Supporting Information

**Asymmetric Synthesis of Spiro[4*H*-Chromene-3,3′-oxindoles] via Squaramide-Organocatalyzed Three-Component Cascade Knoevenagel/ Michael/ Cyclization Sequence**

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1H NMR and 13C NMR spectra… …………………...……………..........S2-S41

HPLC trace.....……………...…………………………...………......….....S42-S61

X-Ray crystal data of compound **3f**……...………………………...........S62-S63

1H NMR and 13C NMR spectra

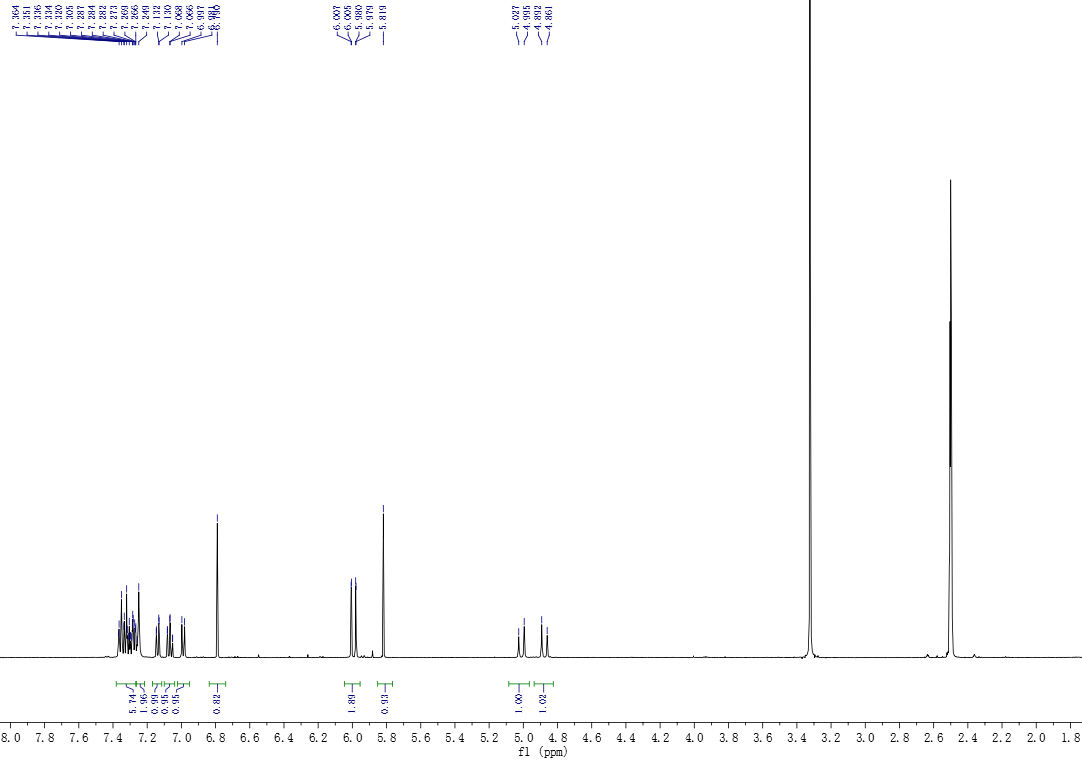


Figure 1. 1H NMR spectrum of **3a**

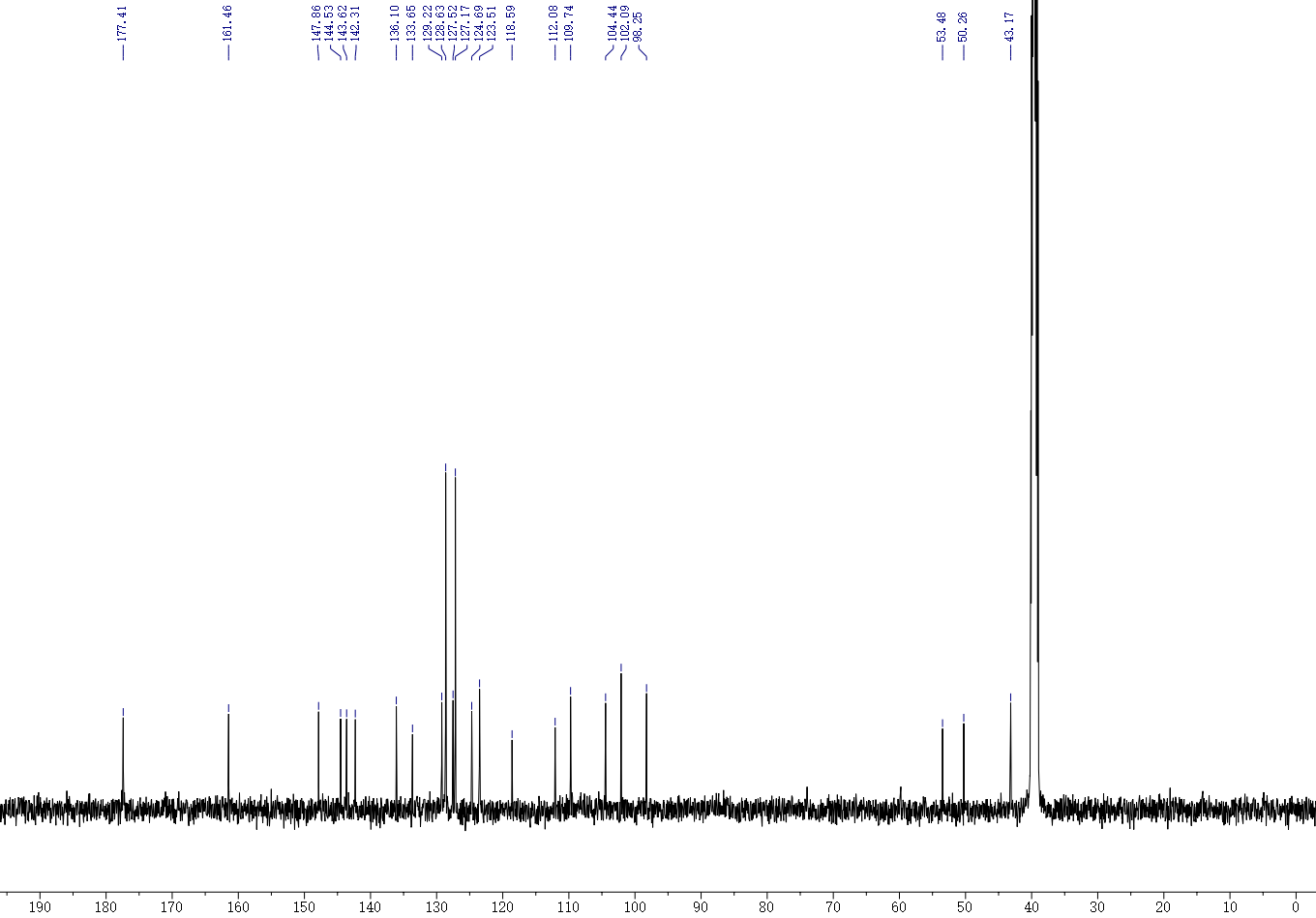


Figure 2. 13C NMR spectrum of **3a**

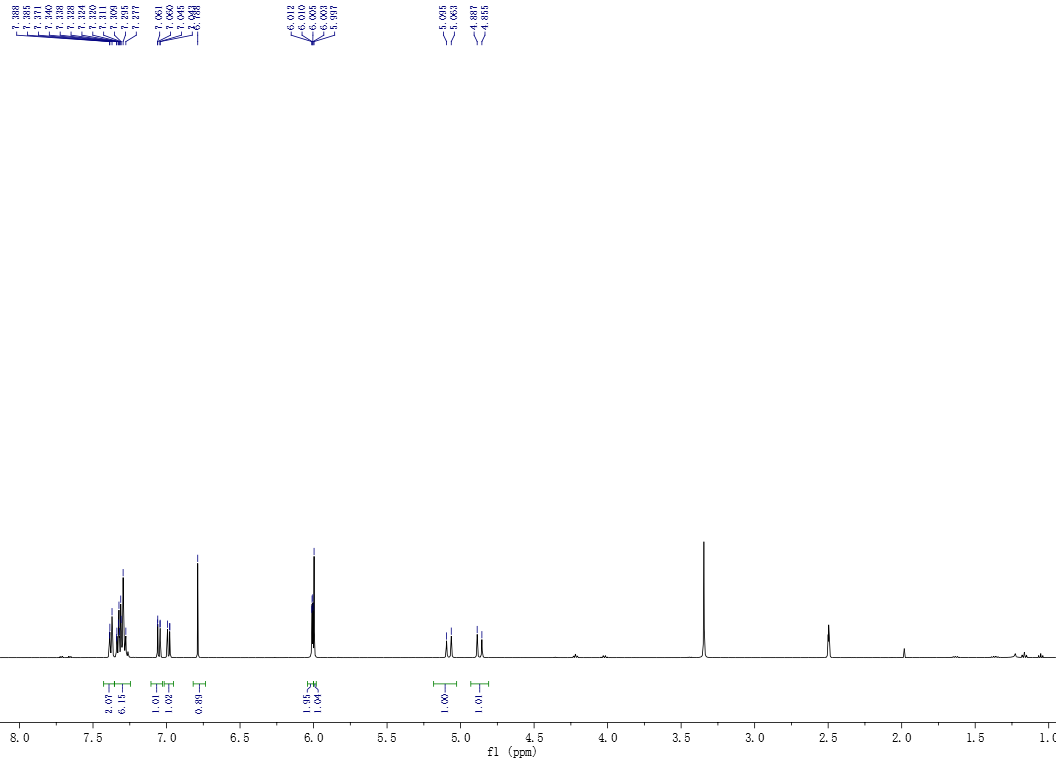


Figure 3. 1H NMR spectrum of **3b**

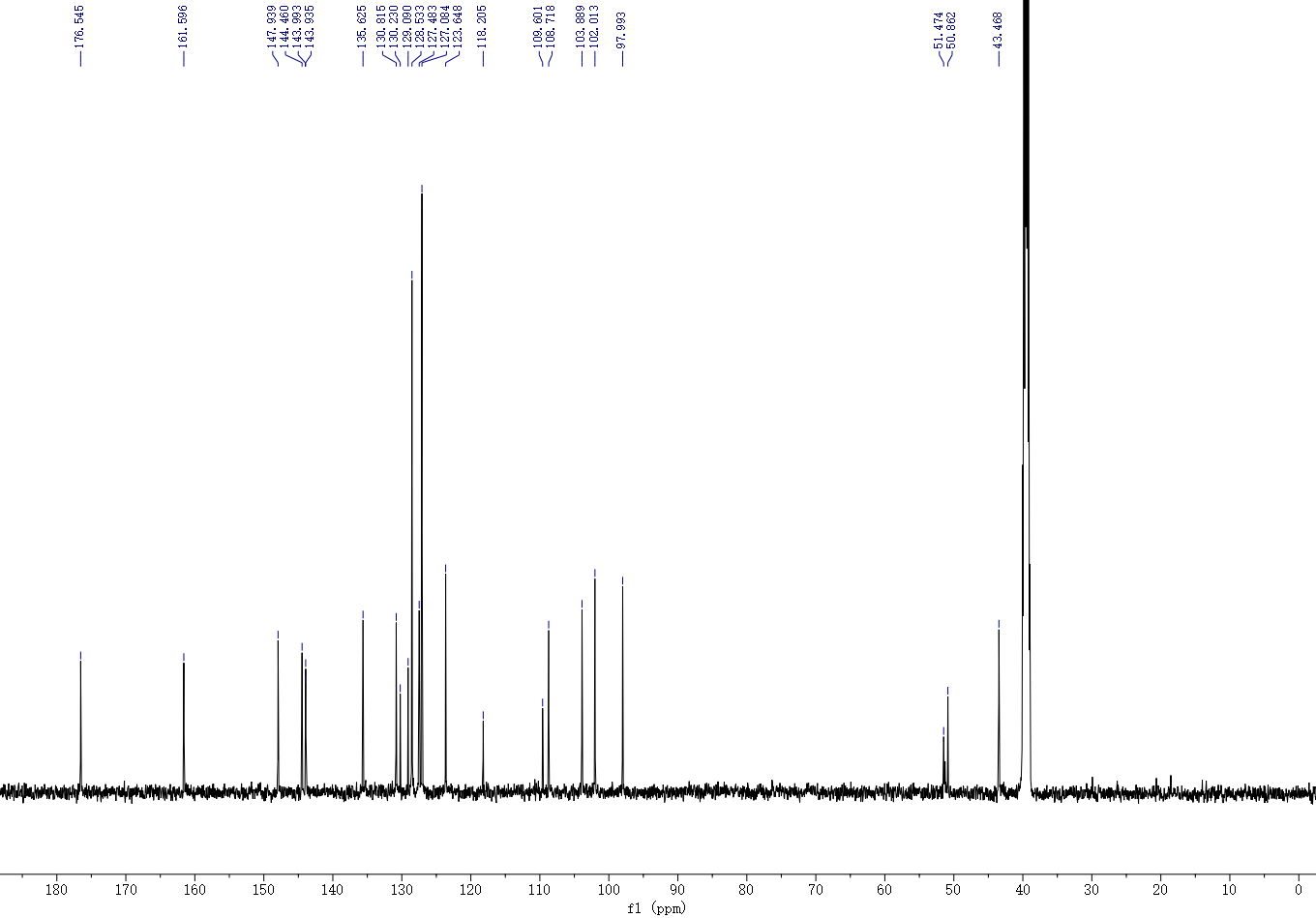


Figure 4. 13C NMR spectrum of **3b**

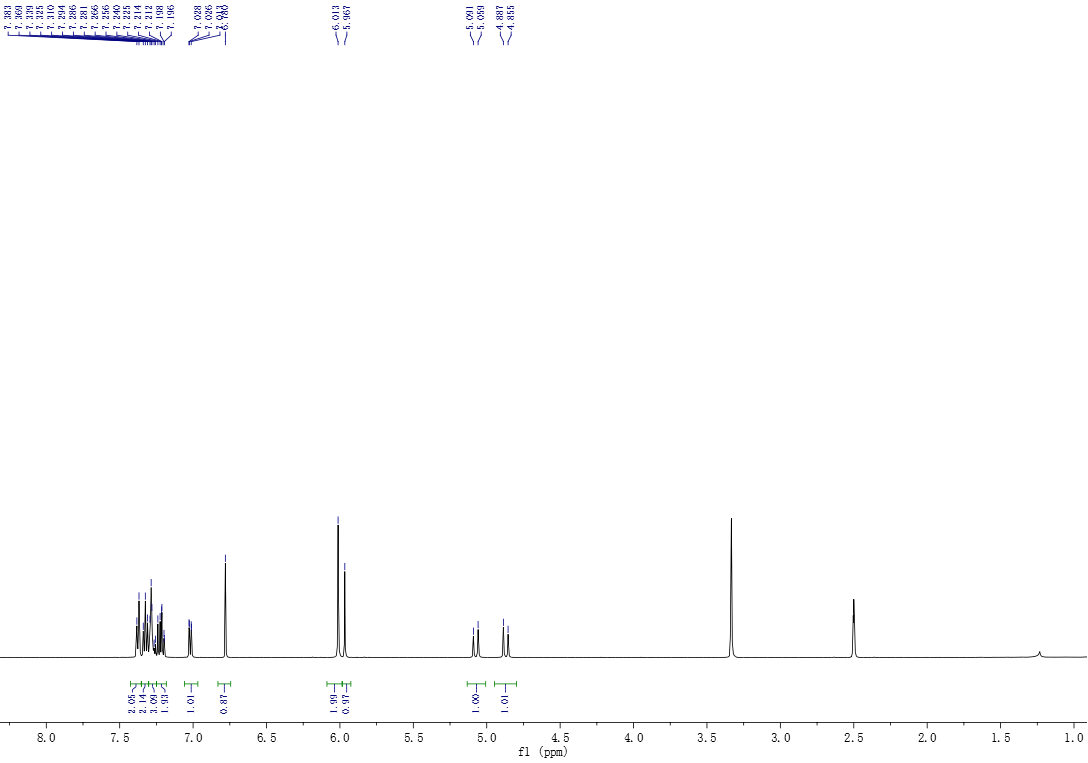


Figure 5. 1H NMR spectrum of **3c**



Figure 6. 13C NMR spectrum of **3c**

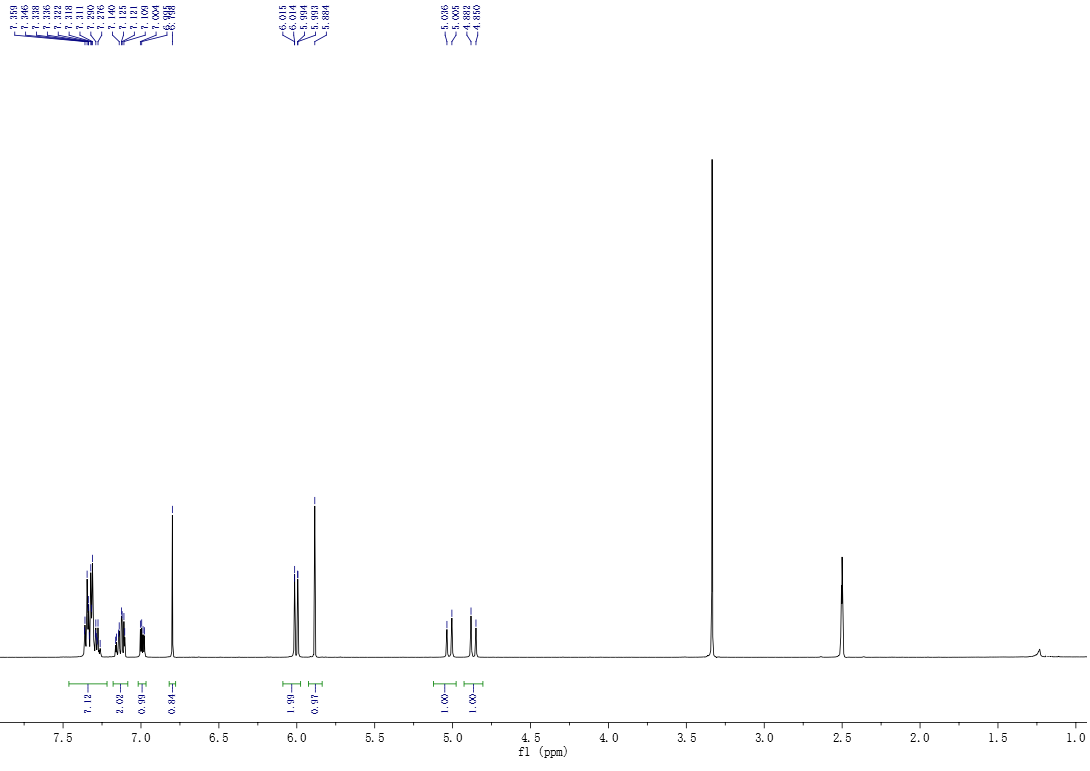


Figure 7. 1H NMR spectrum of **3d**

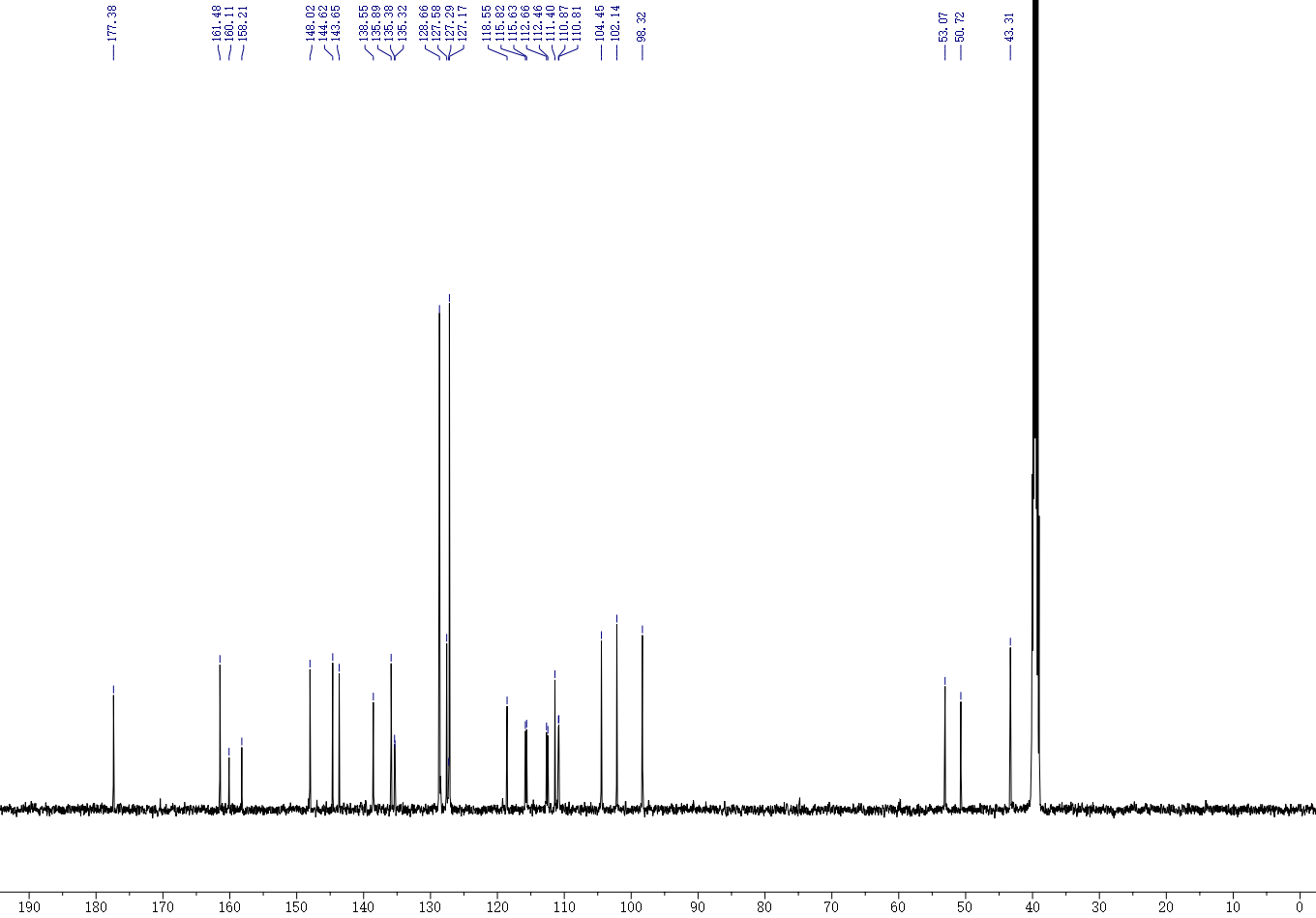


Figure 8. 13C NMR spectrum of **3d**

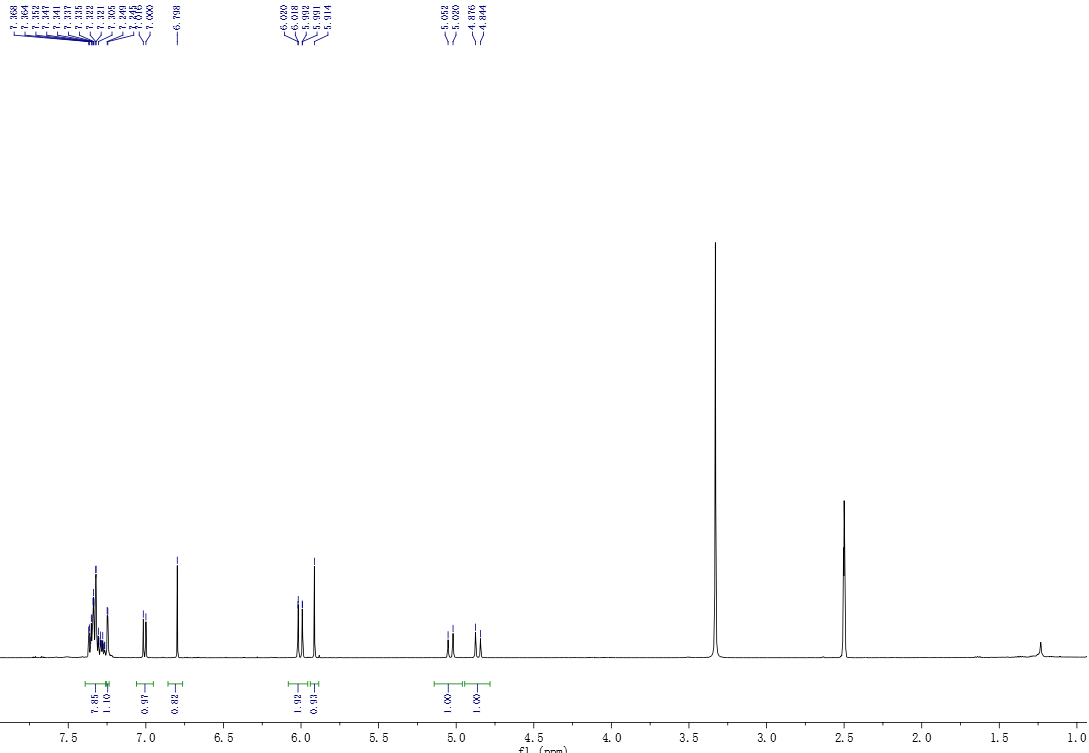
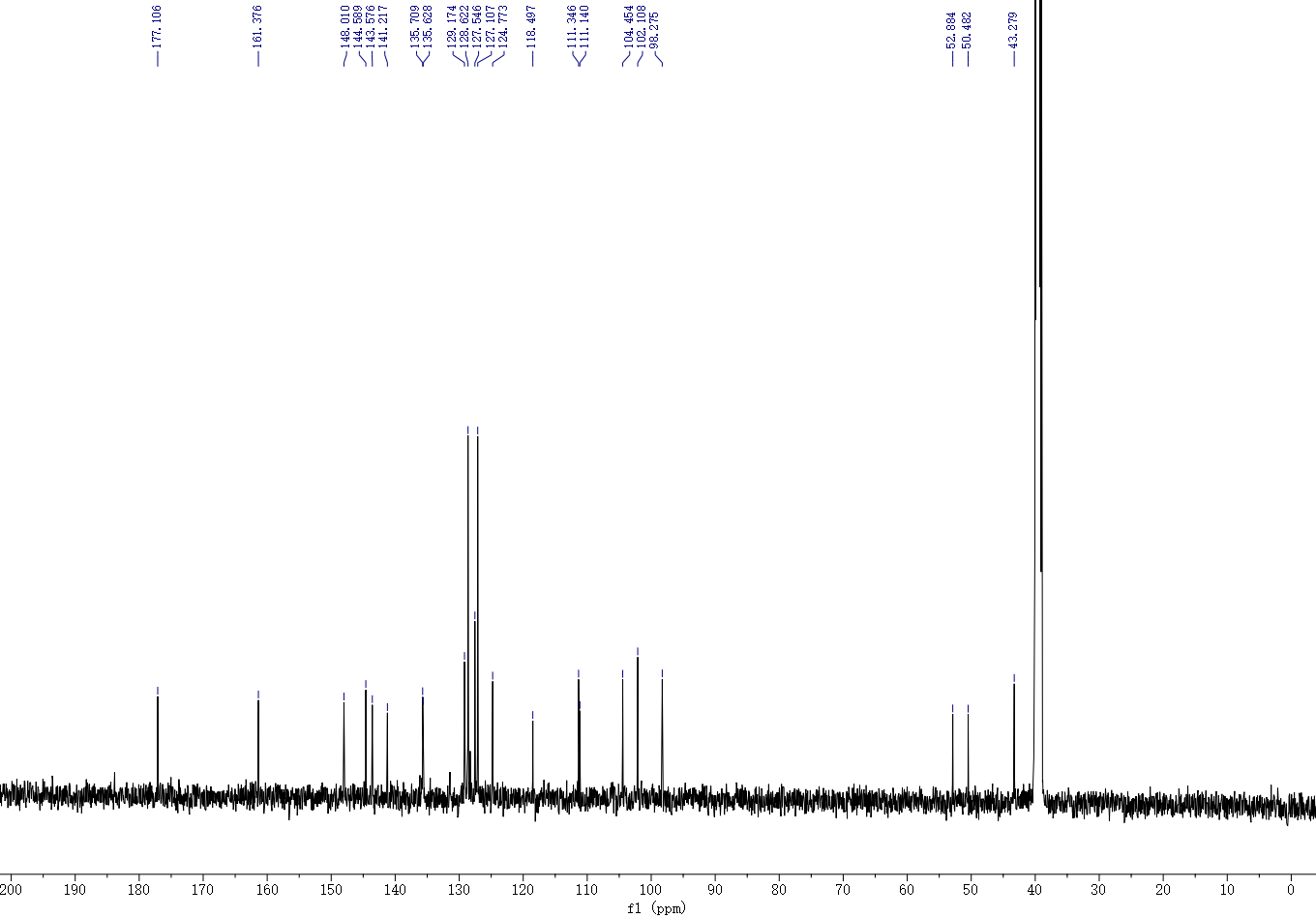
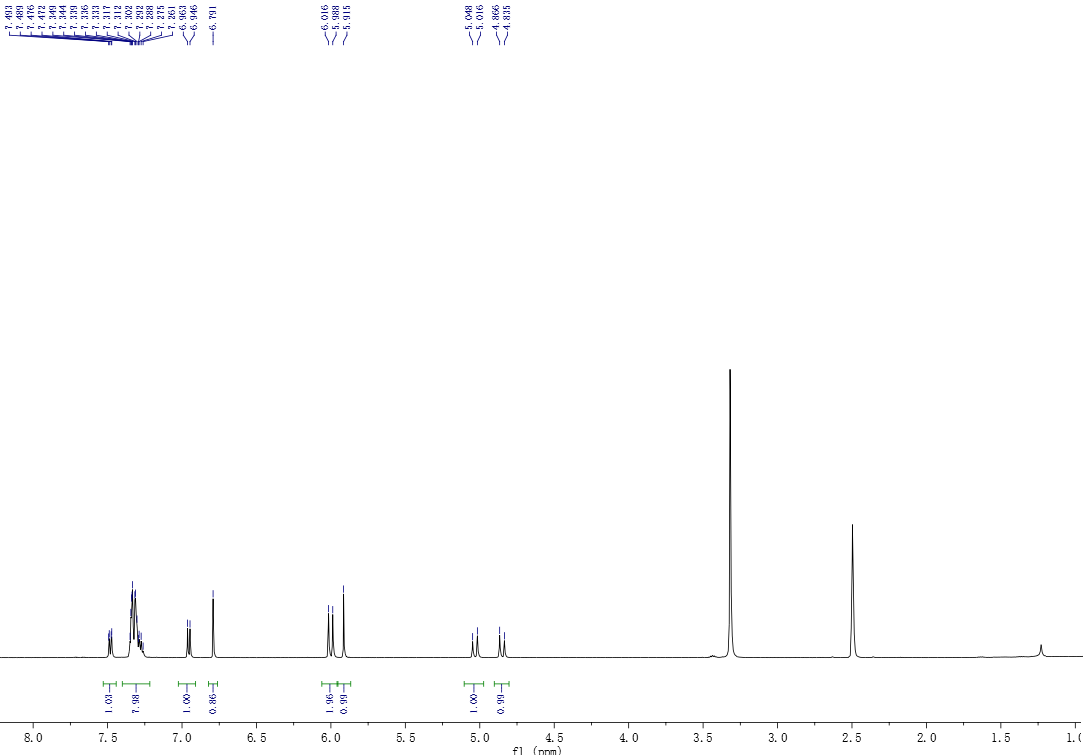


