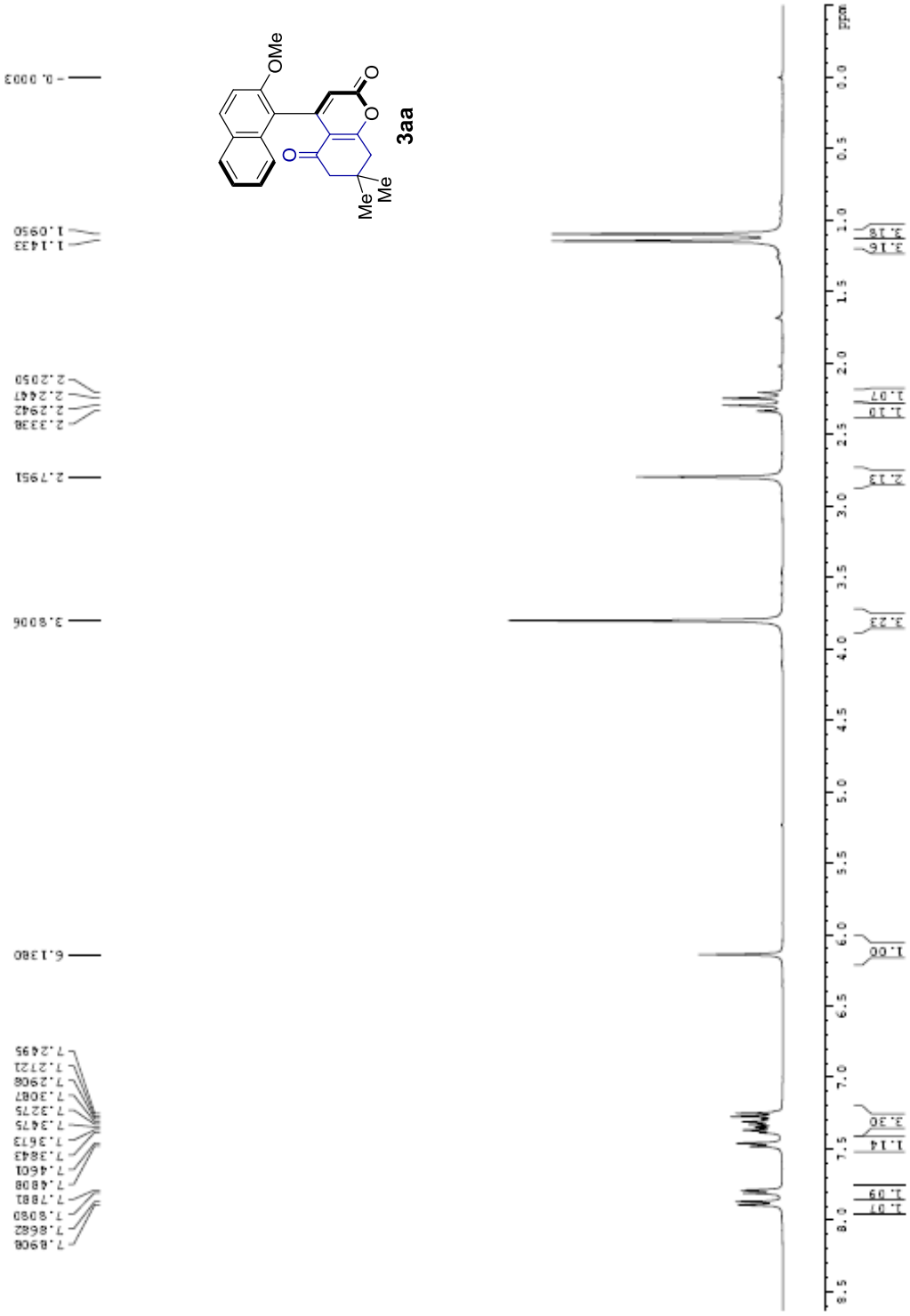
# Enantioselective [3+3] Atroposelective Annulation Catalyzed by N-heterocyclic Carbenes

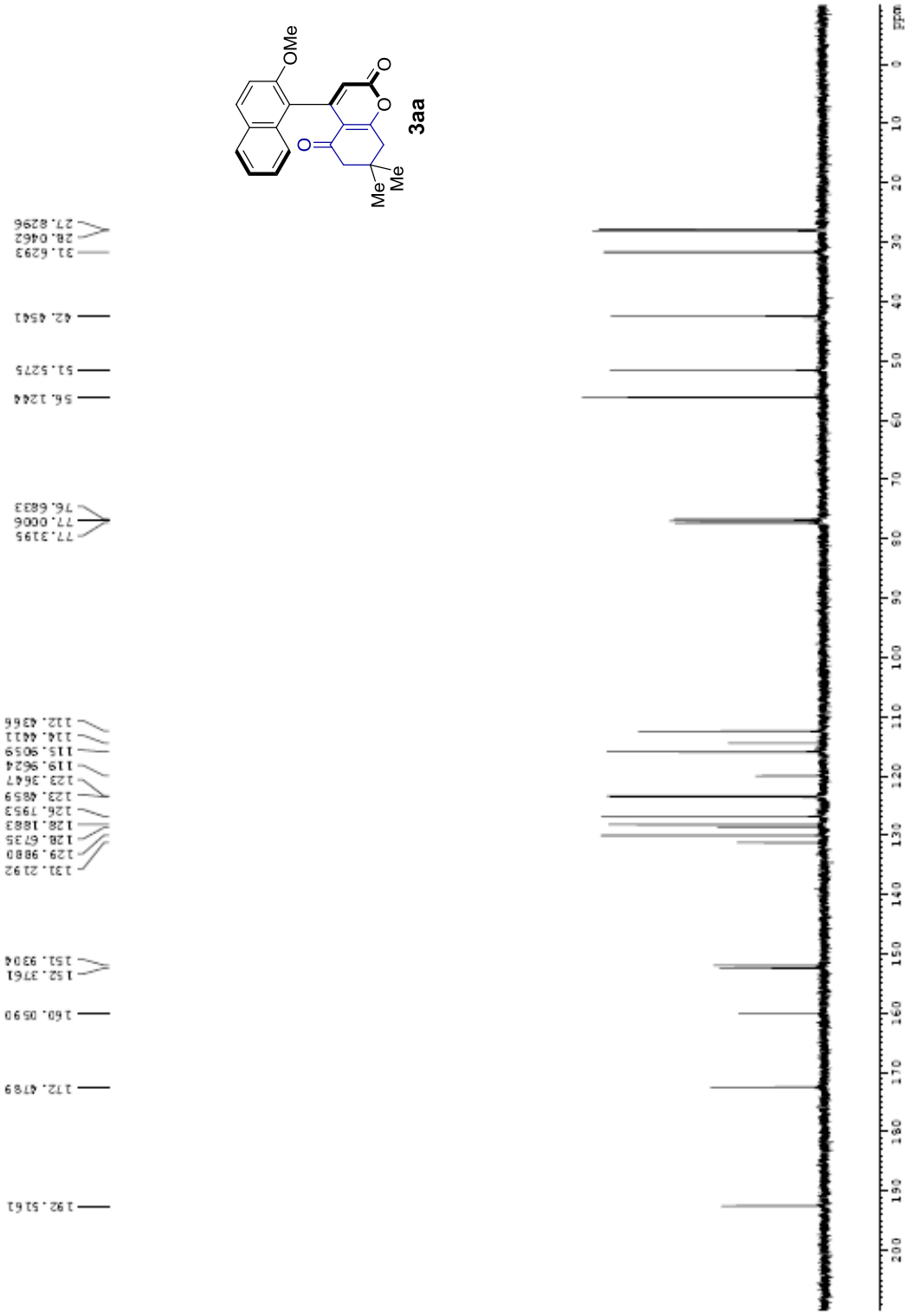
Zhao et al.

# Supplementary Figures

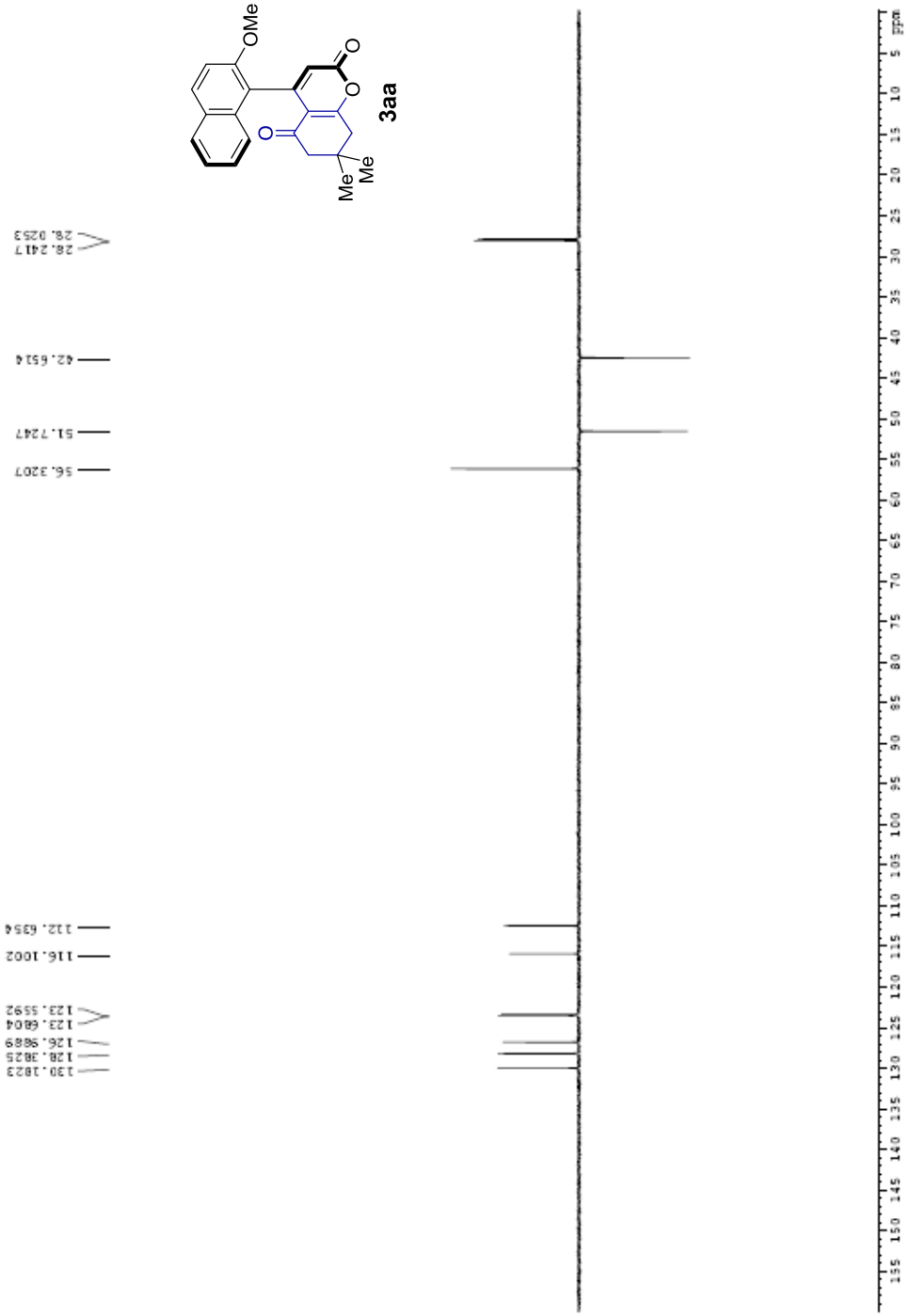
## Supplementary Figure 1. $^{1}$H NMR Spectrum of 3aa



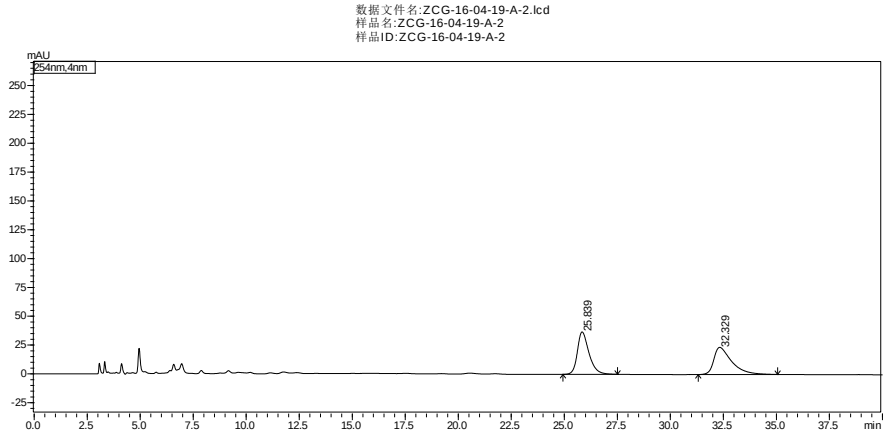
**Supplementary Figure 2. $^{13}$C NMR Spectrum of 3aa**



**Supplementary Figure 3. $^{13}$C NMR Spectrum of 3aa**

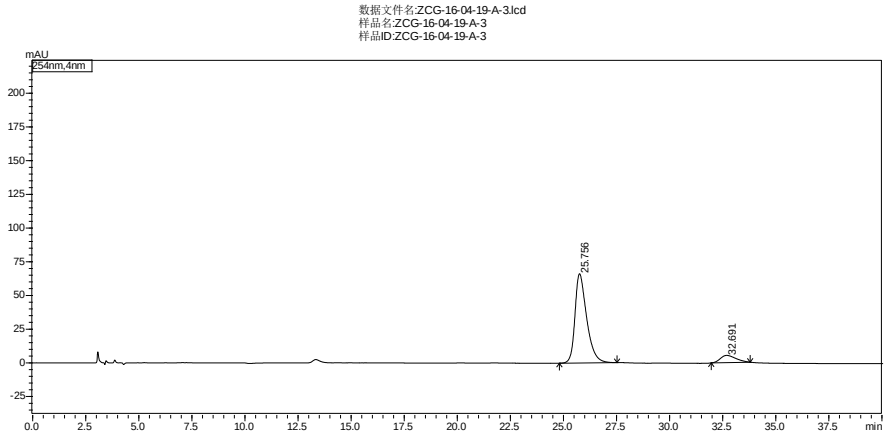


## Supplementary Figure 4. HPLC Spectrum of racemic 3aa



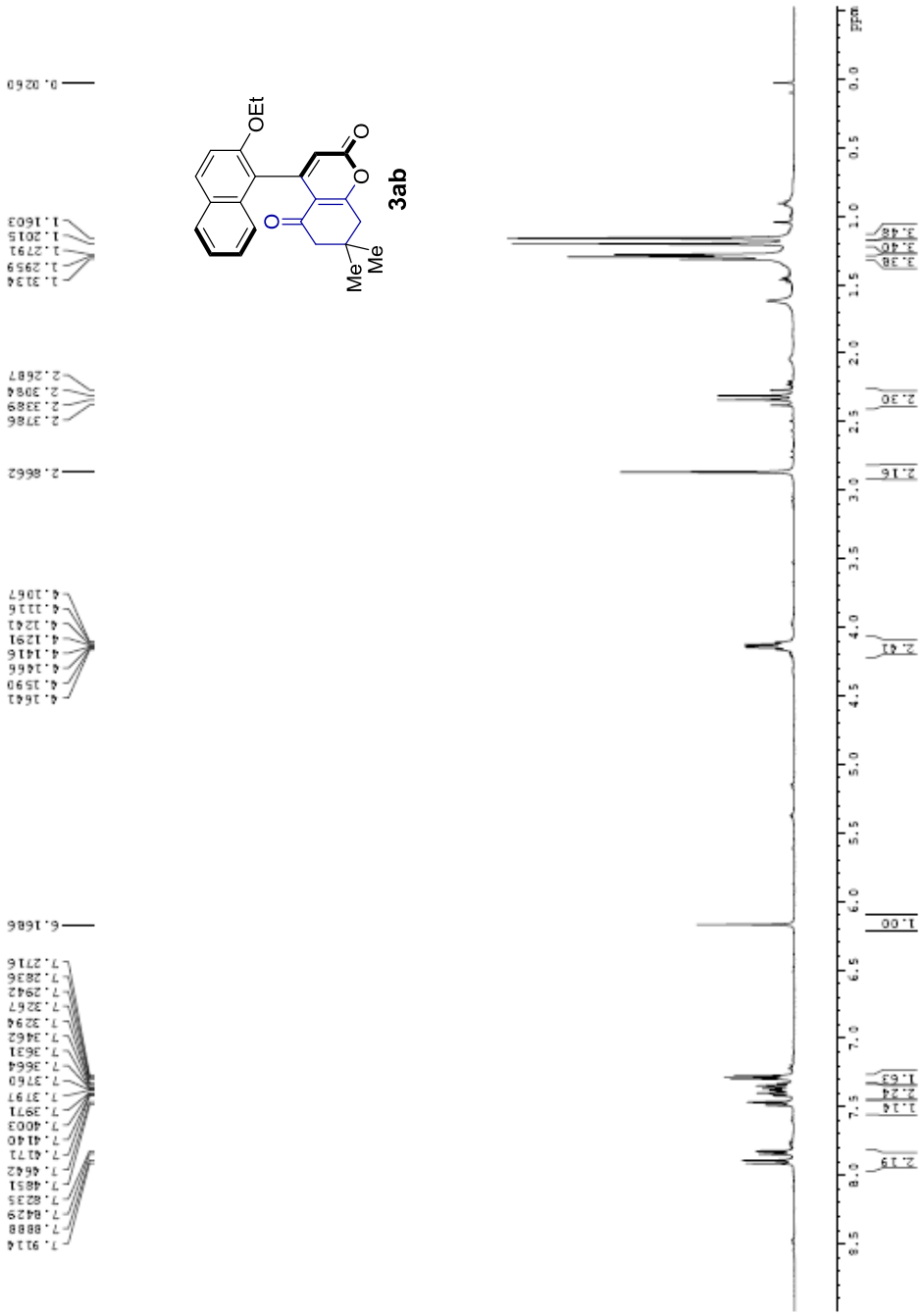

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 25.839 | 1400665 | 36773 | 50.361 | 60.927 |
| 2 | 32.329 | 1380602 | 23583 | 49.639 | 39.073 |
| Total | | 2781267 | 60356 | 100.000 | 100.000 |

## Supplementary Figure 5. HPLC Spectrum of 3aa

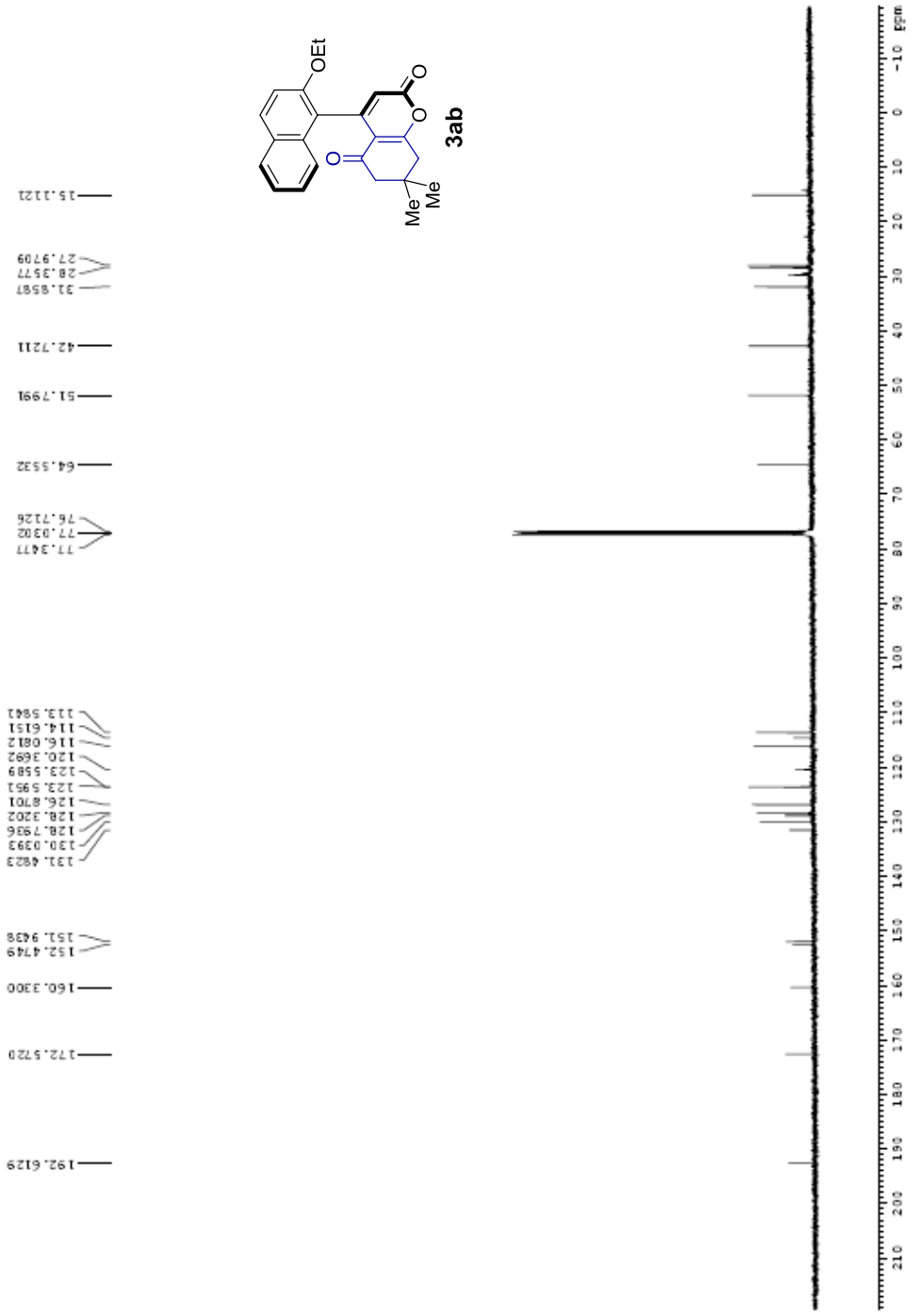



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 25.756 | 2538794 | 66218 | 90.251 | 92.489 |
| 2 | 32.691 | 274241 | 5378 | 9.749 | 7.511 |
| Total | | 2813035 | 71596 | 100.000 | 100.000 |

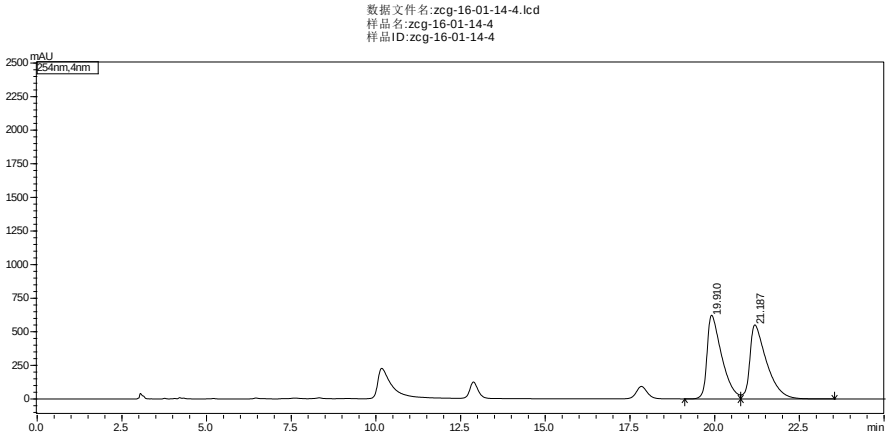
**Supplementary Figure 6. $^{1}$H NMR Spectrum of 3ab**



**Supplementary Figure 7. $^{13}$C NMR Spectrum of 3ab**

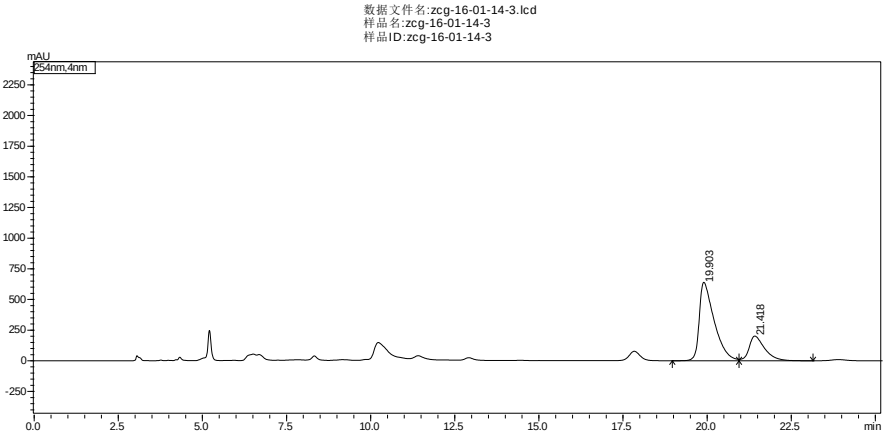


## Supplementary Figure 8. HPLC Spectrum of racemic 3ab



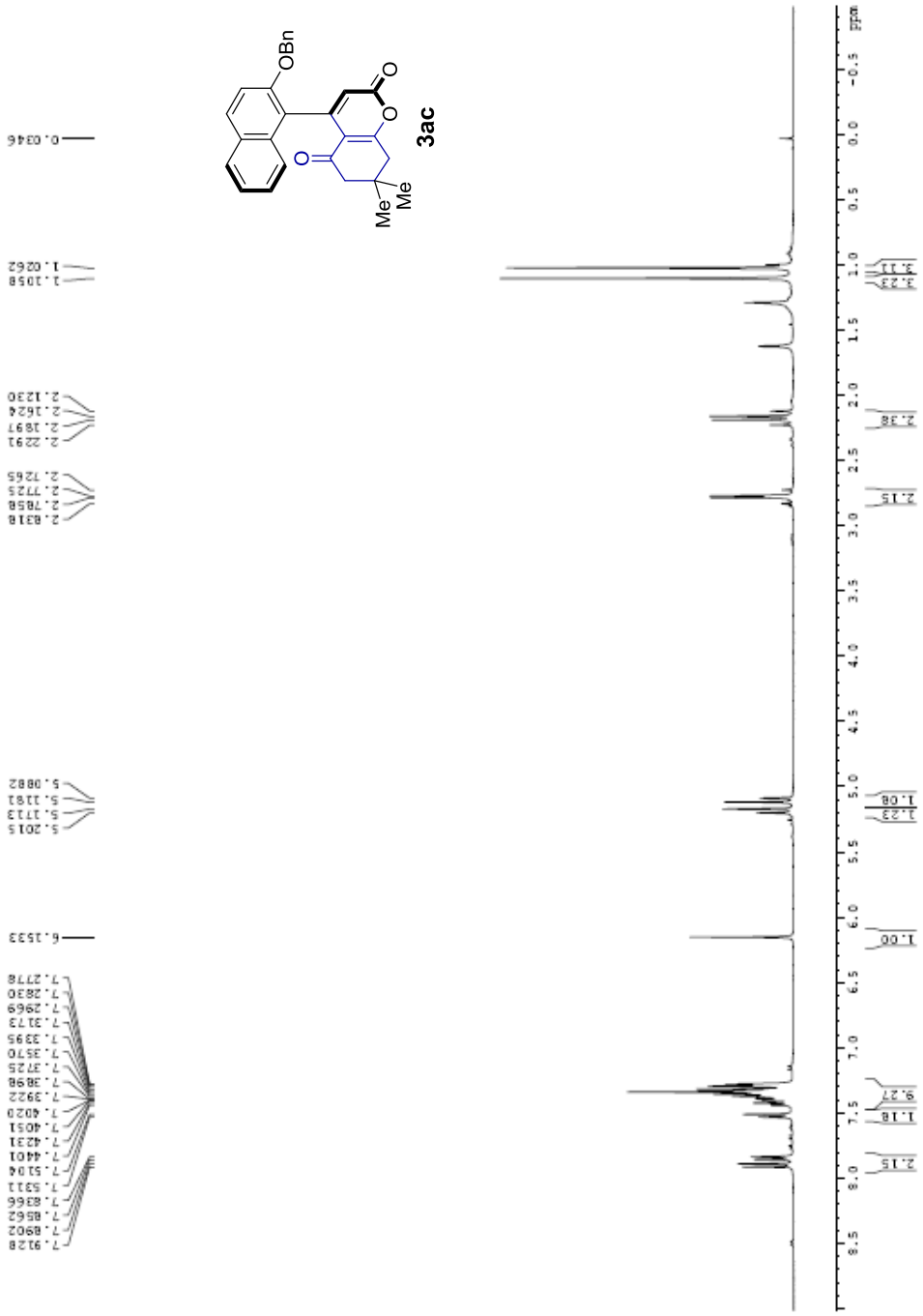

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 19.910 | 18726073 | 622115 | 49.638 | 53.056 |
| 2 | 21.187 | 18999274 | 550444 | 50.362 | 46.944 |
| Total | | 37725347 | 1172559 | 100.000 | 100.000 |

## Supplementary Figure 9. HPLC Spectrum of 3ab

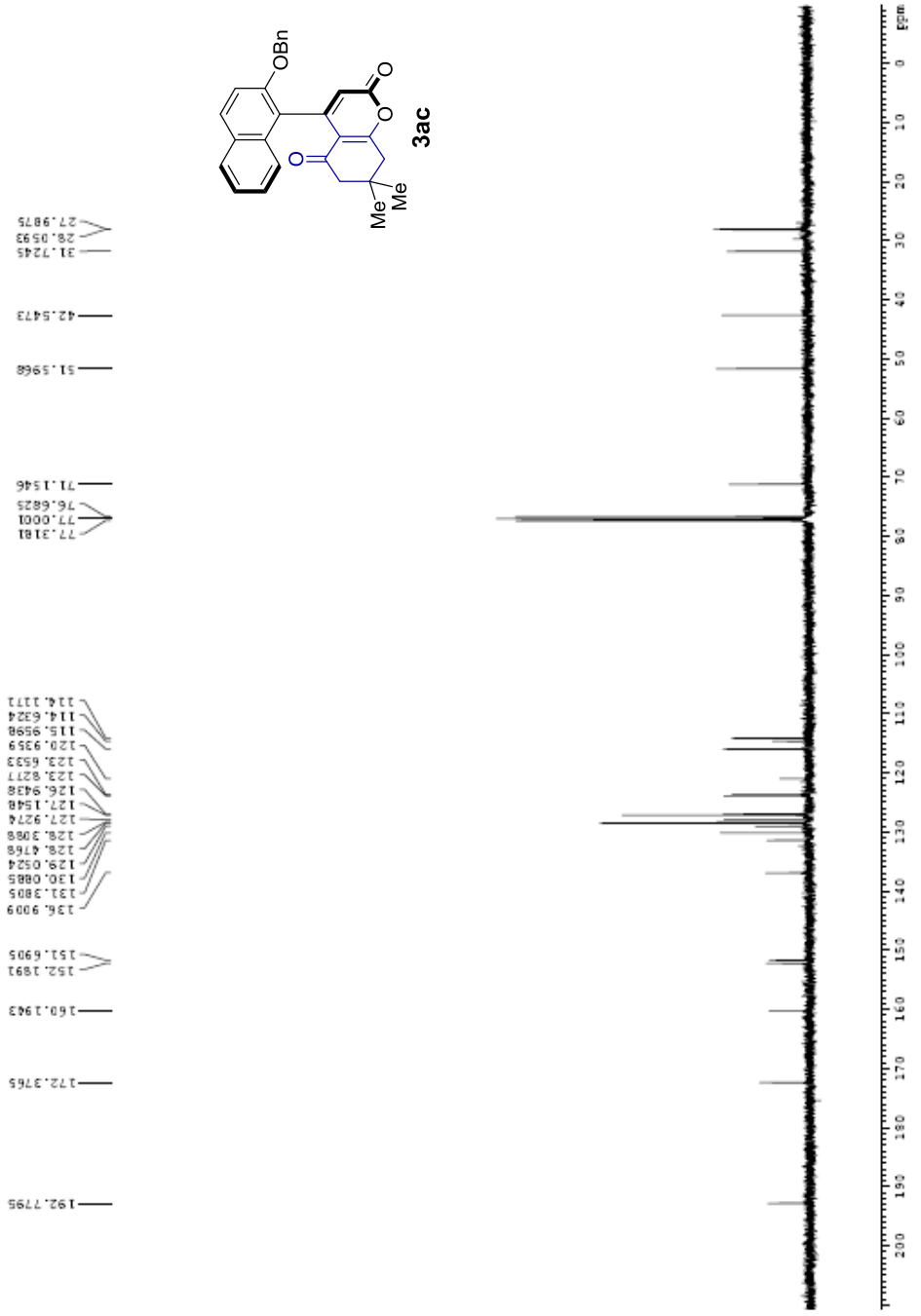



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 19.903 | 19775527 | 639391 | 75.218 | 76.039 |
| 2 | 21.418 | 6515522 | 201484 | 24.782 | 23.961 |
| Total | | 26291049 | 840875 | 100.000 | 100.000 |

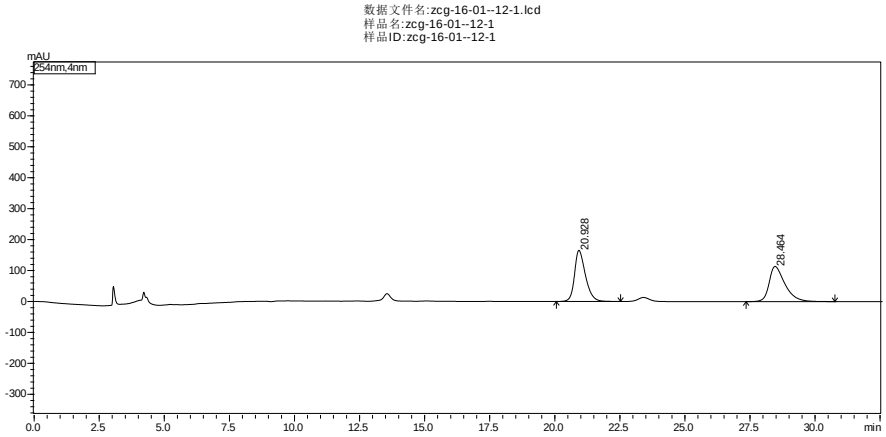
**Supplementary Figure 10. $^{1}$H NMR Spectrum of 3ac**



**Supplementary Figure 11. $^{13}$C NMR Spectrum of 3ac**

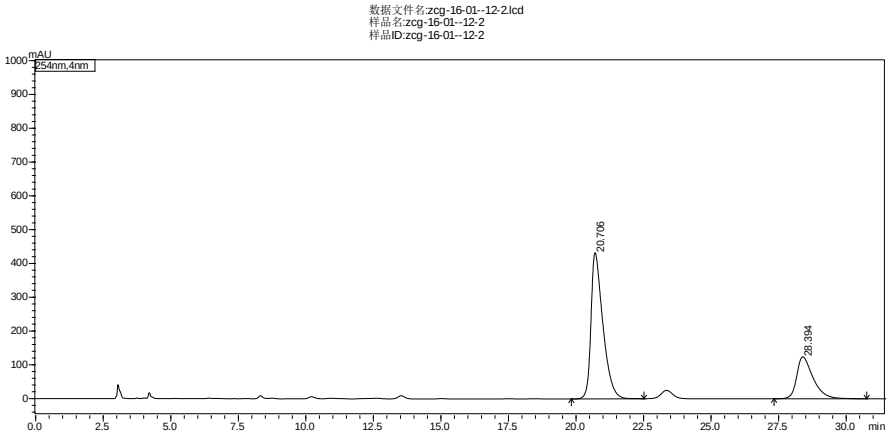


## Supplementary Figure 12. HPLC Spectrum of racemic 3ac



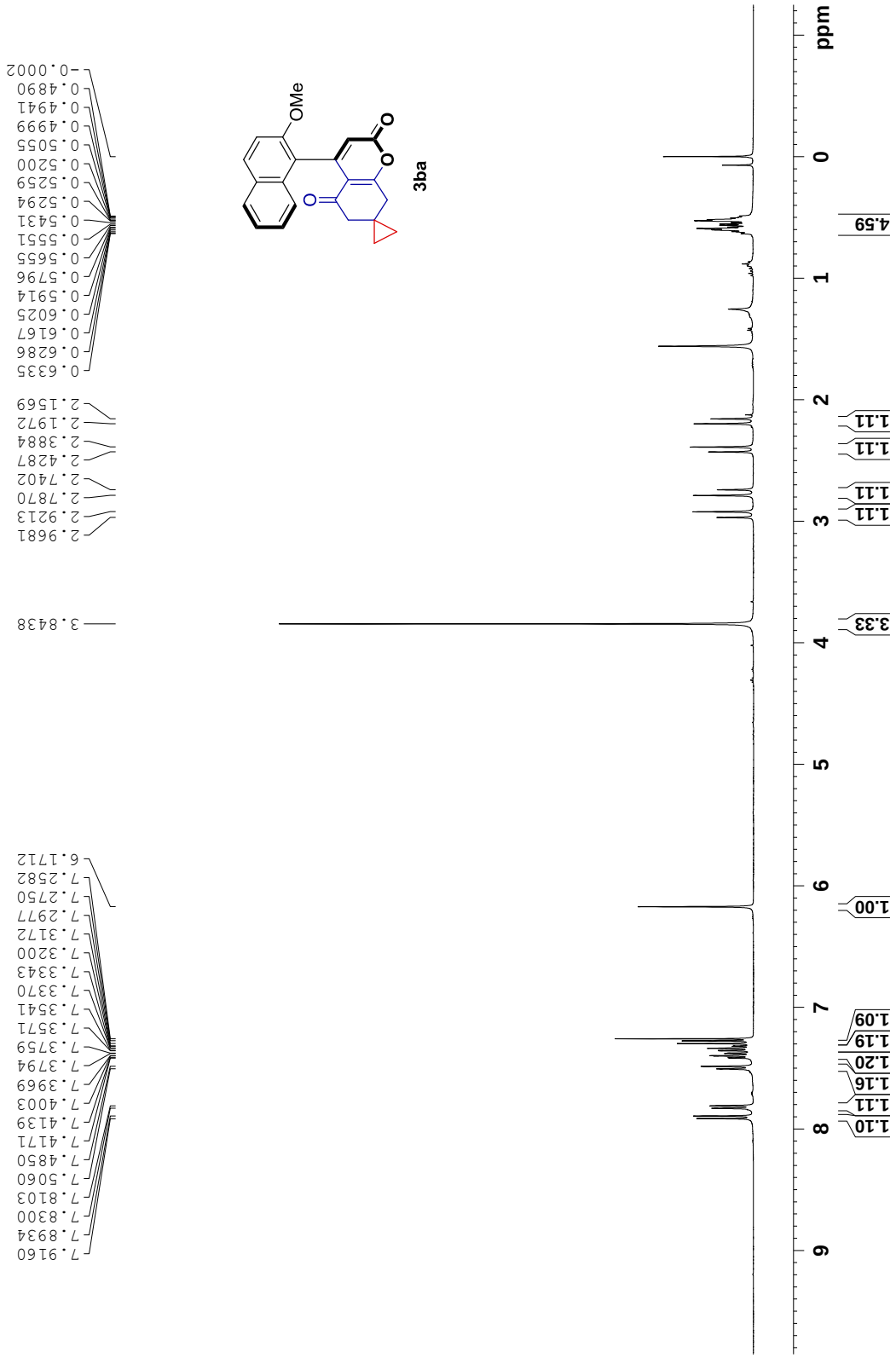

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 20.928 | 4829699 | 165349 | 50.083 | 59.224 |
| 2 | 28.464 | 4813697 | 113844 | 49.917 | 40.776 |
| Total | | 9643396 | 279193 | 100.000 | 100.000 |

## Supplementary Figure 13. HPLC Spectrum of 3ac

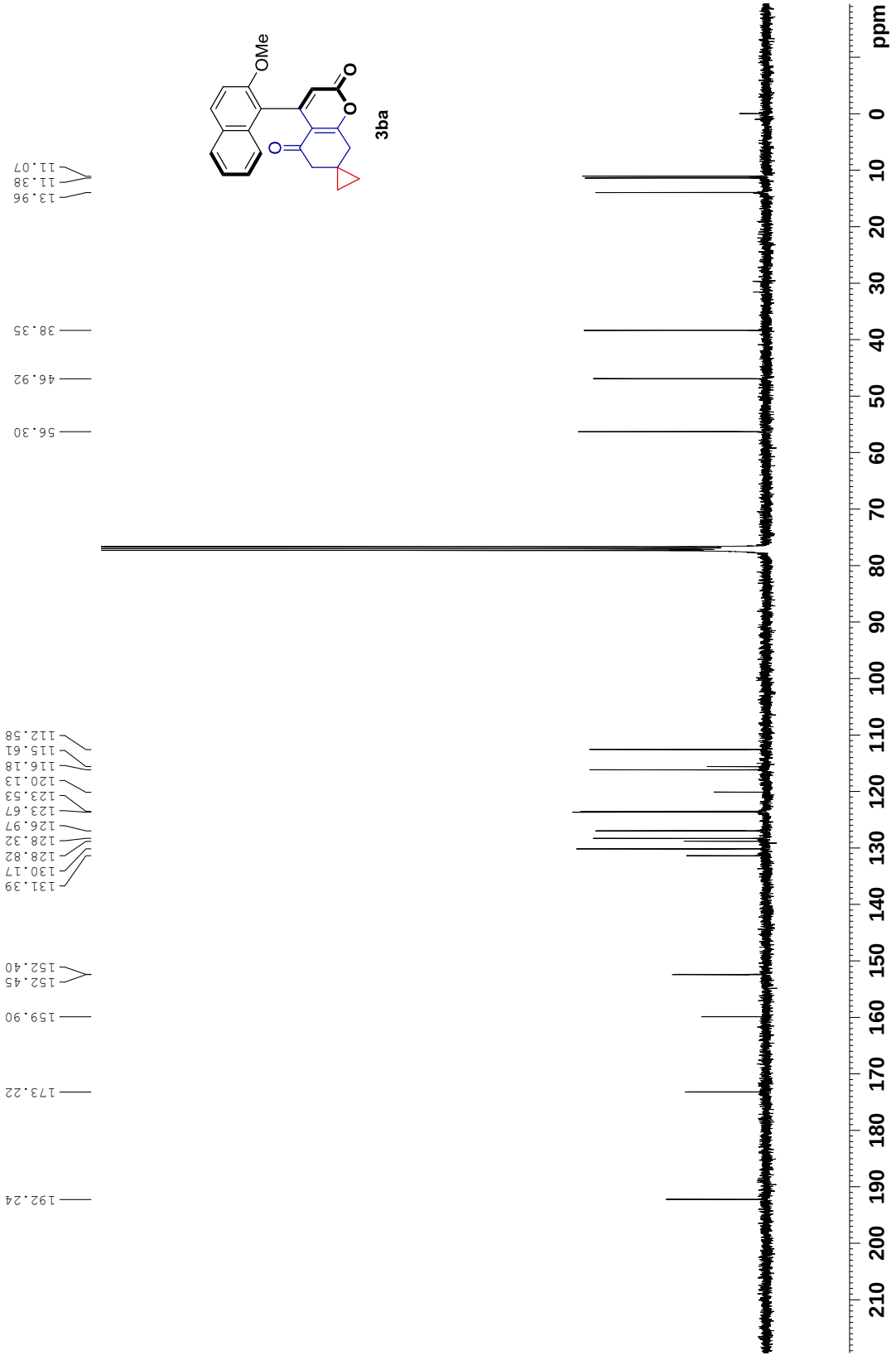



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 20.706 | 13282557 | 432700 | 71.569 | 77.683 |
| 2 | 28.394 | 5276502 | 124307 | 28.431 | 22.317 |
| Total | | 18559059 | 557007 | 100.000 | 100.000 |

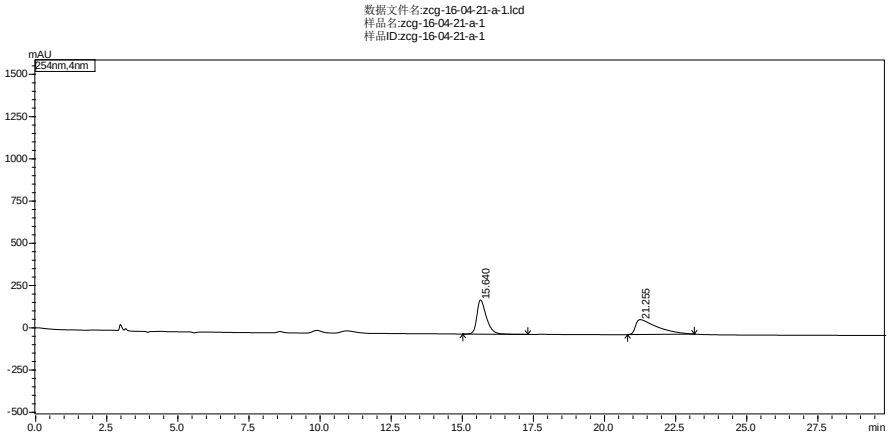
**Supplementary Figure 14. $^{1}$H NMR Spectrum of 3ba**



**Supplementary Figure 15. $^{13}$C NMR Spectrum of 3ba**

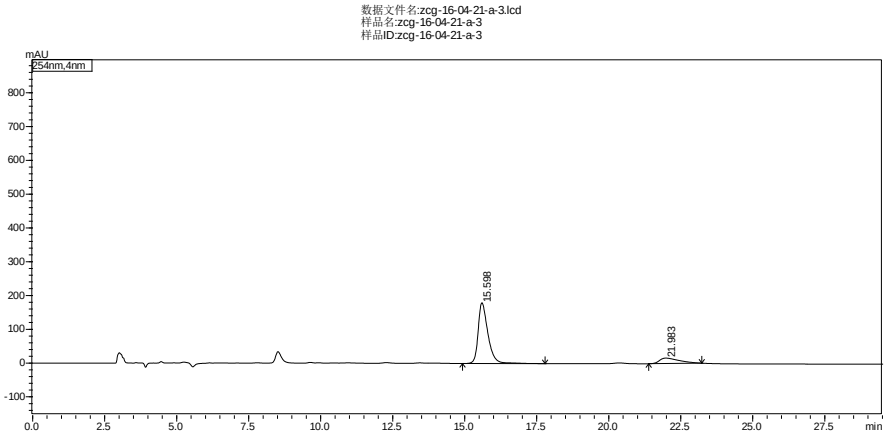


## Supplementary Figure 16. HPLC Spectrum of racemic 3ba



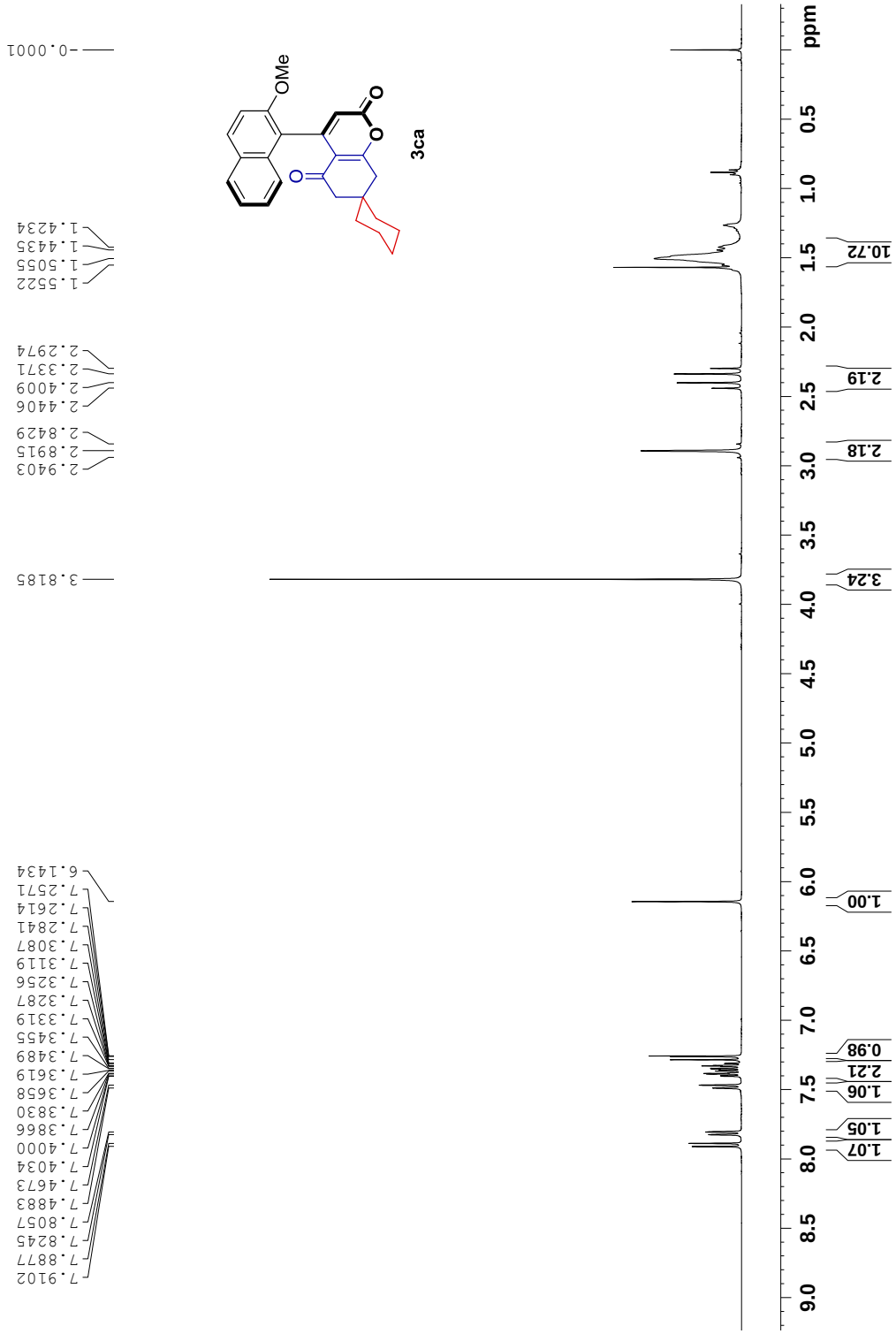

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 15.640 | 4700329 | 202588 | 50.087 | 69.689 |
| 2 | 21.255 | 4684062 | 88115 | 49.913 | 30.311 |
| Total | | 9384391 | 290703 | 100.000 | 100.000 |

## Supplementary Figure 17. HPLC Spectrum of 3ba

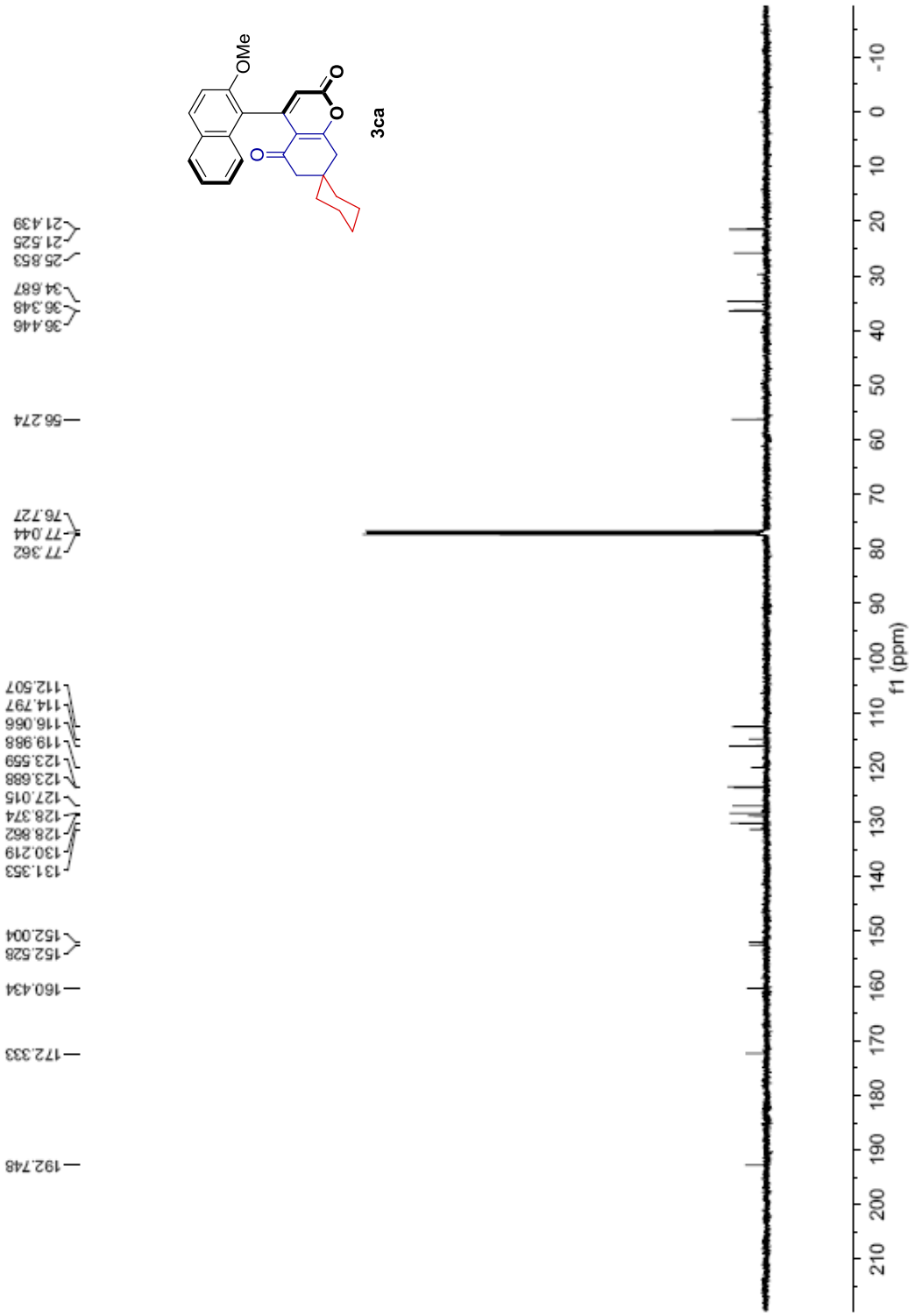



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 15.598 | 4248253 | 179868 | 84.786 | 91.778 |
| 2 | 21.983 | 762314 | 16114 | 15.214 | 8.222 |
| Total | | 5010567 | 195981 | 100.000 | 100.000 |

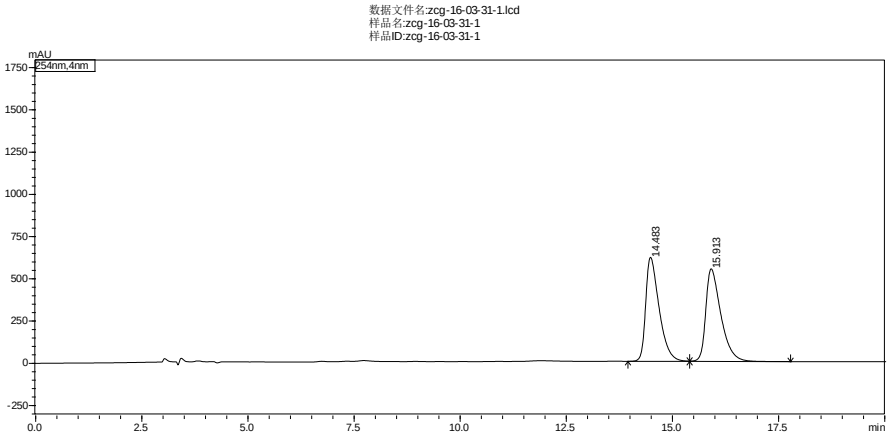
**Supplementary Figure 18. $^{1}$H NMR Spectrum of 3ca**



**Supplementary Figure 19. $^{13}$C NMR Spectrum of 3ca**

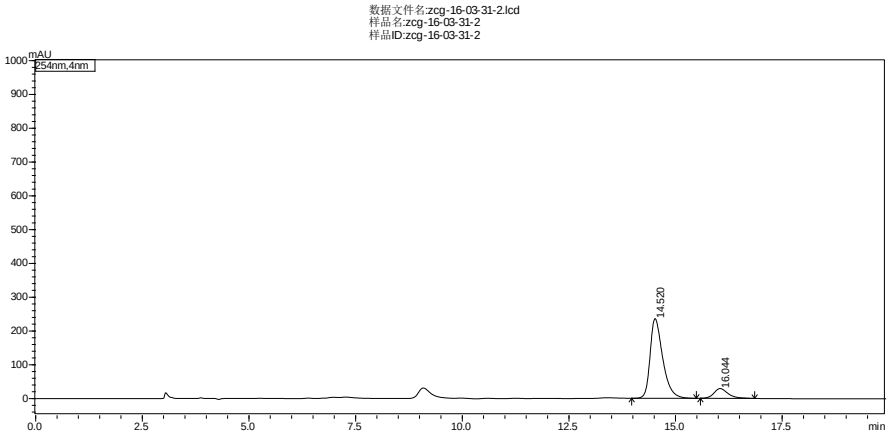


**Supplementary Figure 20. HPLC Spectrum of racemic 3ca**



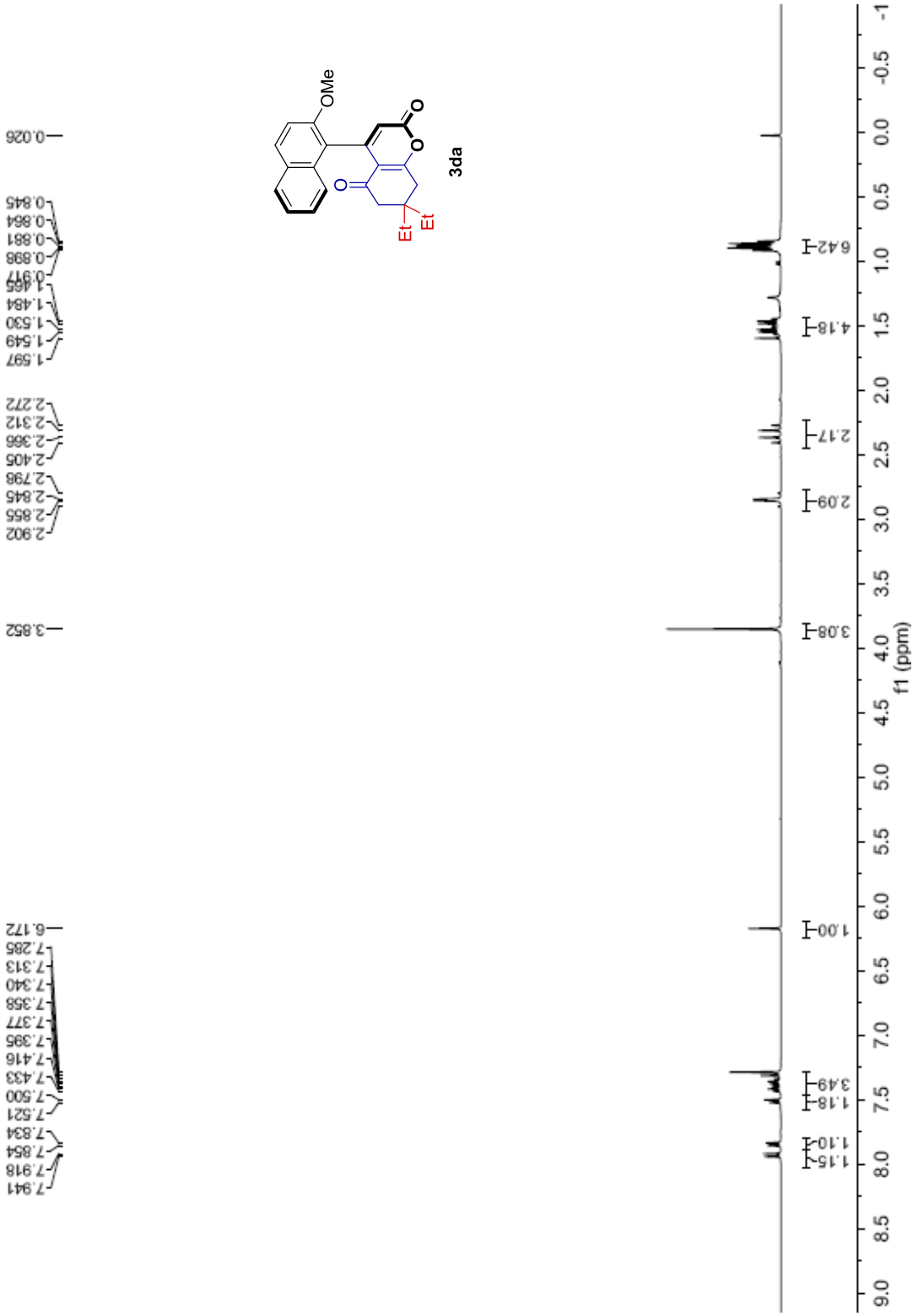

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 14.483 | 13549587 | 615635 | 49.891 | 52.885 |
| 2 | 15.913 | 13608595 | 548458 | 50.109 | 47.115 |
| Total | | 27158182 | 1164093 | 100.000 | 100.000 |

## Supplementary Figure 21. HPLC Spectrum of 3ca

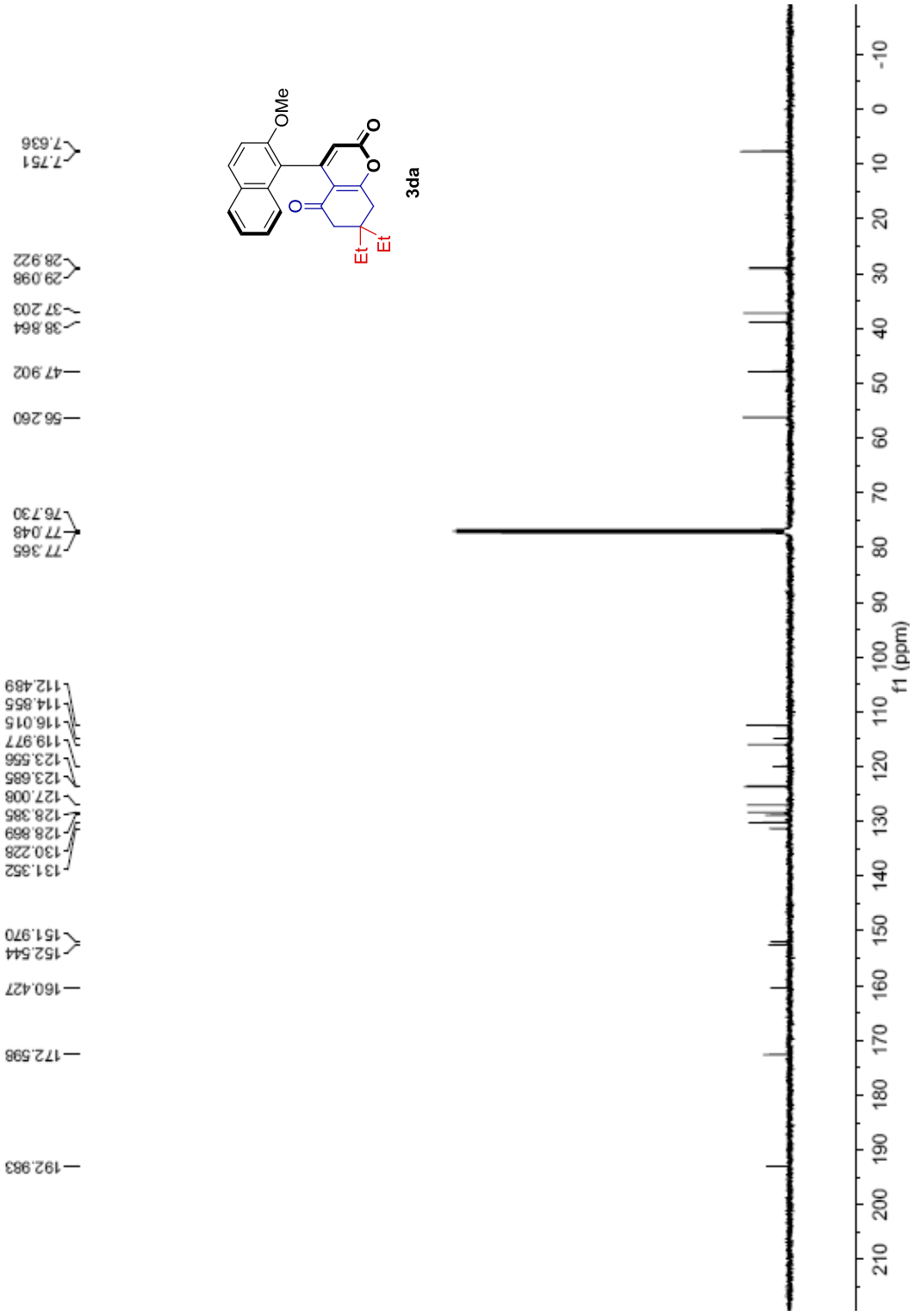



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 14.520 | 4850380 | 235835 | 87.890 | 89.067 |
| 2 | 16.044 | 668331 | 28948 | 12.110 | 10.933 |
| Total | | 5518711 | 264783 | 100.000 | 100.000 |

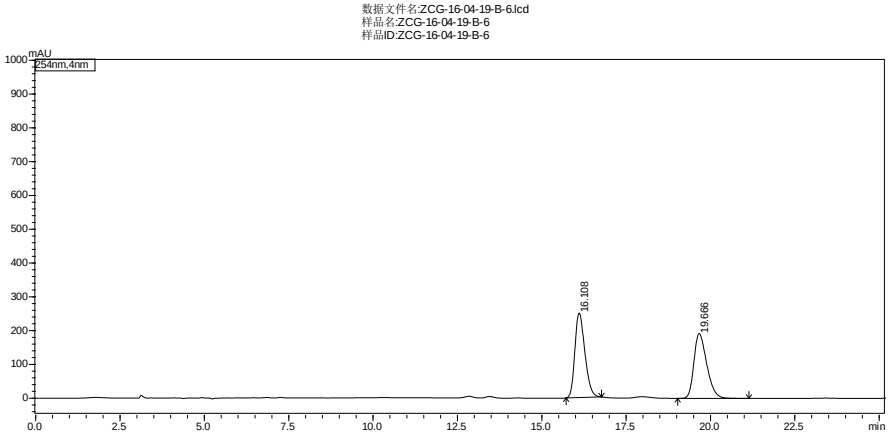
**Supplementary Figure 22. $^{1}$H NMR Spectrum of 3da**



**Supplementary Figure 23. $^{13}$C NMR Spectrum of 3da**

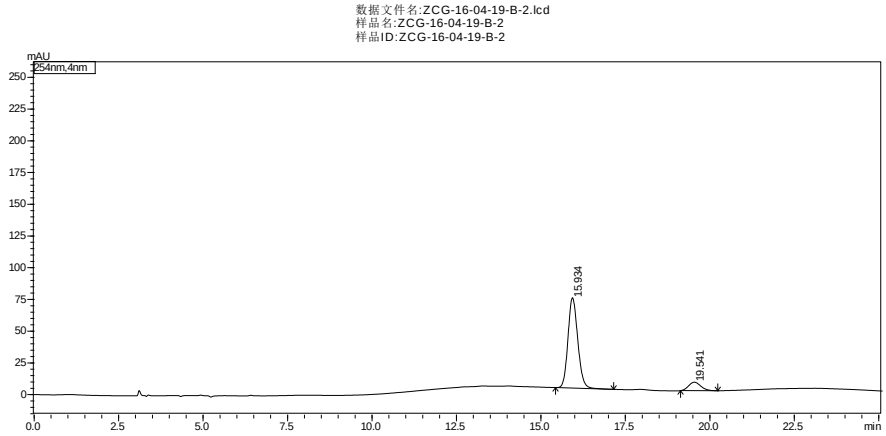


**Supplementary Figure 24. HPLC Spectrum of racemic 3da**



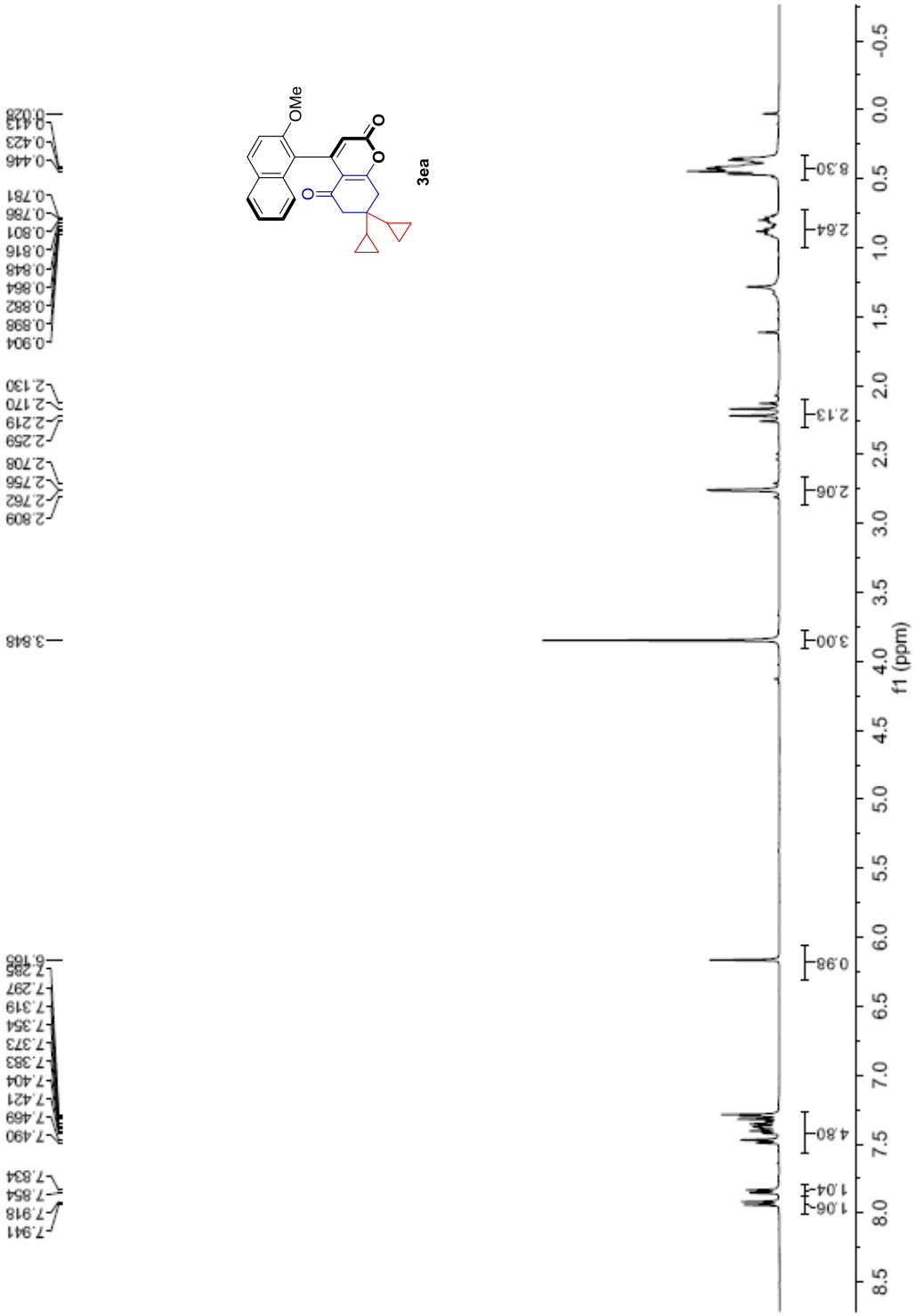

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 16.108 | 5162585 | 250179 | 50.401 | 56.606 |
| 2 | 19.666 | 5080481 | 191788 | 49.599 | 43.394 |
| Total | | 10243066 | 441968 | 100.000 | 100.000 |

## Supplementary Figure 25. HPLC Spectrum of 3da

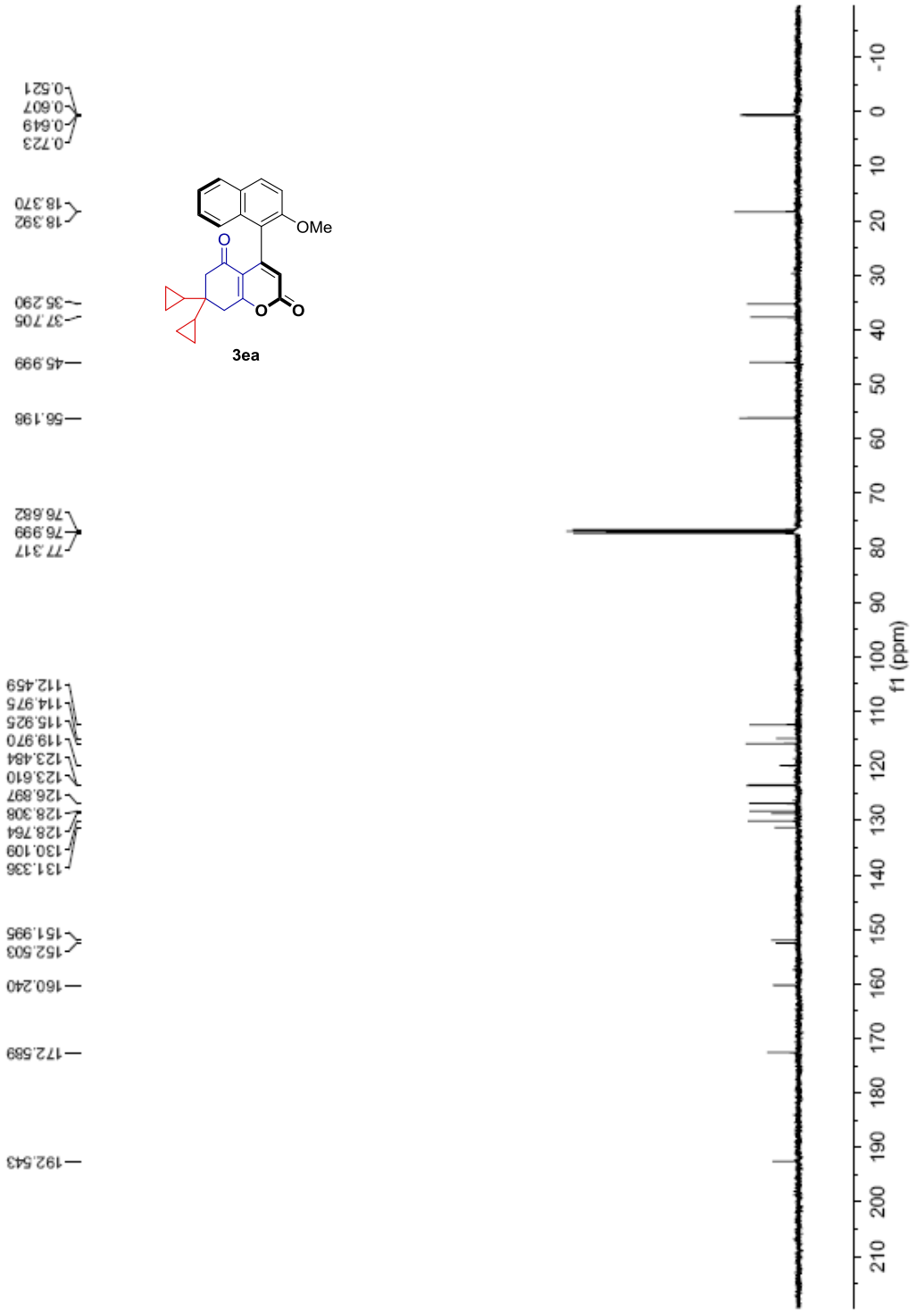



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 15.934 | 1438230 | 71230 | 89.734 | 91.454 |
| 2 | 19.541 | 164532 | 6656 | 10.266 | 8.546 |
| Total | | 1602762 | 77887 | 100.000 | 100.000 |

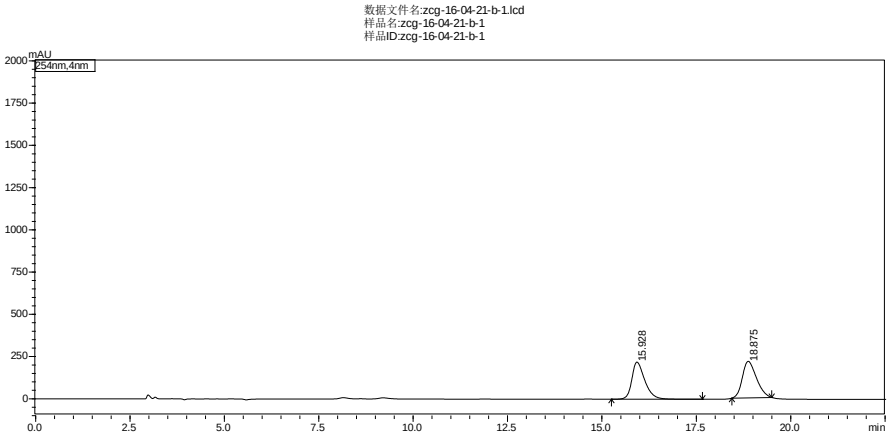
**Supplementary Figure 26. $^{1}$H NMR Spectrum of 3ea**



**Supplementary Figure 27. $^{13}$C NMR Spectrum of 3ea**

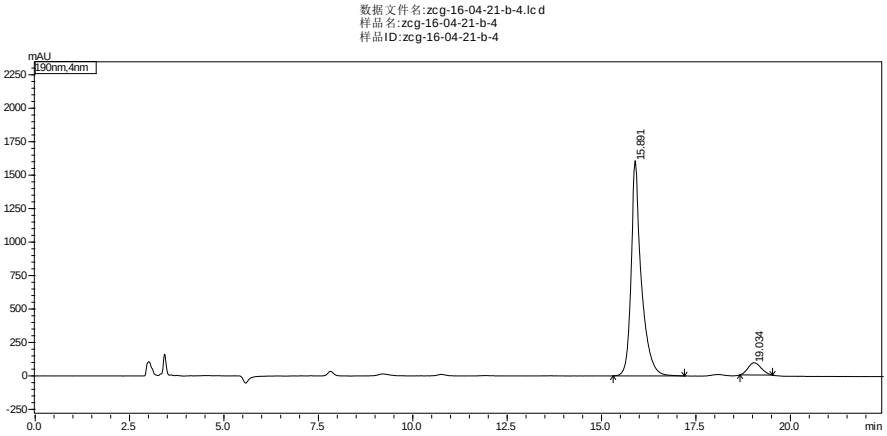


**Supplementary Figure 28. HPLC Spectrum of racemic 3ea**



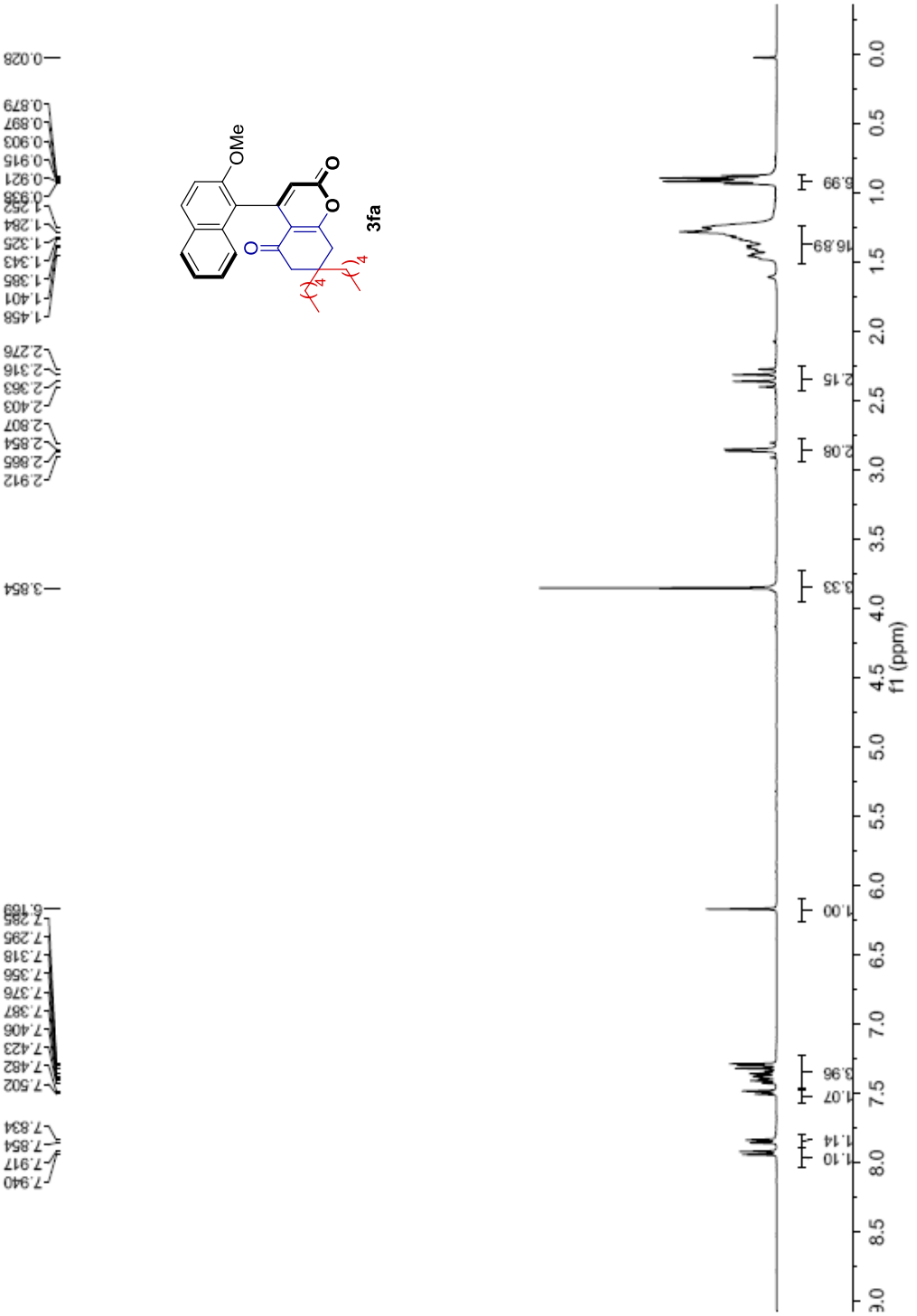

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 15.928 | 5282308 | 219899 | 48.496 | 50.406 |
| 2 | 18.875 | 5609880 | 216358 | 51.504 | 49.594 |
| Total | | 10892188 | 436258 | 100.000 | 100.000 |

