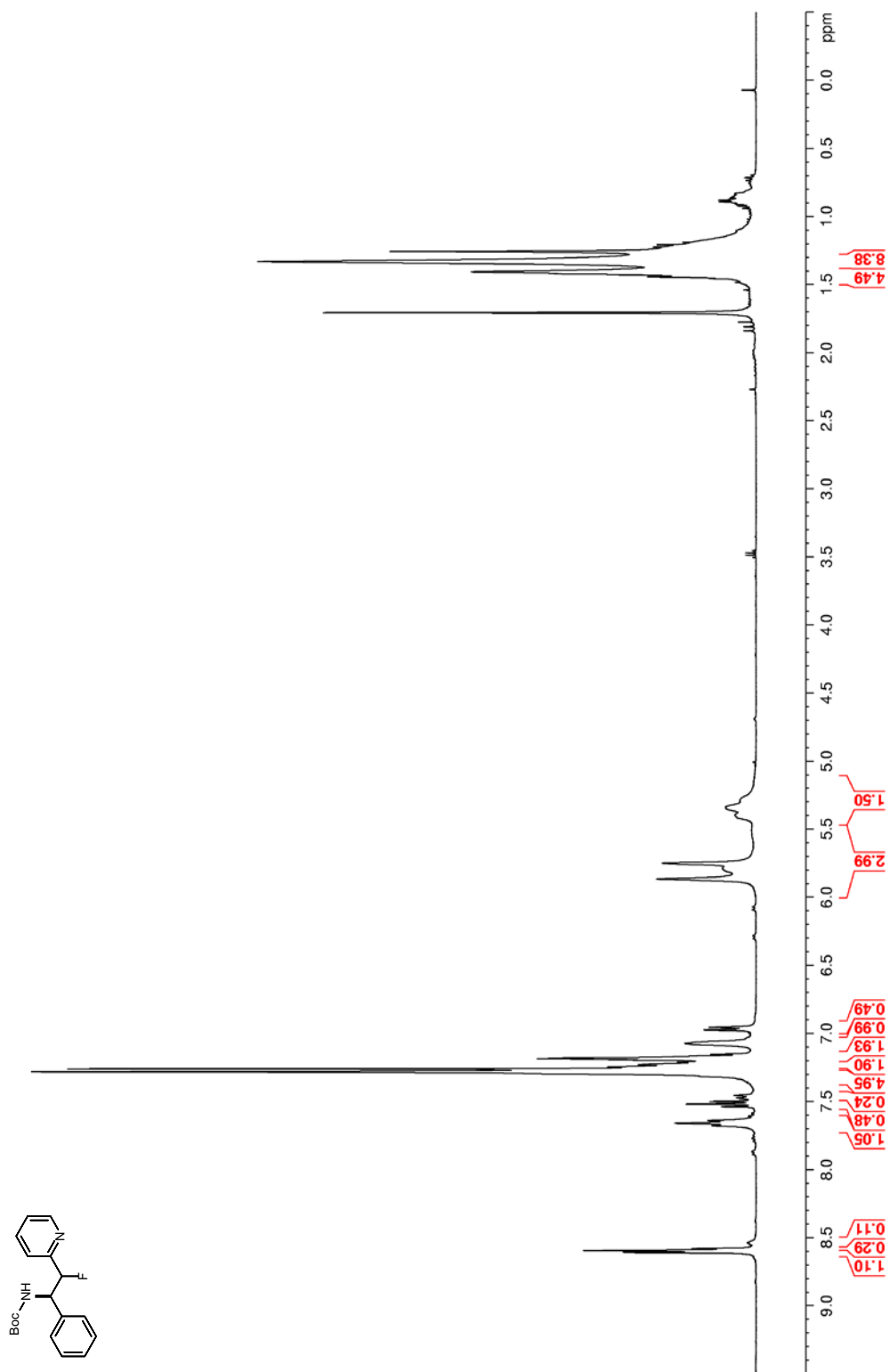


Figure 40. ^{13}C NMR/DEPT135 (100 MHz, CDCl_3) of **S3**

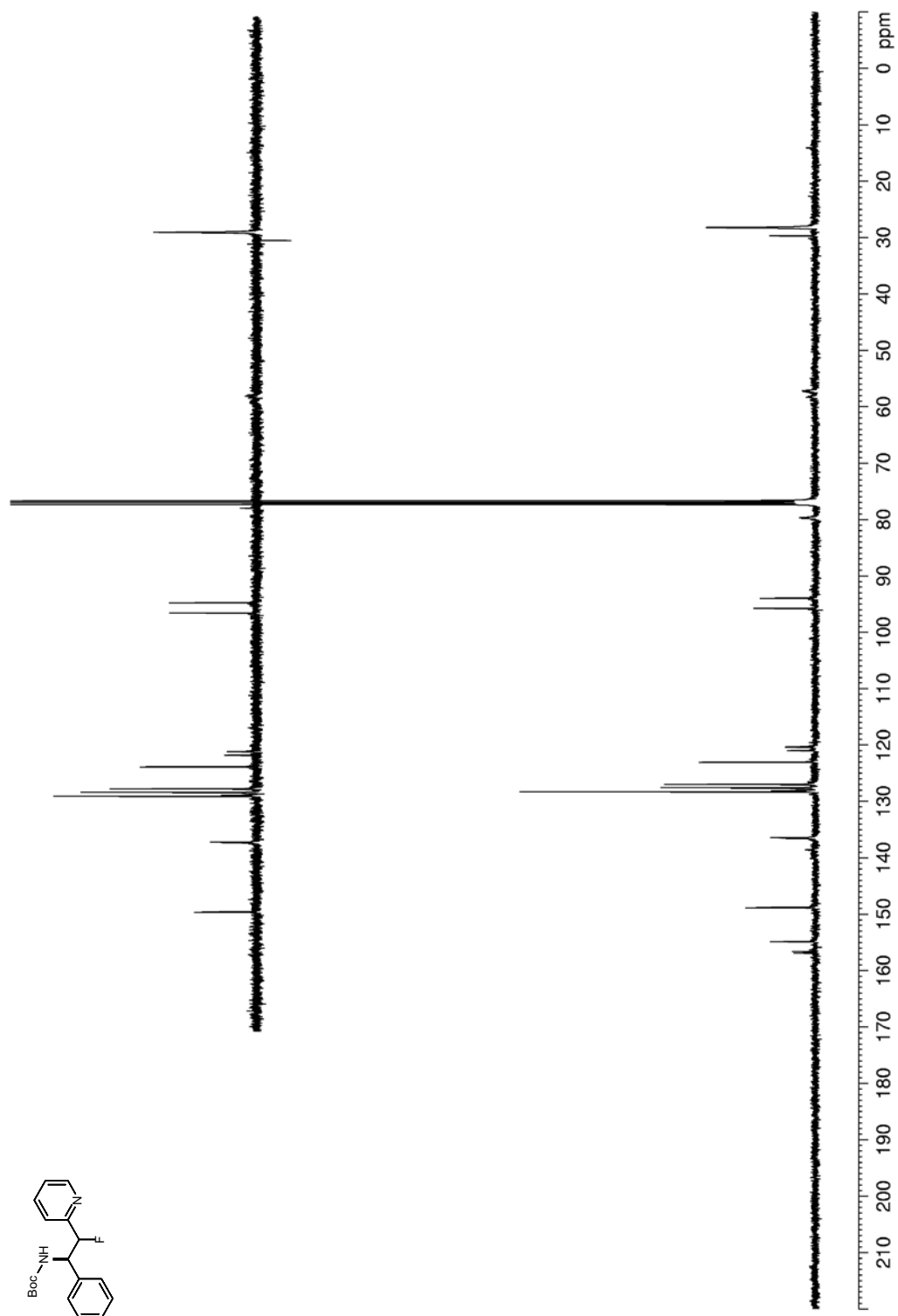


Figure 41. ^1H NMR (400 MHz, MeOD) of S4

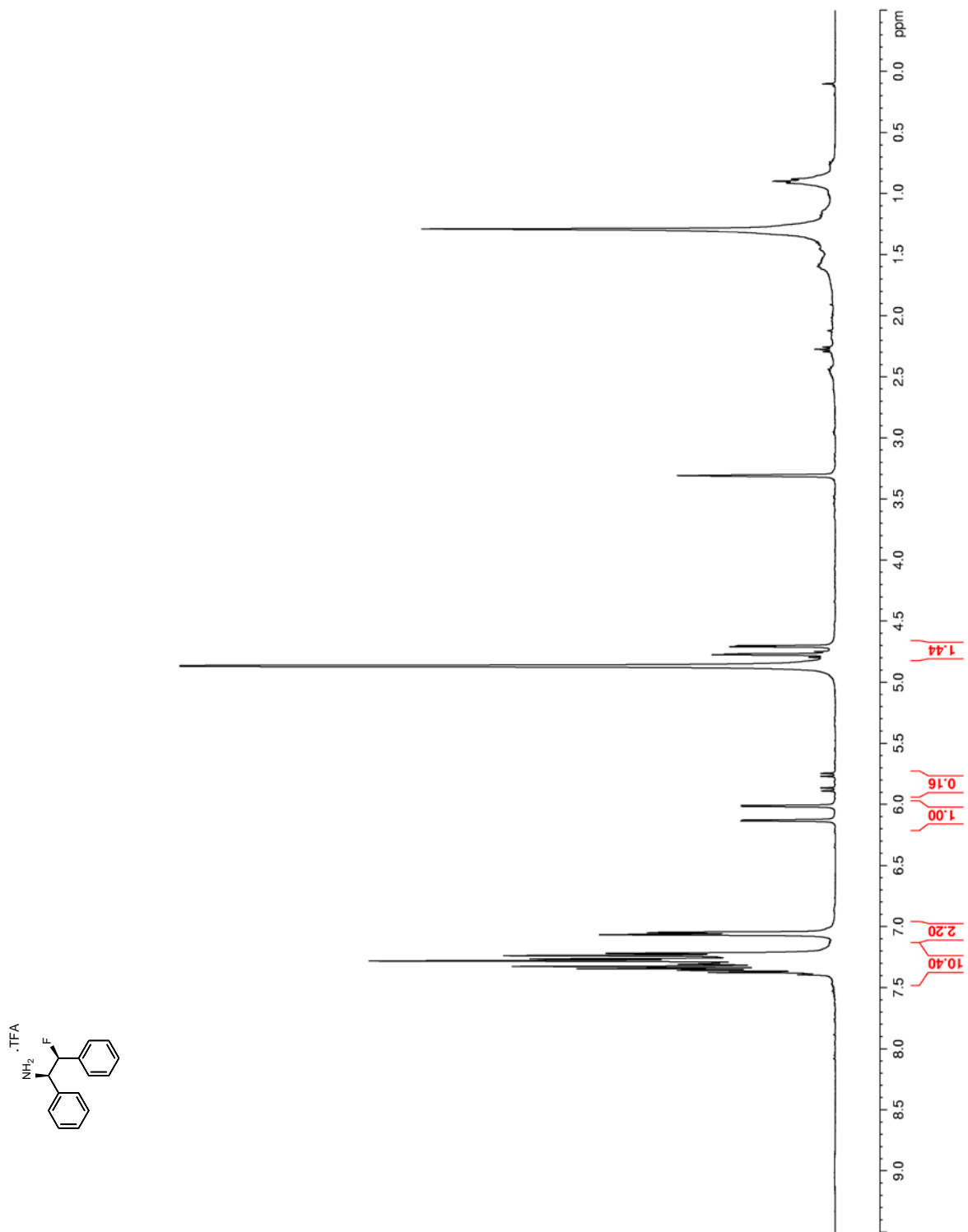


Figure 42. ^{13}C NMR/DEPT135 (100 MHz, MeOD) of **S4**

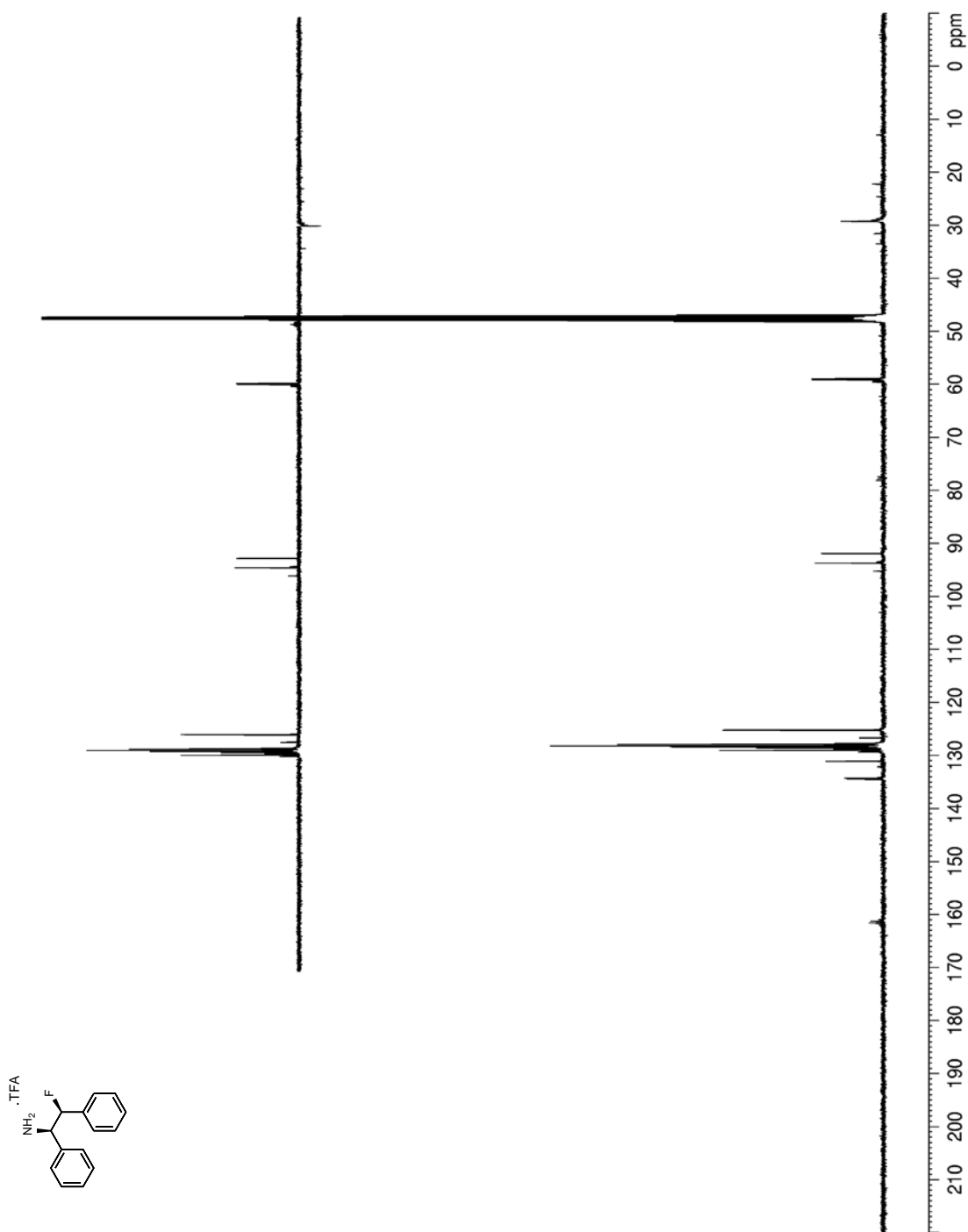
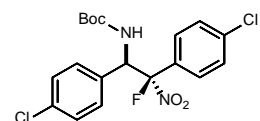
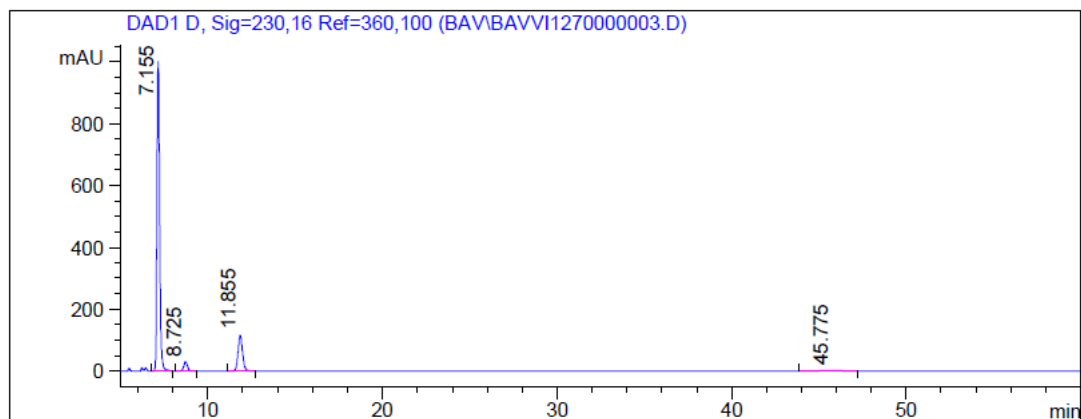