Figure 9. 1H NMR spectrum of **3e**

Figure 10. 13C NMR spectrum of **3e**

Figure 11. 1H NMR spectrum of **3f**

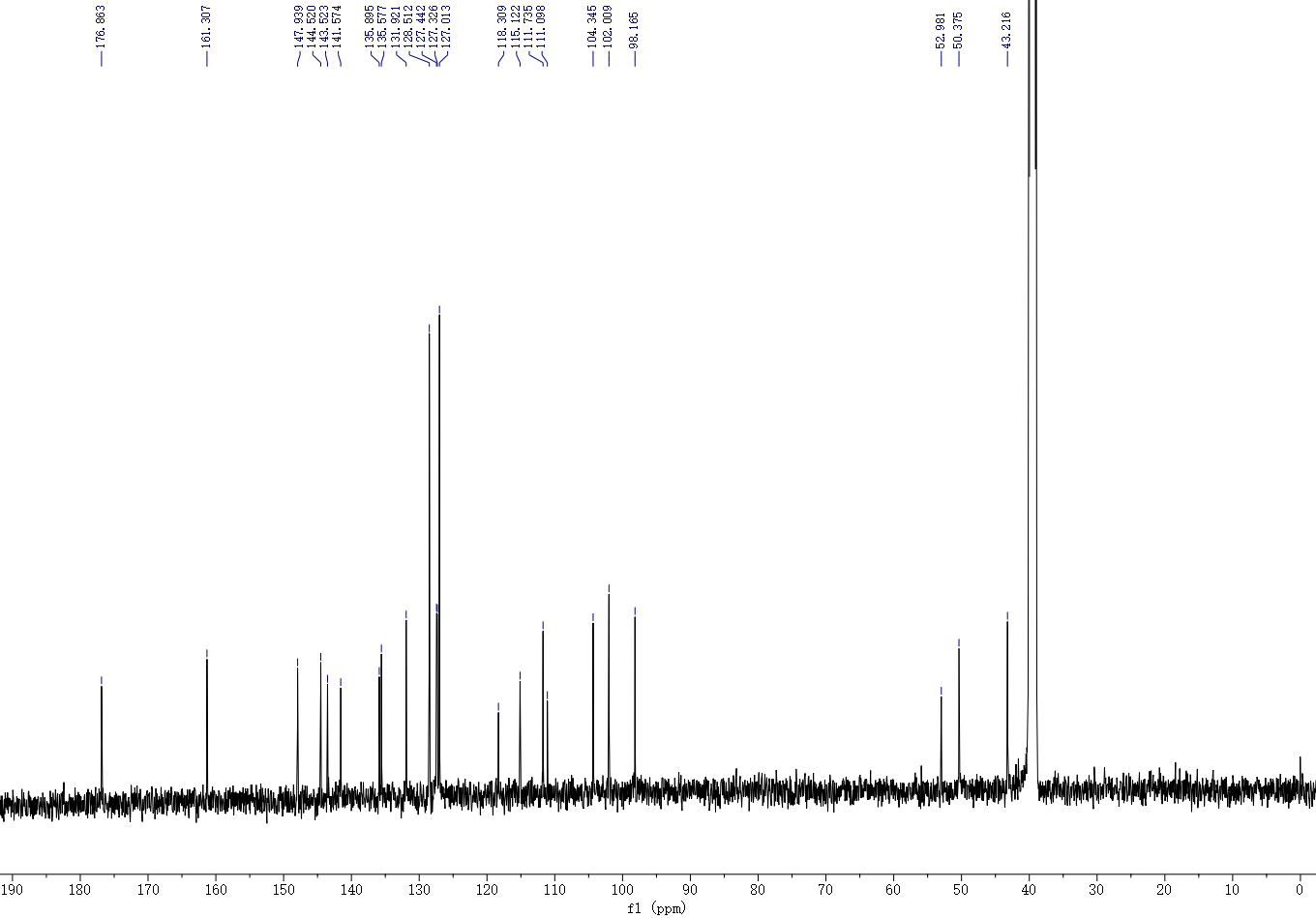


Figure 12. 13C NMR spectrum of **3f**

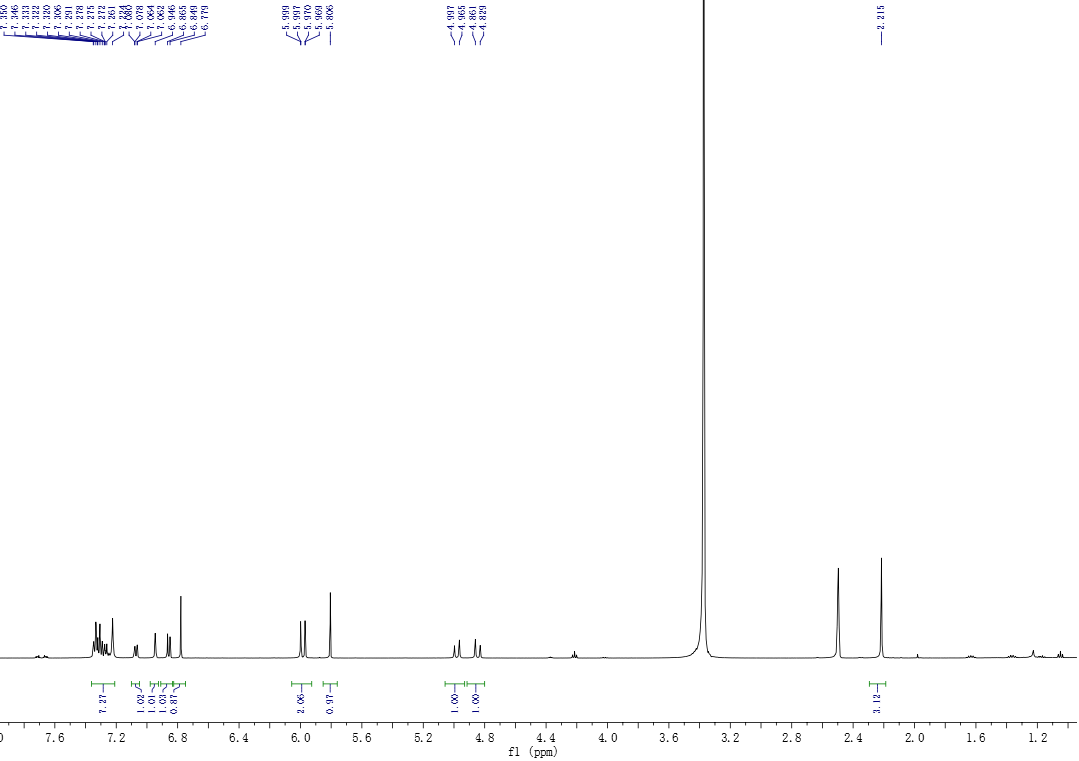


Figure 13 1H NMR spectrum of **3g**

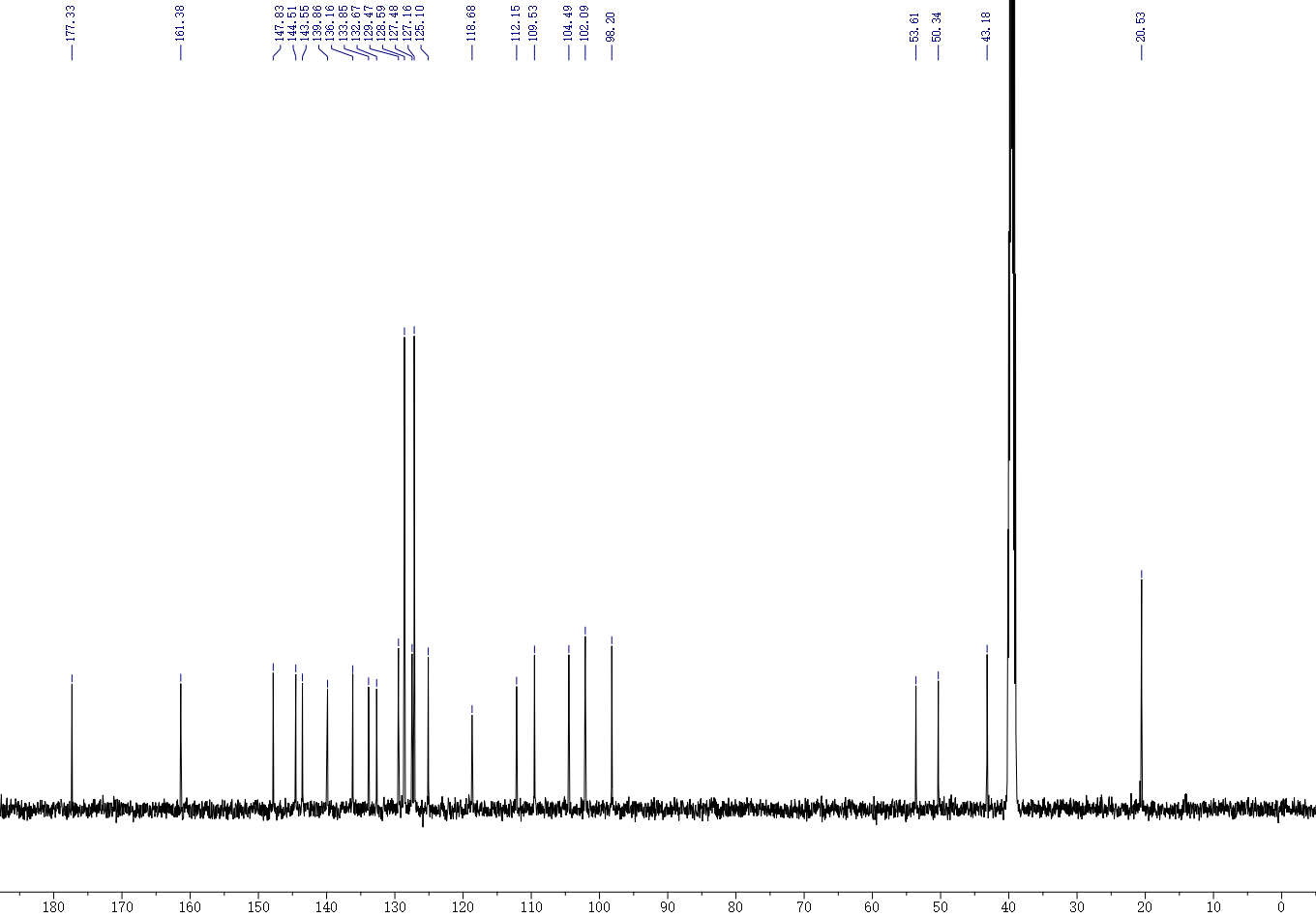


Figure 14. 13C NMR spectrum of **3g**

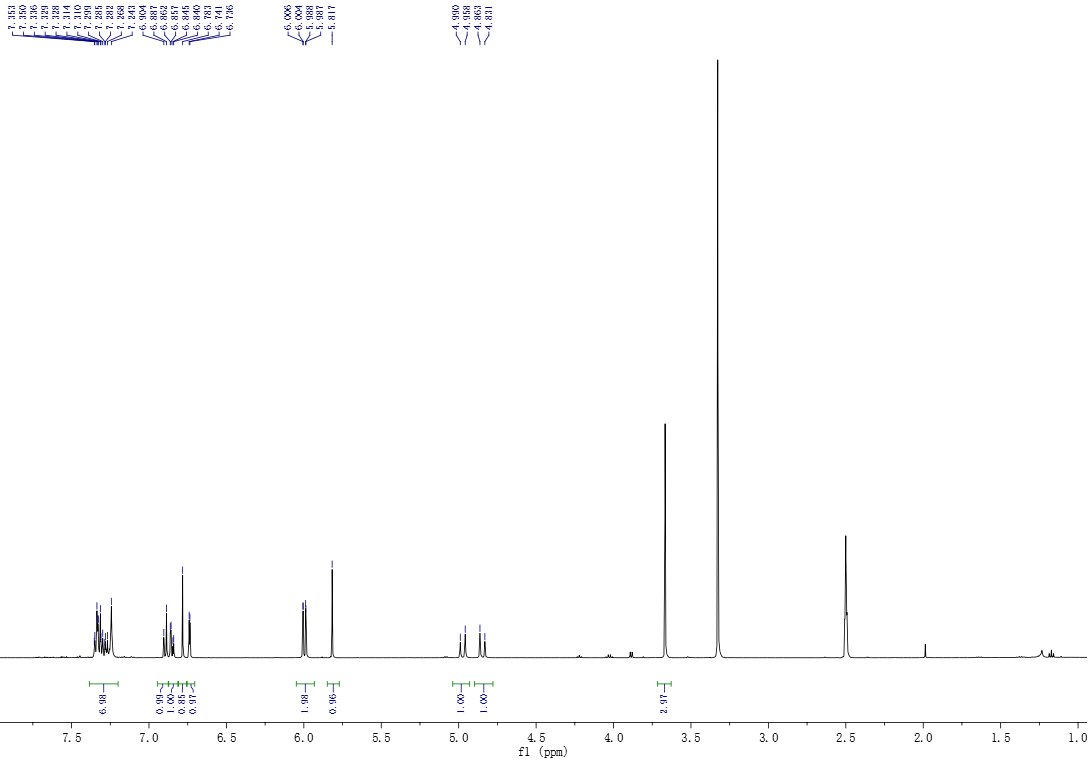


Figure 15. 1H NMR spectrum of **3h**

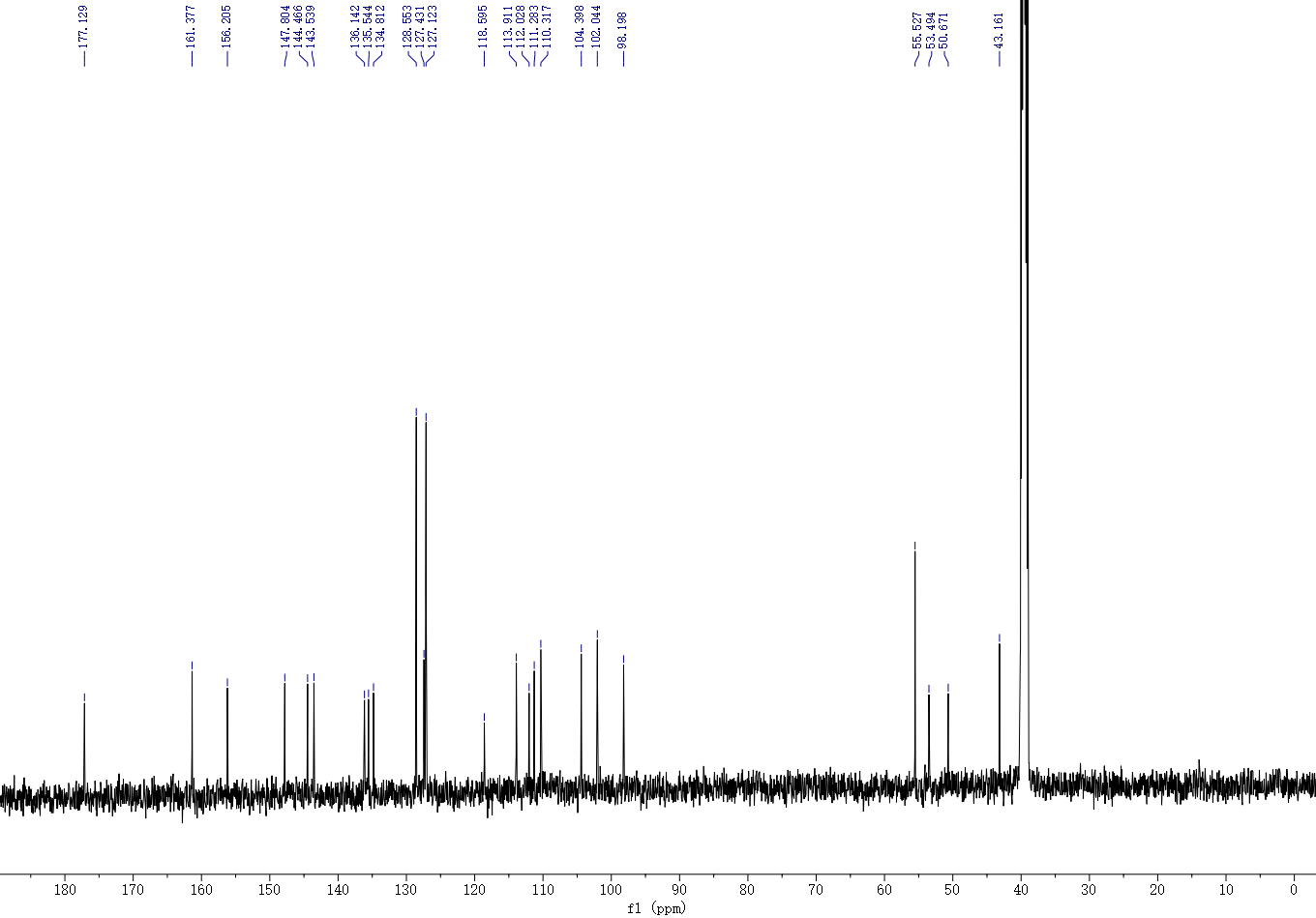


Figure 16. 13C NMR spectrum of **3h**

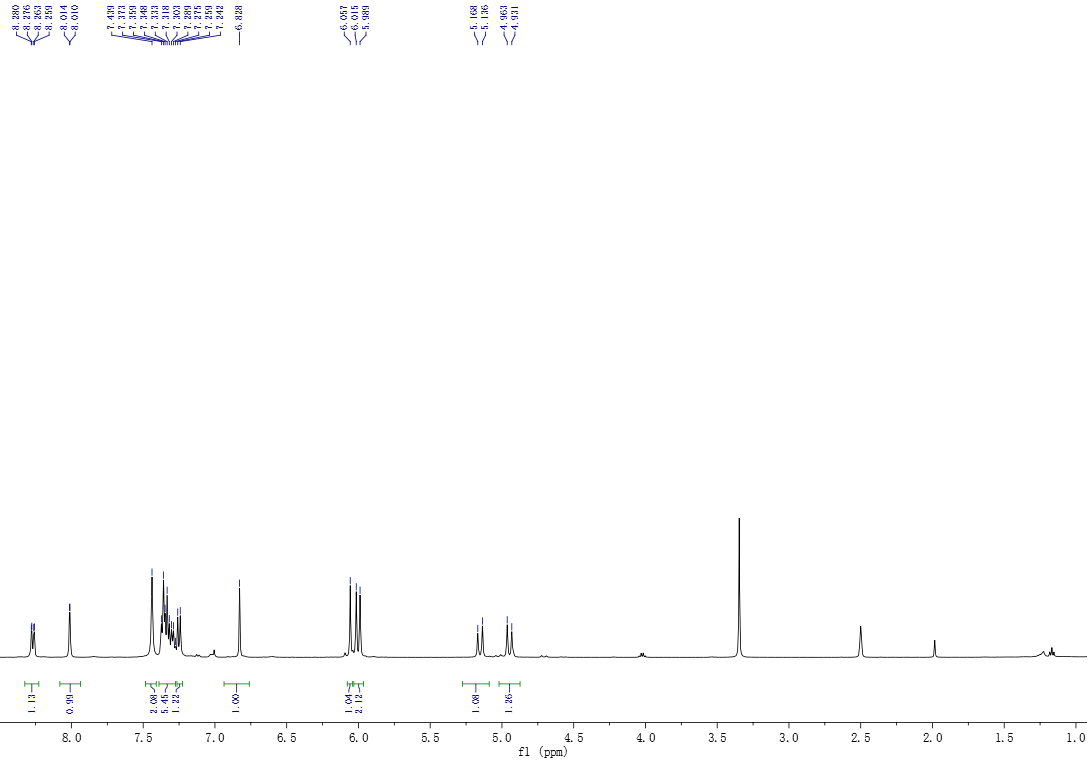


Figure 17. 1H NMR spectrum of **3i**

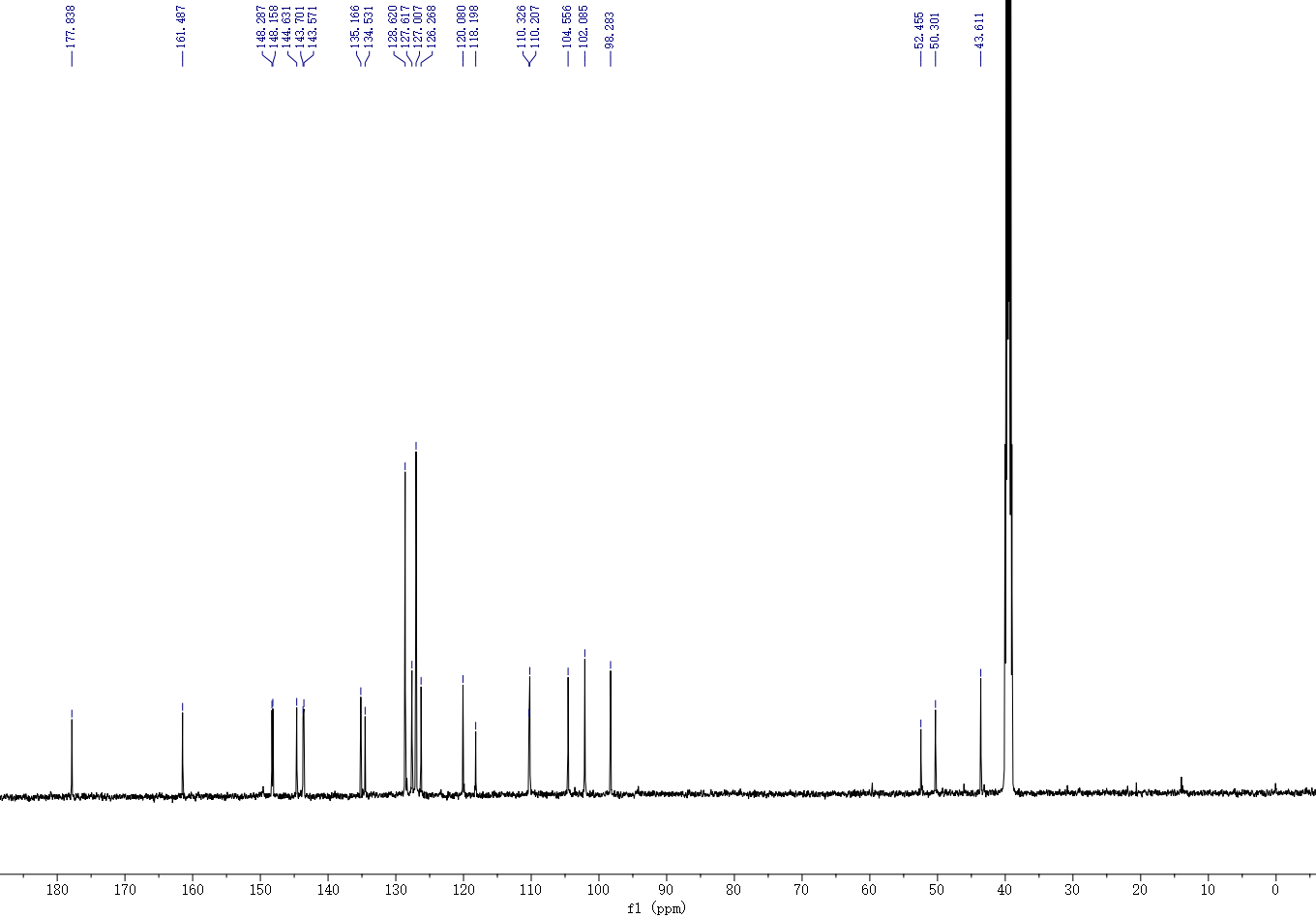


Figure 18. 13C NMR spectrum of **3i**

