

Supporting Information

For

A formal [3+2] Annulation Reaction of Crotonate-derived Sulfur Ylides and β -Ketothioamides: Access to Thiazoline and Spiro[indoline-3,3'-thiophen] Scaffolds

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1. NMR Spectra

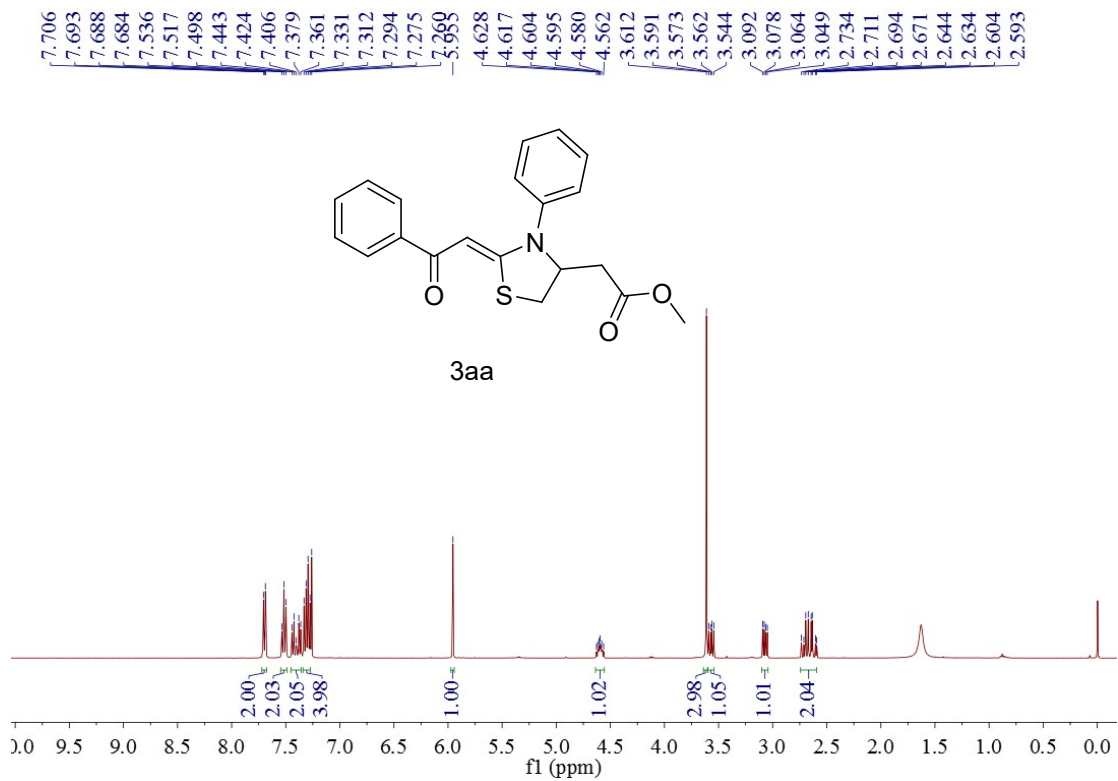


Figure S1. **3aa** (^1H NMR, 400 MHz, CDCl_3)

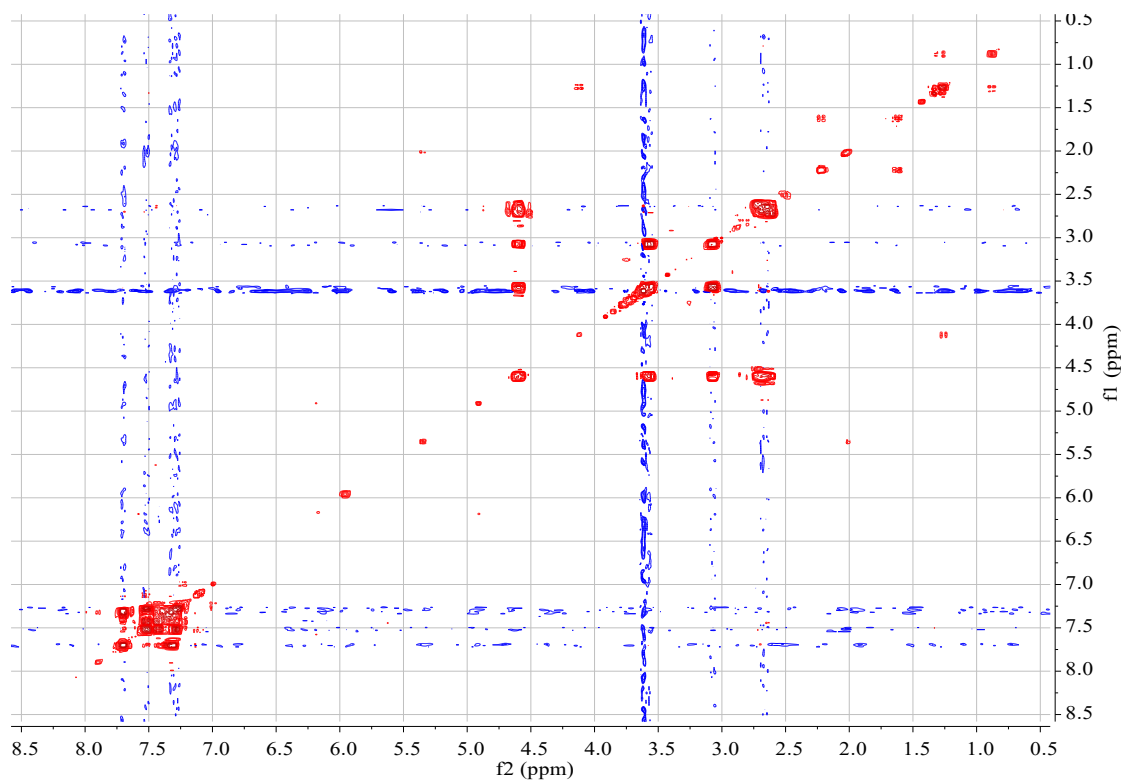


Figure S2. **3aa** (^1H NMR, COSY, 400 MHz, CDCl_3)

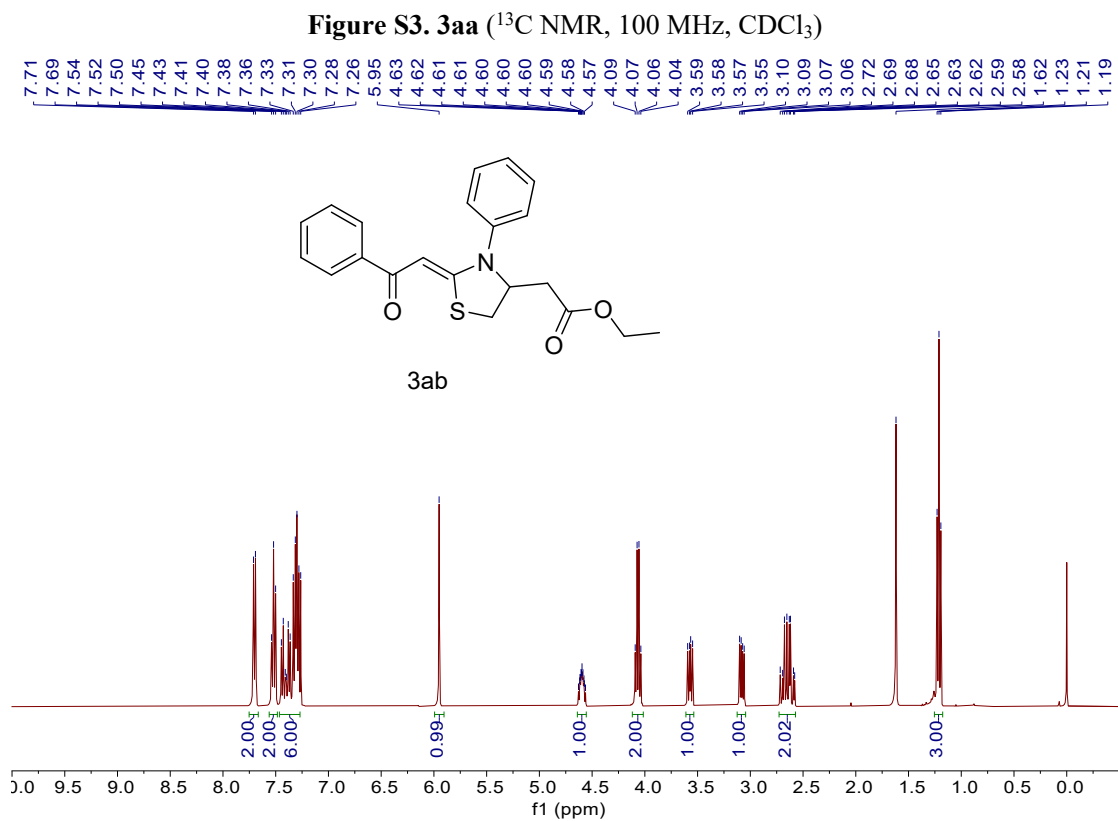
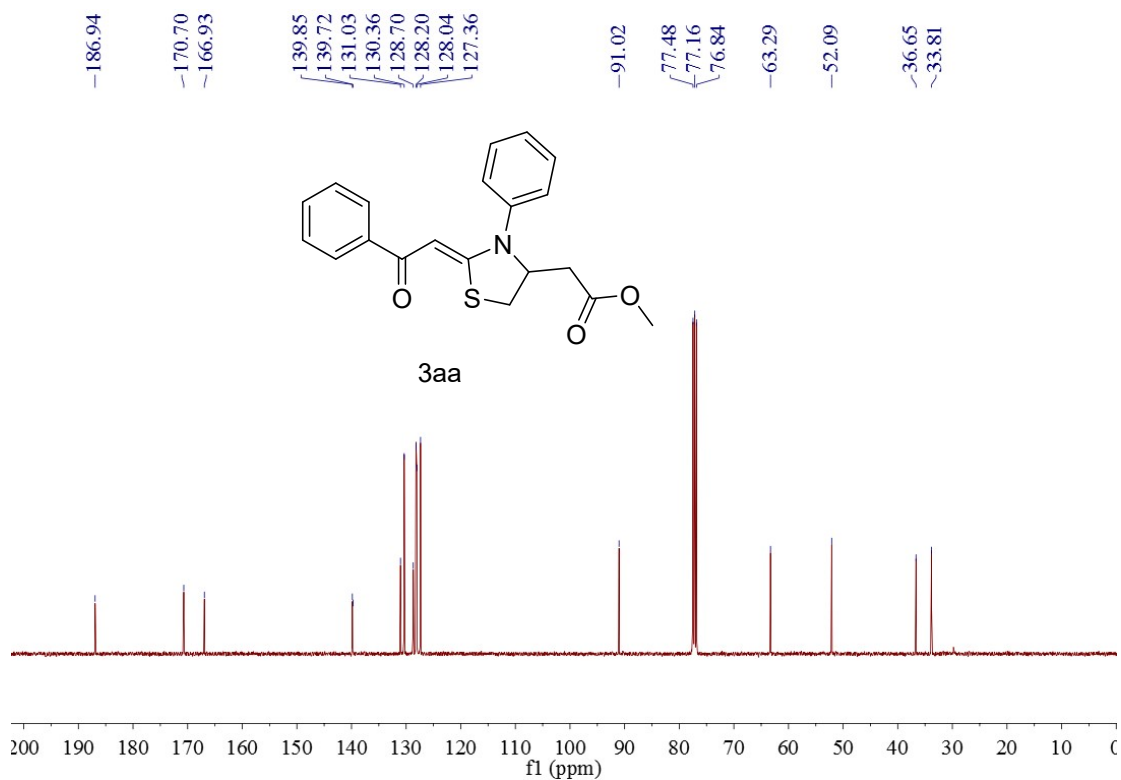


Figure S4. 3ab (^1H NMR, 400 MHz, CDCl_3)

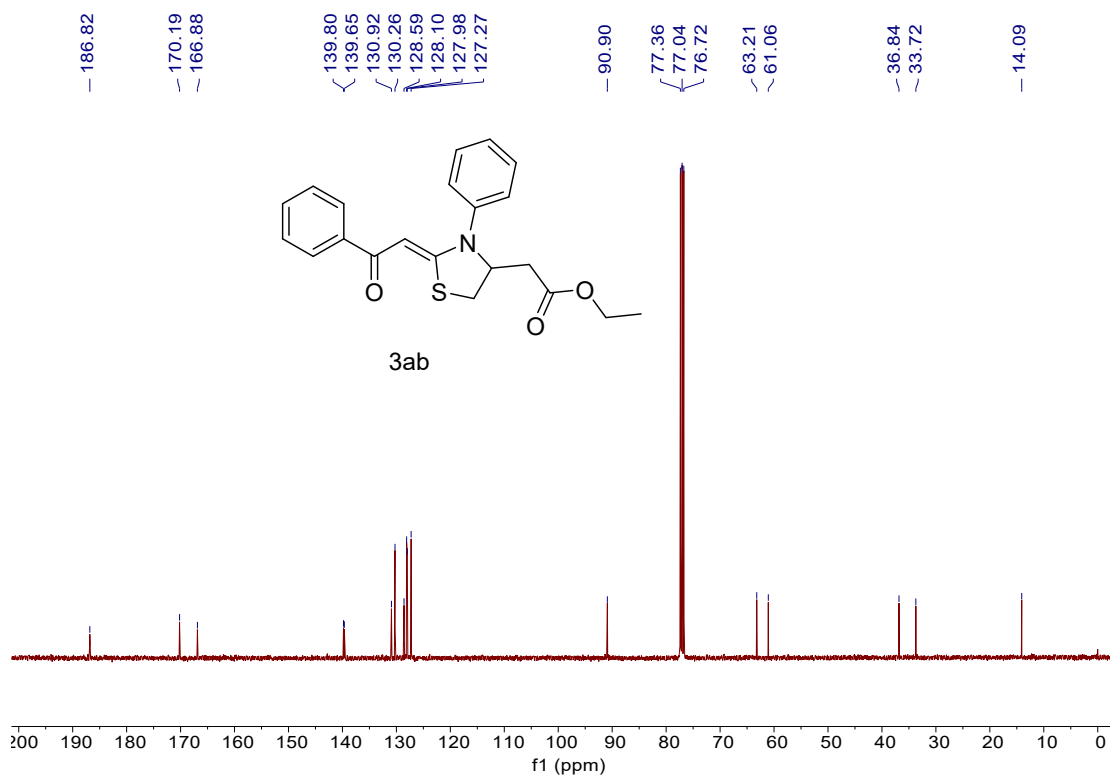


Figure S5. **3ab** (^{13}C NMR, 100 MHz, CDCl_3)

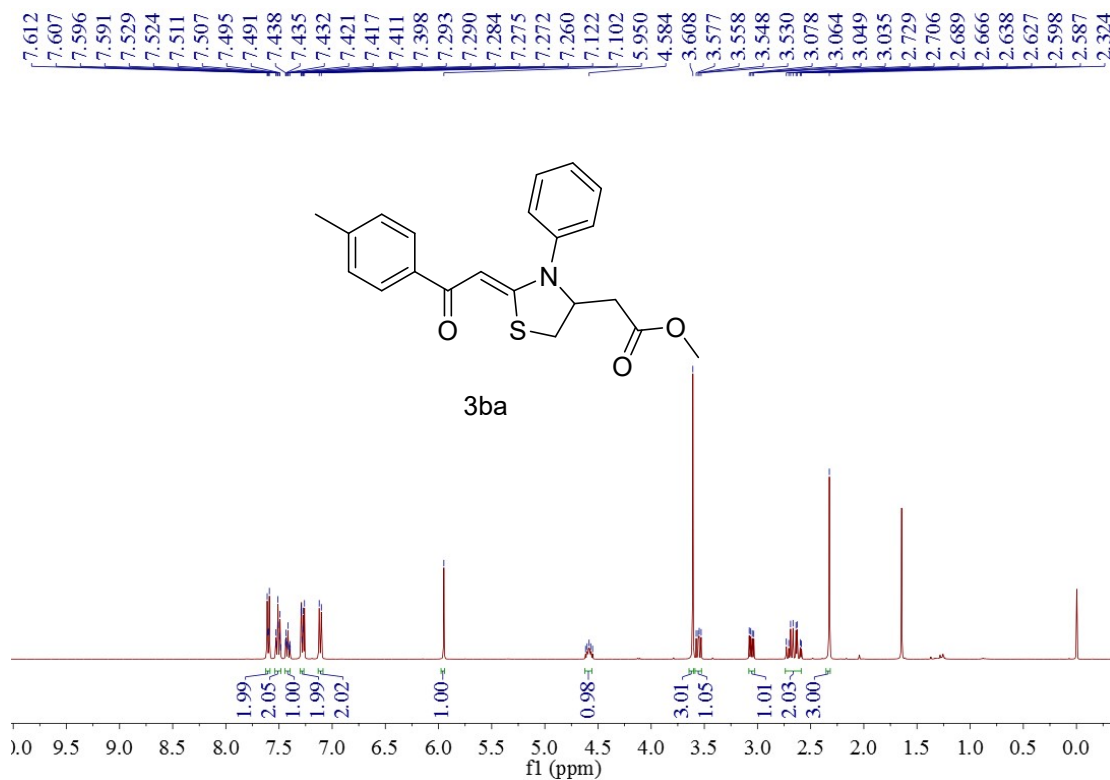


Figure S6. **3ba** (^1H NMR, 400 MHz, CDCl_3)

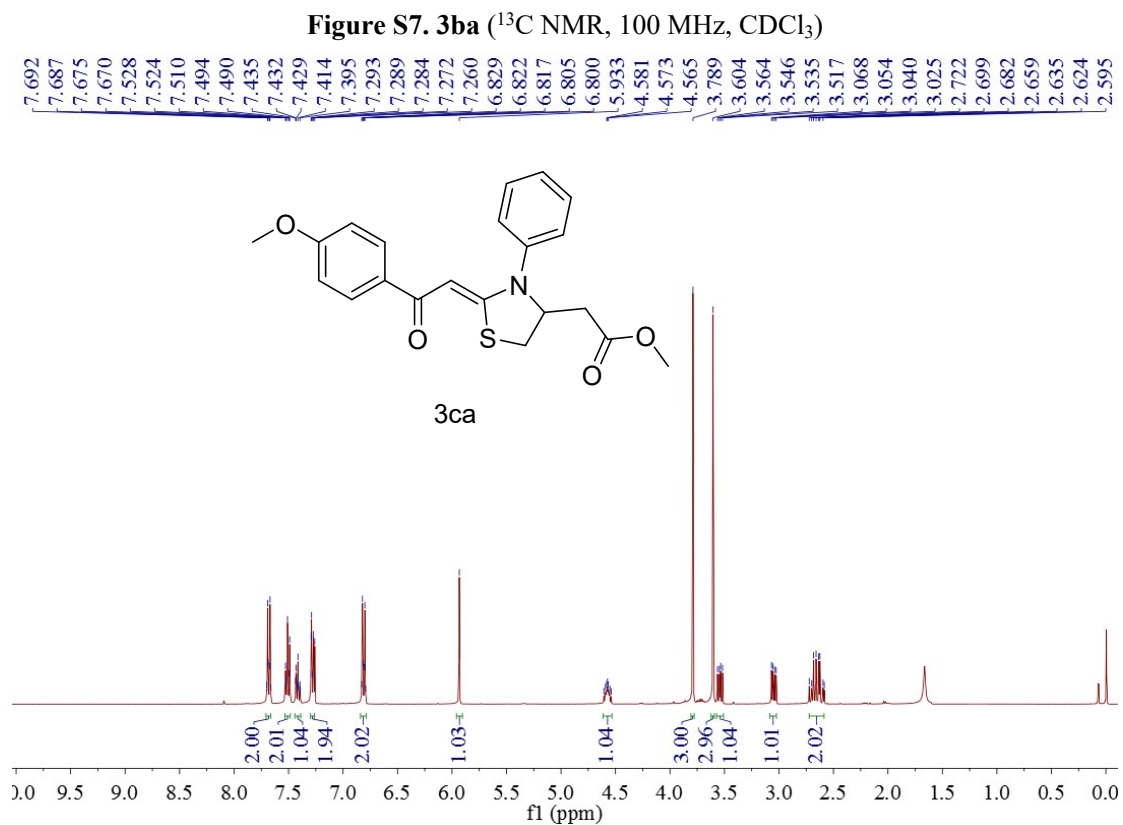
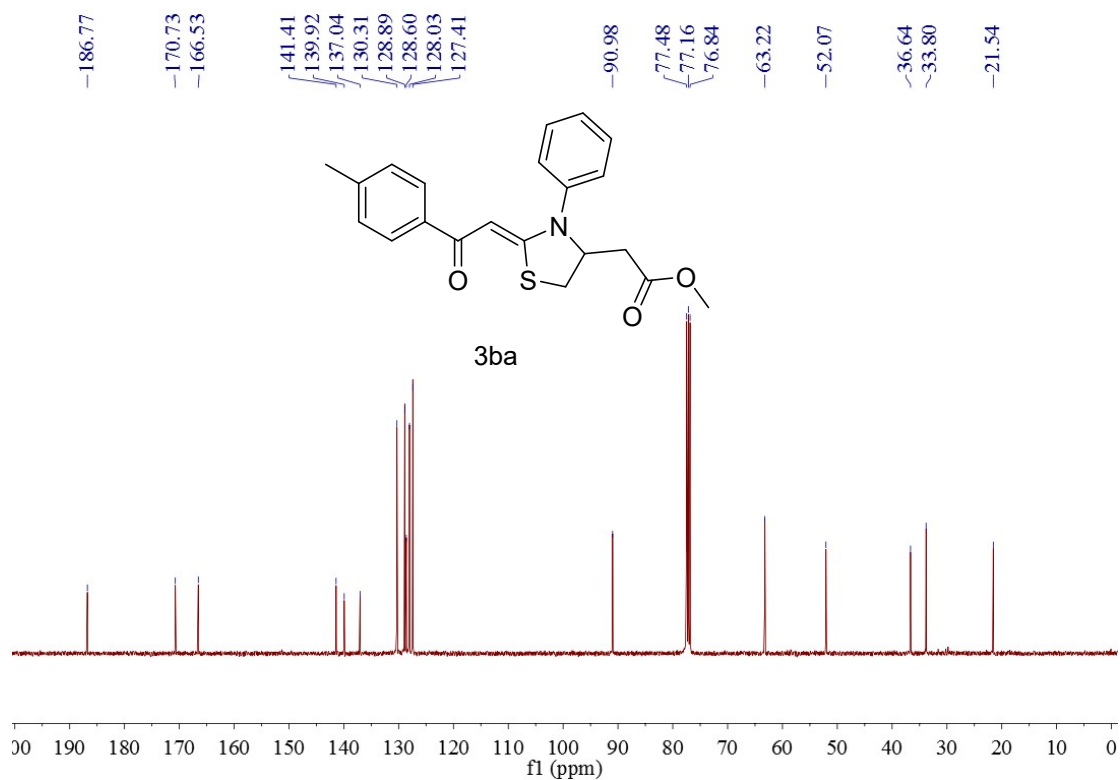


Figure S8. 3ca (^1H NMR, 400 MHz, CDCl_3)

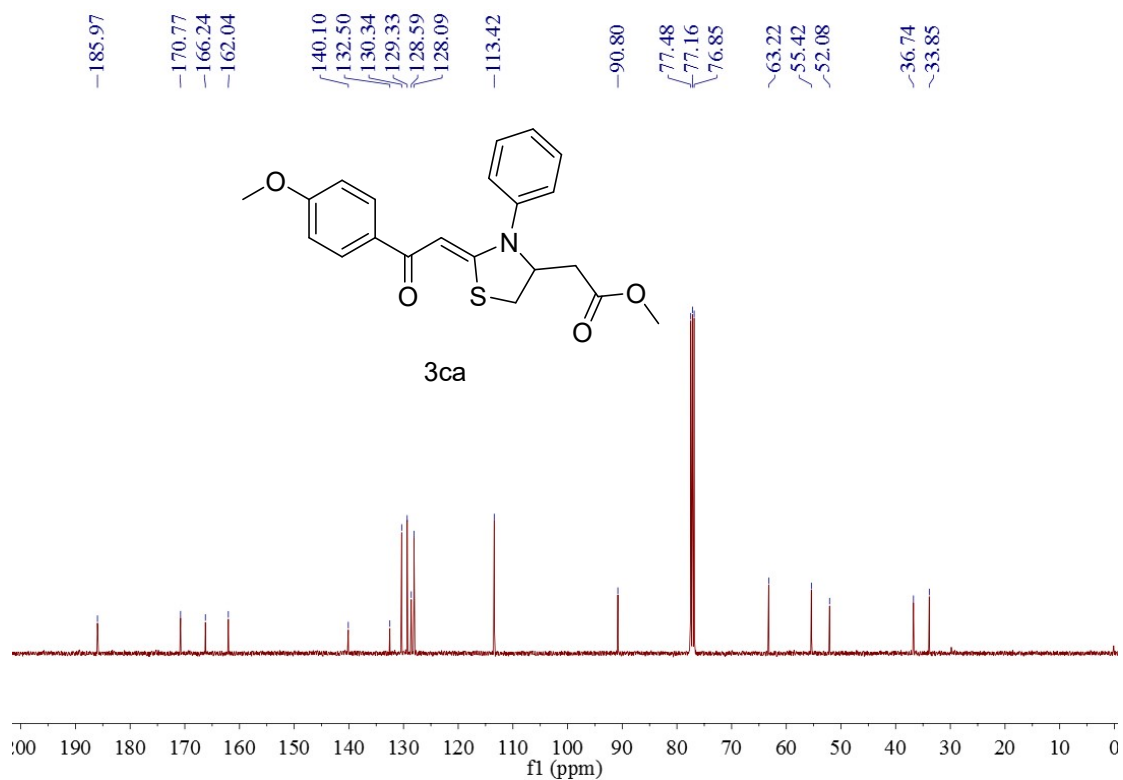


Figure S9. 3ca (^{13}C NMR, 100 MHz, CDCl_3)

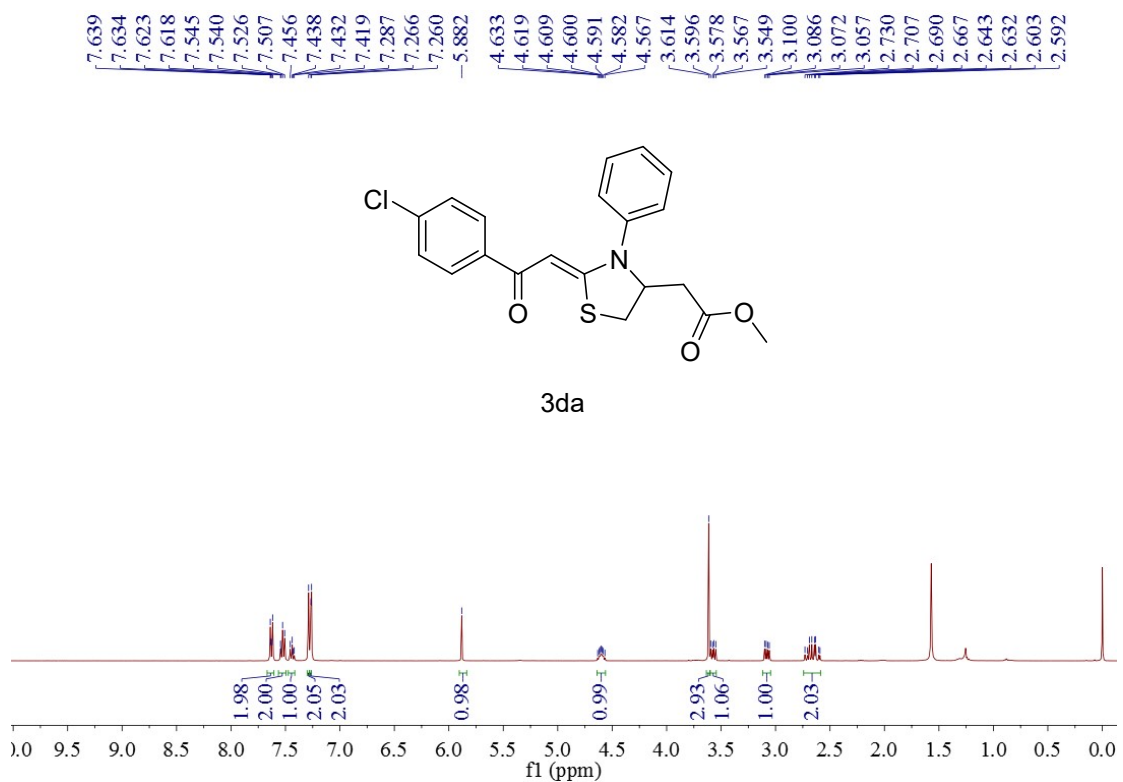


Figure S10. 3da (^1H NMR, 400 MHz, CDCl_3)

