An Easy and Practical Approach to Access Multifunctional Cylcopentadiene- and Cyclopentene-Spirooxindoles via [3+2] Annulation

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General Experimental Section

Unless otherwise stated, all the reagents were purchased from commercial suppliers (Aldrich, TCI, Alfa Aesar, and Spectrochem) and used without purification. All the reactions were carried out in oven dried glassware. Thin-layer chromatography (TLC) was performed using silica gel 60 GF_{254} pre-coated aluminum backed plates (2.5 mm). Visualization was accomplished by irradiation with UV light at 254 nm and the solution of Phosphomolybdic Acid (PMA), $KMnO_4$ was used to stain products. The column chromatography was performed using silica gel (100-200 mesh) eluting with petroleum ether and ethyl acetate. The NMR spectra were recorded using tetramethylsilane as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz, and ^{13}C NMR spectra were recorded at 100 MHz (Bruker and Jeol). Chemical shifts (δ) are reported in ppm downfield from $CDCl_3$ (δ = 7.26 ppm) for ^{1}H NMR and relative to the central $CDCl_3$ resonance (δ = 77.16 ppm) for ^{13}C NMR spectroscopy. For ^{1}H NMR, data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = double doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (*J*) are given in Hz and integration. All the samples were analyzed by high resolution mass spectrometer (HRMS) using ESI TOF. Melting points were measured using BÜCHI M-560 melting point apparatus. All melting points were measured in open glass capillary and values are uncorrected. Morita-Baylis-Hillman carbonates **1a-1j** were prepared according to the literature procedure.[1] Substituted aurones **2a-2t** were synthesized according to the literature procedure.[2] Thioaurones **2aa-2ha** were synthesized according to the literature procedure.[3]

References

1. X. Fan, H. Yang and M. Shi. *Adv. Synth. Catal*. 2017, **359**, 49−57.

2. Z. P. Wang, S. Xiang, P. L. Shao and Y. J. He, *Org. Chem*. 2018, **83**, 10995−11007.

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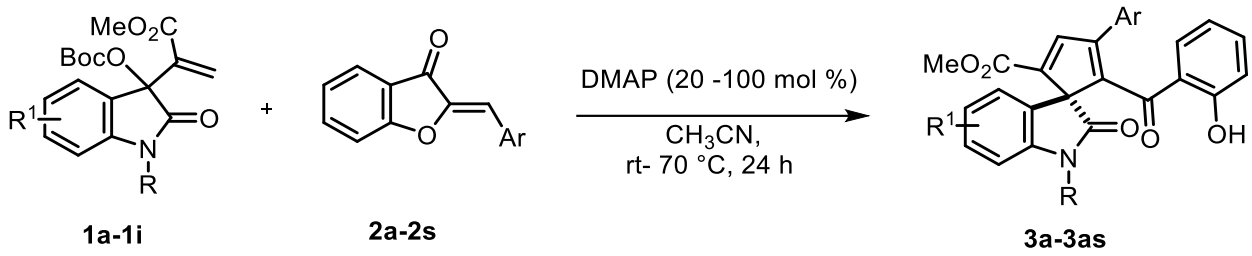
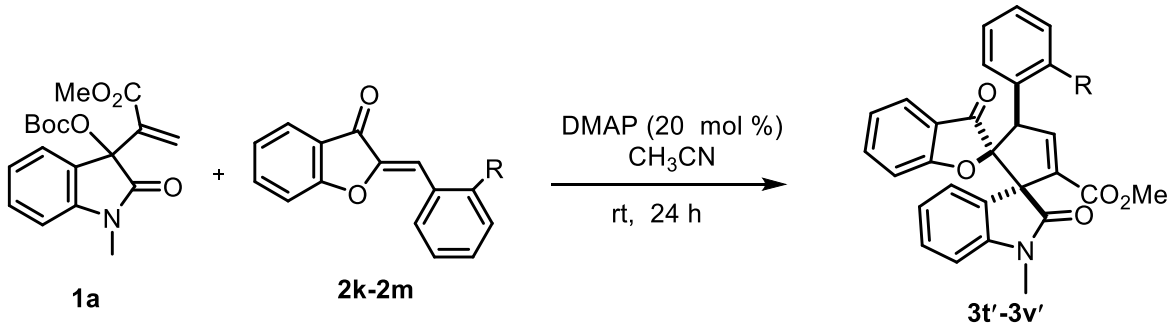
General procedure for the synthesis of spirooxindole cyclopentadiene – GP-1



To the stirred solution of Morita-Baylis-Hillman carbonate of isatin **1a** (0.115 mmol, 1.0 equiv.), aurone **2a** (0.138 mmol, 1.2 equiv.) in 2 mL of acetonitrile, DMAP (0.023 mmol, 0.2 equiv.)* was added at room temperature. Then the resulting reaction mixture was stirred for 24 h at room temperature* or as indicated in manuscript (see Manuscript, Scheme 2, Reaction conditions). After completion of the reaction (monitored by TLC), solvent was evaporated under reduced pressure and the residue was purified on silica gel (100-200 mesh) column chromatography (petroleum ether/ethyl acetate).

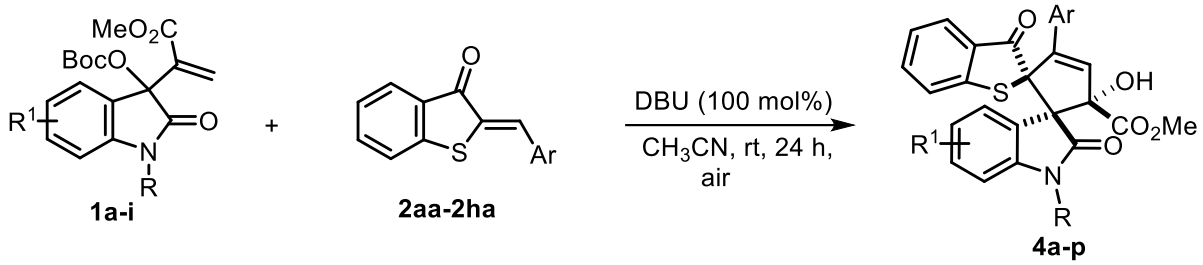
*Synthesis of *ortho* derivatves: **3t** required 20 mol% DMAP at 50 °C or 100 mol% DMAP; **3u** required 100 mol% DMAP at 70 °C and **3v** required 50 mol% DMAP at 70 °C

General procedure for the synthesis of Bis-spirocyclic oxindole – GP-2



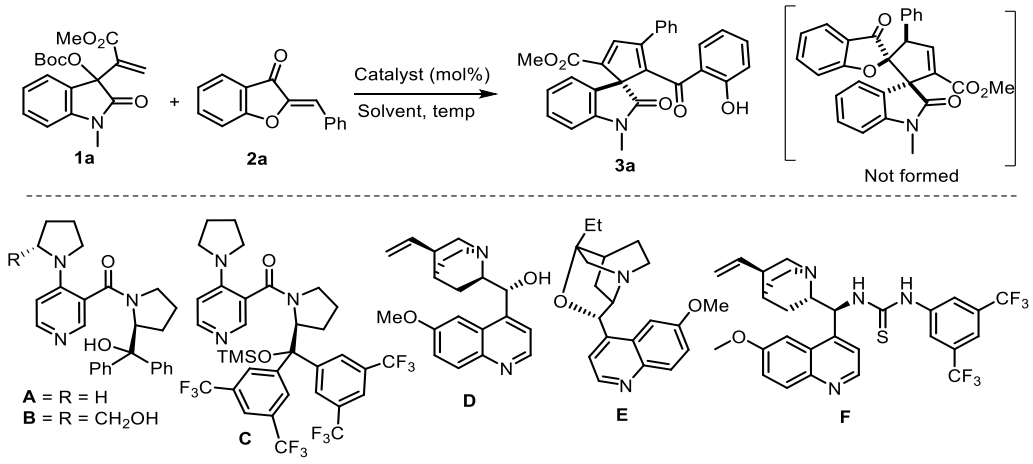
To the stirred solution of Morita-Baylis-Hillman carbonate of isatin **1a** (0.115 mmol, 1.0 equiv.), substituted aurones (**2k** or **2l** or **2m**) (0.138 mmol, 1.2 equiv.) in 2 mL of acetonitrile, DMAP (0.023 mmol, 0.2 equiv.) was added at room temperature. Then the resulting mixture was stirred for 24 h at room temperature. After completion of the reaction (monitored by TLC), solvent was evaporated under reduced pressure and the residue was purified on silica gel (100-200 mesh) column chromatography (petroleum ether/ethyl acetate).

General procedure for the synthesis of dispiro[benzo[*b*]thiophene – GP-3



To the stirred solution of Morita-Baylis-Hillman carbonate of isatin **1a** (0.115 mmol, 1.0 equiv.), thioaurone **2aa** (0.138 mmol, 1.2 equiv.) in 2 mL of acetonitrile, DBU (0.115 mmol, 1.0 equiv.) was added at room temperature. Then the resulting mixture was stirred for 24 h at room temperature. After completion of the reaction (monitored by TLC), solvent was evaporated under reduced pressure and the residue was purified on silica gel (100-200 mesh) column chromatography (petroleum ether/ethyl acetate).

Appendix I: Screening of chiral catalysts and solvents

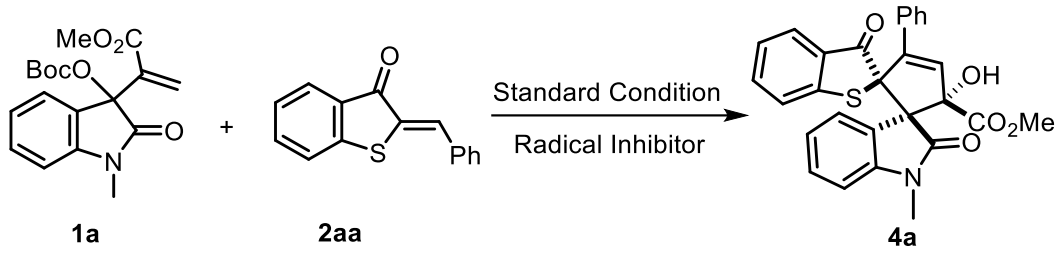


Entry	Catalysts	Solvent	Temp (°C)	Time (h)	Yield (%)
1	A	CH_2Cl_2	rt	36	N.R
2	B	CH_2Cl_2	rt	48	N.R
3	C	CH_2Cl_2	rt	72	N.R
4	A	Toluene	0	24	N.R
5	A	Toluene	-20	24	N.R
6	A	Toluene	60	24	N.R
7	D	CH_2Cl_2	rt	48	N.R
8	E	CH_2Cl_2	rt	48	N.R
9	E	$CHCl_3$	0	36	N.R
10	E	CH_3CN	-20	36	N.R
11	E	CH_3CN	-40	24	N.R
12	E	$CHCl_3$	60	24	N.R
13	F	CH_2Cl_2	rt	36	N.R
14	A+E	CH_2Cl_2	rt	36	N.R

Reaction conditions: [a]The reactions were carried out with **1a** (0.115 mmol, 40 mg), **2a** (0.138 mmol, 26 mg), Cat. (20 mol %) in 2.0 mL of solvent at specified temperature for the specified time. N.R = No reaction

Mechanistic Studies:

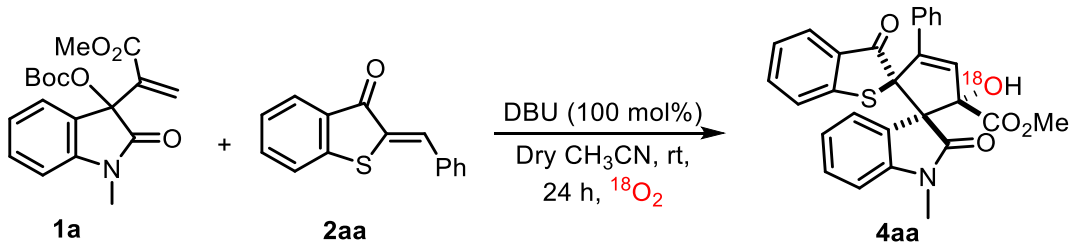
A. Control Experiments



Sr. No.	Radical inhibitor	Yield of **4a** (%)
1	None	56
2	TEMPO	52
3	BHT	50

Reaction conditions- MBH carbonate of isatin **1a** (40 mg, 0.115 mmol), thioaurone **2aa** (33 mg, 0.138 mmol), DBU (17 mg, 0.115 mmol), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 2 equiv.) **or** Butylated hydroxyl toluene (BHT, 2 equiv.), acetonitrile (2.0 mL) were added in a 10 mL round bottom flask and the reaction mixture was stirred under air at room temperature for 24 h. These control experiments afforded compound **4a** in 50-52% yields respectively after purification by column chromatography (See Table above).

B. Procedure for ^{18}O labelling experiment:



In an oven dried 20 mL crimp cap vial Morita-Baylis-Hillman carbonate of isatin **1a** (0.115 mmol, 1.0 equiv.), thioaurone **2aa** (0.138 mmol, 1.2 eqiuv.) were added at room temperature

under argon atmosphere. The vial was purged with argon and sealed with aluminium crimp cap using a crimper. Then 2 mL of dry acetonitrile was added under argon. To this solution DBU (0.115 mmol, 1.0 equiv.) was added under argon and immediately the reaction vial was filled and purged with $^{18}O_2$ gas (98% isotopic purity) and kept it for stirring for 24 h. The percentage of ^{18}O enrichment product **4aa** was examined by HRMS (ESI TOF, +ve ion mode) as shown Figure 1. The calculated data showed 52% of ^{18}O enrichment in **4aa**. **HRMS (**ESI TOF) *m/z* calcd. For $C_{28}H_{21}NO_4$ ^{18}OS $[M+H]^+$ 486.1261, found 486.1260

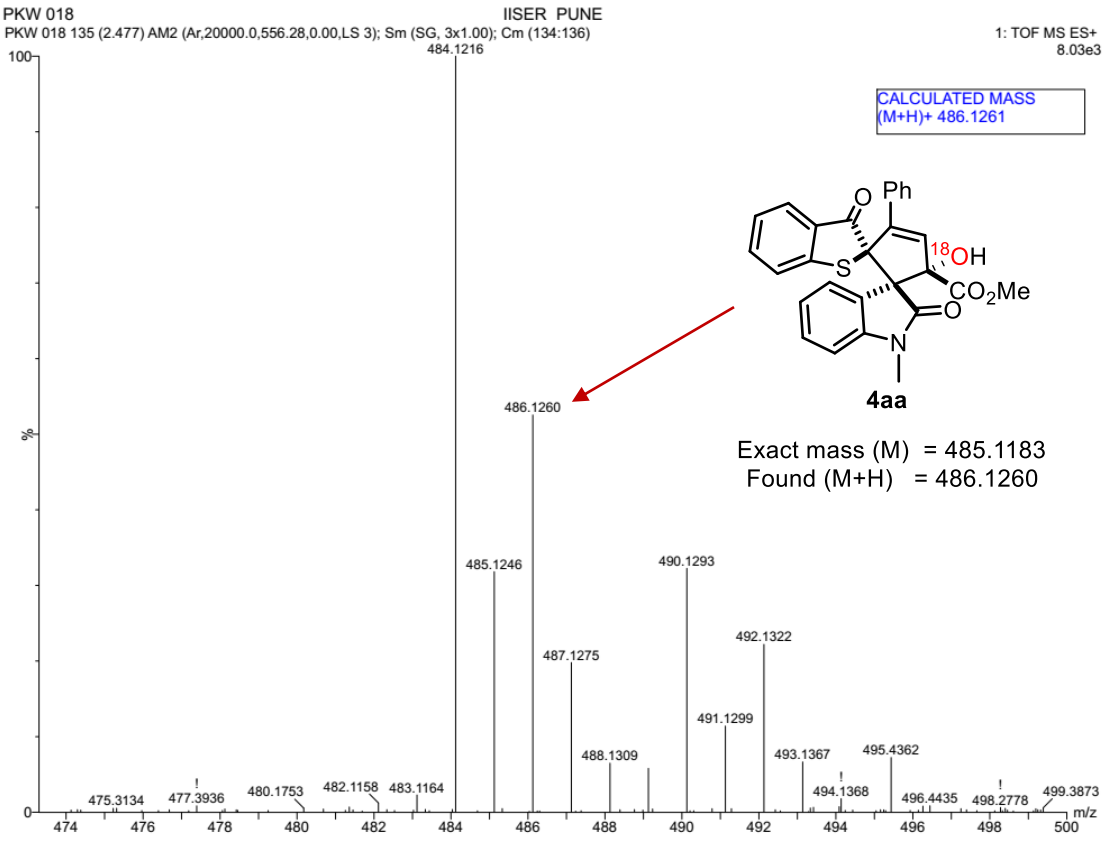


Figure 1. HRMS spectrum of **4aa**- ^{18}O enriched product

C. Detection of intermediate

In an oven dried 20 mL crimp cap vial, Morita-Baylis-Hillman carbonate of isatin **1a** (0.115 mmol, 1.0 equiv.), thioaurone **2aa** (0.138 mmol, 1.2 equiv.) were added at room temperature under argon atmosphere. The vial was purged with argon and sealed with aluminium crimp cap using a crimper. Then 2 mL of dry acetonitrile was added under argon. To this solution DBU (0.115 mmol, 1.0 equiv.) was added under argon (to maintain dry and inert atmosphere). After the compete addition of reagents the reaction vial was filled and purged with argon and kept it for stirring for 24 h. After which, the reaction sample was analysed for HRMS.

The ESI-MS of crude reaction mixture shown Figure 2. Intermediate E was detected based on HRMS. **HRMS (**ESI TOF) *m/z* calcd. For $C_{28}H_{21}NO_4S$ $[M+H]^+$ 468.1269, found 468.1262

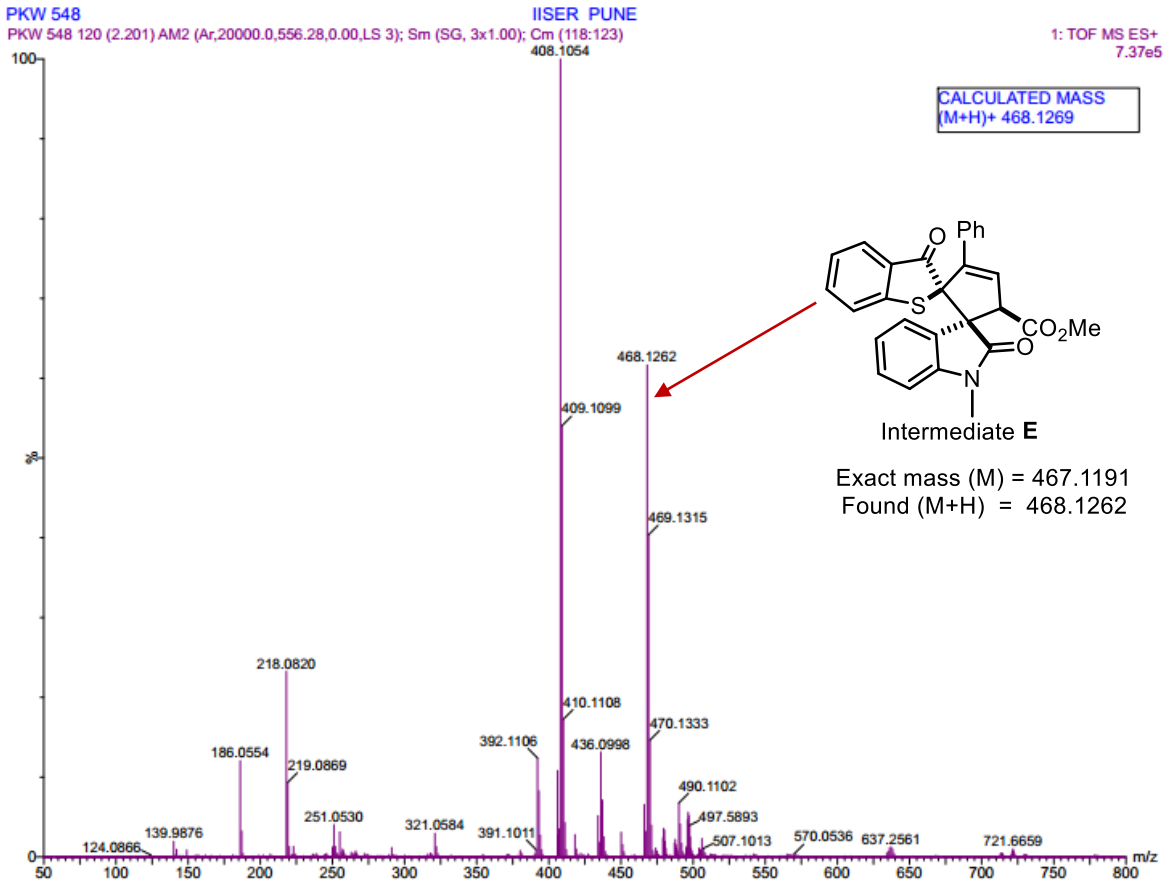


Figure 2. HRMS spectrum of intermediate **E**

D. Computational Details:

All the calculations in this study have been performed with density functional theory (DFT), using Turbomole 7.1 suite of programs,[1] using the PBE functional[2]. The TZVP[3] basis set has been employed. The resolution of identity (RI),[4] along with the multipole accelerated resolution of identity (marij)[5] approximations have been employed for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent corrections were incorporated with optimization calculations using the COSMO model[6] with acetonitrile ($\varepsilon = 37.5$) as the solvent. Also, intrinsic reaction coordinate (IRC)[7] calculations were done with all the transition states to further confirm that they were the correct transition state, yielding the correct reactant and product structures. The values reported are ΔG values, with zero-point energy corrections, internal energy and entropic contributions were included through frequency calculations on the optimized minima, with the temperature taken to be 298.15 K. Harmonic frequency calculations were performed for all stationary points to confirm them as local minima or transition state structures. Then, to find the efficiency of the catalytic cycle in our mechanism, we have calculated the relative efficiency with the AUTOF[8,9] program by employing the "Energetic Span Model" (ESM), developed by Shaik and co-workers[10-12] on all the free energy profiles discussed in the manuscript. The turnover frequency (TOF) calculations take into account the principal rate-determining transition state, potentially rate-influencing transition states and intermediates during the catalysis process. TOF is calculated by the following equation:

$$TOF = \frac{KBT}{h} e^{-\delta E/RT}$$

$\delta E = T_{TDTS} - I_{TDI}$ If TDTS appears after TDI

$\delta E = T_{TDTS} - I_{TDI} - \Delta G_r$ If TDTS appears before TDI

This model has been employed to calculate the TOFs for the free energy profiles obtained for the mechanisms in the solvent phase discussed in the manuscript. This model can also be employed for stoichiometric reactions, where the TOF would correspond to the efficiency of the reaction.

Results and Discussion:

In order to understand the mechanism of the [3+2] annulation of the Morita-Baylis-Hillman (MBH) carbonates of isatin with aurone/thioaurone in the presence of a Lewis base, we have done full quantum chemical calculations using density functional theory (DFT). We have chosen DMAP and DBU for the calculations, because the obtained product yield was the highest for these Lewis bases.

For the case of aurones as shown in Scheme **2**, DMAP has been taken as the Lewis base and *ortho*-substituted (**2k**) as well as *para*-substituted aurone (**2c)** are being considered in the study.

For the *ortho* case, in the first step, DMAP can react with **1a** to give **Int_1**. The nucleophilic DMAP attacks on the MBH carbonate **1a** to form the quaternary ammonium salt **I**, which is a thermodynamically unstable (ΔG = 12.7 kcal/mol) process, (see **Figure 3** below) formed along with the evolution of carbon dioxide and *tert*-butoxide. The *in situ* generated *tert*-butoxide, in turn, reacts with the quaternary ammonium salt **I** to give an allylic nitrogen ylide **I'**. Subsequently, in the second step, **I'** reacts with the aurone **2k** to generate an intermediate **II** with the reaction free energy (ΔG) being -21.5 kcal/mol. This is followed by an intramolecular Michael addition in the third step, leading to the intermediate **III** by eliminating DMAP, with the reaction free energy (ΔG) being -29.5 kcal/mol. Subsequently, in the fourth step, DMAP abstracts the proton from intermediate **III**, leading to the formation of the phenoxide intermediate **IV** *via* ring-opening, with the reaction free energy (ΔG) being unstable by 1.5 kcal/mol. Finally, in the last step, intermediate **IV** leads to the desired compound **3t'**, with reaction free energy (ΔG) being -6.5 kcal/mol *via* protonation and regeneration of DMAP, to complete the catalytic cycle.

A similar mechanism pathway is seen to be followed for the case of the *para*-substituted aurone **2c** (see the Manuscript).

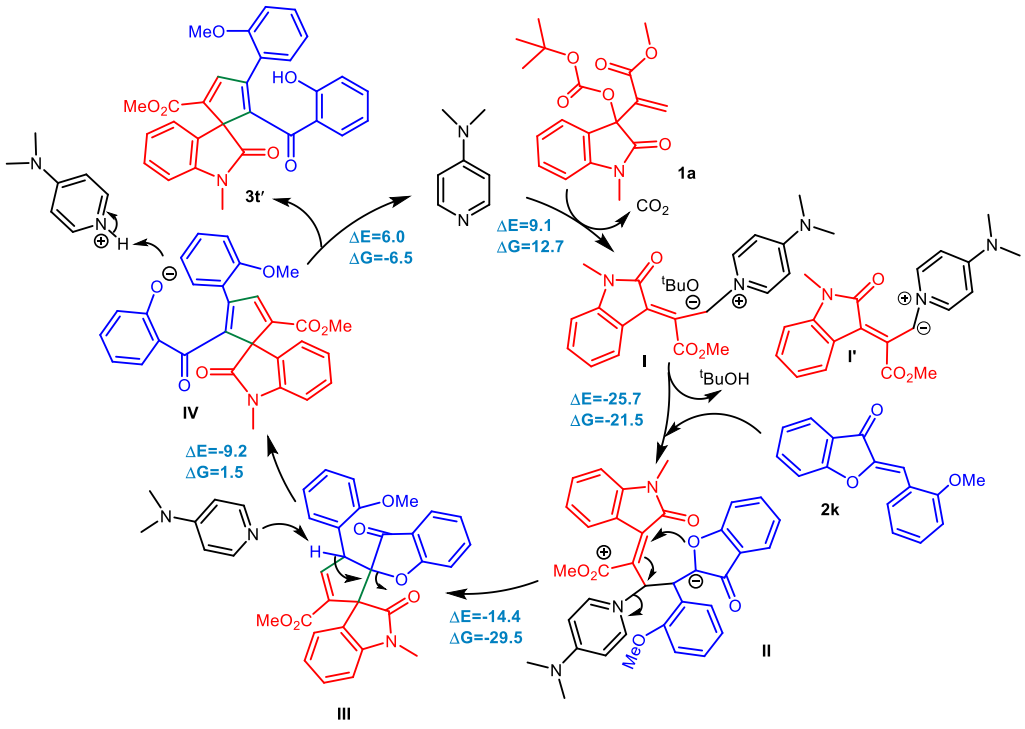


Figure 3. The reaction mechanism for the annulation with the *ortho*-substituted aurone, calculated at the PBE/TZVP level of theory. ΔG (in kcal/mol) represents the Gibbs free energy of the reaction. The thermodynamics for the cycle is shown in this scheme.

Experimentally, it was found that to achieve product (**3t'**) in the *ortho*-substituted aurone **2k** case, a higher concentration of Lewis base, or a higher temperature was required, whereas, for the case of *para*-substituted aurone **2c**, product (**3l**) was achieved at room temperature. It can be seen from the calculations that the formation of intermediate **IV** from intermediate **III** in the case *ortho*-substituted **2k** is unstable by 1.5 kcal/mol whereas, for the *para*-substituted case, it is favorable by 2.0 kcal/mol. To do a detailed study, we have also calculated the transition states, and thus the barriers, for both the cases from intermediate **III** to intermediate **IV**, as shown in Figure **4a** and Figure **4b** below. If we compare both mechanisms, the barrier for **TS_1** with respect to intermediate **III** is 15.7 kcal/mol for the *para* case, whereas for the *ortho*-substituted case, it is 16.9 kcal/mol, which is approximately 1.2 kcal/mol higher than the *para*-substituted mechanism. Furthermore, in order to check the efficiency of the catalytic cycle, we have also calculated the turnover frequency (TOF) for both the processes. It is to be noted that in the current case, the TOF has been calculated with an assumption: that the barriers for all the steps for the two cases studied: *ortho*-substituted as well as *para*-substituted aurone **2**, are similar. This assumption is based on calculations of the relative

barriers for the transformation from **III** to **IV** for both the cases, which were seen to be almost the same. Since this is the critical step in this process (occurs for the *para*-substituted aurone, but not for the *ortho*-substituted case), the similarity in the barriers suggests that considering the rest of the barriers in the two cycles to be similar is a reasonable assumption.

The TOF values (**Appendix II**) indicate that the mechanism with the *para*-substituted aurone is approximately 6.4 times more efficient than for the *ortho*-substituted aurone.

Appendix II. The values for the turnover frequencies (TOFs) obtained for both *ortho* and *para*-substituted aurones **2**.

Mechanism	Turnover Frequency (TOF)
ortho substituted aurone **2k**	3.01 s^{-1}
para substituted aurone **2c**	1.93* 10^{1} s^{-1}

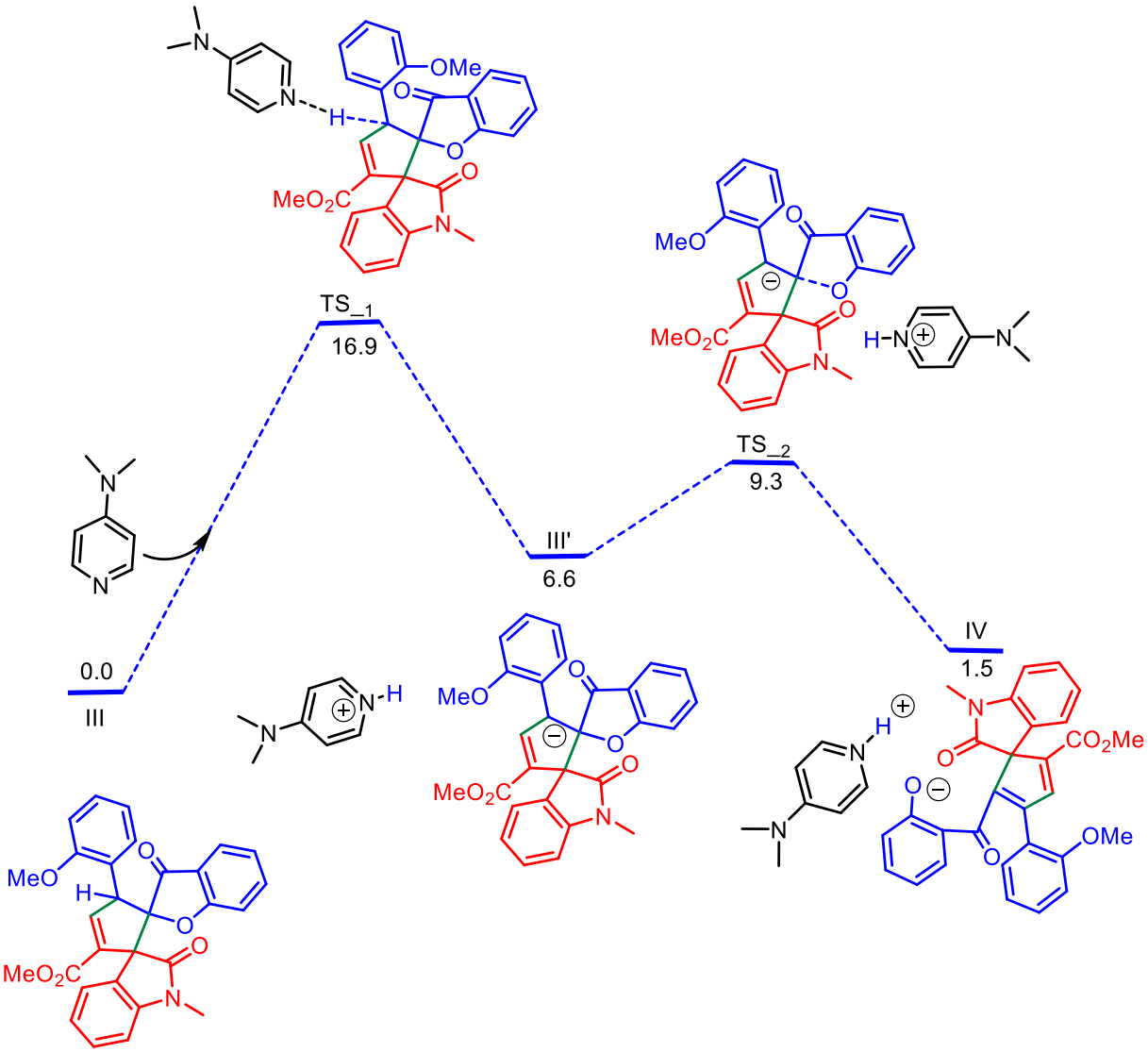


Figure 4a. The reaction mechanism for the annulation with the *ortho*-substituted aurone, calculated at the PBE/TZVP level of theory and ΔG (in kcal/mol) represents Gibbs free energy of the reaction. The kinetics for the cycle is shown in this scheme.

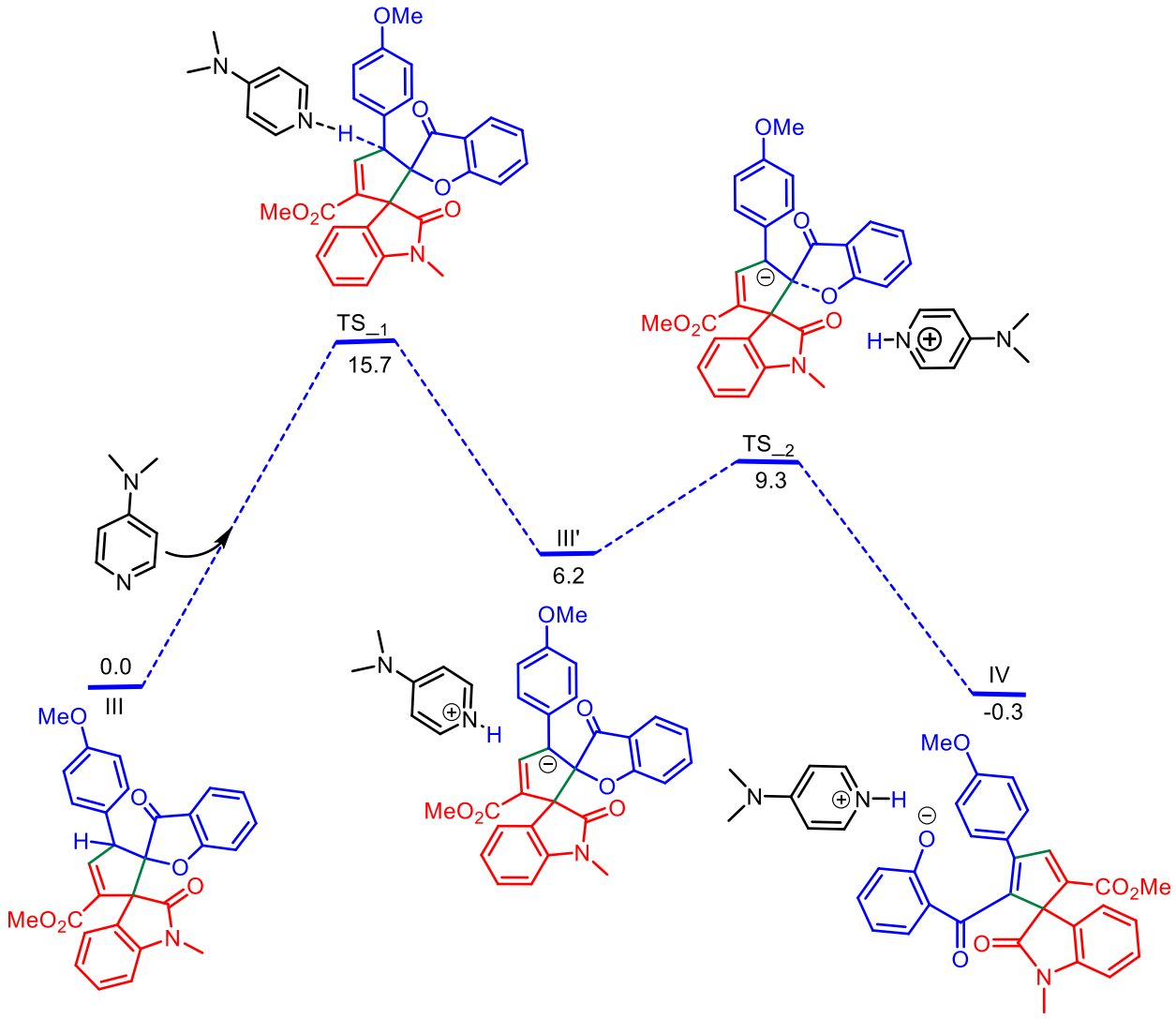


Figure 4b. The reaction mechanism for the annulation with the *ortho*-substituted aurone, calculated at the PBE/TZVP level of theory. ΔG (in kcal/mol) represents the Gibbs free energy of the reaction. The kinetics for the cycle is shown in this scheme.

References:

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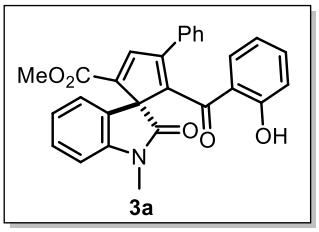
12. S. Kozuch, S. Shaik, *Acc. Chem. Res*. **2010**, *44*, 101.

Experimental Data:

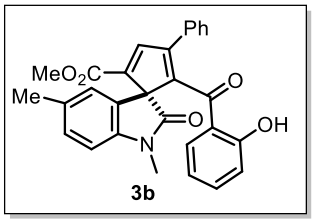
Methyl -2-(2-hydroxybenzoyl)-1'-methyl-2'-oxo-3-phenyl spiro[cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3a)



The compound **3a** was prepared following the general procedure **GP-1**

Yellow solid (40 mg, 76%), R_f = 0.15 (petroleum ether/EtOAc 70:30), MP: 171-173 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (s, 1H), 7.84 (s, 1H), 7.36 – 7.26 (m, 3H), 7.24 – 7.14 (m, 5H), 6.98 – 6.85 (m, 3H), 6.76 (d, *J* = 8.6 Hz, 1H), 6.42 – 6.35 (m, 1H), 3.65 (s, 3H), 3.39 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 196.6, 170.9, 162.4, 161.8, 150.9, 146.2, 145.5, 142.5, 141.8, 136.3, 132.7, 132.3, 129.6, 129.4, 128.6, 128.6, 123.3, 122.5, 122.5, 118.7, 118.6, 117.7, 109.0, 70.3, 52.0, 27.4. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{22}NO_5$ $[M+H]^+$ 452.1498, found 452.1501

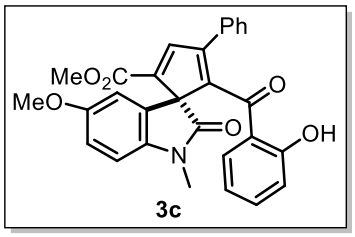
Methyl -2-(2-hydroxybenzoyl)-1', 5'-dimethyl-2'-oxo-3-phenylspiro[cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3b)



The compound **3b** was prepared following the general procedure **GP-1**

Yellow solid (39 mg, 72%), R_f = 0.24 (petroleum ether/EtOAc 70:30), MP: 167-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (s, 1H), 7.83 (s, 1H), 7.34 – 7.29 (m, 2H), 7.24 – 7.14 (m, 5H), 7.07 (d, *J* = 7.9 Hz, 1H), 6.83 – 6.71 (m, 3H), 6.39 (t, *J* = 7.6 Hz, 1H), 3.66 (s, 3H), 3.36 (s, 3H), 2.18 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 196.8, 170.9, 162.5, 162.0, 150.9, 146.2, 143.3, 142.7, 142.1, 136.4, 132.9, 132.5, 132.1, 129.9, 129.7, 128.7, 123.5, 123.4, 118.9, 118.7, 117.8, 108.8, 70.6, 52.1, 27.6, 21.2. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{24}NO_5$ $[M+H]^+$ 466.1654, found 466.1656

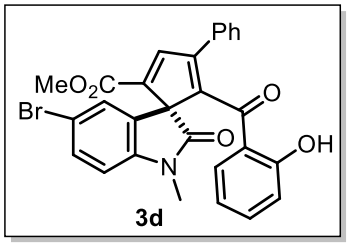
Methyl-2-(2-hydroxybenzoyl)-5'-methoxy-1'-methyl-2'-oxo-3-phenylspiro[cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3c)



The compound **3c** was prepared following the general procedure **GP-1**.

Yellow solid (38 mg, 69%), R_f = 0.15 (petroleum ether/EtOAc 70:30), MP: 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.46 (s, 1H), 7.83 (s, 1H), 7.34 – 7.29 (m, 2H), 7.23 – 7.15 (m, 5H), 6.85 – 6.74 (m, 3H), 6.52 (d, *J* = 2.3 Hz, 1H), 6.42 – 6.35 (m, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 3.36 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 196.7, 170.6, 162.5, 162.0, 155.8, 151.0, 146.3, 142.6, 142.0, 139.2, 136.5, 132.8, 132.5, 129.7, 128.8, 124.8, 118.9, 118.7, 117.9, 113.5, 110.3, 109.3, 70.7, 55.7, 52.1, 27.7. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{24}NO_6$ $[M+H]^+$ 482.16.4, found 482.1604

Methyl -5'-bromo-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxo-3-phenylspiro[cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3d)

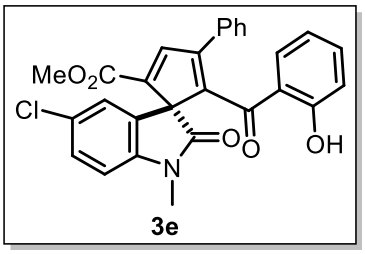


The compound **3d** was prepared following the general procedure **GP-1**.

Yellow solid (43 mg, 70%), R_f = 0.30 (petroleum ether/EtOAc 70:30), MP: 162-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 7.83 (s, 1H), 7.40 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.31 (dd, *J* = 7.5, 2.0 Hz, 2H), 7.27 – 7.12 (m, 5H), 7.03 (d, *J* = 1.9 Hz, 1H), 6.85 – 6.75 (m, 2H), 6.40 (s, 1H), 3.68 (s, 3H), 3.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 196.3, 170.6, 162.5, 161.8, 151.6, 146.6, 144.8, 142.1, 141.6, 136.6, 132.7, 132.4, 132.3, 129.9, 128.8, 128.8, 125.8, 125.8, 118.9, 118.7, 117.9, 115.0, 110.5, 70.0, 52.2, 27.7.HRMS (ESI

TOF) *m/z* calcd. For $C_{28}H_{21}BrNO_5$ $[M+H]^+$ 530.0603 and 532.0583, found 530.0601 and 532.0588

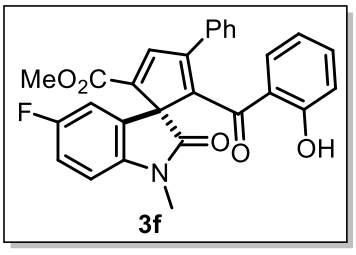
Methyl -5'-chloro-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxo-3-phenylspiro[cyclopentane-1, 3'-indoline]-2,4-diene-5-carboxylate (3e)



The compound **3e** was prepared following the general procedure **GP-1**.

Yellow solid (44 mg, 79%), R_f = 0.18 (petroleum ether/EtOAc 70:30), MP: 163-165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 11.39 (s, 1H), 7.83 (s, 1H), 7.34 – 7.29 (m, 2H), 7.26 – 7.13 (m, 6H), 6.90 (d, *J* = 2.1 Hz, 1H), 6.86 (d, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 8.3 Hz, 1H), 6.43 – 6.36 (m, 1H), 3.68 (s, 3H), 3.37 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 196.2, 170.5, 162.4, 161.7, 151.5, 146.5, 144.2, 141.9, 141.5, 136.5, 132.5, 132.3, 129.8, 129.3, 128.7, 128.7, 127.7, 125.3, 123.0, 118.7, 118.6, 117.8, 109.8, 69.9, 52.1, 27.6. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}ClNO_5$ $[M+H]^+$ 486.1108, found 486.1107

Methyl - 5'-fluoro-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxo-3-phenylspiro[cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3f)

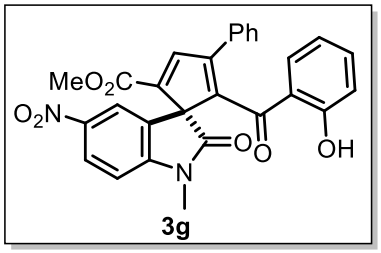


The compound **3f** was prepared following the general procedure **GP-1**.

Yellow solid (44 mg, 82%), R_f = 0.18 (petroleum ether/EtOAc 70:30), MP: 161-163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.42 (s, 1H), 7.84 (s, 1H), 7.34 – 7.29 (m, 2H), 7.25 – 7.13 (m, 5H), 6.99 (td, *J* = 8.9, 2.6 Hz, 1H), 6.86 (dd, *J* = 8.6, 4.1 Hz, 1H), 6.83 – 6.75 (m, 1H), 6.68

(dd, *J* = 7.6, 2.5 Hz, 1H), 6.39 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 3.67 (s, 3H), 3.38 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 196.3, 170.3, 162.4, 161.7, 158.8(d, $J_{(C-F)}$ = 241.1 Hz), 151.3, 146.5, 141.6, 141.6, 141.5, 136.5, 132.5, 132.3, 129.8, 128.7, 128.7, 125.2, 125.1, 118.7, 118.6, 117.8, 115.6(d, $J_{(C-F)}$ = 23.4 Hz), 110.8(d, $J_{(C-F)}$ = 25.2 Hz), 109.4, 109.3, 70.3, 52.1, 27.6. ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -120.4. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}FNO_5$ $[M+H]^+$ 470.1404, found 470.1406.

Methyl-2-(2-hydroxybenzoyl)-1'-methyl-5'-nitro-2'-oxo-3-phenylspiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3g)

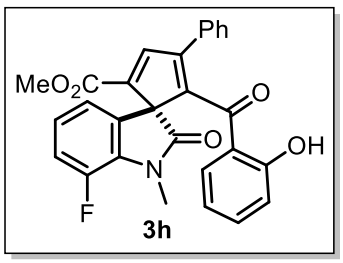


3g

The compound **3g** was prepared following the general procedure **GP-1**

Yellow solid (37 mg, 65%), R_f = 0.17 (petroleum ether/EtOAc 70:30), MP: 218-220 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 1H), 8.28 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.87 (s, 1H), 7.81 (d, *J* = 2.3 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.28 – 7.13 (m, 5H), 7.02 (d, *J* = 8.7 Hz, 1H), 6.80 – 6.77 (m, 1H), 6.38 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 3.69 (d, *J* = 0.6 Hz, 3H), 3.47 (s, 3H). $^{3}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 195.8, 171.1, 162.4, 161.6, 152.4, 151.3, 147.0, 143.2, 141.4, 141.2, 136.8, 132.3, 132.1, 130.1, 128.8, 128.8, 126.7, 124.9, 118.9, 118.4, 118.3, 117.9, 108.4, 69.2, 52.2, 27.9. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}N_2O_7$ $[M+H]^+$ 497.1349, found 497.1350

Methyl -7'-fluoro-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxo-3-phenylspiro[cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3h)

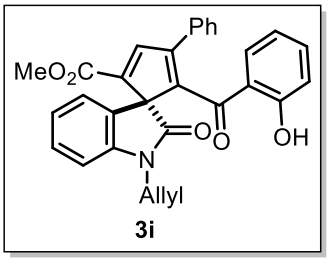


3h

The compound **3h** was prepared following the general procedure **GP-1**.

