Electronic Supplementary Material (ESI) for New Journal of Chemistry.


# Supporting Information

# Enantioselective Synthesis of Monocyclic 2,3-Dihydrofurans With Bifunctional Quinine/Squaramide Organocatalyst

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# 1. $^{1}$H and $^{13}$C NMR Spectra

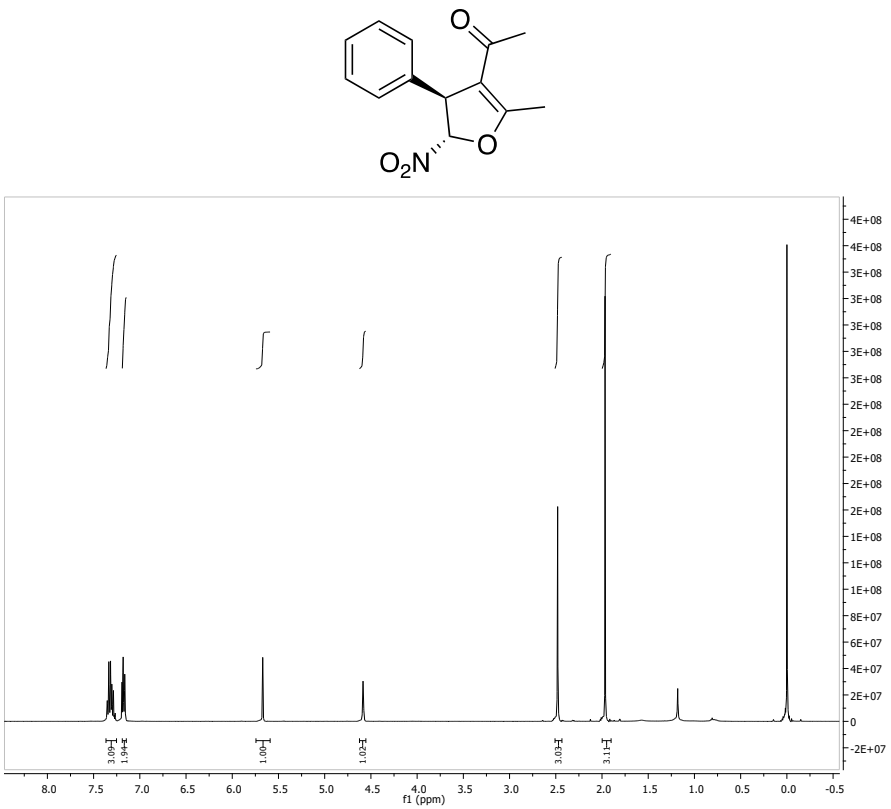



Figure 1. $^{1}$H NMR Spectrum of **3aa**

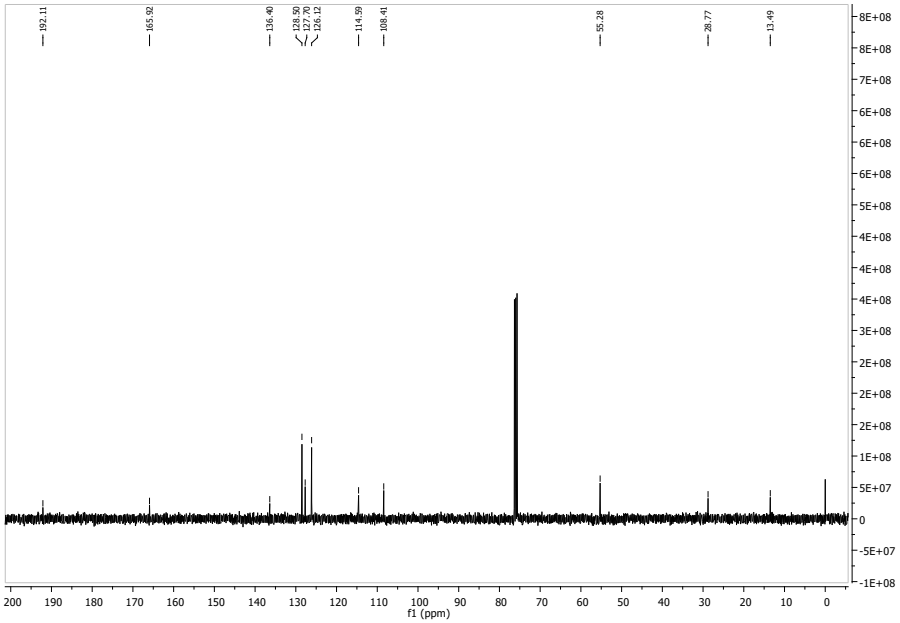
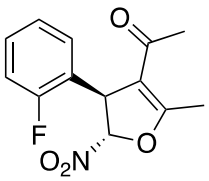



Figure 2. $^{13}$C NMR Spectrum of **3aa**



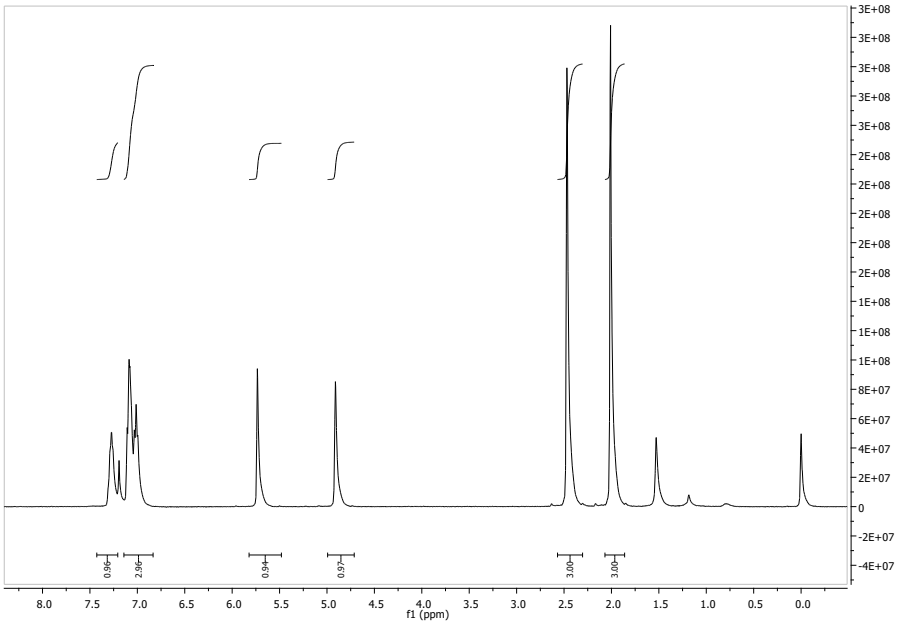




Figure 3. $^{1}$H NMR Spectrum of **3ab**

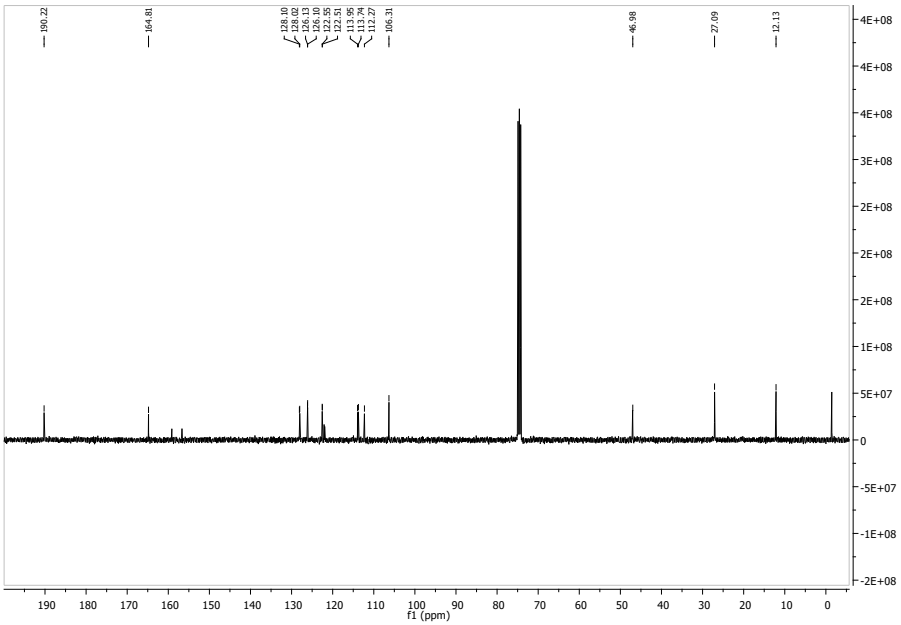
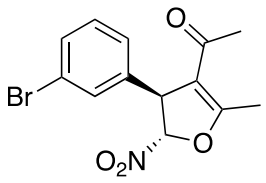



Figure 4. $^{13}$C NMR Spectrum of **3ab**



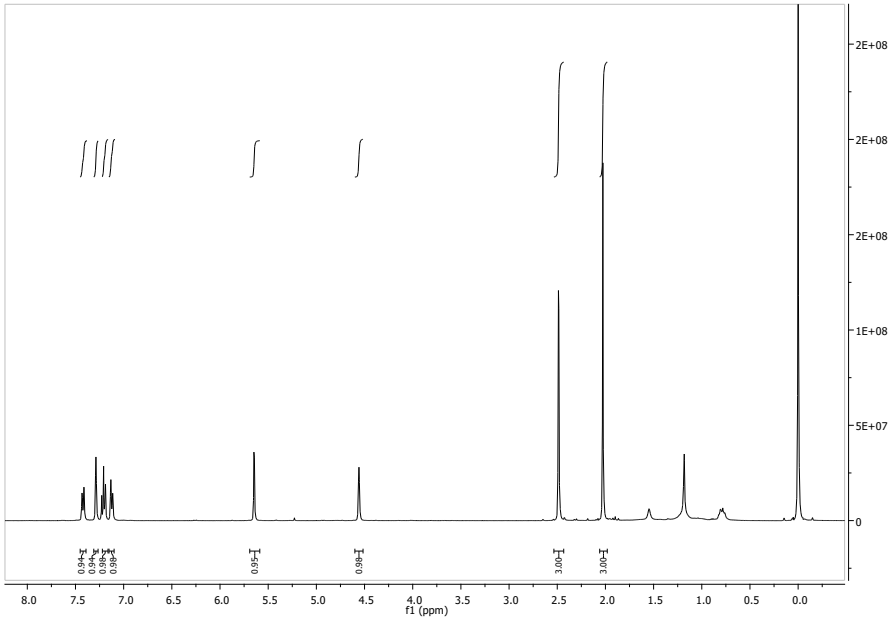




Figure 5. $^{1}$H NMR Spectrum of **3ac**

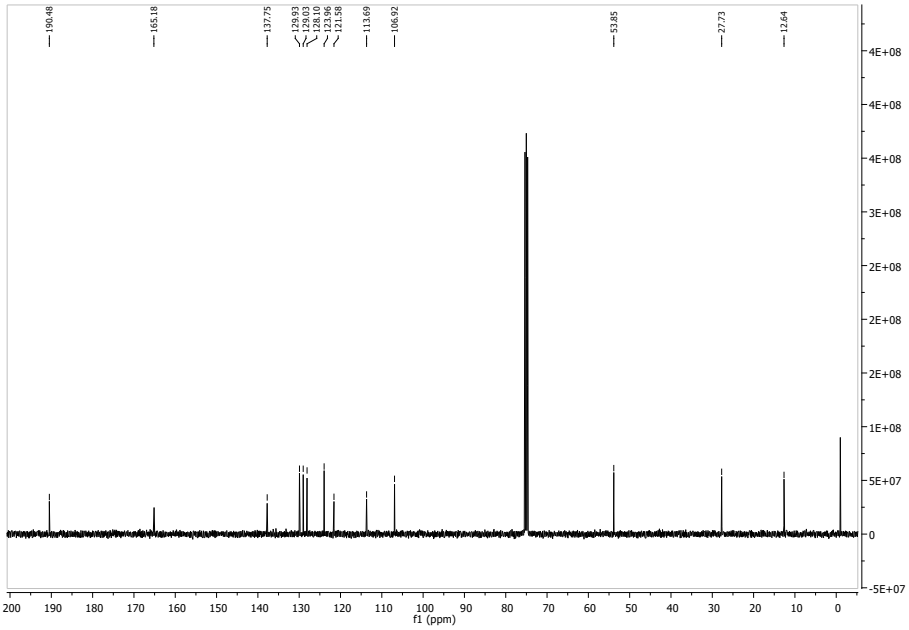
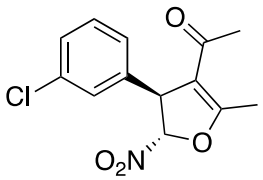



Figure 6. $^{13}$C NMR Spectrum of **3ac**



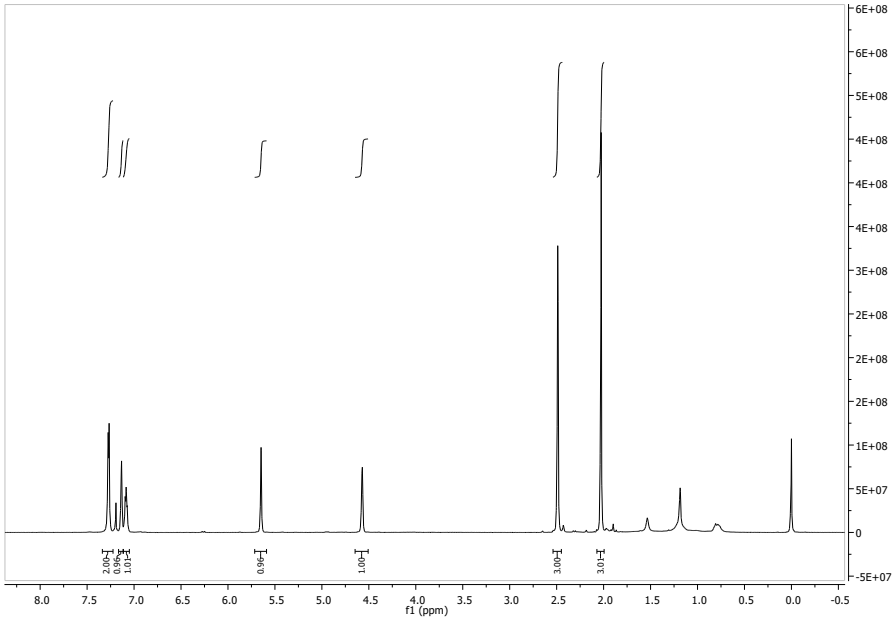




Figure 7. $^{1}$H NMR Spectrum of **3ad**

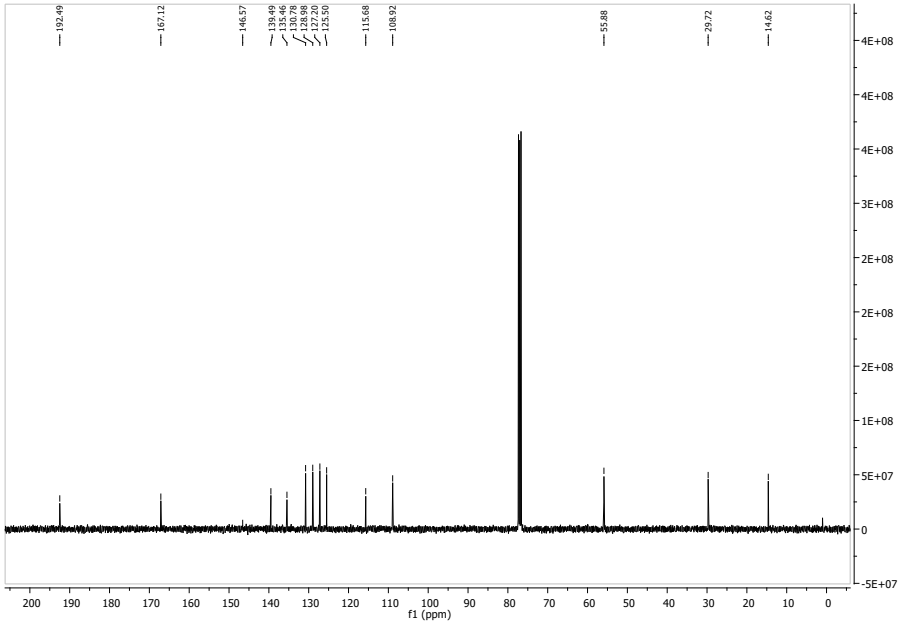
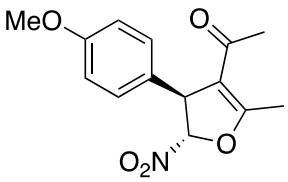



Figure 8. $^{13}$C NMR Spectrum of **3ad**



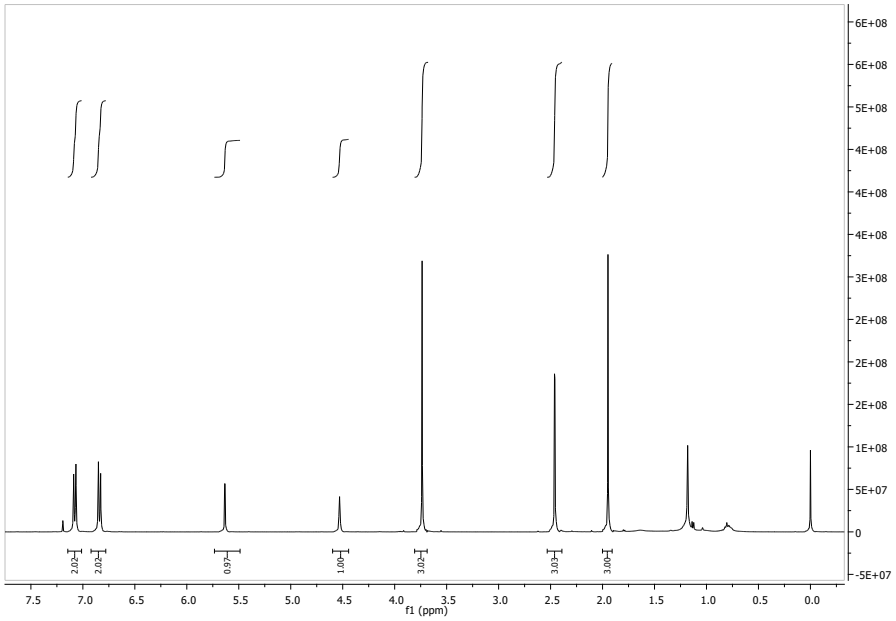




Figure 9. $^{1}$H NMR Spectrum of **3ae**

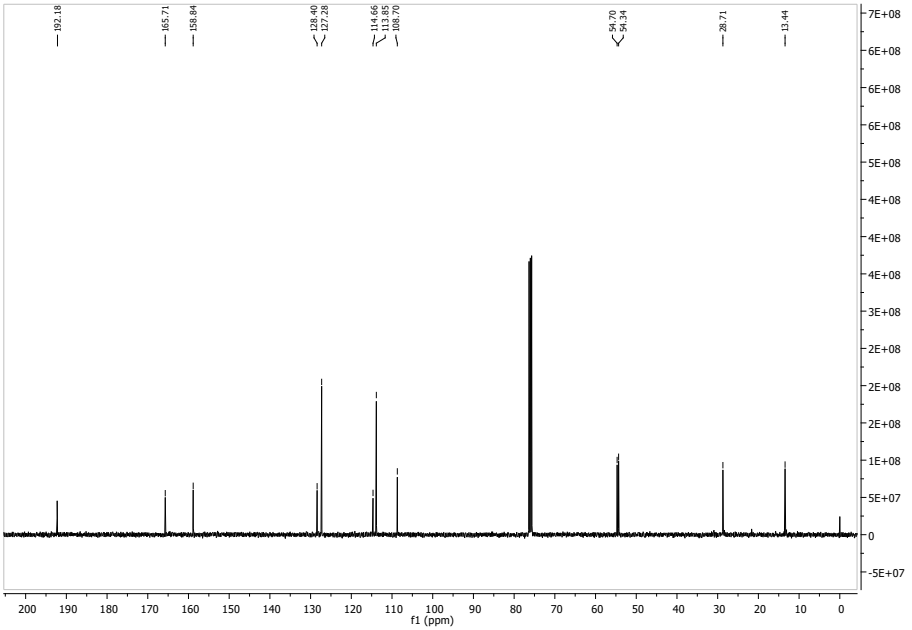



Figure 10. $^{13}$C NMR Spectrum of **3ae**

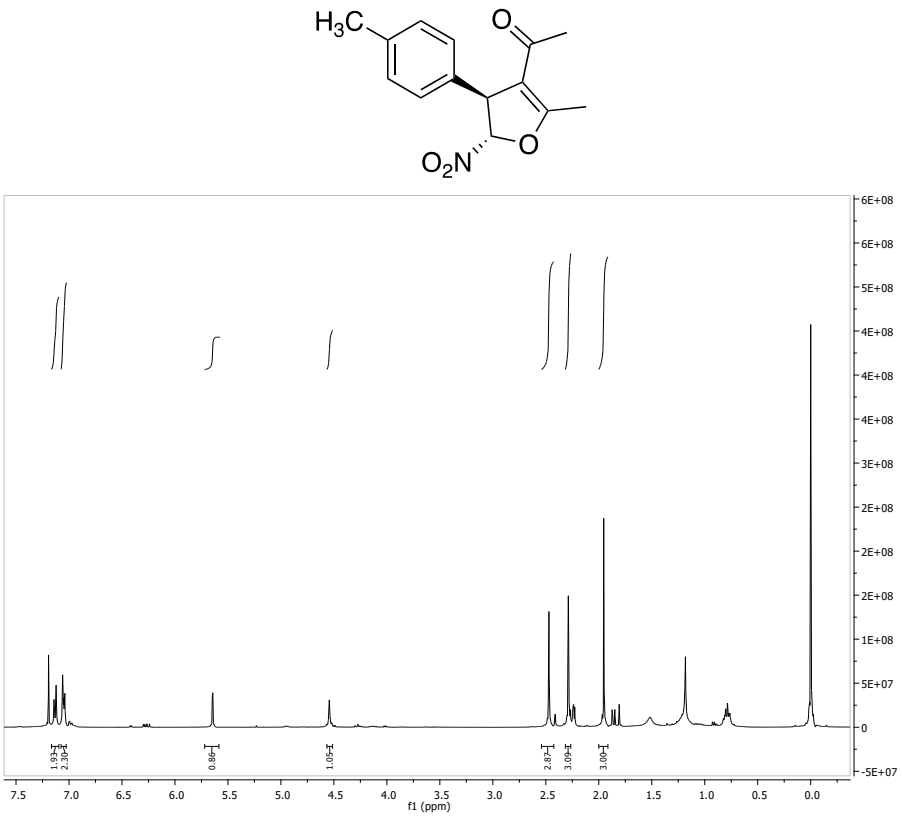



Figure 11. $^{1}$H NMR Spectrum of **3af**

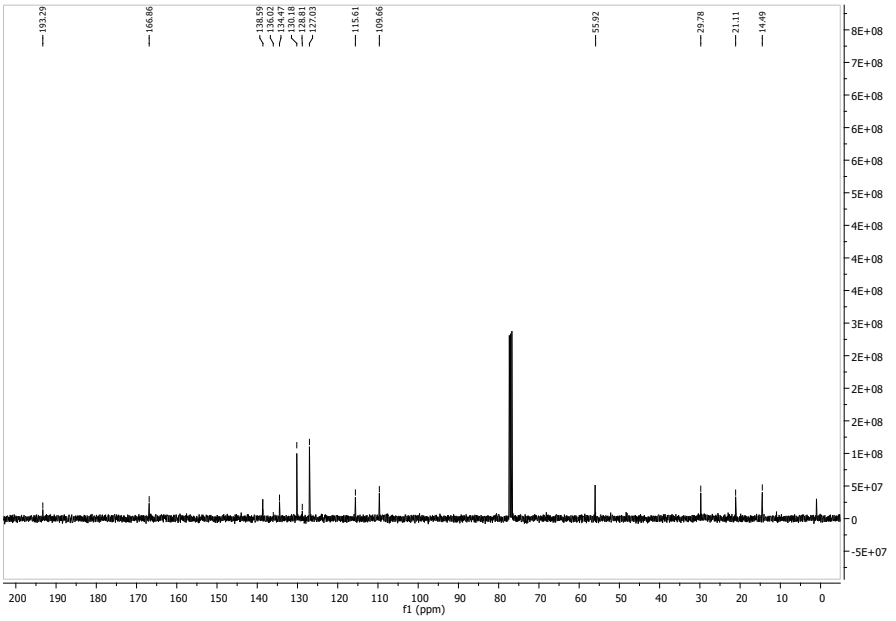
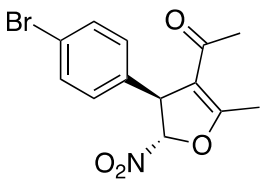



