

Supporting information

Facile synthesis of benzo[*b*]thiophenes *via* metal-free radical-triggered intramolecular C-S bond formation

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General Information

Melting points were determined in open capillaries and were uncorrected. IR spectra were taken on a FT-IR-Tensor 27 spectrometer in KBr pellets and reported in cm^{-1} . ^1H NMR (^{13}C NMR) spectra were measured on a Bruker DPX 400 MHz spectrometer in $\text{DMSO-}d_6$ or $\text{DMF-}d_7$ with chemical shift (δ) given in ppm relative to TMS as internal standard [(s = singlet, d = doublet, t = triplet, brs = broad singlet, m = multiplet), coupling constant (Hz)]. HRMS (ESI) was determined by using microTOF-Q II HRMS/MS instrument (BRUKER). X-Ray crystallographic analysis was performed with a Siemens SMART CCD and a Siemens P4 diffractometer.

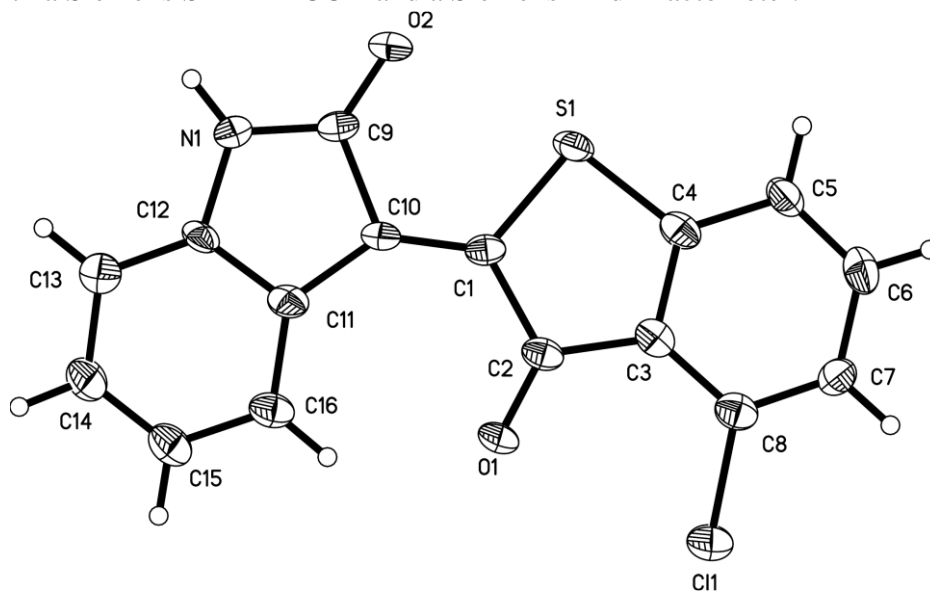
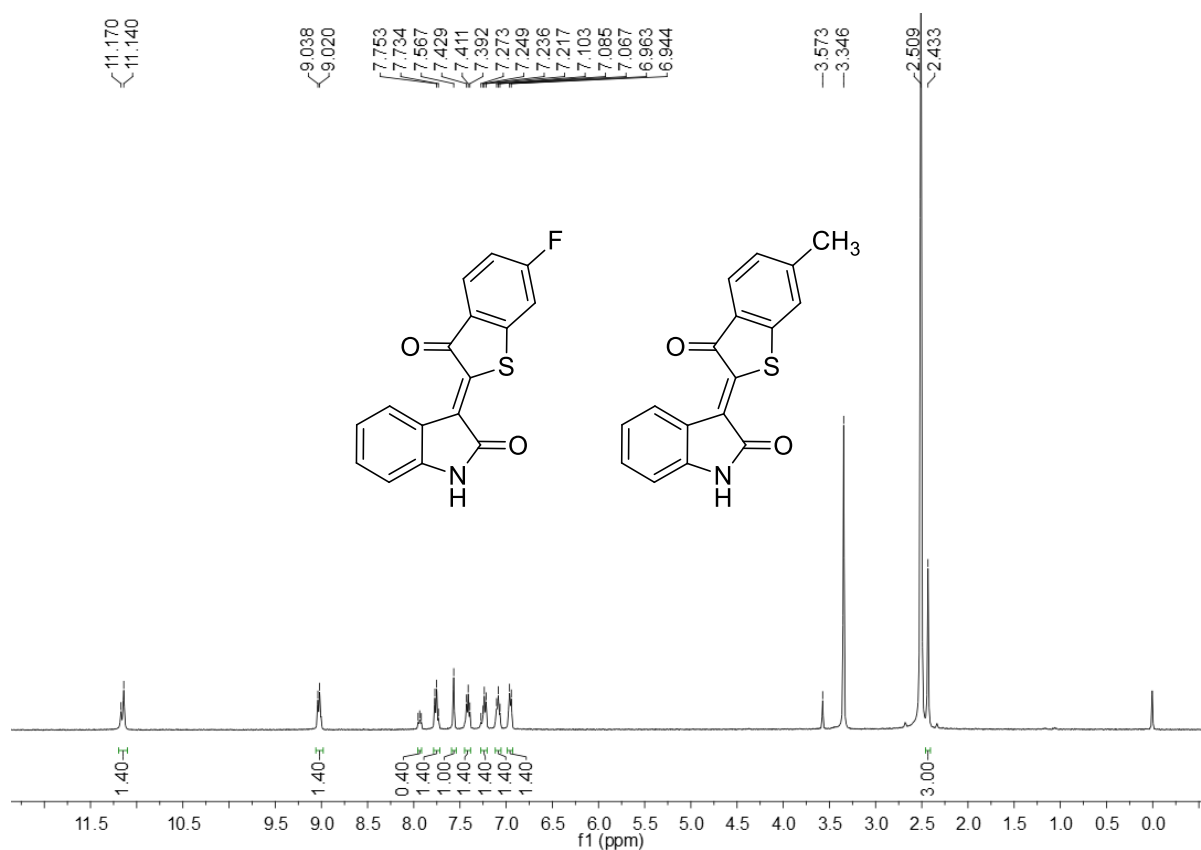
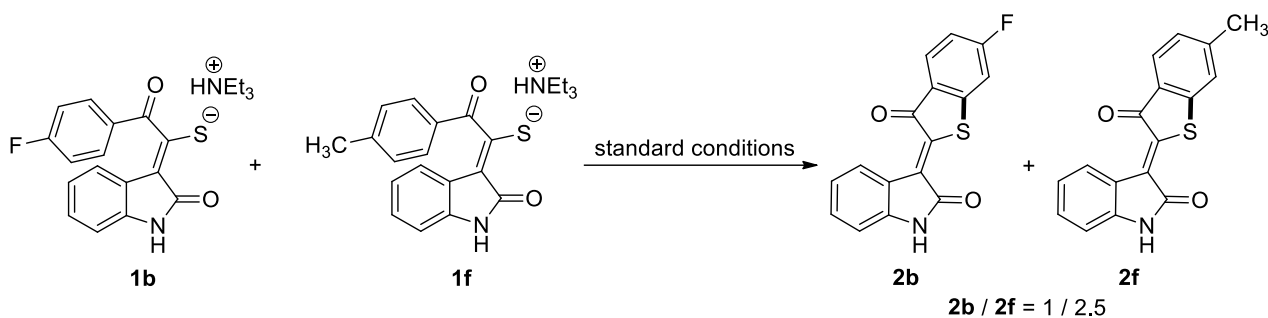


Fig 1, X-ray Structure of 2d

Crystal data for **2d**: $\text{C}_{16}\text{H}_8\text{ClNO}_2\text{S}$, $M_r = 313.74$, Monoclinic, $a = 3.8280(2)$ Å, $b = 13.3111(11)$ Å, $c = 25.038(2)$ Å, $U = 1275.64(17)$ Å³, $T = 298(2)$ K, space group $\text{P2}(1)/n$, $Z = 4$, 6131 reflections measured, 2219 unique ($R_{\text{int}} = 0.1893$) which were used in all calculation. The final $wR(F_2)$ was 0.2492 (all data)

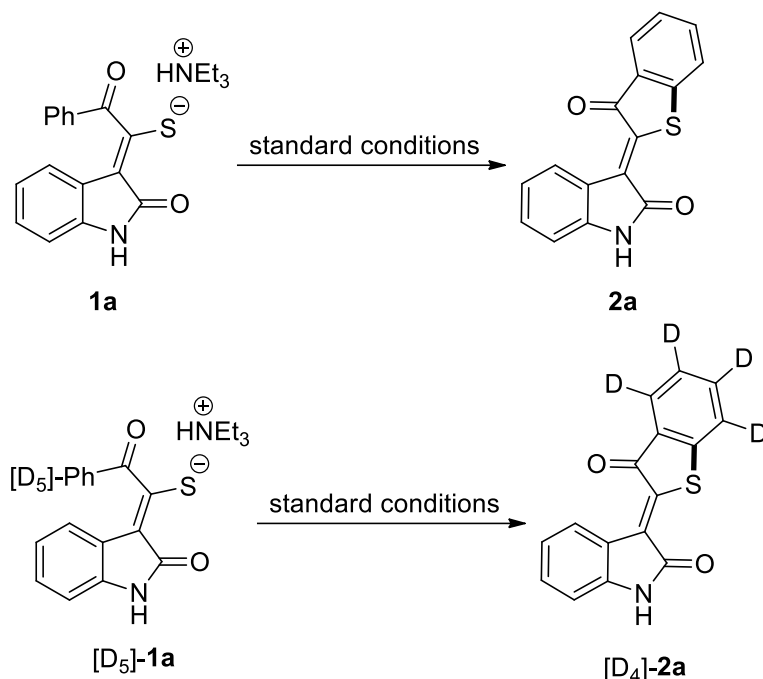
Intermolecular Competition Experiments

Triethylammonium (*Z*)-2-(4-fluorophenyl)-2-oxo-1-(2-oxoindolin-3-ylidene)ethanethiolate (**1b**, 1.0 mmol, 400 mg) and triethylammonium (*Z*)-2-oxo-1-(2-oxoindolin-3-ylidene)-2-(*p*-tolyl)ethanethiolate (**1f**, 1.0 mmol, 396 mg) were introduced into a 10-mL reaction vial. Then I₂ (0.2 mmol, 50.8 mg) and 1,4-dioxane (2.0 mL) were successively added, and the mixture stirred at 120 °C under microwave conditions for 1 h. After completion of the reaction (monitored by TLC), the reaction mixture was down to room temperature. The solid products were collected by Büchner filtration to give **2b** and **2f**.

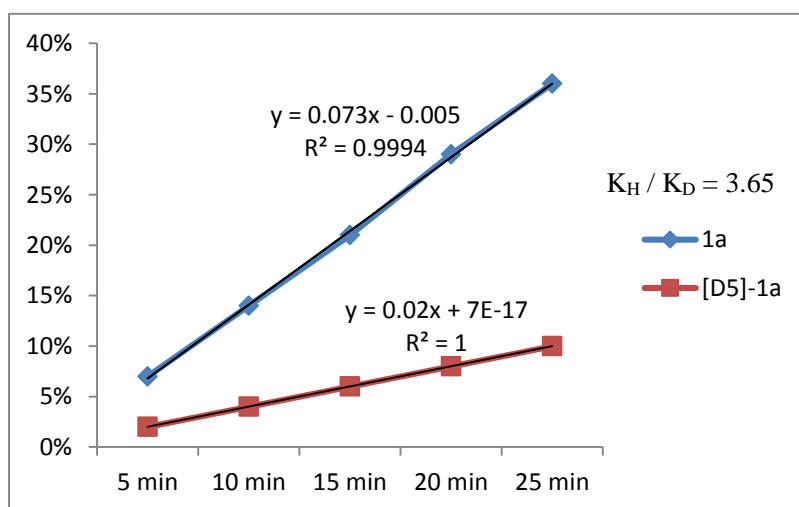


Deuterium Kinetic Isotope Effect

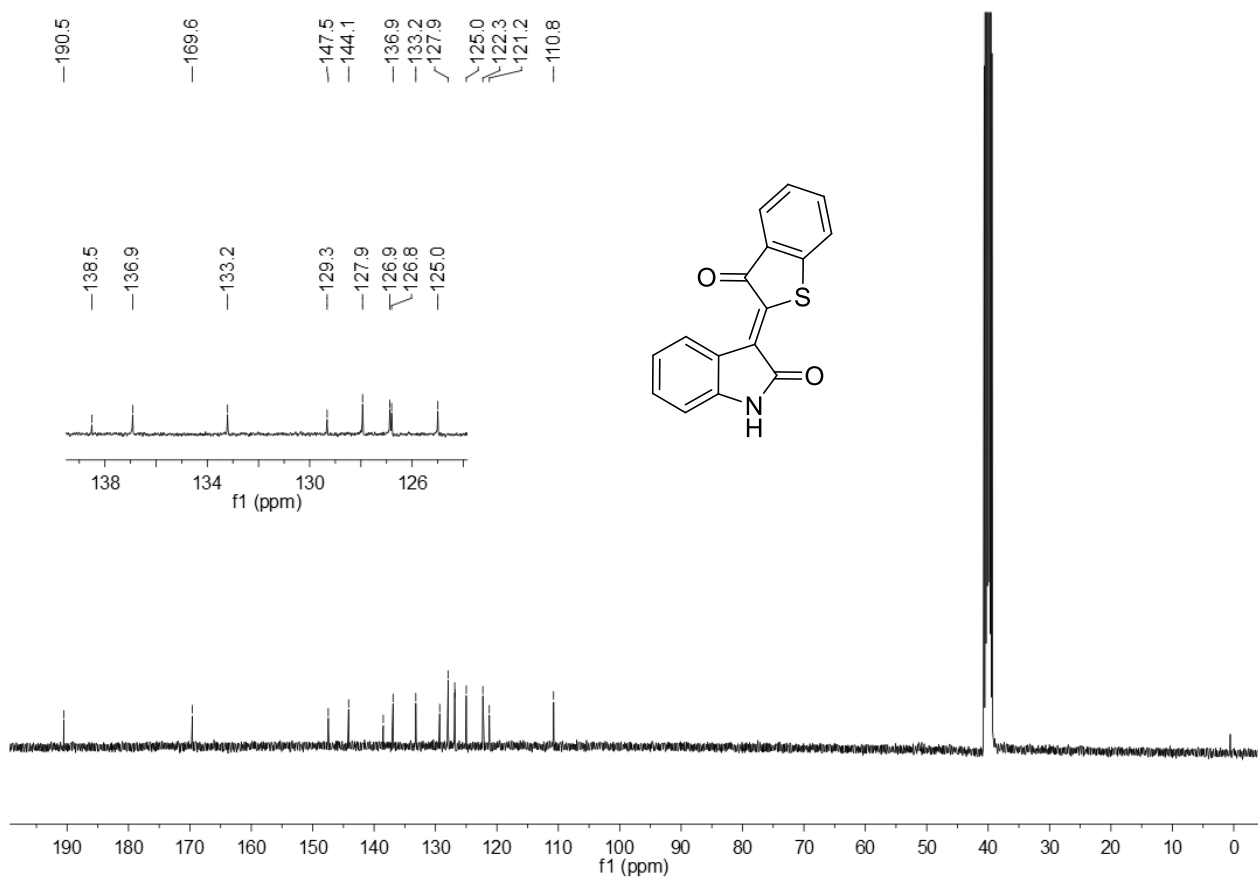
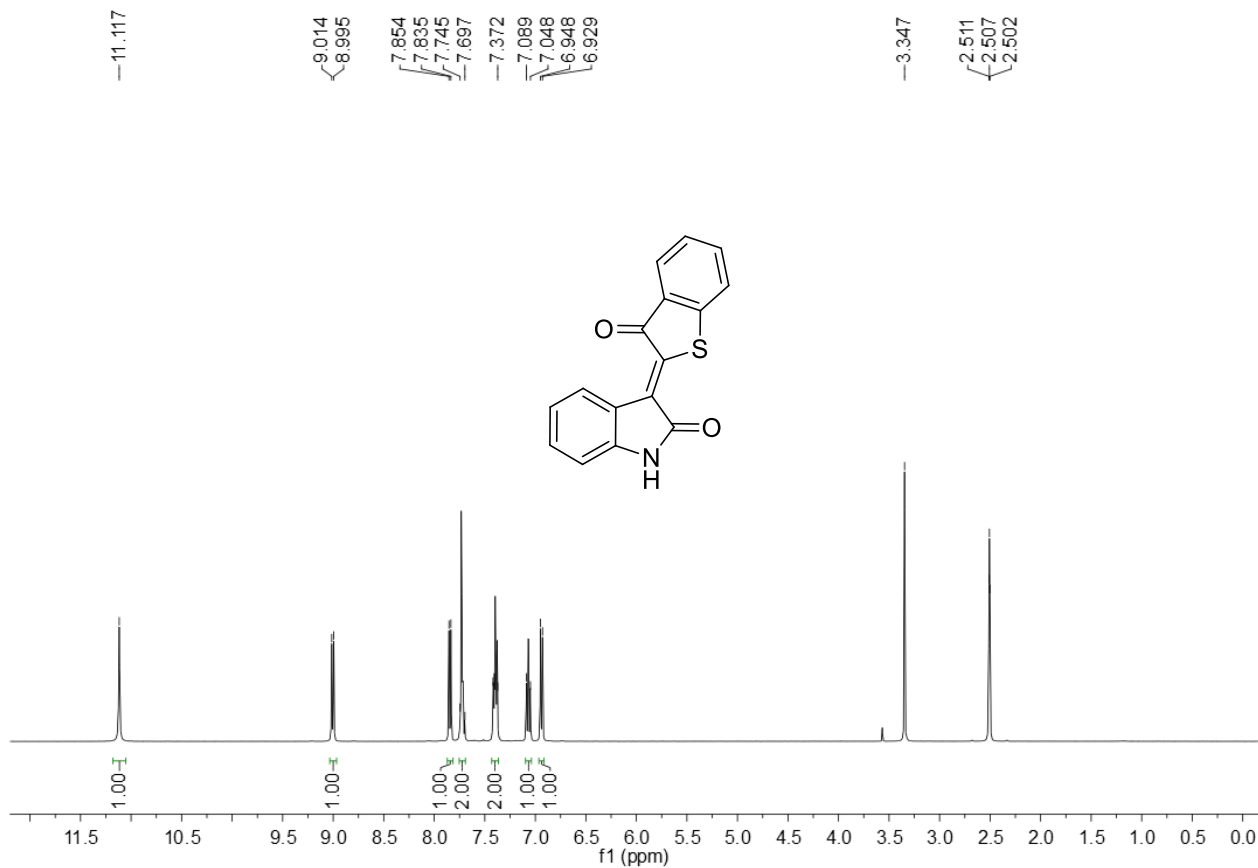
Triethylammonium (*Z*)-2-oxo-1-(2-oxoindolin-3-ylidene)-2-phenylethanethiolate (**1a**, 0.1 mmol, 38.2 mg) or triethylammonium (*Z*)-2-oxo-1-(2-oxoindolin-3-ylidene)-2-phenyl-*d*₅-ethanethiolate ([*D*₅]-**1a**, 0.1 mmol, 38.7 mg) was introduced into a 10-mL reaction vial. Then I₂ (0.02 mmol, 5.08 mg) and 1,4-dioxane (2.0 mL) were successively added, and the mixture stirred at 120 °C under microwave conditions for 5-25 min. After completion of the reaction (monitored by TLC), the reaction mixture was down to room temperature. The solid product was collected by Büchner filtration to give almost pure product **2a** or [*D*₄]-**2a**.



