

Electronic Supplementary Information

**Cu(I) catalysed annulation of isothiocyanates/ isocyanates with 2-iodo-sulfonamides:
Synthesis of benzodithiazines, benzothiadiazinones, benzothiazinylidene-anilines and
benzothiazolylidene-anilines**

*K. Sandeep, Alla Siva Reddy and K. C. Kumara Swamy**

School of Chemistry, University of Hyderabad

Hyderabad 500 046, Telangana, India.

e-mail: kckssc@uohyd.ac.in, kckssc@yahoo.com

1	X-ray data for Compounds 3aa , 3cc , 3fb' , 5ad and 9b	S2-S3
2	Copies of $^1\text{H}/^{13}\text{C}\{^1\text{H}\}$ NMR spectra for compounds 3aa-3ii , 5aa-5hb , 7a-7h and 9a-9k	S4-S65

X-ray data:

Crystallographic data were collected on a Bruker APX-II-SMART using Mo-K α radiation (λ = 0.71073 Å) and have been deposited at the Cambridge Crystallographic Data Center (CCDC). The structures were solved and refined by standard methods.^[1] Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Compound 3aa

Colorless block, C₁₅H₁₄N₂O₂S₂, M_r = 318.40, Orthorhombic, space group *Pbca*, a = 11.4990(8), b = 8.4660(6), c = 31.300(2) Å, V = 3047.1(4) Å³, Z = 8, μ = 0.354 mm⁻¹, Data/restraints/parameters: 2649/0/192. R indices ($I > 2\sigma(I)$): R1 = 0.0338, wR2 (all data) = 0.0919. CCDC No. 1857227.

Compound 3cc

Colorless block, C₁₉H₁₉F₃N₂O₂S₂, M_r = 428.48, Monoclinic, space group *P2(1)/c*, a = 14.5408(7), b = 10.0380(5), c = 14.7642(7) Å, V = 1984.88(17) Å³, β = 112.918(2), Z = 4, μ = 0.313 mm⁻¹, Data/restraints/parameters: 4036/0/257. R indices ($I > 2\sigma(I)$): R1 = 0.0364, wR2 (all data) = 0.1046. CCDC No. 1857231.

Compound 3fb'

Colorless block, C₁₉H₁₆N₂O₃S₂, M_r = 384.46, Orthorhombic, space group *Pbca*, a = 7.507(4), b = 16.207(10), c = 29.663(19) Å, V = 3609(4) Å³, Z = 8, μ = 0.317 mm⁻¹, Data/restraints/parameters: 3166/0/238. R indices ($I > 2\sigma(I)$): R1 = 0.0722, wR2 (all data) = 0.2270. CCDC No. 1857229. Although we could refine the structure satisfactorily, the quality of the data was only moderate.

Compound **5ad**

Colorless block, $C_{15}H_{13}FN_2O_3S$, $M_r = 320.33$, Monoclinic, space group $P2(1)/c$, $a = 12.557(2)$, $b = 18.579(2)$, $c = 13.015(2)$ Å, $V = 2942.3(8)$ Å³, $\beta = 104.300(19)$, $Z = 4$, $\mu = 2.198$ mm⁻¹, Data/restraints/parameters: 4959/0/401. R indices ($I > 2\sigma(I)$): $R1 = 0.1065$, $wR2$ (all data) = 0.3647. CCDC No. 1857230.

Compound **9b**

Colorless block, $C_{21}H_{15}F_3N_2O_2S_2$, $M_r = 448.47$, Monoclinic, space group $P2(1)/c$, $a = 18.7734(9)$, $b = 12.5873(5)$, $c = 8.6595(4)$ Å, $V = 2036.71(16)$ Å³, $\beta = 95.548(2)$, $Z = 4$, $\mu = 0.309$ mm⁻¹, Data/restraints/parameters: 3563/0/272. R indices ($I > 2\sigma(I)$): $R1 = 0.0439$, $wR2$ (all data) = 0.1194. CCDC No. 1857228.

- (1) (a) G. M. Sheldrick, *SADABS, Siemens Area Detector Absorption Correction*; University of Göttingen: Göttingen, Germany, 1996; b) Sheldrick, G. M. *SHELX-97, A Program for Crystal Structure Solution and Refinement*; University of Göttingen, *SHELXTL NT Crystal Structure Analysis Package*, version 5.10; Bruker AXS: Madison, WI, 1999.