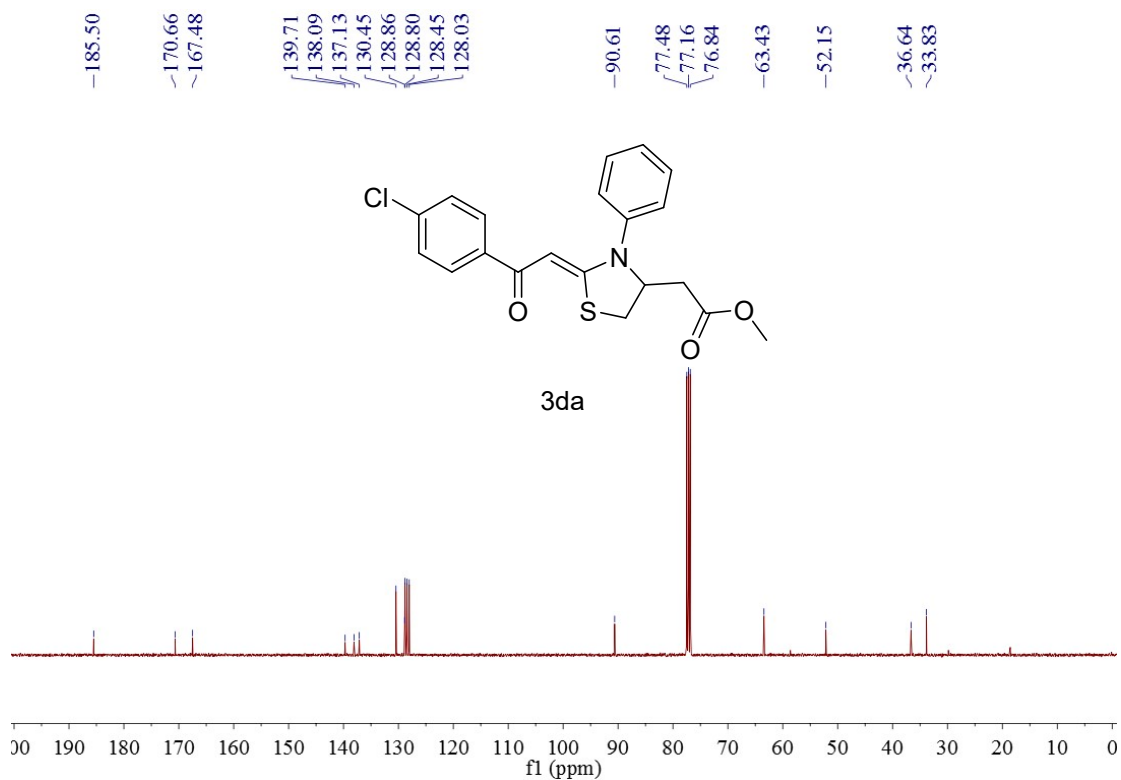


Figure S11. 3da (¹³C NMR, 100 MHz, CDCl₃)

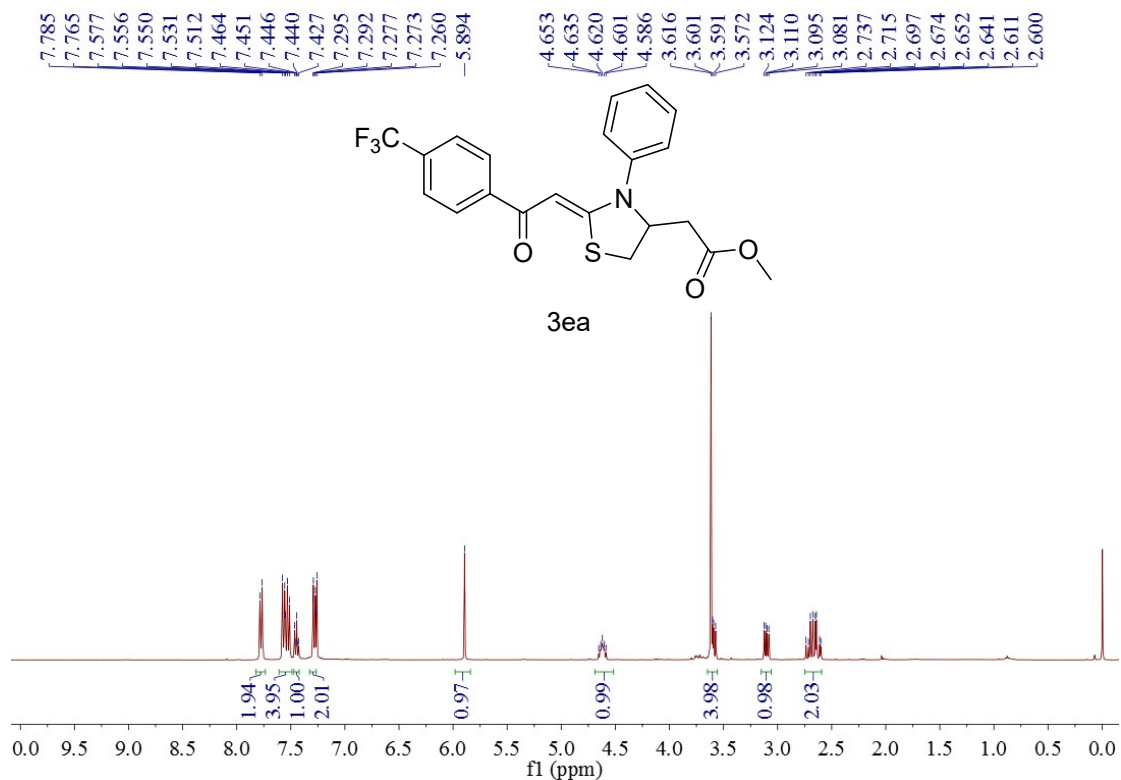


Figure S12. 3ea (¹H NMR, 400 MHz, CDCl₃)

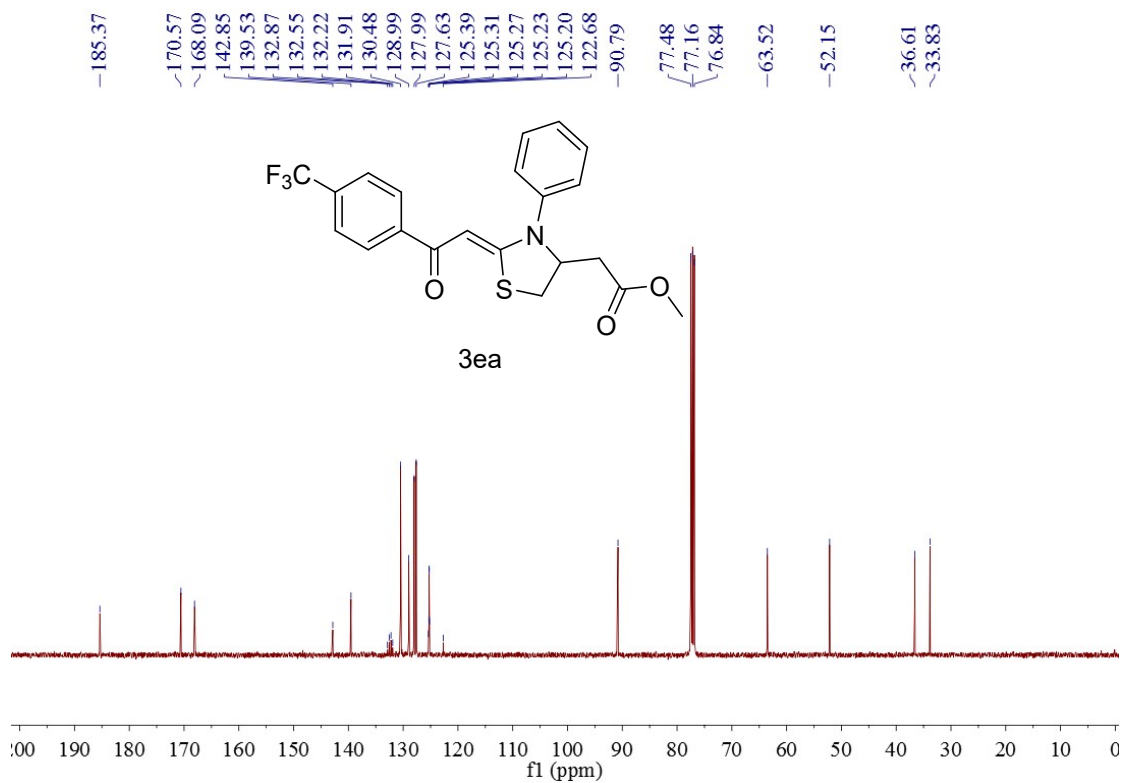


Figure S13. **3ea** (^{13}C NMR, 100 MHz, CDCl_3)

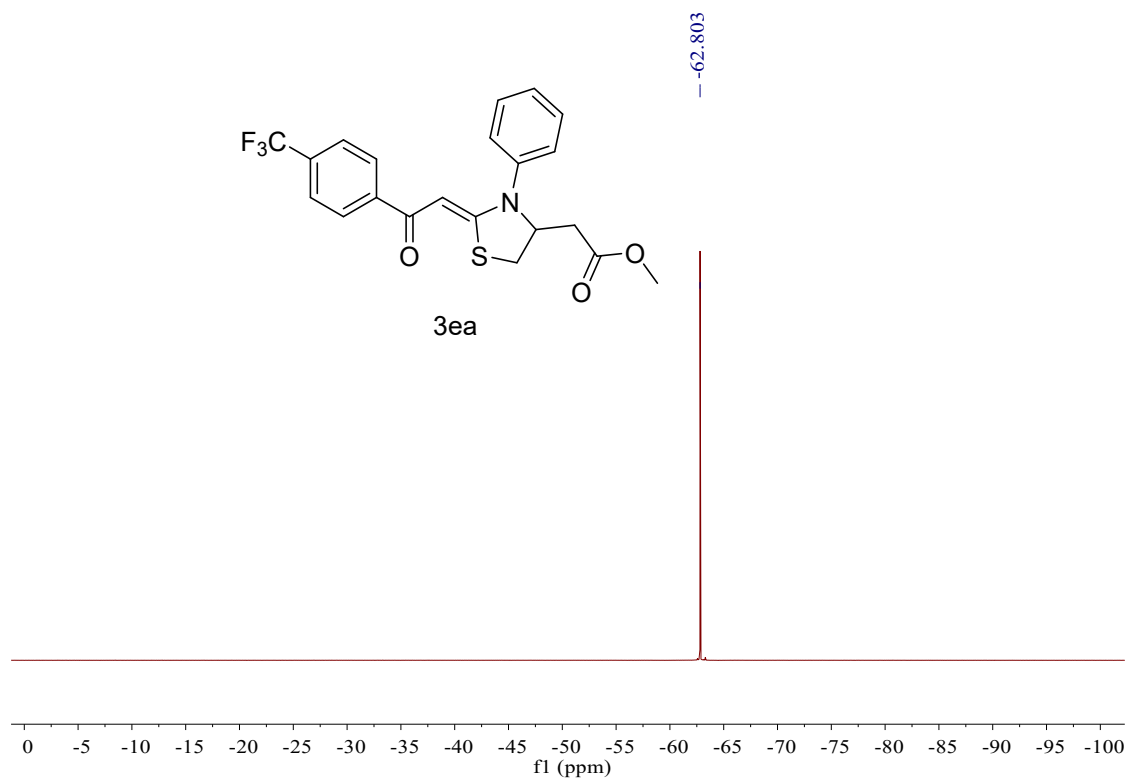


Figure S14. **3ea** (^{19}F NMR, 376 MHz, CDCl_3)

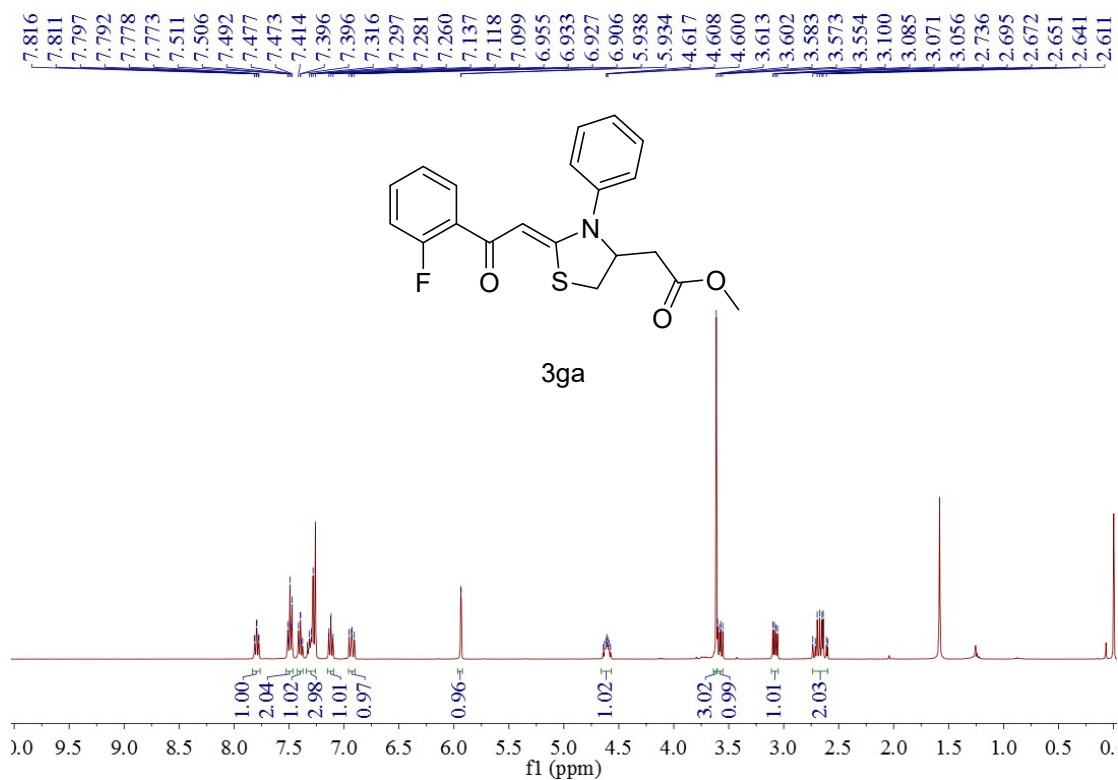


Figure S15. 3ga (^1H NMR, 400 MHz, CDCl_3)

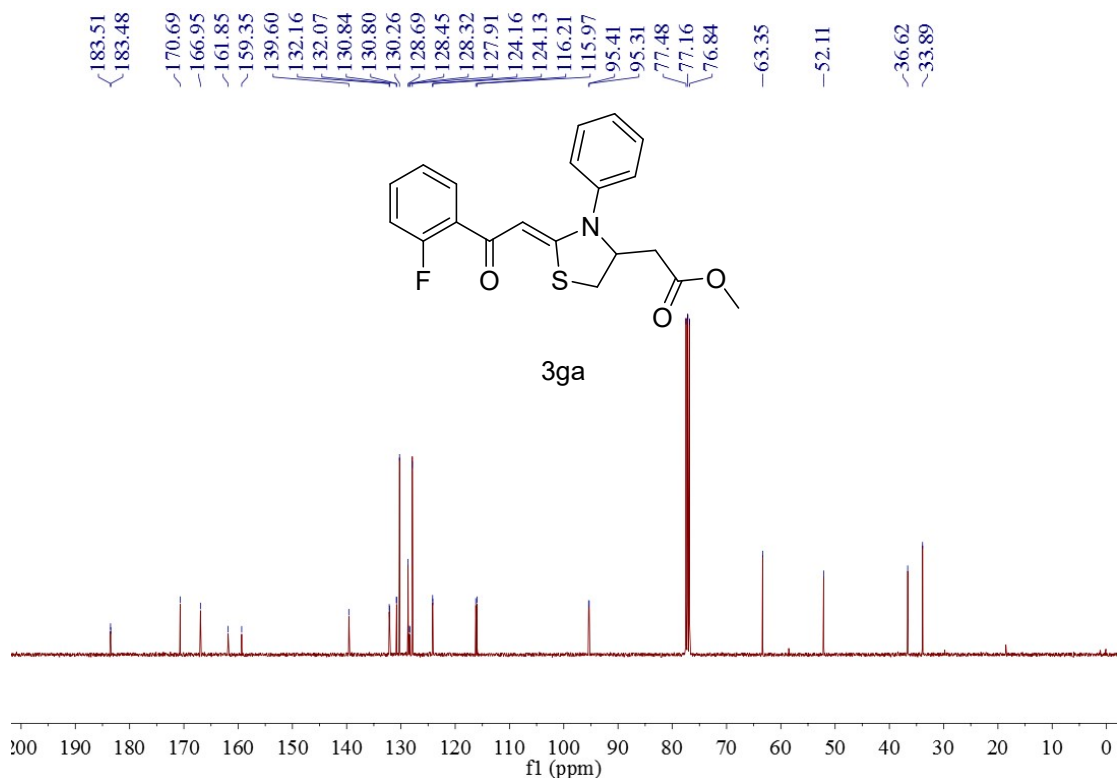


Figure S16. 3ga (^{13}C NMR, 100 MHz, CDCl_3)

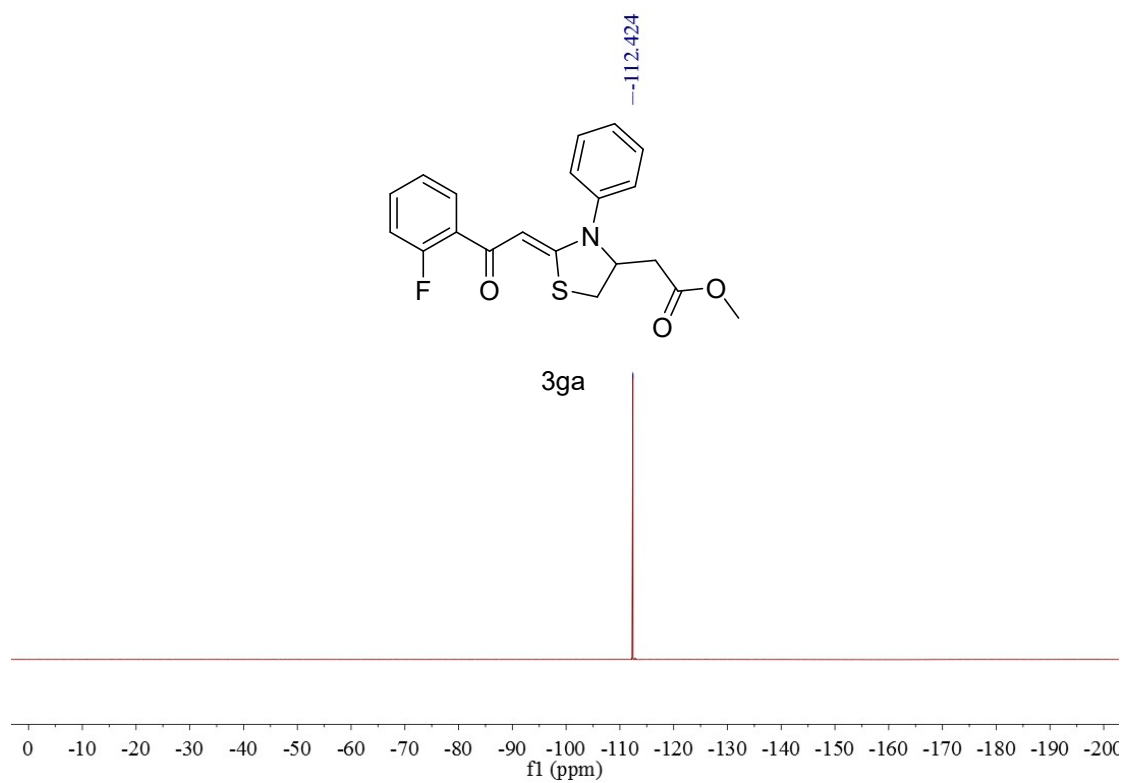


Figure S17. 3ga (¹⁹F NMR, 376 MHz, CDCl₃)

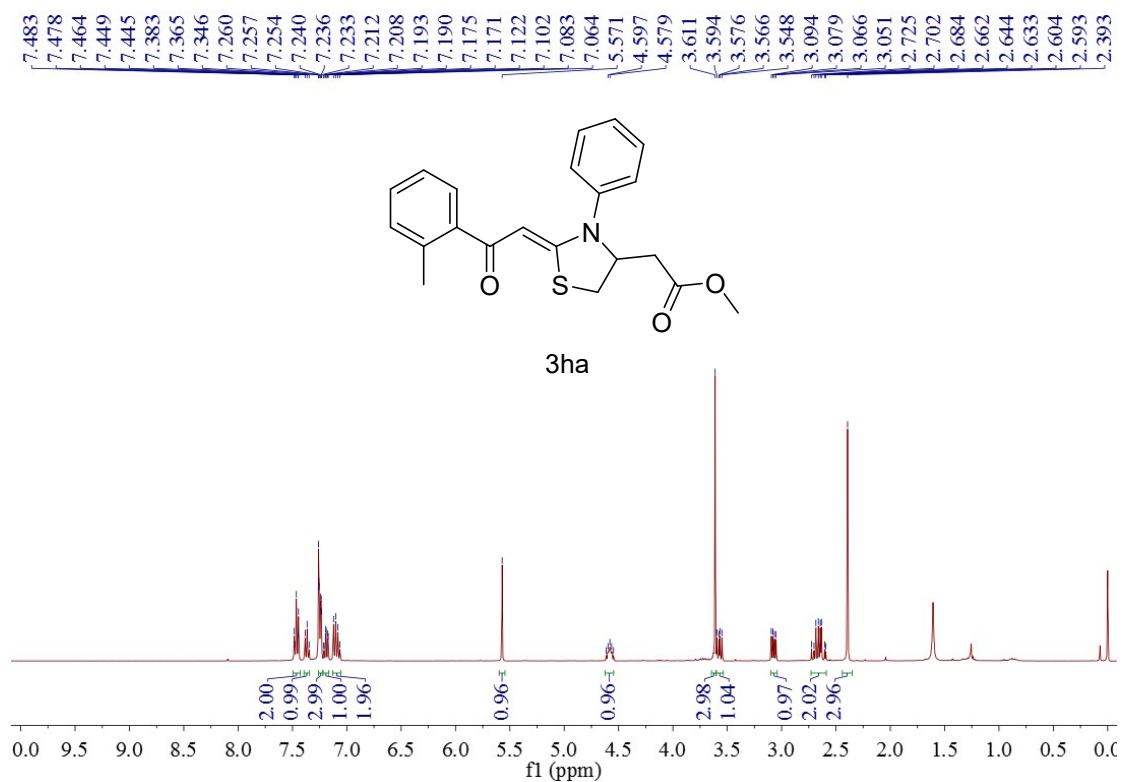


Figure S18. 3ha (¹H NMR, 400 MHz, CDCl₃)

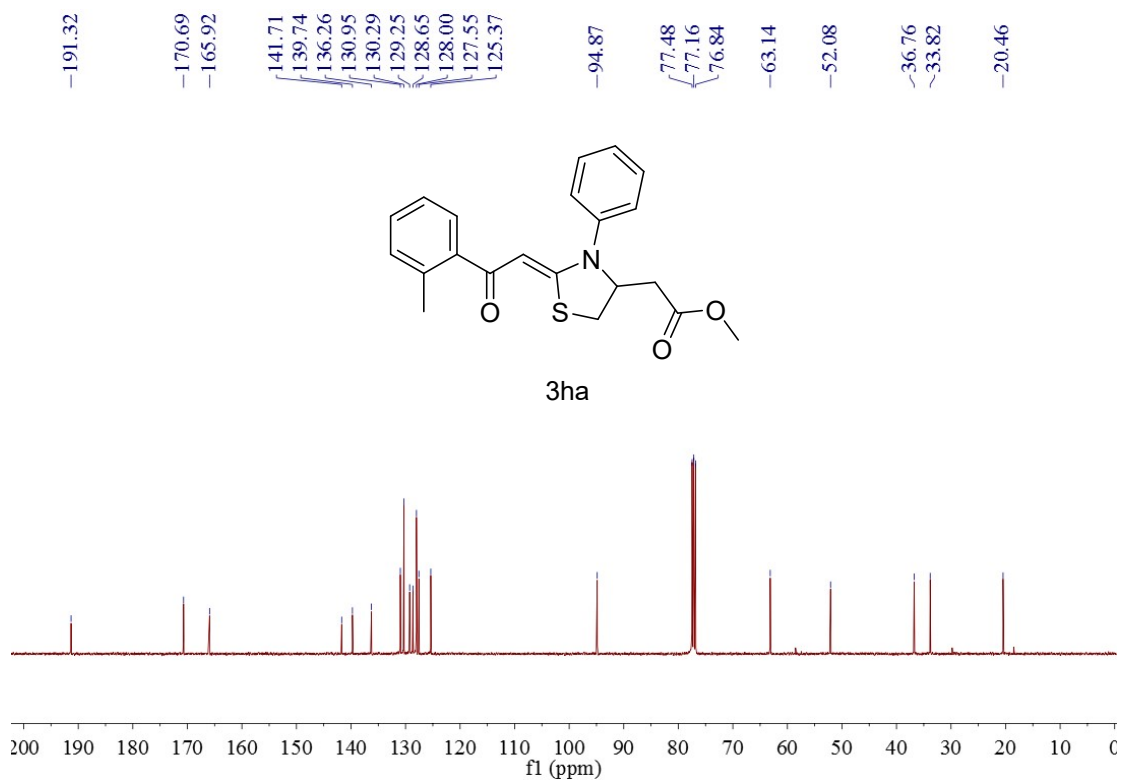


Figure S19. 3ha (^{13}C NMR, 100 MHz, CDCl_3)

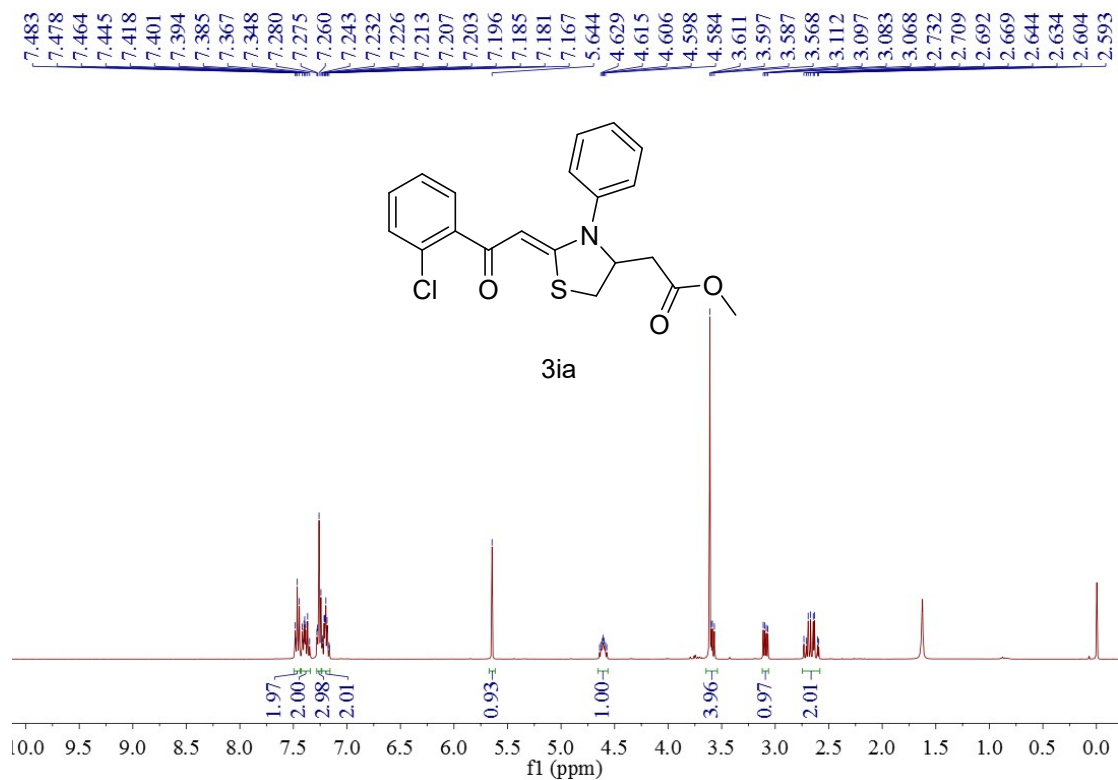


Figure S20. 3ia (^1H NMR, 400 MHz, CDCl_3)

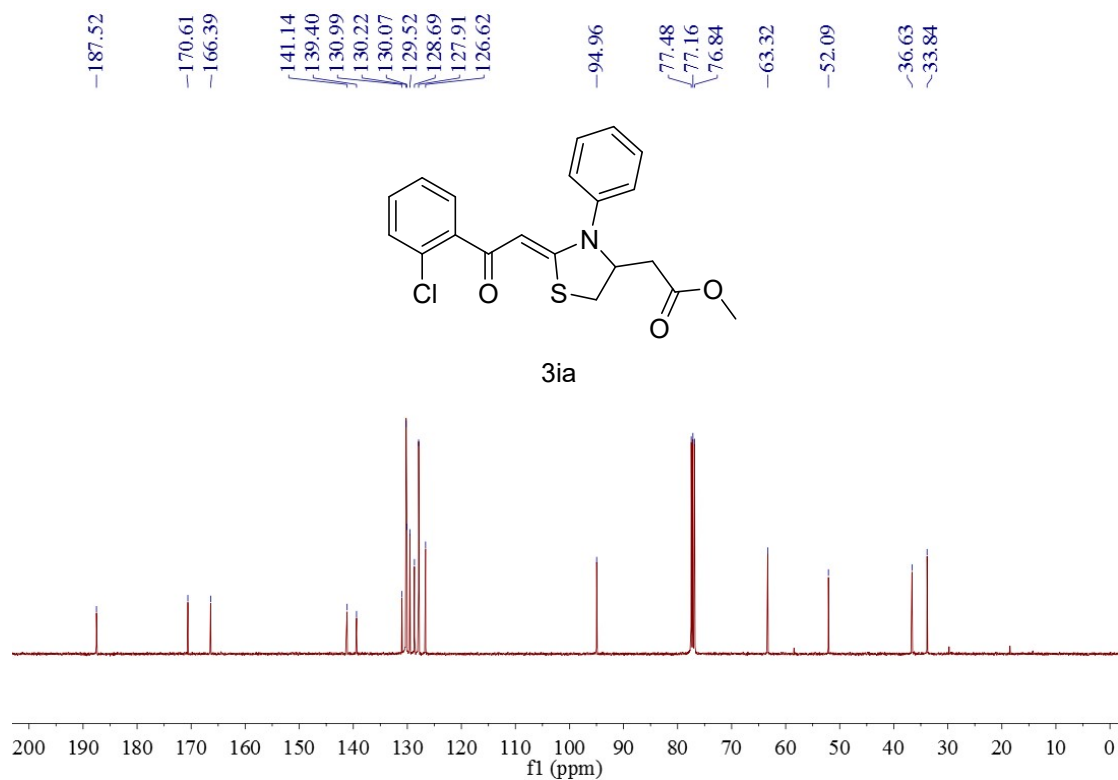


Figure S21. **3ia** (^{13}C NMR, 100 MHz, CDCl_3)

