

Supporting Information

Enantioselective Mannich Reaction between Rhodanines and Isatin-Derived Ketimines to Construct Vicinal Quaternary Stereocenters

Han Xu, Tian-Chen Kang, Feng Sha, Xin-Yan Wu*

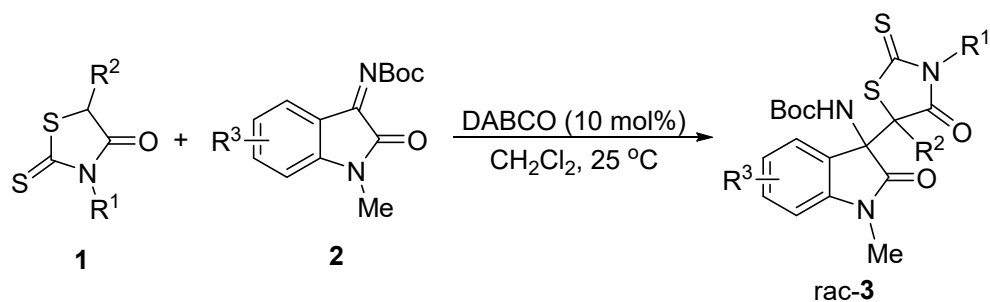
*Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of
Chemistry & Molecular Engineering, East China University of Science and
Technology, Shanghai 200237, P. R. China*

xinyanwu@ecust.edu.cn

Table of Contents

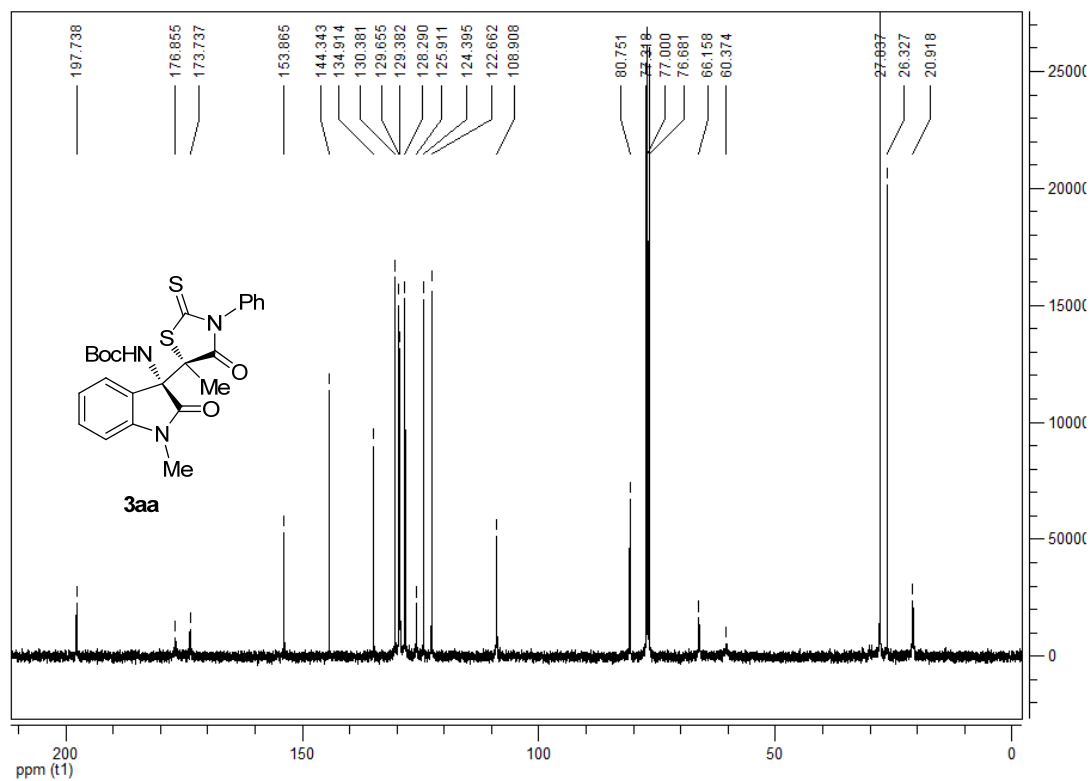
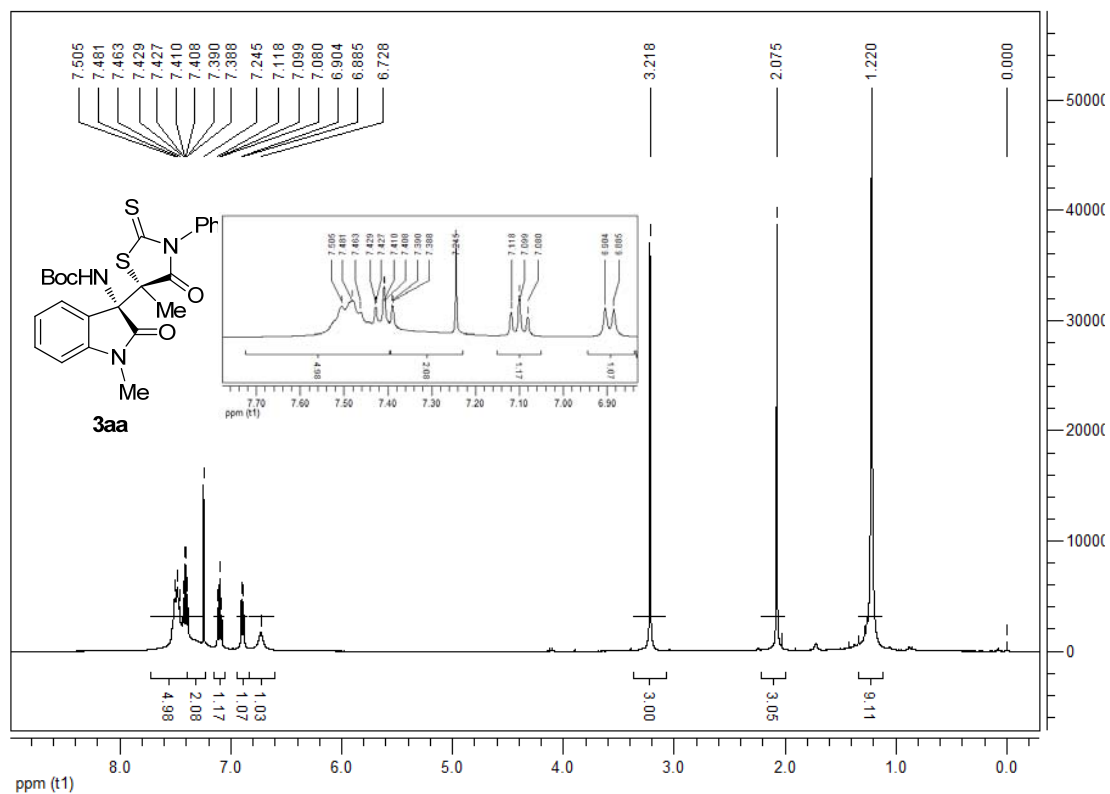
| | |
|---|-----------|
| 1. General Procedure for the Preparation of the Racemic Products | 2 |
| 2. Copies of NMR Spectra of the Products | 3 |
| 3. Copies of HPLC Spectra of the Products | 24 |
| 4. X-ray Analysis of Product 3ba | 45 |
| 5. CD Spectra of the Products | 47 |

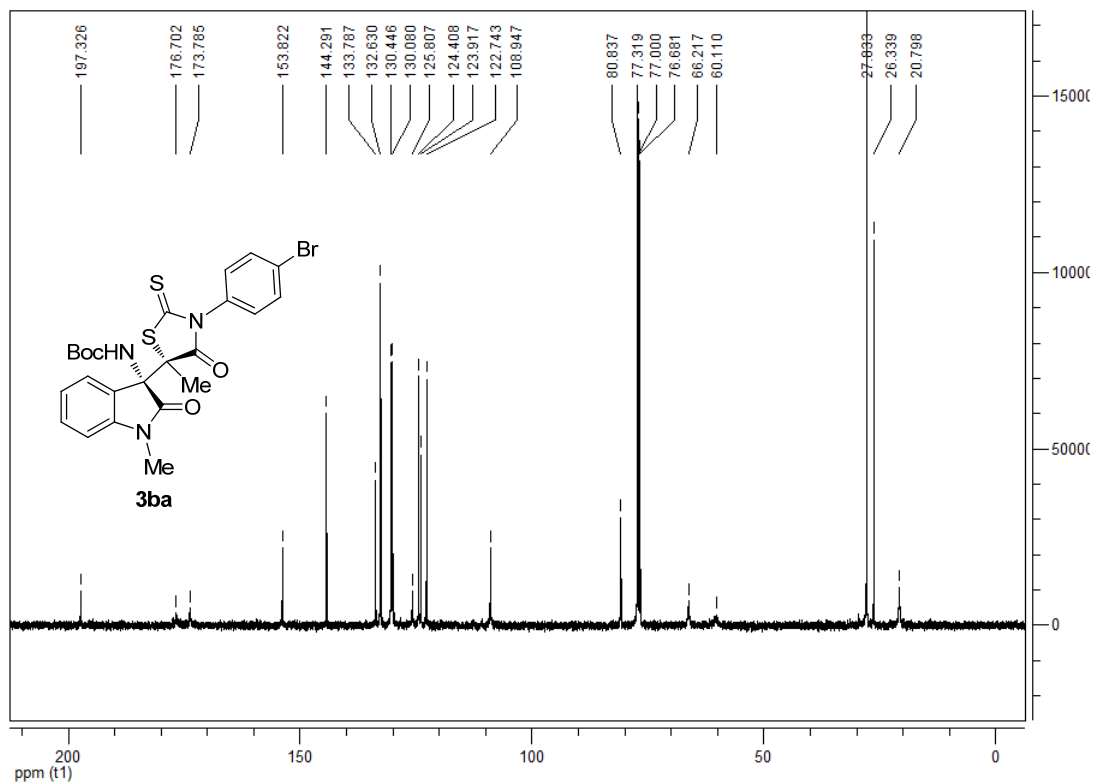
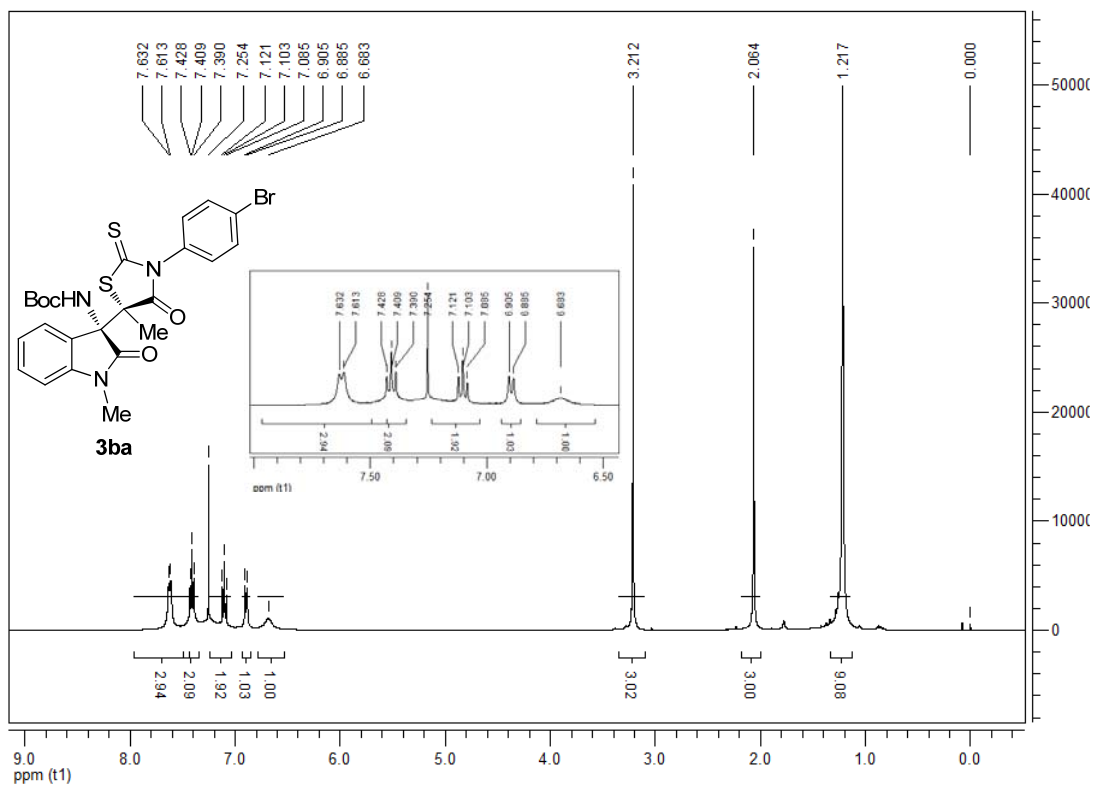
1. General Procedure for the Preparation of the Racemic Products

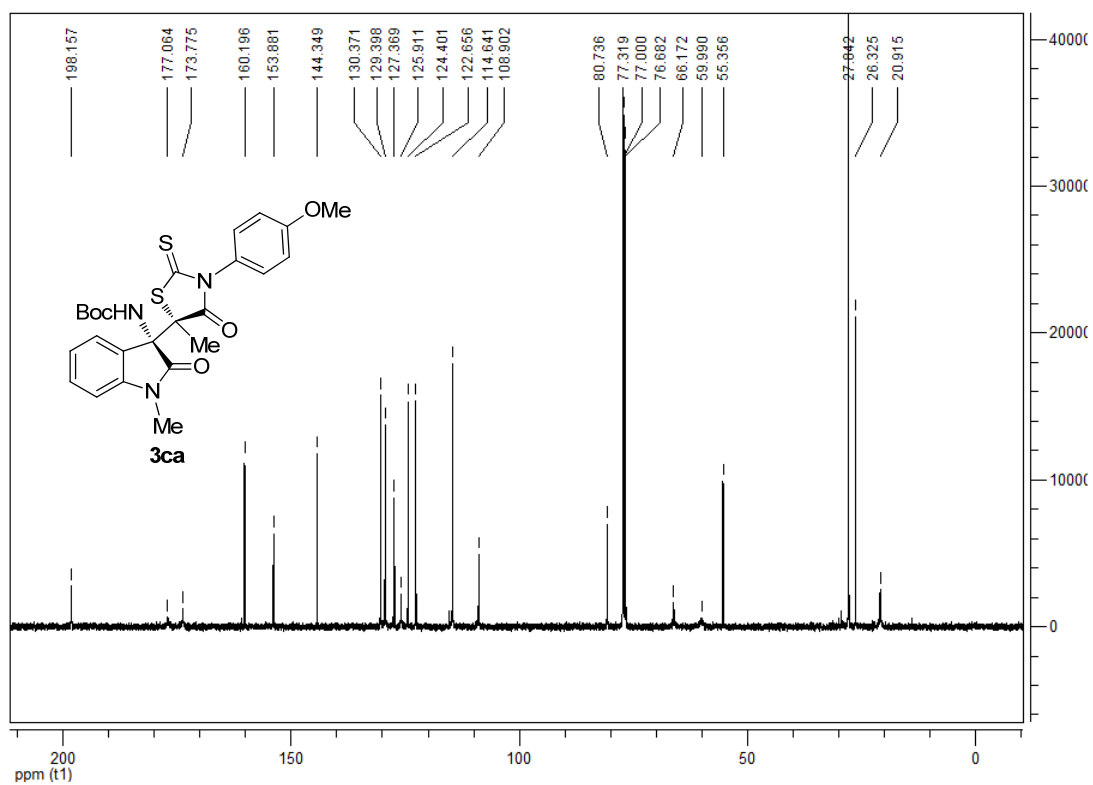
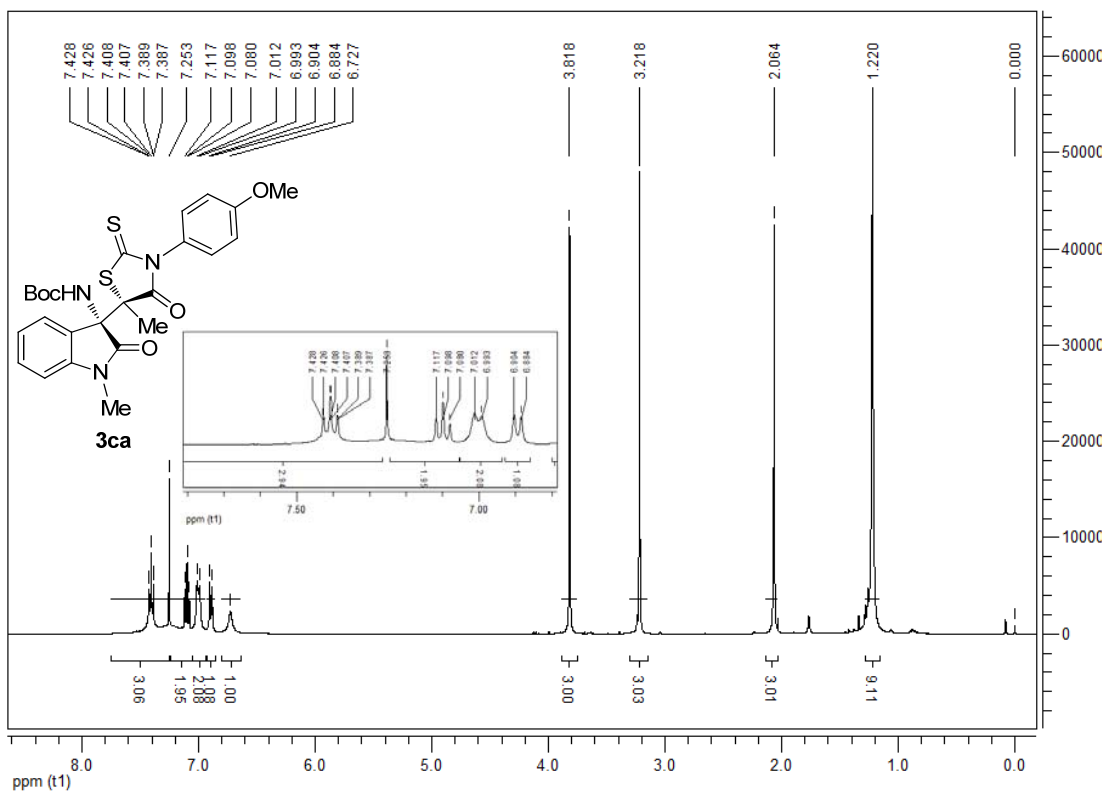