Figure 12. $^{13}$C NMR Spectrum of **3af**



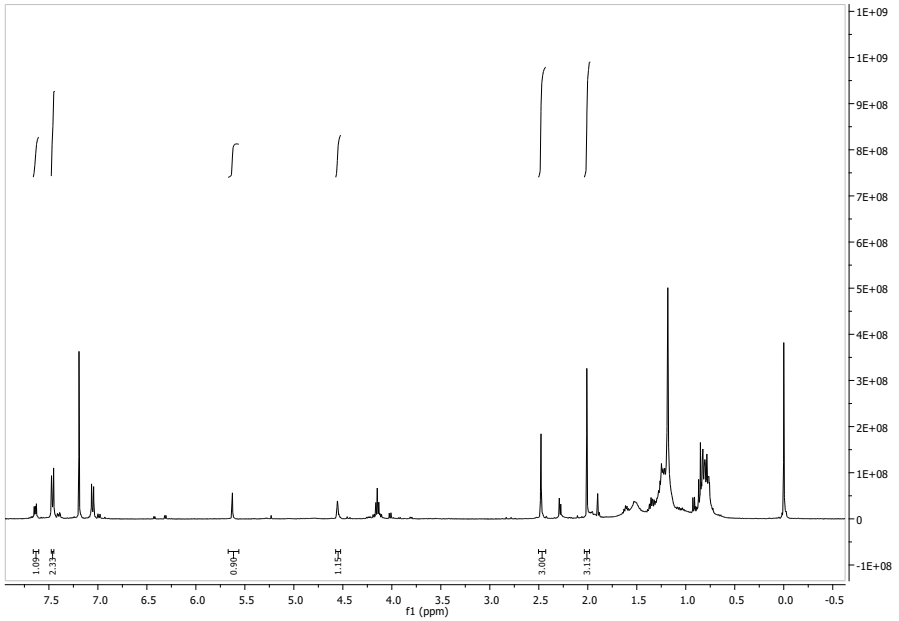




Figure 13. $^{1}$H NMR Spectrum of **3ag**

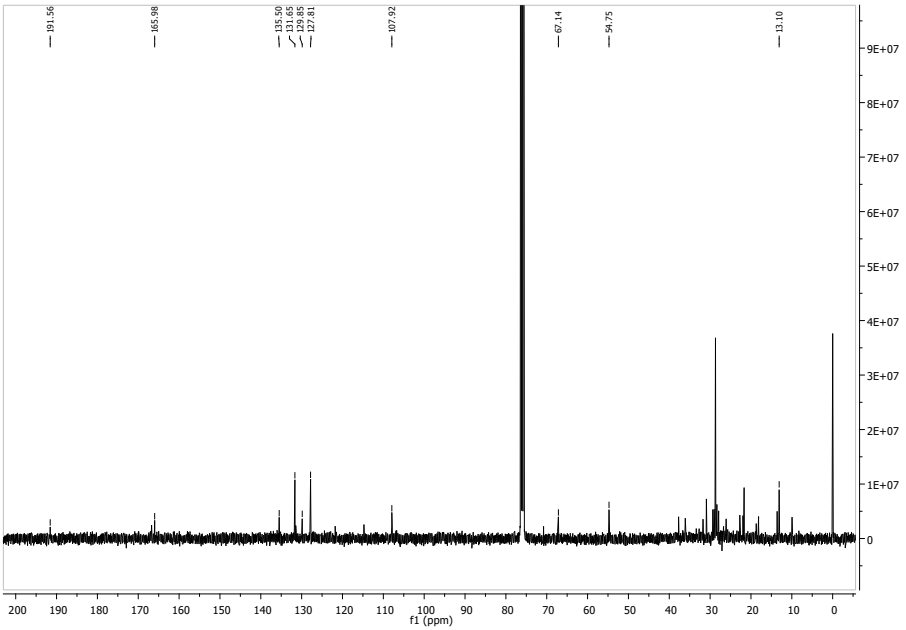
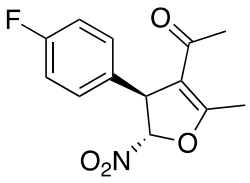



Figure 14. $^{13}$C NMR Spectrum of **3ag**



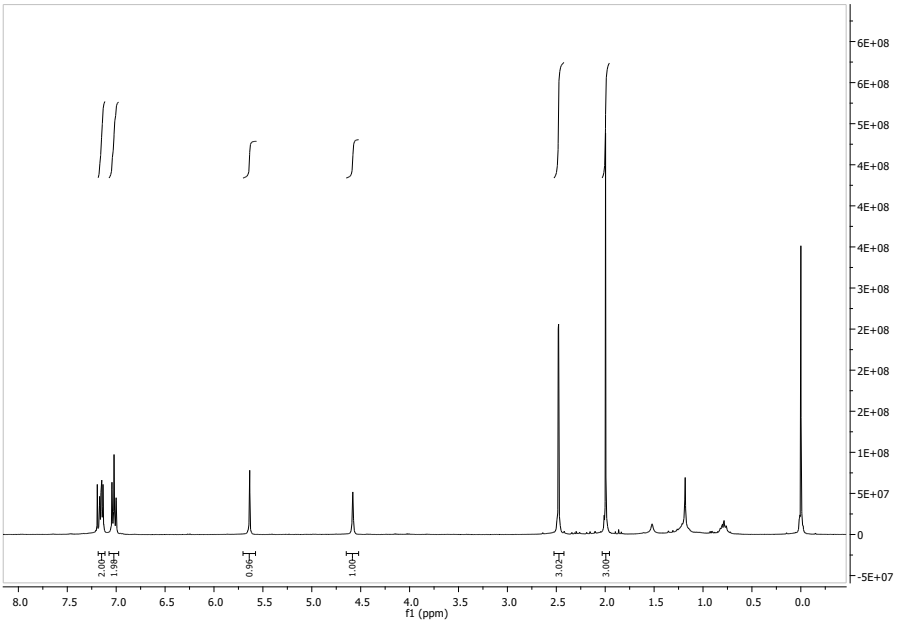




Figure 15. $^{1}$H NMR Spectrum of **3ah**

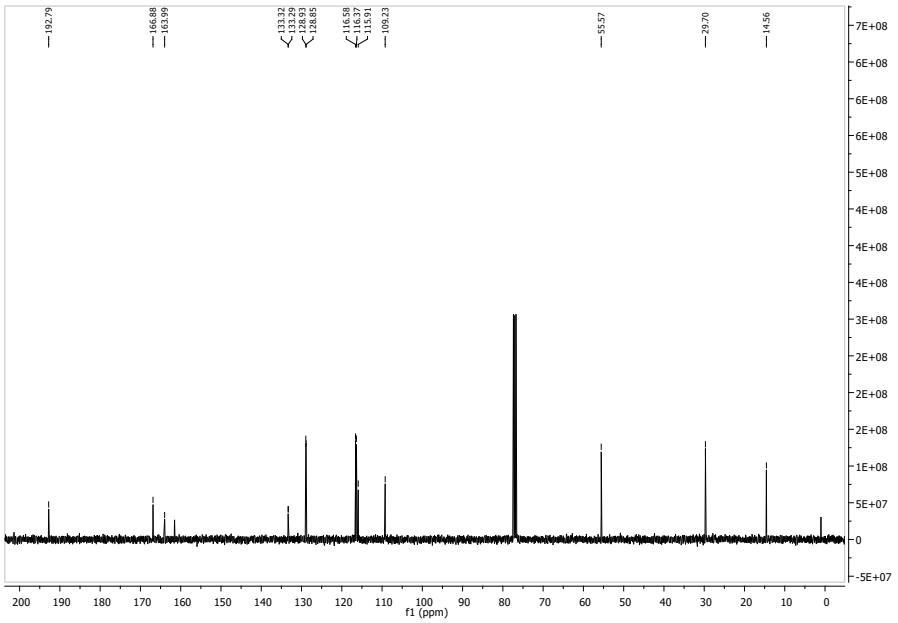
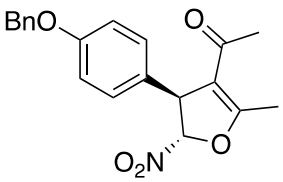



Figure 16. $^{13}$C NMR Spectrum of **3ah**



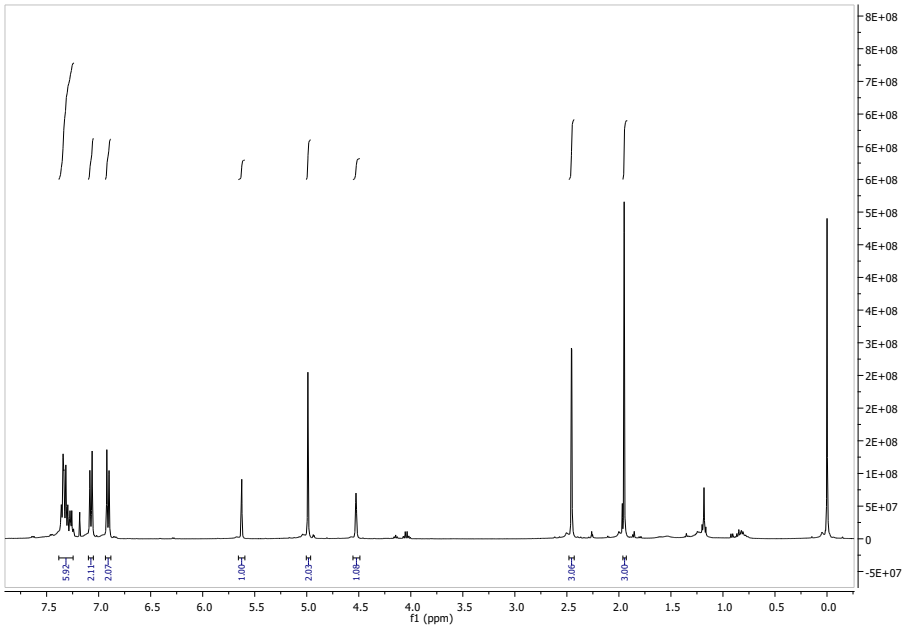




Figure 17. $^{1}$H NMR Spectrum of **3ai**

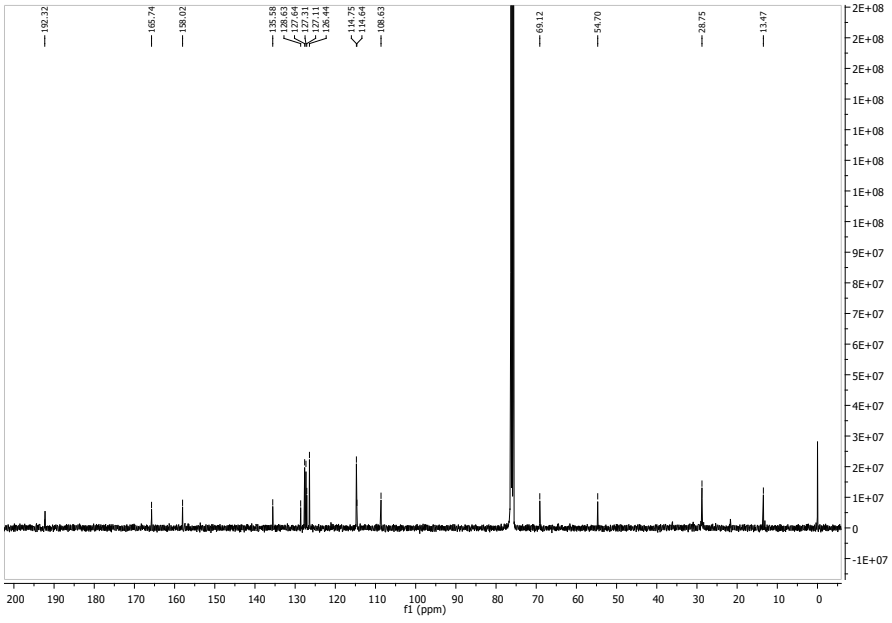



Figure 18. $^{13}$C NMR Spectrum of **3ai**

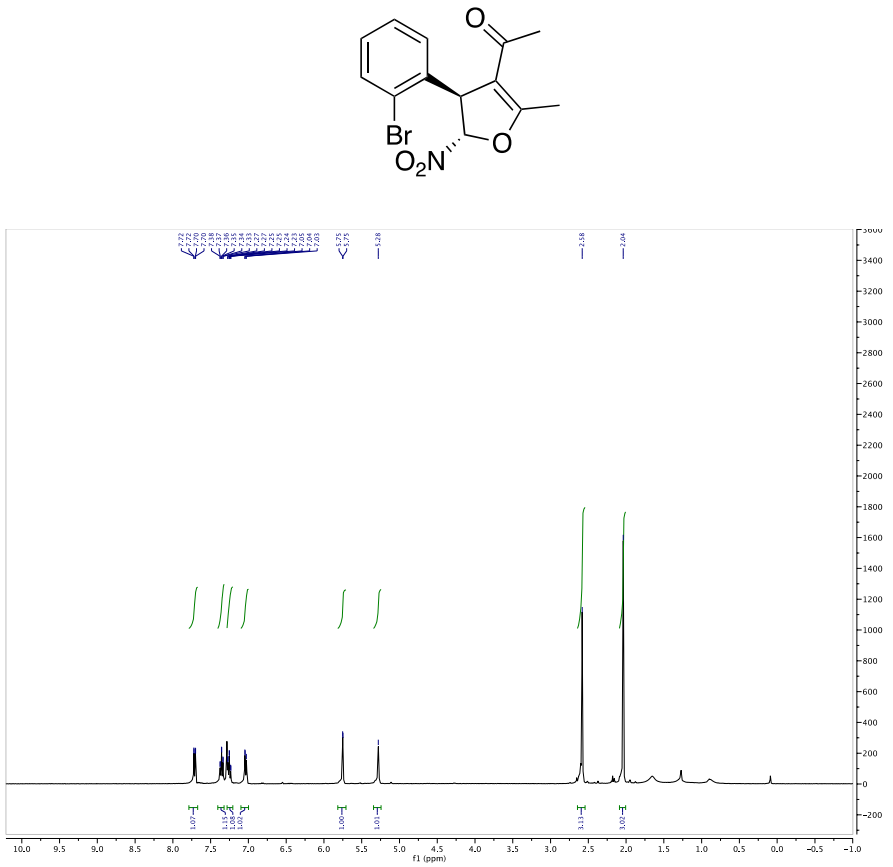


Figure 19. $^{1}$H NMR Spectrum of **3aj**

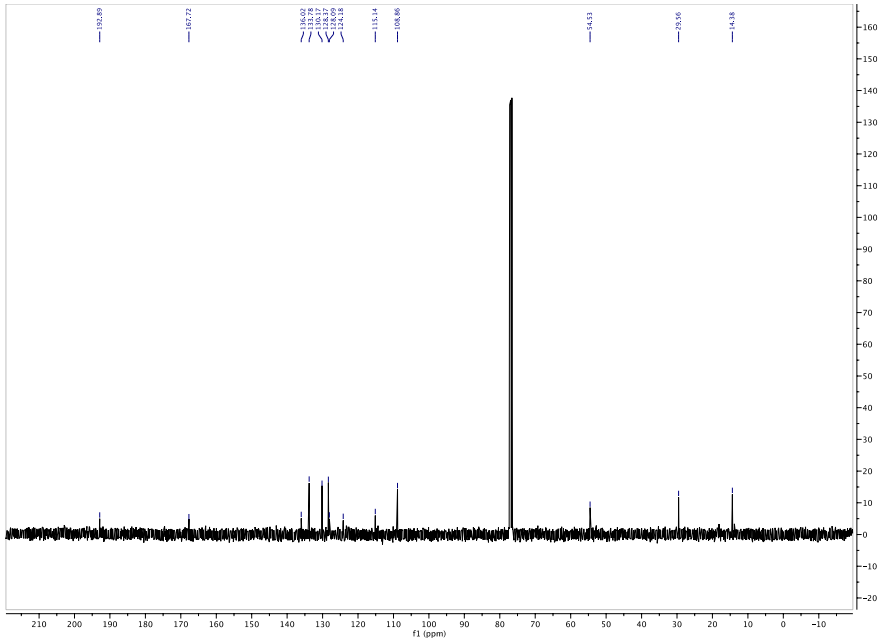


Figure 20. $^{13}$C NMR Spectrum of **3aj**

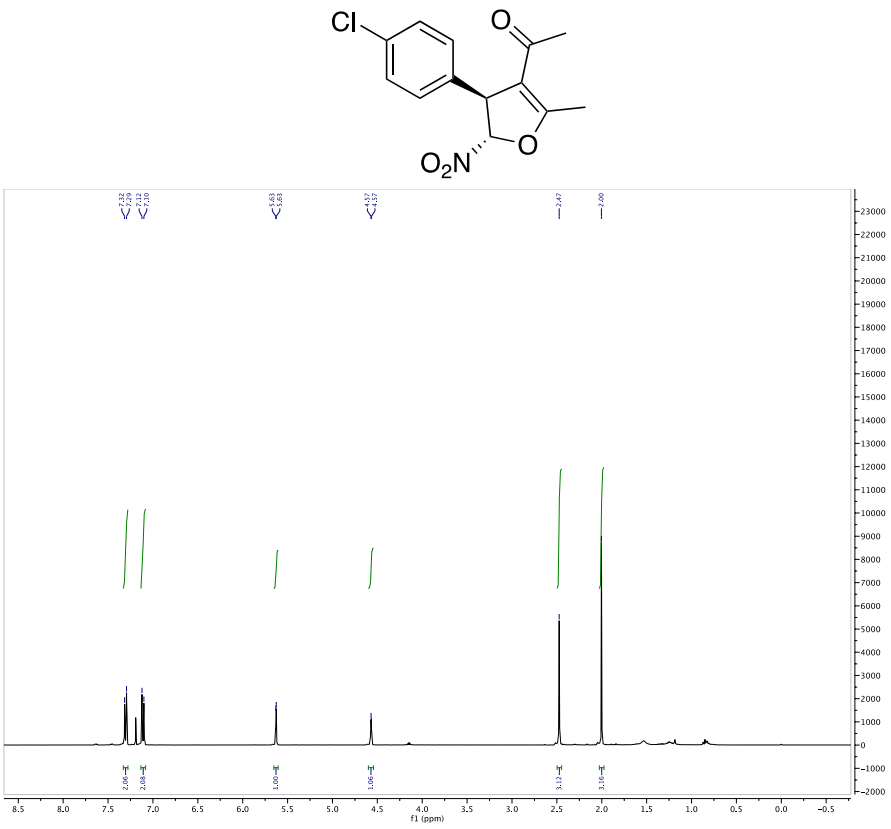



Figure 21. $^{1}$H NMR Spectrum of **3ak**

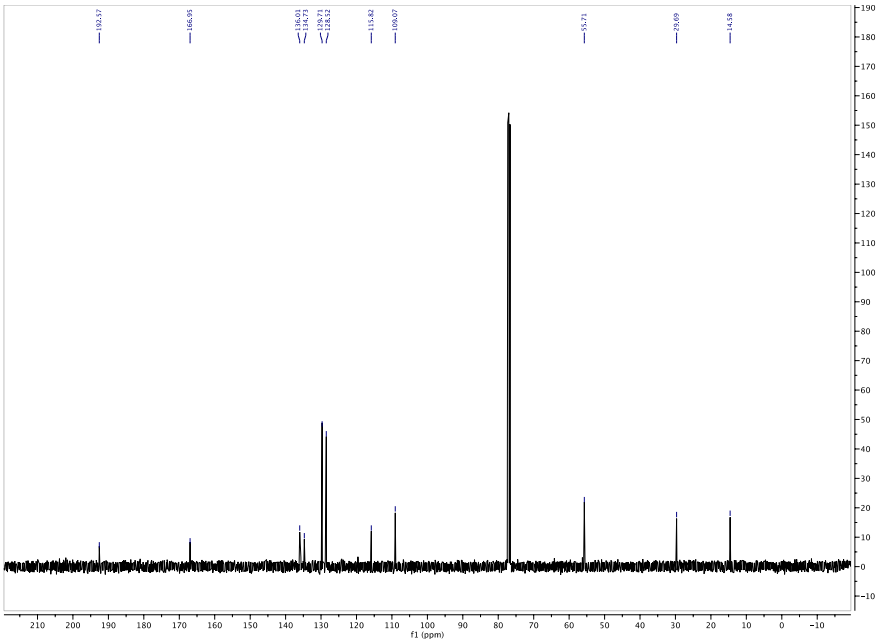
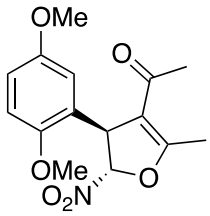