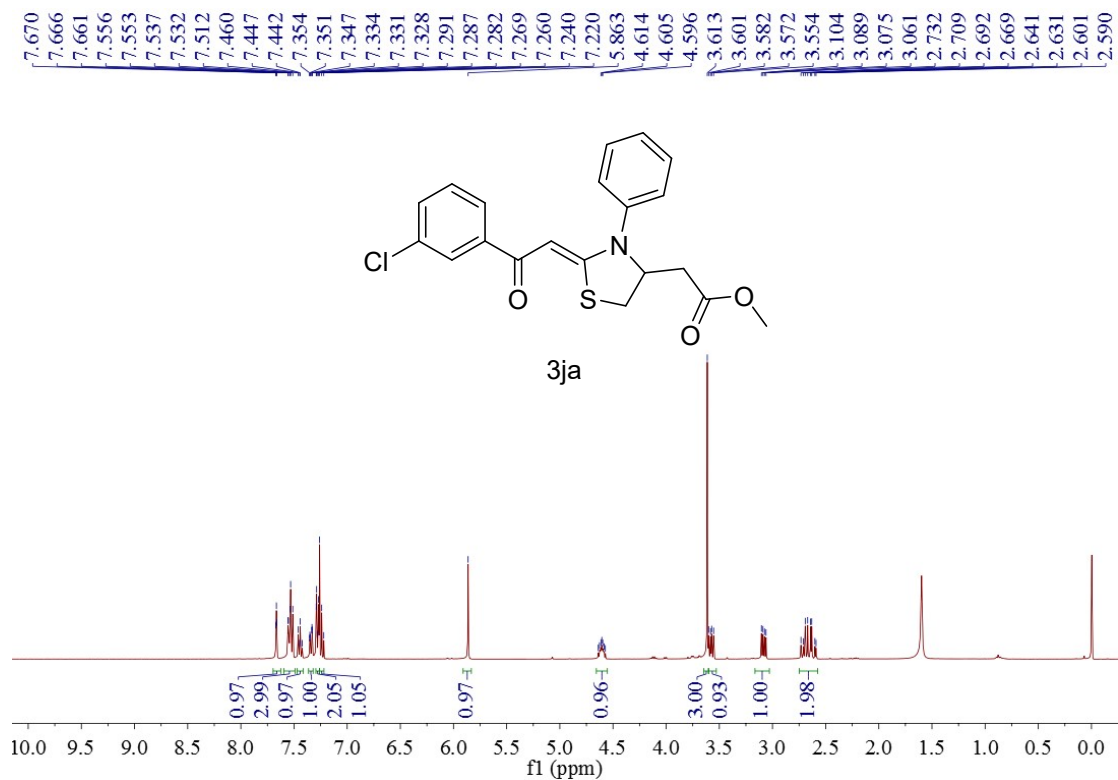


Figure S22. **3ja** (^1H NMR, 400 MHz, CDCl_3)

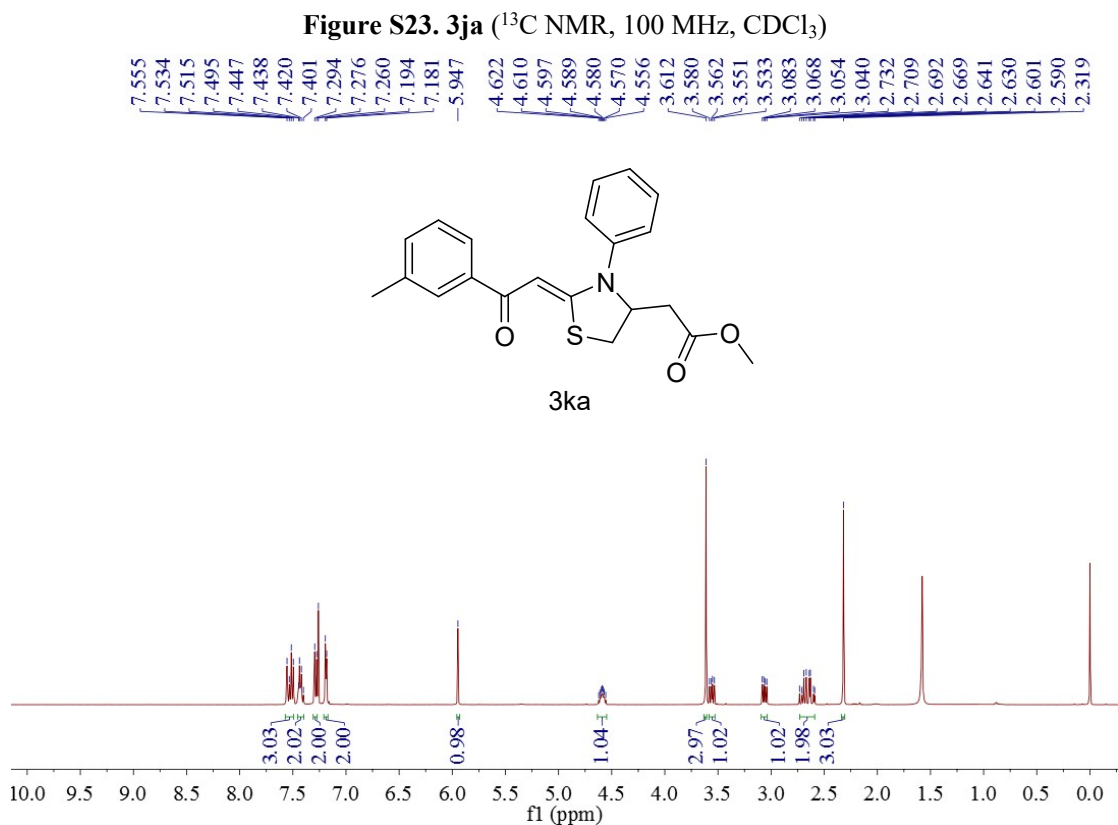
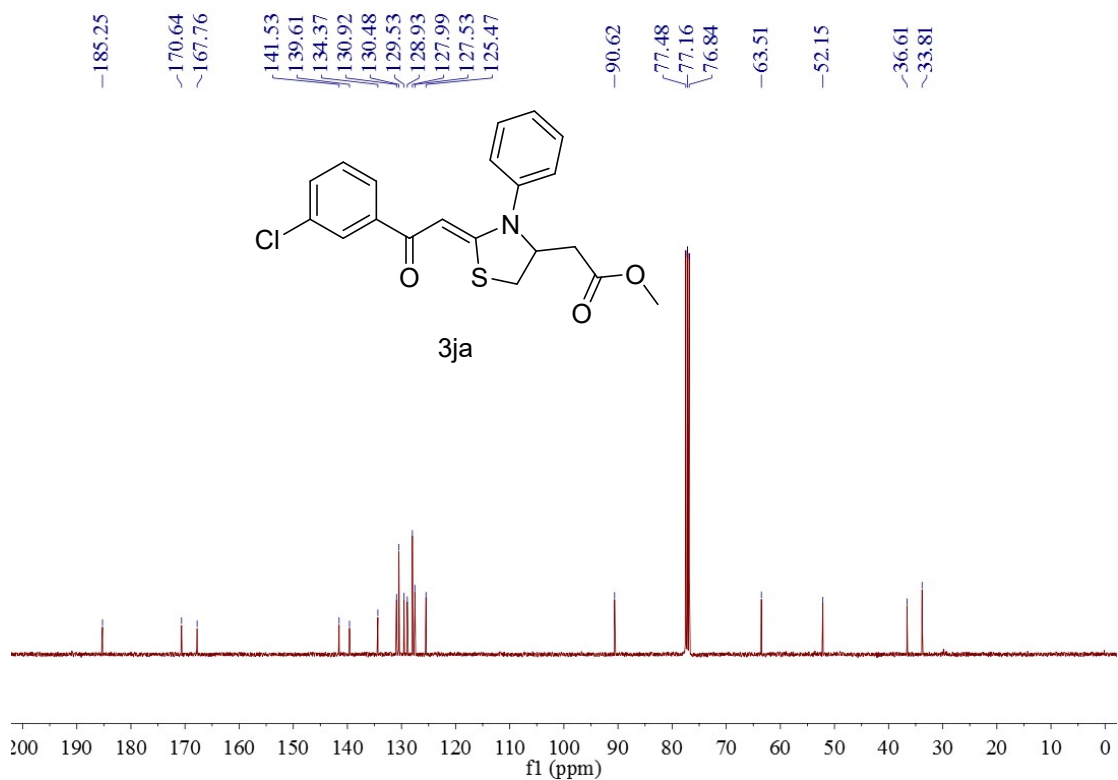


Figure S24. 3ka (^1H NMR, 400 MHz, CDCl_3)

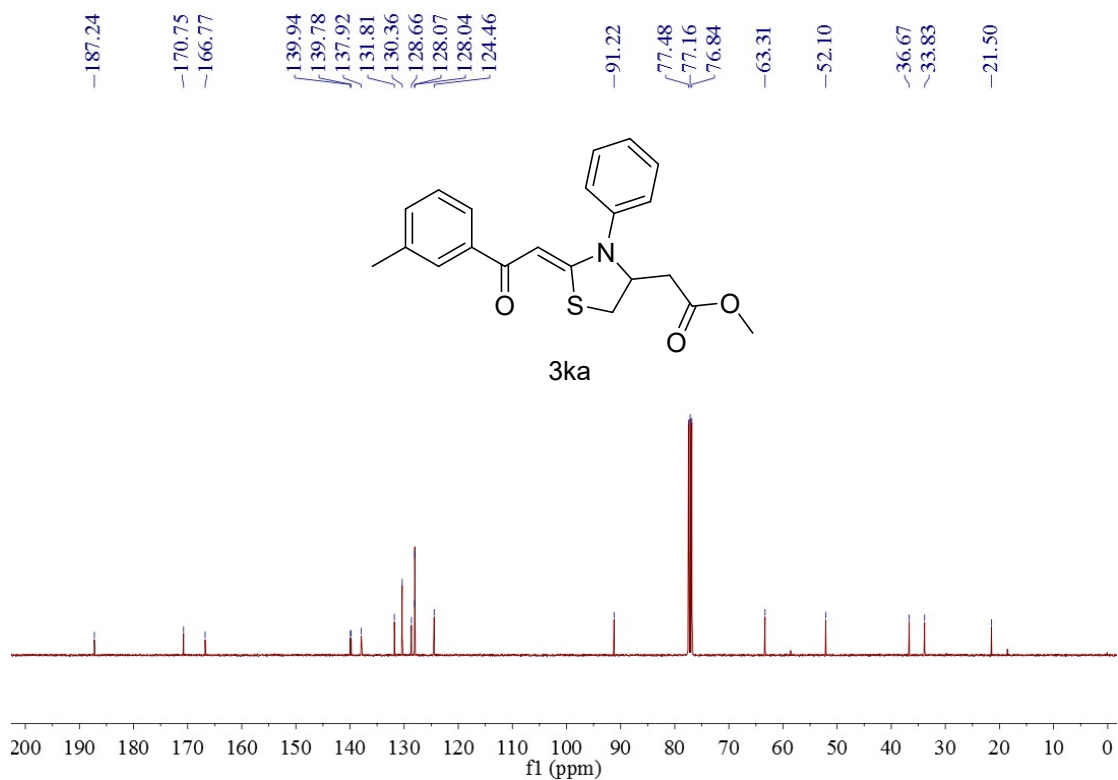


Figure S25. 3ka (^{13}C NMR, 100 MHz, CDCl_3)

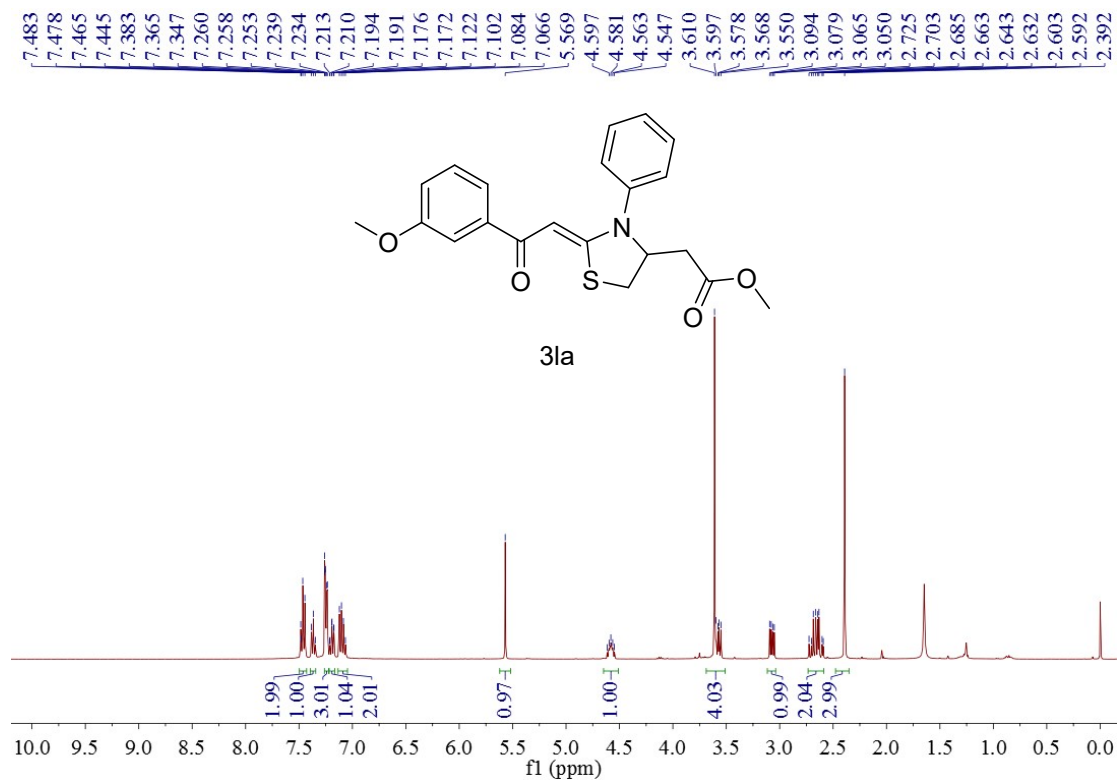


Figure S26. 3la (^1H NMR, 400 MHz, CDCl_3)

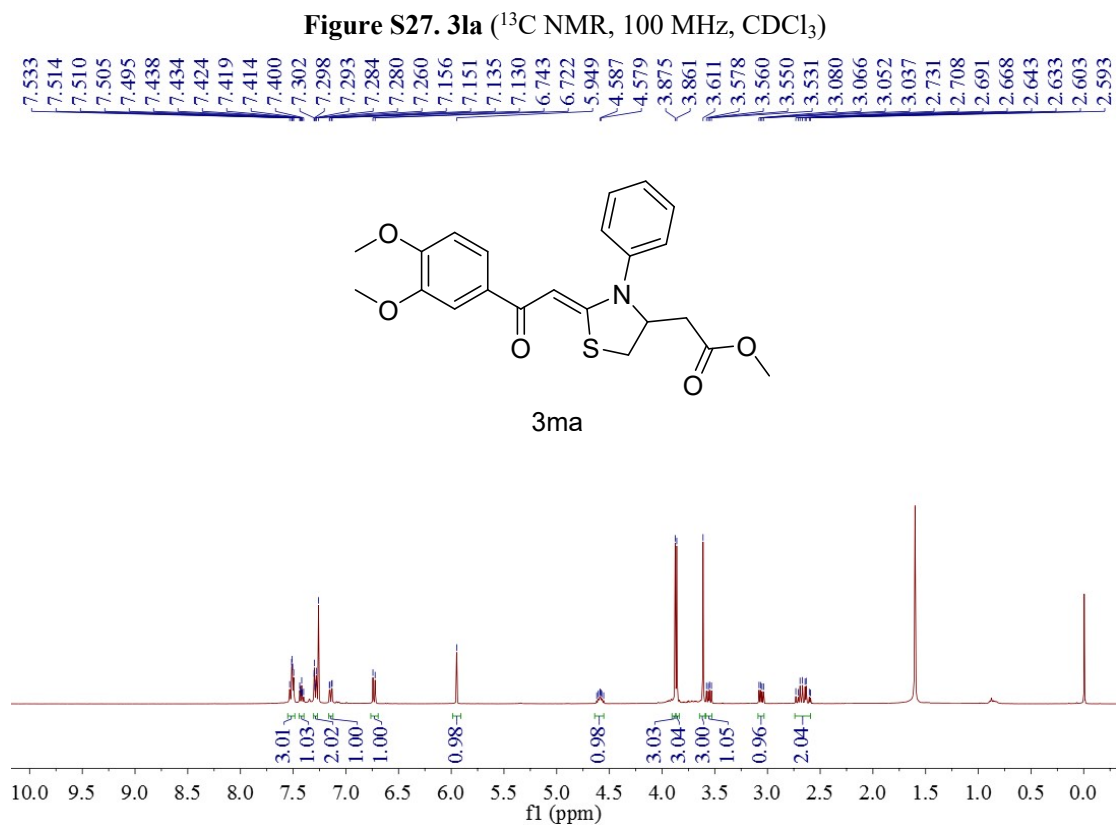
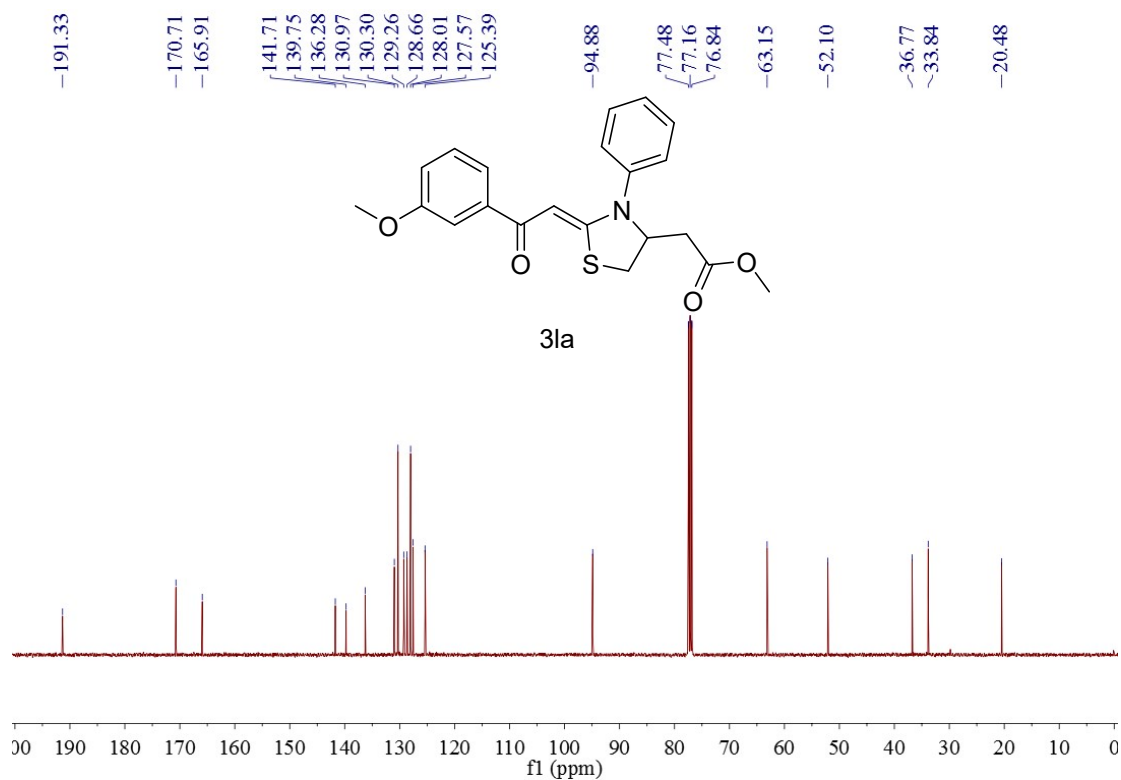


Figure S28. 3ma (^1H NMR, 400 MHz, CDCl_3)

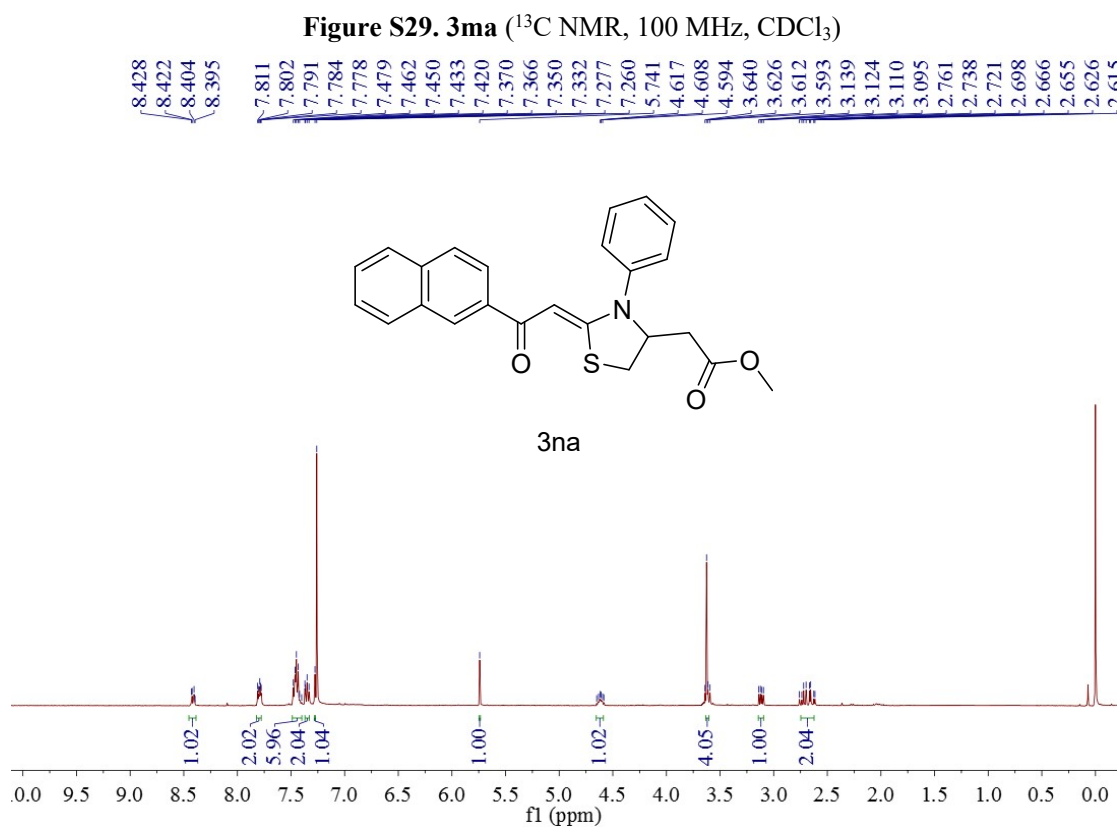
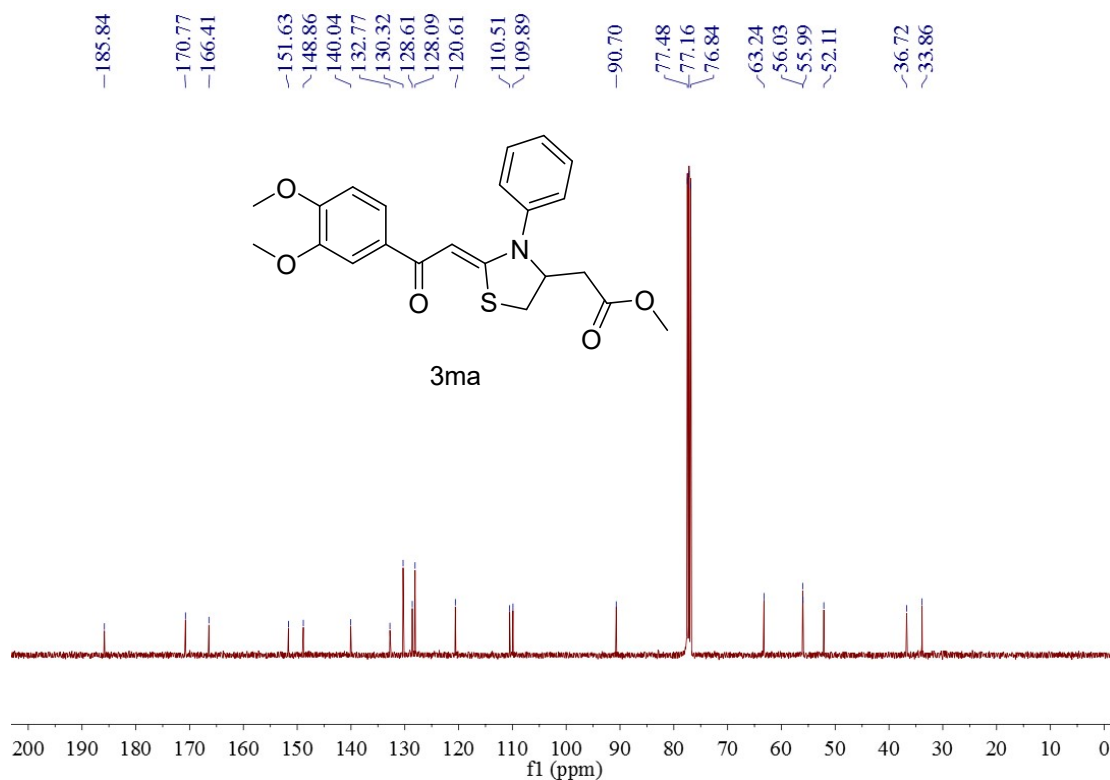


Figure S30. 3na (^1H NMR, 400 MHz, CDCl_3)

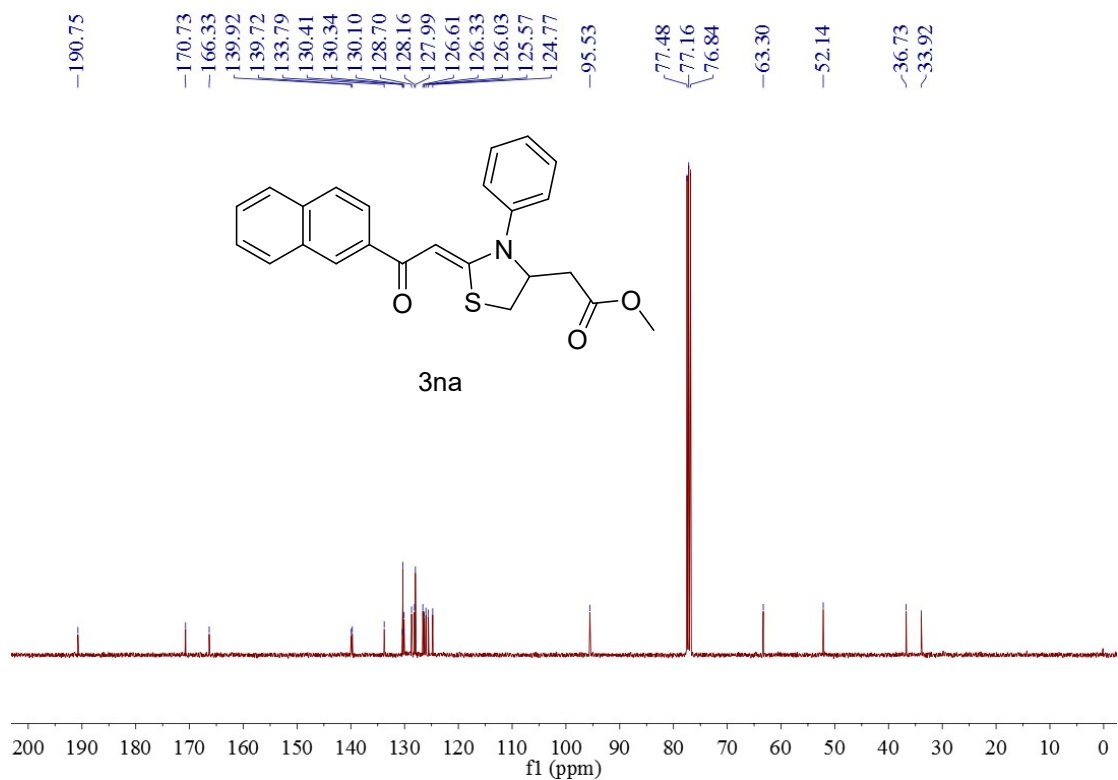


Figure S31. 3na (¹³C NMR, 100 MHz, CDCl₃)