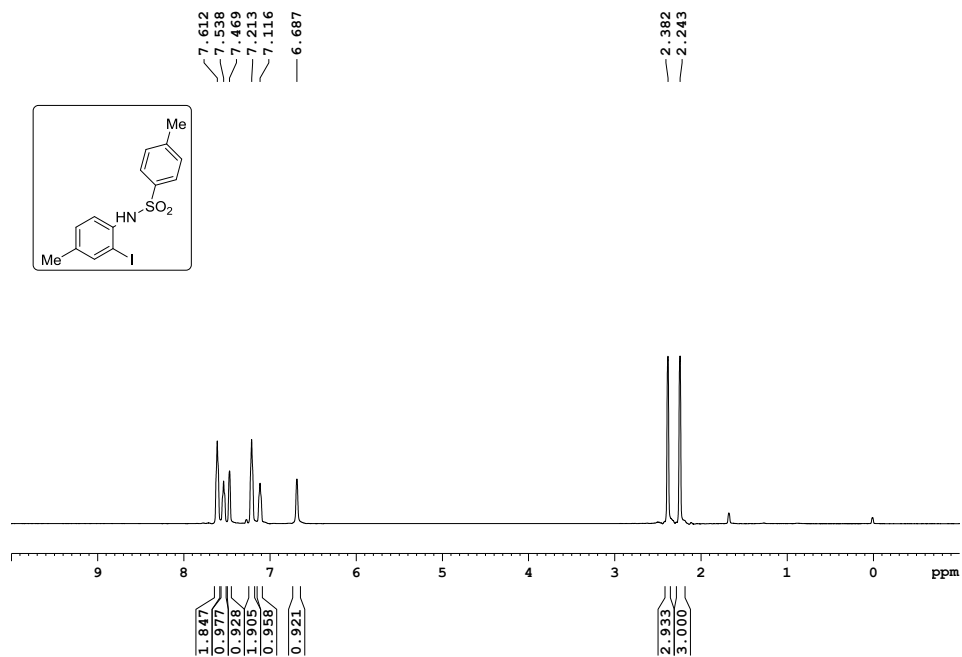


Figure S1. ¹H NMR spectrum of compound **8b**

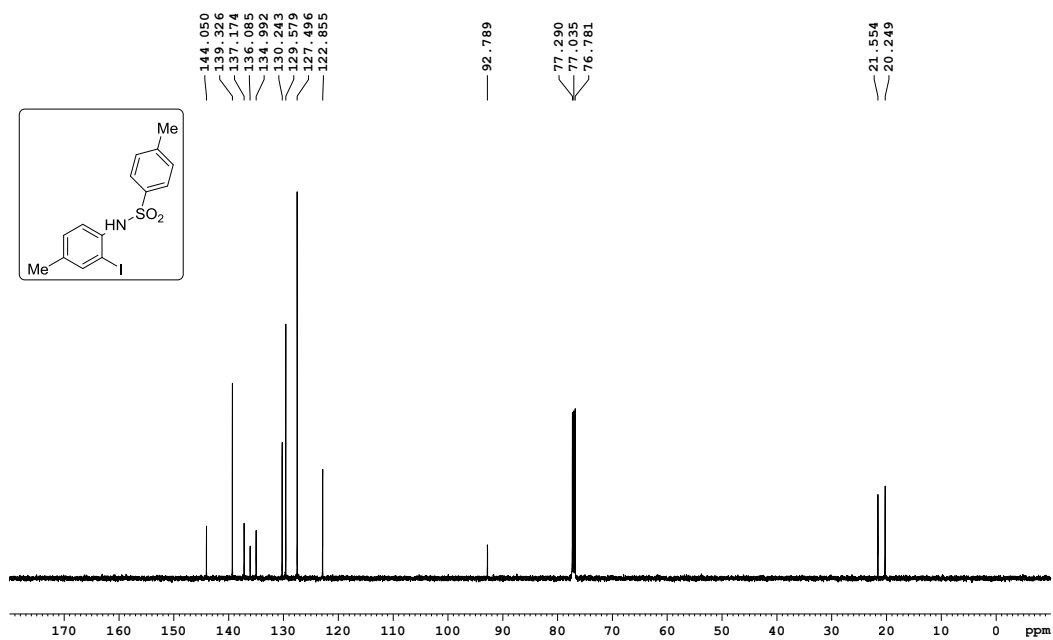


Figure S2. ¹³C NMR spectrum of compound **8b**

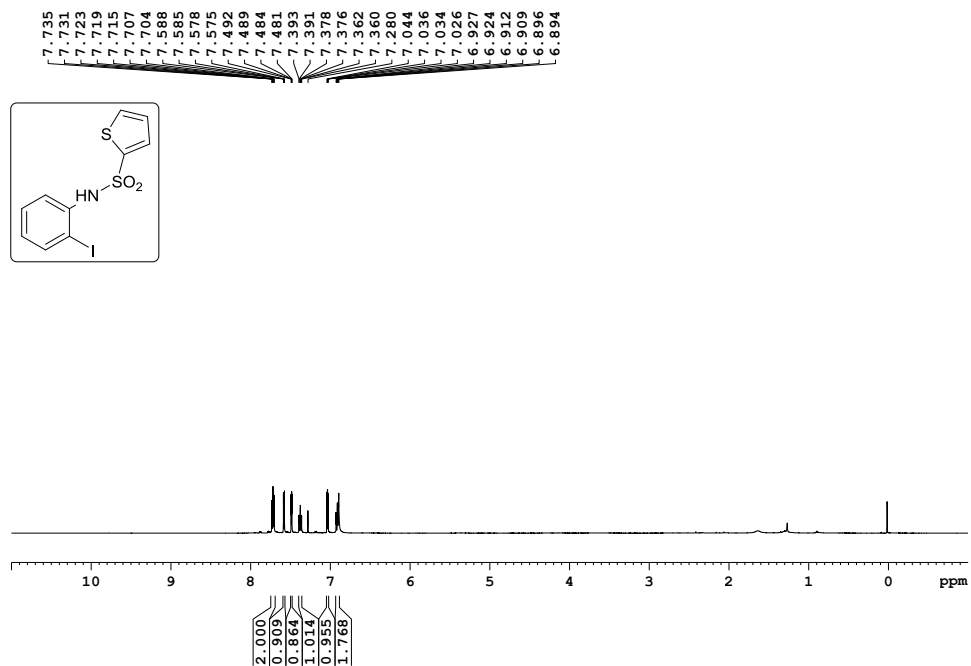


Figure S3. ¹H NMR spectrum of compound **8d**

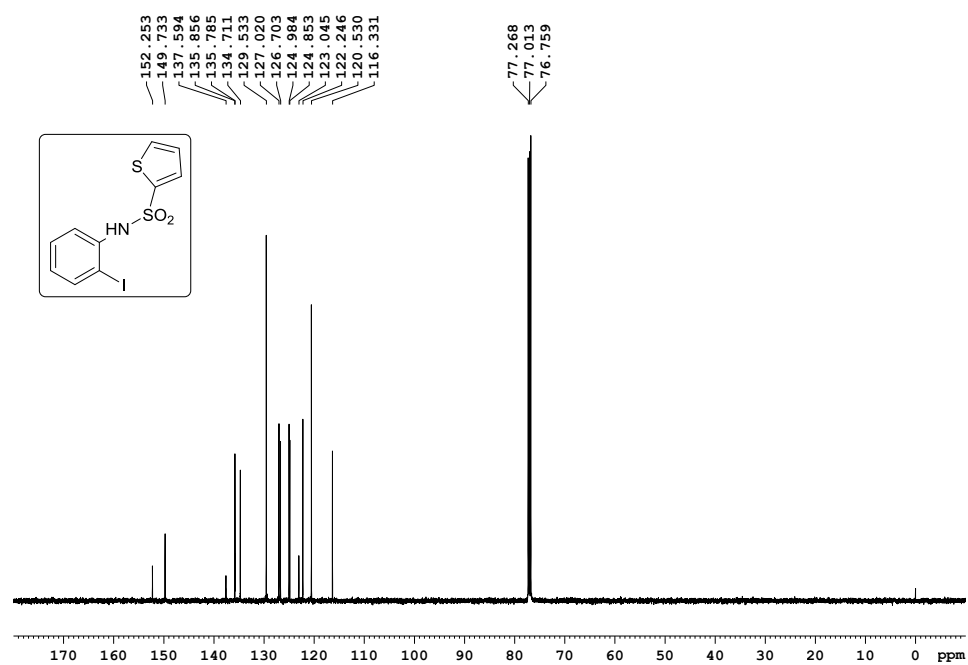


Figure S4. ¹³C NMR spectrum of compound **8d**

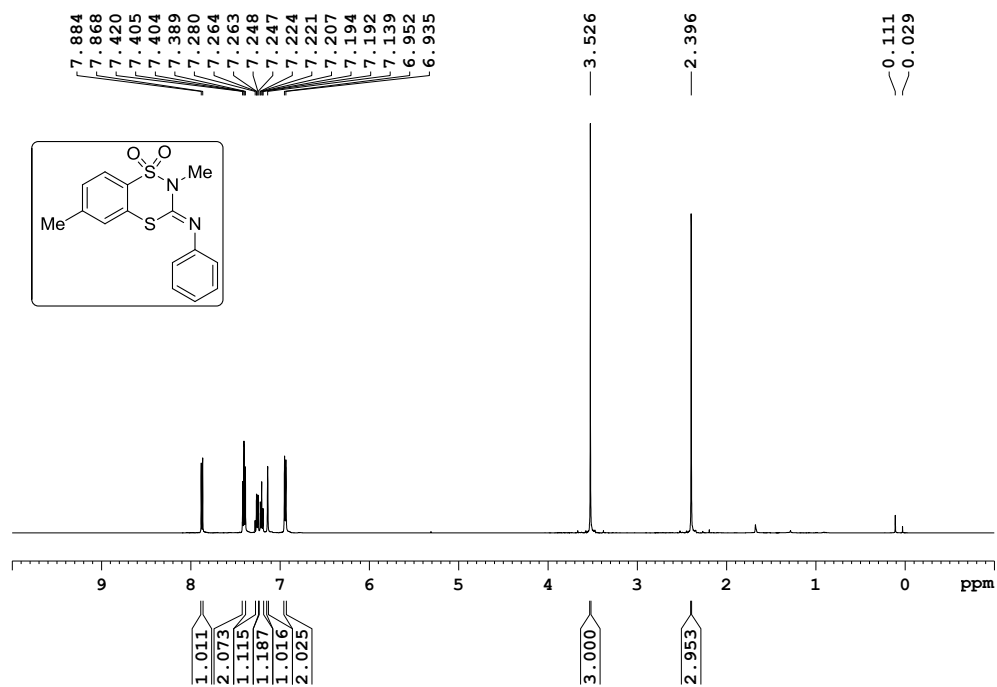


Figure S5. ¹H NMR spectrum of compound 3aa

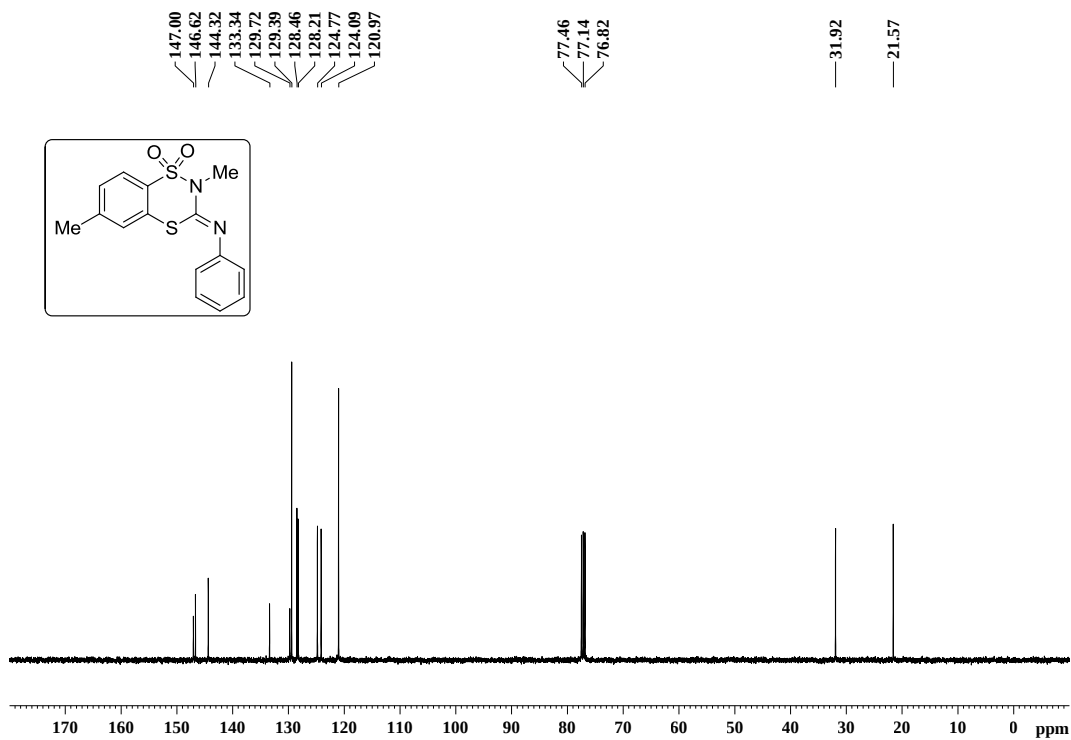


Figure S6. ¹³C NMR spectrum of compound 3aa

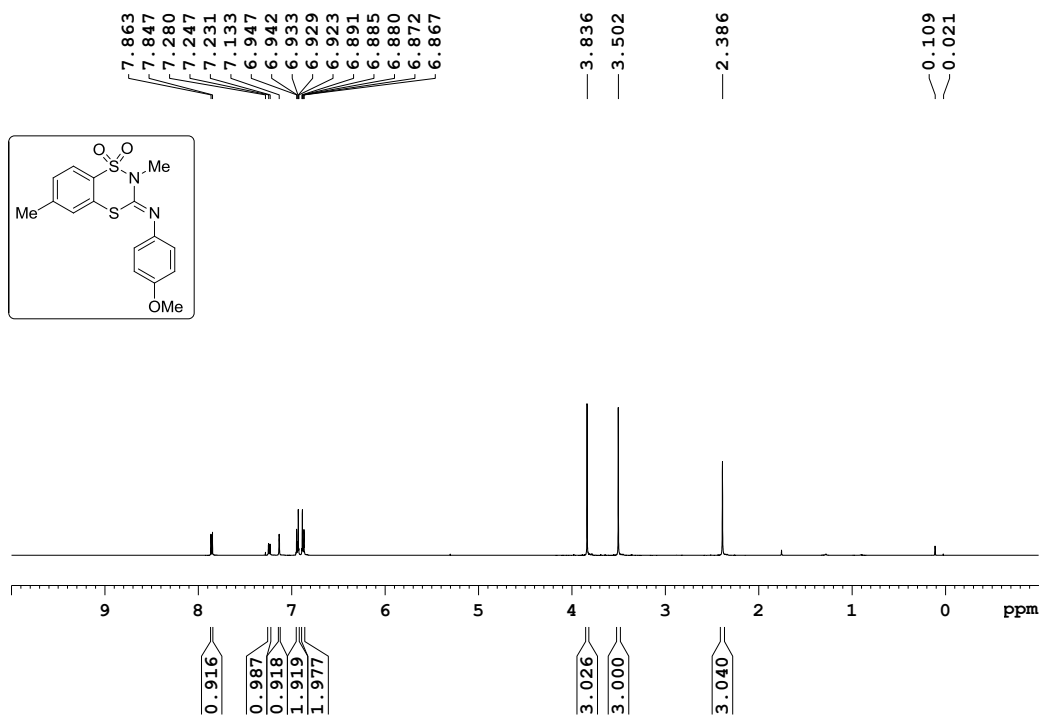


Figure S7. ¹H NMR spectrum of compound **3ab**

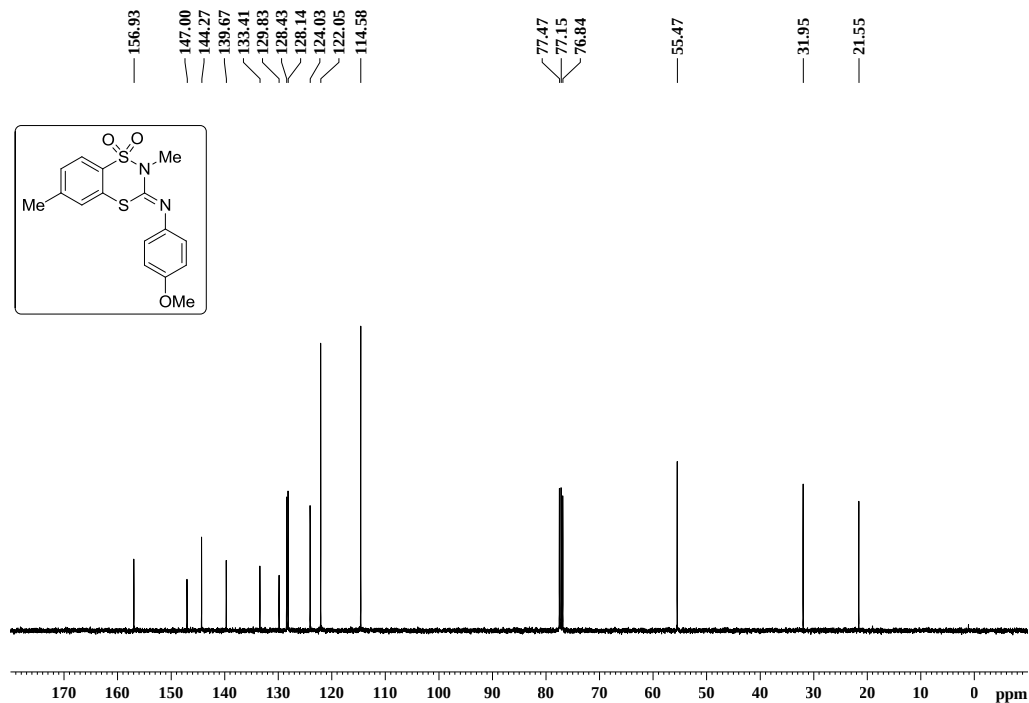


Figure S8. ¹³C NMR spectrum of compound **3ab**

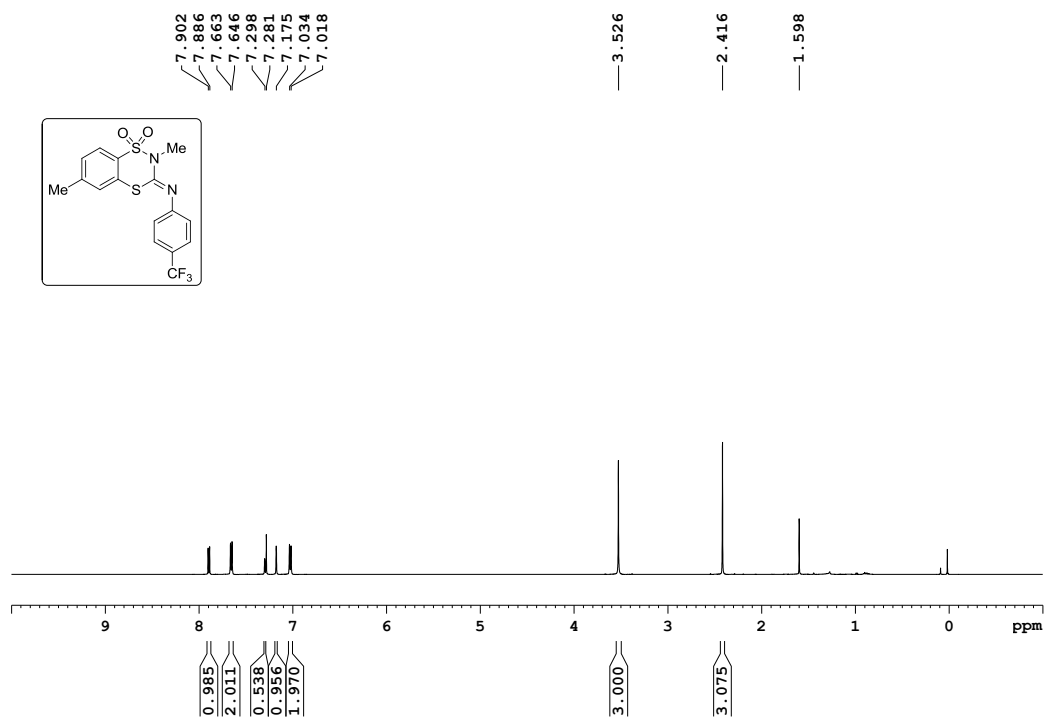


Figure S9. ¹H NMR spectrum of compound 3ac

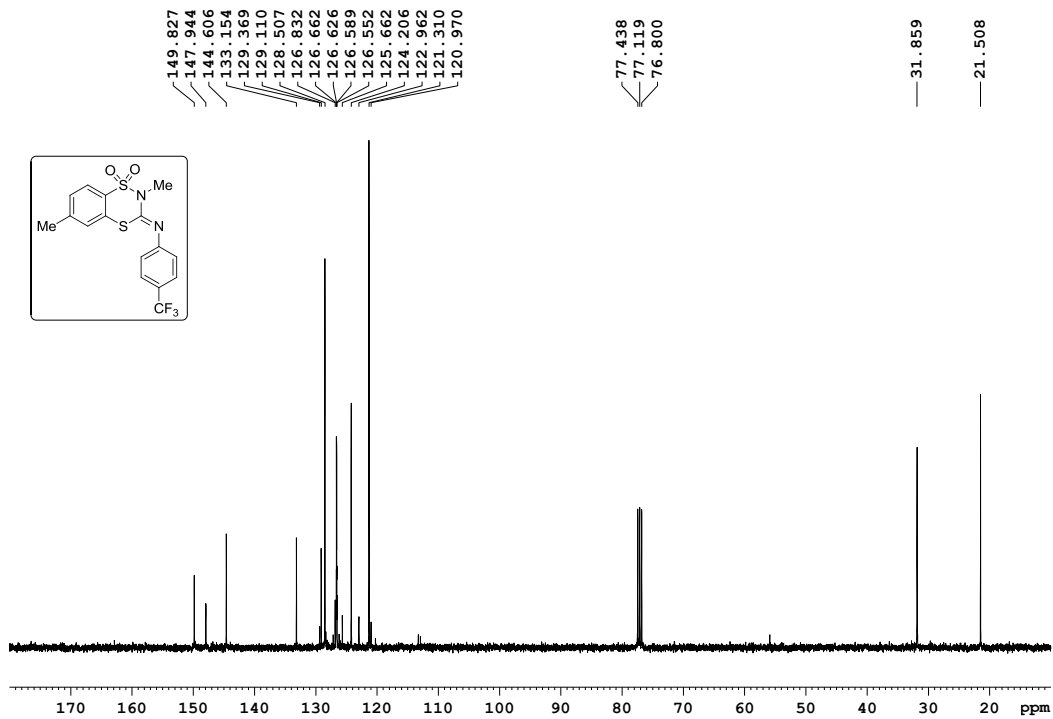


Figure S10. ¹³C NMR spectrum of compound 3ac

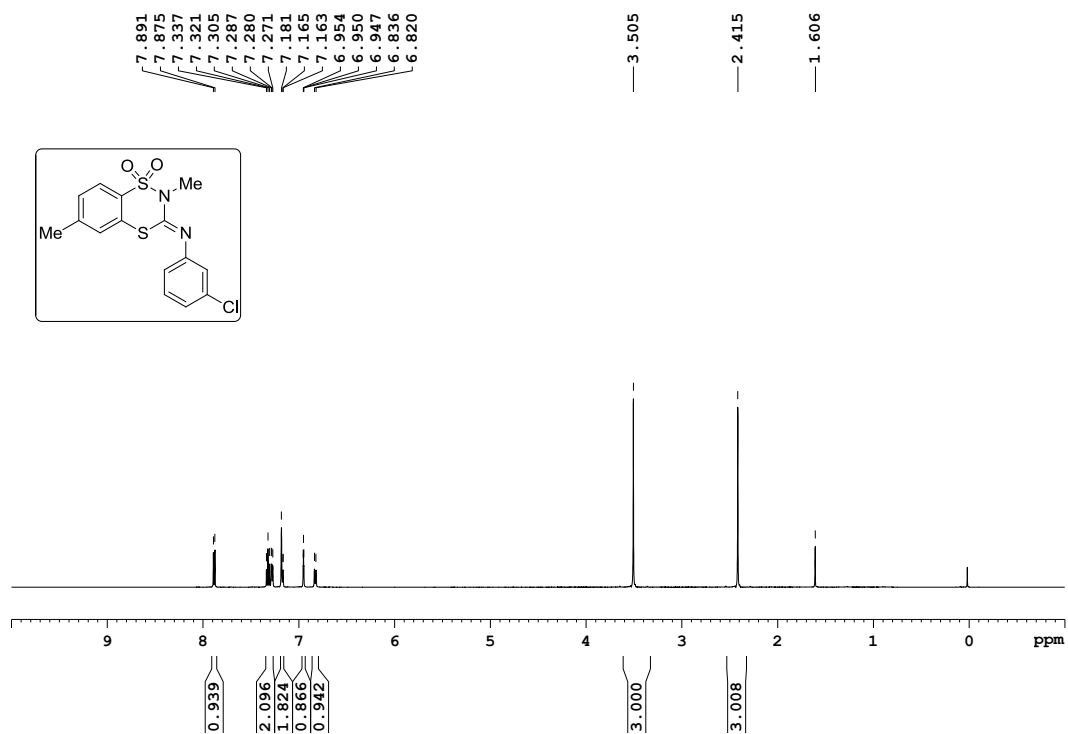


Figure S11. ¹H NMR spectrum of compound 3ad

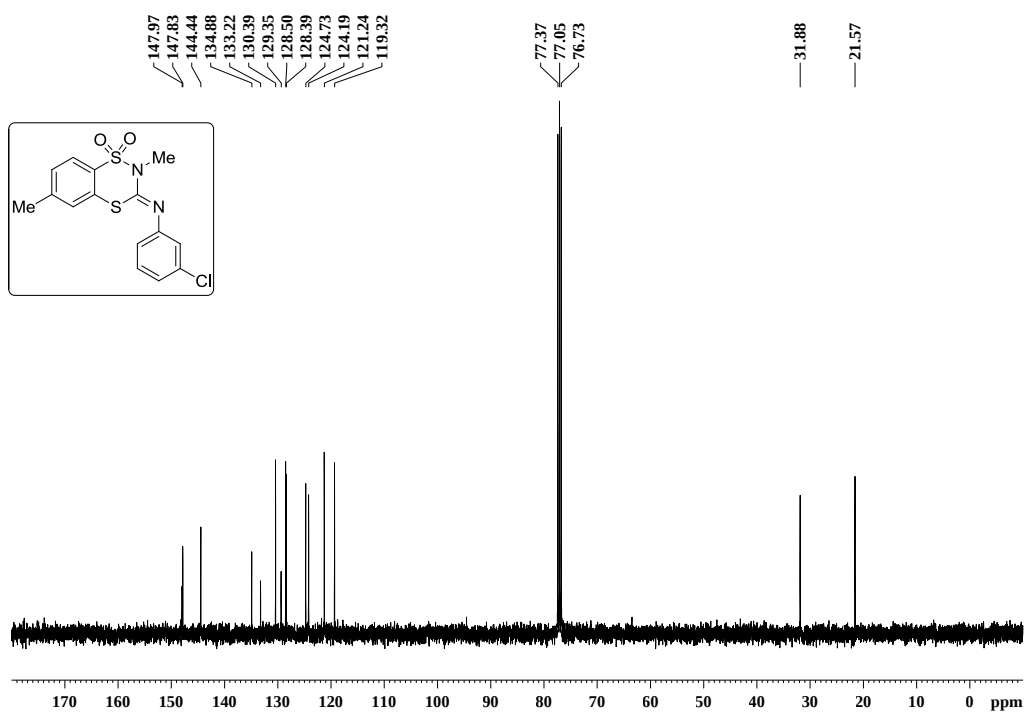


Figure S12. ¹³C NMR spectrum of compound 3ad

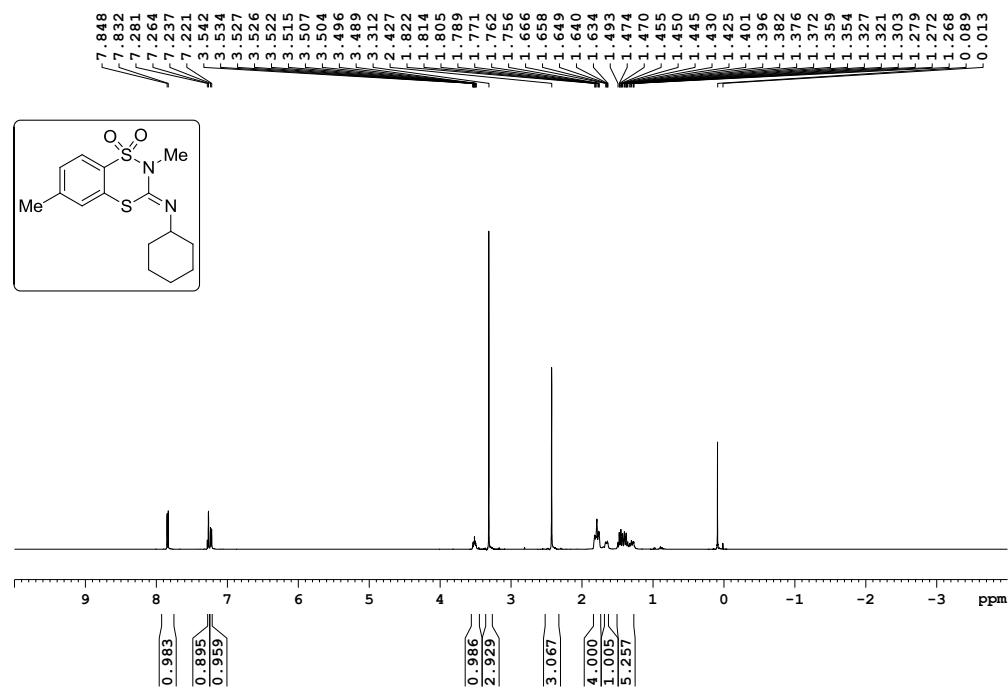


Figure S13. ¹H NMR spectrum of compound 3ae

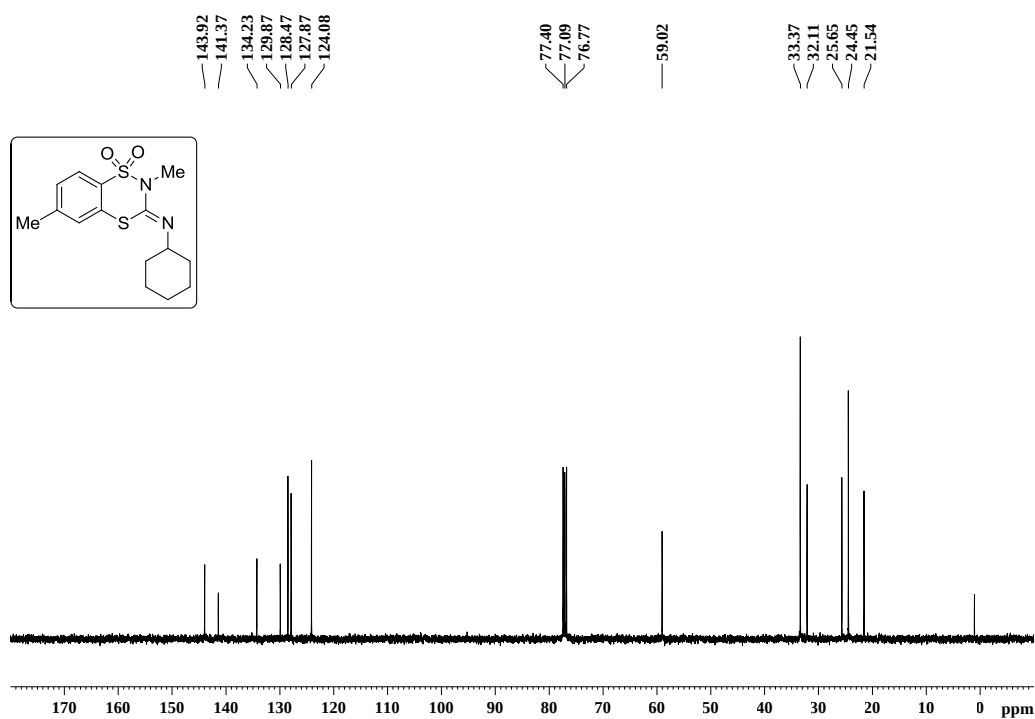


Figure S14. ¹³C NMR spectrum of compound 3ae

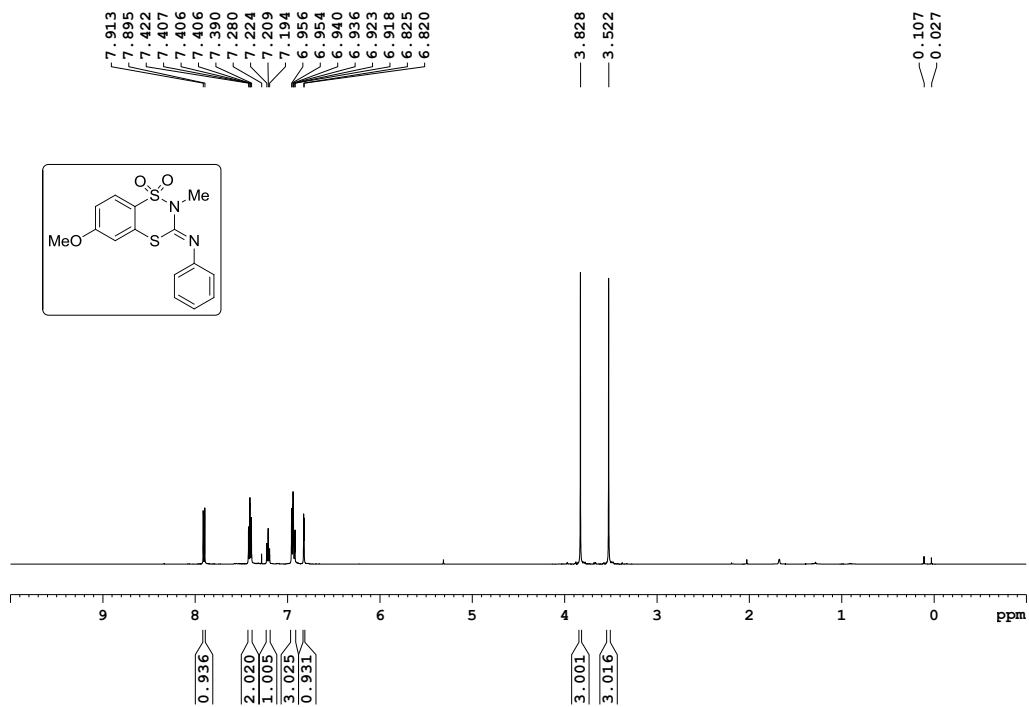


Figure S15. ¹H NMR spectrum of compound **3ba**

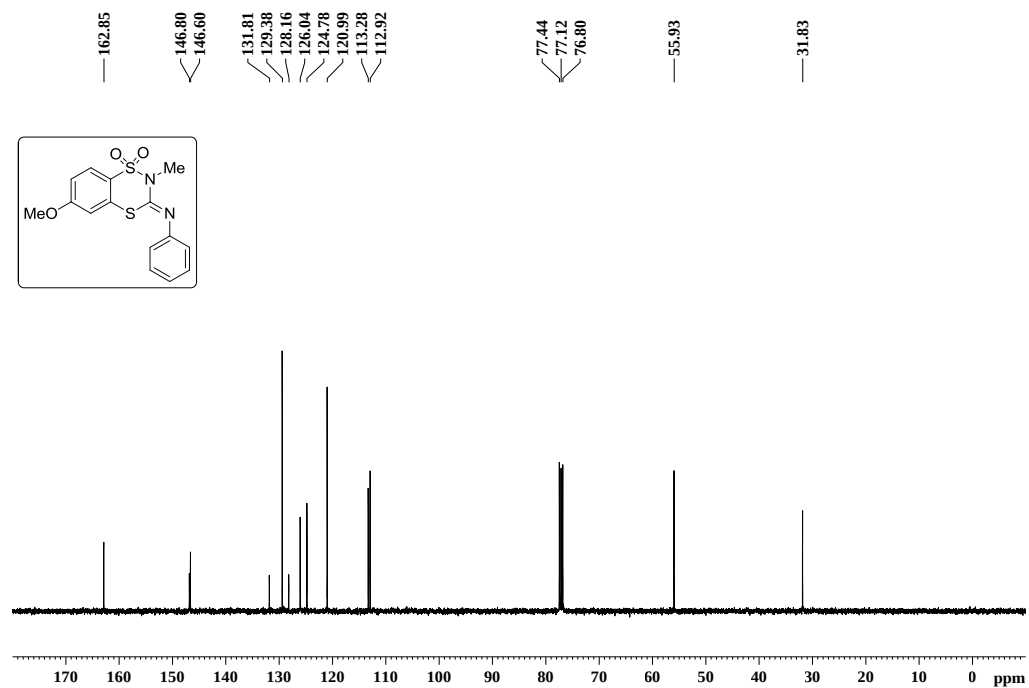


Figure S16. ¹³C NMR spectrum of compound **3ba**

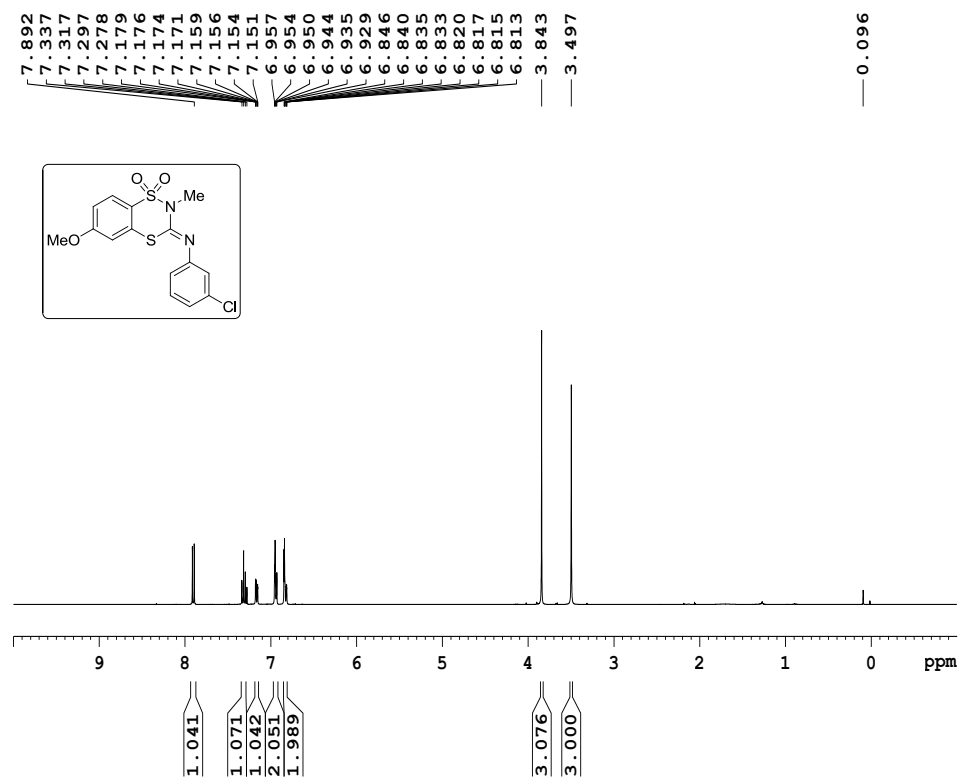


Figure S17. ¹H NMR spectrum of compound **3bd**

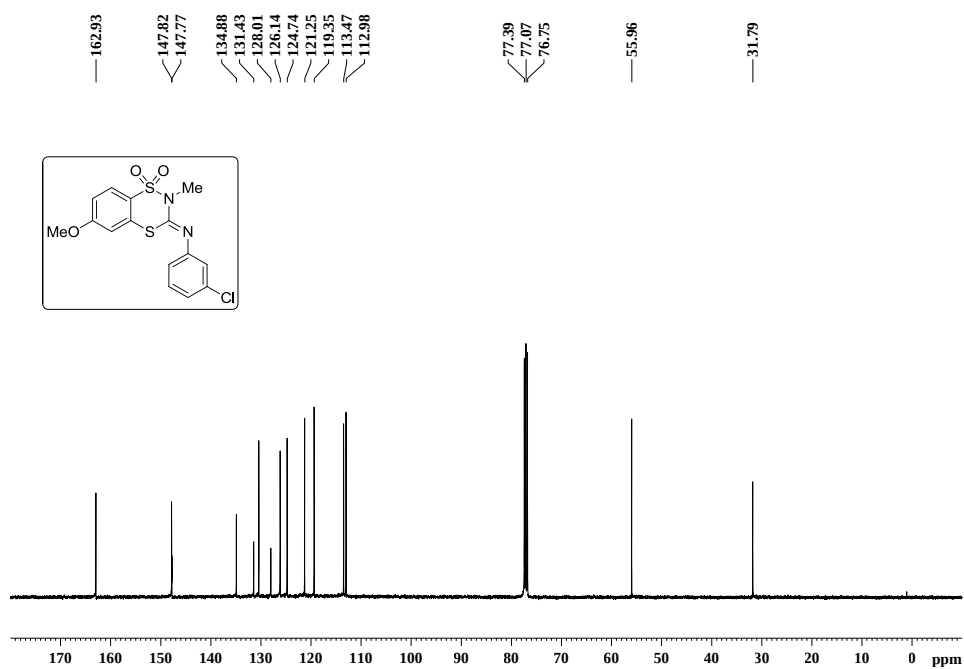


Figure S18. ¹³C NMR spectrum of compound **3bd**

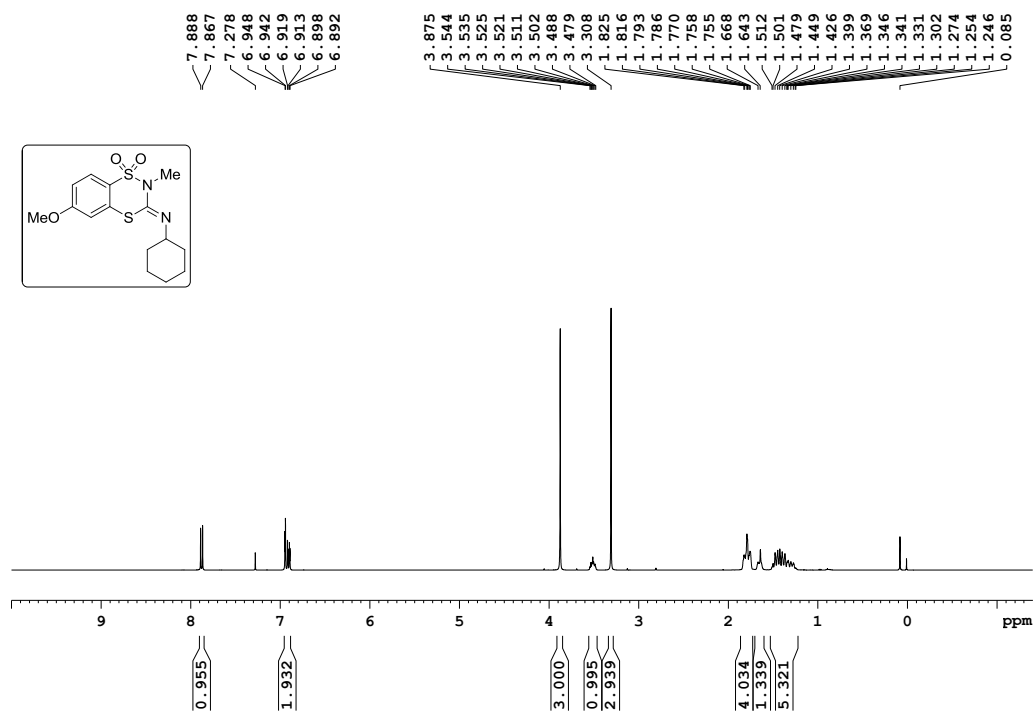
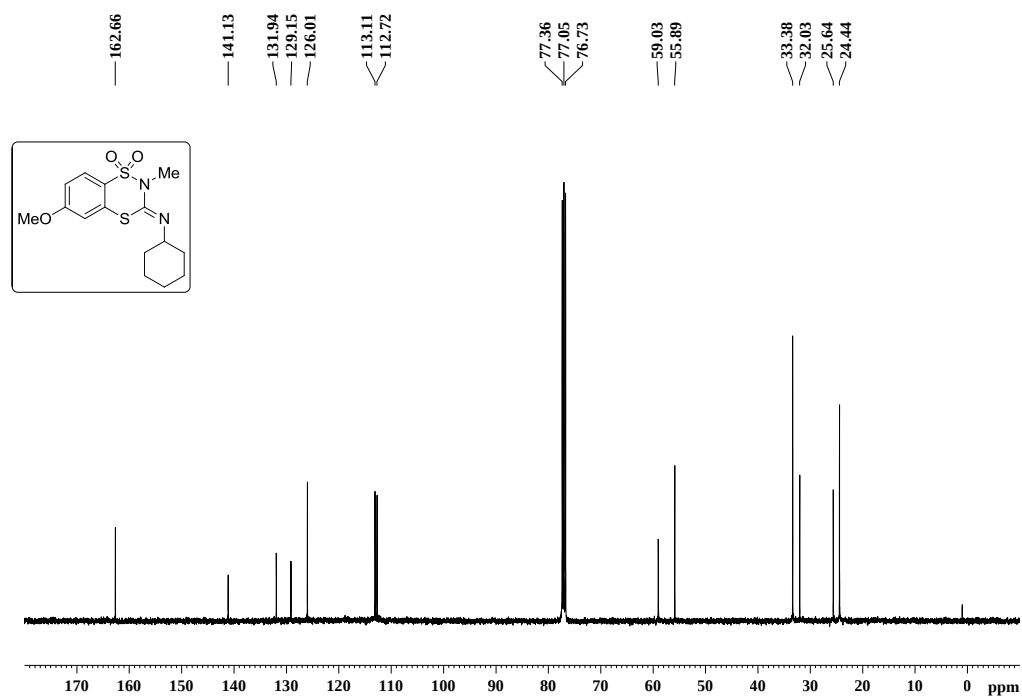