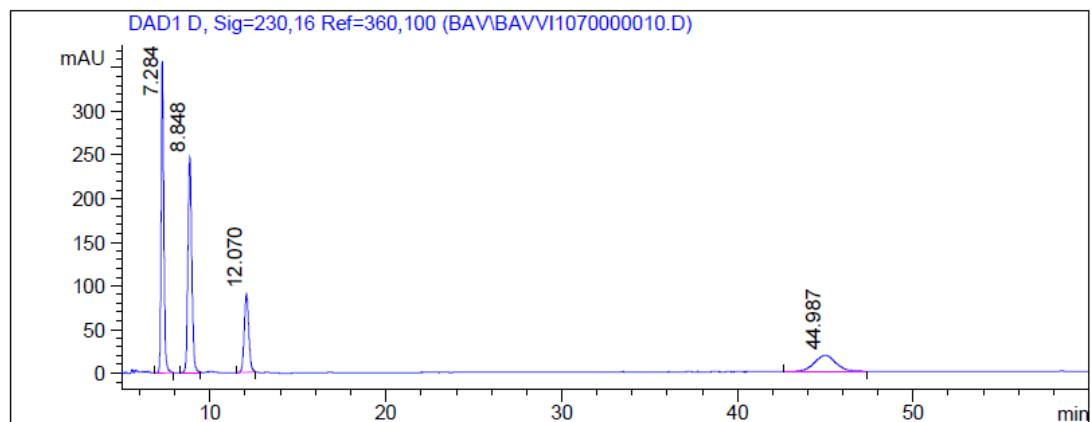


Figure 43. HPLC trace of **3**.



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

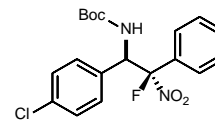
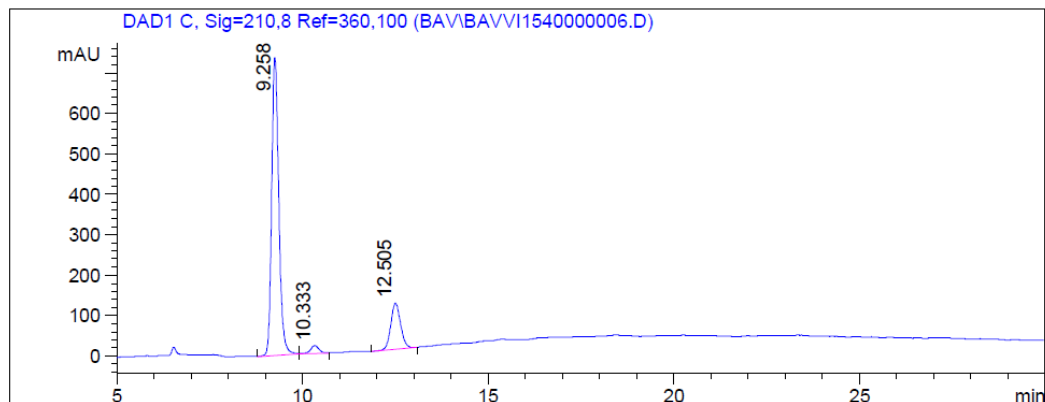
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|-----------|--------|
| 1 | 7.155 | 0.176 | 10599.966 | 79.39 |
| 2 | 8.725 | 0.252 | 454.341 | 3.40 |
| 3 | 11.855 | 0.298 | 2085.416 | 15.62 |