## Supplementary Figure 29. HPLC Spectrum of 3ea

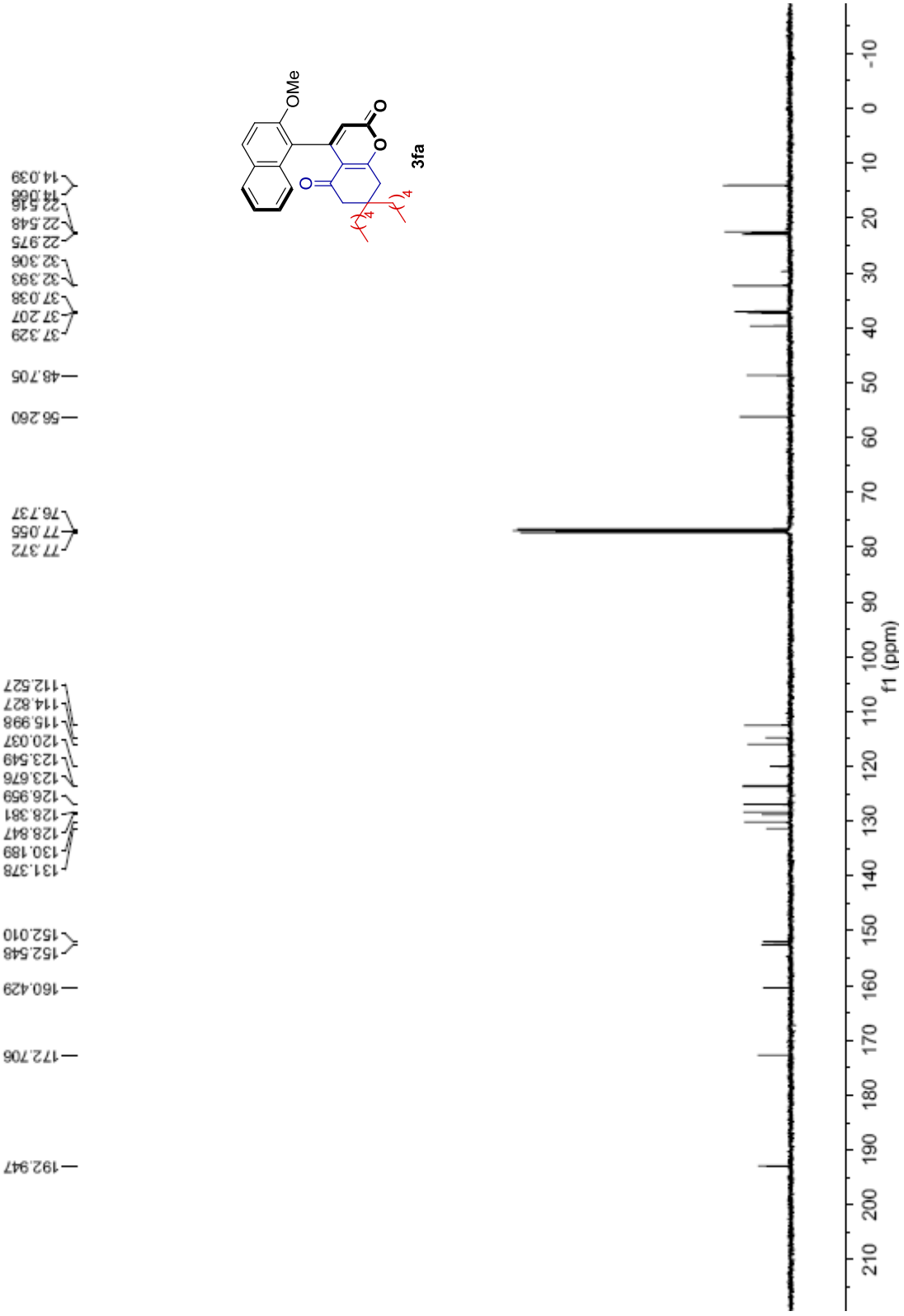



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 15.891 | 29942799 | 1607886 | 93.062 | 94.601 |
| 2 | 19.034 | 2232152 | 91764 | 6.938 | 5.399 |
| Total | | 32174951 | 1699649 | 100.000 | 100.000 |

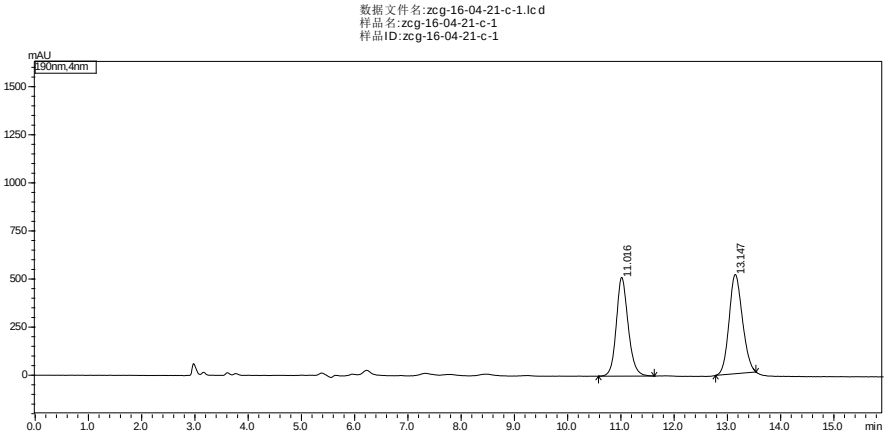
**Supplementary Figure 30. $^{1}$H NMR Spectrum of 3fa**



**Supplementary Figure 31. $^{13}$C NMR Spectrum of 3fa**

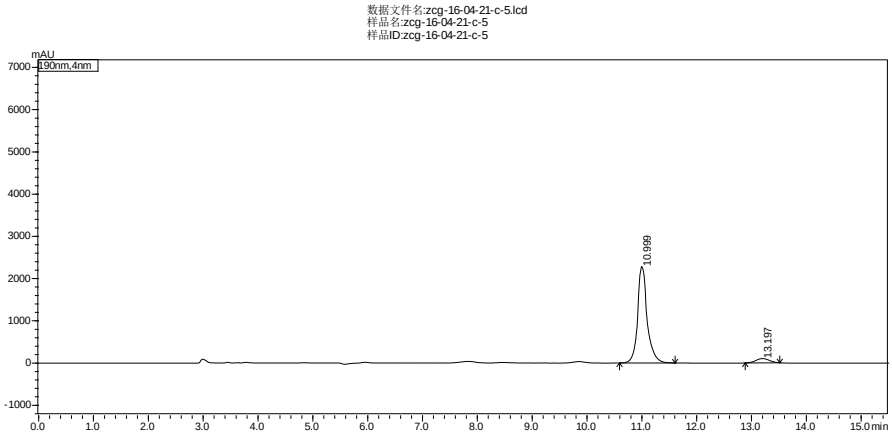


**Supplementary Figure 32. HPLC Spectrum of racemic 3fa**



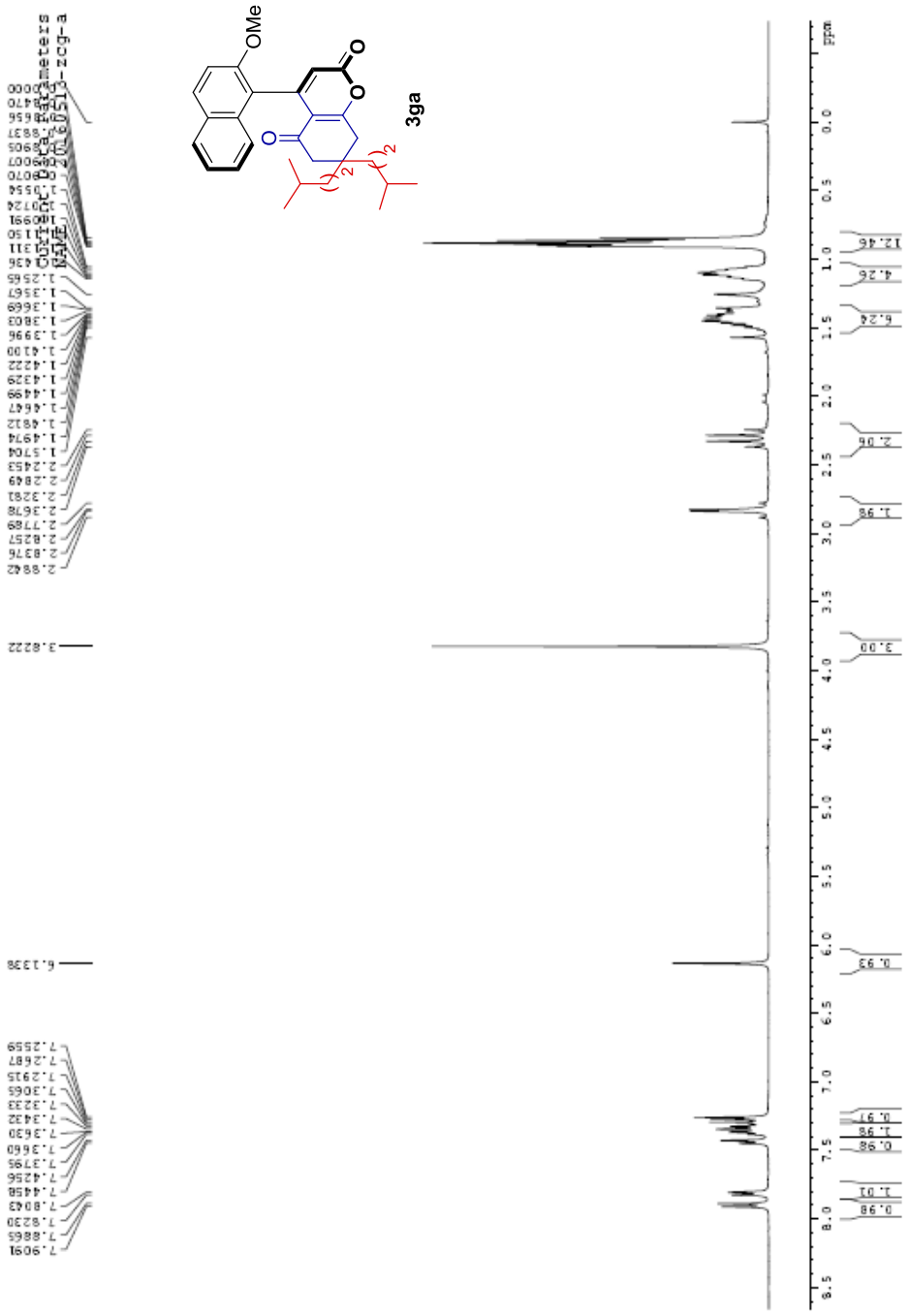

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 11.017 | 2524199 | 159427 | 47.733 | 50.165 |
| 2 | 13.149 | 2763949 | 158377 | 52.267 | 49.835 |
| Total | | 5288147 | 317803 | 100.000 | 100.000 |

## Supplementary Figure 33. HPLC Spectrum of 3fa

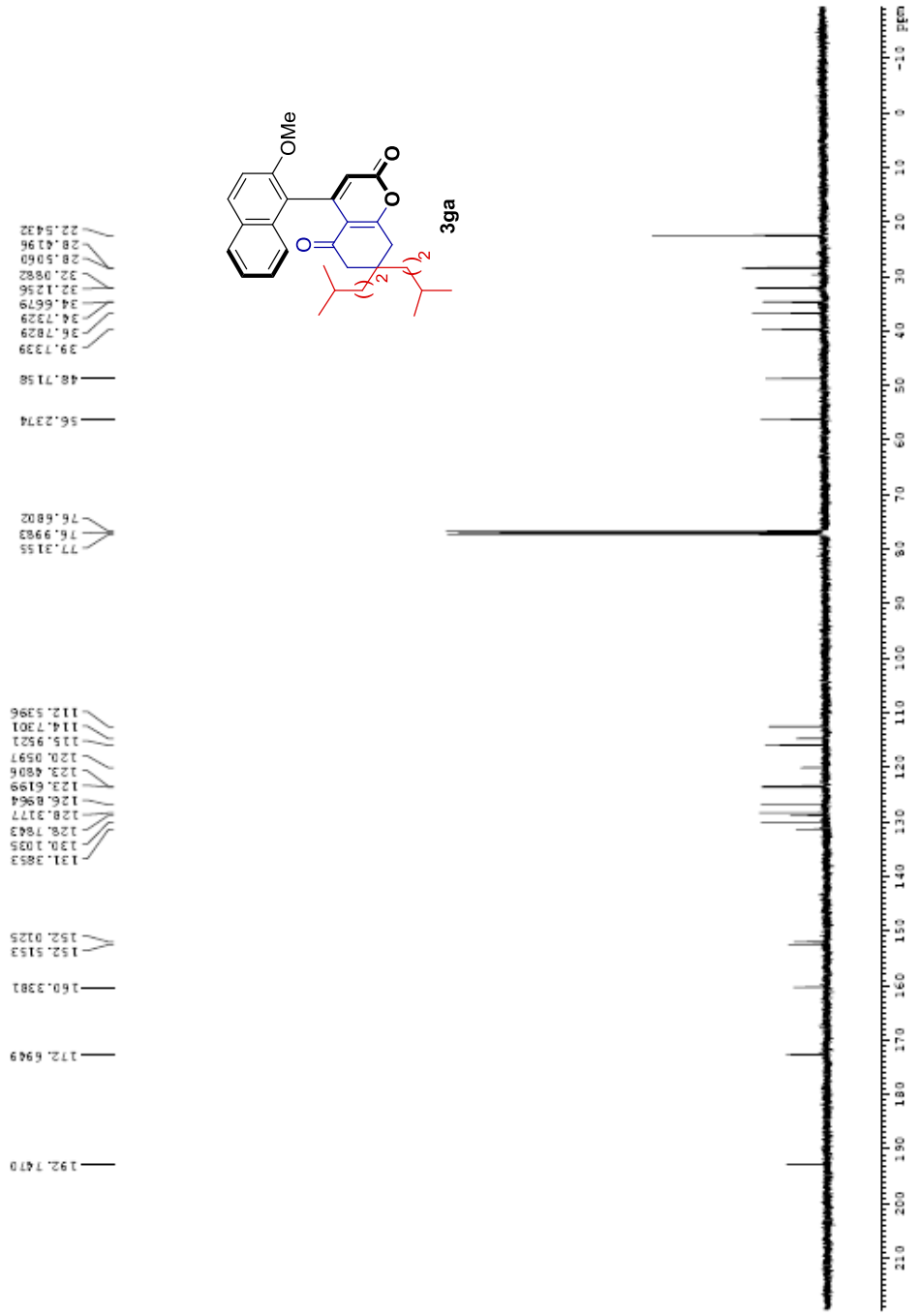



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 10.999 | 27720307 | 2286103 | 94.079 | 95.728 |
| 2 | 13.197 | 1744652 | 102032 | 5.921 | 4.272 |
| Total | | 29464960 | 2388135 | 100.000 | 100.000 |

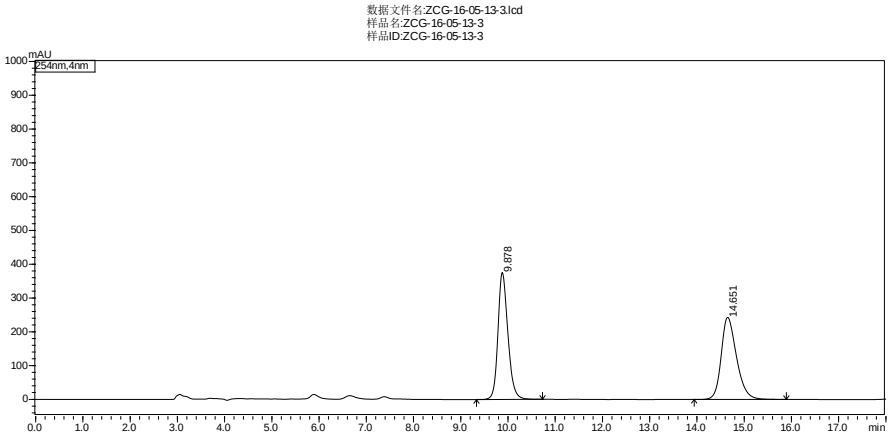
**Supplementary Figure 34. $^{1}$H NMR Spectrum of 3ga**



**Supplementary Figure 35. $^{13}$C NMR Spectrum of 3ga**

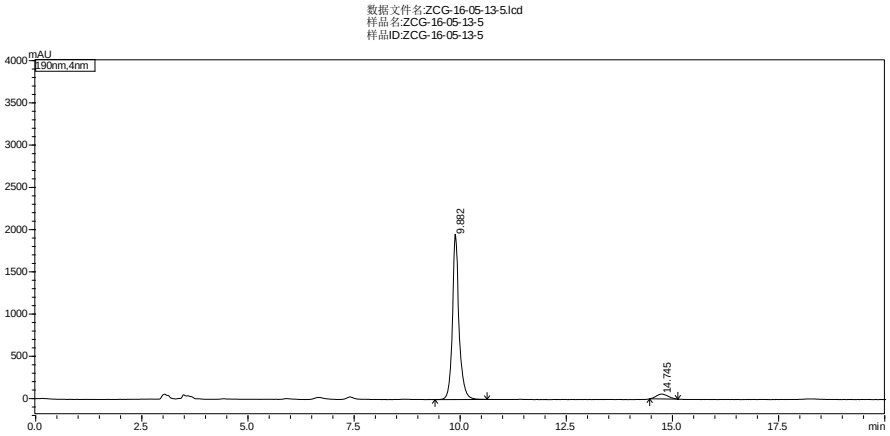


## Supplementary Figure 36. HPLC Spectrum of racemic 3ga



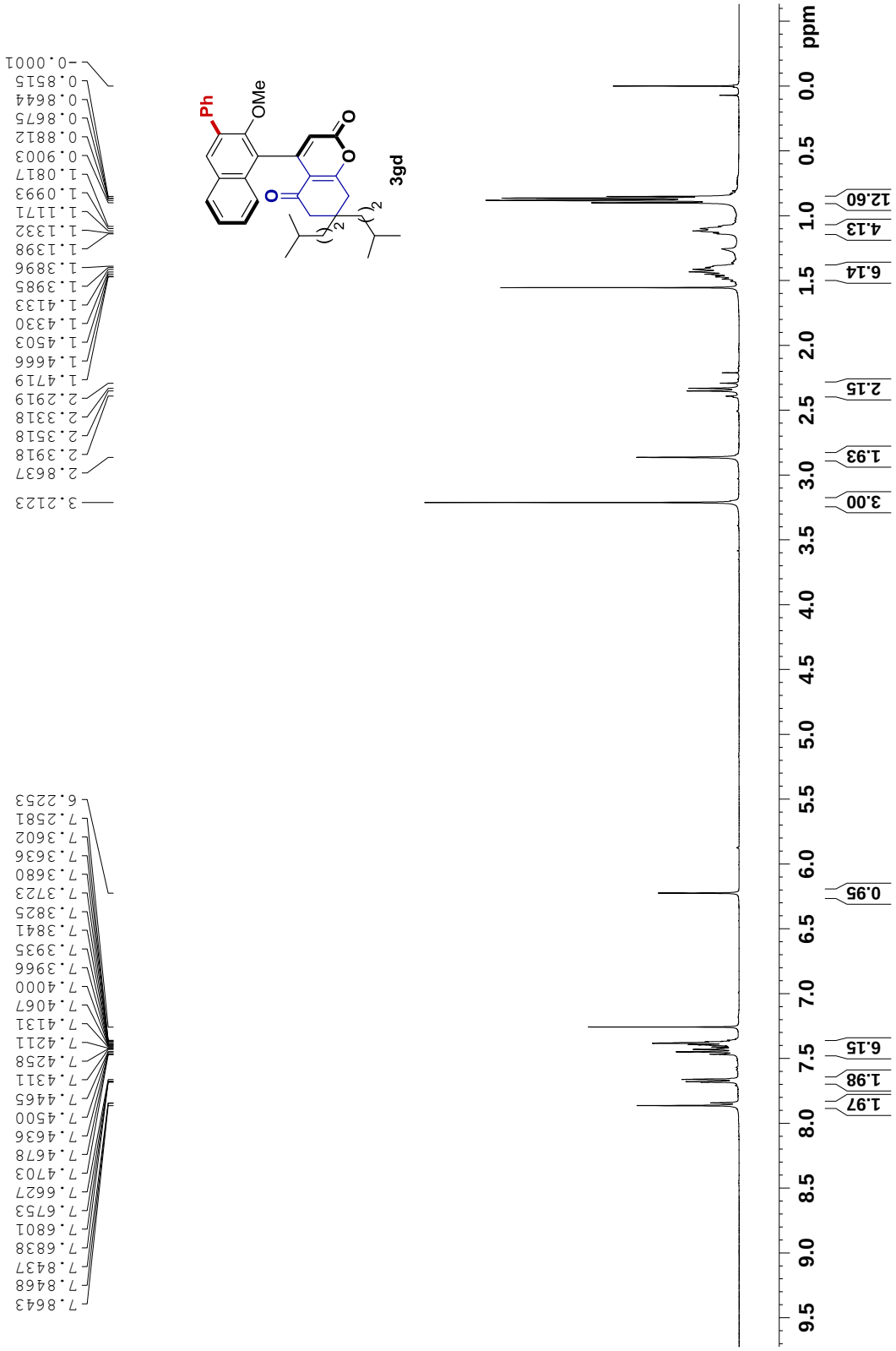

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 9.878 | 5504169 | 375739 | 50.168 | 60.712 |
| 2 | 14.651 | 5467217 | 243148 | 49.832 | 39.288 |
| Total | | 10971386 | 618887 | 100.000 | 100.000 |

## Supplementary Figure 37. HPLC Spectrum of 3ga

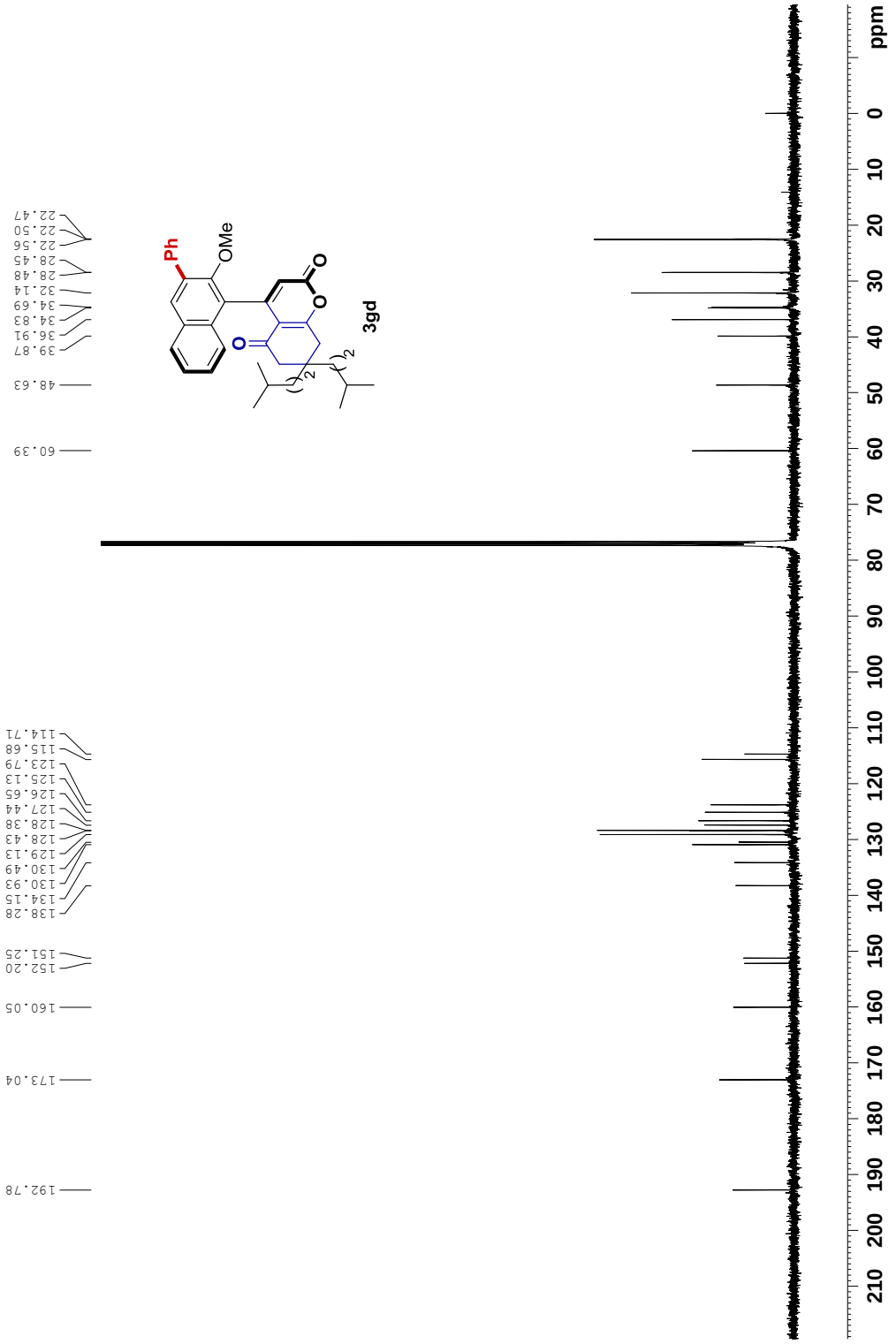



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 9.882 | 21124512 | 1957896 | 95.042 | 97.144 |
| 2 | 14.745 | 1102025 | 57569 | 4.958 | 2.856 |
| Total | | 22226537 | 2015465 | 100.000 | 100.000 |

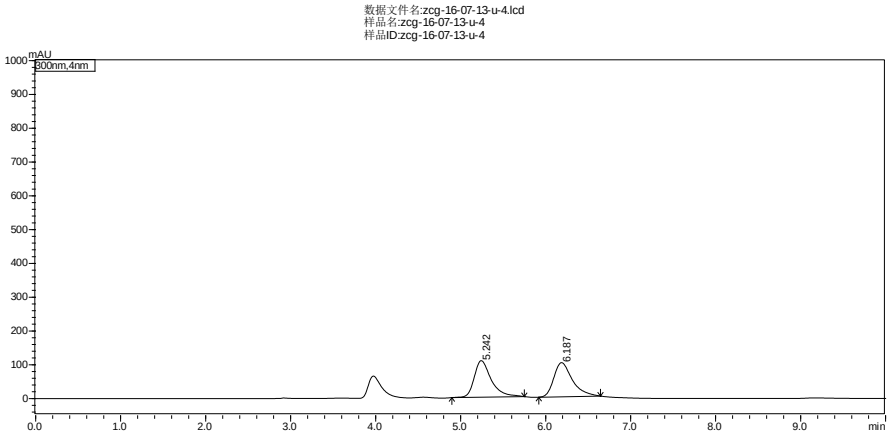
**Supplementary Figure 38. $^{1}$H NMR Spectrum of 3gd**



**Supplementary Figure 39. $^{13}$C NMR Spectrum of 3gd**

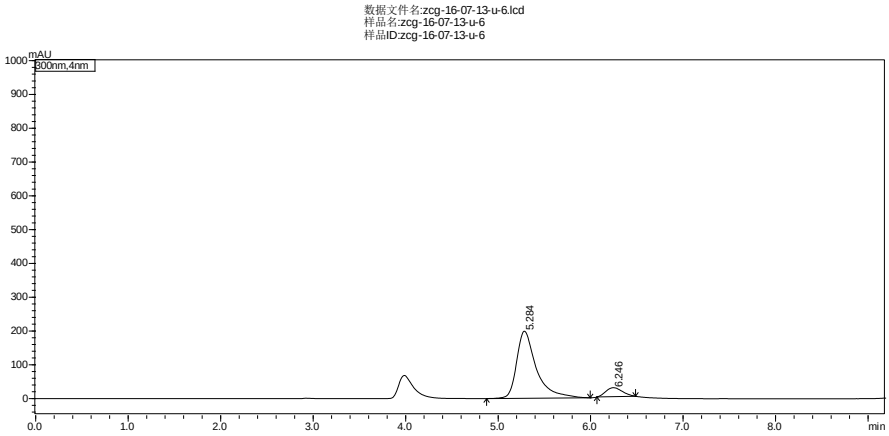


## Supplementary Figure 40. HPLC Spectrum of racemic 3gd



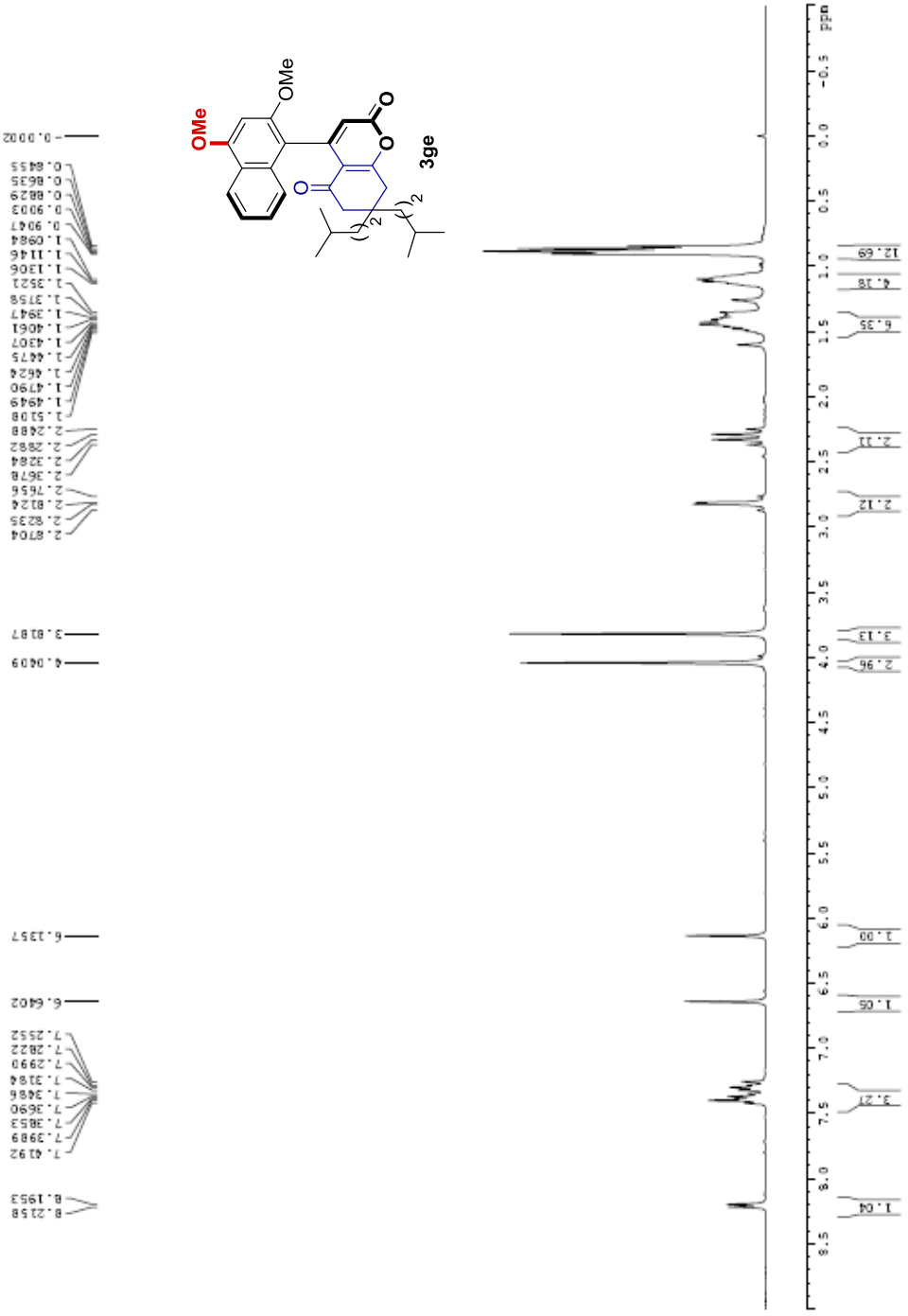

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 5.242 | 1509264 | 108000 | 49.565 | 51.638 |
| 2 | 6.187 | 1535751 | 101147 | 50.435 | 48.362 |
| Total | | 3045016 | 209147 | 100.000 | 100.000 |

## Supplementary Figure 41. HPLC Spectrum of 3gd

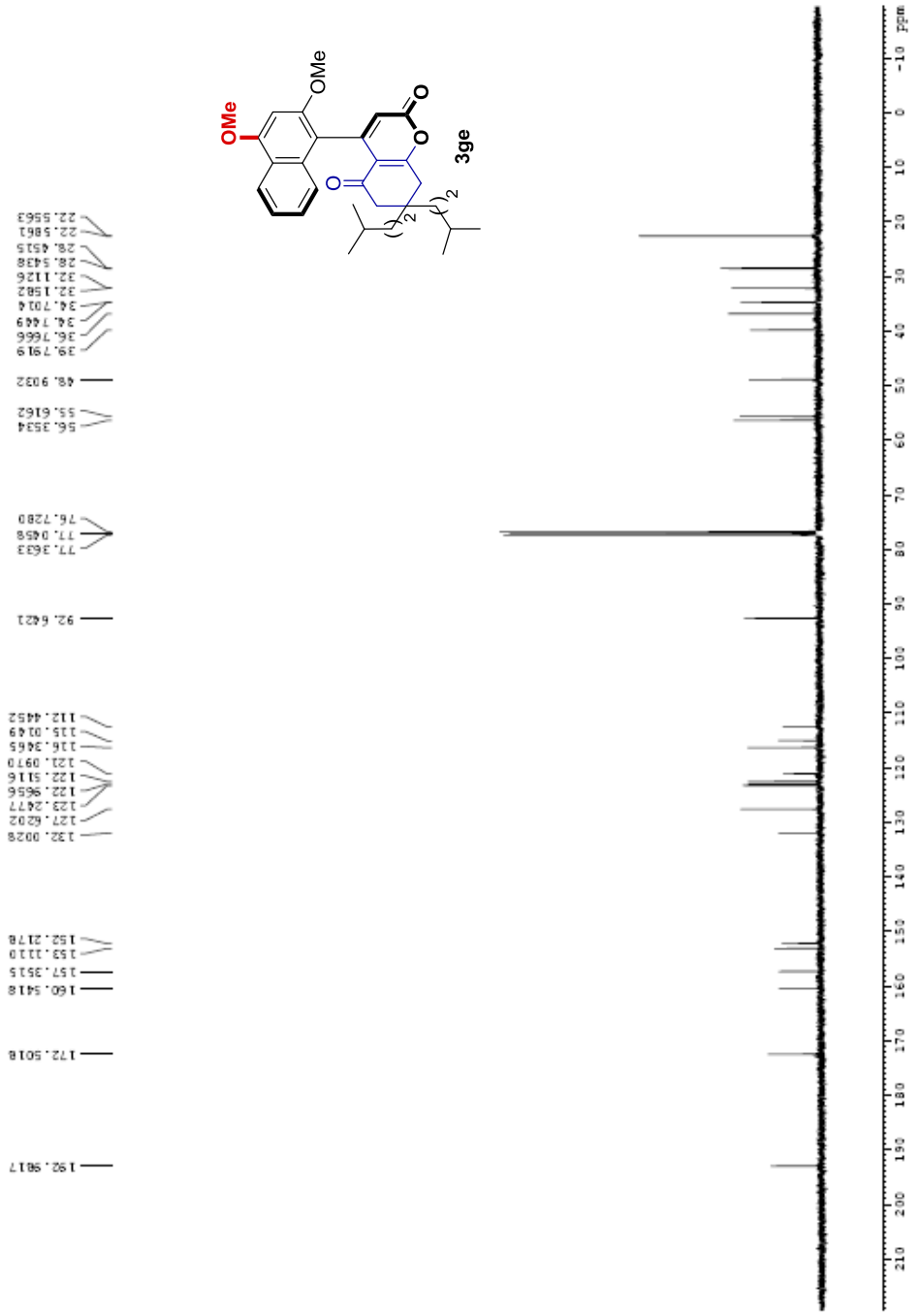



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 5.284 | 2945838 | 198470 | 89.871 | 88.161 |
| 2 | 6.246 | 332027 | 26652 | 10.129 | 11.839 |
| Total | | 3277865 | 225123 | 100.000 | 100.000 |

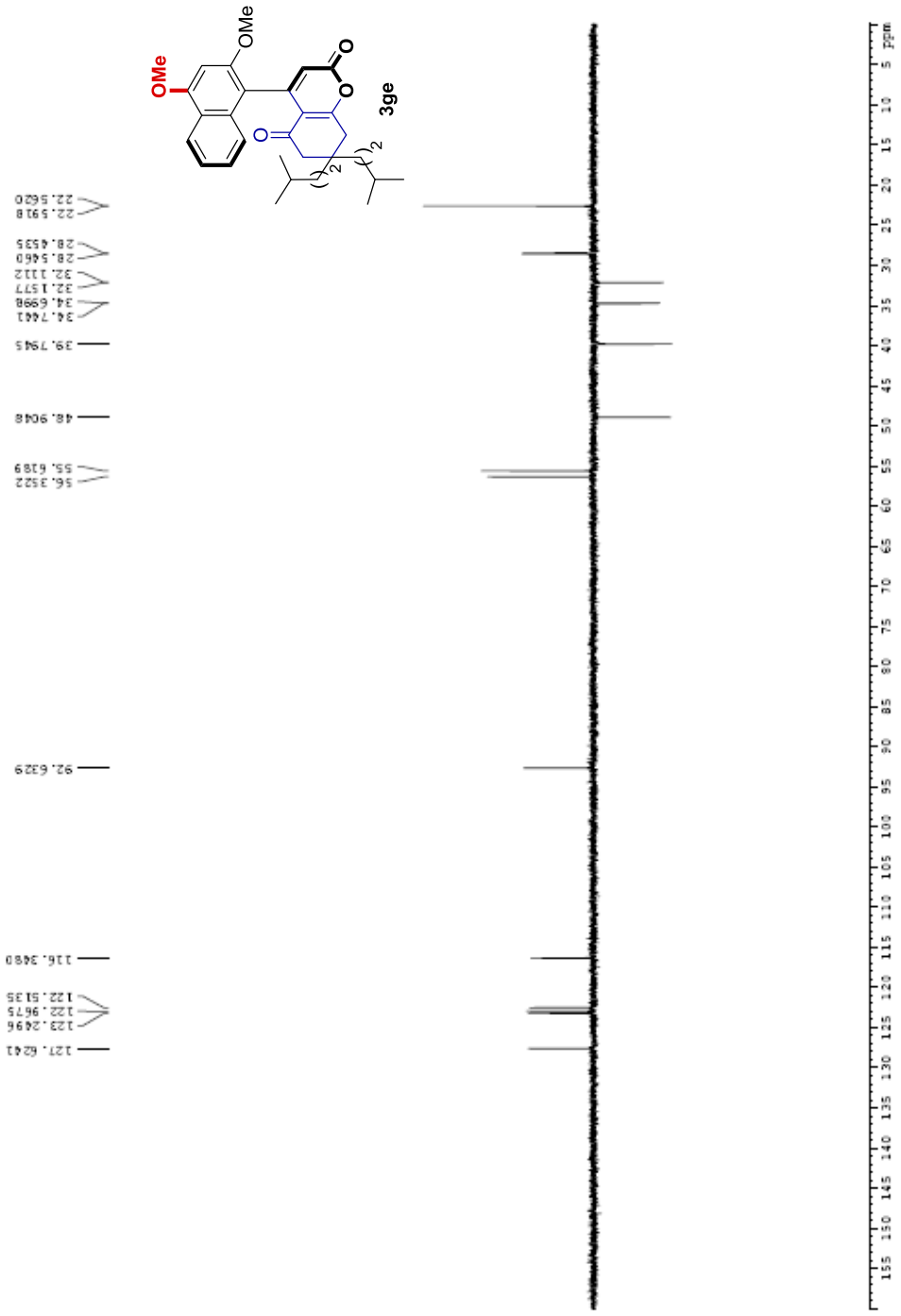
**Supplementary Figure 42. $^{1}$H NMR Spectrum of 3ge**



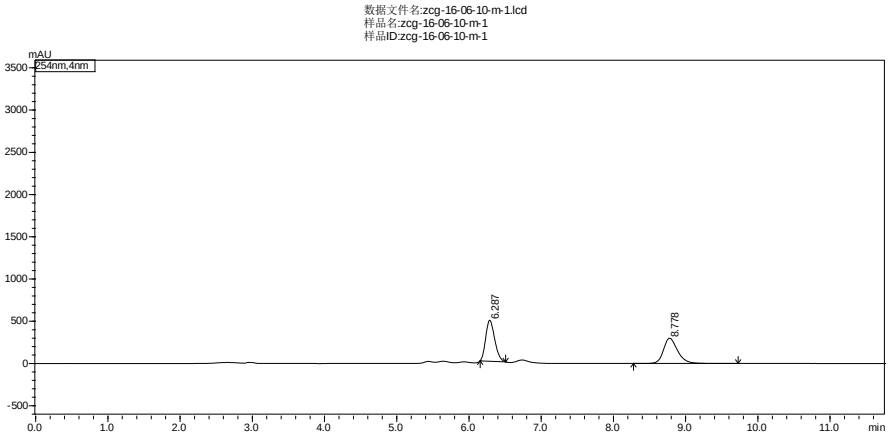
**Supplementary Figure 43. $^{13}$C NMR Spectrum of 3ge**



**Supplementary Figure 44.** $^{13}$C NMR Spectrum of 3ge

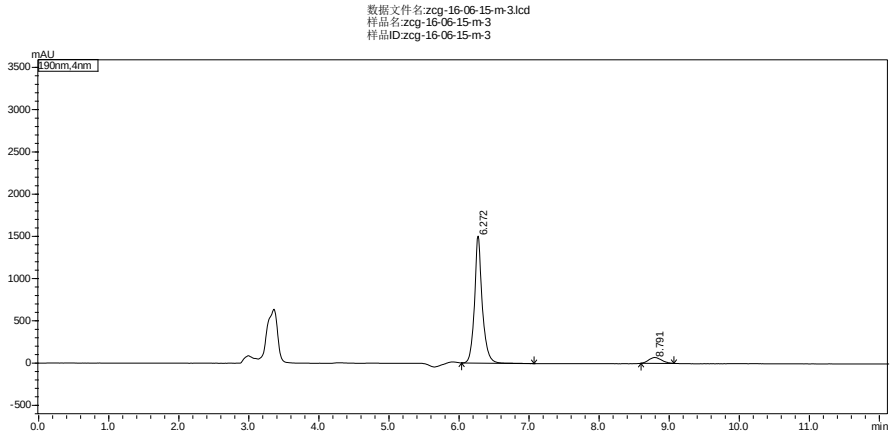


**Supplementary Figure 45. HPLC Spectrum of racemic 3ge**



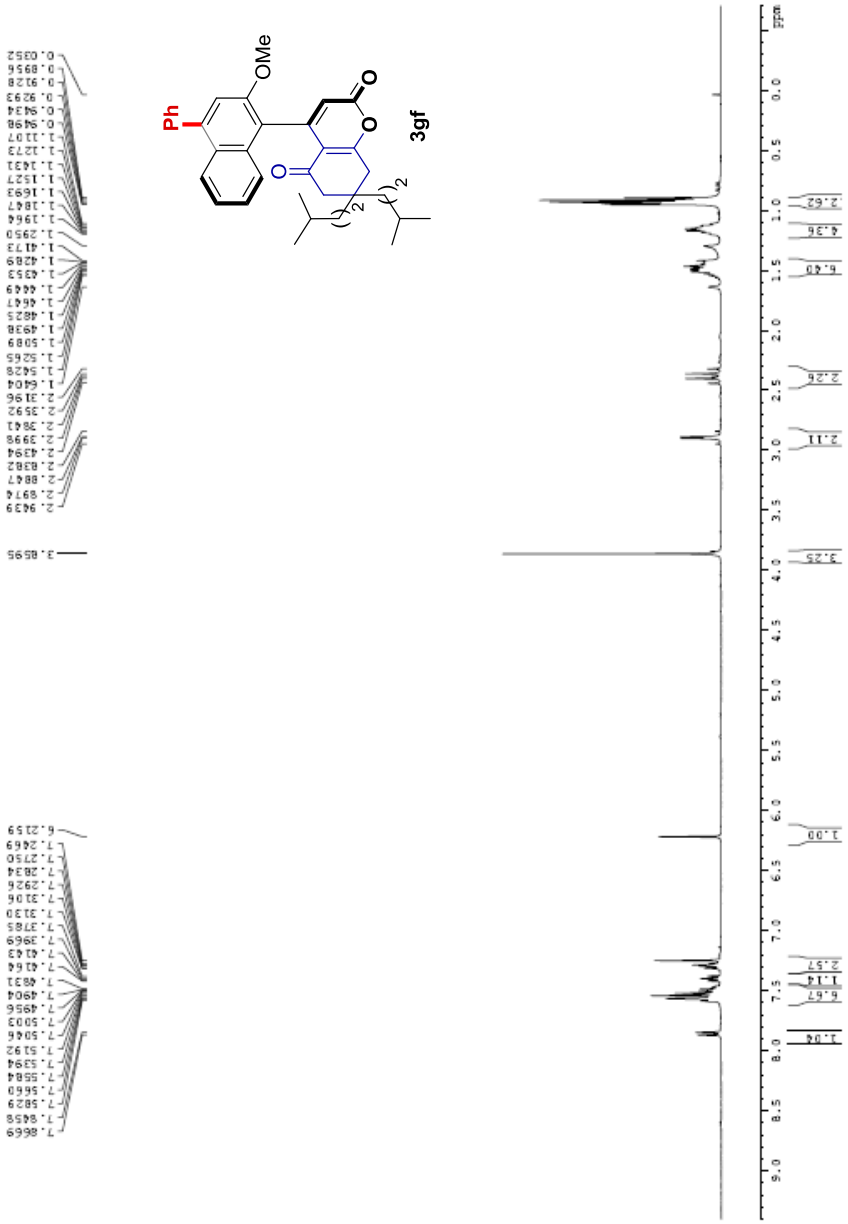

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.287 | 4205010 | 486577 | 50.790 | 61.901 |
| 2 | 8.778 | 4074138 | 299485 | 49.210 | 38.099 |
| Total | | 8279148 | 786062 | 100.000 | 100.000 |

## Supplementary Figure 46. HPLC Spectrum of 3ge

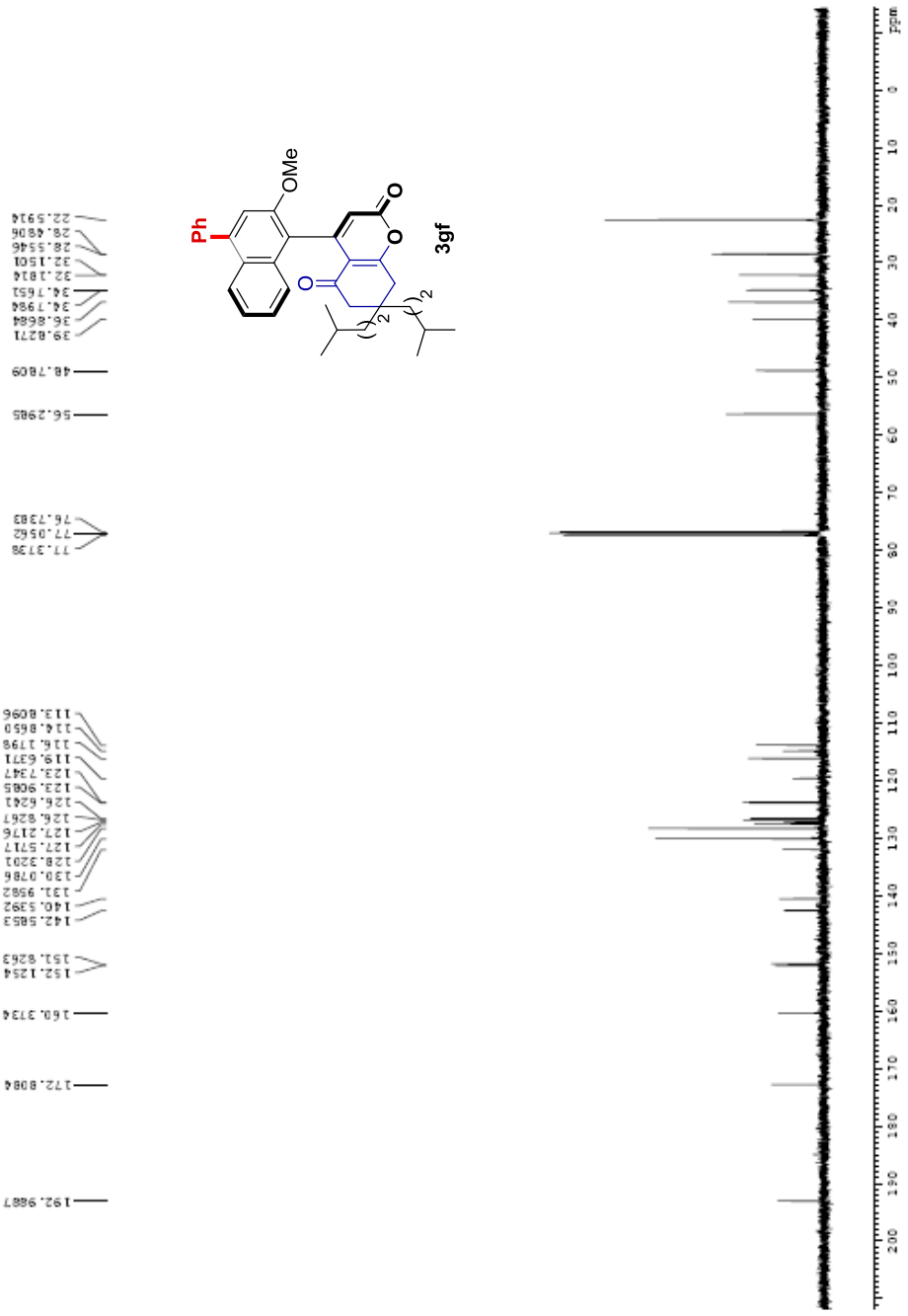



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.272 | 11518515 | 1504360 | 92.945 | 95.619 |
| 2 | 8.791 | 874269 | 68921 | 7.055 | 4.381 |
| Total | | 12392783 | 1573281 | 100.000 | 100.000 |

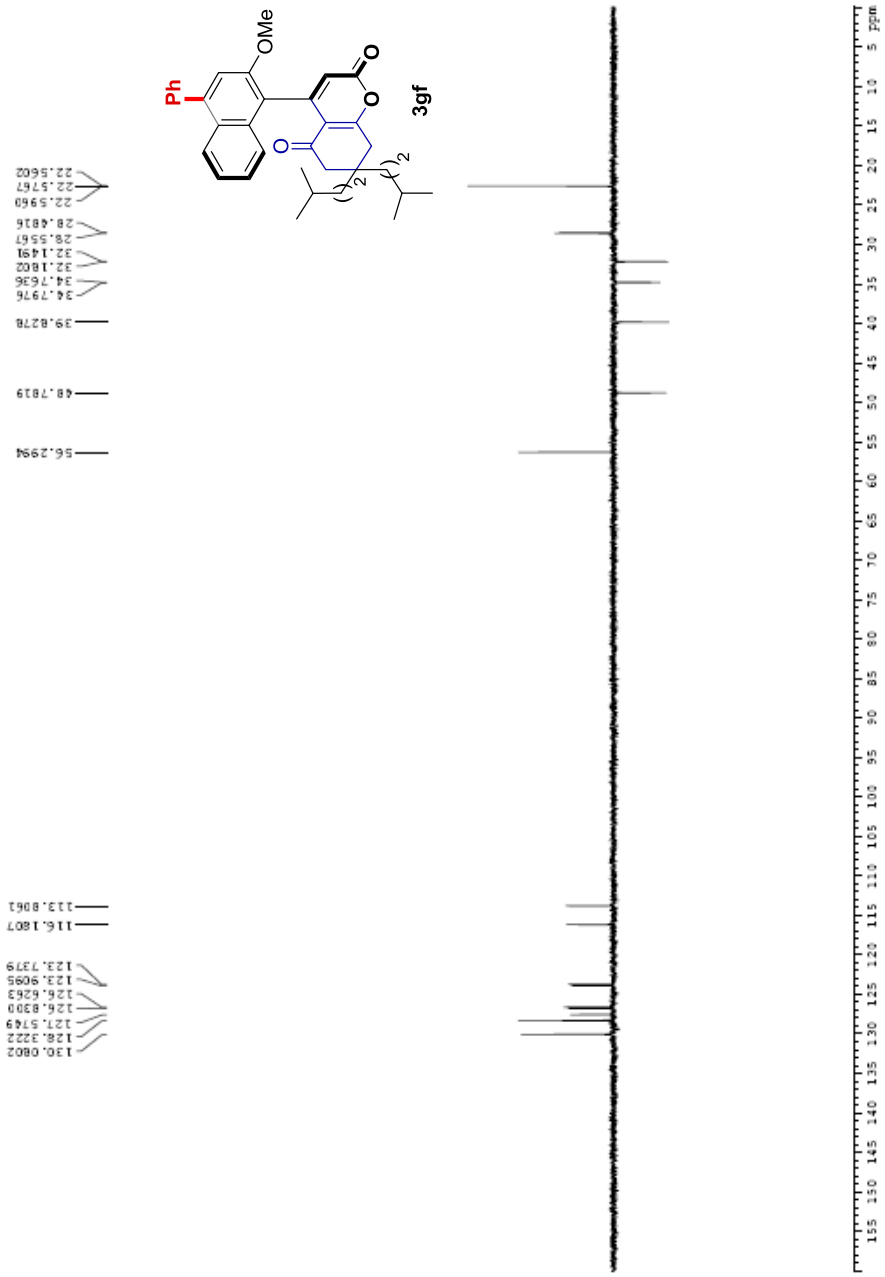
**Supplementary Figure 47. $^{1}$H NMR Spectrum of 3gf**



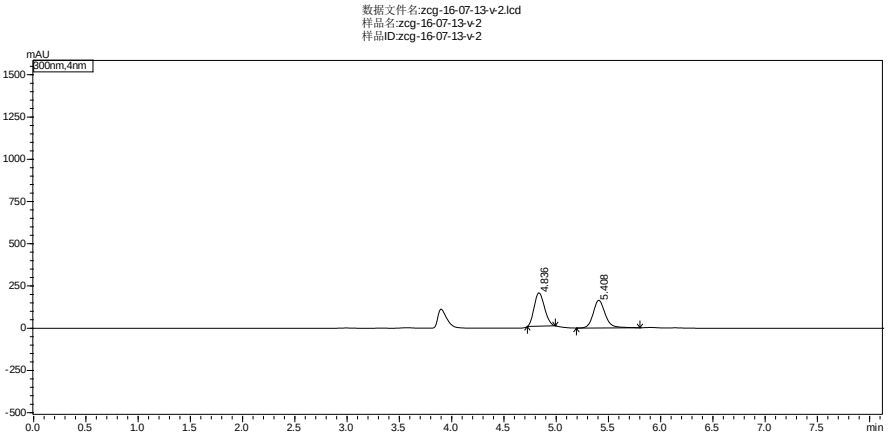
**Supplementary Figure 48. $^{13}$C NMR Spectrum of 3gf**



**Supplementary Figure 49. $^{13}$C NMR Spectrum of 3gf**

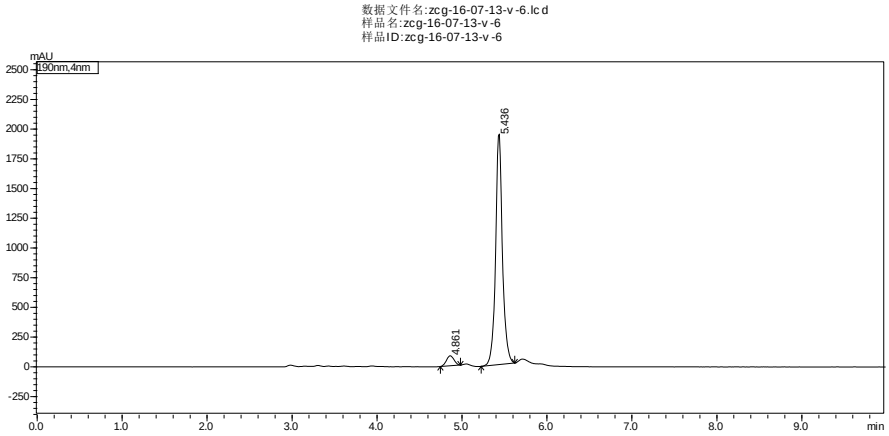


**Supplementary Figure 50. HPLC Spectrum of racemic 3gf**



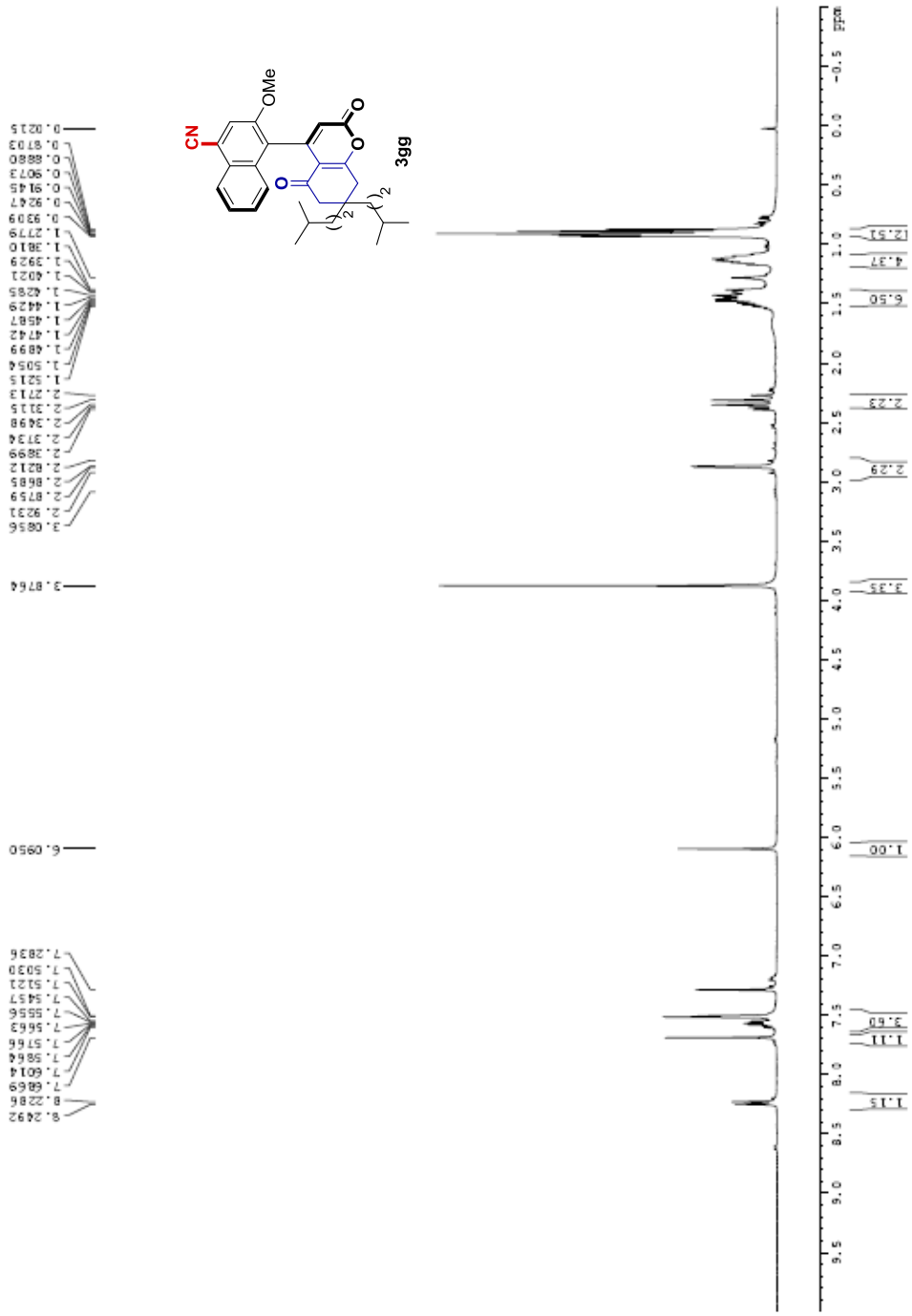

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 4.836 | 1365001 | 197201 | 50.914 | 54.517 |
| 2 | 5.408 | 1316015 | 164522 | 49.086 | 45.483 |
| Total | | 2681015 | 361724 | 100.000 | 100.000 |

## Supplementary Figure 51. HPLC Spectrum of 3gf

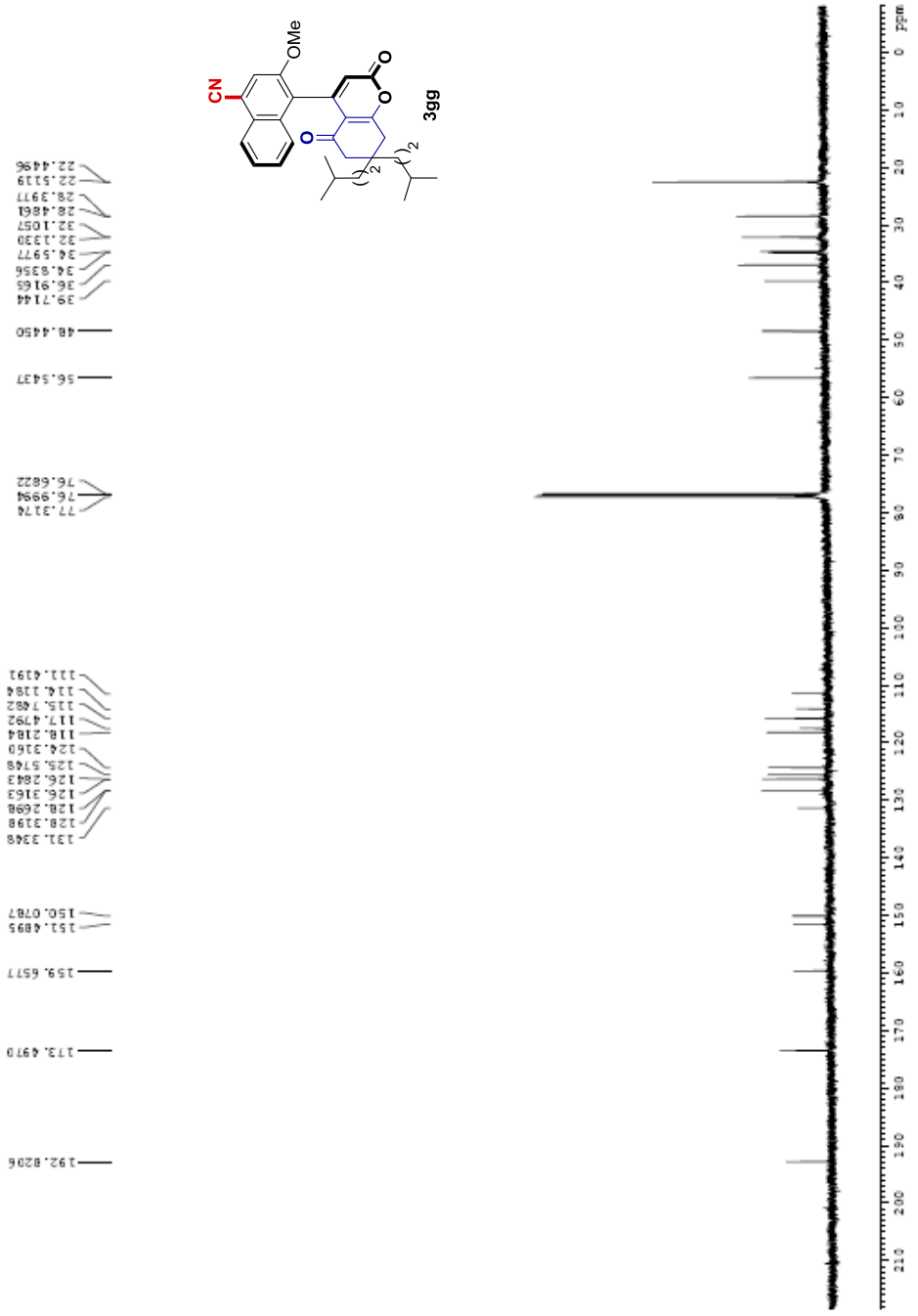



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 4.861 | 526963 | 83904 | 4.630 | 4.144 |
| 2 | 5.436 | 10855714 | 1940907 | 95.370 | 95.856 |
| Total | | 11382677 | 2024811 | 100.000 | 100.000 |

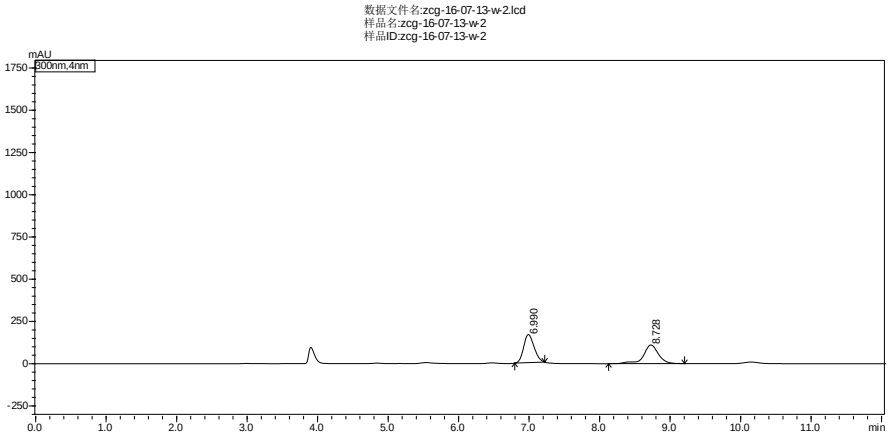
**Supplementary Figure 52. $^{1}$H NMR Spectrum of 3gg**



**Supplementary Figure 53. $^{13}$C NMR Spectrum of 3gg**

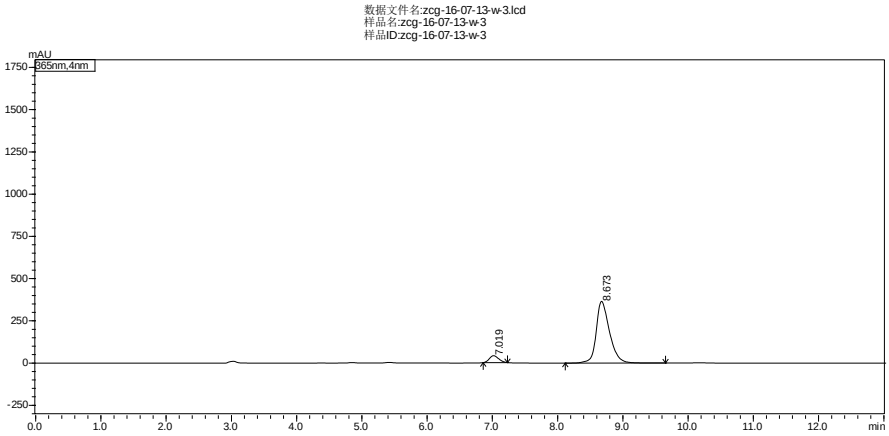


**Supplementary Figure 54. HPLC Spectrum of racemic 3gg**



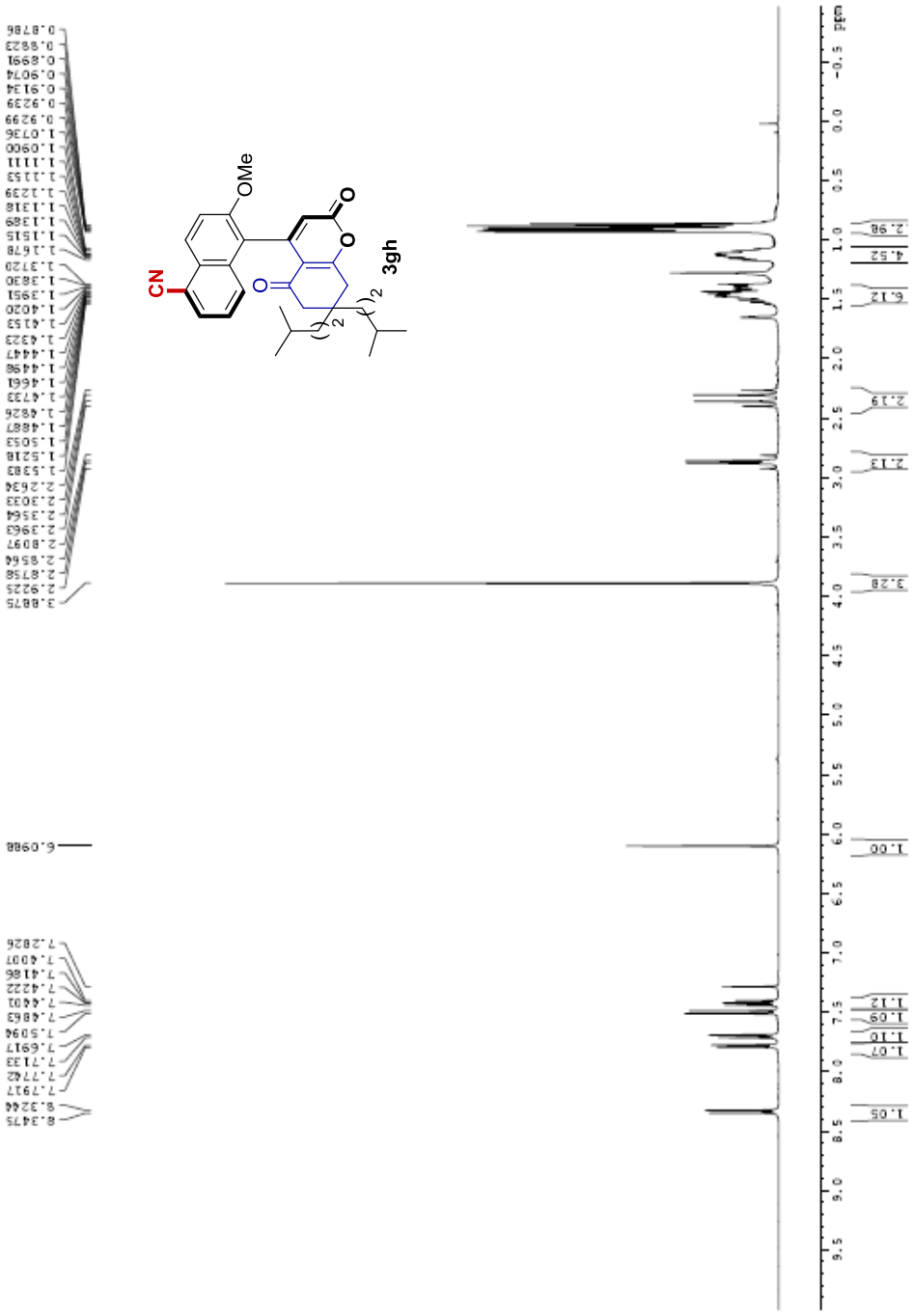

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.990 | 1721891 | 166243 | 51.421 | 60.063 |
| 2 | 8.728 | 1626730 | 110539 | 48.579 | 39.937 |
| Total | | 3348621 | 276782 | 100.000 | 100.000 |

## Supplementary Figure 55. HPLC Spectrum of 3gg

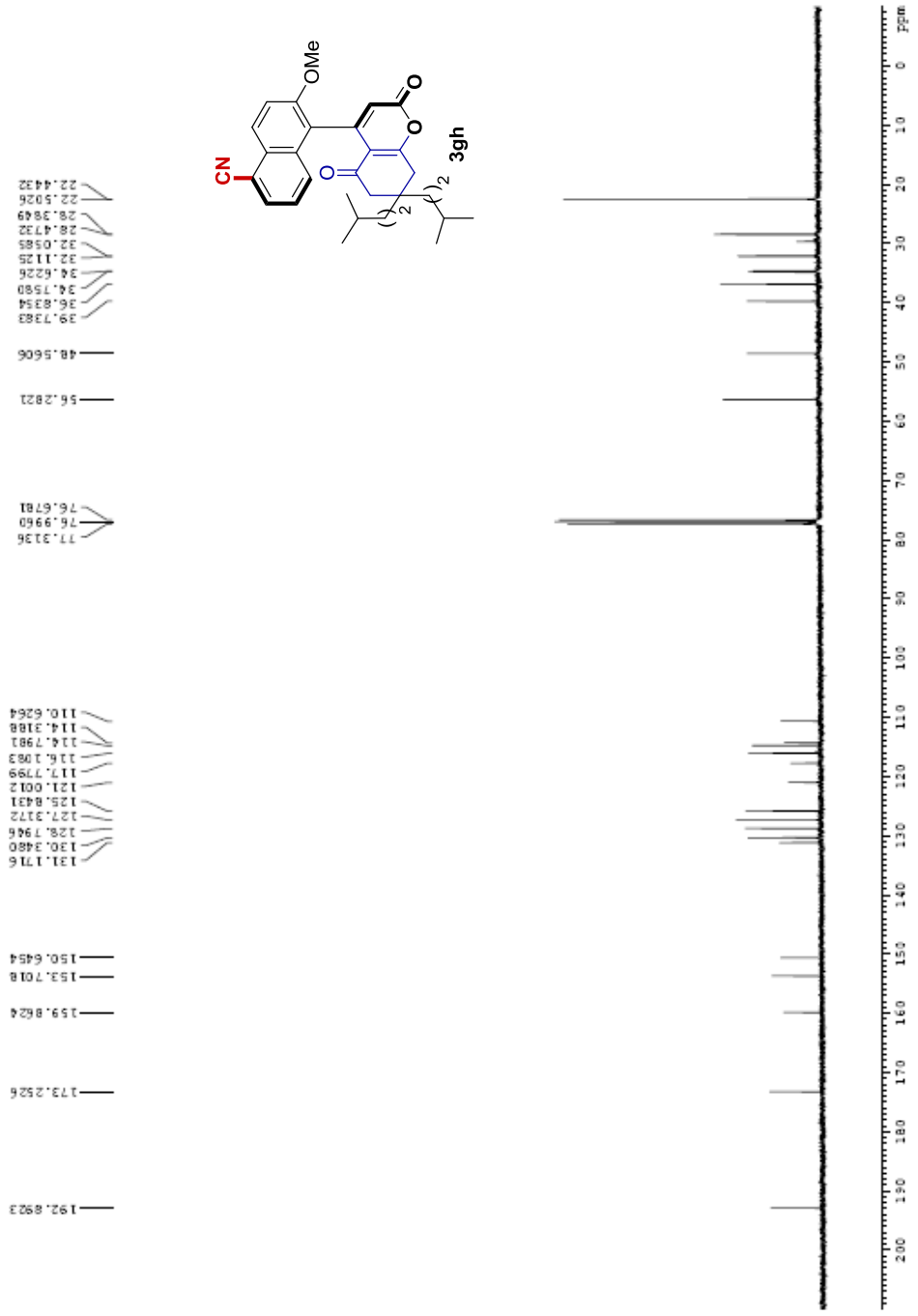



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 7.019 | 404578 | 40739 | 7.252 | 10.017 |
| 2 | 8.673 | 5174470 | 365981 | 92.748 | 89.983 |
| Total | | 5579048 | 406720 | 100.000 | 100.000 |

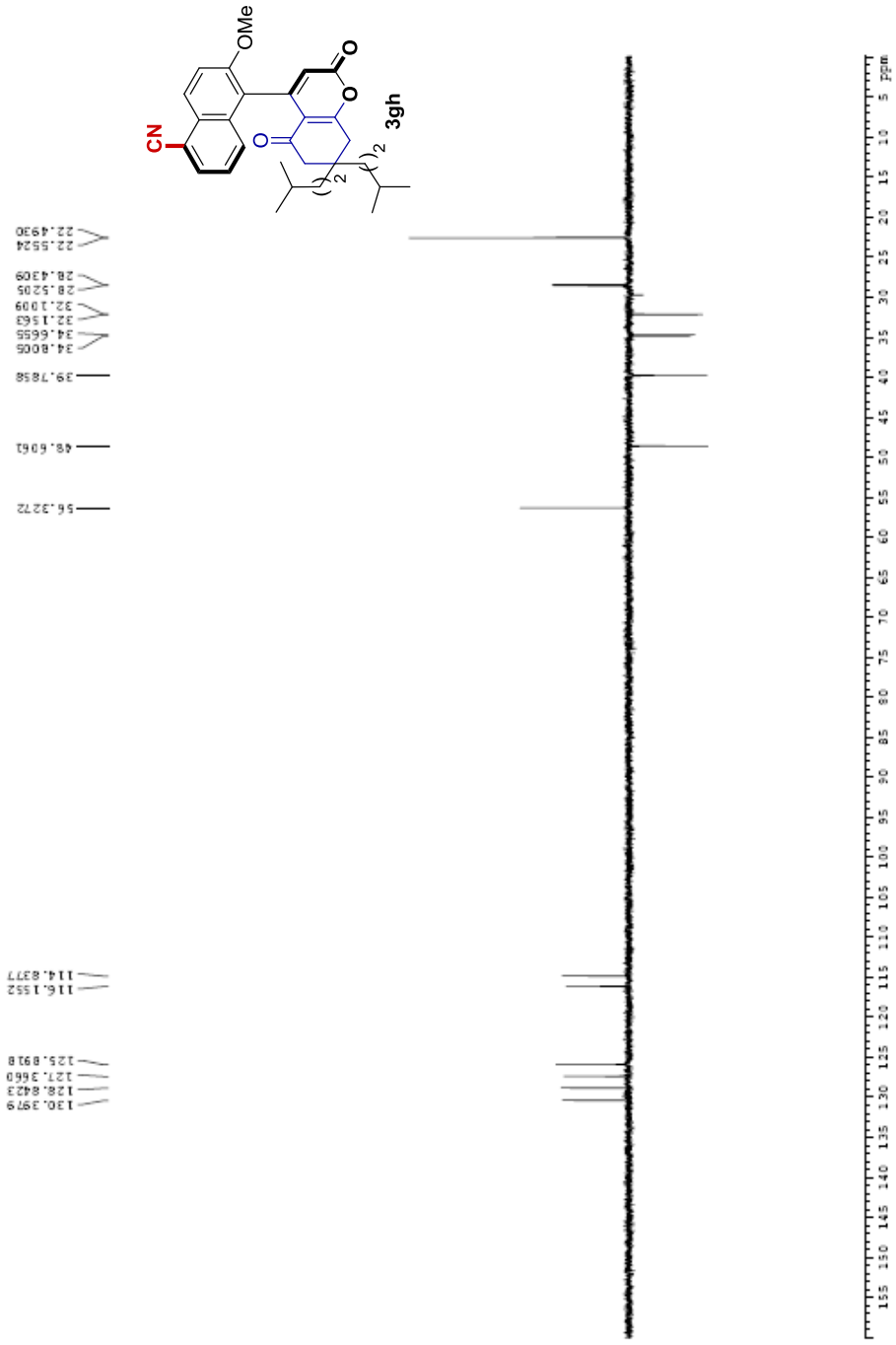
**Supplementary Figure 56. $^{1}$H NMR Spectrum of 3gh**



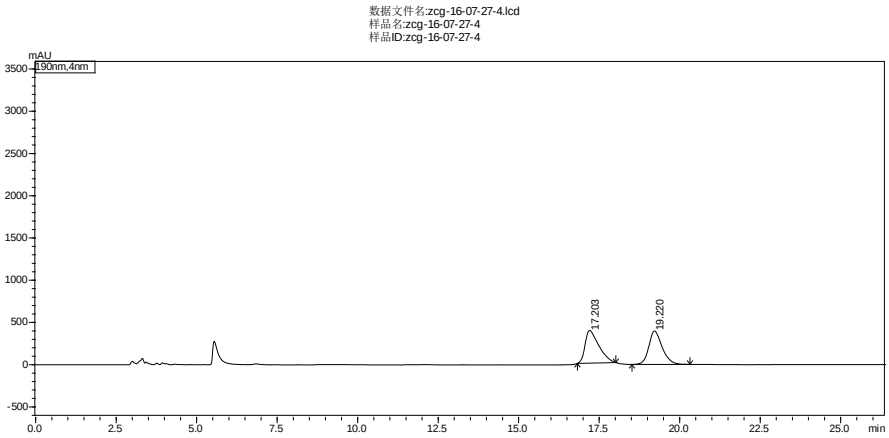
**Supplementary Figure 57. $^{13}$C NMR Spectrum of 3gh**



**Supplementary Figure 58. $^{13}$C NMR Spectrum of 3gh**

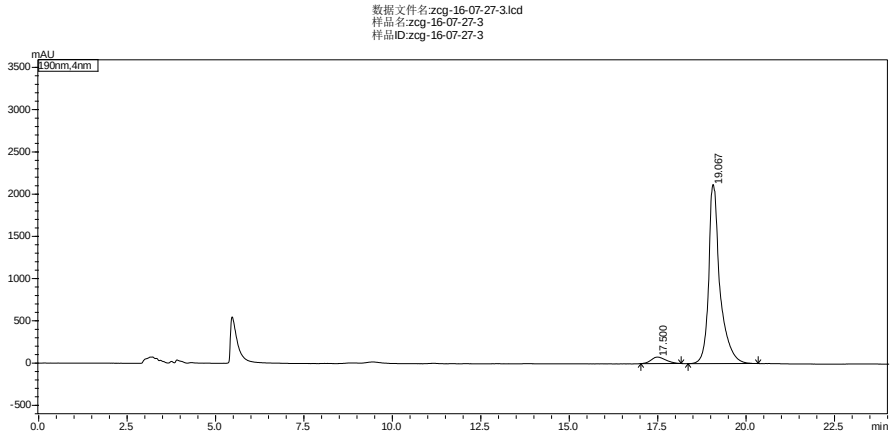


**Supplementary Figure 59. HPLC Spectrum of racemic 3gh**



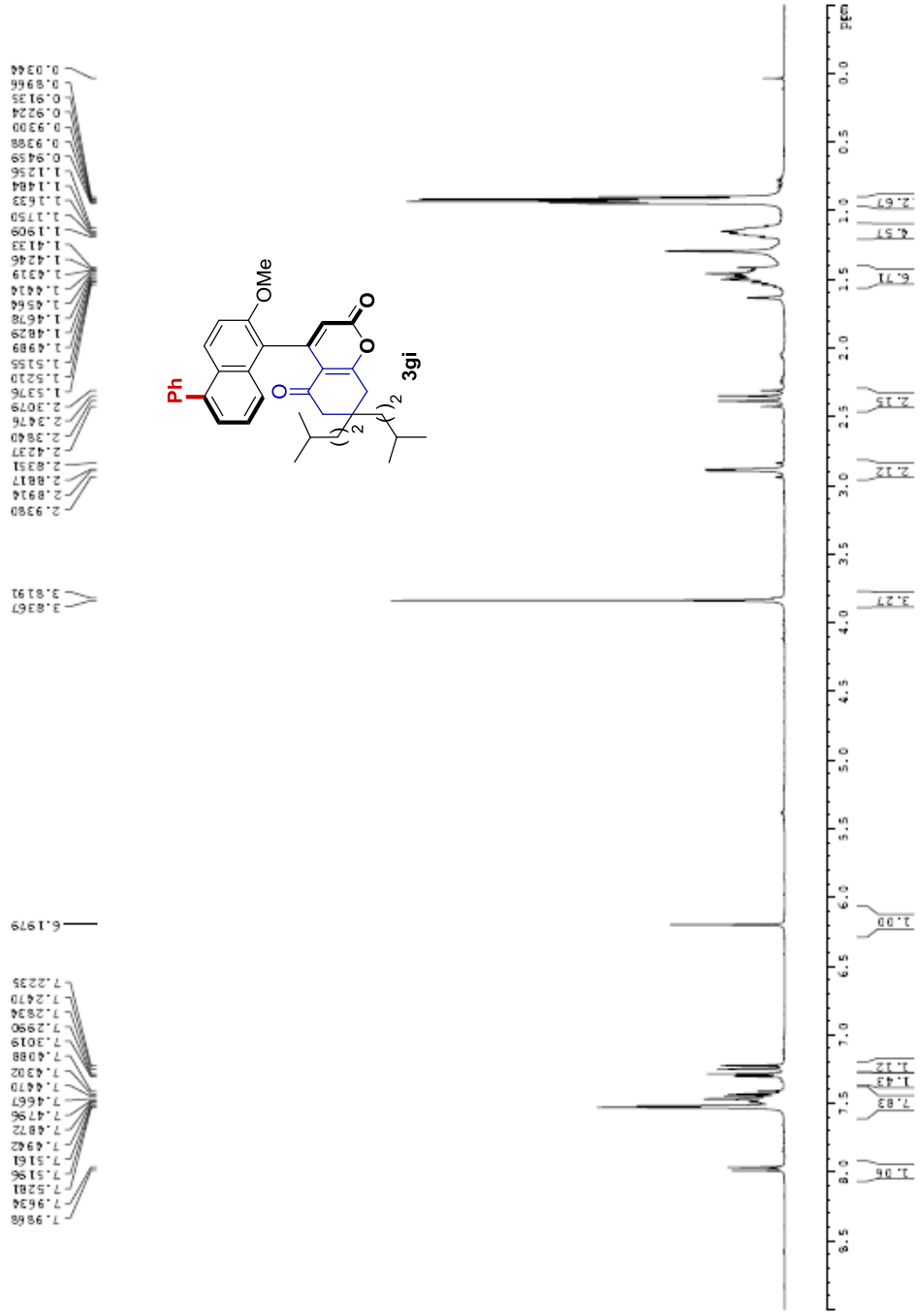

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 17.203 | 11487058 | 387720 | 49.937 | 49.429 |
| 2 | 19.220 | 11516237 | 396686 | 50.063 | 50.571 |
| Total | | 23003294 | 784405 | 100.000 | 100.000 |