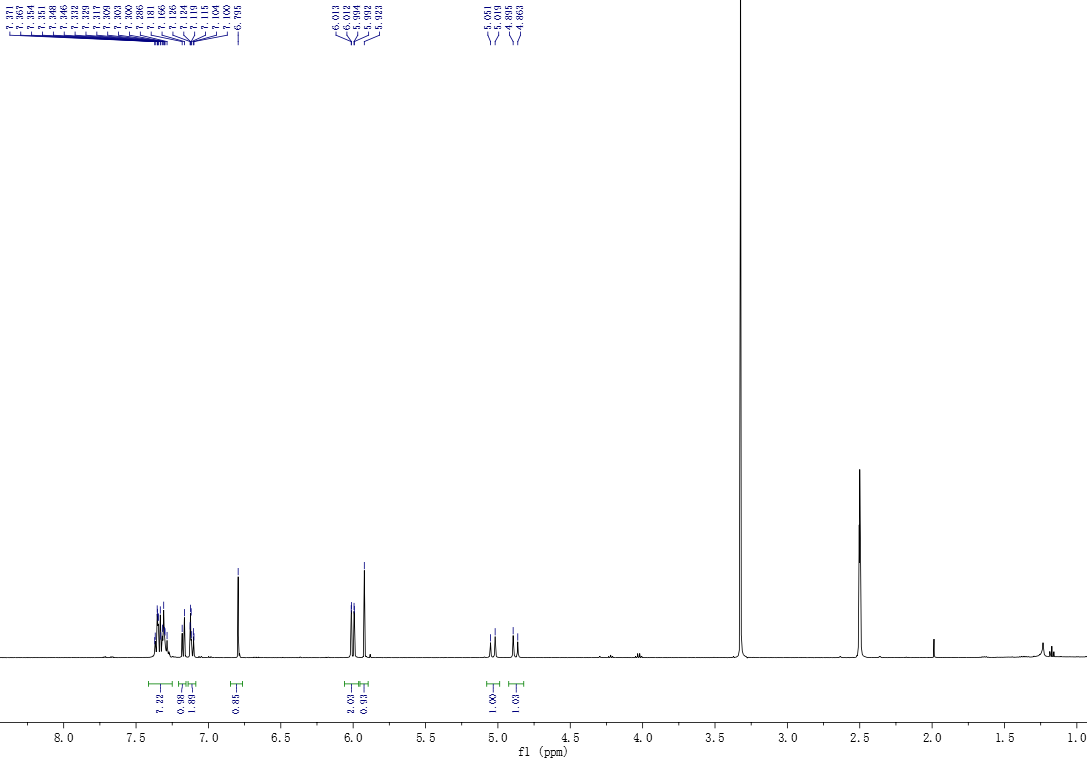


Figure 19. 1H NMR spectrum of **3j**

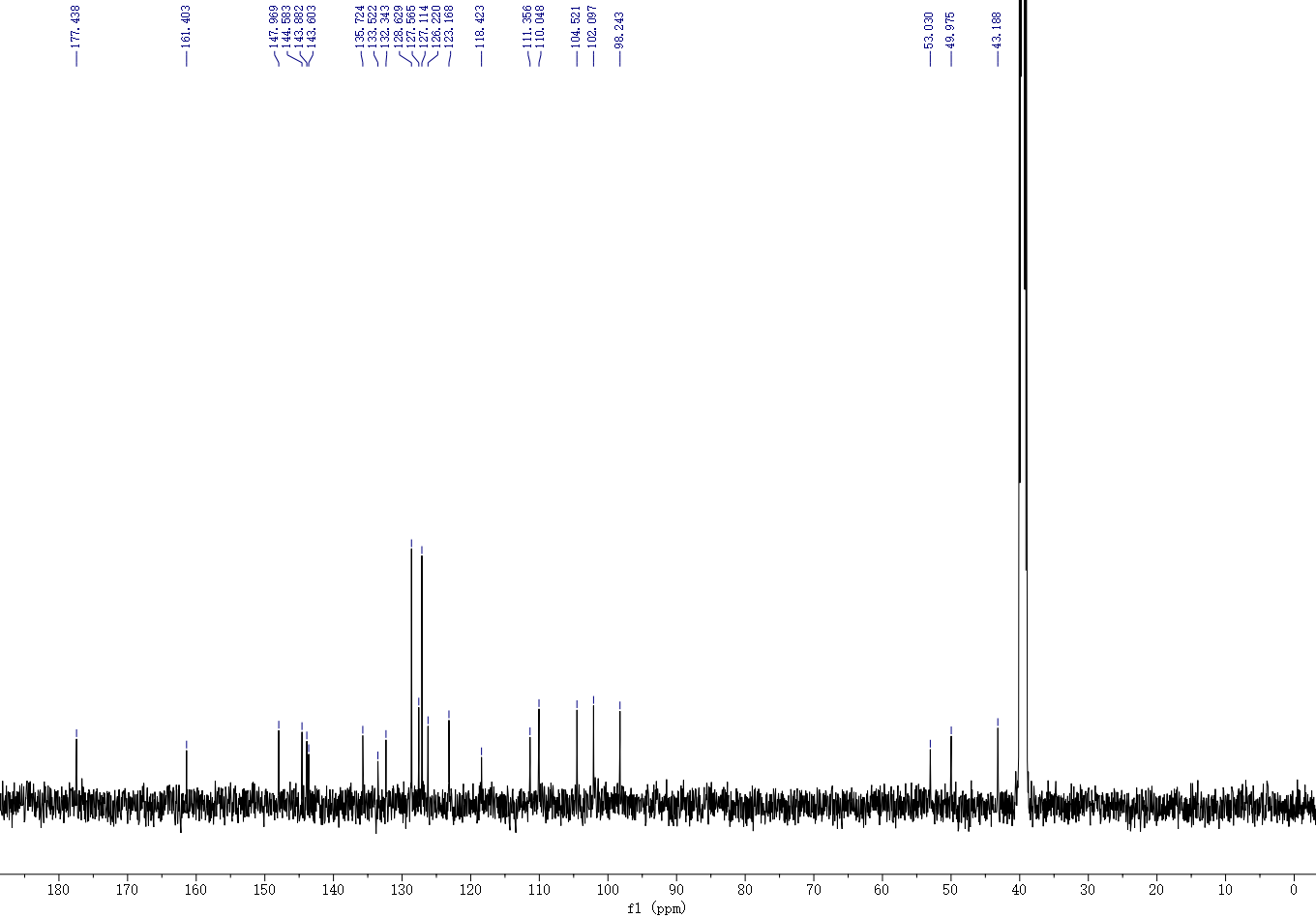


Figure 20. 13C NMR spectrum of **3j**

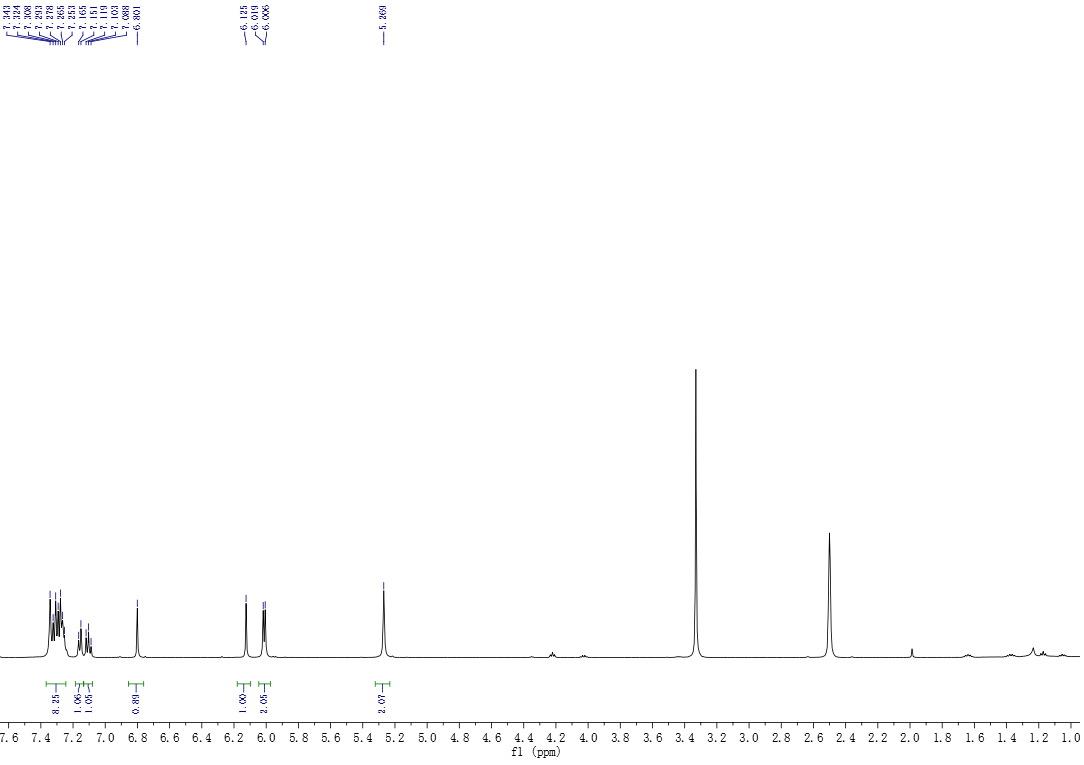


Figure 21. 1H NMR spectrum of **3k**

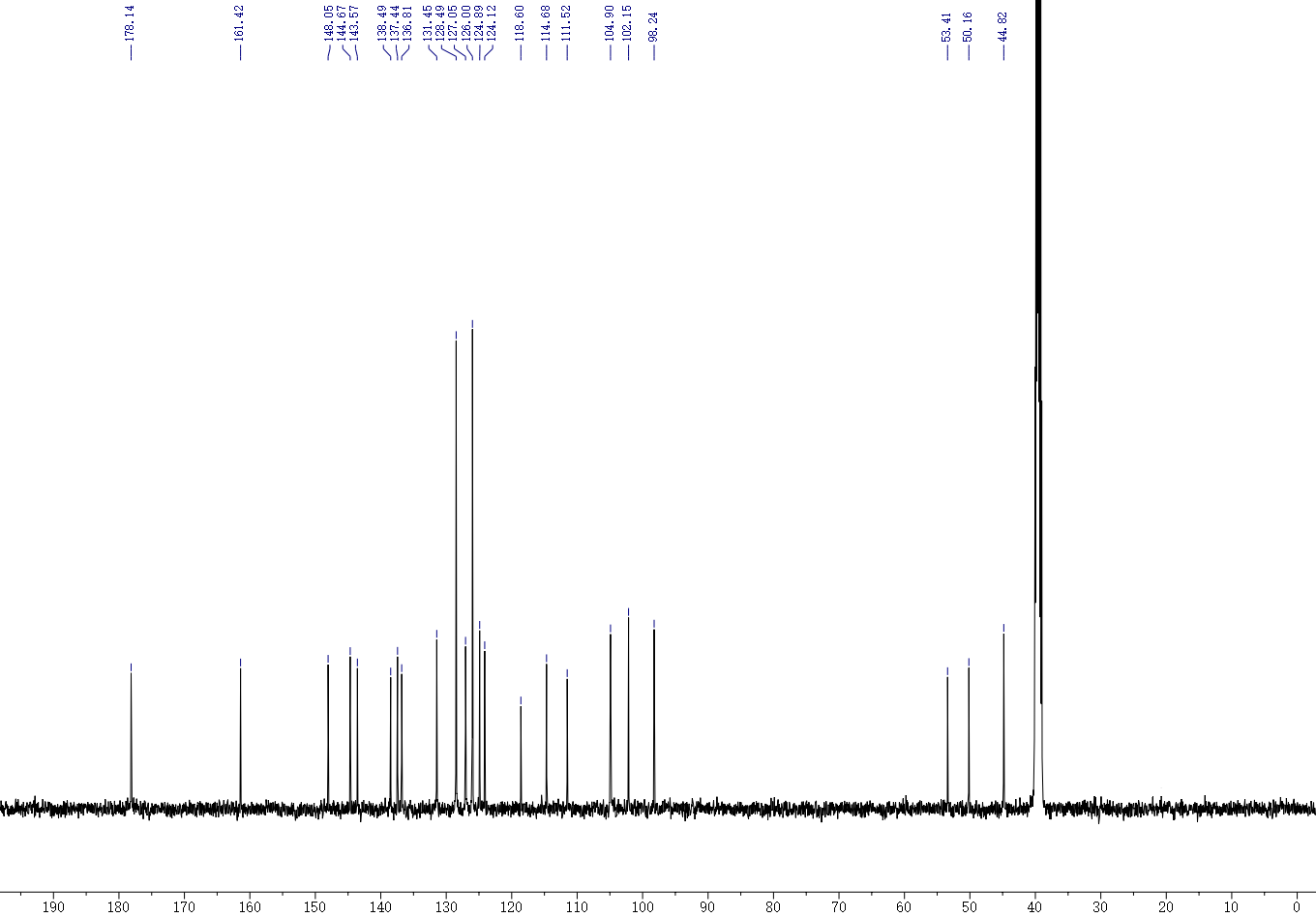


Figure 22. 13C NMR spectrum of **3k**

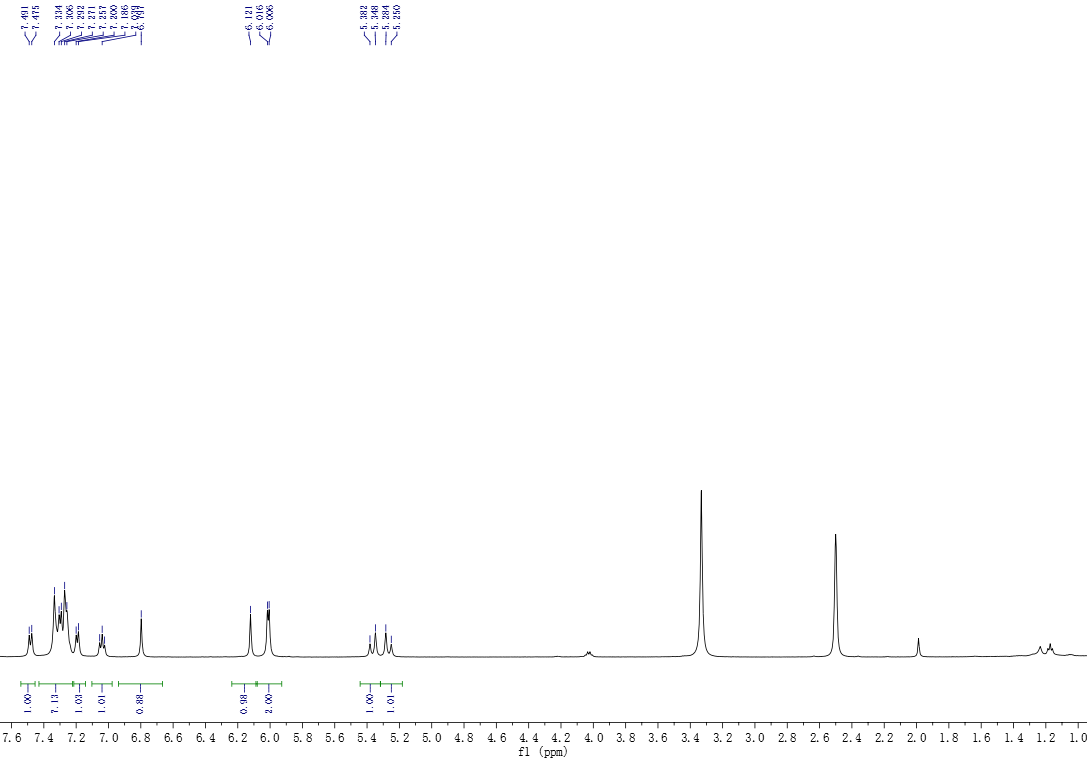


Figure 23. 1H NMR spectrum of **3l**

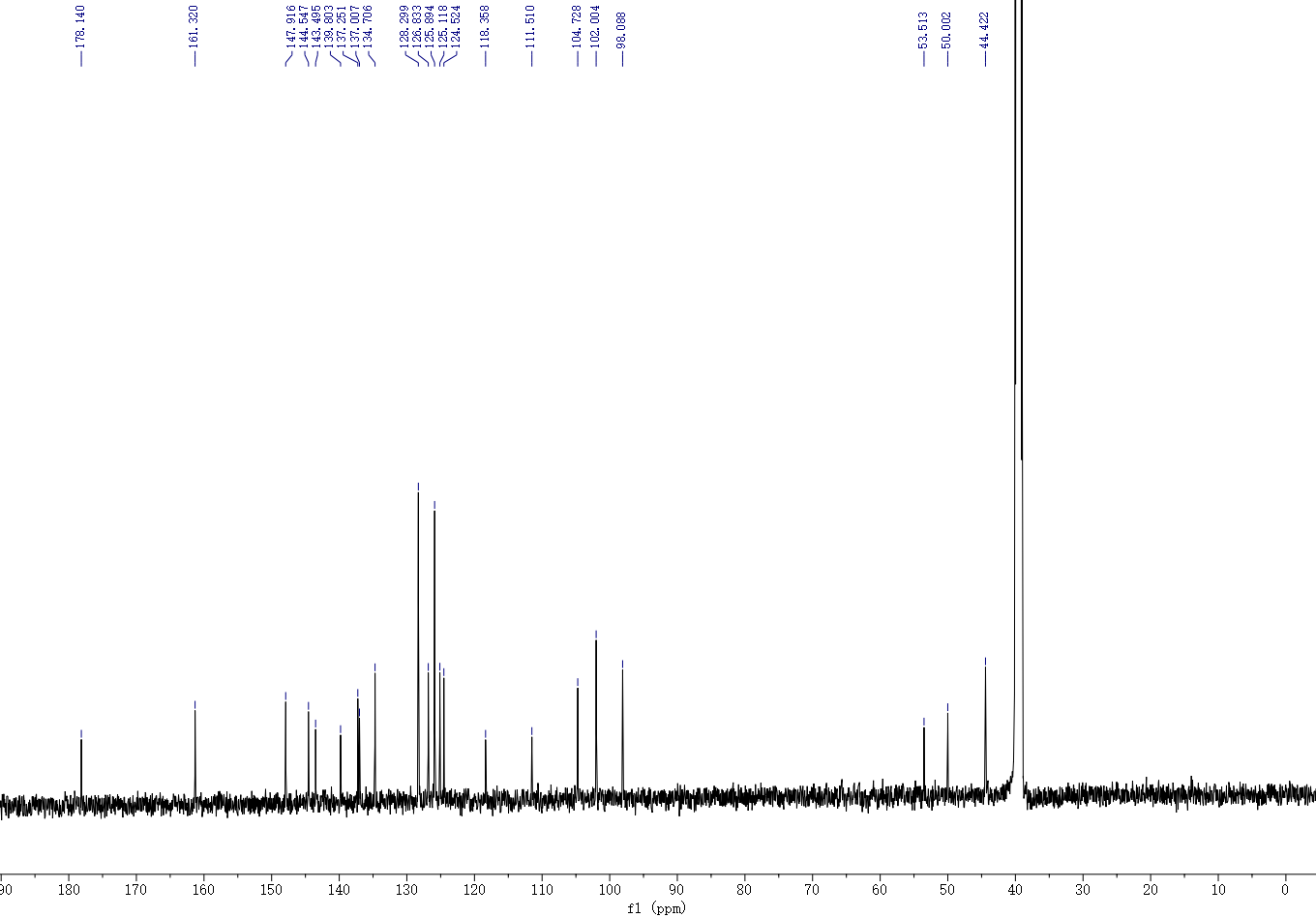


Figure 24. 13C NMR spectrum of **3l**

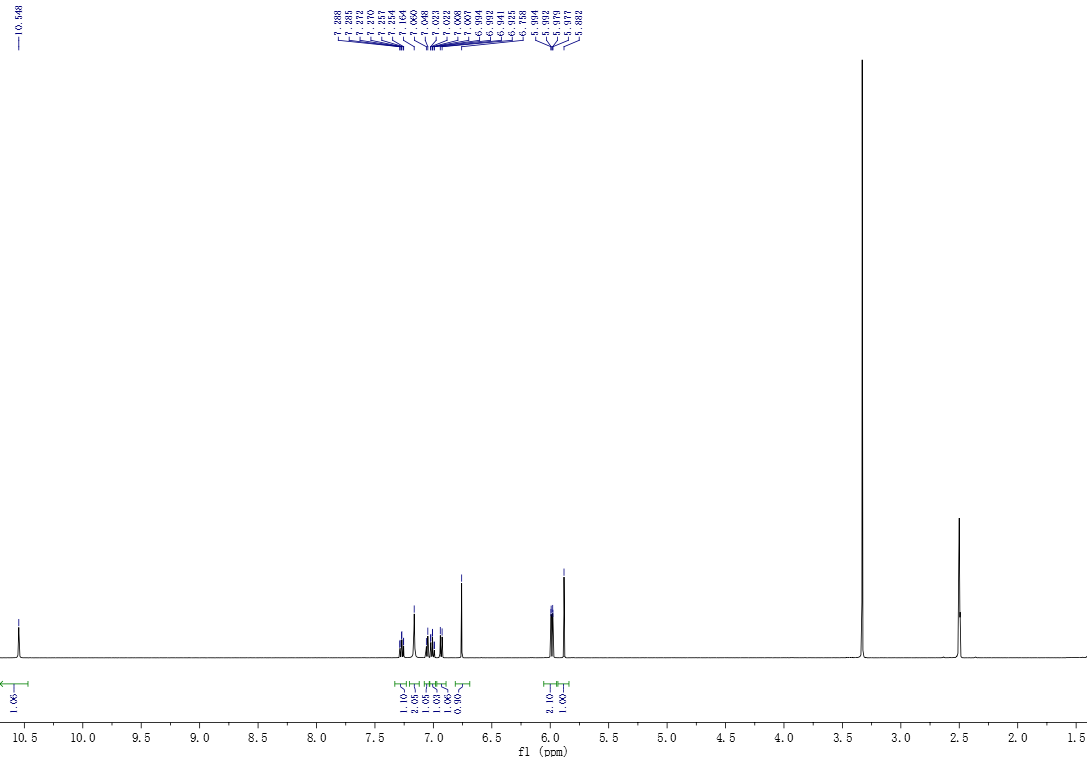


Figure 251H NMR spectrum of **3m**

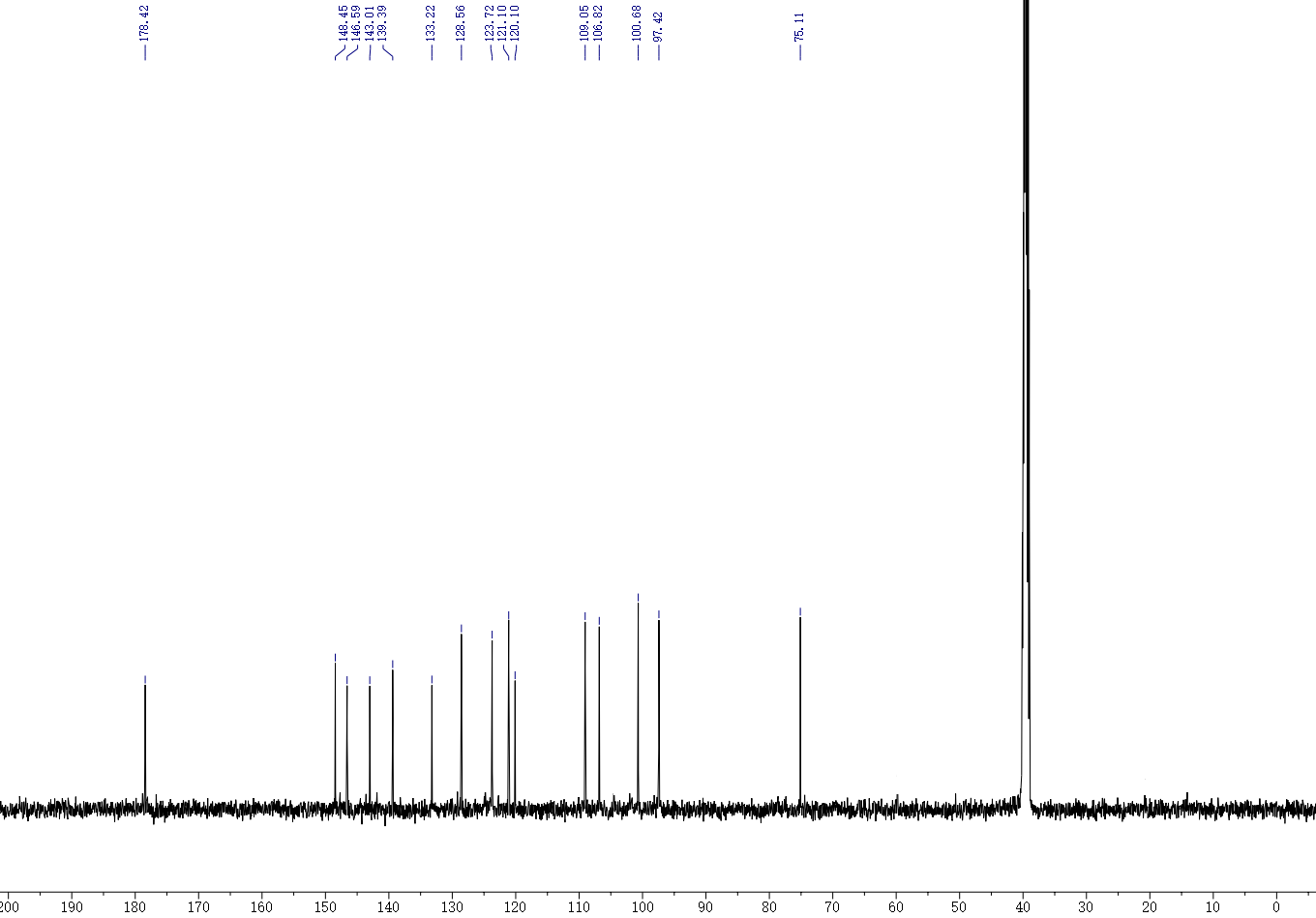


Figure 26. 13C NMR spectrum of **3m**

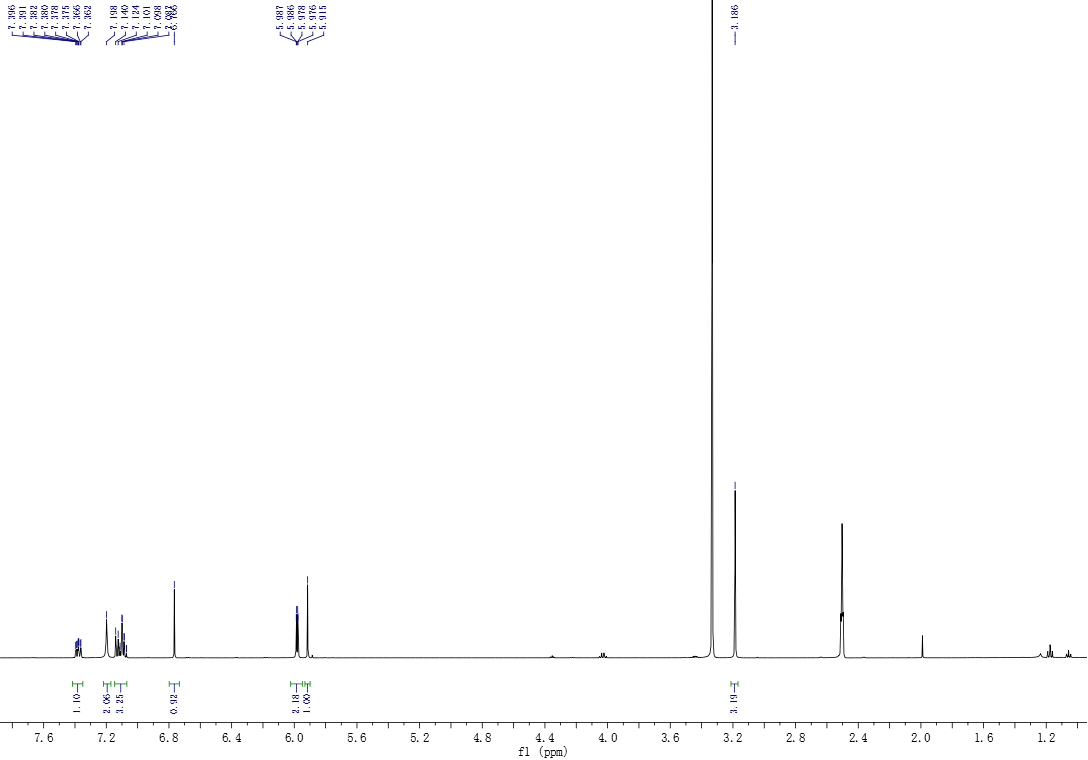


Figure 27 1H NMR spectrum of **3n**