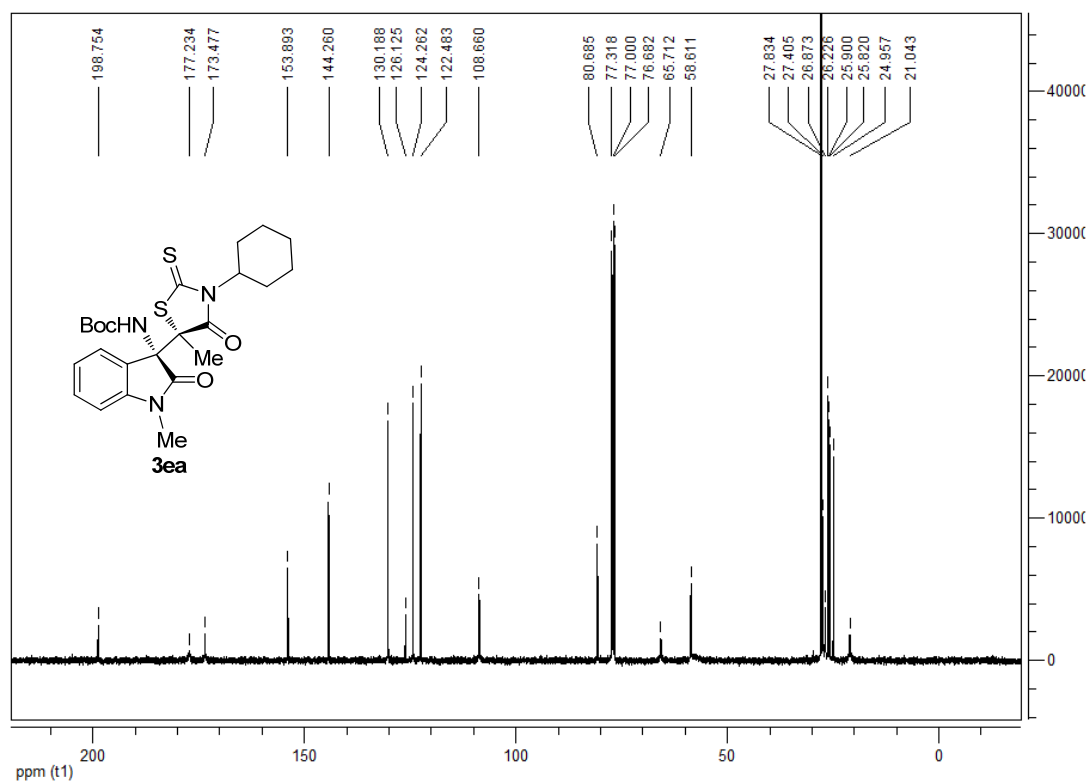
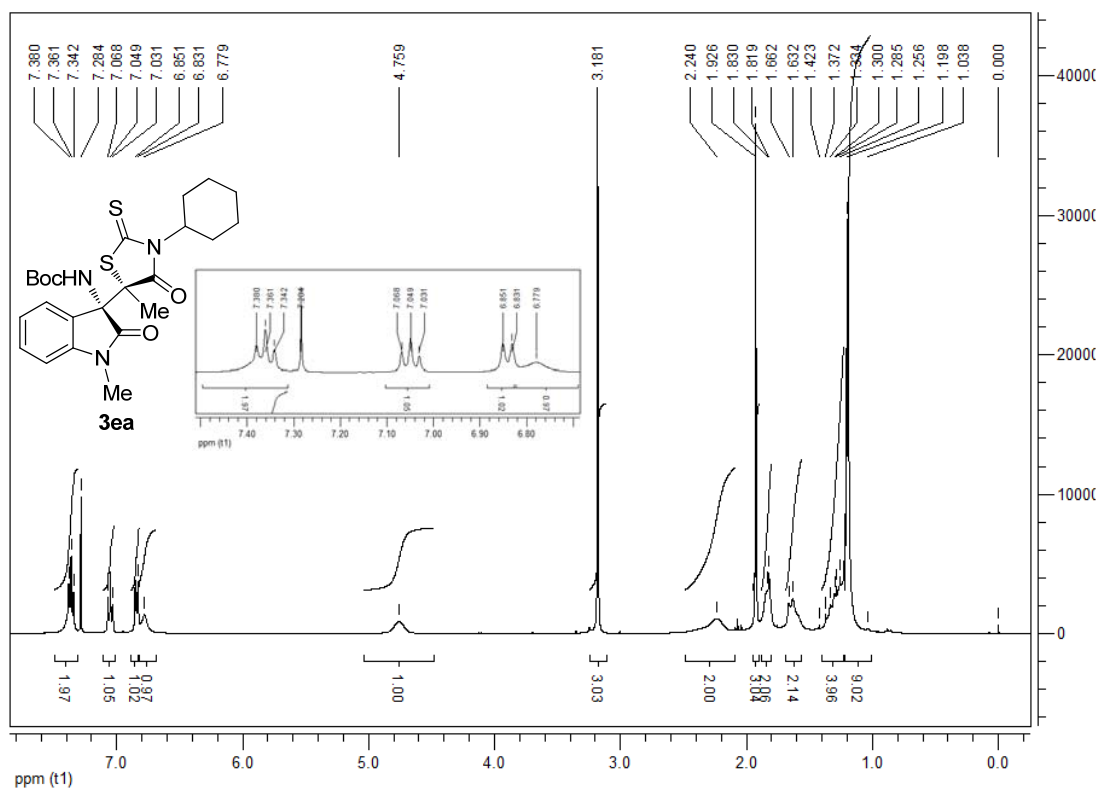
To a solution of rhodanine **1** (0.24 mmol) and DABCO (0.02 mmol, 10 mol%) in 1 mL of CH₂Cl₂ was added isatin-derived ketimine **2** (0.2 mmol) at 25 °C, then the resulting mixture was stirred at this temperature until the reaction completed (monitored by TLC). The solvent was concentrated under reduced pressure and the residue was purified by column chromatography (6:1 petroleum ether/ethyl acetate) to give the racemic product **rac-3**.

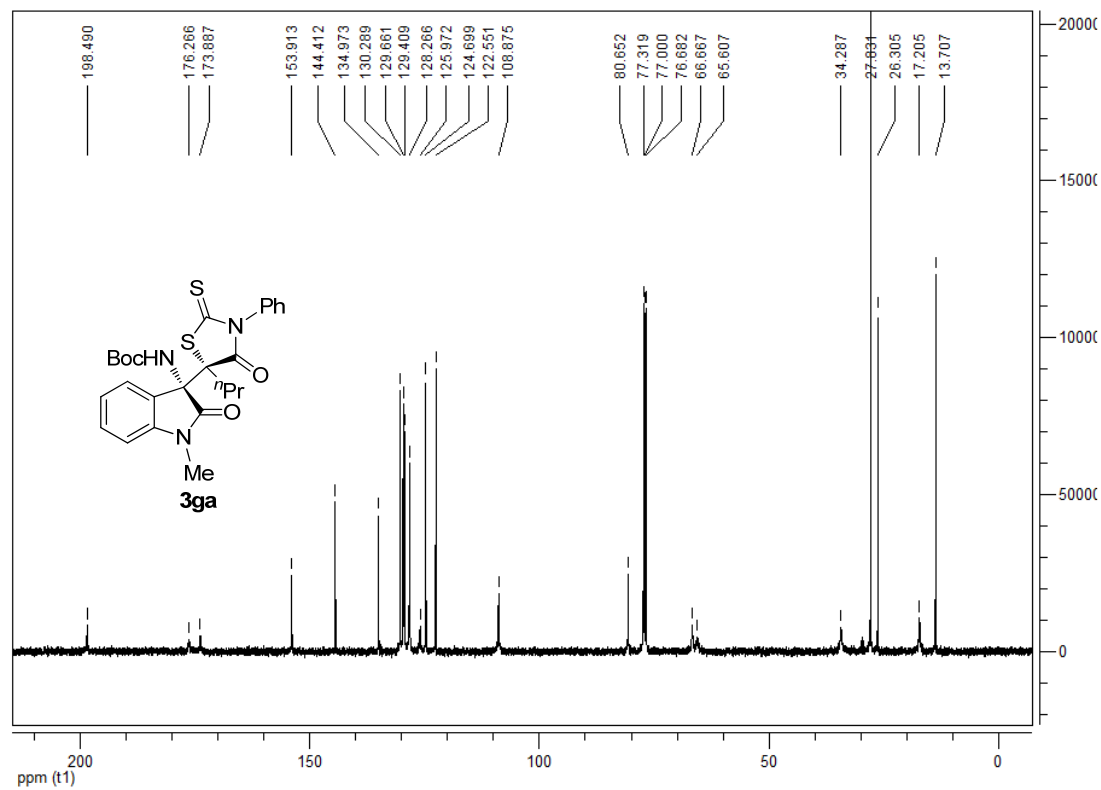
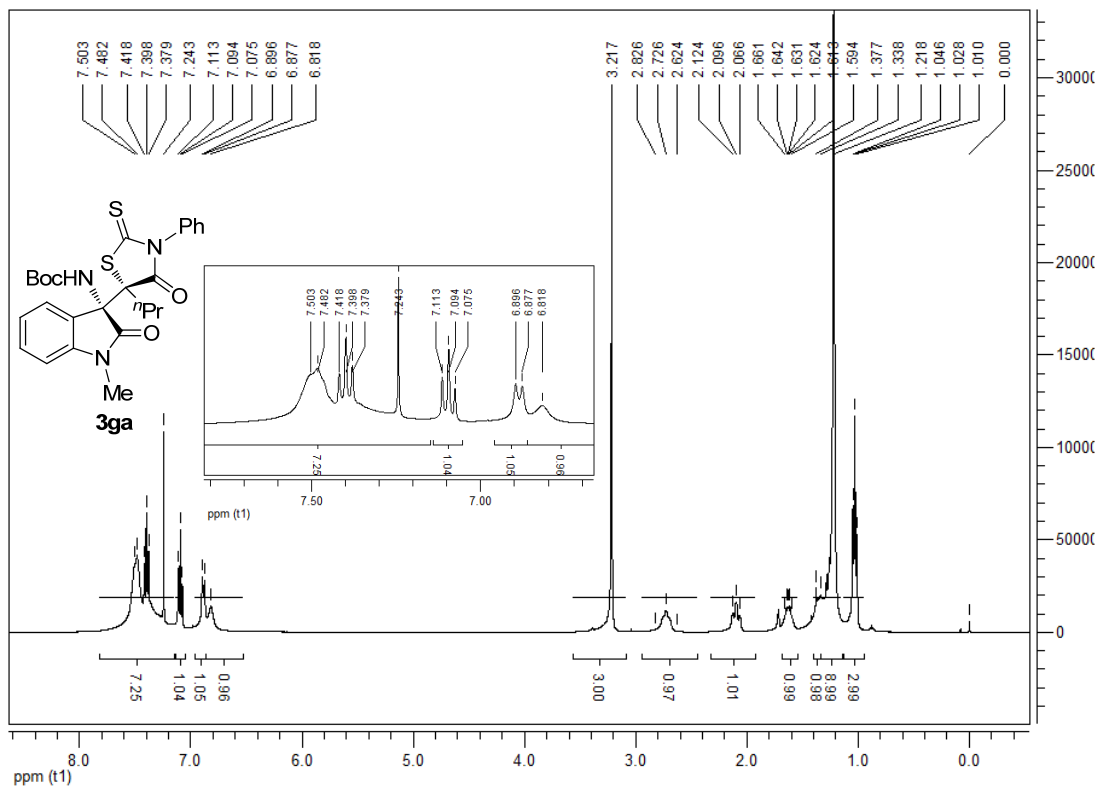
2. Copies of NMR Spectra of the Products

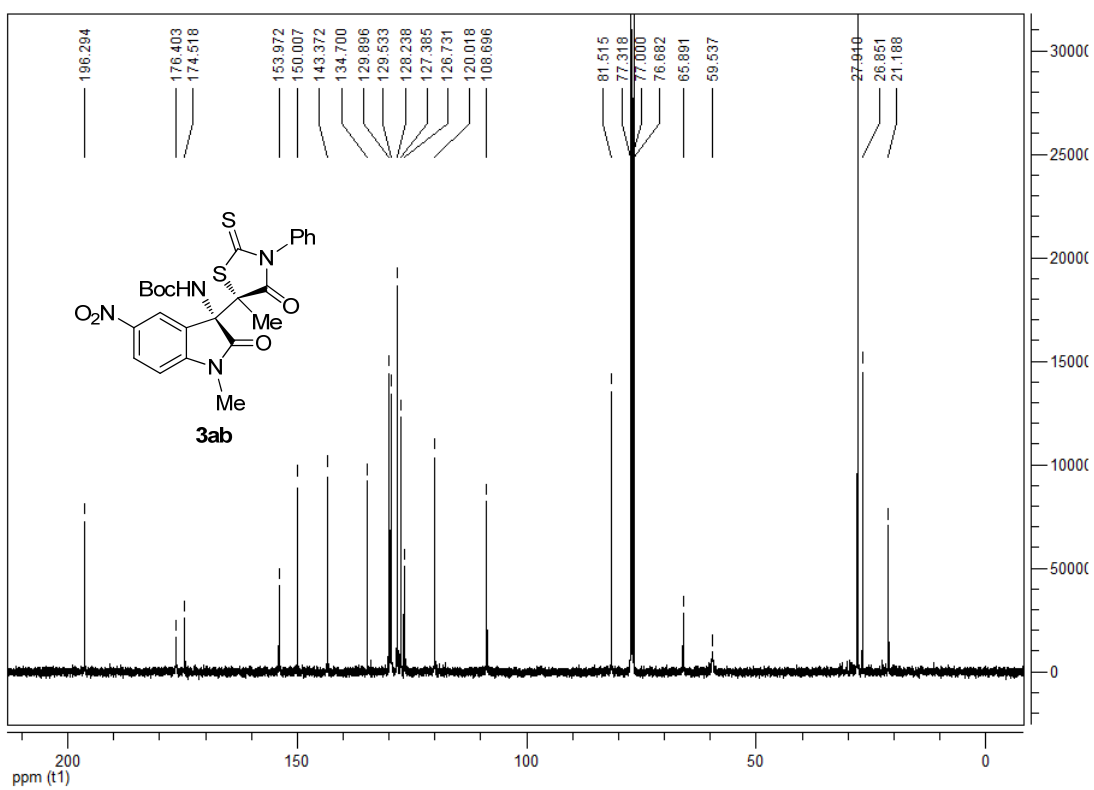
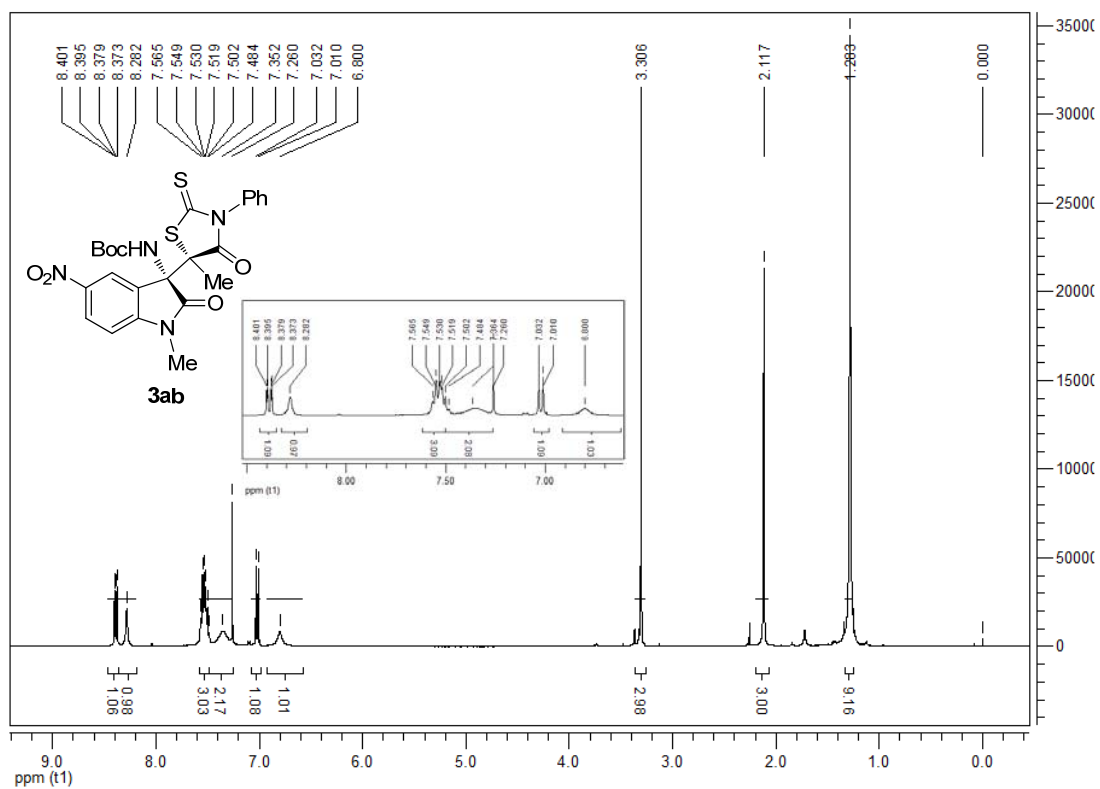


