Supporting Information

Forging Spiro-Dibenzoxazepane Indano-Succinimides through Direct Diastereoselective [3+2] Annulation

Koushik Naskar, Dibas Dandapat, Imtiaj Mondal, Gracy Salam, Sudip Karmakar, Kushal Chowdhury and Indubhusan Deb*

Organic and Medicinal Chemistry Division, CSIR-Indian Institute of Chemical Biology, 4 Raja S. C. Mullick Road, Jadavpur, Kolkata 700032, India.

*Corresponding Author E-mail: indubhusandeb@iicb.res.in, indubhusandeb@gmail.com.

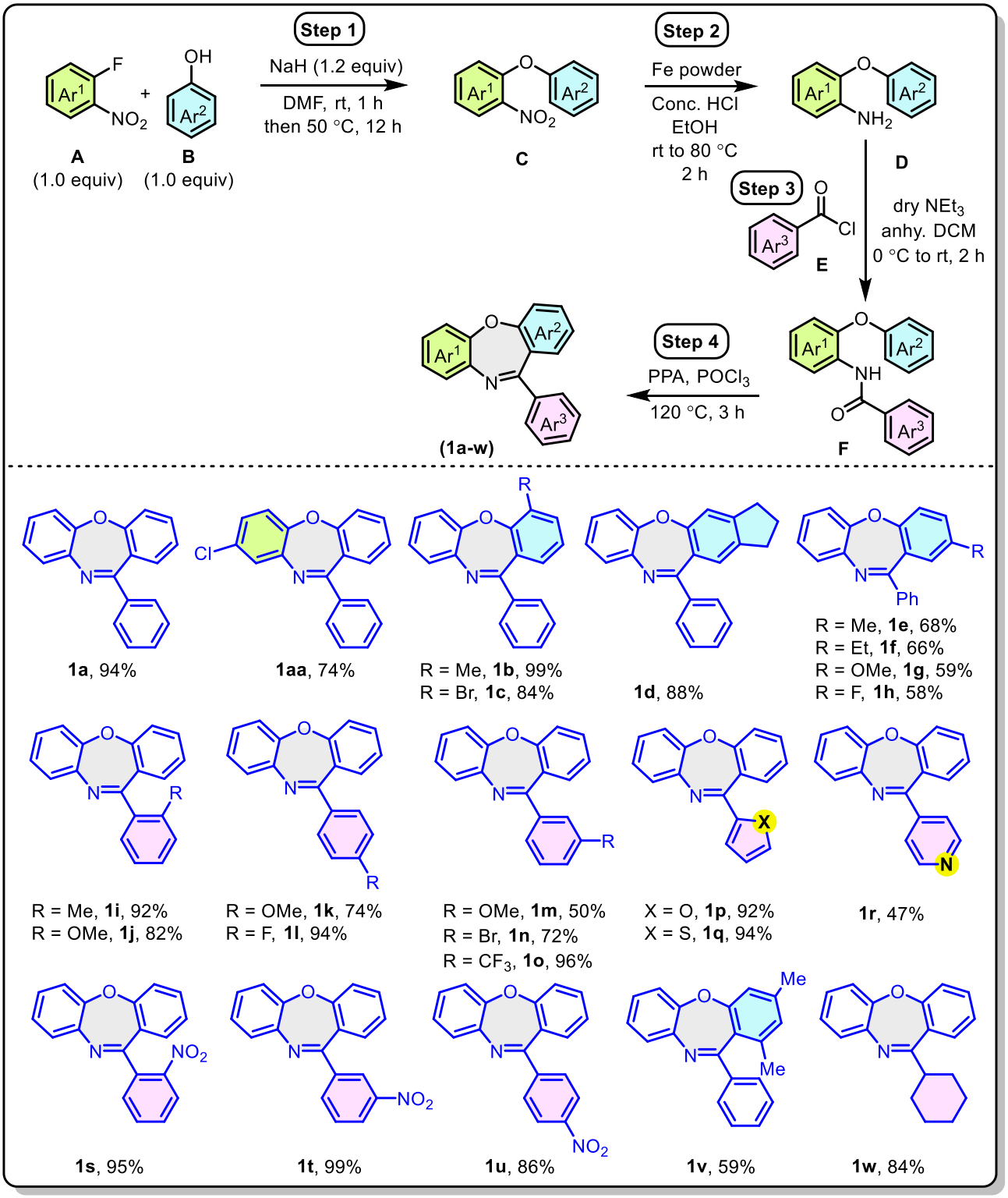
Table of contents

General information:

All reactions were carried out in oven-dried reaction vessels under air atmosphere unless otherwise mentioned. All reagents, including the transition metal catalyst, silver salt, other additives, and solvents used both in the preparation of starting materials and in the final reactions were purchased from commercial suppliers at the highest available grade and used as received, without further purification. The corresponding starting materials *e.g.*, dibenzo[*b,f*][1,4]oxazepines and *N*-substituted maleimides were prepared according to literature procedures. Thin-layer chromatography (TLC) was performed on Merck silica gel 60 F_{254} plates with visualization via ultraviolet light. The synthesized compounds were purified by column chromatography on silica gel (230-400 mesh), using an appropriate eluent mixture of distilled petroleum ether and ethyl acetate. Pressure was applied using an air pump to facilitate the process. NMR spectra were recorded on JEOL spectrometer (600 or 400 MHz for ^{1}H-NMR, 151 or 101 MHz for ^{13}C-NMR, and 376 MHz for ^{19}F-NMR). The chemical shifts (δ) are reported in parts per million (ppm), and multiplicities are abbreviated as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = complex. Internal standards or residual solvent signals were used as references. High resolution mass spectra (HRMS) were recorded on Waters (Xevo G2-XS Q-Tof) using ESI (Q-Tof, positive ion) mass spectrometry. Melting points were determined in a capillary melting point apparatus and are uncorrected. Single crystals of the spiro-dibenzoxazepane containing indano-succinimide product (**3a**, **4e**) was obtained by taking 5 mg of the sample in 5 mL vials using DCM/hexane bi-solvent system or EtOH, applying the solvent diffusion technique. Single-crystal X-ray diffraction (SCXRD) data were collected on Bruker D8 Venture with microfocus optics using Cu K_{α} radiation. The CIF files were submitted to CCDC 2538523, 2554145 and can be obtained at https://summary.ccdc.cam.ac.uk/structure-summary-form.

General procedure for the preparation of staring materials:

(a) Preparation of dibenzo[*b,f*][1,4]oxazepines as directing group:



Step 1: A dropwise addition of phenol (**B**, 1.0 equiv) in *N,N*-Dimethylformamide (DMF) was made to a reaction mixture of sodium hydride (NaH) (1.2 equiv) and DMF (10 mL), which was then stirred for 1 hour at room temperature. The mixture above was then gradually added into *o*-fluoro nitrobenzene (**A**, 1.0 equiv) in DMF (2.0 mL) and stirred for an additional hour at room temperature before being stirred for 12 hours at 50 ºC. Following normal workup procedure using ethyl acetate (EtOAc), water and brine, the crude product was refined using EtOAc/petroleum ether in column chromatography on silica gel to yield the corresponding derivatives of 2-nitrodiaryl ether (**C**).

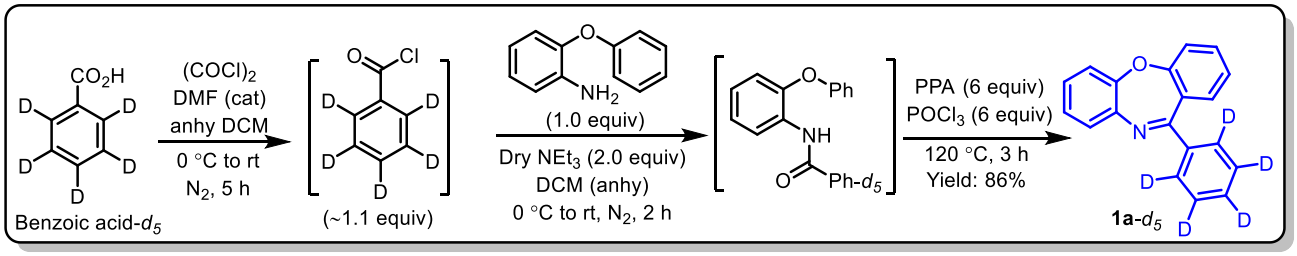
Step 2: At room temperature, 10 equivalents of iron power were added to a solution of 2-nitrodiaryl ether (**C**) in absolute ethanol (0.6 M). The reaction mixture was then heated up to 80 °C, and 1.0 mL of concentrated hydrochloric acid (HCl) was added dropwise over the course of 10 minutes. The reaction mixture was brought to room temperature after 2 hours and then made alkaline by adding an aqueous sodium hydroxide (NaOH) solution. The amine was then extracted from the filtrate of the solid mass using EtOAc. Under reduced pressure, the solvent was withdrawn, and the produced 2-aminodiaryl ether (**D**) was then put through the next process after purification in column chromatography on silica gel using EtOAc/petroleum ether as eluent.

Step 3: Prepared or commercially available 2-aminodiaryl ether derivative (**D**, 1.0 equiv, 10.8 mmol) was dissolved in 30 mL of anhydrous dichloromethane (DCM) and cooled to 0 ºC. The corresponding acid chloride (**E**, 1.05 equiv) was added slowly to the solution followed by the addition of dry triethylamine (Et_3N) (2.0 equiv). Then the temperature of the reaction mixture was allowed to reach room temperature and further stirred. After the reaction was completed, water (40 mL) was added to the reaction mixture. The organic layer was washed with brine (2 × 20 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography over SiO_2 using mixtures of EtOAc and petroleum ether (2% to 5% EtOAc/petroleum ether) to obtain the product **F**. In many cases, these derivatives were used in the synthetic protocol without any further purification.

Step 4: The corresponding dibenzoxazepine (**1a-z**) derivatives were synthesized by continuing the literature procedure.[1] Compound **F** (1.0 equiv, 11.4 mmol) was added to a mixture of polyphosphoric acid (PPA) (6.0 equiv) and phosphorus oxychloride ($POCl_3$) (6.0 equiv). The reaction mixture was heated at 120 ºC and the dense solution was stirred for 3 h. The reaction mixture was allowed to cool down to room temperature. The original dense reaction mixture was diluted by DCM and slowly poured into ice water. The aqueous solution was neutralized with an ammonia solution (30%) and extracted with CH_2Cl_2 (30 mL). The organic solution was washed with brine (2 x 30 mL) and dried over anhydrous Na_2SO_4, concentrated under vacuum. The crude mixture was purified by column chromatography over SiO_2 eluting with 5-30% EtOAc/petroleum ether to give the desired derivative of 11-phenyldibenzo[*b,f*][1,4]oxazepine up to 47-99% yield in final step (**1a-w**).

(b) Preparation of deuterated dibenzo[*b,f*][1,4]oxazepine:

Following a literature procedure the corresponding 11-(phenyl-d_5)dibenzo[*b,f*][1,4]oxazepine (**1a-*d*$_5$**) was synthesized.[1]

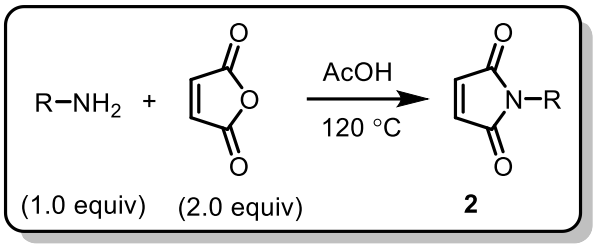


Benzoic acid-d_5 (1.0 equiv) was dissolved in dry DCM (0.5 M) with a catalytic amount of DMF under N_2 and cooled to 0 °C. Oxalyl chloride (1.2 equiv) was added dropwise, and the mixture was stirred at room temperature for 5 h. After removal of solvent under reduced pressure, the resulting deuterated acid chloride was obtained quantitatively and used directly in the next step.

The acid chloride was dissolved in dry DCM (10 mL) at 0 °C under N_2, followed by the addition of 2-phenoxyaniline (1.0 equiv) and dry Et_3N (2.0 equiv). The mixture was stirred at room temperature for 2 h. After TLC confirmation, the crude product was directly subjected to cyclization using PPA (6.0 equiv) and $POCl_3$ (6.0 equiv) at 120 °C for 3 h. The spectral data of **1a**-d_5 was matched the reported values.

(c) Preparation of *N*-substituted maleimides:

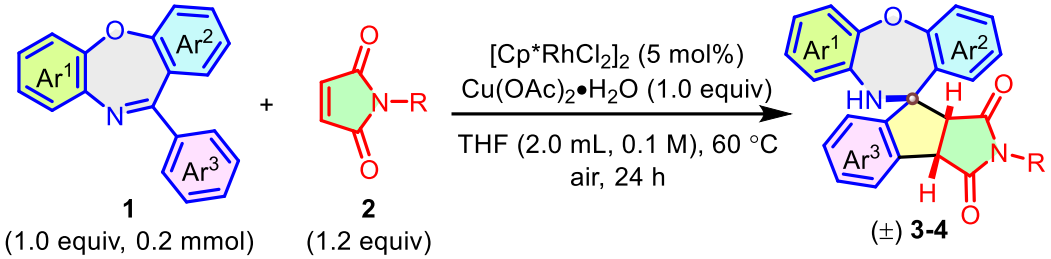
The commercially available *N*-substituted maleimides were used as received without further purification, while the remaining *N*-substituted maleimides were synthesized following the reported literature procedure. [2]



To a solution of maleic anhydride (2.0 equiv) in acetic acid (1.0 M), the corresponding amine or aniline (1.0 equiv) was added. The reaction mixture was refluxed at 120 °C for 5-18 hours. Upon completion of the reaction (as determined by TLC), the acetic acid was removed under reduced pressure. The resulting mixture was then neutralized to pH 6-7 by the dropwise addition of aqueous $NaHCO_3$. The reaction mixture was extracted with ethyl acetate, and the combined organic layers were dried over Na_2SO_4 and concentrated under vacuum. The crude residue was purified by column chromatography on silica gel using 30-50% ethyl acetate/petroleum ether as the eluent to afford the corresponding *N*-substituted maleimides (**2**).

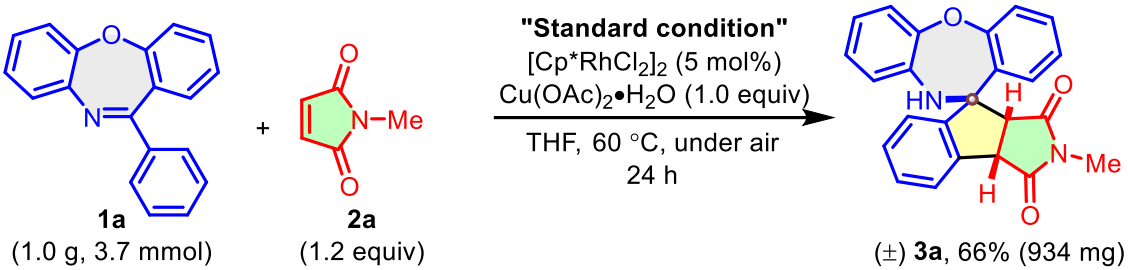
General procedure for [3+2]-spiroannulation between dibenzoxazepines and *N*-substituted maleimides:

(a) 0.2 mmol Scale:



In an oven dried screw cap reaction vial, Dibenzoxazepine (**1**) (0.2 mmol, 1.0 equiv), *N*-substituted Maleimide (**2**) (0.22 mmol, 1.2 equiv), Copper(II) acetate monohydrate [$Cu(OAc)_2•H_2O$] (0.2 mmol, 1.0 equiv) and Pentamethylcyclopentadienyl rhodium dichloride dimer [$Cp^*RhCl_2]_2$ (0.01 mmol, 0.05 equiv) were taken and 2.0 mL of Tetrahydrofuran (THF) solvent (0.1 M) was added. The screw cap reaction vial was capped under air and kept on stirring in a heating block at 60 ºC. After 24 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite using EtOAc and concentrated under reduced pressure. The crude reaction mixture was directly purified by column chromatography over silica gel using 20-50% EtOAc/petroleum ether as eluent to obtain the corresponding spiro-dibenzoxazepane indano-succinimide (**3-4**).

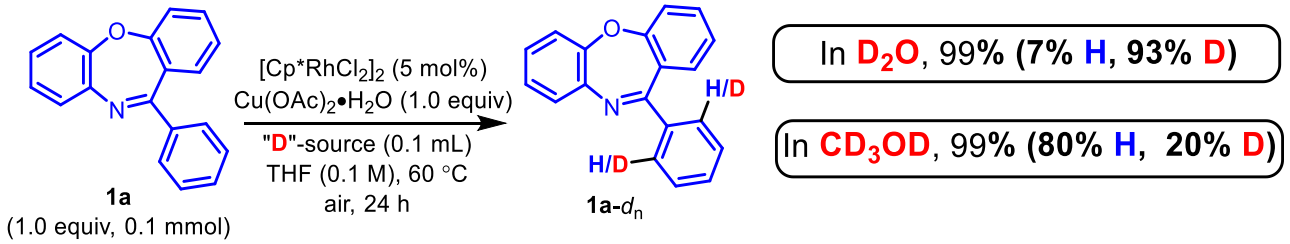
(b) Gram scale:



The scale-up procedure was conducted in accordance with the general protocol for 0.2 mmol reactions. An oven-dried 50 mL round-bottom flask was used in place of a screw-cap reaction vial. The flask was charged with **1a** (1.0 g, 3.7 mmol, 1.0 equiv), **2a** (1.2 equiv), [$Cp^*RhCl_2]_2$ (5 mol%), and $Cu(OAc)_2•H_2O$ (1.0 equiv), followed by the addition of dry THF (0.1 M). The reaction vessel was sealed with a glass stopper and stirred in a preheated oil bath at 60 °C for 24 h. After filtration through Celite and purification by column chromatography following the standard protocol, product **3a** was obtained as an off-white solid in 66% yield (934 mg).

Mechanistic experiments:

(a) Procedure for H/D exchange experiment:



In an oven dried screw cap reaction vial charged with 11-phenyldibenzo[*b*,*f*][1,4]oxazepine (**1a**) (27.1 mg, 0.1 mmol, 1.0 equiv), $Cu(OAc)_2.H_2O$ (20.0 mg, 0.1 mmol, 1.0 equiv) and [$Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 0.05 equiv) were taken and 1.0 mL (0.1 M) of THF was added. To it, 0.1 mL of D_2O or CD_3OD was added as D-source (excess). The screw cap reaction vials were closed under air and stirred in a heating block for 24 h. After 24 h, the reactions were stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite using EtOAc and concentrated under reduced pressure. The deuterated product (**1a**-d_n) was isolated by purifying through column

chromatography over silica gel using 10% EtOAc/petroleum ether as eluent. Compound **1a**-d_n was isolated 99% (93% "D" incorporation) for D_2O and 99% (20% "D" incorporation) for CD_3OD, respectively. The percentage of deuterium incorporation was determined by using ^1H NMR spectroscopy ($CDCl_3$, 400 MHz) (ESI, figure 1).

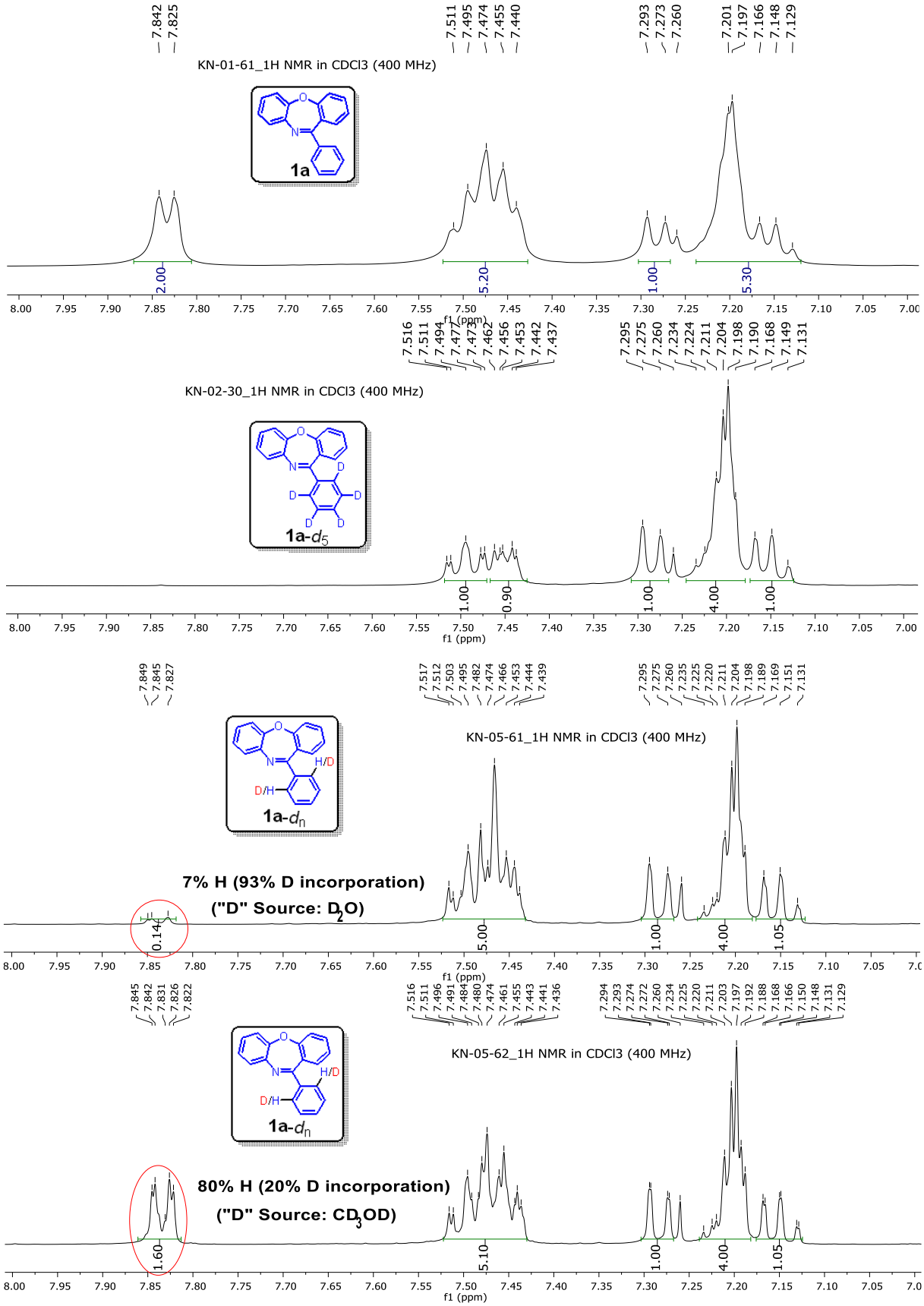
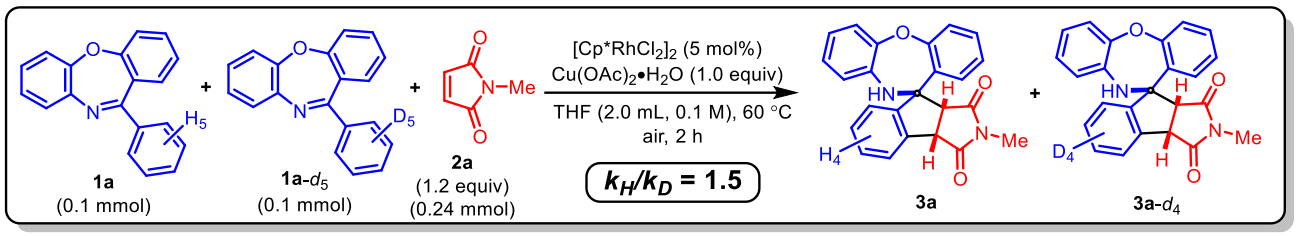


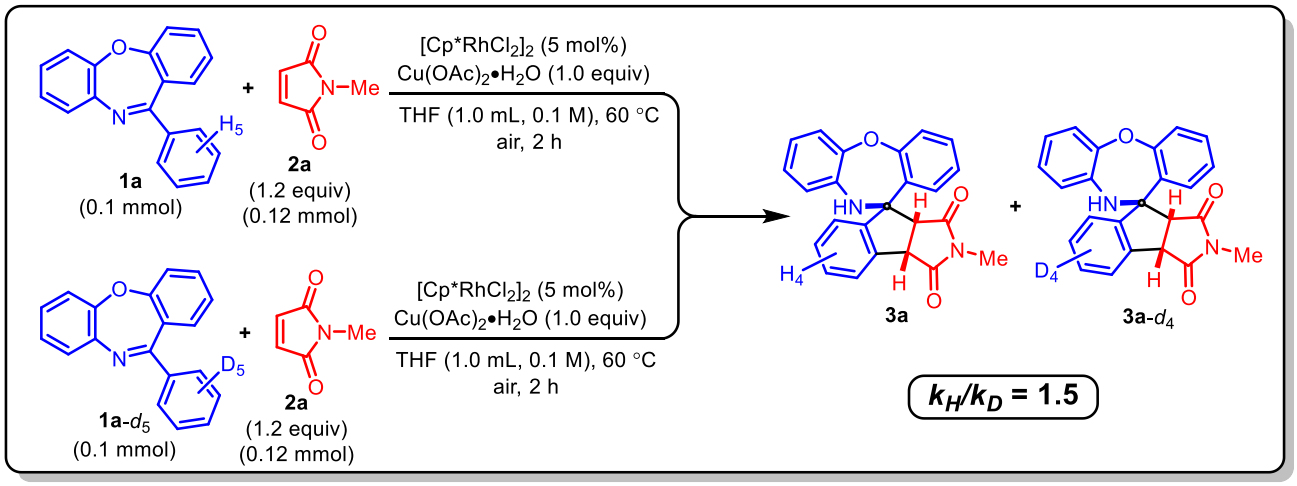
Figure 1. ^1H NMR of **1a**, **1a**-d_5 and **1a**-d_n in $CDCl_3$ (400 MHz) for H/D exchange experiment experiments.

(b) Procedure for competitive kinetic isotopic experiment:



In an oven dried screw cap reaction vial, 11-phenyldibenzo[*b*,*f*][1,4]oxazepine (**1a**) (27.1 mg, 0.1 mmol, 1.0 equiv), 11-(phenyl-d_5)dibenzo[*b*,*f*][1,4]oxazepine (**1a-*d*$_5$**) (27.6 mg, 0.1 mmol, 1.0 equiv), *N*-methyl maleimide (**2a**) (26.7 mg, 0.24 mmol, 1.2 equiv), $Cu(OAc)_2.H_2O$ (40.0 mg, 0.2 mmol, 1.0 equiv) and $[Cp^*RhCl_2]_2$ (6.2 mg, 0.01 mmol, 0.05 equiv) were taken and 2.0 mL of THF (0.1 M) solvent was added. The screw cap reaction vial was capped under air and kept on stirring in a preheated heating block at 60 °C. After 2 h, the reaction was quickly quenched by adding EtOAc keeping in an ice bath. The reaction mixture was filtered through a short pad of celite and concentrated under vacuum. The crude reaction mixture was directly subjected to column chromatography on silica gel for partial purification, using 10% EtOAc in petroleum ether as the eluent. The ratio of **3a** and **3a-*d*$_4$** was determined by ^{1}H NMR spectroscopy (ESI, figure 2). No primary kinetic isotopic effect was found as $k_H/k_D \approx 1.5$.

(c) Procedure for parallel kinetic isotopic experiment:



In two separate oven dried screw cap reaction vial, 11-phenyldibenzo[*b*,*f*][1,4]oxazepine (**1a**) (27.1 mg, 0.1 mmol, 1.0 equiv) or 11-(phenyl-d_5)dibenzo[*b*,*f*][1,4]oxazepine (**1a-*d*$_5$**) (27.6 mg, 0.1 mmol, 1.0 equiv), *N*-methyl maleimide (**2a**) (13.4 mg, 0.12 mmol, 1.2 equiv), $Cu(OAc)_2.H_2O$ (20.0 mg, 0.1 mmol, 1.0 equiv) and $[Cp^*RhCl_2]_2$ (3.1 mg, 0.005 mmol, 0.05 equiv) were taken and 1.0 mL of THF solvent (0.1 M) was added, separately. The screw cap reaction vials were capped under air and kept on stirring in a preheated heating block at 60 °C. After 2 h, the reactions were quickly quenched by adding EtOAc keeping in an ice bath. The combined reaction mixture was filtered through a short pad of celite and concentrated together under vacuum. The crude reaction mixture was directly subjected to column chromatography on silica gel for partial purification, using 10% EtOAc in petroleum ether as the eluent. The ratio of **3a** and **3a-*d*$_4$** was determined by ^{1}H NMR spectroscopy (ESI, figure 2). No primary kinetic isotopic effect was found as $k_H/k_D \approx 1.5$.

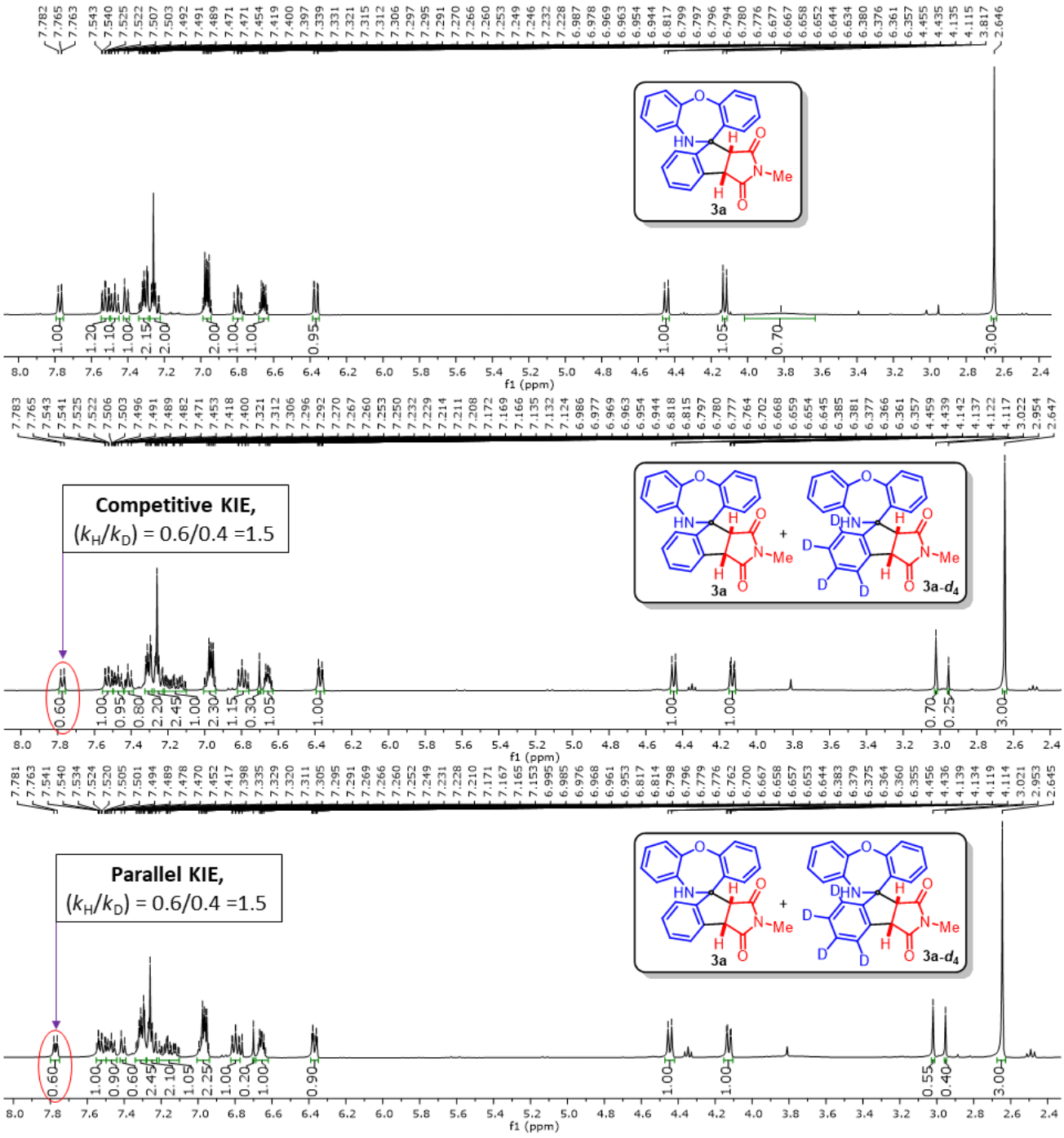
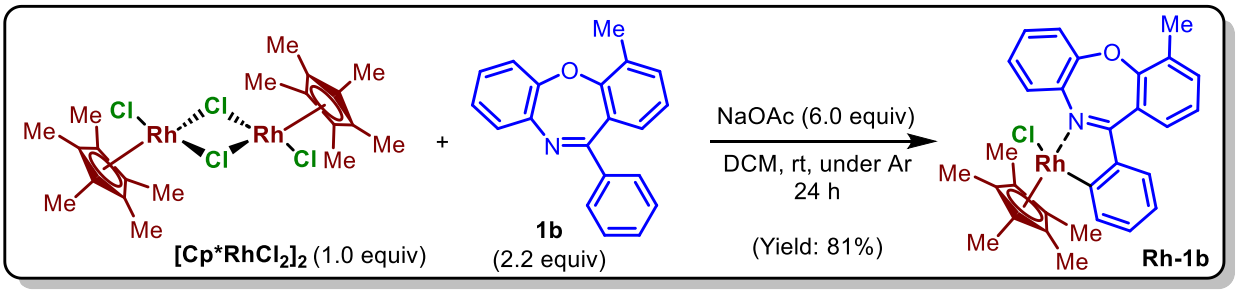


Figure 2. ^{1}H NMR of compound [**3a** + **3a**-d_4] in $CDCl_3$ for competitive and parallel kinetic isotopic experiments (KIE).

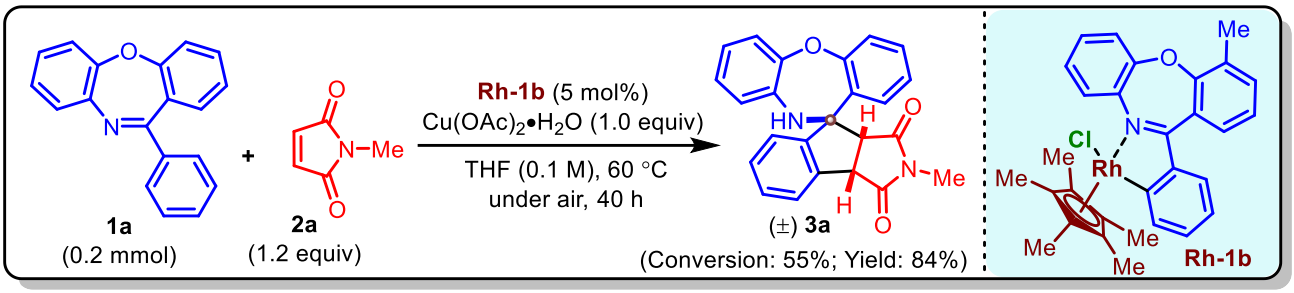
(d) Procedure for the preparation of the rhodacyclic complex:



Following an identical reported literature procedure,[1] the cyclometalated rhodacyclic complex (**Rh-1b**) was synthesized. A mixture of $[Cp^*RhCl_2]_2$ (1.0 equiv), 4-methyl-11-phenyldibenzo[*b,f*][1,4]oxazepine (**1b**) (2.2 equiv), and NaOAc (6.0 equiv) in dry DCM (0.004 M) was stirred under an argon atmosphere at room temperature (≈28 °C) overnight. Upon completion, the reaction mixture was passed through a short pad of celite, concentrated under reduced pressure, washed with hexane, and finally vacuum-dried to afford the cyclometalated complex (**Rh-1b**).

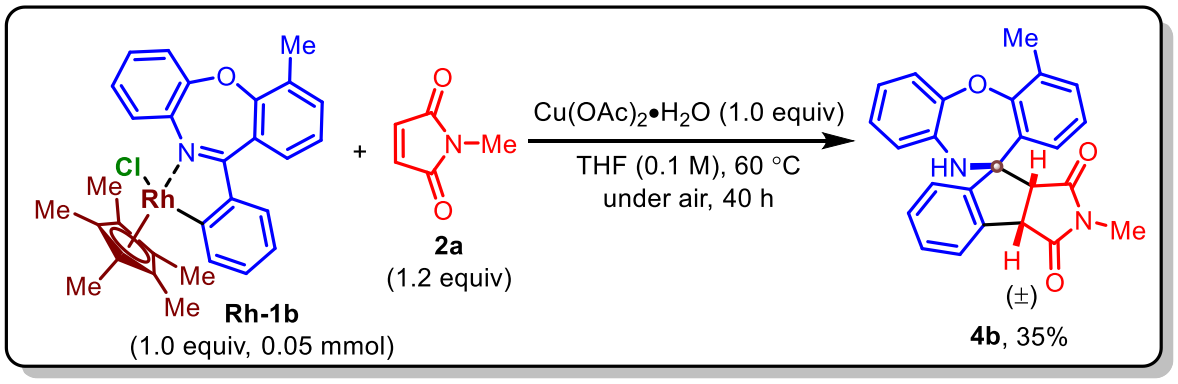
The characterization data, including ^1H and ^{13}C NMR, ESI-HRMS, and the X-ray crystallographic structure [3] (CCDC 2226413), have been previously reported by our group (Deb *et al.*, 2023) and were consistent with the reported data. [1]

(e) Procedure for the treatment of the rhodacyclic complex (Rh-1b) as catalyst:



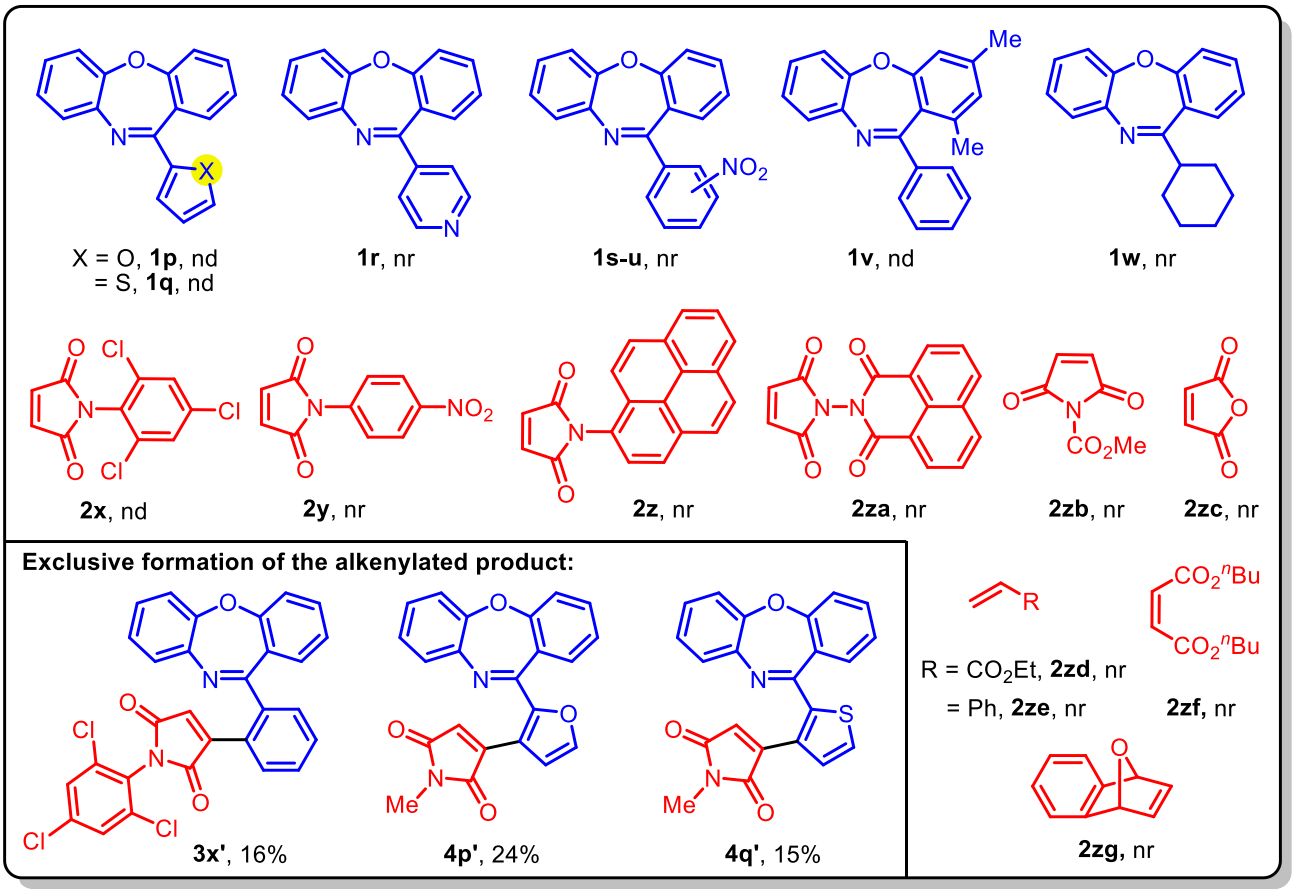
In a dried screw-capped reaction vial, 11- phenyldibenzo[*b,f*][1,4]oxazepane (**1a**) (54.3 mg, 0.2 mmol, 1.0 equiv), *N*-methyl maleimide (**2a**) (26.7 mg, 0.24 mmol, 1.2 equiv), $Cu(OAc)_2.H_2O$ (40.0 mg, 0.2 mmol, 1.0 equiv) and Cp*Rh-complex (**Rh-1b**) as catalyst (5.6 mg, 0.001 mmol, 0.05 equiv) were taken and 2.0 mL of THF (0.1 M) was added. The screw cap reaction vial was closed under air and kept on stirring in a preheated heating block at 60 ºC. After 40 h, the reaction was stopped and cooled to room temperature. The reaction mixture was diluted using ethyl acetate and filtered through a short pad of celite, then concentrated under reduced pressure. The crude reaction mixture was directly purified by column chromatography on silica gel using petroleum ether/ethyl acetate (5:1 to 7:3) as eluent to obtain 2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (**3a**) (35.0 mg, off white solid). In this experiment, 24.6 mg of **1a** was recovered as unreacted starting material (conversion = 55%), with **3a** obtained in a conversion yield of 84%, corresponding to an overall yield of 46%.

(f) Procedure for the treatment of the stoichiometric rhodacyclic complex (Rh-1b) as substrate:

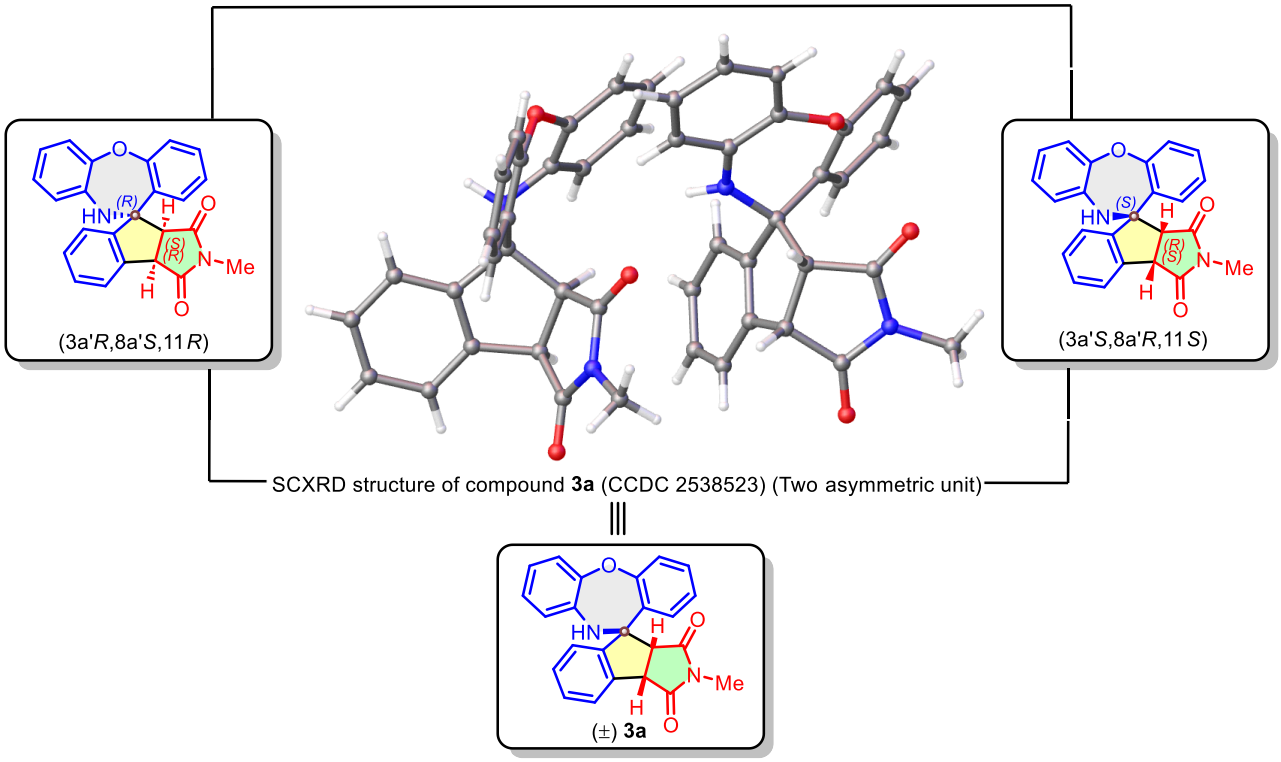


In a dried screw-capped reaction vial, stoichiometric rhodacyclic complex (**Rh-1b**) as substrate (27.9 mg, 0.05 mmol, 1.0 equiv), *N*-methyl maleimide (**2a**) (6.7 mg, 0.06 mmol, 1.2 equiv), $Cu(OAc)_2.H_2O$ (10.0 mg, 0.05 mmol, 1.0 equiv) were taken and 0.5 mL of THF was added. The screw cap reaction vial was closed under air and kept on stirring in a preheated heating block at 60 ºC. After 40 h, the reaction was stopped and cooled to room temperature. The reaction mixture was diluted using ethyl acetate and filtered through a short pad of celite, then concentrated under reduced pressure. The crude reaction mixture was directly purified by column chromatography on silica gel using petroleum ether/ethyl acetate (7:3) as eluent to obtain 2',4-dimethyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (**4b**) (7.0 mg, yield = 35%).

Unsuccessful substrates for the [3+2]-spiroannulation:

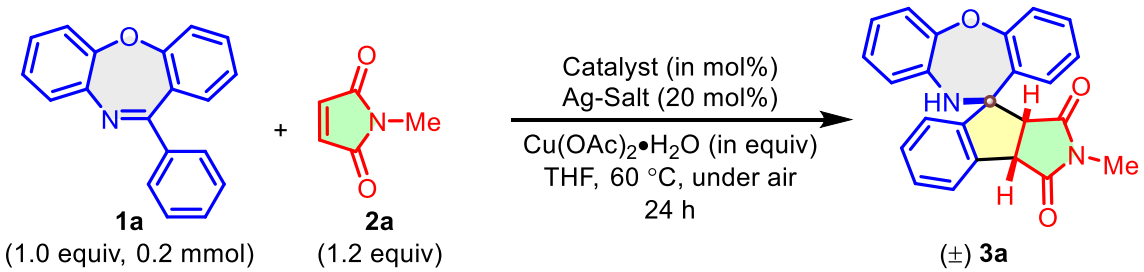


Determination of the relative stereochemistry of the spirocyclic product by SCXRD analysis:



The relative stereochemistry of compound **3a** (CCDC 2538523) was determined by X-ray crystallographic analysis.[4a] We found that the orientation between the two characteristic C–H bonds of indano-succinimide and the C–NH bond of dibenzo[*b*,*f*][1,4]oxazepine is relatively syn. To further confirm the relative stereochemistry, an additional SCXRD structure of compound **4e** (CCDC 2554145) was obtained and analyzed.[b]

Table S1. Additional screening of the reaction conditions:



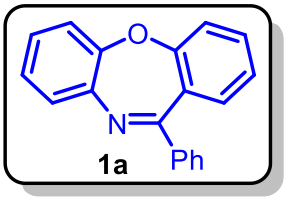
Entry	Catalyst (in mol%)	Ag-Salt (20 mol%)	$Cu(OAc)_2•H_2O$ (equiv)	Isolated yield of **3a** (%)
01	$[Cp^*RhCl_2]_2$ (5)	$AgSbF_6$, or $AgNTf_2$, or AgOTf (20)	0.3	nr
02	$[Cp^*RhCl_2]_2$ (5)	AgOTs (20)	0.3	30
03	$[Cp^*RhCl_2]_2$ (5)	AgOTs (20)	0.5	43
04	$[Cp^*RhCl_2]_2$ (5)	-	0.5	36
05	$[Cp^*RhCl_2]_2$ (5)	AgOTs (20)	1.0	60
06	$[Cp^*RhCl_2]_2$ (5)	-	1.0	89
07	$[Cp^*RhCl_2]_2$ (5)	AgOTs (20)	-	nr
08	$Cp^*Rh(OAc)_2$ (10)	-	-	nr
09	$Cp^*Rh(OAc)_2$ (10)	-	1.0	nr

References:

1. K. Naskar, S. Karmakar, I. Mondal, W. Sarkar, S. Roy, A. Roy and I. Deb, *Chem. Commun.*, 2023, **59**, 7751–7754.
2. (a) R. Mandal, B. Emayavaramban and B. Sundararaju, *Org. Lett.*, 2018, **20**, 2835–2838; (b) I. Mondal, K. Naskar, S. Roy, A. Purkait and I. Deb, *Org. Lett.*, 2024, **26**, 9859–9864.
3. Crystal structure determination of **Rh-1b**: CCDC 2226413.
4. (a) Crystal structure determination of (±) **3a**: CCDC 2538523; (b) Crystal structure determination of (±) **4e**: CCDC 2554145.

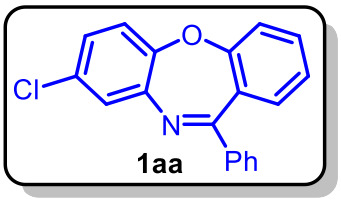
Characterization data of dibenzo[*b,f*][1,4]oxazepines as starting materials:

11-phenyldibenzo[*b,f*][1,4]oxazepine (1a):



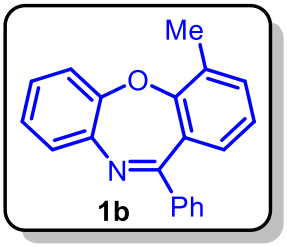
Yield: 94% (2.10 g); Pale yellow solid; **R_f** 0.69 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 98-100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (app d, *J* = 6.8 Hz, 2H), 7.51–7.44 (comp, 5H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.20–7.13 (comp, 5H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.0, 161.9, 152.4, 140.8, 140.0, 132.9, 131.2, 130.3, 129.6, 128.1 (x 2), 127.4, 127.3, 125.5, 124.4, 120.9, 120.6; **HRMS** (ESI, m/z) calcd for $C_{19}H_{14}NO$ $[M+H]^+$ 272.1075, found 272.1079.

8-chloro-11-phenyldibenzo[*b,f*][1,4]oxazepine (1aa):



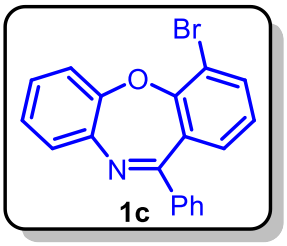
Yield: 74% (1.39 g); Yellow solid; **R_f** 0.67 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 98-100 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (app d, *J* = 7.2 Hz, 2H), 7.51–7.43 (comp, 5H), 7.26–7.09 (comp, 5H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 168.2, 161.8, 151.0, 141.8, 139.6, 133.2, 131.4, 130.7, 130.5, 129.7, 128.2, 127.7, 127.12, 127.08, 124.7, 121.6, 120.8; **HRMS** (ESI, m/z) calcd for $C_{19}H_{13}NOCl$ $[M+H]^+$ 306.0686, found 306.0689.

4-methyl-11-phenyldibenzo[*b,f*][1,4]oxazepine (1b):



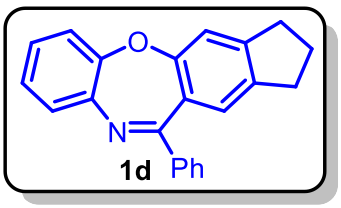
Yield: 99% (975 mg); Yellow solid; **R_f** 0.67 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 19:1; **mp:** 86-88 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (app d, *J* = 6.8 Hz, 2H), 7.48–7.43 (comp, 4H), 7.37–7.35 (m, 1H), 7.26–7.16 (comp, 3H), 7.05–7.00 (comp, 2H), 2.56 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.5, 159.9, 152.2, 141.2, 140.3, 134.1, 130.3, 129.7, 129.0, 128.2, 128.1, 127.4, 127.1, 125.4, 124.0, 120.9, 16.3; **HRMS** (ESI, m/z) calcd for $C_{20}H_{16}NO$ $[M+H]^+$ 286.1232, found 286.1228.

4-bromo-11-phenyldibenzo[*b,f*][1,4]oxazepine (1c):



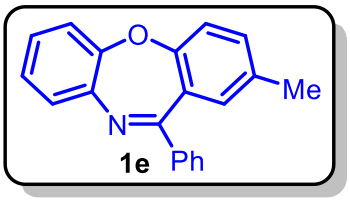
Yield: 84% (1.20 g); Yellow solid; **R_f** 0.67 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 92-94 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (app d, *J* = 6.8 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.29–7.24 (comp, 5H), 7.02–7.02 (comp, 2H), 6.92 (d, *J* = 7.2 Hz, 1H), 6.80–6.77 (m, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 166.0, 157.4, 151.7, 140.4, 139.7, 135.9, 130.6, 130.4, 129.6, 128.8, 128.2, 128.0, 127.6, 125.9, 125.3, 121.5, 115.7; **HRMS** (ESI, m/z) calcd for $C_{19}H_{13}NOBr$ $[M+H]^+$ 350.0181, found 350.0179.

11-phenyl-2,3-dihydro-1*H*-benzo[*b*]indeno[5,6-*f*][1,4]oxazepine (1d):



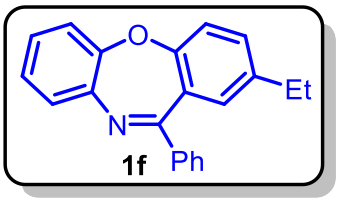
Yield: 88% (1.73 g); Yellow solid; **R_f** 0.67 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 19:1; **mp:** 114-116 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.84 (comp, 2H), 7.49–7.42 (comp, 4H), 7.21–7.17 (comp, 3H), 7.14 (s, 1H), 6.99 (s, 1H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 2.08 (p, *J* = 7.4 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.4, 160.8, 152.6, 150.2, 141.0, 140.4, 140.2, 130.1, 129.6, 128.0, 127.9, 127.2, 126.2, 125.3, 125.1, 120.5, 116.6, 33.0, 32.0, 25.6; **HRMS** (ESI, m/z) calcd for $C_{22}H_{18}NO$ $[M+H]^+$ 312.1388, found 312.1380.

2-methyl-11-phenyldibenzo[*b,f*][1,4]oxazepine (1e):



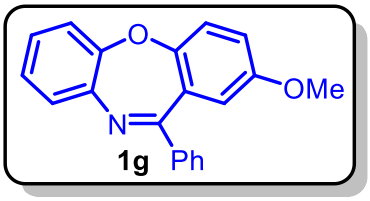
Yield: 68% (1.06 g); Off-white solid; **R$_f$** 0.67 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 138-140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (app d, *J* = 7.6 Hz, 2H), 7.53–7.44 (comp, 4H), 7.29 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.22–7.16 (comp, 4H), 6.98 (s, 1H), 2.26 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.2, 159.9, 152.6, 140.7, 140.1, 134.1, 133.6, 131.3, 130.3, 129.7, 128.13, 128.09, 127.4, 126.9, 125.4, 120.5 (x 2), 20.7; **HRMS** (ESI, m/z) calcd for $C_{20}H_{16}NO$ $[M+H]^+$ 286.1232, found 286.1231.

2-ethyl-11-phenyldibenzo[*b,f*][1,4]oxazepine (1f):



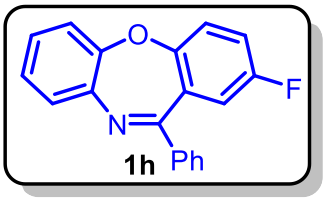
Yield: 66% (377 mg); Off-white solid; **R$_f$** 0.67 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 104-106 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.84 (comp, 2H), 7.52–7.42 (comp, 4H), 7.32 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.22–7.18 (comp, 4H), 7.00 (d, *J* = 2.0 Hz, 1H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.13 (t, *J* = 7.6 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.3, 160.1, 152.6, 140.8, 140.5, 140.1, 132.5, 130.39, 130.36, 129.7, 128.14 (x 2), 128.11, 127.5, 127.0, 125.4, 120.6, 28.1, 15.6; **HRMS** (ESI, m/z) calcd for $C_{21}H_{18}NO$ $[M+H]^+$ 300.1388, found 300.1396.

2-methoxy-11-phenyldibenzo[*b,f*][1,4]oxazepine (1g):



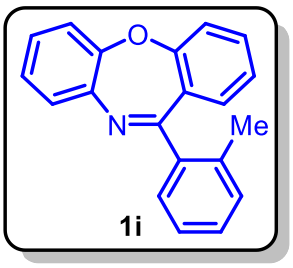
Yield: 59% (1.10 g); Orange solid; **R$_f$** 0.56 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 124-126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90–7.87 (comp, 2H), 7.52–7.44 (comp, 4H), 7.23–7.19 (comp, 4H), 7.02 (dd, *J* = 8.8, 3.2 Hz, 1H), 6.69 (d, *J* = 2.8 Hz, 1H), 3.67 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 166.6, 155.9, 155.8, 152.6, 140.6, 139.7, 130.4, 129.7, 128.2, 128.1, 127.6, 127.5, 125.4, 121.5, 120.4, 118.6, 115.4, 55.7; **HRMS** (ESI, m/z) calcd for $C_{20}H_{16}NO_2$ $[M+H]^+$ 302.1181, found 302.1186.

2-fluoro-11-phenyldibenzo[*b,f*][1,4]oxazepine (1h):



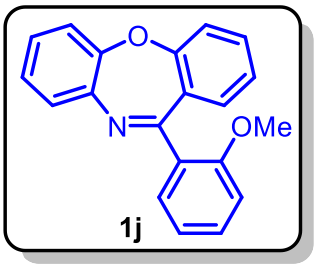
Yield: 58% (1.20 g); Off-white solid; **R$_f$** 0.60 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 126-128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.84 (comp, 2H), 7.54–7.44 (comp, 4H), 7.26–7.16 (comp, 5H), 6.89 (dd, *J* = 8.8, 2.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 165.6, 158.8 (d, $^1J_{CF}$ = 245.4 Hz) , 157.8 (d, $^4J_{CF}$ = 2.3 Hz), 152.2, 140.4, 139.3, 130.6, 129.5, 128.4, 128.30, 128.26, 127.8, 125.7, 122.2 (d, $^3J_{CF}$ = 8.5 Hz), 120.5, 119.7 (d, $^2J_{CF}$ = 24.2 Hz), 117.2 (d, $^2J_{CF}$ = 24.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –117.1; **HRMS** (ESI, m/z) calcd for $C_{19}H_{13}NOF$ $[M+H]^+$ 290.0981, found 290.0990.

11-(*o*-tolyl)dibenzo[*b,f*][1,4]oxazepine (1i):



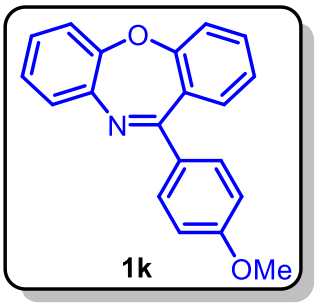
Yield: 92% (713 mg); Off-white solid; **R$_f$** 0.74 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 96-98 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.48–7.43 (comp, 2H), 7.38–7.33 (m, 1H), 7.32–7.28 (m, 1H), 7.26–7.19 (comp, 5H), 7.09–7.05 (m, 1H), 6.93 (dd, *J* = 7.6, 1.6 Hz, 1H), 2.25 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 169.0, 160.9, 152.4, 140.6, 136.4, 133.1, 130.7, 130.6, 129.4, 129.3, 129.0, 128.9, 128.5, 128.0, 125.8, 125.6, 125.0, 120.82, 120.76, 20.0; **HRMS** (ESI, m/z) calcd for $C_{20}H_{16}NO$ $[M+H]^+$ 286.1232, found 286.1229.

11-(2-methoxyphenyl)dibenzo[*b,f*][1,4]oxazepine (1j):



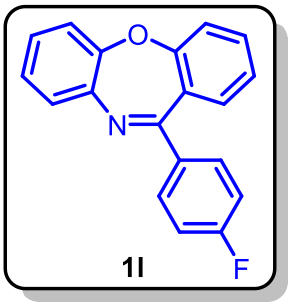
Yield: 82% (669 mg); Yellow solid; **R_f** 0.59 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 128-130 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.46–7.40 (comp, 3H), 7.24–7.18 (comp, 4H), 7.11 (app t, *J* = 7.4 Hz, 1H), 7.06–7.03 (m, 1H), 7.00 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 3.62 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 166.9, 160.5, 157.8, 152.6, 132.6, 131.2, 130.7, 129.9, 129.4, 128.5, 127.8, 125.4, 124.6, 120.8 (x 2), 120.7 (x 2), 120.5, 111.8, 55.8; **HRMS** (ESI, m/z) calcd for $C_{20}H_{16}NO_2$ $[M+H]^+$ 302.1181, found 302.1178.

11-(4-methoxyphenyl)dibenzo[*b,f*][1,4]oxazepine (1k):



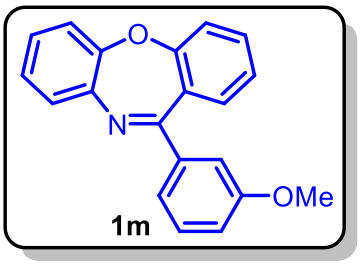
Yield: 74% (350 mg); Yellow solid; **R_f** 0.39 (in 10% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 108-110 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (app d, *J* = 8.8 Hz, 2H), 7.50–7.42 (m, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.24 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.21–7.13 (comp, 4H), 6.97 (app d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 166.4, 161.9, 161.6, 152.5, 140.8, 132.9, 132.43, 132.39, 131.4, 127.9, 127.3, 127.1, 125.5, 124.4, 120.9, 120.6, 113.5, 55.4; **HRMS** (ESI, m/z) calcd for $C_{20}H_{16}NO_2$ $[M+H]^+$ 302.1181, found 302.1189.

11-(4-fluorophenyl)dibenzo[*b,f*][1,4]oxazepine (1l):



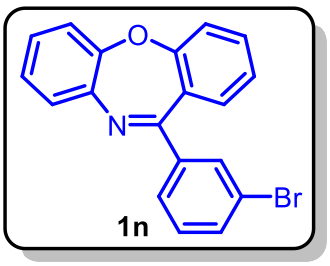
Yield: 94% (730 mg); Yellow solid; **R_f** 0.60 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 19:1; **mp:** 82-84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87–7.82 (comp, 2H), 7.52–7.48 (m, 1H), 7.44–7.40 (m, 1H), 7.29–7.27 (m, 1H), 7.23–7.11 (comp, 7H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 165.8, 164.2 (d, $^1J_{CF}$ = 252.5 Hz), 161.9, 152.3, 140.7, 136.2 (d, $^4J_{CF}$ = 2.8 Hz), 133.1, 131.7 (d, $^3J_{CF}$ = 8.6 Hz), 131.0, 128.1, 127.6, 127.1, 125.6, 124.5, 121.0, 120.7, 115.2 (d, $^2J_{CF}$ = 21.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –110.0; **HRMS** (ESI, m/z) calcd for $C_{19}H_{13}NOF$ $[M+H]^+$ 290.0981, found 290.0983.

11-(3-methoxyphenyl)dibenzo[*b,f*][1,4]oxazepine (1m):



Yield: 50% (825 mg); Yellow solid; **R_f** 0.63 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 100-102 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51–7.46 (comp, 3H), 7.37–7.34 (comp, 2H), 7.29 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.24–7.19 (comp, 4H), 7.17–7.13 (m, 1H), 7.08–7.03 (m, 1H), 3.88 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 166.8, 161.9, 159.4, 152.3, 141.4, 140.6, 132.9, 131.2, 129.0, 128.1, 127.5, 127.3, 125.5, 124.4, 122.4, 120.8, 120.6, 116.4, 114.5, 55.3; **HRMS** (ESI, m/z) calcd for $C_{20}H_{16}NO_2$ $[M+H]^+$ 302.1181, found 302.1189.

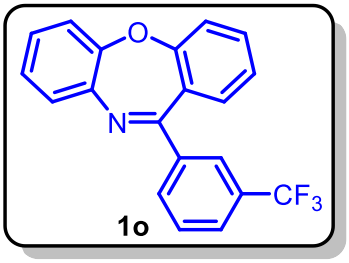
11-(3-bromophenyl)dibenzo[*b,f*][1,4]oxazepine (1n):



Yield: 72% (1.65 g); Yellow solid; **R_f** 0.68 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 126-128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (app t, *J* = 1.8 Hz, 1H), 7.72–7.70 (m, 1H), 7.64–7.61 (m, 1H), 7.53–7.49 (m, 1H), 7.47–7.43 (m, 1H), 7.33–7.28 (comp, 2H), 7.24–7.20 (comp, 3H), 7.17–7.16 (comp, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 165.4, 161.9, 152.3, 142.0, 140.4,

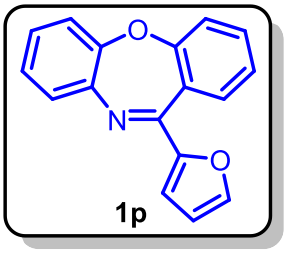
133.2 (x 2), 132.4, 130.9, 129.6, 128.4, 128.2, 127.9, 126.8, 125.6, 124.6, 122.5, 121.1, 120.7; **HRMS** (ESI, m/z) calcd for $C_{19}H_{13}NOBr$ $[M+H]^+$ 350.0181, found 350.0183.

11-(3-(trifluoromethyl)phenyl)dibenzo[*b,f*][1,4]oxazepine (1o):



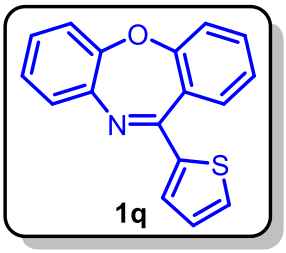
Yield: 96% (877 mg); Yellow solid; **R$_f$** 0.67 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 19:1; **mp:** 94-96 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.58 (app t, *J* = 7.8 Hz, 1H), 7.55–7.51 (m, 1H), 7.48–7.44 (m, 1H), 7.31 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.25–7.20 (comp, 3H), 7.17 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.14 (dd, *J* = 7.6, 2.0 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 165.4, 162.0, 152.3, 140.8, 140.4, 133.4, 132.9, 130.8 (d, $^2J_{CF}$ = 32.3 Hz), 130.7, 128.7, 128.3, 128.0, 126.9 (d, J_{CF} = 3.6 Hz), 126.8 (d, J_{CF} = 2.4 Hz), 126.4–126.3 (m), 125.7, 124.7, 124.0 (d, $^1J_{CF}$ = 273.7 Hz), 121.2, 120.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.4; **HRMS** (ESI, m/z) calcd for $C_{20}H_{13}NOF_3$ $[M+H]^+$ 340.0949, found 340.0959.

11-(furan-2-yl)dibenzo[*b,f*][1,4]oxazepine (1p):



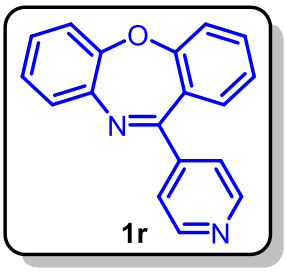
Yield: 92% (644 mg); Yellow solid; **R$_f$** 0.50 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 90-92 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.774–7.770 (m, 1H), 7.65 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.62–7.57 (m, 1H), 7.56–7.53 (m, 1H), 7.36–7.25 (comp, 5H), 6.95 (d, *J* = 3.2 Hz, 1H), 6.65 (dd, *J* = 3.4, 1.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 162.1, 156.1, 152.5, 152.3, 145.6, 140.6, 133.2, 130.3, 128.2, 127.4, 125.9, 125.7, 124.6, 120.9, 120.6, 116.8, 112.0; **HRMS** (ESI, m/z) calcd for $C_{17}H_{12}NO_2$ $[M+H]^+$ 262.0868, found 262.0876.

11-(thiophen-2-yl)dibenzo[*b,f*][1,4]oxazepine (1q):



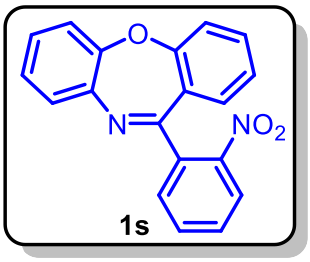
Yield: 94% (702 mg); Bright yellow solid; **R$_f$** 0.42 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 19:1; **mp:** 84-86 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58–7.50 (comp, 3H), 7.40–7.38 (m, 1H), 7.33 (d, *J* = 2.8 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H),7.21–7.17 (comp, 3H), 7.11–7.09 (m, 1H).; **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 161.8, 160.7, 152.2, 145.8, 140.6, 133.1, 131.6, 130.6, 130.5, 128.0, 127.6, 127.3, 126.4, 125.6, 124.6, 121.1, 120.6; **HRMS** (ESI, m/z) calcd for $C_{17}H_{12}NOS$ $[M+H]^+$ 278.0640, found 278.0637.

11-(pyridin-4-yl)dibenzo[*b,f*][1,4]oxazepine (1r):



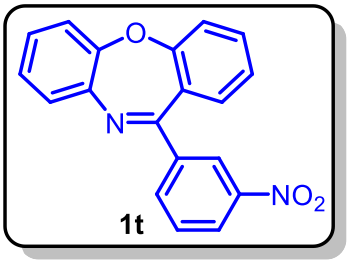
Yield: 47% (184 mg); Yellow solid; **R$_f$** 0.45 (in 50% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 1:1; **mp:** 90-92 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (app d, *J* = 6.0 Hz, 2H), 7.72–7.70 (comp, 2H), 7.55–7.50 (m, 1H), 7.47–7.42 (m, 1H), 7.29 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.25–7.19 (comp, 3H), 7.17 (dd, *J* = 7.2, 0.8 Hz, 1H), 7.13 (dd, *J* = 7.8, 1.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 164.8, 162.1, 152.2, 150.0 (x 2), 147.0, 140.3, 133.5, 130.5, 128.5, 126.3, 125.8, 124.7, 123.5, 121.3, 120.9; **HRMS** (ESI, m/z) calcd for $C_{18}H_{13}N_2O$ $[M+H]^+$ 273.1028, found 273.1030.

11-(2-nitrophenyl)dibenzo[*b,f*][1,4]oxazepine (1s):



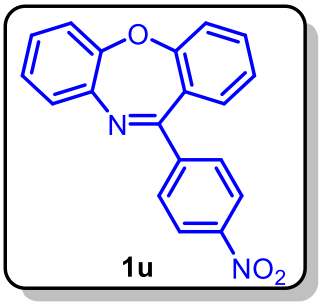
Yield: 95% (811 mg); Light brown solid; **R_f** 0.53 (in 30% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 7:3; **mp:** 124-126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.73–7.70 (comp, 2H), 7.64–7.60 (m, 1H), 7.50–7.46 (m, 1H), 7.38–7.36 (m, 1H), 7.28–7.24 (comp, 2H), 7.22–7.18 (comp, 2H), 7.07 (app td, *J* = 7.6, 1.1 Hz, 1H), 6.93 (dd, *J* = 8.0, 1.6 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 164.7, 161.6, 152.4, 149.2, 139.9, 136.1, 133.7, 132.9, 131.6, 130.2, 129.6, 128.8, 128.6, 127.6, 125.8, 124.9, 124.6, 121.13, 121.06; **HRMS** (ESI, m/z) calcd for $C_{19}H_{13}N_2O_3$ $[M+H]^+$ 317.0926, found 317.0923.

11-(3-nitrophenyl)dibenzo[*b,f*][1,4]oxazepine (1t):



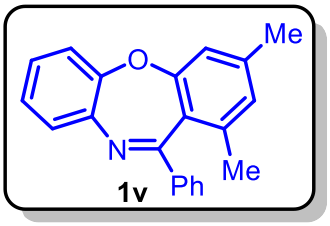
Yield: 99% (967 mg); Pale yellow solid; **R_f** 0.40 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 128-130 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (app t, *J* = 1.8 Hz, 1H), 8.36–8.33 (m, 1H), 8.18–8.16 (m, 1H), 7.64 (app t, *J* = 8.0 Hz, 1H), 7.57–7.53 (m, 1H), 7.50–7.45 (m, 1H), 7.32 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.25–7.21 (comp, 3H), 7.20–7.18 (m, 1H), 7.15–7.12 (dd, *J* = 7.8, 1.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 164.4, 162.1, 152.2, 148.3, 141.7, 140.3, 135.4, 133.6, 130.4, 129.2, 128.4 (x 2), 126.5, 125.8, 124.90, 124.87, 124.5, 121.4, 120.9; **HRMS** (ESI, m/z) calcd for $C_{19}H_{13}N_2O_3$ $[M+H]^+$ 317.0926, found 317.0929.

11-(4-nitrophenyl)dibenzo[*b,f*][1,4]oxazepine (1u):



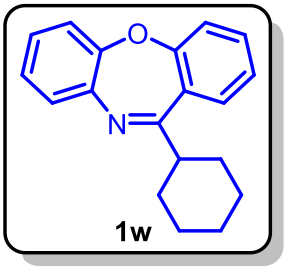
Yield: 86% (820 mg); Bright yellow solid; **R_f** 0.61 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 130-132 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.31 (app d, *J* = 7.2 Hz, 2H), 8.02 (app d, *J* = 7.6 Hz, 2H), 7.57–7.53 (m, 1H), 7.48–7.47 (m, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 7.25–7.16 (comp, 4H), 7.11 (d, *J* = 7.2 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 164.9, 162.1, 152.2, 148.9, 145.6, 140.2, 133.7, 130.61, 130.58, 128.6, 128.5, 126.6, 125.8, 124.8, 123.4, 121.4, 120.9; **HRMS** (ESI, m/z) calcd for $C_{19}H_{13}N_2O_3$ $[M+H]^+$ 317.0926, found 317.0930.

1,3-dimethyl-11-phenyldibenzo[*b,f*][1,4]oxazepine (1v):



Yield: 59% (450 mg); Yellow solid; **R_f** 0.67 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 9:1; **mp:** 126-128 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (app d, *J* = 6.4 Hz, 2H), 7.44–7.39 (comp, 4H), 7.21–7.11 (comp, 3H), 6.96 (s, 1H), 6.82 (s, 1H), 2.34 (s, 3H), 1.81 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 168.1, 164.2, 152.7, 142.3, 141.4, 141.3, 138.4, 130.1, 128.8, 128.4, 128.1, 126.8, 126.7, 125.4, 123.4, 120.5, 118.3, 21.6, 21.1; **HRMS** (ESI, m/z) calcd for $C_{21}H_{18}NO$ $[M+H]^+$ 300.1388, found 300.1385.

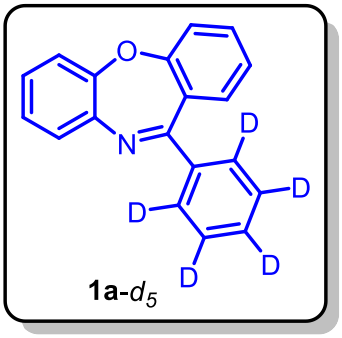
11-cyclohexyldibenzo[*b,f*][1,4]oxazepine (1w):



Yield: 84% (632 mg); Pale yellow solid; **R_f** 0.48 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 19:1; **mp:** 84-86 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.44–7.38 (m, 1H), 7.30–7.28 (m, 1H), 7.22–7.11 (comp, 5H), 2.92 (tt, *J* = 11.4, 3.3 Hz, 1H), 2.01–1.97 (m, 2H), 1.90–1.86 (m, 2H), 1.76–1.72 (m, 1H), 1.68–1.58 (comp, 2H), 1.44–1.24 (m, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 161.7,

152.6, 132.2, 128.6, 127.6 (x 2), 126.8, 125.4 (x 2), 125.0, 120.7, 120.4 (x 2), 46.8, 31.4, 26.4, 26.1; **HRMS** (ESI, m/z) calcd for $C_{19}H_{20}NO$ $[M+H]^+$ 278.1545, found 278.1548.

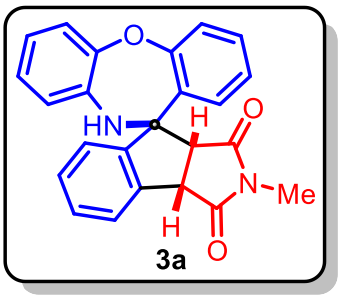
11-(phenyl-*d*$_5$)dibenzo[*b,f*][1,4]oxazepine (1a-*d*$_5$):



Yield: 86% (951 mg); Pale yellow solid; **R$_f$** 0.65 (in 5% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 19:1; **mp:** 82-84 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52–7.47 (m, 1H), 7.46–7.44 (m, 1H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.23–7.19 (comp, 4H), 7.17–7.13 (m, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.0, 162.0, 152.4, 140.8, 139.9, 133.0, 131.3, 129.5, 129.1 (d, *J* = 24.6 Hz), 128.2, 127.8 (d, *J* = 24.4 Hz), 127.5, 127.4, 125.5, 124.4, 120.9, 120.7; **HRMS** (ESI, m/z) calcd for $C_{19}H_9D_5NO$ $[M+H]^+$ 277.1389, found 277.1386.

Characterization data of [3+2] spiroannulated products:

2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3a):



Yield: 89% (68 mg); Off-white solid (Crystallization in DCM/hexane using slow solvent diffusion technique); $\mathbf{R_f}$ 0.3 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 7:3; **mp:** 78-80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78–7.76 (m, 1H), 7.52 (app td, *J* = 7.4, 1.4 Hz, 1H), 7.49–7.45 (m, 1H), 7.42–7.40 (m, 1H), 7.34–7.29 (comp, 2H), 7.27–7.23 (m, 1H), 6.99–6.94 (comp, 2H), 6.82–6.78 (m, 1H), 6.68–6.63 (m, 1H), 6.37 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.45 (d, *J* = 8.0 Hz, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 3.82 (br s, 1NH), 2.65 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.0, 174.1, 156.0, 147.5, 146.2, 137.6, 136.3, 130.2, 129.7, 129.6, 129.5, 128.2, 126.6, 125.7, 124.4, 122.8, 122.2, 121.7, 121.3, 120.9, 74.7, 56.6, 50.3, 24.7; **HRMS** (ESI, m/z) calcd for $C_{24}H_{19}N_2O_3$ $[M+H]^+$ 383.1396, found 383.1380.

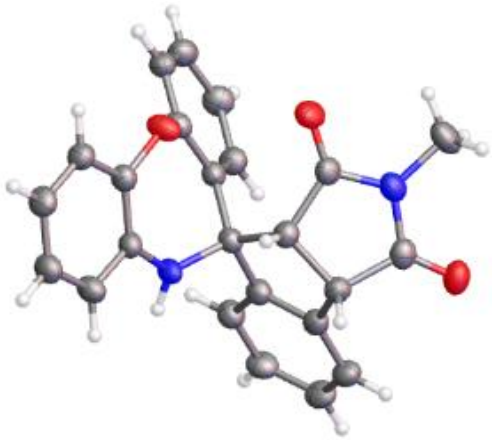
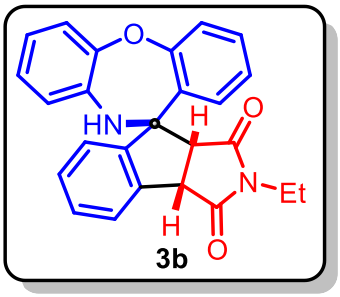


Figure 3. X-ray crystal structure of **3a** (ellipsoid contour at 50% probability level)

Table S2: ***Crystal data and structure refinement for*** [**3a** ($C_{24}H_{18}N_2O_3$) + 0.25 solvent (DCM)], **CCDC No. 2538523**

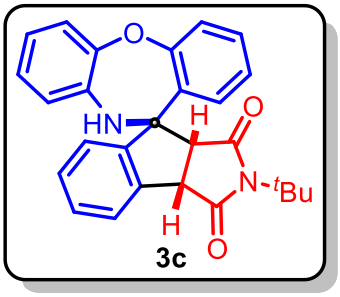
Identification code	ORTHOP_a	μ/mm^{-1}	1.385
Empirical formula	$C_{24.25}H_{18.5}Cl_{0.5}N_2O_3$	F(000)	1684.0
Formula weight	403.63	Crystal size/mm^3	0.15 × 0.02 × 0.005
Temperature/K	130.00	Radiation	Cu Kα (λ = 1.54178)
Crystal system	orthorhombic	2Θ range for data collection/°	6.596 to 133.368
Space group	$P2_12_12$	Index ranges	-22 ≤ h ≤ 22, -22 ≤ k ≤ 22, -12 ≤ l ≤ 12
a/Å	18.7913(17)	Reflections collected	63069
b/Å	19.1175(18)	Independent reflections	6702 [R_{int} = 0.1114, R_{sigma} = 0.0557]
c/Å	10.5622(10)	Data/restraints/parameters	6702/0/526
α/°	90	Goodness-of-fit on F^2	1.052
β/°	90	Final R indexes [I>=2σ (I)]	R_1 = 0.0559, wR_2 = 0.1484
γ/°	90	Final R indexes [all data]	R_1 = 0.0629, wR_2 = 0.1544
Volume/Å^3	3794.4(6)	Largest diff. peak/hole / e Å^{-3}	0.60/-0.35
Z	8	Flack parameter	1.15(10)
ρ_{calc}g/cm^3	1.413		

2'-ethyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3b):



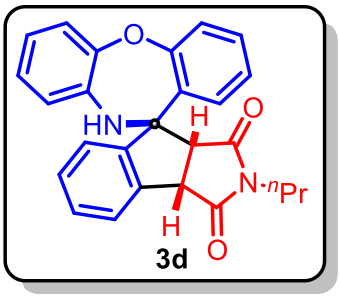
Yield: 84% (66.6 mg); Off-white solid; **R_f** 0.3 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 78-80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.56–7.50 (m, 1H), 7.49–7.45 (m, 1H), 7.40–7.37 (m, 1H), 7.33–7.28 (comp, 2H), 7.25–7.21 (m, 1H), 7.02–6.95 (comp, 2H), 6.77–6.73 (m, 1H), 6.70–6.66 (m, 1H), 6.29 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.41 (d, *J* = 8.0 Hz, 1H), 4.03 (d, *J* = 8.0 Hz, 1H), 3.82 (br s, 1 N-H), 3.29–3.12 (m, 2H), 0.81 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.8, 173.8, 155.7, 147.8, 146.6, 137.5, 136.3, 130.2, 129.8, 129.43, 129.36, 128.6, 126.5, 125.7, 124.3, 123.1, 122.0, 121.7, 121.20, 121.16, 75.0, 56.6, 50.4, 33.8, 12.5; **HRMS** (ESI, m/z) calcd for $C_{25}H_{21}N_2O_3$ $[M+H]^+$ 397.1545, found 397.1539.

