

# Experimental and theoretical investigations of regioselective functionalization of 3-hydroxybisindoles with thiols

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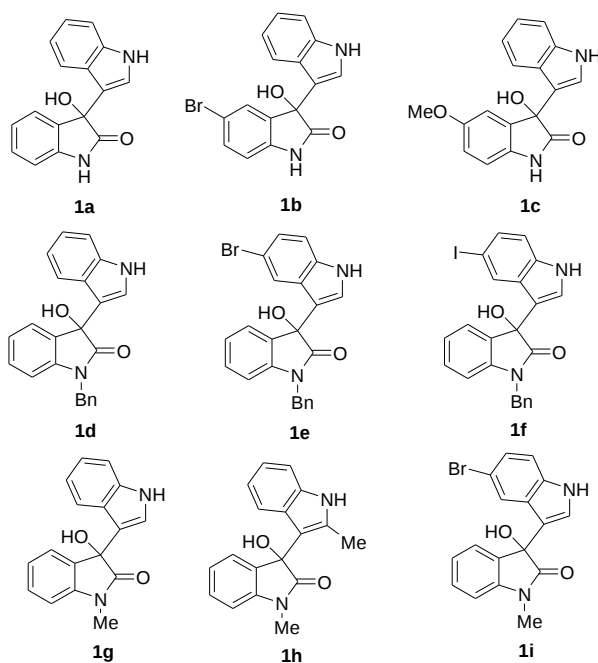
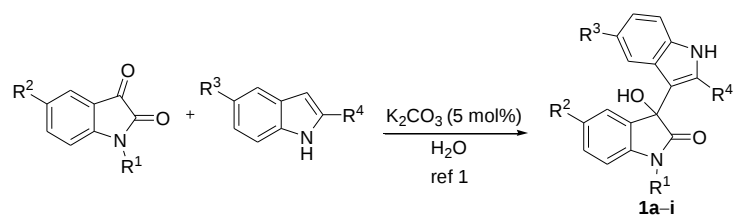
## SUPPORTING INFORMATION

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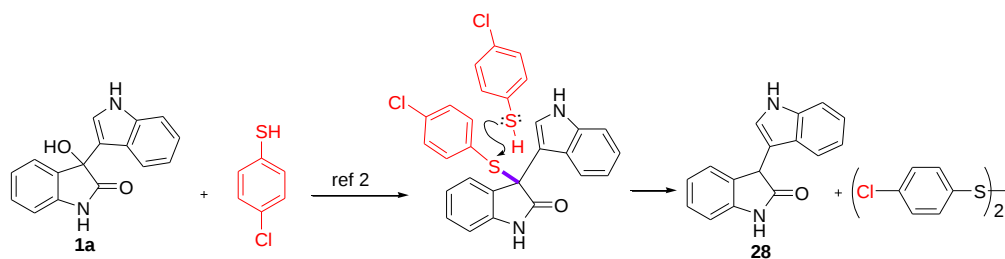
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## Synthesis of 3-hydroxy bisindoles **1**

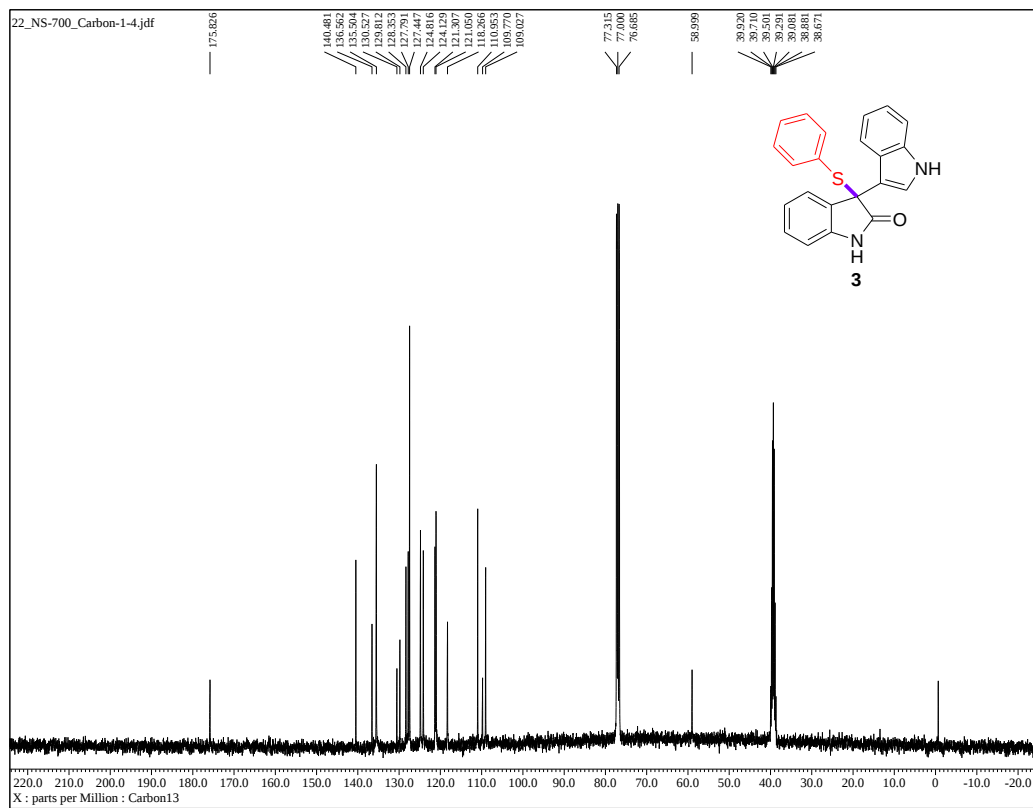
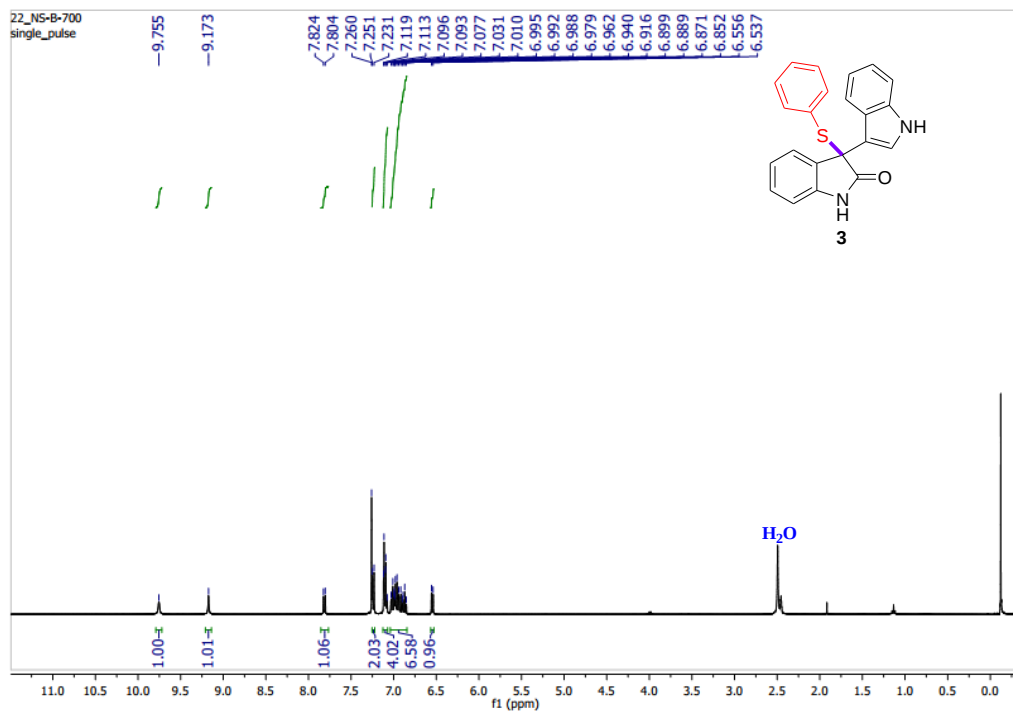


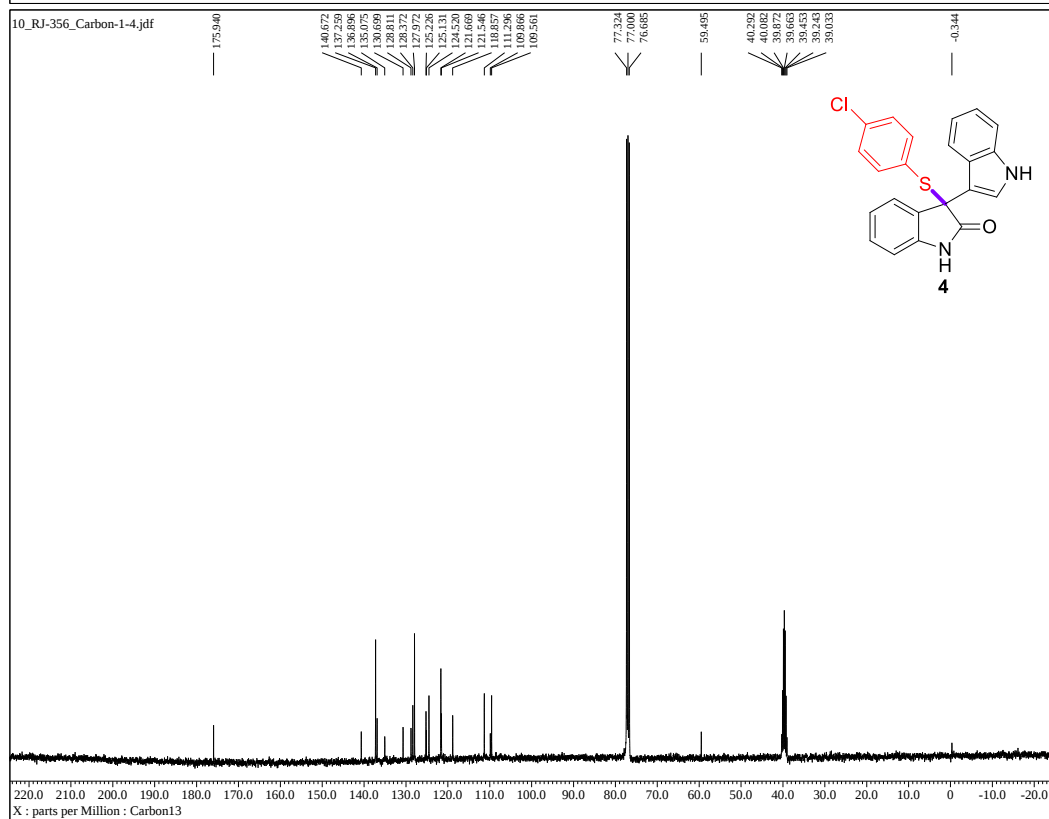
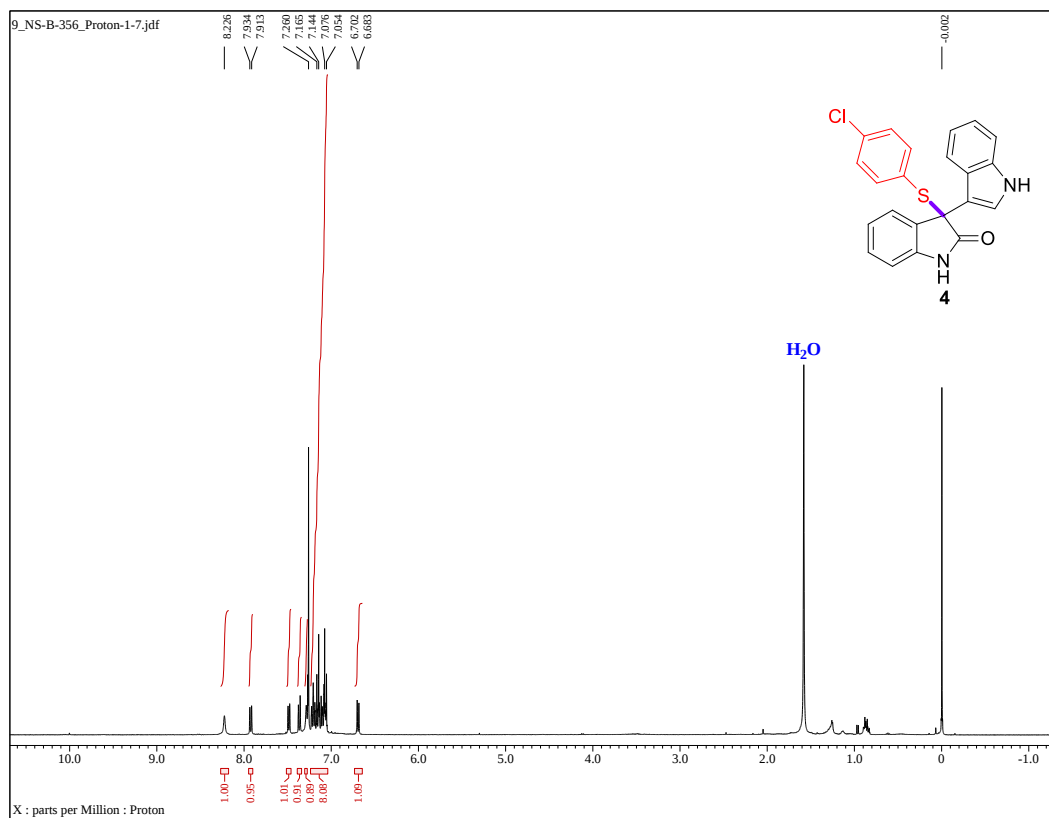
## Plausible mechanism for the synthesis of **28**

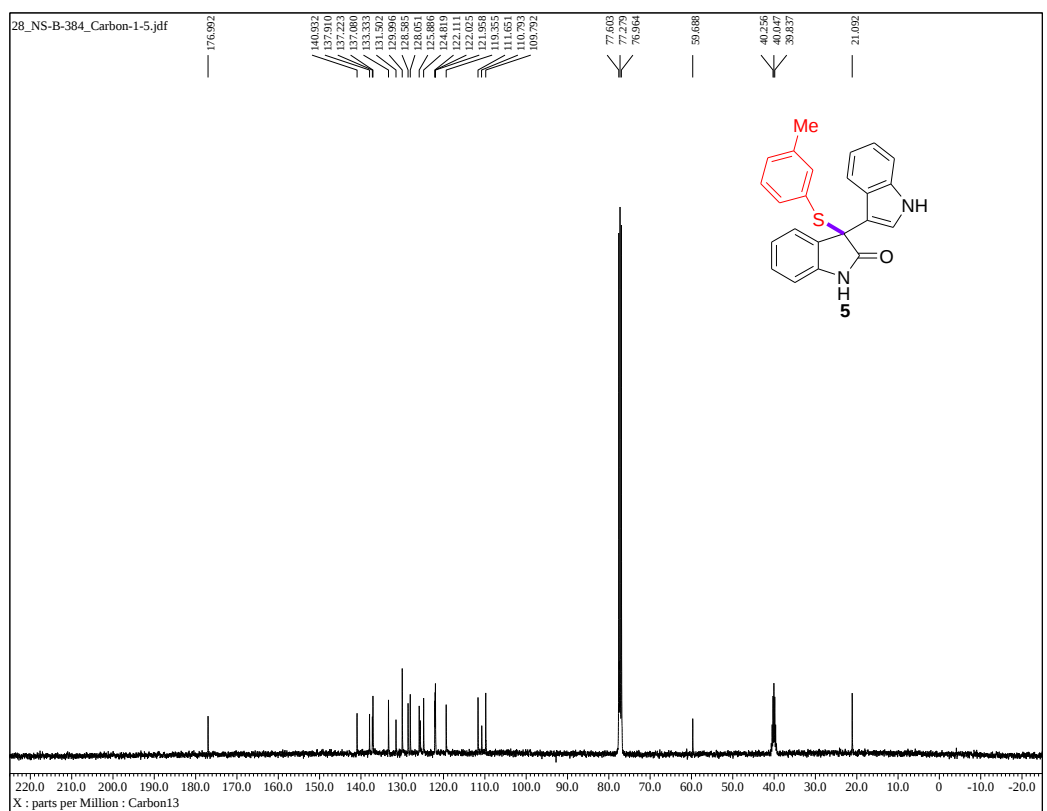
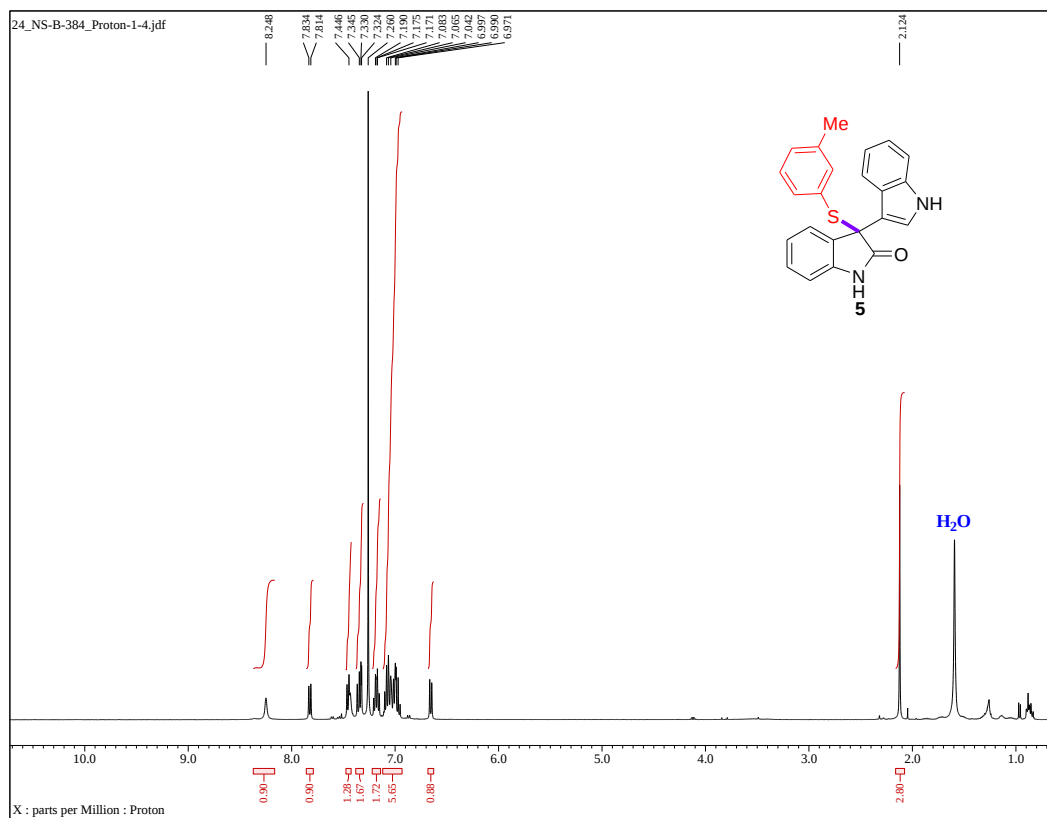