| 4 | 45.775 | 1.615 | 212.238 | 1.59 |



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

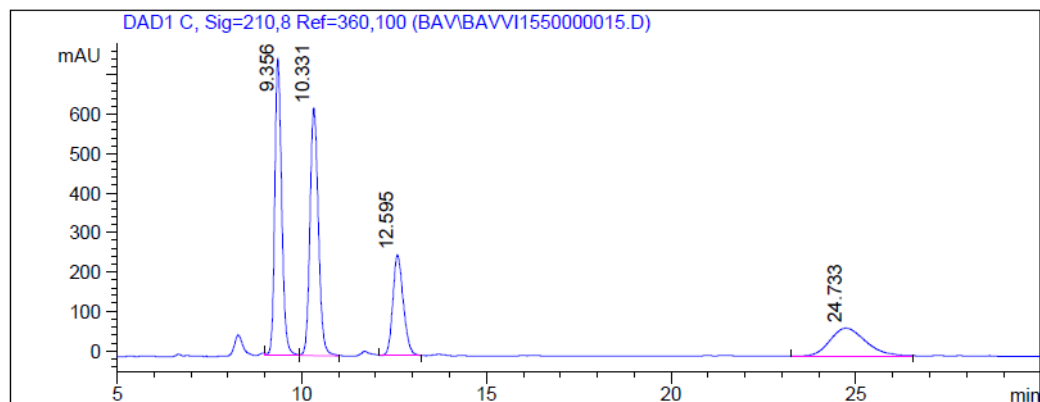
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 7.284 | 0.174 | 3740.637 | 34.65 |
| 2 | 8.848 | 0.255 | 3772.445 | 34.94 |
| 3 | 12.070 | 0.295 | 1607.546 | 14.89 |
| 4 | 44.987 | 1.487 | 1676.373 | 15.53 |

Figure 44. HPLC trace of **7a**.