Figure 22. $^{13}$C NMR Spectrum of **3ak**



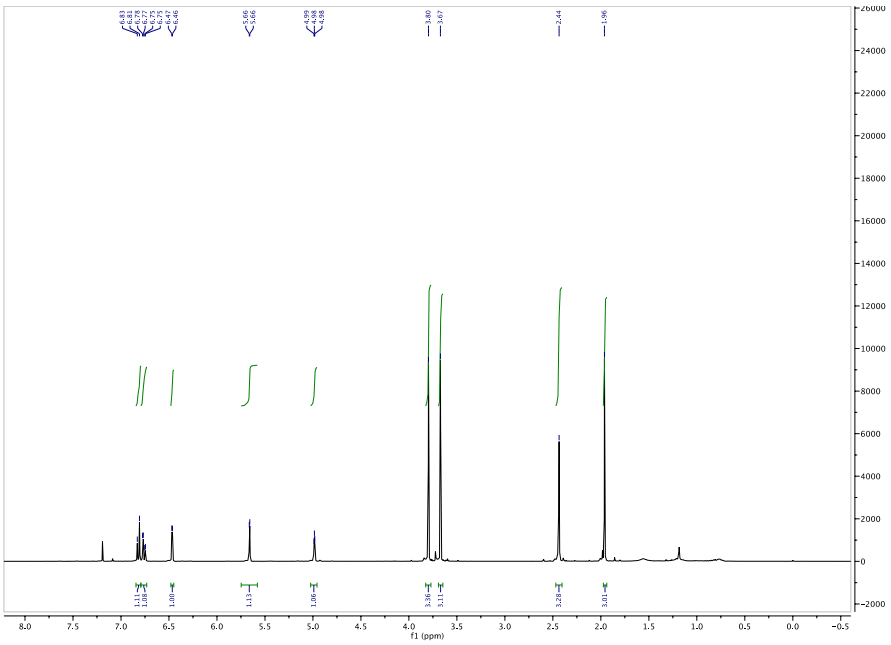



Figure 23. $^{1}$H NMR Spectrum of **3al**

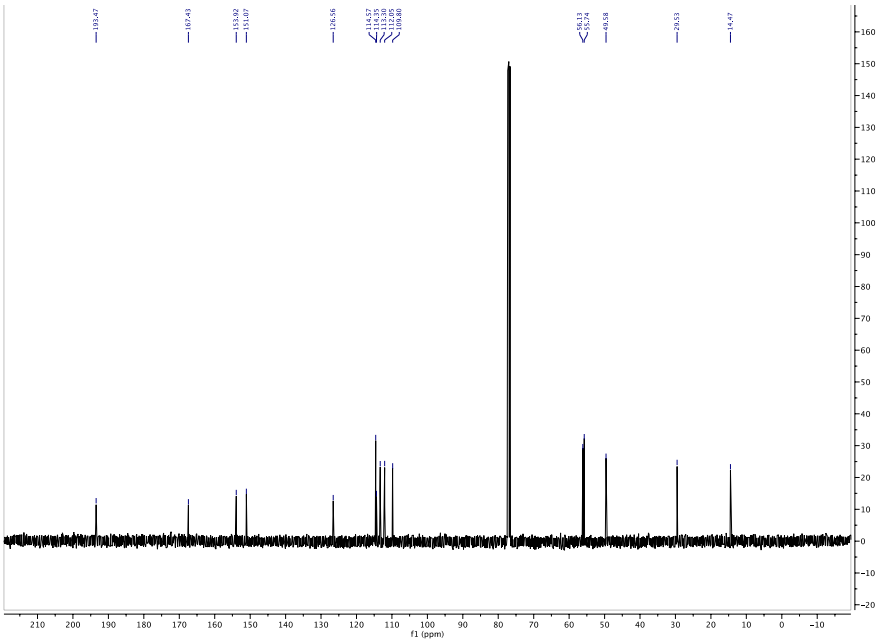


Figure 24. $^{13}$C NMR Spectrum of **3al**

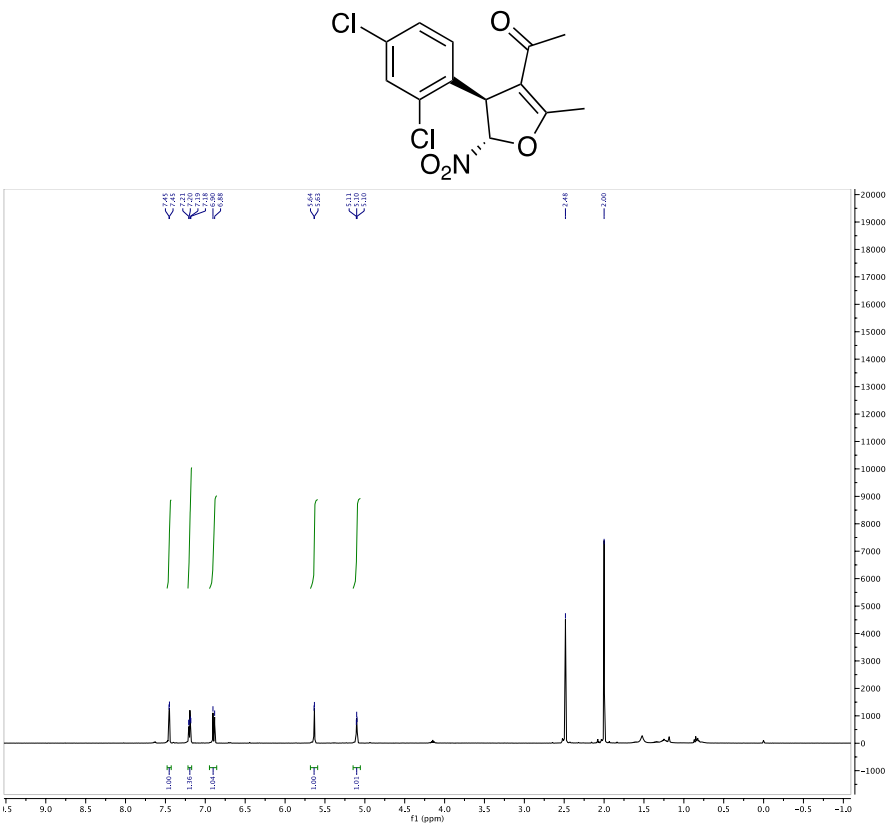



Figure 25. $^{1}$H NMR Spectrum of **3am**

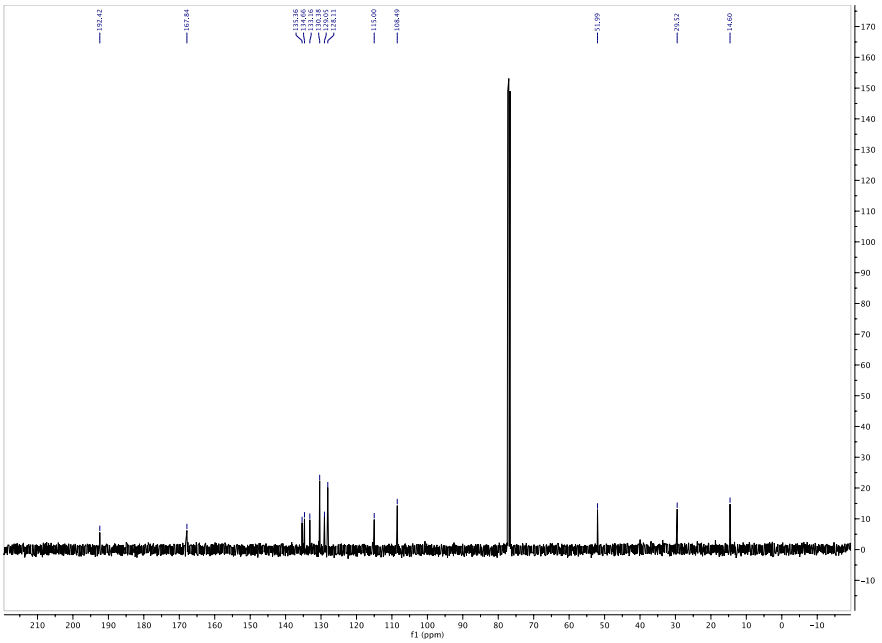



Figure 26. $^{13}$C NMR Spectrum of **3am**

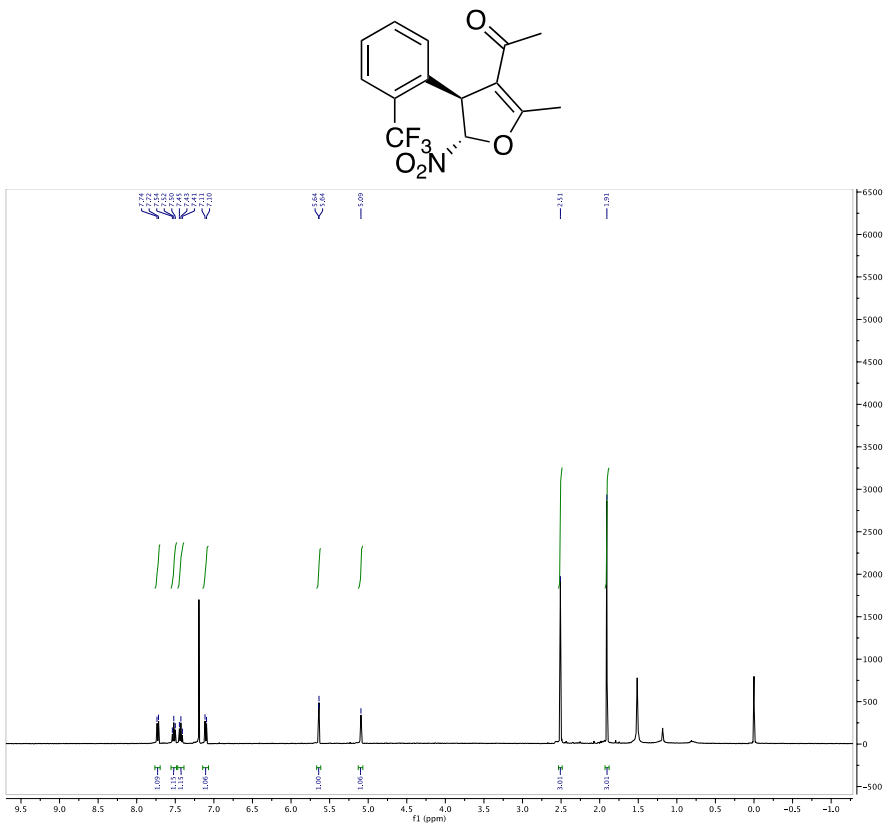


Figure 27. $^{1}$H NMR Spectrum of **3an**

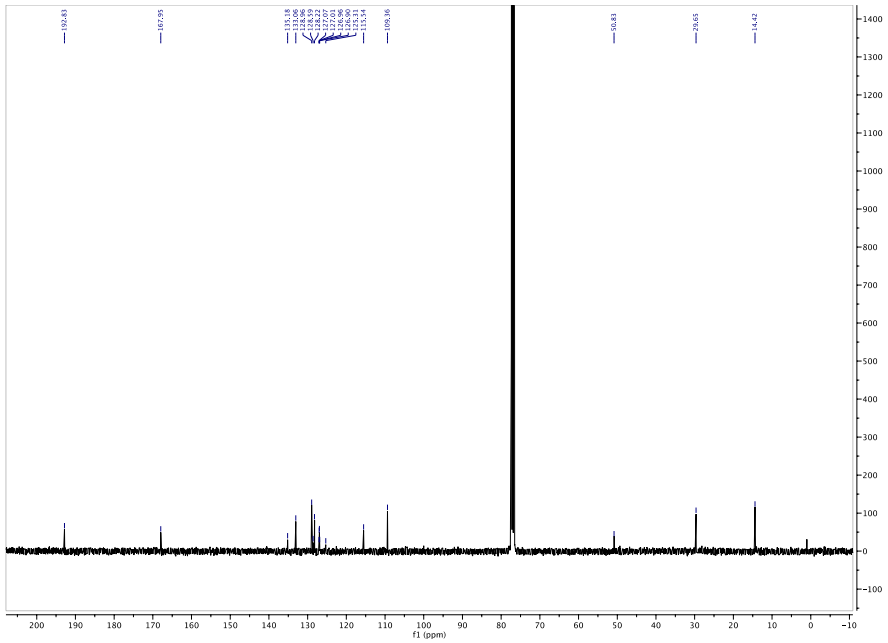


Figure 28. $^{13}$C NMR Spectrum of **3an**

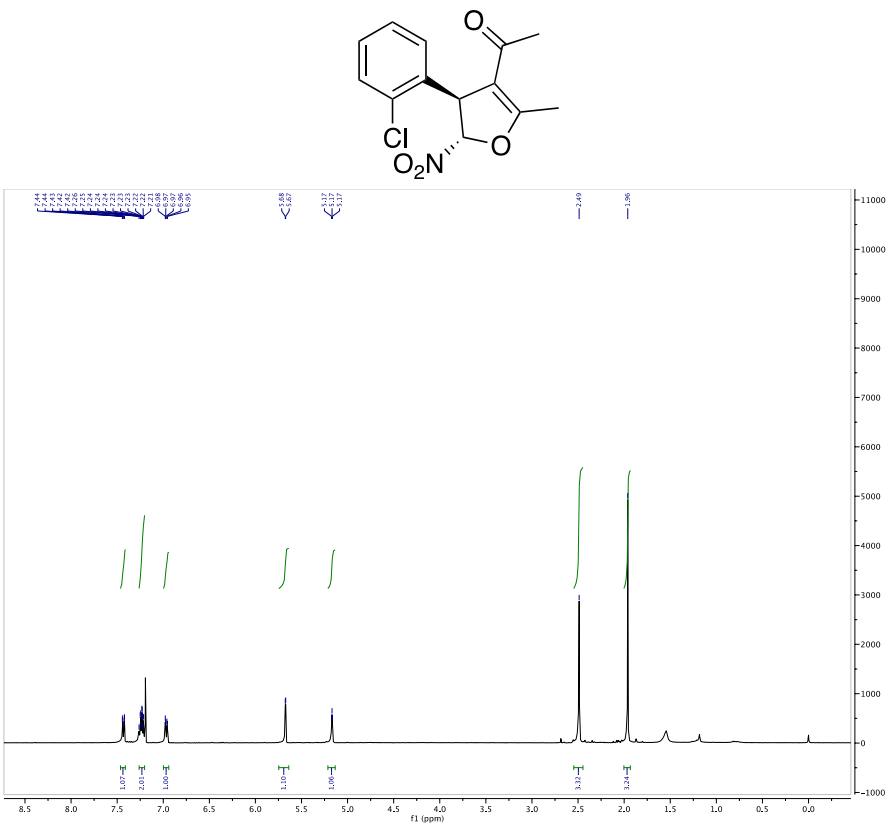


Figure 29. $^{1}$H NMR Spectrum of **3ao**

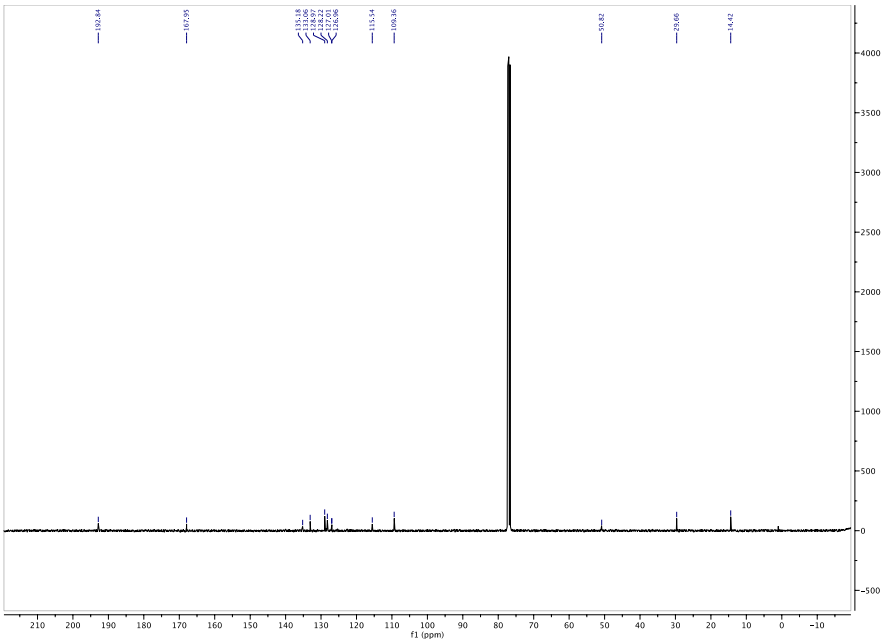
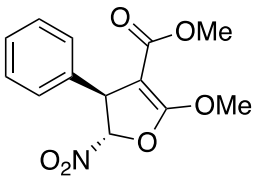