## Supplementary Figure 60. HPLC Spectrum of 3gh

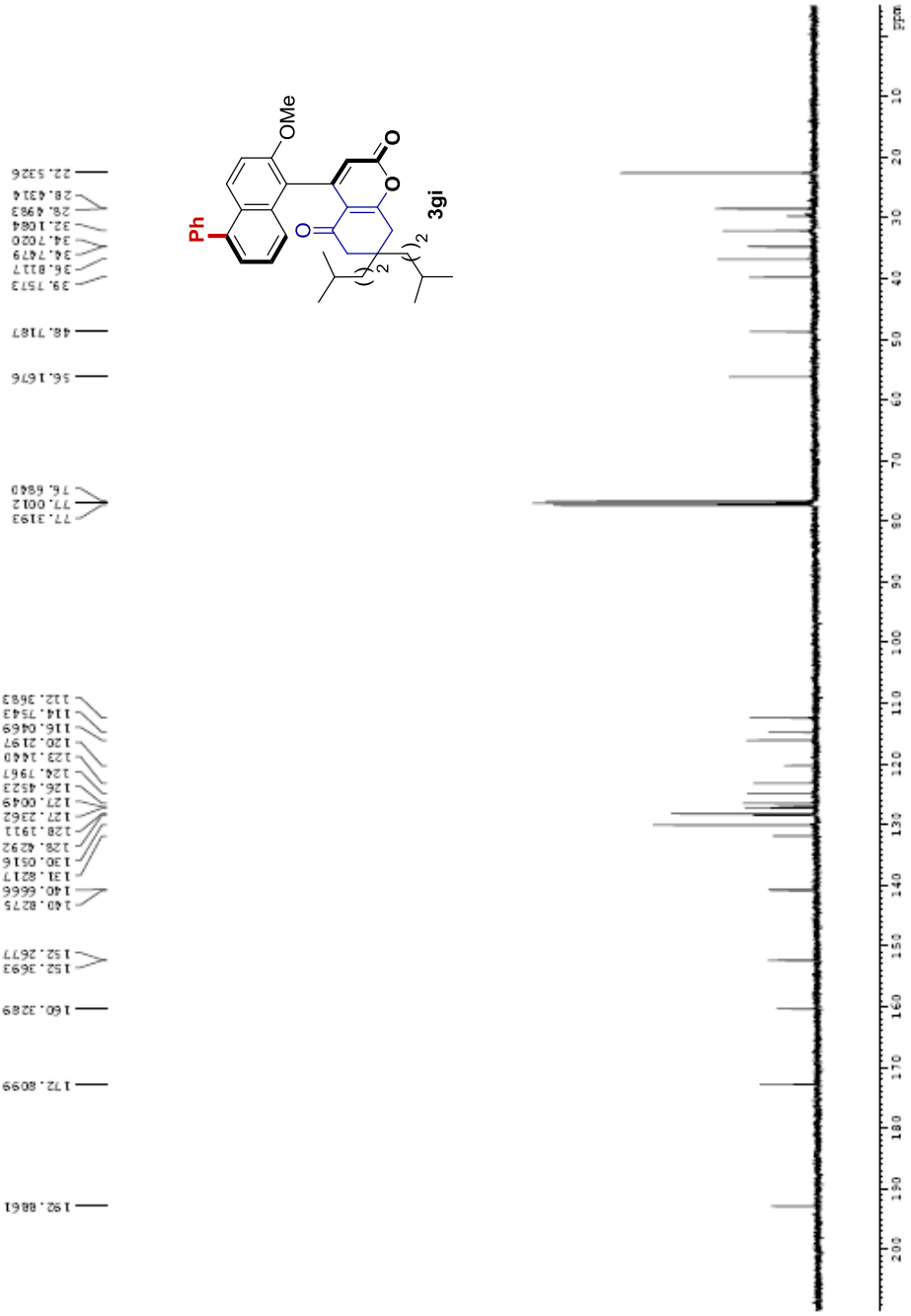



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 17.500 | 2227939 | 76837 | 4.531 | 3.497 |
| 2 | 19.067 | 46946120 | 2120381 | 95.469 | 96.503 |
| Total | | 49174059 | 2197218 | 100.000 | 100.000 |

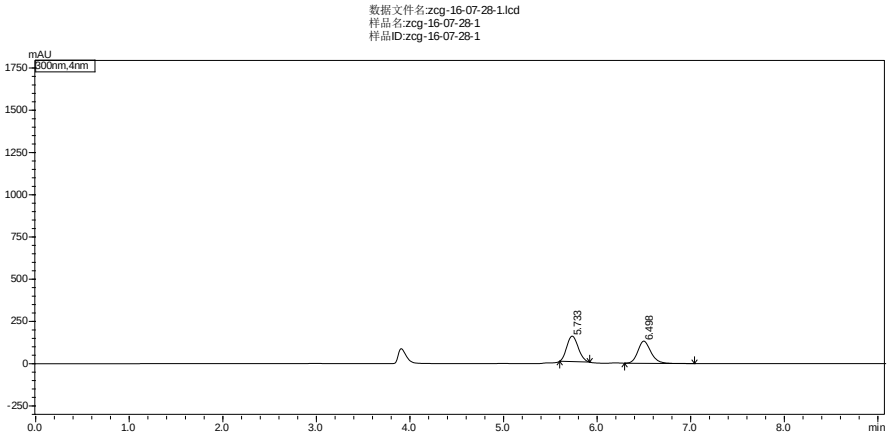
**Supplementary Figure 61. $^{1}$H NMR Spectrum of 3gi**



**Supplementary Figure 62. $^{13}$C NMR Spectrum of 3gi**

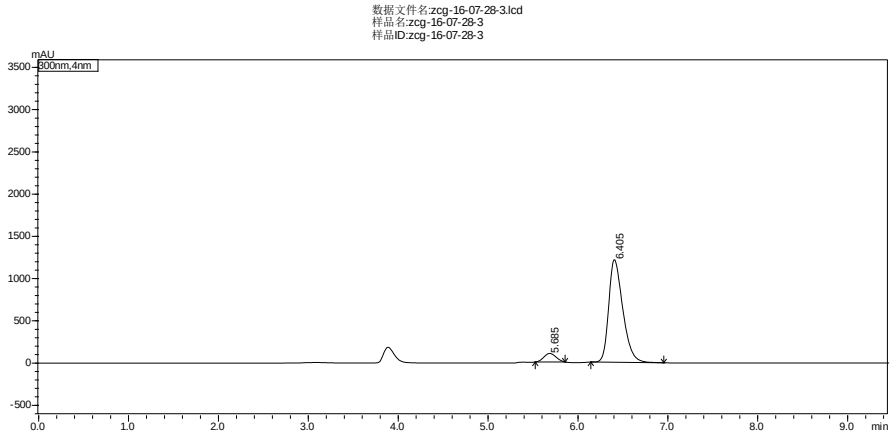


**Supplementary Figure 63. HPLC Spectrum of racemic 3gi**



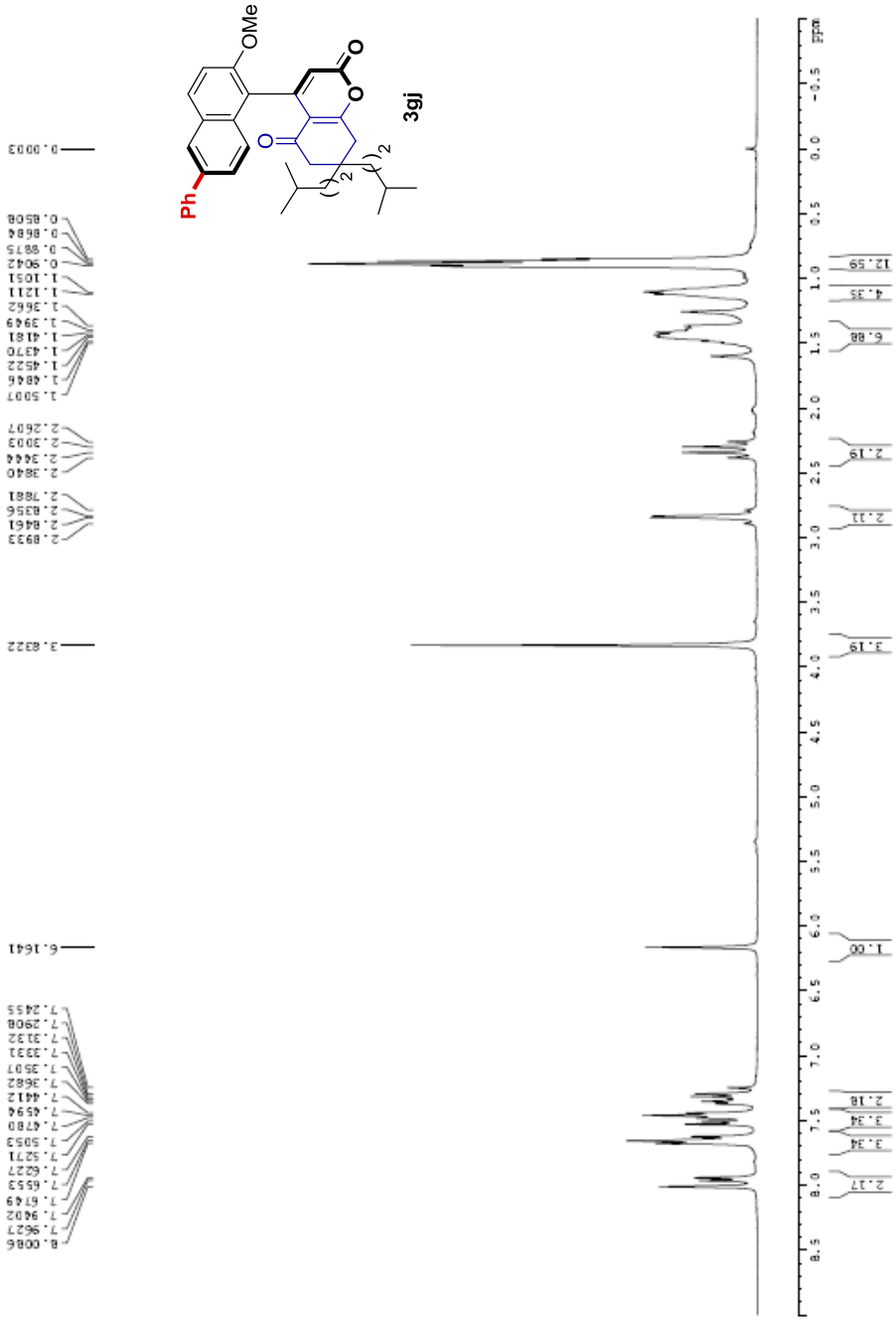

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 5.733 | 1280854 | 150715 | 50.291 | 53.419 |
| 2 | 6.498 | 1266028 | 131423 | 49.709 | 46.581 |
| Total | | 2546881 | 282138 | 100.000 | 100.000 |

## Supplementary Figure 64. HPLC Spectrum of 3gi

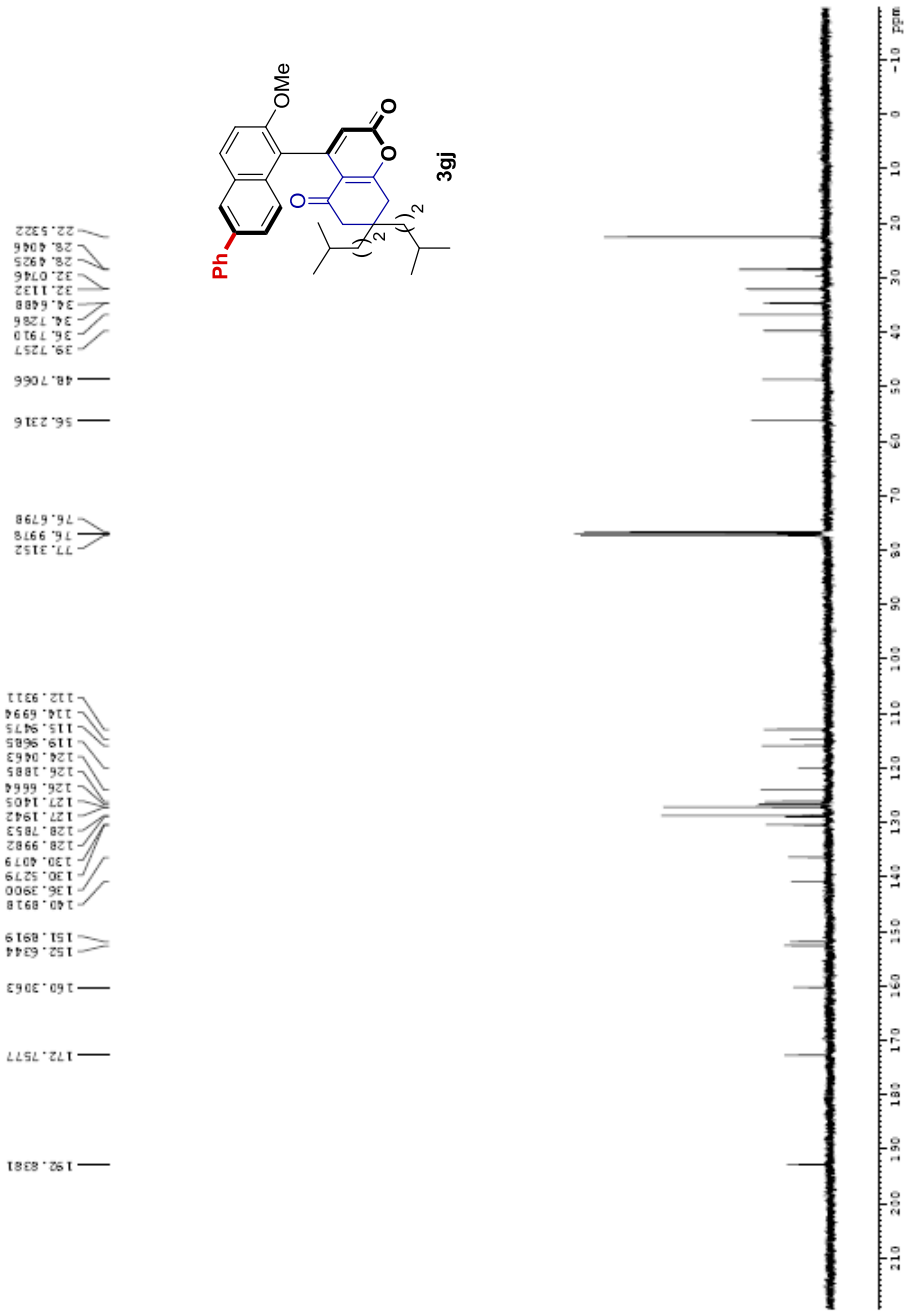



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 5.685 | 952256 | 101183 | 6.705 | 7.695 |
| 2 | 6.405 | 13248874 | 1213725 | 93.295 | 92.305 |
| Total | | 14201129 | 1314908 | 100.000 | 100.000 |

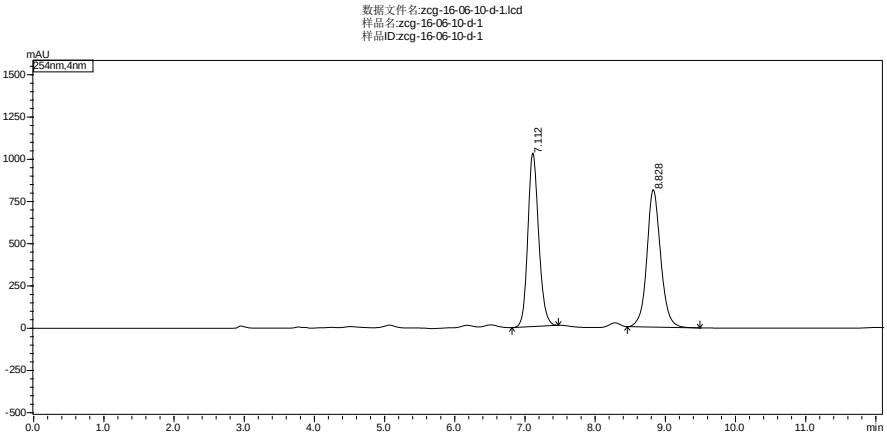
**Supplementary Figure 65. $^{1}$H NMR Spectrum of 3gj**



**Supplementary Figure 66. $^{13}$C NMR Spectrum of 3gj**

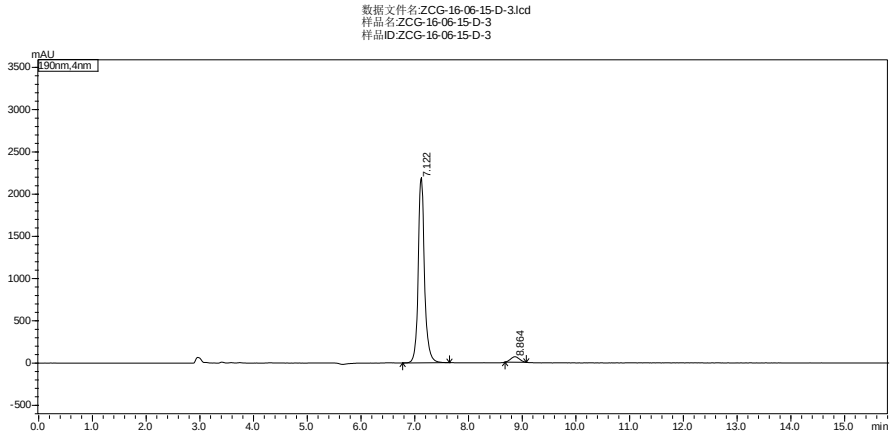


**Supplementary Figure 67. HPLC Spectrum of racemic 3gj**



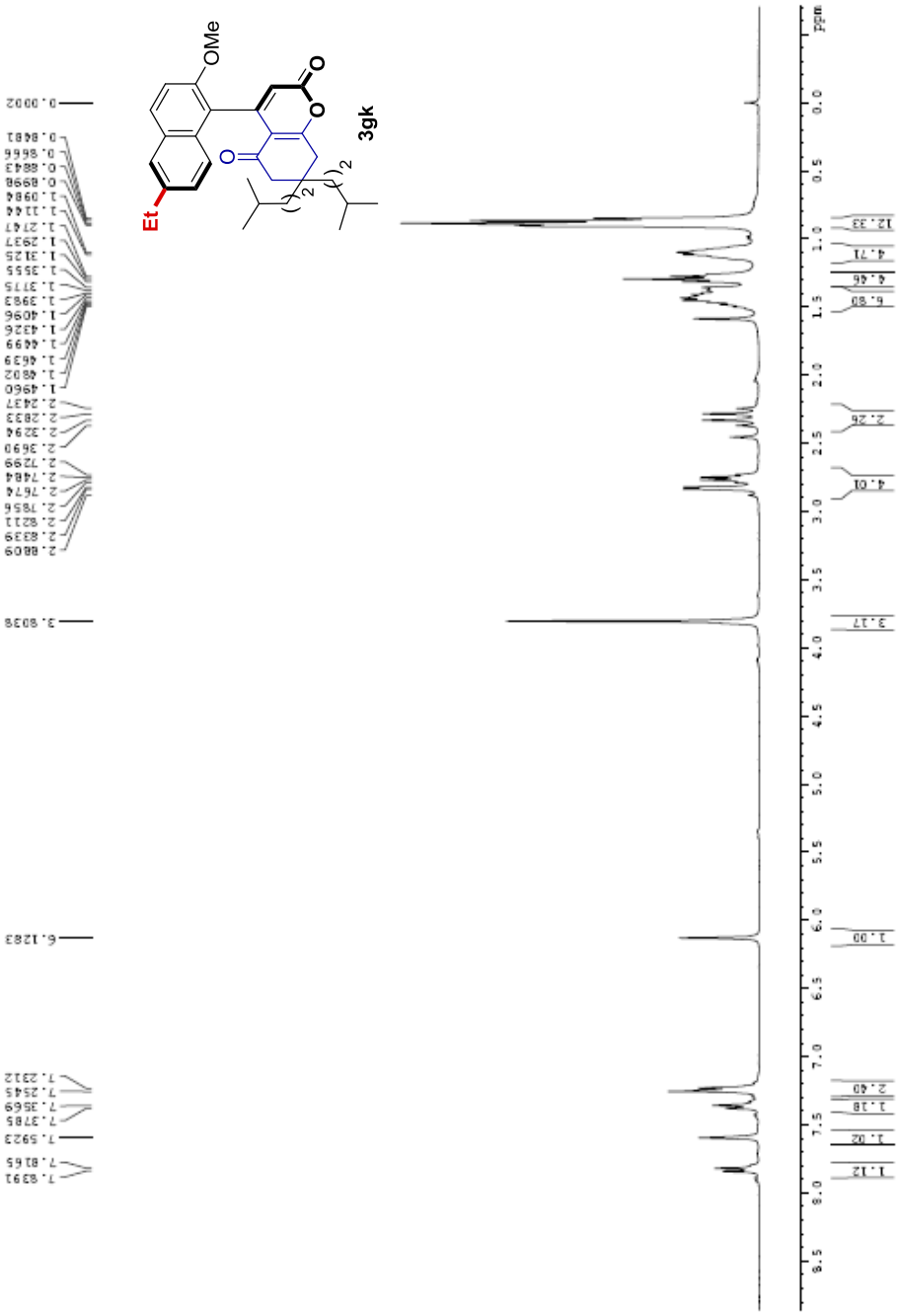

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 7.112 | 11063381 | 1027867 | 49.839 | 55.831 |
| 2 | 8.828 | 11134856 | 813166 | 50.161 | 44.169 |
| Total | | 22198236 | 1841034 | 100.000 | 100.000 |

## Supplementary Figure 68. HPLC Spectrum of 3gj

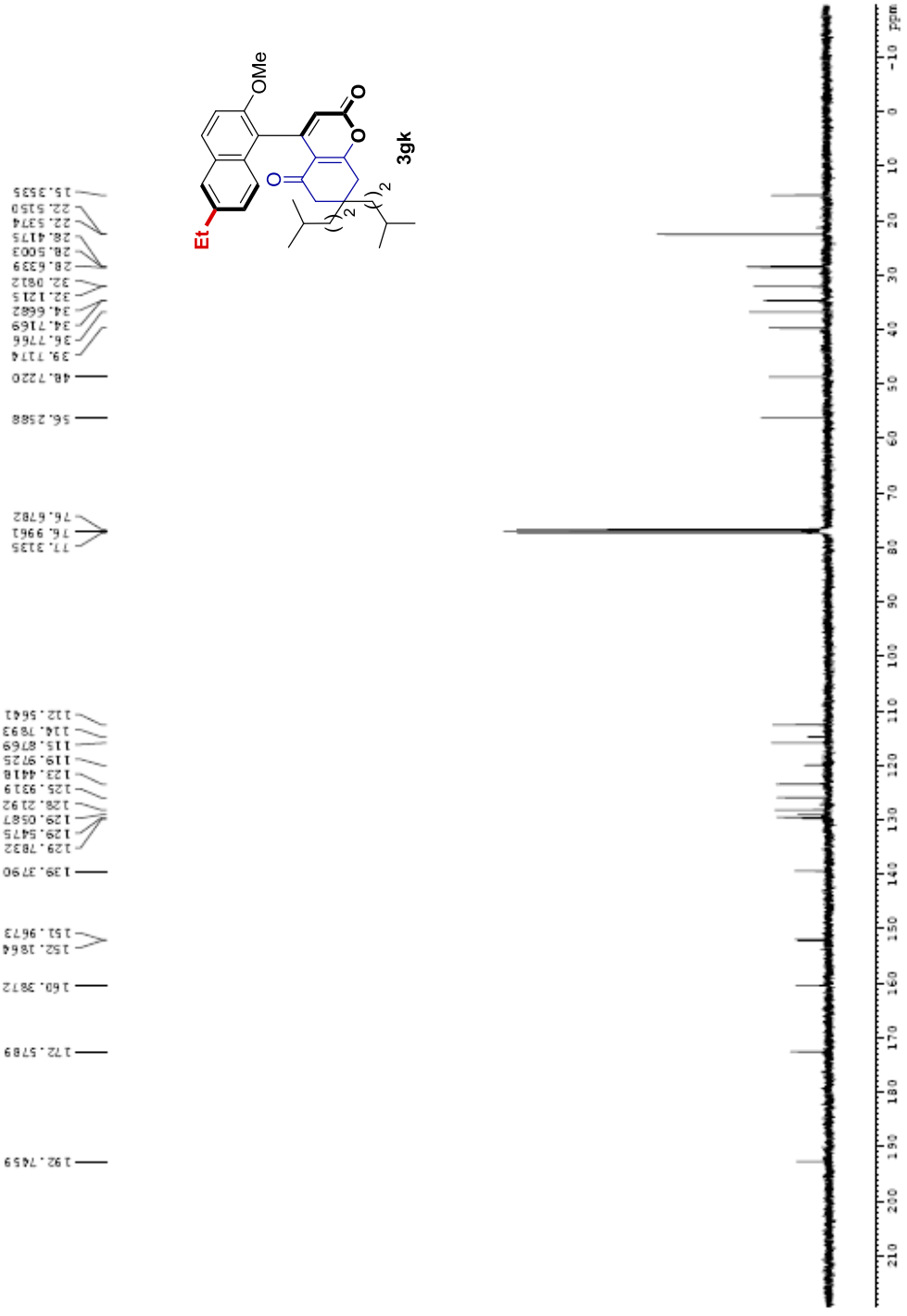



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 7.122 | 17978023 | 2195255 | 96.026 | 97.146 |
| 2 | 8.864 | 744049 | 64485 | 3.974 | 2.854 |
| Total | | 18722072 | 2259740 | 100.000 | 100.000 |

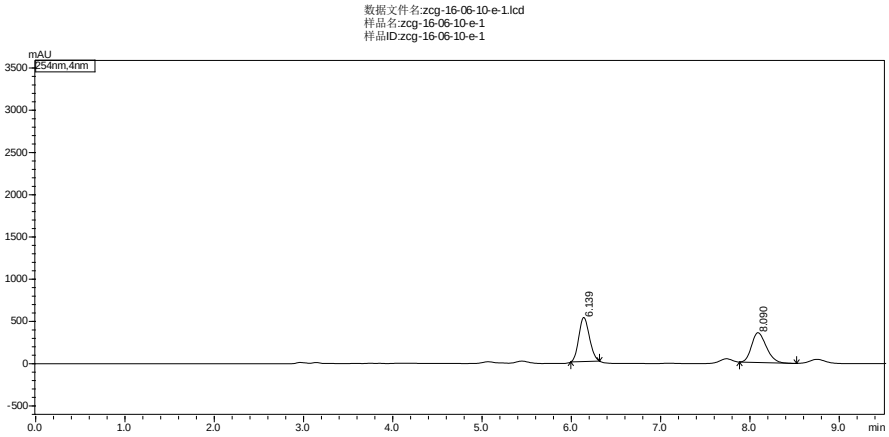
**Supplementary Figure 69. $^{1}$H NMR Spectrum of 3gk**



**Supplementary Figure 70. $^{13}$C NMR Spectrum of 3gk**

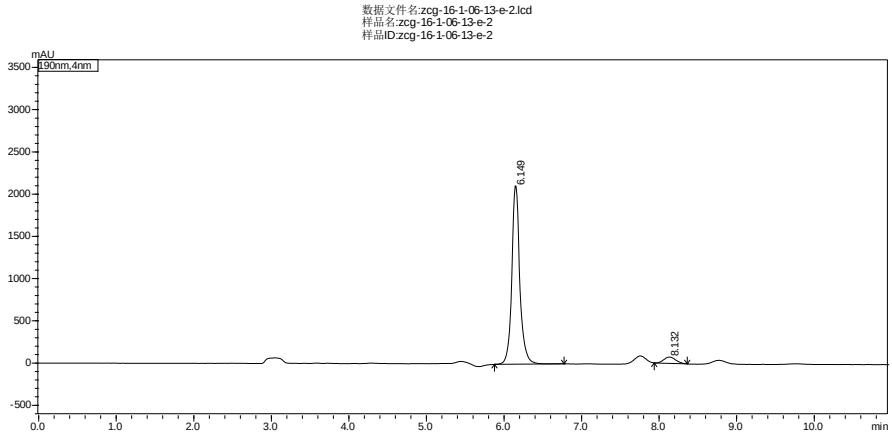


**Supplementary Figure 71. HPLC Spectrum of racemic 3gk**



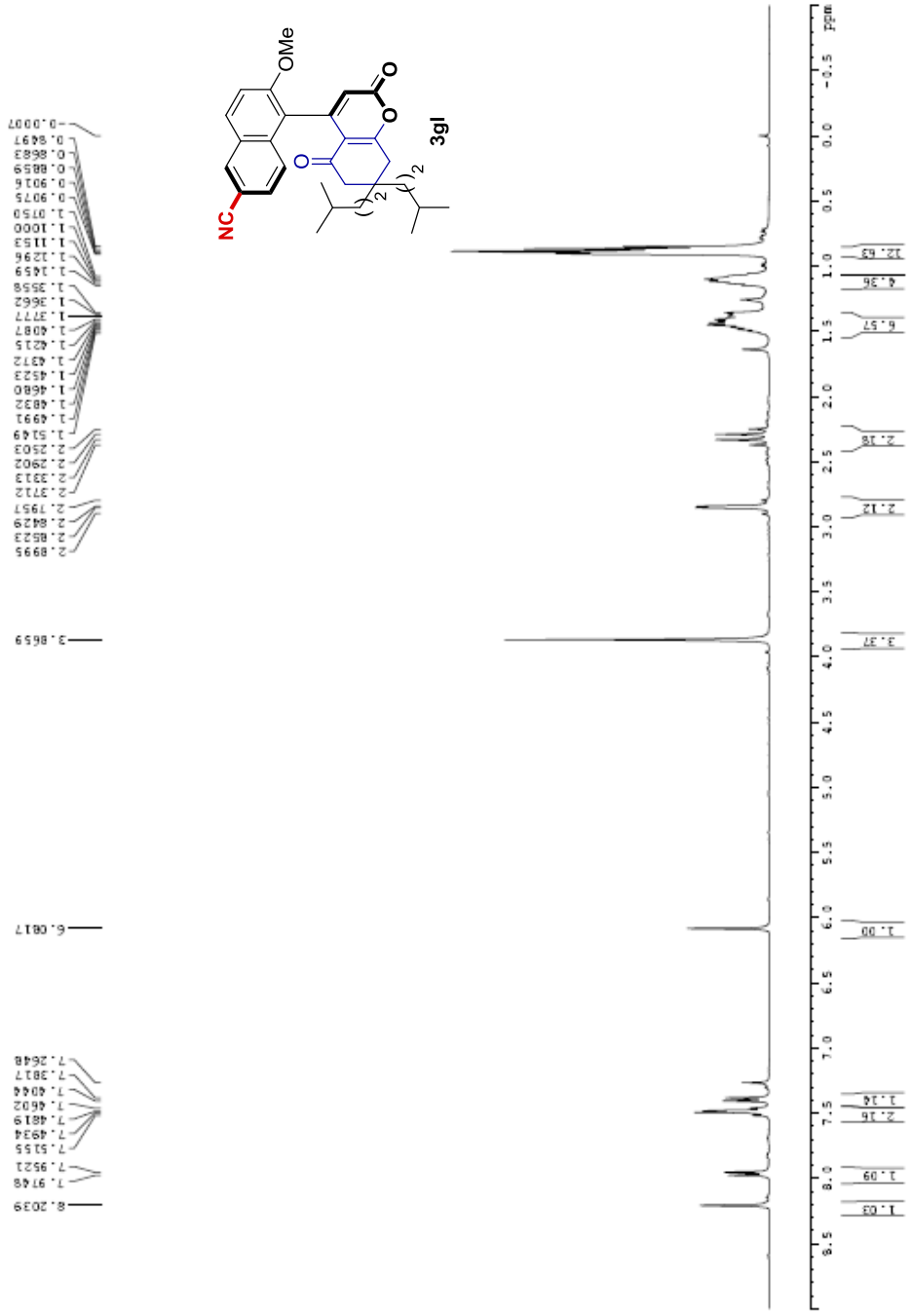

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.139 | 4285266 | 520570 | 51.561 | 59.647 |
| 2 | 8.090 | 4025802 | 352186 | 48.439 | 40.353 |
| Total | | 8311068 | 872756 | 100.000 | 100.000 |

## Supplementary Figure 72. HPLC Spectrum of 3gk

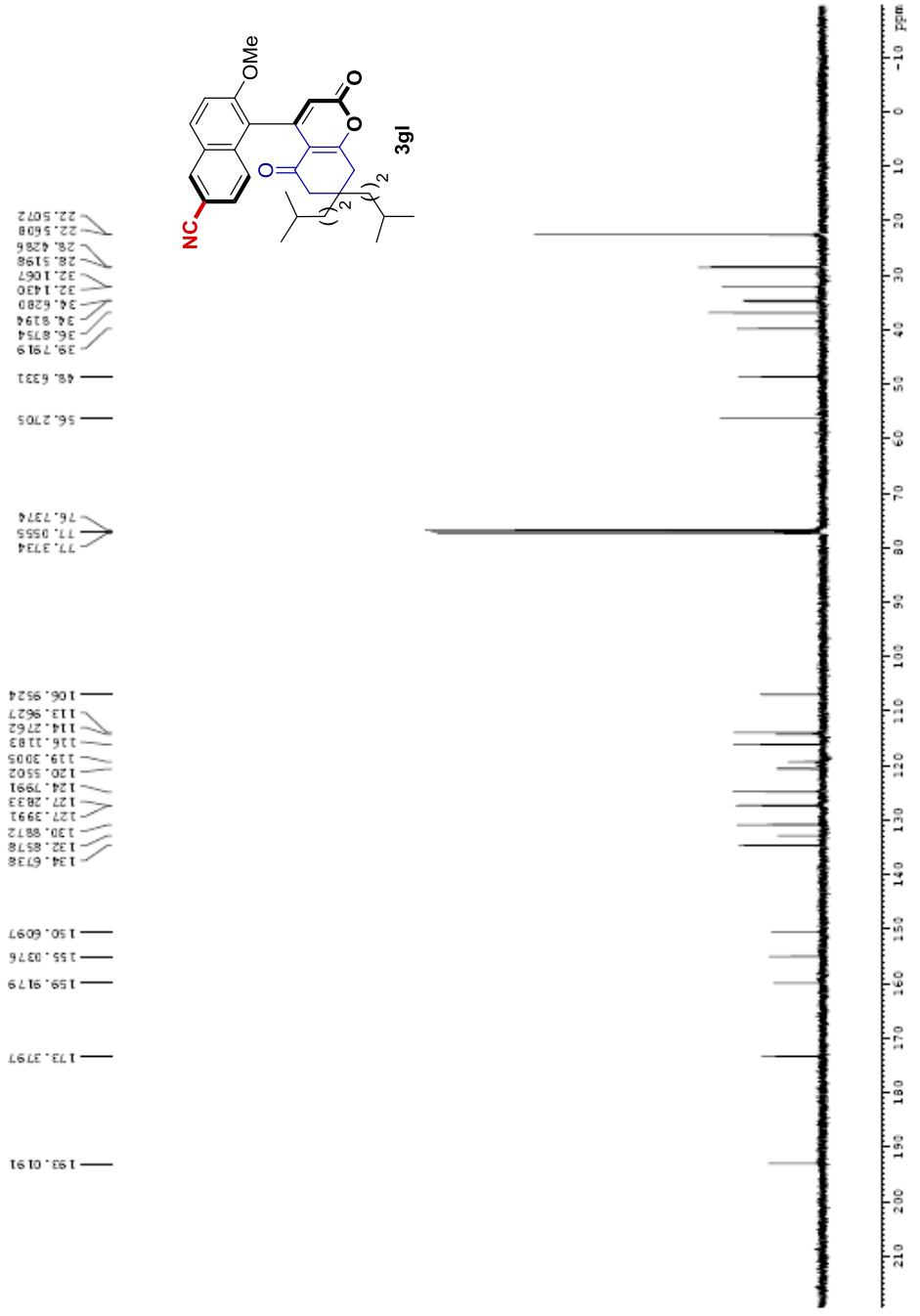



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.149 | 15098195 | 2112835 | 94.974 | 96.593 |
| 2 | 8.132 | 798923 | 74526 | 5.026 | 3.407 |
| Total | | 15897118 | 2187361 | 100.000 | 100.000 |

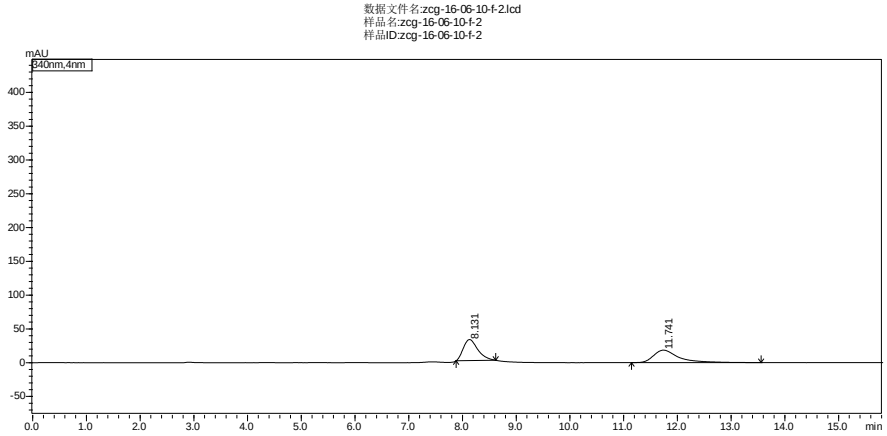
**Supplementary Figure 73. $^{1}$H NMR Spectrum of 3gl**



**Supplementary Figure 74. $^{13}$C NMR Spectrum of 3gl**

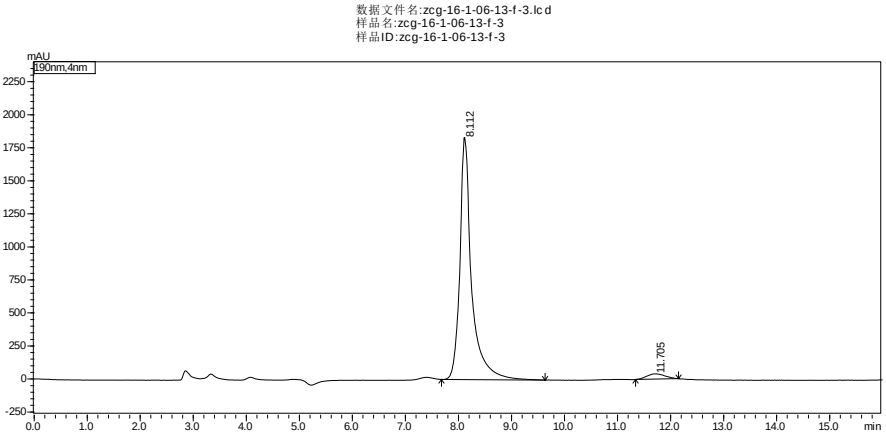


**Supplementary Figure 75. HPLC Spectrum of racemic 3gl**



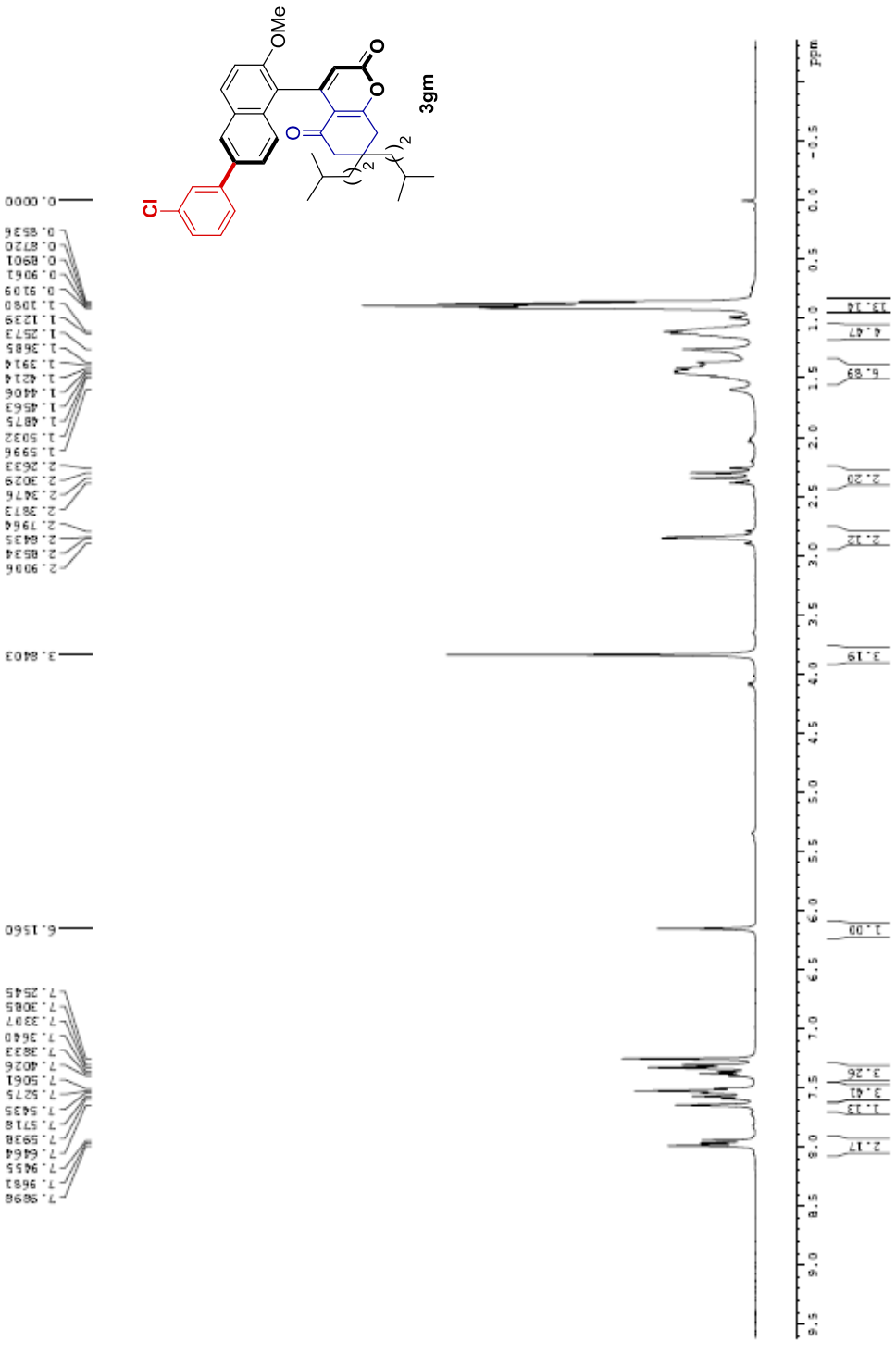

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 8.131 | 587408 | 31133 | 49.491 | 62.851 |
| 2 | 11.741 | 599478 | 18402 | 50.509 | 37.149 |
| Total | | 1186886 | 49535 | 100.000 | 100.000 |

## Supplementary Figure 76. HPLC Spectrum of 3gl

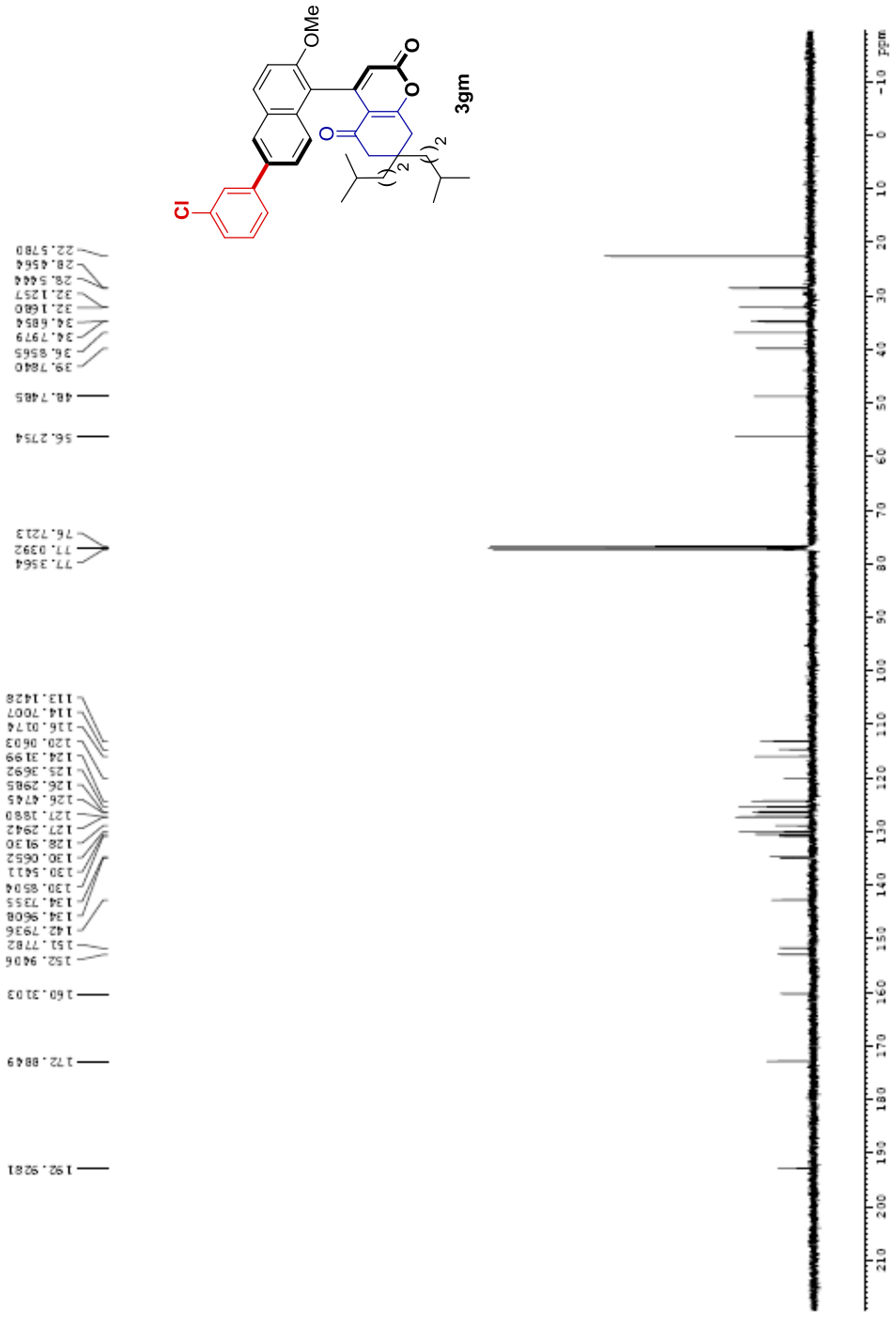



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 8.112 | 28314251 | 1831659 | 96.789 | 97.893 |
| 2 | 11.705 | 939237 | 39423 | 3.211 | 2.107 |
| Total | | 29253488 | 1871082 | 100.000 | 100.000 |

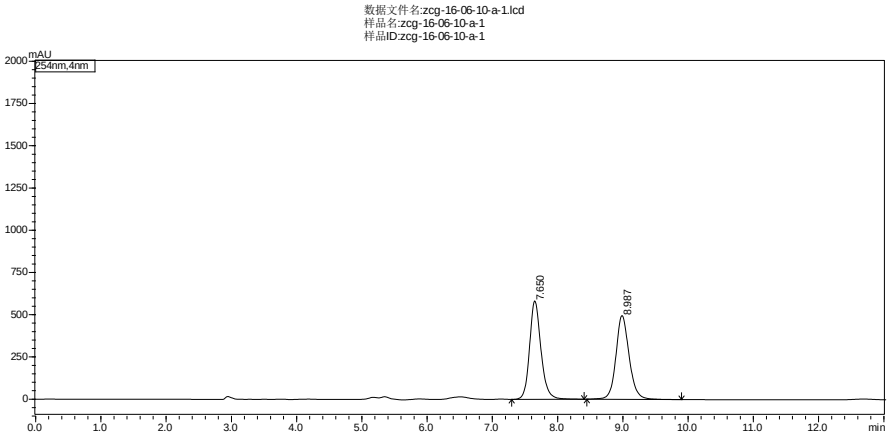
**Supplementary Figure 77. $^{1}$H NMR Spectrum of 3gm**



**Supplementary Figure 78. $^{13}$C NMR Spectrum of 3gm**

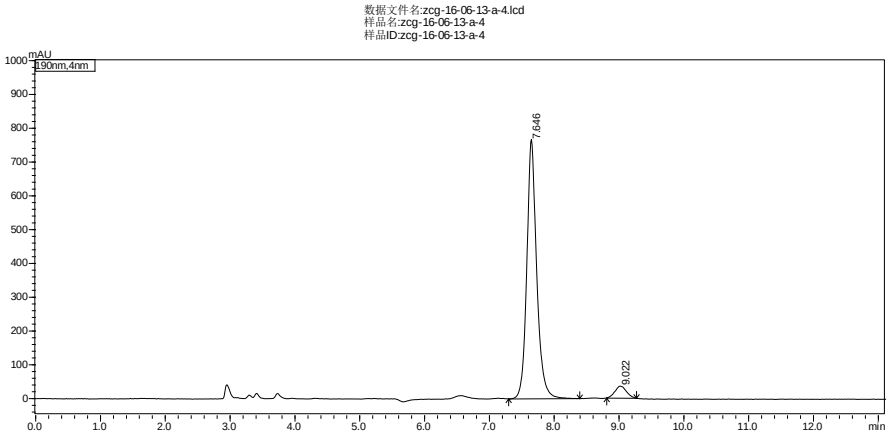


**Supplementary Figure 79. HPLC Spectrum of racemic 3gm**



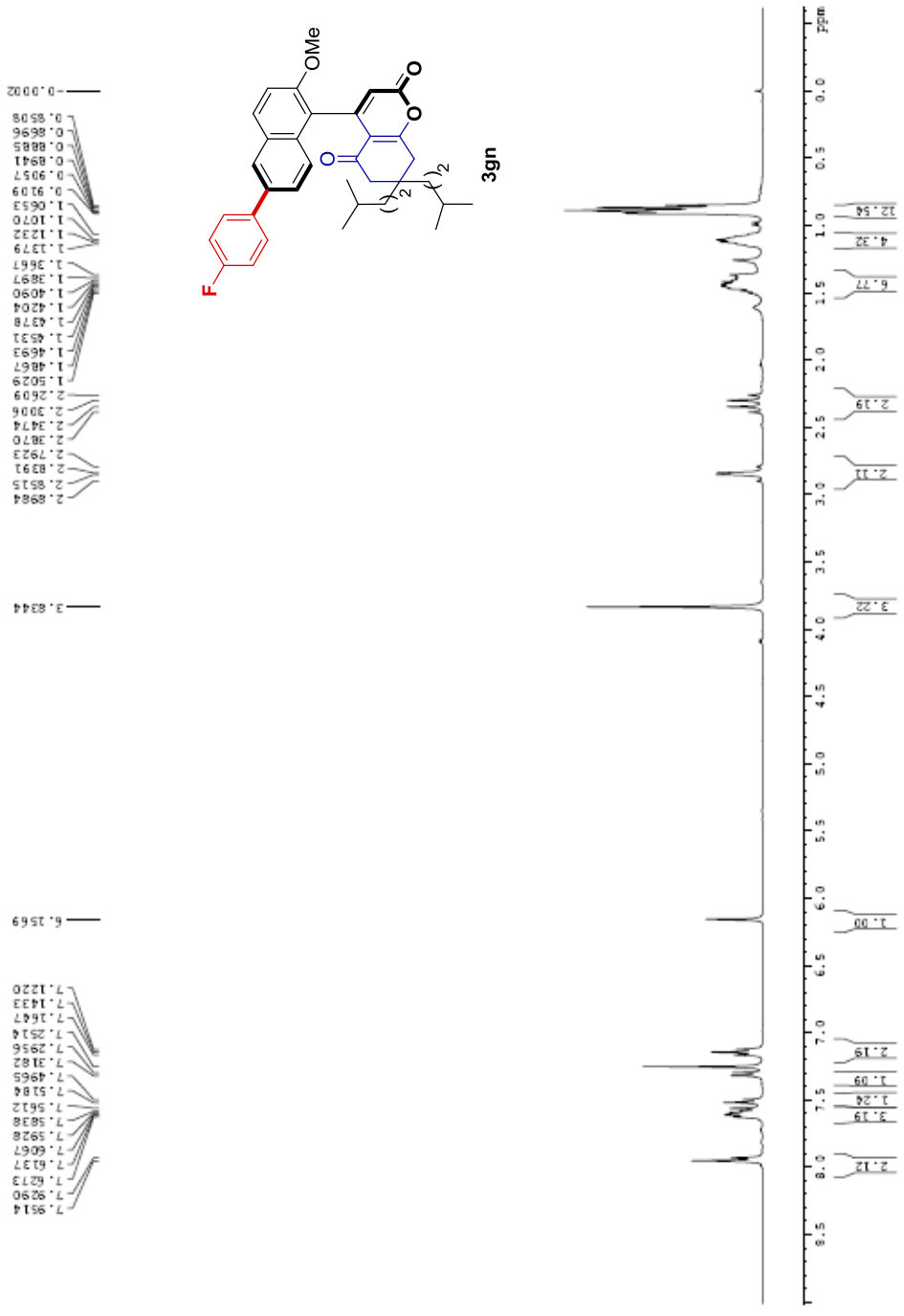

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 7.650 | 7077812 | 582844 | 50.279 | 54.061 |
| 2 | 8.987 | 6999163 | 495284 | 49.721 | 45.939 |
| Total | | 14076975 | 1078128 | 100.000 | 100.000 |

## Supplementary Figure 80. HPLC Spectrum of 3gm

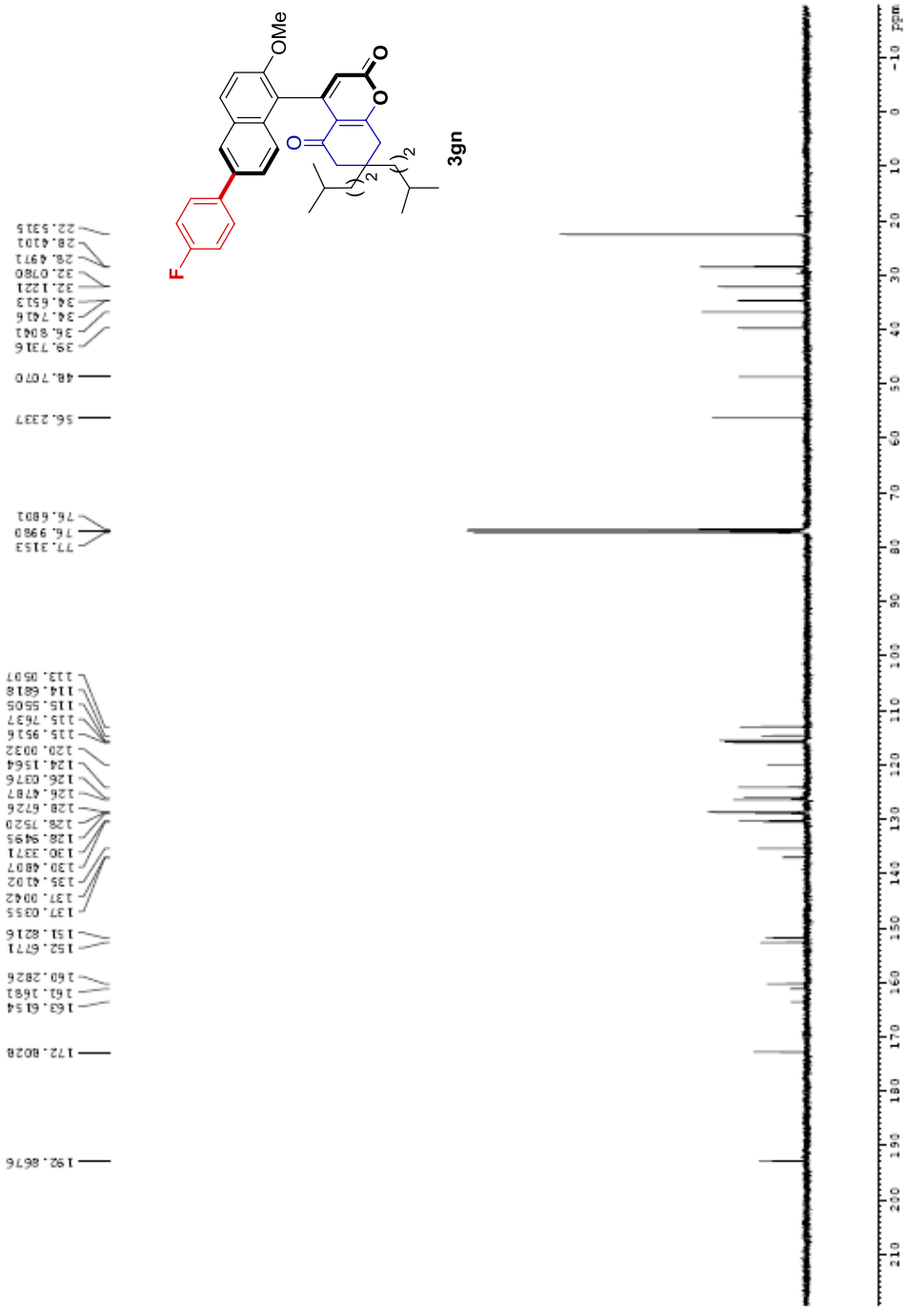



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 7.646 | 8154268 | 768209 | 94.861 | 95.587 |
| 2 | 9.022 | 441758 | 35464 | 5.139 | 4.413 |
| Total | | 8596026 | 803673 | 100.000 | 100.000 |

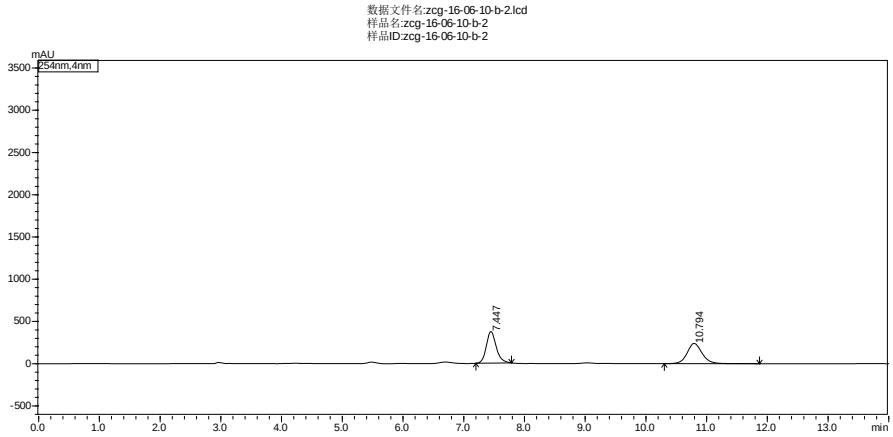
**Supplementary Figure 81. $^{1}$H NMR Spectrum of 3gn**



**Supplementary Figure 82. $^{13}$C NMR Spectrum of 3gn**

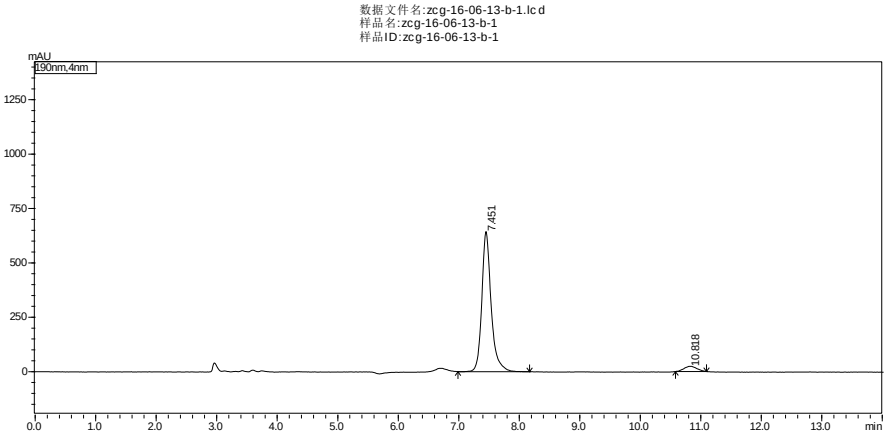


**Supplementary Figure 83. HPLC Spectrum of racemic 3gn**



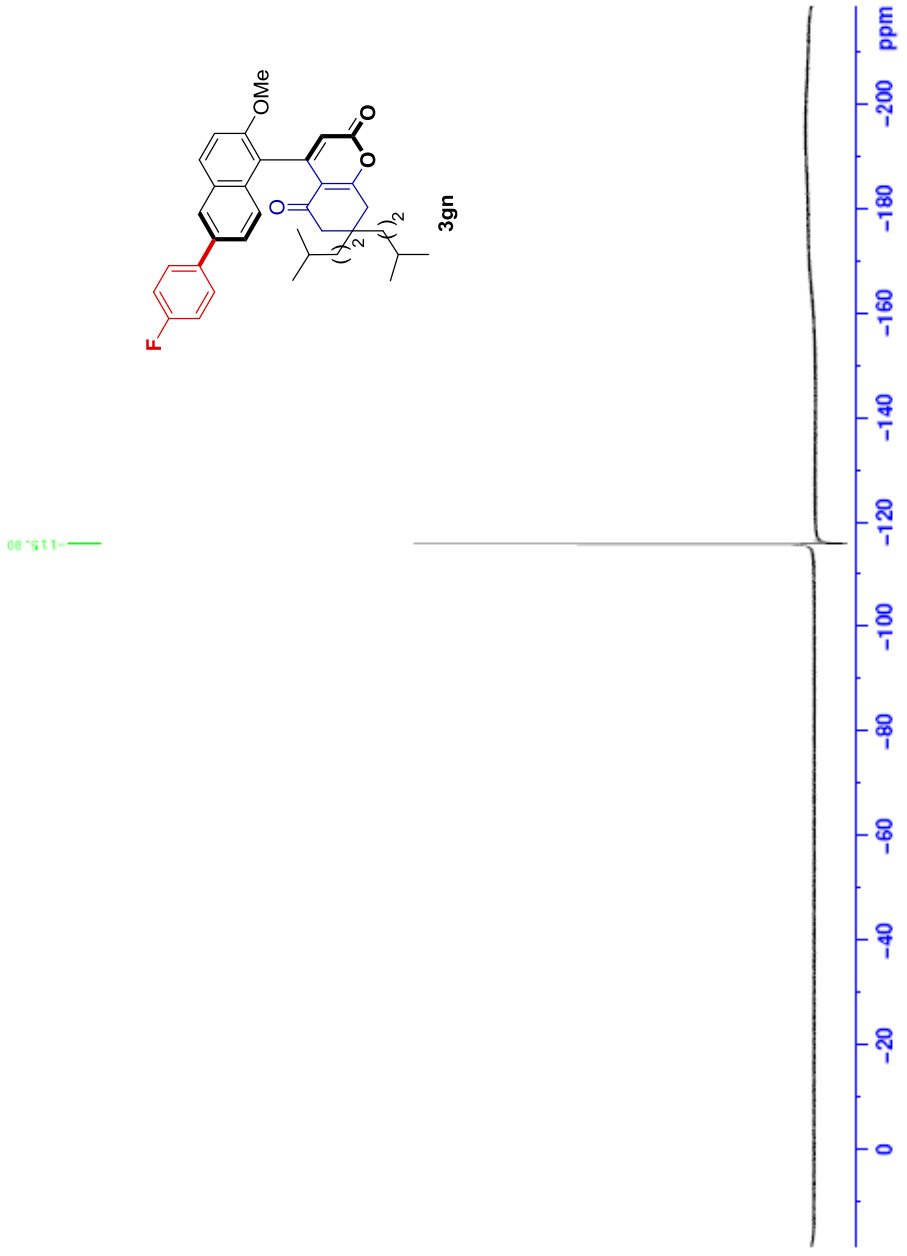

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 7.447 | 4271126 | 373837 | 50.981 | 60.969 |
| 2 | 10.794 | 4106737 | 239327 | 49.019 | 39.031 |
| Total | | 8377862 | 613164 | 100.000 | 100.000 |

## Supplementary Figure 84. HPLC Spectrum of 3gn

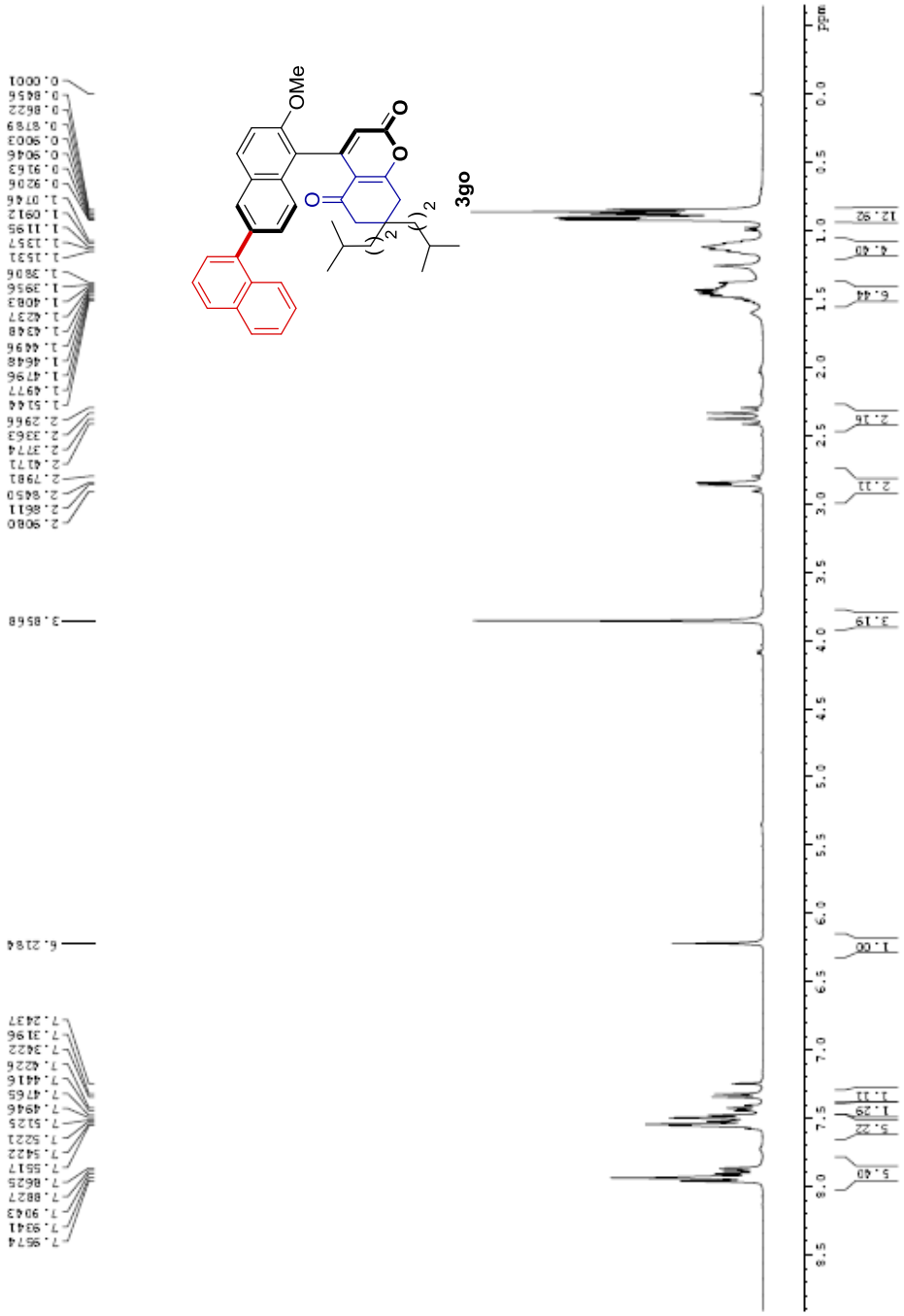



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 7.451 | 6933821 | 643907 | 95.157 | 96.390 |
| 2 | 10.818 | 352928 | 24113 | 4.843 | 3.610 |
| Total | | 7286749 | 668021 | 100.000 | 100.000 |

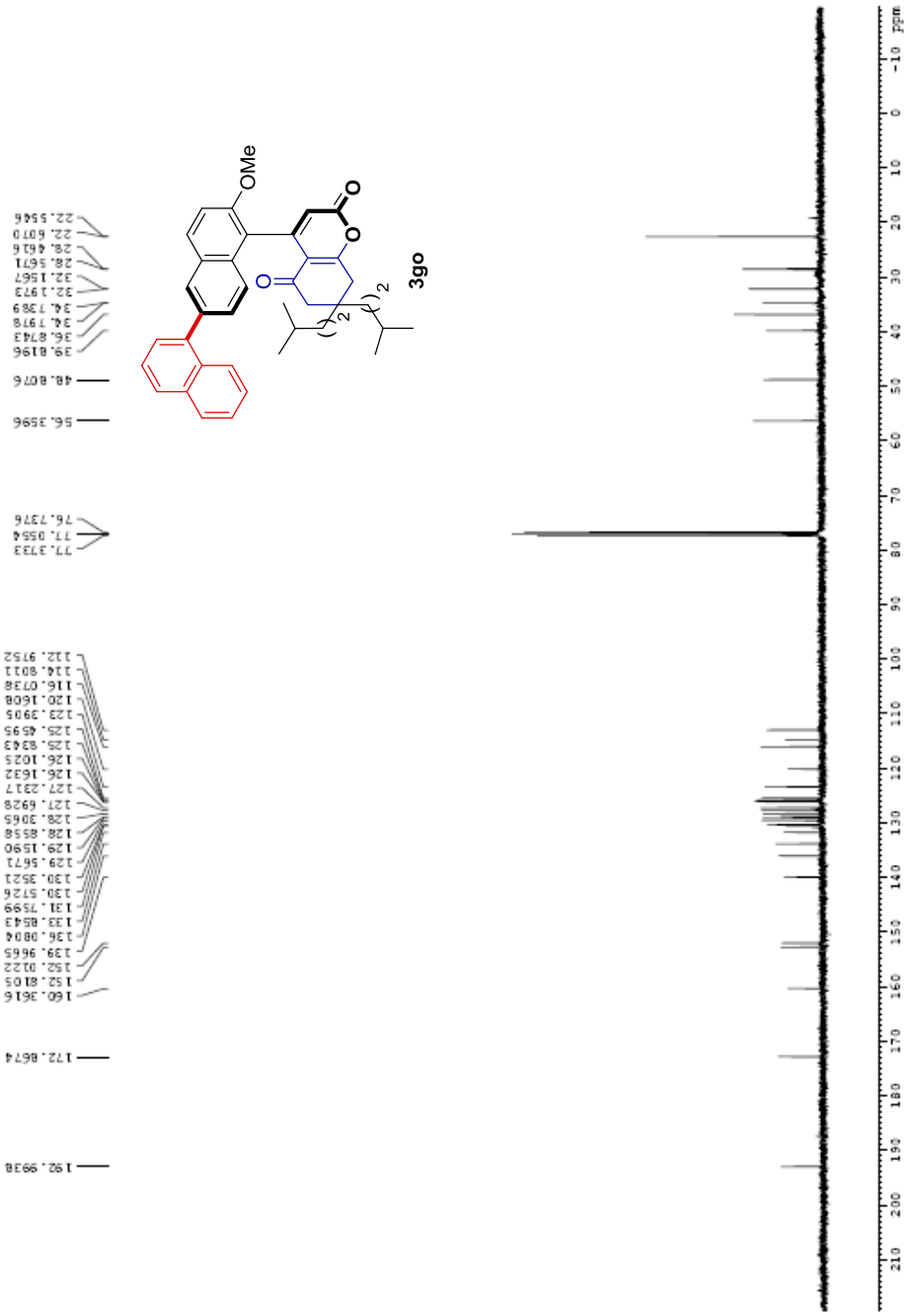
**Supplementary Figure 85. $^{19}$F NMR Spectrum of 3gn**



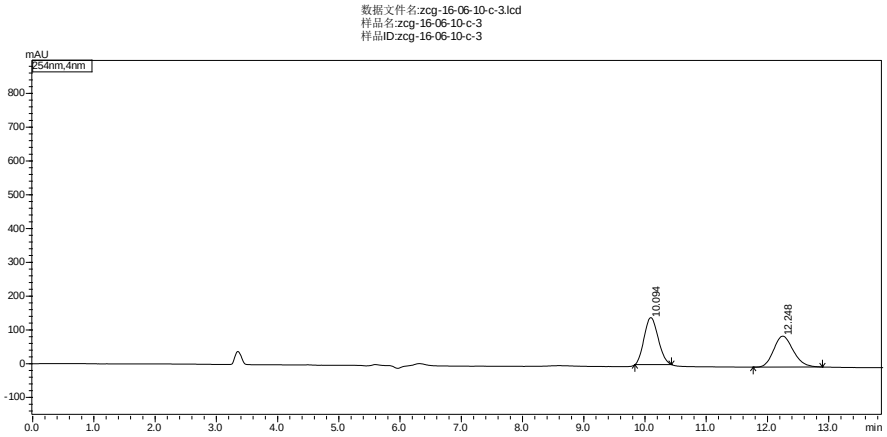
**Supplementary Figure 86. $^{1}$H NMR Spectrum of 3go**



**Supplementary Figure 87. $^{13}$C NMR Spectrum of 3go**

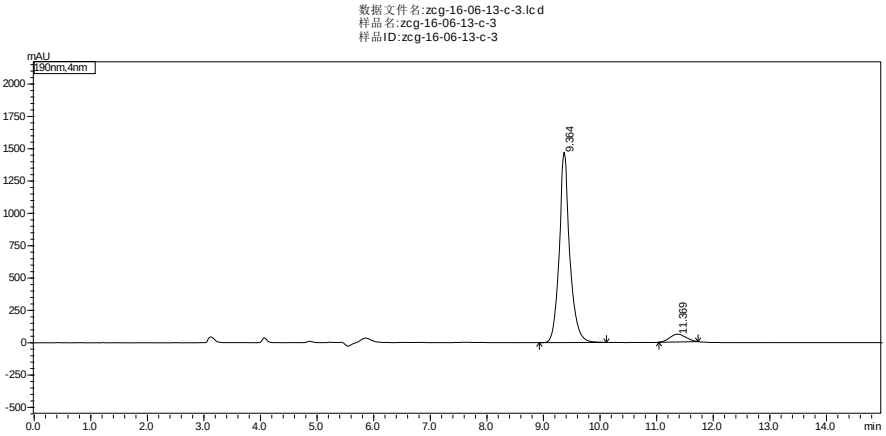


**Supplementary Figure 88. HPLC Spectrum of racemic 3go**



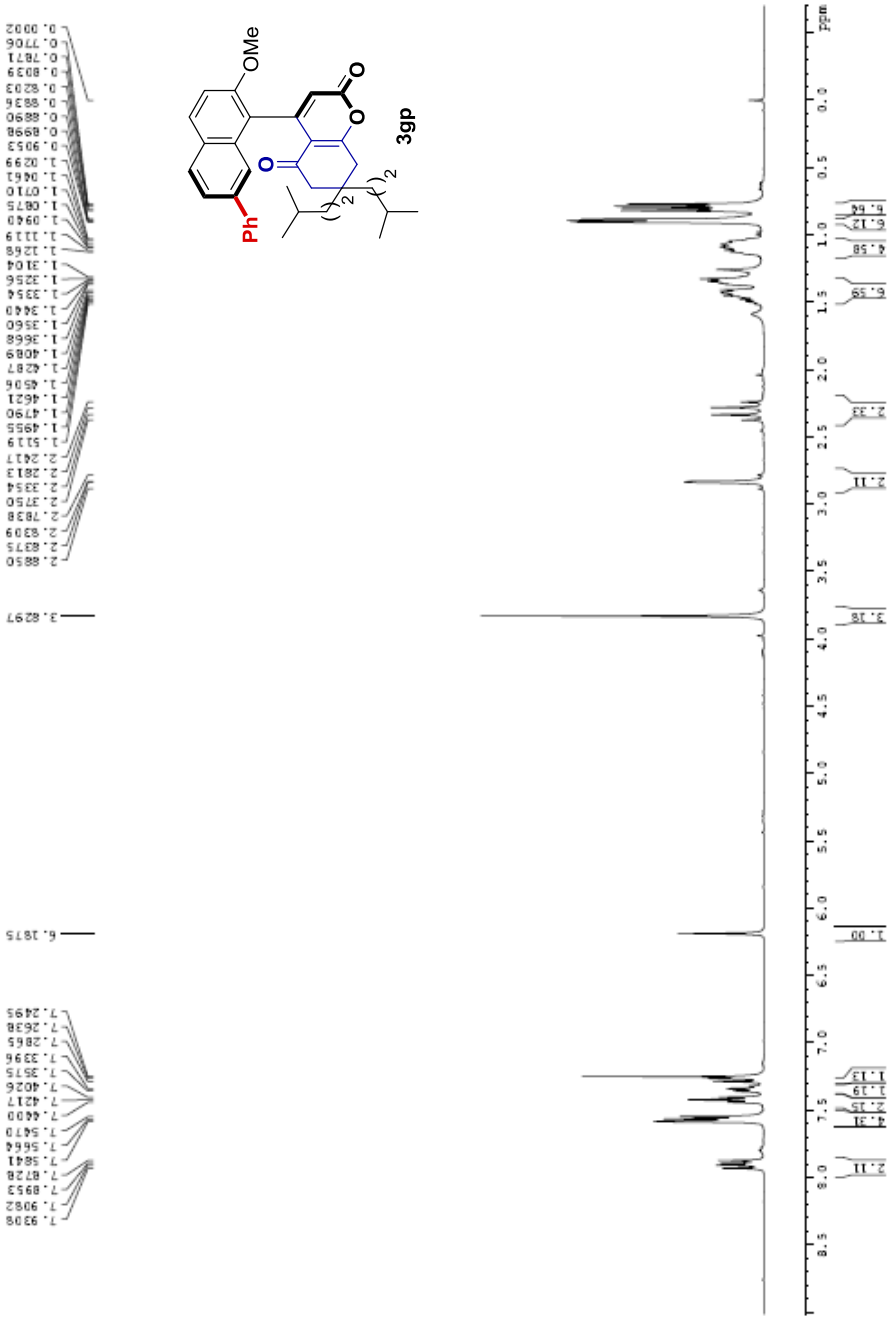

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 10.094 | 2221219 | 139039 | 52.106 | 60.283 |
| 2 | 12.248 | 2041701 | 91605 | 47.894 | 39.717 |
| Total | | 4262920 | 230643 | 100.000 | 100.000 |

## Supplementary Figure 89. HPLC Spectrum of 3go

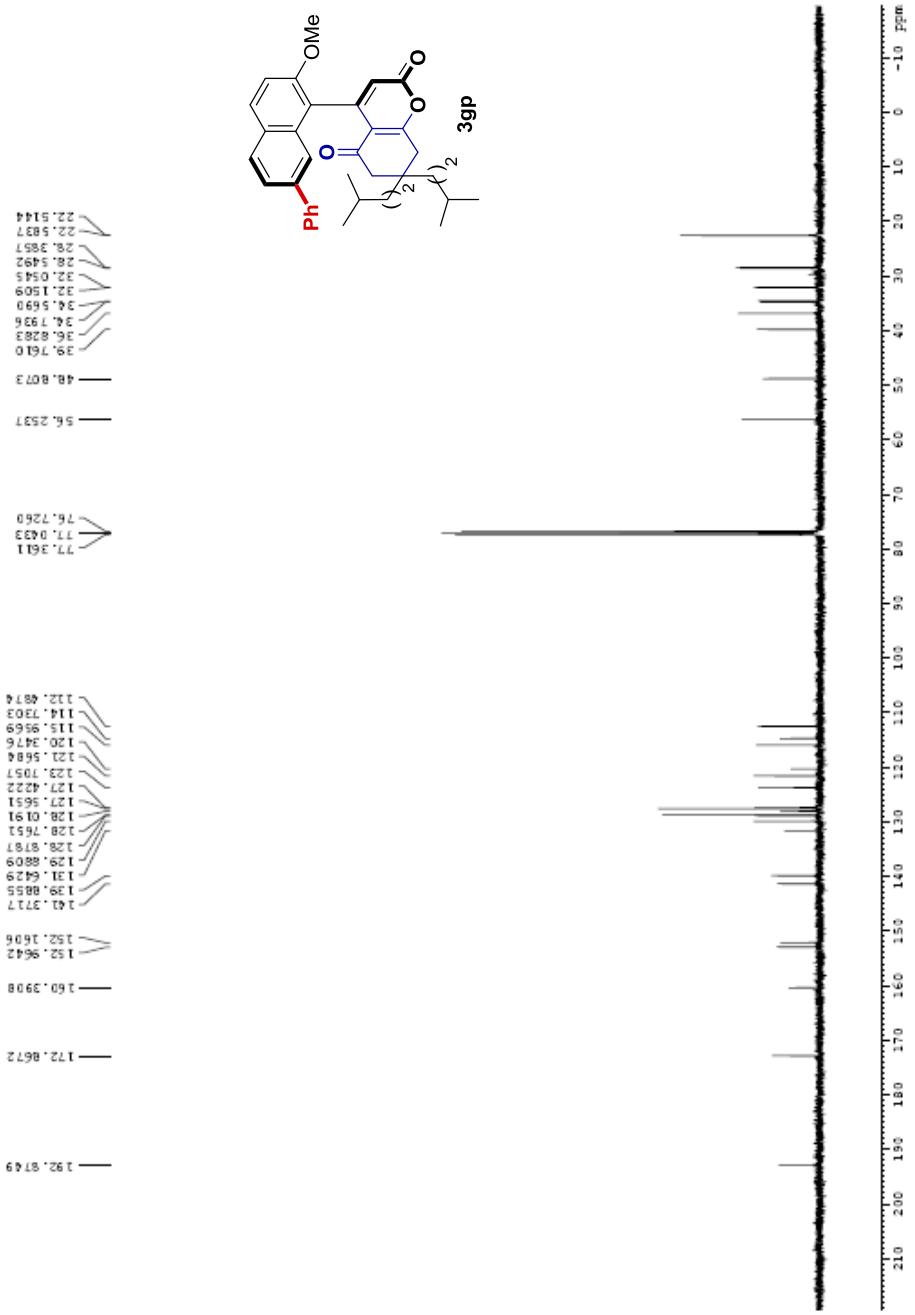



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 9.364 | 18923994 | 1471967 | 94.056 | 96.084 |
| 2 | 11.369 | 1195912 | 59997 | 5.944 | 3.916 |
| Total | | 20119906 | 1531964 | 100.000 | 100.000 |

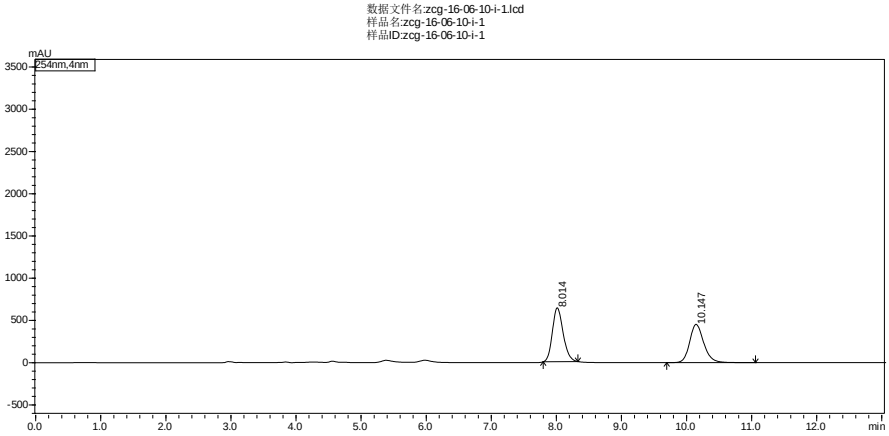
**Supplementary Figure 90. $^{1}$H NMR Spectrum of 3gp**