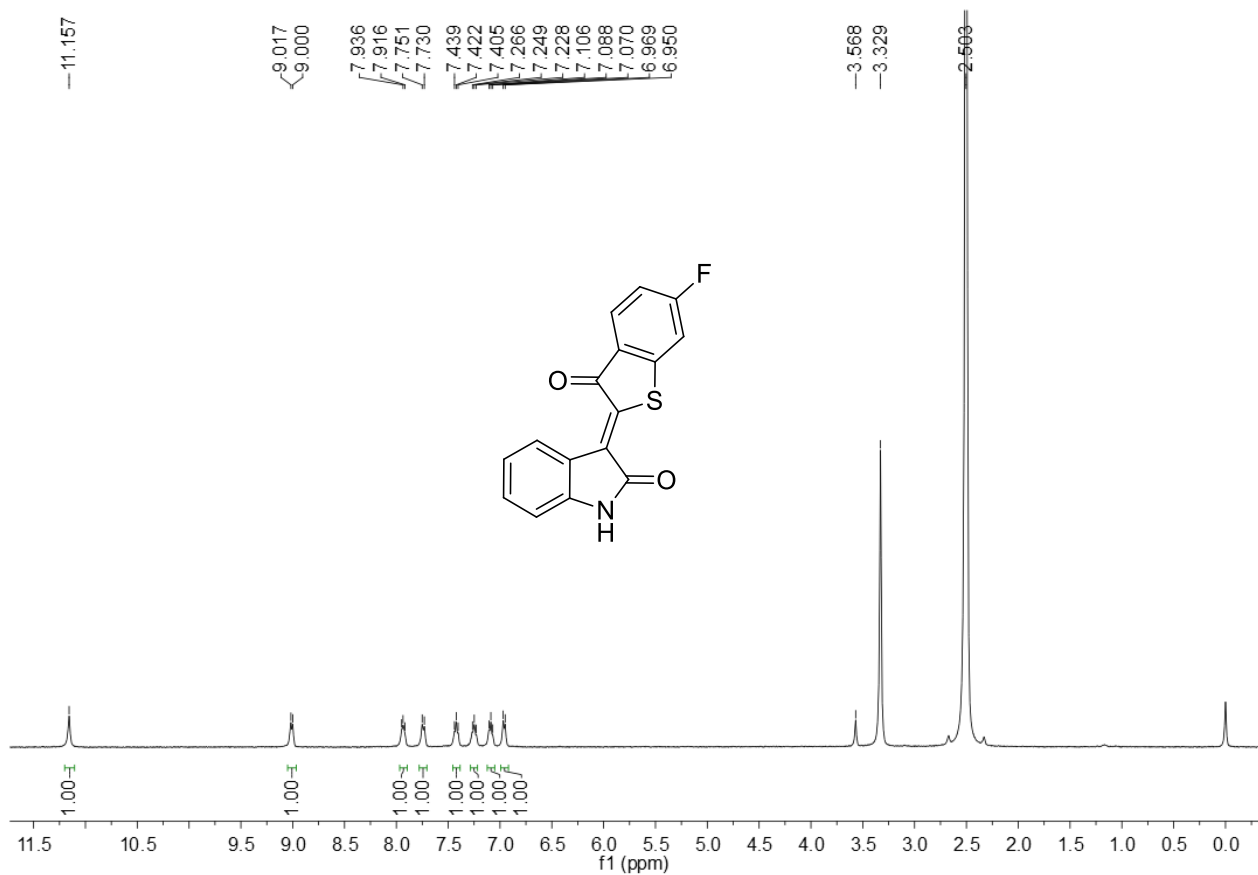
	Yield of 2a or [<i>D</i> ₄]- 2a				
	5 min	10 min	15 min	20 min	25 min
1a	7%	14%	21%	29%	36%
[<i>D</i> ₅]- 1a	2%	4%	6%	8%	10%



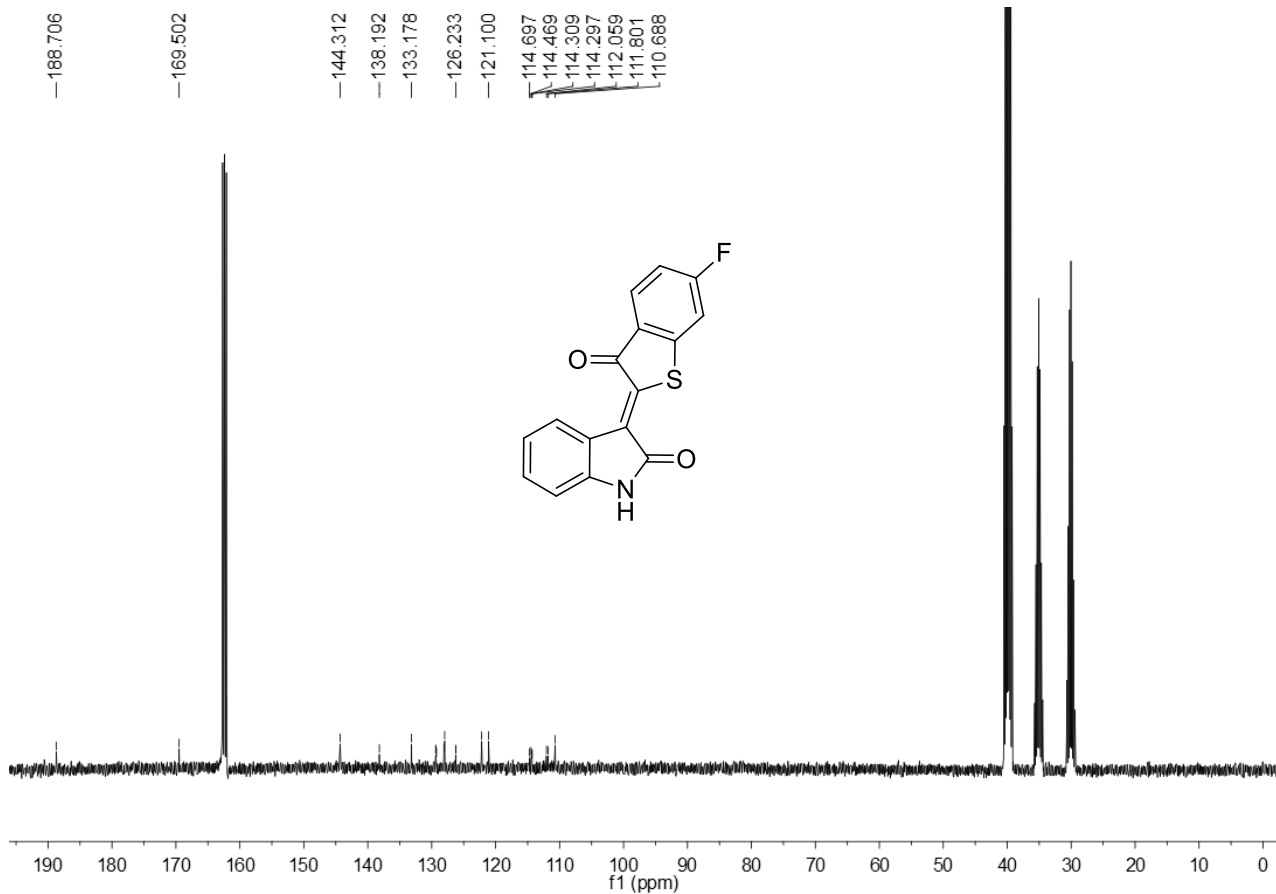
initial rate of **1a** and [*D*₅]-**1a**



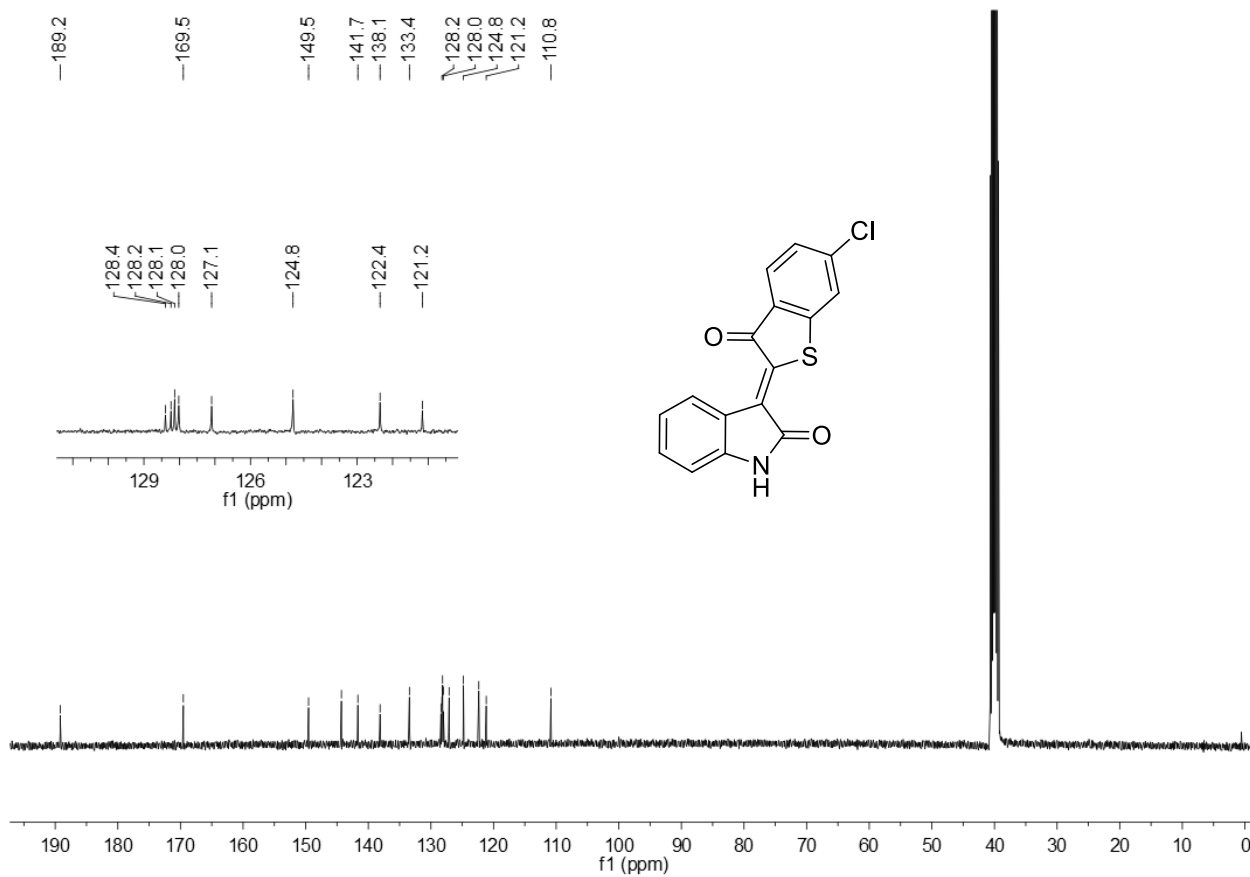
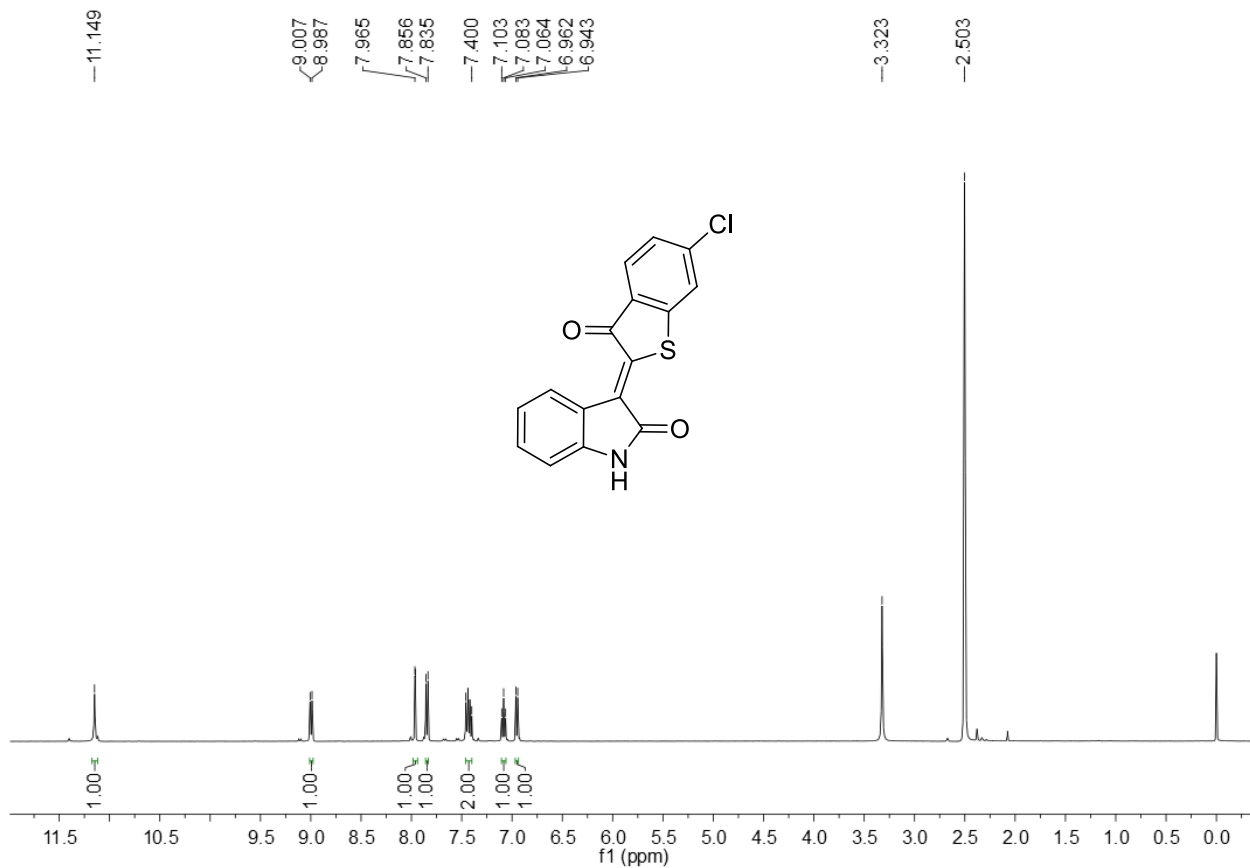
¹³C NMR Spectrum of Compound 2a