Figure 30. $^{13}$C NMR Spectrum of **3an**



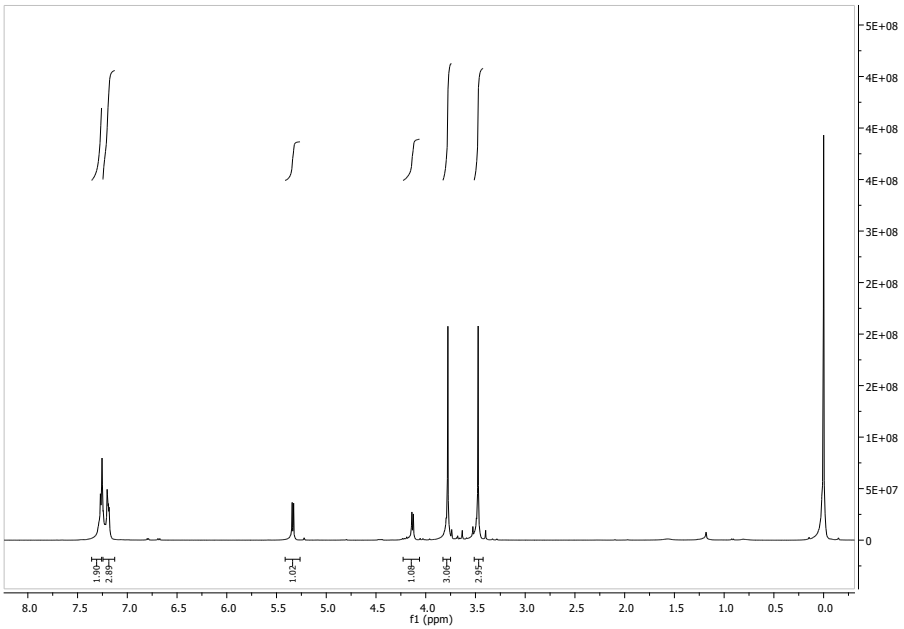




Figure 31. $^{1}$H NMR Spectrum of **3ba**

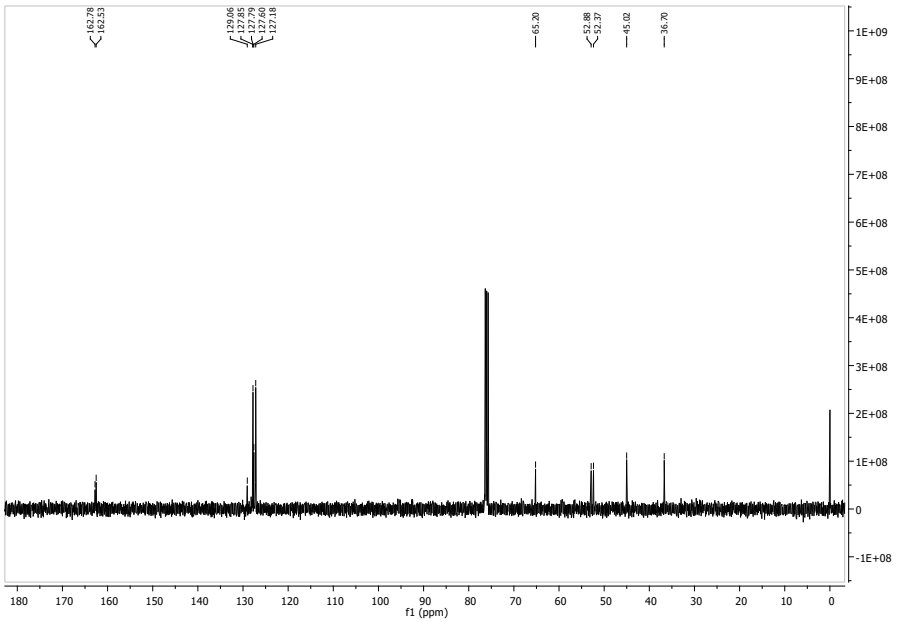



Figure 32. $^{13}$C NMR Spectrum of **3ba**

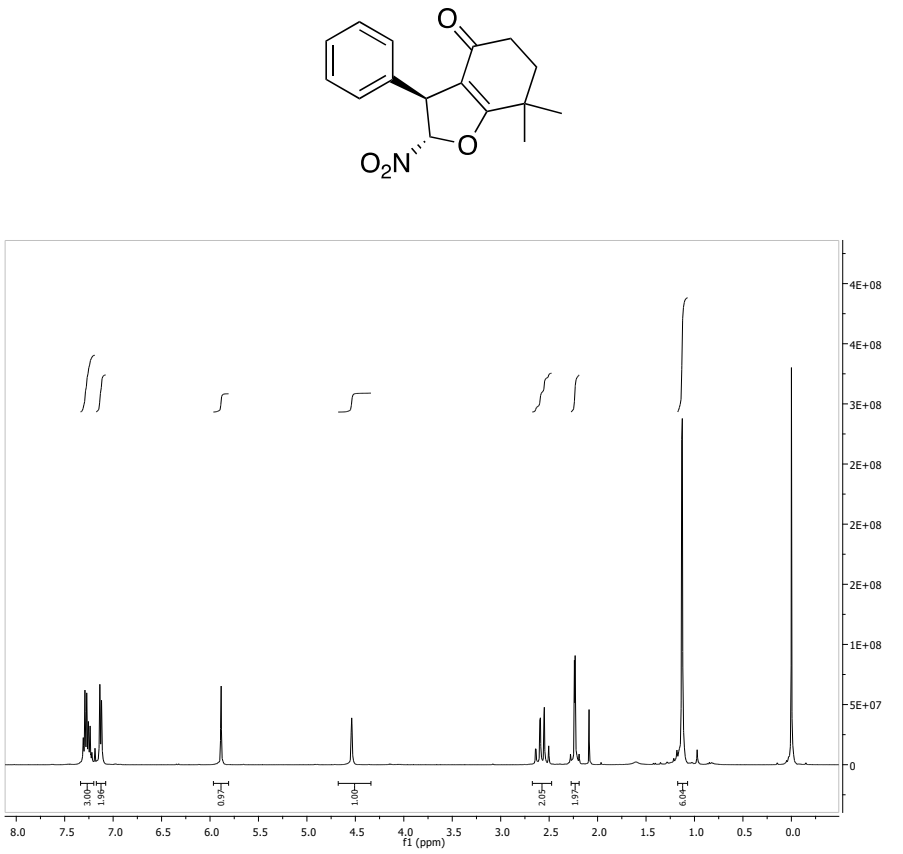



Figure 33. $^{1}$H NMR Spectrum of **3ca**

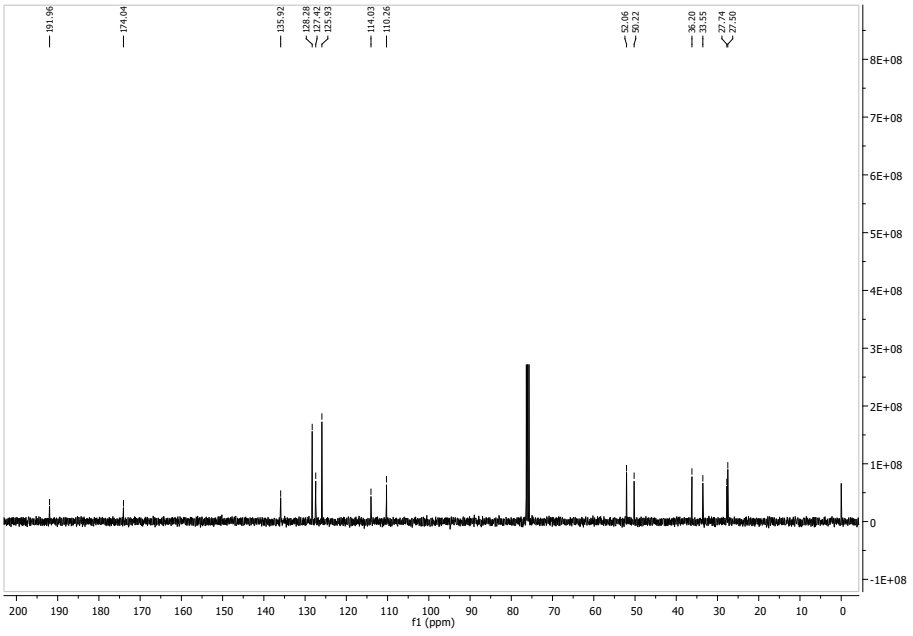
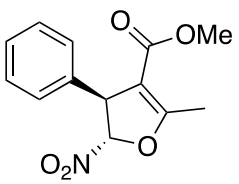



Figure 34. $^{13}$C NMR Spectrum of **3ca**



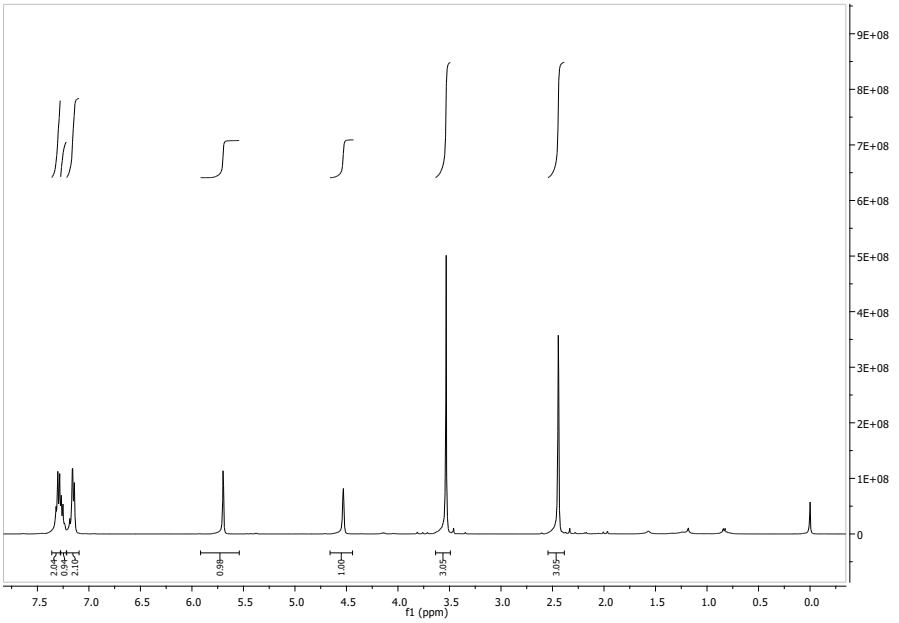




Figure 35. $^{1}$H NMR Spectrum of **3da**

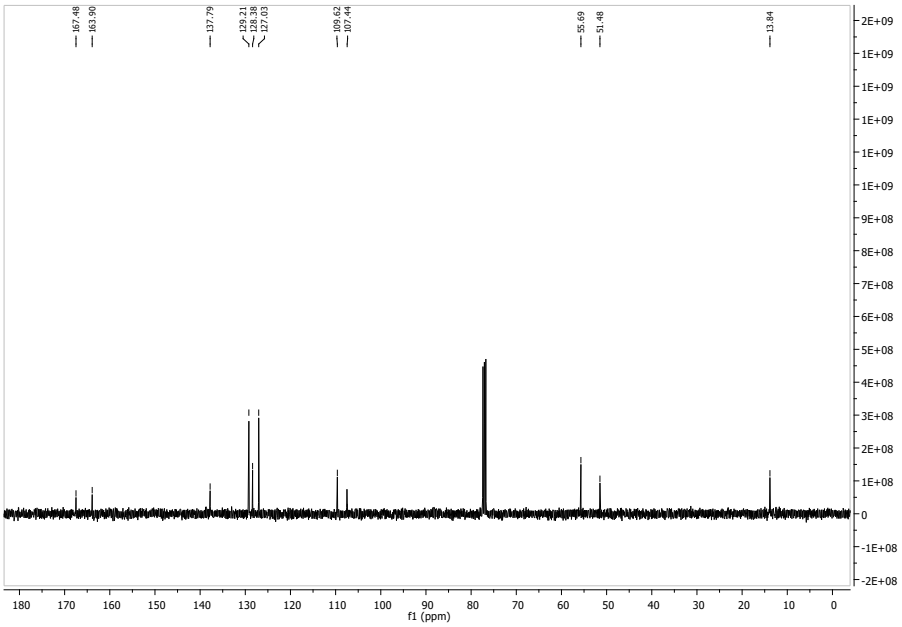
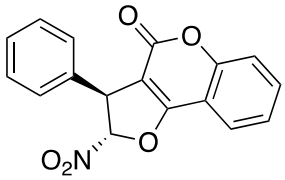



Figure 36. $^{13}$C NMR Spectrum of **3da**



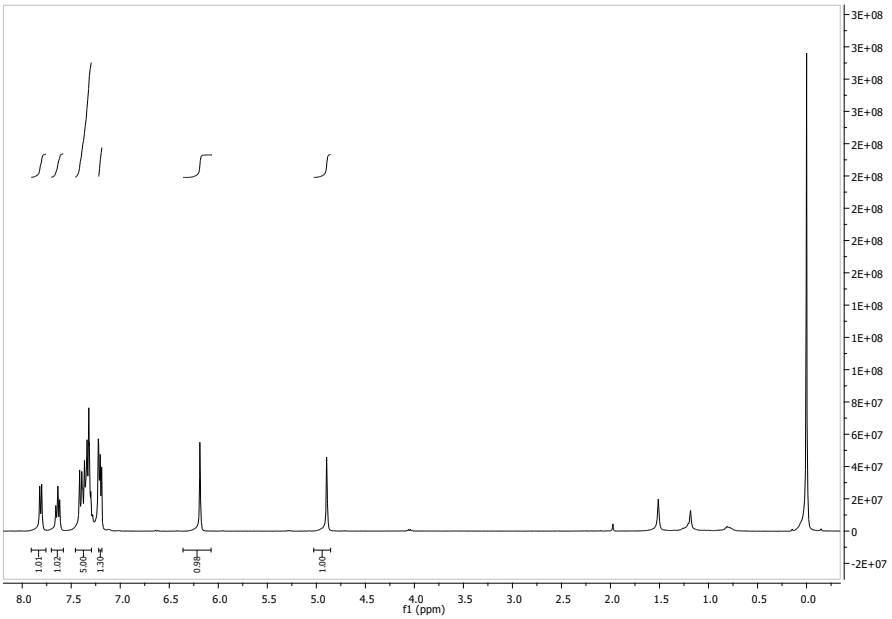




Figure 37. $^{1}$H NMR Spectrum of **3ea**

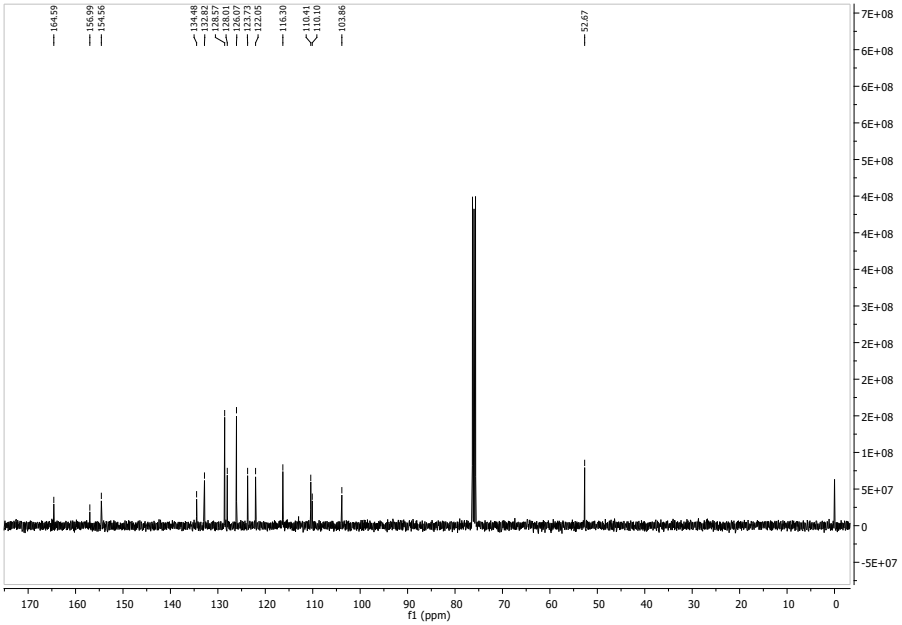



Figure 38. $^{13}$C NMR Spectrum of **3ea**

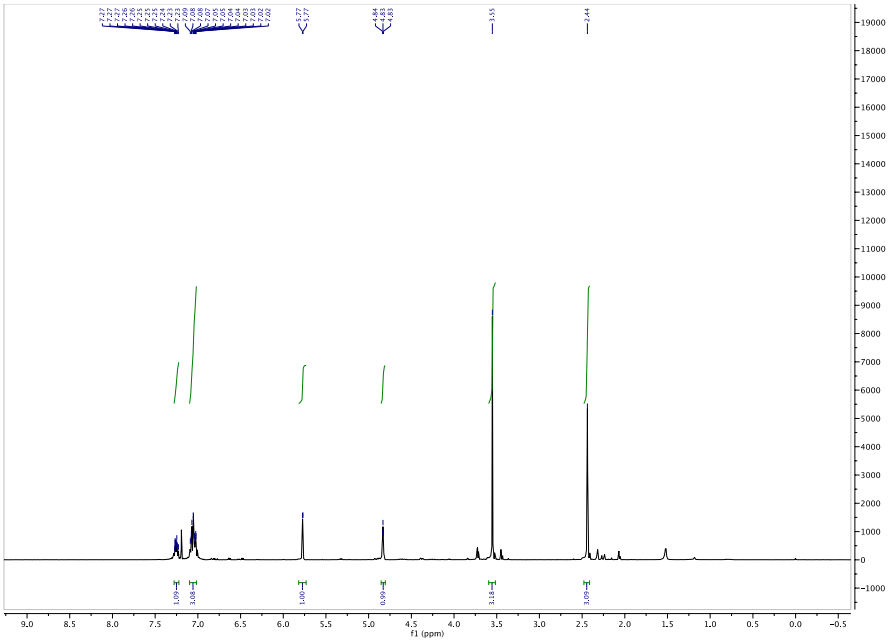


Figure 39. $^{1}$H NMR Spectrum of **3db**

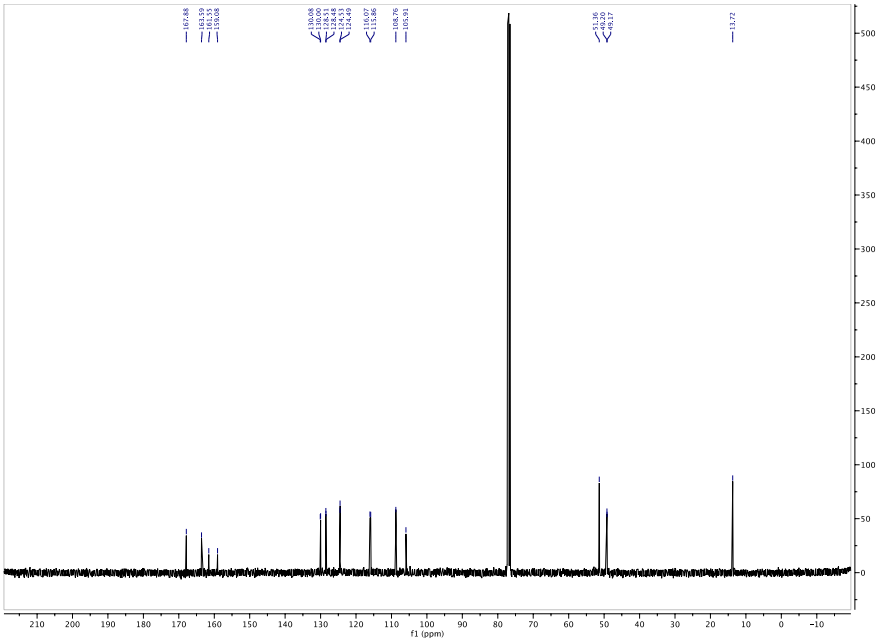
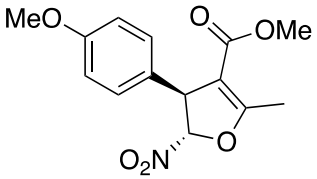


Figure 40. $^{13}$C NMR Spectrum of **3db**



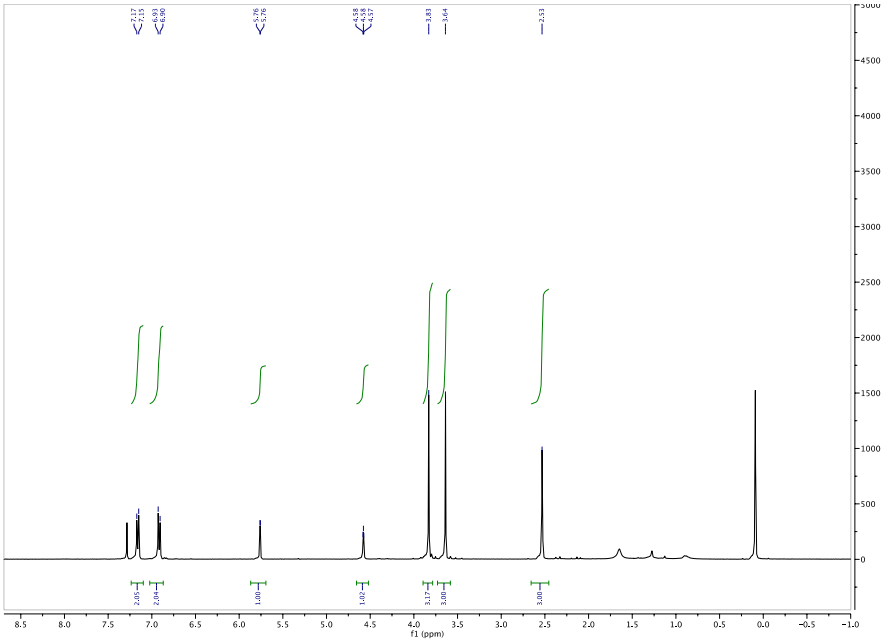




Figure 41. $^{1}$H NMR Spectrum of **3de**

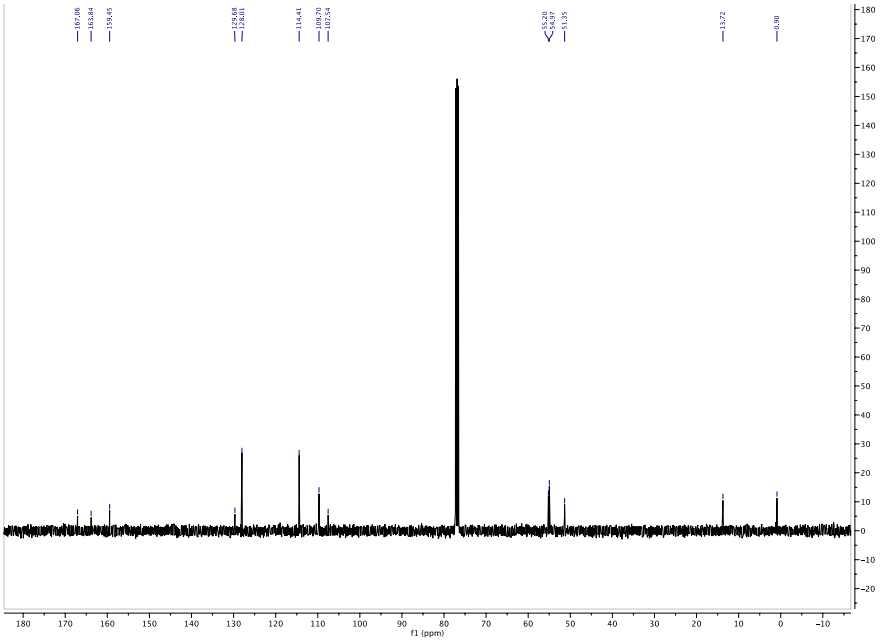
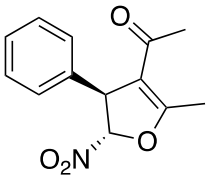



Figure 42. $^{13}$C NMR Spectrum of **3de**

## 2. HPLC Chromatograms



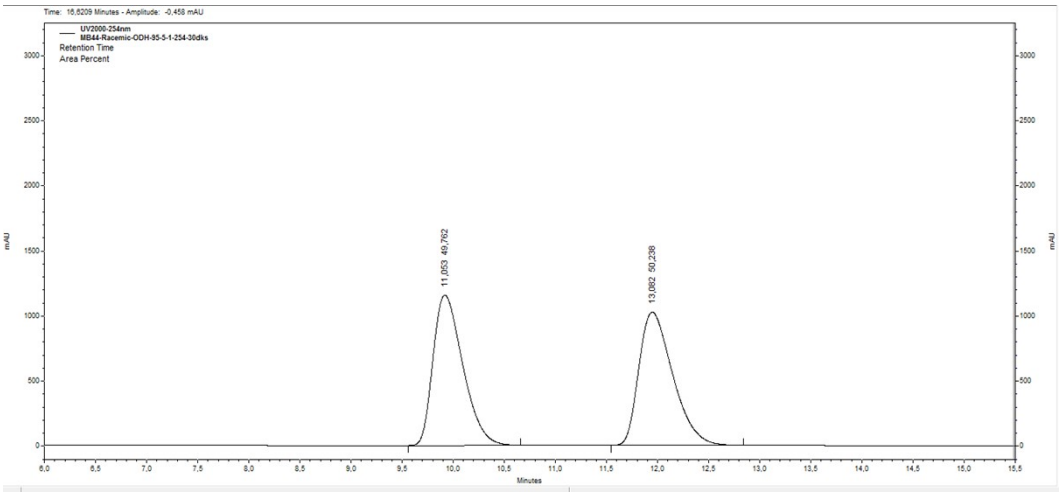




Figure 43. HPLC Chromatogram of racemic **3aa**

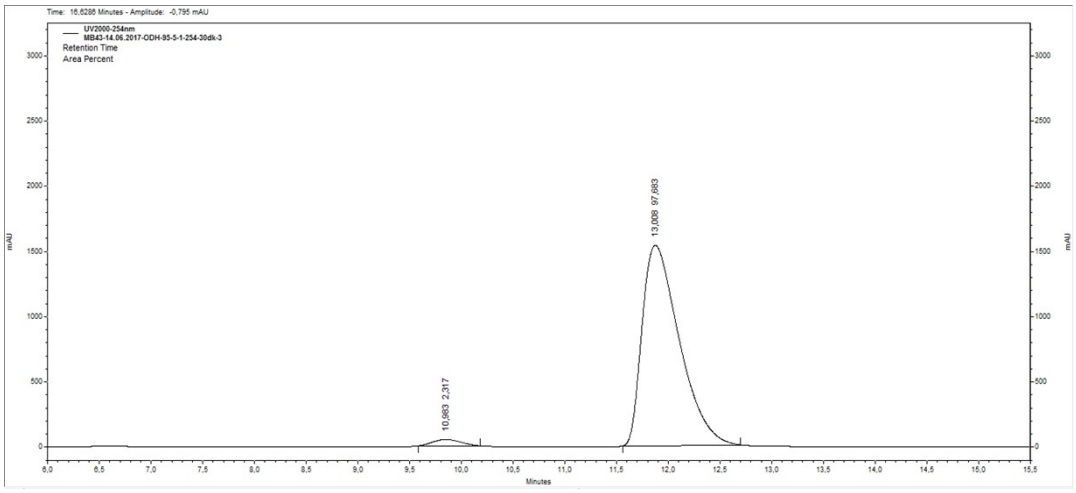
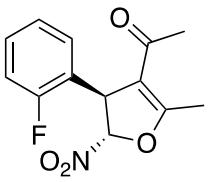