Yellow solid (42 mg, 78%), R_f = 0.36 (petroleum ether/EtOAc 70:30), MP: 170-171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.44 (s, 1H), 7.83 (s, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.12 (m, 5H), 7.00 (dd, *J* = 11.5, 8.4 Hz, 1H), 6.86 – 6.77 (m, 2H), 6.70 (dd, *J* = 7.4, 1.0 Hz, 1H), 6.37 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 3.68 (s, 3H), 3.60 (d, *J* = 2.6 Hz, 3H). ^{13}C{^{1}H} NMR(100 MHz, $CDCl_3$): δ (ppm) 196.5, 170.6, 162.5, 161.9, 151.3, 148.07 (d, *J* = 244.2 Hz), 146.5, 142.05(d, $J_{(C-F)}$ = 45 Hz), 136.6, 132.7, 132.5, 132.4, 129.9, 128.8, 128.8, 126.3, 126.3, 123.1, 123.1, 118.8, 118.5, 118.5, 117.9, 117.65 (d, $J_{(C-F)}$ = 19.4 Hz), 70.2, 52.2, 30.06 (d, $J_{(C-F)}$ = 5.9 Hz). ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -135.0. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}FNO_5$ $[M+H]^+$ 470.1404, found 470.1406

Methyl -1'-allyl-2-(2-hydroxybenzoyl)-2'-oxo-3-phenylspiro[cyclopentane-1, 3'-indoline]-2,4-diene-5-carboxylate (3i)

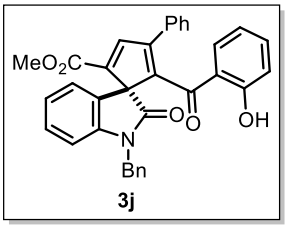


3i

The compound **3i** was prepared following the general procedure **GP-1**

Yellow solid (33 mg, 60%), R_f = 0.33 (petroleum ether/EtOAc 70:30), MP: 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.47 (s, 1H), 7.86 (s, 1H), 7.36 – 7.30 (m, 2H), 7.25 – 7.15 (m, 6H), 6.94 – 6.85 (m, 3H), 6.77 (dd, *J* = 8.8, 1.1 Hz, 1H), 6.39 (ddd, *J* = 8.1, 7.3, 1.1 Hz, 1H), 6.03 – 5.88 (m, 1H), 5.51 – 5.42 (m, 1H), 5.28 (dq, *J* = 10.4, 1.5 Hz, 1H), 4.50 (ddt, *J* = 5.3, 3.6, 1.8 Hz, 2H), 3.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.7, 170.5, 162.4, 161.8, 150.8, 146.3, 144.7, 142.5, 141.9, 136.4, 132.7, 132.4, 131.2, 129.6, 129.2, 128.6, 128.6, 123.3, 122.6, 122.5, 118.7, 118.6, 117.7, 117.7, 110.0, 70.2, 51.9, 43.5. HRMS (ESI TOF) *m/z* calcd. For $C_{30}H_{24}NO_5$ $[M+H]^+$ 478.1654, found 478.1656

Methyl-1'-benzyl-2-(2-hydroxybenzoyl)-2'-oxo-3-phenylspiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3j)

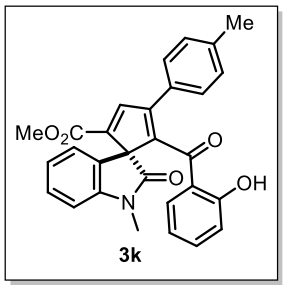


3j

The compound **3j** was prepared following the general procedure **GP-1**

Red solid (24 mg, 40%), R_f = 0.50 (petroleum ether/EtOAc 70:30), MP: 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.53 (s, 1H), 7.90 (s, 1H), 7.45 (d, J = 7.2 Hz, 2H), 7.38 – 7.31 (m, 4H), 7.30 – 7.27 (m, 1H), 7.25 – 7.12 (m, 6H), 6.93 (dd, J = 7.4, 1.0 Hz, 1H), 6.87 (td, J = 7.5, 0.9 Hz, 1H), 6.82 – 6.71 (m, 2H), 6.40 (td, J = 7.7, 1.1 Hz, 1H), 5.11 (d, J = 15.8 Hz, 1H), 5.04 (d, J = 15.8 Hz, 1H), 3.61 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, CDCl3): δ (ppm) 197.0, 171.1, 162.6, 162.0, 150.7, 146.6, 144.8, 142.5, 142.0, 136.6, 135.8, 132.8, 132.6, 129.8, 129.4, 128.8, 128.7, 127.7, 127.6, 123.5, 122.8, 122.7, 118.9, 118.8, 117.9, 110.3, 70.4, 52.1, 45.2. HRMS (ESI TOF) *m/z* calcd. For $C_{34}H_{25}NO_5$ $[M+H]^+$ 528.1811 found 528.1812

Methyl -2-(2-hydroxybenzoyl)-1'-methyl-2'-oxo-3-(p-tolyl)spiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3k)



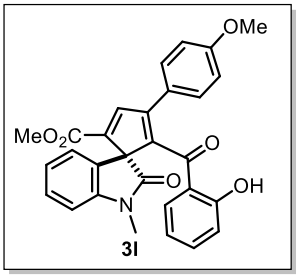
3k

The compound **3k** was prepared following the general procedure **GP-1**

Yellow solid (35 mg, 65%), R_f = 0.21 (petroleum ether/EtOAc 70:30), MP: 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.50 (s, 1H), 7.83 (s, 1H), 7.27 (ddd, *J* = 7.9, 6.4, 2.5 Hz, 1H), 7.24 – 7.12 (m, 4H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.97 – 6.84 (m, 3H), 6.81 – 6.73 (m, 1H), 6.40 (td, *J* = 7.7, 1.1 Hz, 1H), 3.64 (s, 3H), 3.38 (s, 3H), 2.25 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz,

$CDCl_3$): δ (ppm) 197.0, 171.1, 162.5, 162.0, 150.9, 146.5, 145.6, 141.7, 141.7, 140.0, 136.4, 132.5, 129.9, 129.5, 129.4, 128.7, 123.6, 122.7, 122.6, 118.9, 118.8, 117.8, 109.1, 70.4, 52.1, 27.6, 21.4. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{24}NO_5$ $[M+H]^+$ 466.1654, found 466.1654

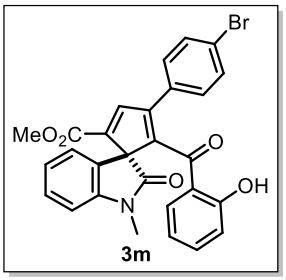
Methyl-2-(2-hydroxybenzoyl)-3-(4-methoxyphenyl)-1'-methyl-2'-oxospiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3l)



The compound **3l** was prepared following the general procedure **GP-1**

Yellow solid (38 mg, 68%), R_f = 0.12 (petroleum ether/EtOAc 70:30), MP: 150-152 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 11.49 (s, 1H), 7.83 (s, 1H), 7.31 – 7.26 (m, 2H), 7.25 – 7.16 (m, 3H), 6.96 – 6.86 (m, 3H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.75 – 6.69 (m, 2H), 6.45 – 6.39 (m, 1H), 3.73 (s, 3H), 3.64 (s, 3H), 3.39 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ (ppm) 196.8, 171.2, 162.3, 161.9, 160.6, 150.5, 146.4, 145.5, 141.6, 140.7, 136.2, 132.4, 130.3, 129.3, 125.2, 123.6, 122.5, 122.5, 118.7, 118.7, 117.7, 114.1, 108.9, 70.2, 55.3, 51.9, 27.4. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{24}NO_6$ $[M+H]^+$ 482.1604, found 482.1601

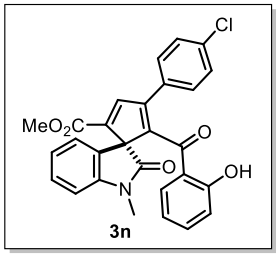
Methyl -3-(4-bromophenyl)-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxospiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3m)



The compound **3m** was prepared following the general procedure **GP-1**

Yellow solid (39 mg, 63%), R_f = 0.21 (petroleum ether/EtOAc 70:30), MP: 176-178 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.40 (s, 1H), 7.78 (s, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.29 (dd, J = 8.0, 4.2 Hz, 1H), 7.25 – 7.14 (m, 4H), 6.95 – 6.88 (m, 3H), 6.79 (d, J = 8.3 Hz, 1H), 6.45 (t, J = 7.6 Hz, 1H), 3.65 (s, 3H), 3.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 196.5, 170.7, 162.6, 161.9, 149.4, 145.6, 145.6, 143.0, 142.2, 136.8, 132.3, 132.0, 131.7, 130.1, 129.6, 124.1, 123.2, 122.7, 122.7, 119.0, 118.7, 118.0, 109.2, 70.6, 52.2, 27.6. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}BrNO_5$ $[M+H]^+$ 530.0603 and 532.0583, found 530.0600 and 532.0587

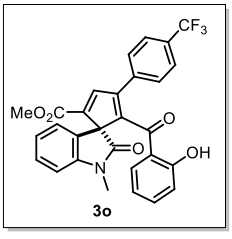
Methyl -3-(4-chlorophenyl)-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxospiro[cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3n)



The compound **3n** was prepared following the general procedure **GP-1**

Yellow solid (39 mg, 70%), R_f = 0.18 (petroleum ether/EtOAc 70:30), MP: 177-179 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.41 (s, 1H), 7.79 (s, 1H), 7.31 – 7.22 (m, 4H), 7.22 – 7.15 (m, 3H), 6.95 – 6.86 (m, 3H), 6.82 – 6.76 (m, 1H), 6.49 – 6.39 (m, 1H), 3.65 (s, 3H), 3.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.5, 170.7, 162.6, 161.9, 149.4, 145.7, 145.6, 143.0, 142.2, 136.8, 135.8, 132.3, 131.3, 129.9, 129.6, 129.1, 123.2, 122.7, 122.7, 118.9, 118.7, 118.0, 109.2, 70.6, 52.1, 27.6. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}ClNO_5$ $[M+H]^+$ 486.1108, found 486.1112

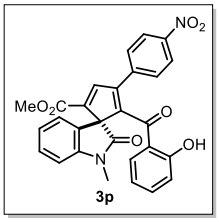
Methyl -2-(2- hydroxybenzoyl) -1' – methyl - 2'-oxo- 3-(4-(trifluoromethyl) phenyl) spiro[cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3o)



The compound **3o** was prepared following the general procedure **GP-1**

Yellow solid (48 mg, 80%), R_f = 0.21 (petroleum ether/EtOAc 70:30), MP: 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.35 (s, 1H), 7.81 (s, 1H), 7.51 – 7.40 (m, 4H), 7.30 (ddd, *J* = 7.9, 5.6, 3.3 Hz, 1H), 7.21 (ddd, *J* = 8.6, 7.3, 1.7 Hz, 1H), 7.13 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.97 – 6.90 (m, 3H), 6.79 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.41 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 3.66 (s, 3H), 3.39 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 196.2, 170.5, 162.5, 161.8, 149.0, 145.6, 145.3, 144.4, 142.4, 136.9, 136.3, 132.2, 131.3 (q, $J_{(C-F)}$ = 33 Hz) , 129.7, 128.9, 125.75 (q, $J_{(C-F)}$ = 3Hz), 123.69 (q, $J_{(C-F)}$ = 271 Hz) 122.9, 122.8, 122.3, 118.9, 118.7, 118.1, 109.3, 70.7, 52.2, 27.6. ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -63.0. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{21}F_3NO_5$ $[M+H]^+$ 520.1372, found 520.1367

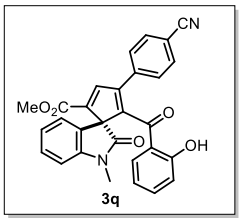
Methyl -2-(2-hydroxybenzoyl)-1'-methyl-3-(4-nitrophenyl)-2'-oxospiro[cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3p)



The compound **3p** was prepared following the general procedure **GP-1**

Yellow solid (37 mg, 65%), R_f = 0.12 (petroleum ether/EtOAc 70:30), MP: 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (s, 1H), 8.15 – 8.04 (m, 2H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.31 (dq, *J* = 8.1, 4.0, 3.5 Hz, 1H), 7.26 – 7.19 (m, 1H), 7.13 (d, *J* = 8.0 Hz, 1H), 7.02 – 6.89 (m, 3H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.48 – 6.38 (m, 1H), 3.67 (s, 3H), 3.39 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 195.8, 170.0, 162.5, 161.5, 147.9, 147.8, 145.4, 145.3, 144.6, 142.5, 138.9, 137.1, 131.8, 129.7, 129.4, 123.9, 122.7, 122.5, 118.9, 118.5, 118.2, 109.3, 70.9, 52.1, 27.6. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}N_2O_7$ $[M+H]^+$ 497.1349, found 497.1355

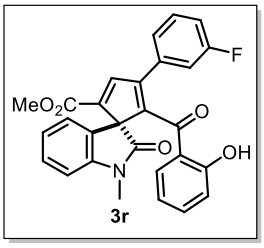
Methyl -3-(4-cyanophenyl)-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxospiro [cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3q)



The compound **3q** was prepared following the general procedure **GP-1**

Yellow solid (41 mg, 74%), R_f = 0.10 (petroleum ether/EtOAc 70:30), MP: 226-228 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.31 (s, 1H), 7.79 (s, 1H), 7.54 – 7.48 (m, 2H), 7.45 – 7.40 (m, 2H), 7.30 (ddd, *J* = 8.0, 5.1, 3.9 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.11 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.96 – 6.90 (m, 3H), 6.83 – 6.78 (m, 1H), 6.46 – 6.39 (m, 1H), 3.66 (s, 3H), 3.38 (s, 3H). ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 195.8, 170.1, 162.5, 161.6, 148.4, 145.4, 144.9, 144.7, 142.5, 137.1, 137.0, 132.4, 131.9, 129.7, 129.0, 122.7, 122.7, 122.6, 118.9, 118.5, 118.1, 118.0, 113.1, 109.2, 70.7, 52.1, 27.5. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{21}N_2O_5$ $[M+H]^+$ 477.1450, found 477.1454

Methyl -3-(3-fluorophenyl)-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxospiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3r)

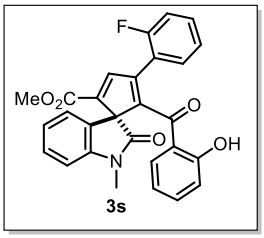


The compound **3r** was prepared following the general procedure **GP-1**

Yellow solid (44 mg, 81%), R_f = 0.21 (petroleum ether/EtOAc 70:30), MP: 222-223 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.40 (s, 1H), 7.79 (s, 1H), 7.32 – 7.27 (m, 1H), 7.26 – 7.12 (m, 3H), 7.10 – 7.02 (m, 2H), 6.97 – 6.89 (m, 4H), 6.81 – 6.76 (m, 1H), 6.44 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 3.65 (s, 3H), 3.38 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 196.3, 170.5, 162.6 (d, $J_{(C-F)}$ = 246 Hz), 162.4, 161.7, 149.2, 149.2, 145.5, 145.5, 143.4, 142.0,

136.6, 134.8, 134.7, 132.1, 130.4, 130.3, 129.5, 124.6, 124.6, 123.0, 122.6, 122.6, 118.7, 118.7, 117.9, 116.54 (d, $J_{(C-F)}$ = 21.1 Hz), 115.19 (d, $J_{(C-F)}$ = 22.6 Hz), 109.1, 70.5, 52.0, 27.5 ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -111.8. HRMS (ESI TOF) *m/z* calcd. $C_{28}H_{21}FNO_5$ $[M+H]^+$ 470.1404, found 470.1407

Methyl -3-(2-fluorophenyl)-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxospiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3s)

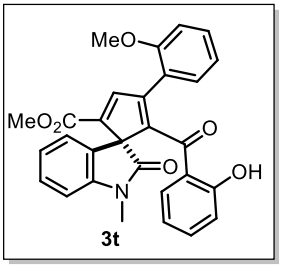


The compound **3s** was prepared following the general procedure **GP-1**

Yellow solid (40 mg, 74%), R_f = 0.21 (petroleum ether/EtOAc 70:30), MP: 166-168 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.27 (s, 1H), 7.79 (d, *J* = 2.4 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.19 (dddd, *J* = 13.8, 8.8, 6.9, 3.5 Hz, 4H), 7.02 – 6.88 (m, 5H), 6.78 – 6.73 (m, 1H), 6.41 (ddd, *J* = 8.3, 7.4, 1.1 Hz, 1H), 3.65 (s, 3H), 3.41 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$):δ (ppm) 195.8, 170.8, 162.2, 161.9, 159.9 (d, $J_{(C-F)}$ = 250.1 Hz), 146.44 (d, $J_{(C-F)}$ = 2.8 Hz), 145.9, 145.7, 145.1, 141.8, 131.9, 131.8, 131.7, 131.0 (d, $J_{(C-F)}$ = 2.8 Hz),, 129.6, 124.5 (d, $J_{(C-F)}$ = 3.6 Hz), 123.3, 122.7 (d, $J_{(C-F)}$ = 5.7 Hz), 121.4, 121.3, 119.0, 118.6, 117.9, 116.1 (d, $J_{(C-F)}$ = 21.6 Hz), 109.2, 69.9, 52.1, 27.6. ^{19}F NMR (377MHz, $CDCl_3$): δ (ppm) -112.0. HRMS (ESI TOF) *m/z* calcd. $C_{28}H_{21}FNO_5$ $[M+H]^+$ 470.1404, found 470.1407

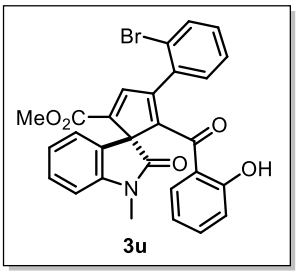
Methyl-2-(2-hydroxybenzoyl)-3-(2-methoxyphenyl)-1'-methyl-2'-oxospiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3t)



The compound **3t** was prepared following the general procedure **GP-1**

Yellow solid (32 mg, 58%), R_f = 0.12 (petroleum ether/EtOAc 70:30), MP: 180-182 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 7.79 (s, 1H), 7.29 – 7.26 (m, 1H), 7.25 (dd, *J* = 3.3, 1.5 Hz, 1H), 7.21 – 7.10 (m, 3H), 6.93 (dd, *J* = 7.6, 1.1 Hz, 2H), 6.89 (td, *J* = 7.3, 1.0 Hz, 1H), 6.82 (td, *J* = 7.5, 1.0 Hz, 1H), 6.73 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.35 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 3.66 (s, 3H), 3.63 (s, 3H), 3.41 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 196.0, 171.5, 162.1, 161.7, 156.6, 148.1, 147.9, 145.7, 143.5, 141.1, 135.8, 131.9, 131.3, 130.3, 129.3, 124.0, 122.6, 122.5, 122.5, 120.8, 119.4, 118.3, 117.4, 110.9, 109.0, 69.6, 55.1, 52.0, 27.6. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{24}NO_6$ $[M+H]^+$ 482.1604 found 482.1604

Methyl -3-(2-bromophenyl)-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxospiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3u)



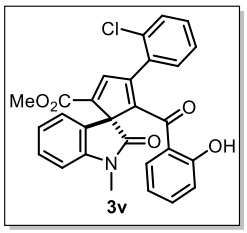
3u

The compound **3u** was prepared following the general procedure **GP-1**

Yellow solid (37 mg, 61%), R_f = 0.26 (petroleum ether/EtOAc 70:30), MP: 181-183 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.14 (s, 1H), 7.79 (s, 1H), 7.56 – 7.52 (m, 1H), 7.34 – 7.26 (m, 2H), 7.17 – 7.03 (m, 4H), 7.01 – 6.88 (m, 3H), 6.70 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.46 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 3.65 (s, 3H), 3.43 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 195.3, 171.0, 162.0, 161.9, 151.7, 147.0, 145.8, 145.7, 140.8, 136.4, 134.6, 133.1, 132.1, 132.0, 130.9, 129.6, 127.8, 123.3, 122.7, 122.6, 122.1, 119.4, 118.5, 117.7, 109.2, 69.3, 52.1, 27.6. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}BrNO_5$ $[M+H]^+$ 530.0603 and 532.0583, found 530.0599 and 532.0583

Methyl -3-(2-chlorophenyl)-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxospiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3v)



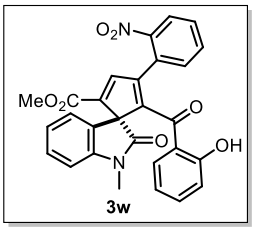
The compound **3v** was prepared following the general procedure **GP-1**

Yellow solid (40 mg, 72%), R_f = 0.26 (petroleum ether/EtOAc 70:30), MP: 183-185 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.17 (s, 1H), 7.78 (s, 1H), 7.34 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.29 (td, *J* = 7.7, 1.4 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.18 – 7.09 (m, 3H), 7.03 – 6.89 (m, 4H), 6.70 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.44 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 3.65 (s, 3H), 3.43 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 195.3, 171.0, 162.0, 161.9, 150.3, 146.9, 146.0, 145.7, 141.1, 136.4, 132.6, 132.5, 131.9, 131.7, 130.8, 129.9, 129.6, 127.2, 123.2, 122.7, 122.6, 119.4, 118.5, 117.7, 109.2, 69.4, 52.1, 27.6. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}ClNO_5$ $[M+H]^+$ 486.1108, found 486.1104

Methyl -2-(2-hydroxybenzoyl)-1'-methyl-3-(2-nitrophenyl)-2'-oxospiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate) (3w)

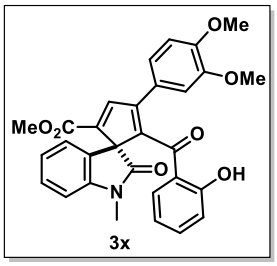


The compound **3w** was prepared following the general procedure **GP-1**

Yellow solid (30 mg, 53%), R_f = 0.11 (petroleum ether/EtOAc 70:30), MP: 195-197 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 11.07 (s, 1H), 8.15 – 8.08 (m, 1H), 7.47 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.44 – 7.35 (m, 3H), 7.30 (td, *J* = 7.8, 1.2 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.17 – 7.09 (m, 2H), 6.98 – 6.91 (m, 2H), 6.69 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.40 (ddd, *J* = 8.2, 7.3, 1.1 Hz, 1H), 3.64 (s, 3H), 3.44 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 195.0, 171.1, 162.0, 161.8, 149.8, 146.9, 145.6, 145.2, 145.1, 141.3, 136.6, 134.2, 133.1, 131.5, 130.6, 129.7, 129.6,

125.3, 123.0, 122.9, 122.9, 119.8, 118.9, 117.9, 109.3, 69.4, 52.1, 27.6. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}N_2O_7$ $[M+H]^+$ 497.1349, found 497.1347

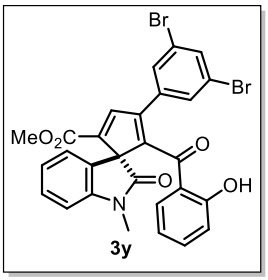
Methyl -3-(3, 4-dimethoxyphenyl)-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxospiro [cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3x)



The compound **3x** was prepared following the general procedure **GP-1**

Yellow solid (32 mg, 54%), R_f = 0.06 (petroleum ether/EtOAc 70:30), MP: 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (s, 1H), 7.85 (s, 1H), 7.30 – 7.28 (m, 1H), 7.24 – 7.19 (m, 2H), 7.04 (dd, J = 8.3, 2.1 Hz, 1H), 6.94 – 6.90 (m, 3H), 6.80 – 6.75 (m, 2H), 6.64 (d, J = 2.0 Hz, 1H), 6.45 – 6.41 (m, 1H), 3.83 (s, 3H), 3.65 (s, 3H), 3.58 (s, 3H), 3.40 (s, 3H).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 197.1, 171.3, 162.3, 162.0, 150.4, 148.8, 146.3, 145.6, 141.8, 140.8, 136.6, 132.4, 129.5, 125.4, 123.8, 122.7, 121.6, 119.2, 119.0, 117.8, 112.3, 111.0, 109.1, 70.3, 56.0, 55.8, 52.1, 27.6. HRMS (ESI TOF) *m/z* calcd. For $C_{30}H_{26}NO_7$ $[M+H]^+$ 512.1709, found 512.1707

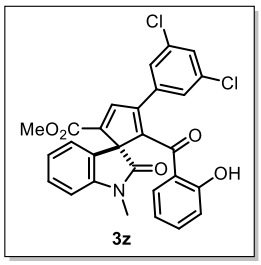
Methyl-3-(3, 5-dibromophenyl)-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxospiro [cyclopentane-1, 3'-indoline]-2, 4-diene-5-carboxylate (3y)



The compound **3y** was prepared following the general procedure **GP-1**

Yellow solid (42 mg, 60%), R_f = 0.30 (petroleum ether/EtOAc 70:30), MP: 167-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.19 (s, 1H), 7.74 (s, 1H), 7.51 (t, *J* = 1.7 Hz, 1H), 7.39 (d, *J* = 1.7 Hz, 2H), 7.33 – 7.26 (m, 2H), 7.13 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.00 – 6.88 (m, 3H), 6.84 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.50 (ddd, *J* = 8.2, 7.2, 1.1 Hz, 1H), 3.66 (s, 3H), 3.39 (s, 3H). ^{13}C {^{1}H} NMR(100 MHz, $CDCl_3$): δ (ppm) 195.5, 170.3, 162.4, 161.6, 147.7, 145.5, 144.7, 144.7, 142.5, 136.9, 135.9, 134.8, 131.6, 130.2, 129.6, 123.1, 122.7, 122.6, 118.8, 118.5, 118.1, 109.2, 70.6, 52.1, 27.5. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{20}Br_2NO_5$ $[M+H]^+$ 607.9708, 609.9688 found 607.9706; 609.9689 and 611.9671

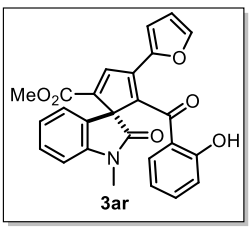
Methyl-3- (3, 5-dichlorophenyl)-2-(2-hydroxybenzoyl)-1'-methyl- 2'-oxospiro [cyclopentane-1, 3'-indoline]-2,4-diene-5-carboxylate (3z)



The compound **3z** was prepared following the general procedure **GP-1**

Yellow solid (38 mg, 64%), R_f = 0.30 (petroleum ether/EtOAc 70:30), MP: 173-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.06 (s, 1H), 7.72 (s, 1H), 7.35 – 7.26 (m, 1H), 7.29 – 7.07 (m, 5H), 7.00 – 6.88 (m, 3H), 6.80 – 6.73 (m, 1H), 6.52 – 6.43 (m, 1H), 3.65 (s, 3H), 3.43 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 194.9, 170.7, 162.1, 161.8, 148.6, 146.7, 146.1, 145.7, 141.6, 136.6, 134.0, 133.2, 131.6, 131.2, 131.0, 130.9, 130.7, 129.7, 123.0, 122.8, 122.6, 119.3, 118.6, 118.0, 109.3, 69.6, 52.2, 27.7. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{20}Cl_2NO_5$ $[M+H]^+$ 520.0719, found 520.0720

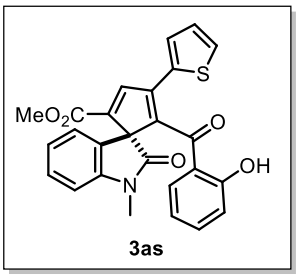
Methyl-3-(furan-2-yl)-2-(2-hydroxybenzoyl)-1'-methyl-2'-oxospiro[cyclopentane-1,3'-indoline]-2, 4-diene-5-carboxylate (3ar)



The compound **3ar** was prepared following the general procedure **GP-1**

Yellow solid (26 mg, 51%), R_f = 0.21 (petroleum ether/EtOAc 70:30), MP: 149-151 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.49 (s, 1H), 7.84 (s, 1H), 7.45 (dd, J = 8.0, 1.4 Hz, 1H), 7.34 (ddd, J = 8.6, 7.3, 1.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.21 (dd, J = 1.8, 0.6 Hz, 1H), 6.89 (ddd, J = 6.5, 5.7, 2.1 Hz, 4H), 6.69 – 6.62 (m, 1H), 6.52 (dd, J = 3.5, 0.6 Hz, 1H), 6.35 (dd, J = 3.5, 1.8 Hz, 1H), 3.64 (s, 3H), 3.34 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 196.7, 171.0, 162.3, 161.9, 147.3, 145.5, 144.8, 143.4, 141.5, 137.8, 137.5, 136.6, 132.4, 129.5, 123.7, 123.0, 122.7, 120.0, 119.0, 118.1, 113.8, 112.2, 109.1, 70.3, 52.1, 27.6. HRMS (ESI TOF) *m/z* calcd. For $C_{23}H_{20}N_3O_5$ $[M+H]^+$ 442.1291, found 442.1299

Methyl -2-(2-hydroxybenzoyl)-1'-methyl-2'-oxo-3-(thiophen-2-yl)spiro[cyclopentane-1,3'-indoline]-2,4-diene-5-carboxylate (3as)

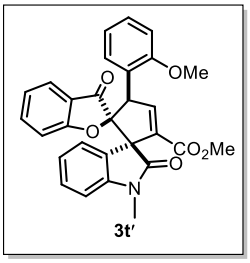


3as

The compound **3as** was prepared following the general procedure **GP-1**

Yellow solid (27 mg, 50%), R_f = 0.23 (petroleum ether/EtOAc 70:30), MP: 157-159 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.48 (s, 1H), 7.82 (s, 1H), 7.46 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.09 (dd, *J* = 3.7, 1.1 Hz, 1H), 6.97 – 6.83 (m, 5H), 6.64 – 6.56 (m, 1H), 3.65 (s, 3H), 3.35 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 196.8, 170.9, 162.6, 161.9, 145.7, 145.4, 142.0, 141.4, 139.7, 136.9, 134.8, 132.5, 130.1, 129.6, 129.2, 128.0, 123.5, 123.0, 122.7, 119.3, 119.3, 118.1, 109.1, 70.5, 52.1, 27.5. HRMS (ESI TOF) *m/z* calcd. For $C_{26}H_{20}NO_5S$ $[M+H]^+$ 458.1062, found 458.1060

Methyl-5'-(2-methoxyphenyl)-1''-methyl-2'',3-dioxo-3*H*-dispiro[benzofuran-2,1'-cyclopentane-2', 3''-indolin]-3'-ene-3'-carboxylate (3t')

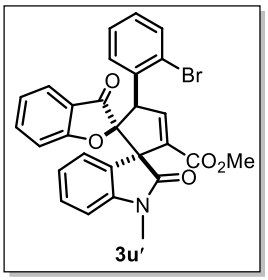


3t'

The compound **3t'** was prepared following the general procedure **GP-2**

White solid (23 mg, 42%), R_f = 0.15 (petroleum ether/EtOAc 70:30), MP: 206-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.47 (ddd, *J* = 7.7, 1.4, 0.6 Hz, 1H), 7.44 (d, *J* = 2.6 Hz, 1H), 7.38 (ddd, *J* = 8.6, 7.2, 1.5 Hz, 1H), 7.30 (dd, *J* = 7.5, 0.8 Hz, 1H), 7.25 – 7.14 (m, 2H), 6.99 (dtd, *J* = 20.6, 7.6, 1.0 Hz, 2H), 6.93 – 6.86 (m, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.67 – 6.58 (m, 2H), 5.02 (d, *J* = 2.5 Hz, 1H), 3.60 (s, 3H), 3.09 (s, 3H), 3.09 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 200.0, 173.7, 171.8, 162.5, 157.1, 147.7, 144.7, 137.7, 136.5, 130.2, 129.2, 129.2, 126.5, 125.6, 124.3, 122.3, 121.9, 120.4, 112.8, 109.2, 107.9, 95.2, 65.3, 54.2, 52.4, 52.0, 26.9. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{24}NO_6$ $[M+H]^+$ 482.1604 found 482.1600

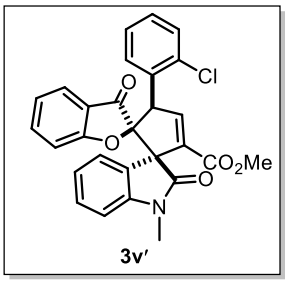
Methyl -5'-(2-bromophenyl)-1''-methyl-2'',3-dioxo-3*H*-dispiro[benzofuran-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (3u')



The compound **3u'** was prepared following the general procedure **GP-2**

Brown solid (22 mg, 36%), R_f = 0.18 (petroleum ether/EtOAc 70:30), MP: 192-194 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.45 – 7.35 (m, 4H), 7.33 – 7.30 (m, 1H), 7.24 – 7.20 (m, 1H), 7.15 (tdd, *J* = 7.7, 2.3, 1.5 Hz, 2H), 6.98 – 6.86 (m, 2H), 6.85 – 6.80 (m, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 5.15 (d, *J* = 2.7 Hz, 1H), 3.60 (s, 3H), 3.11 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 200.2, 174.0, 172.0, 162.4, 147.6, 144.7, 138.1, 136.7, 135.5, 132.4, 132.2, 129.7, 129.3, 127.2, 126.4, 126.1, 125.3, 124.4, 122.5, 122.5, 120.3, 113.0, 107.9, 94.9, 65.4, 56.5, 52.1, 26.9. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}BrNO_5$ $[M+H]^+$ 530.0603 and 532.0583, found 530.0608 and 532.0590

Methyl-5'-(2-chlorophenyl)-1''-methyl-2'',3-dioxo-3*H*-dispiro[benzofuran-2,1'-cyclopentane-2',3''-indolin]-3'-ene-3'-carboxylate (3v')



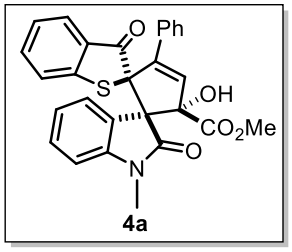
The compound **3v'** was prepared following the general procedure **GP-2**

White solid (30 mg, 54%), R_f = 0.12 (petroleum ether/EtOAc 70:30), MP: 273-275 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.80 (m, 1H), 7.43 – 7.34 (m, 3H), 7.33 (d, *J* = 2.7 Hz, 1H), 7.26 – 7.20 (m, 3H), 7.16 (td, *J* = 7.7, 1.2 Hz, 1H), 6.99 – 6.87 (m, 2H), 6.85 – 6.79 (m, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 5.15 (d, *J* = 2.6 Hz, 1H), 3.61 (s, 3H), 3.10 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 200.0, 173.9, 171.9, 162.4, 147.3, 144.7, 138.1, 136.9, 135.1, 133.7, 132.1, 129.4, 129.3, 128.9, 126.7, 126.4, 125.3, 124.4, 122.5, 122.5, 120.1, 112.9, 108.0, 95.0, 65.4, 54.1, 52.1, 26.9. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}ClNO_5$ $[M+H]^+$ 486.1108, found 486.1119

Methyl-5'-hydroxy-1''-methyl-2'', 3-dioxo-3'-phenyl-3*H*-dispiro[benzo[*b*]thiophene-2, 2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4a)

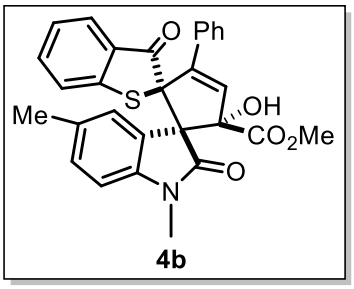


The compound **4a** was prepared following the general procedure **GP-3**

Yellow solid (31 mg, 56%), dr >20:1. R_f = 0.34 (petroleum ether/EtOAc 60:40), MP: 219-221 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.35 (m, 1H), 7.23 – 7.18 (m, 3H), 7.17 – 7.11 (m, 3H), 7.10 – 7.04 (m, 3H), 6.94 (s, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 5.10 (s, 1H), 3.60 (s, 2H), 3.13 (s, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.8, 175.5, 169.2, 154.3, 148.5, 145.5, 137.3, 135.5, 133.4, 129.5, 129.4,

129.1, 128.5, 128.0, 127.5, 127.0, 125.5, 124.2, 122.8, 122.6, 108.1, 87.4, 77.7, 64.7, 52.8, 26.5. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}NO_5SNa$ $[M+Na]^+$ 506.1038, found 506.1037

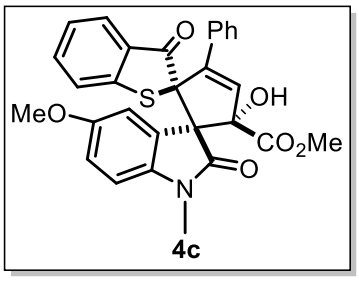
Methyl-5'-hydroxy-1'',5''-dimethyl-2'',3-dioxo-3'-phenyl-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4b)



The compound **4b** was prepared following the general procedure **GP-3**

Yellow solid (28mg, 49%), dr >20:1, R_f = 0.33 (petroleum ether/EtOAc 60:40), MP: 257-259 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.23 – 7.13 (m, 3H), 7.13 – 7.04 (m, 4H), 7.02 (s, 1H), 6.93 (d, *J* = 4.9 Hz, 2H), 6.59 (d, *J* = 7.9 Hz, 1H), 5.07 (s, 1H), 3.60 (s, 3H), 3.10 (s, 3H), 2.12 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.9, 175.3, 169.2, 154.4, 148.4, 143.1, 137.2, 135.5, 133.4, 131.9, 129.8, 129.5, 129.0, 128.5, 128.3, 127.8, 126.9, 125.4, 124.2, 122.7, 107.8, 87.3, 77.8, 64.8, 52.8, 26.5, 21.4. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{24}NO_5S$ $[M+H]^+$ 498.1375, found 498.1377

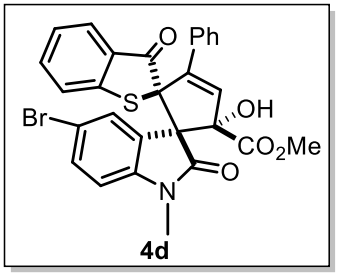
Methyl-5'-hydroxy-5''-methoxy-1''-methyl-2'',3-dioxo-3'-phenyl-*3H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4c)



The compound **4c** was prepared following the general procedure **GP-3**

Yellow solid (30 mg, 51%), dr >20:1, R_f = 0.21 (petroleum ether/EtOAc 60:40), MP: 249-251 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (ddd, *J* = 7.8, 1.3, 0.7 Hz, 1H), 7.46 (ddd, *J* = 7.9, 7.3, 1.4 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.11 (m, 6H), 7.00 (s, 1H), 6.92 (d, *J* = 2.5 Hz, 1H), 6.75 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.68 (d, *J* = 8.5 Hz, 1H), 5.15 (s, 1H), 3.68 (s, 3H), 3.68 (s, 3H), 3.17 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.9, 175.1, 169.1, 155.5, 154.4, 148.5, 139.0, 137.3, 135.4, 133.4, 129.5, 129.1, 128.5, 127.9, 126.9, 126.9, 126.9, 125.6, 124.3, 123.9, 114.9, 114.3, 108.3, 87.3, 77.7, 64.9, 55.8, 52.8, 26.6. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{23}NO_6SNa$ $[M+Na]^+$ 536.1144, found 536.1143

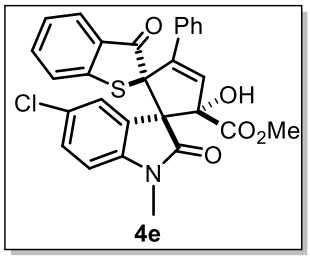
Methyl-5''-bromo-5'-hydroxy-1''-methyl-2'',3-dioxo-3'-phenyl-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4d)



The compound **4d** was prepared following the general procedure **GP-3**

Yellow solid (28 mg, 43%), dr >20:1, R_f = 0.33 (petroleum ether/EtOAc 60:40), MP: 230-232 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 1.7 Hz, 1H), 7.34 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.24 – 7.08 (m, 7H), 6.99 (s, 1H), 6.66 (d, *J* = 8.3 Hz, 1H), 5.07 (s, 1H), 3.70 (s, 3H), 3.18 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.5, 175.1, 169.1, 154.0, 148.4, 144.6, 137.5, 135.2, 133.2, 132.4, 130.6, 129.3, 129.2, 128.5, 128.1, 126.9, 125.8, 124.9, 124.2, 115.2, 109.5, 87.5, 77.6, 64.5, 53.0, 26.6. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{20}BrNO_5SNa$ $[M+Na]^+$ 584.0143, found 584.0150

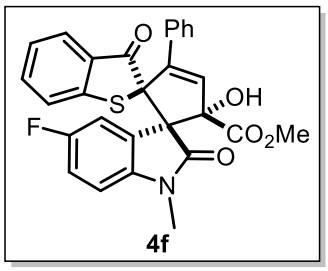
Methyl-5''-chloro-5'-hydroxy-1''-methyl-2'',3-dioxo-3'-phenyl-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4e)



The compound **4e** was prepared following the general procedure **GP-3**

Yellow solid (25 mg, 42%), dr >20:1, R_f = 0.3 (petroleum ether/EtOAc 60:40), MP: 236-238 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.75 (m, 1H), 7.47 – 7.38 (m, 1H), 7.19 (d, *J* = 2.7 Hz, 2H), 7.17 – 7.08 (m, 5H), 7.07 – 7.03 (m, 2H), 6.92 (s, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 5.04 (s, 1H), 3.63 (s, 3H), 3.11 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.5, 175.2, 169.1, 154.0, 148.5, 144.1, 137.5, 135.2, 133.1, 129.5, 129.3, 129.2, 128.5, 128.1, 127.9, 127.9, 126.9, 126.9, 125.8, 124.5, 124.2, 109.0, 87.5, 77.5, 64.6, 53.0, 26.7. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}ClNO_5S$ $[M+H]^+$ 518.0829, found 518.0823

Methyl-5''-fluoro-5'-hydroxy-1''-methyl-2'',3-dioxo-3'-phenyl-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4f*)*

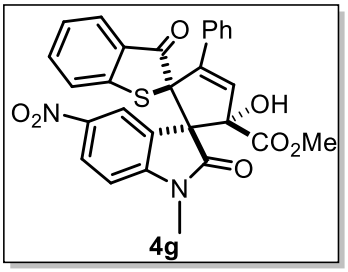


The compound **4f** was prepared following the general procedure **GP-3**

Yellow solid (26 mg, 45%), dr >20:1, R_f = 0.3 (petroleum ether/EtOAc 60:40), MP: 184-186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H), 7.42 (td, *J* = 8.0, 1.4 Hz, 1H), 7.23 – 7.19 (m, 1H), 7.17 – 7.07 (m, 4H), 7.05 (dd, *J* = 7.2, 1.6 Hz, 2H), 6.99 (dd, *J* = 8.9, 2.6 Hz, 1H), 6.92 (s, 1H), 6.86 (td, *J* = 8.7, 2.6 Hz, 1H), 6.63 (dd, *J* = 8.5, 4.3 Hz, 1H), 5.06 (s, 1H), 3.62 (s, 3H), 3.12 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.6, 175.3, 169.1,

158.81 (d, $J_{(C-F)}$ = 239.7 Hz), 154.2, 148.6, 141.5, 137.5, 135.2, 133.2, 129.3, 129.2, 128.5, 128.2, 126.9, 125.7, 124.4, 124.3, 124.2, 115.9 (d, $J_{(C-F)}$ = 26 Hz), 115.8(d, $J_{(C-F)}$ = 23 Hz), 108.40 (d, $J_{(C-F)}$ = 8.2 Hz), 87.4, 77.6, 64.7, 52.9, 26.7. ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -120.3. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{20}FNO_5SNa$ $[M+Na]^+$ 524.0944, found 524.0941

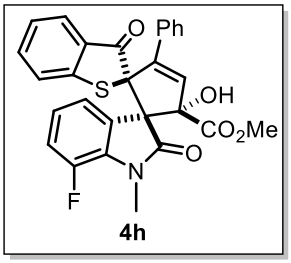
Methyl-5'-hydroxy-1''-methyl-5''-nitro-2'',3-dioxo-3'-phenyl-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4g)



The compound **4g** was prepared following the general procedure **GP-3**

Yellow solid (25mg, 41%), dr >20:1, R_f = 0.23 (petroleum ether/EtOAc 60:40), MP: 227-229 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.6, 2.2 Hz, 1H), 8.16 (d, *J* = 2.2 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.48 (q, *J* = 6.7, 5.5 Hz, 1H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.25 – 7.10 (m, 6H), 7.00 (s, 1H), 6.87 (d, *J* = 8.7 Hz, 1H), 5.18 (s, 1H), 3.72 (s, 3H), 3.27 (s, 3H). ^{13}C {^{1}H} NMR(100 MHz, $CDCl_3$): δ (ppm) 202.1, 175.9, 169.1, 153.5, 151.2, 148.5, 143.2, 141.7, 137.7, 134.8, 132.8, 129.3, 129.0, 128.6, 128.4, 126.8, 126.7, 126.1, 124.2, 123.7, 123.2, 107.7, 87.9, 64.1, 53.1, 26.9. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{20}N_2O_7S$ $[M+H]^+$ 529.1069, found 529.1076

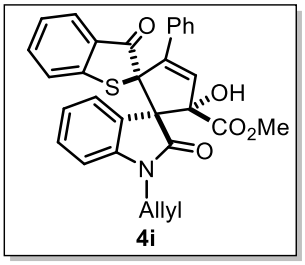
Methyl-7''-fluoro-5'-hydroxy-1''-methyl-2'',3-dioxo-3'-phenyl-3*H*-dispiro[benzo[*b*]thiophene-2, 2'-cyclopentane-1', 3''-indolin]-3'-ene-5'-carboxylate (4h)



The compound **4h** was prepared following the general procedure **GP-3**

Yellow solid (29 mg, 50%), dr >20:1, R_f = 0.5 (petroleum ether/EtOAc 60:40), MP: 188-190 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.20 (dt, *J* = 14.8, 7.4 Hz, 4H), 7.10 (dd, *J* = 18.6, 7.5 Hz, 3H), 7.00 (s, 1H), 6.95 (dd, *J* = 11.4, 8.5 Hz, 1H), 6.80 (td, *J* = 8.1, 4.8 Hz, 1H), 5.11 (s, 1H), 3.71 (s, 3H), 3.42 (d, *J* = 2.8 Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.6, 175.2, 169.1, 154.2, 148.4, 146.4, 136.3 (d, $J_{(C-F)}$ = 221.2 Hz) , 134.4, 133.2, 132.27 (d, $J_{(C-F)}$ = 8.0 Hz), 129.3, 129.2, 128.5, 128.0, 126.9, 125.6, 124.3, 123.4 (d, $J_{(C-F)}$ = 2.9 Hz), 122.8 (d, $J_{(C-F)}$ = 6.4 Hz) , 117.7 (d, $J_{(C-F)}$ = 19.1 Hz)., 87.5, 77.7, 61.1, 53.0, 29.1. ^{19}F NMR (377 MHz, $CDCl_3$): δ (ppm) -136.2. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{20}FNO_5SNa$ $[M+Na]^+$ 524.0944, found 524.0944

Methyl-1''-allyl-5'-hydroxy-2'',3-dioxo-3'-phenyl-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4i)

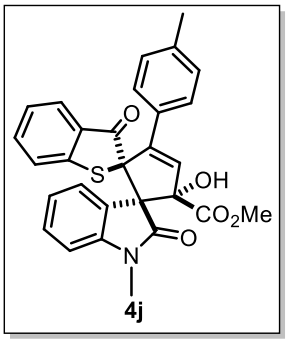


4i

The compound **4i** was prepared following the general procedure **GP-3**

Yellow solid (27 mg, 46%), dr >20:1, R_f = 0.46 (petroleum ether/EtOAc 60:40), MP: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 7.23 – 7.09 (m, 7H), 7.01 (s, 1H), 6.87 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.85 (ddt, *J* = 15.8, 10.5, 5.4 Hz, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.23 (d, *J* = 10.4 Hz, 1H), 5.19 (s, 1H), 4.39 – 4.25 (m, 2H), 3.67 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.8, 175.1, 169.1, 154.3, 148.5, 144.7, 137.3, 135.5, 133.4, 131.5, 129.5, 129.4, 129.0, 128.5, 128.0, 127.6, 126.9, 125.5, 124.2, 122.8, 122.5, 118.1, 109.0, 87.3, 77.9, 64.7, 52.8, 42.9. HRMS (ESI TOF) *m/z* calcd. For $C_{30}H_{23}NO_5SNa$ $[M+Na]^+$ 532.1195, found 532.1192

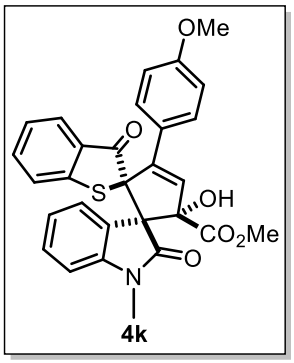
Methyl-5'-hydroxy-1''-methyl-2'',3-dioxo-3'-(p-tolyl)-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4j)



The compound **4j** was prepared following the general procedure **GP-3**

Yellow solid (25 mg, 44%), dr >20:1, R_f = 0.34 (petroleum ether/EtOAc 60:40), MP: 189-191 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.48 – 7.41 (m, 1H), 7.27 – 7.26 (m, 1H), 7.24 – 7.12 (m, 3H), 7.02 (d, *J* = 0.6 Hz, 4H), 6.97 (d, *J* = 0.7 Hz, 1H), 6.87 (t, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 5.15 (d, *J* = 0.7 Hz, 1H), 3.67 (d, *J* = 0.7 Hz, 3H), 3.20 (d, *J* = 0.6 Hz, 3H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.9, 175.5, 169.2, 154.4, 154.4, 148.5, 145.5, 139.1, 137.2, 134.7, 130.5, 129.5, 129.5, 129.2, 128.0, 127.5, 126.8, 126.8, 126.8, 126.8, 126.8, 125.5, 124.2, 122.9, 122.5, 108.1, 87.4, 87.4, 77.7, 64.7, 52.8, 26.5, 21.4. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{24}NO_5S$ $[M+H]^+$ 498.1375, found 498.1374

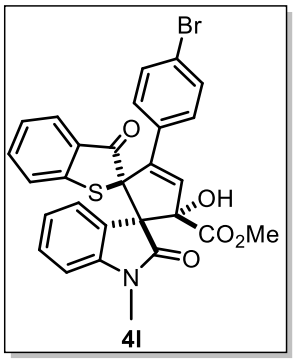
Methyl-5'-hydroxy-3'-(4-methoxyphenyl)-1''-methyl-2'',3-dioxo-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1', 3''-indolin]-3'-ene-5'-carboxylate (4k)



The compound **4k** was prepared following the general procedure **GP-3**

Yellow solid (24 mg, 41%), dr = 90:10. R_f = 0.26 (petroleum ether/EtOAc 60:40), MP: 190-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.28 (s, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.16 (dd, *J* = 7.7, 4.5 Hz, 2H), 7.08 (d, *J* = 8.7 Hz, 2H), 6.93 (s, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 6.76 (dd, *J* = 16.5, 8.3 Hz, 3H), 5.12 (s, 1H), 3.74 (s, 3H), 3.67 (s, 3H), 3.20 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.7, 175.4, 169.1, 160.1, 154.2, 147.9, 145.4, 137.1, 133.8, 129.4, 128.1, 127.8, 127.4, 125.7, 125.3, 124.1, 122.8, 122.4, 113.8, 108.0, 87.2, 77.7, 64.6, 55.2, 52.7, 26.4. HRMS (ESI TOF) *m/z* calcd. For $C_{29}H_{24}NO_6S$ $[M+H]^+$ 514.1324, found 514.1324

Methyl-3'-(4-bromophenyl)-5'-hydroxy-1''-methyl-2'',3-dioxo-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4l)

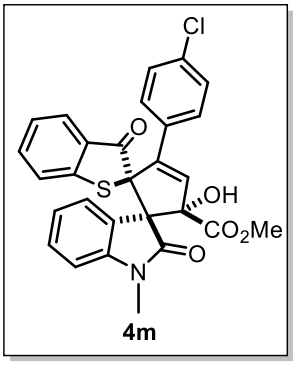


4l

The compound **4l** was prepared following the general procedure **GP-3**

Yellow solid (35 mg, 54%), dr >20:1, R_f = 0.34 (petroleum ether/EtOAc 60:40), MP: 205-206 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 1H), 7.43 – 7.36 (m, 1H), 7.30 – 7.25 (m, 2H), 7.21 (s, 1H), 7.18 – 7.05 (m, 3H), 6.96 – 6.89 (m, 3H), 6.81 (td, *J* = 7.7, 1.0 Hz, 1H), 6.72 (d, *J* = 7.7 Hz, 1H), 5.09 (s, 1H), 3.60 (s, 3H), 3.13 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.6, 175.4, 169.0, 154.1, 147.5, 145.4, 137.5, 136.0, 132.3, 131.7, 129.6, 129.3, 128.6, 128.0, 127.5, 125.7, 124.2, 123.3, 122.6, 108.2, 87.3, 77.6, 64.7, 52.9, 26.5. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}BrNO_5S$ $[M+H]^+$ 562.0324 and 564.0303 found 562.0323 and 564.0317

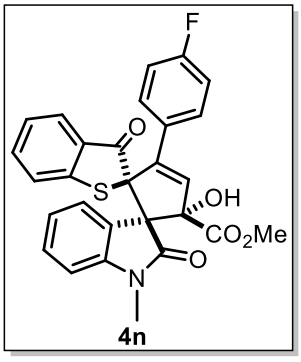
Methyl-3'-(4-chlorophenyl)-5'-hydroxy-1''-methyl-2'', 3-dioxo-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1', 3''-indolin]-3'-ene-5'-carboxylate (4m)



The compound **4m** was prepared following the general procedure **GP-3**

Yellow solid (28 mg, 47%), dr >20:1, R_f = 0.37 (petroleum ether/EtOAc 60:40), MP: 175-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 1H), 7.50 – 7.43 (m, 1H), 7.29 – 7.26 (m, 1H), 7.23 – 7.14 (m, 5H), 7.08 – 7.05 (m, 2H), 6.99 (s, 1H), 6.89 (td, *J* = 7.7, 1.0 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.16 (s, 1H), 3.67 (s, 3H), 3.20 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.6, 175.4, 169.0, 154.2, 147.4, 145.5, 137.5, 136.0, 135.1, 131.9, 129.6, 129.3, 128.9, 128.7, 128.4, 128.0, 127.5, 125.7, 124.3, 122.6, 108.2, 87.3, 77.6, 64.7, 52.9, 26.6. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}ClNO_5S$ $[M+H]^+$ 518.0829, found 518.0831

Methyl-3'-(4-fluorophenyl)-5'-hydroxy-1''-methyl-2'', 3-dioxo-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4n)

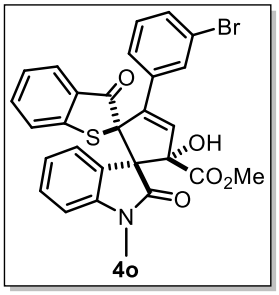


The compound **4n** was prepared following the general procedure **GP-3**

Yellow solid (29 mg, 50%), dr > 20:1, R_f = 0.31 (petroleum ether/EtOAc 60:40), MP: 202-204 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.21 (s, 1H), 7.18 – 7.01 (m, 5H), 6.89 (s, 1H), 6.82 (q, *J* = 7.7, 6.7 Hz, 3H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.08 (s, 1H), 3.60 (s, 3H), 3.13 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.7, 175.4, 169.1, 163.2 (d, $J_{(C-F)}$ = 248.9 Hz), 154.2, 147.5, 145.5, 137.4, 135.5, 129.6, 129.5 (d,

$J_{(C-F)}$ = 3 Hz), 129.3, 129.0, 128.9 (d, $J_{(C-F)}$ = 8.3 Hz), 128.0, 127.5, 125.6, 124.2, 122.7, 122.6, 115.5 (d, $J_{(C-F)}$ = 21.7 Hz), 108.2, 87.2, 77.8, 64.7, 52.8, 26.5. ^{19}F NMR (377 MHz, $CDCl_3$) δ -112.22. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{20}FNO_5S$ $[M+H]^+$ 502.1124, found 502.1121

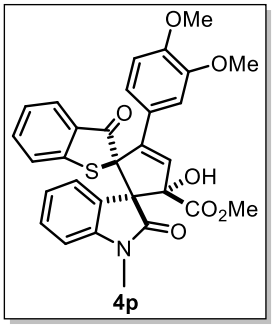
Methyl-3'-(3-bromophenyl)-5'-hydroxy-1''-methyl-2'',3-dioxo-3*H*-dispiro[benzo[*b*]thiophene-2,2'-cyclopentane-1',3''-indolin]-3'-ene-5'-carboxylate (4o)



The compound **4o** was prepared following the general procedure **GP-3**

Yellow solid (32mg, 49%), dr >20:1, R_f = 0.34 (petroleum ether/EtOAc 60:40), MP: 209-211 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.36 (m, 1H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.22 (s, 1H), 7.18 – 7.06 (m, 3H), 6.99 (t, *J* = 7.8 Hz, 1H), 6.94 (s, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 5.12 (s, 1H), 3.61 (s, 3H), 3.13 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.5, 175.4, 169.0, 154.2, 147.2, 145.5, 137.5, 136.6, 135.4, 132.0, 130.3, 130.3, 129.9, 129.6, 129.3, 128.1, 127.5, 125.7, 125.4, 124.2, 122.7, 122.6, 122.6, 122.6, 108.2, 100.1, 87.2, 77.6, 64.6, 52.9, 26.6. HRMS (ESI TOF) *m/z* calcd. For $C_{28}H_{21}BrNO_5S$ $[M+H]^+$ 562.0324 and 564.0303 found 562.0337 and 564.0314

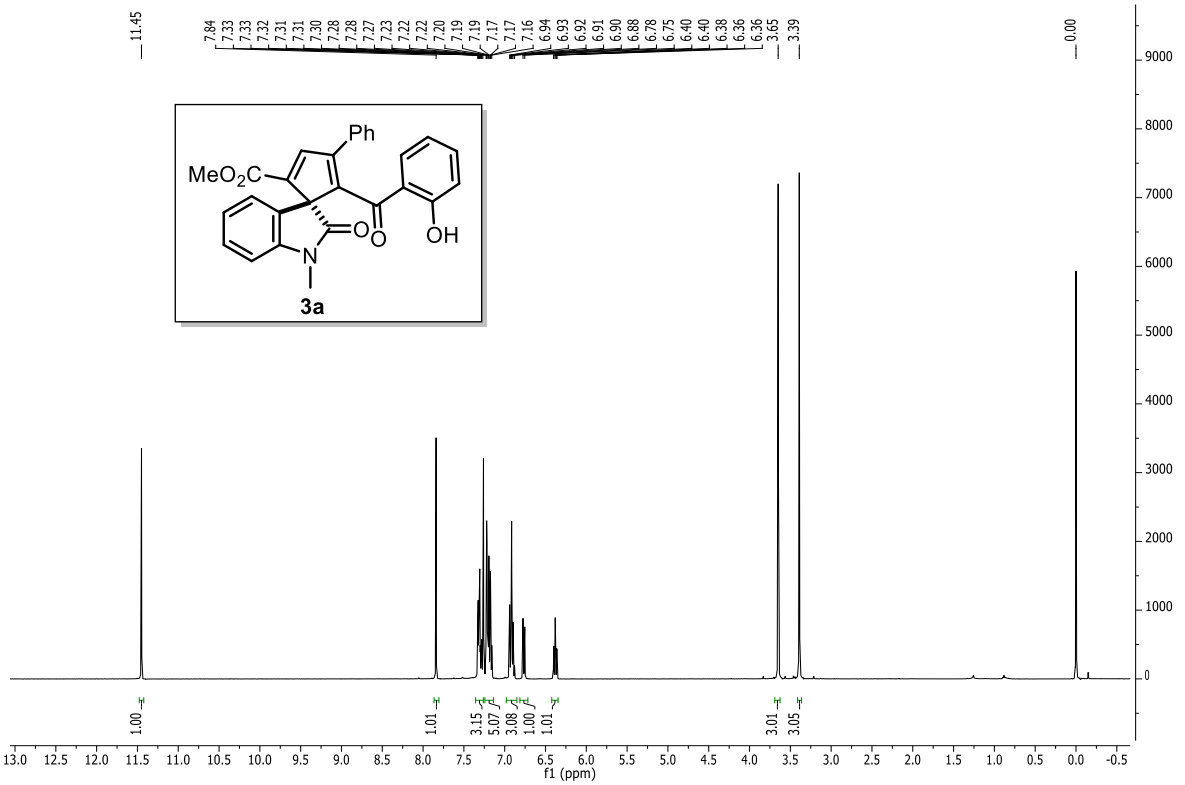
Methyl-3'-(3,4-dimethoxyphenyl)-5'-hydroxy-1''-methyl-2'',3-dioxo-3*H*-dispiro[benzo[*b*]thiophene-2, 2'-cyclopentane-1', 3''-indolin]-3'-ene-5'-carboxylate (4p)



