Supporting Information

$BF_3.Et_2O$ Assisted Synthesis of Sulfinylated Spiro[5.5]trienones from Biaryl ynones

Barnali Roy,[a] Puspendu Kuila,[a] Sangam Jha[a] and Debayan Sarkar [b, *]

[a]Department of Chemistry, National Institute of Technology, Rourkela, Odisha, India-769008. [b]Organic Synthesis and Molecular Engineering Laboratory, Department of Chemistry, Indian Institute of Technology, Indore, Madhya Pradesh, India-453552. E-mail: sarkard@iiti.ac.in.

TABLE OF CONTENT

A. General Information

General Setup: Procedures employing commercially available nitrogen, oxygen, Tarsons magnetic bead, Remi 5MLH stirrer, borosilicate glassware and moisture-sensitive reactions were performed with anhydrous solvents using standard inert atmosphere techniques (atmosphere of anhydrous nitrogen or argon). Room temperature (rt) typically ranged between 25–30 °C, depending on the time of the day.

NMR Spectroscopy: ^{1}H and $^{13}C\{^{1}H\}$ spectra were recorded at 400 MHz and 100 MHz respectively, using a Bruker Advance spectrometer (400 MHz). Spectra were recorded at 298 K (25 °C) on the Bruker. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to residual solvent peaks. Chemical shifts are reported in parts per million (ppm) relative to residual chloroform (δ = 7.28 ppm, ^{1}H; 77.05 ppm, ^{13}C). All $^{13}C\{^{1}H\}$ resonances are assumed to be singlets, unless stated otherwise. Coupling constants, *J*, reported in Hertz (Hz), were calculated using *Mestrenova* to the nearest 0.1 Hz. The following abbreviations (and their combinations) are used to label the multiplicities: br (broad), s (singlet), d (doublet), t (triplet), q (quartet), sept (septet), and m (multiplet).

Infrared Spectroscopy: Infrared (IR) spectra of neat compounds were recorded over the range 4000–650 cm^{-1} using a Shimadzu FTIR Spectrum 100 ATR-FTIR spectrometer. Peaks are reported in cm^{-1}.

Mass Spectrometry: Electrospray ionisation (ESI+) spectra were recorded on a Waters Xevo G2- XS QTof/Tof and 6200 series TOF/6500 series Q-TOF B.09.00 (B9044.1SP1) mass spectrometer with an orthogonal Z-spray-electrospray interface on a micro-mass spectrometer. Data are reported in the form of m/z (intensity relative to the base peak = 556.2771).

Chromatography: Analytical thin-layer chromatography was performed on Merck silica gel 60 F_{254} aluminium-backed plates. Visualisation was accomplished with UV light (long range), iodine (I_2) on silica, ethanolic acidic vanillin solution and/or aqueous basic potassium permanganate ($KMnO_4$). Flash column chromatography (manual) was performed using high purity grade silica gel, pore size 60 Å, 100-200 mesh particle size (Sigma-Aldrich, Cat. No. 288594).

Crystal for X-ray Sample Preparation: Crystal suitable for X-ray were grown by dissolving the sample in a solvent which is soluble in a mixture of CH_2Cl_2 and distilled petroleum ether (3:1). The compound is not soluble in distilled pet ether but soluble in CH_2Cl_2. The solution was kept without any interference causing crystallisation.

Crystallography: Single-crystal X-ray diffraction data (**3w** and **3d**) were collected with a Rigaku X-ray diffractometer equipped with a micro-focus sealed X-ray tube and HyPix3000 CCD a CCD area detector and operated at 250 W power (50 kV, 0.8 mA) to generate Cu Kα (λ = 1.54184) at 100 K. The crystals were placed on top of a nylon Cryoloop (Hampton research) and then mounted in the diffractometer. Samples were initially scanned to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal. CrysAlisPro program software was used suite to carry out overlapping φ and ω scans at detector (2θ) settings (2θ, ~6 to ~60°with 0.3° scans in ω and 10 s per frame exposures). After the data collection, all the reflections were sampled from all regions of the Ewald sphere to re-determine the unit cell parameters for data integration. CrysAlisPro software was also used for the data integration with a narrow frame algorithm. SCALE3 ABSPACK3 scaling algorithm program was used for the subsequent data correction for adsorption. The structure was solved by a direct method and refined using the SHELXL 2016 software suite. Atoms were located from an iterative examination of difference F-maps following least-squares refinements of the earlier models. The final model was refined anisotropically (if the number of data permitted) until full convergence was achieved. The ellipsoids in ORTEP diagrams are displayed at the 50% probability level unless noted.

Solvents: Reaction solvents were dried following standard procedure. Toluene (PhMe), methanol (MeOH), and isopropanol (^{i}PrOH) were dried over sodium metal. Acetonitrile (MeCN) and dichloromethane (DCM) were dried by phosphorus pentoxide (P_2O_5). Dimethyl sulfonyloxide (DMSO) was dried over calcium hydride (CaH_2) and stored all the solvent over 4 Å molecular sieves. Ethylacetate (EtOAc) and pet ether (40–60°) were distilled by potassium carbonate (K_2CO_3) and potassium hydroxide (KOH) respectively for column chromatography. Deuterated chloroform ($CDCl_3$) and CD_3CN were used as received. Solvents for filtration, transfers including acetonitrile (MeCN), dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc) and 40–60° petroleum ether (petrol) were also used after distillation.

Chemicals: Chemicals purchased from commercial suppliers were used as received. Chemicals used are from Avra, HIMEDIA, Sigma, TCI chemicals.

Nomenclature: Atom numbers shown in chemical structures herein correspond to the IUPAC nomenclature, which was used to name each compound.

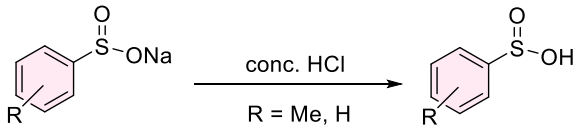
Abbreviations Used: aq. = aqueous, ACN = acetonitrile, DCM = dichloromethane, DMSO = dimethyl sulfoxide, EI = electron ionization, ESI = electrospray ionization, Et_3N = triethylamine, EtOAc = ethyl acetate, equiv. = equivalence, HRMS = high resolution mass spectroscopy, IR = infrared, ^{i}Pr = isopropyl, MeCN = acetonitrile, Na_2SO_4 = sodium sulfate, nBu = n-butyl, NaOH = sodium hydroxide, NMR = nuclear magnetic resonance, TLC = thin-layer chromatography, rt = room temperature, calc. = calculated, conv. = conversion, conc. = concentration, h = hour, alc. = alcohol.

B. Experimental Section:

B.1 General procedure for the synthesis of sulfinic acids

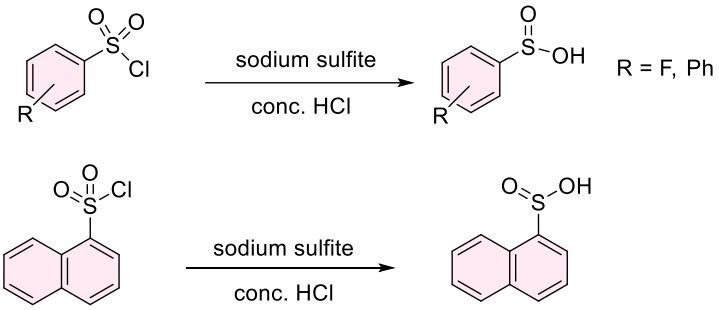
Sulfinic acids were prepared according to the standard literature methods[1a].

Procedure I



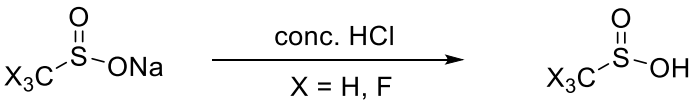
4-methylbenzenesulfinic acid and benzene sulfinic acid were prepared from the corresponding commercially available sodium sulfinates following a general experimental procedure: Sodium 4-methylbenzenesulfinate (10 mmol) or sodium benzenesulfite (10 mmol) was dissolved in H_2O (20 mL), respectively. Then, concentrated HCl was added dropwise to this mixture, the crystals of sulfinic acids were separating out in the beaker. This mixture was stirred in an ice-bath for 30 min. Subsequently, the white precipitate was collected by filtration, and dried. Finally, 4-methylbenzenesulfinic acid (1.29 g, 8.3 mmol, 83%) or benzene sulfinic acid (1.13 g, 8.0 mmol, 80%) was obtained as white solild.

Procedure II



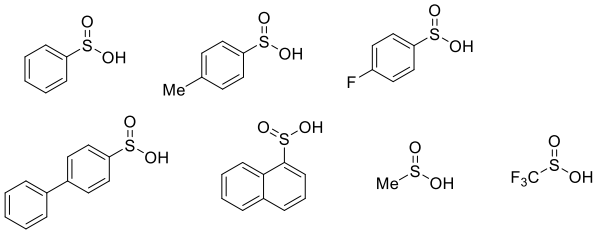
An experimental procedure for the synthesis of other aryl sulfinic acids is shown as following: aryl sulfonyl chloride (1.0 mmol) was added to a solution of anhydrous sodium sulfite (3.0 mmol) in water (5 mL), then, the mixture was stirred at 70-80 °C for overnight. After the reaction was completed, the aqueous layer was washed with $CHCl_3$ (3×10 mL) to remove the residue of sulfonyl chloride. Subsequently, the aqueous part was acidified with excess concentrated HCl solution, and extracted with tert-butyl methyl ether (3×10 mL). Combined organic layer was removed by evaporation, and the residue was dried under reduced pressure (in case of 4-fluorobenzenesulfinic acid which was obtained as white oil). In case of other solid aryl sulfinic acids, the acidified solution was cooled down and then filtered. The white precipitate was recrystallized from water yielding aryl sulfinic acid.

Procedure III

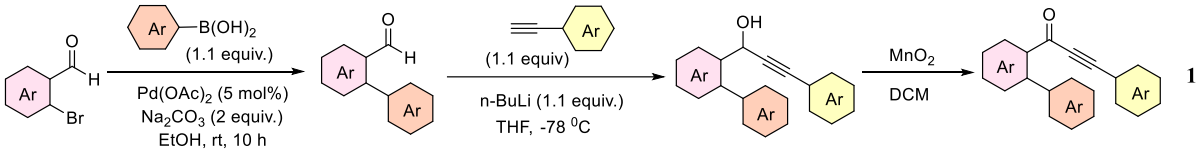


In case of aliphatic sulfinic acids, they were prepared from the corresponding commercially available sulfinates following the procedure I.

The sulfinic acids we prepared



B.2 General procedure for the synthesis of biaryl ynones[1b]



General Procedure for Suzuki Coupling with Arylboronic Acids

In a 100 mL round-bottomed flask with a magnetic bar was charged with 2-bromobenzaldehyde (20 mmol), an arylboronic acid (22 mmol), $Pd(OAc)_2$ (1 mmol), Na_2CO_3 (40 mmol), and EtOH (40 mL). The reaction mixture was stirred at room temperature for 10 h. The solution was filtered through celite and EtOH was evaporated. The solution was then extracted with ethyl acetate (20 mL * 3) and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated using a rotary evaporator, under reduced pressure. The subsequent residue was then purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the 2-(4-methoxyphenyl)benzaldehyde (85% yield).

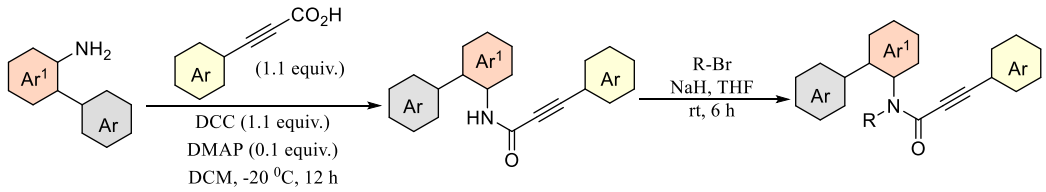
General Procedure for Synthesis of Secondary Alcohols

To a 50 mL two-necked flask charged with alkyne (5.5 mmol) was evacuated and backfilled with nitrogen. Then anhydrous THF (20 mL) was added and cooled to -78 ^oC. n-BuLi (5.5 mmol, 2.5 M in hexane) was then added in 10 min to the solution and the reaction was kept at -78 ^oC for another 1 h. The above aldehyde (5.0 mmol) was added and the mixture was allowed to warm to room temperature and kept for 6 h. The solution was then quenched with saturated aqueous NH_4Cl (20 mL), extracted with ethyl acetate (30 mL * 3). The combined organic layer was washed with saturated NaCl, dried over anhydrous Na_2SO_4. Then it was concentrated and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the 1-(4'-methoxy-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-ol (90% yield).

General Procedure for Oxidation of Biaryl Ynols

To a 100 mL flask charged with the above secondary alcohol (4.0 mmol) was added anhydrous DCM (30 mL) and MnO_2 (40 mmol). The solution was then stirred vigorously at room temperature for 10 h. Afterwards, the solution was filtered through celite and the filtrate was concentrated. The residue was subjected to flash column chromatography on silica gel using ethyl acetate/petroleum ether as eluent to give product 1-[4'-methoxy(1,1'-biphenyl)-2-yl]alkynones **1** (80% yield).

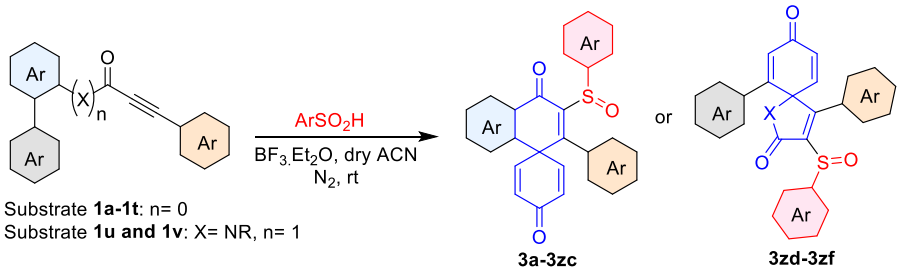
B.3 General procedure for the synthesis of N-([1,1'-biphenyl]-2-yl)-N-alkyl-3-arylpropiolamide derivatives



In a round-bottomed flask, a solution of phenyl propiolic acid (1.1 equiv.) was made by the addition of 10 mL CH_2Cl_2 (DCM); followed by a mixture of 4-dimethylaminopyridine (0.1 equiv.) and dicyclohexylcarbodiimide (1.1 equiv) in 5 mL CH_2Cl_2 was slowly added to the propiolic acid solution and the solution was allowed to stir at -20 °C. Again, a solution of aniline (5.31 mmol, 1.0 equiv.) or phenol (9.4 mmol, 1.0 equiv.) in 5 mL CH_2Cl_2 was then added dropwise. Afterward, the reaction mixture was stirred at room temperature for another 12 h. After completion of the reaction, the crude reaction mixture was washed by 0.5 M aq. HCl, dried over Na_2SO_4, and concentrated under rotary-evaporator. Finally, the crude residue was purified by column chromatography to afford the desired phenylpropiolate or phenylpropiolamide derivatives.

To a stirred solution of phenylpropiolamide (1.0 equiv.) in 10 mL THF, NaH (2.0 equiv.) was added and stirred for 30 min. Then, RBr (2.0 equiv.) was added dropwise. After that, the reaction mixture was left for stirring for next 6 h at rt. The solution was then quenched with saturated aqueous NH_4Cl (20 mL), extracted with ethyl acetate (30 mL * 3). The combined organic layer was washed with saturated NaCl, dried over anhydrous Na_2SO_4. Then it was concentrated and the residue was purified by flash column chromatography on silica gel (eluent: petroleum ether/ethyl acetate) to afford the desired product (56% yield).

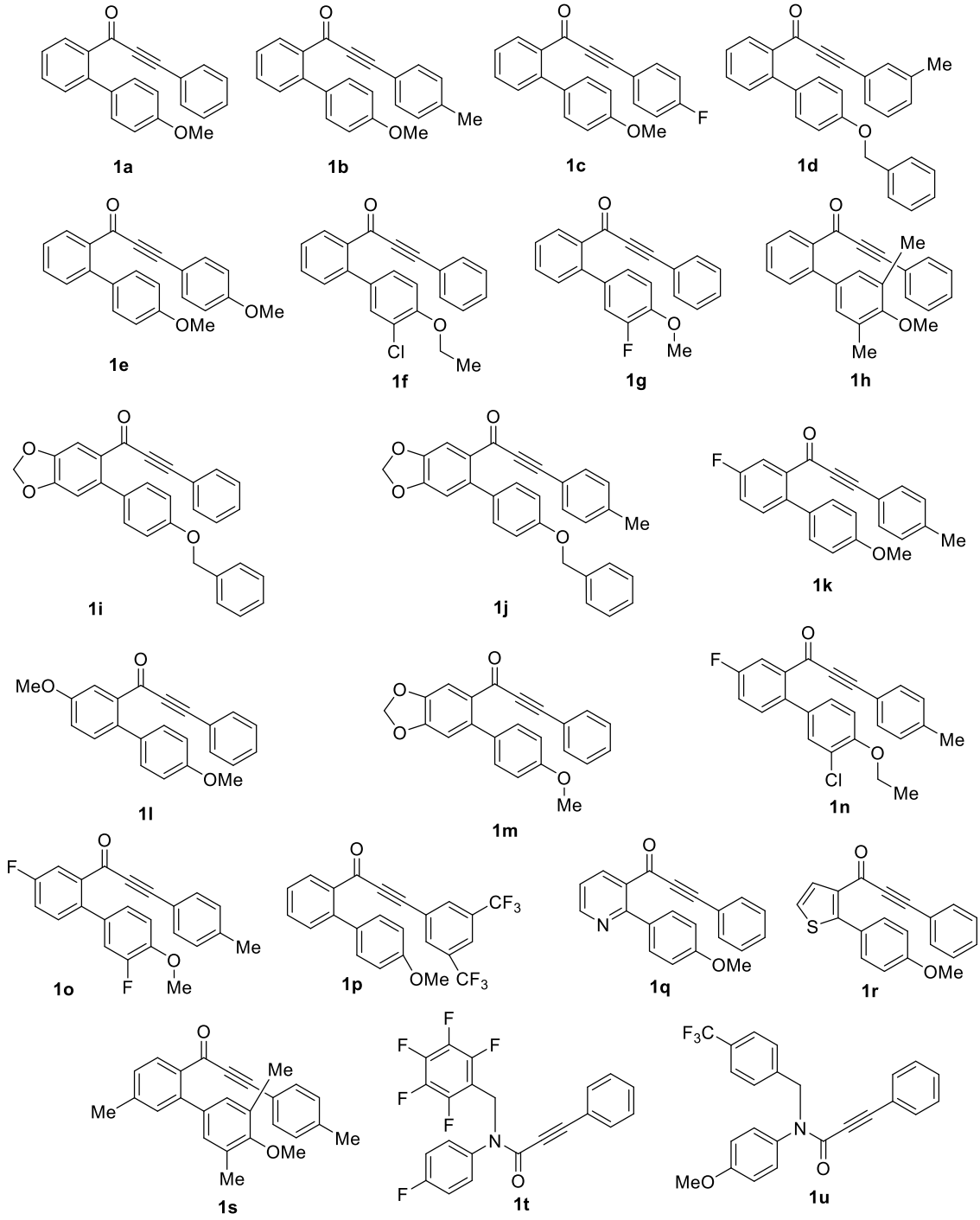
B.4 General procedure for the synthesis of ´3´



Biaryl ynone (**1**, 1.0 equiv.), arylbenzenesulfinic acid (**2**, 1.5 equiv.), and $BF_3{\cdot}Et_2O$ (2.5 equiv.) were added into a round-bottomed flask with 3 mL of anhydrous acetonitrile (ACN). The flask containing the reactants and solvent was stirred at room temperature for 14 h. After the reaction was completed, the mixture was quenched with water (10 mL). The aqueous layer was extracted with EtOAc (3x5 mL), The organic phase was combined and evaporated to remove the solvent in vacuo, and the resulting crude mixture was purified by flash chromatography on silica gel (40% EtOAc in petroleum ether) to provide the desired product (**3**) in good to excellent yield.

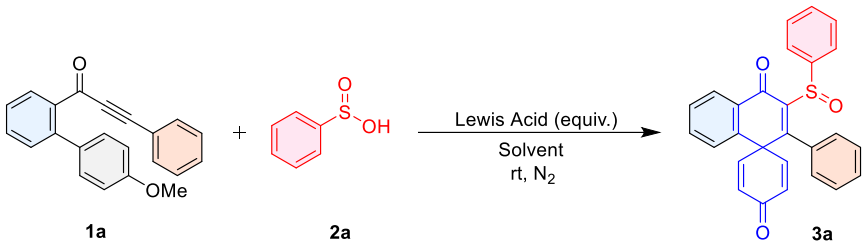
Scope of substrate:

The biaryl ynones **1a** – **1s** and N-aryl ynones **1t** – **1u** used in this study are known compounds and were prepared as described above.[1b]



C. Optimization of Reaction Conditions

Supplementary Table 1. *Optimization of Solvents for Sulfinylation Reaction* [a]

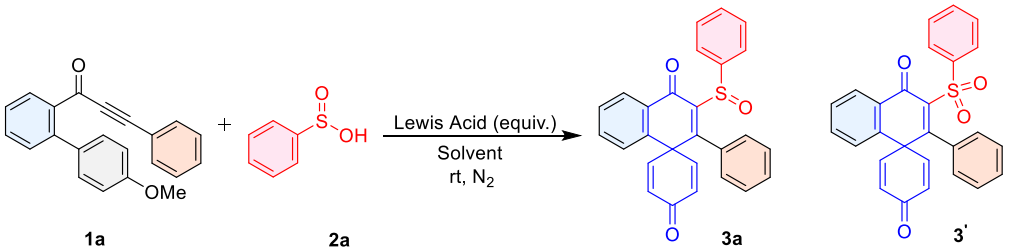


1a 2a 3a

Entry	Solvent	Lewis Acid (equiv.)	Time (h)	Yield (%) [b]
1.	Toluene	$BF_3.Et_2O$ (2.0)	10	52
2.	DCM	$BF_3.Et_2O$ (2.0)	10	43
3.	DCE	$BF_3.Et_2O$ (2.0)	10	46
4.	MeOH	$BF_3.Et_2O$ (2.0)	10	nd
5.	EtOH	$BF_3.Et_2O$ (2.0)	10	nd
6.	EtOAc	$BF_3.Et_2O$ (2.0)	10	nd
7.	Acetone	$BF_3.Et_2O$ (2.0)	10	nd
8.	CH_3CN	$BF_3.Et_2O$ (2.0)	10	66
9.	THF	$BF_3.Et_2O$ (2.0)	10	nd
10.	DMSO	$BF_3.Et_2O$ (2.0)	18	nd
11.	DMF	$BF_3.Et_2O$ (2.0)	18	nd
12.	CH_3CN/H_2O (10:1)	$BF_3.Et_2O$ (2.0)	12	trace

[a] Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **2a** (0.15 mmol), solvent (3.0 mL), 25°C under N_2 atmosphere. [b] Isolated yields.

Supplementary Table 2. *Optimization of Lewis Acids for Sulfinylation Reaction* [a]



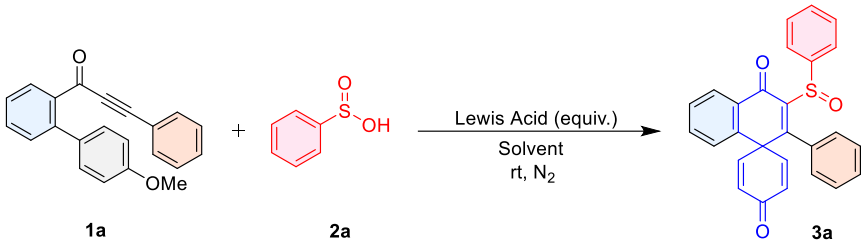
1a 2a 3a 3'

Entry	Solvent	Lewis Acid (equiv.)	Time (h)	Yield (%) [b]
1.	CH_3CN	$BF_3.Et_2O$ (3.0)	14	76
2.	CH_3CN	$TiCl_4$ (3.0)	12	nd
3.	CH_3CN	$AlCl_3$ (3.0)	12	nd (3′, 22)
4.	CH_3CN	$FeCl_3$ (3.0)	12	nd
5.	CH_3CN	PTSA (3.0)	12	nd (3′, 34)
6.	CH_3CN	$SnCl_4$ (3.0)	12	nd
7.	CH_3CN	TFA (3.0)	12	12
8.	CH_3CN	$ZnCl_2$ (3.0)	12	nd
9.	CH_3CN	HCl (3.0)	12	nd

10.	CH_3CN	H_2SO_4 (3.0)	12	nd
11.	CH_3CN	$HgCl_2$ (3.0)	12	nd
12.	CH_3CN	$Sc(OTf)_3$ (3.0)	12	nd
13.	CH_3CN	$BF_3.CH_3CN$ (3.0)	18	60
14.	CH_3CN	$BF_3.THF$ (3.0)	18	50

[a] Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **2a** (0.15 mmol), solvent (3.0 mL), 25°C under N_2 atmosphere. [b] Isolated yields.

Supplementary Table 3. *Optimization of Equivalency of Acids and other reaction conditions for Sulfinylation Reaction* [a]

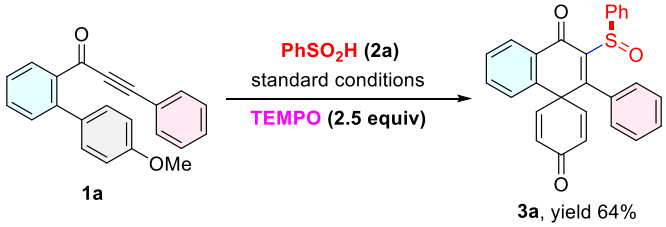


Entry	Solvent	Acid (2a) (equiv.)	Lewis Acid (equiv.)	Time (h)	Yield (%) [b]
1.	CH_3CN	$PhSO_2H$ (1.5)	$BF_3.Et_2O$ (5.0)	10	71
2.	CH_3CN	$PhSO_2H$ (1.5)	$BF_3.Et_2O$ (3.0)	14	76
3.	CH_3CN	$PhSO_2H$ (1.5)	$BF_3.Et_2O$ (2.5)	14	76
4.	CH_3CN	$PhSO_2H$ (1.5)	$BF_3.Et_2O$ (1.2)	18	48
5.	CH_3CN	$PhSO_2H$ (2.5)	$BF_3.Et_2O$ (2.5)	14	45
6.	CH_3CN	$PhSO_2H$ (3.5)	$BF_3.Et_2O$ (2.5)	14	42
7.	CH_3CN	$PhSO_2H$ (1.5)	----	24	nd
8.[c]	CH_3CN	$PhSO_2H$ (1.5)	$BF_3.Et_2O$ (2.5)	14	trace
9.	CH_3CN	$PhSO_2Na$ (2.0)	$BF_3.Et_2O$ (2.5)	14	nd

[a] Reaction conditions unless otherwise noted: **1a** (0.10 mmol), **2a** (0.15 mmol), solvent (3.0 mL), 25°C under N_2 atmosphere. [b] Isolated yields. [c] Under open air.

D. Control Experiment

1. Radical Trapping Experiment

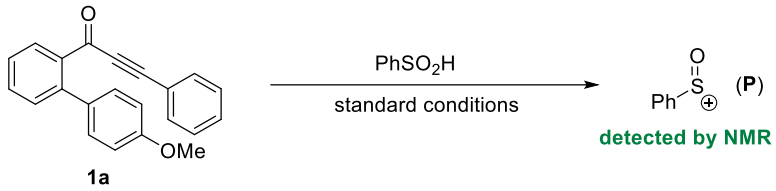


1-(4'-methoxy-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1a**, 0.10 mmol), benzenesulfinic acid (**2a**, 0.15 mmol), $BF_3{\cdot}Et_2O$ (0.25 mmol) and radical scavenger TEMPO (2.0 equiv.) were added into a round-bottomed flask with 3.0 mL of anhydrous acetonitrile (ACN). The flask containing the reactants and solvent was stirred at room temperature for 14 h. The reaction was monitored by TLC and after completion of the reaction, the mixture was quenched with water (10 mL). The aqueous layer was extracted with EtOAc (3x5 mL), The organic phase was combined and evaporated to remove the solvent in vacuo, and the resulting crude mixture was purified by flash chromatography on silica gel (40% EtOAc in petroleum ether) to provide the desired product **3a** in 64% yield.

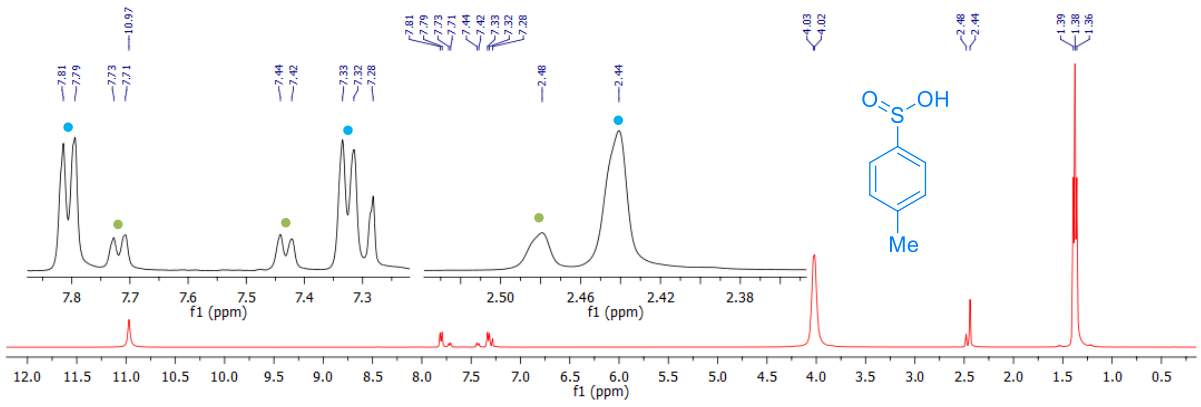
This result suggests that the reaction did not follow radical pathway.

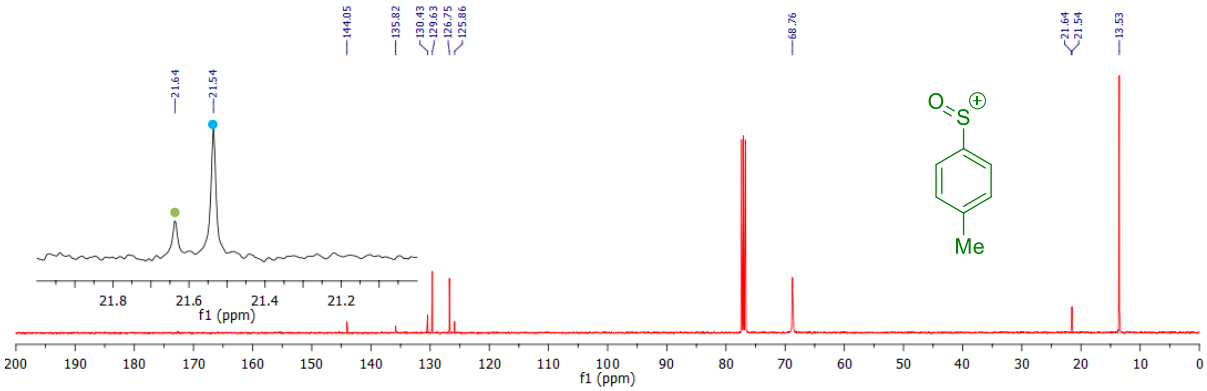
2. The Sulfinyl Cation Trapping Experiment

2.i. In Situ NMR Study



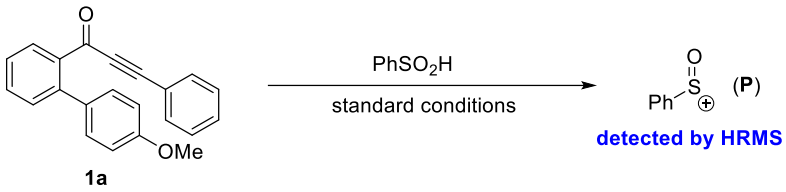
1-(4'-methoxy-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1a**, 0.10 mmol), benzenesulfinic acid (**2a**, 0.15 mmol) and $BF_3{\cdot}Et_2O$ (0.25 mmol) were added into a round-bottomed flask with 3.0 mL of anhydrous acetonitrile (ACN). The flask containing the reactants and solvent was stirred at room temperature for 10 min. The crude reaction mixture was directly detected by HRMS analysis. A sulfinyl cation was detected, as shown in Figure S1.



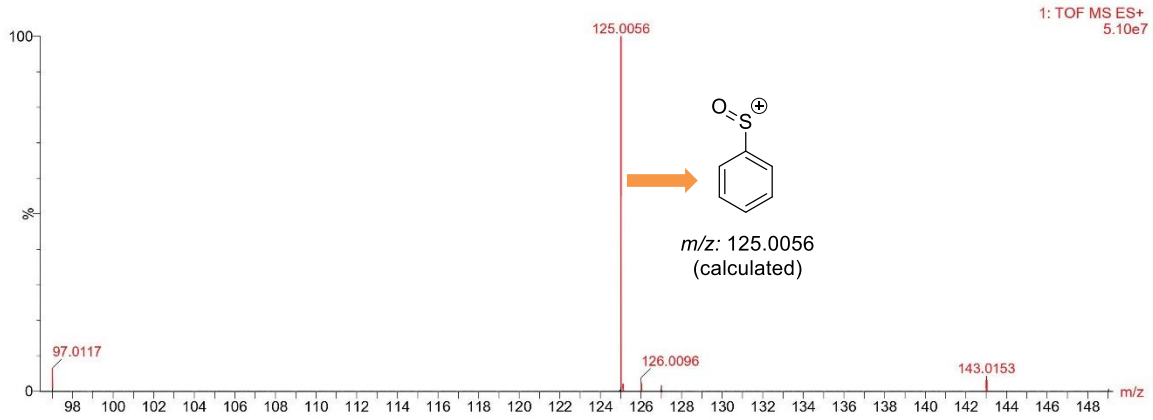


Supplementary Figure 1. In-situ NMR Study to determine the reactive species.

2.ii. In Situ HRMS Study

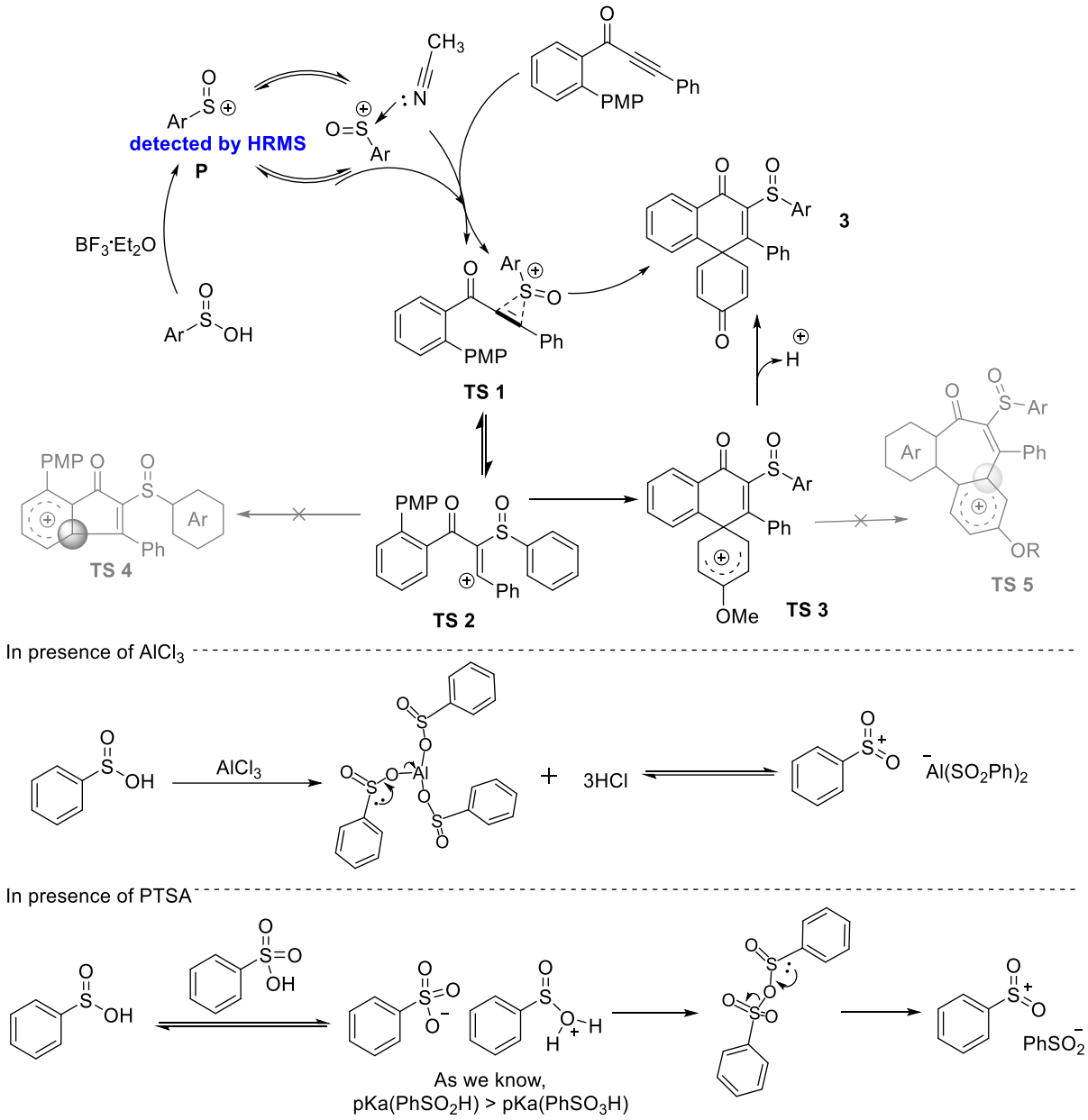


1-(4'-methoxy-[1,1'-biphenyl]-2-yl)-3-phenylprop-2-yn-1-one (**1a**, 0.10 mmol), benzenesulfinic acid (**2a**, 0.15 mmol) and $BF_3{\cdot}Et_2O$ (0.25 mmol) were added into a round-bottomed flask with 3.0 mL of anhydrous acetonitrile (ACN). The flask containing the reactants and solvent was stirred at room temperature for 10 min. The crude reaction mixture was directly detected by HRMS analysis. A sulfinyl cation was detected, as shown in Figure S2.



Supplementary Figure 2. HRMS data of Sulfinyl Cation.

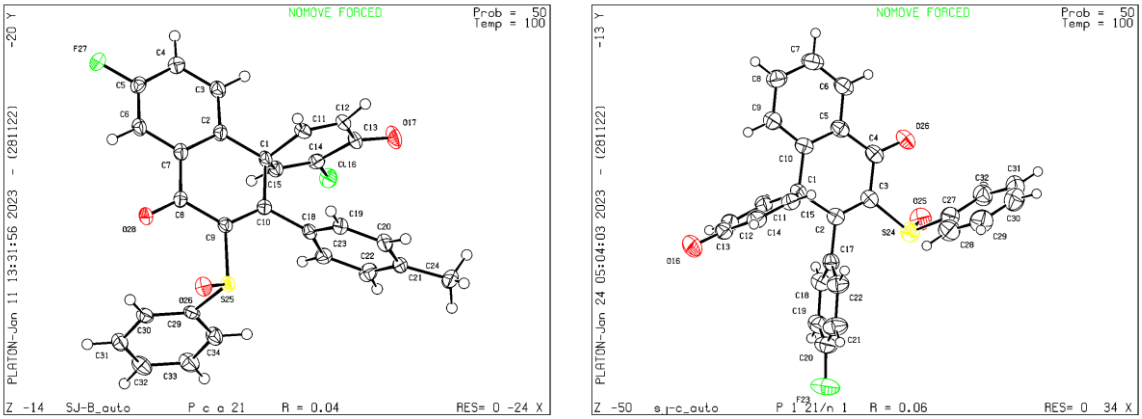
E. Plausible Reaction Mechanism



Supplementary Figure 3. Plausible Reaction Mechanism.