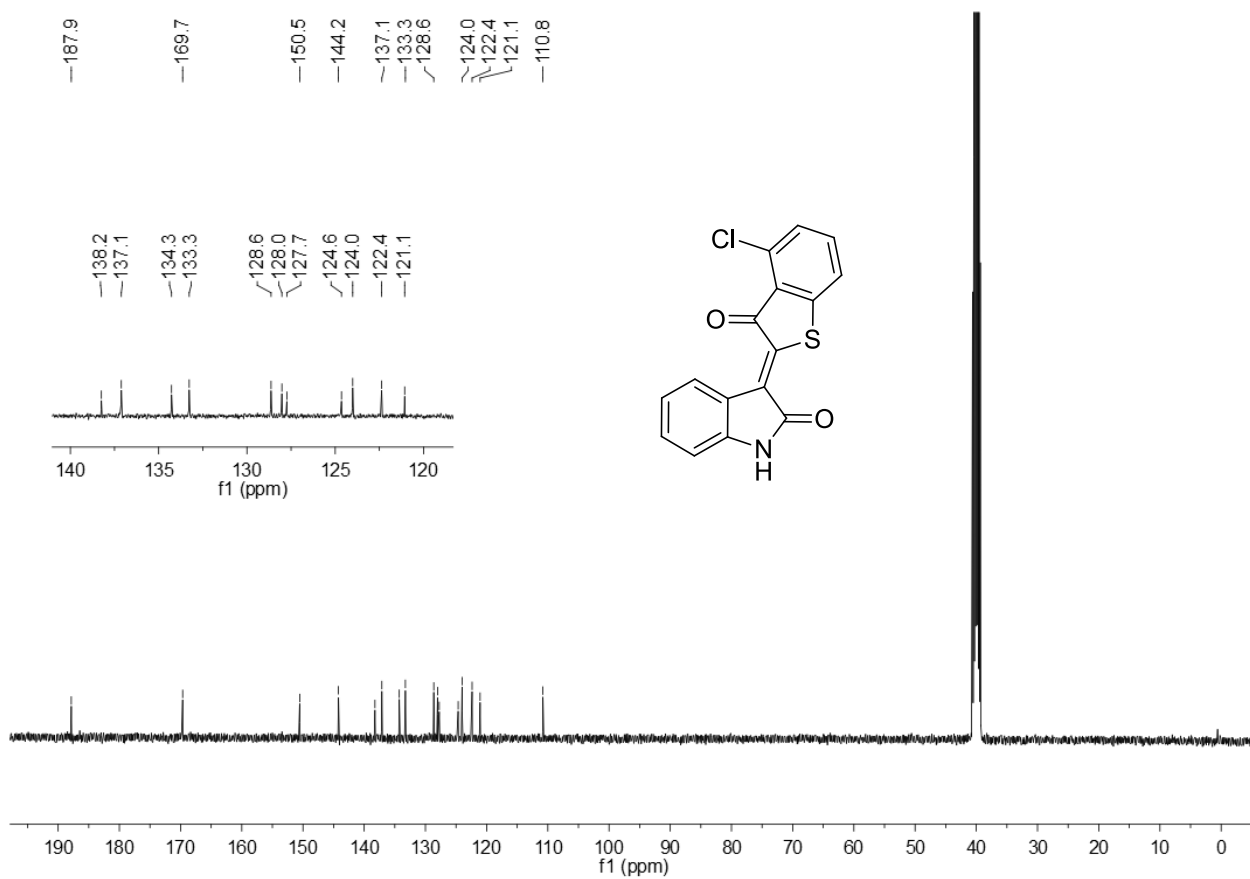
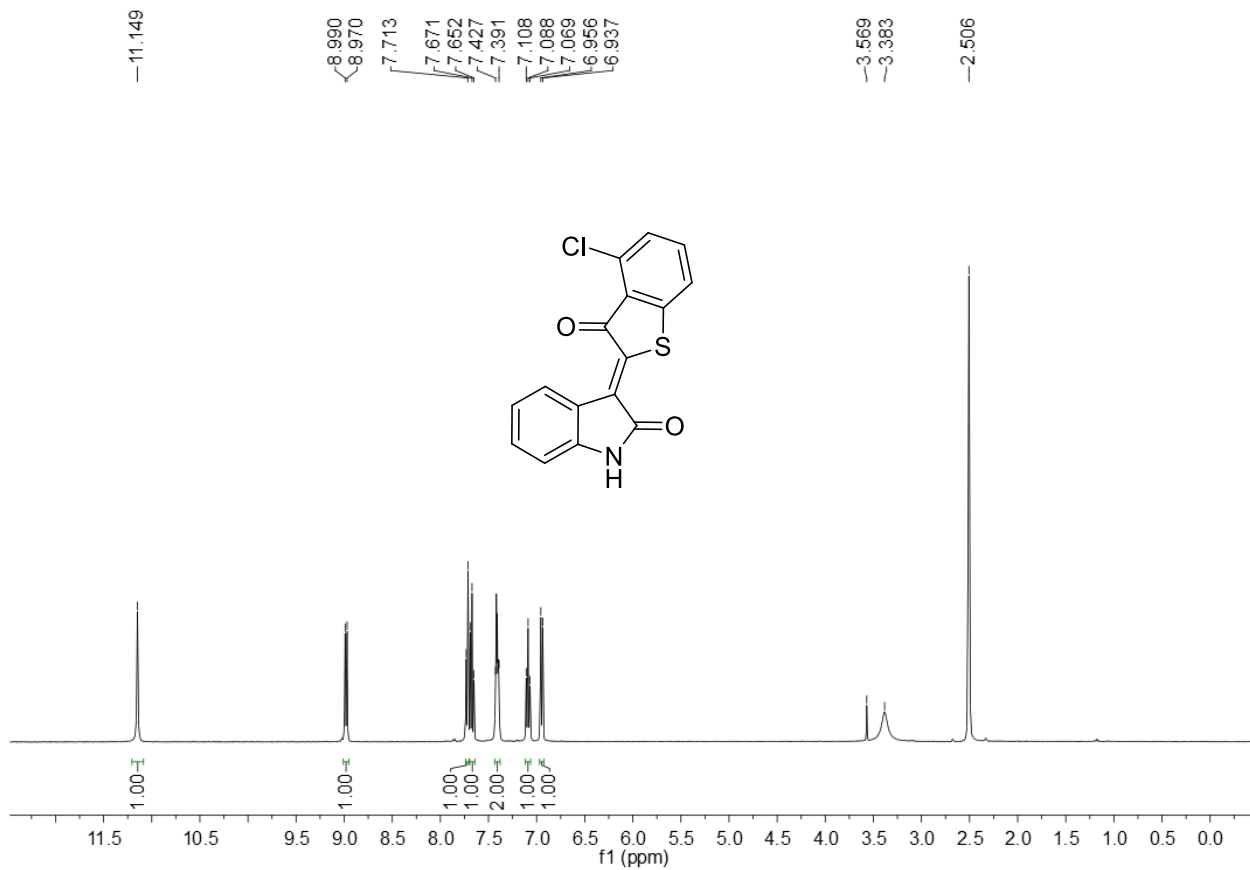
¹H NMR Spectrum of Compound 2b



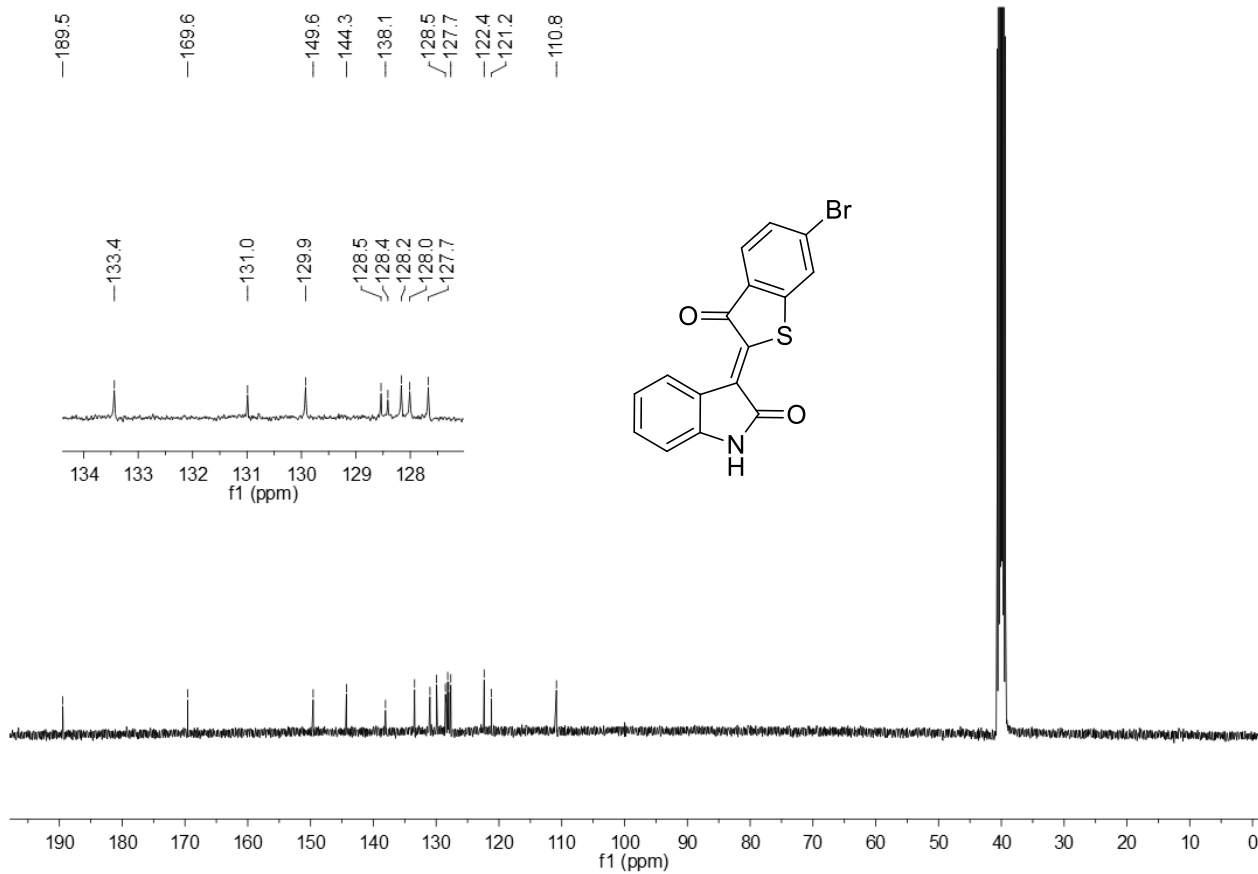
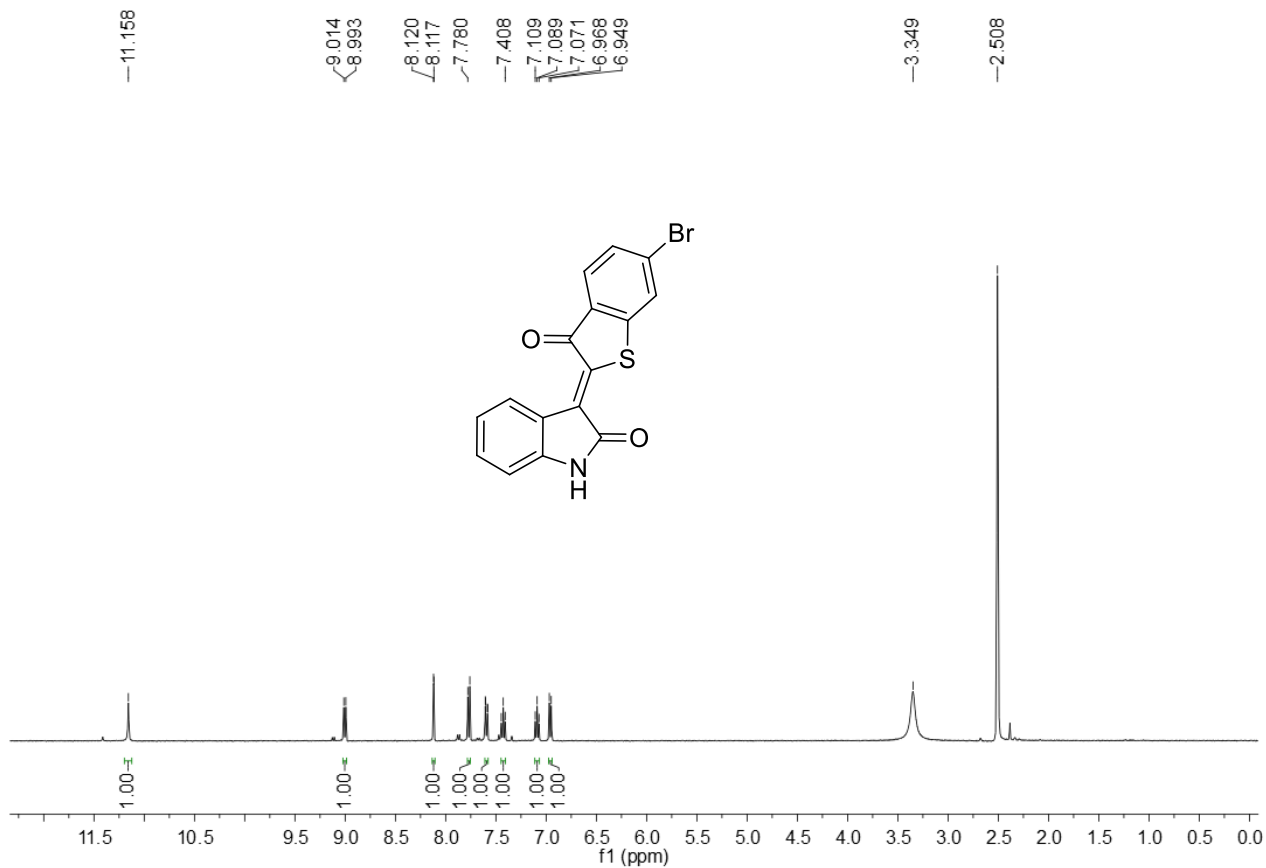
¹³C NMR Spectrum of Compound 2b