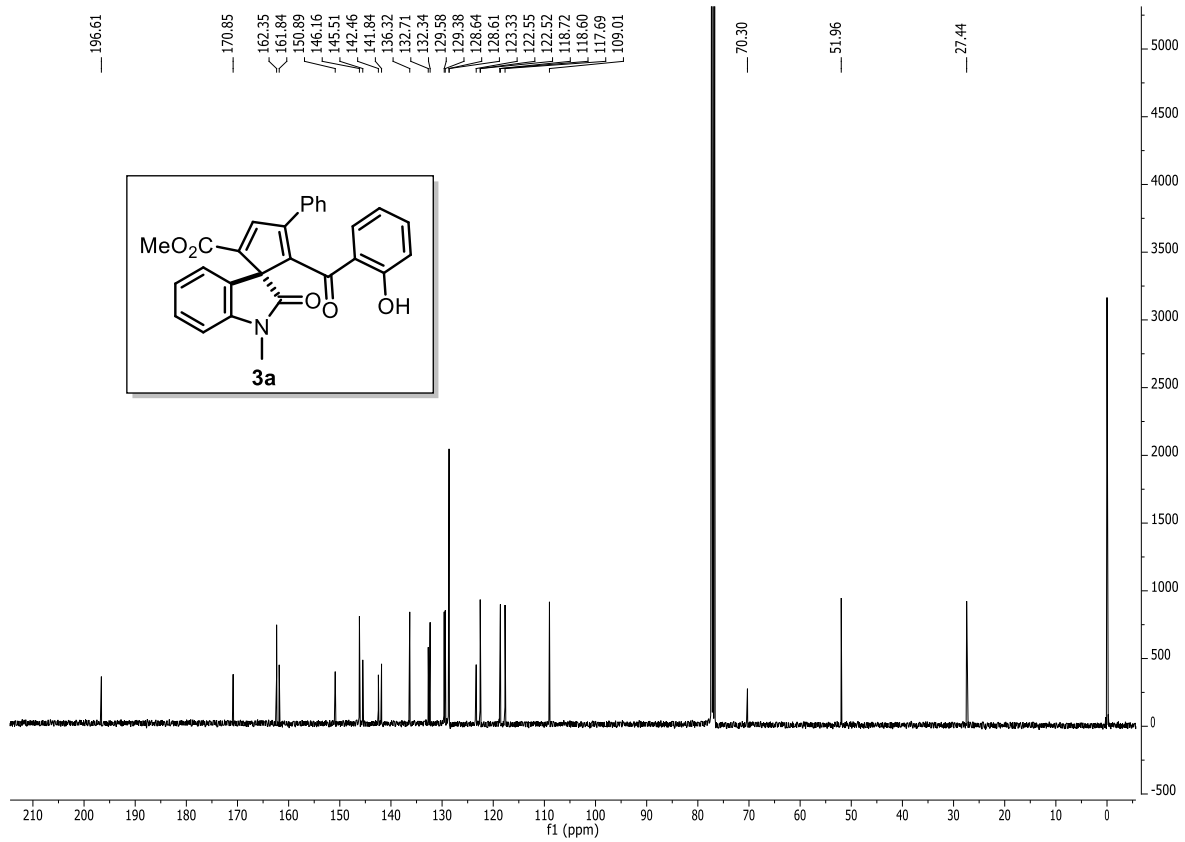
The compound **4p** was prepared following the general procedure **GP-3**

Yellow solid (25 mg, 40%), dr = 84:16 R_f = 0.15 (petroleum ether/EtOAc 60:40), MP: 222-224 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.18 – 7.07 (m, 3H), 6.89 (d, *J* = 11.0 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 6.75 – 6.68 (m, 2H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.49 (d, *J* = 1.9 Hz, 1H), 5.10 (s, 1H), 3.75 (s, 3H), 3.60 (s, 3H), 3.41 (s, 3H), 3.14 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ (ppm) 202.8, 175.5, 169.2, 154.6, 149.7, 148.6, 148.3, 145.5, 137.2, 133.9, 129.6, 129.5, 127.9, 127.6, 126.0, 125.5, 124.2, 122.9, 122.6, 119.6, 111.0, 109.6, 108.2, 87.4, 77.8, 64.6, 56.0, 55.4, 52.8, 26.5. HRMS (ESI TOF) *m/z* calcd. For $C_{30}H_{26}NO_7S$ $[M+H]^+$ 544.1430, found 544.1427

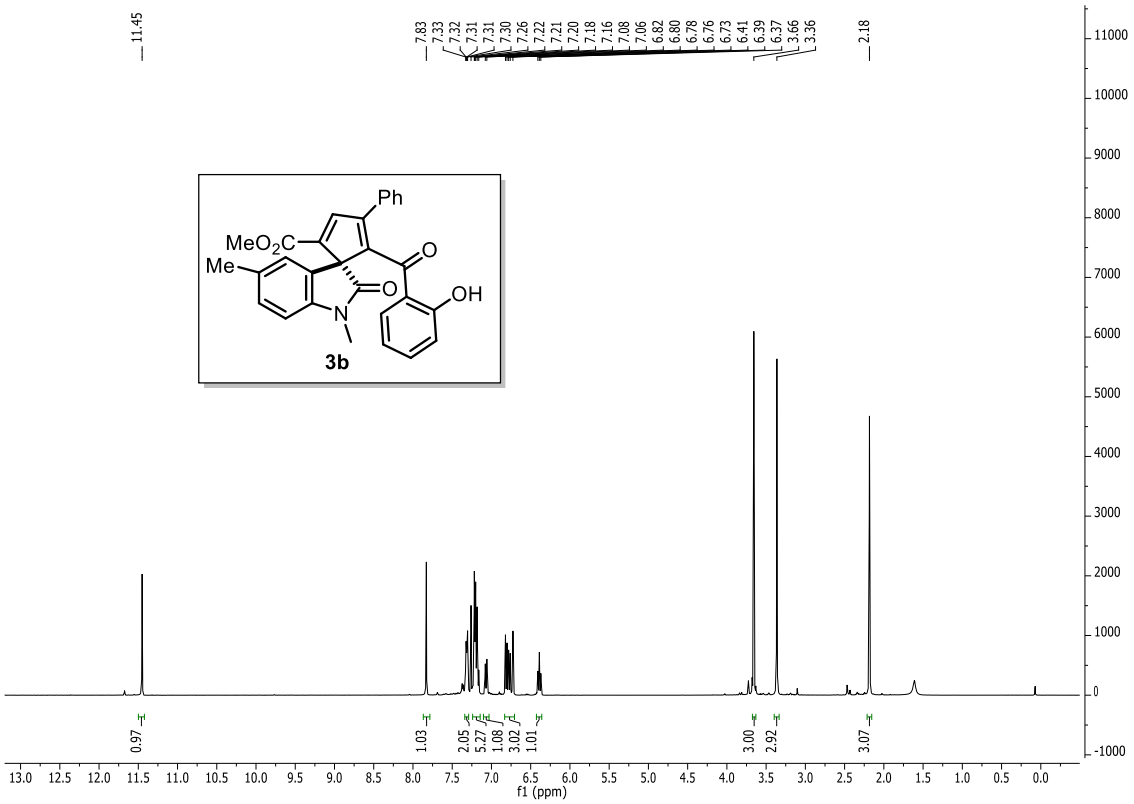
Copies of ^{1}H and ^{13}C NMR Spectra



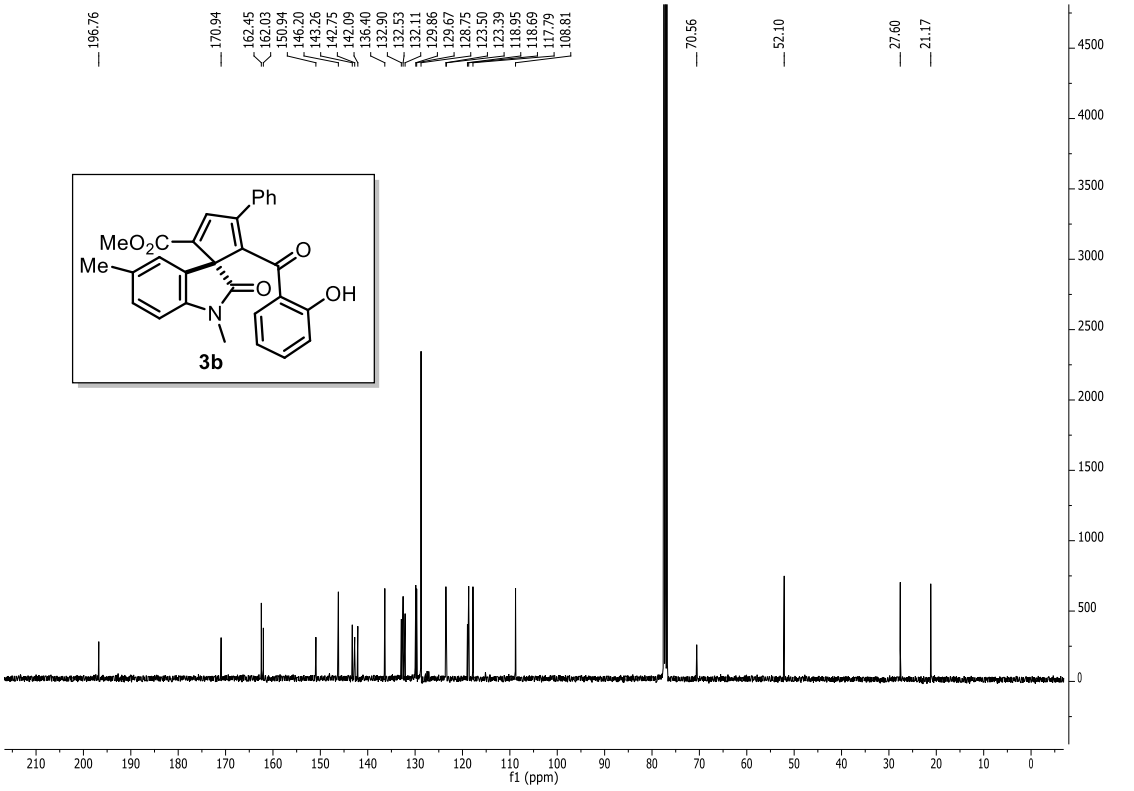
^{1}H NMR (400 MHz, $CDCl_3$)



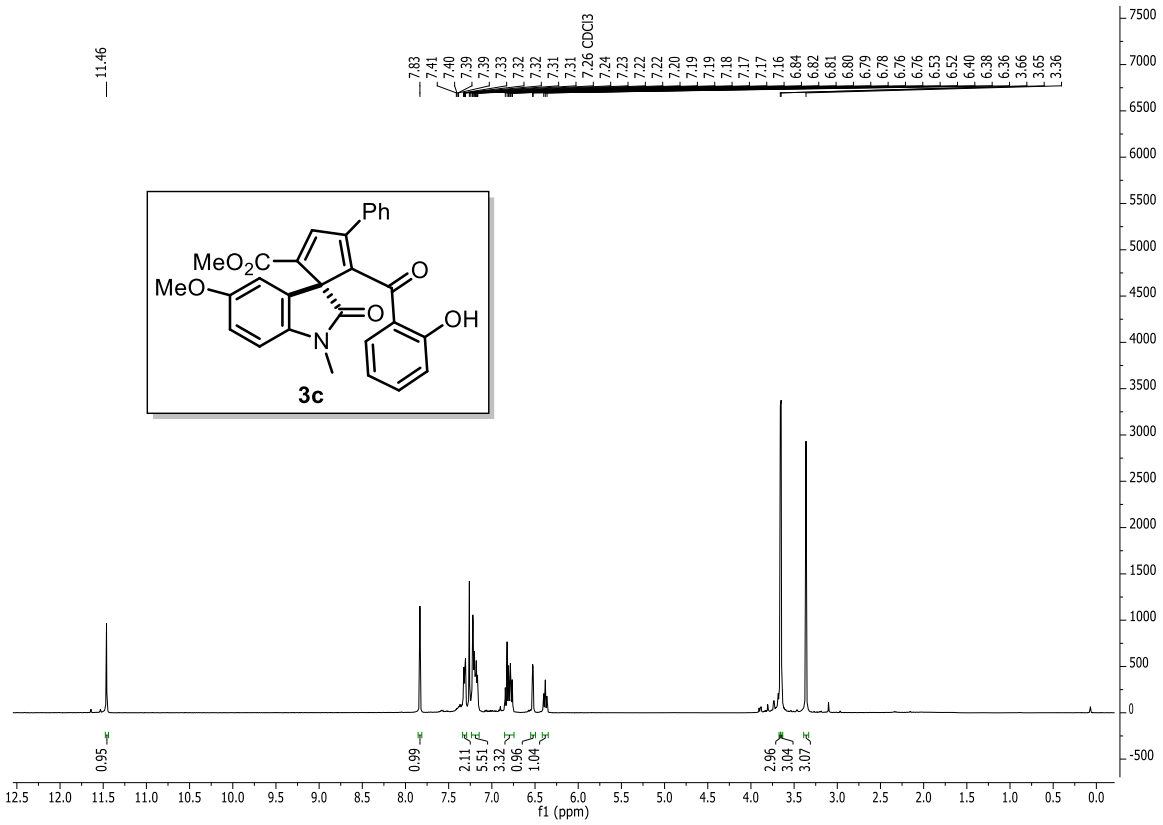
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



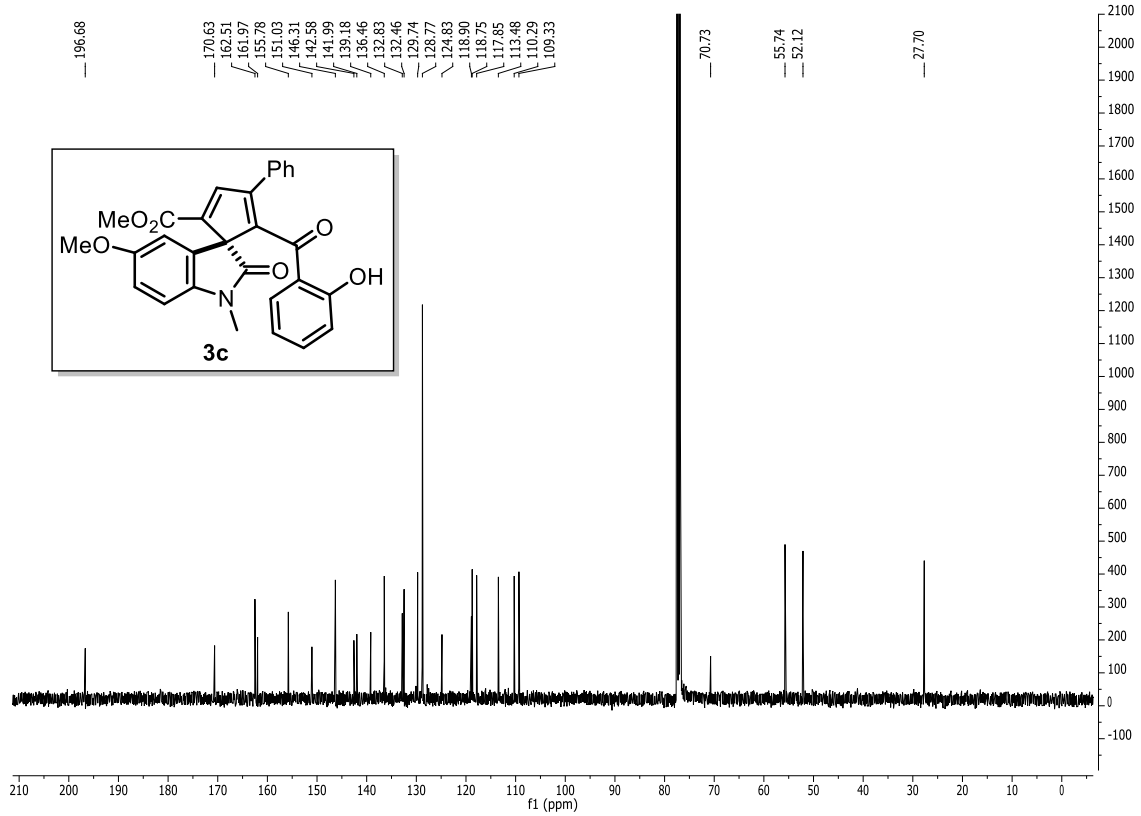
^{1}H NMR (400 MHz, $CDCl_3$)



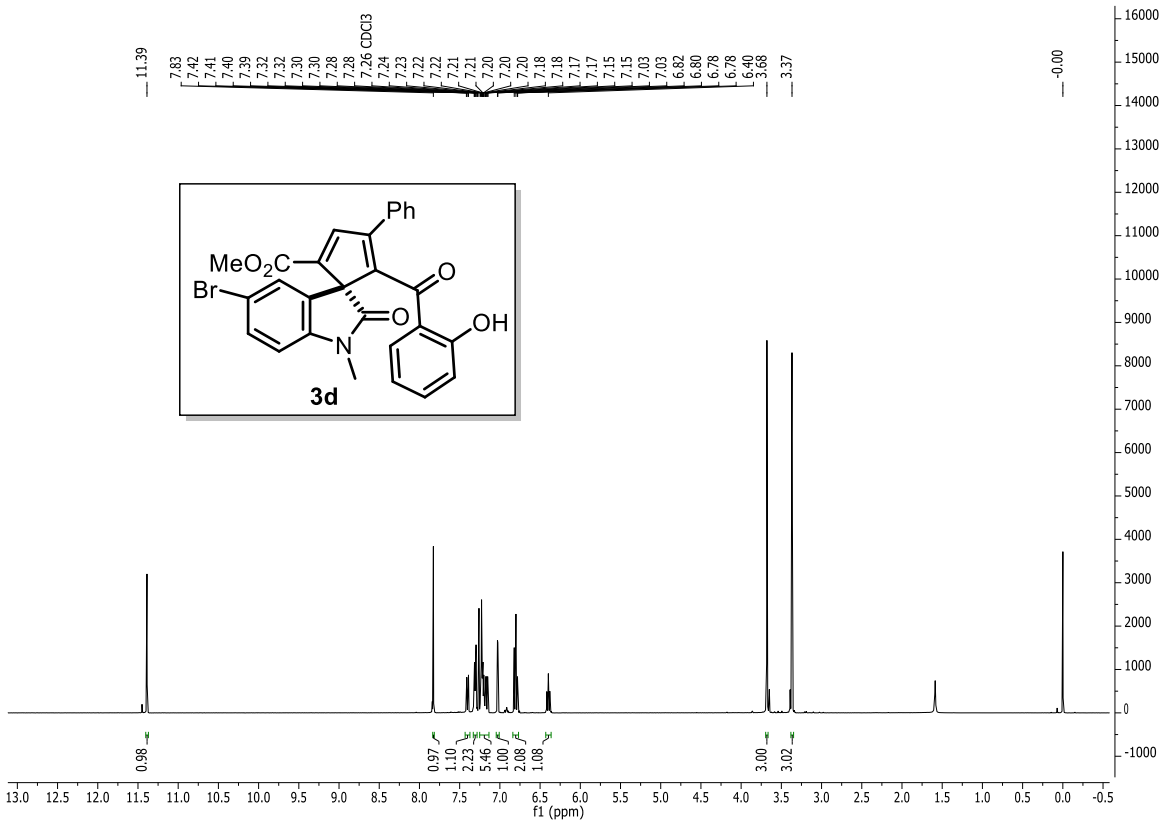
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



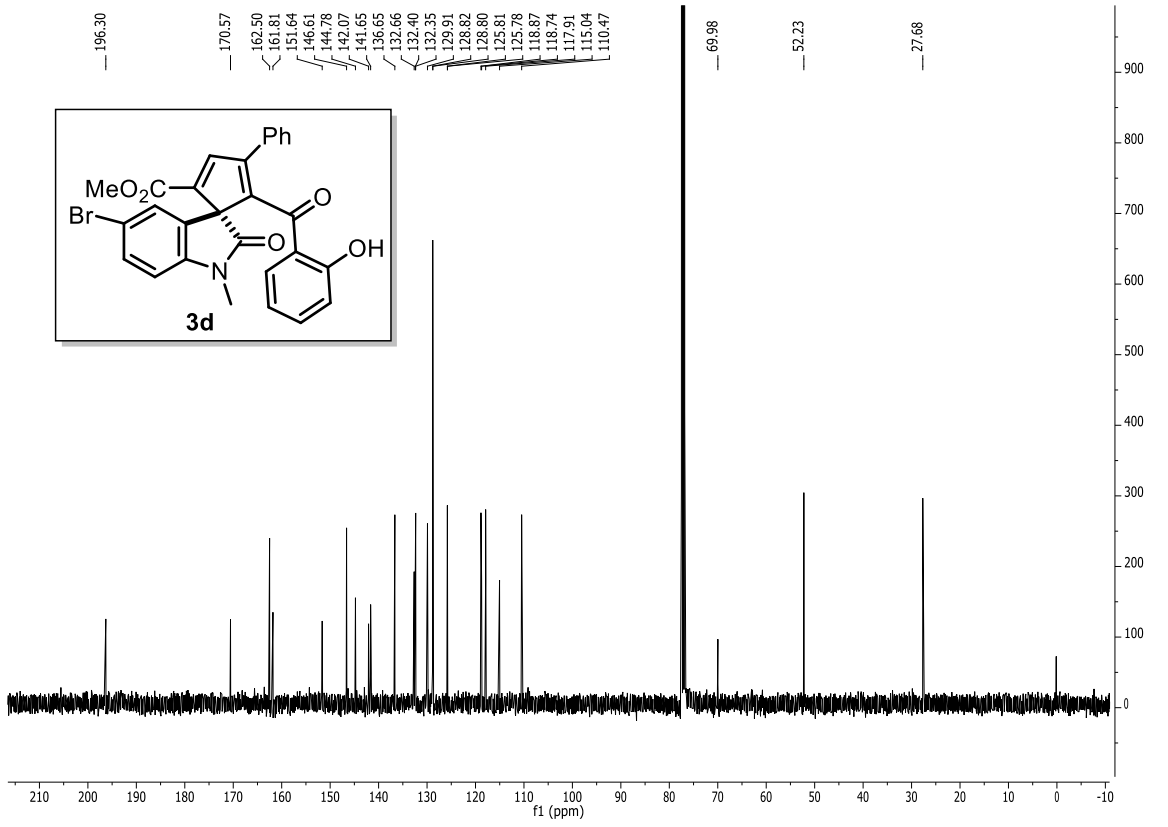
^{1}H NMR (400 MHz, $CDCl_3$)



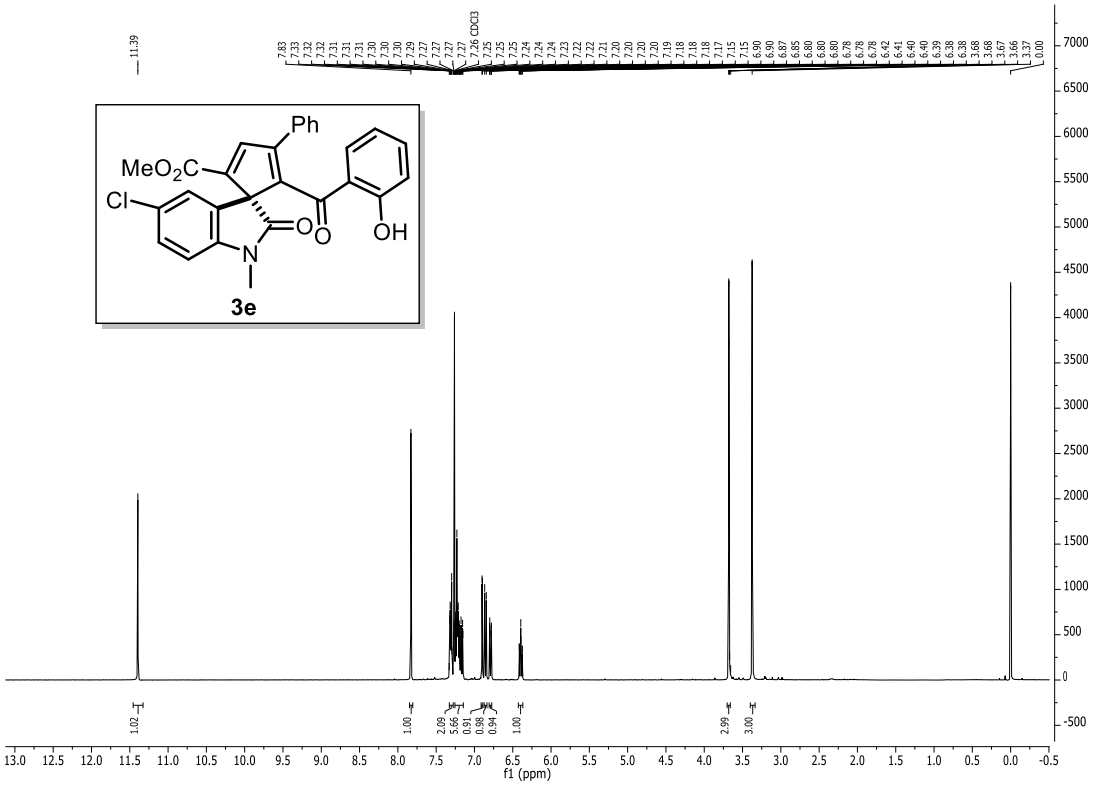
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



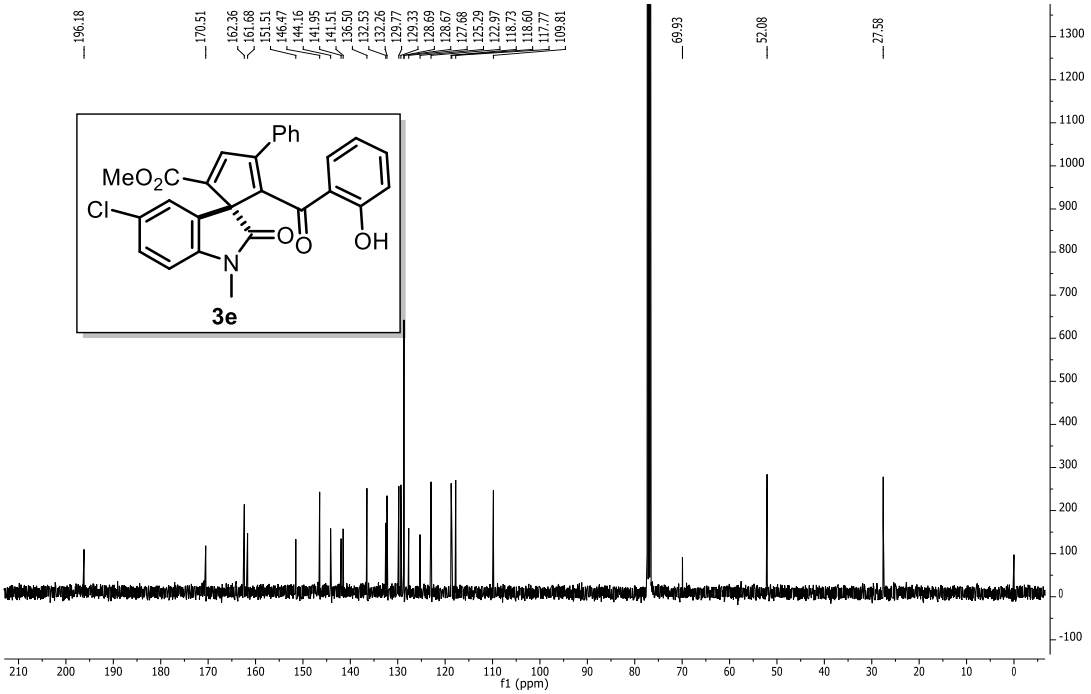
^{1}H NMR (400 MHz, $CDCl_3$)



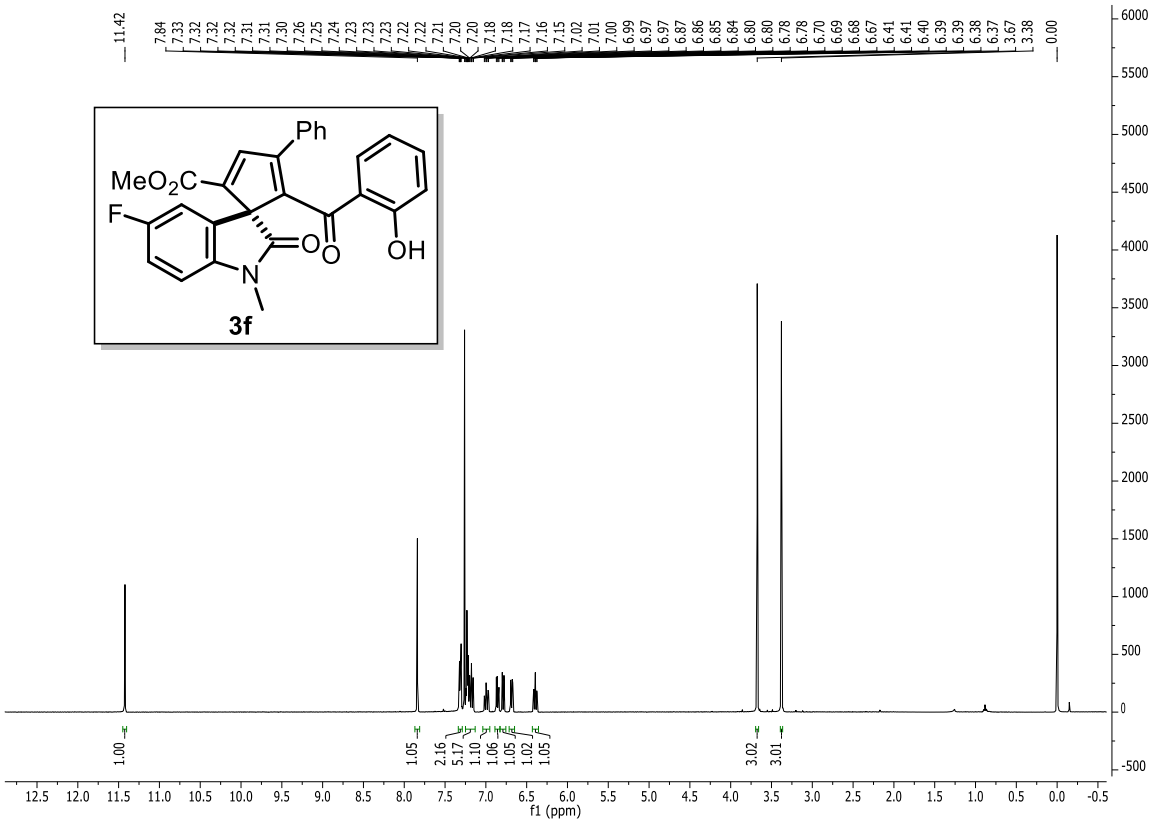
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



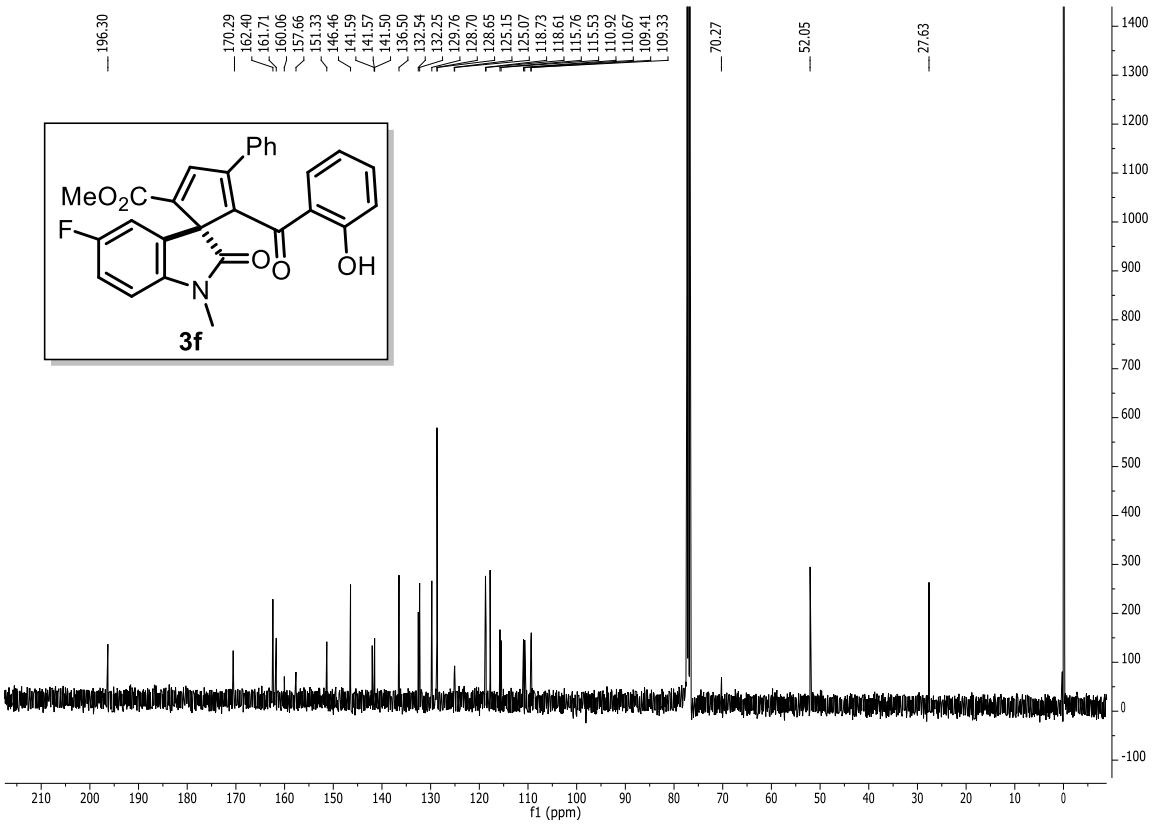
^{1}H NMR (400 MHz, $CDCl_3$)



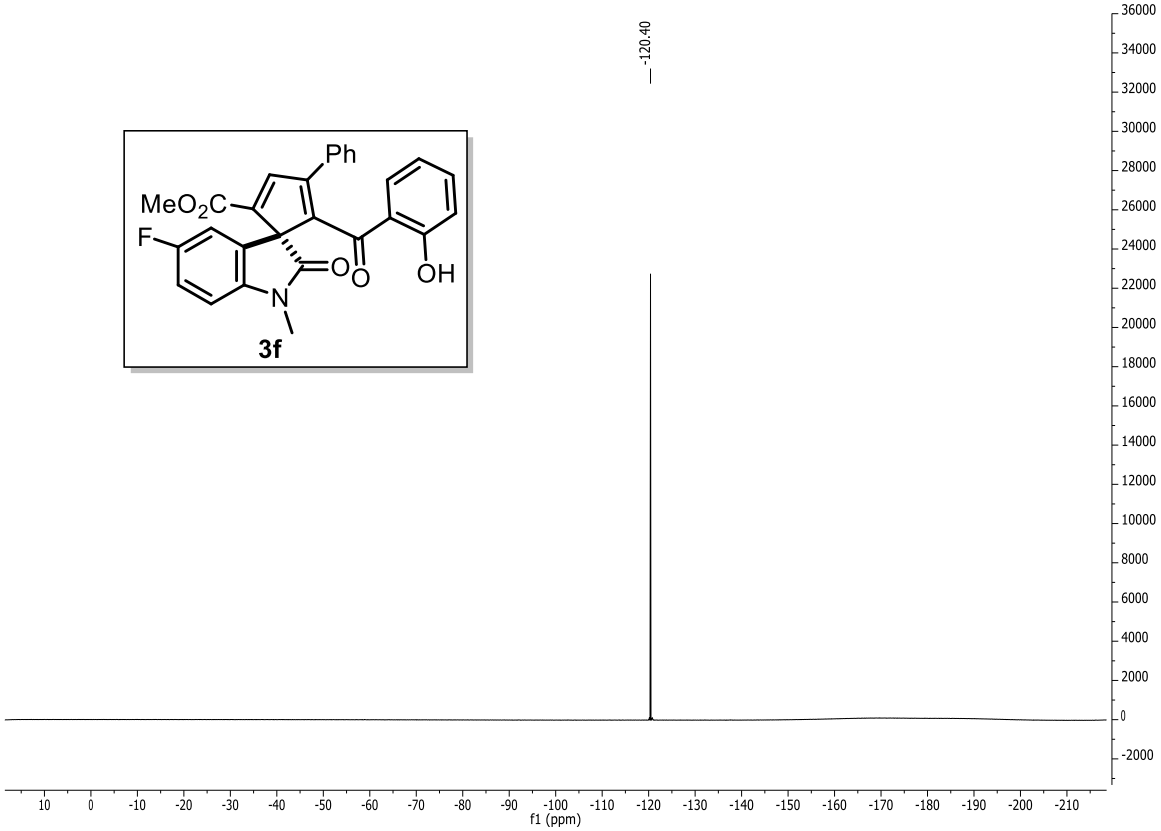
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



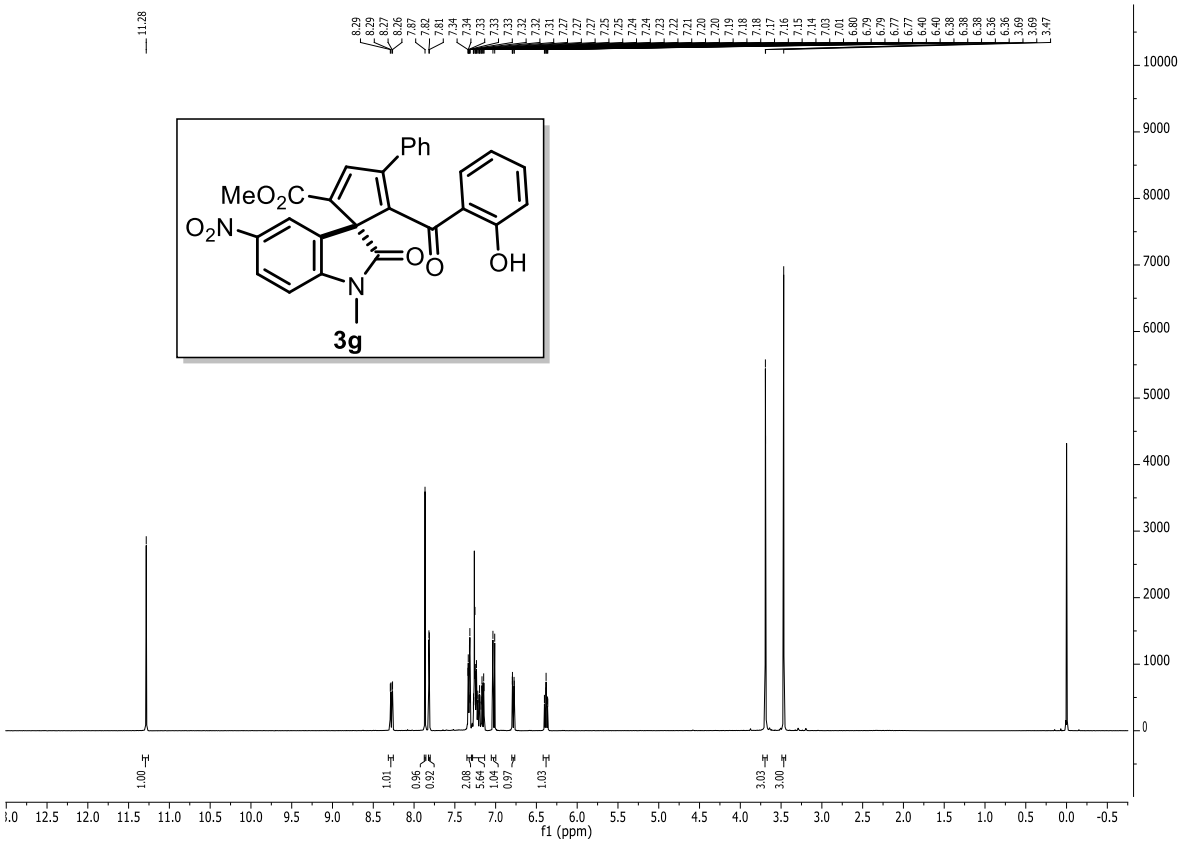
^{1}H NMR (400 MHz, $CDCl_3$)



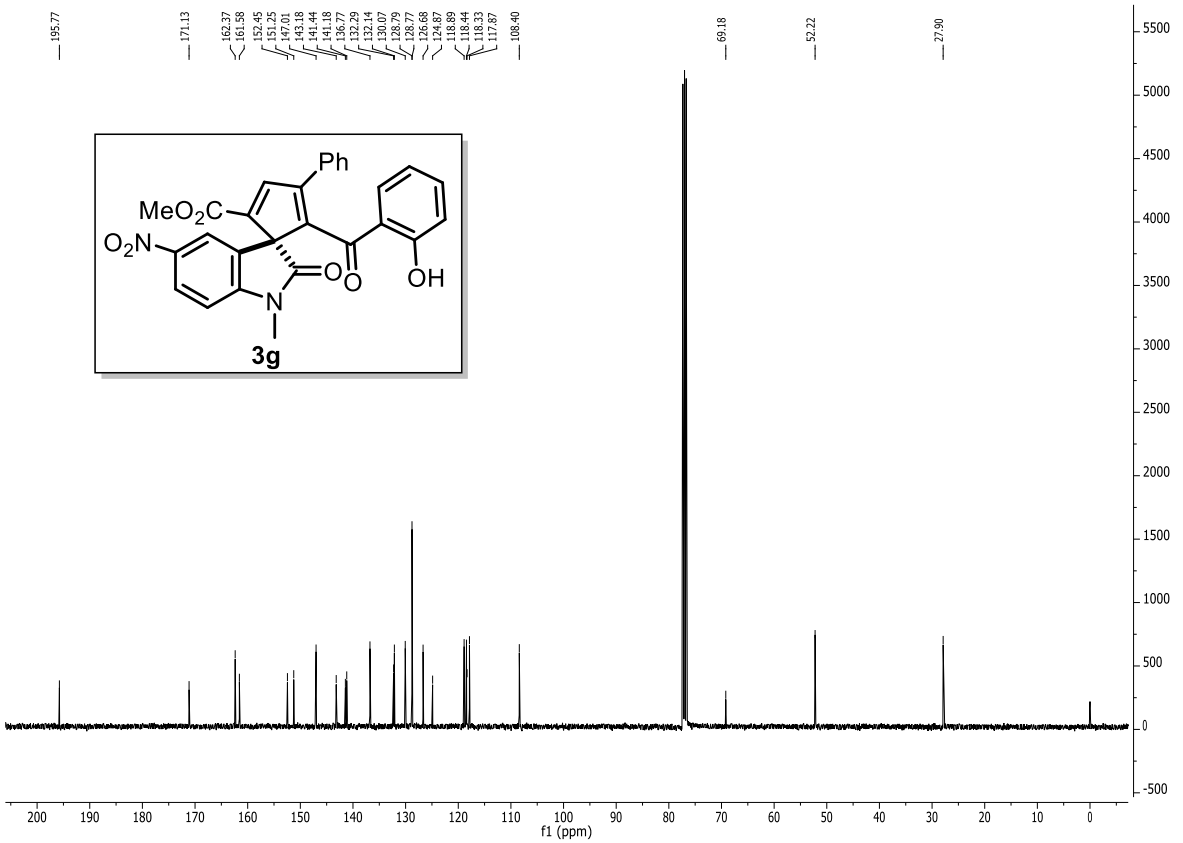
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



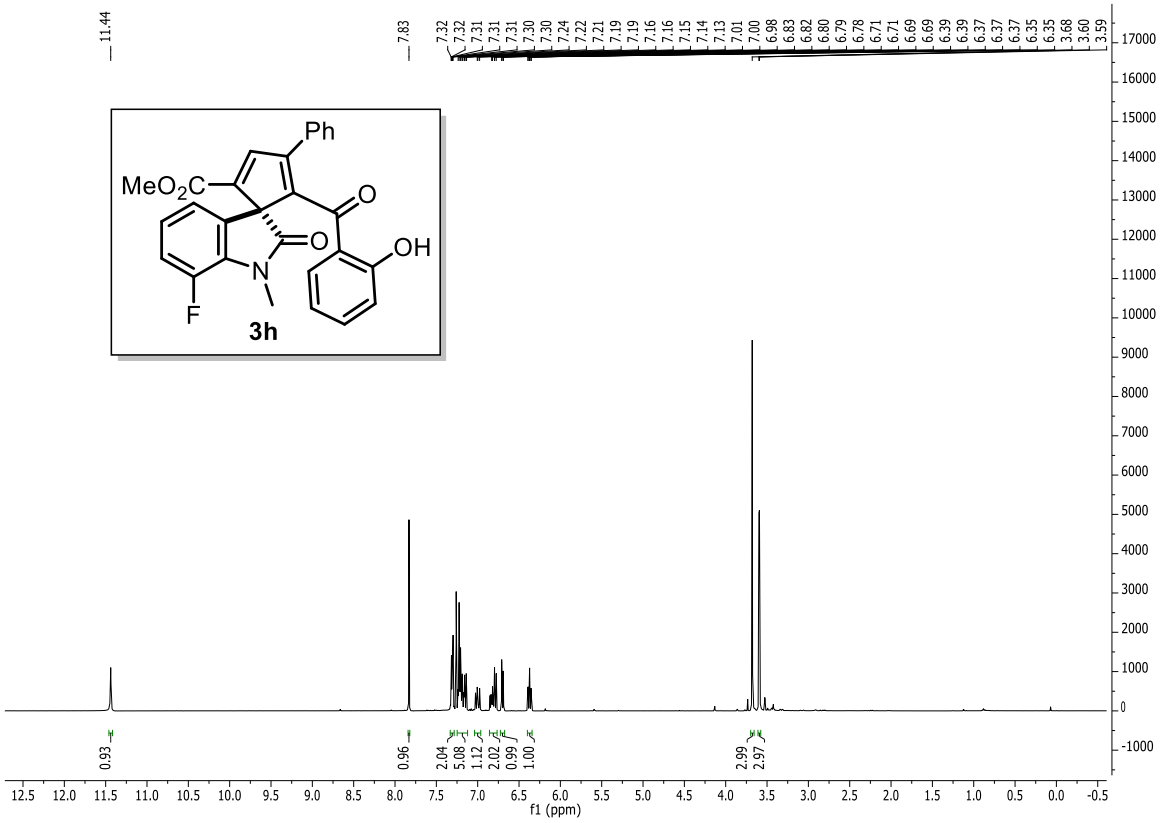
^{19}F NMR (377MHz, $CDCl_3$)



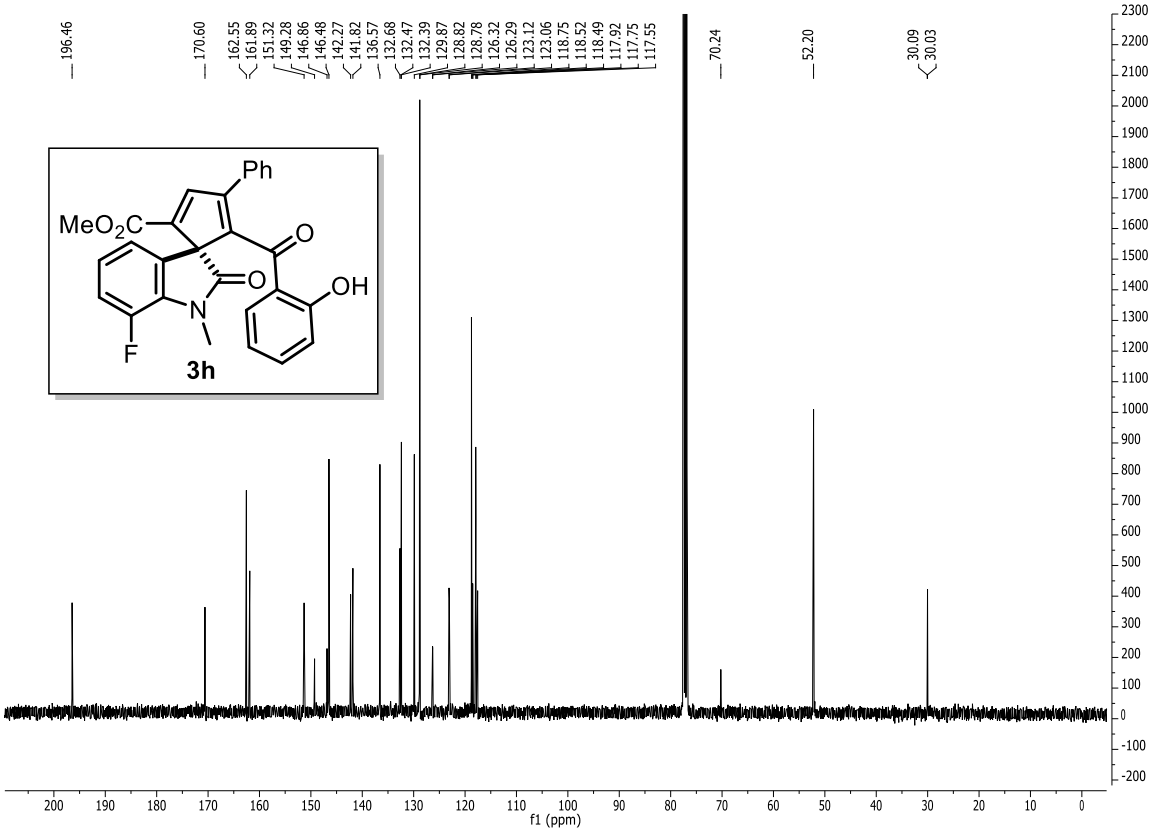
^{1}H NMR (400 MHz, $CDCl_3$)



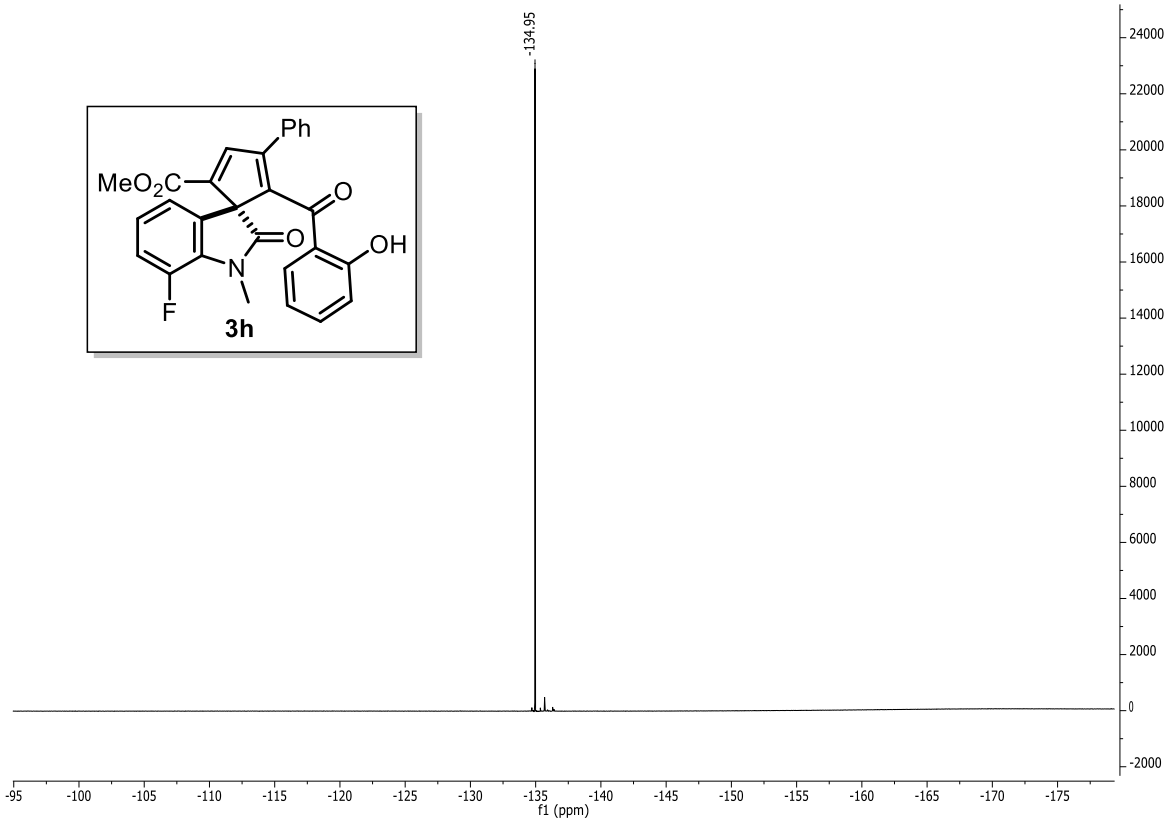
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