**Supplementary Figure 91. $^{13}$C NMR Spectrum of 3gp**

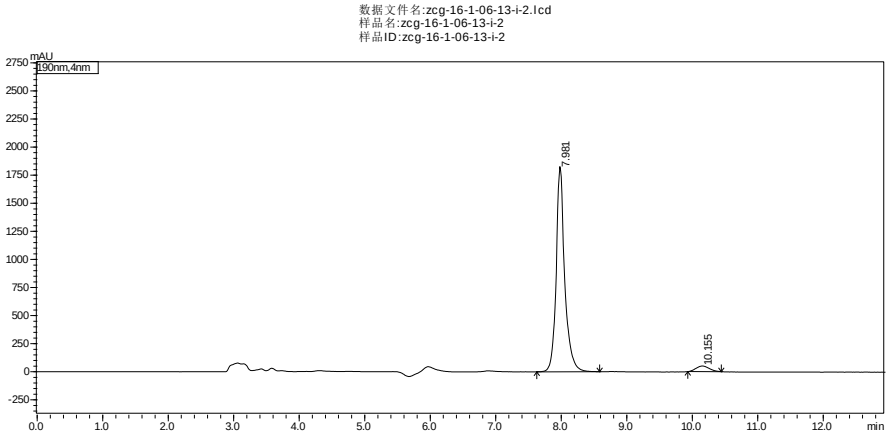


**Supplementary Figure 92. HPLC Spectrum of racemic 3gp**



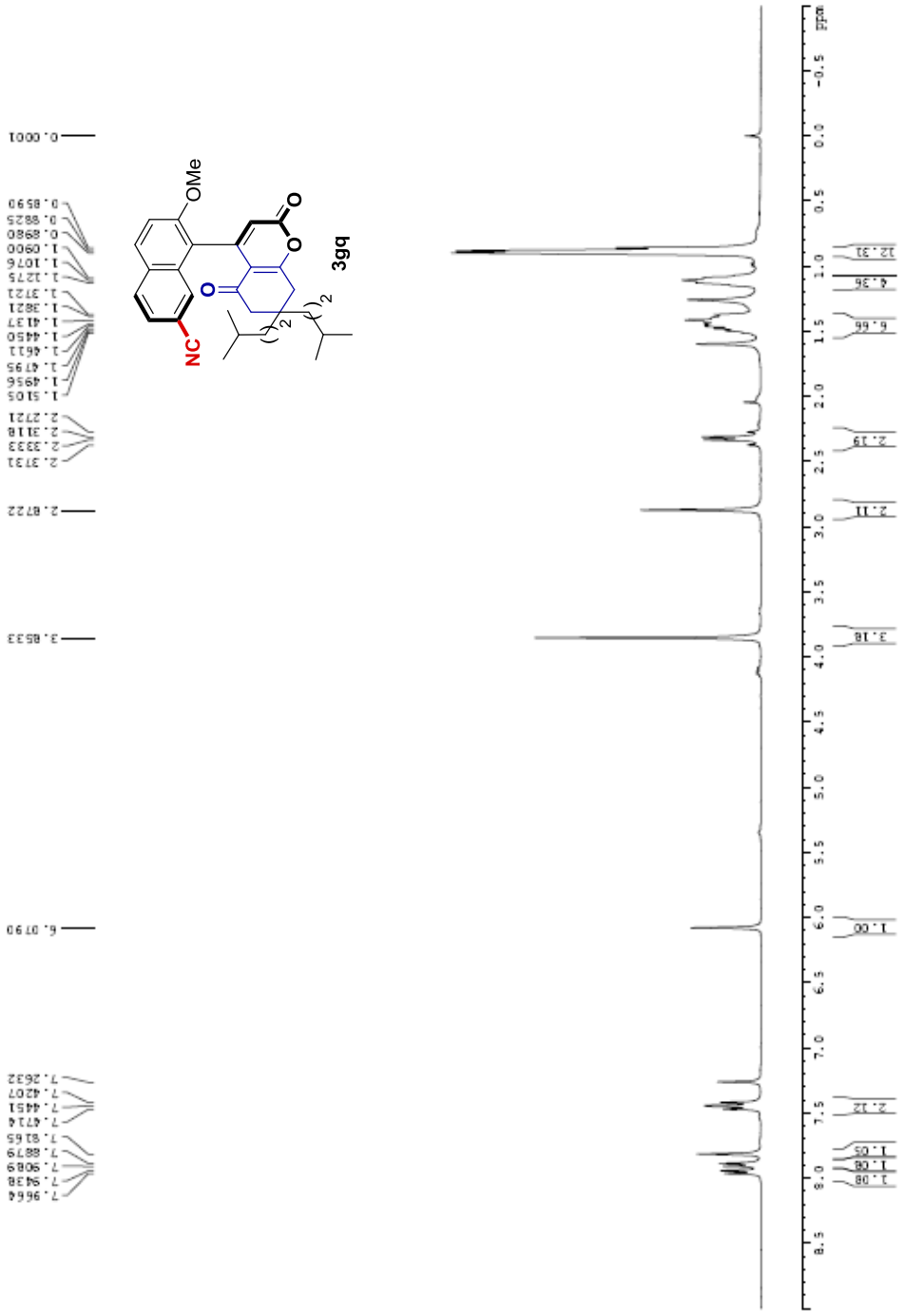

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 8.014 | 7364436 | 638487 | 51.877 | 58.463 |
| 2 | 10.147 | 6831546 | 453629 | 48.123 | 41.537 |
| Total | | 14195982 | 1092117 | 100.000 | 100.000 |

## Supplementary Figure 93. HPLC Spectrum of 3gp

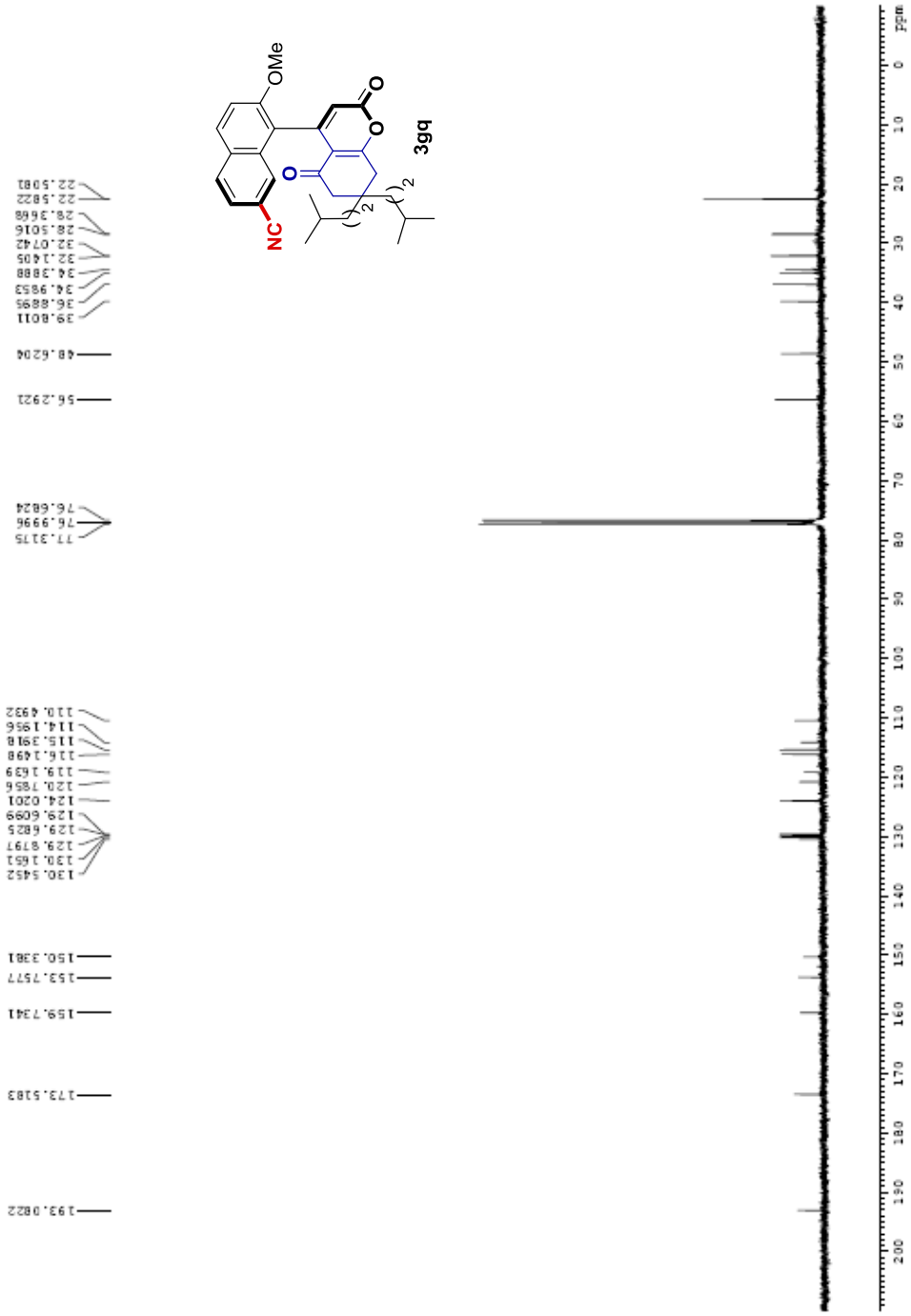



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 7.981 | 16583727 | 1827685 | 95.927 | 97.304 |
| 2 | 10.155 | 704089 | 50645 | 4.073 | 2.696 |
| Total | | 17287816 | 1878330 | 100.000 | 100.000 |

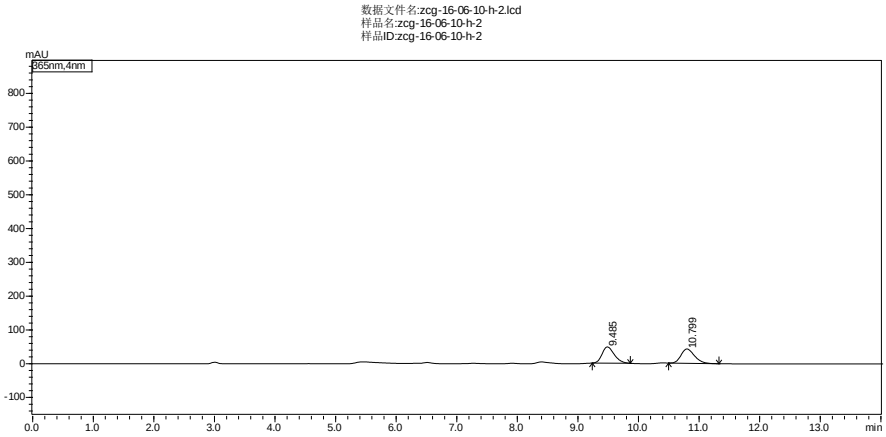
**Supplementary Figure 94. $^{1}$H NMR Spectrum of 3gq**



**Supplementary Figure 95. $^{13}$C NMR Spectrum of 3gq**

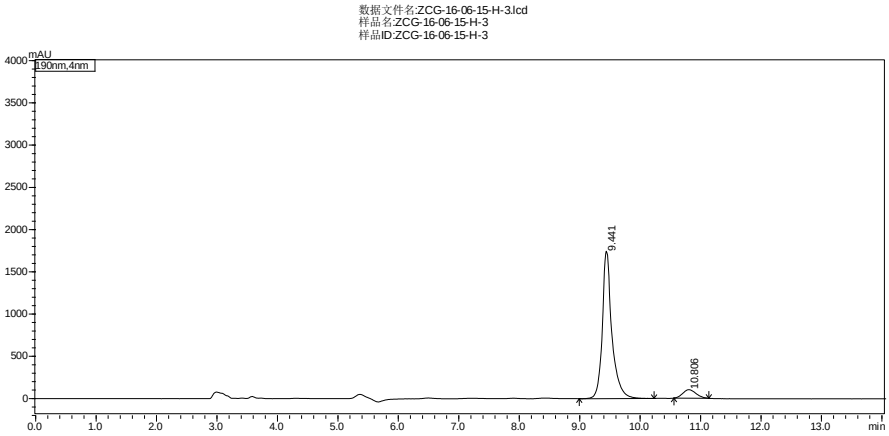


**Supplementary Figure 96. HPLC Spectrum of racemic 3gq**



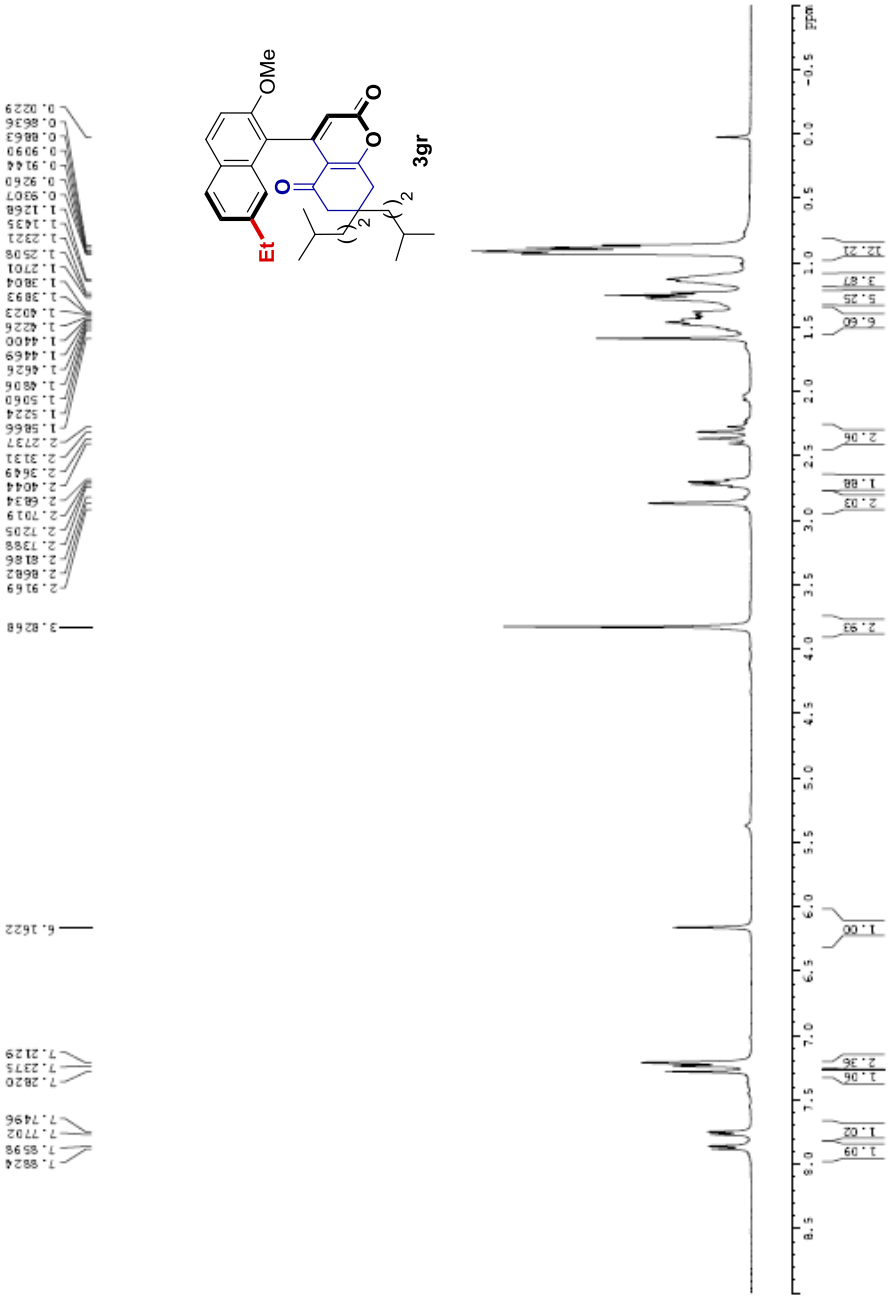

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 9.485 | 676990 | 48172 | 50.573 | 53.134 |
| 2 | 10.799 | 661654 | 42489 | 49.427 | 46.866 |
| Total | | 1338644 | 90661 | 100.000 | 100.000 |

## Supplementary Figure 97. HPLC Spectrum of 3gq

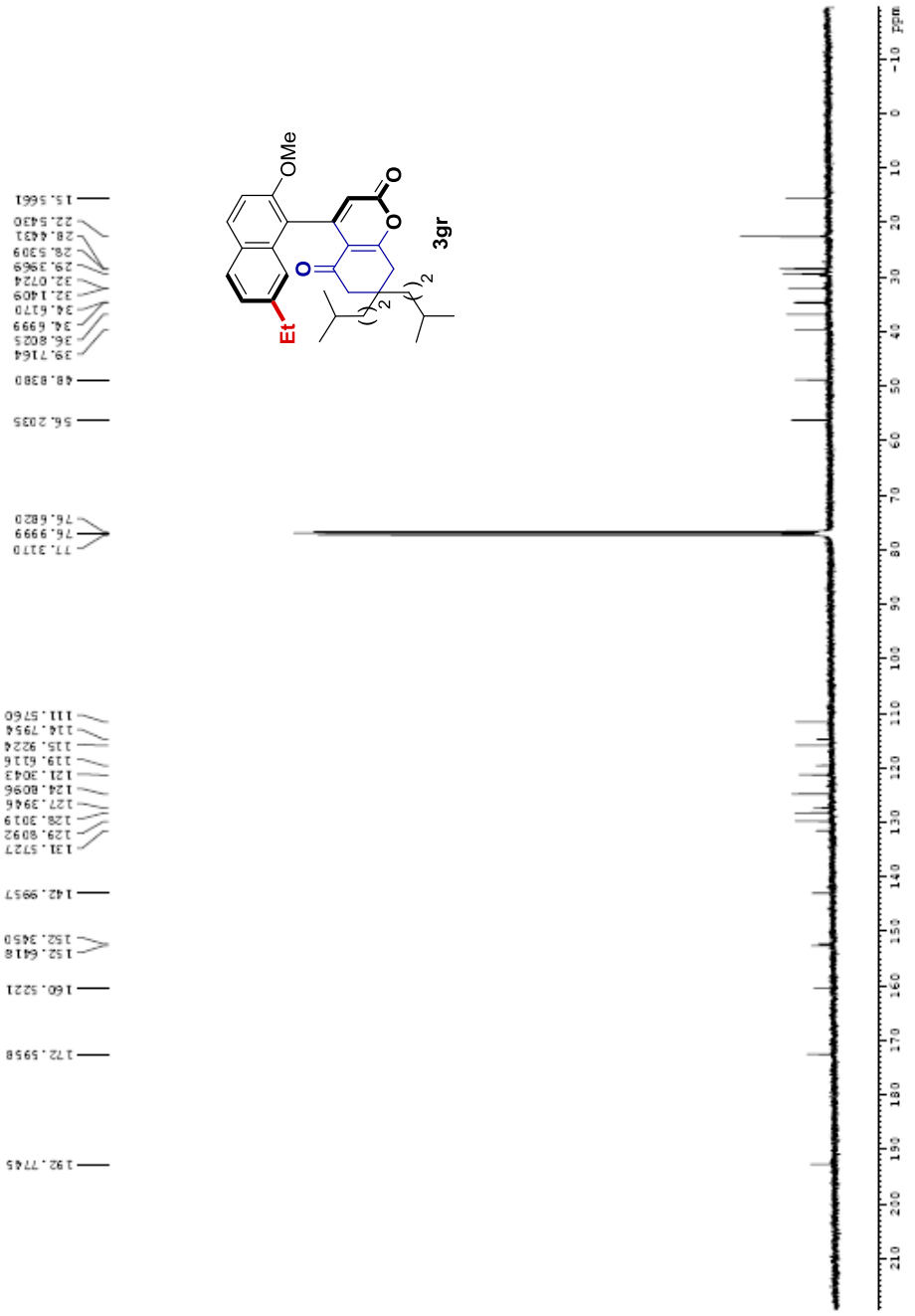



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 9.441 | 19233666 | 1746260 | 92.685 | 94.545 |
| 2 | 10.806 | 1518071 | 100753 | 7.315 | 5.455 |
| Total | | 20751737 | 1847013 | 100.000 | 100.000 |

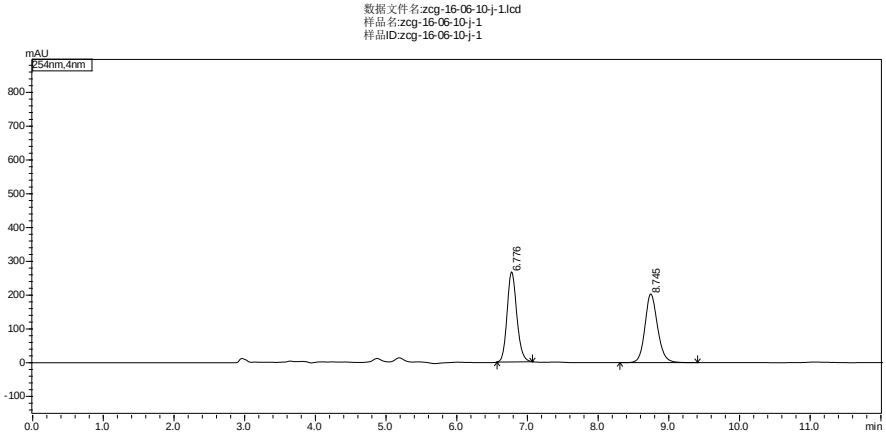
**Supplementary Figure 98. $^{1}$H NMR Spectrum of 3gr**



**Supplementary Figure 99. $^{13}$C NMR Spectrum of 3gr**

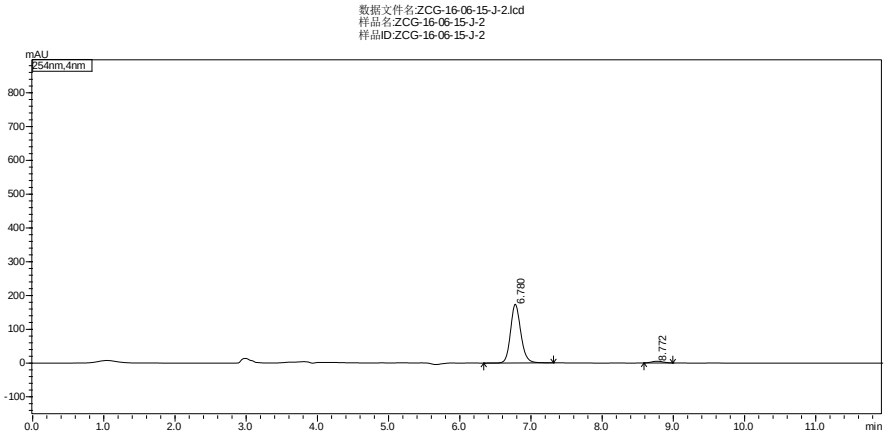


**Supplementary Figure 100. HPLC Spectrum of racemic 3gr**



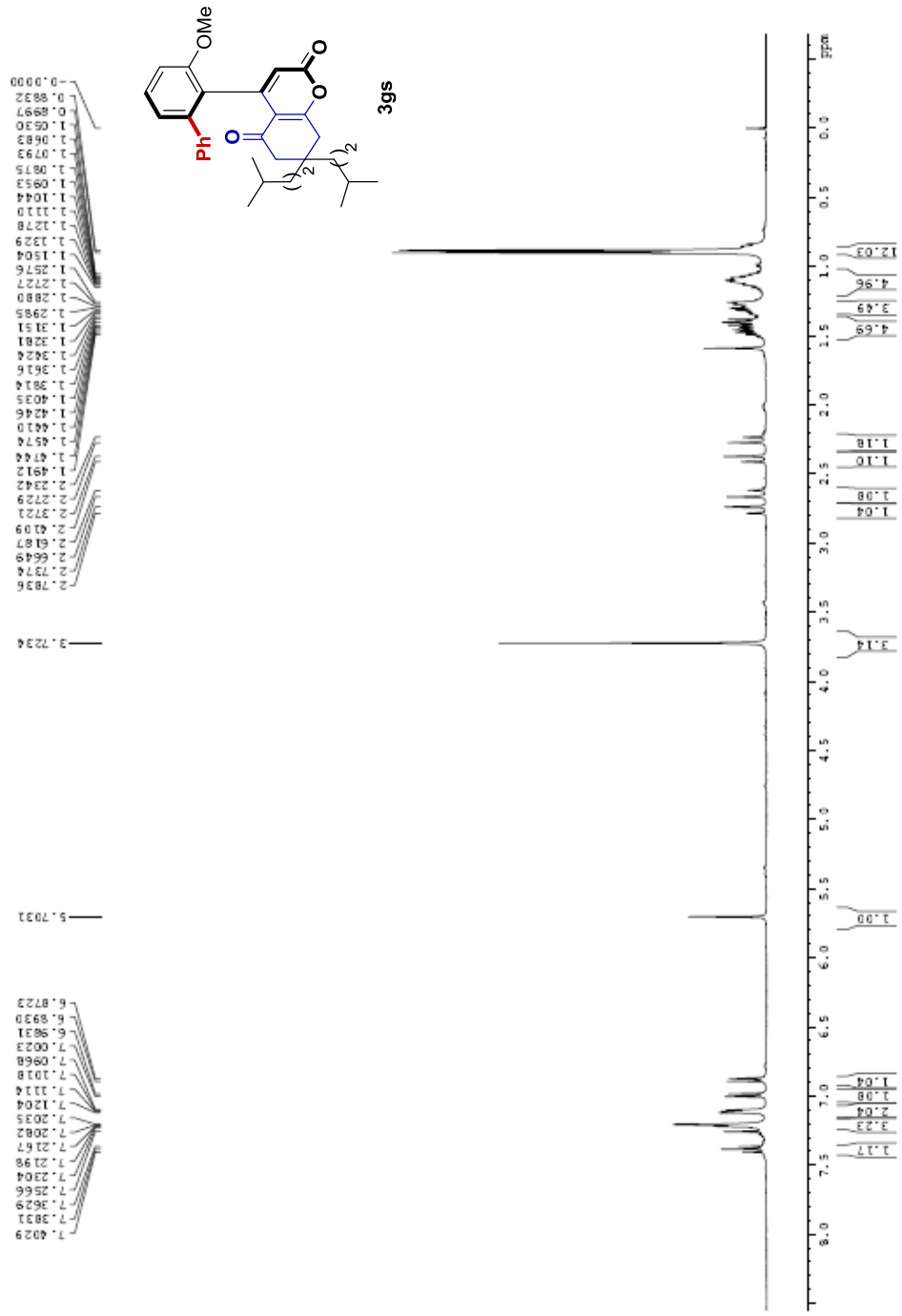

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.776 | 2540743 | 266769 | 50.166 | 56.733 |
| 2 | 8.745 | 2523925 | 203449 | 49.834 | 43.267 |
| Total | | 5064668 | 470218 | 100.000 | 100.000 |

## Supplementary Figure 101. HPLC Spectrum of 3gr

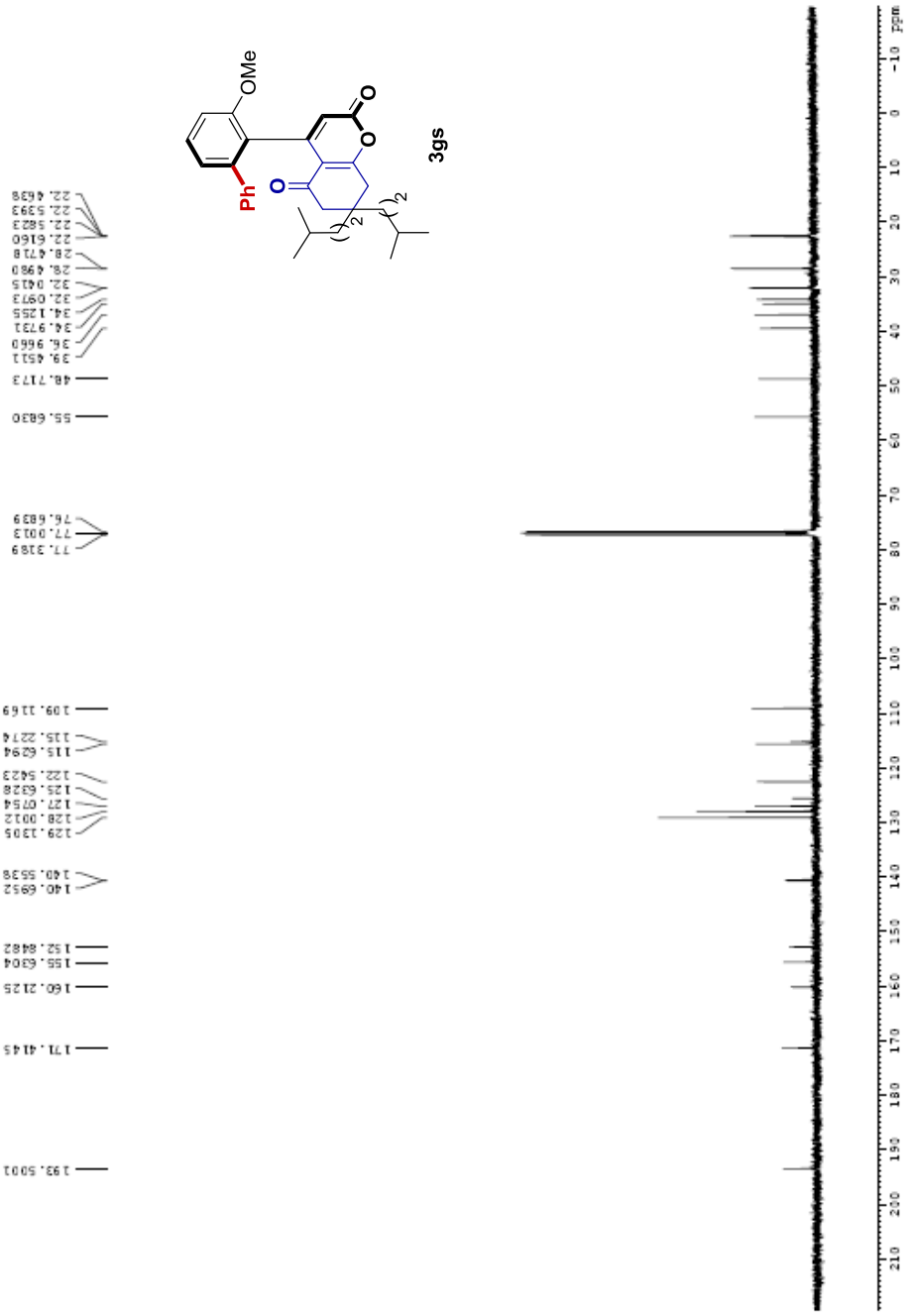



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.780 | 1738998 | 173713 | 96.799 | 97.149 |
| 2 | 8.772 | 57500 | 5098 | 3.201 | 2.851 |
| Total | | 1796497 | 178811 | 100.000 | 100.000 |

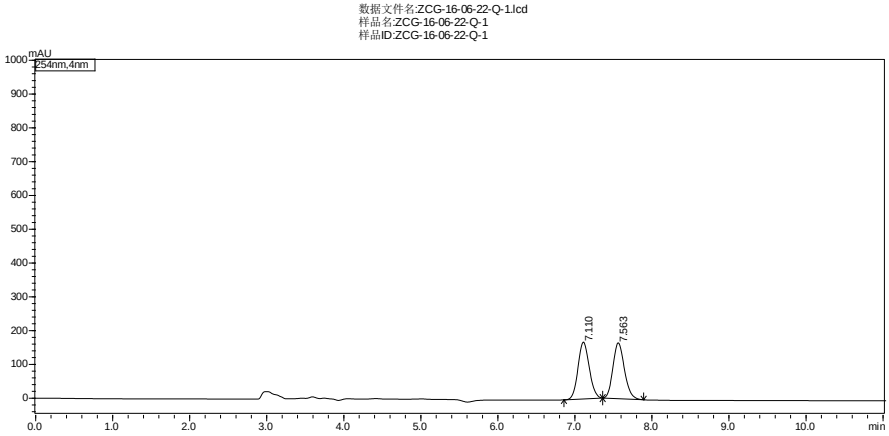
**Supplementary Figure 102. $^{1}$H NMR Spectrum of 3gs**



**Supplementary Figure 103. $^{13}$C NMR Spectrum of 3gs**

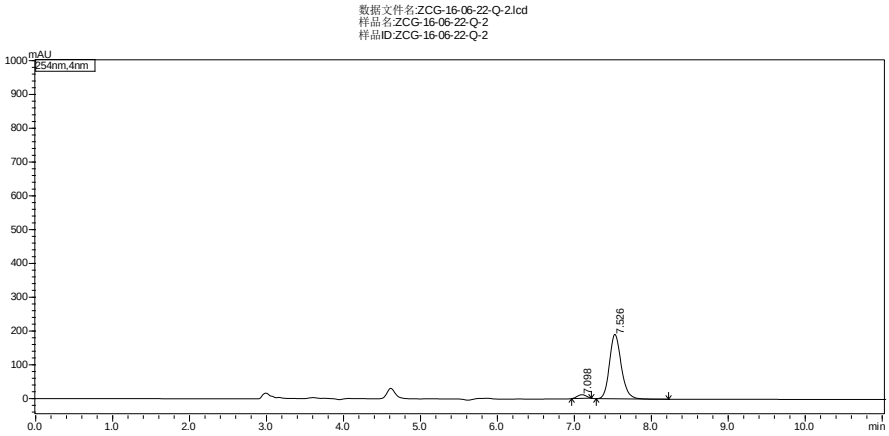


## Supplementary Figure 104. HPLC Spectrum of racemic 3gs



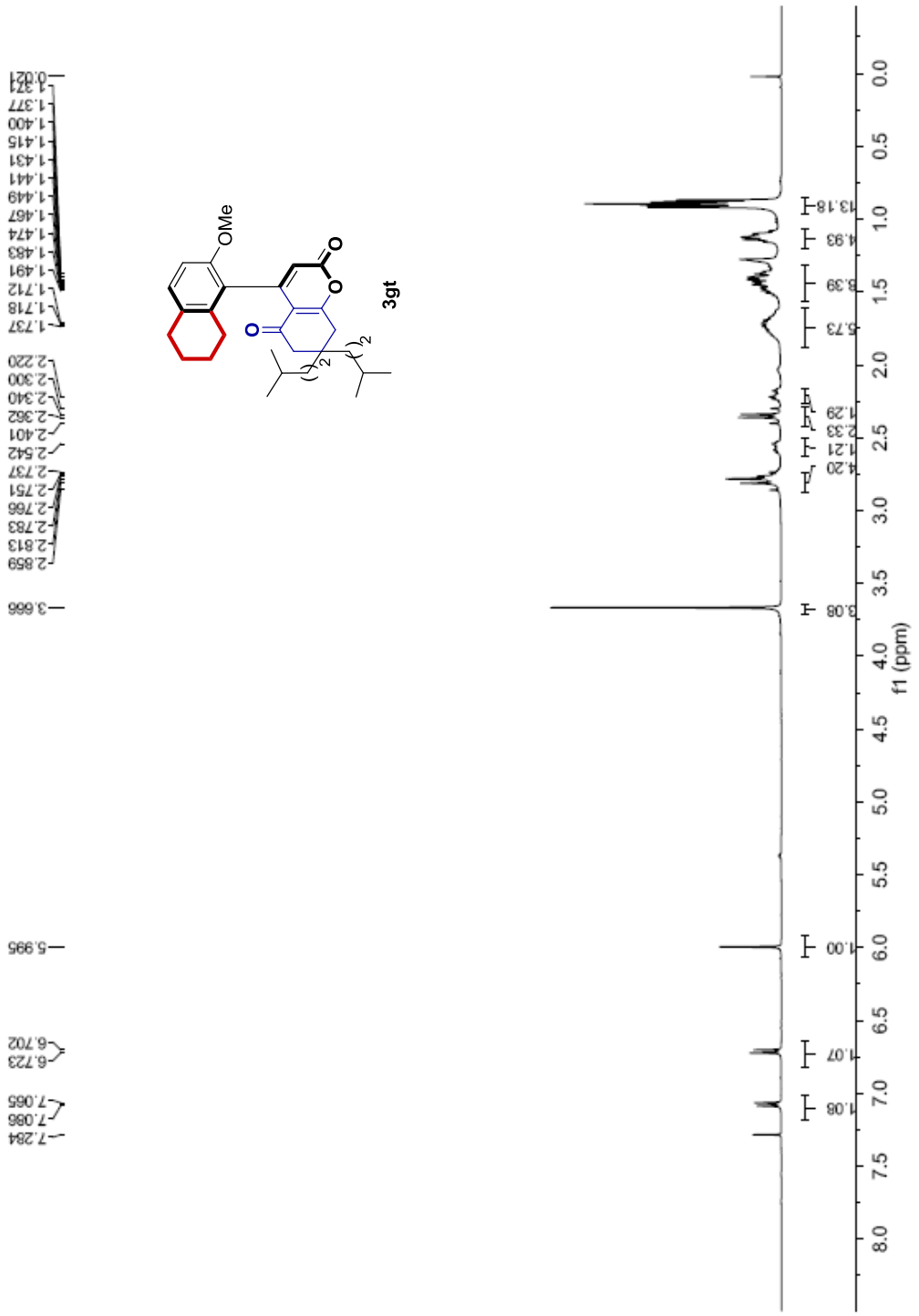

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 7.110 | 1715873 | 168339 | 49.969 | 50.426 |
| 2 | 7.563 | 1717971 | 165496 | 50.031 | 49.574 |
| Total | | 3433844 | 333835 | 100.000 | 100.000 |

## Supplementary Figure 105. HPLC Spectrum of 3gs

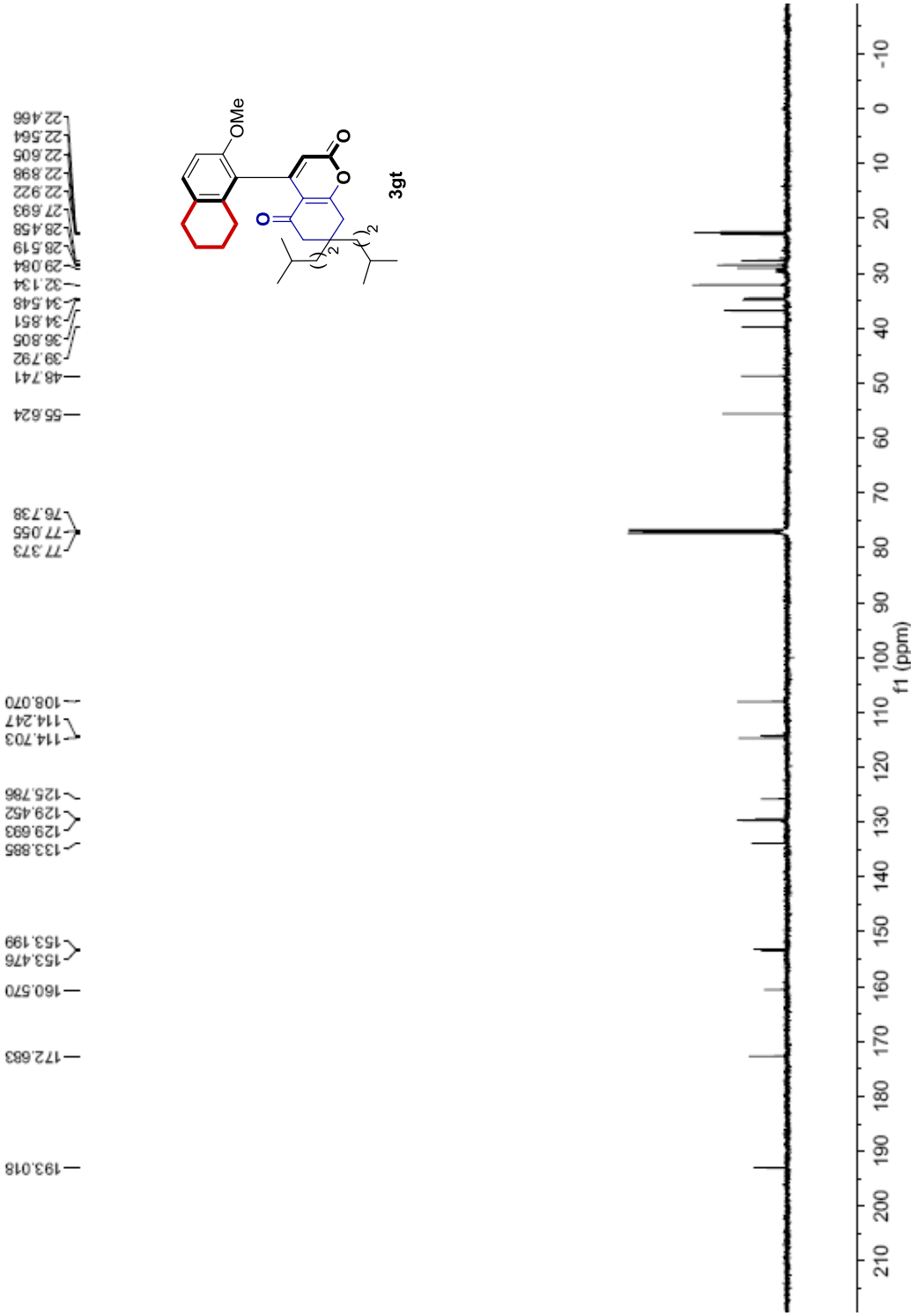



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 7.098 | 87885 | 10767 | 4.135 | 5.341 |
| 2 | 7.526 | 2037287 | 190826 | 95.865 | 94.659 |
| Total | | 2125172 | 201593 | 100.000 | 100.000 |

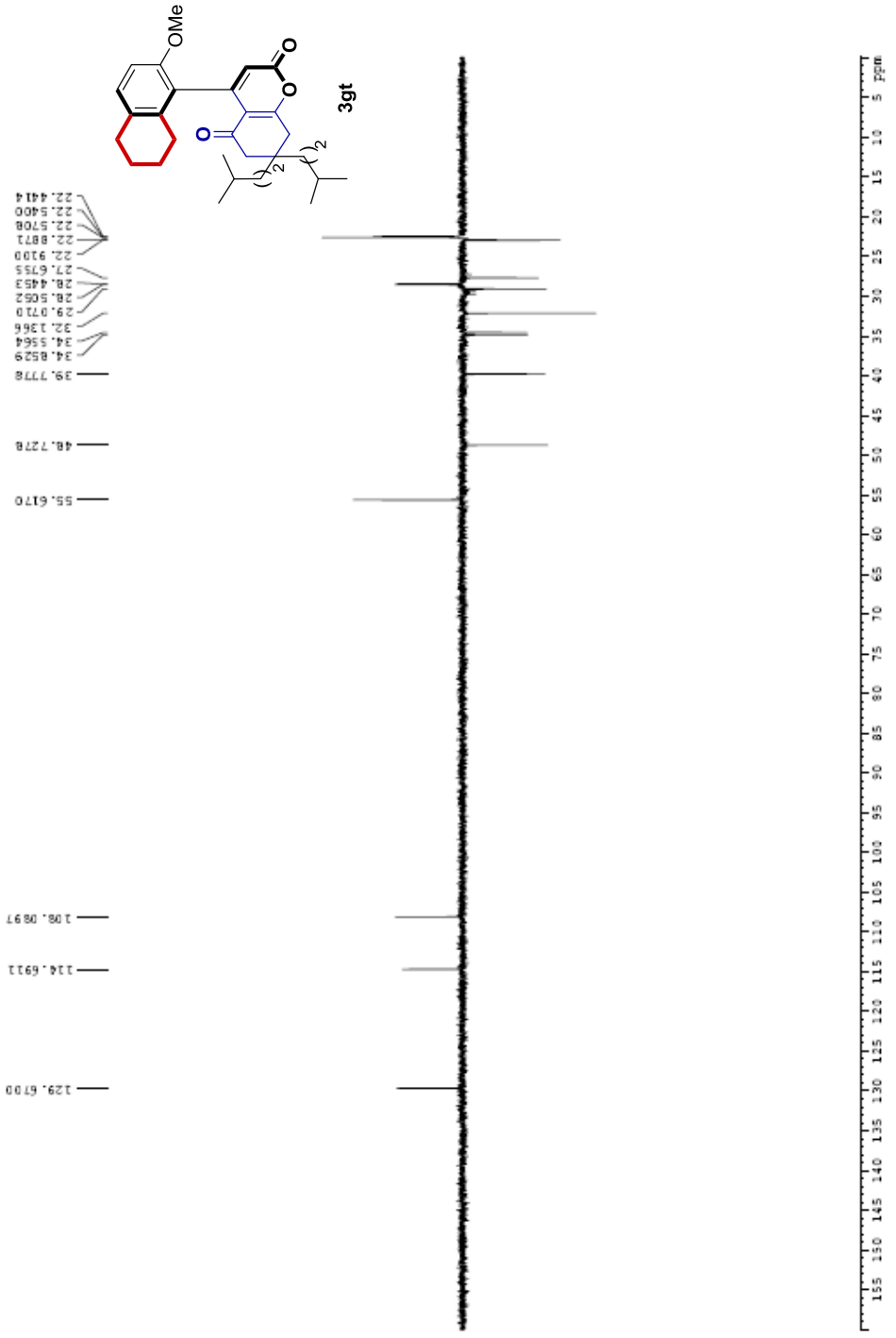
**Supplementary Figure 106. $^{1}$H NMR Spectrum of 3gt**



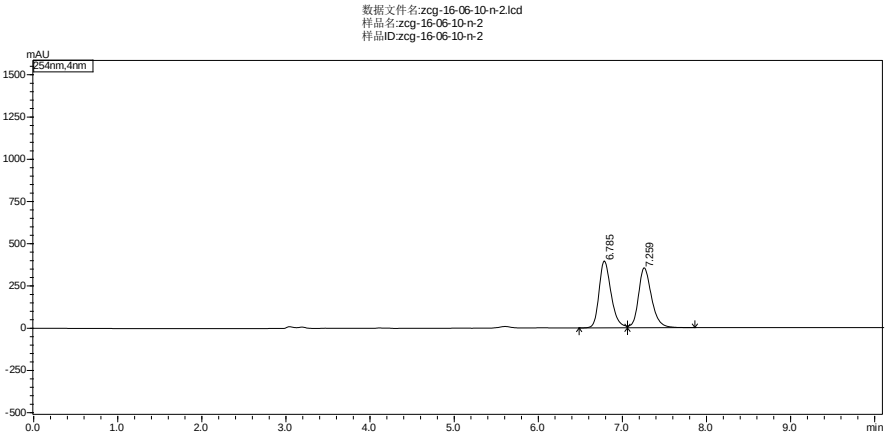
**Supplementary Figure 107. $^{13}$C NMR Spectrum of 3gt**



**Supplementary Figure 108. $^{13}$C NMR Spectrum of 3gt**

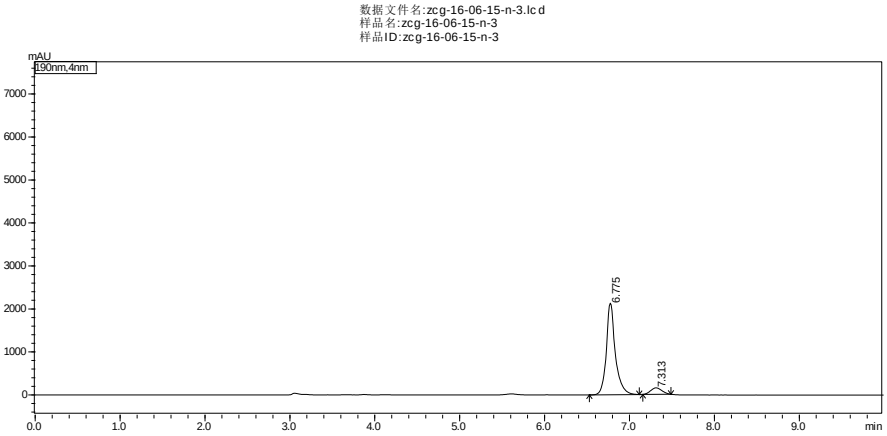


**Supplementary Figure 109. HPLC Spectrum of racemic 3gt**



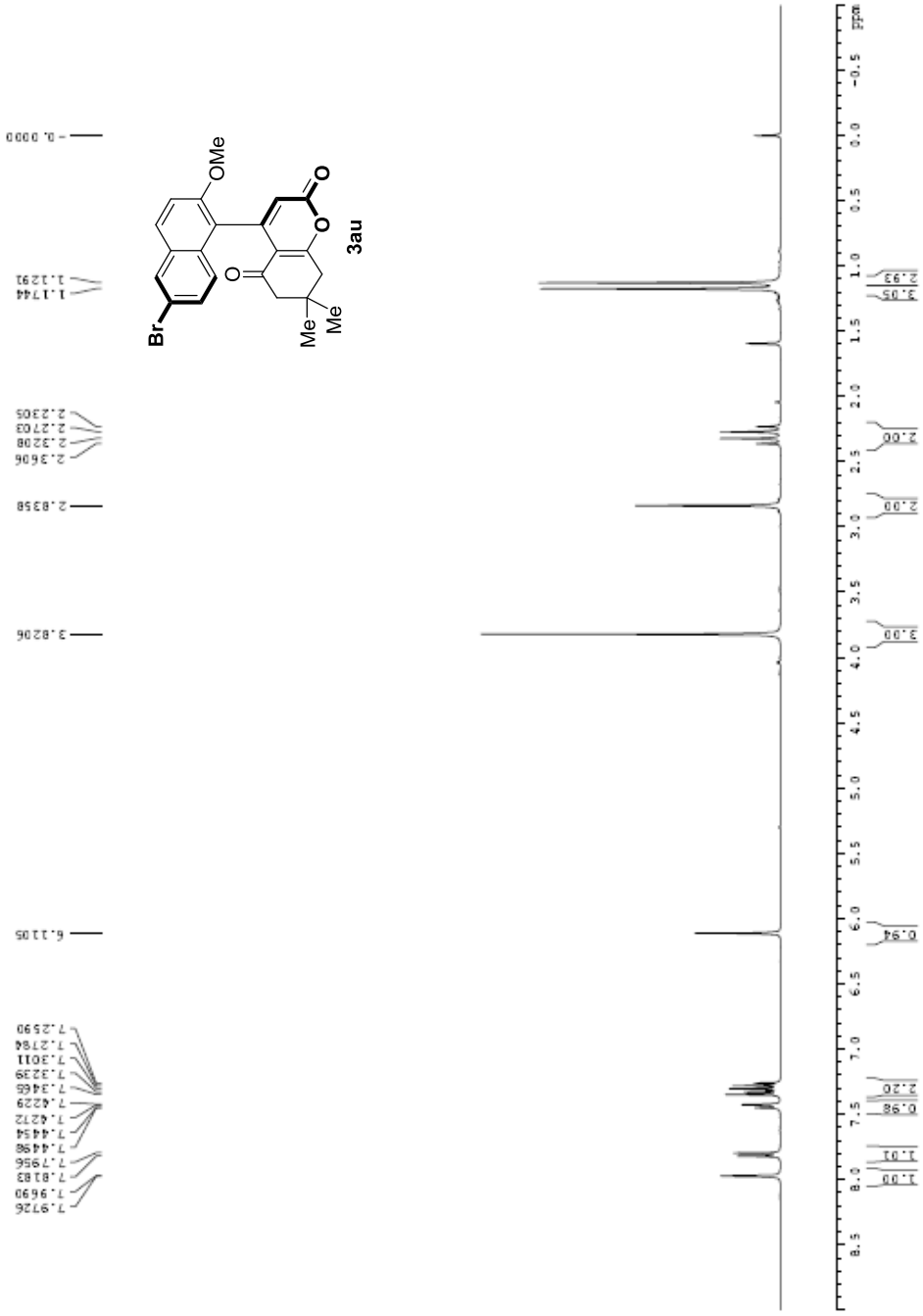

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.785 | 3928716 | 396665 | 50.613 | 52.821 |
| 2 | 7.259 | 3833479 | 354298 | 49.387 | 47.179 |
| Total | | 7762196 | 750964 | 100.000 | 100.000 |

## Supplementary Figure 110. HPLC Spectrum of 3gt

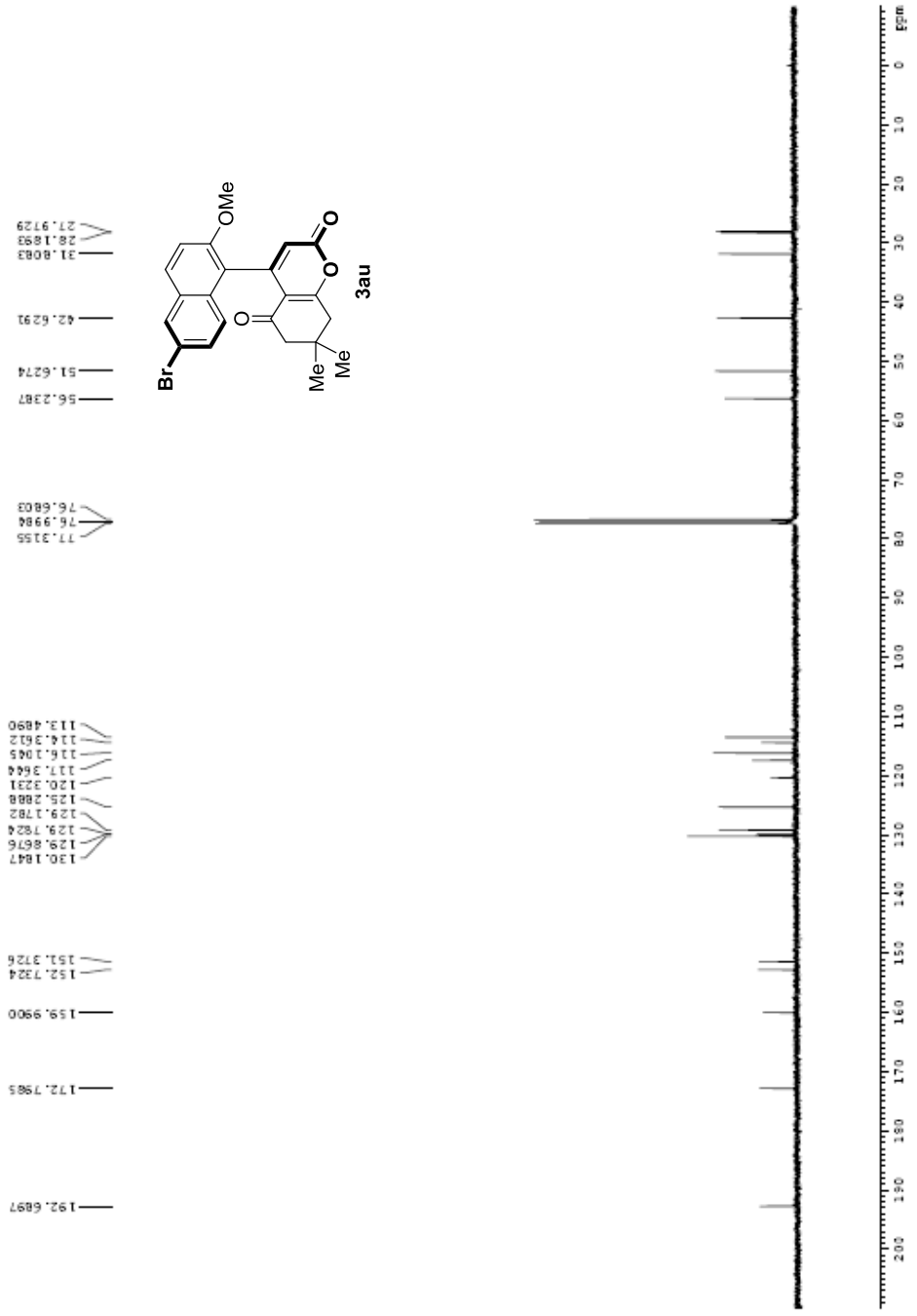



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.775 | 15674564 | 2130564 | 91.932 | 93.436 |
| 2 | 7.313 | 1375667 | 149665 | 8.068 | 6.564 |
| Total | | 17050230 | 2280228 | 100.000 | 100.000 |

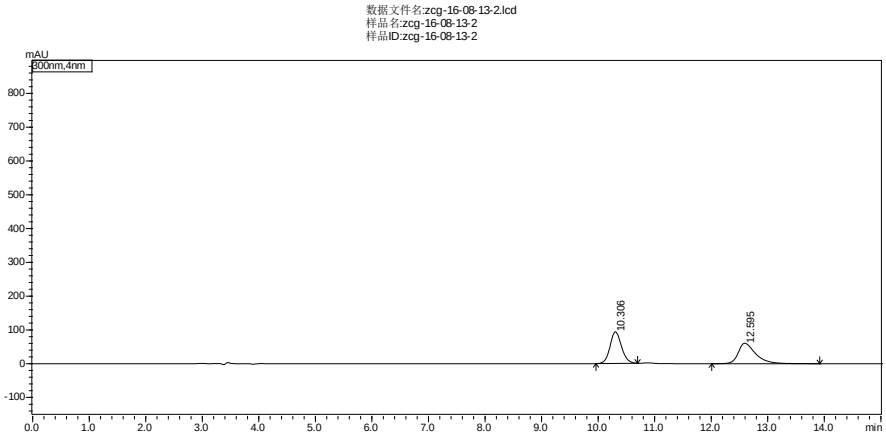
**Supplementary Figure 111. $^{1}$H NMR Spectrum of 3au**



**Supplementary Figure 112. $^{13}$C NMR Spectrum of 3au**

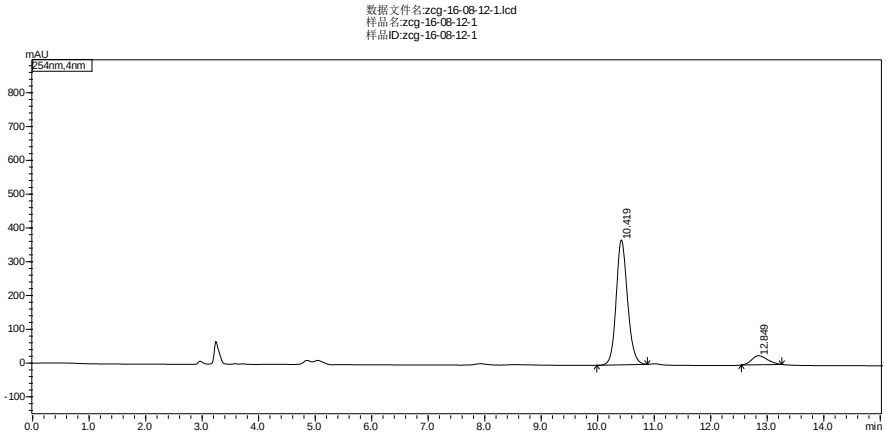


**Supplementary Figure 113. HPLC Spectrum of racemic 3au**



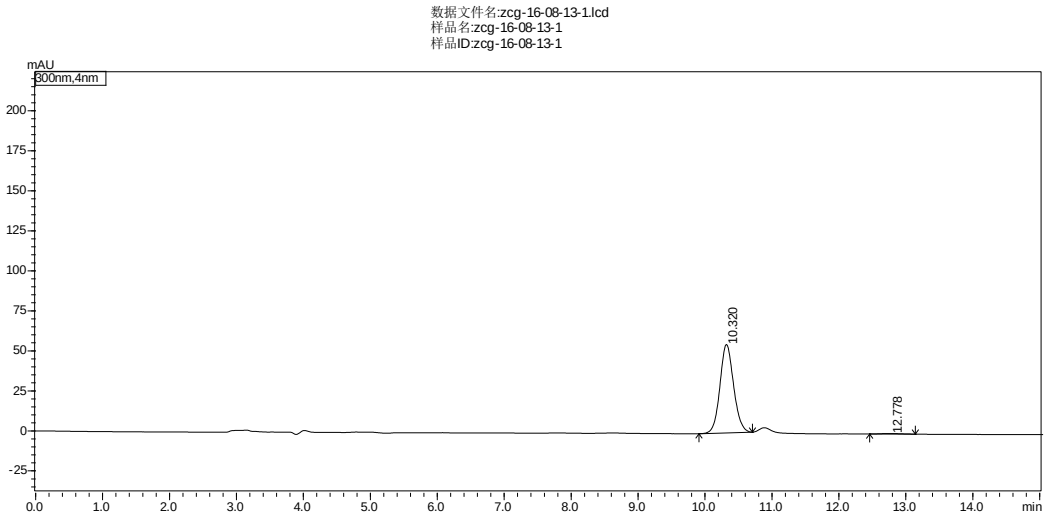

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 10.306 | 1331070 | 93867 | 50.295 | 60.677 |
| 2 | 12.595 | 1315457 | 60832 | 49.705 | 39.323 |
| Total | | 2646527 | 154699 | 100.000 | 100.000 |

## Supplementary Figure 114. HPLC Spectrum of 3au



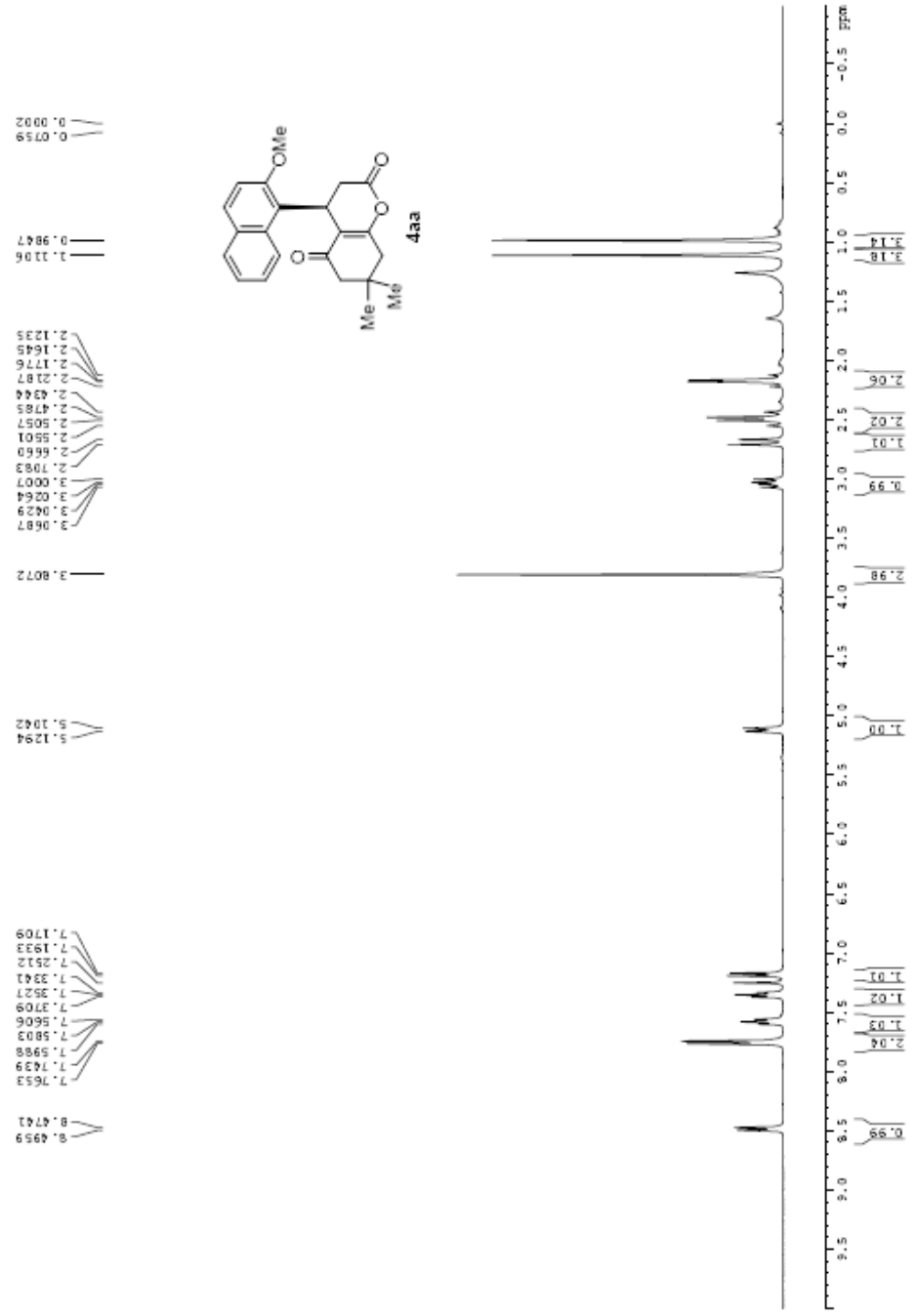

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 10.419 | 5164108 | 369842 | 90.855 | 93.259 |
| 2 | 12.849 | 519786 | 26732 | 9.145 | 6.741 |
| Total | | 5683895 | 396574 | 100.000 | 100.000 |

**Supplementary Figure 115. HPLC Spectrum of 3au after first crystallization**

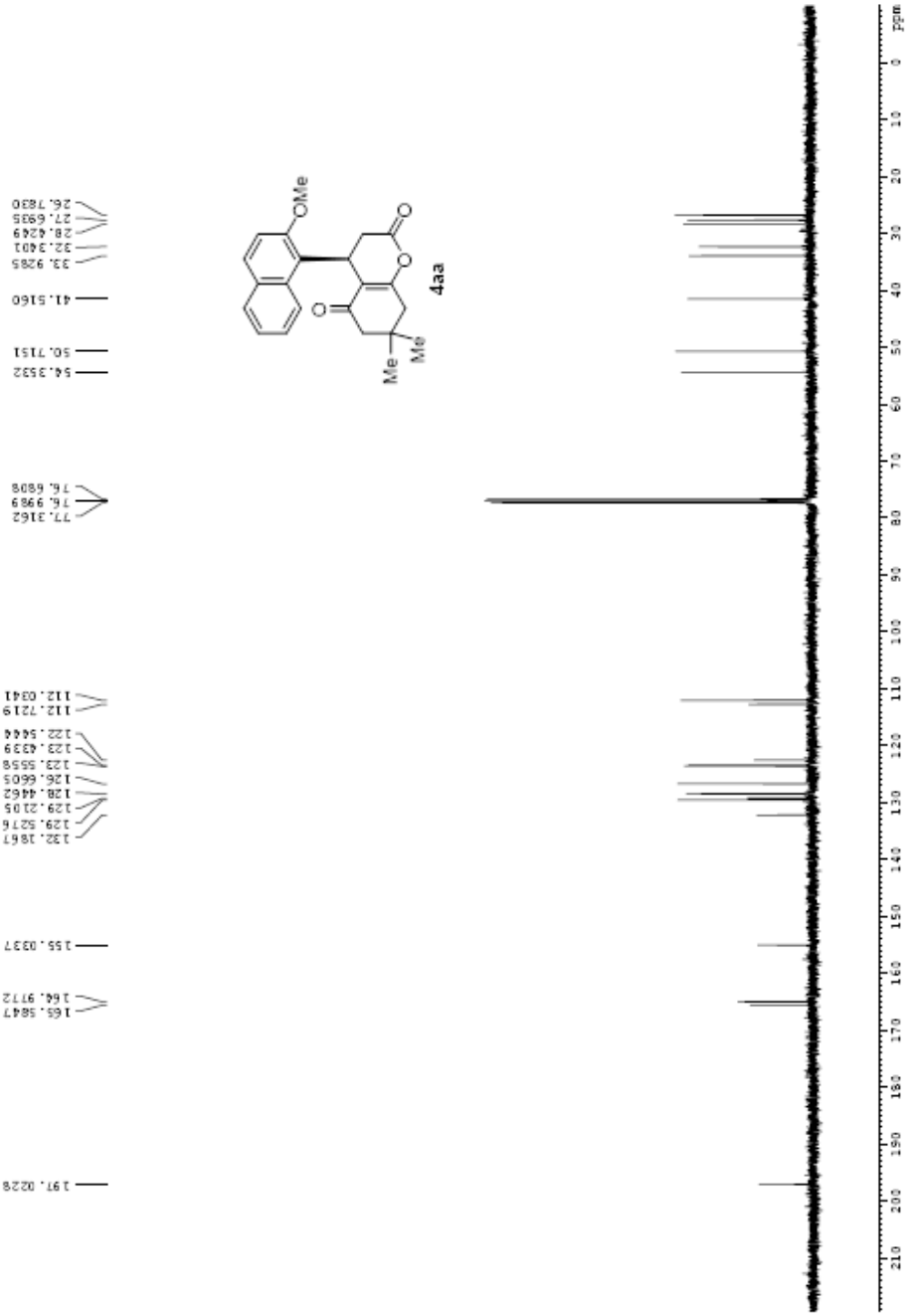



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 10.320 | 785169 | 55222 | 99.070 | 99.317 |
| 2 | 12.778 | 7372 | 380 | 0.930 | 0.683 |
| Total | | 792541 | 55602 | 100.000 | 100.000 |

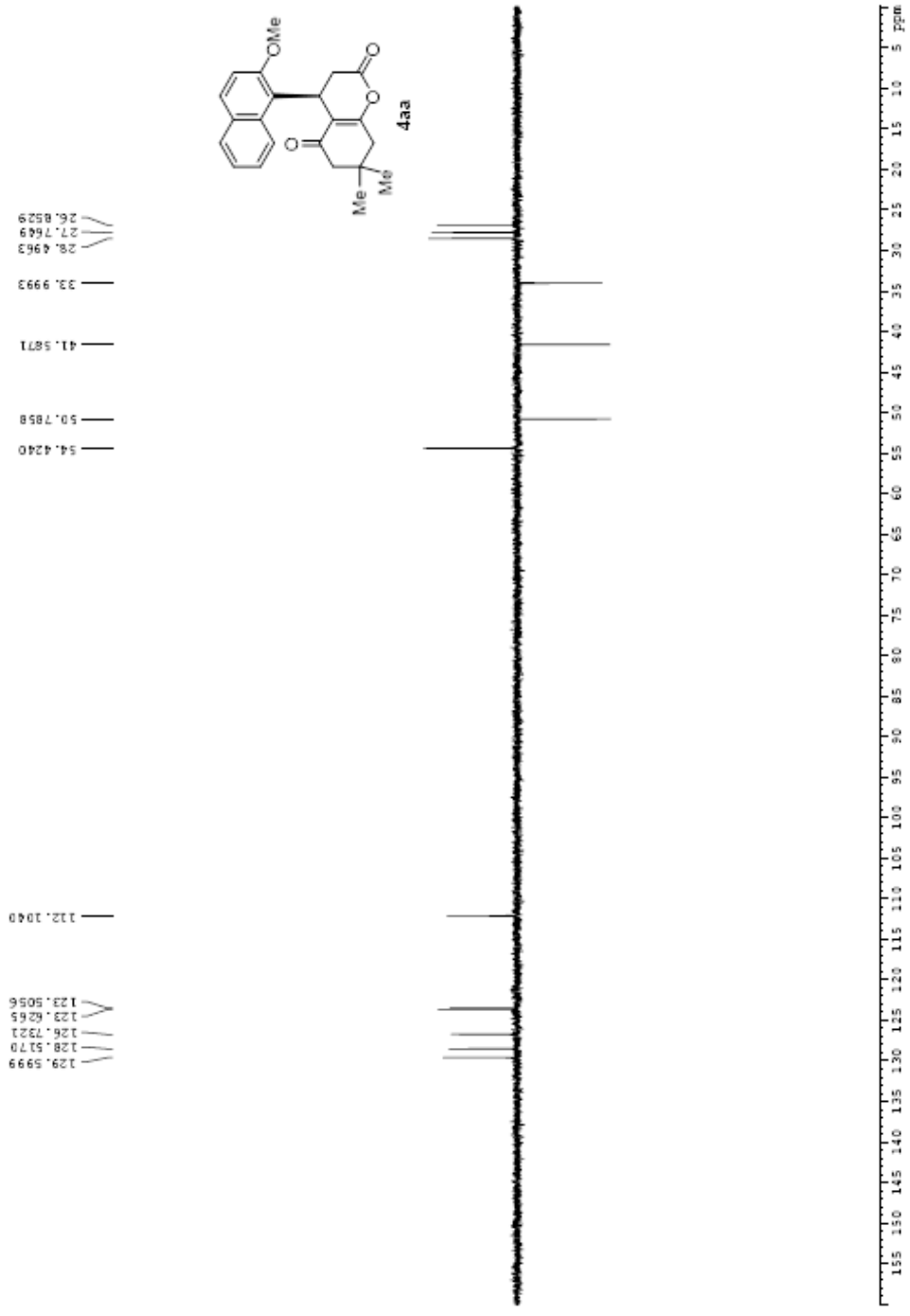
**Supplementary Figure 116. $^{1}$H NMR Spectrum of 4aa**



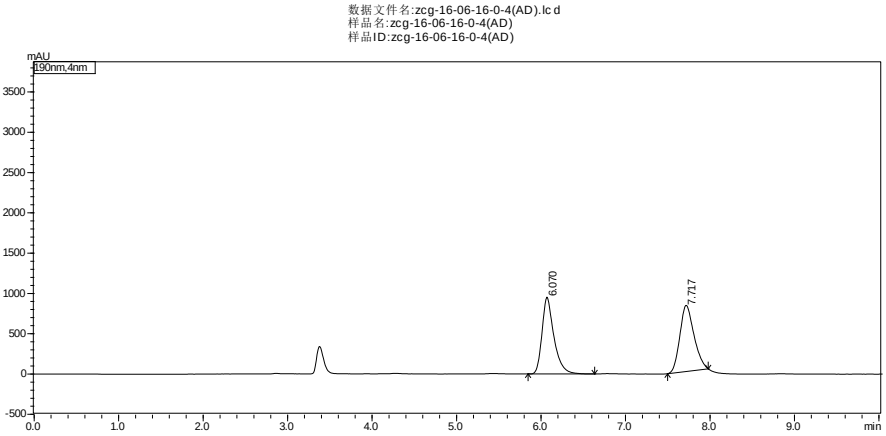
**Supplementary Figure 117. $^{13}$C NMR Spectrum of 4aa**



**Supplementary Figure 118. $^{13}$C NMR Spectrum of 4aa**

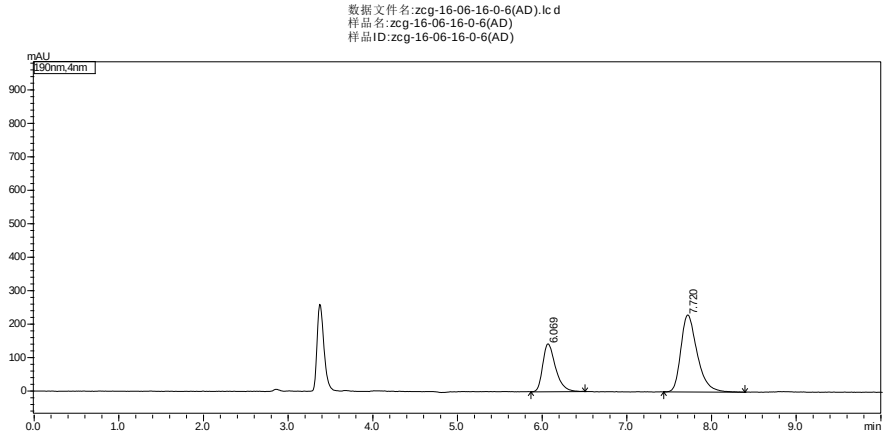


## Supplementary Figure 119. HPLC Spectrum of racemic 4aa



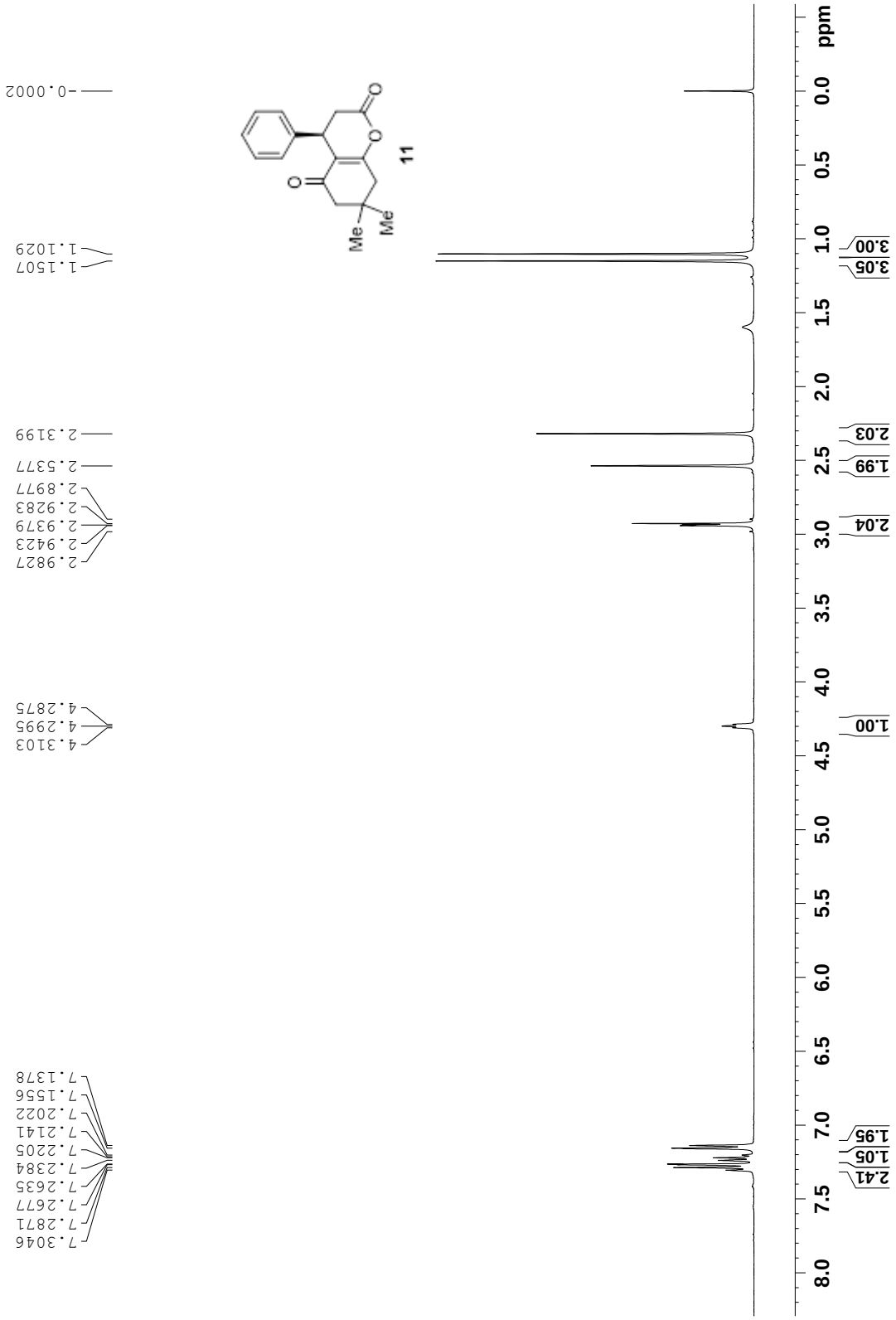

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.070 | 9315359 | 955058 | 49.373 | 53.837 |
| 2 | 7.717 | 9552141 | 818936 | 50.627 | 46.163 |
| Total | | 18867500 | 1773995 | 100.000 | 100.000 |

## Supplementary Figure 120. HPLC Spectrum of 4aa

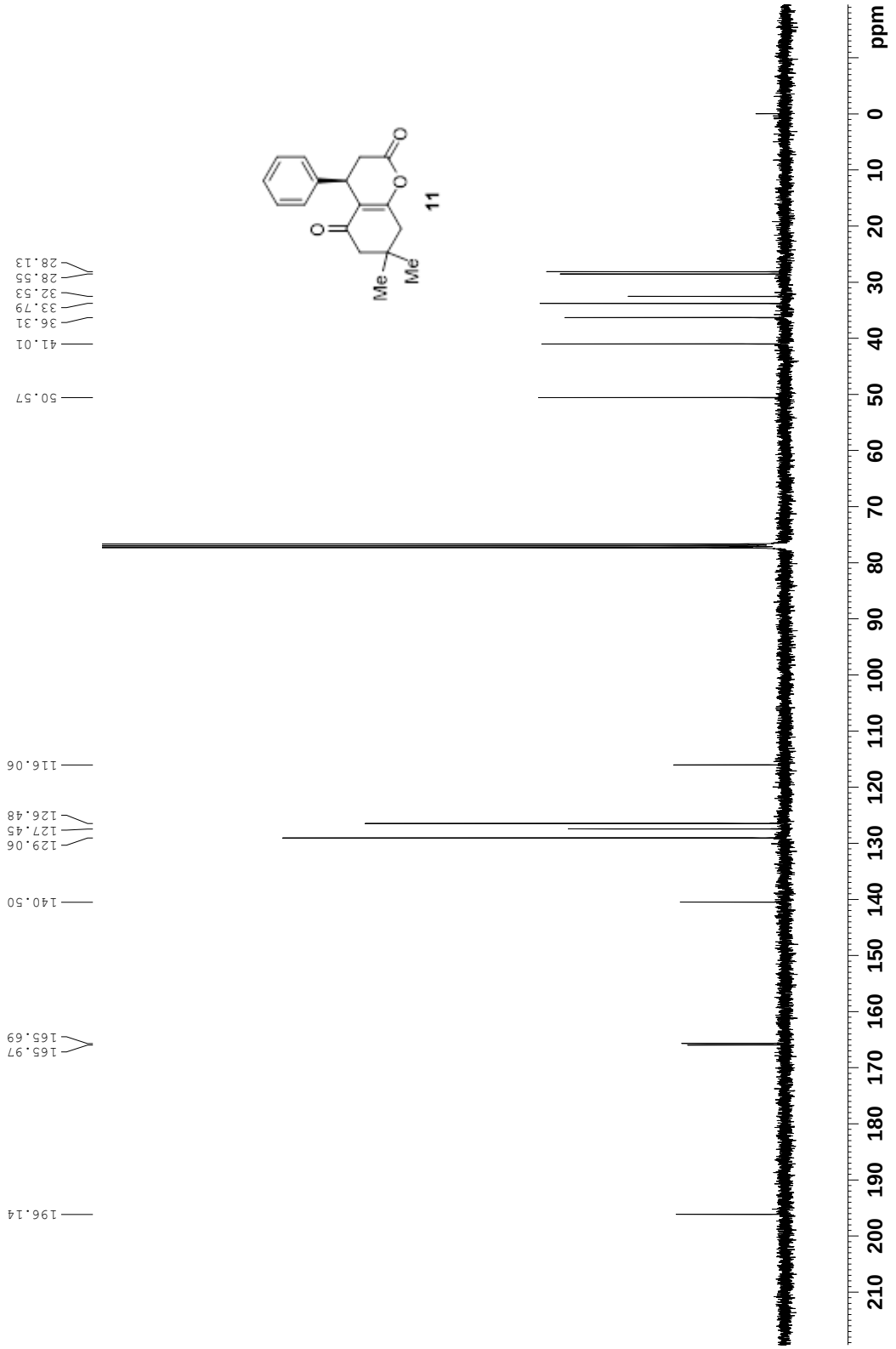



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.069 | 1516859 | 143429 | 32.858 | 38.353 |
| 2 | 7.720 | 3099564 | 230542 | 67.142 | 61.647 |
| Total | | 4616423 | 373971 | 100.000 | 100.000 |

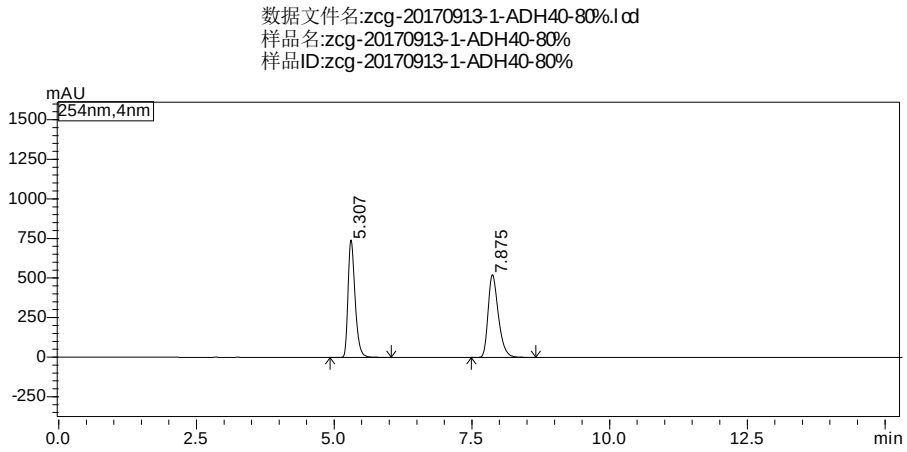
**Supplementary Figure 121. $^{1}$H NMR Spectrum of 11**