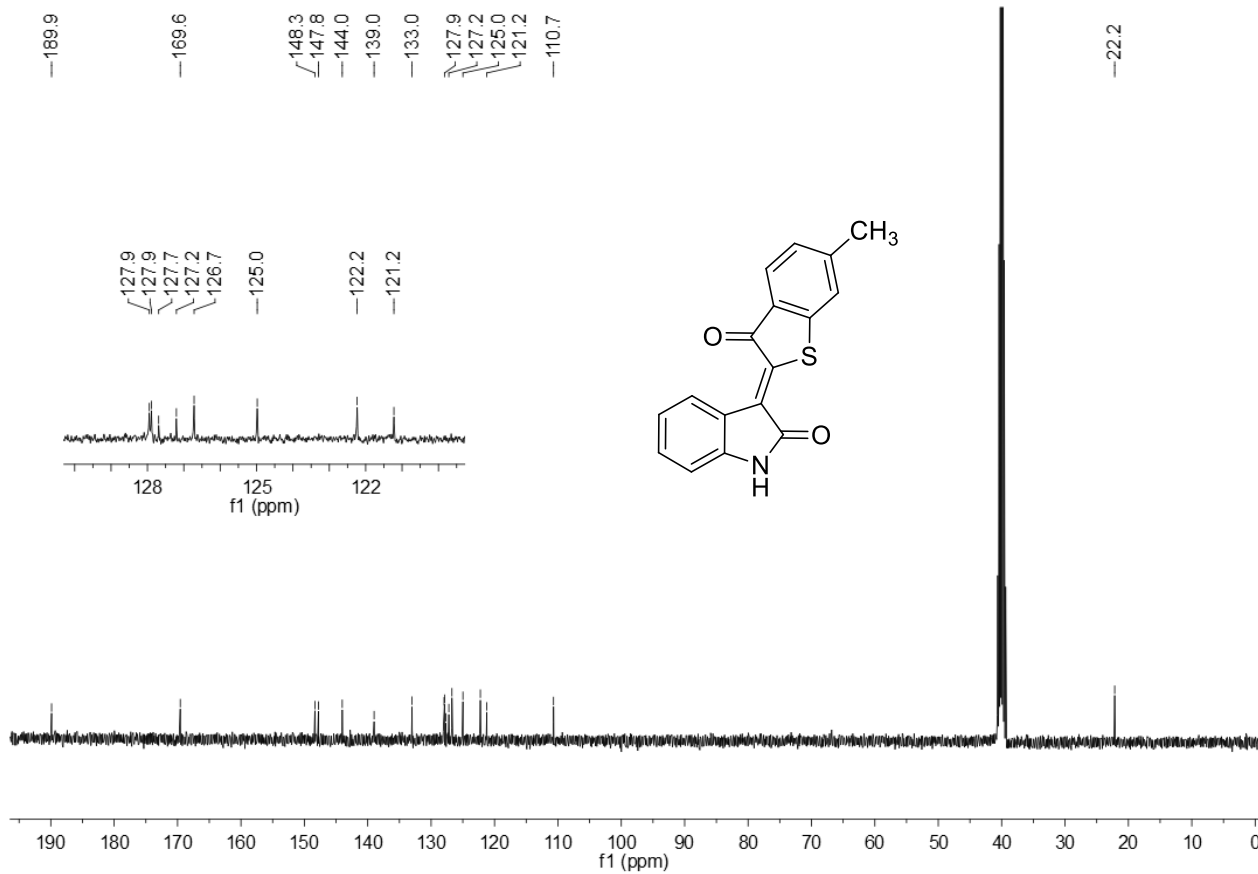
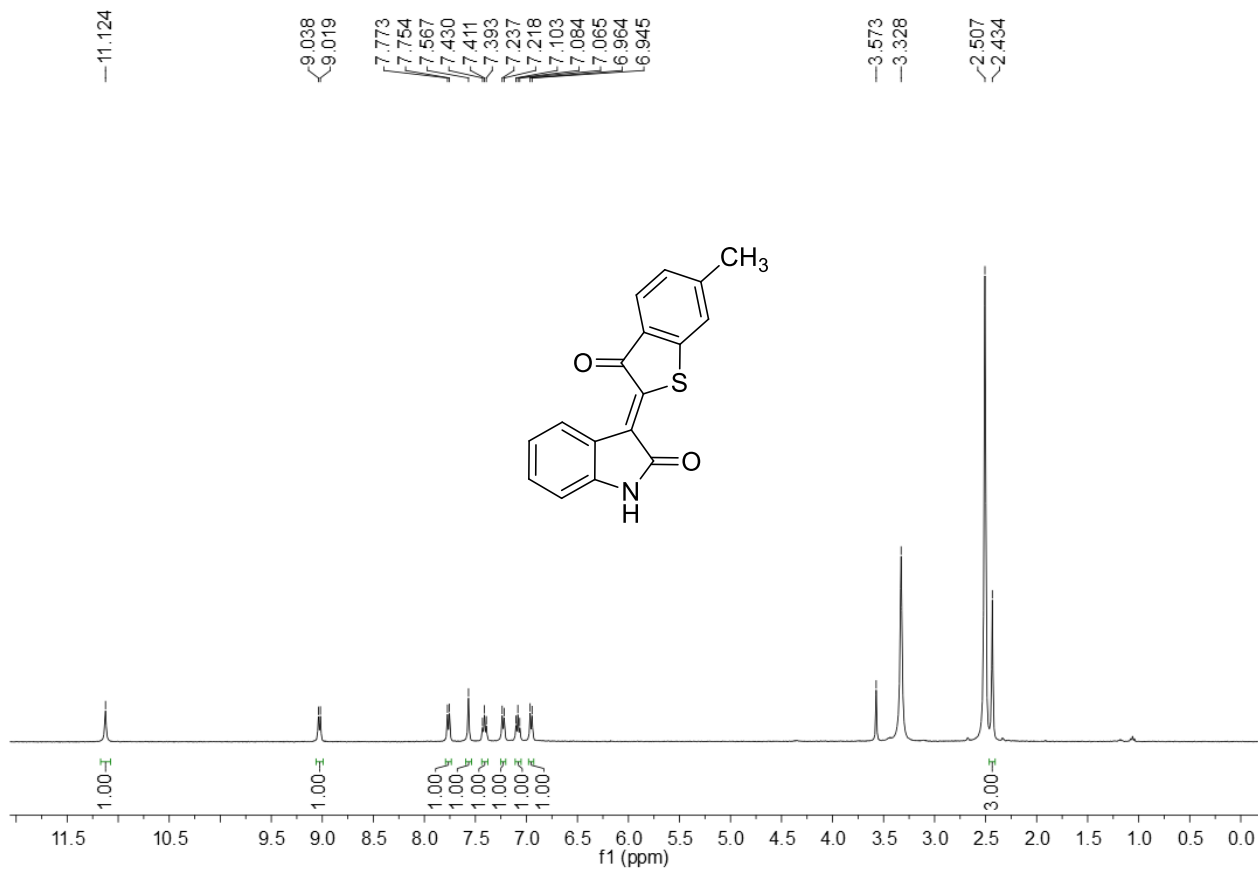
¹³C NMR Spectrum of Compound 2c

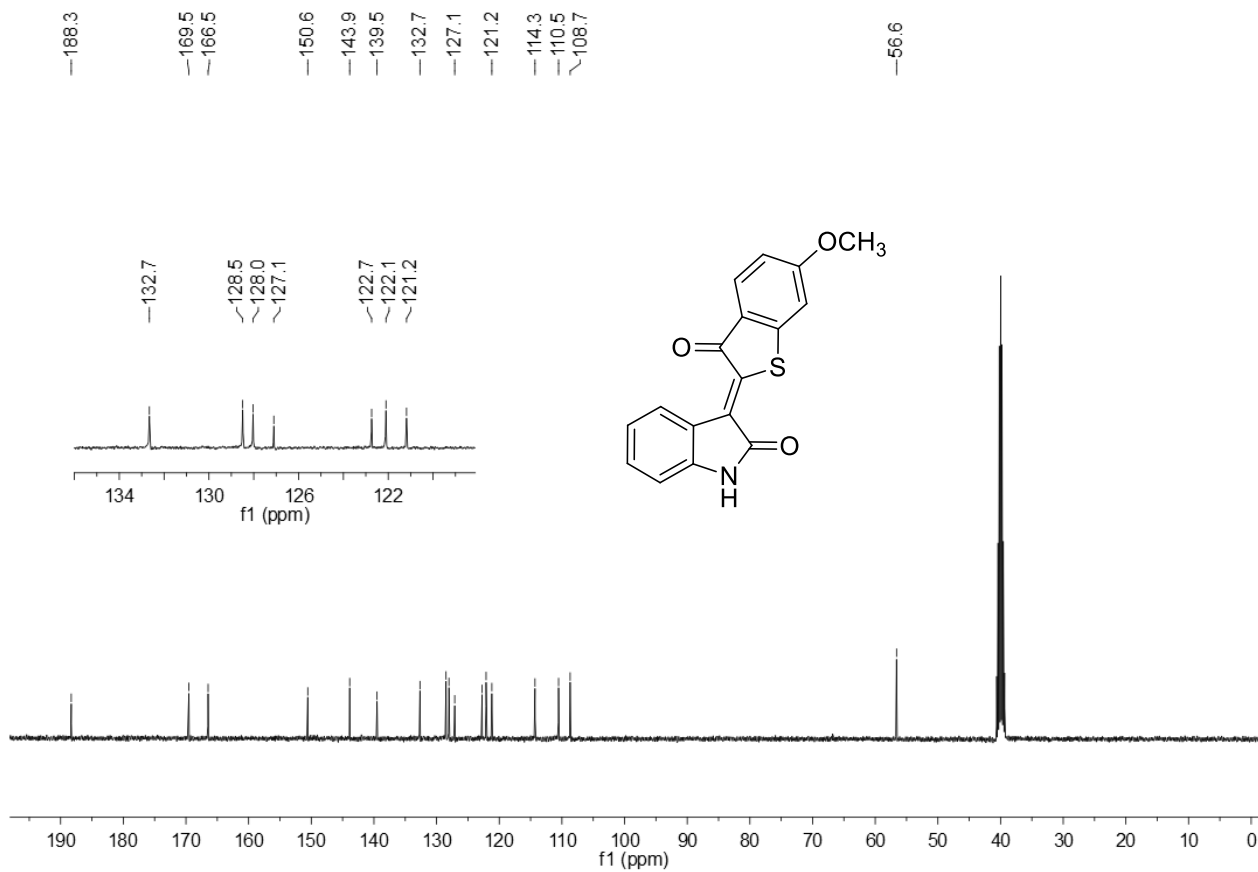
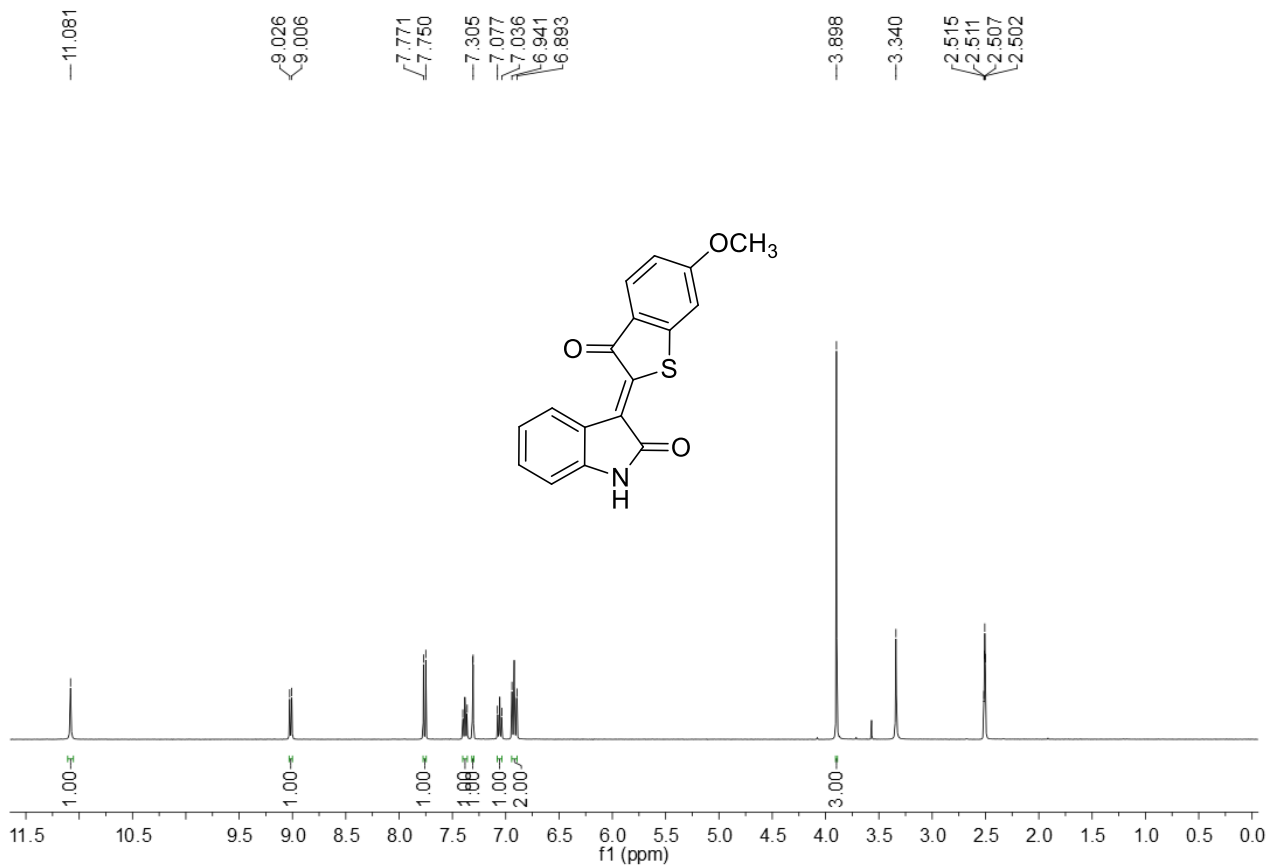