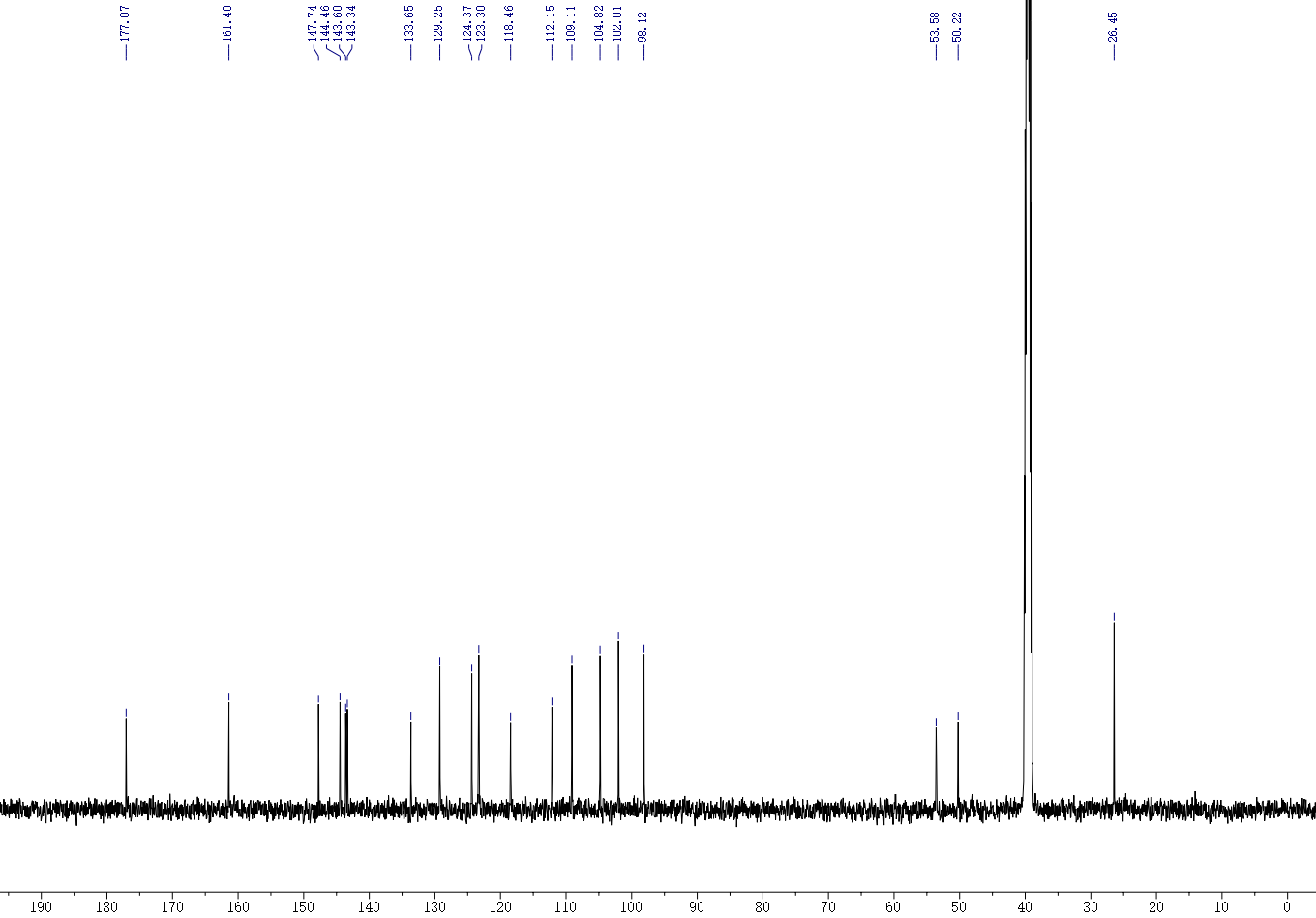


Figure 28. 13C NMR spectrum of **3n**

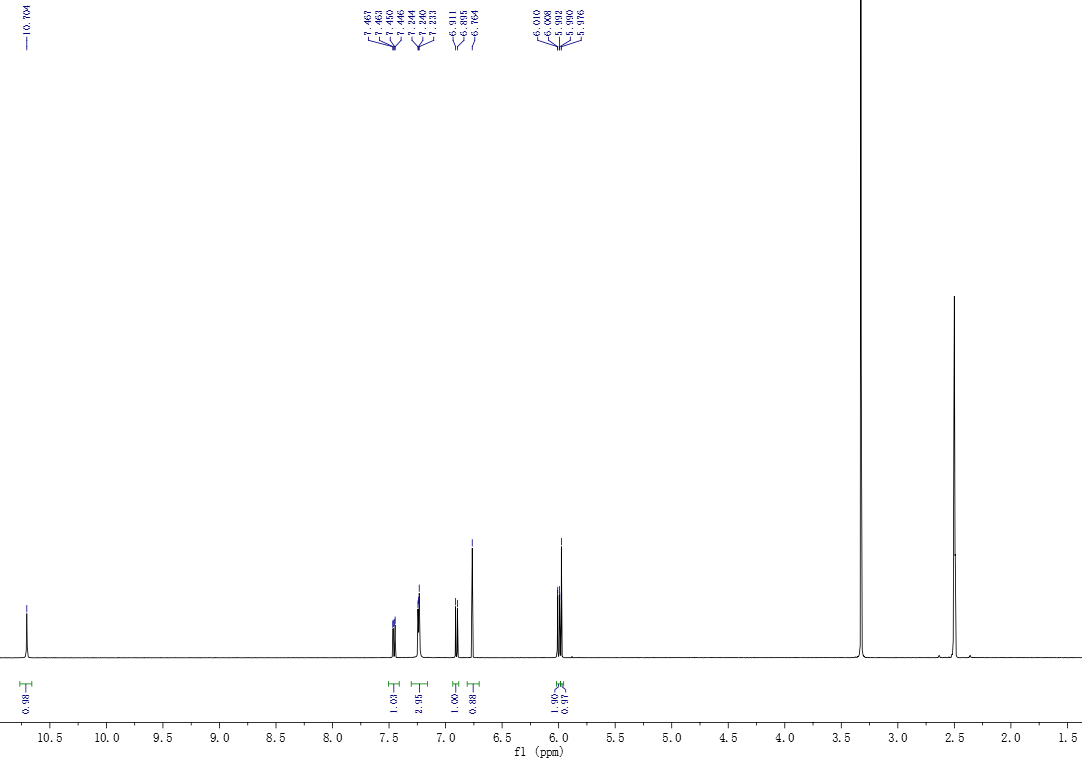


Figure 29 1H NMR spectrum of **3o**

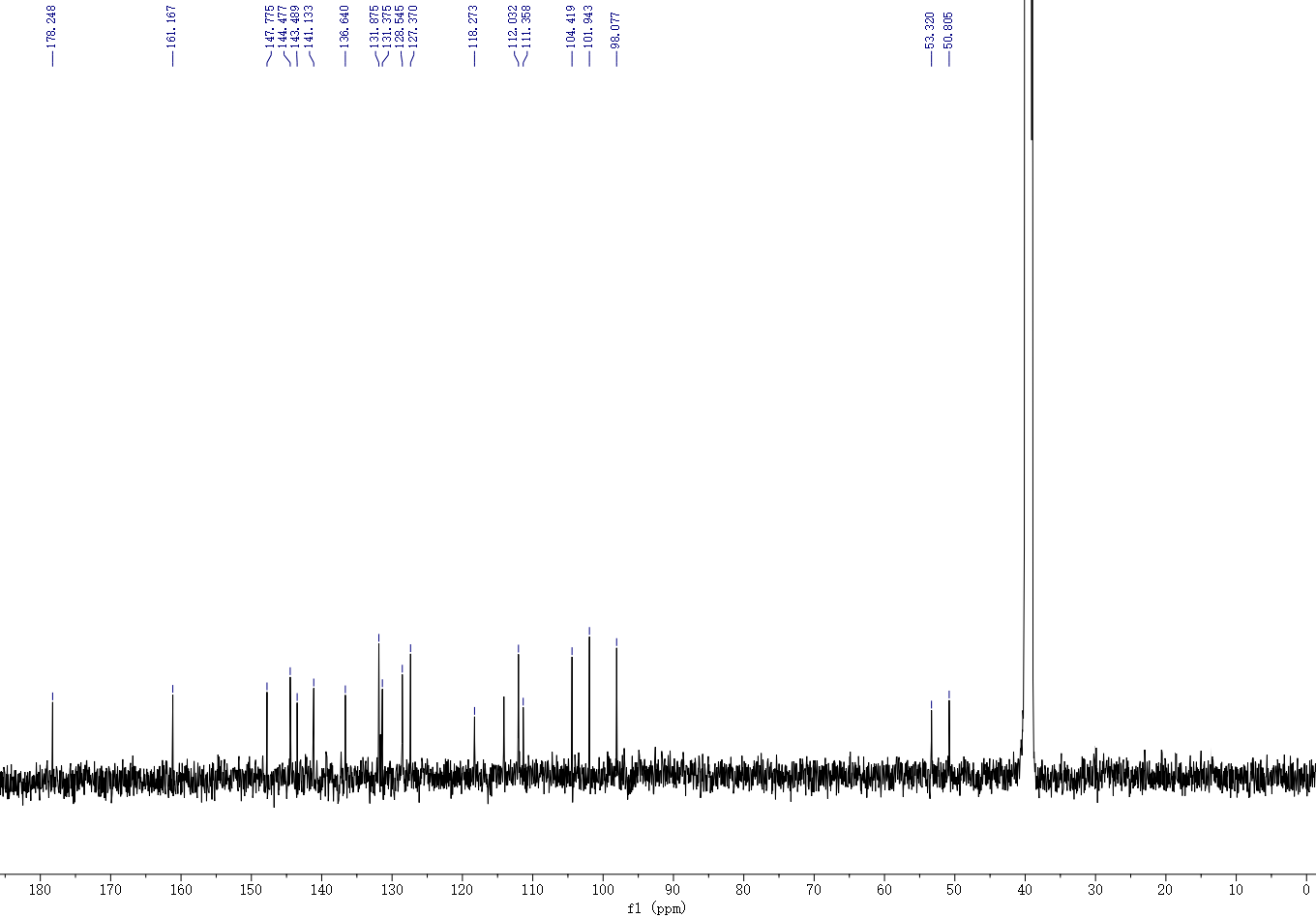


Figure 30 13C NMR spectrum of **3o**

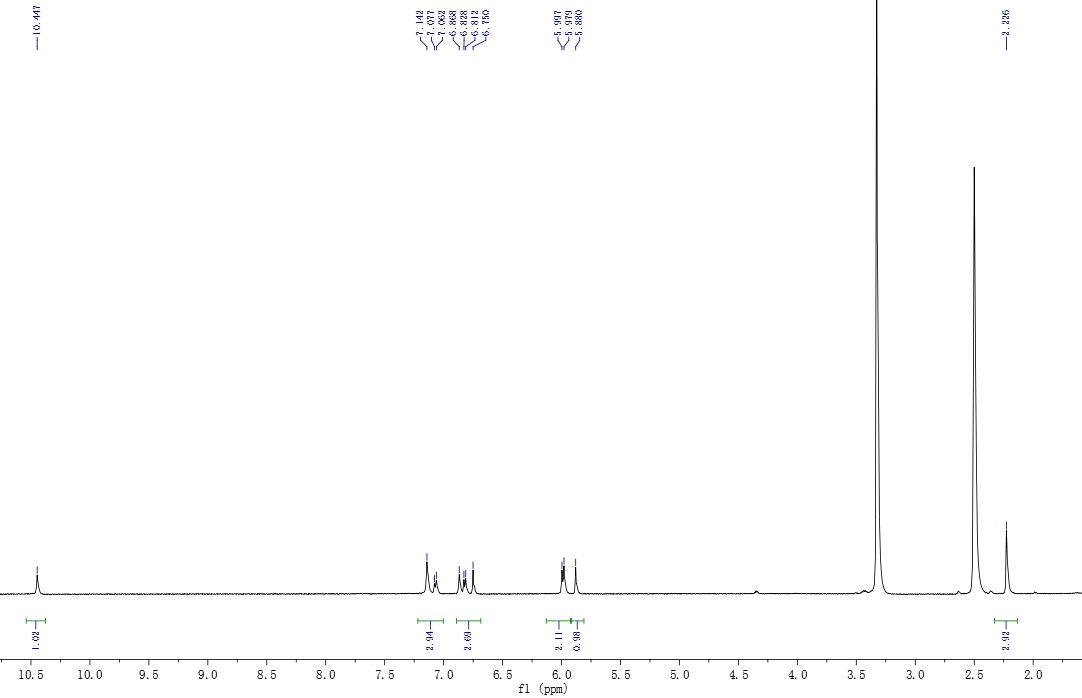


Figure 31 1H NMR spectrum of **3p**

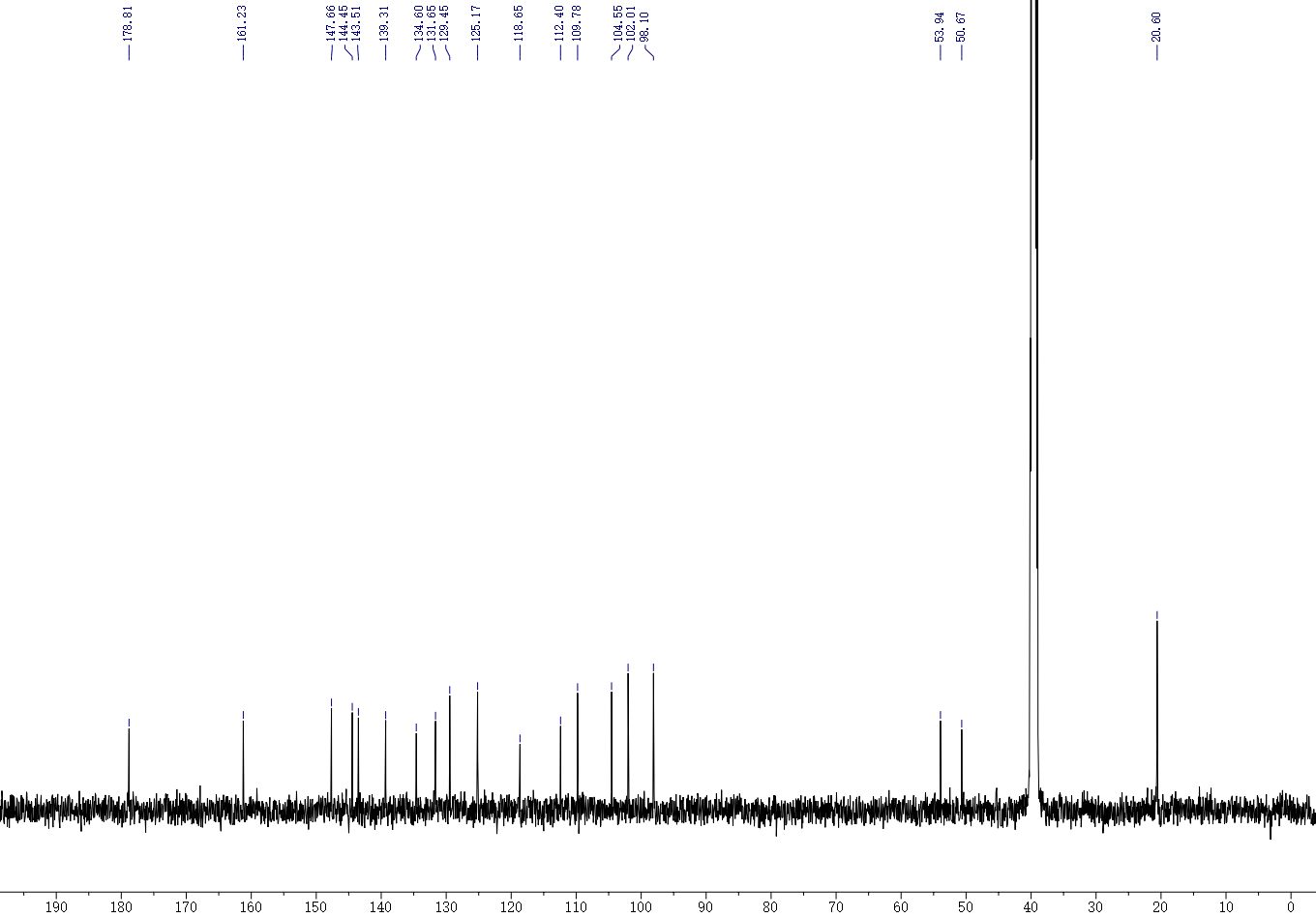


Figure 32 13C NMR spectrum of **3p**

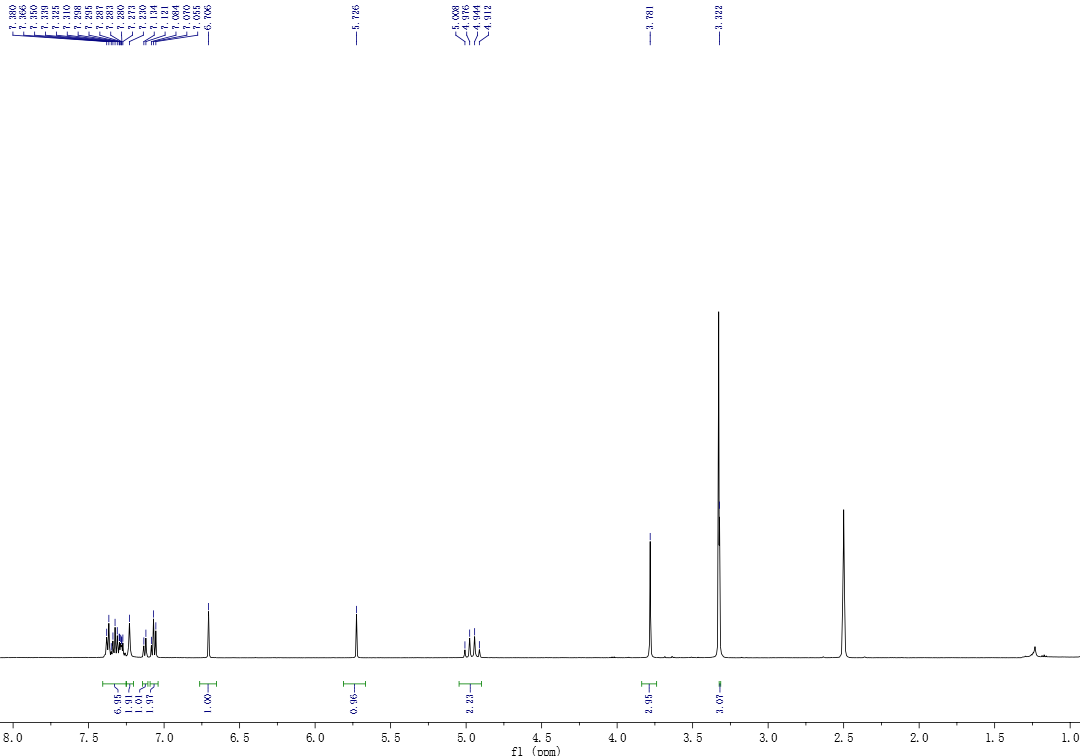


Figure 33 1H NMR spectrum of **4**

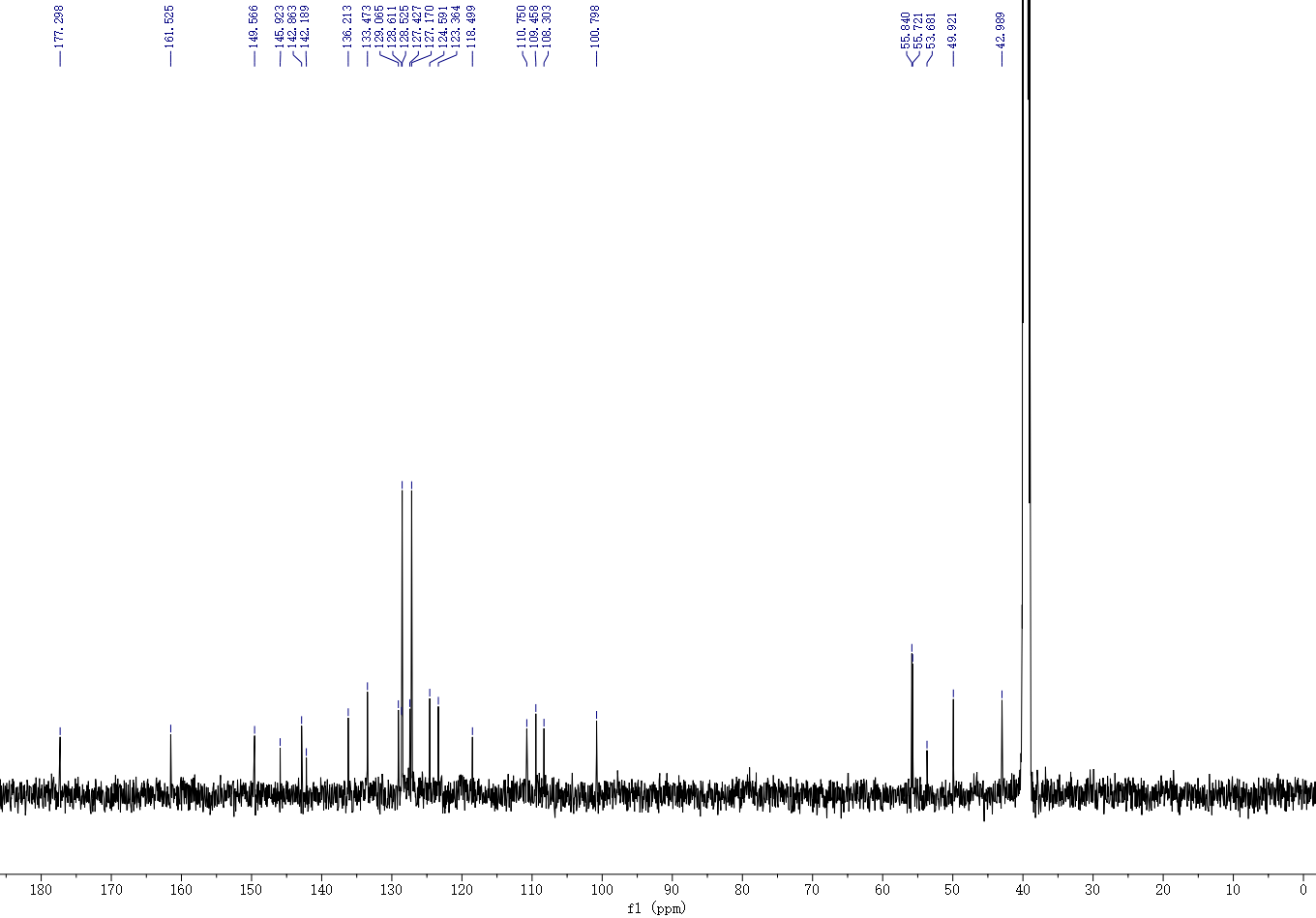


Figure 34 13C NMR spectrum of **4**

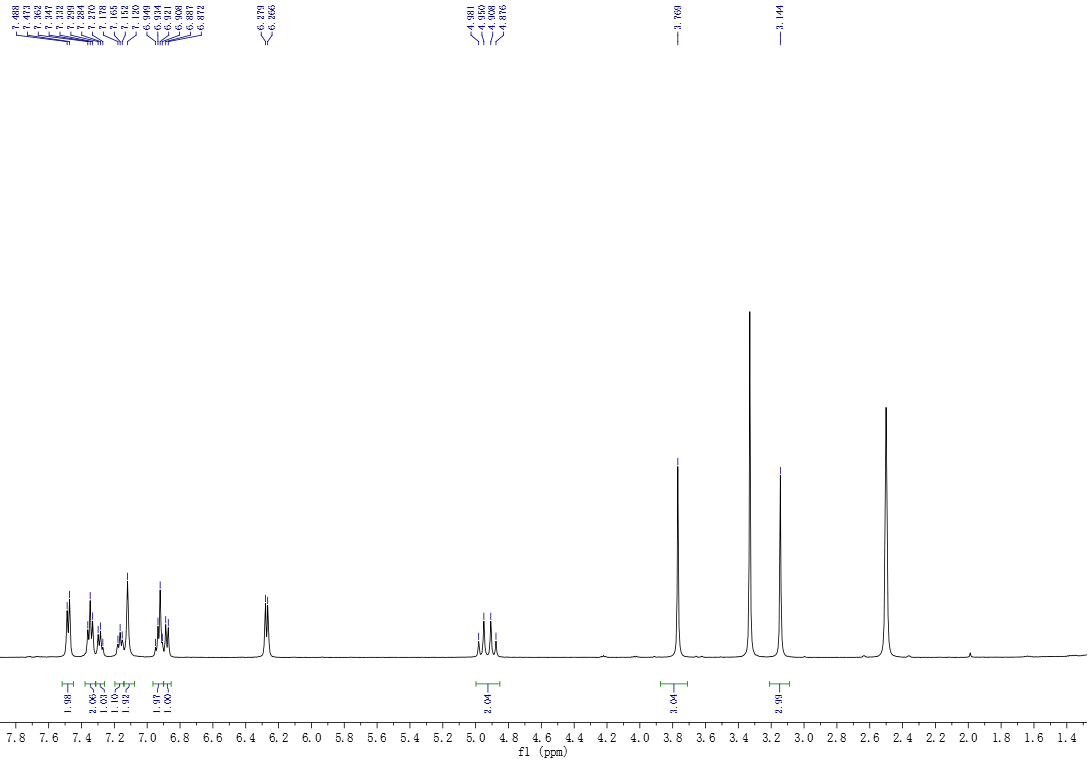


Figure 35 1H NMR spectrum of **5**

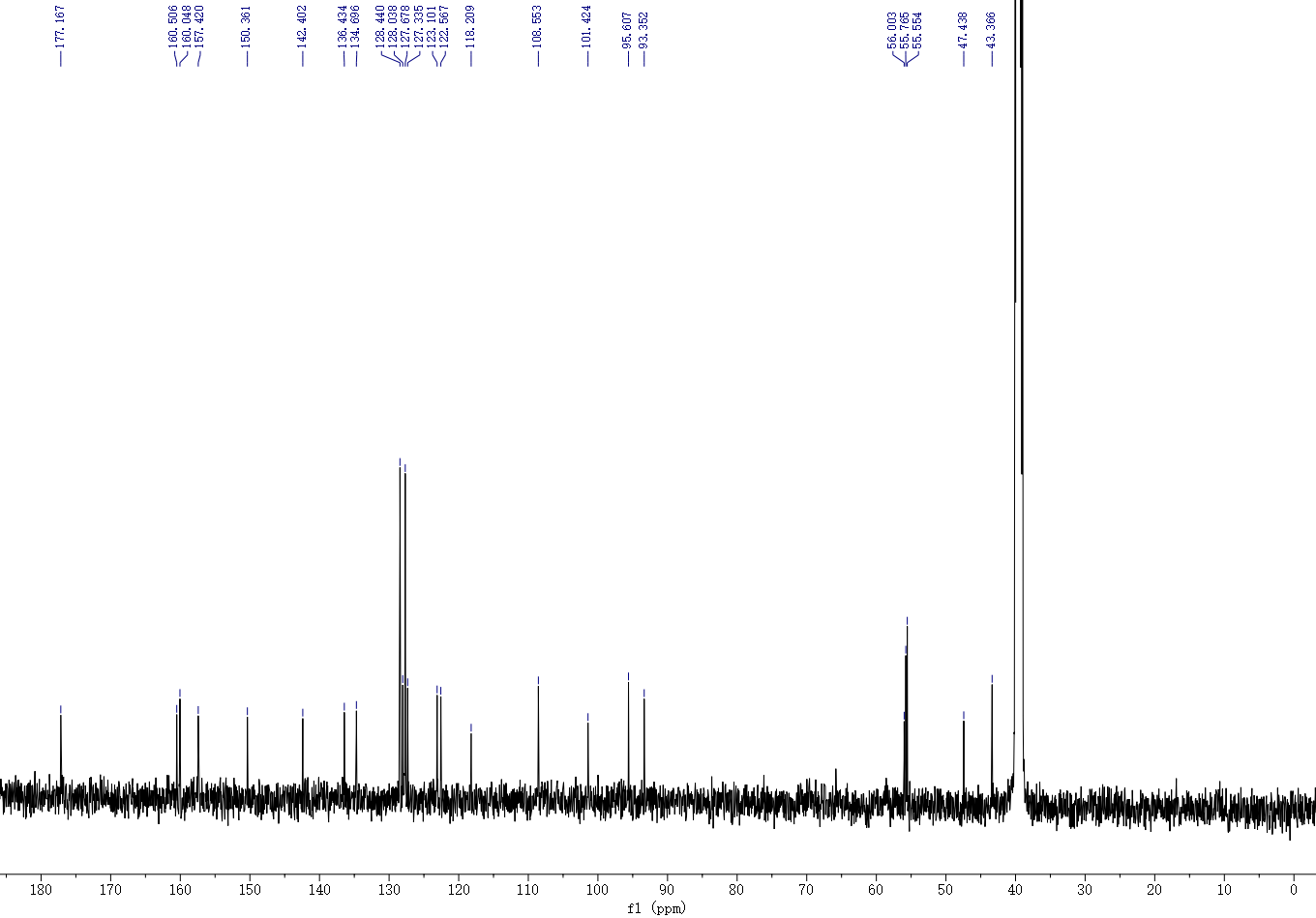