A plausible reaction mechanism has been shown in Supplementary Figure 3. It is believed that the species **P** is generated from sulfinic acid (**2**), which undergoes oxidation, and formation of **TS 1** is a key intermediate. After intramolecular rearrangement, the **TS 1** is converted into **TS 2**. Further neighbouring group participating (NGP of PMP group) nucleophilic addition gave the desired product **3**. Depending upon aryl substitution in PMP, oxygen incorporation of the dearomative core either comes from the Et_2O or from the substrate itself.

F. X-ray Crystallography Data



Supplementary Figure 4. ORTEP diagram of **3w**. X-ray crystallographic coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with the accession code **2226111** [left]. ORTEP diagram of **3d**. X-ray crystallographic coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC) with the accession code **2226112** [right] (the ellipsoids are displayed at a 50% probability level; the compound was recrystallized from DCM/petroleum ether).

Table 1. Crystal data and structure refinement for 3w (CCDC 2226111).

Identification code	SJ-B
Empirical formula	$C_{28}H_{18}ClFO_3S$
Formula weight	488.970
Temperature/K	100.00(10)
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	20.5567(2)
b/Å	11.19093(14)
c/Å	9.50595(12)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2186.83(4)
Z	4
$\rho_{calc}g/cm^3$	1.485
μ/mm^{-1}	2.771
F (000)	1013.889
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/° 3.9350 to 68.1620

Index ranges -16 ≤ h ≤ 24, -13 ≤ k ≤ 13, -11 ≤ l ≤ 11

Reflections collected 16231

Independent reflections 3861 [Rint = 0.0598, Rsigma = 0.0381]

Data/restraints/parameters 3551/1/ 309

Goodness-of-fit on F2 1.0452

Final R indexes [I>=2σ (I)] R1 = 0.0435, wR2 = 0.1261

Largest diff. peak/hole / e $Å^{-3}$ 0.4402/-0.3777

Table 2. Crystal data and structure refinement for 3d (CCDC 2226112).

Identification code	sj-c
Empirical formula	$C_{27}H_{17}FO_3S$
Formula weight	440.46
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.85251(18)
b/Å	9.76803(17)
c/Å	20.3019(3)
α/°	90
β/°	99.4241(17)
γ/°	90
Volume/$Å^3$	2123.11(6)
Z	4
$\rho_{calc}g/cm^3$	1.378
μ/mm^{-1}	1.661
F (000)	912
Radiation	Cu Kα (λ = 1.54184)

2Θ range for data collection/° 4.1250 to 67.8010

Index ranges -13 ≤ h ≤ 12, -11 ≤ k ≤ 11, -24 ≤ l ≤ 24

Reflections collected 21307

Independent reflections 3253 [Rint = 0.0917, Rsigma = 0.0386]

Data/restraints/parameters 3859/0/ 289

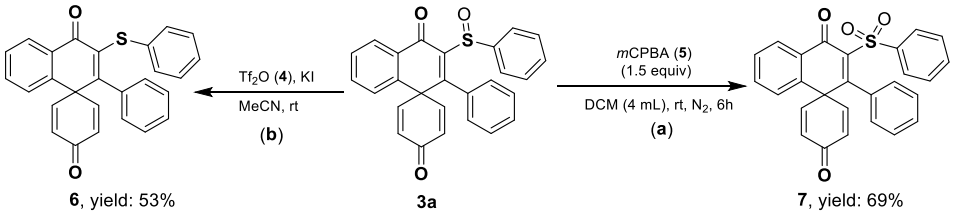
Goodness-of-fit on F2 1.0452

Final R indexes [I>=2σ (I)] R1 = 0.0587, wR2 = 0.1771

Largest diff. peak/hole / e $Å^{-3}$ 0.823/-0.503

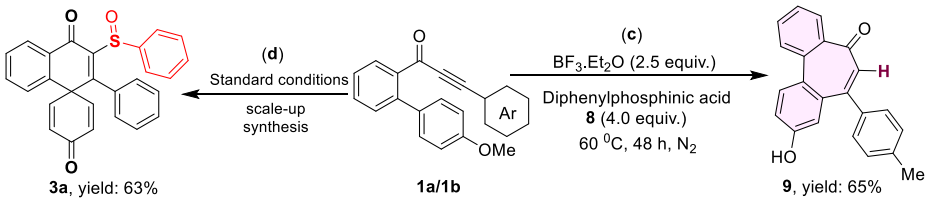
Note: CrysAlisPro 1.171.42.58a (Rigaku Oxford Diffraction, 2020). Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[2] In manuscript the crystal diagrams are drawn using VESTA 3.2.[3]

G. Synthetic Diversification:



Procedure (**a**): A solution of *m*CPBA (0.15 mmol) in DCM (2 mL) was added to a solution of **3a** (42 mg, 0.10 mmol) in DCM (2 mL). The reaction was stirred for 6 h at room temperature. After completion of reaction (monitored by TLC), the mixture was diluted with saturated $NaHCO_3$ and extracted by DCM. The combined DCM extracts were washed with water (2 × 30 mL), dried over Na_2SO_4, and concentrated to afford the desired product. Flash chromatography on silica gel yielded **7** (69% yield) of pure sulfone as yellow solid.

Procedure (**b**): **3a** (42 mg) and KI (3.0 equiv.) were added into a reaction vial with 3.0 mL acetonitrile. Tf_2O (1.0 equiv.) was then added dropwise and the mixture was stirred at room temperature for 6 h. After the reaction was completed, the mixture was quenched with $NaHCO_3$ and extracted by EtOAc. The combined EtOAc extracts were washed with water (2 × 30 mL), dried over Na_2SO_4, and concentrated. Flash chromatography on silica gel yielded the desired thiolated product **6** in 53% yield.

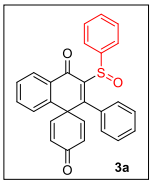


Procedure (**c**): **1b** (0.25 mmol) and **8** (1.0 mmol) were added into a round bottomed flask with 4.0 mL ACN. $BF_3.Et_2O$ (0.63 mmol) was then added and the mixture was stirred at 60 ˚C for 48 h under N_2 atmosphere. After the reaction was completed, the mixture was quenched with H_2O and extracted by EtOAc. The combined EtOAc extracts were washed with water (2 × 30 mL), dried over Na_2SO_4, and concentrated. Flash chromatography on silica gel afforded the desired product **9** in 65% yield.

Procedure (**d**): Scale-up synthesis of **3a** (532 mg) in 63% yield was achieved from **1a** (2.0 mmol) following the standard procedure mentioned under **Experimental Section B4**.

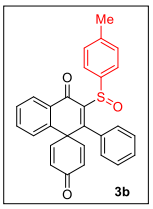
H. NMR Data

2'-phenyl-3'-(phenylsulfinyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3a)



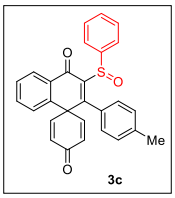
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 35% ethyl acetate in petroleum ether afforded yellow liquid, **1a** (30 mg, 0.096 mmol) → **3a** (31 mg, 0.073 mmol); 76% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3059, 1967, 1664, 1624, 1595, 1138, 1041, 854 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.59 (td, *J* = 7.7, 1.5 Hz, 1H), 7.46 (m, 7H), 7.21 (m, 3H), 6.81 – 6.71 (m, 2H), 6.48 – 6.40 (m, 1H), 6.38 – 6.30 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.25, 178.07, 161.27, 147.07, 146.96, 142.95, 142.60, 137.32, 133.97, 133.32, 131.06, 130.87, 130.53, 130.39, 129.63, 129.35, 128.88, 128.32, 128.18, 128.13, 128.01, 127.81, 127.69, 124.63, 52.04. **HRMS** (ESI) calc'd for $C_{27}H_{19}O_3S$ $[M+H]^+$: 423.1055, Found : 423.1051.

2'-phenyl-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3b)



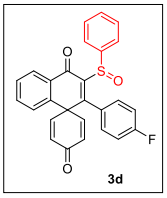
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 35% ethyl acetate in petroleum ether afforded yellow solid, **1a** (30 mg, 0.096 mmol) → **3b** (35 mg, 0.079 mmol); 83% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3035, 1662, 1630, 1570, 1072, 997 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.6 Hz, 1H), 7.62 – 7.48 (m, 4H), 7.41 (d, *J* = 4.6 Hz, 3H), 7.26 (dd, *J* = 11.4, 5.9 Hz, 4H), 7.16 (s, 1H), 6.84 – 6.67 (m, 2H), 6.43 (d, *J* = 9.7 Hz, 1H), 6.37 – 6.28 (m, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.26, 178.15, 160.79, 147.14, 147.02, 143.03, 140.82, 139.34, 137.31, 133.89, 133.39, 131.00, 130.84, 130.62, 129.60, 129.58, 129.30, 128.19, 128.09, 127.81, 124.73, 52.01, 21.41. **HRMS** (ESI) calc'd for $C_{28}H_{21}O_3S$ $[M+H]^+$: 437.1211, Found : 437.1206.

3'-(phenylsulfinyl)-2'-(p-tolyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3c)



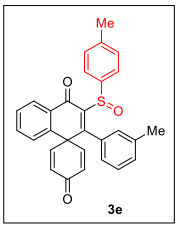
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 35% ethyl acetate in petroleum ether afforded yellow liquid, **1b** (22 mg, 0.067 mmol) → **3c** (21 mg, 0.048 mmol); 71% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.75 – 7.62 (m, 2H), 7.59 (td, *J* = 7.6, 1.5 Hz, 1H), 7.55 – 7.38 (m, 4H), 7.14 (d, *J* = 51.4 Hz, 5H), 6.75 (ddd, *J* = 15.8, 9.8, 3.1 Hz, 2H), 6.45 (dd, *J* = 9.8, 1.6 Hz, 1H), 6.36 (dd, *J* = 9.8, 1.6 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.36, 177.99, 161.67, 147.23, 147.12, 142.78, 139.78, 137.34, 133.86, 130.99, 130.81, 130.59, 130.30, 129.28, 128.82, 128.19, 128.08, 124.64, 52.16, 21.36. **HRMS** (ESI) calc'd for $C_{28}H_{21}O_3S$ $[M+H]^+$: 437.1211, Found : 437.1214.

2'-(4-fluorophenyl)-3'-(phenylsulfinyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3d)



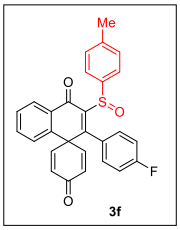
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 35% ethyl acetate in petroleum ether afforded off-white solid, **1c** (30 mg, 0.091 mmol) → **3d** (32 mg, 0.072 mmol); 79% yield. **TLC**; R_f = 0.3 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3315, 1874, 1789, 1720, 1656, 1620, 1138, 1063, 835 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 1H), 7.72 – 7.35 (m, 8H), 7.25 (d, *J* = 7.8 Hz, 1H), 7.21 – 6.97 (m, 3H), 6.79 – 6.65 (m, 2H), 6.45 (d, *J* = 9.7 Hz, 1H), 6.35 (d, *J* = 10.0 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.06, 178.51, 164.38, 163.80, 161.89, 159.88, 146.88, 143.69, 142.59, 137.39, 134.10, 131.23, 130.98, 130.54, 130.32, 129.43, 128.95, 128.18, 124.59, 52.24. **HRMS** (ESI) calc'd for $C_{27}H_{18}O_3SF$ $[M+H]^+$: 441.0961, Found : 441.0963.

2'-(m-tolyl)-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3e)



Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded yellow solid, **1d** (30 mg, 0.075 mmol) → **3e** (27 mg, 0.060 mmol); 81% yield. **TLC**; R_f = 0.3 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3466, 3032, 1950, 1660, 1622, 1479, 1165, 1055 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.47 (m, 4H), 7.33 – 7.20 (m, 6H), 7.13 – 6.88 (m, 2H), 6.81 – 6.67 (m, 2H), 6.50 – 6.39 (m, 1H), 6.35 (d, *J* = 9.9 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.38, 178.16, 161.17, 147.29, 147.10, 142.90, 140.73, 139.38, 138.09, 137.31, 133.86, 133.34, 130.88, 130.73, 130.65, 130.38, 129.58, 129.28, 128.73, 128.33, 128.19, 128.07, 127.88, 127.56, 125.15, 124.95, 124.77, 124.66, 51.99, 21.56, 21.42. **HRMS** (ESI) calc'd for $C_{29}H_{22}O_3SNa$ $[M+Na]^+$: 473.1187, Found : 473.1182.

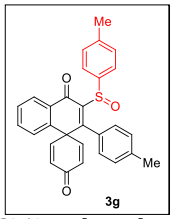
2'-(4-fluorophenyl)-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3f)



Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 35% ethyl acetate in petroleum ether afforded yellow liquid, **1c** (30 mg, 0.091 mmol) → **3f** (38 mg, 0.084 mmol); 92% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3043, 1959, 1712, 1658, 1625, 1597, 1176, 1051, 860 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 – 8.20 (m, 1H), 7.60 (td, *J* = 7.8, 1.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 3H), 7.26 (dd, *J* = 10.9, 8.0 Hz, 3H), 7.20 – 7.11 (m, 2H), 7.06 (t, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 9.9 Hz, 2H), 6.50 – 6.40 (m, 1H), 6.40 – 6.27 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.04, 178.59, 164.36, 161.87, 159.33, 146.96, 146.92, 143.83, 140.98, 139.46, 137.42, 134.02, 131.17, 130.95, 130.41, 130.14, 129.65, 129.37, 128.97, 128.93, 128.15, 124.69, 52.21, 21.38. **HRMS** (ESI) calc'd for $C_{28}H_{20}O_3SF$ $[M+H]^+$: 455.1117, Found : 455.1118.

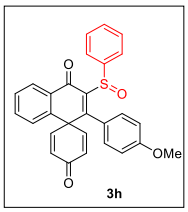
2'-(p-tolyl)-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3g)

Total reaction time = 12 h. Temperature of reaction = room temperature. Elution with 35% ethyl acetate in petroleum ether afforded yellow liquid, **1b** (30 mg, 0.092 mmol) → **3g** (37 mg, 0.082 mmol); 89% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **^{1}H NMR** (400



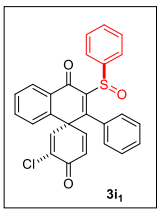
MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.63 – 7.45 (m, 4H), 7.31 – 7.13 (m, 6H), 7.05 (s, 1H), 6.74 (ddd, *J* = 21.9, 9.9, 3.1 Hz, 2H), 6.39 (ddd, *J* = 33.0, 9.9, 1.6 Hz, 2H), 2.39 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.42, 178.04, 161.31, 147.33, 147.21, 142.99, 140.73, 139.71, 139.38, 137.30, 133.81, 130.93, 130.78, 130.66, 129.56, 129.25, 128.17, 128.07, 124.72, 52.12, 21.41, 21.38. **HRMS** (ESI) calc'd for $C_{29}H_{23}O_3S$ $[M+H]^+$: 451.1368, Found : 451.1411.

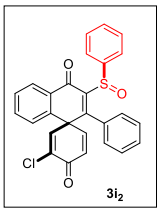
2'-(4-methoxyphenyl)-3'-(phenylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3h)



Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded brownish liquid, **1e** (34 mg, 0.099 mmol) → **3h** (33 mg, 0.073 mmol); 74% yield. **TLC**; R_f = 0.3 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3057, 2312, 1654, 1598, 1514, 1186, 1028, 840 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.67 – 7.45 (m, 3H), 7.36 – 7.26 (m, 4H), 6.89 – 6.73 (m, 6H), 6.49 (s, 1H), 6.47 (s, 1H), 3.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.27, 183.66, 160.70, 156.12, 150.10, 138.38, 133.27, 130.83, 130.27, 130.04, 129.69, 128.94, 128.80, 128.25, 127.36, 113.79, 55.32, 50.76. **HRMS** (ESI) calc'd for $C_{28}H_{21}O_4S$ $[M+H]^+$: 453.1161, Found : 453.1162.

3-chloro-2'-phenyl-3'-(phenylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3i, 1:3**)**



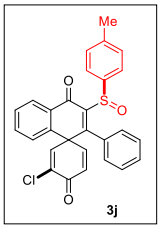


Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 35-40% ethyl acetate in petroleum ether afforded yellow liquid, **1f** (63 mg, 0.175 mmol) → **3i$_1$** (14 mg, 0.032 mmol) and **3i$_2$** (42 mg, 0.093 mmol); 71% overall yield. **TLC**; R_f = 0.5 (i_1) and 0.4 (i_2) (50% ethyl acetate in petroleum ether).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.73 – 7.60 (m, 3H), 7.56 (td, *J* = 7.7, 1.2 Hz, 1H), 7.53 – 7.33 (m, 6H), 7.27 – 7.23 (m, 1H), 7.22 – 7.17 (m, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.95 (d, *J* = 2.9 Hz, 1H), 6.77 (dd, *J* = 9.7, 2.9 Hz, 1H), 6.51 (d, *J* = 9.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.01, 177.33, 159.76, 147.17, 142.66, 142.50, 136.42, 135.23, 134.20, 132.61, 130.54, 130.30, 130.12, 129.83, 129.74, 128.93, 128.43, 128.03, 127.71, 124.71, 53.85. **HRMS** (ESI) calc'd for $C_{27}H_{18}O_3SCl$ $[M+H]^+$: 457.0665, Found : 457.0668.

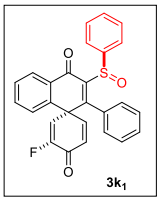
(Major isomer) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.64 (ddd, *J* = 9.2, 8.1, 1.5 Hz, 3H), 7.57 – 7.38 (m, 7H), 7.27 – 7.20 (m, 2H), 7.18 – 7.10 (m, 1H), 6.95 (d, *J* = 2.9 Hz, 1H), 6.80 (dd, *J* = 9.8, 2.9 Hz, 1H), 6.41 (d, *J* = 9.8 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.86, 177.27, 159.79, 147.15, 143.30, 142.52, 142.43, 136.30, 135.45, 134.18, 132.78, 130.53, 130.35, 129.94, 129.84, 129.73, 128.93, 128.43, 128.08, 127.87, 127.62, 124.68, 53.72. **HRMS** (ESI) calc'd for $C_{27}H_{18}O_3SCl$ $[M+H]^+$: 457.0665, Found : 457.0674.

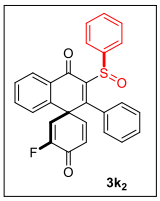
3-chloro-2'-phenyl-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3j)



Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded yellow liquid, **1f** (18 mg, 0.050 mmol) → **3j** (18 mg, 0.039 mmol); 78% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3045, 2320, 1673, 1650, 1586, 1238, 1085, 839 cm^{-1}. (Major isomer) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 6.8 Hz, 1H), 7.62 (t, *J* = 6.9 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 3H), 7.44 (s, 4H), 7.28 (s, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.12 (d, *J* = 6.3 Hz, 1H), 6.92 (d, *J* = 2.8 Hz, 1H), 6.79 (dd, *J* = 9.8, 2.8 Hz, 1H), 6.41 (d, *J* = 9.8 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.90, 177.30, 159.39, 147.22, 143.30, 142.61, 141.02, 139.06, 136.26, 135.38, 134.12, 132.85, 130.41, 130.07, 129.91, 129.79, 129.69, 129.66, 128.42, 128.18, 128.05, 127.82, 127.61, 124.76, 53.68, 21.44. **HRMS** (ESI) calc'd for $C_{28}H_{20}O_3SCl$ $[M+H]^+$: 471.0822, Found : 471.0820.

3-fluoro-2'-phenyl-3'-(phenylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3k, 1:4**)**



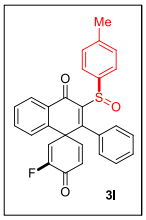


Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded yellow liquid, **1g** (40 mg, 0.121 mmol) → **3k$_1$** (8 mg, 0.018 mmol) and **3k$_2$** (29 mg, 0.066 mmol); 69% overall yield. **TLC**; R_f = 0.5 (k_1) and 0.4 (k_2) (50% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 1H), 7.64 (dd, *J* = 13.7, 7.5 Hz, 3H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.52 – 7.38 (m, 6H), 7.28 – 7.20 (m, 2H), 7.14 (d, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 9.7 Hz, 1H), 6.52 – 6.43 (m, 1H), 6.38 (d, *J* = 11.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.92, 177.09, 176.88, 160.12, 156.54, 153.85, 147.80, 143.22, 142.49, 136.65, 134.19, 132.72, 130.76, 130.71, 130.52, 130.28, 129.84, 129.69, 128.92, 128.57, 128.41, 128.01, 127.88, 127.72, 124.68, 123.93, 123.77, 52.72, 52.65. **HRMS** (ESI) calc'd for $C_{27}H_{18}O_3SF$ $[M+H]^+$: 441.0961, Found : 441.0965.

(Major isomer) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 7.8 Hz, 1H), 7.64 (dd, *J* = 16.1, 7.6 Hz, 3H), 7.59 – 7.40 (m, 7H), 7.28 – 7.14 (m, 4H), 6.79 (d, *J* = 9.8 Hz, 1H), 6.43 – 6.33 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.79, 177.05, 176.83, 160.24, 156.65, 153.96, 147.75, 147.73, 143.12, 142.38, 136.61, 134.16, 132.76, 130.64, 130.59, 130.53, 130.32, 129.83, 129.66, 128.93, 128.40, 128.01, 127.93, 127.88, 124.67, 123.85, 123.70, 52.46, 52.40. **HRMS** (ESI) calc'd for $C_{27}H_{18}O_3SF$ $[M+H]^+$: 441.0961, Found : 441.0974.

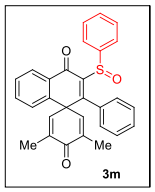
3-fluoro-2'-phenyl-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3l)

(Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded yellow solid, **1g** (22 mg, 0.067 mmol) → **3l** (21 mg, 0.047 mmol); 73% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3439, 1982, 1678, 1653, 1595, 1165, 1049, 871 cm^{-1}. (Major isomer) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 – 8.18 (m, 1H), 7.67 – 7.51 (m, 4H), 7.47 – 7.39 (m, 2H), 7.24 (ddd, *J* = 37.2, 20.3, 6.9 Hz, 4H), 6.77 (dd, *J* = 9.8, 2.9 Hz, 1H), 6.44 – 6.27 (m, 2H), 2.40 (s, 3H). **^{13}C NMR** 100 MHz,



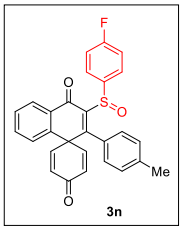
$CDCl_3$) δ 177.85, 177.06, 176.84, 159.78, 156.62, 153.93, 147.81, 143.16, 141.00, 139.07, 136.60, 134.09, 132.83, 130.61, 130.56, 130.40, 129.78, 129.65, 129.62, 128.40, 128.35, 128.04, 127.96, 127.89, 127.83, 124.76, 123.92, 123.76, 52.42, 52.36, 21.43. **HRMS** (ESI) calc'd for $C_{28}H_{19}O_3SFNa$ $[M+Na]^+$: 477.0937, Found :477.0939.

3,5-dimethyl-2'-phenyl-3'-(phenylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3m)



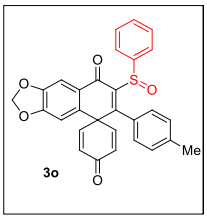
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 35% ethyl acetate in petroleum ether afforded off-white liquid, **1h** (30 mg, 0.088 mmol) → **3m** (30 mg, 0.066 mmol); 75% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **IR** (KBr) 2960, 1660, 1635, 1597, 1157, 1042, 866 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.50 – 7.42 (m, 4H), 7.40 – 7.32 (m, 3H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.07 (d, *J* = 6.5 Hz, 1H), 6.55 – 6.46 (m, 2H), 1.91 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.49, 178.31, 162.92, 142.80, 142.28, 141.74, 141.60, 139.00, 137.98, 137.71, 133.72, 133.47, 130.43, 130.25, 129.26, 128.87, 128.81, 128.14, 128.01, 127.95, 127.90, 127.21, 124.63, 51.83, 16.10, 15.92. **HRMS** (ESI) calc'd for $C_{29}H_{23}O_3S$ $[M+H]^+$: 451.1368, Found : 451.1356.

3'-((4-fluorophenyl)sulfinyl)-2'-(p-tolyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3n)



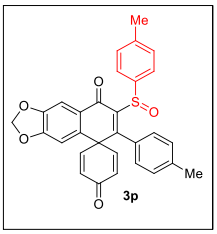
Total reaction time = 12 h. Temperature of reaction = room temperature. Elution with 50% ethyl acetate in petroleum ether afforded reddish gel, **1b** (30 mg, 0.092 mmol) → **3n** (33 mg, 0.074 mmol); 80% yield. **TLC**; R_f = 0.3 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3026, 1665, 1630, 1450, 1041, 881 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.72 – 7.62 (m, 2H), 7.59 (td, *J* = 7.7, 1.5 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.19 (dt, *J* = 17.3, 8.3 Hz, 6H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.74 (ddd, *J* = 17.0, 9.8, 3.1 Hz, 2H), 6.43 (dd, *J* = 9.8, 1.5 Hz, 1H), 6.35 (dd, *J* = 9.8, 1.5 Hz, 1H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.36, 178.10, 165.18, 162.68, 161.88, 147.09, 147.02, 142.67, 139.90, 137.80, 137.34, 134.00, 131.05, 130.86, 130.50, 130.42, 129.35, 129.08, 128.47, 128.15, 128.12, 127.87, 127.56, 127.12, 127.03, 116.25, 116.02, 52.16, 21.40. **HRMS** (ESI) calc'd for $C_{28}H_{20}O_3SF$ $[M+H]^+$: 455.1117, Found : 455.1107.

6'-phenyl-7'-(phenylsulfinyl)-8'H-spiro[cyclohexa[2,5]diene-1,5'-naphtho[2,3-d][1,3]dioxole]-4,8'-dione (3o)



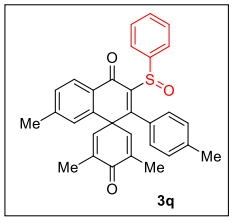
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded yellow liquid, **1j** (35 mg, 0.078 mmol) → **3o** (29 mg, 0.060 mmol); 77% yield. **TLC**; R_f = 0.3 (40% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.5 Hz, 2H), 7.56 (s, 1H), 7.47 (dd, J = 13.5, 5.9 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.18 (dd, J = 22.5, 7.5 Hz, 1H), 6.74 – 6.65 (m, 2H), 6.61 (s, 1H), 6.46 – 6.38 (m, 1H), 6.36 – 6.27 (m, 1H), 6.07 (d, J = 2.5 Hz, 2H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.10, 176.82, 169.93, 160.28, 152.89, 149.14, 147.08, 147.01, 142.74, 138.24, 133.89, 133.24, 131.09, 130.87, 130.33, 129.55, 128.84, 128.73, 128.13, 127.96, 127.87, 127.55, 126.21, 124.61, 107.11, 106.54, 102.49, 52.16, 23.28. **HRMS** (ESI) calc'd for $C_{29}H_{20}O_5SNa$ $[M+Na]^+$: 503.0929, Found : 503.0922.

7'-(phenylsulfinyl)-6'-(p-tolyl)-8'H-spiro[cyclohexa[2,5]diene-1,5'-naphtho[2,3-d][1,3]dioxole]-4,8'-dione (3p)



Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 50% ethyl acetate in petroleum ether afforded yellow liquid, **1j** (58 mg, 0.129 mmol) → **3p** (51 mg, 0.103 mmol); 79% yield. **TLC**; R_f = 0.2 (40% ethyl acetate in petroleum ether). (inseparable mixture of 3p and benzyl alcohol (BA) as a side product, 1:1) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 – 7.49 (m, 3H), 7.33 (ddd, *J* = 24.4, 14.4, 6.9 Hz, 10H), 7.13 (d, *J* = 6.9 Hz, 1H), 6.76 – 6.64 (m, 2H), 6.60 (s, 1H), 6.41 (d, *J* = 9.7 Hz, 1H), 6.32 (d, *J* = 9.8 Hz, 1H), 6.06 (s, 2H), 2.39 (s, 3H), 2.04 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.16, 176.86, 170.00, 159.93, 152.84, 149.11, 147.18, 147.08, 142.70, 140.77, 139.34, 138.25, 133.82, 133.32, 131.04, 130.85, 129.59, 129.53, 128.72, 128.21, 128.15, 127.94, 127.87, 127.58, 127.53, 126.27, 124.68, 107.10, 106.55, 102.49, 52.10, 43.76, 23.29, 21.43. **HRMS** (ESI) calc'd for $C_{30}H_{23}O_5S$ $[M+H]^+$: 495.1266, Found : 495.1271.

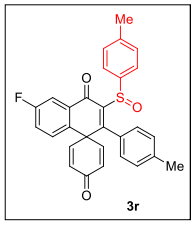
3,5,7'-trimethyl-3'-(phenylsulfinyl)-2'-(p-tolyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3q)



Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 30% ethyl acetate in petroleum ether afforded off-white liquid, **1s** (40 mg, 0.108 mmol) → **3q** (40 mg, 0.083 mmol); 77% yield. **TLC**; R_f = 0.4 (30% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.45 (dt, *J* = 14.3, 7.5 Hz, 3H), 7.26 (s, 1H), 7.20 – 7.04 (m, 3H), 6.93 (d, *J* = 8.3 Hz, 2H), 6.49 (d, *J* = 10.0 Hz, 2H), 2.37 (s, 6H), 1.92 (s, 3H), 1.83 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.83, 178.01, 163.09, 144.82, 142.87, 142.25, 142.16, 142.01, 139.22, 138.95, 137.75, 137.49, 130.76, 130.14, 130.03, 128.76, 128.61, 128.18, 128.05, 127.94, 127.81, 124.60, 51.86, 21.88, 21.38, 16.19, 16.01. **HRMS** (ESI) calc'd for $C_{31}H_{27}O_3S$ $[M+H]^+$: 479.1681, Found : 479.1684.

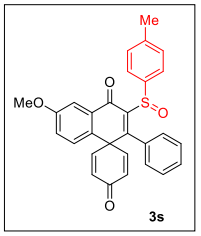
6'-fluoro-2'-(p-tolyl)-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3r)

Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded reddish liquid, **1k** (30 mg, 0.087 mmol) → **3r** (34 mg, 0.073 mmol); 84% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3234, 2850, 1715, 1654, 1626, 1591, 1226, 1054, 887 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H),



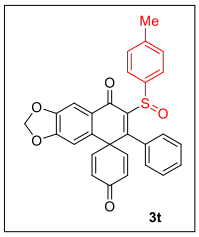
7.33 – 7.11 (m, 8H), 7.04 (s, 1H), 6.73 (dd, *J* = 9.9, 3.1 Hz, 1H), 6.68 (dd, *J* = 9.8, 3.1 Hz, 1H), 6.43 (dd, *J* = 9.9, 1.4 Hz, 1H), 6.35 (dd, *J* = 9.9, 1.4 Hz, 1H), 2.39 (d, *J* = 1.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.16, 177.08, 164.05, 161.73, 161.55, 146.91, 146.81, 142.74, 140.94, 139.90, 139.03, 133.13, 133.10, 132.80, 132.73, 131.06, 130.90, 130.64, 130.56, 130.46, 129.61, 129.07, 128.45, 127.88, 127.64, 124.74, 121.76, 121.53, 114.18, 113.95, 51.72, 21.43, 21.39. **HRMS** (ESI) calc'd for $C_{29}H_{22}O_3SF$ $[M+H]^+$: 469.1274, Found : 469.1268.

6'-methoxy-2'-phenyl-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3s)



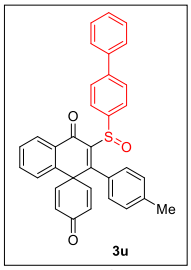
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded brown liquid, **1l** (30 mg, 0.088 mmol) → **3s** (30 mg, 0.065 mmol); 74% yield. **TLC**; R_f = 0.3 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3066, 2956, 1655, 1624, 1452, 1038, 918 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.41 (dd, *J* = 12.0, 6.3 Hz, 4H), 7.28 (s, 2H), 7.15 (t, *J* = 4.3 Hz, 3H), 6.71 (ddd, *J* = 18.1, 9.9, 3.0 Hz, 2H), 6.41 (dd, *J* = 9.8, 1.3 Hz, 1H), 6.32 (dd, *J* = 9.9, 1.3 Hz, 1H), 3.85 (s, 3H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.35, 178.01, 161.23, 160.20, 147.28, 147.16, 142.77, 140.81, 139.22, 133.48, 131.89, 130.81, 130.65, 129.61, 129.58, 129.53, 129.32, 124.65, 122.76, 109.53, 55.75, 51.65, 21.42. **HRMS** (ESI) calc'd for $C_{29}H_{22}O_4SNa$ $[M+Na]^+$: 489.1136, Found : 489.1134.

6'-phenyl-7'-(p-tolylsulfinyl)-8'H-spiro[cyclohexane-1,5'-naphtho[2,3-d][1,3]dioxole]-2,5-diene-4,8'-dione (3t)



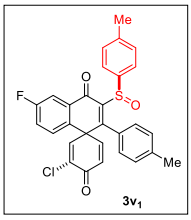
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 50% ethyl acetate in petroleum ether afforded yellow liquid, **1m** (30 mg, 0.084 mmol) → **3t** (33 mg, 0.068 mmol); 81% yield. **TLC**; R_f = 0.3 (60% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 – 7.49 (m, 3H), 7.39 (dd, *J* = 13.2, 6.5 Hz, 3H), 7.28 (d, *J* = 6.6 Hz, 2H), 7.18 (dd, *J* = 42.6, 6.7 Hz, 2H), 6.70 (ddd, *J* = 18.1, 9.9, 3.0 Hz, 2H), 6.61 (s, 1H), 6.42 (dd, *J* = 9.8, 1.4 Hz, 1H), 6.32 (dd, *J* = 9.9, 1.4 Hz, 1H), 6.07 (d, *J* = 1.4 Hz, 2H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.13, 176.89, 159.88, 152.83, 149.11, 147.17, 147.07, 142.76, 140.76, 139.40, 133.85, 133.31, 131.04, 130.85, 129.57, 129.51, 128.18, 127.96, 127.56, 126.30, 124.71, 107.09, 106.57, 102.47, 52.12, 21.40. **HRMS** (ESI) calc'd for $C_{29}H_{21}O_5S$ $[M+H]^+$: 481.1110, Found : 481.1099.

3'-([1,1'-biphenyl]-4-ylsulfinyl)-2'-(p-tolyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3u)

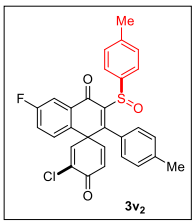


Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 35% ethyl acetate in petroleum ether afforded yellow liquid, **1b** (30 mg, 0.092 mmol) → **3u** (38 mg, 0.075 mmol); 82% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **IR** (KBr) 3317, 2922, 1725, 1671, 1620, 1053, 876 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.72 (q, *J* = 8.5 Hz, 4H), 7.58 (dd, *J* = 11.3, 4.5 Hz, 3H), 7.54 – 7.43 (m, 4H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.27 – 7.17 (m, 4H), 7.10 (s, 1H), 6.81 – 6.73 (m, 2H), 6.48 – 6.43 (m, 1H), 6.39 – 6.34 (m, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.41, 178.06, 161.76, 147.26, 147.14, 143.37, 142.90, 141.31, 139.91, 139.83, 137.36, 133.92, 131.00, 130.84, 130.62, 130.60, 129.32, 128.94, 128.19, 128.13, 128.00, 127.58, 127.23, 125.22, 52.20, 21.41. **HRMS** (ESI) calc'd for $C_{34}H_{25}O_3S$ $[M+H]^+$: 513.1524, Found : 513.1529.

3-chloro-6'-fluoro-2'-(p-tolyl)-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3v, 1:2**)**



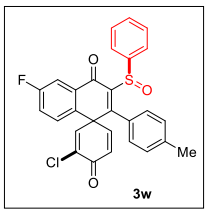
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded yellow semi-solid, **1n** (50 mg, 0.127 mmol) → **3v$_1$** (16 mg, 0.033 mmol) and **3v$_2$** (34 mg, 0.067 mmol); 79% overall yield. **TLC**; R_f = 0.5 (k_1) and 0.4 (k_2) (50% ethyl acetate in petroleum ether).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.27 – 7.16 (m, 3H), 7.12 (d, *J* = 6.8 Hz, 1H), 6.99 (d, *J* = 6.9 Hz, 1H), 6.92 (d, *J* = 2.9 Hz, 1H), 6.71 (dd, *J* = 9.7, 2.8 Hz, 1H), 6.49 (d, *J* = 9.8 Hz, 1H), 2.40 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.08, 165.00, 161.79, 160.05, 146.95, 143.34, 142.42, 141.02, 140.06, 139.29, 135.29, 132.36, 130.44, 130.36, 130.09, 129.73, 129.58, 127.83, 124.88, 121.89, 121.66, 114.43, 114.20, 53.58, 21.32. **HRMS** (ESI) calc'd for $C_{29}H_{20}O_3SClFNa$ $[M+Na]^+$: 525.0703, Found : 525.0713.



(Major isomer) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.30 (dd, *J* = 11.7, 3.5 Hz, 3H), 7.24 (dd, *J* = 8.8, 6.4 Hz, 3H), 7.17 (s, 1H), 6.99 (d, *J* = 6.9 Hz, 1H), 6.88 (d, *J* = 2.9 Hz, 1H), 6.76 (dd, *J* = 9.8, 2.9 Hz, 1H), 6.41 (d, *J* = 9.8 Hz, 1H), 2.40 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.20, 176.80, 164.26, 161.78, 160.26, 147.01, 143.10, 142.32, 141.11, 140.15, 138.86, 135.47, 132.67, 132.60, 132.09, 130.58, 130.50, 129.97, 129.91, 129.66, 129.15, 128.60, 128.06, 127.43, 124.77, 121.99, 121.76, 114.48, 114.25, 53.39, 21.44, 21.41. **HRMS** (ESI) calc'd for $C_{29}H_{20}O_3SClFNa$ $[M+Na]^+$: 525.0703, Found : 525.0705.

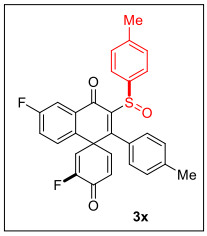
3-chloro-6'-fluoro-3'-(phenylsulfinyl)-2'-(p-tolyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3w, 1:2**)**

Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40-45% ethyl acetate in petroleum ether afforded yellow solid, **1n** (60 mg, 0.153 mmol) → **3w$_1$** (20 mg, 0.040 mmol) and **3w$_2$** (38 mg, 0.078 mmol); 77% overall yield. **TLC**; R_f = 0.4 (k_1) and 0.3 (k_2) (50% ethyl acetate in petroleum ether).



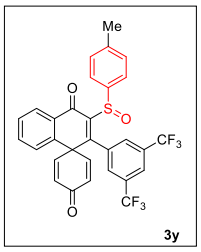
(Major isomer) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.5, 3.1 Hz, 1H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.48 (dt, *J* = 19.8, 7.0 Hz, 3H), 7.36 – 7.14 (m, 5H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.90 (d, *J* = 2.8 Hz, 1H), 6.77 (dd, *J* = 9.8, 3.1 Hz, 1H), 6.42 (d, *J* = 9.8 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.17, 176.79, 164.27, 161.76, 160.66, 146.94, 143.08, 142.24, 140.20, 135.54, 132.60, 132.53, 132.09, 130.59, 130.53, 129.99, 129.85, 129.19, 128.93, 128.64, 128.03, 127.42, 124.68, 122.04, 121.81, 114.47, 114.24, 77.35, 77.03, 76.72, 53.43, 21.41. **HRMS** (ESI) calc'd for $C_{28}H_{19}O_3SClF$ $[M+H]^+$: 489.0727, Found : 489.0728.