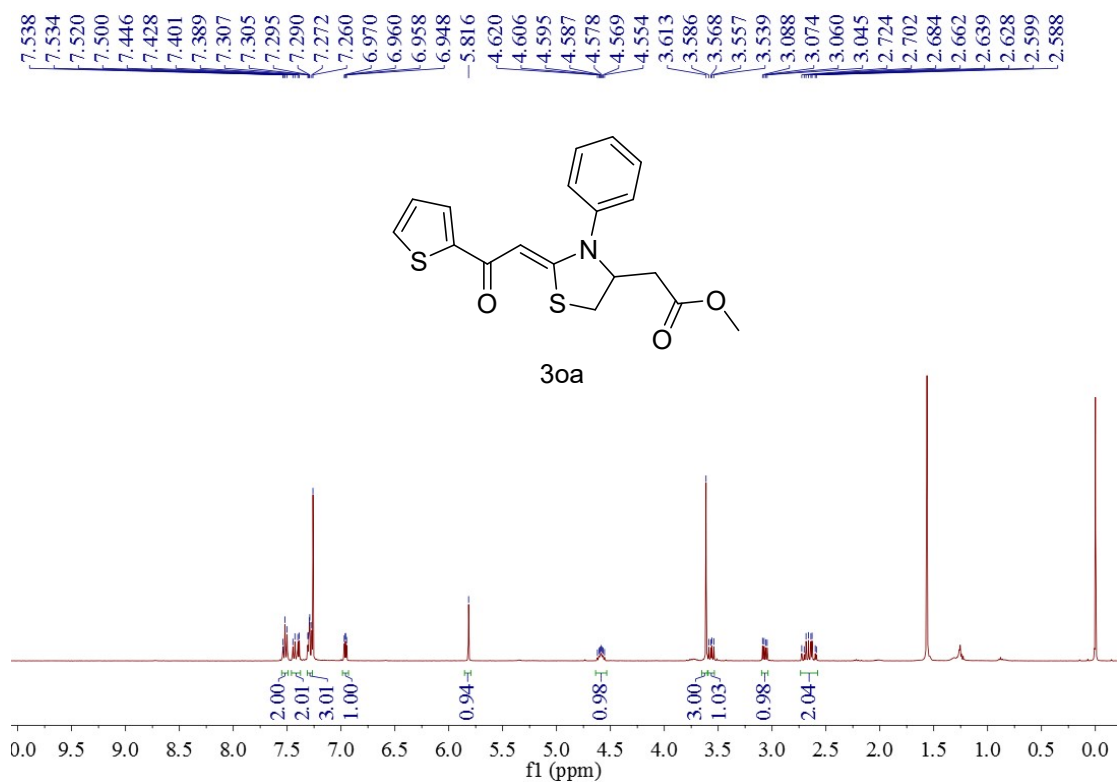


Figure S32. 3oa (¹H NMR, 400 MHz, CDCl₃)

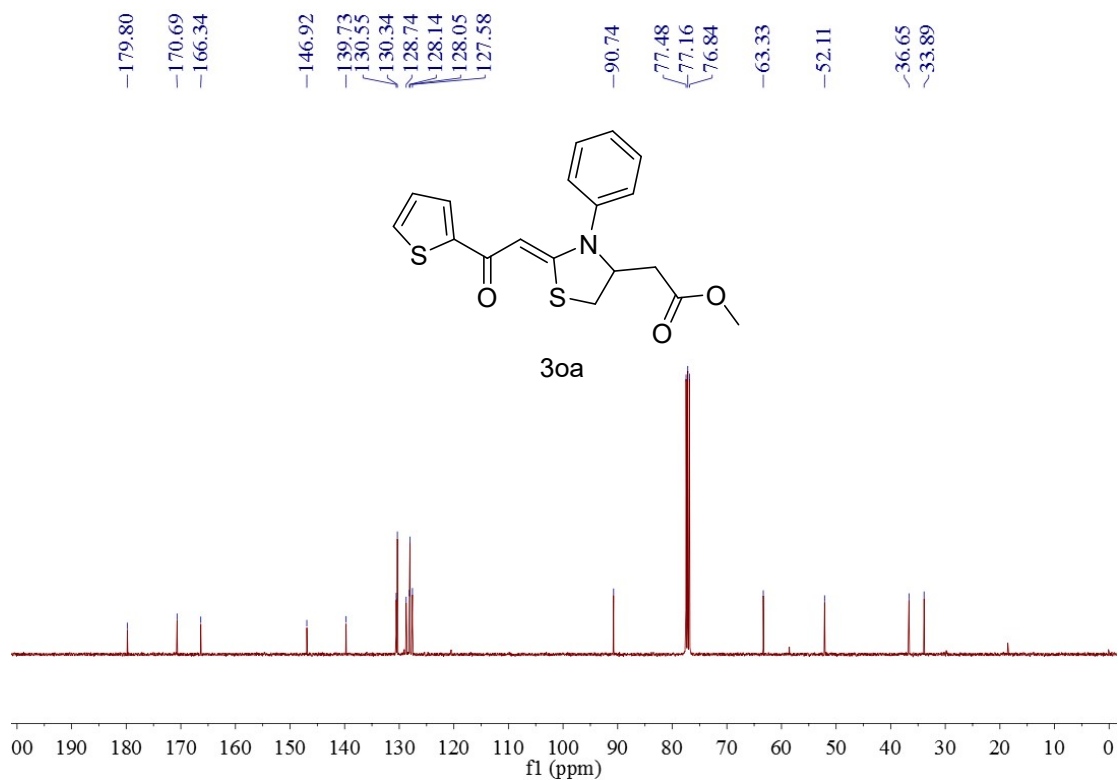


Figure S33. 30a (^{13}C NMR, 100 MHz, CDCl_3)

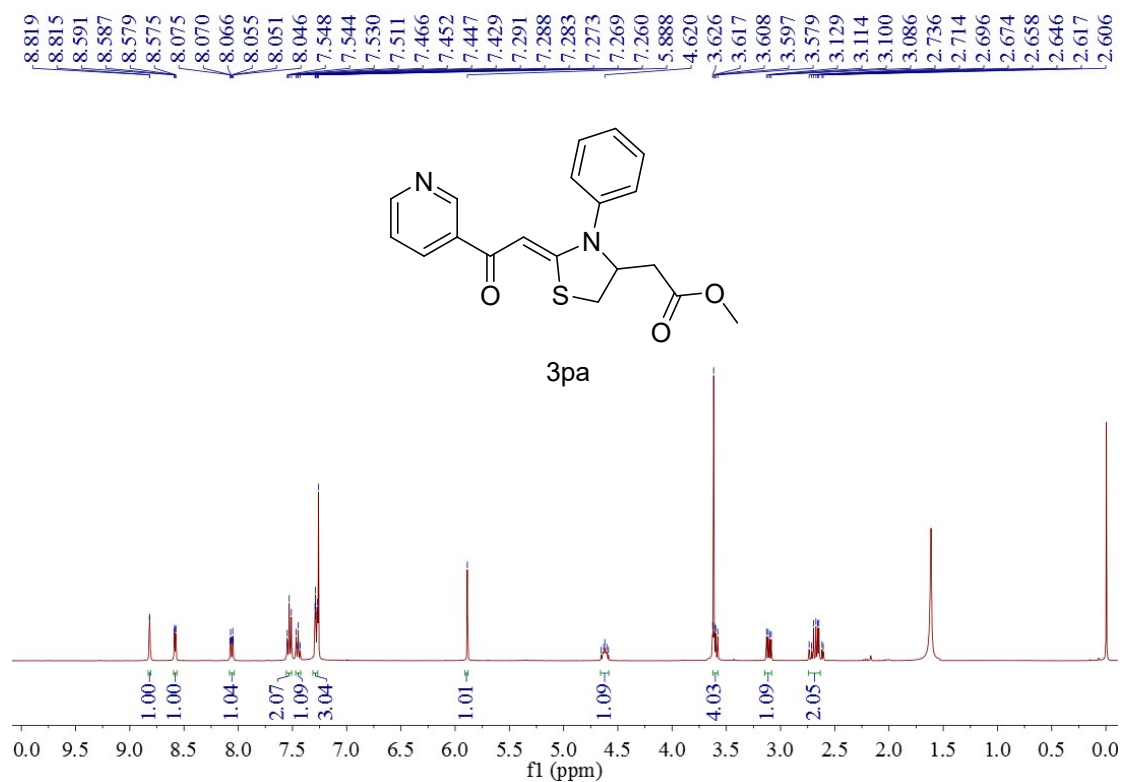


Figure S34. 3pa (^1H NMR, 400 MHz, CDCl_3)

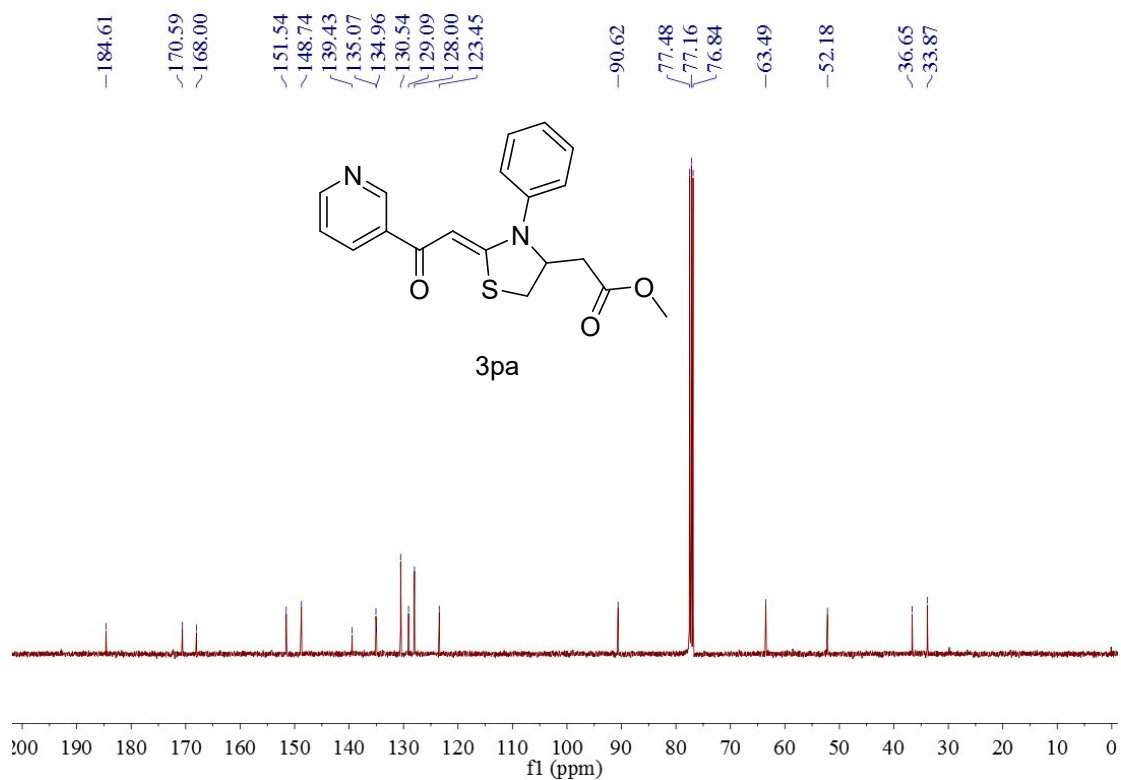


Figure S35. 3pa (^{13}C NMR, 100 MHz, CDCl_3)

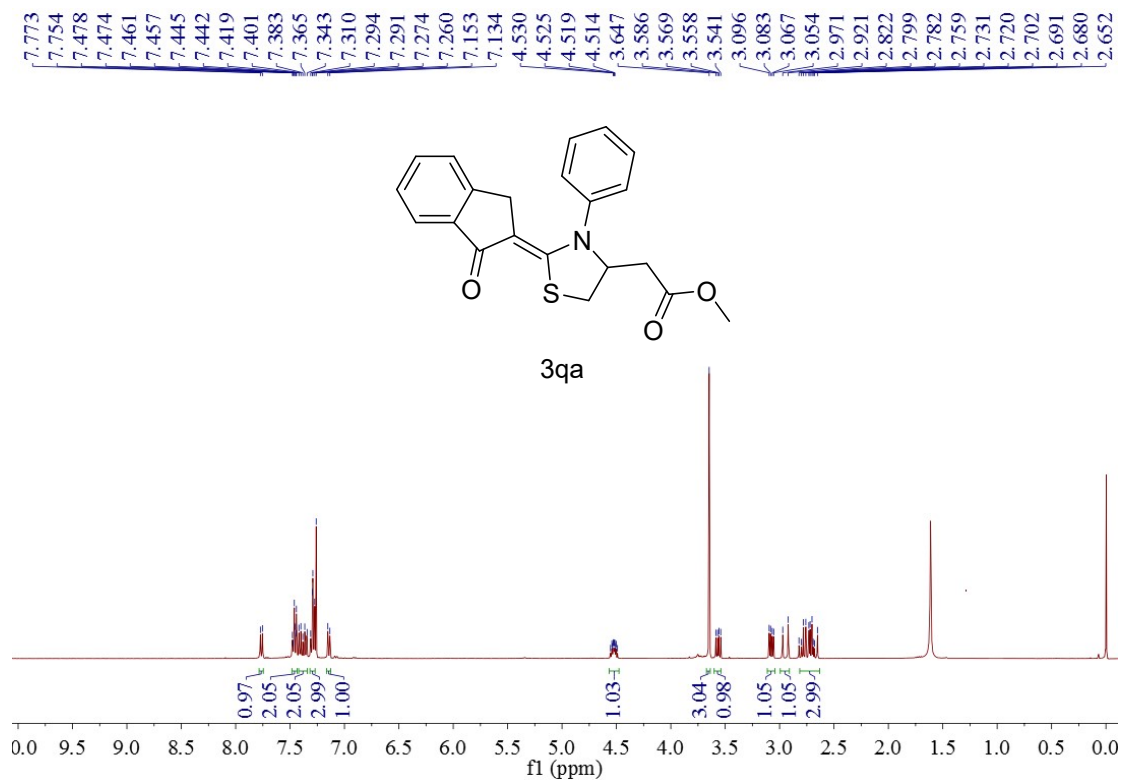


Figure S36. 3qa (^1H NMR, 400 MHz, CDCl_3)

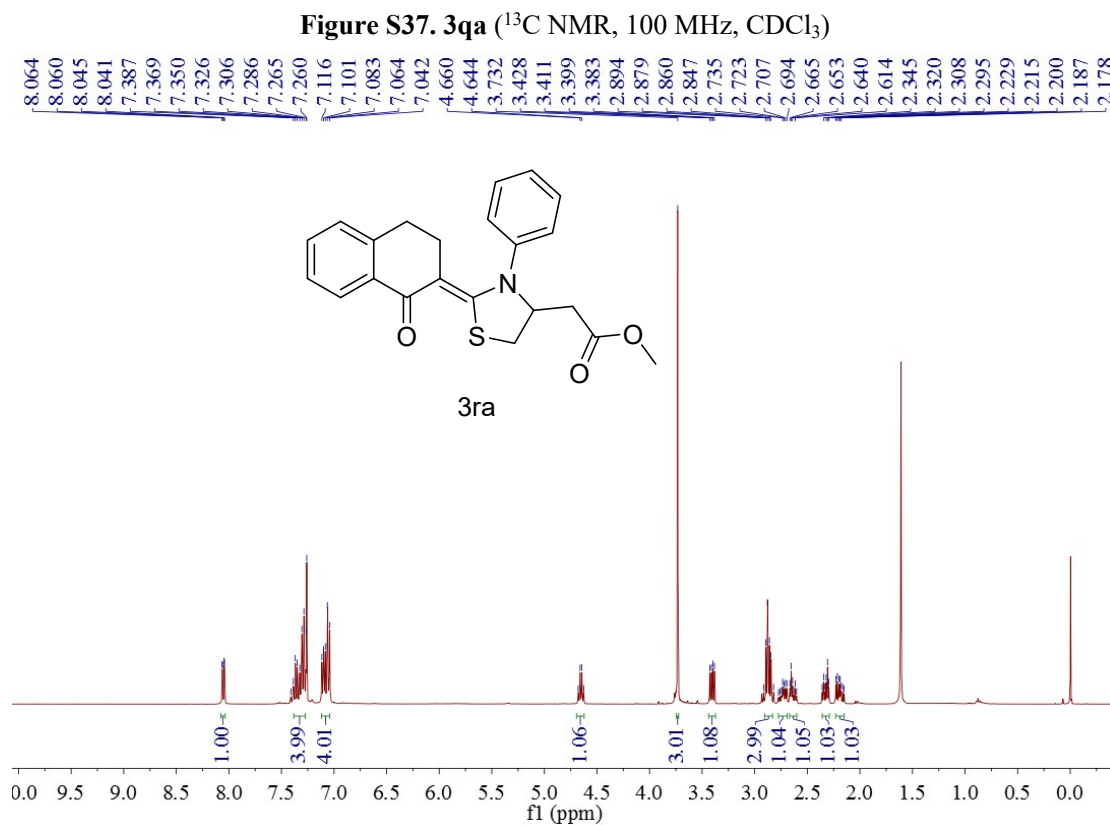
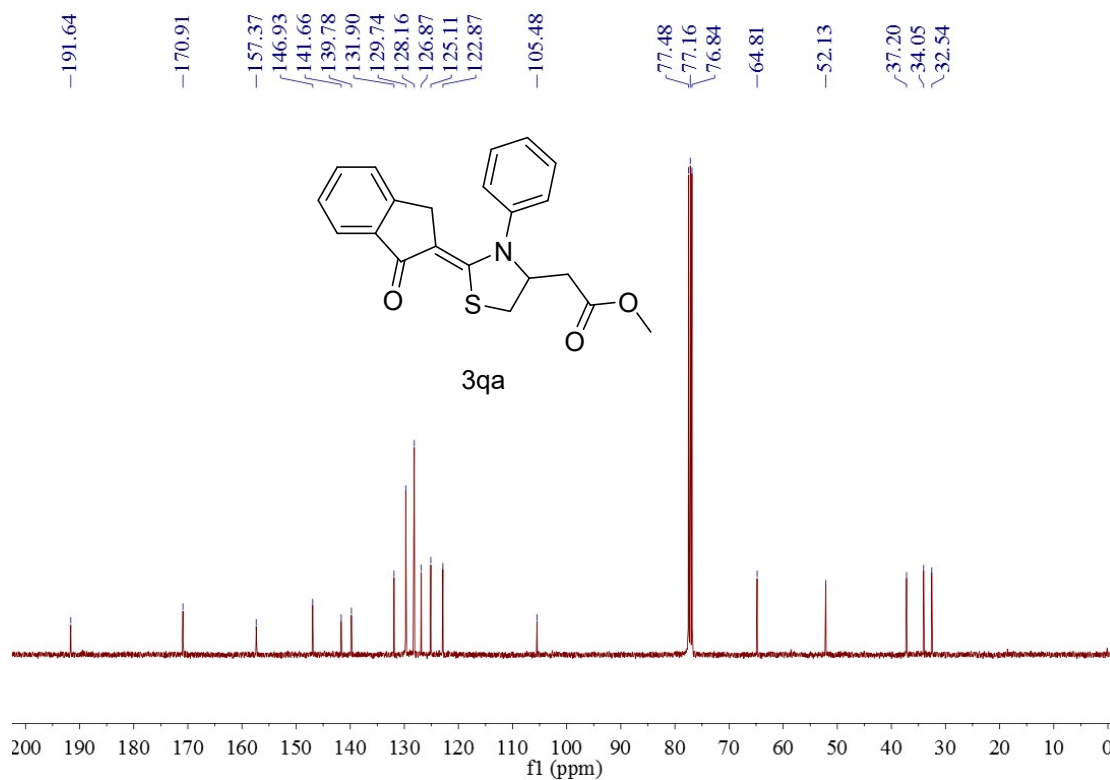


Figure S38. 3ra (¹H NMR, 400 MHz, CDCl₃)

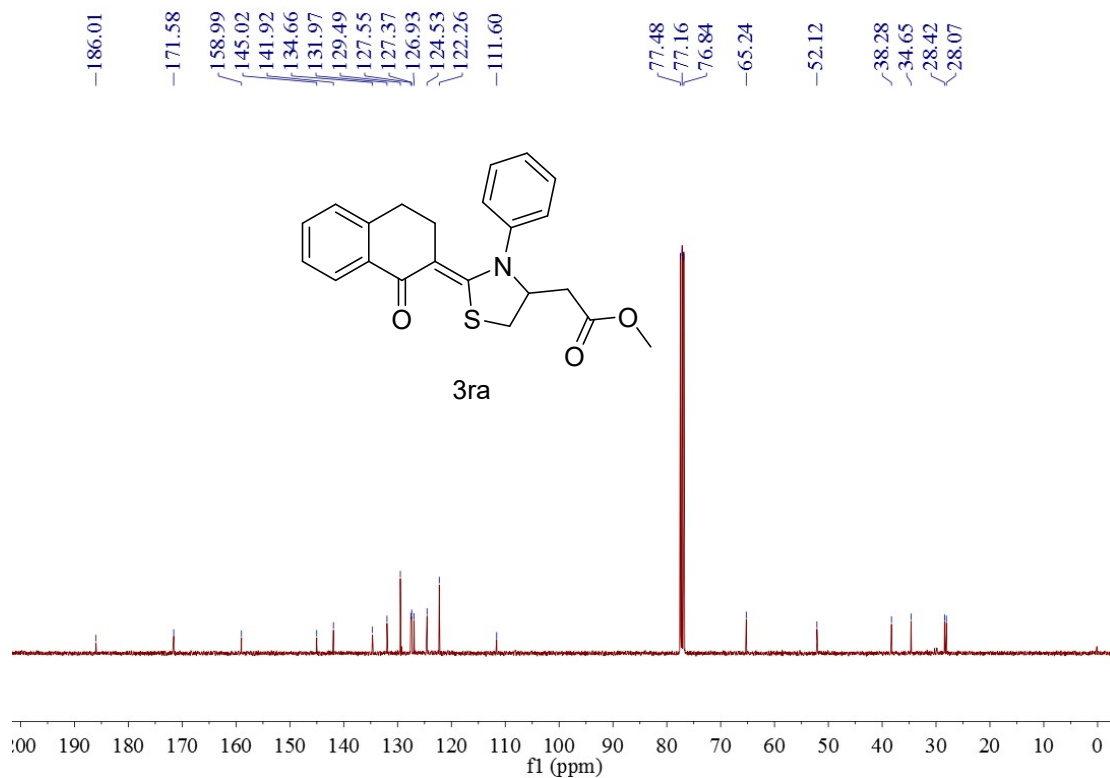


Figure S39. 3ra (¹³C NMR, 100 MHz, CDCl₃)

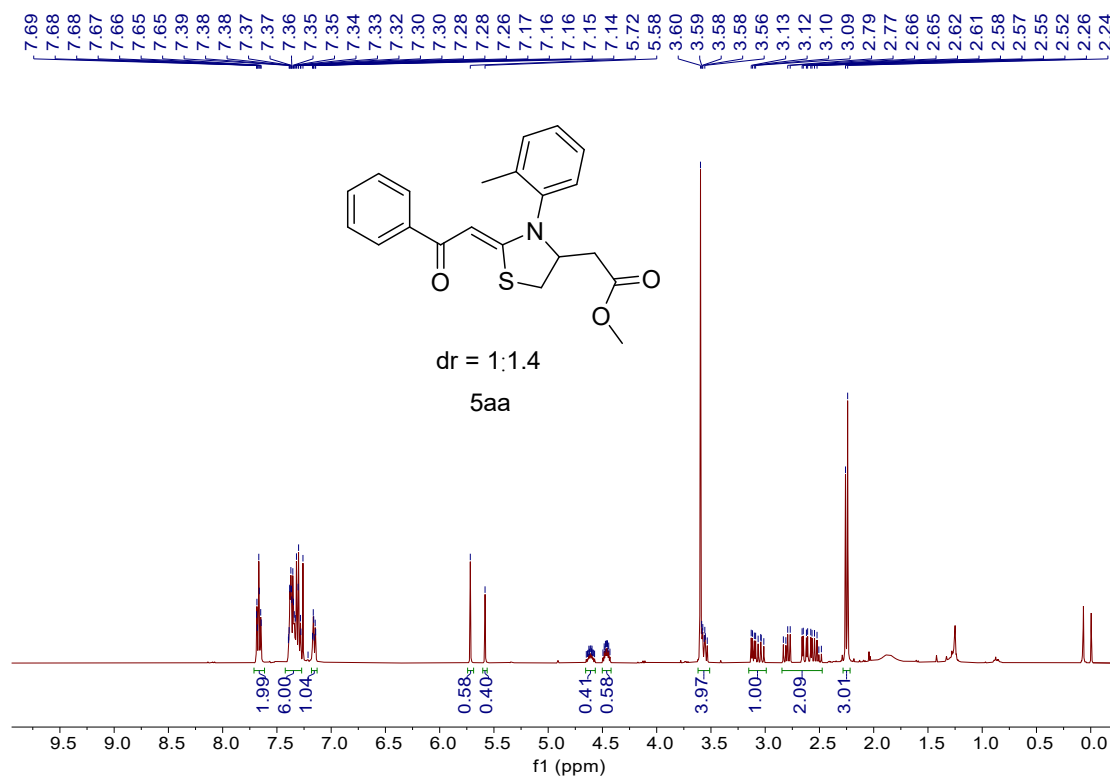


Figure S40. 5aa (¹H NMR, 400 MHz, CDCl₃)

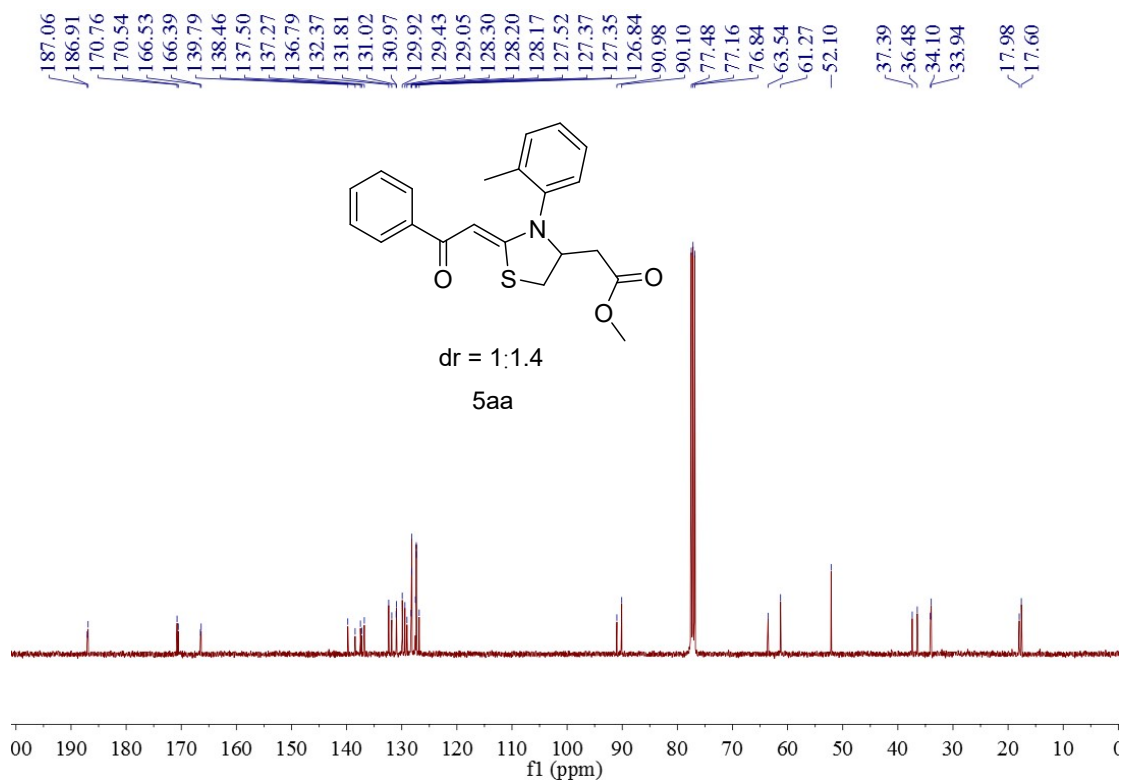


Figure S41. 5aa (^{13}C NMR, 100 MHz, CDCl_3)

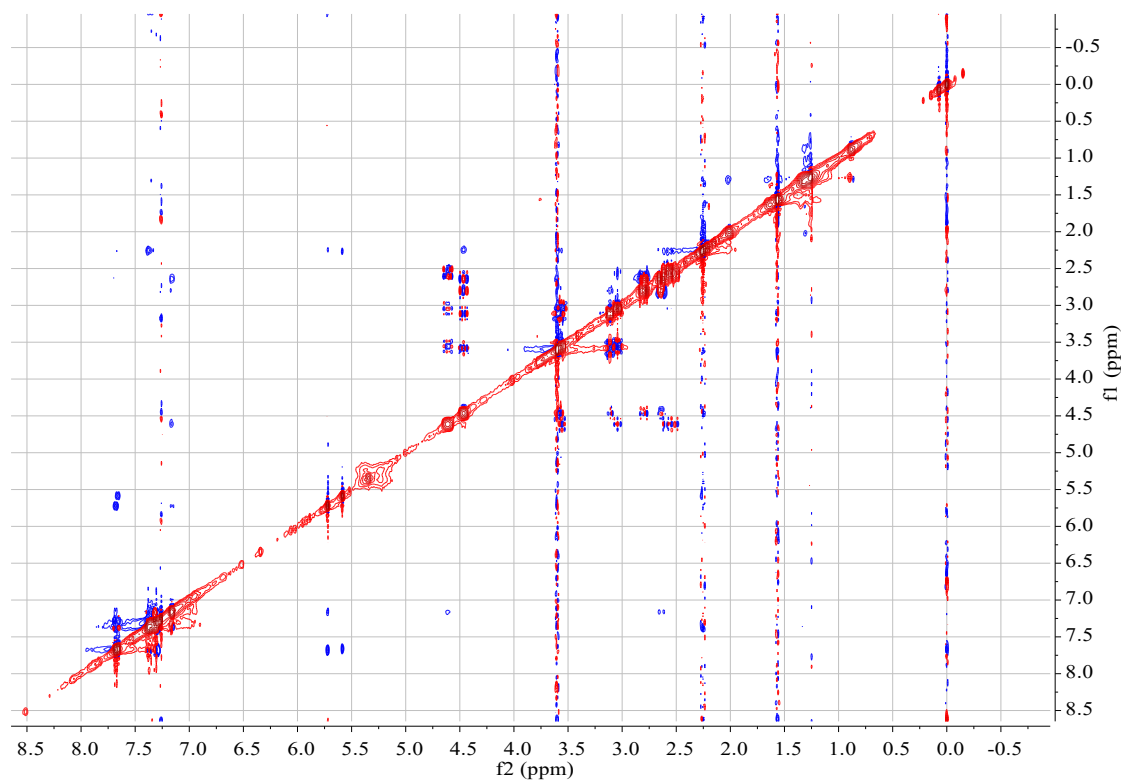


Figure S42. 5aa (^1H NMR, NOESY, 400 MHz, CDCl_3)

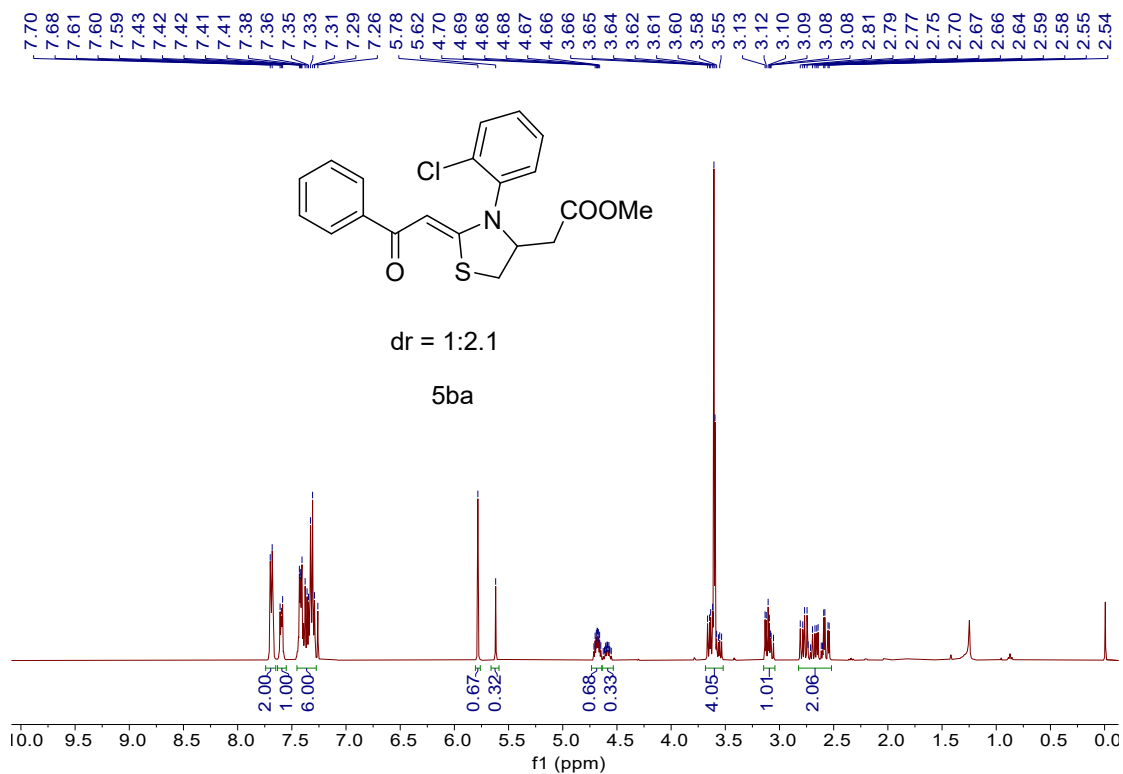


Figure S43. 5ba (^1H NMR, 400 MHz, CDCl_3)

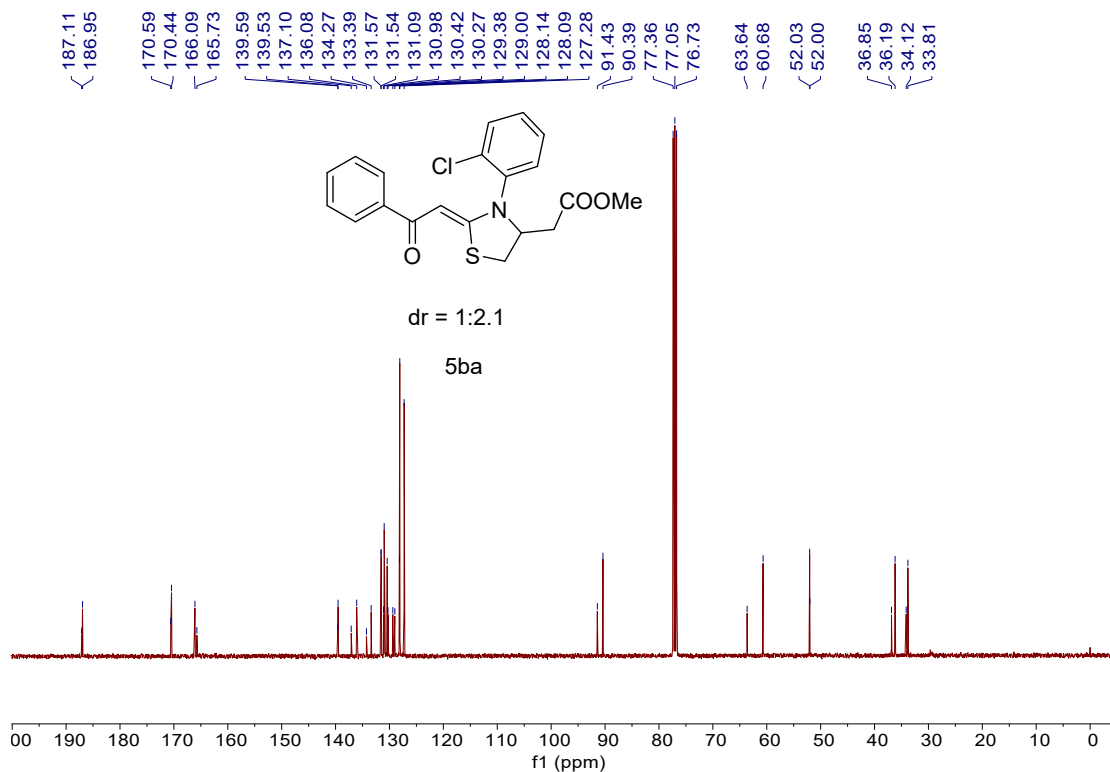


Figure S44. 5ba (^{13}C NMR, 100 MHz, CDCl_3)

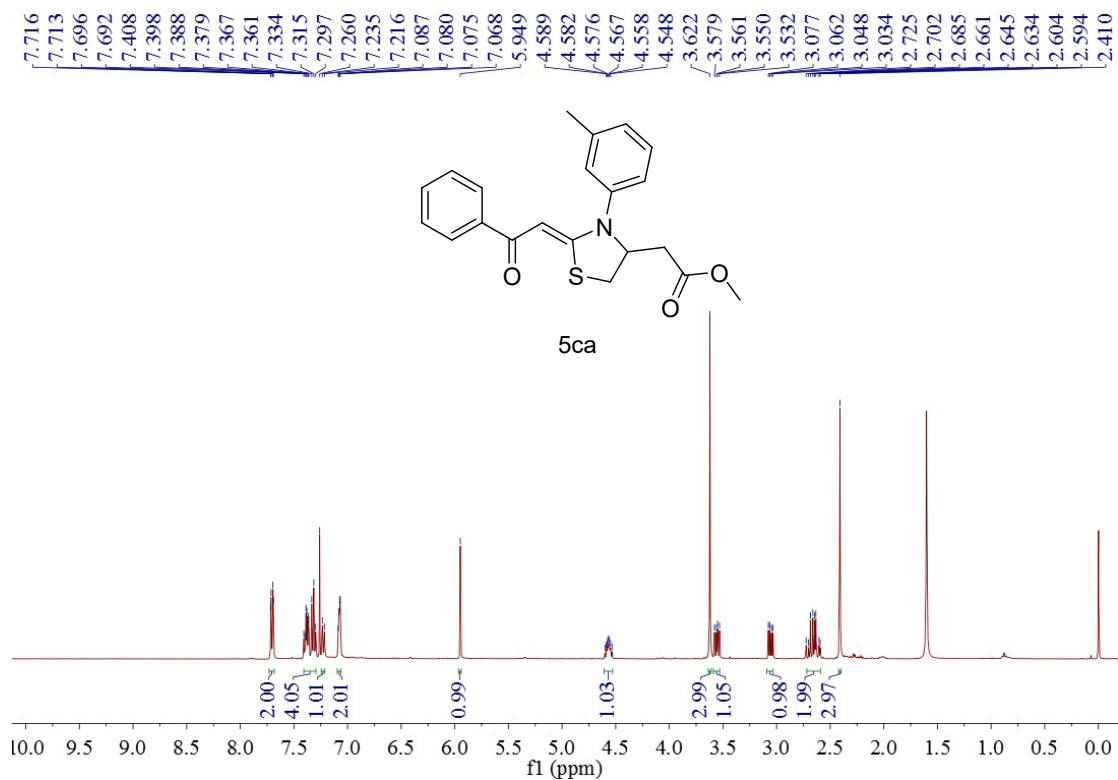


Figure S45. 5ca (¹H NMR, 400 MHz, CDCl₃)

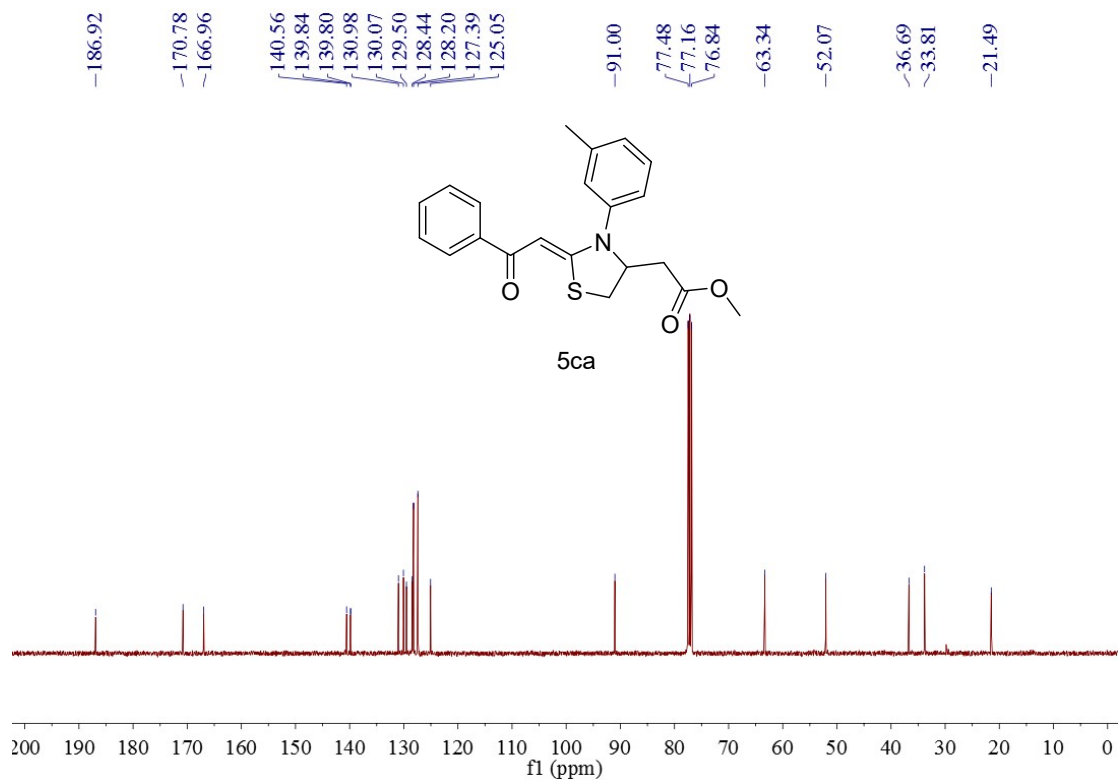


Figure S46. 5ca (¹³C NMR, 100 MHz, CDCl₃)

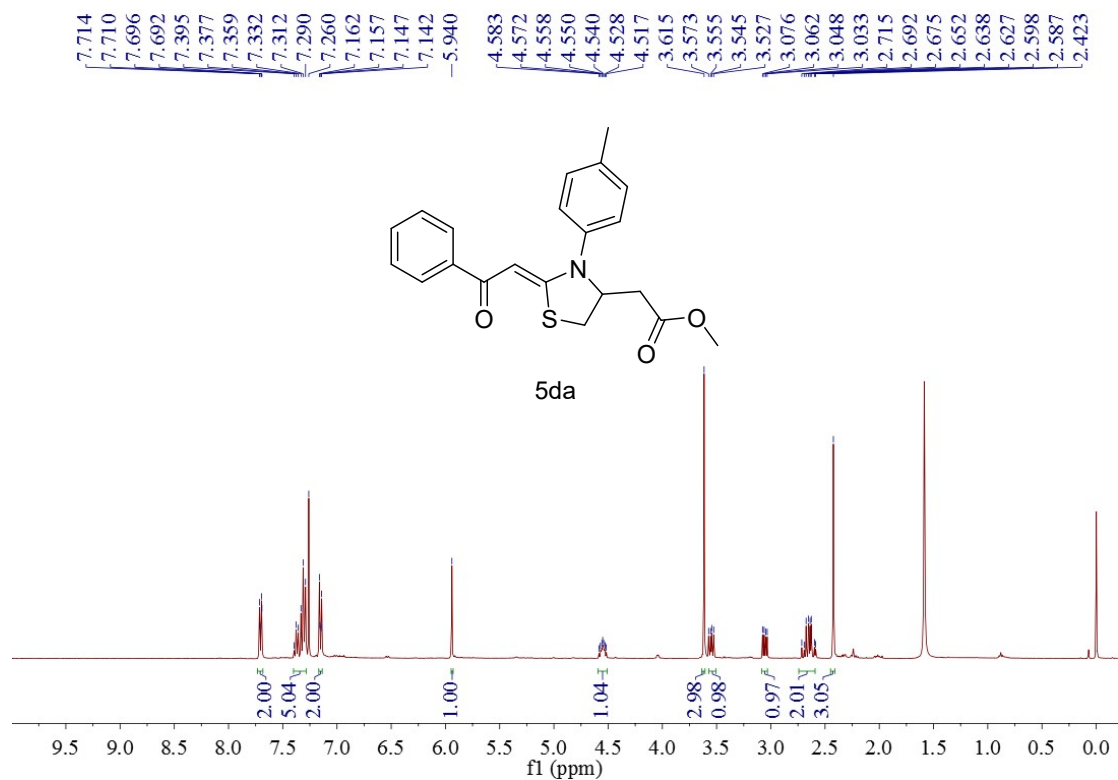


Figure S47. 5da (^1H NMR, 400 MHz, CDCl_3)

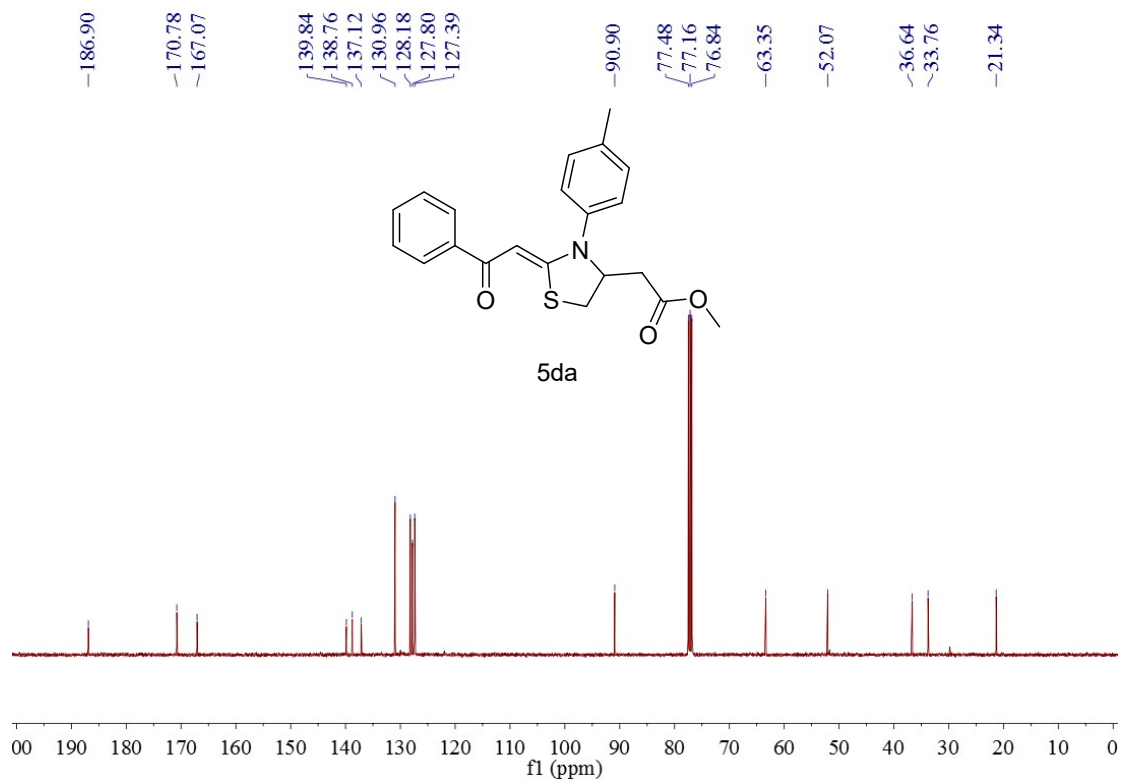


Figure S48. 5da (^{13}C NMR, 100 MHz, CDCl_3)

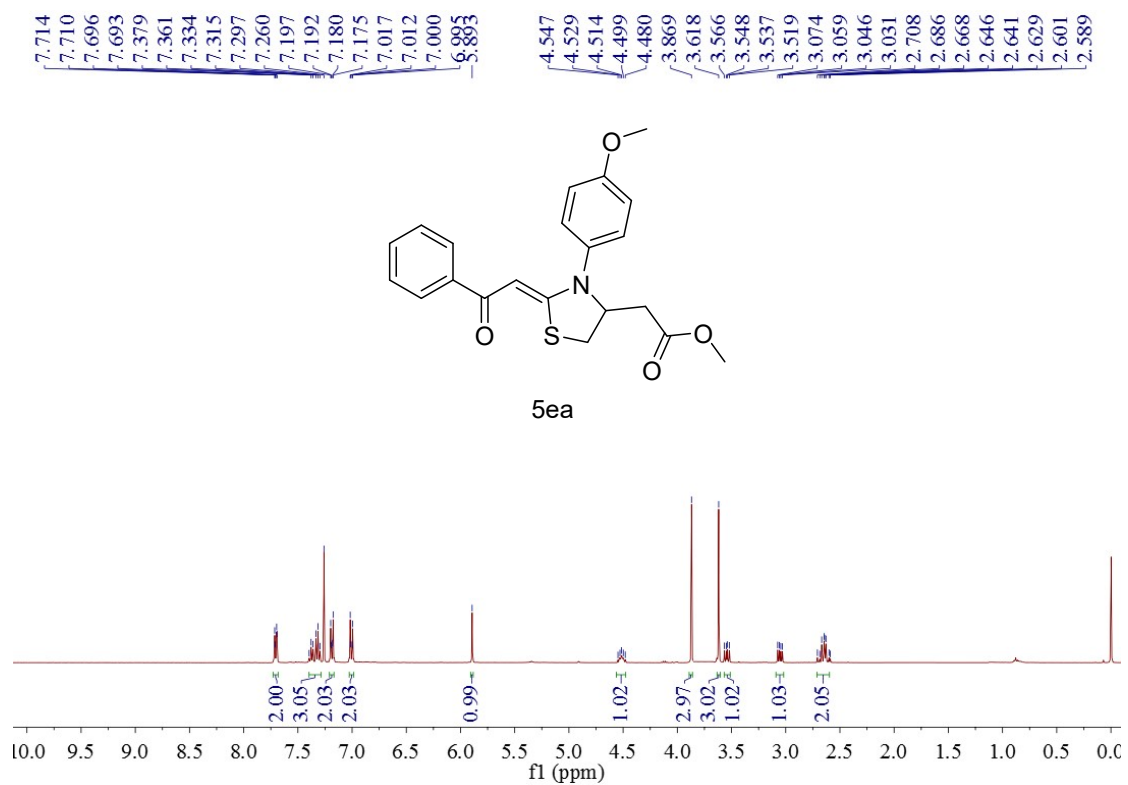


Figure S49. **5ea** (^1H NMR, 400 MHz, CDCl_3)

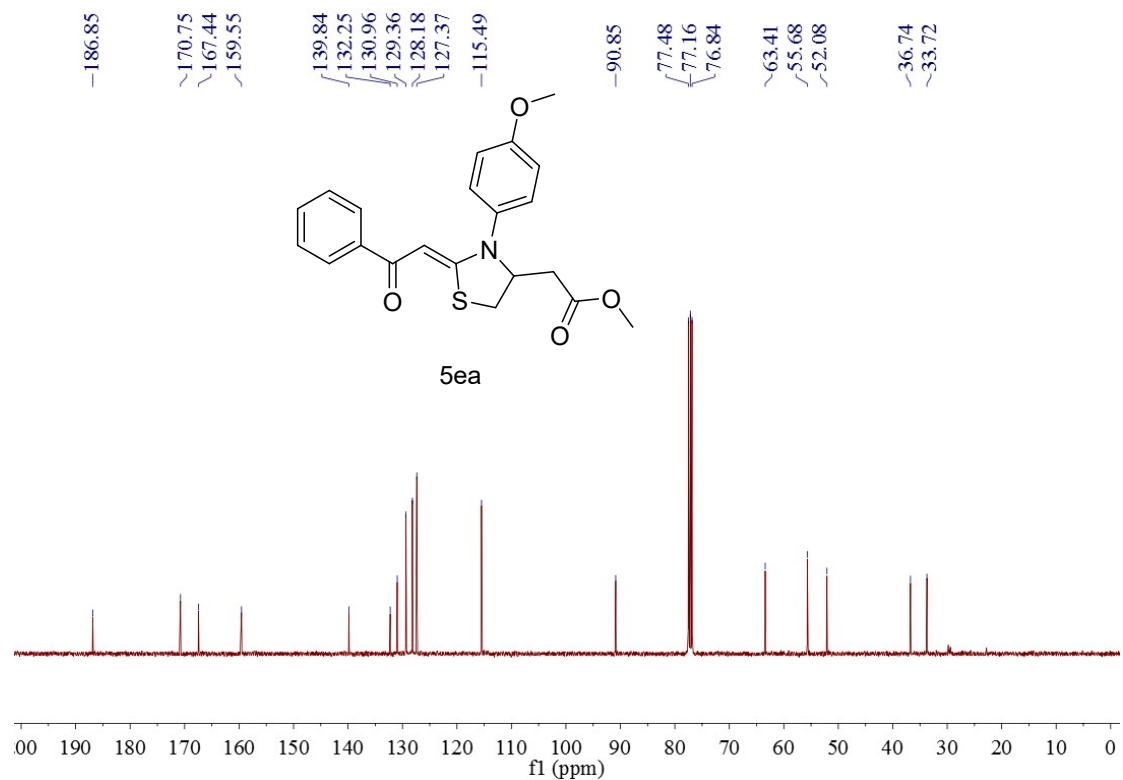


Figure S50. **5ea** (^{13}C NMR, 100 MHz, CDCl_3)

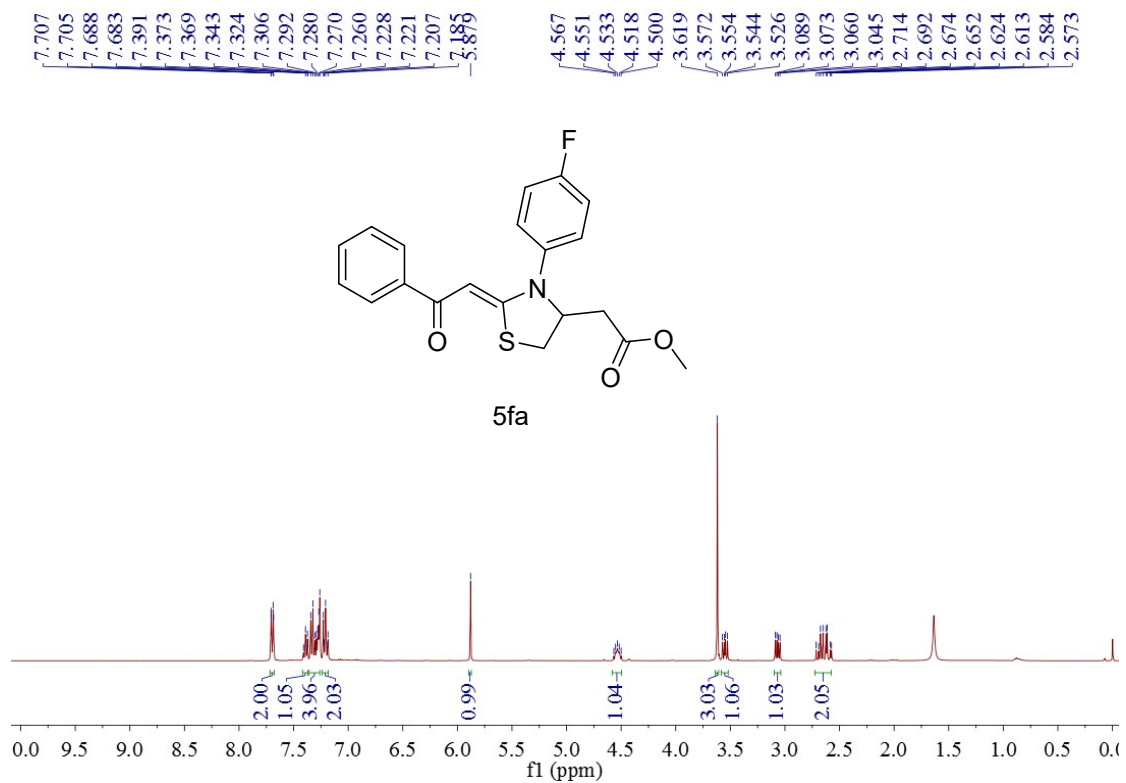


Figure S51. 5fa (¹H NMR, 400 MHz, CDCl₃)

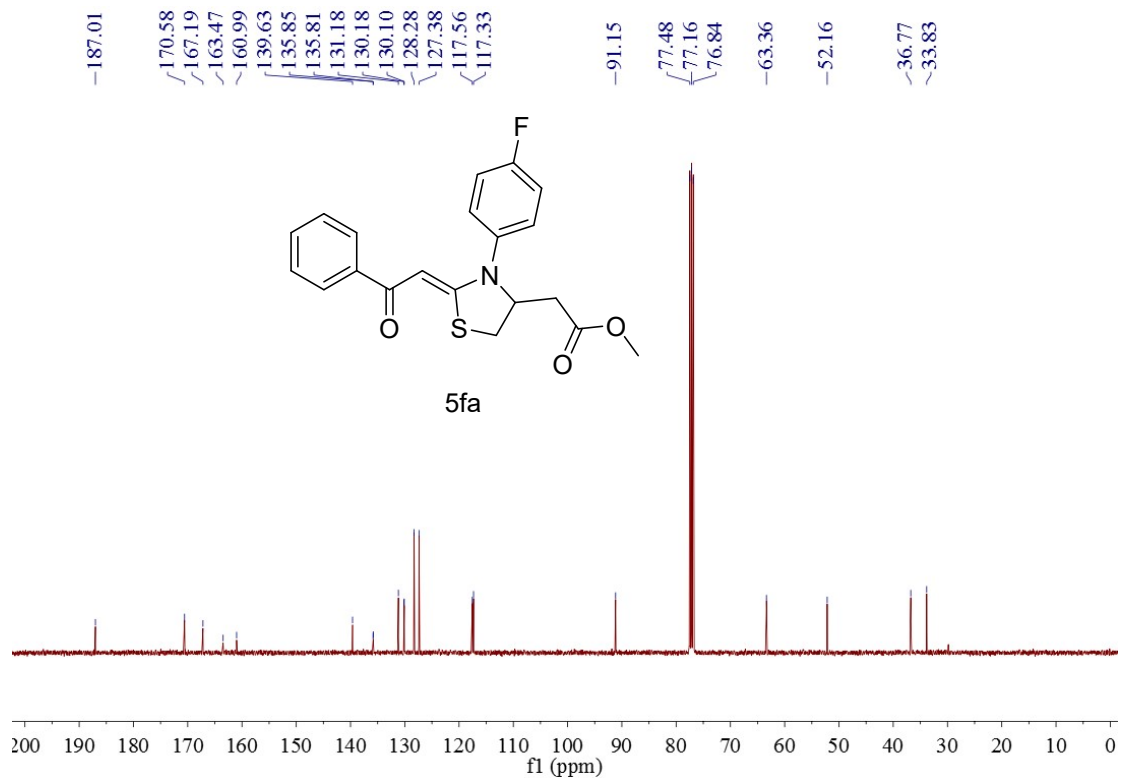


Figure S52. 5fa (¹³C NMR, 100 MHz, CDCl₃)