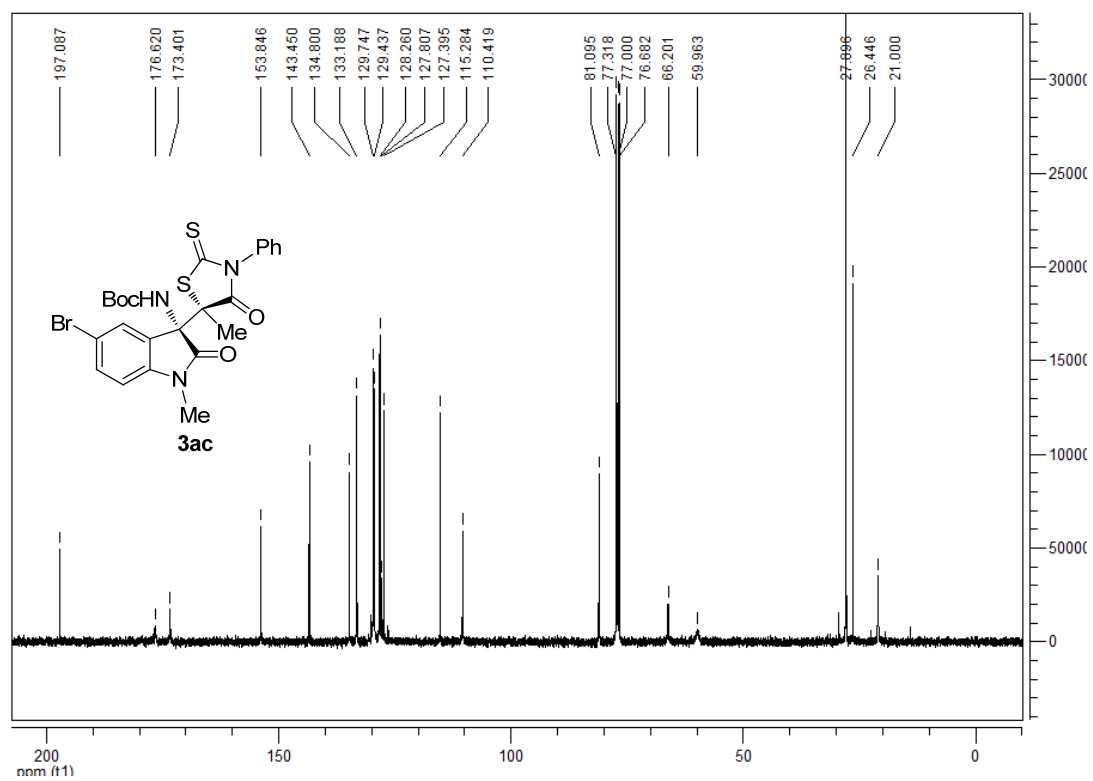
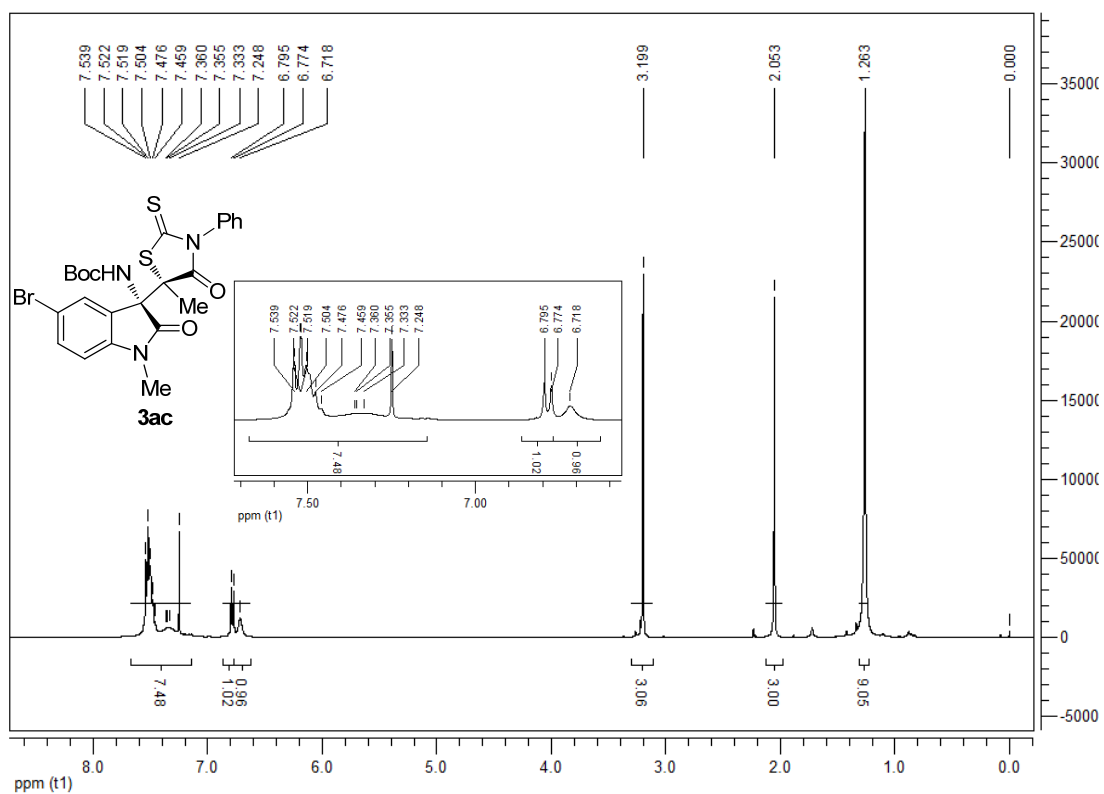


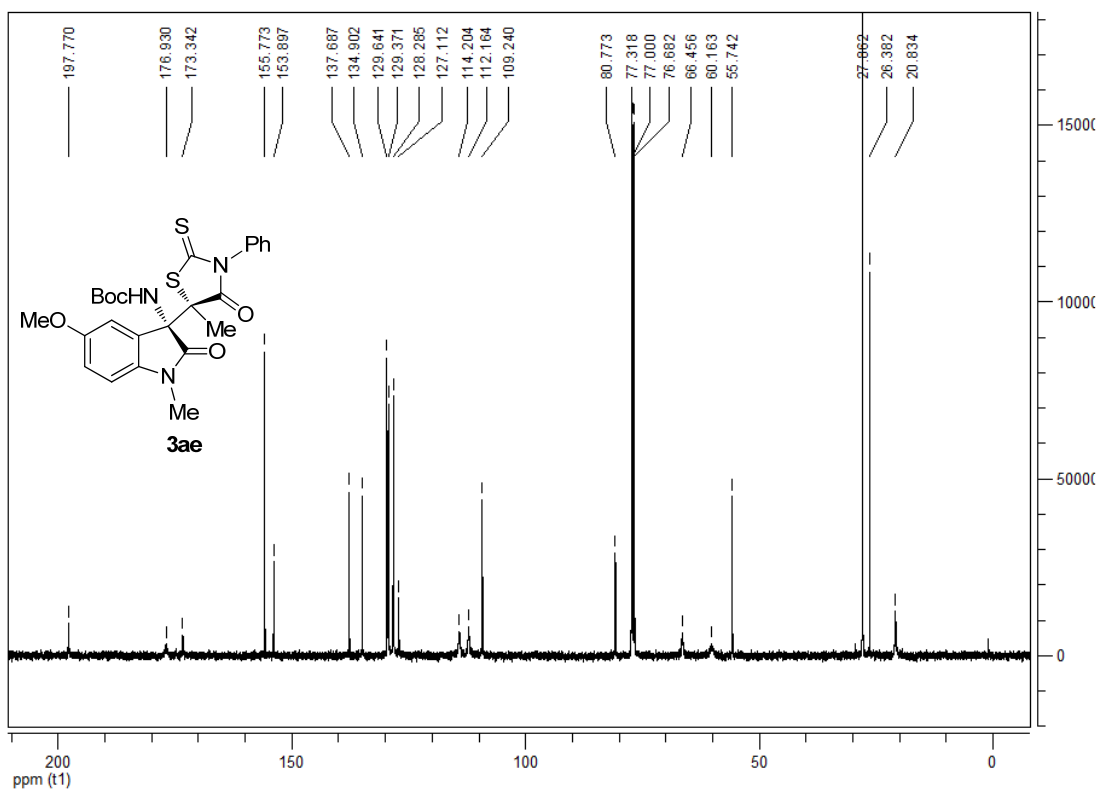
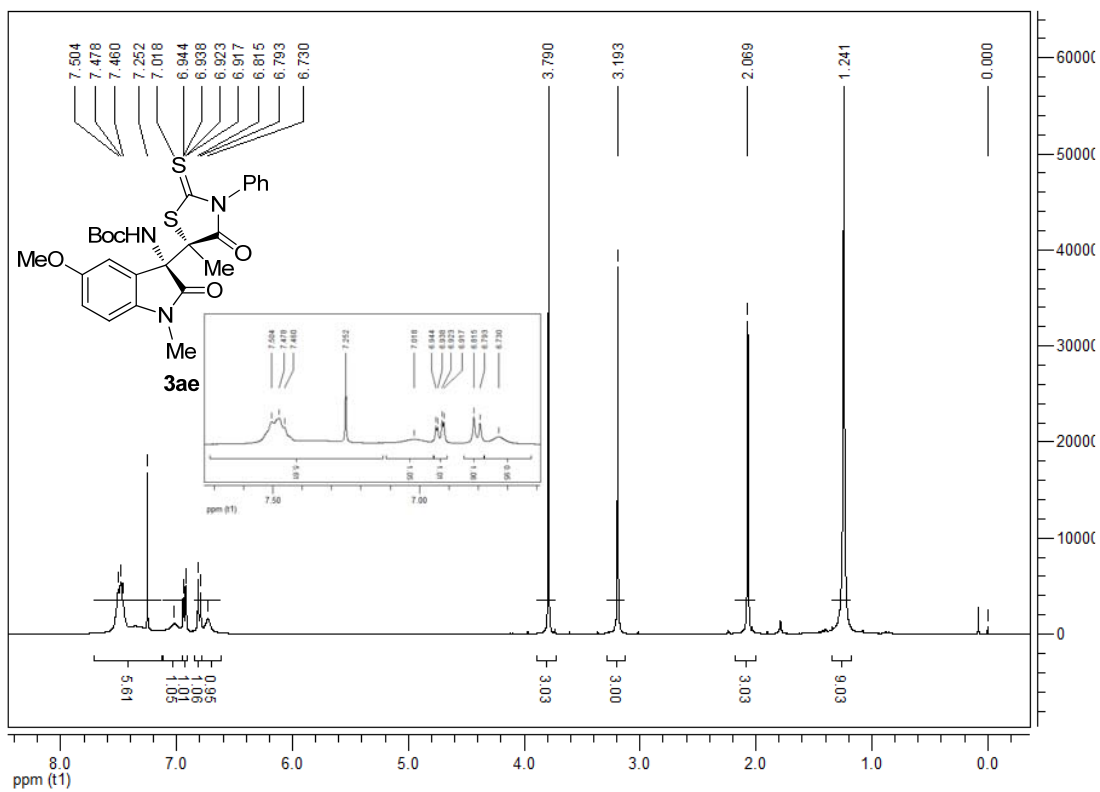


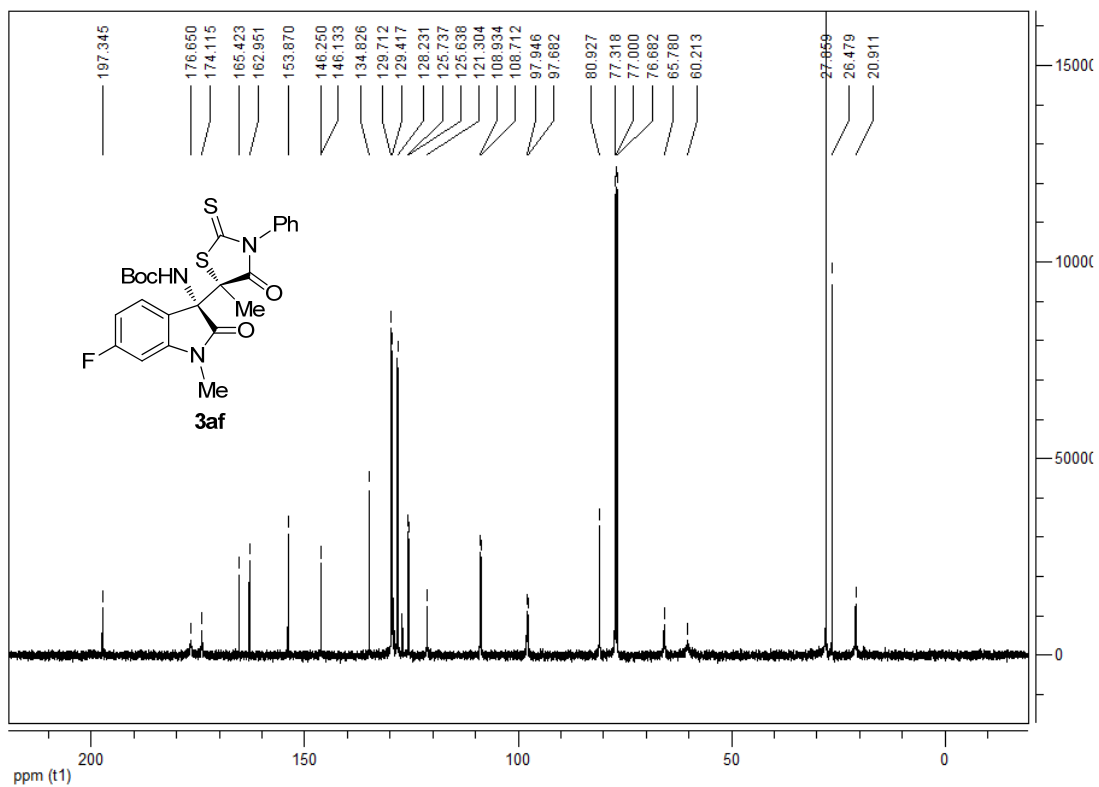
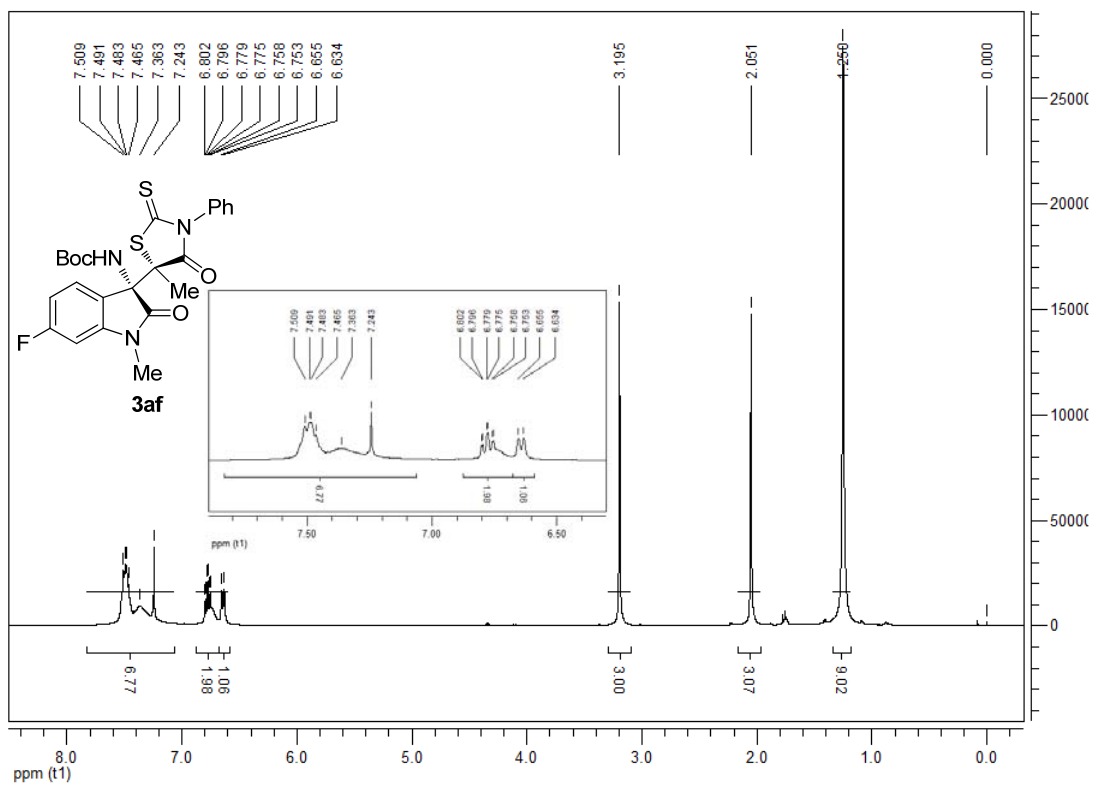


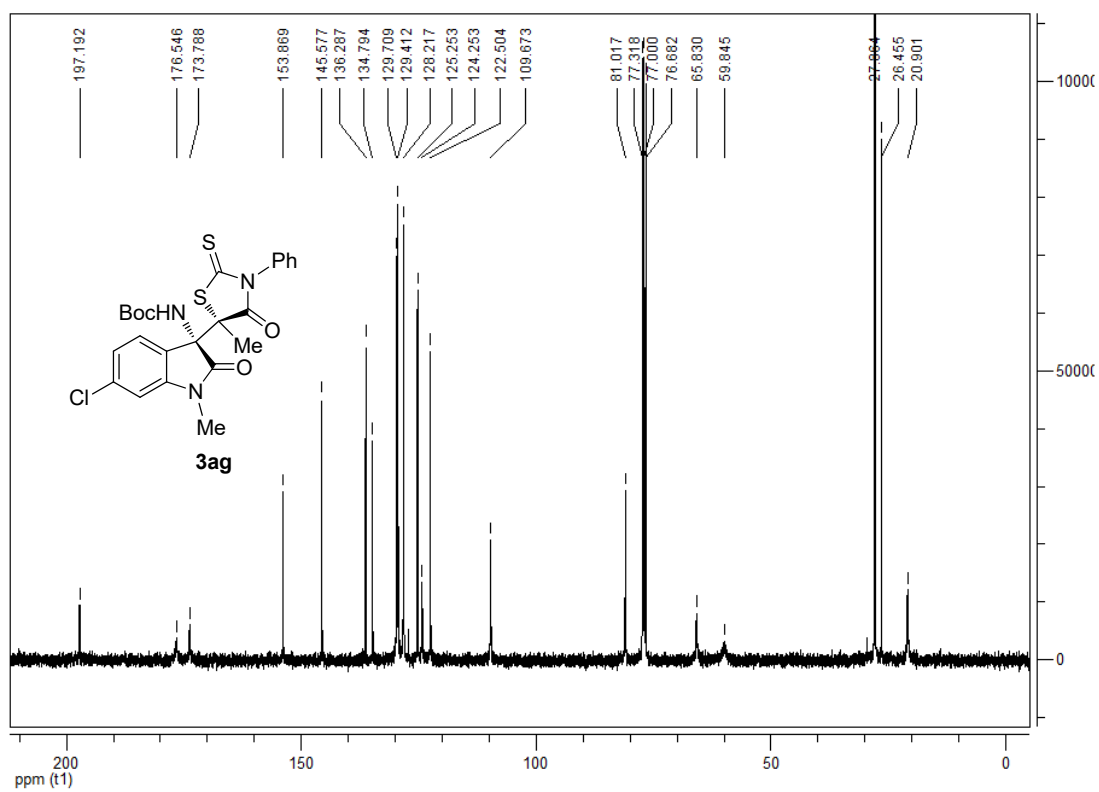
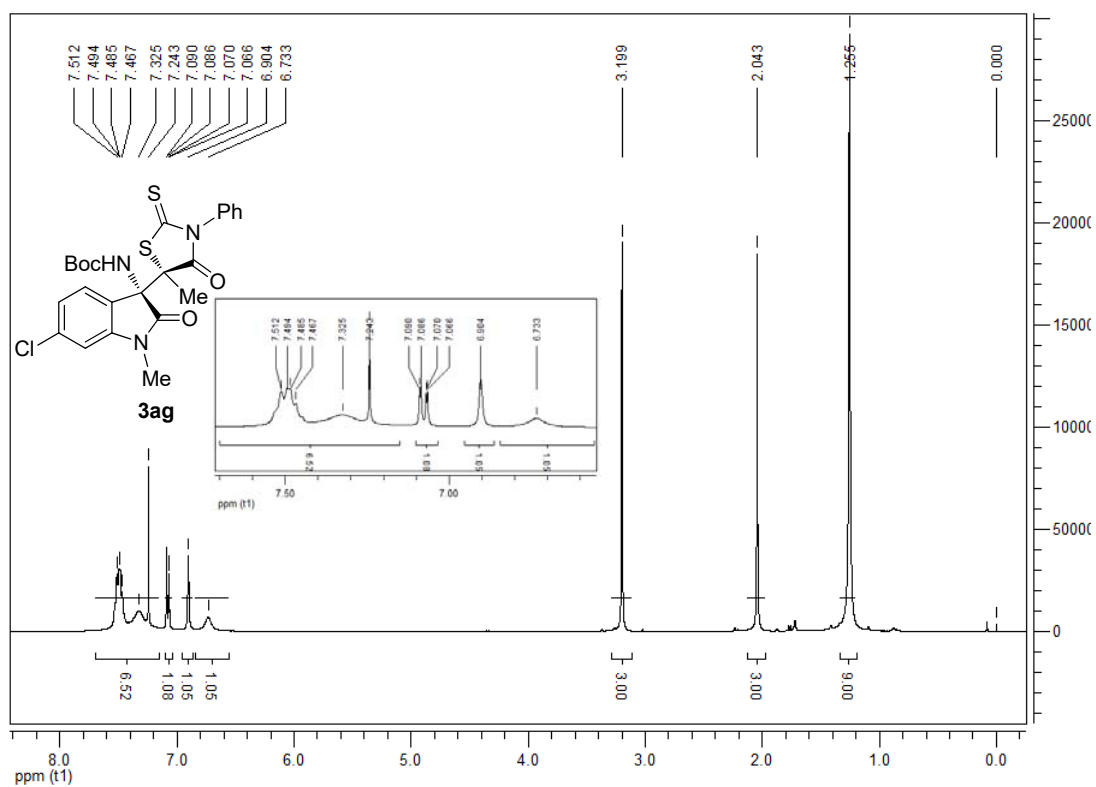