3,6'-difluoro-2'-(p-tolyl)-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3x)



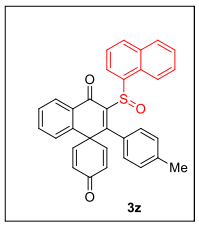
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 35% ethyl acetate in petroleum ether afforded yellow liquid, **1o** (22 mg, 0.061 mmol) → **3x** (20 mg, 0.042 mmol); 70% yield. **TLC**; R_f = 0.5 (50% ethyl acetate in petroleum ether). (Major isomer) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.36 – 7.20 (m, 7H), 7.09 (dd, *J* = 50.9, 7.1 Hz, 2H), 6.75 (dd, *J* = 9.8, 2.7 Hz, 1H), 6.34 (ddd, *J* = 14.2, 10.6, 4.7 Hz, 2H), 2.40 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.95, 176.77, 176.74, 164.21, 161.70, 160.66, 156.61, 153.92, 147.57, 142.96, 141.09, 140.14, 138.85, 132.64, 130.67, 130.62, 130.43, 130.35, 129.89, 129.65, 129.13, 128.61, 127.88, 124.77, 123.68, 123.53, 121.95, 121.73, 114.43, 114.20, 52.17, 52.11, 21.43, 21.40. **HRMS** (ESI) calc'd for $C_{29}H_{21}F_2O_3S$ $[M+H]^+$: 487.1179, Found : 487.1165.

2'-(3,5-bis(trifluoromethyl)phenyl)-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3y)



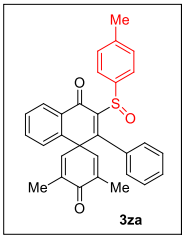
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 20% ethyl acetate in petroleum ether afforded light yellow liquid, **1p** (48 mg, 0.107 mmol) → **3y** (44 mg, 0.077 mmol); 72% yield. **TLC**; R_f = 0.6 (30% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.32 (d, *J* = 7.7 Hz, 1H), 7.90 (s, 1H), 7.64 (dq, *J* = 15.0, 7.5 Hz, 3H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 3H), 7.13 (s, 1H), 6.77 (d, *J* = 9.9 Hz, 1H), 6.60 (d, *J* = 9.9 Hz, 1H), 6.45 (d, *J* = 9.9 Hz, 1H), 6.28 (d, *J* = 10.0 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.43, 180.62, 153.89, 146.14, 145.95, 145.31, 141.64, 139.60, 137.70, 134.63, 133.02, 131.72, 131.32, 130.41, 130.30, 130.08, 129.98, 129.72, 129.55, 129.01, 128.46, 128.29, 128.07, 124.36, 124.27, 122.94, 122.90, 122.86, 121.54, 52.33, 21.35. **HRMS** (ESI) calc'd for $C_{30}H_{19}O_3SF_6$ $[M+H]^+$: 573.0959, Found : 573.0947.

3'-(naphthalen-1-ylsulfinyl)-2'-(p-tolyl)-4'H-spiro[cyclohexa[2,5]diene-1,1'-naphthalene]-4,4'-dione (3z)



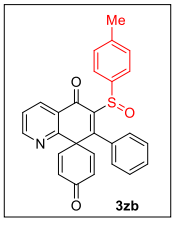
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 50% ethyl acetate in petroleum ether afforded yellow liquid, **1b** (22 mg, 0.067 mmol) → **3z** (23 mg, 0.048 mmol); 71% yield. **TLC**; R_f = 0.3 (50% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 – 8.15 (m, 2H), 7.93 – 7.86 (m, 3H), 7.62 – 7.55 (m, 4H), 7.51 - 7.48 (td, *J* = 7.7, 1.3 Hz, 1H), 7.43 – 7.21 (m, 3H), 7.16-7.11 (dd, *J* = 7.0, 1.8 Hz, 2H), 6.78 - 6.73 (dt, *J* = 10.2, 3.1 Hz, 2H), 6.47 – 6.44 (m, 1H), 6.36 – 6.34 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.45, 178.20, 161.92, 147.27, 147.17, 142.79, 139.85, 139.54, 137.31, 134.06, 133.92, 132.86, 131.00, 130.81, 130.52, 130.43, 129.31, 128.97, 128.81, 128.62, 128.44, 128.17, 128.11, 127.98, 127.76, 127.59, 127.10, 125.41, 120.53, 52.26, 21.42. **HRMS** (ESI) calc'd for $C_{32}H_{23}O_3S$ $[M+H]^+$: 487.1368, Found : 487.1359.

3,5-dimethyl-2'-phenyl-3'-(p-tolylsulfinyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (3za)



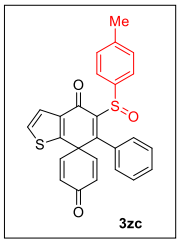
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 30% ethyl acetate in petroleum ether afforded yellow liquid, **1h** (45 mg, 0.132 mmol) → **3za** (51 mg, 0.109 mmol); 83% yield. **TLC**; R_f = 0.4 (30% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 3H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.36 (d, *J* = 10.9 Hz, 3H), 7.31 – 7.25 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.0 Hz, 1H), 6.50 (d, *J* = 13.8 Hz, 2H), 2.39 (s, 3H), 1.90 (s, 3H), 1.81 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 185.57, 178.35, 162.59, 142.23, 141.82, 141.69, 140.68, 139.36, 138.93, 137.92, 137.68, 133.69, 133.55, 130.47, 129.57, 129.24, 128.86, 128.13, 128.03, 127.96, 127.90, 127.20, 124.70, 51.77, 21.44, 16.14, 15.96. **HRMS** (ESI) calc'd for $C_{30}H_{25}O_3S$ $[M+H]^+$: 465.1524, Found : 465.1512.

7'-phenyl-6'-(p-tolylsulfinyl)-5'H-spiro[cyclohexa[2,5]diene-1,8'-quinoline]-4,5'-dione (3zb)



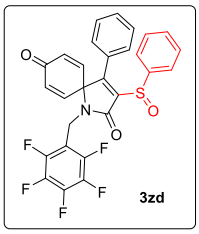
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 50% ethyl acetate in petroleum ether afforded reddish liquid, **1q** (30 mg, 0.096 mmol) → **3zb** (32 mg, 0.073 mmol); 76% yield. **TLC**; R_f = 0.4 (60% ethyl acetate in petroleum ether). **IR** (KBr) 3327, 2922, 1894, 1718, 1664, 1624, 1141, 1051, 802 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (dd, *J* = 4.6, 1.7 Hz, 1H), 8.44 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.39 (m, 4H), 7.30 (d, *J* = 9.8 Hz, 3H), 7.17 (s, 1H), 6.78 (dd, *J* = 10.0, 3.1 Hz, 1H), 6.68 (dd, *J* = 9.9, 3.1 Hz, 1H), 6.49 (dd, *J* = 9.9, 1.2 Hz, 1H), 6.40 (dd, *J* = 10.0, 1.2 Hz, 1H), 2.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.40, 178.36, 162.25, 157.31, 154.29, 145.21, 145.07, 142.61, 141.04, 138.91, 136.02, 133.27, 132.40, 131.97, 129.74, 129.66, 127.94, 126.86, 124.74, 124.48, 54.82, 21.42. **HRMS** (ESI) calc'd for $C_{27}H_{20}O_3SN$ $[M+H]^+$: 438.1164, Found : 438.1168.

6-phenyl-5-(p-tolylsulfinyl)-4H-spiro[benzo[b]thiophene-7,1'-cyclohexa[2,5]diene]-4,4'-dione (3zc)



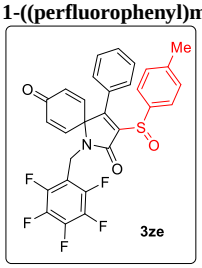
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded yellowish brown liquid, **1r** (32 mg, 0.100 mmol) → **3zc** (37 mg, 0.083 mmol); 83% yield. **TLC**; R_f = 0.3 (40% ethyl acetate in petroleum ether). **IR** (KBr) 3439, 1973, 1691, 1656, 1624, 1114, 1045, 869 cm^{-1}. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 5.1 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 6.3 Hz, 3H), 7.32 – 7.25 (m, 3H), 7.16 (s, 1H), 6.84 (d, *J* = 5.1 Hz, 1H), 6.75 – 6.63 (m, 2H), 6.49 – 6.41 (m, 1H), 6.40 – 6.31 (m, 1H), 2.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.95, 173.12, 160.86, 145.17, 144.51, 143.00, 140.95, 139.02, 137.04, 135.28, 133.16, 131.49, 131.18, 129.66, 129.60, 128.03, 127.13, 124.83, 51.90, 21.43. **HRMS** (ESI) calc'd for $C_{26}H_{19}O_3S_2$ $[M+H]^+$: 443.0776, Found : 443.0772.

1-((perfluorophenyl)methyl)-4-phenyl-3-(phenylsulfinyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3zd)



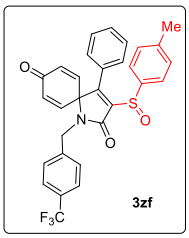
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded reddish liquid, **1t** (32 mg, 0.076 mmol) → **3zd** (30 mg, 0.055 mmol); 72% yield. **TLC**; R_f = 0.4 (60% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.58 – 7.50 (m, 3H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.3 Hz, 2H), 6.45 – 6.28 (m, 4H), 4.68 (d, *J* = 15.2 Hz, 1H), 4.57 (d, *J* = 15.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.85, 164.24, 160.22, 142.17, 141.25, 139.11, 133.93, 133.57, 131.40, 130.86, 129.24, 128.46, 128.40, 128.09, 124.95, 68.00, 31.93. **HRMS** (ESI) calc'd for $C_{28}H_{16}O_3SNNaF_5$ $[M+Na]^+$: 564.0669, Found : 564.0671.

1-((perfluorophenyl)methyl)-4-phenyl-3-(p-tolylsulfinyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3ze)



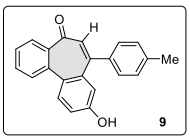
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 40% ethyl acetate in petroleum ether afforded reddish liquid, **1t** (32 mg, 0.076 mmol) → **3ze** (32 mg, 0.058 mmol); 77% yield. **TLC**; R_f = 0.4 (60% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.42 – 7.30 (m, 4H), 7.20 (d, *J* = 7.3 Hz, 2H), 6.45 – 6.26 (m, 4H), 4.69 (d, *J* = 15.1 Hz, 1H), 4.56 (d, *J* = 15.1 Hz, 1H), 2.44 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 182.87, 164.28, 159.69, 142.26, 142.04, 139.23, 138.03, 133.88, 133.52, 130.80, 129.98, 128.42, 128.16, 125.09, 67.94, 31.92, 21.53. **HRMS** (ESI) calc'd for $C_{29}H_{18}O_3SNNaF_5$ $[M+Na]^+$: 578.0825, Found : 578.0824.

4-phenyl-3-(p-tolylsulfinyl)-1-(4-(trifluoromethyl)benzyl)-1-azaspiro[4.5]deca-3,6,9-triene-2,8-dione (3zf)



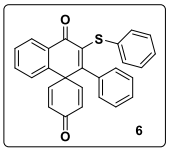
Total reaction time = 14 h. Temperature of reaction = room temperature. Elution with 35% ethyl acetate in petroleum ether afforded yellow liquid, **1u** (28 mg, 0.068 mmol) → **3zf** (29 mg, 0.054 mmol); 79% yield. **TLC**; R_f = 0.4 (50% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.36 (td, *J* = 14.3, 7.8 Hz, 6H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.44 – 6.18 (m, 4H), 4.65 (d, *J* = 15.3 Hz, 1H), 4.36 (d, *J* = 15.3 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 183.35, 164.88, 160.08, 143.23, 143.10, 142.06, 140.85, 139.18, 137.87, 133.70, 133.16, 130.84, 130.00, 129.10, 128.51, 128.41, 128.36, 125.65, 125.61, 125.14, 68.26, 44.14, 21.56. **HRMS** (ESI) calc'd for $C_{30}H_{23}O_3SNF_3$ $[M+H]^+$: 534.1351, Found : 534.1350.

9-hydroxy-7-(p-tolyl)-5H-dibenzo[a,c][7]annulen-5-one (9)



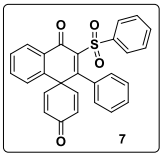
Total reaction time = 48 h. Temperature of reaction = room temperature. Elution with 20% ethyl acetate in petroleum ether afforded off-white liquid, **1b** (81 mg, 0.25 mmol) → **9** (51 mg, 0.16 mmol); 65% yield. **TLC**; R_f = 0.5 (30% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 1H), 7.79 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.76 – 7.66 (m, 2H), 7.56 – 7.50 (m, 1H), 7.15 – 7.03 (m, 5H), 6.69 (d, *J* = 2.7 Hz, 1H), 6.65 (s, 1H), 6.23 (t, *J* = 90.2 Hz, 1H), 2.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.43, 154.84, 149.89, 141.70, 138.96, 138.67, 137.53, 136.83, 133.38, 132.13, 131.69, 131.46, 130.18, 129.49, 129.14, 128.74, 128.50, 127.66, 127.54, 117.39, 117.04, 21.20. **HRMS** (ESI) calc'd for $C_{22}H_{17}O_2$ $[M+H]^+$: 313.1229, Found : 313.1243.

2'-phenyl-3'-(phenylthio)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (6) [4]



Total reaction time = 6 h. Elution with 15% ethyl acetate in petroleum ether afforded yellow solid, **3a** (42 mg, 0.099 mmol) → **6** (21 mg, 0.053 mmol); 53% yield. **TLC**; R_f = 0.5 (20% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.54 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 – 7.22 (m, 5H), 7.21 – 7.15 (m, 4H), 7.06 – 6.98 (m, 2H), 6.84 – 6.76 (m, 2H), 6.41 – 6.31 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.66, 179.96, 159.31, 148.35, 137.71, 137.10, 136.85, 135.40, 133.53, 130.52, 130.27, 129.32, 129.26, 129.18, 128.92, 128.70, 128.55, 128.08, 127.88, 127.31, 126.50, 52.19.

2'-phenyl-3'-(phenylsulfonyl)-4'H-spiro[cyclohexane-1,1'-naphthalene]-2,5-diene-4,4'-dione (7) [4]



Total reaction time = 6 h. Elution with 25% ethyl acetate in petroleum ether afforded off-white solid, **3a** (42 mg, 0.099 mmol) → **7** (30 mg, 0.068 mmol); 69% yield. **TLC**; R_f = 0.5 (30% ethyl acetate in petroleum ether). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.8, 1.9 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.66 – 7.58 (m, 2H), 7.54 (ddd, *J* = 7.0, 5.9, 2.6 Hz, 3H), 7.47 – 7.35 (m, 3H), 7.25 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.20 – 7.14 (m, 2H), 6.74 – 6.69 (m, 2H), 6.39 – 6.33 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 184.10, 178.72, 162.52, 146.72, 141.36, 140.10, 137.09, 134.19, 133.62, 133.54, 131.01, 130.28, 129.39, 128.90, 128.68, 128.16, 127.94, 127.21, 127.09, 52.77.

I. References

(1) (a) According to Manuscript ref. no. 4. (b) According to Manuscript ref. no. 9a.

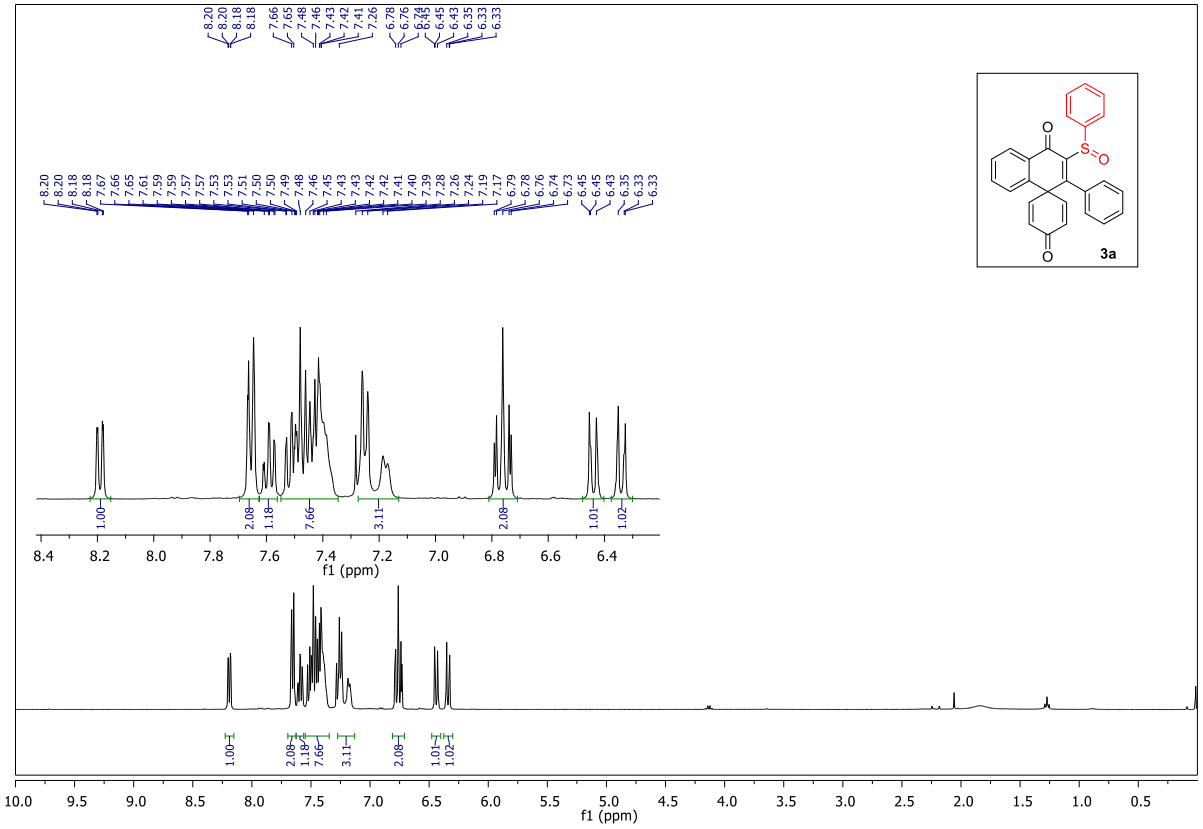
(2) K. Momma and F. Izumi, *J. Appl. Cryst.* 2011, **44**, 1272-1276.

(3) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339-341.

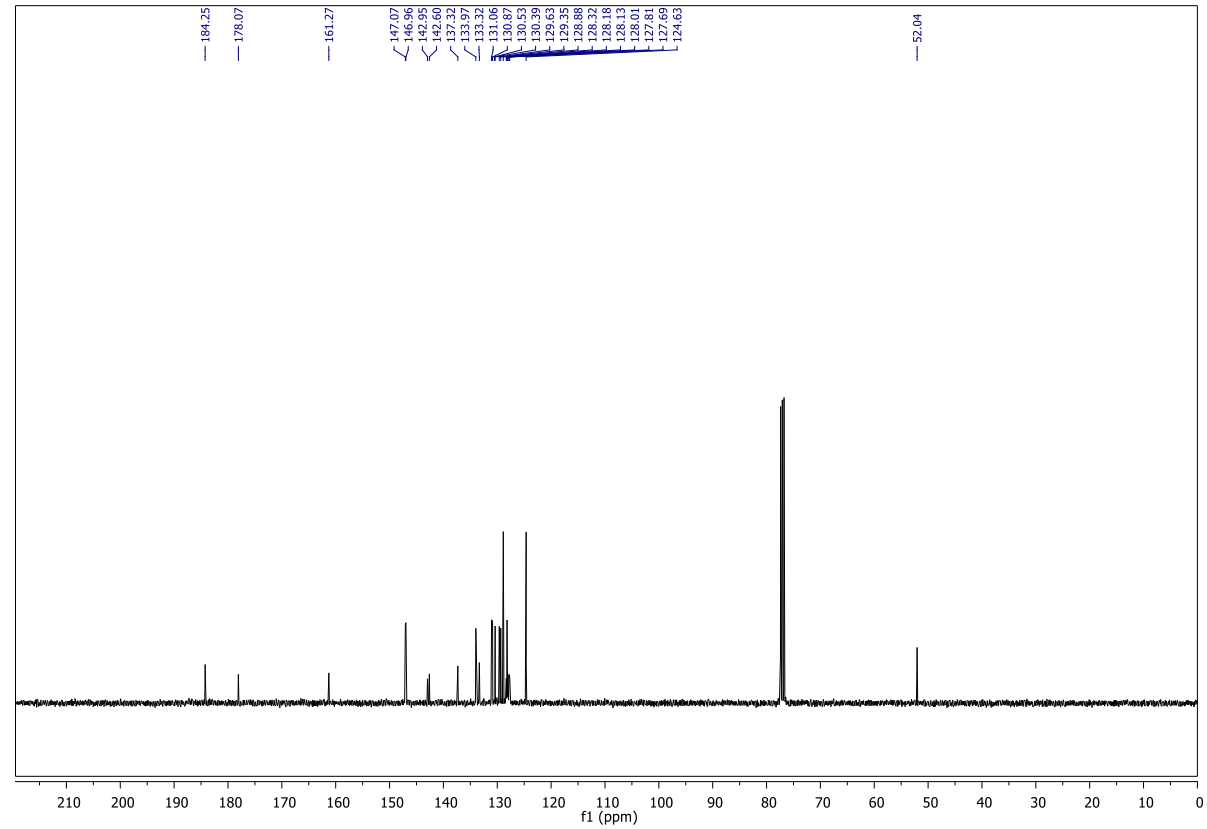
(4) (a) Manuscript ref. no. 9b. (b) Z. Chen, Y. Feng, P. Gao, F. Lv, X. Guo and X. Xie, 2023, **8** (e202303201). (c) S. Chen, Q. Yan, J. Fan, L. Li, Z.-Q. Liu and Z. Li, *Synlett* 2022, **33**, 1733-1738.

J. ^{1}H and ^{13}C Spectra

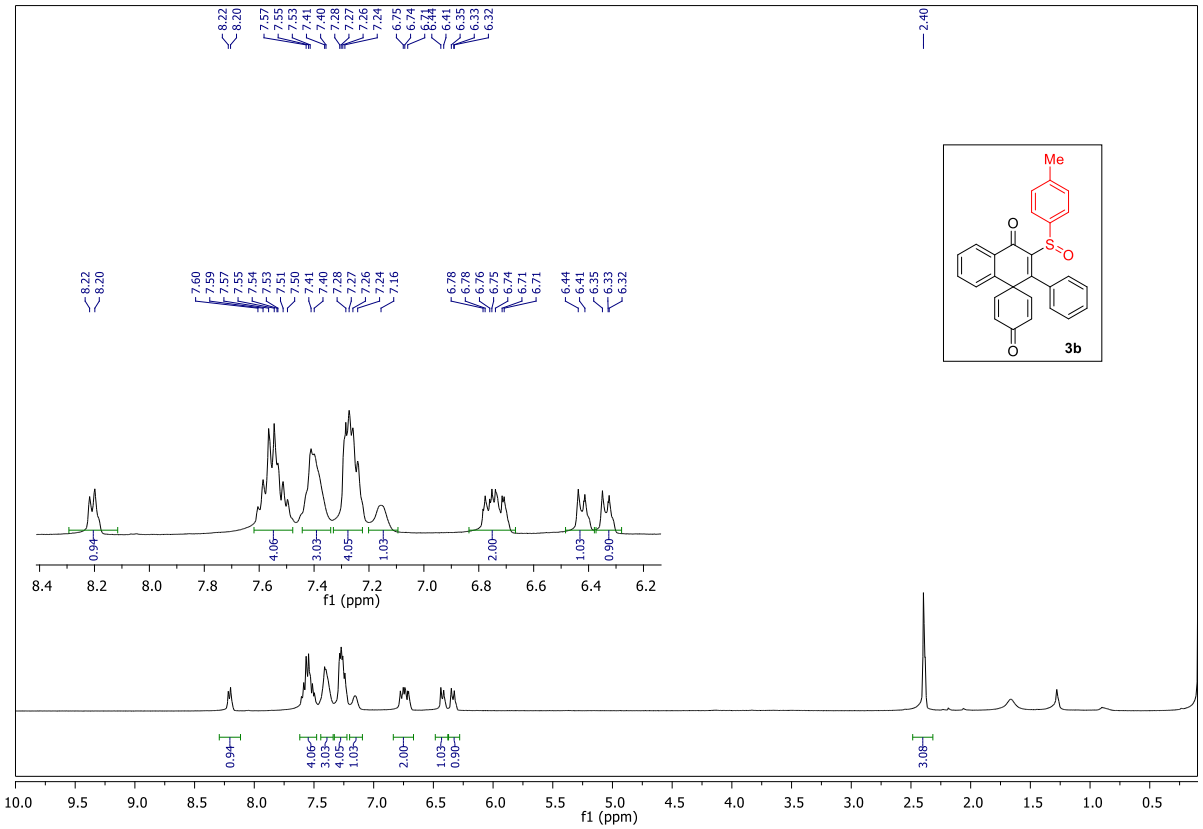
3a, ^{1}H NMR ($CDCl_3$, 400 MHz)



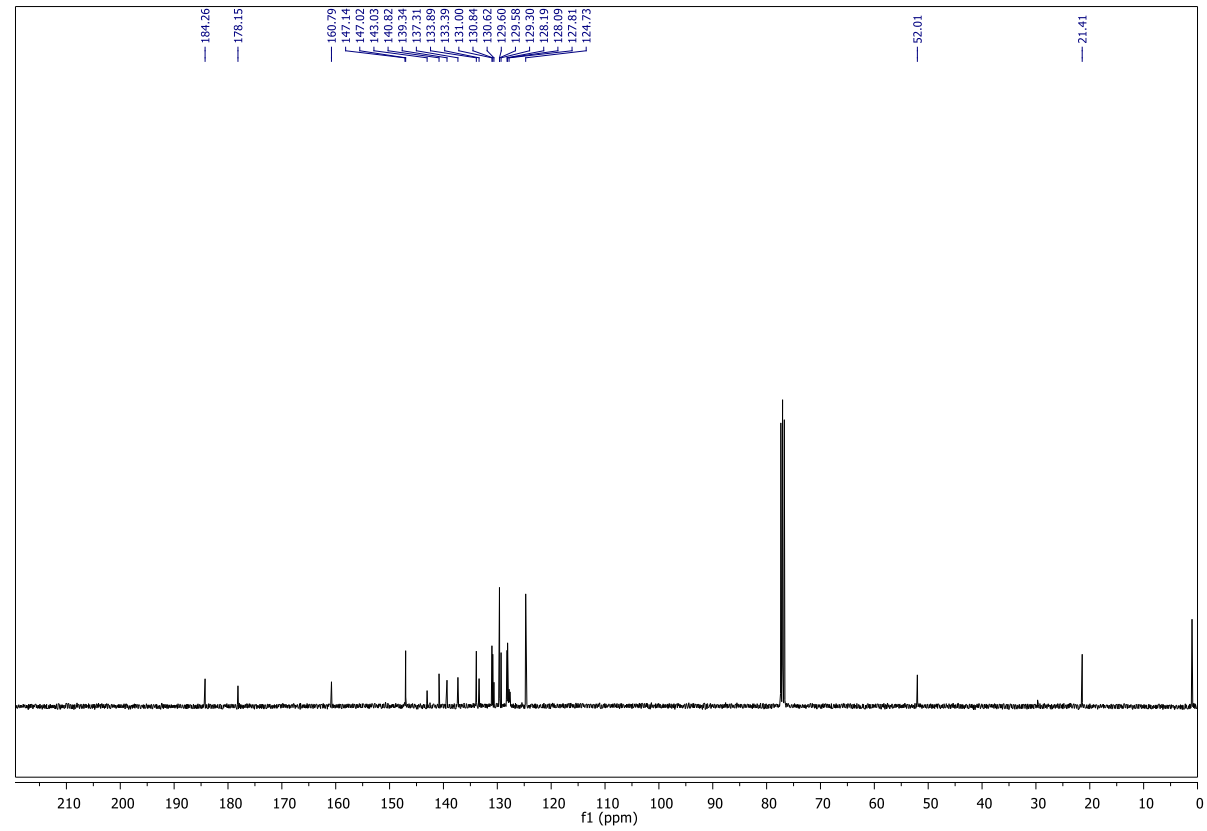
3a, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



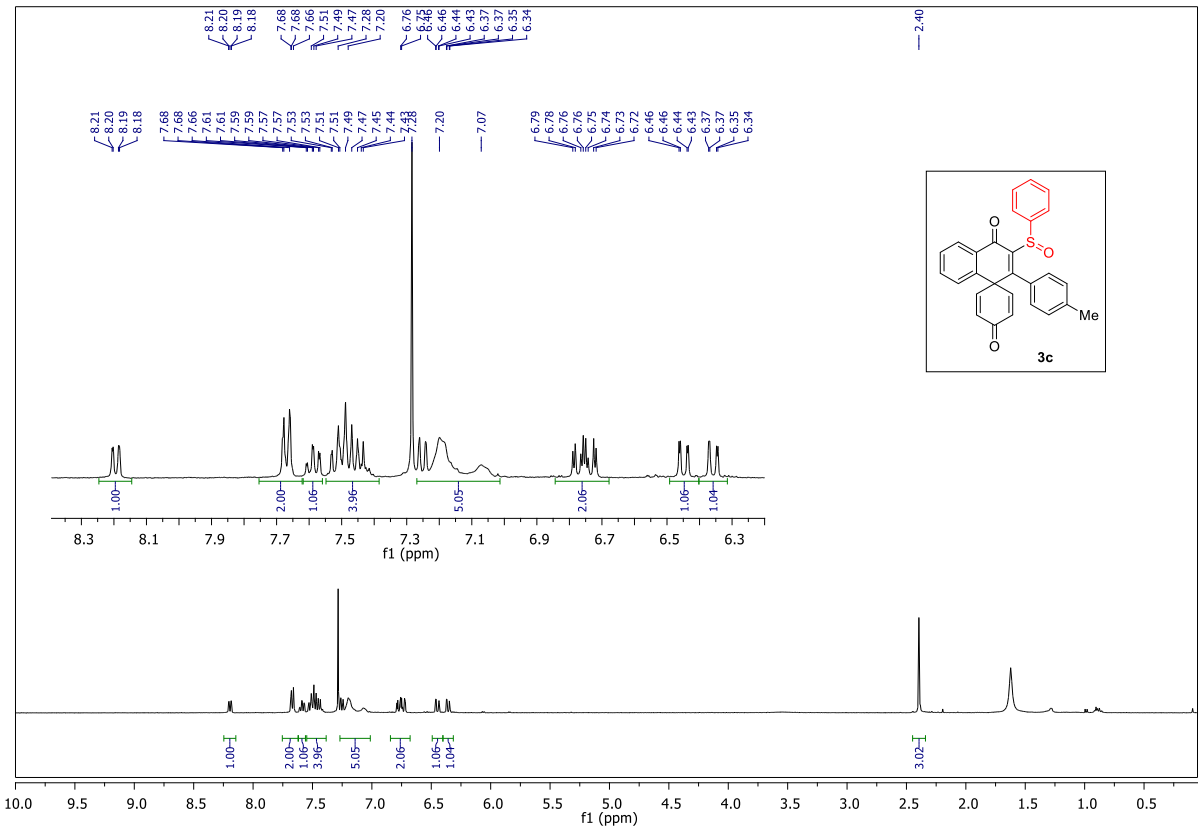
3b, ^{1}H NMR ($CDCl_3$, 400 MHz)



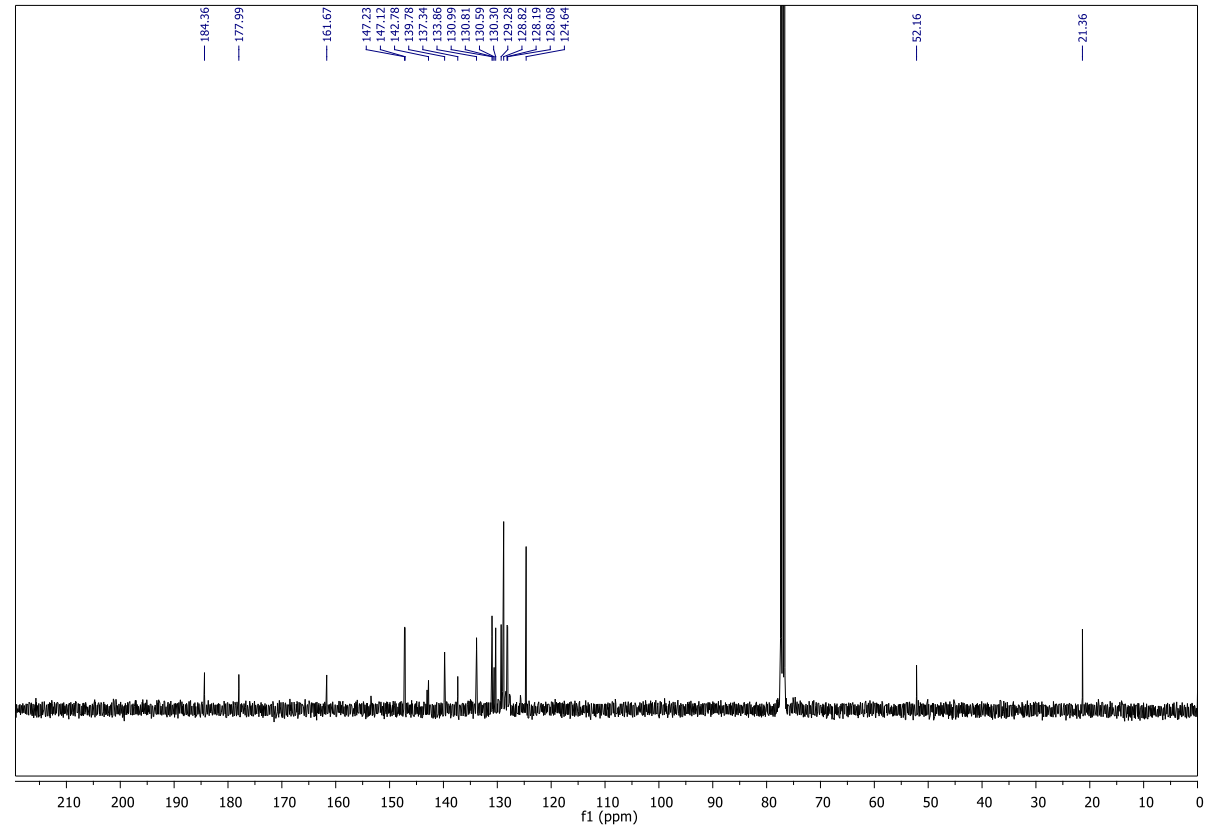
3b, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



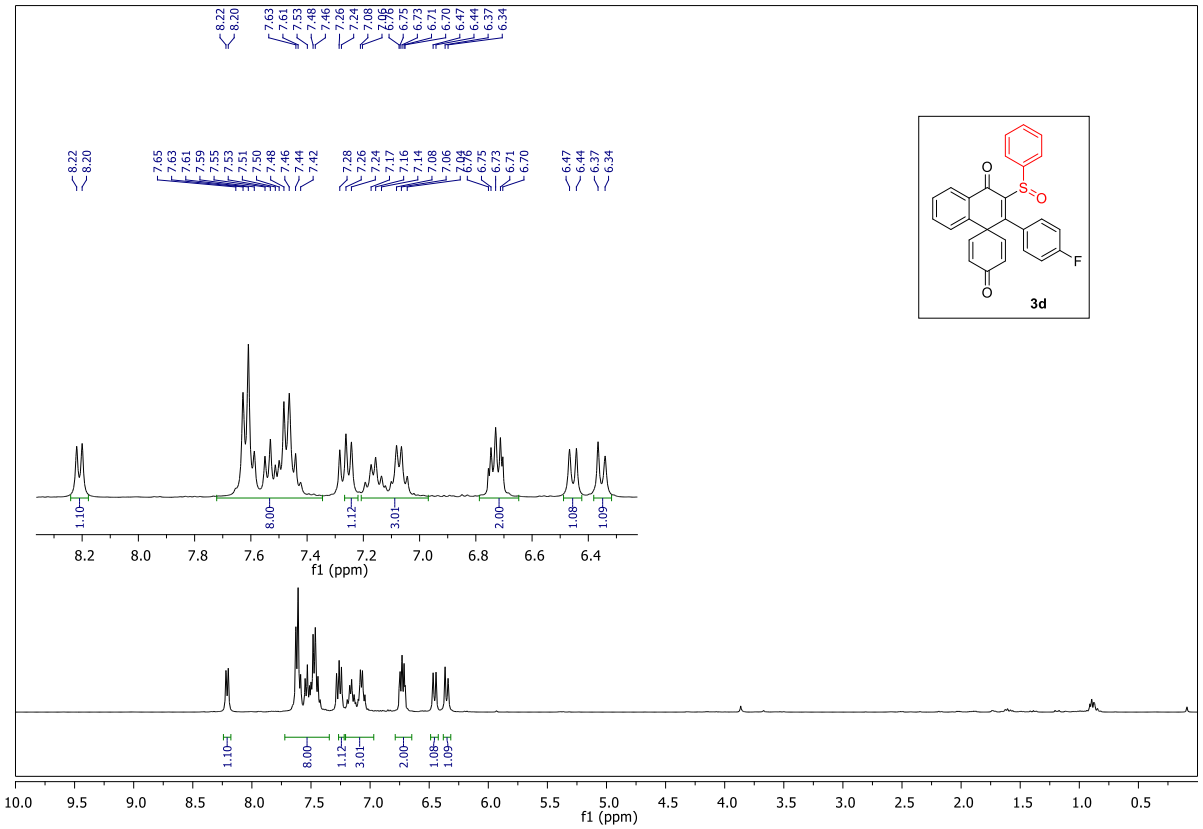
3c, ^{1}H NMR ($CDCl_3$, 400 MHz)



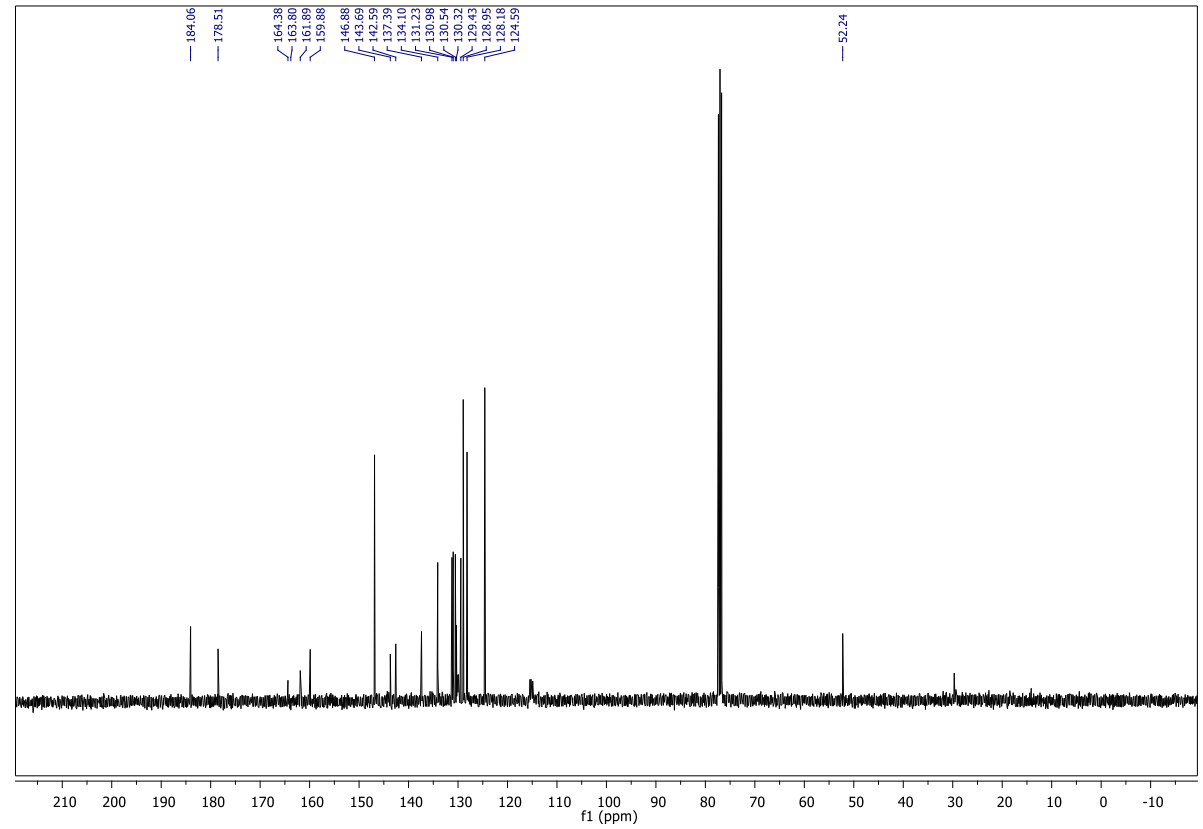
3c, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