Figure S19. ¹H NMR spectrum of compound **3be**



S20. ¹³C NMR spectrum of compound **3be**

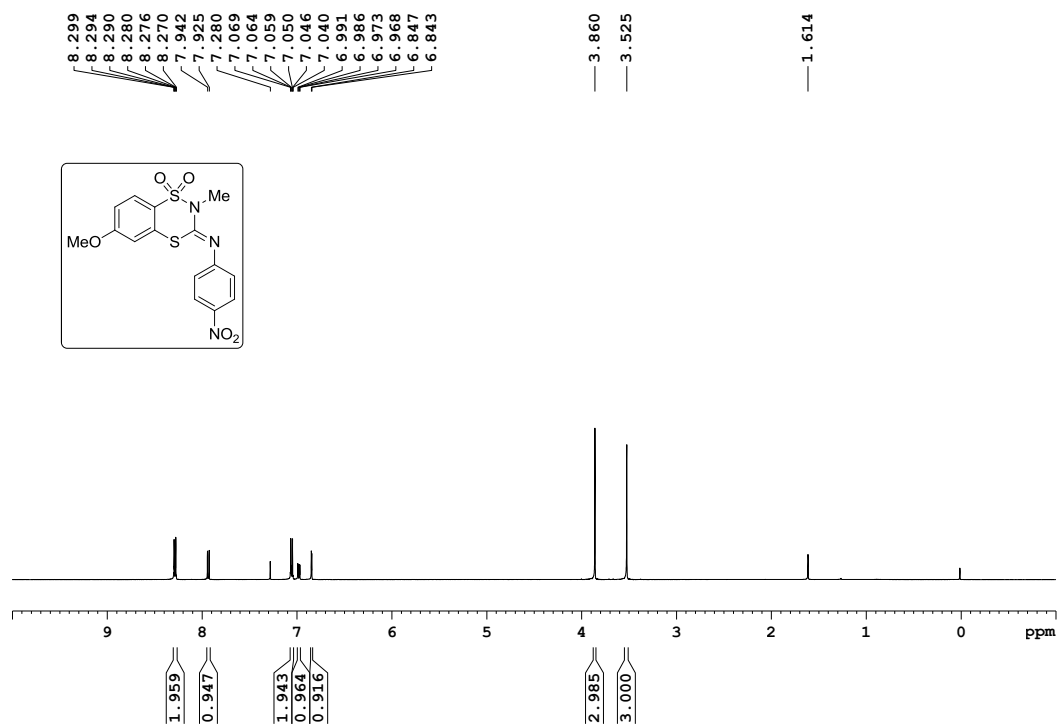


Figure S21. ¹H NMR spectrum of compound **3bf**

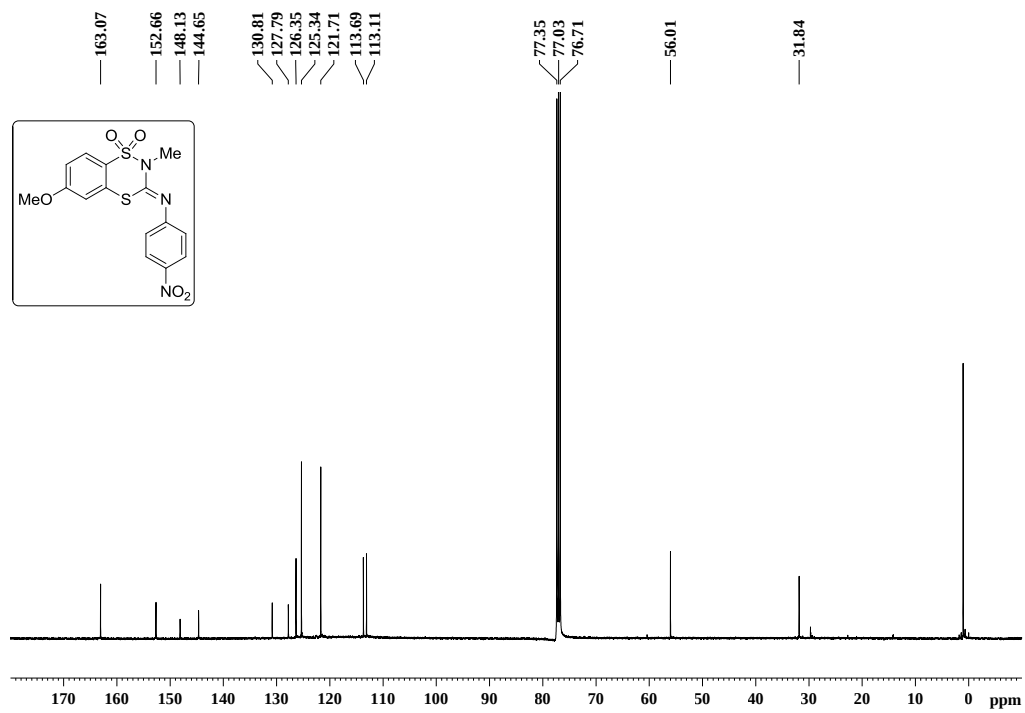


Figure S22. ¹³C NMR spectrum of compound **3bf**

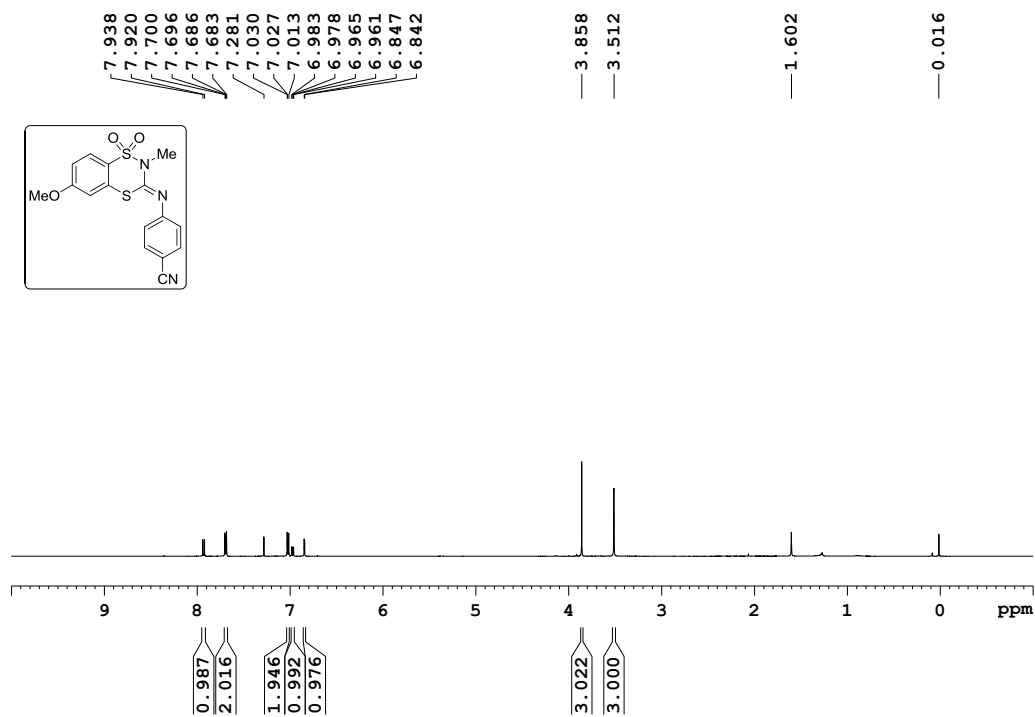


Figure S23. ¹H NMR spectrum of compound **3bg**

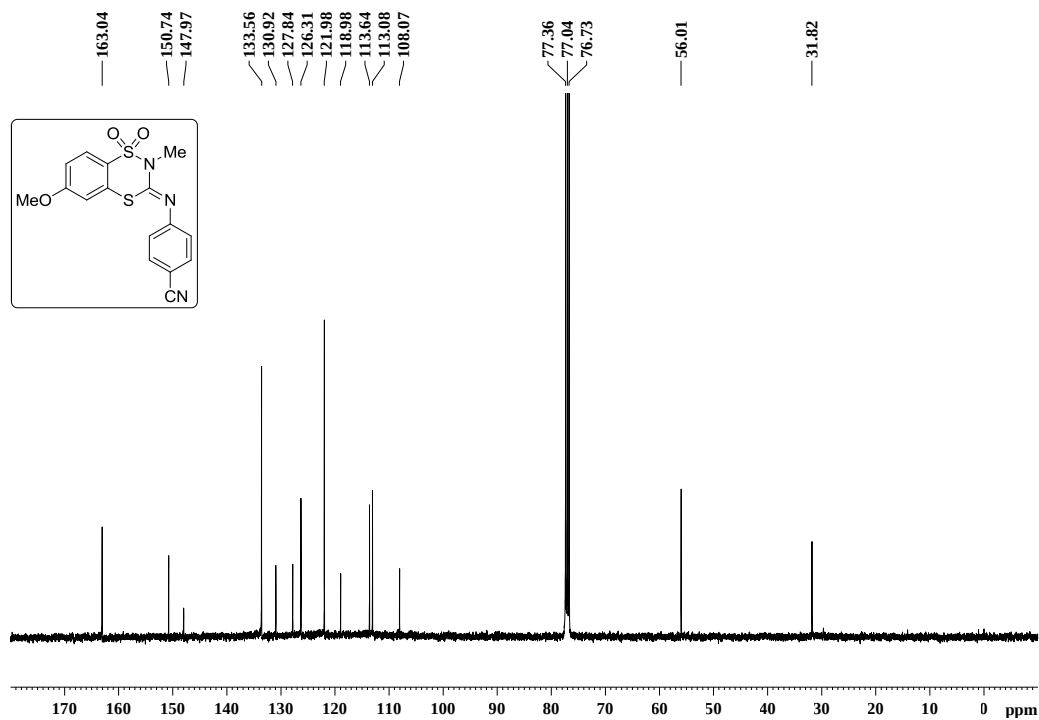


Figure S24. ¹³C NMR spectrum of compound **3bg**

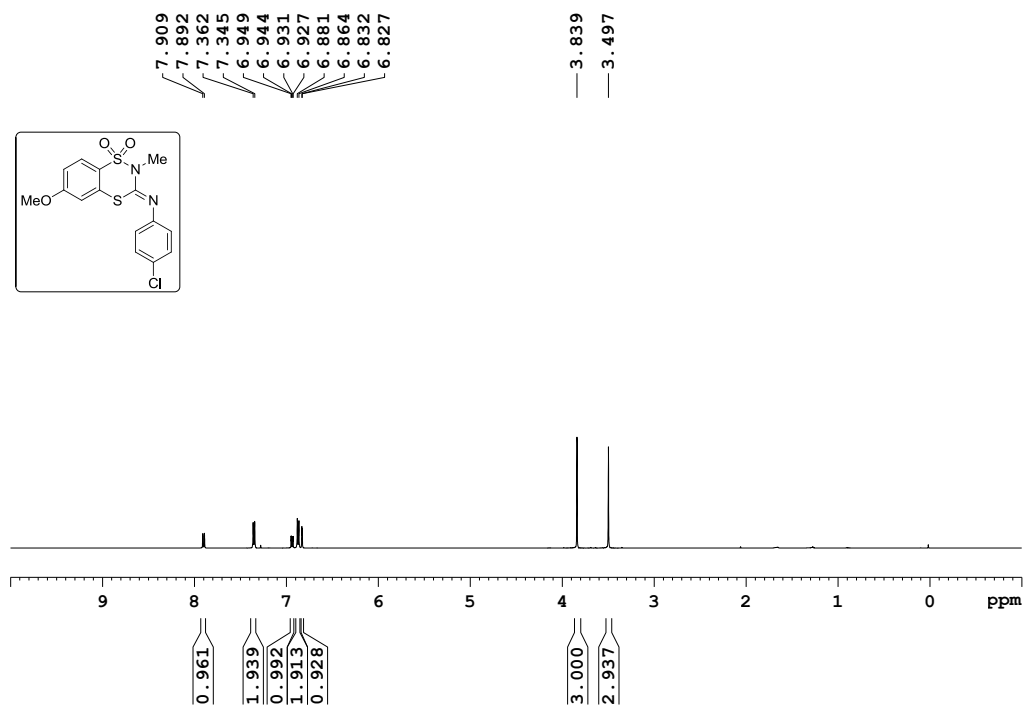


Figure S25. ¹H NMR spectrum of compound **3bh**

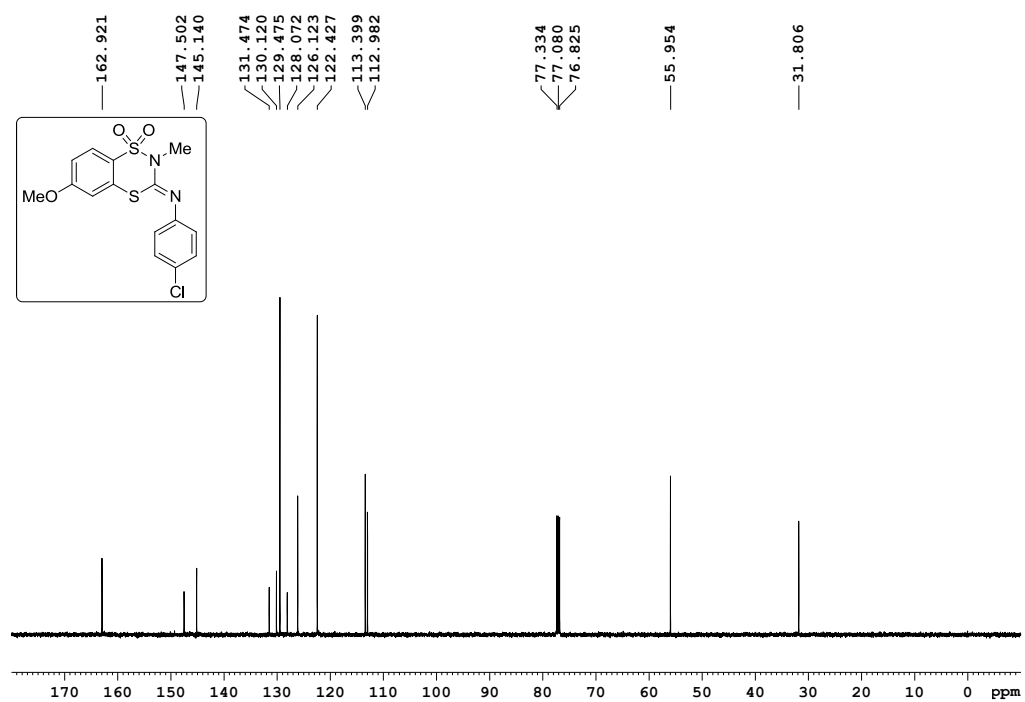


Figure S26. ¹³C NMR spectrum of compound **3bh**

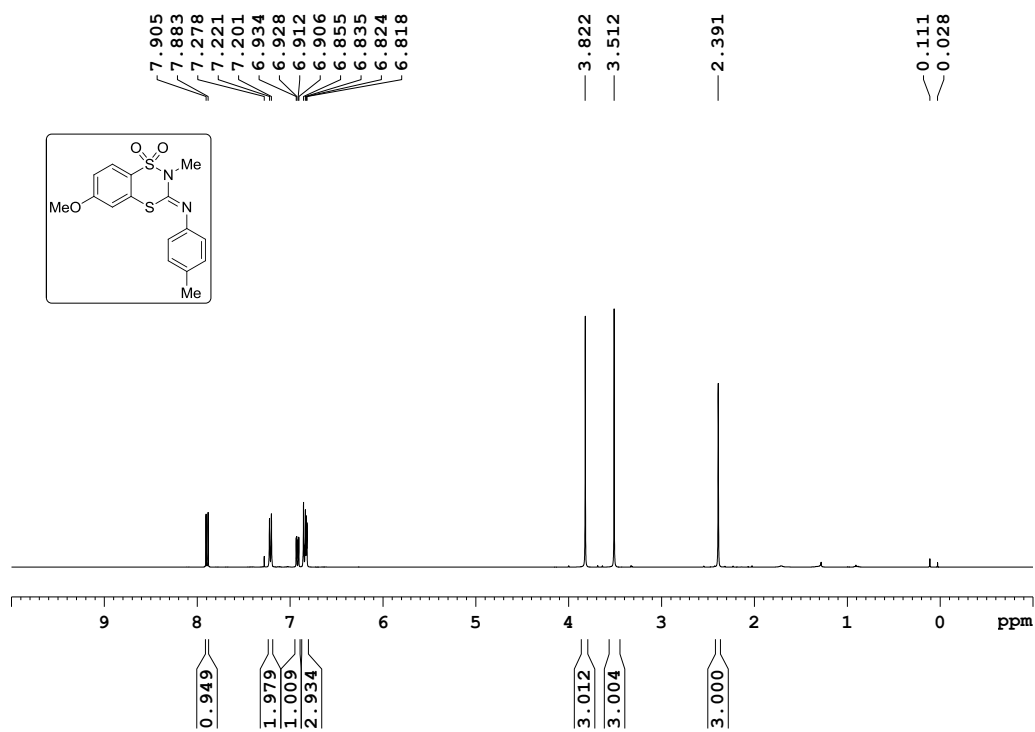


Figure S27. ¹H NMR spectrum of compound **3bi**

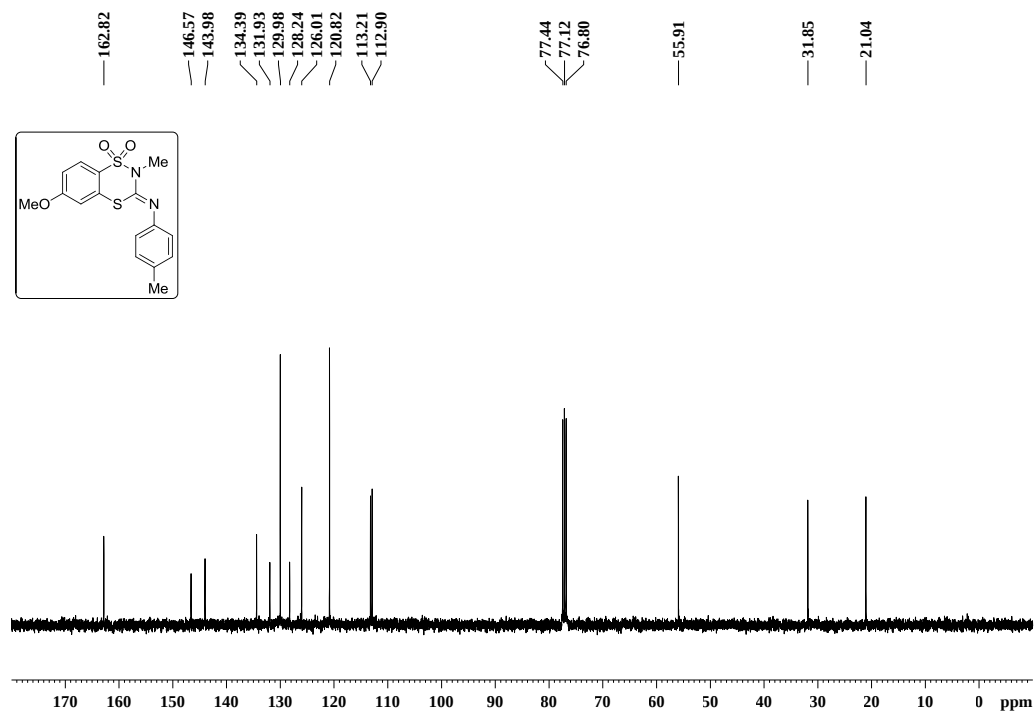


Figure S28. ¹³C NMR spectrum of compound **3bi**

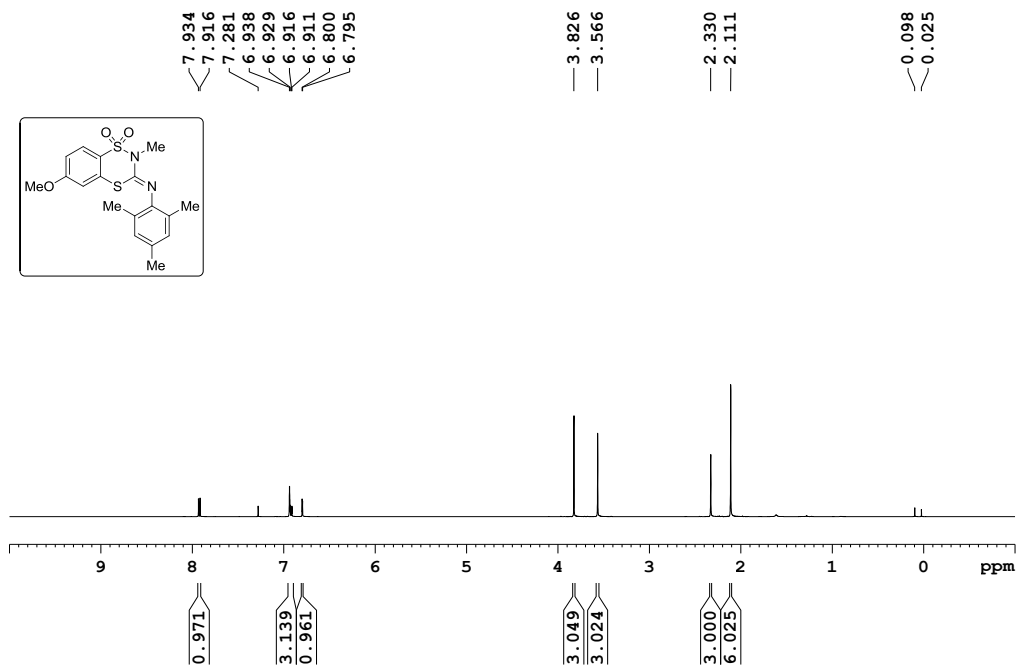


Figure S29. ¹H NMR spectrum of compound **3bj**

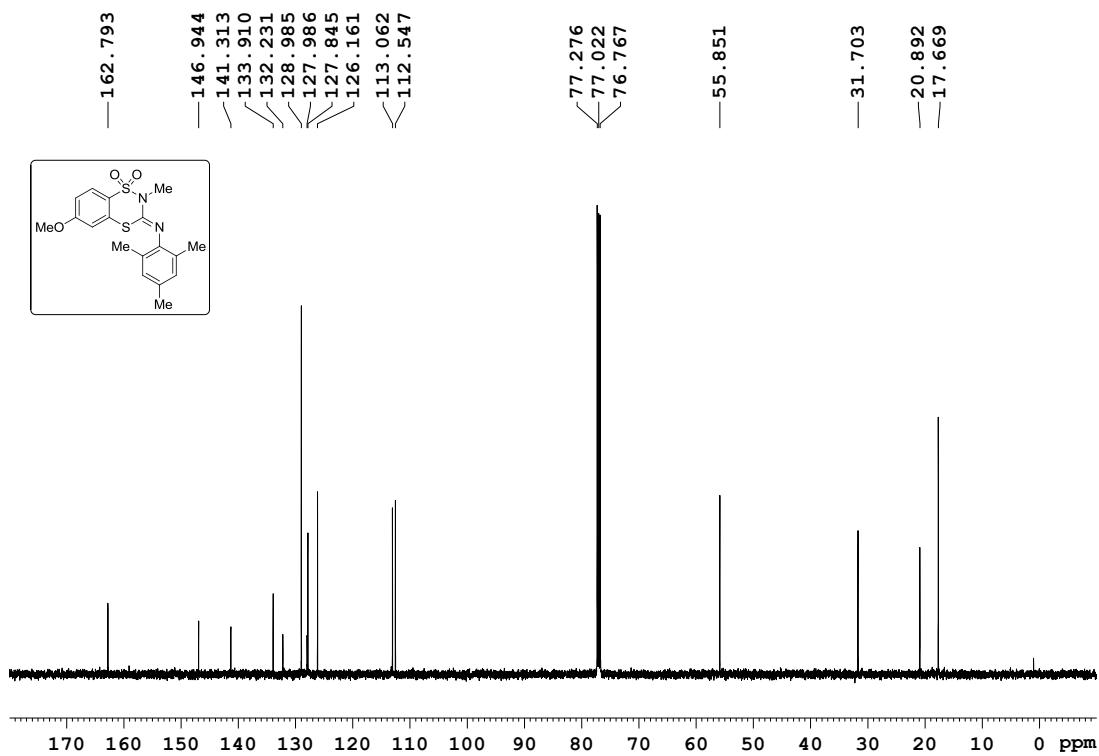


Figure S30. ¹³C NMR spectrum of compound **3bj**

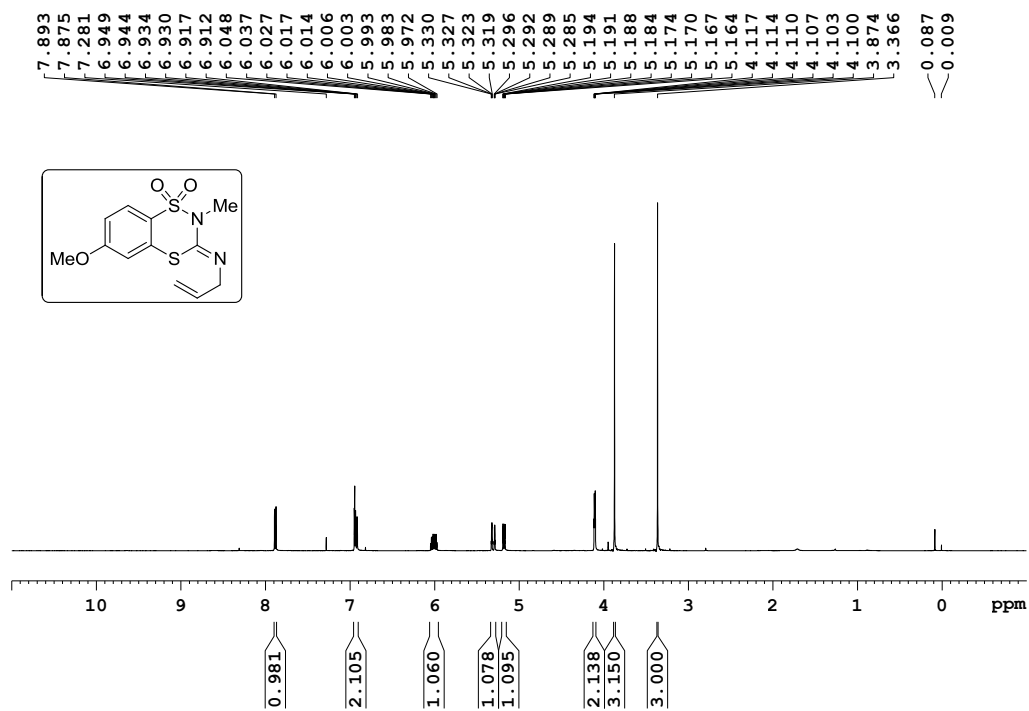


Figure S31. ¹H NMR spectrum of compound **3bk**

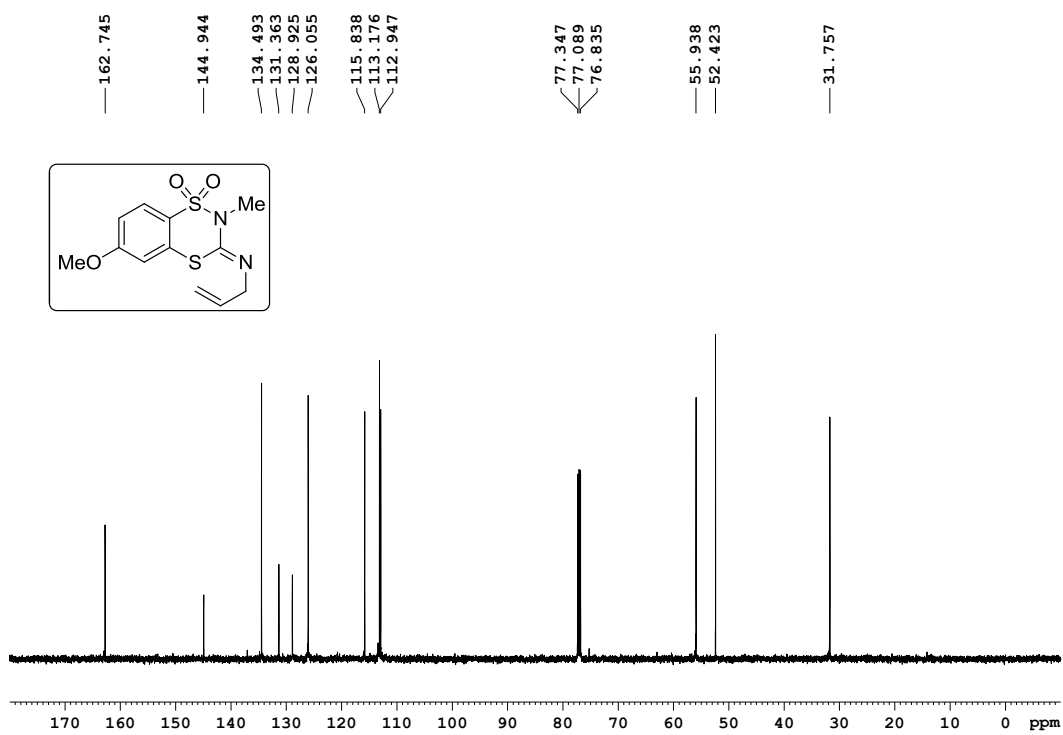


Figure S32. ¹³C NMR spectrum of compound **3bk**

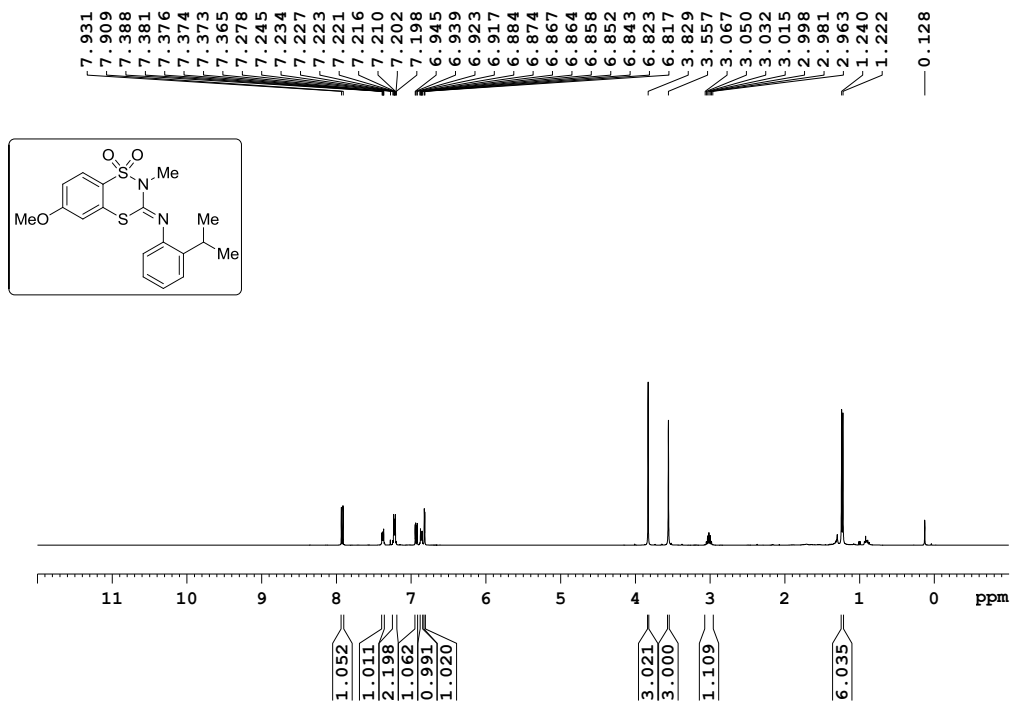


Figure S33. ¹H NMR spectrum of compound 3bl

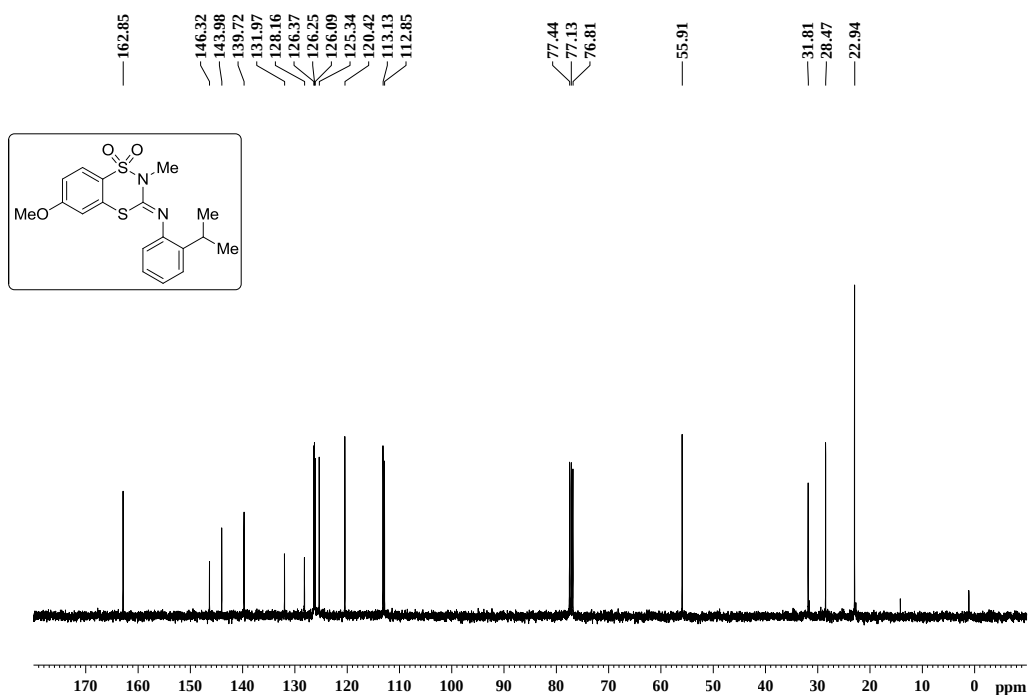


Figure S34. ¹³C NMR spectrum of compound 3bl

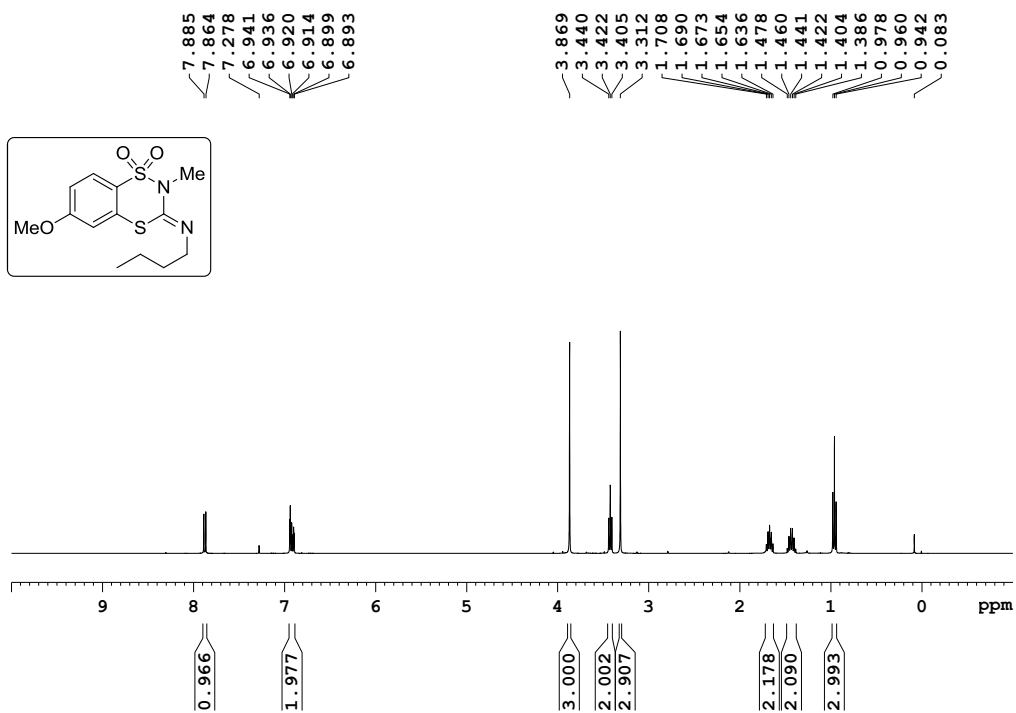


Figure S35. ¹H NMR spectrum of compound 3bm

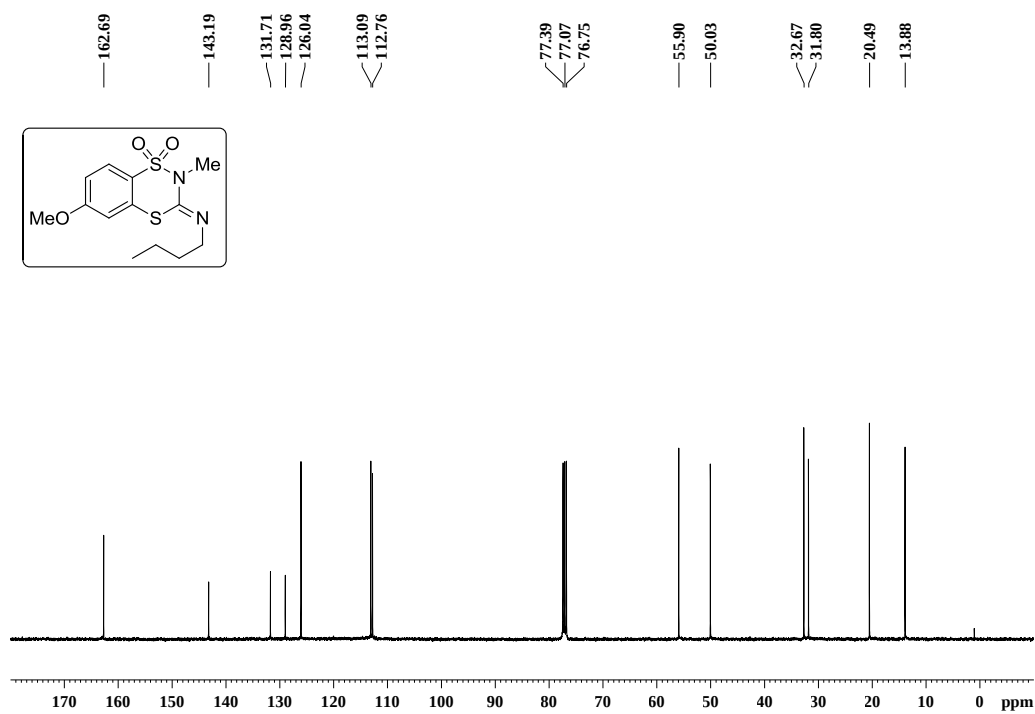


Figure S36. ¹³C NMR spectrum of compound 3bm

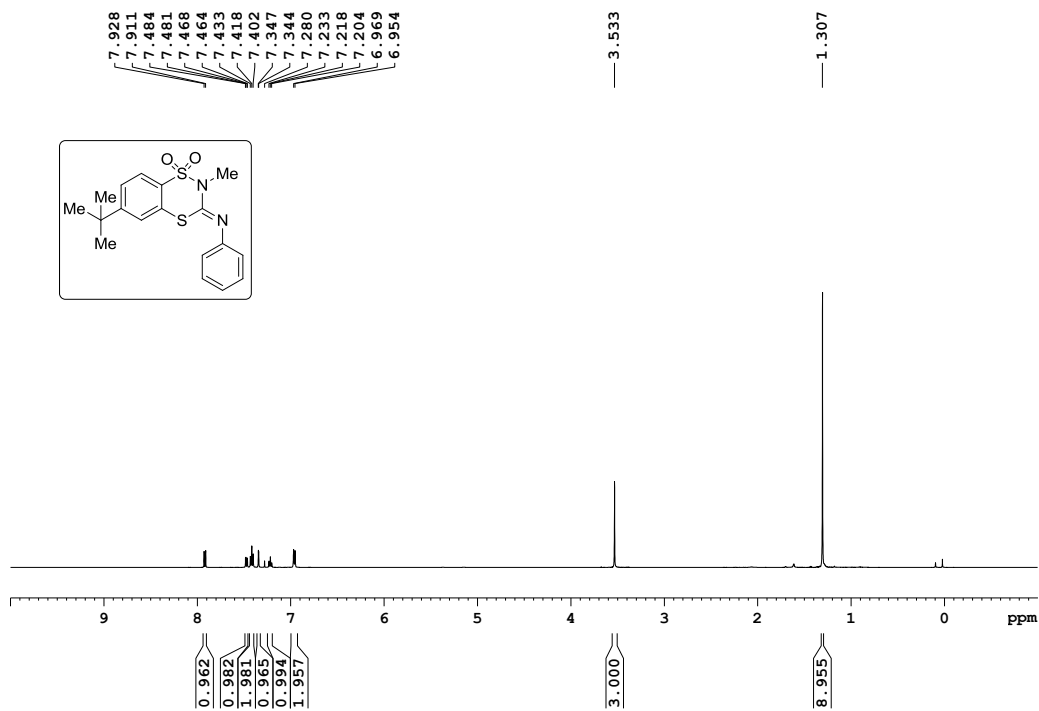


Figure S37. ¹H NMR spectrum of compound **3ca**

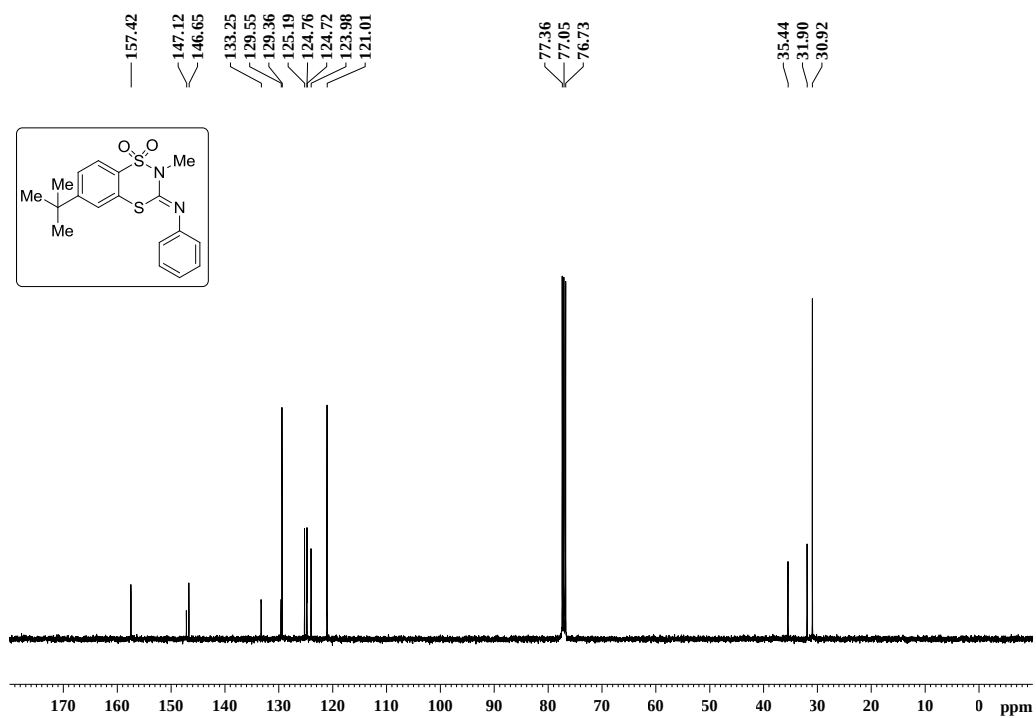


Figure S38. ¹³C NMR spectrum of compound **3ca**

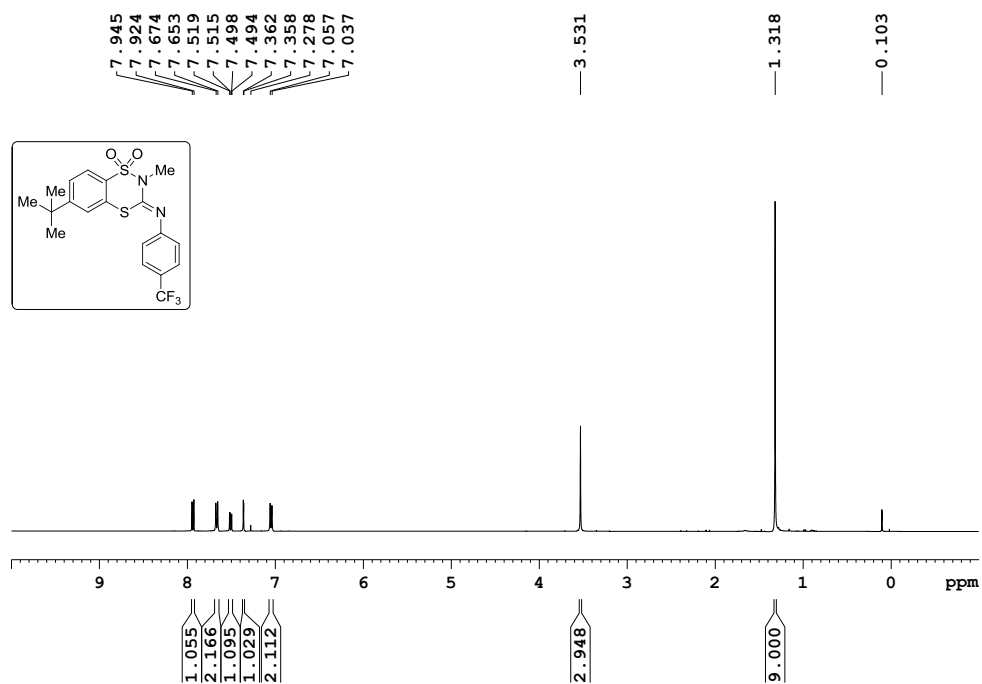


Figure S39. ¹H NMR spectrum of compound 3cc

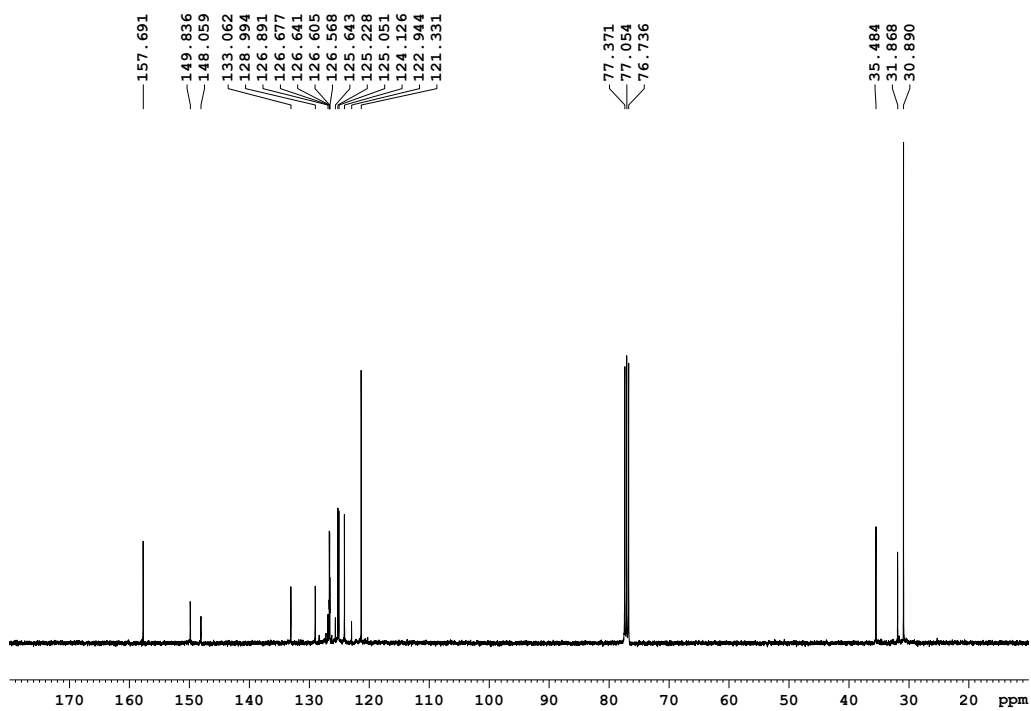


Figure S40. ¹³C NMR spectrum of compound 3cc

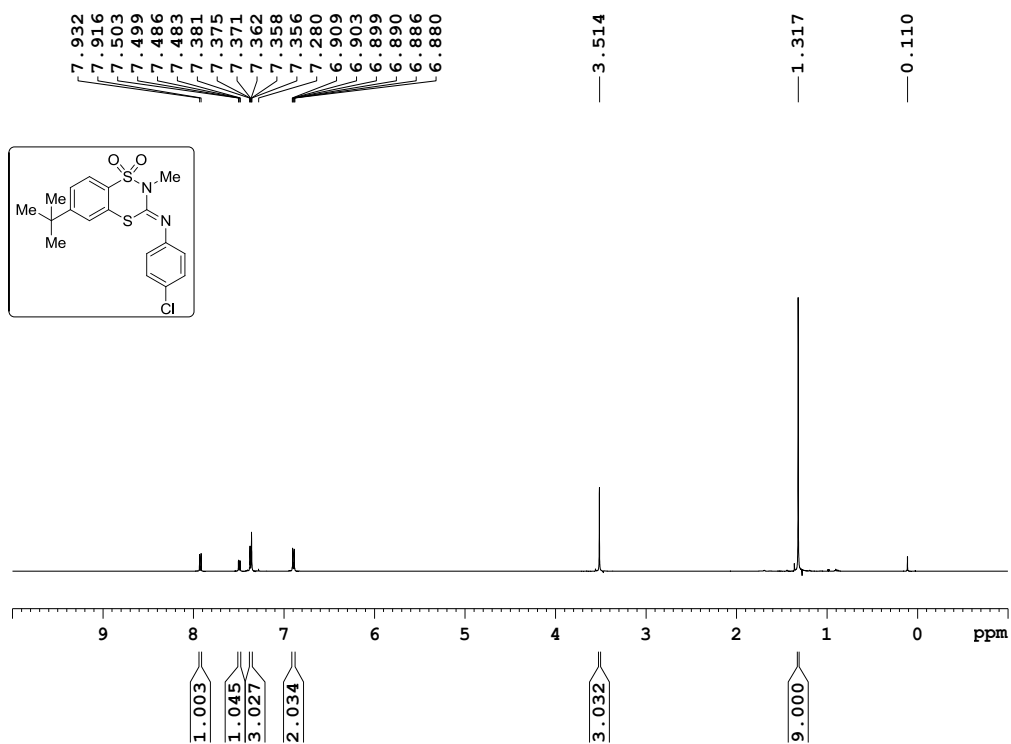