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

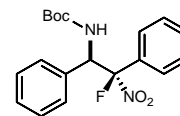
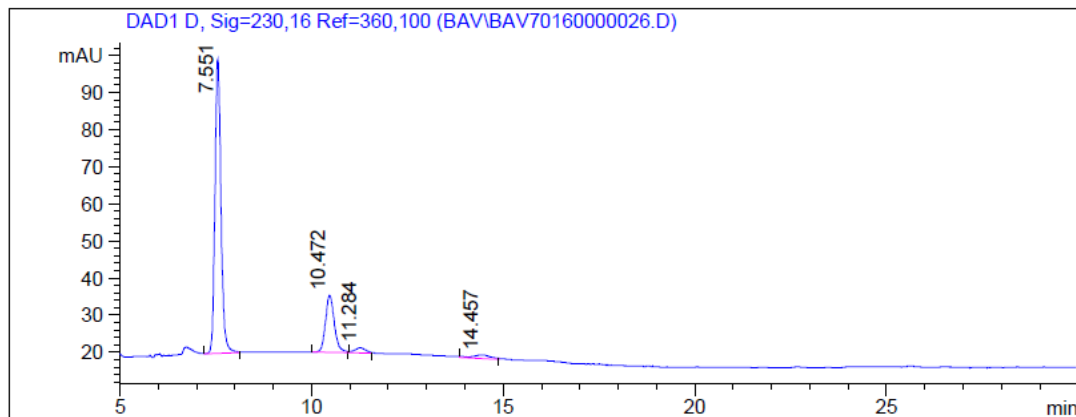
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 9.258 | 0.221 | 9778.399 | 80.29 |
| 2 | 10.333 | 0.259 | 297.102 | 2.44 |
| 3 | 12.505 | 0.307 | 2103.689 | 17.27 |



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

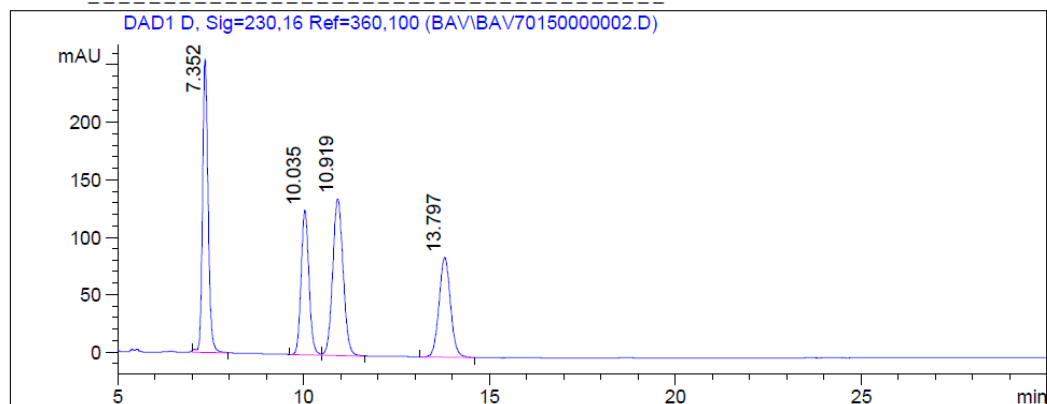
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 9.356 | 0.216 | 9783.243 | 33.19 |
| 2 | 10.331 | 0.264 | 9932.305 | 33.69 |
| 3 | 12.595 | 0.329 | 5031.937 | 17.07 |
| 4 | 24.733 | 1.110 | 4731.183 | 16.05 |

Figure 45. HPLC trace of **7b**.



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

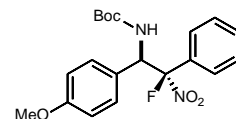
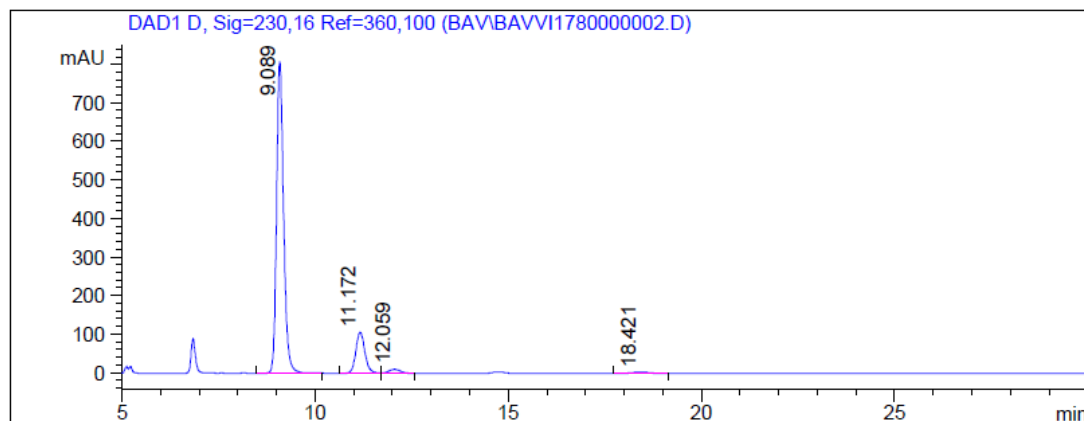
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|---------|--------|
| 1 | 7.551 | 0.181 | 862.144 | 74.04 |
| 2 | 10.472 | 0.266 | 244.085 | 20.96 |
| 3 | 11.284 | 0.335 | 27.027 | 2.32 |
| 4 | 14.457 | 0.543 | 31.196 | 2.68 |



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

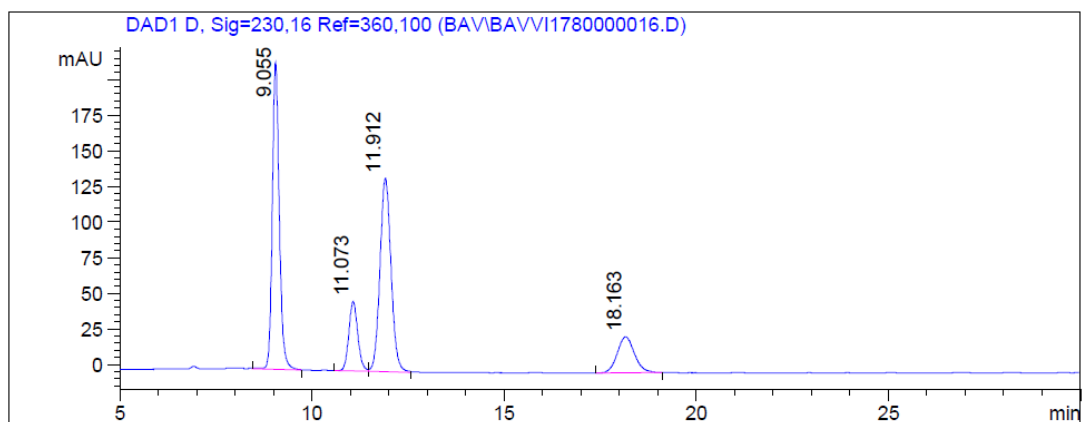
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 7.352 | 0.173 | 2654.923 | 29.36 |
| 2 | 10.035 | 0.245 | 1855.349 | 20.52 |
| 3 | 10.919 | 0.326 | 2666.948 | 29.49 |
| 4 | 13.797 | 0.358 | 1865.698 | 20.63 |

Figure 46. HPLC trace of **7c**.