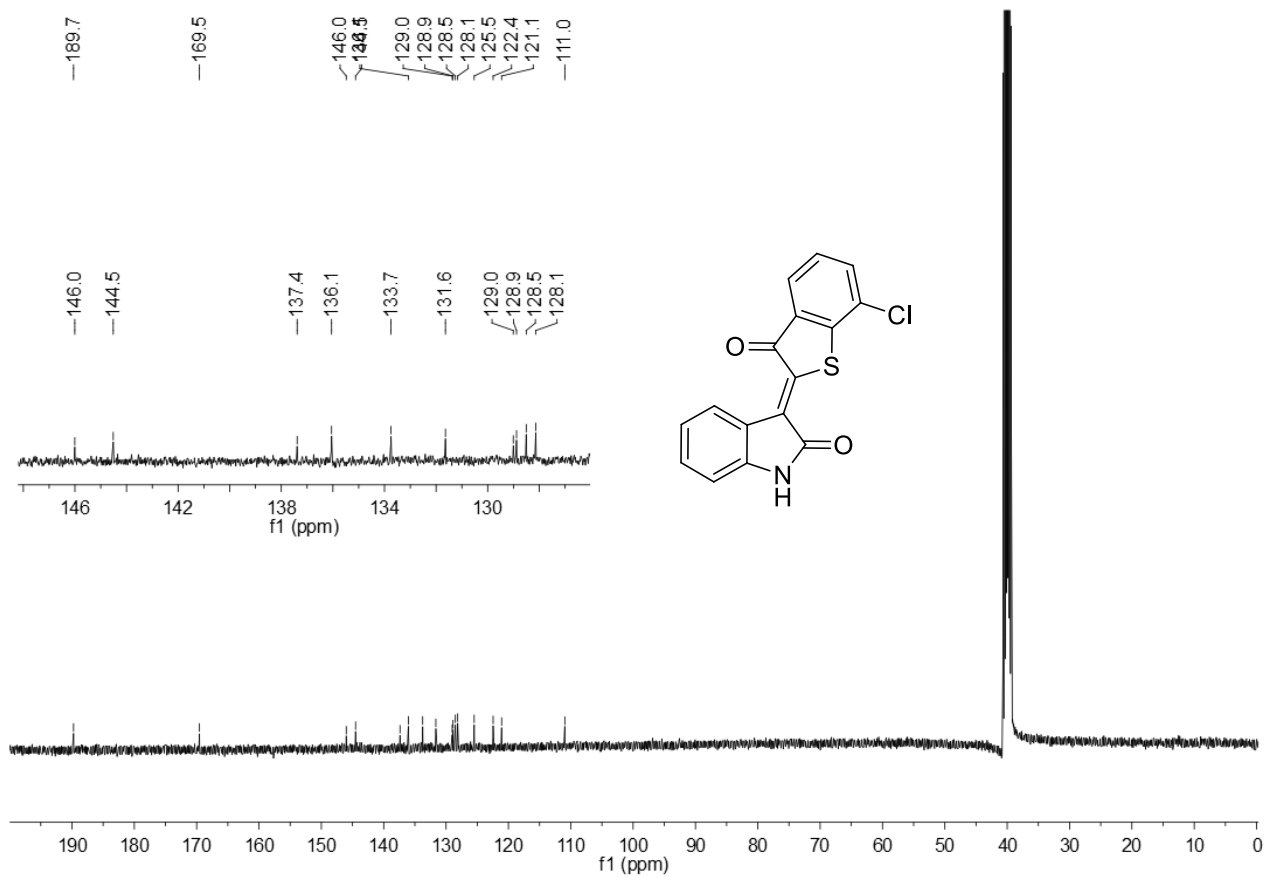
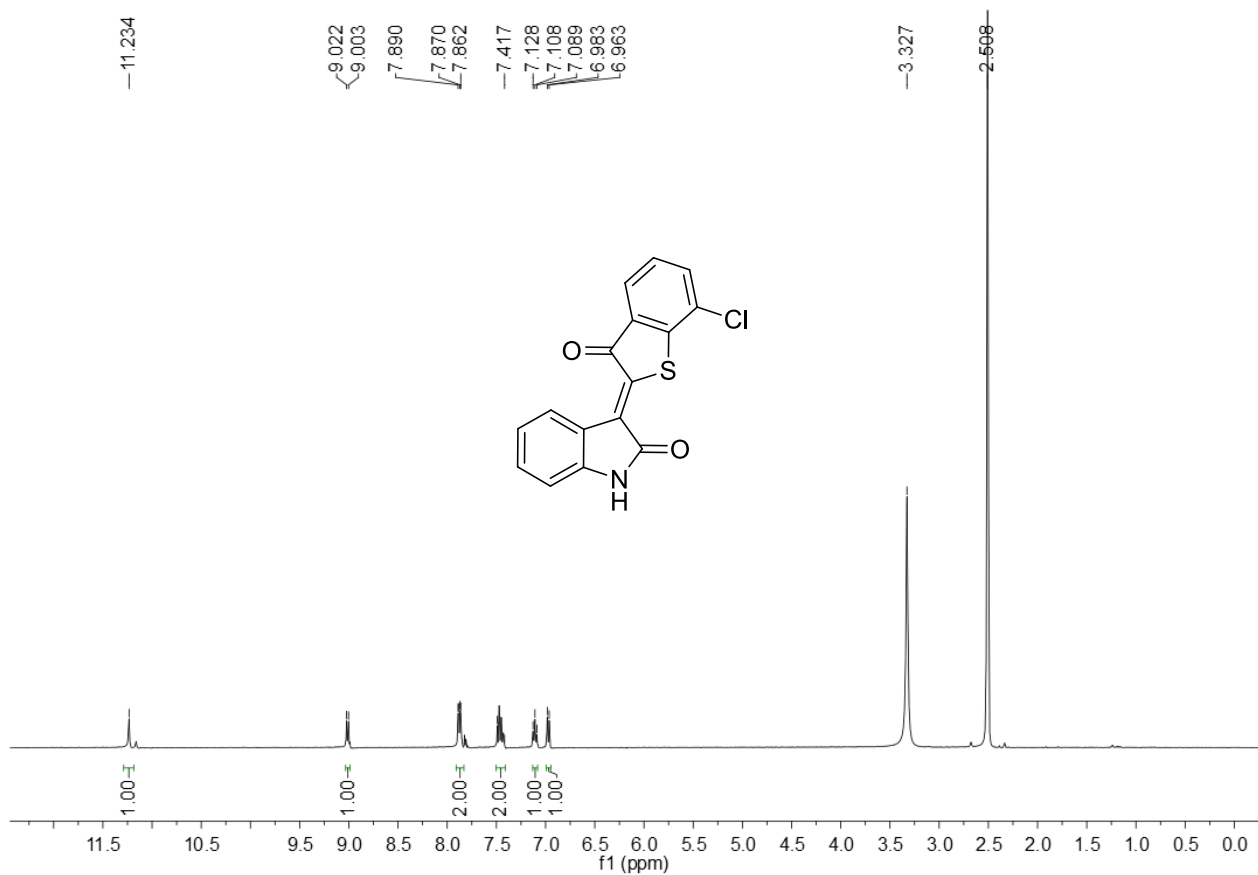
¹³C NMR Spectrum of Compound 2d



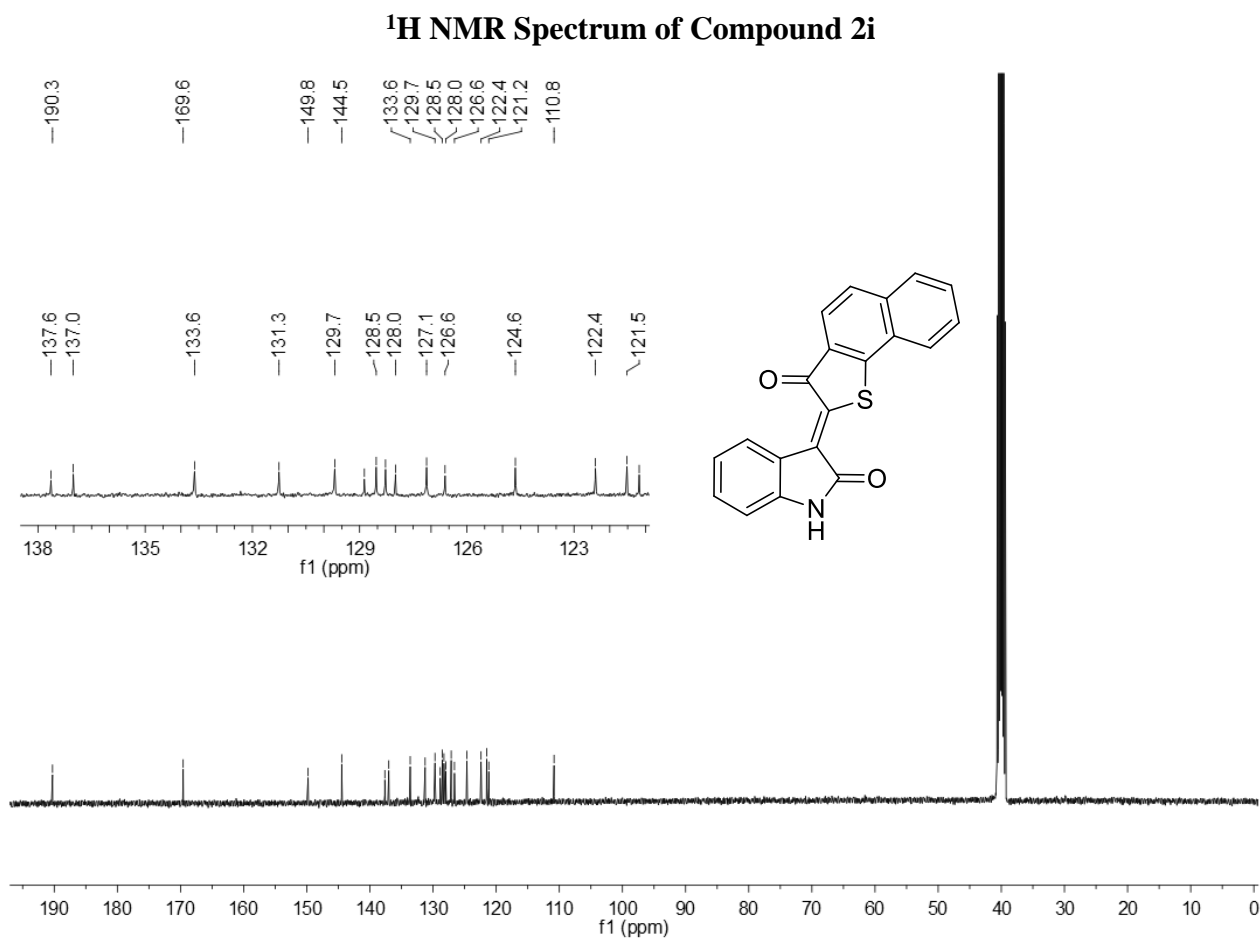
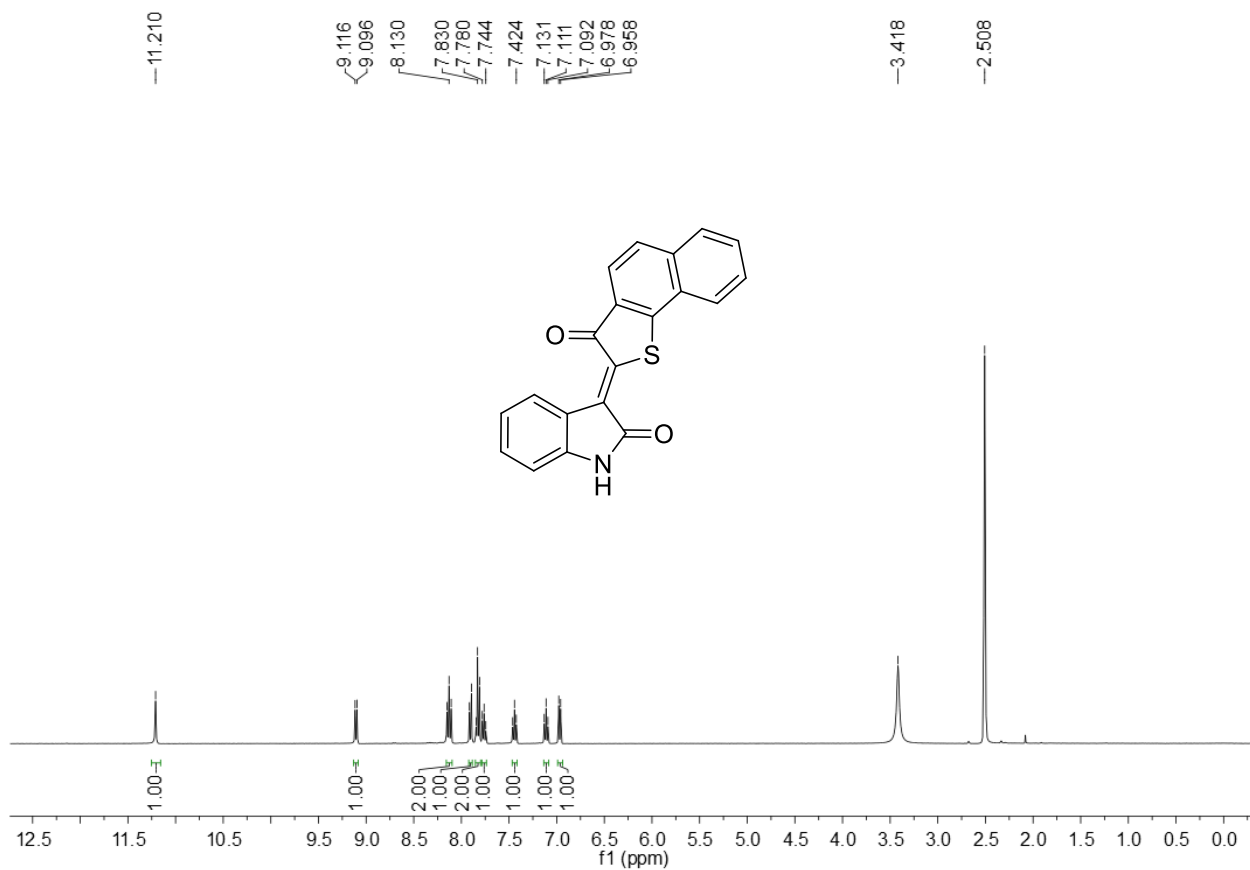
¹³C NMR Spectrum of Compound 2e