**Supplementary Figure 122. $^{13}$C NMR Spectrum of 11**

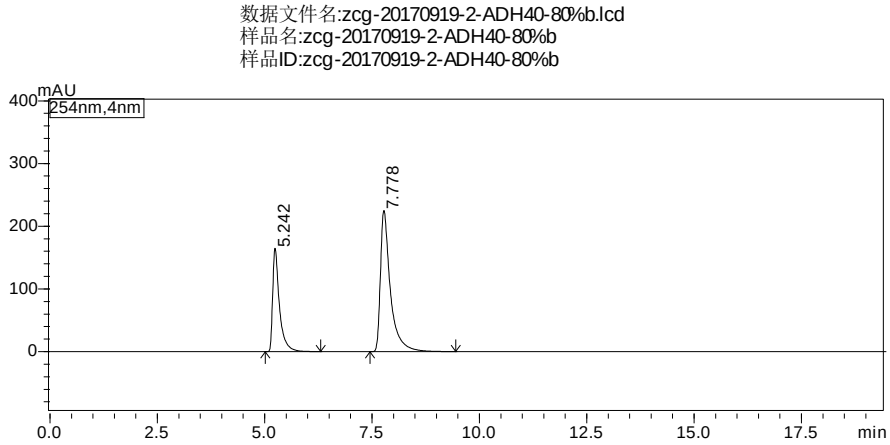


**Supplementary Figure 123. HPLC Spectrum of racemic 11**



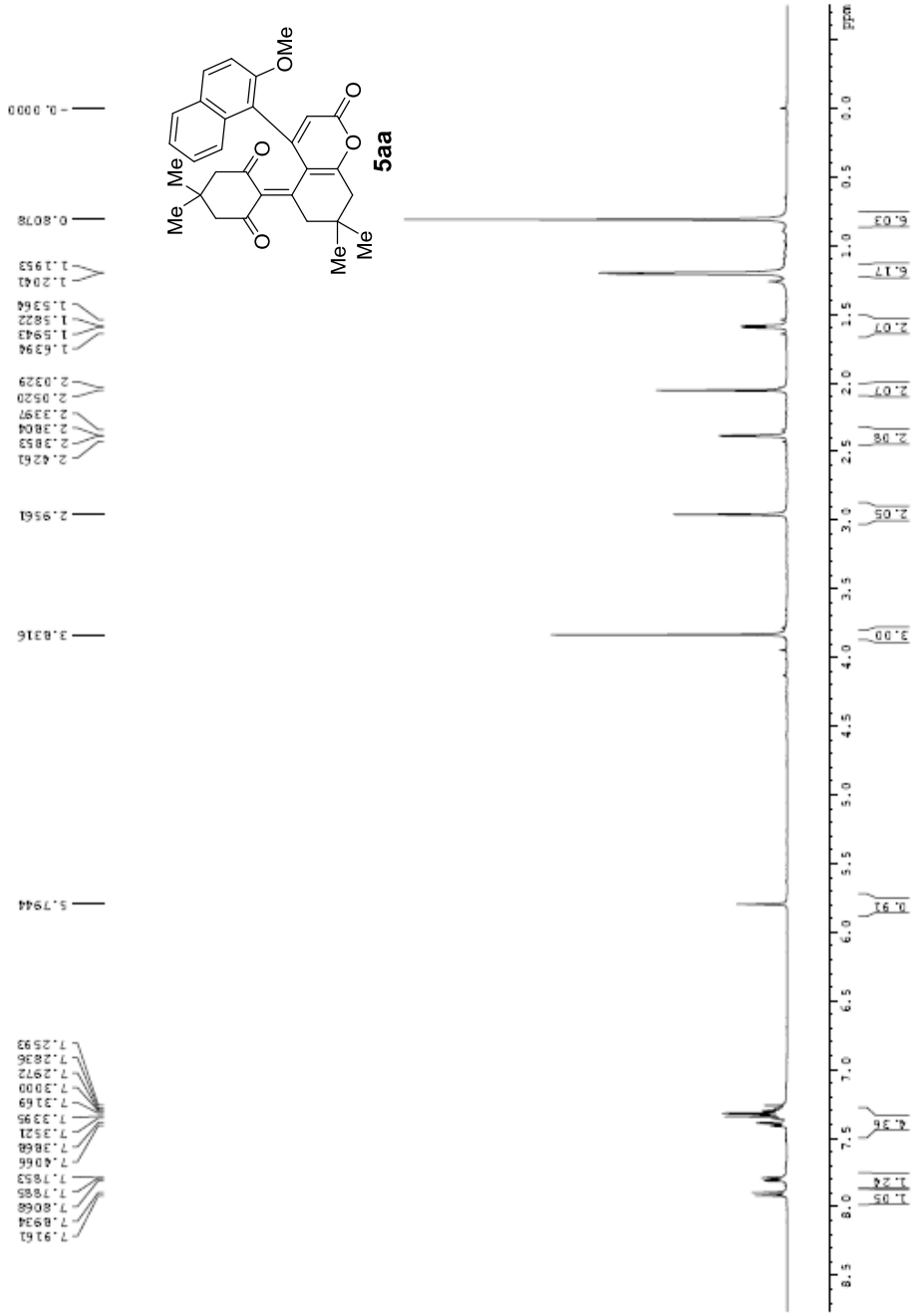

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 5.307 | 6572017 | 741111 | 49.280 | 58.635 |
| 2 | 7.875 | 6764154 | 522830 | 50.720 | 41.365 |
| Total | | 13336171 | 1263942 | 100.000 | 100.000 |

## Supplementary Figure 124. HPLC Spectrum of 11

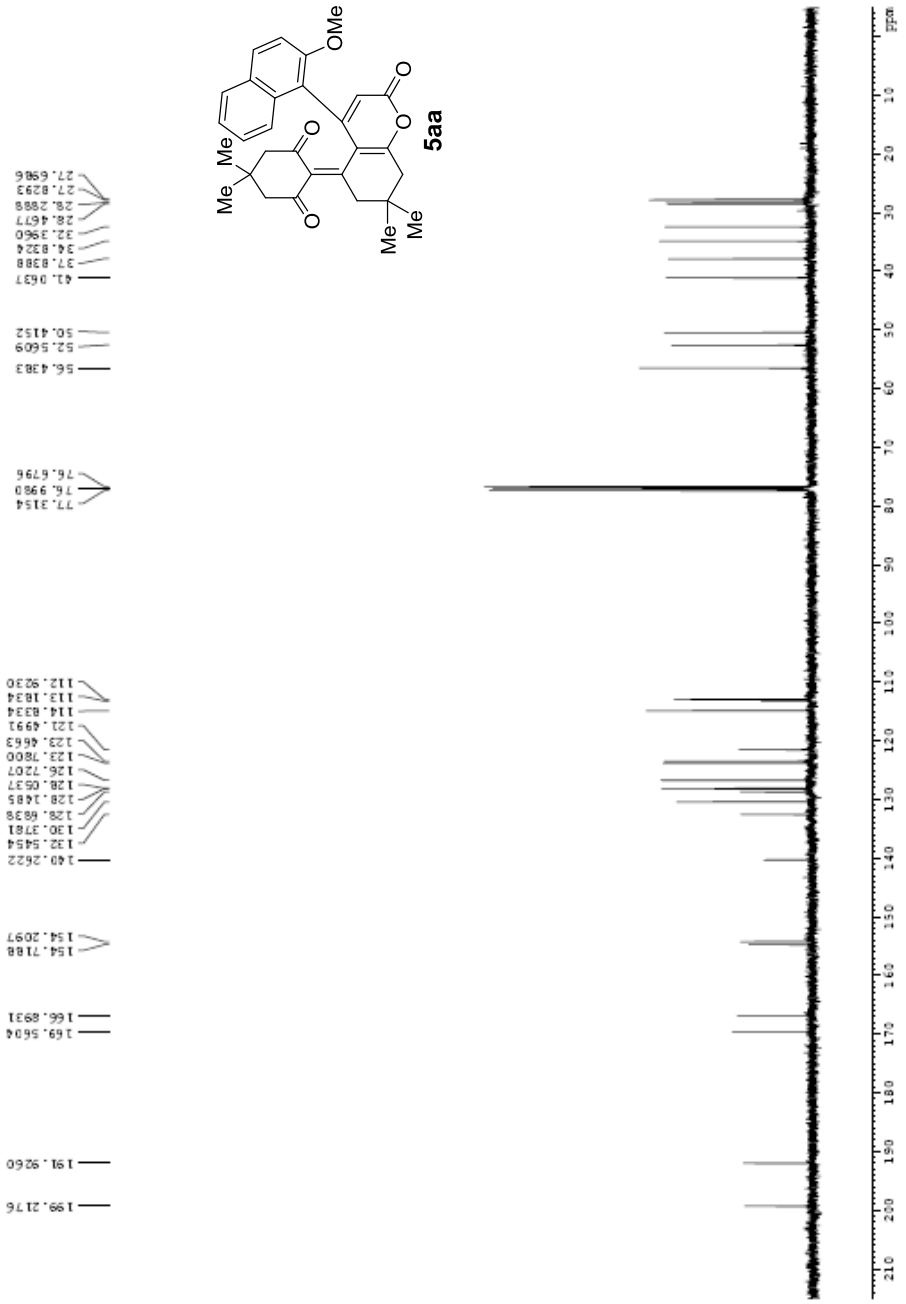



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 5.242 | 1812216 | 164708 | 33.294 | 42.258 |
| 2 | 7.778 | 3630915 | 225061 | 66.706 | 57.742 |
| Total | | 5443130 | 389770 | 100.000 | 100.000 |

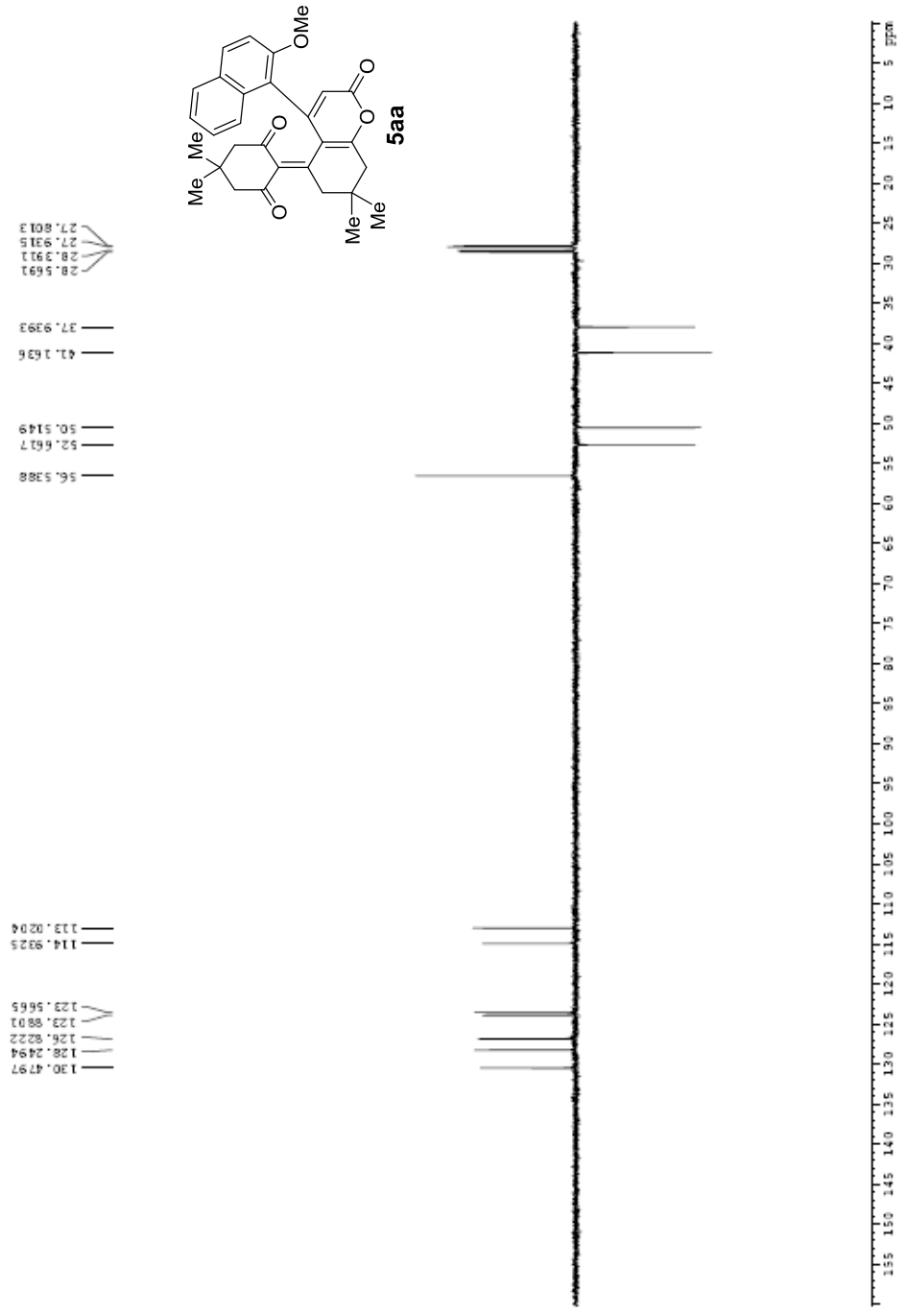
**Supplementary Figure 125. $^{1}$H NMR Spectrum of 5aa**



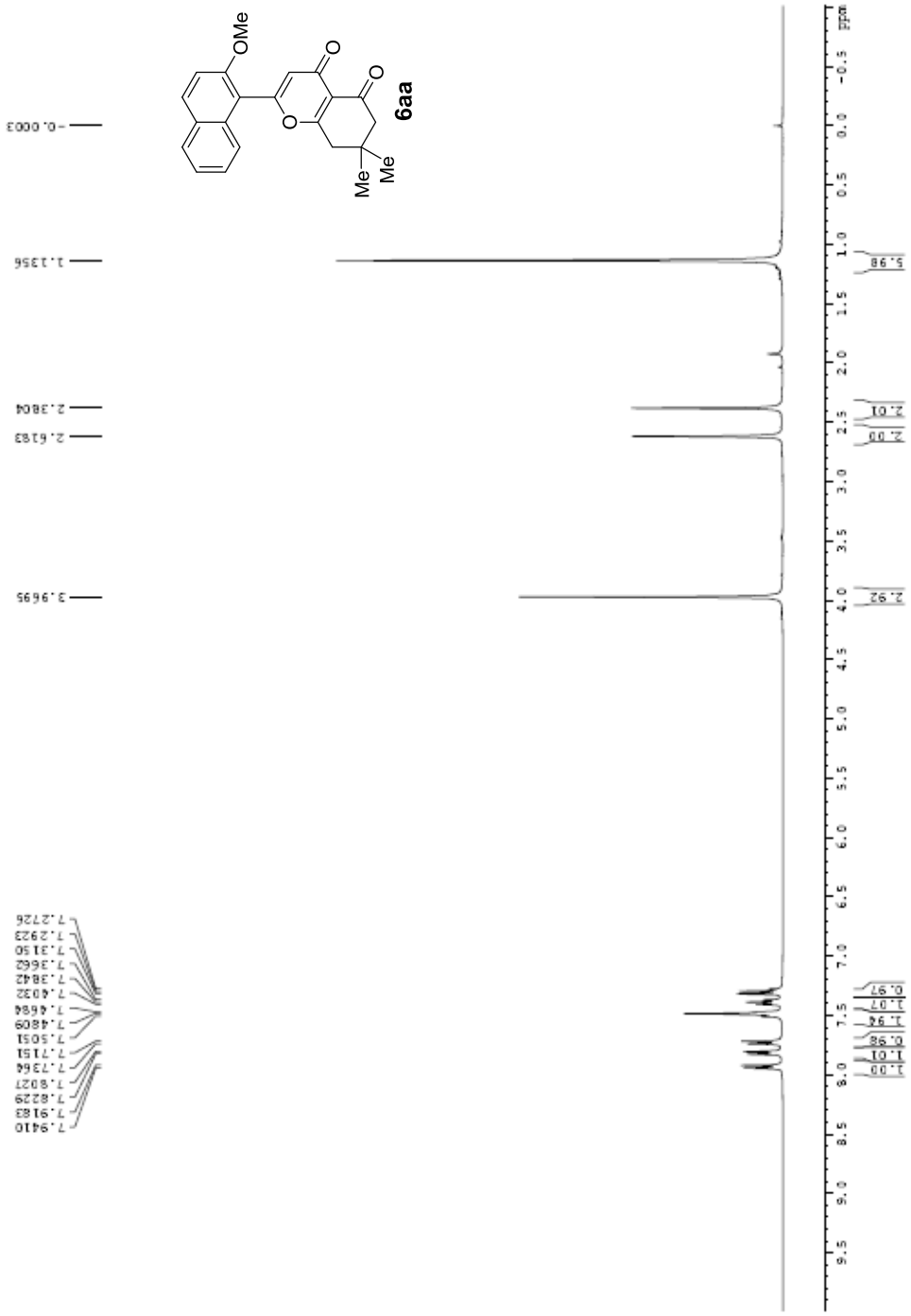
**Supplementary Figure 126. $^{13}$C NMR Spectrum of 5aa**



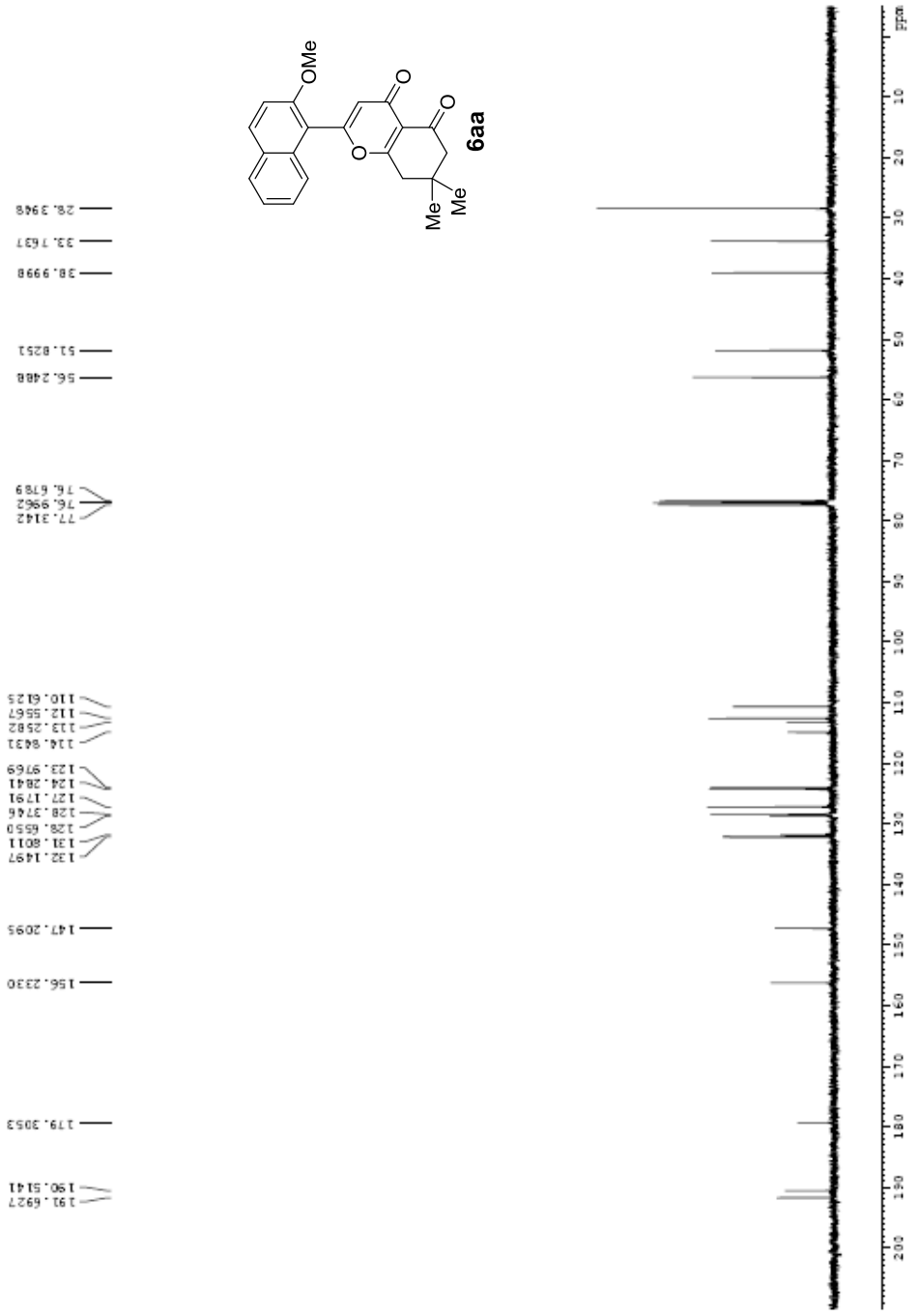
**Supplementary Figure 127. $^{13}$C NMR Spectrum of 5aa**



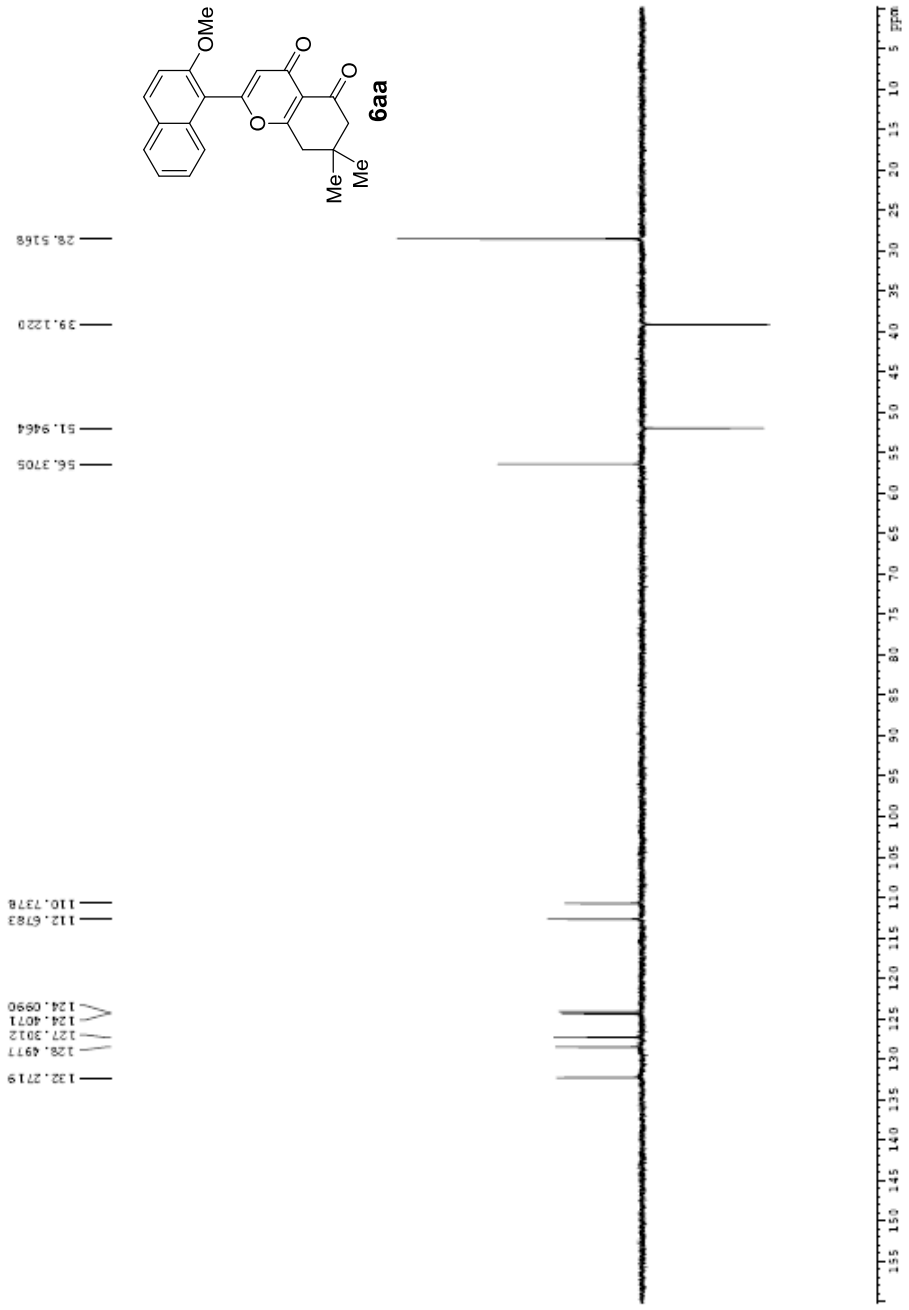
**Supplementary Figure 128. $^{1}$H NMR Spectrum of 6aa**



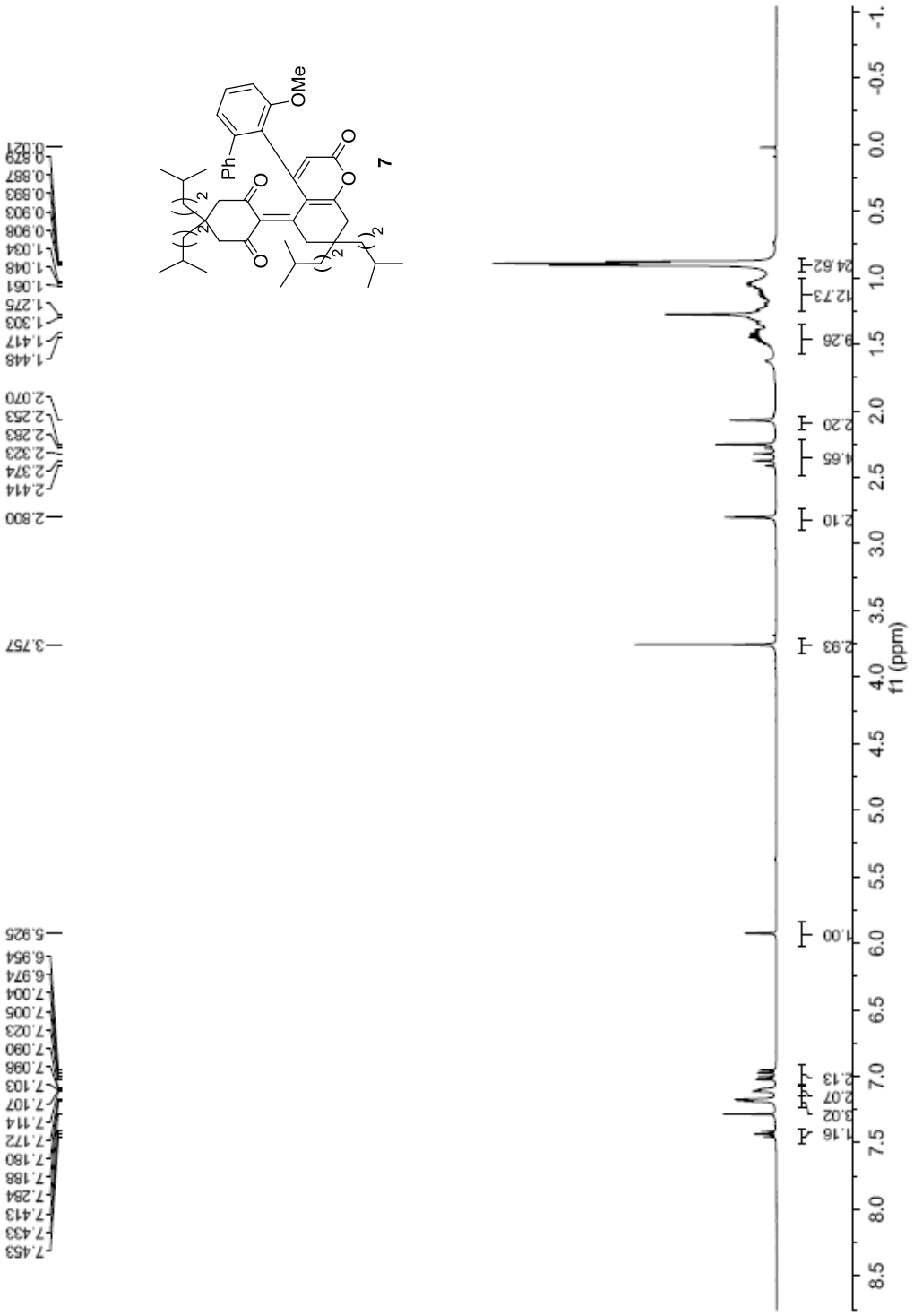
**Supplementary Figure 129. $^{13}$C NMR Spectrum of 6aa**



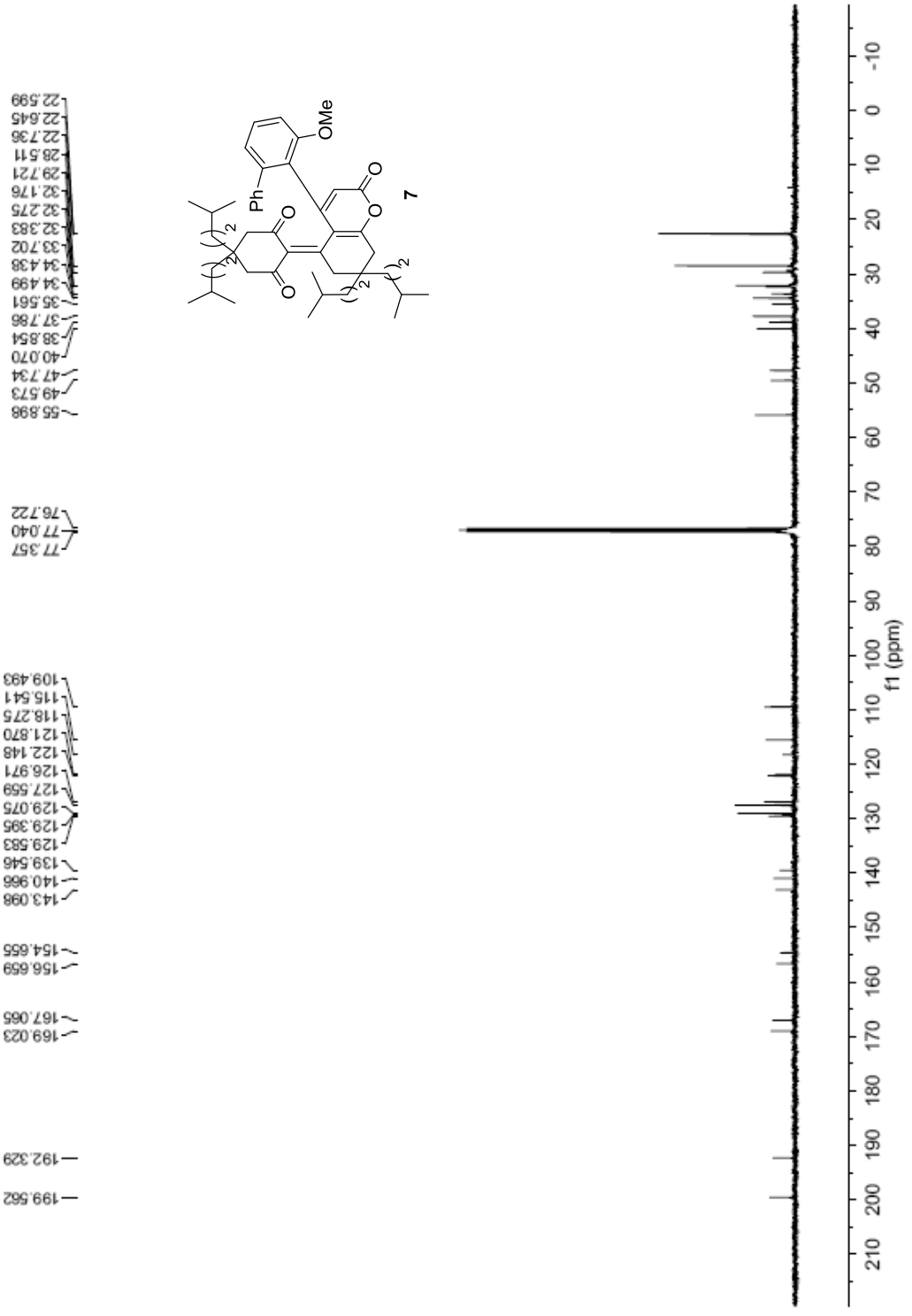
**Supplementary Figure 130. $^{13}$C NMR Spectrum of 6aa**



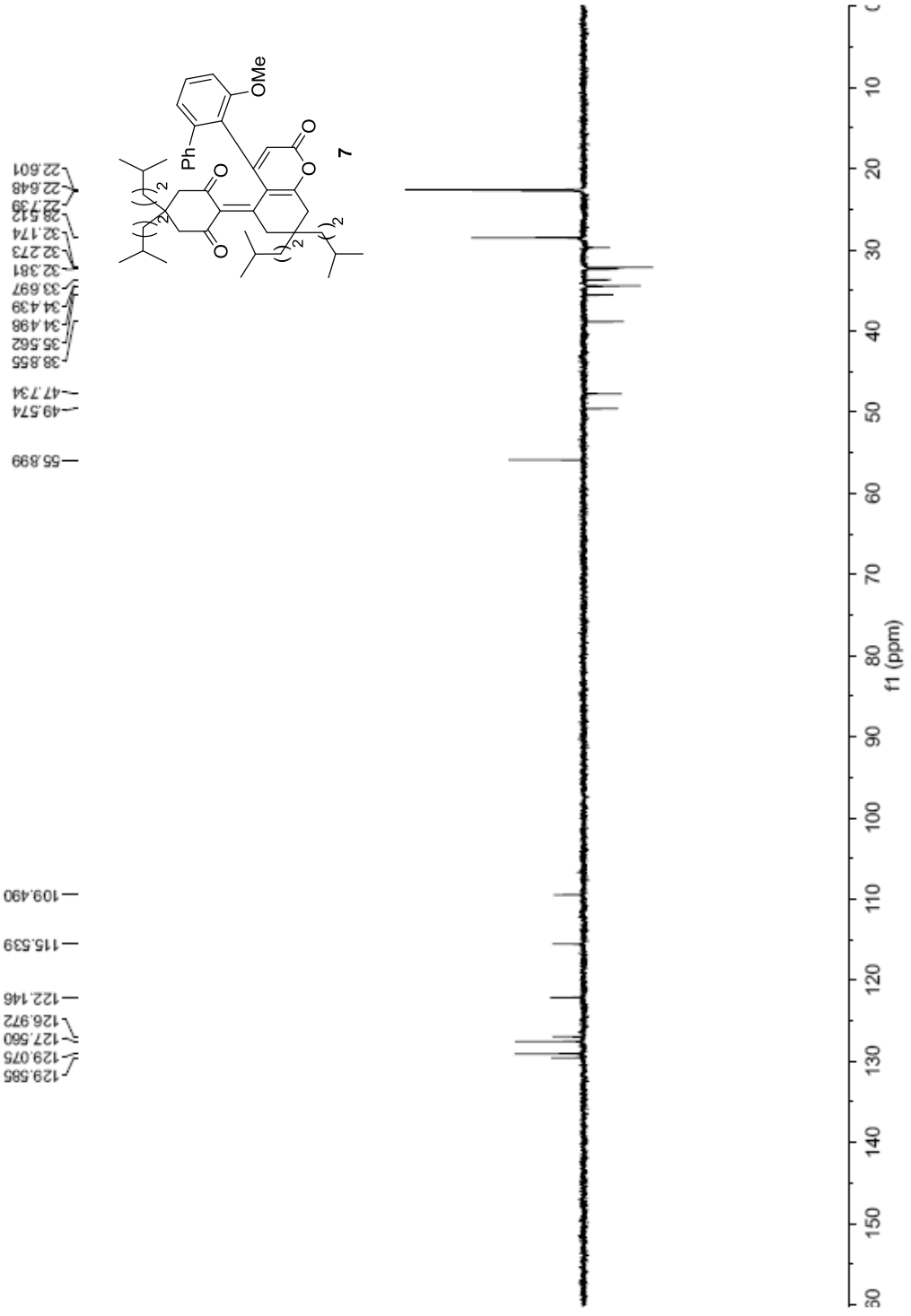
**Supplementary Figure 131. $^{1}$H NMR Spectrum of 7**



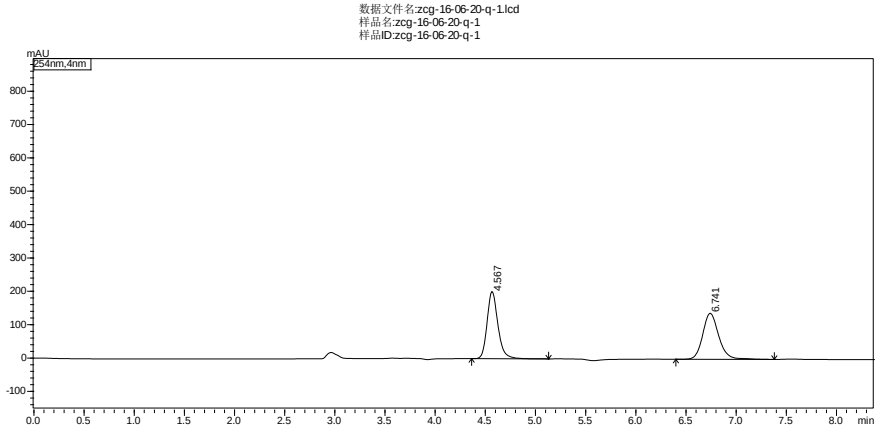
**Supplementary Figure 132. $^{13}$C NMR Spectrum of 7**



**Supplementary Figure 133. $^{13}$C NMR Spectrum of 7**

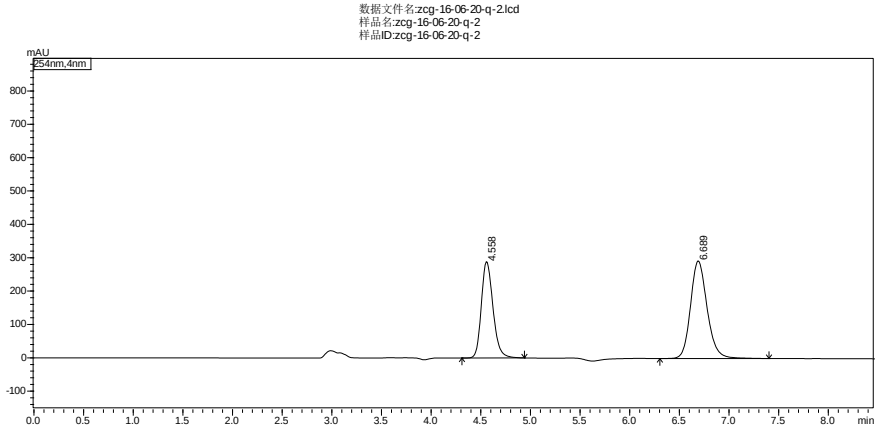


**Supplementary Figure 134. HPLC Spectrum of racemic 7**



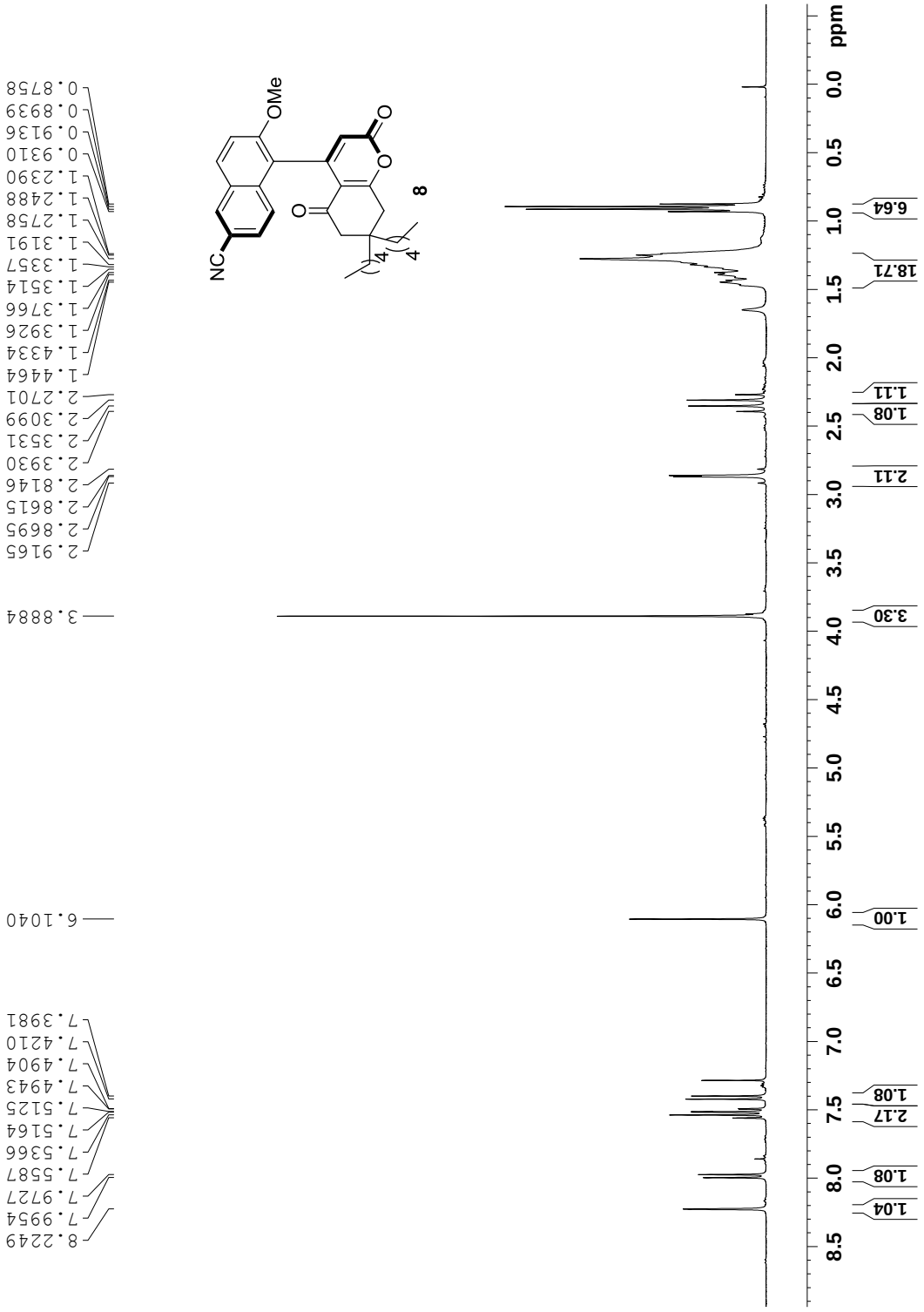

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 4.567 | 1518426 | 201541 | 49.658 | 59.301 |
| 2 | 6.741 | 1539320 | 138321 | 50.342 | 40.699 |
| Total | | 3057746 | 339862 | 100.000 | 100.000 |

## Supplementary Figure 135. HPLC Spectrum of 7

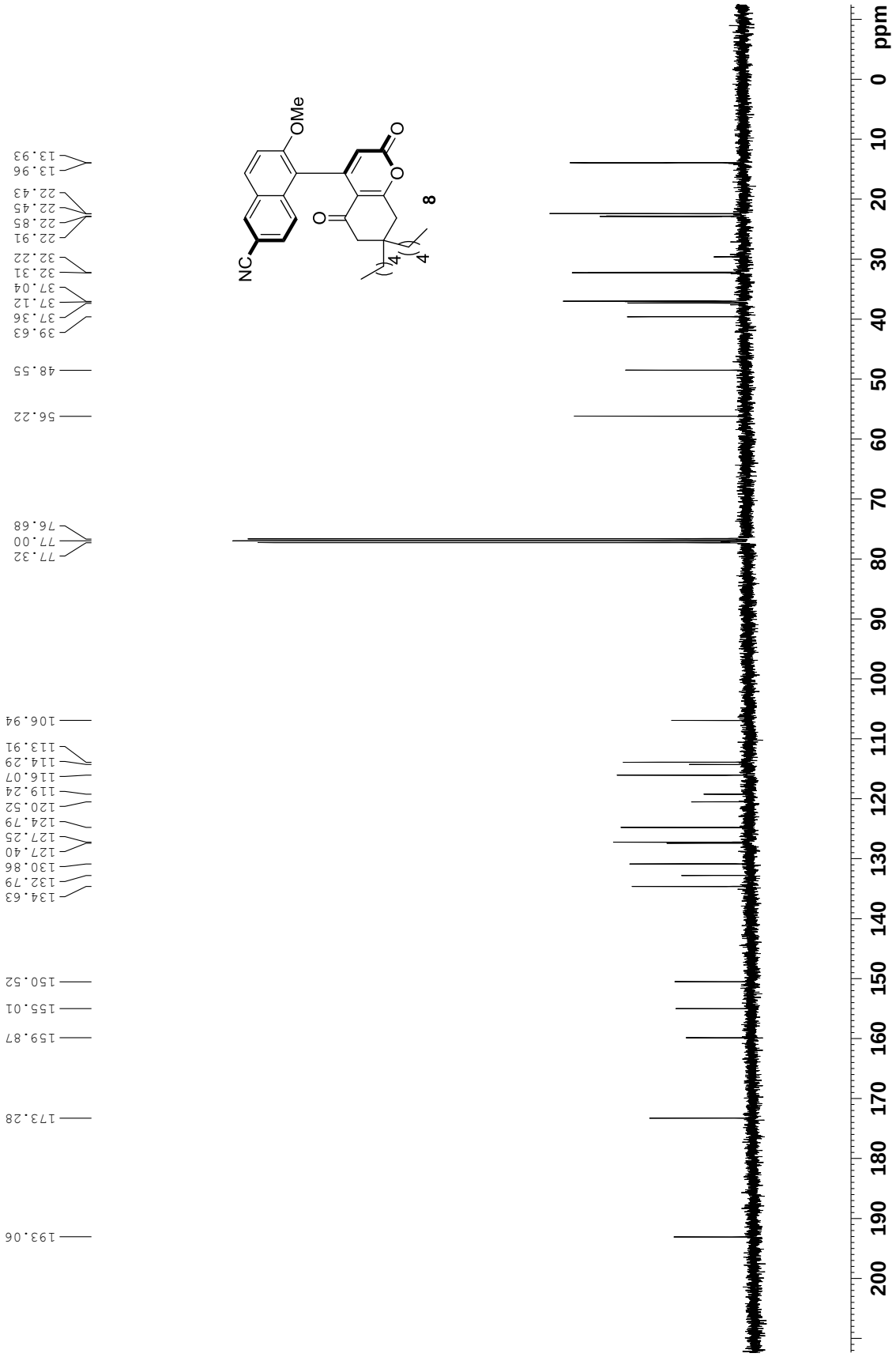



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 4.558 | 2362045 | 289010 | 40.993 | 49.678 |
| 2 | 6.689 | 3399994 | 292757 | 59.007 | 50.322 |
| Total | | 5762040 | 581766 | 100.000 | 100.000 |

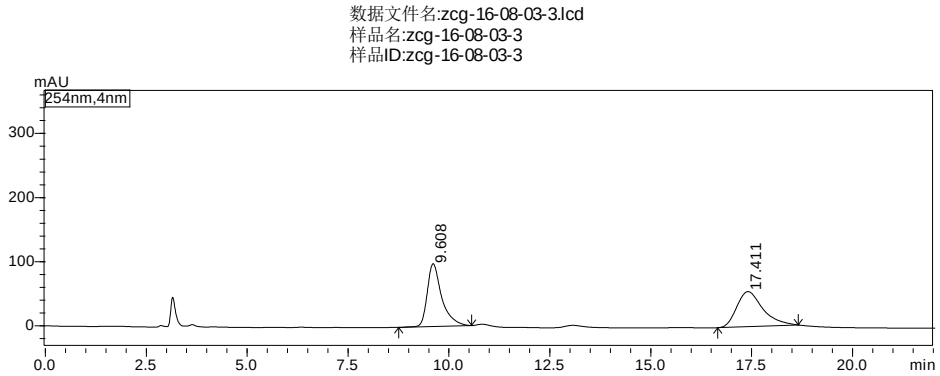
**Supplementary Figure 136. $^{1}$H NMR Spectrum of 8**



**Supplementary Figure 137. $^{13}$C NMR Spectrum of 8**

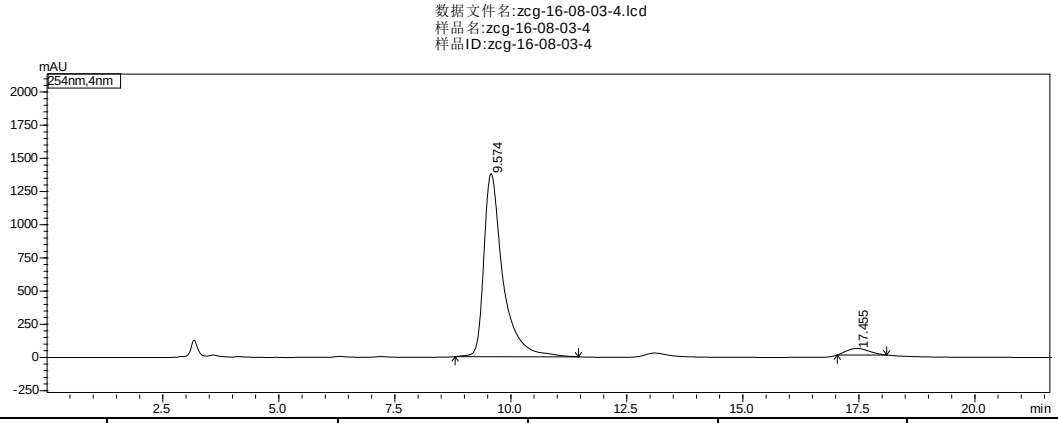


**Supplementary Figure 138. HPLC Spectrum of racemic 8**



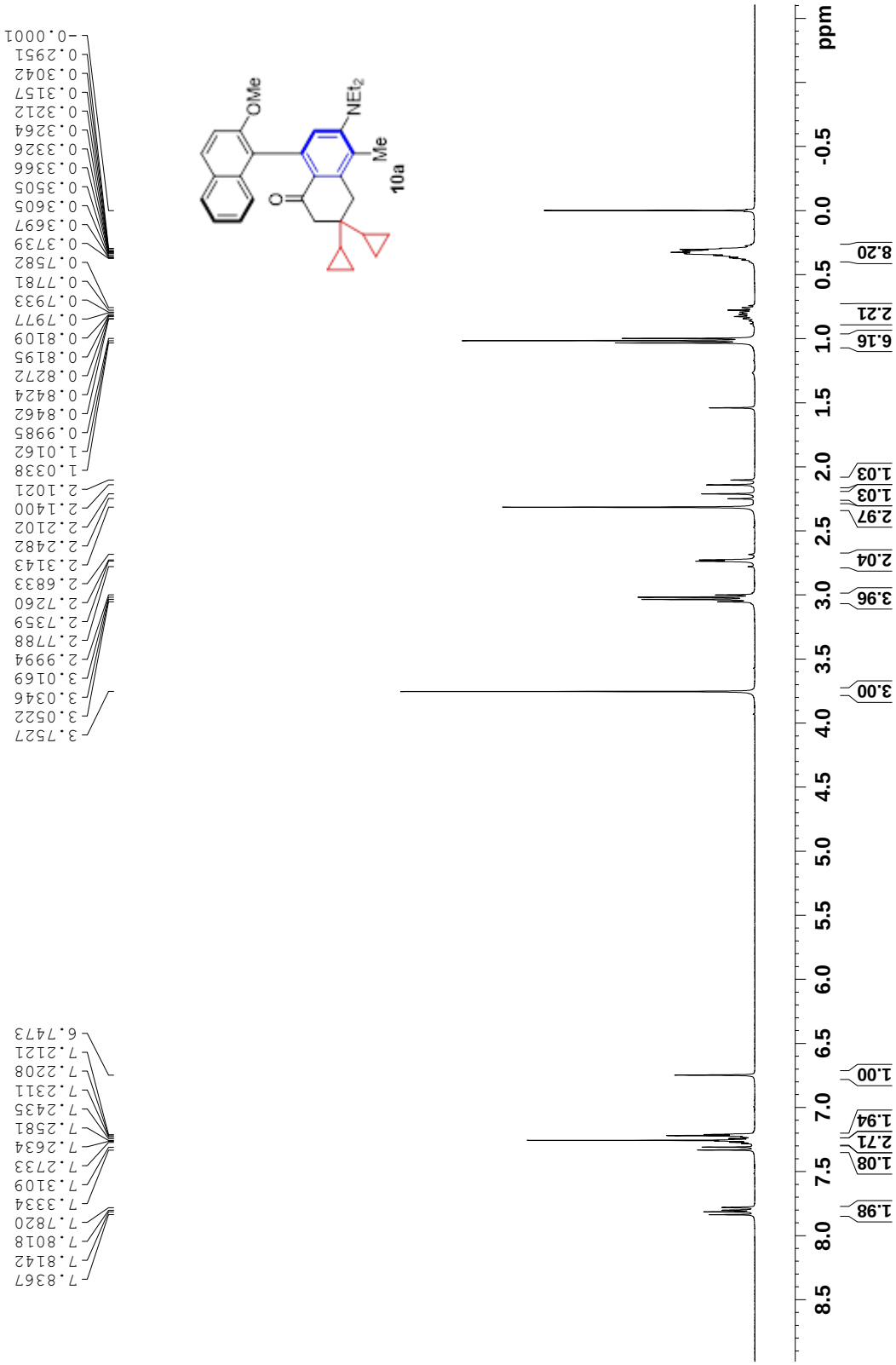

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 9.608 | 2446895 | 98076 | 49.825 | 64.197 |
| 2 | 17.411 | 2464079 | 54698 | 50.175 | 35.803 |
| Total | | 4910973 | 152774 | 100.000 | 100.000 |

## Supplementary Figure 139. HPLC Spectrum of 8

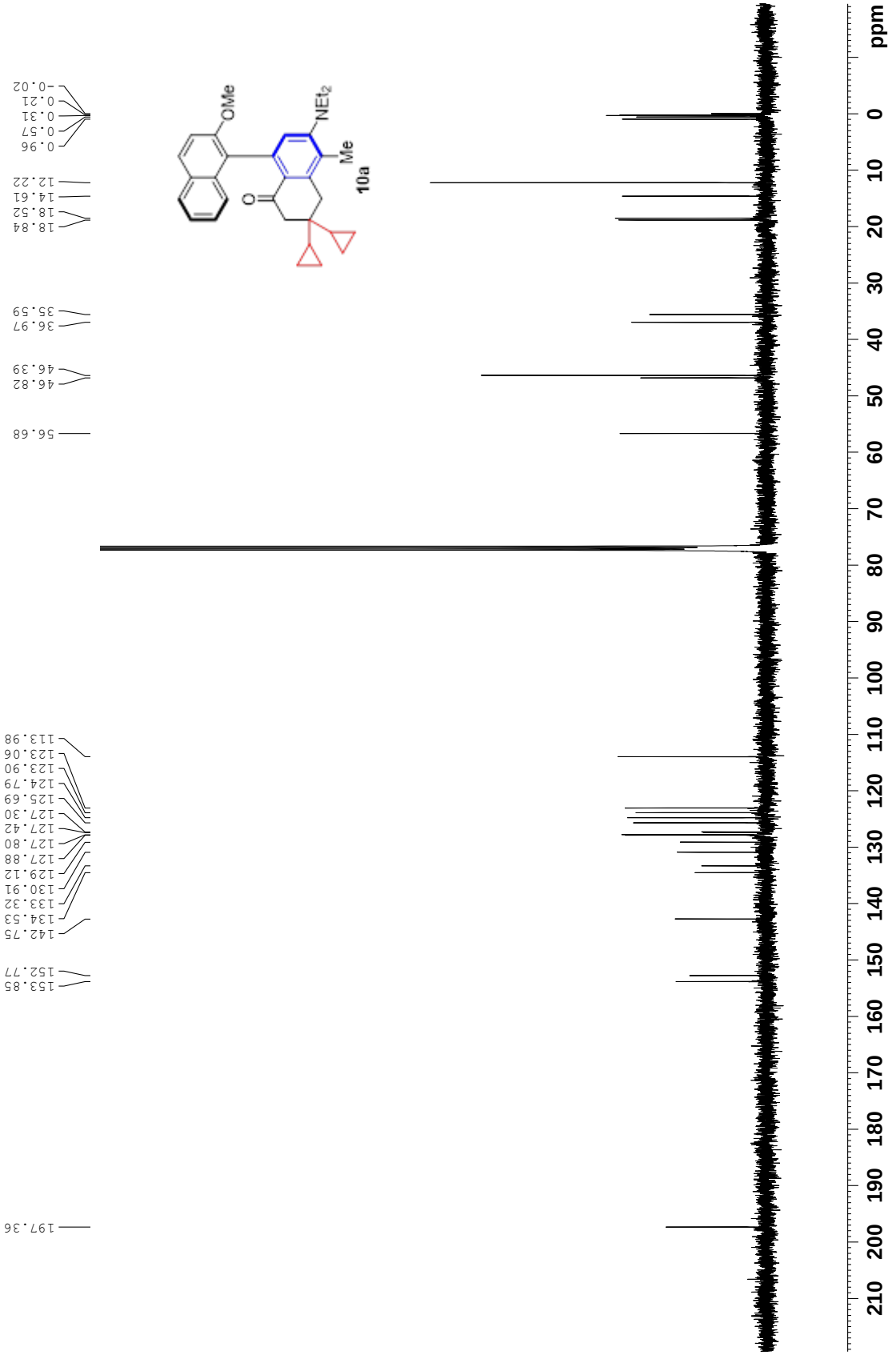



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 9.574 | 39228581 | 1378247 | 95.895 | 96.525 |
| 2 | 17.455 | 1679209 | 49617 | 4.105 | 3.475 |
| Total | | 40907791 | 1427863 | 100.000 | 100.000 |

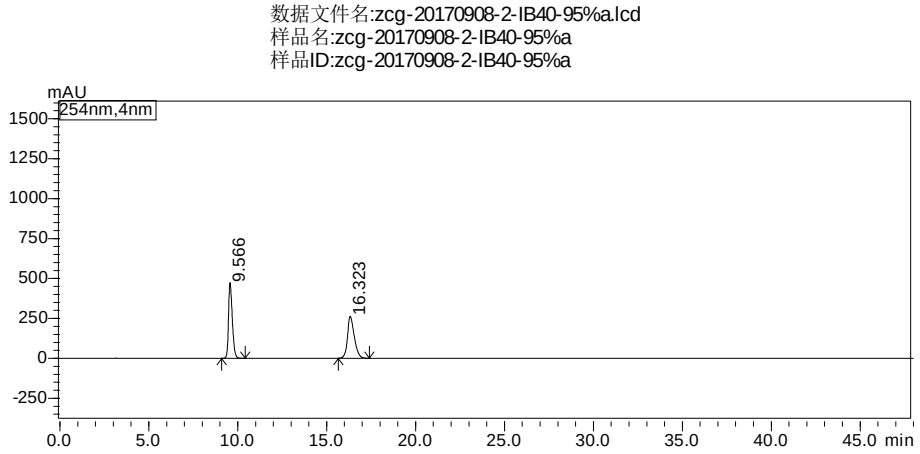
**Supplementary Figure 140. $^{1}$H NMR Spectrum of 10a**



**Supplementary Figure 141. $^{13}$C NMR Spectrum of 10a**



**Supplementary Figure 142. HPLC Spectrum of racemic 10a**




| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 9.566 | 7000121 | 473590 | 50.084 | 64.367 |
| 2 | 16.323 | 6976682 | 262176 | 49.916 | 35.633 |
| Total | | 13976803 | 735766 | 100.000 | 100.000 |

## Supplementary Figure 143. HPLC Spectrum of 10a

数据文件名:zcg-20170922-1-IB40-95%.lcd
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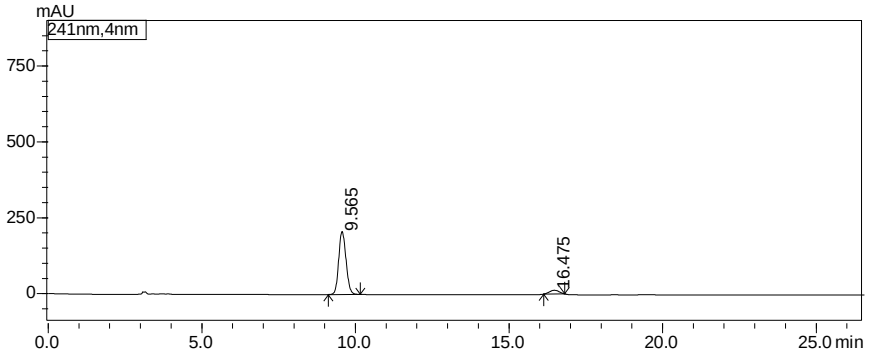
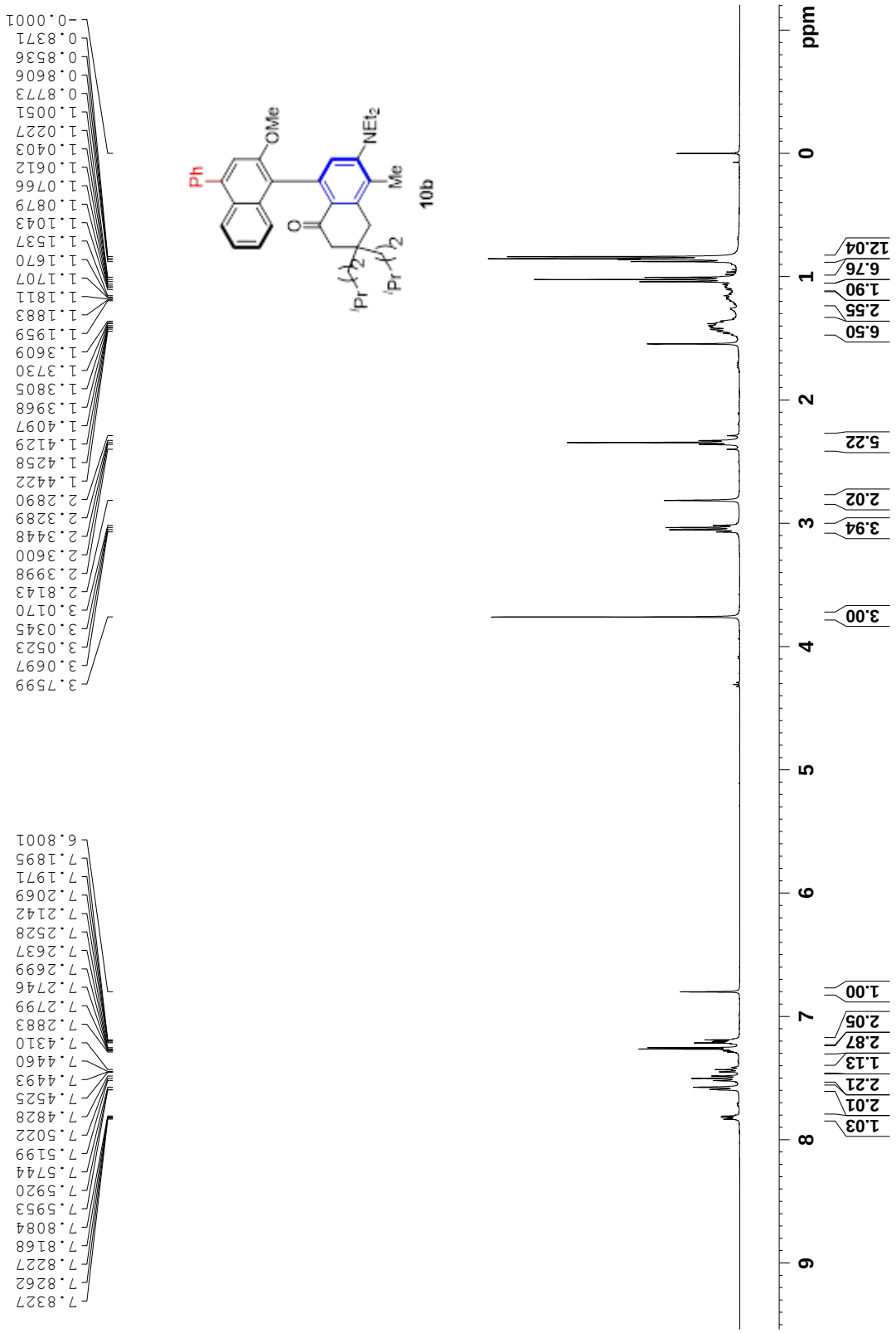
样品ID:zcg-20170922-1-IB40-95%

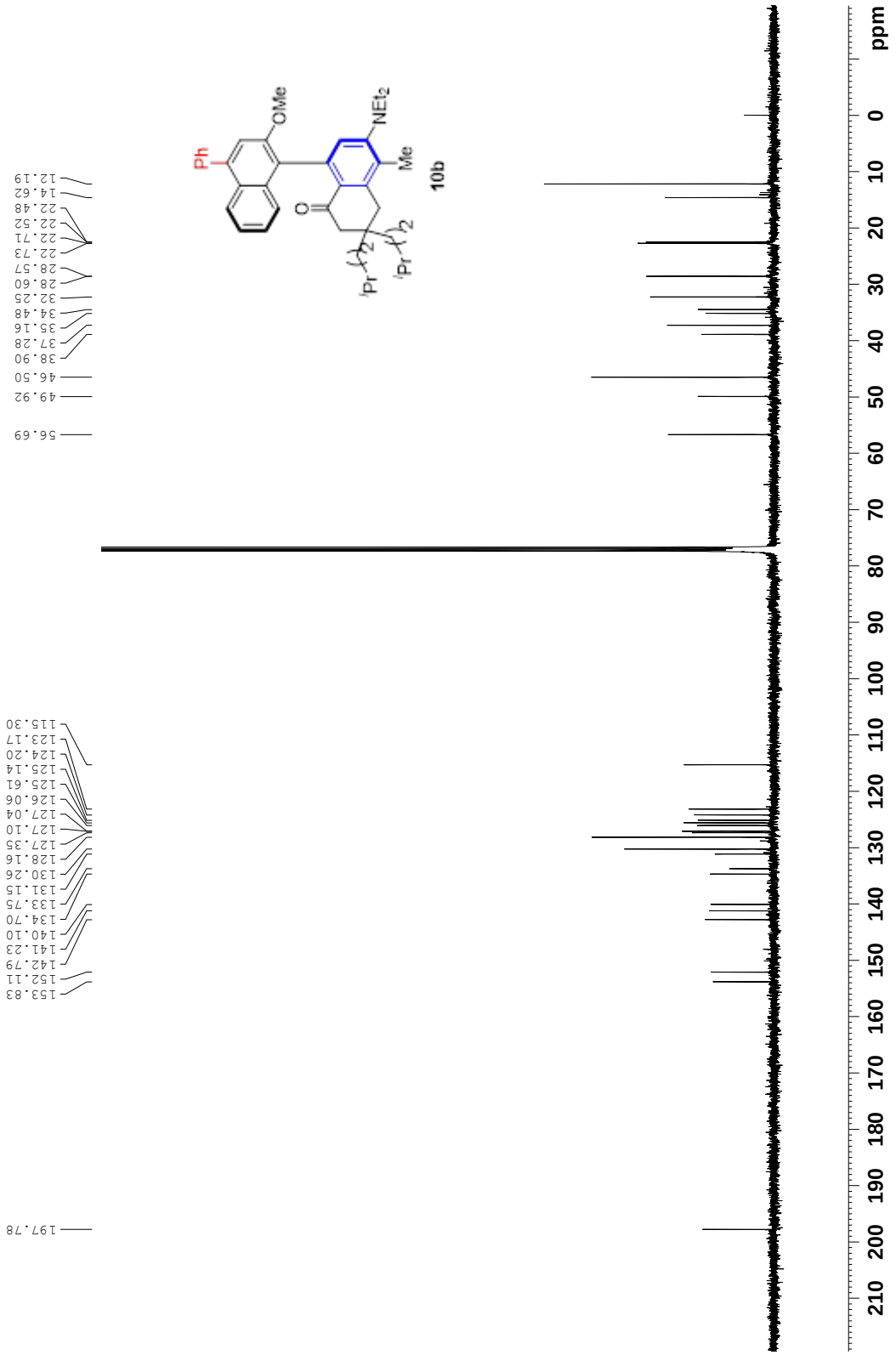



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 9.565 | 3456980 | 207485 | 92.694 | 94.307 |
| 2 | 16.475 | 272463 | 12525 | 7.306 | 5.693 |
| Total | | 3729443 | 220010 | 100.000 | 100.000 |

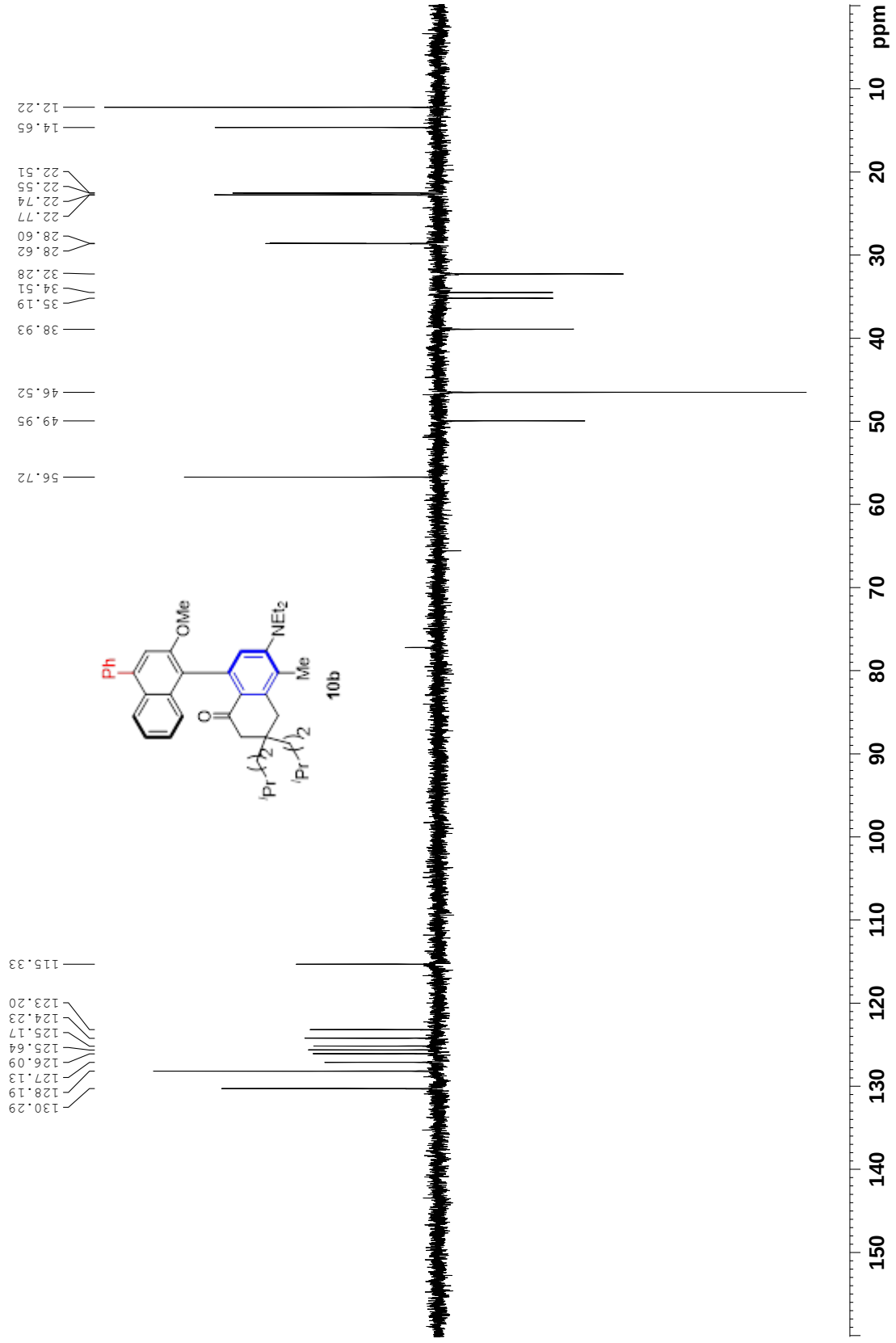
**Supplementary Figure 144. $^{1}$H NMR Spectrum of 10b**



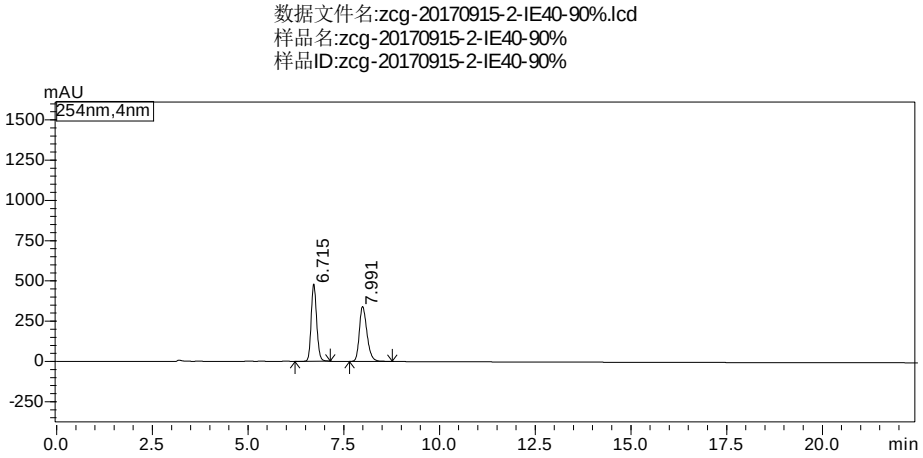
**Supplementary Figure 145. $^{13}$C NMR Spectrum of 10b**



**Supplementary Figure 146. $^{13}$C NMR Spectrum of 10b**

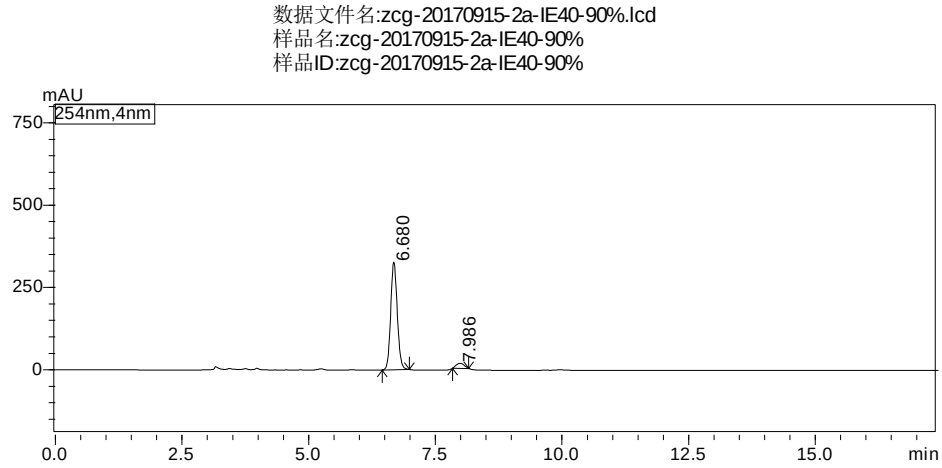


**Supplementary Figure 147. HPLC Spectrum of racemic 10b**



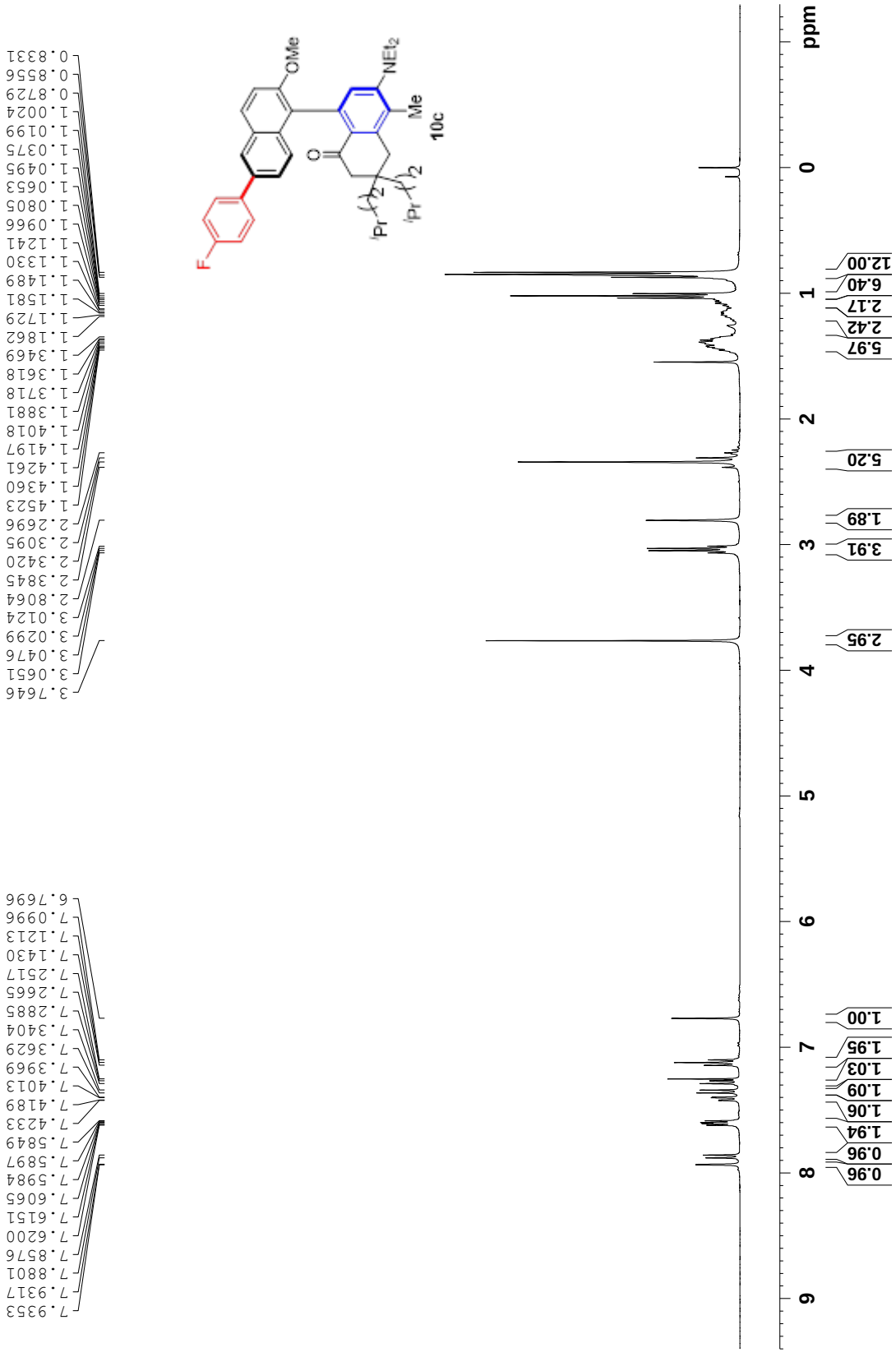

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.715 | 4767825 | 478543 | 50.117 | 58.330 |
| 2 | 7.991 | 4745523 | 341863 | 49.883 | 41.670 |
| Total | | 9513349 | 820406 | 100.000 | 100.000 |

## Supplementary Figure 148. HPLC Spectrum of 10b

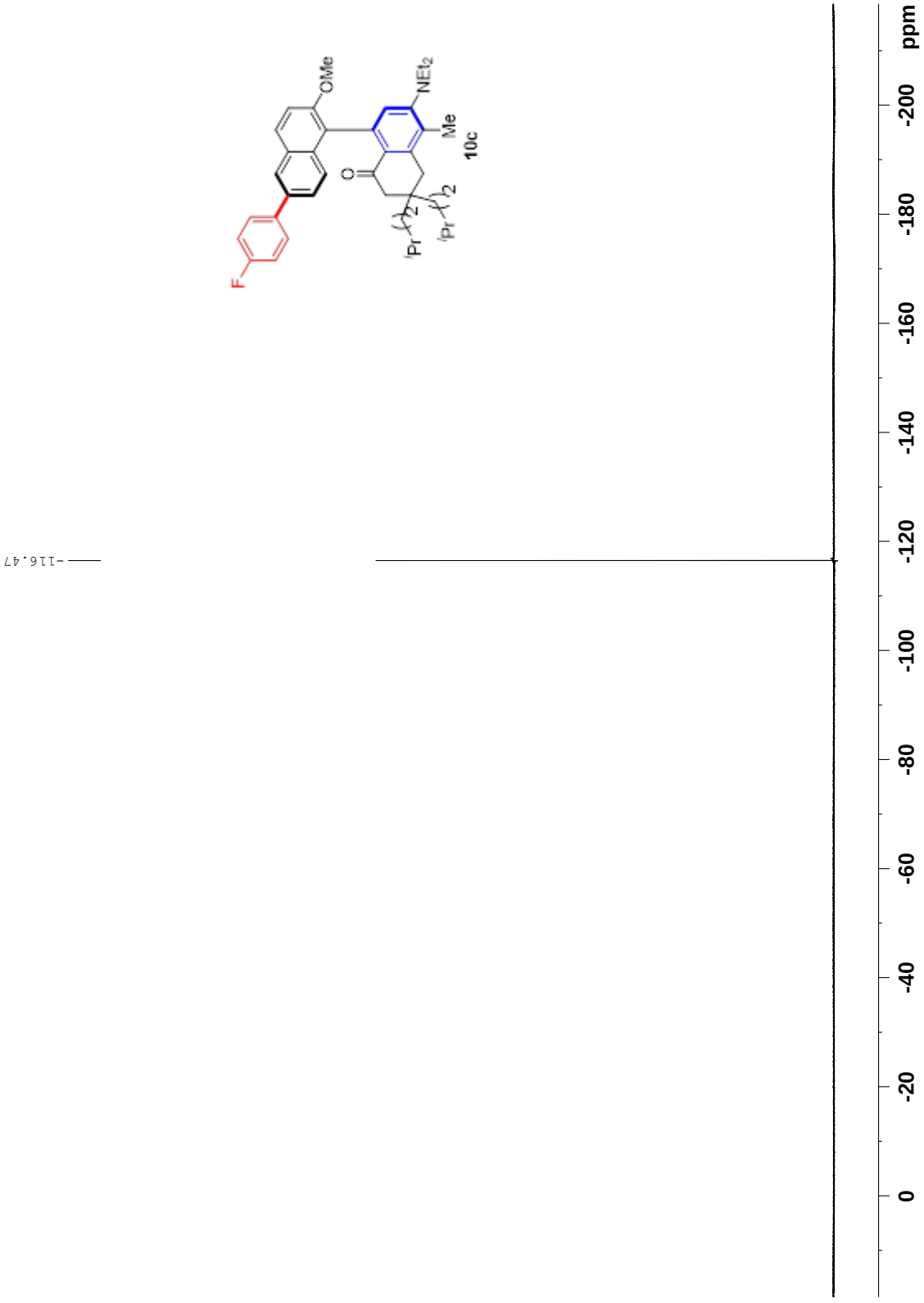



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 6.680 | 2956597 | 326990 | 94.708 | 95.591 |
| 2 | 7.986 | 165196 | 15082 | 5.292 | 4.409 |
| Total | | 3121794 | 342072 | 100.000 | 100.000 |