Figure S41. ¹H NMR spectrum of compound 3ch

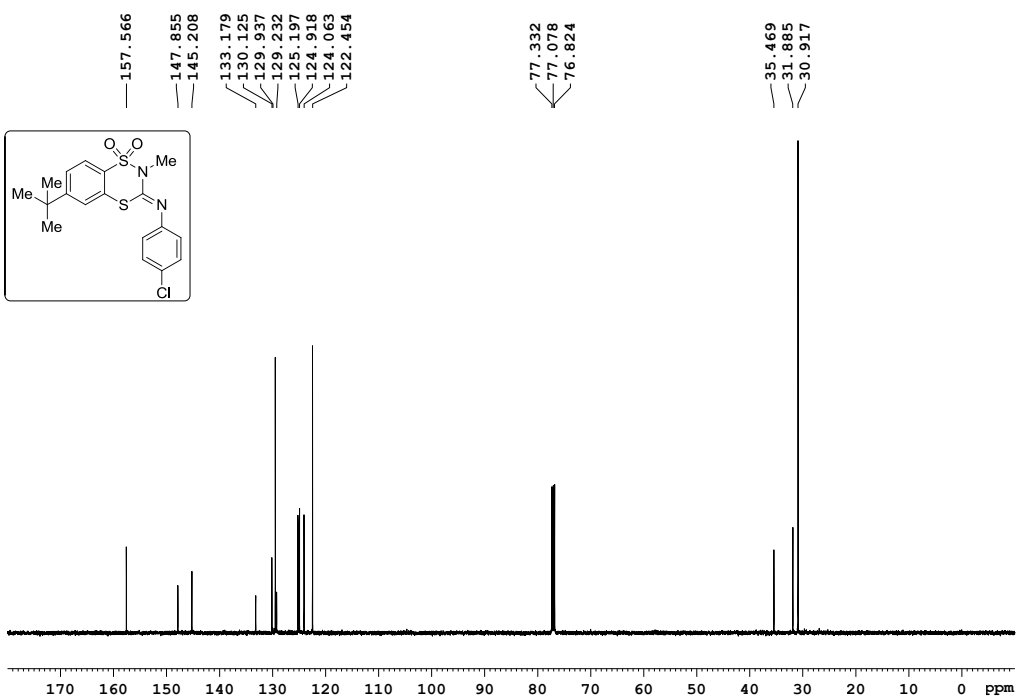


Figure S42. ¹³C NMR spectrum of compound 3ch

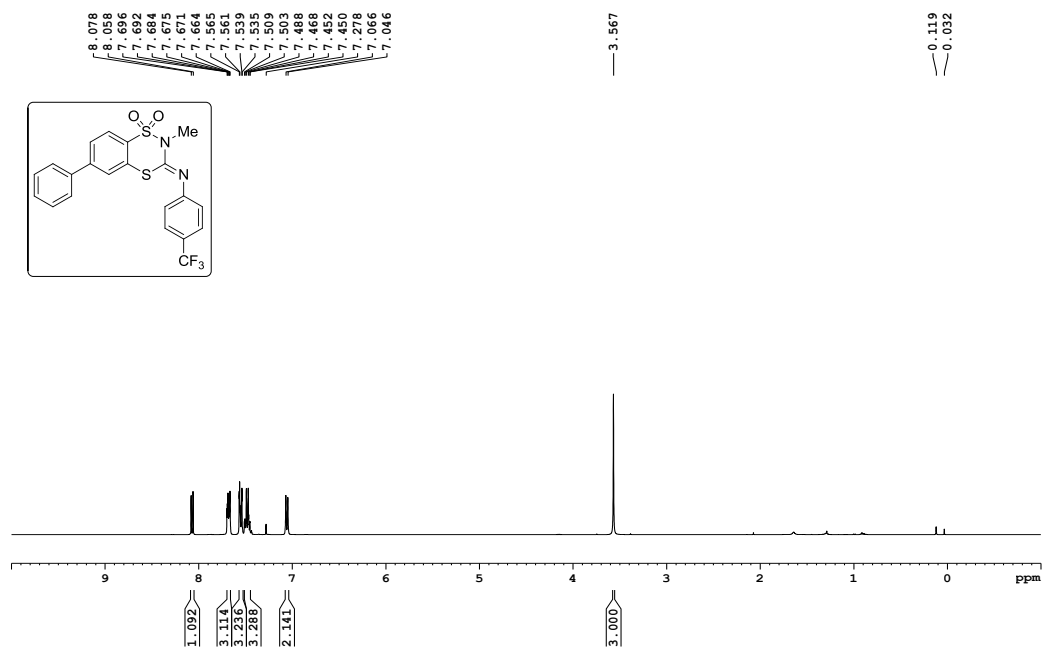


Figure S43. ¹H NMR spectrum of compound **3dc**

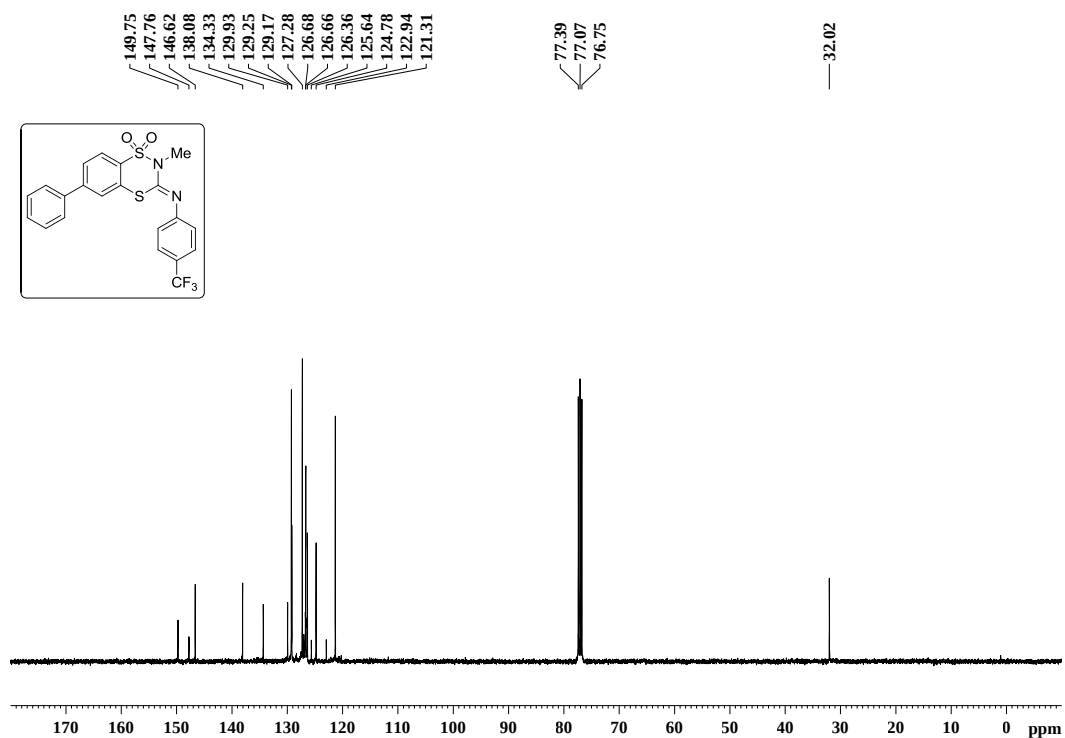


Figure S44. ¹³C NMR spectrum of compound **3dc**

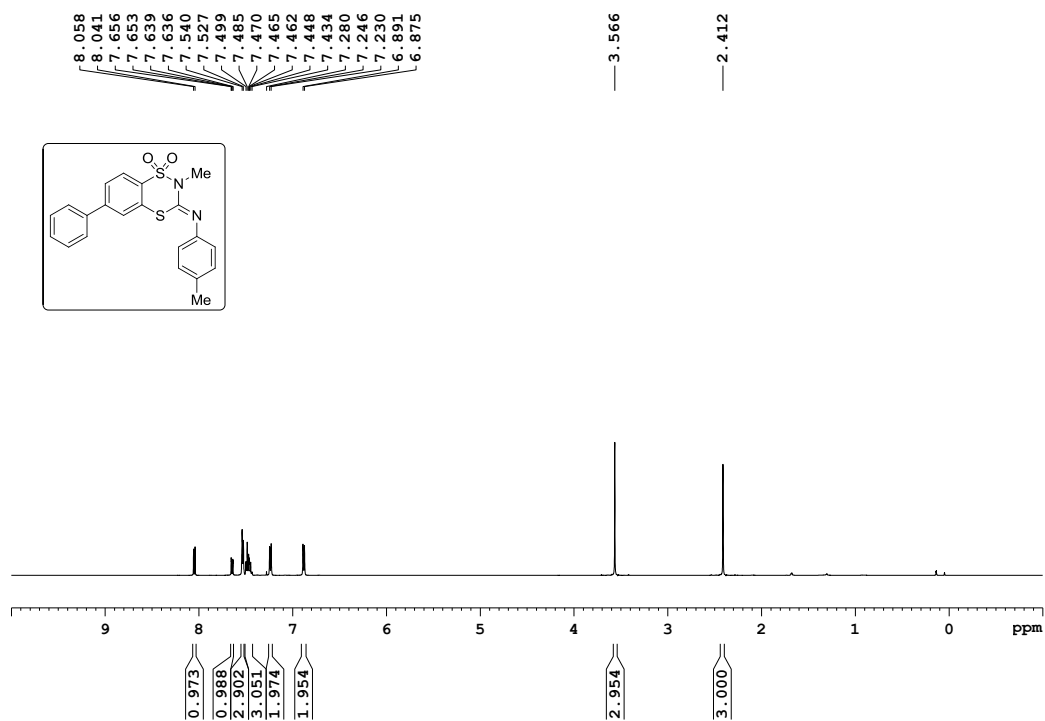


Figure S45. ¹H NMR spectrum of compound **3di**

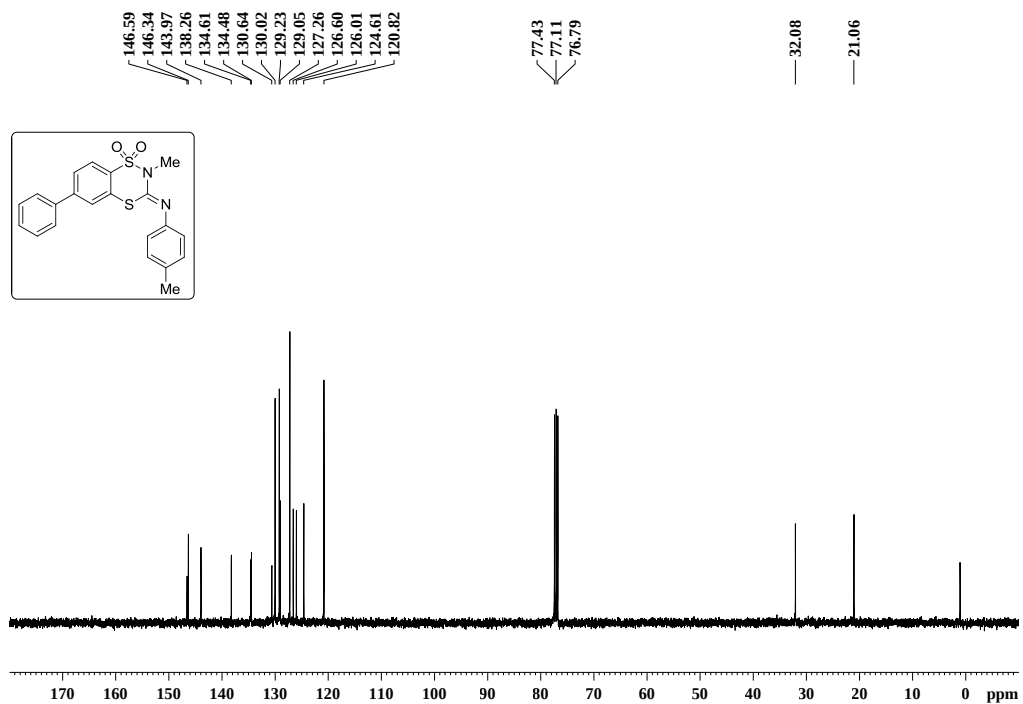


Figure S46. ¹³C NMR spectrum of compound **3di**

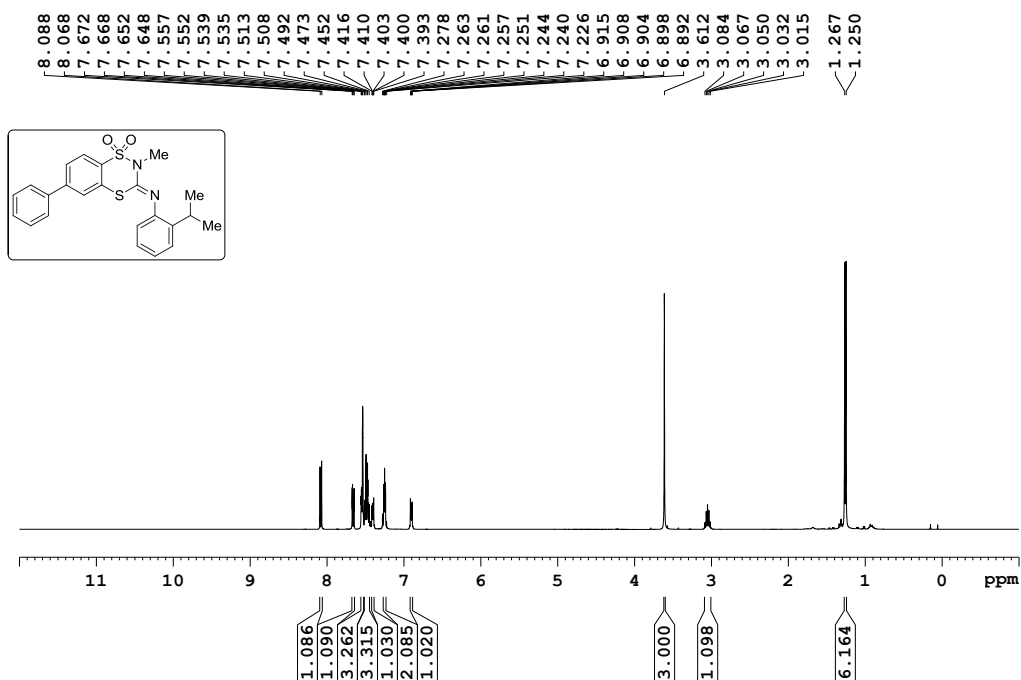


Figure S47. ¹H NMR spectrum of compound **3dl**

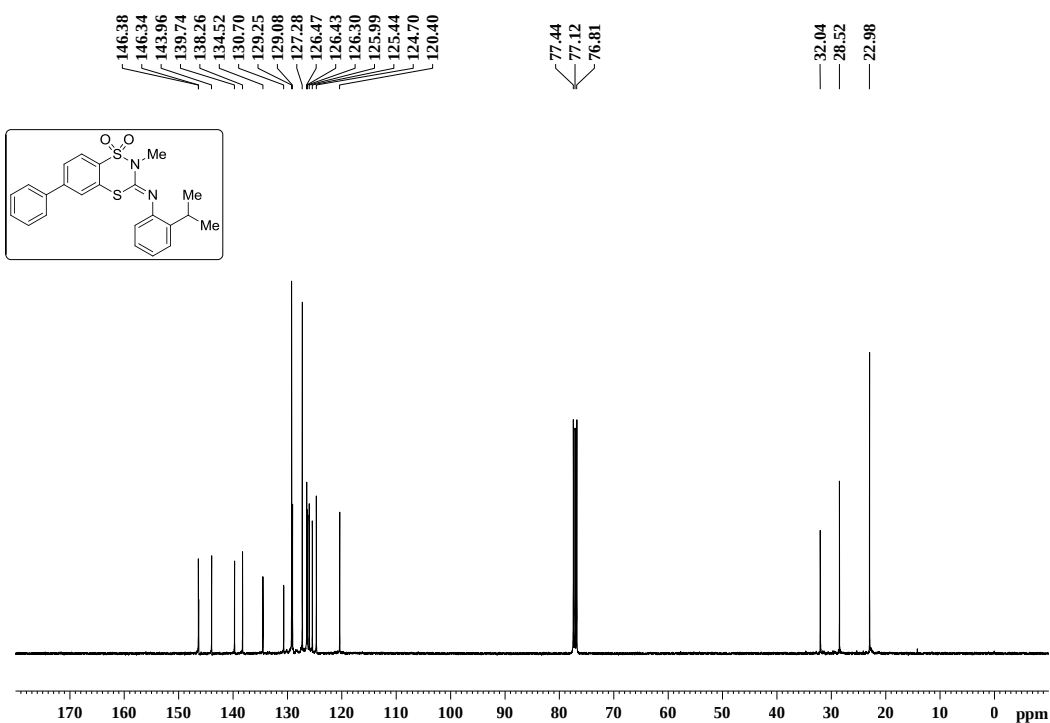


Figure S48. ¹³C NMR spectrum of compound **3dl**

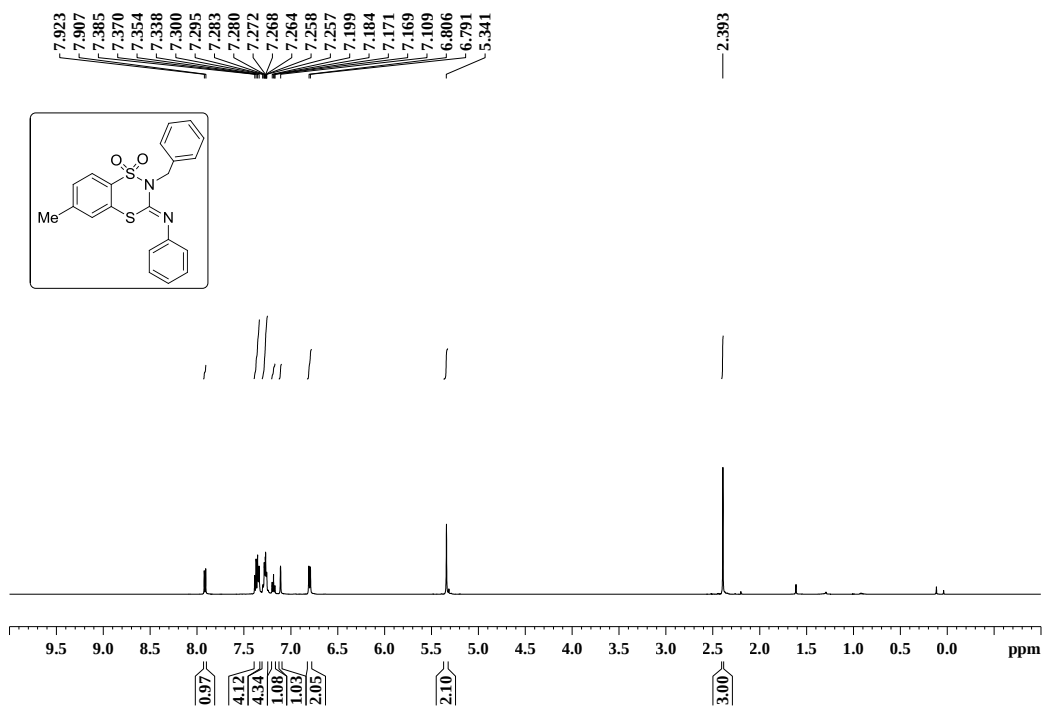


Figure S49. ¹H NMR spectrum of compound **3ea**

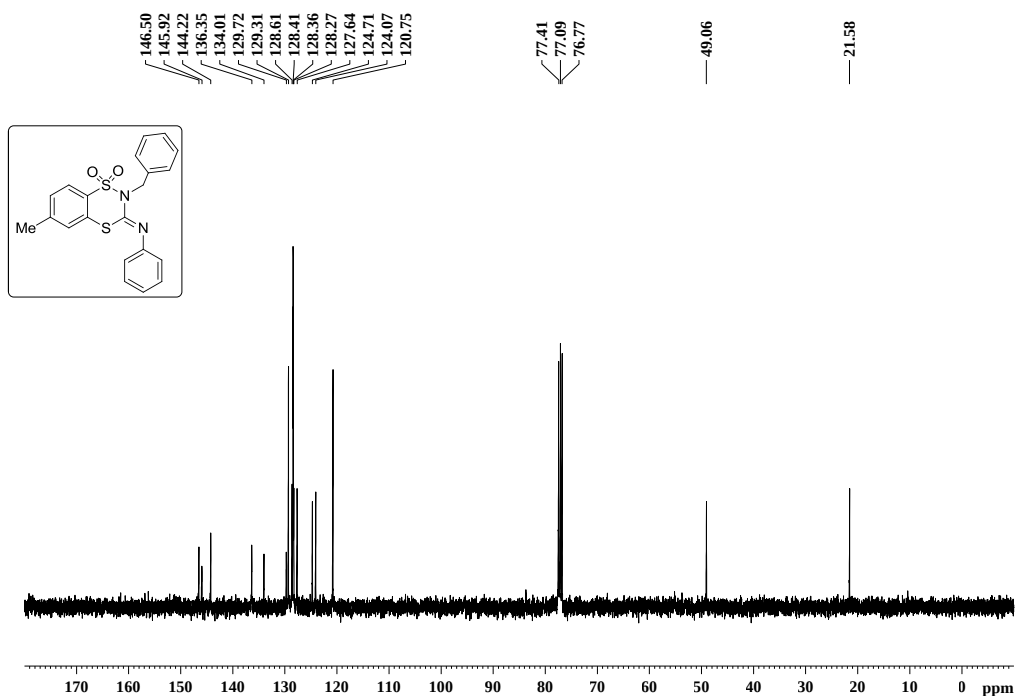


Figure S50. ¹³C NMR spectrum of compound **3ea**

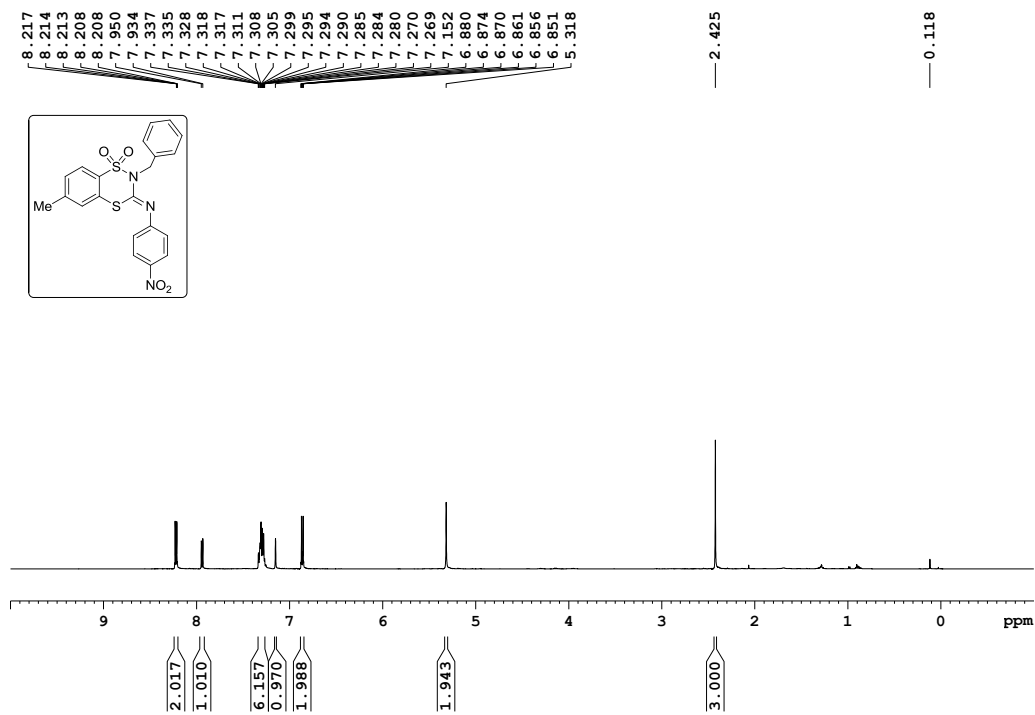


Figure S51. ¹H NMR spectrum of compound **3ef**

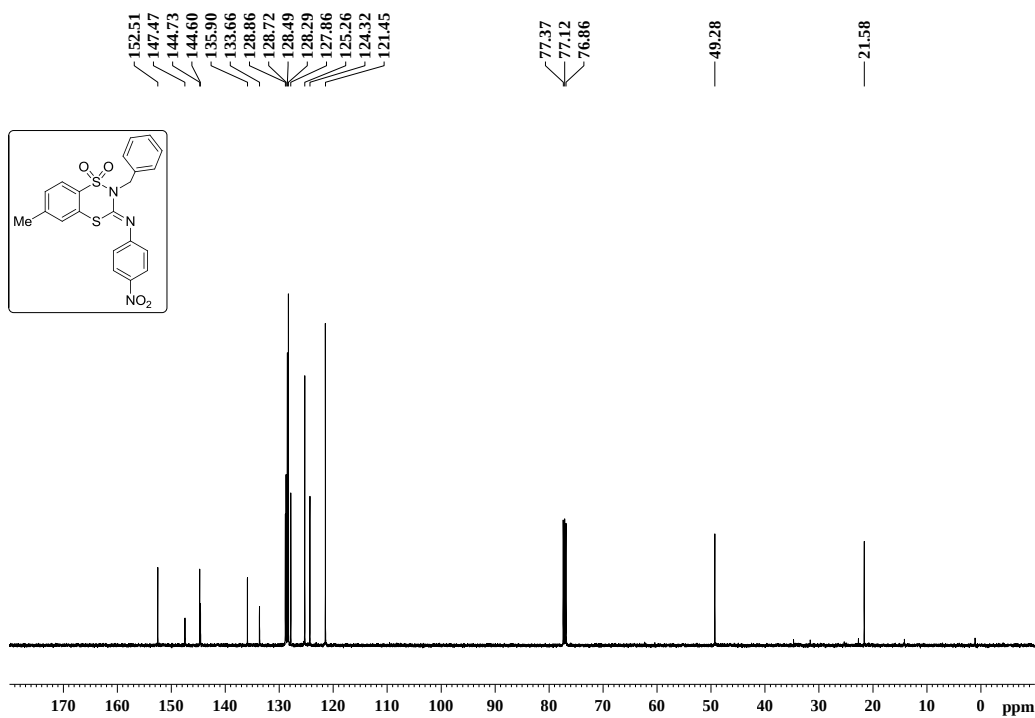


Figure S52. ¹³C NMR spectrum of compound **3ef**

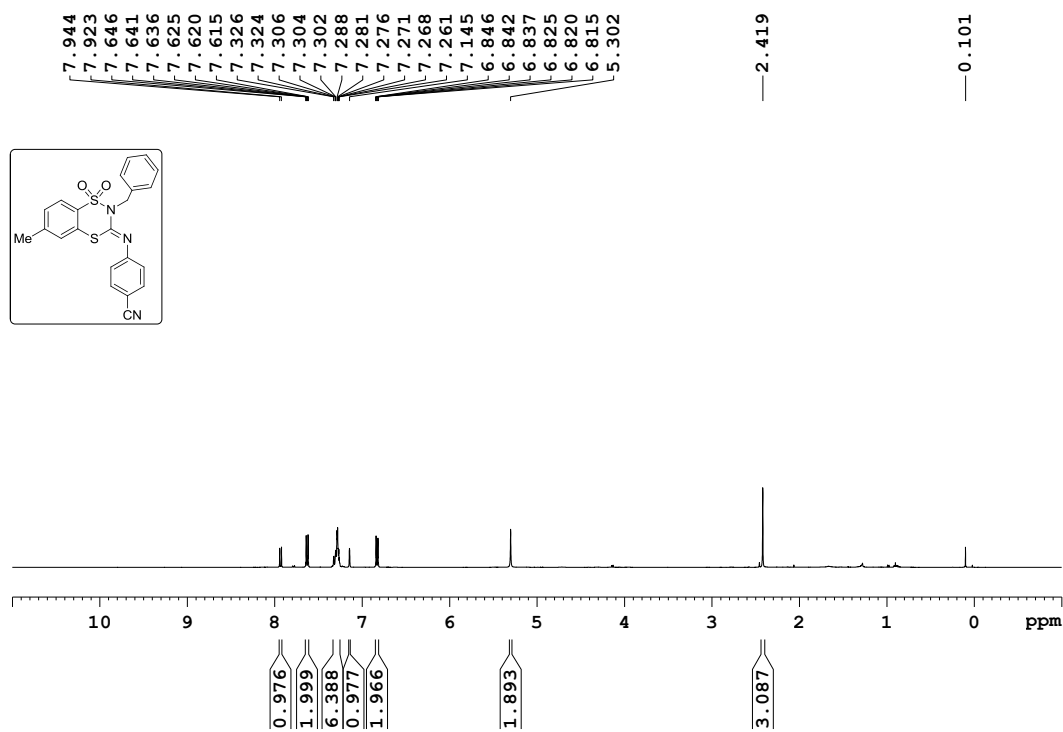


Figure S53. ¹H NMR spectrum of compound **3eg**

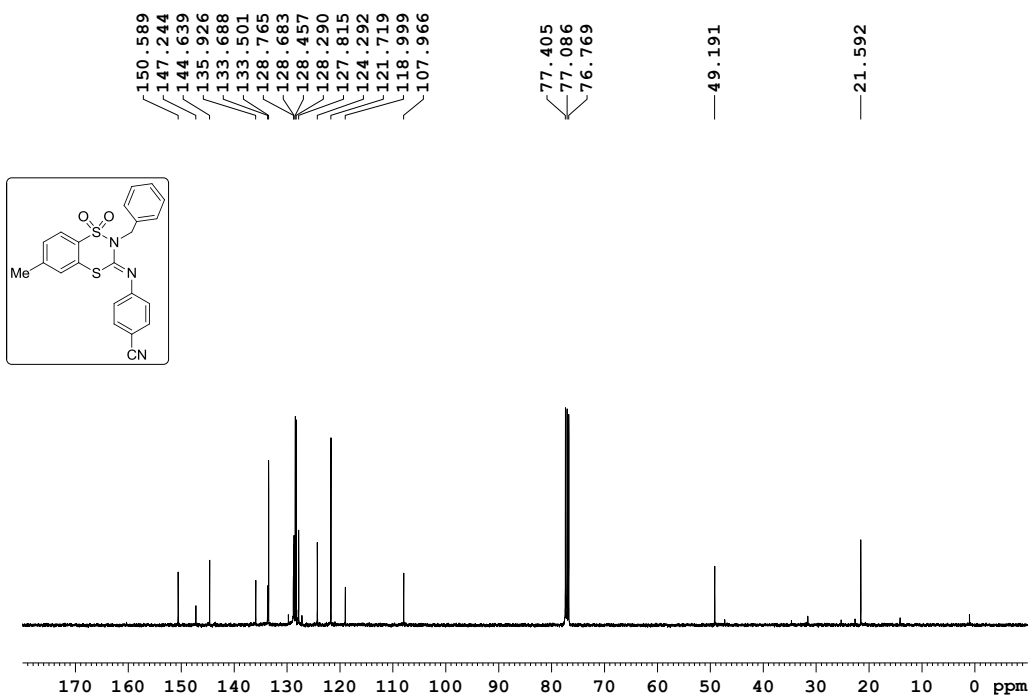


Figure S54. ¹³C NMR spectrum of compound **3eg**

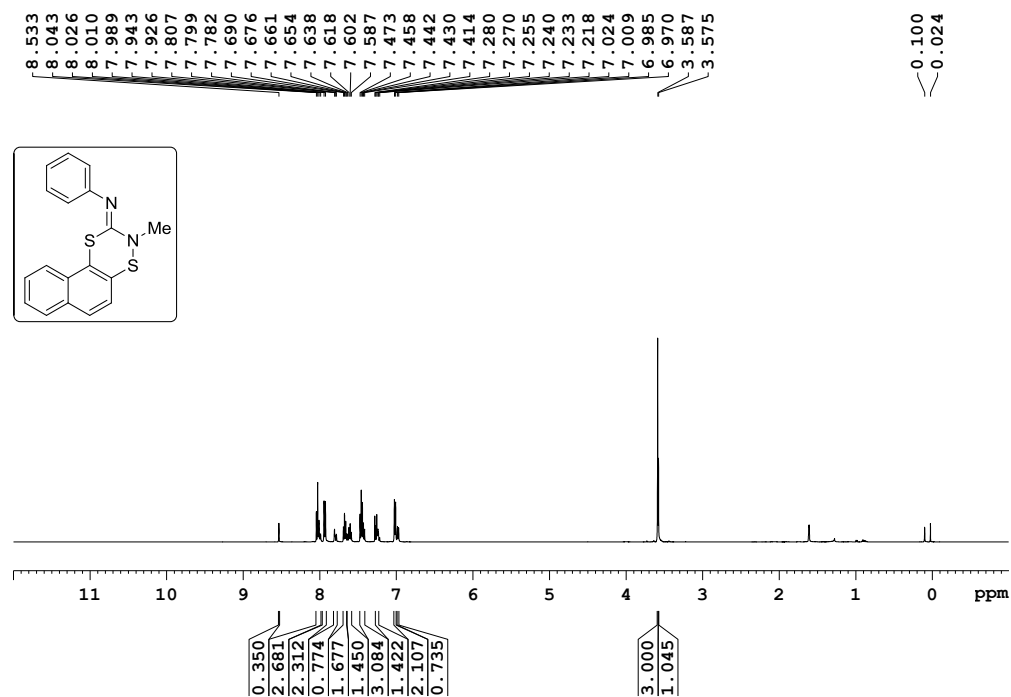


Figure S55. ¹H NMR spectrum of compound **3fa**

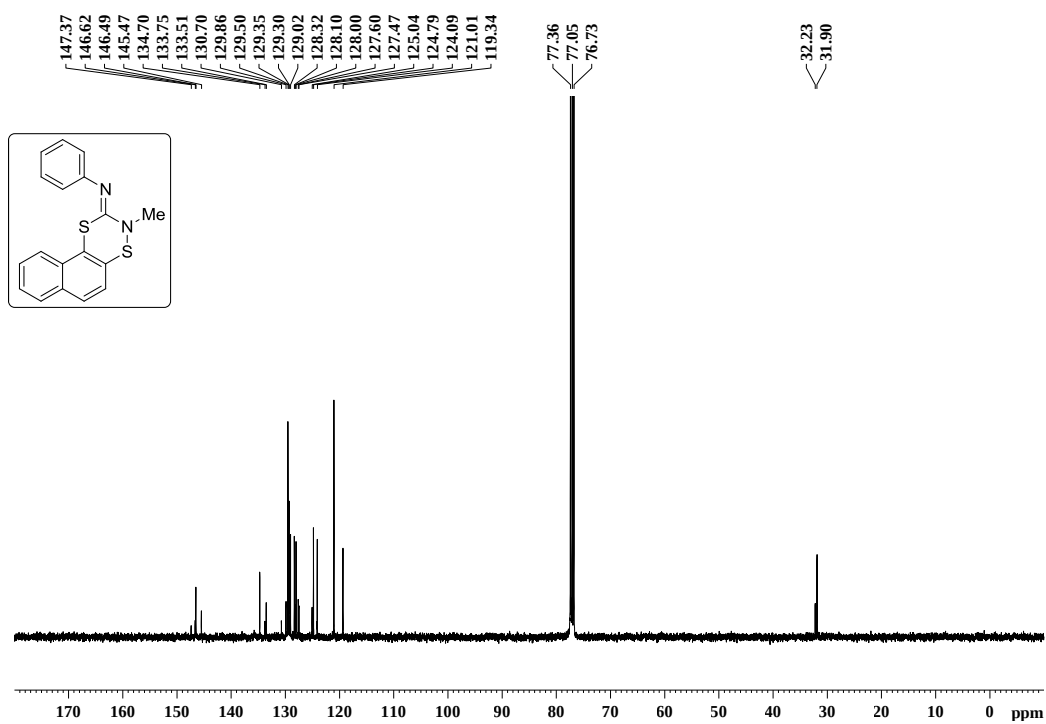


Figure S56. ¹³C NMR spectrum of compound **3fa**

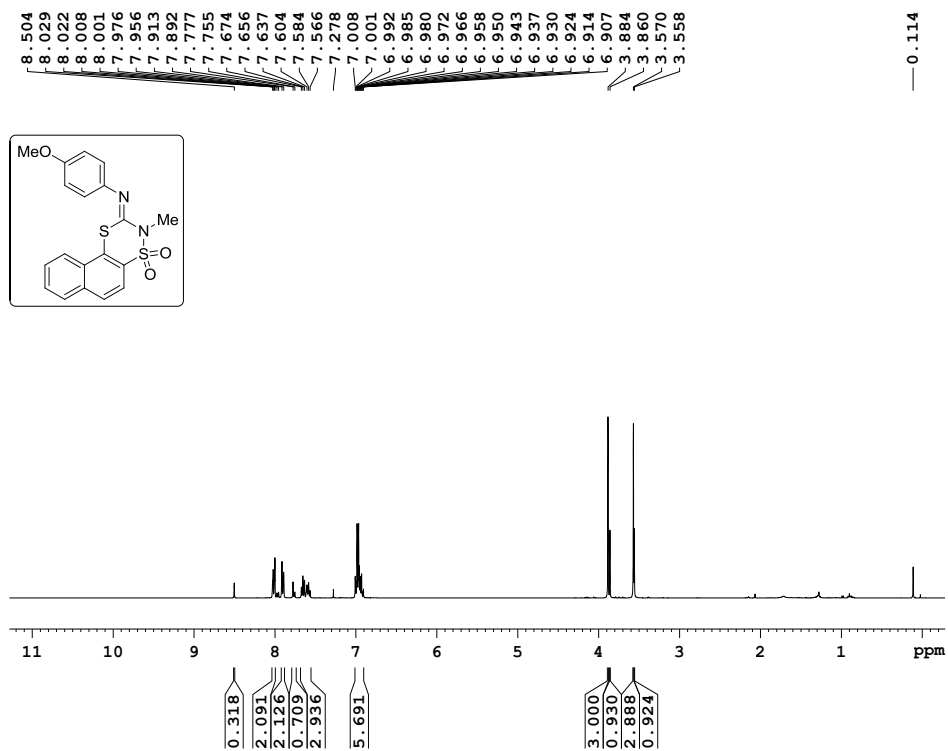


Figure S57. ¹H NMR spectrum of compound **3fb**

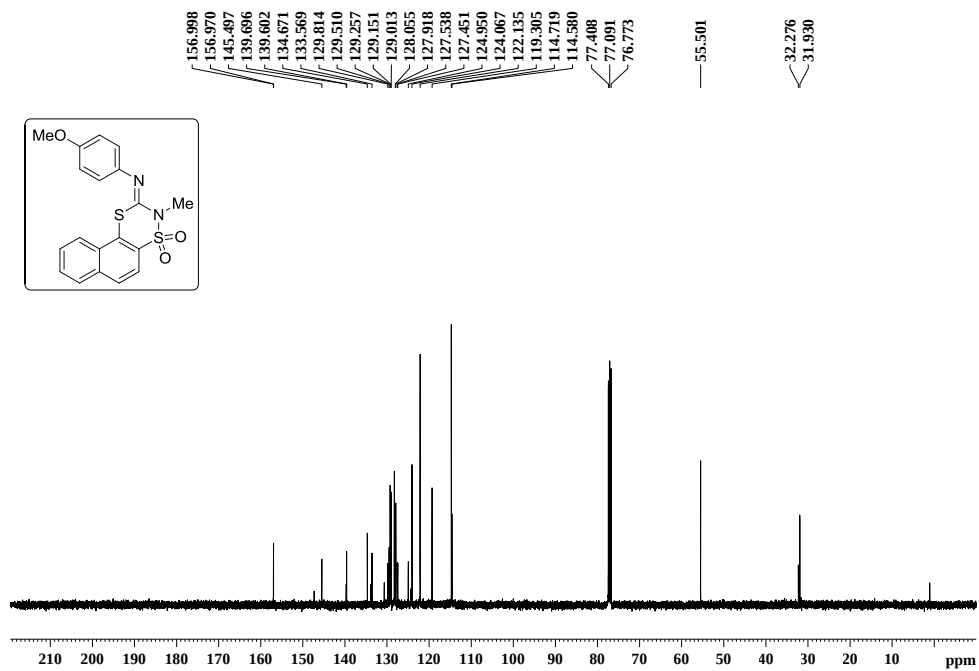


Figure S58. ¹³C NMR spectrum of compound **3fb**

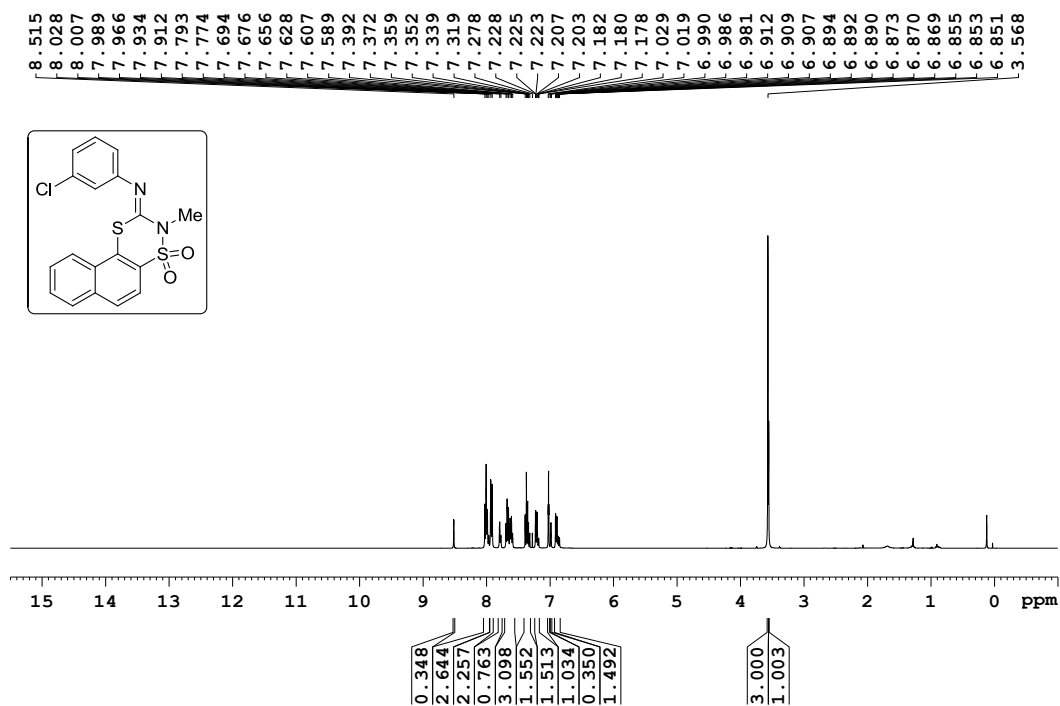


Figure S59. ¹H NMR spectrum of compound 3fd

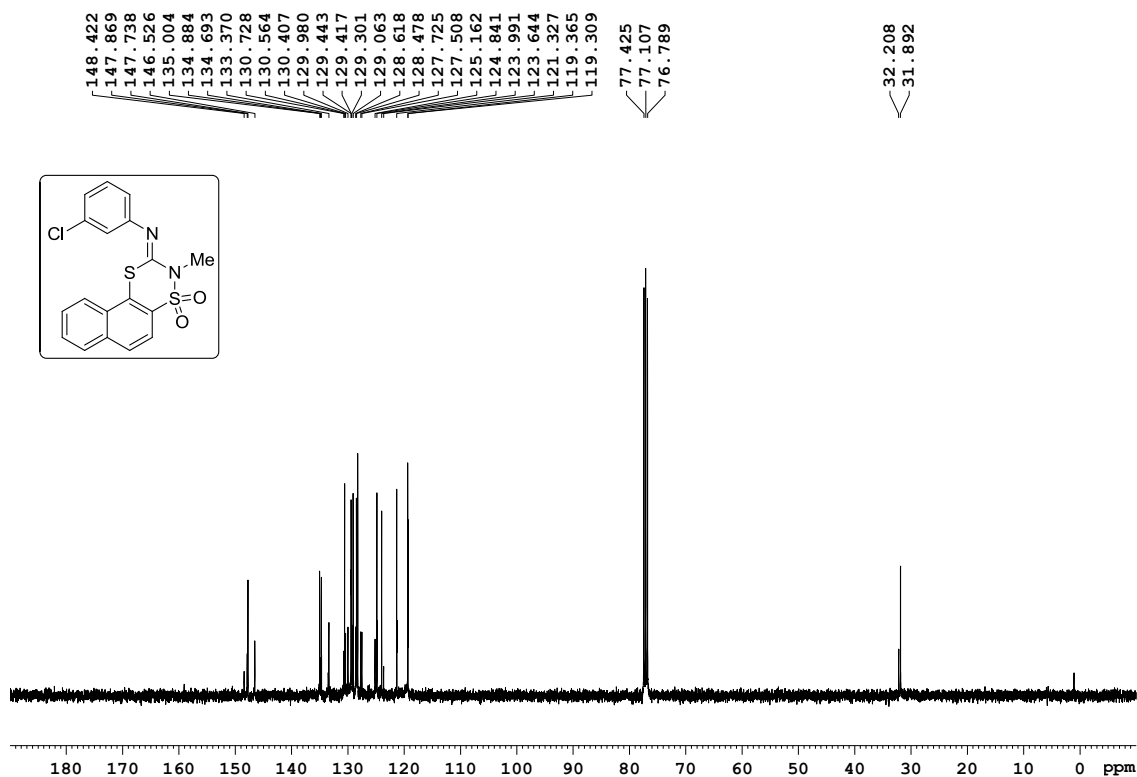


Figure S60. ¹³C NMR spectrum of compound 3fd

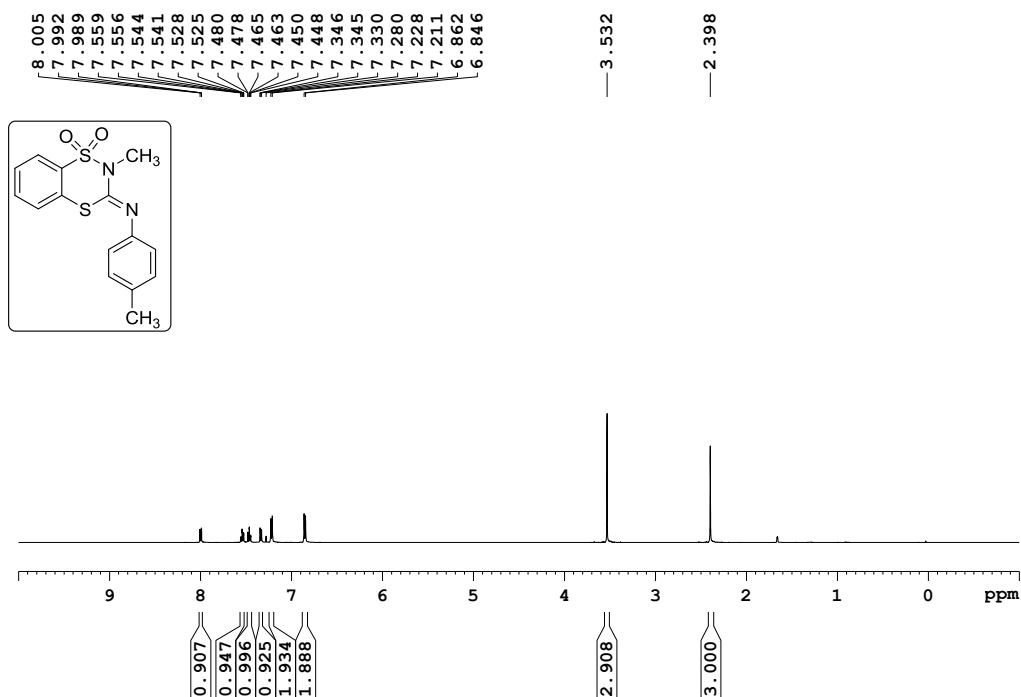


Figure S61. ¹H NMR spectrum of compound **3gi** (using **1g**)

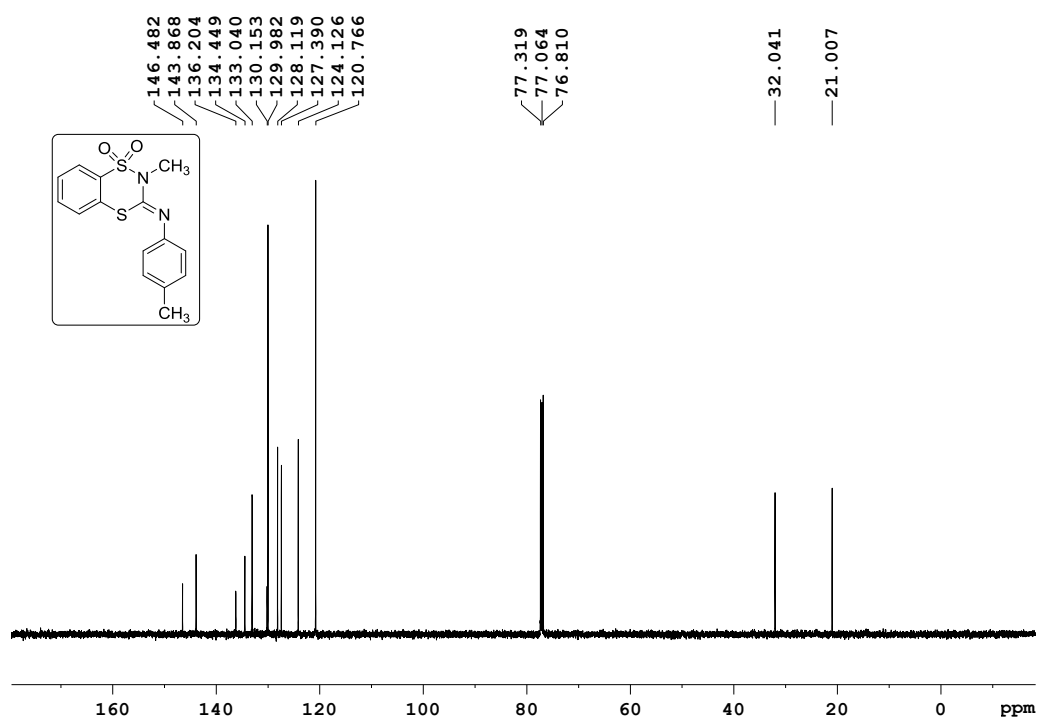


Figure S62. ¹³C NMR spectrum of compound **3gi** (using **1g**)