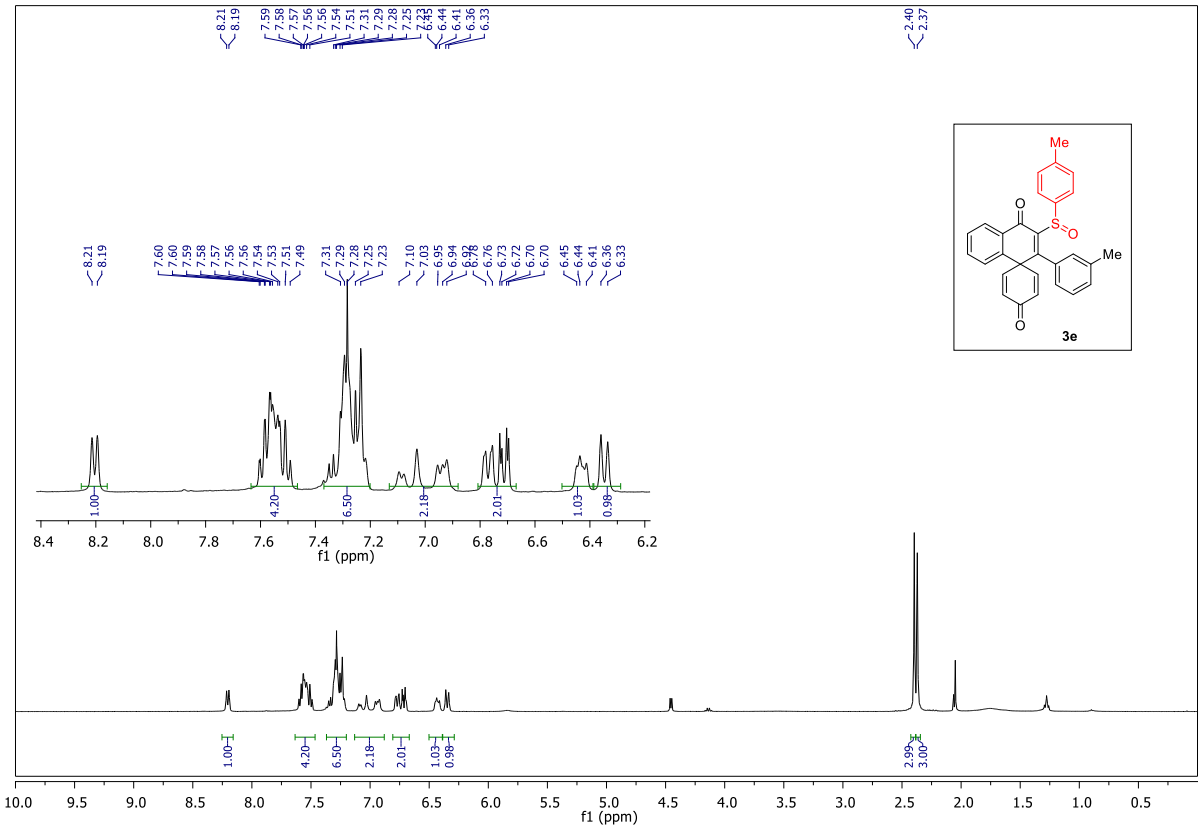
3d, ^{1}H NMR ($CDCl_3$, 400 MHz)



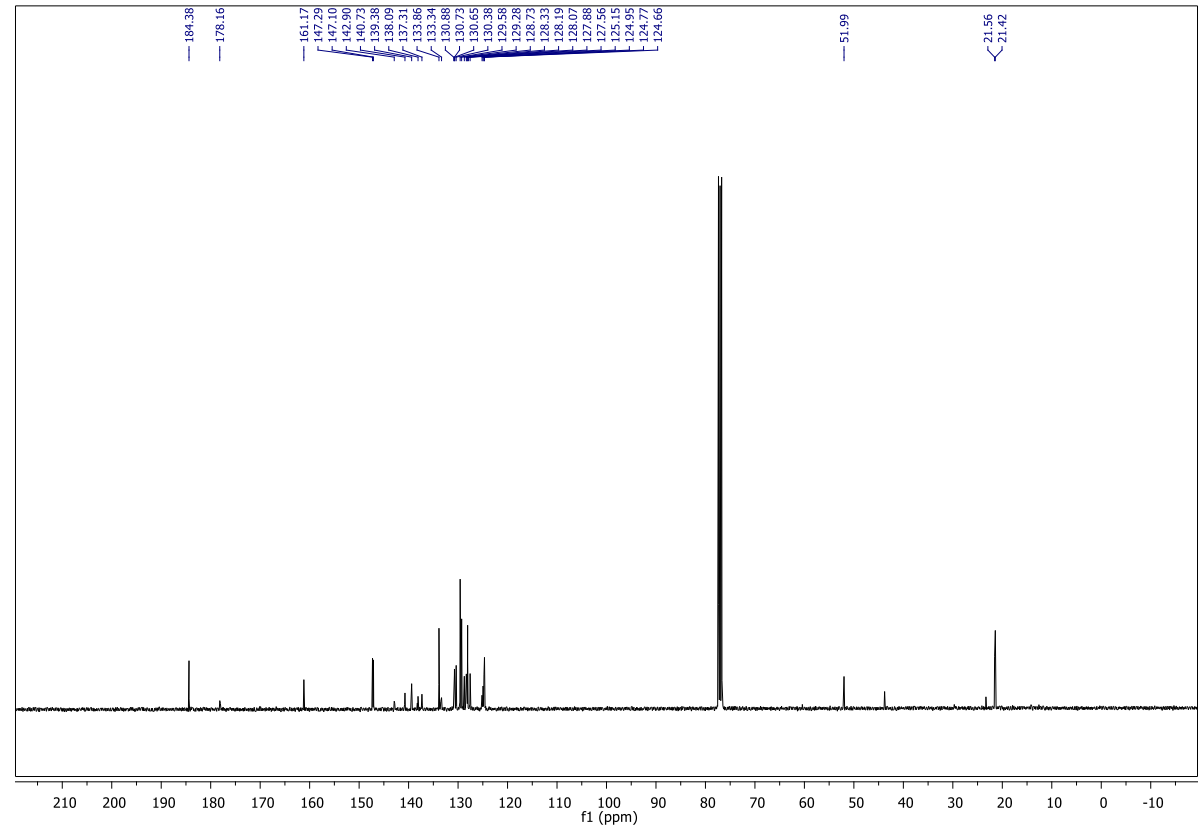
3d, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



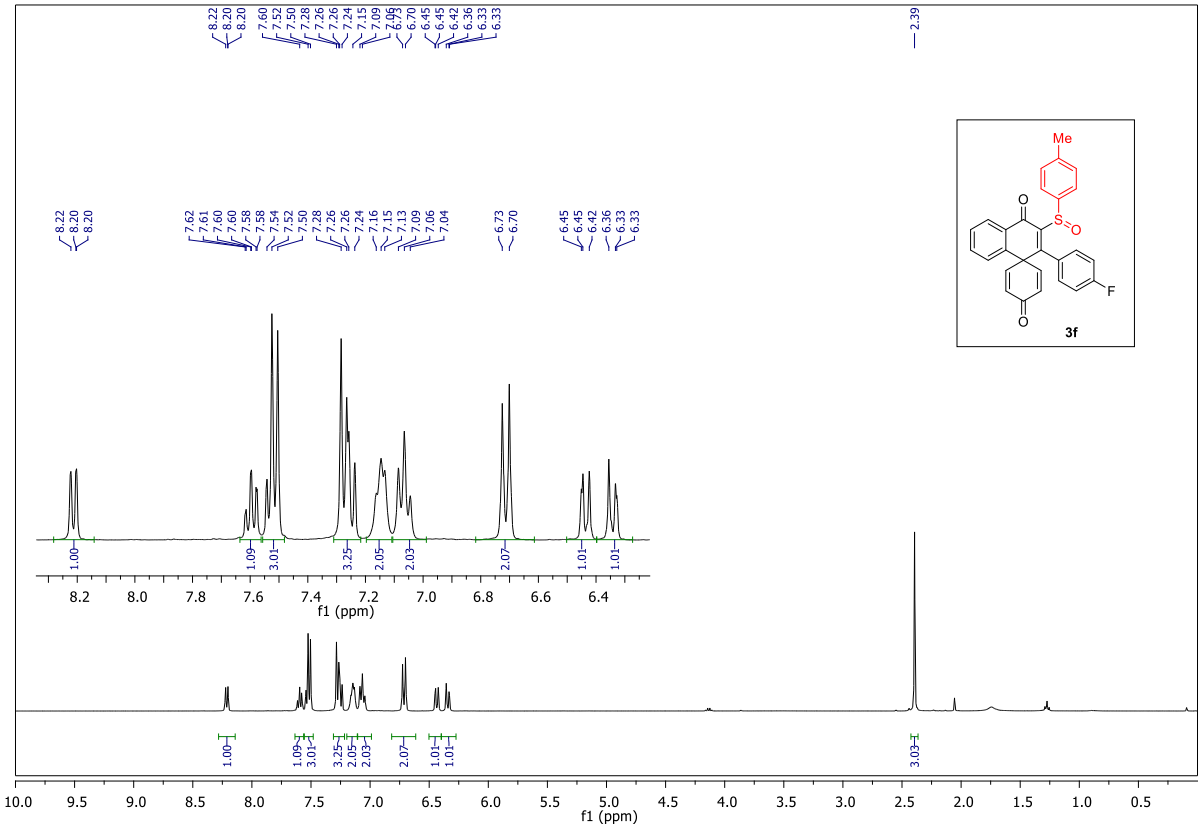
3e, ^{1}H NMR ($CDCl_3$, 400 MHz)



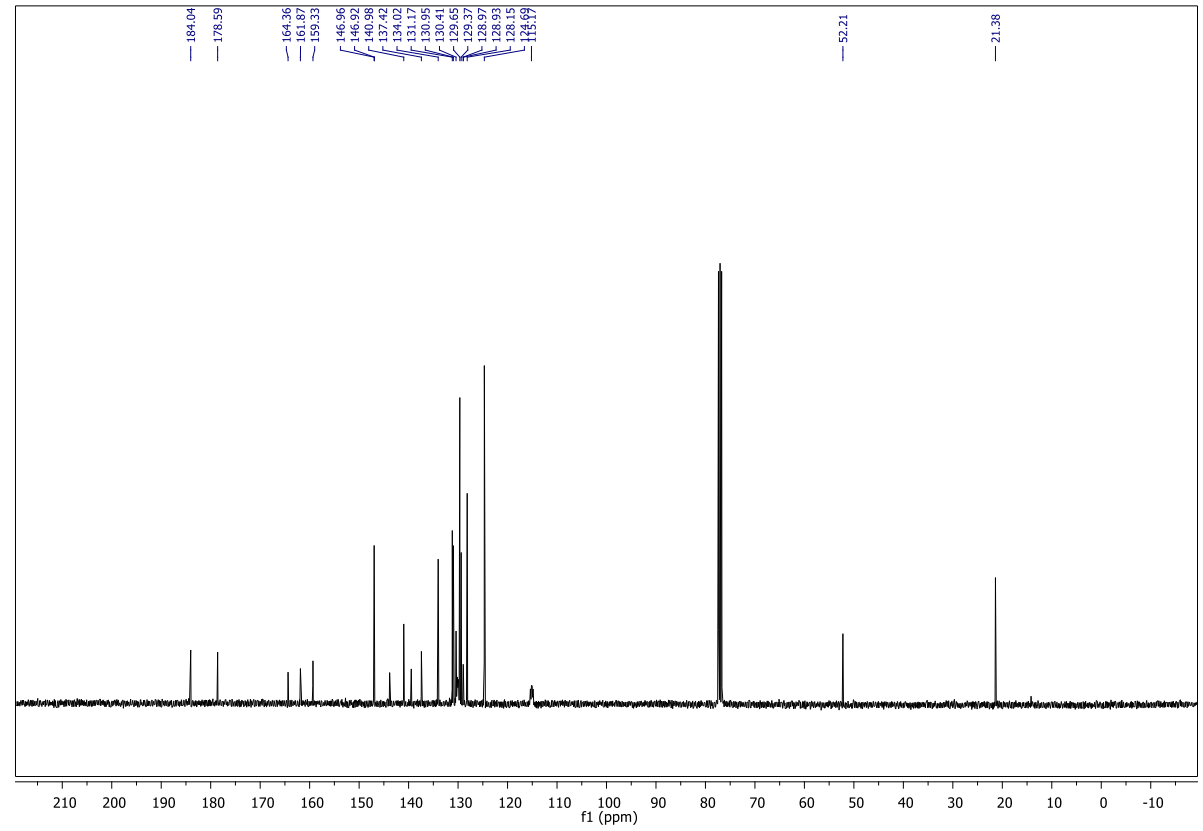
3e, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



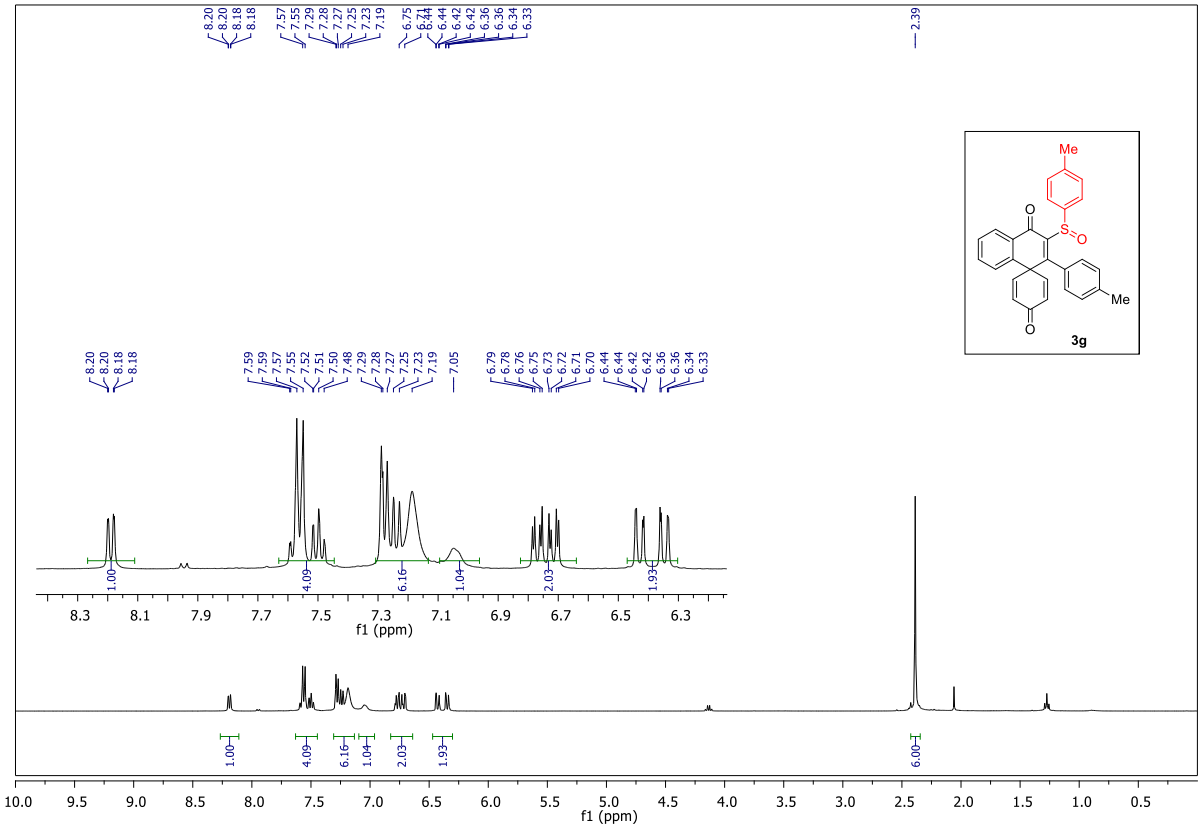
3f, ^{1}H NMR ($CDCl_3$, 400 MHz)



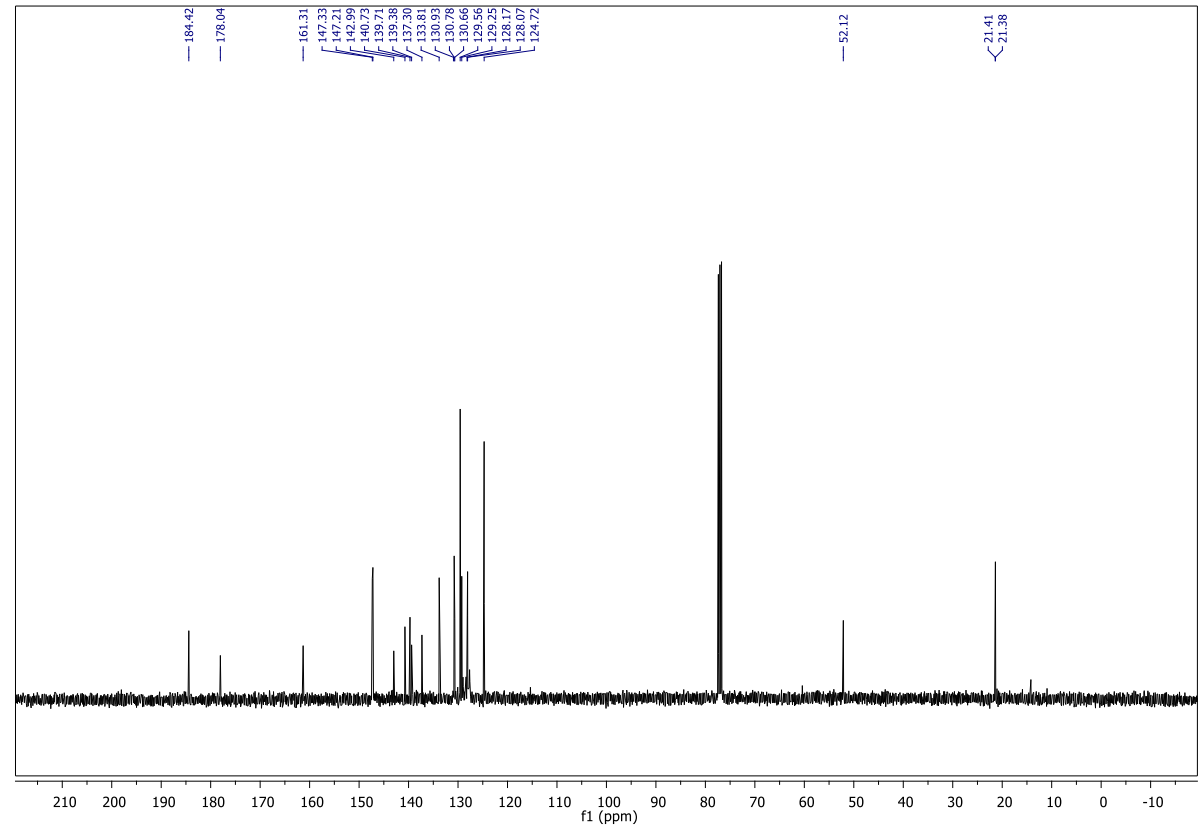
3f, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



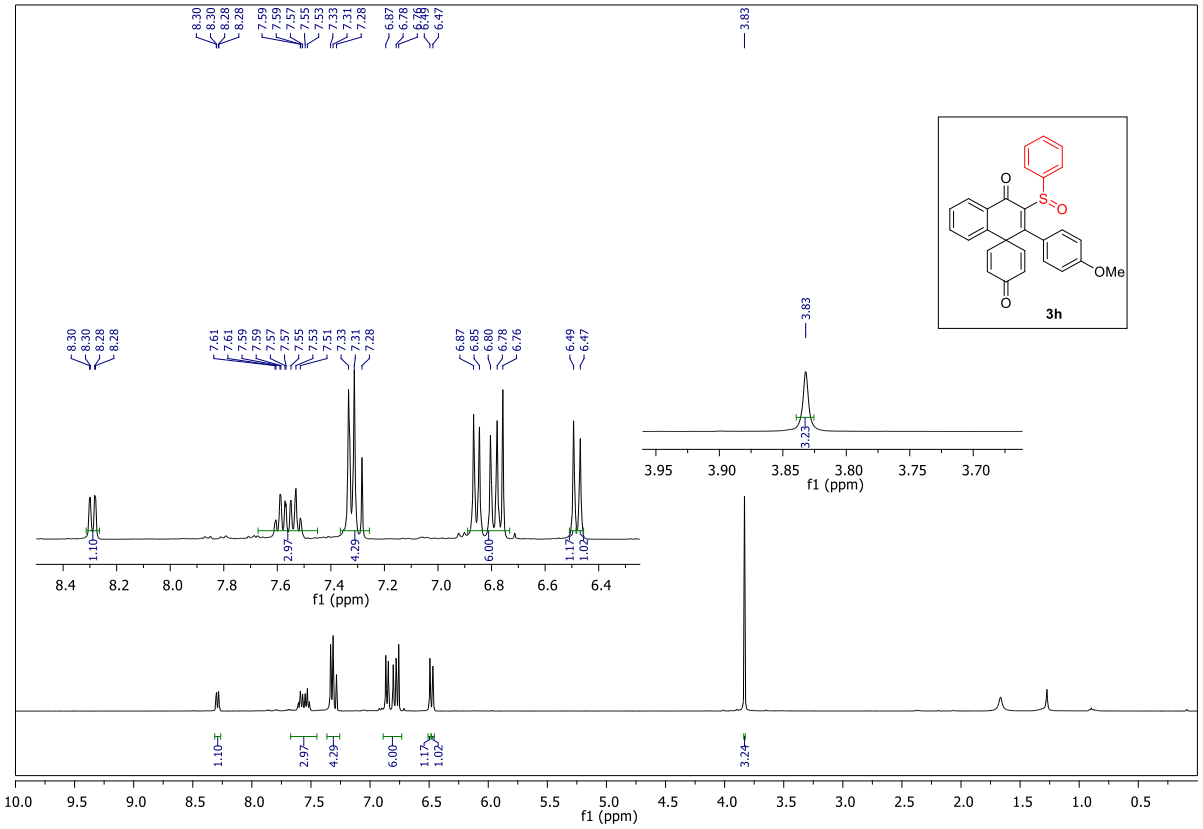
3g, ^{1}H NMR ($CDCl_3$, 400 MHz)



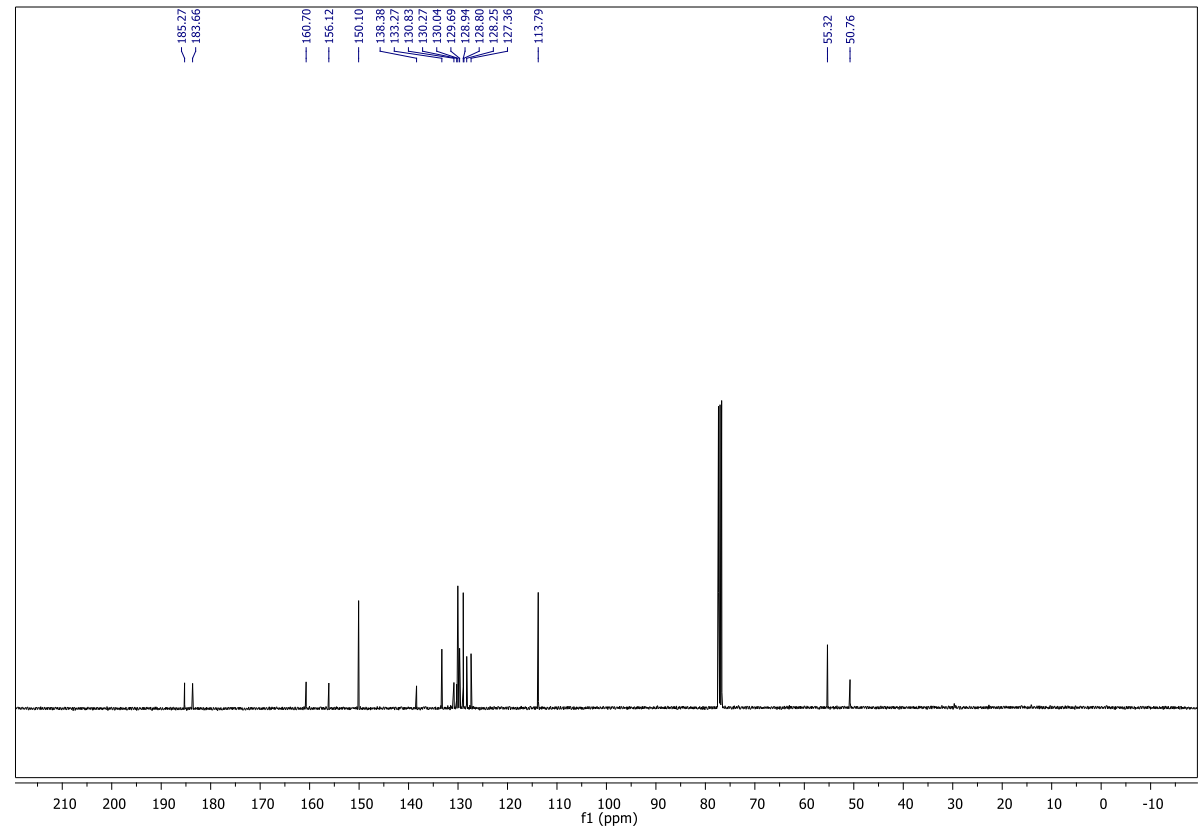
3g, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



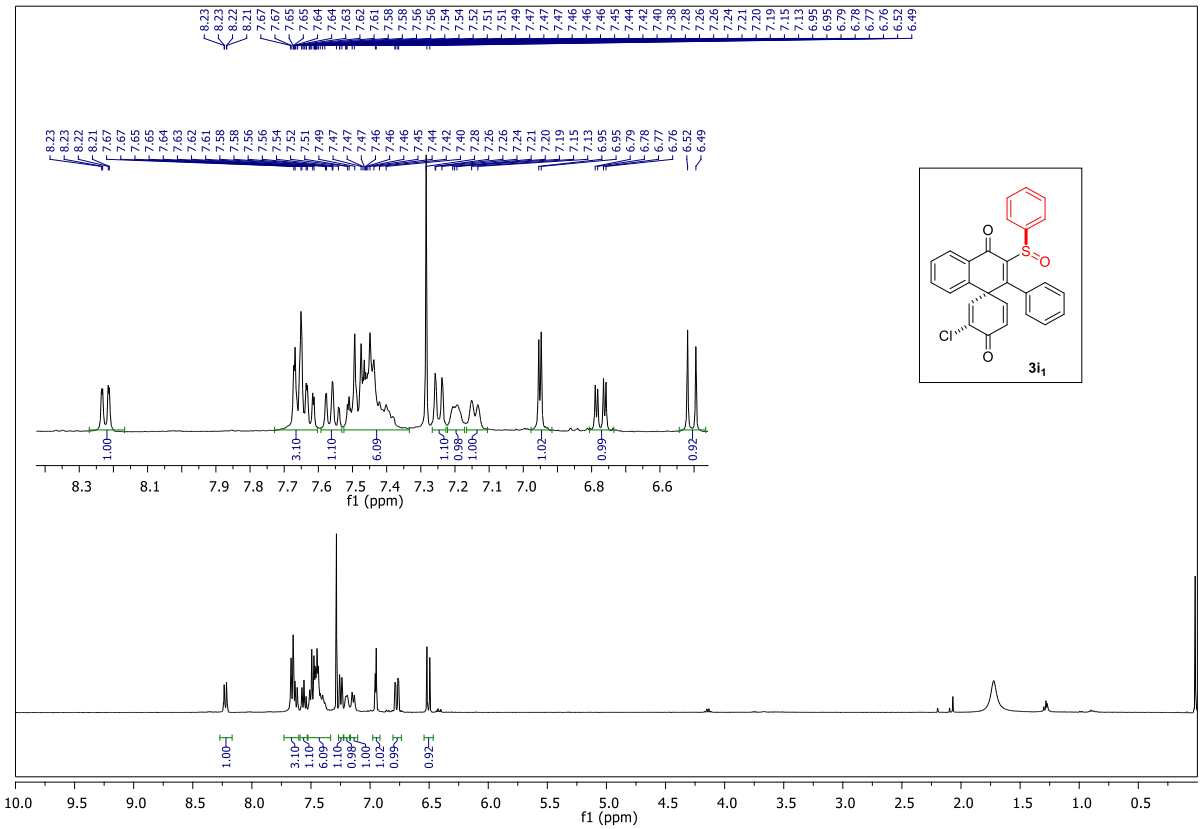
3h, ^{1}H NMR ($CDCl_3$, 400 MHz)



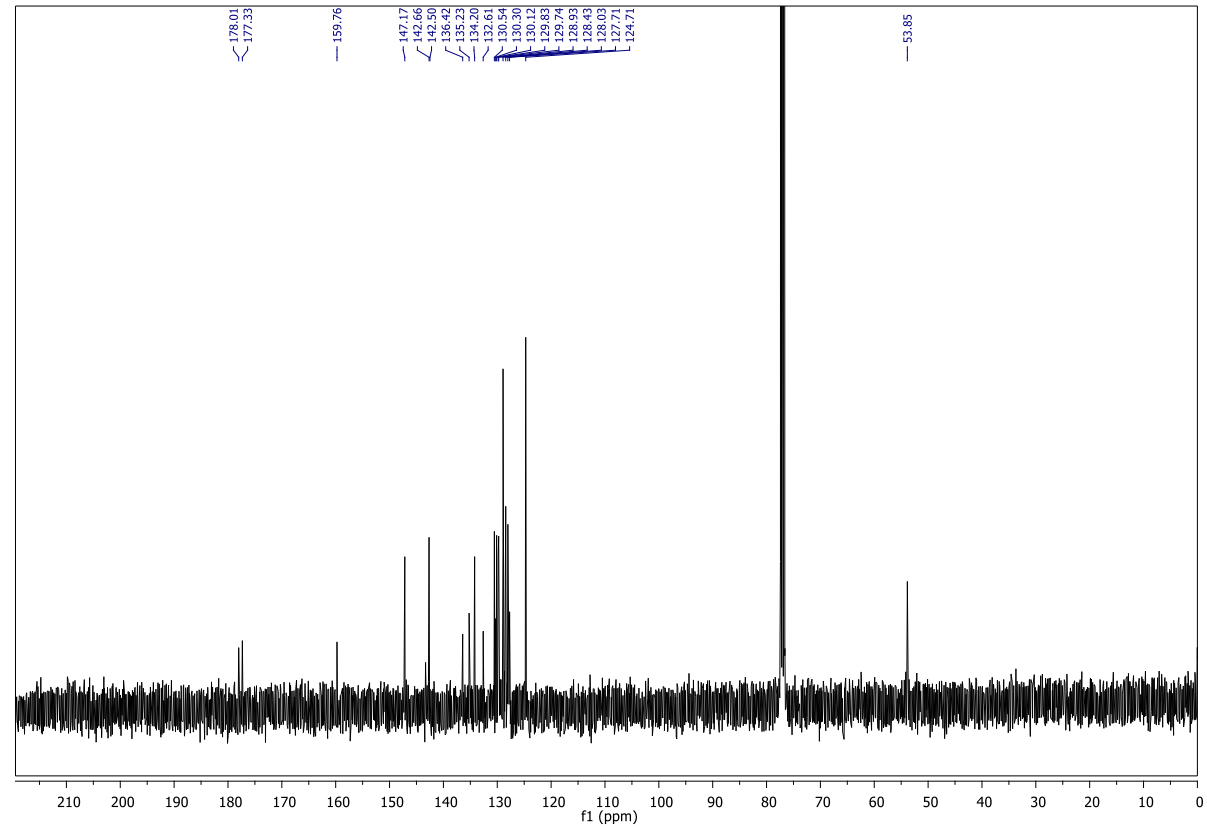
3h, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



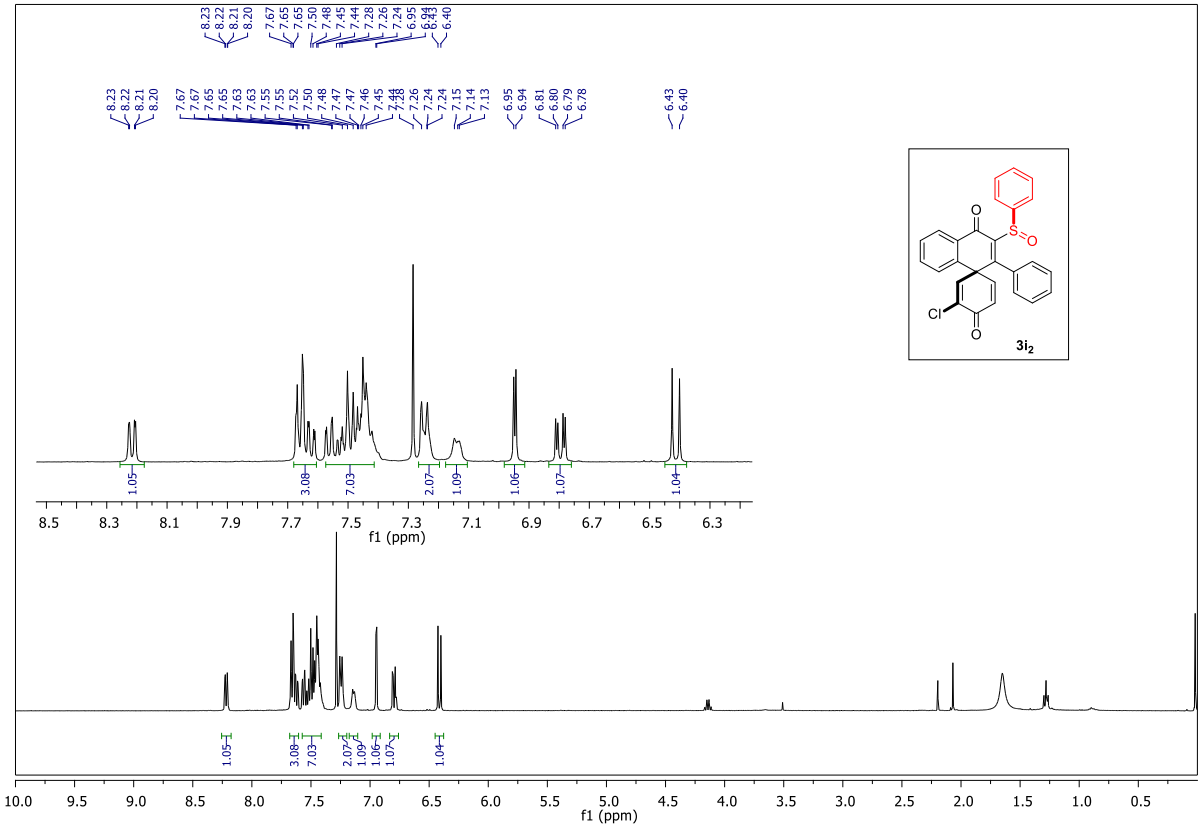
3i$_1$, ^{1}H NMR ($CDCl_3$, 400 MHz)



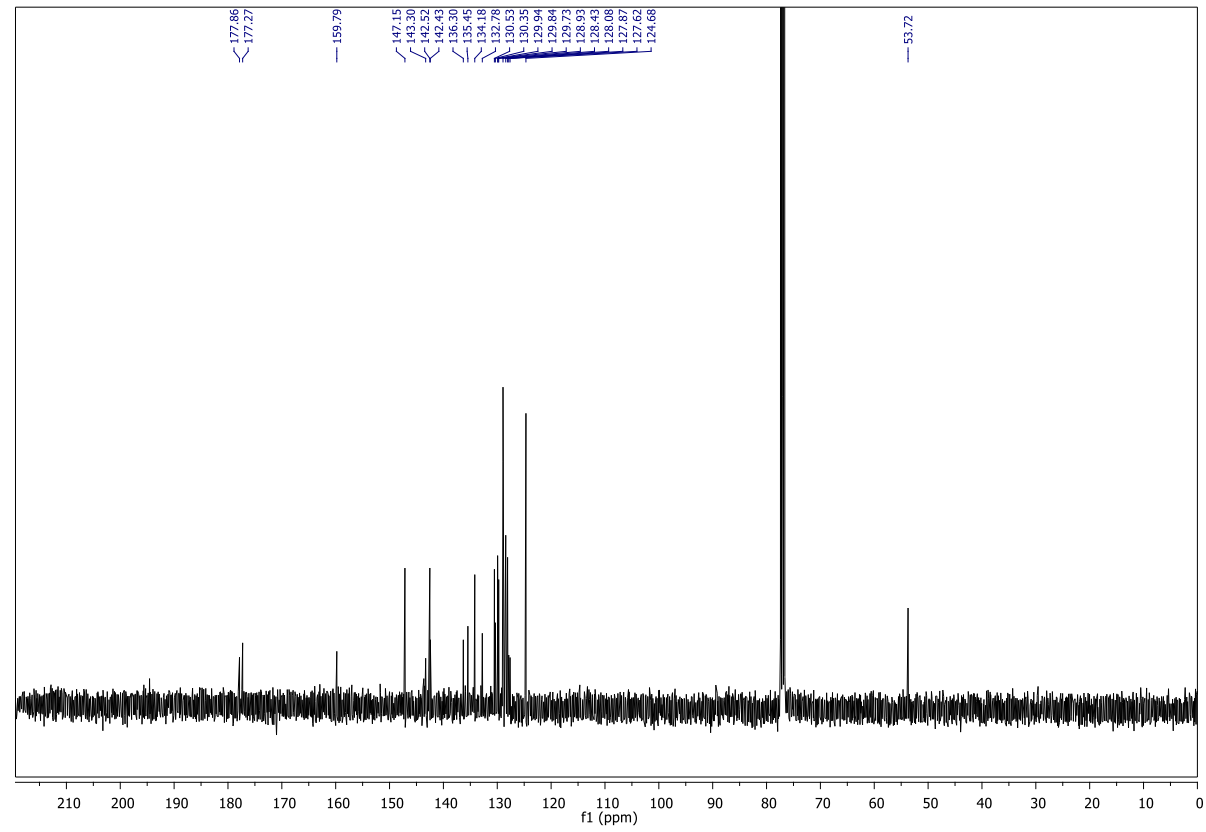
3i$_1$, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