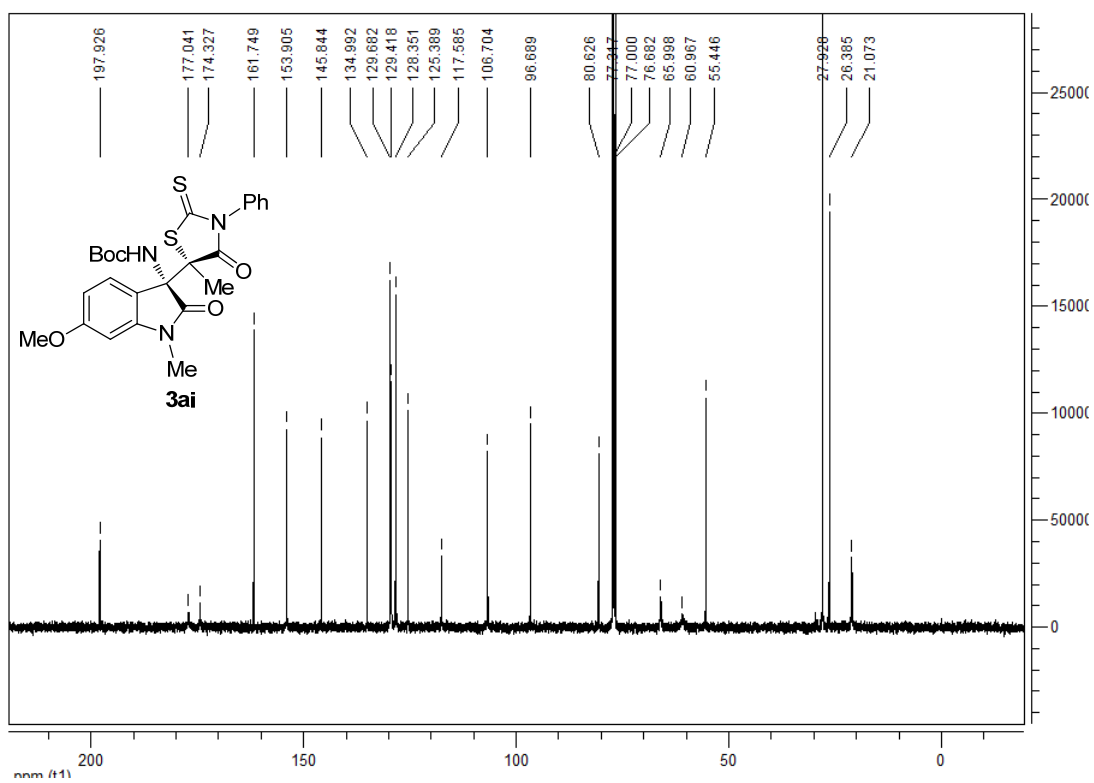
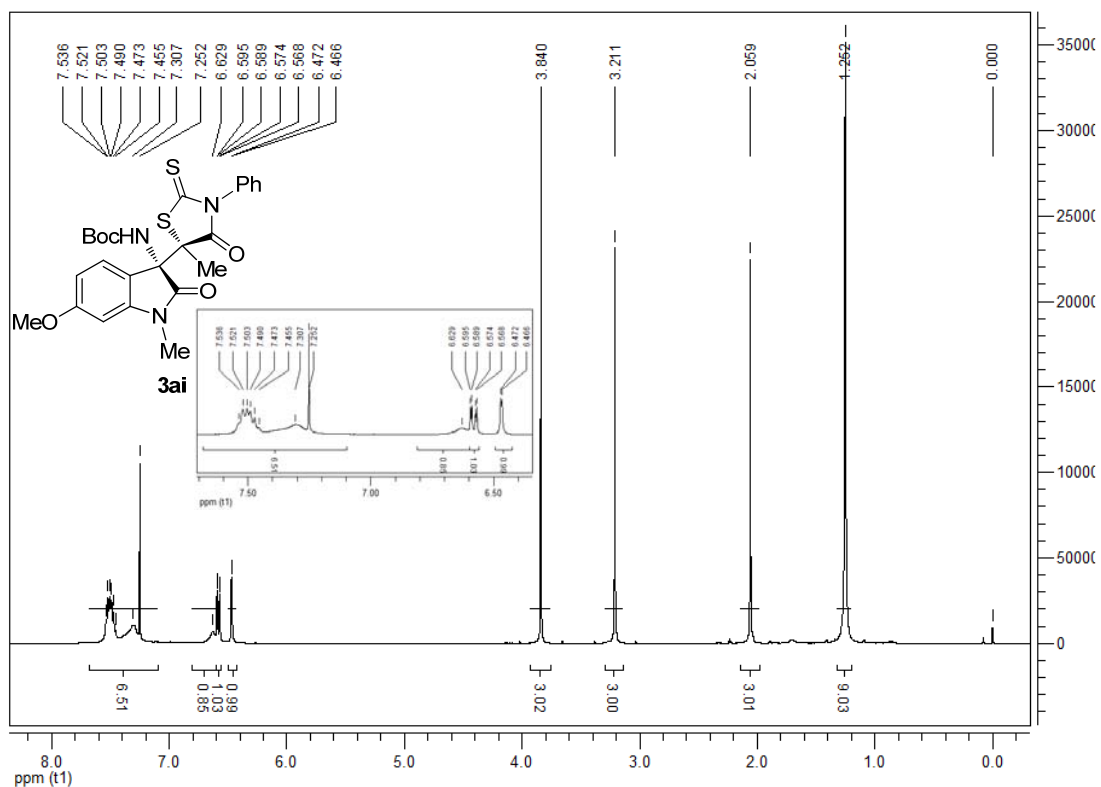


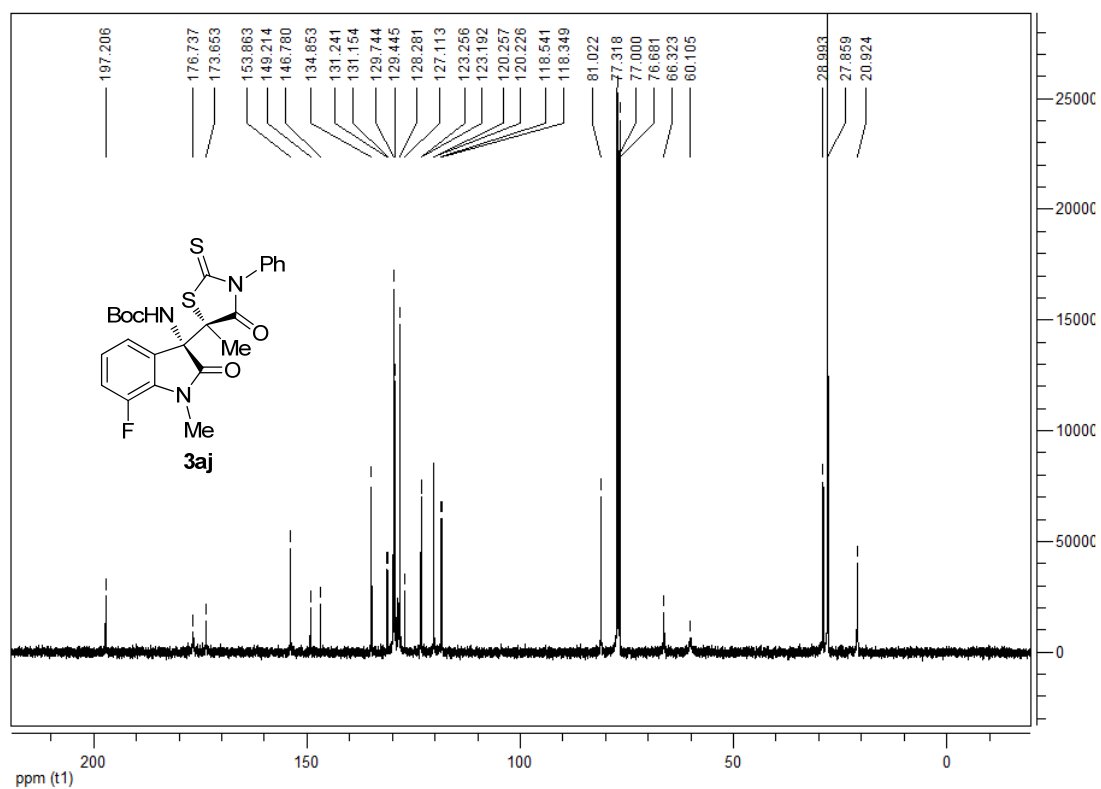
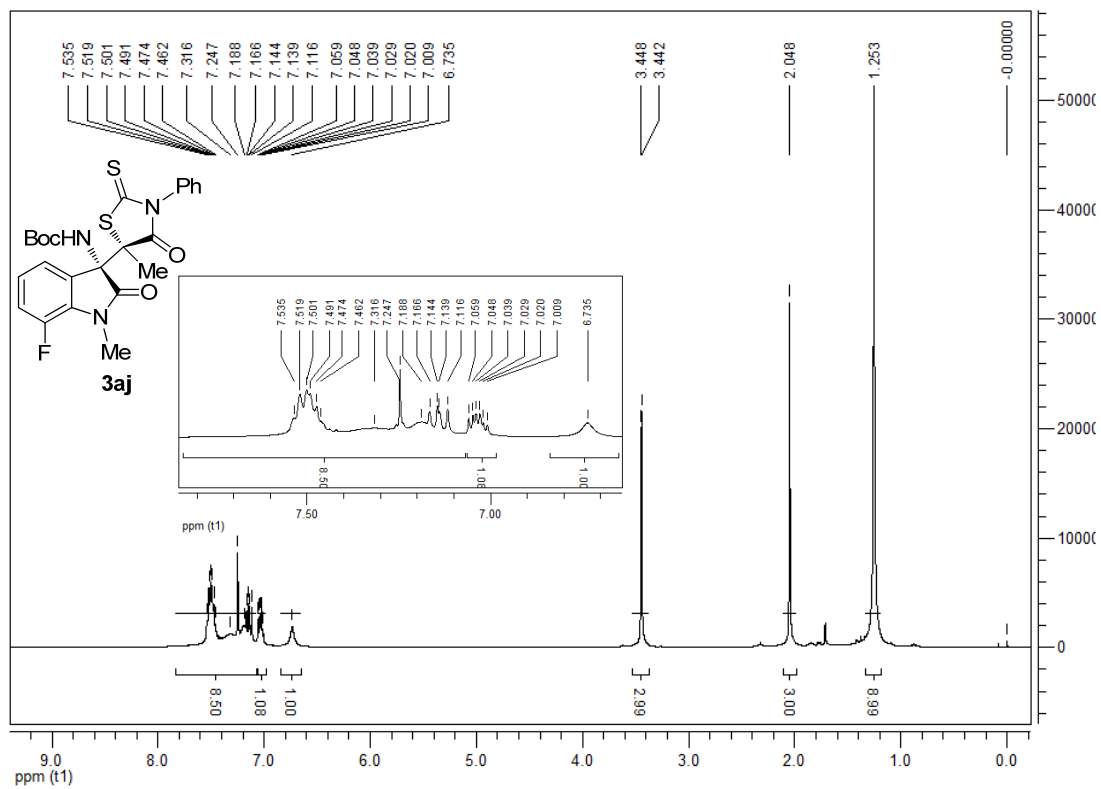


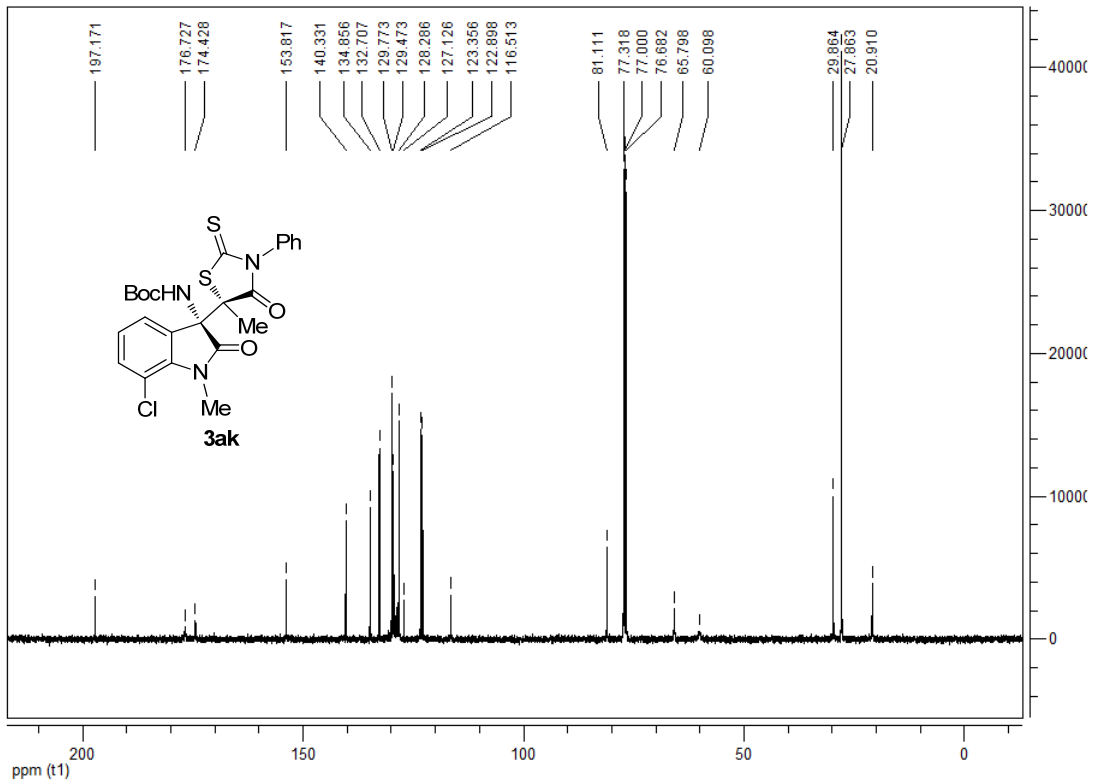
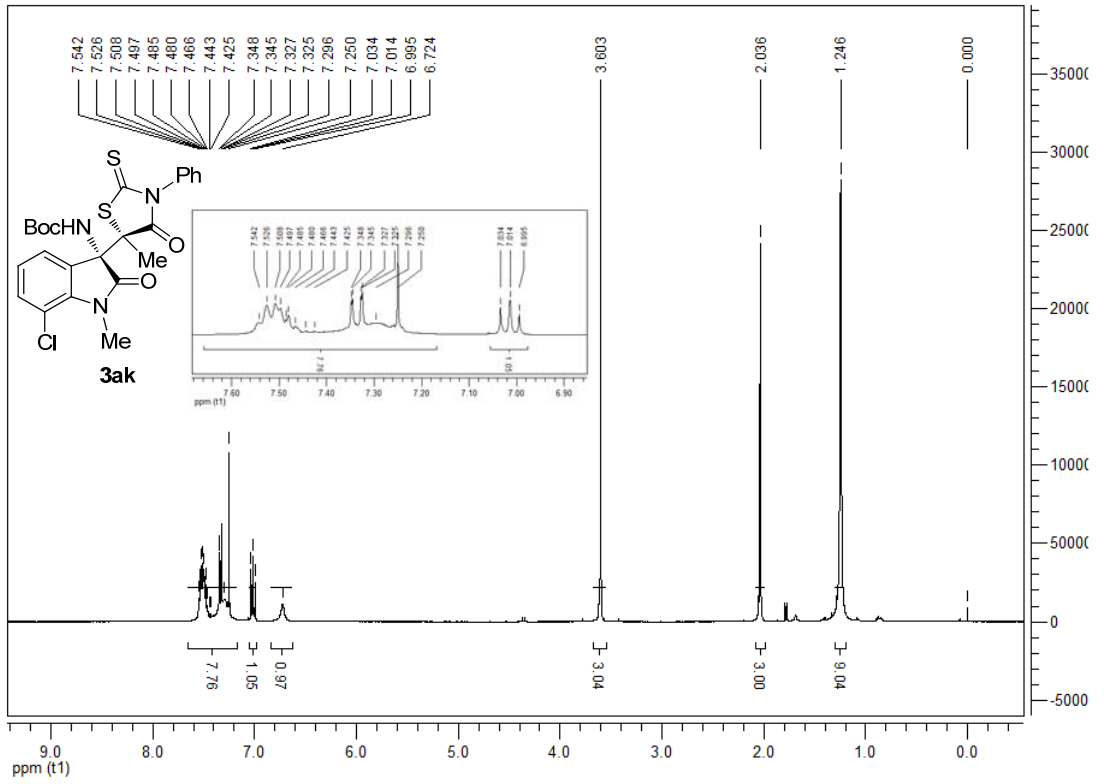