Figure 44. HPLC Chromatogram of chiral **3aa**



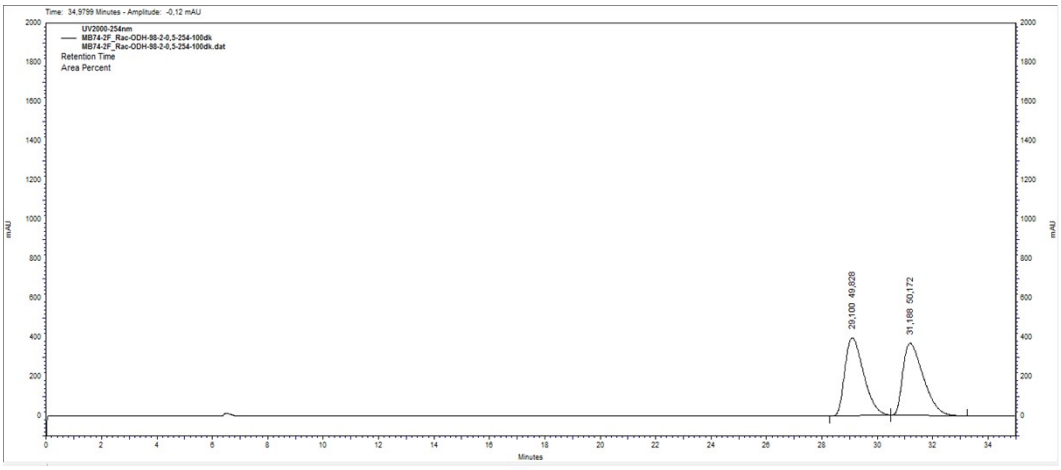




Figure 45. HPLC Chromatogram of racemic **3ab**

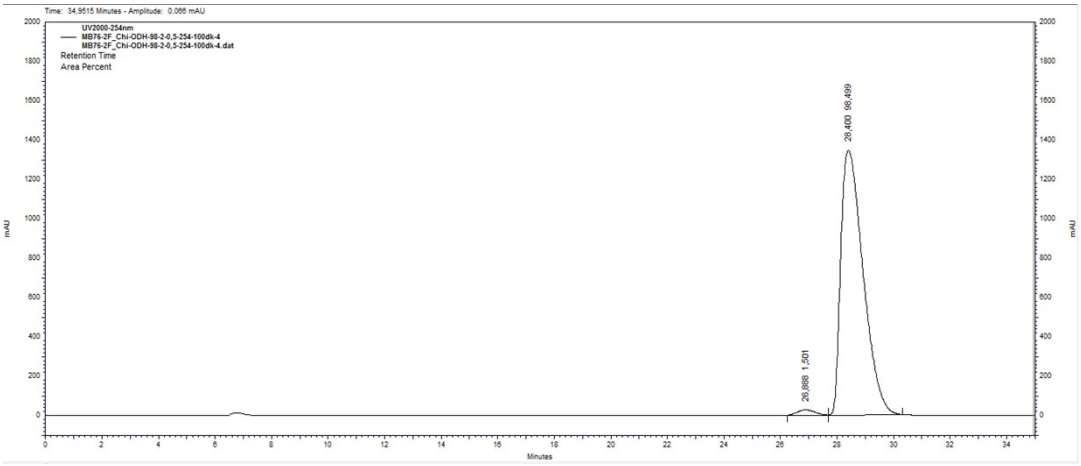
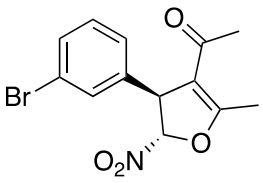



Figure 46. HPLC Chromatogram of chiral **3ab**



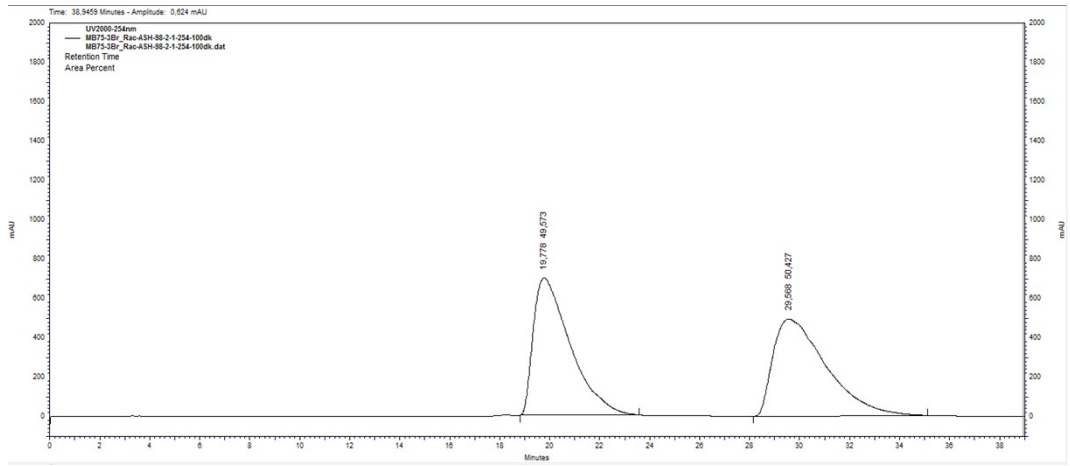




Figure 47. HPLC Chromatogram of racemic **3ac**

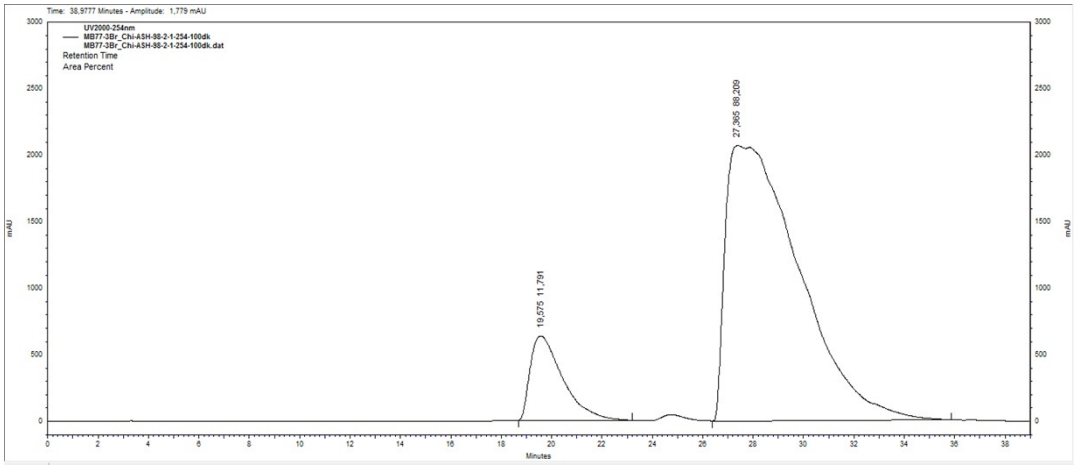
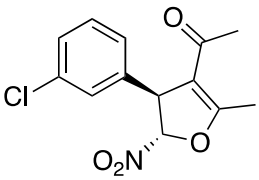



Figure 48. HPLC Chromatogram of chiral **3ac**



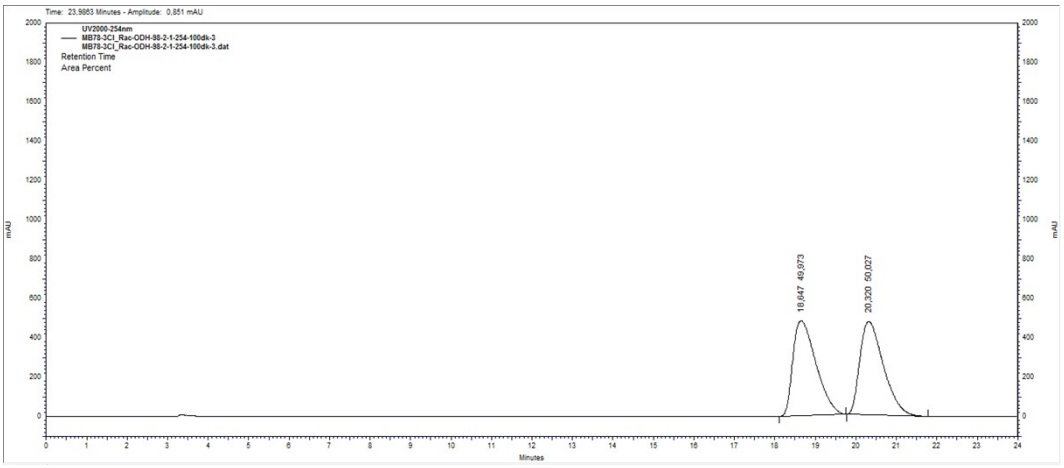




Figure 49. HPLC Chromatogram of racemic **3ad**

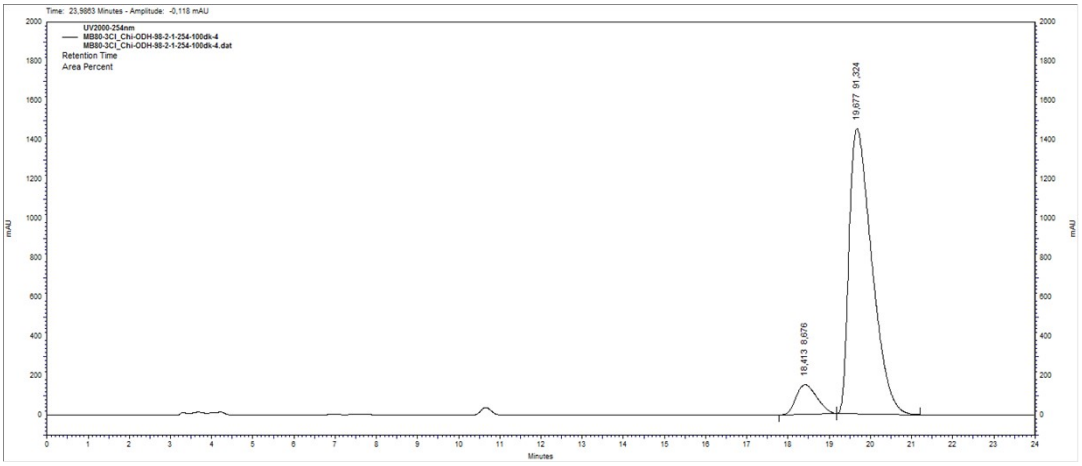
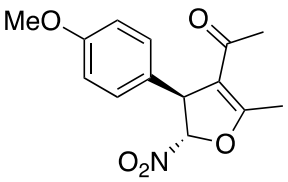



Figure 50. HPLC Chromatogram of chiral **3ad**



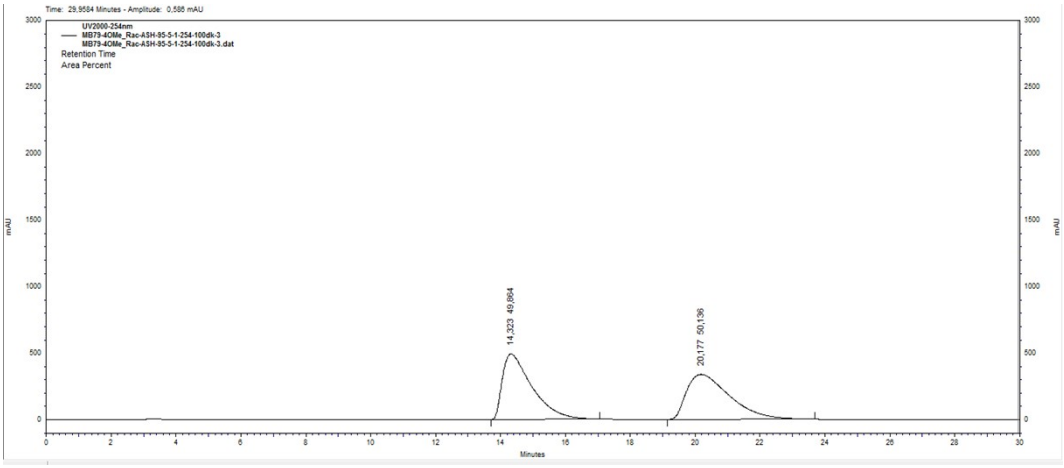




Figure 51. HPLC Chromatogram of racemic **3ae**

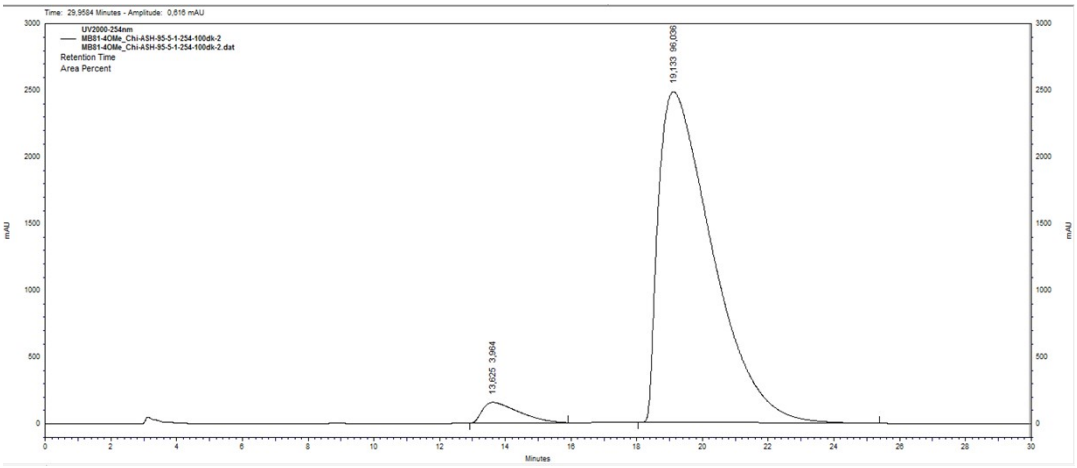
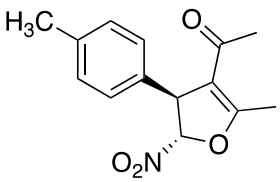



Figure 52. HPLC Chromatogram of chiral **3ae**



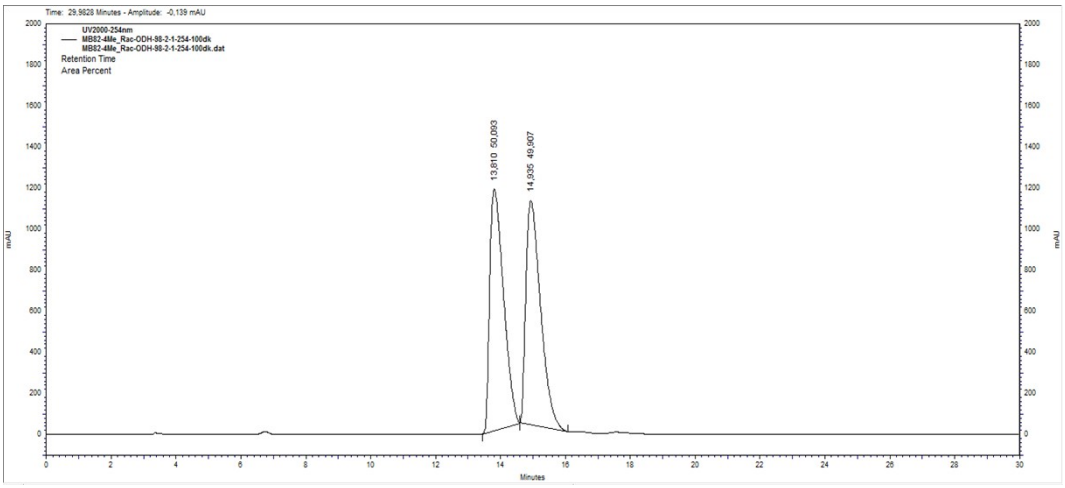




Figure 53. HPLC Chromatogram of racemic **3af**

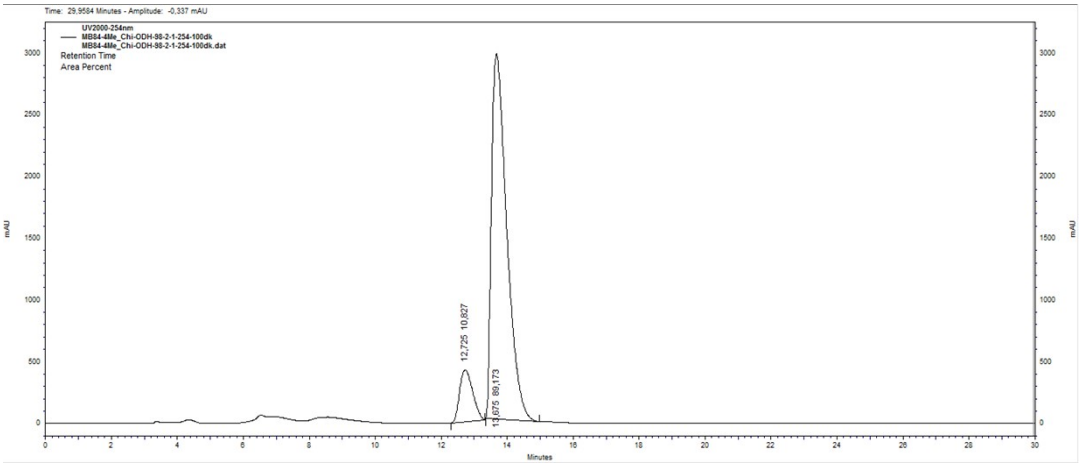
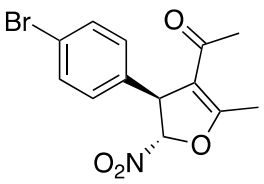



Figure 54. HPLC Chromatogram of chiral **3af**



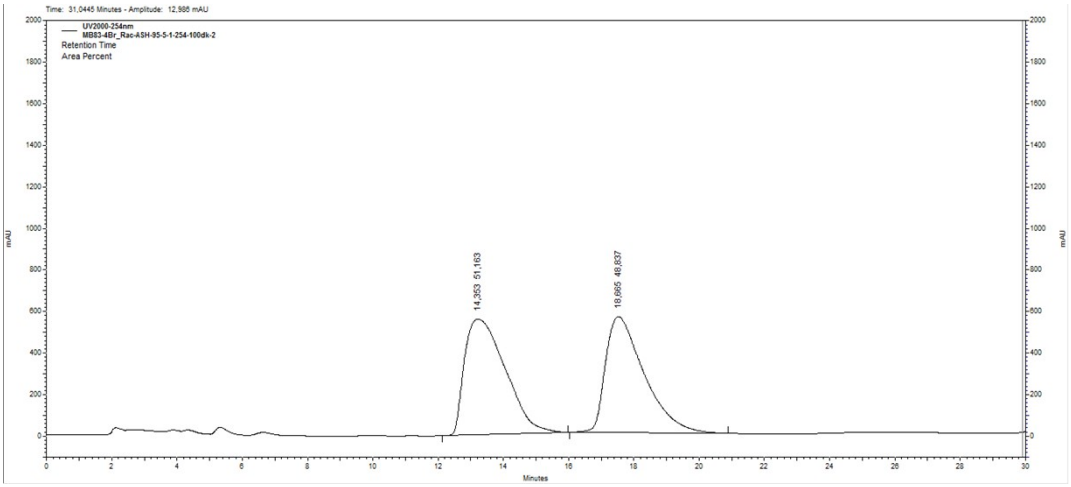




Figure 55. HPLC Chromatogram of racemic **3ag**

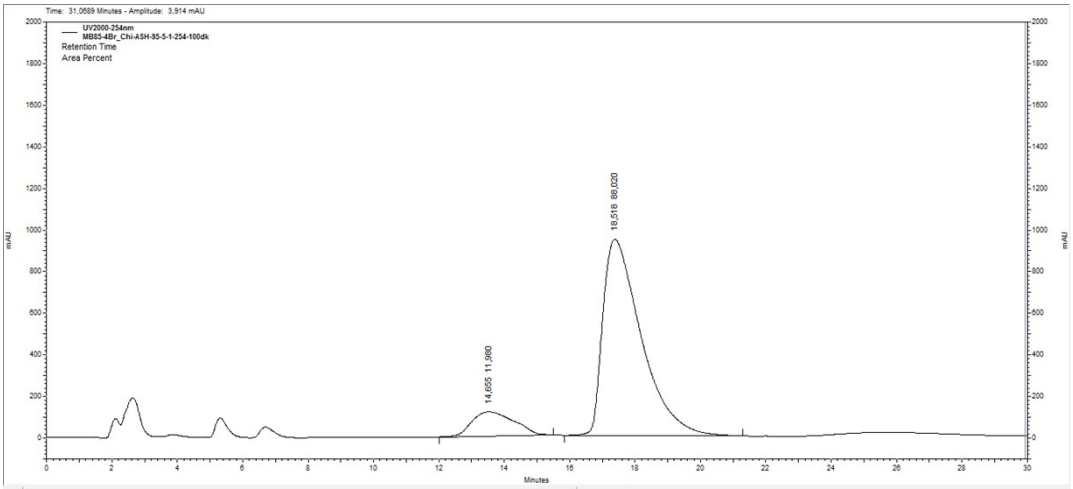
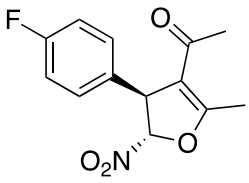