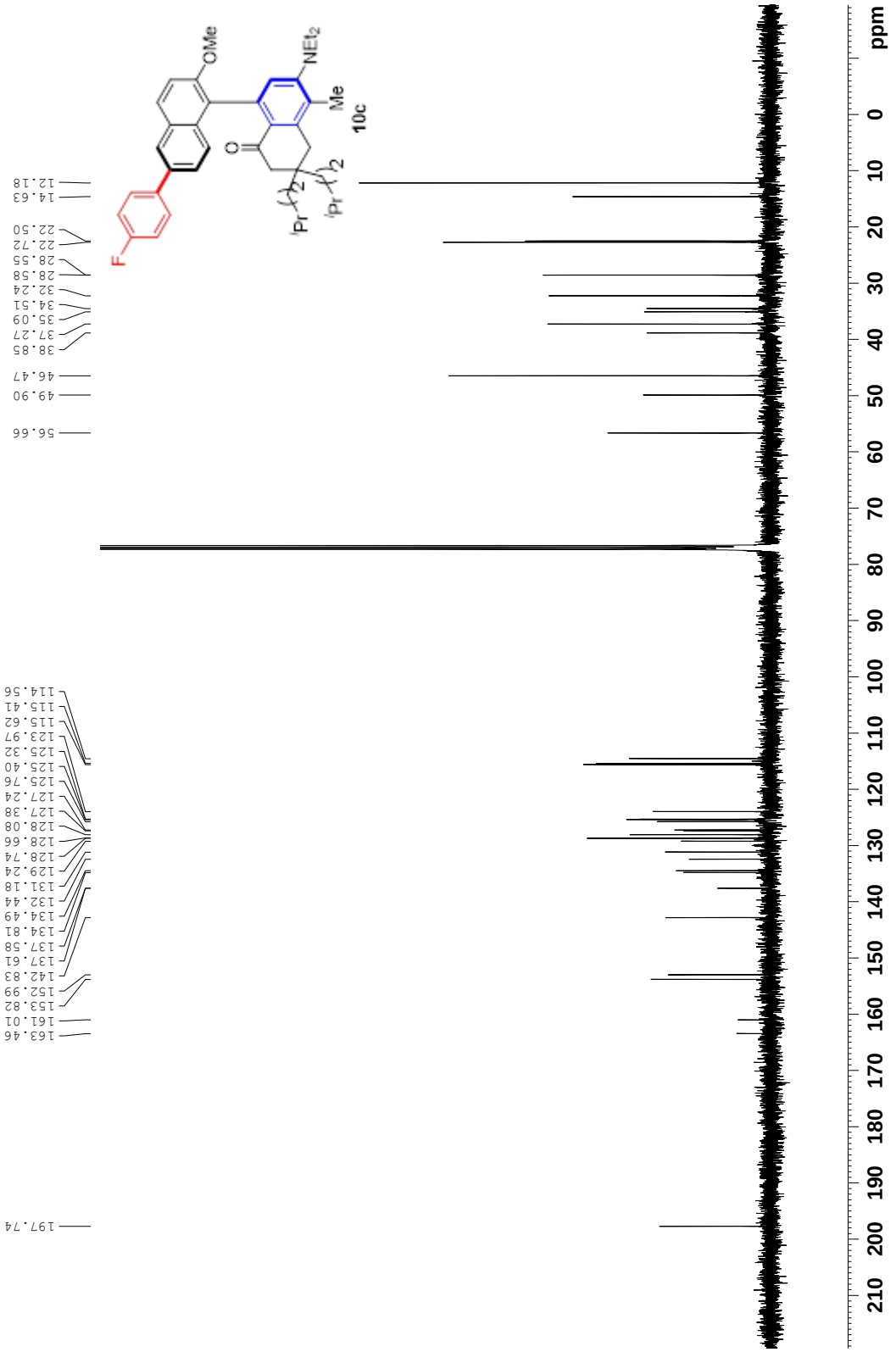
**Supplementary Figure 149. $^{1}$H NMR Spectrum of 10c**



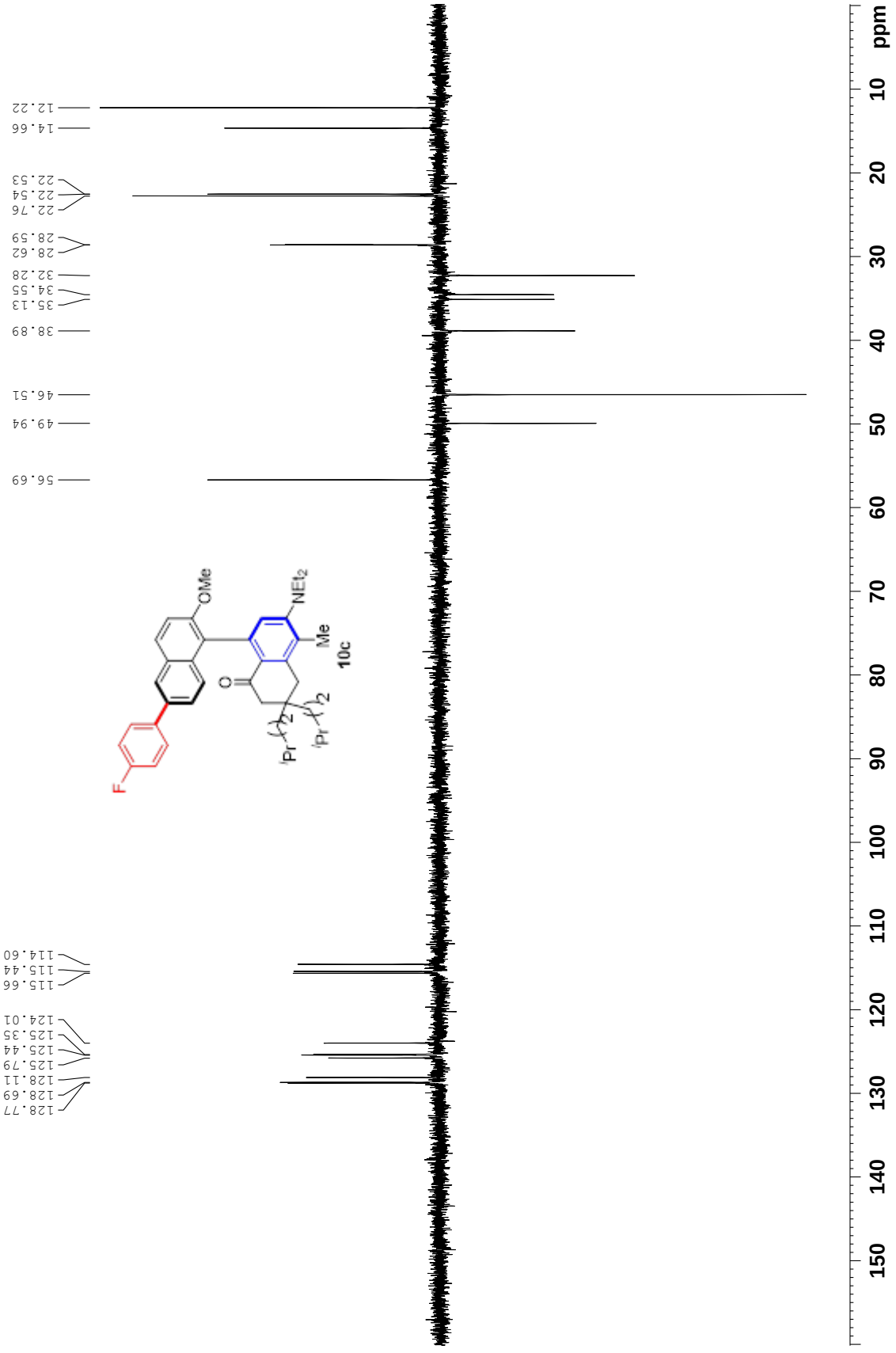
**Supplementary Figure 150. $^{19}$F NMR Spectrum of 10c**



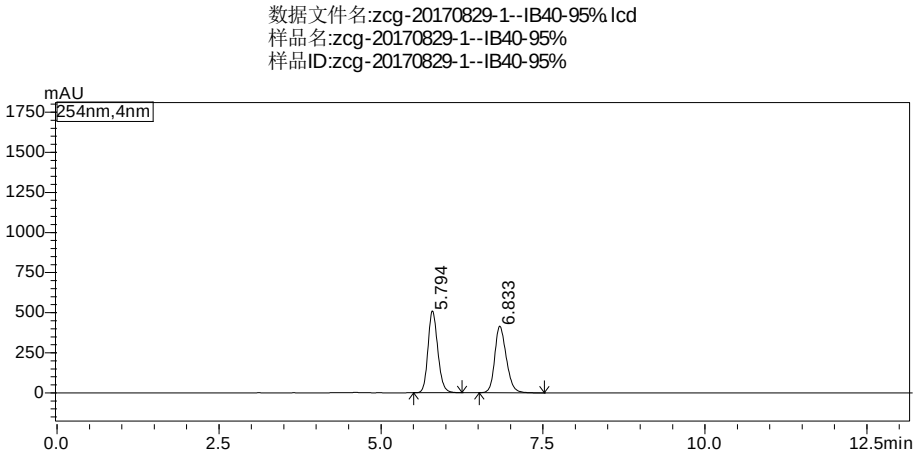
**Supplementary Figure 151. $^{13}$C NMR Spectrum of 10c**



**Supplementary Figure 152. $^{13}$C NMR Spectrum of 10c**

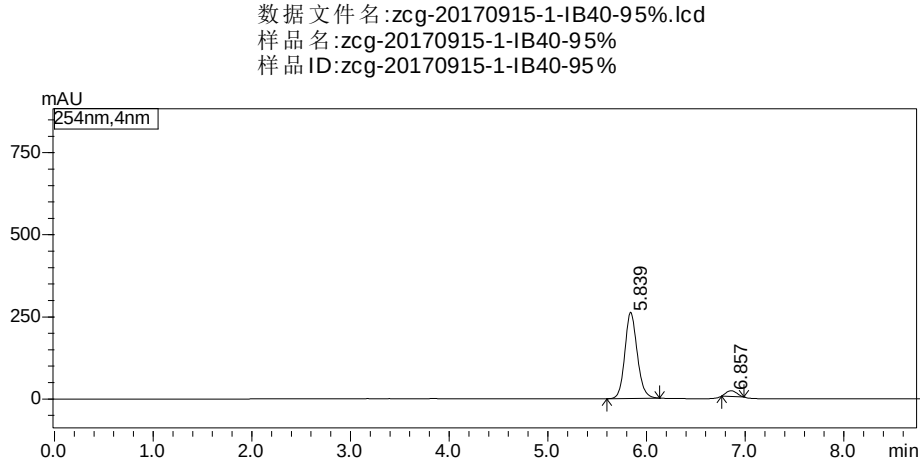


**Supplementary Figure 153. HPLC Spectrum of racemic 10c**



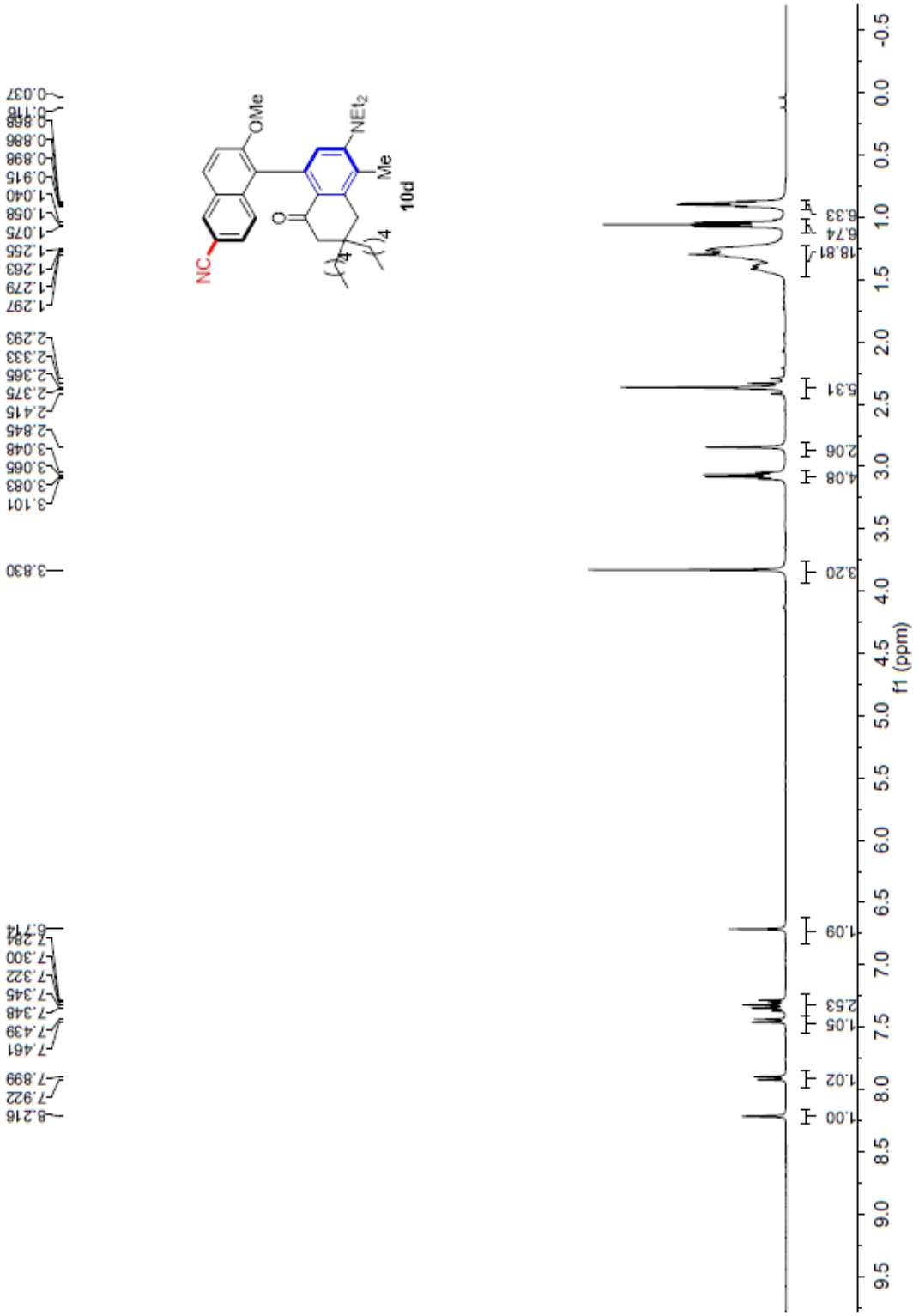

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 5.794 | 5378207 | 511182 | 50.999 | 55.179 |
| 2 | 6.833 | 5167519 | 415218 | 49.001 | 44.821 |
| Total | | 10545726 | 926400 | 100.000 | 100.000 |

## Supplementary Figure 154. HPLC Spectrum of 10c

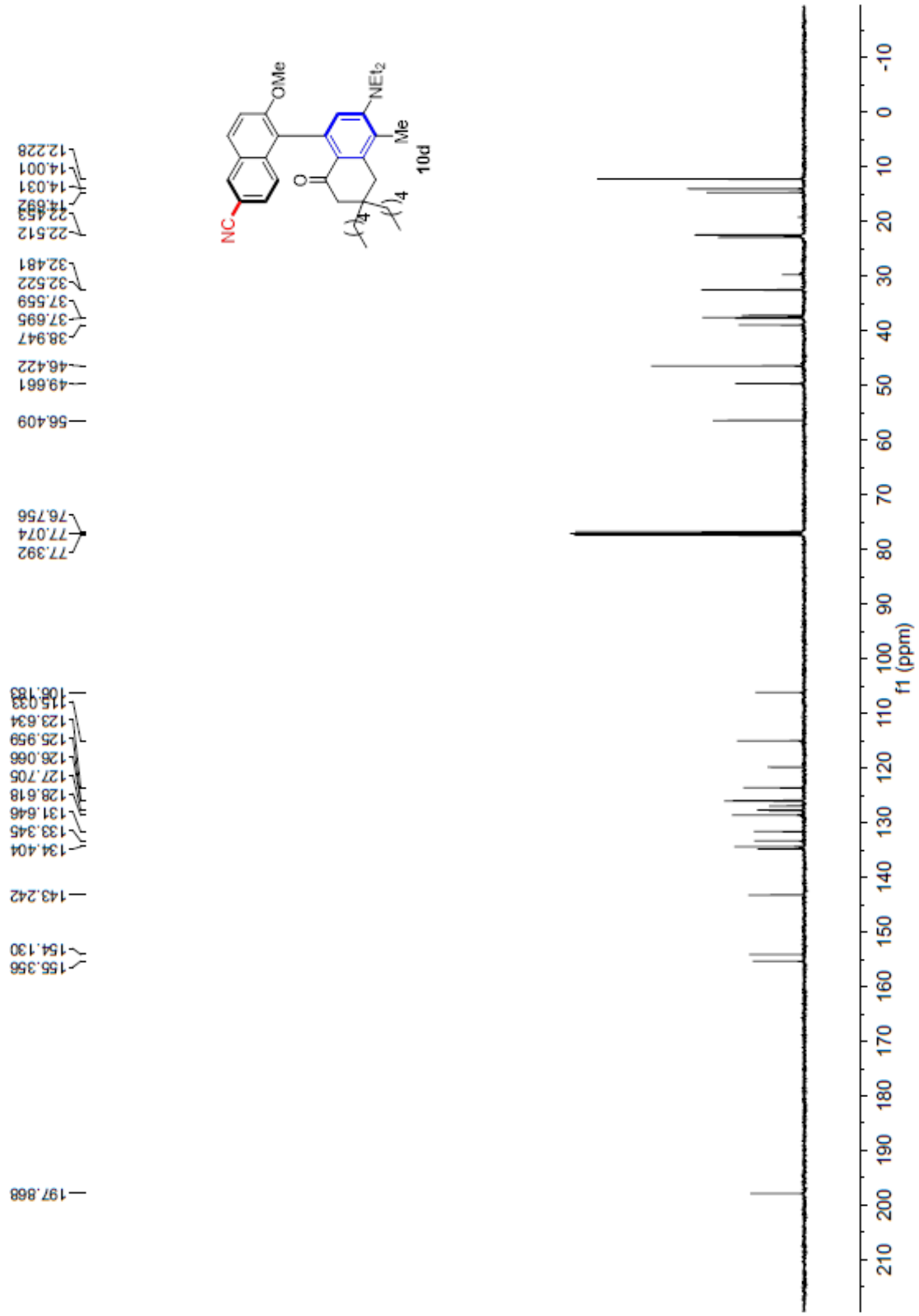



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 5.839 | 2286055 | 262530 | 93.048 | 92.874 |
| 2 | 6.857 | 170789 | 20144 | 6.952 | 7.126 |
| Total | | 2456845 | 282675 | 100.000 | 100.000 |

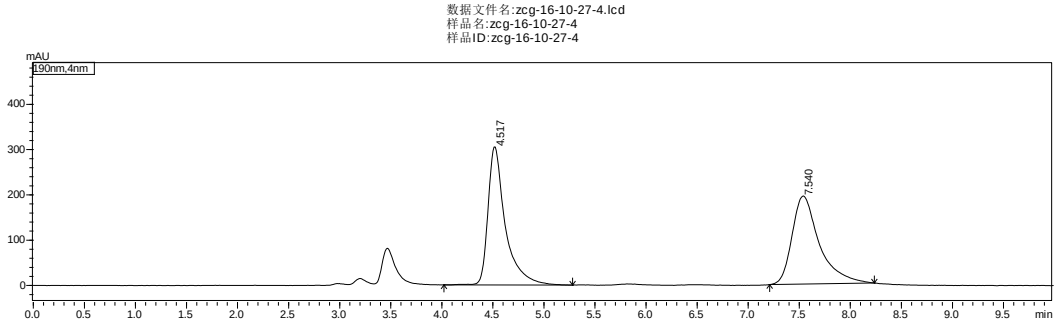
**Supplementary Figure 155. $^{1}$H NMR Spectrum of 10d**



**Supplementary Figure 156. $^{13}$C NMR Spectrum of 10d**

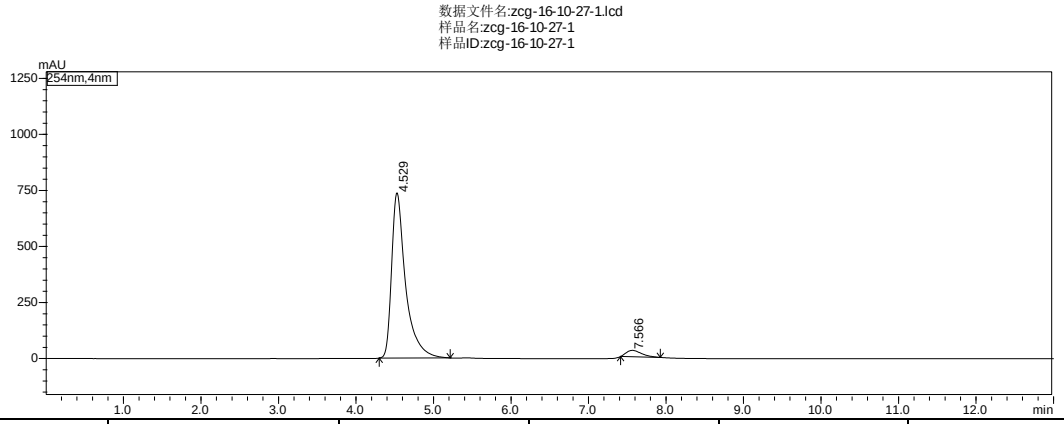


**Supplementary Figure 157. HPLC Spectrum of racemic 10d**



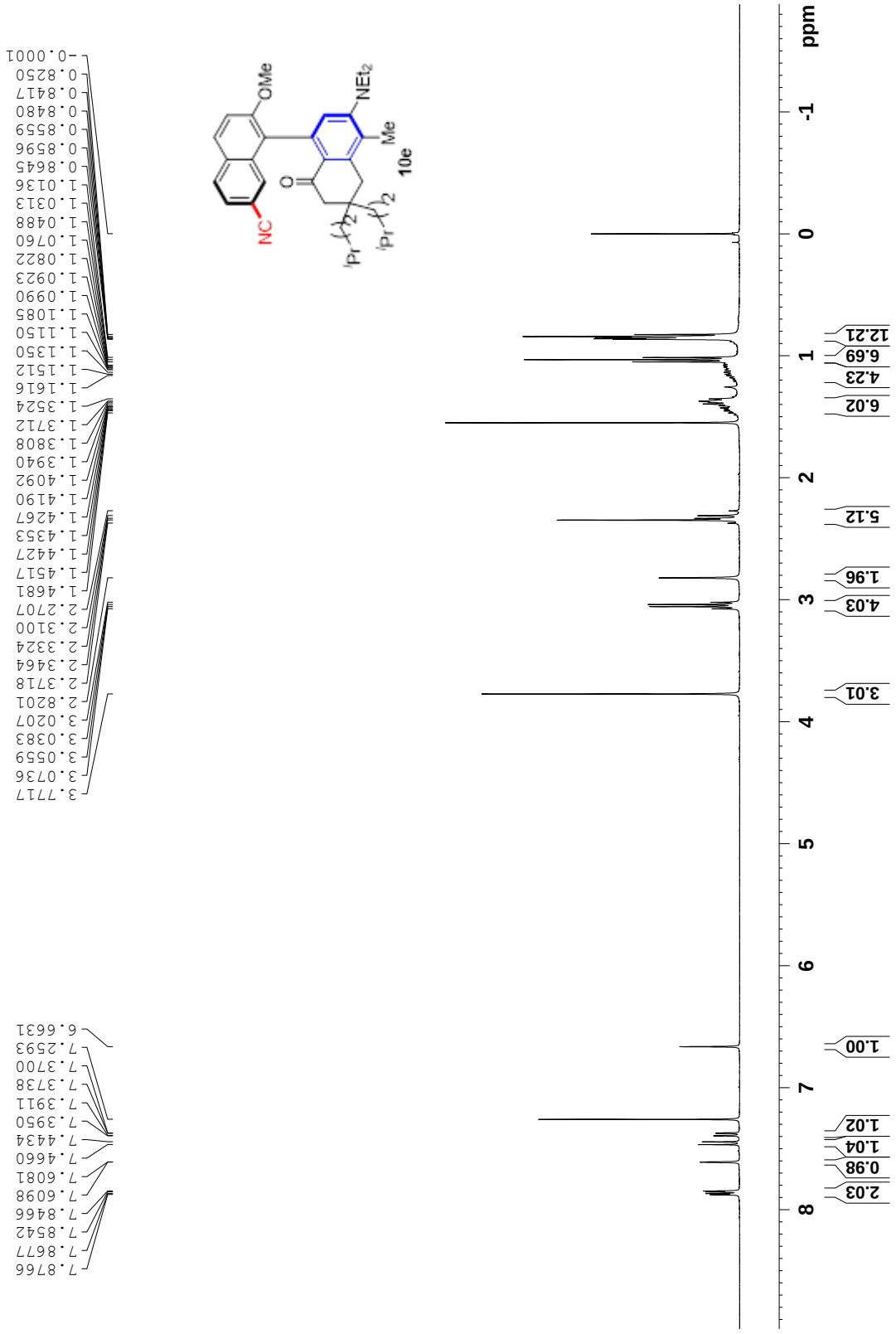

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 4.517 | 3602478 | 304856 | 49.961 | 61.052 |
| 2 | 7.540 | 3608147 | 194479 | 50.039 | 38.948 |
| Total | | 7210625 | 499334 | 100.000 | 100.000 |

## Supplementary Figure 158. HPLC Spectrum of 10d

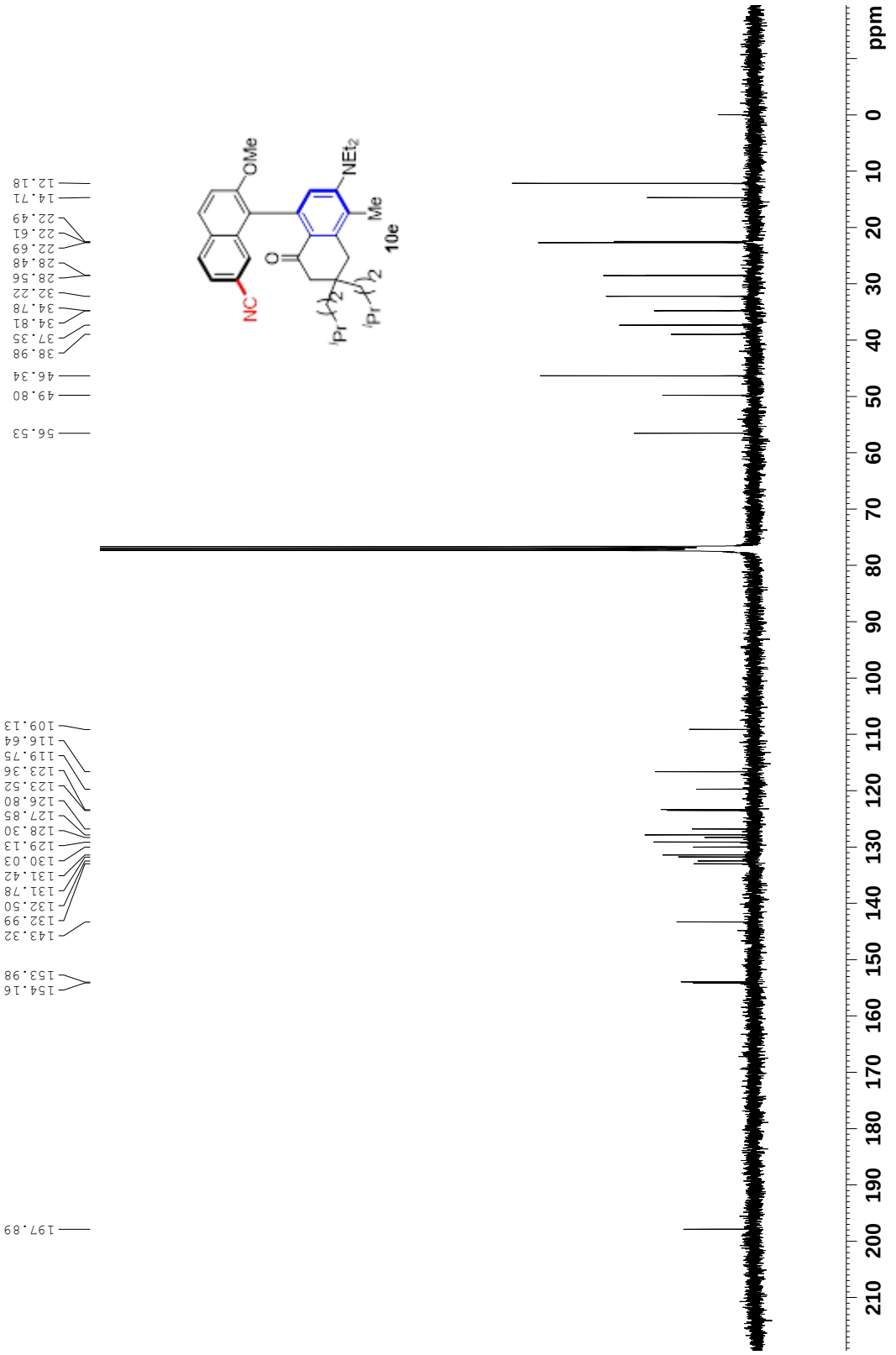



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 4.529 | 9250521 | 736931 | 95.883 | 96.235 |
| 2 | 7.566 | 397235 | 28832 | 4.117 | 3.765 |
| Total | | 9647756 | 765763 | 100.000 | 100.000 |

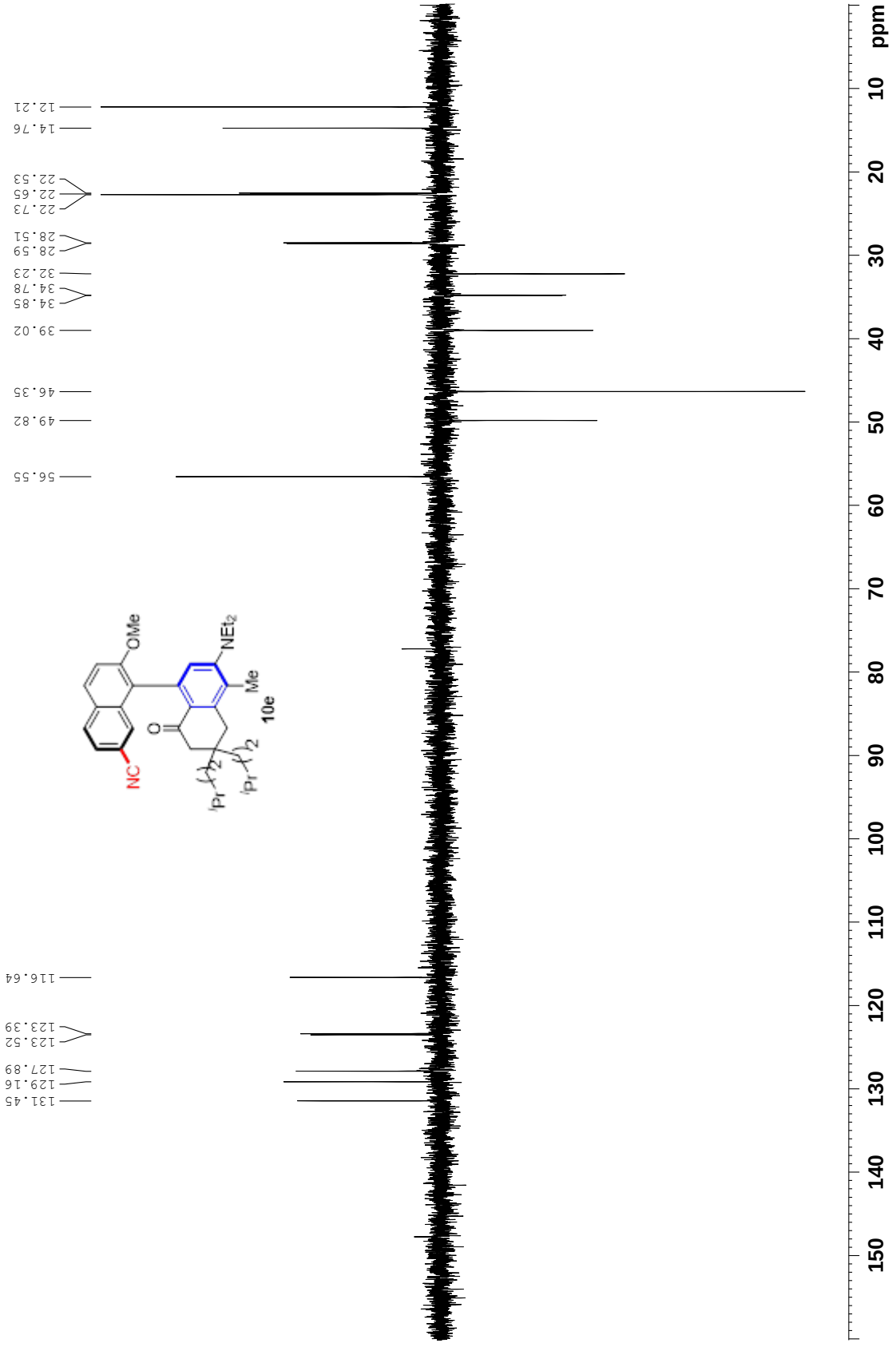
**Supplementary Figure 159. $^{1}$H NMR Spectrum of 10e**



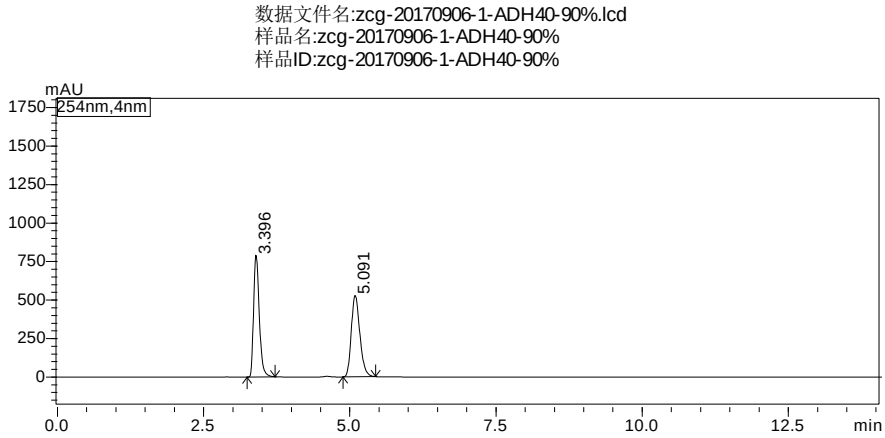
**Supplementary Figure 160. $^{13}$C NMR Spectrum of 10e**



**Supplementary Figure 161. $^{13}$C NMR Spectrum of 10e**

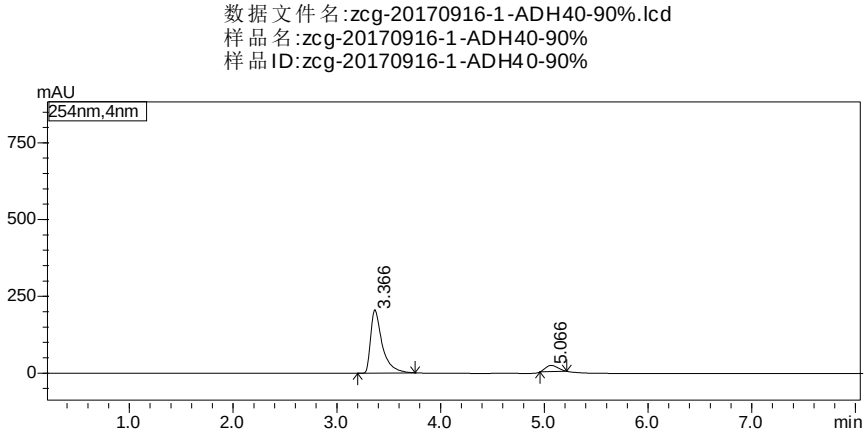


## Supplementary Figure 162. HPLC Spectrum of racemic 10e



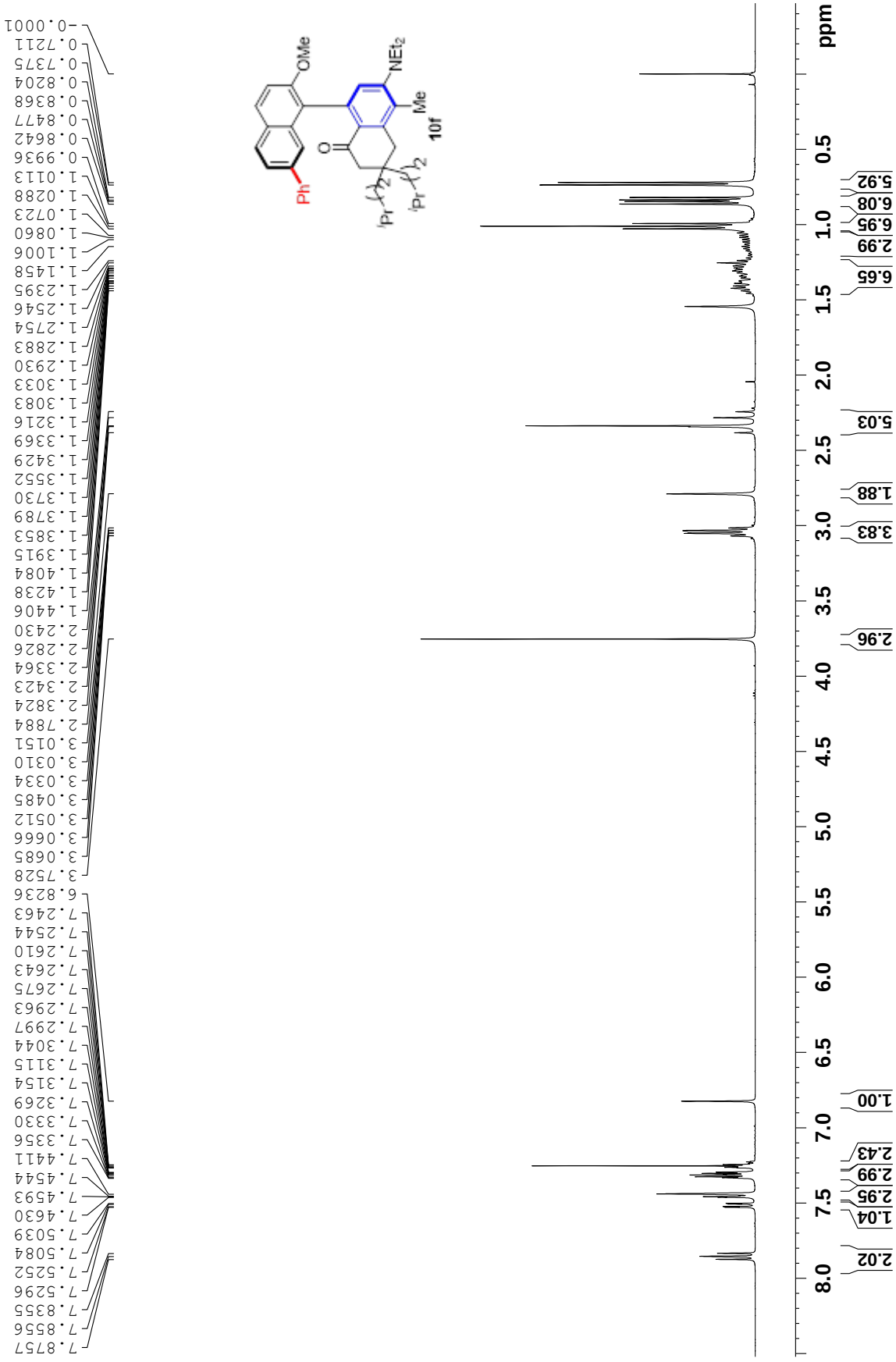

| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 3.396 | 5370929 | 790228 | 49.928 | 59.919 |
| 2 | 5.091 | 5386396 | 528592 | 50.072 | 40.081 |
| Total | | 10757326 | 1318820 | 100.000 | 100.000 |

## Supplementary Figure 163. HPLC Spectrum of 10e

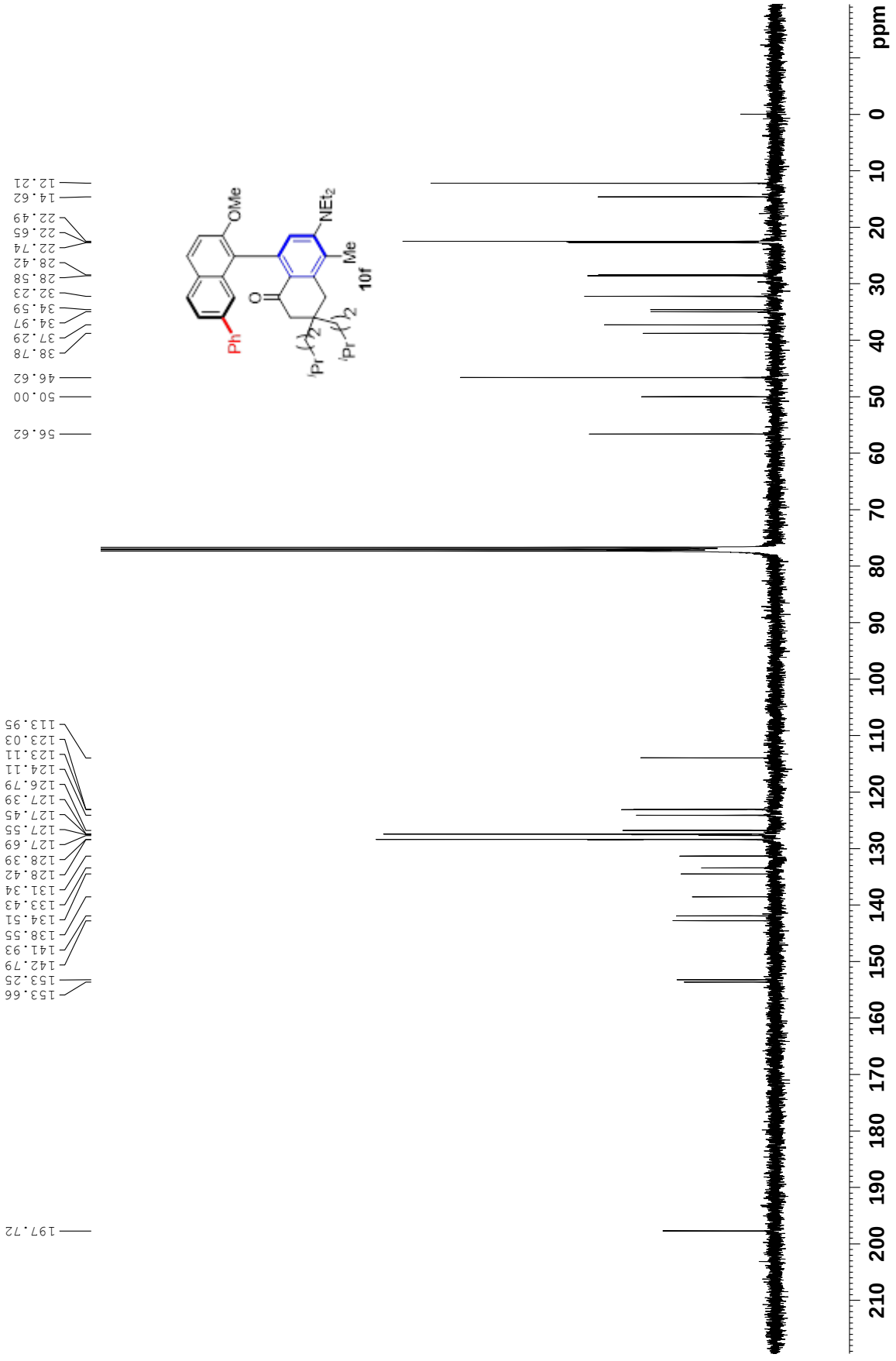



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 3.366 | 1606805 | 206745 | 90.580 | 91.104 |
| 2 | 5.066 | 167098 | 20187 | 9.420 | 8.896 |
| Total | | 1773903 | 226932 | 100.000 | 100.000 |

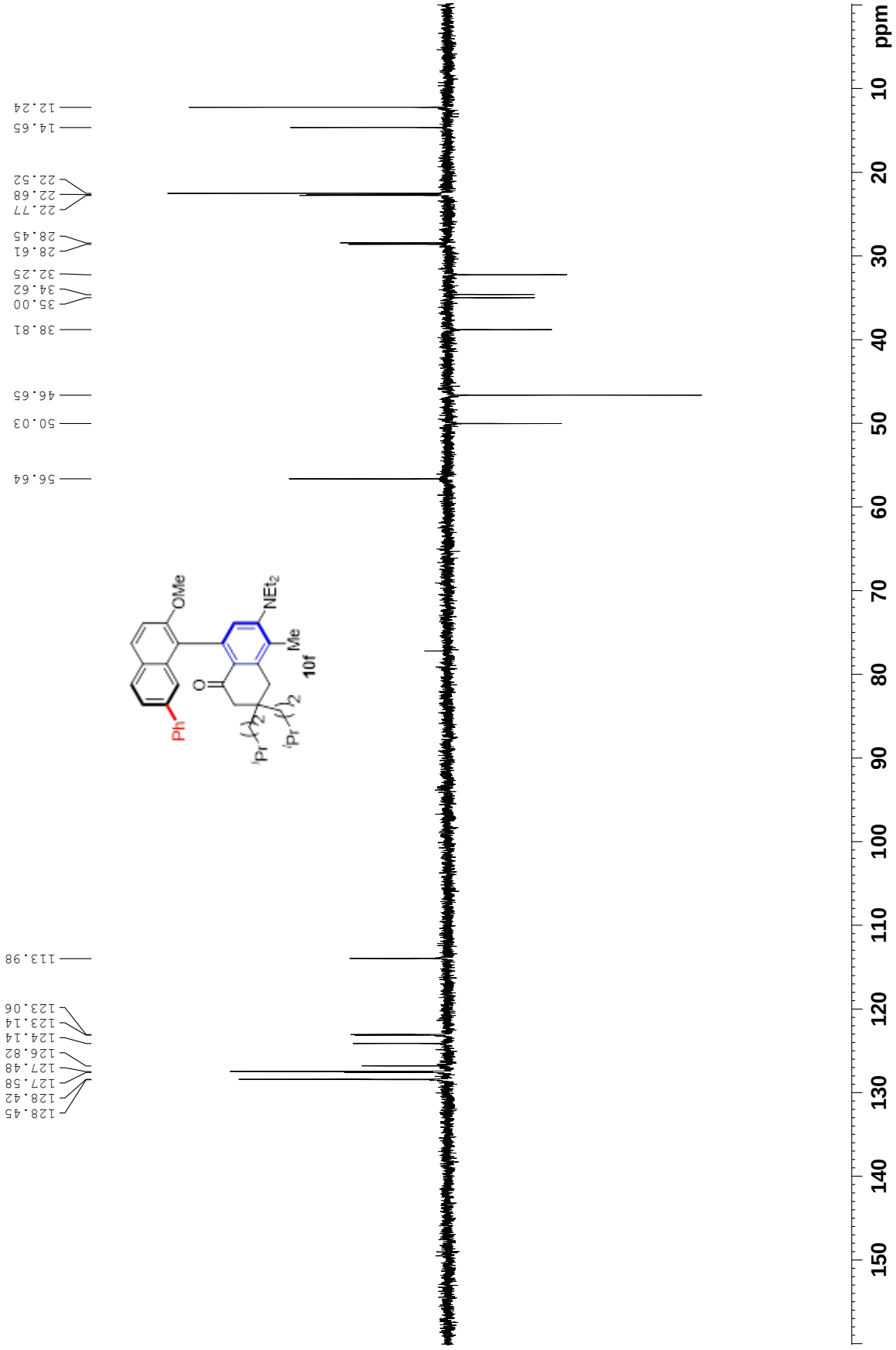
**Supplementary Figure 164. $^{1}$H NMR Spectrum of 10f**



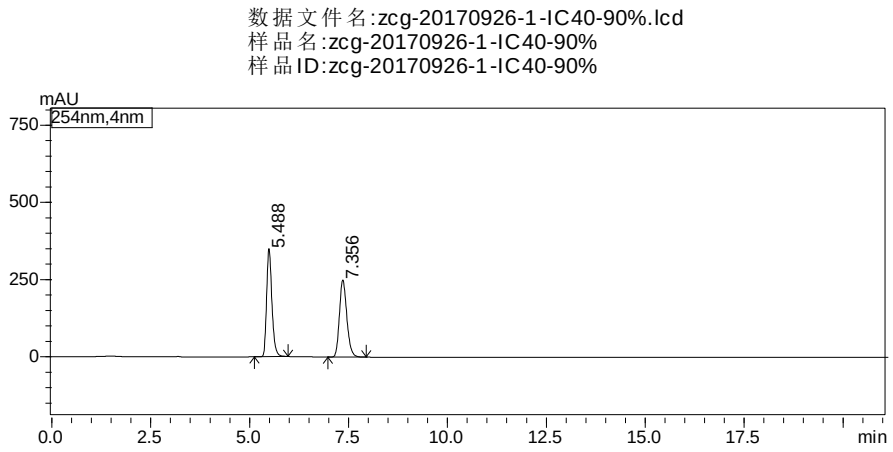
**Supplementary Figure 165. $^{13}$C NMR Spectrum of 10f**



**Supplementary Figure 166. $^{13}$C NMR Spectrum of 10f**



**Supplementary Figure 167. HPLC Spectrum of racemic 10f**




| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 5.488 | 3258170 | 349886 | 50.058 | 58.381 |
| 2 | 7.356 | 3250581 | 249425 | 49.942 | 41.619 |
| Total | | 6508751 | 599311 | 100.000 | 100.000 |

## Supplementary Figure 168. HPLC Spectrum of 10f

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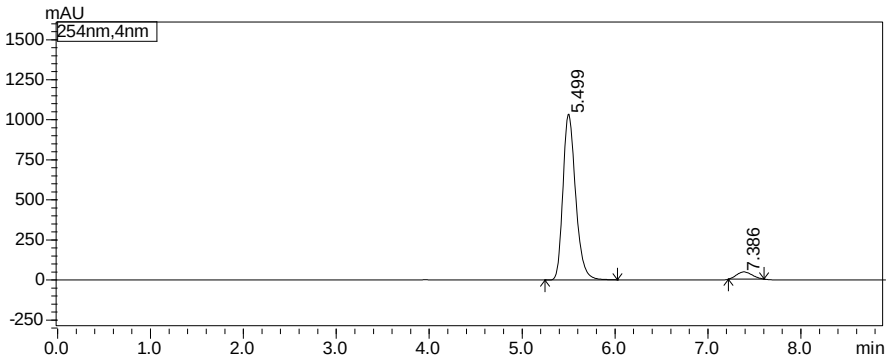
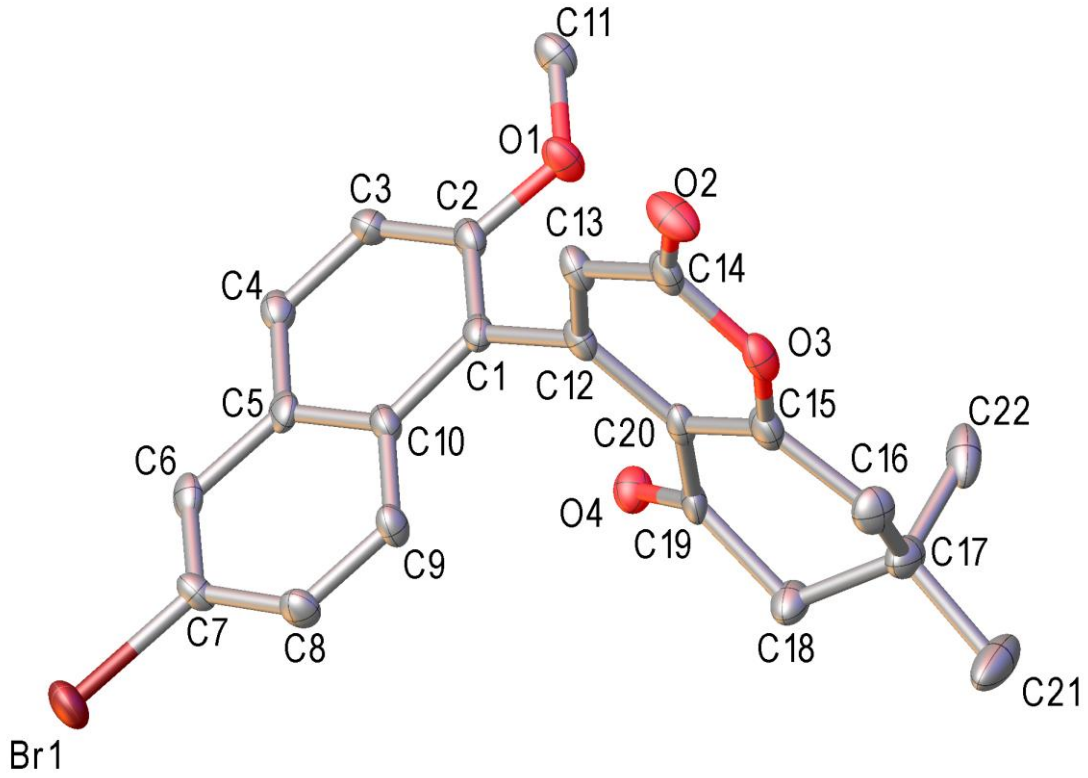



| Peak# | Ret. Time | Area | Height | Area% | Height% |
|---|---|---|---|---|---|
| 1 | 5.499 | 9828855 | 1034129 | 94.923 | 95.798 |
| 2 | 7.386 | 525704 | 45355 | 5.077 | 4.202 |
| Total | | 10354559 | 1079485 | 100.000 | 100.000 |

**Supplementary Figure 169. X-ray of 3au**




## Supplementary Tables

**Supplementary Table 1. Crystal data and structure refinement for 3au.**

| | | |
|---|---|---|
| Identification code | a | |
| Empirical formula | C22 H19 Br O4 | |
| Formula weight | 427.28 | |
| Temperature | 173.1500 K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P 21 21 21 | |
| Unit cell dimensions | a = 11.666(2) Å | = 90°. |
| | b = 12.090(2) Å | = 90°. |
| | c = 13.715(3) Å | = 90°. |
| Volume | 1934.4(6) $Å^3$ | |
| Z | 4 | |

| | |
|---|---|
| Density (calculated) | 1.467 $Mg/m^3$ |
| Absorption coefficient | 2.149 $mm^{-1}$ |
| F(000) | 872 |
| Crystal size | 0.385 x 0.276 x 0.174 $mm^3$ |
| Theta range for data collection | 2.246 to 27.483 °. |
| Index ranges | -15<=h<=15, -15<=k<=15, -17<=l<=17 |
| Reflections collected | 20386 |
| Independent reflections | 4432 [R(int) = 0.1690] |
| Completeness to theta = 25.242 ° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 1.00000 and 0.58344 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4432 / 0 / 248 |
| Goodness-of-fit on $F^2$ | 1.147 |
| Final R indices [I>2sigma(I)] | R1 = 0.0852, wR2 = 0.2416 |
| R indices (all data) | R1 = 0.1375, wR2 = 0.3162 |
| Absolute structure parameter | 0.06(3) |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.047 and -1.211 $e.Å^{-3}$ |

**Supplementary Table 2. Atomic coordinates (x $10^4$) and equivalent isotropic displacement parameters ($Å^2$x $10^3$) for 3au.**

U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| | x | y | z | U(eq) |
|---|---|---|---|---|
| Br1 | 3427(1) | 1560(1) | -1572(1) | 50(1) |
| O1 | 3650(6) | 5700(7) | 3181(6) | 42(2) |
| O2 | -799(7) | 5520(7) | 3099(6) | 51(2) |
| O3 | -83(6) | 4028(6) | 3798(5) | 38(2) |
| O4 | 3660(6) | 2594(6) | 3363(5) | 39(2) |
| C1 | 2988(8) | 4337(8) | 2137(7) | 31(2) |
| C2 | 3813(9) | 5110(9) | 2353(7) | 35(2) |
| C3 | 4780(9) | 5260(8) | 1743(7) | 36(2) |
| C4 | 4881(9) | 4632(9) | 912(7) | 36(2) |
| C5 | 4038(9) | 3807(9) | 664(7) | 35(2) |
| C6 | 4124(9) | 3177(9) | -201(7) | 36(2) |
| C7 | 3327(8) | 2393(8) | -411(7) | 32(2) |
| C8 | 2425(9) | 2185(9) | 236(7) | 37(2) |
| C9 | 2313(8) | 2803(9) | 1071(7) | 34(2) |
| C10 | 3110(9) | 3647(8) | 1299(7) | 32(2) |
| C11 | 4457(9) | 6561(10) | 3406(7) | 41(2) |
| C12 | 1939(8) | 4234(8) | 2757(7) | 33(2) |
| C13 | 1096(9) | 4982(10) | 2639(7) | 37(2) |
| C14 | -4(10) | 4929(10) | 3144(7) | 41(2) |
| C15 | 766(10) | 3278(10) | 3940(7) | 41(2) |
| C16 | 449(9) | 2402(11) | 4652(8) | 43(2) |
| C17 | 1490(11) | 1810(9) | 5071(9) | 48(3) |
| C18 | 2298(11) | 1482(9) | 4240(8) | 45(3) |
| C19 | 2659(10) | 2498(9) | 3646(6) | 36(2) |
| C20 | 1781(8) | 3328(8) | 3447(6) | 31(2) |
| C21 | 1120(17) | 753(13) | 5611(13) | 86(7) |
| C22 | 2111(12) | 2561(13) | 5799(8) | 59(4) |

**Supplementary Table 3. Bond lengths [Å] and angles [ ٩] for 3au.**

| | |
|---|---|
| Br1-C7 | 1.888(9) |
| O1-C2 | 1.354(12) |
| O1-C11 | 1.437(13) |
| O2-C14 | 1.172(14) |
| O3-C14 | 1.415(14) |
| O3-C15 | 1.356(14) |
| O4-C19 | 1.236(13) |
| C1-C2 | 1.373(14) |
| C1-C10 | 1.428(12) |
| C1-C12 | 1.495(13) |
| C2-C3 | 1.416(14) |
| C3-H3 | 0.9300 |
| C3-C4 | 1.375(14) |
| C4-H4 | 0.9300 |
| C4-C5 | 1.442(15) |
| C5-C6 | 1.413(14) |
| C5-C10 | 1.403(14) |
| C6-H6 | 0.9300 |
| C6-C7 | 1.358(14) |
| C7-C8 | 1.399(13) |
| C8-H8 | 0.9300 |
| C8-C9 | 1.374(13) |
| C9-H9 | 0.9300 |
| C9-C10 | 1.415(14) |
| C11-H11A | 0.9600 |
| C11-H11B | 0.9600 |
| C11-H11C | 0.9600 |
| C12-C13 | 1.346(14) |
| C12-C20 | 1.460(14) |
| C13-H13 | 0.9300 |
| C13-C14 | 1.460(14) |
| C15-C16 | 1.488(16) |
| C15-C20 | 1.366(13) |
| C16-H16A | 0.9700 |
| C16-H16B | 0.9700 |
| C16-C17 | 1.523(17) |

| | |
|---|---|
| C17-C18 | 1.531(14) |
| C17-C21 | 1.538(17) |
| C17-C22 | 1.53(2) |
| C18-H18A | 0.9700 |
| C18-H18B | 0.9700 |
| C18-C19 | 1.533(15) |
| C19-C20 | 1.459(14) |
| C21-H21A | 0.9600 |
| C21-H21B | 0.9600 |
| C21-H21C | 0.9600 |
| C22-H22A | 0.9600 |
| C22-H22B | 0.9600 |
| C22-H22C | 0.9600 |

| | |
|---|---|
| C2-O1-C11 | 118.1(8) |
| C15-O3-C14 | 123.9(8) |
| C2-C1-C10 | 120.1(9) |
| C2-C1-C12 | 120.5(8) |
| C10-C1-C12 | 119.4(9) |
| O1-C2-C1 | 116.2(9) |
| O1-C2-C3 | 122.6(10) |
| C1-C2-C3 | 121.3(9) |
| C2-C3-H3 | 120.4 |
| C4-C3-C2 | 119.2(9) |
| C4-C3-H3 | 120.4 |
| C3-C4-H4 | 119.4 |
| C3-C4-C5 | 121.3(9) |
| C5-C4-H4 | 119.4 |
| C6-C5-C4 | 121.5(9) |
| C10-C5-C4 | 118.4(9) |
| C10-C5-C6 | 120.1(10) |
| C5-C6-H6 | 119.8 |
| C7-C6-C5 | 120.4(10) |
| C7-C6-H6 | 119.8 |
| C6-C7-Br1 | 120.6(7) |
| C6-C7-C8 | 120.4(8) |
| C8-C7-Br1 | 119.0(7) |
| C7-C8-H8 | 119.9 |

| | |
|---|---|
| C9-C8-C7 | 120.2(9) |
| C9-C8-H8 | 119.9 |
| C8-C9-H9 | 119.6 |
| C8-C9-C10 | 120.9(9) |
| C10-C9-H9 | 119.6 |
| C5-C10-C1 | 119.8(9) |
| C5-C10-C9 | 118.0(8) |
| C9-C10-C1 | 122.2(9) |
| O1-C11-H11A | 109.5 |
| O1-C11-H11B | 109.5 |
| O1-C11-H11C | 109.5 |
| H11A-C11-H11B | 109.5 |
| H11A-C11-H11C | 109.5 |
| H11B-C11-H11C | 109.5 |
| C13-C12-C1 | 118.3(9) |
| C13-C12-C20 | 119.4(9) |
| C20-C12-C1 | 122.3(8) |
| C12-C13-H13 | 118.1 |
| C12-C13-C14 | 123.8(11) |
| C14-C13-H13 | 118.1 |
| O2-C14-O3 | 116.8(10) |
| O2-C14-C13 | 130.1(12) |
| O3-C14-C13 | 113.1(10) |
| O3-C15-C16 | 112.8(9) |
| O3-C15-C20 | 122.3(10) |
| C20-C15-C16 | 124.9(11) |
| C15-C16-H16A | 109.1 |
| C15-C16-H16B | 109.1 |
| C15-C16-C17 | 112.6(9) |
| H16A-C16-H16B | 107.8 |
| C17-C16-H16A | 109.1 |
| C17-C16-H16B | 109.1 |
| C16-C17-C18 | 109.4(10) |
| C16-C17-C21 | 110.4(12) |
| C16-C17-C22 | 110.2(10) |
| C18-C17-C21 | 108.5(10) |
| C18-C17-C22 | 110.3(11) |
| C22-C17-C21 | 108.1(13) |

| | |
|---|---|
| C17-C18-H18A | 109.5 |
| C17-C18-H18B | 109.5 |
| C17-C18-C19 | 110.9(9) |
| H18A-C18-H18B | 108.0 |
| C19-C18-H18A | 109.5 |
| C19-C18-H18B | 109.5 |
| O4-C19-C18 | 120.1(10) |
| O4-C19-C20 | 122.7(9) |
| C20-C19-C18 | 117.2(9) |
| C15-C20-C12 | 117.6(10) |
| C15-C20-C19 | 119.1(9) |
| C19-C20-C12 | 123.3(8) |
| C17-C21-H21A | 109.5 |
| C17-C21-H21B | 109.5 |
| C17-C21-H21C | 109.5 |
| H21A-C21-H21B | 109.5 |
| H21A-C21-H21C | 109.5 |
| H21B-C21-H21C | 109.5 |
| C17-C22-H22A | 109.5 |
| C17-C22-H22B | 109.5 |
| C17-C22-H22C | 109.5 |
| H22A-C22-H22B | 109.5 |
| H22A-C22-H22C | 109.5 |
| H22B-C22-H22C | 109.5 |

---

Symmetry transformations used to generate equivalent atoms:

**Supplementary Table 4**. **Anisotropic displacement parameters ($Å^2$x $10^3$) for 3au.**

The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| Br1 | 62(1) | 57(1) | 32(1) | -17(1) | 6(1) | -1(1) |
| O1 | 36(4) | 52(4) | 37(4) | -16(3) | 2(3) | -9(3) |
| O2 | 44(4) | 58(5) | 50(5) | -16(4) | -14(4) | 25(4) |
| O3 | 28(3) | 56(4) | 30(3) | -12(3) | 6(3) | -3(3) |
| O4 | 34(3) | 47(4) | 36(4) | 4(3) | 5(3) | 7(3) |
| C1 | 41(5) | 30(4) | 22(4) | 4(4) | 5(3) | 8(4) |
| C2 | 47(5) | 37(5) | 21(4) | -1(4) | -1(4) | 6(4) |
| C3 | 46(5) | 30(4) | 32(5) | -4(4) | 3(4) | -3(4) |
| C4 | 42(5) | 37(5) | 29(5) | 1(4) | 8(4) | 10(4) |
| C5 | 46(5) | 36(5) | 21(4) | 9(4) | 1(4) | 6(4) |
| C6 | 40(5) | 47(5) | 20(4) | 8(4) | 2(4) | 12(4) |
| C7 | 30(4) | 35(4) | 30(4) | -11(4) | -1(4) | 3(4) |
| C8 | 37(5) | 38(5) | 35(5) | -8(4) | -2(4) | -7(4) |
| C9 | 31(4) | 44(5) | 26(4) | -7(4) | 6(4) | -3(4) |
| C10 | 41(5) | 34(5) | 22(4) | -3(3) | 4(3) | 6(4) |
| C11 | 40(5) | 50(5) | 34(5) | -11(5) | -5(4) | 1(4) |
| C12 | 34(4) | 43(5) | 22(4) | -10(4) | 0(3) | 1(4) |
| C13 | 36(5) | 51(6) | 25(4) | -9(4) | 3(4) | 3(4) |
| C14 | 47(6) | 51(6) | 23(4) | -13(4) | 2(4) | -7(5) |
| C15 | 48(6) | 49(6) | 25(4) | -10(4) | 2(4) | -4(5) |
| C16 | 30(4) | 51(6) | 47(6) | 2(5) | 8(4) | -5(4) |
| C17 | 56(7) | 39(6) | 48(6) | 5(5) | 22(6) | 4(5) |
| C18 | 53(6) | 39(5) | 42(6) | 10(5) | 15(5) | 15(5) |
| C19 | 46(5) | 44(5) | 17(4) | -3(4) | 7(4) | -2(4) |
| C20 | 31(4) | 43(5) | 19(4) | -6(4) | 3(3) | -9(4) |
| C21 | 114(15) | 53(8) | 92(12) | 31(8) | 68(12) | 30(9) |
| C22 | 62(8) | 83(10) | 33(6) | 18(6) | 12(5) | 34(8) |

**Supplementary Table 5. Hydrogen coordinates (x $10^4$) and isotropic displacement parameters ($Å^2$x $10^3$) for 3au.**

| | x | y | z | U(eq) |
|---|---|---|---|---|
| H3 | 5339 | 5778 | 1903 | 44 |
| H4 | 5506 | 4742 | 502 | 43 |
| H6 | 4730 | 3299 | -628 | 43 |
| H8 | 1901 | 1626 | 101 | 44 |
| H9 | 1705 | 2665 | 1493 | 40 |
| H11A | 4492 | 7075 | 2874 | 62 |
| H11B | 5201 | 6242 | 3509 | 62 |
| H11C | 4217 | 6940 | 3986 | 62 |
| H13 | 1221 | 5566 | 2211 | 45 |
| H16A | -42 | 1865 | 4332 | 51 |
| H16B | 16 | 2732 | 5181 | 51 |
| H18A | 1916 | 956 | 3816 | 54 |
| H18B | 2974 | 1127 | 4507 | 54 |
| H21A | 571 | 939 | 6106 | 130 |
| H21B | 1778 | 416 | 5908 | 130 |
| H21C | 781 | 246 | 5157 | 130 |
| H22A | 2180 | 3291 | 5529 | 88 |
| H22B | 2860 | 2269 | 5930 | 88 |
| H22C | 1681 | 2595 | 6395 | 88 |

**Supplementary Table 6. Torsion angles [ ٩] for 3au.**

| | |
|---|---|
| Br1-C7-C8-C9 | -178.0(8) |
| O1-C2-C3-C4 | -179.7(9) |
| O3-C15-C16-C17 | -160.4(9) |
| O3-C15-C20-C12 | 0.7(14) |
| O3-C15-C20-C19 | 179.3(8) |
| O4-C19-C20-C12 | 11.4(14) |
| O4-C19-C20-C15 | -167.1(10) |
| C1-C2-C3-C4 | 1.1(15) |
| C1-C12-C13-C14 | 175.3(9) |
| C1-C12-C20-C15 | -176.6(9) |
| C1-C12-C20-C19 | 4.9(14) |
| C2-C1-C10-C5 | -3.9(14) |
| C2-C1-C10-C9 | 176.9(9) |
| C2-C1-C12-C13 | 77.9(12) |
| C2-C1-C12-C20 | -105.0(11) |
| C2-C3-C4-C5 | -1.6(15) |
| C3-C4-C5-C6 | 178.5(9) |
| C3-C4-C5-C10 | -0.7(14) |
| C4-C5-C6-C7 | 179.1(9) |
| C4-C5-C10-C1 | 3.4(14) |
| C4-C5-C10-C9 | -177.4(9) |
| C5-C6-C7-Br1 | 179.3(7) |
| C5-C6-C7-C8 | -1.4(15) |
| C6-C5-C10-C1 | -175.8(8) |
| C6-C5-C10-C9 | 3.4(14) |
| C6-C7-C8-C9 | 2.7(16) |
| C7-C8-C9-C10 | -0.9(16) |
| C8-C9-C10-C1 | 177.1(9) |
| C8-C9-C10-C5 | -2.2(15) |
| C10-C1-C2-O1 | -177.6(9) |
| C10-C1-C2-C3 | 1.6(14) |
| C10-C1-C12-C13 | -100.2(11) |
| C10-C1-C12-C20 | 76.9(12) |
| C10-C5-C6-C7 | -1.7(14) |
| C11-O1-C2-C1 | -176.5(9) |
| C11-O1-C2-C3 | 4.3(14) |
| C12-C1-C2-O1 | 4.3(14) |
| C12-C1-C2-C3 | -176.4(9) |
| C12-C1-C10-C5 | 174.2(9) |
| C12-C1-C10-C9 | -5.0(14) |
| C12-C13-C14-O2 | -179.6(11) |
| C12-C13-C14-O3 | 1.9(14) |

| | |
|---|---|
| C13-C12-C20-C15 | 0.5(13) |
| C13-C12-C20-C19 | -178.0(9) |
| C14-O3-C15-C16 | -178.7(9) |
| C14-O3-C15-C20 | -0.6(14) |
| C15-O3-C14-O2 | -179.3(9) |
| C15-O3-C14-C13 | -0.7(13) |
| C15-C16-C17-C18 | -47.8(14) |
| C15-C16-C17-C21 | -167.1(11) |
| C15-C16-C17-C22 | 73.6(12) |
| C16-C15-C20-C12 | 178.6(9) |
| C16-C15-C20-C19 | -2.8(15) |
| C16-C17-C18-C19 | 57.3(14) |
| C17-C18-C19-O4 | 139.2(11) |
| C17-C18-C19-C20 | -40.3(14) |
| C18-C19-C20-C12 | -169.1(9) |
| C18-C19-C20-C15 | 12.4(13) |
| C20-C12-C13-C14 | -1.9(15) |
| C20-C15-C16-C17 | 21.5(16) |
| C21-C17-C18-C19 | 177.7(13) |
| C22-C17-C18-C19 | -64.1(13) |

Symmetry transformations used to generate equivalent atoms:

**Supplementary Table 7. Hydrogen bonds for 3au [Å and ¶.**

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|

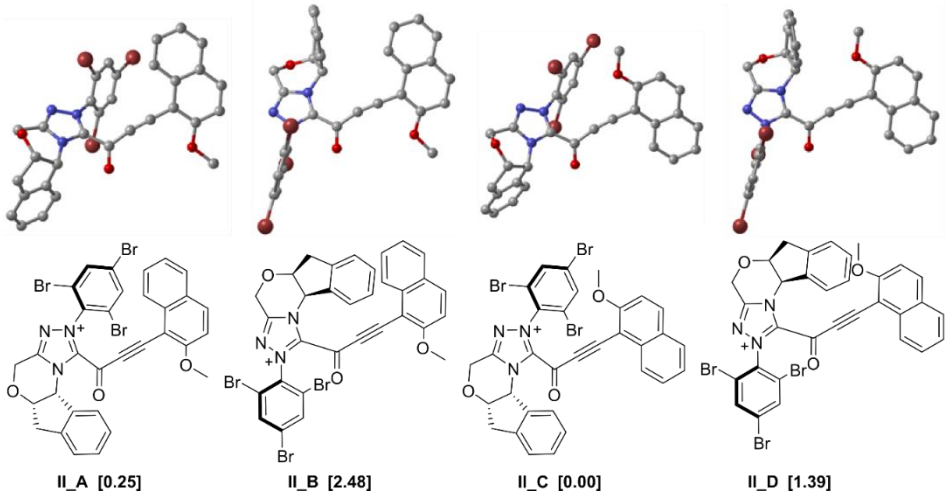
# Supplementary Discussion

## Computational Details

All structures were optimized at the B3LYP/6-31G(d,p) level of theory. Minima were confirmed by frequency calculations (1 imaginary frequency for transition state, 0 imaginary frequency for intermediates).

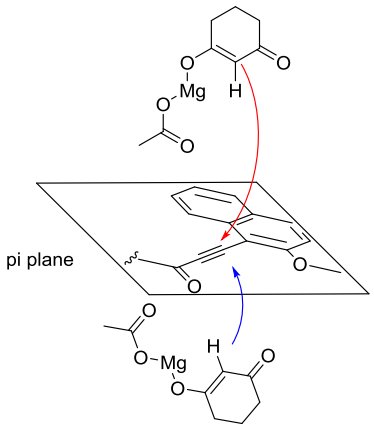
## Conformers

As intermediate **VI**, acyl azolium, has been ruled out by equation (2), only path A starting from **II** was investigated. **II** has four conformers denoted A, B, C, and D (Supplementary Figure 170). **II_A** and **II_C** with the carbonyl group pointing towards the indane ring is favored over **II_B** and **II_D** where the carbonyl group is towards the tribromophenyl group. Attention was focused on **II_A** as the methoxy group is in the same direction as the carbonyl group for an important favorable coordination to magnesium during the reaction.



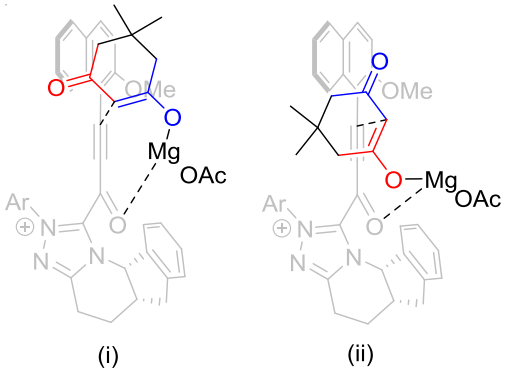

**Supplementary Figure 170. Optimized conformers of II and relative Gibbs Free Energies given in kcal/mol.**

The alkynyl azolium creates a twisted plane in which the ketoenolate can attack from two different sides (Supplementary Figure 171);



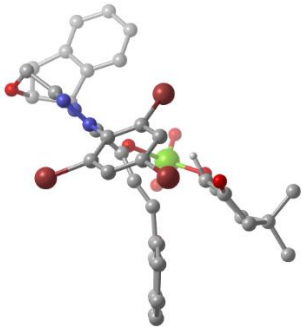
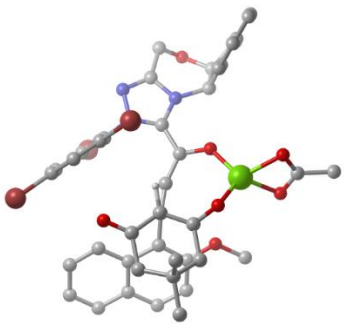

**Supplementary Figure 171. The attack by the ketoenolate can happen from either sides.**

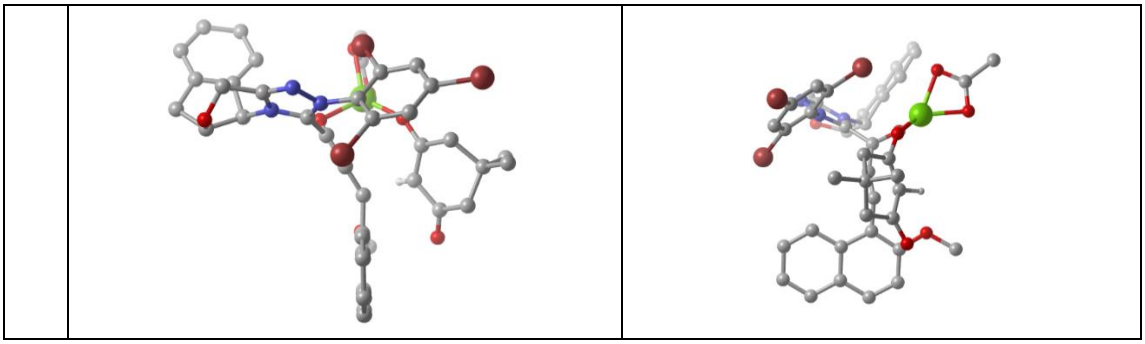
Furthermore, the Mg-coordinated ketoenolate has two enantio-faces for the nucleophilic attack (Supplementary Figure 172). The attack via **TS1(i)** will lead to an allenolate ready for the next proton transfer, while the attack via **TS1(ii)** results in an allenolate with the proton pointing away from the allene moiety and creates a higher energy barrier (2.78 kcal/mole higher, Supplementary Table 8).



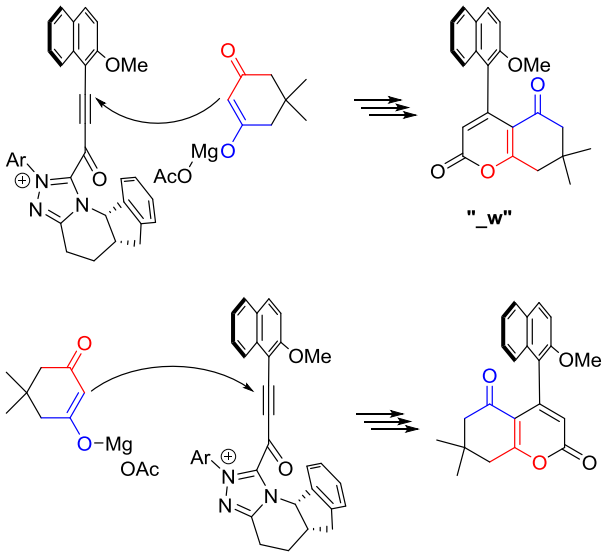

**Supplementary Figure 172. The ketoenolate can attack in two different ways, (i) and (ii).**

**Supplementary Table 8. Comparison between TS1(i) and TS1(ii).**

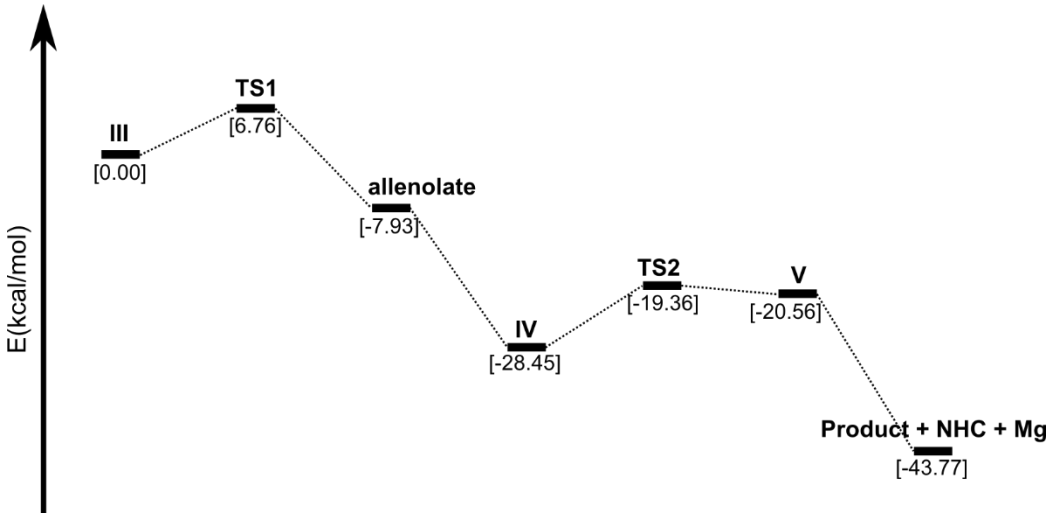
| | | |
|---|---|---|
| | **TS1(i)** (0 kcal/mol) | |
| i |  |  |
| ii | **TS1(ii)** (+2.78 kcal/mol) | |



We hypothesize that enantioselectivity is determined by the attack on the pi plane by the ketoenolate (Figure 172 and 173).




**Supplementary Figure 173. The attack by the ketoenolate on the alkyne bond .**




**Supplementary Figure 174.** Energy profile of Path A from Figure 6 for **A**.

## Geometries and Energies

### II_A

E(RB3LYP/6-31G(d,p)) = -9336.82746821 A.U.

Temp. 298.150 K 1.00000 Atm.

| | |
|---|---|
| E + zero-point Energies | = -9336.367804 |
| E + thermal Energies | = -9336.333140 |
| E + thermal Enthalpies | = -9336.332196 |
| E + thermal Free Energies | = -9336.439358 |

Geometry at E(RB3LYP/6-31G(d,p))

Charge: 1 Multiplicity: 1

C -2.767866000000 2.595911000000 -0.119090000000
C -3.162194000000 3.638569000000 -0.993607000000
C -4.482027000000 4.144260000000 -0.940775000000
C -5.381047000000 3.627133000000 -0.035805000000
H -4.789158000000 4.936122000000 -1.611440000000
H -6.392080000000 4.024168000000 -0.008346000000
C -1.460270000000 2.109576000000 -0.210746000000
C -0.311127000000 1.689094000000 -0.308282000000
C 1.067187000000 1.444050000000 -0.450926000000
O 1.859225000000 2.132159000000 -1.095722000000
C 3.087946000000 -0.999698000000 1.363656000000
C 1.660039000000 0.262641000000 0.284806000000
N 2.050760000000 -1.769876000000 1.172964000000
N 2.894019000000 0.248563000000 0.822785000000
C 3.975300000000 1.262586000000 0.847739000000
H 3.499679000000 2.235544000000 0.717467000000
C 4.328322000000 -1.211627000000 2.171164000000
H 5.190968000000 -1.417918000000 1.523743000000
H 4.193260000000 -2.046543000000 2.859860000000
C 4.756160000000 1.171803000000 2.219352000000
H 4.423490000000 1.959852000000 2.896670000000
O 4.492139000000 -0.031668000000 2.947504000000
C 6.248806000000 1.326372000000 1.836126000000
H 6.585243000000 2.348950000000 2.046554000000
H 6.863768000000 0.661041000000 2.450376000000
C 5.030766000000 0.994451000000 -0.208854000000
C 6.309034000000 1.030877000000 0.356809000000
C 4.844120000000 0.770231000000 -1.573618000000
C 7.431979000000 0.834978000000 -0.447810000000
C 5.970414000000 0.565871000000 -2.371165000000

H 3.847827000000 0.755510000000 -2.002434000000
C 7.253466000000 0.598930000000 -1.811944000000
H 8.430162000000 0.862187000000 -0.020941000000
H 5.851602000000 0.386306000000 -3.434913000000
H 8.119541000000 0.440100000000 -2.446831000000
N 1.163035000000 -0.967571000000 0.495341000000
C -0.053759000000 -1.535060000000 0.008117000000
C -1.065925000000 -1.901908000000 0.904321000000
C -0.217919000000 -1.801862000000 -1.359182000000
C -2.229258000000 -2.513083000000 0.450435000000
C -1.380773000000 -2.404161000000 -1.827943000000
C -2.375576000000 -2.755471000000 -0.915476000000
H -3.008260000000 -2.790587000000 1.147944000000
H -1.504353000000 -2.604209000000 -2.884247000000
Br -0.876060000000 -1.546654000000 2.755232000000
Br 1.146030000000 -1.353869000000 -2.600439000000
Br -3.957725000000 -3.582183000000 -1.543719000000
C -3.707268000000 2.066336000000 0.842026000000
C -5.034233000000 2.592131000000 0.872427000000
C -5.967706000000 2.079292000000 1.809352000000
C -5.604691000000 1.084831000000 2.691393000000
C -4.288143000000 0.574970000000 2.666123000000
H -3.994158000000 -0.201905000000 3.365798000000
C -3.359951000000 1.055227000000 1.764010000000
H -6.322702000000 0.698161000000 3.407014000000
H -6.974004000000 2.488003000000 1.821548000000
H -2.350385000000 0.663413000000 1.767958000000
O -2.228160000000 4.081942000000 -1.847166000000
C -2.539699000000 5.142388000000 -2.758070000000
H -1.622683000000 5.318900000000 -3.318459000000
H -3.339174000000 4.849198000000 -3.446005000000
H -2.822140000000 6.053325000000 -2.220873000000

**II_B**

E(RB3LYP/6-31G(d,p)) = -9336.82149543 A.U.