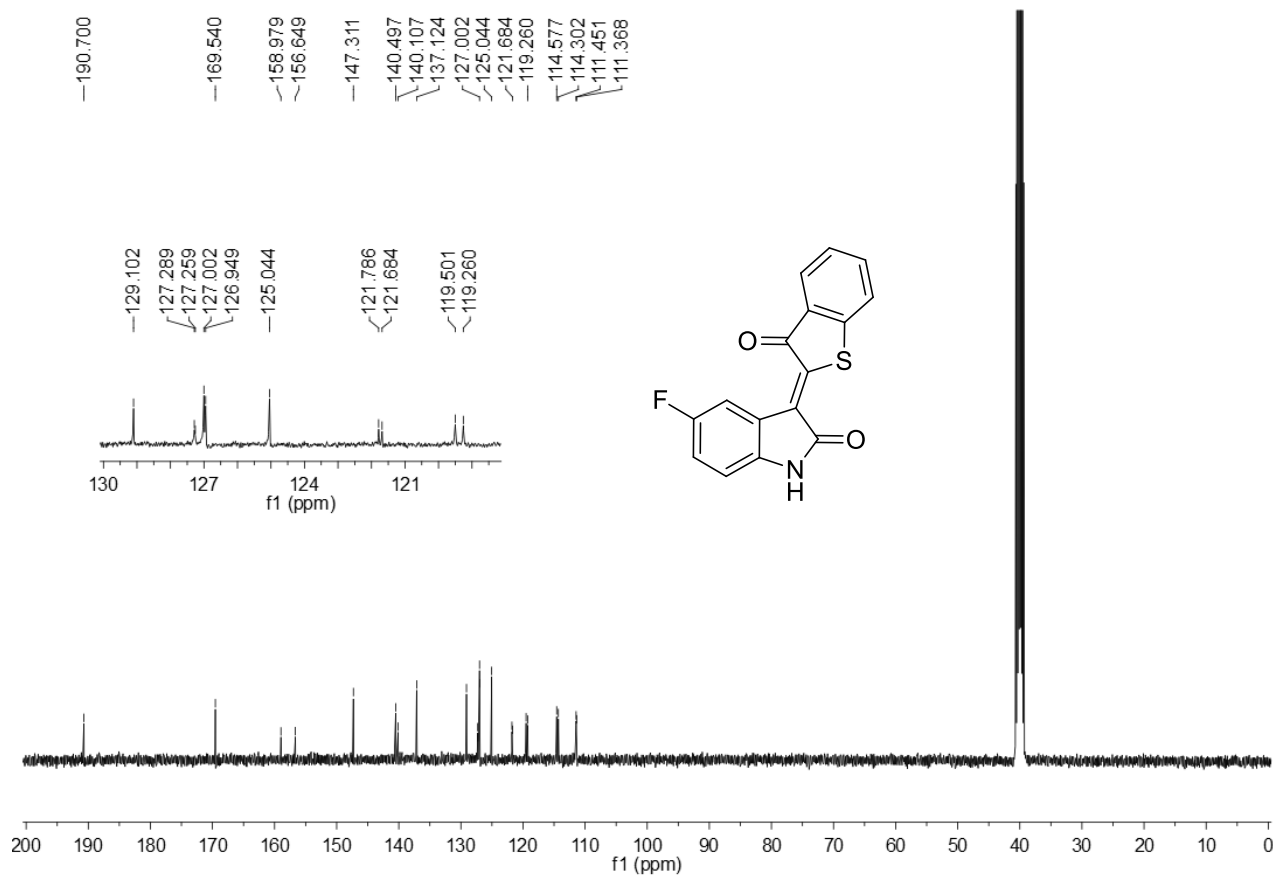
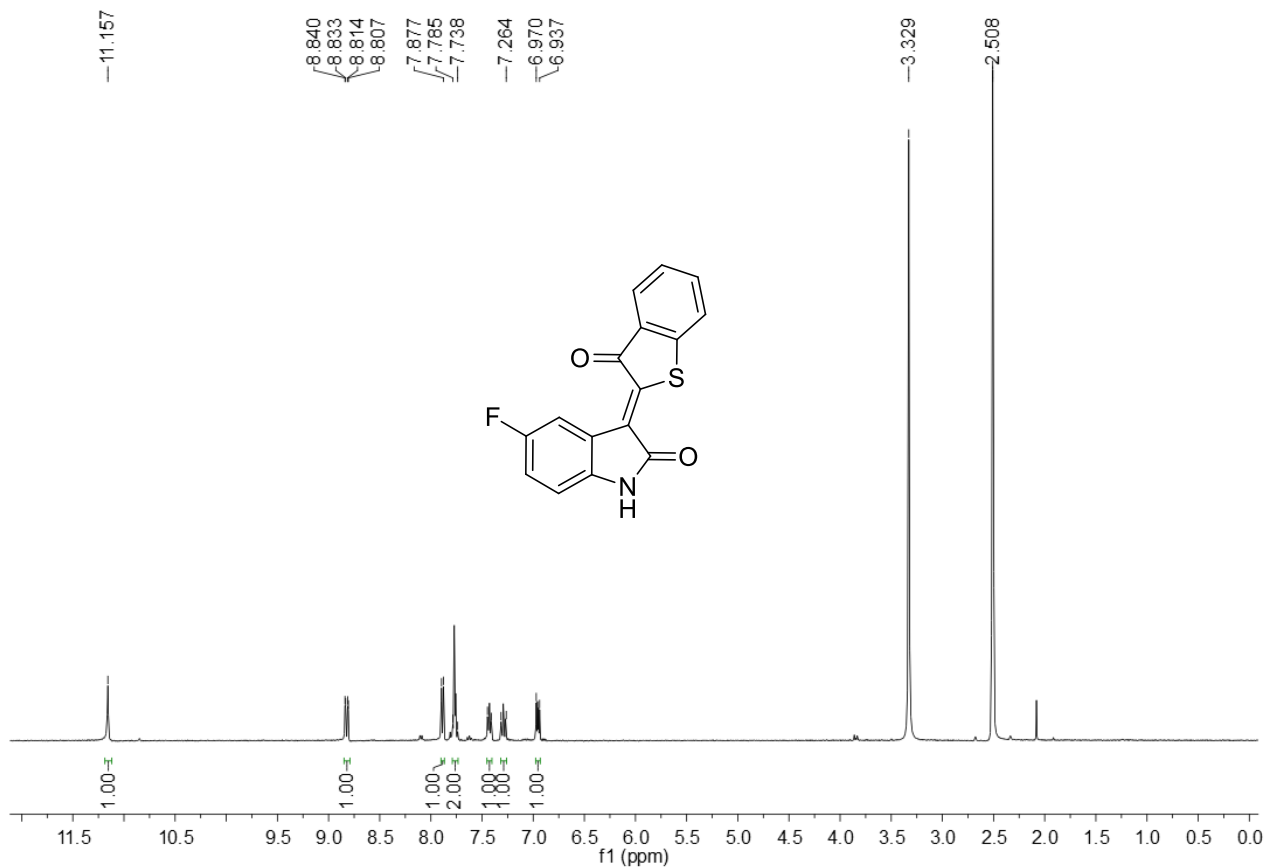




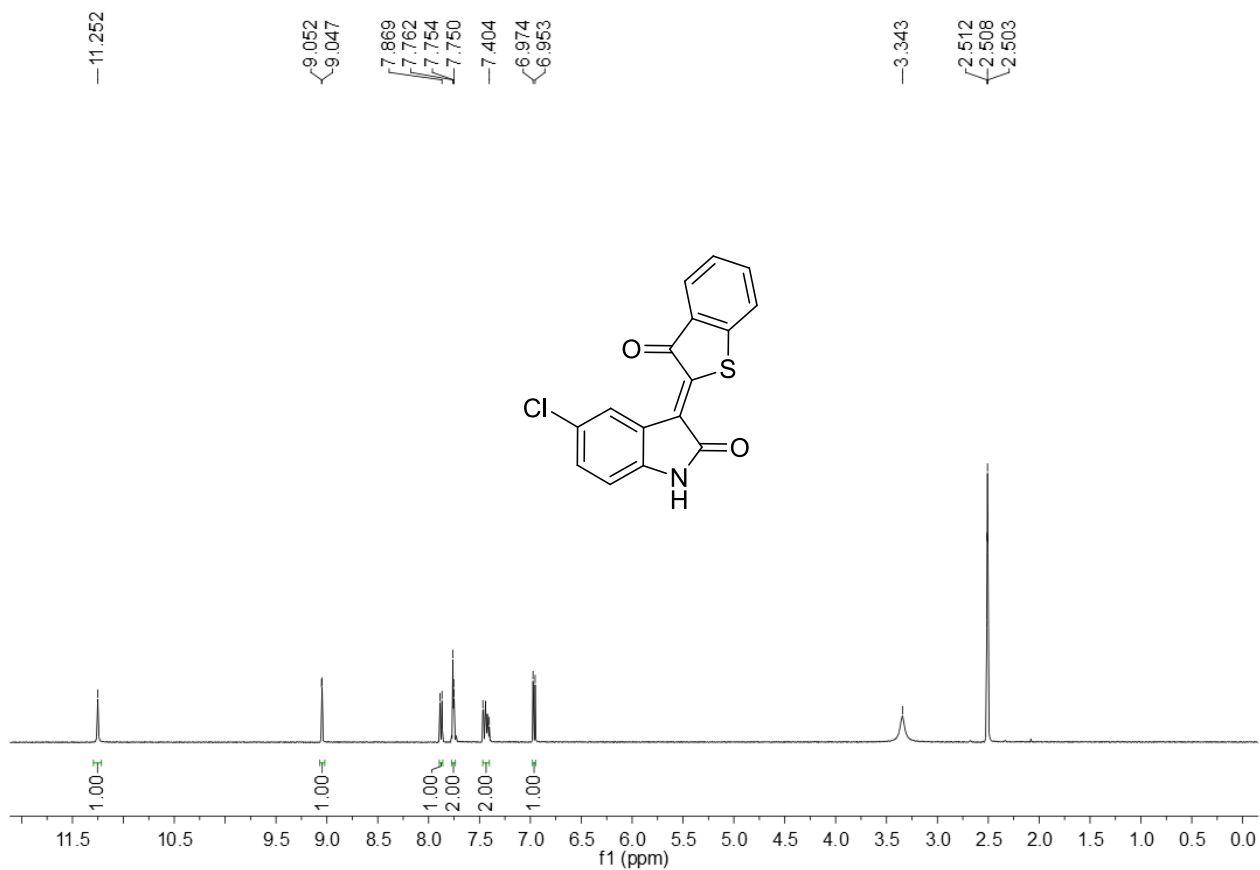
¹³C NMR Spectrum of Compound 2h



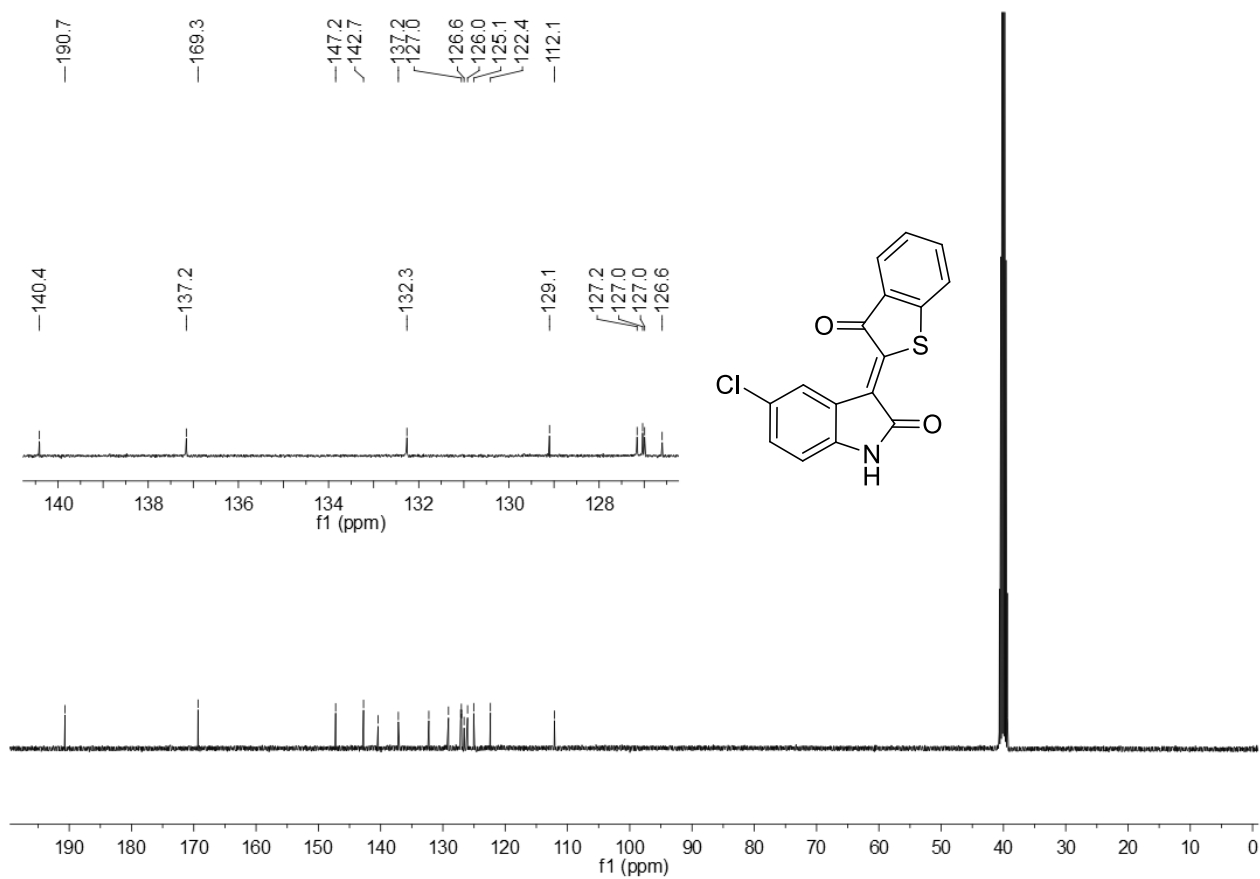
¹³C NMR Spectrum of Compound 2i



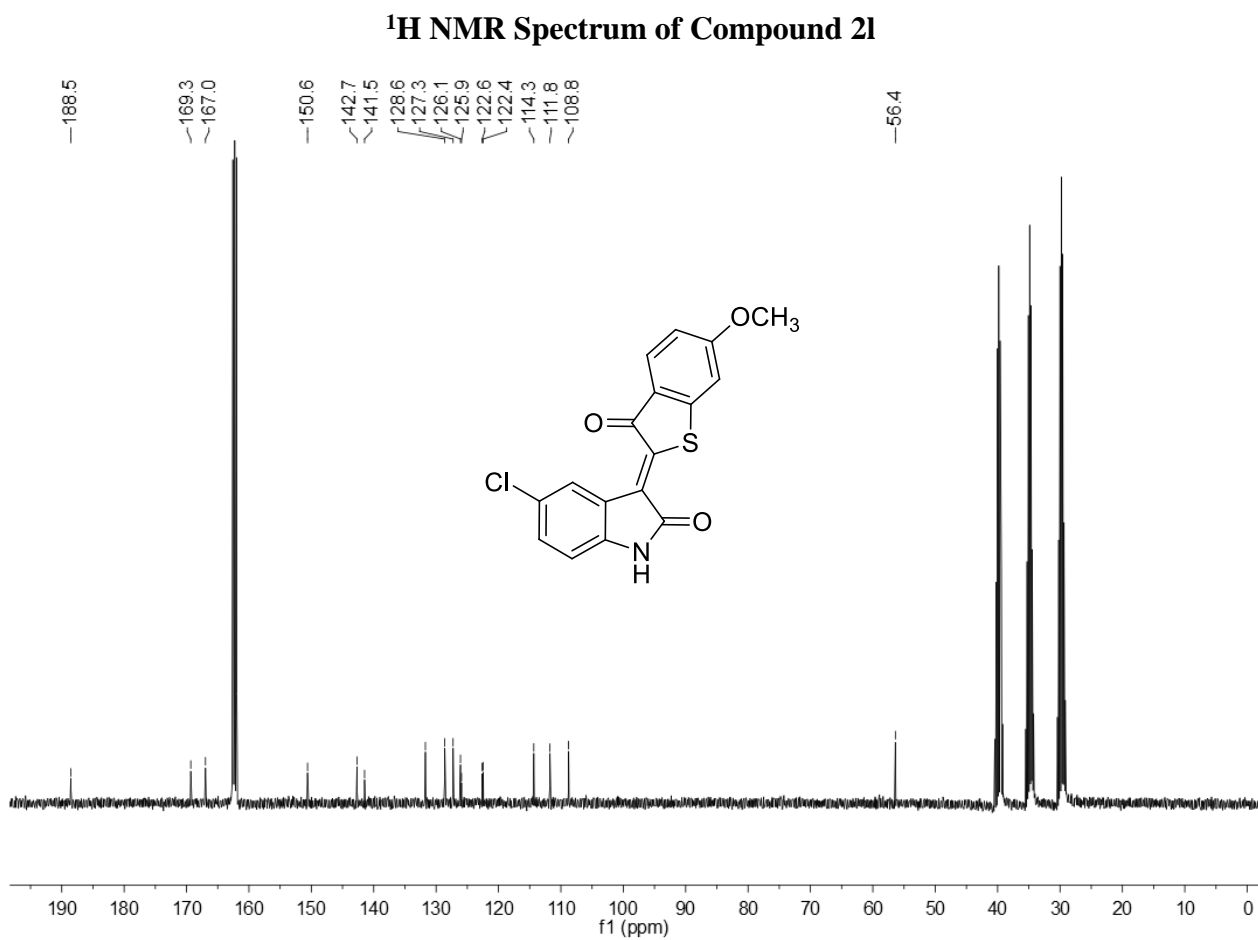
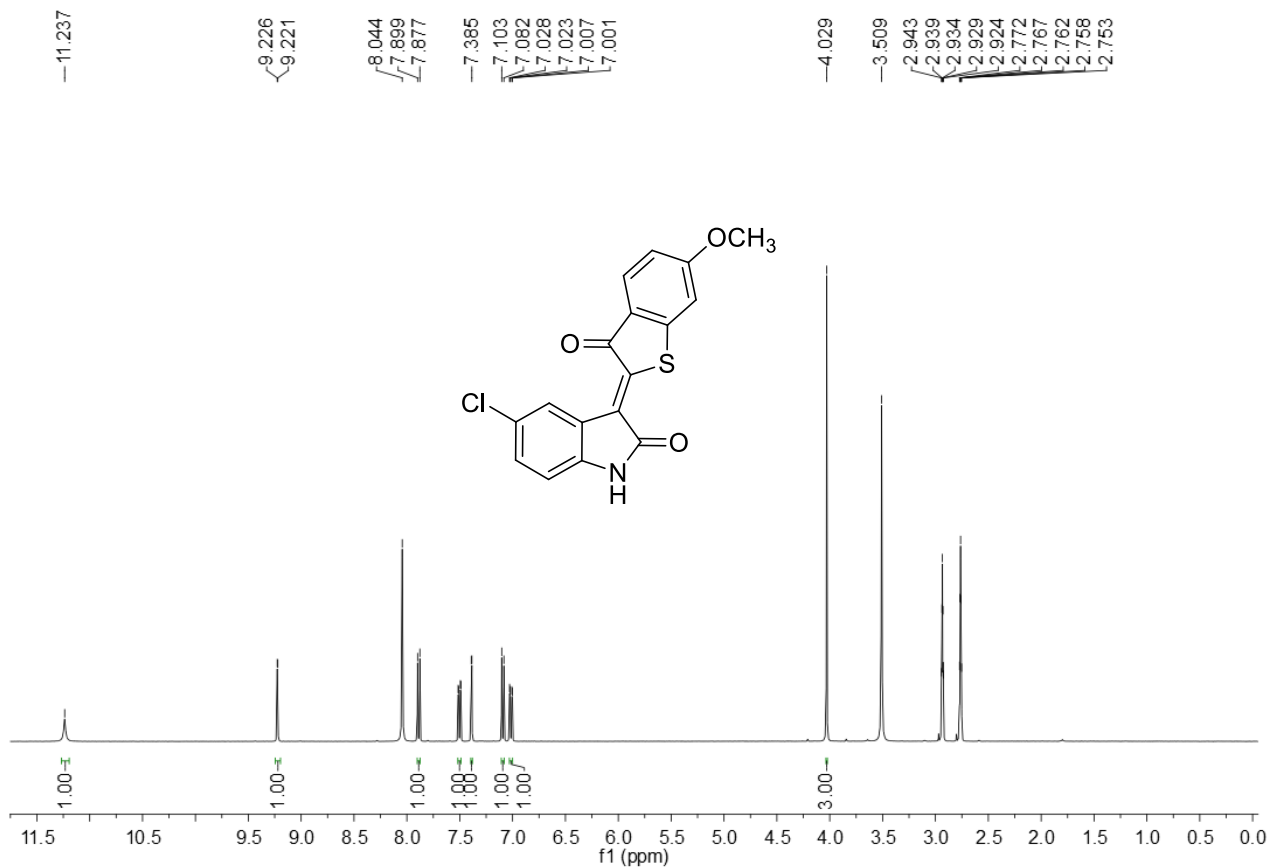
¹³C NMR Spectrum of Compound 2j