Figure 56. HPLC Chromatogram of chiral **3ag**



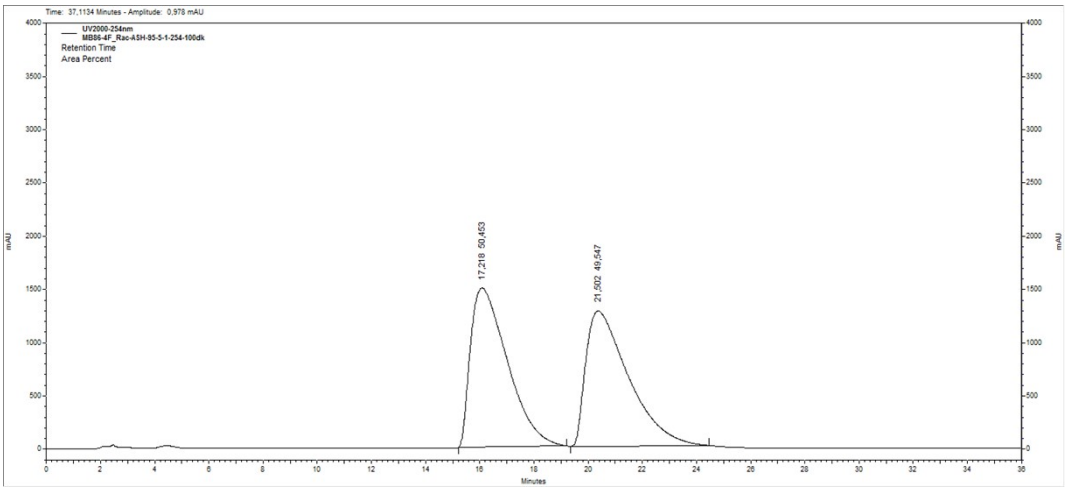




Figure 57. HPLC Chromatogram of racemic **3ah**

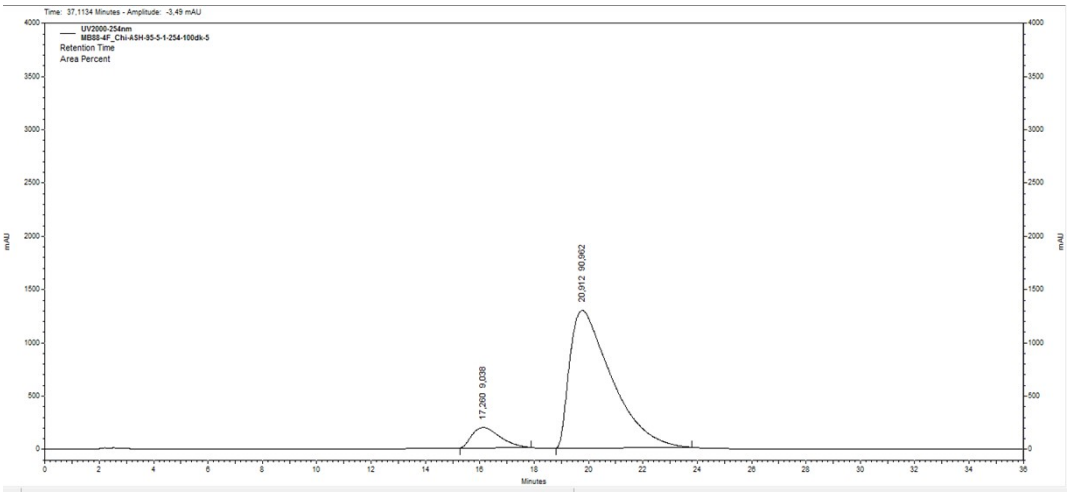
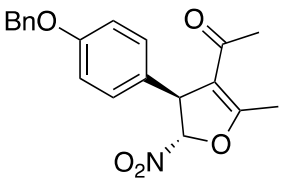



Figure 58. HPLC Chromatogram of chiral **3ah**



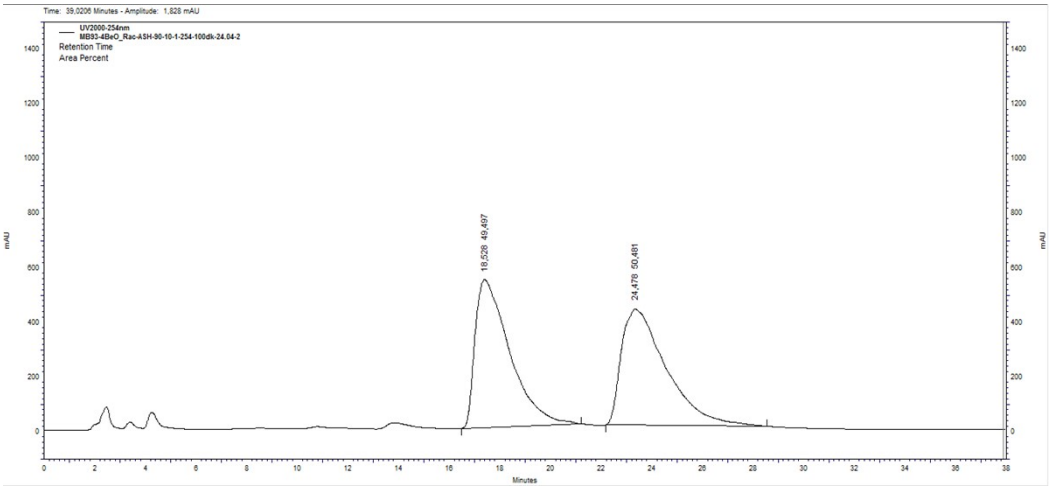




Figure 59. HPLC Chromatogram of racemic **3ai**

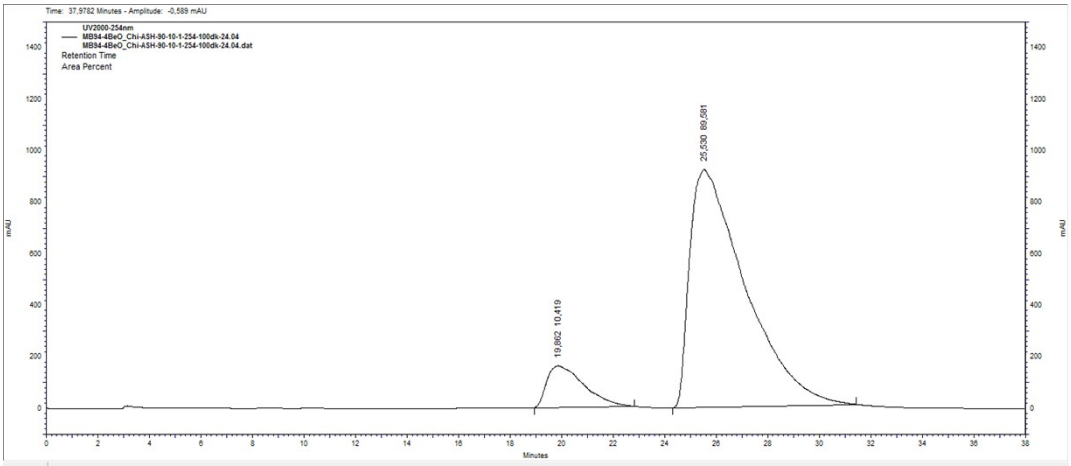
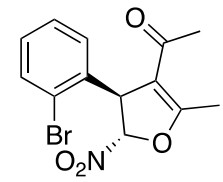
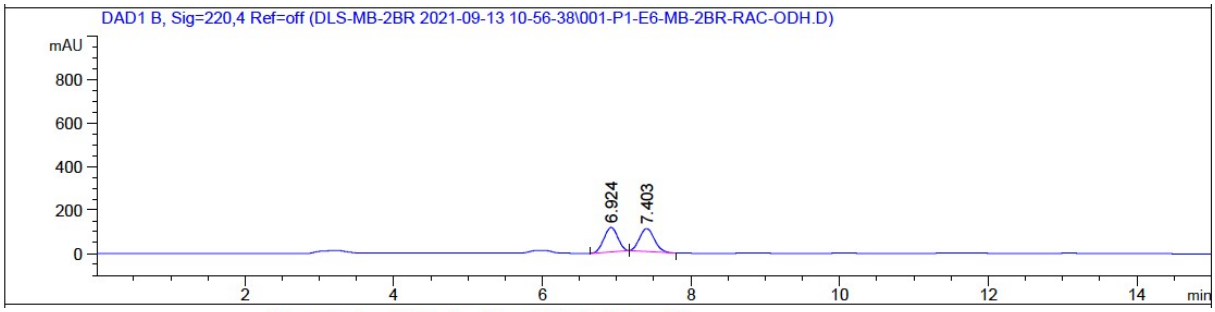



Figure 60. HPLC Chromatogram of chiral **3ai**

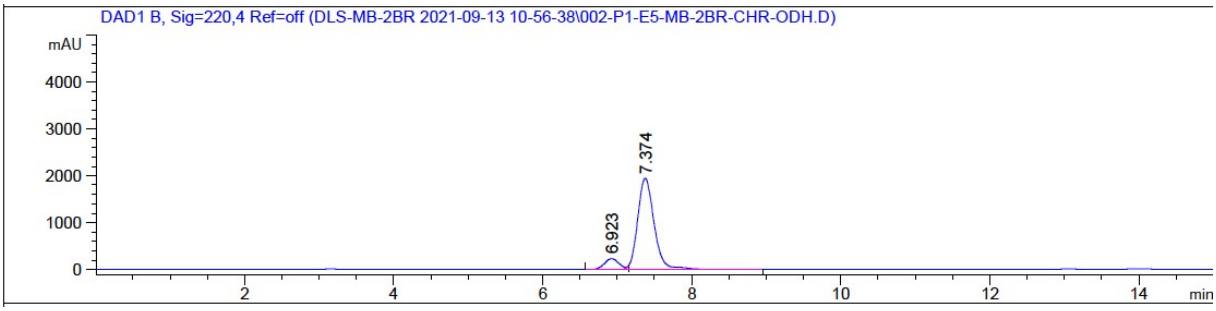



Signal 2: DAD1 B, Sig=220,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.924 | BB | 0.2021 | 1456.10999 | 112.77587 | 49.8779 |
| 2 | 7.403 | BB | 0.2162 | 1463.23804 | 106.23509 | 50.1221 |
| Totals : | | | | 2919.34802 | 219.01096 | |

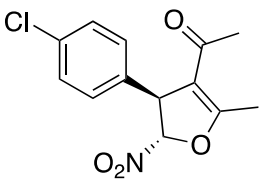
Figure 61. HPLC Chromatogram of racemic **3aj**

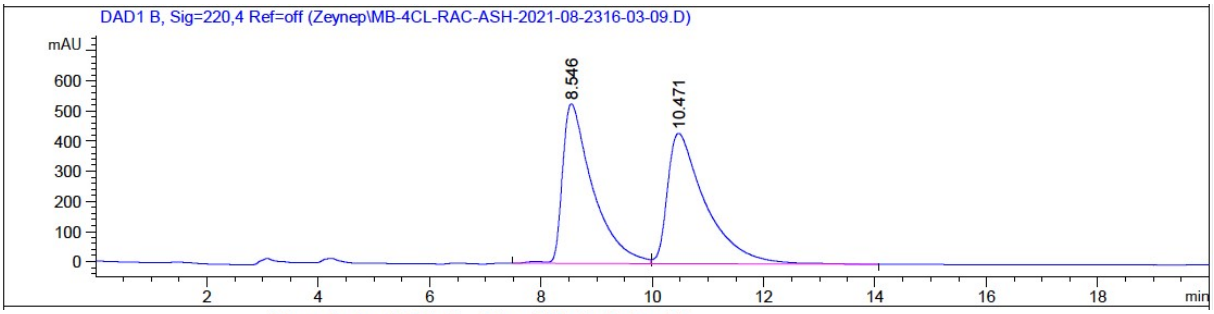



Signal 2: DAD1 B, Sig=220,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.923 | BV E | 0.2055 | 3077.72607 | 233.90144 | 9.3224 |
| 2 | 7.374 | VB R | 0.2371 | 2.99365e4 | 1944.77429 | 90.6776 |
| Totals : | | | | 3.30142e4 | 2178.67574 | |

Figure 62. HPLC Chromatogram of chiral **3aj**

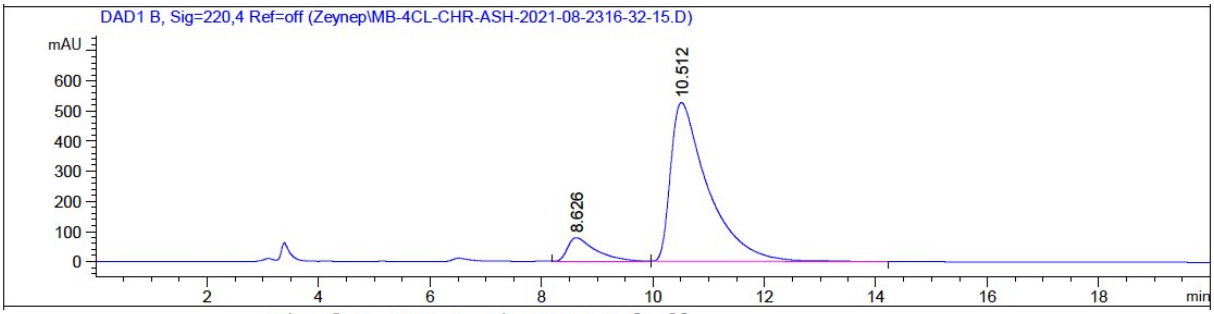



Signal 2: DAD1 B, Sig=220,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.546 | BV | 0.5422 | 2.01092e4 | 529.91113 | 49.4155 |
| 2 | 10.471 | VB | 0.6784 | 2.05849e4 | 433.16159 | 50.5845 |
| Totals : | | | | 4.06941e4 | 963.07272 | |

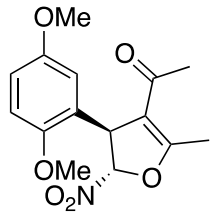
Figure 63. HPLC Chromatogram of racemic **3ak**

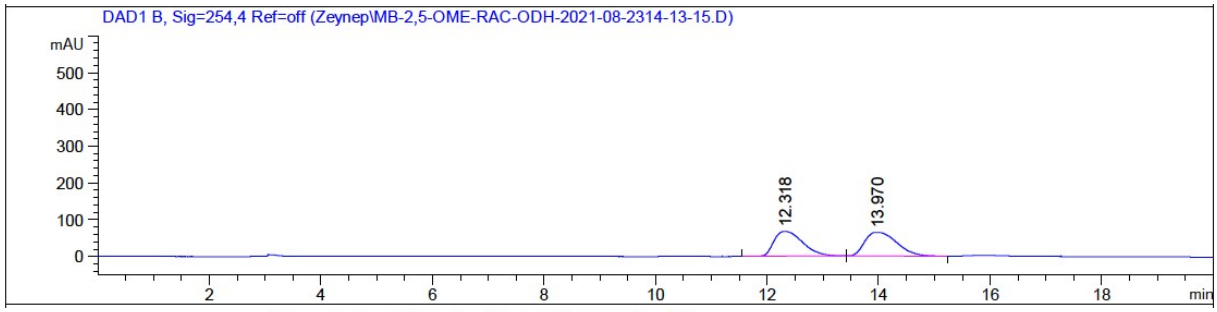



Signal 2: DAD1 B, Sig=220,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 8.626 | BB | 0.4822 | 2730.71338 | 78.42255 | 10.0015 |
| 2 | 10.512 | BB | 0.6584 | 2.45722e4 | 527.11200 | 89.9985 |
| Totals : | | | | 2.73029e4 | 605.53455 | |

Figure 64. HPLC Chromatogram of chiral **3ak**

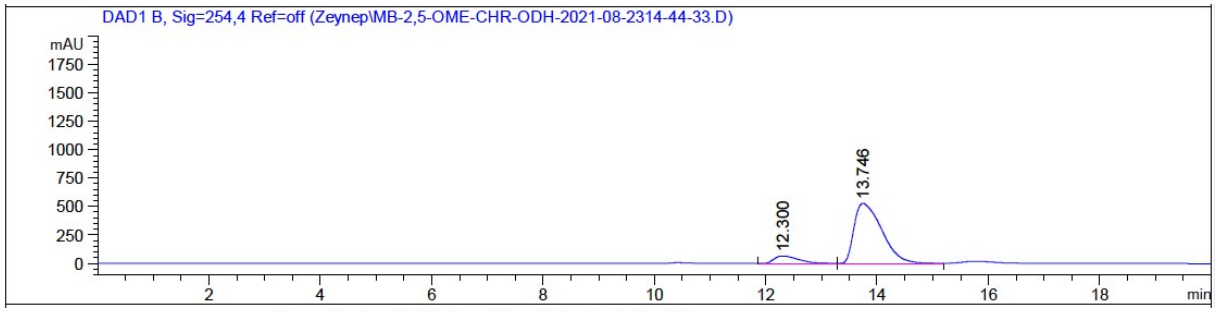



Signal 2: DAD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.318 | BB | 0.5284 | 2446.85742 | 68.15111 | 48.3754 |
| 2 | 13.970 | BB | 0.5463 | 2611.20605 | 65.18950 | 51.6246 |
| Totals : | | | | 5058.06348 | 133.34061 | |

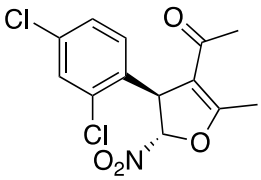
Figure 65. HPLC Chromatogram of racemic **3al**

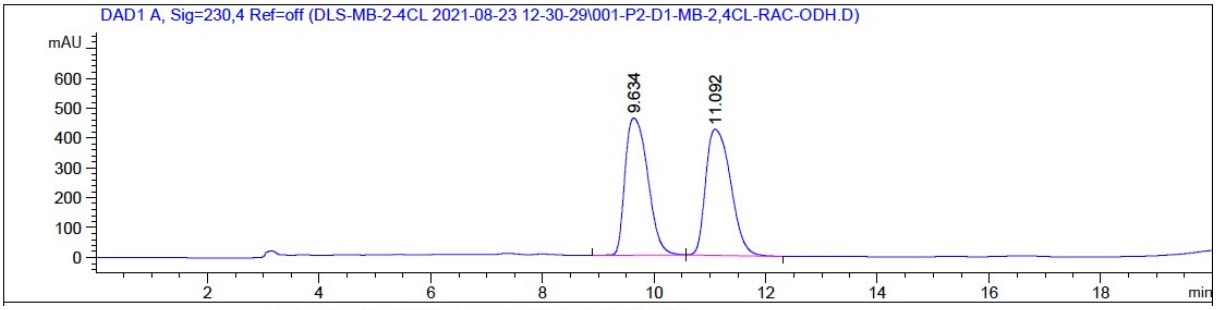



Signal 2: DAD1 B, Sig=254,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 12.300 | BB | 0.4603 | 1976.97620 | 64.90945 | 9.8208 |
| 2 | 13.746 | BB | 0.5518 | 1.81535e4 | 526.46313 | 90.1792 |
| Totals : | | | | 2.01305e4 | 591.37259 | |

Figure 66. HPLC Chromatogram of chiral **3al**

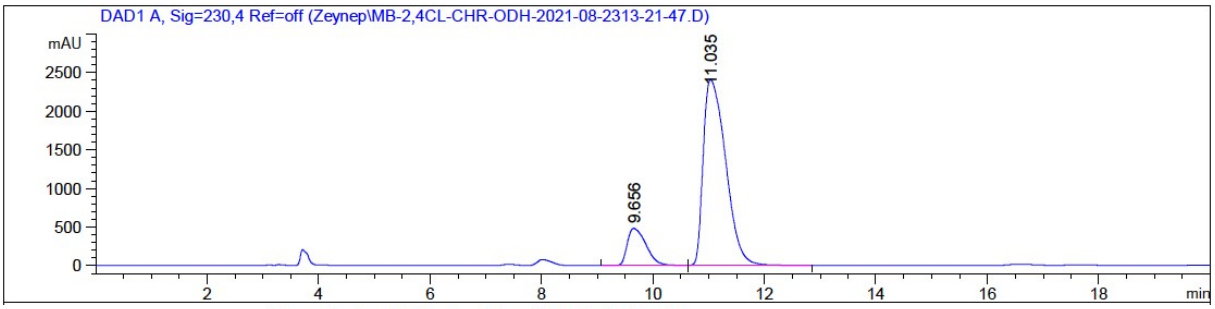



Signal 1: DAD1 A, Sig=230,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.634 | BB | 0.4575 | 1.29292e4 | 458.50415 | 49.7038 |
| 2 | 11.092 | BB | 0.5041 | 1.30833e4 | 421.57480 | 50.2962 |
| Totals : | | | | 2.60125e4 | 880.07895 | |

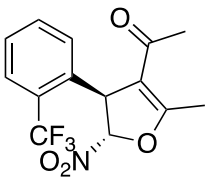
Figure 67. HPLC Chromatogram of racemic **3am**

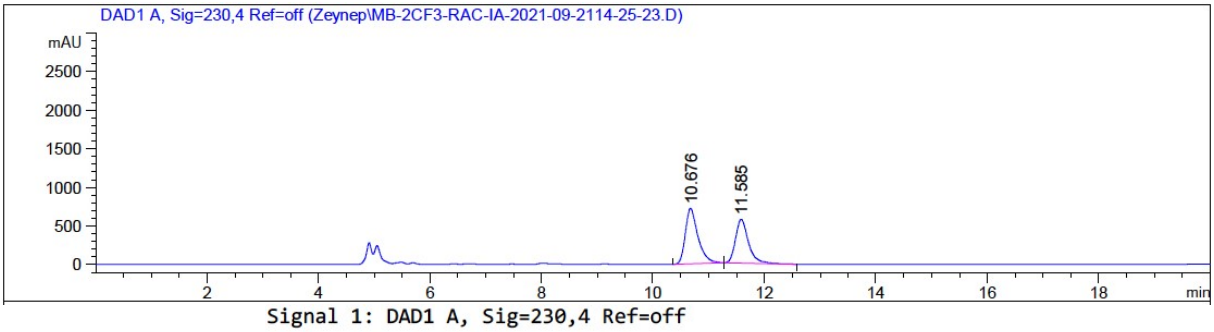



Signal 1: DAD1 A, Sig=230,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 9.656 | BB | 0.3761 | 1.11497e4 | 479.90674 | 14.2402 |
| 2 | 11.035 | BB | 0.3770 | 6.71474e4 | 2406.89673 | 85.7598 |
| Totals : | | | | 7.82970e4 | 2886.80347 | |