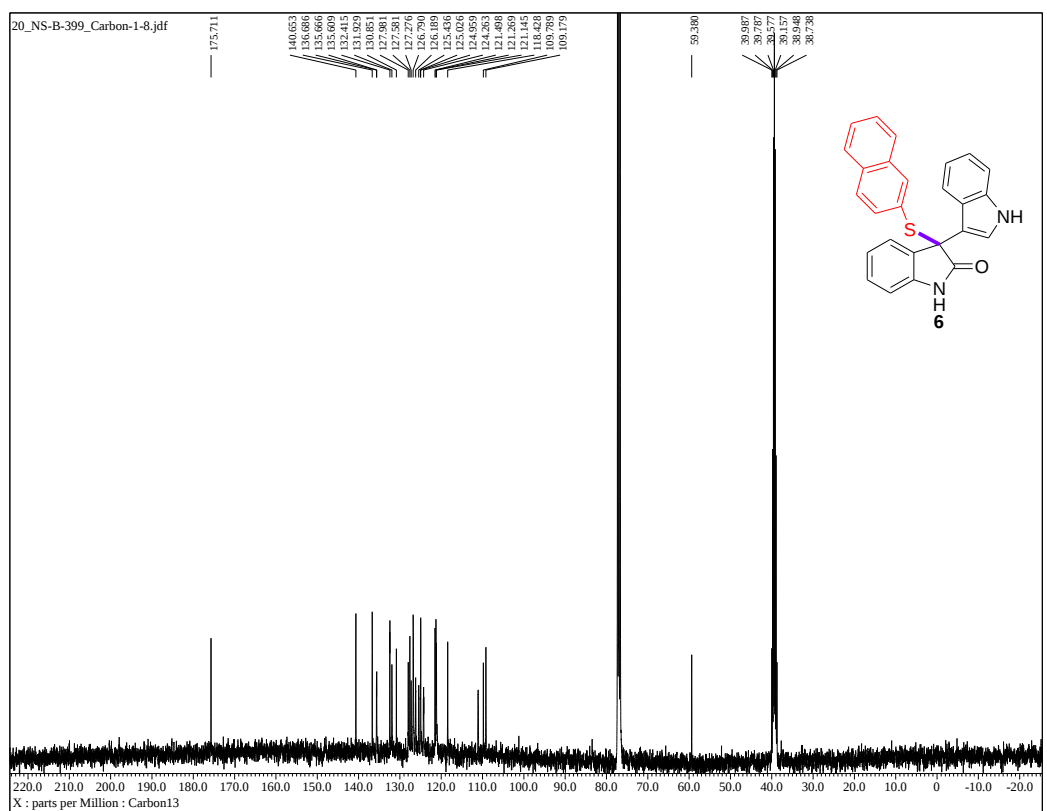
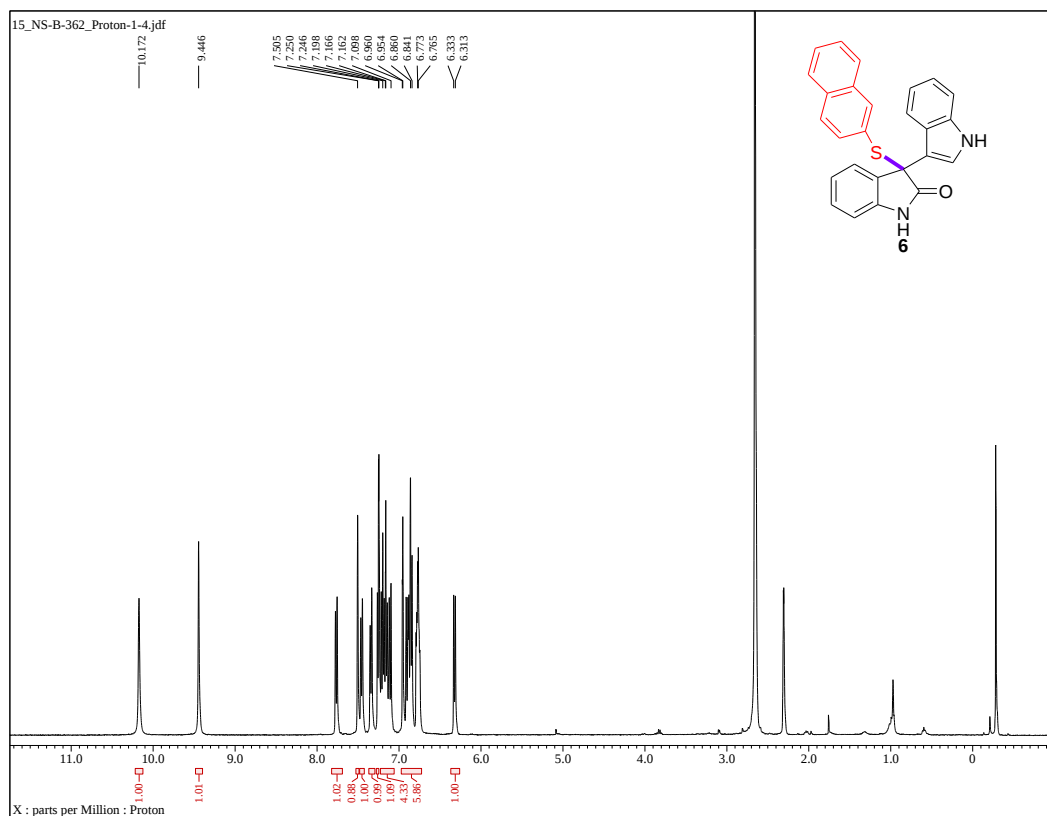
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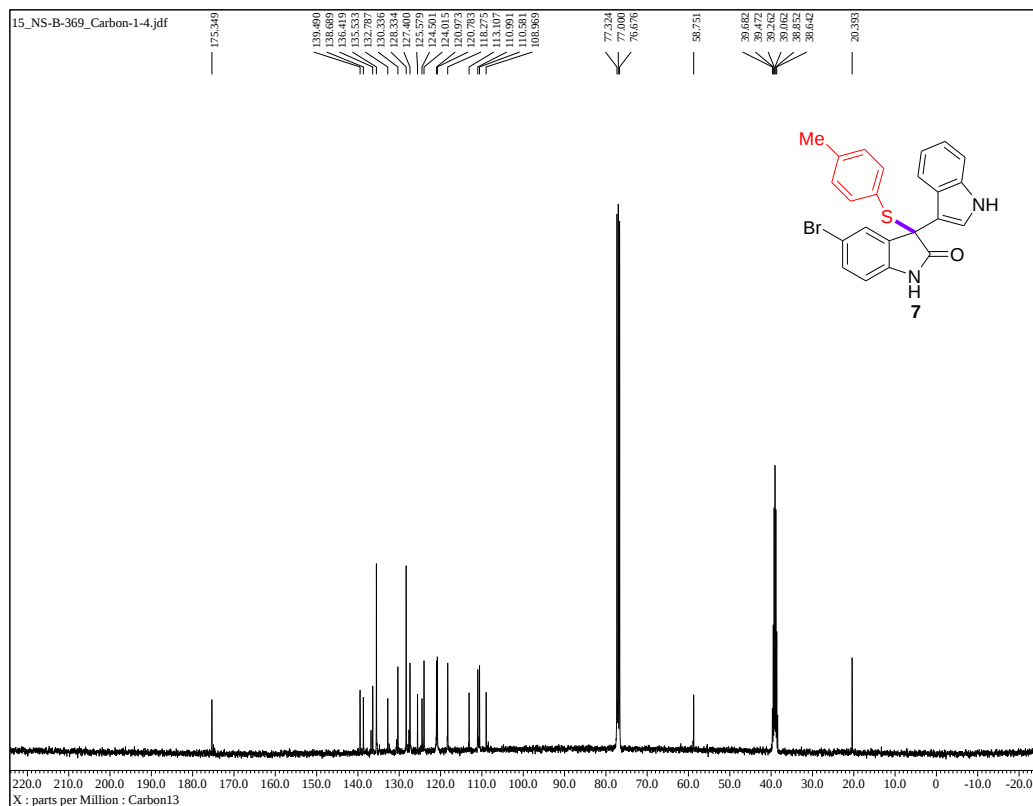
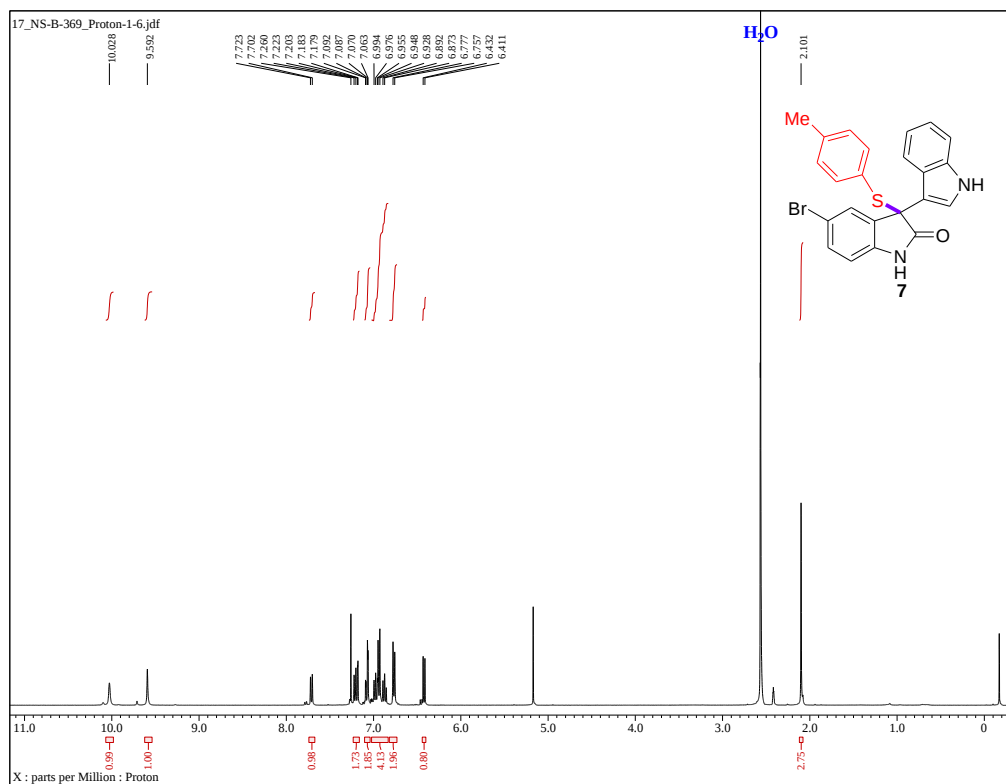
1. G. Shanthi, N. Vidyalakshmi, P.T. Perumal, *Arkivoc* **2009**, 121.
2. F. Zhu, F. Zhou, Z. Y. Cao, C. Wang, Y. X. Zhang, C. H. Wang, J. Zhou, *Synthesis* **2012**, 44, 3129.

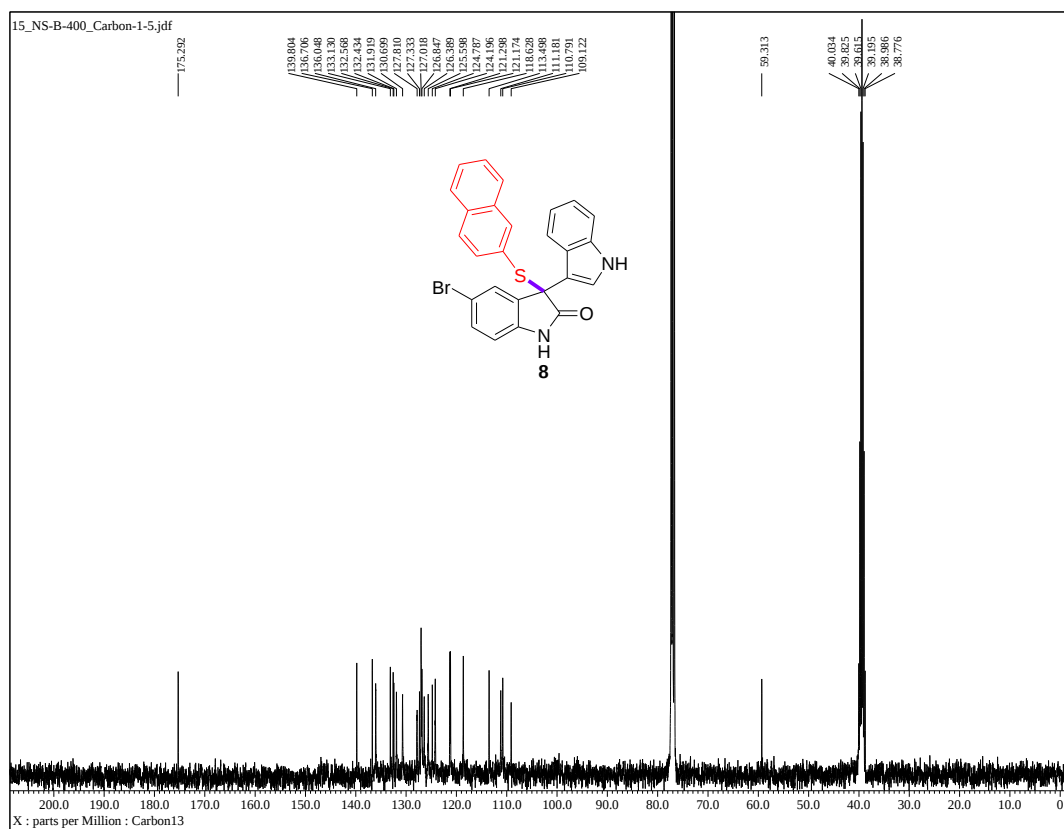
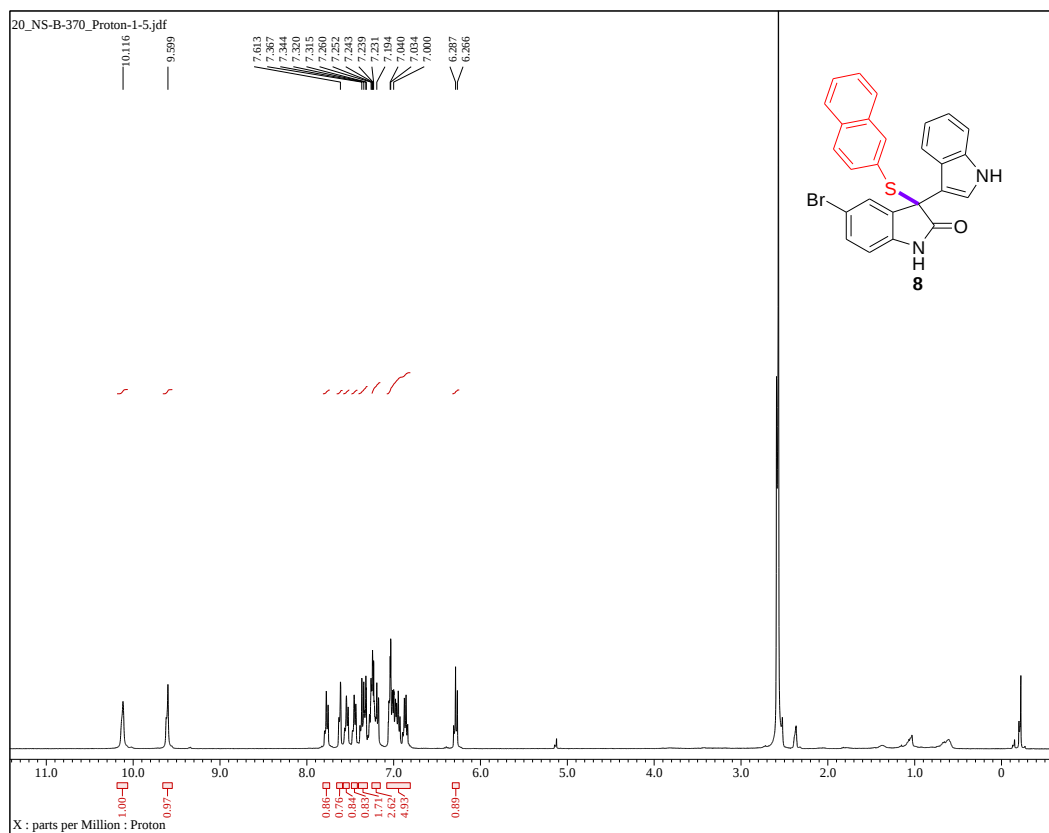


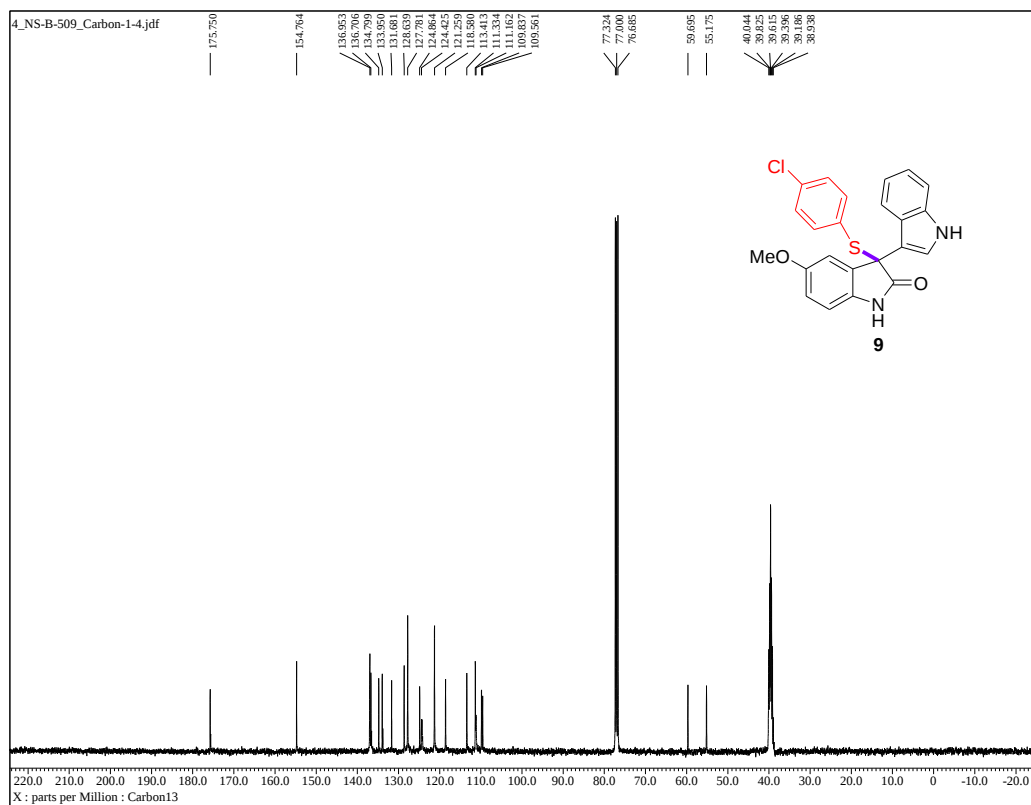
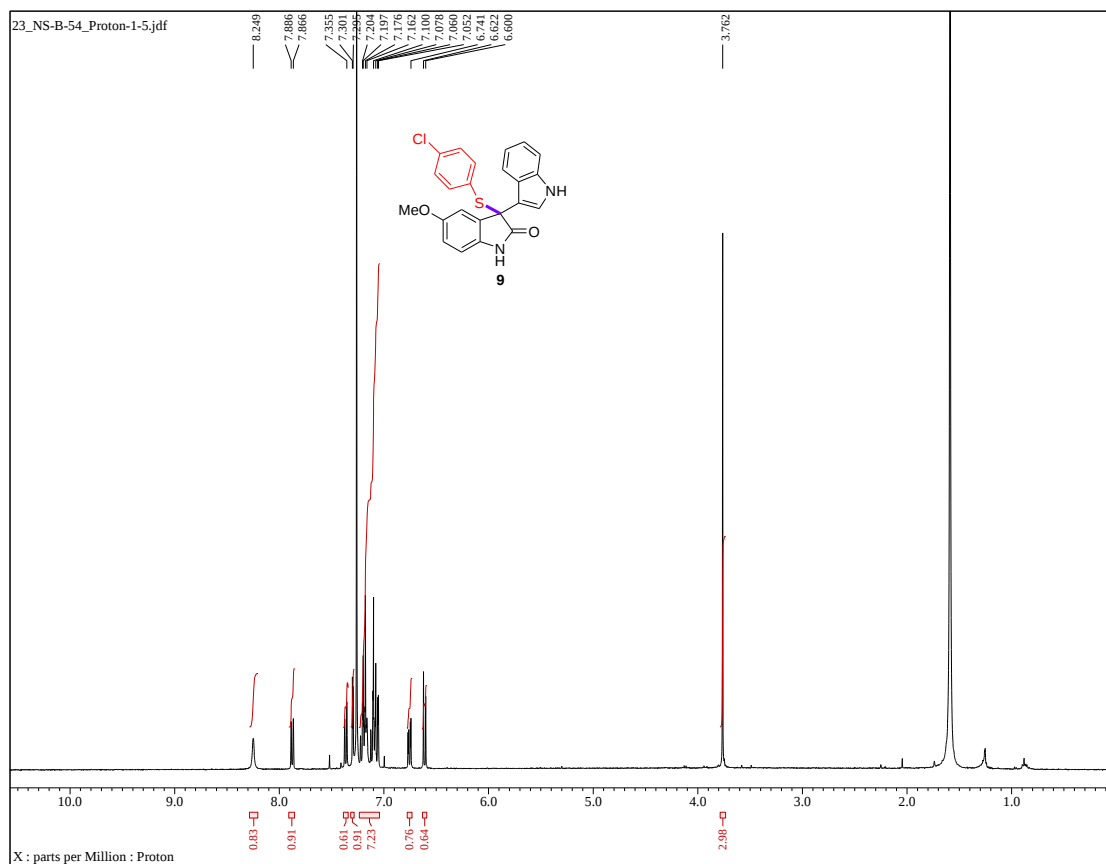