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

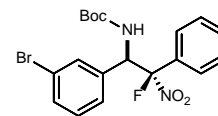
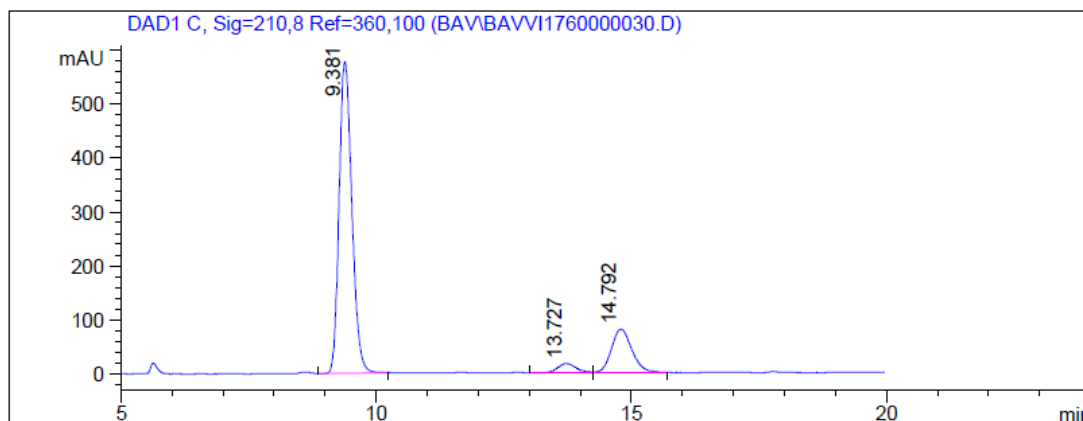
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|-----------|--------|
| 1 | 9.089 | 0.210 | 10206.280 | 82.98 |
| 2 | 11.172 | 0.272 | 1750.505 | 14.23 |
| 3 | 12.059 | 0.347 | 219.357 | 1.78 |
| 4 | 18.421 | 0.544 | 123.147 | 1.00 |



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

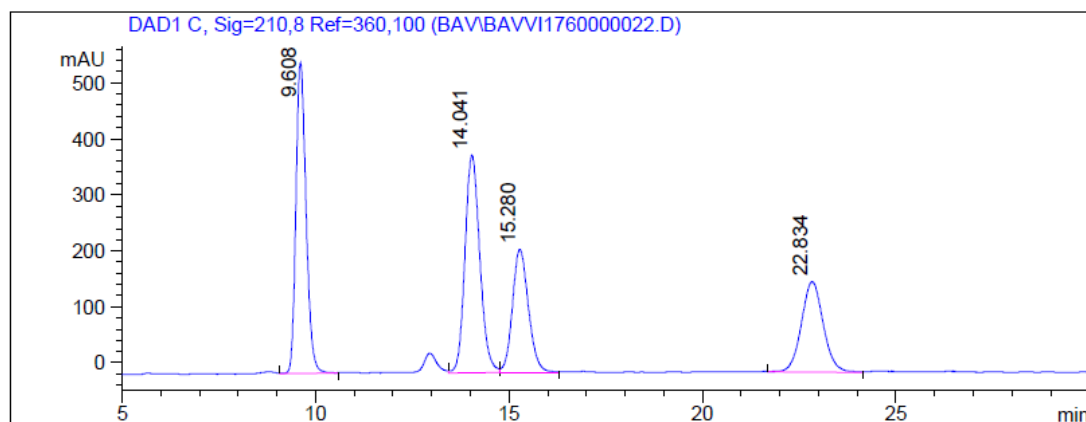
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 9.055 | 0.210 | 2722.281 | 38.80 |
| 2 | 11.073 | 0.269 | 785.431 | 11.19 |
| 3 | 11.912 | 0.334 | 2723.632 | 38.82 |
| 4 | 18.163 | 0.520 | 784.835 | 11.19 |

Figure 47. HPLC trace of 7d.



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

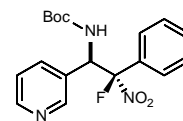
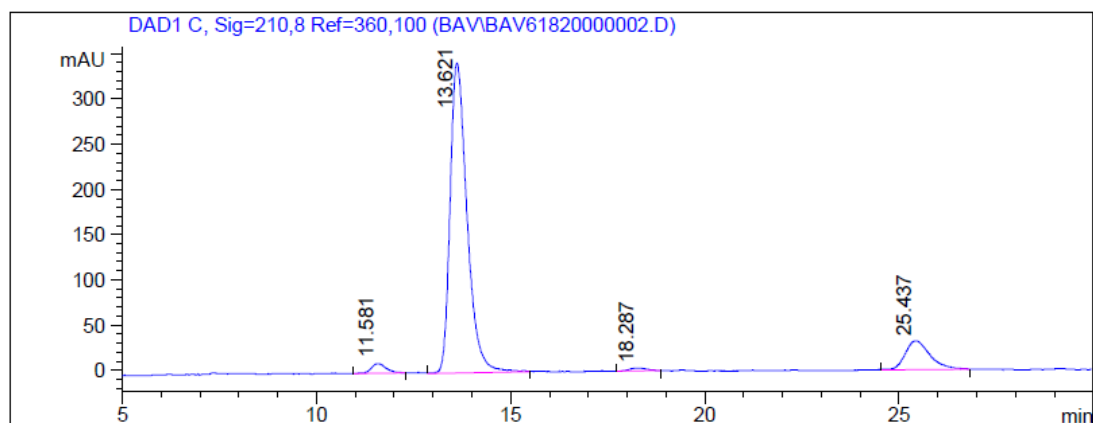
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|-----------|--------|
| 1 | 9.381 | 0.290 | 10049.248 | 79.12 |
| 2 | 13.727 | 0.419 | 415.758 | 3.27 |
| 3 | 14.792 | 0.462 | 2236.555 | 17.61 |



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

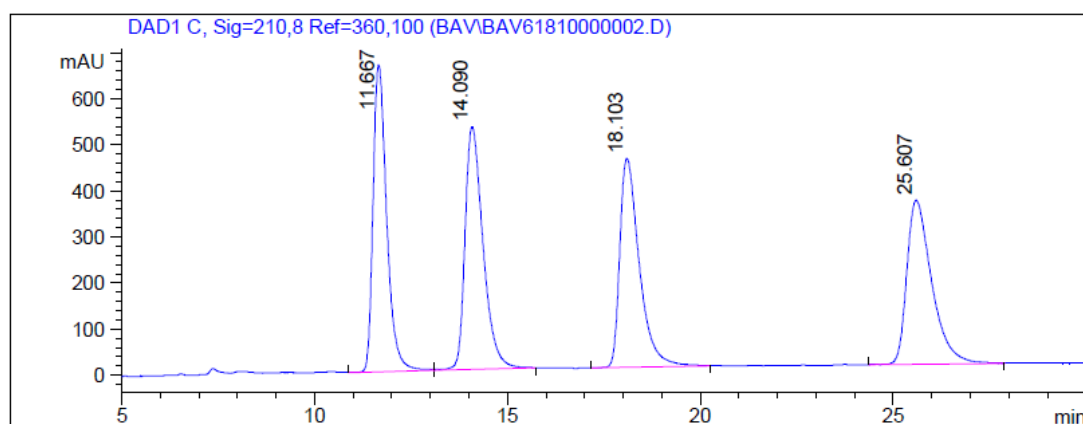
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|-----------|--------|
| 1 | 9.608 | 0.304 | 10116.866 | 30.50 |
| 2 | 14.041 | 0.445 | 10369.546 | 31.27 |
| 3 | 15.280 | 0.479 | 6310.808 | 19.03 |
| 4 | 22.834 | 0.656 | 6368.974 | 19.20 |

Figure 48. HPLC trace of **7e**.