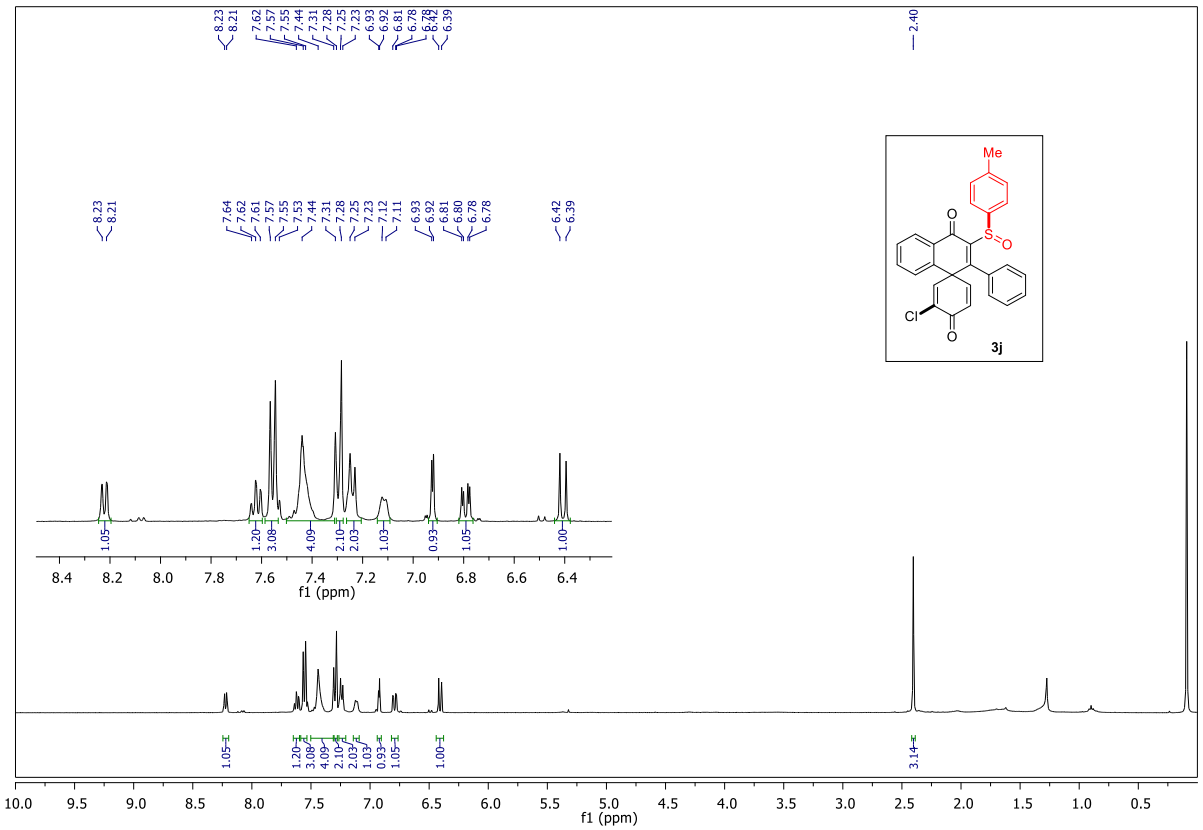
3i$_2$, ^{1}H NMR ($CDCl_3$, 400 MHz)



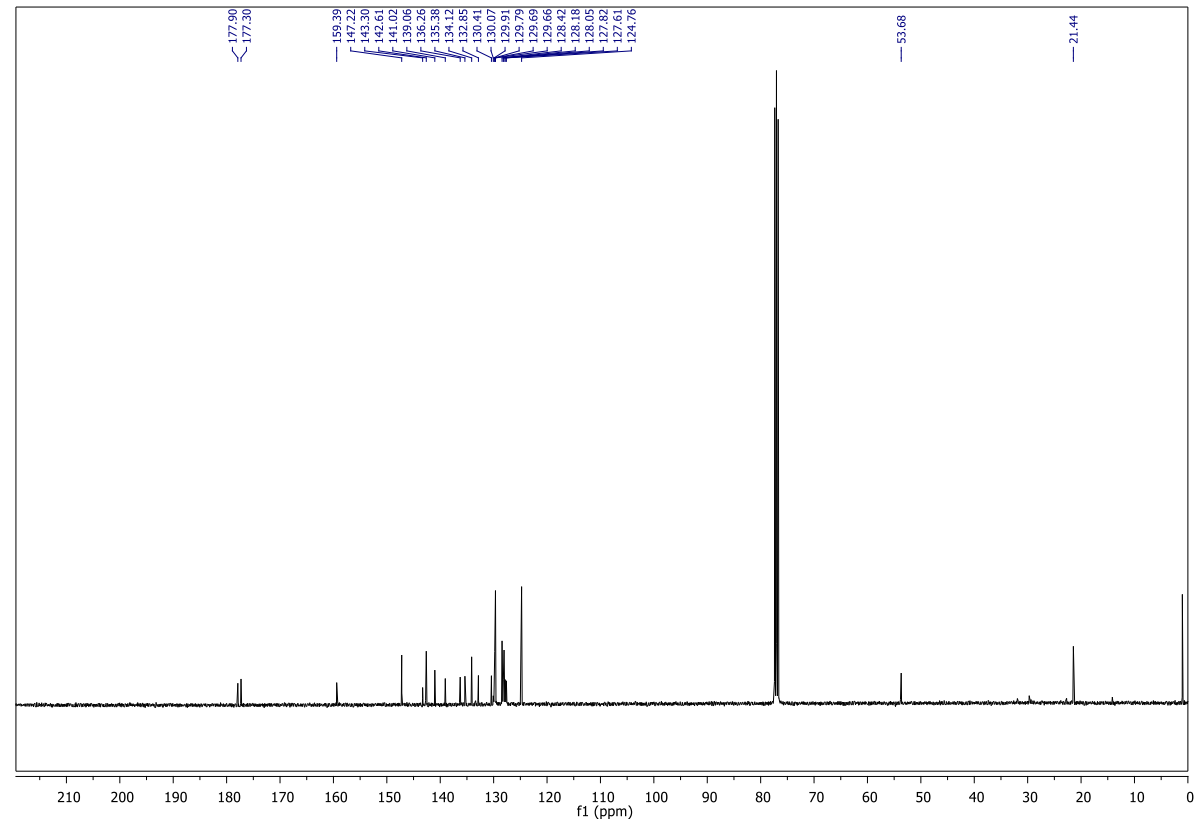
3i$_2$, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



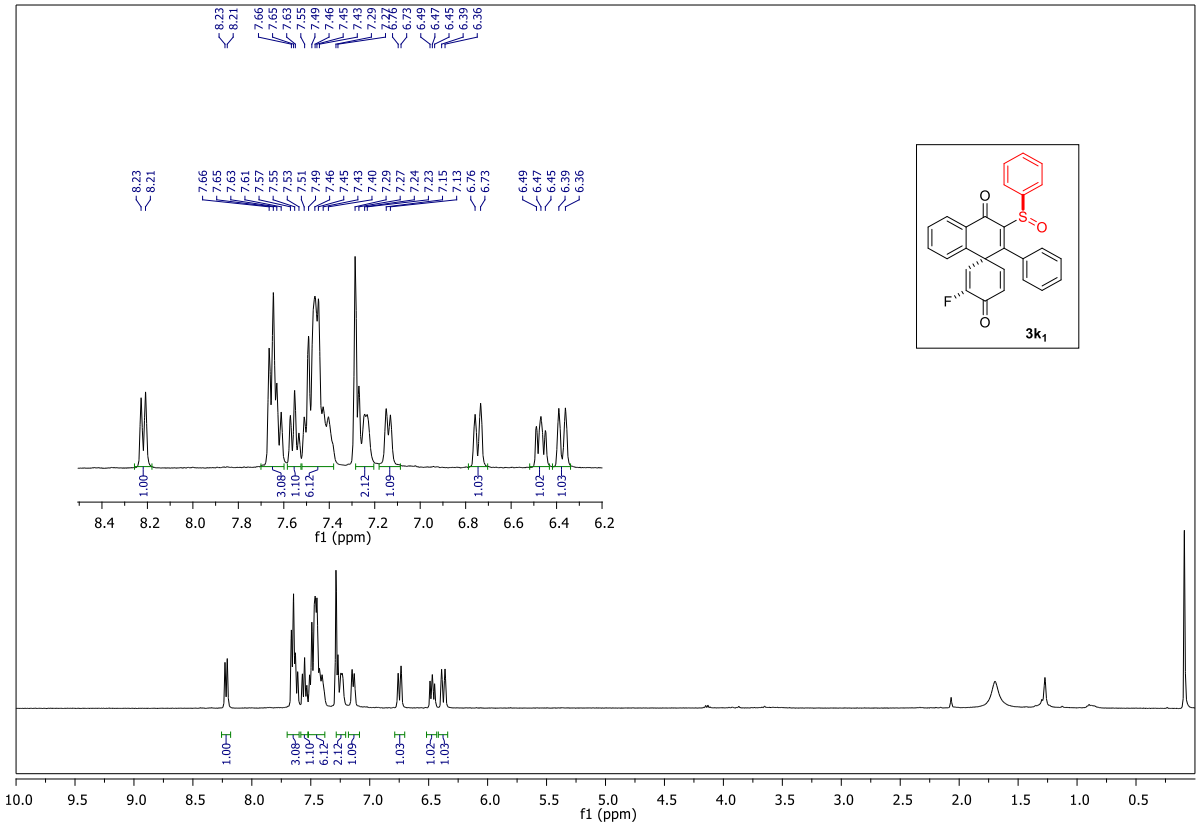
3j, ^{1}H NMR ($CDCl_3$, 400 MHz)



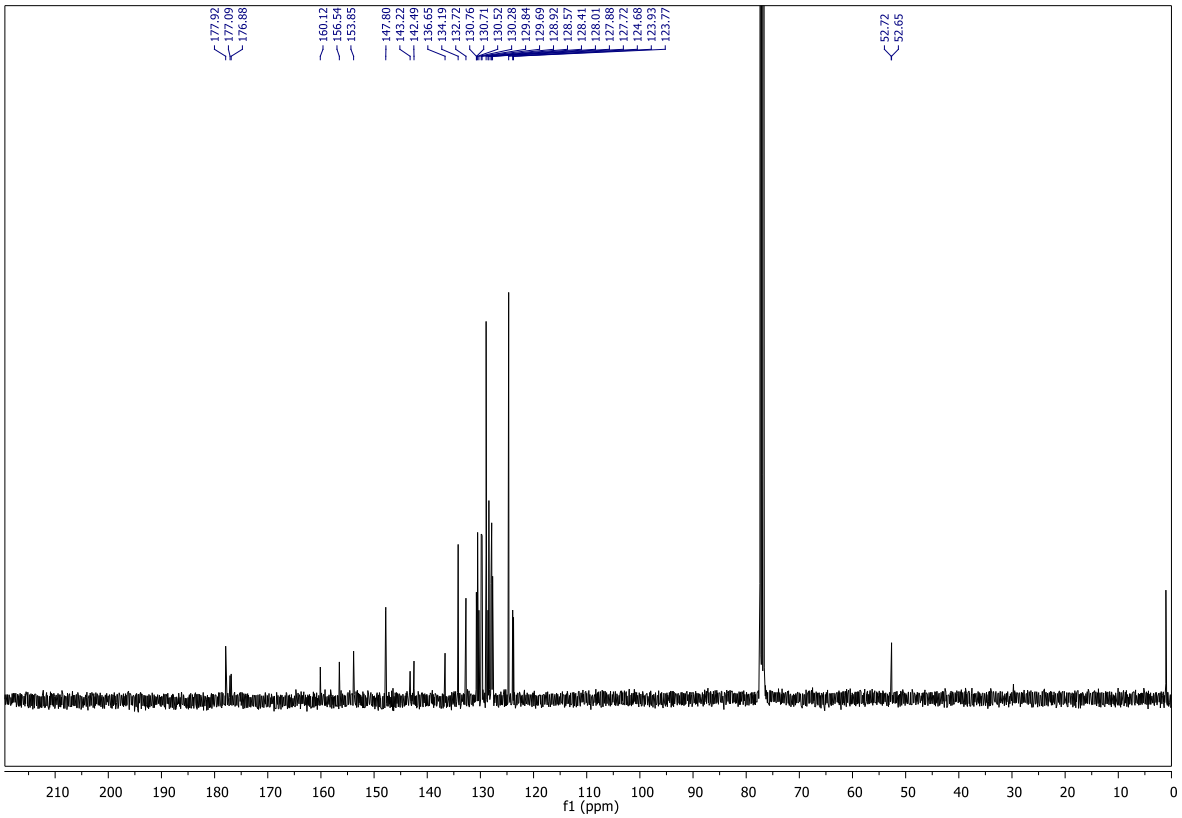
3j, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



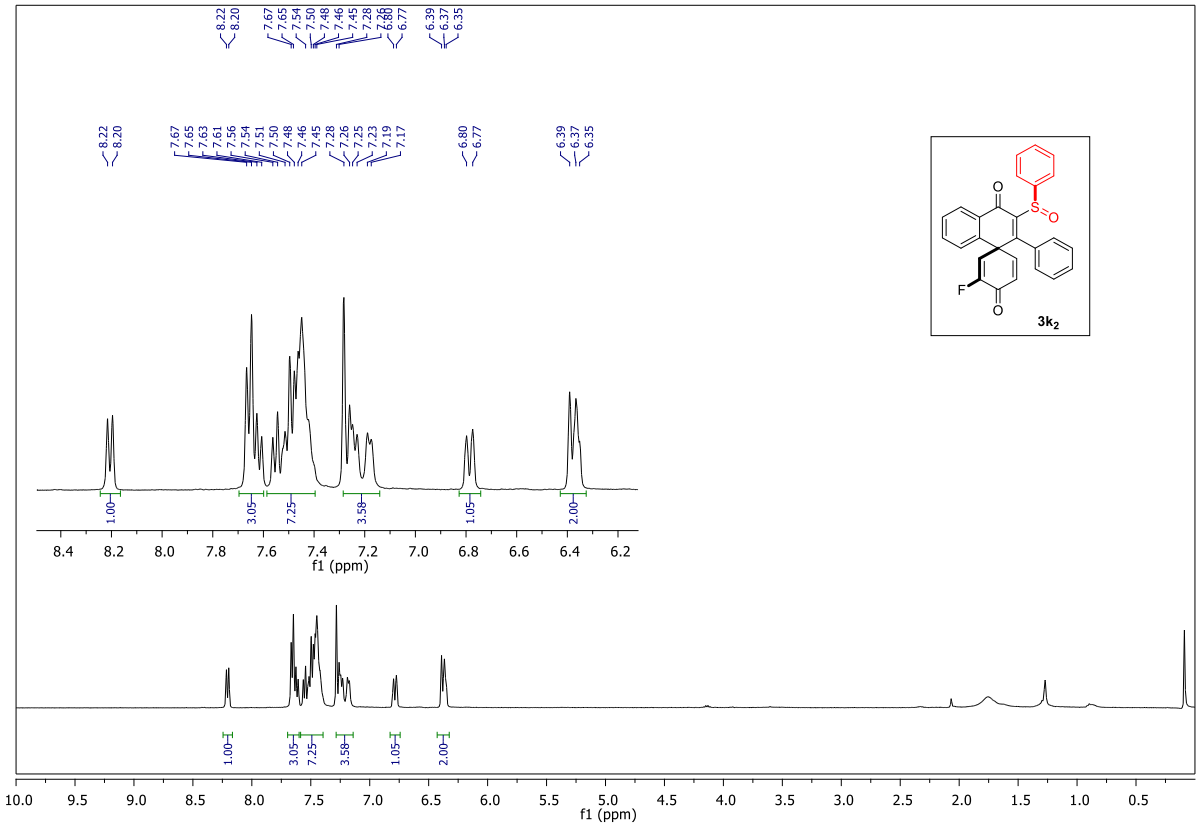
3k$_1$, ^{1}H NMR ($CDCl_3$, 400 MHz)



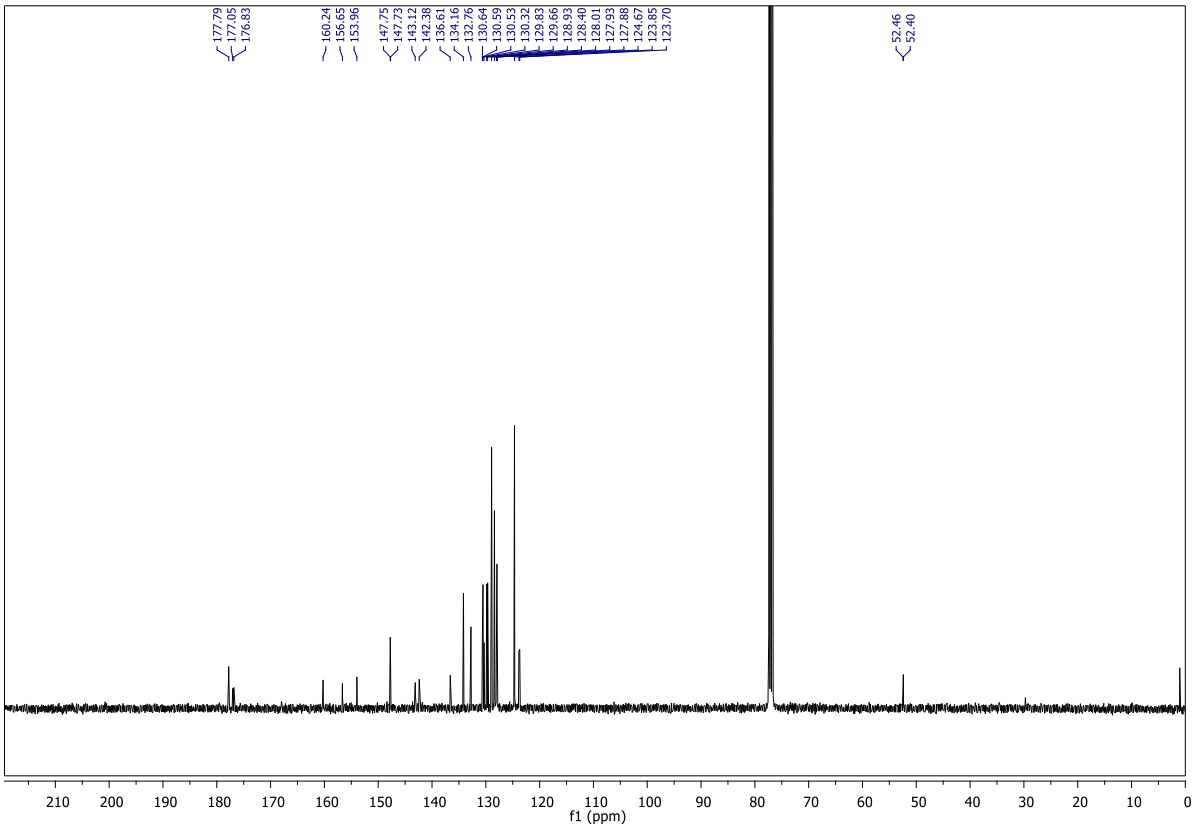
3k$_1$, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



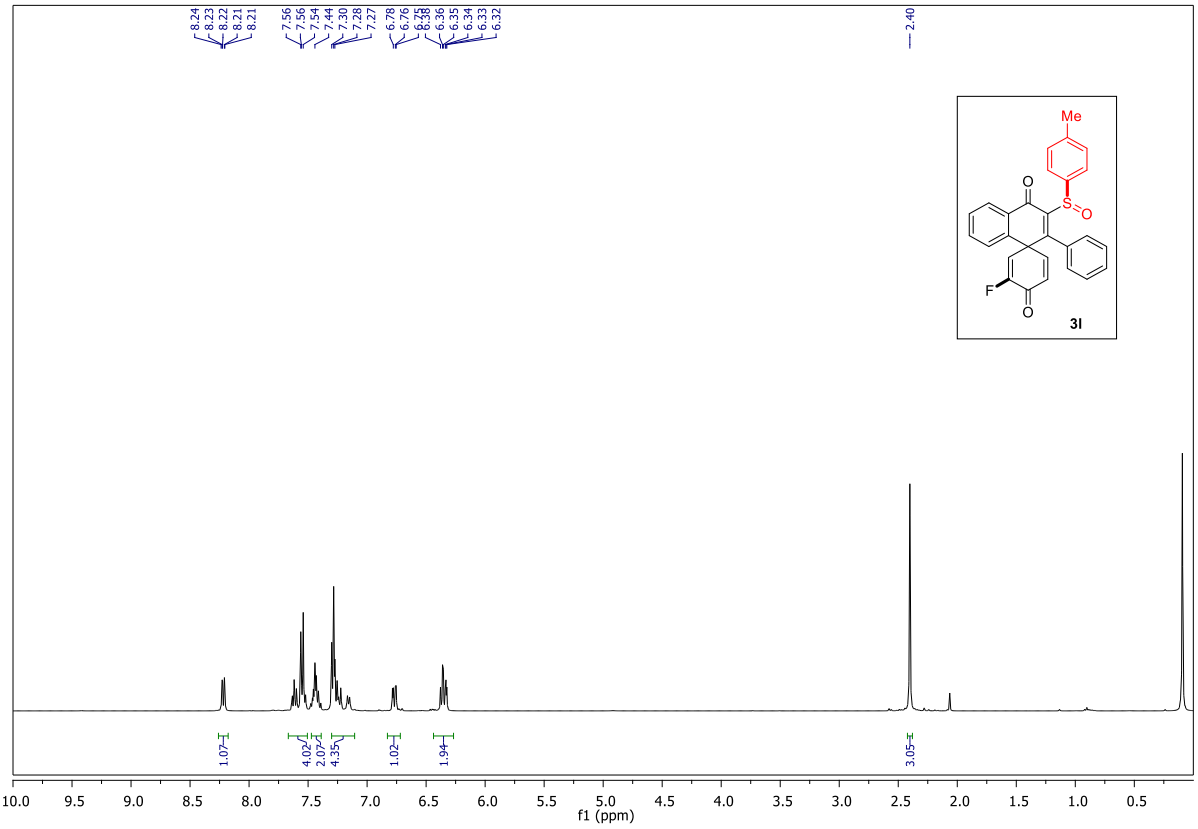
3k$_2$, ^{1}H NMR ($CDCl_3$, 400 MHz)



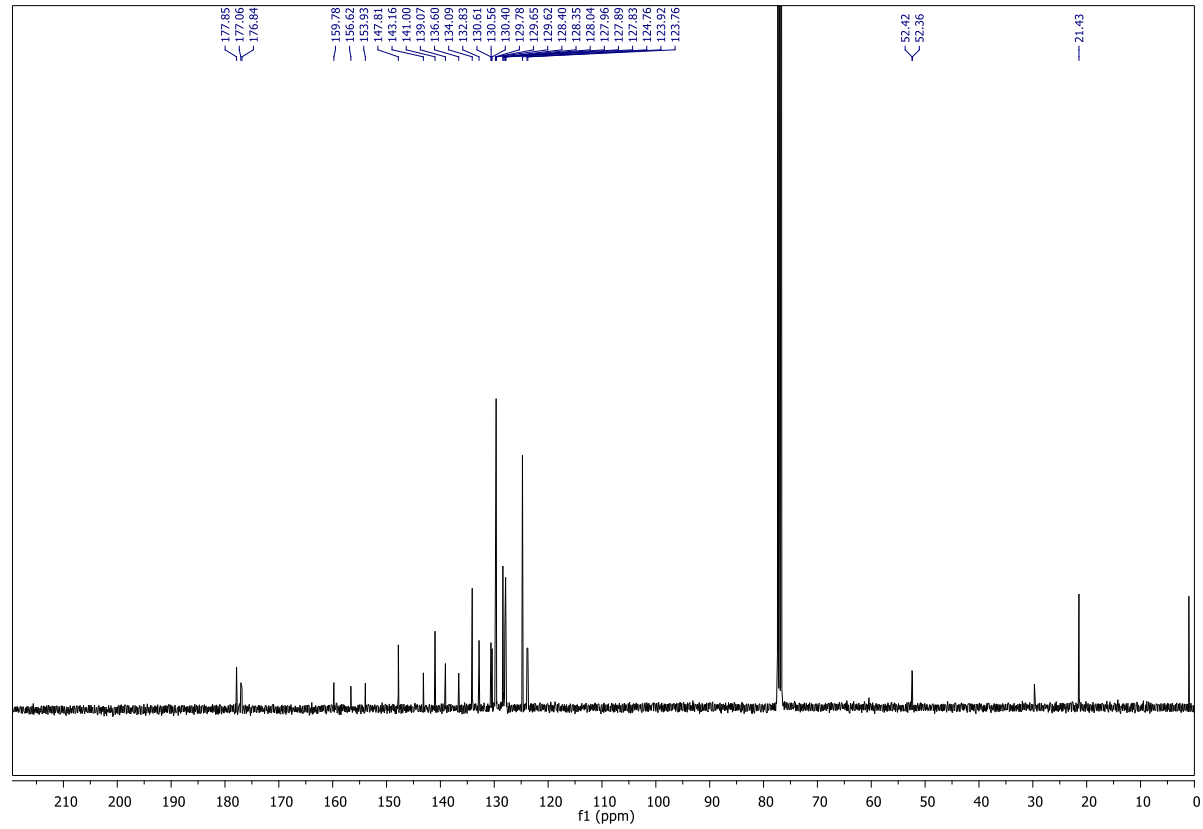
3k$_2$, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



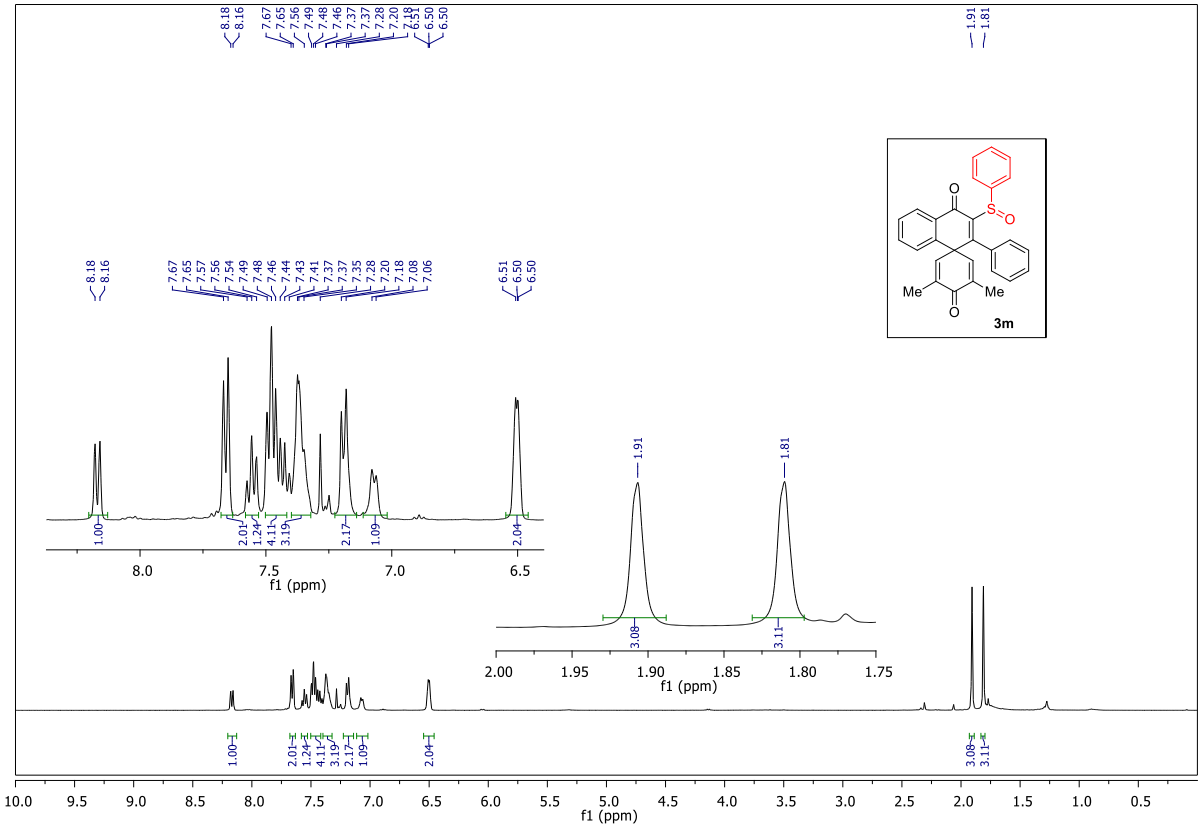
3l, ^{1}H NMR ($CDCl_3$, 400 MHz)



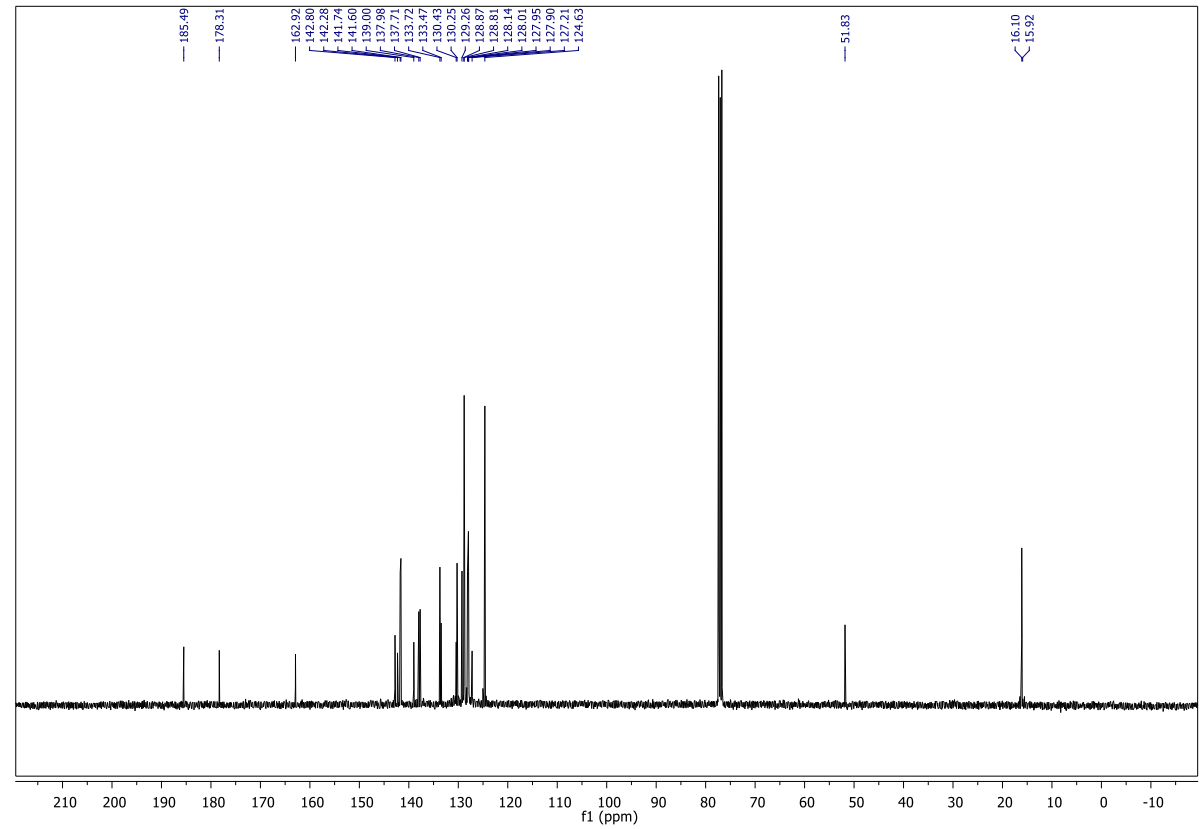
3l, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



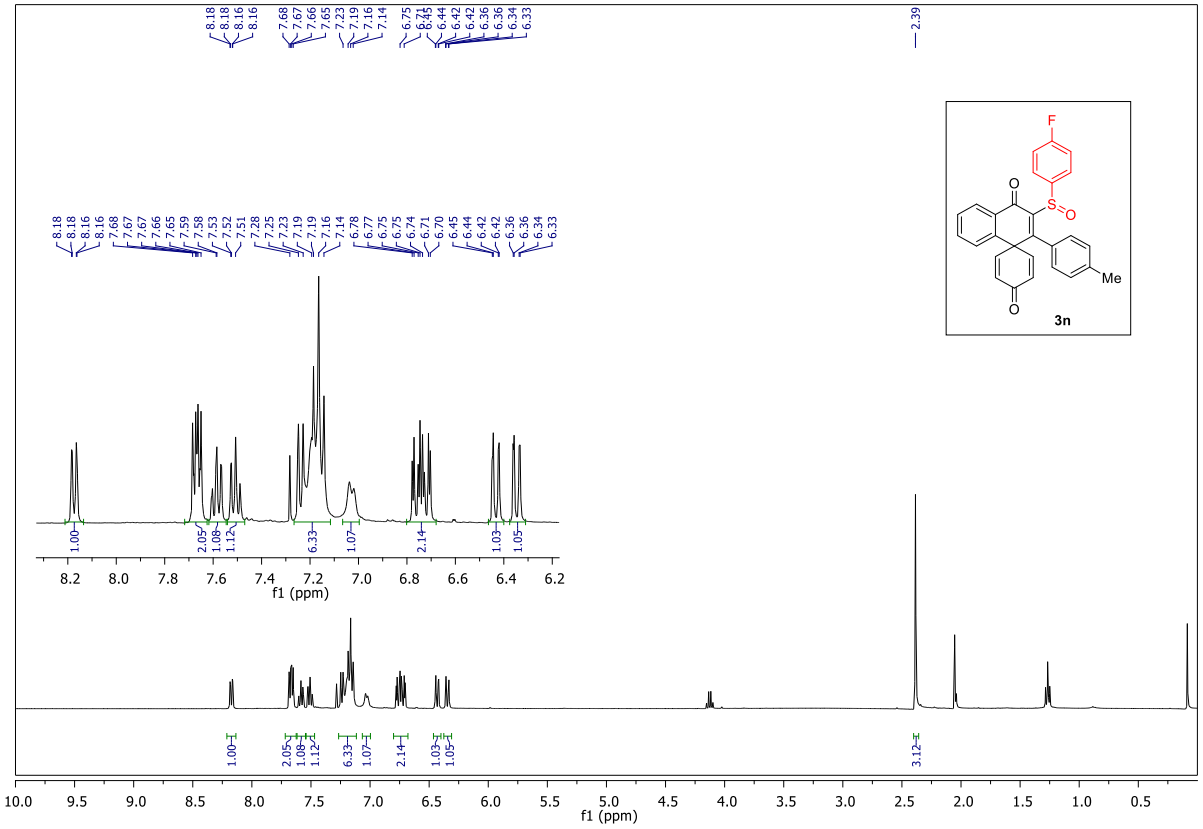
3m, ^{1}H NMR ($CDCl_3$, 400 MHz)



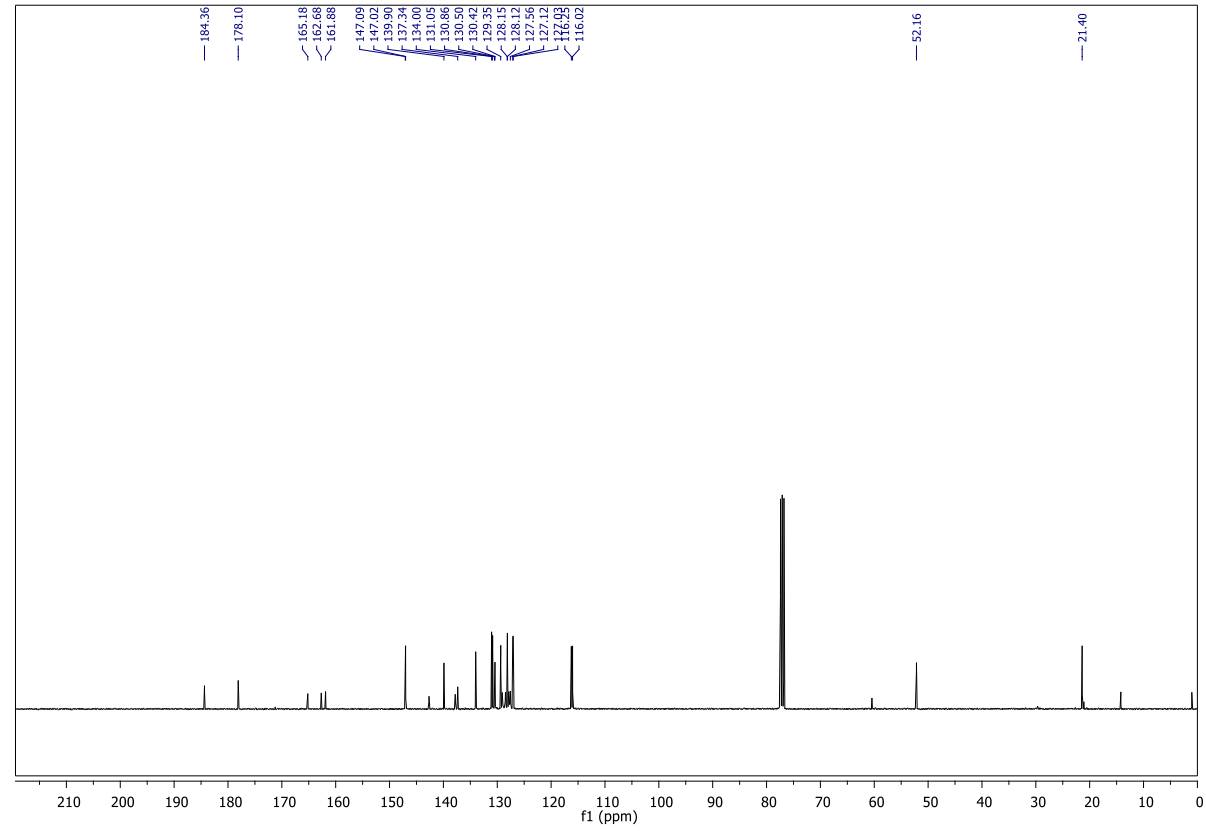
3m, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



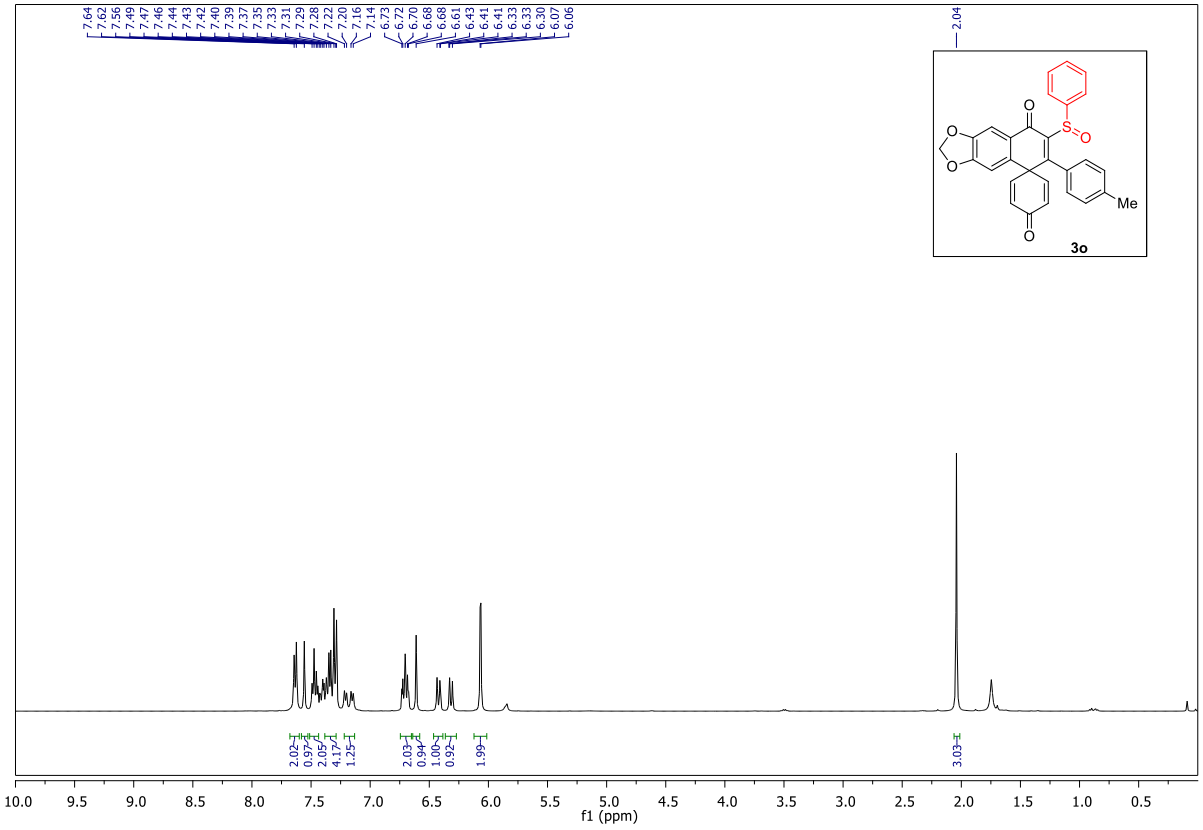
3n, ^{1}H NMR ($CDCl_3$, 400 MHz)