Figure 36 13C NMR spectrum of **5**

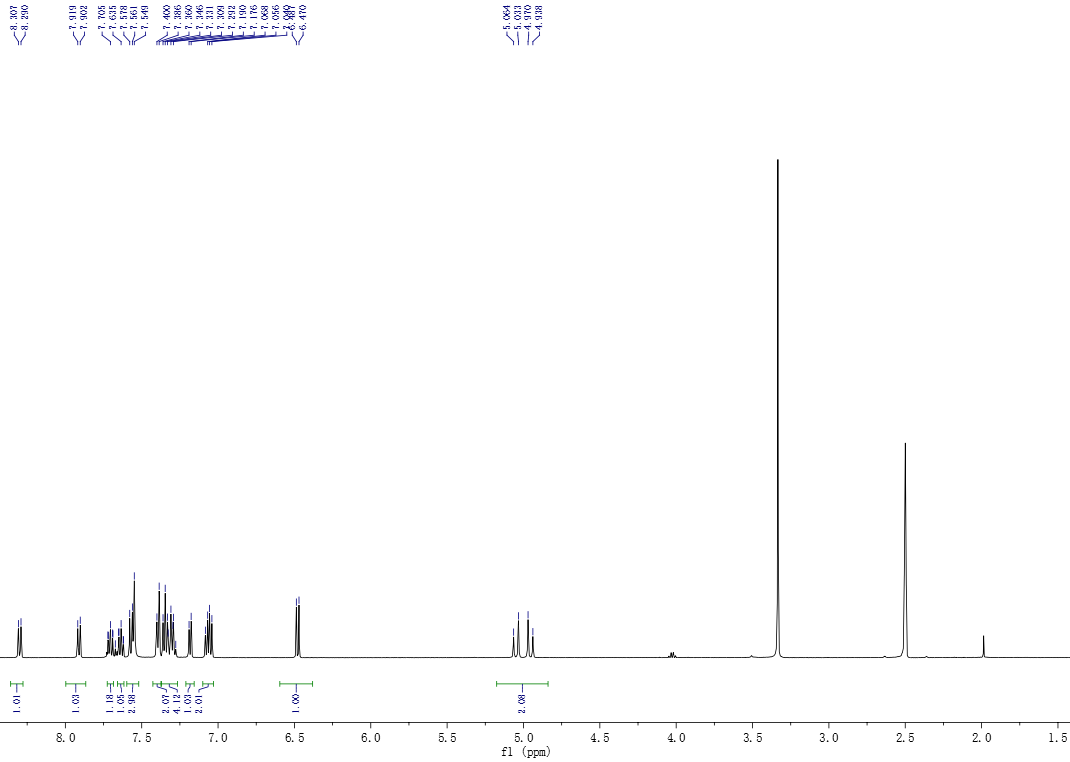


Figure 37 1H NMR spectrum of **6**

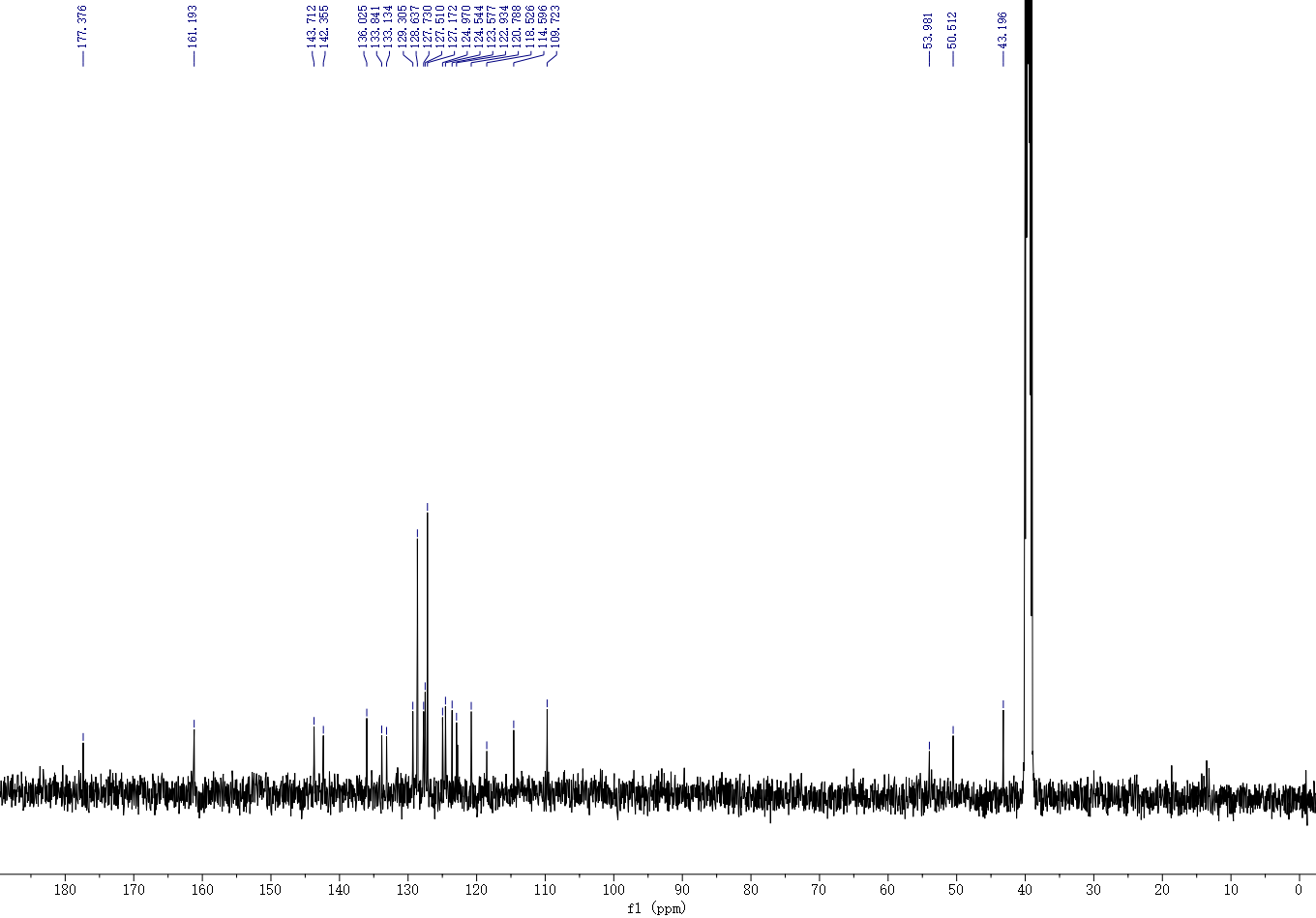


Figure 38 13C NMR spectrum of **6**

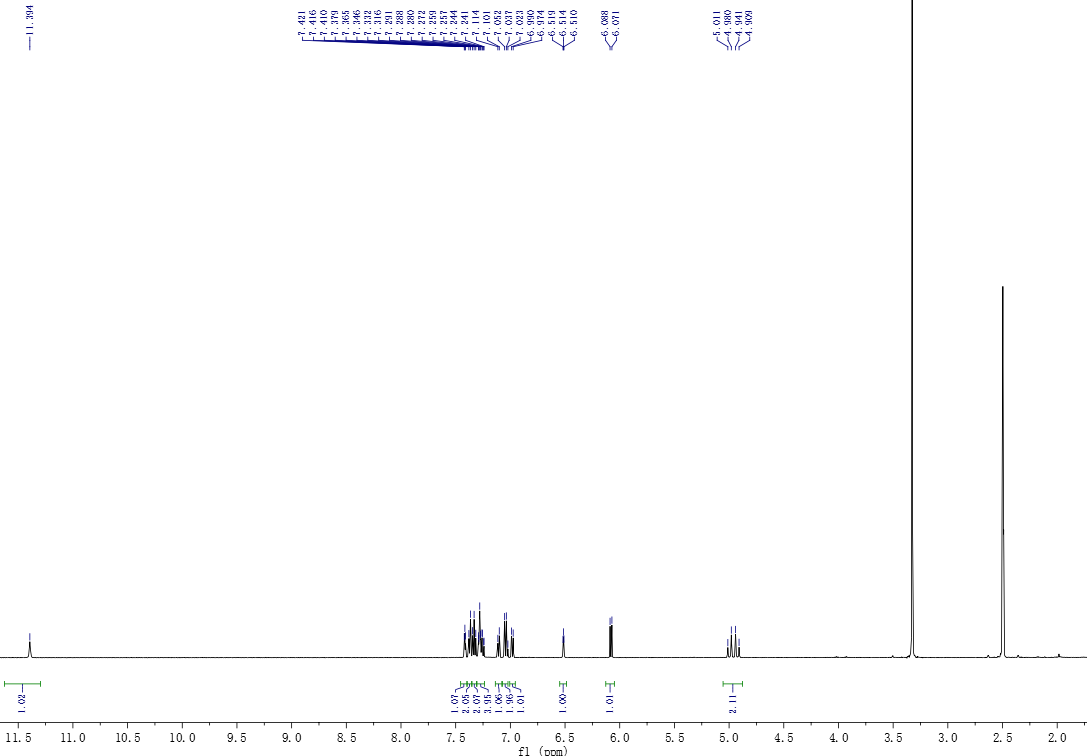


Figure 39 1H NMR spectrum of **7**

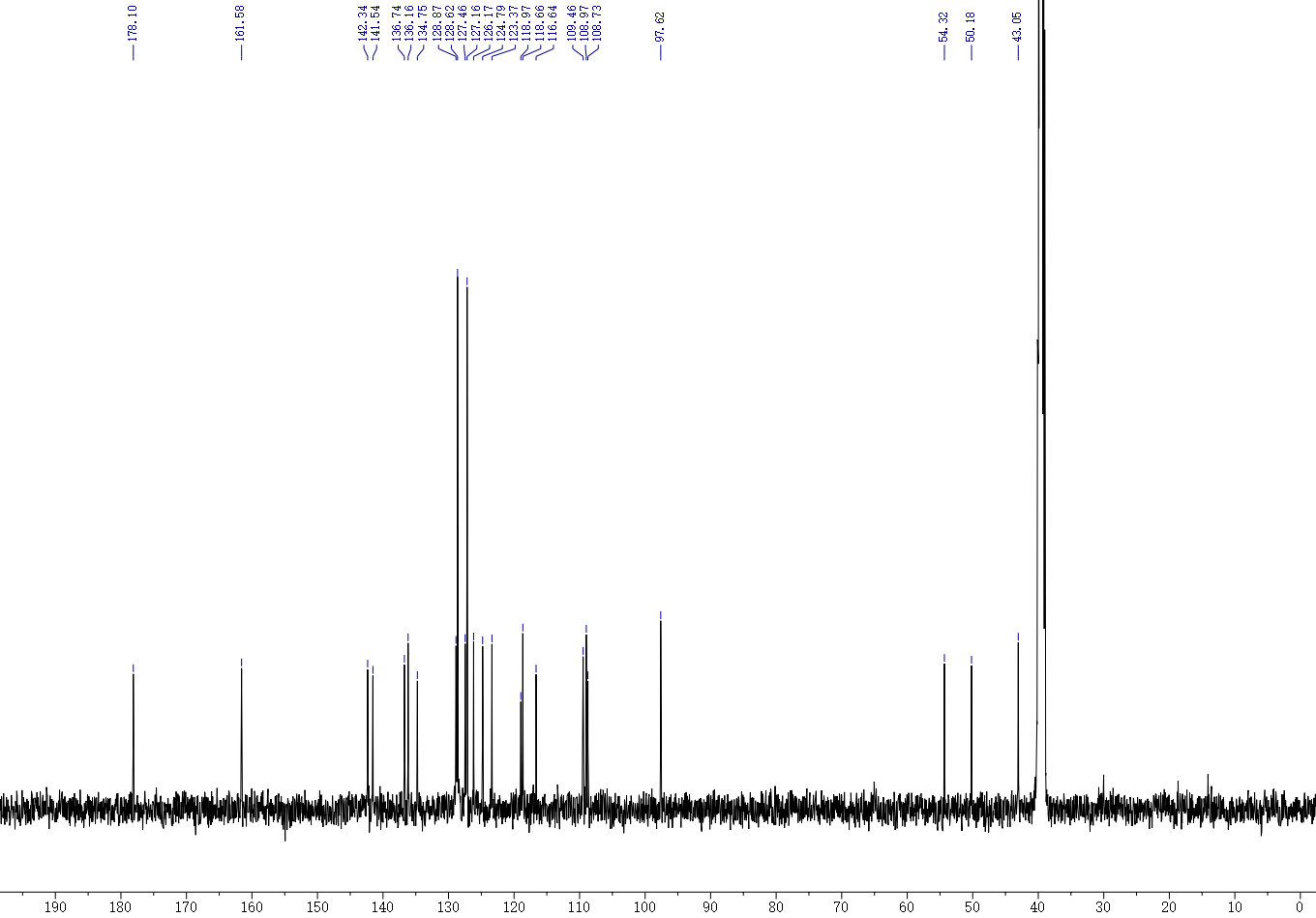


Figure 40 13C NMR spectrum of **7**

HPLC trace

**3a**

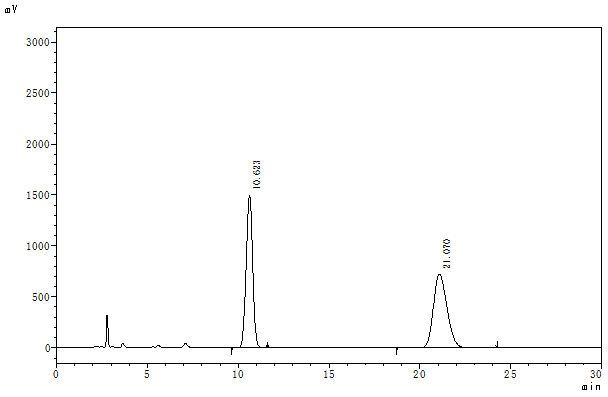


Figure 41. HPLC trace of racemic **3a**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 10.623 | 37492069 | 1496472 | 49.869 |
| 2 | 21.070 | 37689745 | 723931 | 50.131 |
| Total |  | 75181814 | 2220402 | 100.000 |

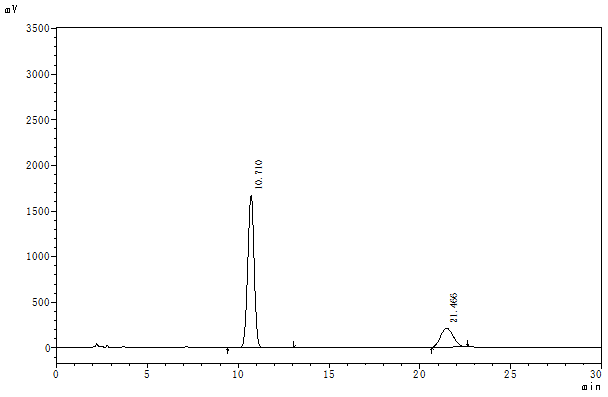