Temp. 298.150 K 1.00000 Atm.

E + zero-point Energies = -9336.362132
E + thermal Energies = -9336.327292
E + thermal Enthalpies = -9336.326348
E + thermal Free Energies = -9336.435796

Geometry at E(RB3LYP/6-31G(d,p))

Charge: 1 Multiplicity: 1
C 3.610653000000 2.463564000000 0.215033000000
C 3.603099000000 3.853385000000 0.492609000000
C 4.815302000000 4.582366000000 0.491429000000
C 6.001505000000 3.940964000000 0.219090000000
H 4.813537000000 5.642550000000 0.708588000000
H 6.926157000000 4.511432000000 0.226083000000
C 2.389572000000 1.781541000000 0.276614000000
C 1.302583000000 1.217612000000 0.363792000000
C -0.056980000000 0.848560000000 0.491396000000
O -0.986440000000 1.644065000000 0.584772000000
C -0.507687000000 -2.791781000000 0.835853000000
C -0.416740000000 -0.618810000000 0.548094000000
N -1.746176000000 -2.433468000000 0.627341000000
N 0.339719000000 -1.710615000000 0.787834000000
C 1.796707000000 -1.914459000000 0.891731000000
H 2.237913000000 -0.957607000000 1.178039000000
C 0.074742000000 -4.111495000000 1.228880000000
H 0.543488000000 -4.607615000000 0.368485000000
H -0.704879000000 -4.761094000000 1.628996000000
C 2.118555000000 -3.024569000000 1.964599000000
H 2.384128000000 -2.566948000000 2.919065000000
O 0.995482000000 -3.849479000000 2.281443000000
C 3.300909000000 -3.818379000000 1.354028000000
H 4.246735000000 -3.474065000000 1.790534000000
H 3.206860000000 -4.880296000000 1.600535000000
C 2.381289000000 -2.459441000000 -0.399144000000
C 3.245596000000 -3.525125000000 -0.126861000000
C 2.158808000000 -2.015672000000 -1.703609000000
C 3.920281000000 -4.156127000000 -1.172630000000
C 2.831010000000 -2.655693000000 -2.746495000000
H 1.462585000000 -1.208529000000 -1.915324000000
C 3.708247000000 -3.713651000000 -2.480636000000
H 4.590978000000 -4.987443000000 -0.976575000000
H 2.670639000000 -2.332610000000 -3.769934000000
H 4.221359000000 -4.203195000000 -3.302432000000
N -1.675267000000 -1.078879000000 0.445364000000
C -2.863426000000 -0.367232000000 0.087251000000
C -3.794682000000 -0.011966000000 1.066395000000
C -3.119007000000 -0.070181000000 -1.254813000000
C -4.977623000000 0.627509000000 0.711937000000
C -4.293822000000 0.572587000000 -1.626050000000
C -5.214438000000 0.910999000000 -0.633192000000
H -5.697911000000 0.904282000000 1.470609000000

H -4.489765000000 0.804038000000 -2.664753000000
Br -3.427468000000 -0.372888000000 2.886580000000
Br -1.841175000000 -0.525480000000 -2.586283000000
Br -6.821301000000 1.784276000000 -1.125434000000
C 6.134814000000 -0.175204000000 -0.703286000000
H 6.162286000000 -1.229698000000 -0.960698000000
C 7.333834000000 0.569352000000 -0.673646000000
C 7.294721000000 1.912617000000 -0.369744000000
C 4.922331000000 0.422523000000 -0.419840000000
C 4.853358000000 1.795399000000 -0.092461000000
C 6.063781000000 2.553689000000 -0.078512000000
O 2.407546000000 4.397435000000 0.758784000000
C 2.307192000000 5.795029000000 1.055854000000
H 2.871841000000 6.047314000000 1.959114000000
H 2.653645000000 6.402875000000 0.214076000000
H 1.246929000000 5.977078000000 1.225317000000
H 8.206969000000 2.501998000000 -0.353221000000
H 8.278627000000 0.085498000000 -0.898010000000
H 4.008383000000 -0.157666000000 -0.474452000000

**II_C**

E(RB3LYP/6-31G(d,p)) = -9336.82755746 A.U.

Temp. 298.150 K 1.00000 Atm.

| | |
|---|---|
| E + zero-point Energies | = -9336.367816 |
| E + thermal Energies | = -9336.333179 |
| E + thermal Enthalpies | = -9336.332235 |
| E + thermal Free Energies | = -9336.439756 |

Geometry at E(RB3LYP/6-31G(d,p))

Charge: 1 Multiplicity: 1

C -2.988892000000 2.116043000000 0.583153000000
C -3.826011000000 1.336597000000 1.414409000000
C -5.169034000000 1.720089000000 1.624000000000
C -5.662243000000 2.854683000000 1.017910000000
H -5.815677000000 1.127273000000 2.257385000000
H -6.698171000000 3.135787000000 1.186526000000
C -1.655402000000 1.748889000000 0.384789000000
C -0.475991000000 1.496882000000 0.158169000000
C 0.907132000000 1.441151000000 -0.091444000000
O 1.577307000000 2.329954000000 -0.620445000000
C 3.252079000000 -1.105290000000 1.070348000000
C 1.655007000000 0.210296000000 0.357719000000

N 2.252659000000 -1.909266000000 0.822019000000
N 2.930609000000 0.200329000000 0.786530000000
C 3.938835000000 1.279129000000 0.916662000000
H 3.387936000000 2.215388000000 1.014539000000
C 4.571321000000 -1.359488000000 1.726557000000
H 5.383439000000 -1.379078000000 0.987587000000
H 4.551853000000 -2.311584000000 2.258309000000
C 4.853397000000 1.002410000000 2.176445000000
H 4.542464000000 1.630475000000 3.012643000000
O 4.729828000000 -0.327104000000 2.691244000000
C 6.291210000000 1.334241000000 1.704945000000
H 6.590364000000 2.320119000000 2.081159000000
H 6.998780000000 0.611407000000 2.123412000000
C 4.901563000000 1.299890000000 -0.255813000000
C 6.224212000000 1.328403000000 0.196778000000
C 4.596183000000 1.324522000000 -1.617465000000
C 7.272814000000 1.376154000000 -0.722659000000
C 5.649224000000 1.363722000000 -2.531650000000
H 3.565546000000 1.313281000000 -1.956378000000
C 6.976372000000 1.389565000000 -2.086617000000
H 8.304606000000 1.399790000000 -0.384712000000
H 5.438244000000 1.380794000000 -3.596122000000
H 7.784345000000 1.421813000000 -2.810867000000
N 1.259071000000 -1.072045000000 0.374449000000
C 0.040745000000 -1.631719000000 -0.117520000000
C -0.890921000000 -2.177627000000 0.773212000000
C -0.199036000000 -1.704501000000 -1.497149000000
C -2.044176000000 -2.793251000000 0.299745000000
C -1.356551000000 -2.302436000000 -1.983328000000
C -2.266251000000 -2.845632000000 -1.076113000000
H -2.757223000000 -3.224334000000 0.989646000000
H -1.540511000000 -2.352527000000 -3.048489000000
Br -0.592271000000 -2.069777000000 2.638384000000
Br 1.051701000000 -0.985085000000 -2.729669000000
Br -3.839594000000 -3.673385000000 -1.727855000000
C -3.502636000000 3.314762000000 -0.046856000000
C -4.865813000000 3.676704000000 0.180305000000
C -5.392224000000 4.844601000000 -0.429441000000
C -4.599671000000 5.632099000000 -1.234224000000
C -3.251467000000 5.274128000000 -1.454640000000
H -2.628747000000 5.898795000000 -2.087519000000
C -2.711760000000 4.141197000000 -0.877516000000
H -5.005112000000 6.525182000000 -1.698005000000
H -6.430802000000 5.106039000000 -0.248401000000

H -1.674000000000 3.881689000000 -1.056444000000
O -3.266981000000 0.247859000000 1.976645000000
C -4.025797000000 -0.517139000000 2.920632000000
H -3.339340000000 -1.281213000000 3.281412000000
H -4.355128000000 0.105110000000 3.758656000000
H -4.892066000000 -0.988818000000 2.444969000000

**II_D**

E(RB3LYP/6-31G(d,p)) = -9336.82439084 A. U.

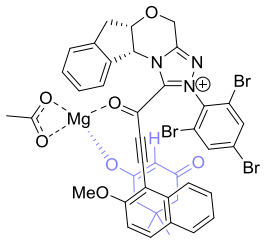
Temp. 298.150 K 1.00000 Atm.

| | |
|---|---|
| E + zero-point Energies | = -9336.364738 |
| E + thermal Energies | = -9336.330013 |
| E + thermal Enthalpies | = -9336.329069 |
| E + thermal Free Energies | = -9336.437547 |

Geometry at E(RB3LYP/6-31G(d,p))
Charge: 1 Multiplicity: 1
C 3.896300000000 1.967374000000 0.176735000000
C 5.014206000000 1.110364000000 0.074608000000
C 6.315977000000 1.650455000000 -0.000483000000
C 6.493566000000 3.017017000000 0.025902000000
H 7.177396000000 0.999797000000 -0.074491000000
H 7.501182000000 3.419619000000 -0.030207000000
C 2.608226000000 1.427245000000 0.246494000000
C 1.460776000000 1.000823000000 0.320025000000
C 0.074153000000 0.741720000000 0.390898000000
O -0.794031000000 1.609330000000 0.386104000000
C -0.612099000000 -2.849759000000 0.818164000000
C -0.385203000000 -0.692247000000 0.502896000000
N -1.830580000000 -2.409404000000 0.652761000000
N 0.306100000000 -1.830998000000 0.726445000000
C 1.752264000000 -2.135469000000 0.774926000000
H 2.275332000000 -1.214777000000 1.037059000000
C -0.113943000000 -4.202822000000 1.211093000000
H 0.287862000000 -4.745202000000 0.344684000000
H -0.924122000000 -4.787543000000 1.648762000000
C 2.031185000000 -3.270601000000 1.837167000000
H 2.390960000000 -2.835050000000 2.770688000000
O 0.859522000000 -3.988912000000 2.225891000000
C 3.097592000000 -4.176299000000 1.170887000000
H 4.090572000000 -3.942731000000 1.574706000000
H 2.900378000000 -5.225552000000 1.411400000000

C 2.250186000000 -2.714058000000 -0.536963000000
C 3.017773000000 -3.860131000000 -0.304190000000
C 2.042245000000 -2.227296000000 -1.827569000000
C 3.599547000000 -4.536988000000 -1.377700000000
C 2.620059000000 -2.911894000000 -2.897924000000
H 1.429262000000 -1.348549000000 -2.007805000000
C 3.394927000000 -4.055814000000 -2.672900000000
H 4.192172000000 -5.432015000000 -1.212268000000
H 2.466534000000 -2.556027000000 -3.911575000000
H 3.834749000000 -4.579785000000 -3.515714000000
N -1.675197000000 -1.065726000000 0.451554000000
C -2.828006000000 -0.279912000000 0.134257000000
C -3.679965000000 0.163342000000 1.148461000000
C -3.131293000000 0.000799000000 -1.201273000000
C -4.832625000000 0.876269000000 0.835977000000
C -4.276526000000 0.715000000000 -1.531025000000
C -5.118695000000 1.142237000000 -0.503114000000
H -5.491947000000 1.221376000000 1.621623000000
H -4.509626000000 0.934037000000 -2.564723000000
Br -3.246118000000 -0.182666000000 2.957667000000
Br -1.956567000000 -0.577676000000 -2.577701000000
Br -6.685134000000 2.113100000000 -0.939736000000
C 4.078978000000 3.402251000000 0.202690000000
C 5.407333000000 3.923004000000 0.125185000000
C 5.611558000000 5.326953000000 0.149781000000
C 4.541557000000 6.187971000000 0.245980000000
C 3.229371000000 5.670313000000 0.321010000000
H 2.388666000000 6.352948000000 0.396040000000
C 2.998531000000 4.308854000000 0.300855000000
H 4.701221000000 7.260906000000 0.264468000000
H 6.626718000000 5.708663000000 0.091331000000
H 1.984475000000 3.928023000000 0.359198000000
O 4.753385000000 -0.214828000000 0.054106000000
C 5.831542000000 -1.130660000000 -0.171174000000
H 5.367522000000 -2.112612000000 -0.253810000000
H 6.354985000000 -0.900137000000 -1.104137000000
H 6.539090000000 -1.121997000000 0.664503000000

**III_ A_i**




**III**

E(RB3LYP/6-31G(d,p)) = -10227.5228534 A. U.

Temp. 298.150 K 1.00000 Atm.

E + zero-point Energies = -10226.832762

E + thermal Energies = -10226.779821

E + thermal Enthalpies = -10226.778877

E + thermal Free Energies = -10226.928725

Geometry at E(RB3LYP/6-31G(d,p))

Charge: 1 Multiplicity: 1

C -3.351654000000 -2.706544000000 -0.503470000000

C -1.857142000000 -1.107130000000 -0.576885000000

N -2.208452000000 -3.313707000000 -0.324133000000

N -3.185156000000 -1.352732000000 -0.654227000000

C -4.371008000000 -0.469352000000 -0.771236000000

H -4.034493000000 0.457883000000 -1.232436000000

C -4.726614000000 -3.263384000000 -0.689122000000

H -5.322194000000 -3.149244000000 0.226525000000

H -4.671079000000 -4.321998000000 -0.946163000000

C -5.486994000000 -1.170249000000 -1.639578000000

H -5.466519000000 -0.788512000000 -2.661676000000

O -5.287356000000 -2.577277000000 -1.800173000000

C -6.814515000000 -0.825158000000 -0.919076000000

H -7.315834000000 0.002220000000 -1.436268000000

H -7.496032000000 -1.680675000000 -0.959248000000

C -5.029529000000 -0.233487000000 0.575354000000

C -6.411160000000 -0.425082000000 0.480137000000

C -4.427919000000 0.150526000000 1.774160000000

C -7.219425000000 -0.221787000000 1.599003000000

C -5.240296000000 0.345116000000 2.891919000000

H -3.351628000000 0.271066000000 1.849863000000

C -6.625422000000 0.164038000000 2.802041000000

H -8.294034000000 -0.366409000000 1.539021000000

H -4.795472000000 0.640476000000 3.836609000000

H -7.244194000000 0.320751000000 3.679970000000

N -1.282800000000 -2.306774000000 -0.371935000000

C 0.068472000000 -2.606141000000 -0.019674000000
C 0.900822000000 -3.269943000000 -0.928341000000
C 0.521701000000 -2.334429000000 1.278727000000
C 2.173387000000 -3.673765000000 -0.541670000000
C 1.808388000000 -2.694221000000 1.667340000000
C 2.606796000000 -3.380598000000 0.753129000000
H 2.815484000000 -4.200129000000 -1.235622000000
H 2.177050000000 -2.421952000000 2.646344000000
Br 0.297355000000 -3.608777000000 -2.690682000000
Br -0.630204000000 -1.499804000000 2.525025000000
Br 4.344338000000 -3.934380000000 1.276347000000
C 2.325611000000 1.512598000000 -1.883331000000
C 2.188892000000 2.794211000000 -2.499538000000
C 3.320351000000 3.426706000000 -3.060440000000
C 4.553396000000 2.817030000000 -2.992440000000
H 3.220701000000 4.386668000000 -3.548847000000
H 5.412382000000 3.316121000000 -3.432752000000
C 1.169308000000 0.894854000000 -1.434546000000
C 0.094571000000 0.364966000000 -1.125045000000
C -1.224731000000 0.224910000000 -0.730125000000
C 3.633037000000 0.898475000000 -1.773768000000
C 4.754090000000 1.564633000000 -2.353589000000
C 6.041854000000 0.982694000000 -2.255896000000
C 6.221981000000 -0.210538000000 -1.587434000000
C 5.117742000000 -0.851104000000 -0.990379000000
H 5.260145000000 -1.770923000000 -0.433339000000
C 3.847089000000 -0.309363000000 -1.081836000000
H 7.210881000000 -0.649142000000 -1.506493000000
H 6.885543000000 1.498550000000 -2.704936000000
H 3.012817000000 -0.797293000000 -0.592043000000
O 0.957850000000 3.308703000000 -2.544585000000
C 0.729877000000 4.578186000000 -3.193586000000
H -0.335042000000 4.765066000000 -3.073114000000
H 0.996045000000 4.514237000000 -4.252677000000
H 1.308145000000 5.365935000000 -2.702285000000
O -1.994351000000 1.219825000000 -0.546482000000
Mg -1.591220000000 3.197730000000 -0.248576000000
O -0.089660000000 3.549959000000 0.832915000000
C 0.931935000000 3.076481000000 1.486976000000
C 1.060500000000 1.752576000000 1.843581000000
C 2.023217000000 4.071586000000 1.823786000000
C 2.226981000000 1.220636000000 2.507378000000
H 0.252084000000 1.060216000000 1.645138000000
C 2.925588000000 3.657152000000 3.009562000000

H 1.548760000000 5.041495000000 2.011353000000
H 2.638317000000 4.205362000000 0.920004000000
C 3.368097000000 2.192184000000 2.801530000000
H 4.060258000000 2.137742000000 1.947299000000
H 3.917370000000 1.812063000000 3.668737000000
C 2.153518000000 3.795210000000 4.338017000000
H 1.849025000000 4.834244000000 4.504124000000
H 2.783095000000 3.493555000000 5.181747000000
H 1.252861000000 3.174617000000 4.353676000000
C 4.161089000000 4.572100000000 3.054946000000
H 3.870336000000 5.619847000000 3.189928000000
H 4.745498000000 4.501400000000 2.130368000000
H 4.818241000000 4.300093000000 3.887710000000
O 2.343150000000 0.019980000000 2.791246000000
O -3.417999000000 4.079691000000 -0.074675000000
C -3.223258000000 4.593717000000 -1.224072000000
C -4.225905000000 5.544757000000 -1.819901000000
H -5.215026000000 5.378040000000 -1.392750000000
H -4.246955000000 5.447796000000 -2.906661000000
H -3.917607000000 6.568508000000 -1.580838000000
O -2.143861000000 4.313779000000 -1.860128000000

**TS1(i)**

Imaginary Frequency = -254.0239 $cm^{-1}$

E(RB3LYP/6-31G(d,p)) = -10227.5152368

Temp. 298.150 K 1.00000 Atm.

E + zero-point Energies = -10226.825403

E + thermal Energies = -10226.773537

E + thermal Enthalpies = -10226.772593

E + thermal Free Energies = -10226.917958

Geometry at E(RB3LYP/6-31G(d,p))

Charge: 1 Multiplicity: 1

C 3.390782000000 -2.671890000000 0.610528000000
C 1.904781000000 -1.061861000000 0.474319000000
N 2.275427000000 -3.282974000000 0.321012000000
N 3.213798000000 -1.312733000000 0.708085000000
C 4.377204000000 -0.430920000000 0.958353000000
H 3.984816000000 0.503381000000 1.356581000000
C 4.733633000000 -3.224202000000 0.964963000000
H 5.434886000000 -3.121920000000 0.125881000000
H 4.647915000000 -4.279199000000 1.228358000000
C 5.371983000000 -1.116348000000 1.973133000000

H 5.217979000000 -0.721656000000 2.978881000000
O 5.160838000000 -2.522969000000 2.125522000000
C 6.781654000000 -0.774565000000 1.427238000000
H 7.207828000000 0.064127000000 1.991613000000
H 7.455126000000 -1.625341000000 1.570372000000
C 5.204738000000 -0.213209000000 -0.294531000000
C 6.562780000000 -0.399241000000 -0.019404000000
C 4.762987000000 0.149966000000 -1.566962000000
C 7.508411000000 -0.213600000000 -1.028305000000
C 5.712301000000 0.327383000000 -2.574332000000
H 3.704958000000 0.269846000000 -1.778760000000
C 7.074296000000 0.150161000000 -2.304445000000
H 8.566411000000 -0.355045000000 -0.828144000000
H 5.392930000000 0.606722000000 -3.573163000000
H 7.800905000000 0.292832000000 -3.098172000000
N 1.354407000000 -2.267859000000 0.233702000000
C 0.030536000000 -2.576087000000 -0.192841000000
C -0.837996000000 -3.269248000000 0.659222000000
C -0.385960000000 -2.257465000000 -1.492818000000
C -2.103012000000 -3.642961000000 0.218155000000
C -1.656814000000 -2.596328000000 -1.938659000000
C -2.498962000000 -3.294933000000 -1.072778000000
H -2.772879000000 -4.179462000000 0.876978000000
H -1.993766000000 -2.301970000000 -2.921928000000
Br -0.312649000000 -3.679186000000 2.430848000000
Br 0.781213000000 -1.319891000000 -2.664074000000
Br -4.244210000000 -3.749895000000 -1.647919000000
C -2.256498000000 1.449075000000 1.601396000000
C -2.034227000000 2.642847000000 2.323525000000
C -3.000634000000 3.095786000000 3.253198000000
C -4.166996000000 2.389214000000 3.437338000000
H -2.824839000000 3.997516000000 3.824572000000
H -4.899071000000 2.750808000000 4.154025000000
C -1.205542000000 0.968595000000 0.769525000000
C -0.062447000000 0.438455000000 0.697497000000
C 1.273181000000 0.273801000000 0.483409000000
C -3.491023000000 0.726014000000 1.767082000000
C -4.453128000000 1.205313000000 2.710572000000
C -5.669624000000 0.497676000000 2.889330000000
C -5.938770000000 -0.634756000000 2.152846000000
C -4.996034000000 -1.097531000000 1.208582000000
H -5.215505000000 -1.971451000000 0.603479000000
C -3.797570000000 -0.437768000000 1.023187000000
H -6.874975000000 -1.166383000000 2.287882000000

H -6.388422000000 0.870604000000 3.613302000000
H -3.097633000000 -0.790992000000 0.276195000000
O -0.871081000000 3.293273000000 2.094209000000
C -0.569789000000 4.483543000000 2.846118000000
H 0.409828000000 4.804874000000 2.497114000000
H -0.534962000000 4.264294000000 3.917782000000
H -1.312626000000 5.263041000000 2.648563000000
O 2.098015000000 1.266241000000 0.352027000000
Mg 1.648856000000 3.128984000000 -0.146835000000
O 0.006435000000 3.266282000000 -1.145663000000
C -1.200555000000 2.896615000000 -1.292837000000
C -1.561489000000 1.531192000000 -1.455133000000
C -2.281749000000 3.948221000000 -1.240872000000
C -2.921730000000 1.150944000000 -1.871346000000
H -0.785996000000 0.834679000000 -1.746374000000
C -3.521692000000 3.638006000000 -2.112656000000
H -1.834065000000 4.911839000000 -1.502977000000
H -2.589972000000 4.022063000000 -0.185420000000
C -4.007915000000 2.210599000000 -1.770825000000
H -4.382421000000 2.193220000000 -0.736490000000
H -4.836845000000 1.901958000000 -2.414051000000
C -3.154639000000 3.733894000000 -3.607006000000
H -2.807515000000 4.741319000000 -3.858904000000
H -4.024960000000 3.513609000000 -4.233069000000
H -2.362433000000 3.029698000000 -3.883238000000
C -4.631274000000 4.653585000000 -1.794796000000
H -4.304334000000 5.675220000000 -2.016286000000
H -4.921061000000 4.613225000000 -0.738881000000
H -5.524688000000 4.453521000000 -2.394934000000
O -3.164554000000 0.014115000000 -2.272394000000
O 3.249139000000 4.215377000000 -0.756476000000
C 3.130510000000 4.893463000000 0.317114000000
C 4.038249000000 6.061131000000 0.591795000000
H 4.221767000000 6.157546000000 1.663113000000
H 3.539860000000 6.976328000000 0.253644000000
H 4.973991000000 5.957627000000 0.042164000000
O 2.205447000000 4.585096000000 1.152212000000

**TS1(ii)**

Imaginary Frequency = -283.2260 $cm^{-1}$

E(RB3LYP/6-31G(d,p)) = -10227.5117001

Temp. 298.150 K 1.00000 Atm.

E + zero-point Energies = -10226.821985

E + thermal Energies = -10226.770310
E + thermal Enthalpies = -10226.769366
E + thermal Free Energies = -10226.913528

Geometry at E(RB3LYP/6-31G(d,p))
Charge: 1 Multiplicity: 1

| | | | |
|---|---|---|---|
| C | -3.143721000000 | -0.332946000000 | -2.499936000000 |
| C | -1.692980000000 | 0.138279000000 | -0.922132000000 |
| N | -2.200466000000 | -1.219376000000 | -2.654783000000 |
| N | -2.880950000000 | 0.505002000000 | -1.441823000000 |
| C | -3.834880000000 | 1.565587000000 | -1.053422000000 |
| H | -3.273596000000 | 2.298077000000 | -0.469567000000 |
| C | -4.319443000000 | 0.009948000000 | -3.357374000000 |
| H | -5.257663000000 | -0.326934000000 | -2.897619000000 |
| H | -4.218499000000 | -0.449216000000 | -4.341402000000 |
| C | -4.452922000000 | 2.216402000000 | -2.355307000000 |
| H | -3.941572000000 | 3.150751000000 | -2.592675000000 |
| O | -4.268691000000 | 1.421642000000 | -3.532137000000 |
| C | -5.945915000000 | 2.438658000000 | -2.014894000000 |
| H | -6.115280000000 | 3.486878000000 | -1.738763000000 |
| H | -6.564484000000 | 2.241376000000 | -2.895943000000 |
| C | -5.036363000000 | 1.026093000000 | -0.295555000000 |
| C | -6.222271000000 | 1.521848000000 | -0.847807000000 |
| C | -5.050751000000 | 0.188926000000 | 0.821503000000 |
| C | -7.451850000000 | 1.173082000000 | -0.288451000000 |
| C | -6.284231000000 | -0.164626000000 | 1.369748000000 |
| H | -4.129197000000 | -0.178036000000 | 1.258033000000 |
| C | -7.474802000000 | 0.323526000000 | 0.818993000000 |
| H | -8.378288000000 | 1.552855000000 | -0.709106000000 |
| H | -6.316027000000 | -0.820361000000 | 2.233960000000 |
| H | -8.426211000000 | 0.040035000000 | 1.258339000000 |
| N | -1.300221000000 | -0.920990000000 | -1.650202000000 |
| C | -0.216553000000 | -1.817952000000 | -1.413812000000 |
| C | 0.857338000000 | -1.877525000000 | -2.311990000000 |
| C | -0.263690000000 | -2.722873000000 | -0.342568000000 |
| C | 1.879485000000 | -2.806354000000 | -2.138441000000 |
| C | 0.746199000000 | -3.661037000000 | -0.161134000000 |
| C | 1.812688000000 | -3.688186000000 | -1.059981000000 |
| H | 2.709069000000 | -2.840945000000 | -2.832588000000 |
| H | 0.705634000000 | -4.355366000000 | 0.667868000000 |
| Br | 0.929528000000 | -0.688208000000 | -3.783130000000 |
| Br | -1.698699000000 | -2.681439000000 | 0.902338000000 |
| Br | 3.215839000000 | -4.929185000000 | -0.787173000000 |
| C | 1.997580000000 | 3.147810000000 | 0.133462000000 |

| | | | |
|---|---|---|---|
| C | 2.123039000000 | 4.188512000000 | 1.077710000000 |
| C | 2.939315000000 | 5.311022000000 | 0.802389000000 |
| C | 3.614494000000 | 5.389299000000 | -0.390558000000 |
| H | 3.034159000000 | 6.105459000000 | 1.530838000000 |
| H | 4.240318000000 | 6.253994000000 | -0.592703000000 |
| C | 1.216516000000 | 2.007328000000 | 0.463906000000 |
| C | 0.158908000000 | 1.360127000000 | 0.181289000000 |
| C | -1.069541000000 | 0.801709000000 | 0.256387000000 |
| C | 2.704087000000 | 3.228400000000 | -1.124438000000 |
| C | 3.522881000000 | 4.372188000000 | -1.379128000000 |
| C | 4.226869000000 | 4.470309000000 | -2.605768000000 |
| C | 4.135171000000 | 3.475424000000 | -3.554819000000 |
| C | 3.324654000000 | 2.348039000000 | -3.303957000000 |
| H | 3.243619000000 | 1.562857000000 | -4.049851000000 |
| C | 2.625224000000 | 2.226493000000 | -2.119835000000 |
| H | 4.679080000000 | 3.557181000000 | -4.490122000000 |
| H | 4.843641000000 | 5.346782000000 | -2.782988000000 |
| H | 1.995462000000 | 1.360262000000 | -1.959029000000 |
| O | 1.392949000000 | 4.059662000000 | 2.199005000000 |
| C | 1.690247000000 | 4.895704000000 | 3.327242000000 |
| H | 1.054361000000 | 4.530088000000 | 4.132945000000 |
| H | 1.442044000000 | 5.941194000000 | 3.119827000000 |
| H | 2.742171000000 | 4.791669000000 | 3.604619000000 |
| O | -1.876527000000 | 0.902523000000 | 1.278328000000 |
| Mg | -1.241521000000 | -0.176525000000 | 2.810851000000 |
| O | 0.607034000000 | -0.651574000000 | 2.353587000000 |
| C | 1.796614000000 | -0.282201000000 | 2.107032000000 |
| C | 2.195298000000 | 1.077672000000 | 2.197980000000 |
| C | 2.774687000000 | -1.324508000000 | 1.617983000000 |
| C | 3.622249000000 | 1.439169000000 | 2.121157000000 |
| H | 1.582731000000 | 1.738946000000 | 2.801717000000 |
| C | 4.253896000000 | -1.044318000000 | 1.971334000000 |
| H | 2.669836000000 | -1.365649000000 | 0.523618000000 |
| H | 2.452027000000 | -2.298102000000 | 1.998964000000 |
| C | 4.582240000000 | 0.405972000000 | 1.551423000000 |
| H | 5.595330000000 | 0.692075000000 | 1.847266000000 |
| H | 4.533470000000 | 0.488653000000 | 0.454950000000 |
| C | 5.150170000000 | -2.026055000000 | 1.198512000000 |
| H | 4.901507000000 | -3.064293000000 | 1.442158000000 |
| H | 6.204470000000 | -1.866018000000 | 1.445003000000 |
| H | 5.036409000000 | -1.903776000000 | 0.115518000000 |
| C | 4.479803000000 | -1.226351000000 | 3.485496000000 |
| H | 4.255910000000 | -2.253608000000 | 3.791826000000 |
| H | 3.850914000000 | -0.556010000000 | 4.081067000000 |

| | | | |
|---|---|---|---|
| H | 5.521991000000 | -1.019623000000 | 3.747875000000 |
| O | 4.006682000000 | 2.553806000000 | 2.461967000000 |
| C | -3.375463000000 | -0.945270000000 | 5.925430000000 |
| H | -4.381614000000 | -1.256314000000 | 5.639555000000 |
| H | -2.906037000000 | -1.782922000000 | 6.452889000000 |
| H | -3.407541000000 | -0.087557000000 | 6.597260000000 |
| O | -2.712250000000 | -1.316356000000 | 3.628620000000 |
| O | -1.682018000000 | 0.297594000000 | 4.727823000000 |
| C | -2.557488000000 | -0.631958000000 | 4.703150000000 |

**TS1'(i)**

Imaginary Frequency = -256.6398 $cm^{-1}$

E(RB3LYP/6-31G(d,p)) = -10227.5112208 A.U.

Temp. 298.150 K 1.00000 Atm.

E + zero-point Energies = -10226.821359

E + thermal Energies = -10226.769557

E + thermal Enthalpies = -10226.768613

E + thermal Free Energies = -10226.914152

Geometry at E(RB3LYP/6-31G(d,p))

Charge: 1 Multiplicity: 1

C -2.540998000000 1.185443000000 -1.046911000000

C -2.438741000000 1.985313000000 -2.208238000000

C -3.567318000000 2.167142000000 -3.043441000000

C -4.771459000000 1.589492000000 -2.715195000000

H -3.486770000000 2.762622000000 -3.942702000000

H -5.629034000000 1.742722000000 -3.364278000000

C -1.354039000000 0.962312000000 -0.291041000000

C -0.207682000000 0.433143000000 -0.233881000000

C 1.144993000000 0.340272000000 -0.094529000000

C 3.210464000000 -2.067965000000 1.660971000000

C 1.778126000000 -0.814334000000 0.568822000000

N 2.173557000000 -2.838988000000 1.478202000000

N 3.016399000000 -0.821268000000 1.118788000000

C 4.107934000000 0.184673000000 1.151827000000

H 3.638941000000 1.161627000000 1.052040000000

C 4.453555000000 -2.298440000000 2.457313000000

H 5.307829000000 -2.514853000000 1.801389000000

H 4.311052000000 -3.136305000000 3.140982000000

C 4.915654000000 0.069357000000 2.506239000000

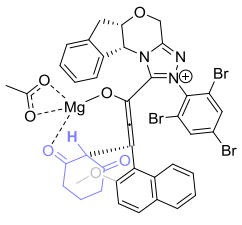
H 4.613047000000 0.863694000000 3.190243000000

O 4.645309000000 -1.127555000000 3.238720000000

C 6.404288000000 0.199455000000 2.093139000000
H 6.768216000000 1.208879000000 2.319806000000
H 7.016961000000 -0.493900000000 2.678199000000
C 5.139258000000 -0.066095000000 0.068112000000
C 6.429305000000 -0.061154000000 0.606549000000
C 4.921553000000 -0.251149000000 -1.297771000000
C 7.531882000000 -0.251975000000 -0.227321000000
C 6.027055000000 -0.449148000000 -2.125824000000
H 3.917099000000 -0.240932000000 -1.708627000000
C 7.321714000000 -0.449988000000 -1.592989000000
H 8.539235000000 -0.250176000000 0.178425000000
H 5.882812000000 -0.599039000000 -3.191095000000
H 8.171975000000 -0.605114000000 -2.249852000000
N 1.288725000000 -2.049568000000 0.788636000000
C 0.087208000000 -2.656566000000 0.313884000000
C -1.073473000000 -2.639205000000 1.093833000000
C 0.109918000000 -3.379498000000 -0.885405000000
C -2.197721000000 -3.355418000000 0.692895000000
C -1.009492000000 -4.089340000000 -1.304416000000
C -2.150056000000 -4.076148000000 -0.500036000000
H -3.096060000000 -3.343699000000 1.295238000000
H -0.991371000000 -4.646074000000 -2.232086000000
Br -1.147100000000 -1.571531000000 2.651386000000
Br 1.678897000000 -3.383479000000 -1.951302000000
Br -3.675796000000 -5.056420000000 -1.048859000000
C -3.807468000000 0.597543000000 -0.689552000000
C -4.934553000000 0.803895000000 -1.546011000000
C -6.186851000000 0.228471000000 -1.209528000000
C -6.331365000000 -0.518516000000 -0.061817000000
C -5.220440000000 -0.716025000000 0.787334000000
H -5.340131000000 -1.291445000000 1.700395000000
C -3.986229000000 -0.176429000000 0.482665000000
H -7.293136000000 -0.950456000000 0.194409000000
H -7.031182000000 0.392890000000 -1.872828000000
H -3.151500000000 -0.332423000000 1.154771000000
O -1.234517000000 2.538548000000 -2.478894000000
C -1.066642000000 3.291075000000 -3.696204000000
H -0.028163000000 3.615836000000 -3.694919000000
H -1.266628000000 2.660861000000 -4.568145000000
H -1.727546000000 4.163621000000 -3.705560000000
O 1.967537000000 1.254627000000 -0.509380000000
Mg 1.535364000000 3.162275000000 -0.811058000000
O 0.110652000000 3.754713000000 0.348853000000
C -1.008563000000 3.493304000000 0.890782000000

C -1.252262000000 2.282455000000 1.598442000000
C -2.130329000000 4.487873000000 0.724104000000
C -2.444826000000 2.136495000000 2.455087000000
H -0.398241000000 1.701758000000 1.920275000000
C -3.105498000000 4.561475000000 1.924155000000
H -1.689598000000 5.464016000000 0.499678000000
H -2.688210000000 4.180383000000 -0.175773000000
C -3.581325000000 3.126247000000 2.247720000000
H -4.193032000000 2.751506000000 1.414127000000
H -4.210913000000 3.102680000000 3.141582000000
C -2.394297000000 5.177107000000 3.145974000000
H -2.049858000000 6.192905000000 2.925862000000
H -3.075662000000 5.232638000000 4.000693000000
H -1.523171000000 4.590150000000 3.456892000000
C -4.312022000000 5.434529000000 1.543253000000
H -3.996953000000 6.453730000000 1.295253000000
H -4.844528000000 5.025113000000 0.677757000000
H -5.021730000000 5.498824000000 2.374104000000
O -2.506266000000 1.244828000000 3.297381000000
O 3.233850000000 4.273261000000 -0.896037000000
C 2.956337000000 4.498907000000 -2.119962000000
C 3.836222000000 5.387313000000 -2.955615000000
H 3.467415000000 6.415911000000 -2.875692000000
H 4.861944000000 5.365487000000 -2.586272000000
H 3.791570000000 5.092962000000 -4.004979000000
O 1.895836000000 3.980297000000 -2.626065000000

**Allenolate_ A_i**



Allenolate

E(RB3LYP/6-31G(d,p)) = -10227.5410639 A.U.

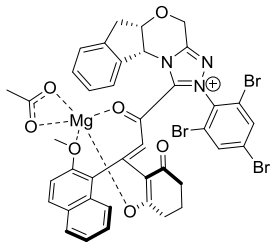
Temp. 298.150 K 1.00000 Atm.
E + zero-point Energies = -10226.848947
E + thermal Energies = -10226.797217
E + thermal Enthalpies = -10226.796272
E + thermal Free Energies= -10226.941362

Geometry at E(RB3LYP/6-31G(d,p))
Charge: 1 Multiplicity: 1
C 3.148233000000 -2.885654000000 0.416093000000
C 1.770356000000 -1.171134000000 0.371262000000
N 2.011163000000 -3.398324000000 0.043283000000
N 3.051336000000 -1.529307000000 0.624702000000
C 4.254588000000 -0.753939000000 1.004631000000
H 3.898657000000 0.166014000000 1.464886000000
C 4.437190000000 -3.552742000000 0.772140000000
H 5.184625000000 -3.420215000000 -0.021476000000
H 4.275379000000 -4.619551000000 0.931653000000
C 5.151078000000 -1.590627000000 1.997241000000
H 4.970692000000 -1.276804000000 3.026860000000
O 4.848701000000 -2.989025000000 2.010854000000
C 6.606162000000 -1.298398000000 1.550472000000
H 7.054375000000 -0.541598000000 2.206306000000
H 7.216248000000 -2.201810000000 1.648219000000
C 5.159454000000 -0.482254000000 -0.182233000000
C 6.486884000000 -0.785666000000 0.134708000000
C 4.809105000000 0.025050000000 -1.433161000000
C 7.492646000000 -0.579515000000 -0.810038000000
C 5.817351000000 0.222728000000 -2.377748000000
H 3.774272000000 0.248509000000 -1.672410000000
C 7.148834000000 -0.075947000000 -2.066194000000
H 8.527501000000 -0.812403000000 -0.576713000000
H 5.567962000000 0.613391000000 -3.359077000000
H 7.922538000000 0.083027000000 -2.810901000000
N 1.158297000000 -2.317205000000 0.007368000000
C -0.189908000000 -2.536242000000 -0.393478000000
C -1.057295000000 -3.244170000000 0.449576000000
C -0.642023000000 -2.129819000000 -1.655898000000
C -2.348569000000 -3.552821000000 0.034940000000
C -1.937614000000 -2.406598000000 -2.075542000000
C -2.774354000000 -3.125342000000 -1.221264000000
H -3.014063000000 -4.100338000000 0.688969000000
H -2.292045000000 -2.057239000000 -3.034947000000
Br -0.494445000000 -3.768098000000 2.178556000000
Br 0.508834000000 -1.153750000000 -2.813483000000
Br -4.554209000000 -3.493754000000 -1.756652000000
C -2.052107000000 1.493421000000 1.558412000000
C -1.650039000000 2.538868000000 2.391366000000
C -2.422720000000 2.891499000000 3.527617000000
C -3.578246000000 2.206061000000 3.817207000000
H -2.108458000000 3.700142000000 4.173982000000

H -4.162722000000 2.486772000000 4.688717000000
C -1.199044000000 1.131445000000 0.379718000000
C -0.074647000000 0.461741000000 0.495636000000
C 1.234845000000 0.198325000000 0.438809000000
C -3.248861000000 0.767089000000 1.859565000000
C -4.029360000000 1.138648000000 3.004002000000
C -5.225966000000 0.431184000000 3.296462000000
C -5.650040000000 -0.602488000000 2.494261000000
C -4.879629000000 -0.977532000000 1.368751000000
H -5.211879000000 -1.787973000000 0.727103000000
C -3.707643000000 -0.320034000000 1.066180000000
H -6.569541000000 -1.132047000000 2.721782000000
H -5.802823000000 0.725738000000 4.168708000000
H -3.129158000000 -0.633649000000 0.206856000000
O -0.505938000000 3.217319000000 2.048496000000
C -0.060193000000 4.282480000000 2.905163000000
H 0.854890000000 4.663902000000 2.455526000000
H 0.151735000000 3.909314000000 3.912175000000
H -0.807639000000 5.081365000000 2.958713000000
O 2.165993000000 1.146322000000 0.469598000000
Mg 1.890049000000 2.986450000000 -0.035456000000
O 0.166020000000 3.400523000000 -0.995205000000
C -1.045041000000 3.152503000000 -1.034151000000
C -1.514967000000 1.704548000000 -1.045130000000
C -2.049088000000 4.264423000000 -1.006755000000
C -2.954746000000 1.508100000000 -1.560172000000
H -0.870841000000 1.155458000000 -1.737995000000
C -3.346976000000 4.006938000000 -1.809803000000
H -1.551878000000 5.191946000000 -1.305135000000
H -2.303331000000 4.368060000000 0.061375000000
C -3.933934000000 2.642377000000 -1.365468000000
H -4.188269000000 2.685539000000 -0.296845000000
H -4.845785000000 2.400860000000 -1.917342000000
C -3.036453000000 3.992768000000 -3.319925000000
H -2.622288000000 4.953741000000 -3.640805000000
H -3.945715000000 3.808695000000 -3.899771000000
H -2.313924000000 3.213767000000 -3.592174000000
C -4.355163000000 5.125112000000 -1.499182000000
H -3.953547000000 6.103405000000 -1.782773000000
H -4.603947000000 5.156131000000 -0.433134000000
H -5.283867000000 4.972430000000 -2.057200000000
O -3.233121000000 0.475108000000 -2.135983000000
O 3.387344000000 3.993876000000 -0.966278000000
C 3.404365000000 4.778785000000 0.038118000000

C 4.345297000000 5.950860000000 0.089782000000
H 5.094543000000 5.882042000000 -0.698076000000
H 4.820830000000 6.001683000000 1.071959000000
H 3.768883000000 6.872803000000 -0.039669000000
O 2.590447000000 4.568029000000 1.009780000000

**IV_A_i**




**IV**

E(RB3LYP) = -10227.5751754

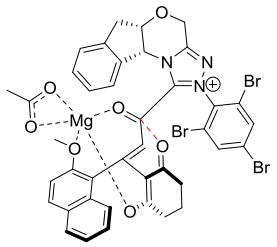
Temperature 298.150 Kelvin. Pressure 1.00000 Atm.
E + zero-point Energies = -10226.882619
E + thermal Energies = -10226.831288
E + thermal Enthalpies = -10226.830343
E + thermal Free Energies = -10226.974064

Charge: 1 Multiplicity: 1
C 2.555198000000 -2.802958000000 1.330150000000
C 1.157446000000 -1.239804000000 0.690157000000
N 1.418189000000 -3.426366000000 1.180050000000
N 2.442723000000 -1.465866000000 1.033042000000
C 3.633984000000 -0.587099000000 1.057722000000
H 3.286353000000 0.441803000000 1.152218000000
C 3.858002000000 -3.276255000000 1.889063000000
H 4.590548000000 -3.449209000000 1.089275000000
H 3.715728000000 -4.203580000000 2.445397000000
C 4.574985000000 -0.992831000000 2.258456000000
H 4.430226000000 -0.312010000000 3.098974000000
O 4.279961000000 -2.279139000000 2.811735000000
C 6.011096000000 -0.900108000000 1.684130000000
H 6.481199000000 0.037492000000 2.005220000000
H 6.626995000000 -1.713668000000 2.080245000000
C 4.498580000000 -0.763114000000 -0.177658000000
C 5.838807000000 -0.932611000000 0.184255000000
C 4.103481000000 -0.729507000000 -1.516040000000
C 6.814017000000 -1.075180000000 -0.803662000000

C 5.082838000000 -0.881704000000 -2.499164000000
H 3.061250000000 -0.592069000000 -1.784747000000
C 6.426641000000 -1.051812000000 -2.145106000000
H 7.858137000000 -1.208204000000 -0.535849000000
H 4.800639000000 -0.862706000000 -3.547050000000
H 7.175844000000 -1.168313000000 -2.922099000000
N 0.552944000000 -2.439039000000 0.772877000000
C -0.740436000000 -2.809716000000 0.292974000000
C -1.808356000000 -2.991464000000 1.176366000000
C -0.924367000000 -3.052039000000 -1.074614000000
C -3.053865000000 -3.398420000000 0.711176000000
C -2.165498000000 -3.453211000000 -1.557500000000
C -3.215820000000 -3.624677000000 -0.656165000000
H -3.878588000000 -3.535024000000 1.398162000000
H -2.307703000000 -3.632623000000 -2.614954000000
Br -1.565834000000 -2.640994000000 3.023271000000
Br 0.519591000000 -2.836182000000 -2.275121000000
Br -4.908726000000 -4.179126000000 -1.304091000000
C -1.686002000000 2.604428000000 1.369570000000
C -0.777043000000 3.221402000000 2.213514000000
C -1.193968000000 4.092082000000 3.244026000000
C -2.536466000000 4.324800000000 3.430666000000
H -0.468909000000 4.588143000000 3.876050000000
H -2.859691000000 4.994834000000 4.221761000000
C -1.190519000000 1.694720000000 0.288304000000
C 0.580377000000 0.067714000000 0.276737000000
C -3.087625000000 2.846276000000 1.548051000000
C -3.513851000000 3.717840000000 2.604272000000
C -4.901484000000 3.953681000000 2.798063000000
C -5.838449000000 3.351269000000 1.992336000000
C -5.421882000000 2.479014000000 0.958685000000
H -6.166902000000 1.997880000000 0.332289000000
C -4.085095000000 2.230589000000 0.741259000000
H -6.896093000000 3.537597000000 2.147962000000
H -5.208336000000 4.619867000000 3.599318000000
H -3.786588000000 1.550618000000 -0.048889000000
O 0.582500000000 3.001829000000 1.962936000000
C 1.485323000000 3.131324000000 3.090871000000
H 1.603632000000 4.181042000000 3.368614000000
H 2.444189000000 2.749607000000 2.751004000000
H 1.100349000000 2.554848000000 3.935321000000
O 1.422059000000 0.839587000000 -0.315813000000
Mg 1.460793000000 2.865995000000 -0.054132000000
O -0.037565000000 4.144308000000 -0.751212000000

C -0.969980000000 3.552423000000 -1.347685000000
C -1.184067000000 2.141824000000 -1.031063000000
C -1.709645000000 4.186779000000 -2.481834000000
C -1.355324000000 1.226437000000 -2.206826000000
C -1.591817000000 3.297138000000 -3.759321000000
H -1.316452000000 5.190326000000 -2.660213000000
H -2.769135000000 4.266689000000 -2.203014000000
C -2.052820000000 1.862123000000 -3.410319000000
H -3.129465000000 1.874491000000 -3.183931000000
H -1.911059000000 1.187660000000 -4.259117000000
C -0.135245000000 3.281637000000 -4.264152000000
H 0.205220000000 4.294181000000 -4.501247000000
H -0.056285000000 2.679361000000 -5.174578000000
H 0.565685000000 2.864538000000 -3.532899000000
C -2.507418000000 3.878864000000 -4.849433000000
H -2.202126000000 4.896899000000 -5.111211000000
H -3.551916000000 3.911339000000 -4.521821000000
H -2.457252000000 3.271797000000 -5.758932000000
O -1.047225000000 0.047205000000 -2.195317000000
C -0.710664000000 0.396321000000 0.663635000000
H -1.208970000000 -0.180134000000 1.435202000000
C 5.235210000000 3.455516000000 -0.774874000000
H 5.660417000000 2.466991000000 -0.981700000000
H 5.753385000000 3.874209000000 0.089431000000
H 5.382618000000 4.081776000000 -1.655112000000
C 3.766761000000 3.292405000000 -0.484870000000
O 3.373976000000 3.006187000000 0.706048000000
O 2.906318000000 3.402087000000 -1.411914000000

**IV-V_ A_i**




**IV-V**

E(RB3LYP/6-31G(d,p)) = -10227.5649095 A.U.

E + zero-point Energies = -10226.871614
E + thermal Energies = -10226.821654
E + thermal Enthalpies = -10226.820710

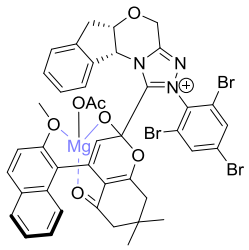
E + thermal Free Energies = -10226.959572

Charge: 1 Multiplicity: 1
C -2.188613000000 -2.927999000000 -1.398694000000
C -1.029644000000 -1.251799000000 -0.594710000000
N -0.986520000000 -3.408431000000 -1.238438000000
N -2.259017000000 -1.608141000000 -1.018610000000
C -3.544950000000 -0.866472000000 -1.111646000000
H -3.307240000000 0.196337000000 -1.174526000000
C -3.387880000000 -3.528266000000 -2.056603000000
H -4.147571000000 -3.812359000000 -1.316227000000
H -3.100240000000 -4.411319000000 -2.628437000000
C -4.346766000000 -1.338360000000 -2.390124000000
H -4.237042000000 -0.602485000000 -3.188017000000
O -3.855352000000 -2.548338000000 -2.973845000000
C -5.817053000000 -1.459435000000 -1.914698000000
H -6.391371000000 -0.588182000000 -2.252224000000
H -6.286094000000 -2.338790000000 -2.367691000000
C -4.467035000000 -1.174868000000 0.052593000000
C -5.744866000000 -1.508891000000 -0.407445000000
C -4.177625000000 -1.118433000000 1.416588000000
C -6.759082000000 -1.802643000000 0.505019000000
C -5.193593000000 -1.421086000000 2.324302000000
H -3.187176000000 -0.839284000000 1.760481000000
C -6.473521000000 -1.761615000000 1.870962000000
H -7.755092000000 -2.064416000000 0.160018000000
H -4.991572000000 -1.387600000000 3.390191000000
H -7.253207000000 -1.994532000000 2.589547000000
N -0.271001000000 -2.351872000000 -0.731456000000
C 1.122592000000 -2.546206000000 -0.478309000000
C 2.056558000000 -2.279265000000 -1.485314000000
C 1.555828000000 -3.089910000000 0.737093000000
C 3.414186000000 -2.497812000000 -1.273883000000
C 2.909089000000 -3.319035000000 0.962389000000
C 3.824958000000 -3.010736000000 -0.043970000000
H 4.132237000000 -2.283757000000 -2.054505000000
H 3.241928000000 -3.734946000000 1.904305000000
Br 1.472312000000 -1.645865000000 -3.176502000000
Br 0.304011000000 -3.527389000000 2.084209000000
Br 5.671071000000 -3.310218000000 0.262495000000
C 1.575956000000 3.110577000000 -0.795017000000
C 0.826581000000 4.080743000000 -1.445854000000
C 1.431906000000 5.224786000000 -2.013115000000
C 2.794977000000 5.383348000000 -1.932134000000

H 0.830352000000 5.984062000000 -2.495508000000
H 3.259149000000 6.264658000000 -2.364775000000
C 0.877459000000 1.959569000000 -0.152270000000
C -0.672331000000 0.139886000000 -0.116296000000
C 2.995943000000 3.268579000000 -0.703608000000
C 3.612773000000 4.422402000000 -1.288112000000
C 5.022893000000 4.576071000000 -1.209769000000
C 5.801291000000 3.629278000000 -0.586785000000
C 5.196353000000 2.481809000000 -0.020578000000
H 5.817432000000 1.732920000000 0.461749000000
C 3.832336000000 2.303406000000 -0.077926000000
H 6.877726000000 3.755337000000 -0.531055000000
H 5.475589000000 5.457613000000 -1.654742000000
H 3.385158000000 1.414011000000 0.351801000000
O -0.560919000000 3.913367000000 -1.487246000000
C -1.289462000000 4.608981000000 -2.529896000000
H -1.367891000000 5.673731000000 -2.295915000000
H -2.276551000000 4.151224000000 -2.546294000000
H -0.786624000000 4.466868000000 -3.489195000000
O -1.668463000000 0.797720000000 0.341569000000
Mg -1.693798000000 2.901617000000 0.079501000000
O -0.488304000000 3.822359000000 1.522441000000
C 0.303509000000 3.014403000000 2.082103000000
C 0.801052000000 1.908266000000 1.316283000000
C 0.585996000000 3.067867000000 3.559525000000
C 0.710068000000 0.668998000000 1.962108000000
C 0.270372000000 1.700128000000 4.242937000000
H -0.005426000000 3.868368000000 4.010761000000
H 1.649429000000 3.303182000000 3.698255000000
C 0.969092000000 0.558995000000 3.444961000000
H 2.053252000000 0.614634000000 3.609724000000
H 0.631413000000 -0.421398000000 3.792041000000
C -1.252483000000 1.462820000000 4.260930000000
H -1.763414000000 2.268581000000 4.796529000000
H -1.485542000000 0.521937000000 4.770254000000
H -1.680109000000 1.409490000000 3.254335000000
C 0.803791000000 1.717495000000 5.683293000000
H 0.322013000000 2.509924000000 6.264964000000
H 1.884926000000 1.889391000000 5.709914000000
H 0.600033000000 0.765996000000 6.185459000000
O 0.334390000000 -0.386208000000 1.317472000000
C 0.341421000000 0.941258000000 -0.864327000000
H 0.504394000000 0.788338000000 -1.925094000000
C -5.557928000000 3.161155000000 -0.479547000000

H -5.832443000000 3.281829000000 -1.528797000000
H -5.980713000000 3.963518000000 0.125947000000
H -5.975055000000 2.212496000000 -0.122944000000
C -4.059730000000 3.114928000000 -0.322577000000
O -3.324542000000 2.629170000000 -1.253094000000
O -3.514140000000 3.527969000000 0.750308000000

**V_ A_i**




**V**

E(RB3LYP/6-31G(d,p)) = -10227.5666918 A.U.

Temp. 298.150 K 1.00000 Atm.

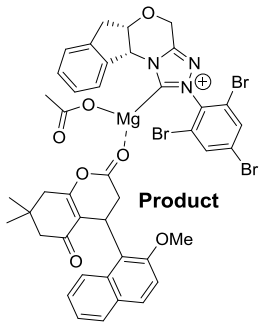
| | |
|---|---|
| E + zero-point Energies | = -10226.872474 |
| E + thermal Energies | = -10226.822091 |
| E + thermal Enthalpies | = -10226.821147 |
| E + thermal Free Energies | = -10226.961491 |

Geometry at E(RB3LYP/6-31G(d,p))
Charge: 1 Multiplicity: 1
C -2.401111000000 -2.855674000000 -1.412416000000
C -1.199159000000 -1.241112000000 -0.552990000000
N -1.231419000000 -3.396603000000 -1.210502000000
N -2.422838000000 -1.532768000000 -1.027278000000
C -3.667094000000 -0.722593000000 -1.148248000000
H -3.352499000000 0.318194000000 -1.221810000000
C -3.604577000000 -3.396173000000 -2.112394000000
H -4.396213000000 -3.659152000000 -1.397706000000
H -3.338209000000 -4.282739000000 -2.689137000000
C -4.483768000000 -1.177157000000 -2.425887000000
H -4.369098000000 -0.435033000000 -3.217040000000
O -4.006344000000 -2.384339000000 -3.025372000000
C -5.955567000000 -1.287433000000 -1.948511000000
H -6.534437000000 -0.432952000000 -2.318743000000
H -6.420179000000 -2.184397000000 -2.371355000000
C -4.609452000000 -0.957850000000 0.014946000000
C -5.890212000000 -1.283770000000 -0.440723000000

C -4.329381000000 -0.844913000000 1.377427000000
C -6.916134000000 -1.520254000000 0.475528000000
C -5.356961000000 -1.088990000000 2.289048000000
H -3.337334000000 -0.563003000000 1.714694000000
C -6.639443000000 -1.427158000000 1.840404000000
H -7.915232000000 -1.774875000000 0.134112000000
H -5.163287000000 -1.010617000000 3.354198000000
H -7.428610000000 -1.614344000000 2.562054000000
N -0.489881000000 -2.377521000000 -0.664589000000
C 0.899979000000 -2.581223000000 -0.399114000000
C 1.837369000000 -2.349419000000 -1.414143000000
C 1.340705000000 -3.026108000000 0.853467000000
C 3.201000000000 -2.468819000000 -1.167401000000
C 2.701961000000 -3.154783000000 1.115358000000
C 3.617204000000 -2.848872000000 0.108055000000
H 3.920003000000 -2.265231000000 -1.949901000000
H 3.040738000000 -3.483449000000 2.089178000000
Br 1.250936000000 -1.868066000000 -3.152536000000
Br 0.094142000000 -3.455403000000 2.208606000000
Br 5.474128000000 -2.942703000000 0.481227000000
C 1.926846000000 2.722439000000 -0.793084000000
C 1.388942000000 3.803054000000 -1.476309000000
C 2.224406000000 4.781047000000 -2.065651000000
C 3.591502000000 4.647168000000 -1.987883000000
H 1.799981000000 5.639062000000 -2.569973000000
H 4.228478000000 5.401226000000 -2.440821000000
C 1.020761000000 1.743028000000 -0.131452000000
C -0.734483000000 0.117272000000 -0.026595000000
C 3.345853000000 2.563139000000 -0.723040000000
C 4.192429000000 3.541069000000 -1.337373000000
C 5.602177000000 3.367452000000 -1.291973000000
C 6.158448000000 2.263958000000 -0.687696000000
C 5.322757000000 1.285466000000 -0.096661000000
H 5.759124000000 0.396769000000 0.350393000000
C 3.954362000000 1.435047000000 -0.106115000000
H 7.236008000000 2.136506000000 -0.667781000000
H 6.234367000000 4.119481000000 -1.755606000000
H 3.325902000000 0.674658000000 0.344001000000
O -0.001145000000 3.893283000000 -1.549821000000
C -0.564033000000 4.812934000000 -2.517471000000
H -1.624797000000 4.574008000000 -2.558090000000
H -0.103643000000 4.651572000000 -3.494946000000
H -0.415214000000 5.845810000000 -2.191742000000
O -1.720442000000 0.949347000000 0.198852000000

Mg -1.418439000000 2.984100000000 -0.091375000000
O -0.132422000000 3.884415000000 1.390056000000
C 0.509801000000 3.017726000000 2.026222000000
C 0.848288000000 1.791823000000 1.331321000000
C 0.732235000000 3.087298000000 3.510454000000
C 0.452596000000 0.657299000000 2.009352000000
C 0.065621000000 1.858359000000 4.215093000000
H 0.316949000000 4.020583000000 3.897939000000
H 1.811922000000 3.073271000000 3.705986000000
C 0.530387000000 0.548144000000 3.506763000000
H 1.574105000000 0.341741000000 3.779560000000
H -0.067503000000 -0.303742000000 3.841444000000
C -1.468404000000 1.975104000000 4.129263000000
H -1.812205000000 2.907338000000 4.587037000000
H -1.942347000000 1.145386000000 4.663769000000
H -1.833810000000 1.957582000000 3.097832000000
C 0.499474000000 1.824981000000 5.687929000000
H 0.171013000000 2.730007000000 6.208407000000
H 1.587845000000 1.753997000000 5.786412000000
H 0.055914000000 0.966582000000 6.203197000000
O -0.078855000000 -0.353671000000 1.339685000000
C 0.385079000000 0.764065000000 -0.805673000000
H 0.546755000000 0.548679000000 -1.855373000000
C -5.107707000000 4.068545000000 -0.761904000000
H -5.744956000000 3.408631000000 -0.164422000000
H -5.383169000000 3.987757000000 -1.813352000000
H -5.276052000000 5.086348000000 -0.401566000000
C -3.665890000000 3.686430000000 -0.544134000000
O -3.122613000000 3.880971000000 0.591118000000
O -2.979817000000 3.154508000000 -1.485508000000

**Product**




E(RB3LYP/6-31G(d,p)) = -10227.5949318

Temp. 298.150 K 1.00000 Atm.

E + zero-point Energies = -10226.902489
E + thermal Energies = -10226.850673
E + thermal Enthalpies = -10226.849729
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Geometry at E(RB3LYP/6-31G(d,p))
Charge: 1 Multiplicity: 1
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C 2.860317000000 -0.524410000000 0.288695000000
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H 3.082400000000 3.341577000000 5.060024000000
C 3.107841000000 1.906835000000 3.493898000000
O 2.964260000000 2.232922000000 2.263455000000
O 2.611619000000 0.802888000000 3.905528000000

**Supplementary Table 9. Data of enantiomerisation barrier determation**[a]

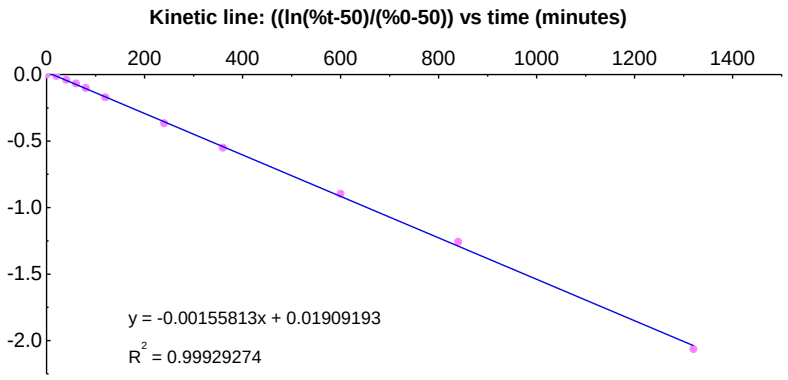
| Time (min) | % second eluted enantiomer (%t) | ln ((%t-50)/(%0-50)) |
|---|---|---|
| 0 | 95.50 | 0 |
| 20 | 95.01 | -0.01083 |
| 40 | 93.72 | -0.03991 |
| 60 | 92.53 | -0.0675 |
| 80 | 91.12 | -0.10122 |
| 120 | 88.33 | -0.17148 |
| 240 | 81.56 | -0.36582 |
| 360 | 76.23 | -0.55081 |
| 600 | 68.58 | -0.89563 |
| 840 | 62.94 | -1.25739 |
| 1320 | 55.78 | -2.06331 |

[a] Conditions: About 3 mg of enantio-enriched (**3gh**) were refluxed in 15 mL of toluene at 85 ℃. Samples of 7 µL of this solution were injected on Chiralpak IC (heptane / *i*PrOH = 80/20, 1 mL/min, UV detection at 254 nm) to monitor the percentage decrease of the second eluted enantiomer over time.

**Supplementary Table 10. Statistical results.**

| | |
|---|---|
| k racemization = | 2.59688E-05 $s^{-1}$ |
| k enantiomerisation = | 1.29844E-05 $s^{-1}$ |
| $\Delta G^{\neq}$ enantiomerisation = | 119.71 $KJ.mol^{-1}$ |
| | 28.6 $kcal.mol^{-1}$ |
| half-life time[a] $t_{1/2}$ = | 26692 s |
| | 444.87 min |
| | 7.41 h |
| | 0.309 d |

[a] T = 85 °C, $t_{1/2}$ = 7.41 h, T = 25 °C, $t_{1/2}$ = 1.67 year.



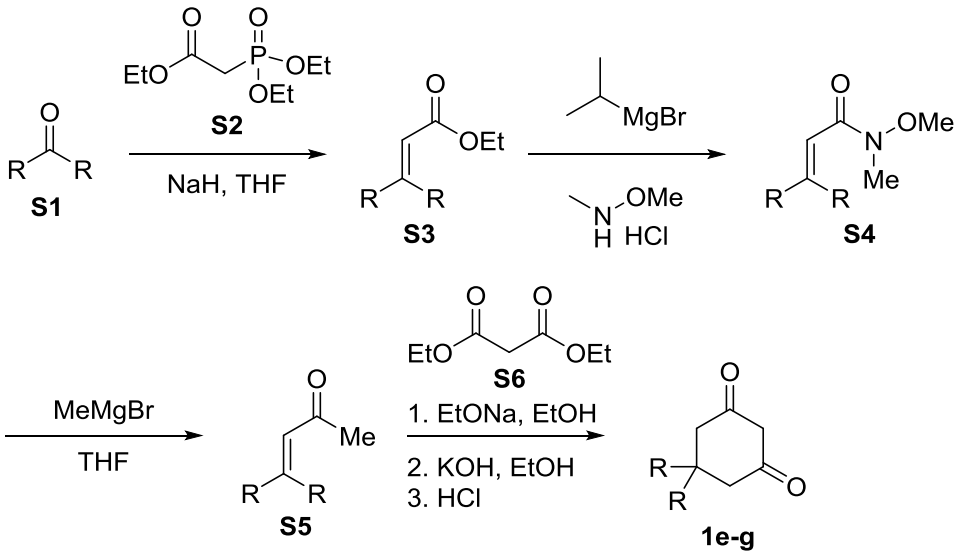

**Supplementary Figure 175. Kinetic line based on the data in Supplementary Table 9.**

## Supplementary Methods

## General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker ACF400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0) or tetramethylsilane (TMS δ 0.00) was used as a reference. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), bs (broad singlet). Coupling constants were reported in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. The enantiomeric excesses of products were determined by chiral phase HPLC analysis. Optical rotations were recorded on Jasco DIP-1000 polarimeter.

## General procedure for the synthesis of 1e-g.



To a solution of **S2** (40.0 mmol) in THF (60 mL) was added NaH (1.6 g, 40 mmol, 60%) at 0 $^{o}$C. The reaction mixture was stirred for 30 min. **S1** (20.0 mmol) in THF (20 mL) was added. The reaction mixture was warmed to 70 $^{o}$C and stirred for 48 h. The reaction was then quenched by addition of $NH_4Cl$. The reaction mixture was extracted with $Et_2O$ (3 x 80 mL) and washed with brine, dried over sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography to afford the **S3**.

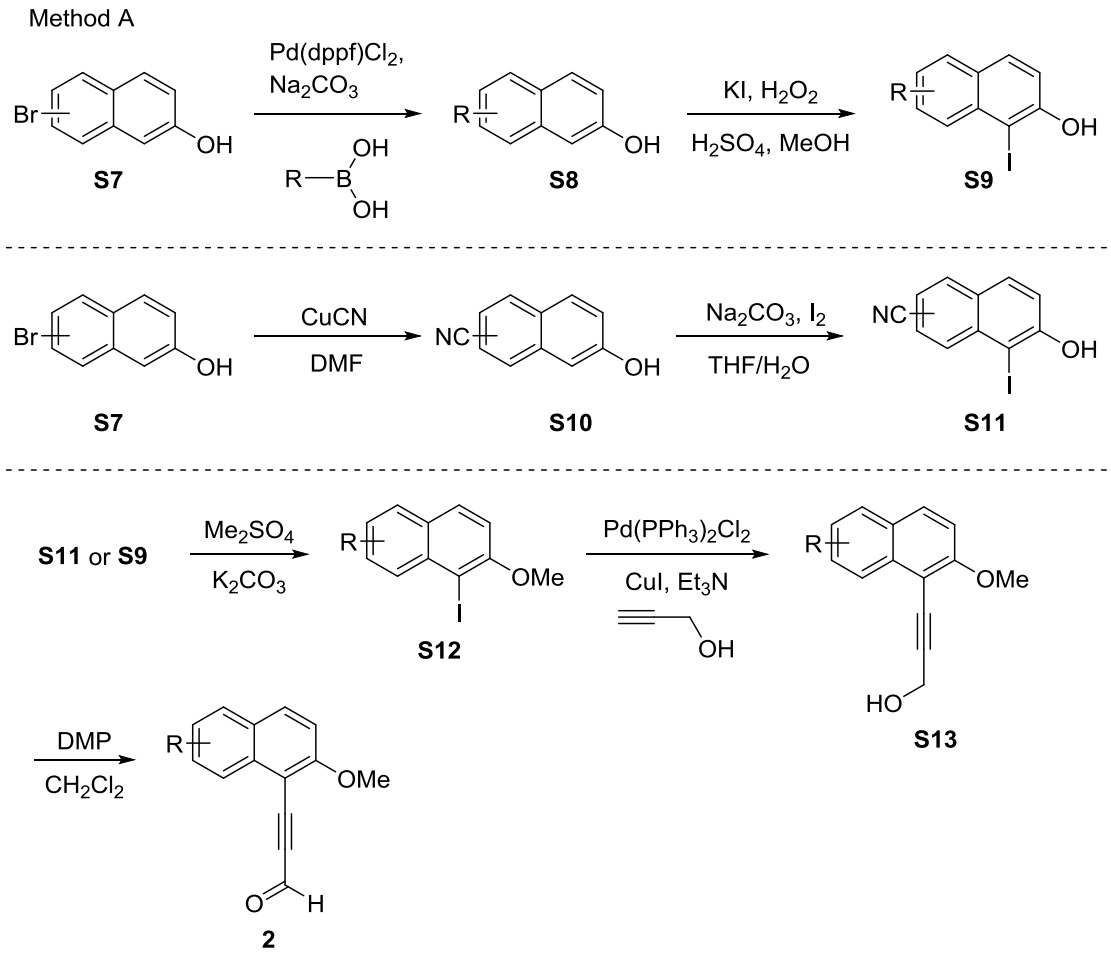
To the above product **S3** (20.0 mmol), N-methoxymethanamine (40.0 mmol) in THF (60 mL) was added $^{i}$PrMgBr (40.0 mL, 2.0 M in THF) at -20 $^{o}$C under $N_2$, the mixture was warmed to RT and stirred for 2 h. The reaction was then quenched by addition of $NH_4Cl$. The reaction mixture was extracted with EtOAc (3 x 80 mL) and washed with brine, dried over sodium sulfate. The solvent was removed under reduced pressure, and the residue was used directly for the next step.

To the above product **S4** (20.0 mmol) in THF (40 mL) was added MeMgBr (20.0 mL, 2.0 M in THF) at -20 $^{o}$C under $N_2$, the mixture was warmed to 0 $^{o}$C and stirred for 2 h. The reaction was then quenched by addition of $NH_4Cl$, the reaction mixture was extracted with EtOAc (3 x 80 mL) and washed with brine, dried over sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography to afford the **S5**.

Sodium metal (460 mg, 20.0 mmol) was added to ethanol (30 mL) at rt under argon. After the sodium dissolved completely, diethyl malonate **S6** (3.20 g, 20.0 mmol) was added to the sodium ethoxide solution followed by addition of **S5** (10.0 mmol) at rt. The solution was warmed to reflux. After 24 h reflux, the solution was cooled to rt and a solution of potassium hydroxide (5.6 g, 100 mmol) in $H_2O$ (20 mL) was added. The resulting solution was warmed to reflux for 48 h. The solution was cooled to 0 ℃ and acidified with 6 N HCl to pH 3. The EtOH was evaporated, and the residue was extracted with EtOAc (3 x 100 mL) and washed with brine, dried over sodium sulfate. The solvent was evaporated, and the residue was purified by column chromatography to afford the **1e-g**.

**1b-d** were prepared according to references [1] and [2].

## General procedure for the synthesis of 2.




**2a, 2b, 2c, 2e, 2f, 2g, 2h, 2i, 2j, 2k, 2l, 2m, 2n, 2o, 2p, 2q, 2r, 2t,** and **2u** were synthesized by method A.

**Method A:**

To a solution of **S7** (10.0 mmol) in 1,4-dioxane (40 mL) was added 2 M aqueous $Na_2CO_3$ (10 mL, 20 mmol), boric acid (15.0 mmol) and $PdCl_2$(dppf) (183 mg, 0.25 mmol). The flask was flushed with nitrogen gas. The solution was warmed to reflux for 4 h. The reaction mixture was cooled to RT. The 1,4-dioxane was evaporated, and the residue was extracted with EtOAc (3 x 30 mL) and washed with brine, dried over sodium sulfate. The solvent was evaporated, and the residue was purified by column

chromatography to afford **S8**.

To MeOH (50 mL) being stirred at 0 ℃ in a round-bottom flask was added sulfuric acid (95.8%, 0.56 mL, 15.0 mmol), **S7** (10.0 mmol), KI (1.67 g, 10.0 mmol), and $H_2O_2$ (31.6%, 2.0 mL, 21.0 mmol). The dark mixture was kept stirring at 0 ℃ for 9 h at which time the substrate appeared consumed (TLC). The mixture was quenched by adding excess saturated aqueous $Na_2SO_3$. The MeOH was evaporated, and the residue was extracted with EtOAc (3 x 30 mL) and washed with brine, dried over sodium sulfate. The solvent was evaporated to yield the product **S9** which was used directly for the next step.

A mixture of bromo-2-naphthol **S7** (10.0 mmol) and CuCN (1.34 g, 15.0 mmol) in DMF (20 mL) was vigorously stirred at 150 ℃ for 4.5 h. After cooling to room temperature, the mixture was added 10% NaOH (30 mL) and stirred for 5 min. The reaction was filtered and the filtrate was washed with water (15 mL). Then, 3 N HCl was used to adjust pH to 2-3. The precipitate was collected by filtration to give **S10** as a brown solid which was used directly for the next step.

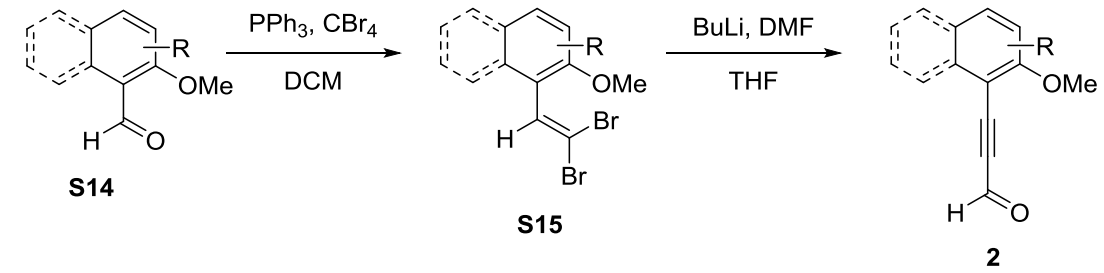
To a solution of **S10** (5.0 mmol) in THF: $H_2O$ (50 mL, 1:4) was added $Na_2CO_3$ (1.06 g, 10.0 mmol), and $I_2$ (1.27 g, 5.0 mmol) at 0 ℃. The reaction was vigorously stirred at RT for 4 h. at which time TLC indicated complete conumption of the naphthol. The mixture was quenched by adding excess saturated aqueous $Na_2SO_3$. The mixture was extracted with EtOAc (3 x 30 mL) and washed with brine, dried over sodium sulfate. The solvent was evaporated to yield the product **S11** which was used directly for the next step.

To a solution of **S11** or **S9** (5.0 mmol) in acetone (20 mL) was added $K_2CO_3$ (1.38 g, 10.0 mmol), dimethyl sulfate (1.0 mL, 10.0 mmol). The solution was warmed to reflux for 4 h at which time TLC indicated complete consumption of the naphthol. The reaction mixture was cooled to RT. $Et_3N$ (5.0 mL) was added, and the reaction was stirred for 1 h. The reaction mixture was filtered through a pad of Celite, the solid was washed with DCM and the solvent was evaporated to yield a yellow solid. The solid was washed with PE for three times to give the product **S12** which was used directly for the next step.

To a solution of **S12** (5.00 mmol) and propargyl alcohol (1.4 g, 25.0 mmol) in triethylamine (20 mL) was added $PdCl_2(PPh_3)_2$ (142 mg, 0.202 mmol) and CuI (76 mg, 0.40 mmol). The flask was flushed with nitrogen gas. The resulting mixture was stirred at room temperature for 40 h. The reaction mixture was filtered and washed with EtOAc. The combined filtrate was concentrated and the residue was purified by a silica gel column chromatography to give **S13**.

To a solution of **S13** (4.0 mmol) in DCM (50 mL) was added $NaHCO_3$ (1.06 g, 10.0 mmol), and Dess-Martin oxidant (2.12 g, 5.0 mmol) at 0 ℃. The reaction was stirred at RT for 2 h. at which time TLC indicated complete conumption of the **S14**. The mixture was quenched by adding excess saturated aqueous $Na_2SO_3$. The mixture was vigorously stirred at RT for 1 h. The mixture was extracted with EtOAc (3 x 30 mL) and washed with brine, dried over sodium sulfate. The solvent was concentrated and the residue was purified by a silica gel column chromatography to give **2**.

Method B



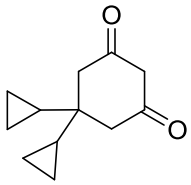

**2d** and **2s** were synthesized by method B.

**Method B:**

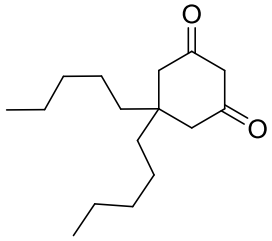
To a solution of **S14** (10.0 mmol) in DCM (50 mL) was added $PPh_3$ (13.1 g, 50.0 mmol), $CBr_4$ (8.3 g, 25.0 mmol) was added slowly at 0 $^oC$. The solution was stirred for 30 mins. Half of the solvent was evaporated, PE: EtOAc (50 mL, 1:1) was added to the mixture. The mixture was filtered through a pad of silica gel, the solid was washed with PE: EtOAc (50 mL, 1:1) for three times and the solvent was evaporated and the residue was purified by a silica gel column chromatography to give **S15**.

To the above product **S15** (8.0 mmol), in THF (30 mL) was added BuLi (7.0 mL, 2.5 M) at -78 $^{o}$C under $N_2$, the mixture was warmed to -30 $^{o}$C and stirred for 1 h. Then DMF (1.19 g, 16.0 mmol) was added to the reaction mixture. The reaction was warmed to RT and stirred for another 2 hours and then quenched by addition of $NH_4Cl$. The reaction mixture was extracted with EtOAc (3 x 30 mL) and washed with brine, dried over sodium sulfate. The solvent was concentrated and the residue was purified by a silica gel column chromatography to give **2**.

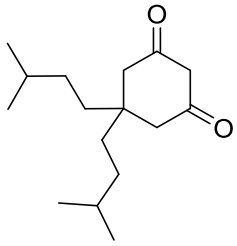
## Characterization data of 1 and 2.



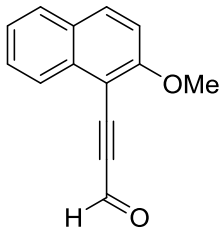
**1e:** White solid: **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 3.35 (s, 2H), 2.41 (s, 4H), 0.67 – 0.60 (m, 2H), 0.42 – 0.32 (m, 8H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 204.3, 57.4, 48.9, 40.8, 35.0, 18.8, 0.4; **HRMS** (ESI): *m/z*: calculated for $C_{12}H_{17}O_2^+$: $[M + H]^+$ 193.1223, found: 193.1229.



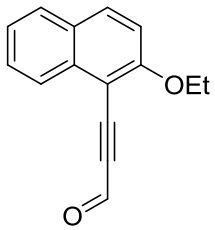
**1f:** White solid: **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 3.33 (s, 2H), 2.53 (s, 4H), 1.38 -1.22 (m, 16H), 0.88 (t, *J* = 6.9 Hz, 6H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 204.2, 57.6, 50.9, 43.1, 37.5, 32.1, 22.7, 22.4, 13.9; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{29}O_2^+$: $[M + H]^+$ 253.2162, found: 253.2170.



**1g:** White solid: **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 3.33 (s, 2H), 2.52 (s, 4H), 1.21 (s, 4H), 1.09 (s, 6H), 0.86 (s, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 204.0, 57.6, 50.9, 35.9, 35.0, 31.9, 28.3, 22.5; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{29}O_2^+$: $[M + H]^+$ 253.2162, found: 253.2171.

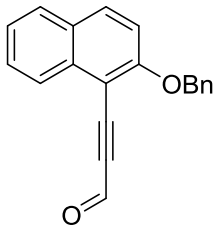


**2a:** Yellow solid; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 7.96 (d, *J* = 9.2 Hz, 1H), 7.79 (d, *J* = 8.1 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.44 – 7.40 (m, 1H), 7.24 (d, *J* = 9.6 Hz, 1H), 4.05 (s, 3H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 176.7, 162.2, 134.9, 134.1, 128.6, 128.5, 128.2, 124.8, 124.7, 112.1, 102.1, 98.5, 91.3, 56.5; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{10}NaO_2^+$: $[M + Na]^+$ 233.0573, found: 233.0579.

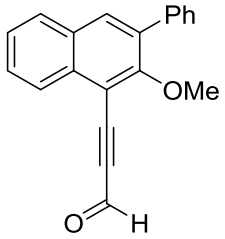


**2b:** Yellow solid; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.21 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 9.0 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 9.1 Hz, 1H), 4.28 (q, *J* = 7.0 Hz, 1H), 1.51 (t, *J* = 7.0 Hz, 1H); **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 176.7, 161.7, 134.9, 133.8, 128.4, 128.3,

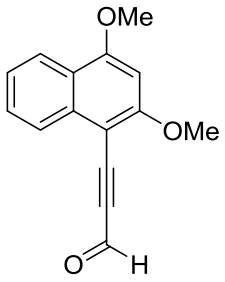
128.1, 124.7, 113.3, 102.5, 98.4, 91.5, 65.2, 14.9; **HRMS** (ESI): *m/z*: calculated for $C_{15}H_{12}NaO_2^+$: $[M + Na]^+$ 247.0730, found: 247.0736.



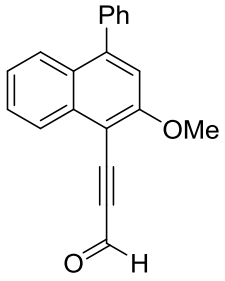

**2c:** Yellow solid; **$^1$H NMR** (400 MHz, $CDCl_3$) δ **$^1$H NMR** (400MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 9.1 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.59 – 7.55 (m, 1H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.42 – 7.36 (m, 3H), 7.33 – 7.29 (m, 1H), 7.23 – 7.20 (m, 1H), 5.33 (s, 2H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.7, 161.4, 136.3, 134.9, 133.9, 128.7, 128.5, 128.5, 128.4, 127.0, 125.0, 124.8, 114.0, 103.3, 98.5, 91.2, 71.2; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{14}NaO_2^+$: $[M + Na]^+$ 309.0886, found: 309.0892.



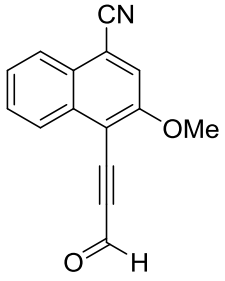

**2d:** White solid; **$^1$H NMR** (400MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.88 (d *J* = 8.1 Hz, 1H), 7.68 – 7.63 (m, 3H), 7.56 – 7.43 (m, 4H), 3.78 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.4, 161.4, 137.1, 134.7, 134.3, 134.0, 130.1, 129.1, 128.4, 128.4, 128.1, 127.8, 126.2, 124.9, 108.8, 97.4, 90.4, 61.9; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{14}NaO_2^+$: $[M + Na]^+$ 309.0886, found: 309.0880.