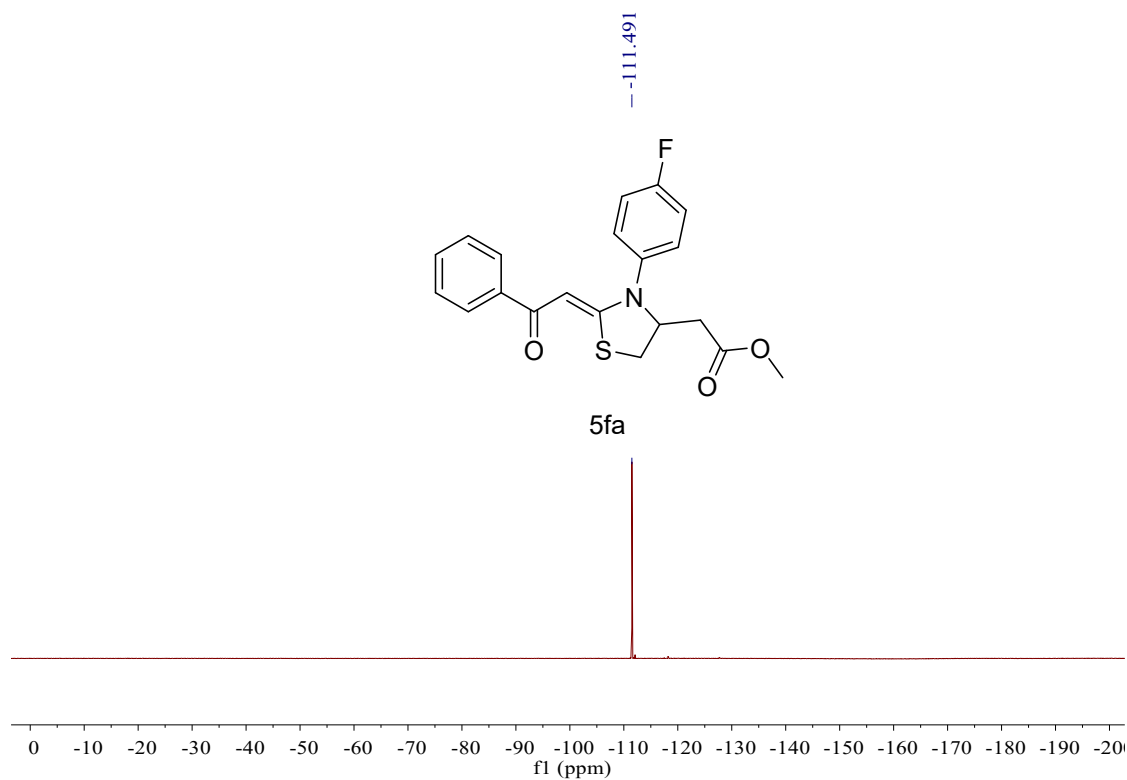


Figure S53. 5fa (^{19}F NMR, 376 MHz, CDCl_3)

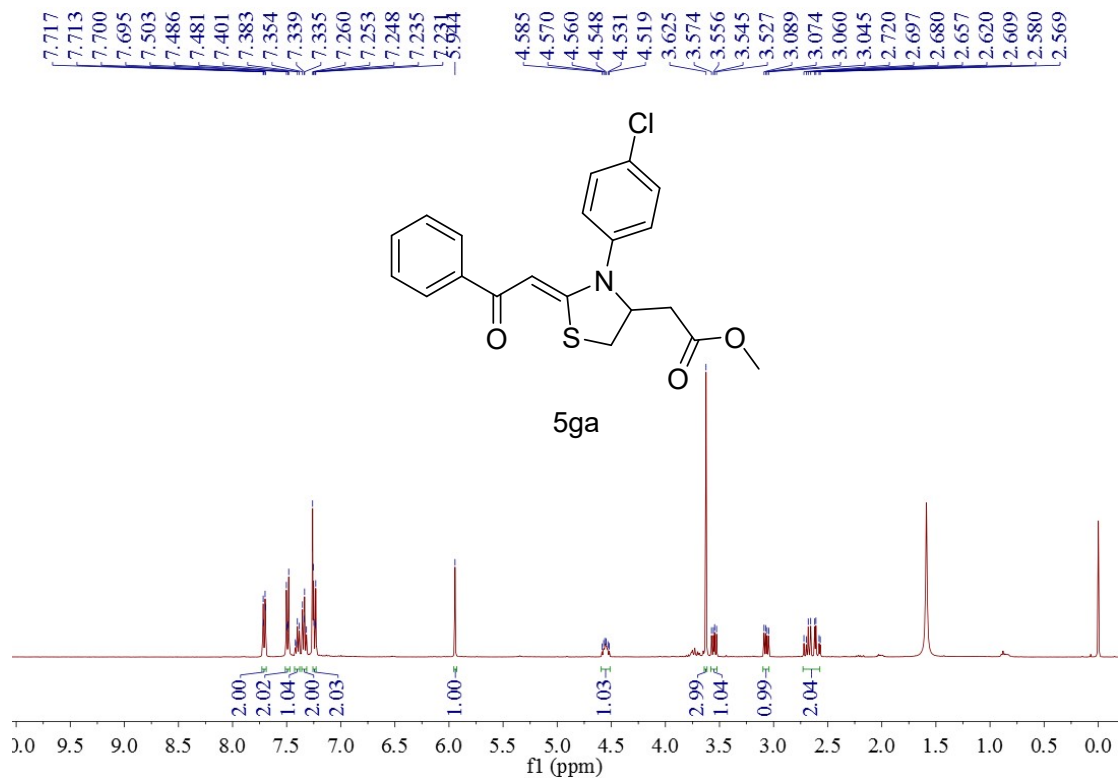


Figure S54. 5ga (^1H NMR, 400 MHz, CDCl_3)

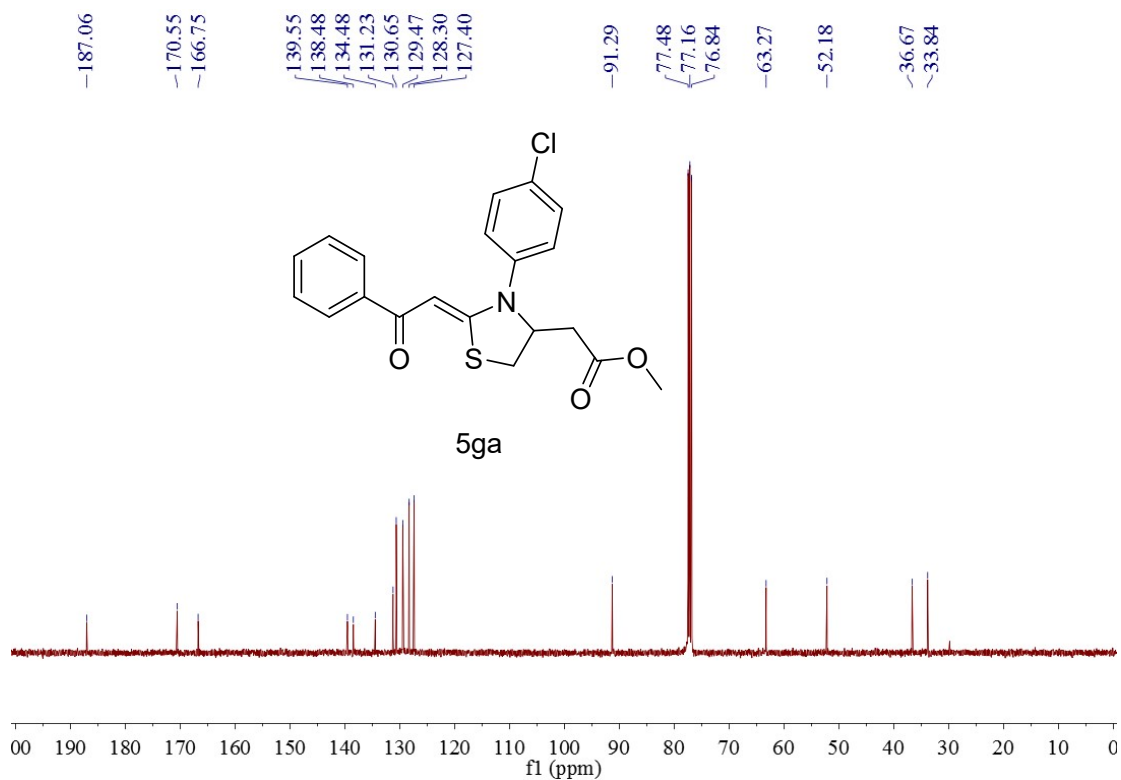


Figure S55. **5ga** (^{13}C NMR, 100 MHz, CDCl_3)

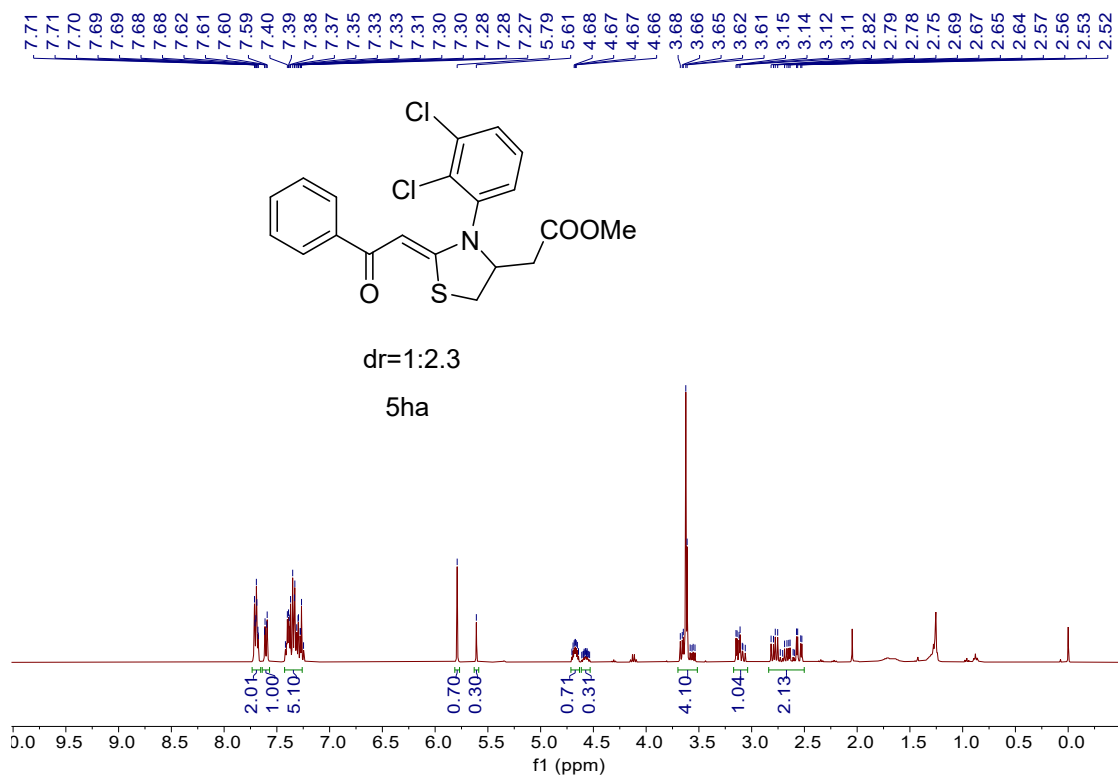


Figure S56. **5ha** (^1H NMR, 400 MHz, CDCl_3)

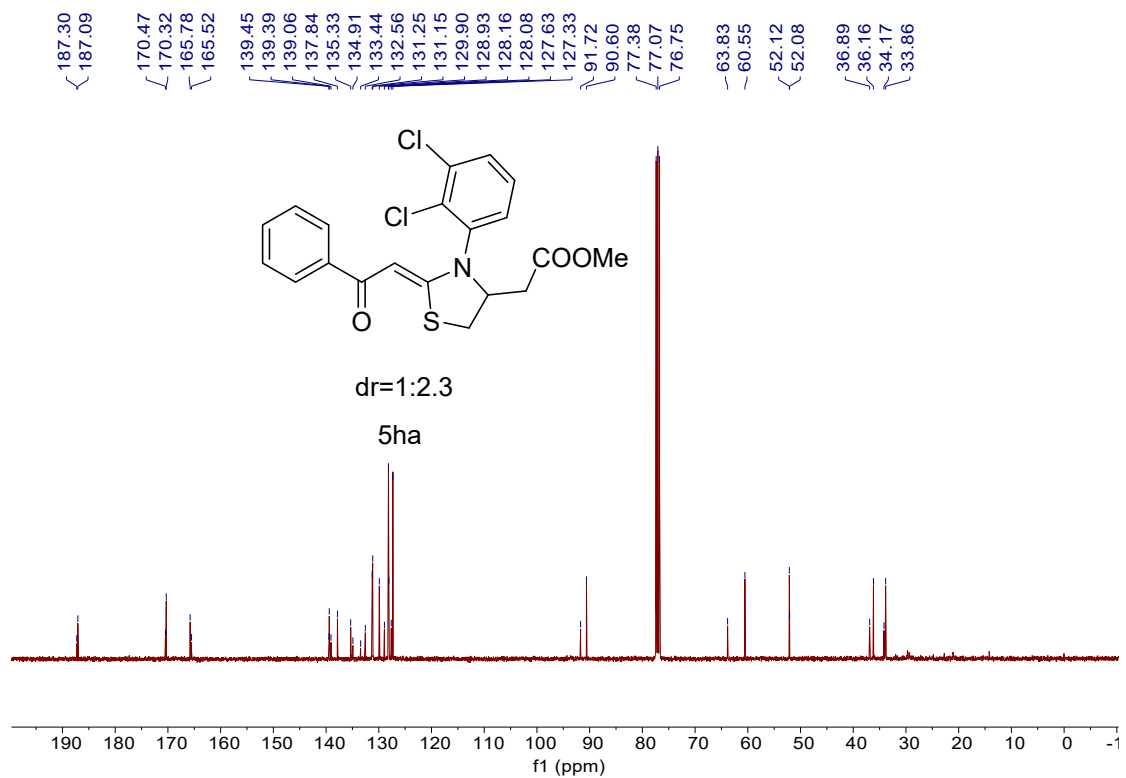


Figure S57. 5ha (^{13}C NMR, 100 MHz, CDCl_3)

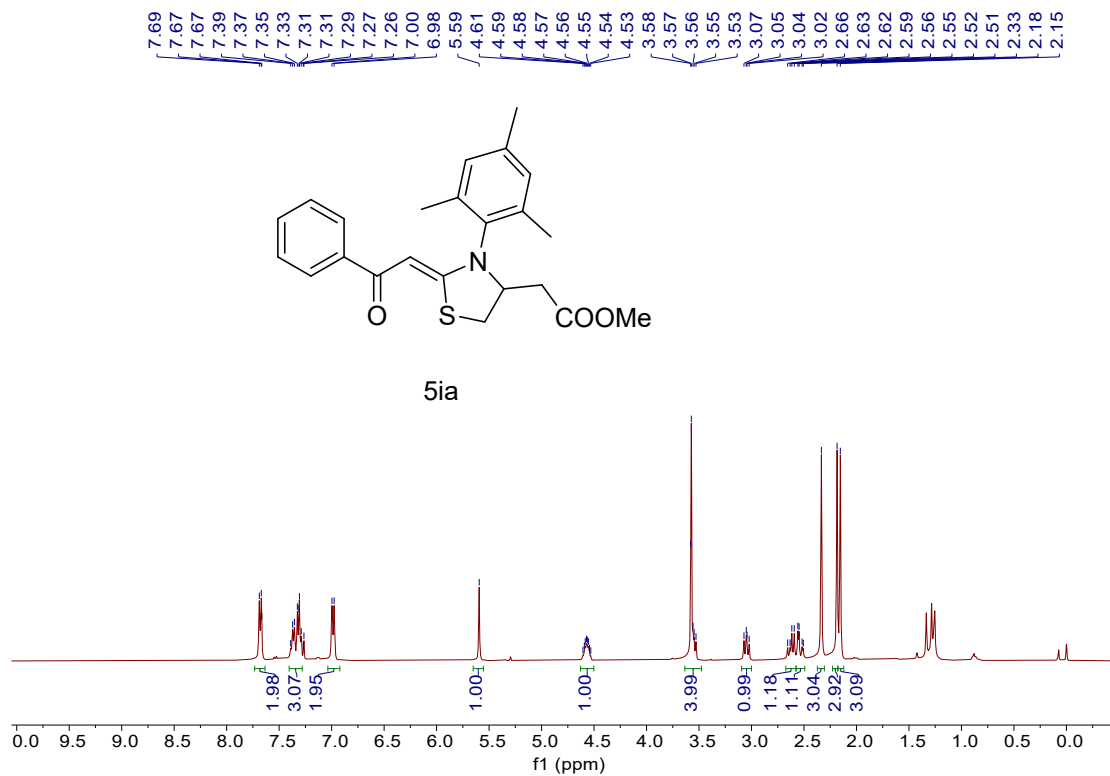


Figure S58. 5ia (^1H NMR, 400 MHz, CDCl_3)

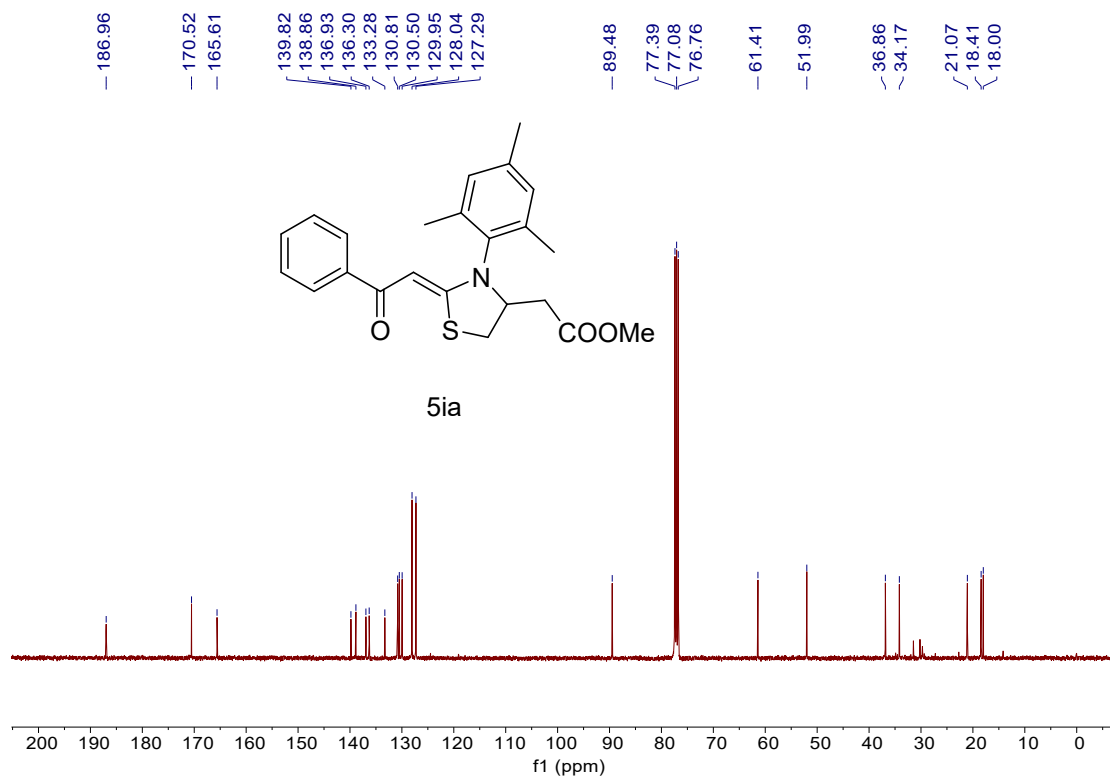


Figure S59. 5ia (¹³C NMR, 100 MHz, CDCl₃)

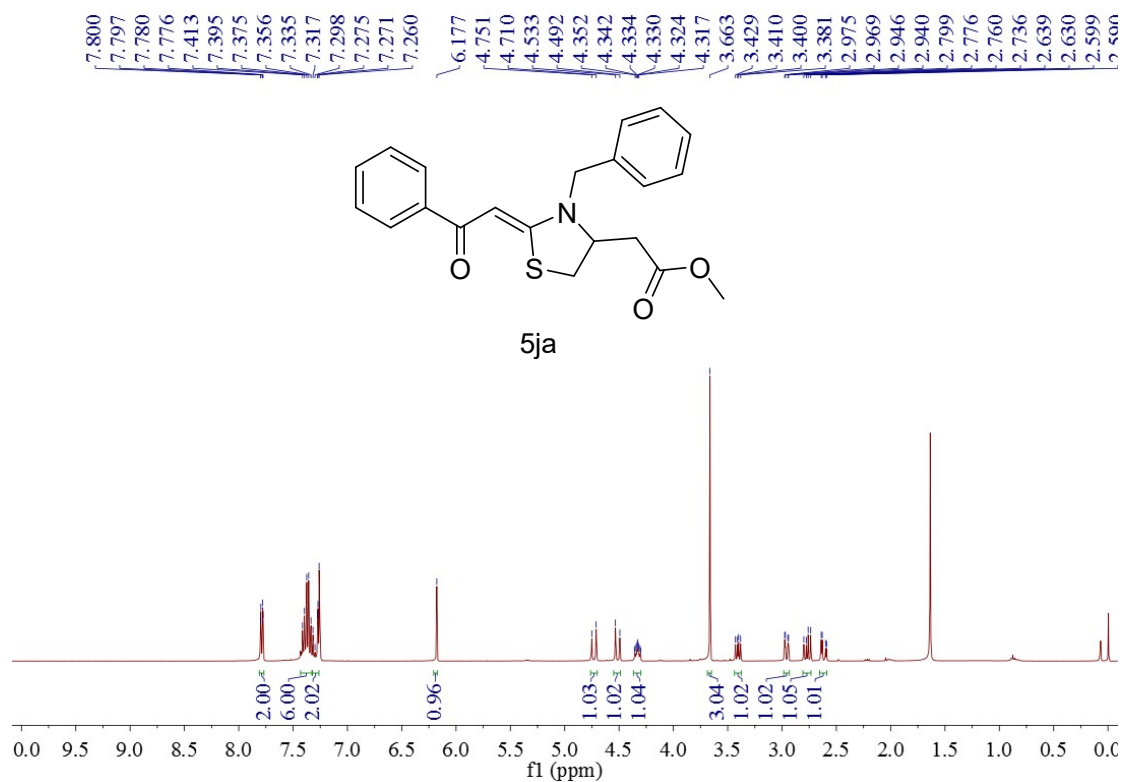


Figure S60. 5ja (¹H NMR, 400 MHz, CDCl₃)

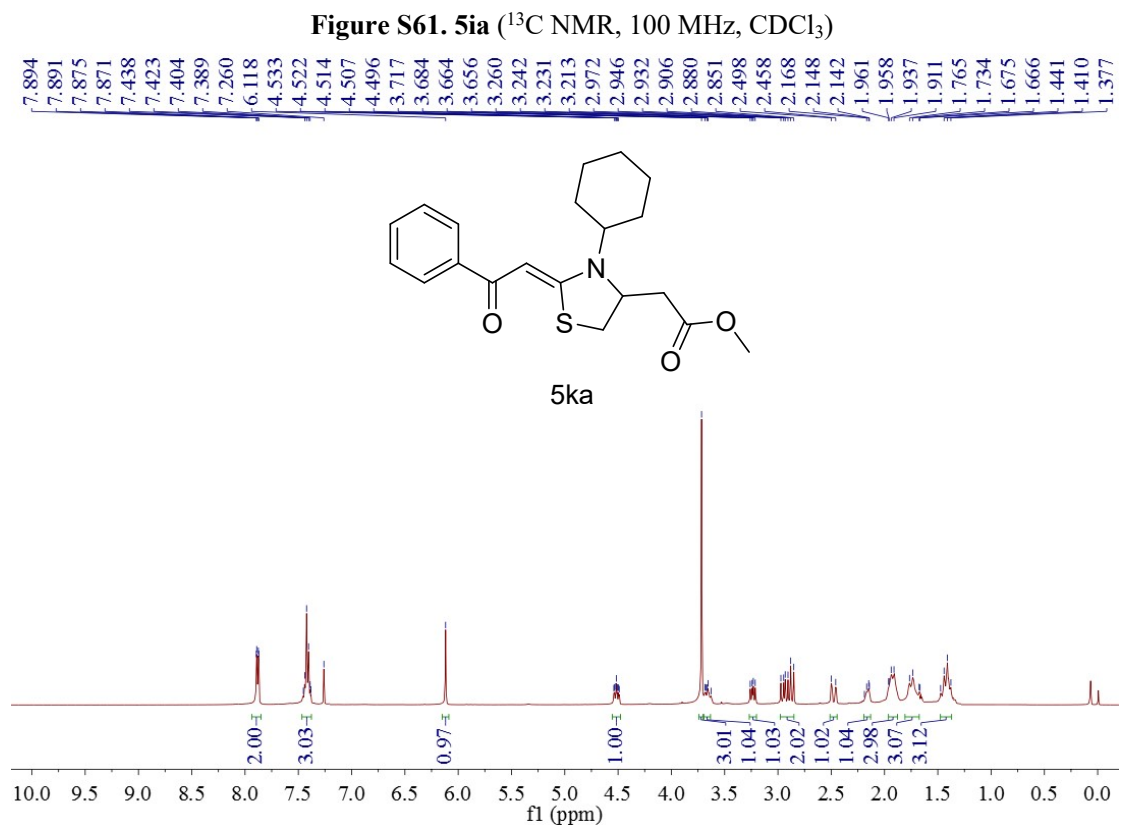
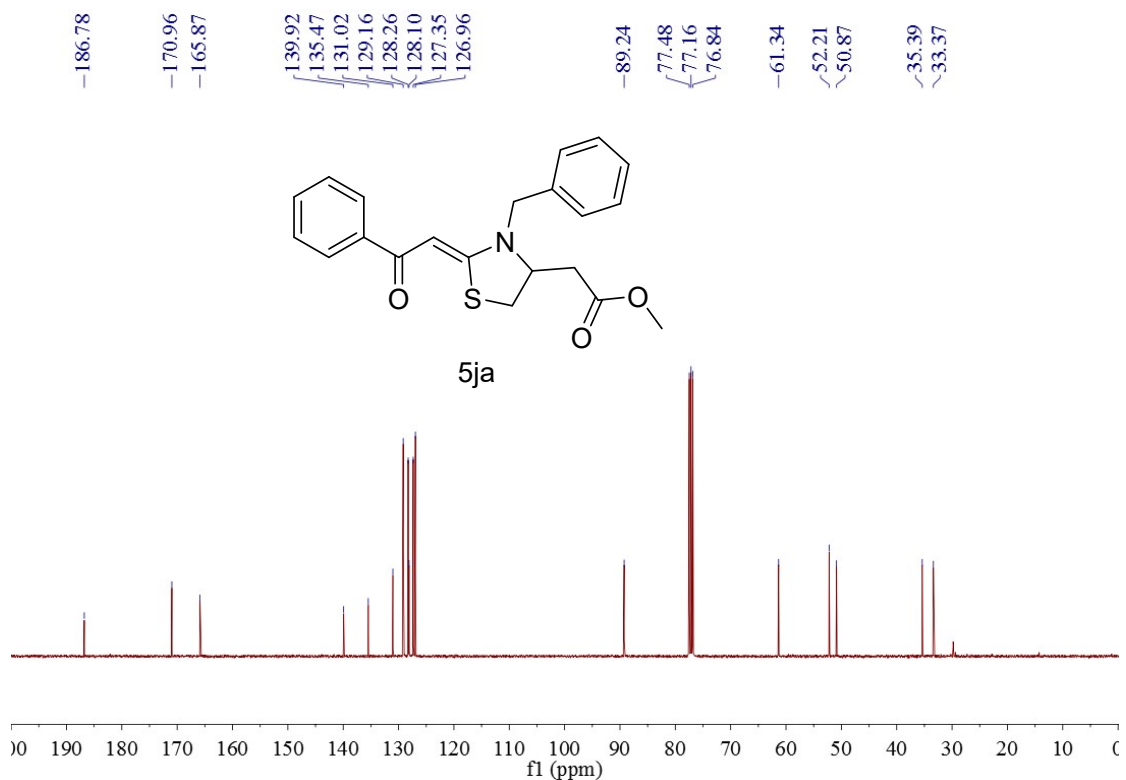


Figure S62. 5ka (^1H NMR, 400 MHz, CDCl_3)

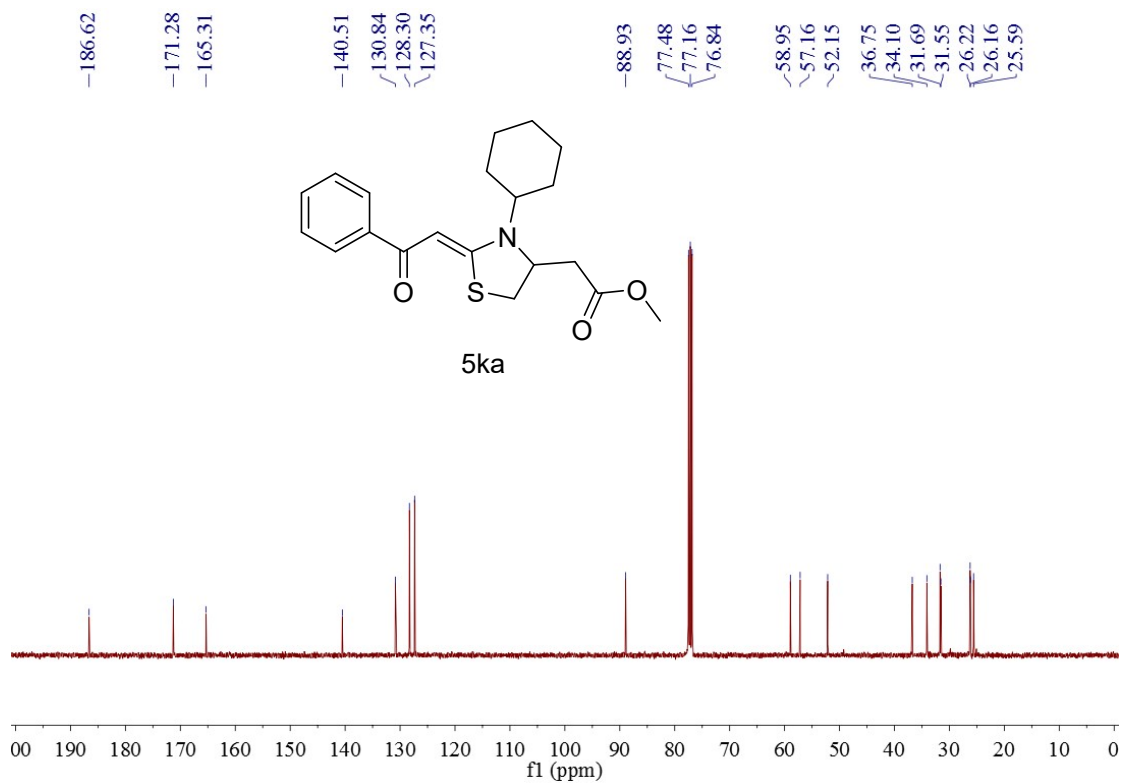


Figure S63. **5ka** (^{13}C NMR, 100 MHz, CDCl_3)