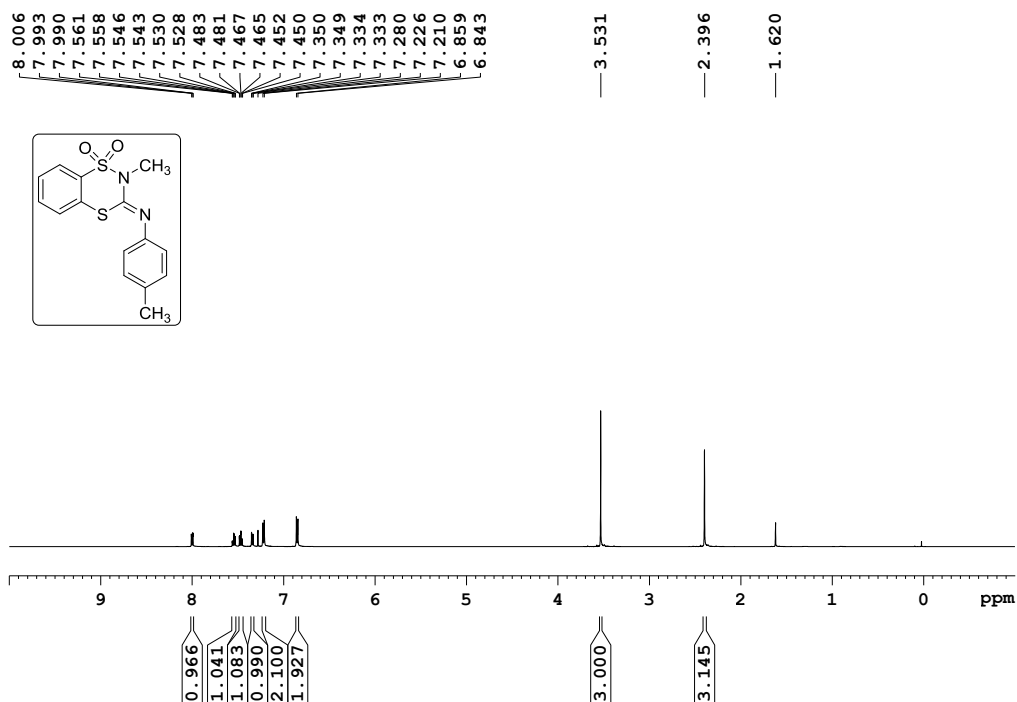


Figure S63. ¹H NMR spectrum of compound **3gi**(using **1i**)

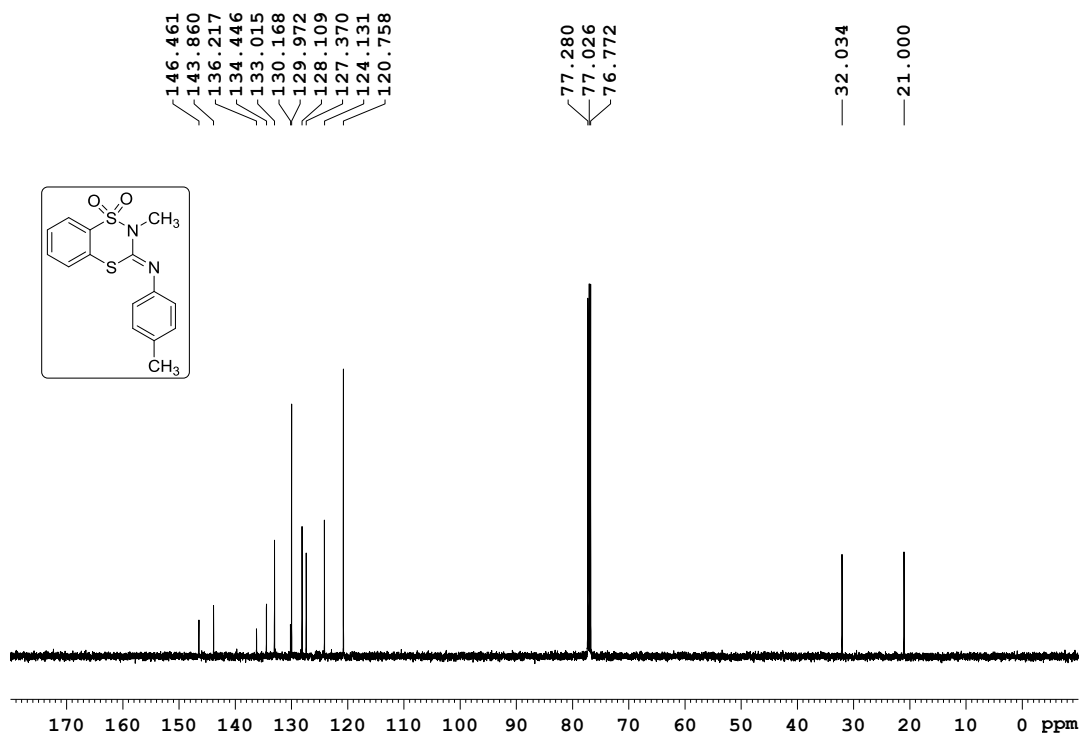


Figure S64. ¹³C NMR spectrum of compound **3gi** (using **1i**)

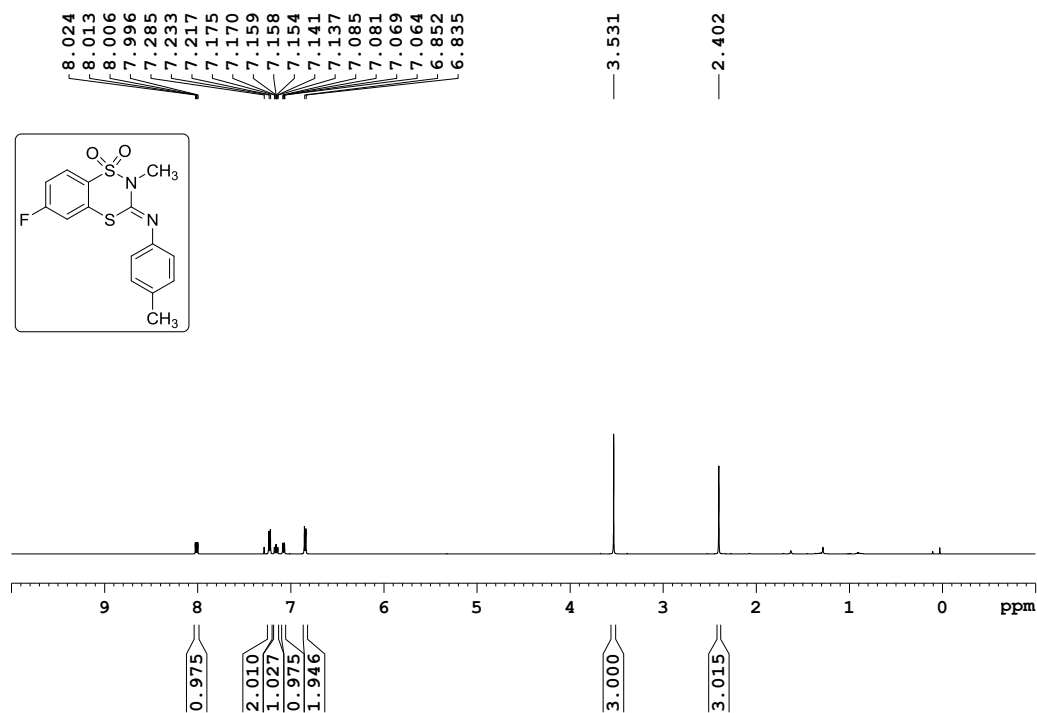


Figure S65. ¹H NMR spectrum of compound **3hi**

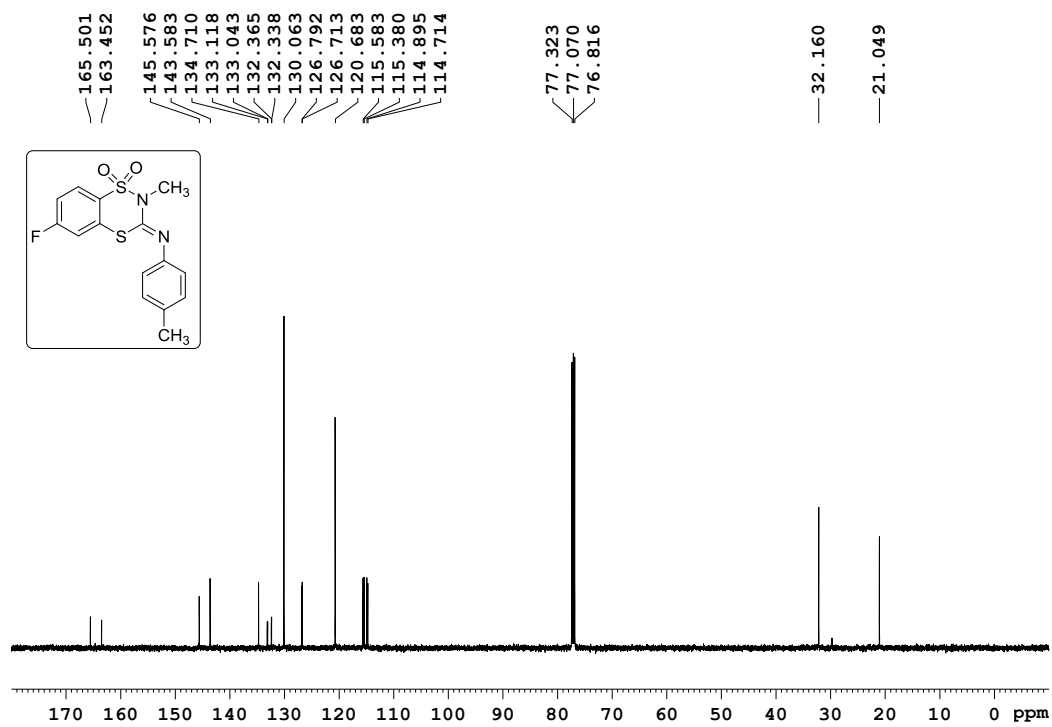


Figure S66. ¹³C NMR spectrum of compound **3hi**

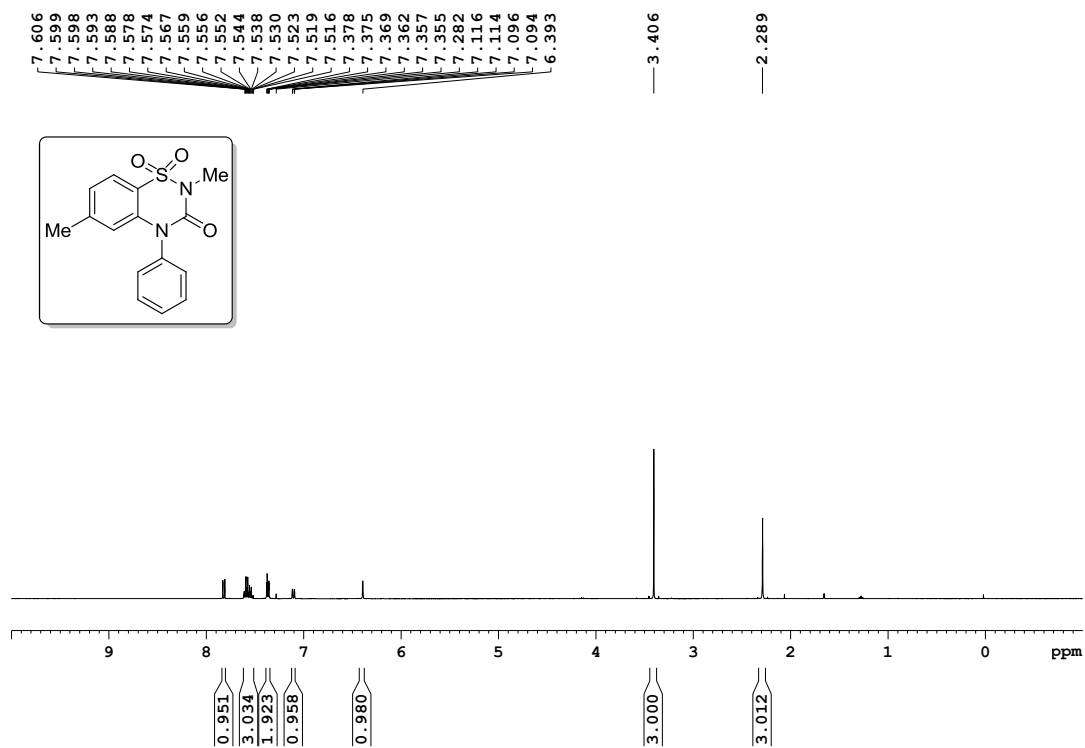


Figure S67. ¹H NMR spectrum of compound 5aa

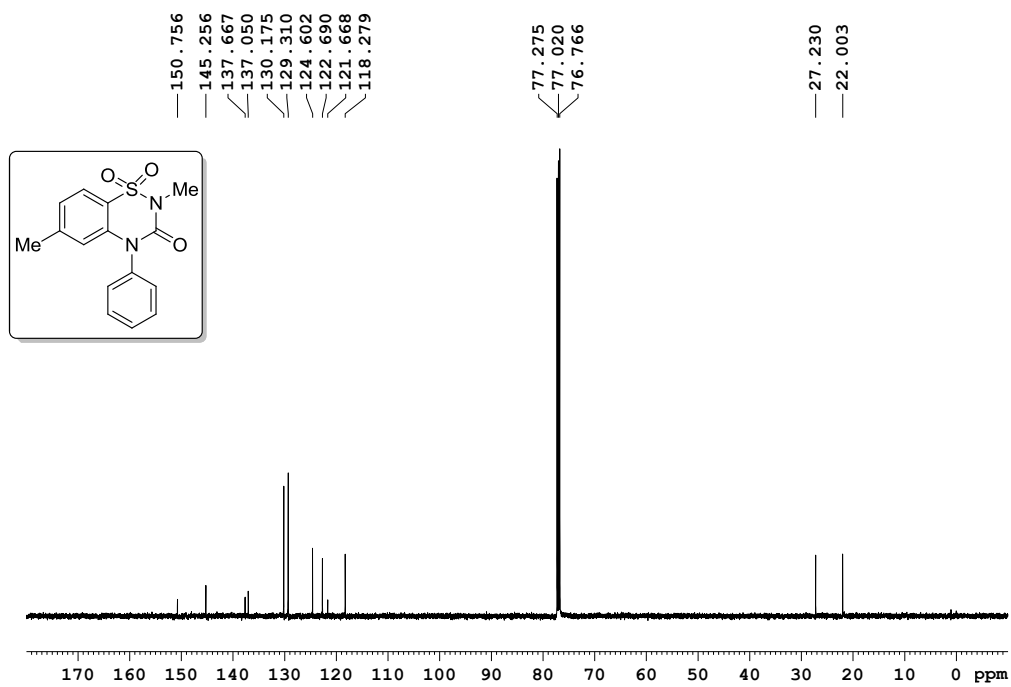


Figure S68. ¹³C NMR spectrum of compound 5aa

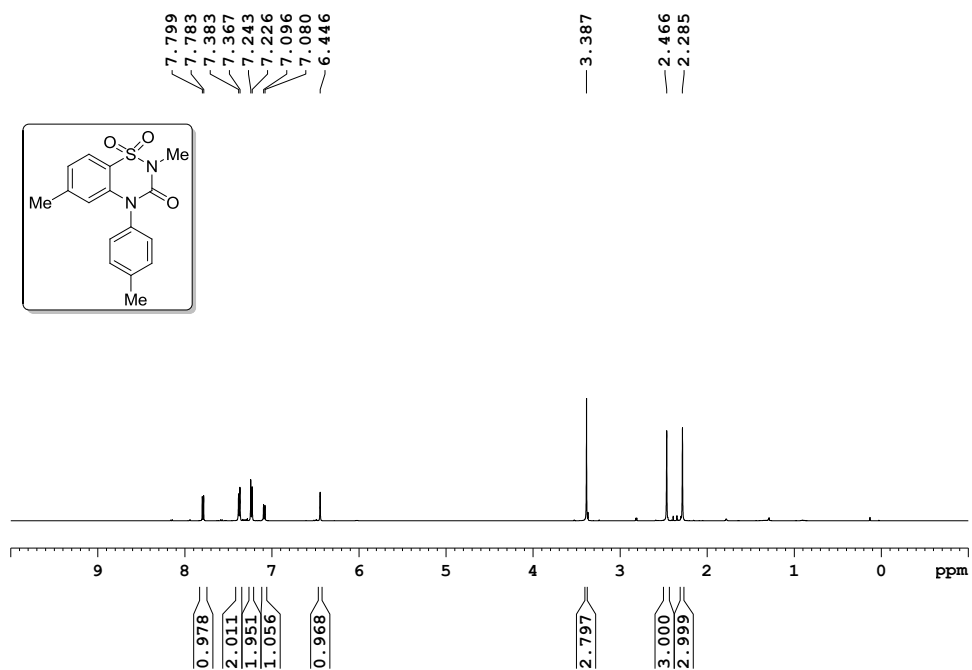


Figure S69. ¹H NMR spectrum of compound 5ab

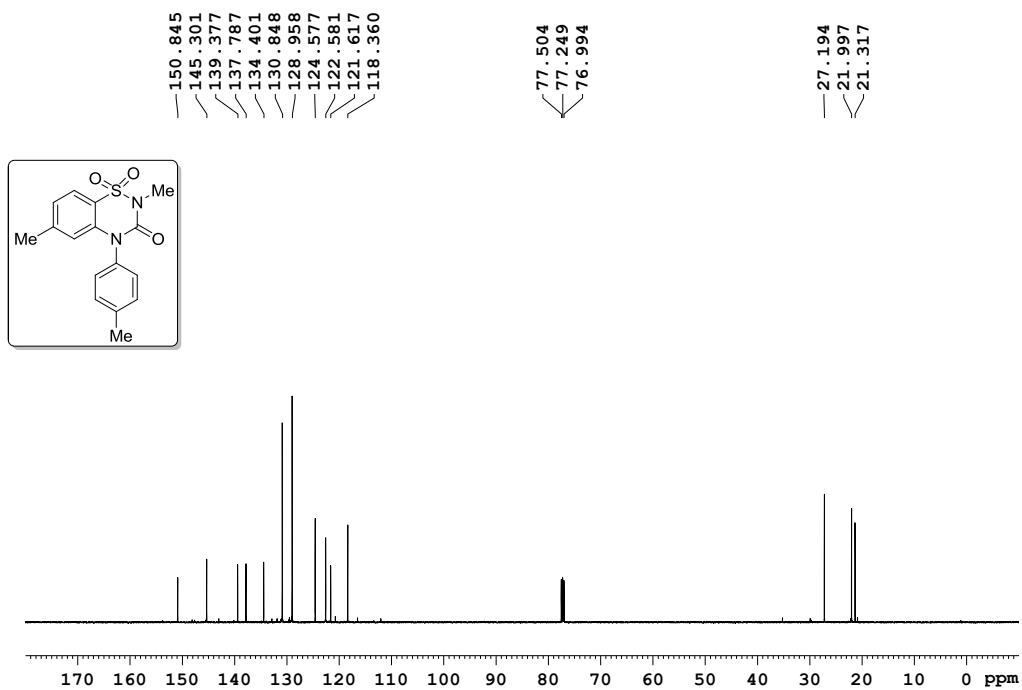


Figure S70. ¹³C NMR spectrum of compound 5ab

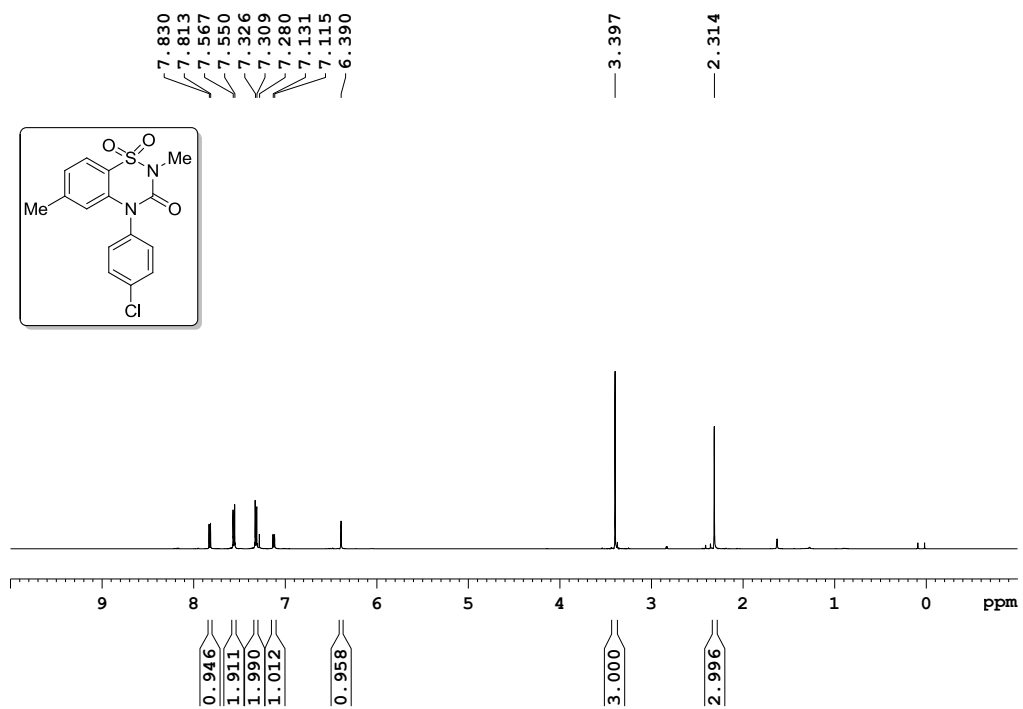


Figure S71. ¹H NMR spectrum of compound 5ac

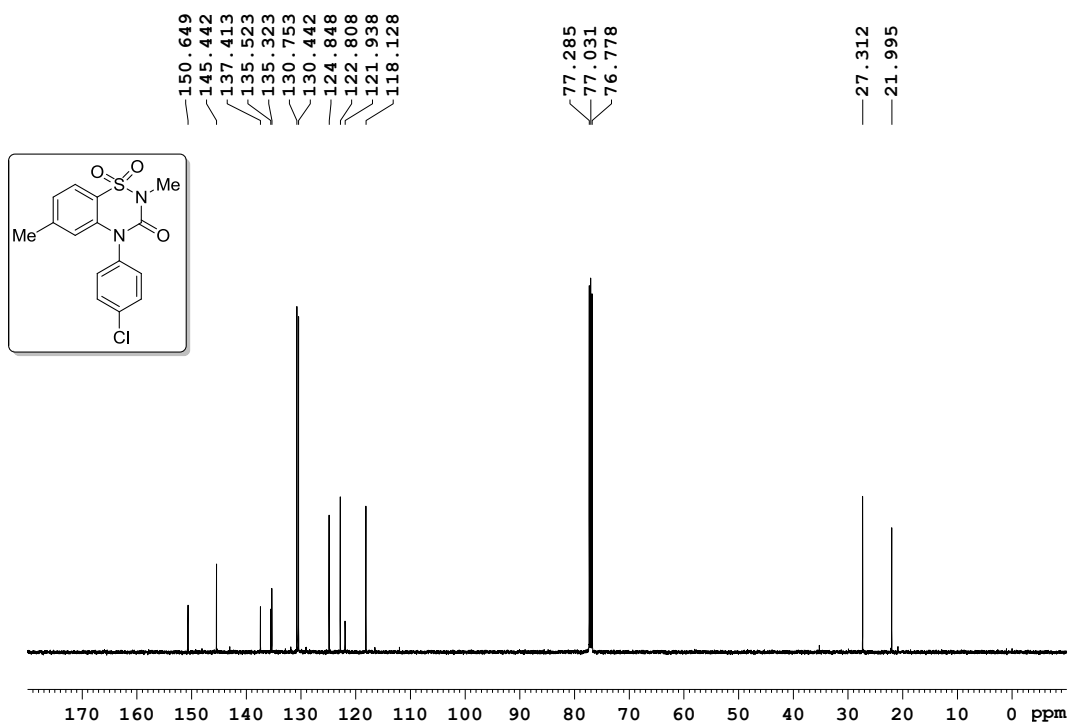


Figure S72. ¹³C NMR spectrum of compound 5ac

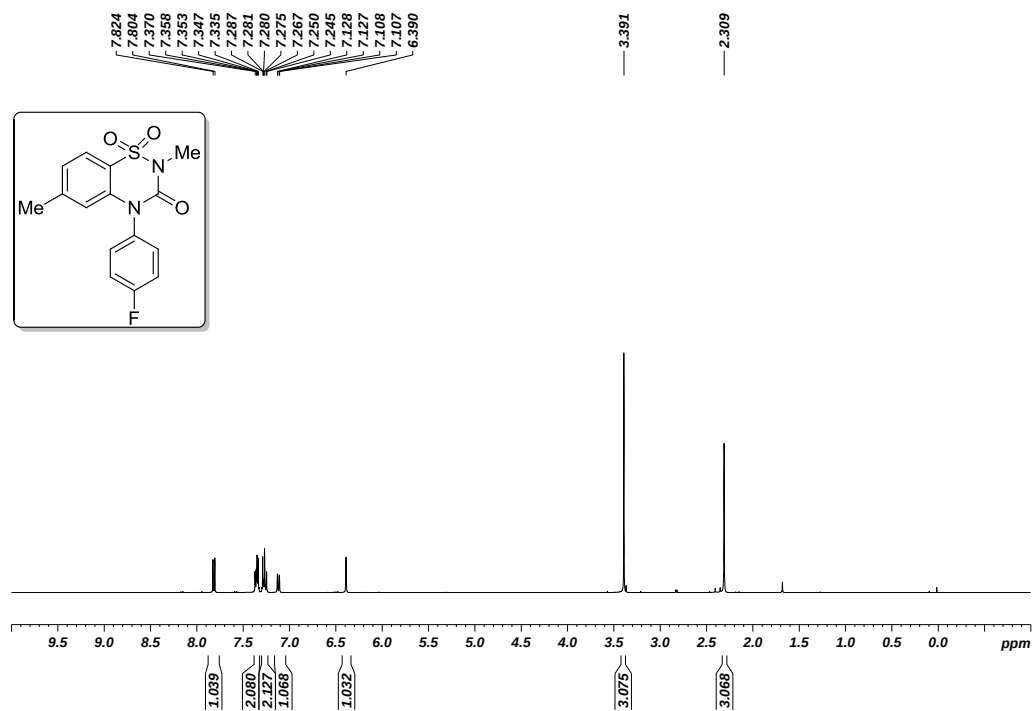


Figure S73. ¹H NMR spectrum of compound 5ad

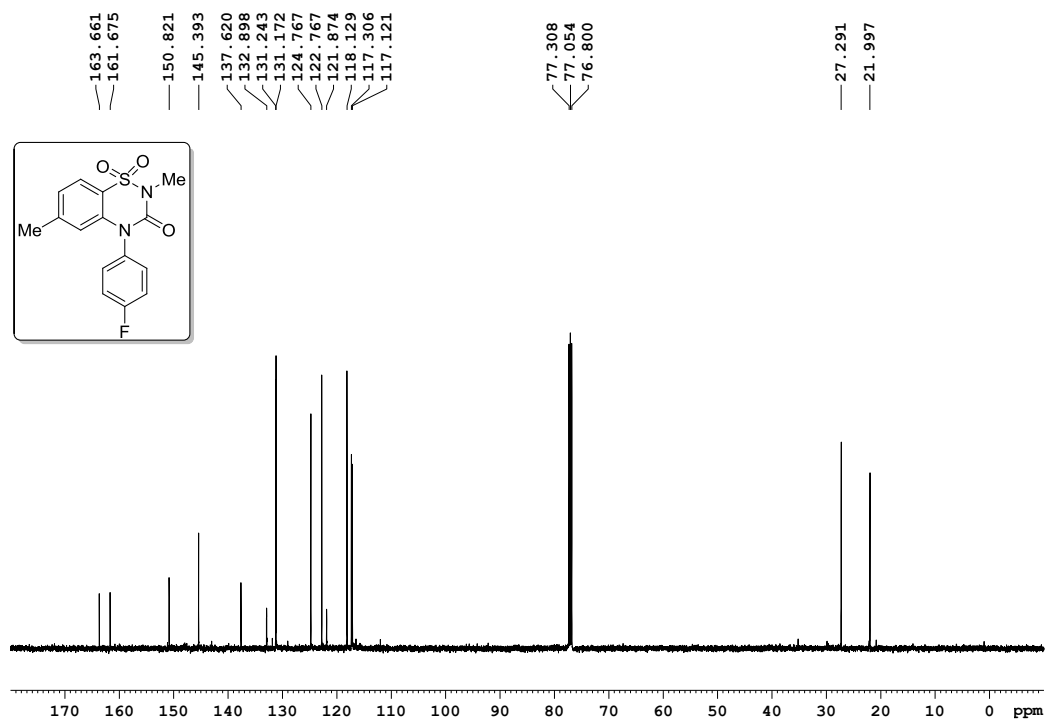


Figure S74. ¹³C NMR spectrum of compound 5ad

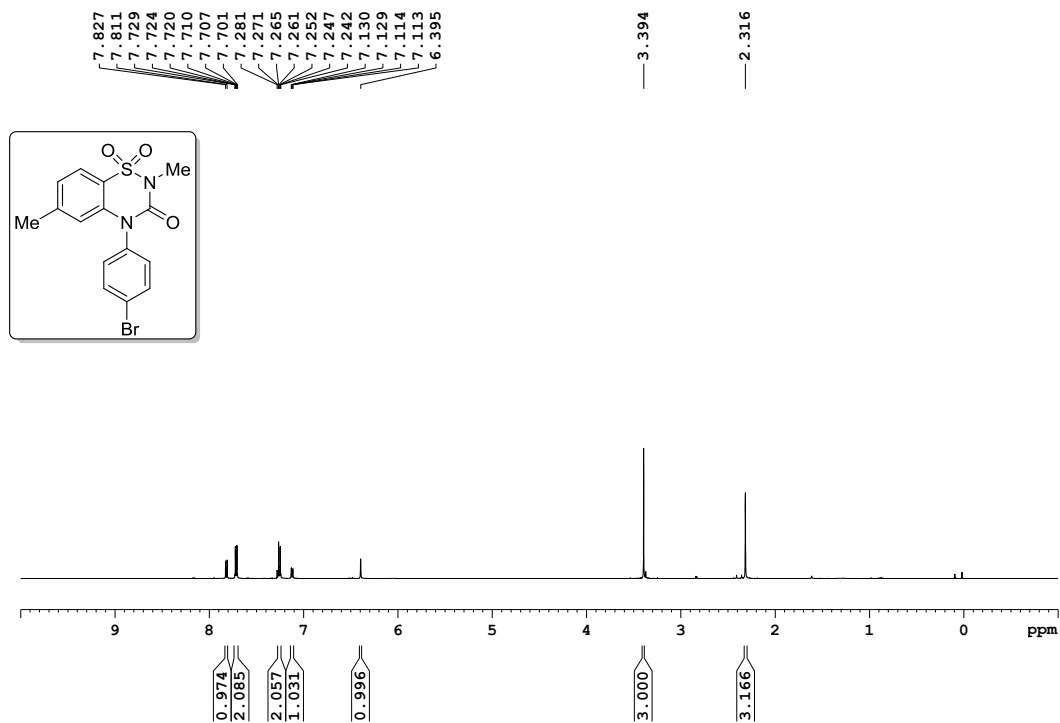


Figure S75. ¹H NMR spectrum of compound 5ae

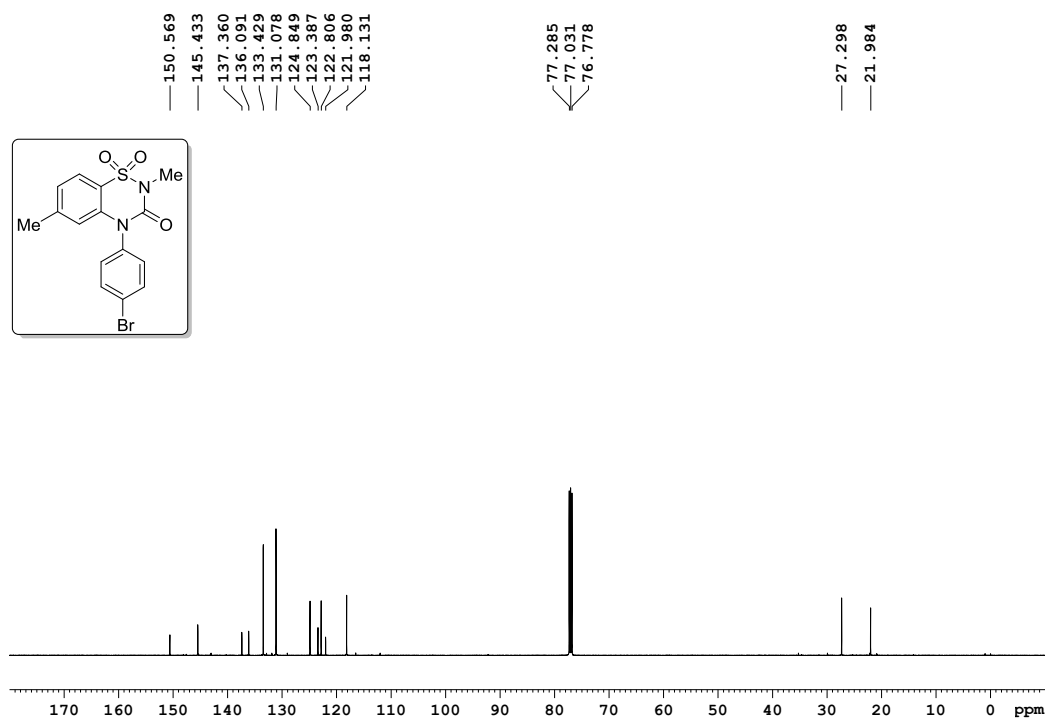


Figure S76. ¹³C NMR spectrum of compound 5ae

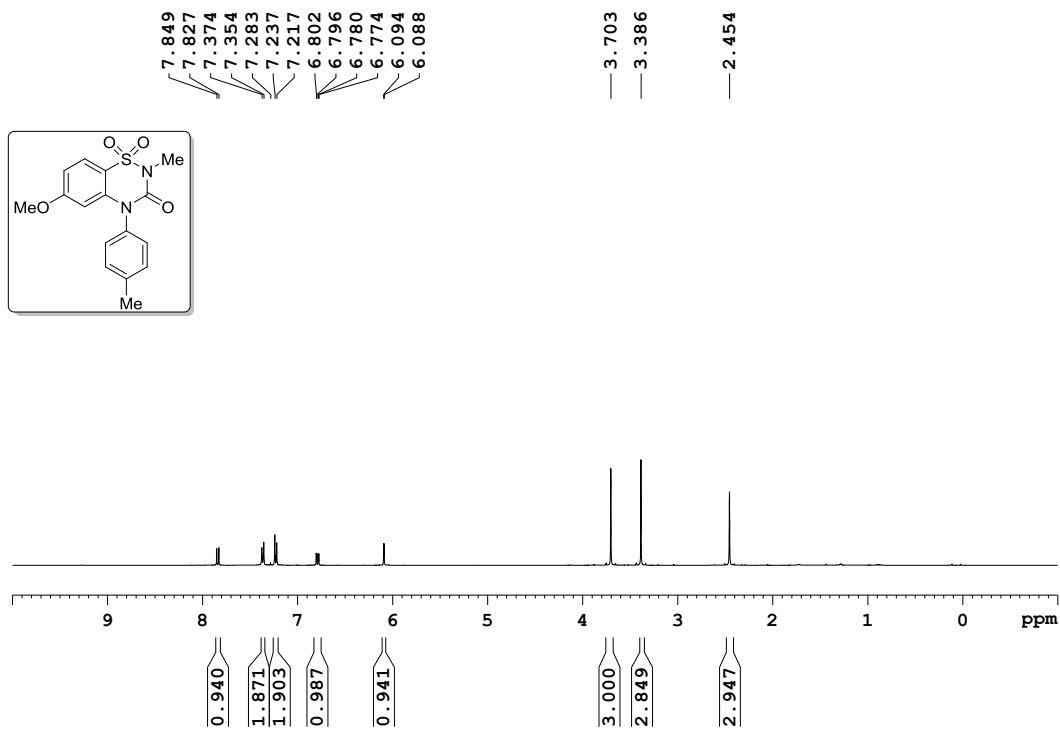


Figure S77. ¹H NMR spectrum of compound **5bb**

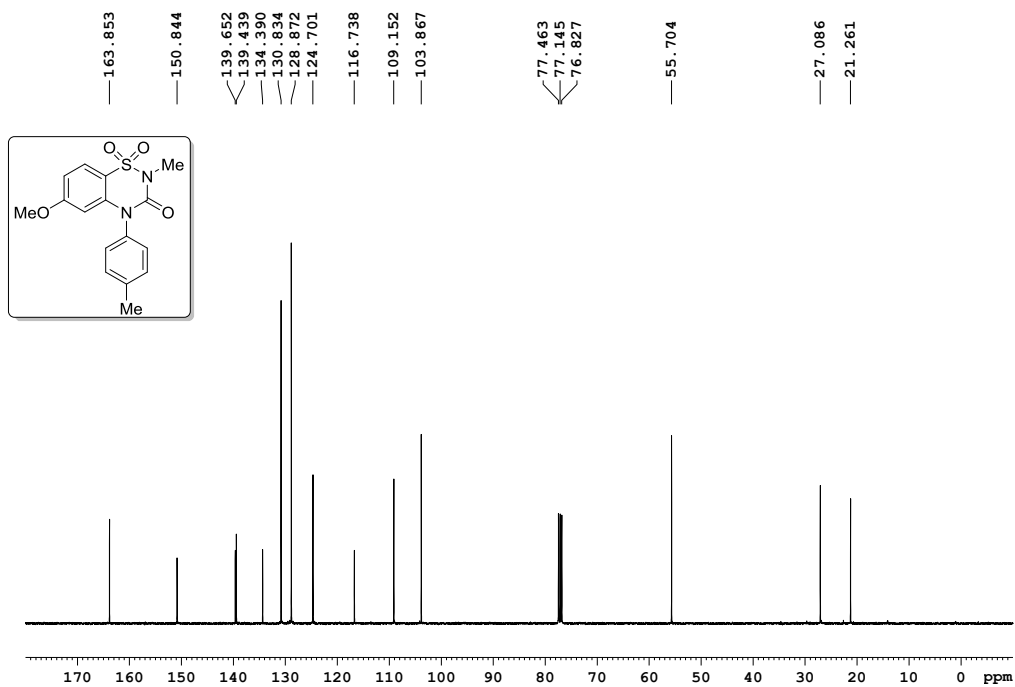
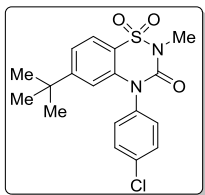


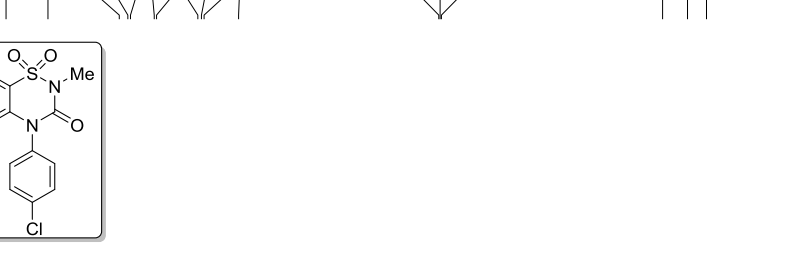
Figure S78. ¹³C NMR spectrum of compound **5bb**



Chemical structure of 2-(4-chlorophenyl)-2-methyl-5-(propan-2-ylsulfonyl)benzimidazole is shown. The structure features a benzimidazole core with a 4-chlorophenyl group at position 2 and an isopropylsulfonyl group at position 5.