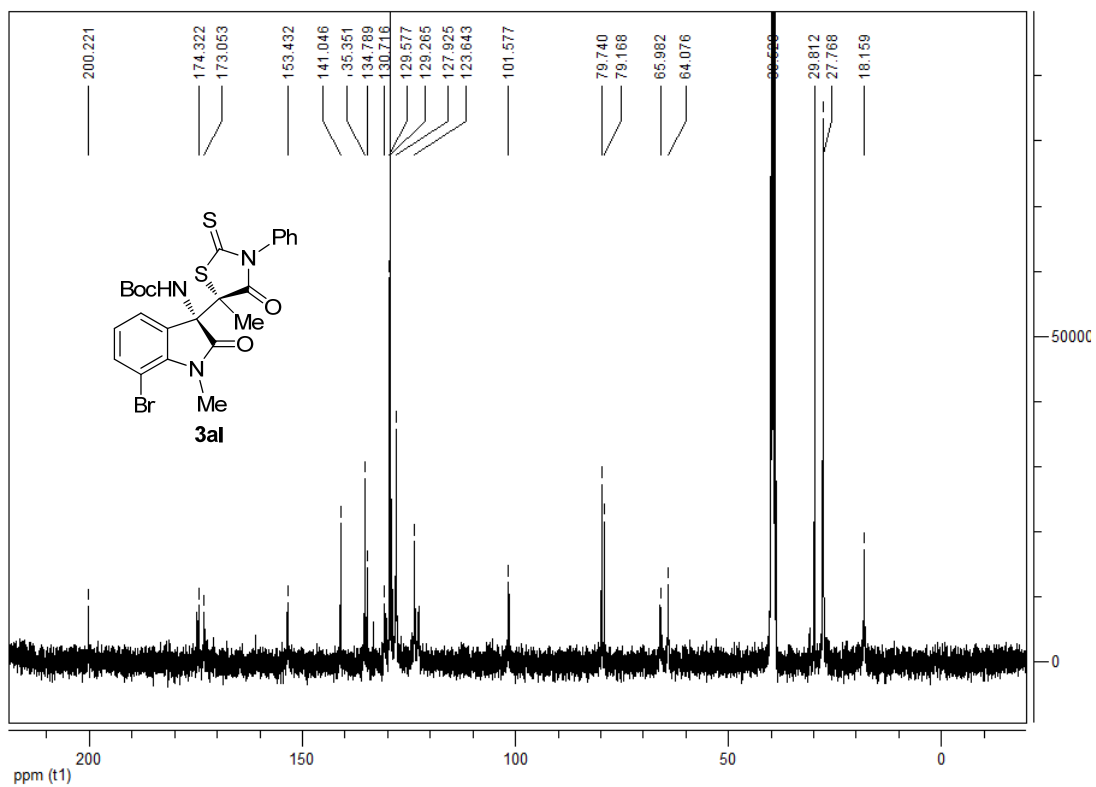
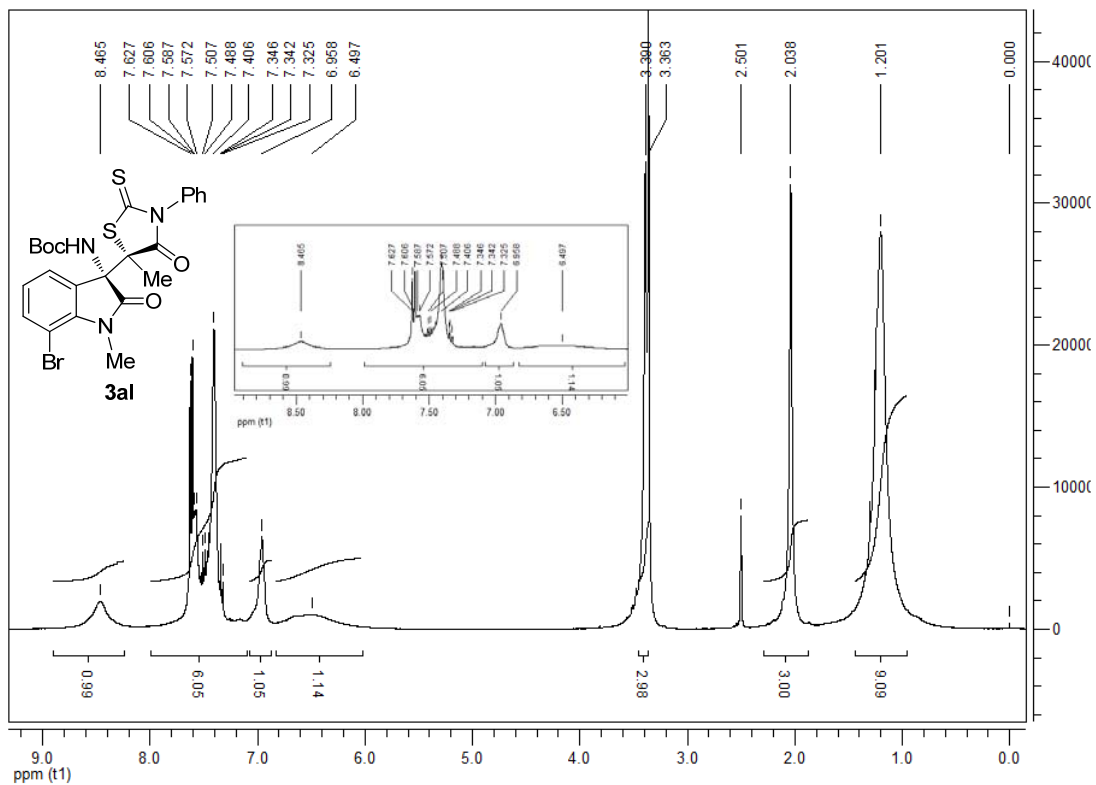


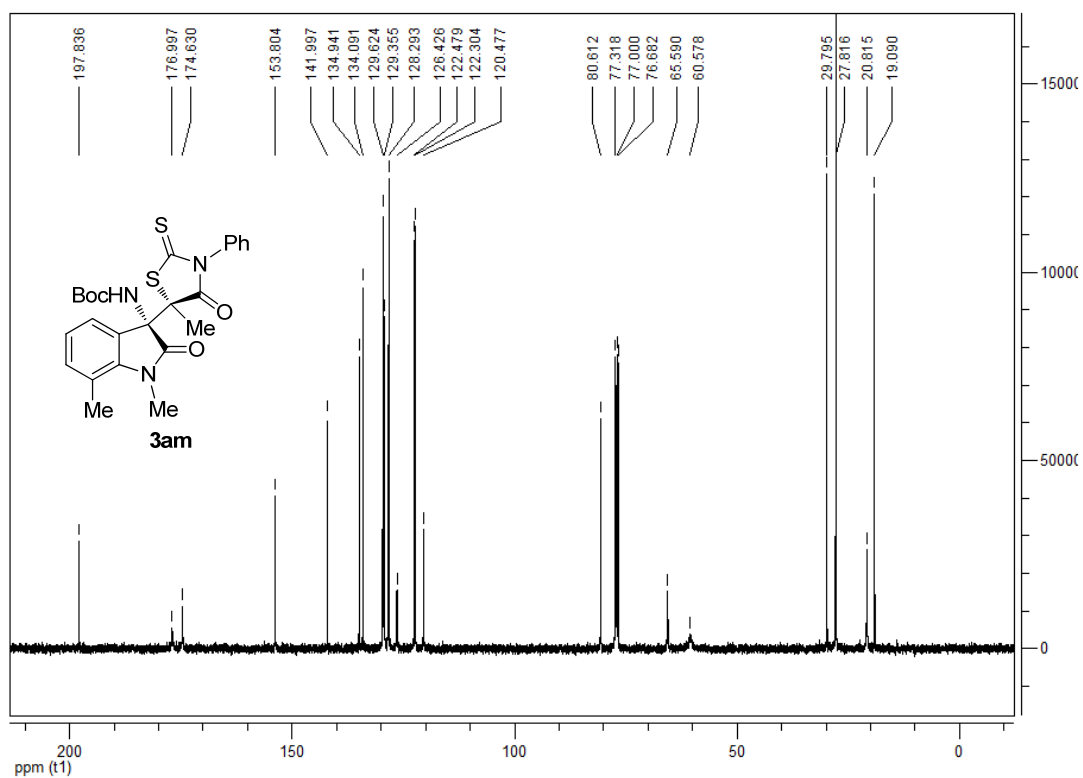
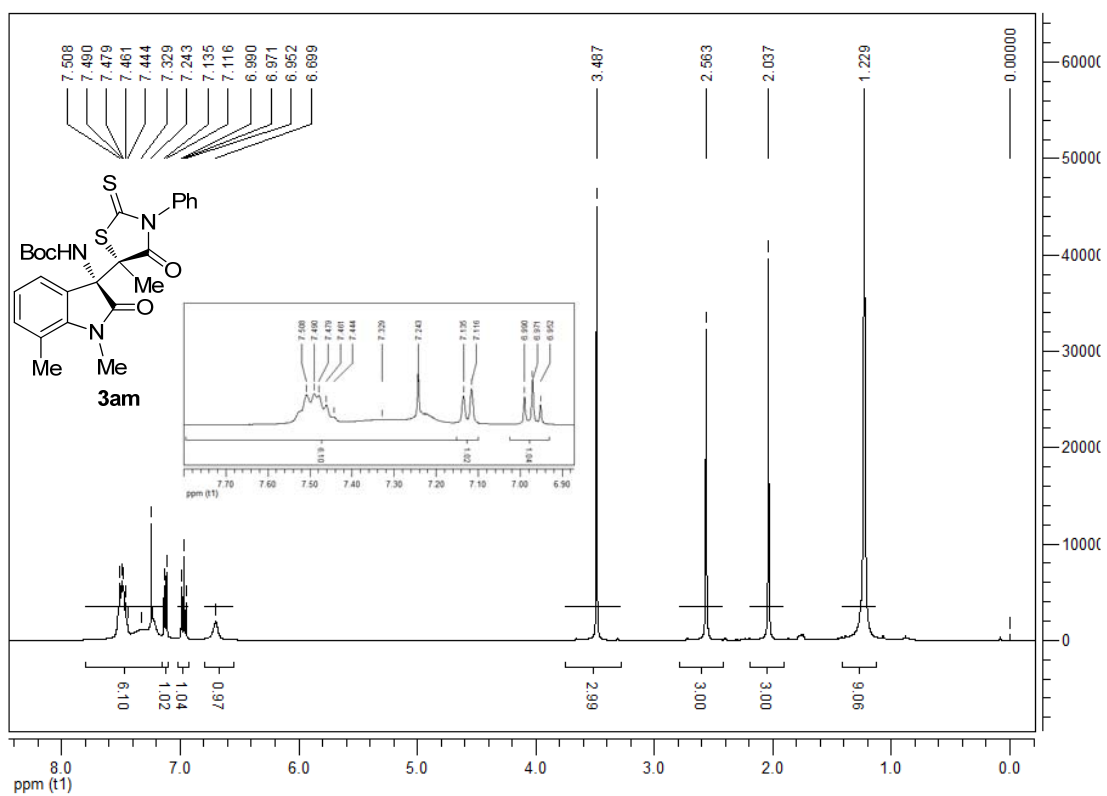




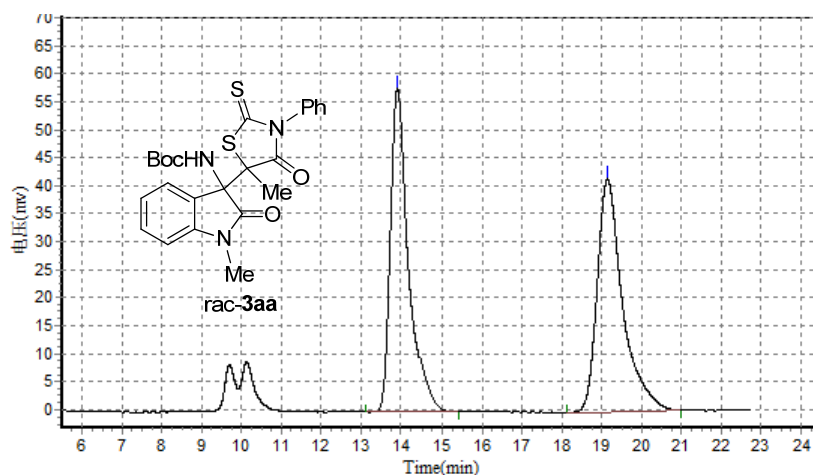






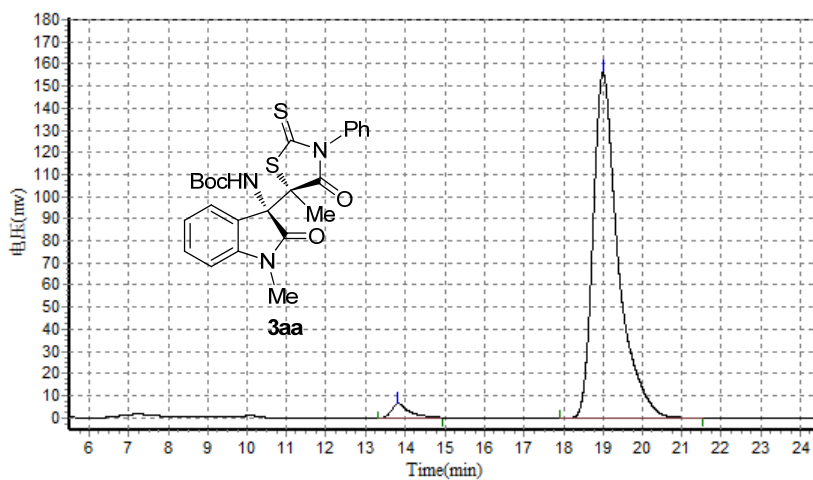


3. Copies of HPLC Spectra of the Products



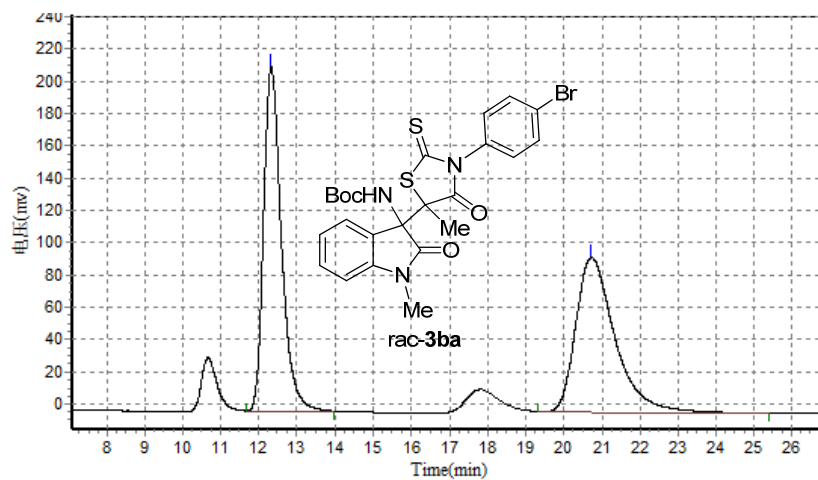
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|-----------|-------------|----------|
| 1 | | 13.910 | 57754.523 | 1798939.000 | 49.6040 |
| 2 | | 19.148 | 41556.852 | 1827658.750 | 50.3960 |
| Total | | | 99311.375 | 3626597.750 | 100.0000 |



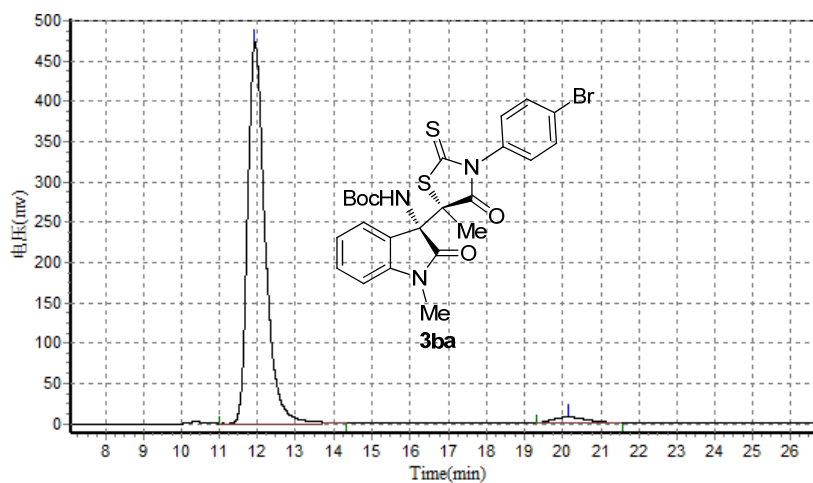
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 13.833 | 6497.349 | 205349.609 | 2.9003 |
| 2 | | 18.995 | 156112.609 | 6875002.000 | 97.0997 |
| Total | | | 162609.958 | 7080351.609 | 100.0000 |



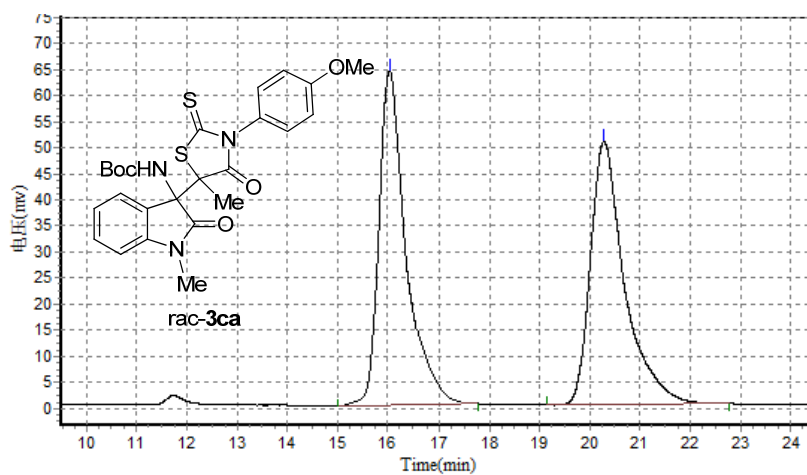
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 12.322 | 213017.047 | 6913549.500 | 50.2494 |
| 2 | | 20.715 | 95891.688 | 6844934.000 | 49.7506 |
| Total | | | 308908.734 | 13758483.500 | 100.0000 |



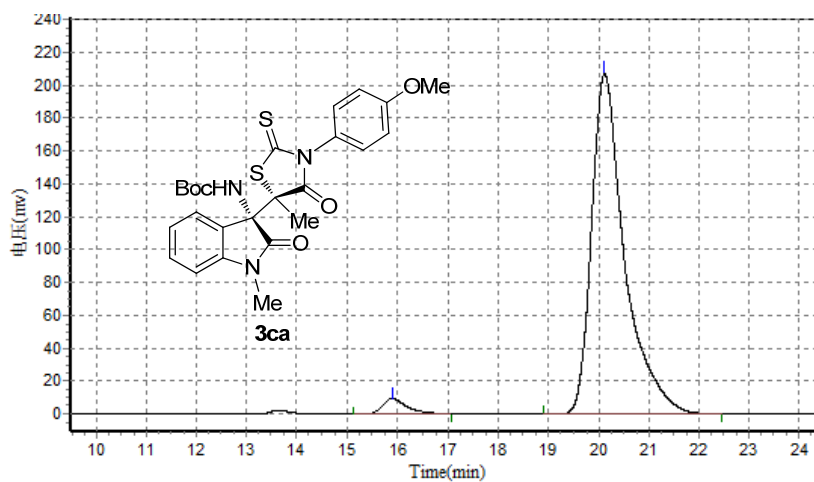
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 11.930 | 473514.625 | 15031673.000 | 97.0925 |
| 2 | | 20.153 | 7201.206 | 450131.469 | 2.9075 |
| Total | | | 480715.831 | 15481804.469 | 100.0000 |



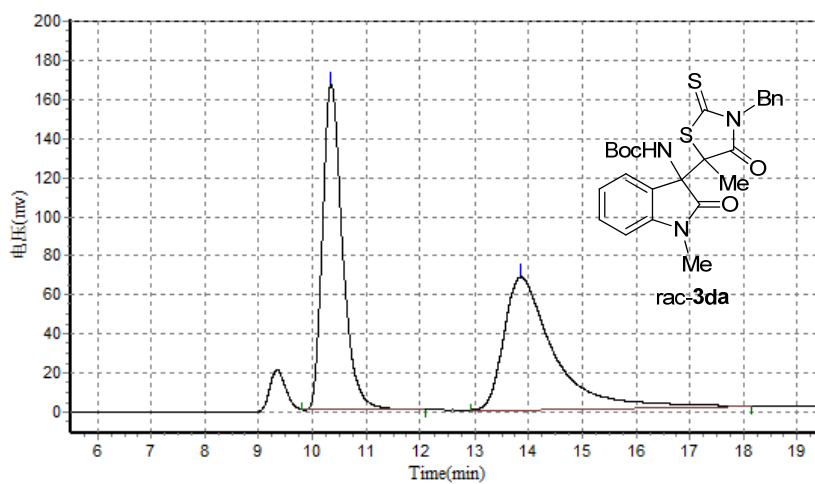
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 16.042 | 64175.895 | 2385000.500 | 50.0517 |
| 2 | | 20.278 | 50469.621 | 2380069.250 | 49.9483 |
| Total | | | 114645.516 | 4765069.750 | 100.0000 |