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

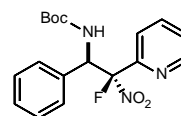
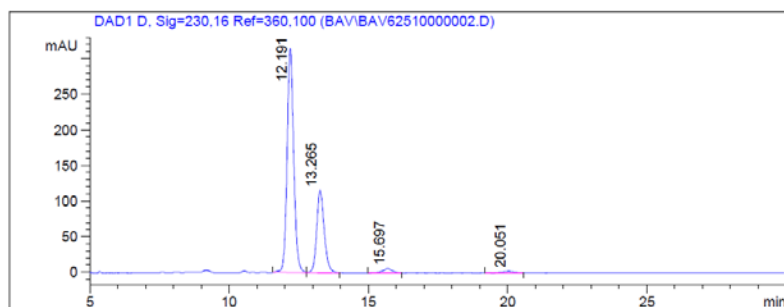
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|-----------|--------|
| 1 | 11.581 | 0.447 | 293.182 | 2.40 |
| 2 | 13.621 | 0.506 | 10395.784 | 85.16 |
| 3 | 18.287 | 0.532 | 114.923 | 0.94 |
| 4 | 25.437 | 0.735 | 1404.119 | 11.50 |



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

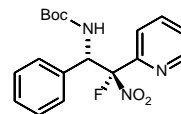
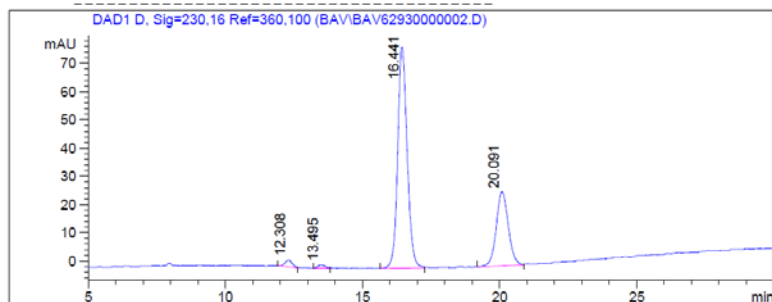
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|-----------|--------|
| 1 | 11.667 | 0.409 | 16332.238 | 24.76 |
| 2 | 14.090 | 0.541 | 17089.305 | 25.90 |
| 3 | 18.103 | 0.587 | 15963.237 | 24.20 |
| 4 | 25.607 | 0.751 | 16014.698 | 24.27 |
| 5 | 44.855 | 0.242 | 572.871 | 0.87 |

Figure 49. HPLC trace of **7f** + *ent*-**7f**.



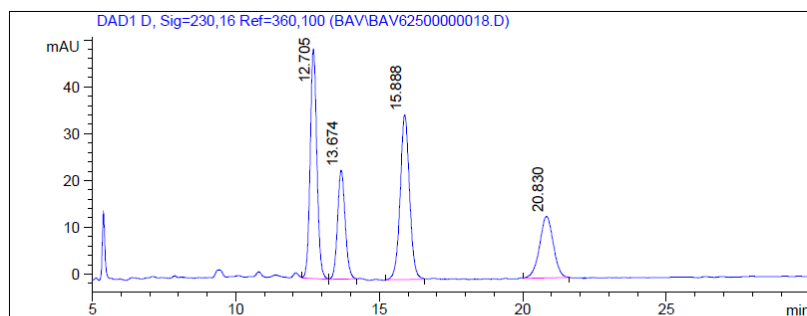
Signal 1: DAD1 D, Sig=230,16 Ref=360,100

| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 12.191 | 0.274 | 5165.790 | 68.55 |
| 2 | 13.265 | 0.312 | 2151.945 | 28.56 |
| 3 | 15.697 | 0.442 | 146.380 | 1.94 |
| 4 | 20.051 | 0.576 | 71.575 | 0.95 |



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

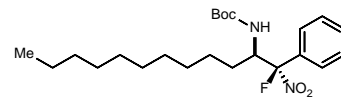
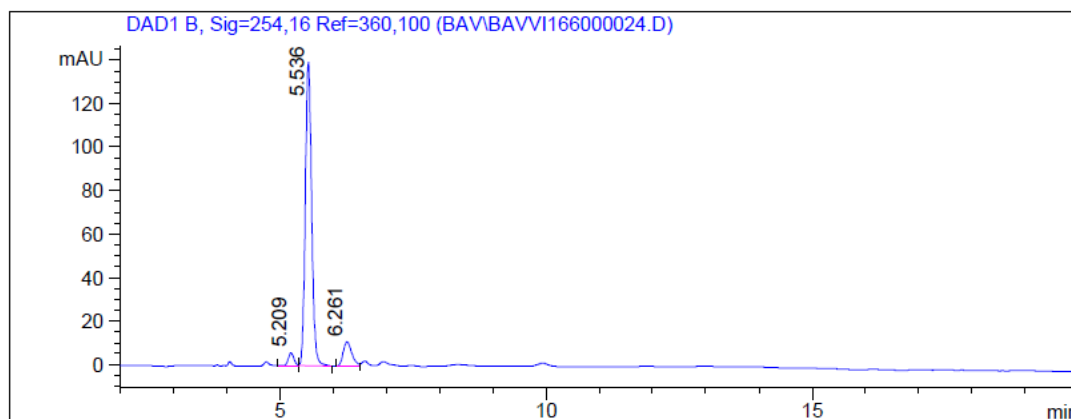
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 12.308 | 0.298 | 42.326 | 1.54 |
| 2 | 13.495 | 0.328 | 25.096 | 0.91 |
| 3 | 16.441 | 0.399 | 1879.701 | 68.39 |
| 4 | 20.091 | 0.509 | 801.416 | 29.16 |



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

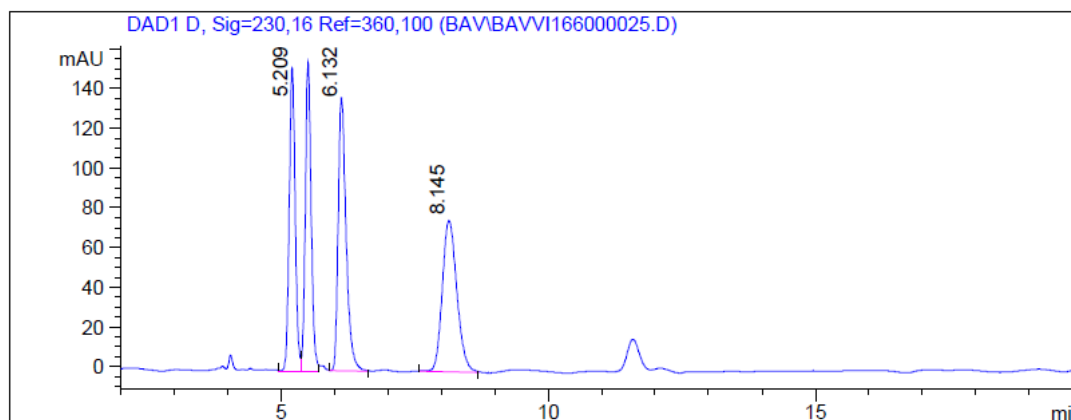
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|---------|--------|
| 1 | 12.705 | 0.269 | 790.160 | 32.13 |
| 2 | 13.674 | 0.308 | 430.599 | 17.51 |
| 3 | 15.888 | 0.379 | 799.429 | 32.51 |
| 4 | 20.830 | 0.555 | 439.100 | 17.85 |

Figure 50. HPLC trace of **7g**.