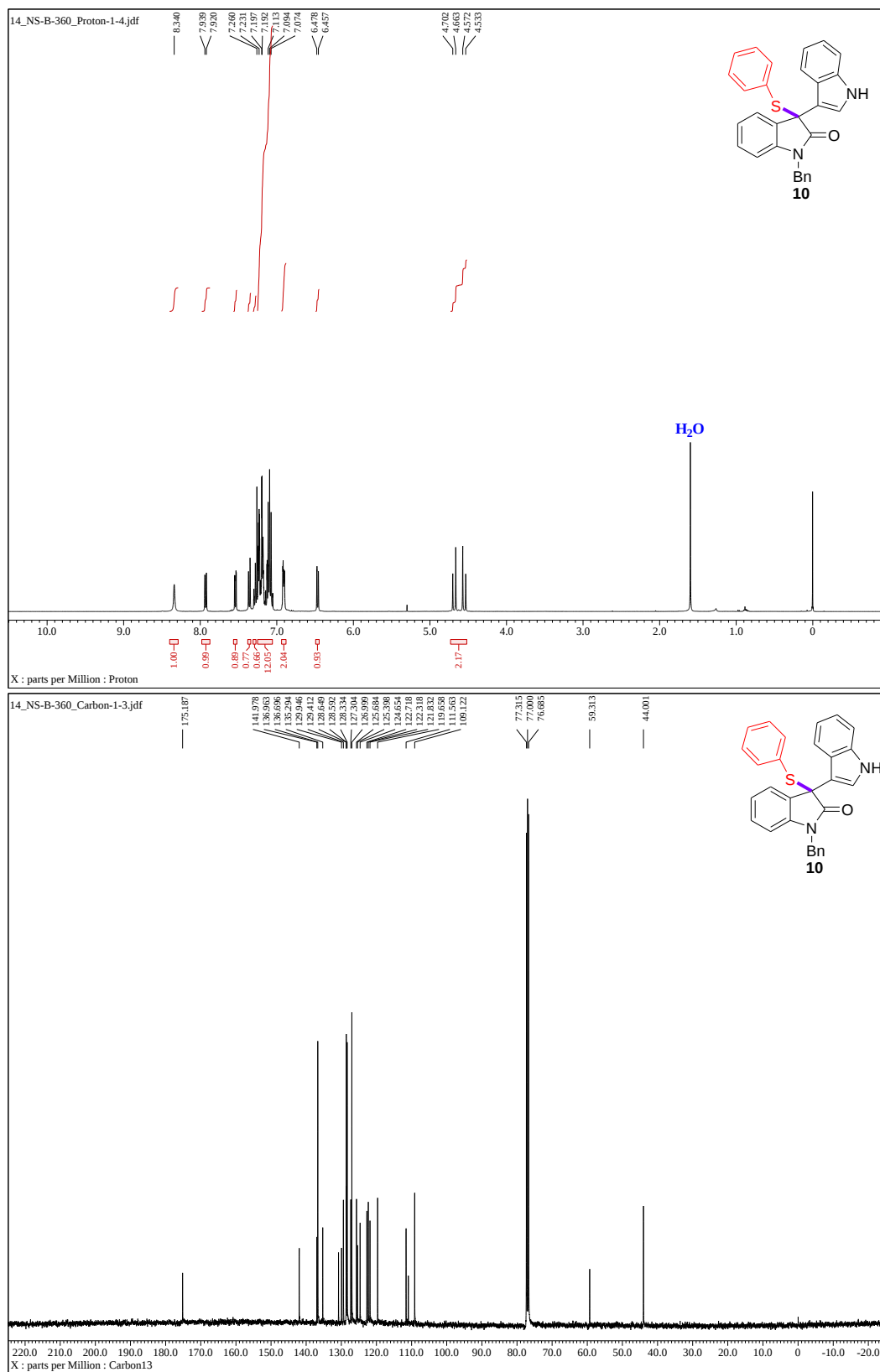


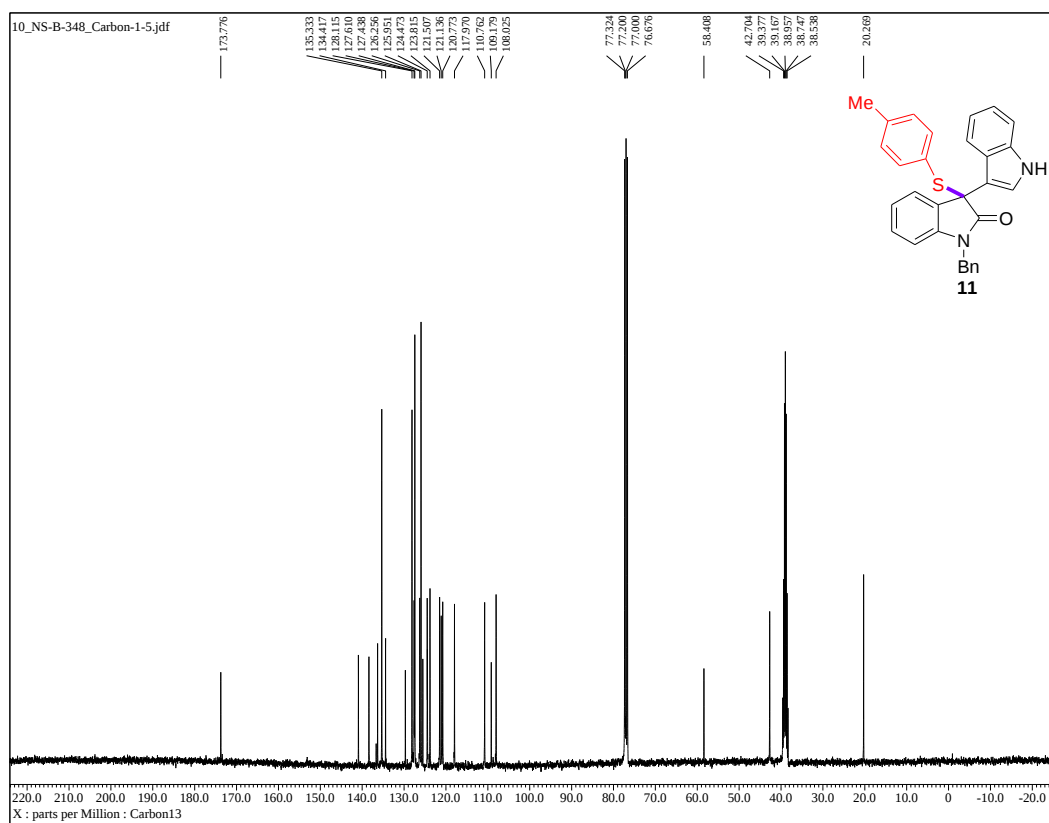
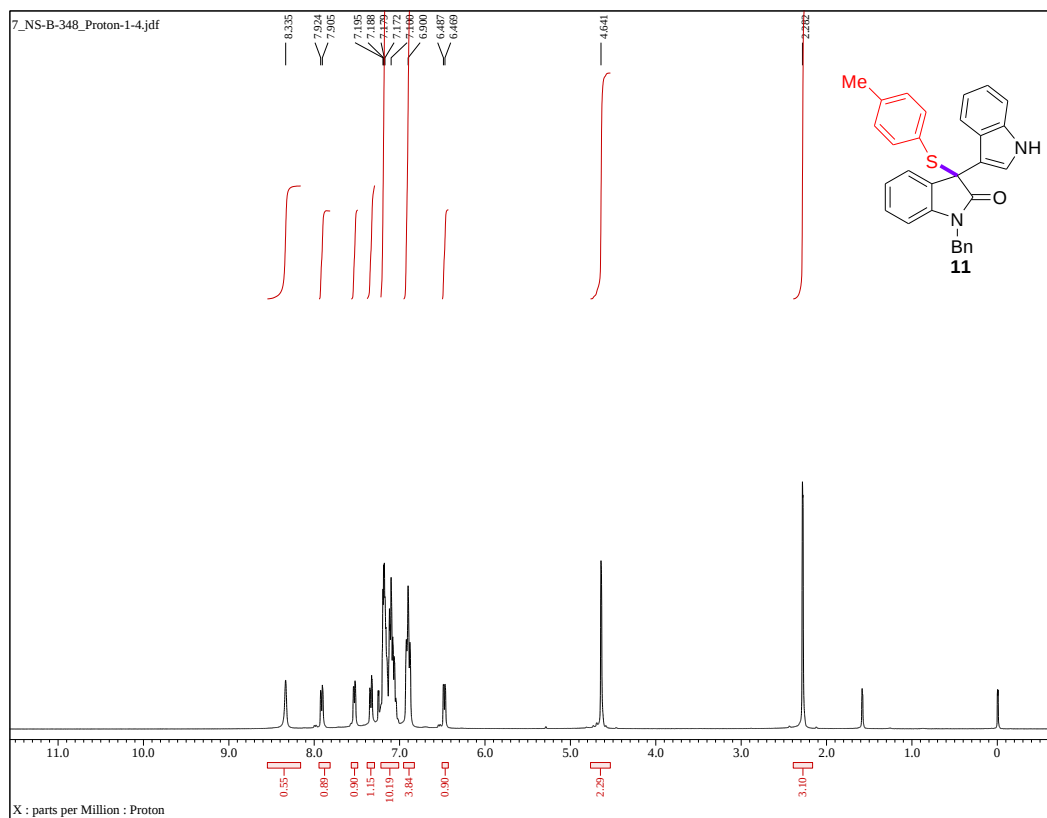


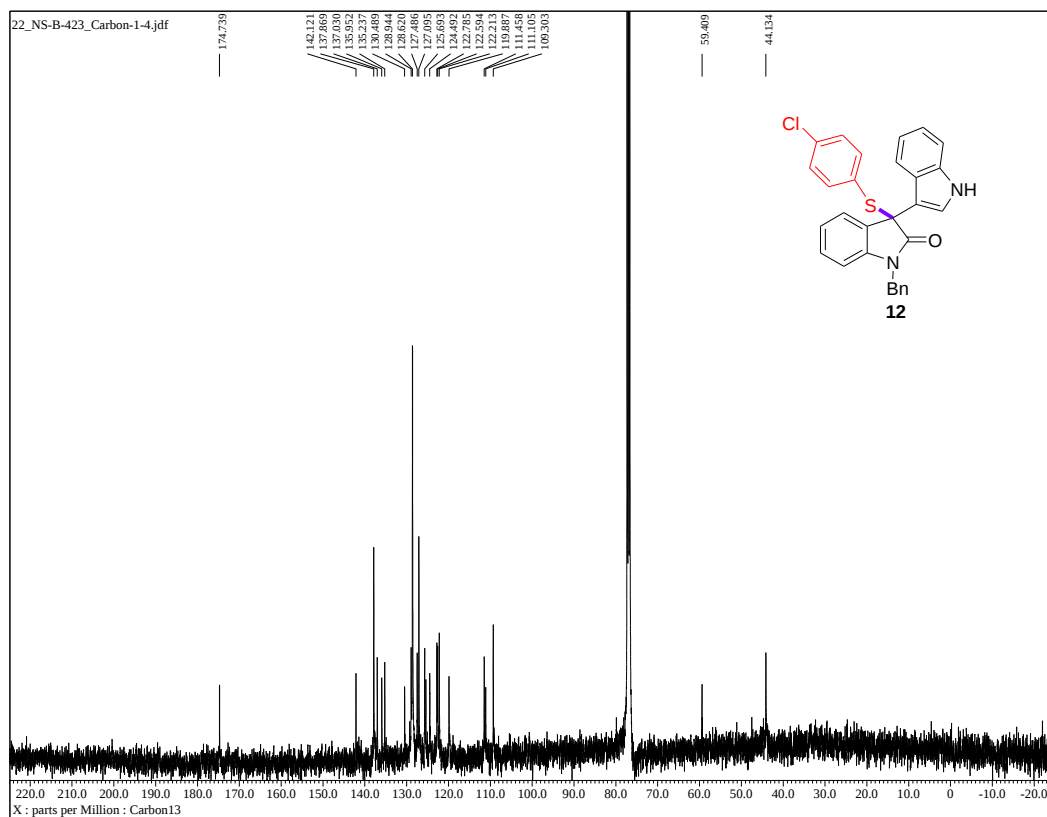
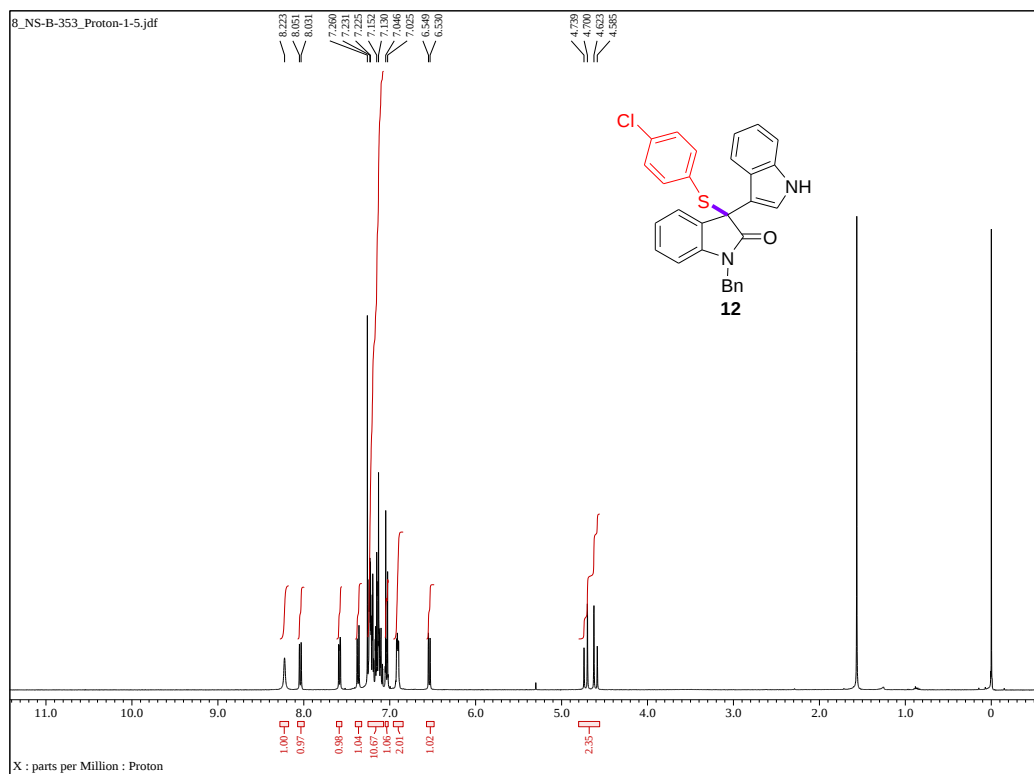


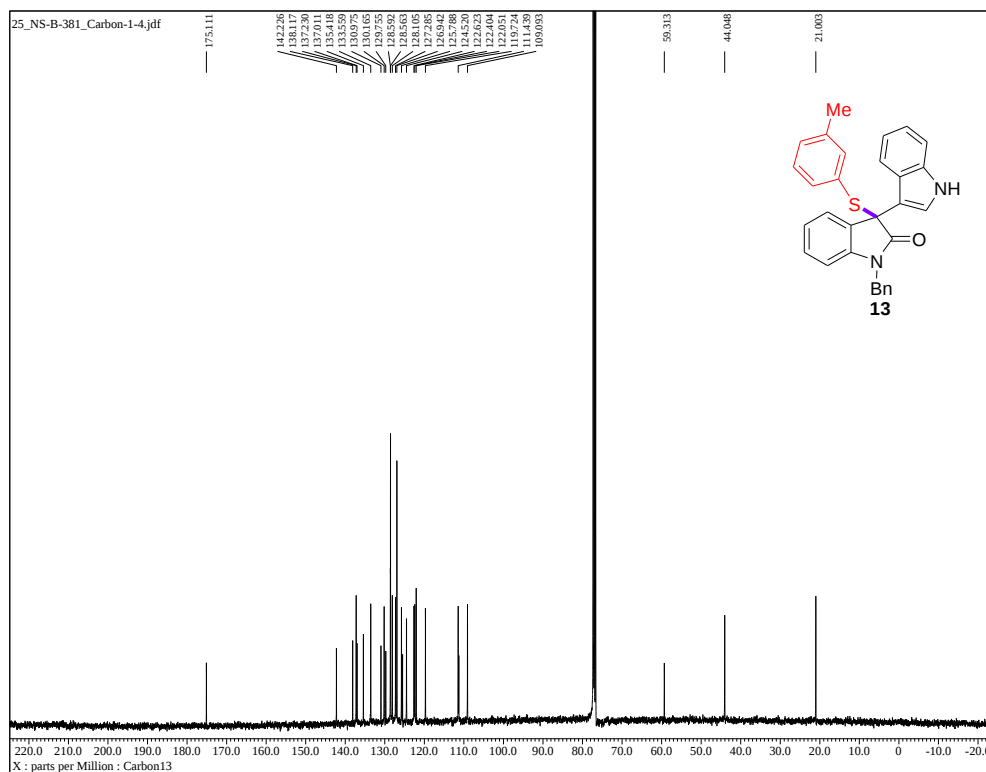
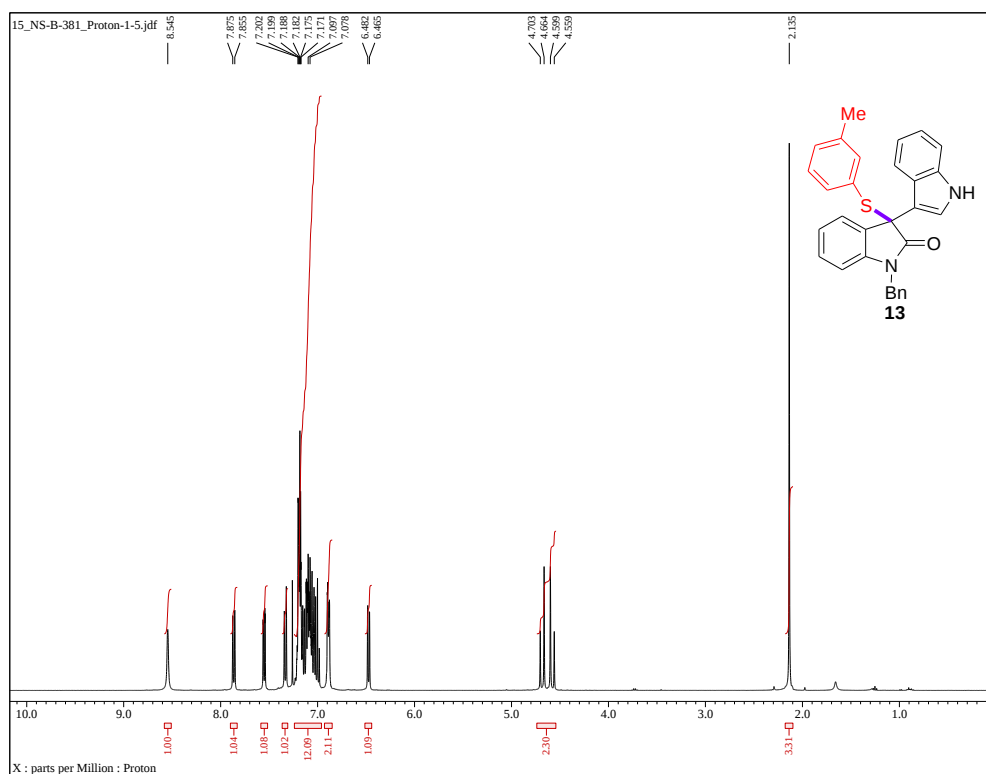