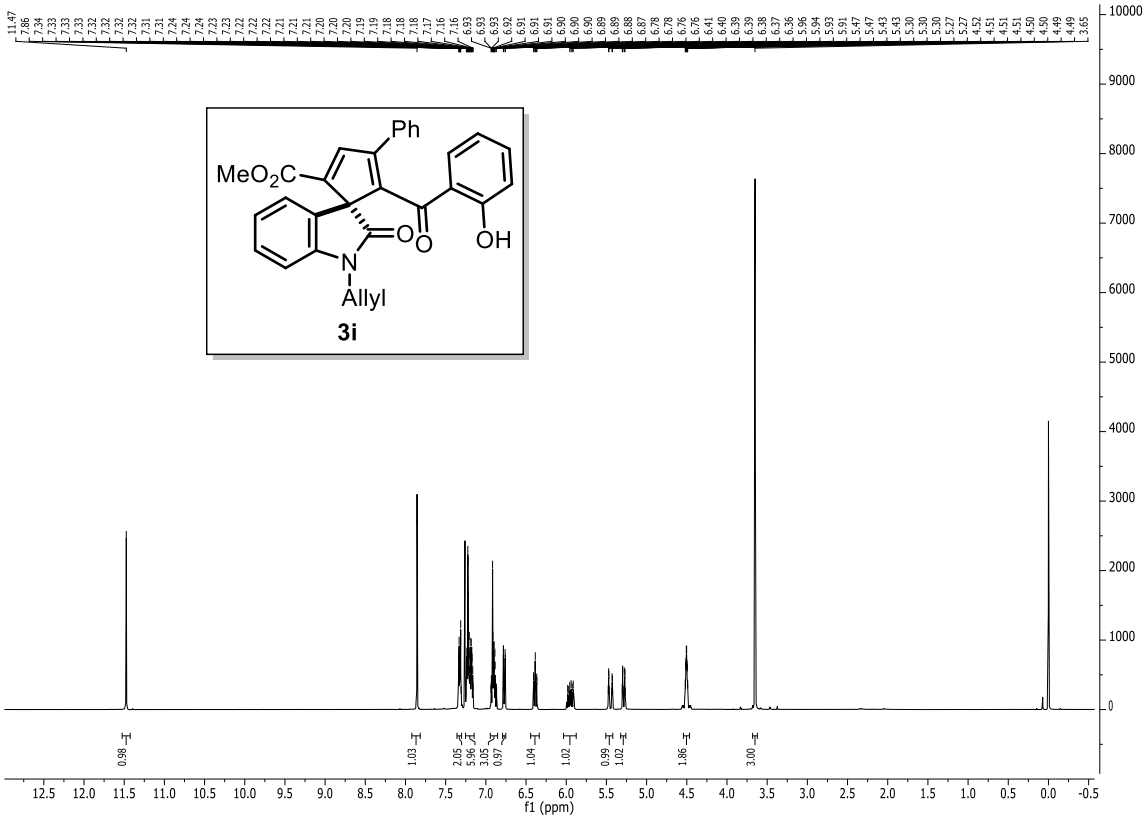
^{1}H NMR (400 MHz, $CDCl_3$)



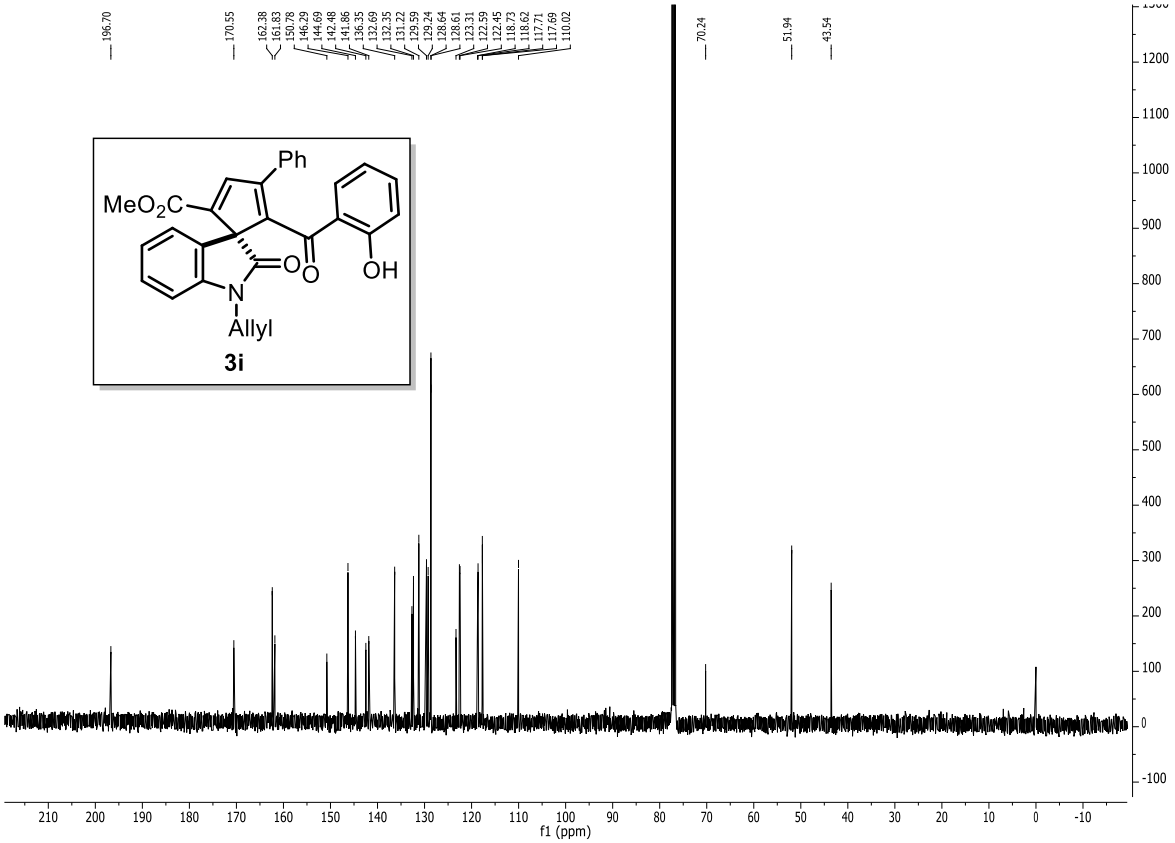
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



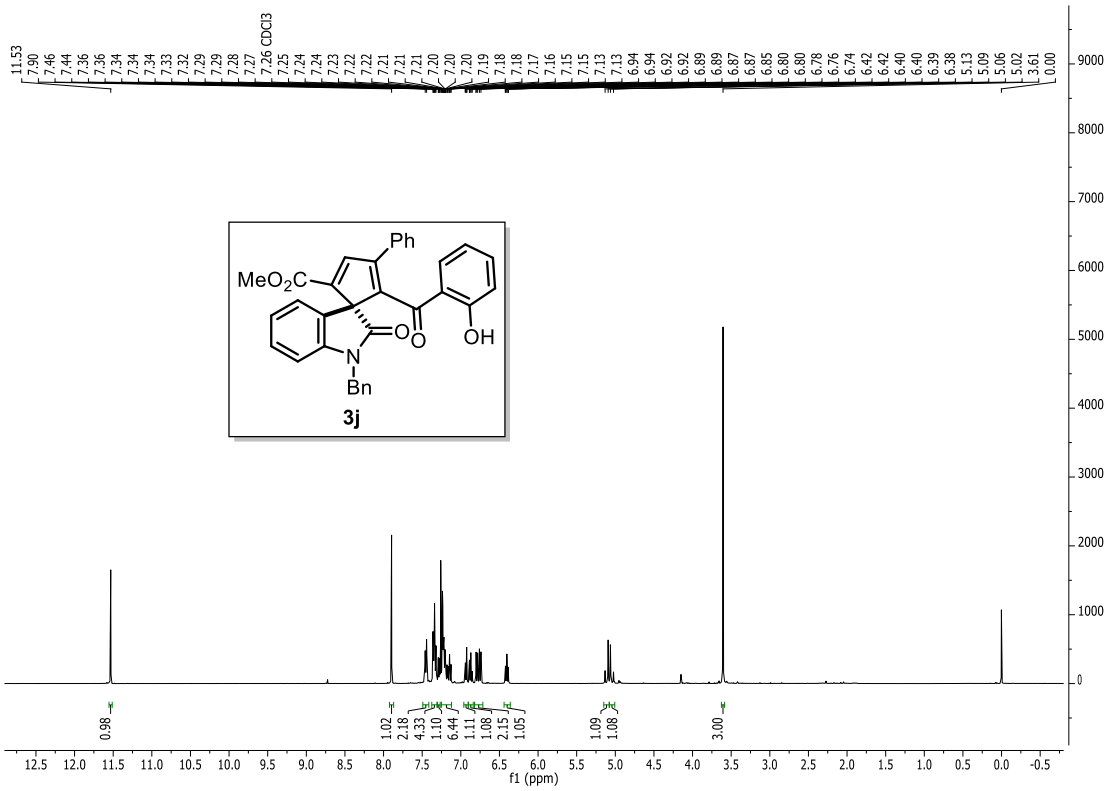
^{13}F NMR (377 MHz, $CDCl_3$)



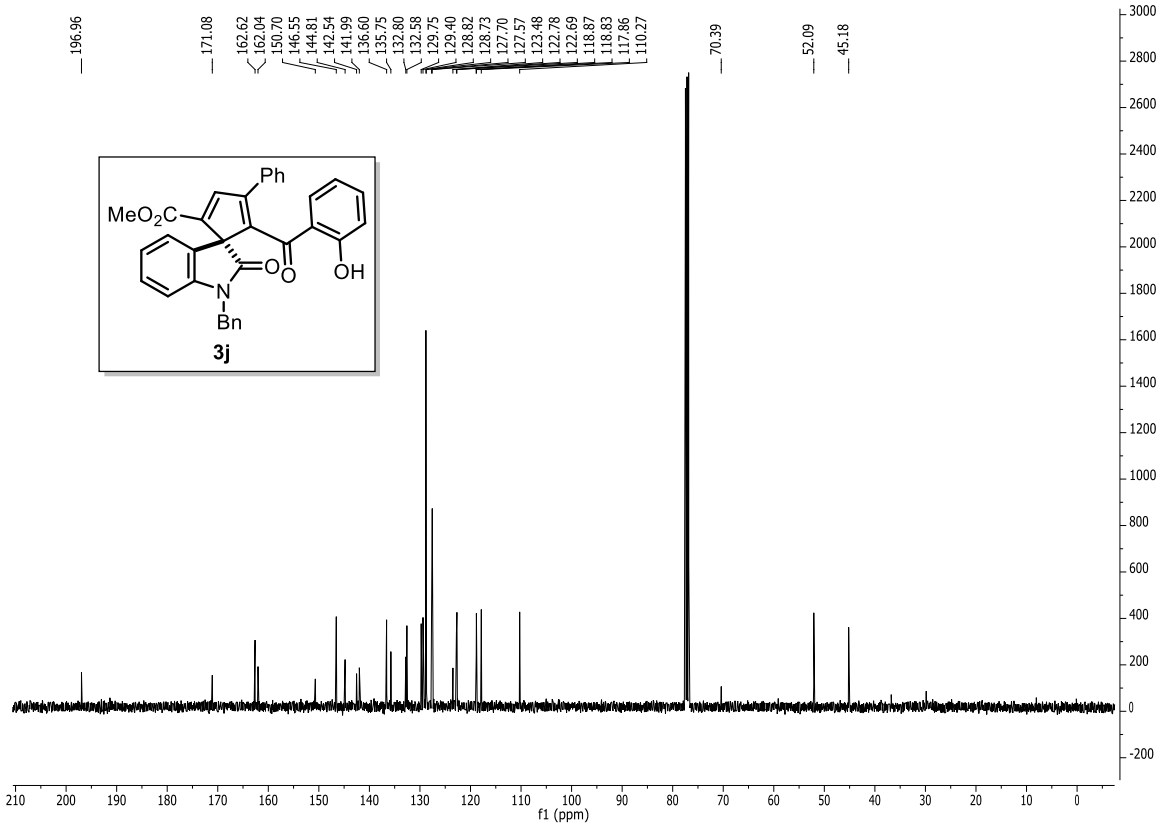
^{1}H NMR (400 MHz, $CDCl_3$)



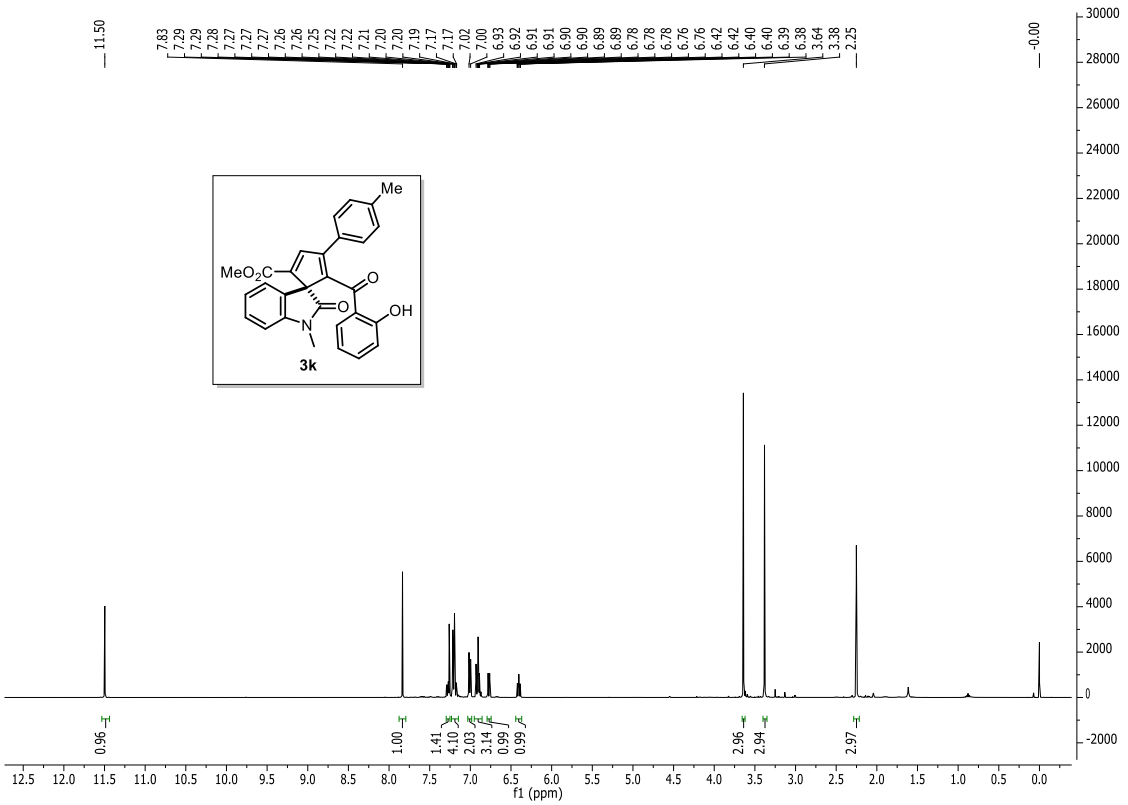
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



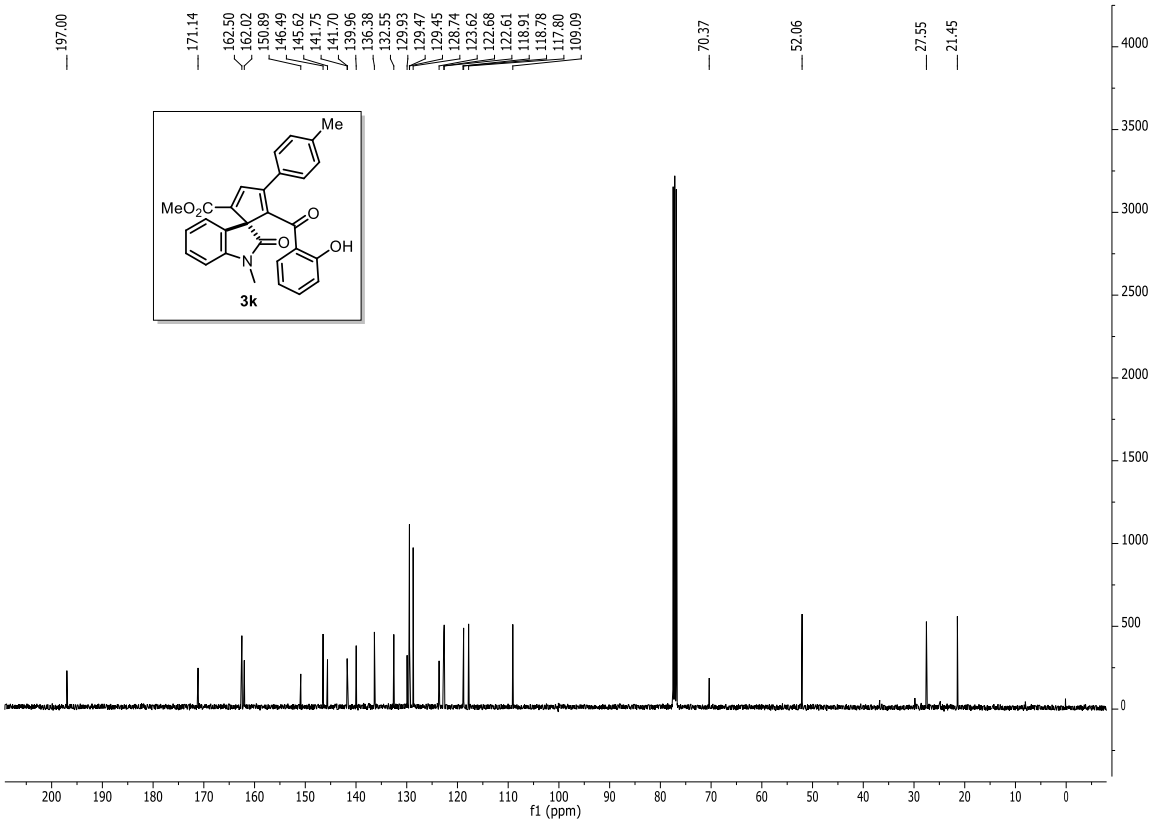
^{1}H NMR (400 MHz, $CDCl_3$)



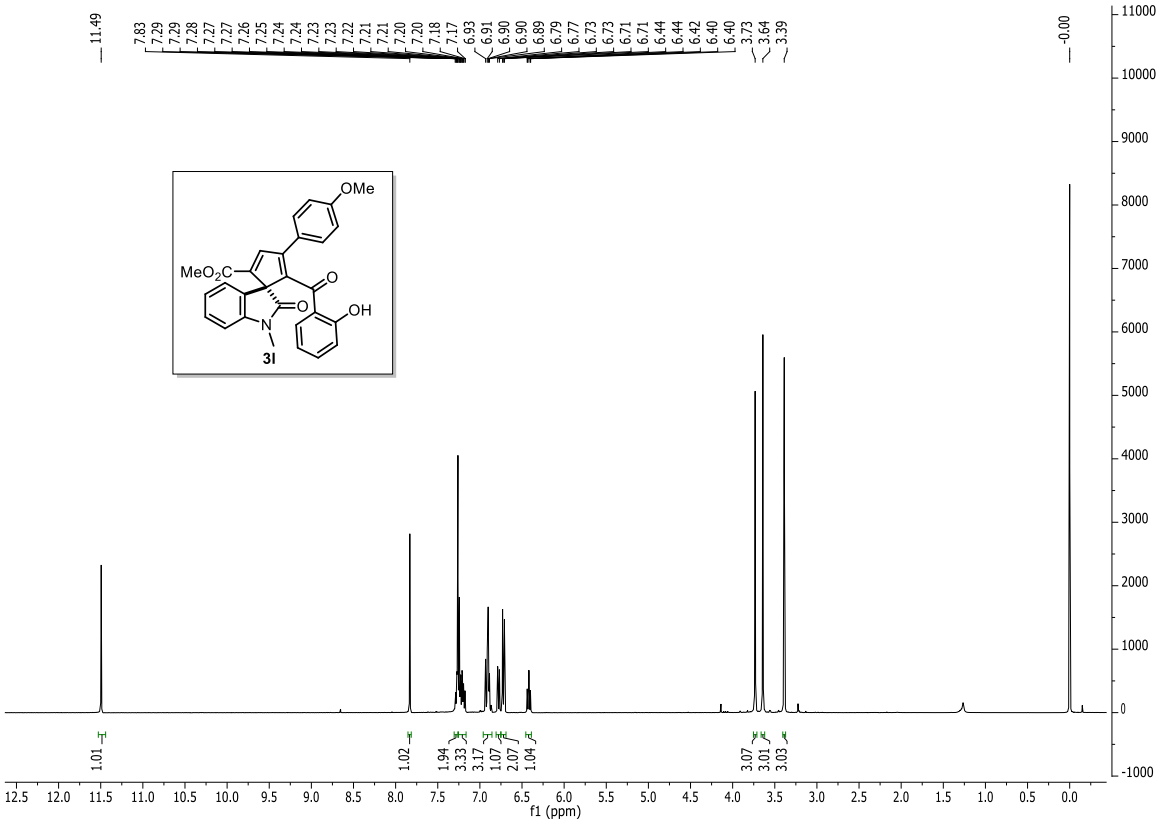
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



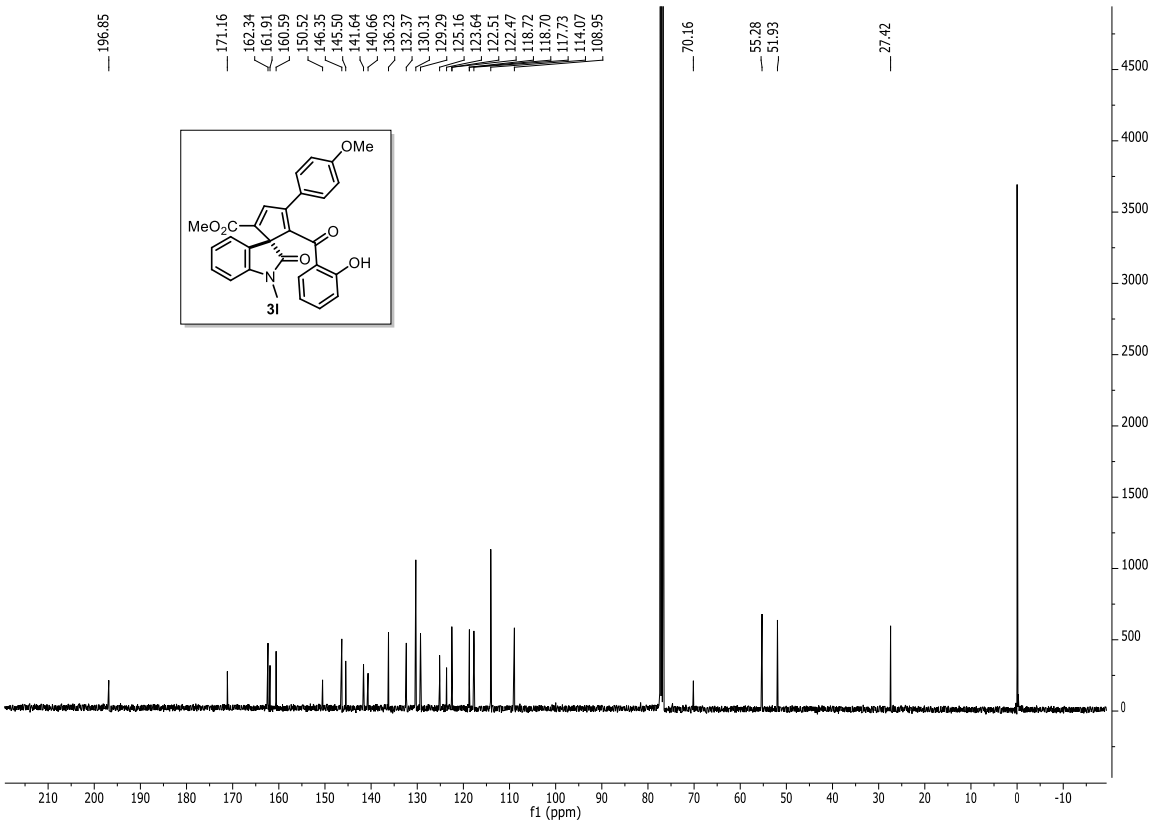
^{1}H NMR (400 MHz, $CDCl_3$)



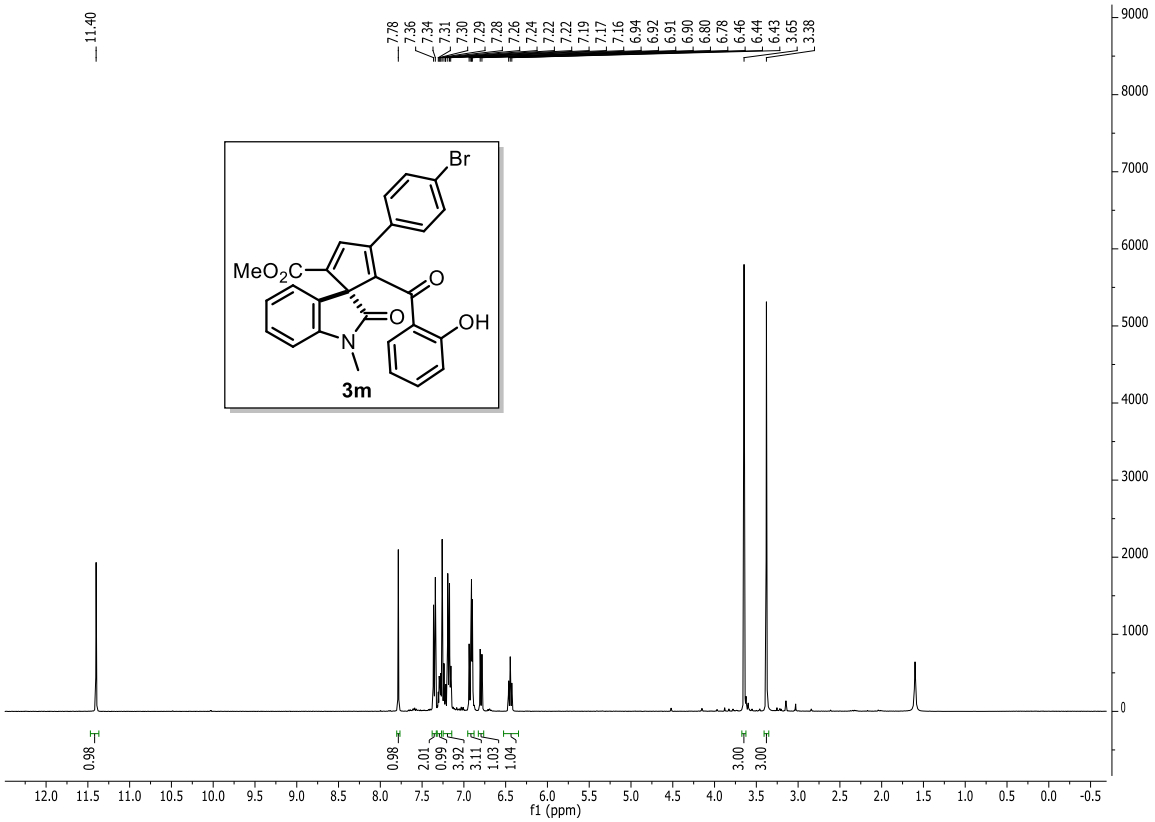
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



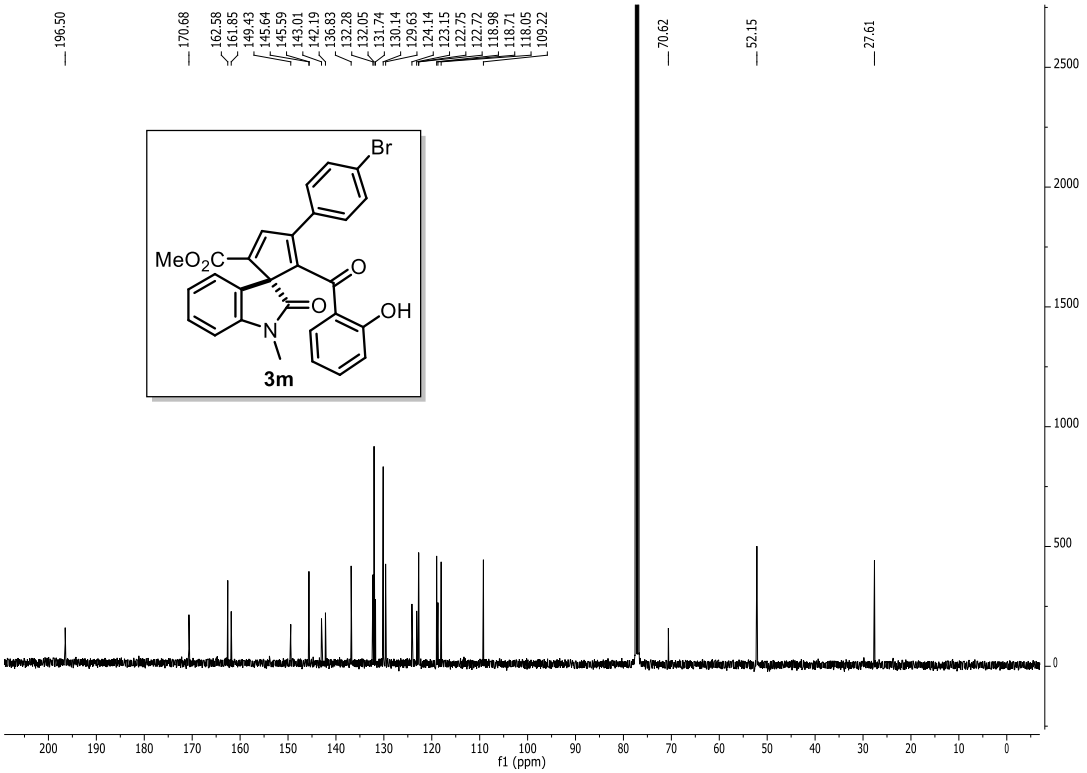
^{1}H NMR (400 MHz, $CDCl_3$)



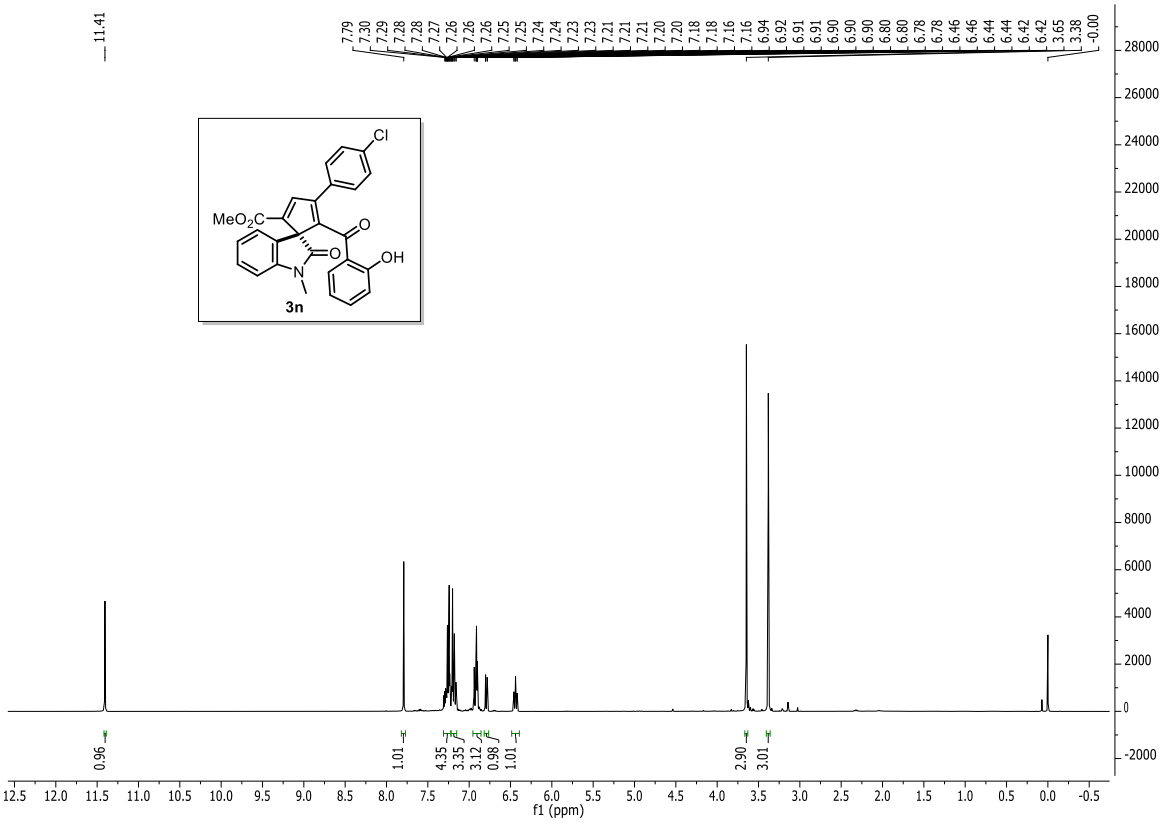
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



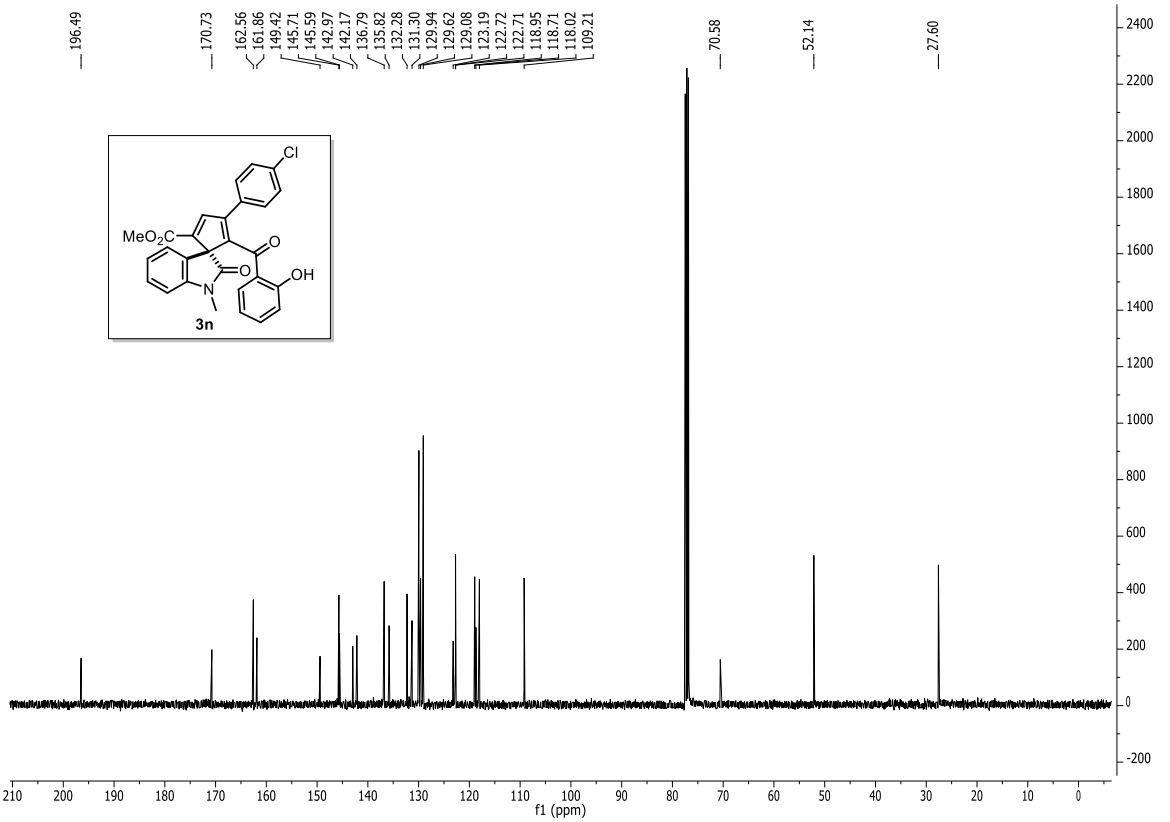
^{1}H NMR (400 MHz, $CDCl_3$)



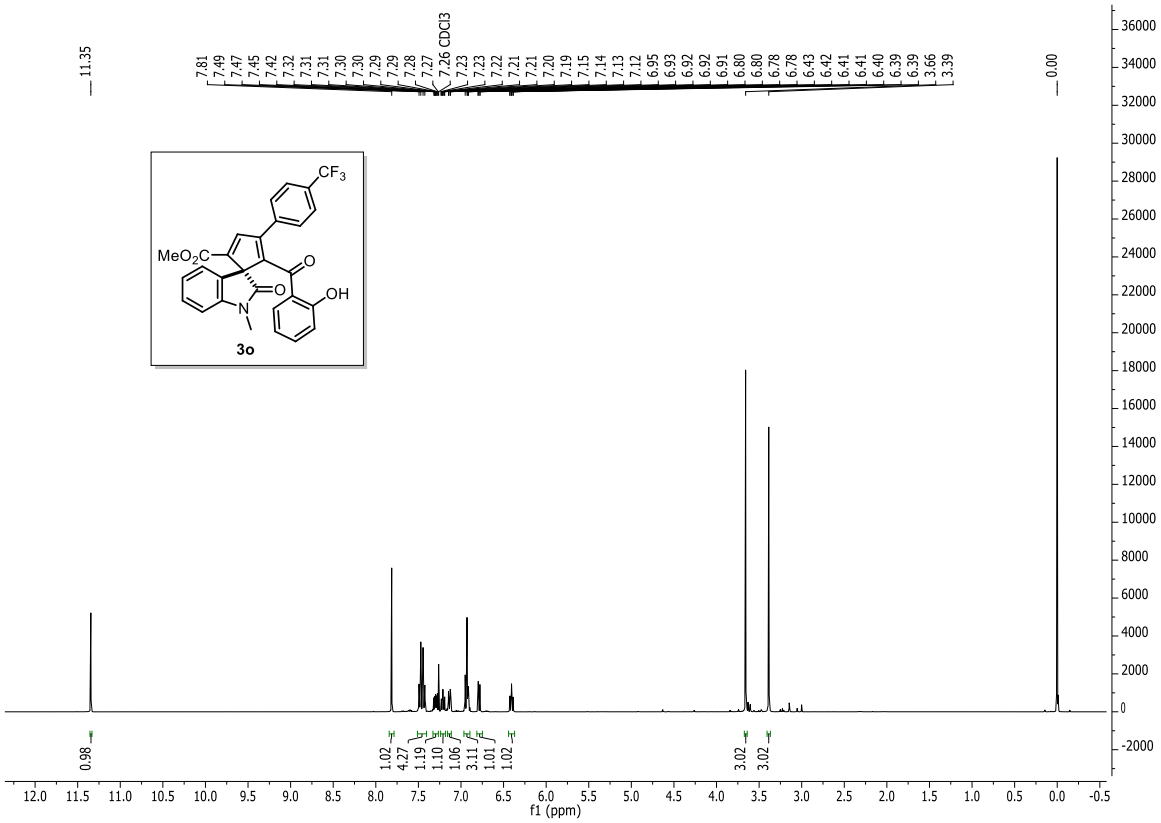
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



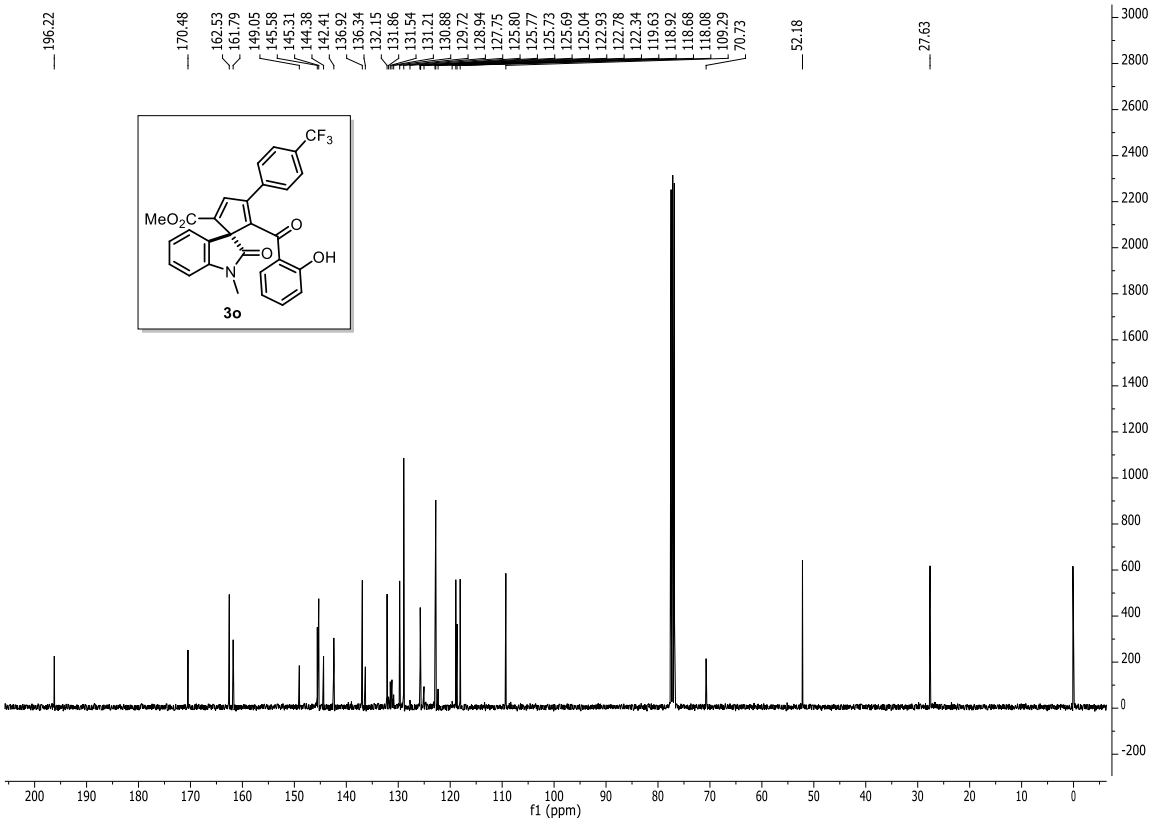
^{1}H NMR (400 MHz, $CDCl_3$)



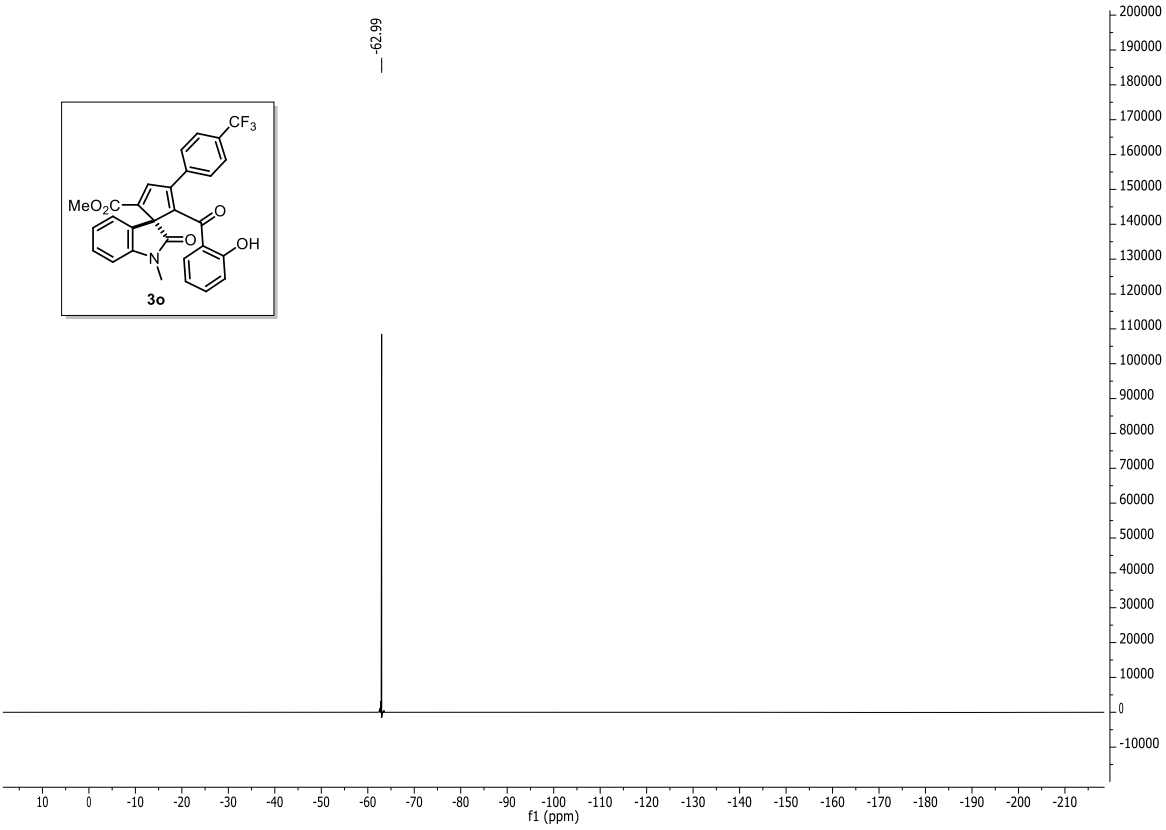
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



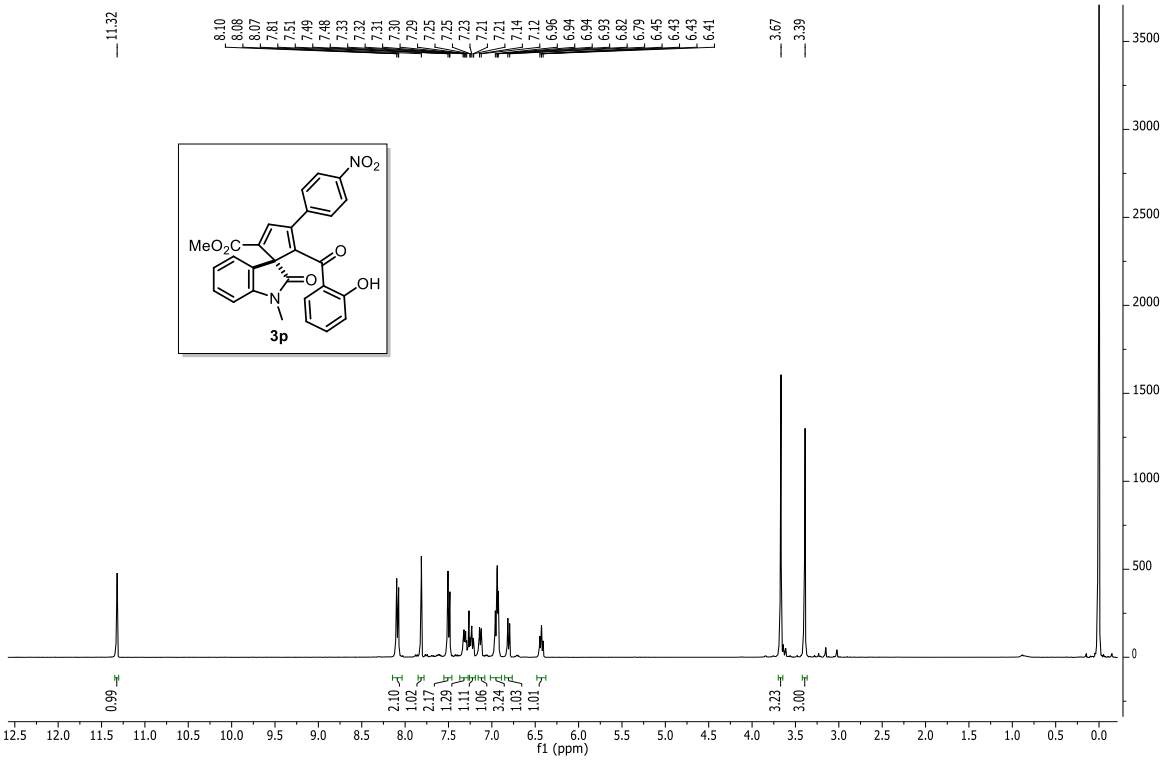
^{1}H NMR (400 MHz, $CDCl_3$)



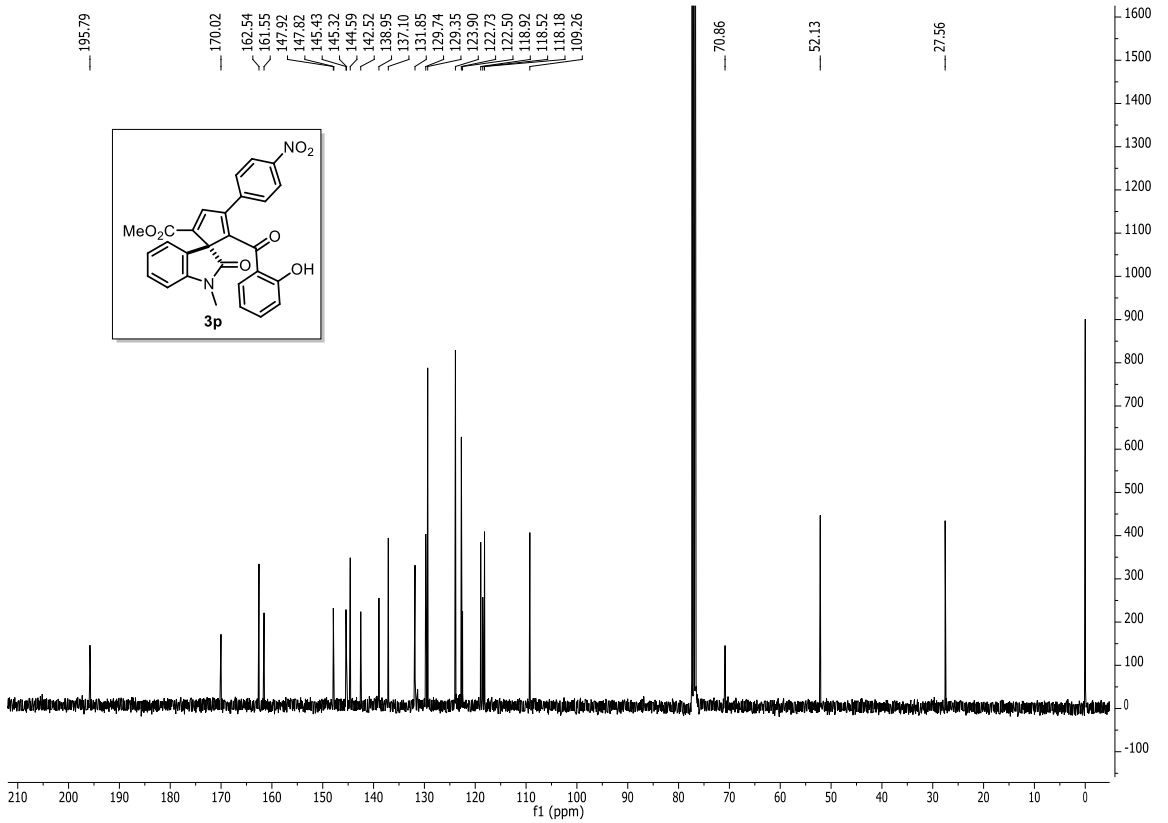
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



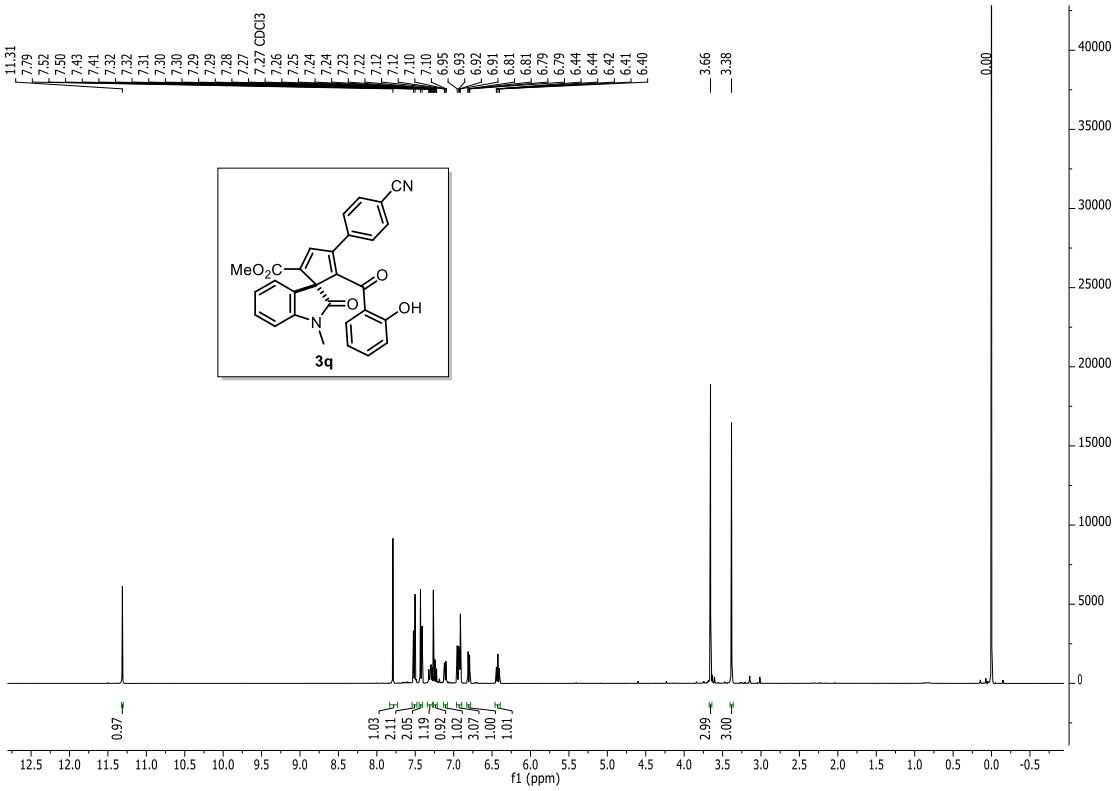
^{19}F NMR (100 MHz, $CDCl_3$)