¹³C NMR spectrum (CDCl₃) showing chemical shifts (ppm) for the structure:

- 158.52, 150.66 (Imidazole ring carbonyl carbons)
- 137.30, 135.68, 135.19, 130.77, 130.32, 122.58, 121.90, 121.40, 114.92 (Aromatic carbons)
- 77.41, 77.15, 76.90 (Solvent triplet, CDCl₃)
- 35.45, 30.78, 27.23 (Isopropyl group carbons)



Chemical Shift (ppm)
158.52
150.66
137.30
135.68
135.19
130.77
130.32
122.58
121.90
121.40
114.92
77.41
77.15
76.90
35.45
30.78
27.23

Figure S80. ^{13}C NMR spectrum of compound **5cc**

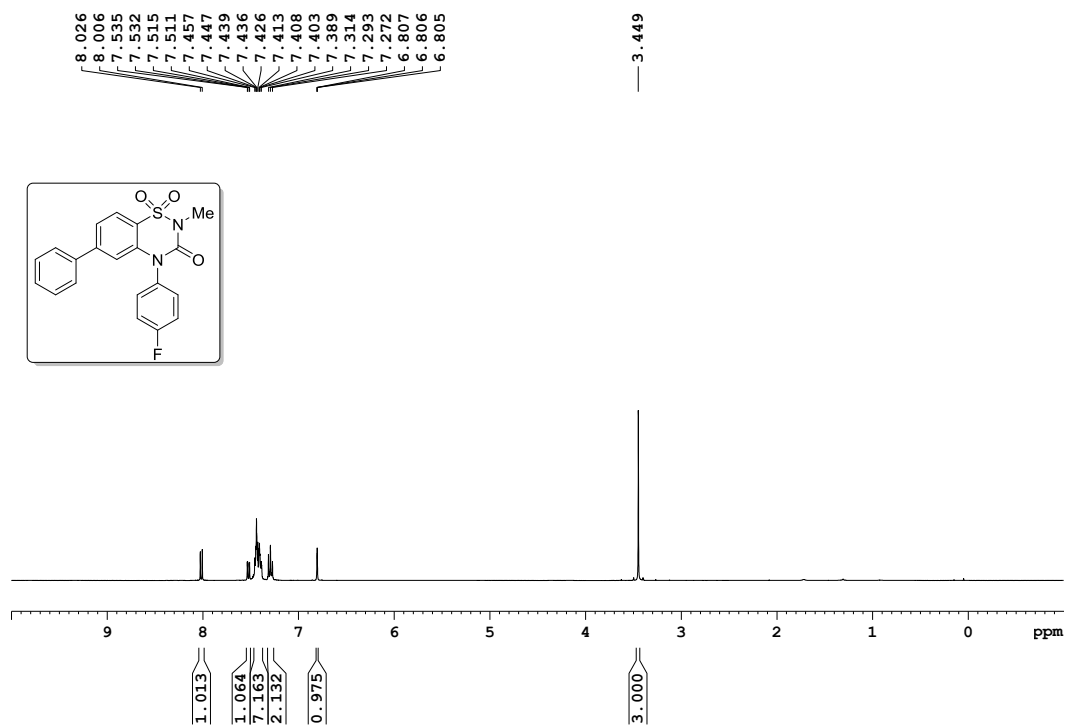


Figure S81. ¹H NMR spectrum of compound 5dd

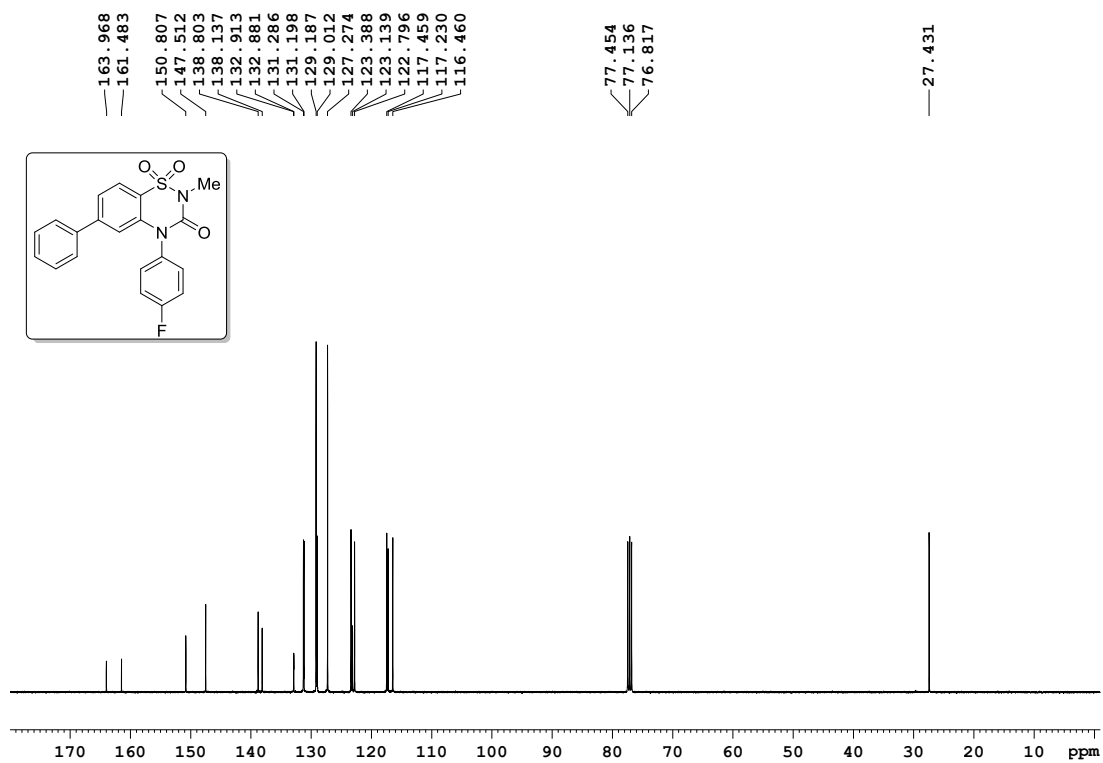


Figure S82. ¹³C NMR spectrum of compound 5dd

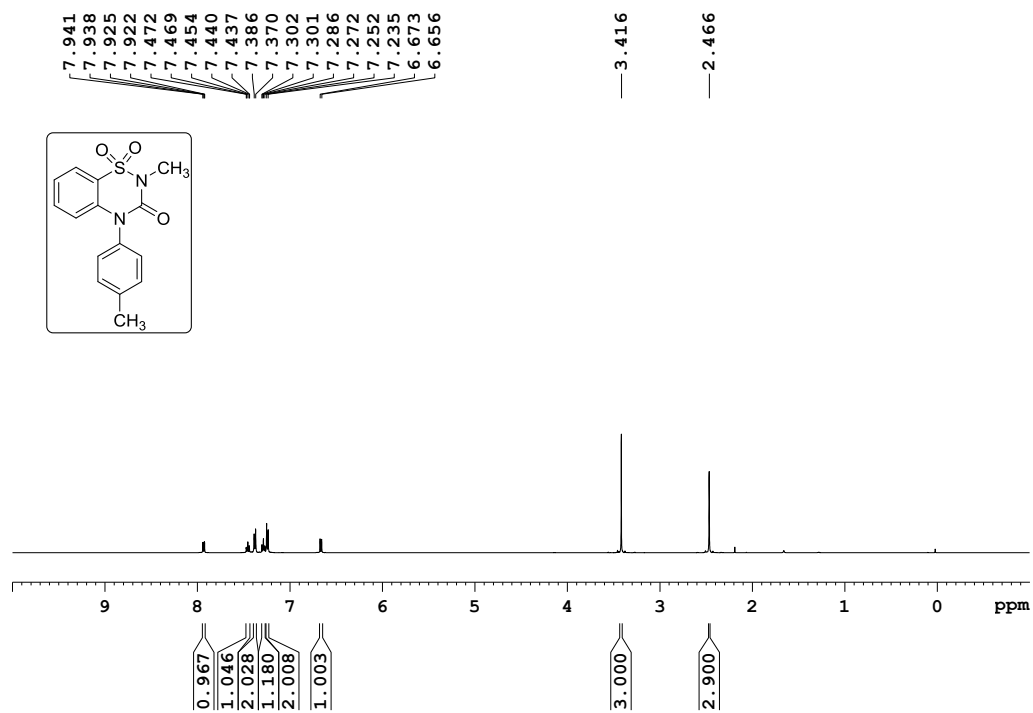


Figure S83. ¹H NMR spectrum of compound 5gb

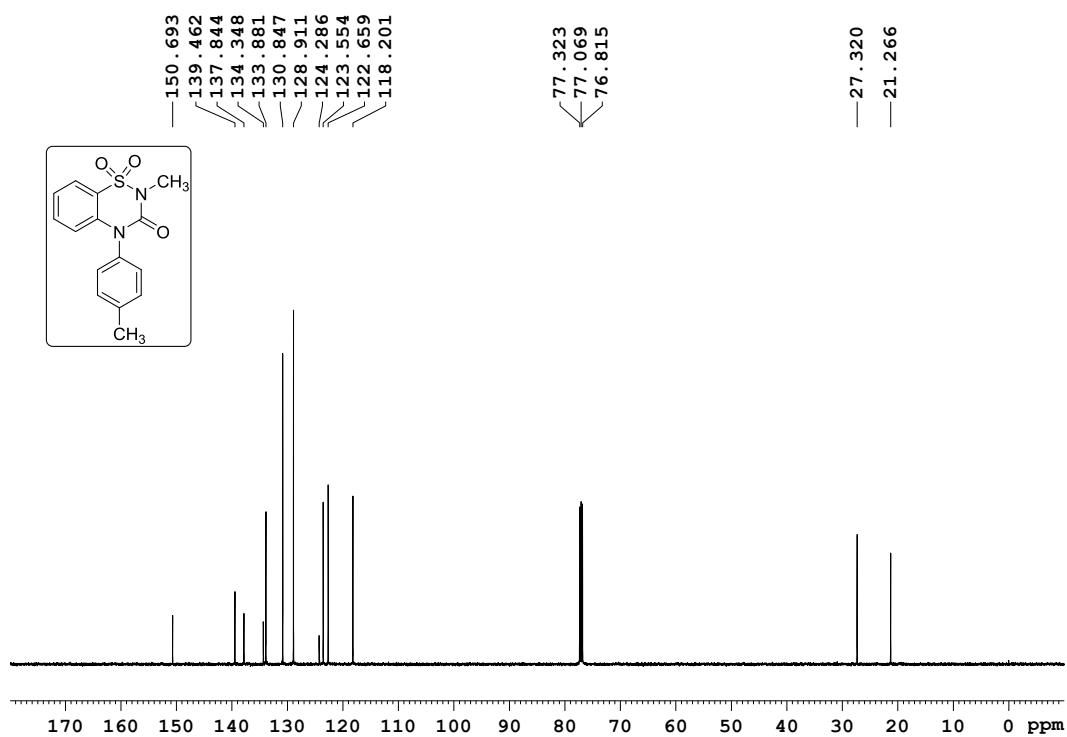


Figure S84. ¹³C NMR spectrum of compound 5gb

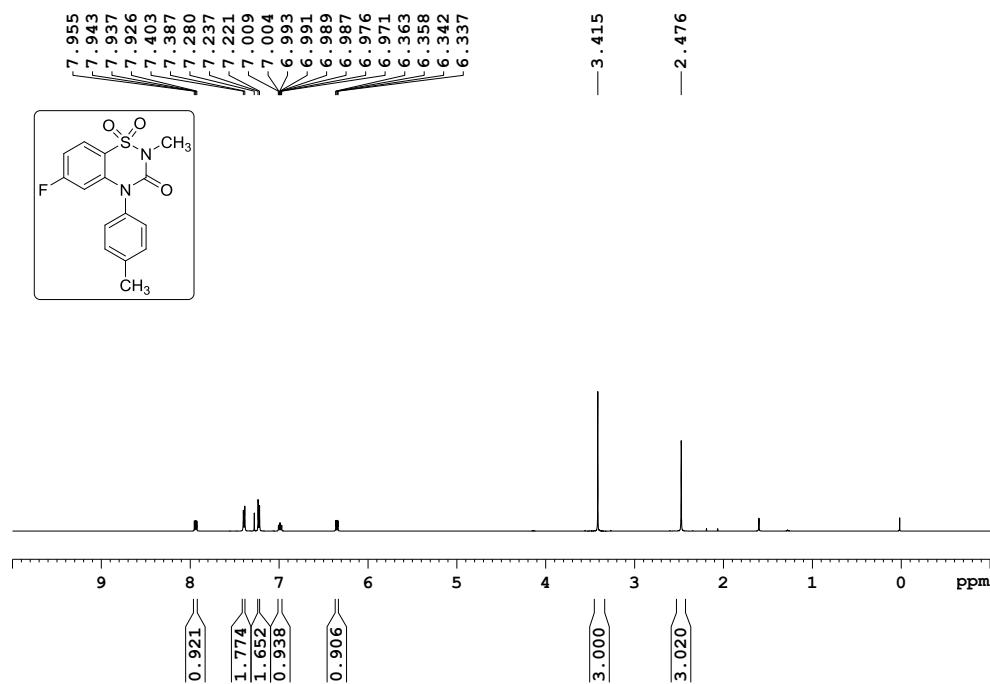


Figure S85. ¹H NMR spectrum of compound **5hb**

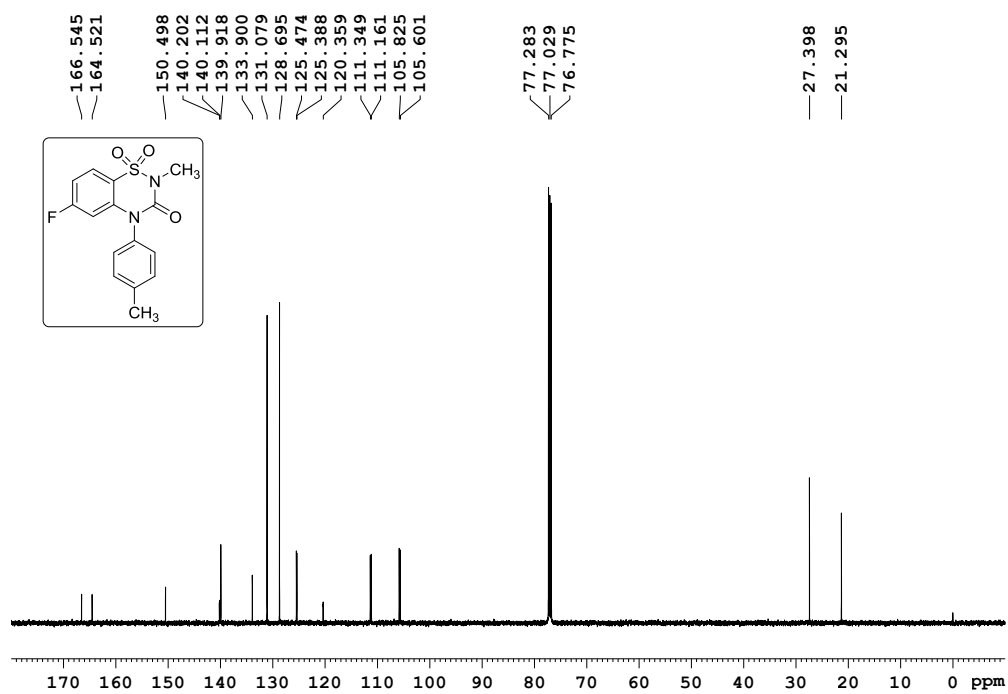


Figure S86. ¹³C NMR spectrum of compound **5hb**

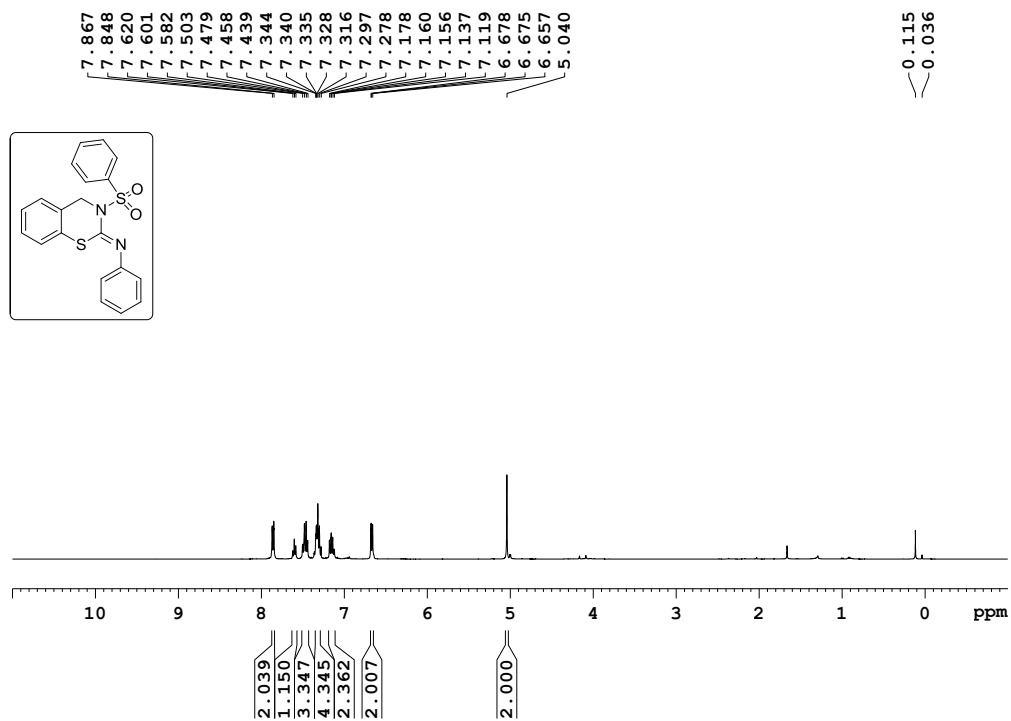


Figure S87. ¹H NMR spectrum of compound 7a

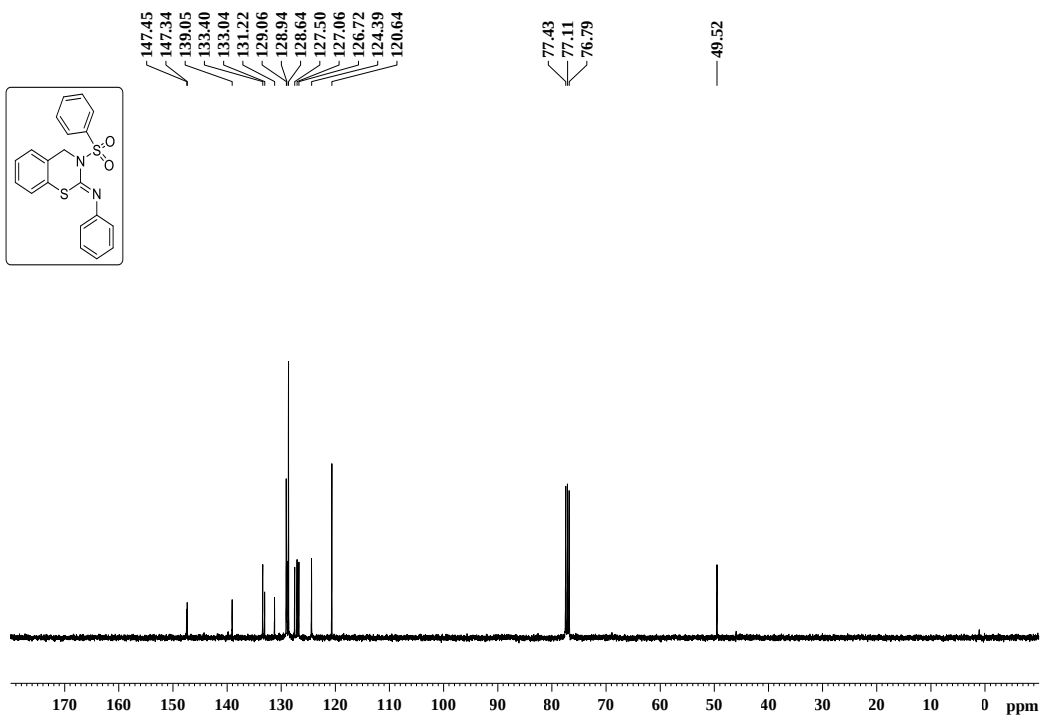


Figure S88. ¹³C NMR spectrum of compound 7a

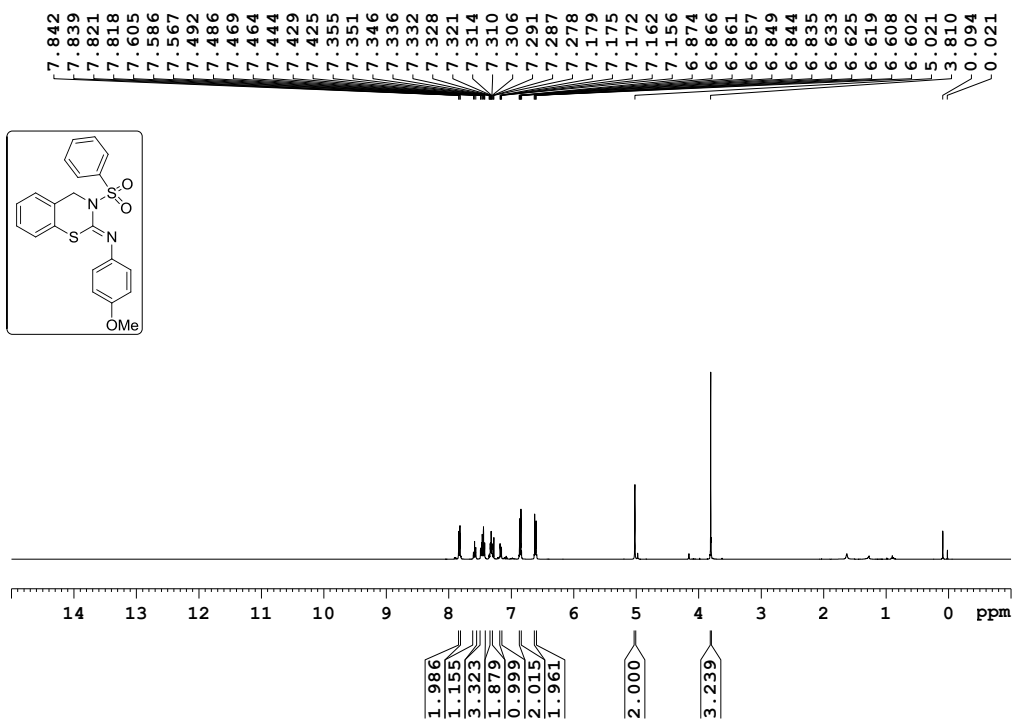


Figure S894. ¹H NMR spectrum of compound 7b

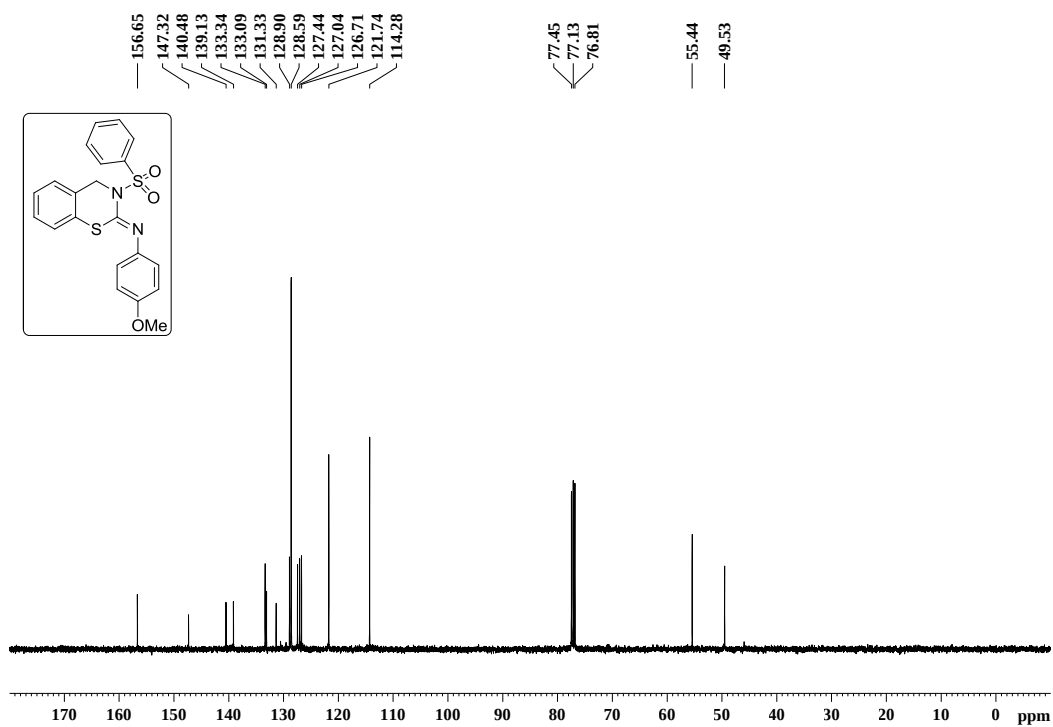


Figure S90. ¹³C NMR spectrum of compound 7b

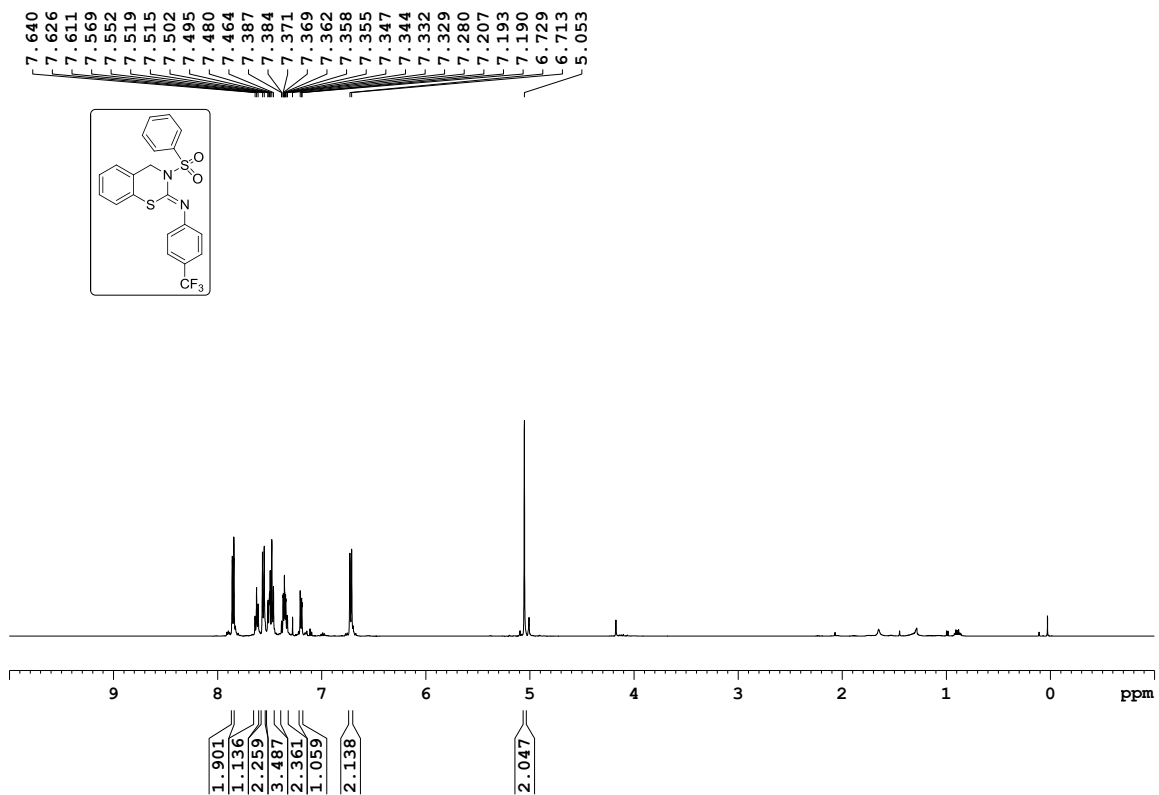


Figure S91. ¹H NMR spectrum of compound 7c