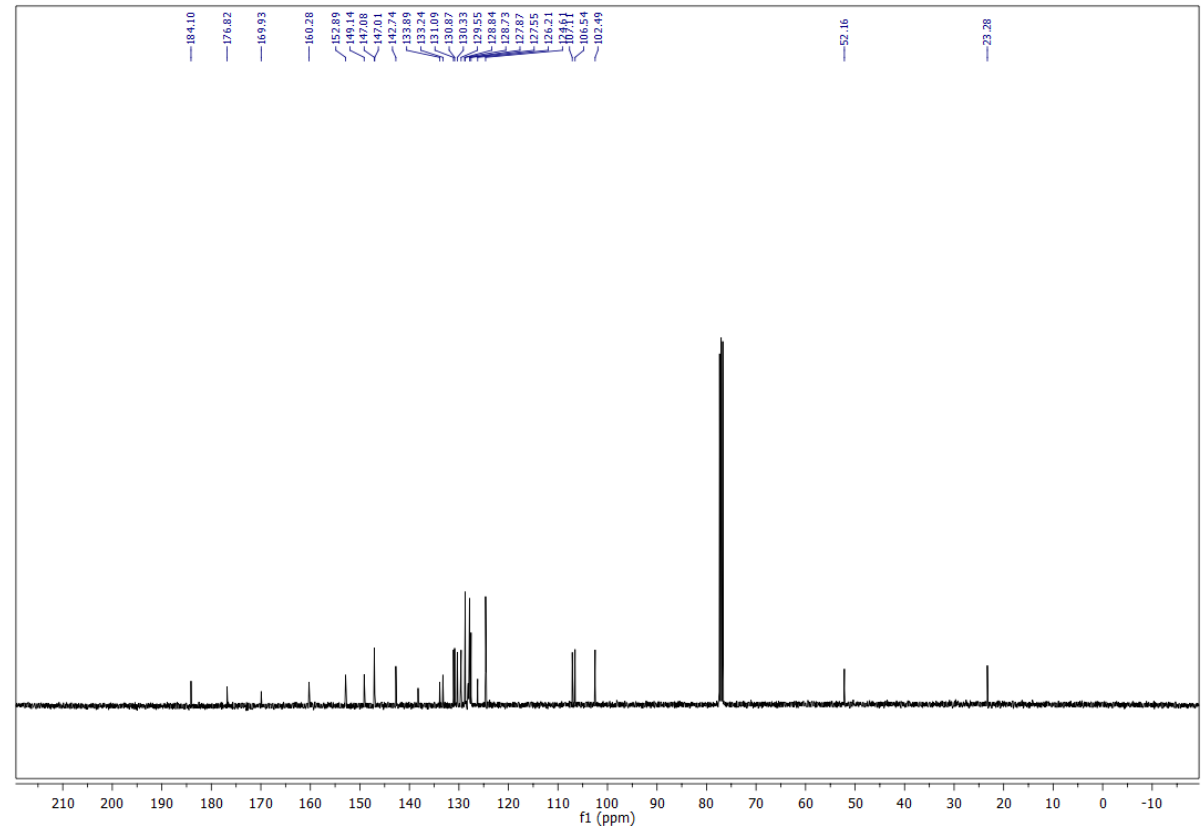
3n, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



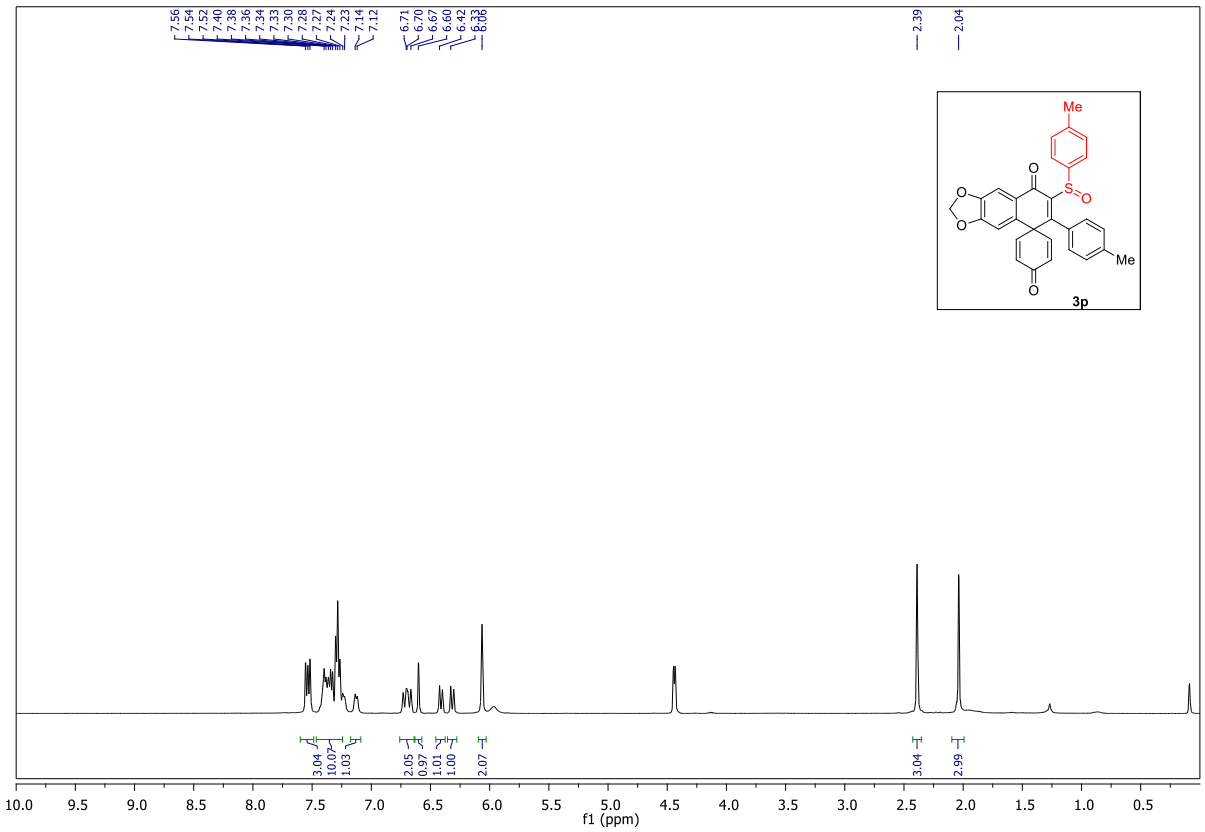
3o, ^{1}H NMR ($CDCl_3$, 400 MHz)



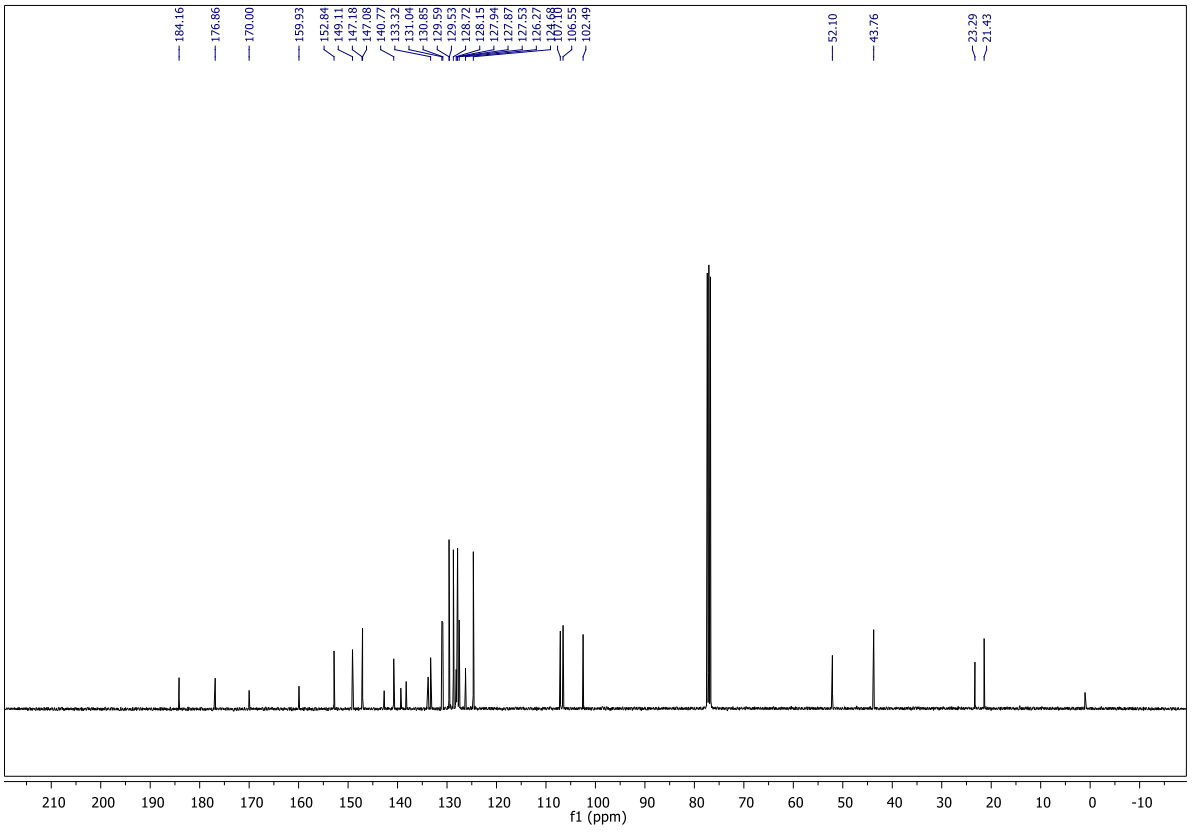
3o, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



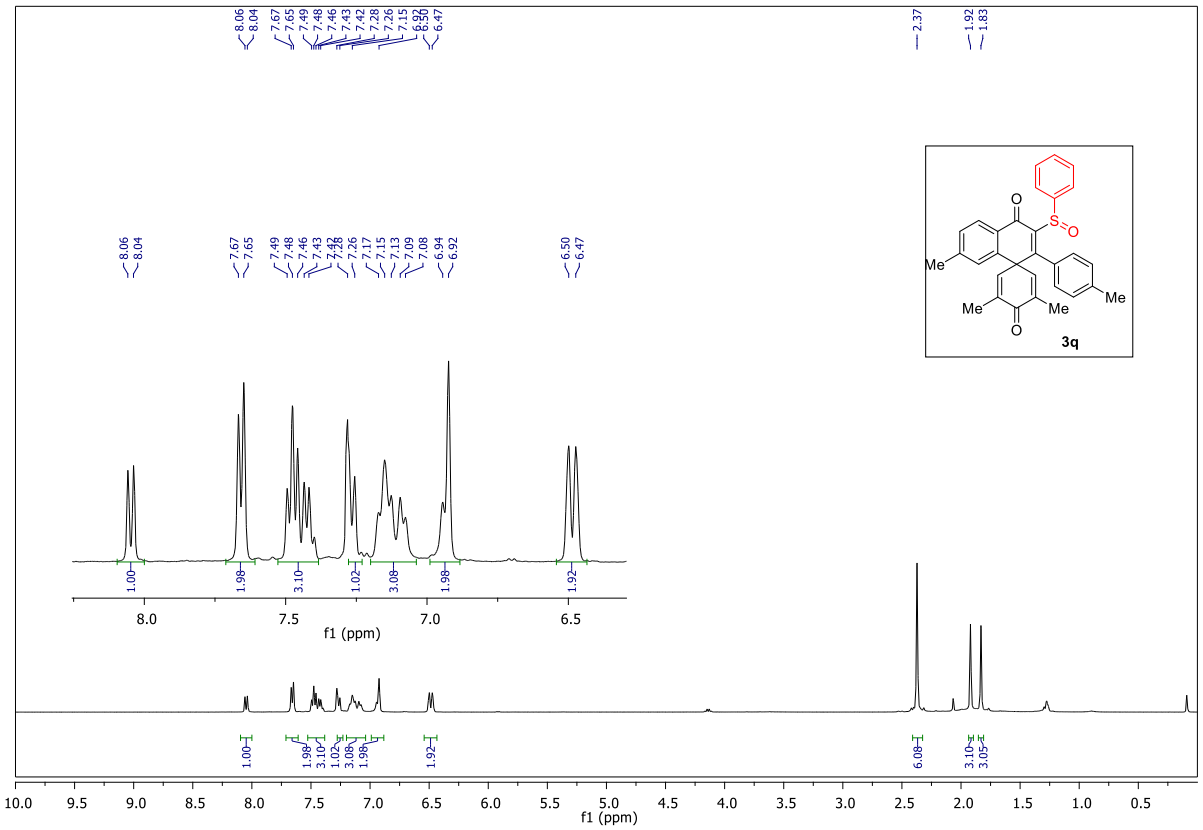
3p, ^{1}H NMR ($CDCl_3$, 400 MHz)



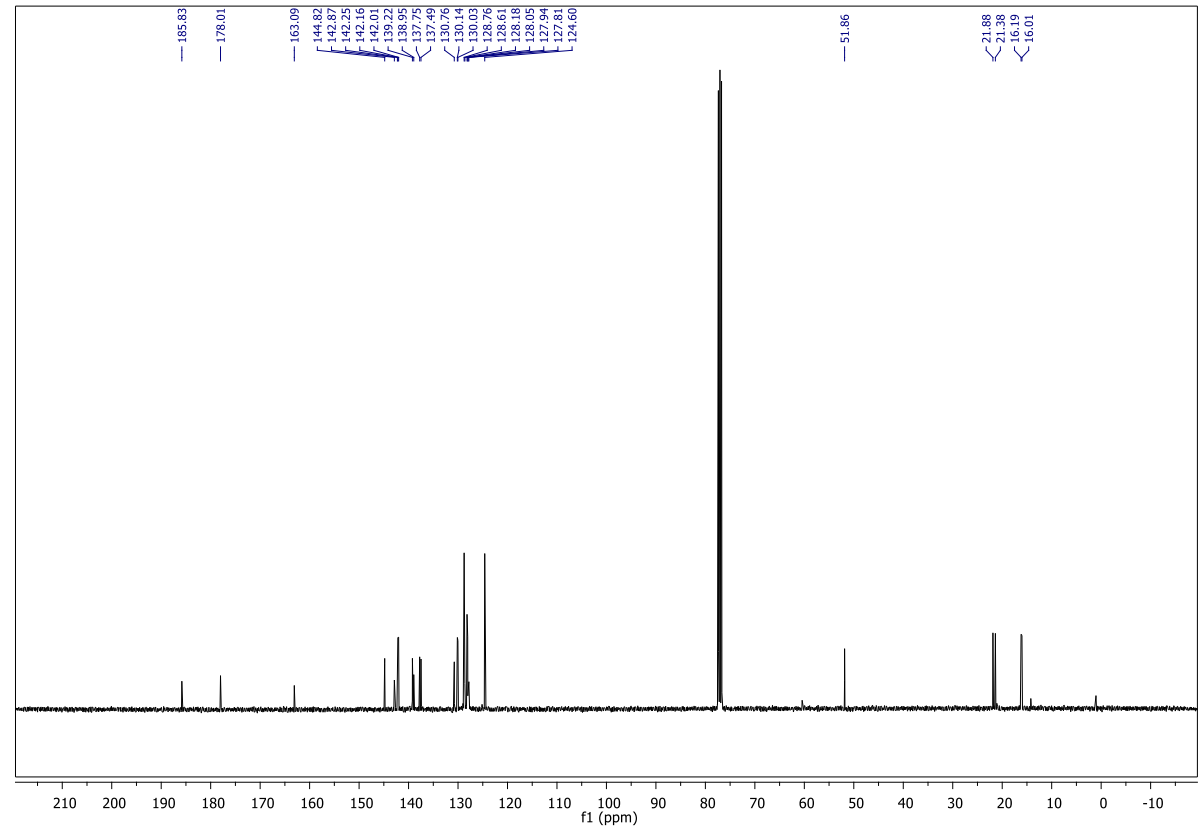
3p, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



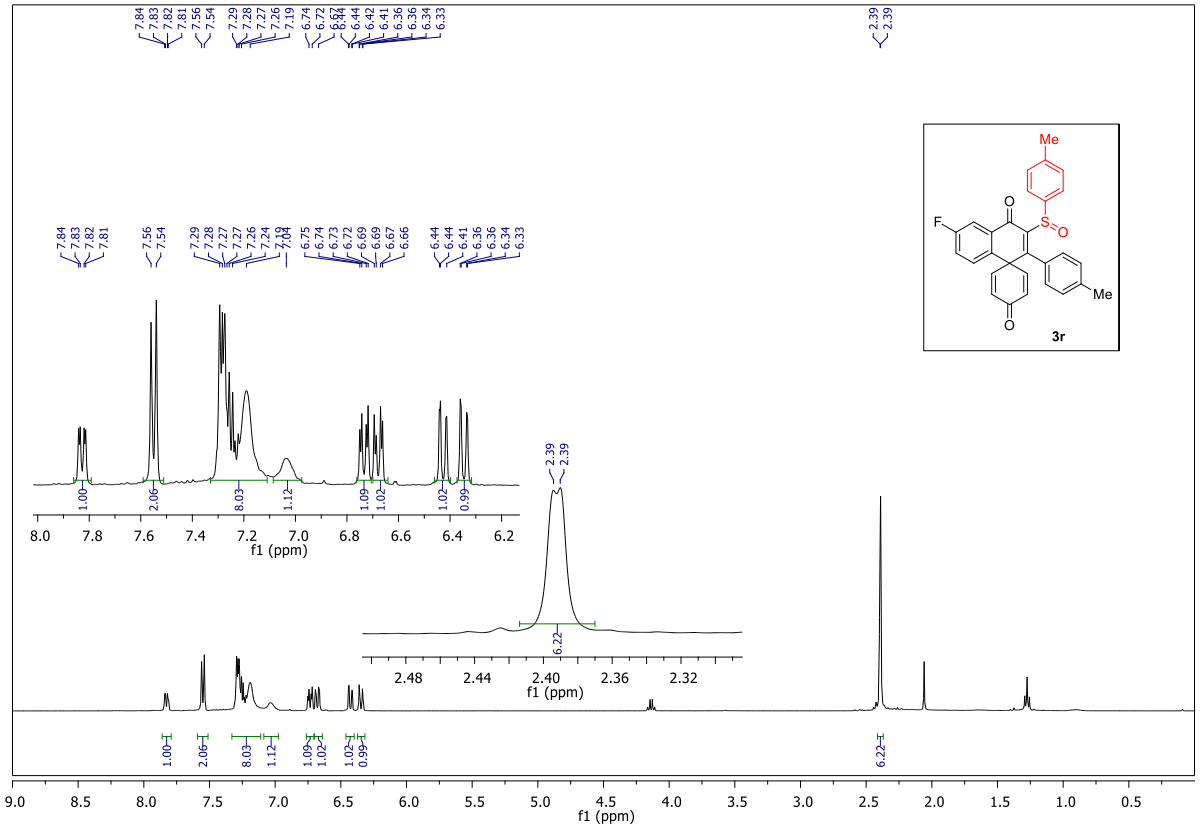
3q, ^{1}H NMR ($CDCl_3$, 400 MHz)



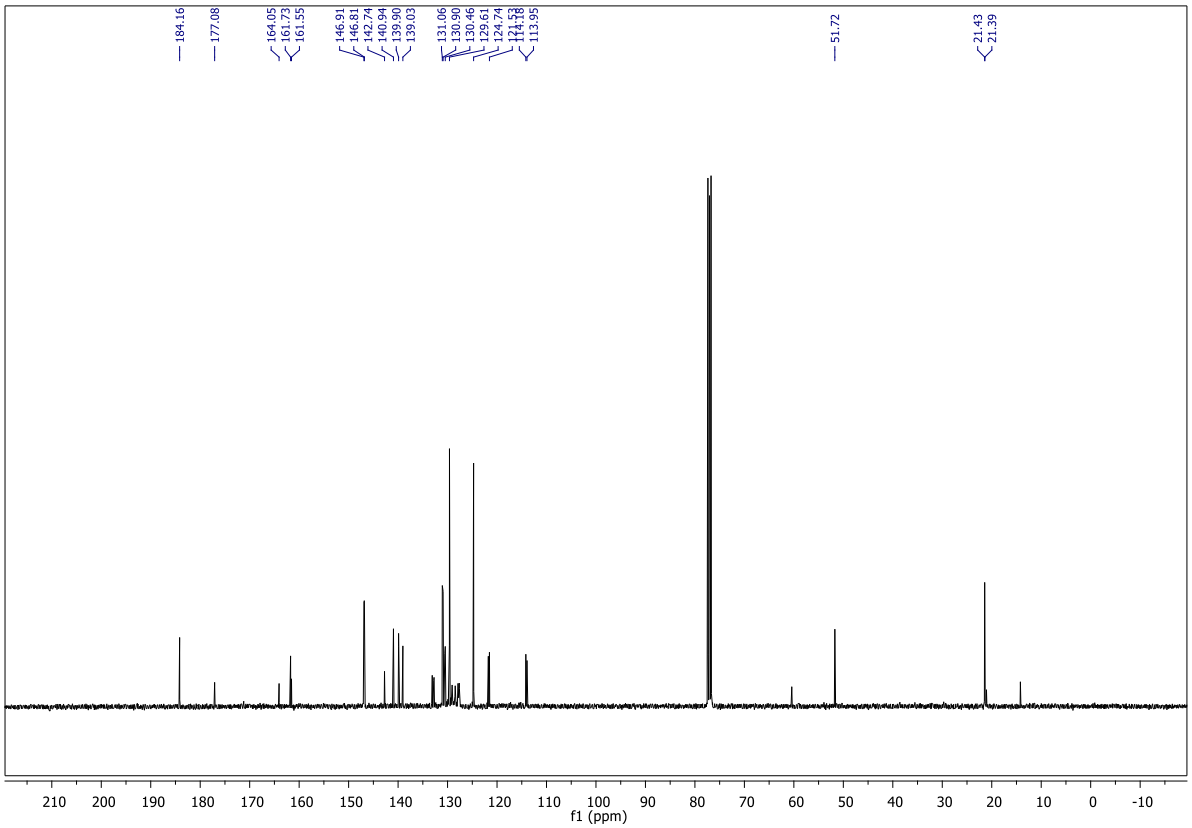
3q, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



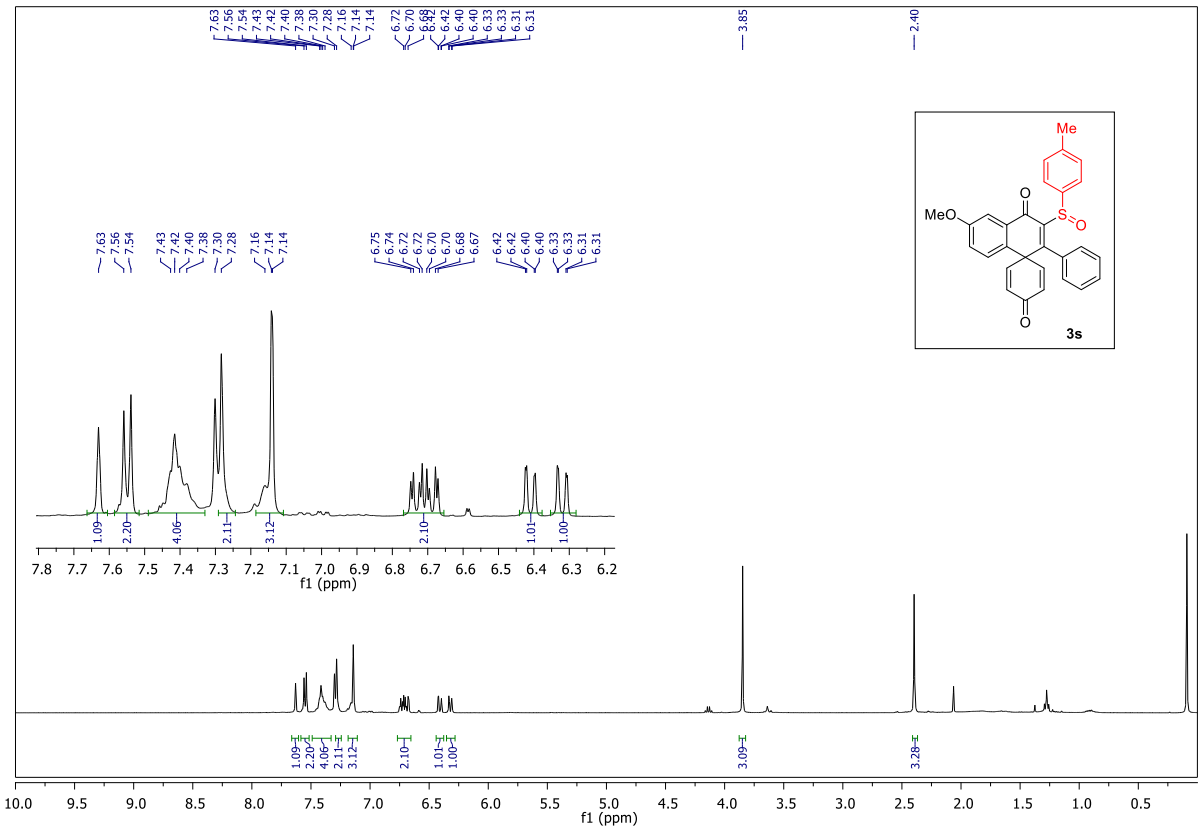
3r, ^{1}H NMR ($CDCl_3$, 400 MHz)



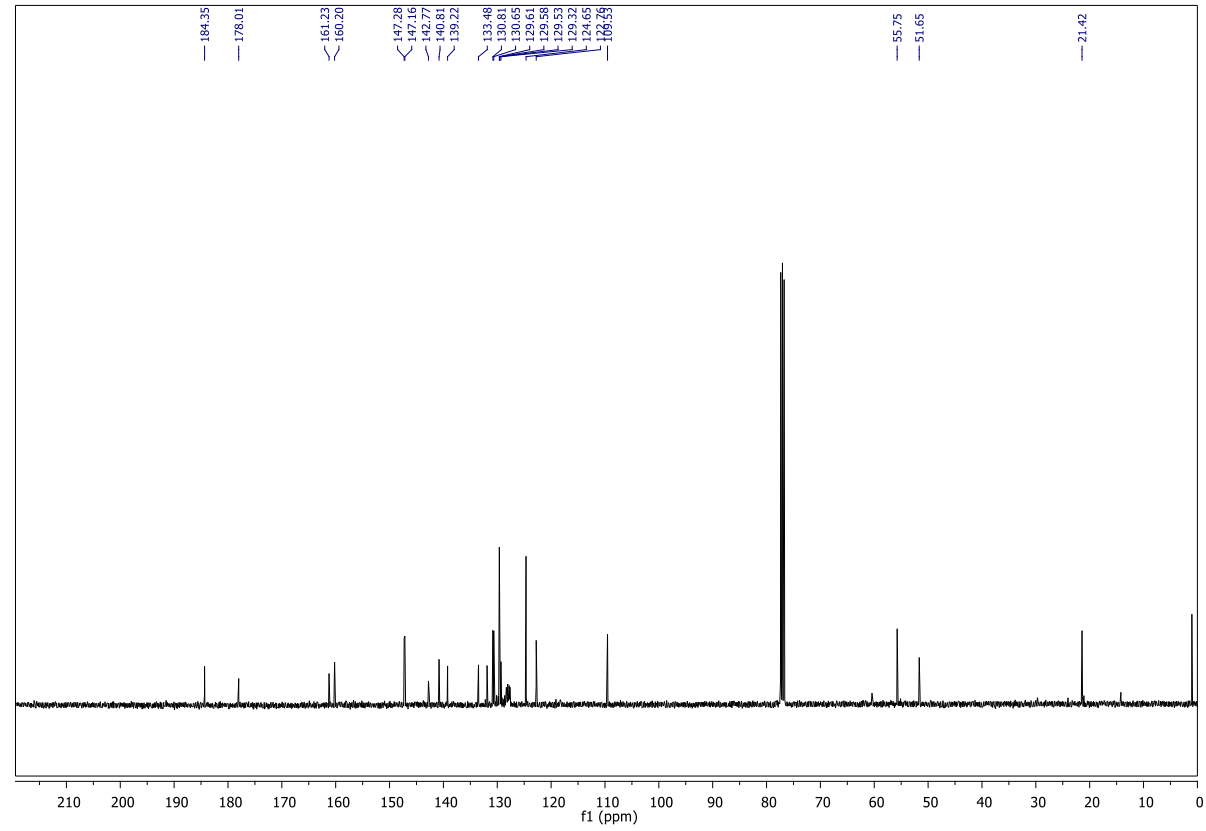
3r, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



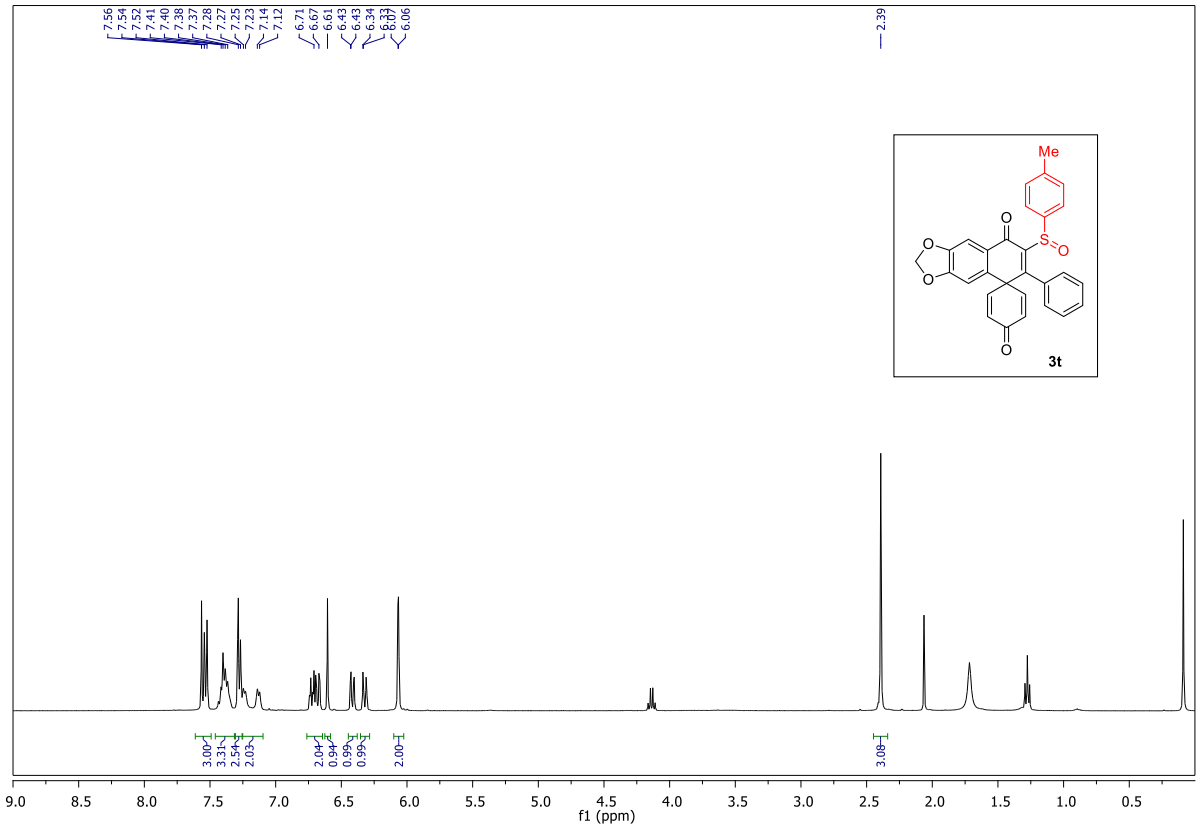
3s, ^{1}H NMR ($CDCl_3$, 400 MHz)



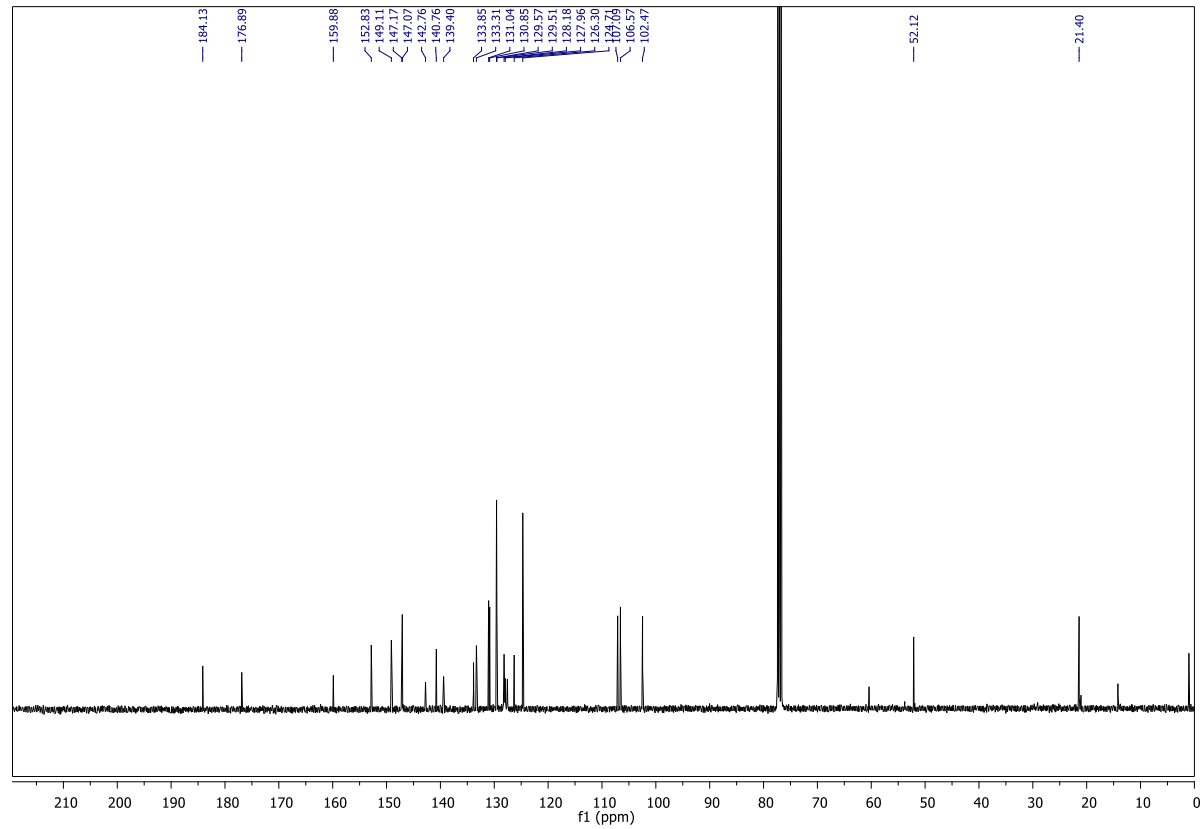
3s, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



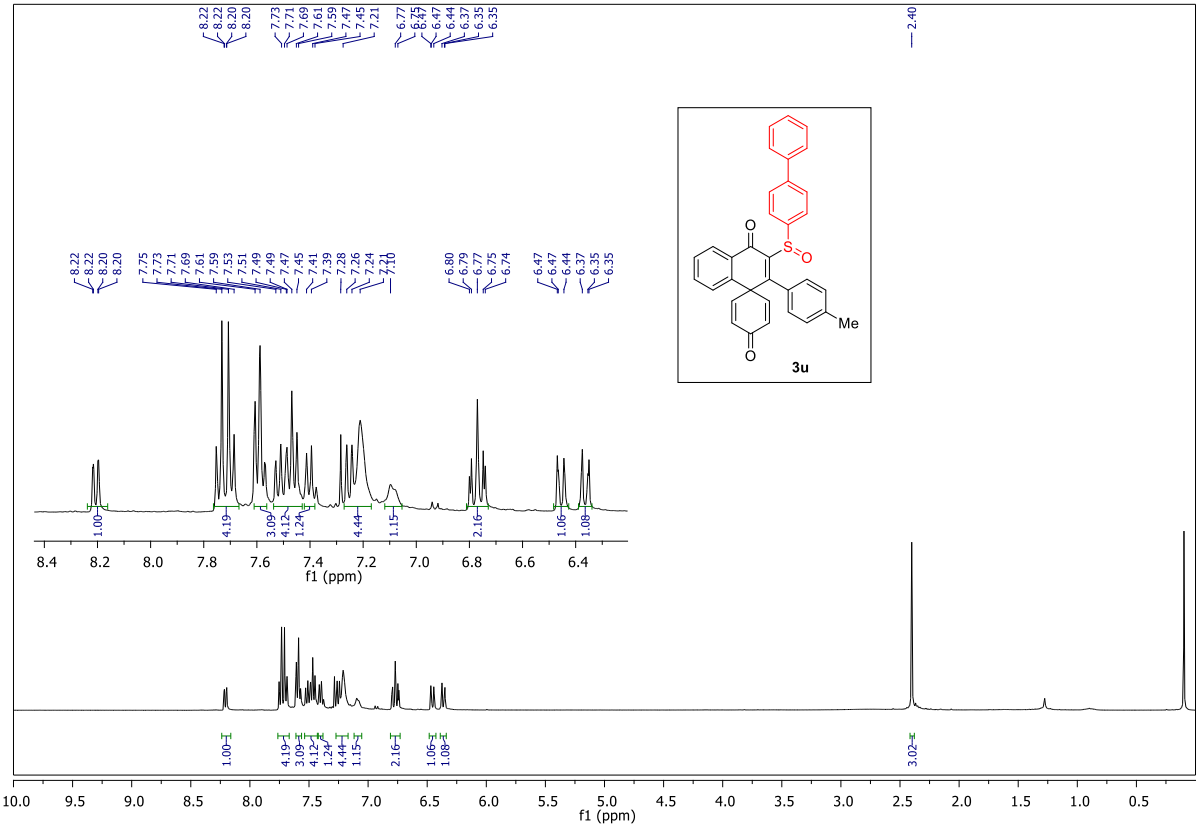
3t, ^{1}H NMR ($CDCl_3$, 400 MHz)



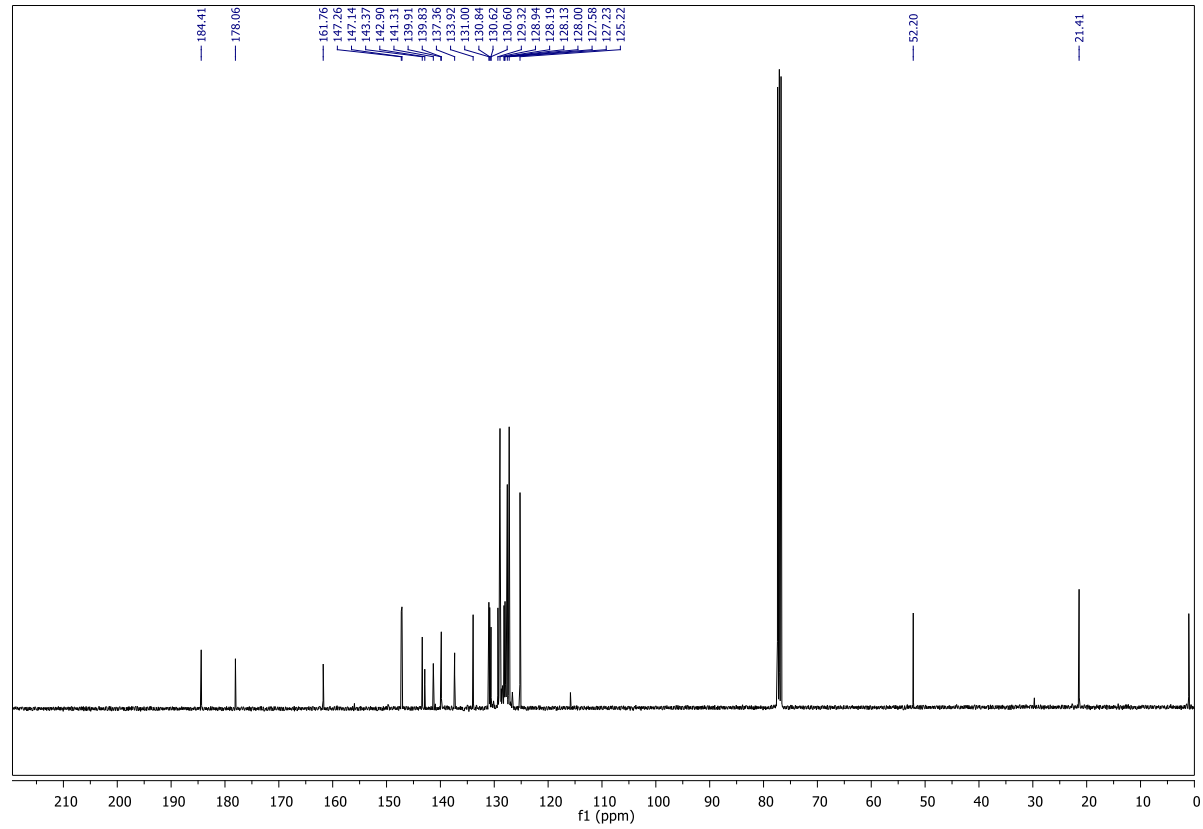
3t, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