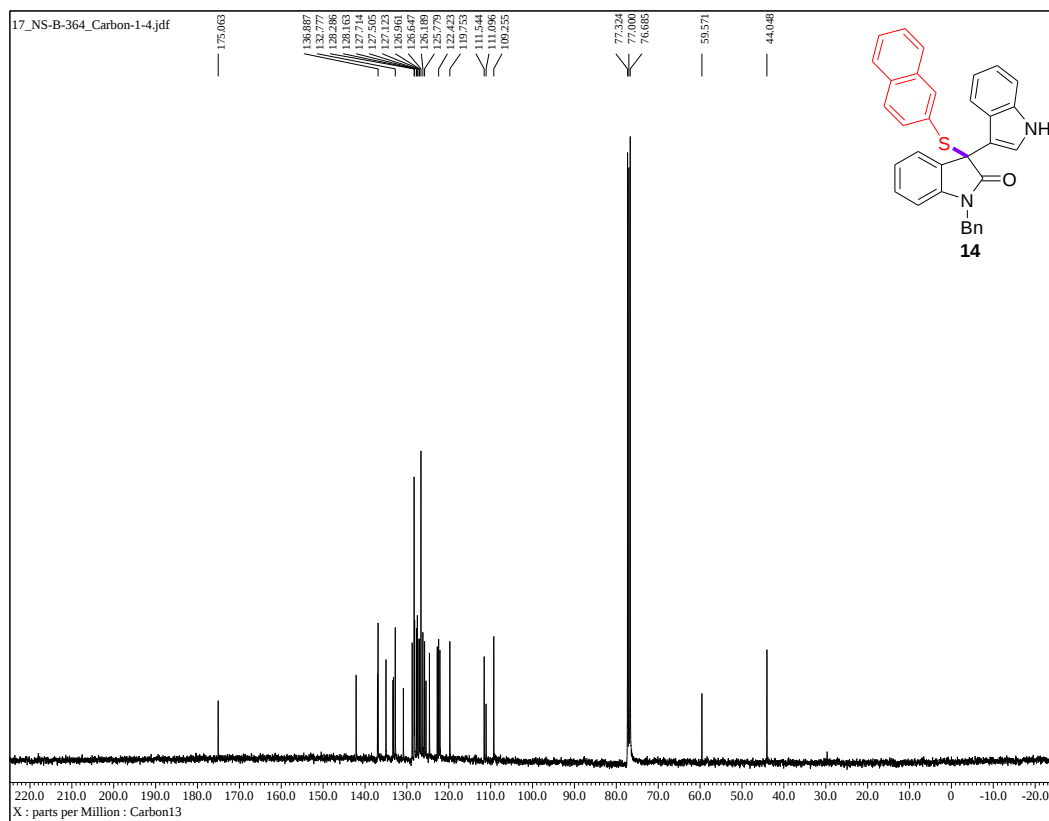
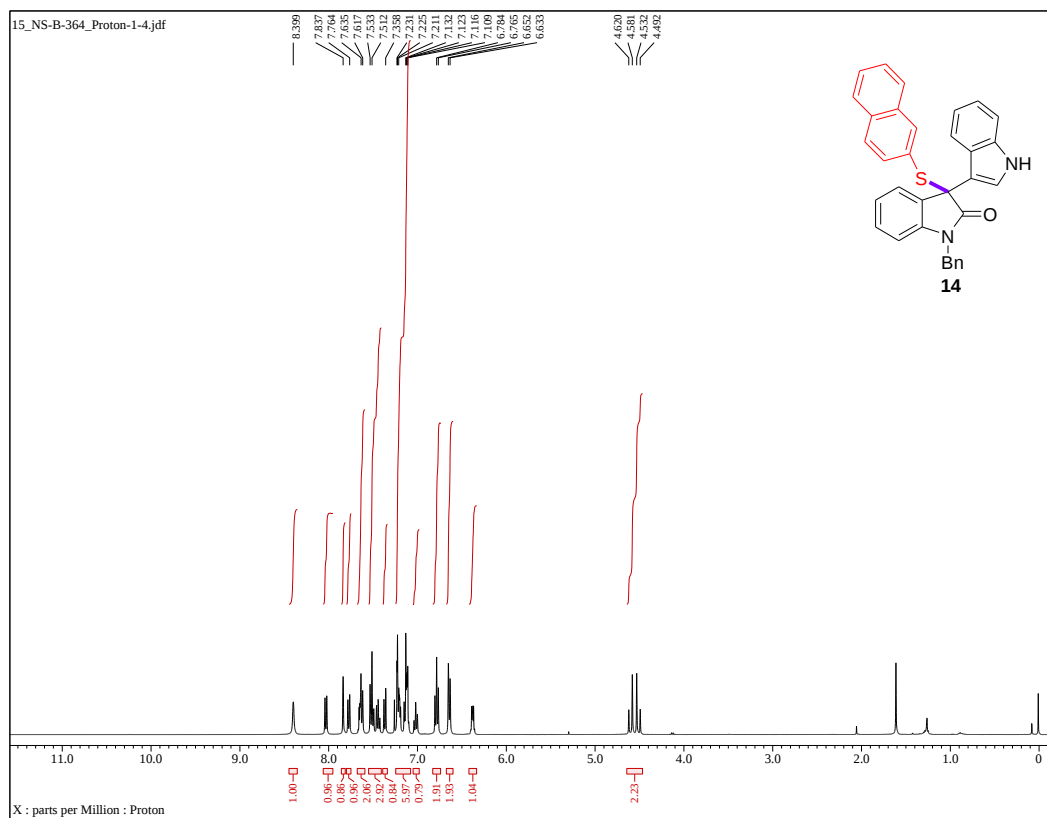


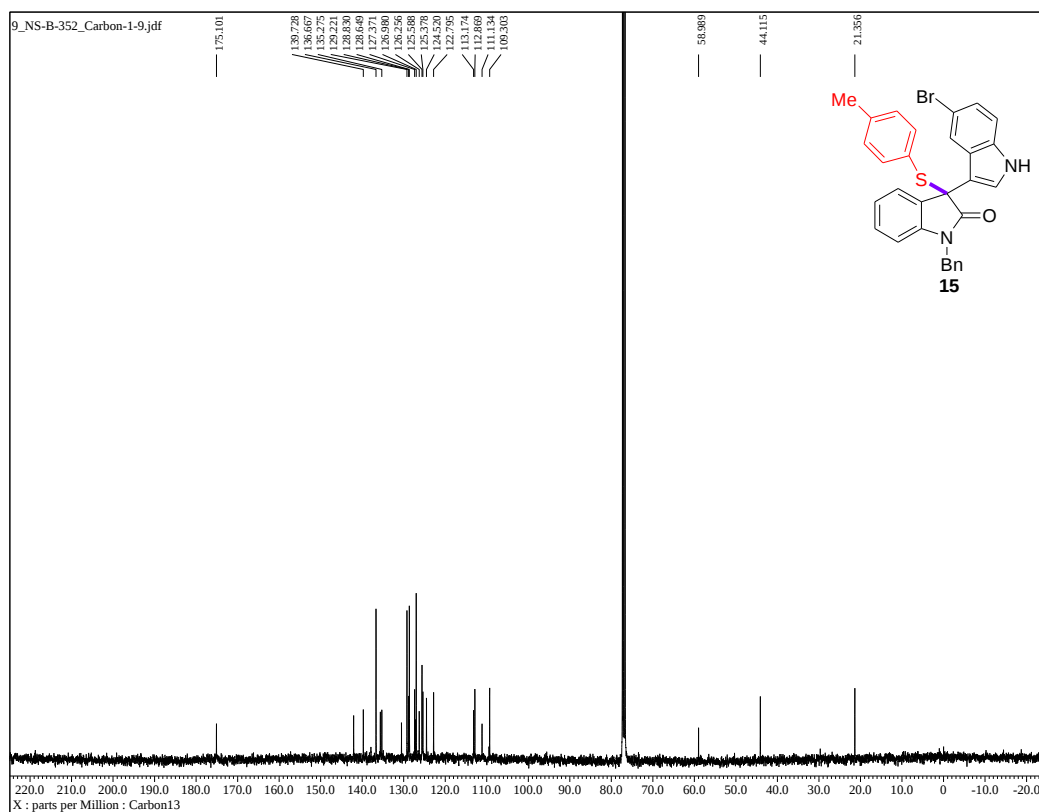
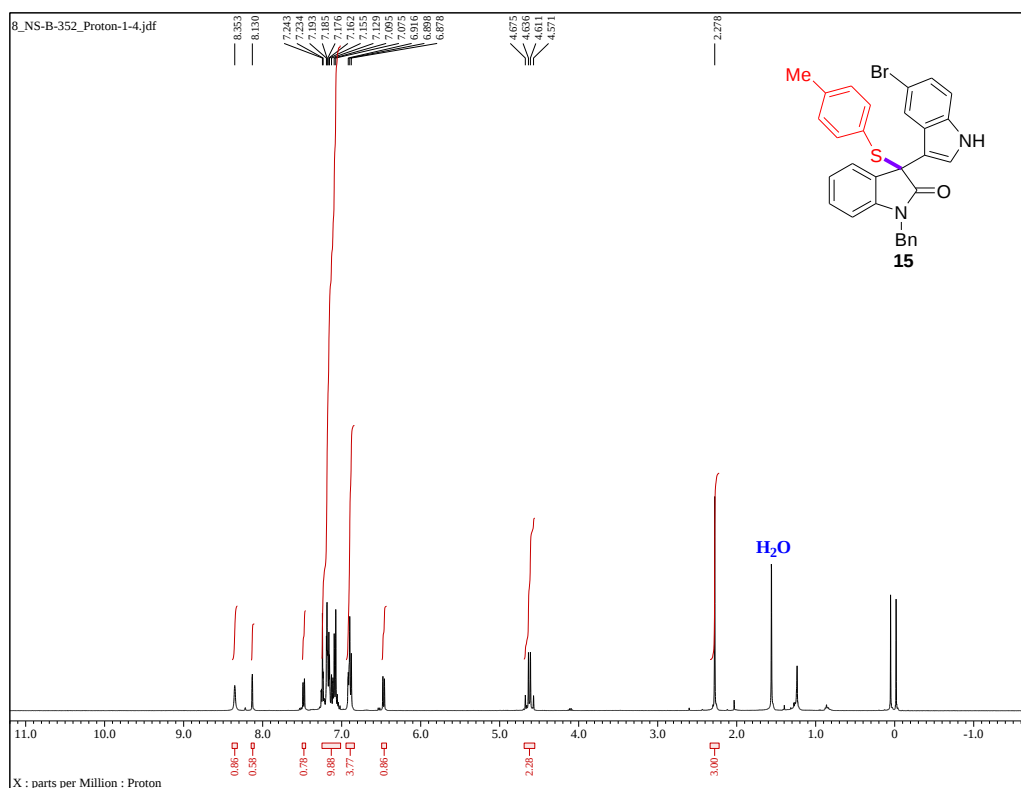


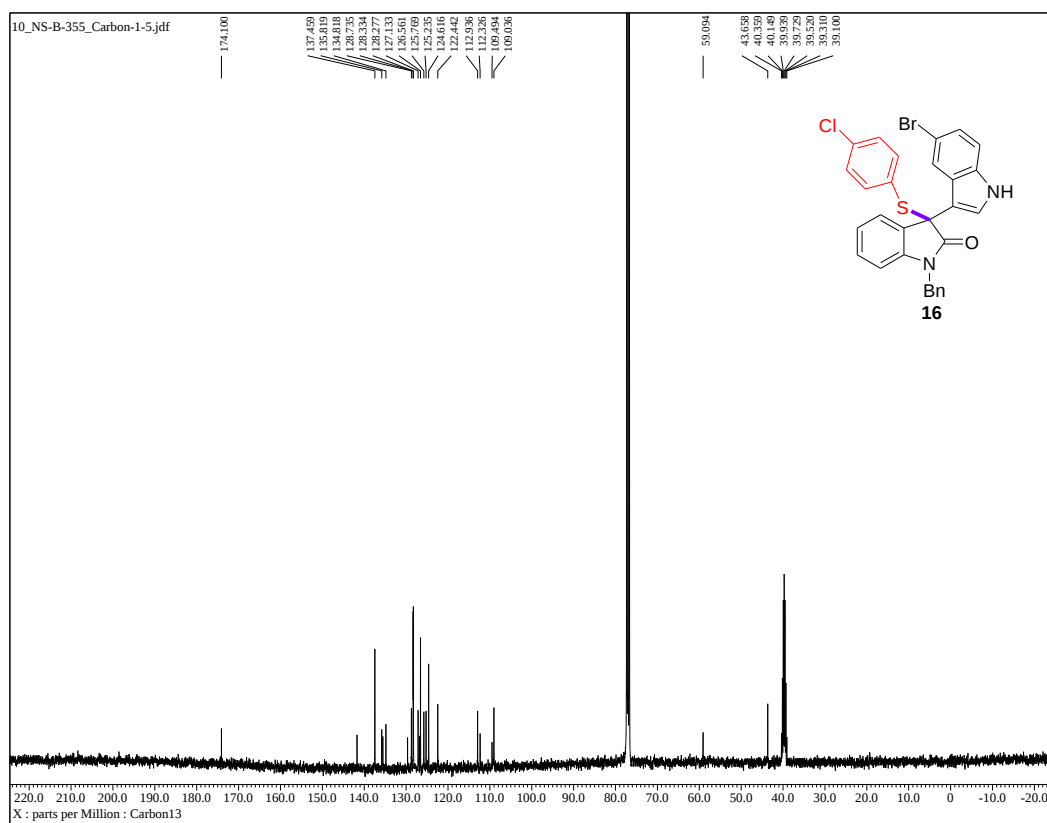
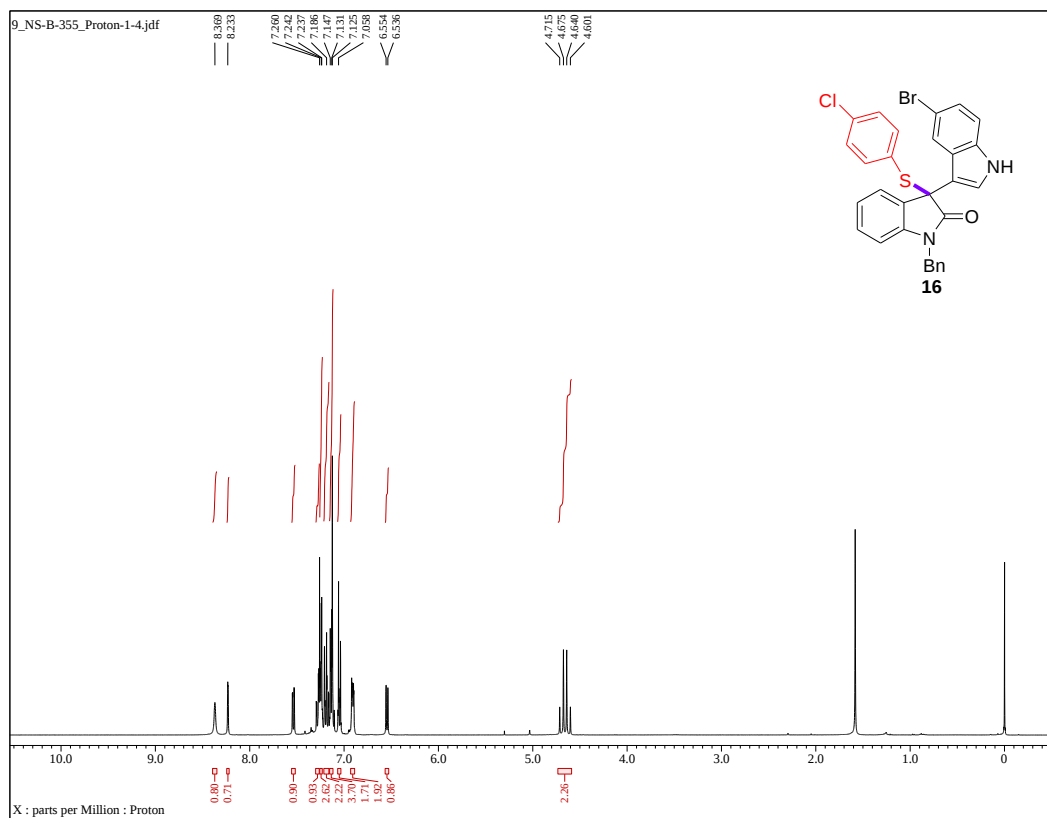


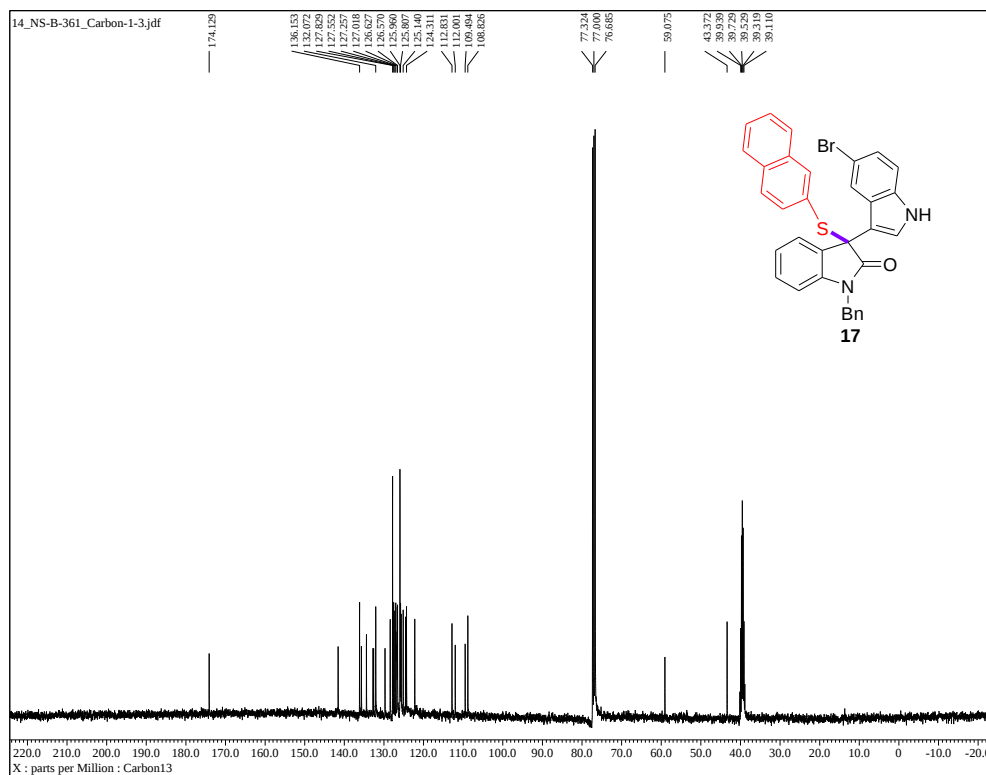
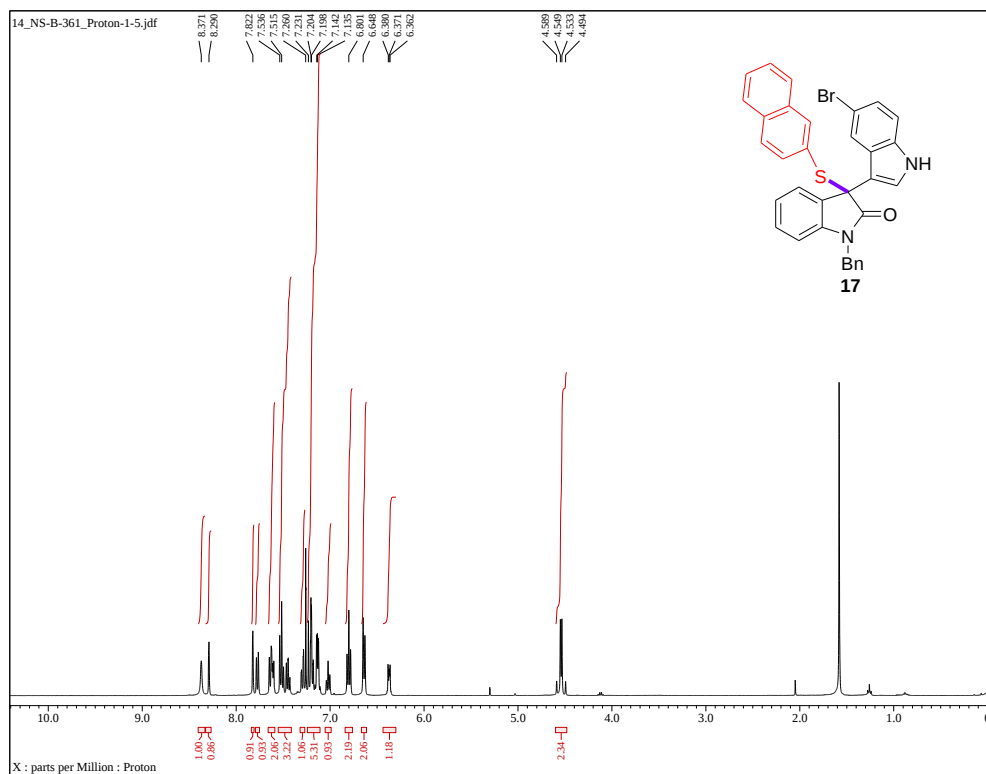