**2e:** Yellow solid; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.16 (s, 2H), 7.60 (s, 1H), 7.39 (d, *J* = 6.8 Hz, 1H), 6.53 (s, 1H), 4.05 (s, 6H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.5, 164.2, 160.8, 135.4, 129.2, 124.5, 124.1, 122.6, 120.9, 98.9, 94.3, 93.3, 91.9, 56.5, 55.9; **HRMS** (ESI): *m/z*: calculated for $C_{15}H_{12}NaO_3^+$: $[M + Na]^+$ 263.0679, found: 263.0672.

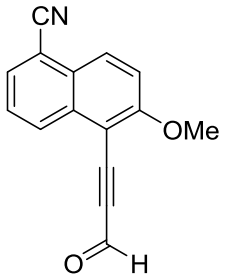



**2f:** White solid; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.54 – 7.47 (m, 5H), 7.37 – 7.33 (m, 1H), 7.19 (s, 1H), 4.04 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.6, 161.4, 146.8, 139.6, 135.4, 129.6, 128.5, 128.4, 128.2, 126.9, 125.1, 124.8, 113.3, 101.5, 98.8, 91.4, 56.5; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{14}NaO_2^+$: $[M + Na]^+$ 309.0886, found: 309.0882.

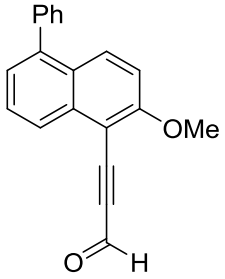



**2g:** Yellow solid; **$^{1}$H NMR** (400MHz, DMSO-$d^6$) δ 9.60 (s, 1H), 8.18 (s, 2H), 8.04 (s,

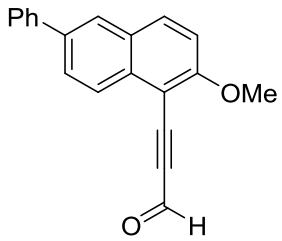
1H), 7.78 (s, 1H), 7.69 (d, *J* = 5.6 Hz, 1H), 4.06 (s, 3H); **$^{13}$C NMR** (101MHz, DMSO-$D_6$) δ 179.0, 160.5, 134.0, 130.5, 127.9, 126.9, 125.5, 125.3, 120.3, 117.1, 113.8, 106.8, 99.8, 87.2, 57.8; **HRMS** (ESI): *m/z*: calculated for $C_{15}H_9NNaO_2^+$: $[M + Na]^+$ 258.0525, found: 258.0530.



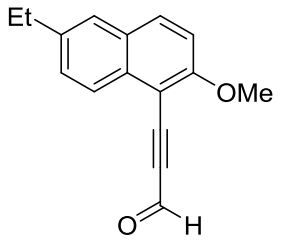

**2h:** Yellow solid**; $^{1}$H NMR** (400MHz, DMSO-$D_6$) δ 9.59 (s, 1H), 8.42 (s, 1H), 8.28 (s, 1H), 8.11 (s, 1H), 7.81 (s, 2H), 4.08 (s, 3H); **$^{13}$C NMR** (101MHz, DMSO-$D_6$) δ 178.9, 163.1, 134.3, 132.3, 130.8, 129.9, 128.7, 126.7, 117.7, 116.6, 110.2, 102.3, 99.0, 88.4, 57.4; **HRMS** (ESI): *m/z*: calculated for $C_{15}H_9NNaO_2^+$: $[M + Na]^+$ 258.0525, found: 258.0518.



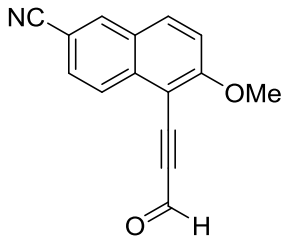

**2i:** Yellow solid**; $^{1}$H NMR** (400MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 9.4 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.51 – 7.43 (m, 5H), 7.35 (d, *J* = 7.1 Hz, 1H), 7.15 (d, *J* = 2.5 Hz, 1H), 4.03 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.7, 162.0, 141.1, 140.1, 135.4, 132.5, 130.0, 128.4, 128.2, 127.6, 126.6, 125.9, 124.3, 102.3, 98.6, 91.4, 56.5; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{14}NaO_2^+$: $[M + Na]^+$ 309.0886, found: 309.0880.




**2j:** Yellow solid**; $^{1}$H NMR** (400MHz, $CDCl_3$) δ 9.63 (s, 1H), 8.30 – 8.27 (m, 1H), 8.01 – 7.98 (m, 2H), 7.88 – 7.85 (m, 1H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.51 (t, *J* = 8.0 Hz, 2H), 7.28 – 7.25 (m, 1H), 4.07 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.6, 162.1, 140.3, 137.5, 134.2, 134.0, 128.9, 128.4, 128.1, 127.5, 127.1, 126.1, 125.2, 112.4, 102.0, 98.4, 91.0, 56.5; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{14}NaO_2^+$: $[M + Na]^+$ 309.0886, found: 309.0892.

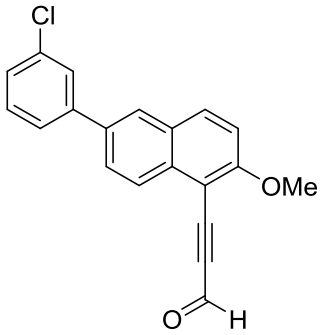



**2k:** Yellow solid**; $^{1}$H NMR** (400MHz, $CDCl_3$) δ 9.61 (s, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 7.90 – 7.87 (m, 1H), 7.57 (s, 1H), 7.46 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.22 – 7.19 (m, 1H), 4.04 (dd, *J* = 4.9, 3.6 Hz, 3H), 2.80 (dd, *J* = 15.2, 7.6 Hz, 2H), 1.35 – 1.31 (m, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.6, 161.6, 140.6, 133.5, 133.2, 129.7, 128.4, 126.0, 124.5, 111.9, 101.8, 98.3, 91.5, 56.4, 28.5, 15.3; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{14}NaO_2^+$: $[M + Na]^+$ 261.0886, found: 261.0881.

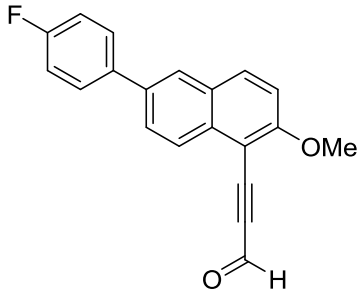



**2l:** White solid**; $^{1}$H NMR** (400MHz, DMSO-$D_6$) δ 9.59 (s, 1H), 8.63 (d, *J* = 1.4 Hz, 1H), 8.33 (d, *J* = 9.3 Hz, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 7.95 (dd, *J* = 8.7, 1.7 Hz, 1H),

7.74 (d, *J* = 9.3 Hz, 1H), 4.10 (s, 3H); **$^{13}$C NMR** (101MHz, DMSO-$D_6$) 178.9, 164.5, 136.3, 135.6, 135.5, 129.6, 127.3, 125.6, 119.4, 115.5, 107.5, 101.4, 98.7, 88.7, 57.5; **HRMS** (ESI): *m/z*: calculated for $C_{15}H_9NNaO_2^+$: $[M + Na]^+$ 258.0525, found: 258.0531.

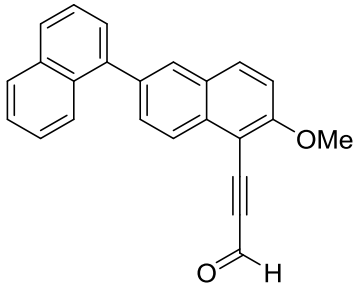



**2m:** Yellow solid**; $^{1}$H NMR** (400MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.23 (d, *J* = 8.7 Hz, 1H), 7.97 (d, *J* = 9.2 Hz, 1H), 7.91 (d, *J* = 1.6 Hz, 1H), 7.76 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.64 (t, *J* = 1.8 Hz, 1H), 7.54 – 7.51 (m, 1H), 7.40 – 7.32 (m, 2H), 7.26 – 7.24 (m, 1H), 4.05 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.6, 162.3, 142.1, 136.0, 134.8, 134.3, 134.2, 130.1, 128.3, 127.7, 127.4, 127.2, 126.3, 125.4, 112.6, 102.1, 98.4, 90.8, 56.5; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{13}ClNaO_2^+$: $[M + Na]^+$ 343.0496, found: 343.0490.

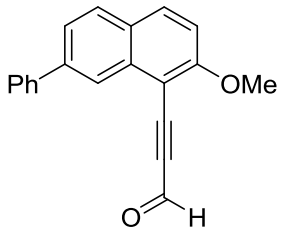



**2n:** Yellow solid**; $^{1}$H NMR** (400MHz, DMSO-$D_6$) δ 9.60 (s, 1H), 8.26 – 8.16 (m, 3H), 7.98 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 7.2 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 2H), 4.06 (s, 3H); **$^{13}$C NMR** (101MHz, DMSO-$D_6$) δ 178.9, 162.7, 136.3, 135.7, 135.3, 133.7, 129.9 (d, *J* = 8.2 Hz), 128.6, 128.2, 126.6, 128.2, 126.6, 125.0, 116.3 (d, *J* = 2.1 Hz), 114.2, 100.8, 98.7, 90.3, 57.1; **$^{19}$F NMR** (376 MHz, DMSO-$D_6$)

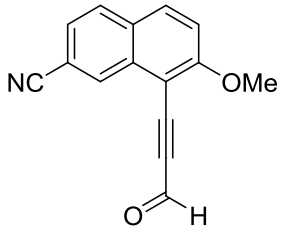
δ -115.2; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{13}FNaO_2^+$: $[M + Na]^+$ 327.0792, found: 327.0799.



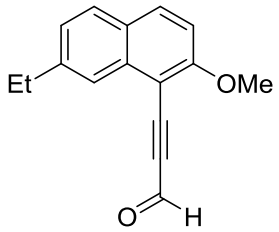

**2o:** Yellow solid**; $^1$H NMR** (400MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.32 (d, *J* = 7.9 Hz, 1H), 7.98 – 7.88 (m, 5H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.41 (m, 4H), 7.26 (d, *J* = 8.6 Hz, 1H), 4.06 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.7, 162.3, 139.4, 137.4, 134.2, 134.1, 133.9, 131.7, 131.2, 129.2, 128.4, 128.3, 128.0, 127.3, 126.3, 126.0, 125.8, 125.5, 124.6, 112.5, 102.2, 98.5, 91.1, 56.6; **HRMS** (ESI): *m/z*: calculated for $C_{24}H_{16}NaO_2^+$: $[M + Na]^+$ 359.1043, found: 359.1049.



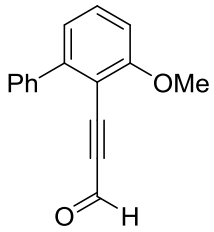

**2p:** White solid; **$^1$H NMR** (400MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.36 (s, 1H), 7.92 (d, *J* = 9.1 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.64 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.49 (t, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 9.1 Hz, 1H), 4.02 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.6, 162.6, 141.3, 140.7, 135.2, 133.8, 129.0, 127.9, 127.6, 127.4, 124.6, 122.5, 112.0, 102.3, 98.8, 91.2, 56.6; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{14}NaO_2^+$: $[M + Na]^+$ 309.0886, found: 309.0881.




**2q:** White solid**; $^{1}$H NMR** (400MHz, DMSO-$D_6$) δ 9.60 (s, 1H), 8.49 (s, 1H), 8.26 (d, *J* = 6.1 Hz, 1H), 8.12 (d, *J* = 4.2 Hz, 1H), 7.72 (d, *J* = 6.5 Hz, 2H), 4.06 (s, 3H); **$^{13}$C NMR** (101MHz, DMSO-$D_6$) δ 179.1, 163.3, 134.8, 133.6, 130.8, 130.0, 129.6, 125.8, 119.4, 116.8, 111.5, 101.5, 99.0, 88.4; **HRMS** (ESI): *m/z*: calculated for $C_{15}H_9NNaO_2^+$: $[M + Na]^+$ 258.0525, found: 258.0520.

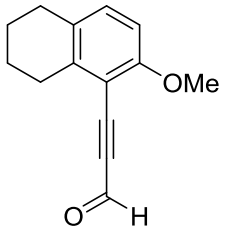



**2r:** Yellow solid; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 9.62 (s, 1H), 7.95 (s, 1H), 7.82 (d, *J* = 9.1 Hz, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.23 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.06 (d, *J* = 9.1 Hz, 1H), 3.95 (s, 3H), 2.81 (dd, *J* = 15.2, 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.5, 162.1, 144.8, 134.8, 133.6, 128.2, 126.4, 125.6, 122.1, 110.8, 101.1, 98.4, 91.6, 29.1, 15.3; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{14}NaO_2^+$: $[M + Na]^+$ 261.0886, found: 261.0891.

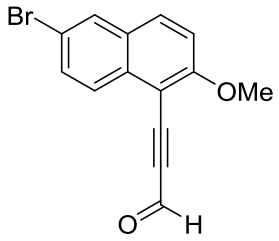



**2s:** White solid; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 9.32 (s, 1H), 7.58 – 7.41 (m, 6H), 7.05 (dd, *J* = 7.7, 0.5 Hz, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 3.98 (s, 3H), **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.6, 162.4, 148.0, 139.2, 132.3, 129.1, 128.1, 128.1, 122.0, 109.3, 107.4,

95.5, 92.3, 56.1; **HRMS** (ESI): *m/z*: calculated for $C_{16}H_{12}NaO_2^+$: $[M + Na]^+$ 259.0730, found: 259.0737.

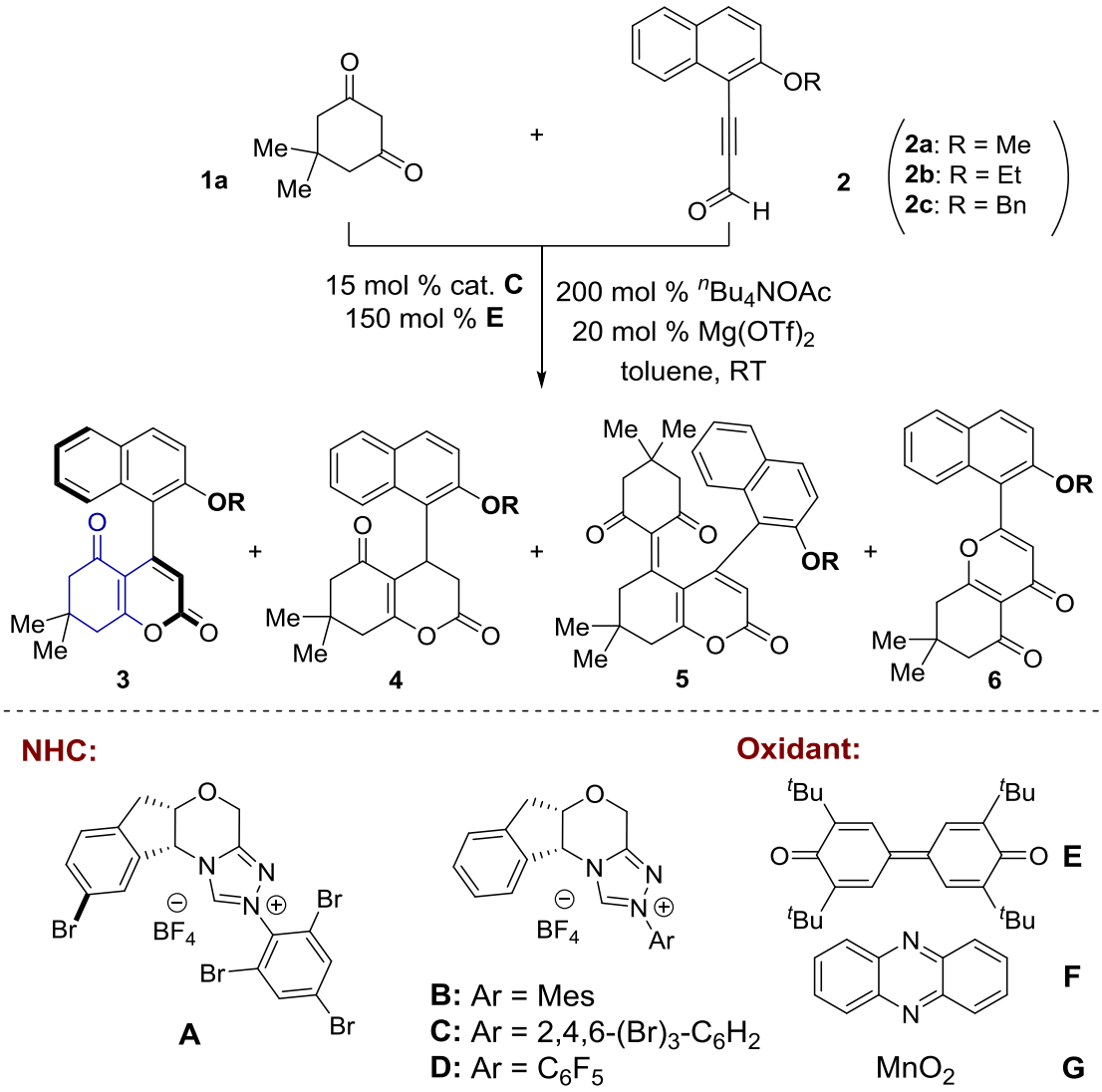



**2t:** Yellow solid; **$^1$H NMR** (400MHz, $CDCl_3$) δ 9.49 (s, 1H), 7.14 (d, *J* = 8.6 Hz, 1H), 6.69 (d, *J* = 8.6 Hz, 1H), 3.88 (s, 3H), 2.88 (t, *J* = 6.0 Hz, 2H), 2.69 (t, *J* = 6.2 Hz, 2H), 1.82 – 1.74 (m, 4H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 176.8, 160.4, 143.1, 133.4, 129.9, 108.1, 107.9, 97.7, 91.5, 55.8, 28.8, 28.2, 22.7, 22.5; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_{14}NaO_2^+$: $[M + Na]^+$ 237.0886, found: 237.0880.




**2u:** White solid; **$^1$H NMR** (400MHz, DMSO-$D_6$) δ 9.57 (s, 1H), 8.23 (d, *J* = 2.0 Hz, 1H), 8.14 (d, *J* = 9.2 Hz, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.75 (dd, *J* = 9.0, 2.1 Hz, 1H), 7.58 (d, *J* = 9.3 Hz, 1H), 4.04 (s, 3H); **$^{13}$C NMR** (101MHz, DMSO-$D_6$) δ 178.8, 162.7, 134.0, 133.1, 132.0, 131.0, 129.4, 126.4, 118.0, 114.8, 101.1, 98.7, 89.5, 57.2; **HRMS** (ESI): *m/z*: calculated for $C_{14}H_9BrNaO_2^+$: $[M + Na]^+$ 310.9678, 312.9658, found: 310.9685, 312.9663.

## Supplementary Table 11. Optimization of the reaction conditions.




| entry | deviation from standard conditions[a] | yield **3** (%)[b] | er **3** (%)[c] | yield **4** (%)[b] | yield **5** (%)[b] | yield **6** (%)[b] |
|---|---|---|---|---|---|---|
| 1[d] | **none** | **70** | **91:9** | <5 | <5 | <5 |
| 2 | no cat. **C** | 0 | - | 0 | 0 | 0 |
| 3 | **A** instead of **C** | 54 | 81:19 | <5 | 20 | 18 |
| 4 | **B** instead of **C** | <5 | - | <5 | <5 | <5 |
| 5 | **D** instead of **A** | <5 | - | <5 | <5 | 60 |
| 6 | no $Mg(OTf)_2$ | 60 | 90:10 | <5 | <5 | 18 |
| 7 | LiCl instead of $Mg(OTf)_2$ | 58 | 90:10 | <5 | <5 | <10 |
| 8 | $In(OTf)_3$ instead of $Mg(OTf)_2$ | 63 | 90:10 | <5 | <5 | <10 |
| 9 | $Sc(OTf)_3$ instead of $Mg(OTf)_2$ | 60 | 90:10 | <5 | <5 | <10 |
| 10 | $Zn(OTf)_2$ instead of $Mg(OTf)_2$ | 61 | 90:10 | <5 | <5 | <10 |
| 11 | $CHCl_3$ as solvent | 40 | 80:20 | <5 | 15 | 23 |

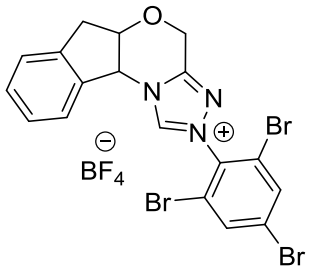
| | | | | | | |
|---|---|---|---|---|---|---|
| 12 | THF as solvent | 54 | 85:15 | <5 | <10 | 19 |
| 13 | Dioxane as solvent | 20 | - | <5 | <5 | 50 |
| 14 | no $^{n}Bu_4NOAc$ | 0 | - | 0 | 0 | 0 |
| 15 | DIPEA as base | 45 | 80:20 | <5 | 17 | 20 |
| 16 | $Cs_2CO_3$ as base | 40 | 75:25 | <5 | 20 | 22 |
| 17 | $KO^{t}Bu$ as base | <10 | - | <5 | <5 | <5 |
| 18 | **F** instead of **E** | <5 | - | 74 | <5 | <5 |
| 19 | **G** instead of **E** | <5 | - | 70 | <5 | <5 |
| 20 | 10 mol % cat. **C** | 69[e] | 91:9 | <5 | <5 | 13 |
| 21 | 100 mol % **E** | 28 | 91:9 | 20 | 20 | 10 |
| 22 | 120 mol % **E** | 56 | 91:9 | <5 | 22 | 10 |
| 23 | 100 mol % base | 40 | 91:9 | <5 | 23 | 25 |
| 24 | 50 mol % base | 30 | 91:9 | <5 | 32 | 28 |
| 25 | 150 mol % **1a** | 31 | 91:9 | <5 | 30 | 28 |
| 26 | 200 mol % **1a** | 28 | 91:9 | <5 | 24 | 40 |
| 27 | 150 mol % **2a** | <5 | - | <5 | <5 | <5 |
| 28 | 200 mol % **2a** | <5 | - | <5 | <5 | <5 |
| 29[e] | **2b** instead of **2a**[f] | 60 | 75:25 | <5 | <5 | 18 |
| 30[f] | **2c** instead of **2a**[g] | 60 | 72:8 | <5 | <5 | <5 |

[a]Standard conditions: **1a** (0.11 mmol), **2a** (0.10 mmol, R = Me), $^{n}Bu_4NOAc$ (0.2 mmol), oxidant **E** (0.15 mmol), $Mg(OTf)_2$ (20 mol %), cat. **C** (15 mol %), toluene (2.0 mL), room temperature, $N_2$, 24 h. [b]Isolated yield. [c]Determined by chiral HPLC. [e] 48 h. [f] **3ab** as major product. [g] **3ac** as major product.

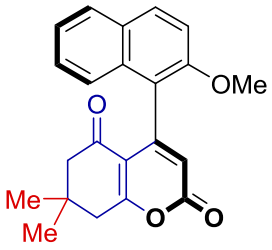
## General procedure for NHC-catalyzed reaction of 1 with 2.

In a glovebox, a flame-dried Schlenk reaction tube equipped with a magnetic stir bar, was added the azolium precatalyst (9.2 mg, 0.015 mmol), $Bu_4NOAc$ (60.2 mg, 0.20 mmol), DQ (62.0 mg), **1** (0.11 mmol) and **2** (0.10 mmol), and freshly distilled toluene (2.0 mL) was added. The mixture was then stirred at rt for 24 h. The reaction mixture was filtered through a pad of Celite, the solid was washed with DCM and the solvent was evaporated and purified by via column chromatography on silica gel to afford the desired product.

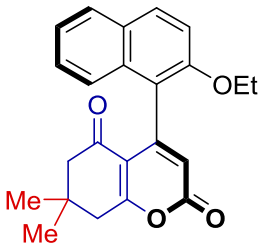
**Note**: Racemic samples for the standard of chiral HPLC spectra were prepared using racemic NHC precursor as catalyst.




## Characterization data of 3, 4, 5, 6, 7, 8, 10.

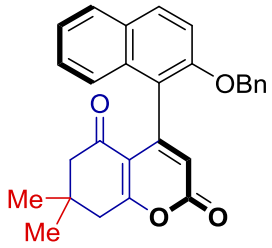



**3aa**: 70%; white solid; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.40 – 7.26 (m, 3H), 6.14 (s, 1H), 3.80 (s, 3H), 2.80 (s, 2H), 2.32 (d, *J* = 15.9 Hz, 1H), 2.22 (d, *J* = 15.9 Hz, 1H), 1.14 (s, 3H), 1.11 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.5, 172.5, 160.1, 152.4, 152.0, 131.2, 130.0, 128.7, 128.2, 126.8, 123.5, 123.4, 120.0, 116.0, 114.5, 112.3, 56.1, 51.6, 42.5, 31.7, 28.0, 27.8; **HRMS** (ESI): *m/z*: calculated for $C_{22}H_{20}NaO_4^+$: $[M + Na]^+$ 371.1254, found: 371.1250; HPLC (Chiralpak IB, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 25.8 min, $t_R$ (minor) = 32.7 min, e.r. = 90:10; $[\alpha]^{25}_D$ = -214.6 (*c* = 1.0, $CHCl_3$).

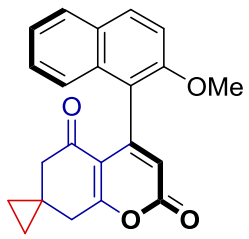



**3ab**: 60%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.27 – 7.24 (m, 1H), 6.14 (s, 1H), 4.14 – 4.08 (m, 2H), 2.84 (s, 2H), 2.30 (dd, *J* = 28.0, 15.9 Hz, 2H), 1.27

(t, *J* = 7.0 Hz, 3H), 1.17 (s, 3H), 1.13 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.6, 172.6, 160.3, 152.5, 152.0, 131.5, 130.0, 128.8, 128.3, 126.9, 123.6, 123.6, 120.4, 116.1, 114.6, 113.6, 64.6, 51.8, 42.7, 31.9, 28.4, 28.0, 15.1; **HRMS** (ESI): *m/z*: calculated for $C_{23}H_{23}O_4^+$: $[M + H]^+$ 363.1591, found: 363.1597; HPLC (Chiralpak IB, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 19.9 min, $t_R$ (minor) = 21.4 min, e.r. = 75:25; $[\alpha]^{25}_D$ = -103.2 (*c* = 1.0, $CHCl_3$).

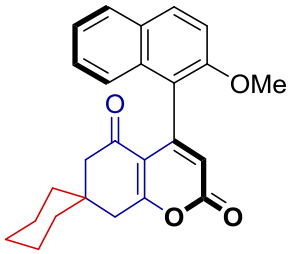



**3ac**: 60%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.87 (dd, *J* = 22.8, 9.2 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.44 – 7.28 (m, 8H), 6.15 (s, 1H), 5.19 (d, *J* = 12.0 Hz, 1H), 5.10 (d, *J* = 12.0 Hz, 1H), 2.78 (dd, *J* = 23.8, 18.4 Hz, 2H), 2.18 (dd, *J* = 26.4, 15.8 Hz, 2H), 1.11 (s, 3H), 1.03 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.7, 172.4, 160.2, 152.2, 151.7, 136.9, 131.4, 130.1, 129.1, 128.5, 128.3, 127.9, 127.1, 126.9, 123.8, 123.7, 121.0, 116.0, 114.6, 114.1, 71.2, 51.6, 42.5, 31.7, 28.0, 28.0; **HRMS** (ESI): *m/z*: calculated for $C_{28}H_{25}O_4^+$: $[M + H]^+$ 425.1747, found: 425.1741; HPLC (Chiralpak IB, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 20.7 min, $t_R$ (minor) = 28.4 min, e.r. = 72.5:8.5; $[\alpha]^{25}_D$ = -83.2 (*c* = 1.0, $CHCl_3$).

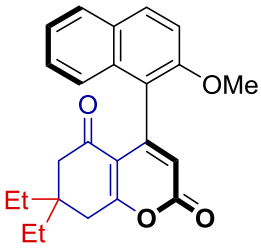



**3ba**: 61%; yellow oil; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 9.0 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.50 (d J = 8.4 Hz, 1H), 7.40 (dt, J = 8.4, 1.4 Hz, 1H), 7.34 (dt, J = 6.8, 1.2 Hz, 1H), 7.29 (d, J = 9.1 Hz, 1H), 6.17 (s, 1H), 3.84 (s, 3H) 2.94 (d, J = 18.7

Hz, 1H), 2.76 (d, J = 18.7 Hz, 1H), 2.41 (d, J =15.8 Hz, 1H), 2.18 (d, J = 16.1 Hz, 1H), 0.63 – 0.49 (m, 4H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.2, 173.2, 159.9, 152.4, 152.4, 131.4, 130.2, 128.8, 128.3, 127.0, 123.7, 123.5, 120.1, 116.2, 115.6, 112.6, 56.3, 46.9, 38.4, 14.0, 11.4, 11.1; **HRMS** (ESI): *m/z*: calculated for $C_{22}H_{18}NaO_4^+$: $[M + Na]^+$ 369.1097, found: 369.1091; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 15.6 min, $t_R$ (minor) = 22.0 min, e.r. = 85:15; $[\alpha]^{25}_D$ = -129.2 (*c* = 1.0, $CHCl_3$).

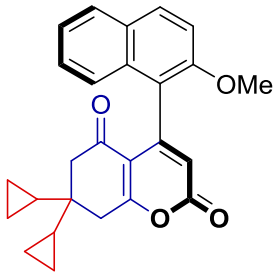



**3ca**: 69%; yellow oil; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, J = 9.0 Hz, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 7.40 – 7.31 (m 2H), 7.26 (d, J = 1.7 Hz, 1H), 6.14 (s, 1H), 3.82 (s, 3H), 2.89 (t, J = 19.5 Hz, 2H), 2.37 (dd, J = 41.6, 15.9 Hz, 2H), 1.55 – 1.42 (m, 10H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.7, 172.3, 160.4, 152.5, 152.0, 131.3, 130.2, 128.8, 128.3, 127.0, 123.6, 123.5, 120.0, 116.0, 114.8, 112.5, 56.2, 49.7, 40.3, 36.4, 36.3, 34.6, 31.6, 25.8, 22.6, 21.5, 21.4; **HRMS** (ESI): *m/z*: calculated for $C_{25}H_{25}O_4^+$: $[M + H]^+$ 389.1747, found: 389.1742; HPLC (Chiralpak IB, *i*-propanol/hexane = 15/85, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 14.5 min, $t_R$ (minor) = 16.0 min, e.r. = 88:12; $[\alpha]^{25}_D$ = -133.6 (*c* = 1.0, $CHCl_3$).

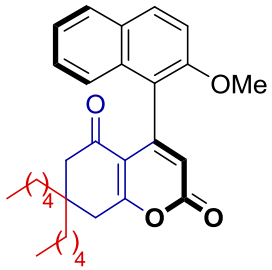



**3da**: 68%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.92 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.43 – 7.29 (m, 3H), 6.17 (s, 1H), 3.85 (s,

3H), 2.85 (dd, *J* = 22.9, 18.7 Hz, 2H), 2.38 (d. *J* = 15.8 Hz, 1H), 2.29 (d, *J* = 15.8 Hz, 1H), 1.60 – 1.45 (m, 4H), 0.92 – 0.84 (m, 6H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 193.0, 172.6, 160.4,152.5, 152.0, 131.3, 130.2, 128.9, 128.4, 127.0, 123.7, 123.6, 120.0, 116.0, 114.9, 112.5, 56.2, 47.9, 38.9, 37.2, 29.1, 28.9, 7.7, 7.6; **HRMS** (ESI): *m/z*: calculated for $C_{24}H_{25}O_4^+$: $[M + H]^+$ 377.1747, found: 377.1753; HPLC (Chiralpak ID, *i*-propanol/hexane = 15/85, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 15.9 min, $t_R$ (minor) = 19.5 min, e.r. = 90:10; $[\alpha]^{25}_D$ = -163.4 (*c* = 1.0, $CHCl_3$).

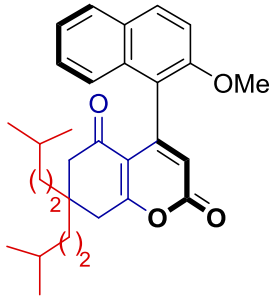



**3ea**: 72%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.29 (m, 3H), 6.16 (s, 1H), 3.85 (s, 3H), 2.76 (dd, *J* = 21.4, 19.0 Hz, 2H), 2.24 (d, *J* = 15.9 Hz, 1H), 2.15 (d, *J* = 15.9 Hz, 1H), 0.92 – 0.77 (m, 2H), 0.47 – 0.35 (m, 8H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.5, 172.6, 160.2, 152.5, 152.0, 131.3, 130.1, 128.8, 128.3, 126.9, 123.6, 123.5, 120.0, 115.9, 115.0, 112.5, 56.2, 46.0, 37.7, 35.2, 18.4, 18.4, 0.7, 0.6, 0.6, 0.5; **HRMS** (ESI): *m/z*: calculated for $C_{26}H_{25}O_4^+$: $[M + H]^+$ 401.1747, found: 401.1752; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 15.9 min, $t_R$ (minor) = 19.0 min, e.r. = 93:7; $[\alpha]^{25}_D$ = -177.2 (*c* = 1.0, $CHCl_3$).

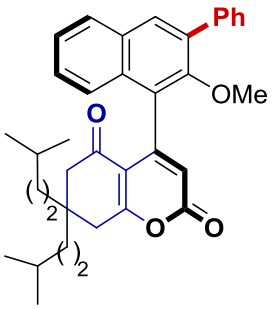



**3fa**: 71%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.0 Hz, 1H), 7.84 (d,

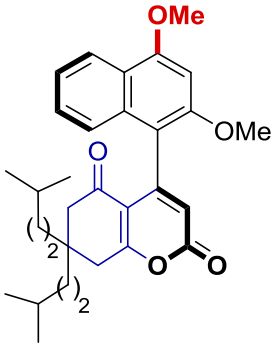
*J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.42 – 7.28 (m, 3H), 6.17 (s, 1H), 3.86 (d, *J* = 6.4 Hz, 3H), 2.86 (dd, *J* = 23.4, 22.6 Hz, 2H), 2.38 (d, *J* = 15.9 Hz, 1H), 2.29 (d, *J* = 15.9 Hz, 1H), 1.46 – 1.25 (m, 18H), 0.94 – 0.88 (m, 6H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.9, 172.7, 160.4, 152.5, 152.0, 131.4, 130.2, 128.8, 128.4, 127.0, 123.7, 123.5, 120.0, 116.0, 114.8, 112.5, 56.3, 48.7, 39.7, 37.3, 37.2, 37.0, 32.4, 32.3, 23.0, 22.9, 22.5, 22.5, 14.1, 14.0; **HRMS** (ESI): *m/z*: calculated for $C_{30}H_{37}O_4^+$: $[M + H]^+$ 461.2686, found: 461.2680; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 11.0 min, $t_R$ (minor) = 13.2 min, e.r. = 94:6; $[\alpha]^{25}_D$ = -106.8 (*c* = 1.0, $CHCl_3$).




**3ga**: 70%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.0 Hz, 1H), 7.81 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.26 (m, 3H), 6.13 (s, 1H), 3.82 (s, 3H), 2.83 (dd, *J* = 23.4, 18.6 Hz, 2H), 2.31 (dd, *J* = 33.2, 15.9 Hz, 2H), 1.50 – 1.36 (m, 6H), 1.14 – 1.06 (m, 4H), 0.91 – 0.85 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.7, 172.7, 160.3, 152.5, 152.0, 131.4, 130.1, 128.8, 128.3, 126.9, 123.6, 123.5, 120.1, 116.0, 114.7, 112.5, 56.2, 48.7, 39.7, 36.8, 34.7, 34.7, 32.1, 32.1, 28.5, 28.4, 22.5; **HRMS** (ESI): *m/z*: calculated for $C_{30}H_{37}O_4^+$: $[M + H]^+$ 461.2686, found: 461.2691; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 9.9 min, $t_R$ (minor) = 14.7 min, e.r. = 95:5; $[\alpha]^{25}_D$ = -189.8 (*c* = 1.0, $CHCl_3$).

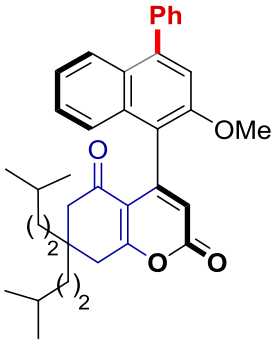



**3gd**: 57%; yellow oil; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.84 (m, 2H), 7.68-7.66 (m, 2H), 7.47 – 7.36 (m, 6H), 6.23 (s, 1H), 3.21 (s, 3H), 2.86 (s, 2H) 3.34 (dd, J = 24.0, 16.0 Hz, 2H), 1.47 – 1.39 (m, 6H), 1.14 – 1.08 (m, 4H), 0.90 – 0.85 (m, 12H) **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.8, 173.0, 160.1, 152.2, 151.3, 138.3, 134.2, 130.9, 130.5, 129.1, 128.4, 128.4, 127.4, 126.6, 125.1, 123.8, 115.7, 114.7, 60.4, 48.6, 39.9, 36.9, 34.8, 34.7, 32.1, 28.5, 28.4, 22.6, 22.5, 22.5; **HRMS** (ESI): *m/z*: calculated for $C_{36}H_{41}O_4^+$: $[M + H]^+$ 537.2999, found: 537.2993; HPLC (Chiralpak IA, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 300 nm): $t_R$ (major) = 5.3 min, $t_R$ (minor) = 6.2 min, e.r. = 90:10; $[\alpha]^{25}_D$ = -173.2 (*c* = 1.0, $CHCl_3$).

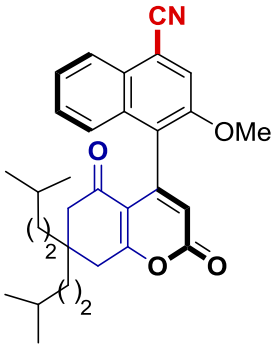



**3ge**: 76%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.26 (m, 3H), 6.64 (s, 1H), 6.14 (s, 1H), 4.04 (s, 3H), 3.82 (s, 3H), 2.82 (dd, *J* = 23.2, 18.8 Hz, 2H), 2.31 (dd, *J* = 31.8, 15.8 Hz, 2H), 1.51 – 1.35 (m, 6H), 1.13 – 1.10 (m, 4H), 0.90 – 0.85 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 193.0, 172.5, 160.5, 157.4, 153.1, 152.2, 132.0, 127.6, 123.2, 123.0, 122.5, 121.1, 116.3, 115.0, 112.4, 92.6, 56.3, 55.6, 48.9, 39.8, 36.8, 34.7, 34.7, 32.2, 32.1, 28.5, 28.5, 22.6, 22.6; **HRMS** (ESI): *m/z*: calculated for $C_{31}H_{39}O_5^+$: $[M + H]^+$ 491.2792, found: 491.2798; HPLC (Chiralpak IB,

*i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 6.3 min, $t_R$ (minor) = 8.8 min, e.r. = 93:7; $[\alpha]^{25}_D$ = -165.4 (*c* = 1.0, $CHCl_3$).

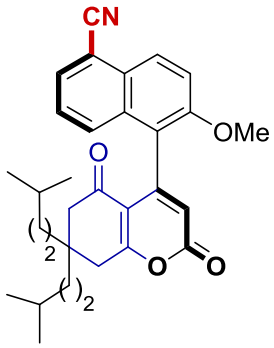



**3gf**: 74%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 1H), 7.58 – 7.48 (m, 6H), 7.41 – 7.38 (m, 1H), 7.31 – 7.25 (m, 2H), 6.22 (s, 1H), 3.86 (s, 3H), 2.89 (dd, *J* = 23.7, 18.6 Hz, 2H), 2.44 – 2,32 (m, 2H), 1.54 – 1.42 (m, 6H), 1.20 – 1.11 (m, 4H), 0.95 – 0.90 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 193.0, 172.8, 160.4, 152.1, 151.8, 142.6, 140.5, 132.0, 130.1, 128.3, 127.6, 127.2, 126.8, 126.6, 123.9, 123.7, 119.6, 116.2, 114.9, 113.8, 56.3, 48.8, 39.8, 36.9, 34.8, 34.8, 32.2, 32.2, 28.6, 28.5, 22.6; **HRMS** (ESI): *m/z*: calculated for $C_{36}H_{41}O_4^+$: $[M + H]^+$ 537.2999, found: 537.2991; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 5.4 min, $t_R$ (minor) = 4.9 min, e.r. = 95:5; $[\alpha]^{25}_D$ = -173.9 (*c* = 1.0, $CHCl_3$).



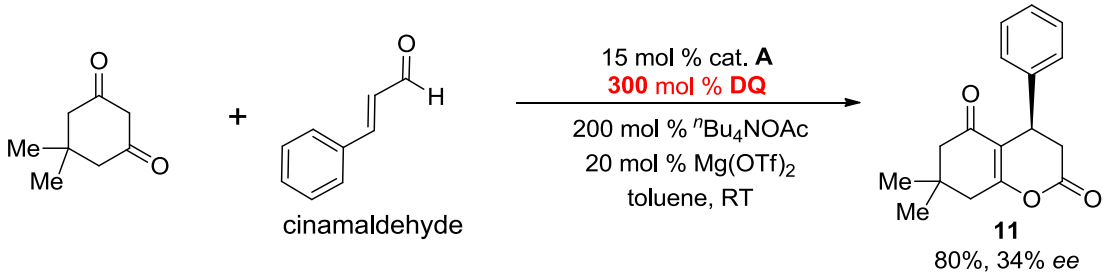

**3gg**: 60%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.2 Hz, 1H), 7.69 (s, 1H), 7.60 – 7.50 (m, 3H), 6.10 (s, 1H), 3.88 (s, 3H), 2.87 (dd, *J* = 21.8, 18.9 Hz, 2H), 2.39 – 2.27 (m, 2H), 1.52 – 1.38 (m, 6H), 1.18 – 1.04 (m, 4H), 0.93 – 0.87 (m, 12H);

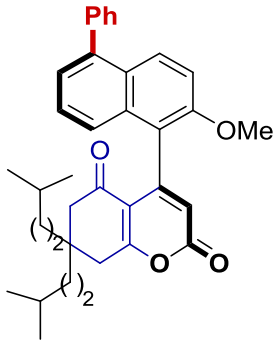
**$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.8, 173.5, 160.0, 151.5, 150.1, 131.3, 128.3, 128.3, 126.3, 126.3, 125.6, 124.3, 118.2, 117.5, 115.7, 114.1, 111.4, 56.5, 48.4, 39.7, 36.9, 34.8, 34.6, 32.1, 32.1, 28.5, 28.4, 22.5, 22.4; **HRMS** (ESI): *m/z*: calculated for $C_{31}H_{36}NO_4^+$: $[M + H]^+$ 486.2639, found: 486.2634; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 365 nm): $t_R$ (major) = 8.6 min, $t_R$ (minor) = 7.0 min, e.r. = 93:7; $[\alpha]^{25}_D$ = -145.8 (*c* = 1.0, $CHCl_3$).



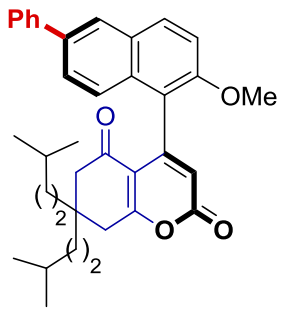

**3gh**: 70%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 8.34 (d, *J* = 9.2 Hz, 1H), 7.78 (d, *J* = 7.0 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.50 (d, *J* = 9.2 Hz, 1H), 7.42 (dd, *J* = 8.6, 7.2 Hz, 1H), 6.10 (s, 1H), 3.89 (s, 3H), 2.86 (dd, *J* = 26.4, 18.7 Hz, 2H), 2.34 (dd, *J* = 37.2, 16.0 Hz, 2H), 1.54 – 1.37 (m, 6H), 1.17 – 1.07 (m, 4H), 0.93 – 0.88 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.9, 173.3, 159.9, 153.7, 150.6, 131.2, 130.3, 128.8, 127.3, 125.8, 121.0, 117.8, 116.1, 114.8, 114.3, 110.6, 56.3, 48.6, 39.7, 36.8, 34.8, 34.6, 32.1, 32.1, 28.5, 28.4, 22.5, 22.4; **HRMS** (ESI): *m/z*: calculated for $C_{31}H_{36}NO_4^+$: $[M + H]^+$ 486.2639, found: 486.2644; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 19.1 min, $t_R$ (minor) = 17.5 min, e.r. = 95.5:4.5; $[\alpha]^{25}_D$ = -198.6 (*c* = 1.0, $CHCl_3$).

**Additional experiment:**



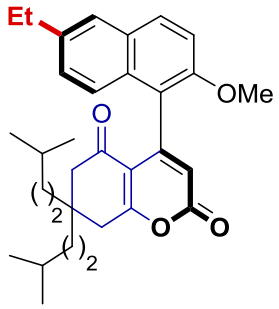



**3gi**: 71%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.4 Hz, 1H), 7.53 – 7.41 (m, 7H), 7.30 (d, *J* = 1.16 Hz, 1H), 7.23 (d, *J* = 9.4 Hz 1H), 6.20 (s, 1H), 3.83 (s, 3H), 2.89 (dd, *J* = 22.5, 18.6 Hz, 2H), 2.37 (dd, *J* = 30.4, 15.9 Hz, 2H), 1.54 – 1.41 (m, 6H), 1.19 – 1.13 (m, 4H), 0.95 – 0.90 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.9, 172.8, 160.3, 152.4, 152.3, 140.8, 140.7, 131.8, 130.1, 128.4, 128.2, 127.2, 127.0, 126.5, 124.8, 123.1, 120.2, 116.0, 114.8, 112.4, 56.2, 48.7, 39.8, 36.8, 34.7, 34.7, 32.1, 28.5, 28.4, 22.5; **HRMS** (ESI): *m/z*: calculated for $C_{36}H_{41}O_4^+$: $[M + H]^+$ 537.2999, found: 537.2993; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 300 nm): $t_R$ (major) = 6.4 min, $t_R$ (minor) = 5.7 min, e.r. = 93:7; $[\alpha]^{25}_D$ = -167.4 (*c* = 1.0, $CHCl_3$).

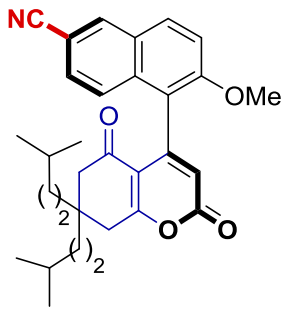



**3gj**: 68%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 8.01 (s, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.67 – 7.53 (m, 3H), 7.53 – 7.44 (m, 3H), 7.37 – 7.29 (m, 2H), 6.16 (s, 1H), 3.83 (s, 3H), 2.84 (dd, *J* = 23.1, 18.9 Hz, 2H), 2.32 (dd, *J* = 33.5, 15.8 Hz, 2H), 1.50 – 1.37 (m, 6H), 1.11 (d, *J* = 6.4 Hz, 4H), 0.90 – 0.85 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.8, 172.8, 160.3, 152.6, 151.9, 140.9, 136.4, 130.5, 130.4, 129.0, 128.8, 127.2, 127.1, 126.7, 126.2, 124.0, 120.0, 115.9, 114.7, 112.9, 56.2, 48.7, 39.7, 36.8, 34.7,

34.6, 32.1, 32.1, 28.5, 28.4, 22.5; **HRMS** (ESI): *m/z*: calculated for $C_{34}H_{37}O_4^+$: [M + H]$^+$ 537.2999, found: 537.2992; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 7.1 min, $t_R$ (minor) = 8.9 min, e.r. = 96:4; $[\alpha]^{25}_D$ = -178.6 (*c* = 1.0, $CHCl_3$).

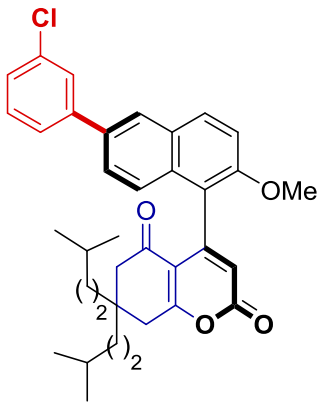



**3gk**: 66%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.83 (d, *J* = 9.0 Hz, 1H), 7.59 (s, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 7.24 (d, *J* = 9.0 Hz, 2H), 6.13 (s, 1H), 3.80 (s, 3H), 2.88 – 2.73 (m, 4H), 2.31 (dd, *J* = 34.3, 15.8 Hz, 2H), 1.50 – 1.36 (m, 6H), 1.31 – 1.27 (m, 3H), 1.27 -1.11 (m, 4H), 0.90 – 0.85 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.7, 172.6, 160.4, 152.2, 152.0, 139.4, 129.8, 129.5, 129.1, 128.2, 125.9, 123.4, 120.0, 115.9, 114.8, 112.6, 56.3, 48.7, 39.7, 36.8, 34.7, 34.7, 32.1, 32.1, 28.6, 28.5, 28.4, 22.5, 22.5, 15.4; **HRMS** (ESI): *m/z*: calculated for $C_{32}H_{41}O_4^+$: [M + H]$^+$ 489.2999, found: 489.2992; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 6.1 min, $t_R$ (minor) = 8.1 min, e.r. = 95:5; $[\alpha]^{25}_D$ = -165.9 (*c* = 1.0, $CHCl_3$).

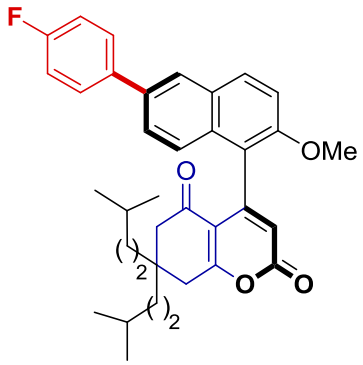



**3gl**: 72%; white solid; **$^1$H NMR** (400MHz, $CDCl_3$) δ 8.20 (s, 1H), 7.96 (d, *J* = 9.1 Hz, 1H), 7.49 (dd, *J* = 13.4, 8.8 Hz, 2H), 7.39 (d, *J* = 9.1 Hz, 1H), 6.08 (s, 1H), 3.87 (s,

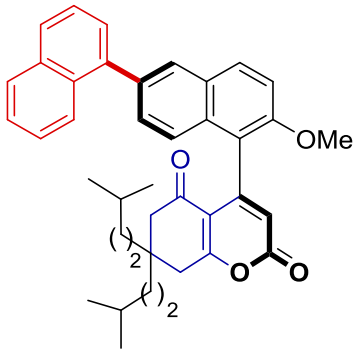
3H), 2.85 (dd, *J* = 22.6, 18.9 Hz, 2H), 2.31 (dd, *J* = 32.4, 16.0 Hz, 2H), 1.51 – 1.36 (m, 6H), 1.15 – 1.08 (m, 4H), 0.91 – 0.85 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 193.0, 173.4, 159.9, 155.0, 150.6, 134.7, 132.9, 130.9, 127.4, 127.3, 124.8, 120.6, 119.3, 116.1, 114.3, 114.0, 107.0, 56.2, 48.6, 39.8, 36.9, 34.8, 34.6, 32.1, 32.1, 28.5, 28.4, 22.6, 22.5; **HRMS** (ESI): *m/z*: calculated for $C_{31}H_{36}NO_4^+$: $[M + H]^+$ 486.2639, found: 486.2634; HPLC (Chiralpak IA, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 8.1 min, $t_R$ (minor) = 11.7 min, e.r. = 96.5:3.5; $[\alpha]^{25}_D$ = -187.0 (*c* = 1.0, $CHCl_3$).




**3gm**: 70%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.99 – 7.95 (m, 2H), 7.65 (s, 1H), 7.94 (d, *J* = 9.0 Hz, 1H), 7.59 – 7.51 (m, 3H), 7.40 – 7.31 (m, 3H), 6.16 (s, 1H), 3.84 (s, 3H), 2.85 (dd, *J* = 22.8, 18.8 Hz, 2H), 2.32 (dd, *J* = 33.8, 15.8 Hz, 2H), 1.50 – 1.37 (m, 6H), 1.12 – 1.11 (m, 4H), 0.91 – 0.86 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.9, 172.9, 160.3, 152.9, 151.8, 142.8, 135.0, 134.7, 130.9, 130.5, 130.1, 128.9, 127.3, 127.2, 126.5, 126.3, 125.4, 124.3, 120.1, 116.0, 114.7, 113.1, 56.3, 48.7, 39.8, 36.9, 34.8, 34.7, 32.2, 32.1, 28.5, 28.5, 22.6; **HRMS** (ESI): *m/z*: calculated for $C_{36}H_{39}ClNaO_4^+$: $[M + Na]^+$ 593.2429, found: 593.2424; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 7.6 min, $t_R$ (minor) = 9.0 min, e.r. = 95:5; $[\alpha]^{25}_D$ = -173.6 (*c* = 1.0, $CHCl_3$).

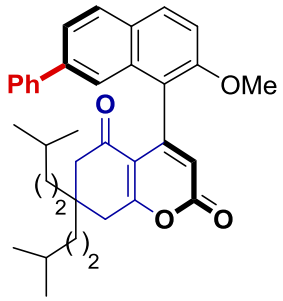



**3gn**: 71%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 2H), 7.63 – 7.56 (m, 3H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 7.14 (t, *J* = 8.6 Hz, 2H), 6.16 (s, 1H), 3.83 (s, 3H), 2.85 (dd, *J* = 23.7, 18.8 Hz, 2H), 2.32 (dd, *J* = 34.6, 15.8 Hz, 2H), 1.50 – 1.37 (m, 6H), 1.14 – 1.07 (m, 4H), 0.91 – 0.85 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.9, 172.8, 162.4 (d, *J* = 244.7 Hz), 160.3, 152.7, 151.8, 137.0 (d, *J* = 3.1 Hz), 135.4, 130.5, 130.3, 128.9, 128.7 (d, *J* = 7.9 Hz), 126.5, 126.0, 134.2, 120.0, 116.0, 115.7 (d, *J* = 21.3 Hz), 114.7, 113.1, 76.7, 56.2, 48.7, 39.7, 36.8, 34.7, 34.7, 32.1, 32.1, 28.5, 28.4, 22.5; **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -115.8; **HRMS** (ESI): *m/z*: calculated for $C_{36}H_{39}FNaO_4^+$: $[M + Na]^+$ 577.2725, found: 577.2730; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 7.5 min, $t_R$ (minor) = 10.8 min, e.r. = 95:5; $[\alpha]^{25}_D$ = -165.4 (*c* = 1.0, $CHCl_3$).

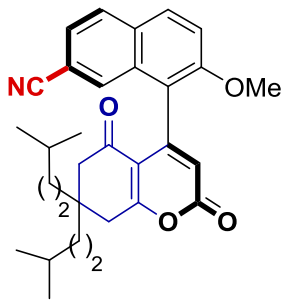



**3go**: 67%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 5H), 7.56 – 7.48 (m, 5H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 9.0 Hz, 1H), 6.22 (s, 1H), 3.86 (s, 3H), 2.85 (dd, *J* = 25.2, 18.8 Hz, 2H), 2.36 (dd, *J* = 32,3, 15.9 Hz, 2H), 1.51 – 1.38 (m, 6H), 1.15 – 1.07 (m, 4H), 0.92 – 0.85 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 193.0,

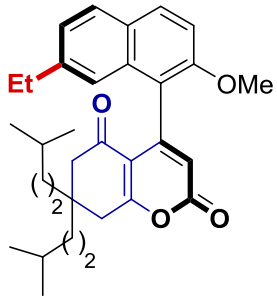
172.9, 160.4, 152.8, 152.0, 140.0, 136.1, 133.9, 131.8, 130.6, 130.4, 129.6, 129.2, 128.9, 128.3, 127.7, 127.2, 126.2, 126.1, 125.8, 125.5, 123.4, 120.2, 116.1, 114.8, 113.0, 56.4, 48.8, 39.8, 36.9, 34.8, 34.7, 32.2, 32.2, 28.6, 28.5, 22.6, 22.6; **HRMS** (ESI): *m/z*: calculated for $C_{40}H_{43}O_4^+$: $[M + H]^+$ 587.3156, found: 587.3151; HPLC (Chiralpak IC, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 9.4 min, $t_R$ (minor) = 11.4 min, e.r. = 94:6; $[\alpha]^{25}_D$ = -179.4 (*c* = 1.0, $CHCl_3$).



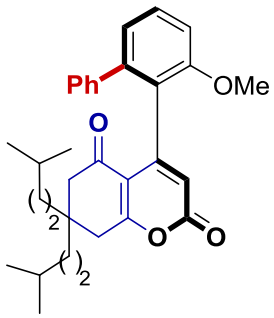

**3gp**: 72%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.90 (dd, *J* = 14.2, 9.0 Hz, 2H), 7.57 (t, 7.1 Hz, 4H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.36 – 7.26 (m, 2H), 6.19 (s, 1H), 3.83 (s, 3H), 2.83 (dd, *J* = 21.6, 19.0 Hz, 2H), 2.31 (dd, *J* = 37.5, 15.8 Hz, 2H), 1.51 – 1.33 (m, 6H), 1.13 – 1.03 (m, 4H), 0.91 – 0.77 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.9, 172.9, 160.4, 153.0, 152.2, 141.4, 139.9, 131.6, 129.9, 128.9, 128.0, 127.6, 127.4, 123.7, 121.6, 120.3, 116.0, 114.7, 112.5, 56.3, 48.8, 39.8, 36.8, 34.8, 32.2, 32.1, 28.5, 28.4, 22.6, 22.5; **HRMS** (ESI): *m/z*: calculated for $C_{34}H_{37}O_4^+$: $[M + H]^+$ 537.2999, found: 537.2993; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 8.0 min, $t_R$ (minor) = 10.2 min, e.r. = 96:4; $[\alpha]^{25}_D$ = -198.6 (*c* = 1.0, $CHCl_3$).



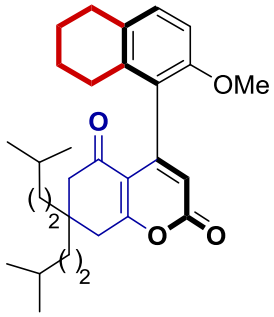
**3gq**: 60%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 7.95 (d, *J* = 9.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.45 (t, *J* = 10.5 Hz, 2H), 6.08 (s, 1H), 3.85 (s, 3H), 2.87 (s, 2H), 2.32 (dd, *J* = 24.5, 15.9 Hz, 2H), 1.51 – 1.37 (m, 6H), 1.13 – 1.09 (m, 4H), 0.90 – 0.86 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 193.1, 173.5, 159.7, 153.8, 150.3, 130.5, 130.2, 129.9, 129.7, 129.6, 124.0, 120.8, 119.2, 116.1, 115.4, 114.2, 110.5, 56.3, 48.6, 39.8, 36.9, 35.0, 34.4, 32.1, 32.1, 28.5, 28.4, 22.6, 22.5; **HRMS** (ESI): *m/z*: calculated for $C_{31}H_{36}NO_4^+$: $[M + H]^+$ 486.2639, found: 486.2644; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 9.4 min, $t_R$ (minor) = 10.8 min, e.r. = 93:7; $[\alpha]^{25}_D$ = -143.7 (*c* = 1.0, $CHCl_3$).




**3gr**: 71%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.28 (s, H), 7.23 (d, *J* = 9.8 Hz, 1H), 6.16 (s, 1H), 3.83 (s, 3H), 2.87 (t, *J* = 19.5 Hz, 2H), 2.71 (dd, *J* = 14.8, 7.3 Hz, 2H), 2.34 (dd, *J* = 36.5, 15.8 Hz, 2H), 1.52 – 1.38 (m, 6H), 1.25 (t, *J* = 7.7 Hz, 3H), 1.14 – 1.13 (m, 4H), 0.93 – 0.86 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.8, 172.6, 160.5, 152.6, 152.3, 143.0, 131.6, 129.8, 128.3, 127.4, 124.8, 121.3, 119.6, 115.9, 114.8, 111.6, 56.2, 48.8, 39.7, 36.8, 34.7, 34.6, 32.1, 32.1, 29.4, 28.5, 28.4, 22.5, 15.6; **HRMS** (ESI): *m/z*: calculated for $C_{32}H_{41}O_4^+$: $[M + H]^+$ 489.2999, found: 489.2993; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 6.8 min, $t_R$ (minor) = 8.8 min, e.r. = 97:3; $[\alpha]^{25}_D$ = -189.6 (*c* = 1.0, $CHCl_3$).

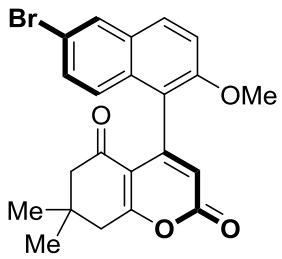



**3gs**: 60%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.9 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.12 – 7.10 (m, 2H), 6.99 (d, *J* = 37.8 Hz, 1H), 6.88 (d, *J* = 8.3 Hz, 1H), 5.70 (s, 1H), 3.72 (s, 3H), 2.76 (d, *J* = 18.5 Hz, 1H), 2.64 (d, *J* = 18.5 Hz, 1H), 2.39 (d, *J* = 15.5 Hz, 1H), 2.25 (d, *J* = 15.5 Hz, 1H), 1.49 – 1.26 (m, 6H), 1.15 – 1.05 (m, 4H), 0.89 (d, *J* = 6.6 Hz, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 193.5, 171.4, 160.2, 155.6, 152.8, 140.7, 140.6, 129.1, 128.0, 127.1, 125.6, 122.5, 115.6, 115.2, 109.1, 55.7, 48.7, 39.5, 37.0, 35.0, 34.1, 32.1, 32.0, 28.5, 28.5, 22.6, 22.6, 22.5, 22.5; **HRMS** (ESI): *m/z*: calculated for $C_{32}H_{39}O_4^+$: $[M + H]^+$ 487.2843, found: 487.2844; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 7.5 min, $t_R$ (minor) = 7.1 min, e.r. = 96:4; $[\alpha]^{25}_D$ = -176.8 (*c* = 1.0, $CHCl_3$).

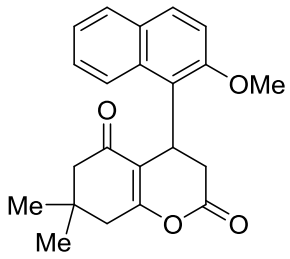



**3gt**: 61%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.4Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 5.97 (s, 1H), 3.64 (s, 3H), 2.84 – 2.72 (m, 4H), 2.54 (d, *J* = 16.9 Hz, 1H), 2.33 (dd, *J* = 24.2, 15.9 Hz, 2H), 2.18 (d, *J* = 16.4 Hz, 1H), 1.71 – 1.63 (m, 4H), 1.48 – 1.36 (m, 6H), 1.11 – 1.10 (m, 4H), 0.89 – 0.86 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.9, 172.6, 160.5, 153.4, 153.2, 133.8, 129.6, 129.4, 125.8, 114.7, 114.2, 108.1, 55.6, 48.7, 39.7, 36.8, 34.8, 34.5, 32.1, 29.0, 28.5, 28.4, 27.6, 22.9, 22.5, 22.5, 22.4; **HRMS** (ESI): *m/z*: calculated for $C_{30}H_{41}O_4^+$: $[M + H]^+$ 465.2999, found:

465.2993; HPLC (Chiralpak IB, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 6.8 min, $t_R$ (minor) = 7.3 min, e.r = 92:8; $[\alpha]^{25}_D$ = -143.2 (*c* = 1.0, $CHCl_3$).

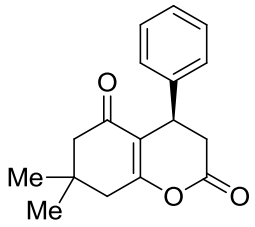



**3au**: 68%; white solid; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.4 Hz, 1H), 7.81 (d, *J* = 9.1 Hz, 1H), 7.44 (dd, *J* = 9.0, 1.8 Hz, 1H), 7.35 – 7.26 (m, 2H), 6.11 (s, 1H), 3.82 (s, 3H), 2.84 (s, 2H), 2.30 (dd, *J* = 36.1, 15.9 Hz, 2H), 1.17 (s, 3H), 1.13 (s, 1H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 192.7, 172.8, 160.0, 152.7, 151.4, 130.2, 129.9, 129.8, 129.2, 125.3, 120.3, 117.4, 116.1, 114.4, 113.5, 56.2, 51.6, 42.6, 31.8, 28.2, 28.0; **HRMS** (ESI): *m/z*: calculated for $C_{20}H_{20}BrO_4^+$: $[M + H]^+$ 427.0539, 429.0519, found: 427.0534, 429.0513; HPLC (Chiralpak IB, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 10.4 min, $t_R$ (minor) = 12.8 min, e.r. = 91:9; $[\alpha]^{25}_D$ = -193.2 (*c* = 1.0, $CHCl_3$).

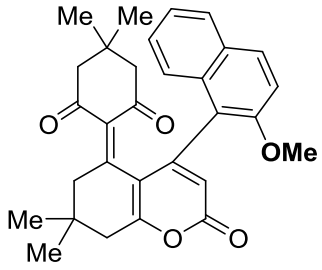



**4aa**: 74%; White solid; **$^1$H NMR** (400MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.7 Hz, 1H), 7.75 (d, *J* = 8.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 1H), 7.18 (d, *J* = 9.0 Hz, 1H), 5.12 (d, *J* = 10.1 Hz, 1H), 3.81 (s, 3H), 3.03 (dd, *J* = 16.9, 10.3 Hz, 1H), 2.69 (d, *J* = 16.9 Hz, 1H), 2.49 (dd, *J* = 28.6, 17.8 Hz, 2H), 2.17 (dd, *J* = 21.7, 16.4 Hz, 2H), 1.11 (s, 3H), 0.98 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 197.0, 165.6, 165.0, 155.0, 132.2, 129.5, 129.2, 128.4, 126.7, 123.6, 123.4, 122.5, 112.7, 112.0,

54.4, 50.7, 41.5, 33.9, 32.3, 28.4, 27.7, 26.8; **HRMS** (ESI): *m/z*: calculated for $C_{22}H_{23}O_4^+$: $[M + H]^+$ 351.1591, found: 351.1596; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 190 nm): $t_R$ (major) = 7.7 min, $t_R$ (minor) = 6.1 min, e.r. = 67:33; $[\alpha]^{25}_D$ = -53.2 (*c* = 1.0, $CHCl_3$).

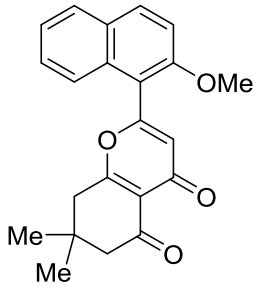



**11**: 80%; white solid; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.20 (m, 3H), 7.15 (d, *J* = 7.2 Hz, 2H), 4.30 (t, *J* = 4.6 Hz, 1H), 2.94 (dd, *J* = 21.8, 16.2 Hz, 1H), 2.93 (s, 1H) 2.54 (s, 2H), 2.32 (s, 2H) 1.15 (s, 3H), 1.10 (s, 3H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 196.1, 166.0, 165.7, 140.5, 129.1, 127.5, 126.5, 116.1, 50.6, 41.0, 36.3, 33.8, 32.5, 28.5, 28.1; **HRMS** (ESI): m/z: calculated for $C_{17}H_{19}O_3^+$: $[M + H]^+$ 271.1329, found: 271.1327; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 7.8 min, $t_R$ (minor) = 5.2 min, e.r. = 67:33; $[\alpha]^{25}_D$ = -110.2 (c = 1.0, $CHCl_3$).

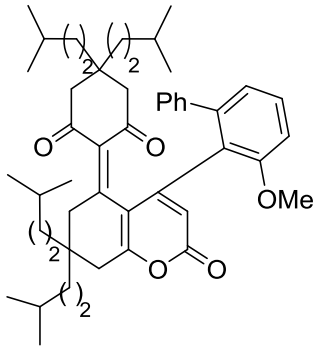



**5aa**: Yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.90 (d, *J* = 9.1 Hz, 1H), 7.80 (d, *J* = 7.3 Hz, 1H), 7.41 – 7.26 (m, 4H), 5.79 (s, 1H), 3.83 (s, 3H), 2.96 (s, 2H), 2.38 (dd, *J* = 18.3, 16.3 Hz, 2H), 2.04 (d, *J* = 7.6 Hz, 2H), 1.58 (dd, *J* = 22.9, 18.0 Hz, 2H), 1.20 (d, *J* = 3.5 Hz, 6H), 0.81 (s, 6H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 199.2, 191.9, 169.6, 166.9, 154.7, 154.2, 140.3, 132.5, 130.4, 128.7, 128.1, 128.1, 126.7, 123.8, 123.5, 121.5, 114.8, 113.2, 112.9, 56.4, 52.6, 50.4, 41.1, 37.8, 34.8, 32.4, 28.5, 28.3, 27.8,

27.7; **HRMS** (ESI): *m/z*: calculated for $C_{30}H_{31}O_5^+$: $[M + H]^+$ 471.2166, found: 471.2161.

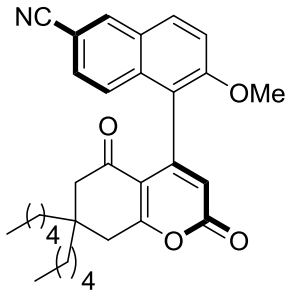



**6aa**: Yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.93 (d, *J* = 9.1 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.51 - 7.47 (m, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 9.1 Hz, 1H), 3.97 (s, 3H), 2.62 (s, 2H), 2.38 (s, 2H), 1.14 (s, 6H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 191.7, 190.5, 179.3, 156.2, 147.2, 132.1, 131.8, 128.7, 128.4, 127.2, 124.3, 124.0, 114.8, 113.3, 112.6, 110.6, 56.2, 51.8, 39.0, 33.8, 28.4; **HRMS** (ESI): *m/z*: calculated for $C_{22}H_{21}O_4^+$: $[M + H]^+$ 349.1434, found: 349.1439.

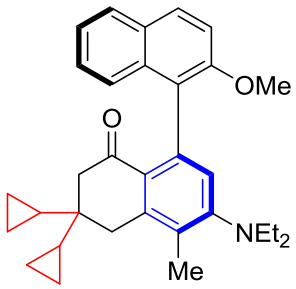



**7**: 20%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 7.93 (t, *J* = 8.0 Hz, 1H), 7.19 - 7.09 (m, 5H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 5.93 (s, 1H), 3.76 (s, 3H), 2.80 (s, 2H), 2.39 (d, *J* = 16.1 Hz, 1H), 2.30 (d, *J* = 16.1 Hz, 1H), 2.25 (s, 2H), 2.07 (s, 2H), 2.48 – 2.10 (m, 20H), 0.96 – 0.88 (m, 24H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 199.6, 192.3, 169.0, 167.1, 156.7, 154.7, 143.1, 141.0, 139.5, 129.6, 129.4, 129.1, 127.6, 127.0, 122.1, 121.9, 118.3, 115.5, 109.5, 55.9, 49.6, 47.7, 40.1, 38.8, 37.8, 35.5, 34.5, 34.4, 33.7, 32.4, 32.3, 32.2, 29.7, 28.5, 22.7, 22.6, 22.6; **HRMS** (ESI): *m/z*: calculated for $C_{48}H_{65}O_5^+$: $[M + H]^+$ 721.4827, found: 721.4821; HPLC (Chiralpak IC,

*i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 6.7 min, $t_R$ (minor) = 4.6 min, e.r. = 59:41; $[\alpha]^{25}_D$ = -11.2 (*c* = 1.0, $CHCl_3$).

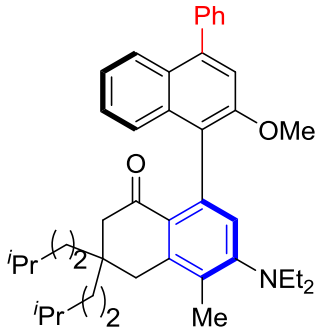



**8**: 71%; yellow oil; **$^1$H NMR** (400MHz, $CDCl_3$) δ 8.22 (t, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 4.4 Hz, 1H), 7.56 – 7.40 (m, 2H), 7.41 (d, *J* = 4.4 Hz, 1H), 6.10 (s, 1H), 3.88 (s, 3H), 2.87 (dd, *J* = 22.0 Hz, 18.8 Hz, 2H), 2.33 (dd, *J* = 33.2 Hz, 16.0 Hz, 2H), 1.45 – 1.24 (m, 18H), 0.90 (dd, *J* = 14.8 Hz, 6.8 Hz, 6H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 193.1, 173.3, 159.9, 155.0, 134.6, 132.8, 130.9. 127.4, 127.3, 120.5, 119.2, 116.1, 114.3, 113.9, 106.9, 56.2, 48.6, 39.6, 37.4, 37.1, 32.3, 32.2, 22.9, 22.8, 22.5, 14.0, 13.9; **HRMS** (ESI): *m/z*: calculated for $C_{31}H_{38}NO_4^+$: $[M + H]^+$ 488.2801, found: 488.2808; HPLC (Chiralpak IA, *i*-propanol/hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 9.6 min, $t_R$ (minor) = 17.5 min, e.r. = 96:4; $[\alpha]^{25}_D$ = -17.6 (*c* = 1.0, $CHCl_3$).

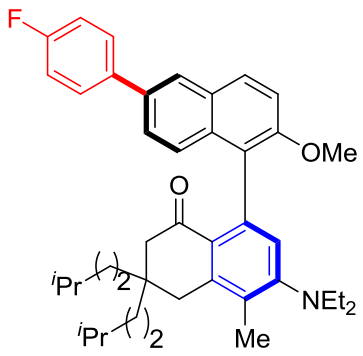



**10a**: 52%; White solid; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.32 (d, *J* = 9.0 Hz, 1H), 7.27 – 7.21 (m, 3H), 6.75 (s, 1H), 3.75 (s, 3H), 3.03 (dd, *J* = 14.1, 7.0 Hz, 4H), 2.73 (dd, *J* = 21.0, 17.1 Hz, 2H), 2.31 (s, 3H), 2.23 (d, *J* = 15.1 Hz, 1H), 2.12 (d, *J* = 15.2 Hz, 1H), 1.02 (t, *J* = 7.1 Hz, 6H), 0.85 – 0.76 (m, 2H), 0.37 – 0.30 (m, 8H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 197.4, 153.8, 152.8, 142.7, 134.5, 133.3,

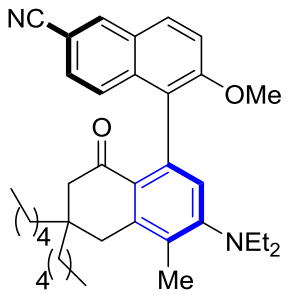
130.9, 129.1, 127.9, 127.8, 127.4, 127.3, 125.7, 124.8, 123.9, 123.1, 114.0, 56.7, 46.8, 46.4, 37.0, 35.6, 18.8, 18.5, 14.6, 12.2, 1.0, 0.6, 0.3, 0.2, 0.0; **HRMS** (ESI): m/z: calculated for $C_{32}H_{38}NO_2^+$: $[M + H]^+$ 468.2897, found: 468.2897; HPLC (Chiralpak IB, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 241 nm): $t_R$ (major) = 9.6 min, $t_R$ (minor) = 16.5 min, e.r. = 93:7; $[\alpha]^{25}_D$ = -140.2 (c = 1.0, $CHCl_3$).




**10b**: 52%; yellow oil; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 – 7.81 (m, 1H), 7.60 – 7.57 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.45 – 7.41 (m, 1H), 7.29 – 7.26 (m, 2H), 7.21 – 7.19 (m, 2H), 6.80 (s, 1H), 3.76 (s, 3H), 3.04 (dd, *J* = 14.1, 7.0 Hz, 4H), 2.81 (s, 2H), 2.35 (dd, *J* = 28.4, 16.0 Hz, 2H), 2.34 (s, 3H), 1.44 – 1.36 (m, 6H), 1.20 – 1.17 (m, 2H), 1.10 – 1.06 (m, 2H), 1.02 (t, *J* = 7.0 Hz, 6H), 0.88 – 0.84 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 197.8, 153.8, 152.1, 142.8, 141.2, 140.1, 134.7, 133.7, 131.1, 130.3, 128.2, 127.4, 127.1, 127.0, 126.1, 125.6, 125.1, 124.2, 123.2, 115.3, 56.7, 49.9, 46.5, 38.9, 37.3, 35.2, 34.5, 32.2, 28.6, 28.6, 22.7, 22.7, 22.5, 22.5, 14.6, 12.2; **HRMS** (ESI): m/z: calculated for C30H37O4$^+$: $[M + H]^+$ 604.4149, found: 604.4147; HPLC (Chiralpak IE, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 6.7 min, $t_R$ (minor) = 8.0 min, e.r. = 95:5; $[\alpha]^{25}_D$ = -122.0 (c = 1.0, $CHCl_3$).

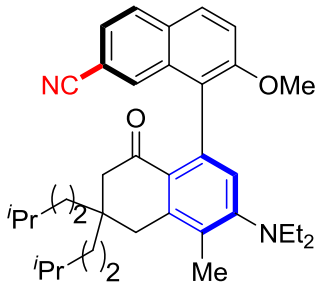



**10c**: 64%; yellow oil; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.4 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.41 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H) 7.12 (t, *J* = 8.7 Hz, 2H), 6.77 (s, 1H), 3.76 (s, 3H), 3.04 (dd, *J* = 14.2, 7.0 Hz, 4H), 2.81 (s, 2H), 2.34 (s, 3H), 2.32 (dd, *J* = 30.0, 16.0 Hz, 2H), 1.45 – 1.35 (m, 6H), 1.18 – 1.12 (m, 2H), 1.10 – 1.05 (m, 2H), 1.02 (t, *J* = 7.02 Hz, 6H), 0.87 – 0.83 (m, 12H); **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -116.47; **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 197.7, 162.2 (*J* = 245.8 Hz), 153.8, 153.0, 142.8, 137.6 (*J* = 3.1 Hz), 134.8, 134.5, 132.4, 131.2, 129.2, 128.7 (*J* = 7.9 Hz), 128.1, 127.4, 127.2, 125.8, 125.4, 125.3, 124.0, 115.5 (*J* = 21.4 Hz), 114.6, 56.7, 49.9, 46.5, 38.8, 37.3, 35.1, 34.5, 32.2, 28.6, 28.6, 22.7, 22.5, 14.6, 12.2; **HRMS** (ESI): m/z: calculated for $C_{42}H_{53}FNO_2^+$: $[M + H]^+$ 622.4055, found: 622.4059; HPLC (Chiralpak IB, *i*-propanol/hexane = 5/95, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 5.8 min, $t_R$ (minor) = 6.9 min, e.r. = 93:7; $[\alpha]^{25}_D$ = -120.0 (c = 1.0, $CHCl_3$).

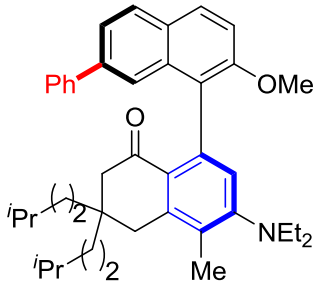



**10d**: 78%; yellow oil; **$^{1}$H NMR** (400MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.91 (d, *J* = 9.2 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 4H), 7.35 – 7.28 (m, 2H), 6.71 (s, 1H), 3.83 (s, 3H), 3.07 (dd, *J* = 14.4 Hz, 7.2 Hz, 2H), 2.85 (s, 1H), 2.42 -2.29 (m, 5H), 1.30 – 1.26 (m, 18H), 1.06

(t, *J* = 6.8 Hz, 6H), 0.89 (dd, *J* = 10.8 Hz, 6.8 Hz, 6H), ; **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 197.9, 155.4, 154.1, 143.2, 134.4, 133.3, 131.6, 128.6, 127.7, 126.1, 126.0, 123.6, 115.0, 106.2, 56.4, 49.7, 46.4,38.9, 37.7, 37.6, 32.5, 32.5, 22.5, 22.4, 14.7, 14.0, 12.2; **HRMS** (ESI): *m/z*: calculated for $C_{37}H_{49}N_2O_2^+$: $[M + H]^+$ 553.3794, found: 553.3795; HPLC (Chiralpak IA, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 4.5 min, $t_R$ (minor) = 7.6 min, e.r. = 96:4; $[\alpha]^{25}_D$ = -16.8 (*c* = 1.0, $CHCl_3$).




**10e**: 80%; yellow oil; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 3.6 Hz, 1H), 7.85 (d, *J* = 3.0 Hz, 1H), 7.61 (s, 1H), 7.45 (d, *J* = 9.0 Hz, 1H), 7.38 (dd, *J* = 8.5, 1.6 Hz, 1H), 6.66 (s, 1H), 3.77 (s, 3H), 3.05 (dd, *J* = 14.1, 7.1 Hz, 4H), 2.82 (s, 2H), 2.35 (s, 3H), 2.32 (dd, *J* = 24.7, 15.8 Hz, 2H), 1.47 – 1.35 (m, 6H), 1.16 – 1.08 (m, 4H), 1.03 (t, *J* = 7.0 Hz, 6H), 0.86 – 0.83 (m, 12H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 197.9, 154.2, 154.0, 143.3, 133.0, 132.5, 131.8, 131.4, 130.0, 129.1, 128.3, 127.9, 126.8, 123.5, 123.4, 119.7, 116.6, 109.1, 56.5, 49.8, 46.3, 39.0, 37.3, 34.8, 34.8, 32.2, 28.6, 28.5, 22.7, 22.6, 22.5, 14.7, 12.2; **HRMS** (ESI): m/z: calculated for $C_{37}H_{49}N_2O_2^+$: $[M + H]^+$ 553.3789, found: 553.3790; HPLC (Chiralpak AD-H, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 3.4 min, $t_R$ (minor) = 5.1 min, e.r. = 90.5:9.5; $[\alpha]^{25}_D$ = -60.0 (c = 1.0, $CHCl_3$).



**10f**: 48%; yellow oil; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.86 (t, *J* = 8.0 Hz, 2H), 7.52 (dd, *J* = 8.5 Hz, 1.8 Hz, 1H), 7.46 – 7.44 (m, 3H), 7.34 – 7.30 (m, 3H), 7.27 – 7.23 (m, 2H), 6.82 (s, 1H), 3.75 (s, 3H), 3.07 – 3.02 (m, 4H), 2.79 (s, 2H), 2.34 (s, 3H), 2.31 (dd, *J* = 39.9 Hz, 15.8 Hz, 2H), 1.44 – 1.24 (m, 6H), 1.17 – 1.07 (m, 2H), 1.01 (t, *J* = 7.0 Hz, 6H), 0.84 (dd, *J* = 11.0, 6.6 Hz, 6H), 0.73 (d, *J* = 6.6 Hz, 6H); **$^{13}$C NMR** (101MHz, $CDCl_3$) δ 197.7, 153.7, 153.2, 142.8, 141.9, 138.6, 134.5, 133.4, 131.3, 128.4, 128.4, 127.7, 127.5, 127.5, 127.4, 126.8, 124.1, 123.1, 123.0, 114.0, 56.6, 50.0, 46.6, 38.8, 37.3, 35.0, 34.6, 32.2, 28.6, 28.4, 22.7, 22.6, 22.5, 14.6, 12.2; **HRMS** (ESI): m/z: calculated for $C_{42}H_{54}NO_2^+$: $[M + H]^+$ 604.4149, found: 604.4147; HPLC (Chiralpak IC, *i*-propanol/hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm): $t_R$ (major) = 5.5 min, $t_R$ (minor) = 7.4 min, e.r. = 95:5; $[\alpha]^{25}_D$ = -72.7 (c = 1.0, $CHCl_3$).

## Supplementary References:


1. Shriner, R. L.; Todd; H. R. *Organic Syntheses*, **1935**, *XV*, 14-16.
2. Jin X, Xu W, Yang J, et al. Short and tandem syntheses of spiro [2.5] octane-5, 7-dione and spiro [3.5] nonane-6, 8-dione via diethyl acetonedicarboxylate. *Tetrahedron Lett*. **56**, 6287-6289 (2015).