Signal 1: DAD1 B, Sig=254,16 Ref=360,100

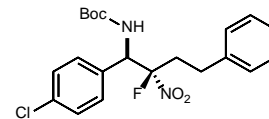
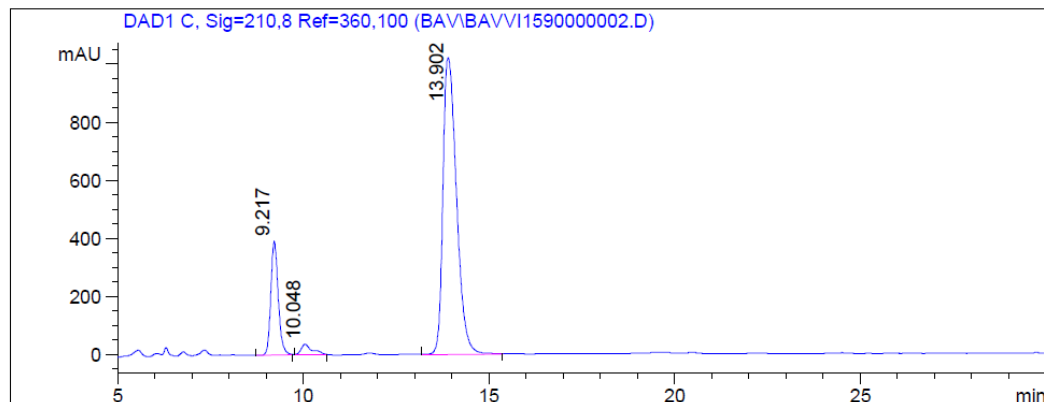
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 5.209 | 0.122 | 43.786 | 3.28 |
| 2 | 5.536 | 0.138 | 1157.429 | 86.69 |
| 3 | 6.261 | 0.195 | 133.858 | 10.03 |



Signal 1: DAD1 D, Sig=230,16 Ref=360,100

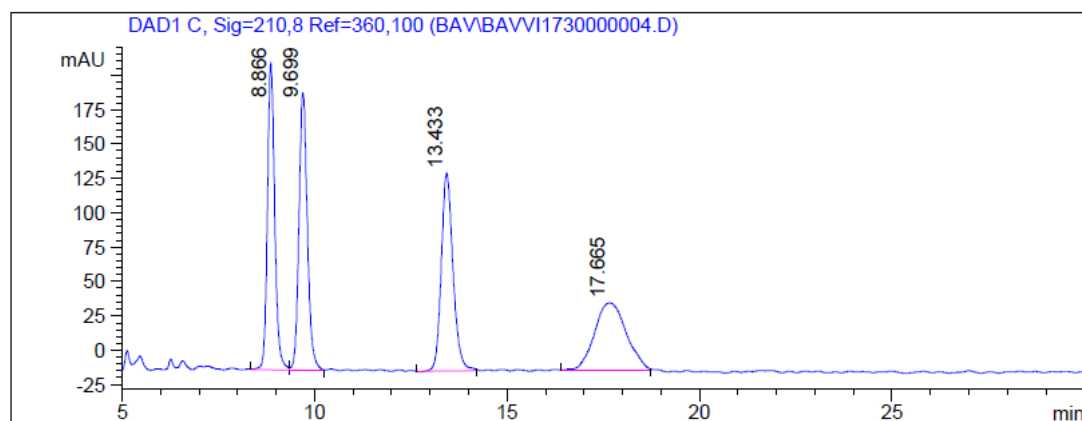
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 5.209 | 0.128 | 1174.427 | 22.45 |
| 2 | 5.508 | 0.127 | 1185.151 | 22.66 |
| 3 | 6.132 | 0.172 | 1421.073 | 27.17 |
| 4 | 8.145 | 0.317 | 1450.498 | 27.73 |

Figure 51. HPLC trace of 7h.



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

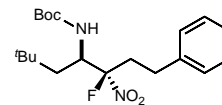
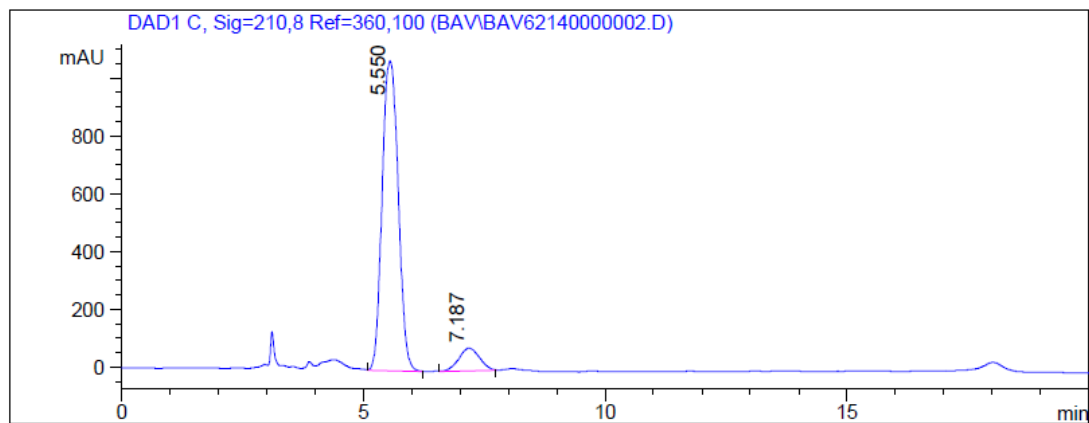
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|-----------|--------|
| 1 | 9.217 | 0.231 | 5444.865 | 16.85 |
| 2 | 10.048 | 0.365 | 807.436 | 2.50 |
| 3 | 13.902 | 0.424 | 26055.645 | 80.65 |



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

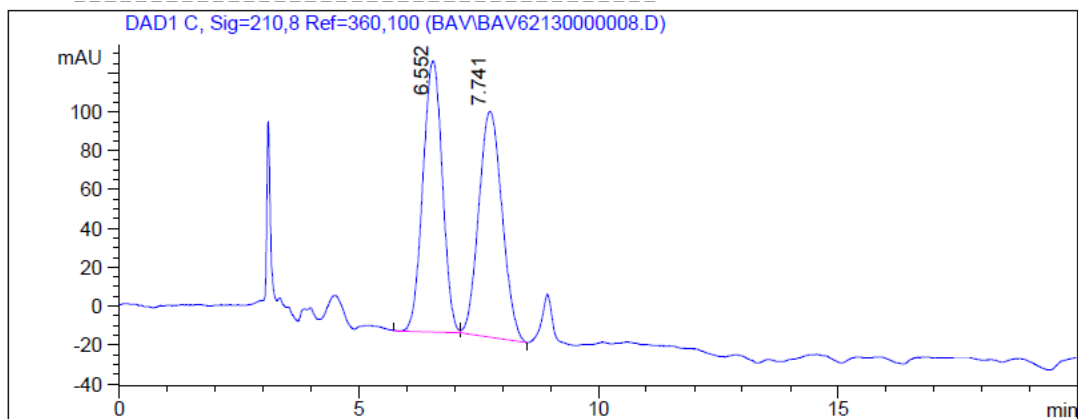
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 8.866 | 0.219 | 2924.311 | 24.68 |
| 2 | 9.699 | 0.253 | 3063.250 | 25.85 |
| 3 | 13.433 | 0.356 | 3067.807 | 25.89 |
| 4 | 17.665 | 0.952 | 2792.467 | 23.57 |

Figure 52. HPLC trace of 7i.