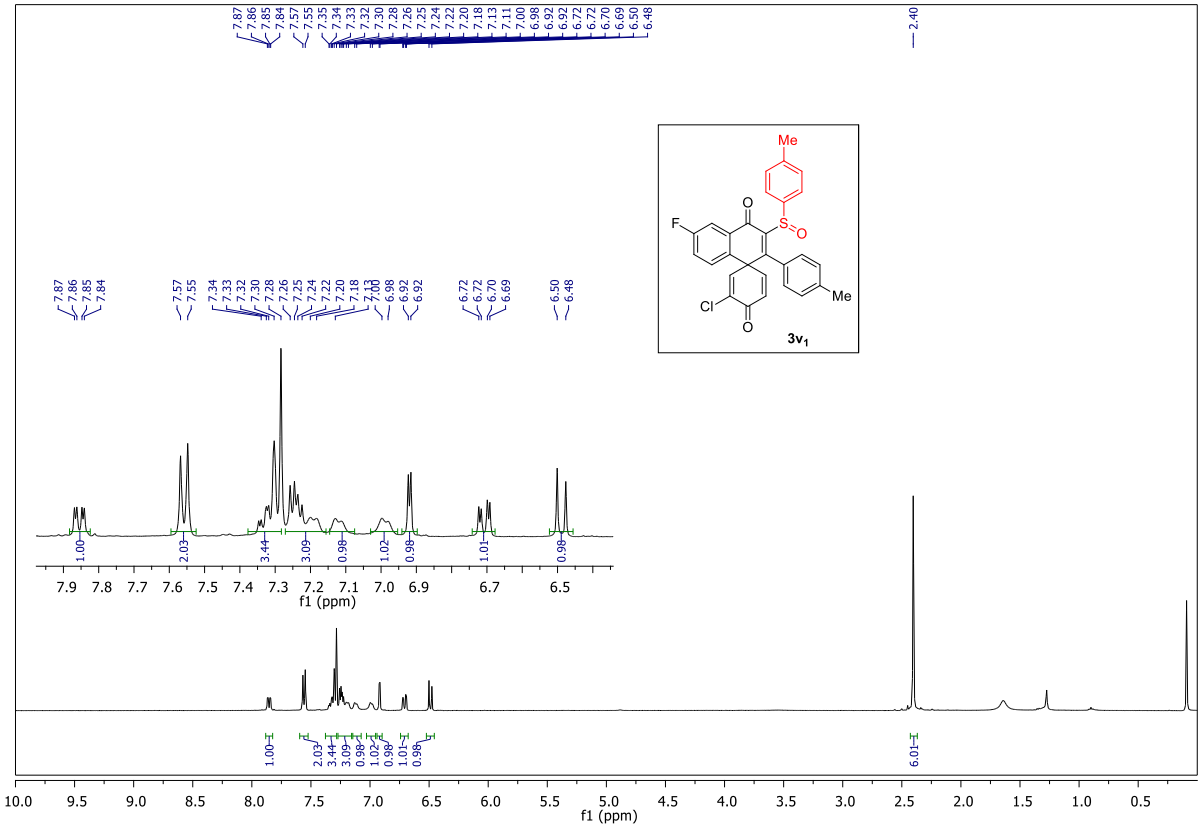
3u, ^{1}H NMR ($CDCl_3$, 400 MHz)



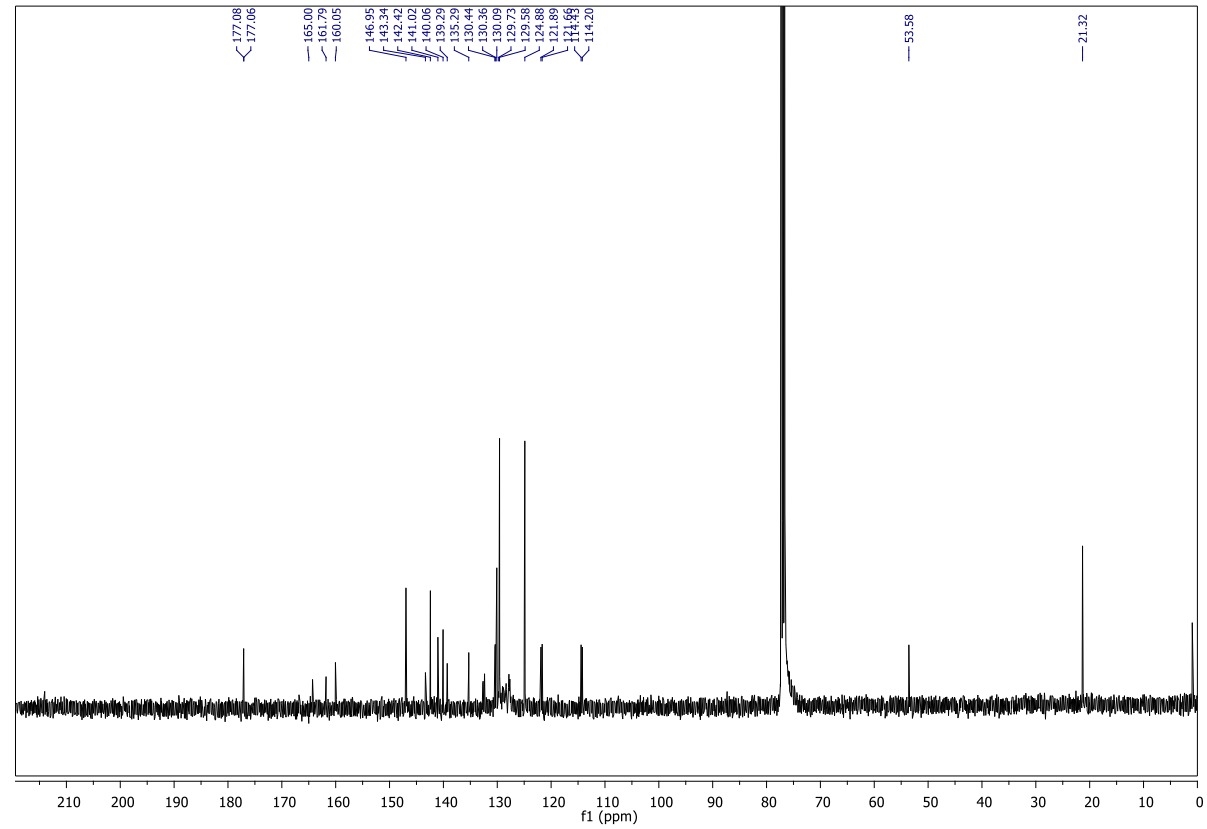
3u, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



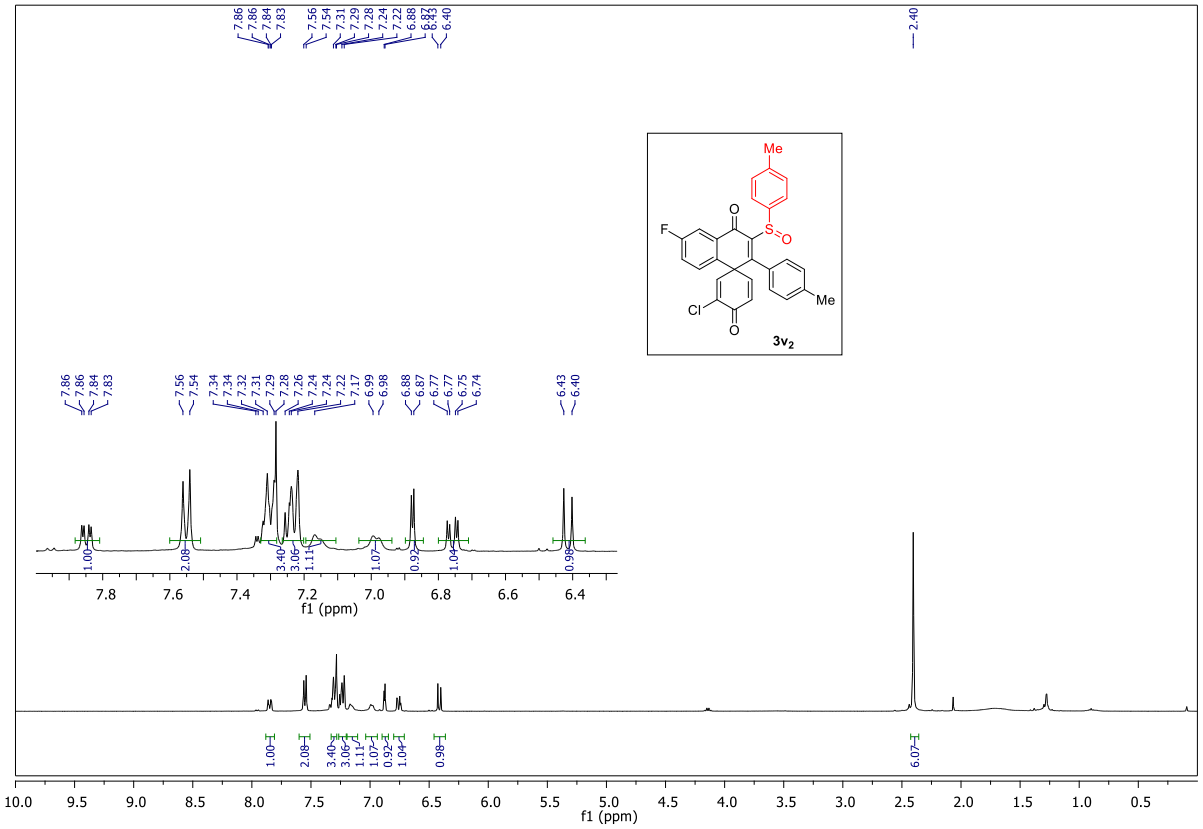
3v$_1$, ^{1}H NMR ($CDCl_3$, 400 MHz)



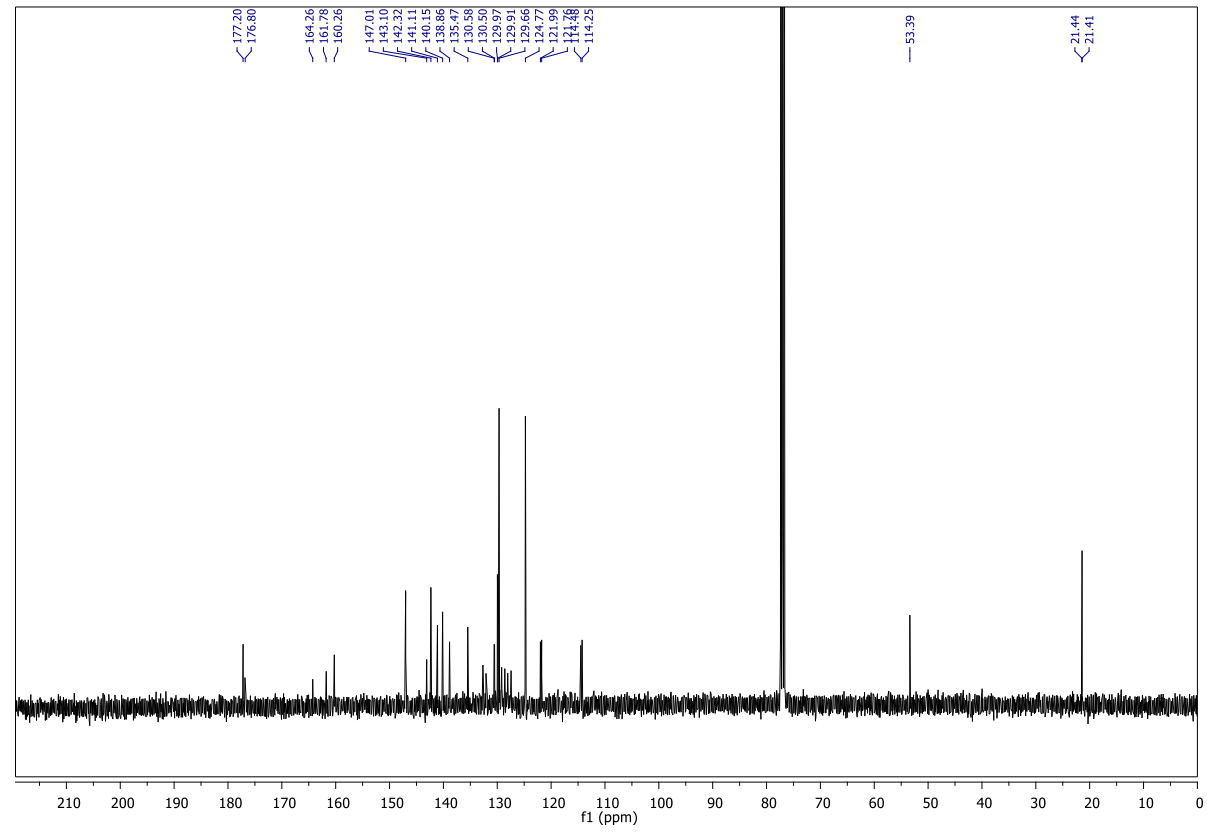
3v$_1$, $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz)



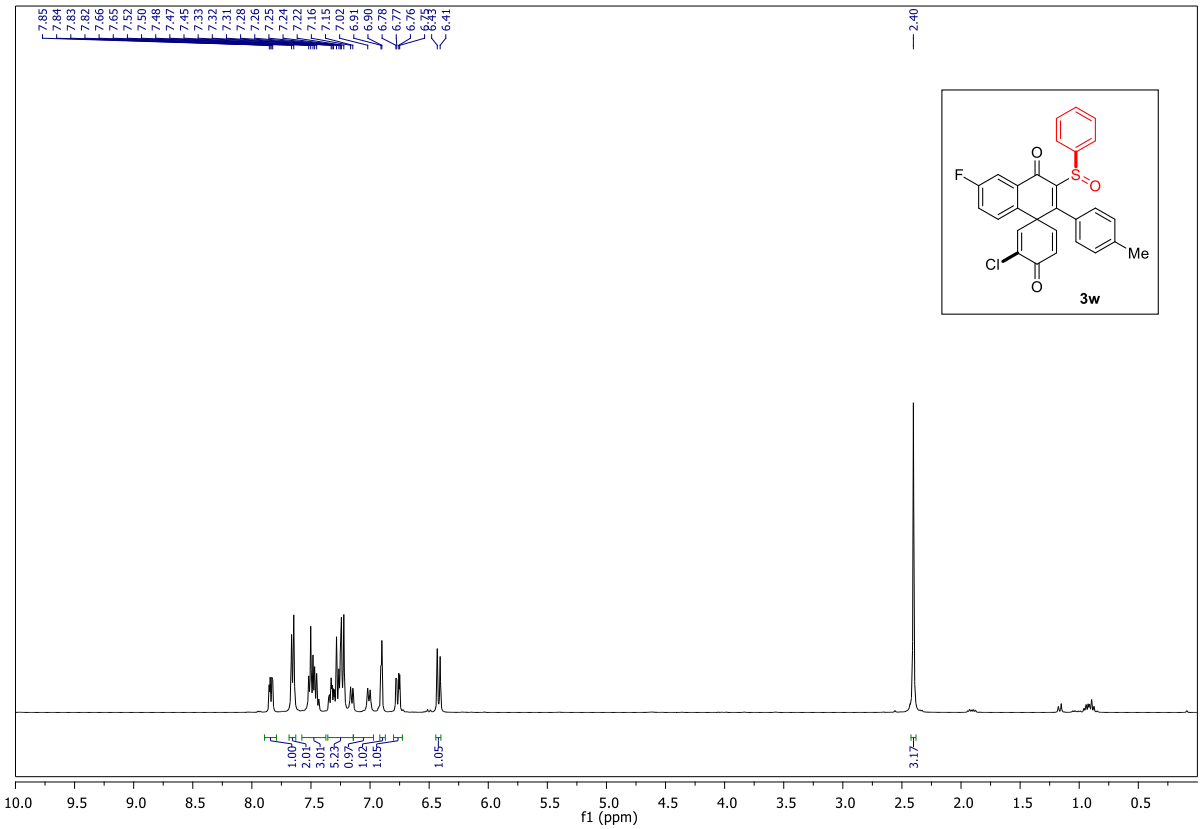
3v$_2$, ^{1}H NMR ($CDCl_3$, 400 MHz)



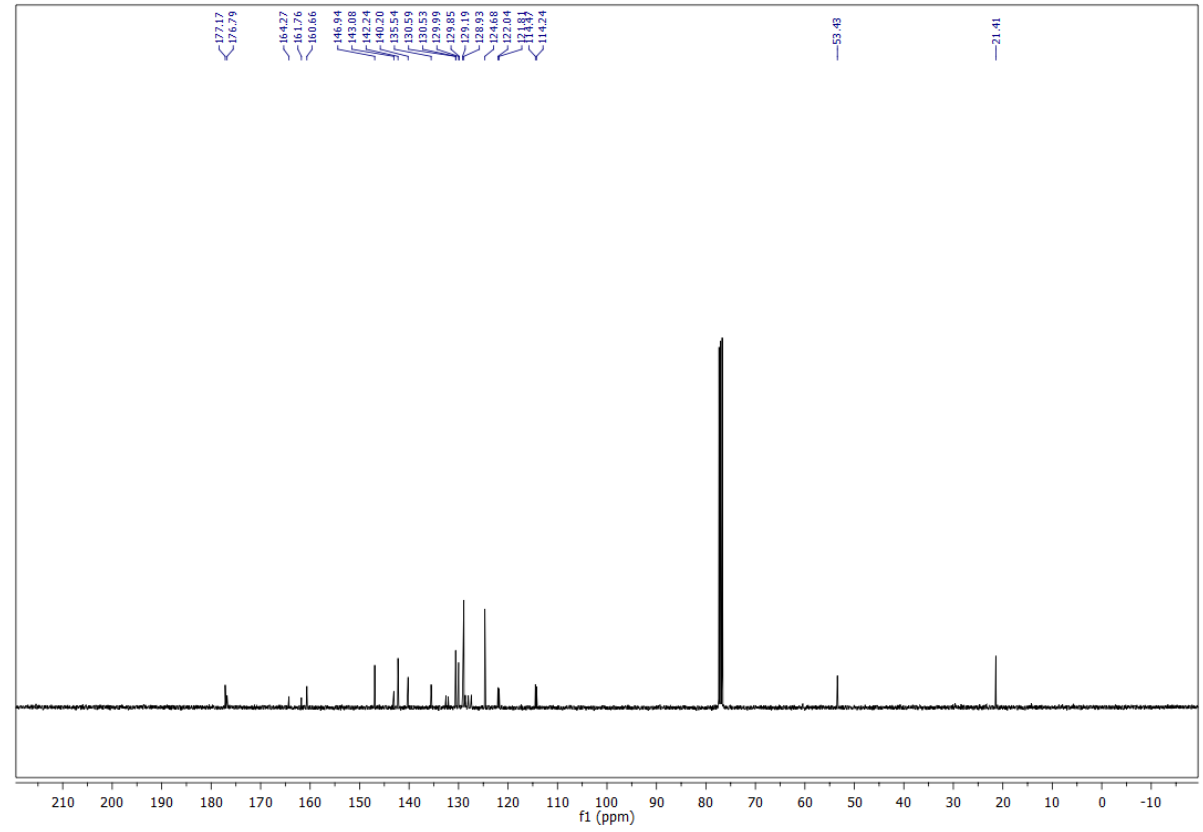
3v$_2$, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



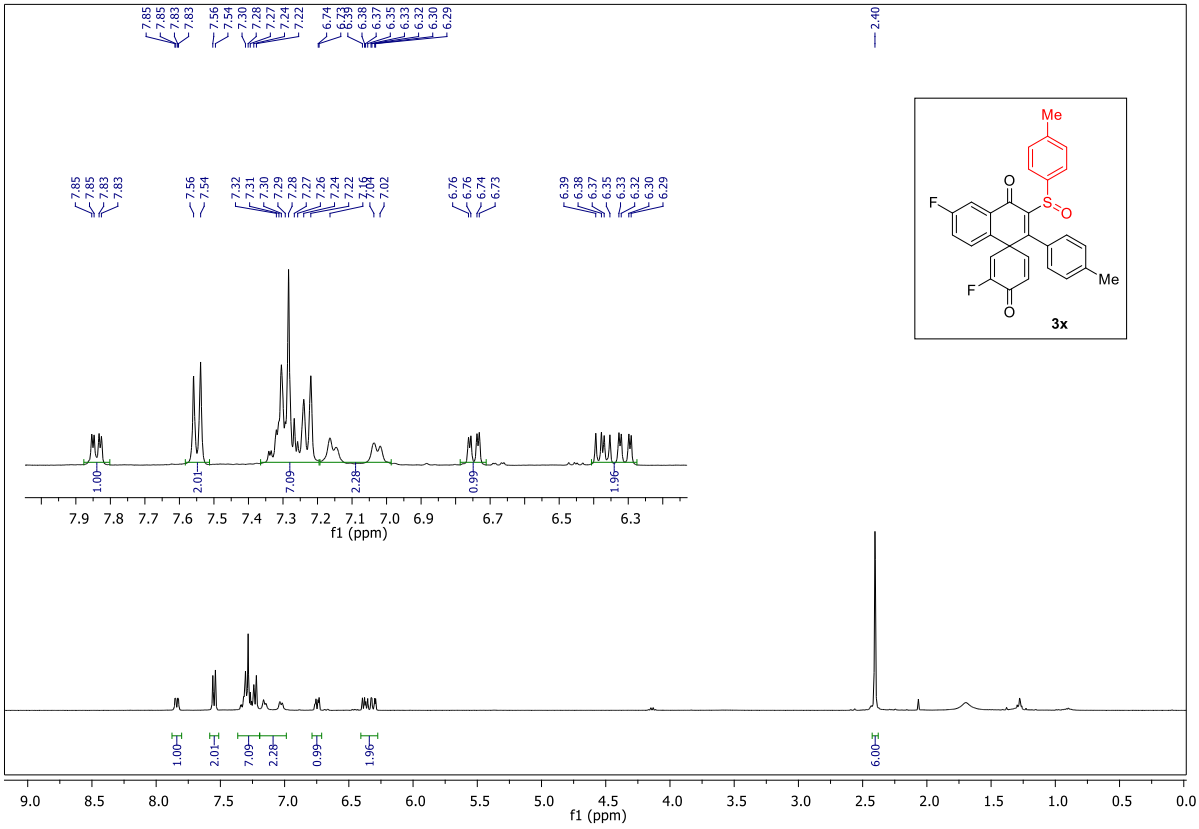
3w, ^{1}H NMR ($CDCl_3$, 400 MHz)



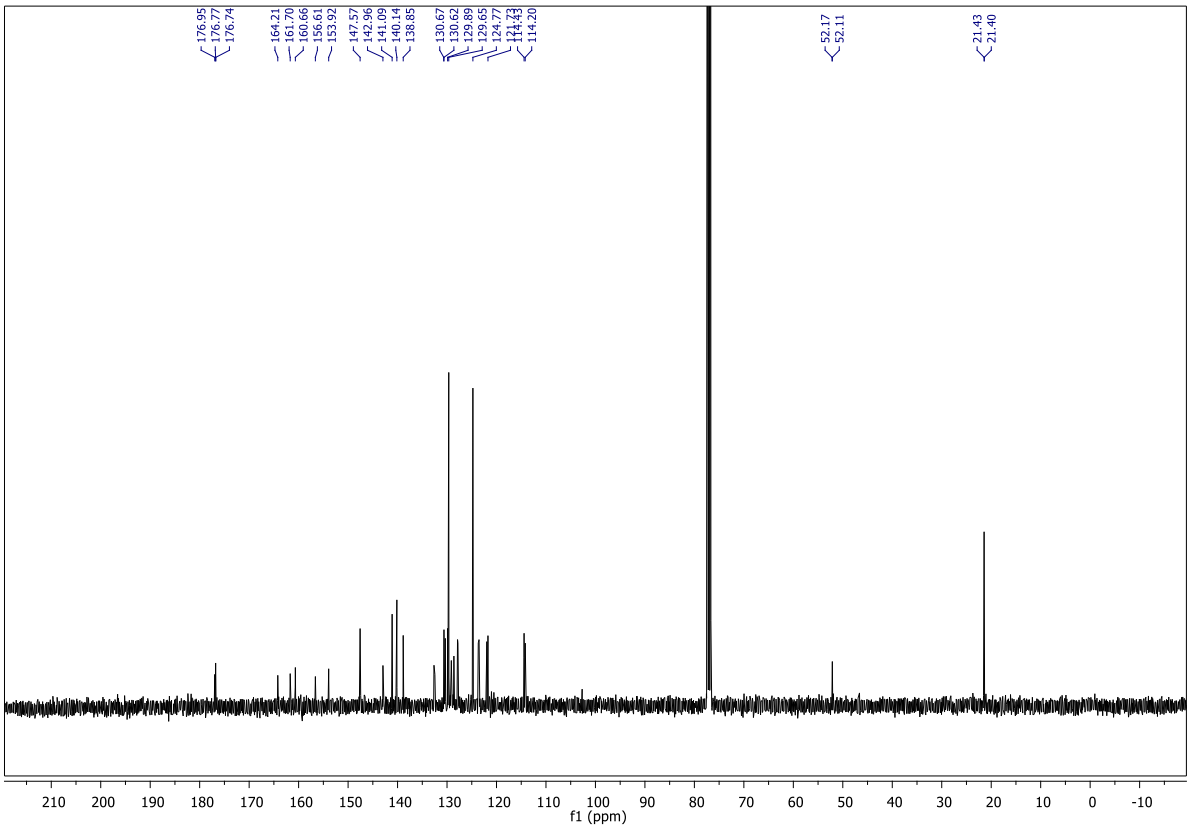
3w, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



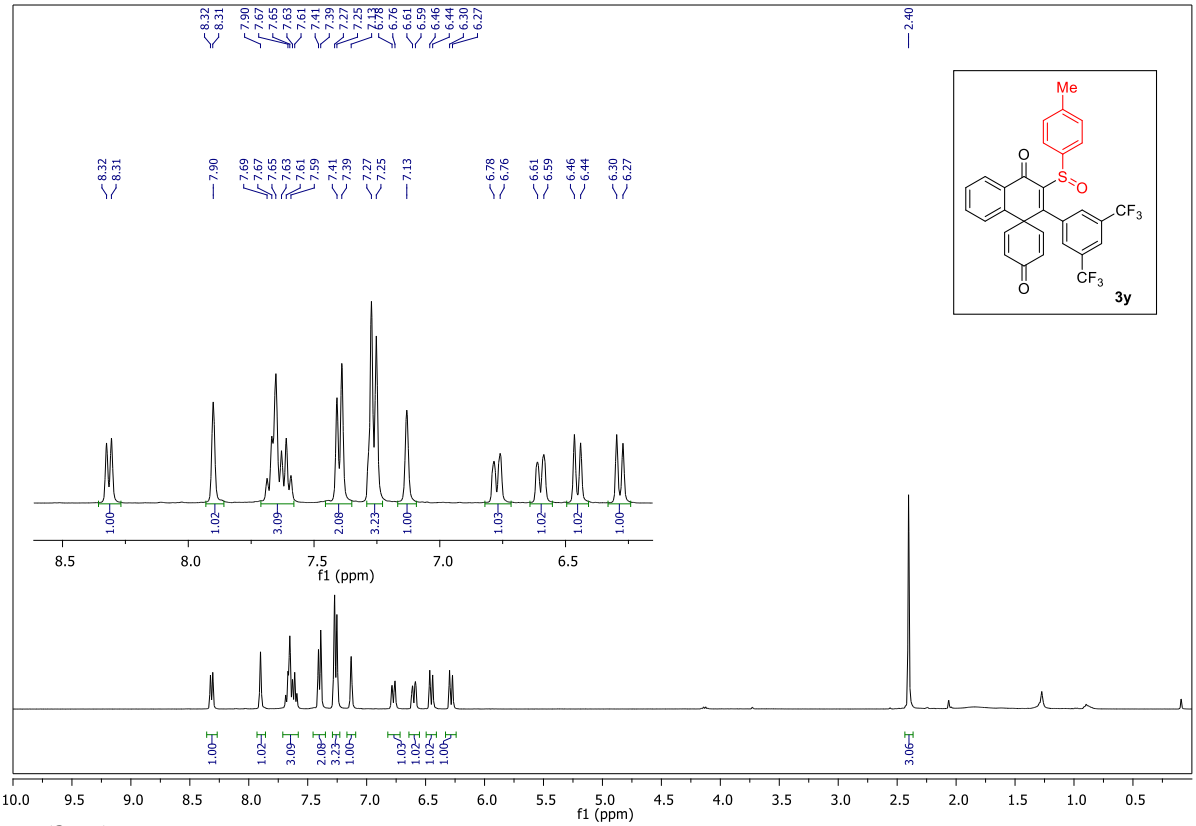
3x, ^{1}H NMR ($CDCl_3$, 400 MHz)



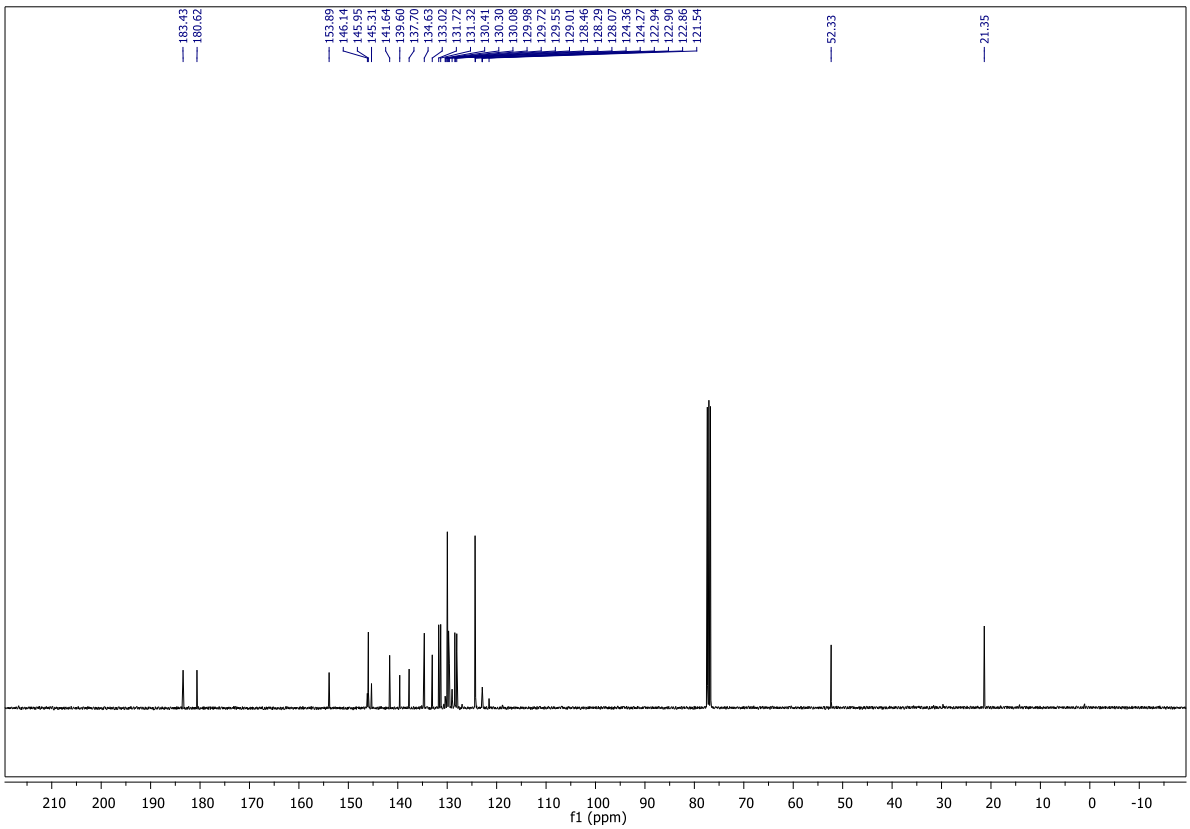
3x, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



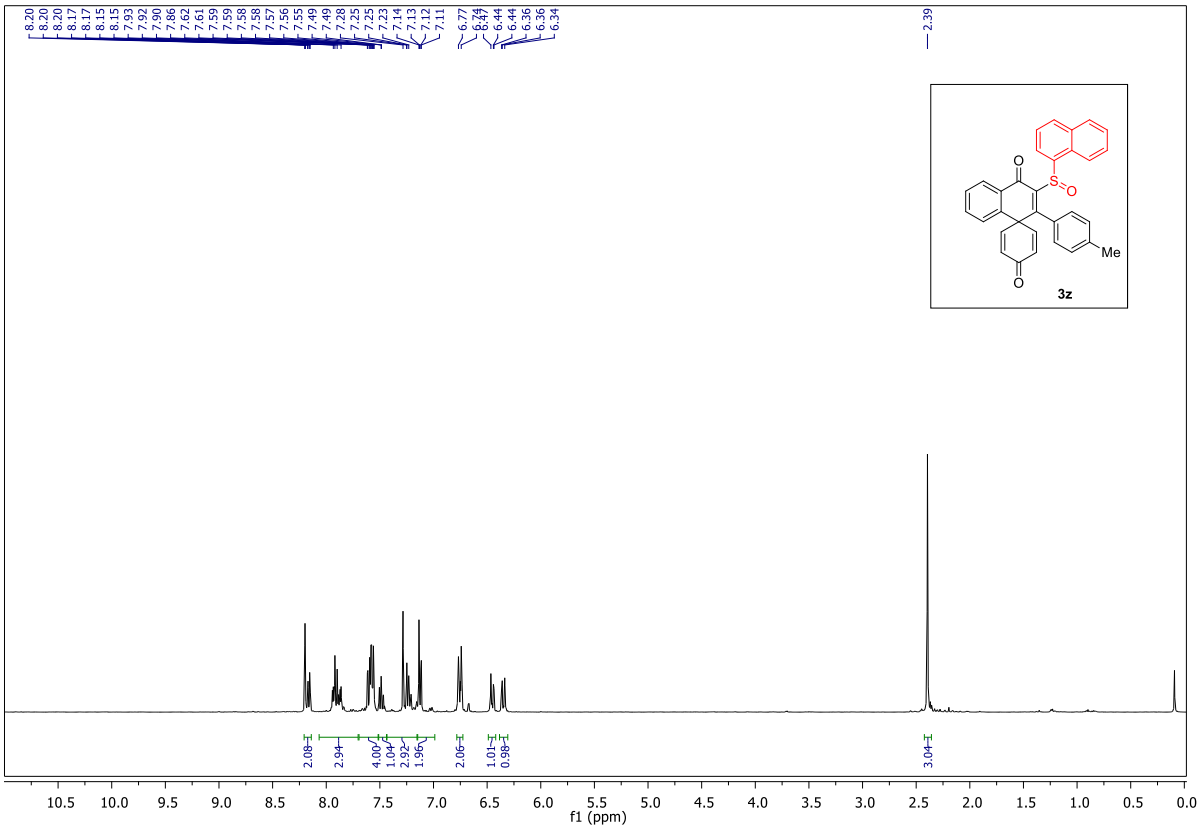
3y, ^{1}H NMR ($CDCl_3$, 400 MHz)



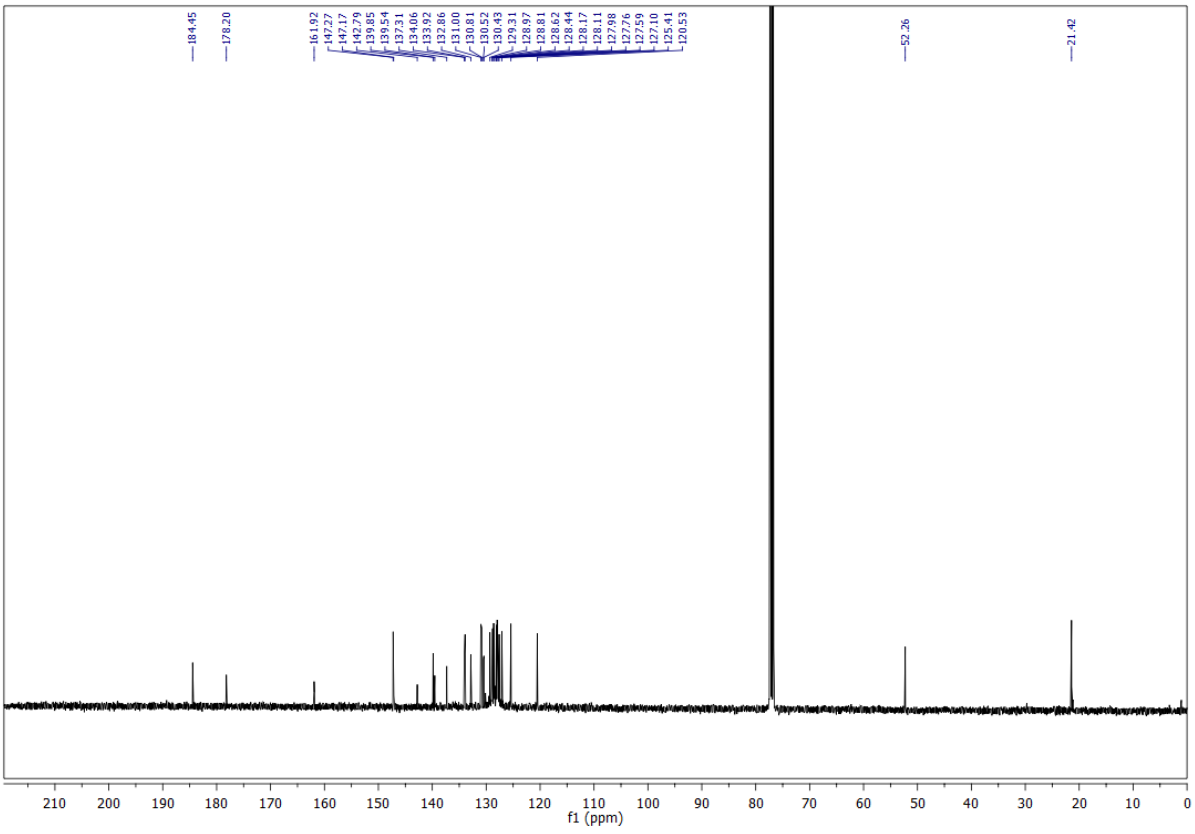
3y, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