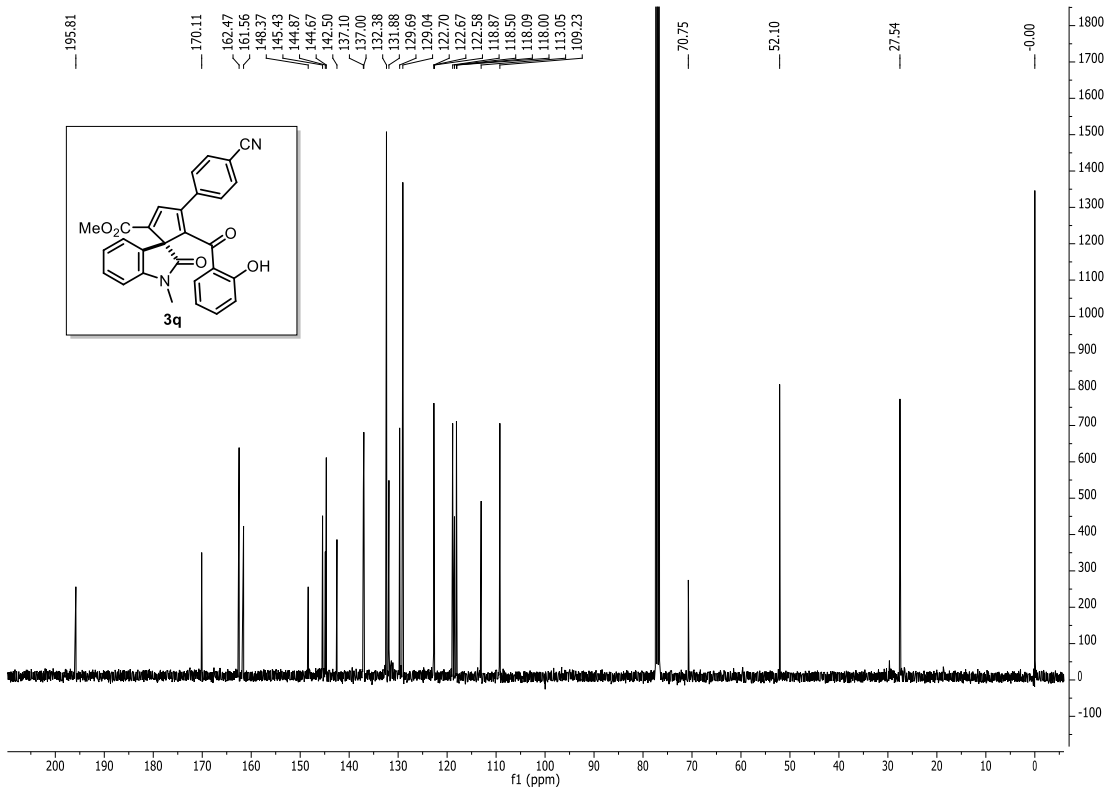
^{1}H NMR (400 MHz, $CDCl_3$)



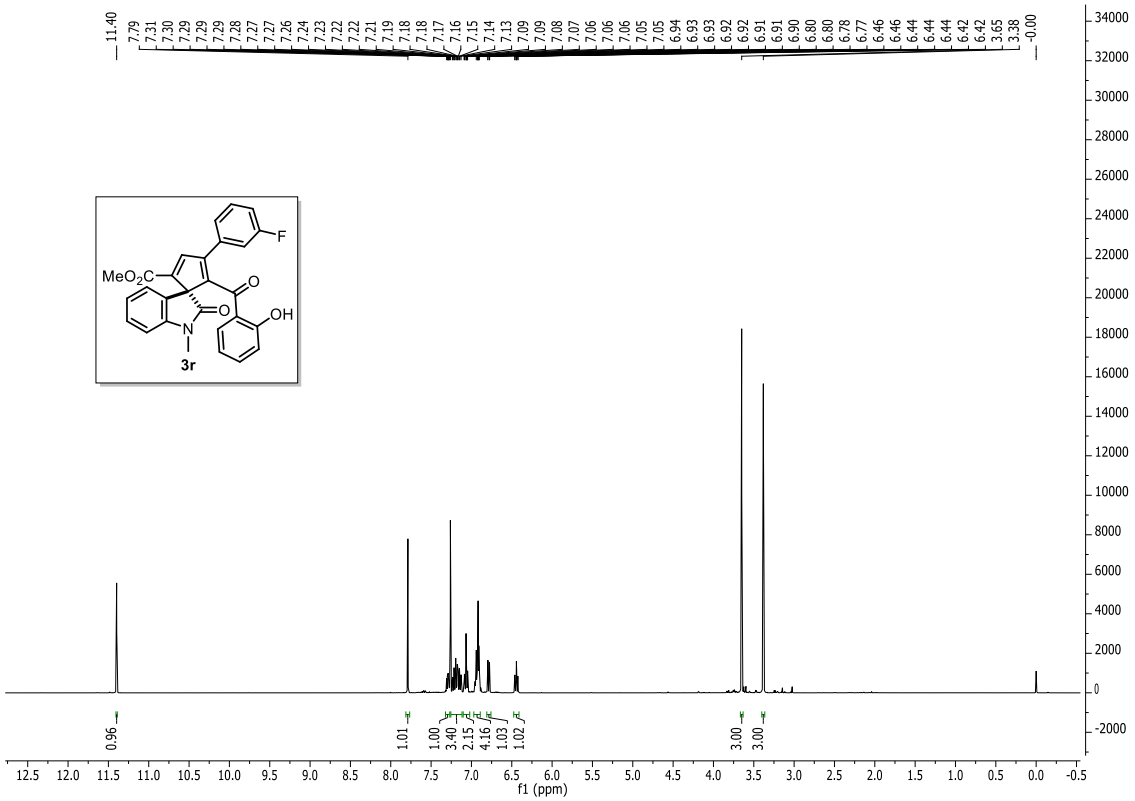
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



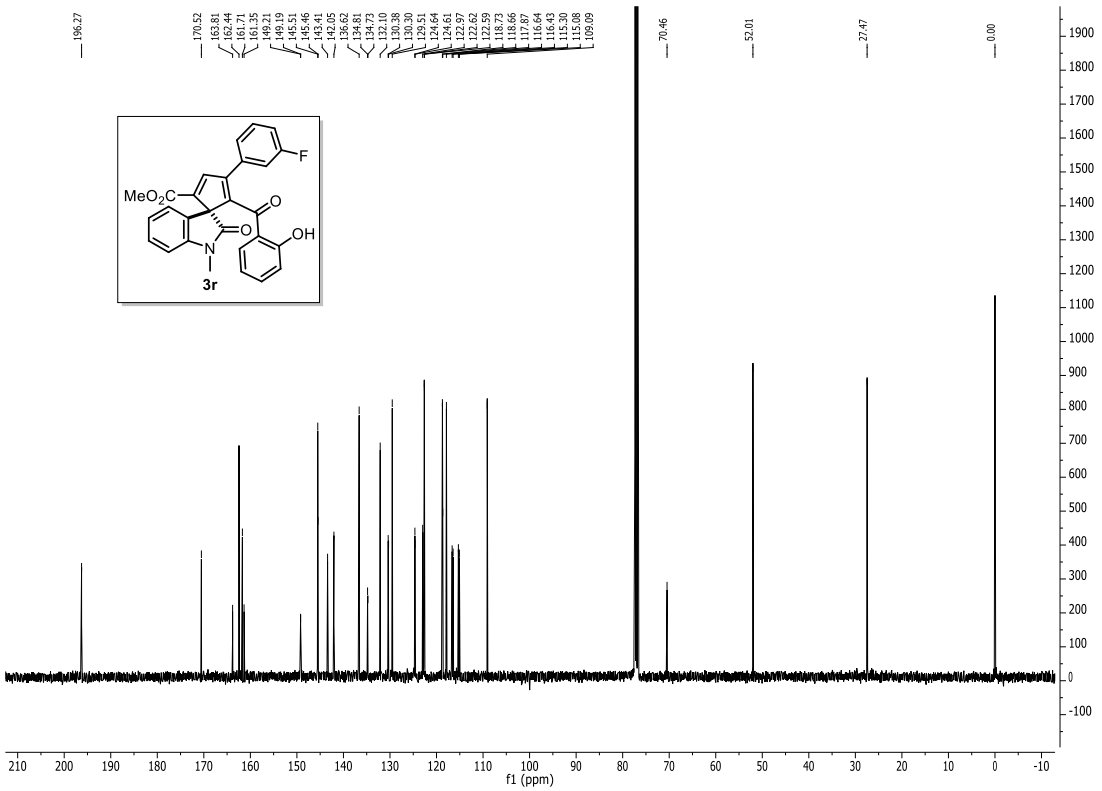
^{1}H NMR (400 MHz, $CDCl_3$)



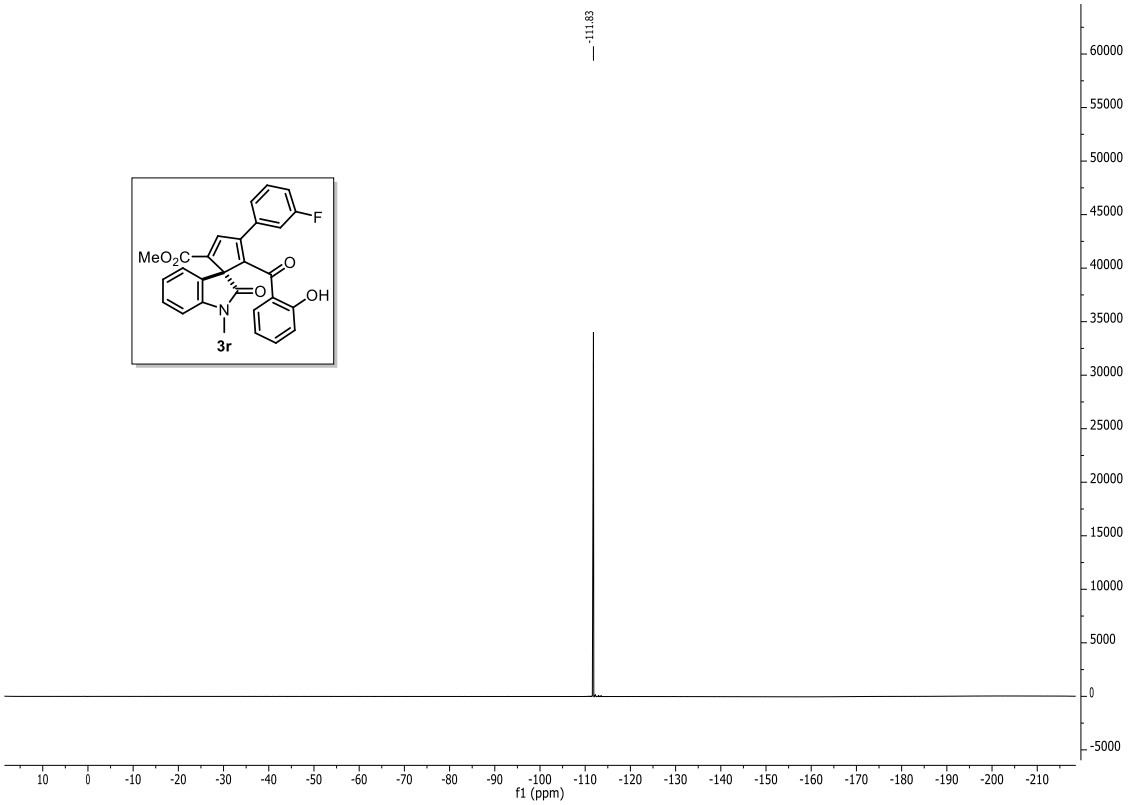
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



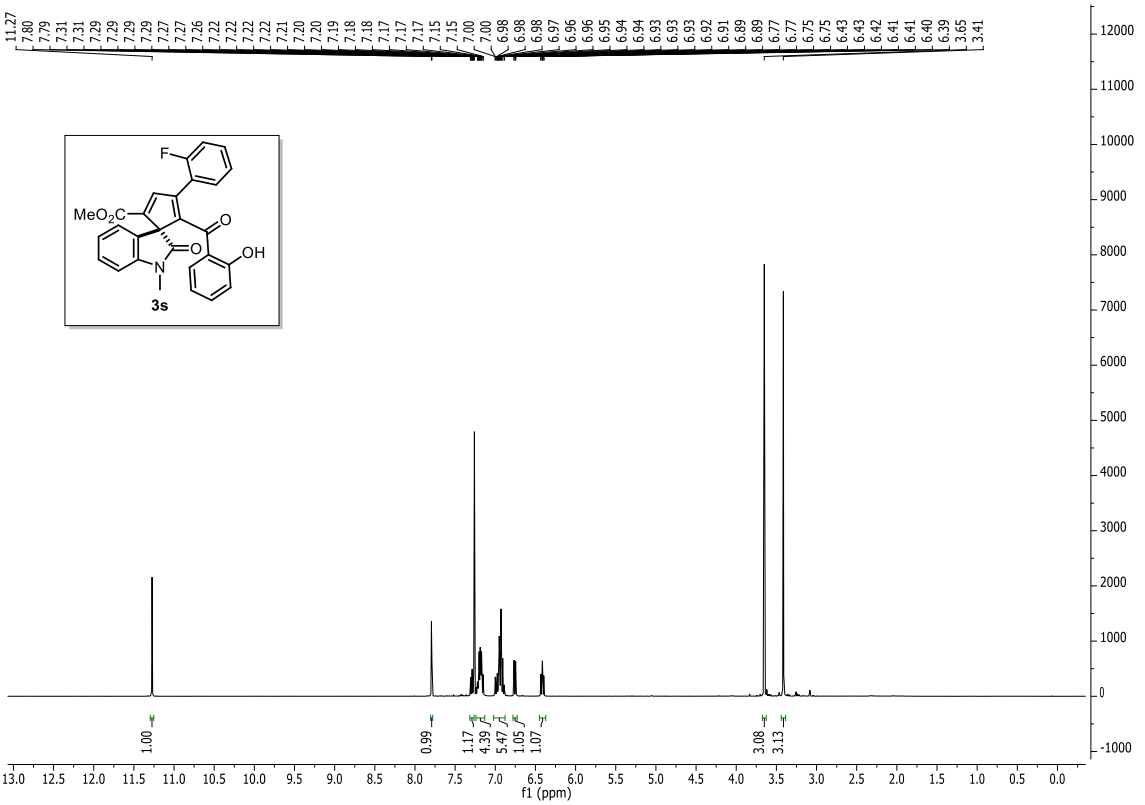
^{1}H NMR (400 MHz, $CDCl_3$)



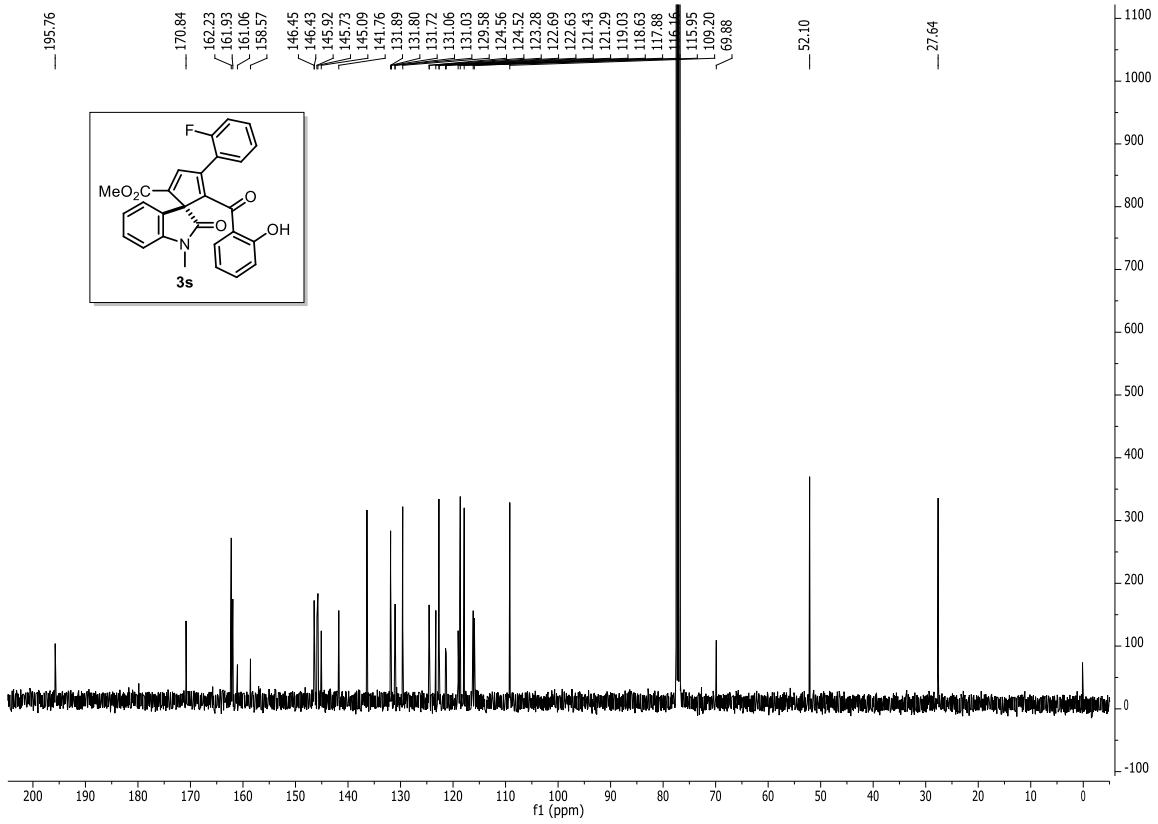
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



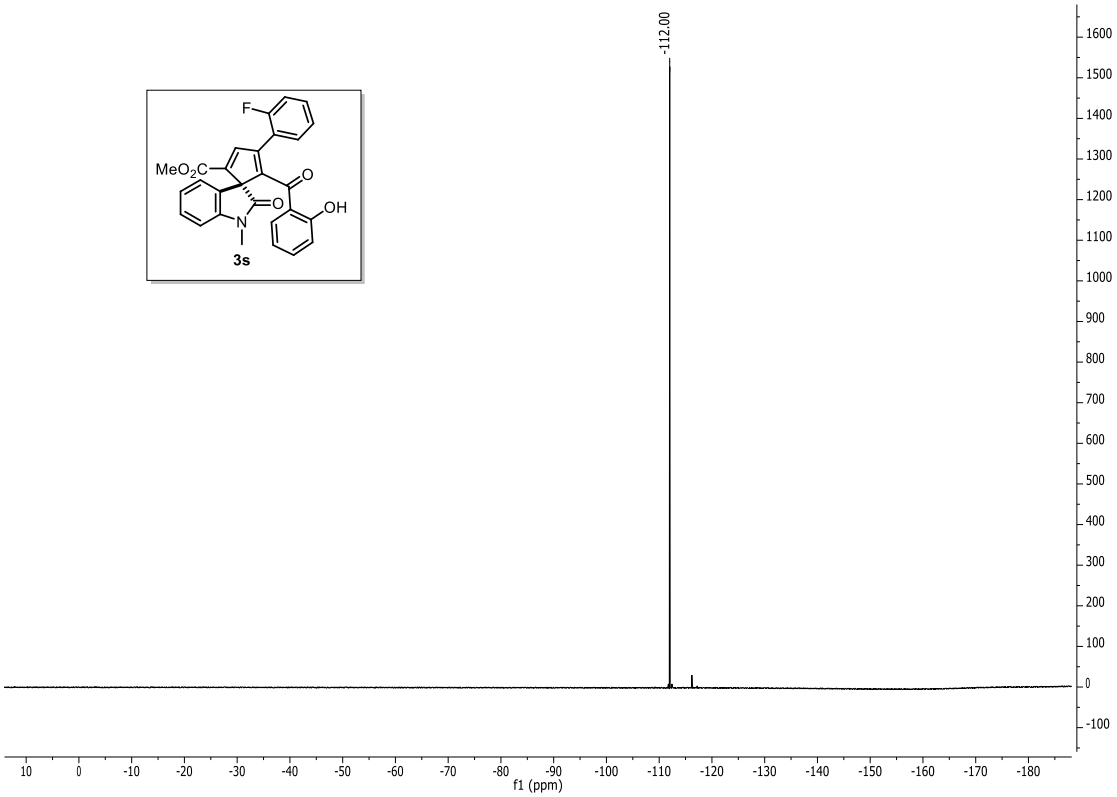
^{19}F NMR (100 MHz, $CDCl_3$)



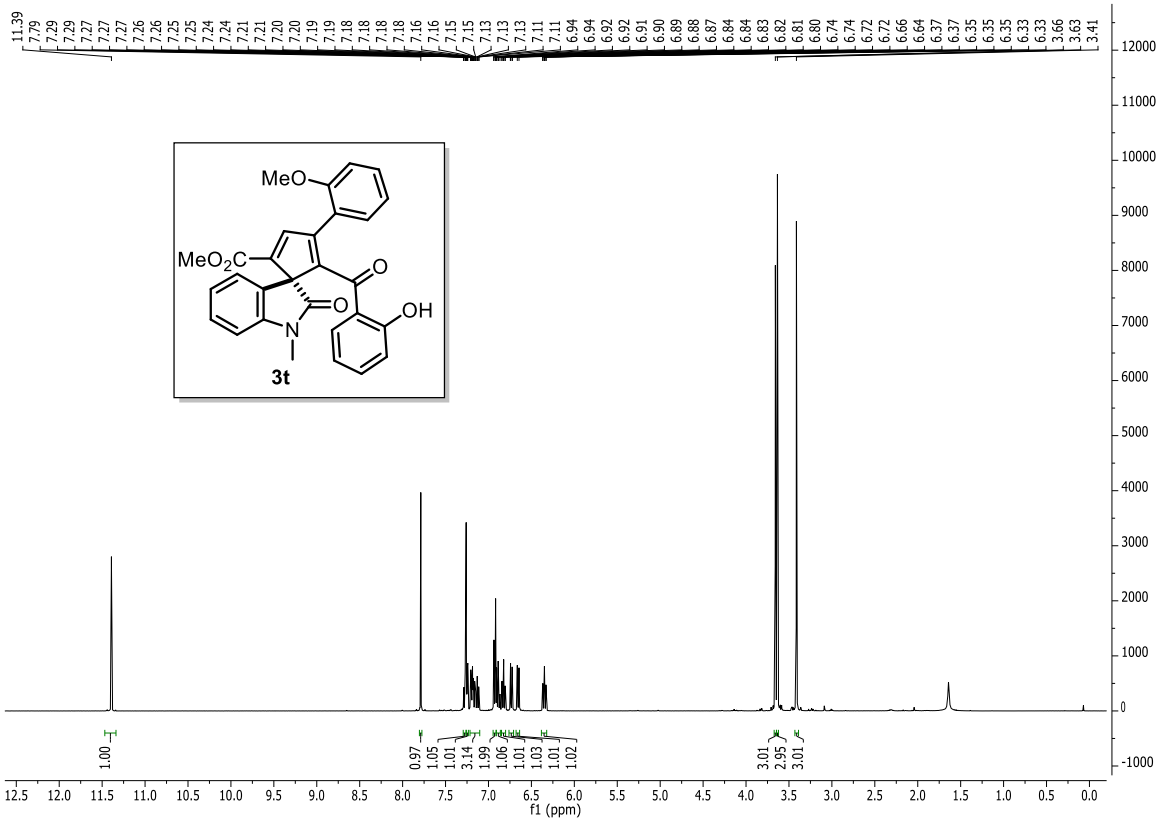
^{1}H NMR (400 MHz, $CDCl_3$)



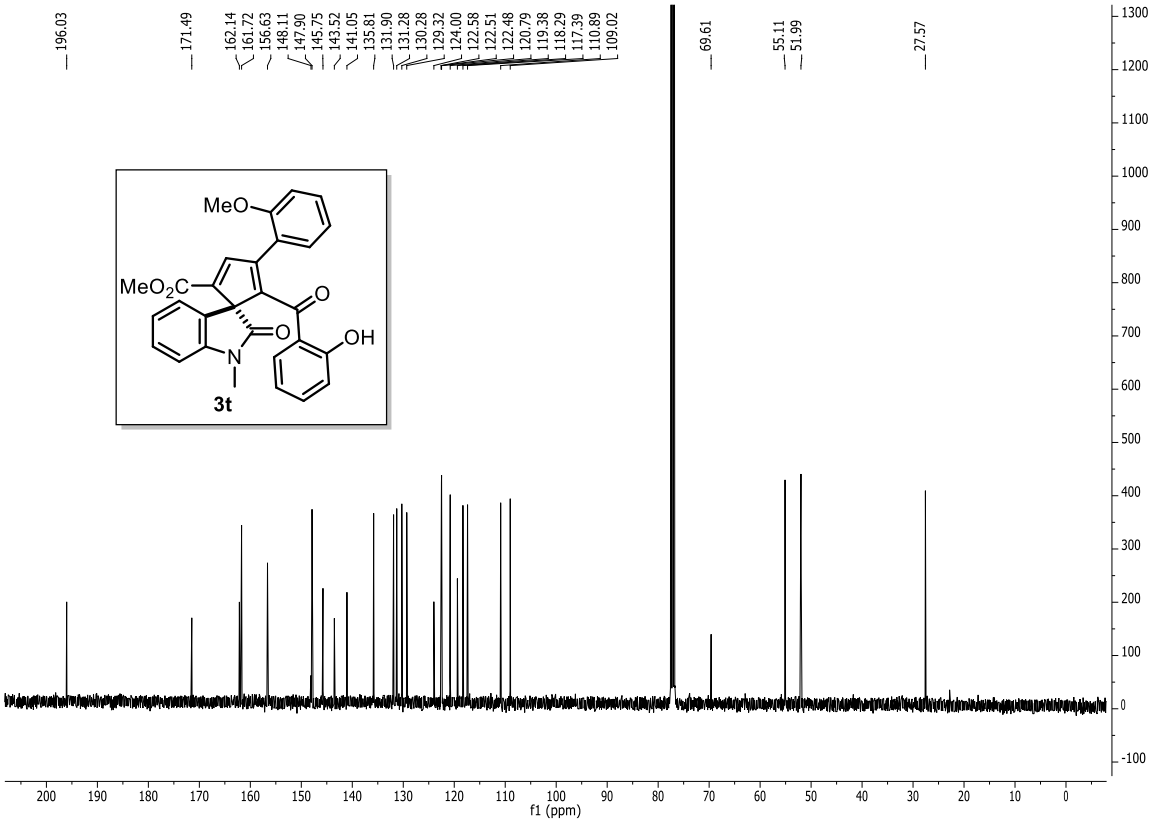
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



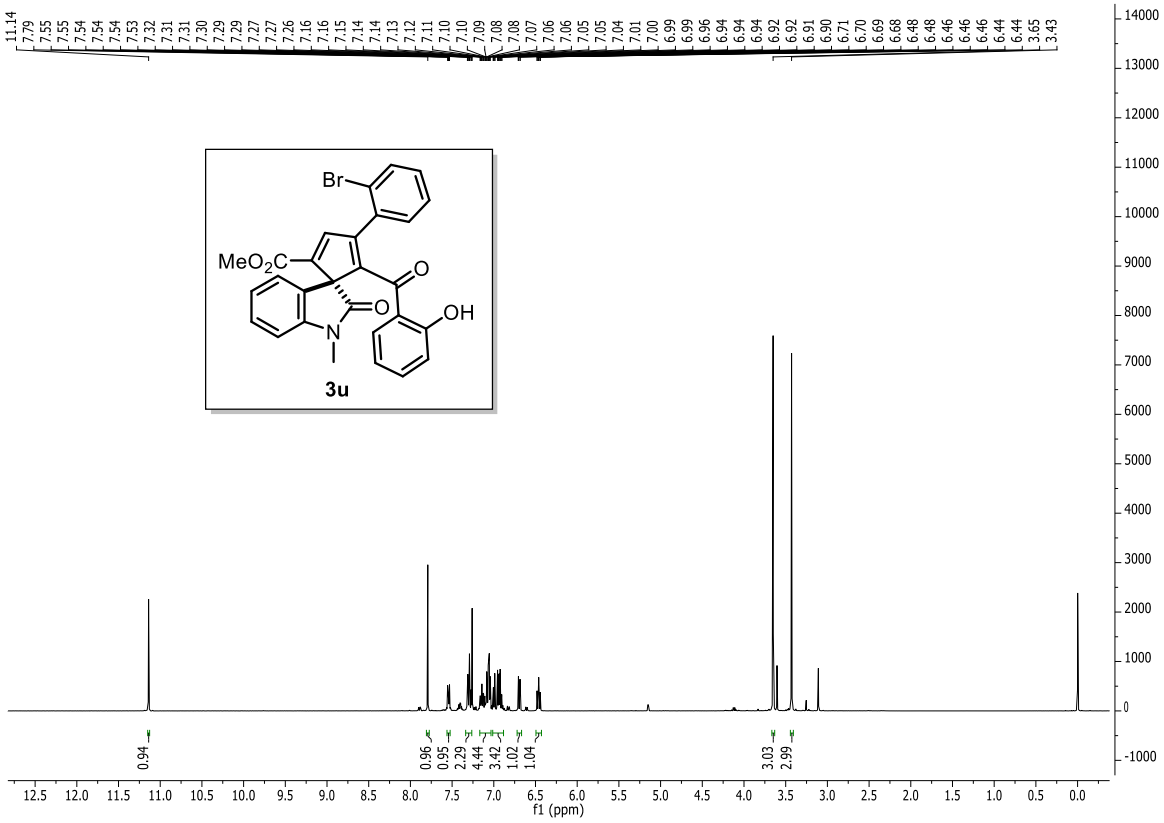
^{19}F NMR (377 MHz, $CDCl_3$)



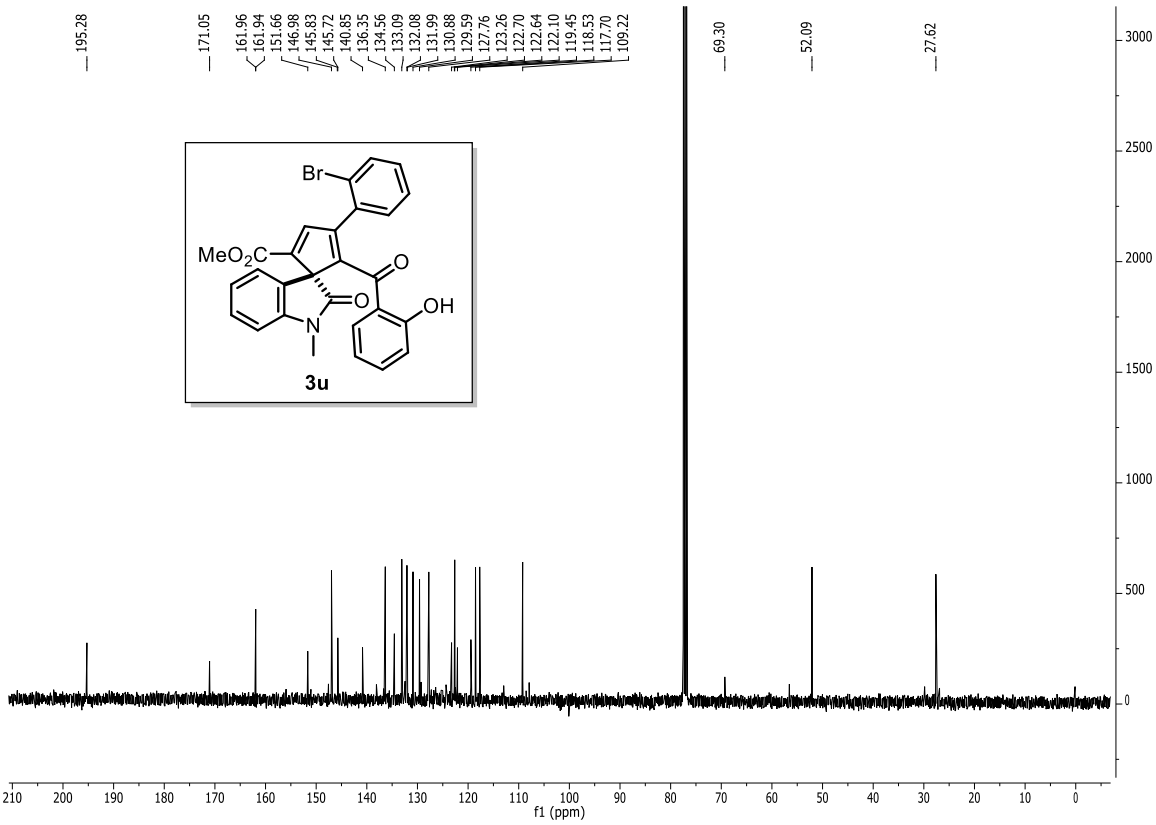
^{1}H NMR (400 MHz, $CDCl_3$)



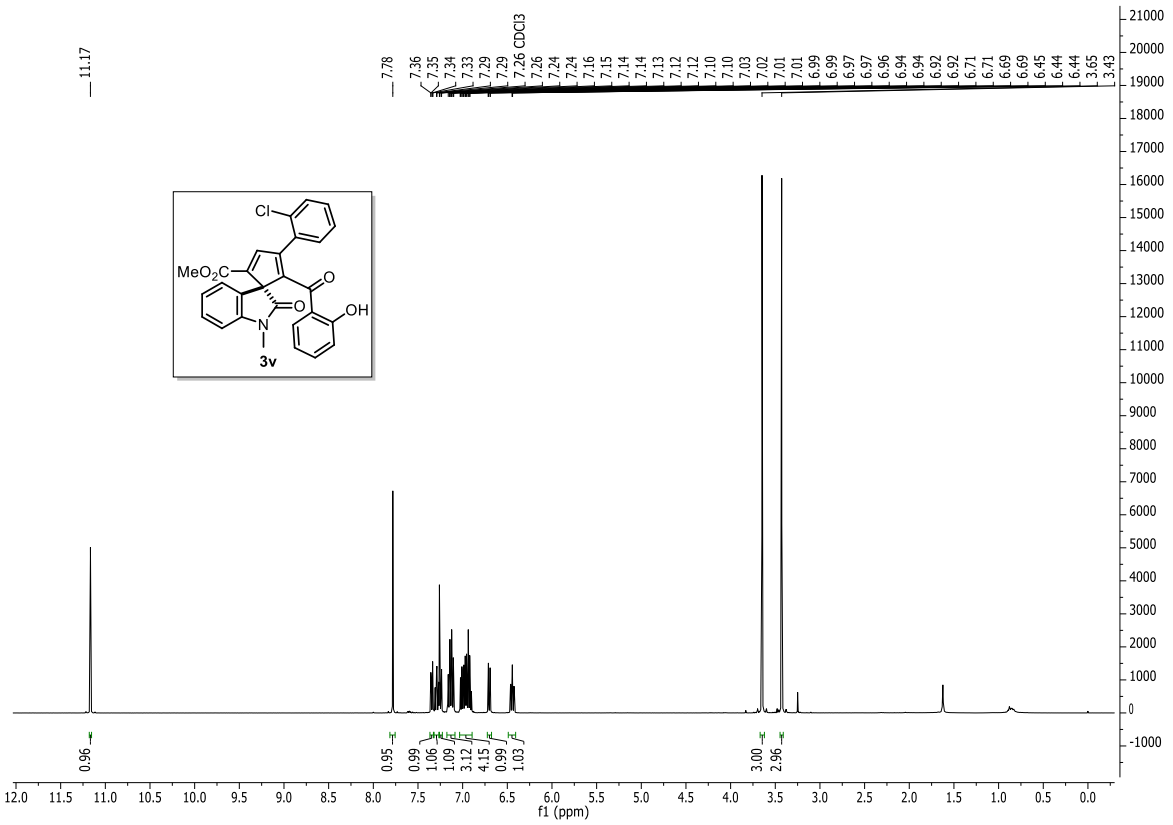
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



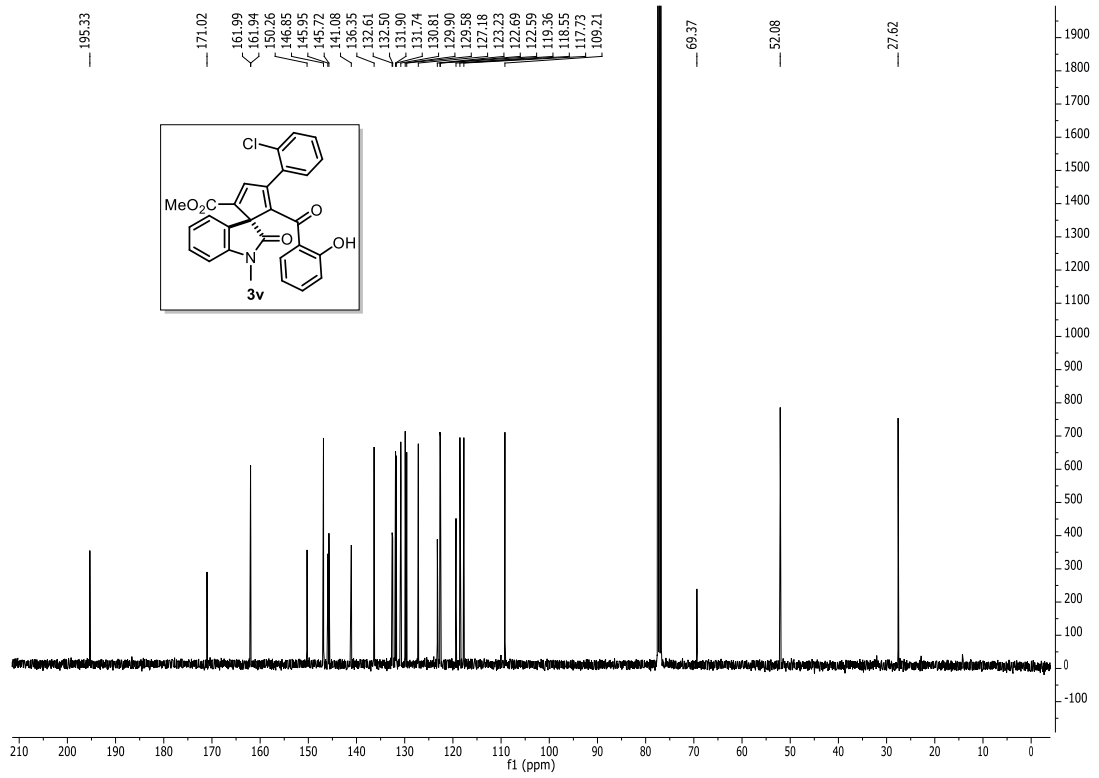
^{1}H NMR (400 MHz, $CDCl_3$)



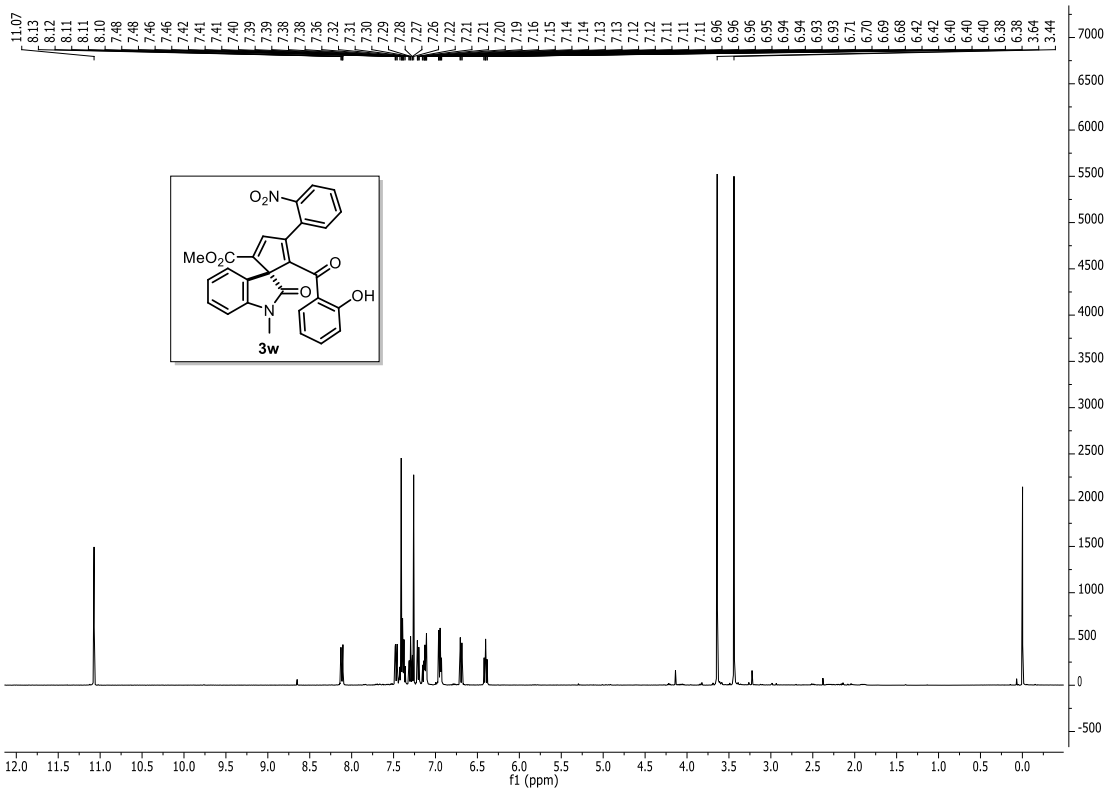
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



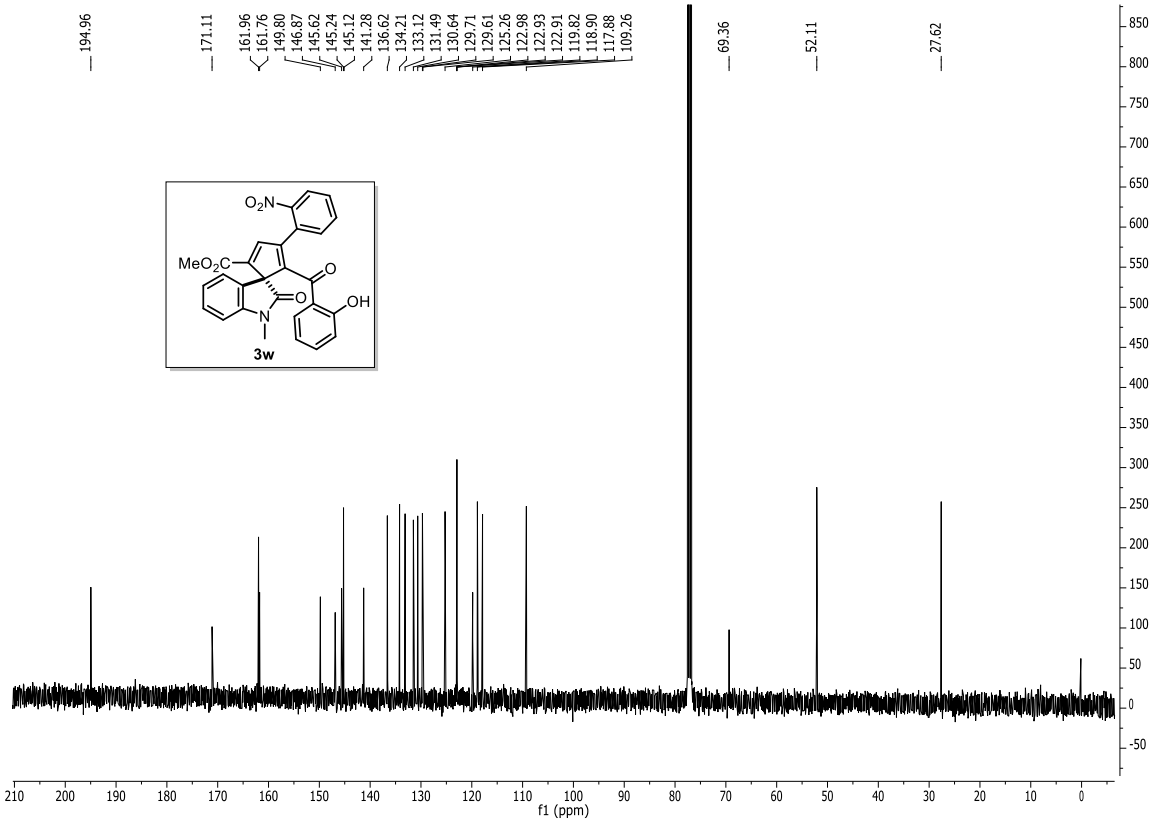
^{1}H NMR (400 MHz, $CDCl_3$)



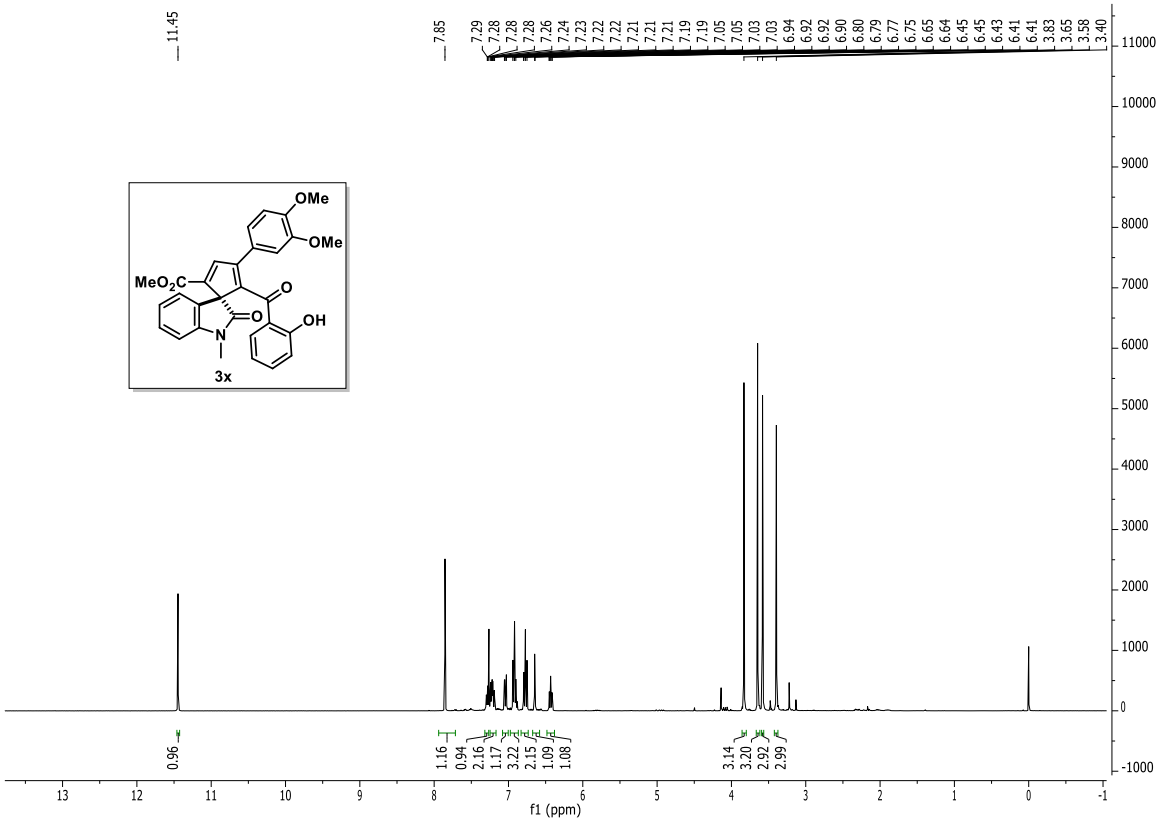
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



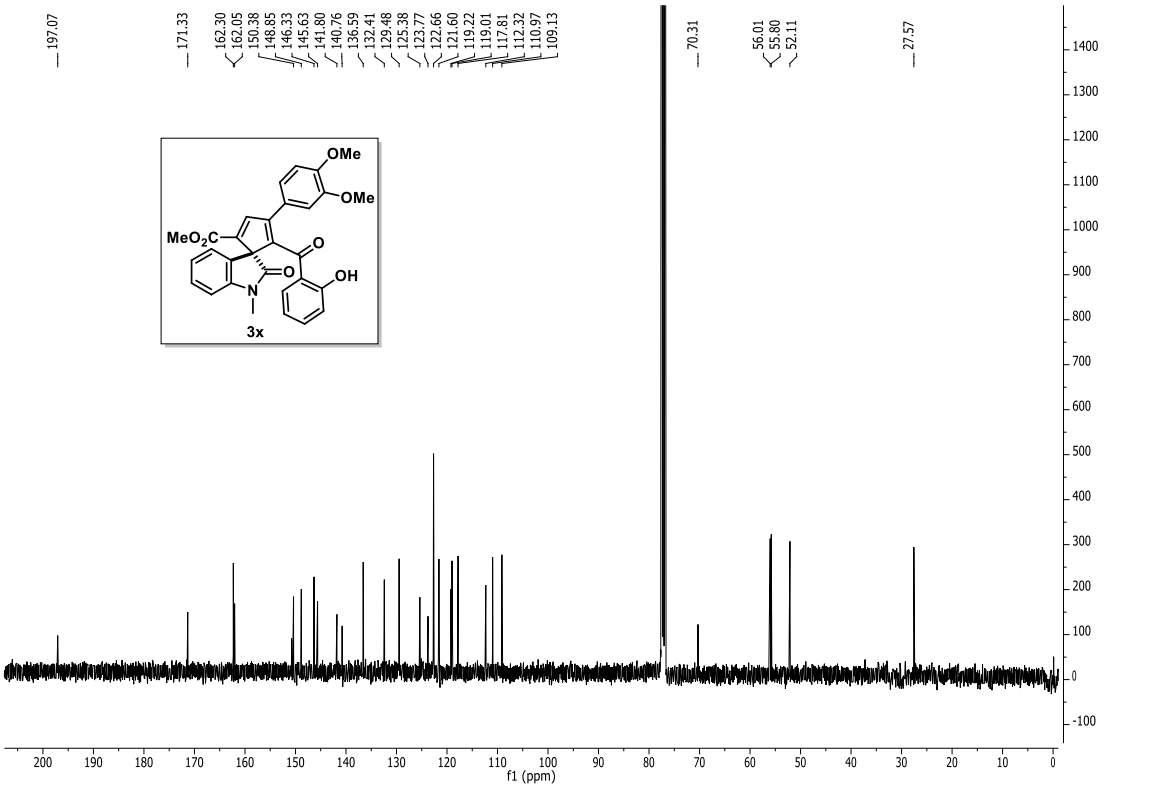
^{1}H NMR (400 MHz, $CDCl_3$)



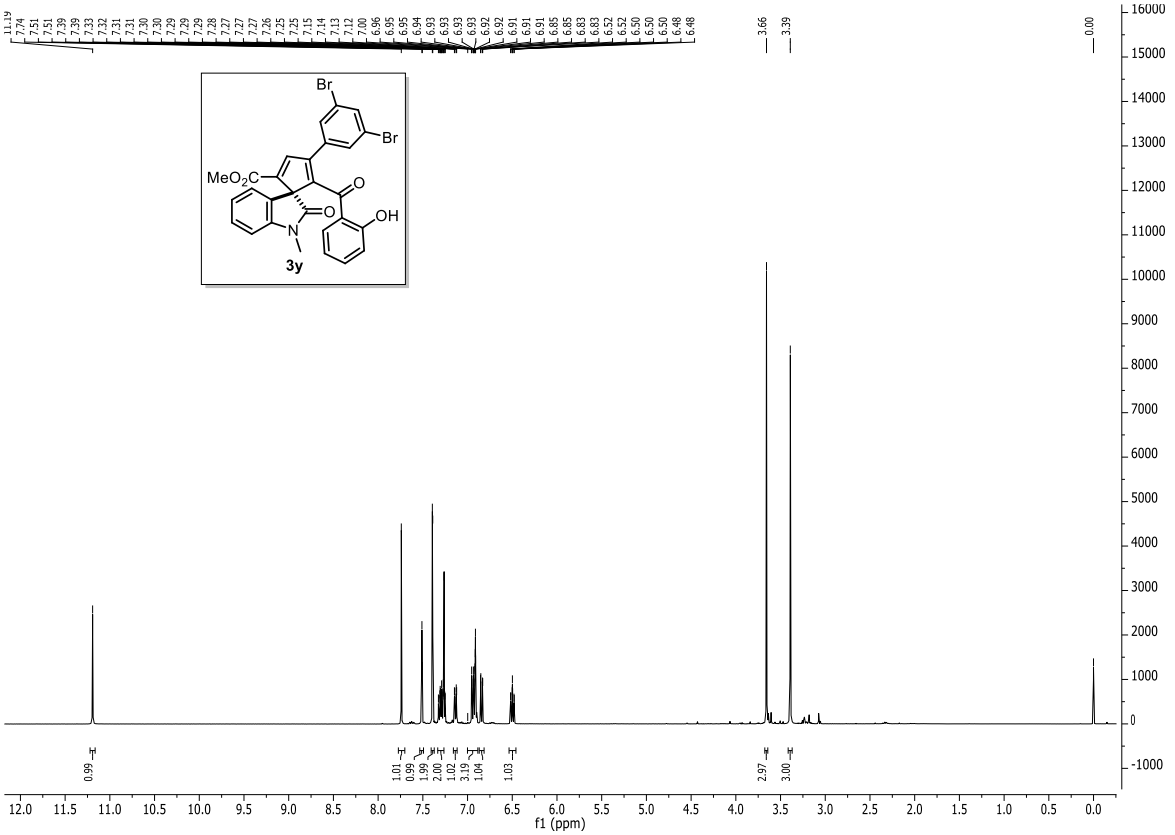
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



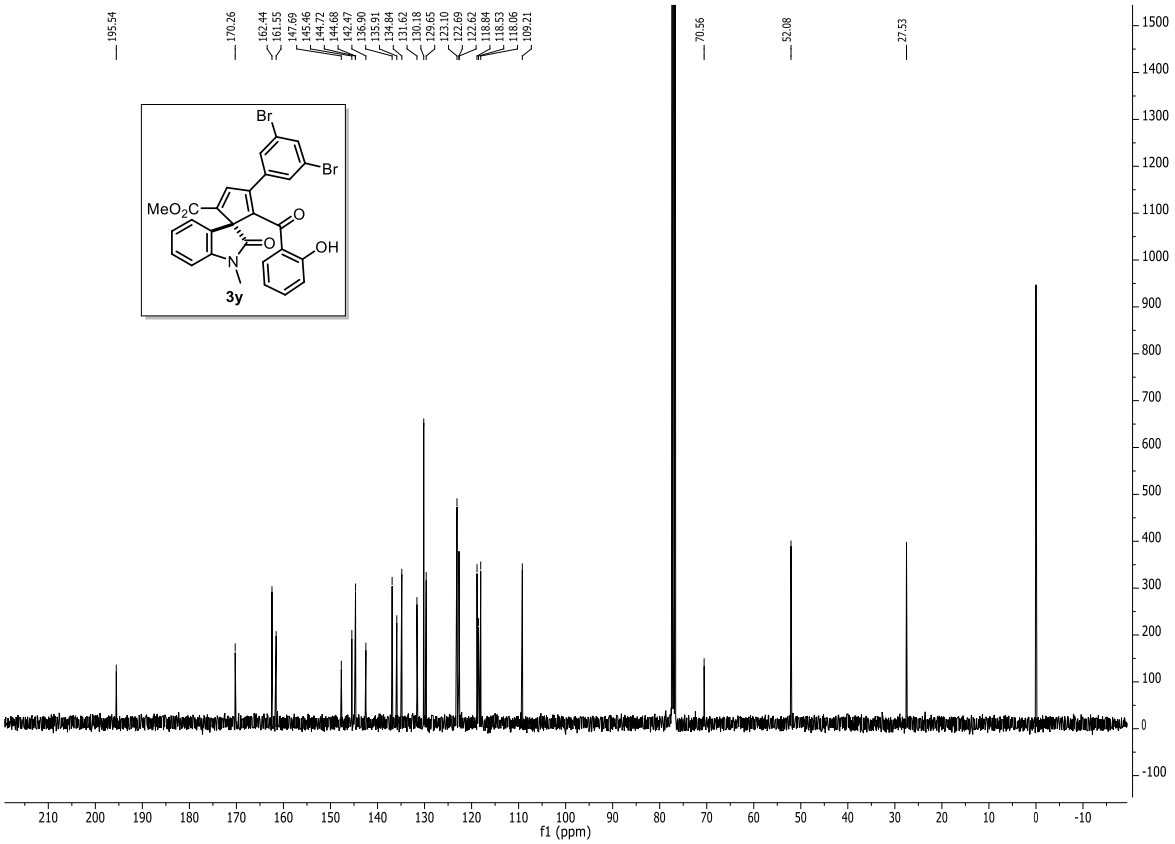
^{1}H NMR (400 MHz, $CDCl_3$)



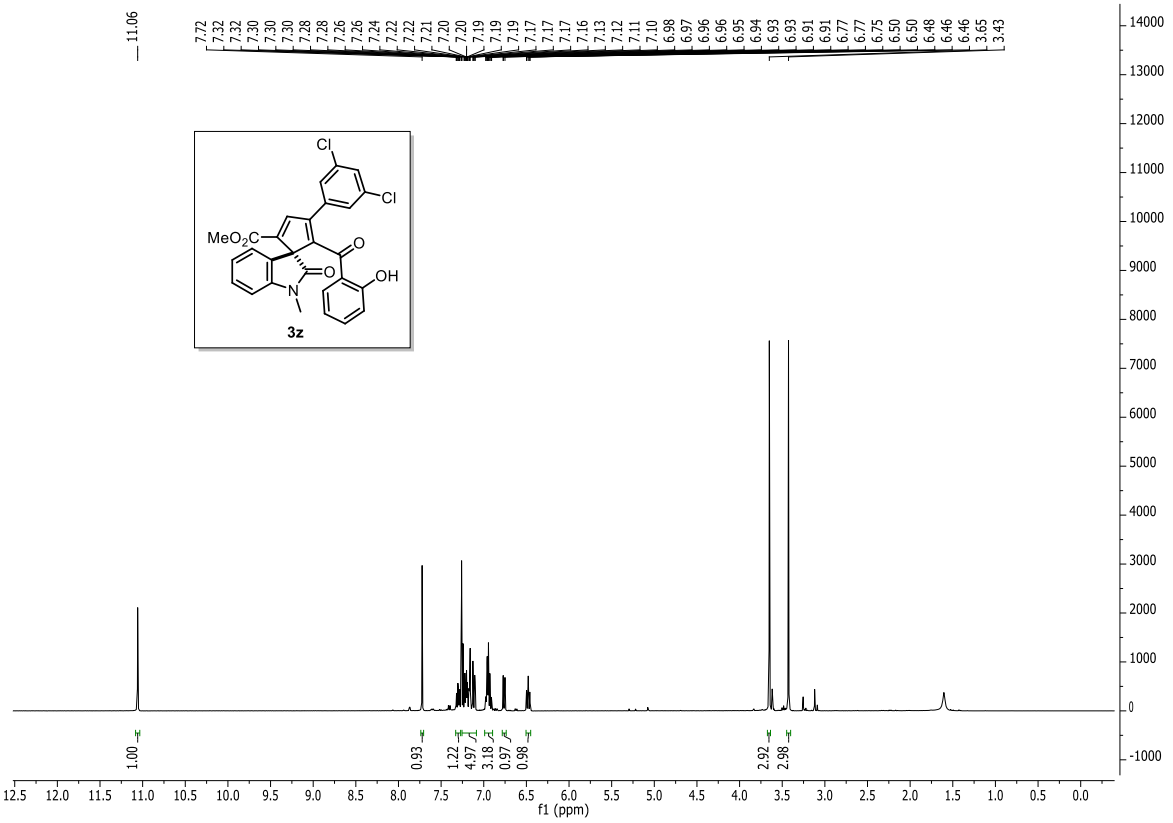
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



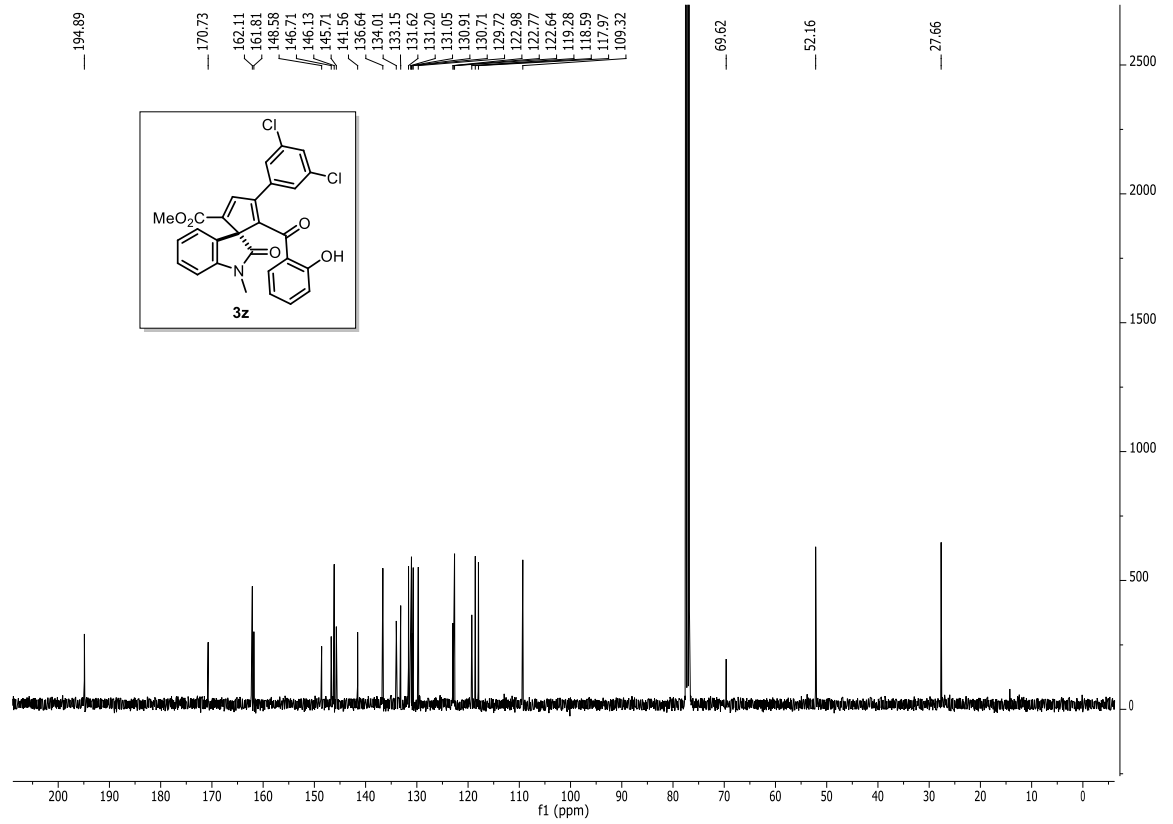
^{1}H NMR (400 MHz, $CDCl_3$)



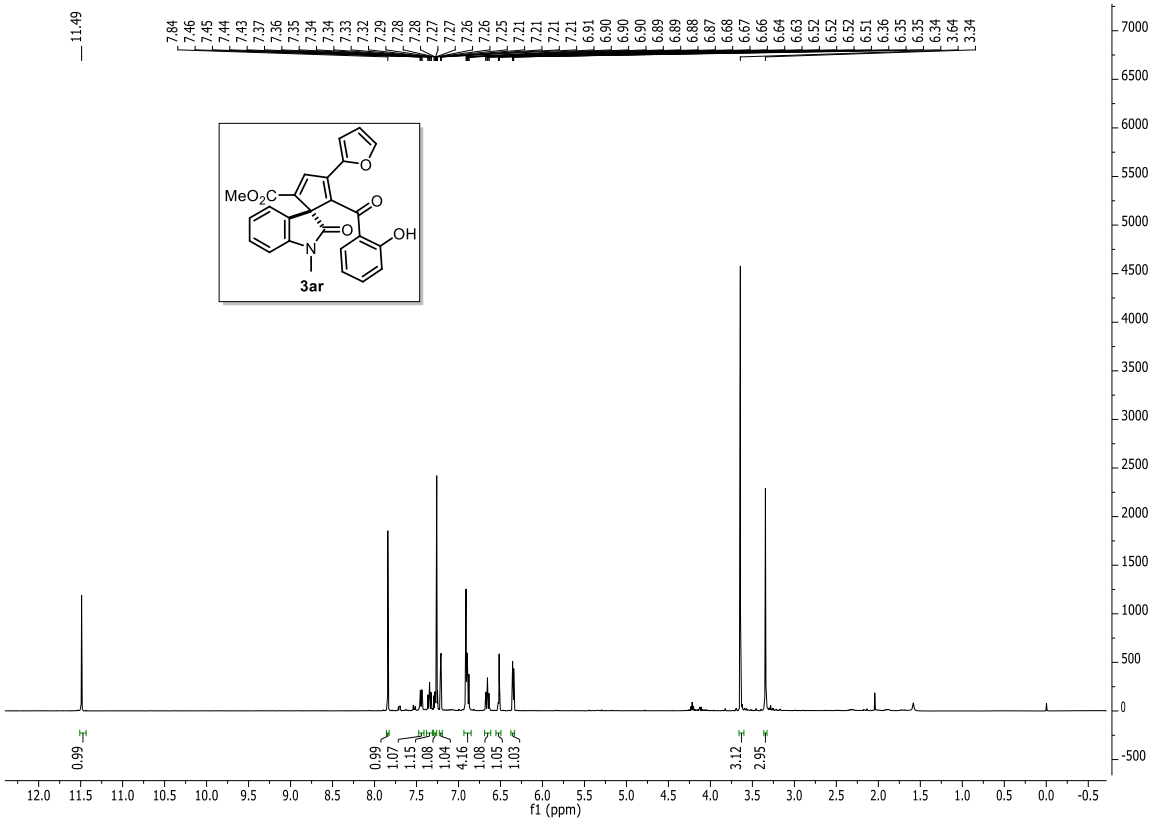
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



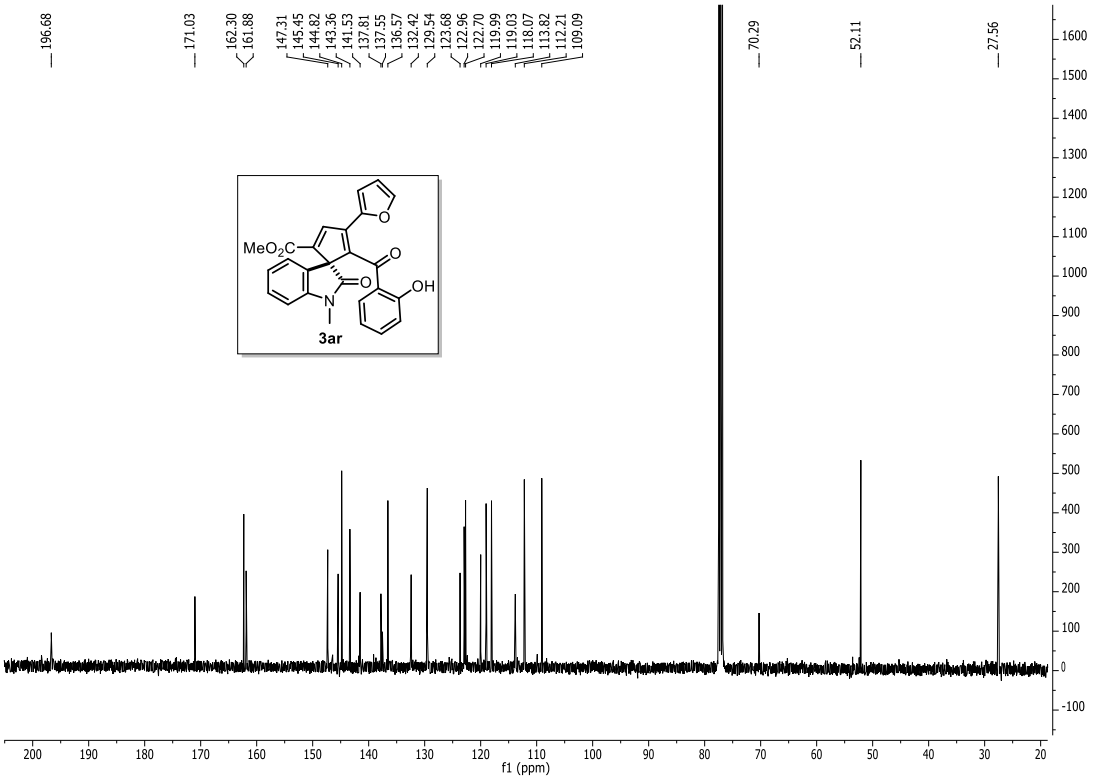
^{1}H NMR (400 MHz, $CDCl_3$)



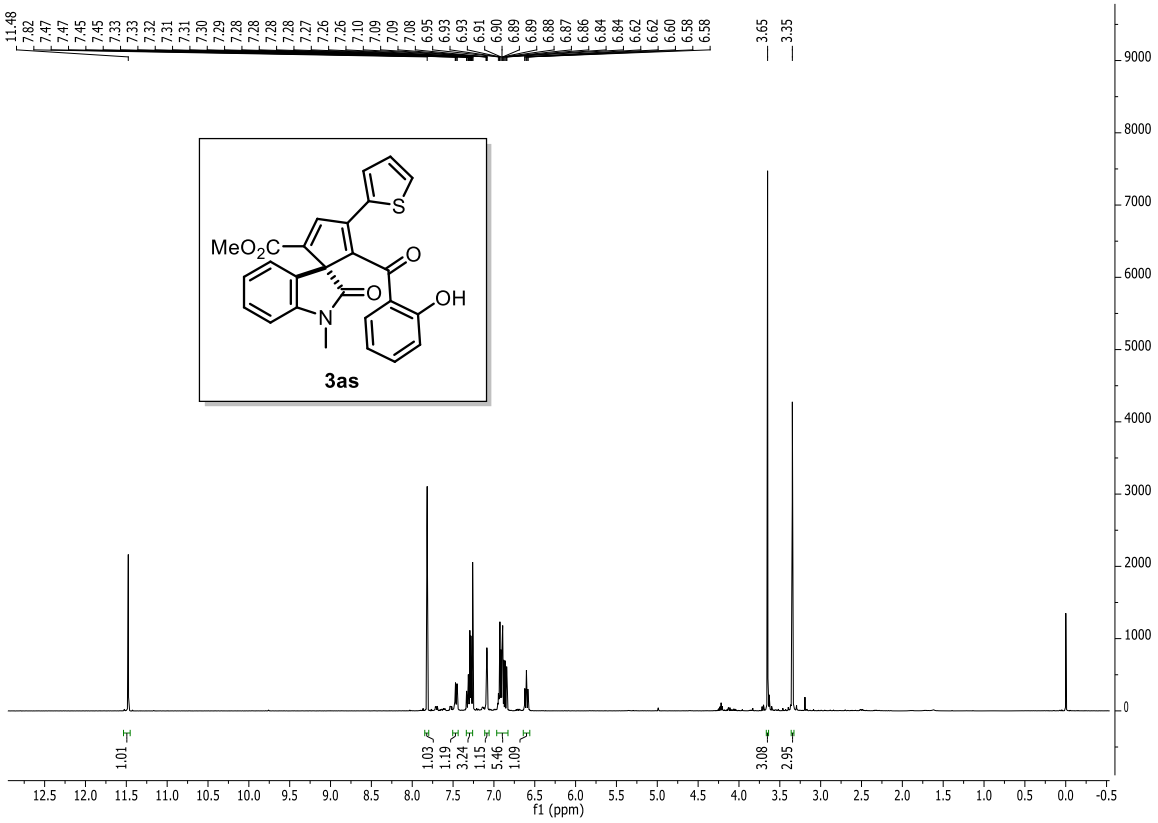
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



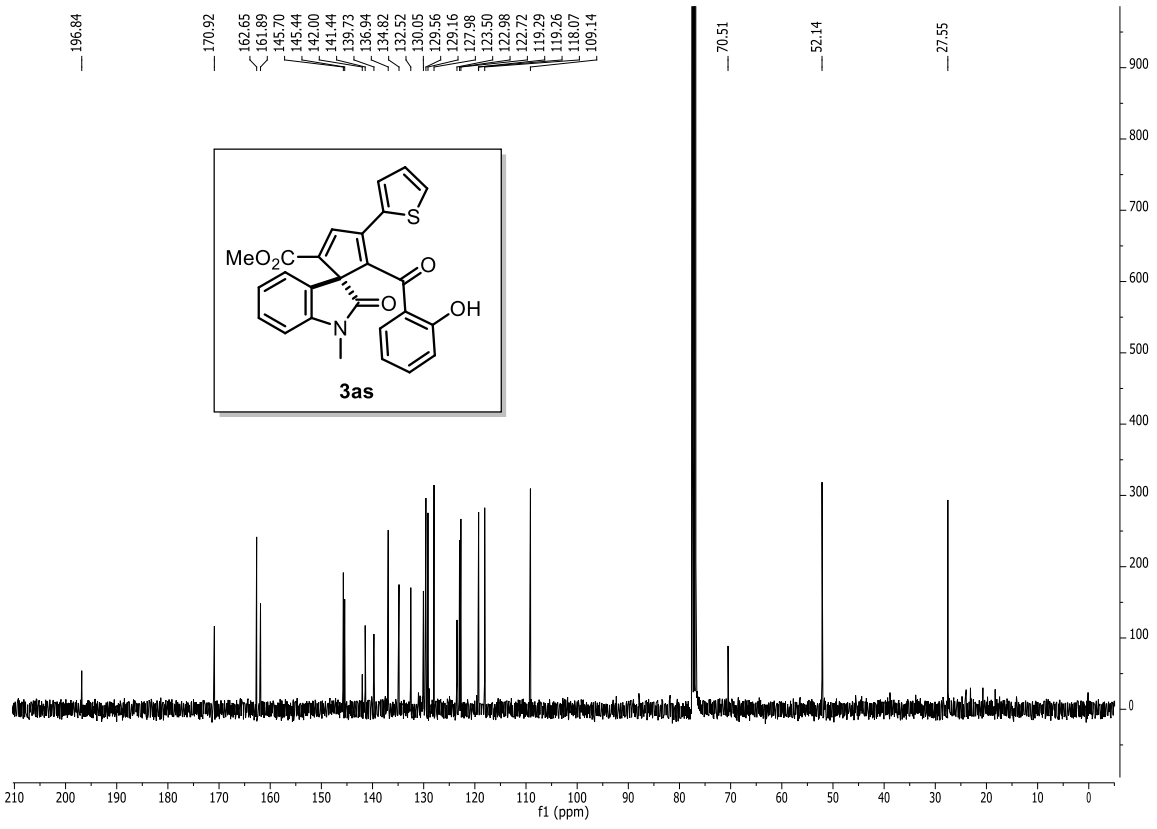
^{1}H NMR (400 MHz, $CDCl_3$)



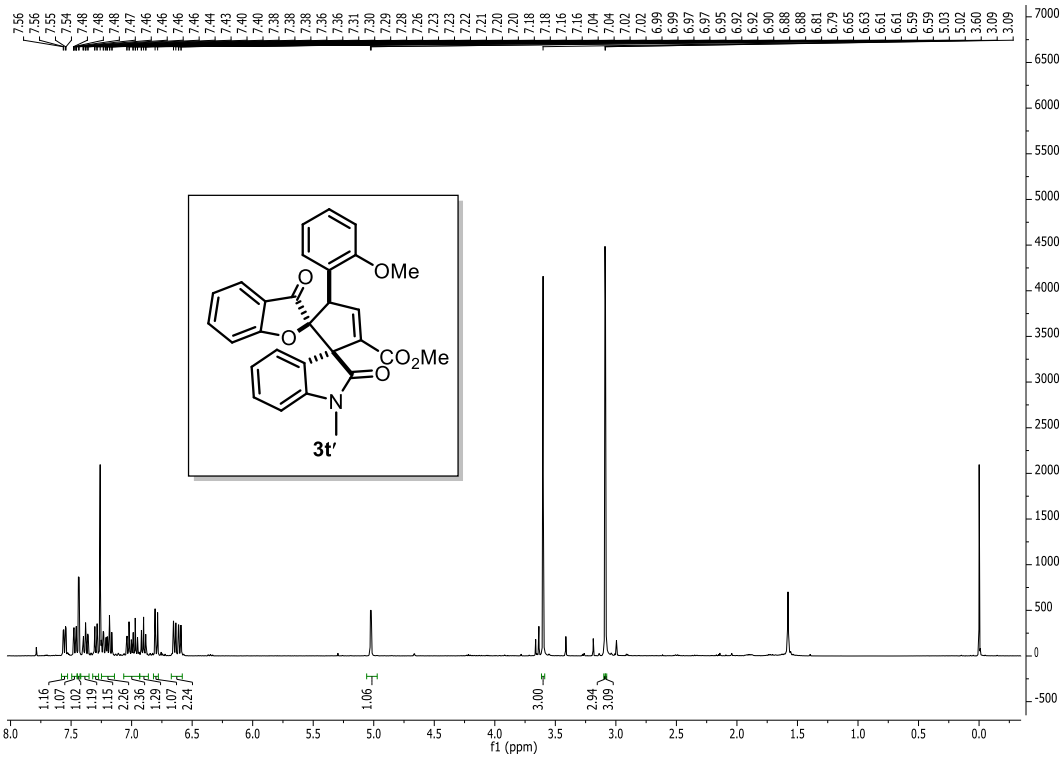
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



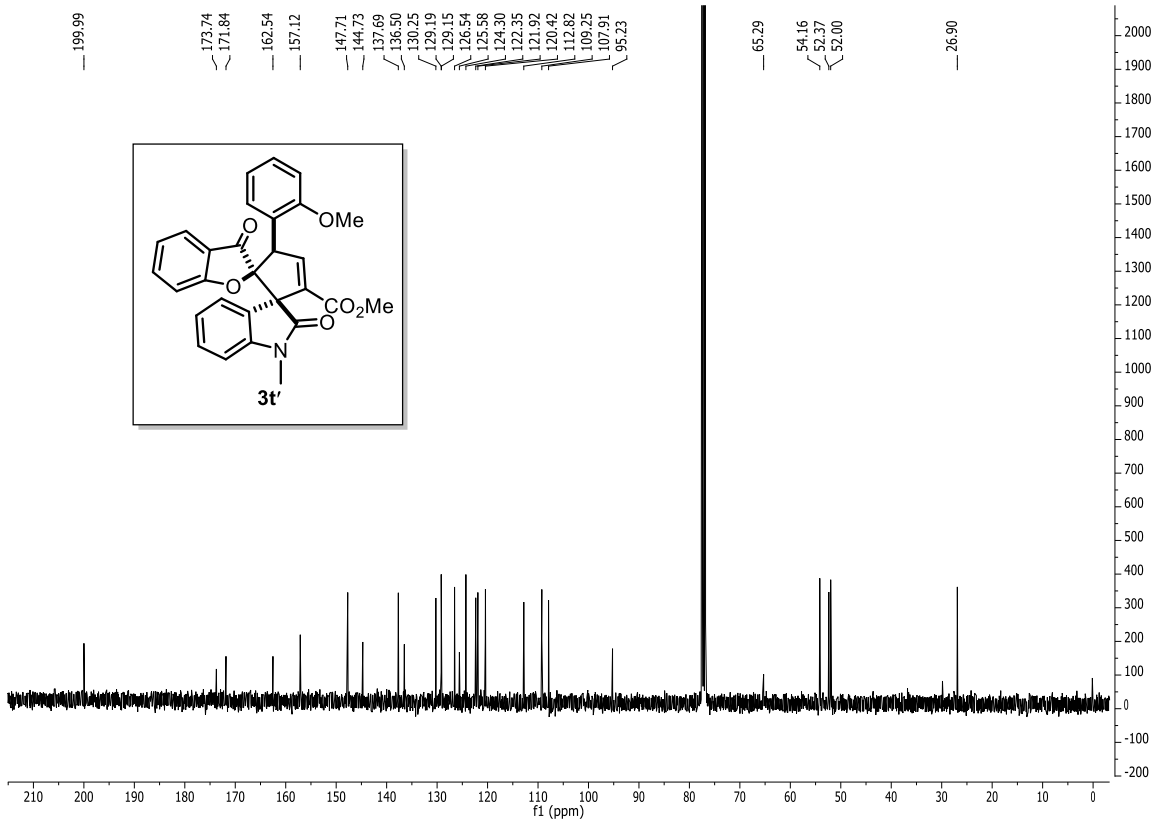
^{1}H NMR (400 MHz, $CDCl_3$)



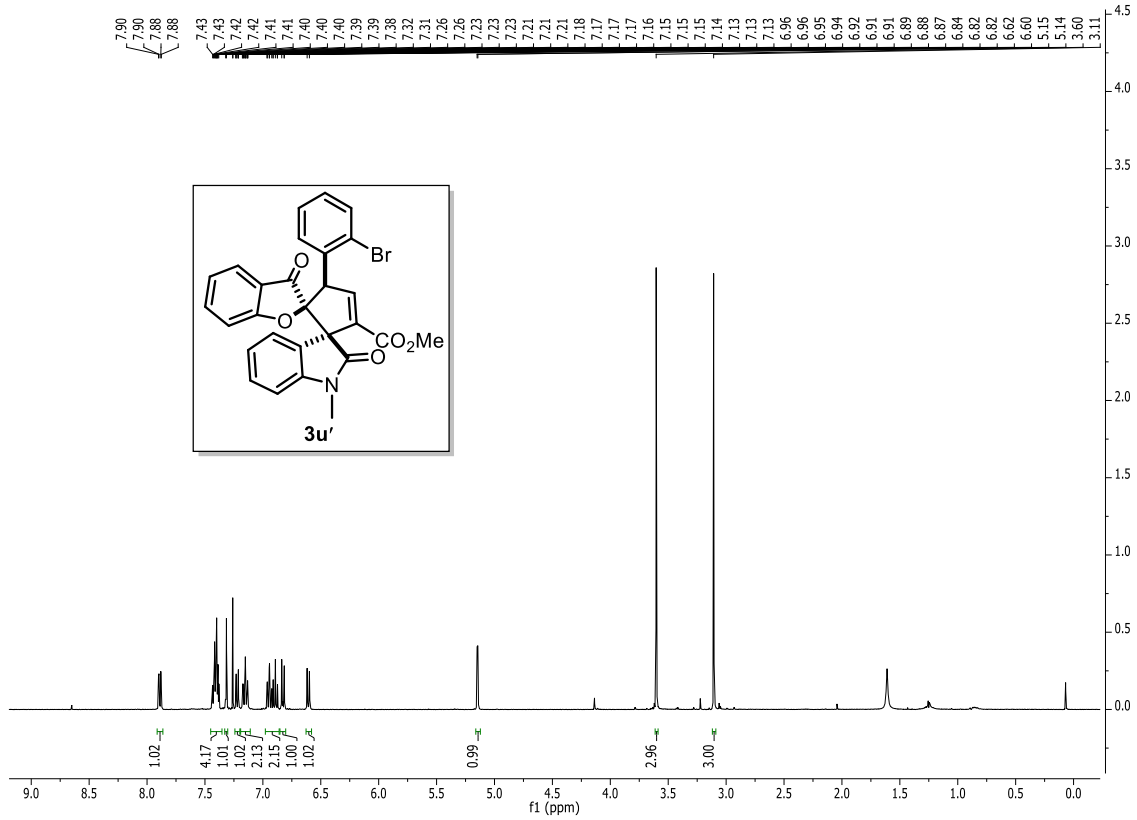
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

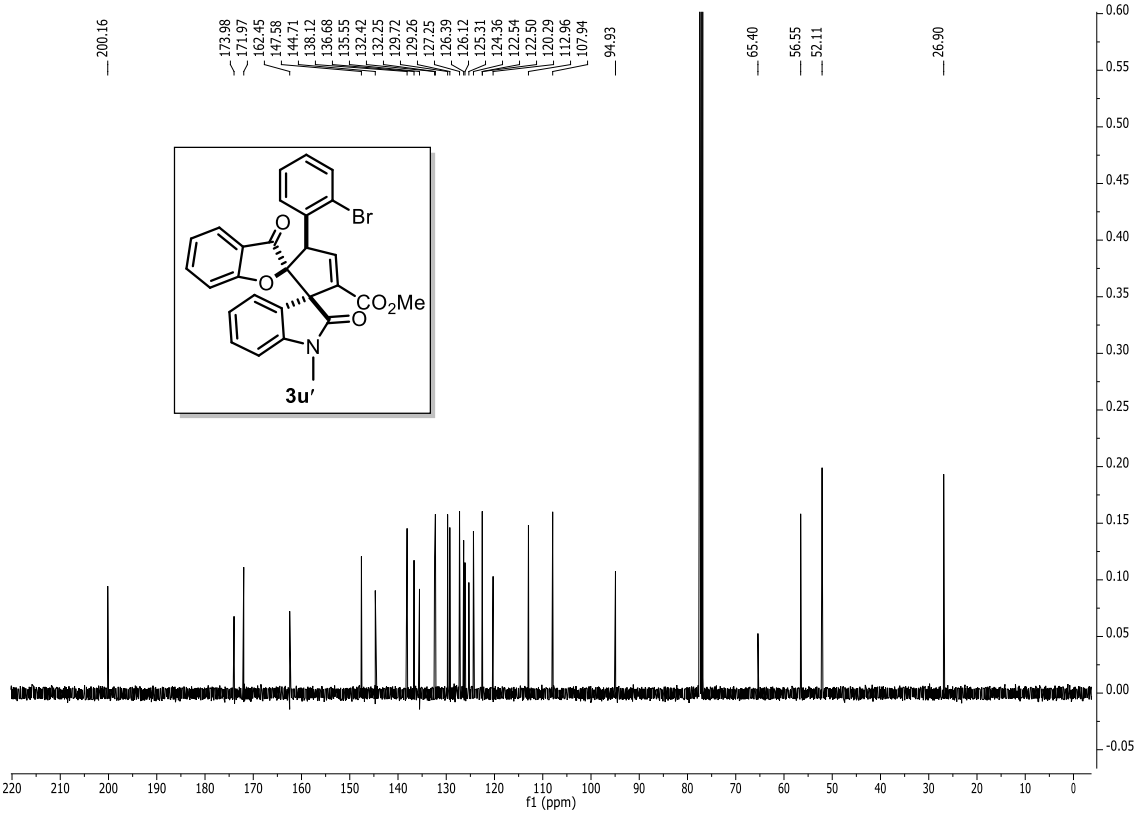


^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



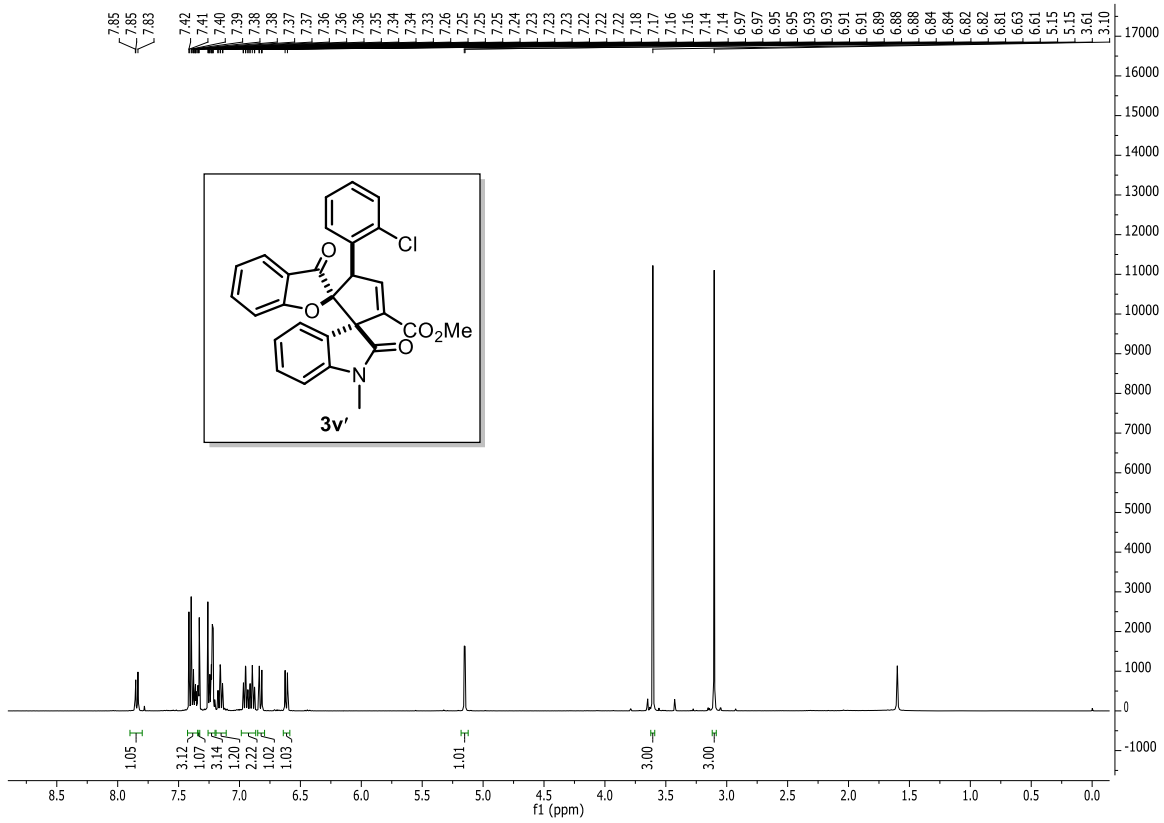
1

H NMR (400 MHz, $CDCl_3$)

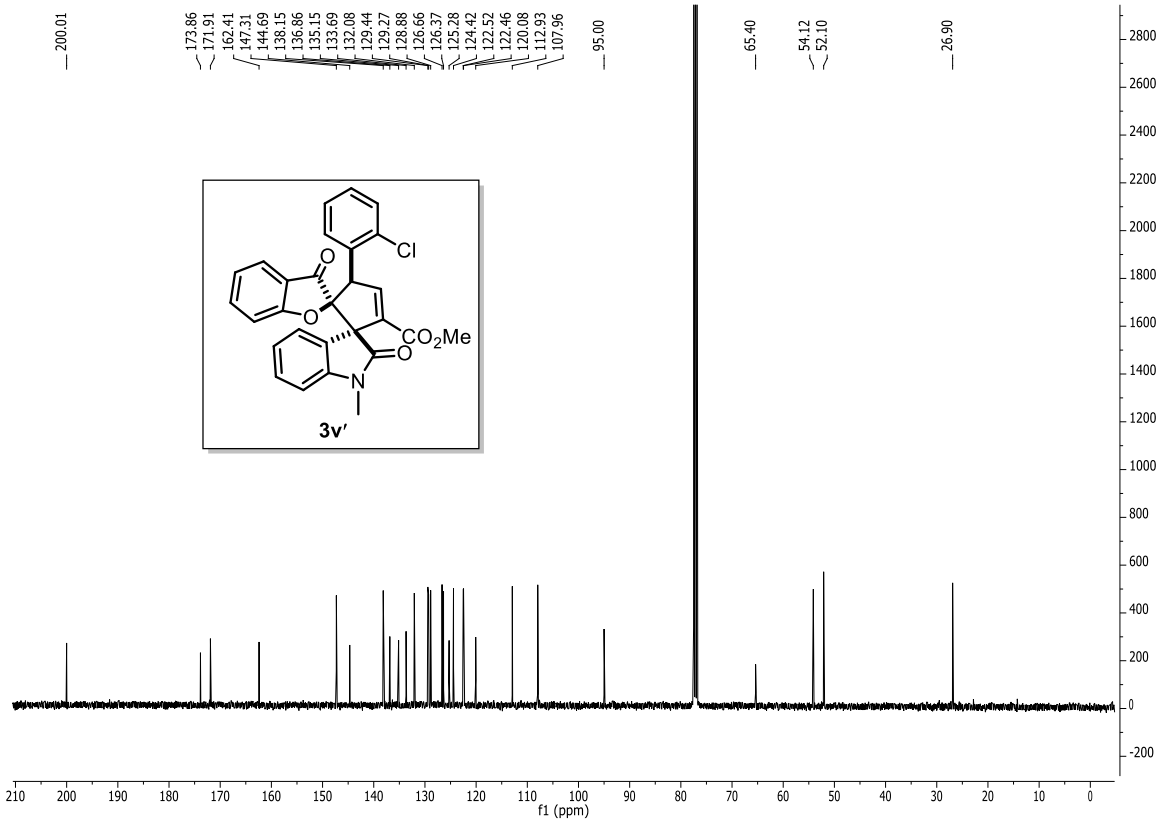


13

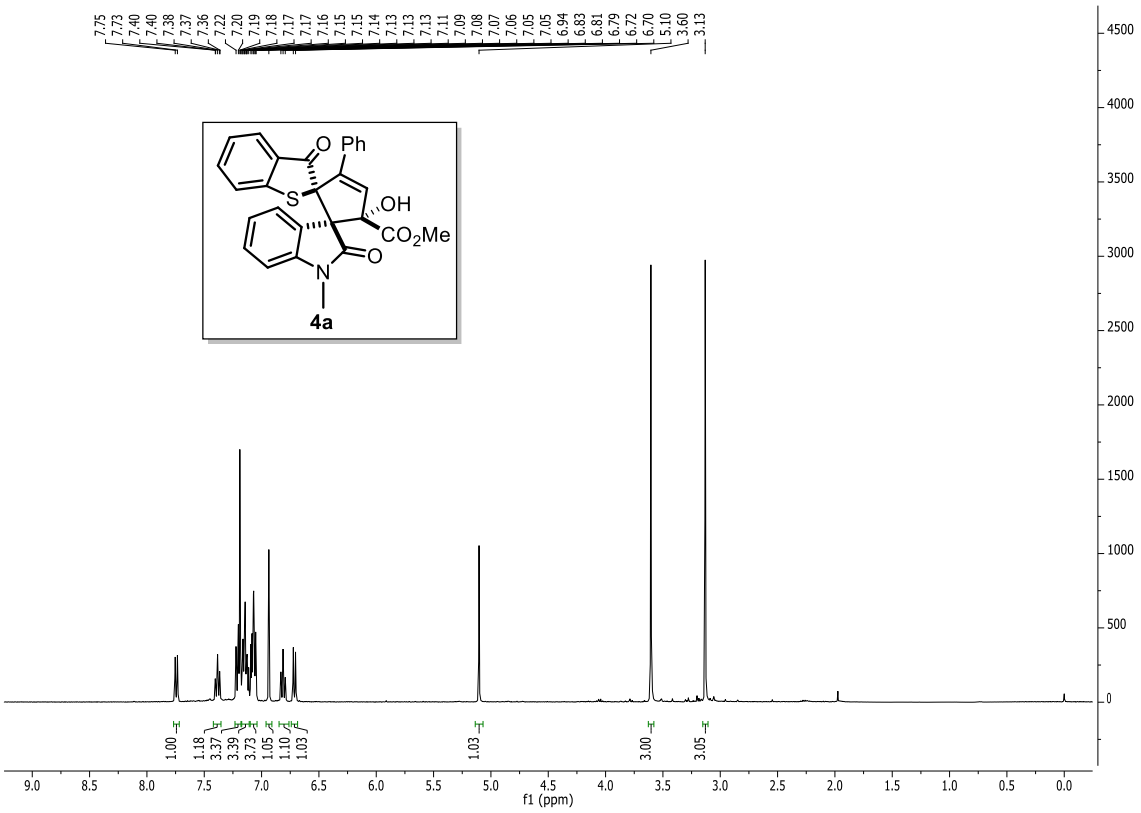
C {^{1}H} NMR (100 MHz, $CDCl_3$)



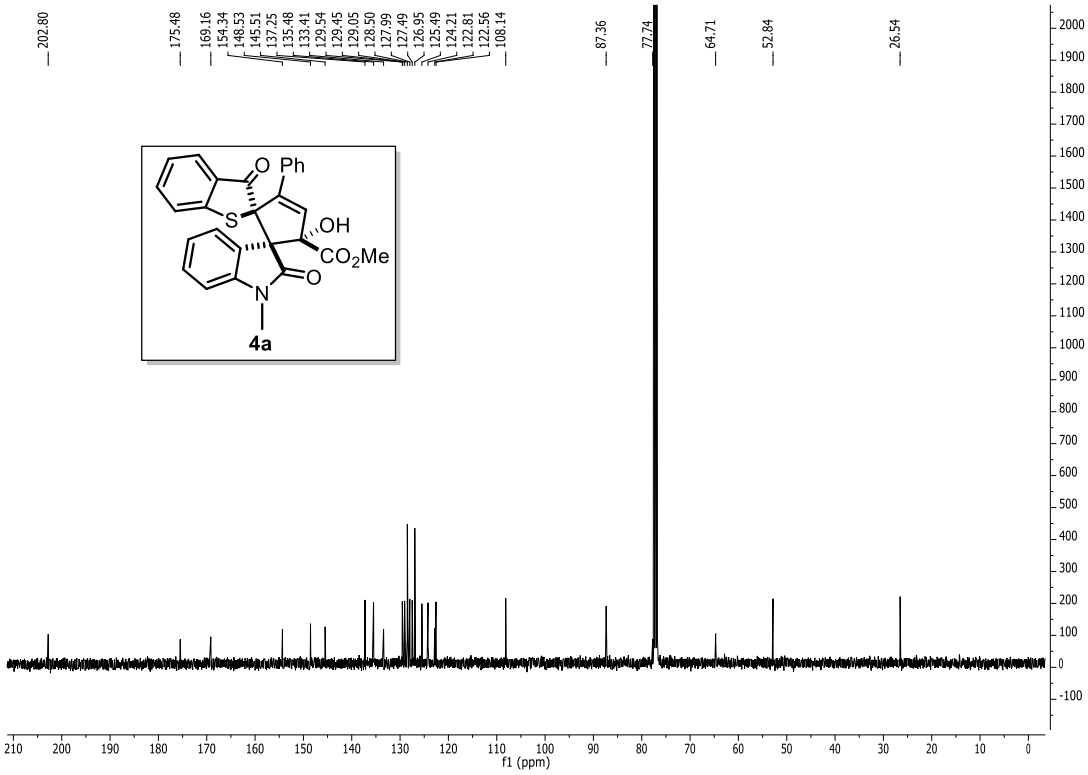
^{1}H NMR (400 MHz, $CDCl_3$)



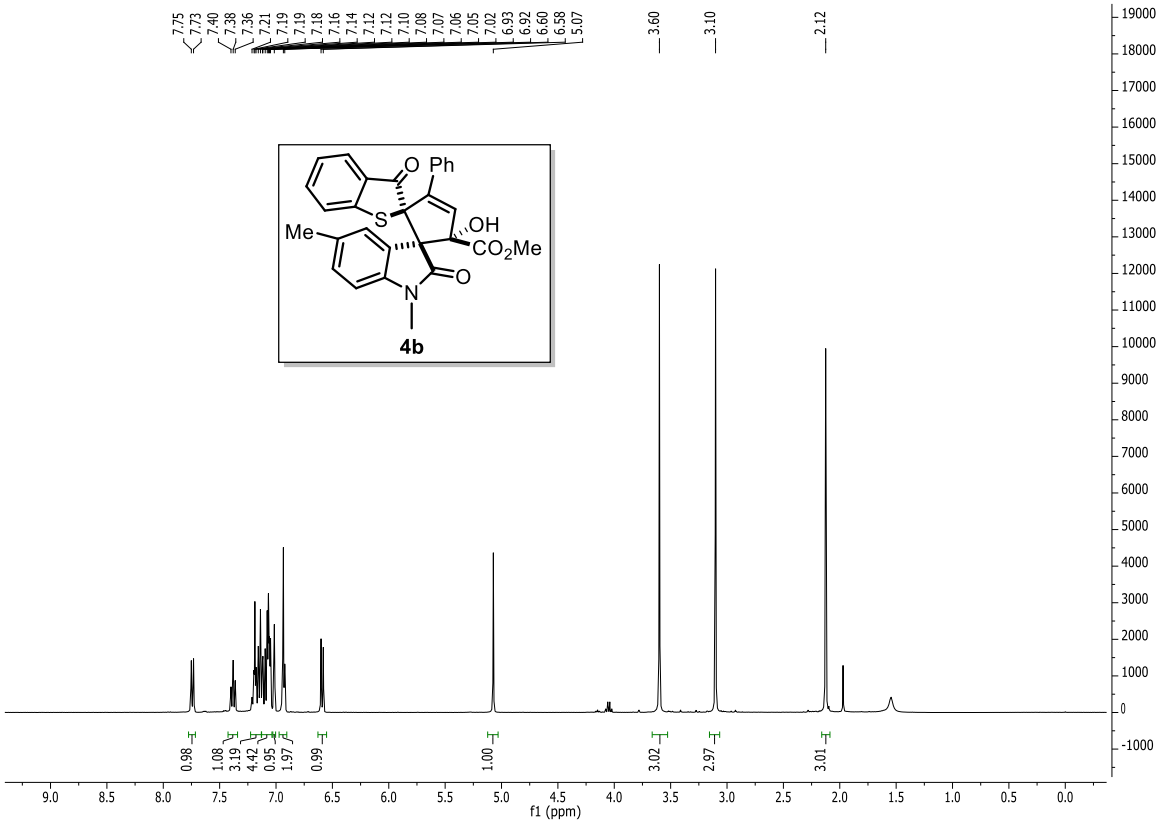
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



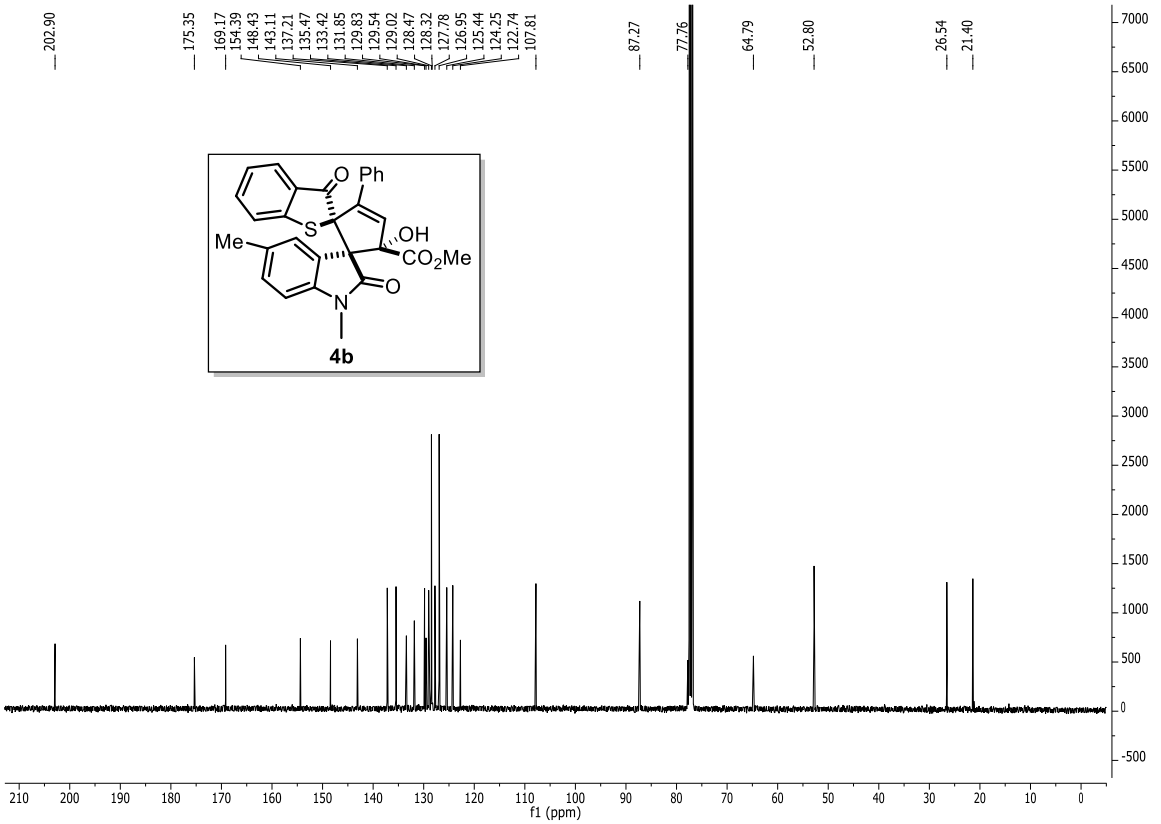
^{1}H NMR (400 MHz, $CDCl_3$)



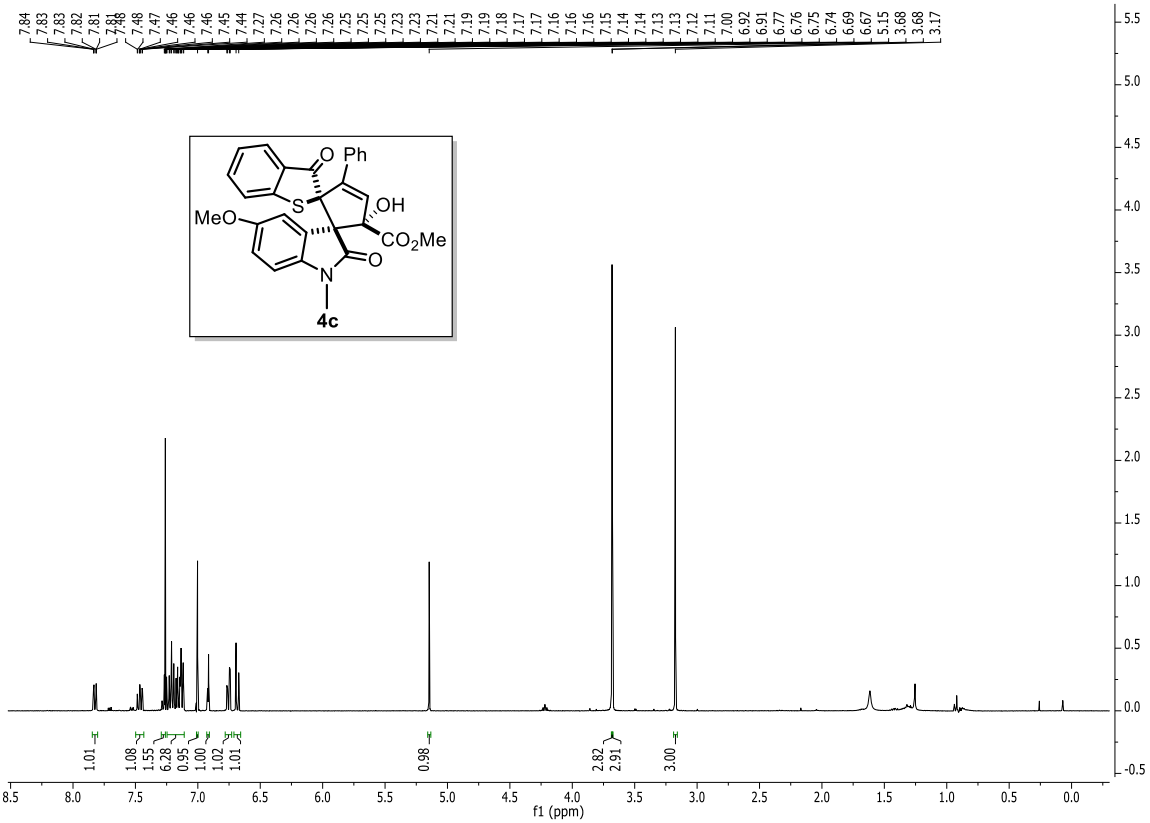
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



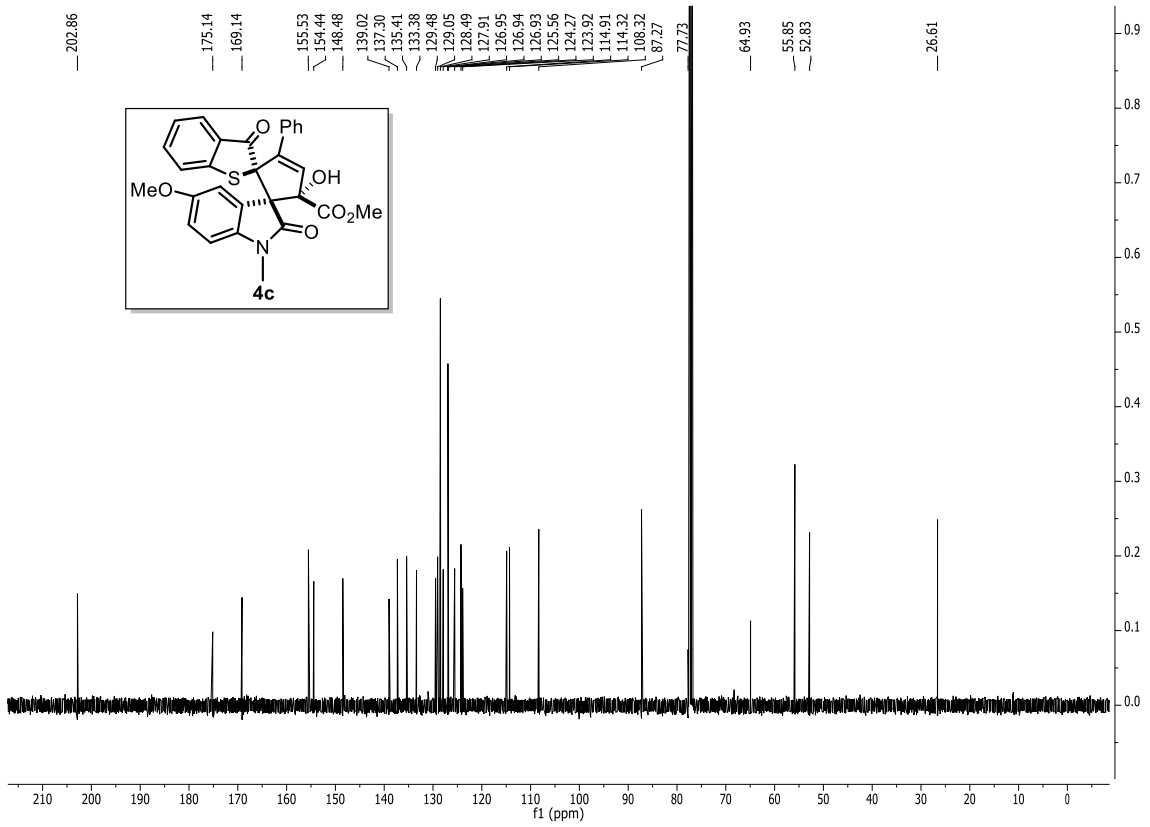
^{1}H NMR (400 MHz, $CDCl_3$)



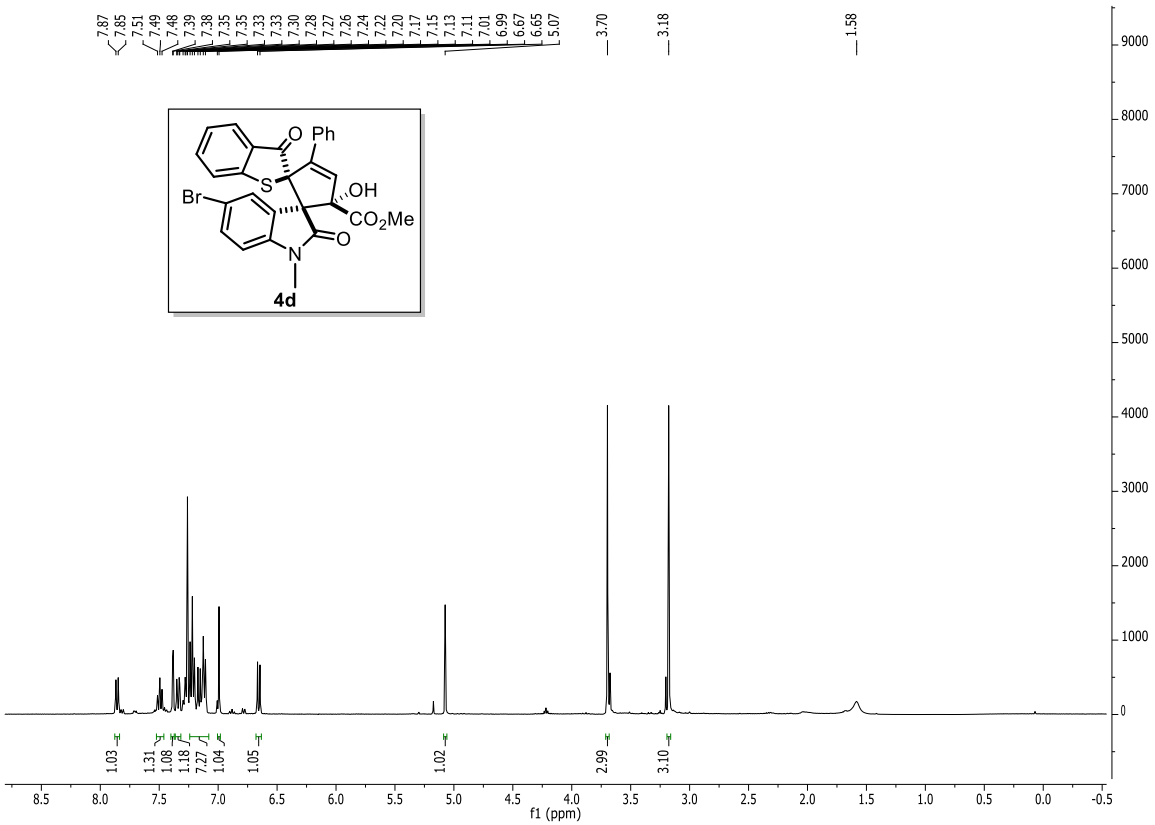
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



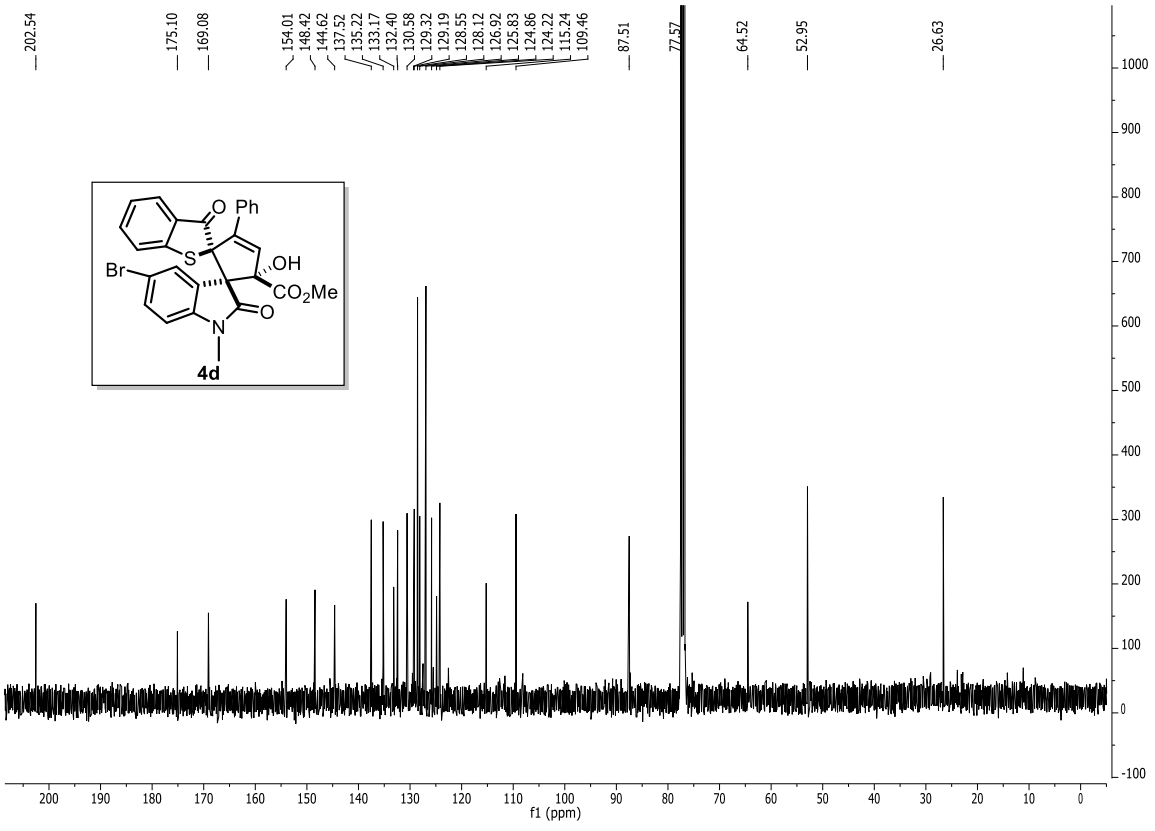
^{1}H NMR (400 MHz, $CDCl_3$)



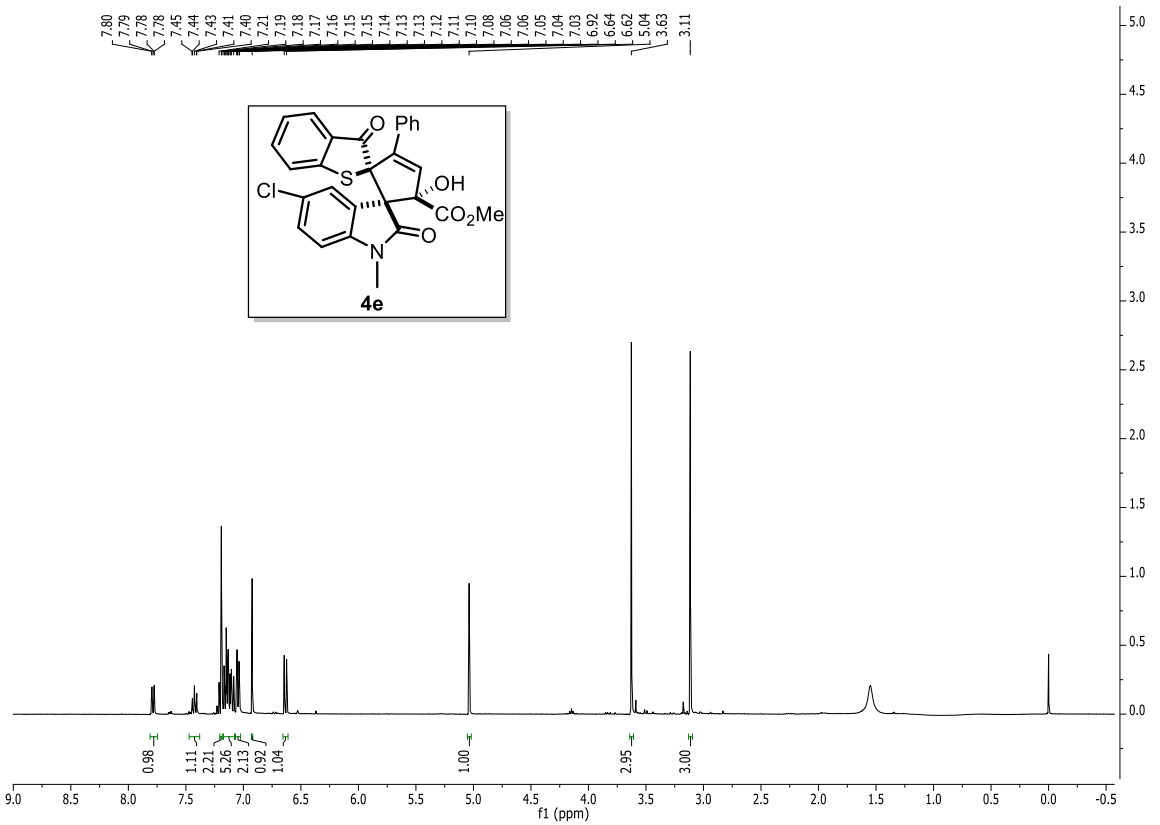
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



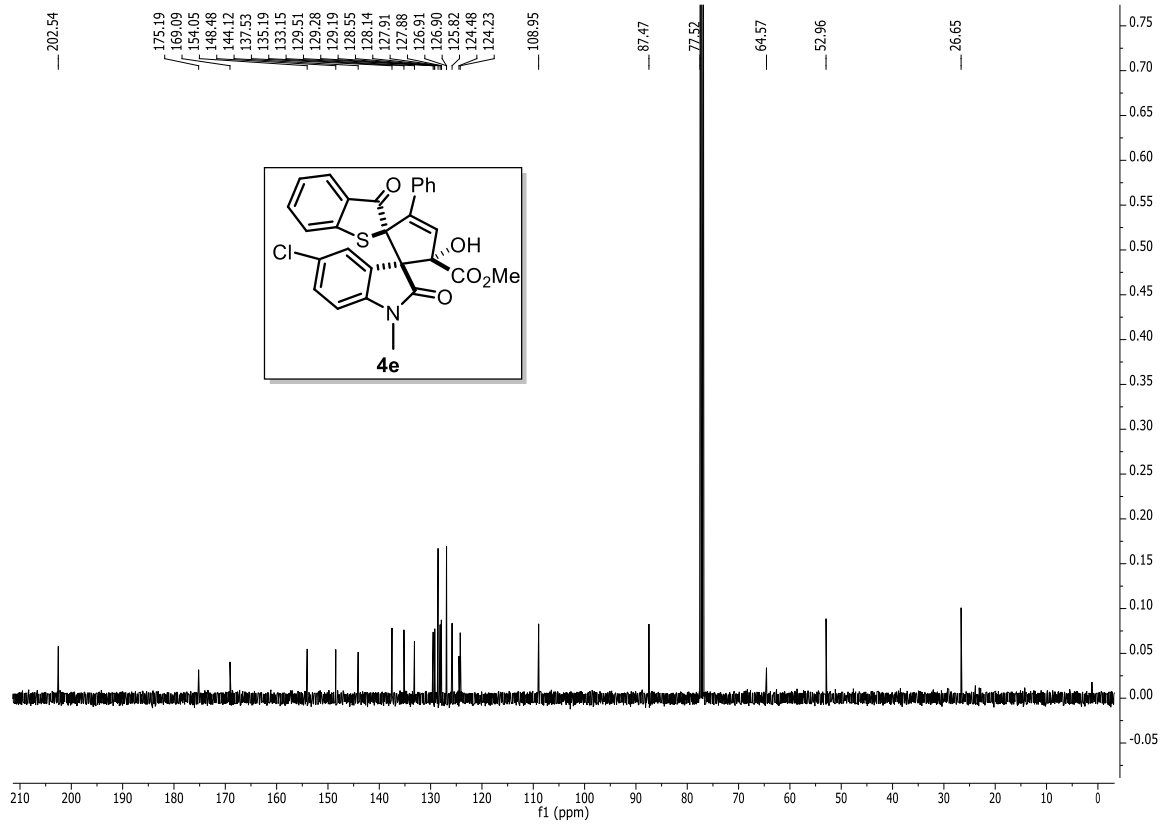
^{1}H NMR (400 MHz, $CDCl_3$)



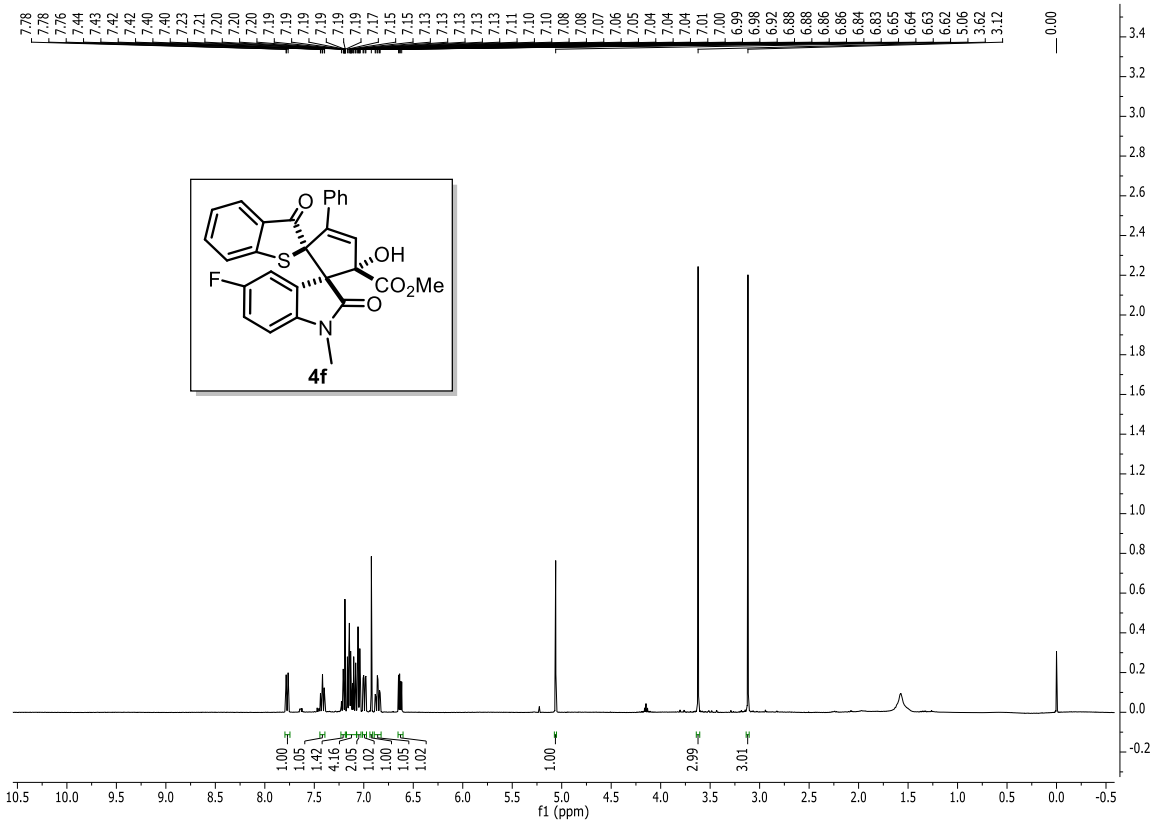
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



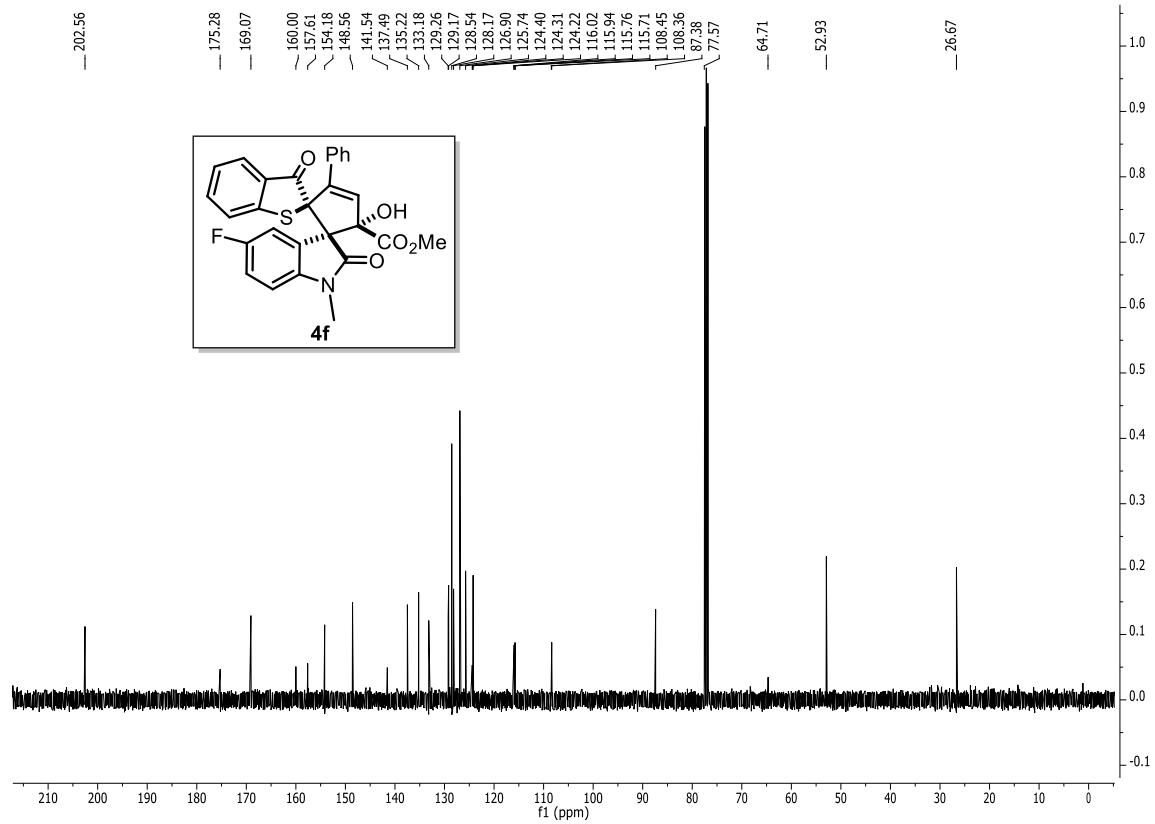
^{1}H NMR (400 MHz, $CDCl_3$)



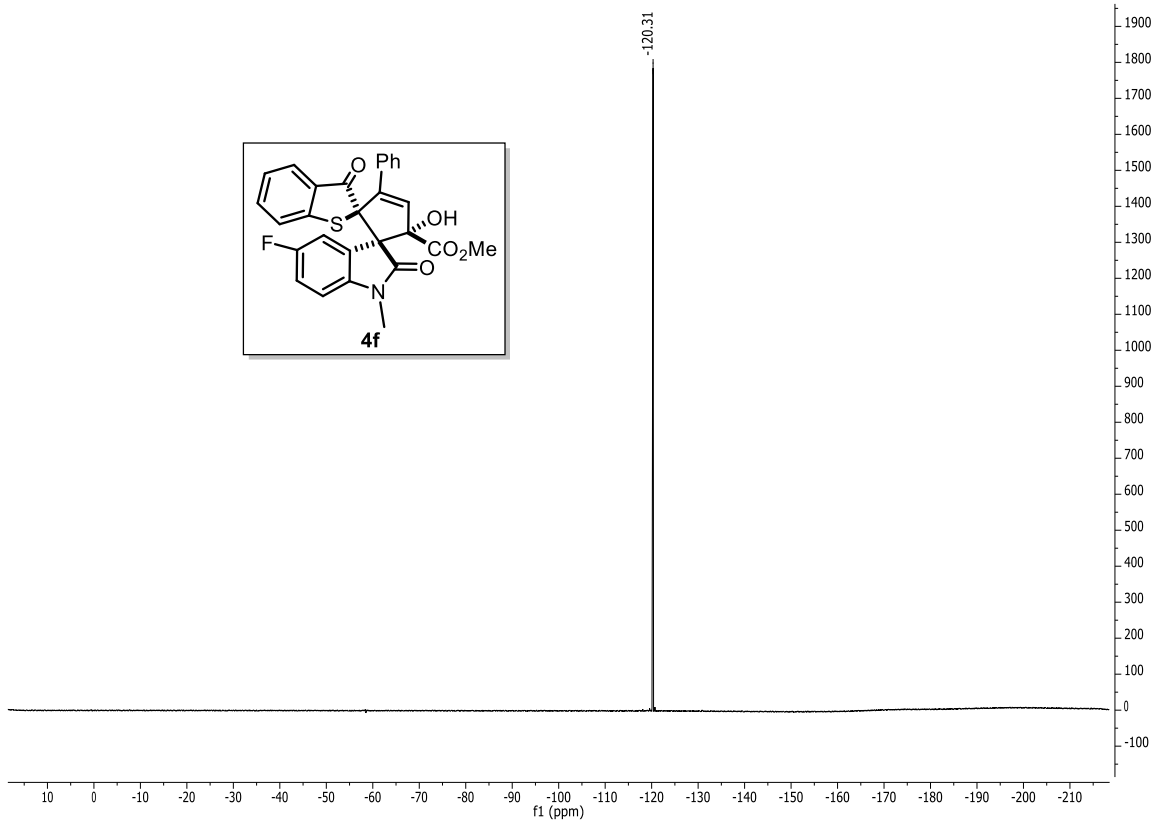
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



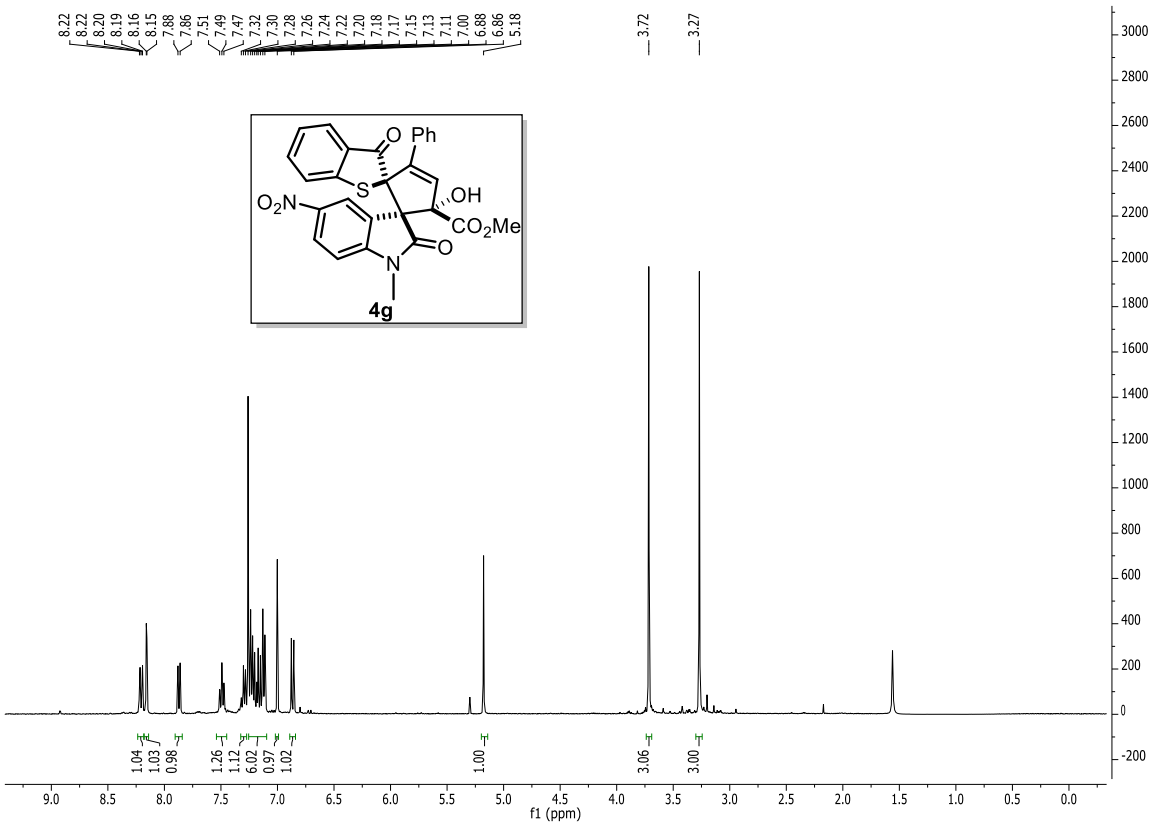
^{1}H NMR (400 MHz, $CDCl_3$)



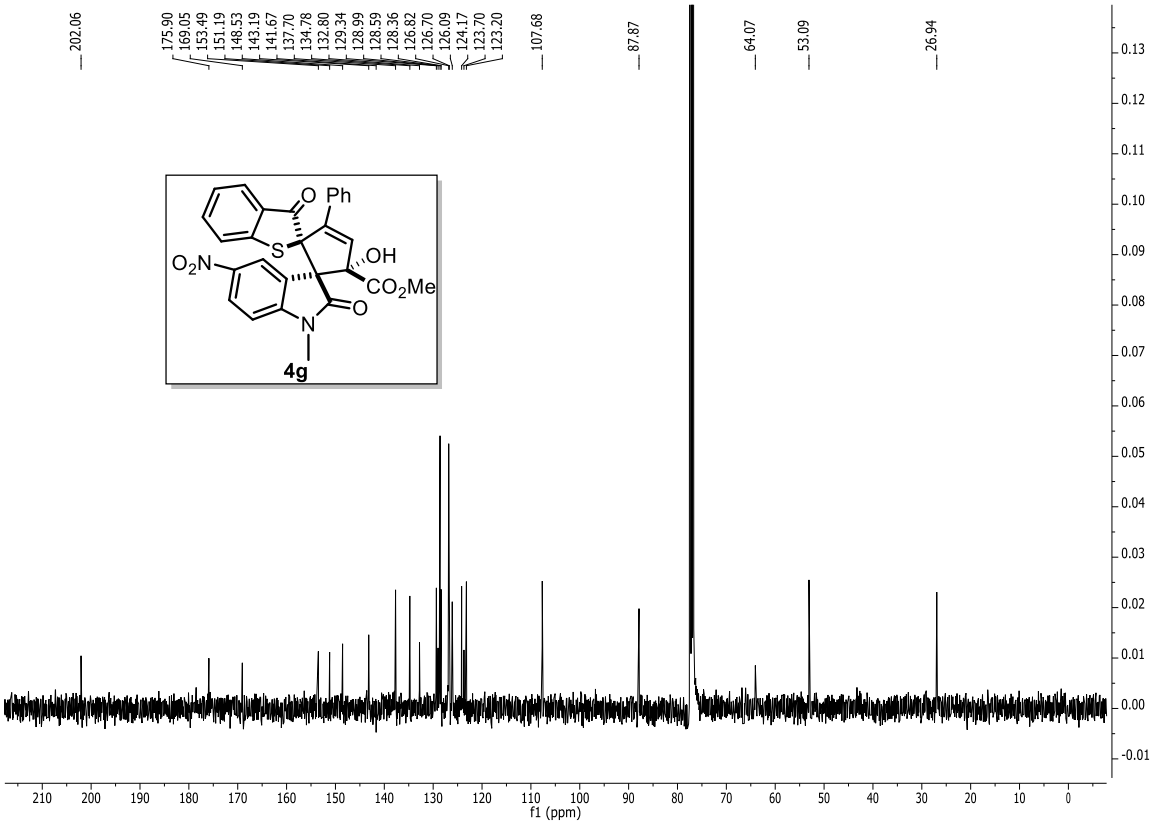
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



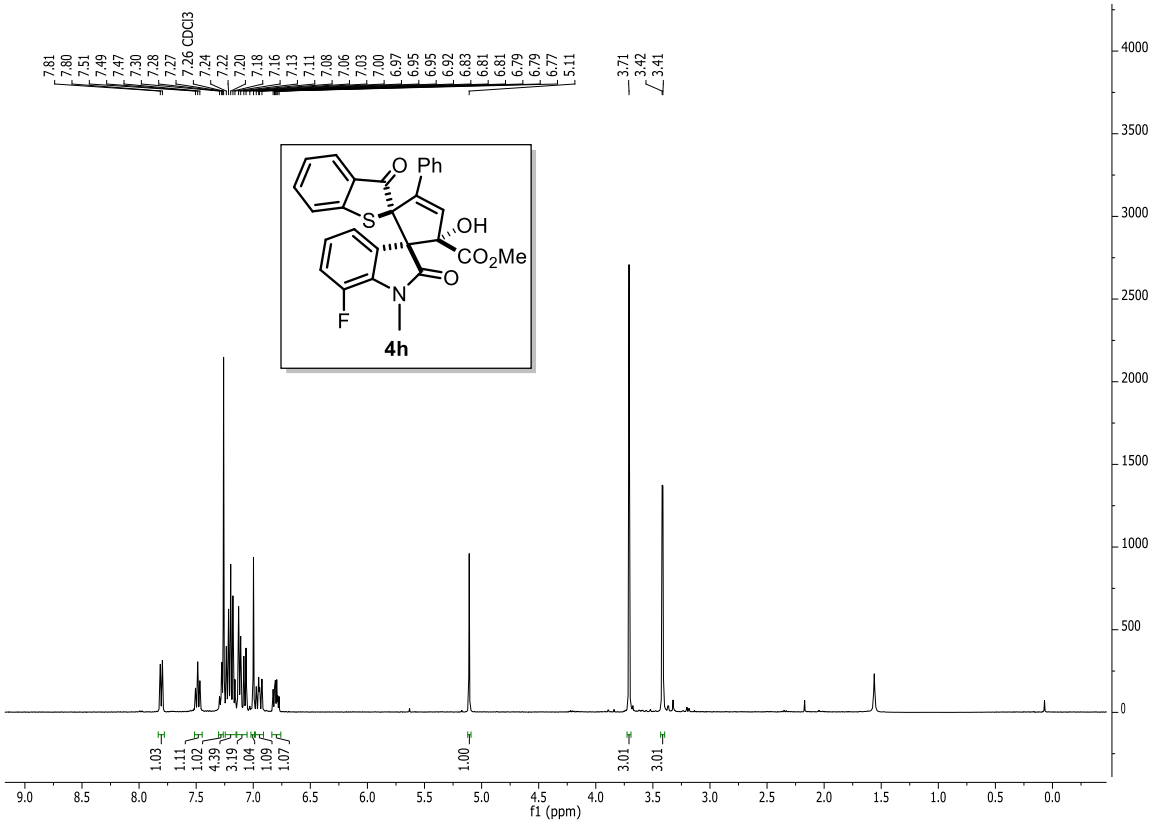
^{19}F NMR (377 MHz, $CDCl_3$)



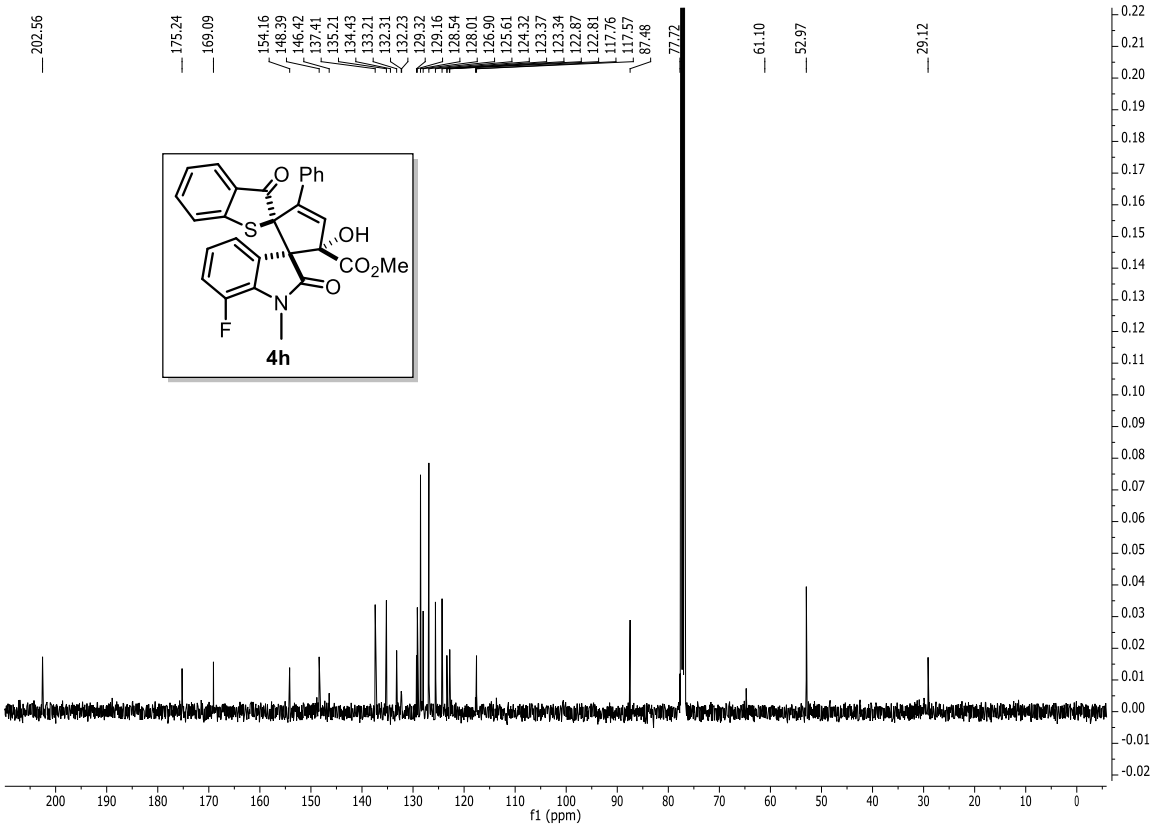
^{1}H NMR (400 MHz, $CDCl_3$)



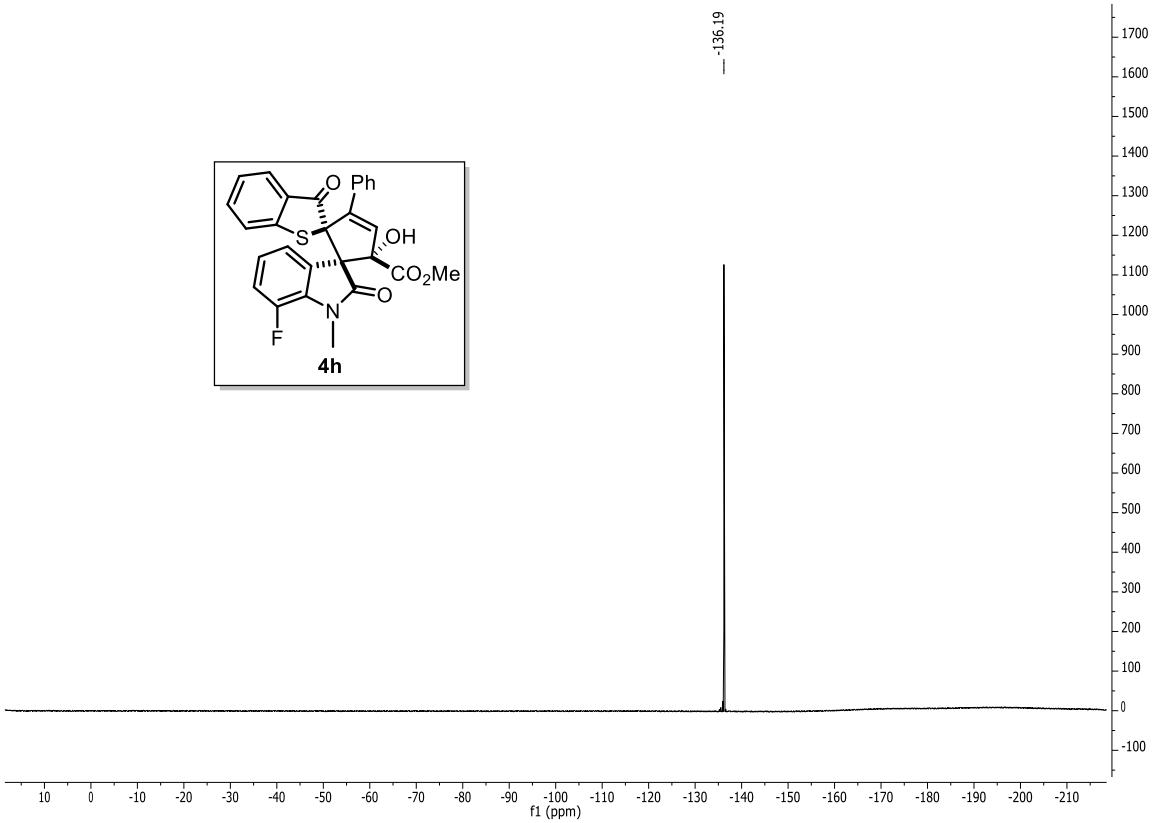
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



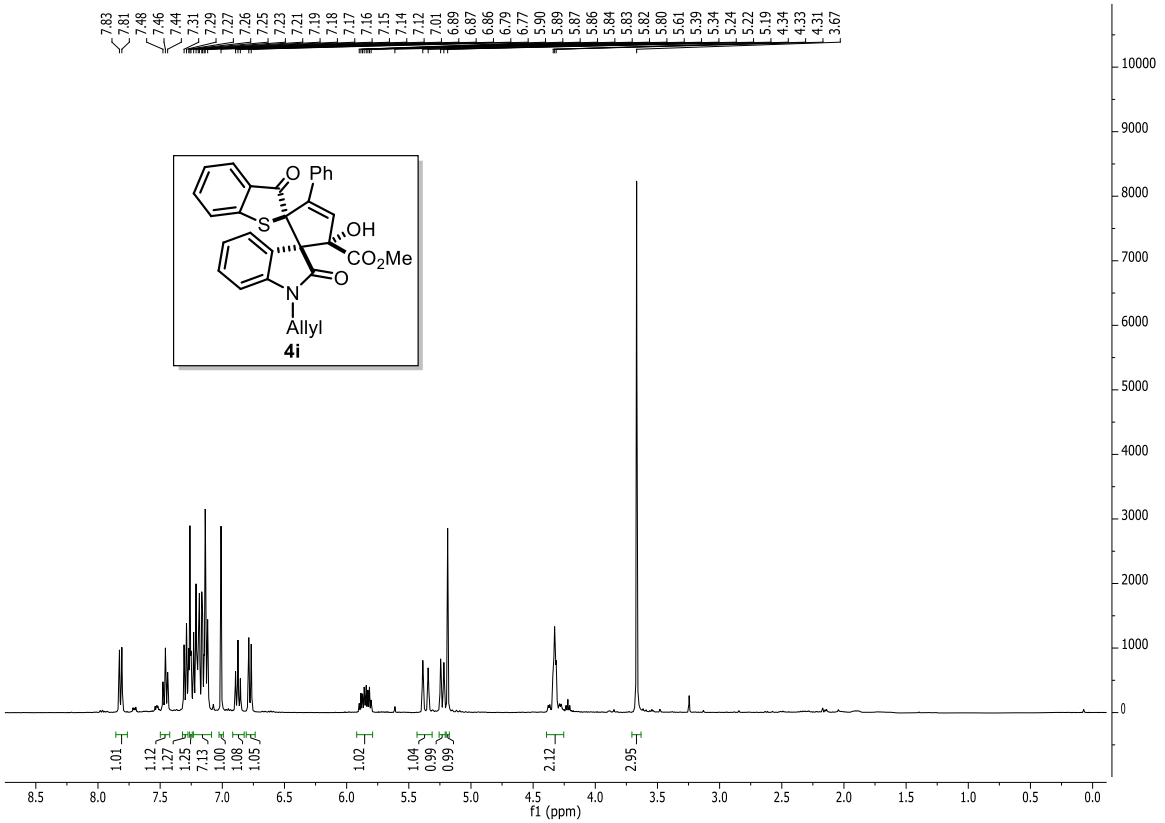
^{1}H NMR (400 MHz, $CDCl_3$)



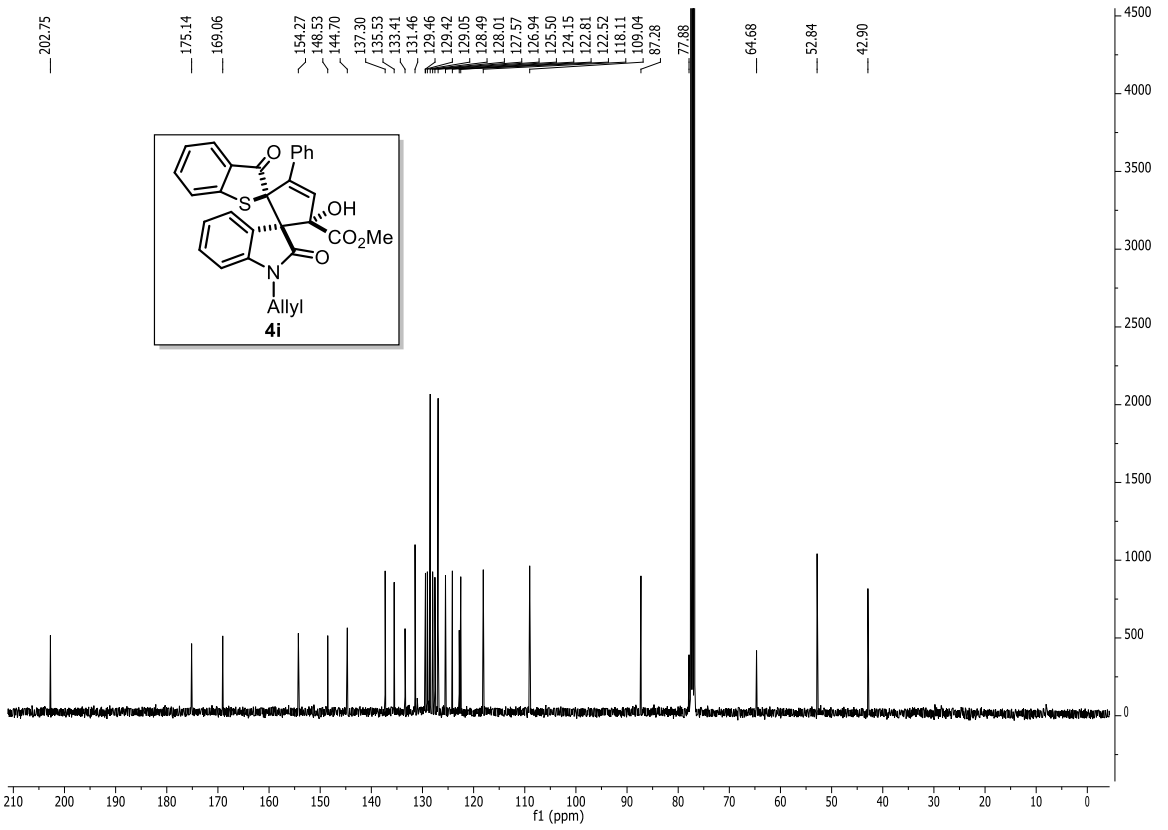
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



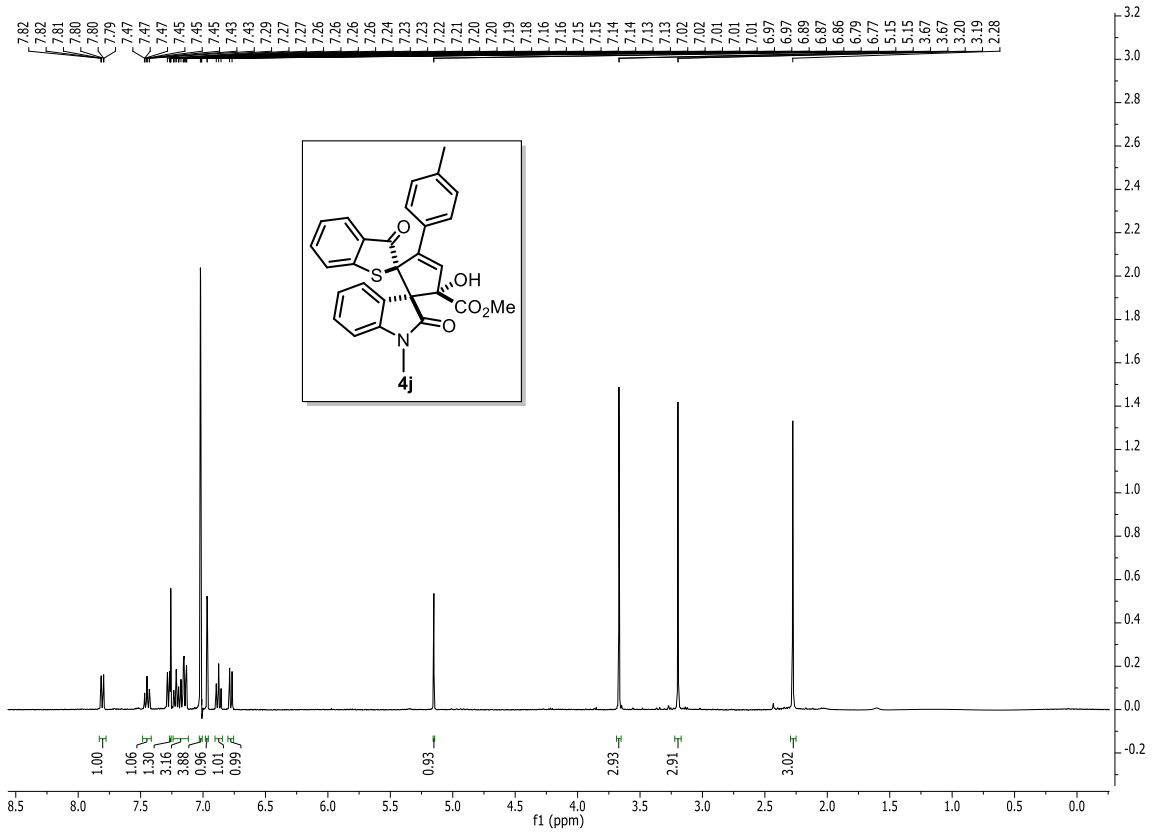
^{19}F NMR (377 MHz, $CDCl_3$)



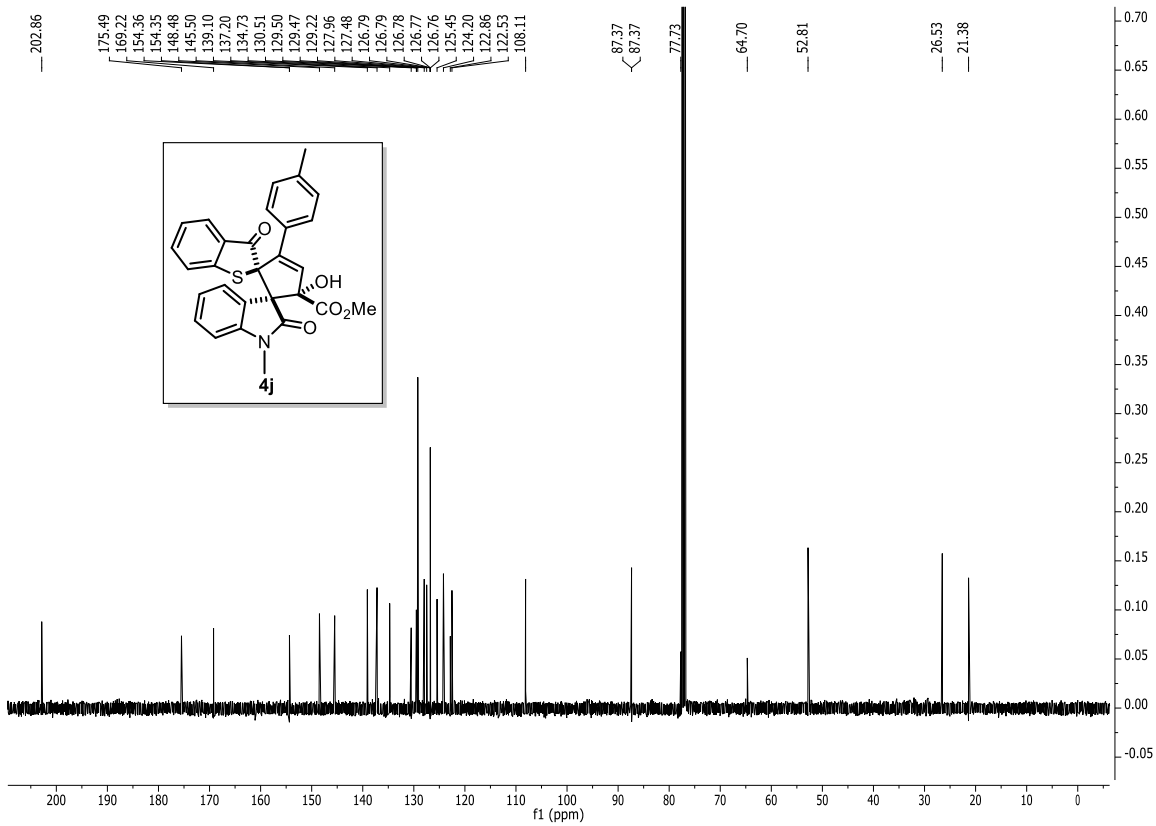
^{1}H NMR (400 MHz, $CDCl_3$)



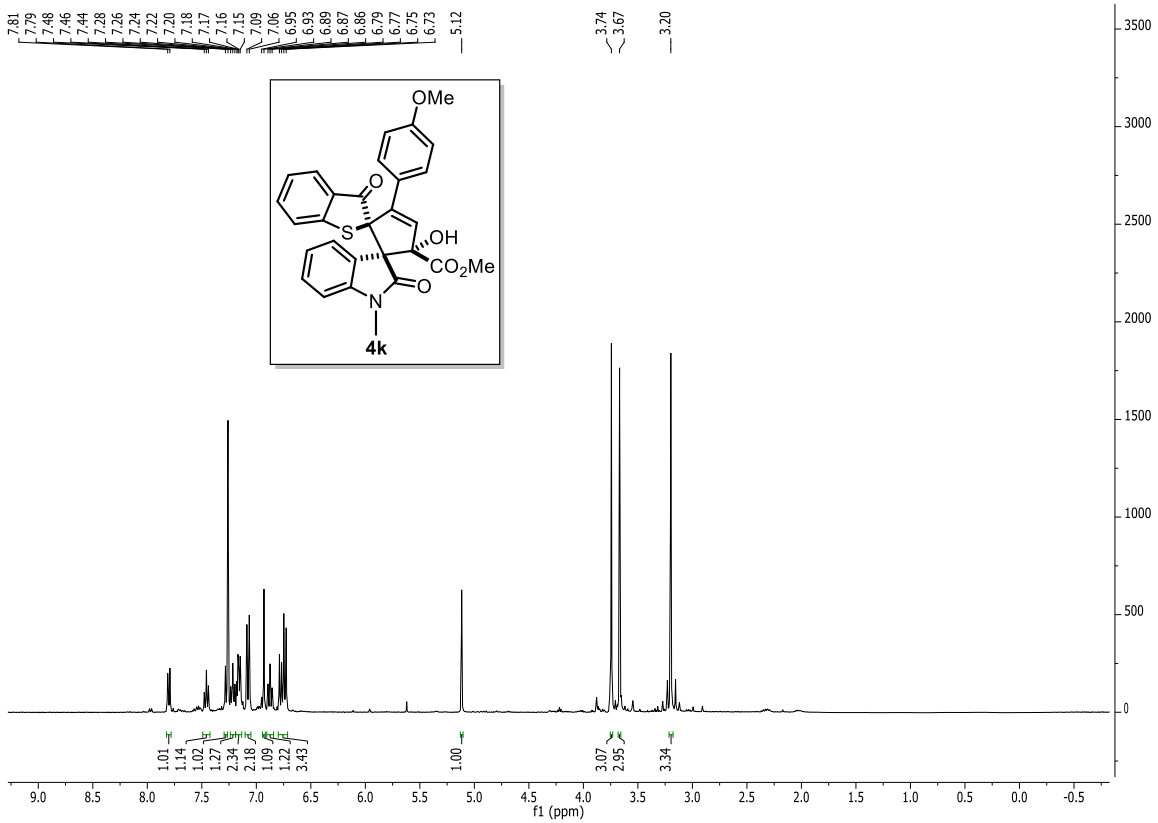
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



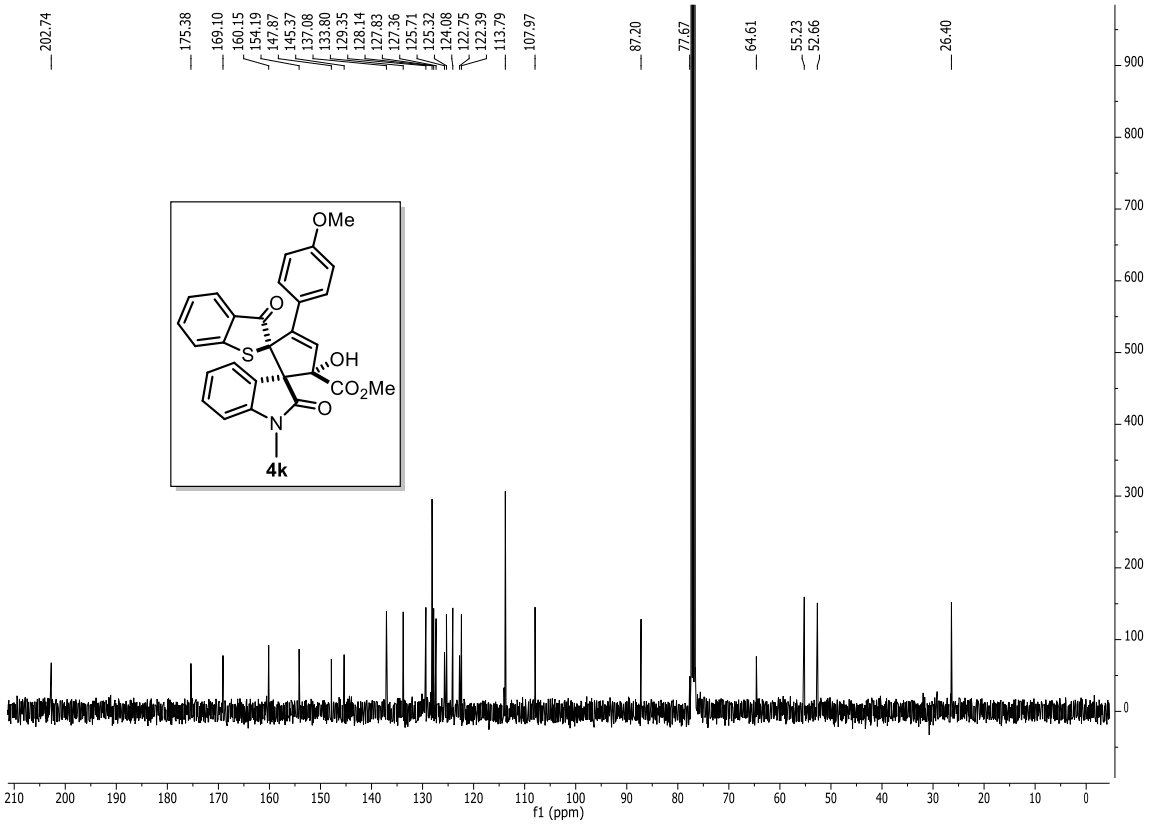
^{1}H NMR (400 MHz, $CDCl_3$)



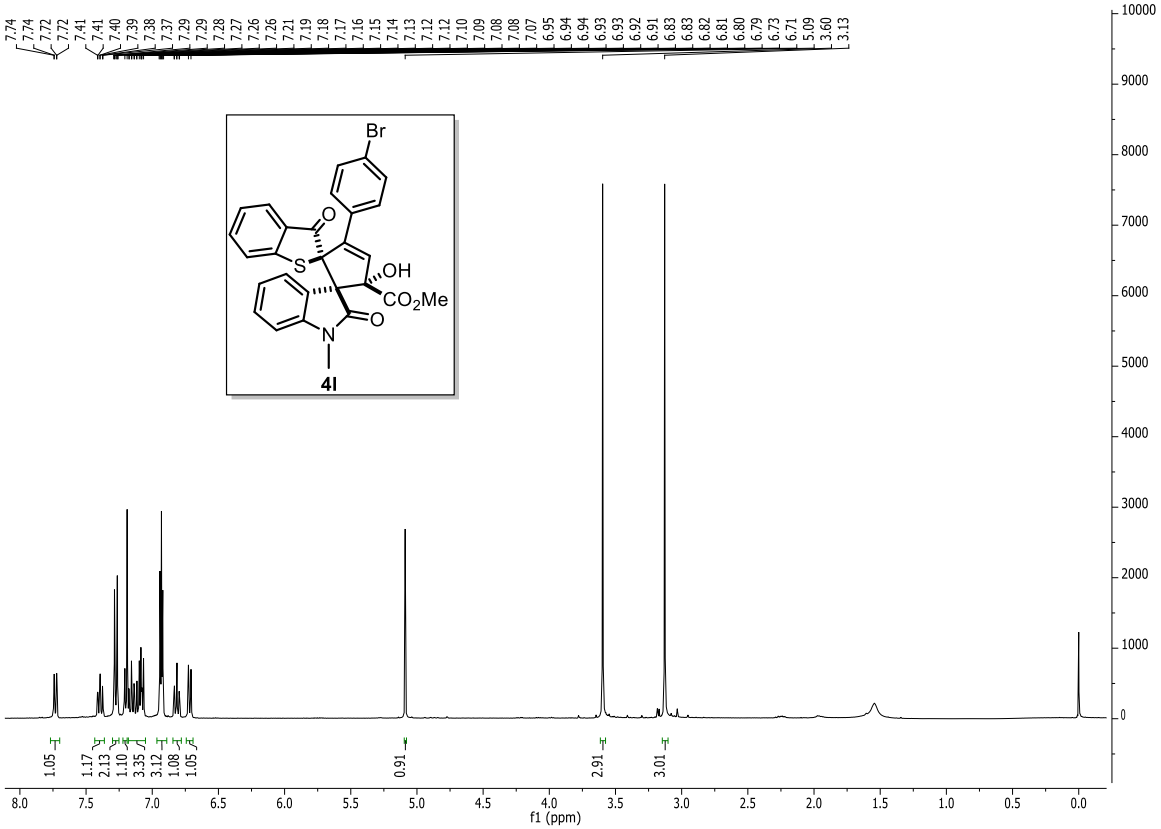
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



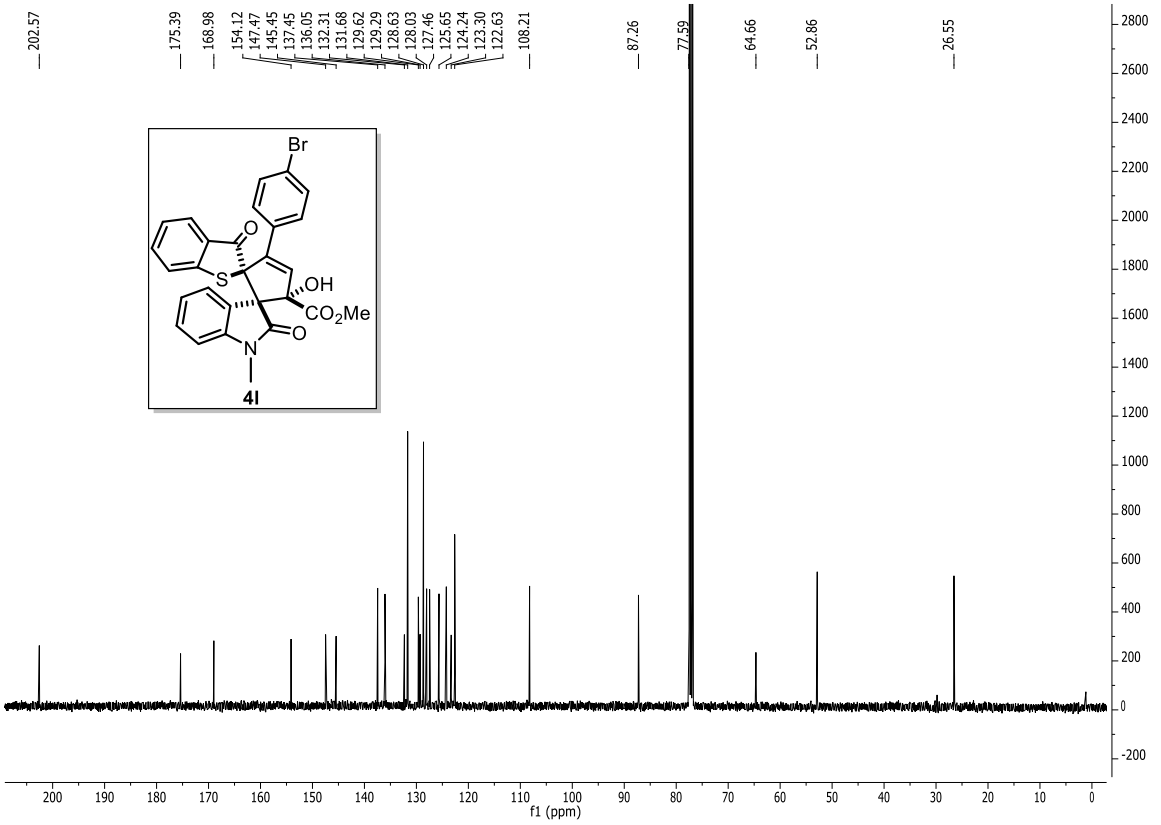
^{1}H NMR (400 MHz, $CDCl_3$)



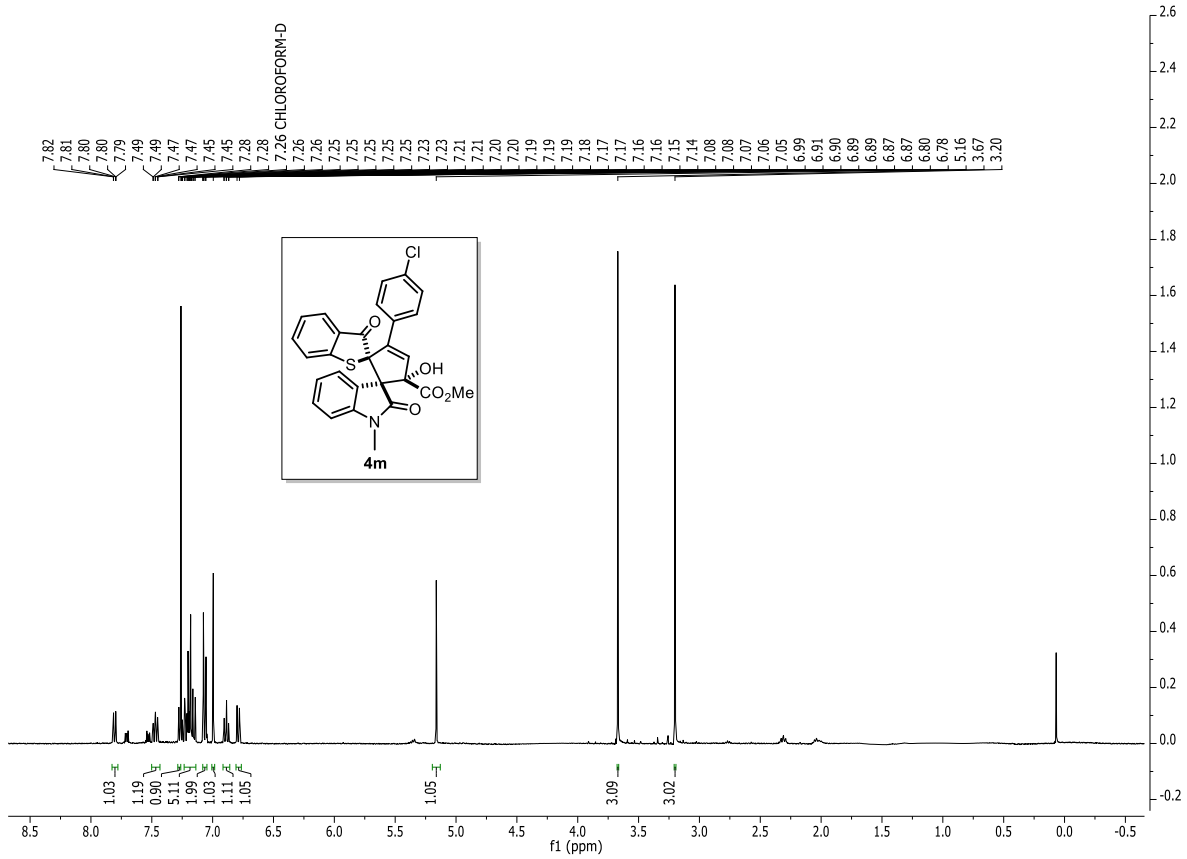
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



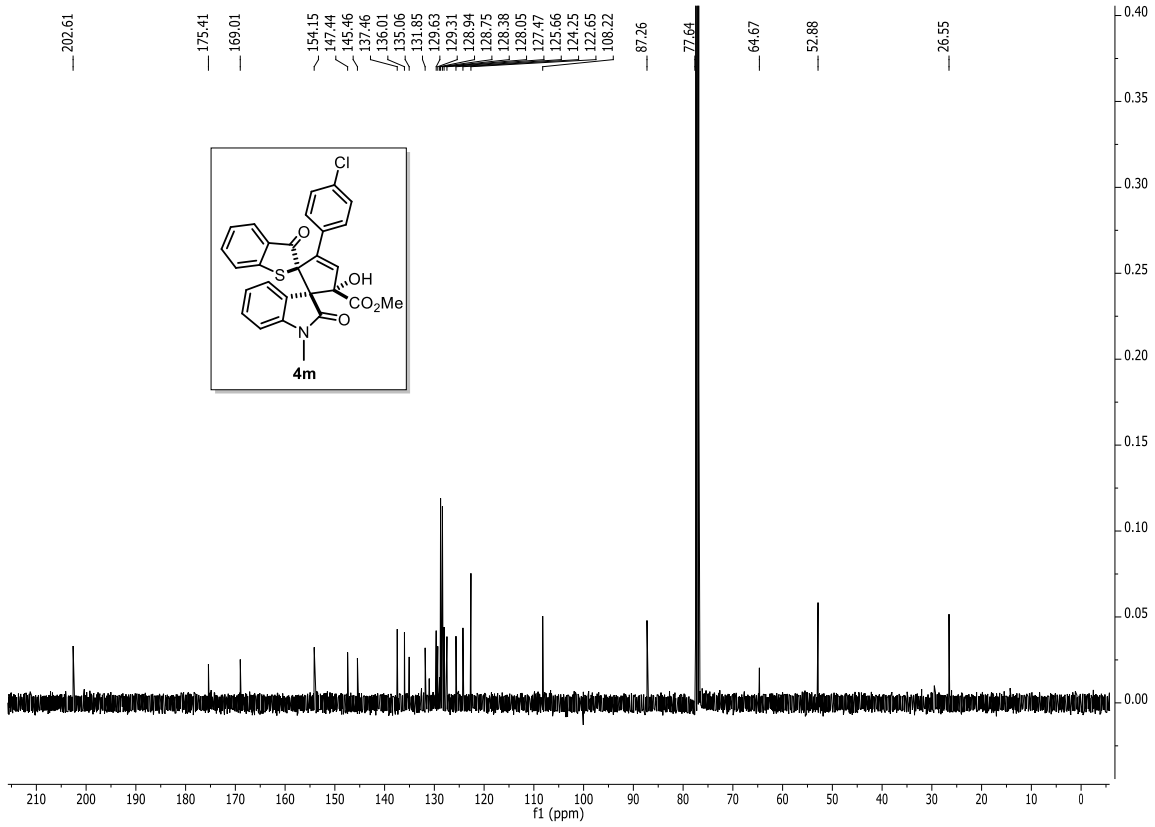
^{1}H NMR (400 MHz, $CDCl_3$)



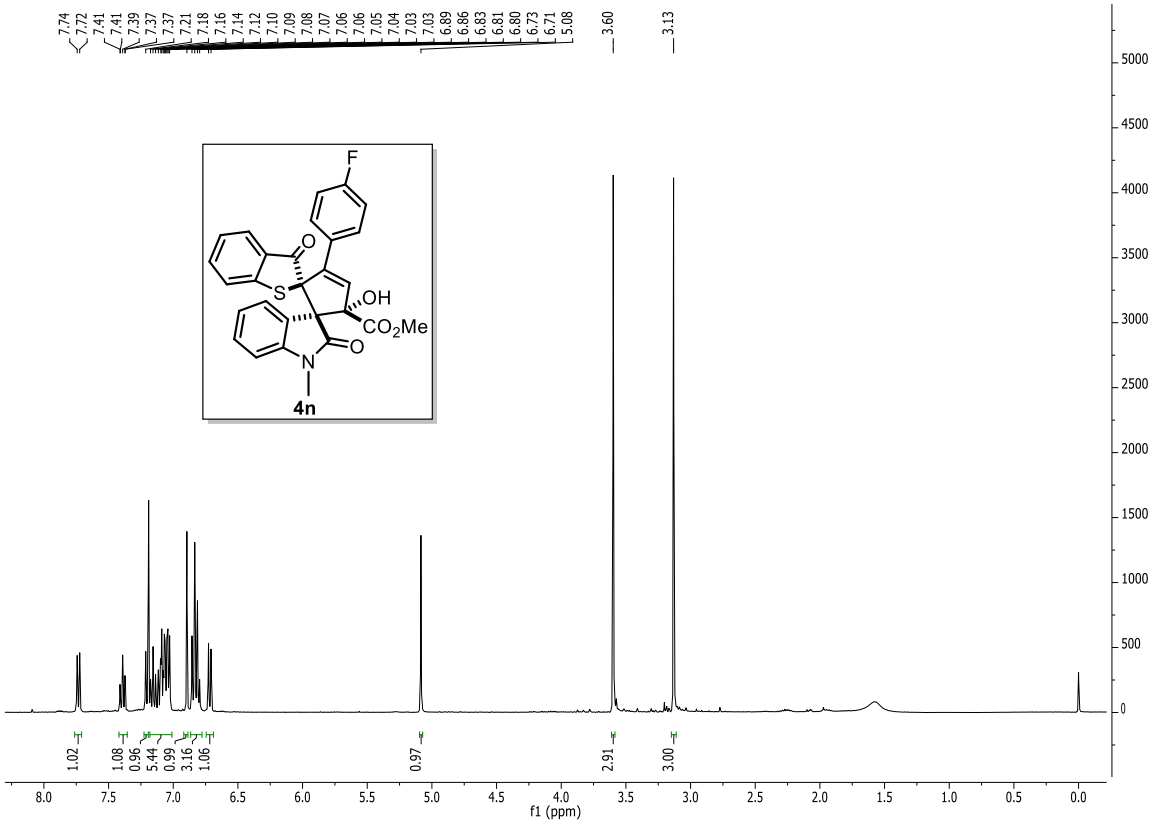
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



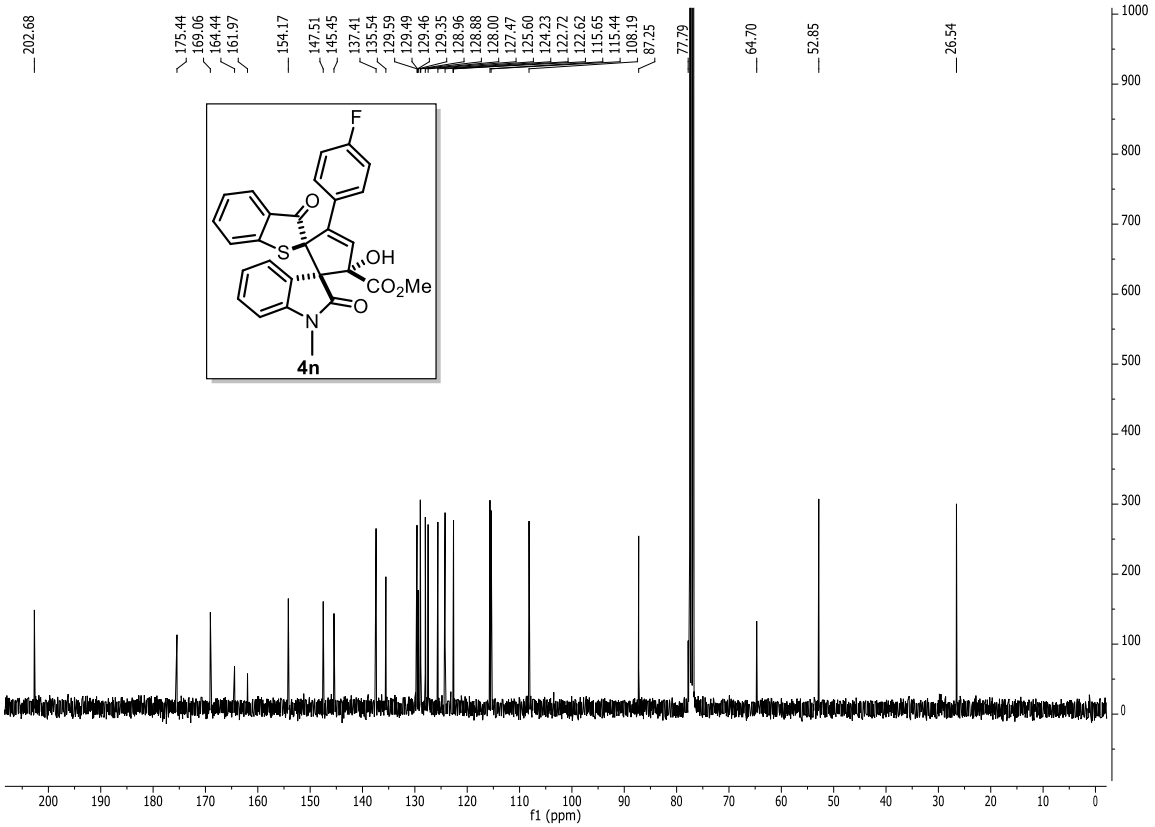
^{1}H NMR (400 MHz, $CDCl_3$)



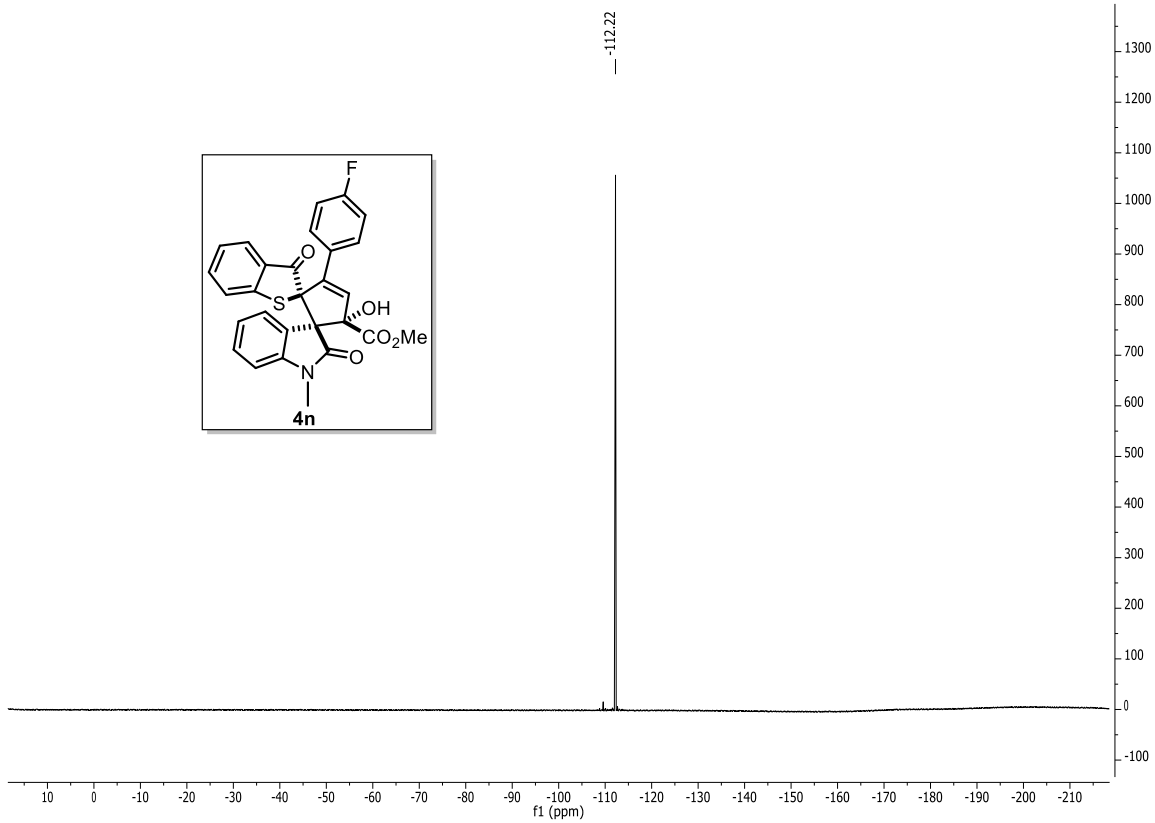
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



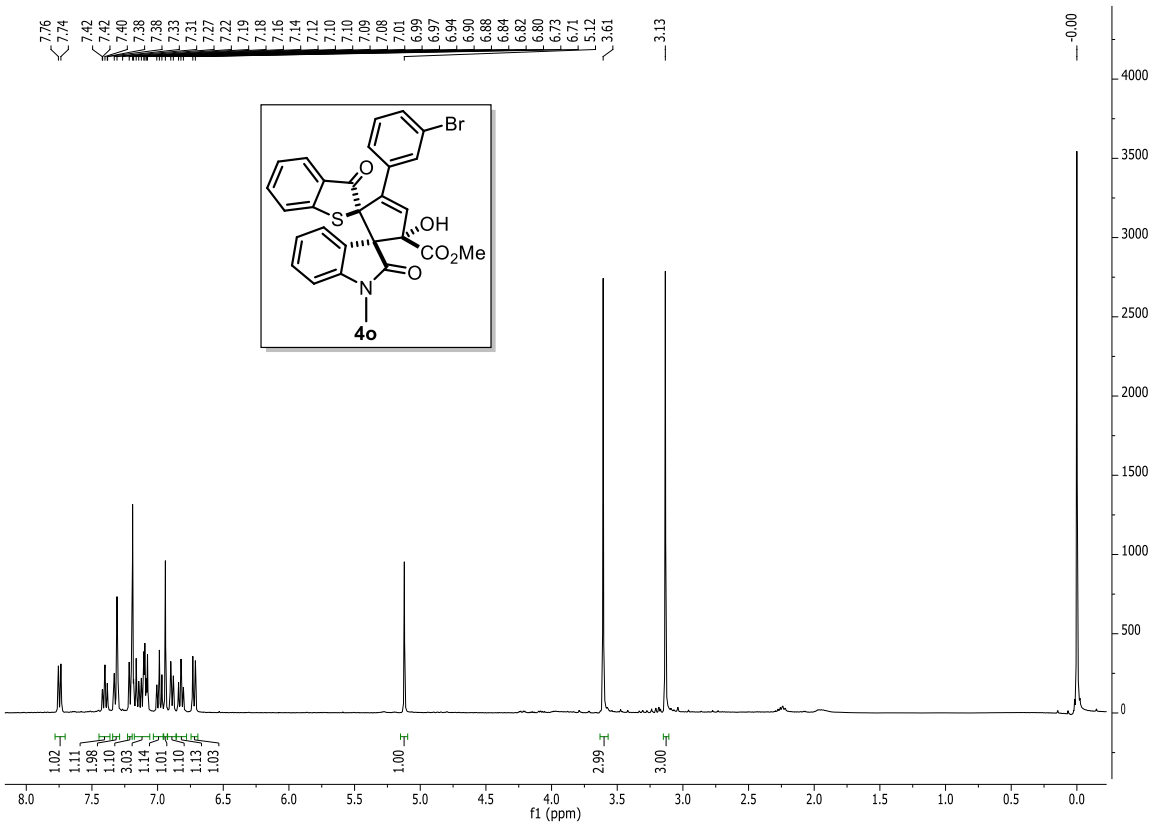
^{1}H NMR (400 MHz, $CDCl_3$)



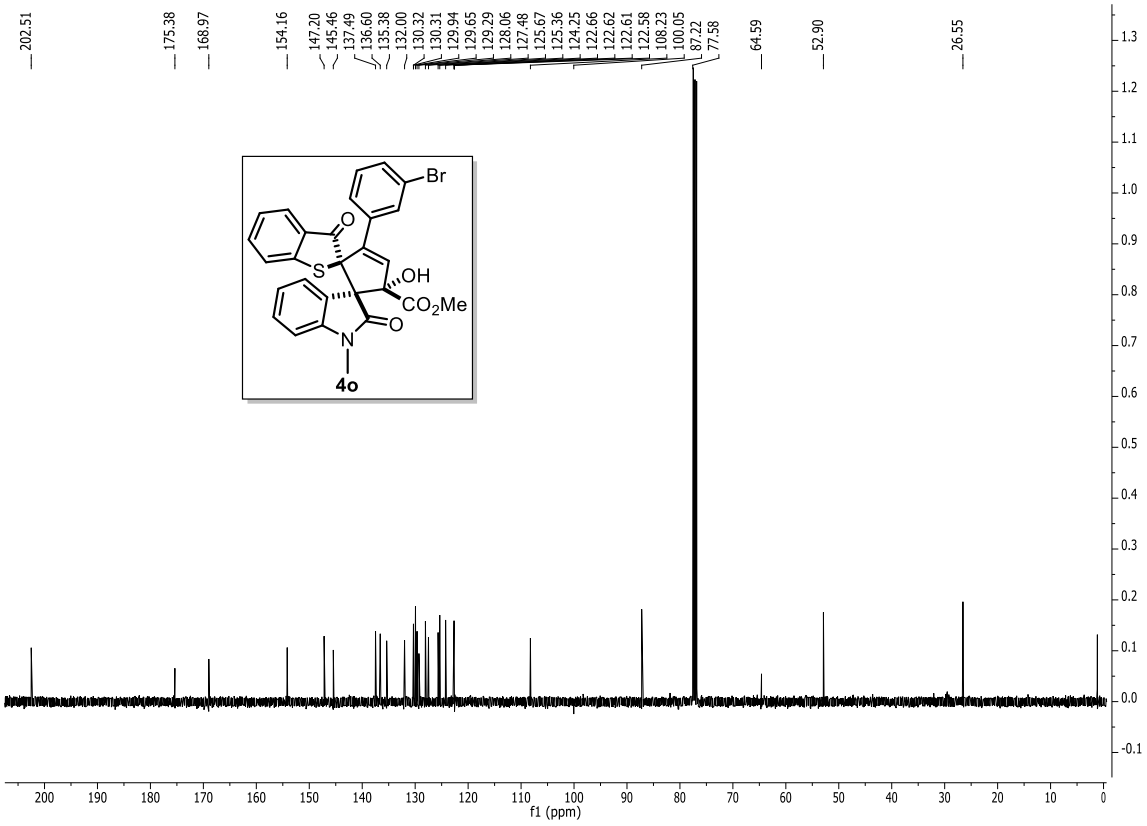
^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



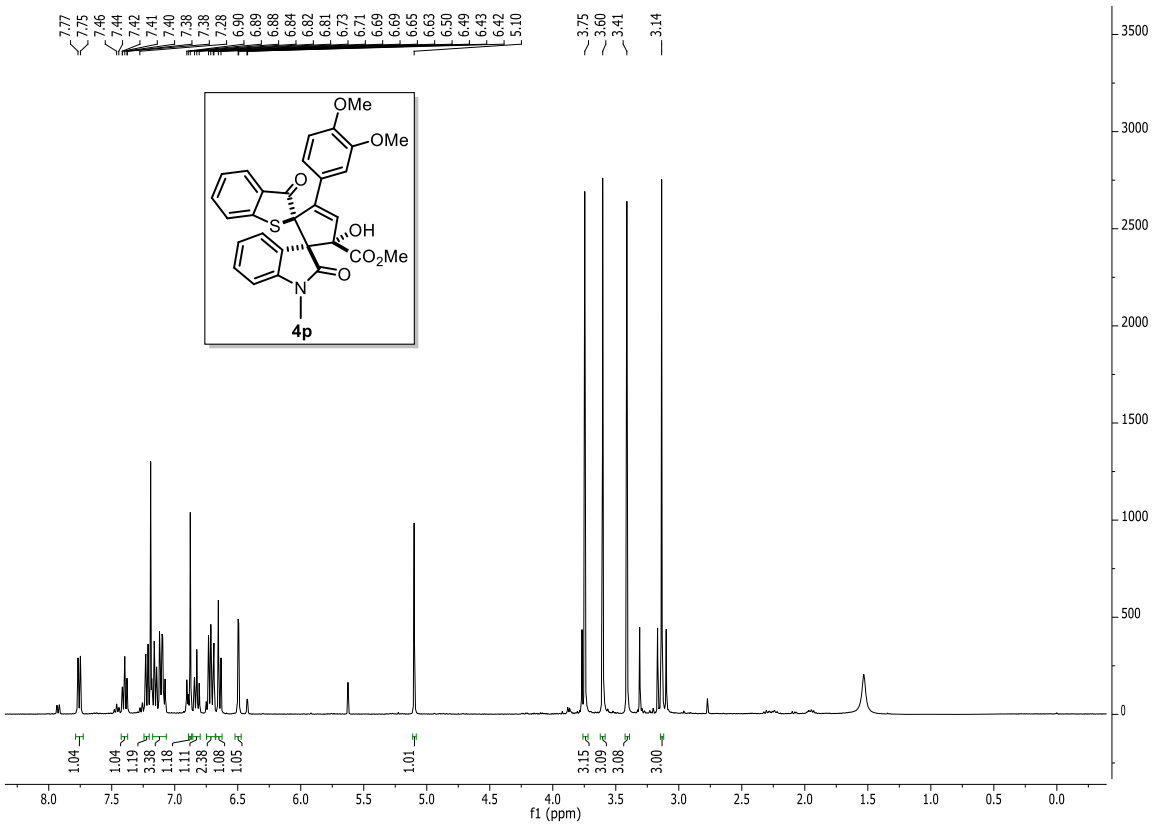
^{19}F NMR (377 MHz, $CDCl_3$)



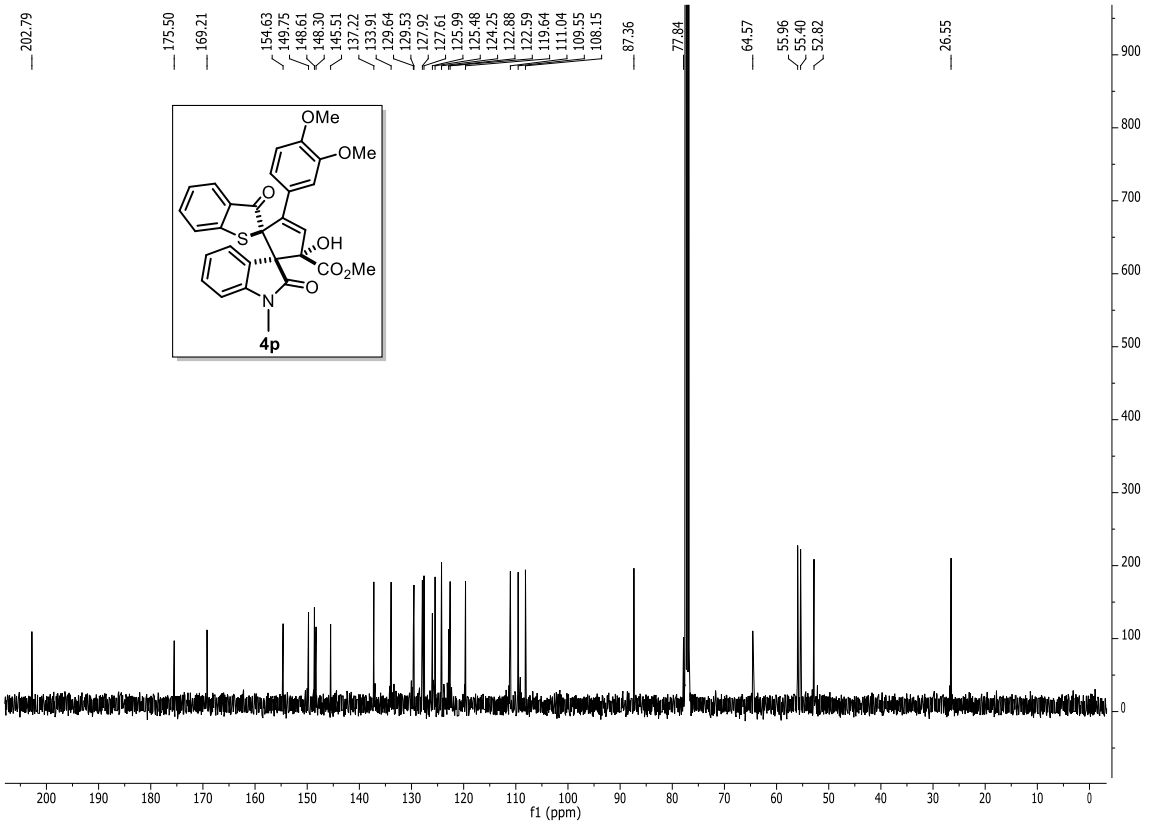
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$)

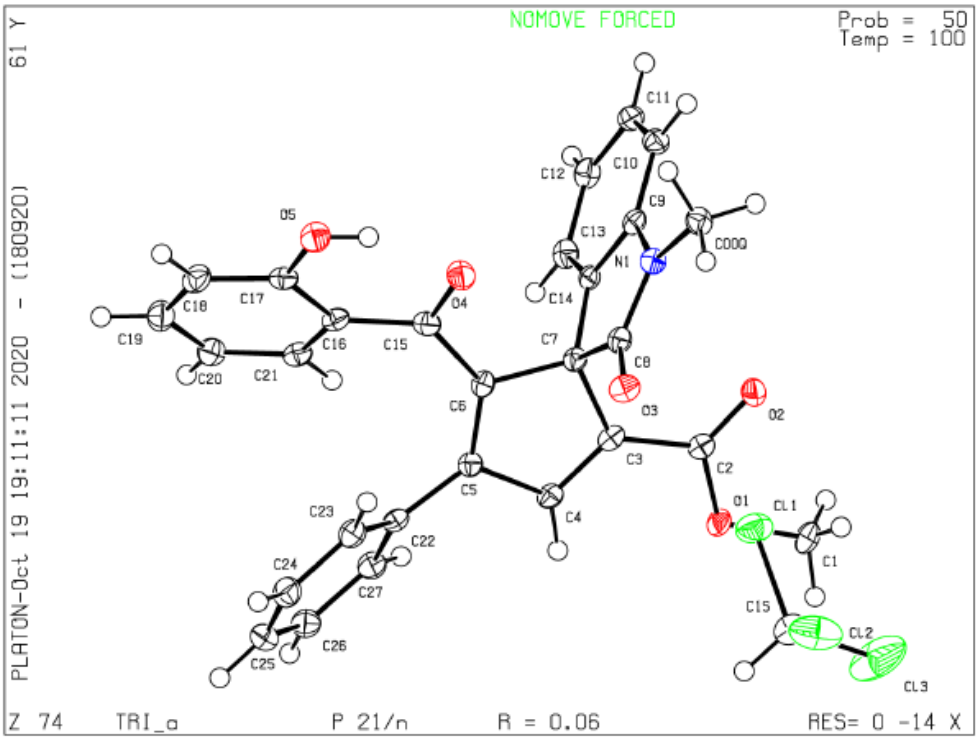
Crystallographic data

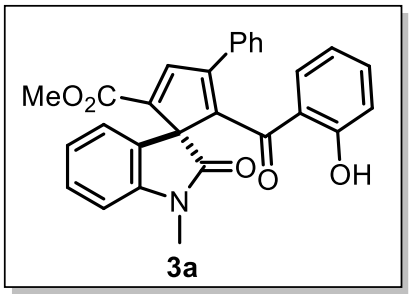
Molecular Structure of compound **3a** using Single Crystal X-ray analysis

Datablock: 3a CCDC 2067873

```
Bond precision:  C-C = 0.0049 A          Wavelength=0.71073

Cell:            a=9.170(14)     b=29.30(4)         c=9.624(15)
                 alpha=90        beta=94.36(2)      gamma=90
Temperature:     100 K

                Calculated                Reported
Volume          2578(7)                   2578(7)
Space group     P 21/n                    P 21/n
Hall group      -P 2yn                    -P 2yn
Moiety formula  C28 H21 N O5, C H Cl3     ?
Sum formula     C29 H22 Cl3 N O5          C29 H22 Cl3 N O5
Mr              570.83                    570.82
Dx,g cm-3       1.471                     1.471
Z               4                         4
Mu (mm-1)       0.398                     0.398
F000            1176.0                    1176.0
F000'           1178.28
h,k,lmax        12,39,12                  12,39,12
Nref            6513                      6463
Tmin,Tmax       0.942,0.965               0.610,0.746
Tmin'           0.942

Correction method= # Reported T Limits: Tmin=0.610 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.992          Theta(max)= 28.473

R(reflections)= 0.0599( 3866)     wR2(reflections)= 0.1580( 6463)

S = 1.029                 Npar= 347
```

Datablock: 3a- Ellipsoid Plot





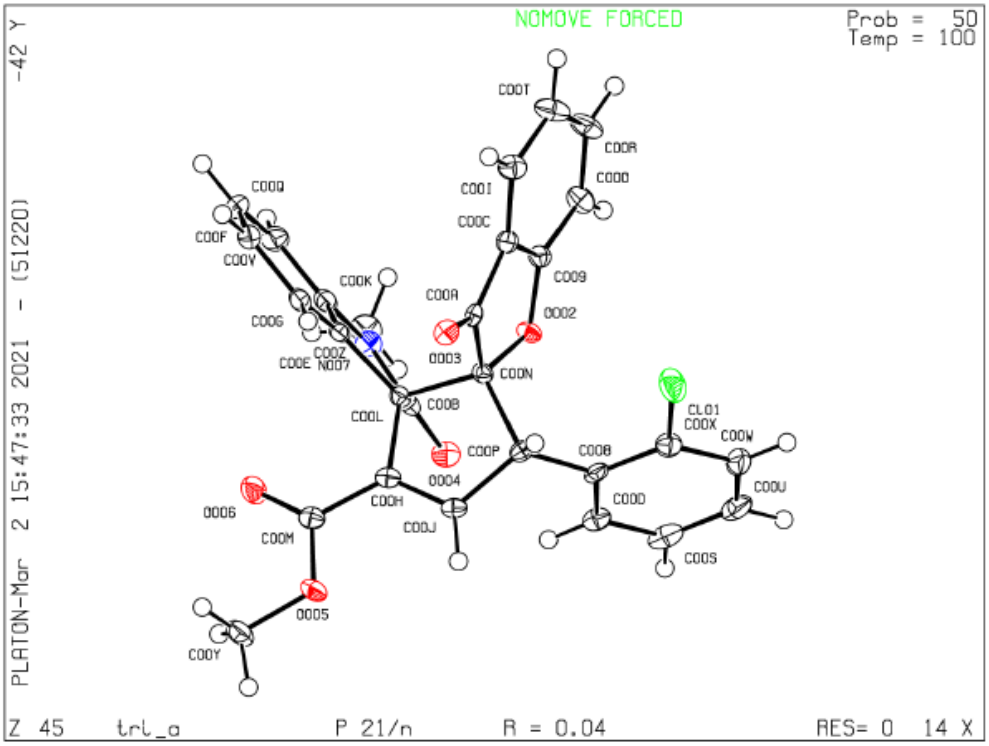
3a

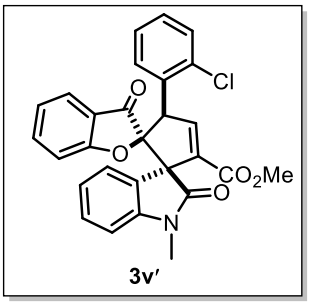
Molecular Structure of compound **3v'** using Single Crystal X-ray analysis

Datablock: 3v' - CCDC 2067878

```
Bond precision:  C-C = 0.0030 A          Wavelength=0.71073

Cell:            a=9.8464(15)     b=16.367(2)        c=14.348(2)
                 alpha=90         beta=94.553(6)     gamma=90
Temperature:     100 K

                 Calculated                Reported
Volume           2305.0(6)                 2305.1(6)
Space group      P 21/n                    P 21/n
Hall group       -P 2yn                    -P 2yn
Moiety formula   C28 H20 Cl N O5           ?
Sum formula      C28 H20 Cl N O5           C28 H20 Cl N O5
Mr               485.90                    485.90
Dx,g cm-3        1.400                     1.400
Z                4                         4
Mu (mm-1)        0.207                     0.207
F000             1008.0                    1008.0
F000'            1009.08
h,k,lmax         11,19,17                  11,19,17
Nref             4066                      4056
Tmin,Tmax        0.973,0.982               0.621,0.746
Tmin'            0.973

Correction method= # Reported T Limits: Tmin=0.621 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.998          Theta(max)= 25.025

R(reflections)= 0.0416( 3245)     wR2(reflections)= 0.0954( 4056)

S = 1.051                 Npar= 318
```

Datablock: 3v'- Ellipsoid Plot



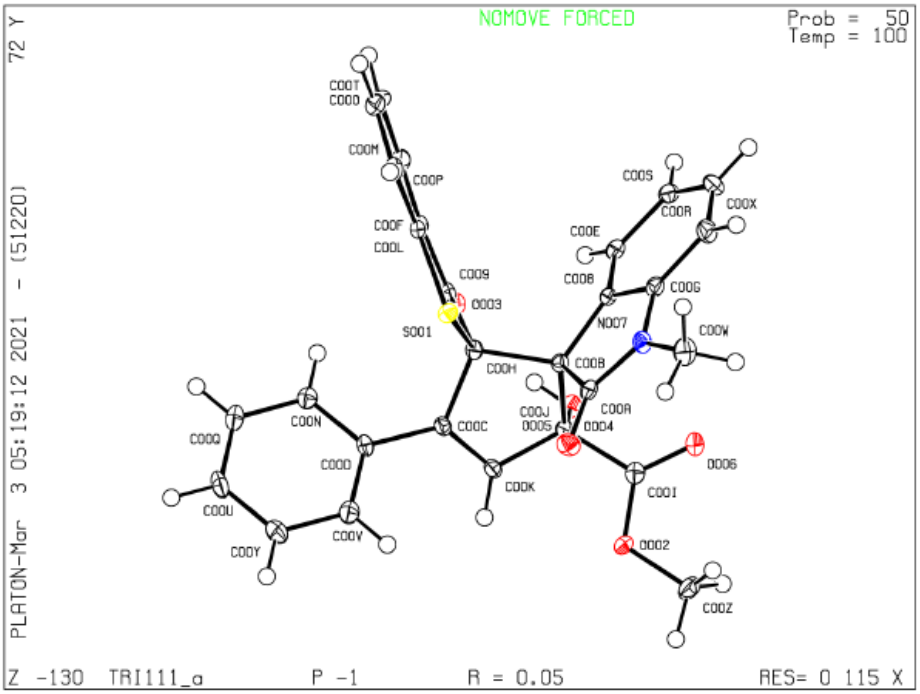


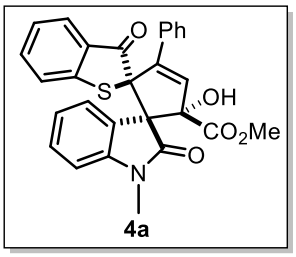
Molecular Structure of compound **4a** using Single Crystal X-ray analysis

Datablock: 4a- CCDC 2067874

```
Bond precision:  C-C = 0.0030 A          Wavelength=0.71073

Cell:          a=9.9440(6)       b=10.1014(5)     c=11.6132(6)
               alpha=79.844(2)   beta=79.371(2)   gamma=84.323(2)
Temperature:   100 K

                Calculated                Reported
Volume          1125.89(11)               1125.89(11)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C28 H21 N O5 S            C28 H21 N O5 S
Sum formula     C28 H21 N O5 S            C28 H21 N O5 S
Mr              483.52                    483.52
Dx,g cm-3       1.426                     1.426
Z               2                         2
Mu (mm-1)       0.186                     0.186
F000            504.0                     504.0
F000'           504.49
h,k,lmax        13,13,15                  13,13,15
Nref            5645                      5434
Tmin,Tmax       0.972,0.983               0.610,0.746
Tmin'           0.972

Correction method= # Reported T Limits: Tmin=0.610 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.963          Theta(max)= 28.388

R(reflections)= 0.0503( 4166)     wR2(reflections)= 0.1532( 5434)

S = 0.910                 Npar= 319
```

Datablock: 4a- Ellipsoid Plot





4a

Molecular Structure of compound **4c** using Single Crystal X-ray analysis

Datablock: 4c- CCDC 2067877

```
Bond precision:        C-C = 0.0022 A                  Wavelength=1.54178
Cell:         a=9.4270(5)       b=10.2071(6)      c=13.7551(8)
              alpha=76.432(2)   beta=74.927(2)    gamma=79.643(2)
Temperature: 100 K
                     Calculated                          Reported
Volume               1232.36(12)                         1232.36(12)
Space group          P -1                                P -1
Hall group           -P 1                                -P 1
Moiety formula       C29 H23 N O6 S                      C29H23No6S
Sum formula          C29 H23 N O6 S                      C29 H23 N O6 S
Mr                   513.54                              513.54
Dx,g cm-3            1.384                               1.384
Z                    2                                   2
Mu (mm-1)            1.556                               1.556
F000                 536.0                               536.0
F000'                538.31
h,k,lmax             11,12,16                            11,12,16
Nref                 4338                                4268
Tmin,Tmax            0.817,0.883                         0.622,0.754
Tmin'                0.817
Correction method= # Reported T Limits: Tmin=0.622 Tmax=0.754
AbsCorr = MULTI-SCAN
Data completeness= 0.984          Theta(max)= 66.593
R(reflections)= 0.0364( 3919)         wR2(reflections)= 0.0937( 4268)
S = 1.031               Npar= 339
```

Datablock: 4c- Ellipsoid Plot