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

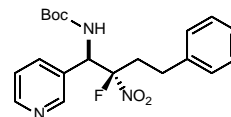
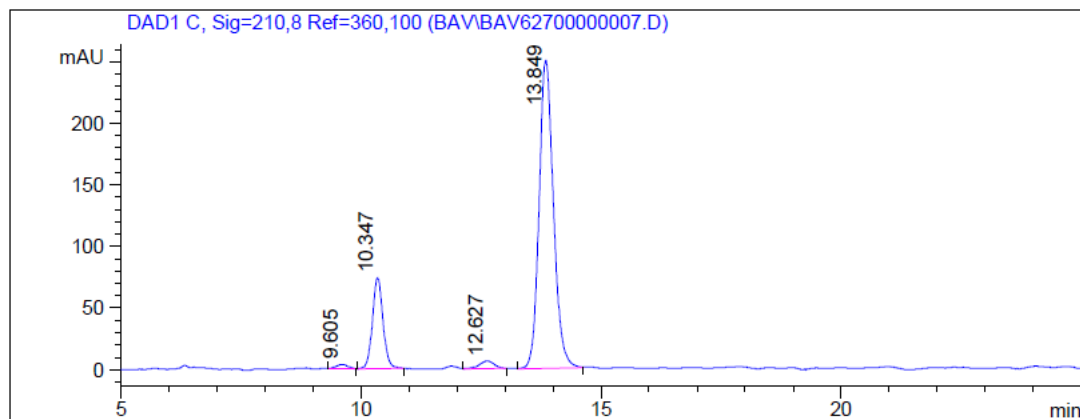
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|-----------|--------|
| 1 | 5.550 | 0.385 | 24709.771 | 91.41 |
| 2 | 7.187 | 0.497 | 2322.444 | 8.59 |



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

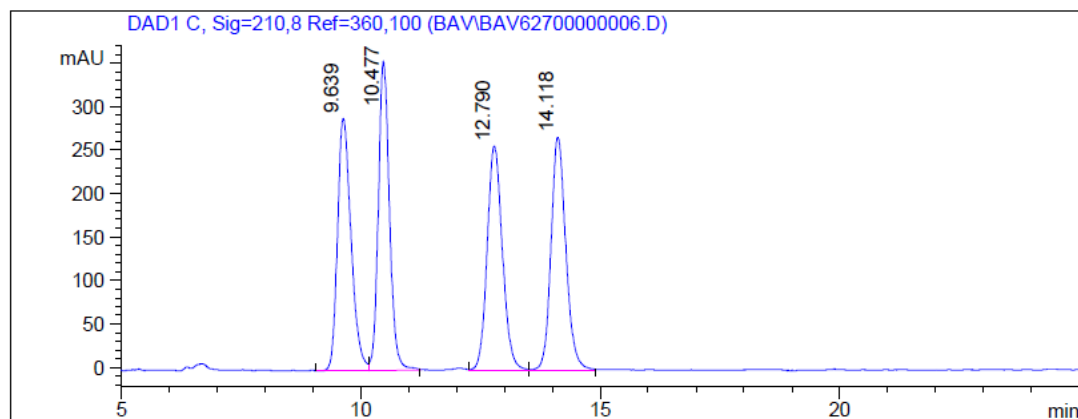
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 6.552 | 0.470 | 3938.330 | 49.98 |
| 2 | 7.741 | 0.565 | 3941.525 | 50.02 |

Figure 53. HPLC trace of **7j**.



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

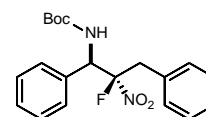
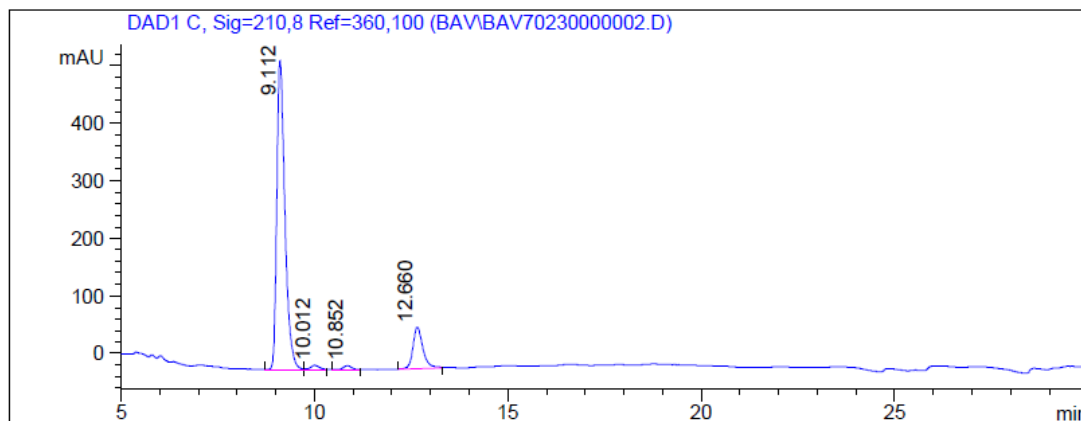
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 9.605 | 0.292 | 61.668 | 0.94 |
| 2 | 10.347 | 0.256 | 1132.465 | 17.35 |
| 3 | 12.627 | 0.362 | 133.279 | 2.04 |
| 4 | 13.849 | 0.346 | 5199.589 | 79.66 |



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

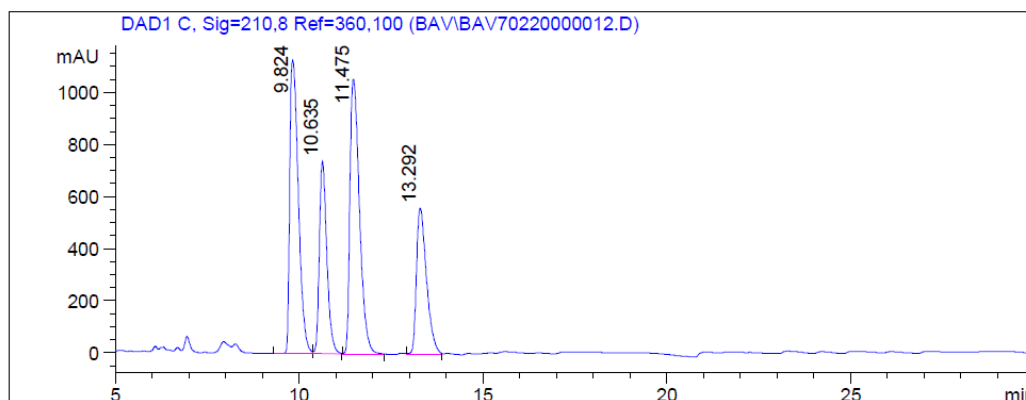
| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 9.639 | 0.328 | 5701.634 | 24.93 |
| 2 | 10.477 | 0.269 | 5739.758 | 25.10 |
| 3 | 12.790 | 0.368 | 5685.617 | 24.86 |
| 4 | 14.118 | 0.358 | 5739.110 | 25.10 |

Figure 54. HPLC trace of **10**.



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|----------|--------|
| 1 | 9.112 | 0.243 | 7845.124 | 83.38 |
| 2 | 10.012 | 0.287 | 144.605 | 1.54 |
| 3 | 10.852 | 0.281 | 118.508 | 1.26 |
| 4 | 12.660 | 0.301 | 1300.506 | 13.82 |



Signal 1: DAD1 C, Sig=210,8 Ref=360,100

| Peak # | RT [min] | Width [min] | Area | Area % |
|--------|----------|-------------|-----------|--------|
| 1 | 9.824 | 0.271 | 18351.621 | 31.46 |
| 2 | 10.635 | 0.235 | 10425.837 | 17.88 |
| 3 | 11.475 | 0.300 | 18996.447 | 32.57 |
| 4 | 13.292 | 0.314 | 10550.926 | 18.09 |