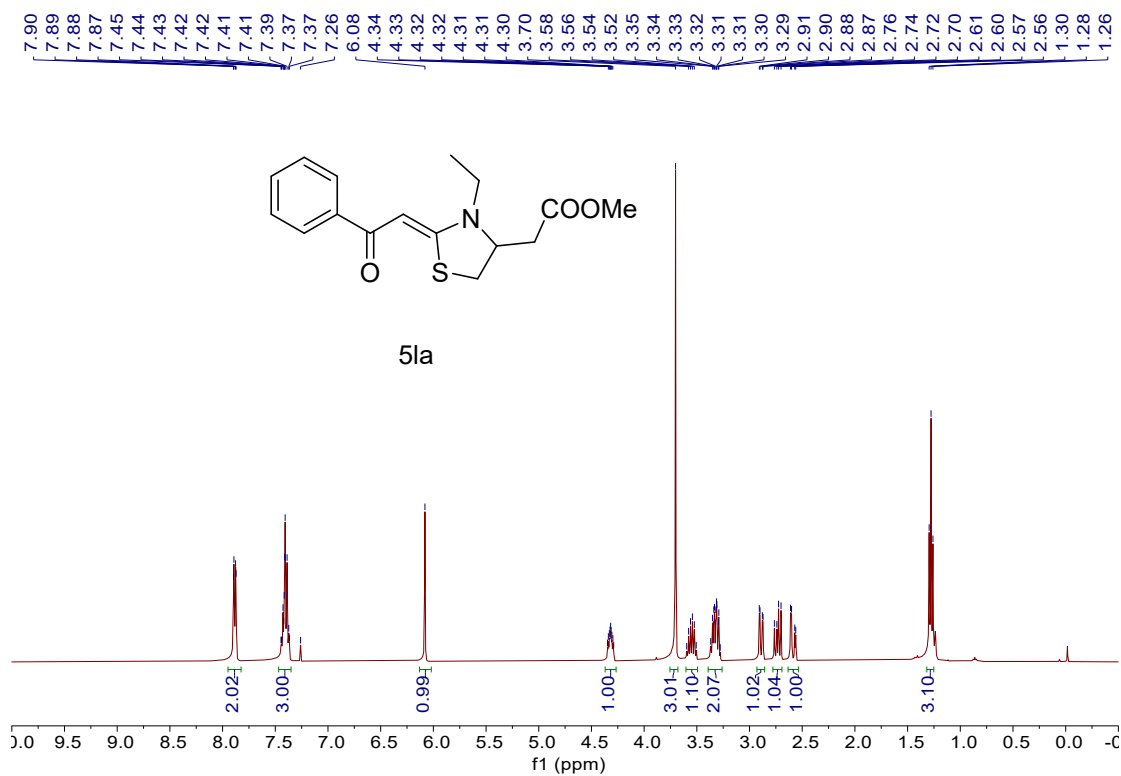


Figure S64. **5la** (^1H NMR, 400 MHz, CDCl_3)

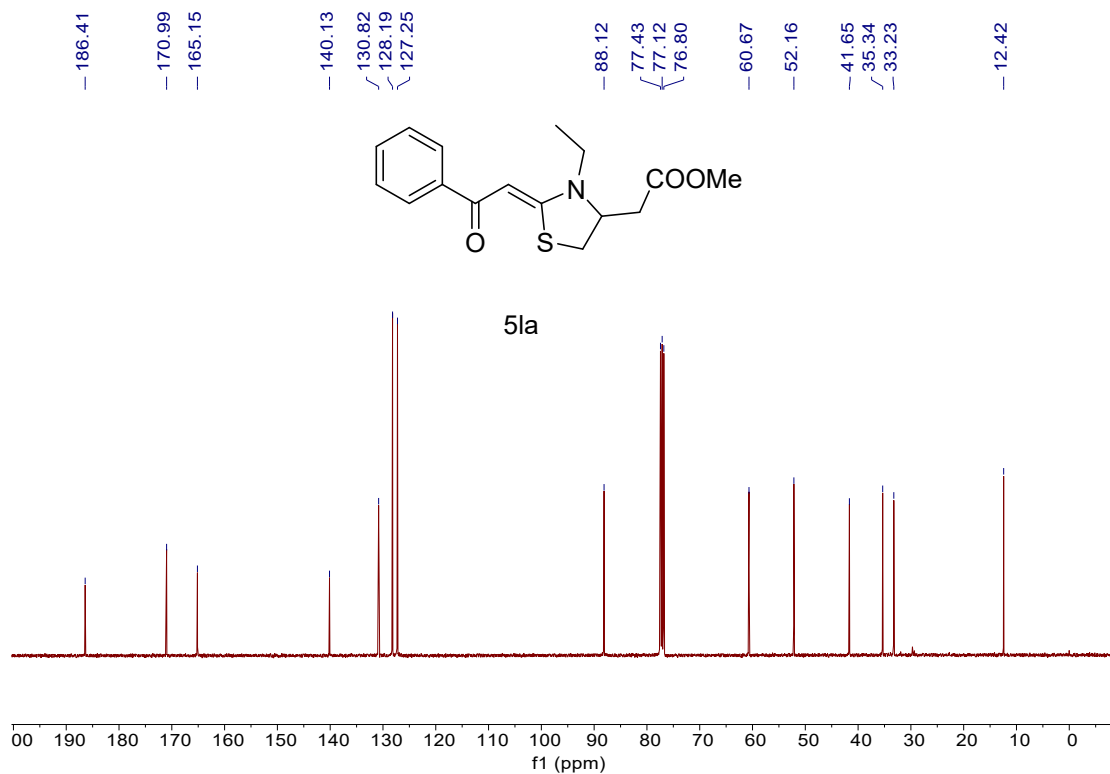


Figure S65. 5la (^{13}C NMR, 100 MHz, CDCl_3)

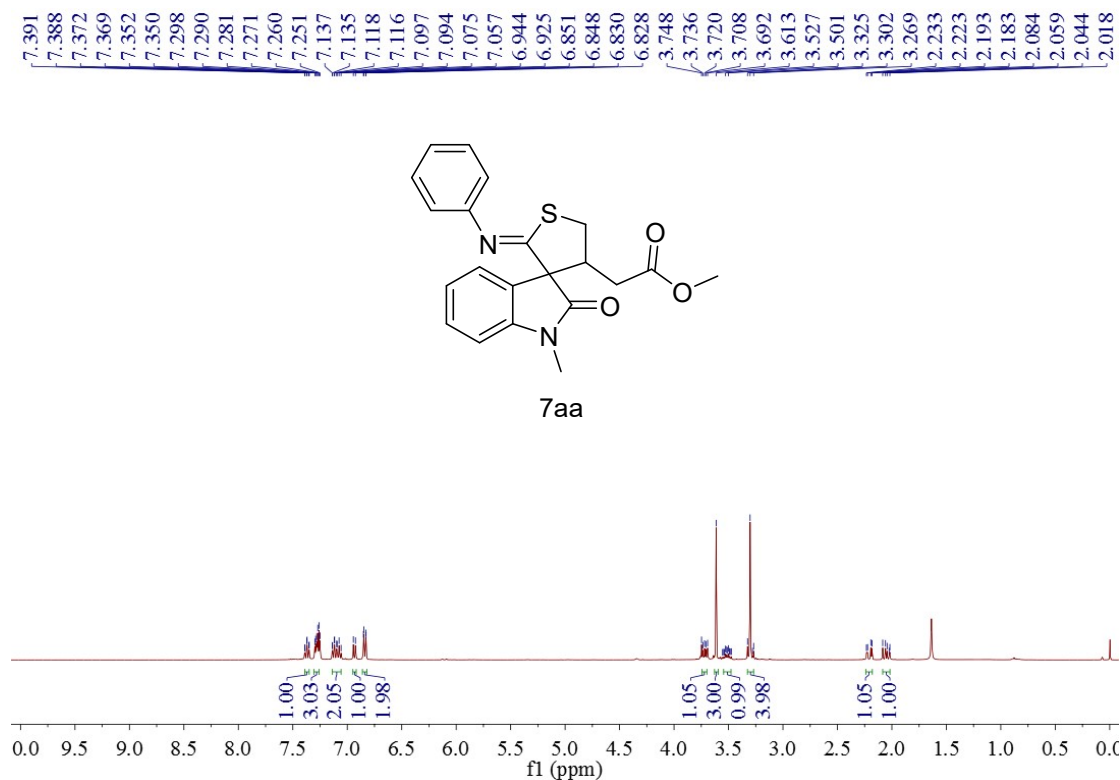


Figure S66. 7aa (^1H NMR, 400 MHz, CDCl_3)

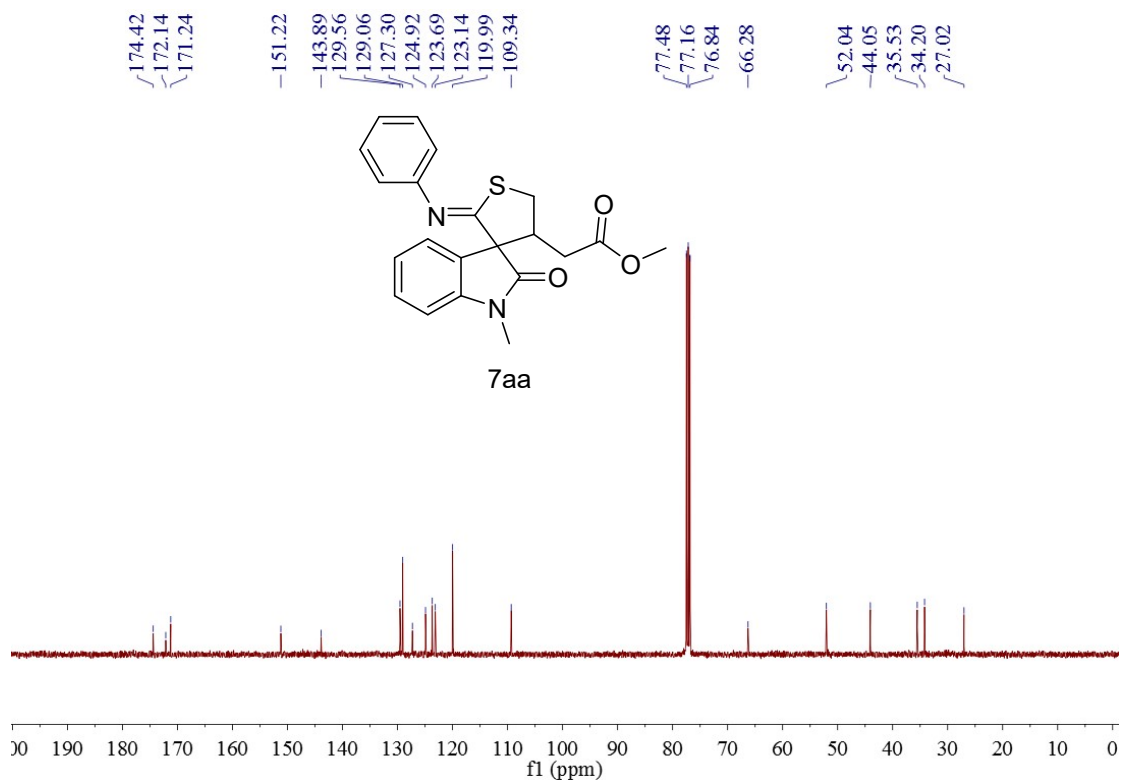


Figure S67. 7aa (^{13}C NMR, 100 MHz, CDCl_3)

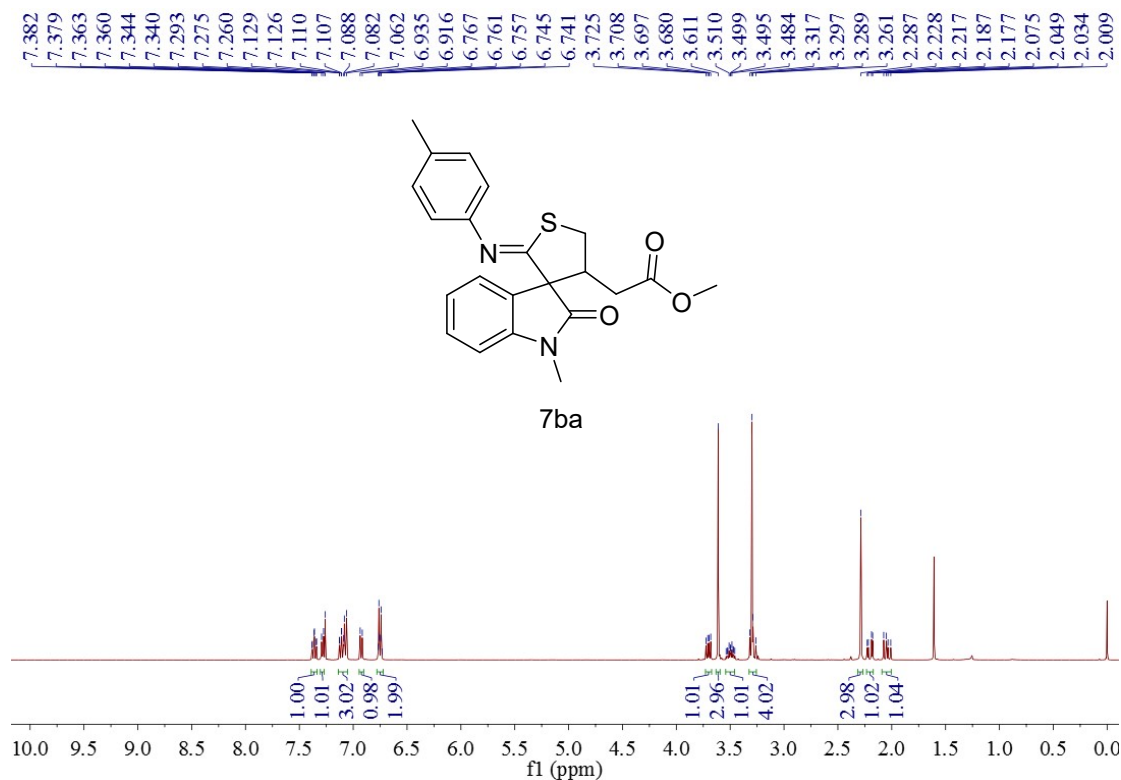


Figure S68. 7ba (^1H NMR, 400 MHz, CDCl_3)

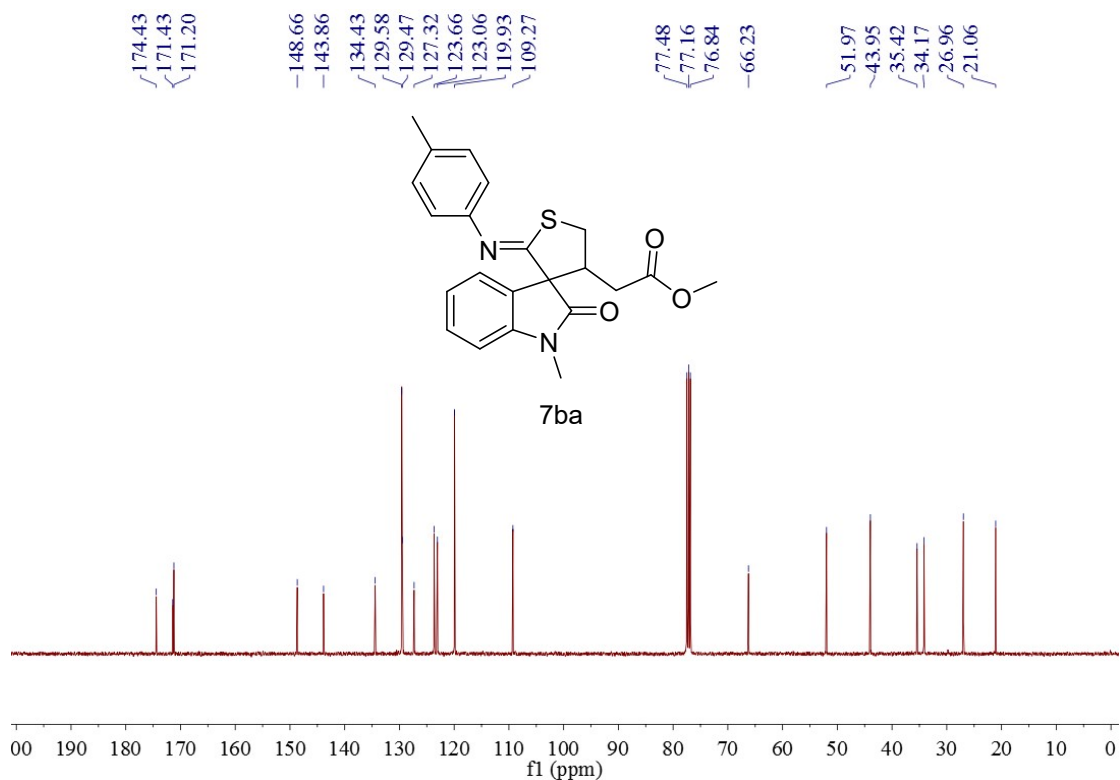


Figure S69. 7ba (¹³C NMR, 100 MHz, CDCl₃)

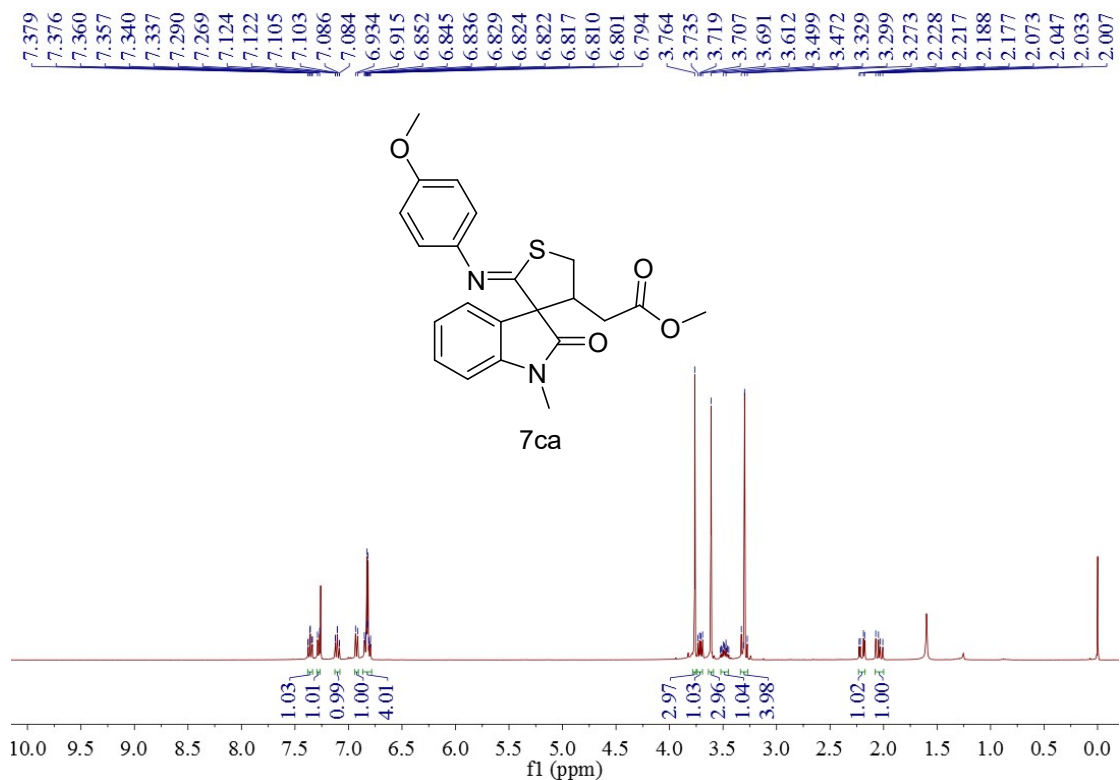


Figure S70. 7ca (¹H NMR, 400 MHz, CDCl₃)

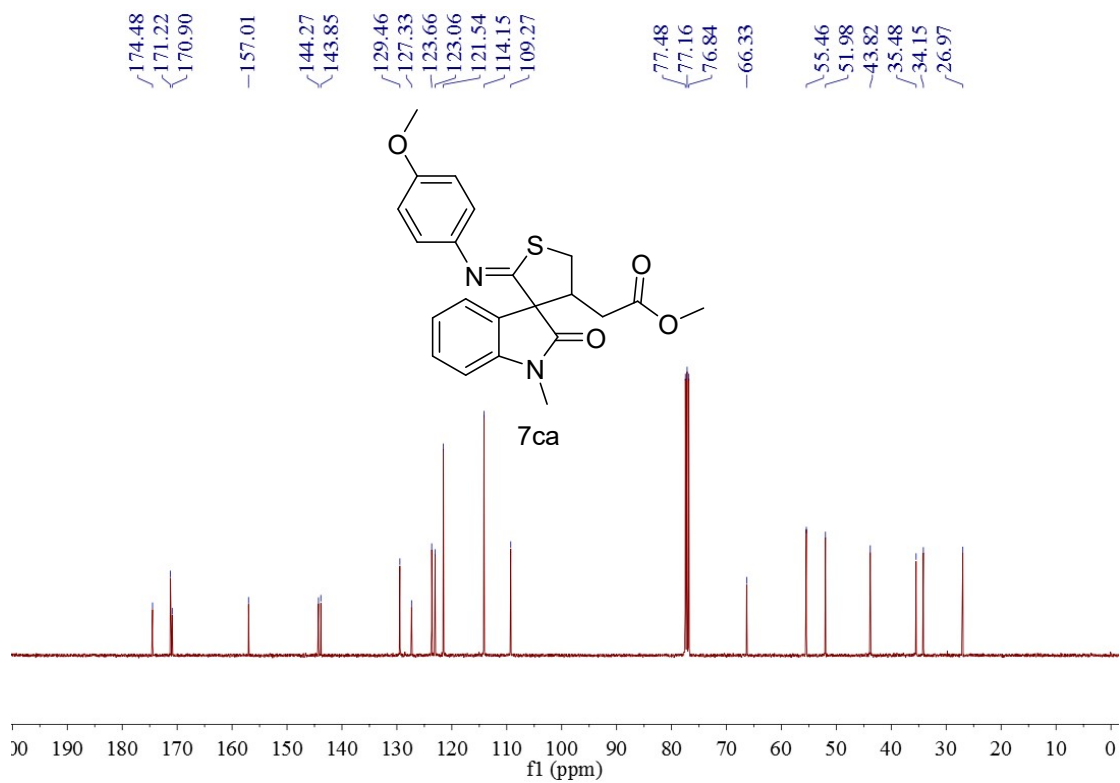


Figure S71. 7ca (¹³C NMR, 100 MHz, CDCl₃)

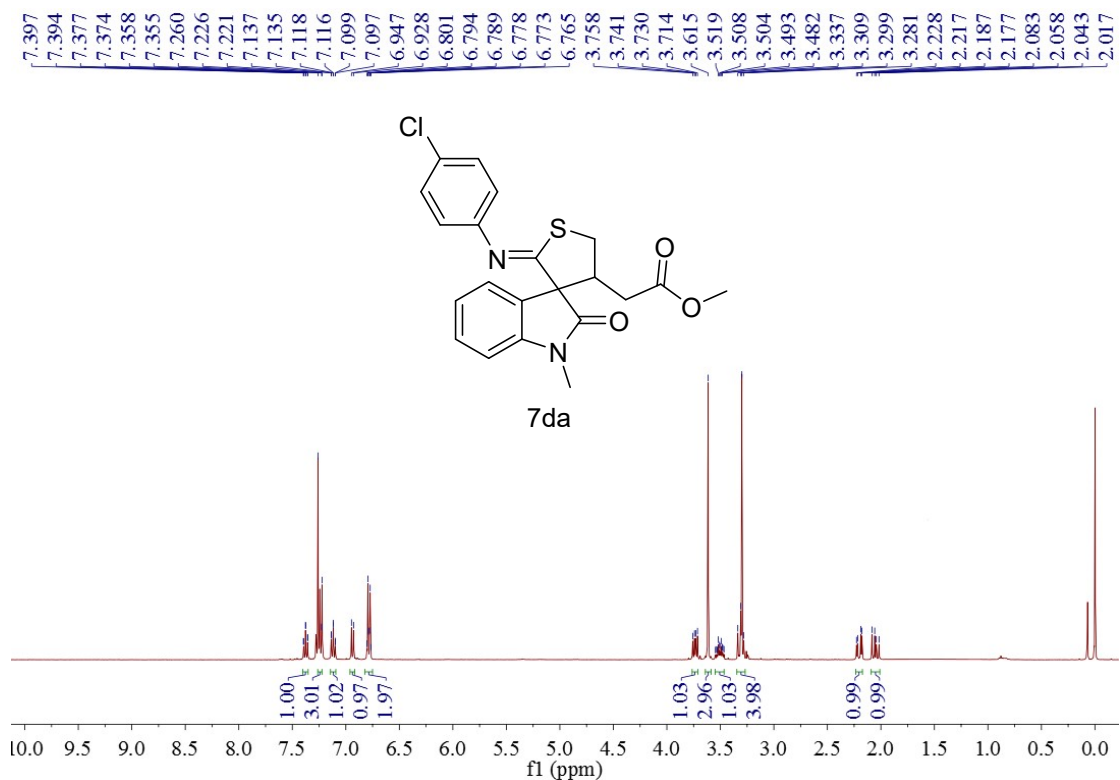


Figure S72. 7da (¹H NMR, 400 MHz, CDCl₃)

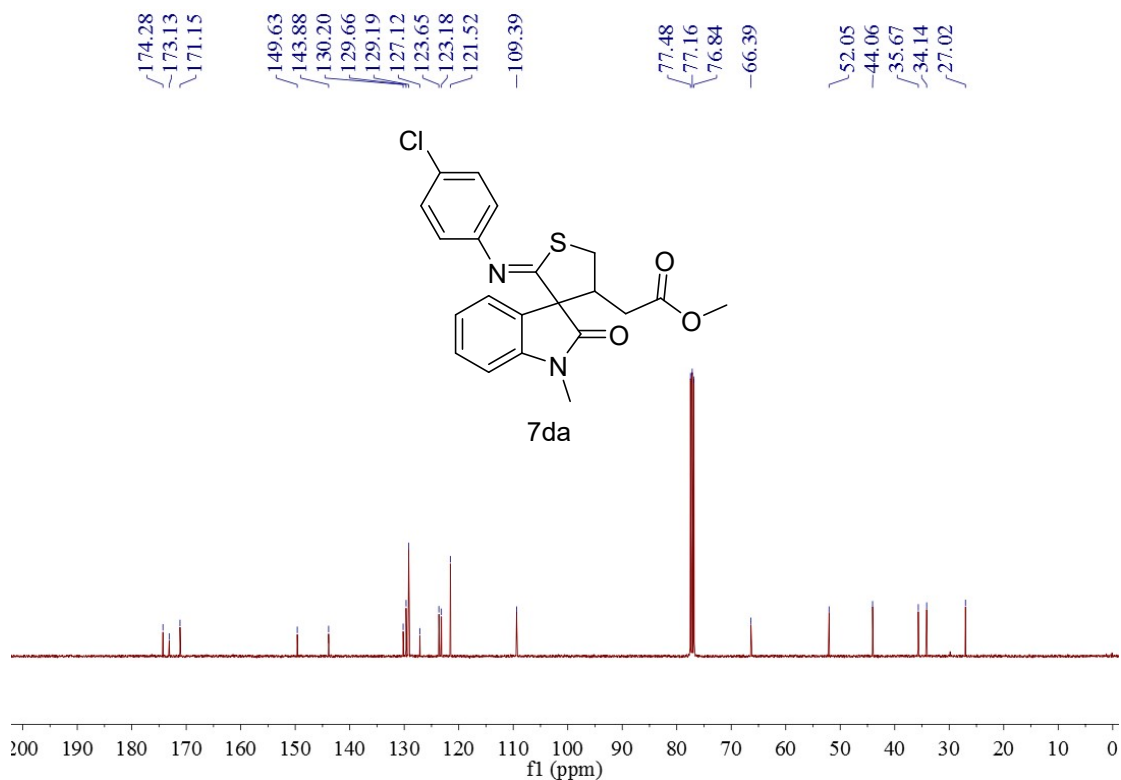


Figure S73. 7da (¹³C NMR, 100 MHz, CDCl₃)