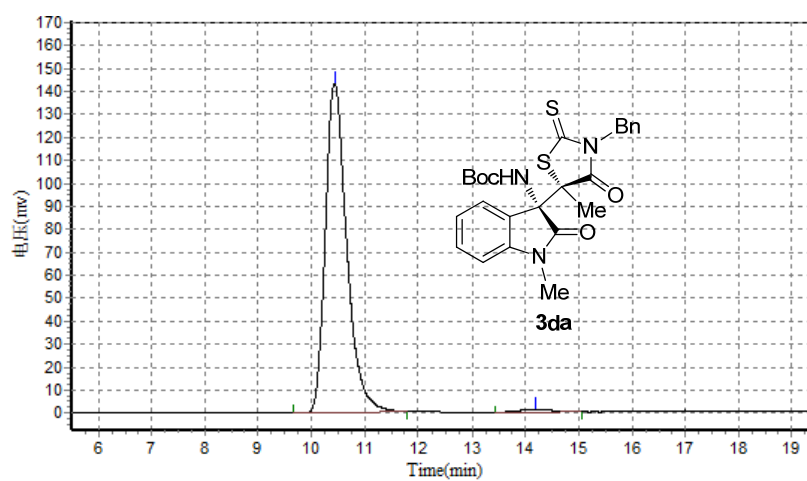
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 15.913 | 9490.627 | 329460.031 | 3.3619 |
| 2 | | 20.112 | 206664.750 | 9470444.000 | 96.6381 |
| Total | | | 216155.377 | 9799904.031 | 100.0000 |



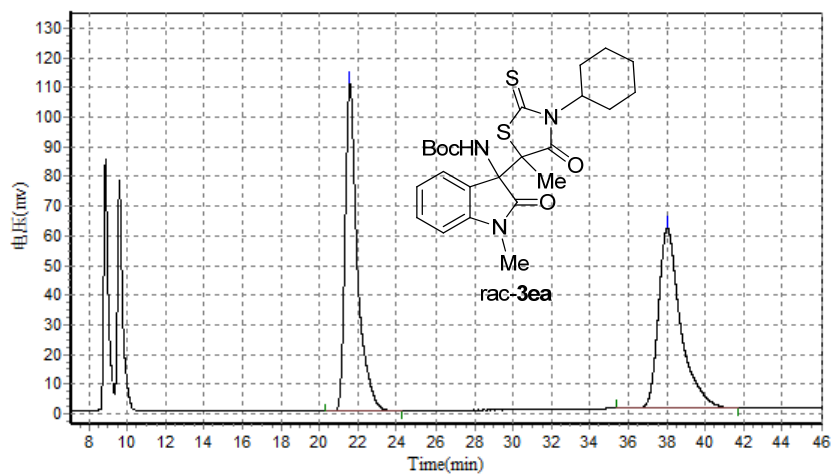
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 10.345 | 166314.813 | 4305499.000 | 49.7924 |
| 2 | | 13.853 | 67681.211 | 4341399.000 | 50.2076 |
| Total | | | 233996.023 | 8646898.000 | 100.0000 |



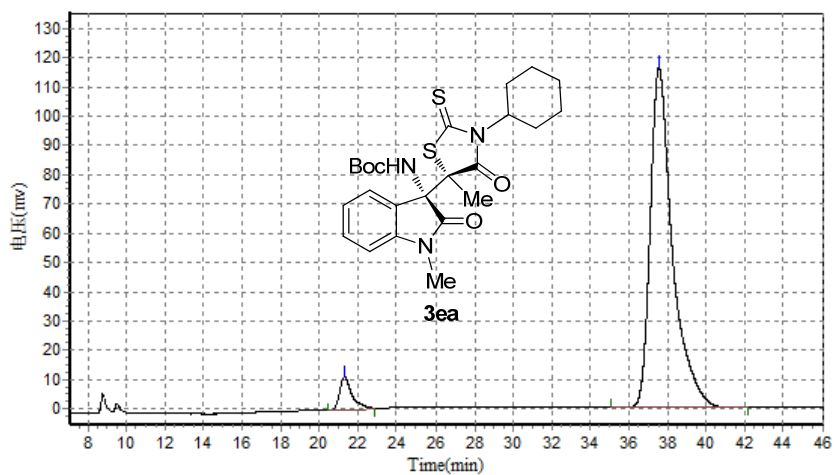
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 10.437 | 143290.547 | 4001920.750 | 98.6442 |
| 2 | | 14.173 | 1080.358 | 55004.199 | 1.3558 |
| Total | | | 144370.905 | 4056924.949 | 100.0000 |



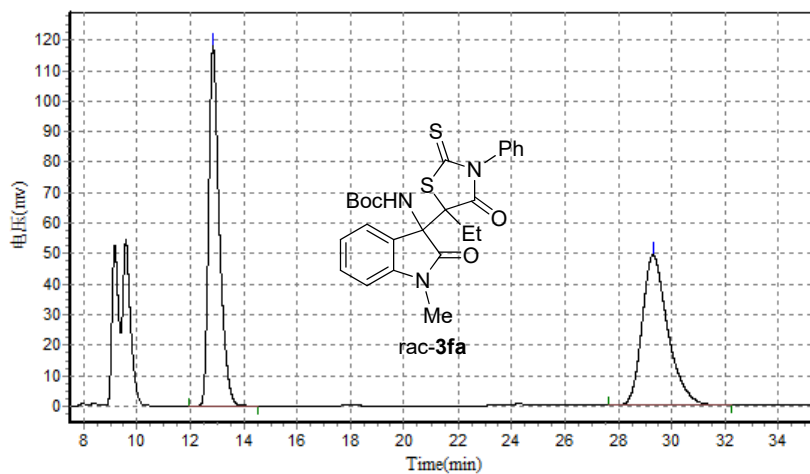
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 21.588 | 109837.258 | 4830878.000 | 49.8988 |
| 2 | | 38.027 | 60721.738 | 4850479.000 | 50.1012 |
| Total | | | 170558.996 | 9681357.000 | 100.0000 |



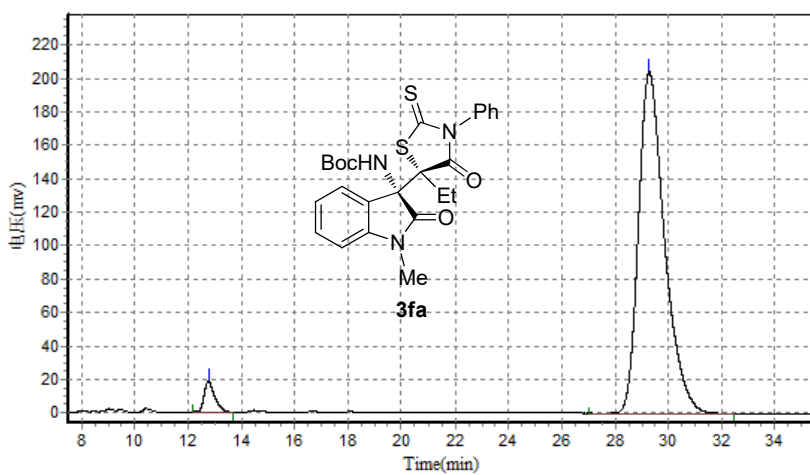
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 21.307 | 11350.021 | 497120.531 | 5.1061 |
| 2 | | 37.557 | 115931.516 | 9238660.000 | 94.8939 |
| Total | | | 127281.536 | 9735780.531 | 100.0000 |



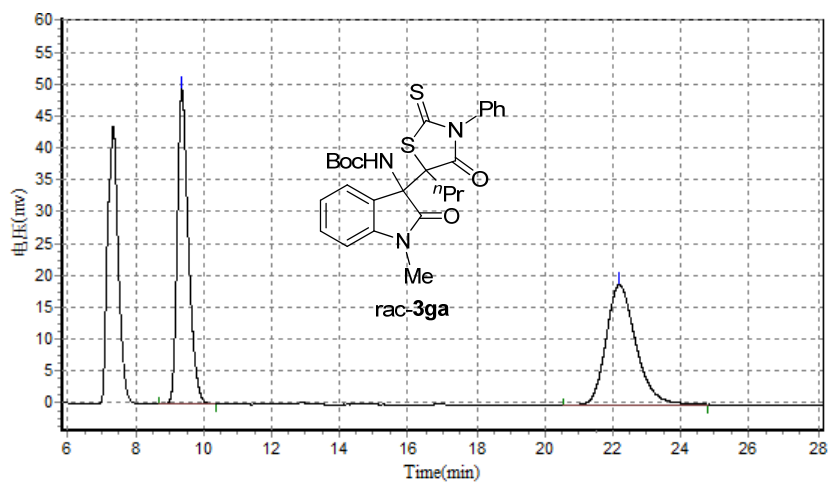
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 12.845 | 117958.484 | 3276080.000 | 50.0219 |
| 2 | | 29.295 | 49220.551 | 3273212.750 | 49.9781 |
| Total | | | 167179.035 | 6549292.750 | 100.0000 |



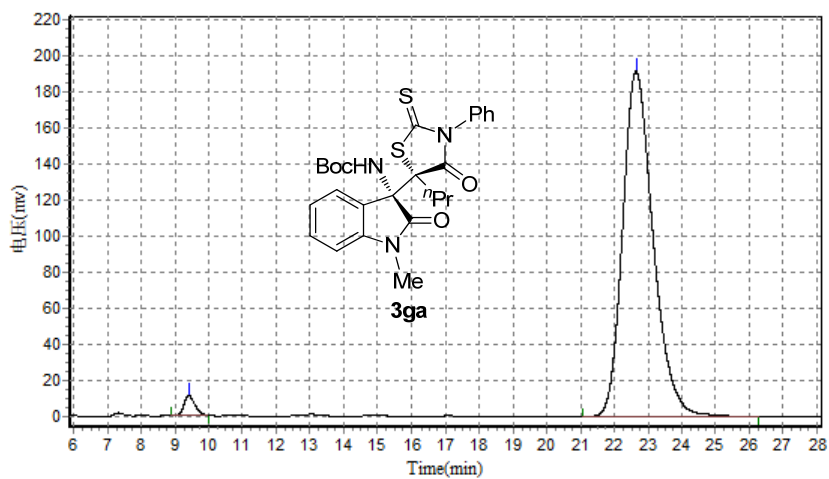
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 12.762 | 18400.363 | 503028.594 | 3.5054 |
| 2 | | 29.282 | 203849.969 | 13846945.000 | 96.4946 |
| Total | | | 222250.332 | 14349973.594 | 100.0000 |



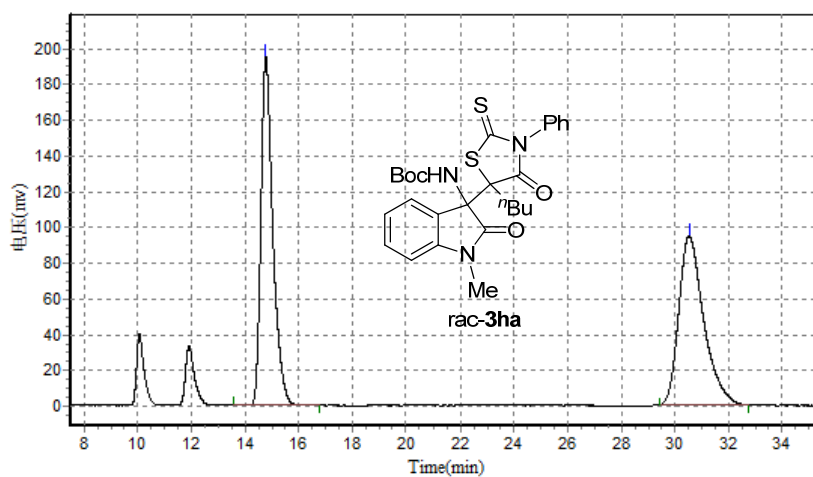
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|-----------|-------------|----------|
| 1 | | 9.358 | 49227.480 | 1118107.375 | 49.5507 |
| 2 | | 22.188 | 18831.018 | 1138385.875 | 50.4493 |
| Total | | | 68058.498 | 2256493.250 | 100.0000 |



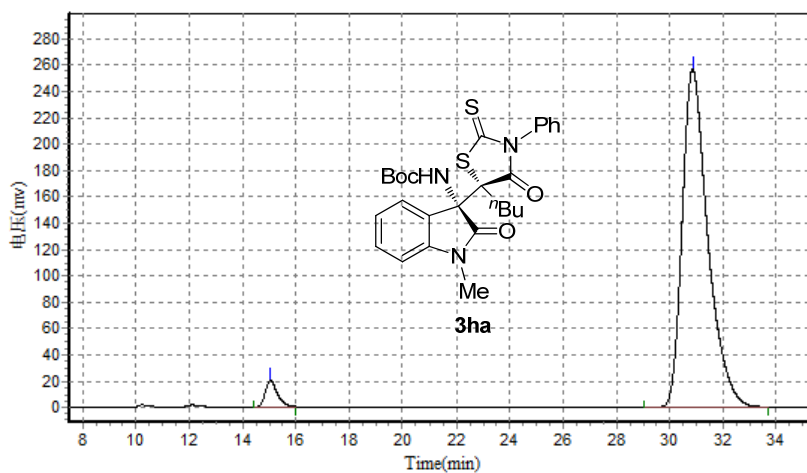
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 9.408 | 11284.080 | 254935.594 | 2.0793 |
| 2 | | 22.642 | 191525.688 | 12005713.000 | 97.9207 |
| Total | | | 202809.768 | 12260648.594 | 100.0000 |



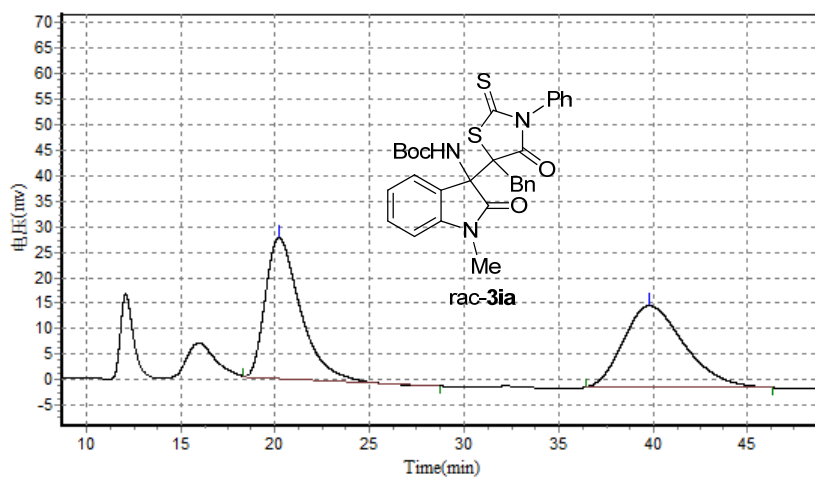
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 14.777 | 194578.625 | 6017683.500 | 49.5334 |
| 2 | | 30.530 | 94587.375 | 6131051.500 | 50.4666 |
| Total | | | 289166.000 | 12148735.000 | 100.0000 |



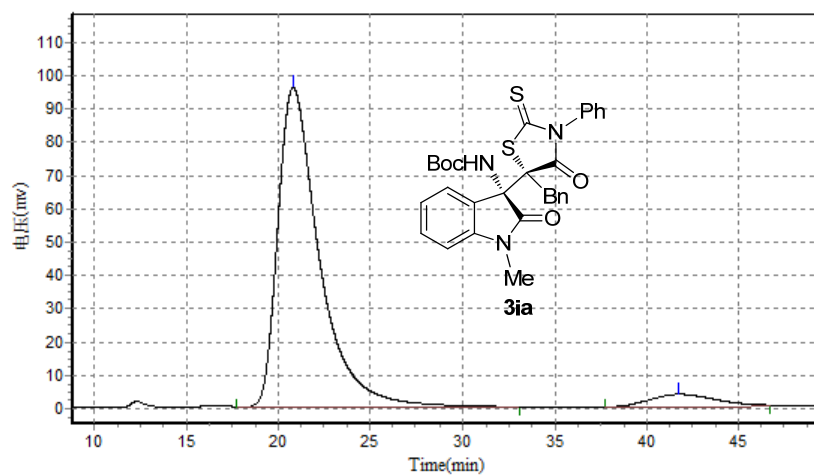
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 15.035 | 20575.514 | 638574.563 | 3.5990 |
| 2 | | 30.862 | 256481.938 | 17104728.000 | 96.4010 |
| Total | | | 277057.451 | 17743302.563 | 100.0000 |



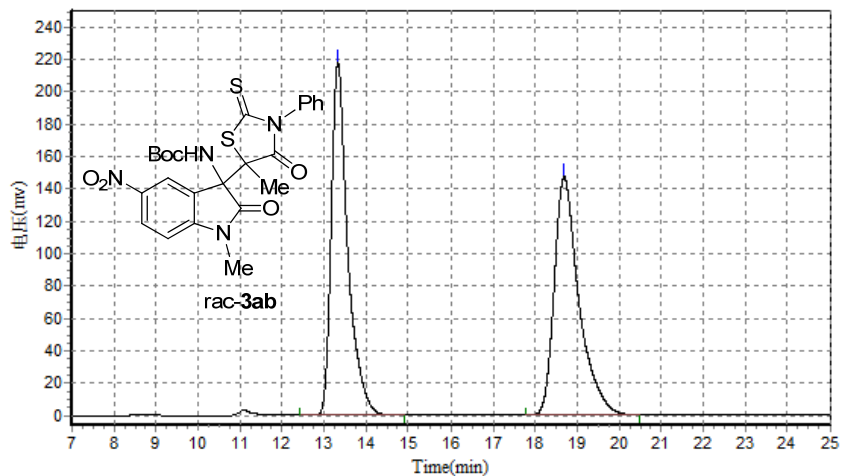
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|-----------|-------------|----------|
| 1 | | 20.210 | 27362.969 | 3506488.000 | 49.4702 |
| 2 | | 39.817 | 15936.980 | 3581596.000 | 50.5298 |
| Total | | | 43299.949 | 7088084.000 | 100.0000 |



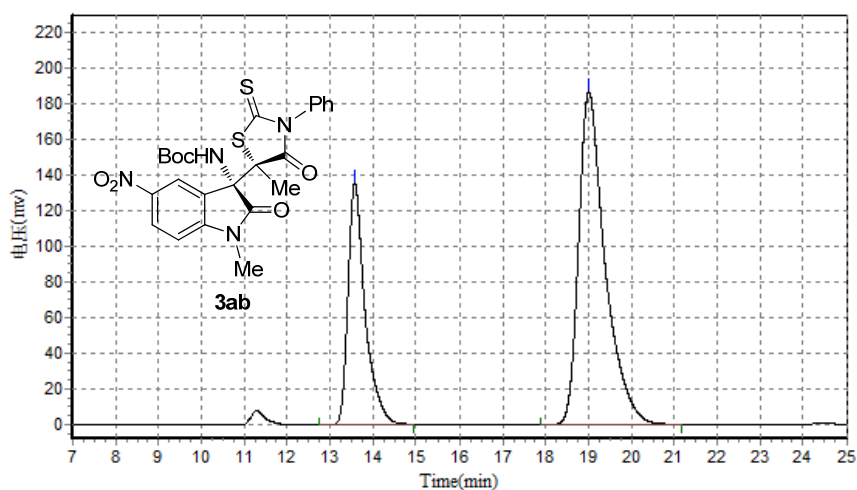
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|-----------|--------------|----------|
| 1 | | 20.815 | 95854.016 | 15049487.000 | 94.5314 |
| 2 | | 41.723 | 3606.221 | 870600.750 | 5.4686 |
| Total | | | 99460.236 | 15920087.750 | 100.0000 |



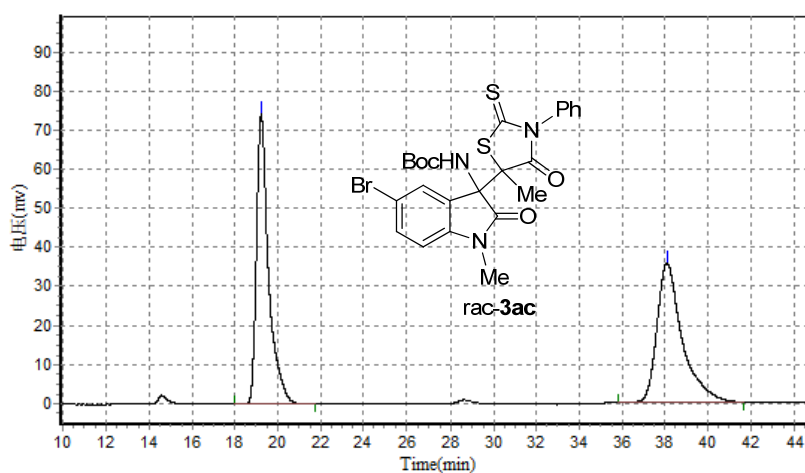
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 13.332 | 217489.391 | 5912936.000 | 49.6199 |
| 2 | | 18.687 | 147170.922 | 6003528.500 | 50.3801 |
| Total | | | 364660.313 | 11916464.500 | 100.0000 |



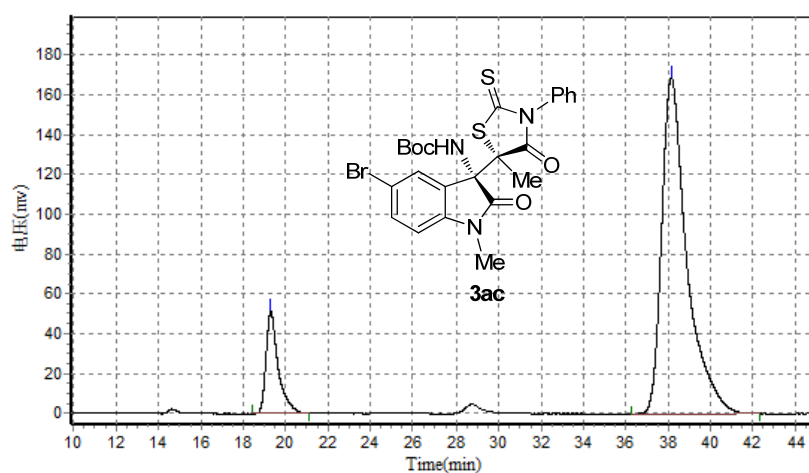
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 13.580 | 135899.547 | 3747138.000 | 31.9303 |
| 2 | | 19.007 | 186914.672 | 7988230.000 | 68.0697 |
| Total | | | 322814.219 | 11735368.000 | 100.0000 |



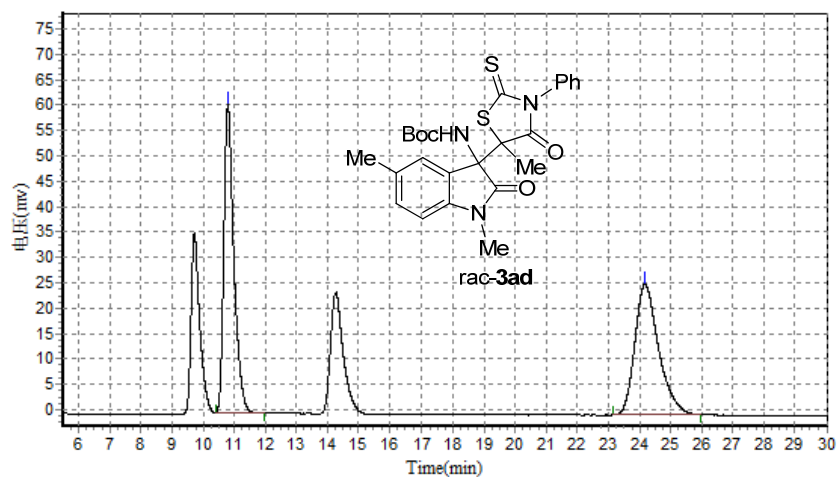
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 19.222 | 74231.617 | 2896113.500 | 49.9339 |
| 2 | | 38.080 | 35656.879 | 2903782.250 | 50.0661 |
| Total | | | 109888.496 | 5799895.750 | 100.0000 |



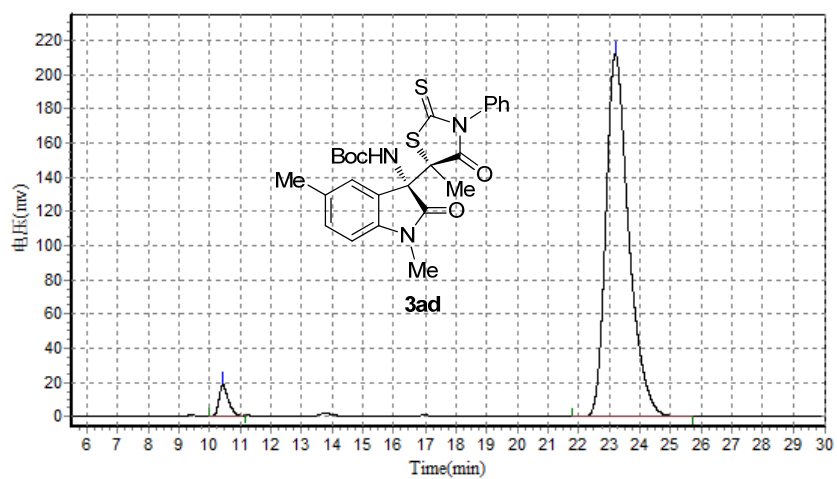
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 19.298 | 51165.059 | 2047268.750 | 12.8488 |
| 2 | | 38.150 | 168556.984 | 13886296.000 | 87.1512 |
| Total | | | 219722.043 | 15933564.750 | 100.0000 |



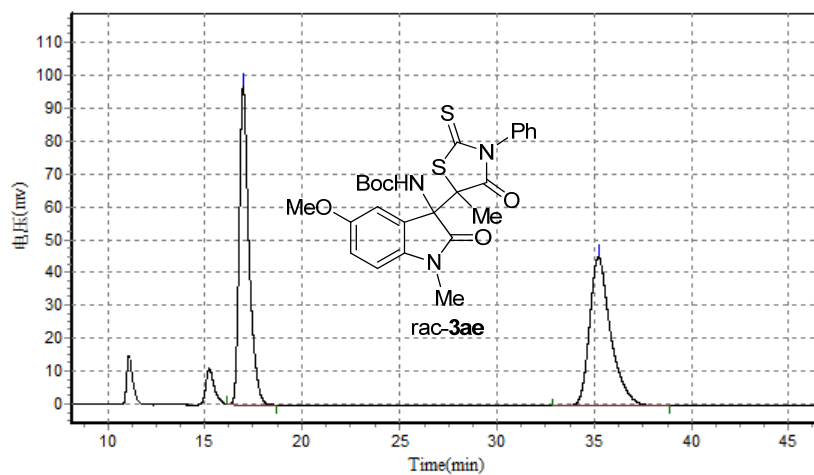
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|-----------|-------------|----------|
| 1 | | 10.793 | 60627.953 | 1354667.000 | 49.7307 |
| 2 | | 24.173 | 25747.865 | 1369338.375 | 50.2693 |
| Total | | | 86375.818 | 2724005.375 | 100.0000 |



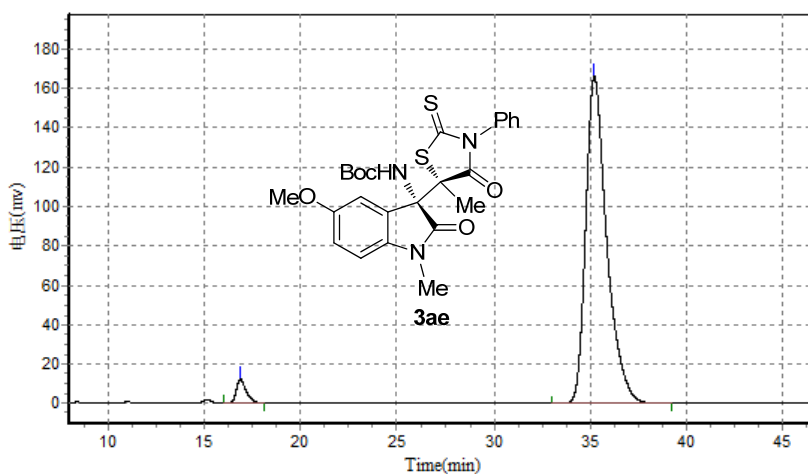
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 10.427 | 18248.025 | 376458.719 | 3.3177 |
| 2 | | 23.198 | 212257.359 | 10970486.000 | 96.6823 |
| Total | | | 230505.385 | 11346944.719 | 100.0000 |



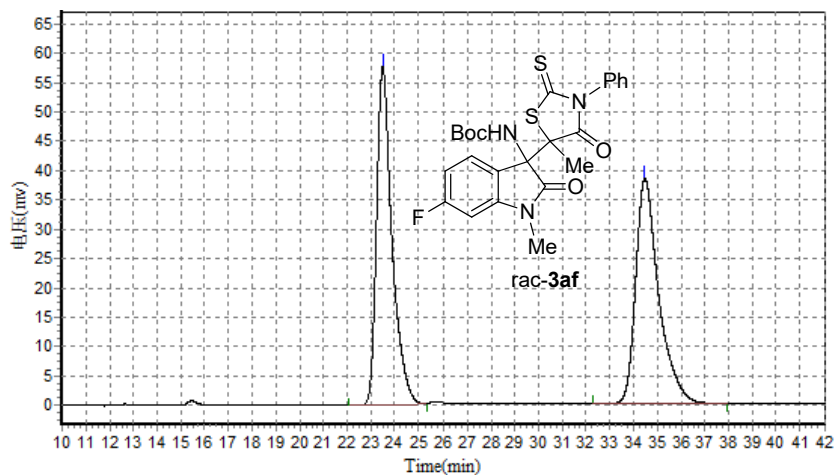
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 16.965 | 97014.367 | 3382969.000 | 49.9358 |
| 2 | | 35.202 | 45222.363 | 3391668.500 | 50.0642 |
| Total | | | 142236.730 | 6774637.500 | 100.0000 |



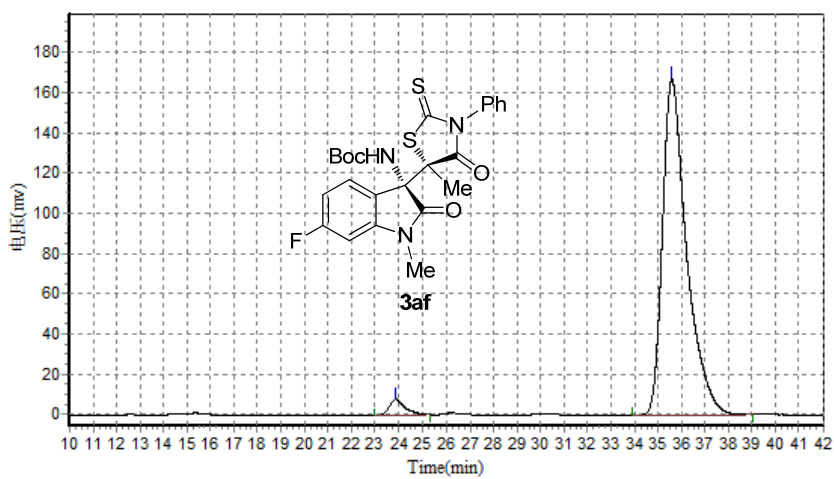
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 16.877 | 12139.603 | 423365.563 | 3.2512 |
| 2 | | 35.210 | 165748.281 | 12598373.000 | 96.7488 |
| Total | | | 177887.884 | 13021738.563 | 100.0000 |



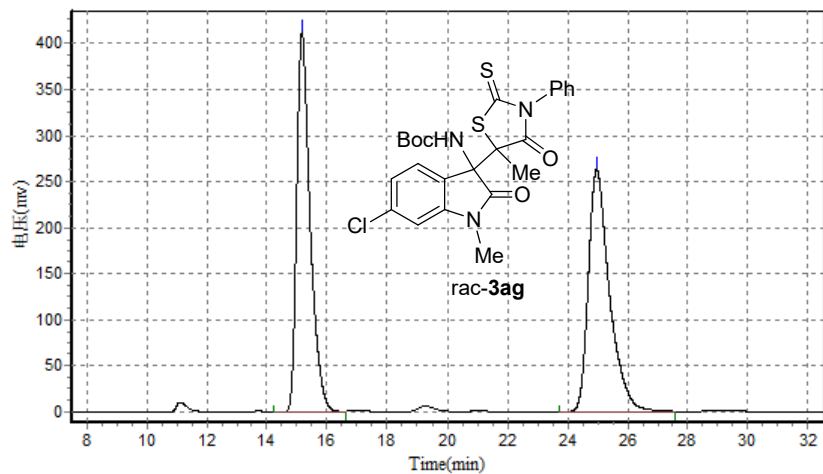
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|-----------|-------------|----------|
| 1 | | 23.497 | 57373.063 | 2573802.750 | 50.0720 |
| 2 | | 34.475 | 38308.828 | 2566405.250 | 49.9280 |
| Total | | | 95681.891 | 5140208.000 | 100.0000 |



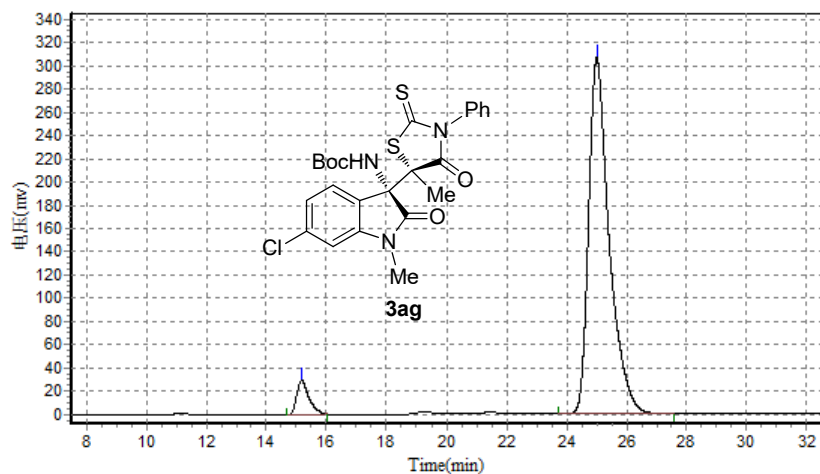
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 23.877 | 7741.628 | 357948.750 | 2.9186 |
| 2 | | 35.600 | 166864.297 | 11906365.000 | 97.0814 |
| Total | | | 174605.925 | 12264313.750 | 100.0000 |



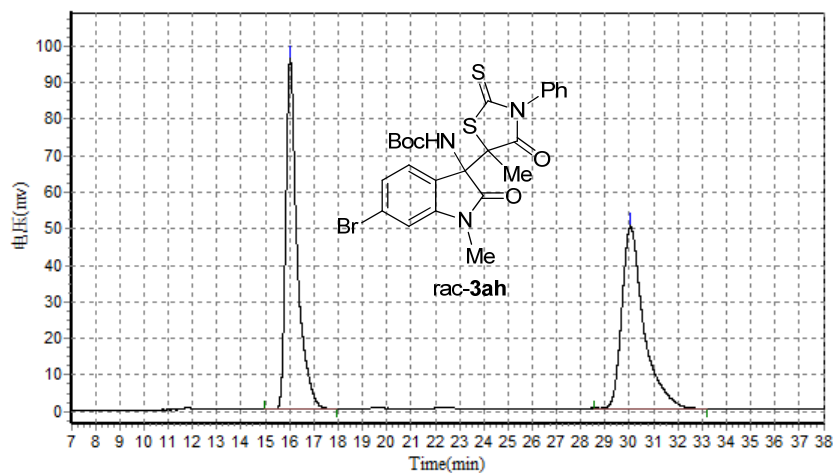
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 15.173 | 411952.531 | 12770349.000 | 49.8221 |
| 2 | | 24.962 | 263303.281 | 12861545.000 | 50.1779 |
| Total | | | 675255.813 | 25631894.000 | 100.0000 |



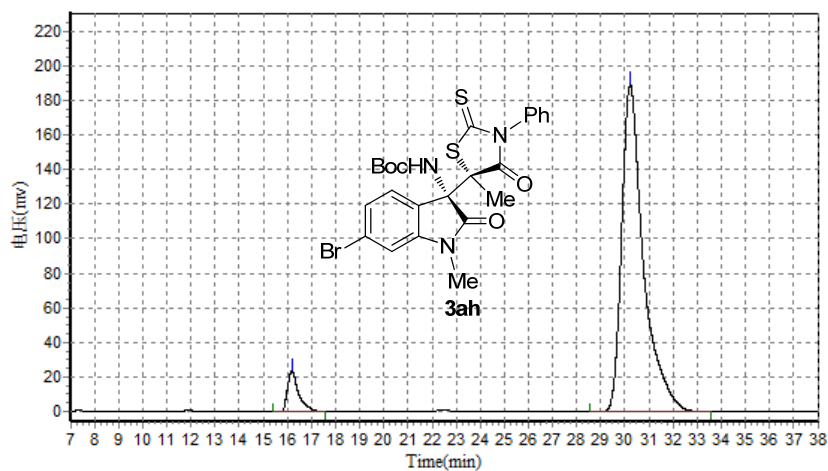
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 15.172 | 30071.213 | 847548.500 | 5.4964 |
| 2 | | 24.995 | 306404.031 | 14572408.000 | 94.5036 |
| Total | | | 336475.244 | 15419956.500 | 100.0000 |