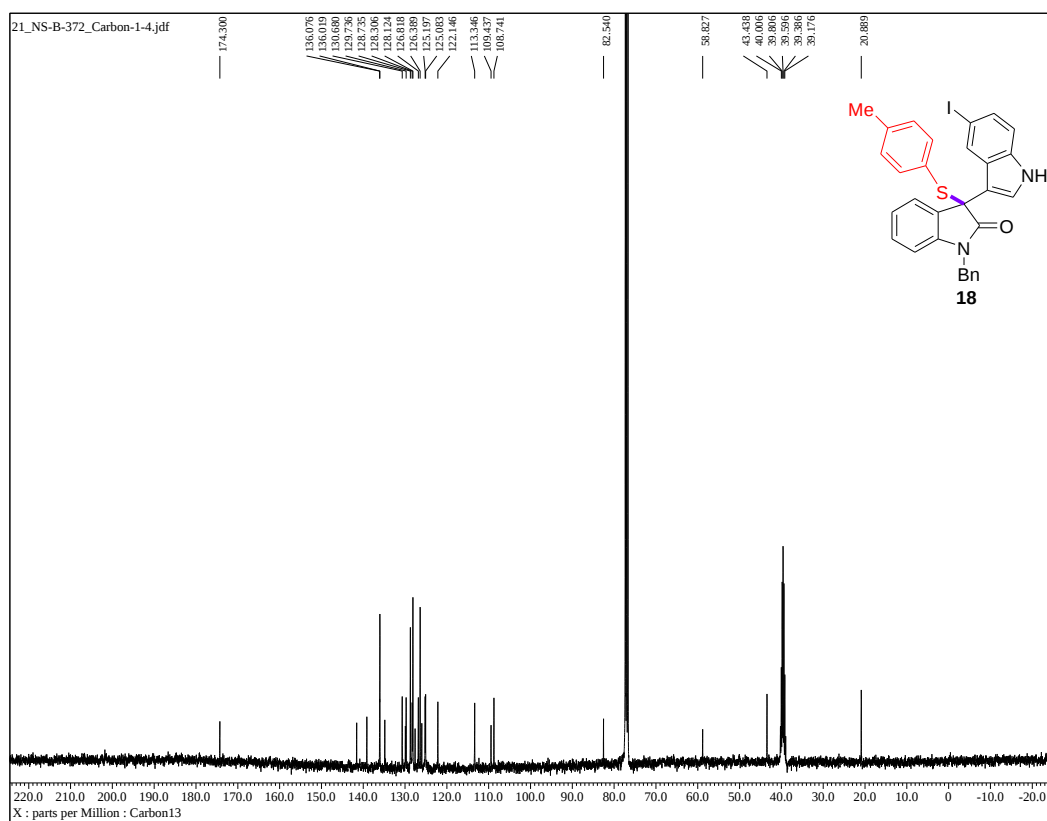
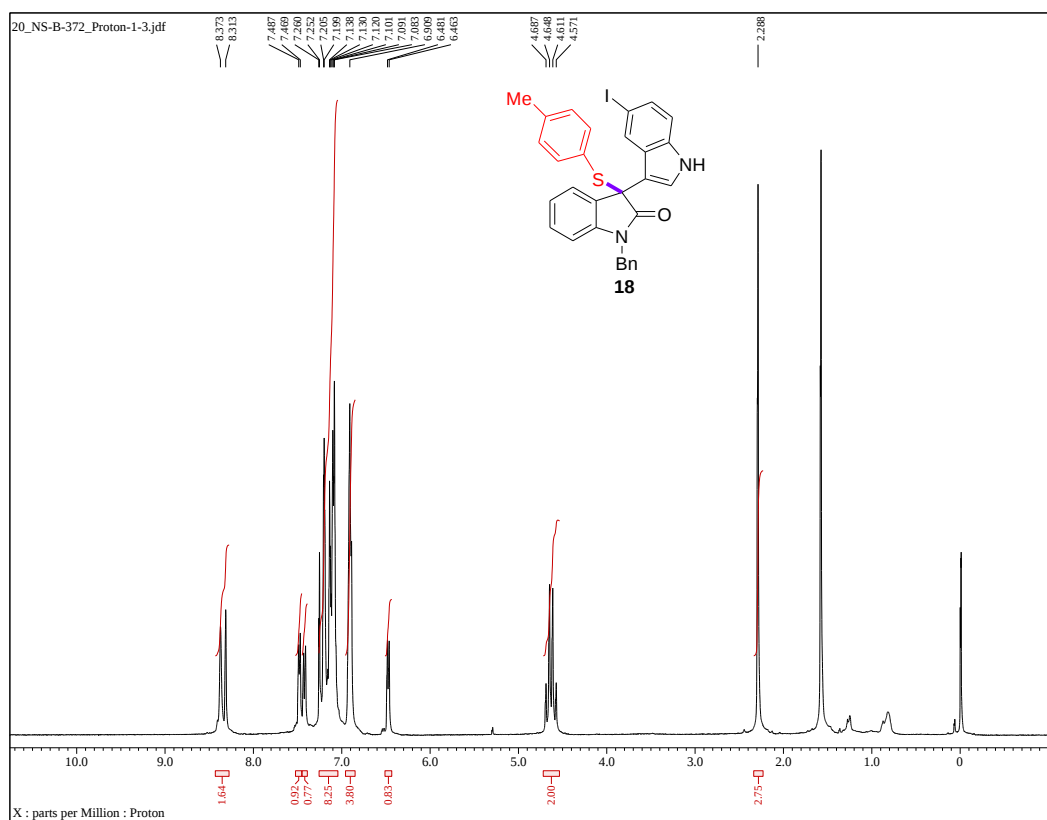


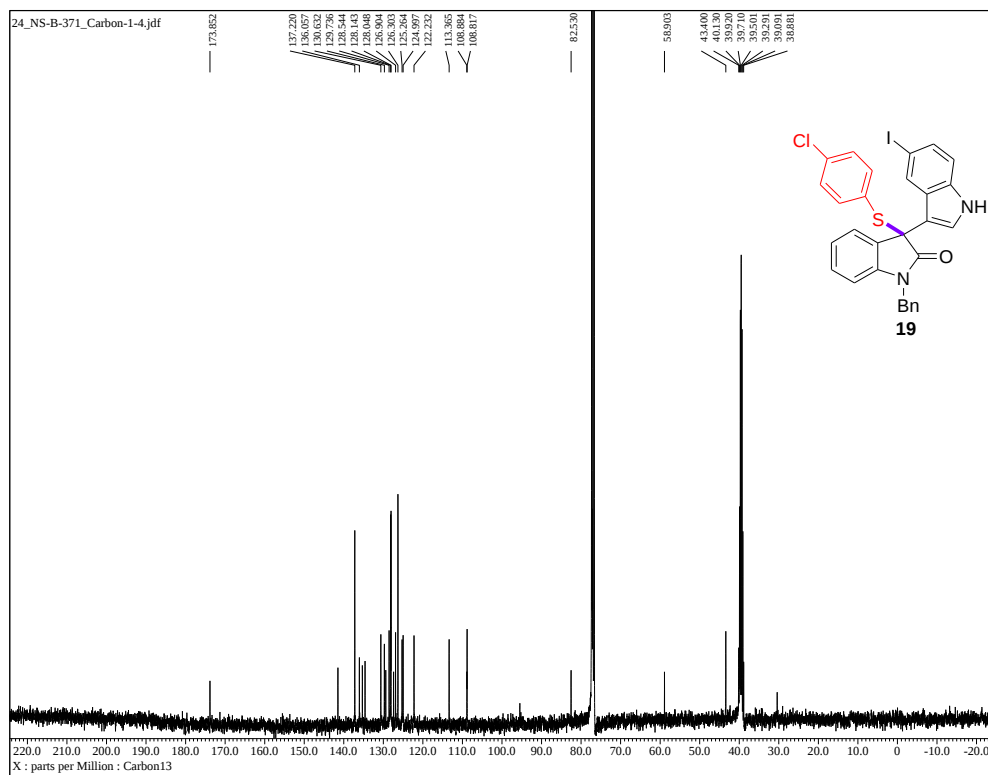
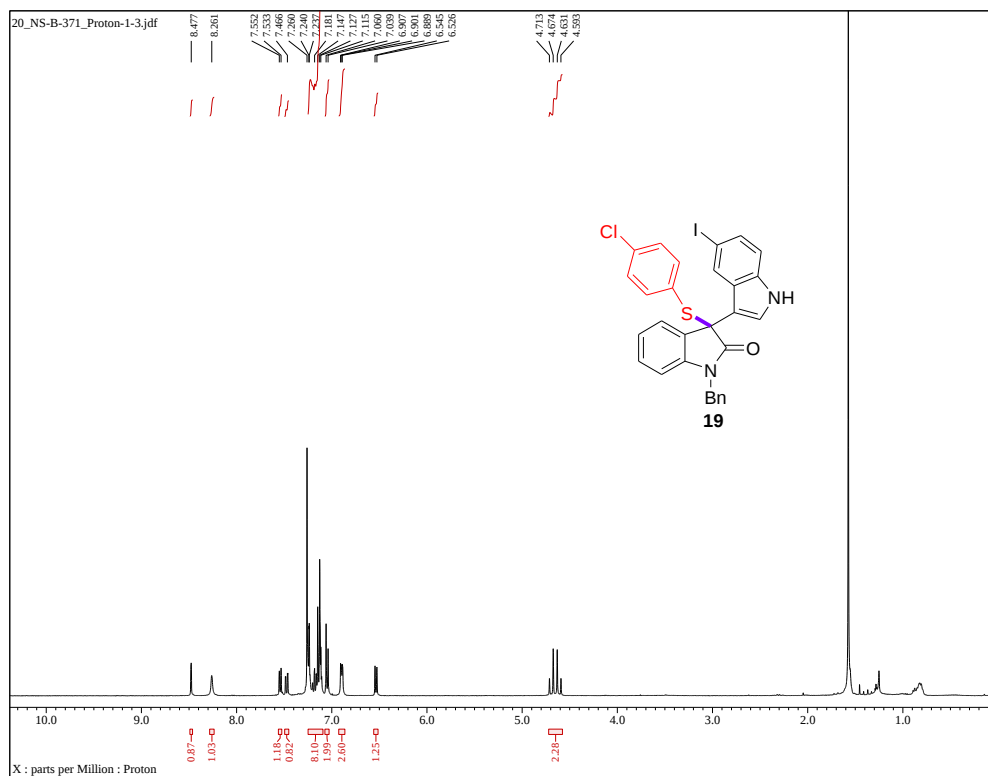


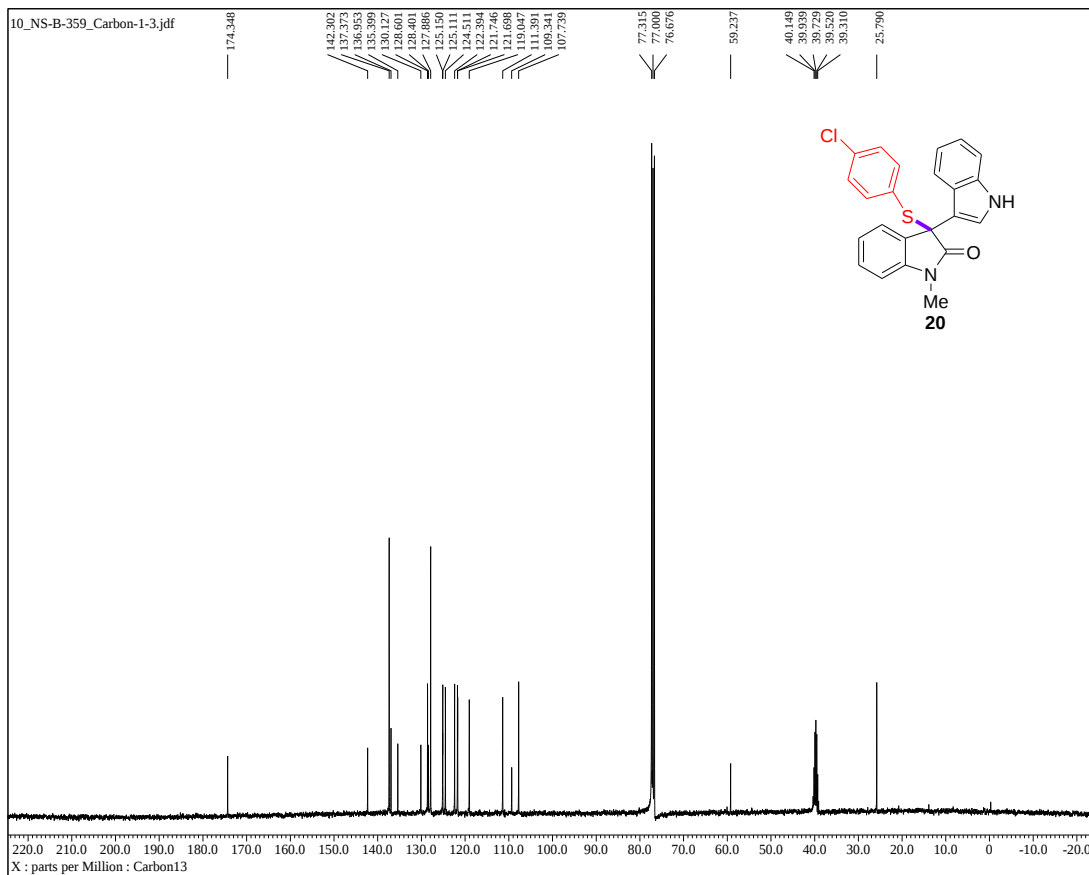
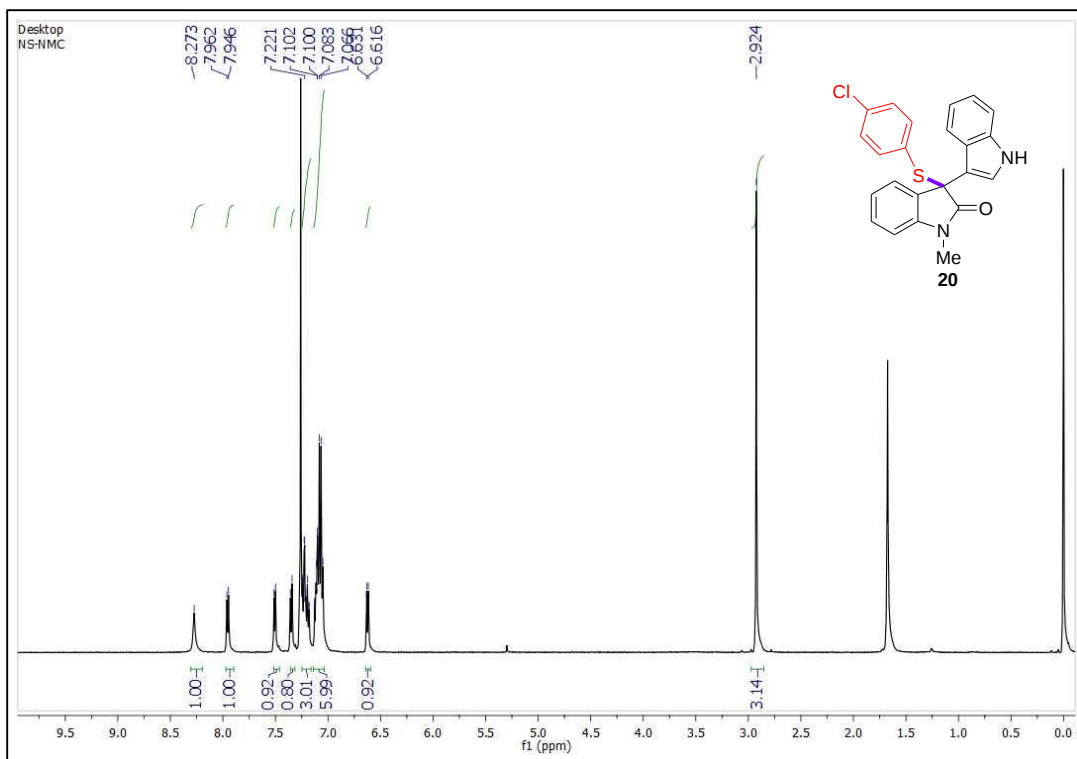


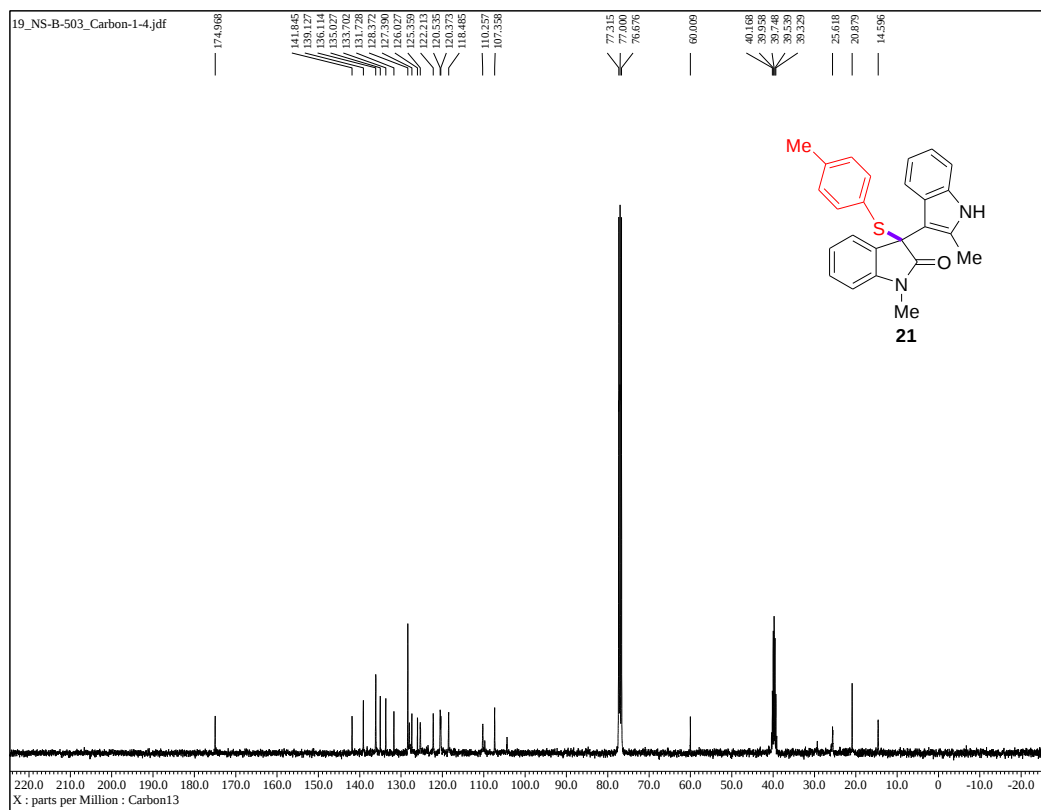
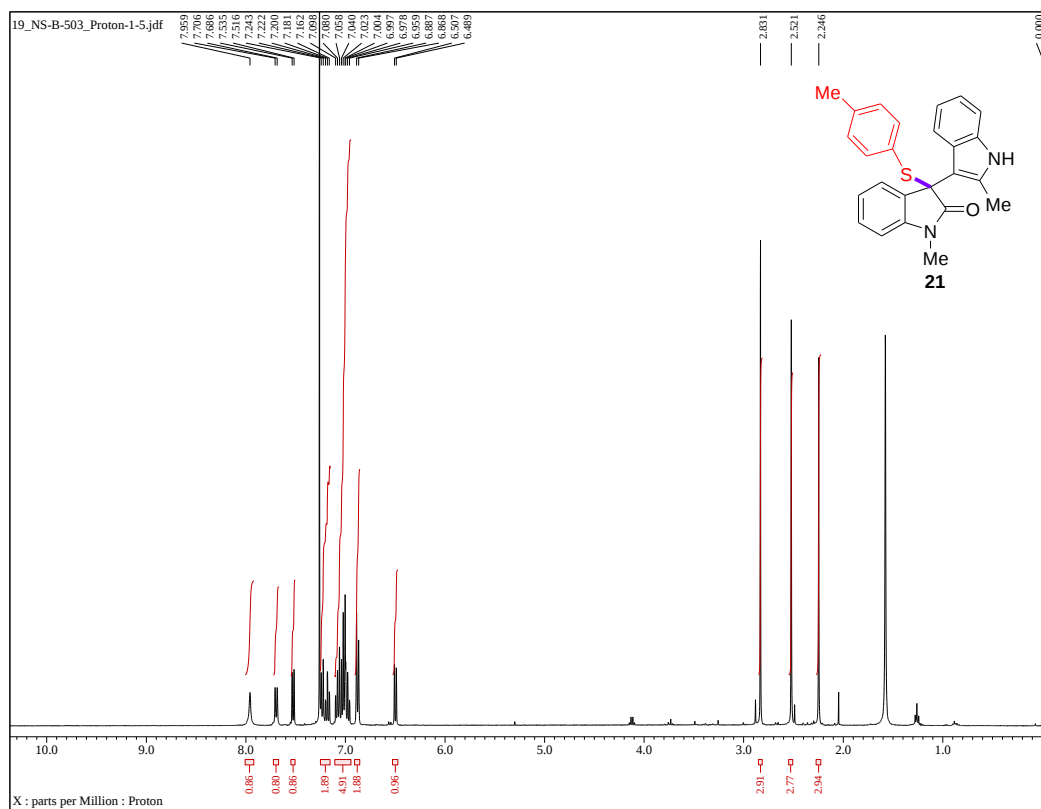