Figure 68. HPLC Chromatogram of chiral **3am**

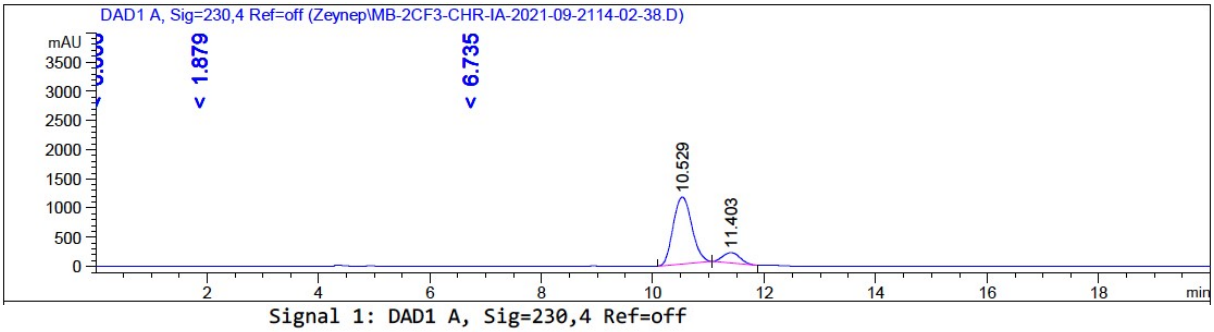



Signal 1: DAD1 A, Sig=230,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.676 | BB | 0.2331 | 1.13124e4 | 718.91040 | 55.1621 |
| 2 | 11.585 | BB | 0.2443 | 9195.13477 | 568.27295 | 44.8379 |
| Totals : | | | | 2.05075e4 | 1287.18335 | |

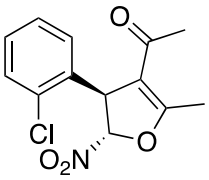
Figure 69. HPLC Chromatogram of racemic **3an**

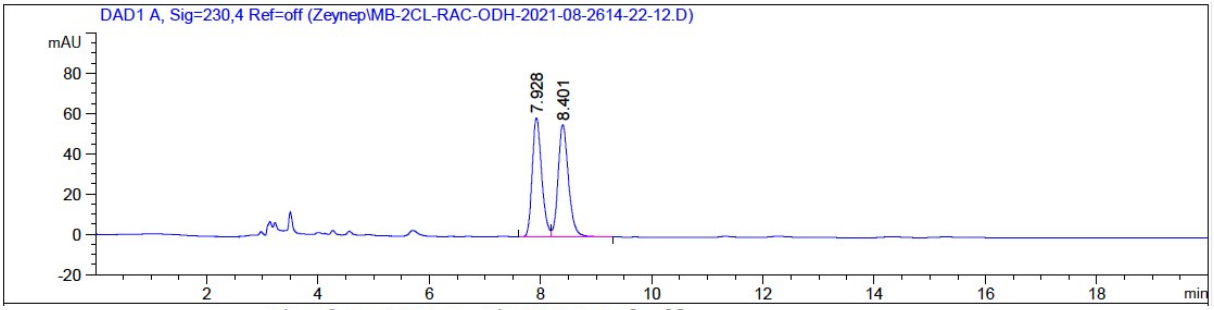



Signal 1: DAD1 A, Sig=230,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 10.529 | BB | 0.3704 | 2.66403e4 | 1147.29211 | 87.4757 |
| 2 | 11.403 | BB | 0.3440 | 3814.21533 | 179.10402 | 12.5243 |
| Totals : | | | | 3.04545e4 | 1326.39613 | |

Figure 70. HPLC Chromatogram of chiral **3an**

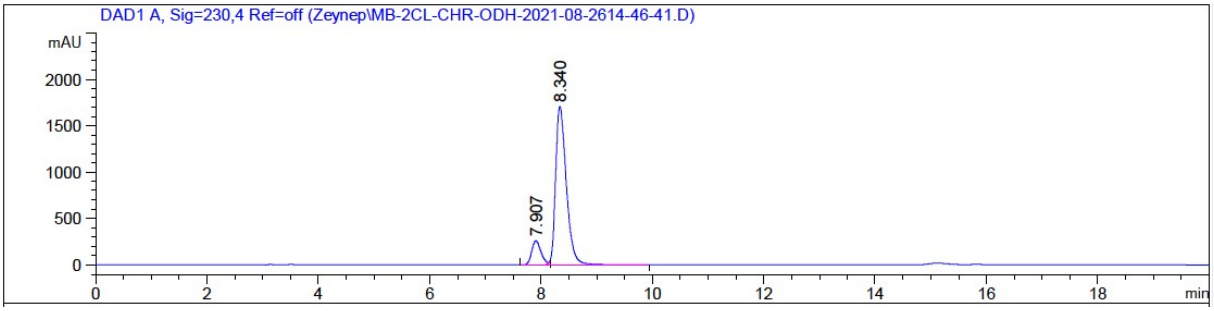



Signal 1: DAD1 A, Sig=230,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.928 | BV | 0.1808 | 699.05145 | 59.17958 | 48.9920 |
| 2 | 8.401 | VB | 0.2002 | 727.81763 | 55.80560 | 51.0080 |
| Totals : | | | | 1426.86908 | 114.98518 | |

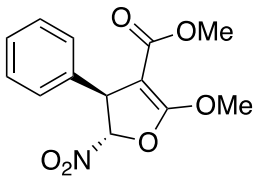
Figure 71. HPLC Chromatogram of racemic **3ao**




Signal 1: DAD1 A, Sig=230,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 7.907 | BV E | 0.1784 | 2986.86621 | 259.20132 | 11.6023 |
| 2 | 8.340 | VB R | 0.2047 | 2.27570e4 | 1704.90503 | 88.3977 |
| Totals : | | | | 2.57438e4 | 1964.10635 | |

Figure 72. HPLC Chromatogram of chiral **3ao**



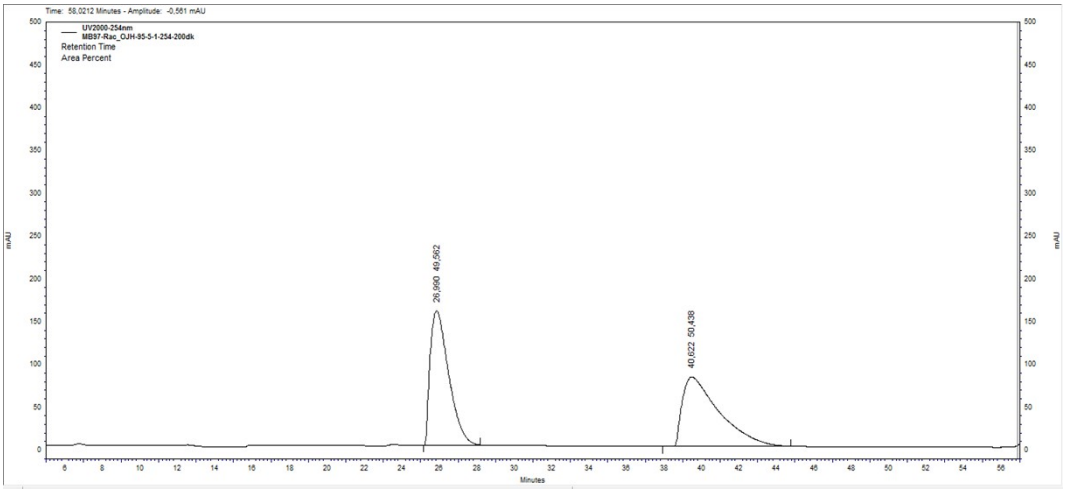




Figure 73. HPLC Chromatogram of racemic **3ba**

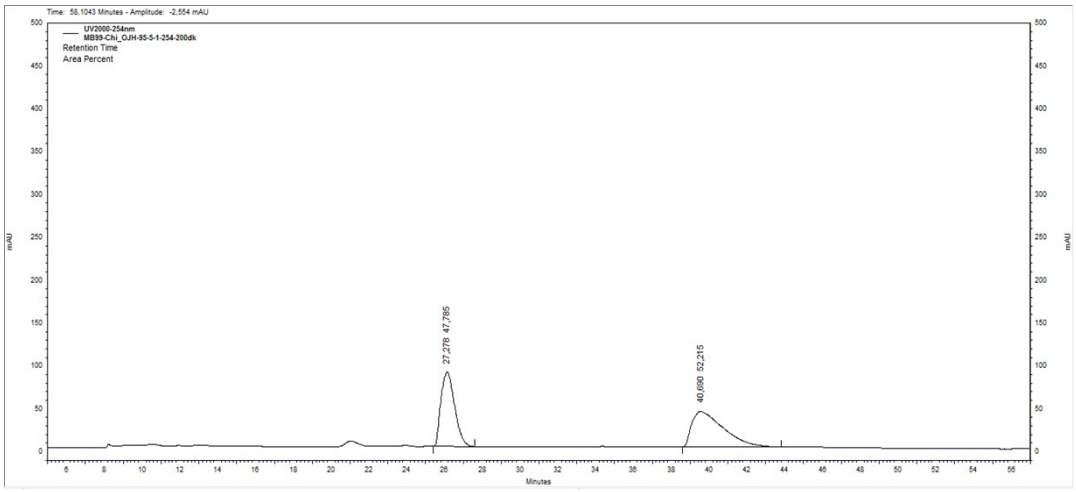
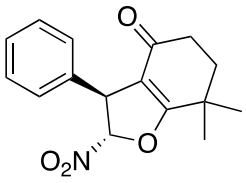



Figure 74. HPLC Chromatogram of chiral **3ba**



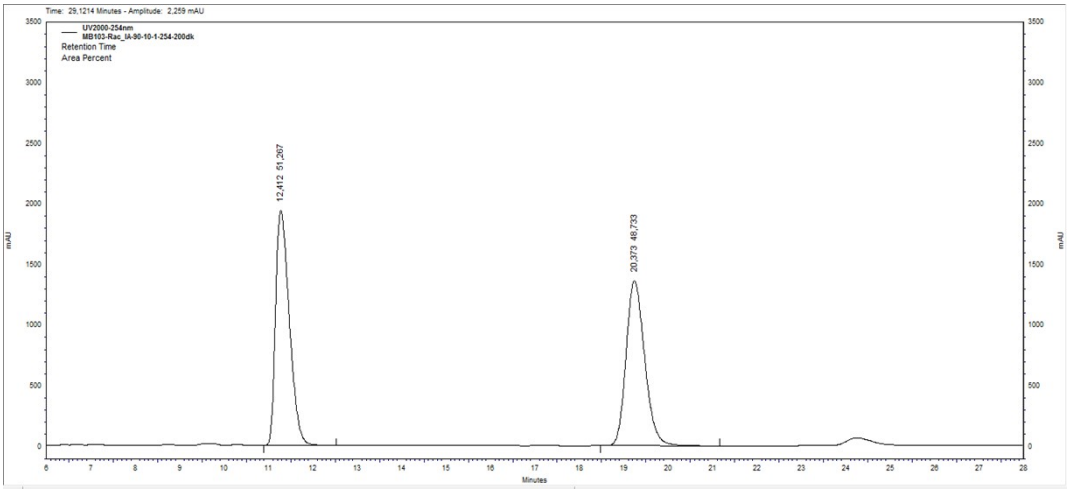




Figure 75. HPLC Chromatogram of racemic **3ca**

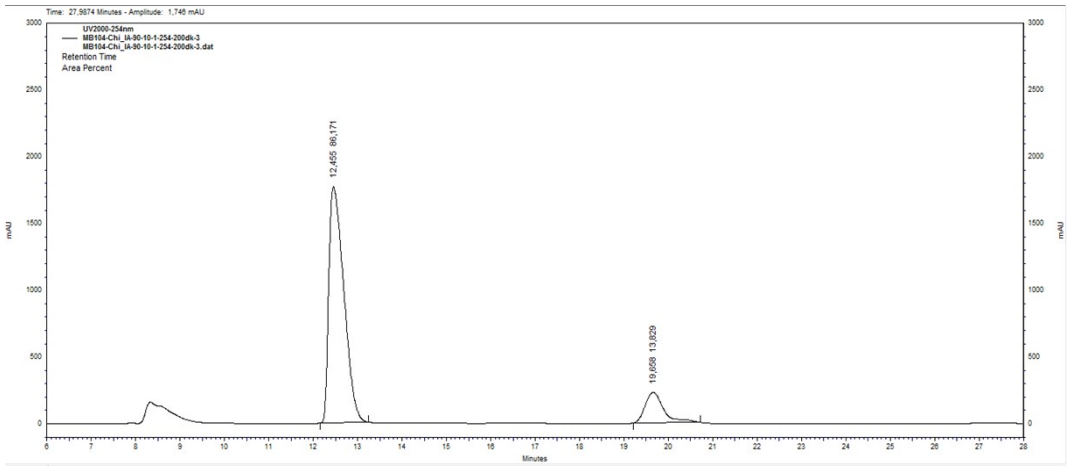
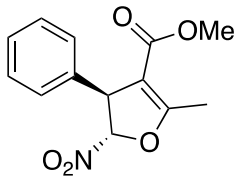



Figure 76. HPLC Chromatogram of chiral **3ca**



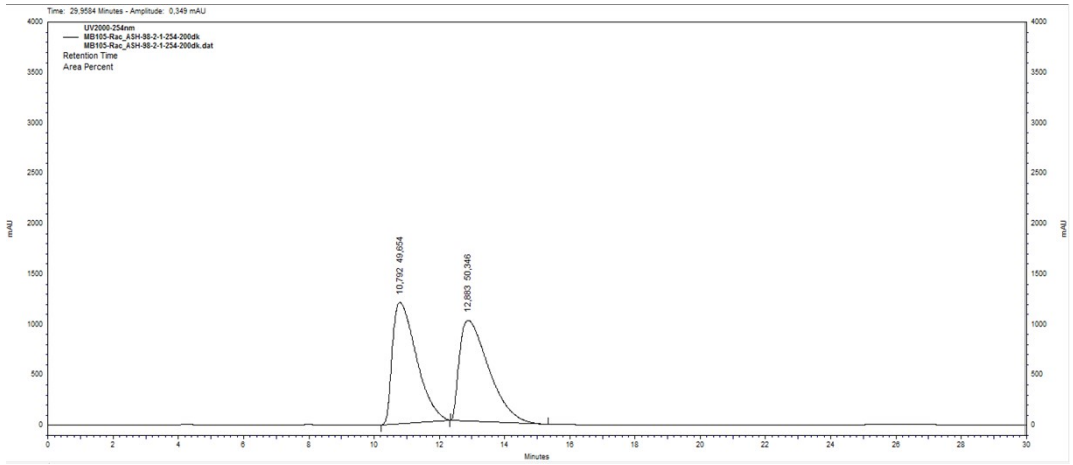




Figure 77. HPLC Chromatogram of racemic **3da**

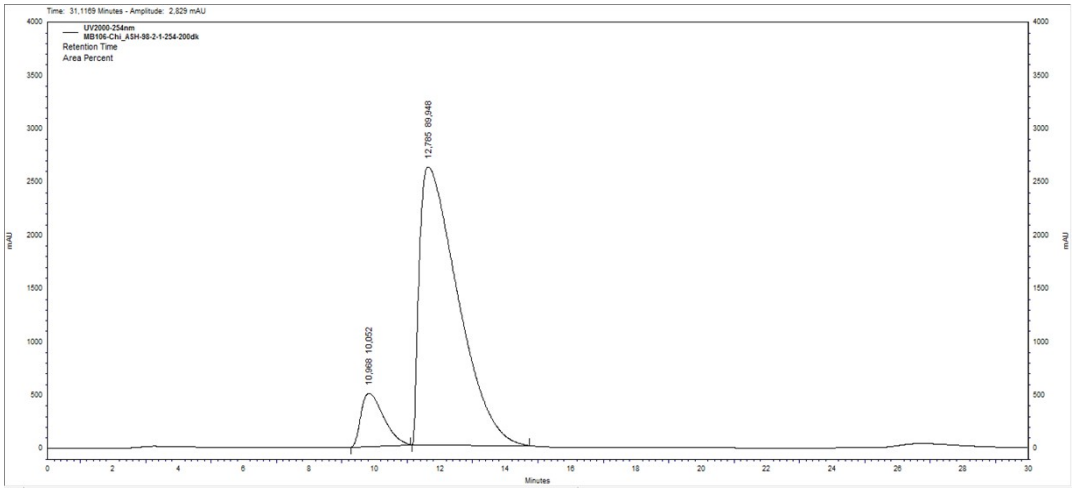
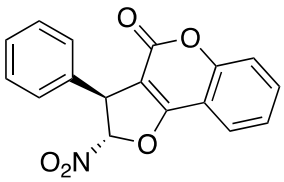



Figure 78. HPLC Chromatogram of chiral **3da**



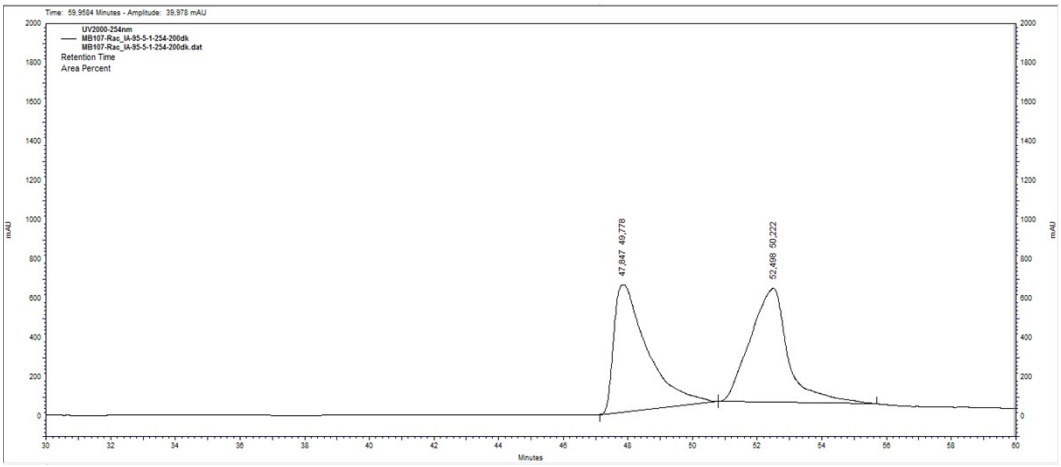




Figure 79. HPLC Chromatogram of racemic **3ea**

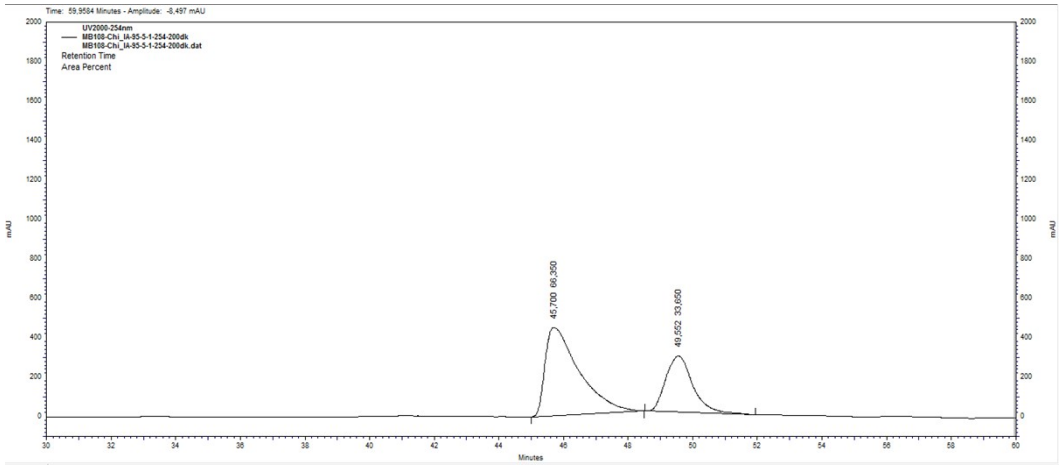
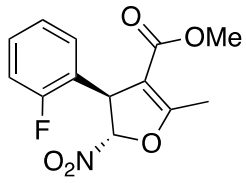
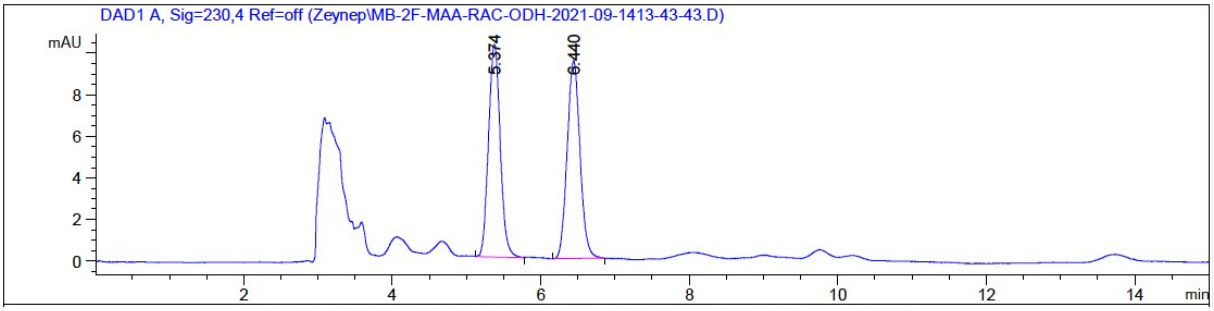