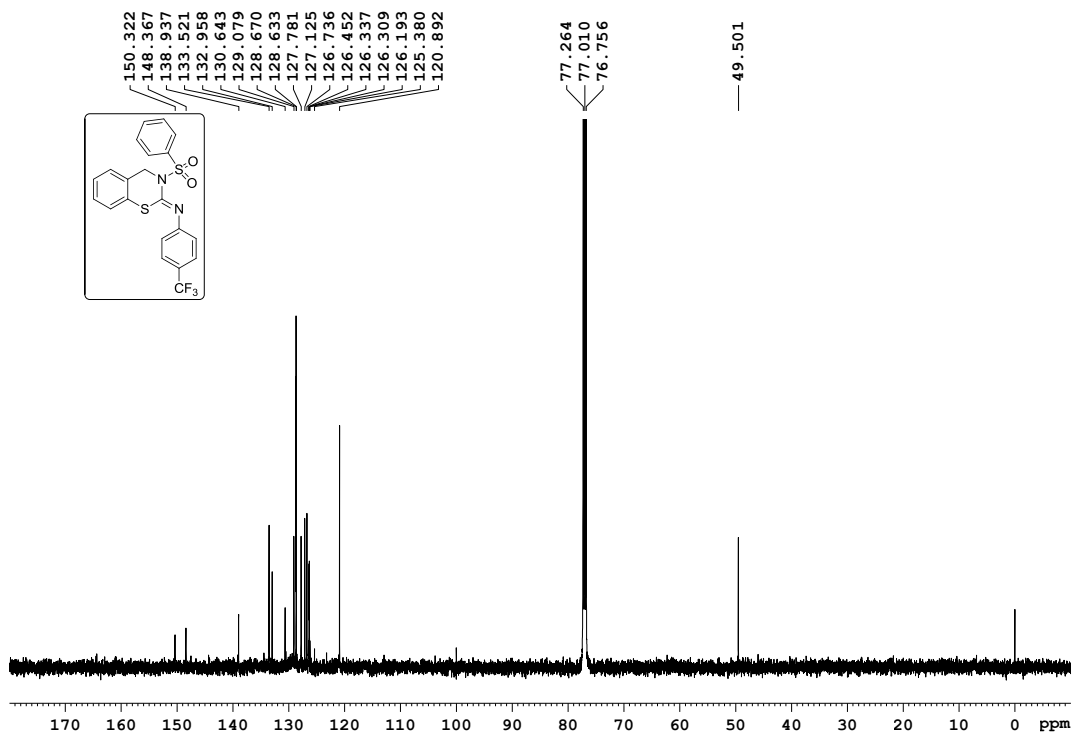


Figure S92. ¹³C NMR spectrum of compound 7c

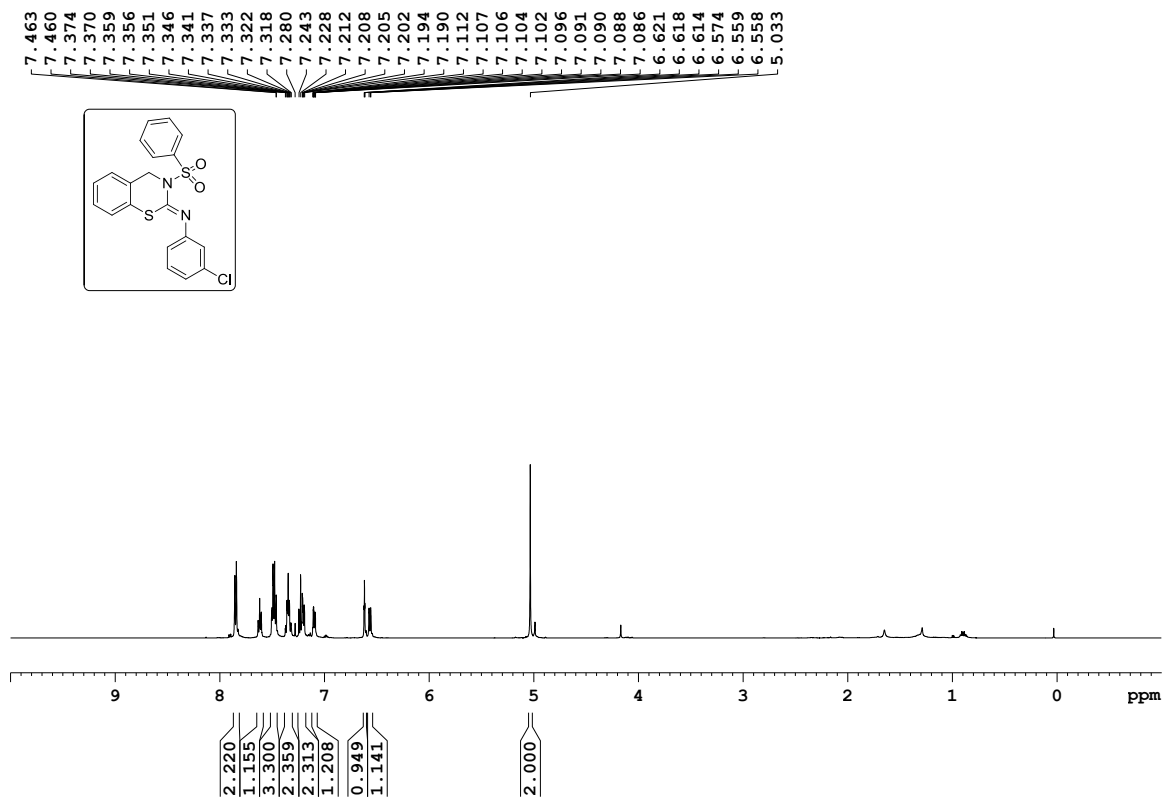


Figure S93. ¹H NMR spectrum of compound 7d

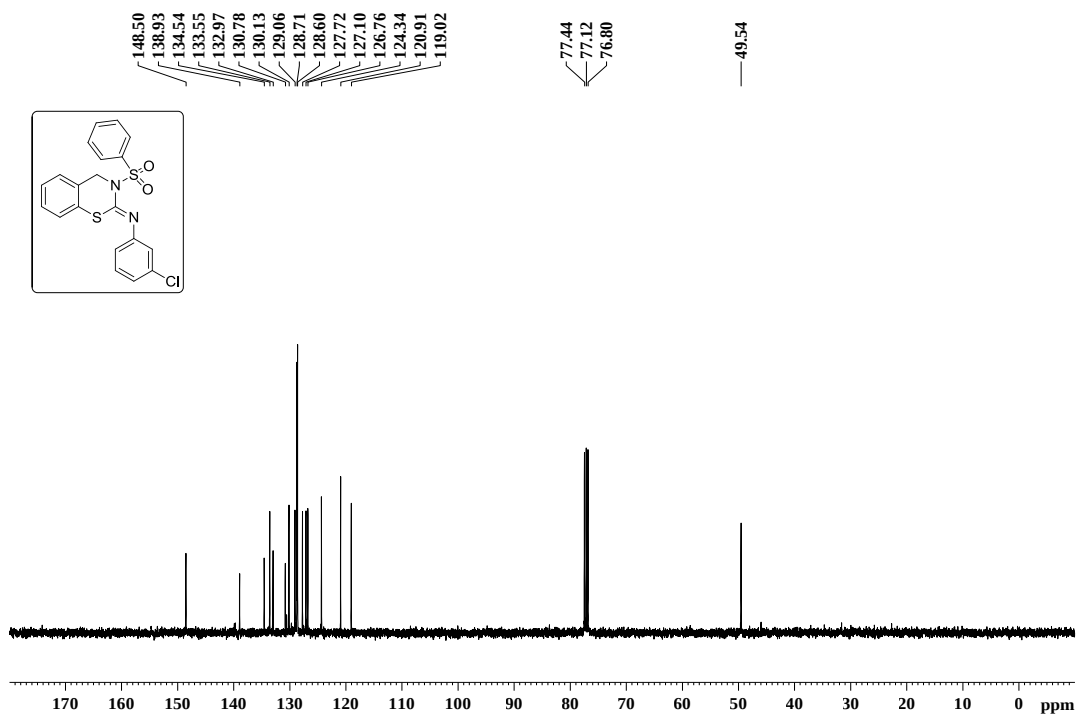


Figure S94. ¹³C NMR spectrum of compound 7d

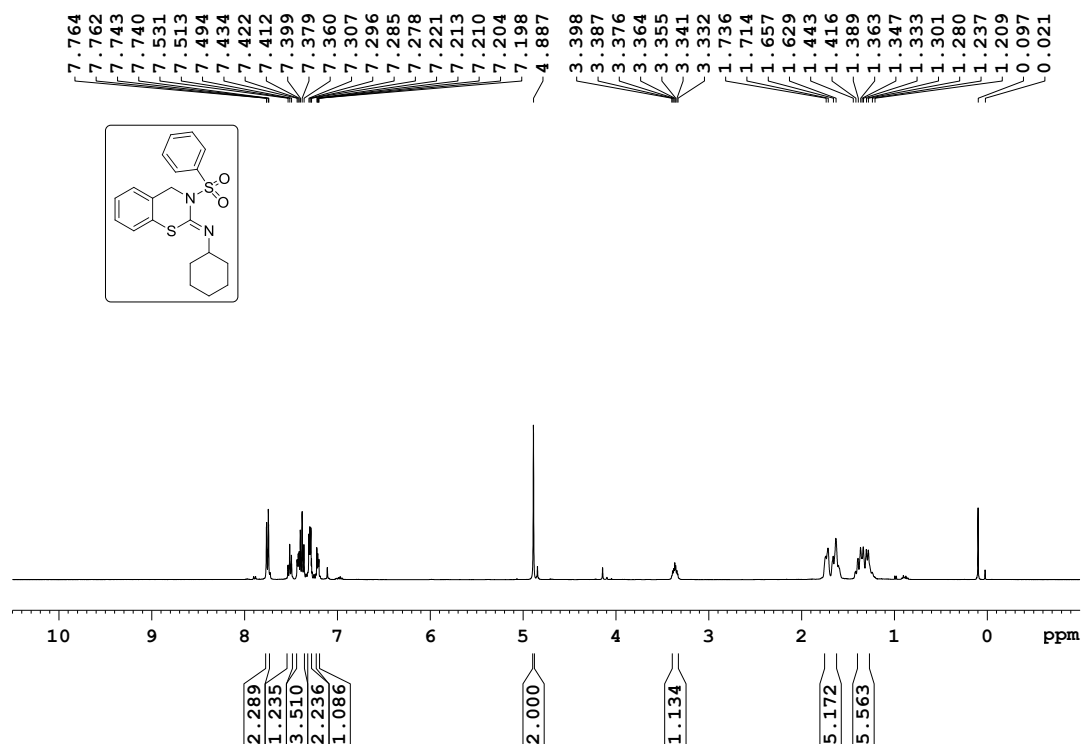


Figure S95. ¹H NMR spectrum of compound **7e**

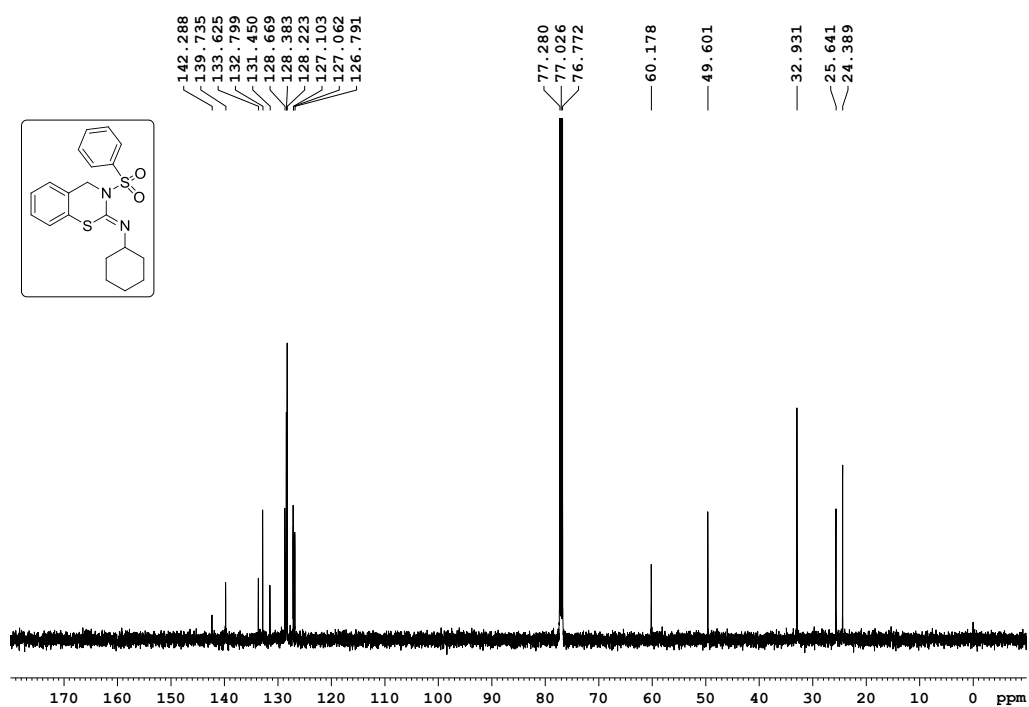


Figure S96. ¹³C NMR spectrum of compound **7e**

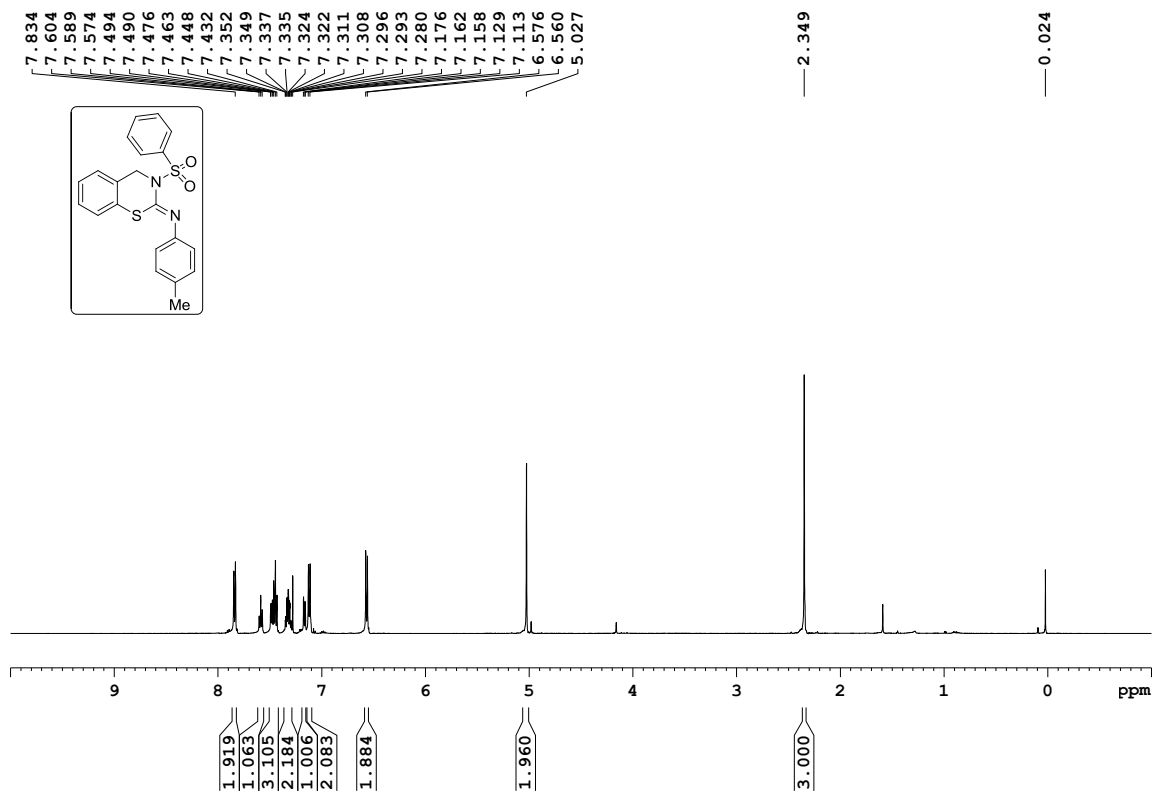


Figure S97. ¹H NMR spectrum of compound **7f**

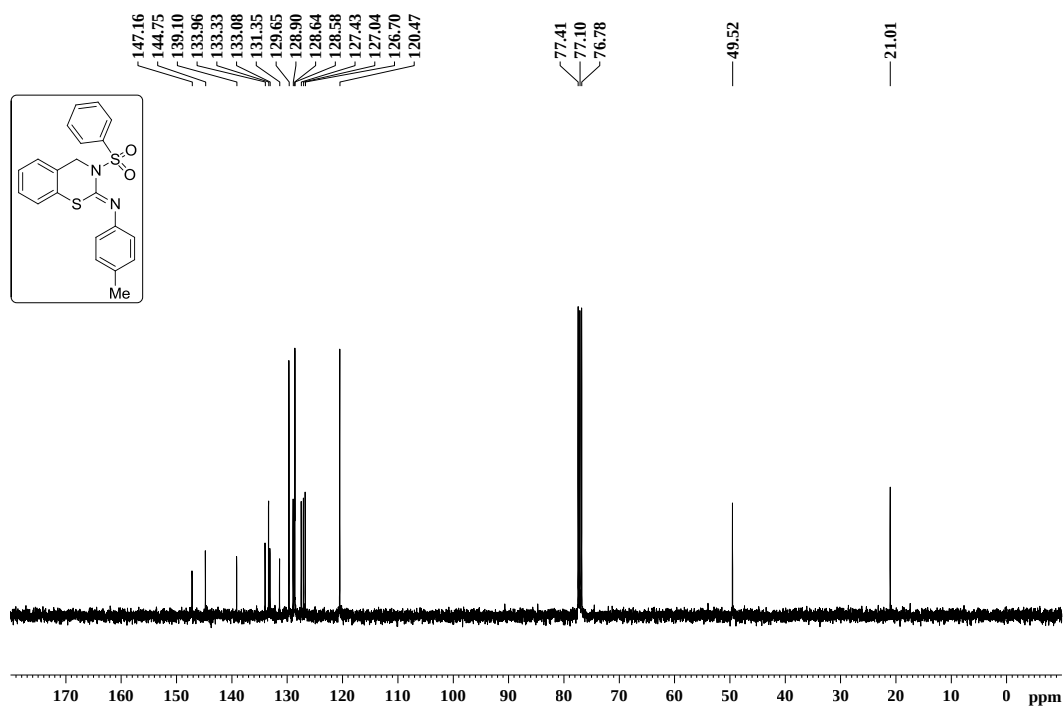


Figure S98. ¹³C NMR spectrum of compound **7f**

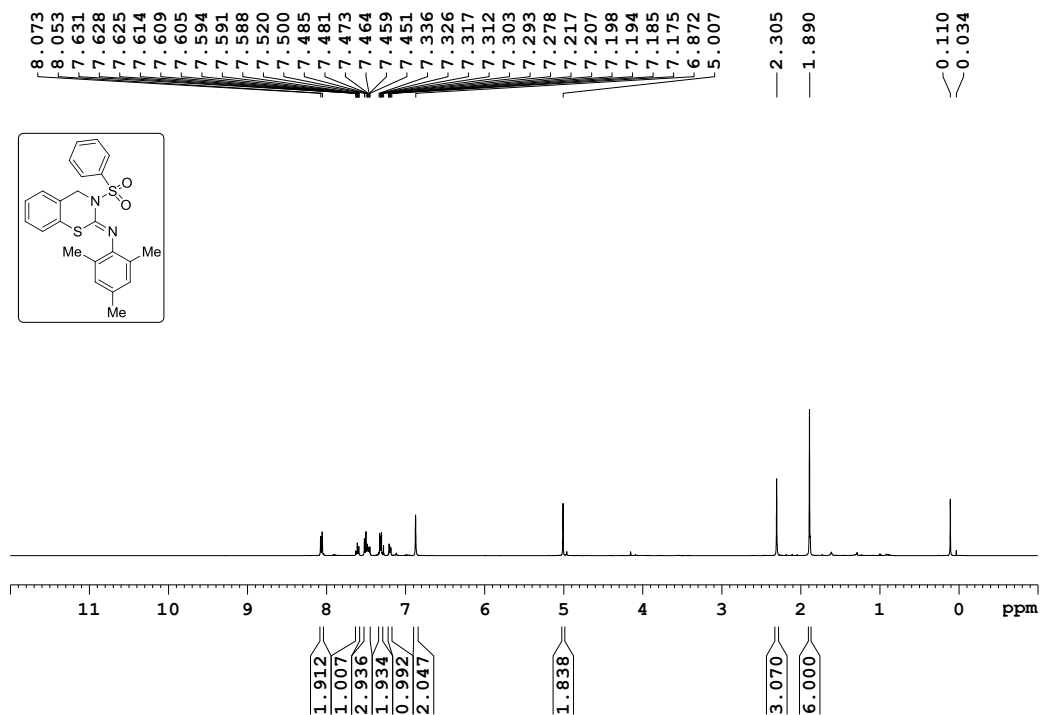


Figure S99. ¹H NMR spectrum of compound **7g**

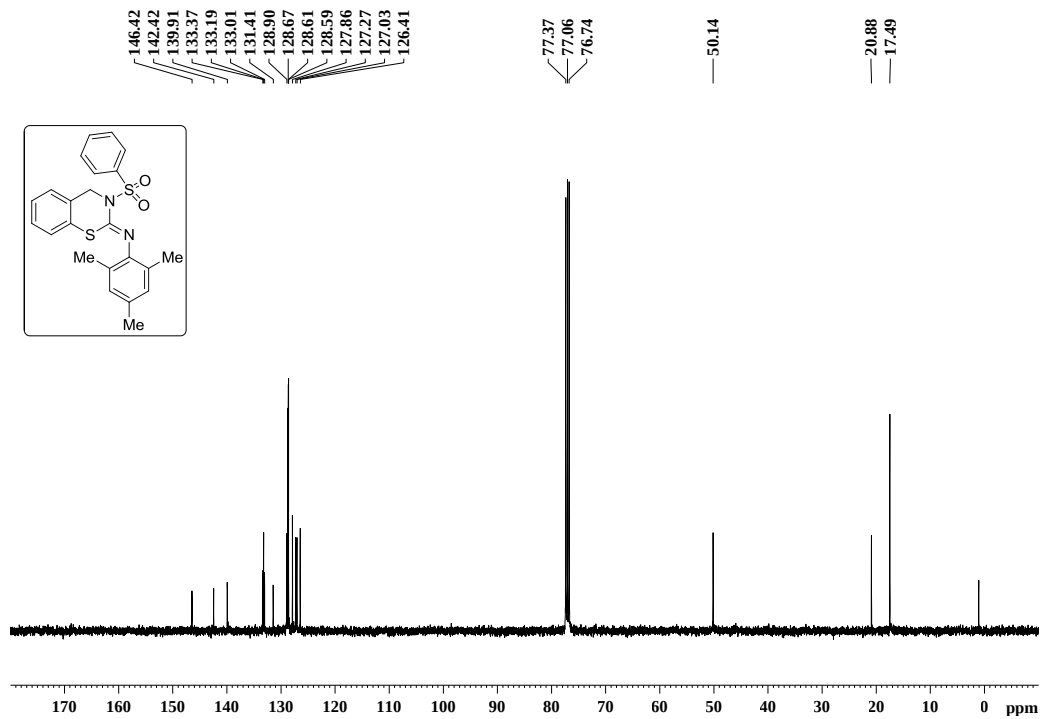


Figure S100. ¹³C NMR spectrum of compound **7g**

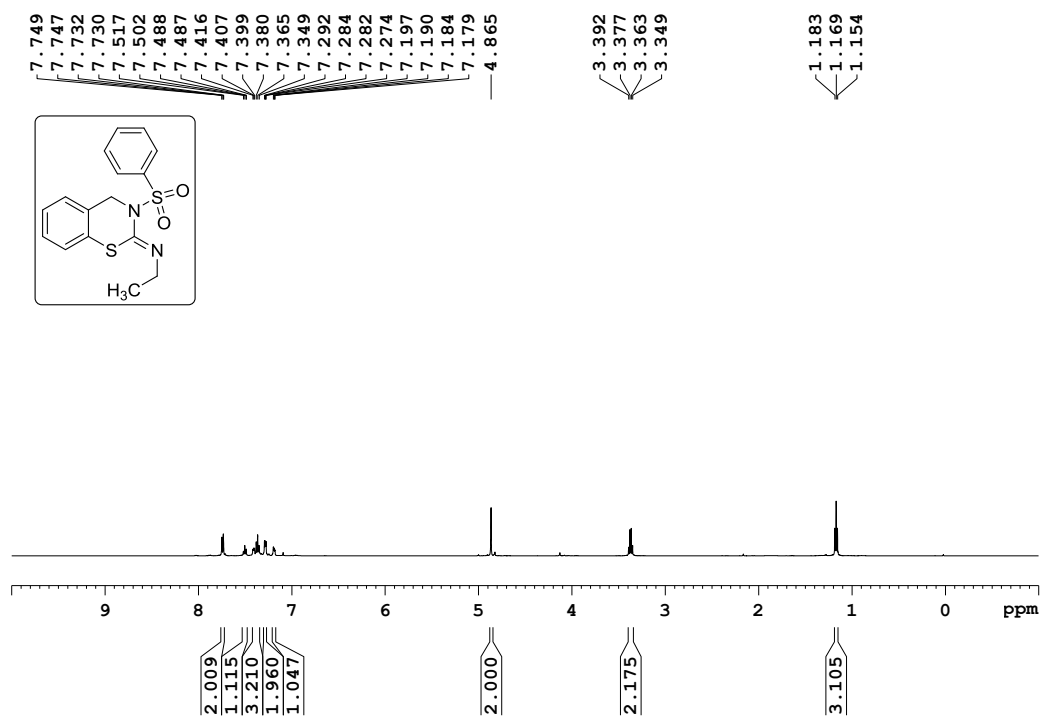


Figure S101. ¹H NMR spectrum of compound 7h

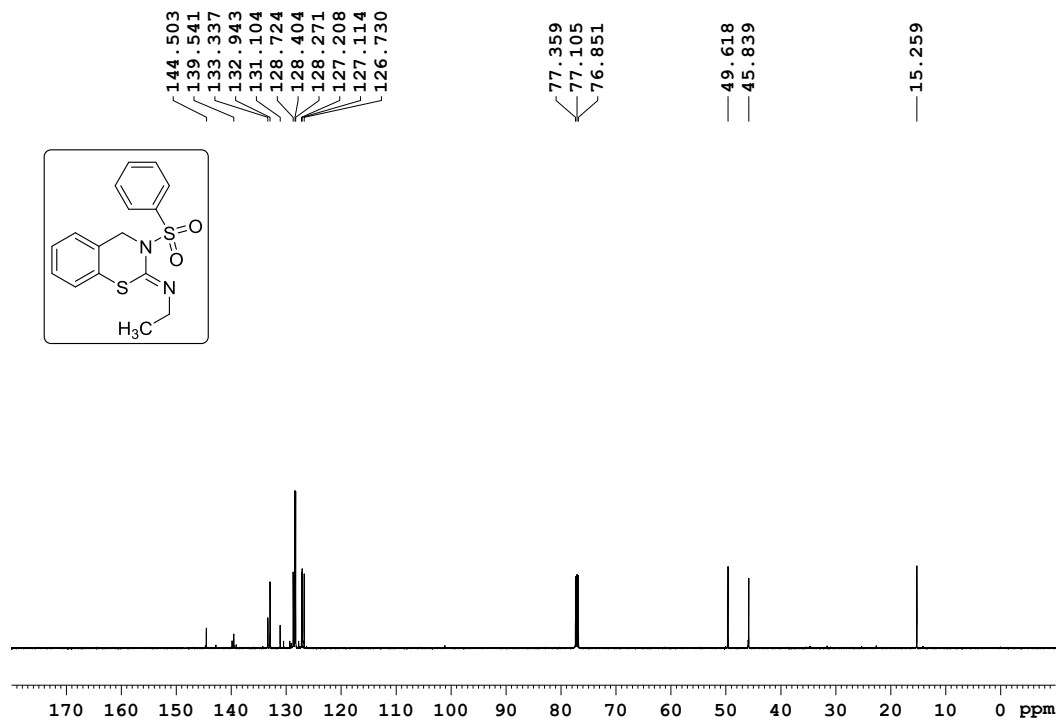


Figure S102. ¹³C NMR spectrum of compound 7h

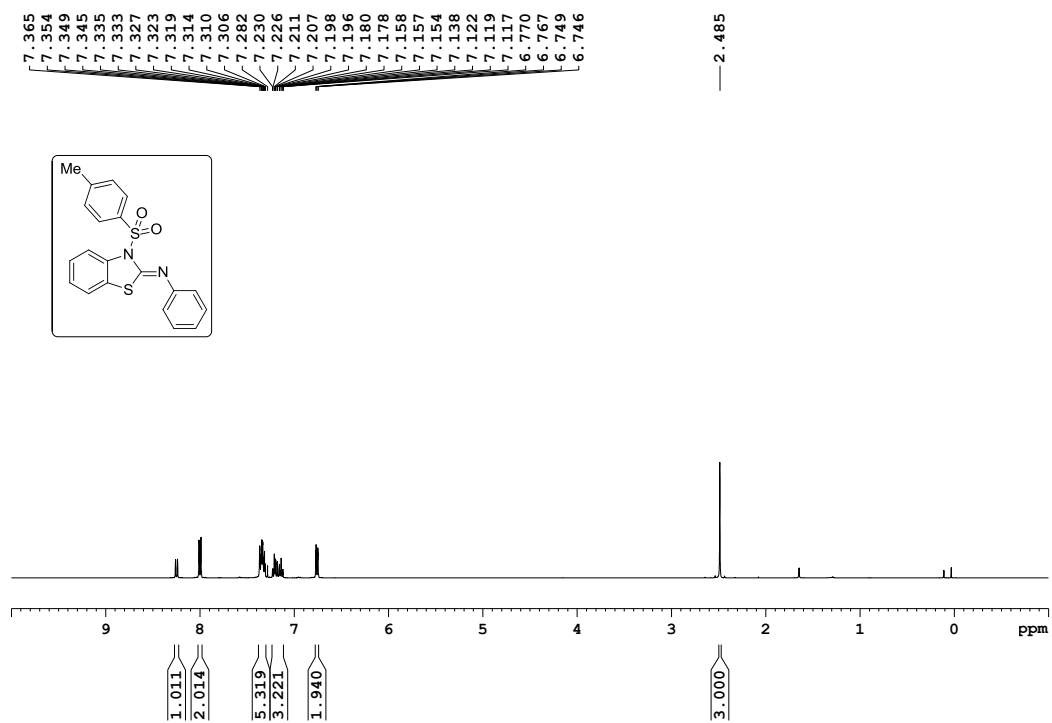


Figure S103. ¹H NMR spectrum of compound **9a**

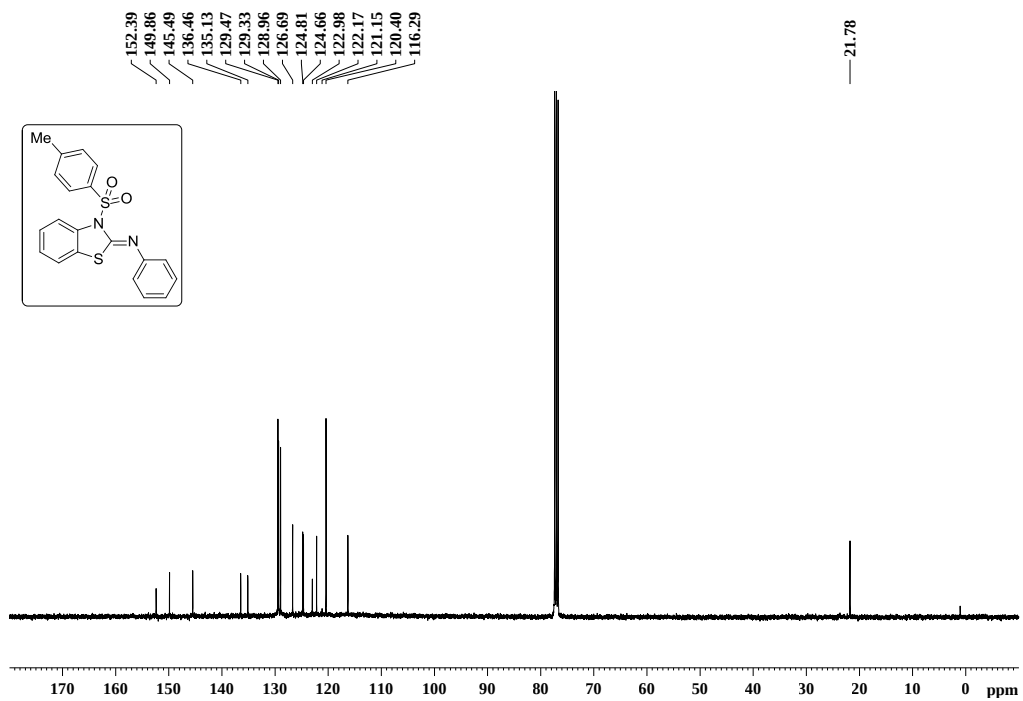


Figure S104. ¹³C NMR spectrum of compound **9a**

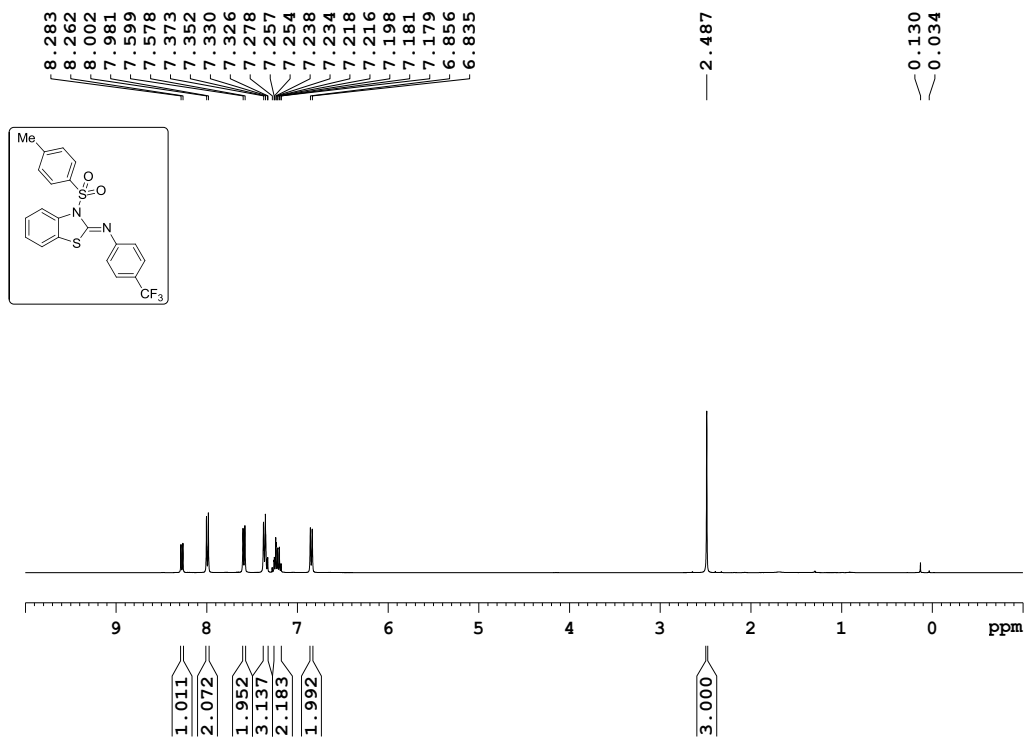


Figure S105. ¹H NMR spectrum of compound **9b**

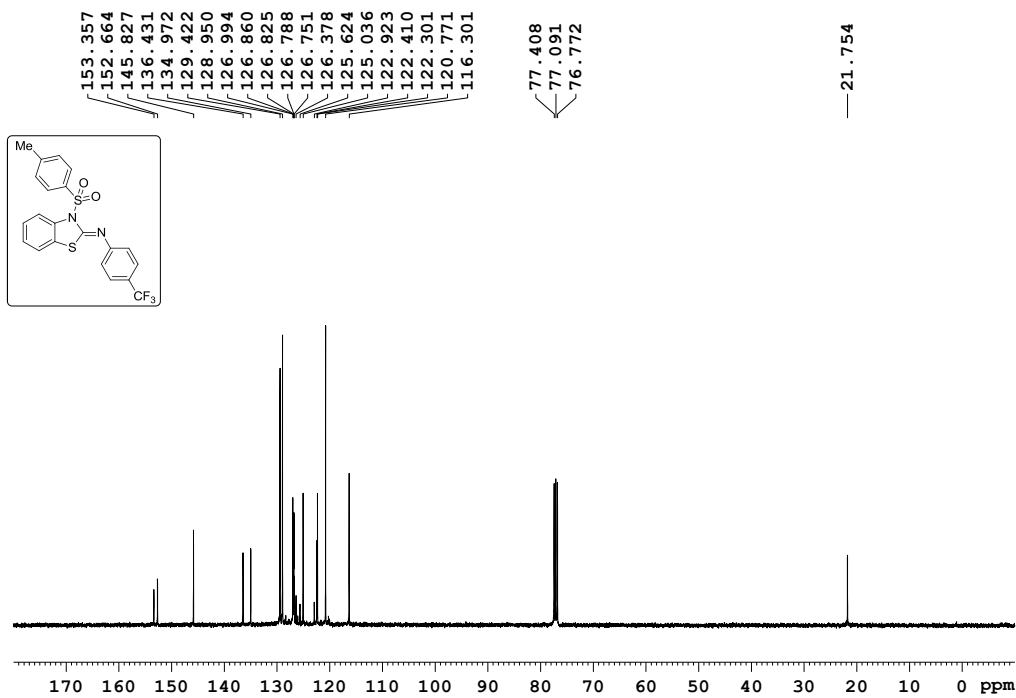


Figure S106. ¹³C NMR spectrum of compound **9b**

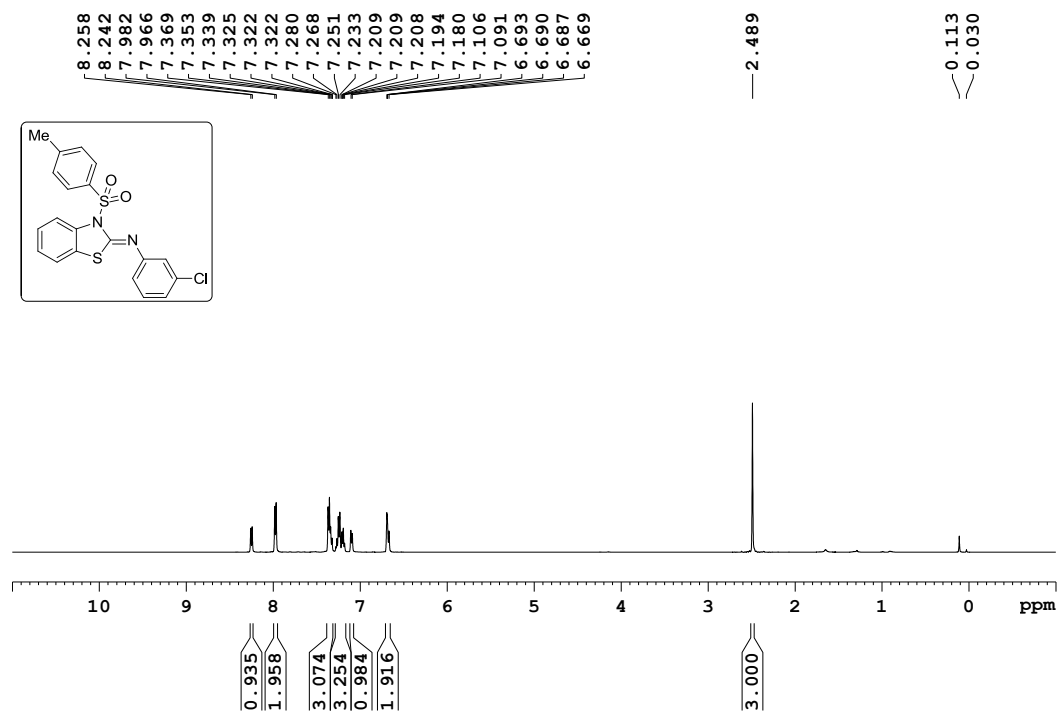


Figure S107. ¹H NMR spectrum of compound **9c**

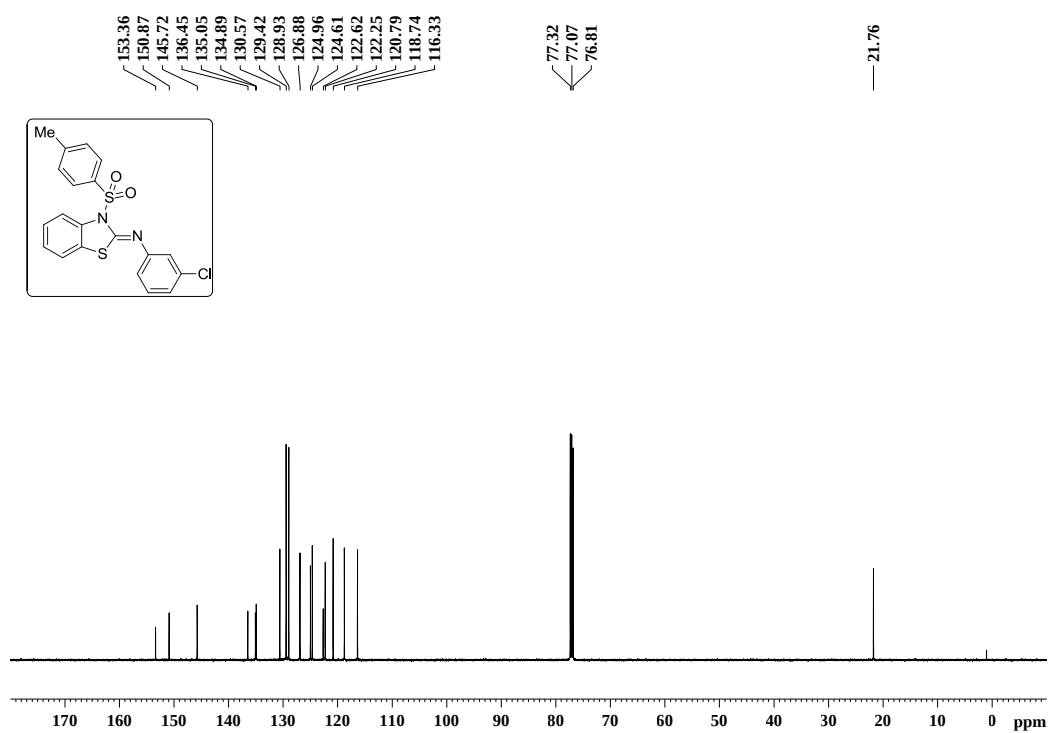