Figure 42. HPLC trace of enantiomeric **3a**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 10.710 | 41296201 | 1671675 | 80.449 |
| 2 | 21.466 | 10035661 | 206371 | 19.551 |
| Total |  | 51331862 | 1878046 | 100.000 |

**3b**



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

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 15.286 | 32435506 | 1063242 | 49.856 |
| 2 | 26.085 | 32622937 | 607935 | 50.144 |
| Total |  | 65058443 | 1671177 | 100.000 |

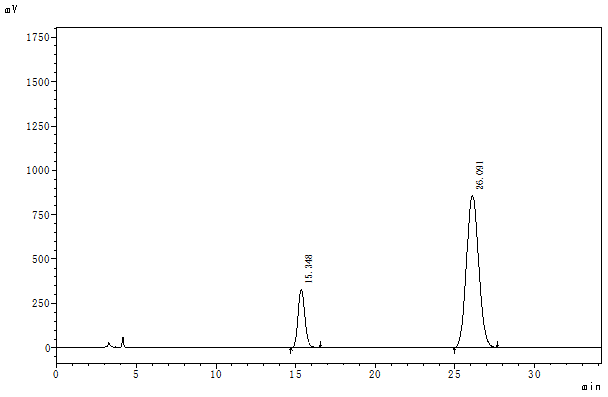


Figure 44. HPLC trace of enantiomeric **3b**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 15.348 | 9833749 | 326542 | 17.672 |
| 2 | 26.091 | 45812104 | 857394 | 82.328 |
| Total |  | 55645854 | 1183937 | 100.000 |