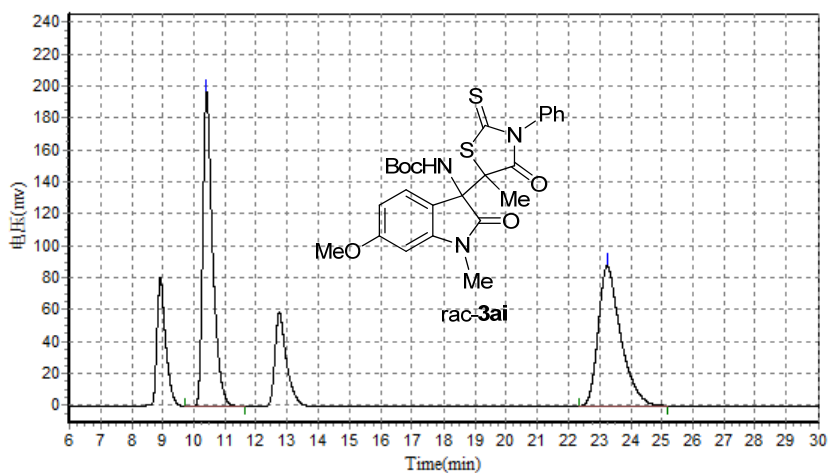
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 16.027 | 95797.656 | 3144903.500 | 50.1551 |
| 2 | | 30.050 | 49883.559 | 3125456.750 | 49.8449 |
| Total | | | 145681.215 | 6270360.250 | 100.0000 |



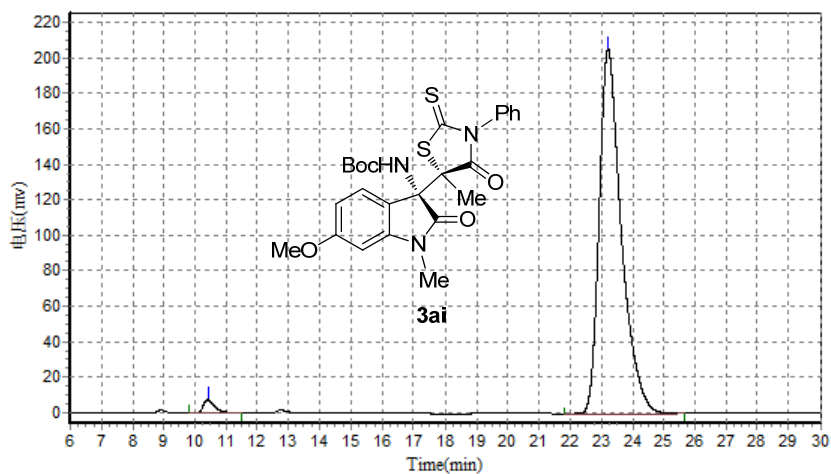
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 16.188 | 23544.170 | 771606.000 | 6.0907 |
| 2 | | 30.225 | 189012.984 | 11897064.000 | 93.9093 |
| Total | | | 212557.154 | 12668670.000 | 100.0000 |



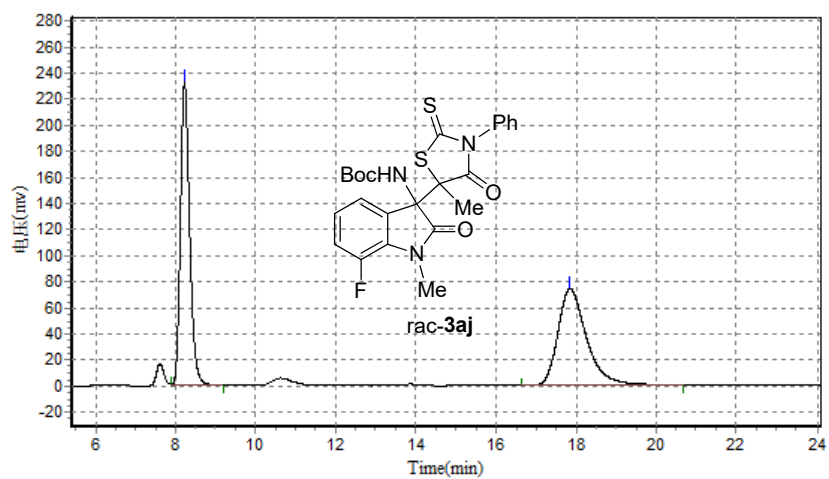
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 10.405 | 196865.219 | 4340590.500 | 49.7609 |
| 2 | | 23.243 | 87592.164 | 4382296.000 | 50.2391 |
| Total | | | 284457.383 | 8722886.500 | 100.0000 |



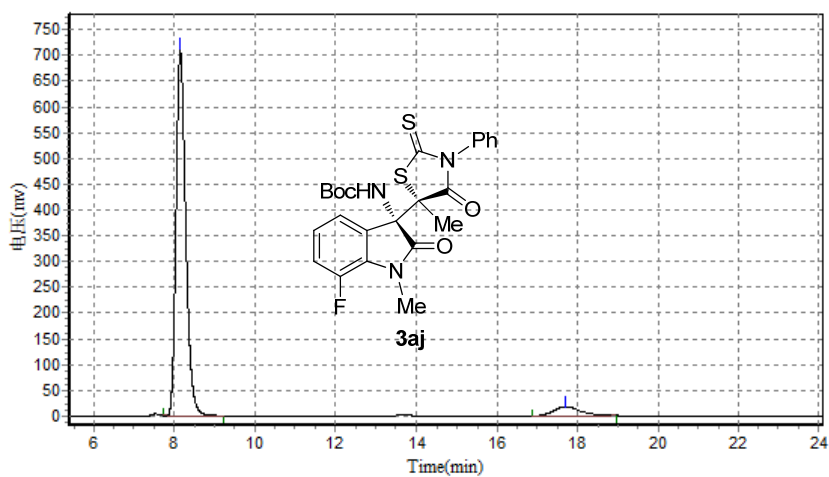
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 10.410 | 7582.823 | 185653.813 | 1.8041 |
| 2 | | 23.208 | 205159.750 | 10104947.000 | 98.1959 |
| Total | | | 212742.573 | 10290600.813 | 100.0000 |



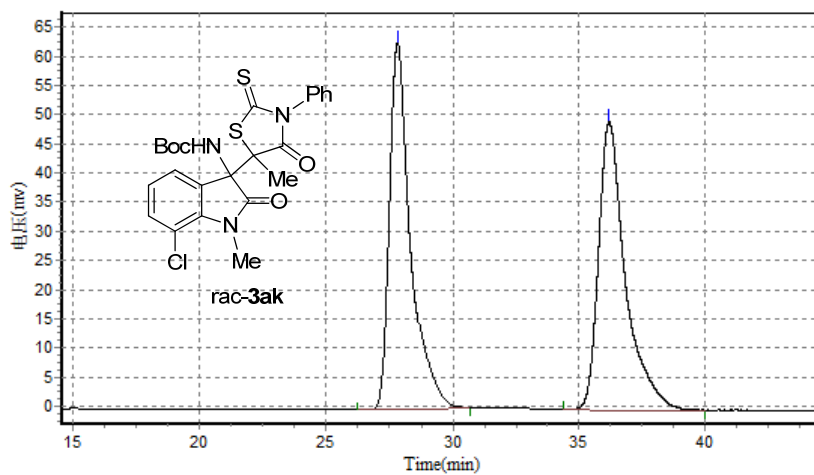
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 8.223 | 231701.000 | 3691100.000 | 50.1080 |
| 2 | | 17.842 | 74011.227 | 3675187.500 | 49.8920 |
| Total | | | 305712.227 | 7366287.500 | 100.0000 |



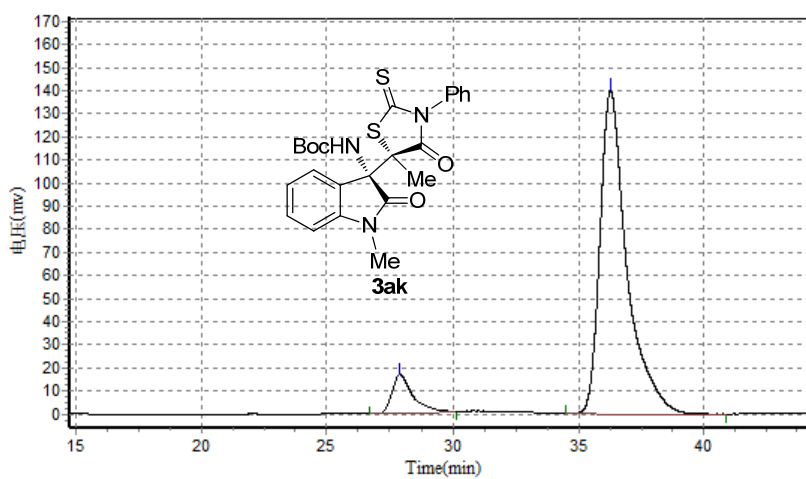
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 8.143 | 707490.125 | 11853879.000 | 93.5148 |
| 2 | | 17.697 | 17155.334 | 822062.375 | 6.4852 |
| Total | | | 724645.459 | 12675941.375 | 100.0000 |



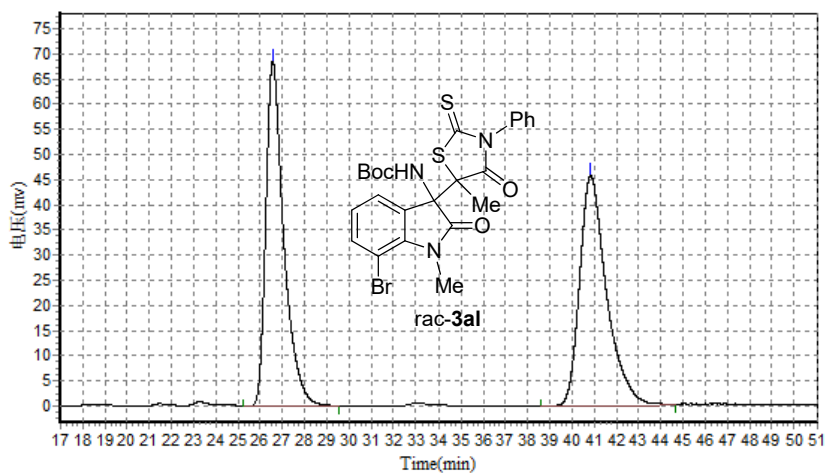
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 27.850 | 62733.578 | 3598807.250 | 49.7606 |
| 2 | | 36.195 | 49310.727 | 3633430.250 | 50.2394 |
| Total | | | 112044.305 | 7232237.500 | 100.0000 |



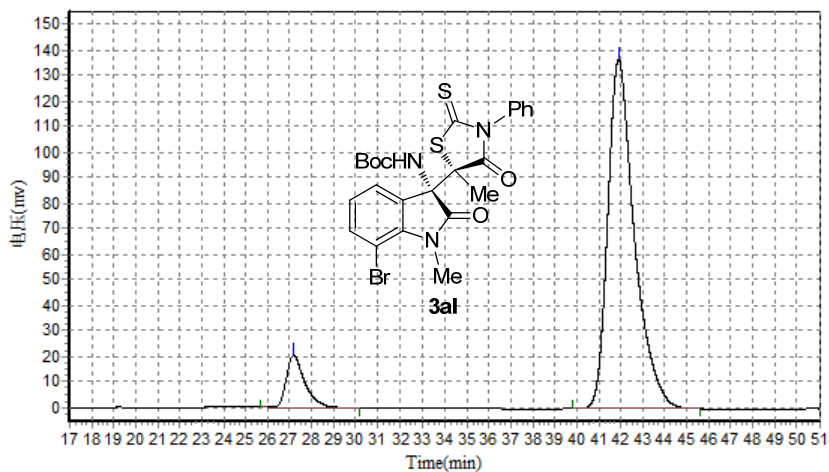
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 27.937 | 16713.631 | 933643.938 | 8.2809 |
| 2 | | 36.272 | 139521.141 | 10341077.000 | 91.7191 |
| Total | | | 156234.771 | 11274720.938 | 100.0000 |



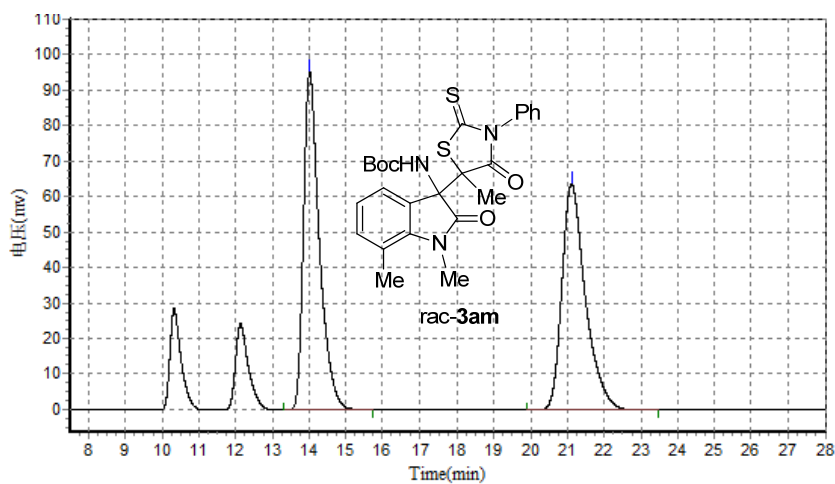
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 26.565 | 68452.383 | 3827727.000 | 50.1036 |
| 2 | | 40.837 | 45673.434 | 3811892.500 | 49.8964 |
| Total | | | 114125.816 | 7639619.500 | 100.0000 |



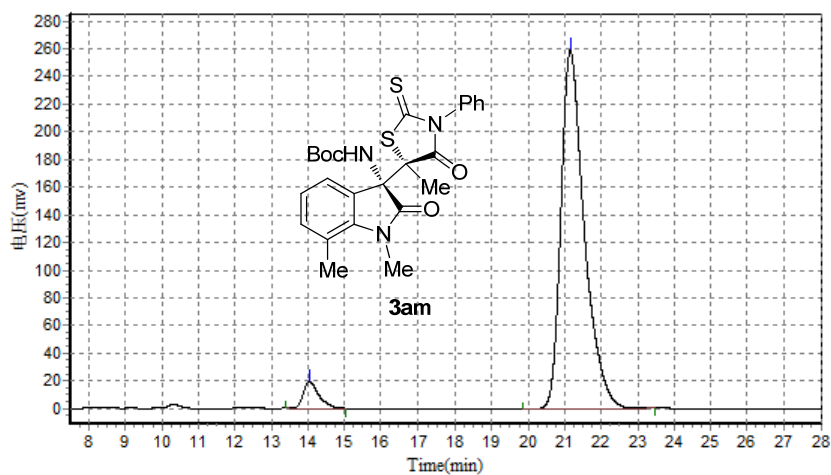
Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 27.172 | 20633.986 | 1196410.750 | 9.4149 |
| 2 | | 41.897 | 136746.516 | 11511266.000 | 90.5851 |
| Total | | | 157380.502 | 12707676.750 | 100.0000 |



Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|-------------|----------|
| 1 | | 14.015 | 95434.500 | 2862088.750 | 50.2672 |
| 2 | | 21.110 | 63797.523 | 2831658.250 | 49.7328 |
| Total | | | 159232.023 | 5693747.000 | 100.0000 |



Results

| Peak No. | Peak ID | Ret Time | Height | Area | Conc. |
|--------------|---------|----------|------------|--------------|----------|
| 1 | | 14.035 | 19620.867 | 581027.250 | 4.8203 |
| 2 | | 21.152 | 258455.375 | 11472775.000 | 95.1797 |
| Total | | | 278076.242 | 12053802.250 | 100.0000 |

4. X-ray Analysis of Product 3ba

The crystal data of compound **3ba** have been deposited in CCDC with number 1569396.

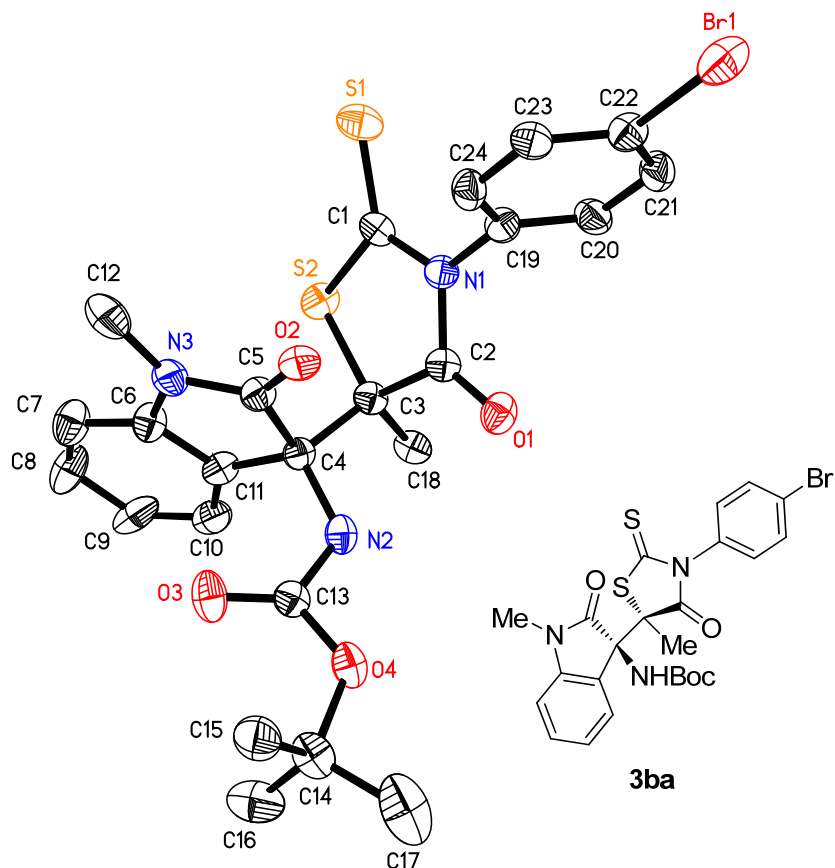


Table 1. Crystal data and structure refinement for **3ba**

| | | |
|----------------------|---|----------|
| Identification code | dm17375 | |
| Empirical formula | C ₂₄ H ₂₄ Br N ₃ O ₄ S ₂ | |
| Formula weight | 562.49 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Orthorhombic | |
| Space group | P 21 21 21 | |
| Unit cell dimensions | a = 8.7914(10) Å | α = 90°. |
| | b = 16.8836(19) Å | β = 90°. |
| | c = 17.728(2) Å | γ = 90°. |
| Volume | 2631.4(5) Å ³ | |
| Z | 4 | |
| Density (calculated) | 1.420 Mg/m ³ | |

| | |
|-----------------------------------|---|
| Absorption coefficient | 1.755 mm ⁻¹ |
| F(000) | 1152 |
| Crystal size | 0.200 x 0.160 x 0.130 mm ³ |
| Theta range for data collection | 2.298 to 25.499°. |
| Index ranges | -10<=h<=10, -20<=k<=20, -20<=l<=21 |
| Reflections collected | 18453 |
| Independent reflections | 4898 [R(int) = 0.0287] |
| Completeness to theta = 25.242° | 100.0 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7456 and 0.5693 |
| Refinement method | Full-matrix least-squares on F ² |
| Data / restraints / parameters | 4898 / 0 / 317 |
| Goodness-of-fit on F ² | 1.015 |
| Final R indices [I>2sigma(I)] | R1 = 0.0322, wR2 = 0.0687 |
| R indices (all data) | R1 = 0.0453, wR2 = 0.0737 |
| Absolute structure parameter | 0.006(4) |
| Extinction coefficient | 0.0069(5) |
| Largest diff. peak and hole | 0.526 and -0.556 e.Å ⁻³ |