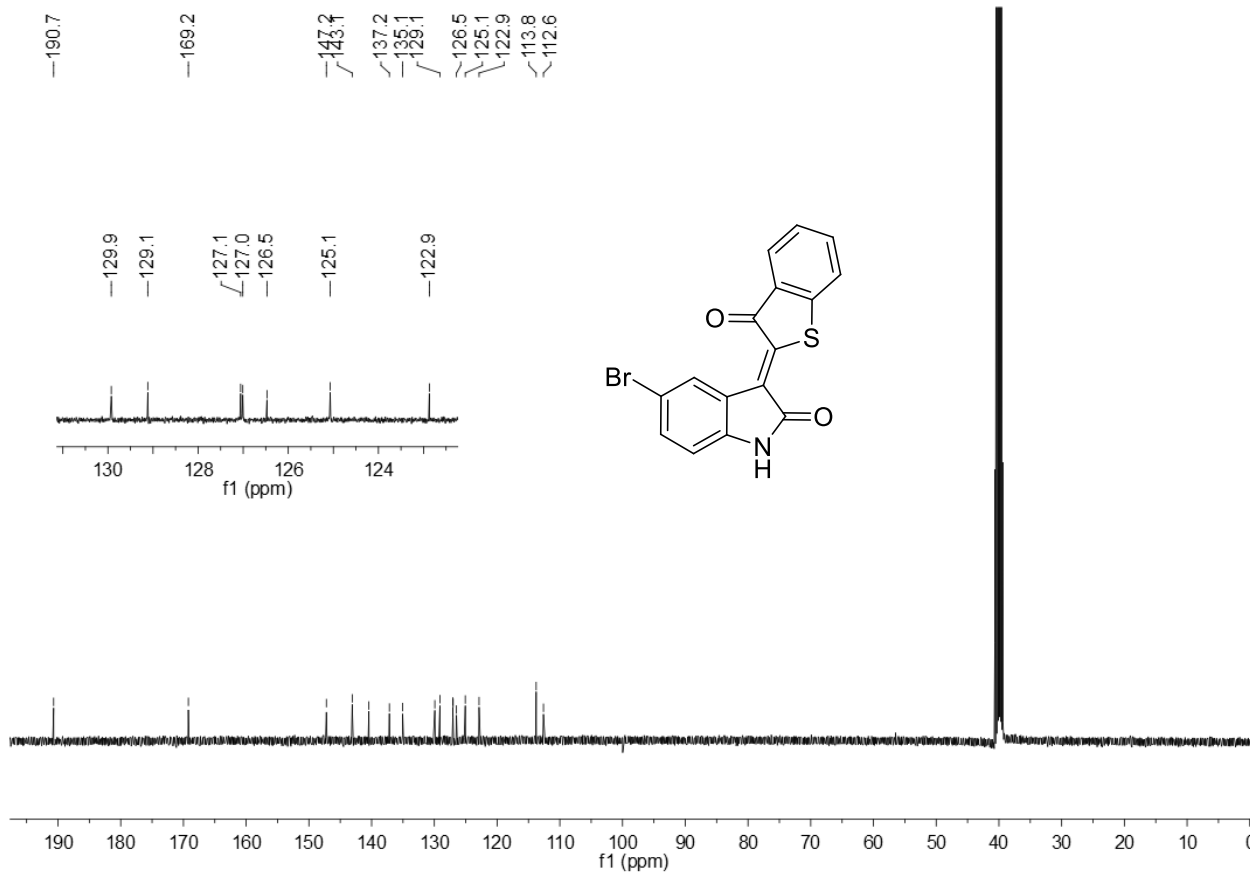
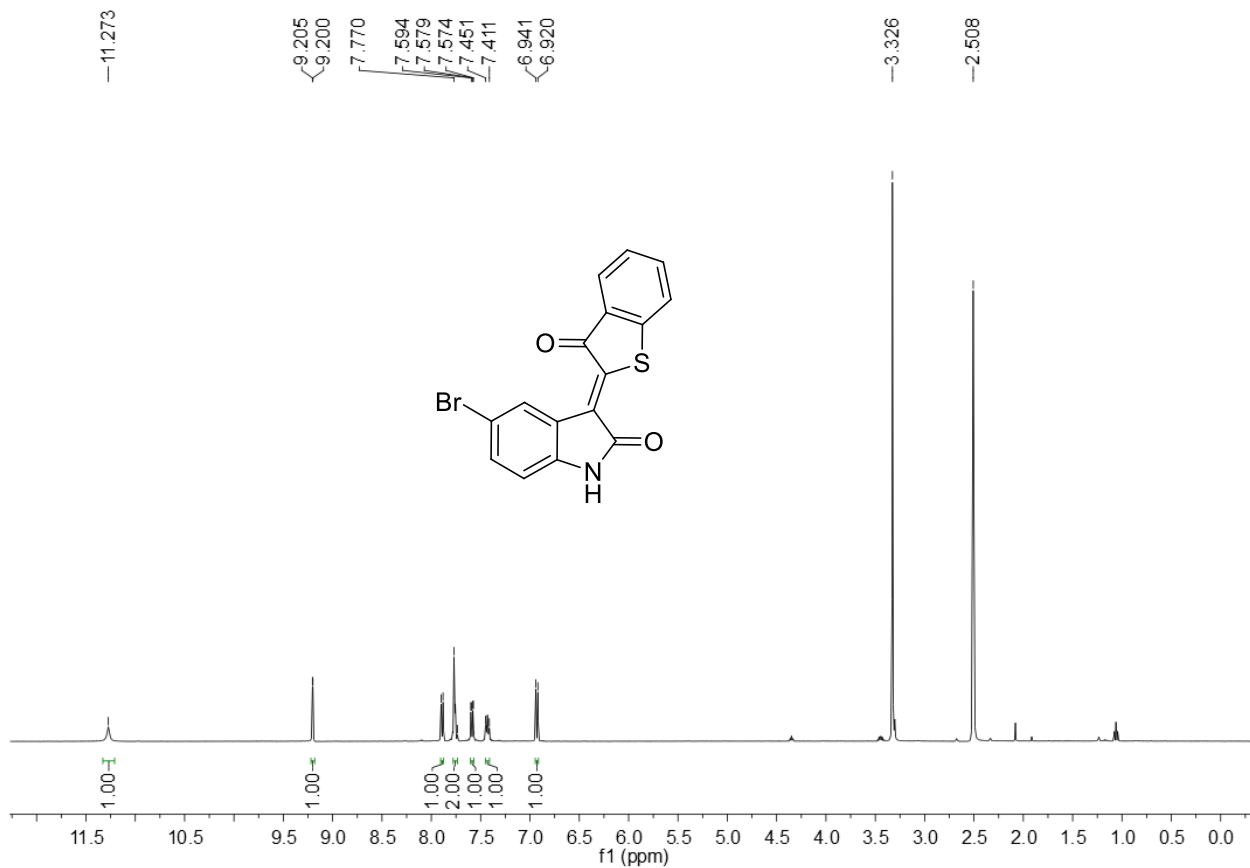


¹H NMR Spectrum of Compound 2k

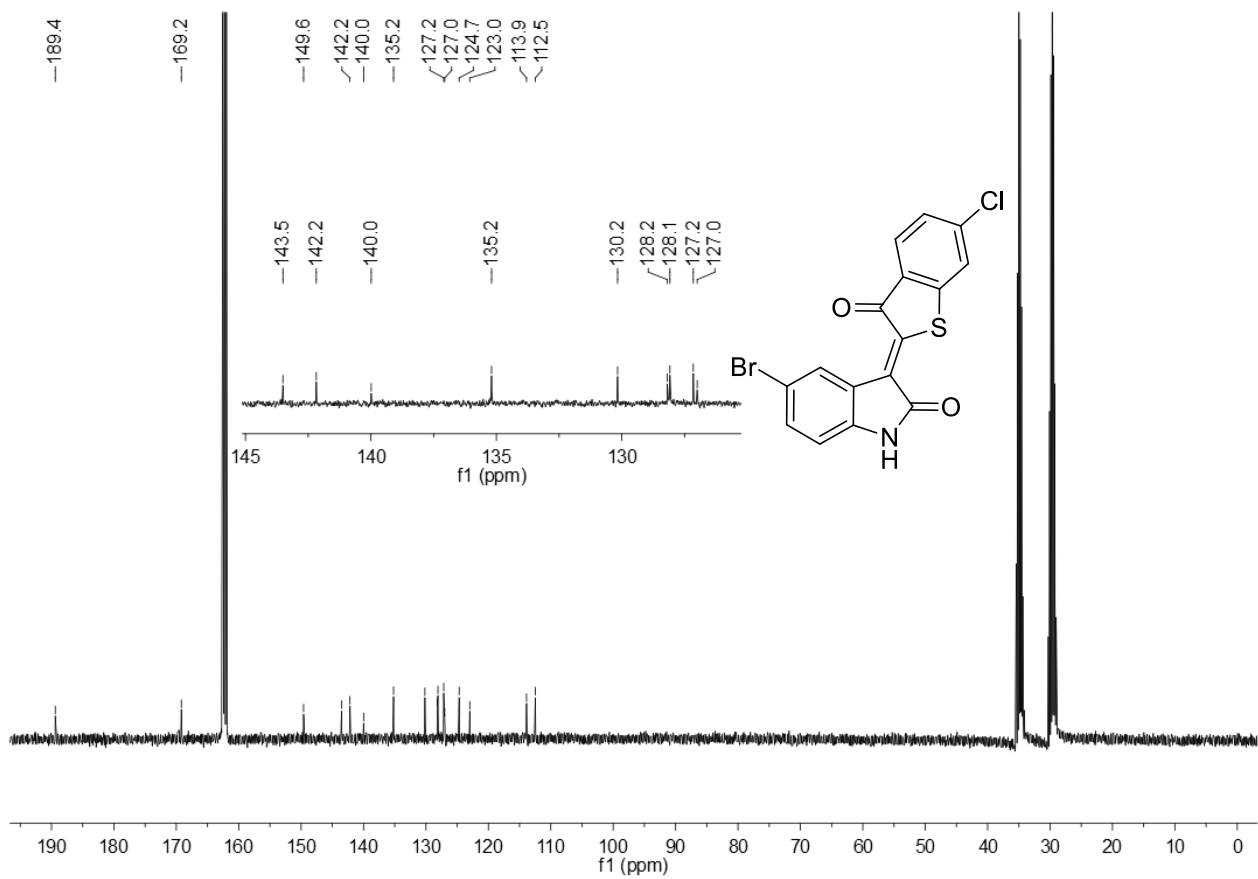
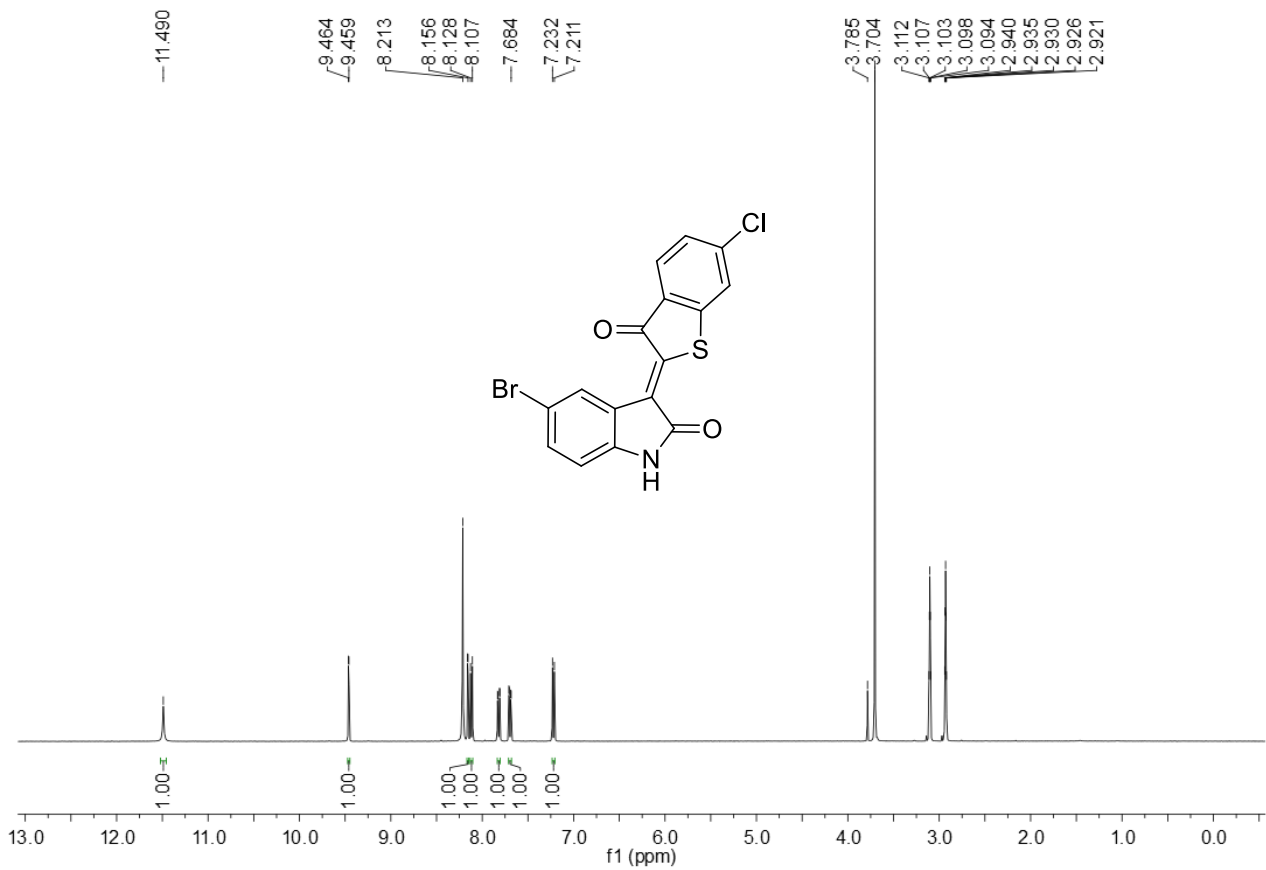