**3c**

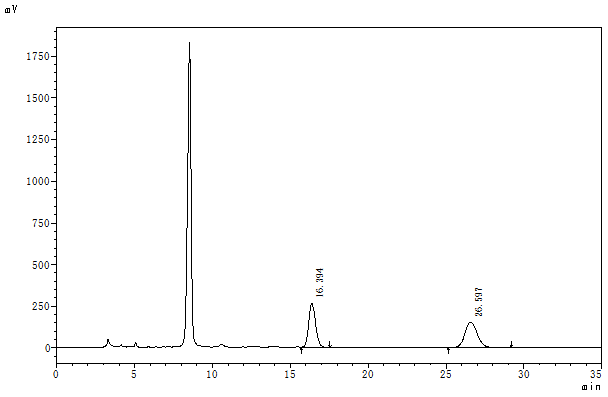


Figure 45. HPLC trace of racemic **3c**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 16.394 | 8298092 | 265808 | 50.077 |
| 2 | 26.597 | 8272419 | 153106 | 49.923 |
| Total |  | 16570511 | 418913 | 100.000 |

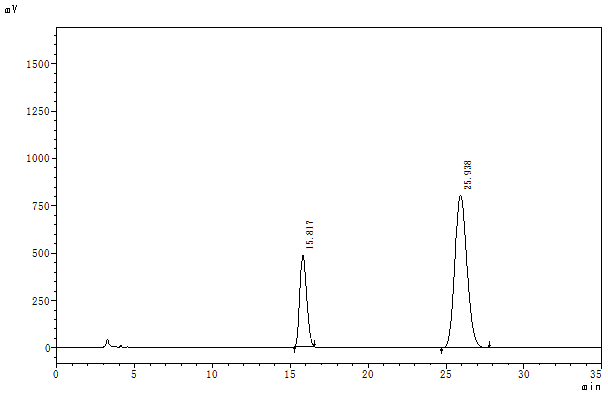


Figure 46. HPLC trace of enantiomeric **3c**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 15.817 | 14914990 | 480511 | 25.400 |
| 2 | 25.938 | 43805339 | 805352 | 74.600 |
| Total |  | 58720329 | 1285863 | 100.000 |

**3d**

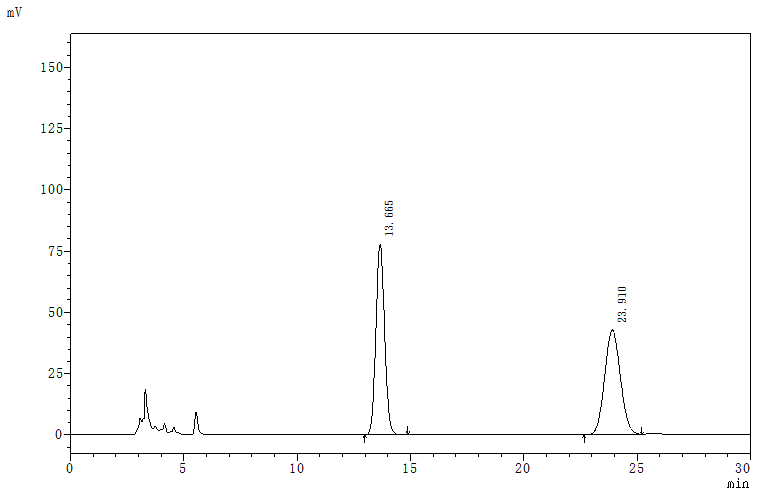


Figure 47. HPLC trace of racemic **3d**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.665 | 2078568 | 77743 | 49.961 |
| 2 | 23.910 | 2081806 | 42826 | 50.039 |
| Total |  | 4160374 | 120569 | 100.000 |

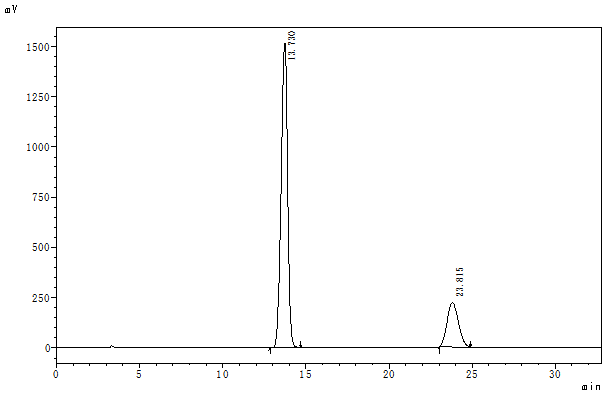


Figure 48. HPLC trace of enantiomeric **3d**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.730 | 41232394 | 1517889 | 79.724 |
| 2 | 23.815 | 10486569 | 221946 | 20.276 |
| Total |  | 51718962 | 1739835 | 100.000 |

**3e**

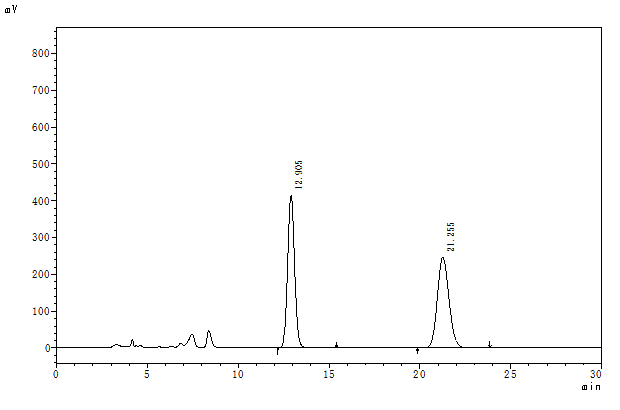


Figure 49. HPLC trace of racemic **3e**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 12.905 | 11116688 | 414345 | 50.183 |
| 2 | 21.255 | 11035638 | 246505 | 49.817 |
| Total |  | 22152326 | 660850 | 100.000 |

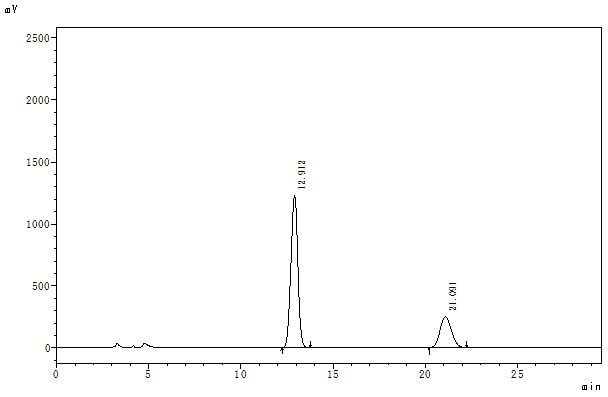


Figure 50. HPLC trace of enantiomeric **3e**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 12.912 | 32048047 | 1228926 | 74.679 |
| 2 | 21.091 | 10866457 | 251249 | 25.321 |
| Total |  | 42914504 | 1480175 | 100.000 |

**3f**

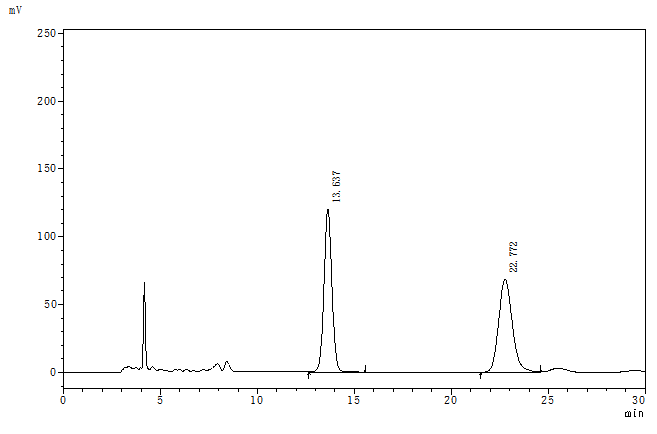


Figure 51. HPLC trace of racemic **3f**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.637 | 3451833 | 120105 | 50.686 |
| 2 | 22.772 | 3358429 | 68544 | 49.314 |
| Total |  | 6810263 | 188649 | 100.000 |

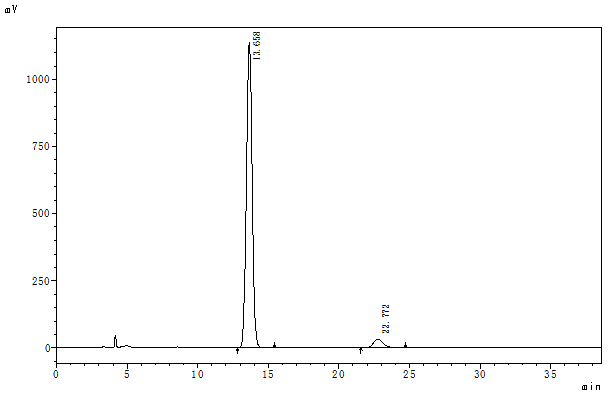


Figure 52. HPLC trace of enantiomeric **3f**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.658 | 32096090 | 1136190 | 95.022 |
| 2 | 22.772 | 1681413 | 32796 | 4.978 |
| Total |  | 33777503 | 1168986 | 100.000 |

**3g**



Figure 53. HPLC trace of racemic **3g**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.744 | 34665264 | 1247873 | 49.913 |
| 2 | 24.121 | 34786407 | 675499 | 50.087 |
| Total |  | 69451672 | 1923371 | 100.000 |

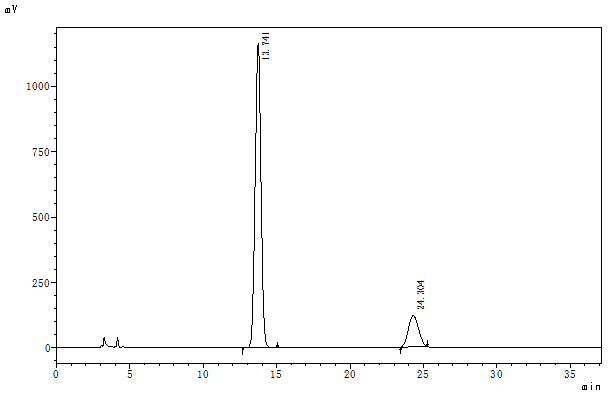


Figure 54. HPLC trace of enantiomeric **3g**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.741 | 32270523 | 1166350 | 84.729 |
| 2 | 24.304 | 5816344 | 120521 | 15.271 |
| Total |  | 38086867 | 1286871 | 100.000 |

**3h**

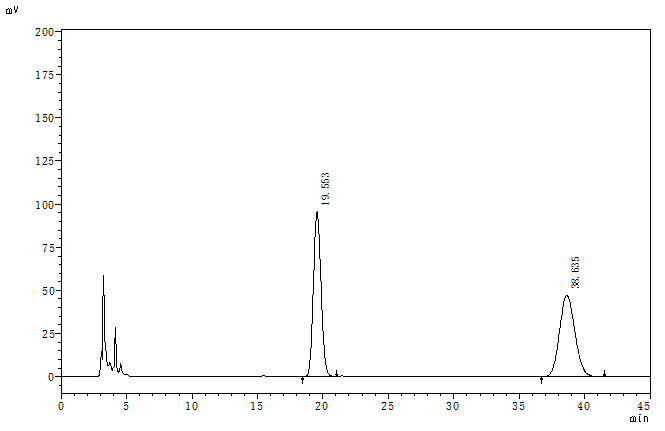


Figure 55. HPLC trace of racemic **3h**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 19.553 | 3876801 | 95723 | 50.056 |
| 2 | 38.635 | 3868176 | 47244 | 49.944 |
| Total |  | 7744977 | 142967 | 100.000 |

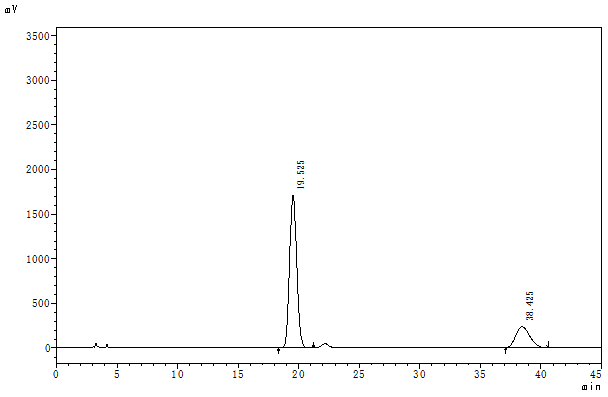


Figure 56. HPLC trace of enantiomeric **3h**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 19.525 | 70237855 | 1710652 | 78.551 |
| 2 | 38.425 | 19178961 | 236751 | 21.449 |
| Total |  | 89416816 | 1947403 | 100.000 |

**3i**

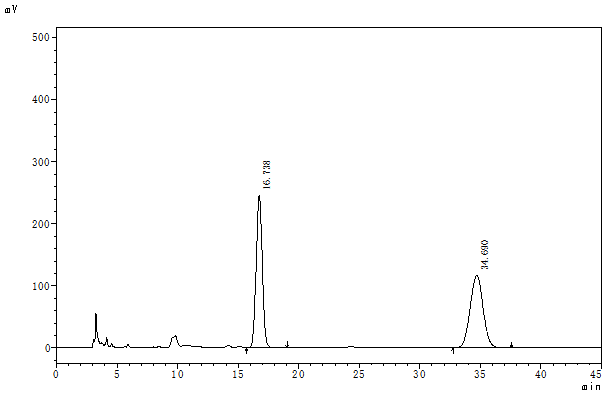


Figure 57. HPLC trace of racemic **3i**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 16.738 | 8677665 | 245786 | 50.050 |
| 2 | 34.690 | 8660371 | 116453 | 49.950 |
| Total |  | 17338036 | 362240 | 100.000 |

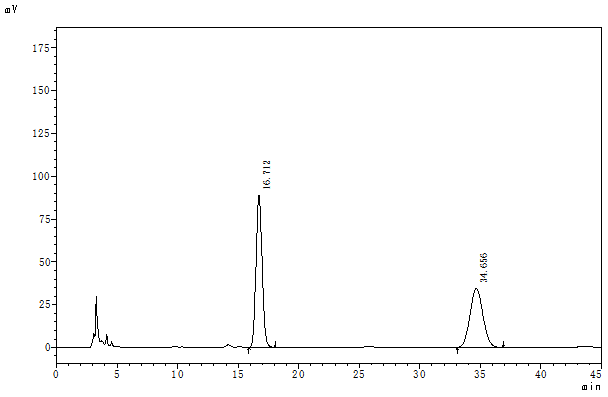


Figure 58. HPLC trace of enantiomeric **3i**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 16.712 | 3112570 | 88788 | 54.951 |
| 2 | 34.656 | 2551649 | 34395 | 45.049 |
| Total |  | 5664219 | 123183 | 100.000 |

**3j**

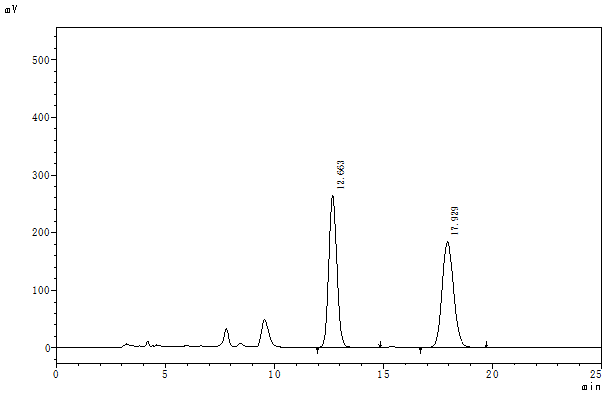


Figure 59. HPLC trace of racemic **3j**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 12.663 | 6781606 | 263562 | 50.124 |
| 2 | 17.929 | 6747966 | 182981 | 49.876 |
| Total |  | 13529572 | 446543 | 100.000 |

**3j**

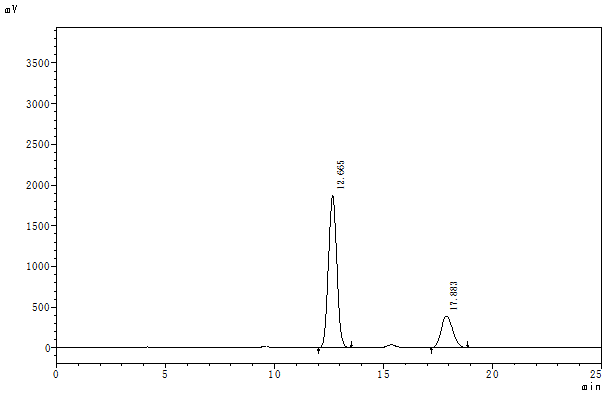


Figure 60. HPLC trace of enantiomeric **3j**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 12.665 | 49971405 | 1872607 | 77.578 |
| 2 | 17.883 | 14442900 | 389017 | 22.422 |
| Total |  | 64414305 | 2261624 | 100.000 |

**3k**

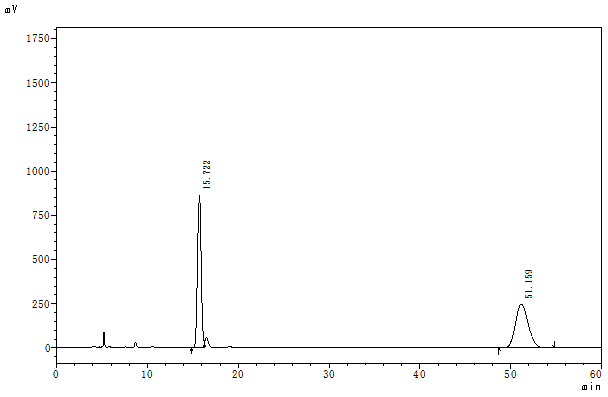


Figure 61. HPLC trace of racemic **3k**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 15.722 | 24079454 | 862839 | 49.922 |
| 2 | 51.159 | 24154274 | 248595 | 50.078 |
| Total |  | 48233728 | 1111434 | 100.000 |

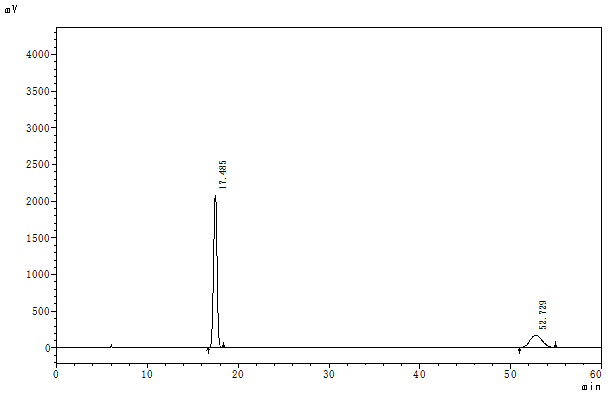


Figure 62. HPLC trace of enantiomeric **3k**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 17.485 | 54352310 | 2077891 | 77.319 |
| 2 | 52.729 | 15944277 | 169599 | 22.681 |
| Total |  | 70296587 | 2247489 | 100.000 |

**3l**

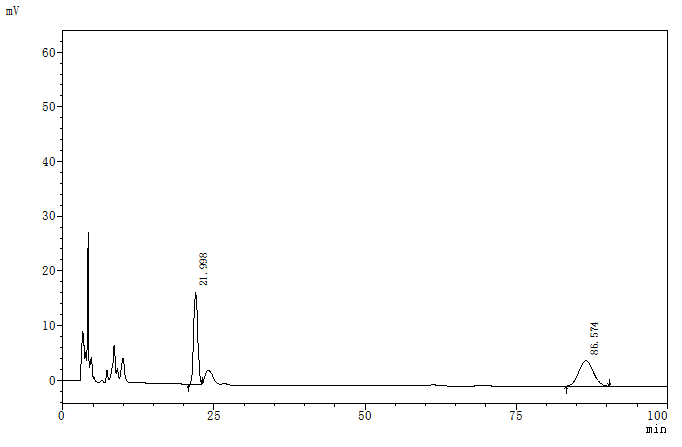


Figure 63. HPLC trace of racemic **3l**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 21.998 | 792211 | 16842 | 50.545 |
| 2 | 86.574 | 775135 | 4664 | 49.455 |
| Total |  | 1567345 | 21505 | 100.000 |

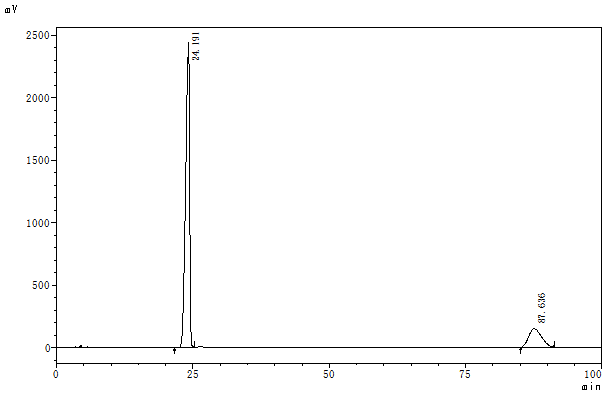


Figure 64. HPLC trace of enantiomeric **3l**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 24.191 | 122255711 | 2439253 | 83.332 |
| 2 | 87.636 | 24453785 | 148816 | 16.668 |
| Total |  | 146709496 | 2588068 | 100.000 |

**3m**

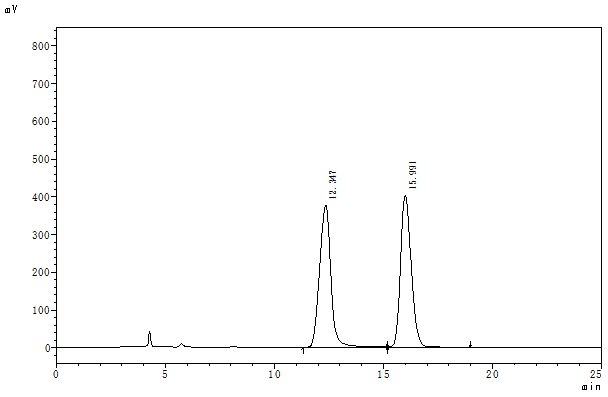


Figure 65. HPLC trace of racemic **3m**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 12.347 | 13508577 | 375754 | 49.669 |
| 2 | 15.991 | 13688556 | 401831 | 50.331 |
| Total |  | 27197133 | 777585 | 100.000 |