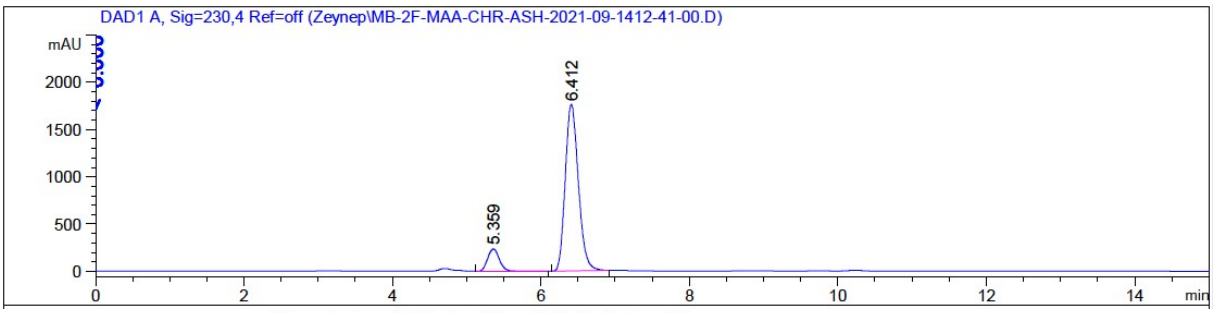

Figure 80. HPLC Chromatogram of chiral **3ea**




| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.374 | BB | 0.1696 | 111.83317 | 10.22275 | 49.3704 |
| 2 | 6.440 | BB | 0.1779 | 114.68555 | 9.52993 | 50.6296 |
| Totals : | | | | 226.51871 | 19.75268 | |

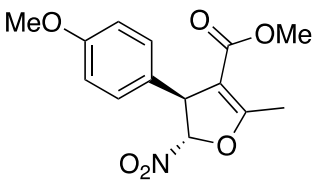
Figure 81. HPLC Chromatogram of racemic **3db**

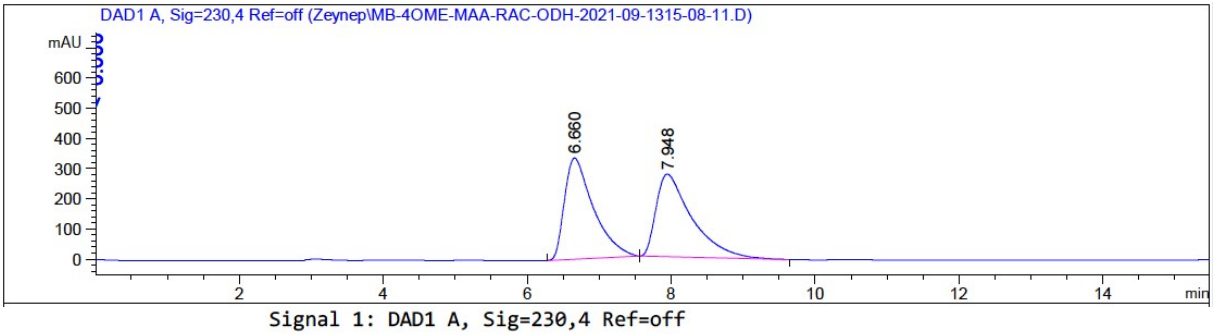



Signal 1: DAD1 A, Sig=230,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 5.359 | BB | 0.1794 | 2638.89746 | 234.37566 | 10.8762 |
| 2 | 6.412 | BB | 0.2003 | 2.16242e4 | 1747.75439 | 89.1238 |
| Totals : | | | | 2.42631e4 | 1982.13005 | |

Figure 82. HPLC Chromatogram of chiral **3db**

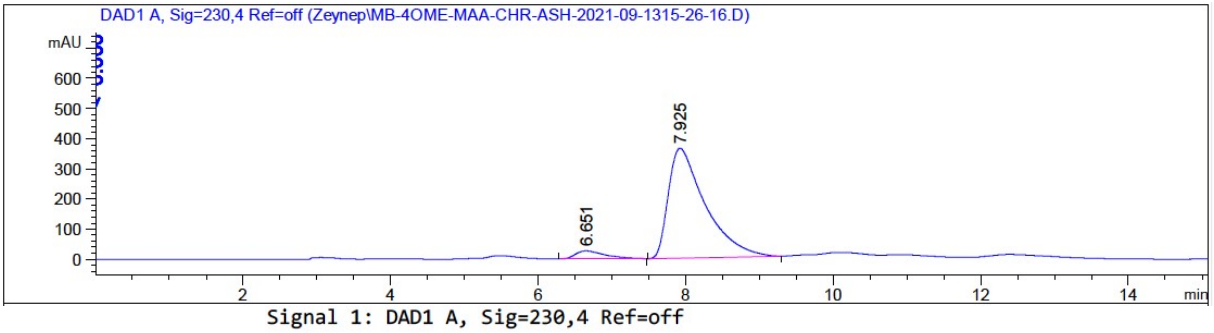



Signal 1: DAD1 A, Sig=230,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.660 | BB | 0.4105 | 9368.52441 | 335.32416 | 49.7533 |
| 2 | 7.948 | BB | 0.5002 | 9461.42090 | 274.08835 | 50.2467 |
| Totals : | | | | 1.88299e4 | 609.41251 | |

Figure 83. HPLC Chromatogram of racemic **3de**




Signal 1: DAD1 A, Sig=230,4 Ref=off

| Peak # | RetTime [min] | Type | Width [min] | Area [mAU*s] | Height [mAU] | Area % |
|---|---|---|---|---|---|---|
| 1 | 6.651 | BB | 0.3896 | 720.57434 | 26.51239 | 5.3963 |
| 2 | 7.925 | BB | 0.5021 | 1.26325e4 | 363.81625 | 94.6037 |
| Totals : | | | | 1.33531e4 | 390.32864 | |

Figure 84. HPLC Chromatogram of chiral **3de**

# 3. X-Ray Crystallography

**Crystal structure determination**

Single crystal X-ray diffraction data for (*Z*)-1-(2-bromo-2-nitrovinyl)-4-methylbenzene ($C_9H_8BrNO_2$) (**1**) and 1-((4*S*,5*S*)-2-methyl-5-nitro-4-phenyl-4,5-dihydrofuran-3-yl)ethan-1-one ($C_{13}H_{13}NO_4$) (**2**) compounds were collected at room temperature on a Rigaku R-AXIS RAPID diffractometer equipped with an imaging plate area detector using graphite monochromated Mo-Kα radiation (λ = 0.71075 Å). The crystal structures were solved by means of direct methods and refined with full-matrix least-squares on Olex 2-1.2 [1, 2].

Non-hydrogen atoms were refined anisotropically while hydrogen atoms were positioned with an idealized geometry and refined using a riding model. Crystal data, data collection, and refinement parameters for (**1**) and (**2**) are listed in Table 1. The Ortep-3 [3] diagrams of both compounds with thermal ellipsoids at the 50% probability level are shown in Figures 83 and 84 for (**1**) and (**2**), respectively. The crystal packings of both compounds projected onto the *bc* plane for (**1**) and the *ab* plane for (**2**) figures were prepared with the use of Mercury visualization software [4] and are shown in Figures 85 and 86 for (**1**) and (**2**), respectively. The selected bond lengths, bond angles and torsion angles of both compounds are reported in Table 2 for (**1**) and Table 3 for (**2**). CCDC 1957076–1957077 contain the supplementary crystallographic data for (**1**) and (**2**), respectively.

**References:**

1. O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann. *J. Appl. Cryst.*, **42**, 339 (2009).

2. G.M. Sheldrick. *Acta Cryst.*, **64**, 112 (2008).

3. Farrugia, L. J. (**2012**). ‘‘WinGX and ORTEP for Windows: an update,’’ J. Appl. Cryst. **45**, 849-854.

4. Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M., van de Streek, J. (**2006**). ‘‘Mercury: visualization and analysis of crystal structures’’, J. Appl. Cryst., **39**, 453-457.

**Table 1** Experimental details

| Crystal data | (**1**) | (**2**) |
|---|---|---|
| Chemical formula | $C_9H_8BrNO_2$ | $C_{13}H_{13}NO_4$ |
| $M_r$ | 242.07 | 247.24 |
| $D_{calc}$ (g cm$^{-3}$) | 1.679 | 1.314 |
| Crystal system, space group | Monoclinic, $P2_1/a$ | Triclinic, $P$-1 |
| Temperature (K) | 293(2) | 293(2) |
| $a$, $b$, $c$ (Å) | 6.8836(13), 14.397(3), 9.6929(19) | 7.4498(3), 8.4498(4), 11.1317(8) |
| α, β, γ (°) | 90, 94.332(7), 90 | 107.098(8), 91.985(7), 109.401(8) |
| $V$ (Å$^3$) | 957.8(3) | 624.89(8) |
| $Z$ | 4 | 2 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| μ (mm$^{-1}$) | 4.26 | 0.10 |
| No. of measured reflections | 24386 | 16255 |
| Refinement | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.065, 0.183, 1.00 | 0.049, 0.137, 1.03 |
| No. of reflections | 2379 | 3088 |
| No. of parameters | 119 | 165 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.29, −0.77 | 0.25, −0.28 |

Computer programs: *SHELXS (Sheldrick, 2008), SHELXL2018/3 (Sheldrick, 2018), Olex2 (Dolomanov et al., 2009)*.

**Table 2** Selected geometric parameters (Å, º) for (**1**)

| | | | |
|---|---|---|---|
| Br1—C9 | 1.845(4) | O2—N1 | 1.207(5) |
| O1—N1 | 1.206(5) | N1—C9 | 1.497(5) |
| O1—N1—O2 | 124.6(4) | C8—C9—N1 | 118.5(4) |
| O1—N1—C9 | 117.5(4) | C8—C9—Br1 | 129.0(3) |
| O2—N1—C9 | 117.9(4) | N1—C9—Br1 | 112.5(3) |
| O2—N1—C9—Br1 | −172.7(4) | C9—C8—C5—C6 | 173.3(5) |
| C4—C3—C2—C1 | 179.9(5) | | |

**Table 3** Selected geometric parameters (Å, º) for (**2**)

| | | | |
|---|---|---|---|
| O1—C9 | 1.3838(16) | O3—N1 | 1.215(2) |
| O1—C10 | 1.3976(17) | O4—N1 | 1.199(2) |
| O2—C12 | 1.2206(18) | N1—C10 | 1.539(2) |
| C10—O1—C9 | 107.88(10) | C11—C9—C8 | 133.53(13) |
| O4—N1—O3 | 124.41(17) | N1—C10—O1 | 108.82(12) |
| C10—N1—O3 | 115.46(14) | C7—C10—O1 | 107.59(11) |
| C10—N1—O4 | 120.09(16) | C7—C10—N1 | 108.01(11) |
| C8—C9—O1 | 112.41(12) | C8—C12—O2 | 121.50(13) |
| C11—C9—O1 | 113.99(12) | C13—C12—O2 | 120.79(13) |
| C7—C4—C5—C6 | −178.3(1) | C7—C8—C12—O2 | −174.1(1) |
| O3—N1—C10—O1 | 169.3(2) | C9—C8—C12—C13 | −173.0(1) |
| O4—N1—C10—C7 | 103.5(2) | C7—C8—C9—C11 | −172.0(2) |
| C4—C7—C10—O1 | −101.8(1) | | |

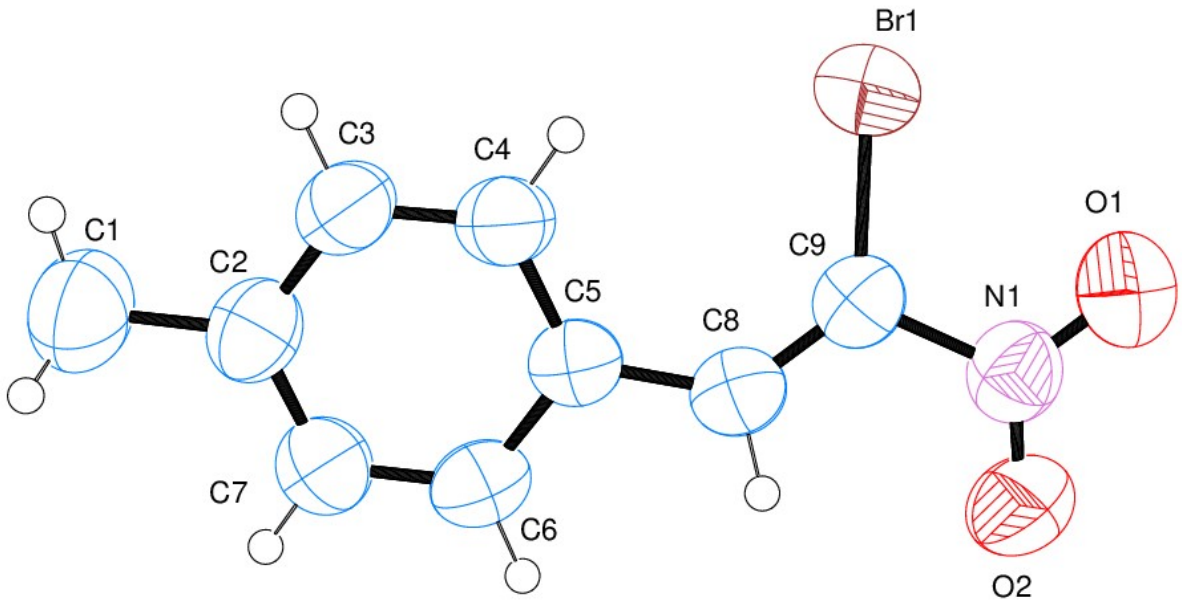



Figure 85. Ortep diagram of (**1**) Thermal ellipsoids are shown at the 50% probability level.

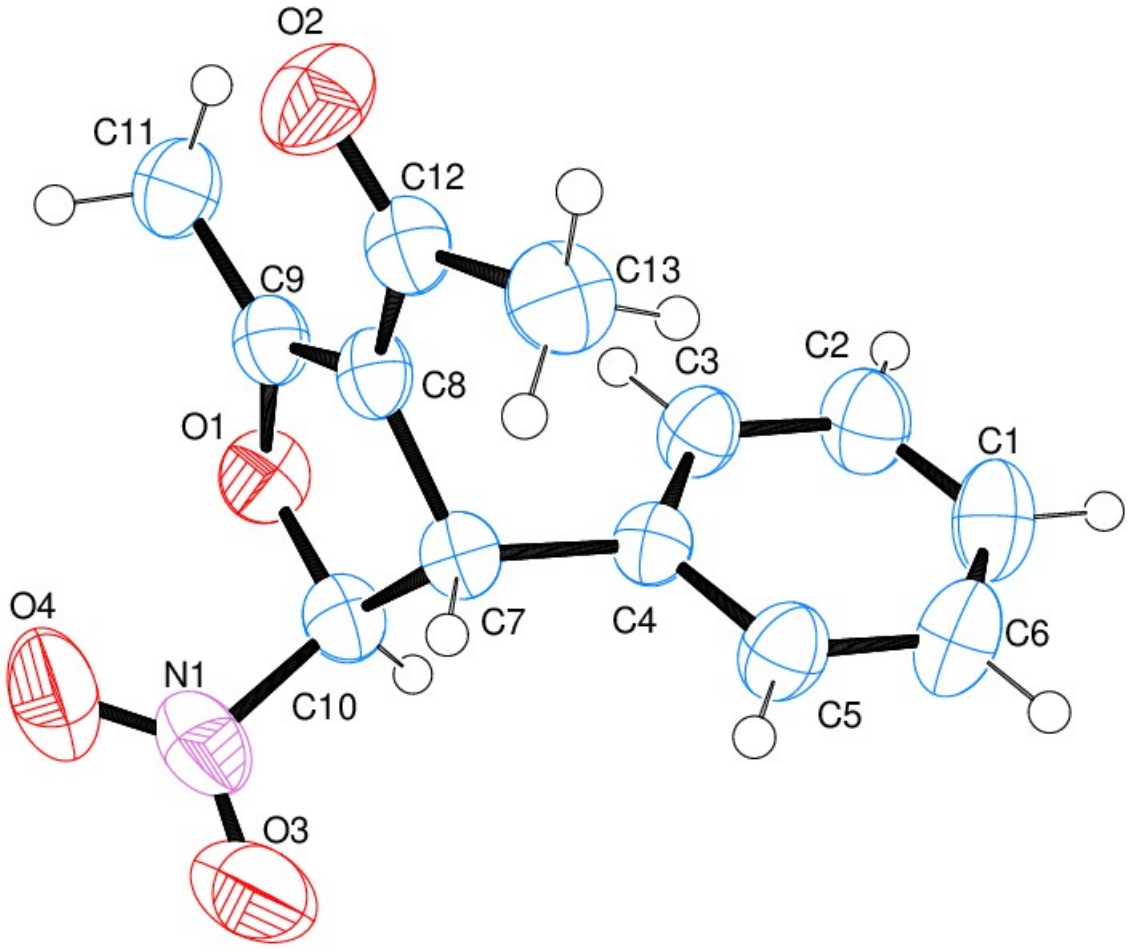



Figure 86. Ortep diagram of (**2**) Thermal ellipsoids are shown at the 50% probability level.

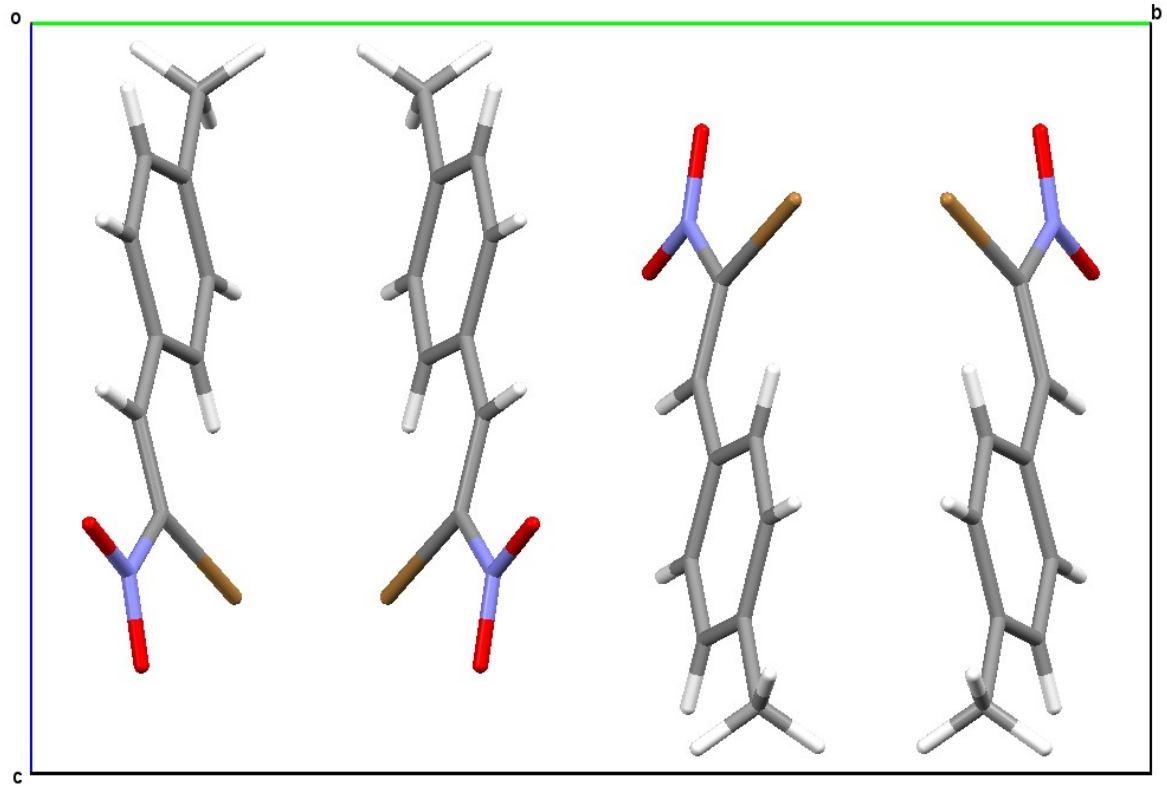



Figure 87. Crystal packing of (**1**) projected onto the *bc* plane

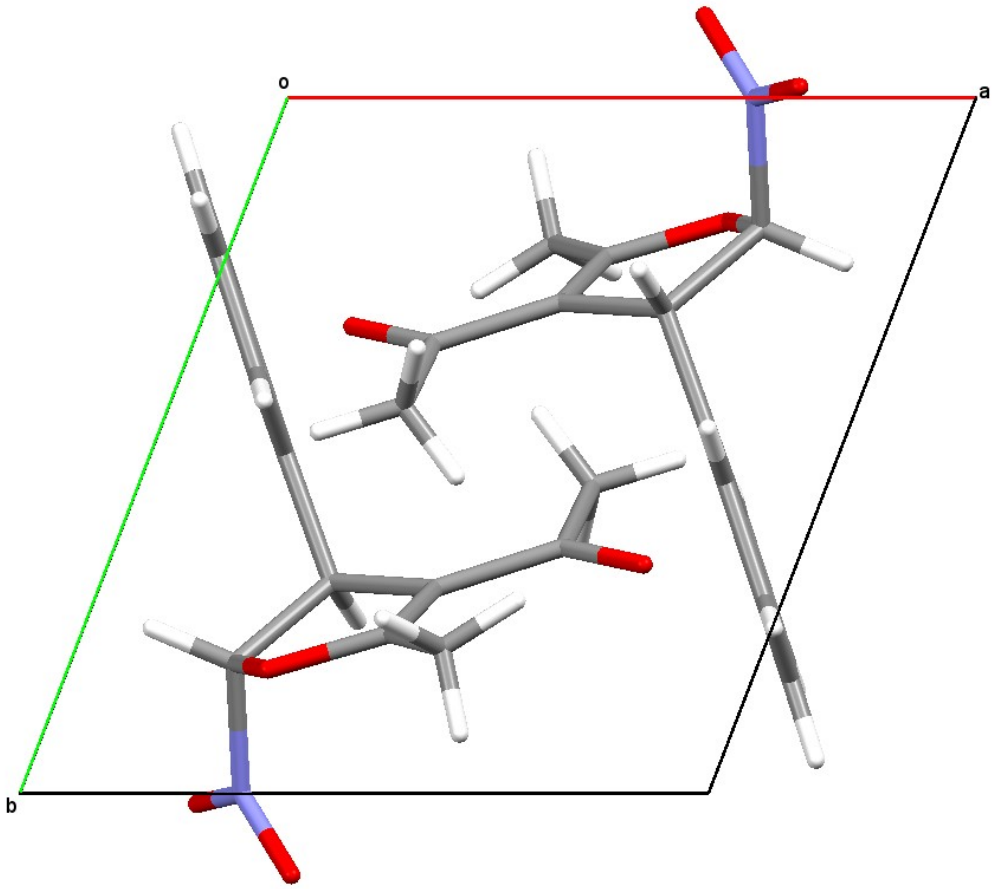



Figure 88. Crystal packing of (**2**) projected onto the *ab* plane