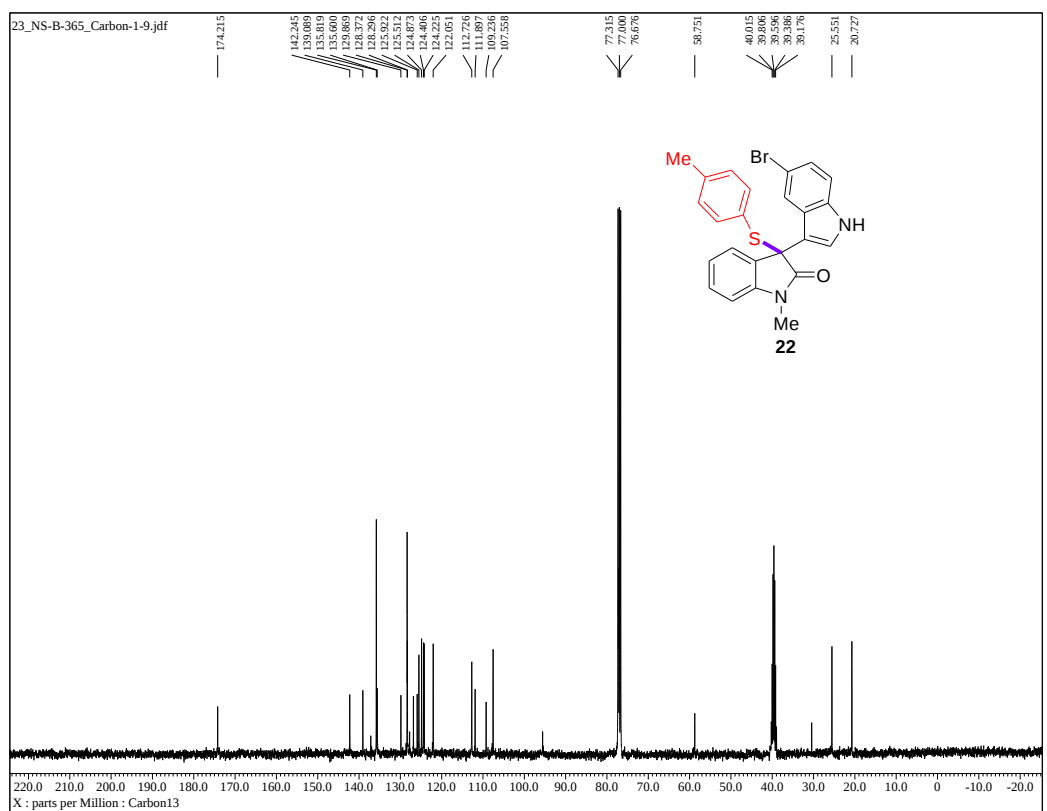
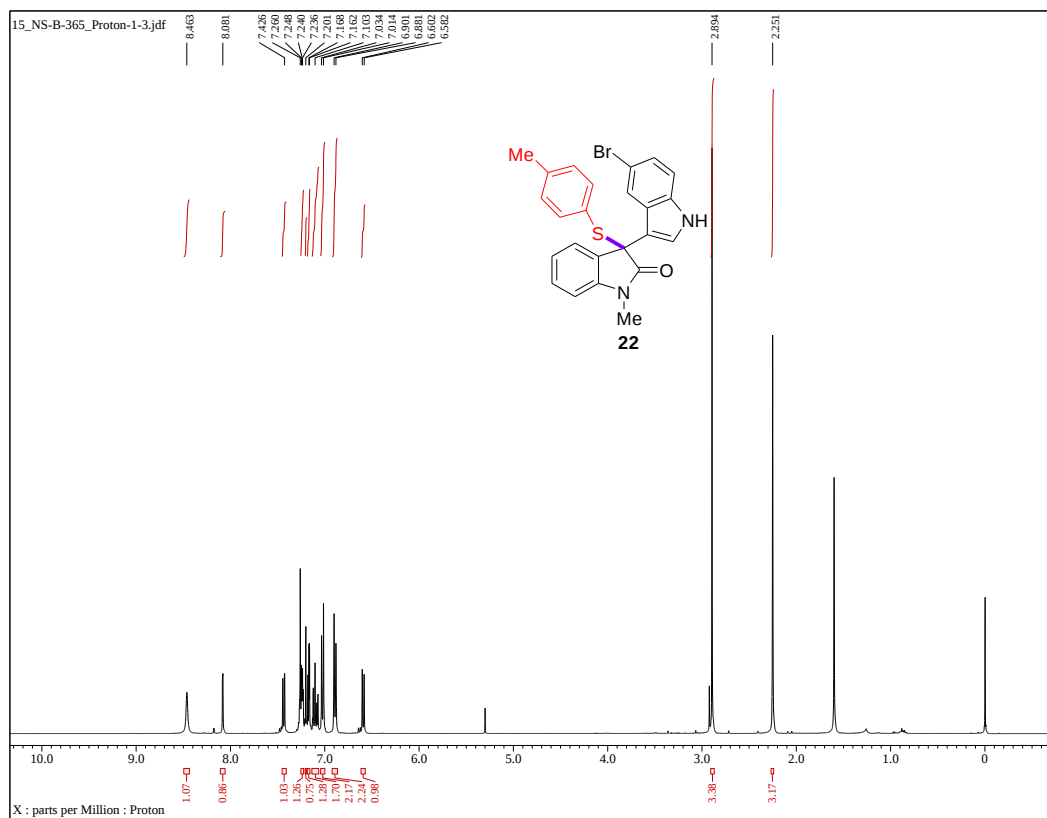


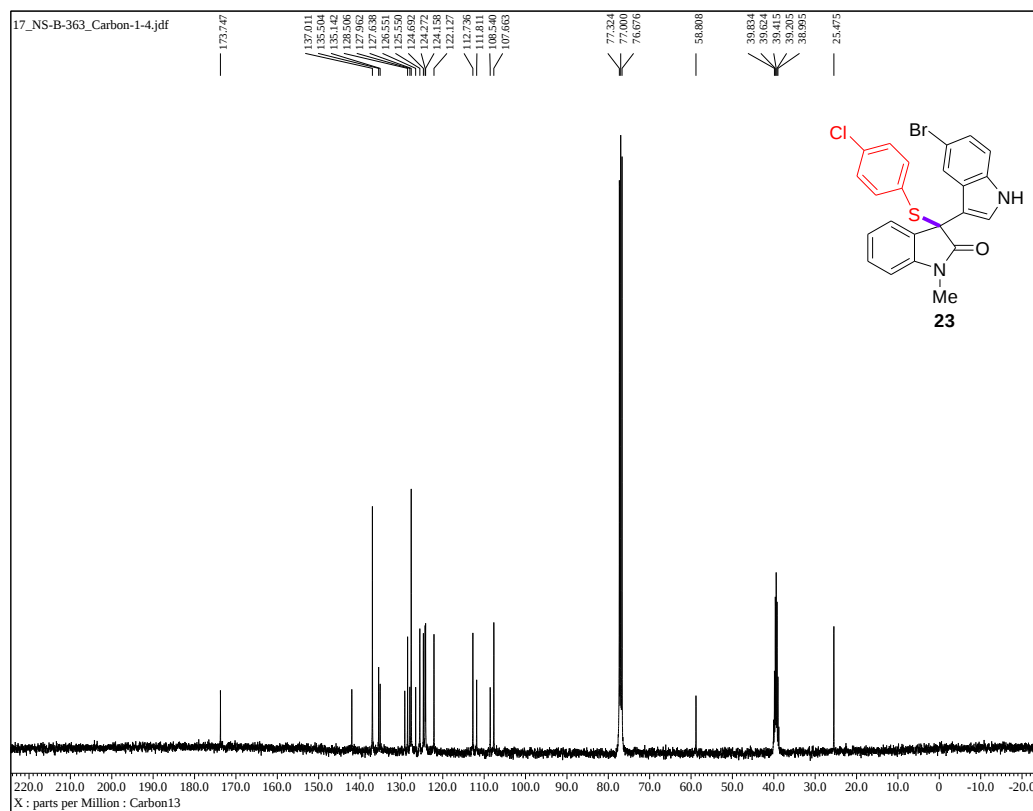
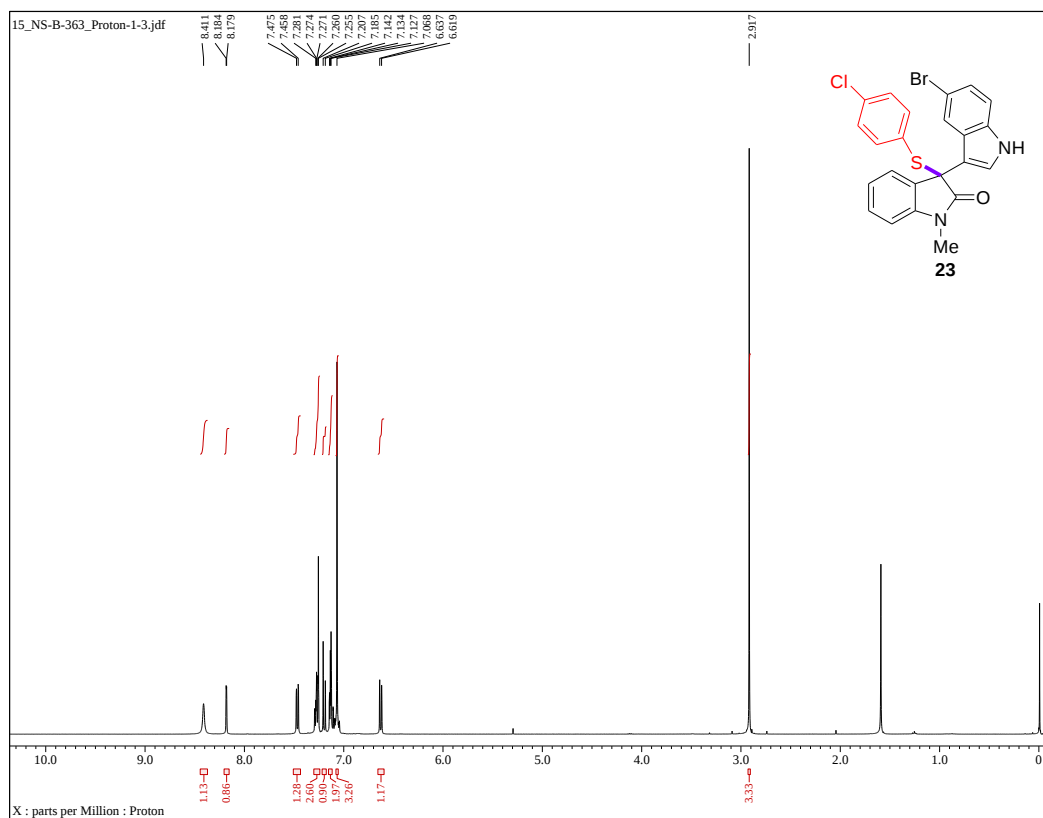


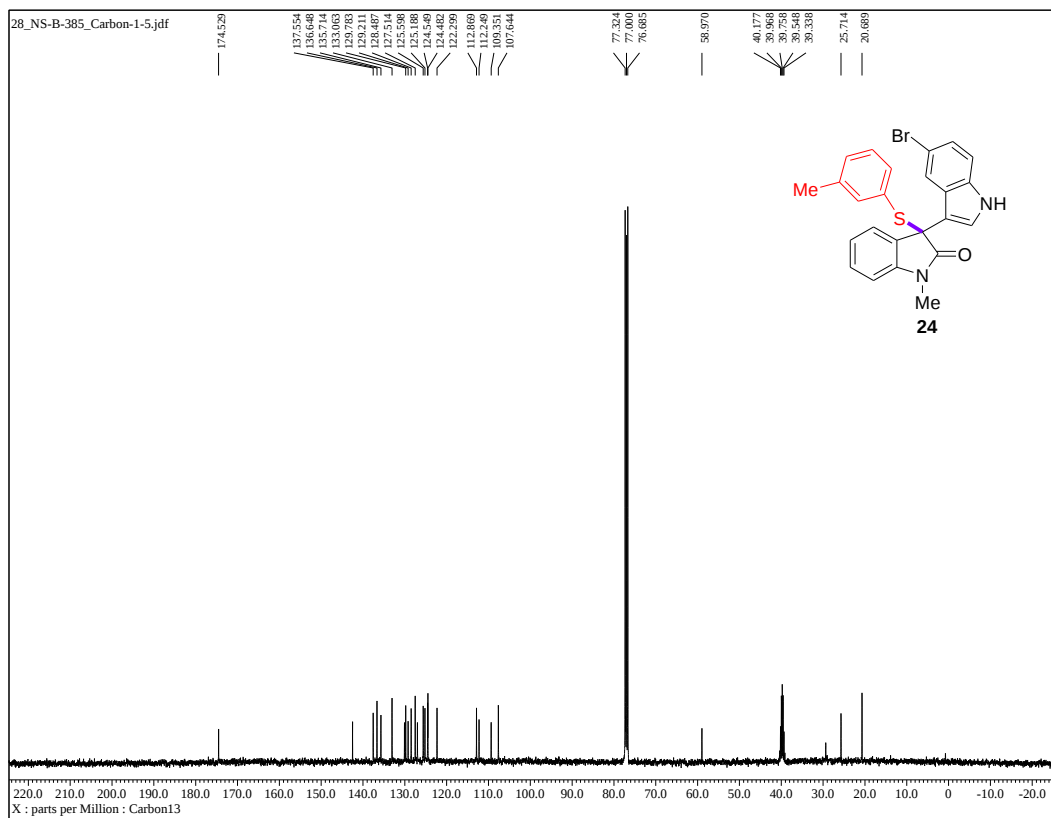
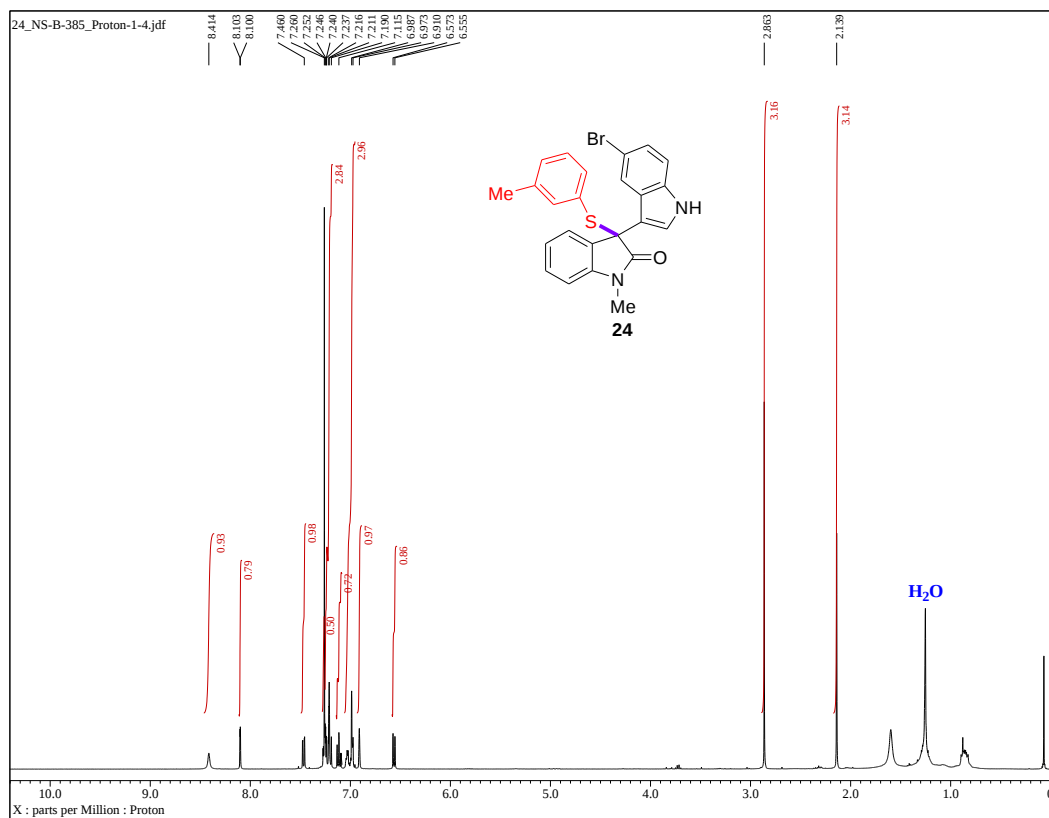


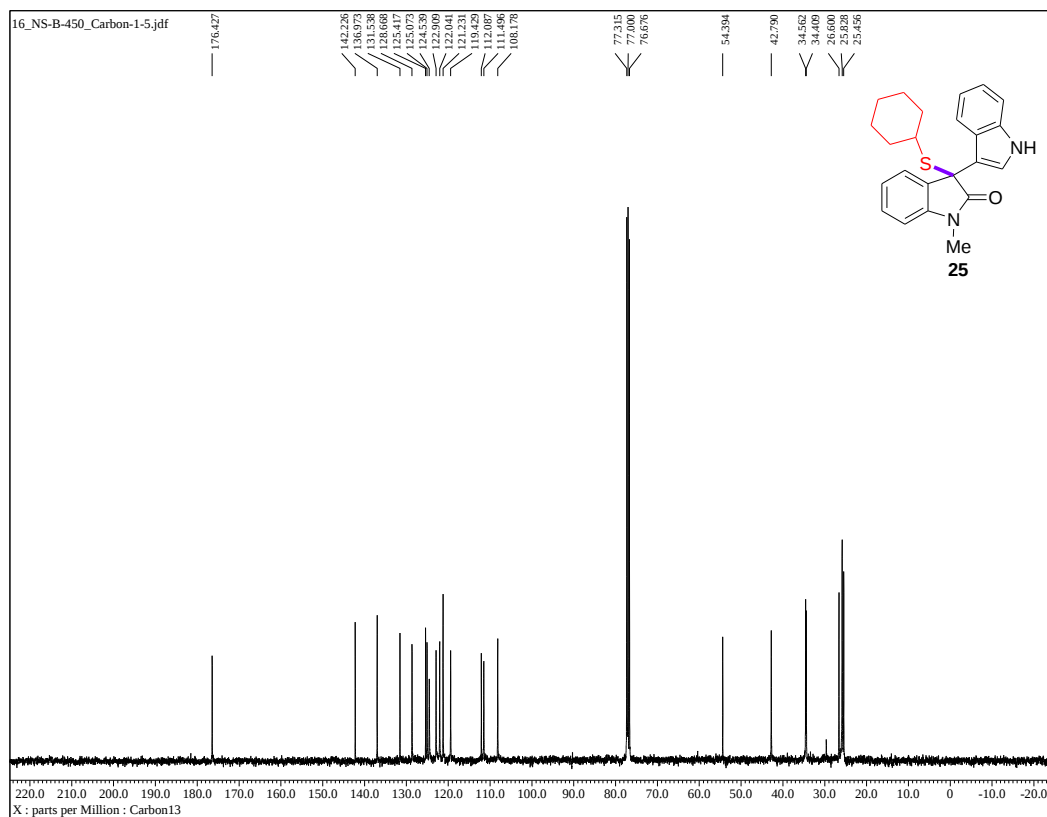
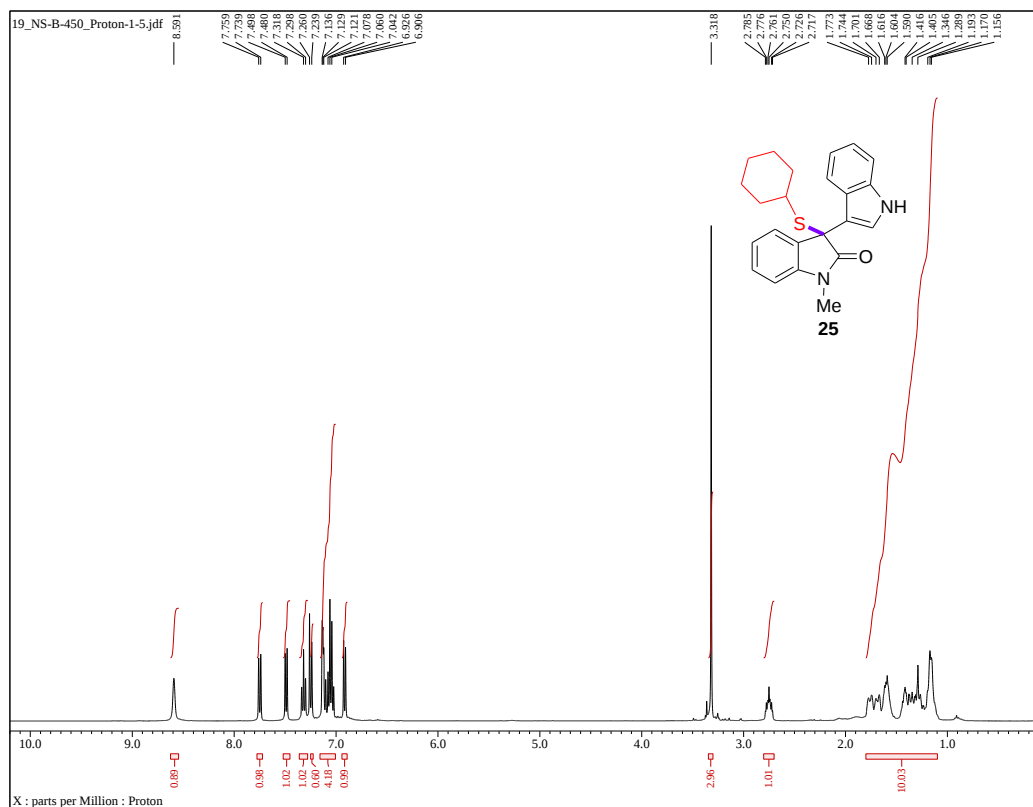


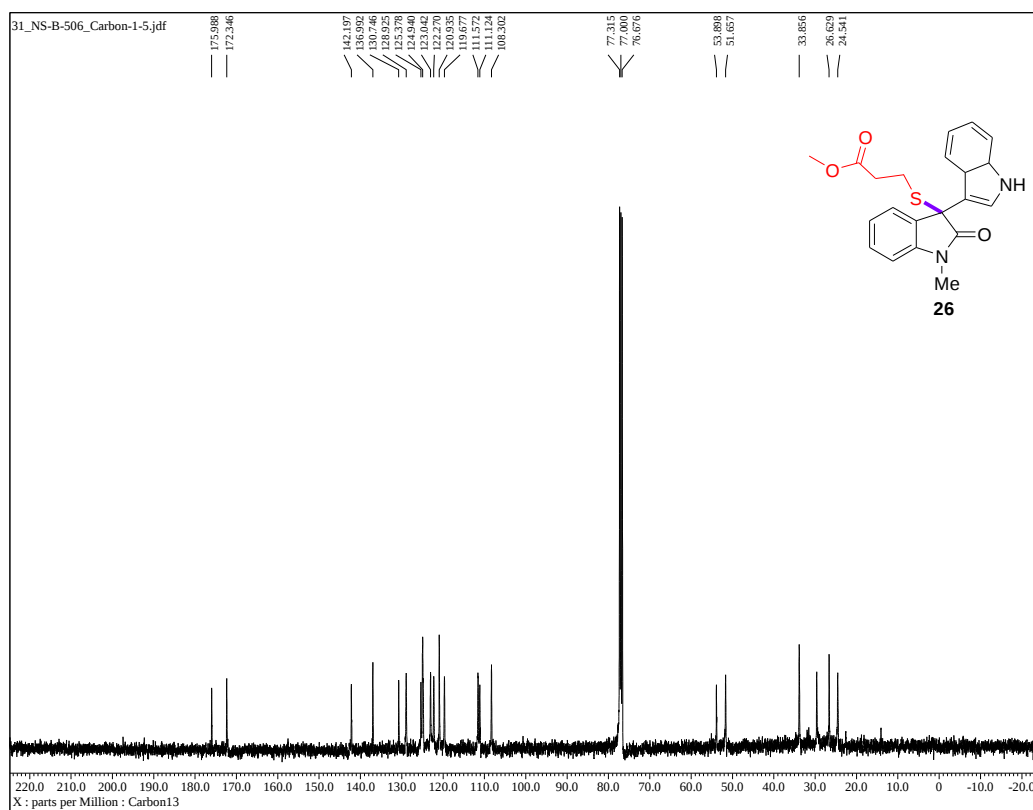
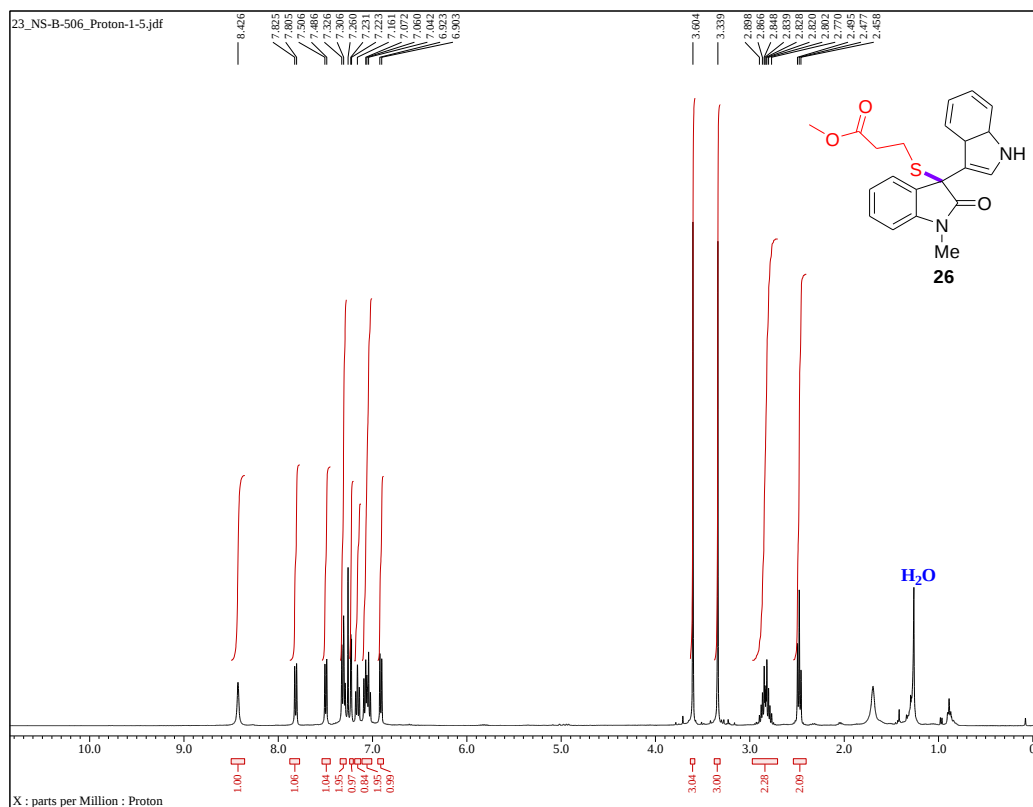


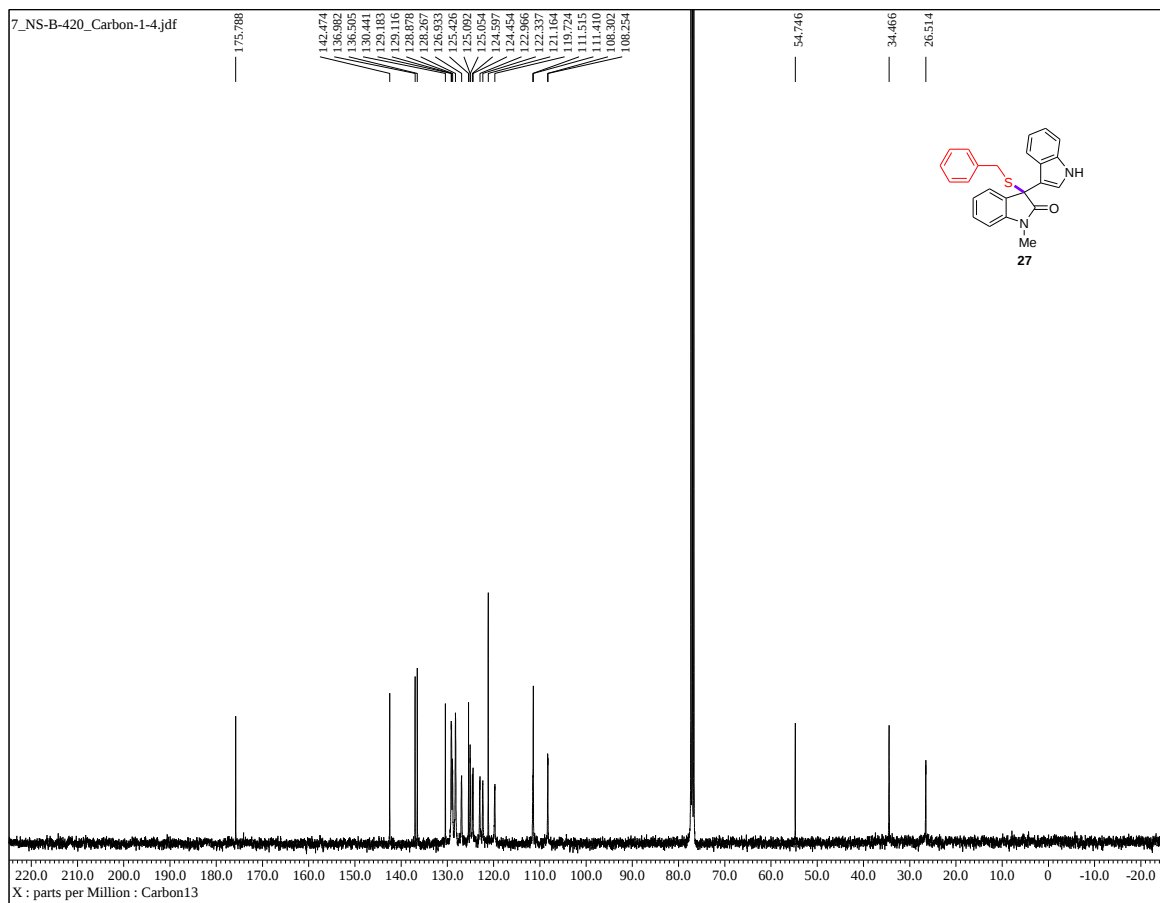
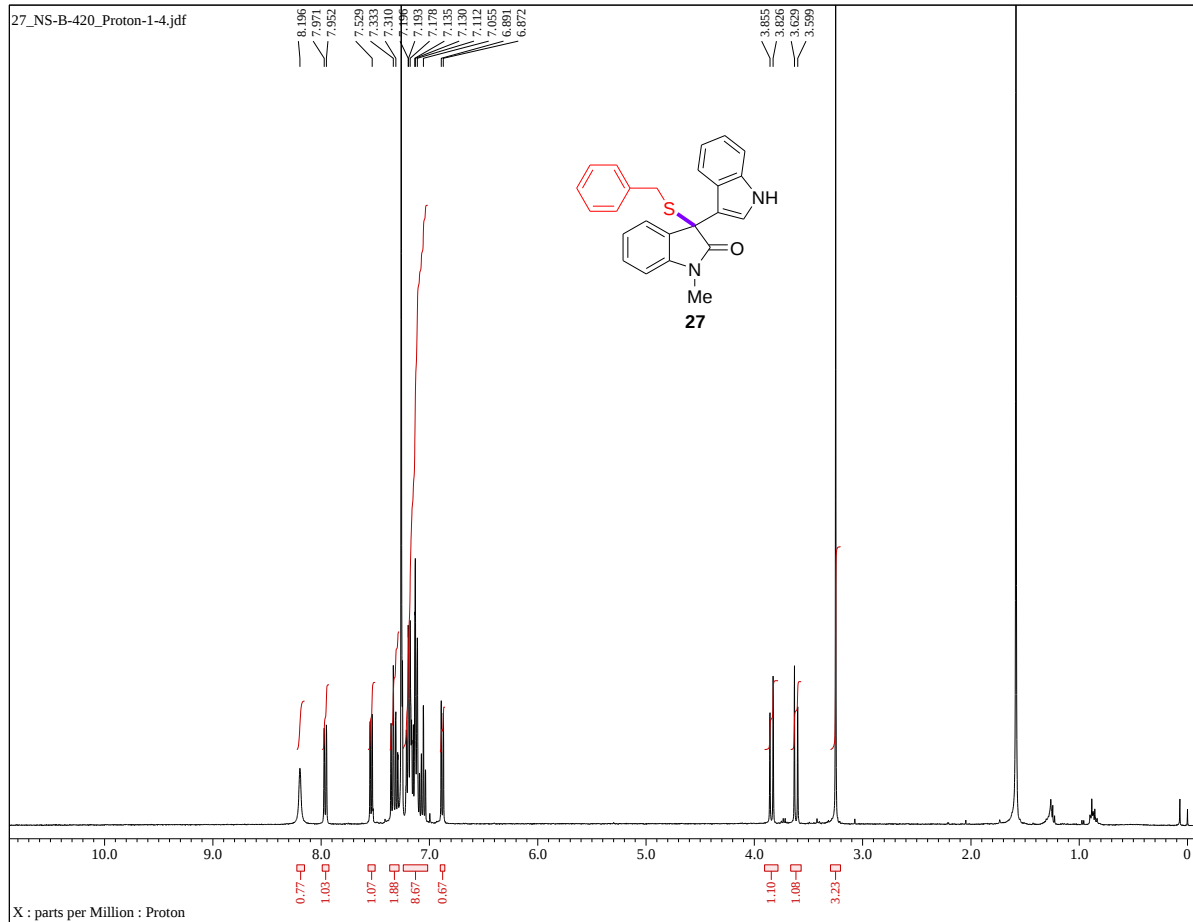


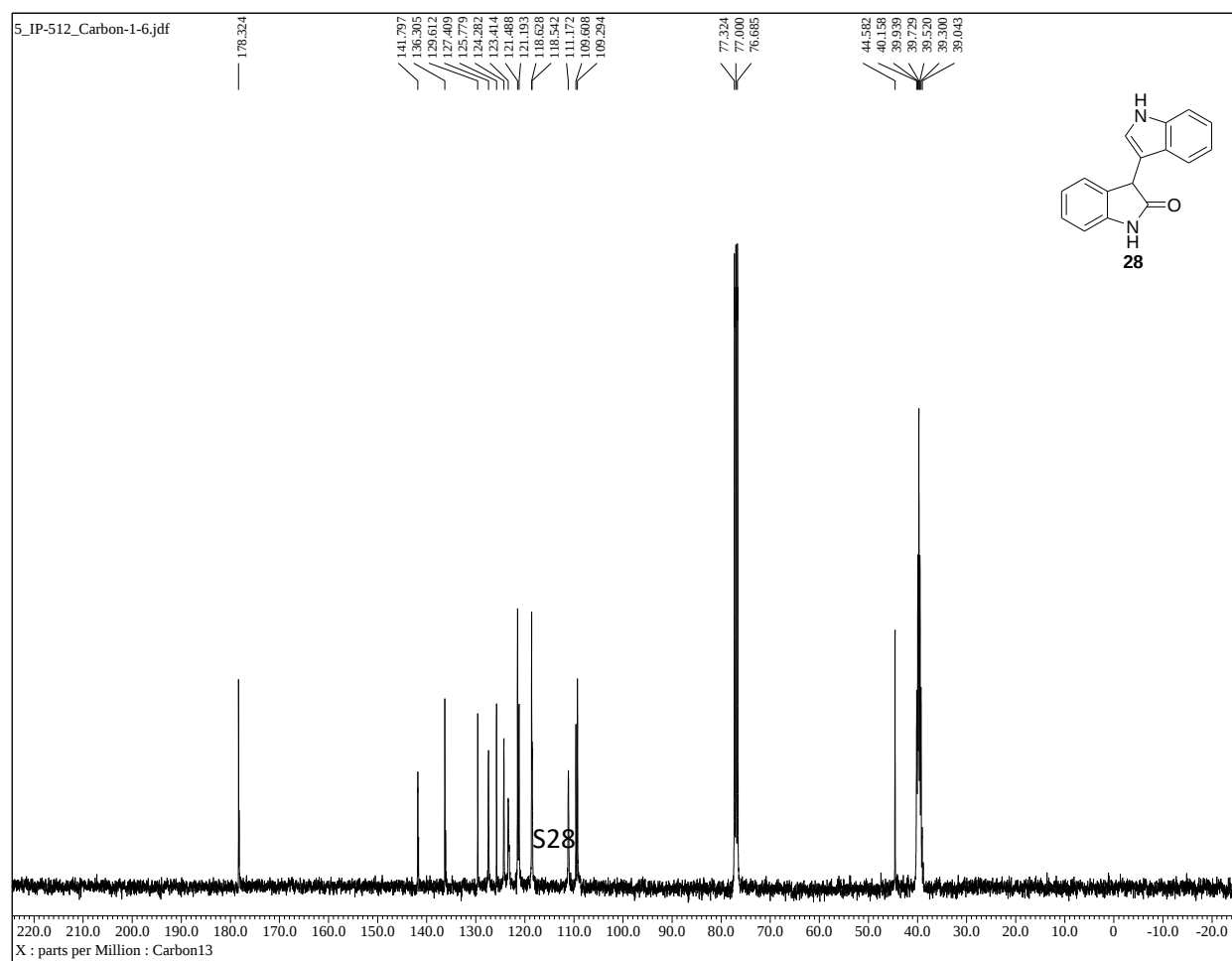
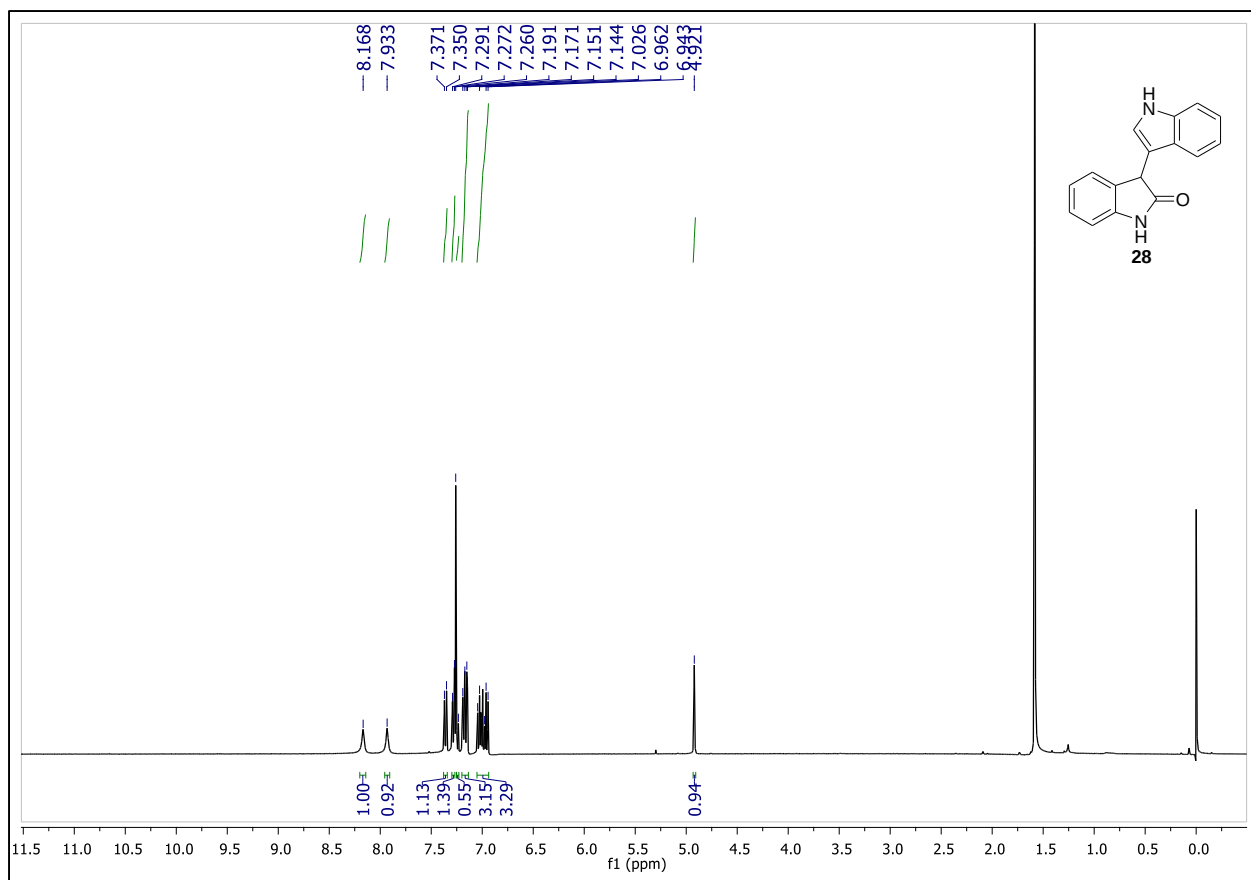






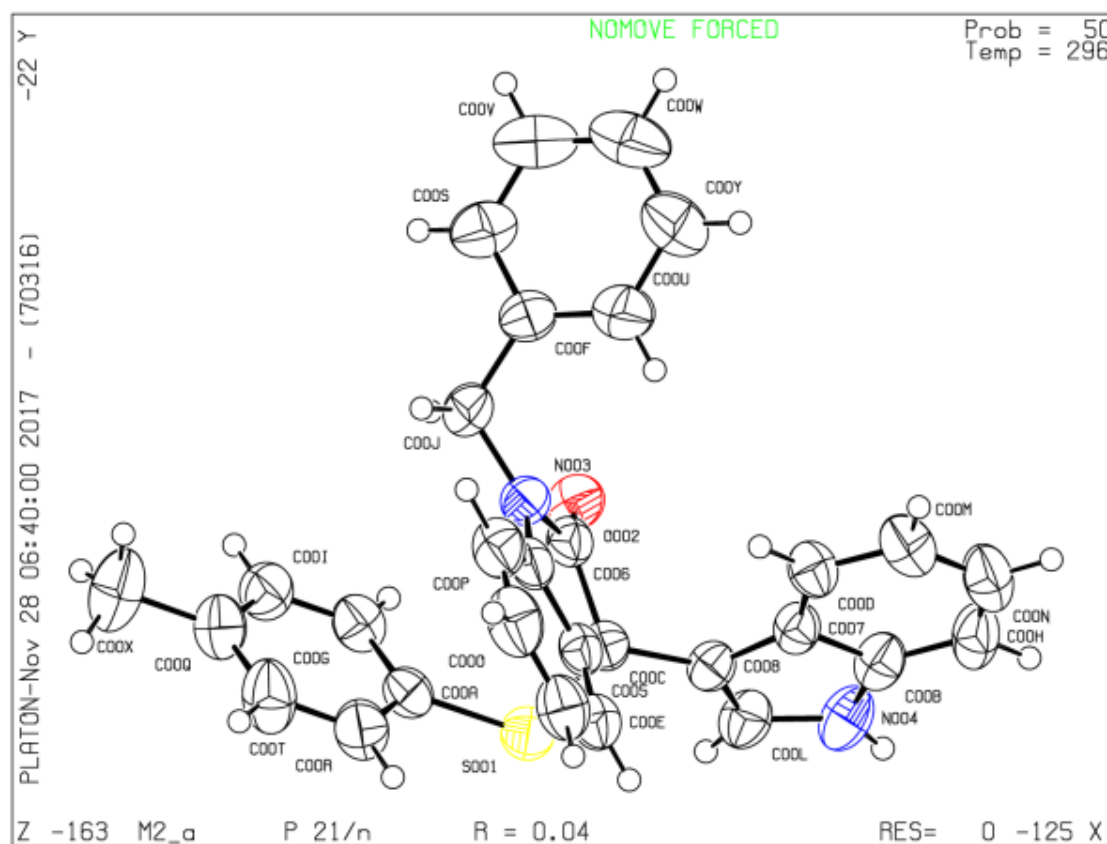






## X-ray crystallographic information of product 11:

Single-crystal of product **11** was procured through slow evaporation of ethanol. The crystal data of sulphenylated oxindole **11** were collected on X-ray diffractometer using graphite monochromated MoK $\alpha$  radiation ( $\lambda = 0.71070 \text{ \AA}$ ) at 296 K. The refinements were carried out by the full-matrix least-squares techniques against  $F^2$  using the SHELXTL program.<sup>3</sup> The non-hydrogen atoms were refined anisotropically. The crystallographic data was deposited at the Cambridge Crystallographic data centre (CCDC) with the supplementary publication numbers of CCDC No.-1823159.



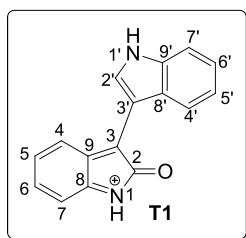
**Figure S-1.** Crystal structure of **11** with thermal ellipsoids set at 50% probability. N: blue; O: red; S: yellow.

**Table S-1** Important crystal data of compound **11**

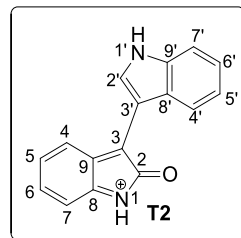
|                   |                                                     |
|-------------------|-----------------------------------------------------|
| Empirical formula | 'C <sub>30</sub> H <sub>24</sub> N <sub>2</sub> OS' |
| Formula weight    | 460.57                                              |
| Temperature       | 296 K                                               |
| Wavelength        | 0.71073                                             |
| Space group       | P 21/n                                              |

|                             |                                                                                                          |
|-----------------------------|----------------------------------------------------------------------------------------------------------|
| Unit cell dimensions        | a = 10.4442(4) Å $\alpha$ = 90<br>b = 14.3318(4) Å $\beta$ = 96.095(1)<br>c = 16.2731(5) Å $\gamma$ = 90 |
| Volume                      | 2422.06 Å <sup>3</sup>                                                                                   |
| Z                           | 4                                                                                                        |
| Density (calculated)        | 1.263 g/cm <sup>3</sup>                                                                                  |
| Absorption coefficient (Mu) | 0.159 mm <sup>-1</sup>                                                                                   |
| F(000)                      | 968.0                                                                                                    |
| h,k,l <sub>max</sub>        | 13, 17, 20                                                                                               |
| N <sub>ref</sub>            | 4964                                                                                                     |
| Data completeness           | 0.993                                                                                                    |
| Absorption correction       | multi-scan                                                                                               |
| Theta <sub>max</sub>        | 26.474                                                                                                   |
| Refinement method           | Full-matrix least-squares on F <sup>2</sup>                                                              |
| R(reflections)              | 0.0413 (3581)                                                                                            |
| wR2(reflections)            | 0.1630 (4964)                                                                                            |

**Table S2.** Cartesian coordinates of of optimized structures of **T1** and **T2**



**T1** B3LYP/6-311G\*\*



**T2** B3LYP/6-311G\*\*

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| 6 | 1.765733  | -0.231934 | 0.047612  | 6 | -2.871513 | 0.786919  | -0.103209 |
| 6 | 2.981770  | 0.440006  | -0.196714 | 6 | -1.956634 | -0.294328 | 0.069722  |
| 6 | 4.226610  | -0.164320 | -0.142709 | 6 | -2.470089 | -1.577177 | 0.359577  |
| 6 | 4.254562  | -1.516628 | 0.194968  | 6 | -3.837642 | -1.768311 | 0.398477  |
| 6 | 3.073589  | -2.202998 | 0.491174  | 6 | -4.713065 | -0.689889 | 0.175455  |
| 6 | 1.830065  | -1.575090 | 0.428184  | 6 | -4.244476 | 0.599941  | -0.064661 |
| 6 | 0.700612  | 0.773385  | -0.060972 | 6 | -0.804300 | 1.754472  | -0.186672 |
| 6 | 1.374990  | 2.010647  | -0.332735 | 6 | -0.633544 | 0.234388  | -0.027886 |
| 6 | -0.684467 | 0.708089  | -0.005055 | 1 | -1.811255 | -2.401972 | 0.596300  |
| 6 | -1.527451 | 1.988983  | 0.205048  | 1 | -4.242753 | -2.745837 | 0.625515  |
| 6 | -1.620603 | -0.363017 | -0.068691 | 1 | -5.782362 | -0.861164 | 0.215202  |
| 6 | -2.924610 | 0.184830  | 0.130041  | 1 | -4.930550 | 1.425570  | -0.205562 |
| 6 | -1.502095 | -1.735844 | -0.374407 | 6 | 0.597247  | -0.411998 | -0.087314 |
| 6 | -2.637934 | -2.522591 | -0.416538 | 6 | 0.702645  | -1.811164 | -0.373370 |
| 6 | -3.900959 | -1.961408 | -0.163850 | 6 | 2.812425  | -1.070547 | -0.149052 |
| 6 | -4.063225 | -0.601360 | 0.102005  | 6 | 1.986389  | 0.058350  | 0.042861  |
| 7 | 2.674208  | 1.792314  | -0.435694 | 6 | 4.195731  | -1.049247 | -0.065970 |
| 7 | -2.831056 | 1.555654  | 0.309206  | 6 | 4.784842  | 0.177987  | 0.231510  |
| 1 | -3.602876 | 2.192839  | 0.442499  | 6 | 3.997869  | 1.314034  | 0.439797  |
| 1 | -2.559347 | -3.575527 | -0.653868 | 6 | 2.605597  | 1.273834  | 0.351887  |
| 1 | -4.777765 | -2.597658 | -0.193687 | 7 | 1.976064  | -2.166348 | -0.415894 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| 1 | -5.046484 | -0.178560 | 0.265185  |
| 1 | -0.540357 | -2.167058 | -0.608759 |
| 1 | 0.944352  | -2.127492 | 0.704911  |
| 1 | 3.124778  | -3.244382 | 0.783892  |
| 1 | 5.204462  | -2.033484 | 0.248025  |
| 1 | 5.138747  | 0.386667  | -0.337420 |
| 8 | -1.144655 | 3.129097  | 0.292593  |
| 1 | 3.355792  | 2.507249  | -0.657720 |
| 1 | 0.934354  | 2.984349  | -0.472560 |

#### T1 PM6

|   |           |           |           |
|---|-----------|-----------|-----------|
| 6 | -1.773320 | -0.249501 | -0.003434 |
| 6 | -3.025509 | 0.453195  | 0.011893  |
| 6 | -4.264063 | -0.179762 | 0.007457  |
| 6 | -4.257170 | -1.579646 | -0.015640 |
| 6 | -3.050607 | -2.291684 | -0.034939 |
| 6 | -1.808873 | -1.637764 | -0.029716 |
| 6 | -0.702167 | 0.765674  | 0.006206  |
| 6 | -1.415123 | 2.060123  | 0.022080  |
| 6 | 0.654998  | 0.692785  | 0.003465  |
| 6 | 1.493961  | 2.010839  | -0.011603 |
| 6 | 1.630352  | -0.368960 | 0.008198  |
| 6 | 2.955588  | 0.208467  | -0.012744 |
| 6 | 1.535902  | -1.766097 | 0.034665  |
| 6 | 2.695174  | -2.542781 | 0.033865  |
| 6 | 3.966127  | -1.950131 | 0.008286  |
| 6 | 4.113782  | -0.555349 | -0.014621 |
| 7 | -2.737474 | 1.865236  | 0.027962  |
| 7 | 2.848166  | 1.626347  | -0.026757 |
| 1 | 3.634833  | 2.270962  | -0.040009 |
| 1 | 2.615215  | -3.633196 | 0.054054  |
| 1 | 4.860410  | -2.584005 | 0.007182  |
| 1 | 5.104806  | -0.099603 | -0.032407 |
| 1 | 0.555635  | -2.257292 | 0.057567  |
| 1 | -0.888057 | -2.231679 | -0.047833 |
| 1 | -3.076407 | -3.386866 | -0.055098 |
| 1 | -5.207842 | -2.123196 | -0.019656 |
| 1 | -5.201838 | 0.377617  | 0.020499  |
| 8 | 1.089823  | 3.147157  | -0.012939 |
| 1 | -3.461538 | 2.581421  | 0.040611  |
| 1 | -0.922942 | 3.051058  | 0.029667  |

#### T1 AM1

|   |           |           |           |
|---|-----------|-----------|-----------|
| 6 | -1.744718 | -0.232684 | -0.052902 |
| 6 | -3.006158 | 0.439117  | 0.153052  |
| 6 | -4.225183 | -0.228881 | 0.104660  |
| 6 | -4.191680 | -1.597108 | -0.185632 |
| 6 | -2.986195 | -2.250574 | -0.442322 |
| 6 | -1.758998 | -1.576268 | -0.390078 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| 1 | 2.304019  | -3.093811 | -0.655430 |
| 7 | -2.167210 | 1.963801  | -0.281525 |
| 1 | -2.564100 | 2.887906  | -0.370247 |
| 8 | 0.047232  | 2.602774  | -0.253452 |
| 1 | 4.791711  | -1.941117 | -0.217476 |
| 1 | 5.862839  | 0.248209  | 0.305234  |
| 1 | 4.479576  | 2.256011  | 0.671282  |
| 1 | 2.023068  | 2.168857  | 0.497995  |
| 1 | -0.078921 | -2.510605 | -0.620184 |

#### T2 PM6

|   |           |           |           |
|---|-----------|-----------|-----------|
| 6 | 2.882033  | 0.812624  | 0.000026  |
| 6 | 1.953197  | -0.289488 | -0.000033 |
| 6 | 2.477976  | -1.593269 | -0.000006 |
| 6 | 3.855171  | -1.781105 | -0.000054 |
| 6 | 4.738909  | -0.683298 | -0.000032 |
| 6 | 4.263493  | 0.630317  | 0.000028  |
| 6 | 0.754962  | 1.771831  | 0.000015  |
| 6 | 0.604304  | 0.228038  | -0.000059 |
| 1 | 1.808297  | -2.457243 | 0.000014  |
| 1 | 4.268720  | -2.793018 | -0.000060 |
| 1 | 5.820171  | -0.865139 | 0.000013  |
| 1 | 4.952023  | 1.476797  | 0.000148  |
| 6 | -0.583268 | -0.434153 | -0.000039 |
| 6 | -0.690235 | -1.900522 | 0.000033  |
| 6 | -2.824733 | -1.114720 | 0.000016  |
| 6 | -1.980233 | 0.046250  | -0.000099 |
| 6 | -4.215644 | -1.053756 | 0.000044  |
| 6 | -4.788573 | 0.222683  | -0.000004 |
| 6 | -3.986085 | 1.372686  | -0.000051 |
| 6 | -2.584859 | 1.298166  | -0.000103 |
| 7 | -1.975507 | -2.276283 | 0.000071  |
| 1 | -2.334010 | -3.228628 | 0.000125  |
| 7 | 2.156509  | 2.026098  | 0.000011  |
| 1 | 2.570196  | 2.955344  | -0.000024 |
| 8 | -0.074998 | 2.637465  | 0.000123  |
| 1 | -4.836960 | -1.949562 | 0.000124  |
| 1 | -5.878848 | 0.323962  | 0.000025  |
| 1 | -4.464456 | 2.359177  | -0.000032 |
| 1 | -1.994748 | 2.224896  | -0.000081 |
| 1 | 0.164100  | -2.588710 | 0.000091  |

#### T2 AM1

|   |           |           |           |
|---|-----------|-----------|-----------|
| 6 | -2.879706 | 0.804036  | -0.085648 |
| 6 | -1.946853 | -0.296680 | 0.055344  |
| 6 | -2.454190 | -1.575872 | 0.299005  |
| 6 | -3.829627 | -1.773288 | 0.339611  |
| 6 | -4.719155 | -0.705501 | 0.158540  |
| 6 | -4.260162 | 0.595304  | -0.045407 |

|   |           |           |           |
|---|-----------|-----------|-----------|
| 6 | -0.697636 | 0.789863  | 0.065432  |
| 6 | -1.427123 | 2.054907  | 0.274997  |
| 6 | 0.658426  | 0.727459  | 0.035419  |
| 6 | 1.517349  | 1.998428  | -0.153796 |
| 6 | 1.607476  | -0.353486 | 0.100814  |
| 6 | 2.928634  | 0.195248  | -0.146525 |
| 6 | 1.491240  | -1.706010 | 0.421597  |
| 6 | 2.629315  | -2.509975 | 0.417536  |
| 6 | 3.887425  | -1.979223 | 0.116595  |
| 6 | 4.058874  | -0.618485 | -0.155967 |
| 7 | -2.744369 | 1.827985  | 0.355627  |
| 7 | 2.844171  | 1.584332  | -0.330651 |
| 1 | 3.619185  | 2.192297  | -0.436130 |
| 1 | 2.538102  | -3.580577 | 0.663223  |
| 1 | 4.770104  | -2.642320 | 0.108133  |
| 1 | 5.059289  | -0.209410 | -0.363264 |
| 1 | 0.520076  | -2.134001 | 0.714713  |
| 1 | -0.834499 | -2.112603 | -0.651629 |
| 1 | -2.996406 | -3.323336 | -0.700257 |
| 1 | -5.139598 | -2.159851 | -0.225842 |
| 1 | -5.181389 | 0.288434  | 0.275366  |
| 8 | 1.116122  | 3.164783  | -0.179080 |
| 1 | -3.458969 | 2.504544  | 0.517239  |
| 1 | -0.969778 | 3.058369  | 0.378973  |

# T1 MP2/3-21g

|   |           |           |           |
|---|-----------|-----------|-----------|
| 6 | 1.759064  | -0.231628 | 0.042464  |
| 6 | 2.992706  | 0.435230  | -0.207632 |
| 6 | 4.239046  | -0.192293 | -0.164776 |
| 6 | 4.247539  | -1.556605 | 0.180122  |
| 6 | 3.047273  | -2.229995 | 0.503542  |
| 6 | 1.800998  | -1.577437 | 0.456954  |
| 6 | 0.694413  | 0.796728  | -0.021293 |
| 6 | 1.381566  | 2.057220  | -0.282465 |
| 6 | -0.684857 | 0.727797  | -0.011268 |
| 6 | -1.546739 | 2.025936  | 0.181735  |
| 6 | -1.615100 | -0.369678 | -0.062912 |
| 6 | -2.930868 | 0.168192  | 0.145060  |
| 6 | -1.467070 | -1.736562 | -0.405329 |
| 6 | -2.604718 | -2.551019 | -0.441060 |
| 6 | -3.885221 | -2.015299 | -0.159608 |
| 6 | -4.062712 | -0.647286 | 0.121396  |
| 7 | 2.689370  | 1.825165  | -0.417607 |
| 7 | -2.857239 | 1.564825  | 0.314701  |
| 1 | -3.650545 | 2.186268  | 0.448579  |
| 1 | -2.509651 | -3.600405 | -0.702650 |
| 1 | -4.754119 | -2.666893 | -0.183821 |
| 1 | -5.056008 | -0.243045 | 0.294948  |
| 1 | -0.497364 | -2.137297 | -0.678447 |
| 1 | 0.902629  | -2.100486 | 0.764179  |

|   |           |           |           |
|---|-----------|-----------|-----------|
| 6 | -0.793906 | 1.758886  | -0.164941 |
| 6 | -0.606535 | 0.236815  | -0.032107 |
| 1 | -1.784927 | -2.427029 | 0.490425  |
| 1 | -4.230534 | -2.782845 | 0.526015  |
| 1 | -5.806480 | -0.894575 | 0.189961  |
| 1 | -4.967219 | 1.430172  | -0.166155 |
| 6 | 0.587080  | -0.413749 | -0.077149 |
| 6 | 0.702505  | -1.861238 | -0.314272 |
| 6 | 2.822730  | -1.101961 | -0.127942 |
| 6 | 1.976467  | 0.056347  | 0.042654  |
| 6 | 4.210992  | -1.036326 | -0.058547 |
| 6 | 4.776968  | 0.216794  | 0.195842  |
| 6 | 3.975921  | 1.343593  | 0.381202  |
| 6 | 2.577445  | 1.275995  | 0.312553  |
| 7 | 1.988354  | -2.235415 | -0.353898 |
| 1 | 2.340142  | -3.151676 | -0.529329 |
| 7 | -2.180269 | 2.002785  | -0.243914 |
| 1 | -2.591649 | 2.902373  | -0.295774 |
| 8 | 0.063991  | 2.635512  | -0.240610 |
| 1 | 4.844433  | -1.925699 | -0.193304 |
| 1 | 5.874658  | 0.307997  | 0.253662  |
| 1 | 4.450966  | 2.318228  | 0.587657  |
| 1 | 1.986191  | 2.192540  | 0.473604  |
| 1 | -0.123954 | -2.564099 | -0.499641 |

# T2 MP2/3-21g

|   |           |           |           |
|---|-----------|-----------|-----------|
| 6 | -2.886148 | 0.798666  | -0.106309 |
| 6 | -1.970147 | -0.292726 | 0.065264  |
| 6 | -2.475188 | -1.586657 | 0.351264  |
| 6 | -3.860136 | -1.784099 | 0.368785  |
| 6 | -4.746644 | -0.703772 | 0.133543  |
| 6 | -4.268969 | 0.599924  | -0.088293 |
| 6 | -0.791072 | 1.790954  | -0.133494 |
| 6 | -0.629313 | 0.246721  | -0.011838 |
| 1 | -1.813488 | -2.404613 | 0.621221  |
| 1 | -4.262849 | -2.767431 | 0.591492  |
| 1 | -5.818560 | -0.878438 | 0.155732  |
| 1 | -4.960302 | 1.426148  | -0.228144 |
| 6 | 0.587281  | -0.410904 | -0.097518 |
| 6 | 0.674536  | -1.844113 | -0.347983 |
| 6 | 2.822724  | -1.100077 | -0.128535 |
| 6 | 1.997191  | 0.055085  | 0.010273  |
| 6 | 4.215970  | -1.082931 | -0.035287 |
| 6 | 4.814987  | 0.164288  | 0.218098  |
| 6 | 4.025425  | 1.326879  | 0.363441  |
| 6 | 2.620621  | 1.292760  | 0.268388  |
| 7 | 1.959795  | -2.216371 | -0.372208 |
| 1 | 2.284936  | -3.163653 | -0.581554 |
| 7 | -2.171905 | 1.999126  | -0.244651 |
| 1 | -2.580629 | 2.925487  | -0.334009 |

|   |           |           |           |   |           |           |           |
|---|-----------|-----------|-----------|---|-----------|-----------|-----------|
| 1 | 3.089950  | -3.269740 | 0.814146  | 8 | 0.089543  | 2.671777  | -0.168657 |
| 1 | 5.192296  | -2.089561 | 0.223290  | 1 | 4.814245  | -1.983903 | -0.142558 |
| 1 | 5.163782  | 0.341615  | -0.366366 | 1 | 5.895521  | 0.230488  | 0.299236  |
| 8 | -1.150862 | 3.206687  | 0.232943  | 1 | 4.514009  | 2.278320  | 0.551860  |
| 1 | 3.383958  | 2.543585  | -0.635063 | 1 | 2.032032  | 2.194954  | 0.347642  |
| 1 | 0.925129  | 3.032731  | -0.371580 | 1 | -0.123197 | -2.530850 | -0.592441 |