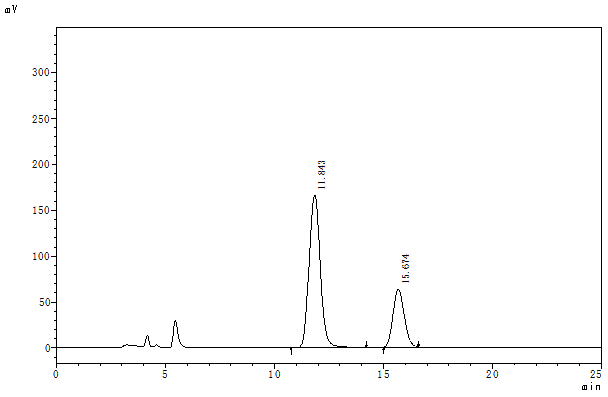


Figure 66. HPLC trace of enantiomeric **3m**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 11.843 | 5936773 | 166098 | 72.478 |
| 2 | 15.674 | 2254412 | 63076 | 27.522 |
| Total |  | 8191185 | 229175 | 100.000 |

**3n**

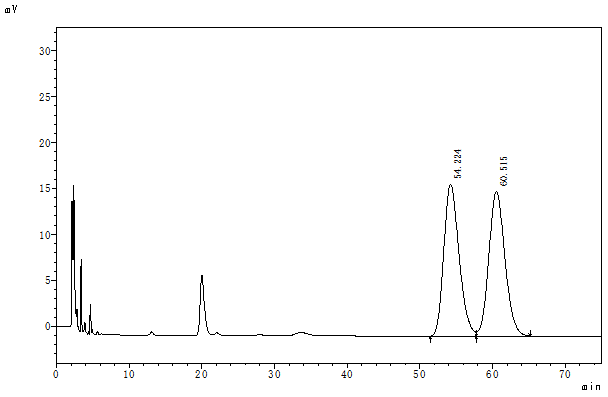


Figure 67. HPLC trace of racemic **3n**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 54.224 | 2417987 | 16523 | 49.844 |
| 2 | 60.515 | 2433170 | 15727 | 50.156 |
| Total |  | 4851158 | 32250 | 100.000 |

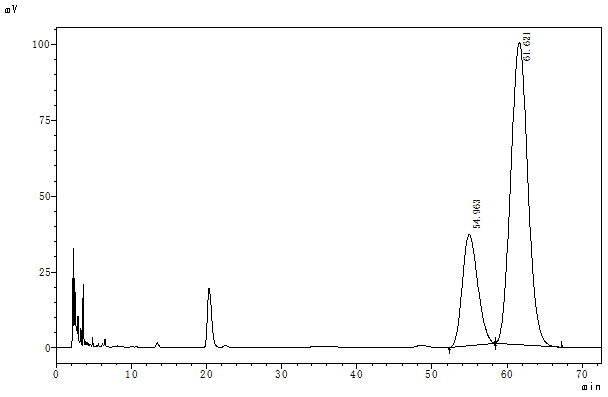


Figure 68. HPLC trace of enantiomeric **3n**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 54.963 | 5228268 | 36668 | 24.871 |
| 2 | 61.621 | 15793017 | 99598 | 75.129 |
| Total |  | 21021285 | 136266 | 100.000 |

**3o**

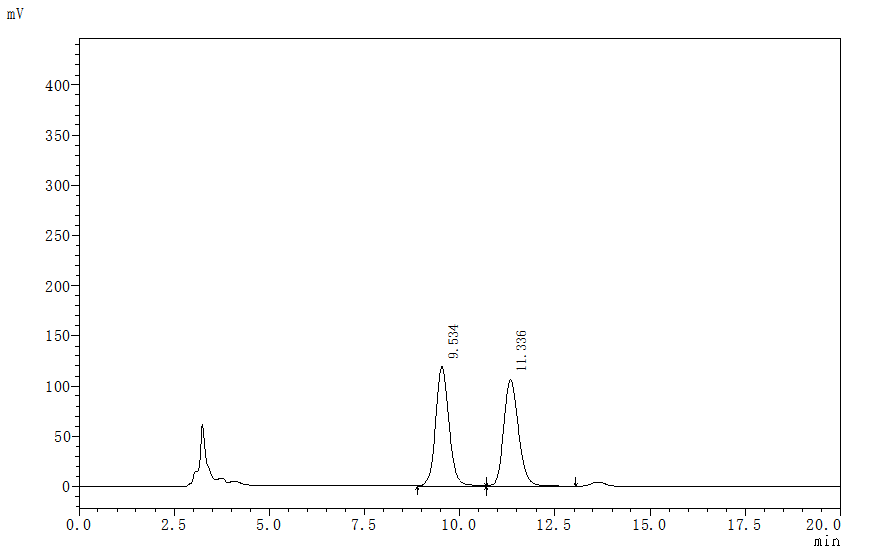


Figure 69. HPLC trace of racemic **3o**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 9.534 | 2969799 | 119595 | 50.482 |
| 2 | 11.336 | 2913055 | 106703 | 49.518 |
| Total |  | 5882854 | 226298 | 100.000 |

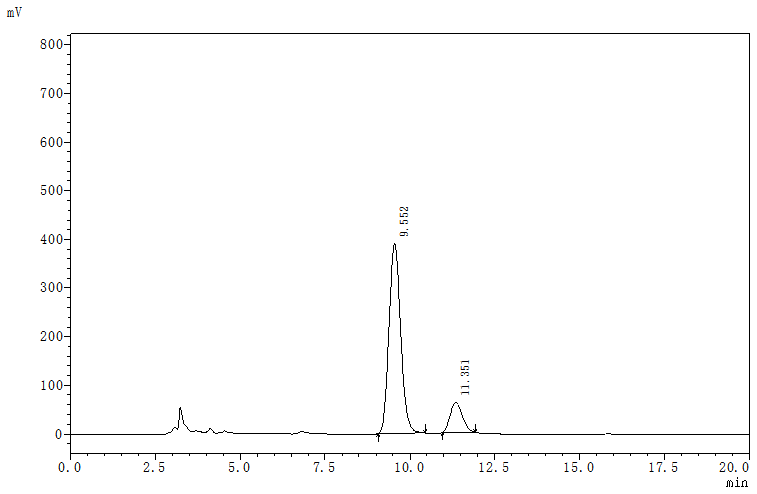


Figure 70. HPLC trace of enantiomeric **3o**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 9.552 | 9338796 | 390241 | 85.965 |
| 2 | 11.351 | 1524712 | 61040 | 14.035 |
| Total |  | 10863508 | 451281 | 100.000 |

**3p**

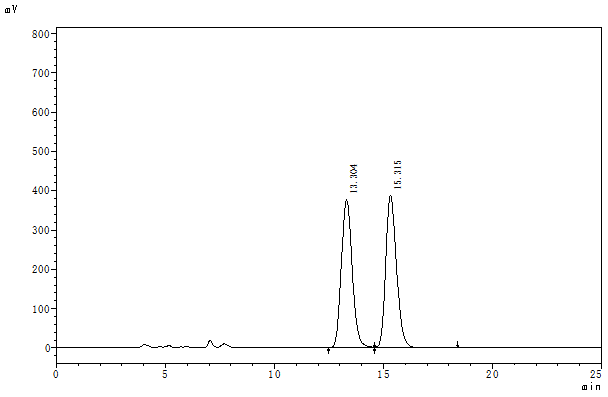


Figure 71. HPLC trace of racemic **3p**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.304 | 13199972 | 376529 | 49.618 |
| 2 | 15.315 | 13403126 | 388170 | 50.382 |
| Total |  | 26603098 | 764698 | 100.000 |

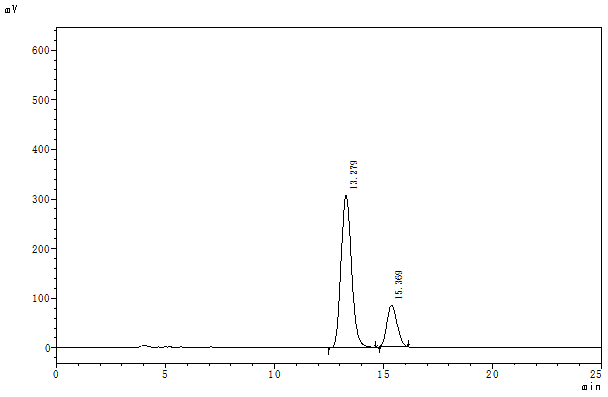


Figure 72. HPLC trace of enantiomeric **3p**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.279 | 10380576 | 307498 | 79.232 |
| 2 | 15.369 | 2720863 | 83717 | 20.768 |
| Total |  | 13101438 | 391215 | 100.000 |

**4**

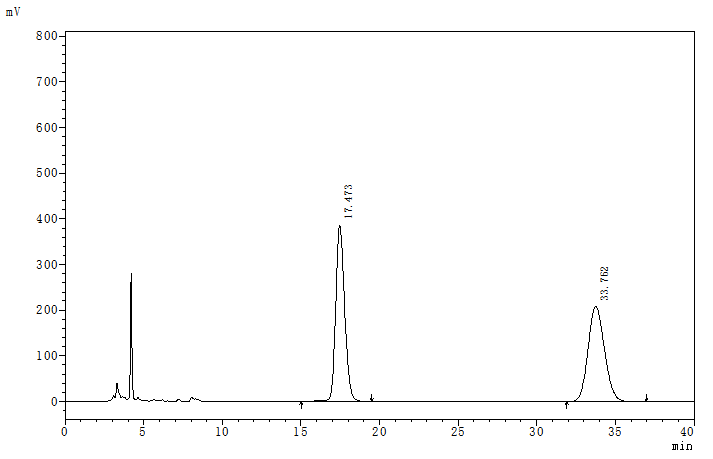


Figure 73. HPLC trace of racemic **4**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 17.473 | 15279611 | 385690 | 50.241 |
| 2 | 33.762 | 15132823 | 208071 | 49.759 |
| Total |  | 30412434 | 593760 | 100.000 |

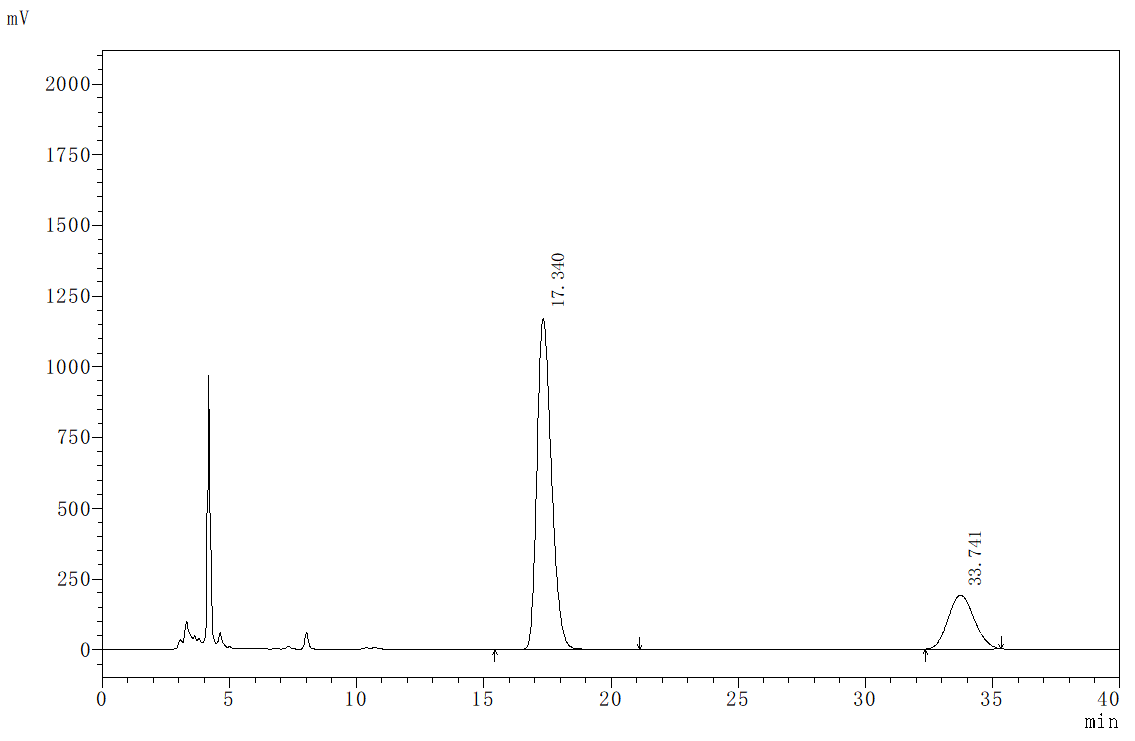


Figure 74. HPLC trace of enantiomeric **4**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 17.340 | 46201545 | 1172933 | 77.314 |
| 2 | 33.741 | 13557029 | 189801 | 22.686 |
| Total |  | 59758573 | 1362734 | 100.000 |

**5**

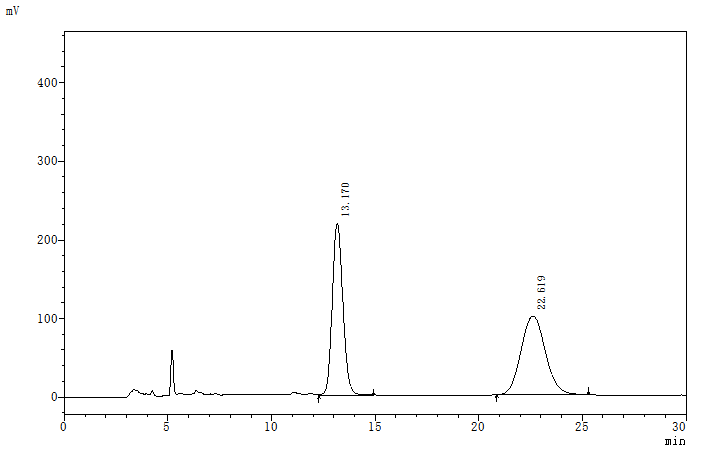


Figure 75. HPLC trace of racemic **5**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.170 | 7922922 | 219983 | 49.114 |
| 2 | 22.619 | 8208709 | 100075 | 50.886 |
| Total |  | 16131632 | 320057 | 100.000 |

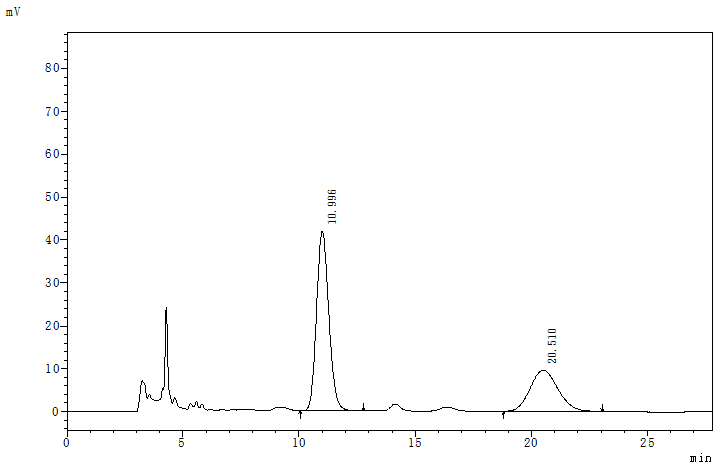


Figure 76. HPLC trace of enantiomeric **5**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 10.996 | 1552755 | 41942 | 65.969 |
| 2 | 20.510 | 801006 | 9619 | 34.031 |
| Total |  | 2353761 | 51561 | 100.000 |

**6**

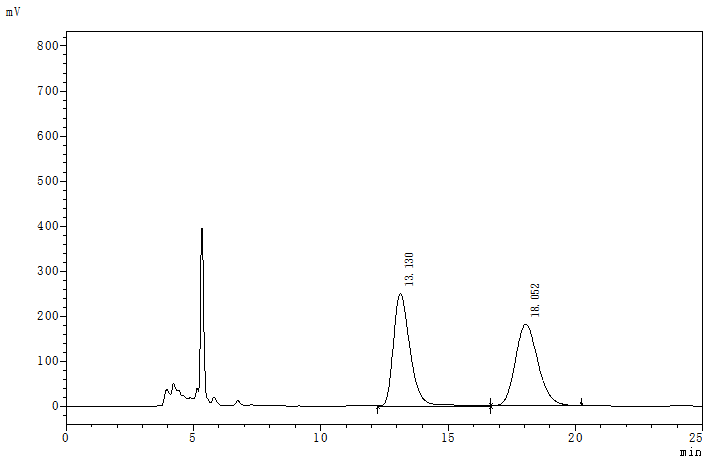


Figure 77. HPLC trace of racemic **6**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.130 | 11414299 | 250160 | 50.464 |
| 2 | 18.052 | 11204580 | 180938 | 49.536 |
| Total |  | 22618879 | 431098 | 100.000 |

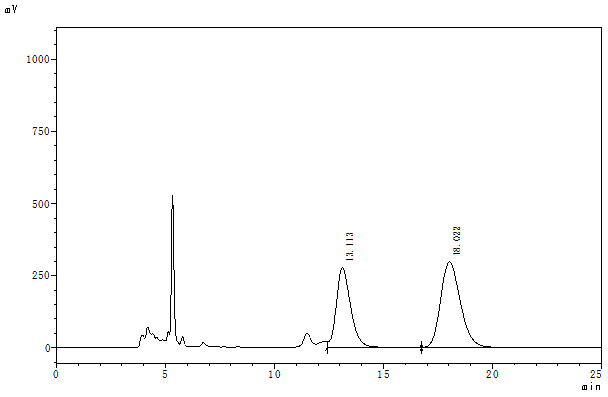


Figure 78. HPLC trace of enantiomeric **6**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 13.113 | 13004424 | 276790 | 40.385 |
| 2 | 18.022 | 19196691 | 297683 | 59.615 |
| Total |  | 32201115 | 574473 | 100.000 |

**7**

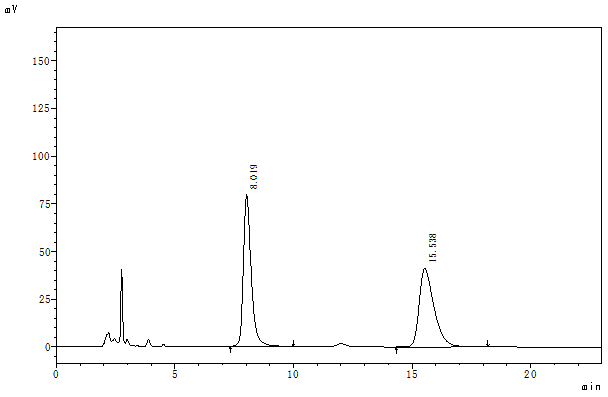


Figure 79. HPLC trace of racemic **7**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 8.019 | 1837960 | 79526 | 50.514 |
| 2 | 15.538 | 1800547 | 41357 | 49.486 |
| Total |  | 3638507 | 120883 | 100.000 |

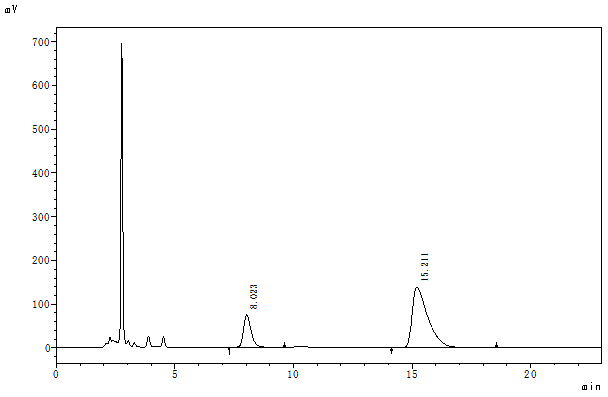


Figure 80. HPLC trace of enantiomeric **7**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Retention Time | Area | Height | Area% |
| 1 | 8.023 | 1821900 | 75834 | 22.022 |
| 2 | 15.211 | 6451092 | 138396 | 77.978 |
| Total |  | 8272992 | 214230 | 100.000 |

**X-Ray crystal data of compound 3f**



|  |  |
| --- | --- |
| **Table 1 Crystal data and structure refinement for 3f** | |
| Identification code | **3f** |
| Empirical formula | C25H16BrN3O4 |
| Formula weight | 502.32 |
| Temperature/K | 173.0 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.5405(6) |
| b/Å | 10.5930(6) |
| c/Å | 11.7435(7) |
| α/° | 74.825(3) |
| β/° | 81.589(3) |
| γ/° | 73.759(3) |
| Volume/Å3 | 1096.31(12) |
| Z | 2 |
| ρcalcg/cm3 | 1.522 |
| μ/mm‑1 | 2.881 |
| F(000) | 508.0 |
| Crystal size/mm3 | 0.301 × 0.287 × 0.285 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 7.824 to 127.626 |
| Index ranges | -11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13 |
| Reflections collected | 20277 |
| Independent reflections | 3600 [Rint = 0.0347, Rsigma = 0.0254] |
| Data/restraints/parameters | 3600/0/306 |
| Goodness-of-fit on F2 | 1.139 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0303, wR2 = 0.0735 |
| Final R indexes [all data] | R1 = 0.0352, wR2 = 0.0758 |
| Largest diff. peak/hole / e Å-3 | 0.39/-0.40 |