Figure S108. ¹³C NMR spectrum of compound **9c**

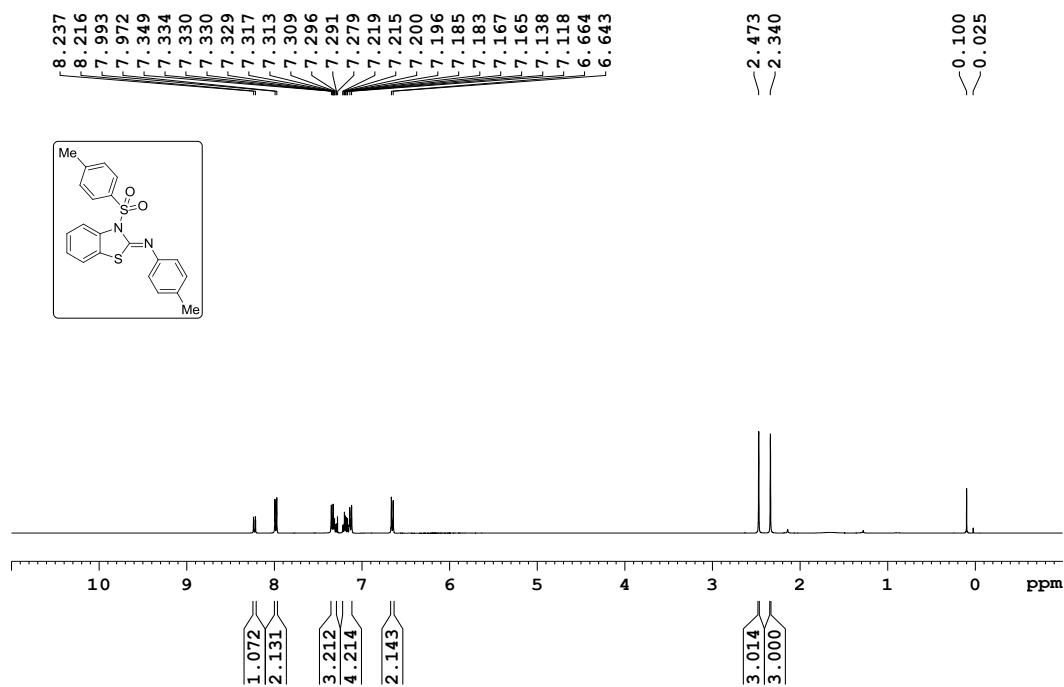


Figure S109. ¹H NMR spectrum of compound 9d

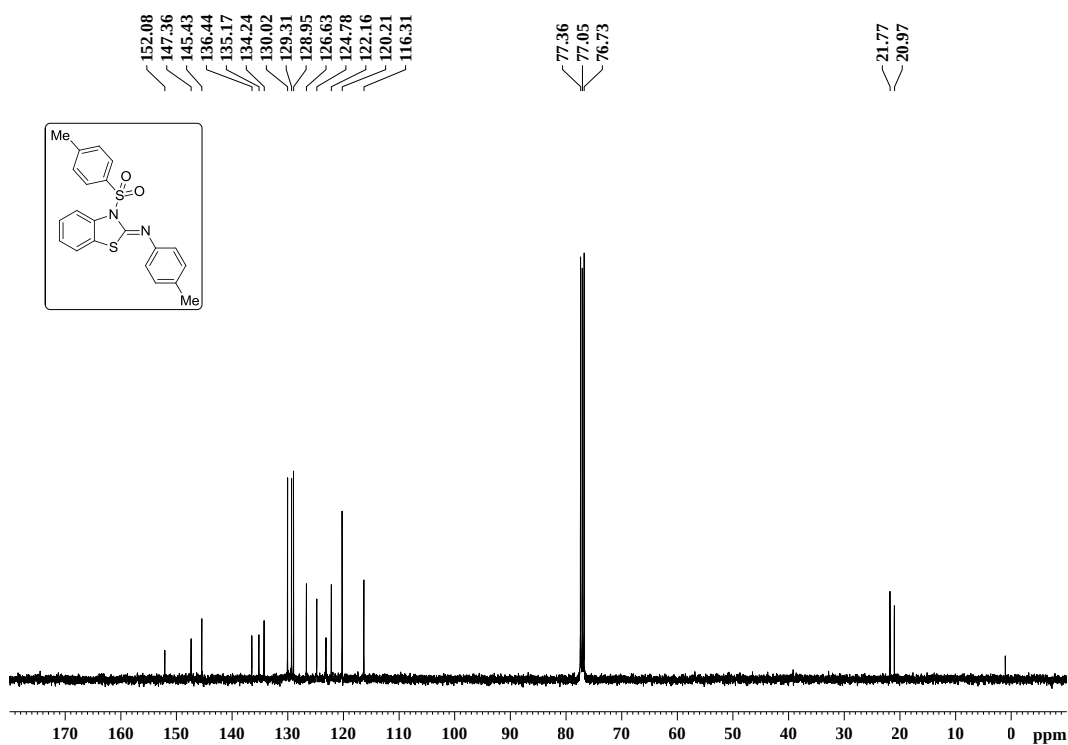


Figure S110. ¹³C NMR spectrum of compound 9d

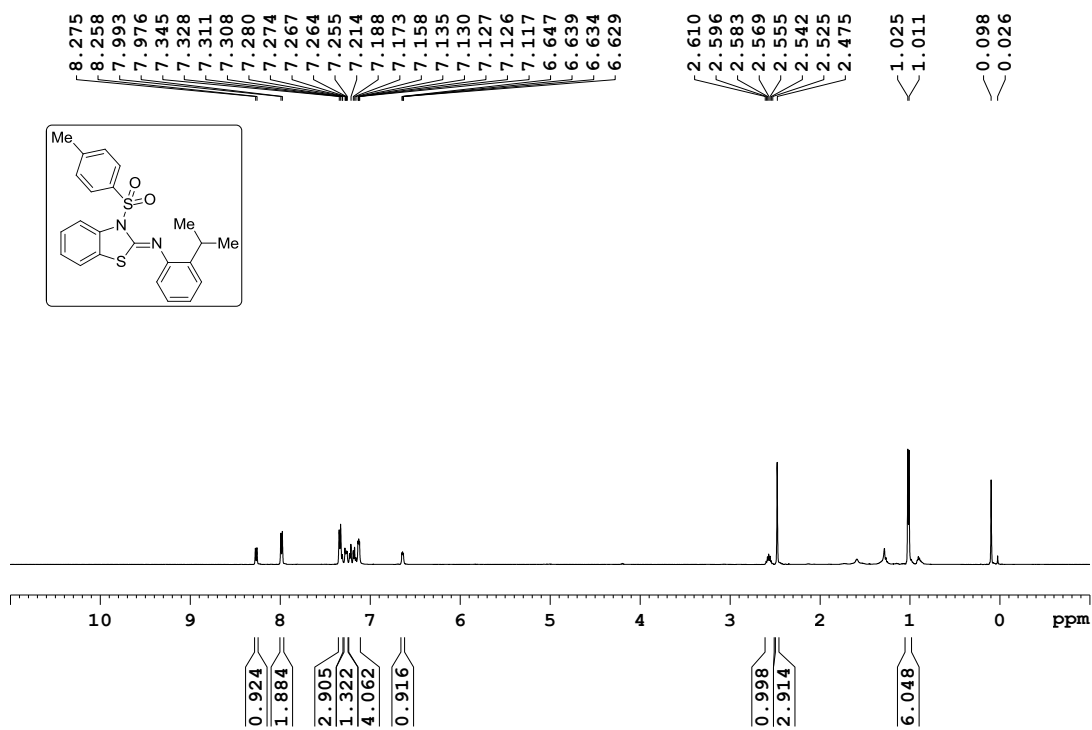


Figure S111. ¹H NMR spectrum of compound **9e**

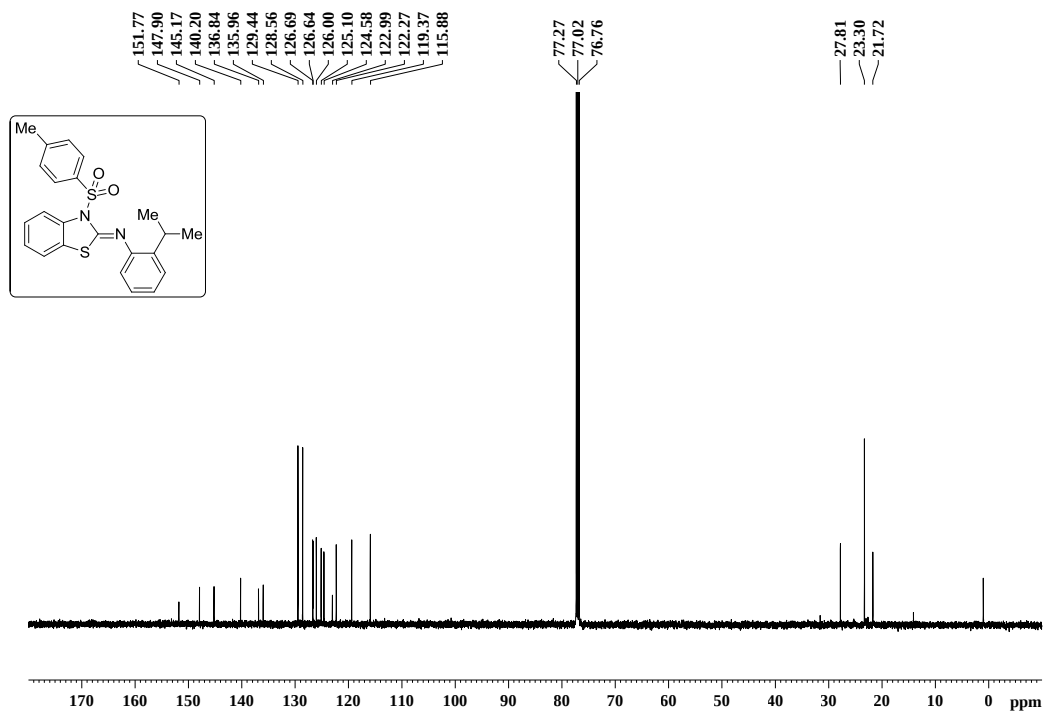


Figure S112. ¹³C NMR spectrum of compound **9e**

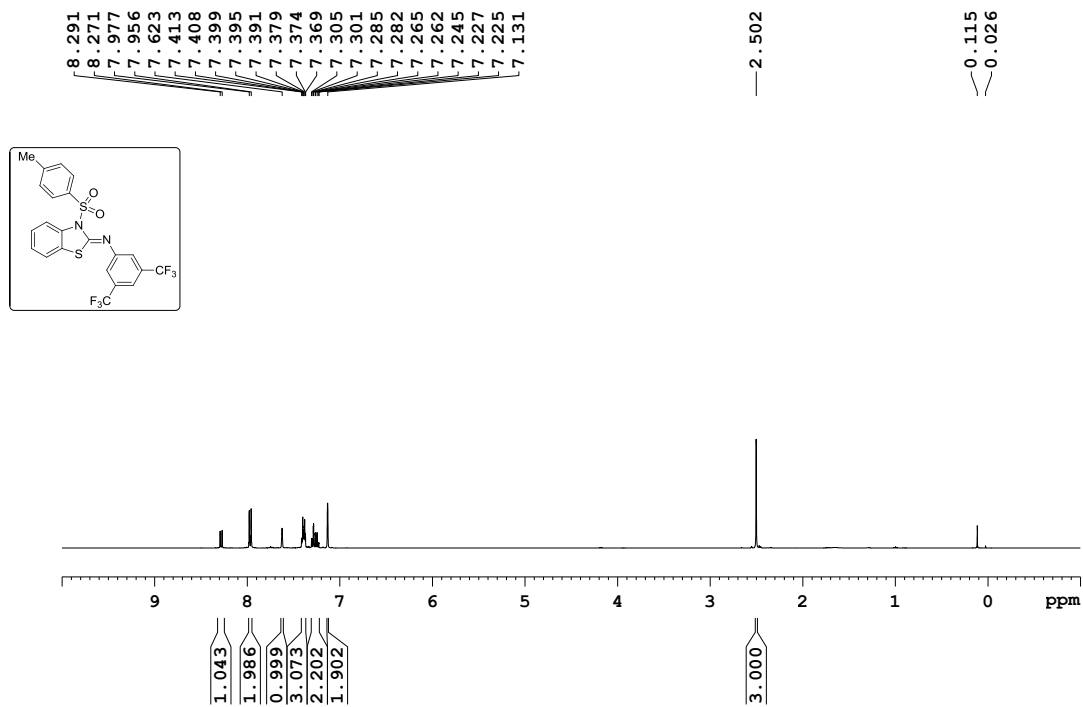


Figure S113. ¹H NMR spectrum of compound **9f**

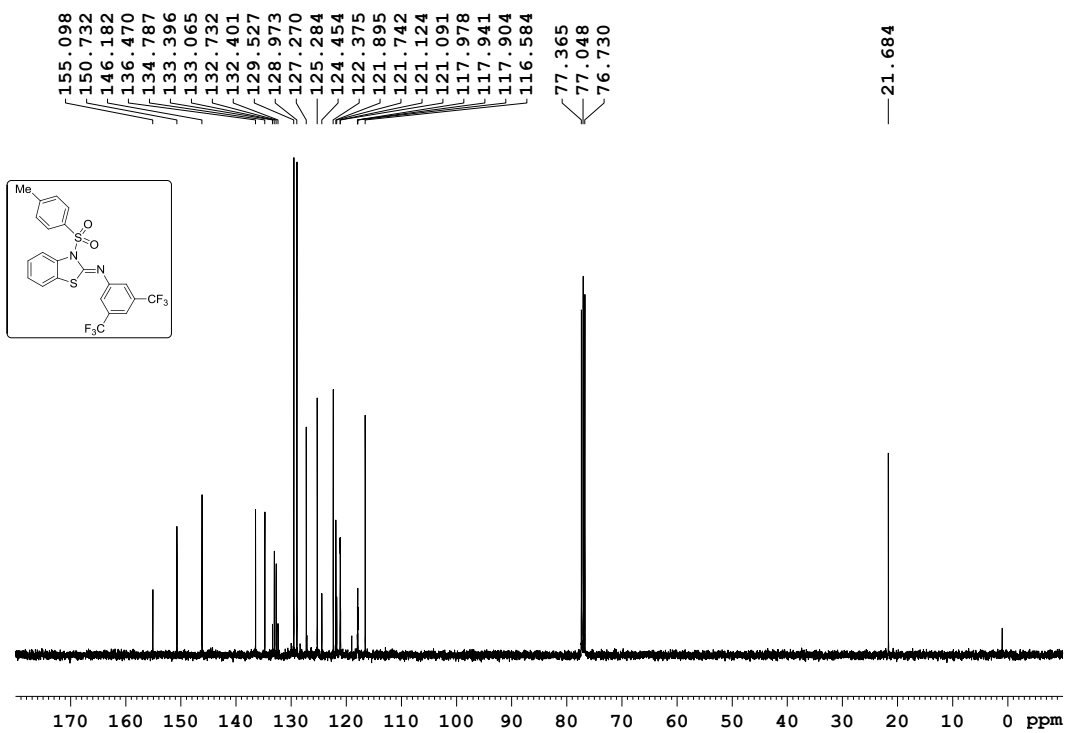


Figure S114. ¹³C NMR spectrum of compound **9f**

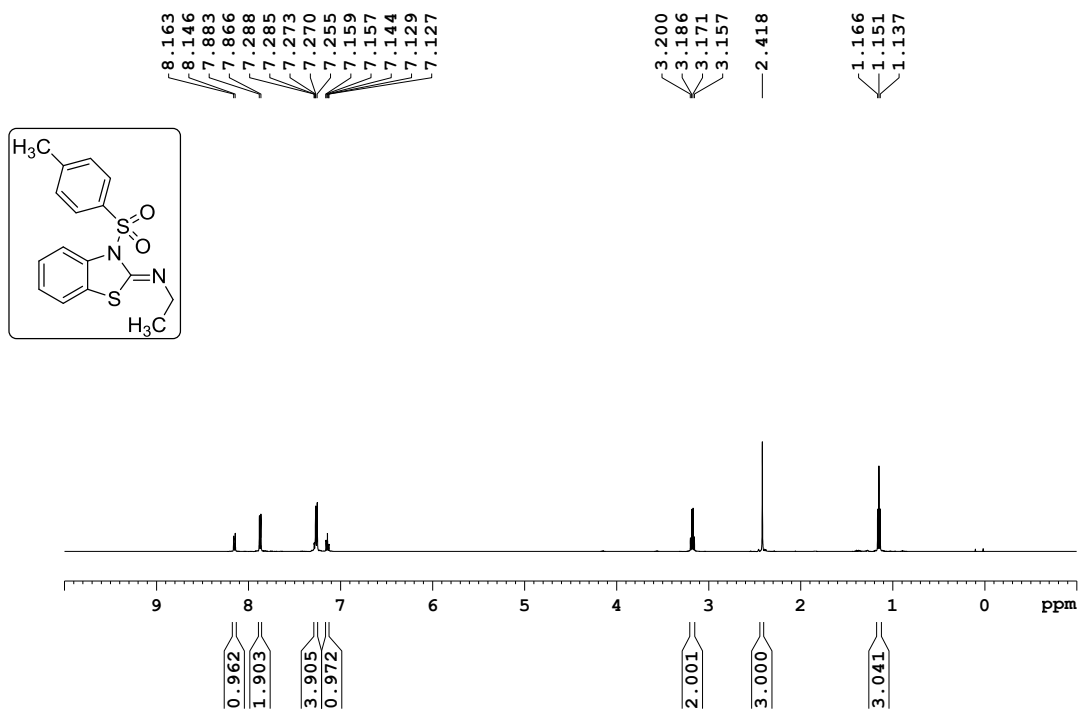


Figure S115. ¹H NMR spectrum of compound **9g**

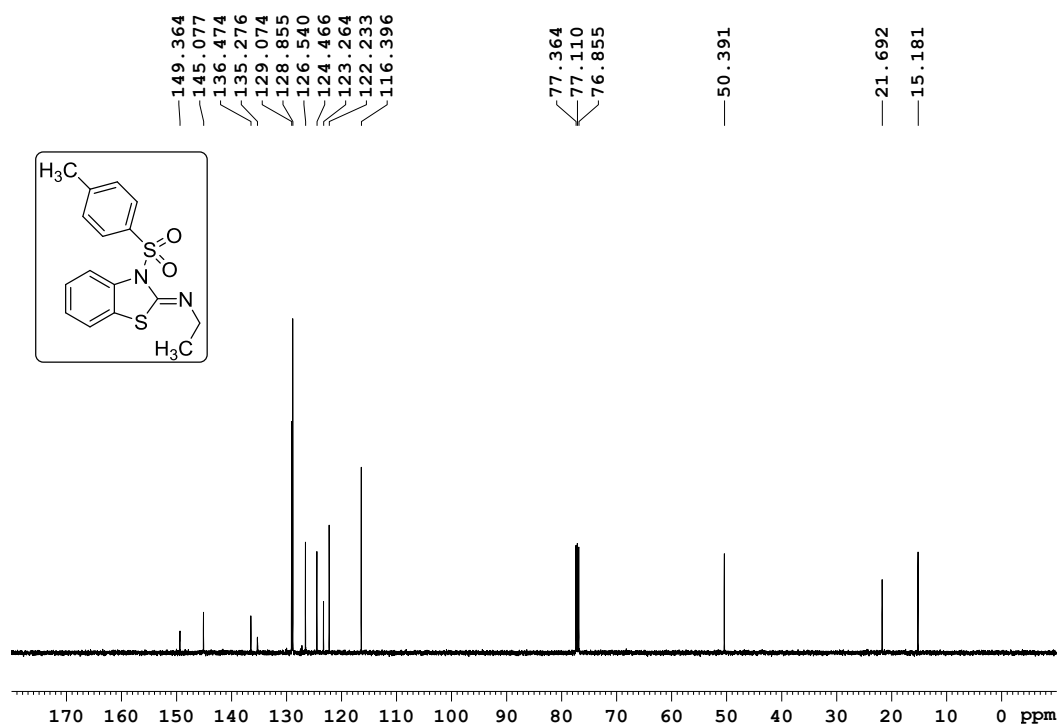


Figure S116. ¹³C NMR spectrum of compound **9g**

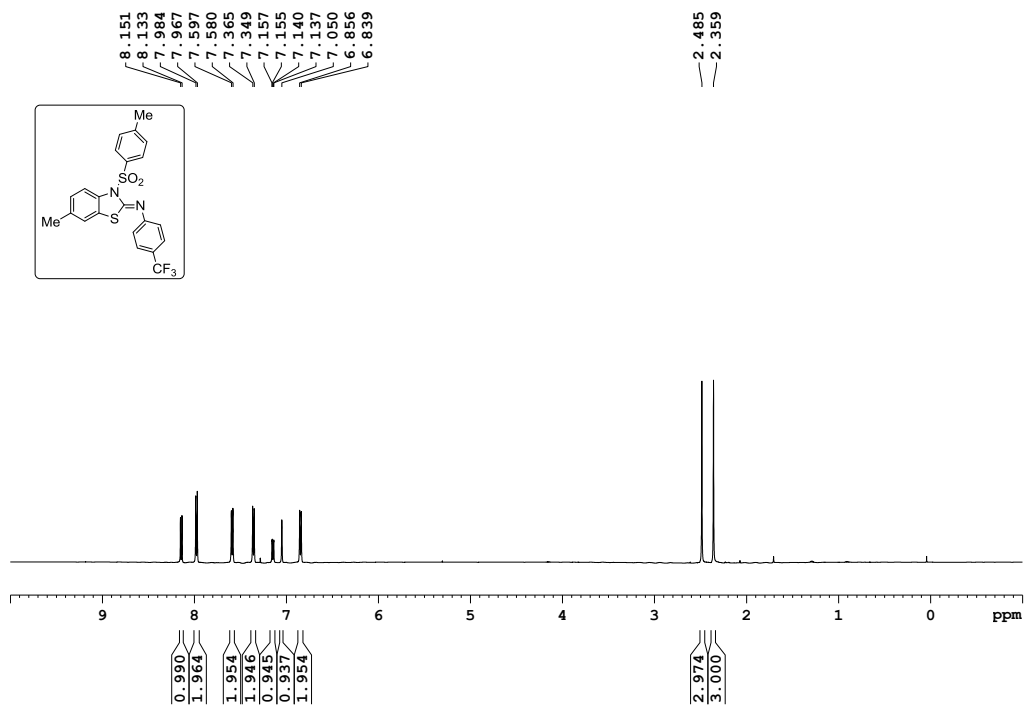


Figure S117. ¹H NMR spectrum of compound **9h**

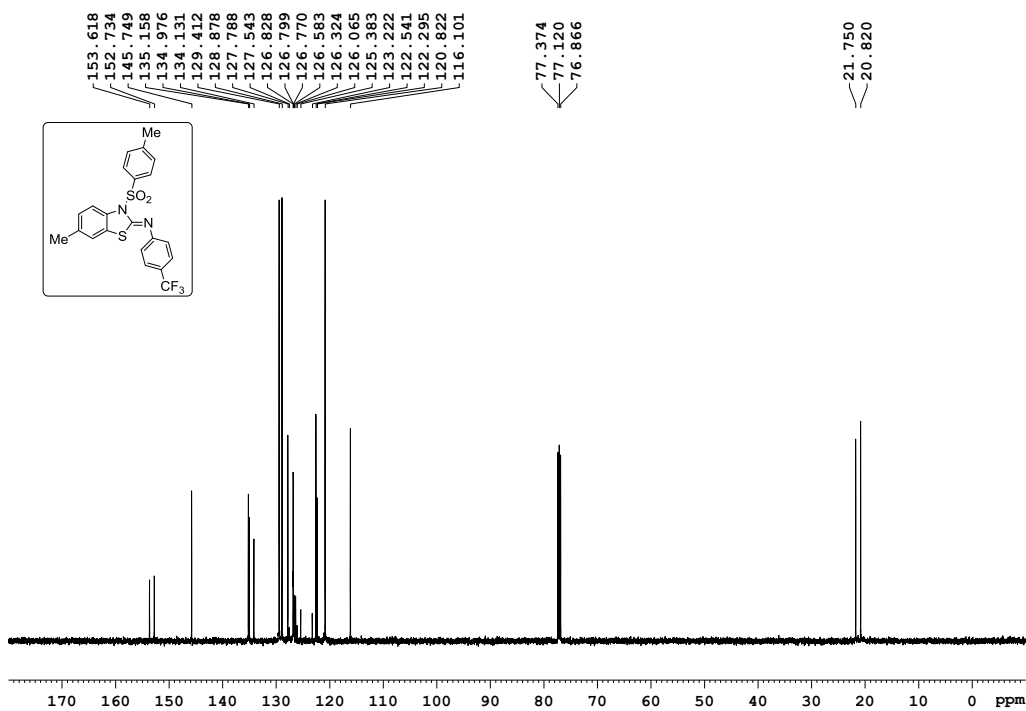


Figure S118. ¹³C NMR spectrum of compound **9h**

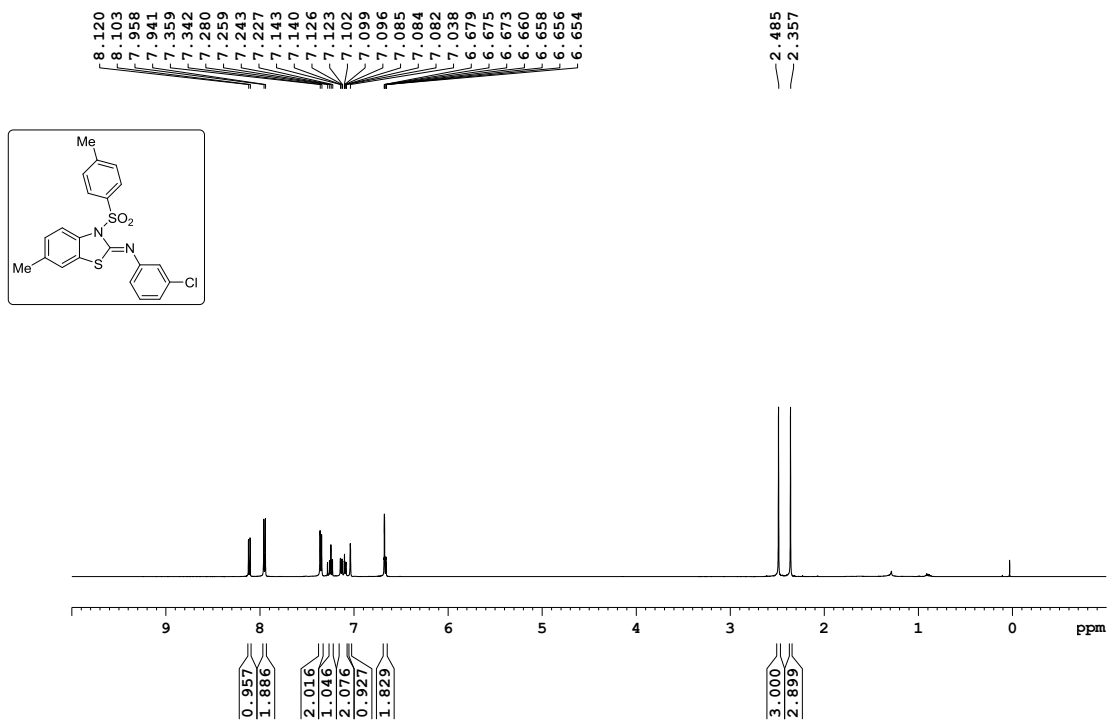


Figure S119. ¹H NMR spectrum of compound **9i**

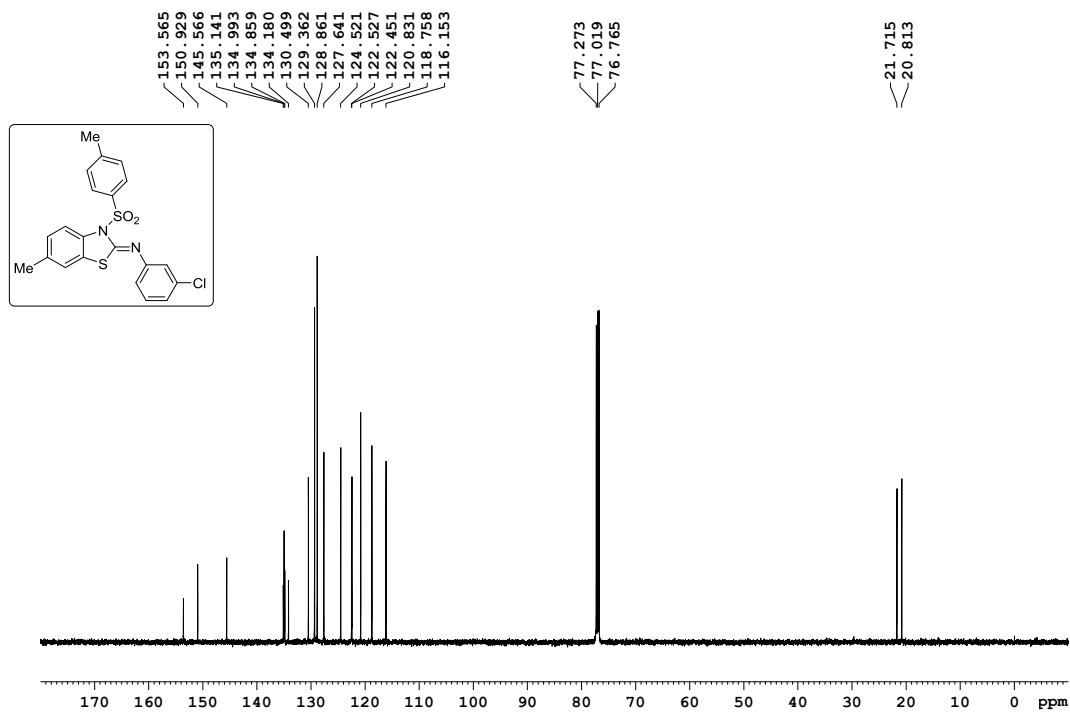


Figure S120. ¹³C NMR spectrum of compound **9i**

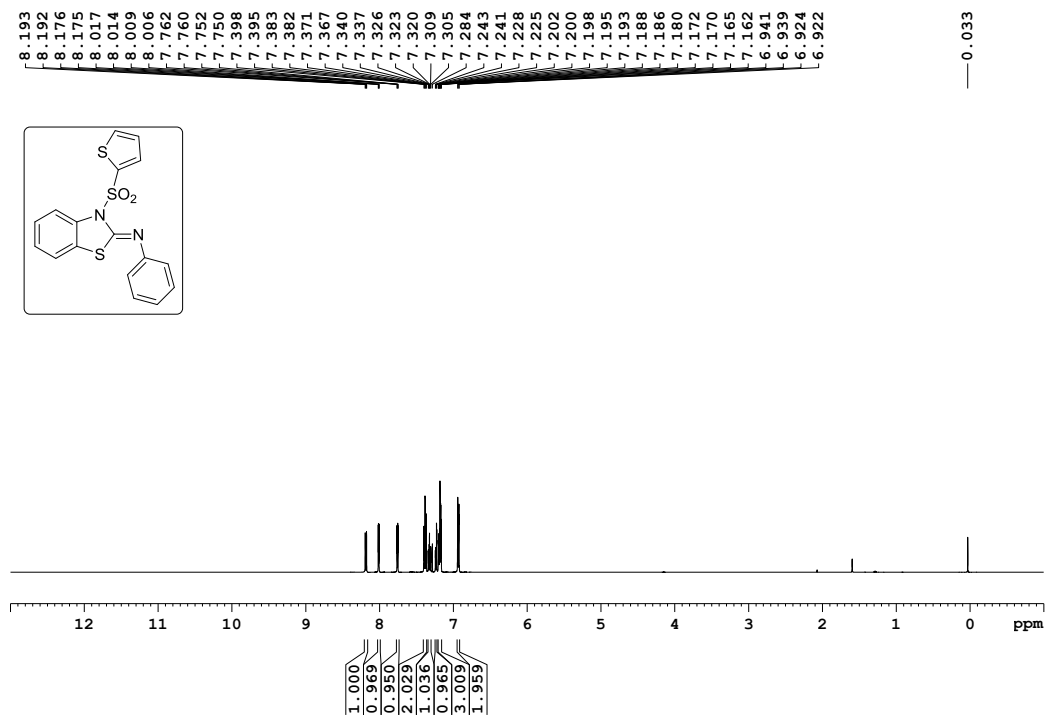


Figure S121. ¹H NMR spectrum of compound **9j**

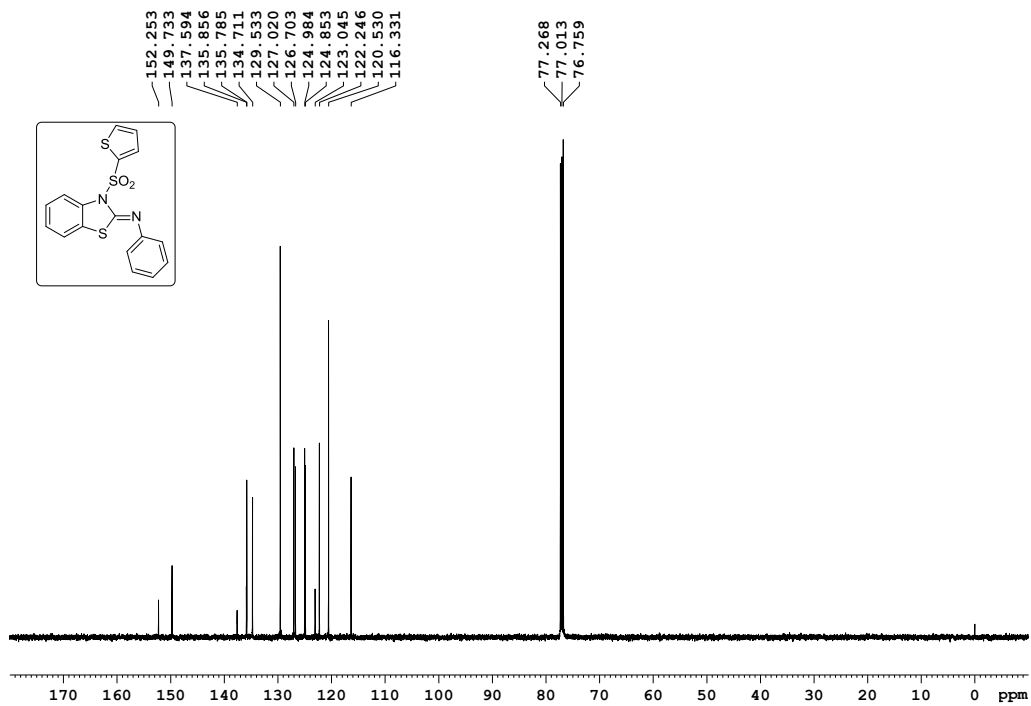


Figure S122. ¹³C NMR spectrum of compound **9j**

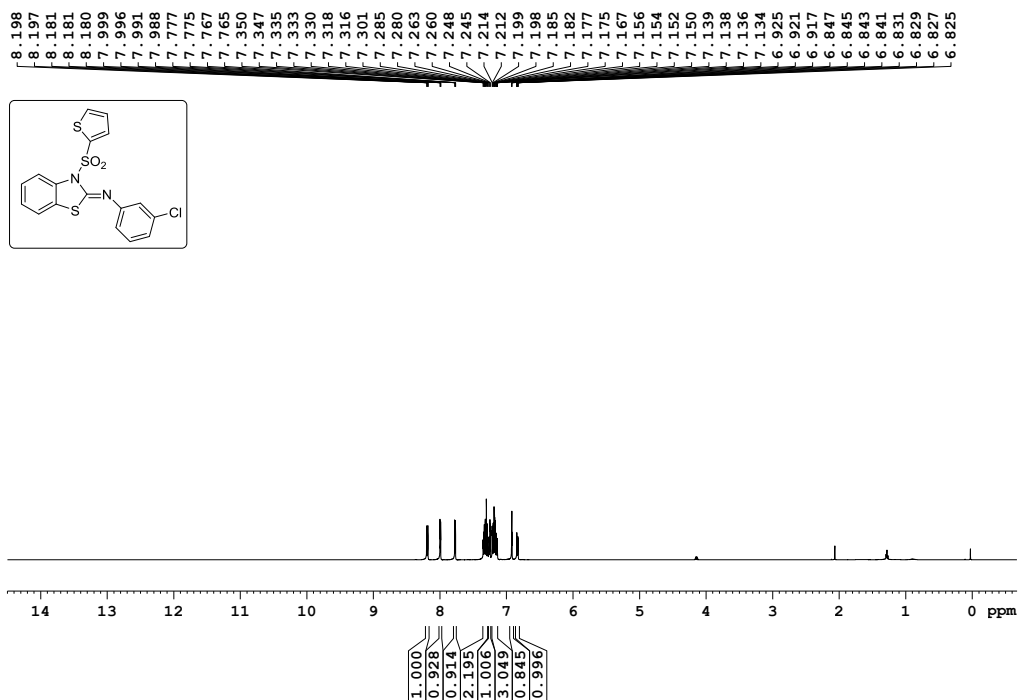


Figure S123. ¹H NMR spectrum of compound 9k

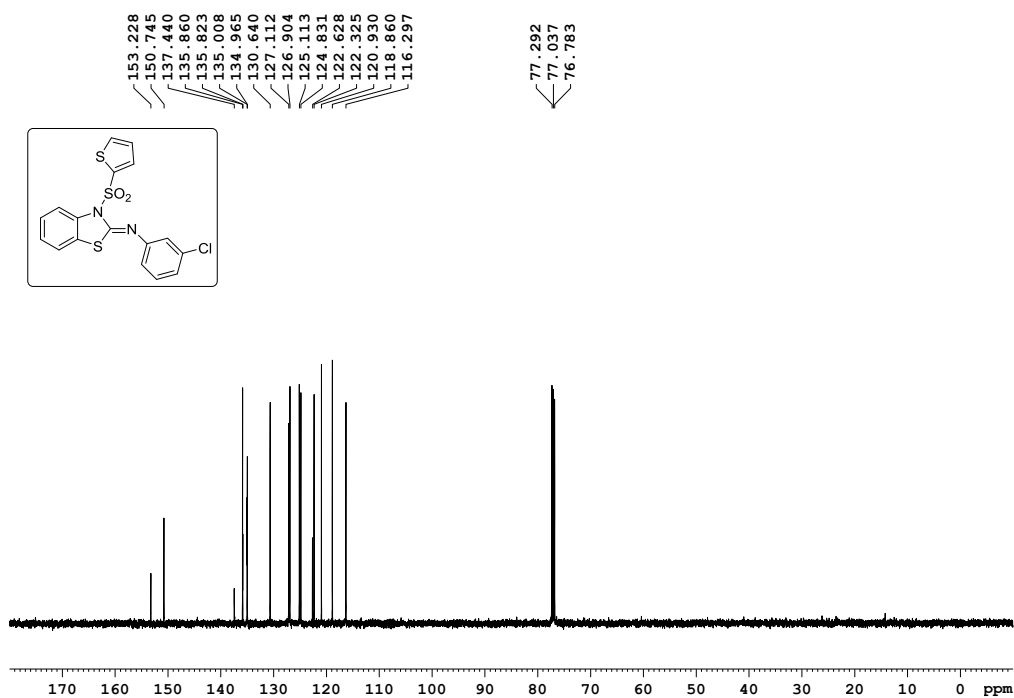


Figure S124. ¹³C NMR spectrum of compound 9k