¹³C NMR Spectrum of Compound 2k

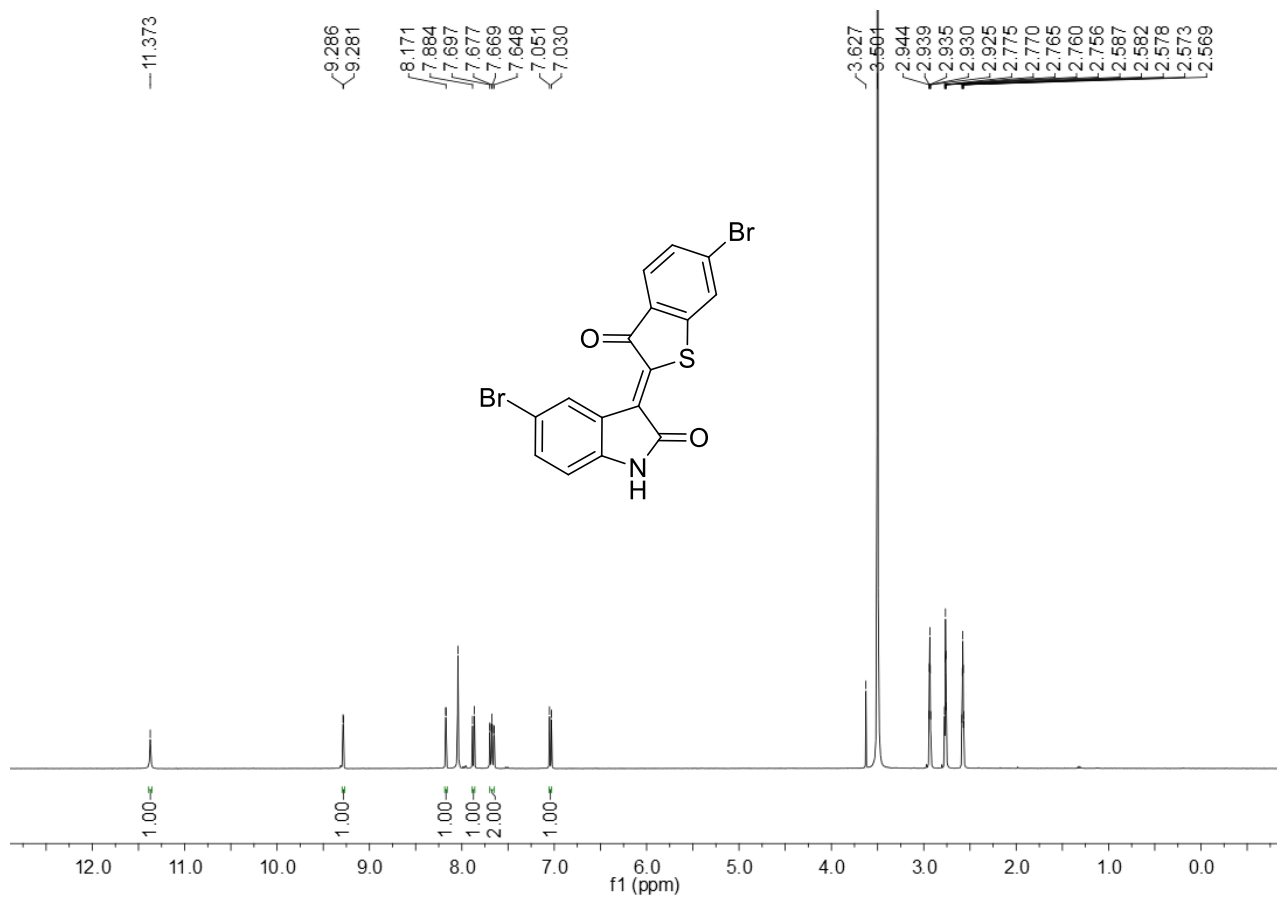




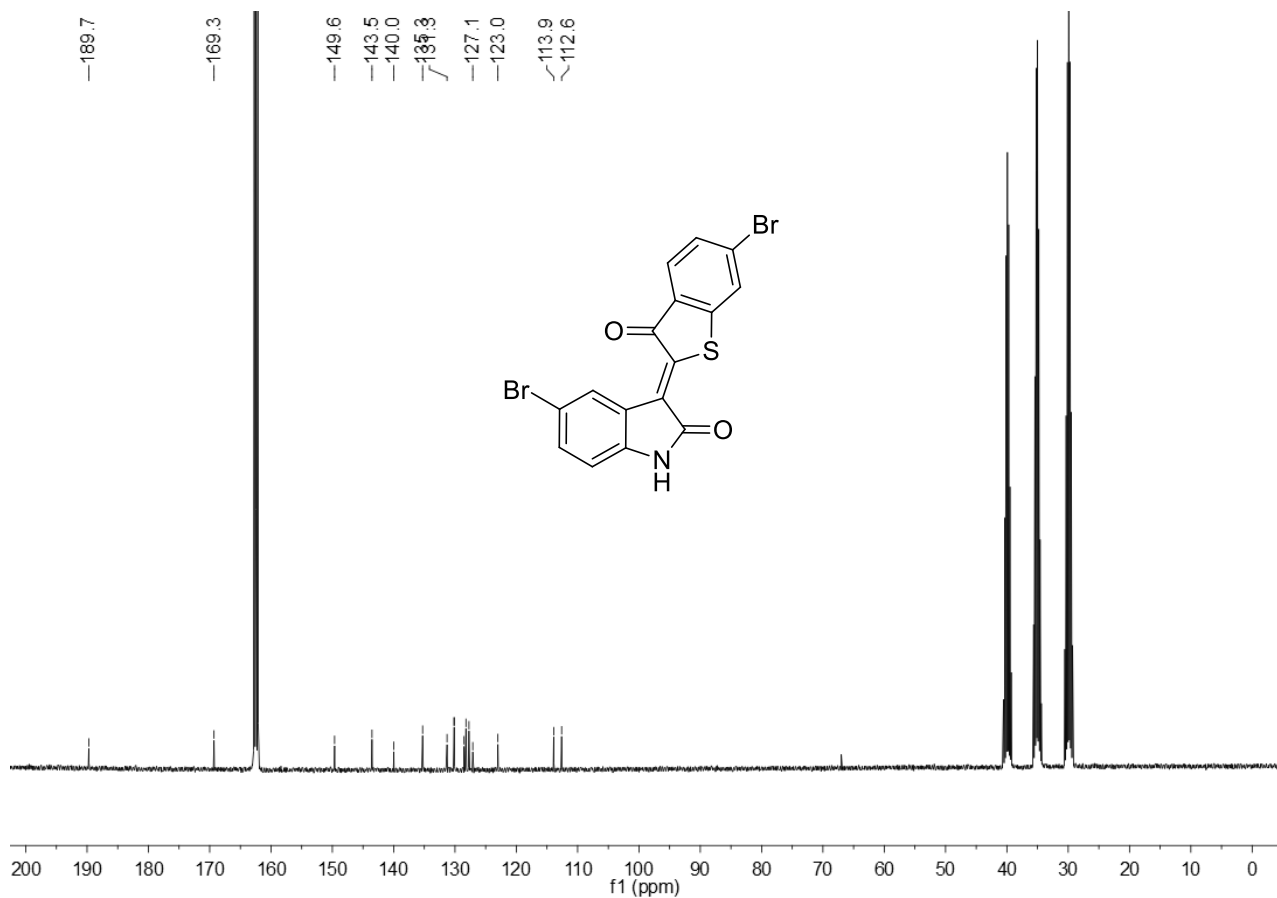
¹³C NMR Spectrum of Compound 2m



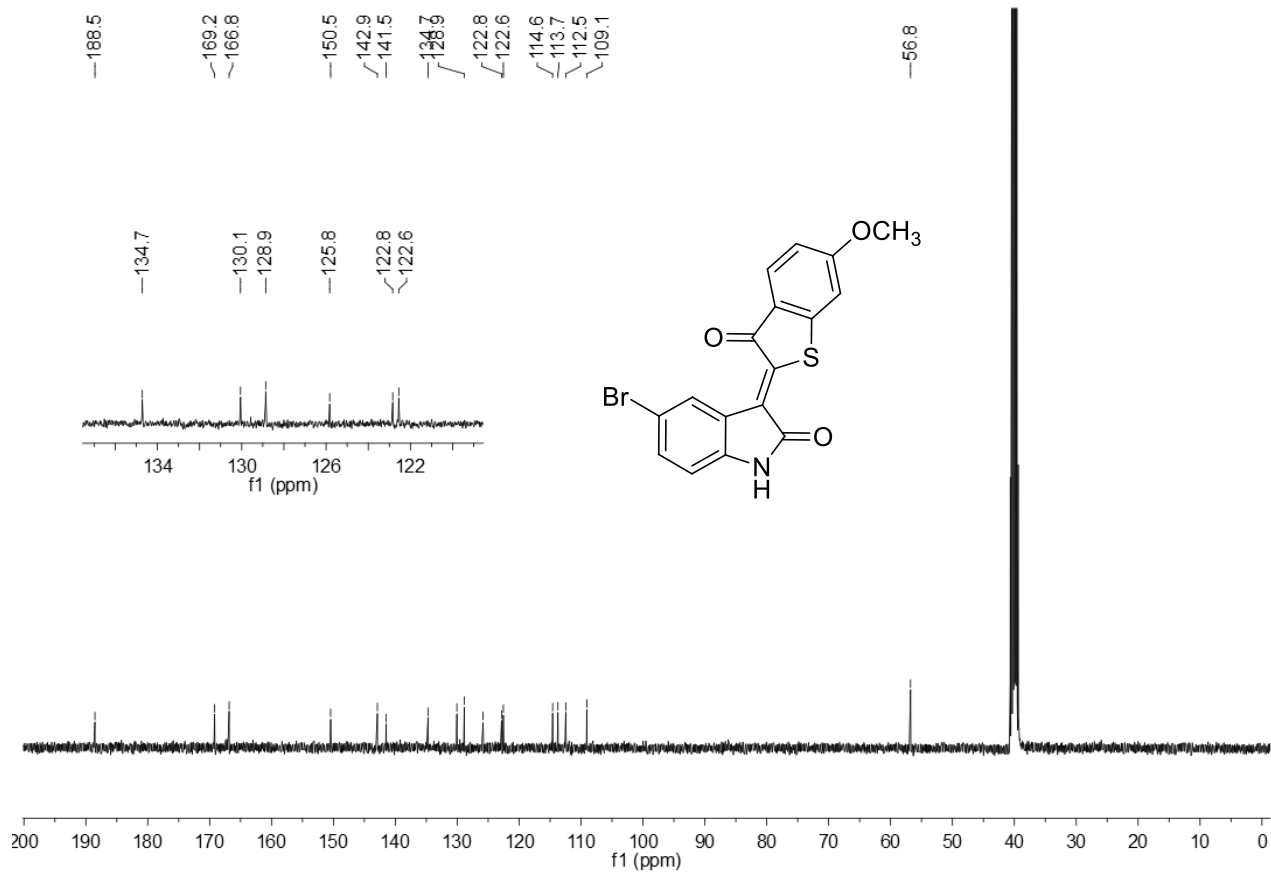
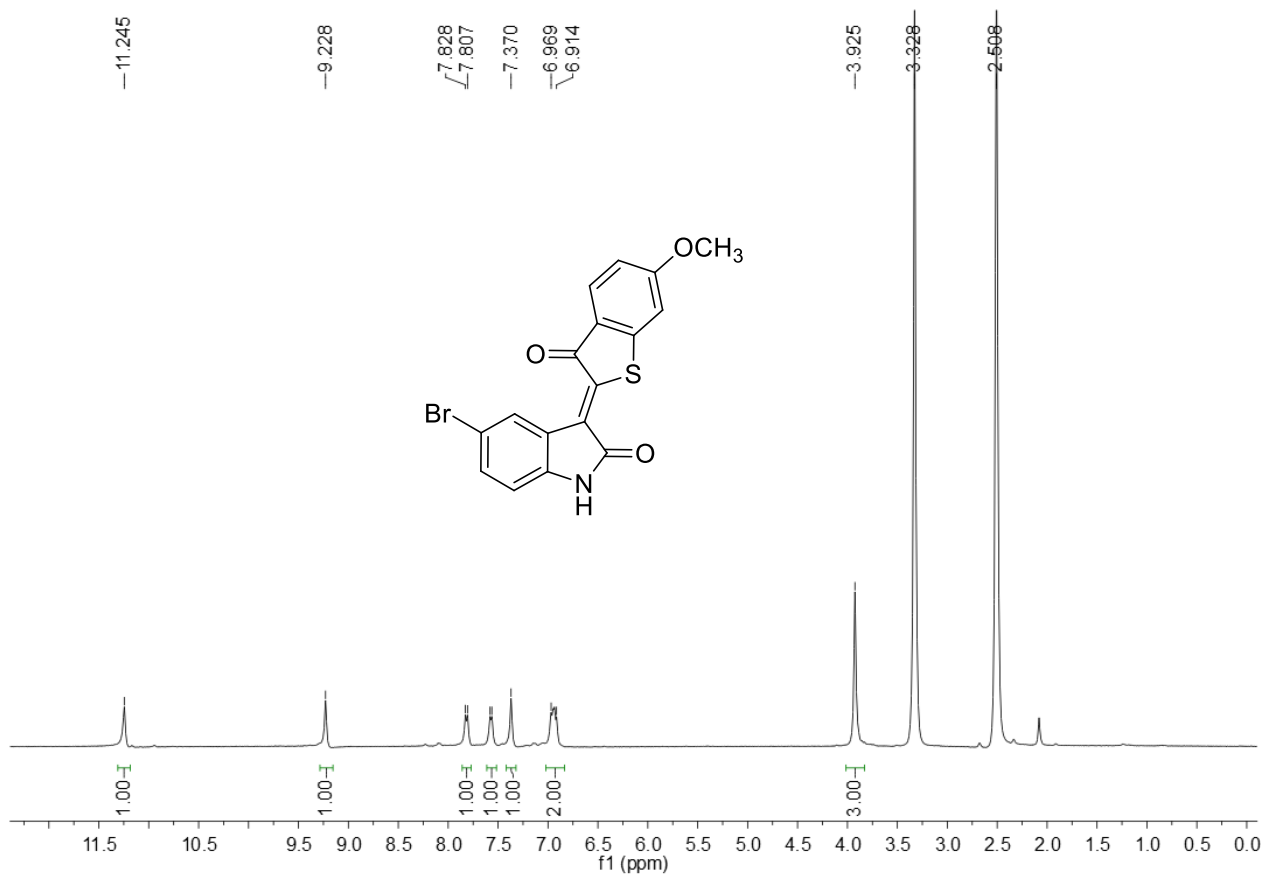
¹³C NMR Spectrum of Compound 2n



¹H NMR Spectrum of Compound 2o



¹³C NMR Spectrum of Compound 2o



¹³C NMR Spectrum of Compound 2p