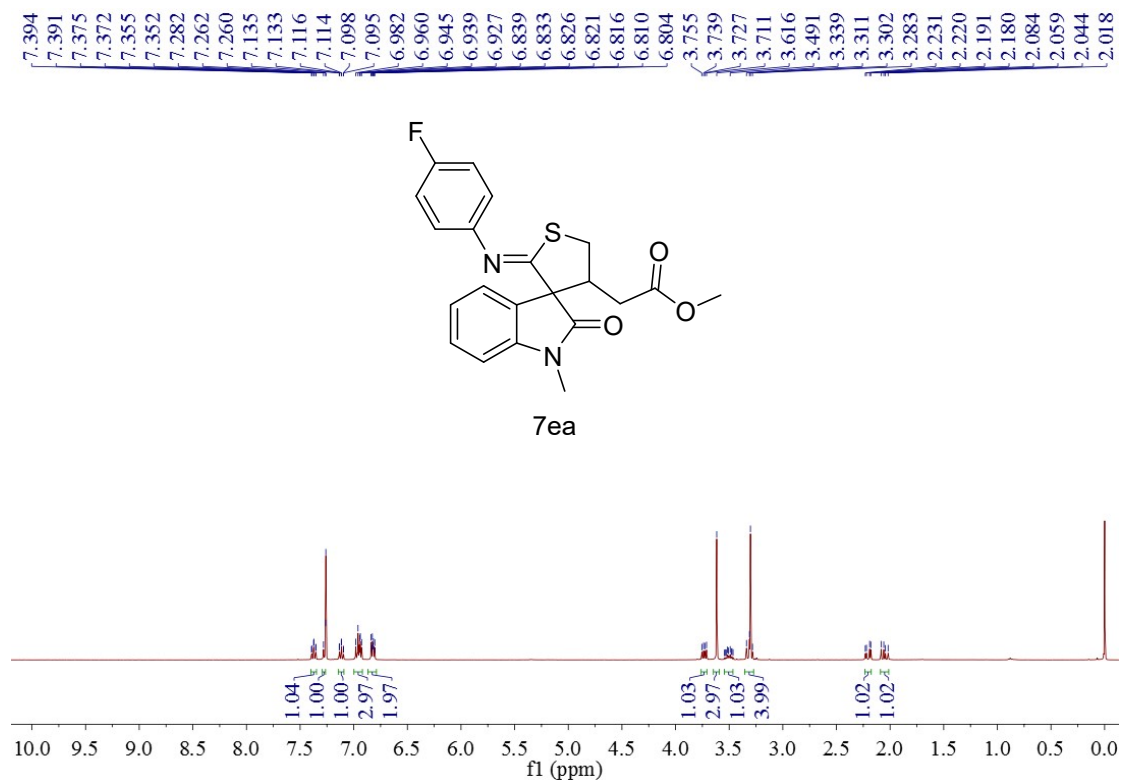


Figure S74. 7ea (¹H NMR, 400 MHz, CDCl₃)

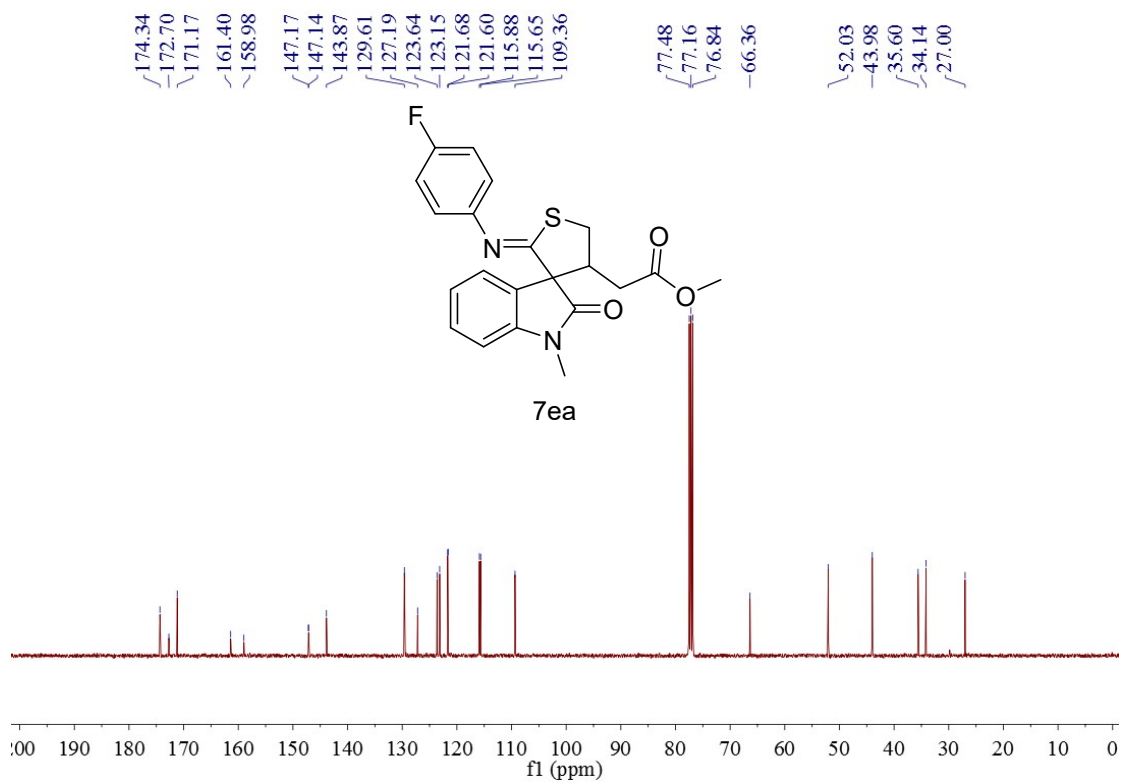


Figure S75. 7ea (^{13}C NMR, 100 MHz, CDCl_3)

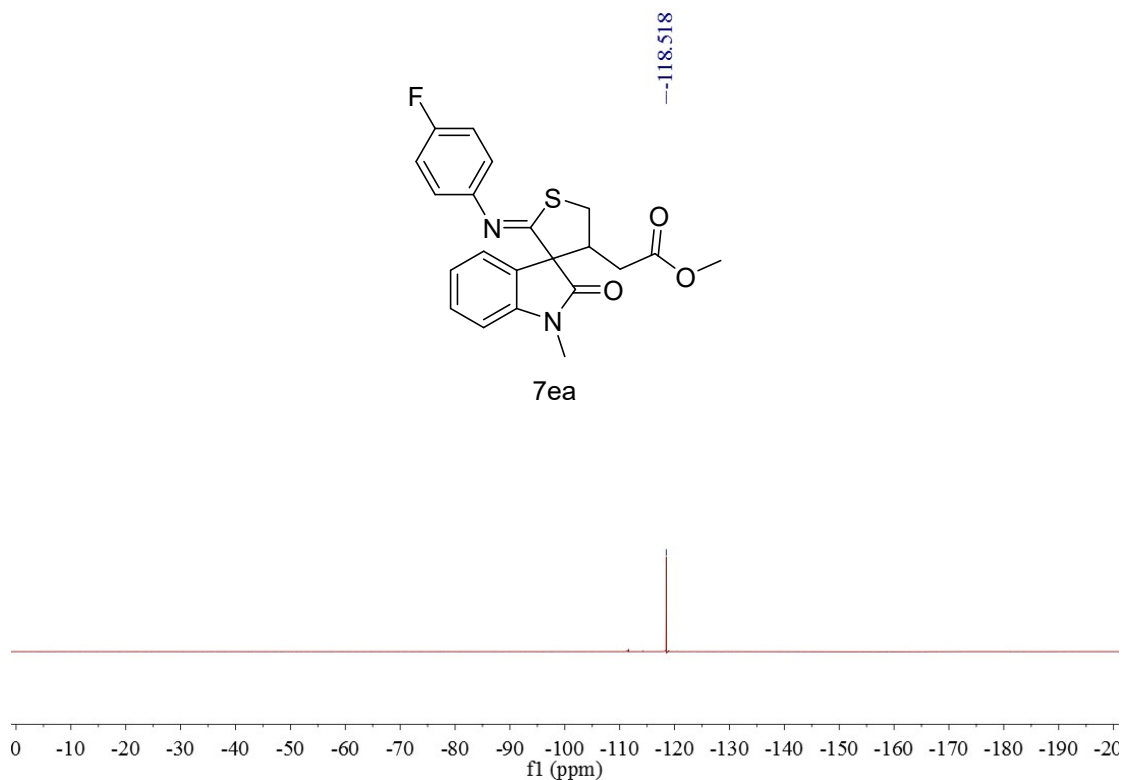


Figure S76. 7ea (^{19}F NMR, 376 MHz, CDCl_3)

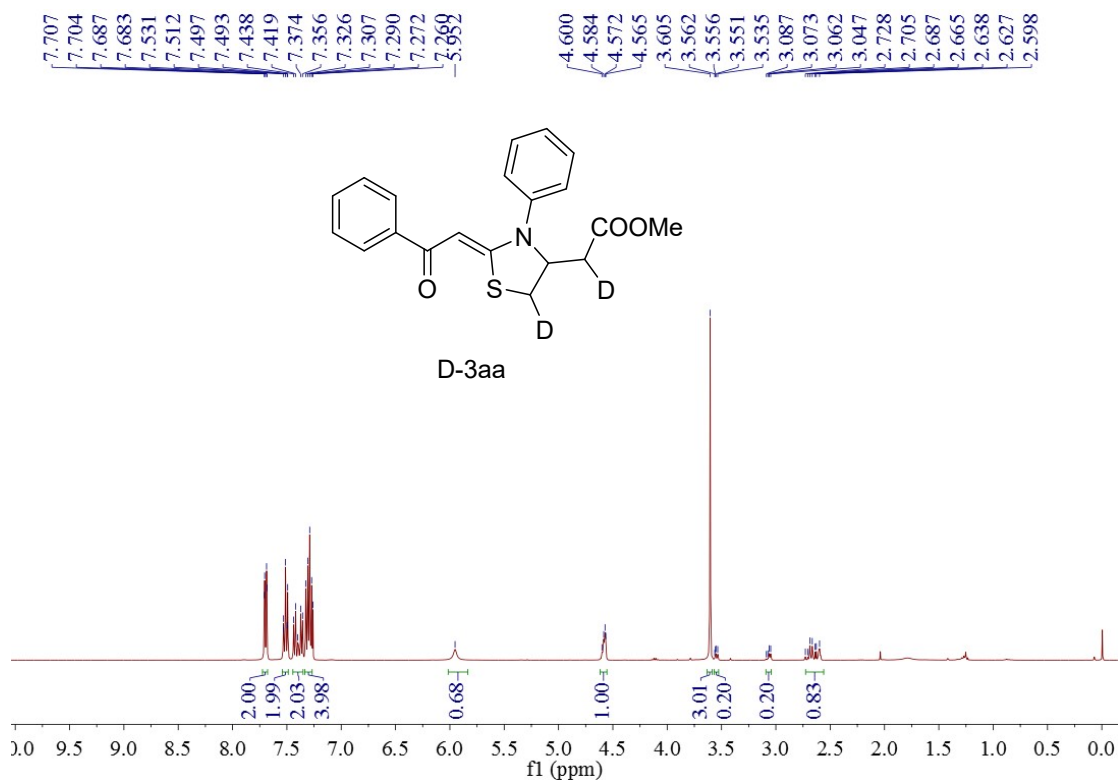


Figure S77. D-3aa (^1H NMR, 400 MHz, CDCl_3)

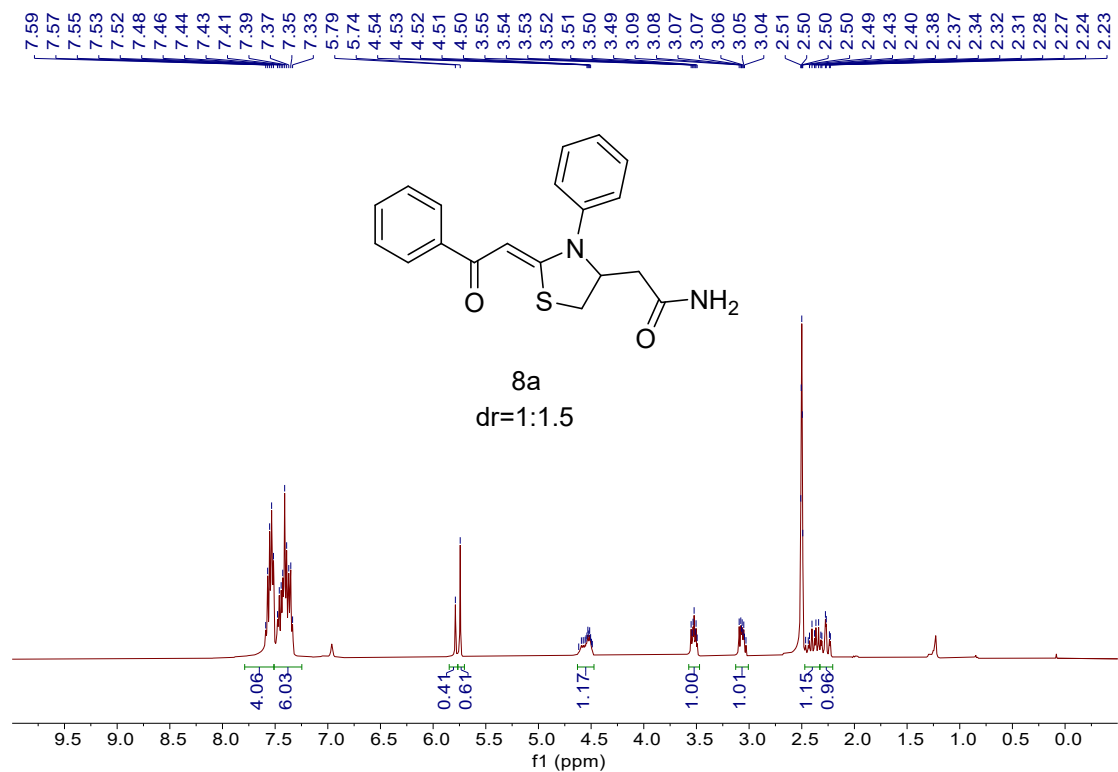


Figure S78. 8a (^1H NMR, 400 MHz, DMSO-d_6)

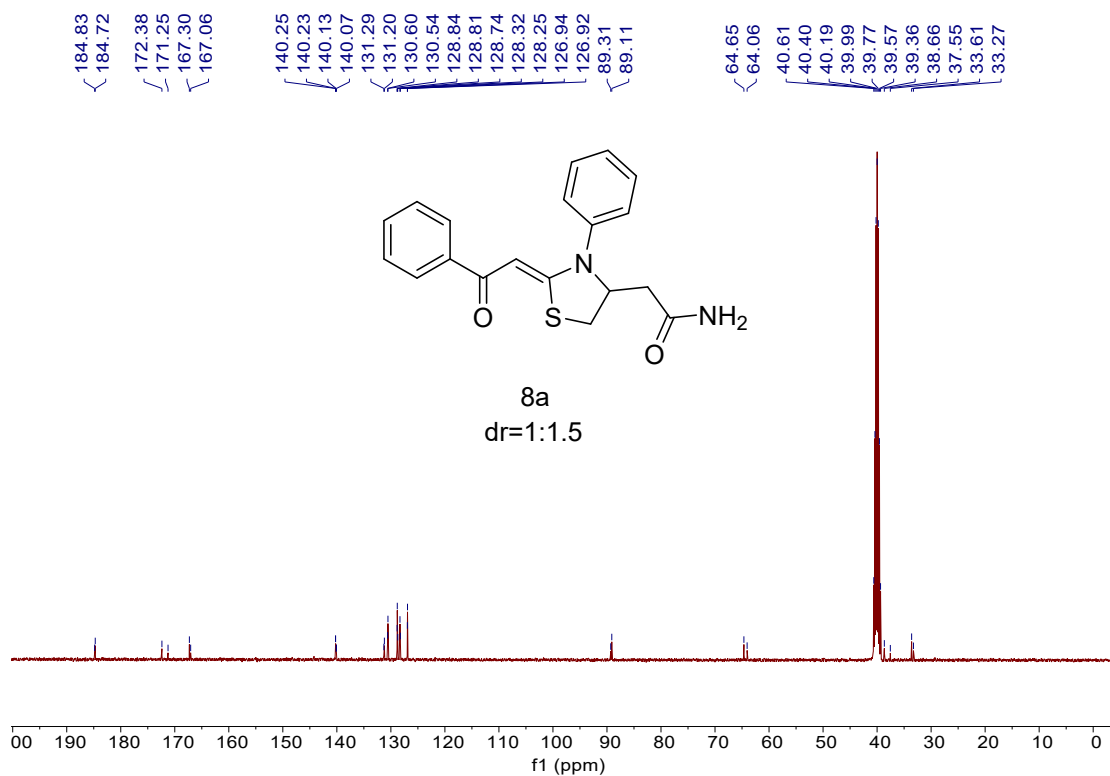


Figure S79. 8a (^{13}C NMR, 100 MHz, DMSO-d_6)

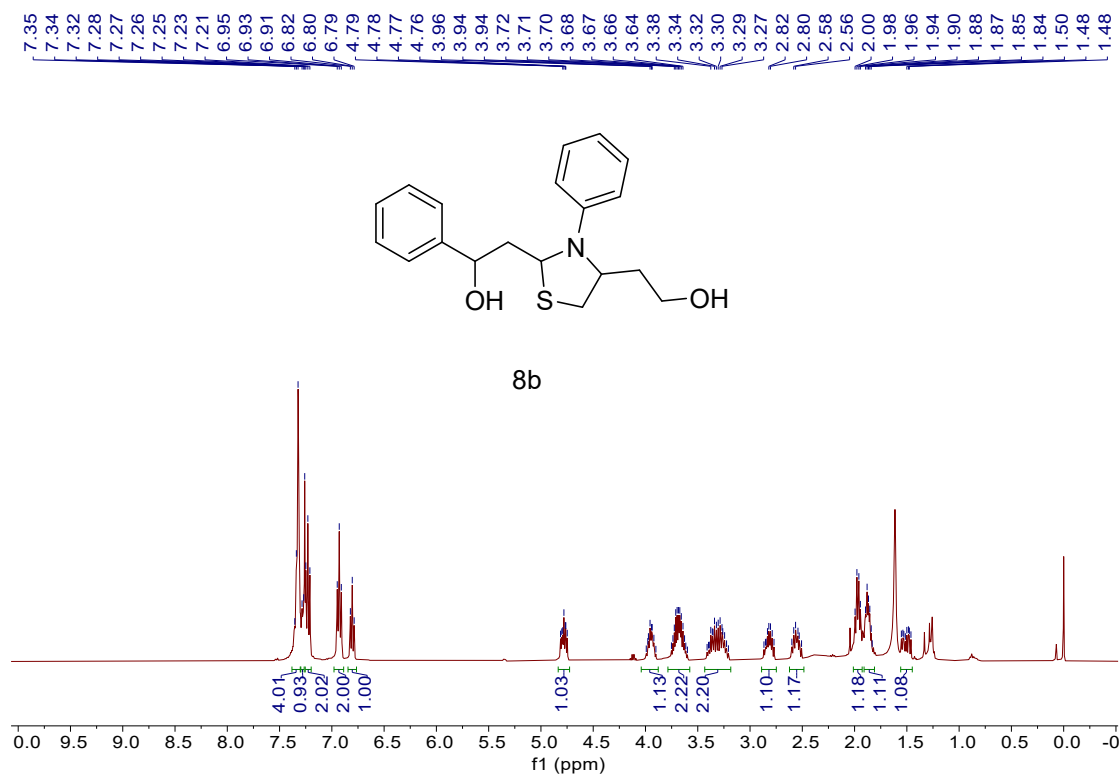


Figure S80. 8b (^1H NMR, 400 MHz, CDCl_3)

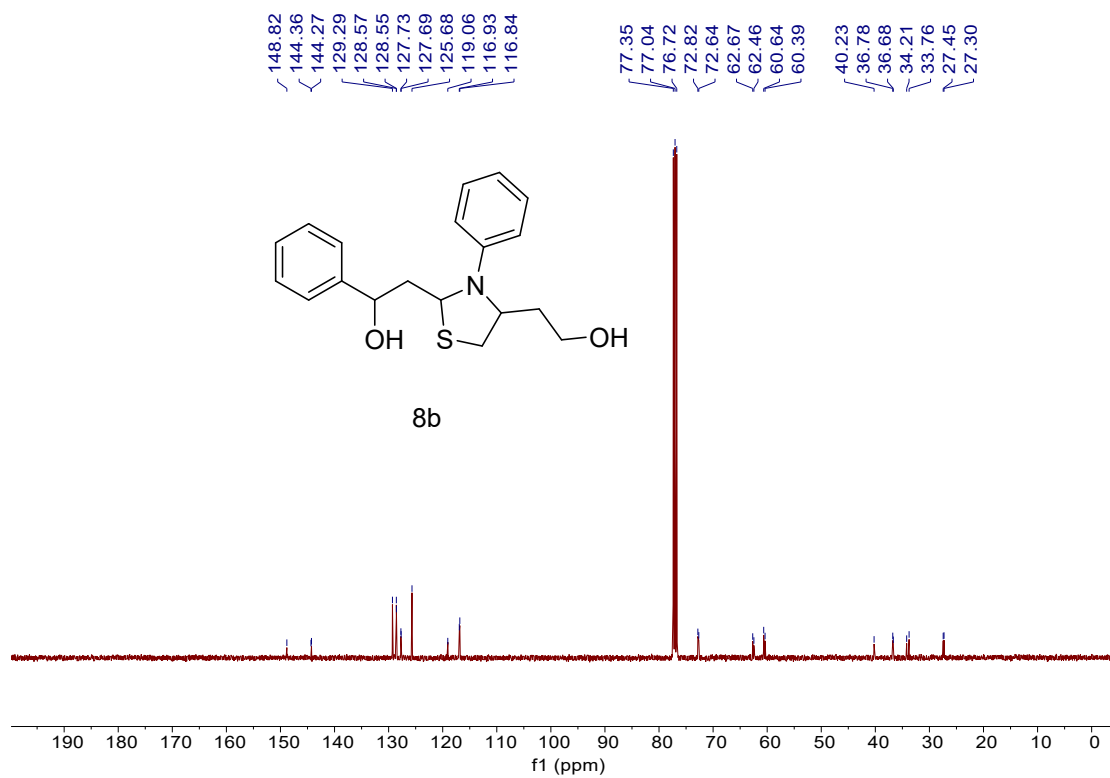


Figure S81. 8b (^{13}C NMR, 100 MHz, CDCl_3)

2. X-raycrystal structure

X-raycrystal structure of **3aa**

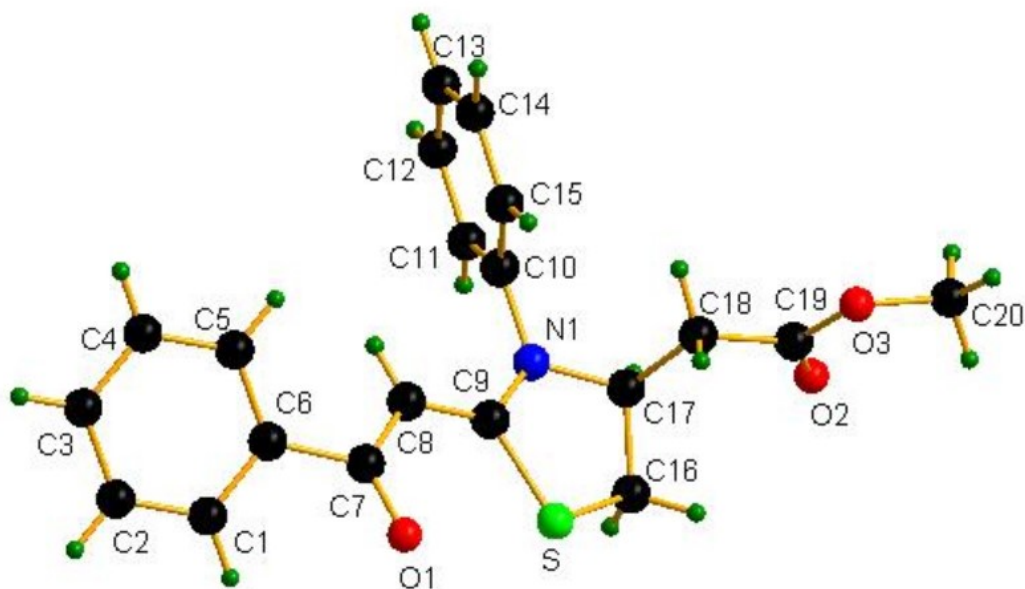


Figure S82. X-raycrystal structure of **3aa**

Single crystals of **3aa** were grown in ethyl acetate and petroleum ether. petroleum ether (2.0 mL) was added to **3aa** (20 mg in a 3 mL vial) followed by 6 drops of ethyl acetate. The 3 mL vial was capped and placed at room temperature in the experimental cabinet for 5 days, whereupon crystals formed. A yellow block shaped crystal of **3aa** was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 193(2) K, on a Rigaku AFC7R diffractometer. The crystal data of **3aa** have been deposited in CCDC with number 2019802 and have been displayed at 50% ellipsoid contour probability level.

Table S1. Crystal data and structure refinement for 3aa.

Identification code	3aa	
Empirical formula	C ₂₀ H ₁₉ N O ₃ S	
Formula weight	353.42	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.424(4) Å	a = 69.255(12)°.
	b = 9.886(4) Å	b = 76.260(14)°.
	c = 10.482(4) Å	g = 89.585(14)°.
Volume	884.0(6) Å ³	
Z	2	
Density (calculated)	1.328 Mg/m ³	
Absorption coefficient	0.202 mm ⁻¹	
F(000)	372	
Crystal size	0.120 x 0.110 x 0.080 mm ³	
Theta range for data collection	2.233 to 28.311°.	
Index ranges	-12<=h<=12, -11<=k<=13, -13<=l<=13	
Reflections collected	8429	
Independent reflections	4233 [R(int) = 0.0264]	
Completeness to theta = 25.242°	97.7 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4233 / 0 / 227	
Goodness-of-fit on F ²	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0540, wR2 = 0.1469	
R indices (all data)	R1 = 0.0626, wR2 = 0.1548	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.798 and -0.378 e. Å ⁻³	

X-raycrystal structure of **7aa**

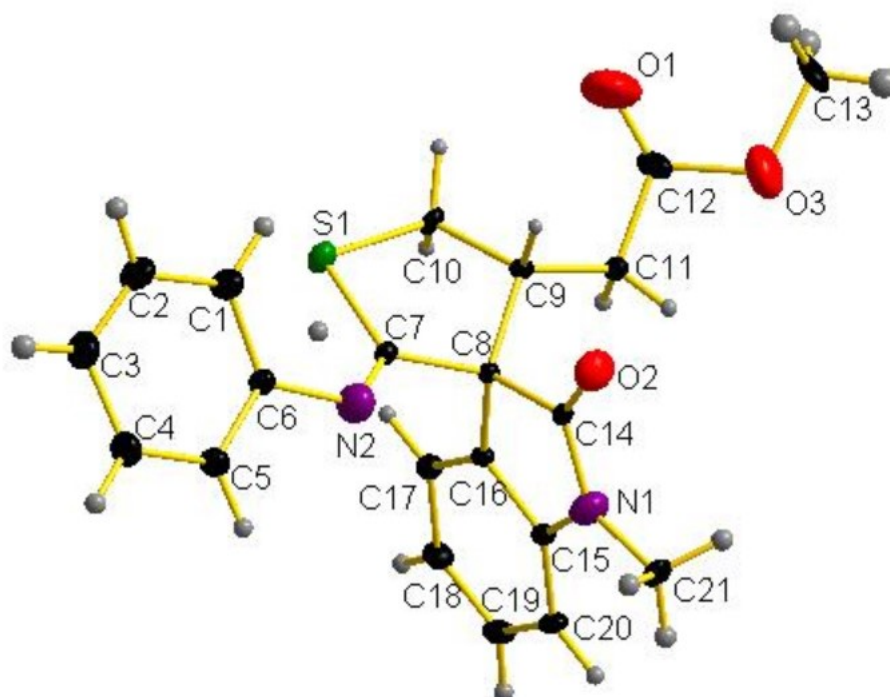


Figure S83. X-raycrystal structure of **7aa**

Single crystals of **7aa** were grown in ethyl acetate and petroleum ether. petroleum ether (2.0 mL) was added to **7aa** (10 mg in a 3 mL vial) followed by 6 drops of ethyl acetate. The 3 mL vial was capped and placed at room temperature in the experimental cabinet for 3 days, whereupon crystals formed. A White block shaped crystal of **7aa** was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 193(2) K, on a Rigaku AFC7R diffractometer. The crystal data of **7aa** have been deposited in CCDC with number 2019886 and have been displayed at 50% ellipsoid contour probability level.

Table S2. Crystal data and structure refinement for 7aa.

Identification code	7aa	
Empirical formula	C ₂₁ H ₂₀ N ₂ O ₃ S	
Formula weight	380.45	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 26.464(11) Å	a = 90°.
	b = 9.374(4) Å	b = 130.263(13)°.
	c = 19.700(10) Å	g = 90°.
Volume	3729(3) Å ³	
Z	8	
Density (calculated)	1.355 Mg/m ³	
Absorption coefficient	0.198 mm ⁻¹	
F(000)	1600	
Crystal size	0.120 x 0.110 x 0.080 mm ³	
Theta range for data collection	2.395 to 27.826°.	
Index ranges	-33<=h<=34, -12<=k<=12, -25<=l<=25	
Reflections collected	14077	
Independent reflections	4284 [R(int) = 0.0462]	
Completeness to theta = 25.242°	97.7 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4284 / 186 / 318	
Goodness-of-fit on F ²	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0728, wR2 = 0.1944	
R indices (all data)	R1 = 0.0939, wR2 = 0.2074	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.705 and -0.601 e. Å ⁻³	