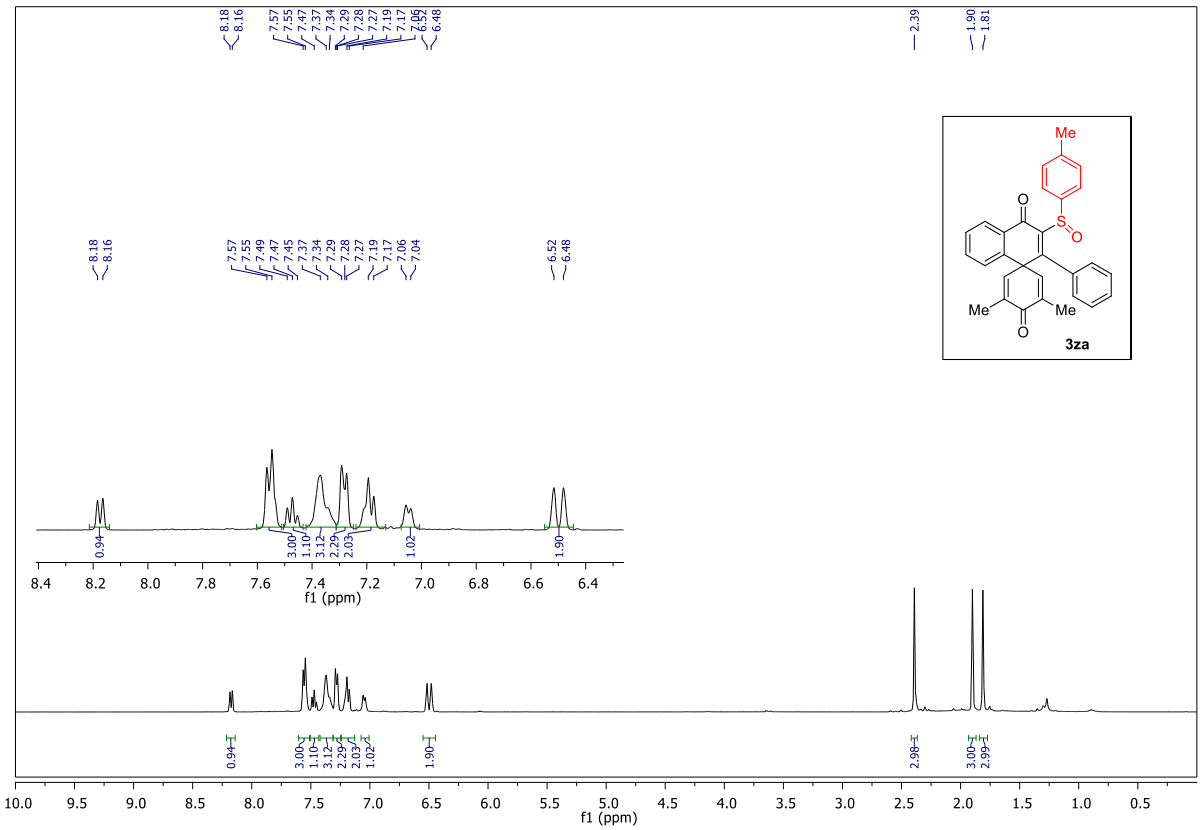
3z, ^{1}H NMR ($CDCl_3$, 400 MHz)



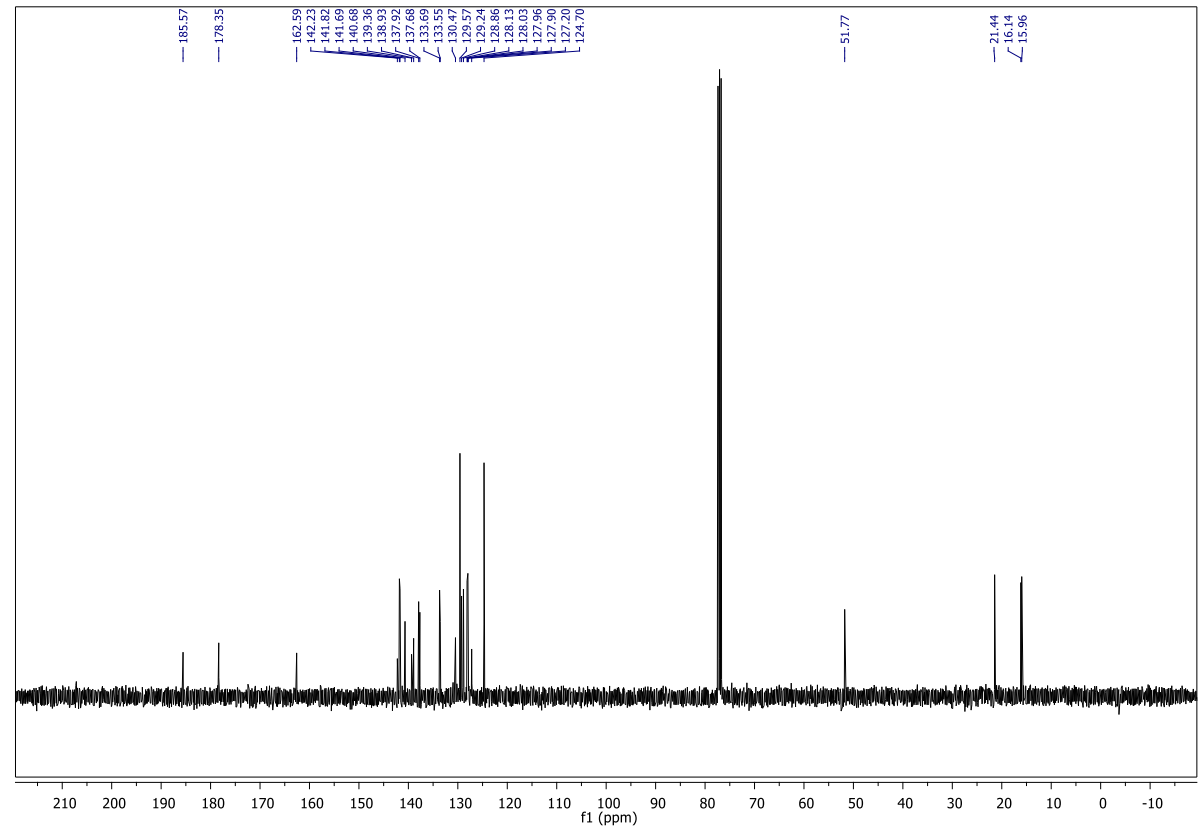
3z, ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz)



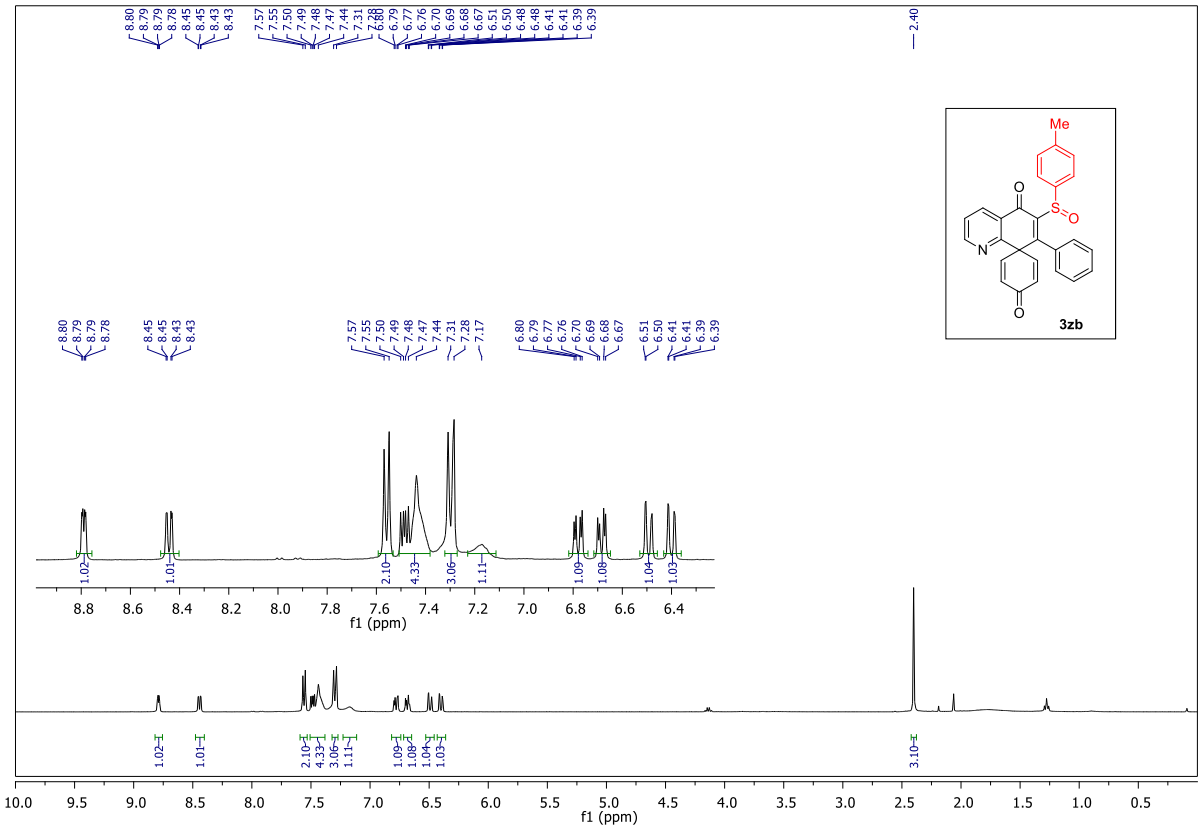
3za, ^{1}H NMR ($CDCl_3$, 400 MHz)



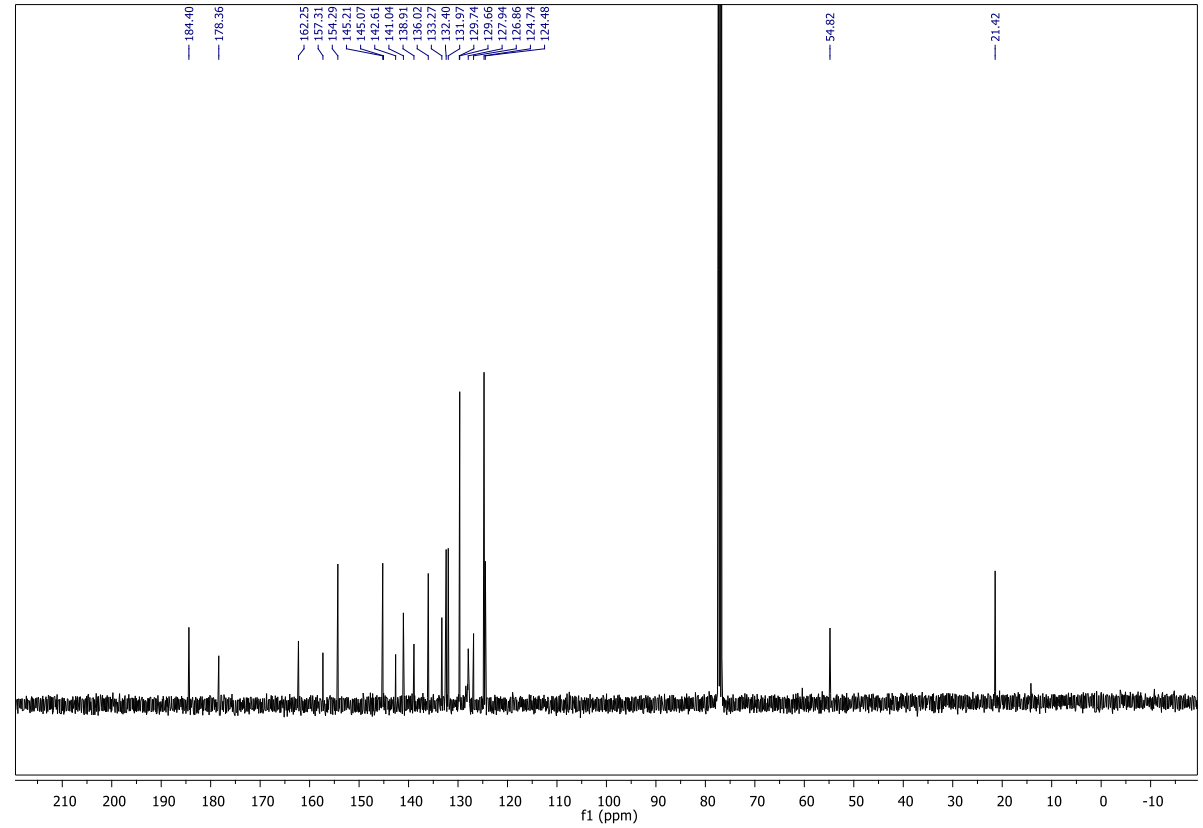
3za, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



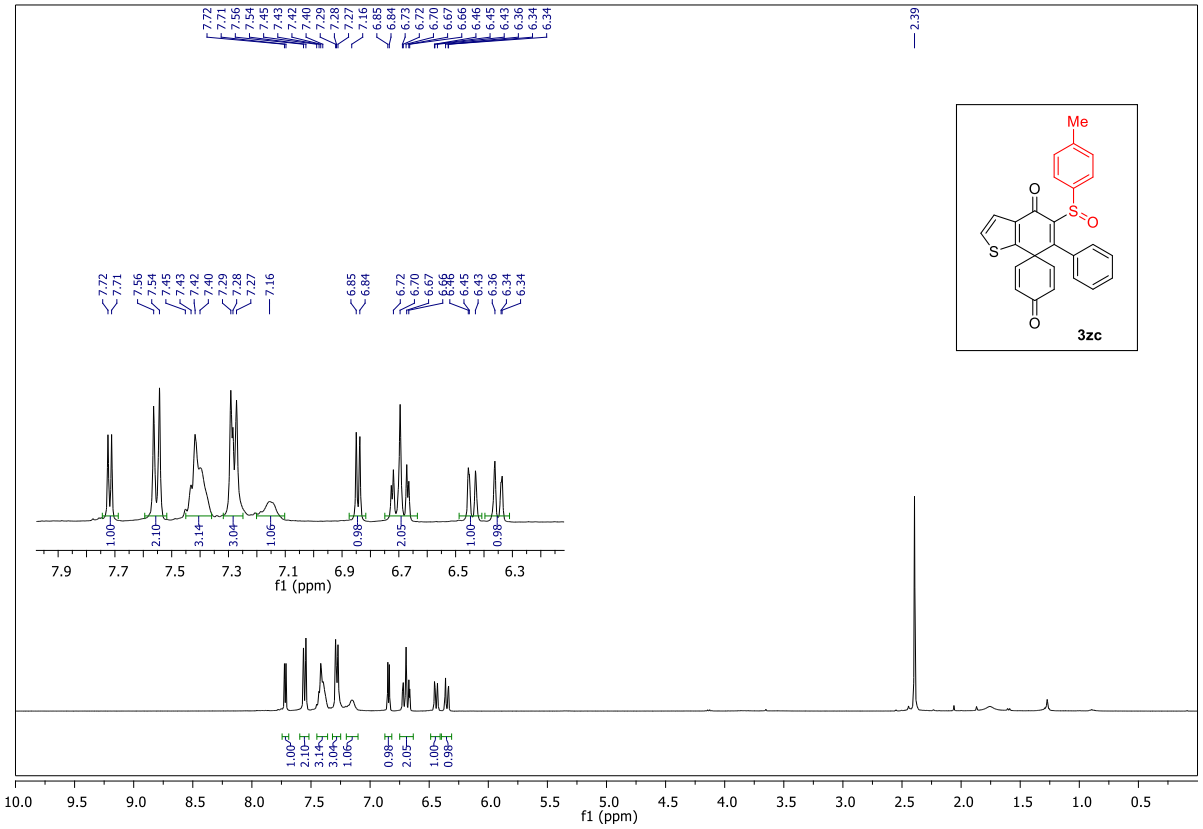
3zb, ^{1}H NMR ($CDCl_3$, 400 MHz)



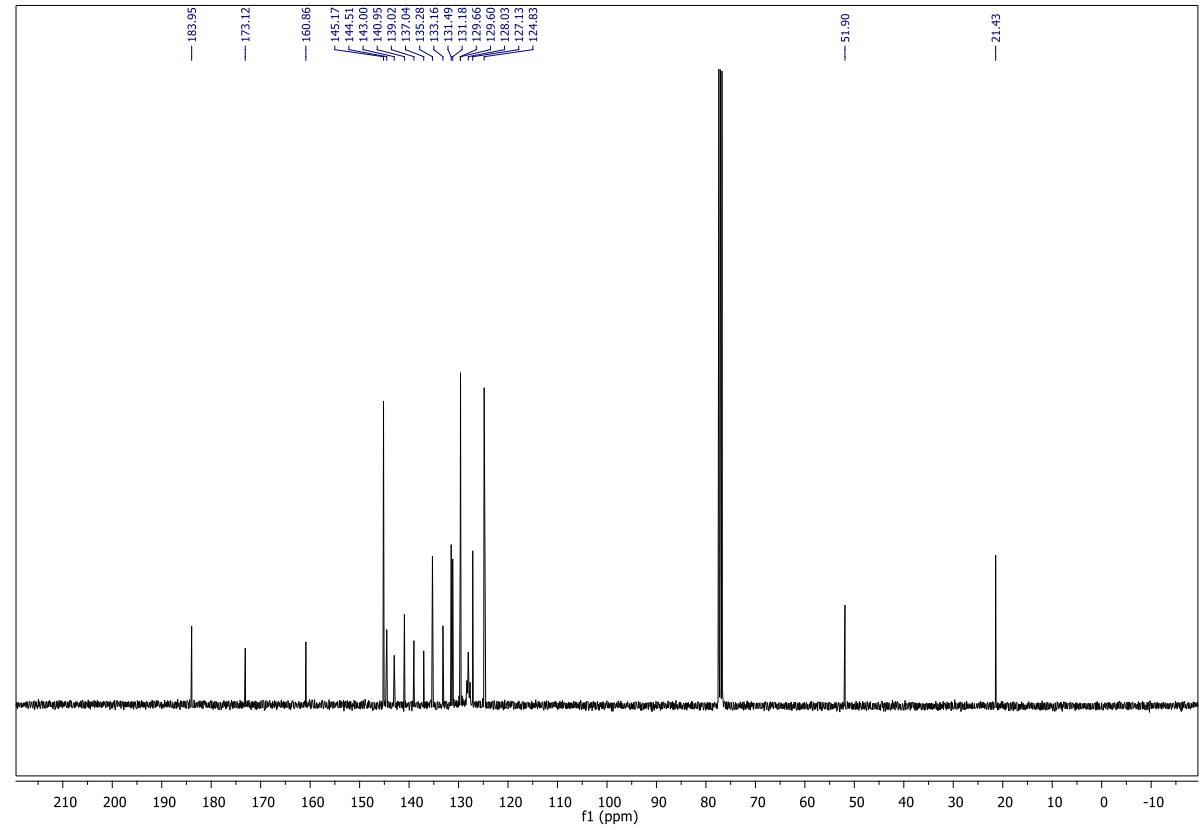
3zb, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



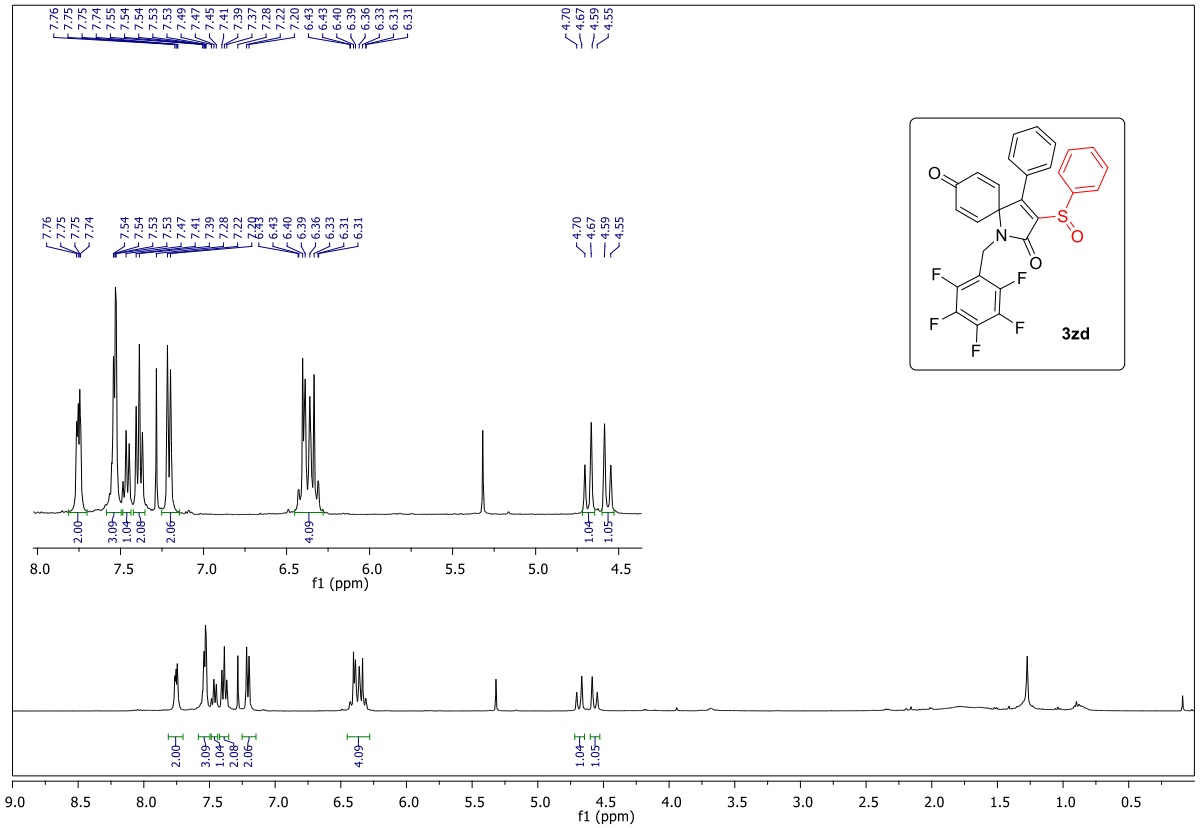
3zc, ^{1}H NMR ($CDCl_3$, 400 MHz)



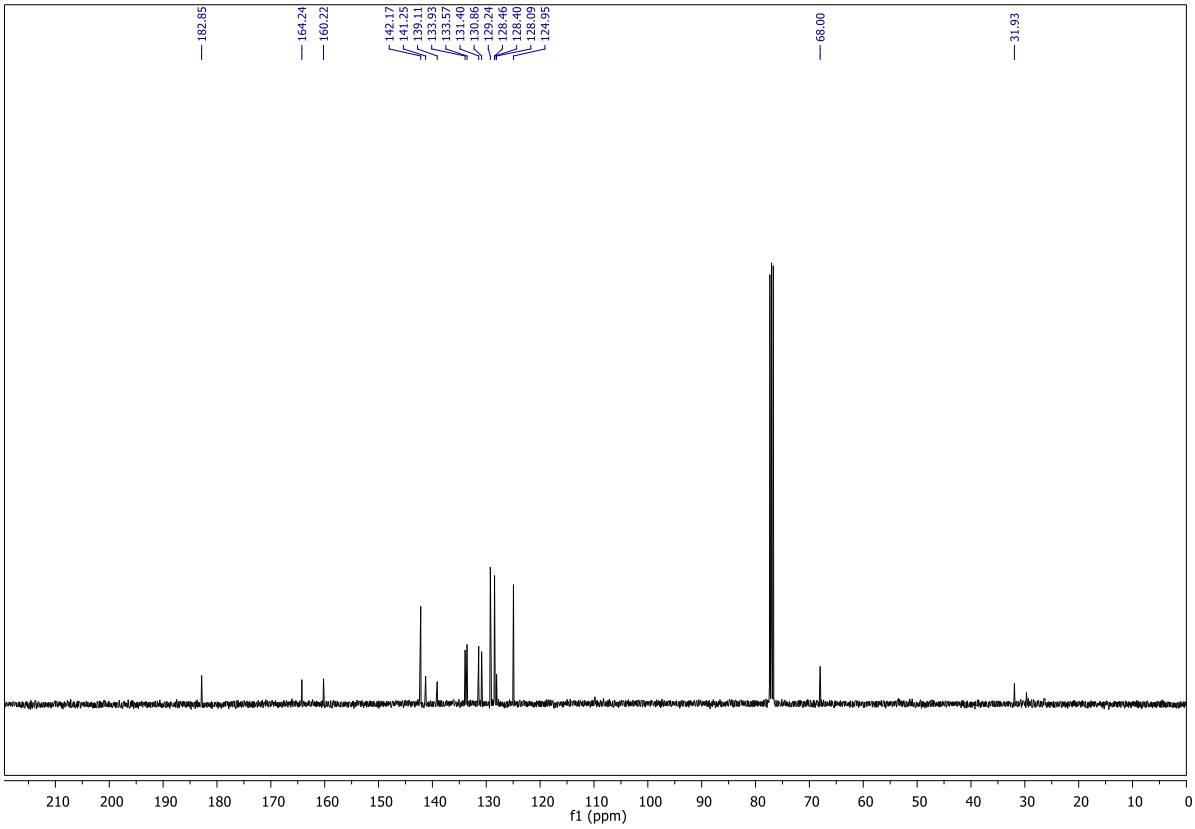
3zc, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



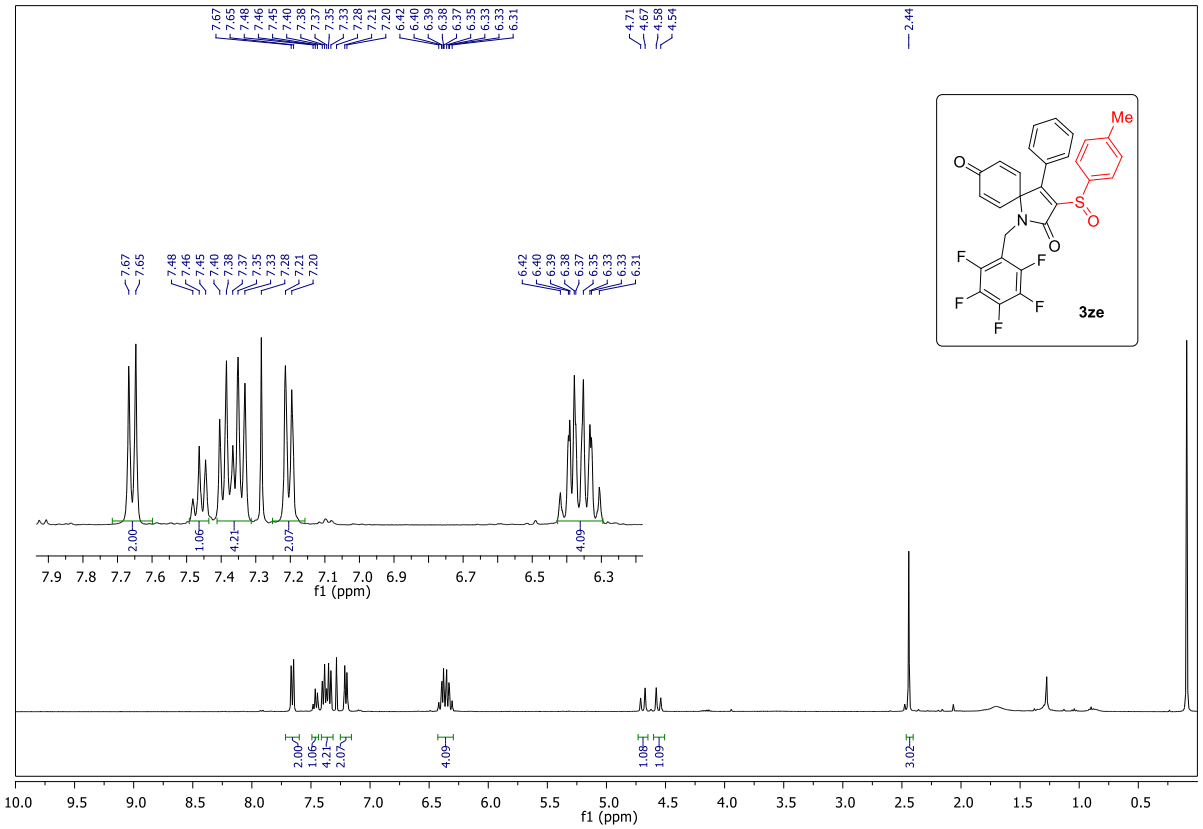
3zd, ^{1}H NMR ($CDCl_3$, 400 MHz)



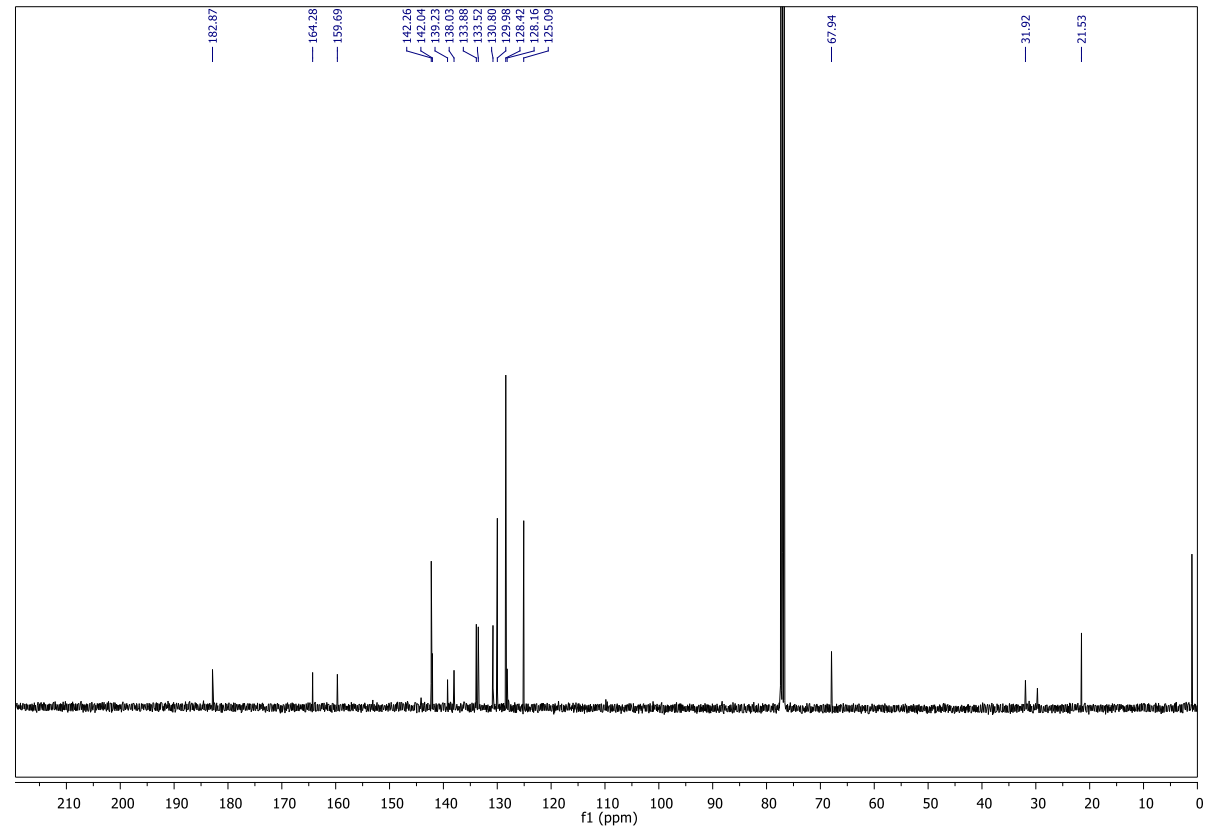
3zd, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



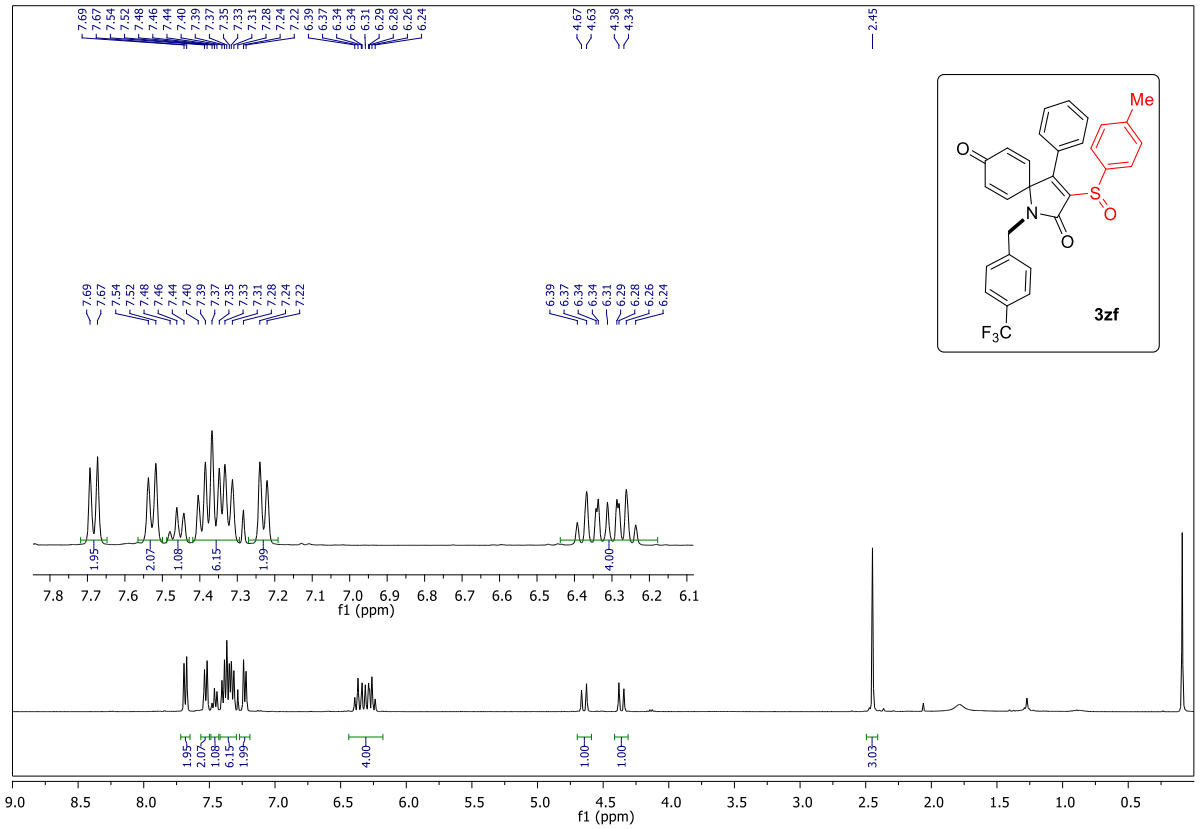
3ze, ^{1}H NMR ($CDCl_3$, 400 MHz)



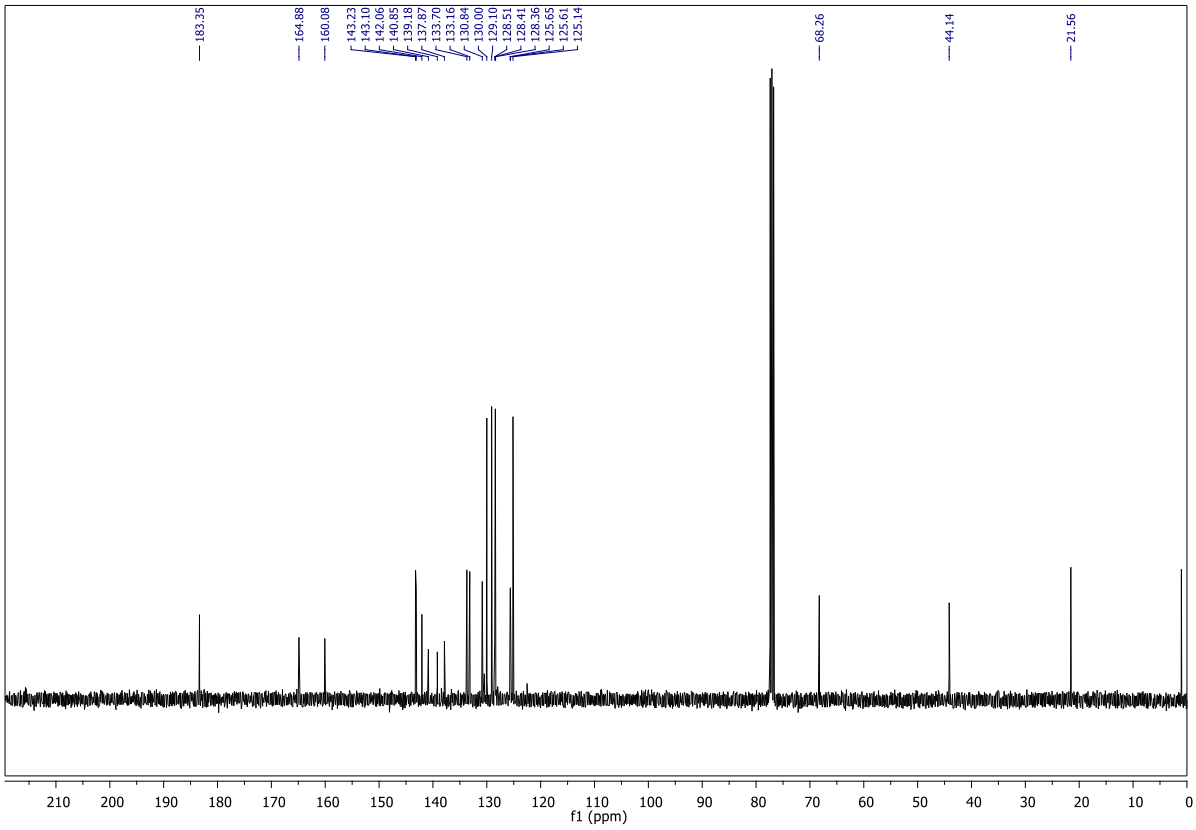
3ze, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



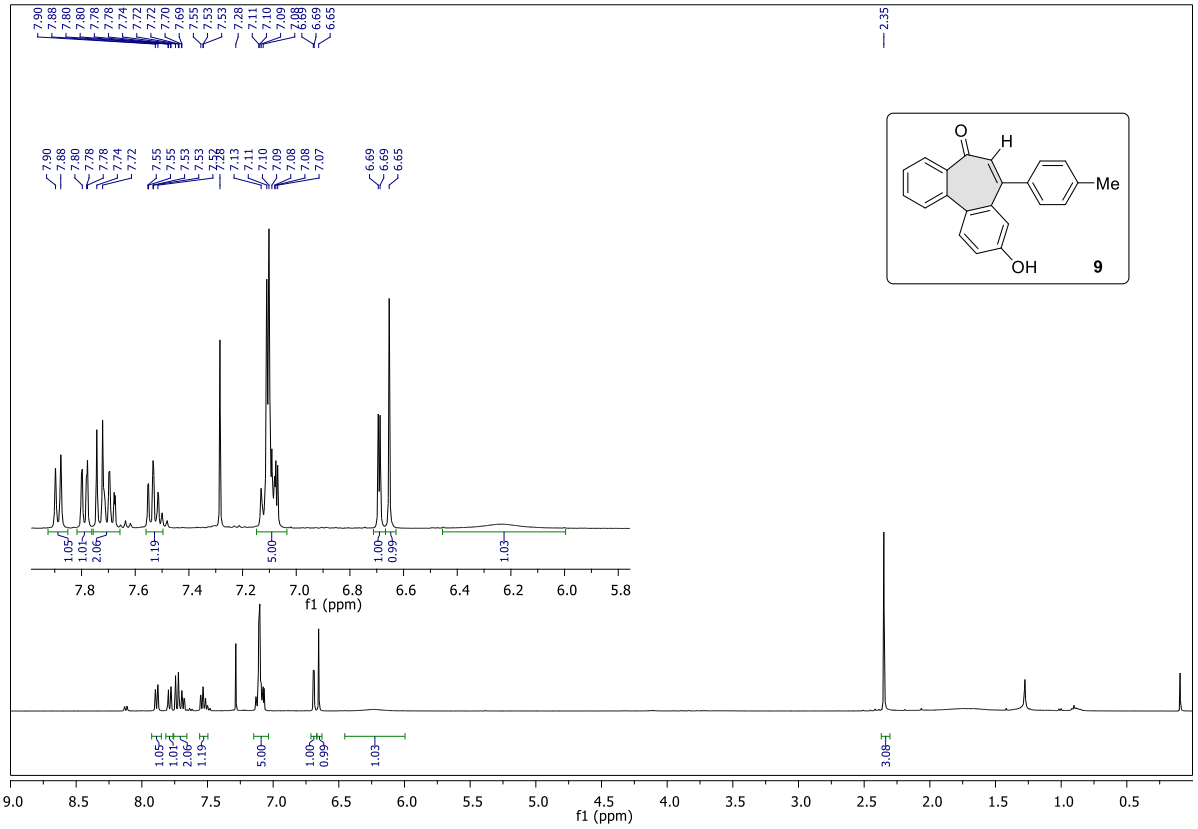
3zf, ^{1}H NMR ($CDCl_3$, 400 MHz)



3zf, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)



9, ^{1}H NMR ($CDCl_3$, 400 MHz)



9, $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz)