

Supporting Information

Cobalt catalysed cross-dehydrogenative coupling of indoles: a photoinduced ligand to metal charge transfer process

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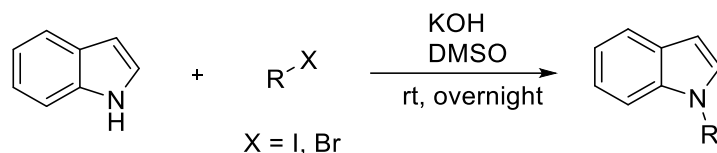
1. General Information

All the photochemical reactions were conducted in a 7 mL reaction via equipped with screw cap purchased from Sigma-Aldrich. UV-Visible experiments were conducted on SHIMADZU-UV-2450 using HPLC grade acetonitrile (MeCN). Chromatographic purification of products was accomplished by column chromatography on silica gel (230-400 mesh) using a proper eluent system. For thin layer chromatography (TLC) analysis throughout this work, Merck pre-coated TLC plates (silica gel 60 GF₂₅₄, 0.25 mm) were employed, using UV light as the visualizing agent. Organic solutions were concentrated under reduced pressure using Heidolph rotary evaporator. The products obtained were characterised using ¹H NMR, ¹³C NMR, and HRMS. The ¹H (400 MHz and 500 MHz), ¹³C (101 MHz and 126 MHz) and ¹⁹F (376 MHz and 471 MHz) nuclear magnetic resonance spectra were recorded on 400 MHz and 500 MHz spectrometers. Chemical shifts (δ) for ¹H and ¹³C are reported in parts per million (ppm) relative to internal standard tetramethylsilane (tetramethylsilane @ 0 ppm) and residual solvent peak in the NMR solvent for ¹H NMR (DMSO @ 2.50 ppm), for ¹³C NMR (DMSO @ 39.52 ppm). Coupling constants are given in Hertz. The following abbreviations are followed to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublets. High-resolution mass spectra (HRMS) were recorded on a Mass Spectrometry Unit using electrospray ionization-time of flight (ESI-TOF) reflectron experiments. All the 2-aryl indoles were synthesized by the reported literature procedures.^{1,2}

2. Materials:

Synthesis grade solvents were used as purchased. Co^{III}(acac)₃ was purchased from Sigma-Aldrich. All the other commercial grade reagents and solvents were purchased from Sigma-Aldrich, BLDpharm and GLR Innovation at the highest commercial quality and used without further purification, unless otherwise stated.

3. General Procedure of Synthesis of *N*-substituted indoles:⁶



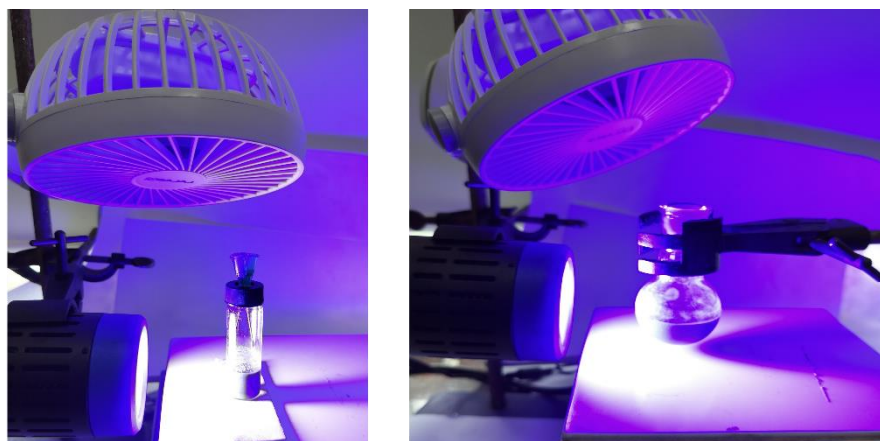
Indole (1.0 equiv.) and potassium hydroxide (2.0 equiv.) were dissolved in DMSO and then alkyl halide (2.0 equiv.) was added dropwise. Then the reaction mixture was stirred for overnight at room temperature. After that the reaction mixture was quenched by water and extracted by DCM (3 times). The combined organic phase was dried over Na₂SO₄ and concentrated under reduced pressure. Then the residue was purified by flash chromatography on silica gel by using hexane/EtOAc.

4. General Procedure for homo cross-dehydrogenative coupling of indoles:

An oven dried 7 mL glass vial equipped with magnetic stirring bar was charged with 0.2 mmol 2-aryl indole **1**, 0.2 mmol sodium pivalate, 0.04 mmol $\text{Co}^{\text{III}}(\text{acac})_3$ and 2.0 mL TFE solvent. Then a needle was inserted into the septum for air required for the reaction. The reaction mixture was then irradiated by a Kessil® PR160-440 nm lamp with an external cooling fan for maintaining ambient temperature. After 24 h the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography using hexane/EtOAc.

5. General Procedure for hetero cross-dehydrogenative coupling of indoles:

An oven dried 7 mL glass vial equipped with magnetic stirring bar was charged with 0.2 mmol 2-aryl indole **1**, 0.6 mmol indole **3**, 0.2 mmol sodium pivalate, 0.04 mmol $\text{Co}^{\text{III}}(\text{acac})_3$ and 2.0 mL TFE solvent. Then a needle was inserted into the septum for air required for the reaction. The reaction mixture was then irradiated by a Kessil® PR160-440 nm lamp with an external cooling fan for maintaining ambient temperature. After 24 h the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography using hexane/EtOAc.



Reaction Setup for 0.2 mmol reaction

Reaction Setup for 1.0 mmol reaction

Figure S1: Reaction setup

6. Scale up Synthesis of **2a**:

An oven dried 25 mL round bottom flask equipped with magnetic stirring bar was charged with 2.0 mmol 2-aryl indole **1a**, 1.0 mmol sodium pivalate, 0.2 mmol $\text{Co}^{\text{III}}(\text{acac})_3$ and 10.0 mL TFE solvent. The reaction mixture was then irradiated by a Kessil® PR160-440 nm lamp with an external cooling fan for maintaining ambient temperature. After 32 h the reaction mixture was concentrated in vacuo. The residue was purified by column chromatography using hexane/EtOAc. The final product **2a** was isolated 67% yield (268.3 mg).

7. Intermediate Detection Experiment:

An oven dried 7 mL glass vial equipped with magnetic stirring bar was charged with 0.2 mmol 2-aryl indole **1a**, 0.2 mmol sodium pivalate, 0.04 mmol $\text{Co}^{\text{III}}(\text{acac})_3$ and 2.0 mL TFE solvent. Then a needle was inserted into the septum for air required for the reaction. The reaction mixture was then irradiated by a Kessil® PR160-440 nm lamp with an external cooling fan for maintaining ambient temperature. After 6 h an aliquot of the reaction mixture was subjected to HRMS analysis. We were able to detect the intermediate 2-phenyl-3-*H*-indole-3-one, which was formed after LMCT process with our metal catalyst followed by reaction with molecular oxygen.

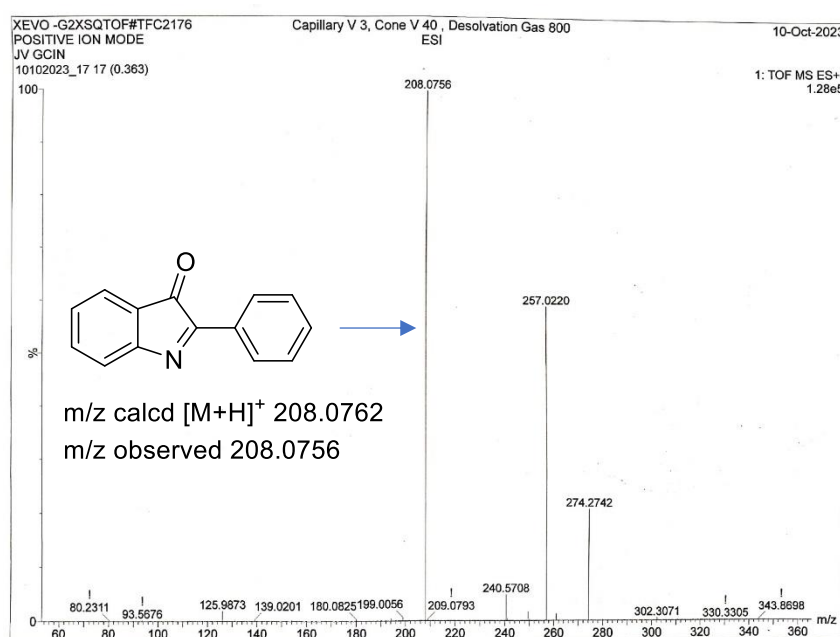


Figure S2: HRMS data of intermediate

8. Radical Trapping Experiment:

An oven dried 7 mL glass vial equipped with magnetic stirring bar was charged with 0.2 mmol 2-aryl indole **1a**, 0.2 mmol sodium pivalate, 0.04 mmol $\text{Co}^{\text{III}}(\text{acac})_3$, 0.4 mmol BHT and 2.0 mL TFE solvent. Then a needle was inserted into the septum for air required for the reaction. The reaction mixture was then irradiated by a 440 nm Kessil lamp with an external cooling fan for maintaining ambient temperature. After 2 h an aliquot of the reaction mixture was subjected to HRMS analysis. We were able to detect radical-BHT adduct which is shown below. (In a similar fashion, when the standard reaction was carried out in presence of TEMPO instead of BHT, no traces of the desired product was formed).

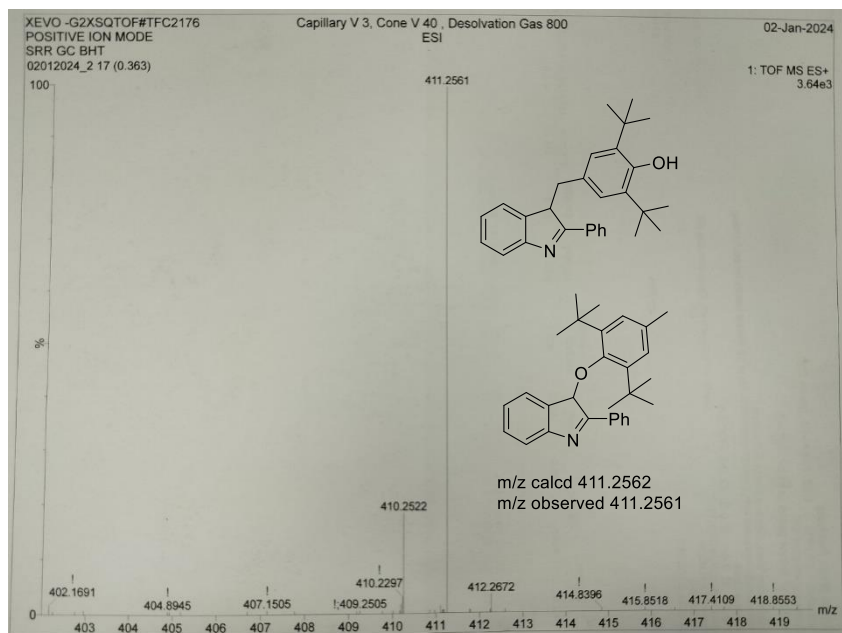


Figure S3: HRMS data of BHT adduct of 2-Phenylindole

9. UV-Visible Spectroscopic Analysis:

We have performed UV-vis spectroscopic studies to prove the visible light-induced LMCT of $\text{Co}(\text{acac})_3$. Initially, UV-vis spectre of a mixture of $\text{Co}(\text{acac})_3$ (1 mM) and **1a** (5 mM) was recorded and a band at 596 nm was observed which is characteristics band of $\text{Co}(\text{acac})_3$. Then the similar mixture was irradiated for 1 min by using 440 nm light source and subjected to UV-visible analysis. To our delight, a decrease in the band 596 nm intensity was observed which clearly justified the decrease in the amount of Co(III) because of the LMCT. In a similar fashion UV-spectra were recorded for 2 min, 3 min, 4 min, 5 min and 6 min excitations. In each and every case, a decrease in the absorbance band around 596 nm was observed.

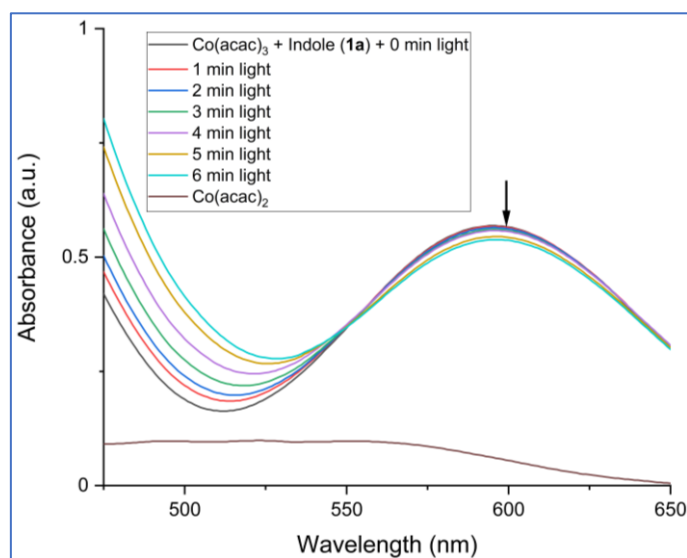


Figure S4: UV-vis spectra of $\text{Co}(\text{acac})_3$ and **1a** in MeCN after light irradiation for a given time interval

10. X-ray Photoelectron Spectroscopy (XPS) Analysis:

The elemental composition analysis was performed using the XPS studies. The measurement was conducted by using an instrument of model AXIS Supra of make Kratos Analytical Ltd. equipped with Al K α radiation $h\nu = 1486.6\text{eV}$. During all the measurements the operational voltage and current were kept constant at 15 kV and 15 mA.

An oven dried 7 mL glass vial equipped with magnetic stirring bar was charged with 0.2 mmol 2-aryl indole **1a**, 0.2 mmol sodium pivalate, 0.04 mmol Co^{III}(acac)₃ and 2.0 mL TFE solvent. Then a needle was inserted into the septum for air required for the reaction. The reaction mixture was then irradiated by a Kessil® PR160-440 nm lamp with an external cooling fan for maintaining ambient temperature. After 6 h light irradiation, the solvent was evaporated using a rotatory evaporator and to ensure proper dryness the residue was dried in high vacuum. The residue was then subjected to the XPS analysis. The formation of Co(III) and Co(II) in the reaction medium was observed.

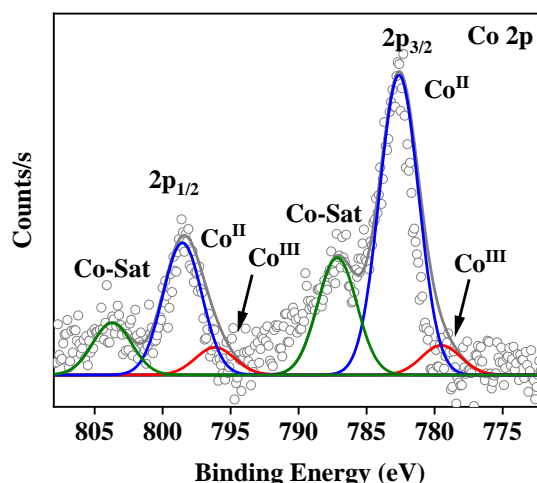


Figure S5: XPS spectra of reaction mixture after irradiation of light

11. Electron Paramagnetic Resonance (EPR) studies:

Continuous wave (CW) EPR spectra were obtained using a Bruker A300-9.5/12/S/W instrument with X-band of 8.75-9.65 GHz. The spectral data was collected at 77 K with the following spectrometer settings: microwave power = 13.73 mW, center field = 3350 G, sweep width = 300 G, sweep time = 163.86 s, modulation frequency = 100 kHz, modulation amplitude = 6.0 G, time constant = 1310.72 ms.

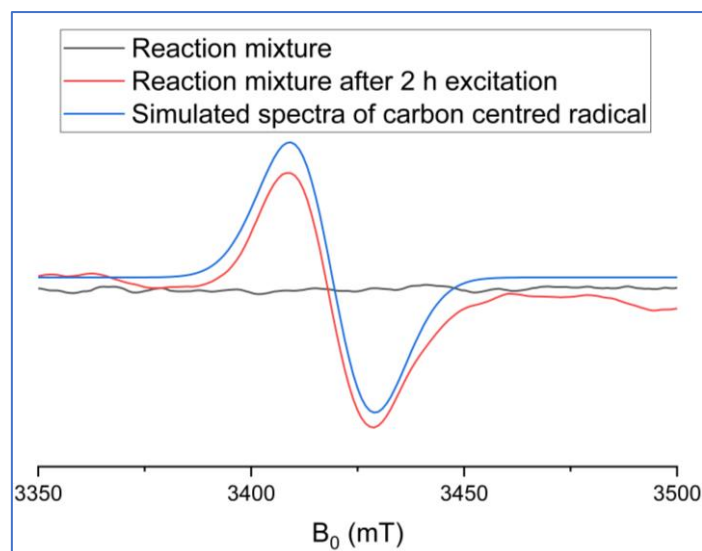


Figure S6: EPR data of reaction mixture

For all EPR measurements, the corresponding sample solution was transferred into the EPR tube and then placed in liquid Nitrogen to freeze the sample solution prior to recording of the spectra. After that, the sample tube was inserted in the EPR cavity which was kept frozen with continuous supply of liquid nitrogen for recording the spectra. For experiments in which the sample was irradiated, the sample tube was kept at 4 cm distance from the 440 nm Kessil lamp.

Initially, an oven dried 7 mL glass vial equipped with magnetic stirring bar was charged with 0.2 mmol 2-aryl indole **1a**, 0.2 mmol sodium pivalate, 0.04 mmol $\text{Co}^{\text{III}}(\text{acac})_3$ and 2.0 mL TFE solvent. The vial was placed into a magnetic stirrer and stirred for 10 minutes to ensure homogeneity. Then, from the reaction mixture, 600 μL solution was transferred into the EPR tube and EPR spectra was recorded (Fig S6, black line) after freezing the solution by using liquid nitrogen (liq. N_2).

Then the tube containing reaction mixture was left 5 minutes to attain room temperature and irradiated for 2h by using 440 nm light. Instantly after irradiation, the EPR spectra was recorded in a similar fashion (Fig S6, red line). To our delight we got an EPR signal which suggest that after photo-induced LMCT $\text{Co}(\text{III})$ converted to $\text{Co}(\text{II})$.

12. Differential Pulse Voltammetry Experiments:

The differential pulse voltammetry (DPV) experiments were carried out using a Metrohm Autolab PGSTAT204 potentiostat in MeCN at room temperature (25° C). ${}^n\text{Bu}_4\text{NPF}_6$ (0.1 M) was used as the supporting electrolyte. IUPAC convention has been used in plotting all the DPV graphs. All the DPV experiments were carried out in the range of 0 V to -1.6 V with a scan rate 100 mV/s using a glassy carbon disk electrode (diameter: 3 mm) as the working electrode, a coiled platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The electrodes were polished using the alumina-water slurry in figure-eight polishing motion before every experiment. The 0.02 M solution of cobalt

catalyst was purged with argon (7 min) to remove the dissolved oxygen and subjected to DPV experiment. Then solution of cobalt catalyst and **1a** (0.1 M) was purged with argon to remove the dissolved oxygen and subjected to DPV experiment. We observed that an anodic shift in cobalt and **1a** solution. This result verifies the ground state interaction between cobalt catalyst and **1a**.

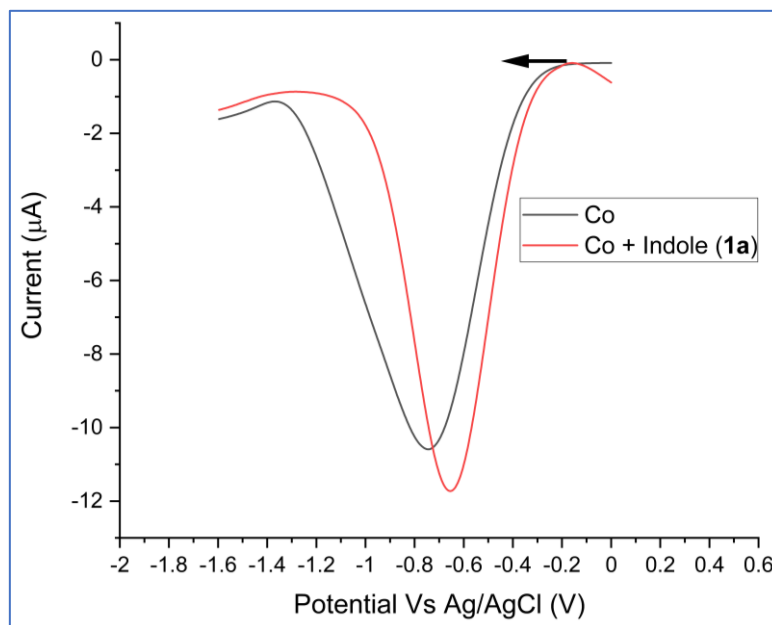


Figure S7: DPV experiment

13. Steady state Fluorescence Experiment:

Fluorescence measurements were carried out using a Varian Cary Eclipse fluorimeter using 2 cm path length quartz cuvette equipped with a Teflon® septum.

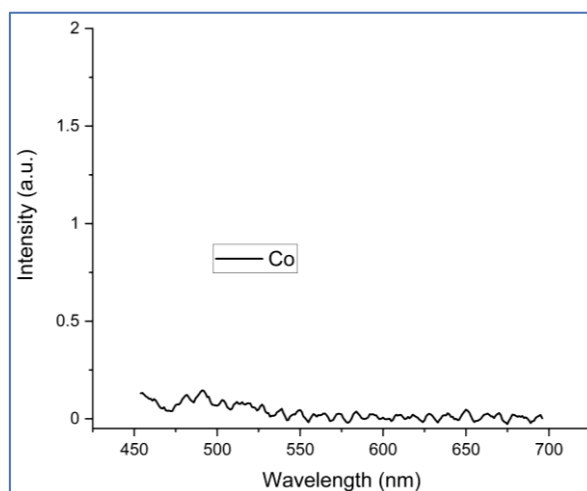
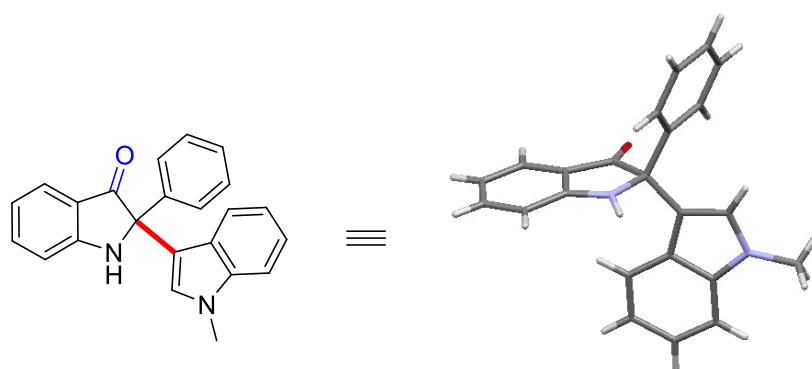


Figure S8: Steady state fluorescence experiments

A 0.02 M stock solution of cobalt was prepared in MeCN and subjected to fluorescence experiment. The excitation and emission slit widths were fixed at 10 nm for data collection. Fluorescence emission spectra of cobalt catalyst were collected from 450 nm to 700 nm with an excitation wavelength of 440 nm. It was observed that cobalt catalyst does not possess any emissive band in this region. This result excludes the possibilities of single electron transfer and energy transfer.

14. Crystallographic Data:

Single crystal X-ray diffraction data of crystals for compound **3v** was collected using a Bruker SMART APEX diffractometer equipped with a 3-axis goniometer. The crystals were covered with Paratone-N and mounted in a glass capillary.



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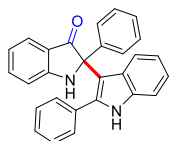
Identification code	GC IND 0ma a
Empirical formula	C _{2.71} H _{2.12} N _{0.24} O _{0.12}
+Formula weight	39.81
Temperature/K	297(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	14.0903(8)
b/Å	10.8057(6)
c/Å	11.6002(6)
α/°	90
β/°	103.060(2)
γ/°	90
Volume/Å ³	1720.51(16)
Z	34
ρ _{calc} /cm ³	1.306
μ/mm ⁻¹	0.081
F(000)	712.0
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.798 to 49.68
Index ranges	-16 ≤ h ≤ 16, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	42311
Independent reflections	2964 [Rint = 0.0625, Rsigma = 0.0244]
Data/restraints/parameters	2964/0/239

Goodness-of-fit on F ²	1.035
Final R indexes [I>2σ(I)]	R1 = 0.0394, wR2 = 0.0962
Final R indexes [all data]	R1 = 0.0509, wR2 = 0.1037
Largest diff. peak/hole / e Å ⁻³	0.15/-0.15

The data was collected at room temperature using Mo K α radiation ($\lambda = 0.71073$). The measured intensities were reduced to F² and corrected for absorption with SAINT. Structure solutions were accomplished by direct methods and refined by full matrix least-square on F² using OLEX2. Non-hydrogen atoms were refined anisotropically. All non-hydrogen atoms were refined anisotropically. The position of hydrogen atoms was fixed according to a riding model and was refined isotropically. Images were created with the program Diamond. The crystal structure was shown 50% thermal probability ellipsoids.

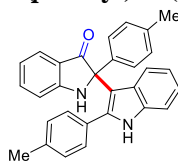
15. Spectral Data:

2-Phenyl-2-(2-phenyl-1*H*-indol-3-yl)indolin-3-one (2a):³ The product was synthesised by general



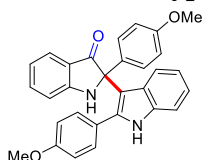
procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **2a** (30 mg, 75% yield) was obtained as a yellow solid. ¹H NMR (500 MHz, DMSO) δ 11.34 (s, 1H), 8.33 (s, 1H), 7.52 (t, J = 7.5 Hz, 1H), 7.38 - 7.34 (m, 3H), 7.25 (d, J = 7.5 Hz, 1H), 7.17 - 7.13 (m, 3H), 7.06 - 7.02 (m, 6H), 6.98 (d, J = 8.1 Hz, 1H), 6.77 - 6.70 (m, 2H), 6.61 (d, J = 7.8 Hz, 1H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO) δ 201.0, 160.6, 140.3, 138.5, 138.0, 136.3, 133.7, 130.0, 128.1, 127.9, 127.8, 127.6, 127.5, 127.5, 124.9, 121.6, 120.8, 119.2, 119.0, 118.0, 112.4, 111.7, 111.5, 71.6 ppm.

2-(*p*-Tolyl)-2-(2-(*p*-tolyl)-1*H*-indol-3-yl)indolin-3-one (2b):³ The product was synthesised by general



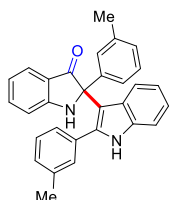
procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **2b** (31.7 mg, 74% yield) was obtained as a yellow solid. ¹H NMR (500 MHz, DMSO) δ 11.26 (s, 1H), 8.27 (s, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.26 - 7.22 (m, 3H), 7.01 (d, J = 7.6 Hz, 3H), 6.96 (d, J = 8.2 Hz, 1H), 6.87 (t, J = 8.0 Hz, 4H), 6.76 - 6.69 (m, 2H), 6.59 (d, J = 8.1 Hz, 1H), 2.22 (s, 3H), 2.16 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO) δ 201.0, 160.4, 138.3, 137.9, 137.4, 137.0, 136.6, 136.2, 130.9, 129.9, 128.7, 128.2, 128.1, 127.5, 124.9, 121.5, 120.8, 119.1, 119.1, 117.8, 112.3, 111.6, 111.4, 71.5, 21.3, 21.0 ppm.

2-(4-Methoxyphenyl)-2-(2-(4-methoxyphenyl)-1*H*-indol-3-yl)indolin-3-one (2c):³ The product was



synthesised by general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **2c** (32.7 mg, 71% yield) was obtained as a yellow solid. ¹H NMR (500 MHz, DMSO) δ 11.25 (s, 1H), 8.27 (s, 1H), 7.52 - 7.49 (m, 1H), 7.33 (d, J = 8.1 Hz, 1H), 7.29 - 7.25 (m, 3H), 7.06 - 7.00 (m, 3H), 6.96 (d, J = 8.2 Hz, 1H), 6.75 (t, J = 7.6 Hz, 1H), 6.70 (t, J = 7.4 Hz, 1H), 6.64 - 6.59 (m, 5H), 3.68 (s, 3H), 3.63 (s, 3H) ppm. ¹³C{¹H} NMR (101 MHz, DMSO) δ 201.4, 160.4, 159.0, 159.0, 138.3, 137.9, 136.2, 132.0, 131.3, 128.8, 128.05, 126.1, 125.0, 121.4, 120.7, 119.1, 117.9, 113.6, 113.1, 112.4, 111.6, 111.4, 71.2, 55.6, 55.5 ppm.

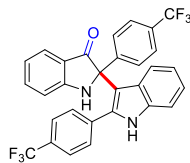
2-(*m*-Tolyl)-2-(2-(*m*-tolyl)-1*H*-indol-3-yl)indolin-3-one (2d): The product was synthesised by



general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **2d** (31.3 mg, 73% yield) was obtained as a yellow solid. ¹H NMR (500 MHz, DMSO) δ 11.31 (s, 1H), 8.35 (s, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 8.1 Hz, 1H), 7.27 (d, J = 7.7 Hz, 1H), 7.21 (d, J = 12.3 Hz, 2H), 7.07-6.94 (m, 6H), 6.87 (d, J = 9.7 Hz, 2H), 6.73 (dt, J = 14.6, 7.4 Hz, 2H), 6.58 (d, J = 8.1 Hz, 1H), 2.09 (s, 3H), 2.01 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO) δ 201.0, 160.3, 140.1, 138.6, 137.9, 136.9, 136.7, 136.2, 133.6, 131.0, 128.4, 128.1, 128.0, 127.9, 127.6, 126.6, 124.8, 124.4,

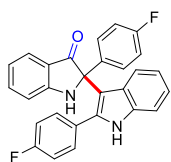
121.5, 120.7, 119.1, 119.1, 117.9, 112.3, 111.7, 111.4, 71.6, 21.6, 21.1 ppm. **HRMS-ESI:** calcd for $C_{30}H_{25}N_2O$ $[M+H]^+$ 429.1967, found 429.1956.

2-(4-(Trifluoromethyl)phenyl)-2-(2-(4-(trifluoromethyl)phenyl)-1H-indol-3-yl)indolin-3-one



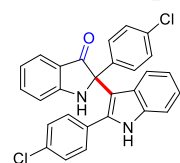
(2e):³ The product was synthesised by general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **2e** (37.6 mg, 70% yield) was obtained as a yellow solid. **¹H NMR** (500 MHz, DMSO) δ 11.59 (s, 1H), 8.57 (s, 1H), 7.61 - 7.54 (m, 3H), 7.43 - 7.29 (m, 8H), 7.12 (t, J = 7.1 Hz, 1H), 7.05 (d, J = 8.3 Hz, 1H), 6.88-6.85 (m, 1H), 6.83-6.79 (m, 2H) ppm. **¹⁹F NMR** (471 MHz, DMSO) δ -61.43(s), -61.50(s) ppm. **¹³C{¹H} NMR** (126 MHz, DMSO) δ 200.8, 161.1, 144.4, 138.6, 137.4, 137.4, 136.3, 130.9, 128.6, 128.5, 128.4, 128.1, 127.9, 127.8, 127.2, 125.6, 125.1, 124.8, 124.8, 124.3, 124.3, 123.5, 122.5, 120.4, 119.8, 118.7, 118.4, 118.3, 112.6, 112.37, 112.1, 71.4 ppm.

2-(4-Fluorophenyl)-2-(2-(4-fluorophenyl)-1H-indol-3-yl)indolin-3-one (2f):³ The product was



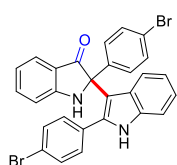
synthesised by general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **2f** (33.2 mg, 76% yield) was obtained as a yellow solid. **¹H NMR** (500 MHz, DMSO) δ 11.41 (s, 1H), 8.40 (s, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.40-7.32 (m, 4H), 7.20 - 7.18 (m, 2H), 7.06 (t, J = 7.6 Hz, 1H), 6.99 (d, J = 8.3 Hz, 1H), 6.89 (dt, J = 23.4, 8.8 Hz, 4H), 6.81 (t, J = 7.6 Hz, 1H), 6.75 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 8.1 Hz, 1H) ppm. **¹⁹F NMR** (471 MHz, DMSO) δ -114.46(s), -116.08(s) ppm. **¹³C{¹H} NMR** (126 MHz, DMSO) δ 201.2, 162.0 (d, J_{C-F} = 245.7 Hz), 161.8 (d, J_{C-F} = 245.7 Hz), 138.2, 137.5, 136.1 132.1 (d, J_{C-F} = 7.6 Hz), 129.9 (d, J_{C-F} = 2.5 Hz), 129.5 (d, J_{C-F} = 8.8 Hz), 127.4, 125.0, 121.8, 120.5, 119.4, 118.6, 118.3, 114.8, 114.7, 114.5, 114.3, 112.4, 111.7 (d, J_{C-F} = 7.6 Hz), 71.0 ppm.

2-(4-Chlorophenyl)-2-(2-(4-chlorophenyl)-1H-indol-3-yl)indolin-3-one (2g):³ The product was



synthesised by general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **2g** (32.8 mg, 70% yield) was obtained as a yellow solid. **¹H NMR** (500 MHz, DMSO) δ 11.44 (s, 1H), 8.40 (s, 1H), 7.55 (t, J = 7.3 Hz, 1H), 7.36 - 7.33 (m, 2H), 7.14 - 7.06 (m, 7H), 6.99 (d, J = 8.0 Hz, 1H), 6.79 (dt, J = 23.3, 7.2 Hz, 2H), 6.69 (d, J = 7.5 Hz, 1H) ppm. **¹³C{¹H} NMR** (126 MHz, DMSO) δ 200.9, 160.7, 139.1, 138.4, 137.3, 136.3, 132.8, 132.5, 132.3, 131.8, 129.4, 128.0, 127.6, 127.4, 125.0, 122.1, 120.6, 119.5, 118.65, 118.4, 112.6, 112.0, 111.8, 71.1 ppm.

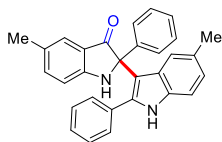
2-(4-Bromophenyl)-2-(2-(4-bromophenyl)-1H-indol-3-yl)indolin-3-one (2h):³ The product was



synthesised by general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **2h** (34.6 mg, 62% yield) was obtained as a yellow solid. **¹H NMR** (500 MHz, DMSO) δ 11.46 (s, 2H), 8.42 (s, 1H), 7.55 (t, J = 7.7 Hz, 1H), 7.37 - 7.23 (m, 8H), 7.08 - 7.06 (m, 3H), 6.99 (d,

J = 8.3 Hz, 1H), 6.82 (t, J = 7.6 Hz, 1H), 6.77 (t, J = 7.4 Hz, 1H), 6.68 (d, J = 8.1 Hz, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.8, 160.7, 139.5, 138.3, 137.3, 136.2, 132.6, 132.0, 130.9, 130.5, 129.8, 127.4, 125.0, 122.0, 121.4, 121.0, 120.5, 119.5, 118.6, 118.4, 112.5, 111.9, 111.6, 71.1 ppm.

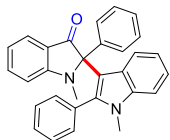
5-Methyl-2-(5-methyl-2-phenyl-1H-indol-3-yl)-2-phenylindolin-3-one (2i):³ The product was synthesised by general procedure and the crude reaction mixture was purified by



flash chromatography on silica gel with hexane/EtOAc as eluent. Product **2i** (32.6 mg, 76% yield) was obtained as a yellow solid. ^1H NMR (500 MHz, DMSO) δ 11.18 (s, 1H), 8.06 (s, 1H), 7.37 - 7.35 (m, 3H), 7.22 (d, J = 8.1 Hz, 1H), 7.15 -

7.11 (m, 3H), 7.05 - 7.03 (m, 6H), 6.91 (d, J = 8.3 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H), 6.40 (s, 1H), 2.22 (s, 3H), 2.11 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 201.0, 159.1, 140.7, 139.3, 138.4, 134.7, 133.9, 130.0, 128.2, 128.0, 127.7, 127.6, 127.3, 127.2, 126.9, 124.0, 123.1, 120.6, 119.2, 112.5, 111.4, 111.2, 72.1, 22.1, 20.6 ppm.

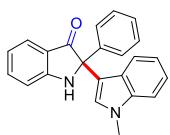
1-Methyl-2-(1-methyl-2-phenyl-1H-indol-3-yl)-2-phenylindolin-3-one (2j):⁴ The product was synthesised by general procedure and the crude reaction mixture was purified by flash



chromatography on silica gel with hexane/EtOAc as eluent. Product **2j** (23.6 mg, 55% yield) was obtained as a yellow solid. ^1H NMR (500 MHz, DMSO) δ 7.20 - 7.17 (m,

2H), 7.97 - 6.91 (m, 7H), 6.84 (dd, J = 14.5, 7.1 Hz, 2H), 6.67 (d, J = 7.6 Hz, 1H), 6.62 - 6.56 (m, 2H), 6.52 - 6.49 (m, 2H), 6.26 (t, J = 7.4 Hz, 1H), 6.10 (d, J = 8.1 Hz, 1H), 3.14 (s, 1H), 2.50 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 199.6, 159.5, 140.4, 138.7, 138.0, 136.9, 131.4, 131.3, 131.1, 128.7, 128.1, 127.8, 127.4, 124.6, 121.7, 121.1, 119.6, 119.0, 116.8, 110.7, 109.3, 108.9, 76.0, 30.9, 29.9 ppm.

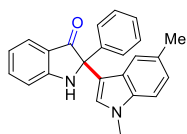
2-(1-Methyl-1H-indol-3-yl)-2-phenylindolin-3-one (4a):⁵ The product was synthesised by general procedure and the crude reaction mixture was purified by flash chromatography on



silica gel with hexane/EtOAc as eluent. Product **4a** (26.4 mg, 78% yield) was obtained as a yellow solid. ^1H NMR (500 MHz, DMSO) δ 8.34 (s, 1H), 7.53 - 7.45 (m, 4H),

7.40 (d, J = 8.2 Hz, 1H), 7.33 - 7.26 (m, 3H), 7.13 - 7.08 (m, 3H), 6.98 (d, J = 8.3 Hz, 1H), 6.89 (t, J = 7.5 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 3.73 (s, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.7, 161.4, 140.4, 138.3, 137.8, 128.8, 128.6, 127.9, 127.1, 126.3, 125.1, 121.9, 120.6, 119.2, 118.0, 117.8, 114.2, 112.5, 110.4, 71.0, 32.8 ppm.

2-(1,5-Dimethyl-1H-indol-3-yl)-2-phenylindolin-3-one (4b): The product was synthesised by general procedure and the crude reaction mixture was purified by flash chromatography on

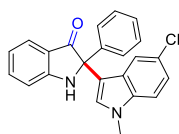


silica gel with hexane/EtOAc as eluent. Product **4b** (25.7 mg, 73% yield) was obtained as a yellow solid. ^1H NMR (500 MHz, DMSO) δ 8.31 (s, 1H), 7.51 - 7.43

(m, 4H), 7.31 - 7.28 (m, 4H), 7.05 - 6.91 (m, 4H), 6.75 - 6.73 (m, 1H), 3.70 (s, 3H), 2.22 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.6, 161.4, 140.5, 138.2, 136.3, 128.8, 128.7, 127.9, 127.6,

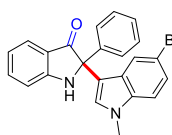
127.0, 126.6, 125.1, 123.5, 120.3, 118.0, 117.7, 113.3, 112.5, 110.2, 71.1, 32.9, 21.8 ppm. **HRMS-ESI:** calcd for C₂₄H₂₀N₂ONa [M+Na]⁺ 375.1473, found 375.1470.

2-(5-Chloro-1-methyl-1H-indol-3-yl)-2-phenylindolin-3-one (4c): The product was synthesised by



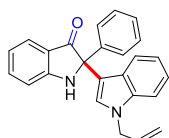
general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4c** (28 mg, 75% yield) was obtained as a yellow solid. ¹H NMR (500 MHz, DMSO) δ 8.43 (s, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 13.7, 8.2 Hz, 2H), 7.40 (d, *J* = 7.4 Hz, 2H), 7.34-7.28 (m, 3H), 7.23 (s, 1H), 7.13 (d, *J* = 12.0 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 1H), 6.75 (t, *J* = 7.3 Hz, 1H), 3.75 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO) δ 200.4, 161.4, 140.2, 138.4, 136.3, 130.4, 128.8, 128.1, 127.3, 127.0, 125.3, 124.0, 121.9, 119.8, 118.2, 117.6, 113.7, 112.4, 112.2, 70.8, 33.1 ppm. **HRMS-ESI:** calcd for C₂₃H₁₈N₂O Cl [M+H]⁺ 373.1108, found 373.1193.

2-(5-Bromo-1-methyl-1H-indol-3-yl)-2-phenylindolin-3-one (4d): The product was synthesised by



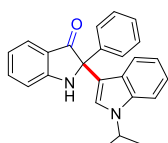
general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4d** (29.6 mg, 71% yield) was obtained as a yellow solid. ¹H NMR (500 MHz, DMSO) δ 8.43 (s, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.42 - 7.38 (m, 3H), 7.34 - 7.29 (m, 3H), 7.26 - 7.23 (m, 2H), 7.21 (s, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 3.75 (s, 4H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO) δ 200.4, 161.4, 140.1, 138.4, 136.6, 130.2, 128.8, 128.1, 128.0, 127.0, 125.2, 124.4, 122.8, 118.2, 117.6, 113.6, 112.6, 112.4, 112.1, 70.8, 33.1 ppm. **HRMS-ESI:** calcd for C₂₃H₁₈N₂O [M+H]⁺ 417.0603, found 417.0602.

2-(1-Allyl-1H-indol-3-yl)-2-phenylindolin-3-one (4e): The product was synthesised by general



procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4e** (26.6 mg, 73% yield) was obtained as a yellow solid. ¹H NMR (500 MHz, DMSO) δ 8.38 (s, 1H), 7.54 - 7.41 (m, 5H), 7.34 - 7.28 (m, 3H), 7.12 - 7.09 (m, 3H), 6.99 (d, *J* = 8.3 Hz, 1H), 6.89 (t, *J* = 7.5 Hz, 1H), 6.75 (t, *J* = 7.4 Hz, 1H), 6.00-5.93 (m, 1H), 5.15-5.03 (m, 2H), 4.80 (d, *J* = 4.7 Hz, 2H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO) δ 200.6, 161.4, 140.4, 138.3, 137.2, 134.8, 128.7, 128.0, 127.8, 127.0, 126.5, 125.2, 122.0, 120.8, 119.4, 118.1, 117.7, 117.4, 114.6, 112.5, 110.8, 71.0, 48.5 ppm. **HRMS-ESI:** calcd for C₂₅H₂₁N₂O [M+H]⁺ 365.1654, found 365.1637.

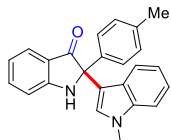
2-(1-Isopropyl-1H-indol-3-yl)-2-phenylindolin-3-one (4f):⁵ The product was synthesised by general



procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4f** (27.5 mg, 75% yield) was obtained as a yellow solid. ¹H NMR (500 MHz, DMSO) δ 8.34 (s, 1H), 7.53 - 7.47 (m, 3H), 7.43-7.41 (m, 2H), 7.32 - 7.26 (m, 3H), 7.16 (s, 1H), 7.11 - 7.08 (m, 2H), 6.98 (d, *J* = 8.3 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.74 (t, *J* = 7.4 Hz, 1H), 4.77 - 4.69 (m, 1H), 1.43 (d, *J* = 6.7 Hz, 1H), 1.40 (d, *J* =

6.7 Hz, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.6, 161.4, 140.5, 138.3, 136.6, 128.7, 127.9, 127.0, 126.5, 125.2, 123.4, 121.8, 120.9, 119.3, 118.0, 117.7, 114.4, 112.5, 110.7, 107.2, 71.1, 22.83, 22.80 ppm.

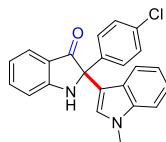
2-(1-Methyl-1H-indol-3-yl)-2-(p-tolyl)indolin-3-one (4g): The product was synthesised by general



procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4g** (25.4 mg, 72% yield) was obtained

as a yellow solid. ^1H NMR (500 MHz, DMSO) δ 8.28 (s, 1H), 7.51 - 7.45 (m, 2H), 7.40 (d, J = 8.2 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.13 - 7.05 (m, 5H), 6.96 (d, J = 8.2 Hz, 1H), 6.88 (t, J = 7.5 Hz, 1H), 6.73 (t, J = 7.3 Hz, 1H), 3.73 (s, 3H), 2.26 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.8, 161.3, 138.2, 137.8, 137.4, 137.0, 129.2, 128.8, 127.0, 126.3, 125.1, 121.9, 120.7, 119.2, 117.9, 117.8, 114.3, 112.4, 110.4, 70.8, 32.8, 21.1 ppm.

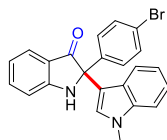
2-(4-Chlorophenyl)-2-(1-methyl-1H-indol-3-yl)indolin-3-one (4h): The crude reaction mixture was



purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4h** (26.1 mg, 70% yield) was obtained as a yellow solid. ^1H NMR (500 MHz, DMSO)

δ 8.36 (s, 1H), 7.54 - 7.46 (m, 4H), 7.40 (t, J = 7.9 Hz, 3H), 7.13 (t, J = 7.6 Hz, 1H), 7.08 - 7.06 (m, 2H), 6.98 (d, J = 8.2 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.76 (t, J = 7.3 Hz, 1H), 3.74 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.3, 161.4, 139.5, 138.4, 137.8, 132.7, 129.0, 128.9, 128.7, 126.2, 125.2, 122.0, 120.4, 119.4, 118.3, 117.6, 113.8, 112.6, 110.5, 70.5, 32.8 ppm. **HRMS-ESI:** calcd for $\text{C}_{23}\text{H}_{18}\text{N}_2\text{O}$ $[\text{M}+\text{H}]^+$ 373.1108, found 373.1097.

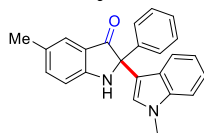
2-(4-Bromophenyl)-2-(1-methyl-1H-indol-3-yl)indolin-3-one (4i): The product was synthesised by



general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4i** (26.7 mg, 64%

yield) was obtained as a yellow solid. ^1H NMR (500 MHz, DMSO) δ 8.35 (s, 1H), 7.54 - 7.47 (m, 1H), 7.42 - 7.38 (m, 3H), 7.13 (t, J = 7.6 Hz, 1H), 7.08 - 7.04 (m, 2H), 6.97 (d, J = 8.3 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.76 (t, J = 7.4 Hz, 1H), 3.74 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.2, 161.4, 139.9, 138.4, 137.8, 131.6, 129.3, 128.9, 126.1, 125.2, 122.0, 121.3, 120.4, 119.4, 118.3, 117.6, 113.7, 112.6, 110.5, 70.5, 32.8 ppm.

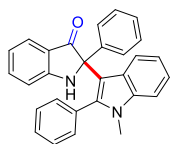
5-Methyl-2-(1-methyl-1H-indol-3-yl)-2-phenylindolin-3-one (4j): The product was synthesised by



general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4j** (27.1 mg,

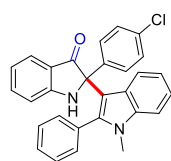
77% yield) was obtained as a yellow solid. ^1H NMR (500 MHz, DMSO) δ 8.10 (s, 1H), 7.45 (d, J = 7.4 Hz, 2H), 7.40 (d, J = 8.2 Hz, 1H), 7.36 (d, J = 8.3 Hz, 1H), 7.32 - 7.27 (m, 4H), 7.12 (t, J = 7.6 Hz, 1H), 7.07 - 7.05 (m, 2H), 6.91 - 6.86 (m, 2H), 3.73 (s, 3H), 2.23 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.7, 159.9, 140.6, 139.7, 137.8, 128.8, 128.6, 127.8, 127.1, 127.0, 126.4, 124.2, 121.9, 120.7, 119.2, 117.9, 114.4, 112.5, 110.4, 71.3, 32.8, 20.6 ppm.

2-(1-Methyl-2-phenyl-1H-indol-3-yl)-2-phenylindolin-3-one (4k): The product was synthesised by



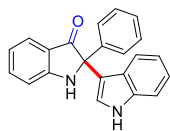
general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4k** (29.4 mg, 71% yield) was obtained as a yellow solid. $^1\text{H NMR}$ (500 MHz, DMSO) δ 8.10 (s, 1H), 7.46 – 7.42 (m, 4H), 7.23-7.19 (m, 3H), 7.13 - 6.97 (m, 7H, m), 6.87 (d, J = 8.3 Hz, 1H), 6.81 (t, J = 7.6 Hz, 1H), 6.63 (t, J = 7.4 Hz, 1H), 6.59 (d, J = 8.1 Hz, 1H), 3.40 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.8, 160.6, 140.5, 139.8, 137.7, 136.8, 131.7, 131.6, 131.2, 128.4, 128.2, 127.80, 127.6, 126.8, 124.7, 121.8, 120.8, 119.5, 118.9, 117.7, 112.7, 112.4, 110.4, 71.5, 30.8 ppm. **HRMS-ESI:** calcd for $\text{C}_{29}\text{H}_{22}\text{N}_2\text{ONa}$ $[\text{M}+\text{Na}]^+$ 437.1630, found 437.1617.

2-(4-Chlorophenyl)-2-(1-methyl-2-phenyl-1H-indol-3-yl)indolin-3-one (4l): The product was



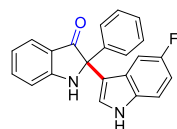
synthesised by general procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4l** (31.4 mg, 70% yield) was obtained as a yellow solid. $^1\text{H NMR}$ (500 MHz, DMSO) δ 8.19 (s, 1H), 7.48 - 7.39 (m, 4H), 7.27 - 7.13 (m, 7H), 7.02 - 6.86 (m, 4H), 6.69 (q, J = 14.5, 7.6 Hz, 2H), 3.41 (s, 3H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.6, 160.8, 140.2, 139.5, 138.0, 136.8, 132.3, 131.8, 131.6, 131.2, 129.4, 128.4, 128.1, 127.9, 127.6, 126.5, 124.8, 122.0, 120.6, 119.7, 118.8, 118.1, 112.6, 112.4, 110.6, 71.1, 30.9 ppm. **HRMS-ESI:** calcd for $\text{C}_{29}\text{H}_{22}\text{N}_2\text{O Cl}$ $[\text{M}+\text{H}]^+$ 449.1421, found 449.1400.

2-(1H-Indol-3-yl)-2-phenylindolin-3-one (4m):⁵ The product was synthesised by general procedure



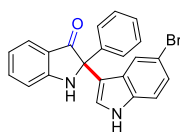
and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4m** (22.7 mg, 70% yield) was obtained as a yellow solid. $^1\text{H NMR}$ (500 MHz, DMSO) δ 11.06 (s, 1H), 8.32 (s, 1H), 7.52 - 7.45 (m, 4H), 7.37 (d, J = 8.1 Hz, 1H), 7.33 - 7.27 (m, 3H), 7.09 - 7.04 (m, 3H), 6.97 (d, J = 8.2 Hz, 1H), 6.84 (t, J = 7.4 Hz, 1H), 6.74 (t, J = 7.3 Hz, 1H) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.8, 161.4, 140.5, 138.2, 137.4, 128.6, 127.9, 127.1, 126.0, 125.1, 124.6, 121.8, 120.4, 119.1, 118.0, 117.8, 115.0, 112.4, 112.2, 71.1 ppm.

2-(5-Fluoro-1H-indol-3-yl)-2-phenylindolin-3-one (4n):⁵ The product was synthesised by general



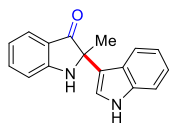
procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4n** (24.3 mg, 71% yield) was obtained as a yellow solid. $^1\text{H NMR}$ (500 MHz, DMSO) δ 11.20 (s, 1H), 8.38 (s, 1H), 7.52 - 7.18 (m, 9H), 6.98 - 6.77 (m, 4H) ppm. $^{19}\text{F NMR}$ (376 MHz, DMSO) δ -124.8(s) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, DMSO) δ 200.7, 161.4, 157.0 (d, $J_{\text{C-F}}$ = 228.1 Hz), 140.3, 138.4, 134.1, 128.8, 128.1, 127.1, 126.5, 126.2 (d, $J_{\text{C-F}}$ = 10.1 Hz), 125.2, 118.2, 117.8, 115.1 (d, $J_{\text{C-F}}$ = 5.0 Hz), 113.3 (d, $J_{\text{C-F}}$ = 12.6 Hz), 112.4, 110.1 (d, $J_{\text{C-F}}$ = 26.5 Hz), 105.1 (d, $J_{\text{C-F}}$ = 23.9 Hz), 71.0 ppm.

2-(5-Bromo-1H-indol-3-yl)-2-phenylindolin-3-one (4o):⁵ The product was synthesised by general



procedure and the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **4o** (26.2 mg, 65% yield) was obtained as a yellow solid. ¹H NMR (500 MHz, DMSO) δ 11.27 (s, 1H), 8.37 (s, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.36 - 7.27 (m, 6H), 7.22 (s, 1H), 7.17 - 7.15 (m, 2H), 6.98 (d, J = 8.3 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO) δ 200.7, 161.4, 140.1, 138.5, 136.1, 128.8, 128.1, 127.7, 126.9, 126.0, 125.2, 124.4, 122.6, 118.3, 117.6, 114.5, 114.3, 112.4, 111.9, 70.9 ppm.

2-(1H-indol-3-yl)-2-methylindolin-3-one (6):⁵ The product was synthesised by general procedure and

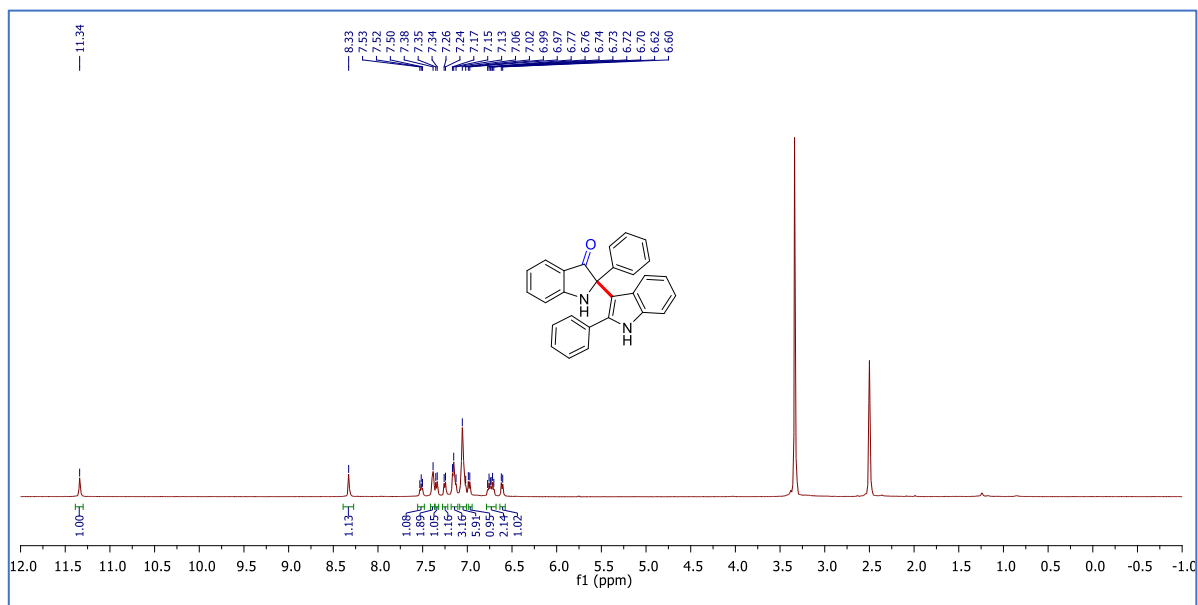


the crude reaction mixture was purified by flash chromatography on silica gel with hexane/EtOAc as eluent. Product **6** (20.5 mg, 78% yield) was obtained as a yellow solid. ¹H NMR (500 MHz, DMSO) δ 11.03 (s, 1H), 7.51 (t, J = 7.3 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.39 (d, J = 2.5 Hz, 1H), 7.35 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 8.0 Hz, 1H), 7.03 (t, J = 7.5 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 6.83 (t, J = 7.5 Hz, 1H), 6.74 (t, J = 7.4 Hz, 1H), 1.65 (s, 3H) ppm. ¹³C{¹H} NMR (126 MHz, DMSO) δ 203.8, 161.1, 138.0, 137.2, 125.4, 124.9, 124.0, 121.6, 120.1, 119.0, 118.4, 117.6, 115.0, 112.4, 112.1, 65.6, 23.8 ppm.

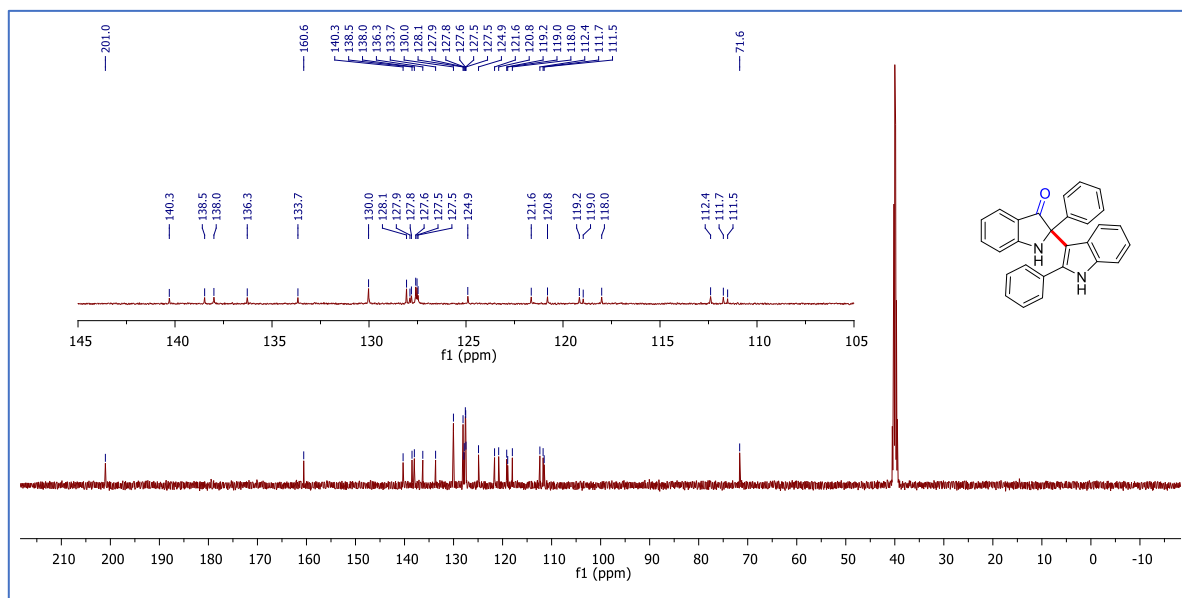
16. References:

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2. S.-D. Yang, C.-L. Sun, Z. Fang, B.-J. Li, Y.-Z. Li and Z.-J. Shi, *Angew. Chem., Int. Ed.*, 2008, **47**, 1473–1476.
3. C. Cremer and F. W. Patureau, *JACS Au*, 2022, **2**, 1318–1323.
4. C. Zhang, S. Li, F. Bureš, R. Lee, X. Ye and Z. Jiang, *ACS Catal.*, 2016, **6**, 6853–6860.
5. X. Jiang, B. Zhu, K. Lin, G. Wang, W.-K. Su and C. Yu, *Org. Biomol. Chem.*, 2019, **17**, 2199–2203.
6. Y. Dong, M.-F. Lan, Y.-Q. Lin, L. Chen, C.-M. Wu, Z.-F. Wang, Z.-C. Shi, G. Deng and B. He, *J. Org. Chem.*, 2024, **89**, 6474–6488.

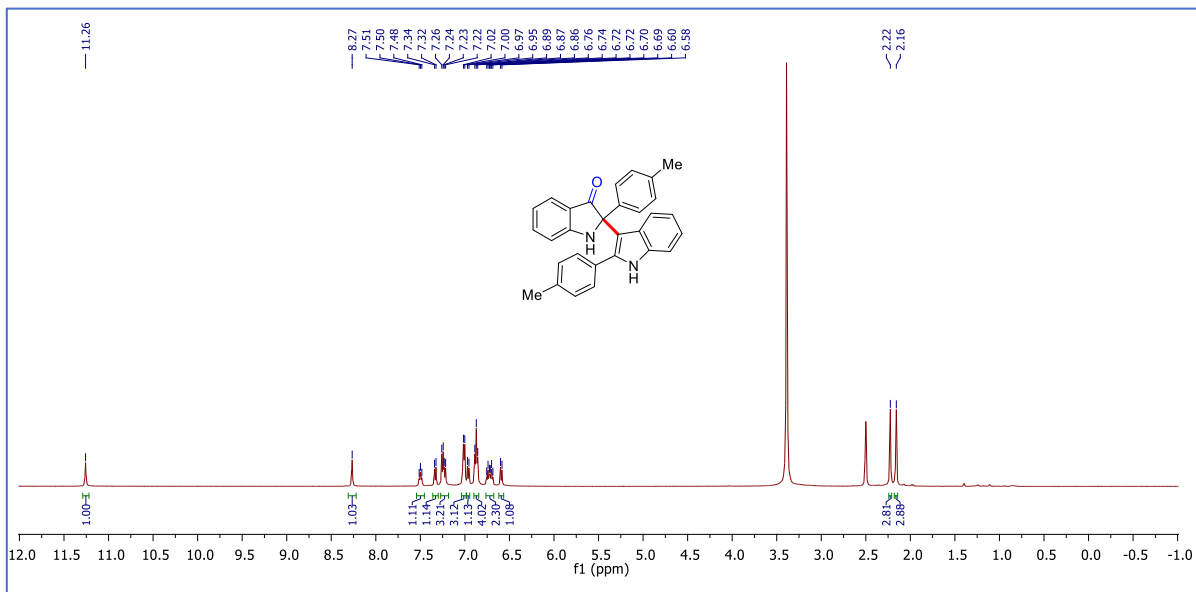
17. ^1H and ^{13}C NMR Spectra:



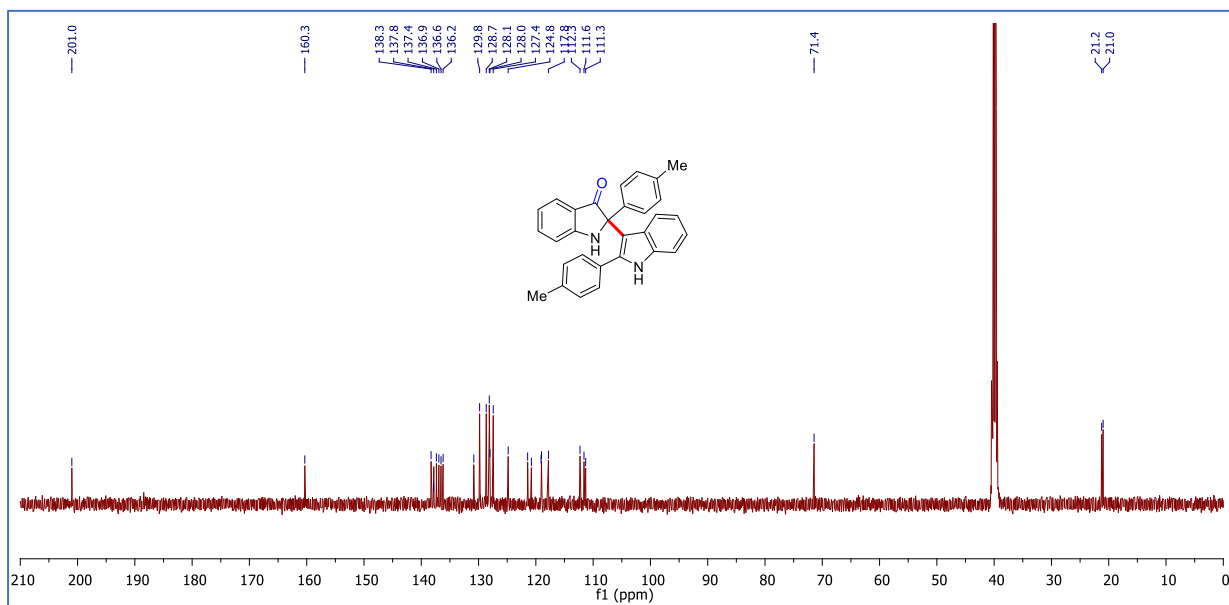
^1H NMR (500 MHz, $\text{DMSO}-d_6$) of compound **2a**



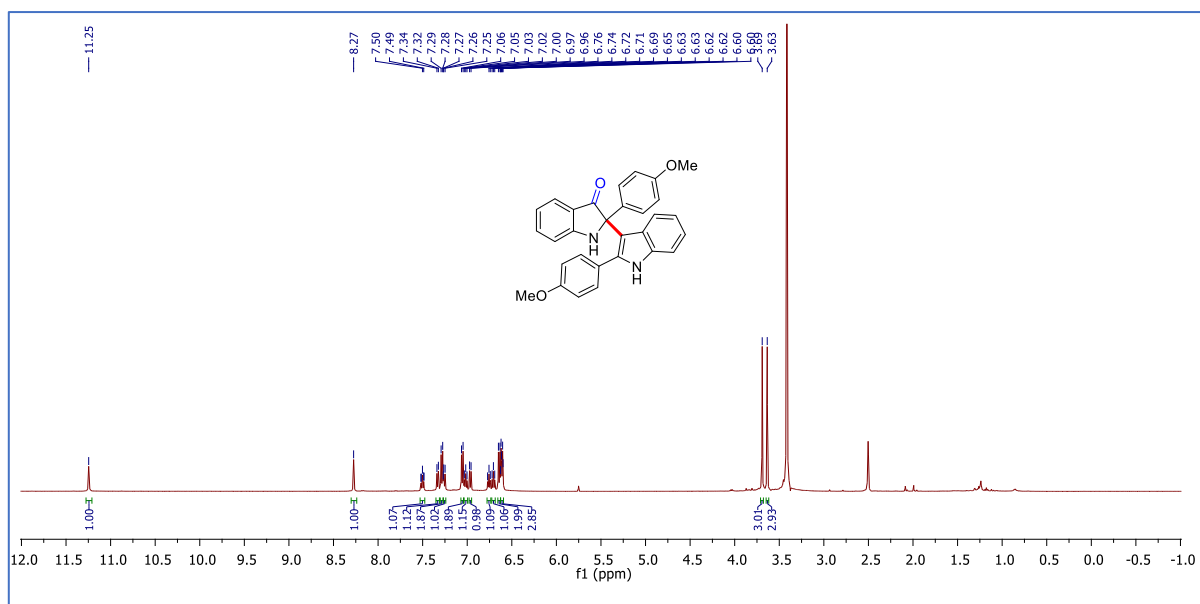
^{13}C NMR (126 MHz, $\text{DMSO}-d_6$) of compound **2a**



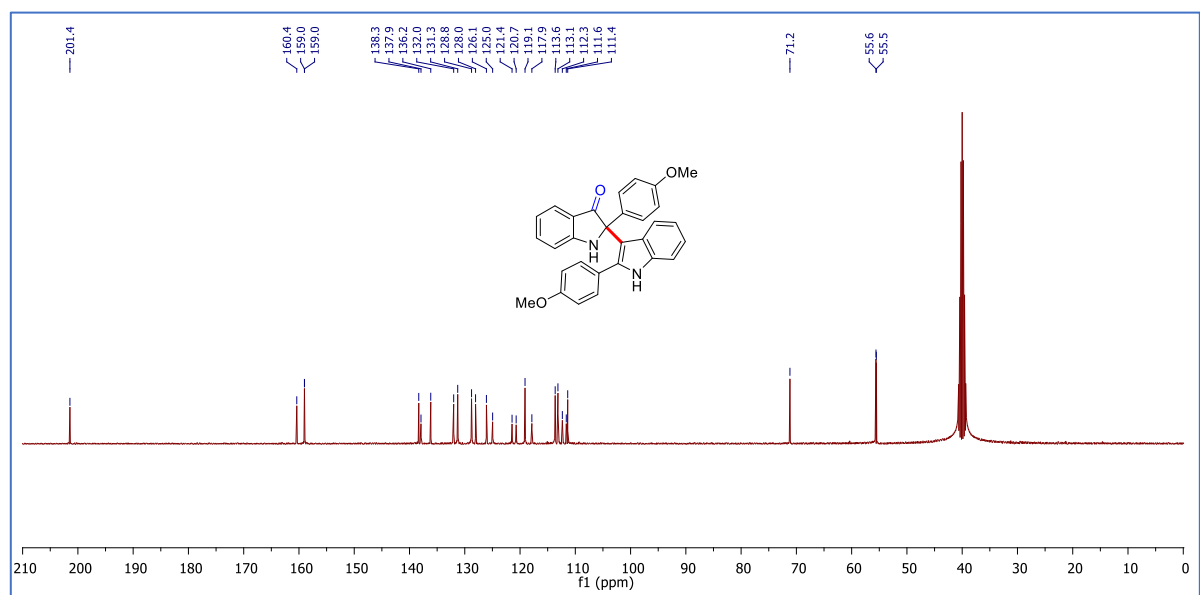
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of compound **2b**



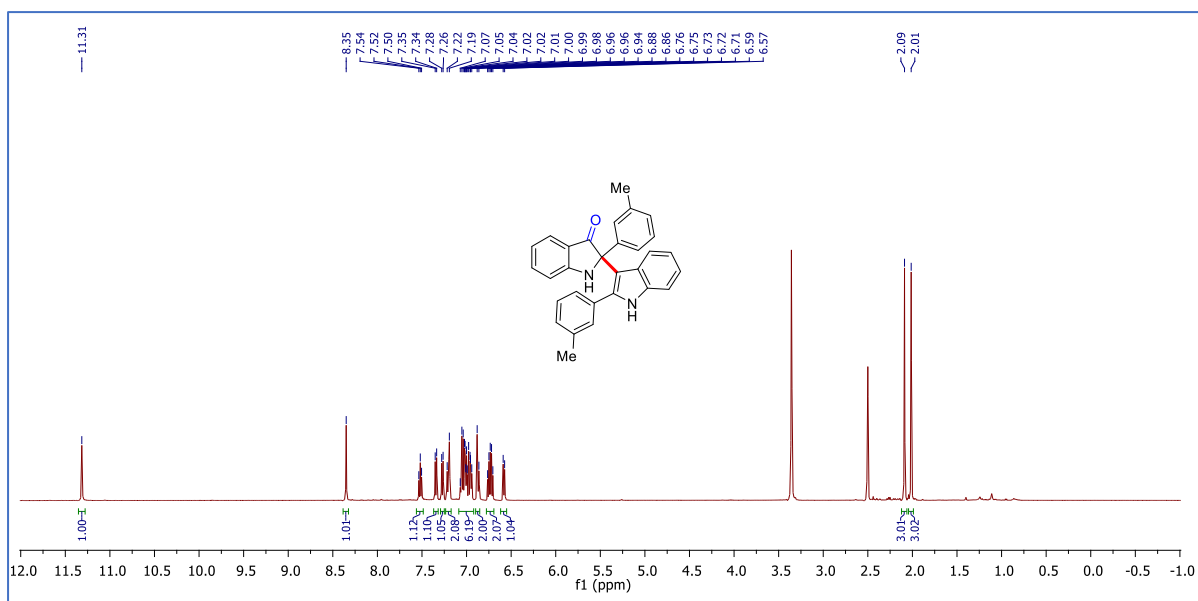
^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) of compound **2b**



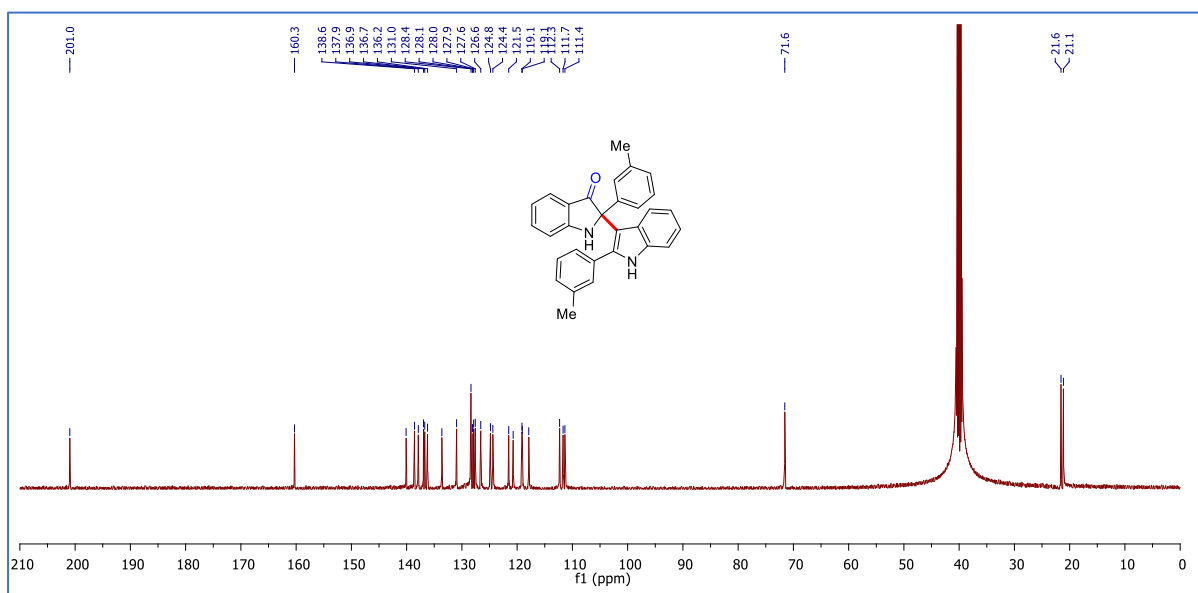
$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) of compound **2c**



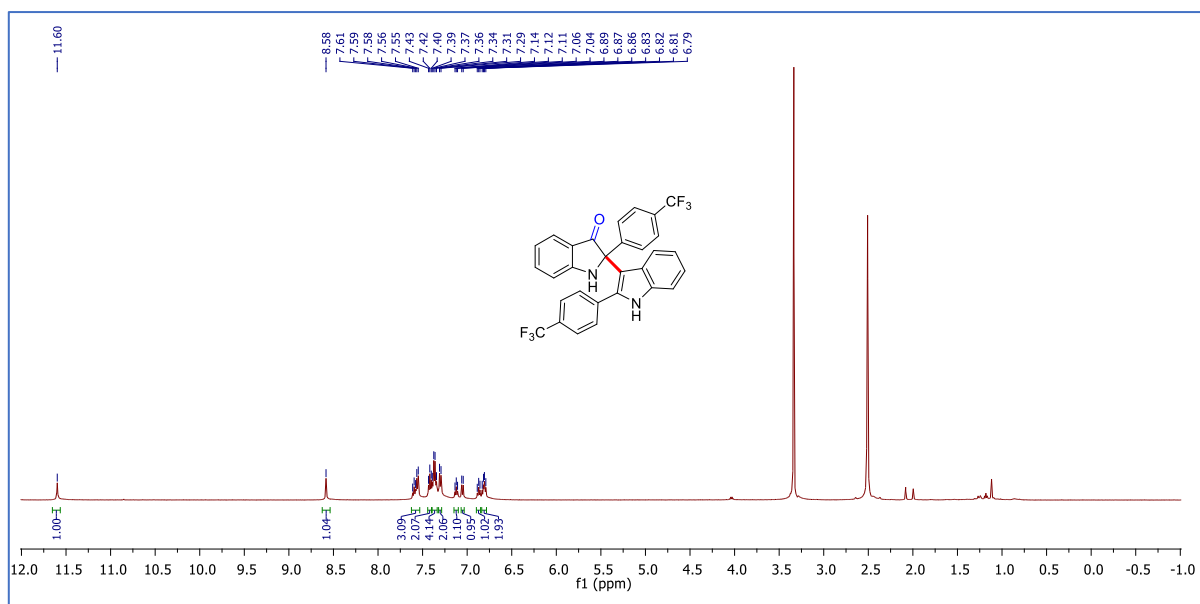
$^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) of compound **2c**



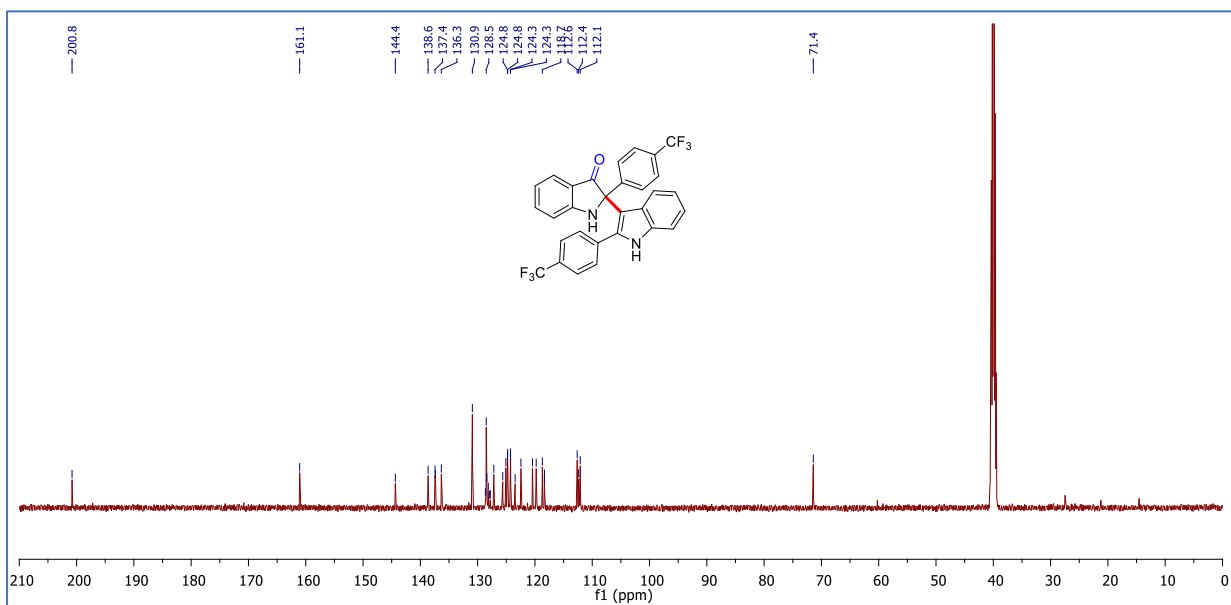
$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) of compound **2d**



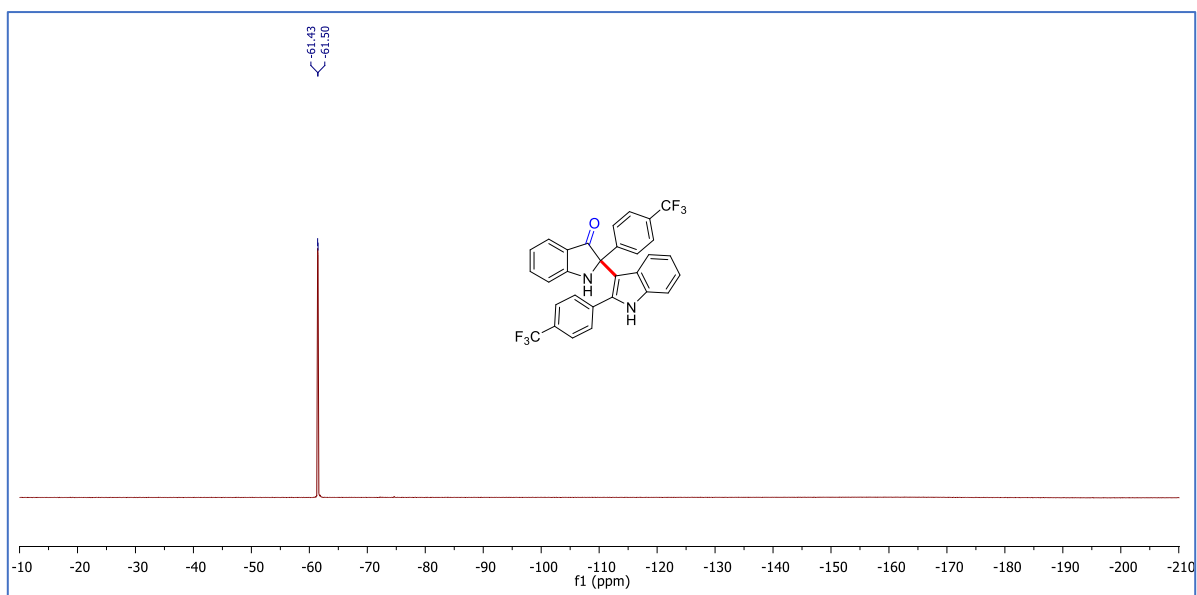
$^{13}\text{C NMR}$ (126 MHz, $\text{DMSO-}d_6$) of compound **2d**

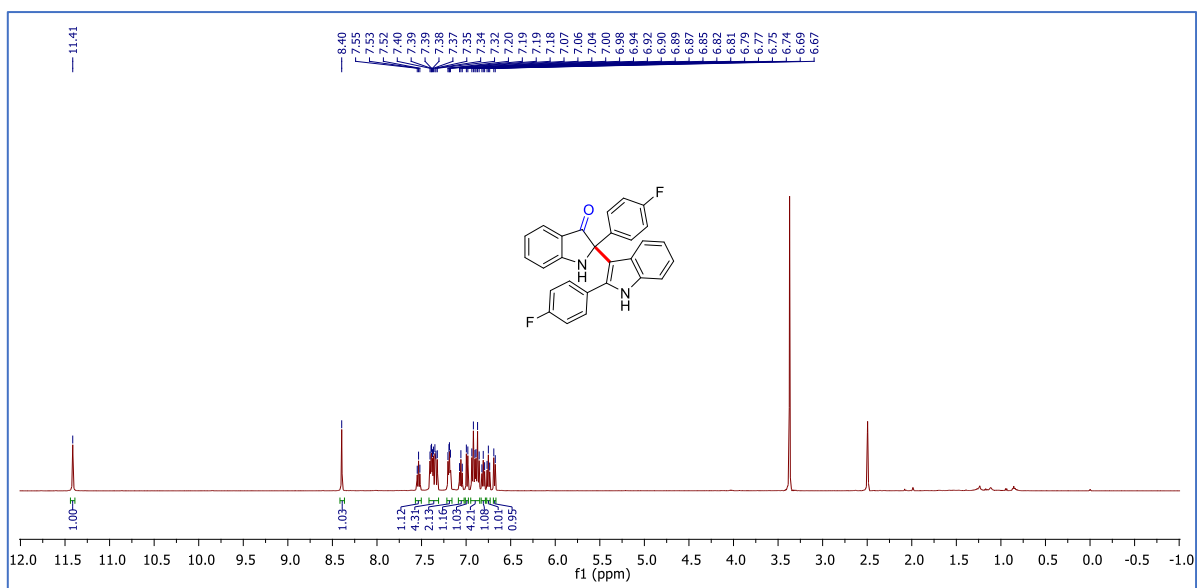


¹H NMR (500 MHz, DMSO-*d*₆) of compound **2e**

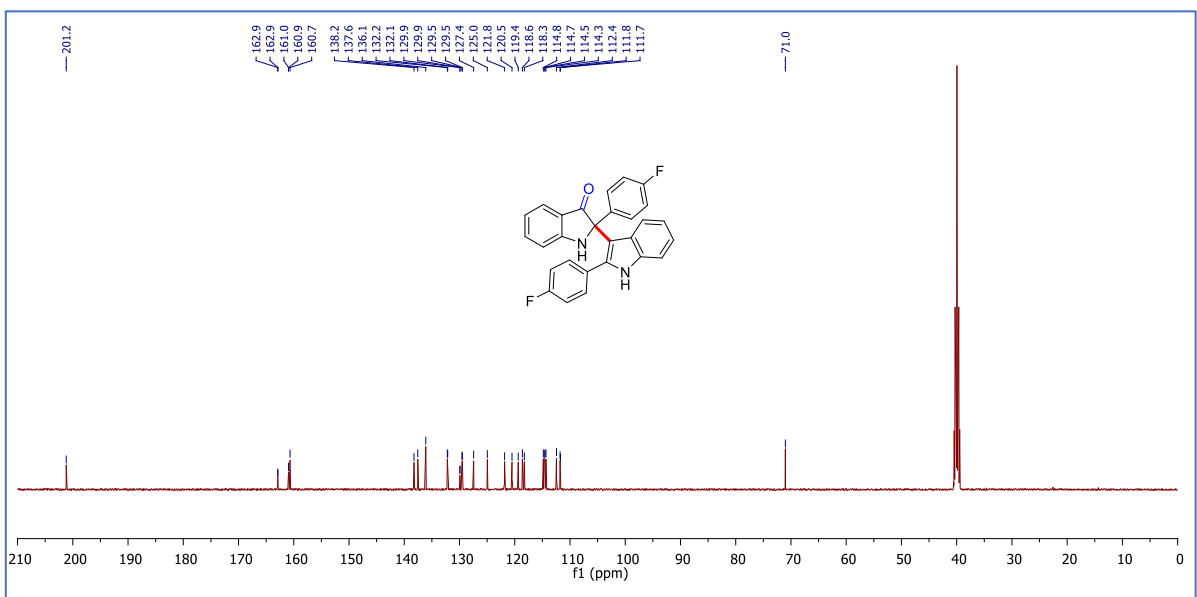


¹³C NMR (126 MHz, DMSO-*d*₆) of compound **2e**

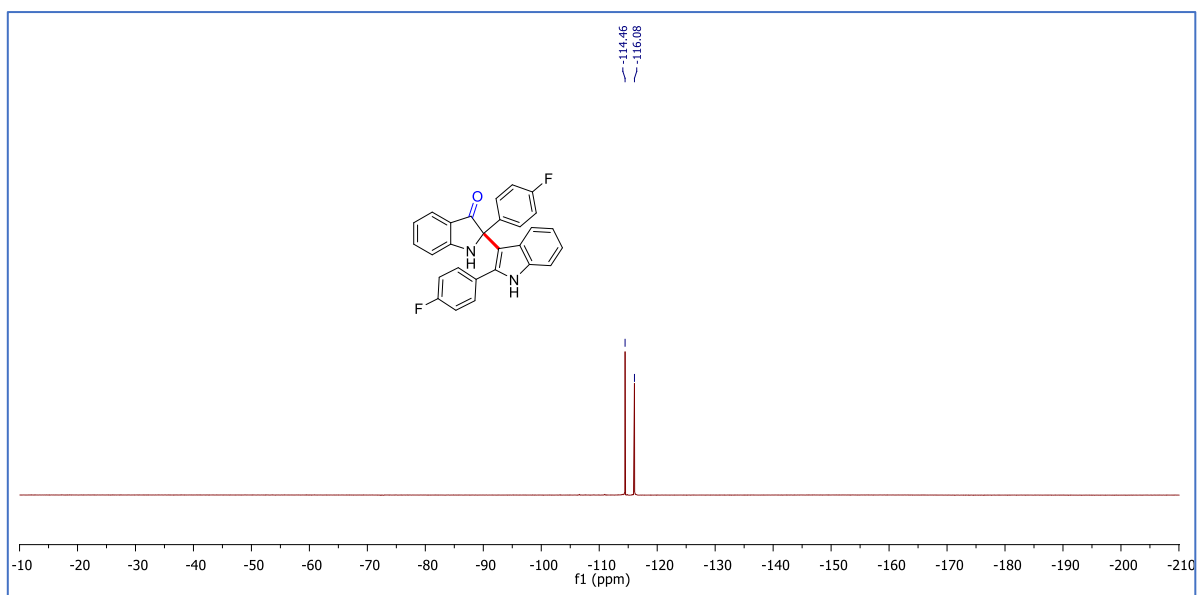




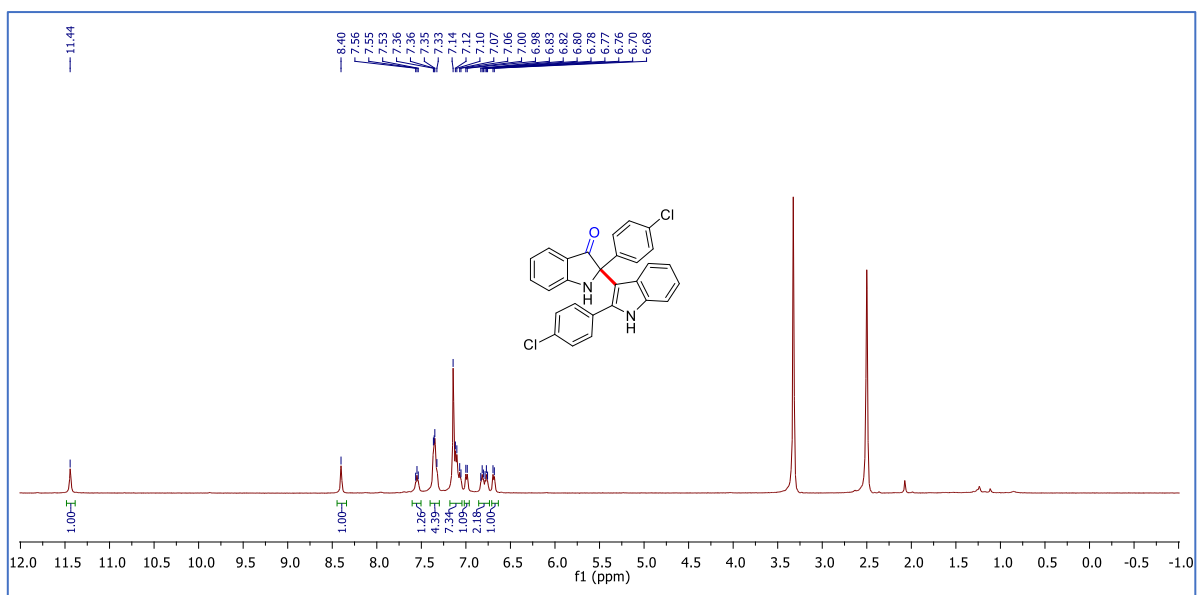
$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) of compound **2f**



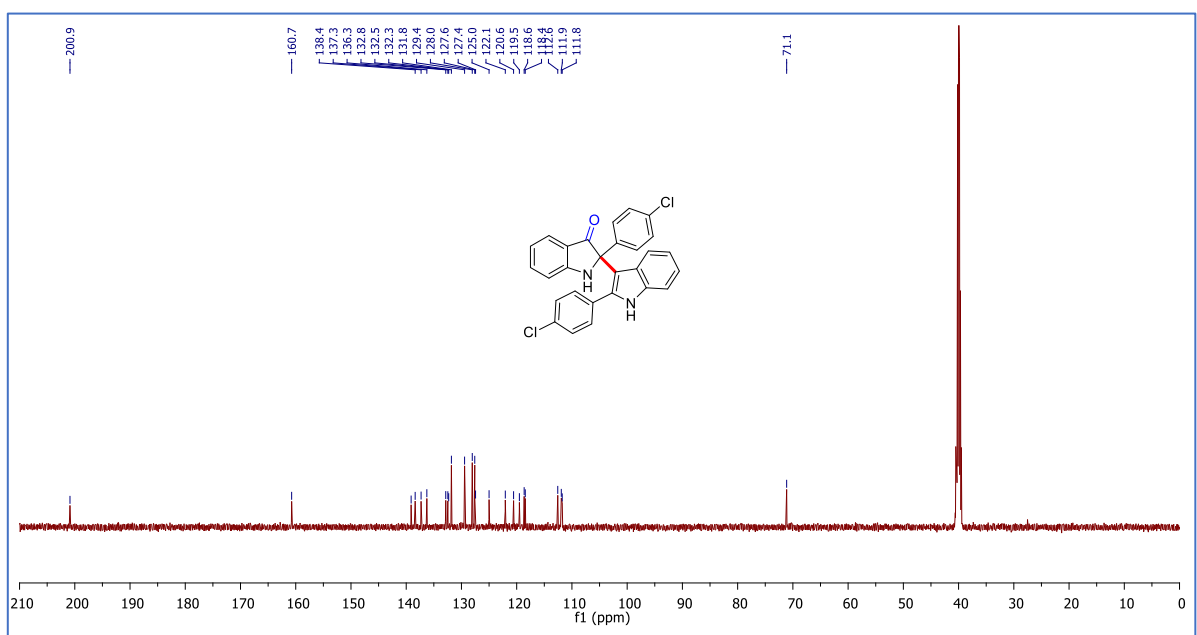
$^{13}\text{C NMR}$ (126 MHz, $\text{DMSO-}d_6$) of compound **2f**



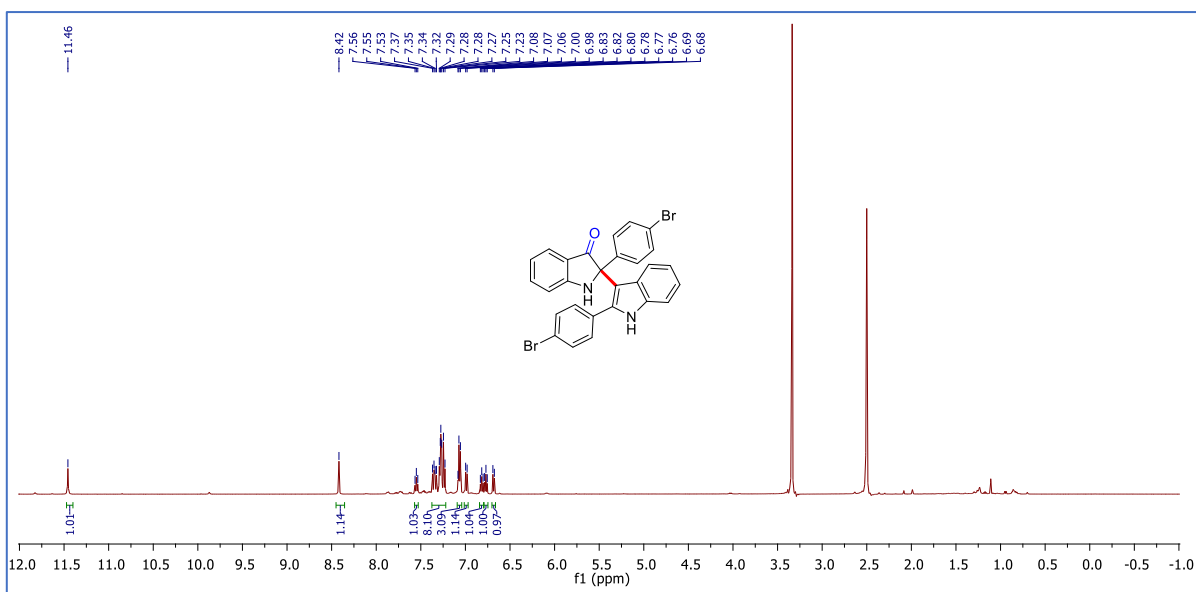
^{19}F NMR (471 MHz, $\text{DMSO}-d_6$) of compound **2f**



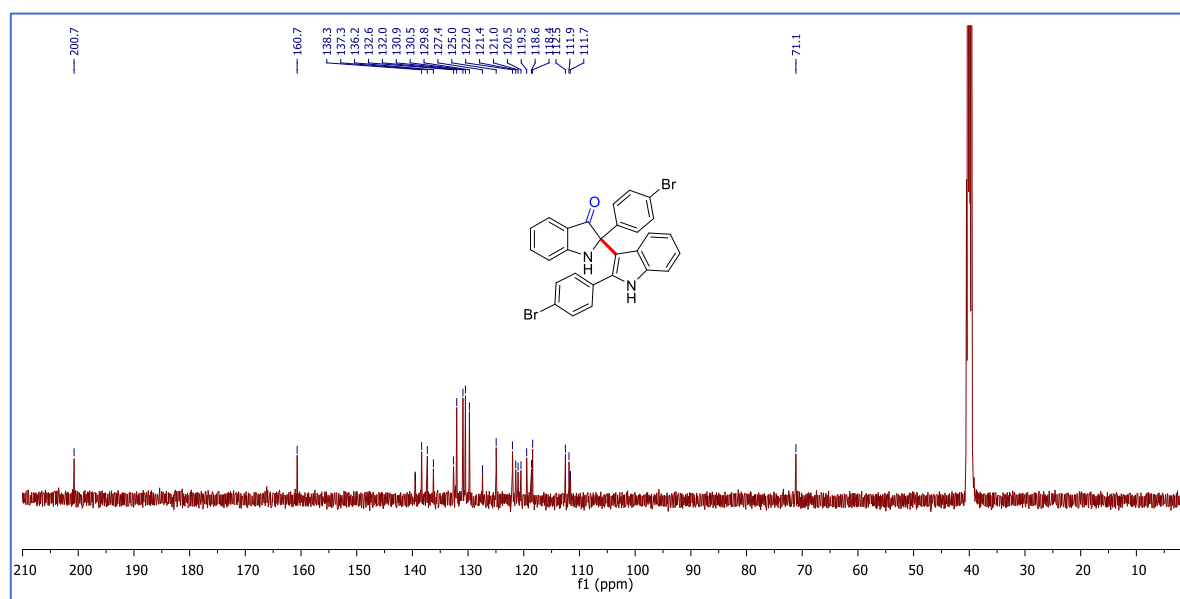
¹H NMR (500 MHz, DMSO-*d*₆) of compound **2g**



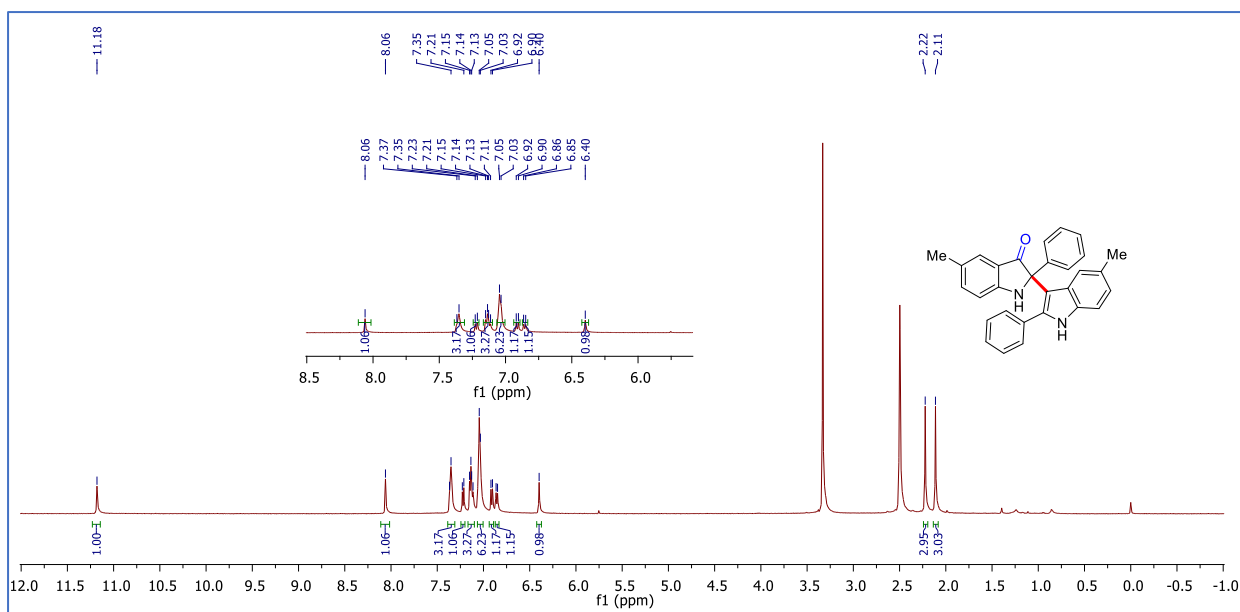
¹³C NMR (126 MHz, DMSO-*d*₆) of compound **2g**



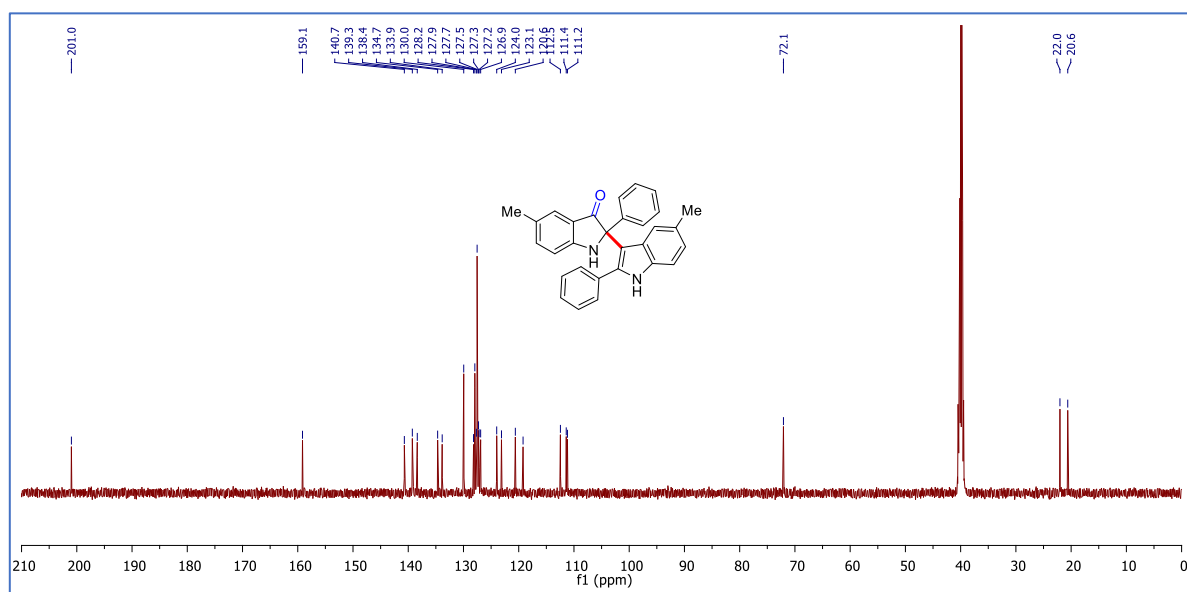
¹H NMR (500 MHz, DMSO-*d*₆) of compound **2h**



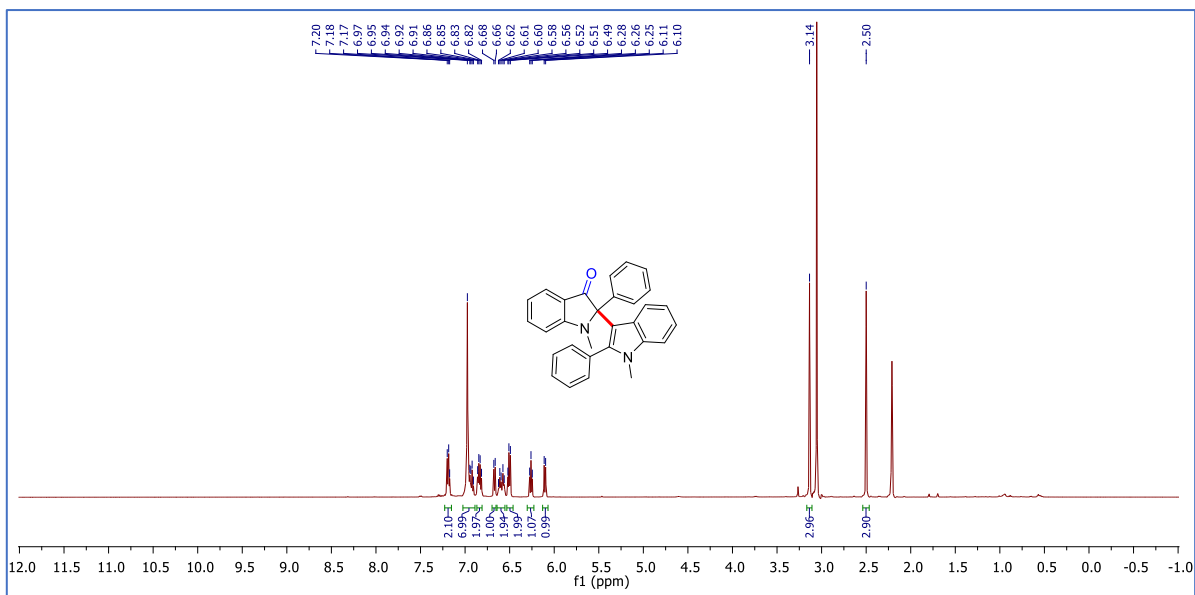
¹³C NMR (126 MHz, DMSO-*d*₆) of compound **2h**



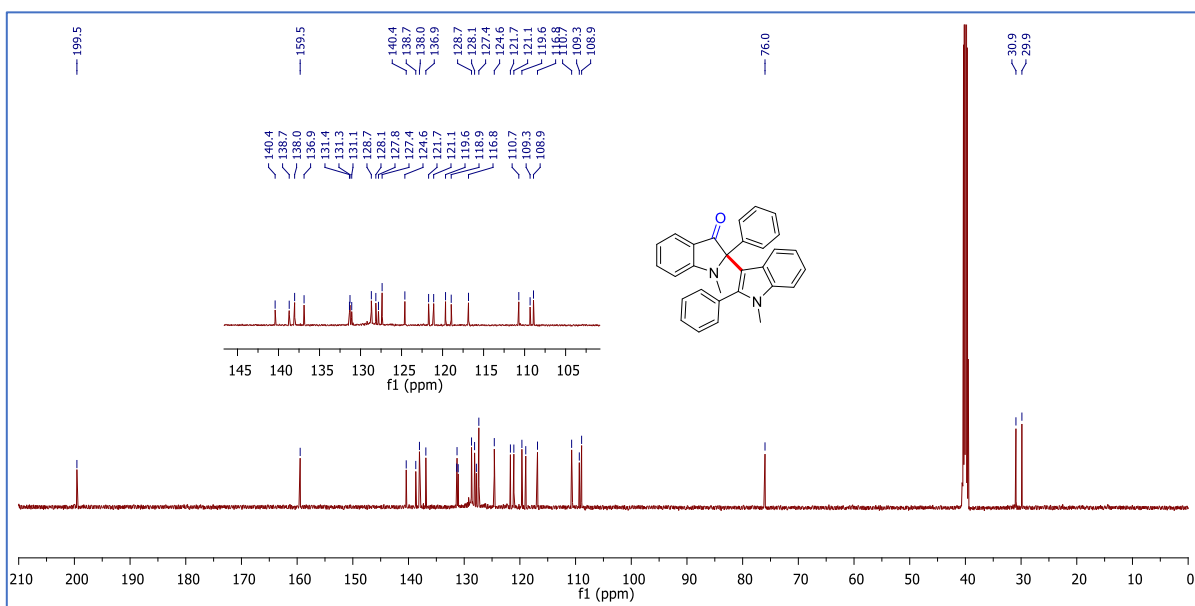
¹H NMR (500 MHz, DMSO-*d*₆) of compound **2i**



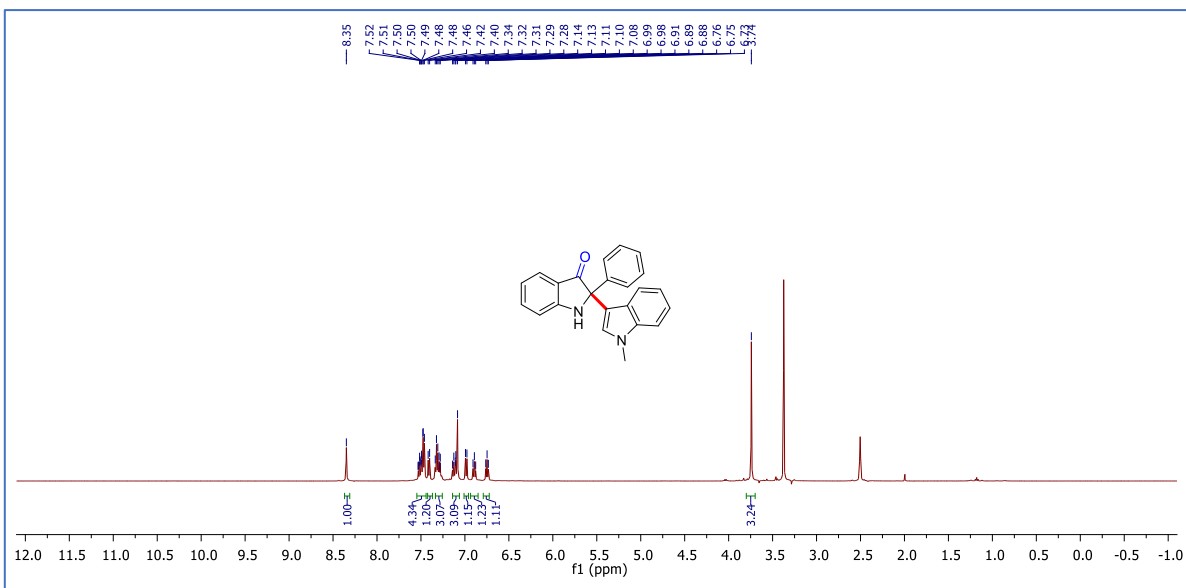
¹³C NMR (126 MHz, DMSO-*d*₆) of compound **2i**



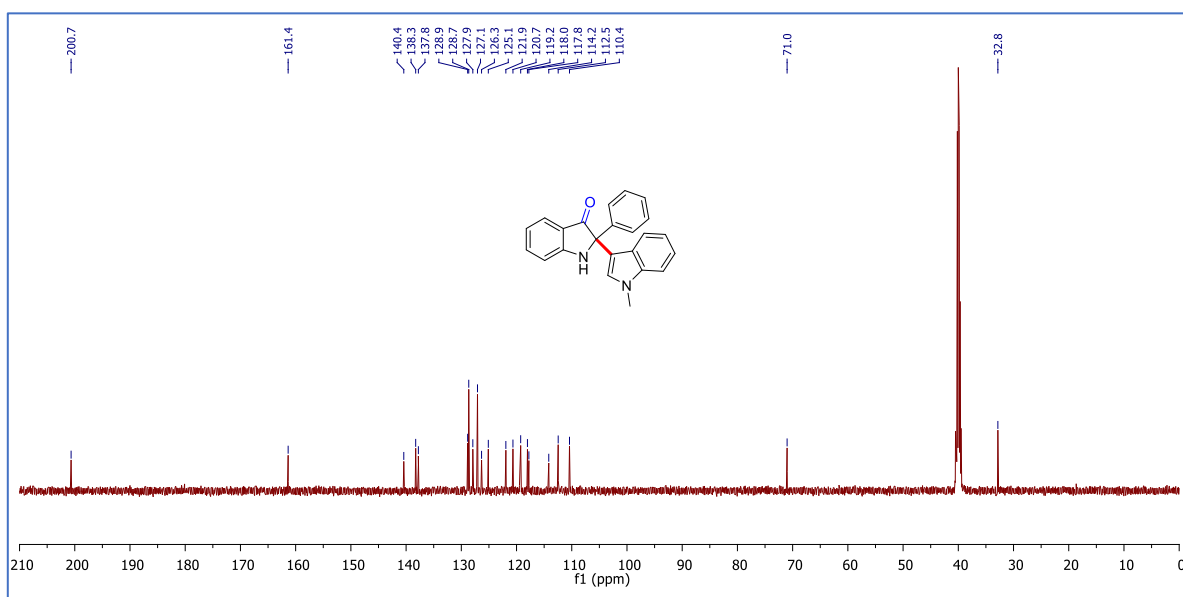
¹H NMR (500 MHz, DMSO-*d*₆) of compound **2j**



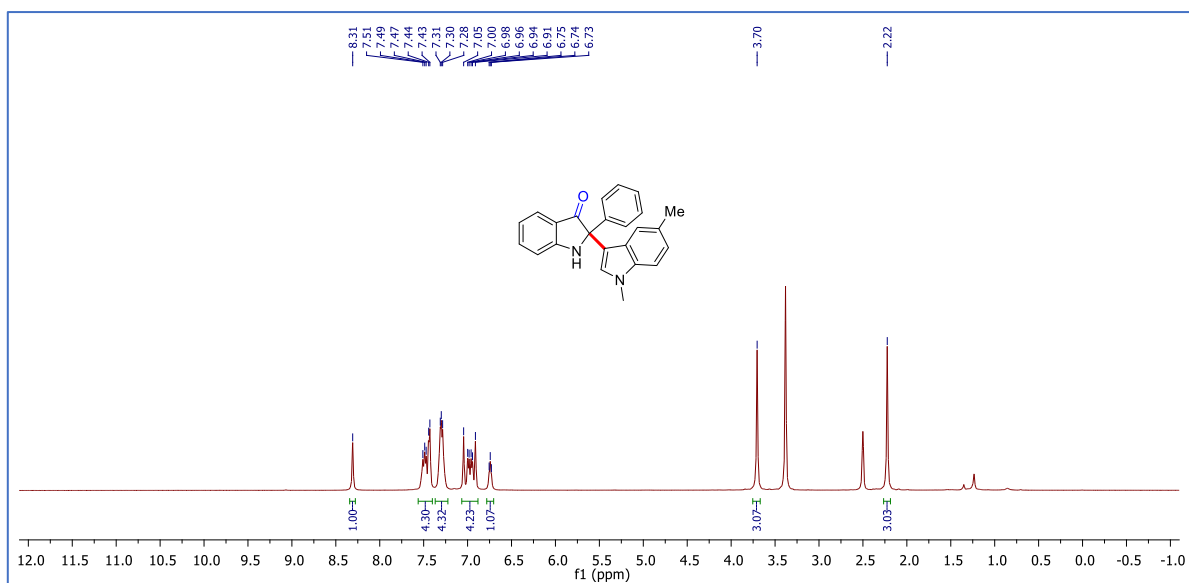
¹³C NMR (101 MHz, DMSO-*d*₆) of compound **2j**



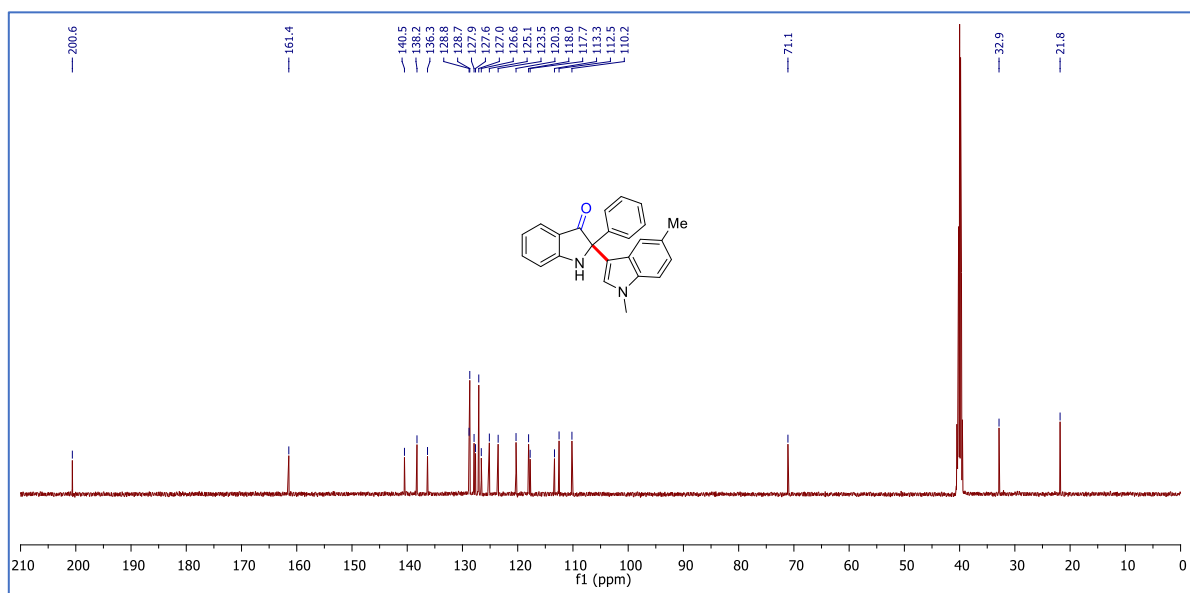
¹H NMR (500 MHz, DMSO-*d*₆) of compound **4a**



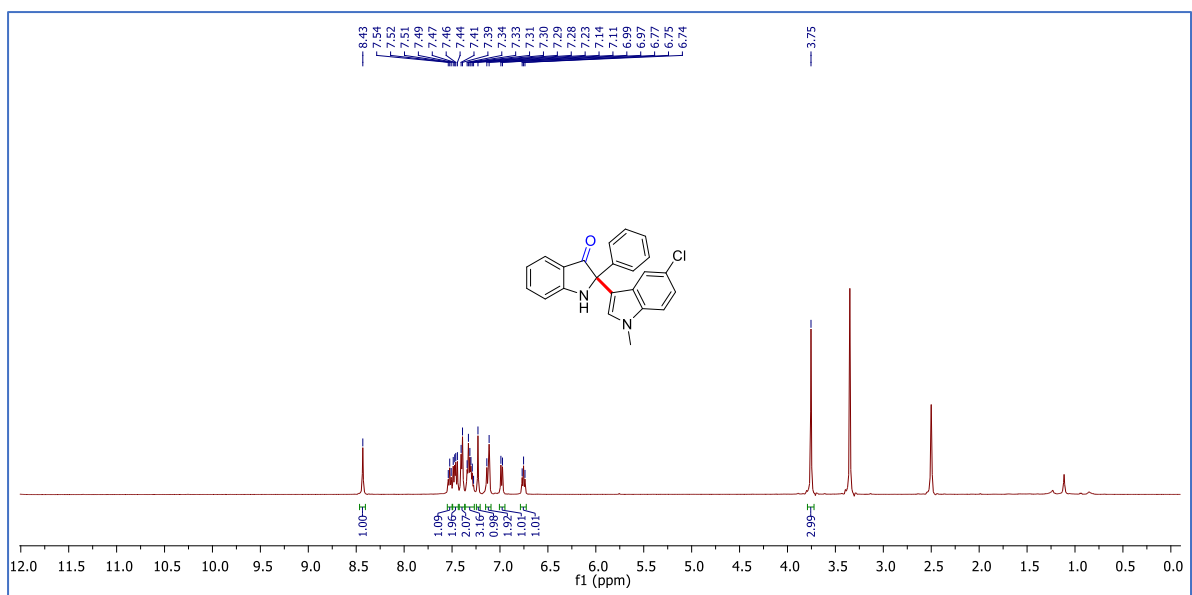
¹³C NMR (126 MHz, DMSO-*d*₆) of compound **4a**



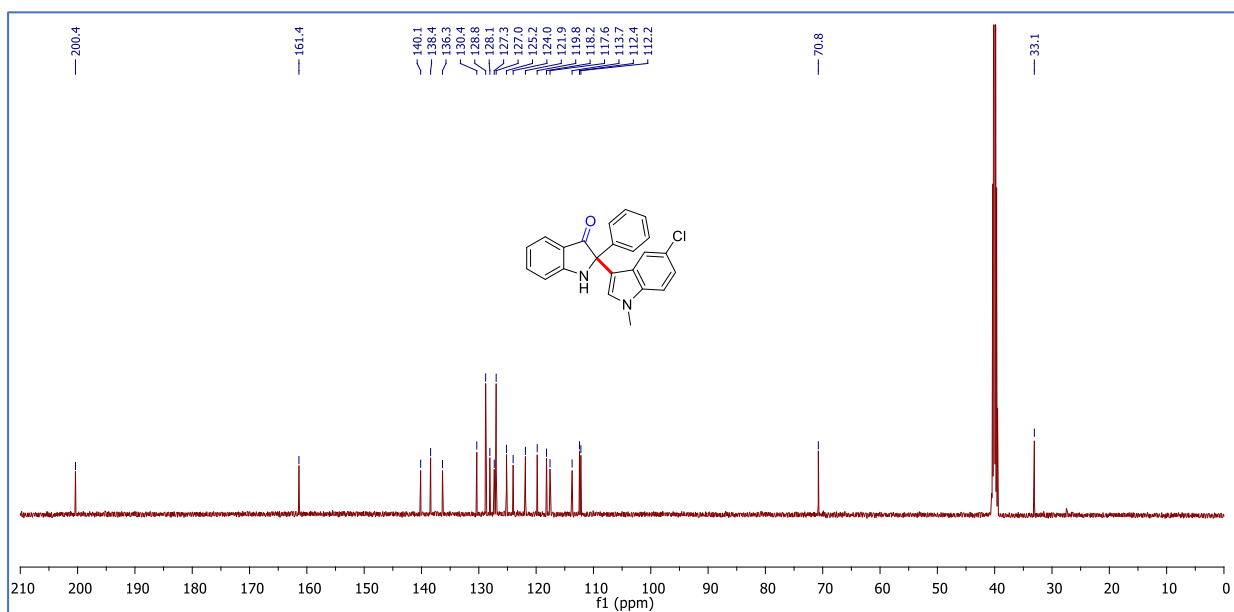
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of compound **4b**



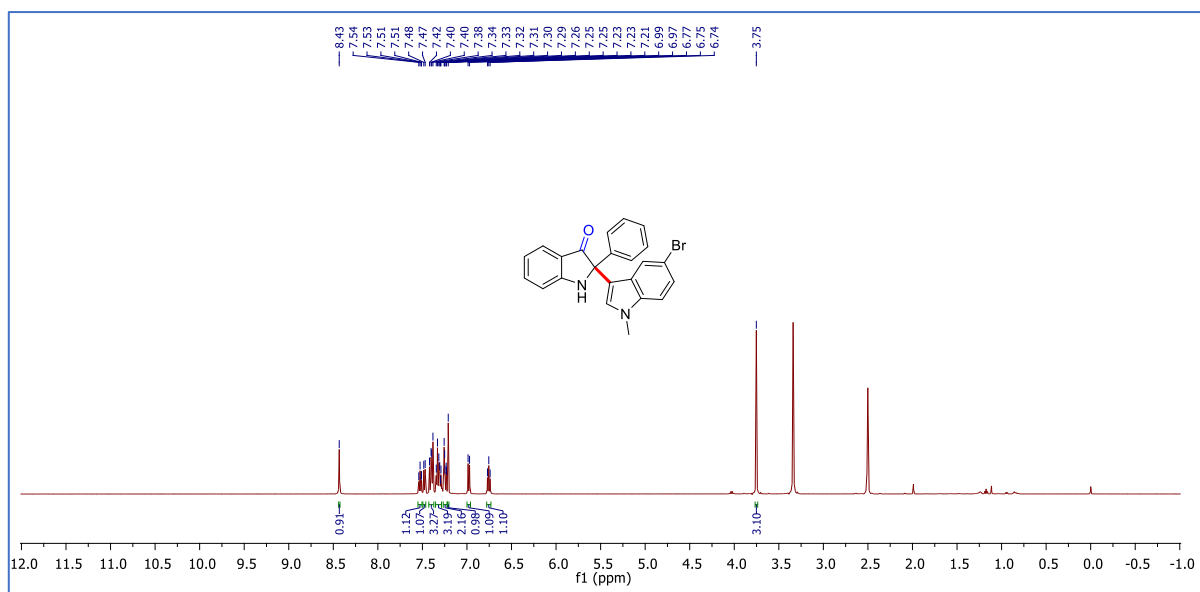
^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) of compound **4b**



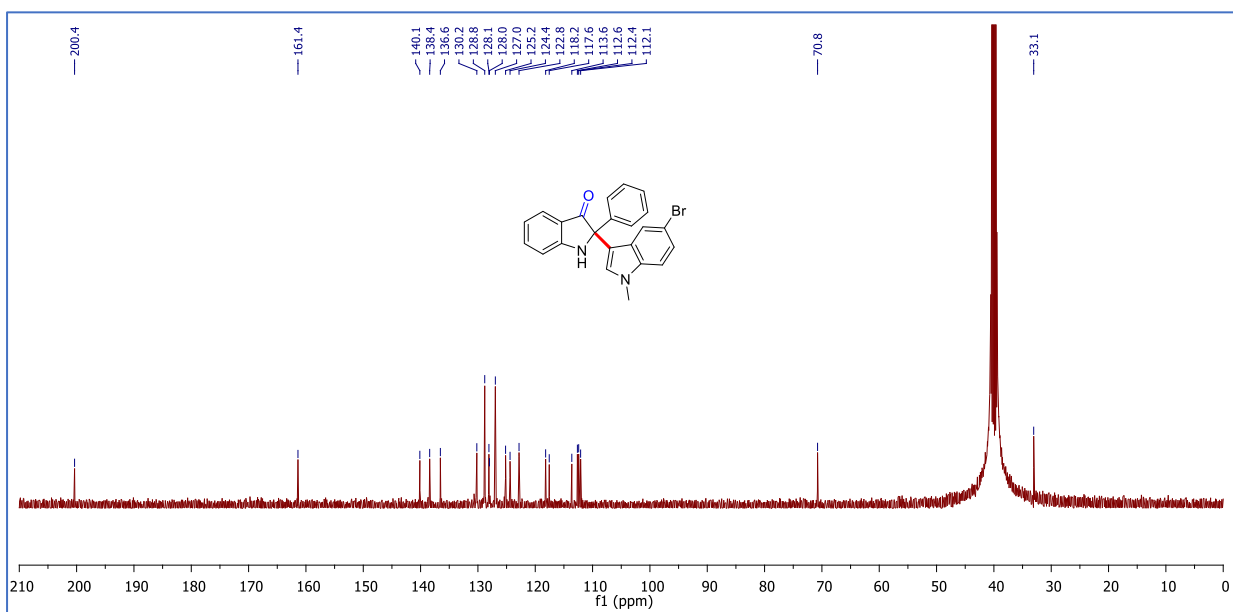
¹H NMR (500 MHz, DMSO-*d*₆) of compound **4c**



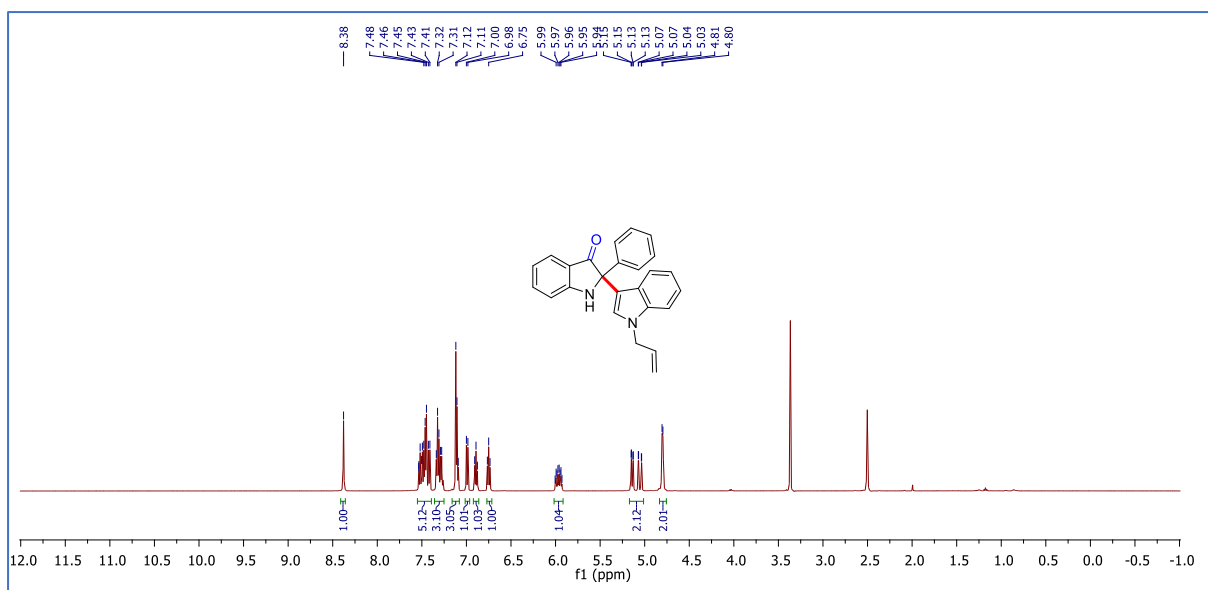
¹³C NMR (126 MHz, DMSO-*d*₆) of compound **4c**



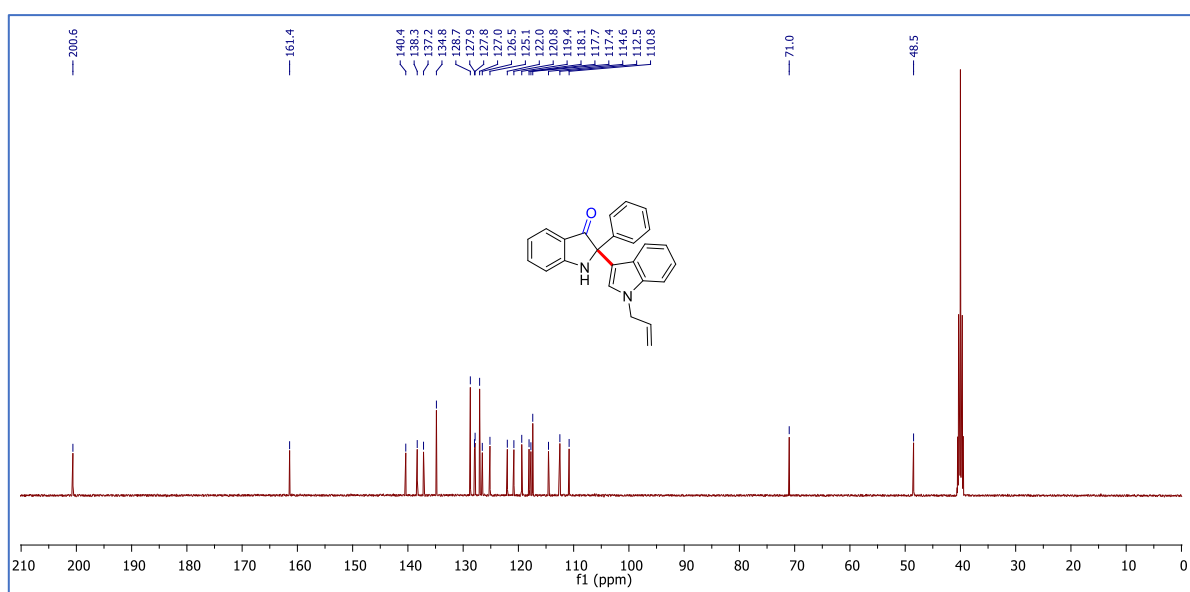
¹H NMR (500 MHz, DMSO-*d*₆) of compound **4d**



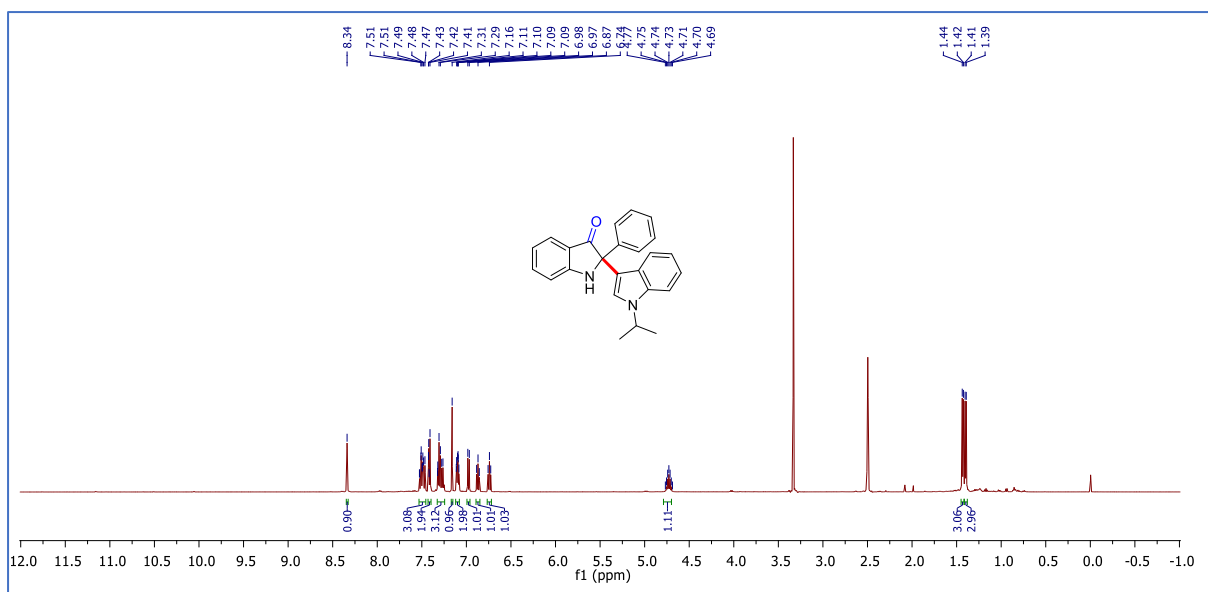
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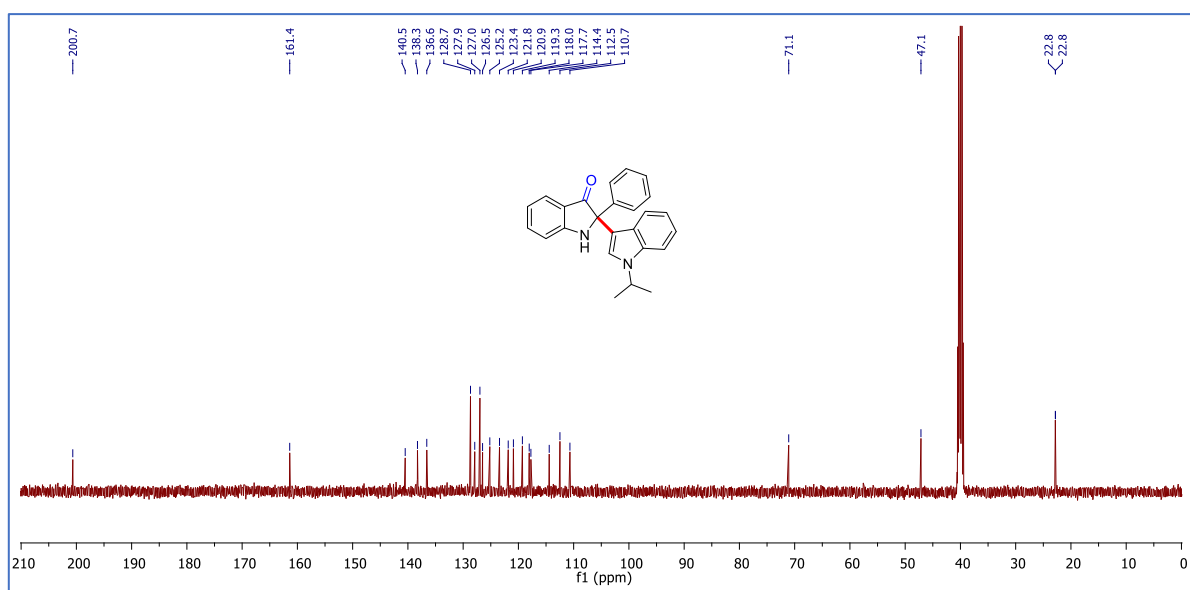
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of compound **4e**



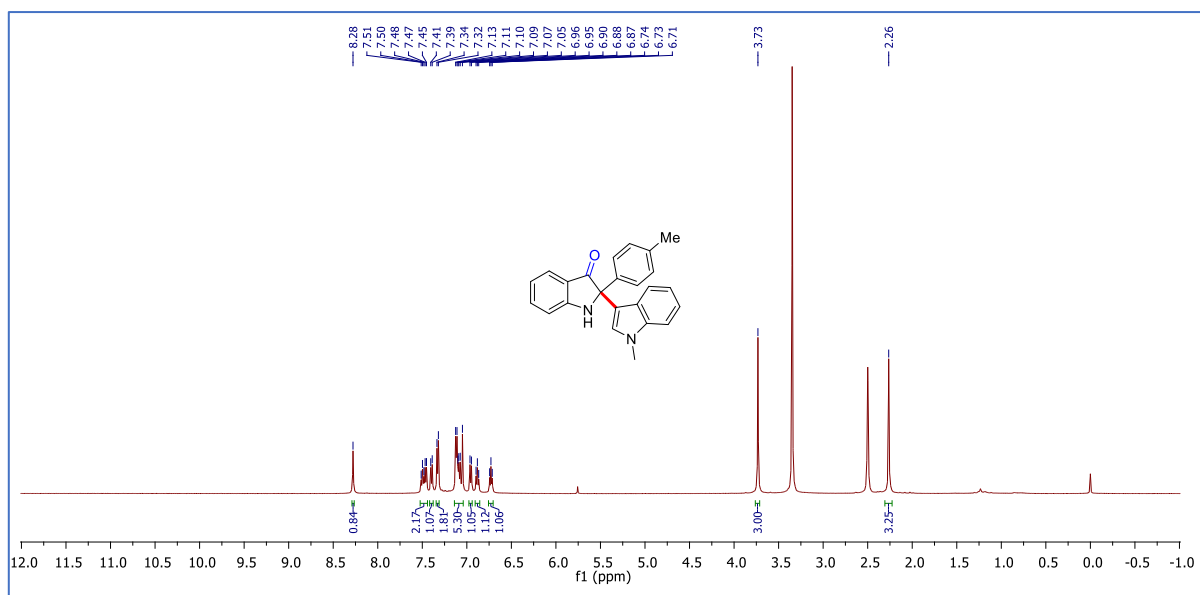
^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) of compound **4e**



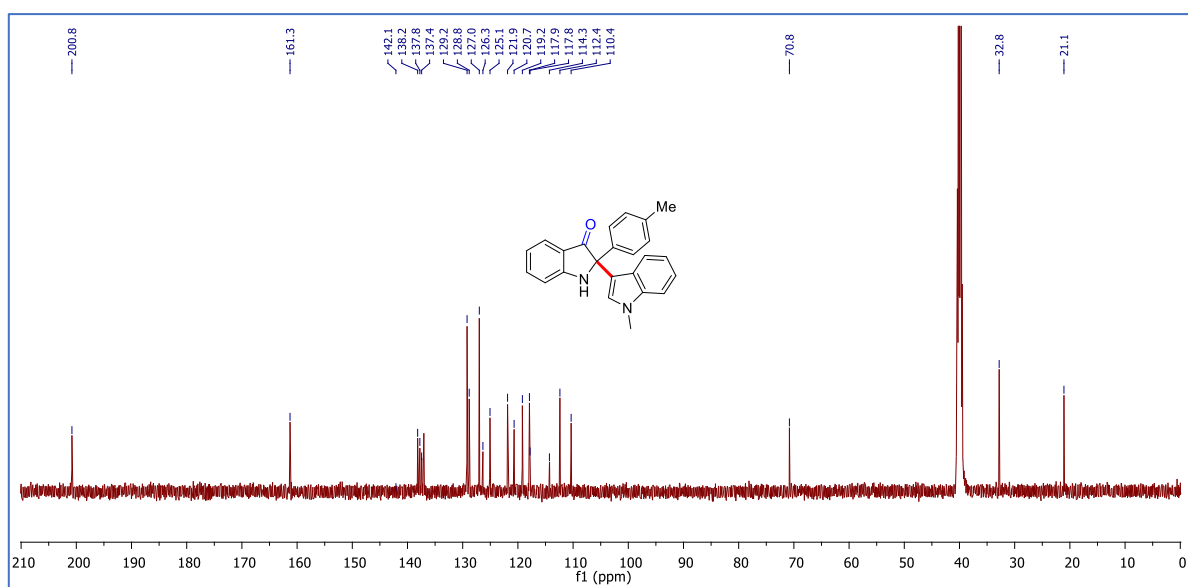
¹H NMR (500 MHz, DMSO-*d*₆) of compound 4f



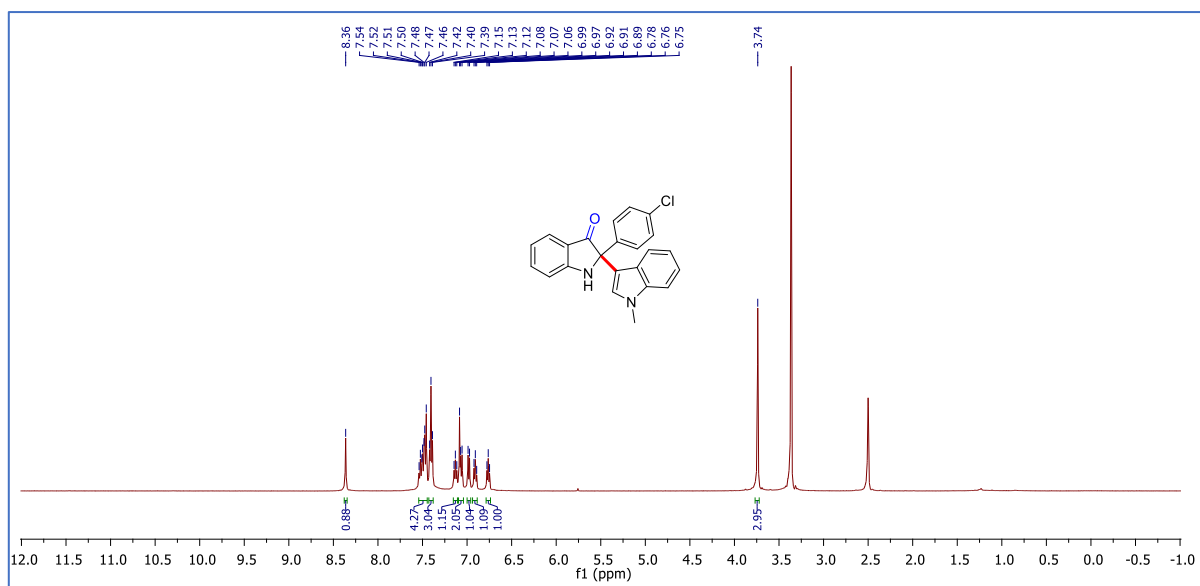
¹³C NMR (126 MHz, DMSO-*d*₆) of compound 4f



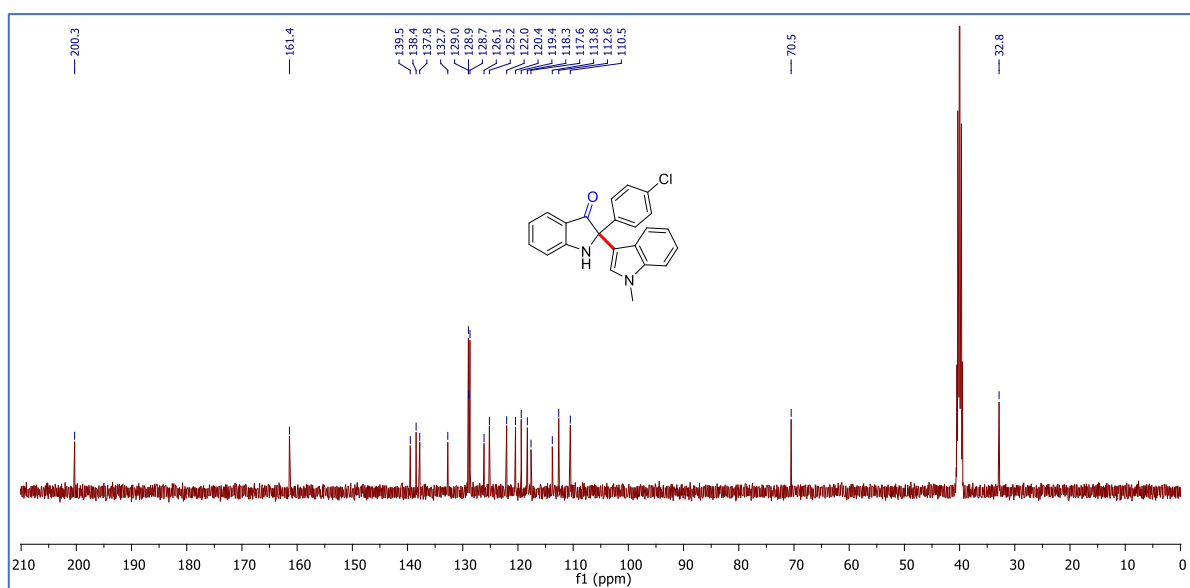
$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) of compound **4g**



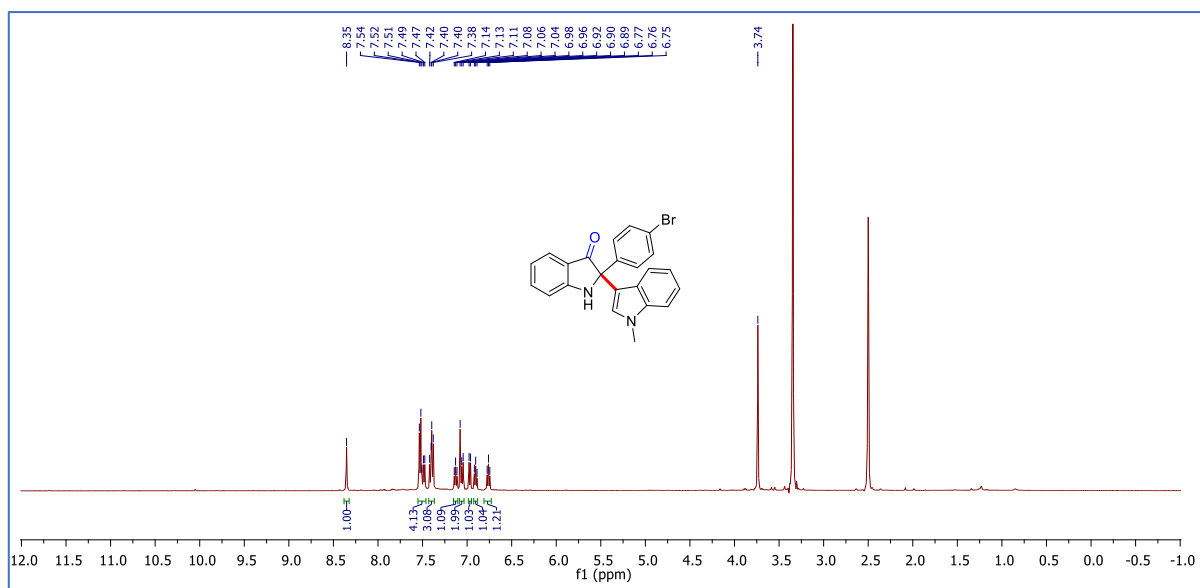
$^{13}\text{C NMR}$ (126 MHz, $\text{DMSO-}d_6$) of compound **4g**



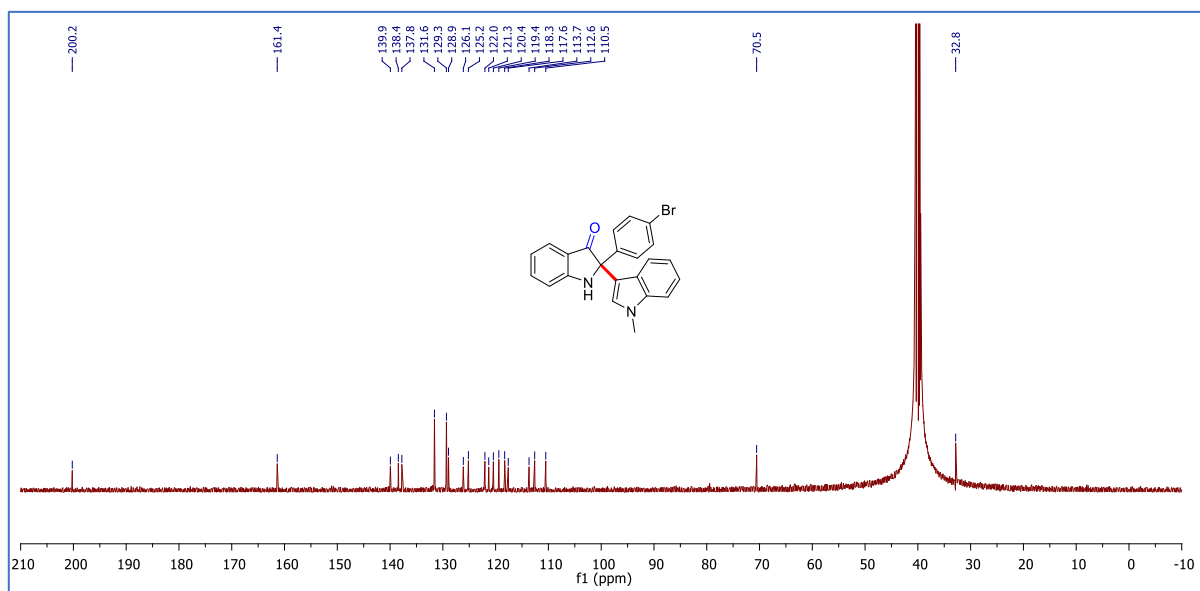
¹H NMR (500 MHz, DMSO-*d*₆) of compound **4h**



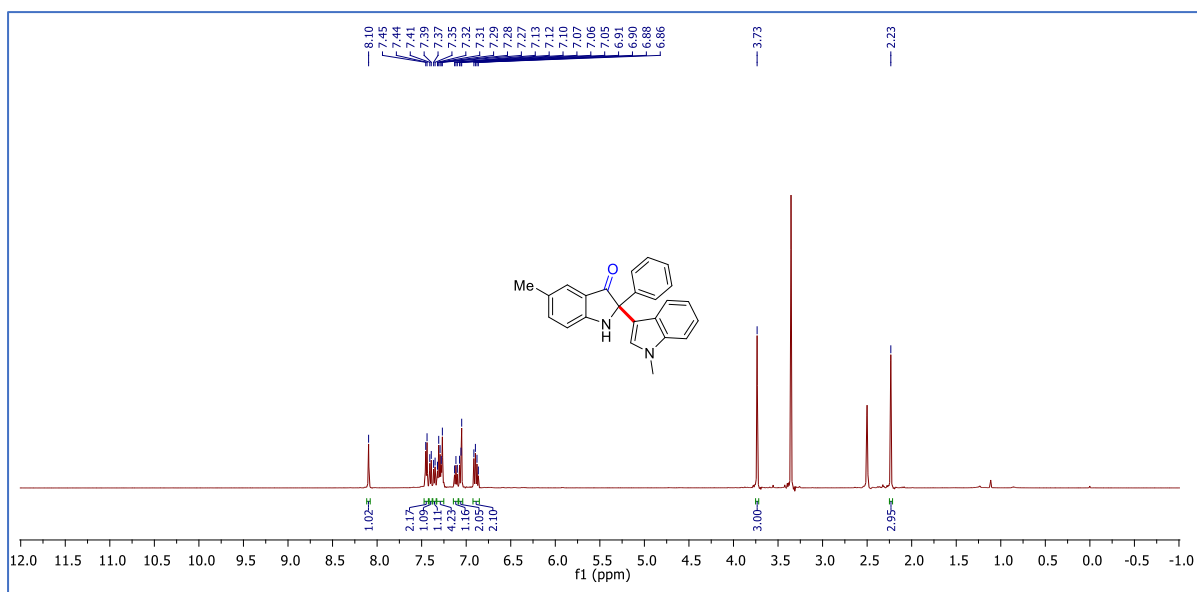
¹³C NMR (126 MHz, DMSO-*d*₆) of compound **4h**



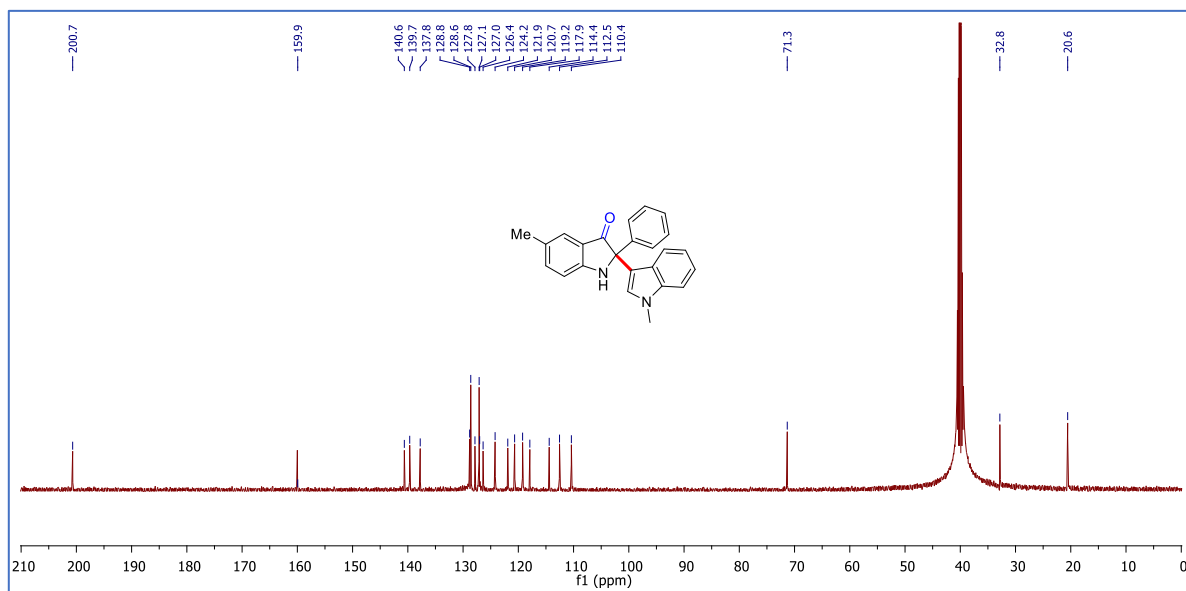
¹H NMR (500 MHz, DMSO-*d*₆) of compound **4i**



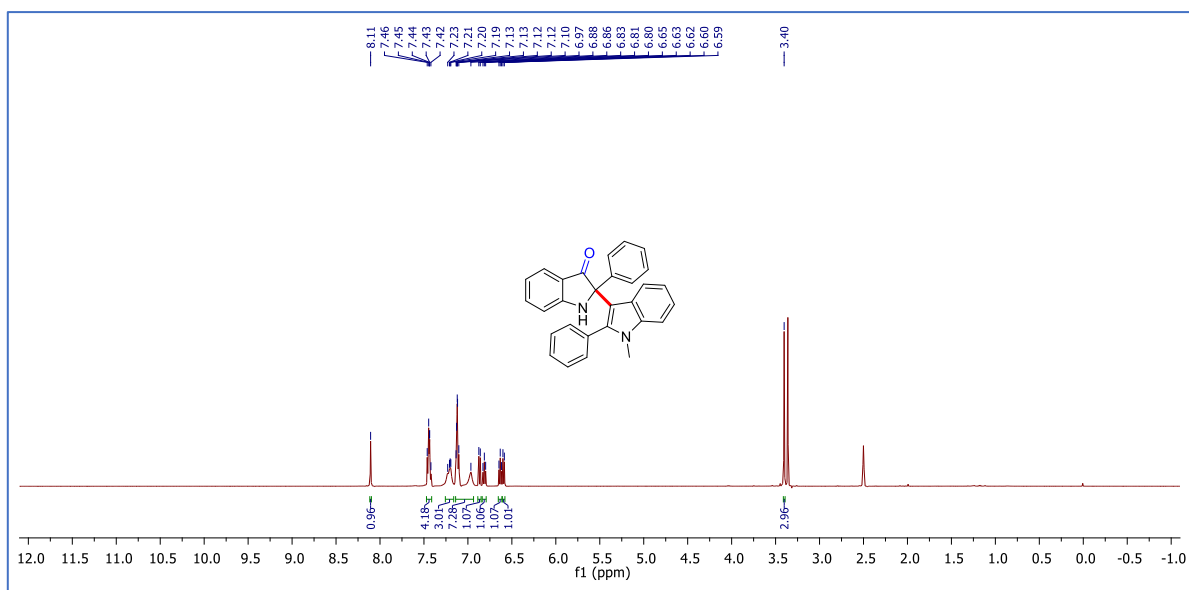
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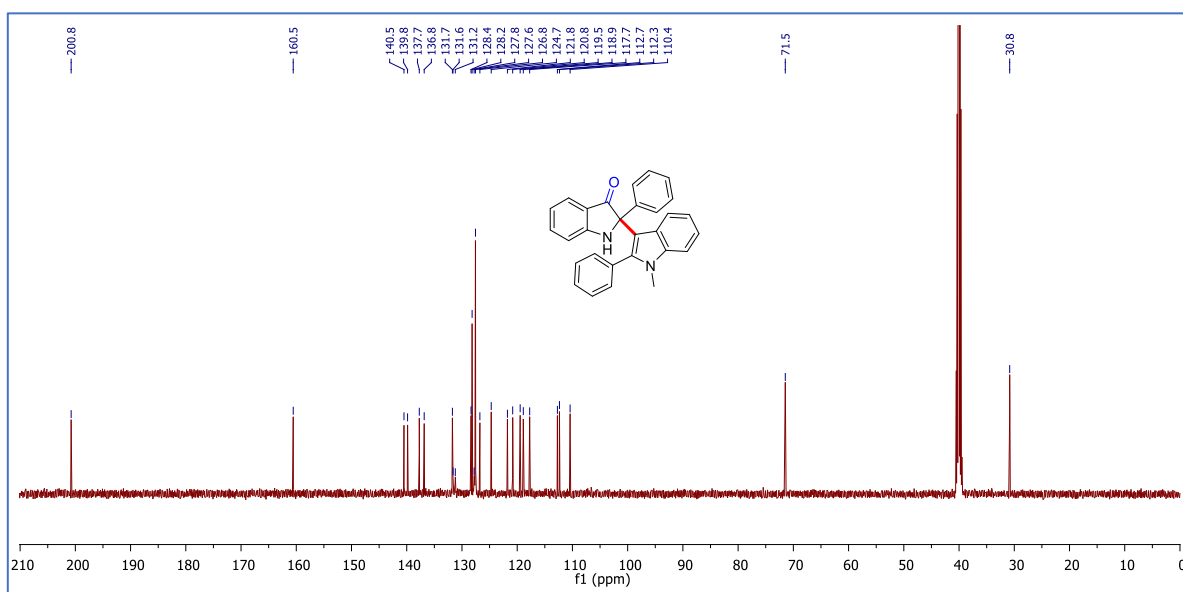
¹H NMR (500 MHz, DMSO-*d*₆) of compound **4j**



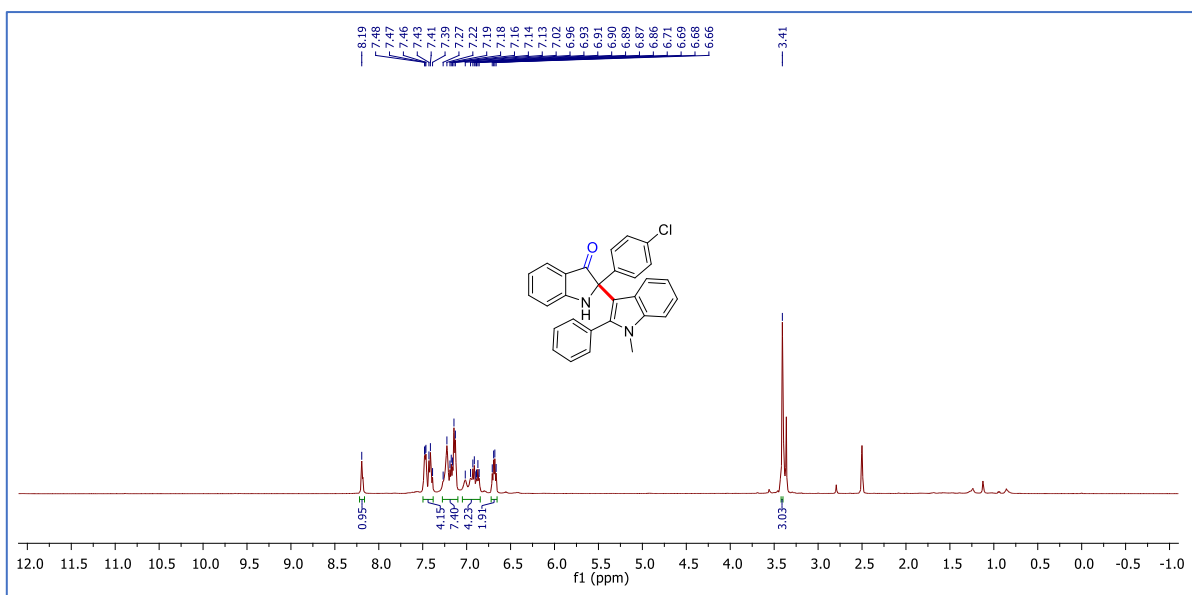
¹³C NMR (126 MHz, DMSO-*d*₆) of compound **4j**



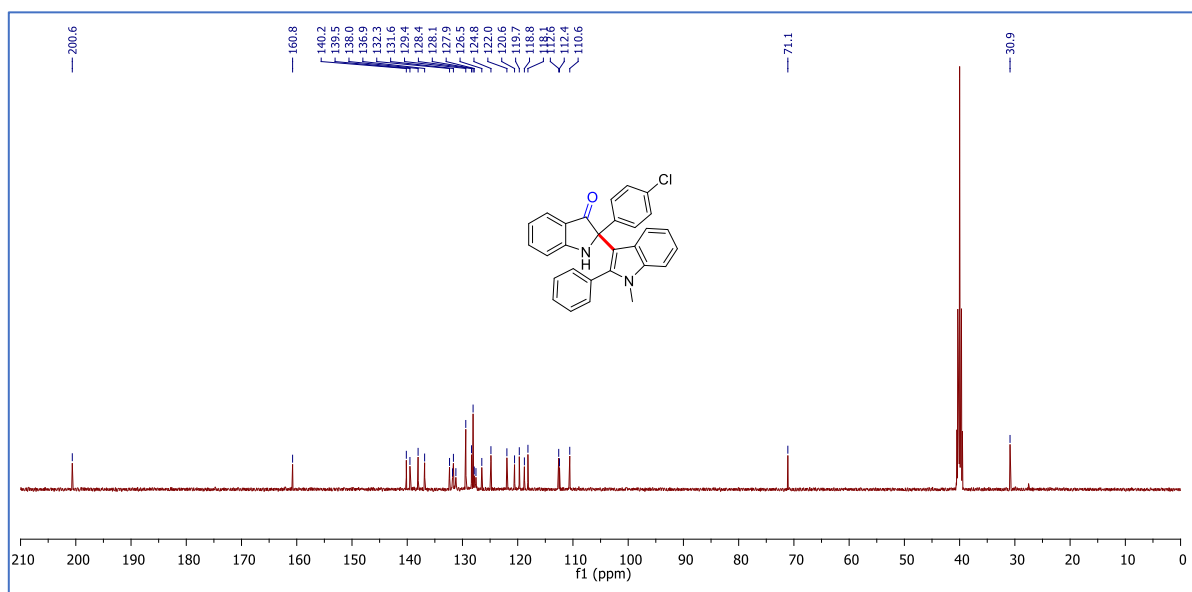
¹H NMR (500 MHz, DMSO-*d*₆) of compound **4k**



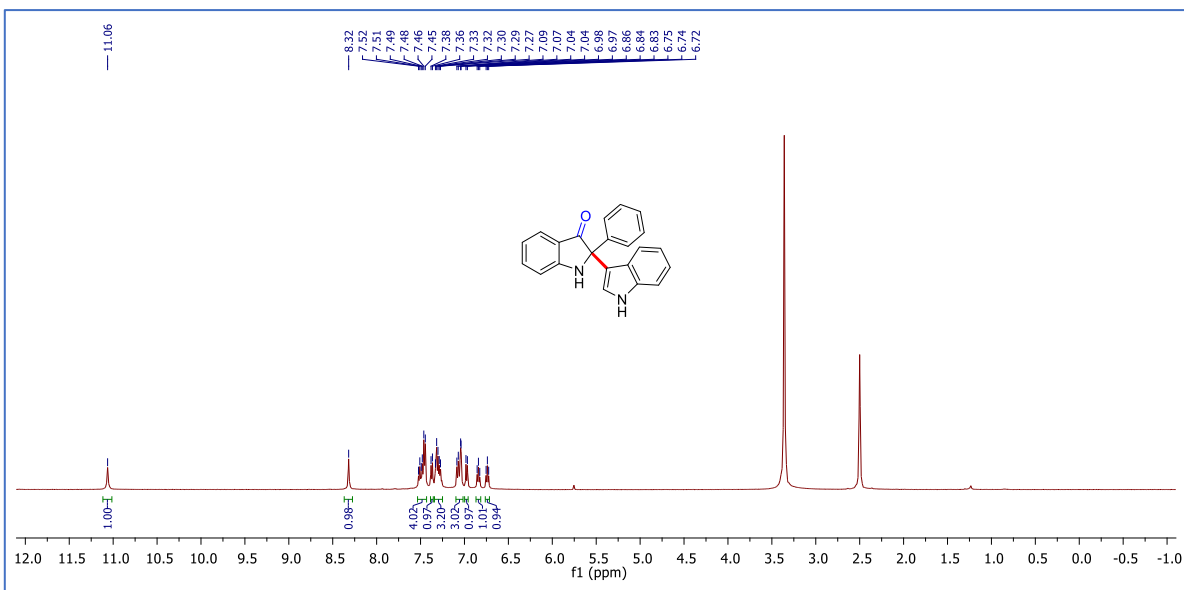
¹³C NMR (126 MHz, DMSO-*d*₆) of compound **4k**



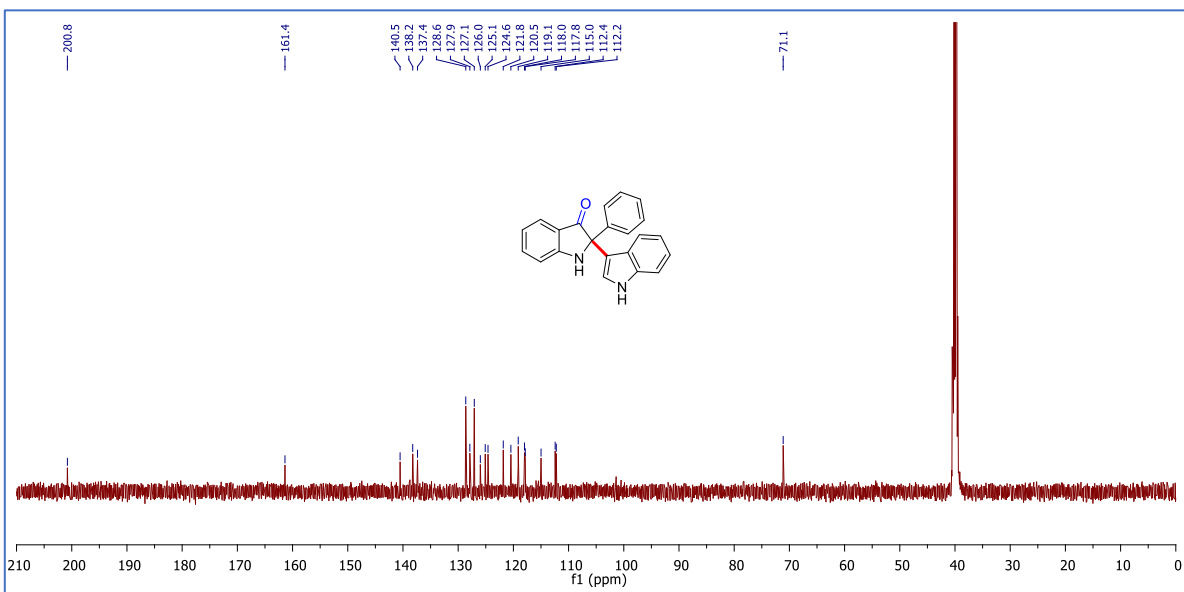
¹H NMR (500 MHz, DMSO-*d*₆) of compound **41**



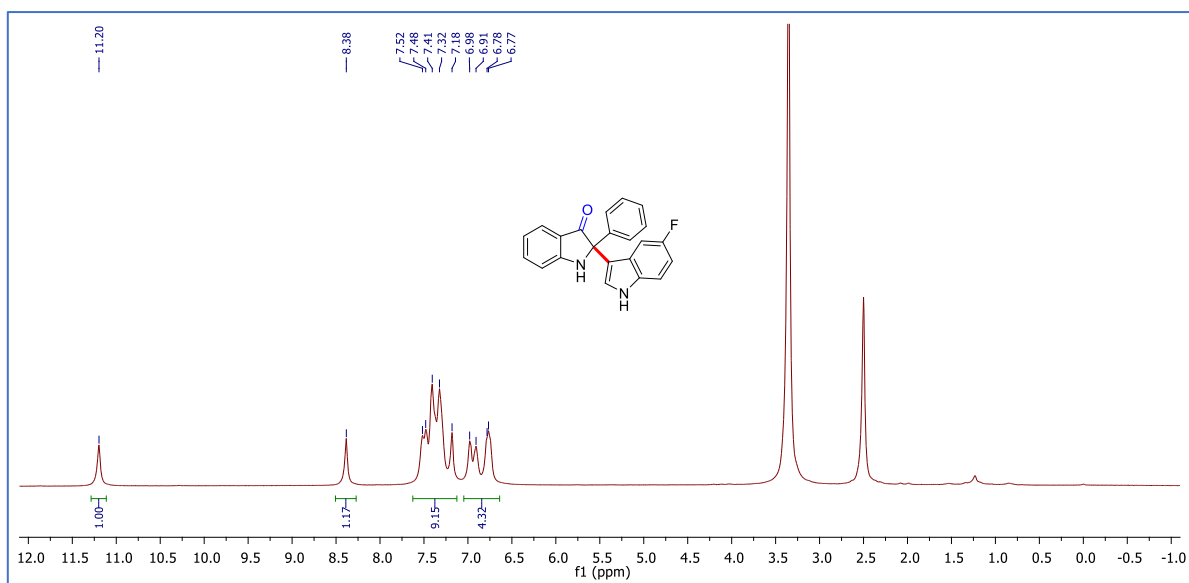
¹³C NMR (126 MHz, DMSO-*d*₆) of compound **41**



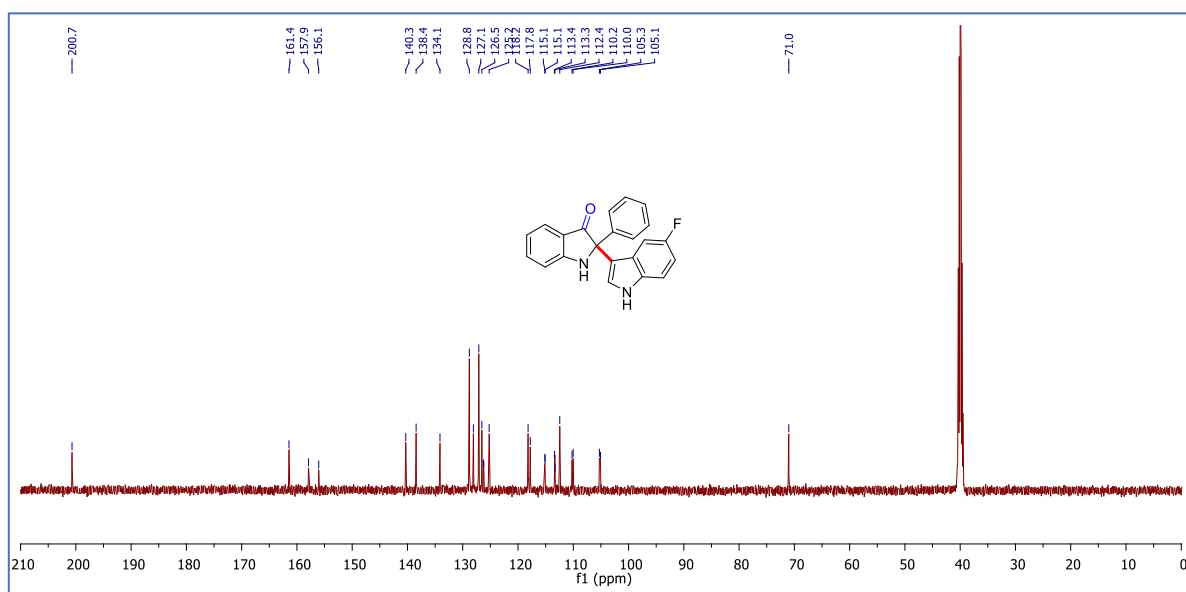
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of compound **4m**



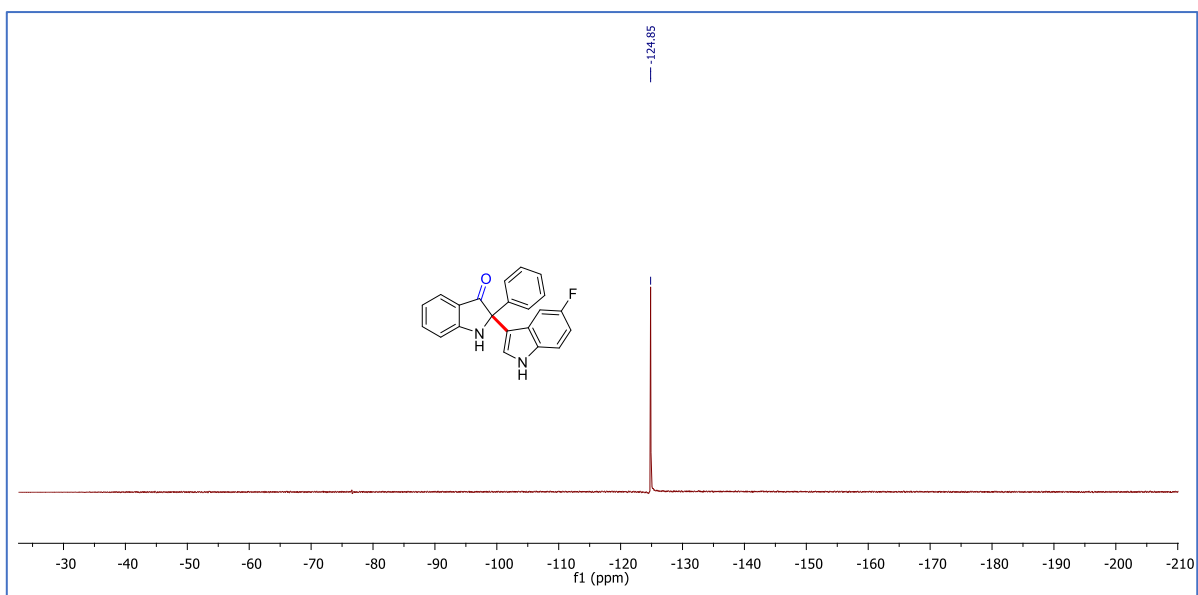
^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) of compound **4m**



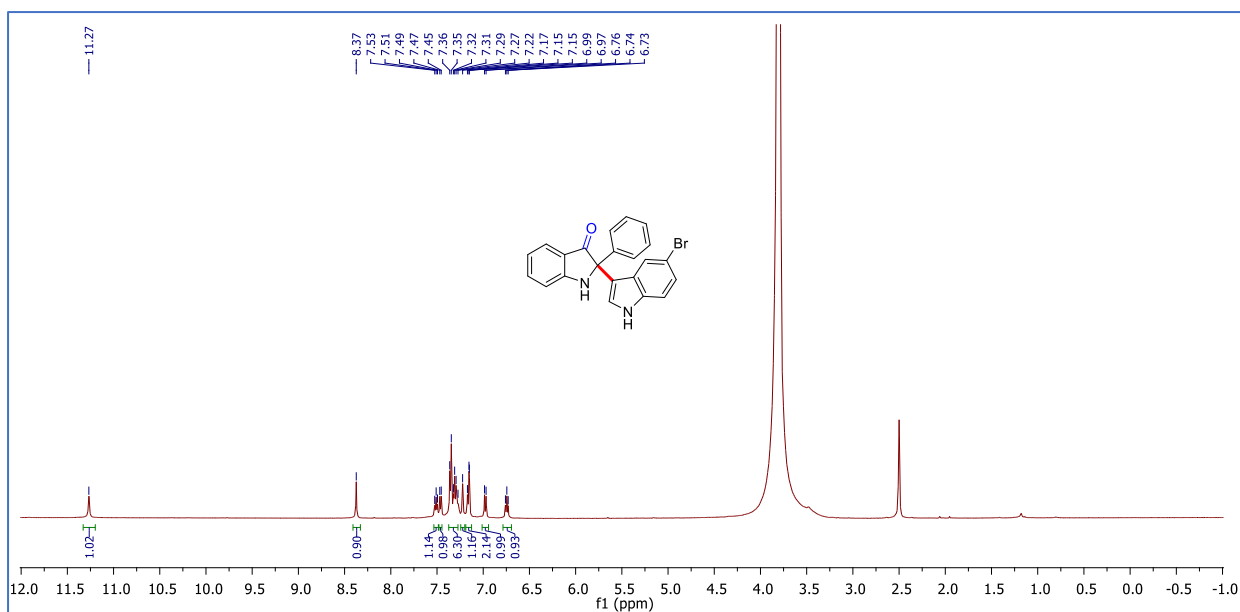
$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) of compound **4n**



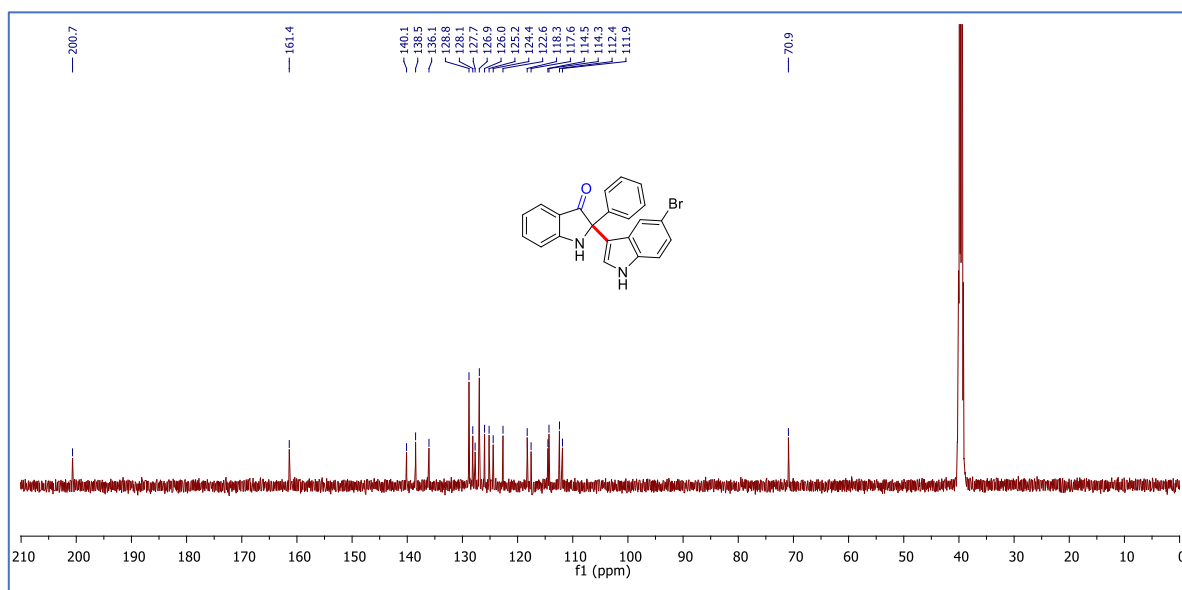
$^{13}\text{C NMR}$ (126 MHz, $\text{DMSO-}d_6$) of compound **4n**



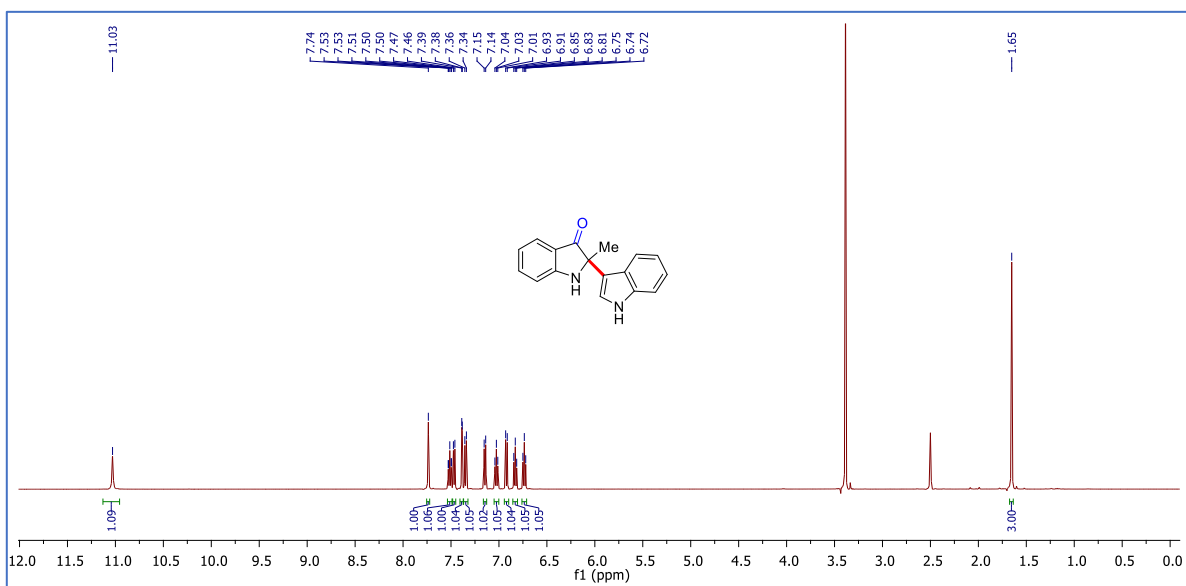
^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) of compound **4n**



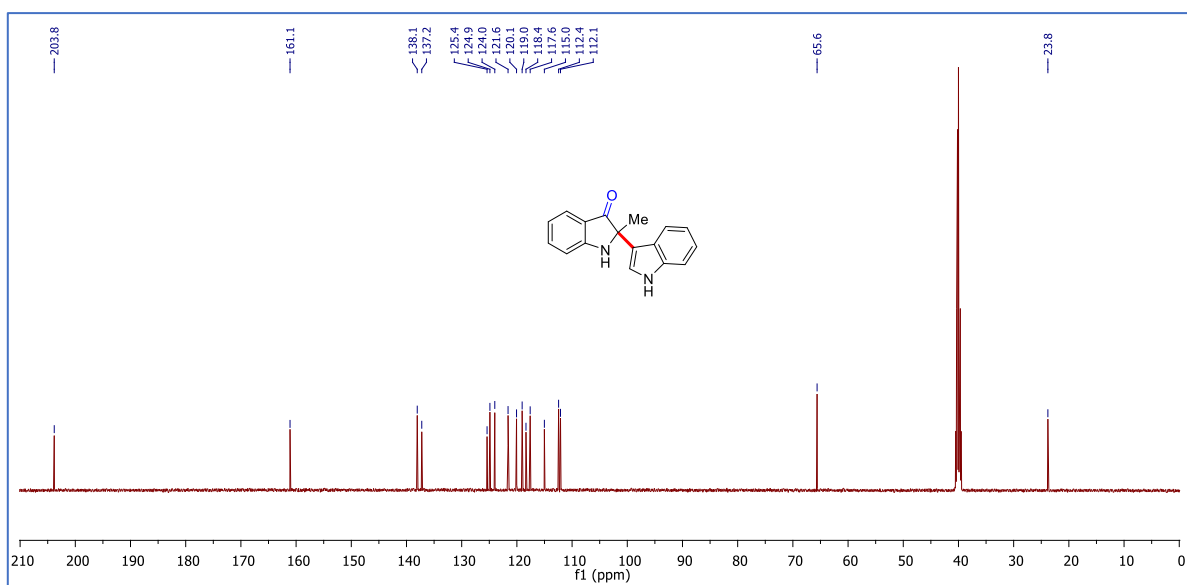
^1H NMR (500 MHz, $\text{DMSO-}d_6$) of compound **4o**



^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) of compound **4o**



^1H NMR (500 MHz, $\text{DMSO-}d_6$) of compound **6**



^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) of compound **6**