2'-(*tert*-butyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3c):



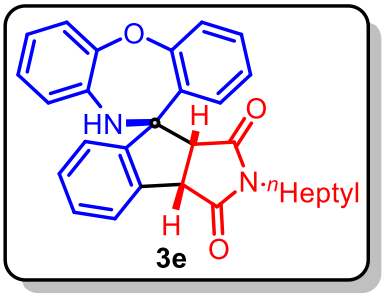
Yield: 82% (69.6 mg); Off-white solid; **R_f** 0.4 (in 30% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 176-178 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 1H), 7.52–7.48 (m, 1H), 7.46–7.42 (m, 1H), 7.34–7.32 (comp, 2H), 7.27–7.24 (m, 1H), 7.21–7.17 (m, 1H), 7.03–6.99 (m, 1H), 6.98–6.94 (m, 1H), 6.75–6.70 (m, 1H), 6.69 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.22 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.25 (d, *J* = 8.4 Hz, 1H), 3.76 (d, *J* = 8.4 Hz, 1H), 1.19 (s, 9H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.9, 174.8, 155.2, 148.1, 146.9, 138.2, 136.2, 130.2, 129.7, 129.25, 129.17 (x 2), 126.4, 125.7, 124.1, 123.4, 121.63, 121.61 (x 2), 121.1, 76.1, 58.3, 57.0, 50.5, 27.8; **HRMS** (ESI, m/z) calcd for $C_{27}H_{25}N_2O_3$ $[M+H]^+$ 425.1865, found 425.1850.

2'-propyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-c]pyrrole]-1',3'(2'*H*)-dione (3d):



Yield: 81% (66.5 mg); Off-white solid; **R_f** 0.3 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 166-168 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.54–7.50 (m, 1H), 7.48–7.45 (m, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.34–7.28 (comp, 2H), 7.26–7.21 (m, 1H), 7.00–6.94 (comp, 2H), 6.78–6.74 (m, 1H), 6.68–6.66 (m, 1H), 6.33 (dd, *J* = 8.0, 1.4 Hz, 1H), 4.42 (d, *J* = 8.0 Hz, 1H), 4.06 (d, *J* = 8.0 Hz, 1H), 3.21–3.04 (m, 2H), 1.29–1.15 (m, 2H), 0.67 (t, *J* = 7.4 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.1, 174.0, 155.8, 147.5, 146.4, 137.7, 136.2, 130.2, 129.7, 129.5, 129.4, 128.5, 126.6, 125.6, 124.3, 122.9, 122.0, 121.7, 121.2, 121.0, 75.0, 56.5, 50.3, 40.4, 20.6, 11.1; **HRMS** (ESI, m/z) calcd for $C_{26}H_{23}N_2O_3$ $[M+H]^+$ 411.1709, found 411.1702.

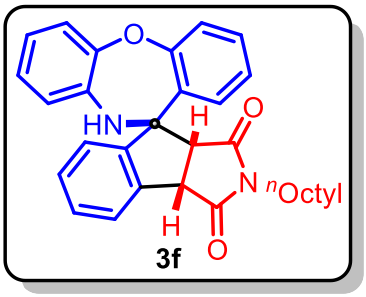
2'-heptyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3e):



Yield: 70% (65.1 mg); Off-white solid; **R_f** 0.4 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 58-60 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.54–7.50 (m, 1H), 7.48–7.45 (m, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.34–7.28 (comp, 2H), 7.26–7.21 (m, 1H), 7.00–6.94 (comp, 2H), 6.78–6.74 (m, 1H), 6.68–6.64 (m, 1H), 6.32 (dd, *J* = 8.0, 1.4 Hz, 1H), 4.41 (d, *J* = 8.4 Hz, 1H), 4.05 (d, *J* = 8.0 Hz, 1H), 3.78 (br s, 1 N-H), 3.20–

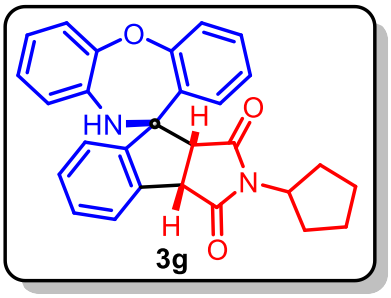
3.07 (m, 2H), 1.24–1.08 (m, 8H), 1.05–0.98 (m, 2H), 0.83 (t, *J* = 7.2 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.0, 174.0, 155.8, 147.5, 146.4, 137.7, 136.3, 130.2, 129.7, 129.5, 129.4, 128.5, 126.6, 125.6, 124.3, 122.9, 122.0, 121.7, 121.2, 121.0, 75.0, 56.5, 50.3, 38.9, 31.5, 28.6, 27.3, 26.5, 22.4, 14.0; **HRMS** (ESI, m/z) calcd for $C_{30}H_{31}N_2O_3$ $[M+H]^+$ 467.2335, found 467.2321.

2'-octyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3f):



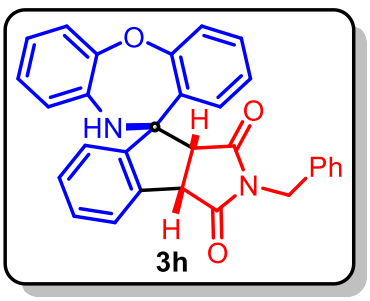
Yield: 73% (70.0 mg); Off-white solid; **R_f** 0.38 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 104-106 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 7.2 Hz, 1H), 7.54–7.50 (m, 1H), 7.48–7.45 (m, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.34–7.28 (comp, 2H), 7.26–7.21 (m, 1H), 7.01–6.94 (comp, 2H), 6.78–6.74 (m, 1H), 6.68–6.66 (m, 1H), 6.32 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.42 (d, *J* = 8.0 Hz, 1H), 4.06 (d, *J* = 8.0 Hz, 1H), 3.20–3.07 (m, 2H), 1.24–1.20 (m, 2H), 1.17–1.08 (m, 8H), 1.05–1.01 (m, 2H), 0.84 (t, *J* = 7.0 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.0, 174.0, 155.8, 147.5, 146.4, 137.7, 136.2, 130.2, 129.7, 129.5, 129.4, 128.5, 126.6, 125.7, 124.3, 123.0, 122.1, 121.7, 121.2, 121.0, 75.0, 56.5, 50.3, 38.9, 31.6, 29.0, 28.9, 27.3, 26.6, 22.6, 14.0; **HRMS** (ESI, m/z) calcd for $C_{31}H_{33}N_2O_3$ $[M+H]^+$ 481.2491, found 481.2483.

2'-cyclopentyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3g):



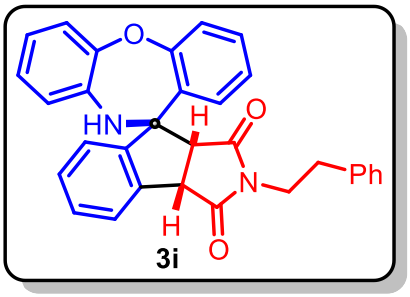
Yield: 77% (67.2 mg); Off-white solid; **R_f** 0.4 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 66-68 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.6 Hz, 1H), 7.53–7.49 (m, 1H), 7.47–7.42 (m, 1H), 7.36–7.33 (comp, 2H), 7.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.23–7.18 (m, 1H), 7.06–6.97 (comp, 2H), 6.74–6.70 (comp, 2H), 6.18 (dd, *J* = 7.8, 1.0 Hz, 1H), 4.38 (d, *J* = 8.0 Hz, 1H), 4.11 (p, *J* = 8.4 Hz, 1H), 3.92 (d, *J* = 8.4 Hz, 1H), 1.75–1.61 (m, 3H), 1.54– 1.33 (m, 5H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.2, 174.0, 155.3, 148.4, 146.8, 137.5, 130.2, 129.8, 129.2 (x 2), 128.9, 126.4, 125.6, 124.2, 123.5, 121.9, 121.7 (x 2), 121.6, 121.1, 75.5, 56.6, 51.7, 50.2, 28.3, 27.6, 24.8 (x 2); **HRMS** (ESI, m/z) calcd for $C_{28}H_{25}N_2O_3$ $[M+H]^+$ 437.1865, found 437.1862.

2'-benzyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3h):



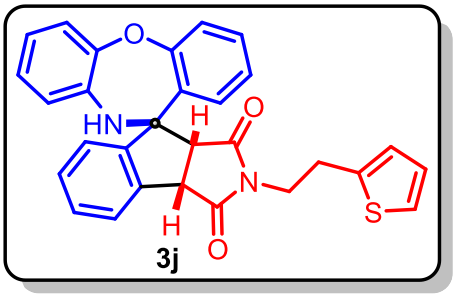
Yield: 88% (80.7 mg); Off-white solid; **R_f** 0.20 (in 10% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 74-76 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.53–7.49 (m, 1H), 7.45–7.42 (m, 1H), 7.36–7.27 (comp, 3H), 7.20–7.14 (comp, 4H), 7.12–7.10 (comp, 2H), 7.01–6.94 (comp, 2H), 6.68 (d, *J* = 5.2 Hz, 1H), 6.54–6.50 (m, 1H), 6.15 (d, *J* = 8.0 Hz, 1H), 4.45 (d, *J* = 8.0 Hz, 1H), 4.36–4.25 (m, 2H), 4.06 (d, *J* = 8.0 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.8, 173.6, 155.6, 147.8, 146.6, 137.4, 136.3, 135.3, 130.2, 129.7, 129.3, 129.2, 129.0, 128.5, 128.4, 127.7, 126.6, 125.6, 124.4, 123.0, 122.1, 121.7, 121.2, 121.1, 75.1, 56.5, 50.3, 42.4; **HRMS** (ESI, m/z) calcd for $C_{30}H_{23}N_2O_3$ $[M+H]^+$ 459.1709, found 459.1696.

2'-phenethyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3i):



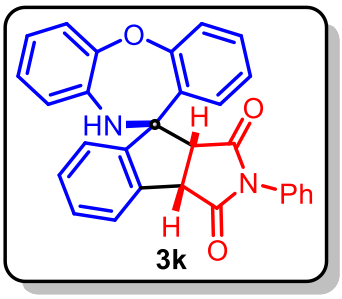
Yield: 89% (84.6 mg); Off-white solid; **R_f** 0.38 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 68-70 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.56–7.46 (comp, 2H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.36–7.30 (comp, 2H), 7.27–7.21 (m, 1H), 7.16–7.13 (comp, 3H), 7.01–6.95 (comp, 4H), 6.79–6.75 (m, 1H), 6.66–6.63 (m, 1H), 6.32 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 4.10 (d, *J* = 8.0 Hz, 1H), 3.79 (br s, 1N-H), 3.48–3.33 (m, 2H), 2.58–2.46 (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.7, 173.8, 156.0, 147.2, 146.2, 137.7, 137.5, 136.2, 130.2, 129.7, 129.52, 129.47, 128.7, 128.5, 128.3, 126.6, 126.4, 125.7, 124.4, 122.7, 122.2, 121.7, 121.2, 120.8, 74.8, 56.3, 50.1, 39.9, 33.1; **HRMS** (ESI, m/z) calcd for $C_{31}H_{25}N_2O_3$ $[M+H]^+$ 473.1865, found 473.1852.

2'-(2-(thiophen-2-yl)ethyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3j):



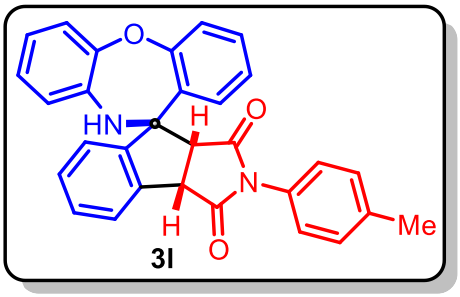
Yield: 61% (58.0 mg); Off-white solid; **R_f** 0.4 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 88-90 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.6 Hz, 1H), 7.55–7.51 (m, 1H), 7.50–7.46 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.34–7.30 (comp, 2H), 7.28–7.23 (m, 1H), 7.04 (dd, *J* = 5.2, 1.2 Hz, 1H), 6.99–6.94 (comp, 2H), 6.81–6.76 (comp, 2H), 6.66–6.62 (m, 1H), 6.61 (dd, *J* = 3.6, 0.8 Hz, 1H), 6.37 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.42 (d, *J* = 8.0 Hz, 1H), 4.12 (d, *J* = 8.0 Hz, 1H), 3.78 (br s, 1N-H), 3.52–3.36 (m, 2H), 2.76–2.72 (m, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.6, 173.8, 156.1, 147.1, 146.1, 139.5, 137.6, 136.2, 130.2, 129.7, 129.5 (x 2), 128.4, 126.8, 126.6, 125.7, 125.5, 124.4, 123.9, 122.7, 122.3, 121.7, 121.3, 120.8, 74.8, 56.3, 50.2, 40, 27.1; **HRMS** (ESI, m/z) calcd for $C_{29}H_{23}N_2O_3S$ $[M+H]^+$ 479.1429, found 479.1419.

2'-phenyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3k):



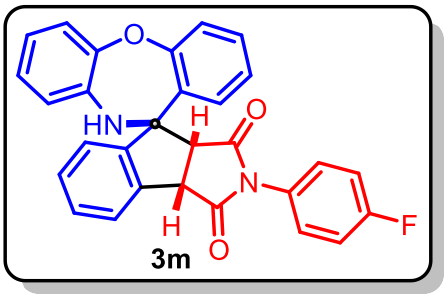
Yield: 85% (75.6 mg); Off-white solid; **R_f** 0.36 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 162-164 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.57–7.53 (m, 1H), 7.52–7.48 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.32–7.26 (comp, 3H), 7.25–7.21 (comp, 3H), 7.04–6.98 (comp, 2H), 6.82–6.77 (comp, 3H), 6.76–6.72 (m, 1H), 6.36 (dd, *J* = 8.0, 1.4 Hz, 1H), 4.59 (d, *J* = 8.4 Hz, 1H), 4.16 (d, *J* = 8.4 Hz, 1H), 3.89 (br s, 1N-H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.9, 173.0, 155.4, 148.2, 146.8, 137.2, 136.3, 131.5, 130.3, 130.0, 129.4, 129.3, 128.8, 128.6, 128.3, 126.4, 126.0, 125.8, 124.3, 123.4, 122.0, 121.8, 121.5, 121.4, 75.7, 57.1, 50.5; **HRMS** (ESI, m/z) calcd for $C_{29}H_{21}N_2O_3$ $[M+H]^+$ 445.1552, found 445.1544.

2'-(*p*-tolyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3l):



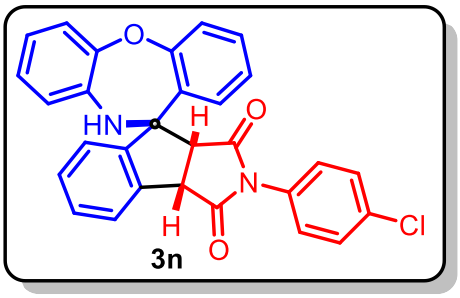
Yield: 70% (64.1 mg); Off-white solid; **R**$_f$ 0.31 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 232-234 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.57–7.53 (m, 1H), 7.51–7.47 (m, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.32–7.27 (comp, 2H), 7.24–7.20 (m, 1H), 7.06 (app d, *J* = 8.4 Hz, 2H), 7.04–6.97 (comp, 2H), 6.80–6.73 (comp, 2H), 6.69 (app d, *J* = 8.4 Hz, 2H), 6.35 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.58 (d, *J* = 8.4 Hz, 1H), 4.14 (d, *J* = 8.4 Hz, 1H), 2.26 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.0, 173.0, 155.4, 148.2, 146.8, 138.3, 137.3, 136.3, 130.3, 130.0, 129.44, 129.40, 129.2, 128.9, 128.7, 126.4, 125.82, 125.78, 124.3, 123.4, 122.0, 121.8, 121.5, 121.4, 75.7, 57.1, 50.5, 21.1; **HRMS** (ESI, m/z) calcd for $C_{30}H_{23}N_2O_3$ $[M+H]^+$ 459.1709, found 459.1712.

2'-(4-fluorophenyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3m):



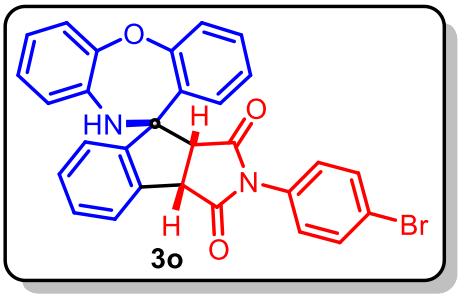
Yield: 56% (52.1 mg); White solid; **R**$_f$ 0.32 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 200-202 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.58–7.53 (m, 1H), 7.52–7.48 (m, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.34–7.28 (comp, 2H), 7.25–7.22 (m, 1H), 7.05–6.99 (comp, 2H), 6.99–6.92 (comp, 2H), 6.81–6.75 (comp, 4H), 6.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.60 (d, *J* = 8.4 Hz, 1H), 4.16 (d, *J* = 8.4 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.8, 172.9, 161.9 (d, *J* = 250.5 Hz), 155.4, 148.2, 146.6, 137.1, 136.1, 130.4, 130.1, 129.5, 129.2, 128.6, 127.8 (d, *J* = 9.0 Hz), 127.4 (d, *J* = 3.0 Hz), 126.4, 125.8, 124.4, 123.6, 122.0, 121.8, 121.6, 121.5, 115.8 (d, *J* = 23.2 Hz), 75.8, 57.1, 50.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –112.4; **HRMS** (ESI, m/z) calcd for $C_{29}H_{20}N_2O_3F$ $[M+H]^+$ 463.1458, found 463.1448.

2'-(4-chlorophenyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3n):



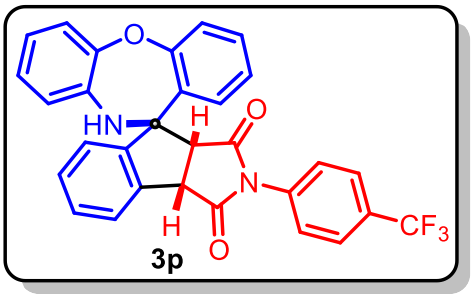
Yield: 60% (57.5 mg); Off-white solid; **R**$_f$ 0.30 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 204-206 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.58–7.53 (m, 1H), 7.50 (m, 1H), 7.42 (d, *J* = 7.2 Hz, 1H), 7.33–7.28 (comp, 2H), 7.25–7.21 (comp, 3H), 7.05–6.98 (comp, 2H), 6.79–6.74 (comp, 4H), 6.32 (dd, *J* = 8.0, 1.4 Hz, 1H), 4.60 (d, *J* = 8.4 Hz, 1H), 4.16 (d, *J* = 8.4 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.6, 172.7, 155.4, 148.2, 146.6, 137.1, 136.1, 134.1, 130.4, 130.1, 129.9, 129.5, 129.2, 129.0, 128.5, 127.2, 126.4, 125.8, 124.4, 123.6, 122.0, 121.8, 121.51, 121.48, 75.8, 57.1, 50.5; **HRMS** (ESI, m/z) calcd for $C_{29}H_{20}N_2O_3Cl$ $[M+H]^+$ 479.1162, found 479.1169.

2'-(4-bromophenyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3o):



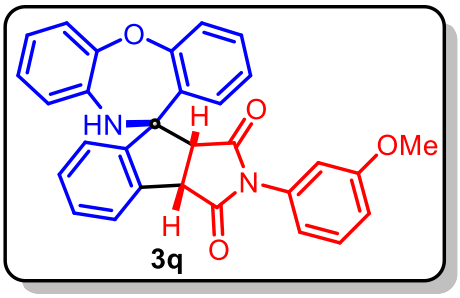
Yield: 59% (61.6 mg); Off-white solid; **R**$_f$ 0.28 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 7:3; **mp:** 214-216 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.58–7.54 (m, 1H), 7.52–7.48 (m, 1H), 7.43–7.37 (comp, 3H), 7.34–7.30 (comp, 2H), 7.25–7.21 (m, 1H), 7.04–6.98 (comp, 2H), 6.79–6.73 (comp, 2H), 6.72–6.68 (comp, 2H), 6.32 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.59 (d, *J* = 8.4 Hz, 1H), 4.16 (d, *J* = 8.4 Hz, 1H), 3.84 (br s, 1N-H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.6, 172.6, 155.4, 148.1, 146.6, 137.0, 136.2, 132.0, 130.5, 130.4, 130.1, 129.5, 129.2, 128.5, 127.5, 126.4, 125.8, 124.4, 123.5, 122.1, 122.0, 121.8, 121.5 (x 2), 75.8, 57.1, 50.5; **HRMS** (ESI, m/z) calcd for $C_{29}H_{20}N_2O_3Br$ $[M+H]^+$ 523.0657, found 523.0662.

2'-(4-(trifluoromethyl)phenyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3p):



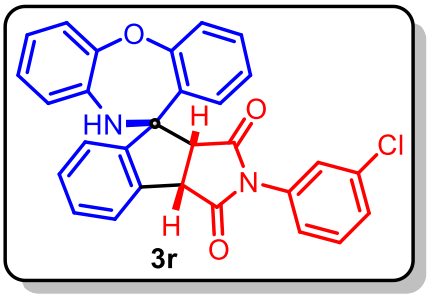
Yield: 50% (53.7 mg); Off-white solid; **R**$_f$ 0.30 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 9:1 to 4:1; **mp:** 210-212 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.59–7.50 (comp, 4H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.34–7.29 (comp, 2H), 7.27–7.22 (m, 1H), 7.05–6.99 (comp, 2H), 6.96 (app d, *J* = 8.4 Hz, 2H), 6.80–6.74 (comp, 2H), 6.34 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.63 (d, *J* = 8.4 Hz, 1H), 4.19 (d, *J* = 8.4 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.4, 172.5, 155.4, 148.1, 146.6, 136.9, 136.2, 134.6, 130.5, 130.21 (d, $^2J_{CF}$ = 32.3 Hz), 130.2, 129.6, 129.2, 128.5, 126.5, 126.2, 125.9 (d, $^3J_{CF}$ = 3.6 Hz), 125.8 (d, $^3J_{CF}$ = 4.0 Hz), 124.4, 123.6 (d, $^1J_{CF}$ = 273.7 Hz), 123.5, 122.0, 121.8, 121.5, 121.4, 75.8, 57.2, 50.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.7; **HRMS** (ESI, m/z) calcd for $C_{30}H_{20}N_2O_3F_3$ $[M+H]^+$ 513.1426, found 513.1420.

2'-(3-methoxyphenyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3q):



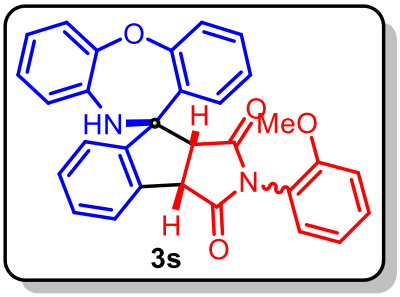
Yield: 62% (58.8 mg); Yellow semi-solid; **R**$_f$ 0.24 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 1:1; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.57–7.53 (m, 1H), 7.50–7.46 (m, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.34–7.30 (comp, 2H), 7.24–7.20 (m, 1H), 7.19–7.14 (m, 1H), 7.06–6.99 (comp, 2H), 6.82–6.77 (comp, 3H), 6.43–6.41 (m, 1H), 6.34 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.28–6.27 (m, 1H), 4.61 (d, *J* = 8.4 Hz, 1H), 4.15 (d, *J* = 8.4 Hz, 1H), 3.66 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.8, 172.9, 159.8, 155.3, 148.2, 146.8, 137.2, 136.2, 132.5, 130.3, 130.0, 129.5, 129.4, 129.2, 128.7, 126.4, 125.8, 124.3, 123.5, 121.9, 121.8, 121.6, 121.4, 118.3, 114.7, 111.5, 75.8, 57.1, 55.3, 50.6; **HRMS** (ESI, m/z) calcd for $C_{30}H_{23}N_2O_3$ $[M+H]^+$ 475.1658, found 475.1662.

2'-(3-chlorophenyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3r):



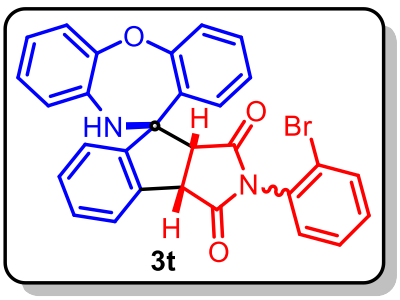
Yield: 72% (68.9 mg); Yellow solid; **R_f** 0.34 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 3:2; **mp:** 192-194 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.58–7.54 (m, 1H), 7.53–7.49 (m, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.34–7.25 (comp, 3H), 7.24–7.17 (comp, 2H), 7.05–6.98 (comp, 2H), 6.82–6.78 (comp, 2H), 6.76–6.72 (comp, 2H), 6.34 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.60 (d, *J* = 8.4 Hz, 1H), 4.17 (d, *J* = 8.4 Hz, 1H), 3.84 (br s, 1N-H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.5, 172.6, 155.4, 148.1, 146.6, 137.0, 136.2, 134.3, 132.5, 130.4, 130.1, 129.7, 129.6, 129.2, 128.5 (x 2), 126.44, 126.35, 125.8, 124.4, 124.2, 123.5, 122.1, 121.8, 121.5, 121.4, 75.8, 57.2, 50.5; **HRMS** (ESI, m/z) calcd for $C_{29}H_{20}N_2O_3Cl$ $[M+H]^+$ 479.1162, found 479.1157.

2'-(2-methoxyphenyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3s):



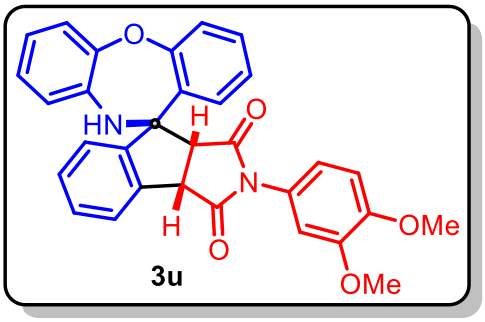
Yield: 69% (dr 5:2) (65.5 mg); Yellow solid; **R_f** 0.31 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 3:2; **mp:** 198-200 °C; **Data for major isomer, ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.57–7.53 (m, 1H), 7.50–7.36 (comp, 2H), 7.31–7.28 (comp, 2H), 7.25–7.19 (comp, 2H), 7.05–6.93 (comp, 2H), 6.87–6.79 (comp, 2H), 6.78–6.70 (comp, 2H), 6.39–6.37 (m, 1H), 6.34 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.64 (d, *J* = 8.4 Hz, 1H), 4.18 (d, *J* = 8.4 Hz, 1H), 3.70 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.8, 172.8, 155.3, 154.5, 148.2, 146.9, 137.4, 130.5, 130.3, 129.9, 129.4, 129.0, 128.8, 128.5, 126.4, 125.9, 124.2, 123.5, 121.8, 121.7, 121.5, 121.4, 121.1, 120.7, 120.6, 111.7, 75.6, 57.5, 55.7, 50.8; **HRMS** (ESI, m/z) calcd for $C_{30}H_{23}N_2O_4$ $[M+H]^+$ 475.1658, found 475.1650.

2'-(2-bromophenyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3t):



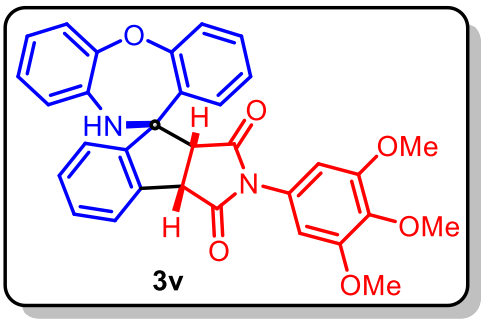
Yield: 64% (dr 3:1) (66.6 mg); Yellow solid; **R_f** 0.31 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 3:2; **mp:** 210-212 °C; **Data for major isomer, ^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.58–7.48 (comp, 3H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.31–7.23 (comp, 3H), 7.20–7.14 (comp, 2H), 7.06–6.99 (comp, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.92–6.88 (m, 1H), 6.86–6.82 (m, 1H), 6.78 (d, *J* = 5.6 Hz, 1H), 6.39–6.36 (comp, 2H), 4.69 (d, *J* = 8.8 Hz, 1H), 4.22 (d, *J* = 8.8 Hz, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 174.0, 172.0, 155.3, 148.1, 146.8, 136.9, 133.2, 130.7, 130.4, 130.1, 130.0, 129.9, 129.5, 129.3, 128.7, 128.2, 127.0, 126.3, 125.9, 124.3, 123.0, 122.0, 121.8, 121.7, 121.5, 121.2, 75.7, 57.7, 50.9; **HRMS** (ESI, m/z) calcd for $C_{29}H_{20}N_2O_3Br$ $[M+H]^+$ 523.0657, found 523.0643.

2'-(3,4-dimethoxyphenyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3u):



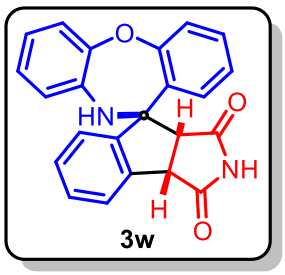
Yield: 71% (71.4 mg); Off-white solid; **R**$_f$ 0.42 (in 50% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 3:2; **mp:** 210-212 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 1H), 7.57–7.53 (m, 1H), 7.51–7.47 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.33–7.31 (m, 1H), 7.29–7.27 (m, 1H), 7.23–7.19 (m, 1H), 7.05–6.98 (comp, 2H), 6.80–6.72 (comp, 3H), 6.41 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.33 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.19 (d, *J* = 2.4 Hz, 1H), 4.57 (d, *J* = 8.4 Hz, 1H), 4.10 (d, *J* = 8.4 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.1, 173.2, 155.3, 148.91 (x 2), 148.86, 148.3, 146.8, 137.2, 136.2, 130.3, 130.0, 129.3, 128.8, 126.4, 125.8, 124.3 (x 2), 123.6, 121.8, 121.7, 121.6, 121.4, 118.6, 110.8, 109.4, 75.8, 57.1, 55.9 (x 2), 50.6; **HRMS** (ESI, m/z) calcd for $C_{31}H_{25}N_2O_5$ $[M+H]^+$ 505.1763, found 505.1752.

2'-(3,4,5-trimethoxyphenyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3v):



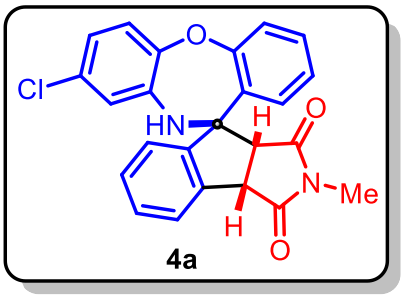
Yield: 63% (67 mg); Off-white solid; **R**$_f$ 0.42 (in 50% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 3:2; **mp:** 198-200 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.58–7.54 (m, 1H), 7.52–7.49 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.34–7.27 (comp, 2H), 7.23–7.18 (m, 1H), 7.06–6.99 (comp, 2H), 6.80–6.76 (comp, 2H), 6.32 (dd, *J* = 8.0, 1.6 Hz, 1H), 5.95 (s, 2H), 4.59 (d, *J* = 8.8 Hz, 1H), 4.10 (d, *J* = 8.4 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 6H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.0, 173.0, 155.2, 153.2, 148.3, 146.8, 137.9, 137.0, 136.2, 130.4, 130.1, 129.3, 129.2, 128.8, 127.0, 126.3, 125.9, 124.3, 123.7, 121.8, 121.7, 121.52, 121.46, 103.8, 75.9, 60.7, 57.2, 56.1, 50.7; **HRMS** (ESI, m/z) calcd for $C_{32}H_{27}N_2O_6$ $[M+H]^+$ 535.1869, found 535.1860.

3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (3w):



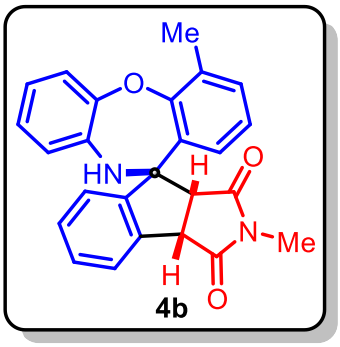
Yield: 65% (48.0 mg); Off-white solid; **R**$_f$ 0.30 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/ethyl acetate = 4:1 to 1:1; **mp:** 192-194 °C; **^{1}H NMR** (600 MHz, DMSO-d_6) δ 11.10 (s, 1N-H), 7.59–7.52 (comp, 3H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.31–7.27 (comp, 2H), 7.08 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.96–6.93 (m, 1H), 6.83–6.80 (m, 1H), 6.73 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.55–6.53 (m, 1H), 6.38 (s, 1N-H), 6.09 (dd, *J* = 7.5, 0.9 Hz, 1H), 4.11 (d, *J* = 7.8 Hz, 1H), 3.95 (d, *J* = 7.2 Hz, 1H); **^{13}C{^{1}H} NMR** (151 MHz, DMSO-d_6) δ 177.9, 175.6, 157.1, 143.9, 143.0, 139.8, 138.4, 137.7, 129.8, 129.6, 128.6, 127.0, 126.4, 124.8, 124.6, 124.4, 121.5, 120.7, 117.7, 116.7, 70.8, 59.8, 50.9; **HRMS** (ESI, m/z) calcd for $C_{23}H_{17}N_2O_3$ $[M+H]^+$ 369.1239, found 369.1247.

8-chloro-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4a):



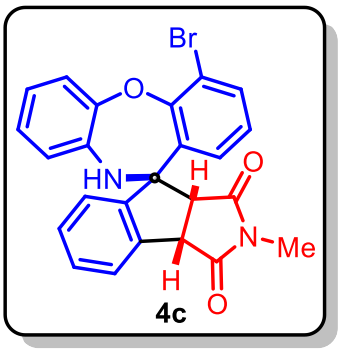
Yield: 64% (53.6 mg); White solid; **R**$_f$ 0.40 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 232-234 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.55–7.51 (m, 1H), 7.50–7.46 (m, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.30–7.25 (comp, 2H), 7.21 (d, *J* = 8.4 Hz, 1H), 6.88–6.82 (comp, 2H), 6.63 (d, *J* = 2.0 Hz, 1H), 6.46–6.44 (m, 1H), 4.46 (d, *J* = 7.6 Hz, 1H), 4.16 (d, *J* = 7.6 Hz, 1H), 2.65 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.8, 173.9, 156.0, 145.5, 145.4, 137.7, 137.3, 130.4, 129.81, 129.77, 129.6, 129.1, 128.0, 126.6, 125.8, 122.8 (x 2), 122.0, 121.2, 119.9, 74.3, 56.6, 50.2, 24.8; **HRMS** (ESI, m/z) calcd for $C_{24}H_{18}N_2O_3Cl$ $[M+H]^+$ 417.1006, found 417.1019.

2',4-dimethyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4b):



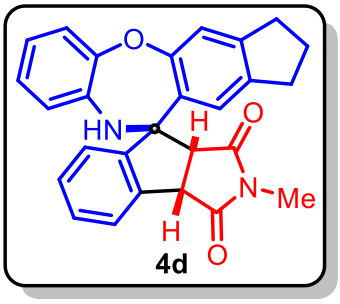
Yield: 67% (53.4 mg); Off-white solid; **R**$_f$ 0.40 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 210-212 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78–7.76 (m, 1H), 7.54–7.48 (comp, 3H), 7.31 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 6.95–6.91 (m, 1H), 6.89–6.85 (m, 1H), 6.80–6.76 (m, 1H), 6.56 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.48 (dd, *J* = 7.8, 1.0 Hz, 1H), 4.46 (d, *J* = 7.6 Hz, 1H), 4.35 (d, *J* = 8.0 Hz, 1H), 3.73 (br s, 1N-H), 2.69 (s, 3H), 2.54 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.0, 174.1, 155.0, 145.8, 145.6, 138.0, 136.8, 131.2, 130.4, 130.3, 130.1, 129.5, 126.9, 125.7, 125.5, 124.6, 122.5, 122.0, 121.3, 119.5, 74.0, 55.9, 50.0, 24.8, 17.2; **HRMS** (ESI, m/z) calcd for $C_{25}H_{21}N_2O_3$ $[M+H]^+$ 397.1552, found 397.1542.

4-bromo-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4c):



Yield: 76% (70.3 mg); Off-white solid; **R**$_f$ 0.30 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 238-240 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 1H), 7.57 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.55–7.47 (comp, 4H), 6.97–6.93 (m, 1H), 6.90–6.86 (m, 1H), 6.80–6.76 (m, 1H), 6.69 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.54 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.48 (d, *J* = 7.6 Hz, 1H), 4.41 (d, *J* = 8.0 Hz, 1H), 3.80 (br s, 1N-H), 2.71 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.8, 173.9, 153.7, 144.9, 144.6, 138.2, 136.2, 133.5, 132.6, 130.4, 129.6, 126.81, 126.77, 125.9, 125.2, 123.9, 122.6, 121.2, 119.2, 116.4, 73.6, 55.5, 49.9, 24.9; **HRMS** (ESI, m/z) calcd for $C_{24}H_{18}N_2O_3Br$ $[M+H]^+$ 461.0501, found 461.0515.

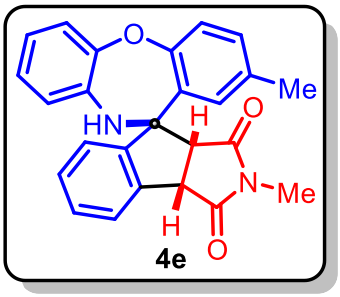
2'-methyl-2,3,3a',8a'-tetrahydro-1*H*,1'*H*,10*H*-spiro[benzo[*b*]indeno[5,6-*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4d):



Yield: 77% (65.2 mg); Off-white solid; **R**$_f$ 0.32 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 198-200 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78–7.77 (m, 1H), 7.54–7.45 (comp, 3H), 7.28–7.25 (m, 1H), 7.18 (s, 1H), 6.94–6.85 (comp, 2H), 6.56 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.39 (s, 1H), 4.46 (d, *J* = 7.6 Hz, 1H), 4.31 (d, *J* = 7.6 Hz, 1H), 2.97–2.81 (m, 2H), 2.69 (s, 3H), 2.68–2.56 (m, 2H), 2.01 (p, *J* = 7.4 Hz, 2H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.1, 174.1, 155.5, 146.8, 146.0, 145.9, 138.7, 137.9, 136.5, 130.1, 129.6, 127.9, 126.9,

125.7, 124.5, 123.0, 121.7, 121.6, 119.9, 117.2, 74.2, 56.3, 50.2, 32.7, 32.2, 25.5, 24.8; **HRMS** (ESI, m/z) calcd for $C_{27}H_{23}N_2O_3$ $[M+H]^+$ 423.1709, found 423.1702.

2,2'-dimethyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4e):



Yield: 82% (64.6 mg); White solid (Crystallization in EtOH under heating using slow diffusion technique); $\mathbf{R_f}$ 0.30 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 114-116 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.55–7.51 (m, 1H), 7.50–7.47 (m, 1H), 7.45–7.42 (m, 1H), 7.29–7.27 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 1H), 7.06 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.96–6.90 (comp, 2H), 6.64–6.59 (m, 1H), 6.23 (d, *J* = 1.6 Hz, 1H), 4.45 (d, *J* = 8.0 Hz, 1H), 4.20 (d, *J* = 8.0 Hz, 1H), 2.68 (s, 3H), 2.09 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.1, 174.1, 154.2, 147.3, 146.0, 137.7, 136.4, 131.9, 130.2, 130.1, 129.7, 129.5, 128.4, 126.7, 125.7, 124.4, 122.3, 121.6, 121.1, 120.5, 74.4, 56.4, 50.2, 24.7, 20.7; **HRMS** (ESI, m/z) calcd for $C_{25}H_{21}N_2O_3$ $[M+H]^+$ 397.1552, found 397.1559.

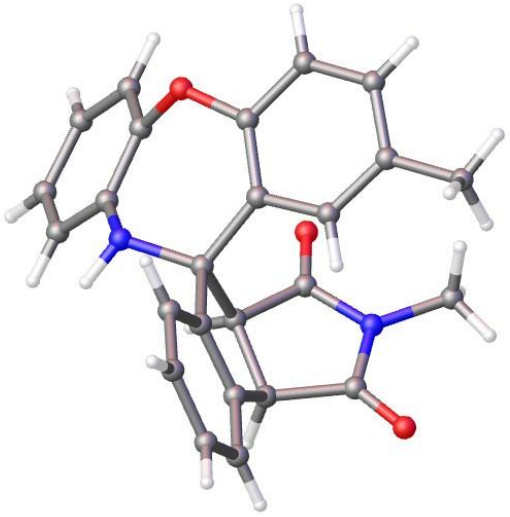
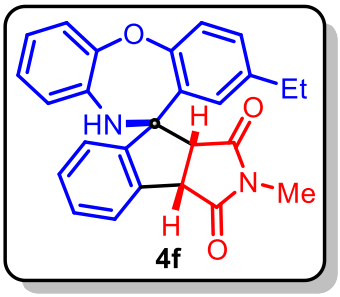


Figure 4. X-ray crystal structure of **4e** (ellipsoid contour at 50% probability level)

Table S3: ***Crystal data and structure refinement for 4e*****, CCDC No. 2554145**

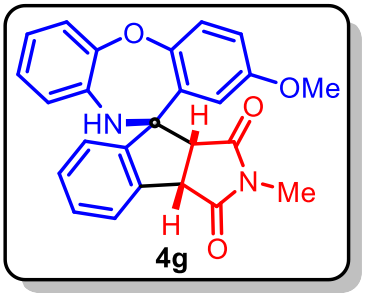
Identification code	IBD_KN_04_191_0m_a	μ/mm^{-1}	0.709
Empirical formula	$C_{25}H_{20}N_2O_3$	F(000)	832.0
Formula weight	396.43	Crystal size/mm^3	0.16 × 0.14 × 0.09
Temperature/K	216.00	Radiation	CuKα (λ = 1.54178)
Crystal system	monoclinic	2Θ range for data collection/°	6.814 to 133.352
Space group	$P2_1/c$	Index ranges	-15 ≤ h ≤ 15, -11 ≤ k ≤ 11, -19 ≤ l ≤ 19
a/Å	13.1329(5)	Reflections collected	24611
b/Å	9.5274(4)	Independent reflections	3509 [R_{int} = 0.0649, R_{sigma} = 0.0460]
c/Å	16.0526(6)	Data/restraints/parameters	3509/0/287
α/°	90	Goodness-of-fit on F^2	1.048
β/°	98.948(2)	Final R indexes [I>=2σ (I)]	R_1 = 0.0432, wR_2 = 0.1095
γ/°	90	Final R indexes [all data]	R_1 = 0.0475, wR_2 = 0.1130
Volume/Å^3	1984.10(14)	Largest diff. peak/hole / e Å^{-3}	0.17/-0.22
Z	4	Flack parameter	0.709
ρ_{calc}g/cm^3	1.327		

2-ethyl-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4f):



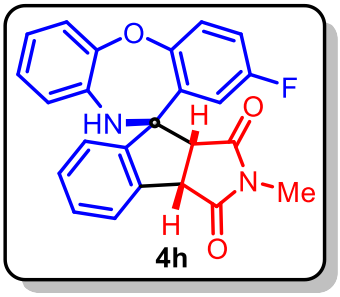
Yield: 79% (64.6 mg); Off-white solid; **R**$_f$ 0.30 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 80-82 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 1H), 7.55–7.51 (m, 1H), 7.49–7.46 (m, 1H), 7.41 (d, *J* = 7.2 Hz, 1H), 7.31–7.28 (m, 1H), 7.22 (d, *J* = 8.0 Hz, 1H), 7.07 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.97–6.93 (comp, 2H), 6.71–6.63 (m, 1H), 6.16 (d, *J* = 2.0 Hz, 1H), 4.45 (d, *J* = 8.0 Hz, 1H), 4.15 (d, *J* = 7.6 Hz, 1H), 2.66 (s, 3H), 2.36 (q, *J* = 7.6 Hz, 2H), 1.00 (t, *J* = 7.6 Hz, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.1, 174.0, 154.1, 147.7, 146.3, 138.2, 137.6, 136.4, 130.2, 129.7, 129.2, 128.8, 127.4, 126.6, 125.7, 124.4, 122.7, 121.7, 121.1, 120.8, 74.7, 56.6, 50.3, 28.0, 24.7, 15.7; **HRMS** (ESI, m/z) calcd for $C_{26}H_{23}N_2O_3$ $[M+H]^+$ 411.1709, found 411.1702.

2-methoxy-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4g):



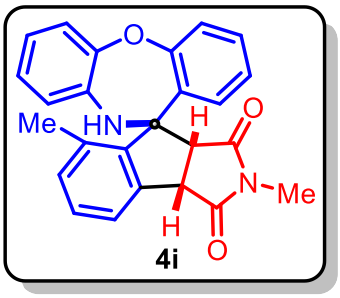
Yield: 76% (62.4 mg); Off-white solid; **R**$_f$ 0.24 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 110-112 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 6.8 Hz, 1H), 7.54–7.48 (comp, 3H), 7.28–7.24 (comp, 2H), 6.95–6.87 (comp, 2H), 6.80 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.58 (d, *J* = 7.2 Hz, 1H), 6.10 (d, *J* = 2.8 Hz, 1H), 4.46 (d, *J* = 7.6 Hz, 1H), 4.29 (d, *J* = 8.0 Hz, 1H), 3.58 (s, 3H), 2.71 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.0, 174.0, 154.7, 150.7, 146.8, 145.5, 137.9, 136.3, 131.1, 130.3, 129.7, 126.7, 125.8, 124.5, 122.0, 121.9, 121.6, 120.1, 114.2, 113.5, 74.0, 56.1, 55.4, 50.1, 24.8; **HRMS** (ESI, m/z) calcd for $C_{25}H_{21}N_2O_4$ $[M+H]^+$ 413.1501, found 413.1504.

2-fluoro-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4h):



Yield: 66% (52.6 mg); Yellow solid; **R**$_f$ 0.28 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 214-216 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.2 Hz, 1H), 7.56–7.45 (comp, 3H), 7.29–7.27 (comp, 2H), 6.99–6.89 (comp, 3H), 6.59 (dd, *J* = 7.2, 1.6 Hz, 1H), 6.29 (dd, *J* = 9.8, 3.0 Hz, 1H), 4.46 (d, *J* = 7.6 Hz, 1H), 4.25 (d, *J* = 8.0 Hz, 1H), 3.76 (br s, 1N-H), 2.72 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.8, 173.9, 157.7 (d, $^1J_{CF}$ = 241.8 Hz), 152.7 (d, $^4J_{CF}$ = 1.7 Hz), 146.4, 145.1, 137.9, 136.1, 131.6 (d, $^3J_{CF}$ = 6.8 Hz), 130.5, 129.9, 126.6, 125.8, 124.7, 122.6 (d, $^3J_{CF}$ = 8.4 Hz), 122.2, 121.7, 120.2, 116.0 (d, $^2J_{CF}$ = 22.9 Hz), 114.5 (d, $^2J_{CF}$ = 25.5 Hz), 73.8, 55.9, 50.0, 24.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –119.4; **HRMS** (ESI, m/z) calcd for $C_{24}H_{18}N_2O_3F$ $[M+H]^+$ 401.1301, found 401.1306.

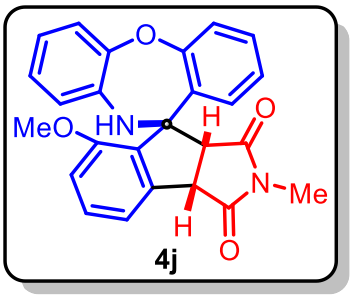
2',7'-dimethyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4i):



Yield: 79% (62.4 mg); White solid; **R**$_f$ 0.38 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 206-208 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.6 Hz, 1H), 7.41 (app t, *J* = 7.6 Hz, 1H), 7.35 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.28 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.22–7.18 (comp, 2H), 7.08–7.00 (comp, 2H), 6.78 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.70–6.66 (m, 1H), 6.06 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.39 (d, *J* = 8.4 Hz, 1H), 3.86 (d, *J* = 8.4 Hz, 1H), 2.59 (s, 3H), 2.10 (s, 3H); **^{13}C{^{1}H}**

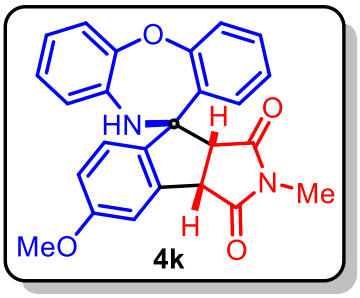
NMR (101 MHz, $CDCl_3$) δ 176.3, 174.2, 154.2, 149.4, 144.8, 137.2, 137.1, 136.6, 132.4, 130.2, 129.0, 127.74, 127.71, 124.3, 124.0, 123.0, 122.2, 121.8, 121.7, 121.2, 76.1, 57.5, 50.5, 24.6, 18.6; **HRMS** (ESI, m/z) calcd for $C_{25}H_{21}N_2O_3$ $[M+H]^+$ 397.1552, found 397.1544.

7'-methoxy-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4j):



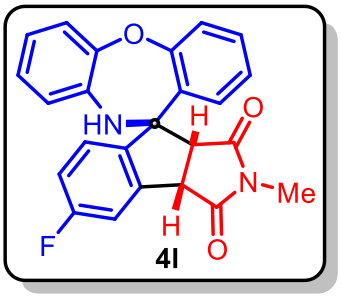
Yield: 89% (73.2 mg); Yellow solid; **R_f** 0.24 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 202-204 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (app t, *J* = 8.0 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 1H), 7.32–7.27 (comp, 2H), 7.22–7.18 (m, 1H), 7.00–6.96 (comp, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.79–6.70 (comp, 2H), 6.27 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.42 (d, *J* = 8.4 Hz, 1H), 4.08 (d, *J* = 8.0 Hz, 1H), 3.64 (s, 3H), 2.62 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.0, 174.0, 156.5, 155.4, 149.5, 139.1, 136.7, 133.5, 131.9, 129.2, 129.0, 127.5, 124.4, 123.3, 122.4, 122.1, 121.6, 121.1, 117.6, 112.0, 74.9, 57.2, 55.6, 50.7, 24.7; **HRMS** (ESI, m/z) calcd for $C_{25}H_{21}N_2O_4$ $[M+H]^+$ 413.1501, found 413.1508.

5'-methoxy-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4k):



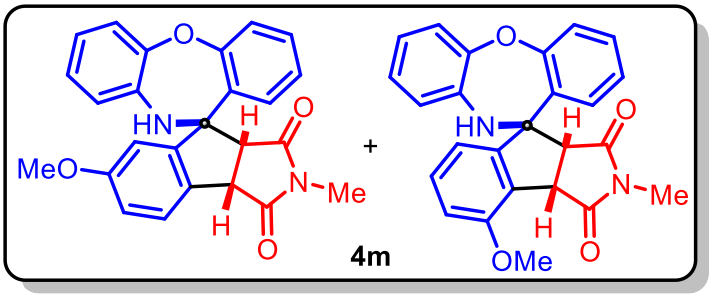
Yield: 88% (72.9 mg); Yellow solid; **R_f** 0.24 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 194-196 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.27 (comp, 4H), 7.24 (d, *J* = 2.4 Hz, 1H), 7.01 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.97–6.92 (comp, 2H), 6.84–6.80 (m, 1H), 6.64–6.62 (m, 1H), 6.47 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 7.6 Hz, 1H), 3.90 (s, 3H), 2.66 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.0, 174.1, 161.4, 156.2, 147.0, 139.2, 138.0, 136.3, 130.0, 129.5, 128.1, 127.4, 124.5, 122.44, 122.39, 121.8, 121.3, 120.6, 117.3, 109.0, 74.0, 56.8, 55.7, 50.2, 24.8; **HRMS** (ESI, m/z) calcd for $C_{25}H_{21}N_2O_4$ $[M+H]^+$ 413.1501, found 413.1491.

5'-fluoro-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4l):



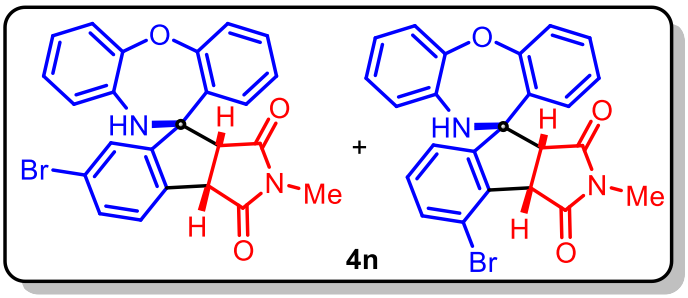
Yield: 88% (70.3 mg); White solid; **R_f** 0.32 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 204-206 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.35 (dd, *J* = 8.6, 5.0 Hz, 1H), 7.32–7.29 (comp, 2H), 7.27–7.23 (m, 1H), 7.19–7.14 (m, 1H), 7.00–6.96 (comp, 2H), 6.82–6.78 (m, 1H), 6.70–6.66 (m, 1H), 6.31 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.41 (d, *J* = 8.0 Hz, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 2.65 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.4, 173.7, 163.9 (d, $^1J_{CF}$ = 250.0 Hz), 155.8, 147.7, 142.0 (d, $^4J_{CF}$ = 2.0 Hz), 139.6 (d, $^3J_{CF}$ = 9.1 Hz), 136.0, 129.6, 129.2, 128.1, 128.0, 124.5, 123.2, 122.3, 121.8, 121.4, 121.1, 117.4 (d, $^2J_{CF}$ = 23.1 Hz), 112.5 (d, $^2J_{CF}$ = 23.0 Hz), 74.2, 57.0, 50.0, 24.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –110.3; **HRMS** (ESI, m/z) calcd for $C_{24}H_{18}N_2O_3F$ $[M+H]^+$ 401.1301, found 401.1304.

6'-methoxy-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4m) and **4'-methoxy-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione:**



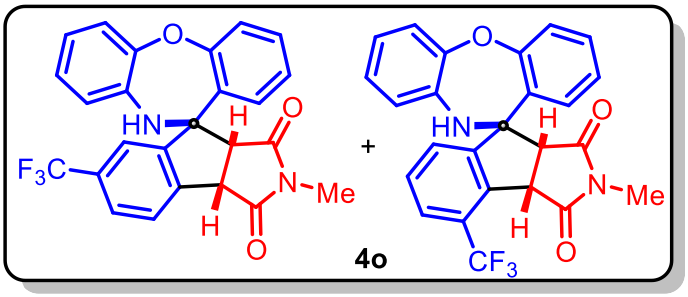
Combined yield: 79% (regioisomeric ratio, 100:23) (65.2 mg); Off-white solid; **R$_f$** 0.28 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 72-74 °C; Data for major isomer, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 1H), 7.32–7.28 (comp, 2H), 7.26–7.22 (m, 1H), 7.07 (dd, *J* = 8.6, 2.6 Hz, 1H), 7.01–6.96 (comp, 2H), 6.86 (d, *J* = 2.4 Hz, 1H), 6.81–6.77 (m, 1H), 6.72–6.67 (m, 1H), 6.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.35 (d, *J* = 8.0 Hz, 1H), 4.07 (d, *J* = 8.4 Hz, 1H), 3.77 (s, 3H), 3.02 (s, 0.69H), 2.62 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 176.4, 174.1, 161.2, 155.7, 147.8, 147.7, 136.3, 134.2, 129.4, 129.3, 129.2, 128.4, 126.4, 124.4, 123.1, 122.2, 121.7, 121.3, 121.2, 117.7, 110.2, 74.9, 57.3, 55.7, 49.6, 24.6; **HRMS** (ESI, m/z) calcd for $C_{25}H_{21}N_2O_4$ $[M+H]^+$ 413.1501, found 413.1490.

6'-bromo-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4n) and **4'-bromo-2'-methyl-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione:**



Combined yield: 61% (regioisomeric ratio, 100:6) (56.6 mg); Off-white solid; **R$_f$** 0.30 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 202-204 °C; Data for major isomer, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (app d, *J* = 0.8 Hz, 2H), 7.53 (s, 1H), 7.32–7.24 (comp, 3H), 7.02–6.96 (comp, 2H), 6.84–6.80 (m, 1H), 6.70–6.67 (m, 1H), 6.29 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.37 (d, *J* = 8.0 Hz, 1H), 4.08 (d, *J* = 8.0 Hz, 1H), 2.64 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.5, 173.7, 155.7, 148.4, 147.9, 136.4, 136.0, 133.5, 129.6 (x 2), 128.8, 128.1, 127.2, 124.5, 123.6, 123.3, 122.4, 121.8, 121.4, 121.2, 74.7, 56.9, 49.8, 24.8; **HRMS** (ESI, m/z) calcd for $C_{24}H_{18}N_2O_3Br$ $[M+H]^+$ 461.0501, found 461.0512.

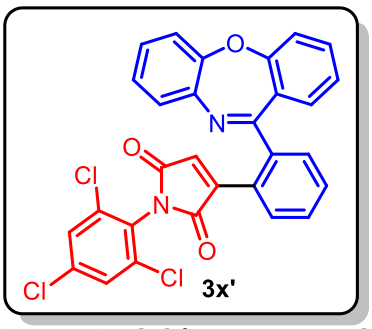
2'-methyl-6'-(trifluoromethyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione (4o) and **2'-methyl-4'-(trifluoromethyl)-3a',8a'-dihydro-1'*H*,10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,8'-indeno[1,2-*c*]pyrrole]-1',3'(2'*H*)-dione:**



Combined yield: 49% (regioisomeric ratio, 100:15) (44.1 mg); Pale yellow solid; **R$_f$** 0.30 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1 to 3:2; **mp:** 228-230 °C; Data for major isomer, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.67 (s, 1H), 7.34–7.31 (comp, 2H), 7.29–7.25 (m, 1H), 7.04–6.97 (comp, 2H), 6.83–6.79 (m, 1H), 6.71–6.69 (m, 1H), 6.22–6.20 (dd, *J* = 7.8, 1.4 Hz, 1H), 4.48 (d, *J* = 8.4 Hz, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 3.76 (br s, 1N-H), 2.65 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 175.1, 173.5, 155.7, 148.0, 147.2, 141.2, 136.0, 132.4 (d, $^2J_{CF}$ = 32.6 Hz), 129.8, 128.6, 128.0, 127.3 (d, $^3J_{CF}$ = 3.0 Hz), 126.4, 124.6, 123.8–123.7 (m), 123.7 (d, $^1J_{CF}$ = 273.7 Hz), 123.5, 122.4, 121.8, 121.6, 121.3, 74.8, 56.8, 50.2, 24.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –62.2, –62.6; **HRMS** (ESI, m/z) calcd for $C_{25}H_{18}N_2O_3F_3$ $[M+H]^+$ 451.1270, found 451.1263.

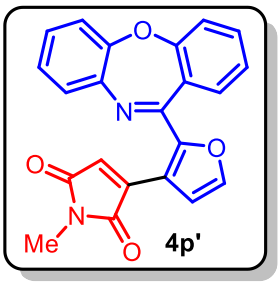
Characterization data of representative by-products:

3-(2-(dibenzo[*b,f*][1,4]oxazepin-11-yl)phenyl)-1-(2,4,6-trichlorophenyl)-1*H*-pyrrole-2,5-dione (3x′):



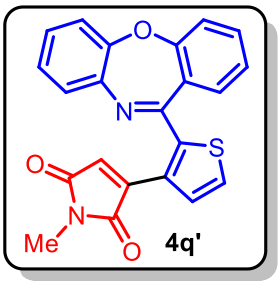
Yield: 16% (17.2 mg); Off-white solid; **R_f** 0.53 (in 40% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 7:3; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72–7.68 (m, 1H), 7.67–7.64 (m, 1H), 7.62–7.58 (comp, 2H), 7.48–7.41 (comp, 2H), 7.38 (app s, 2H), 7.22–7.18 (comp, 3H), 7.17–7.11 (comp, 2H), 7.09–7.07 (m, 1H), 7.04 (s, 1H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.6, 167.2, 167.1, 161.7, 152.1, 146.9, 141.8, 140.2, 136.3, 136.2, 133.6, 131.1, 131.0, 130.9, 130.6, 129.8, 128.6 (x 2), 128.5, 128.4, 127.8, 127.7, 126.8, 125.5, 125.0, 121.0, 120.7; **HRMS** (ESI, m/z) calcd for $C_{29}H_{16}N_2O_3Cl_3$ $[M+H]^+$ 545.0227, found 545.0232.

3-(2-(dibenzo[*b,f*][1,4]oxazepin-11-yl)furan-3-yl)-1-methyl-1*H*-pyrrole-2,5-dione (4p′):



Yield: 24% (17.6 mg); Yellow gel; **R_f** 0.24 (in 20% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 4:1; **Recovered SM (S-1x):** 39.8 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.0 Hz, 1H), 7.52–7.48 (m, 1H), 7.28– 7.24 (comp, 5H), 7.22–7.17 (comp, 4H), 7.14 (d, *J* = 1.6 Hz, 1H), 3.07 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 170.9, 170.4, 161.6, 157.1, 152.5, 152.3, 143.9, 140.1, 137.8, 133.5, 130.4, 128.6, 127.8, 127.6, 126.1, 125.9, 124.8, 121.0, 120.9, 117.1, 113.3, 23.9; **HRMS** (ESI, m/z) calcd for $C_{22}H_{15}N_2O_4$ $[M+H]^+$ 371.1032, found 371.1023.

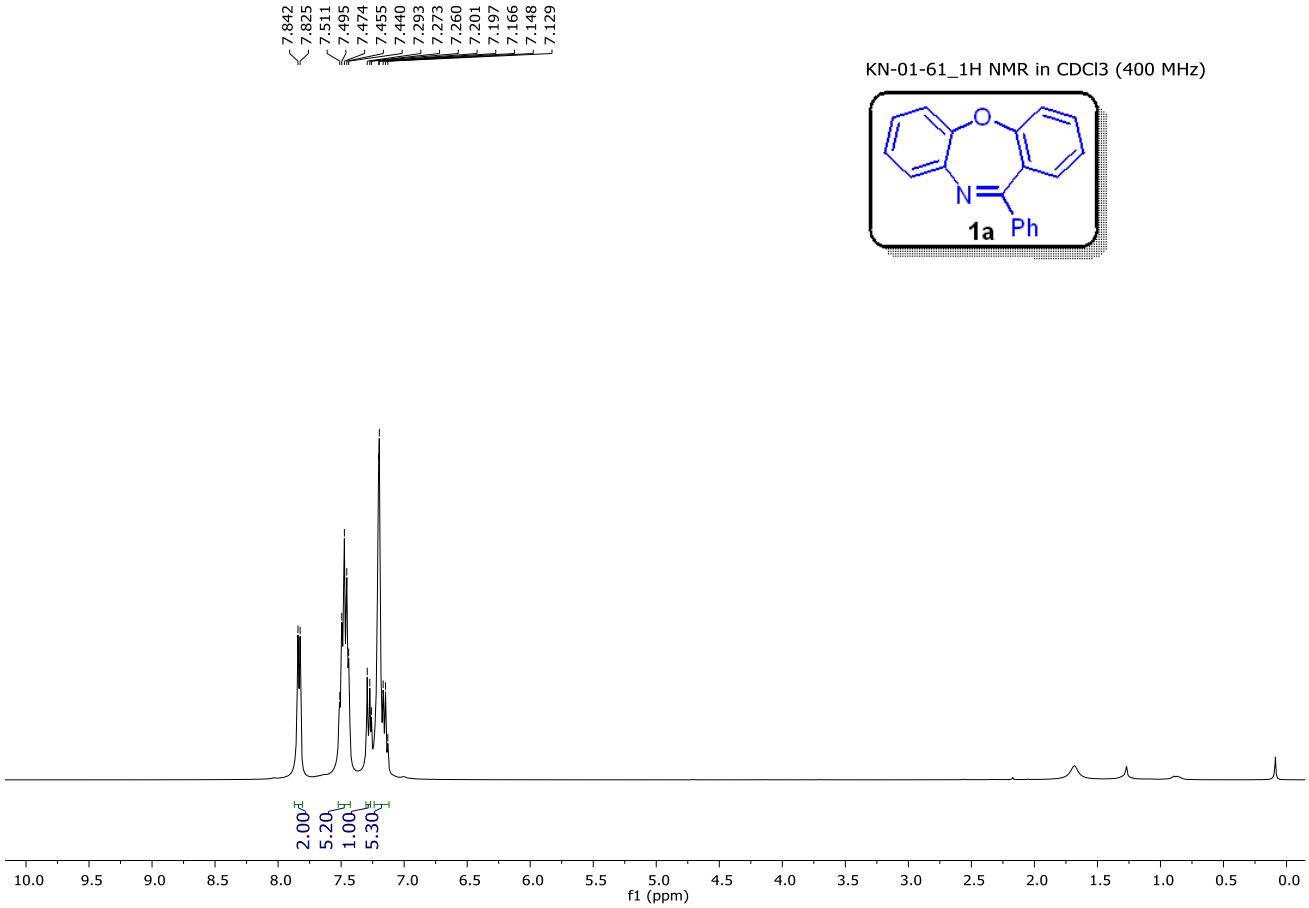
3-(2-(dibenzo[*b,f*][1,4]oxazepin-11-yl)thiophen-3-yl)-1-methyl-1*H*-pyrrole-2,5-dione (4q′):



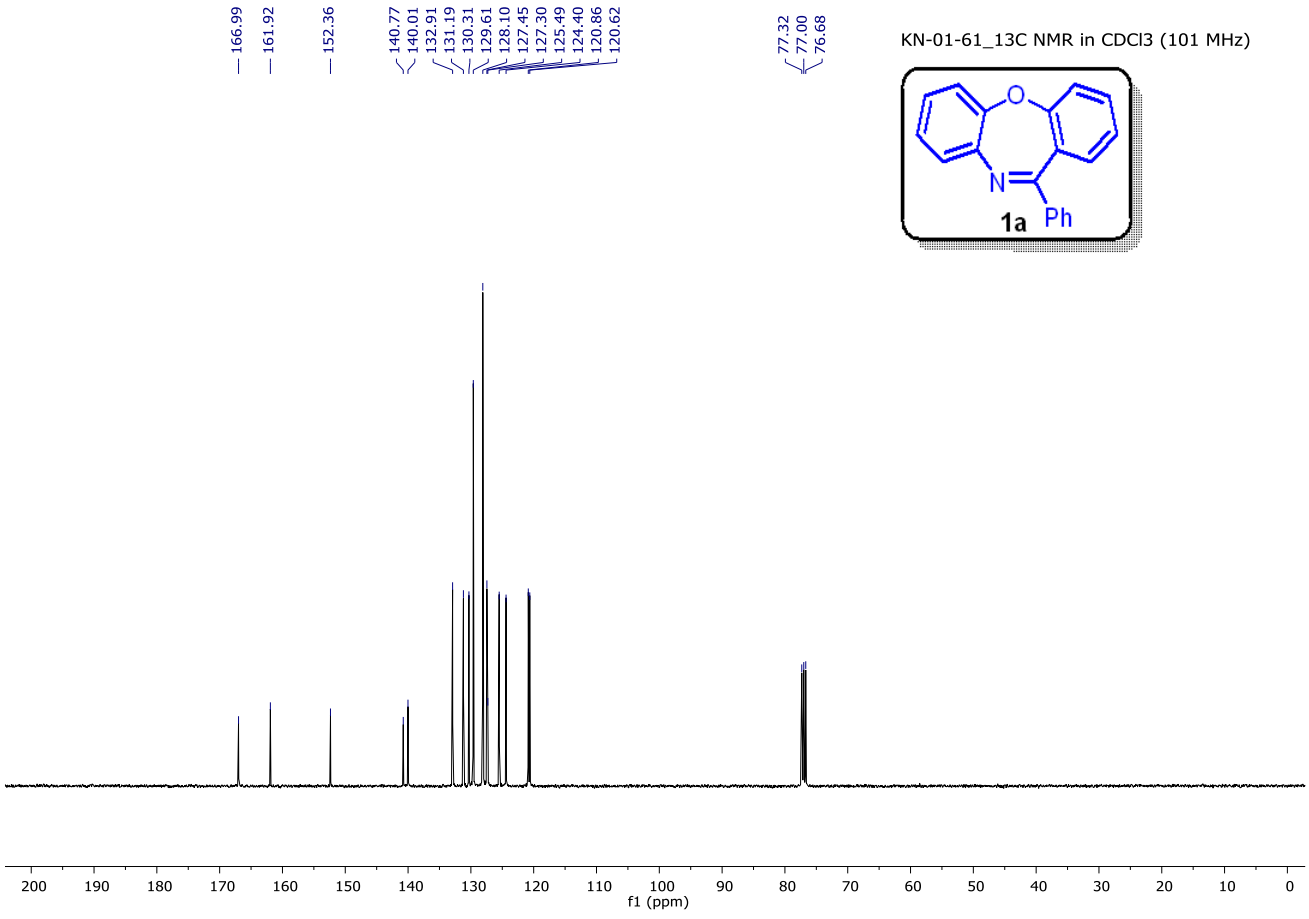
Yield: 15% (11.5 mg); Dark yellow gel; **R_f** 0.25 (in 20% EtOAc/petroleum ether); **Eluent composition:** petroleum ether/EtOAc = 7:3; **Recovered SM (S-1y):** 42.3 mg; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 5.2 Hz, 1H), 7.46–7.42 (m, 1H), 7.36 (d, *J* = 5.2 Hz, 1H), 7.25–7.20 (comp, 3H), 7.20–7.15 (comp, 3H), 7.06 (m, 1H), 6.51 (s, 1H), 2.94 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 170.2, 169.8, 161.9, 160.7, 152.2, 145.2, 141.3, 140.2, 133.7, 130.4, 129.7, 129.4, 128.5, 128.3, 128.0, 127.4, 126.3, 125.8, 124.8, 121.0, 120.8, 23.8; **HRMS** (ESI, m/z) calcd for $C_{22}H_{15}N_2O_3S$ $[M+H]^+$ 387.0803, found 387.0801.

^{1}H, ^{13}C and ^{19}F NMR spectra of dibenzo[*b,f*][1,4]oxazepines (Starting materials):

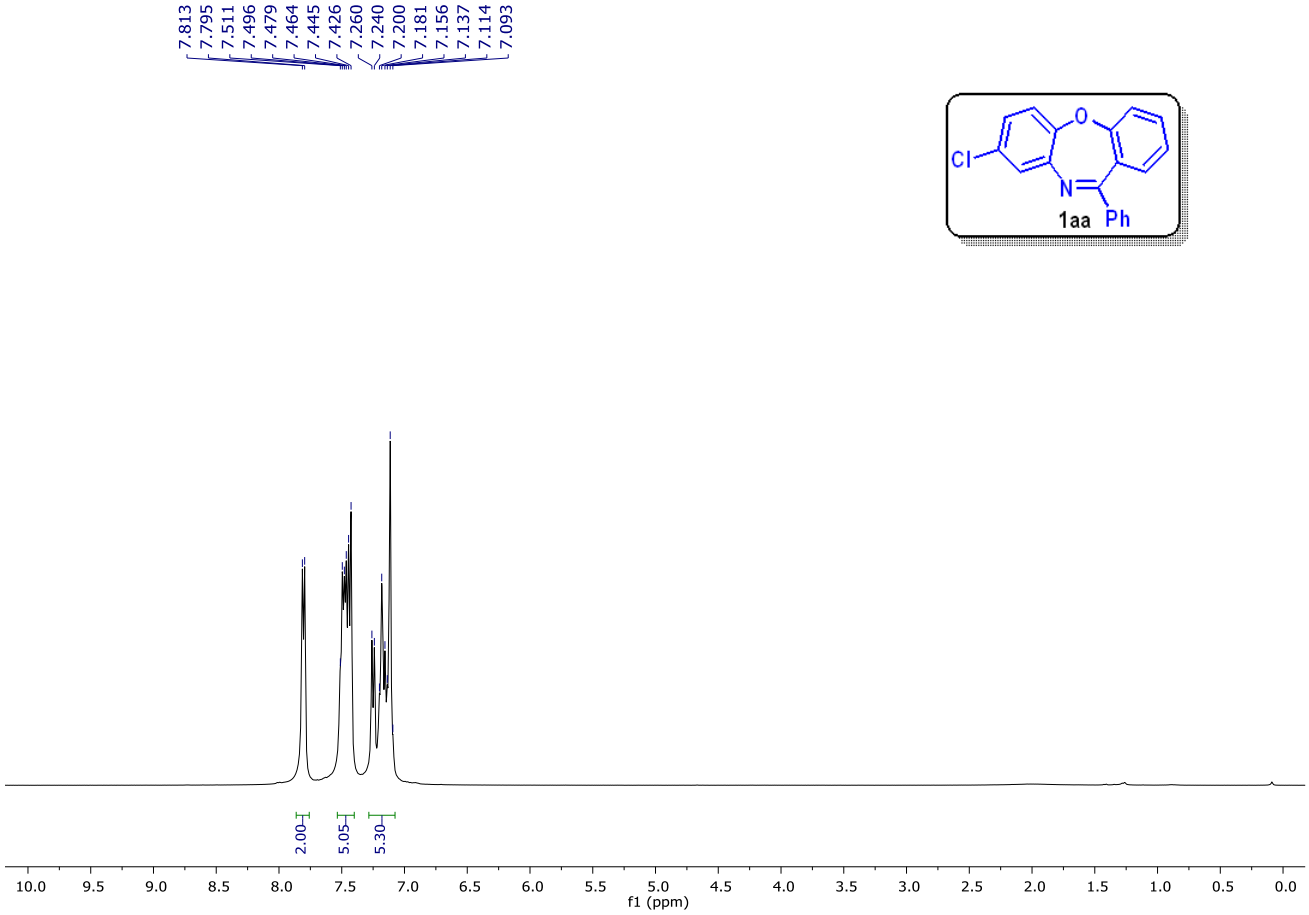
^{1}H NMR of 1a (400 MHz, $CDCl_3$):



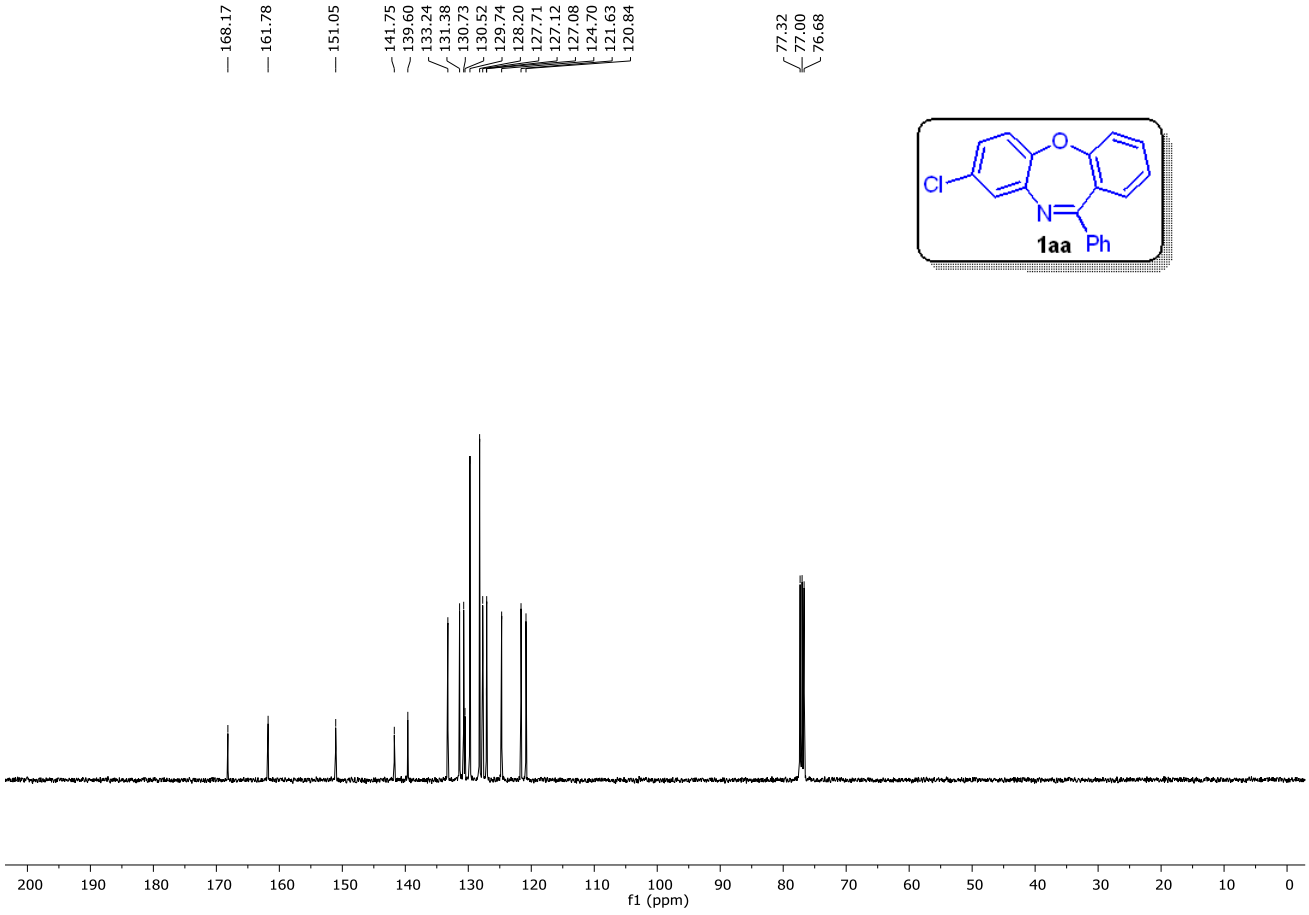
^{13}C{^{1}H} NMR of 1a (101 MHz, $CDCl_3$):



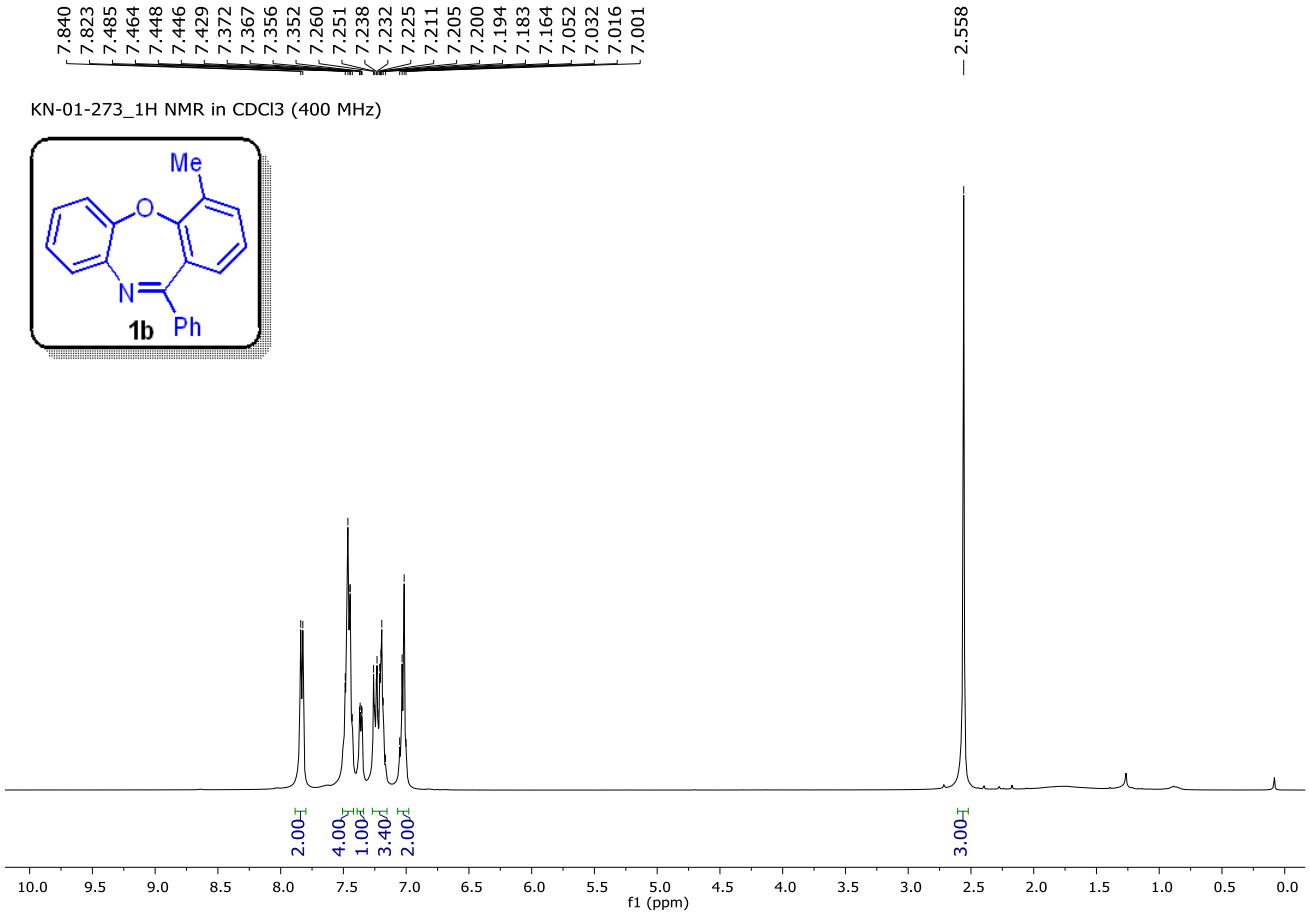
^{1}H NMR of 1aa (400 MHz, $CDCl_3$):



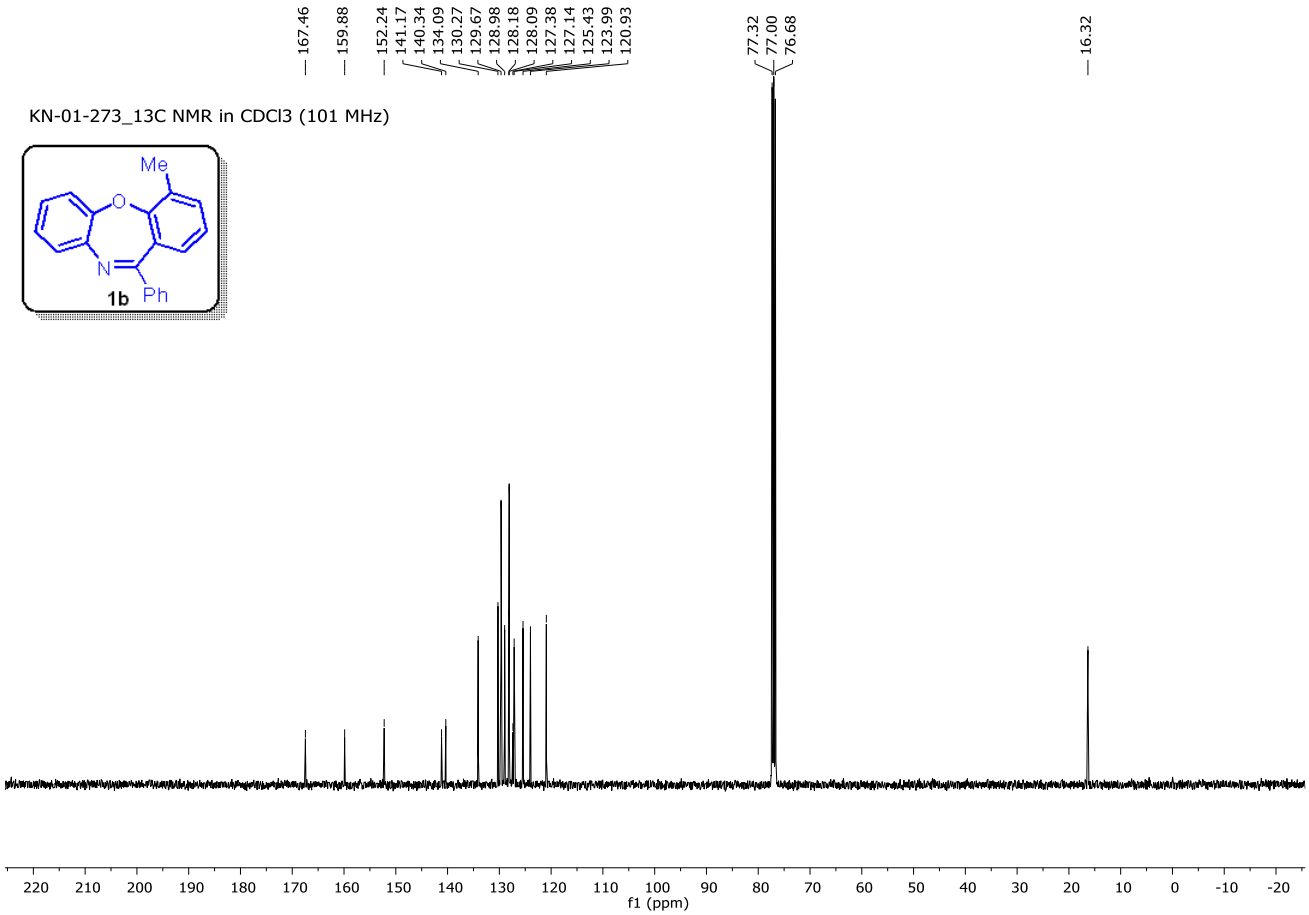
^{13}C{^{1}H} NMR of 1aa (101 MHz, $CDCl_3$):



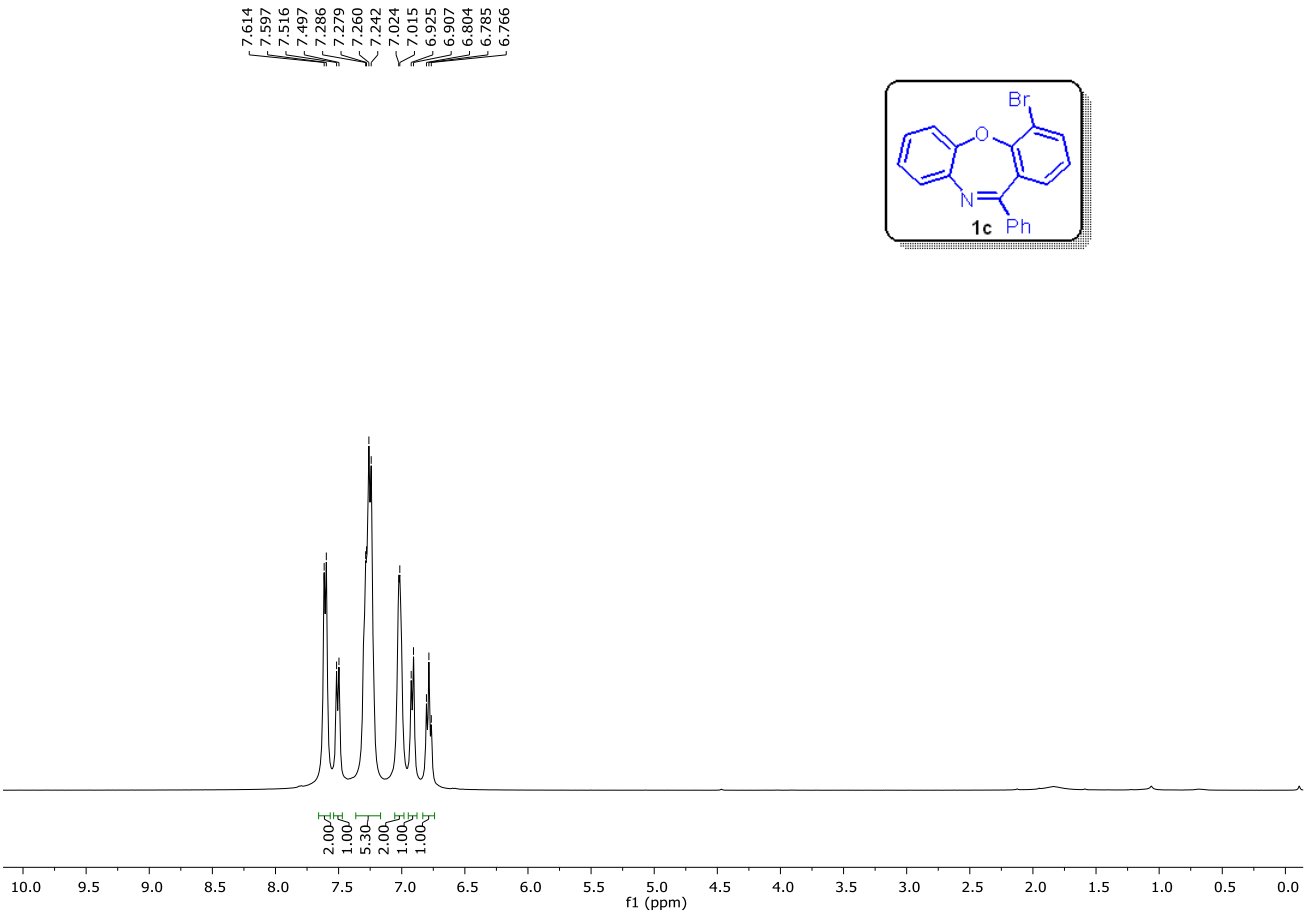
^{1}H NMR of 1b (400 MHz, $CDCl_3$):



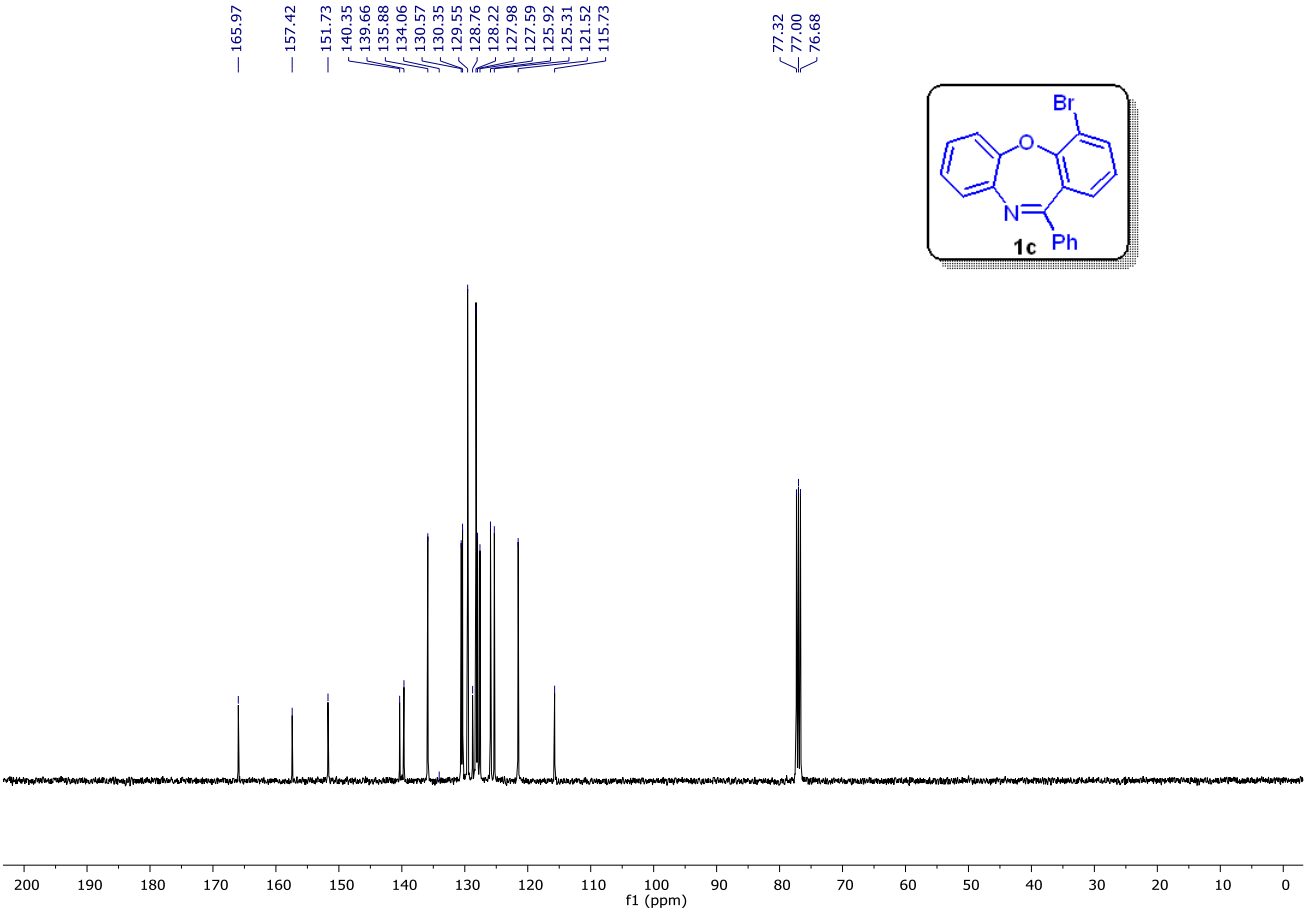
^{13}C{^{1}H} NMR of 1b (101 MHz, $CDCl_3$):



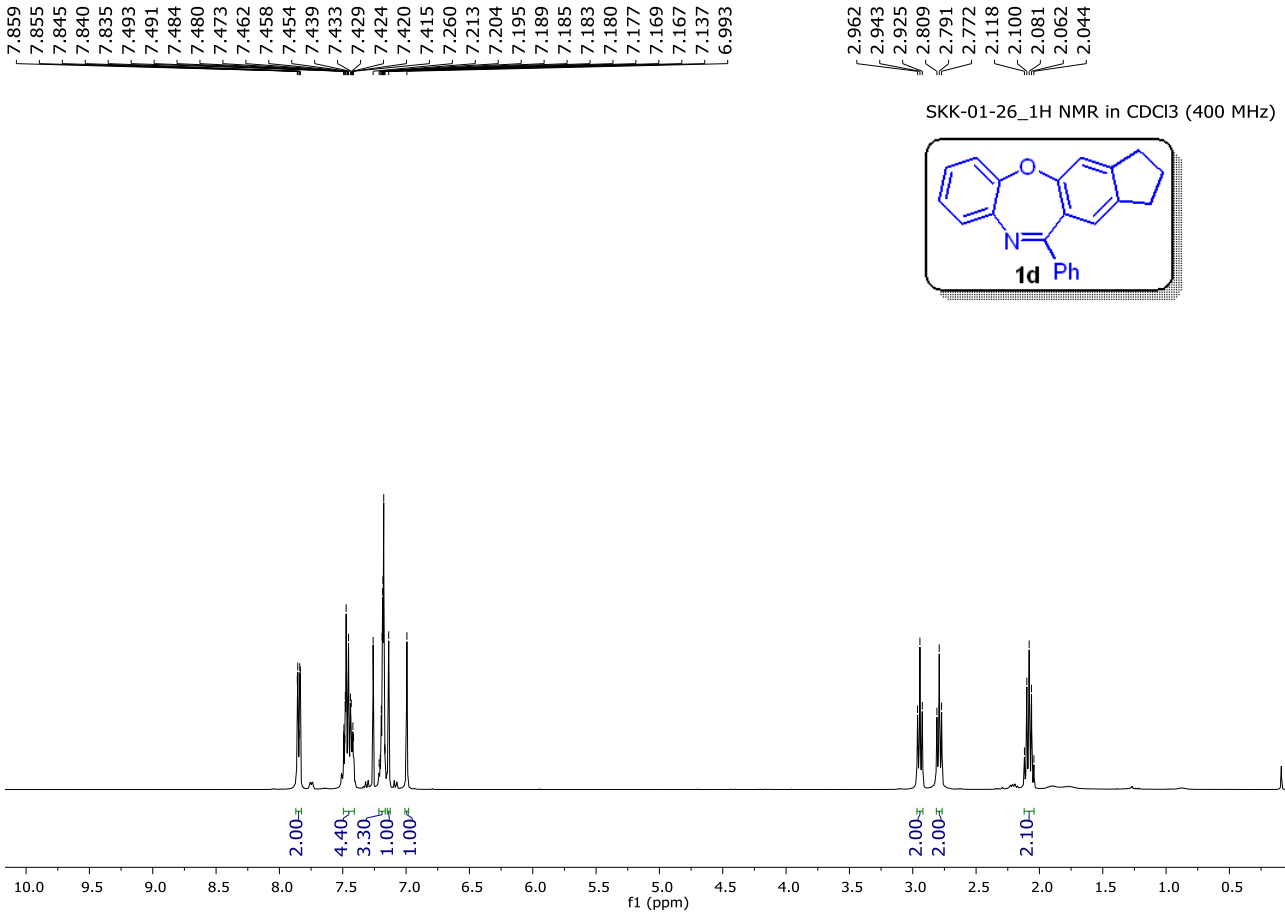
^{1}H NMR of 1c (400 MHz, $CDCl_3$):



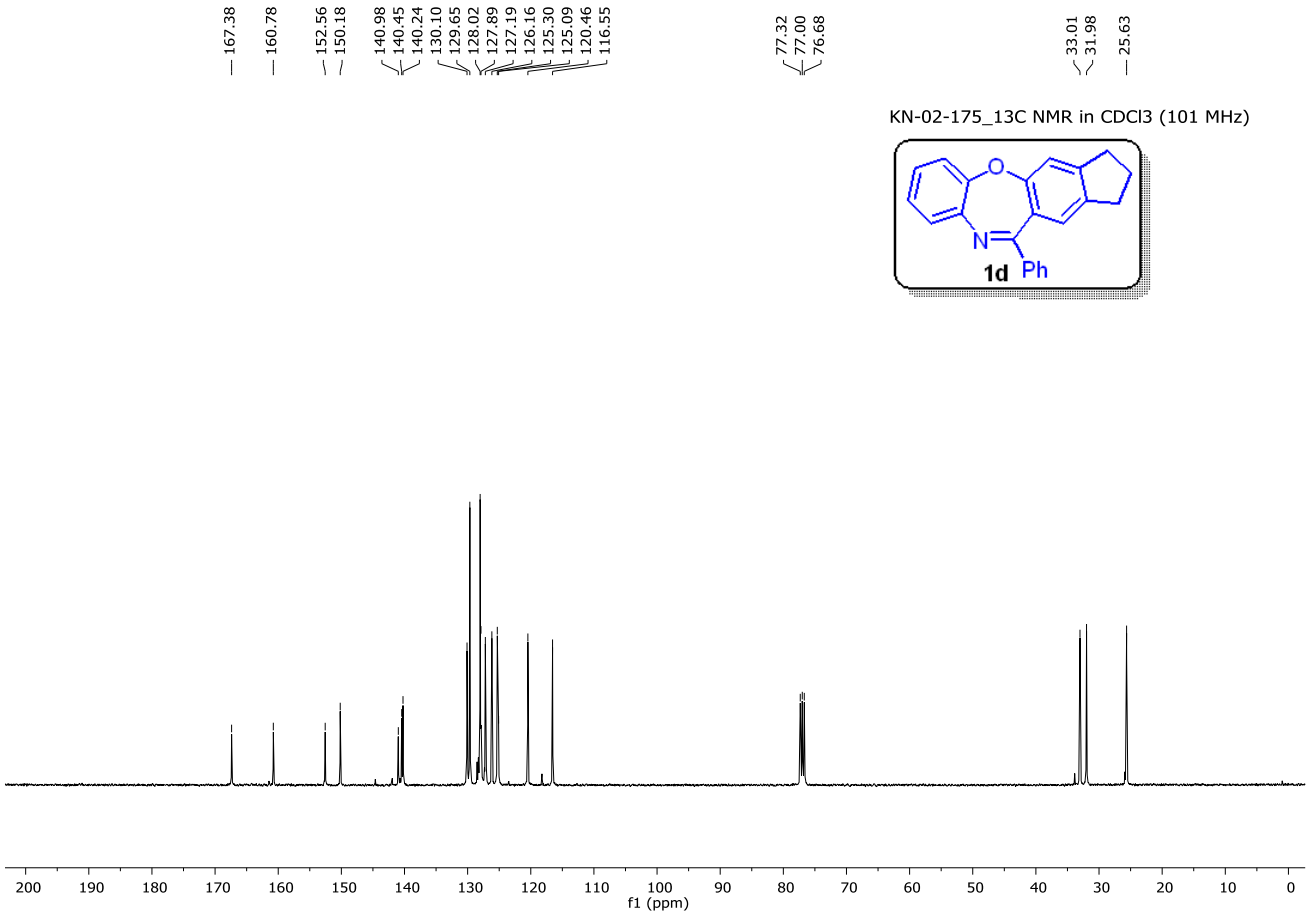
^{13}C{^{1}H} NMR of 1c (101 MHz, $CDCl_3$):



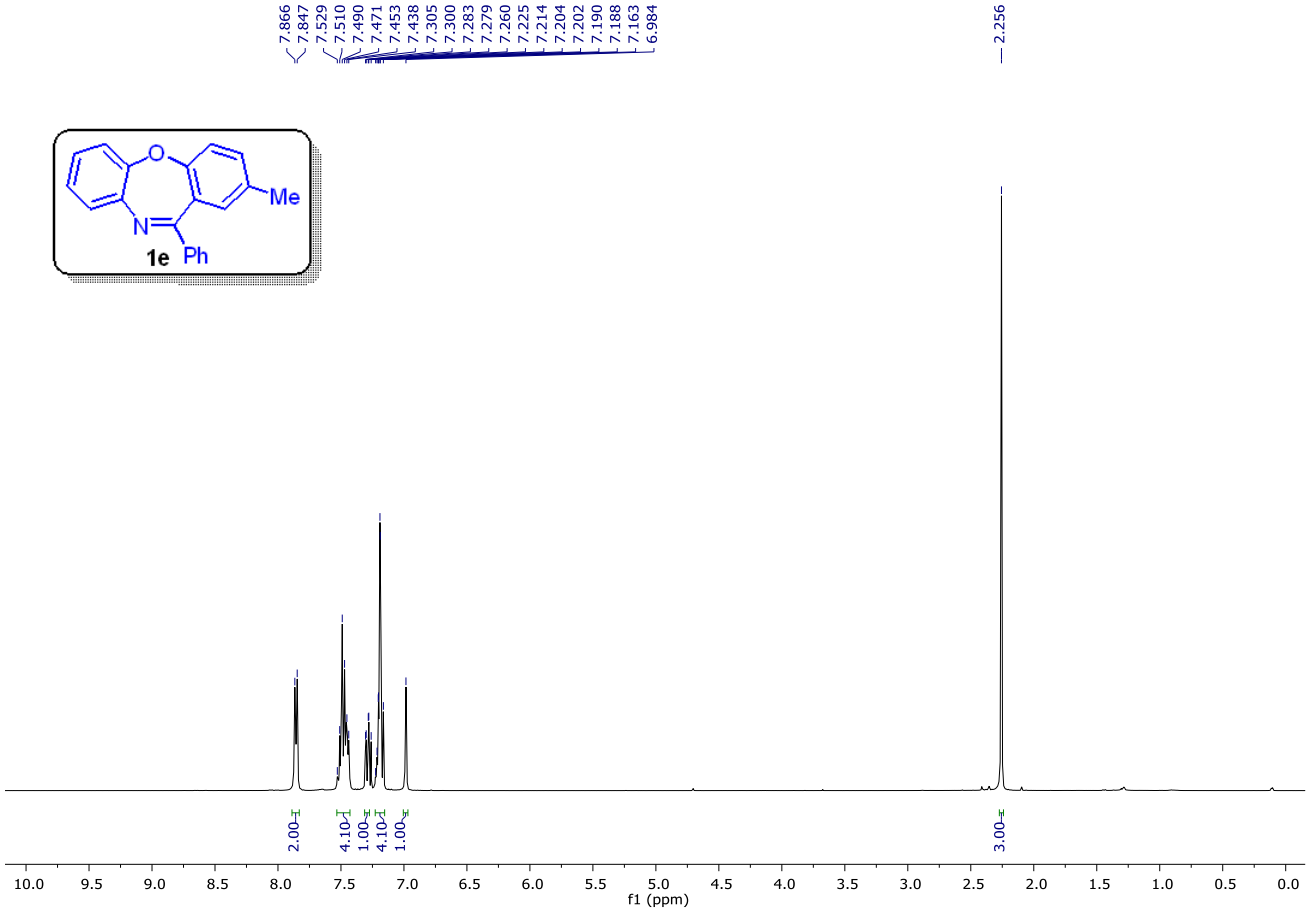
^{1}H NMR of 1d (400 MHz, $CDCl_3$):



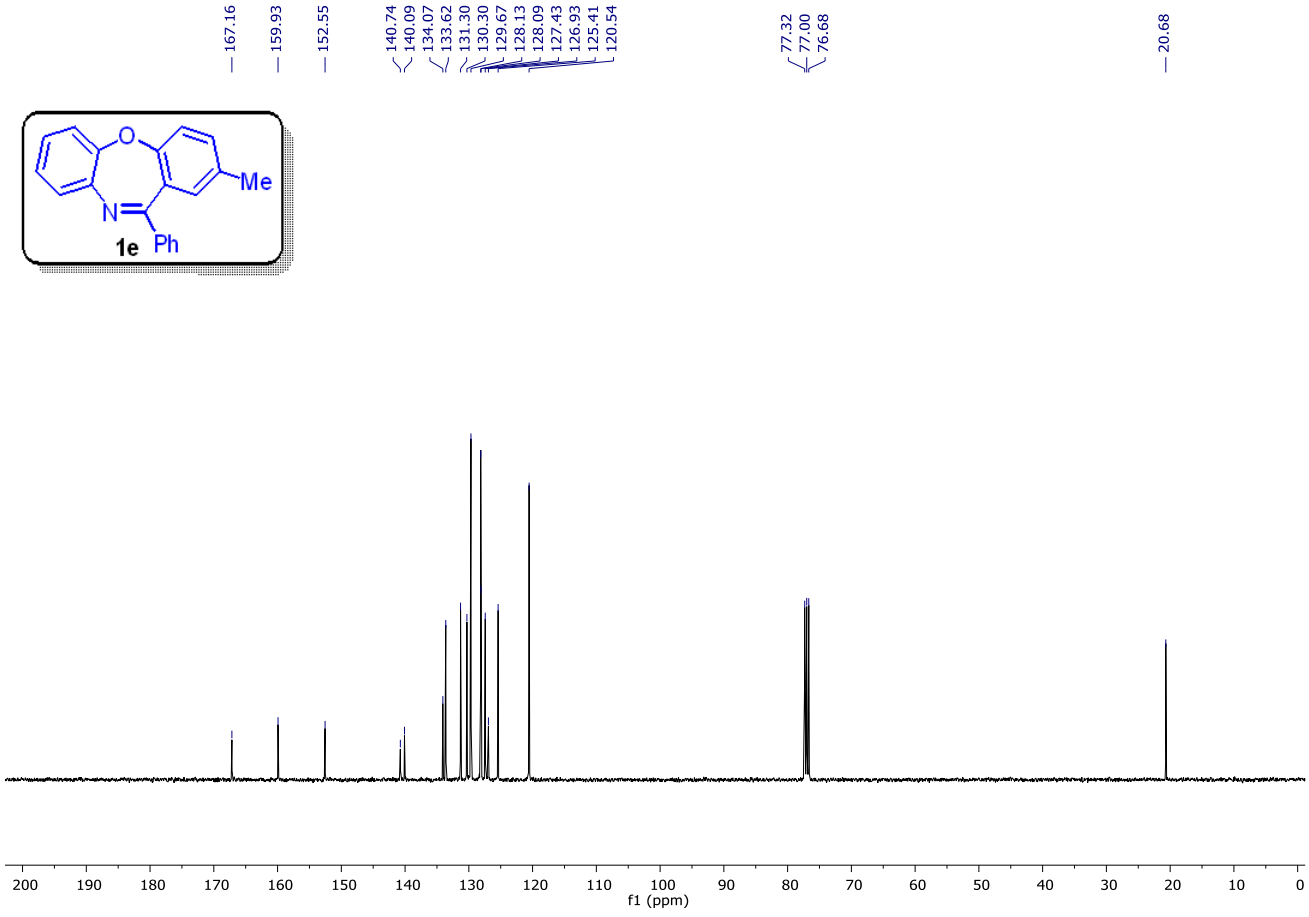
^{13}C{^{1}H} NMR of 1d (101 MHz, $CDCl_3$):



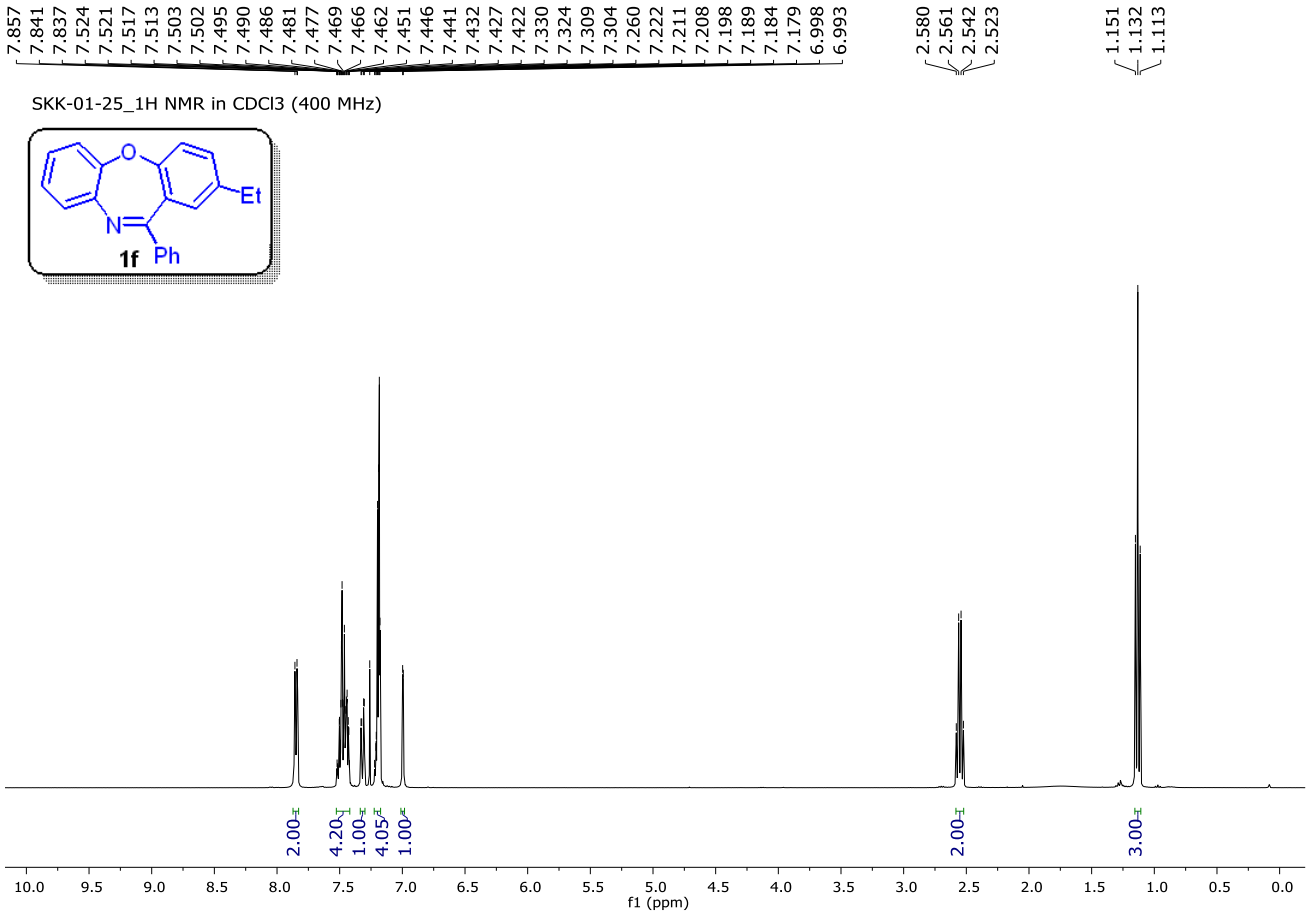
^{1}H NMR of 1e (400 MHz, $CDCl_3$):



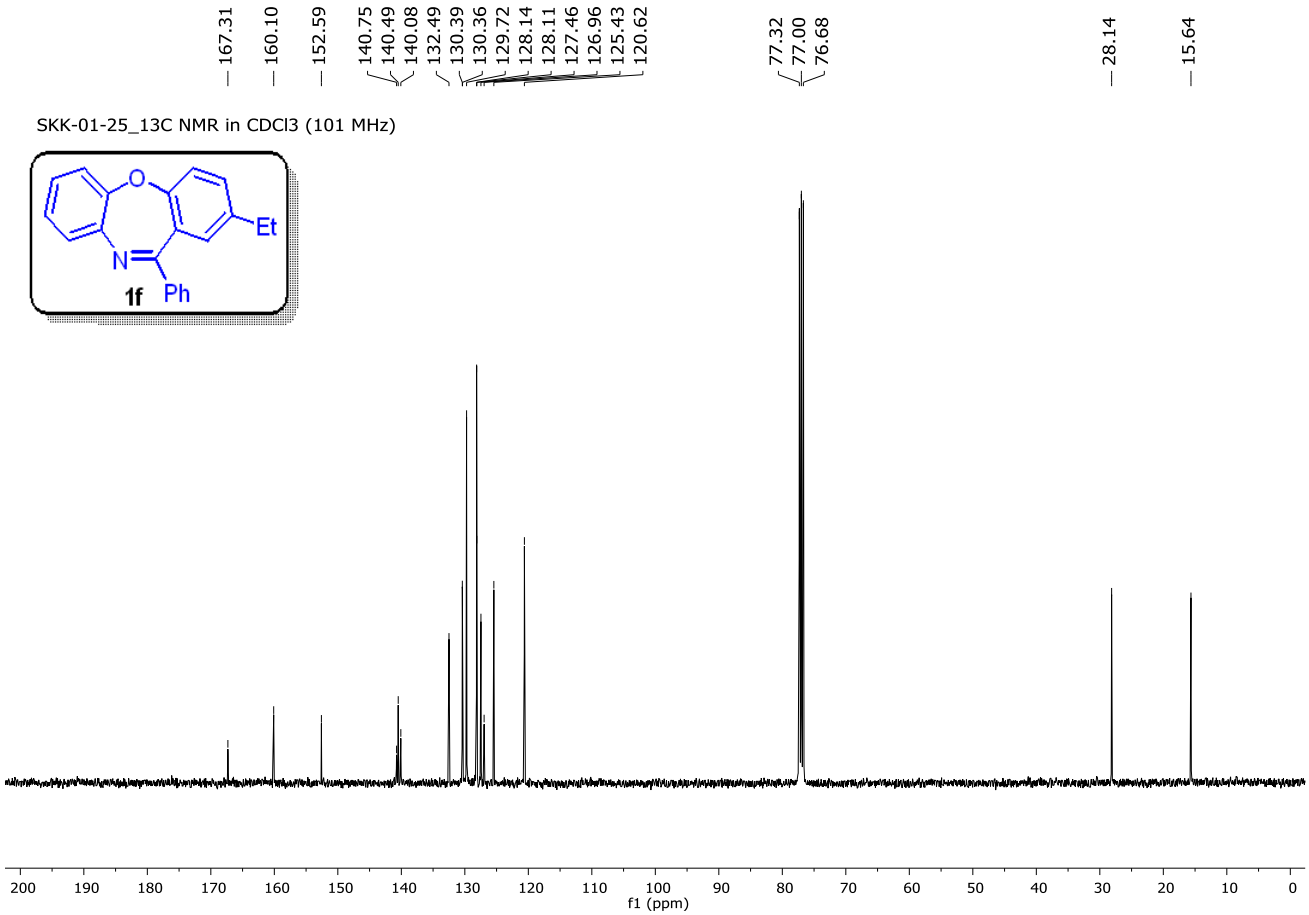
^{13}C{^{1}H} NMR of 1e (101 MHz, $CDCl_3$):



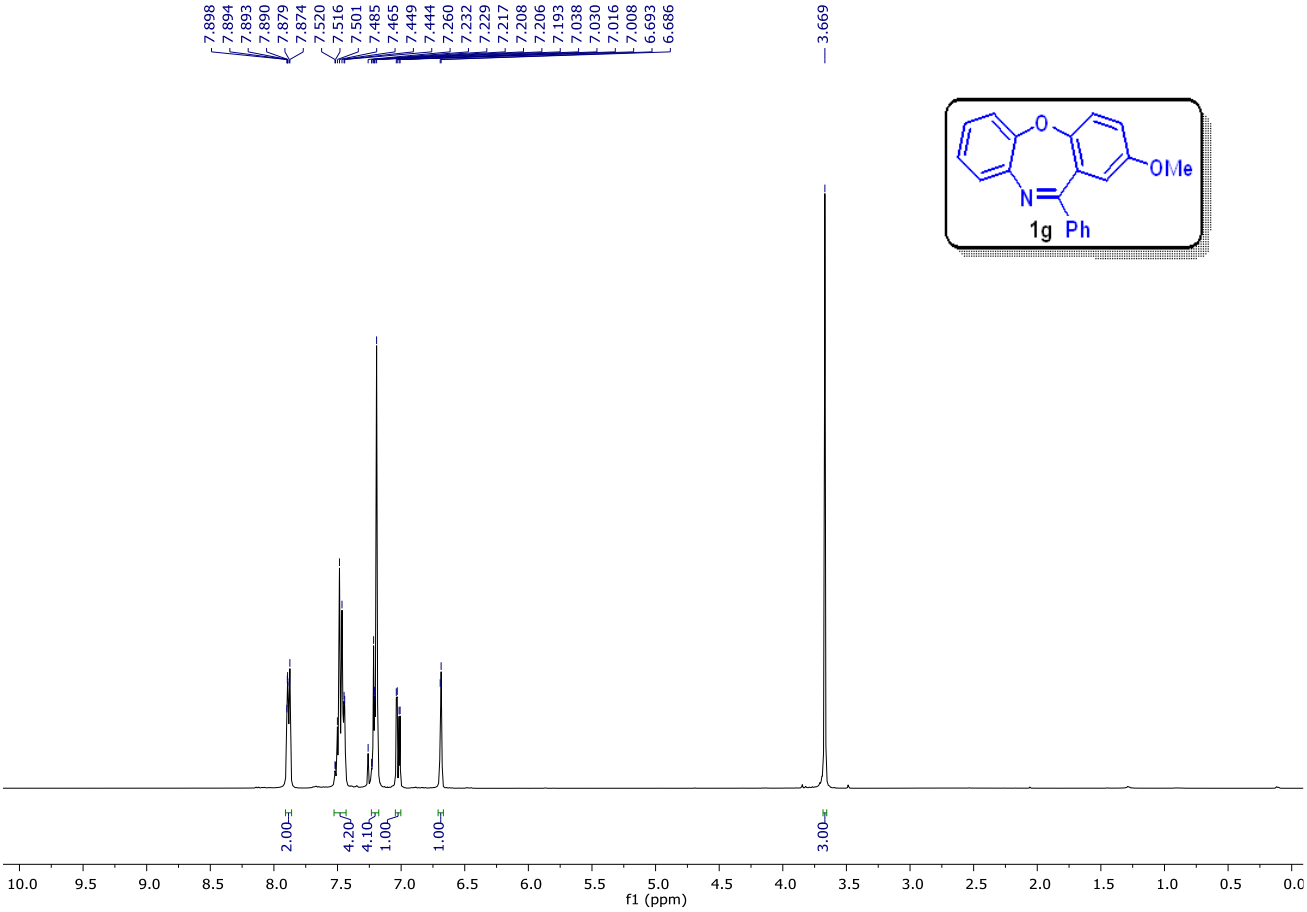
^{1}H NMR of 1f (400 MHz, $CDCl_3$):



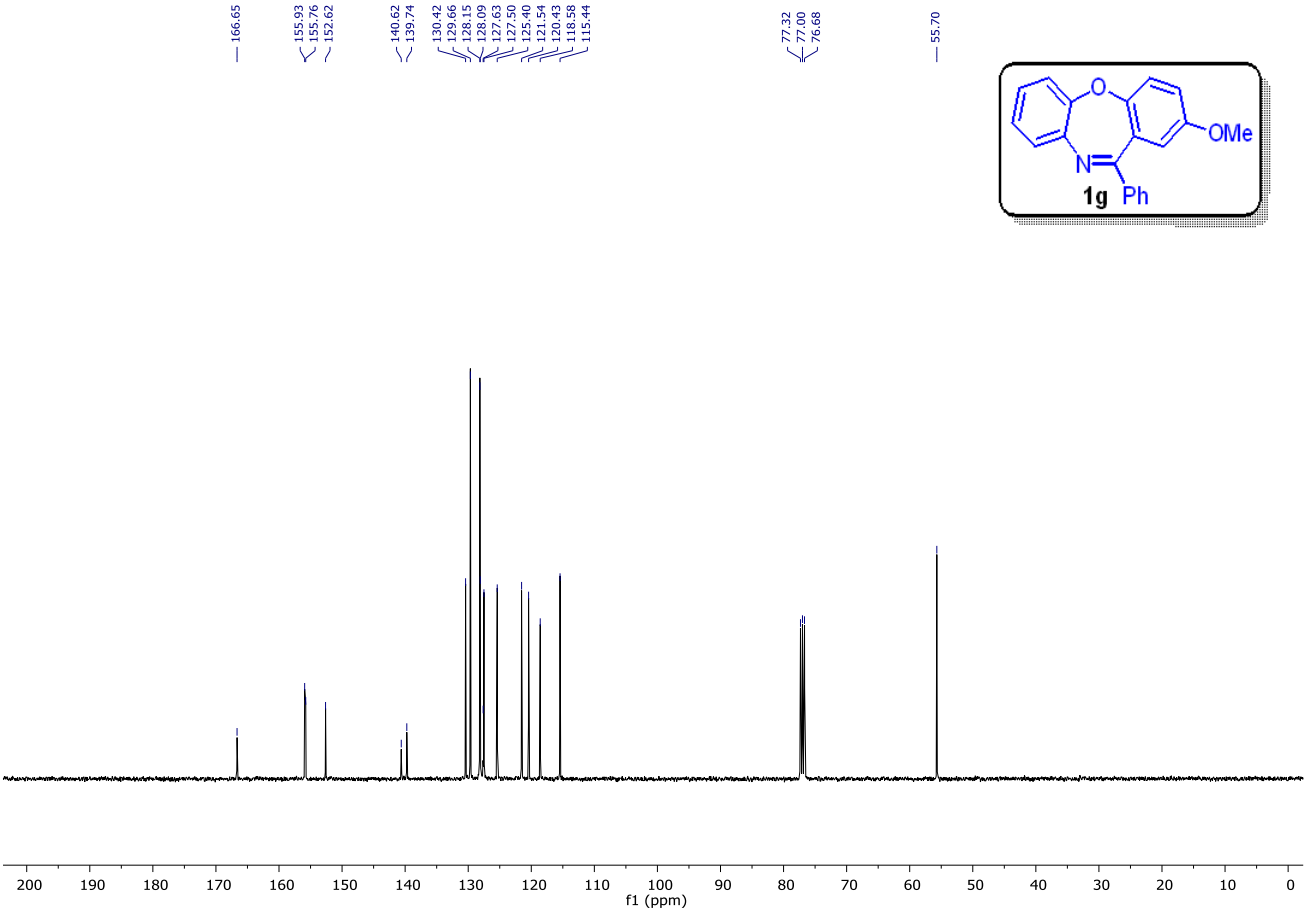
^{13}C{^{1}H} NMR of 1f (101 MHz, $CDCl_3$):



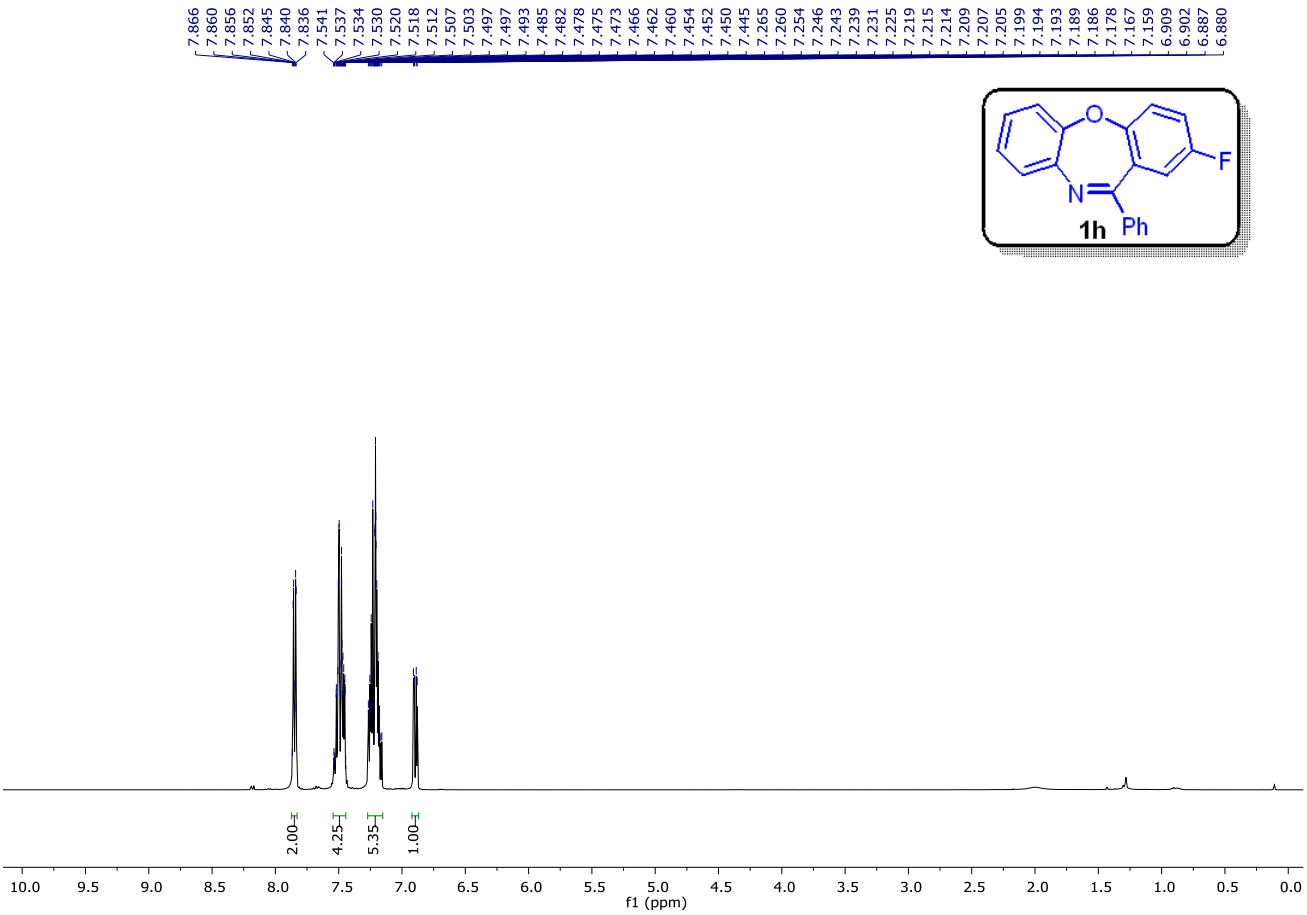
^{1}H NMR of 1g (400 MHz, $CDCl_3$):



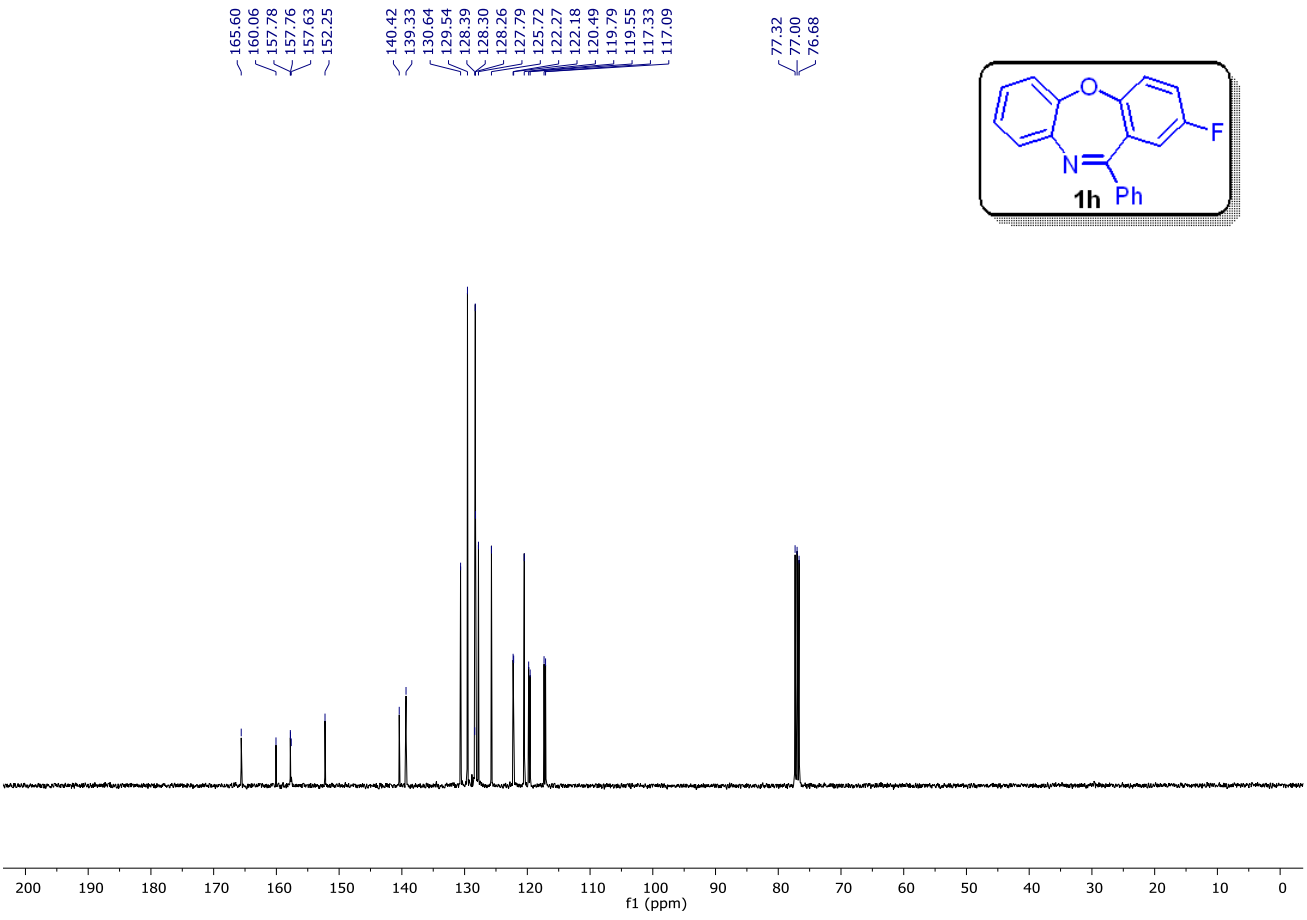
^{13}C{^{1}H} NMR of 1g (101 MHz, $CDCl_3$):



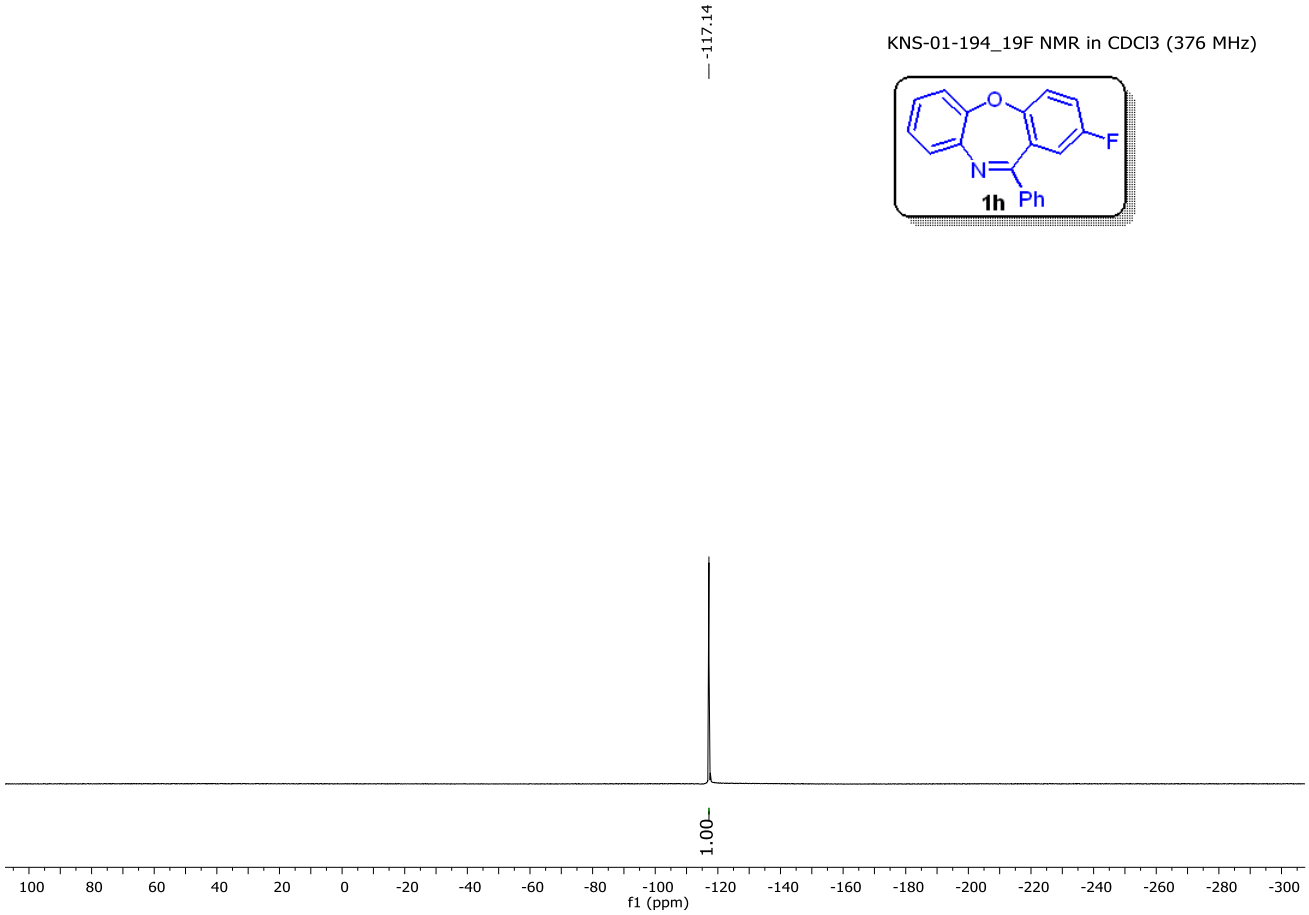
^{1}H NMR of 1h (400 MHz, $CDCl_3$):



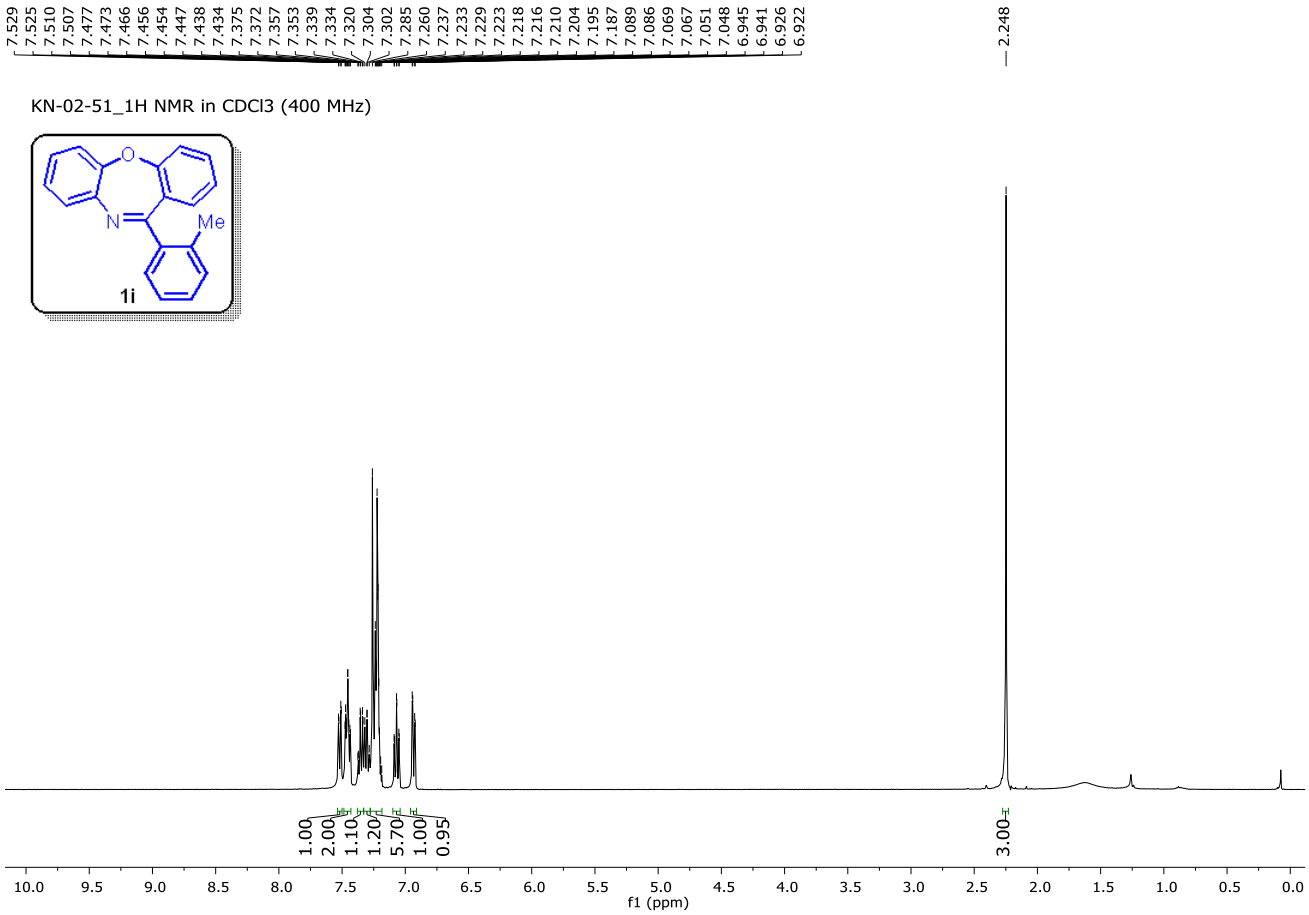
^{13}C{^{1}H} NMR of 1h (101 MHz, $CDCl_3$):



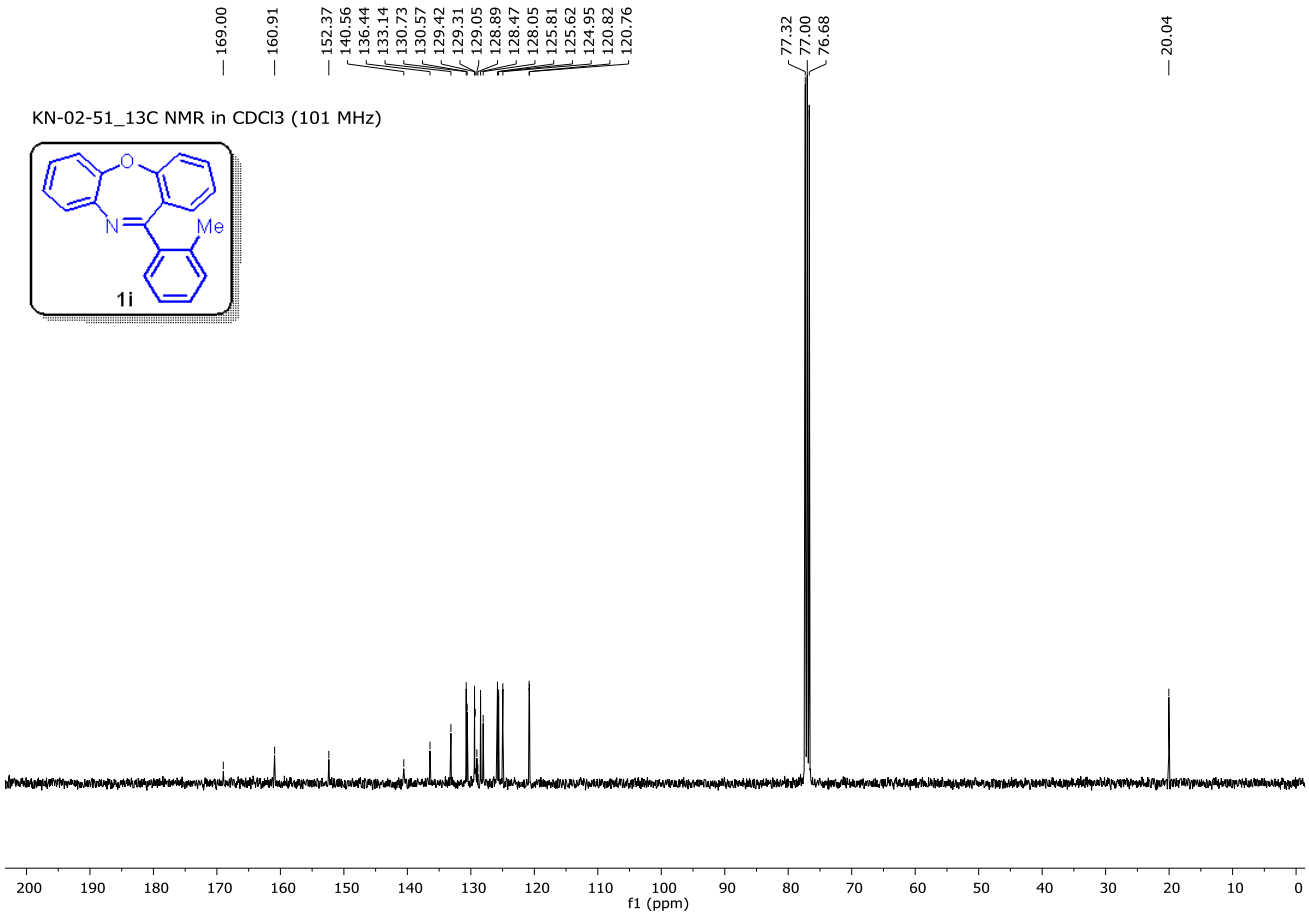
^{19}F NMR of 1h (376 MHz, $CDCl_3$):



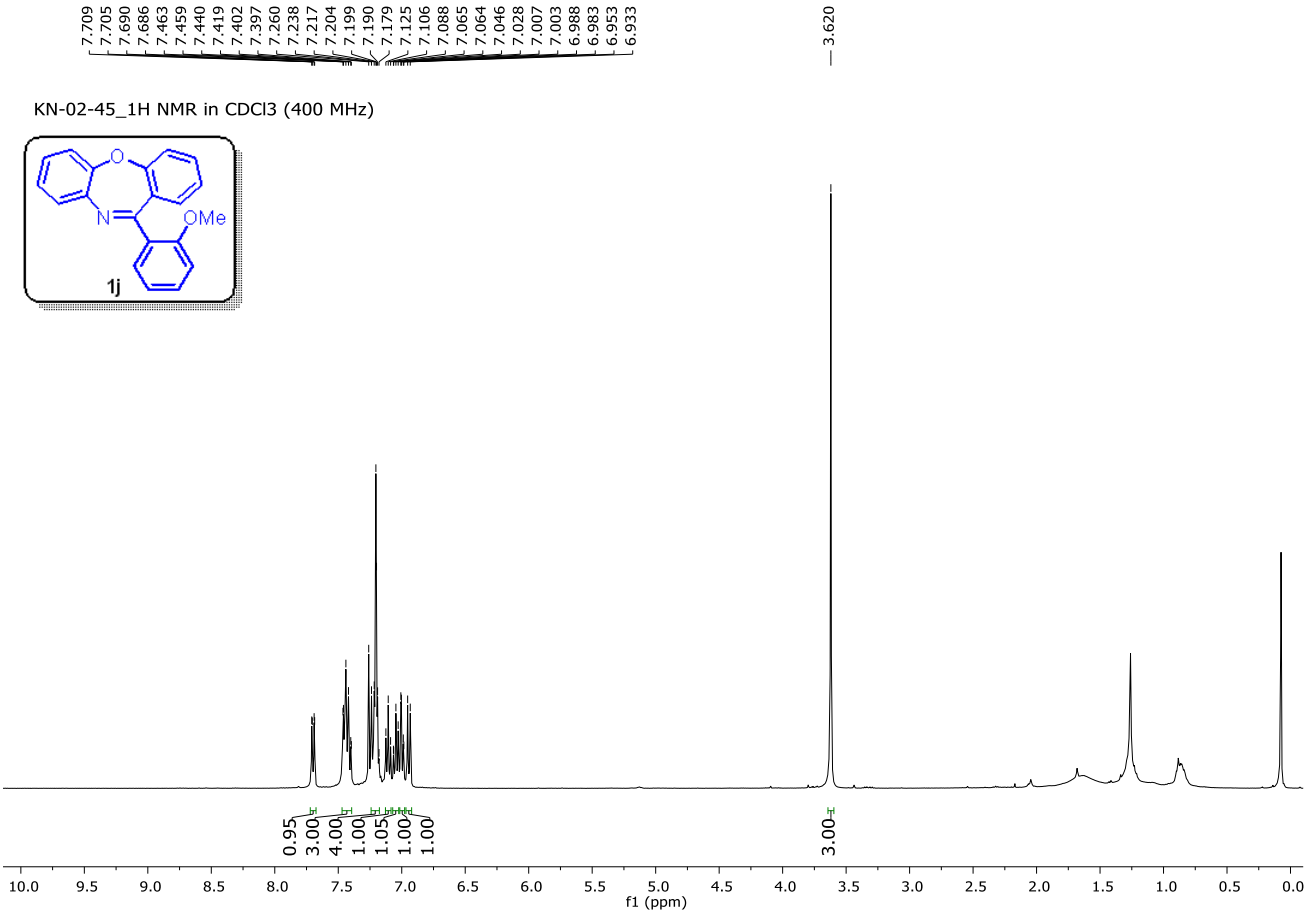
^{1}H NMR of 1i (400 MHz, $CDCl_3$):



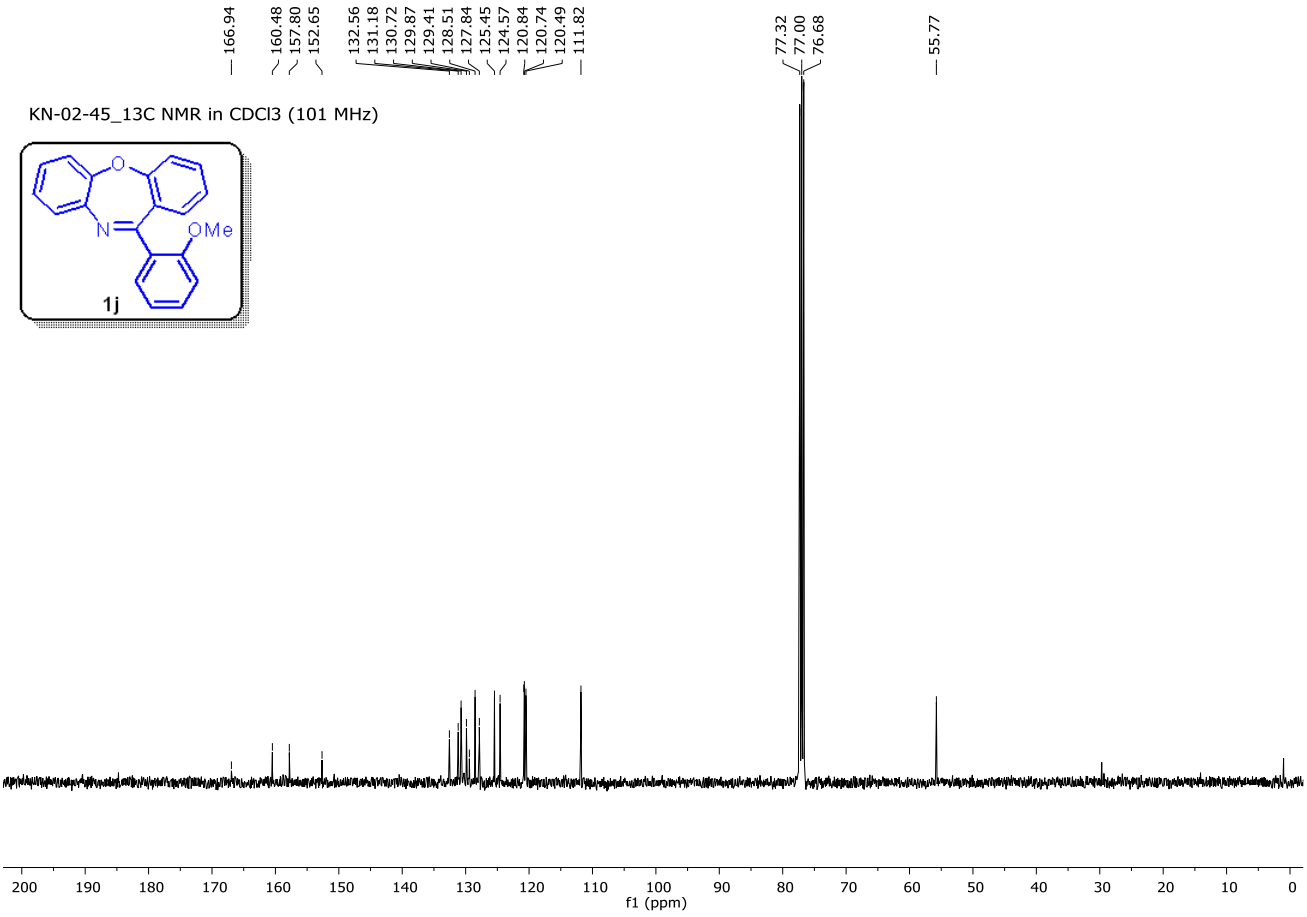
^{13}C{^{1}H} NMR of 1i (101 MHz, $CDCl_3$):



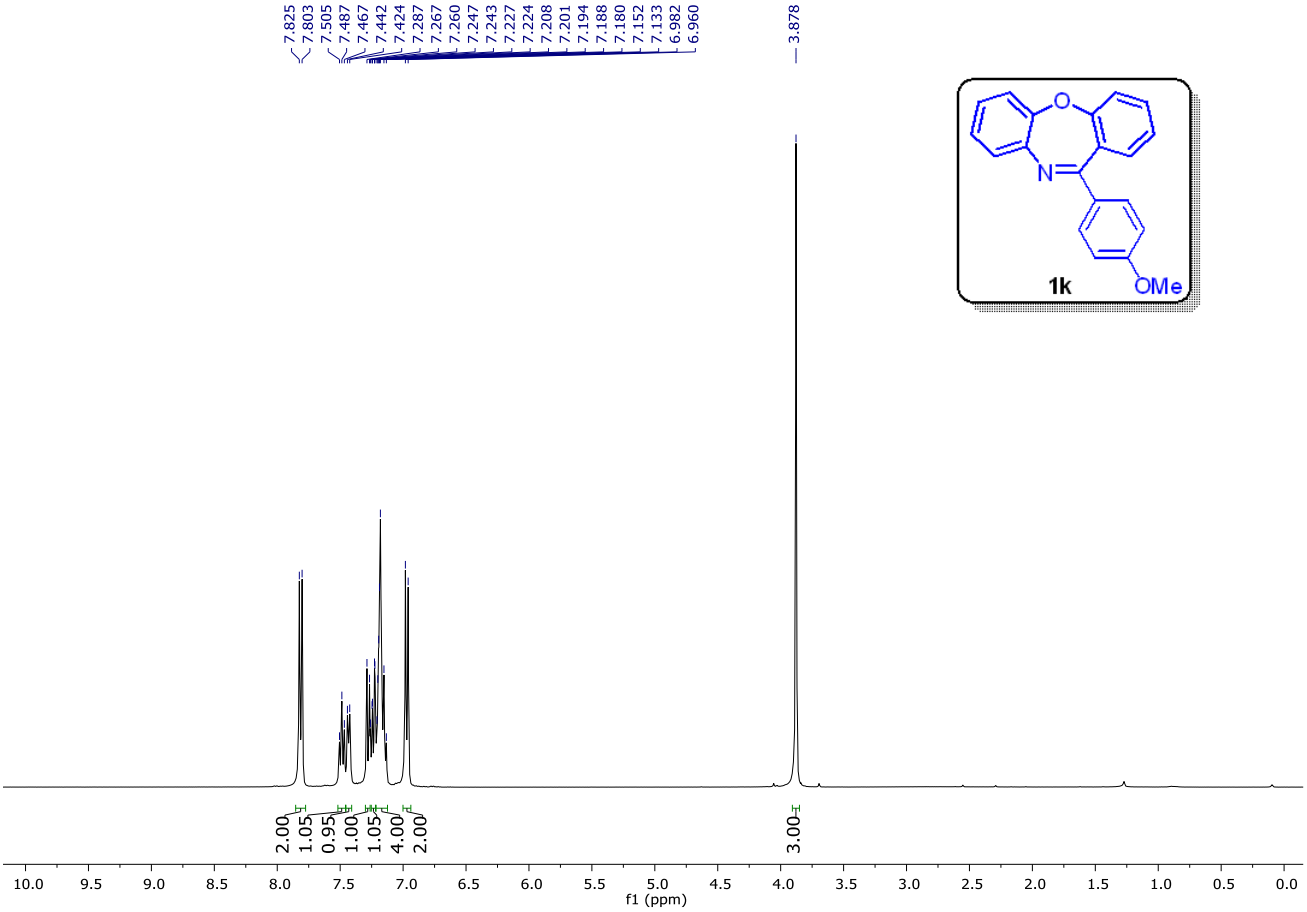
^{1}H NMR of 1j (400 MHz, $CDCl_3$):



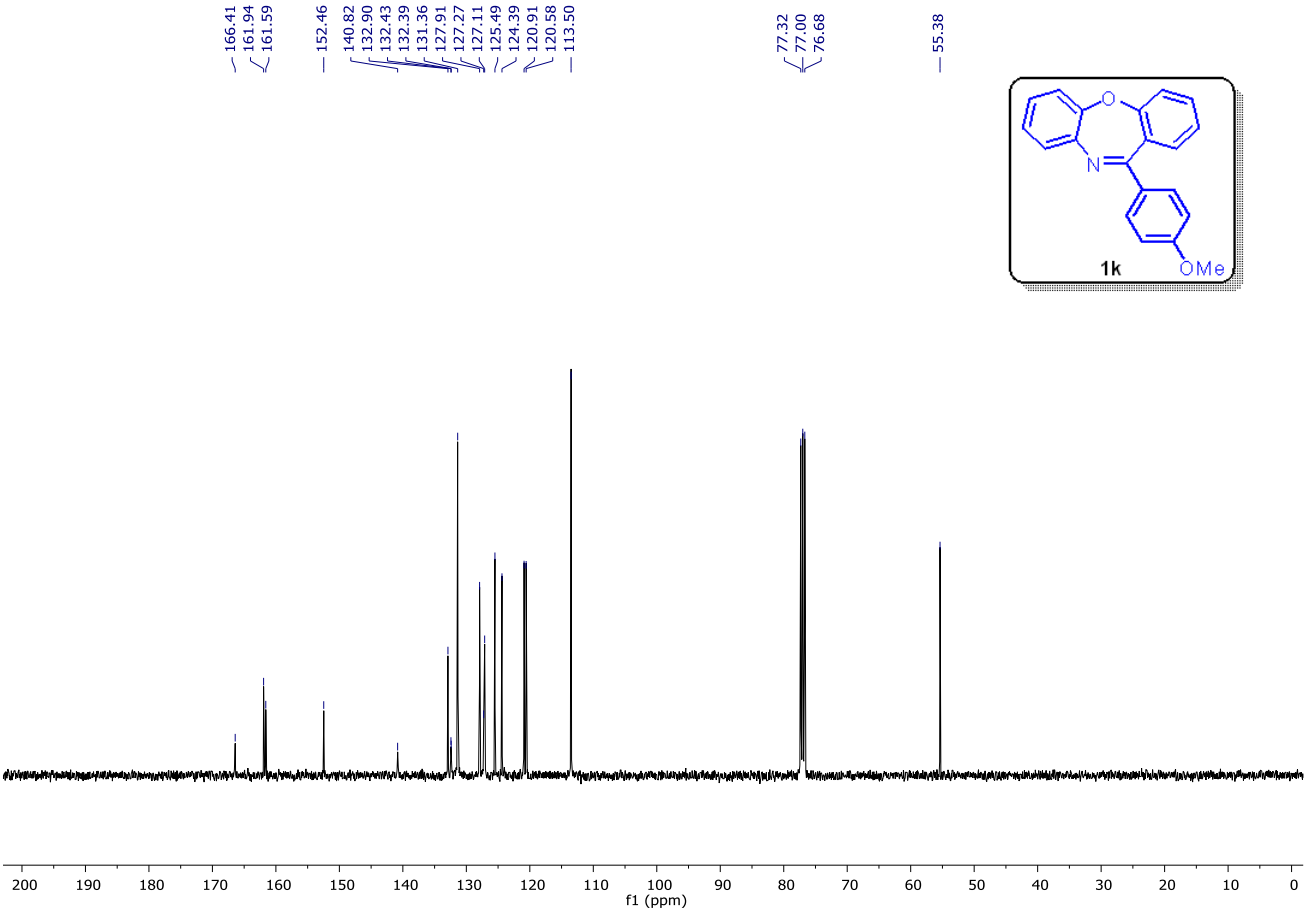
^{13}C{^{1}H} NMR of 1j (101 MHz, $CDCl_3$):



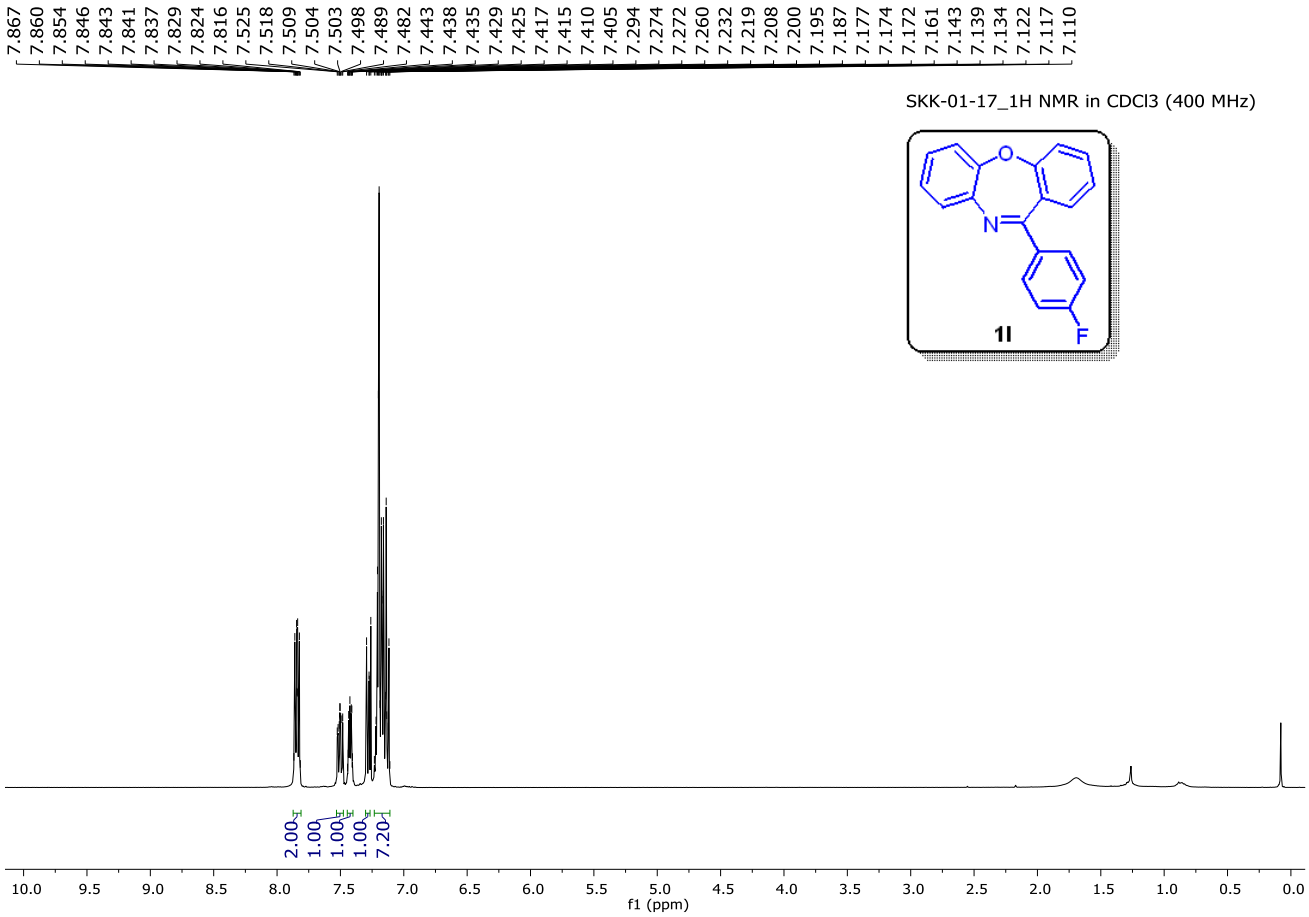
^{1}H NMR of 1k (400 MHz, $CDCl_3$):



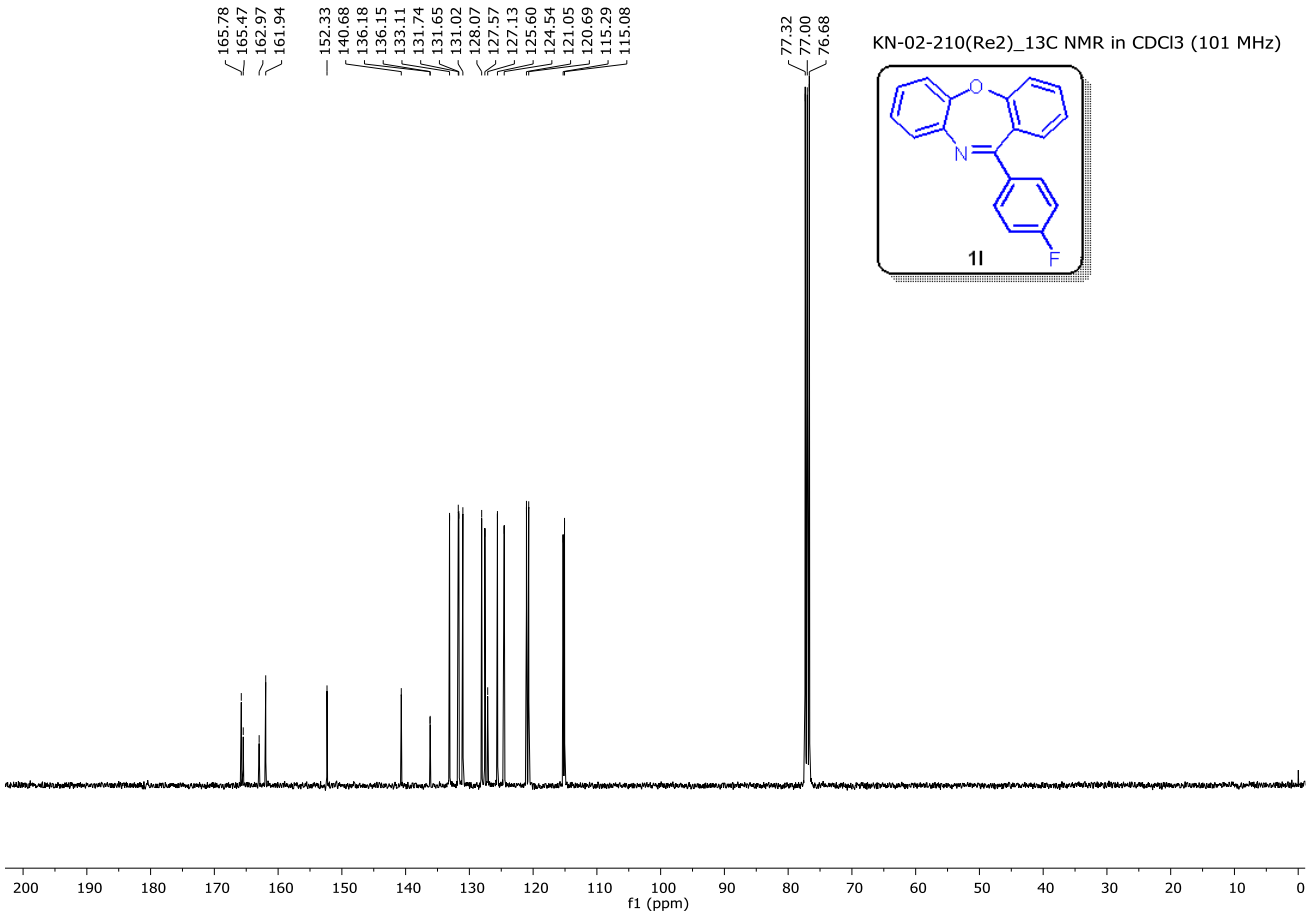
^{13}C{^{1}H} NMR of 1k (101 MHz, $CDCl_3$):



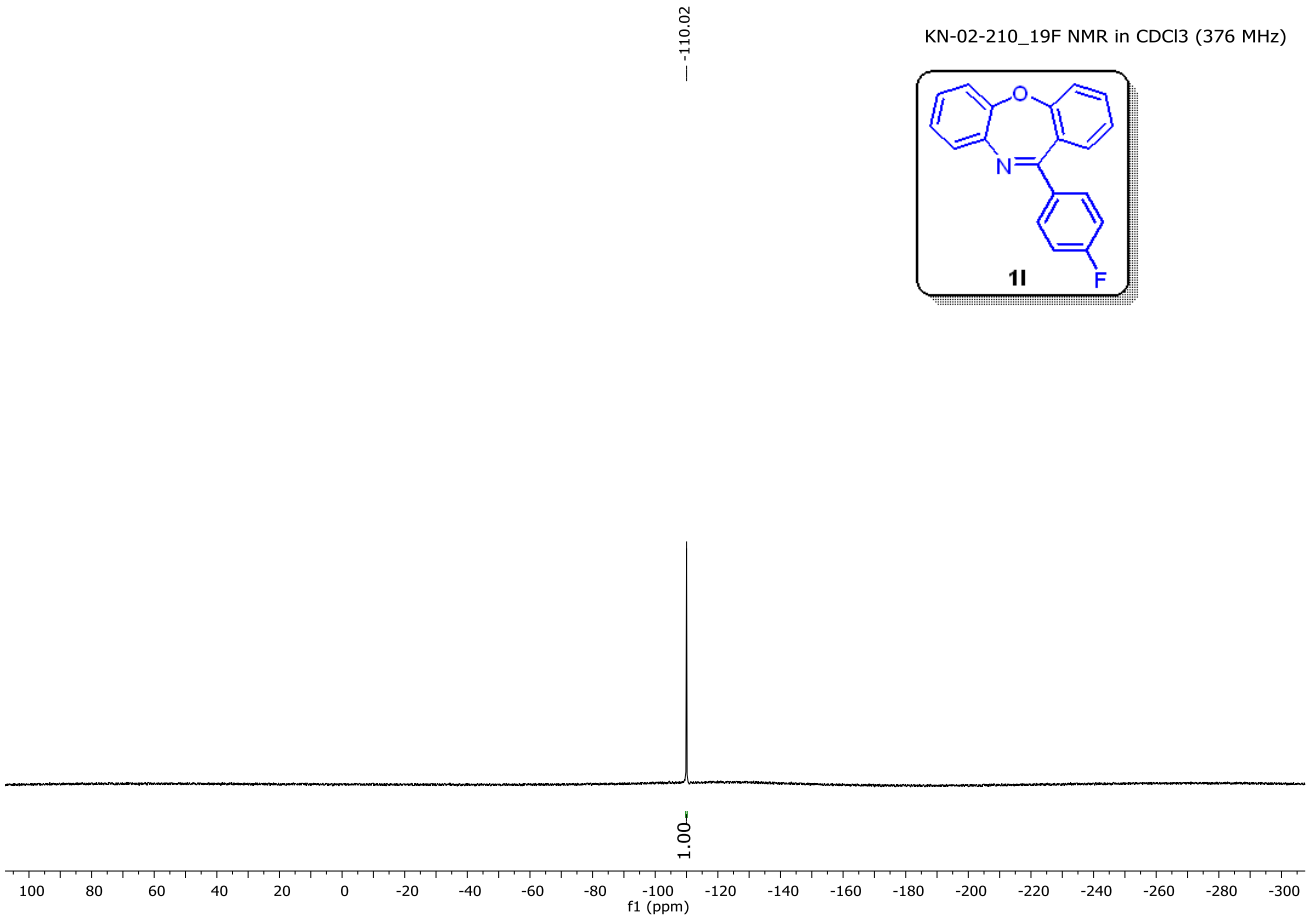
^{1}H NMR of 1l (400 MHz, $CDCl_3$):



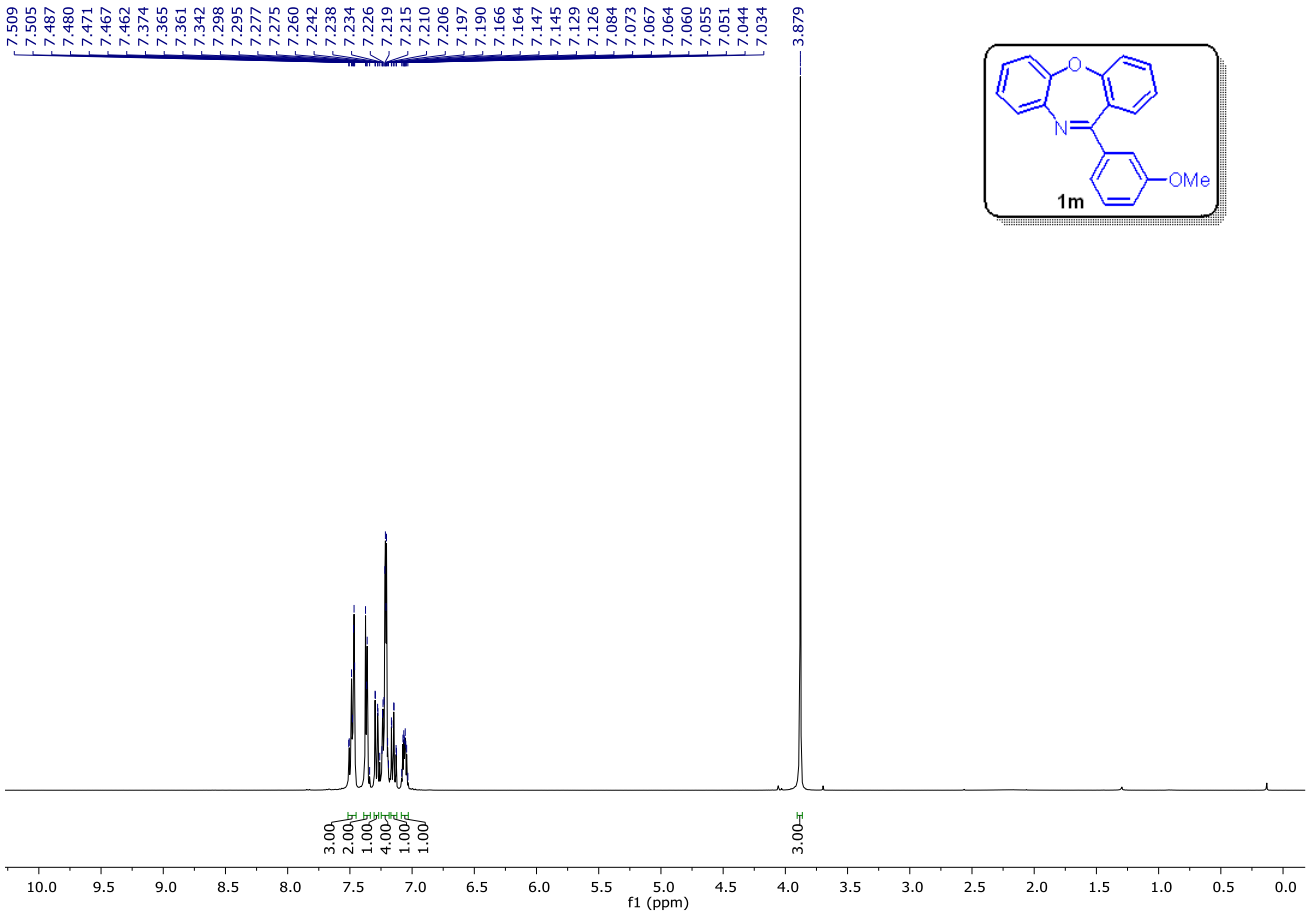
^{13}C{^{1}H} NMR of 1l (101 MHz, $CDCl_3$):



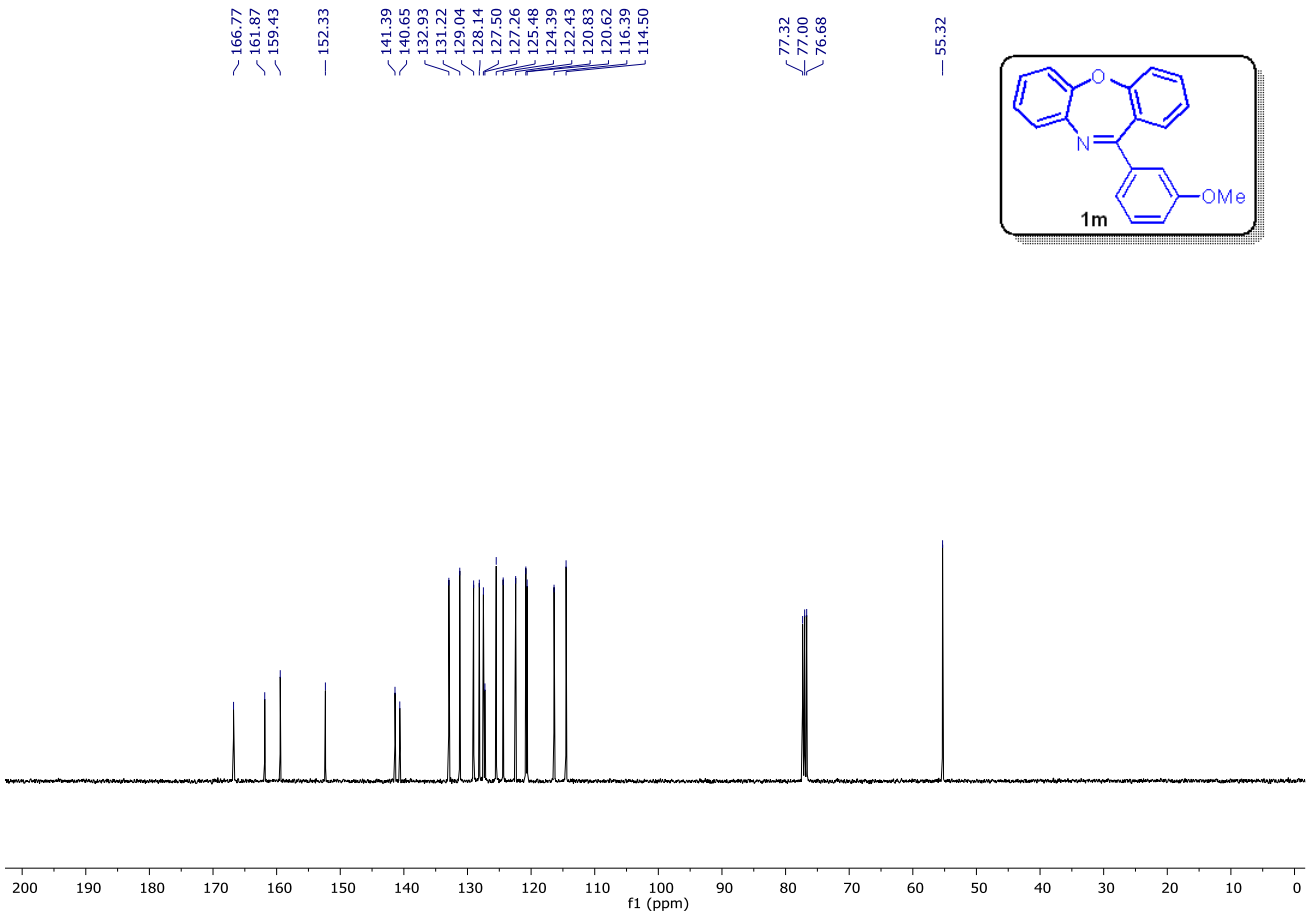
^{19}F NMR of 1l (376 MHz, $CDCl_3$):



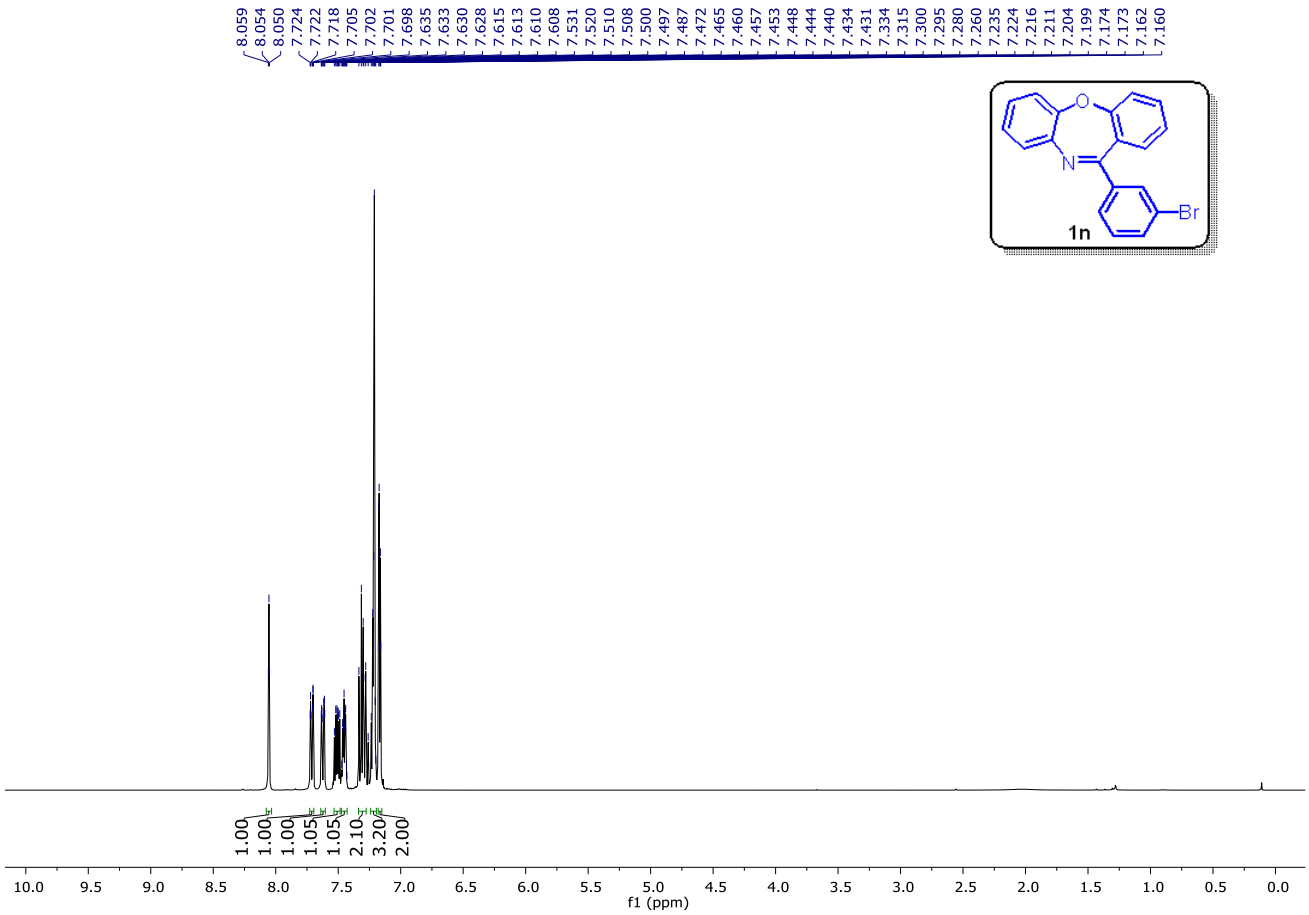
^{1}H NMR of 1m (400 MHz, $CDCl_3$):



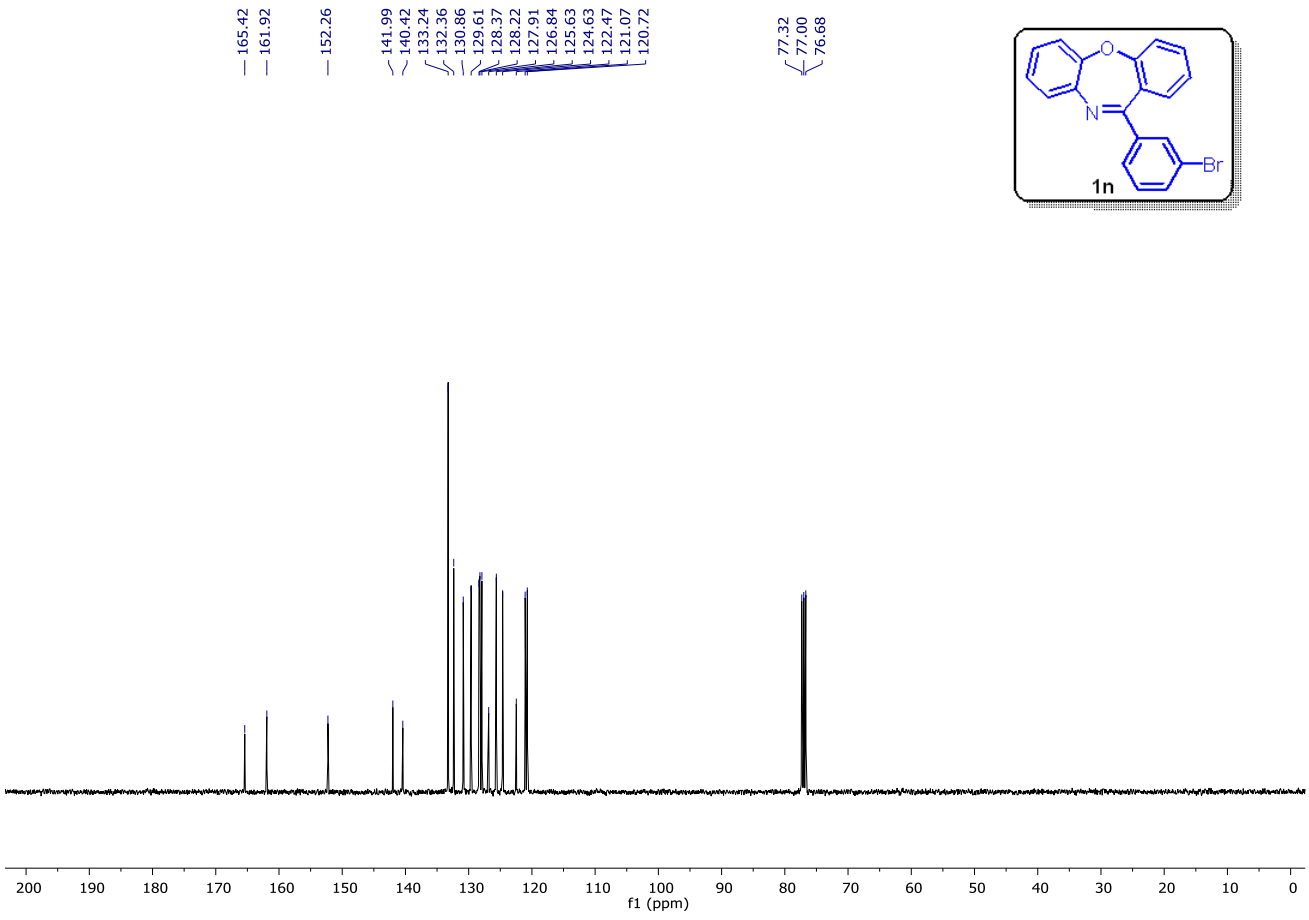
^{13}C{^{1}H} NMR of 1m (101 MHz, $CDCl_3$):



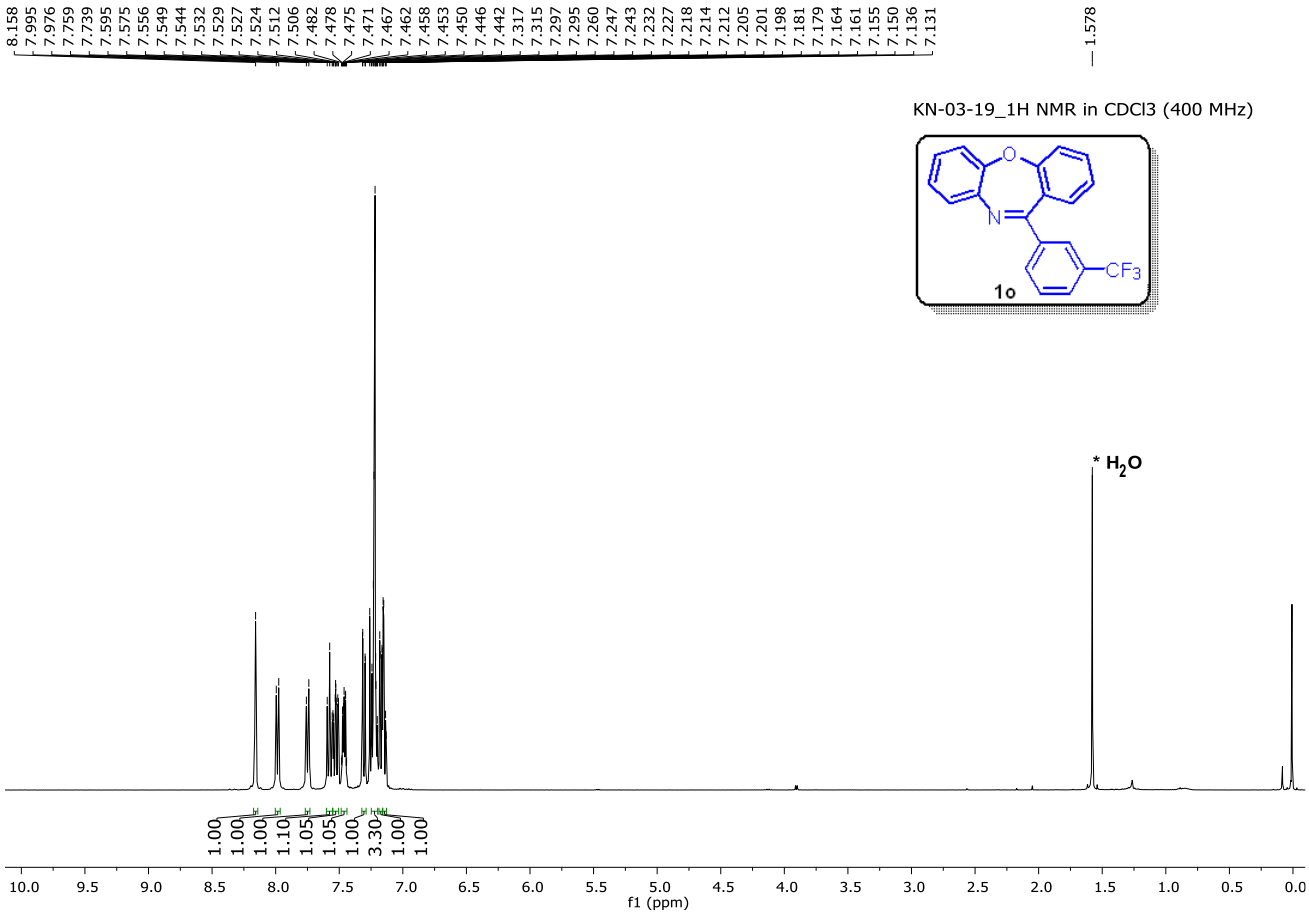
^{1}H NMR of 1n (400 MHz, $CDCl_3$):



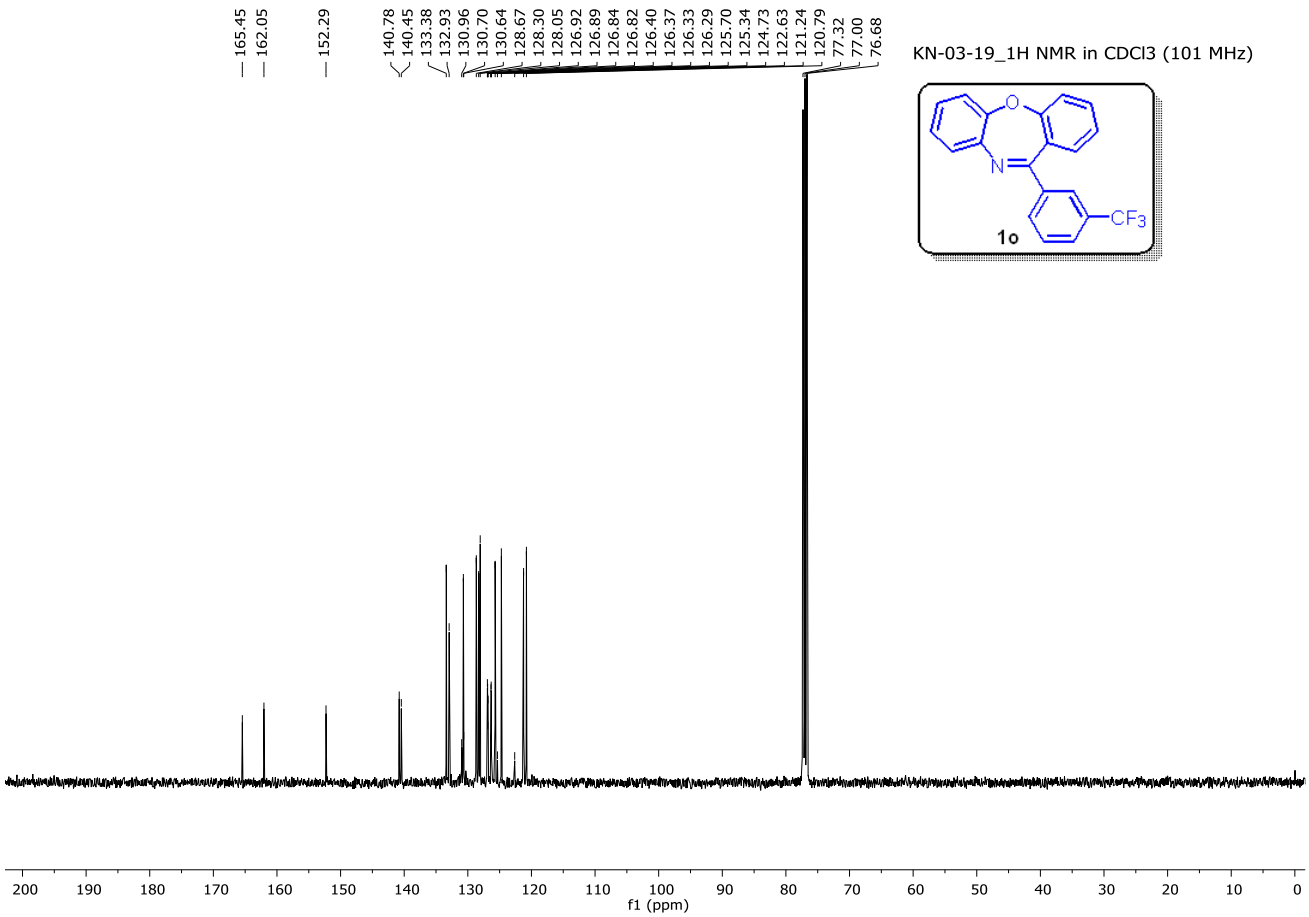
^{13}C{^{1}H} NMR of 1n (101 MHz, $CDCl_3$):



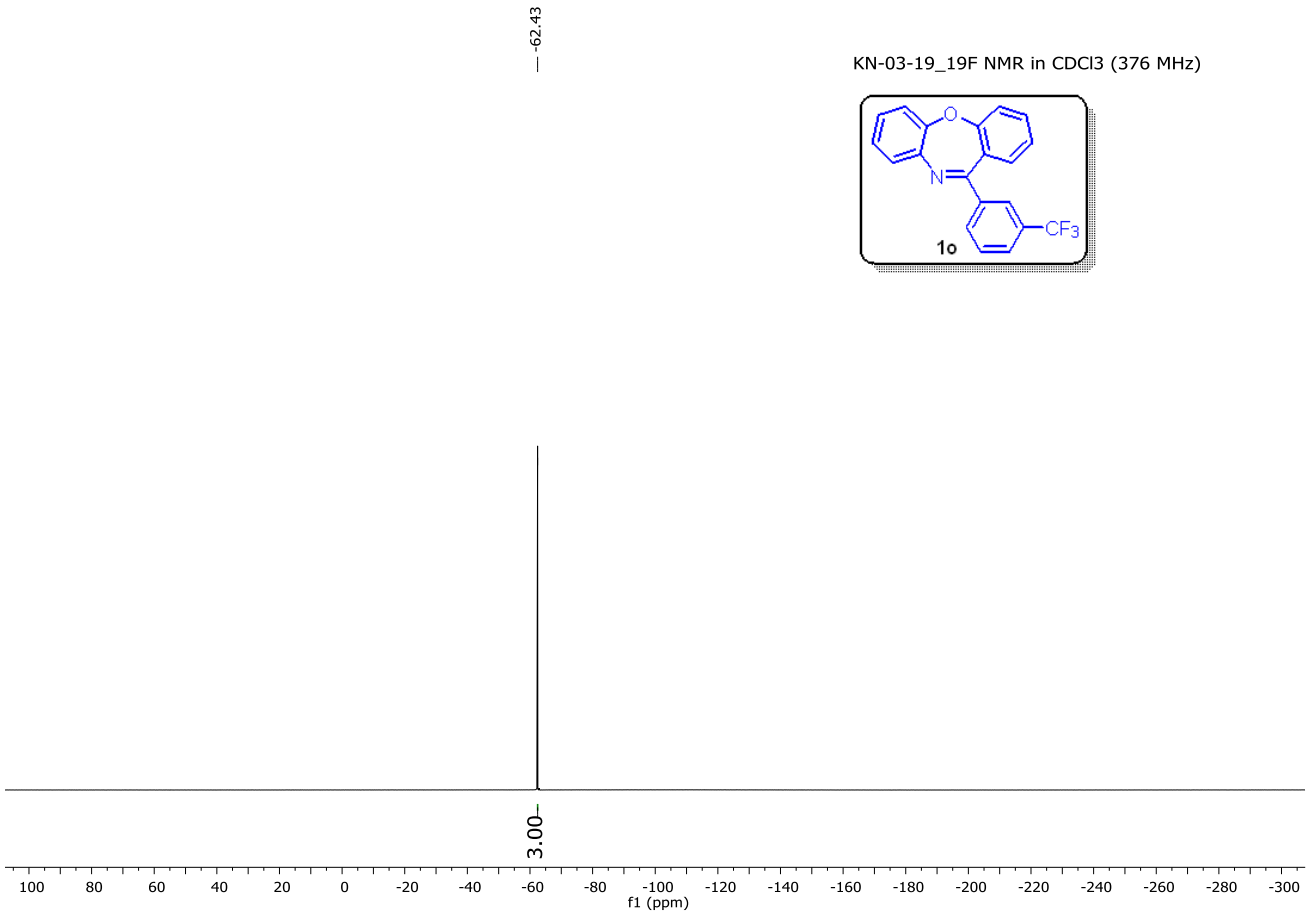
^{1}H NMR of 1o (400 MHz, $CDCl_3$):



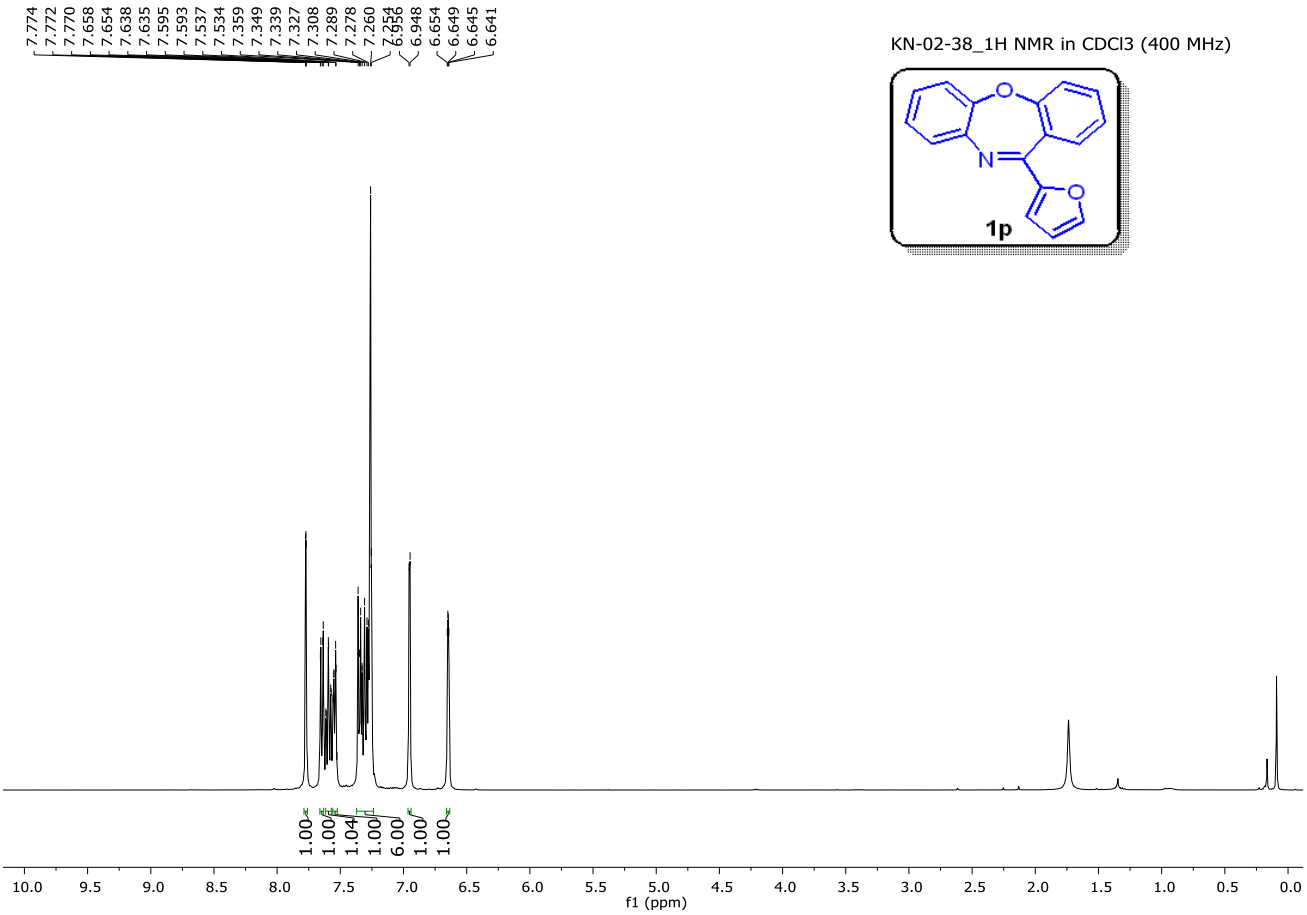
^{13}C{^{1}H} NMR of 1o (101 MHz, $CDCl_3$):



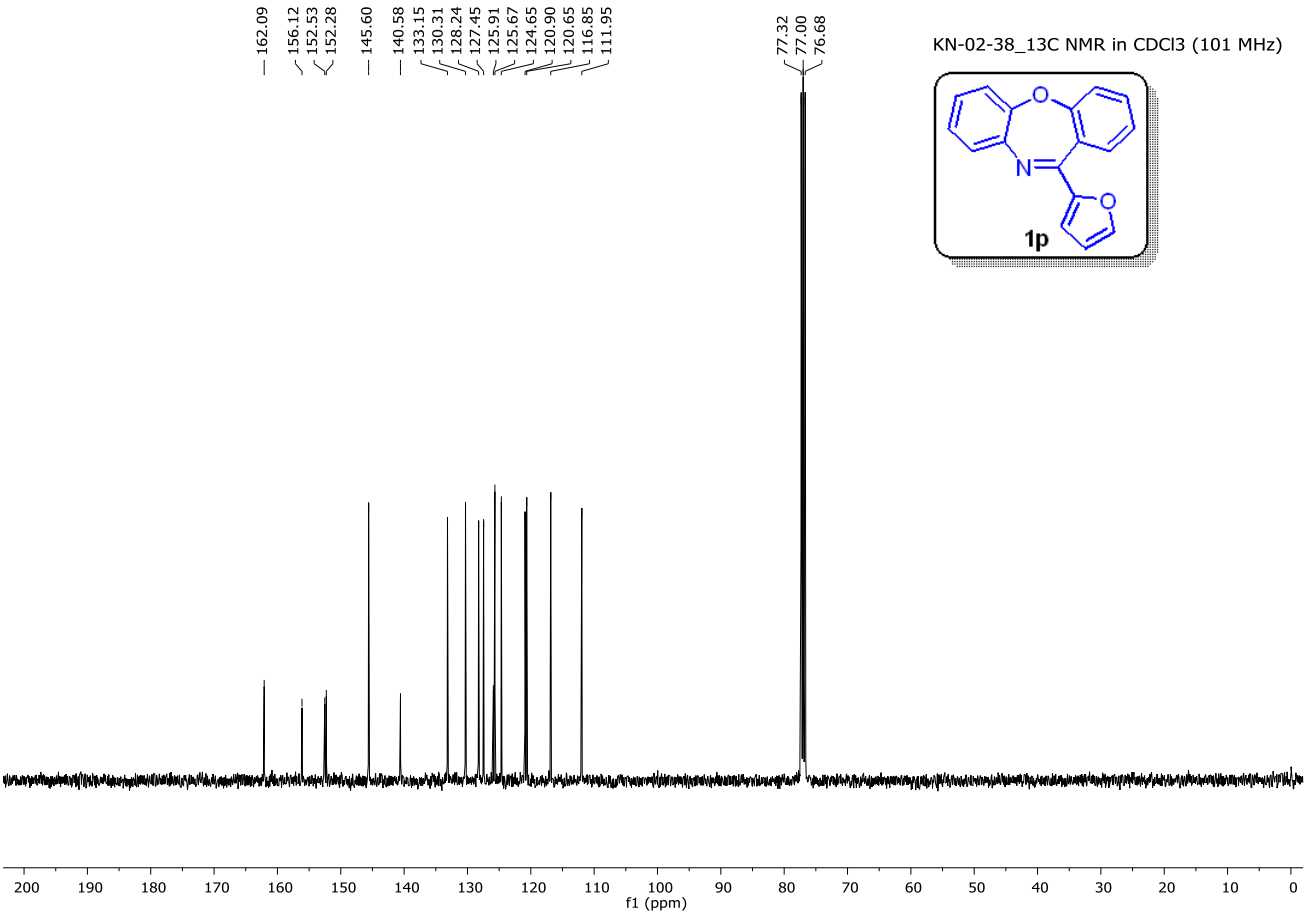
^{19}F NMR of 1o (376 MHz, $CDCl_3$):



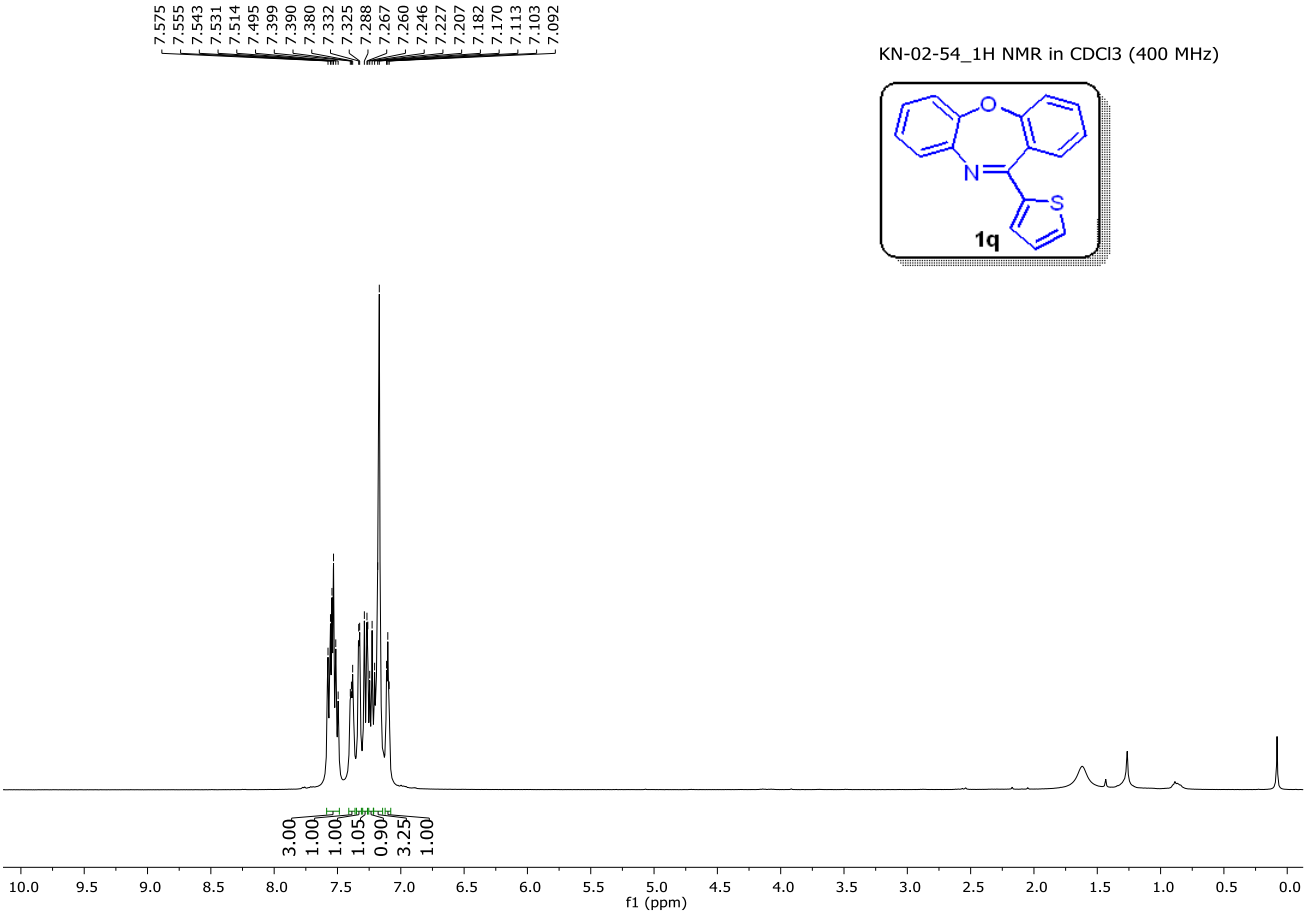
^{1}H NMR of 1p (400 MHz, $CDCl_3$):



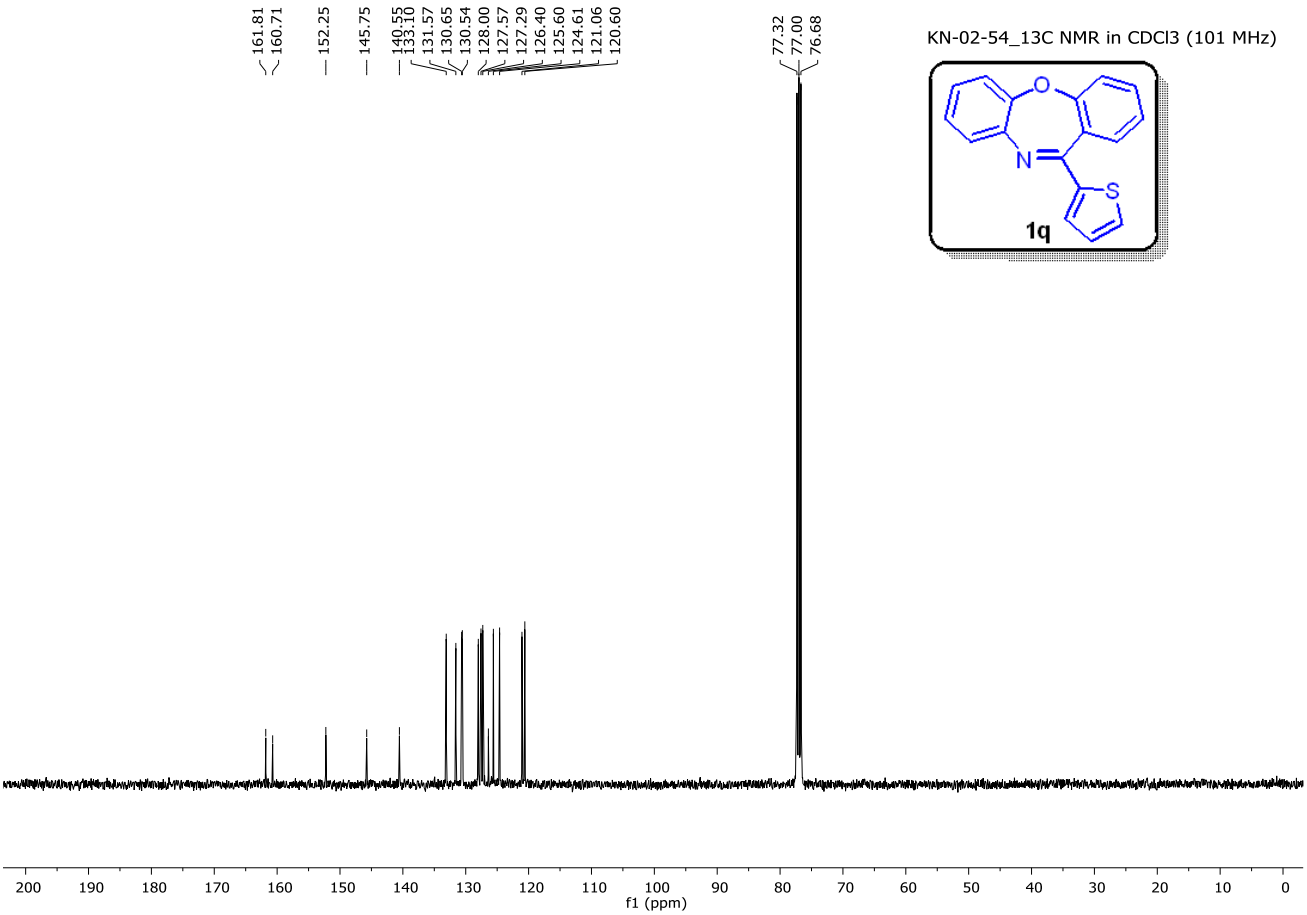
^{13}C{^{1}H} NMR of 1p (101 MHz, $CDCl_3$):



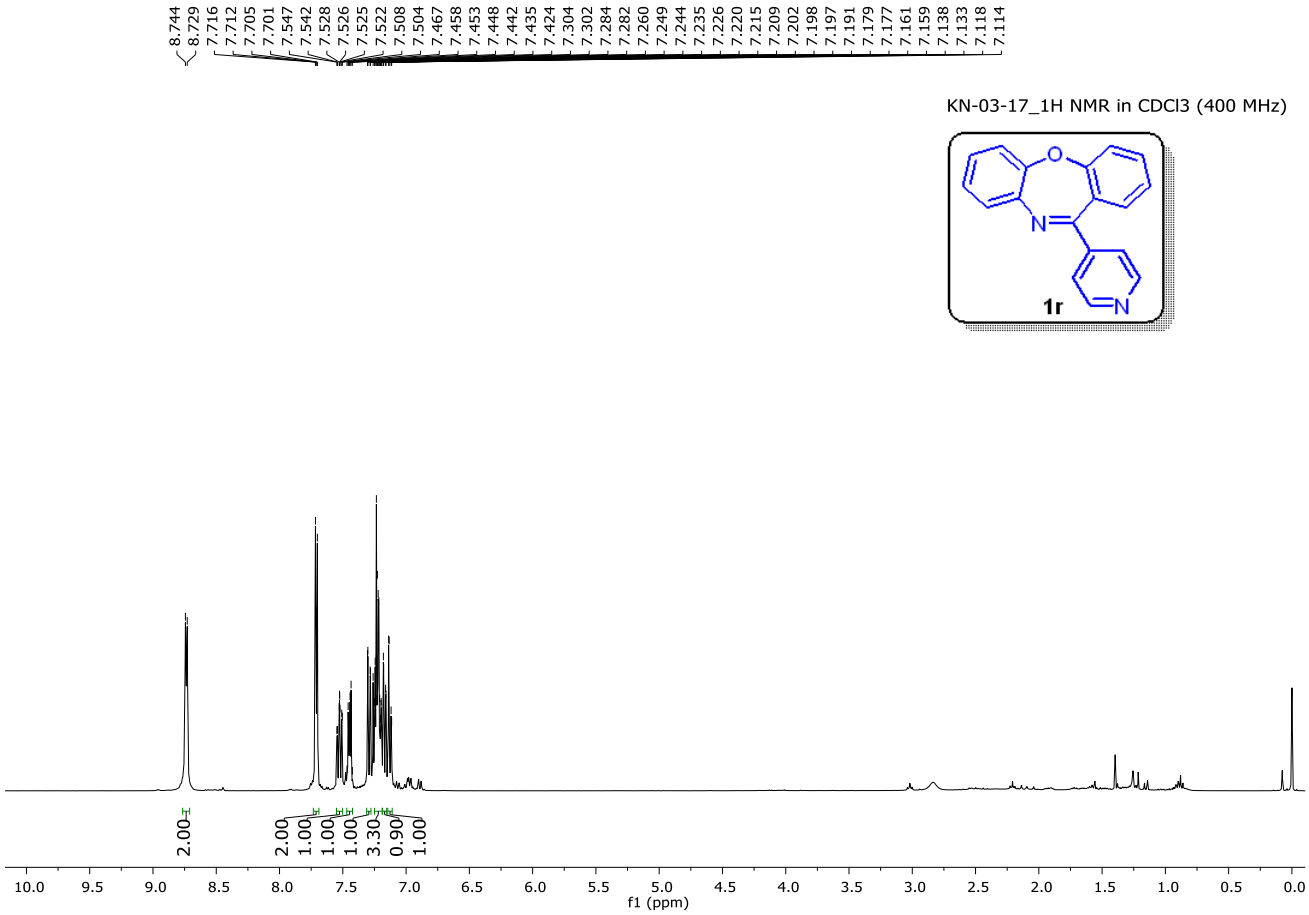
^{1}H NMR of 1q (400 MHz, $CDCl_3$):



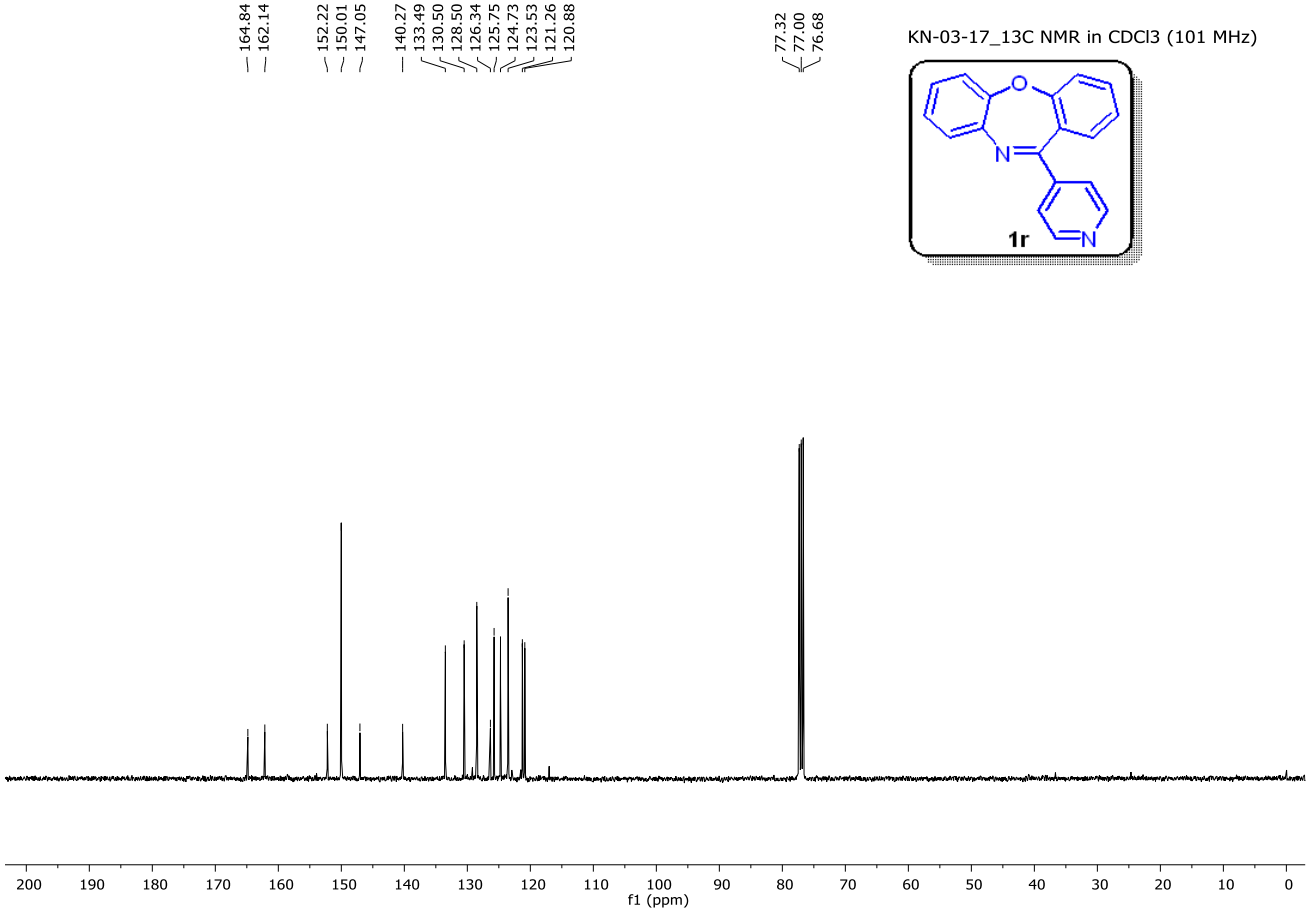
^{13}C{^{1}H} NMR of 1q (101 MHz, $CDCl_3$):



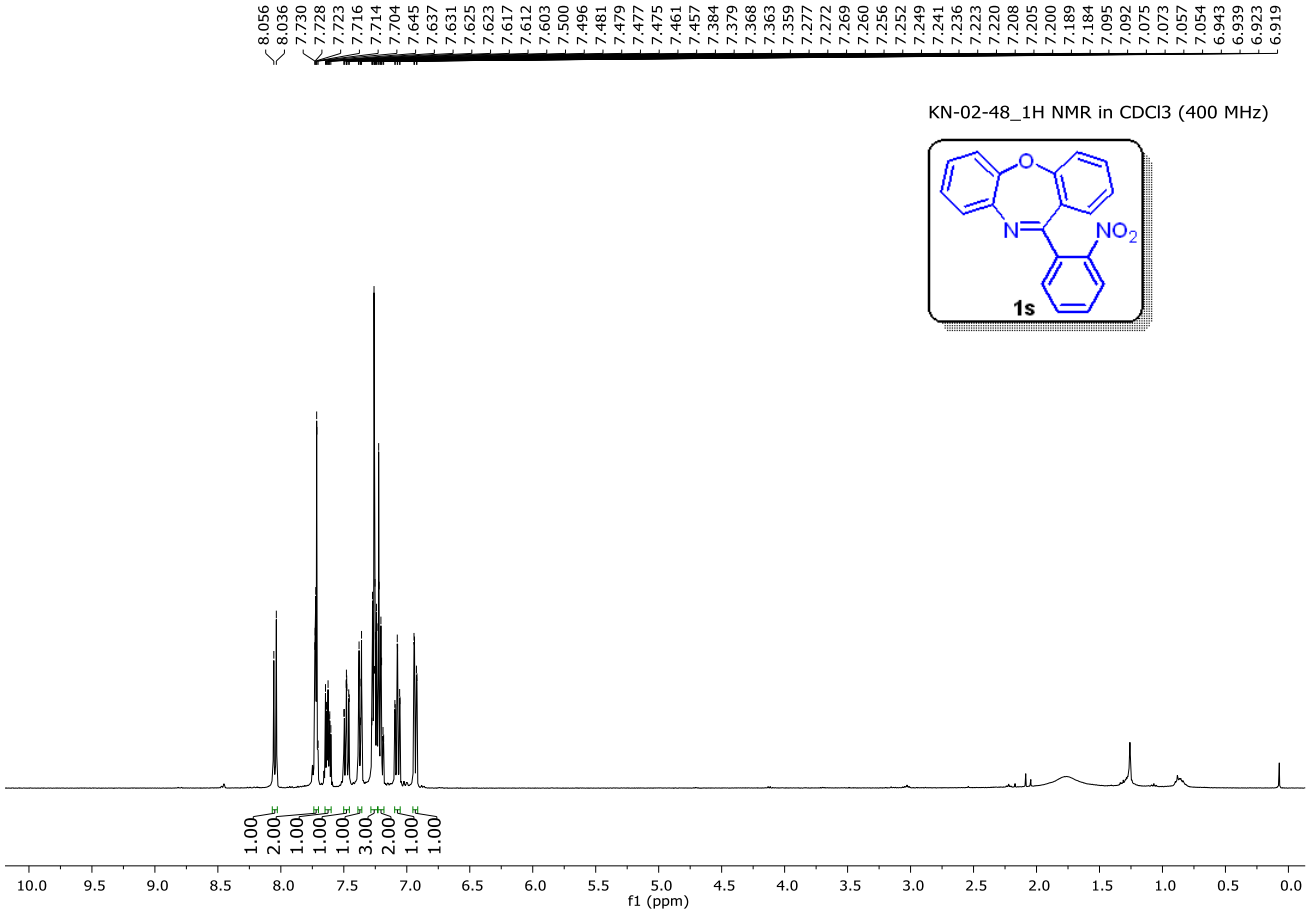
^{1}H NMR of 1r (400 MHz, $CDCl_3$):



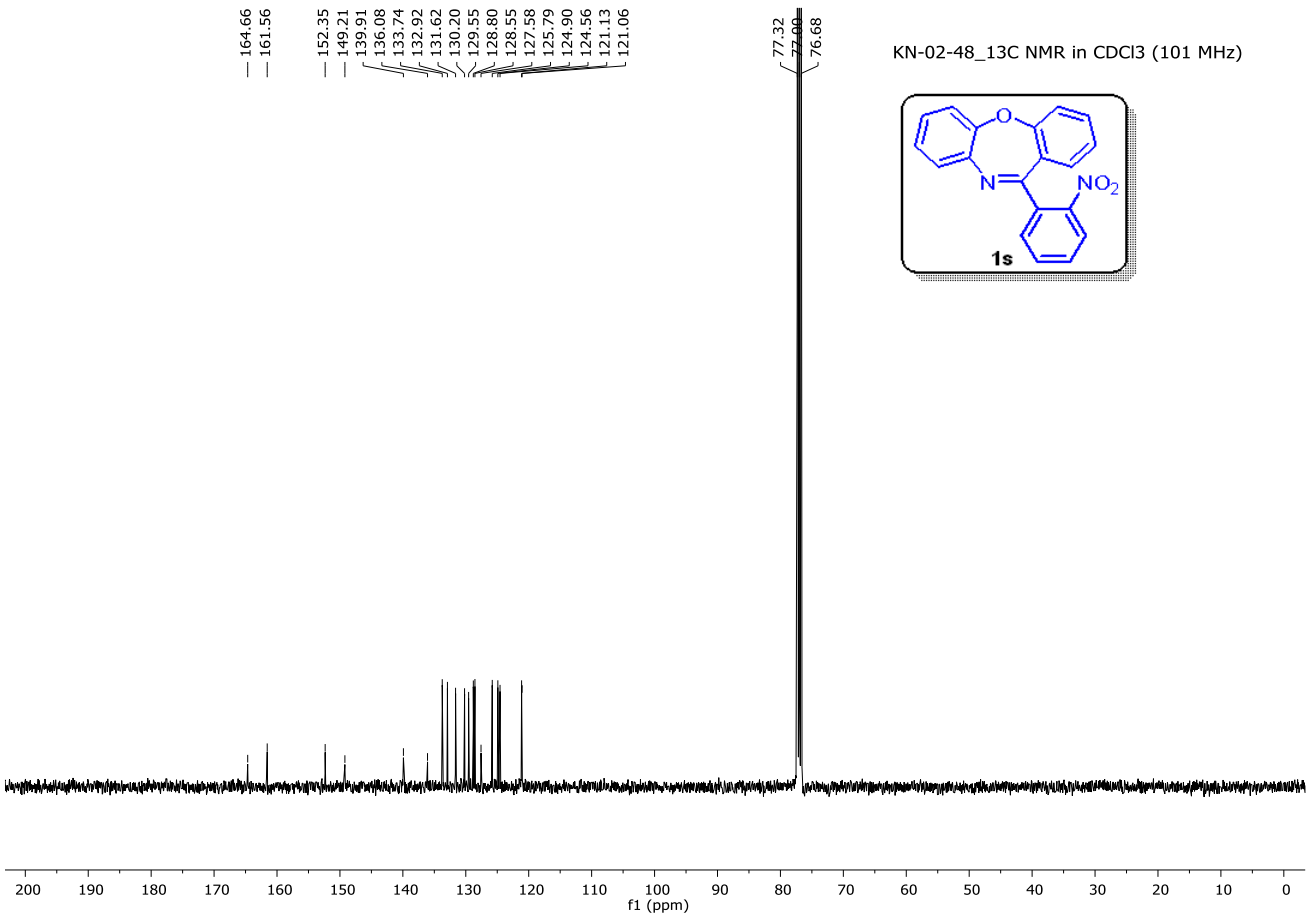
^{13}C{^{1}H} NMR of 1r (101 MHz, $CDCl_3$):



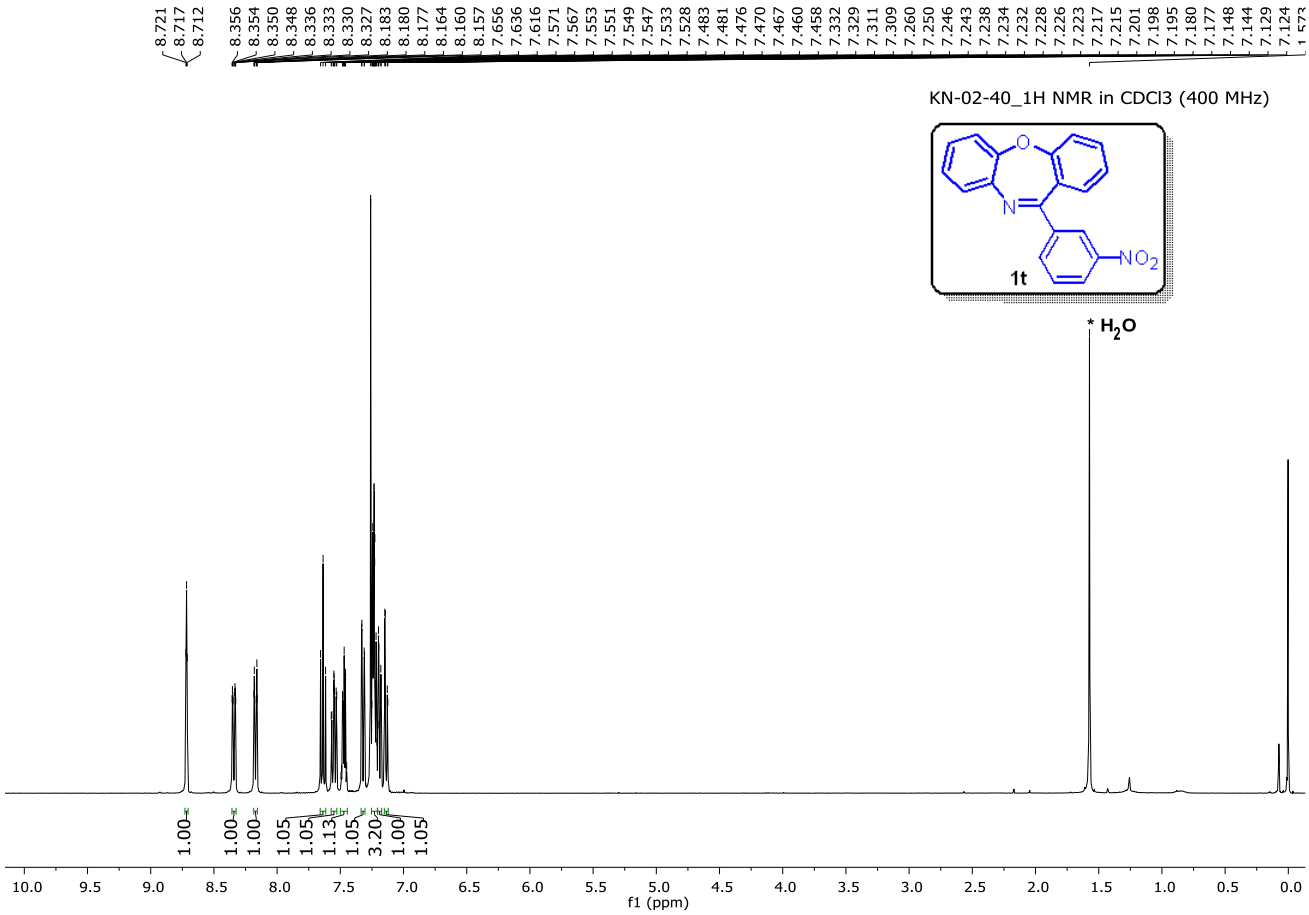
^{1}H NMR of 1s (400 MHz, $CDCl_3$):



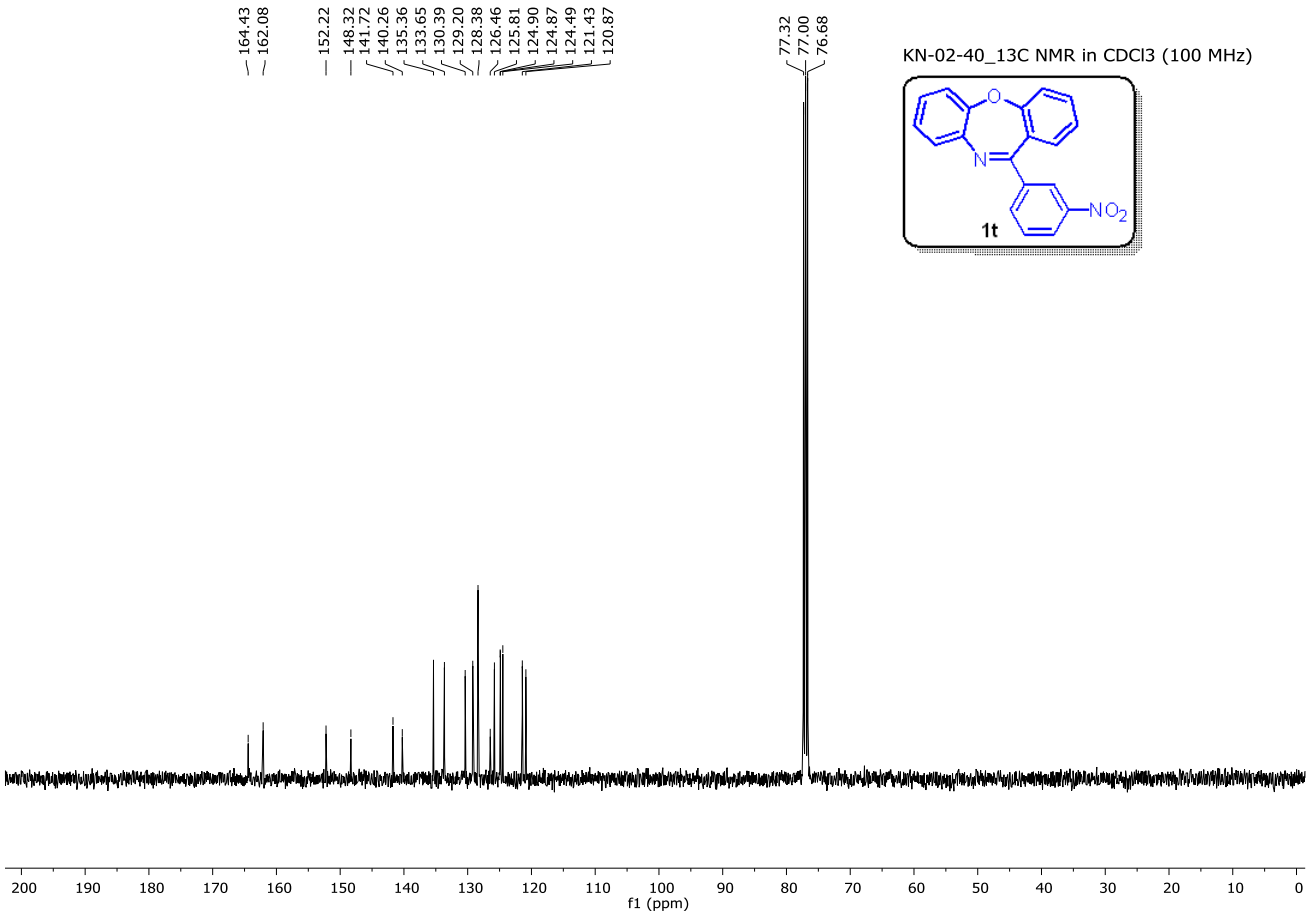
^{13}C{^{1}H} NMR of 1s (101 MHz, $CDCl_3$):



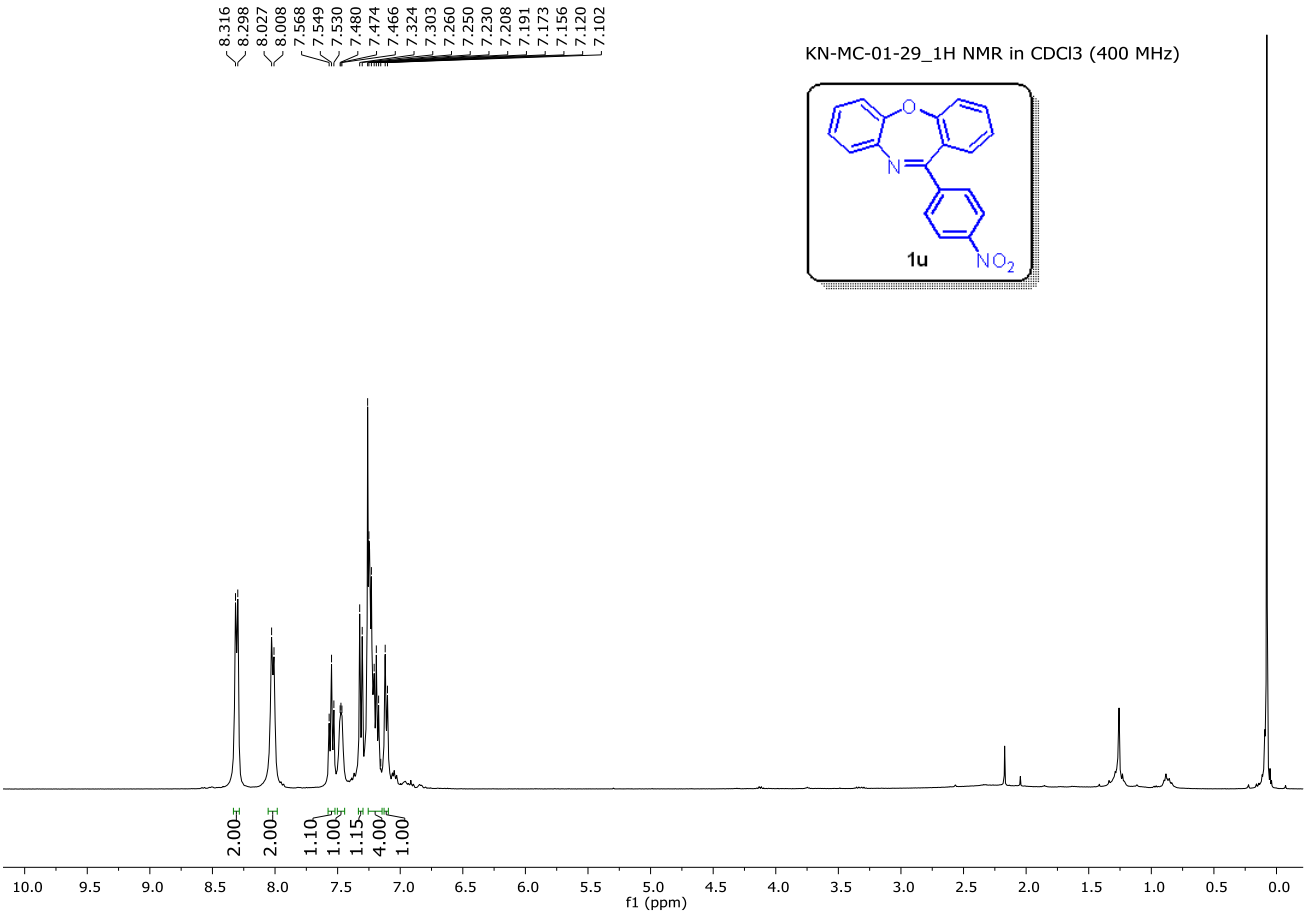
^{1}H NMR of 1t (400 MHz, $CDCl_3$):



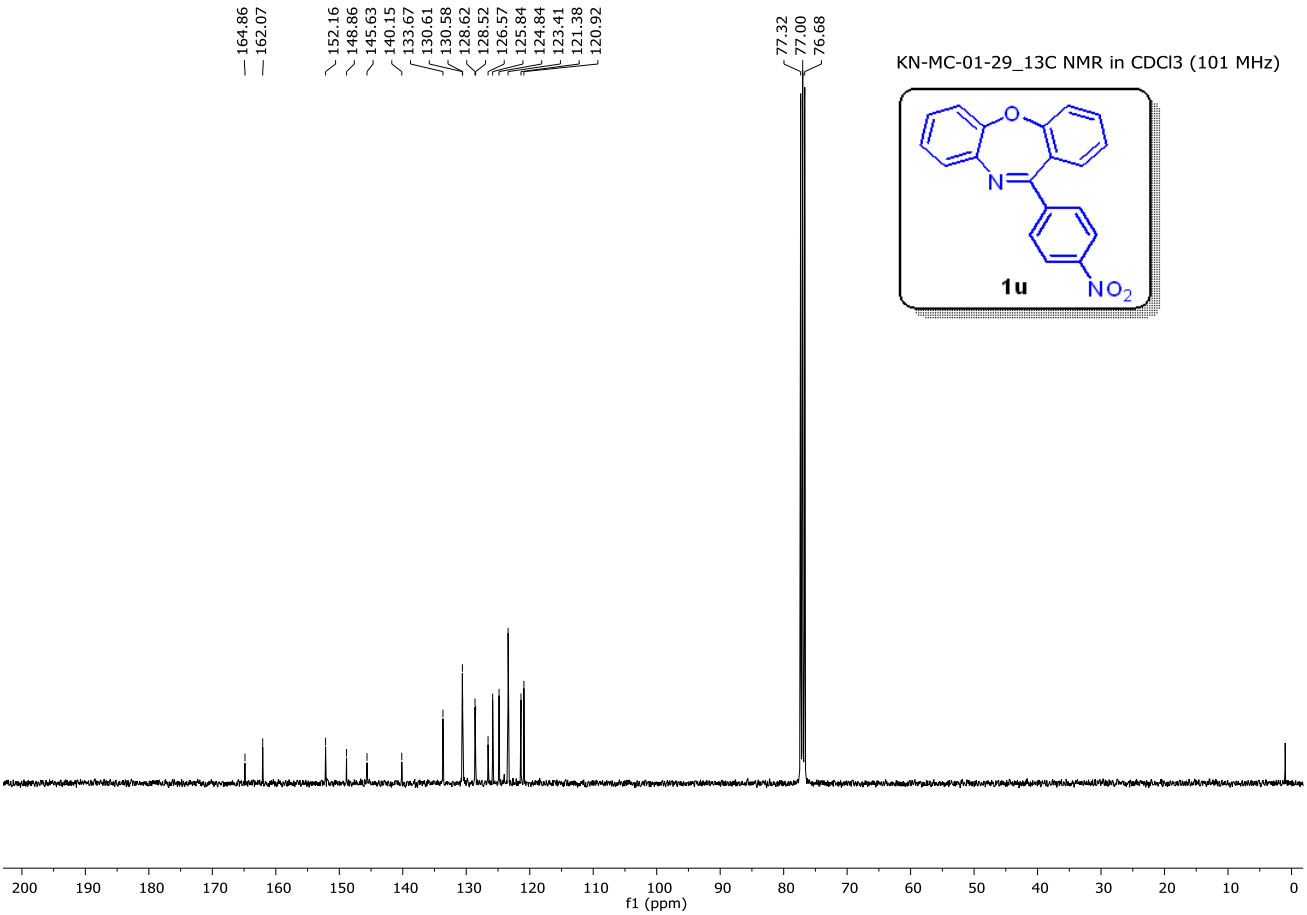
^{13}C{^{1}H} NMR of 1t (101 MHz, $CDCl_3$):



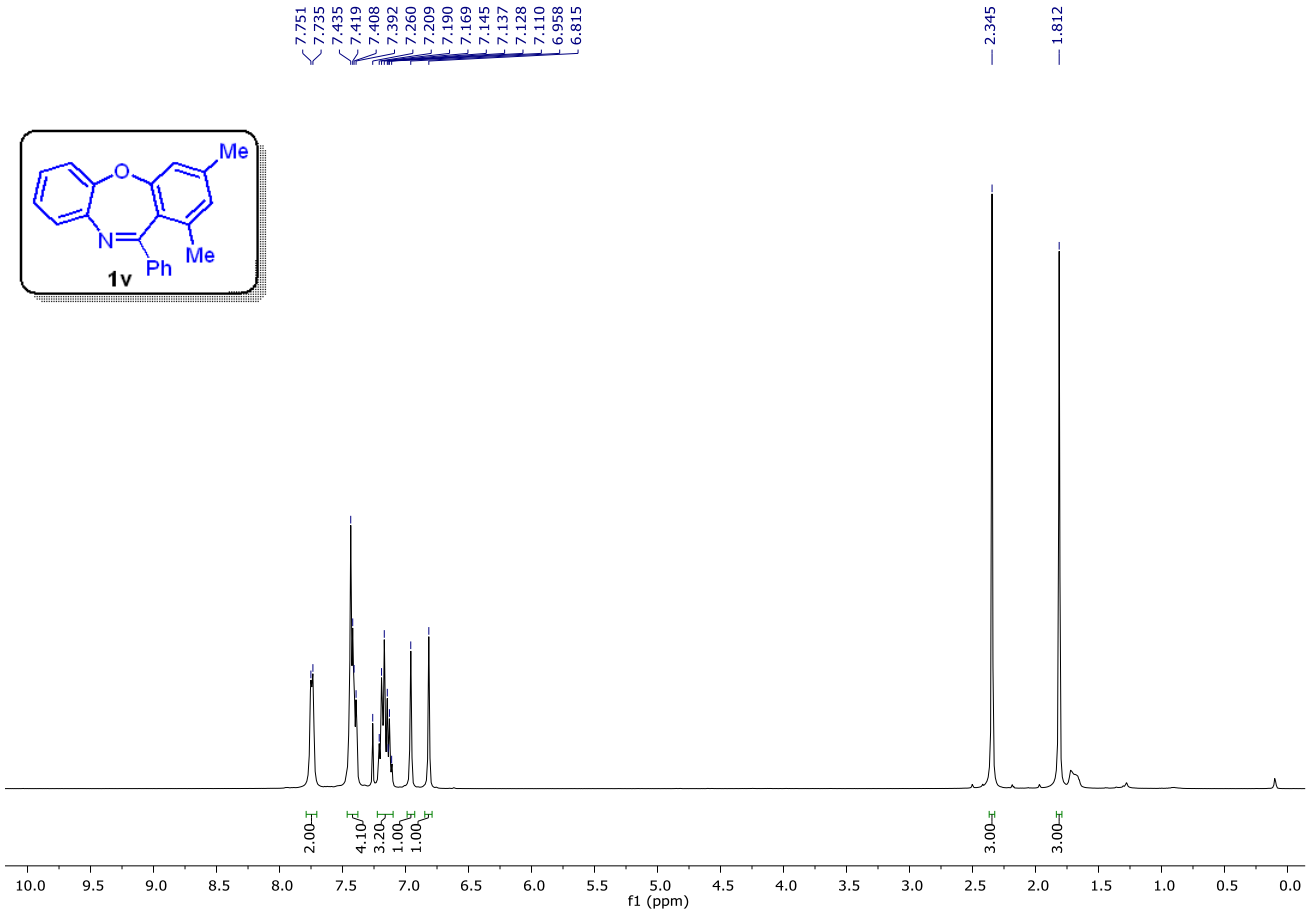
^{1}H NMR of 1u (400 MHz, $CDCl_3$):



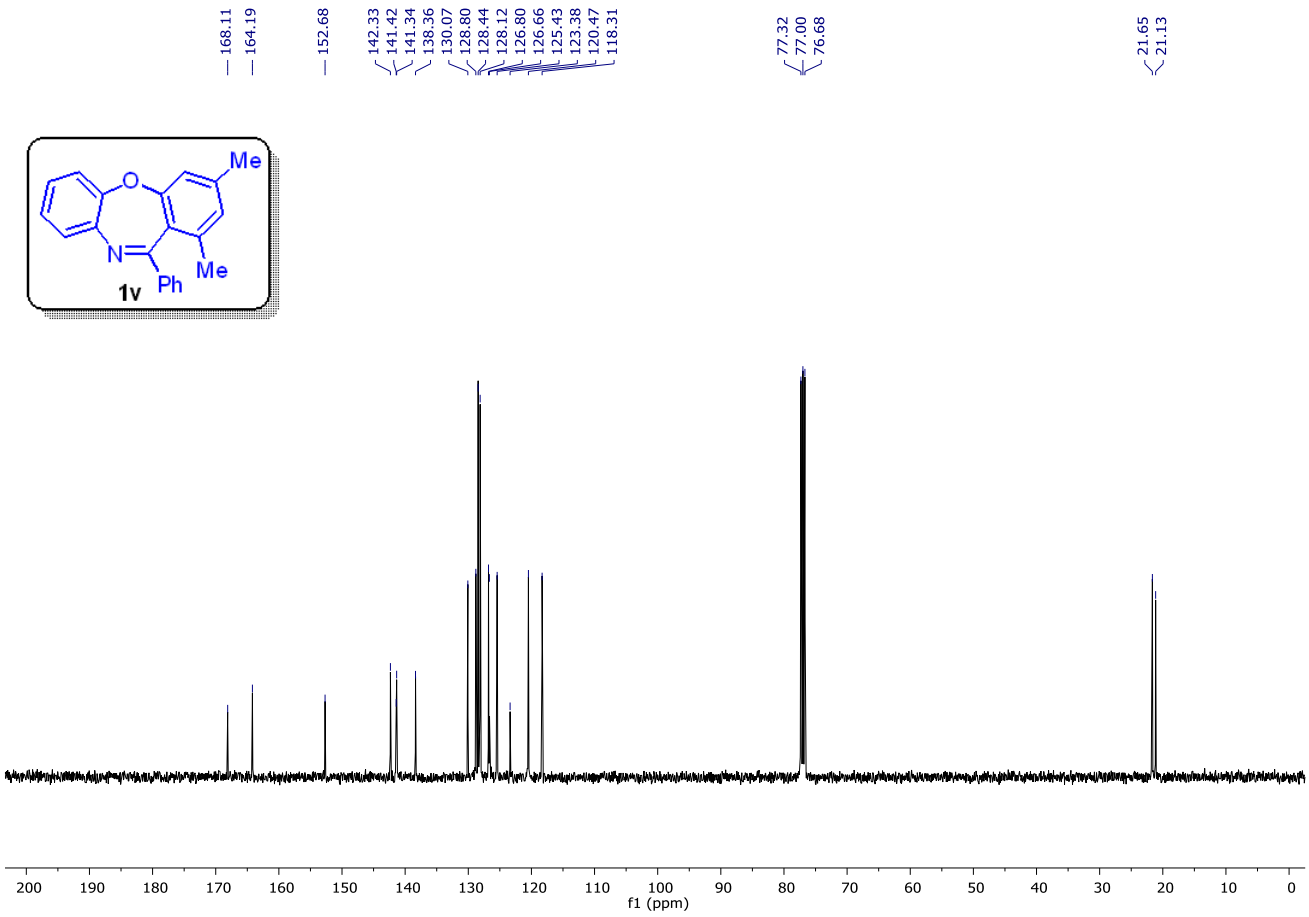
^{13}C{^{1}H} NMR of 1u (101 MHz, $CDCl_3$):



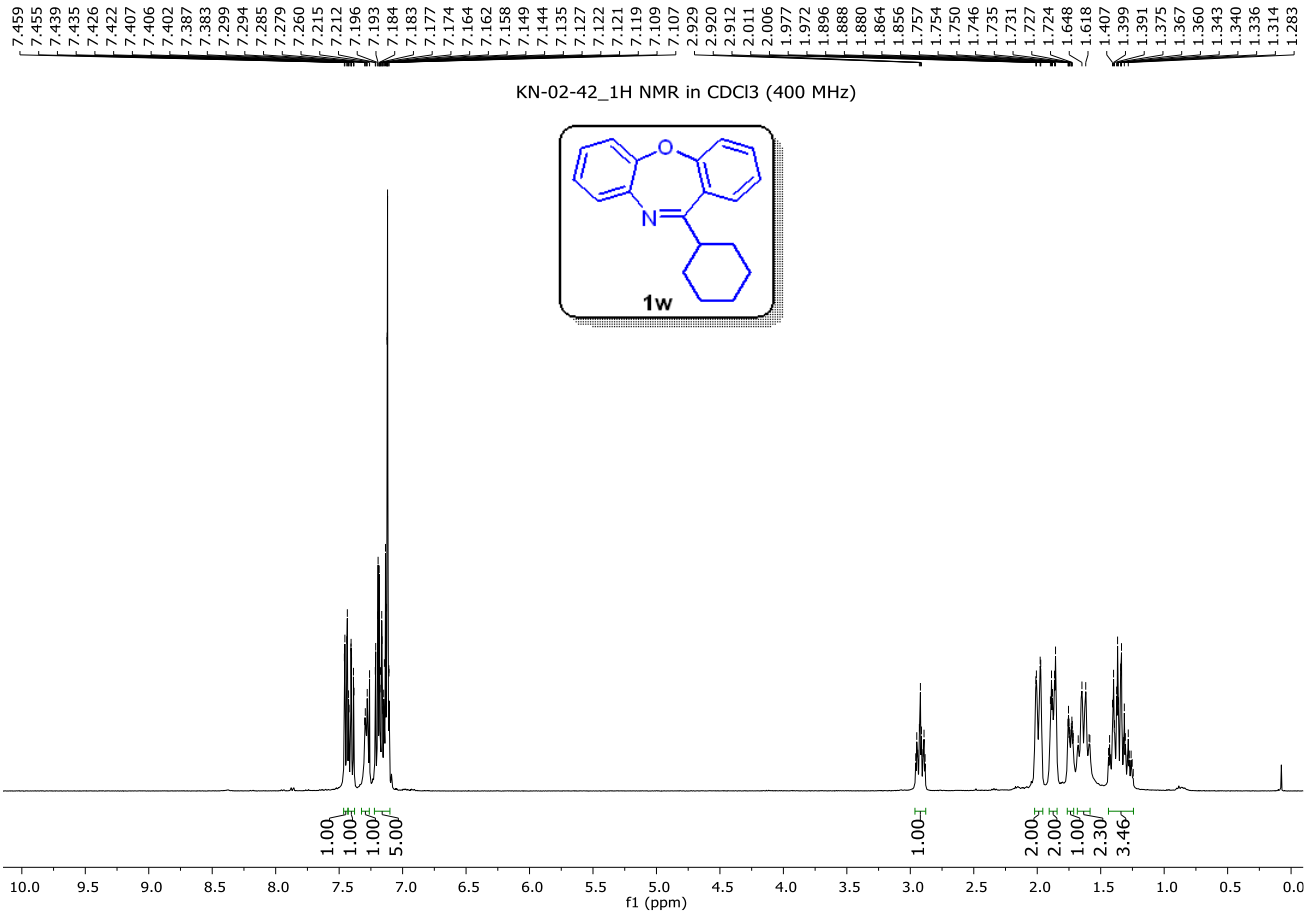
^{1}H NMR of 1v (400 MHz, $CDCl_3$):



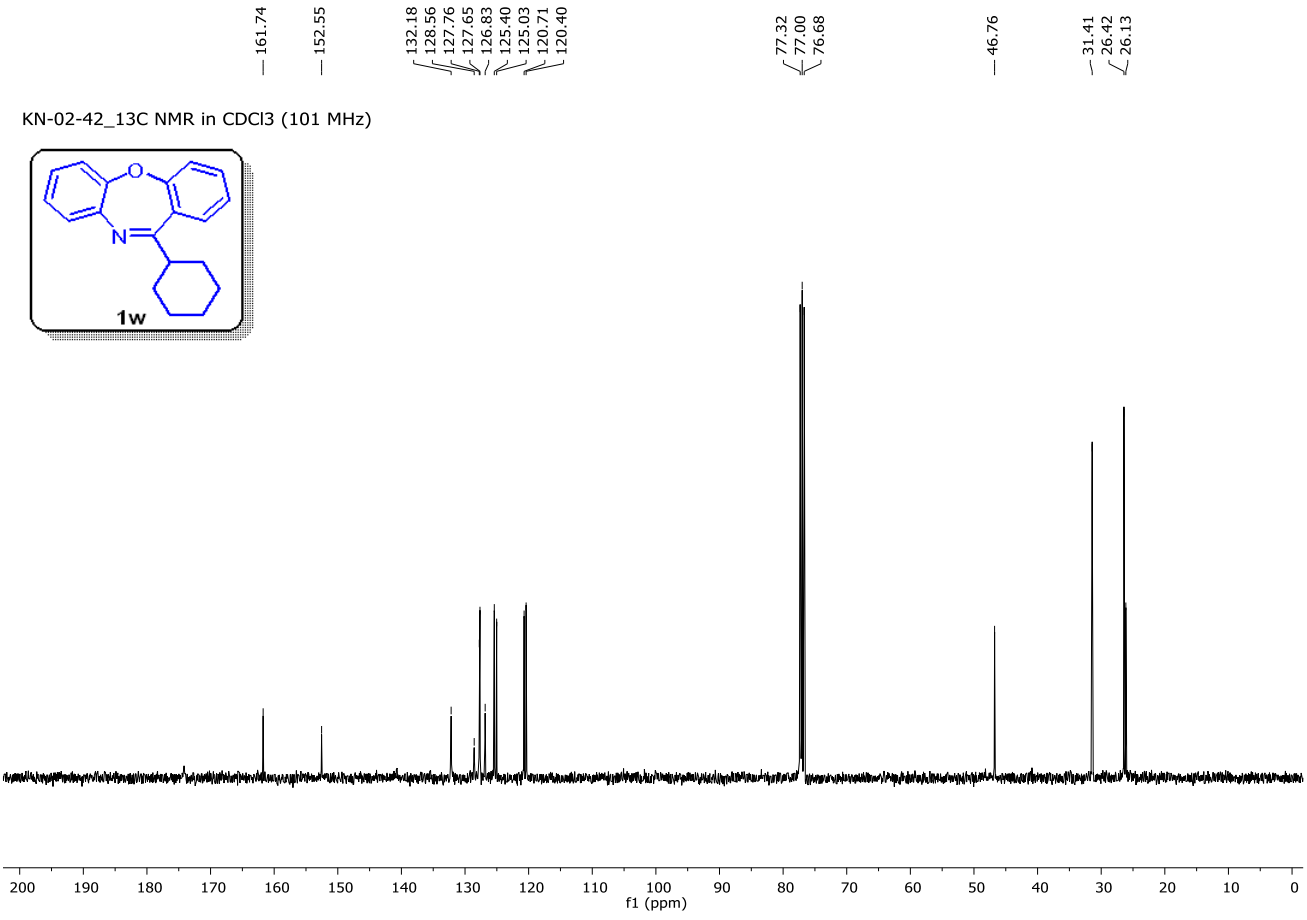
^{13}C{^{1}H} NMR of 1v (101 MHz, $CDCl_3$):



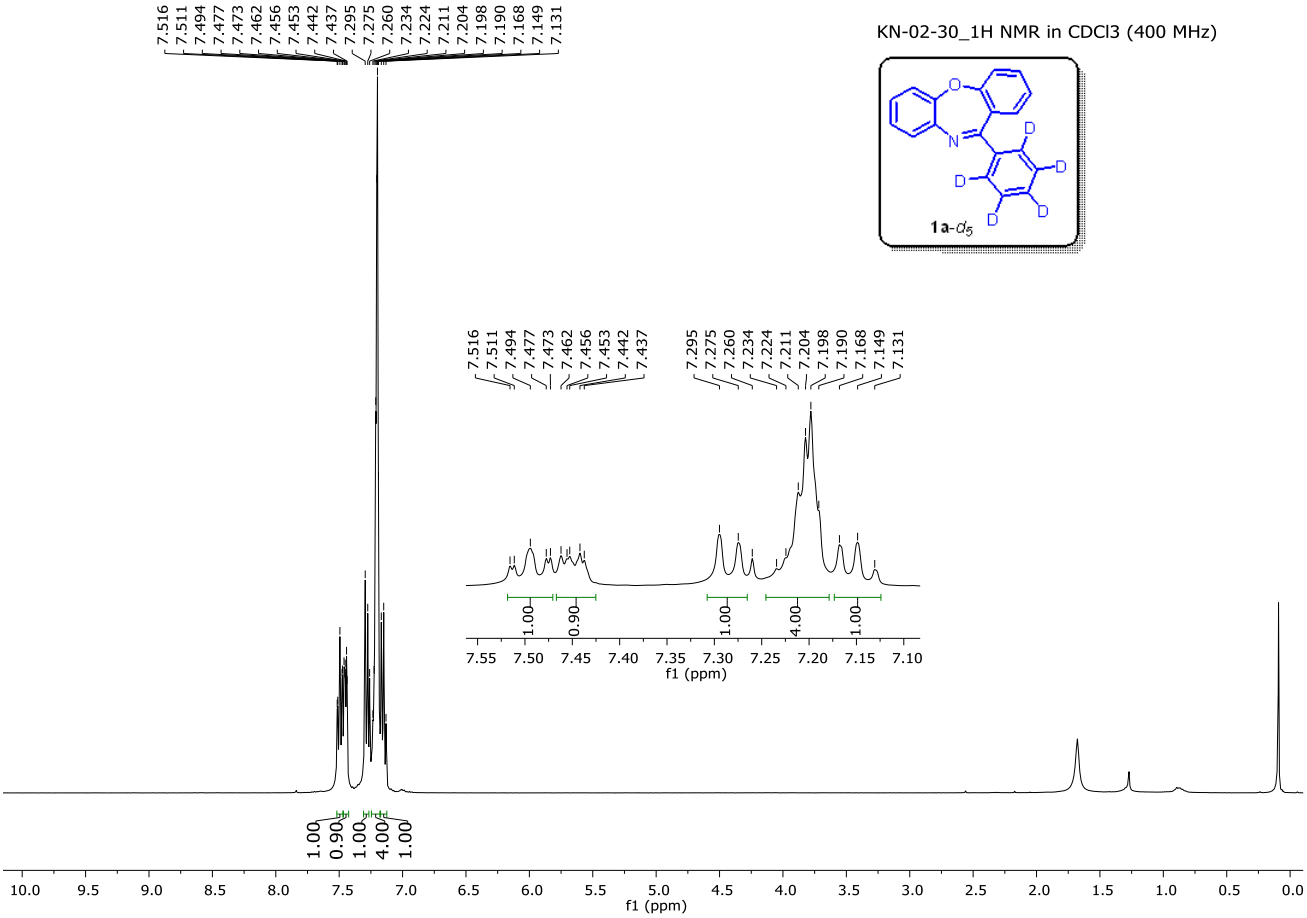
^{1}H NMR of 1w (400 MHz, $CDCl_3$):



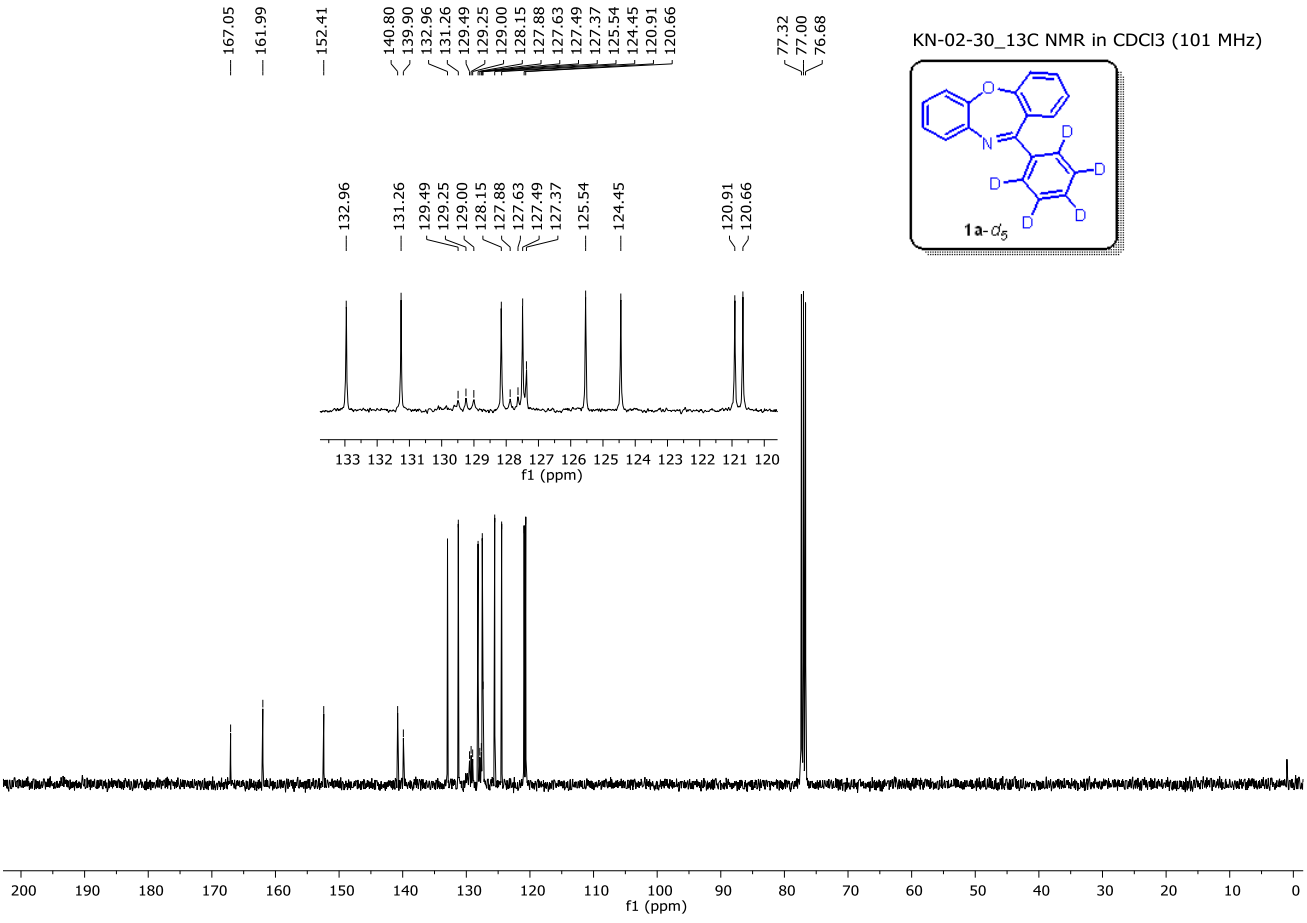
^{13}C{^{1}H} NMR of 1w (101 MHz, $CDCl_3$):



^{1}H NMR of 1a-d_5 (400 MHz, $CDCl_3$):

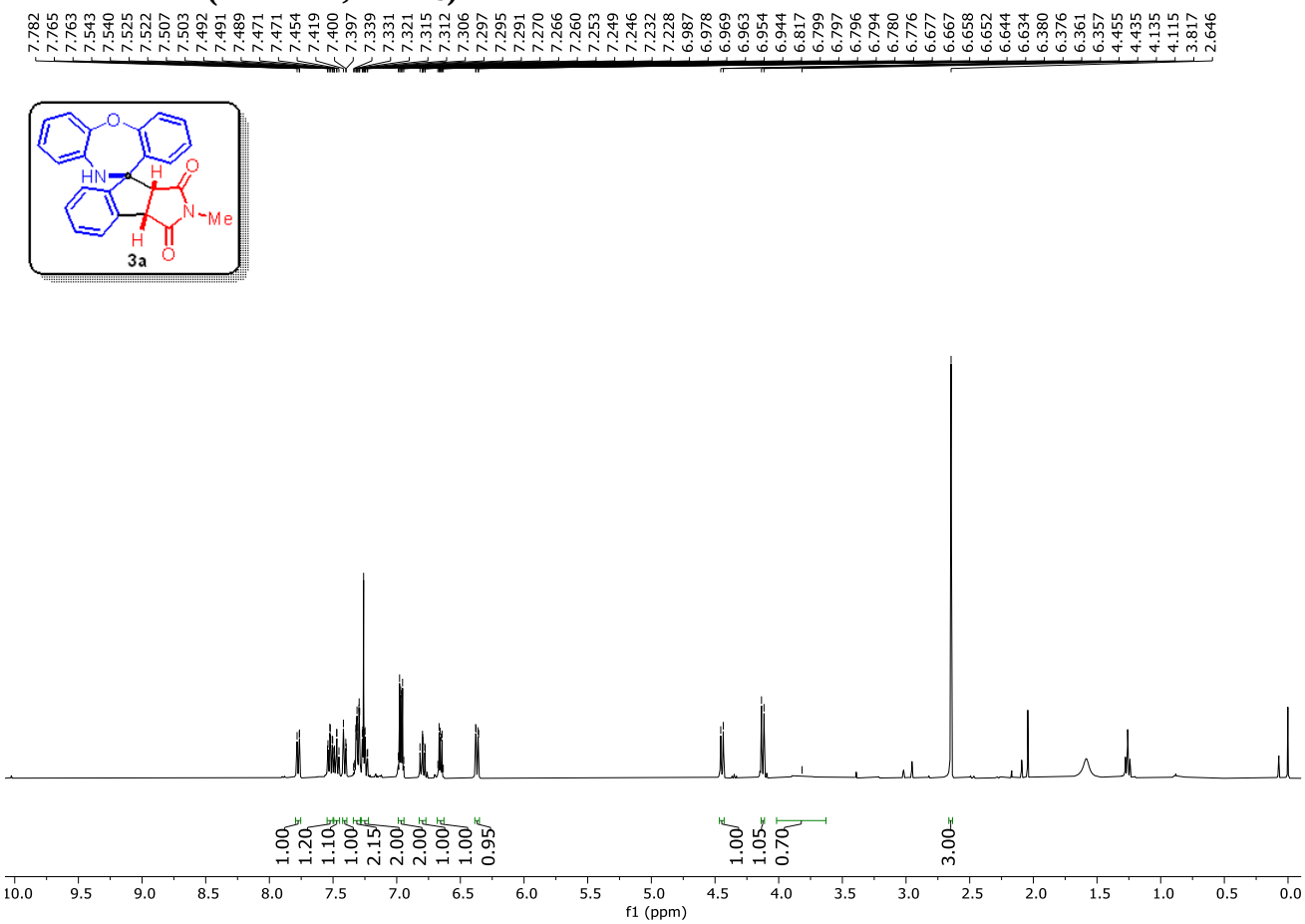


^{13}C{^{1}H} NMR of 1a-d_5 (101 MHz, $CDCl_3$):

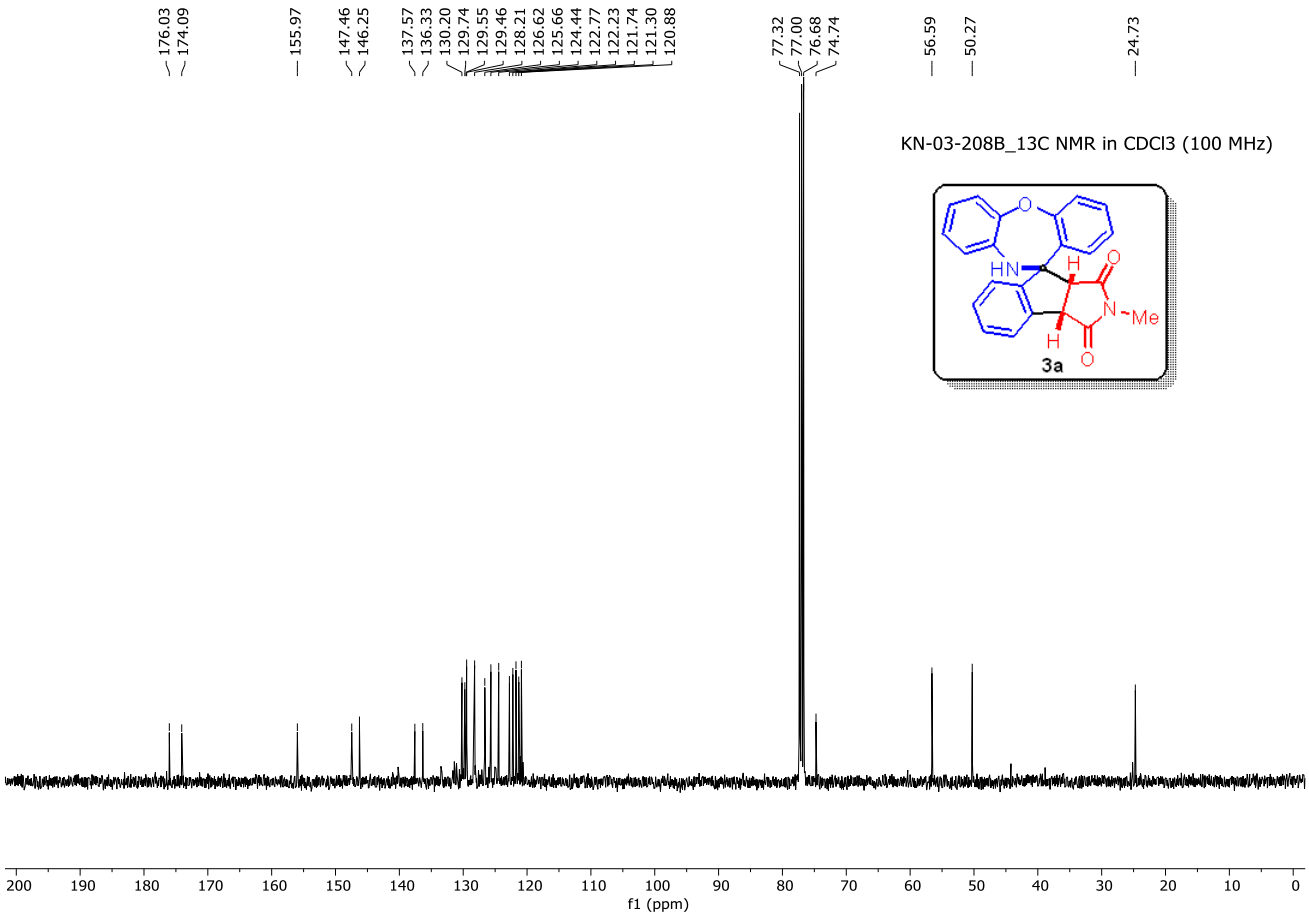


^{1}H, ^{13}C and ^{19}F NMR spectra of [3+2] spiroannulated products:

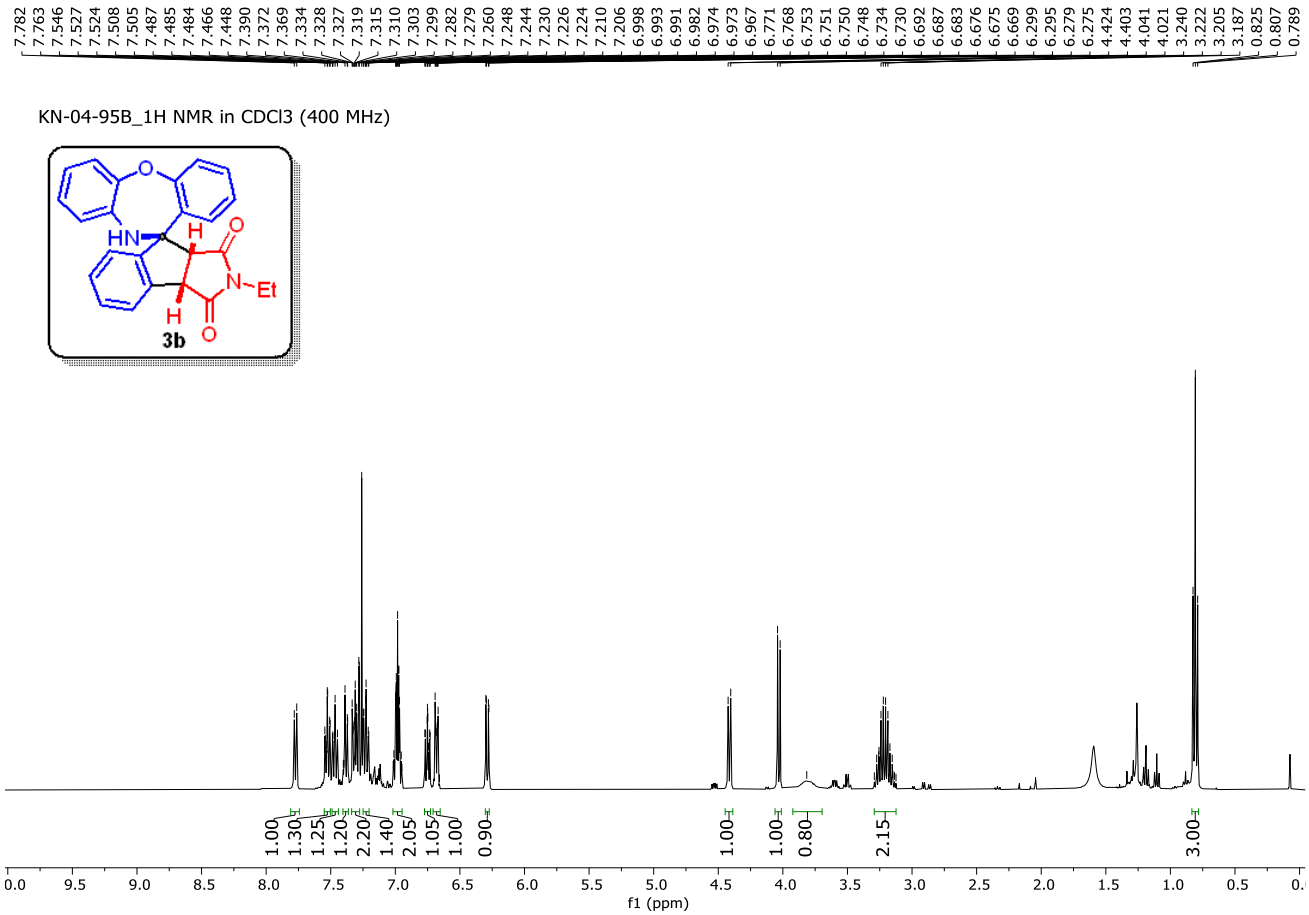
^{1}H NMR of 3a (400 MHz, $CDCl_3$):



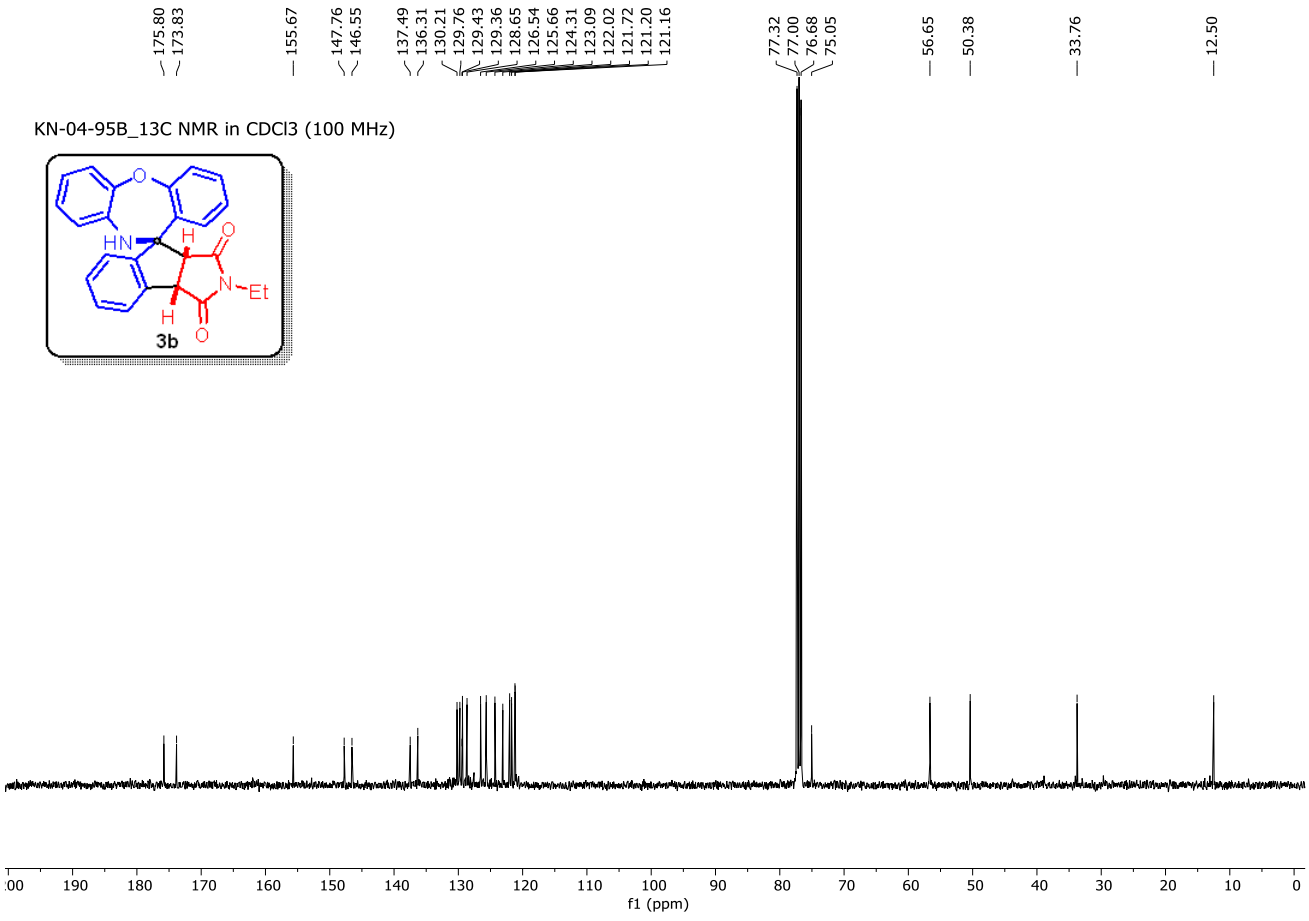
$^{13}C\{^{1}H\}$ NMR of 3a (101 MHz, $CDCl_3$):



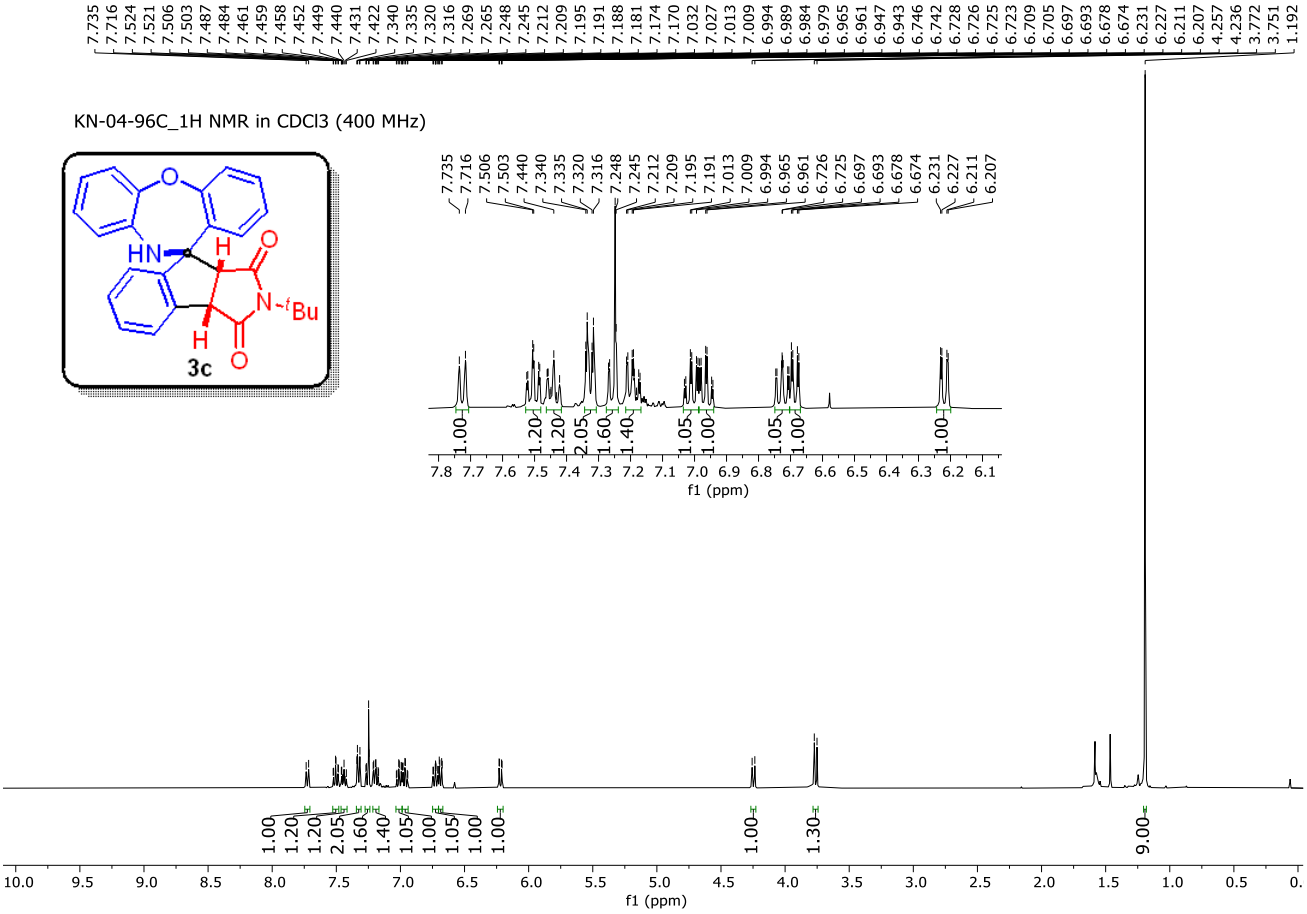
^{1}H NMR of 3b (400 MHz, $CDCl_3$):



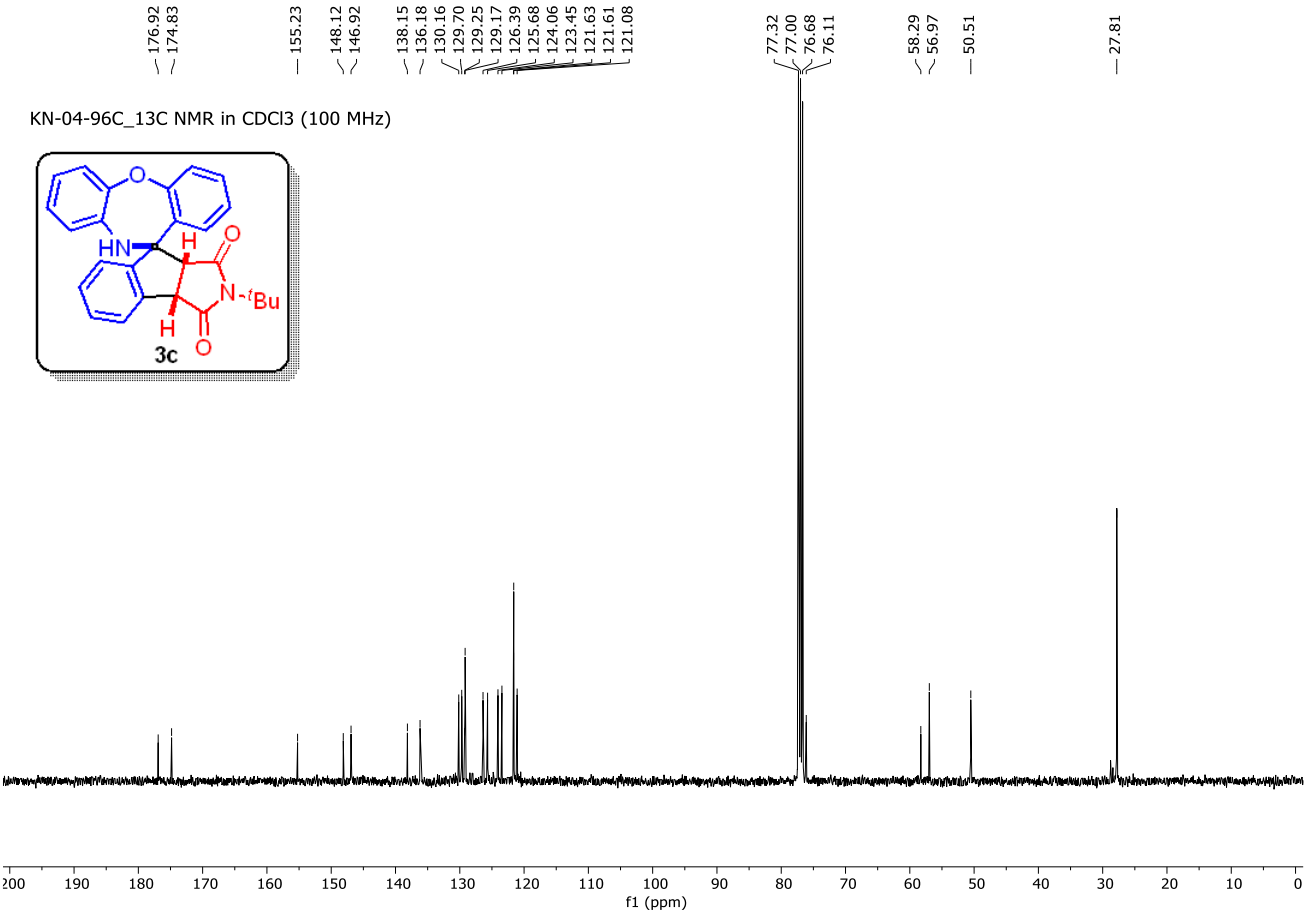
^{13}C{^{1}H} NMR of 3b (101 MHz, $CDCl_3$):



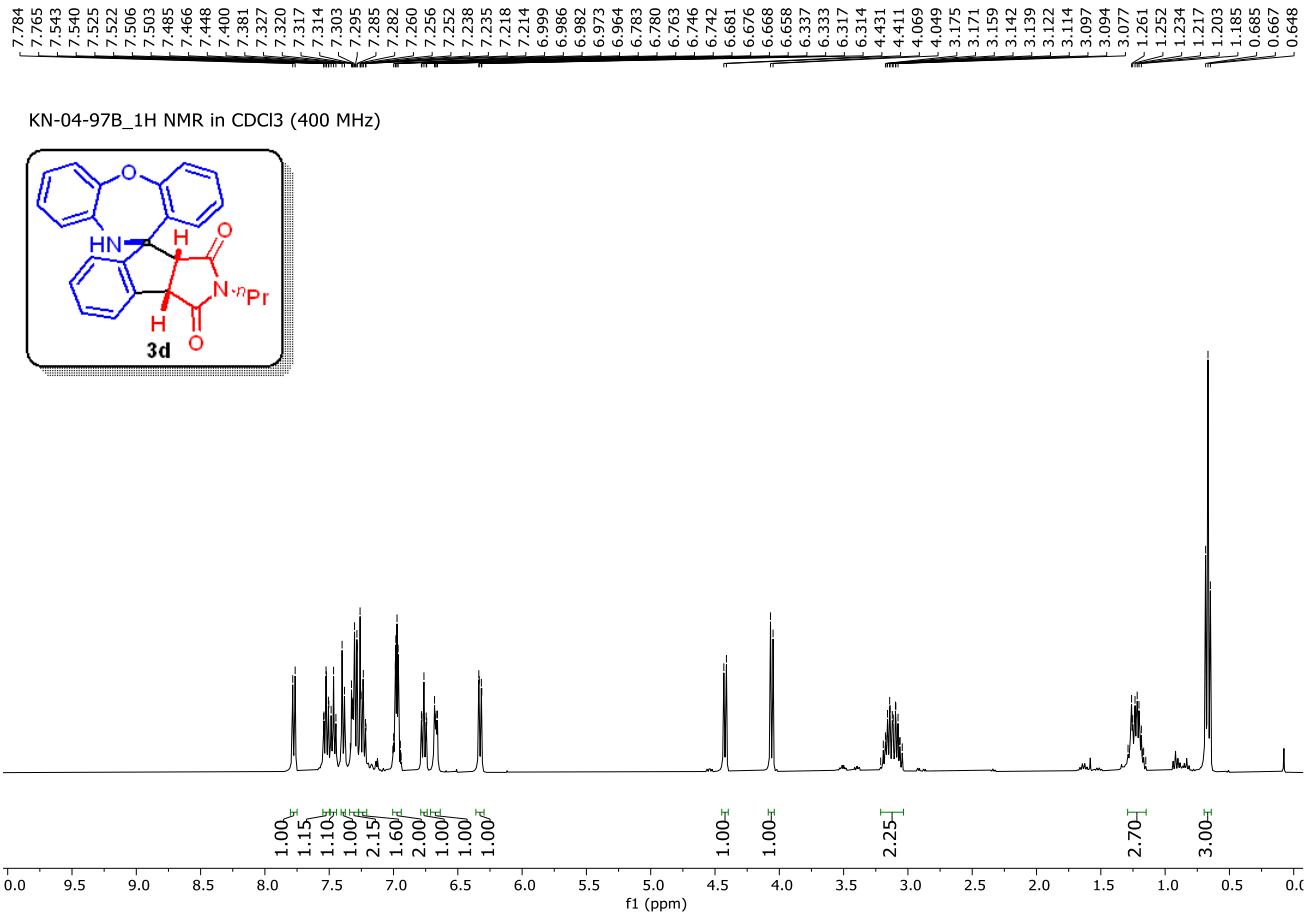
^{1}H NMR of 3c in $CDCl_3$ (400 MHz):



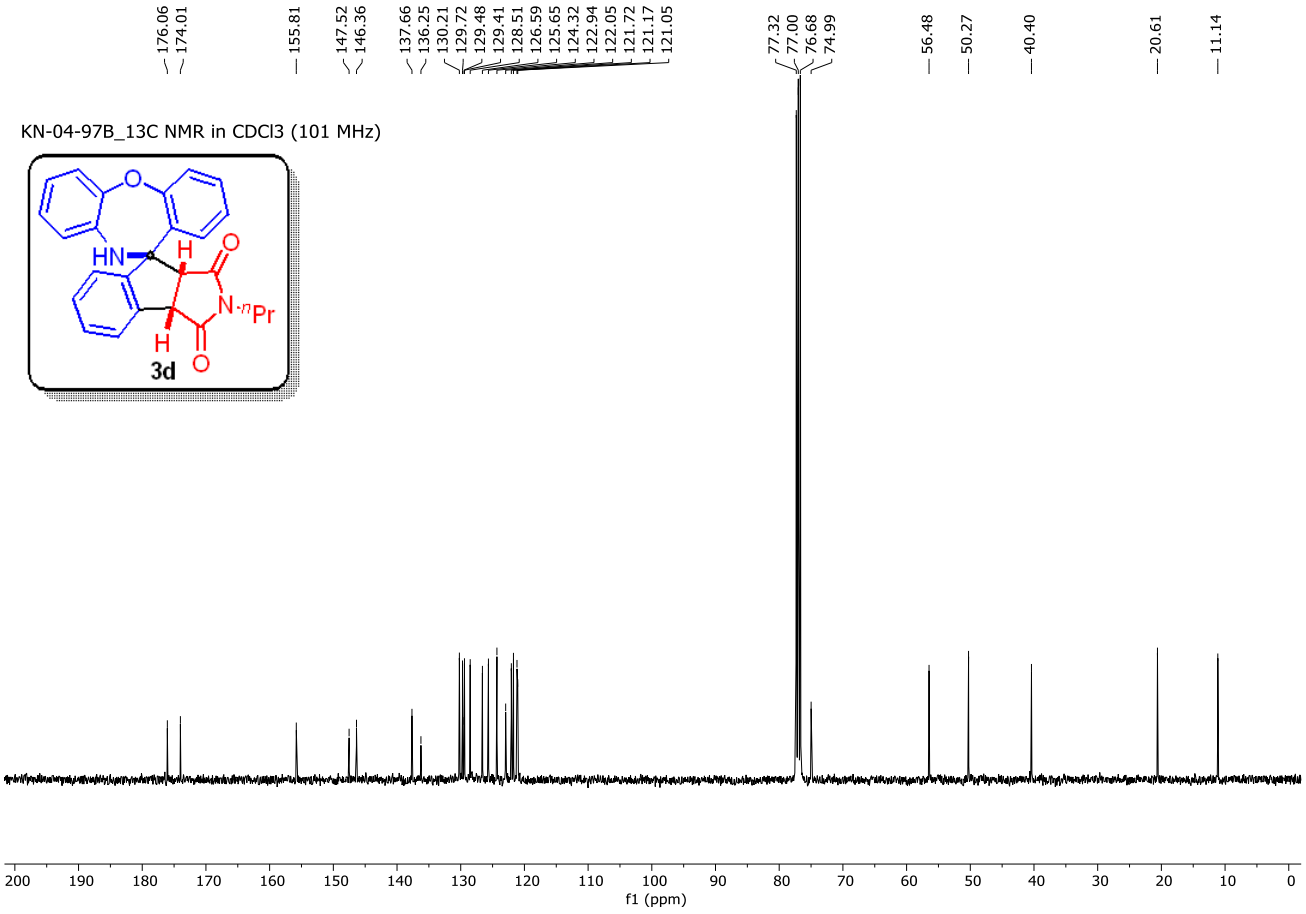
^{13}C{^{1}H} NMR of 3c in $CDCl_3$ (101 MHz):



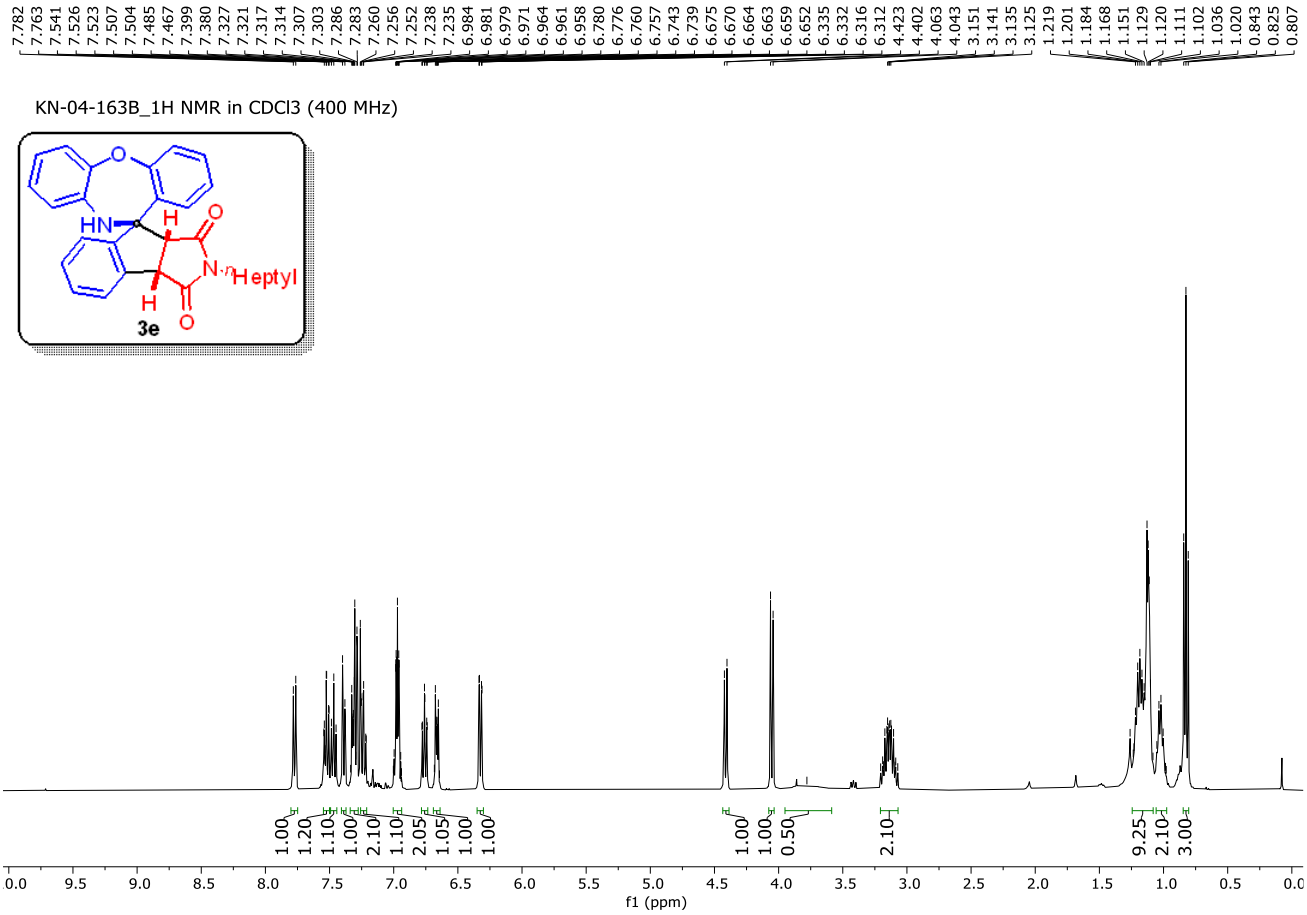
^{1}H NMR of 3d in $CDCl_3$ (400 MHz):



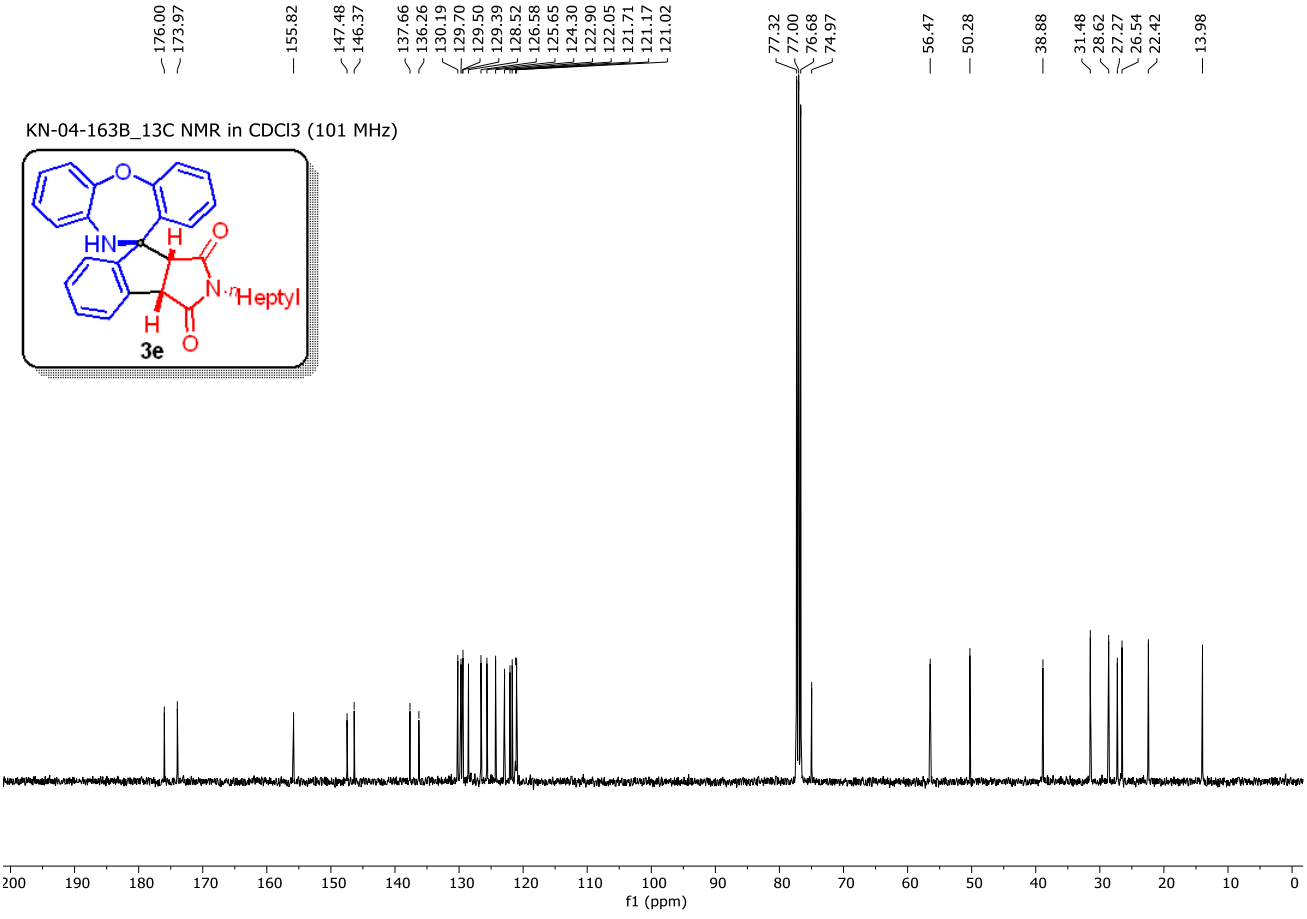
^{13}C{^{1}H} NMR of 3d in $CDCl_3$ (101 MHz):



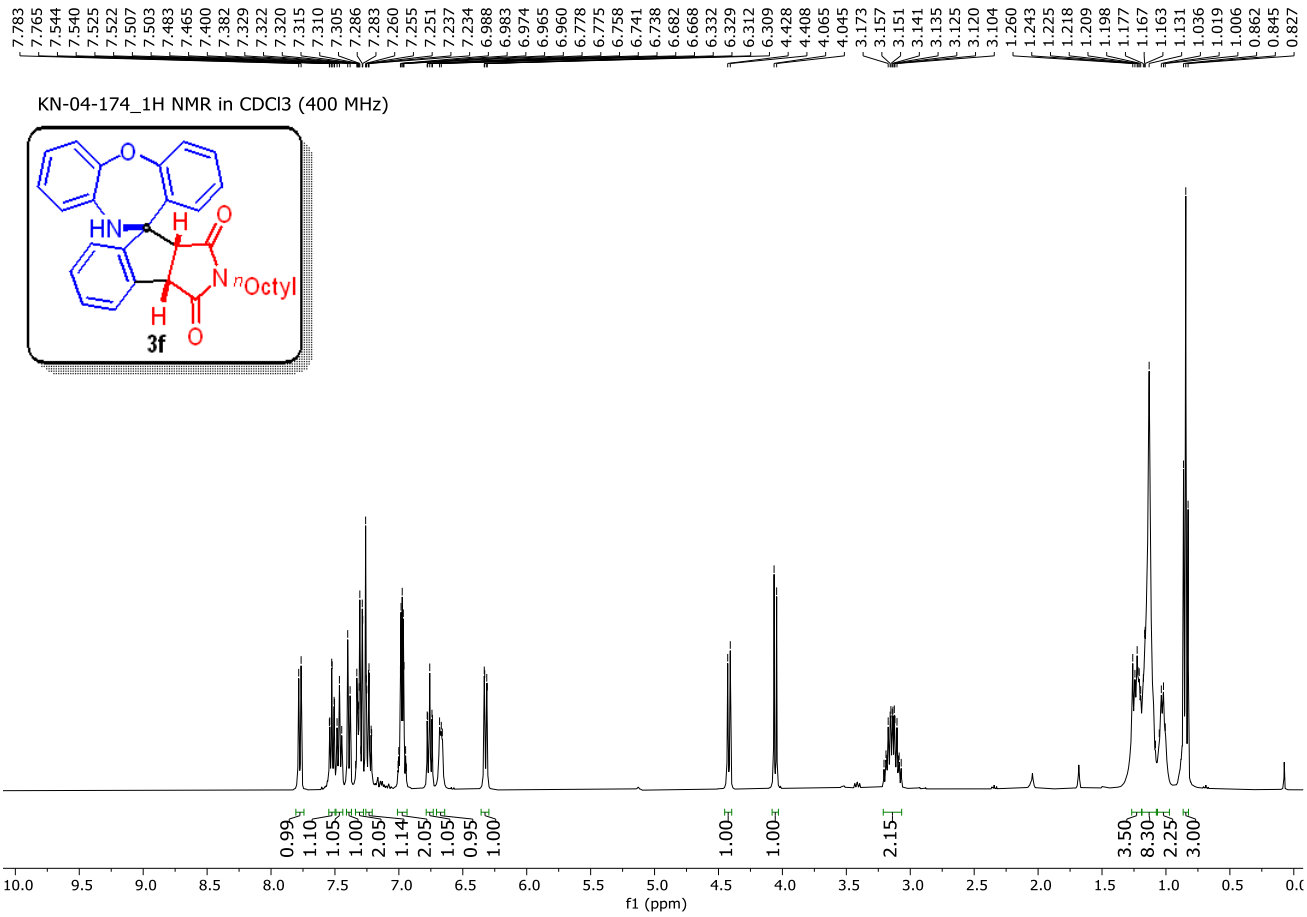
^{1}H NMR of 3e in $CDCl_3$ (400 MHz):



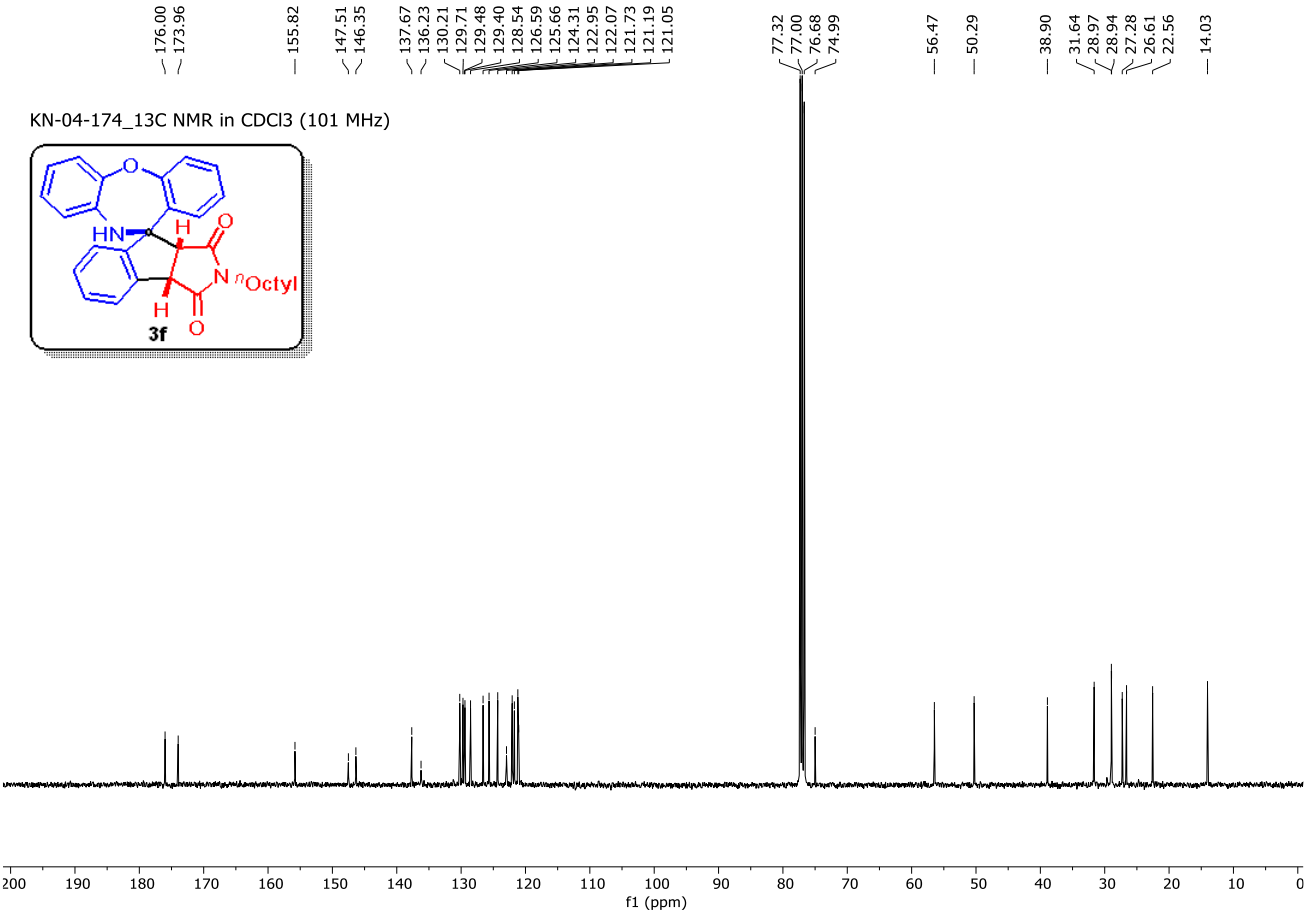
^{13}C{^{1}H} NMR of 3e in $CDCl_3$ (101 MHz):



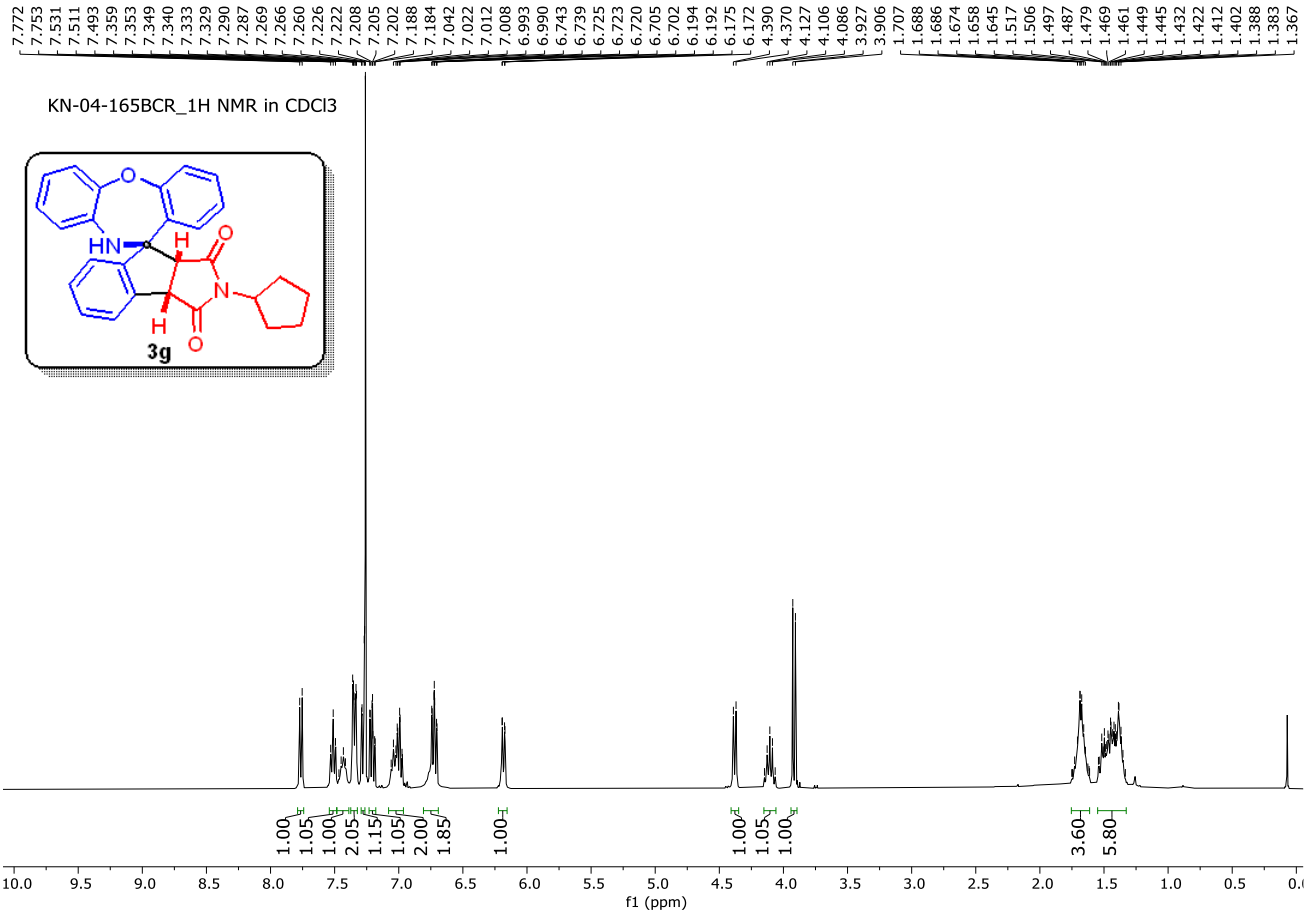
^{1}H NMR of 3f in $CDCl_3$ (400 MHz):



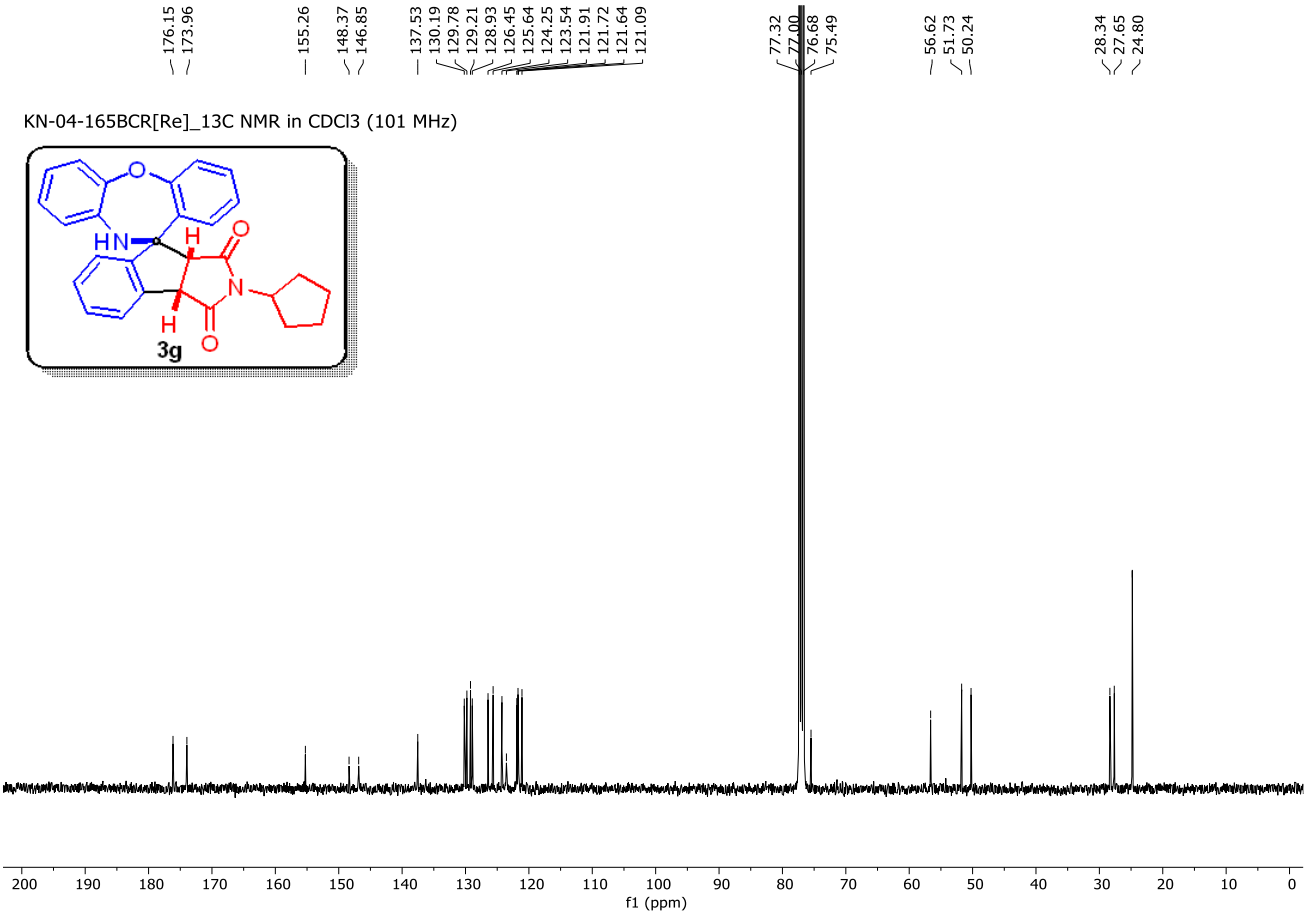
^{13}C{^{1}H} NMR of 3f in $CDCl_3$ (101 MHz):



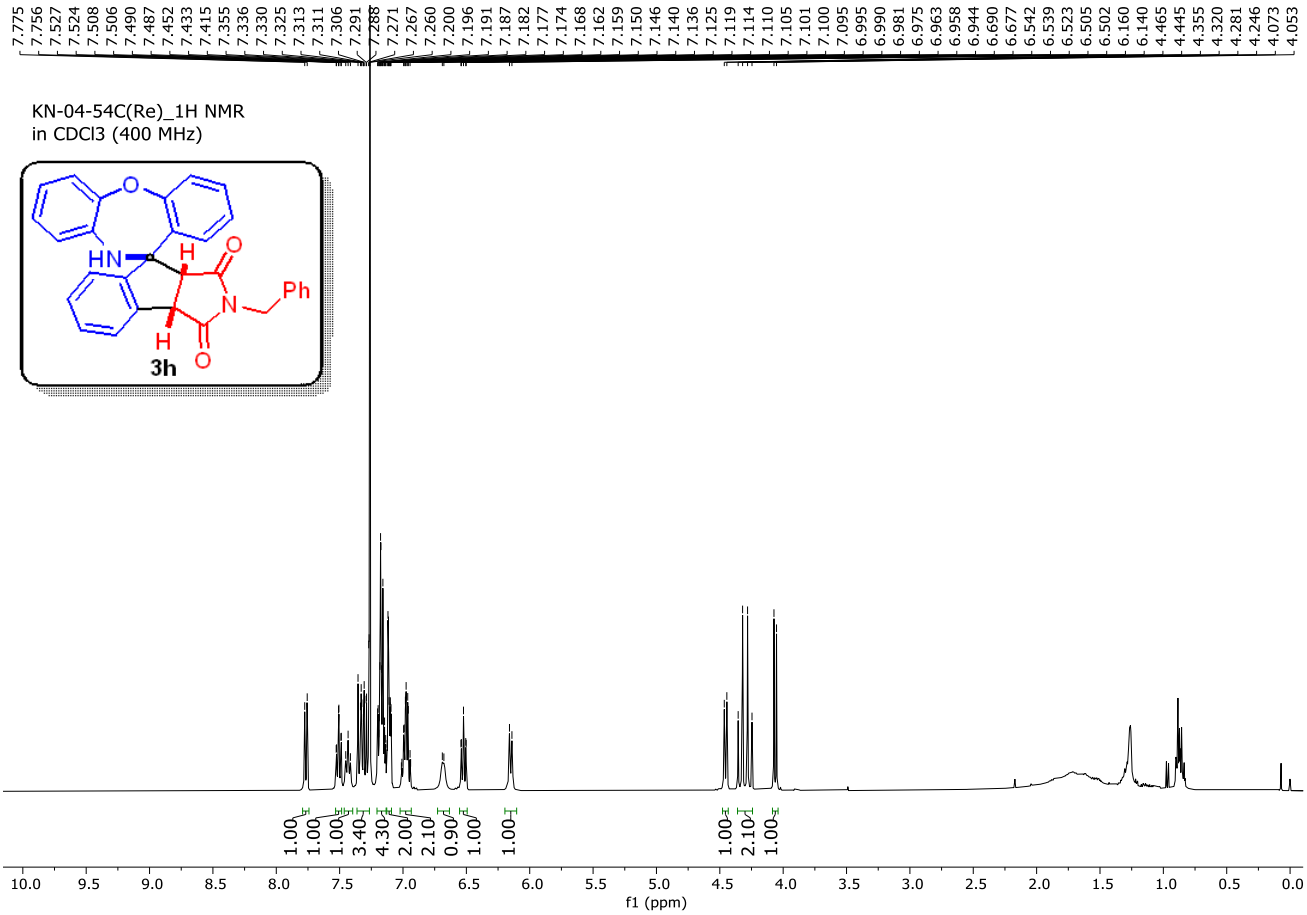
^{1}H NMR of 3g in $CDCl_3$ (400 MHz):



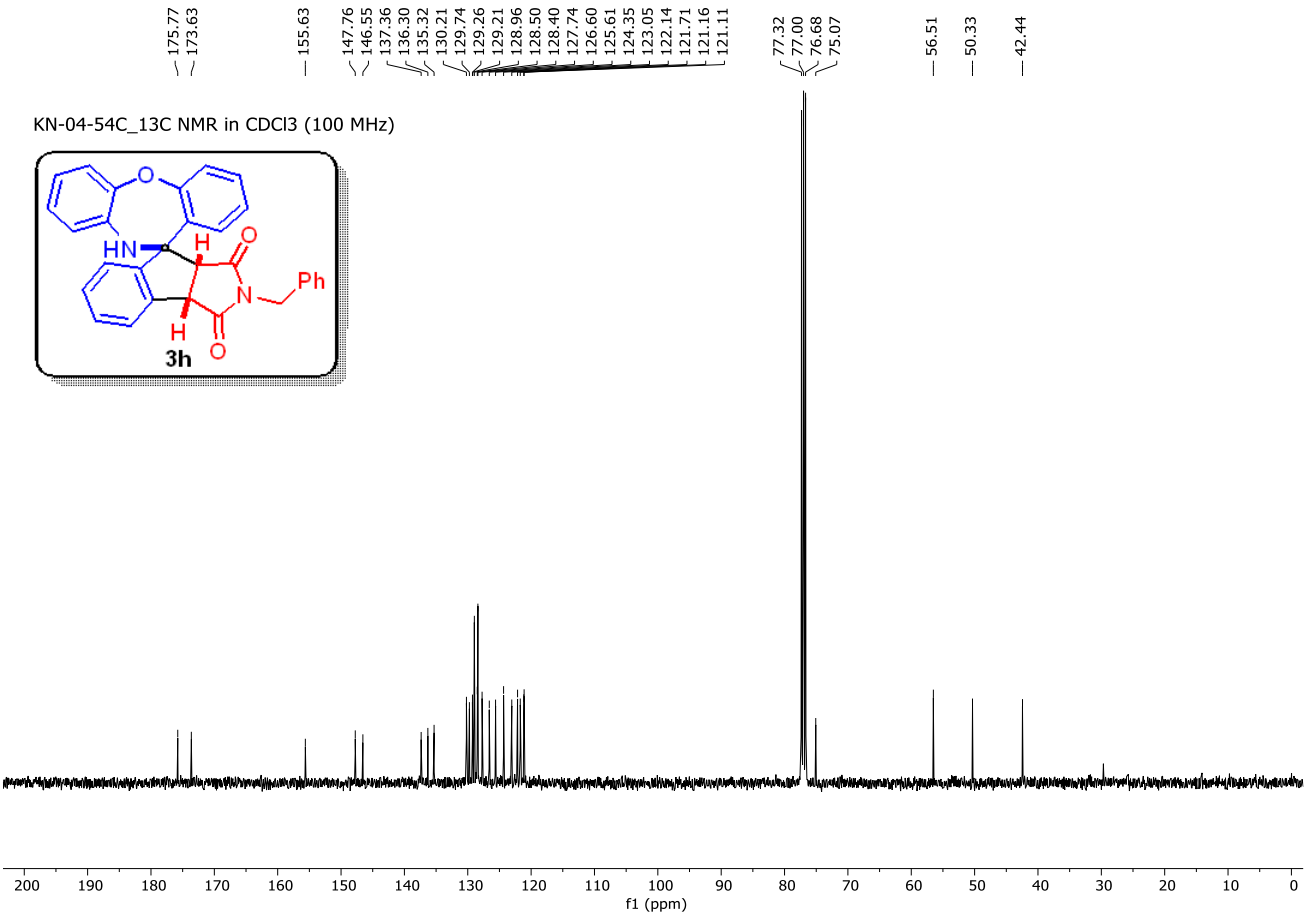
^{13}C{^{1}H} NMR of 3g in $CDCl_3$ (101 MHz):



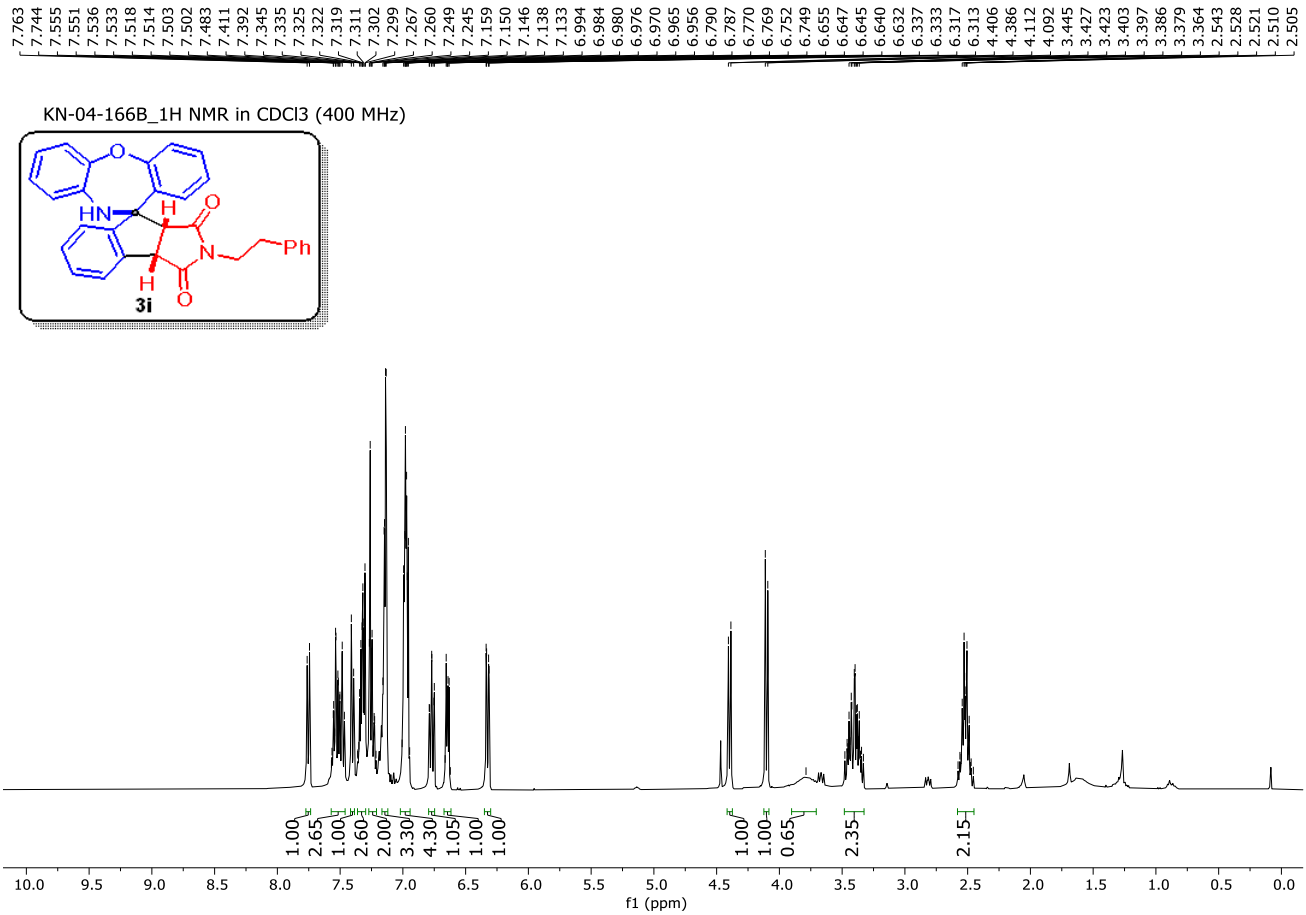
^{1}H NMR of 3h in $CDCl_3$ (400 MHz):



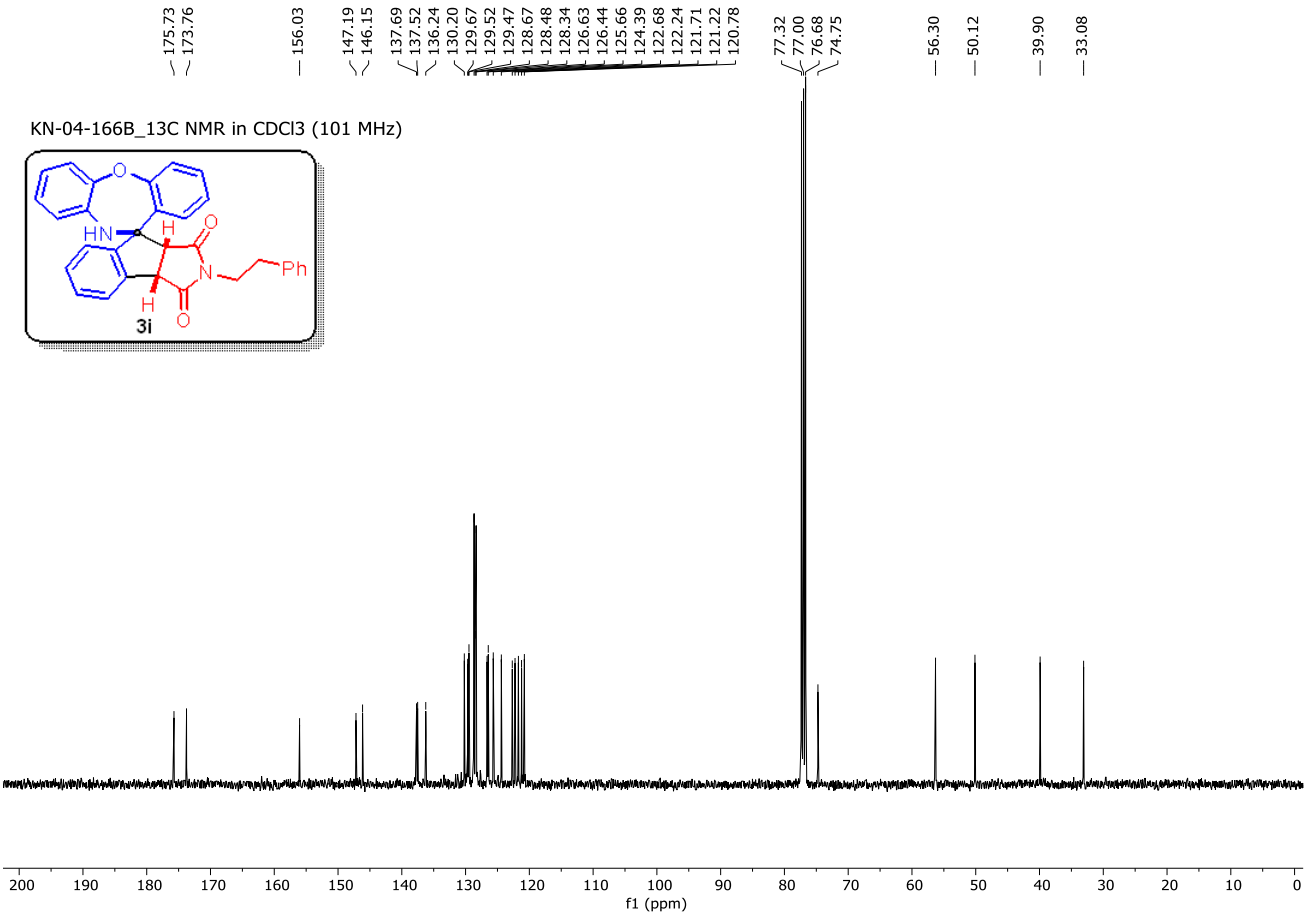
^{13}C{^{1}H} NMR of 3h in $CDCl_3$ (101 MHz):



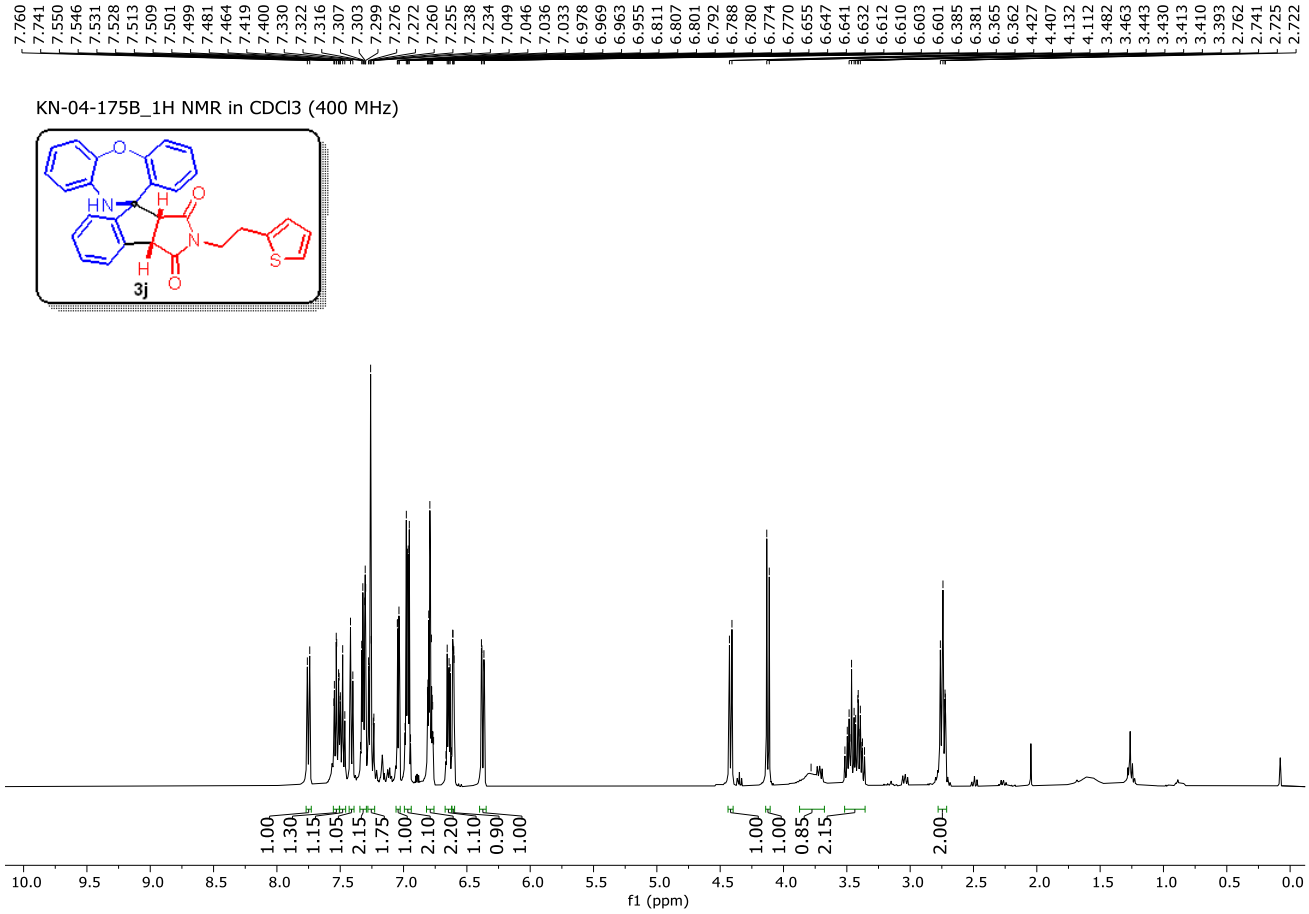
^{1}H NMR of 3i in $CDCl_3$ (400 MHz):



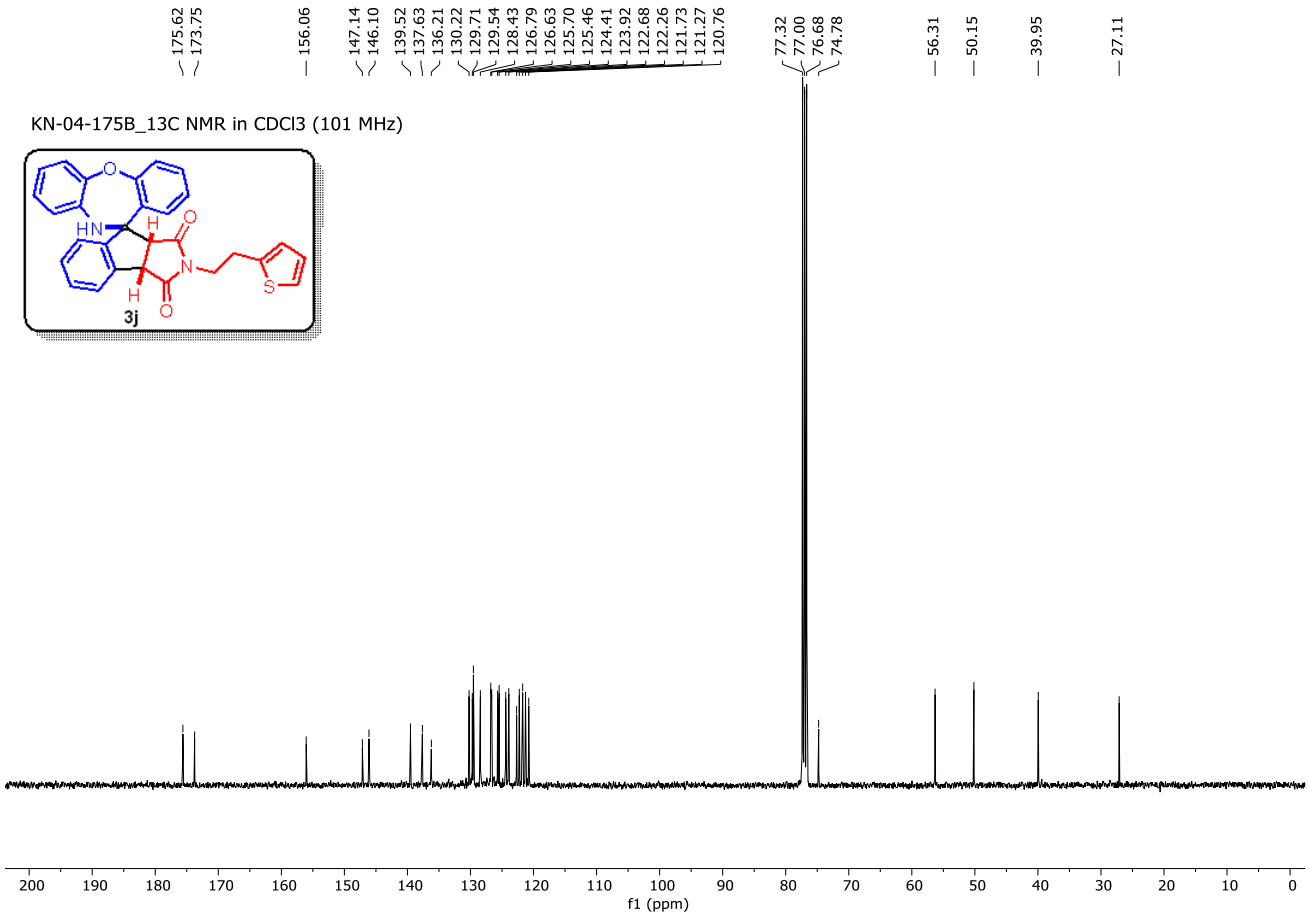
^{13}C{^{1}H} NMR of 3i in $CDCl_3$ (101 MHz):



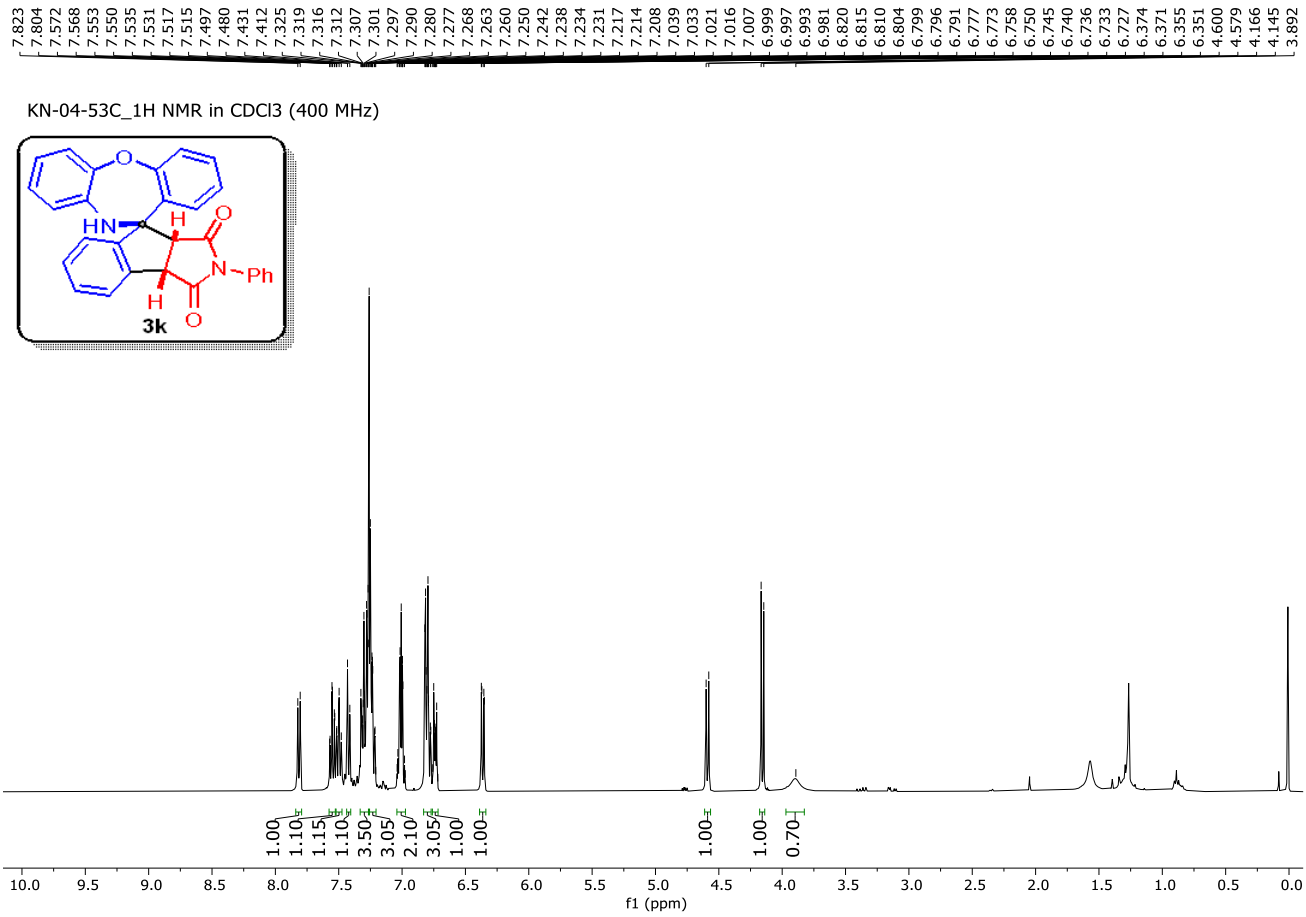
^{1}H NMR of 3j in $CDCl_3$ (400 MHz):



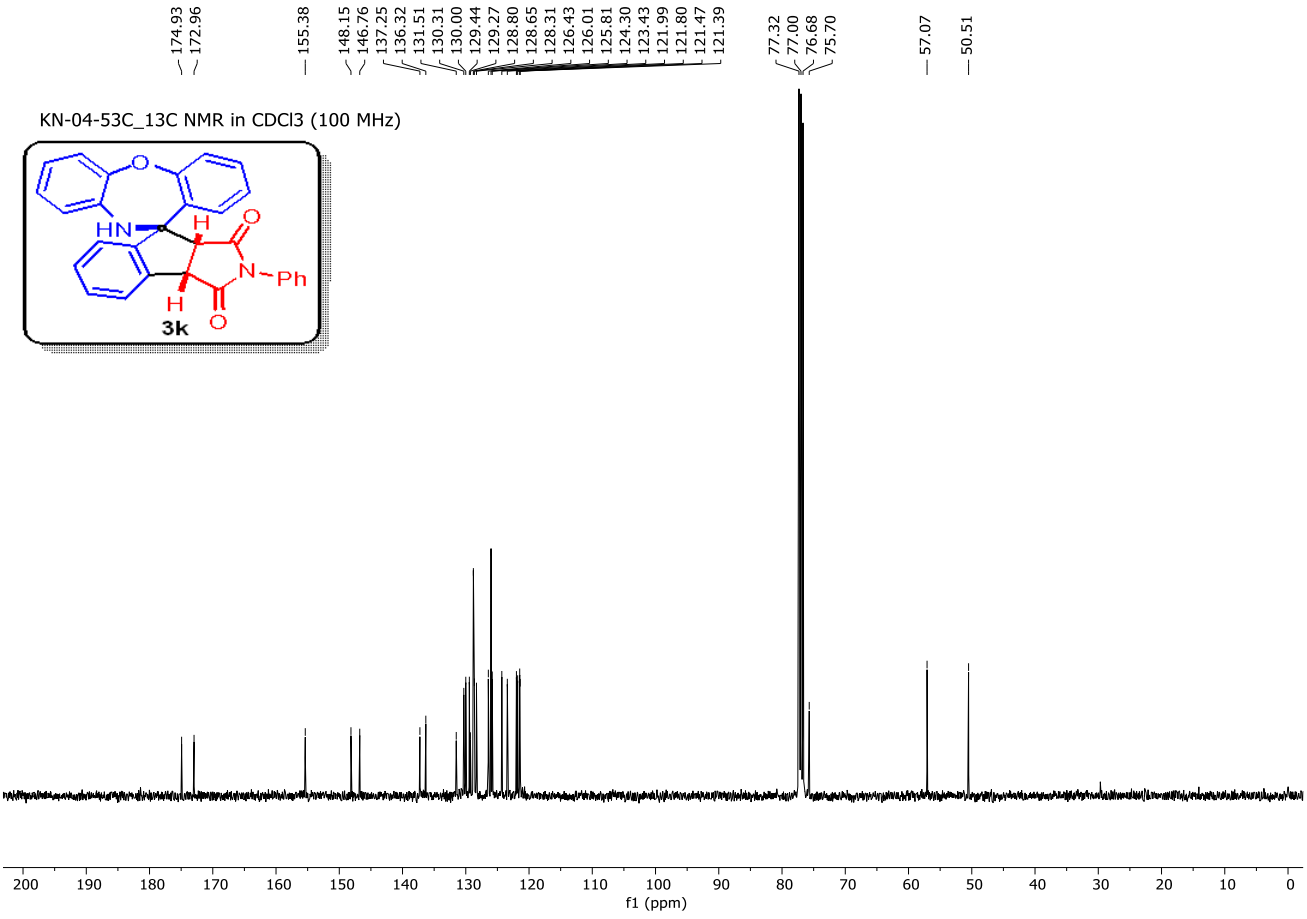
^{13}C{^{1}H} NMR of 3j in $CDCl_3$ (101 MHz):



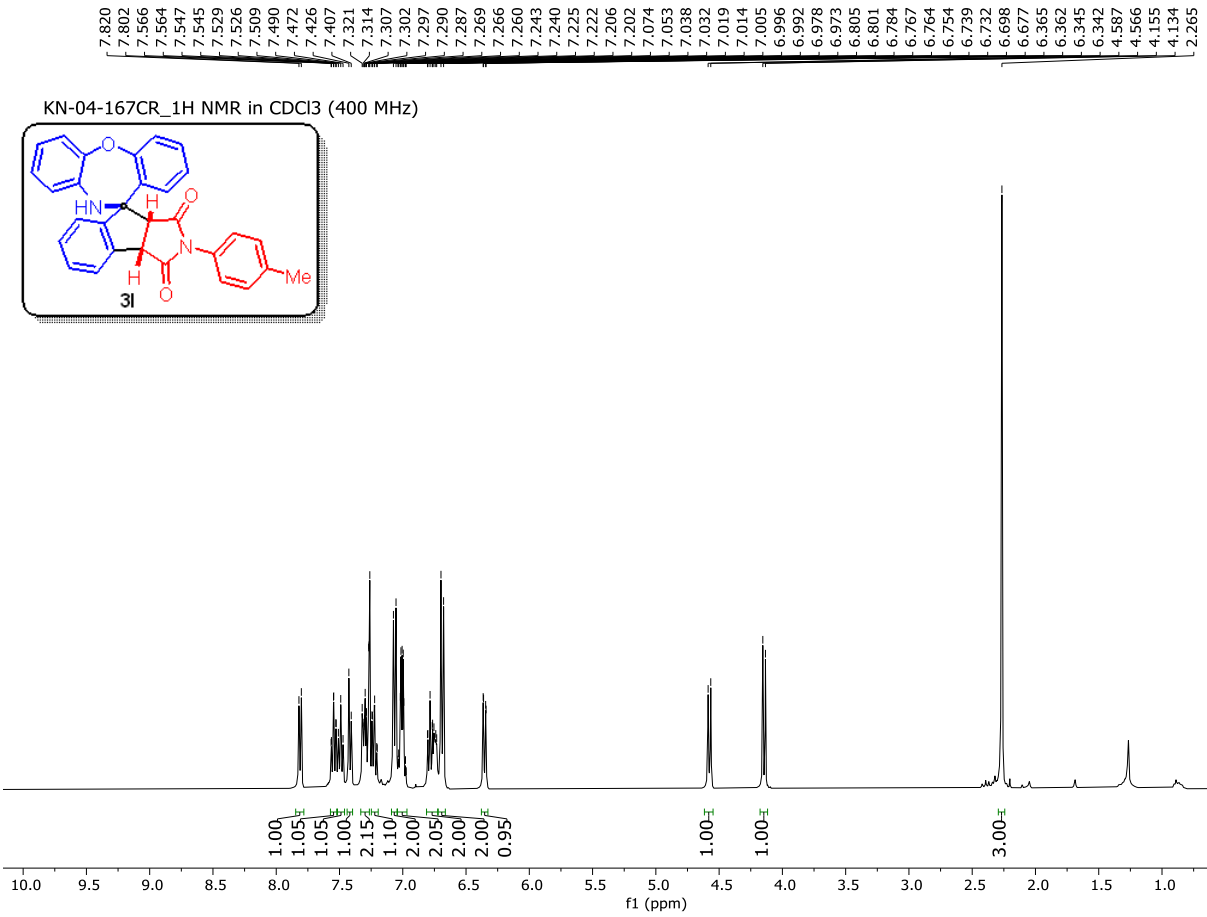
^{1}H NMR of 3k in $CDCl_3$ (400 MHz):



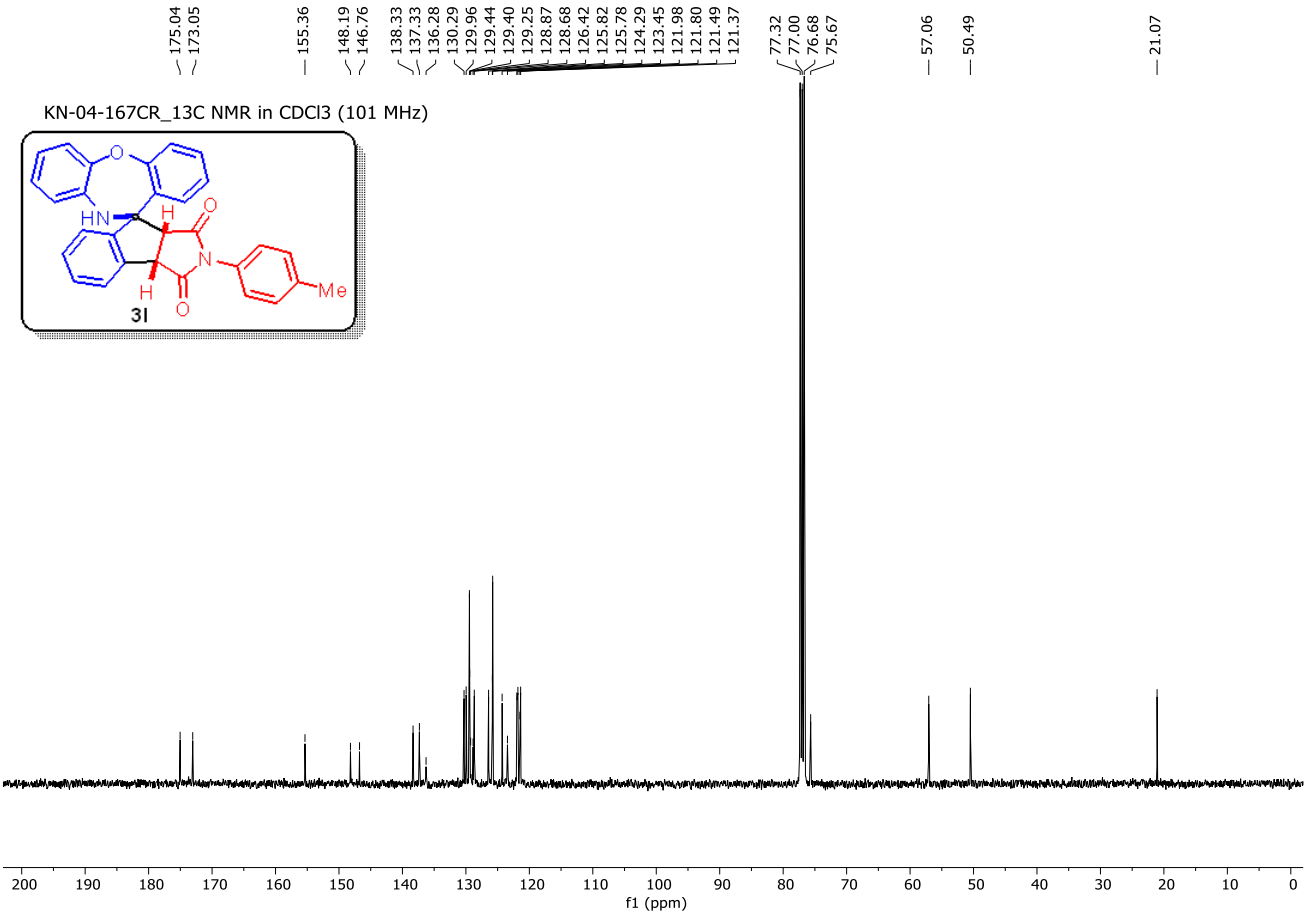
^{13}C{^{1}H} NMR of 3k in $CDCl_3$ (101 MHz):



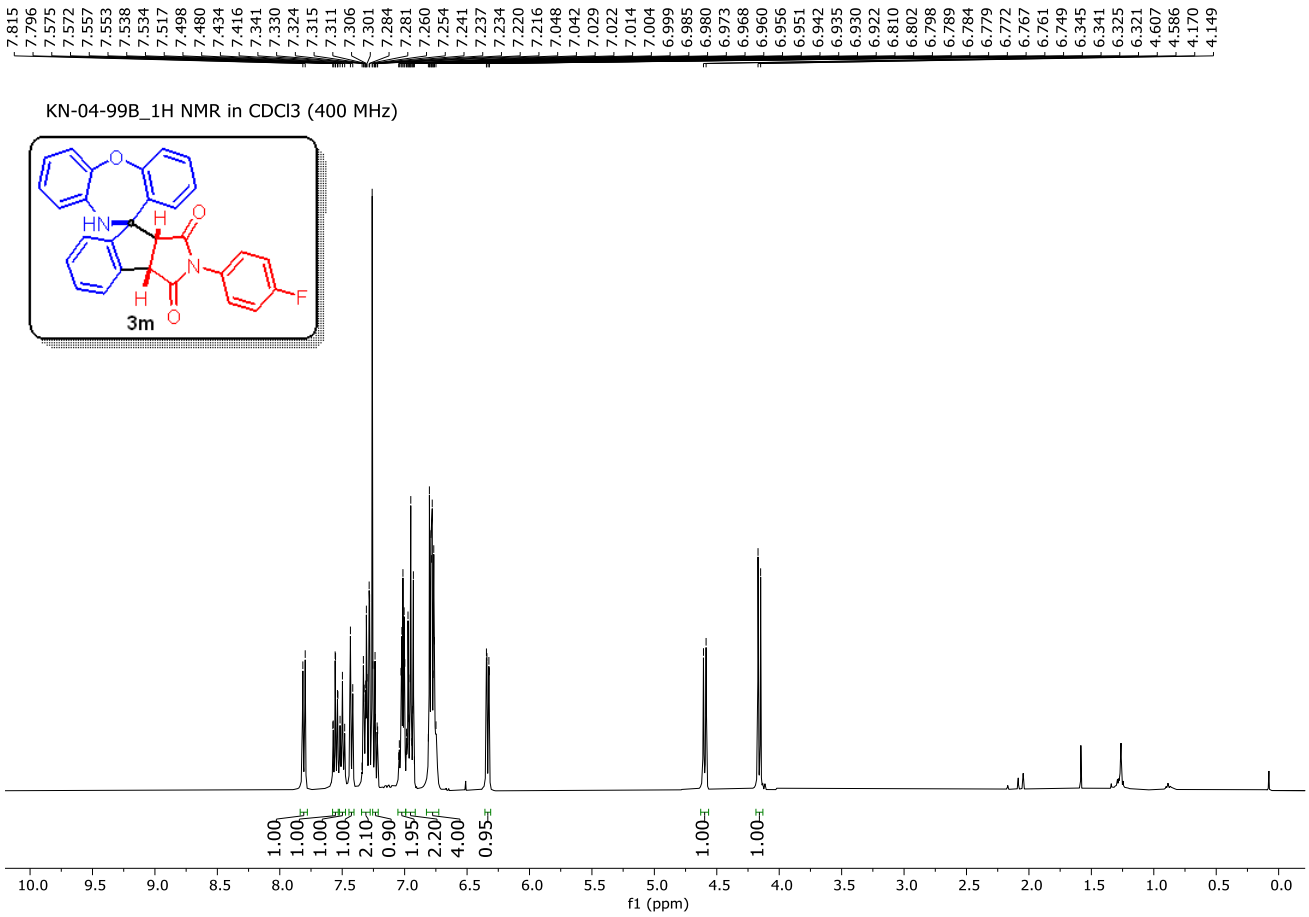
^{1}H NMR of 3l in $CDCl_3$ (400 MHz):



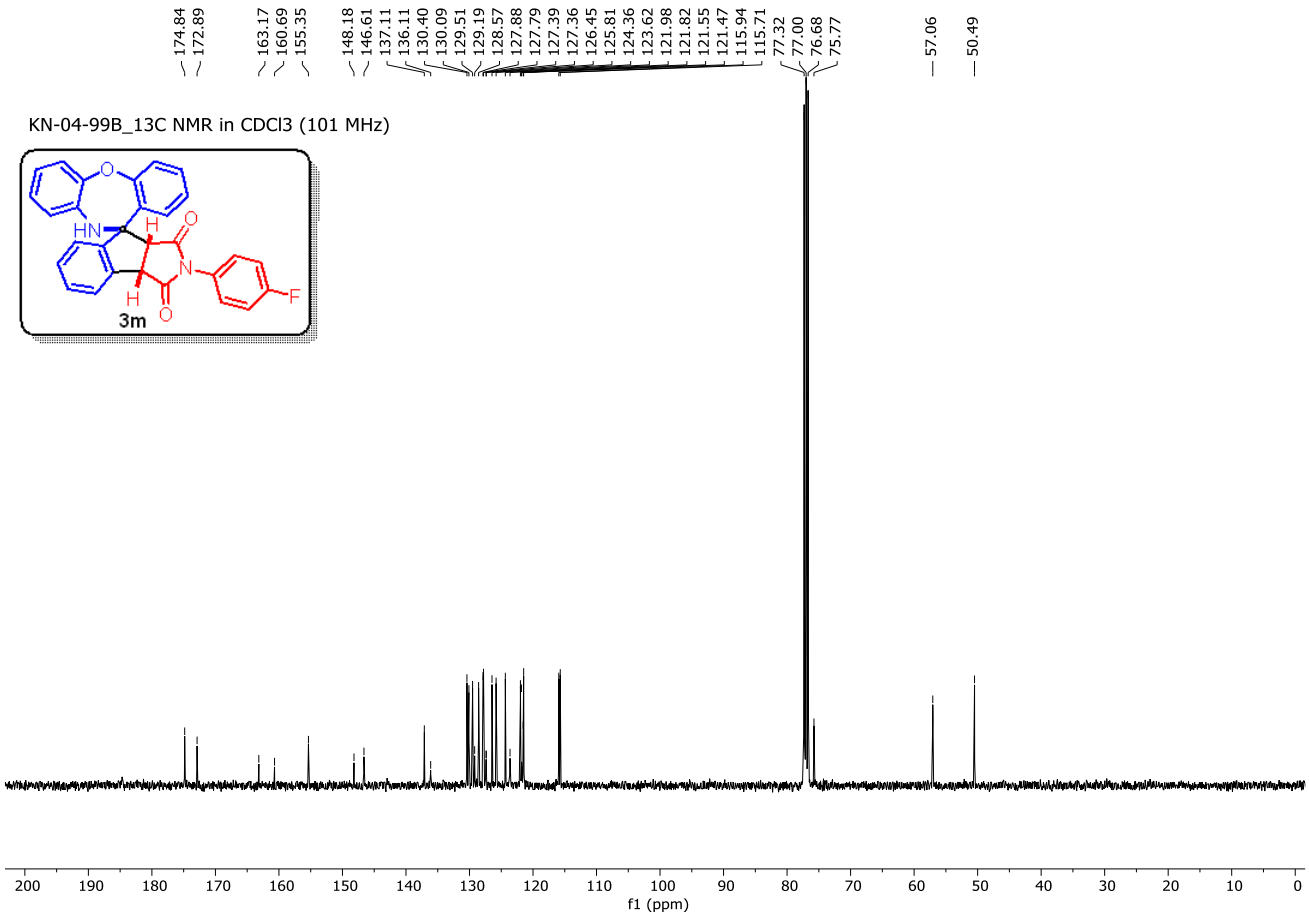
^{13}C{^{1}H} NMR of 3l in $CDCl_3$ (101 MHz):



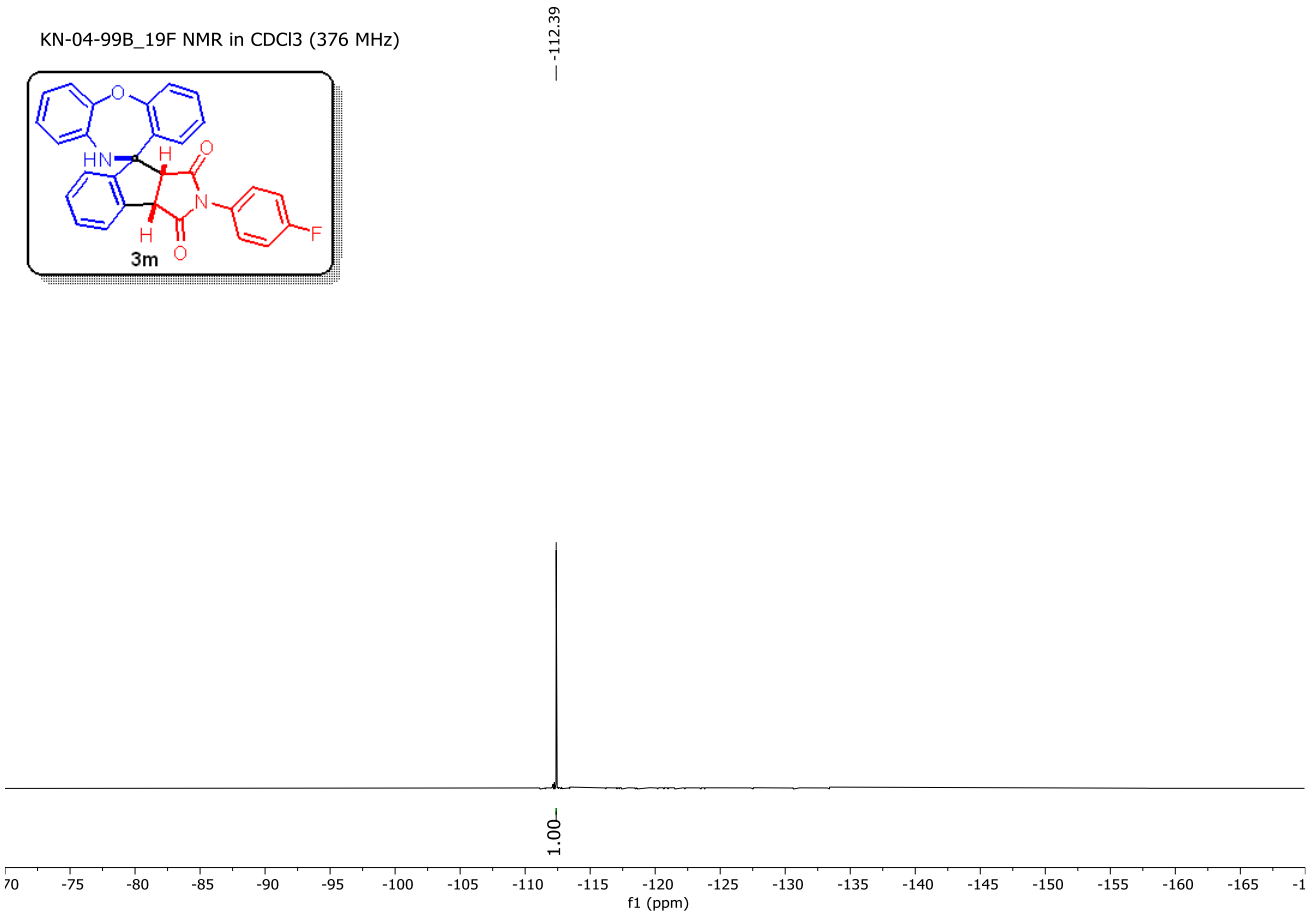
^{1}H NMR of 3m in $CDCl_3$ (400 MHz):



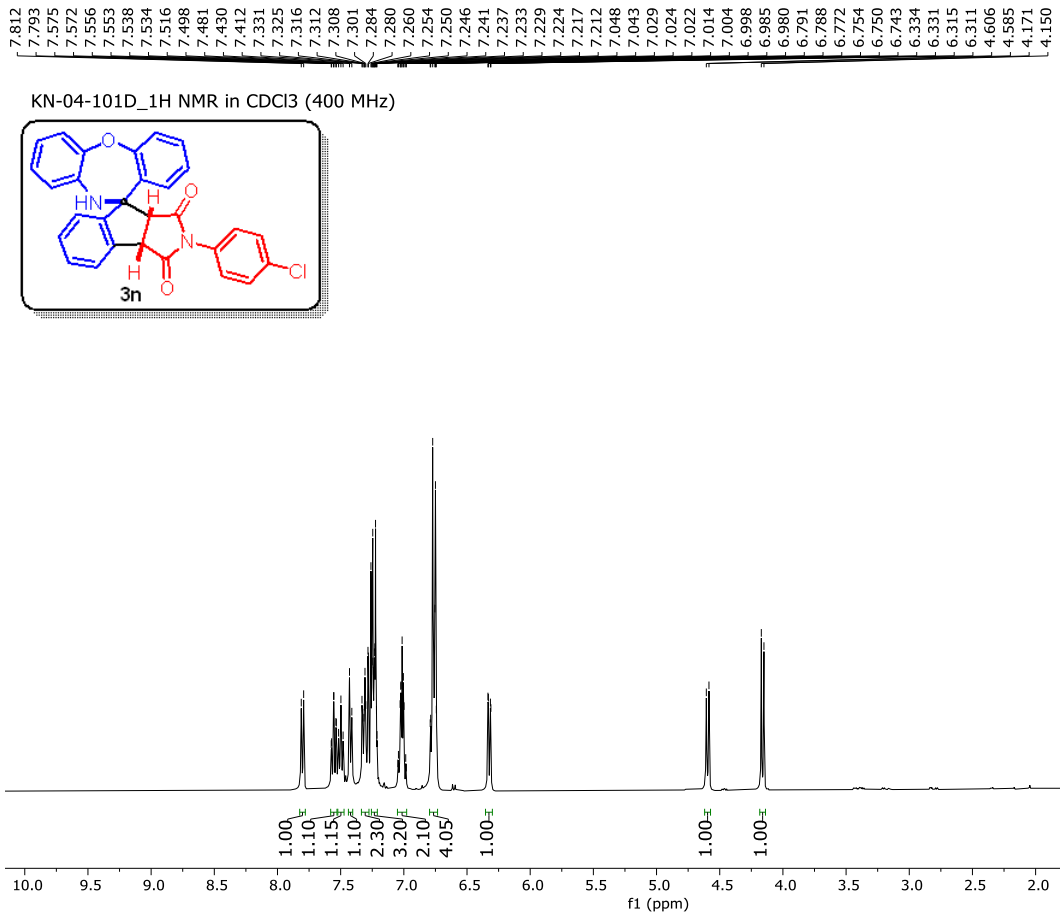
^{13}C{^{1}H} NMR of 3m in $CDCl_3$ (101 MHz):



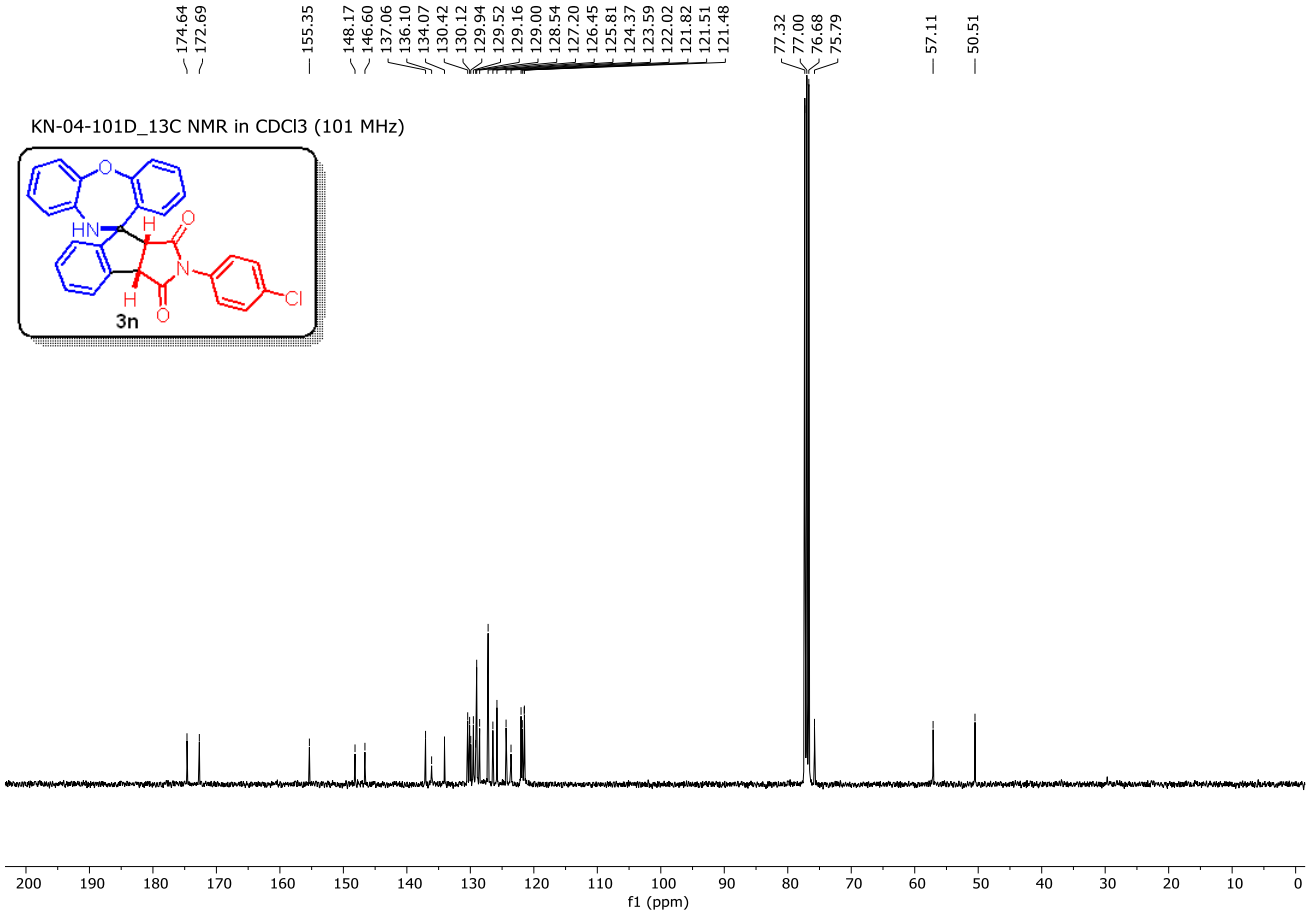
^{19}F NMR of 3m in $CDCl_3$ (376 MHz):



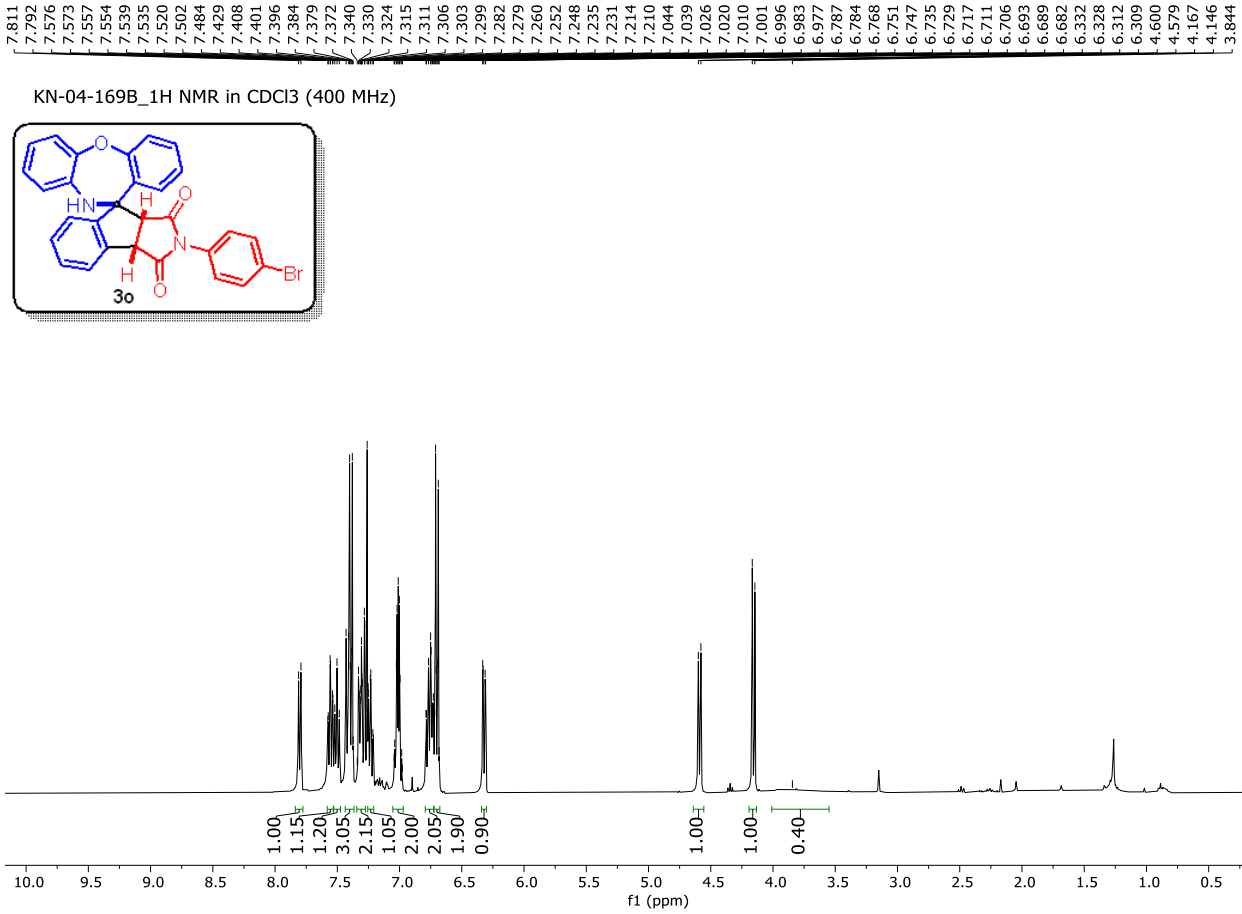
^{1}H NMR of 3n in $CDCl_3$ (400 MHz):



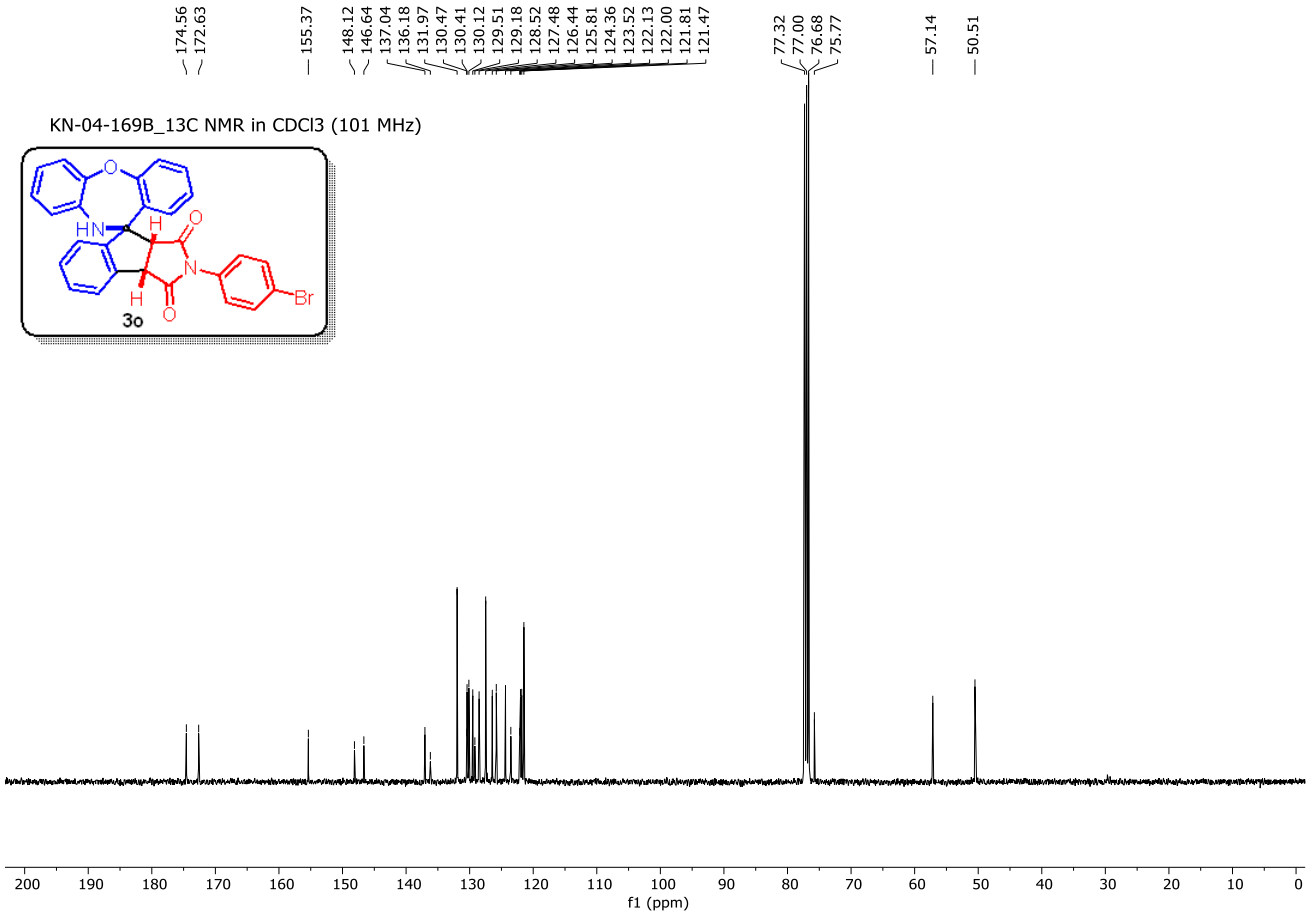
^{13}C{^{1}H} NMR of 3n in $CDCl_3$ (101 MHz):



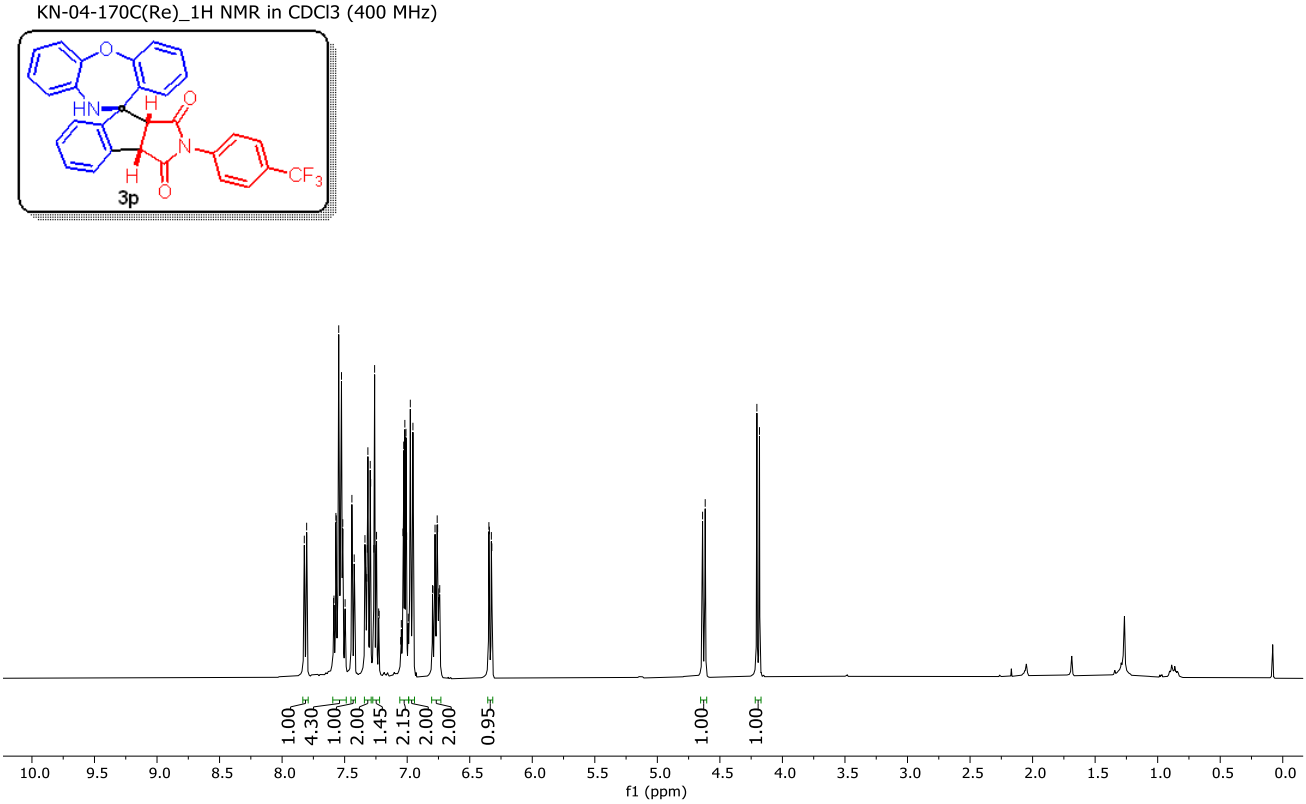
^{1}H NMR of 3o in $CDCl_3$ (400 MHz):



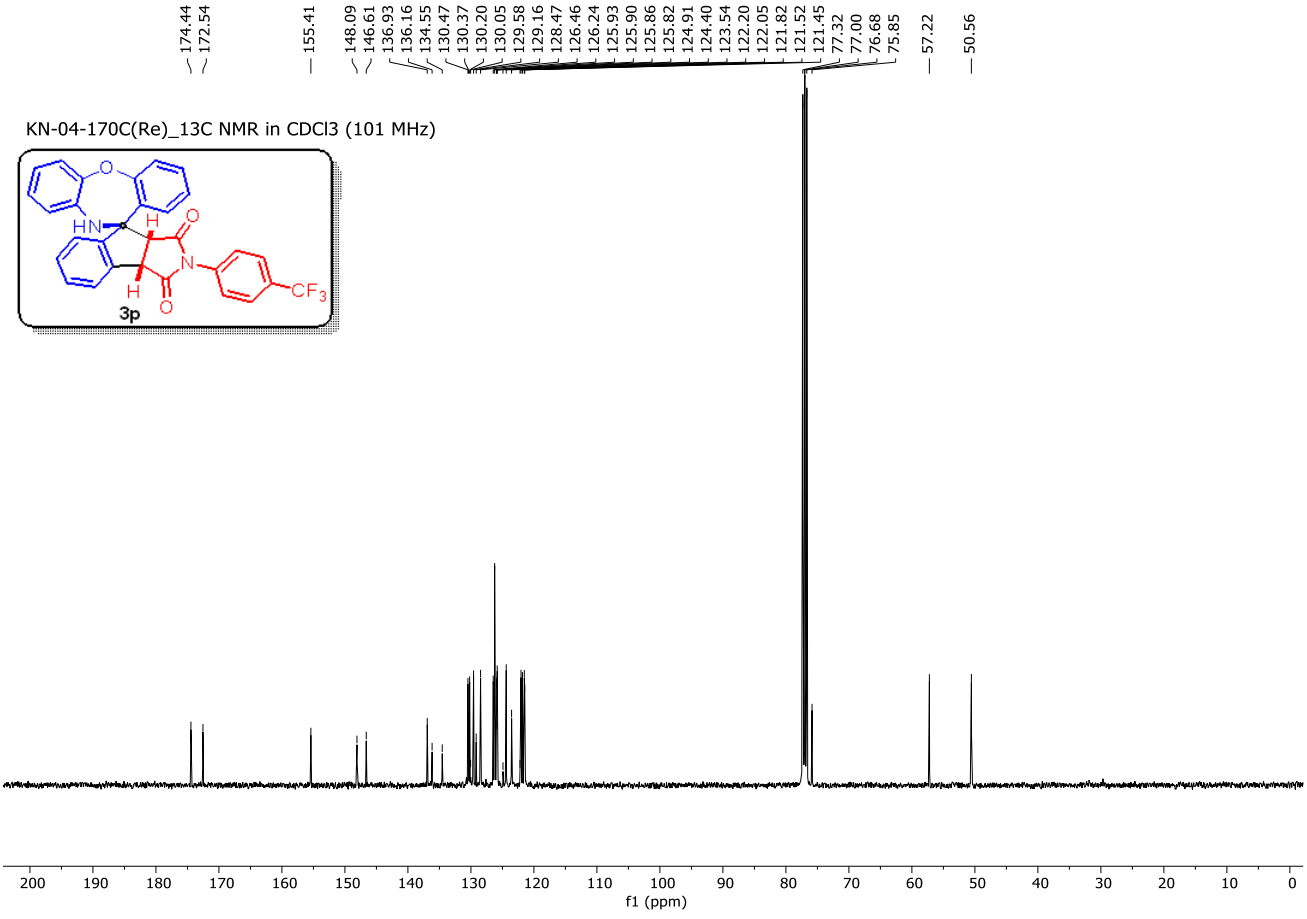
^{13}C{^{1}H} NMR of 3o in $CDCl_3$ (101 MHz):



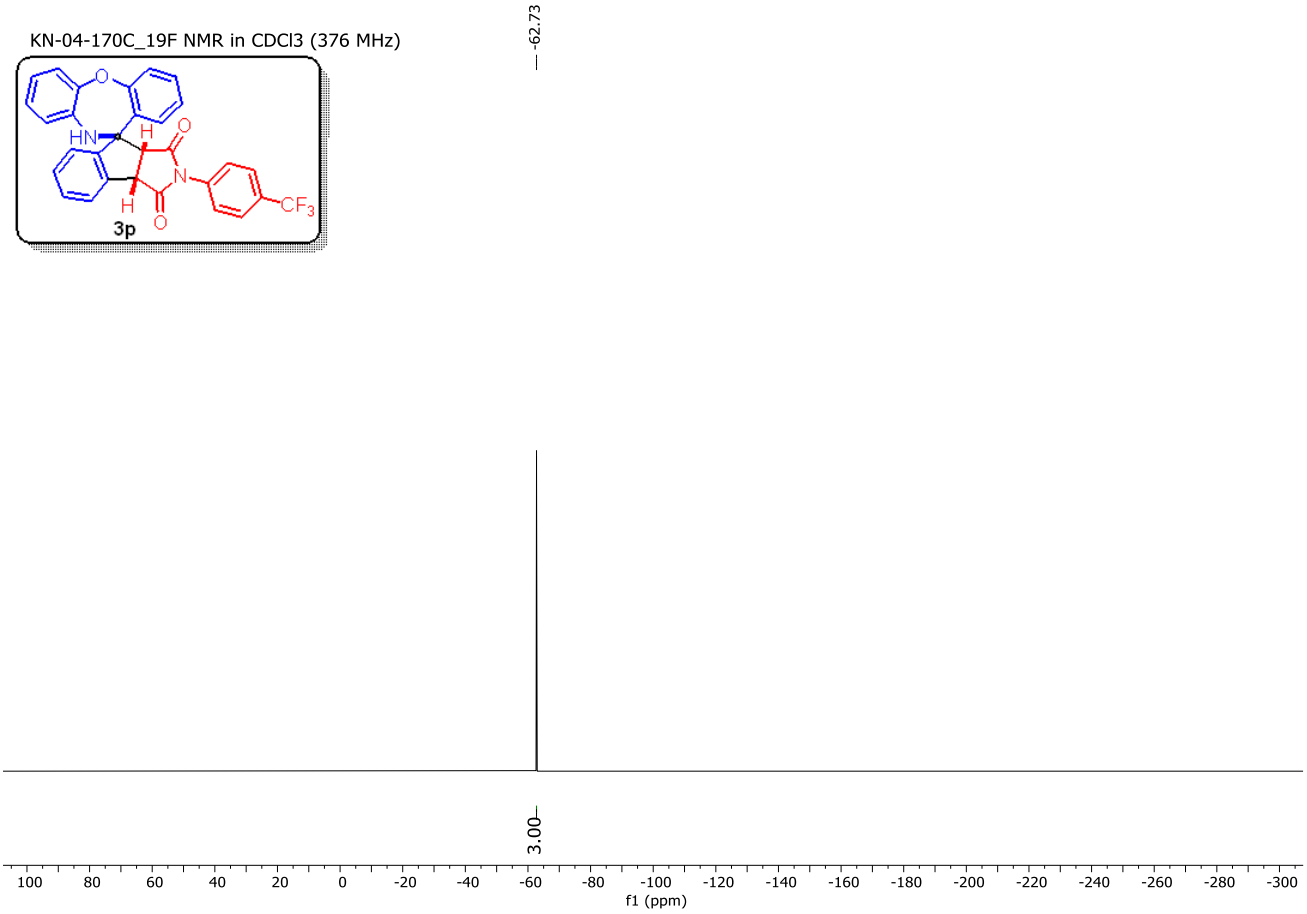
^{1}H NMR of 3p (400 MHz, $CDCl_3$):



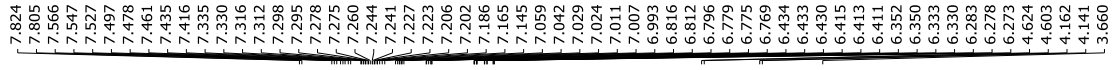
^{13}C{^{1}H} NMR of 3p (101 MHz, $CDCl_3$):

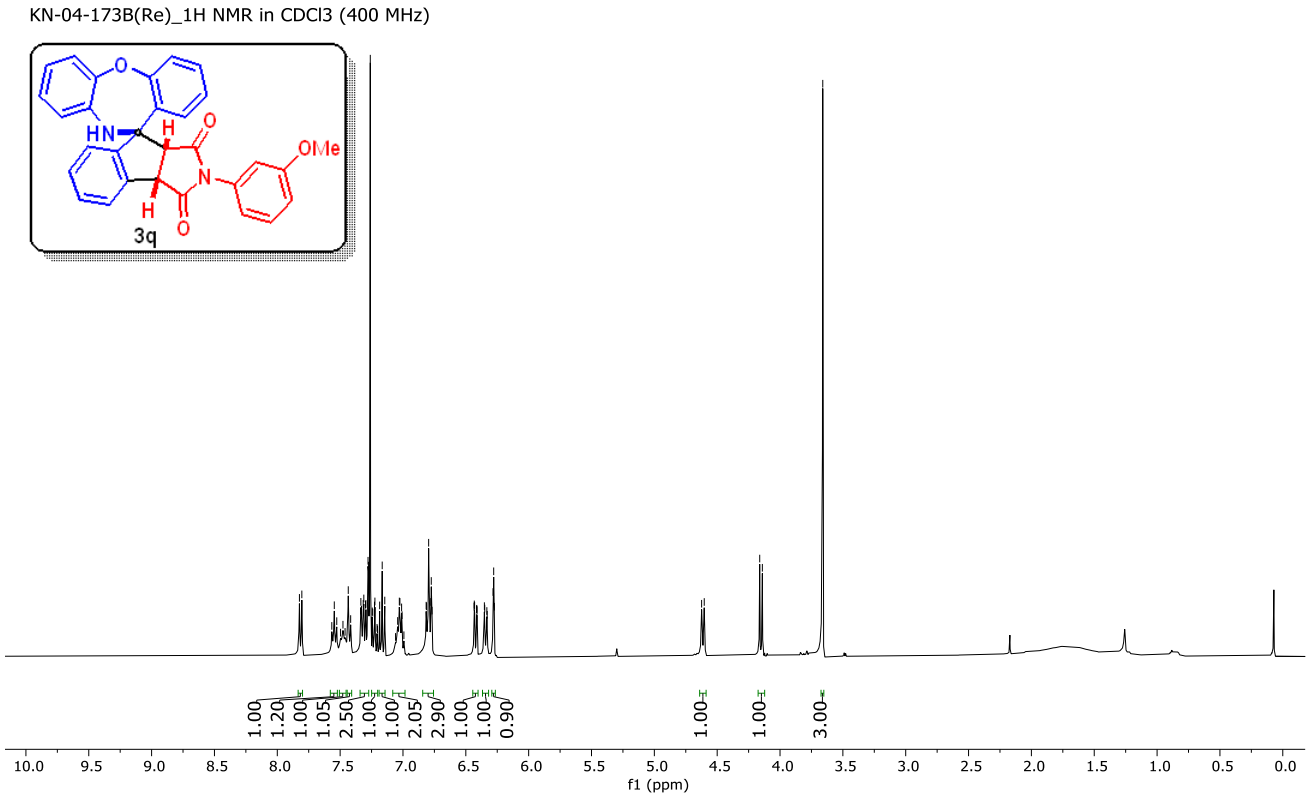


^{19}F NMR of 3p (376 MHz, $CDCl_3$):

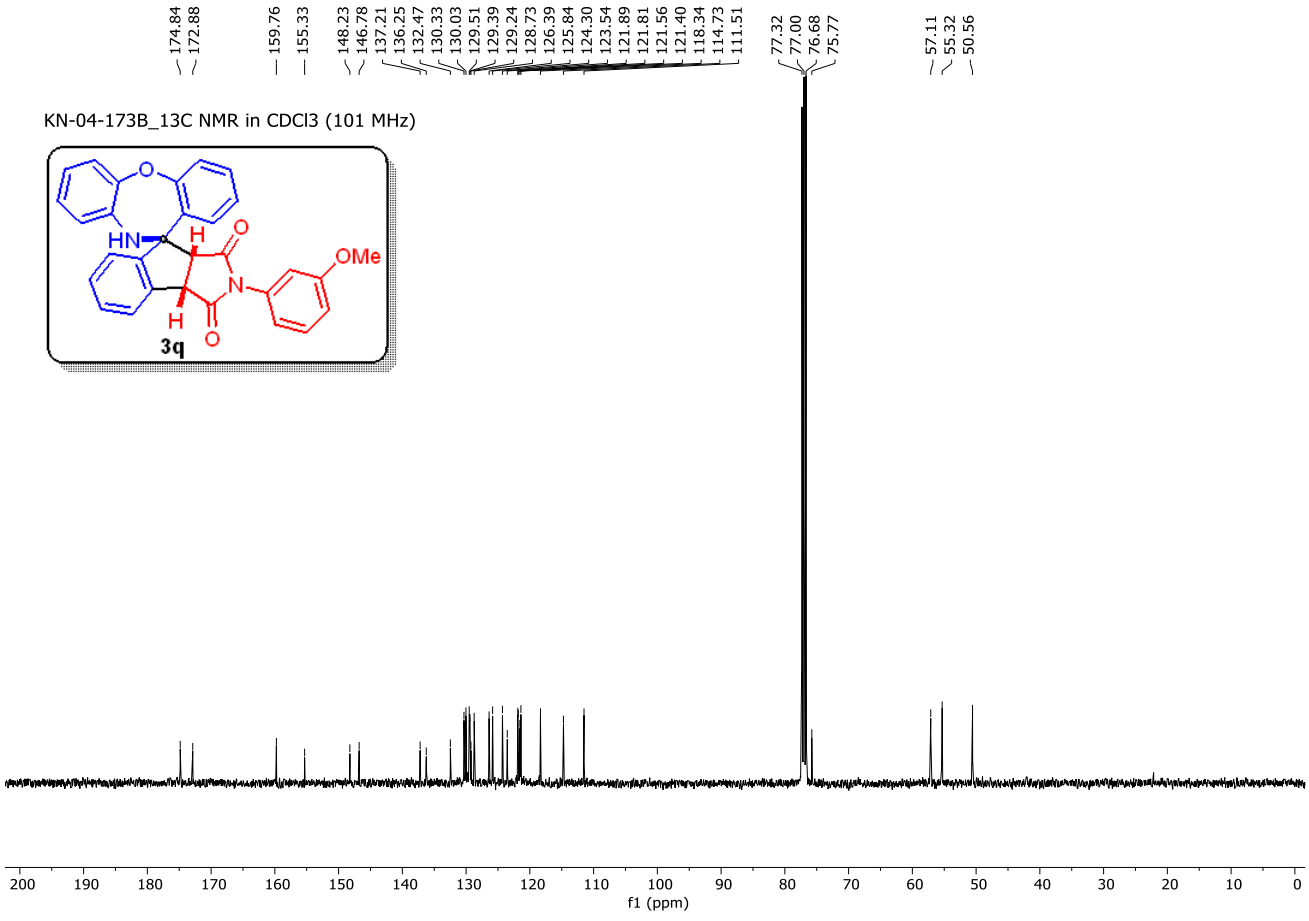


^{1}H NMR of 3q (400 MHz, $CDCl_3$):

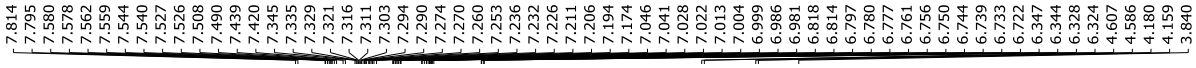




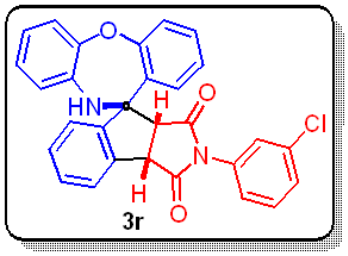
^{13}C{^{1}H} NMR of 3q (101 MHz, $CDCl_3$):

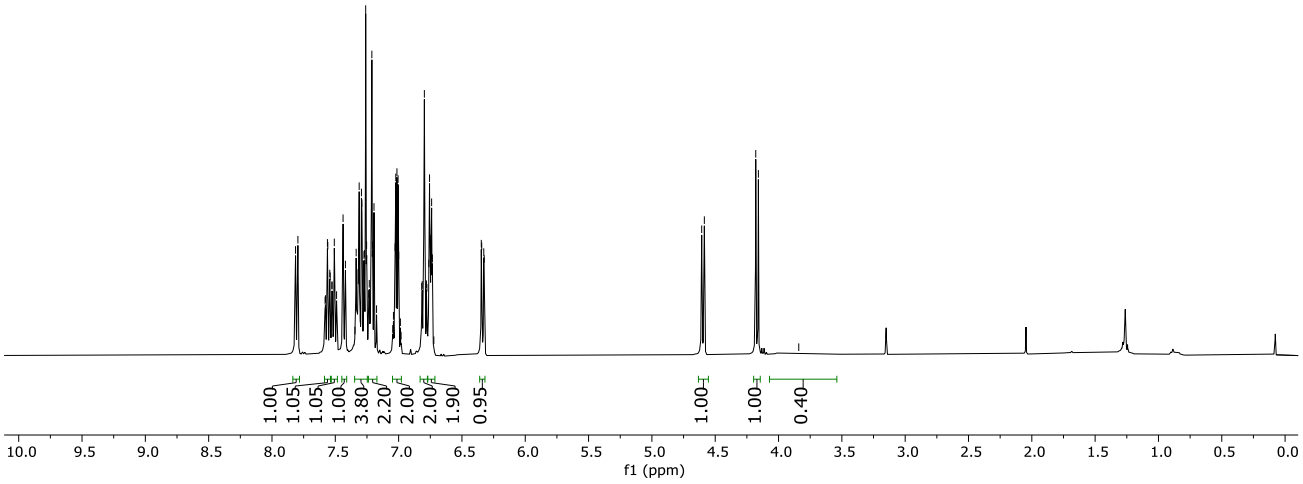


^{1}H NMR of 3r (400 MHz, $CDCl_3$):

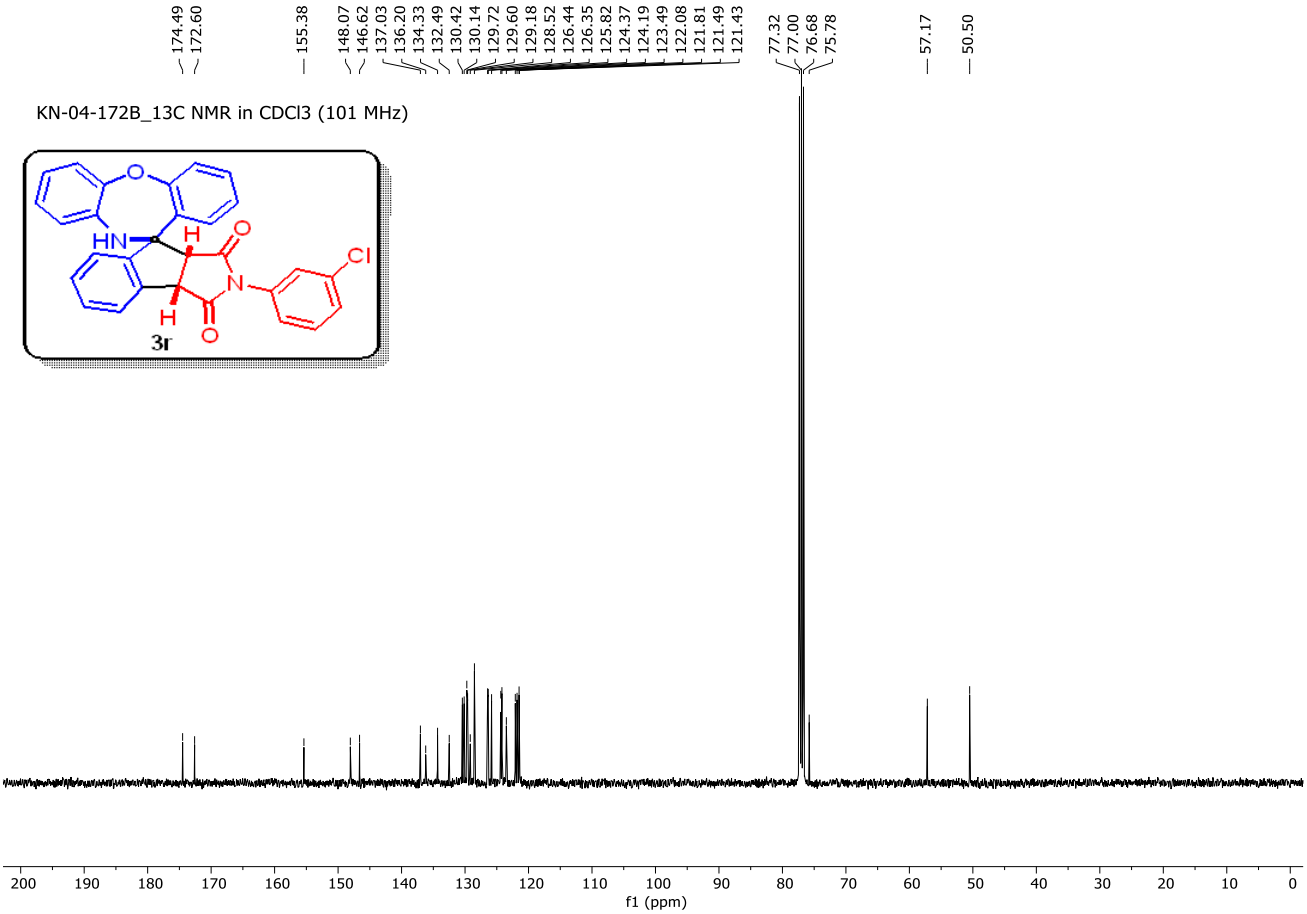


KN-04-172B_1H NMR in CDCl3 (400 MHz)



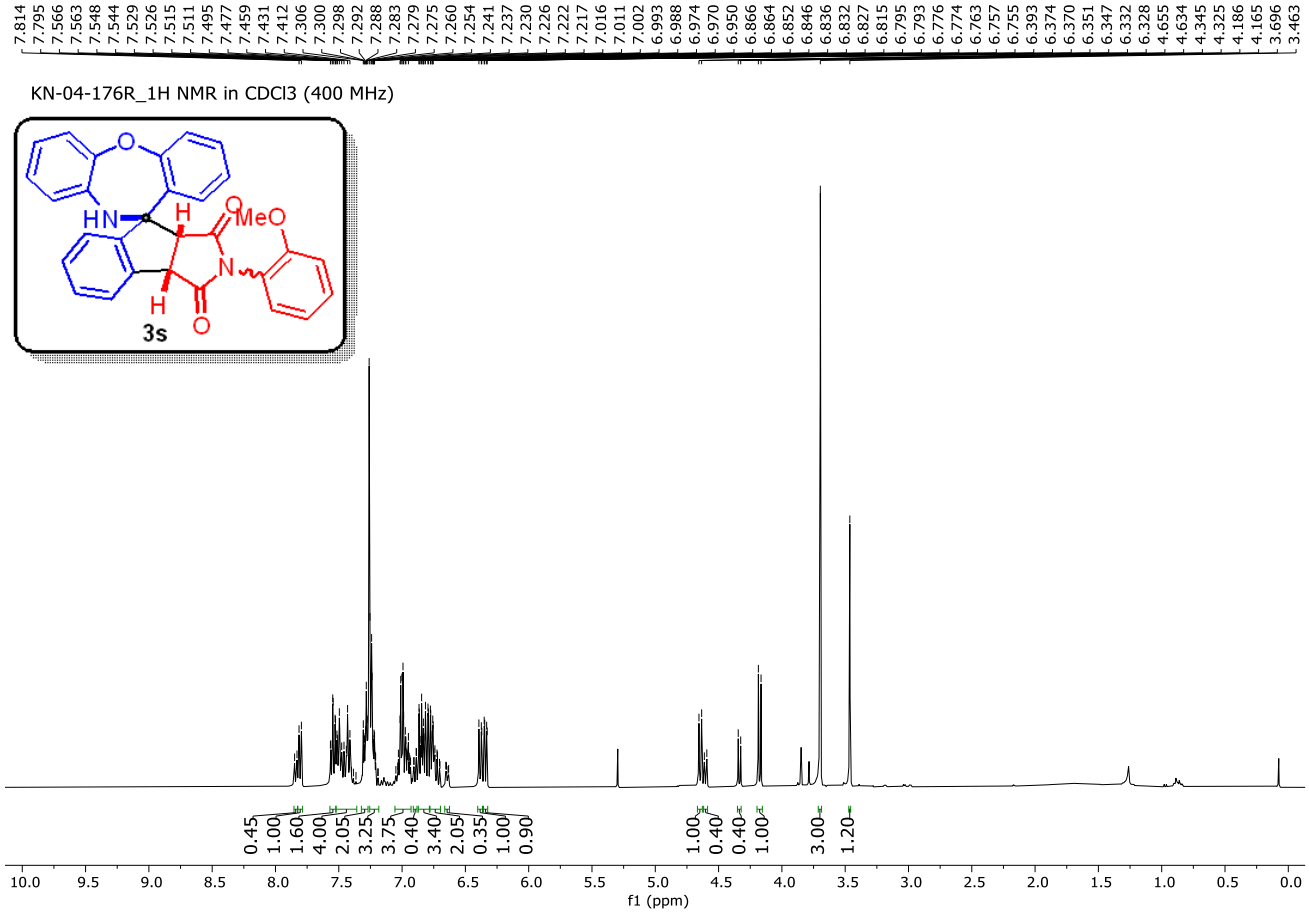


^{13}C{^{1}H} NMR of 3r (101 MHz, $CDCl_3$):

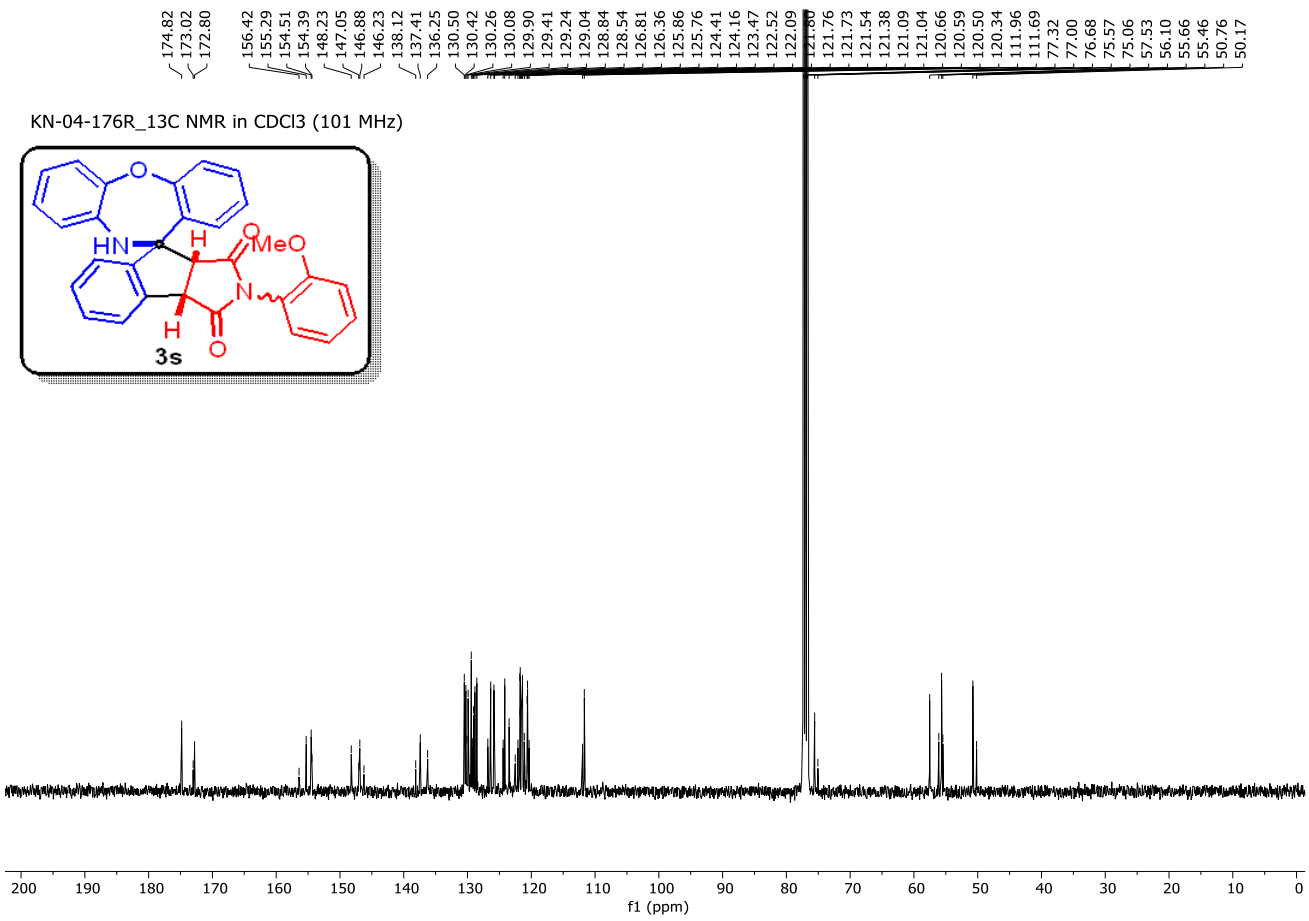


KN-04-172B_13C NMR in CDCl3 (101 MHz)

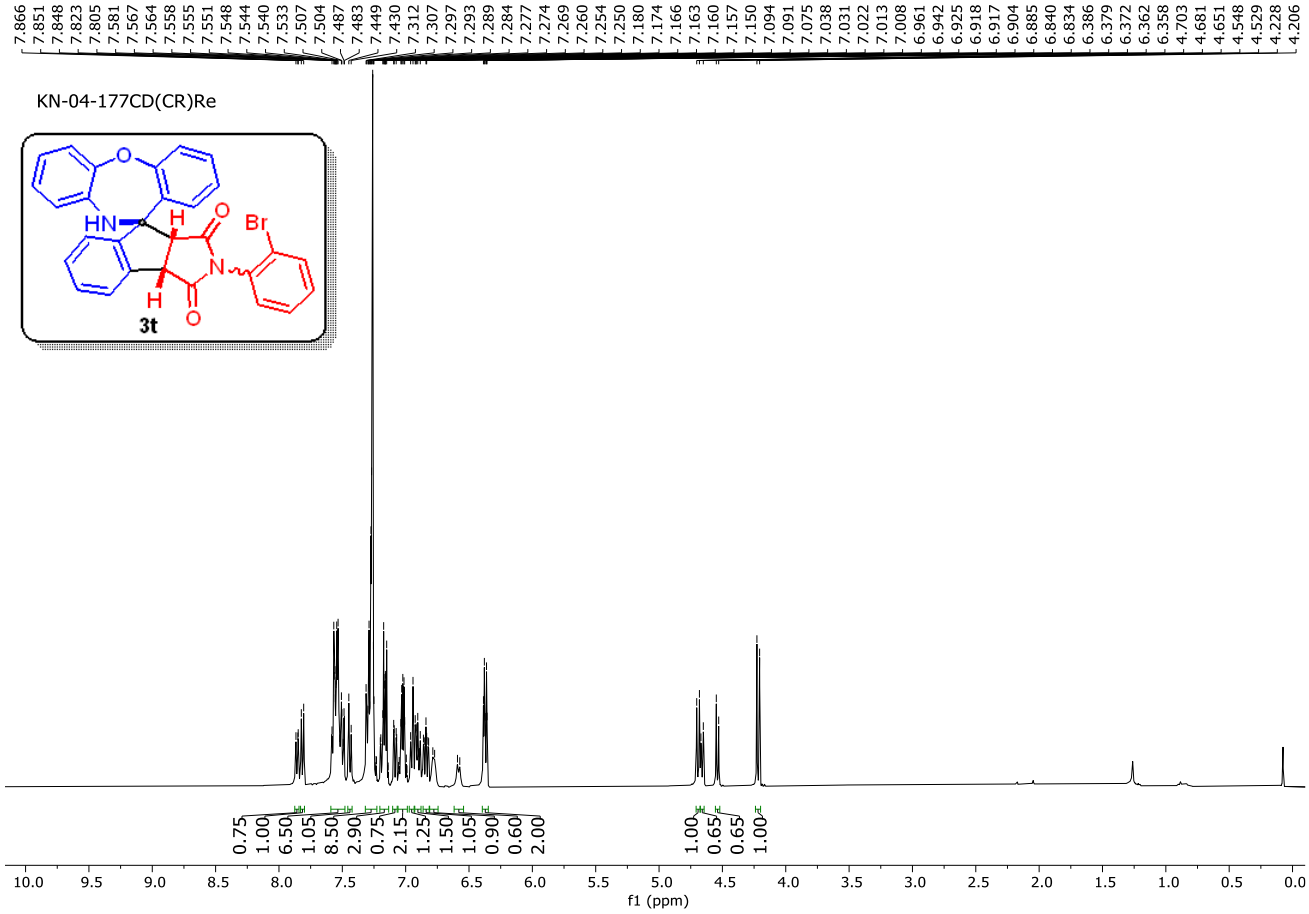
^{1}H NMR of 3s (400 MHz, $CDCl_3$):



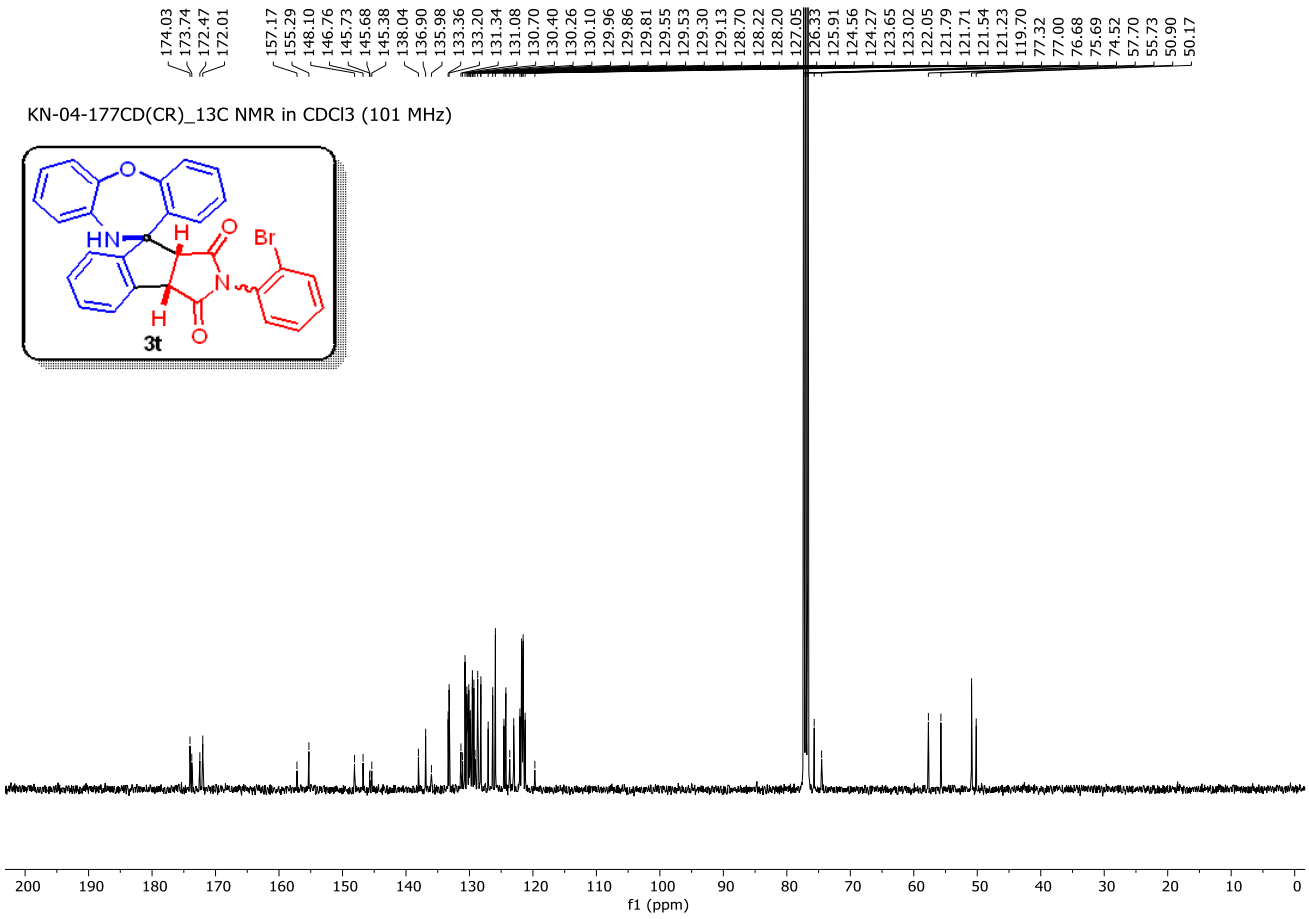
^{13}C{^{1}H} NMR of 3s (101 MHz, $CDCl_3$):



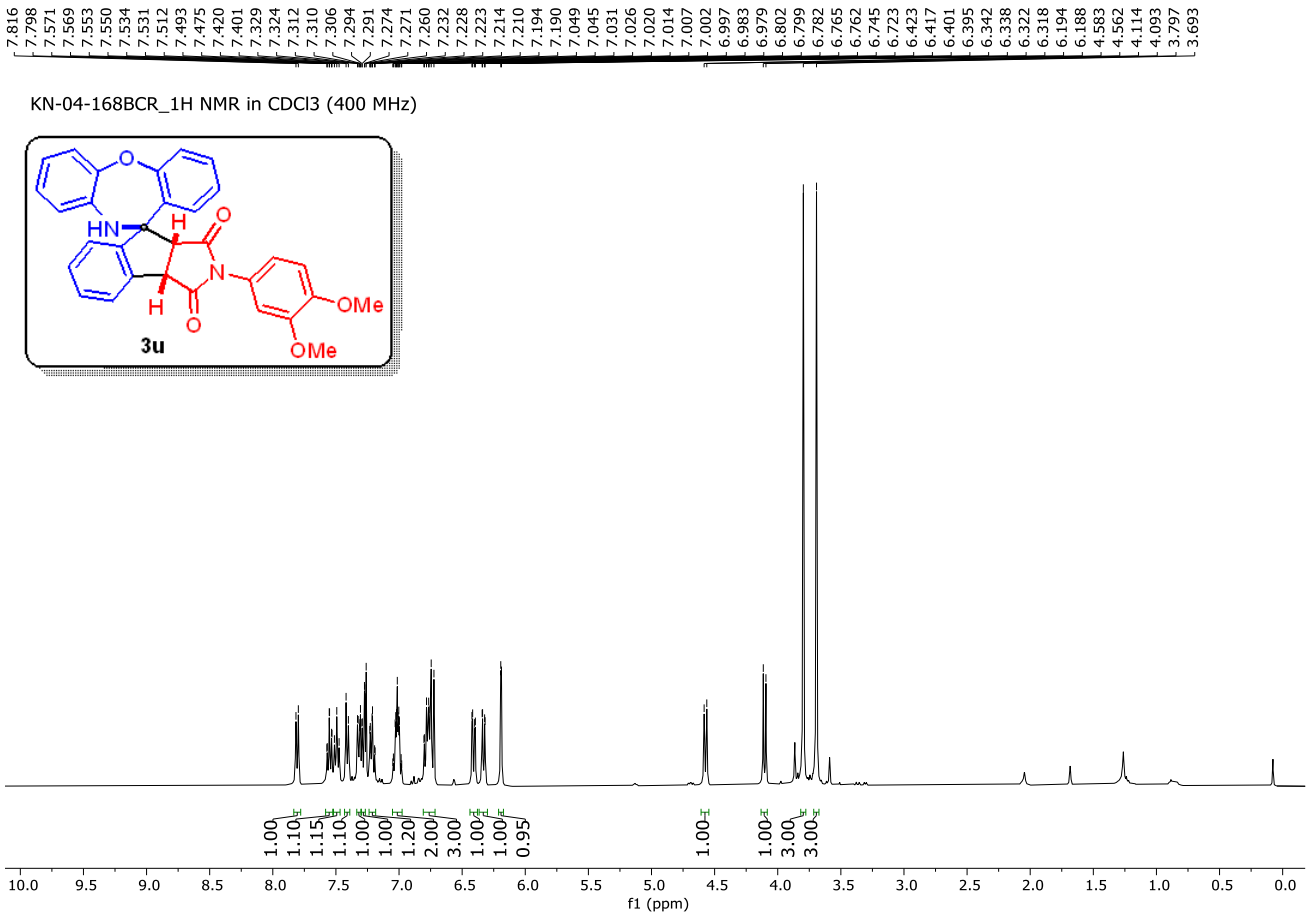
^{1}H NMR of 3t (400 MHz, $CDCl_3$):



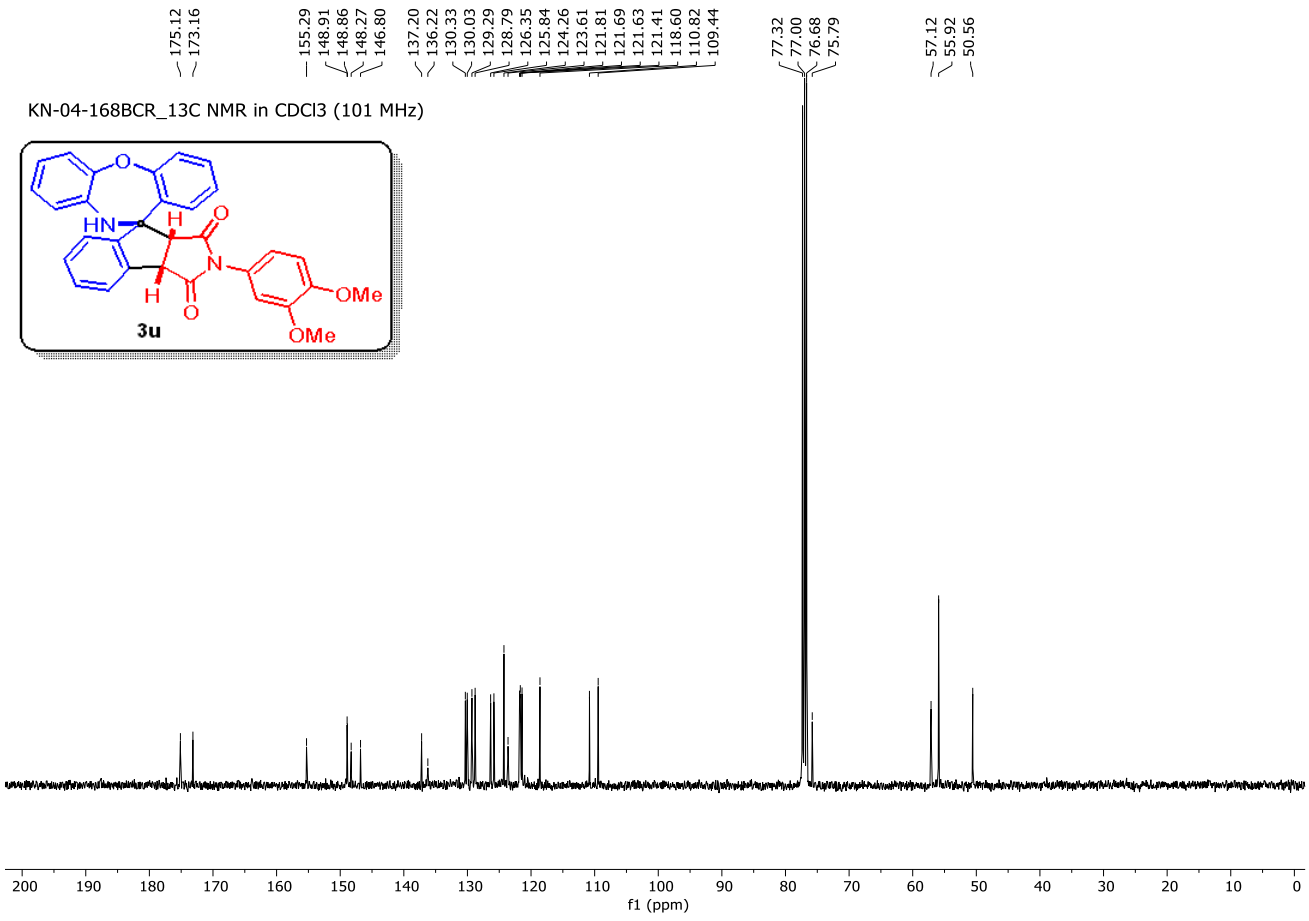
^{13}C{^{1}H} NMR of 3t (101 MHz, $CDCl_3$):



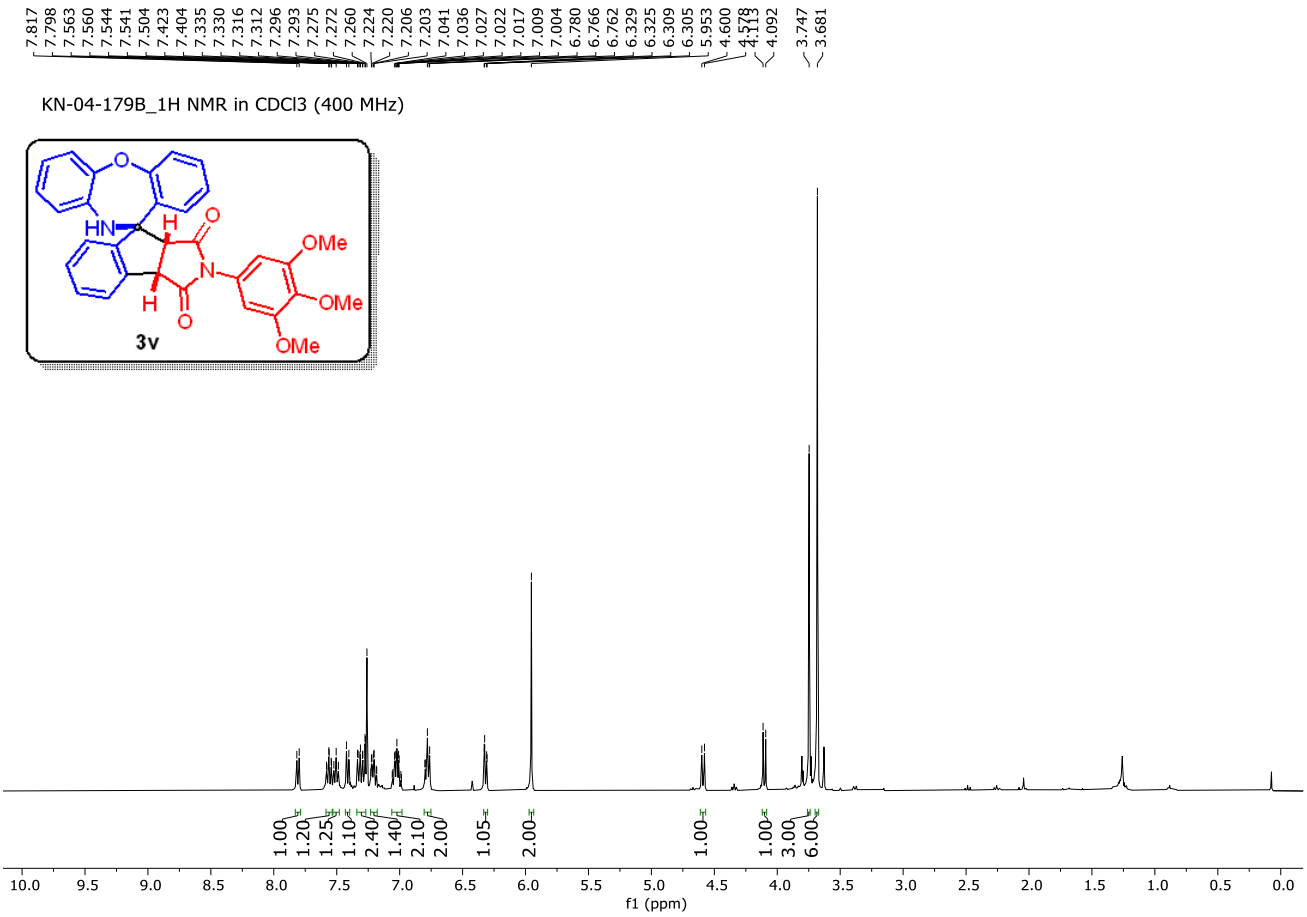
^{1}H NMR of 3u (400 MHz, $CDCl_3$):



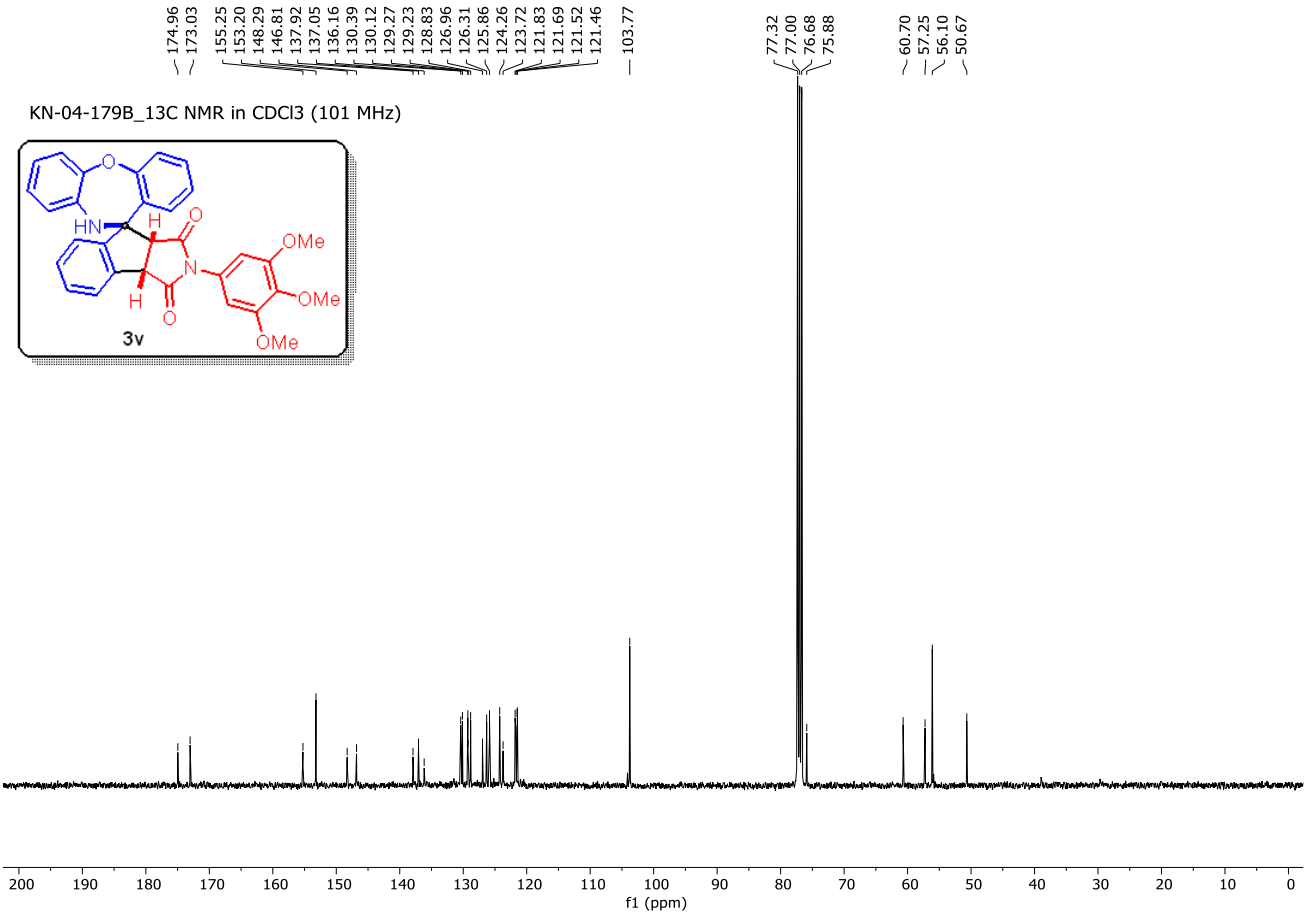
^{13}C{^{1}H} NMR of 3u (101 MHz, $CDCl_3$):



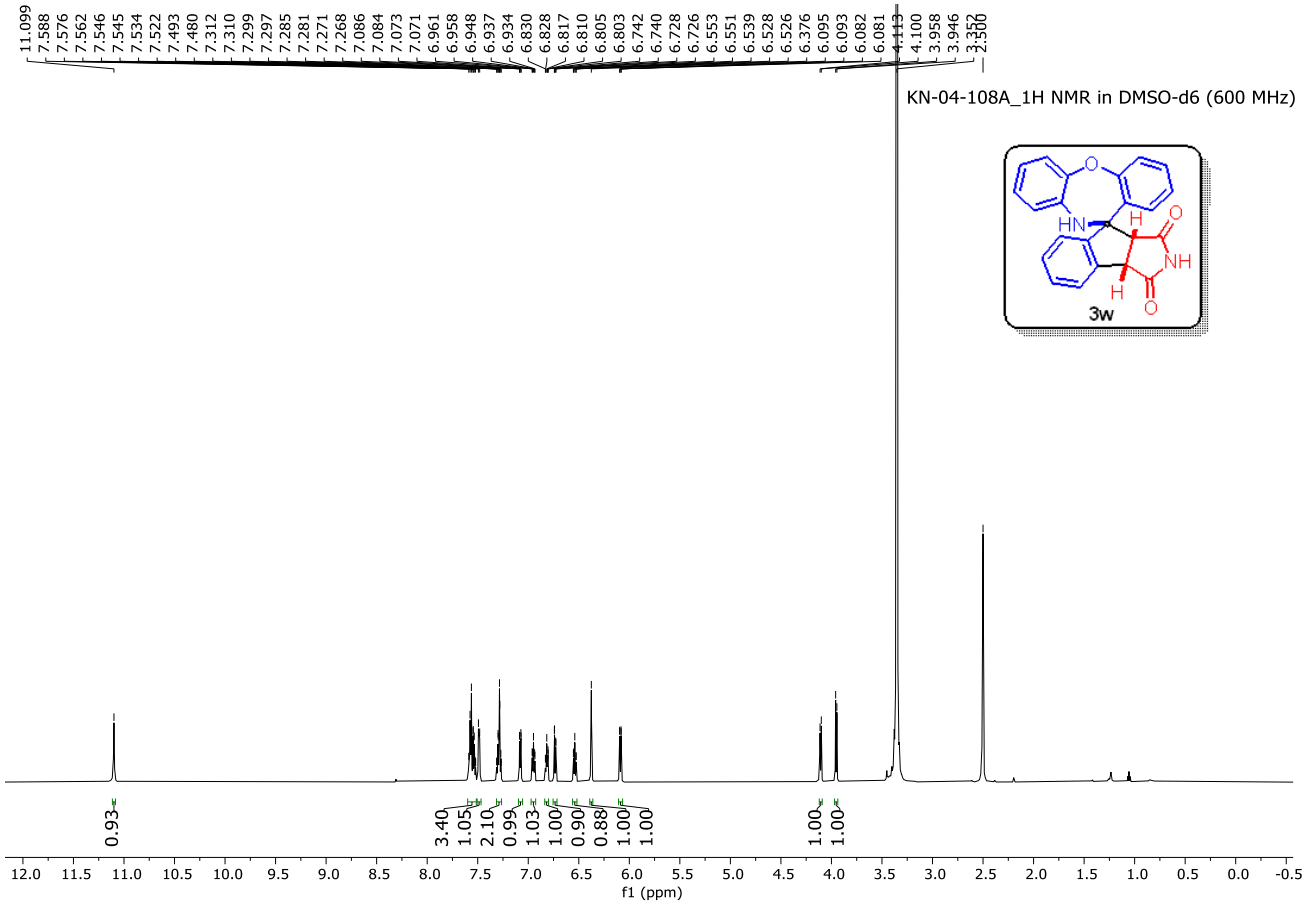
^{1}H NMR of 3v (400 MHz, $CDCl_3$):



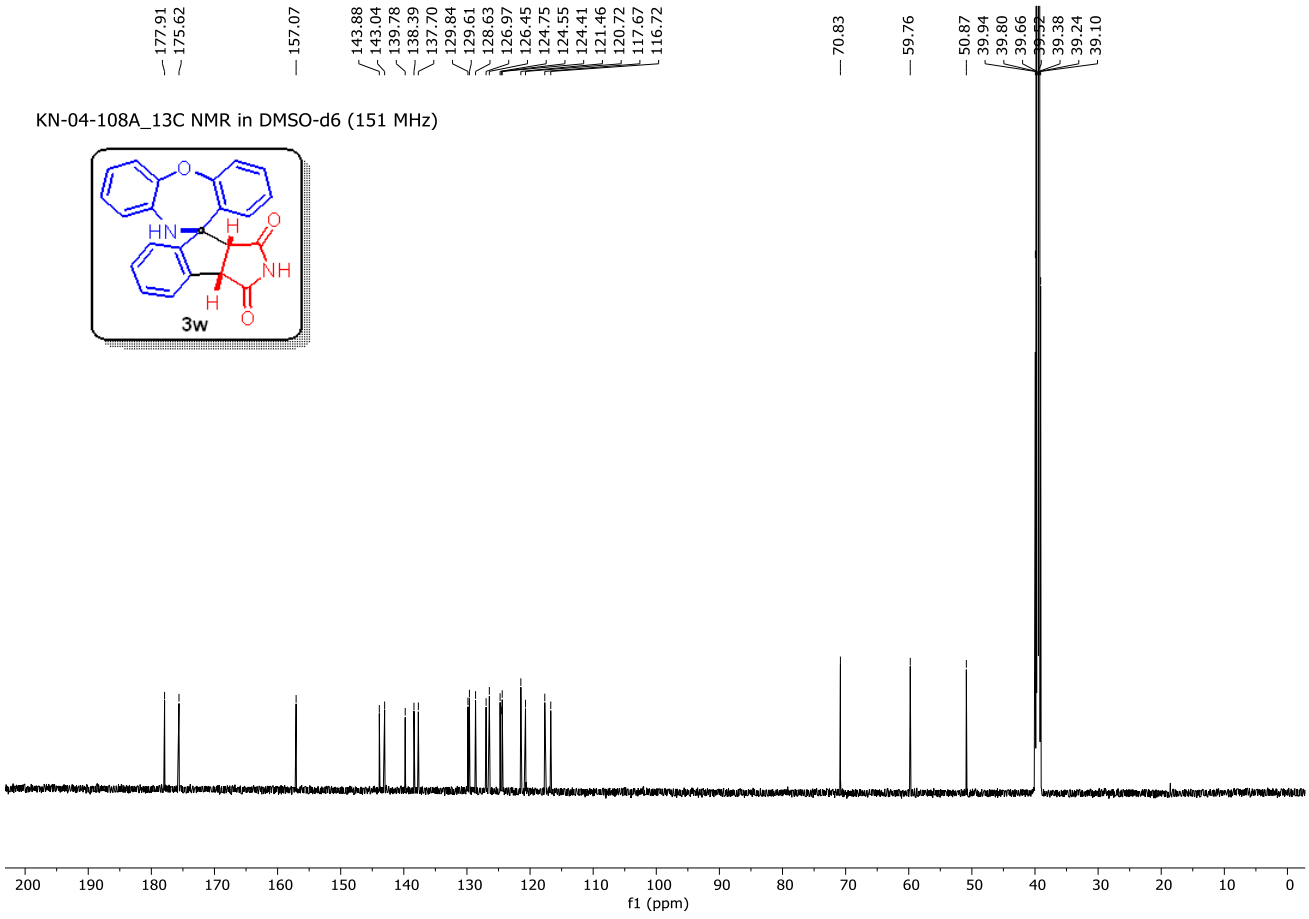
^{13}C{^{1}H} NMR of 3v (101 MHz, $CDCl_3$):



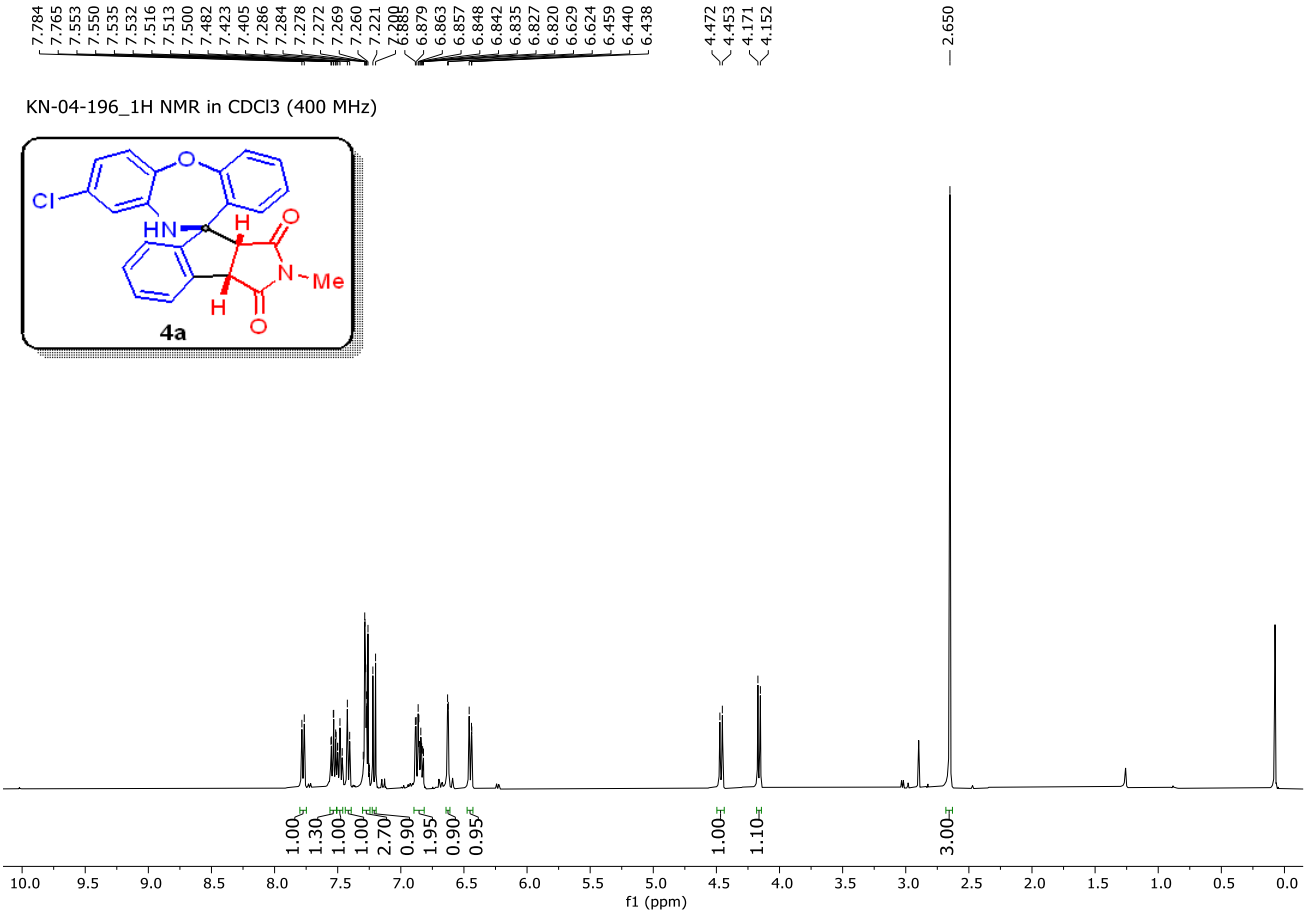
^{1}H NMR of 3w (600 MHz, DMSO-d_6):



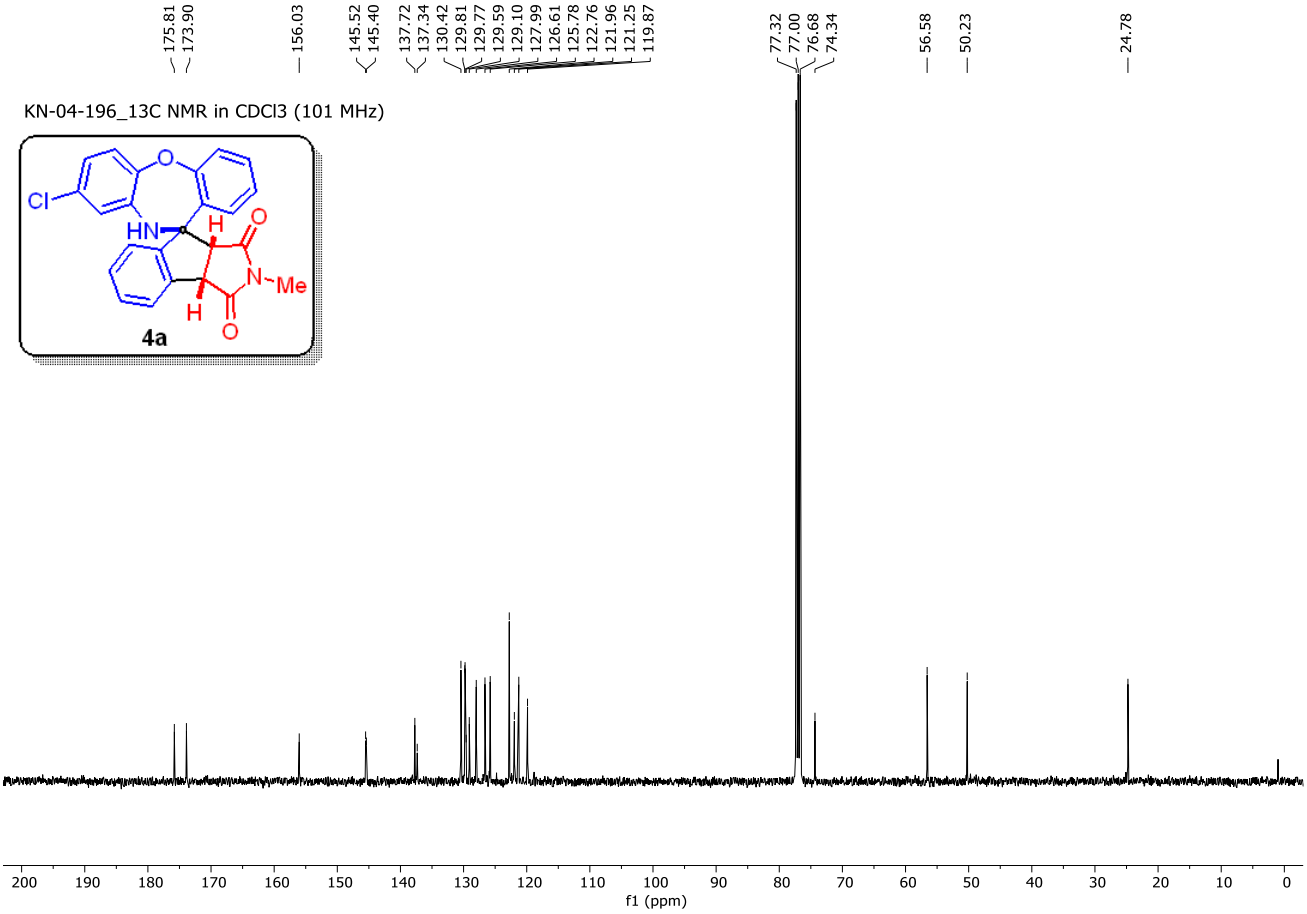
^{13}C{^{1}H} NMR of 3w (151 MHz, DMSO-d_6):



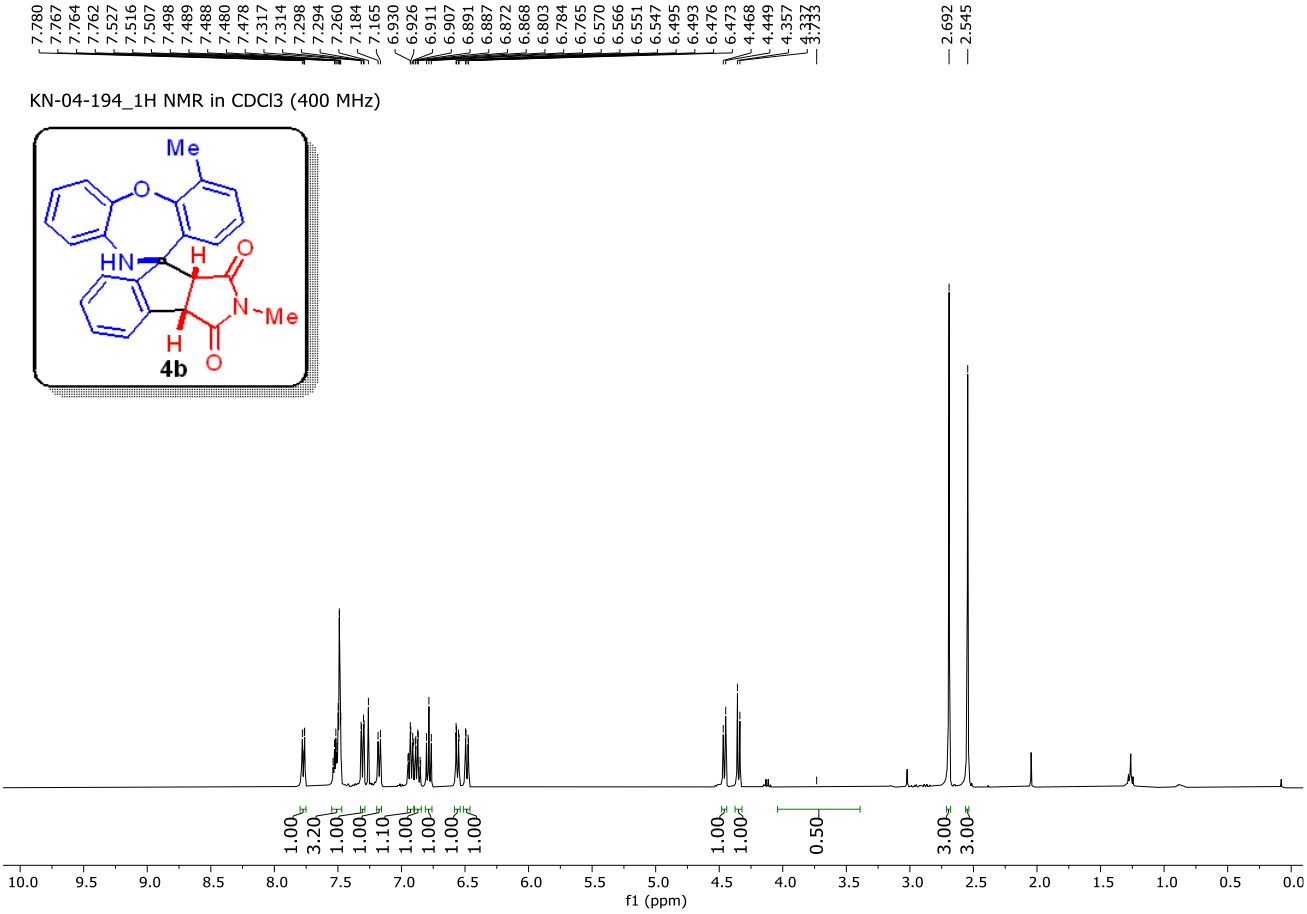
^{1}H NMR of 4a (400 MHz, $CDCl_3$):



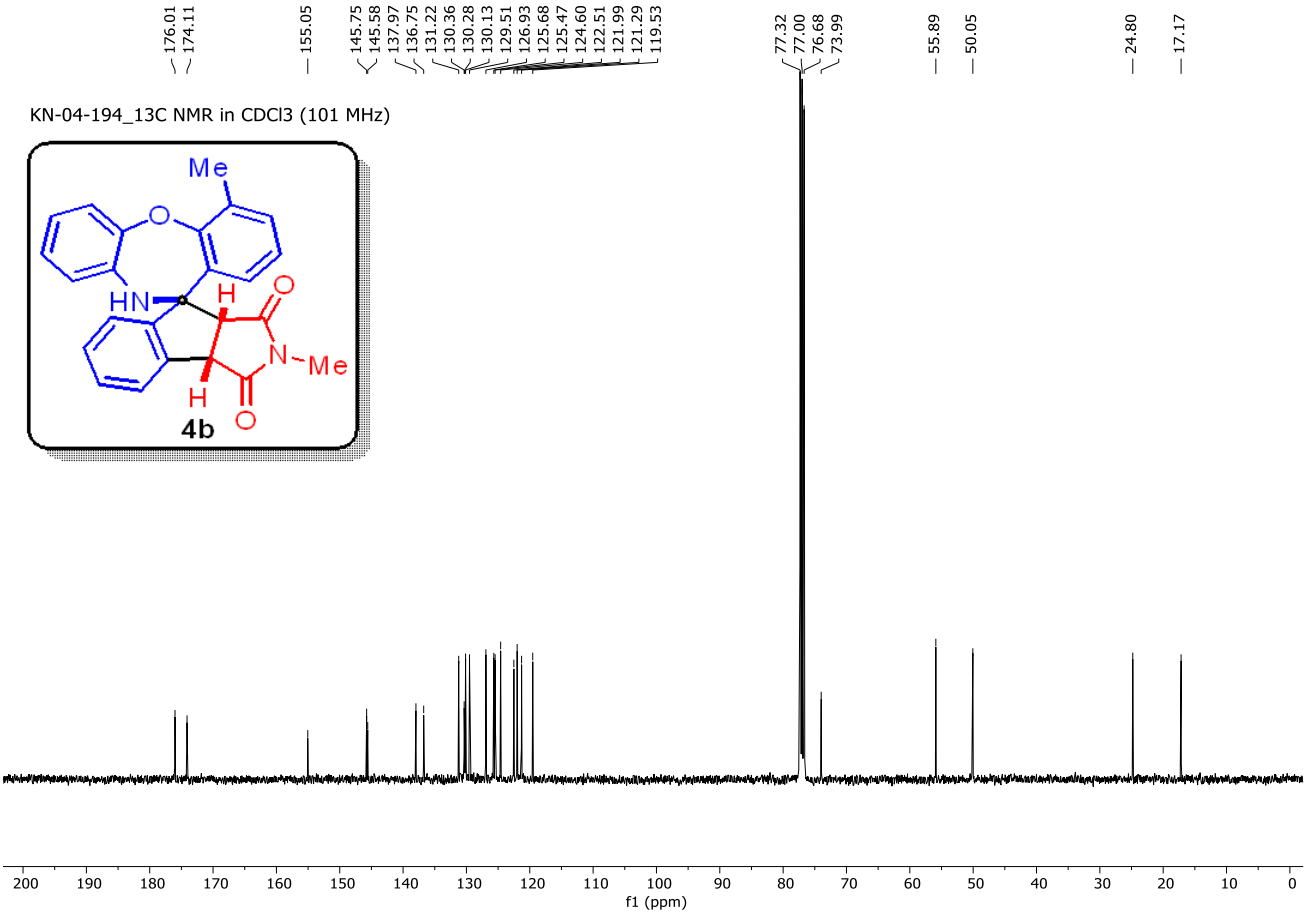
^{13}C{^{1}H} NMR of 4a (101 MHz, $CDCl_3$):



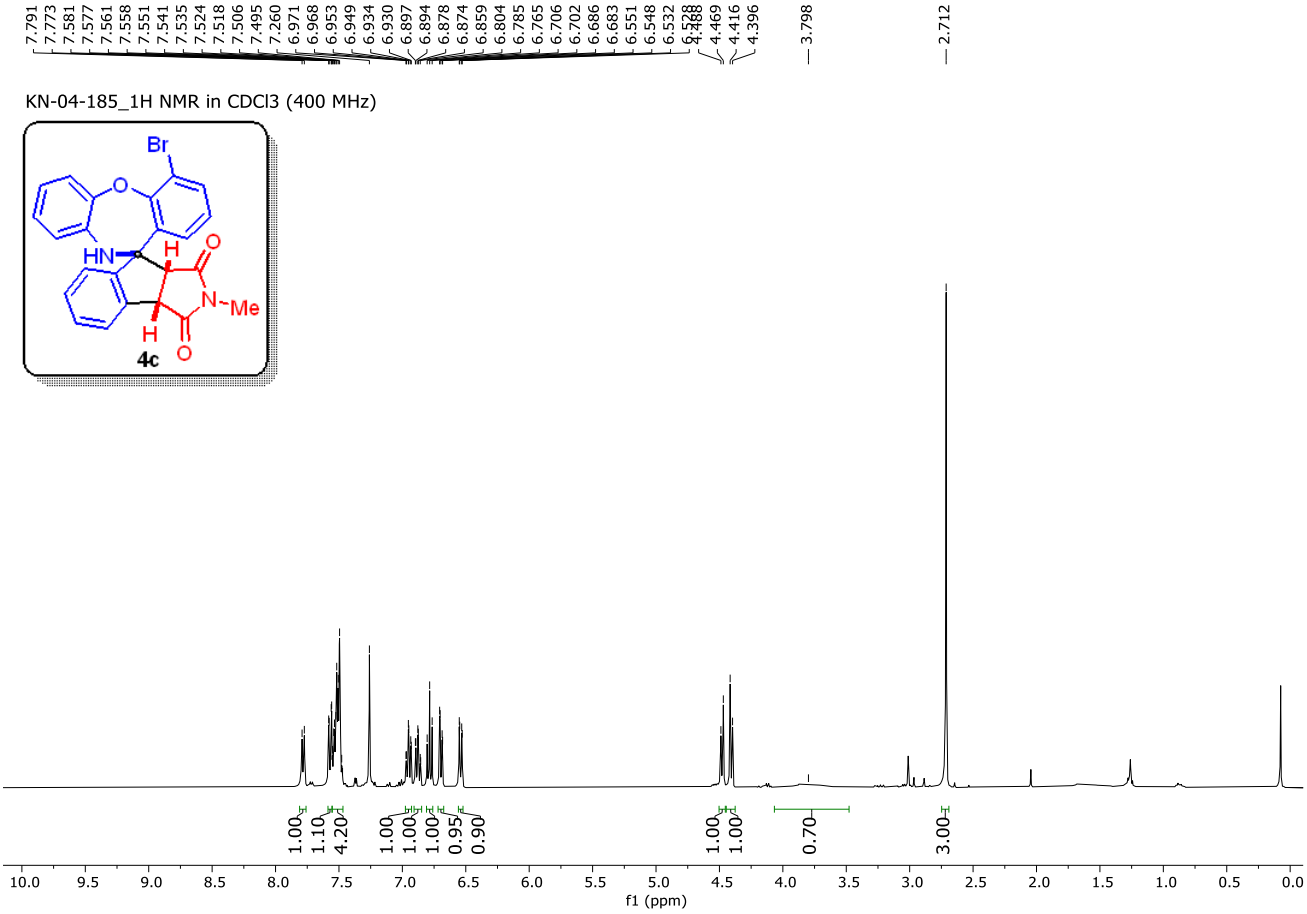
^{1}H NMR of 4b (400 MHz, $CDCl_3$):



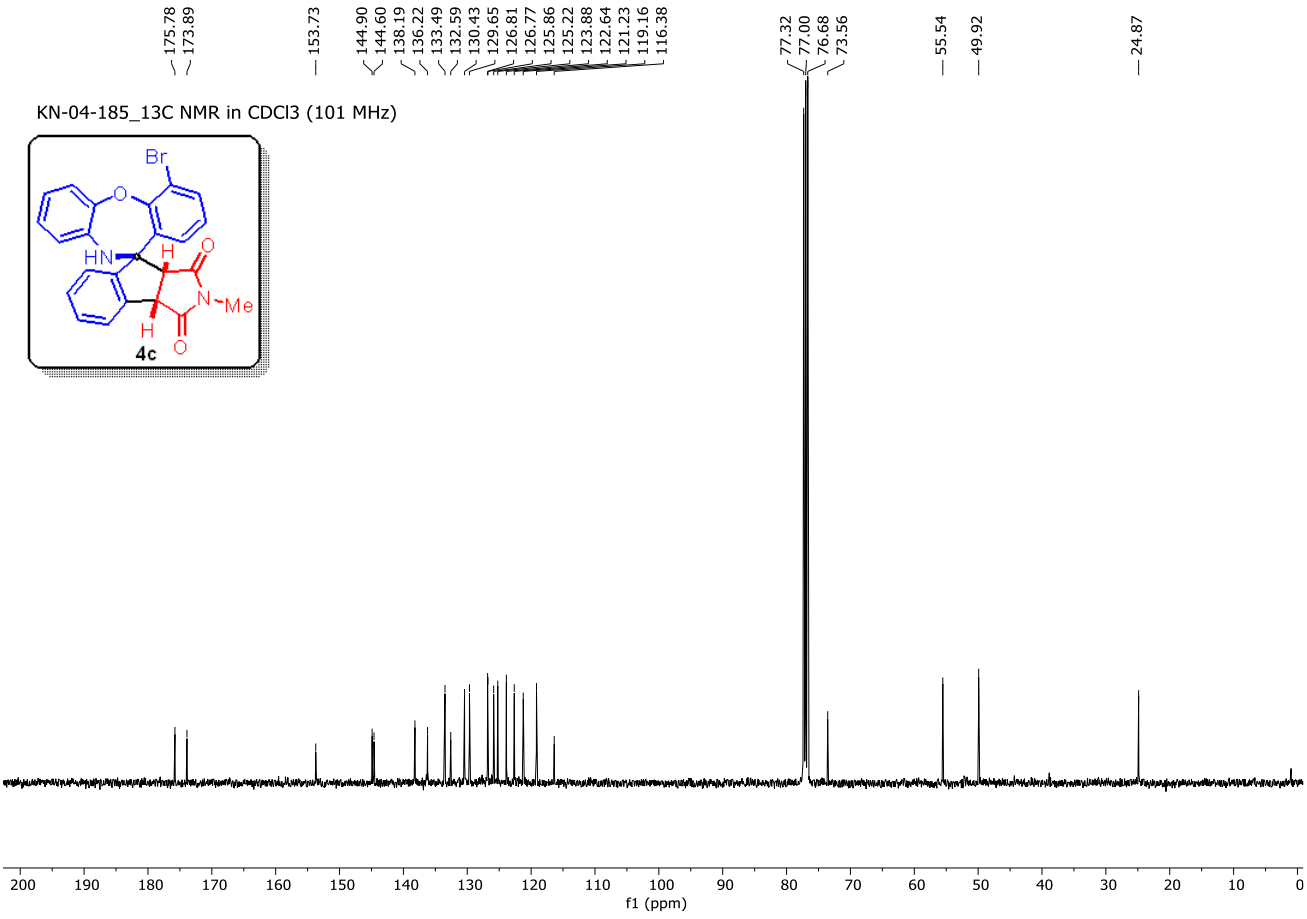
^{13}C{^{1}H} NMR of 4b (101 MHz, $CDCl_3$):



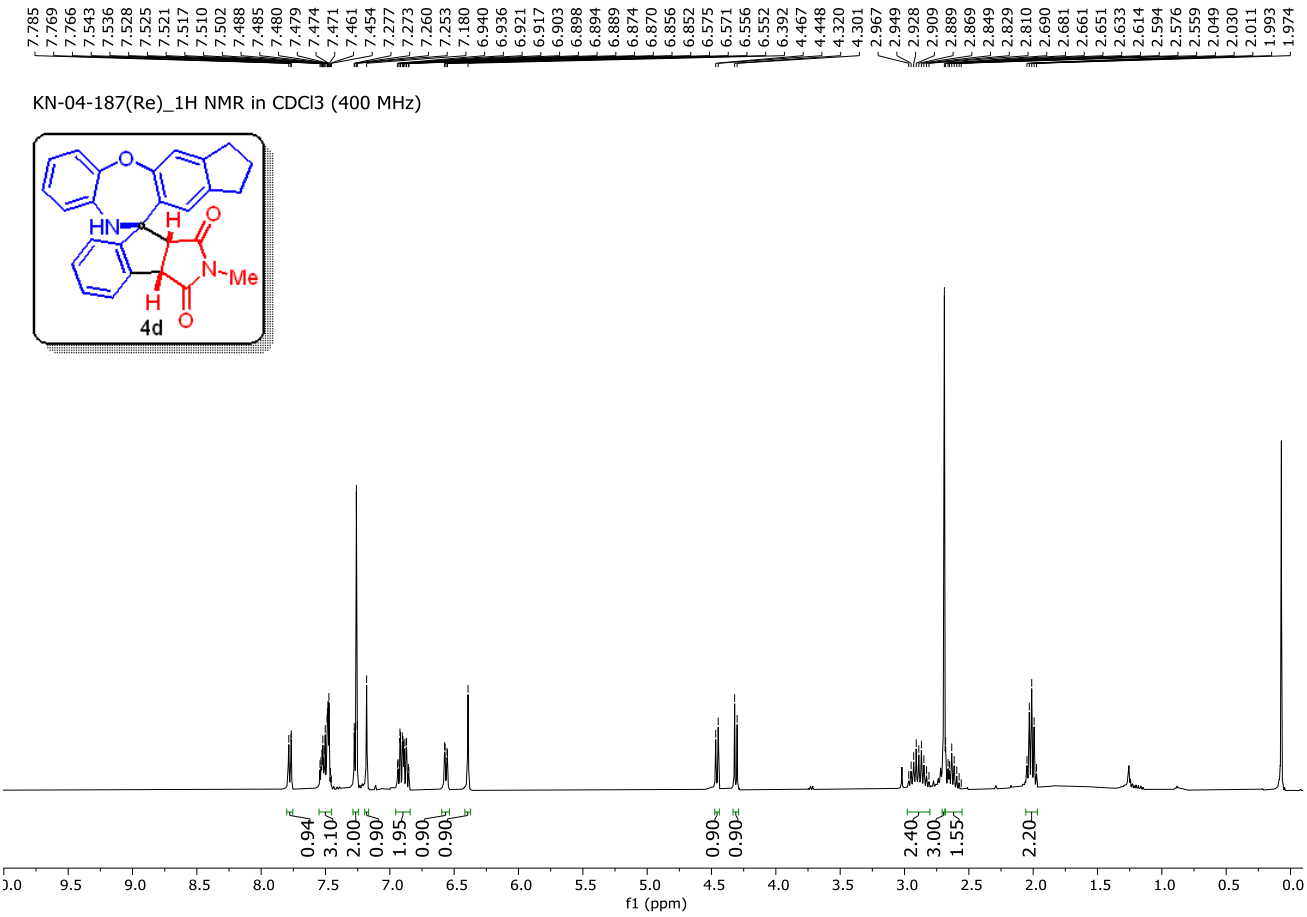
^{1}H NMR of 4c (400 MHz, $CDCl_3$):



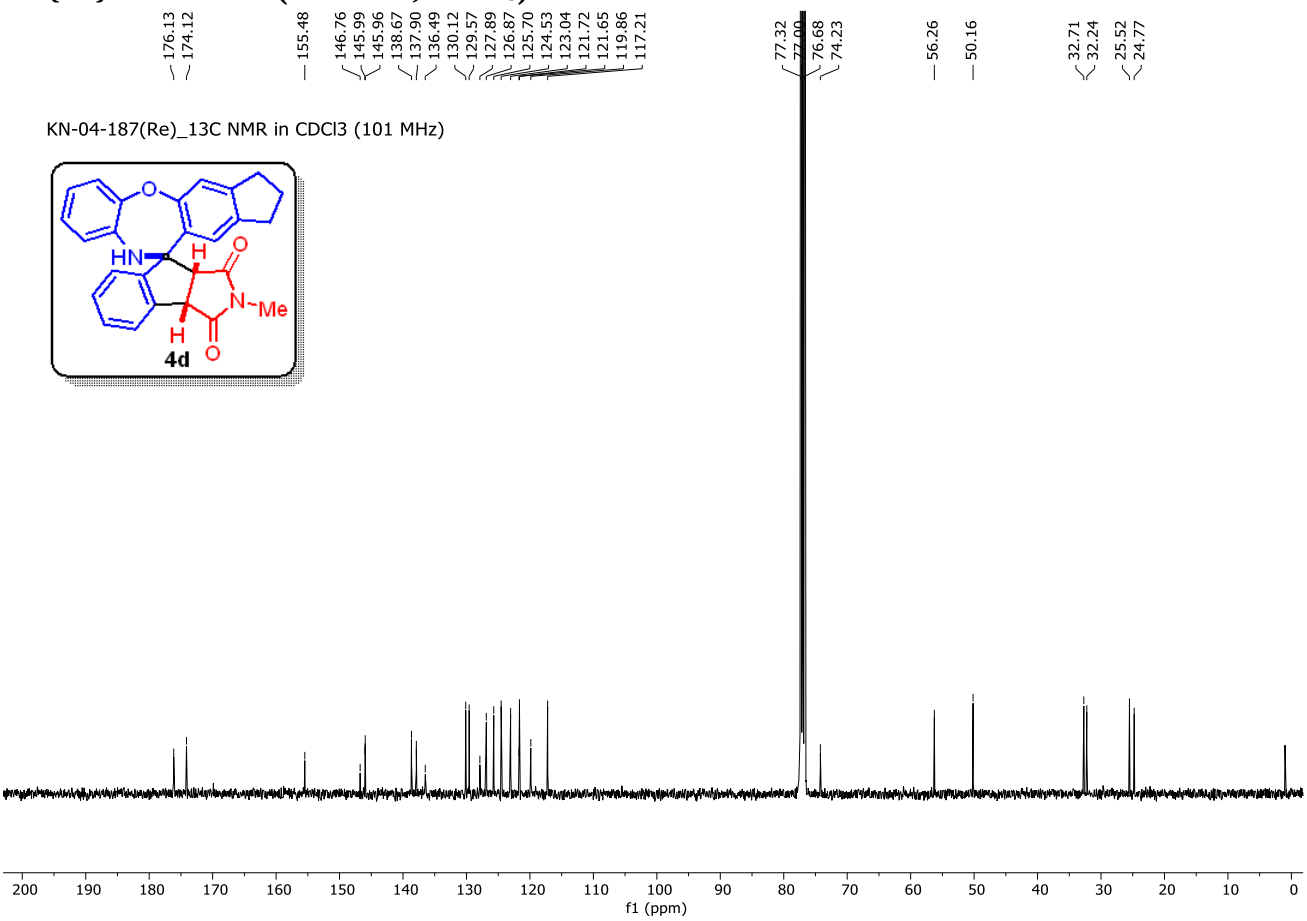
^{13}C{^{1}H} NMR of 4c (101 MHz, $CDCl_3$):



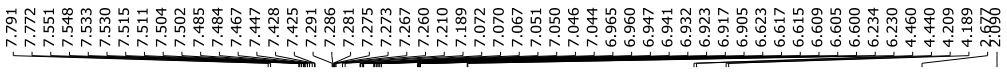
^{1}H NMR of 4d (400 MHz, $CDCl_3$):



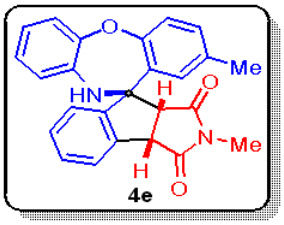
^{13}C{^{1}H} NMR of 4d (101 MHz, $CDCl_3$):



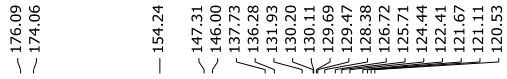
^{1}H NMR of 4e (400 MHz, $CDCl_3$):



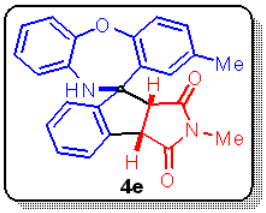
KN-04-191(Re)_1H NMR in CDCl3 (400 MHz)



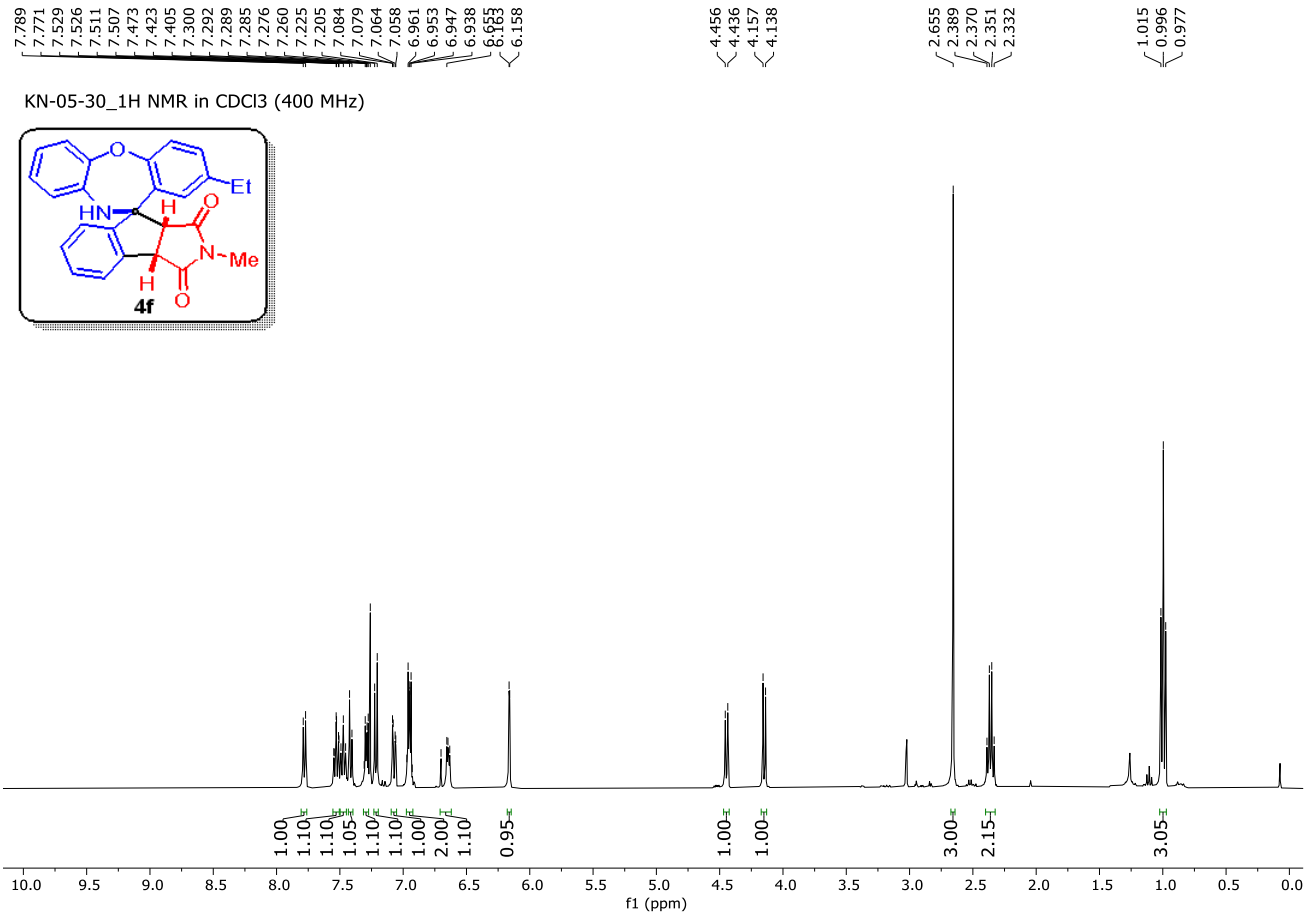
^{13}C{^{1}H} NMR of 4e (101 MHz, $CDCl_3$):



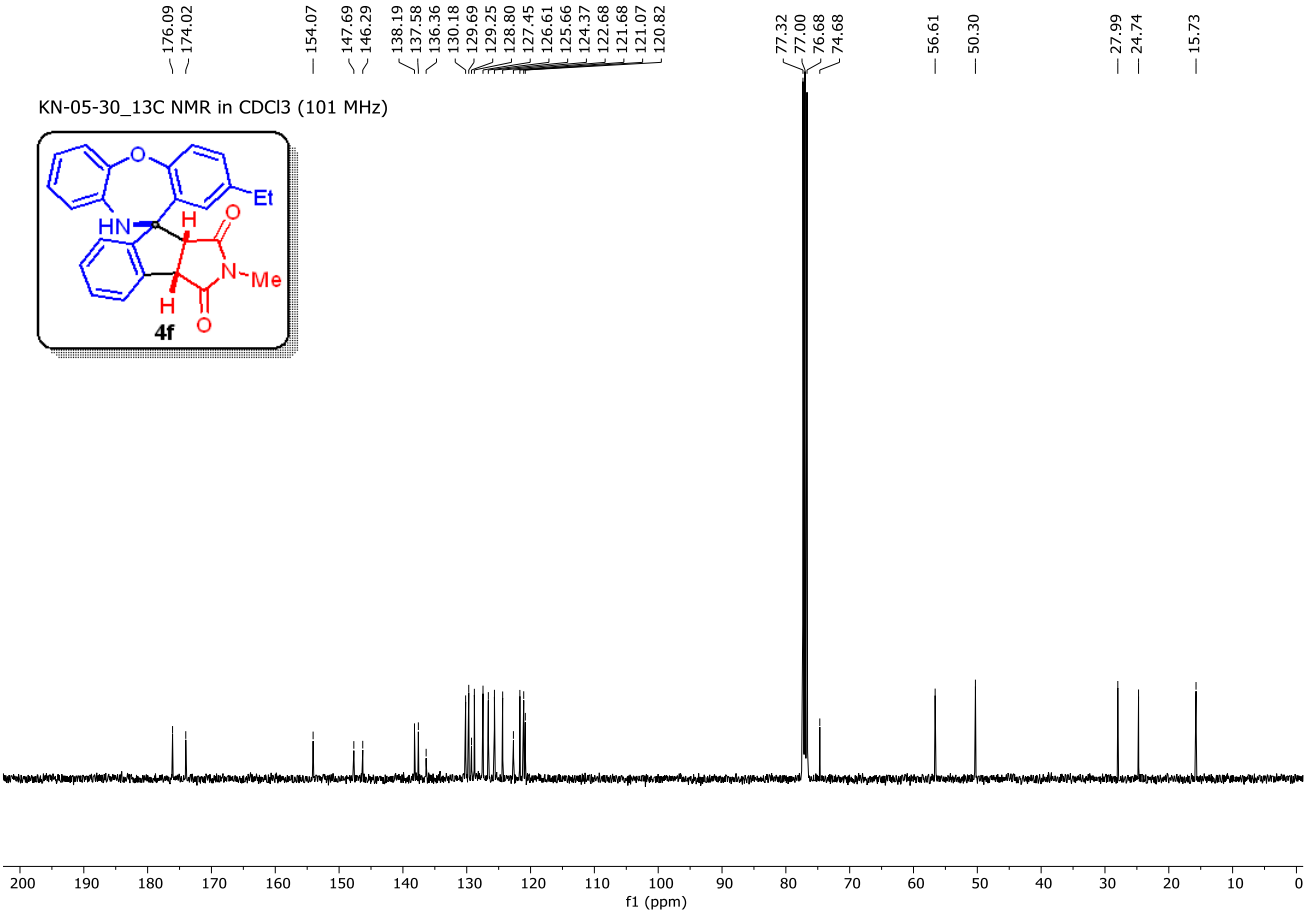
KN-04-191(Re)_13C NMR in CDCl3 (101 MHz)



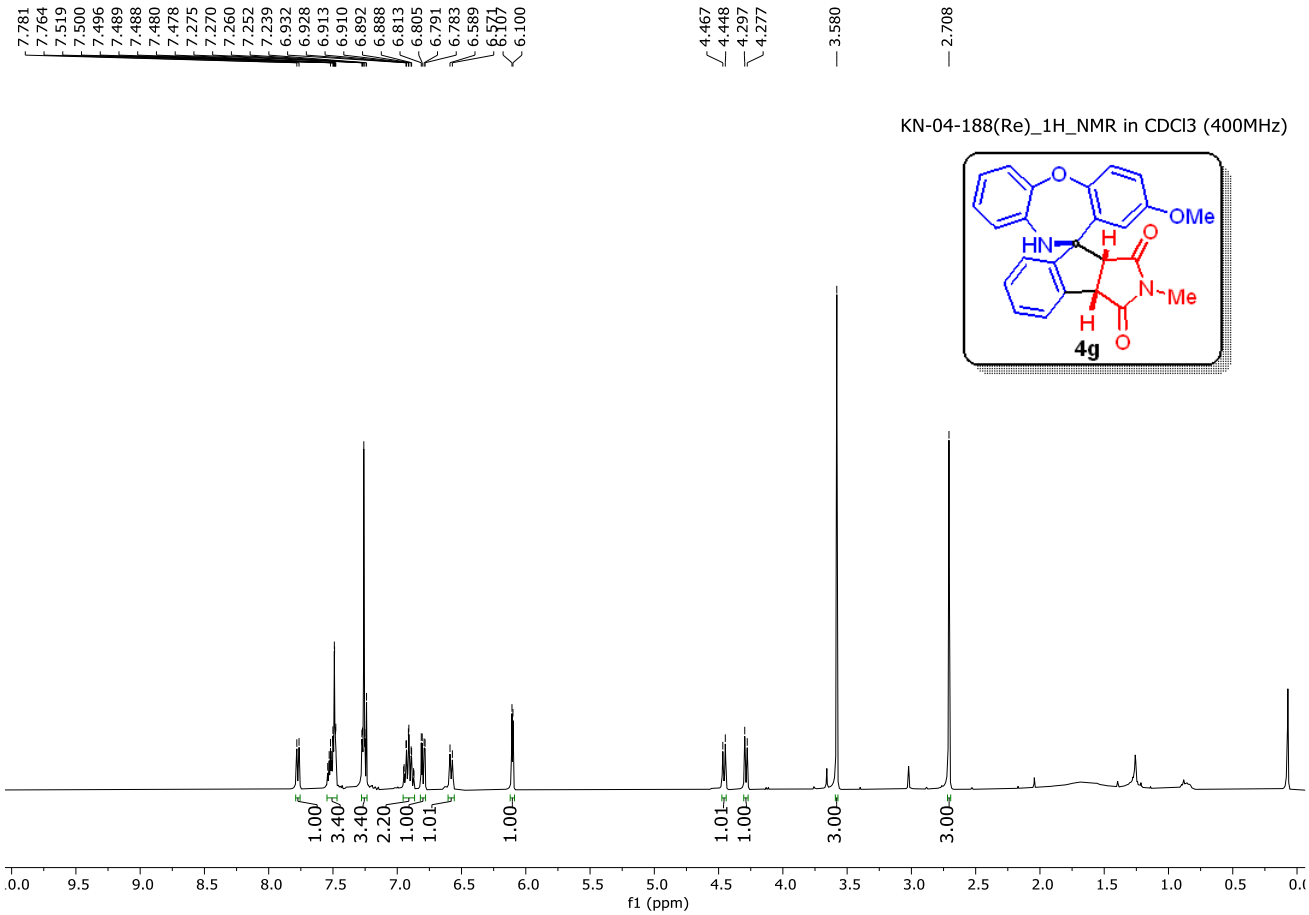
^{1}H NMR of 4f (400 MHz, $CDCl_3$):



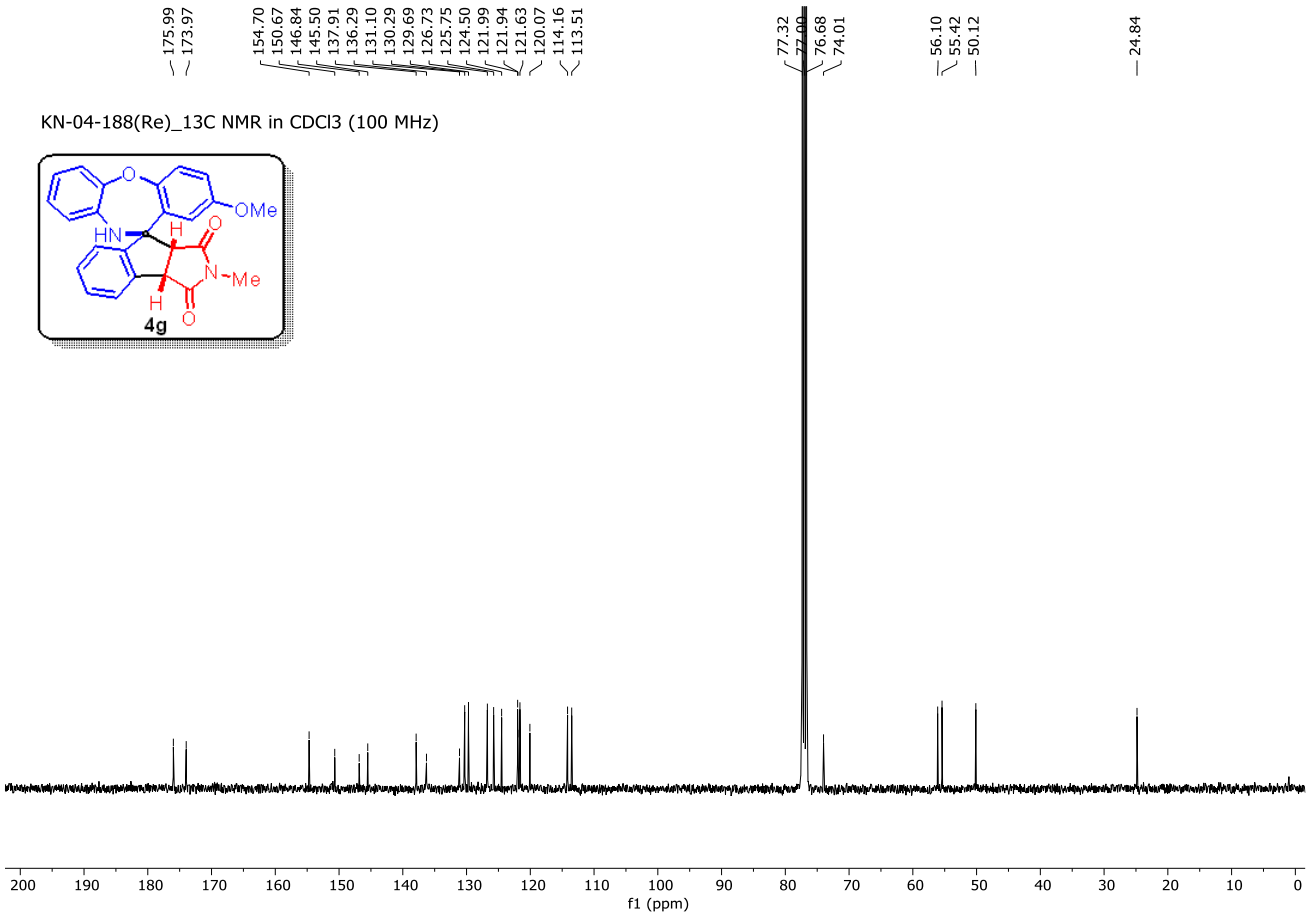
^{13}C{^{1}H} NMR of 4f (101 MHz, $CDCl_3$):



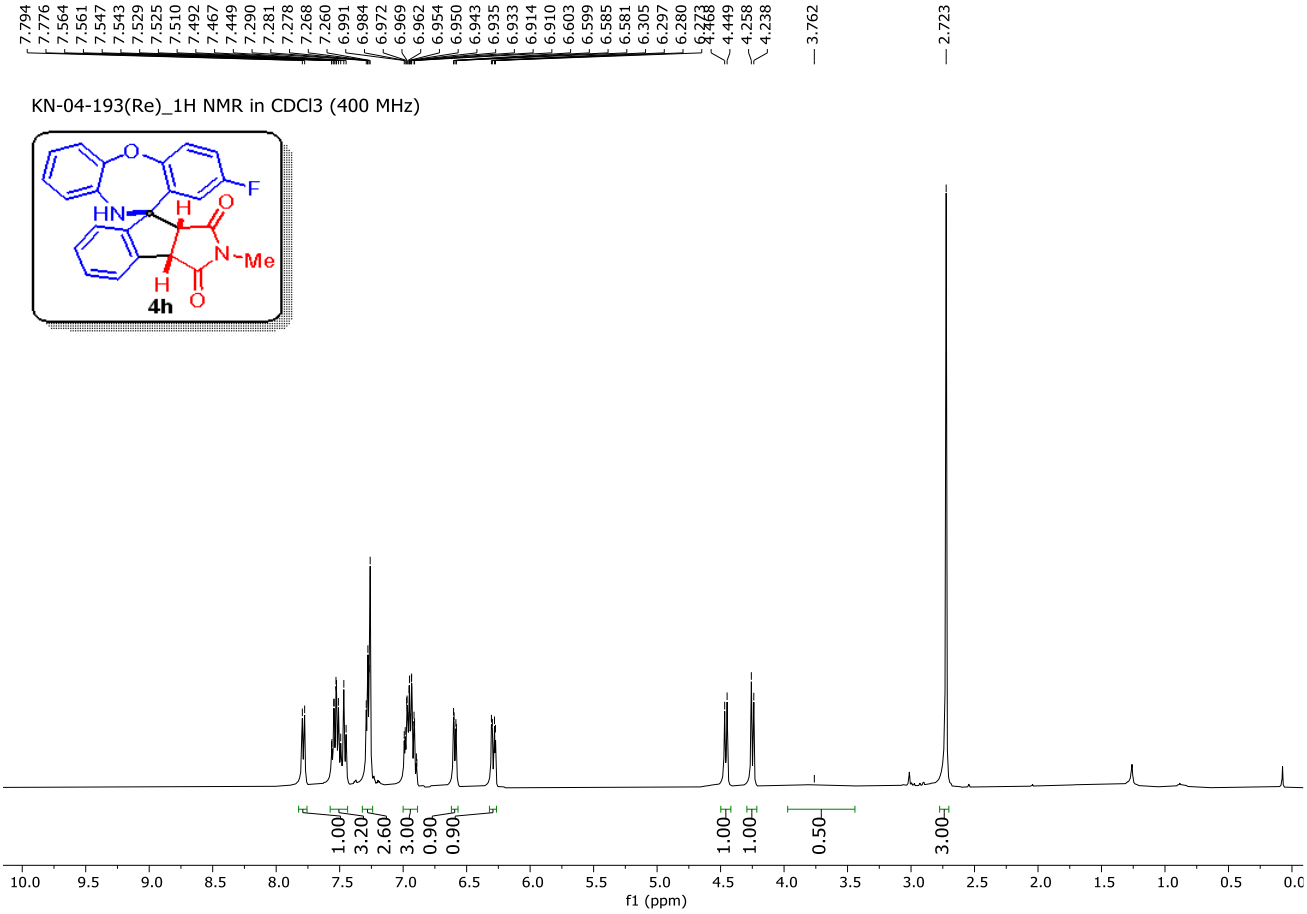
^{1}H NMR of 4g (400 MHz, $CDCl_3$):



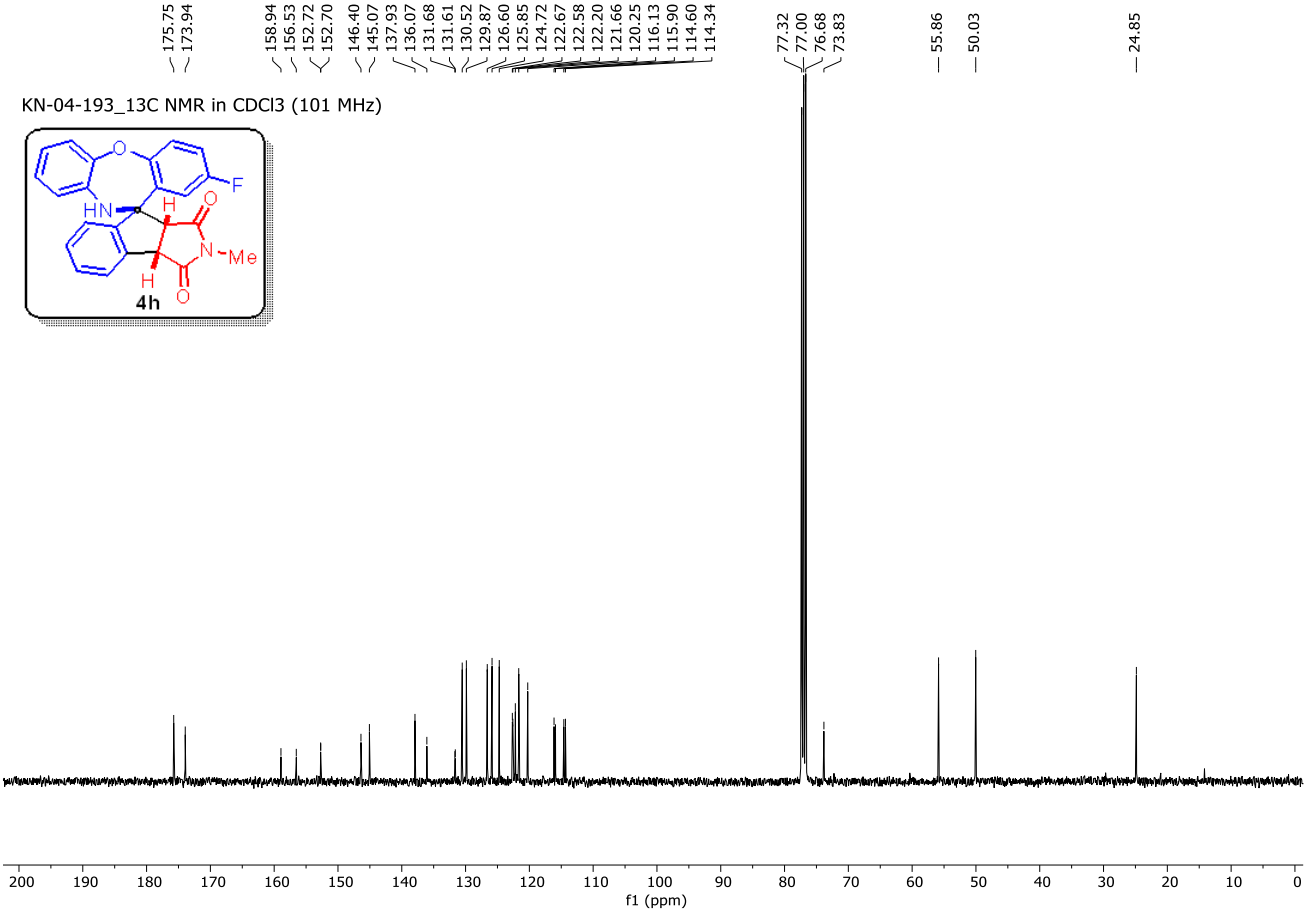
^{13}C{^{1}H} NMR of 4g (101 MHz, $CDCl_3$):



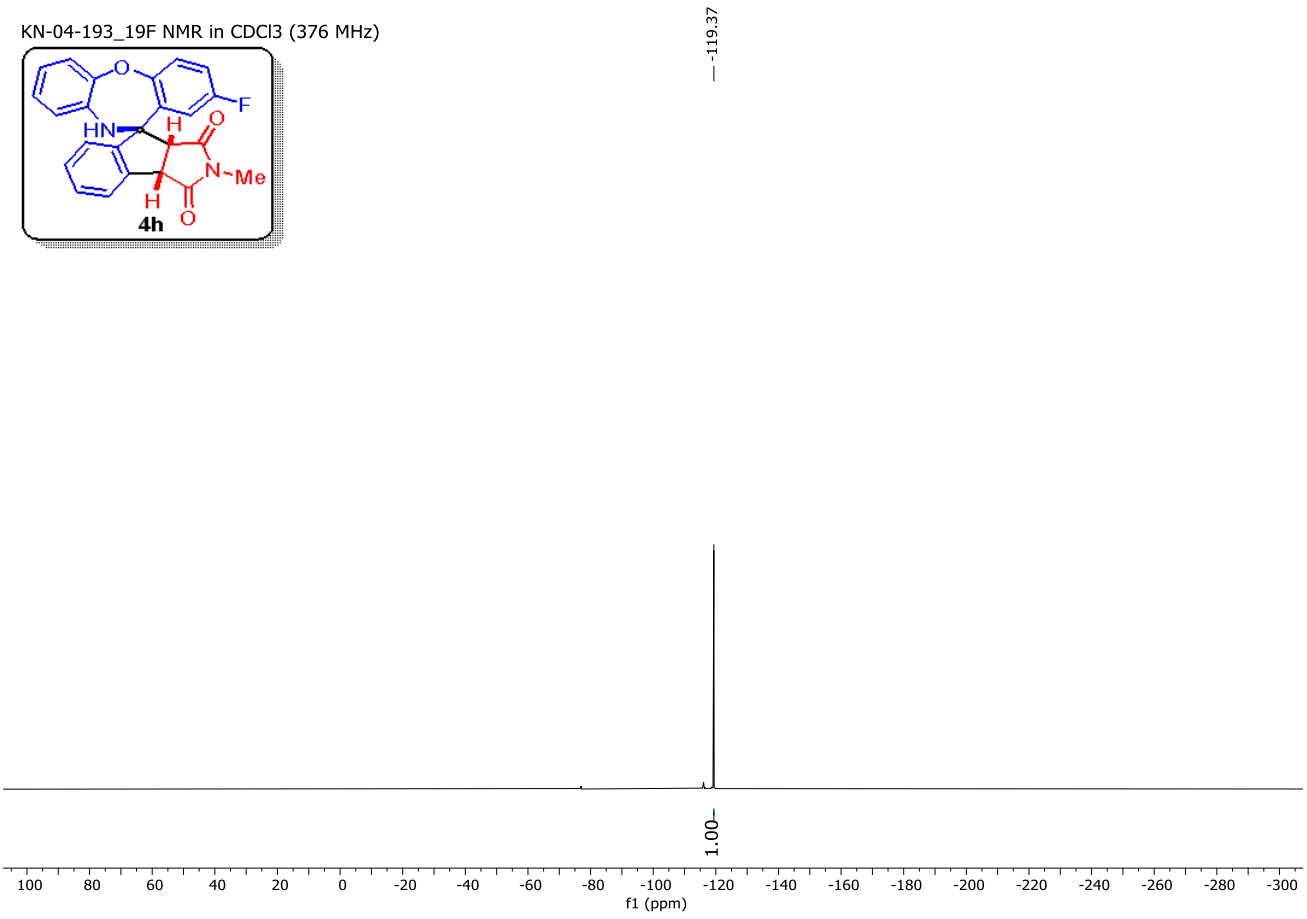
^{1}H NMR of 4h (400 MHz, $CDCl_3$):



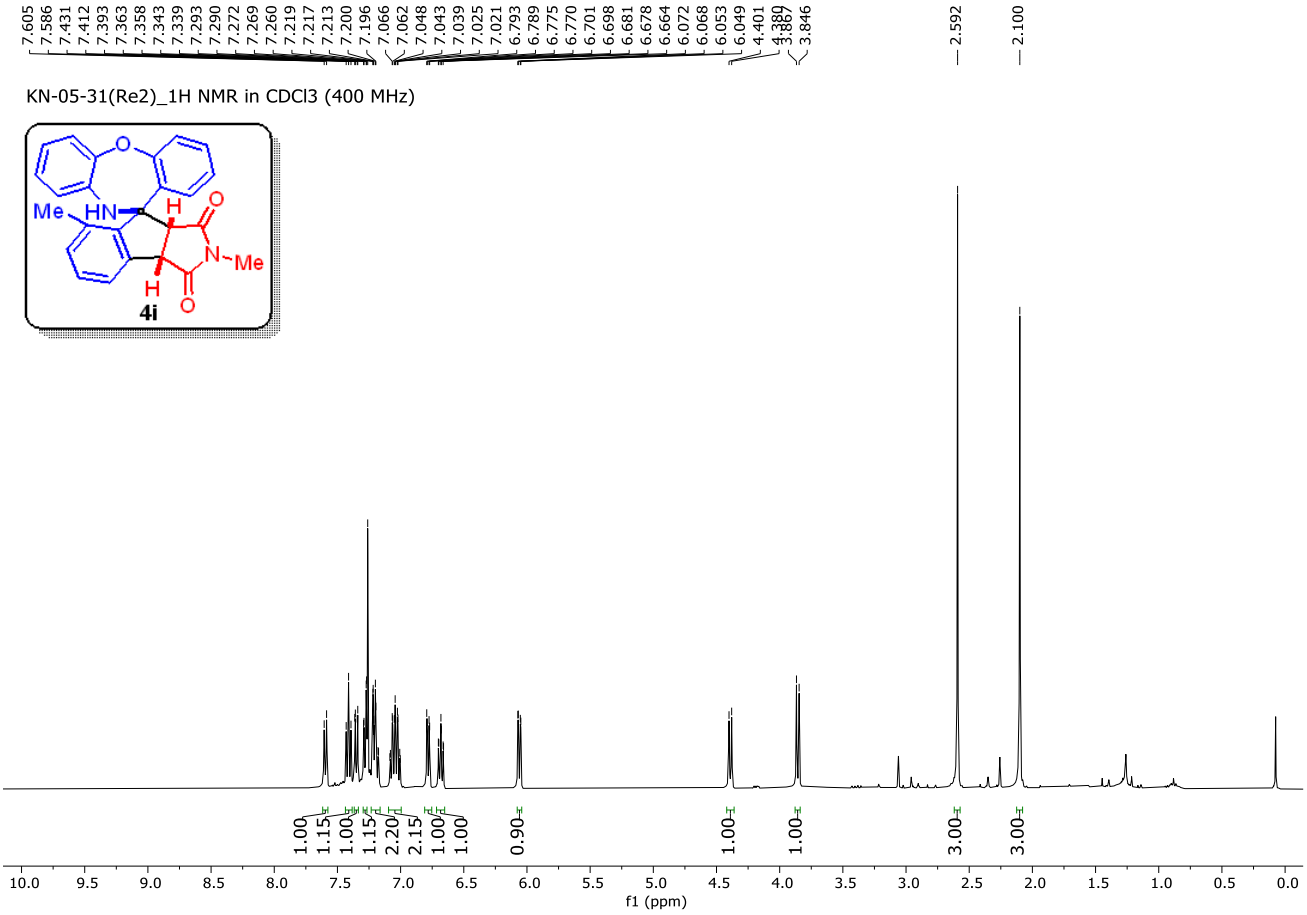
^{13}C{^{1}H} NMR of 4h (101 MHz, $CDCl_3$):



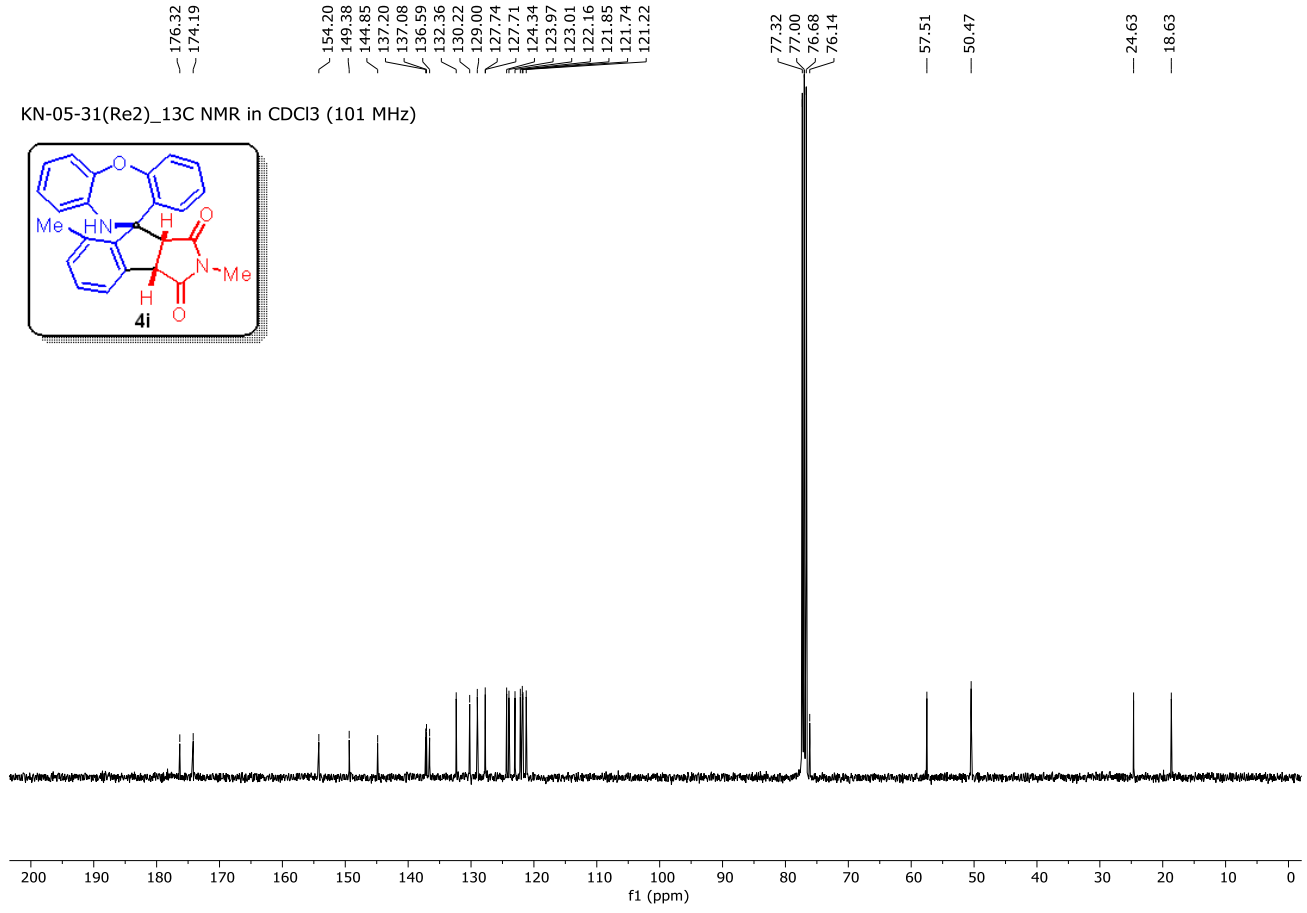
^{19}F NMR of 4h (376 MHz, $CDCl_3$):



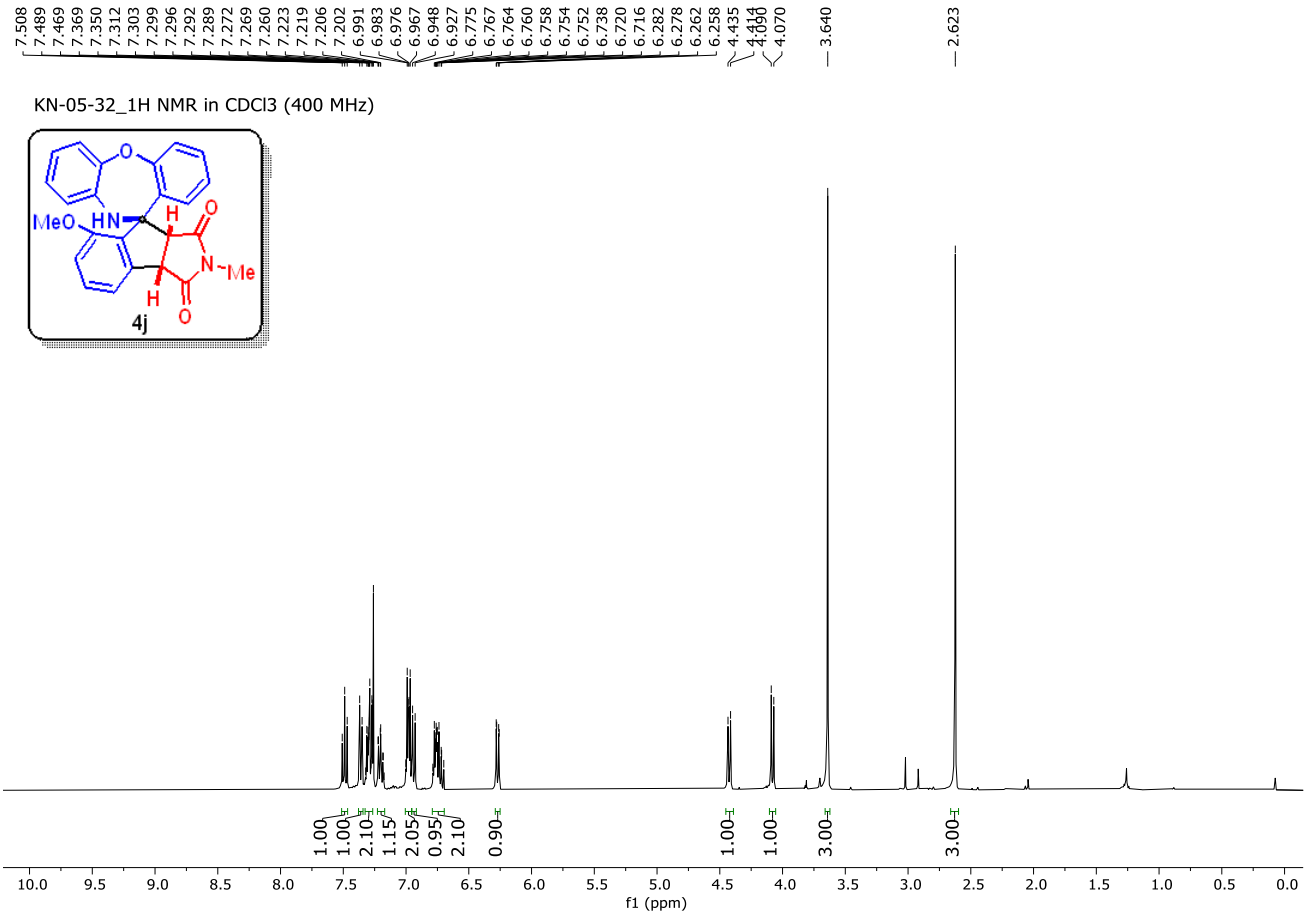
^{1}H NMR of 4i (400 MHz, $CDCl_3$):



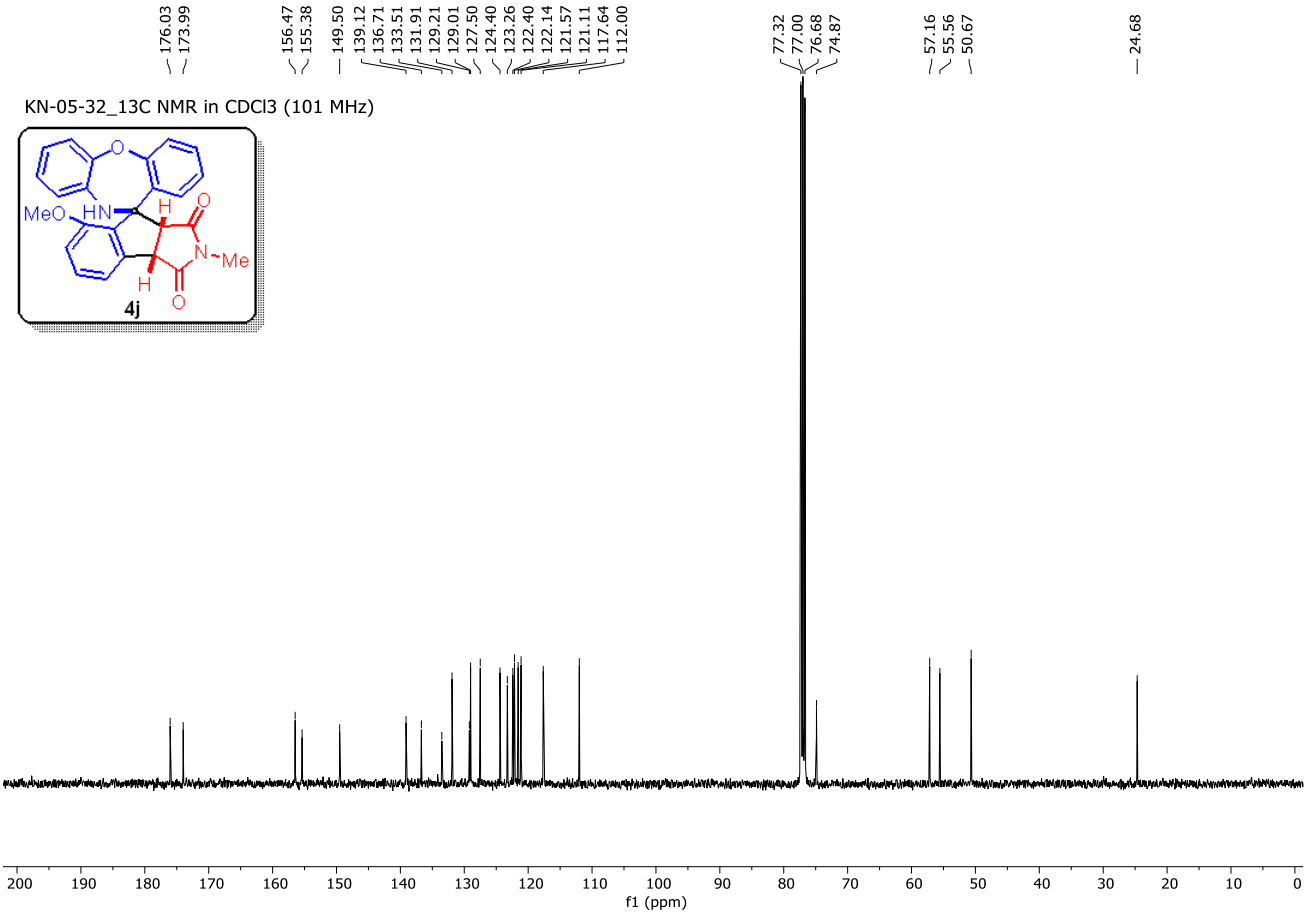
^{13}C{^{1}H} NMR of 4i (101 MHz, $CDCl_3$):



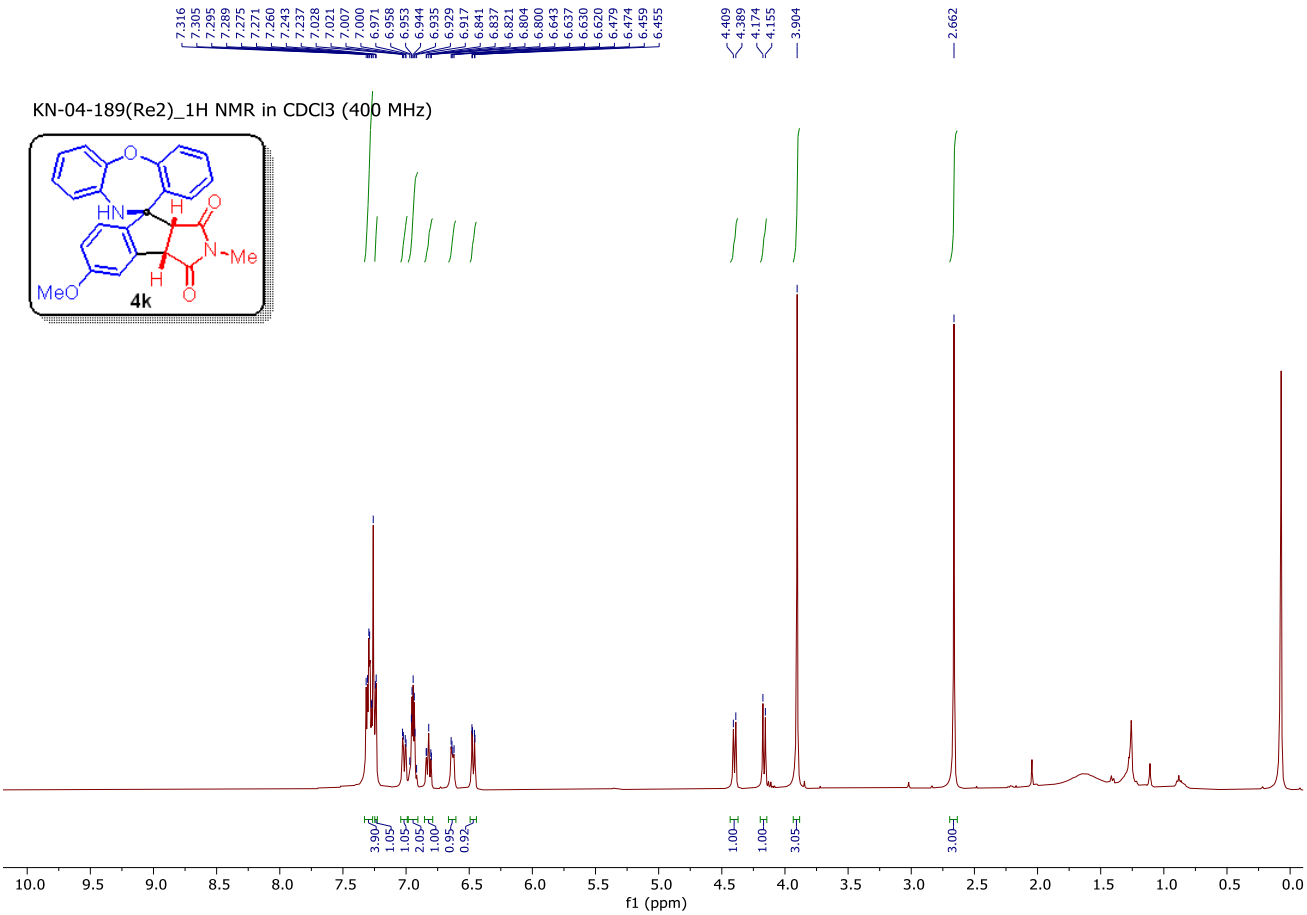
^{1}H NMR of 4j (400 MHz, $CDCl_3$):



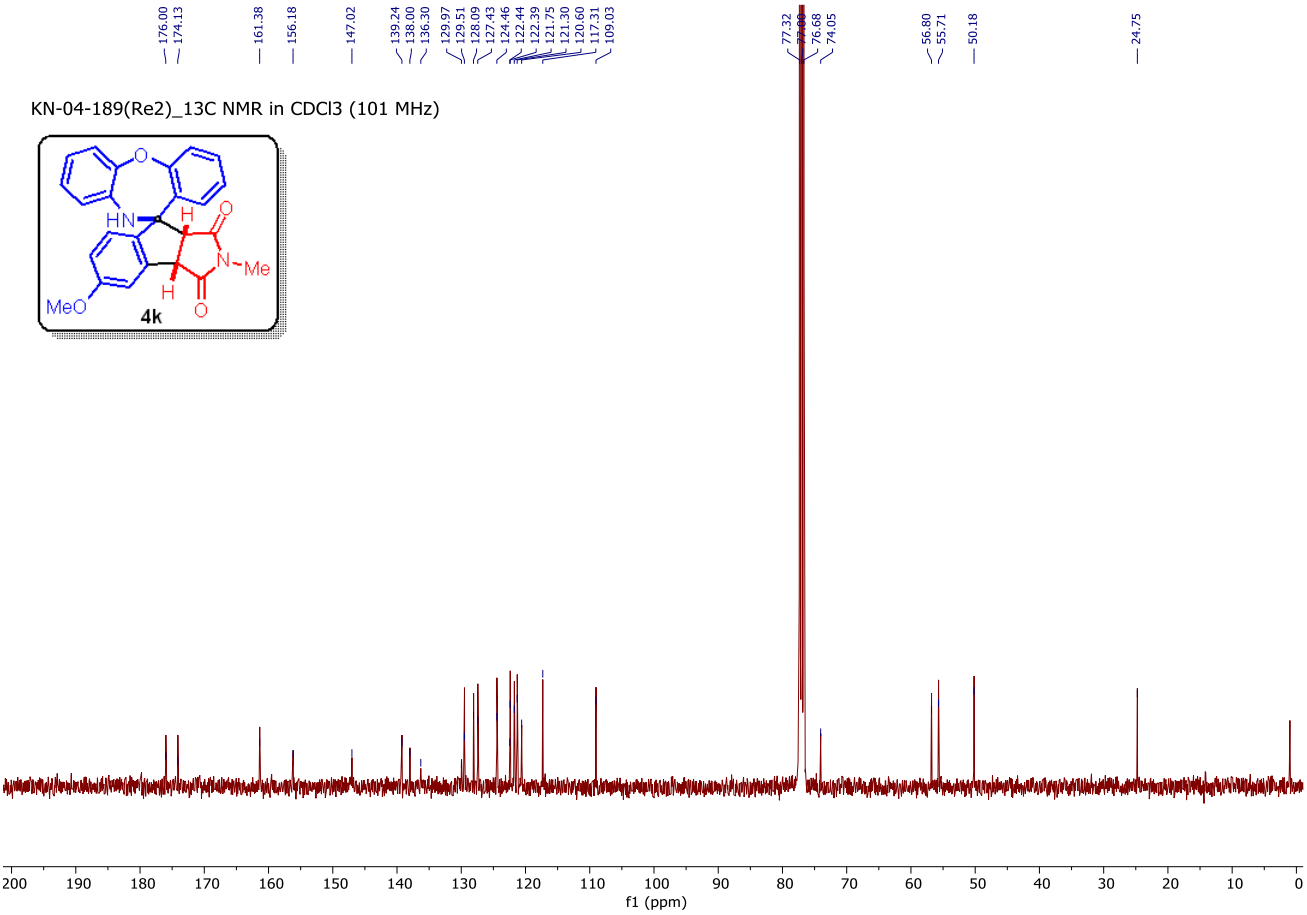
^{13}C{^{1}H} NMR of 4j (101 MHz, $CDCl_3$):



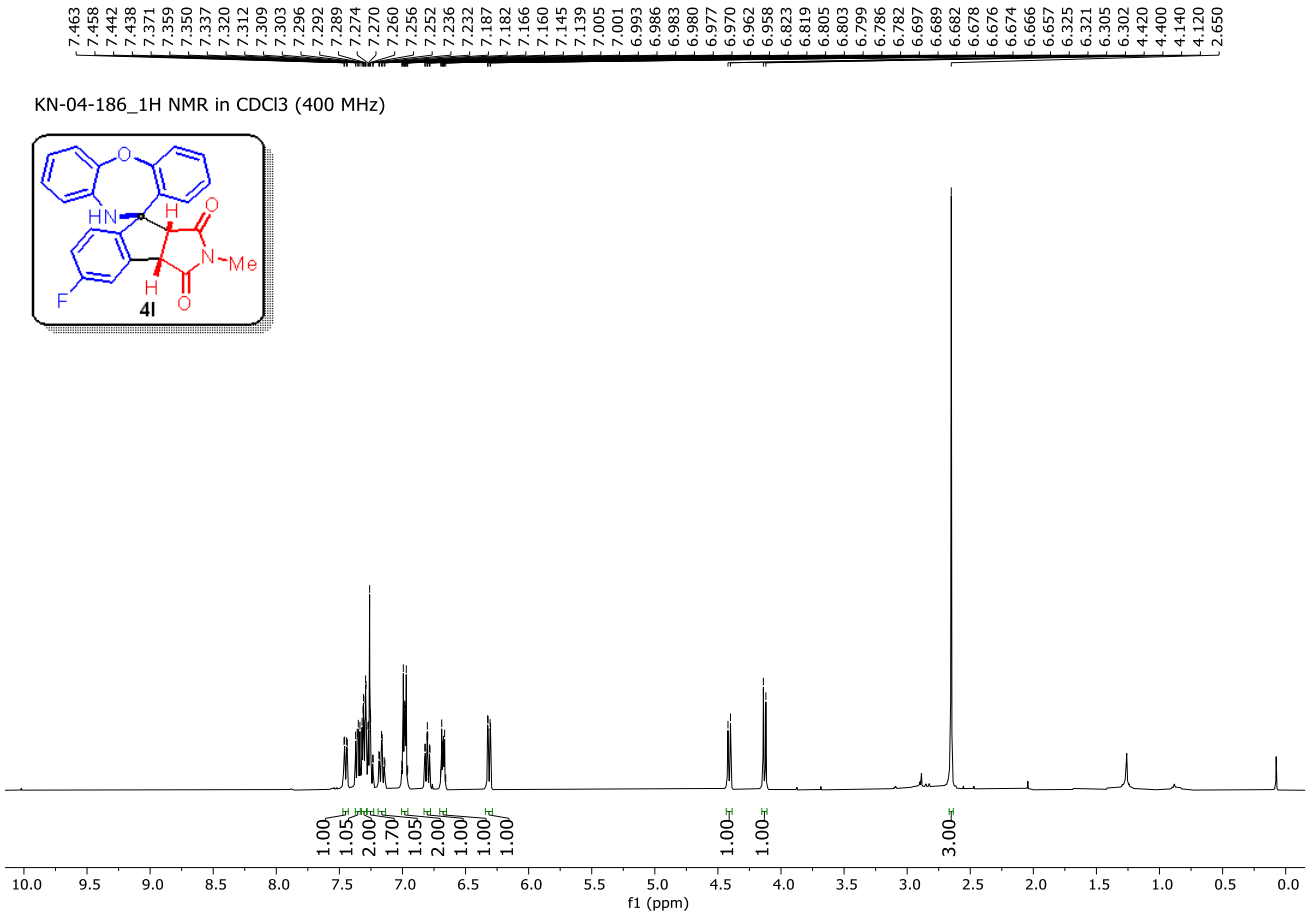
^{1}H NMR of 4k (400 MHz, $CDCl_3$):



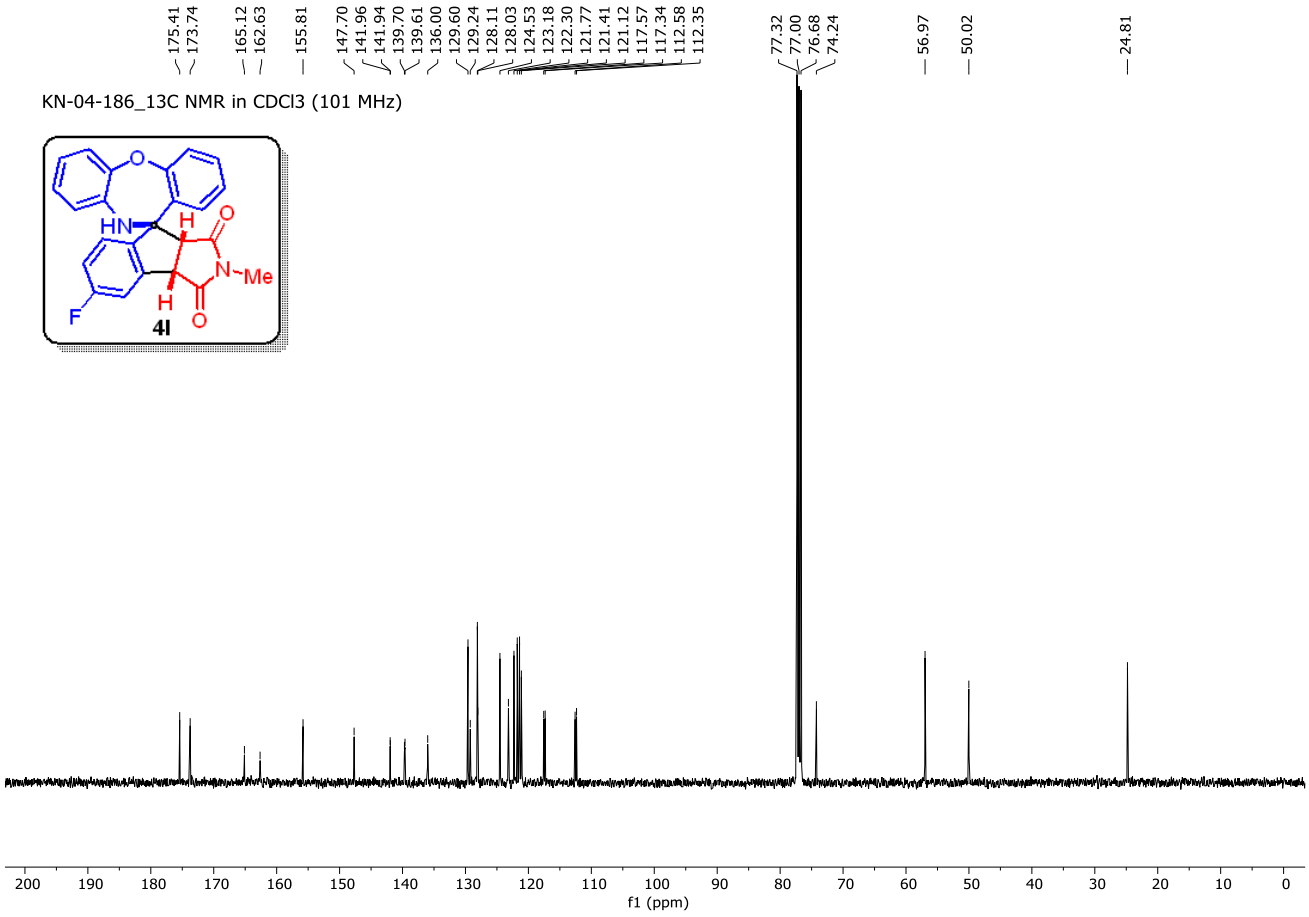
^{13}C{^{1}H} NMR of 4k (101 MHz, $CDCl_3$):



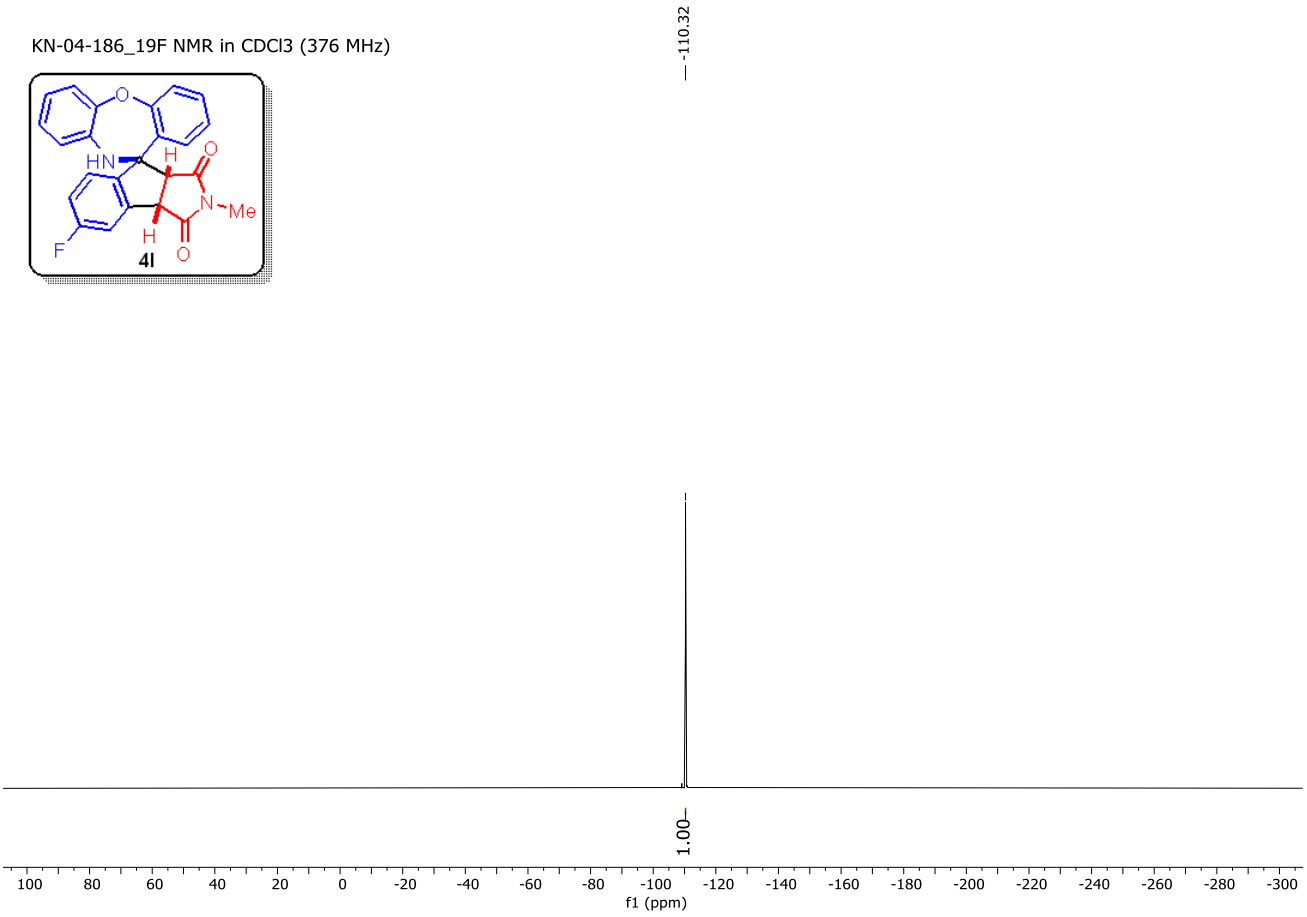
^{1}H NMR of 4l (400 MHz, $CDCl_3$):



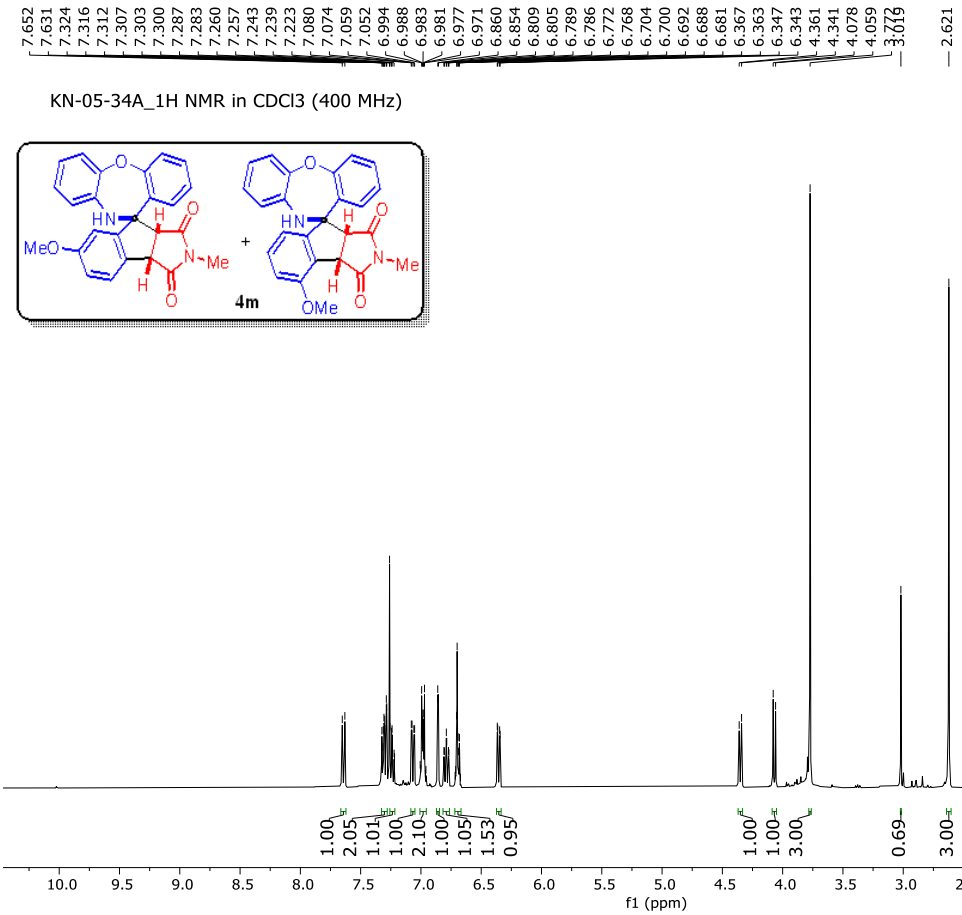
^{13}C{^{1}H} NMR of 4l (101 MHz, $CDCl_3$):



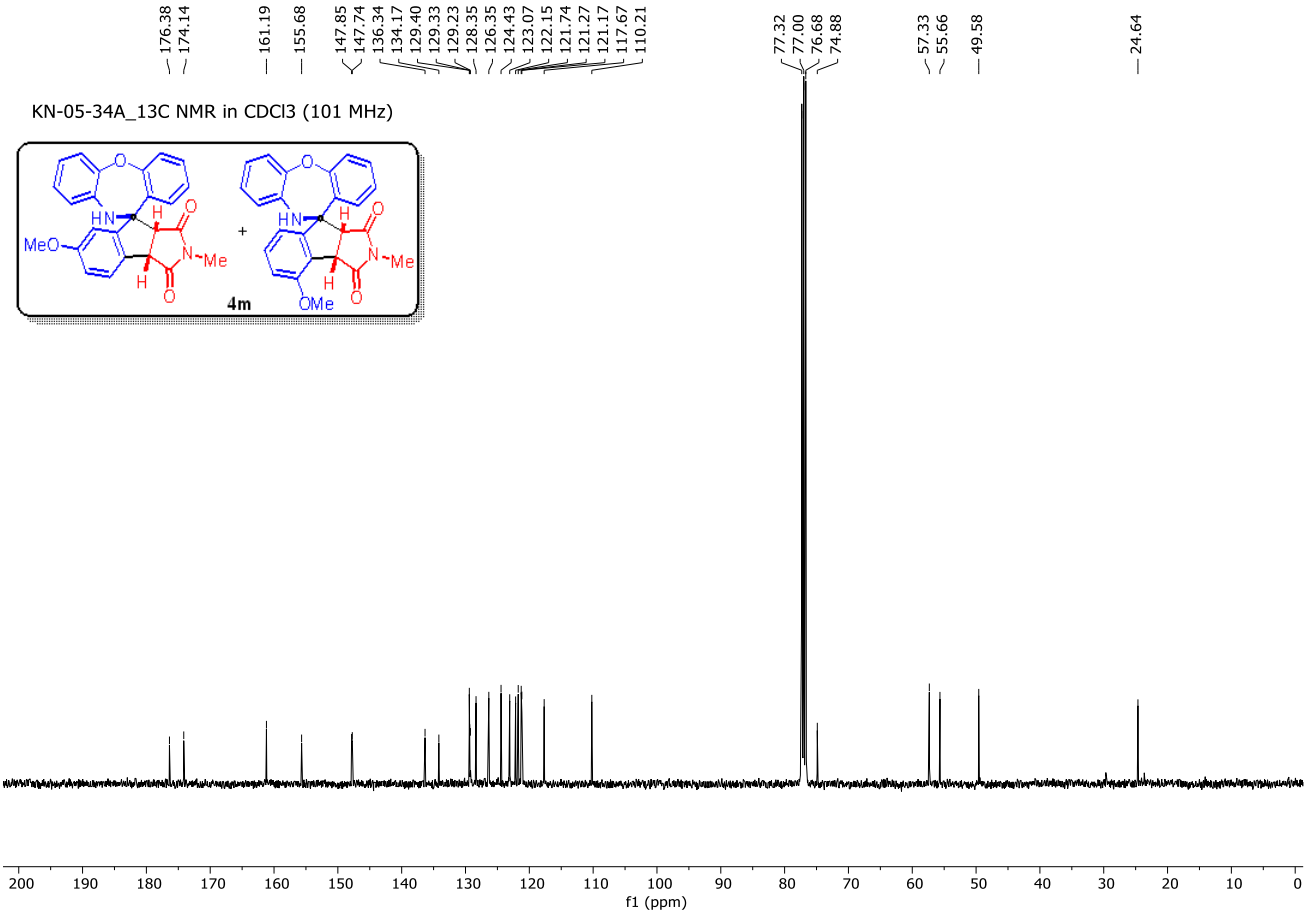
^{19}F NMR of 4l (376 MHz, $CDCl_3$):



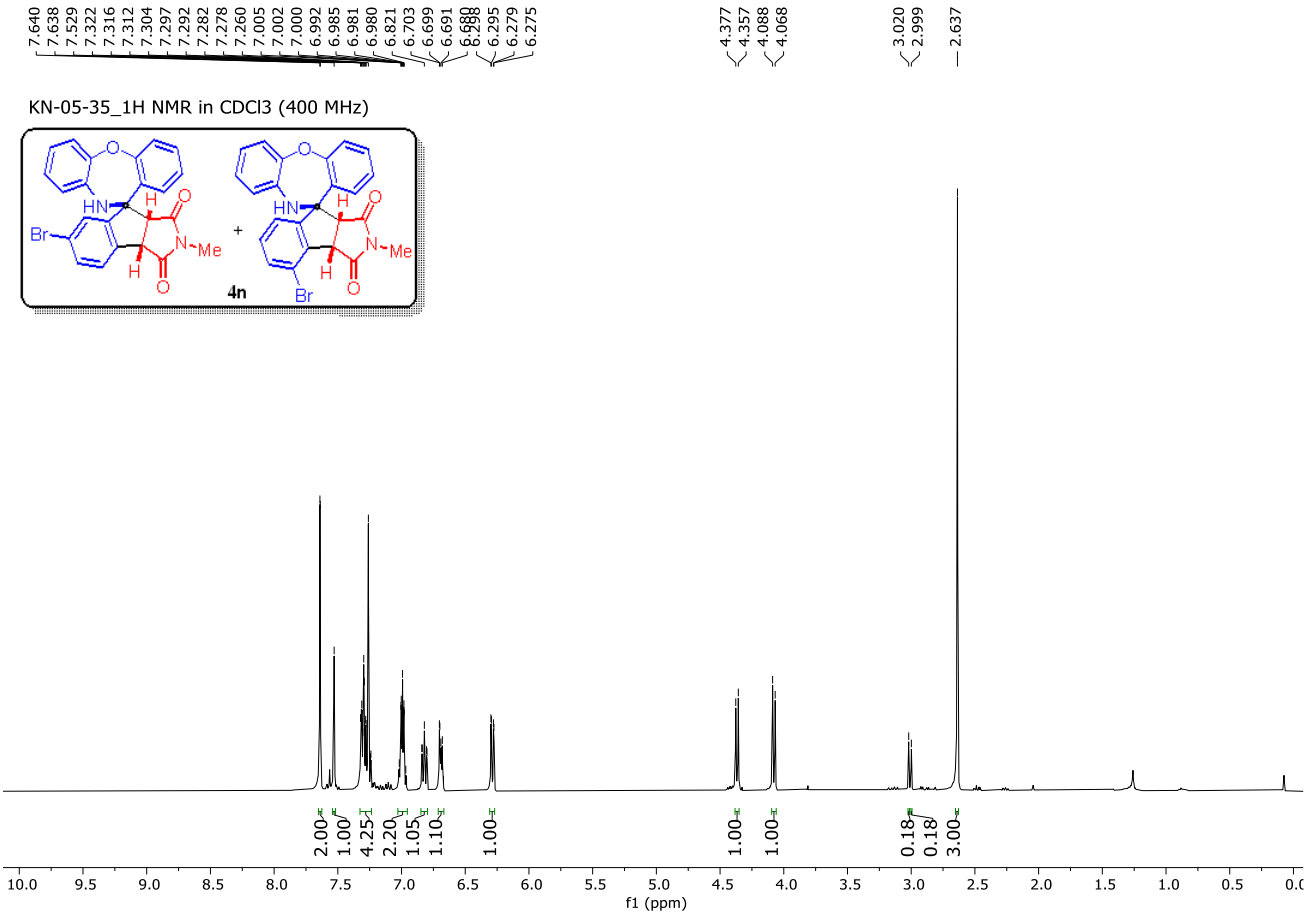
^{1}H NMR of 4m (400 MHz, $CDCl_3$):



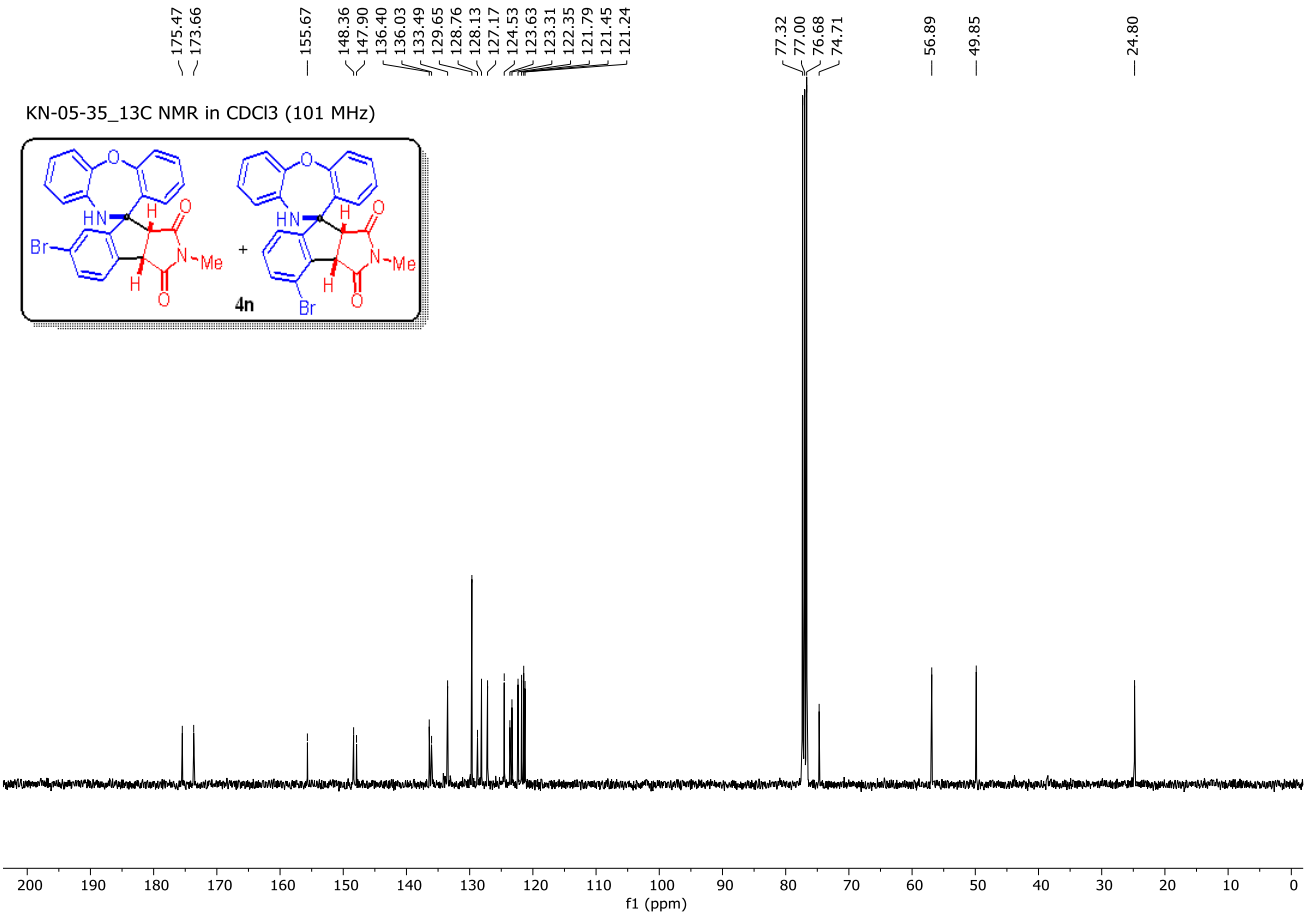
^{13}C{^{1}H} NMR of 4m (100 MHz, $CDCl_3$):



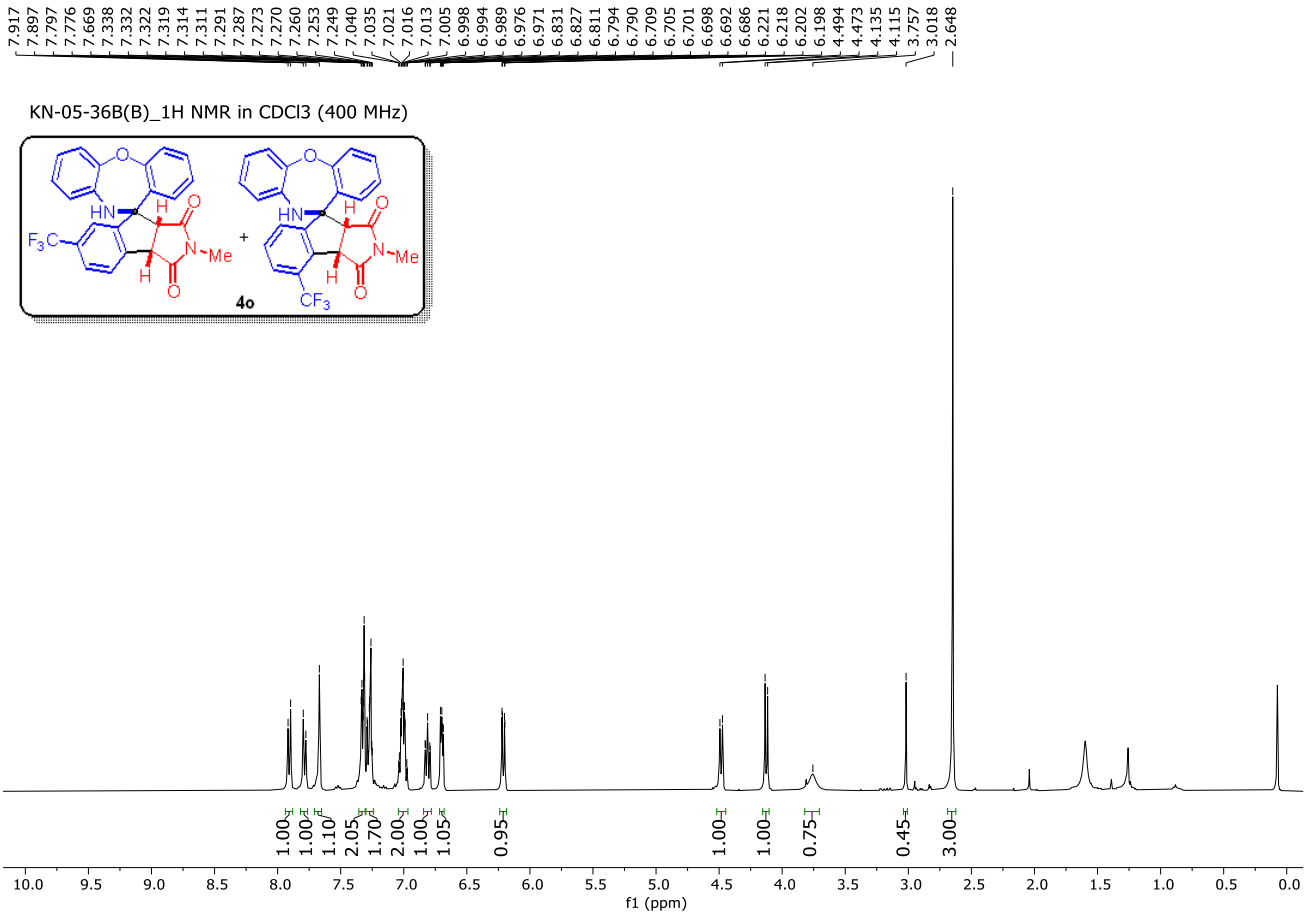
^{1}H NMR of 4n (400 MHz, $CDCl_3$):



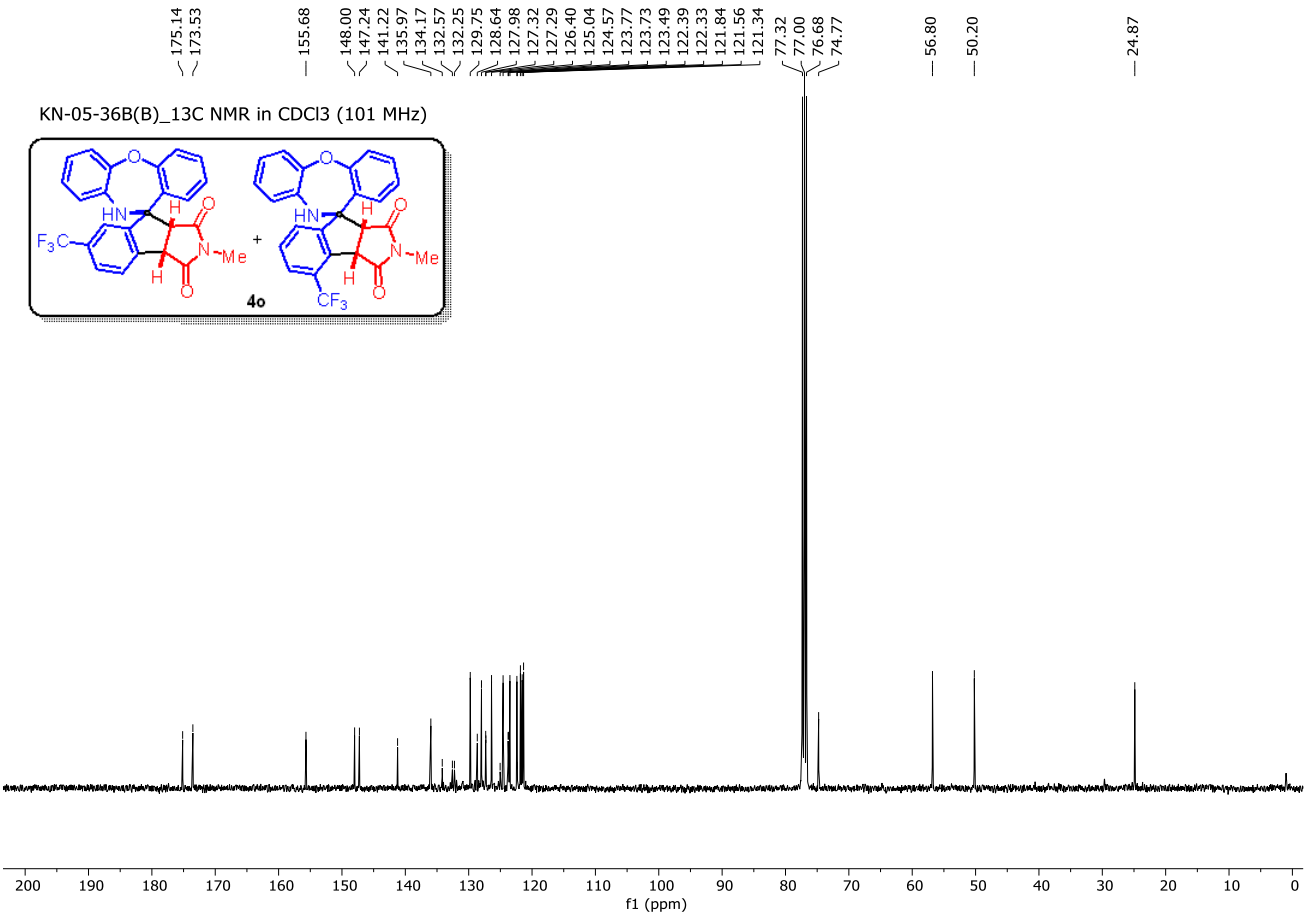
^{13}C{^{1}H} NMR of 4n (101 MHz, $CDCl_3$):



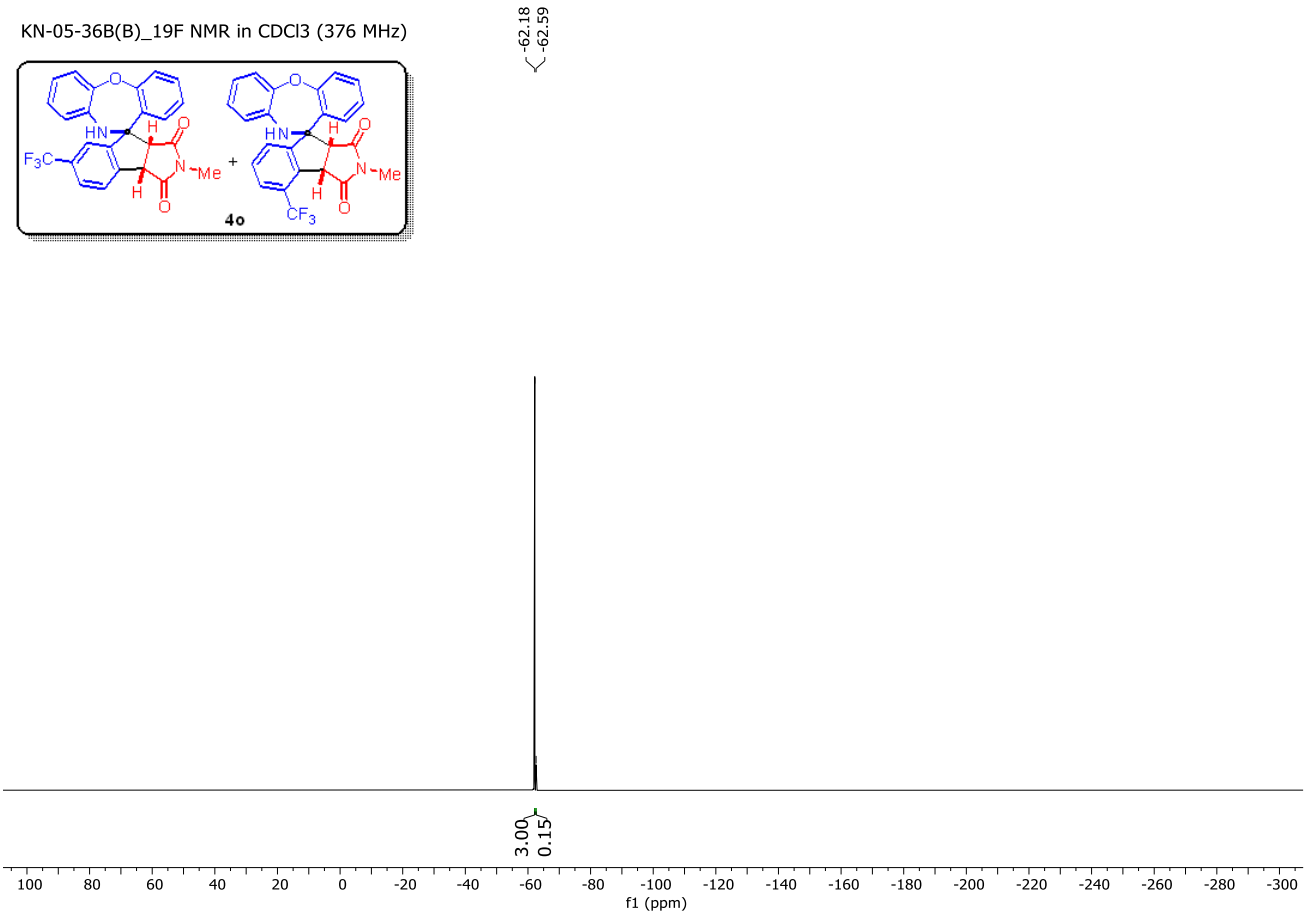
^{1}H NMR of 4o (400 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR of 4o (101 MHz, $CDCl_3$):

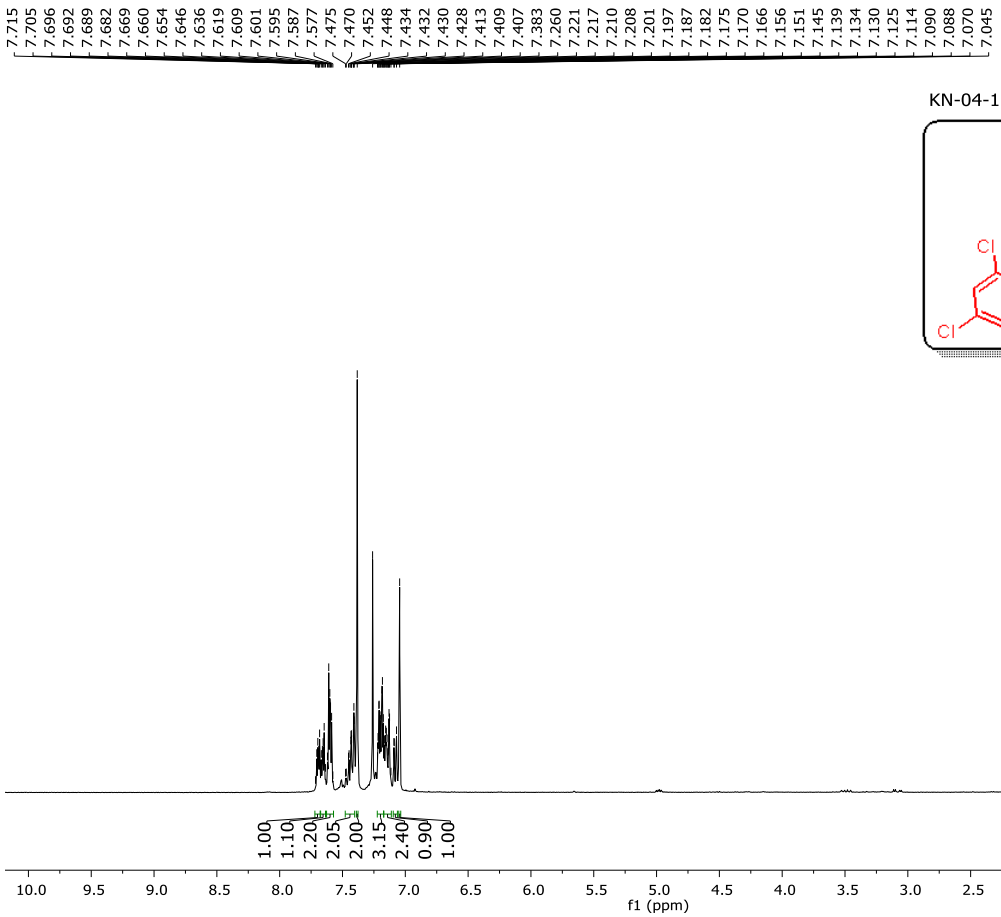


^{19}F NMR of 4o (376 MHz, $CDCl_3$):

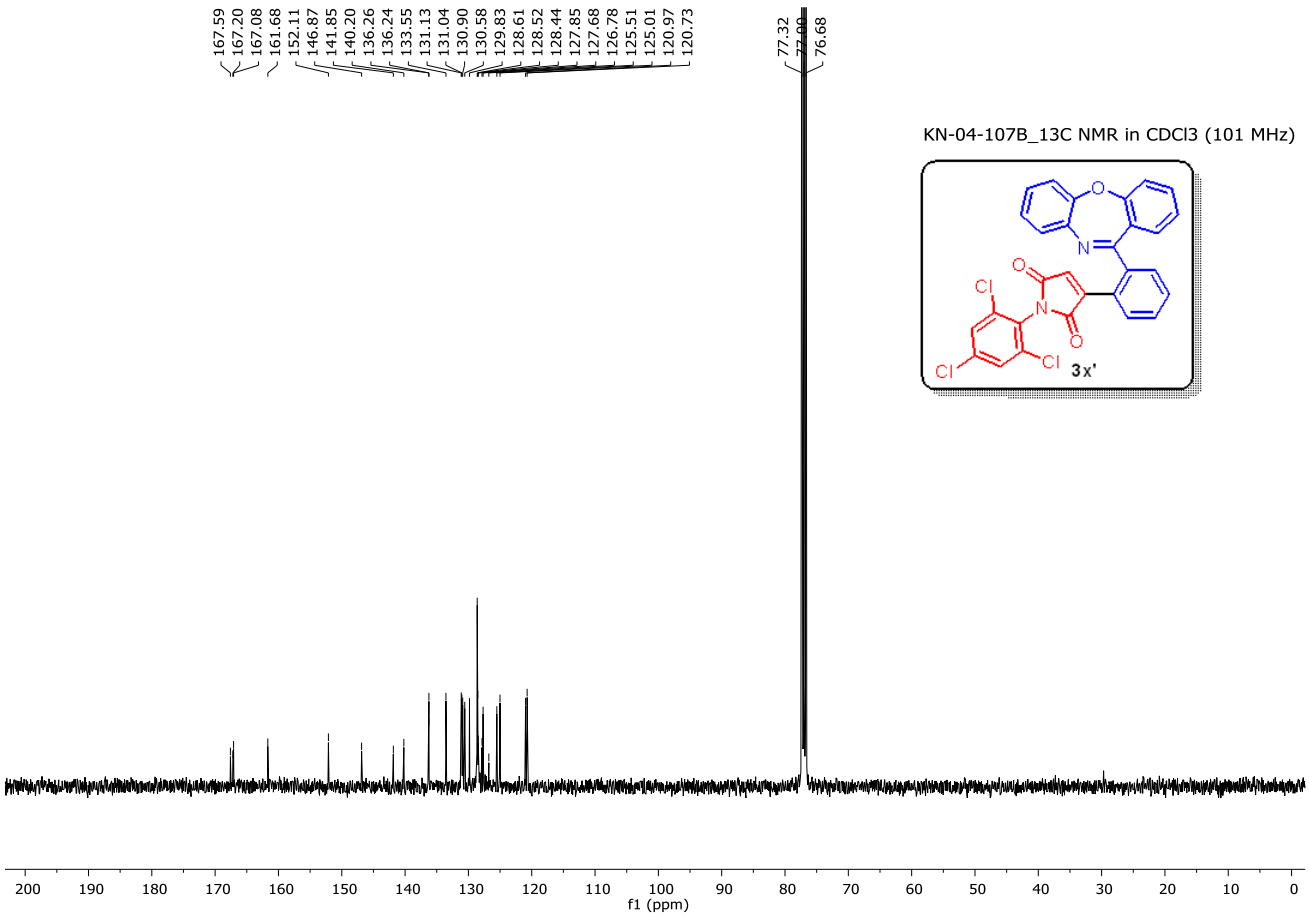


^{1}H and ^{13}C NMR spectra of representative alkenylated by-products

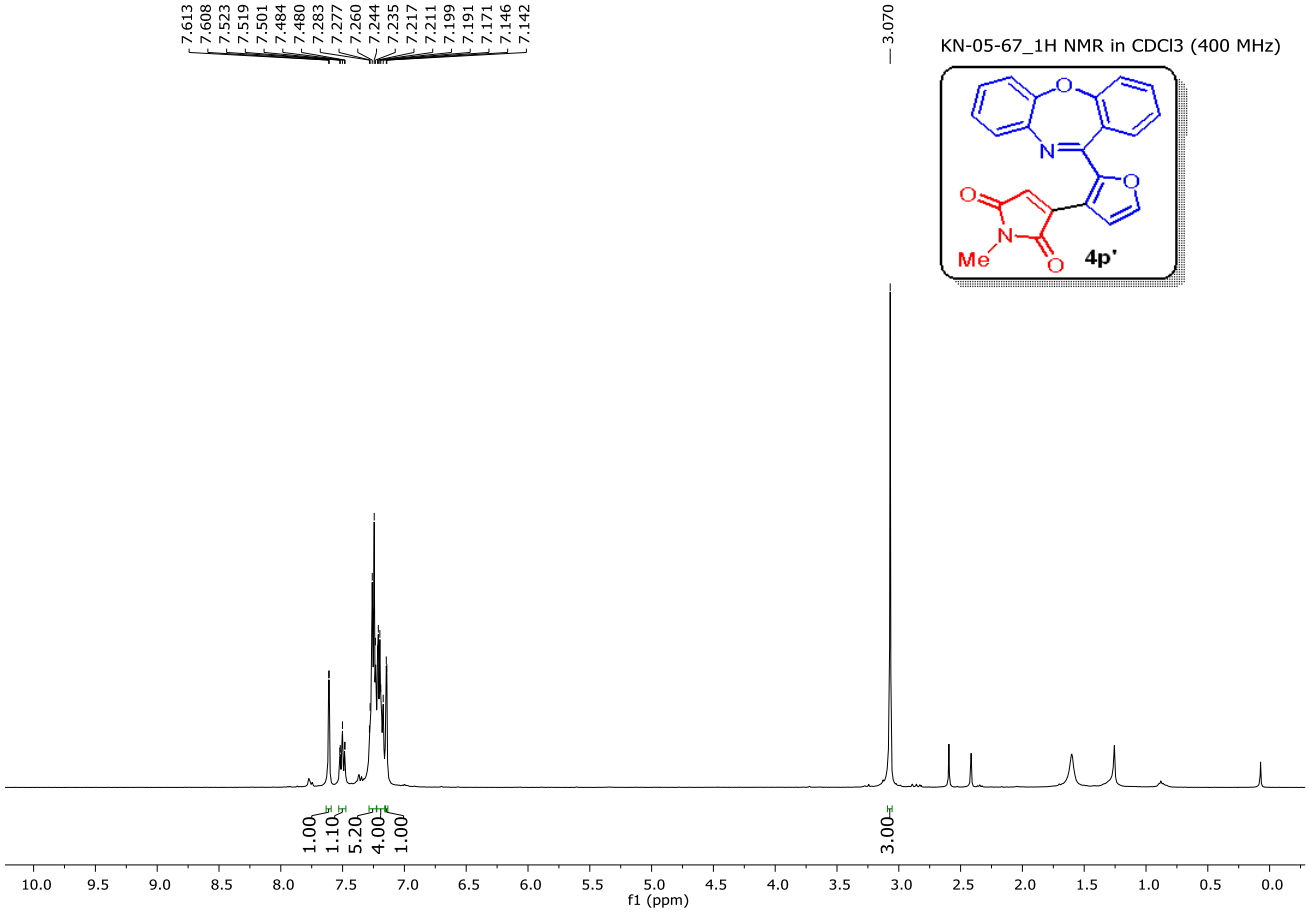
^{1}H NMR of 3x′ (400 MHz, $CDCl_3$):



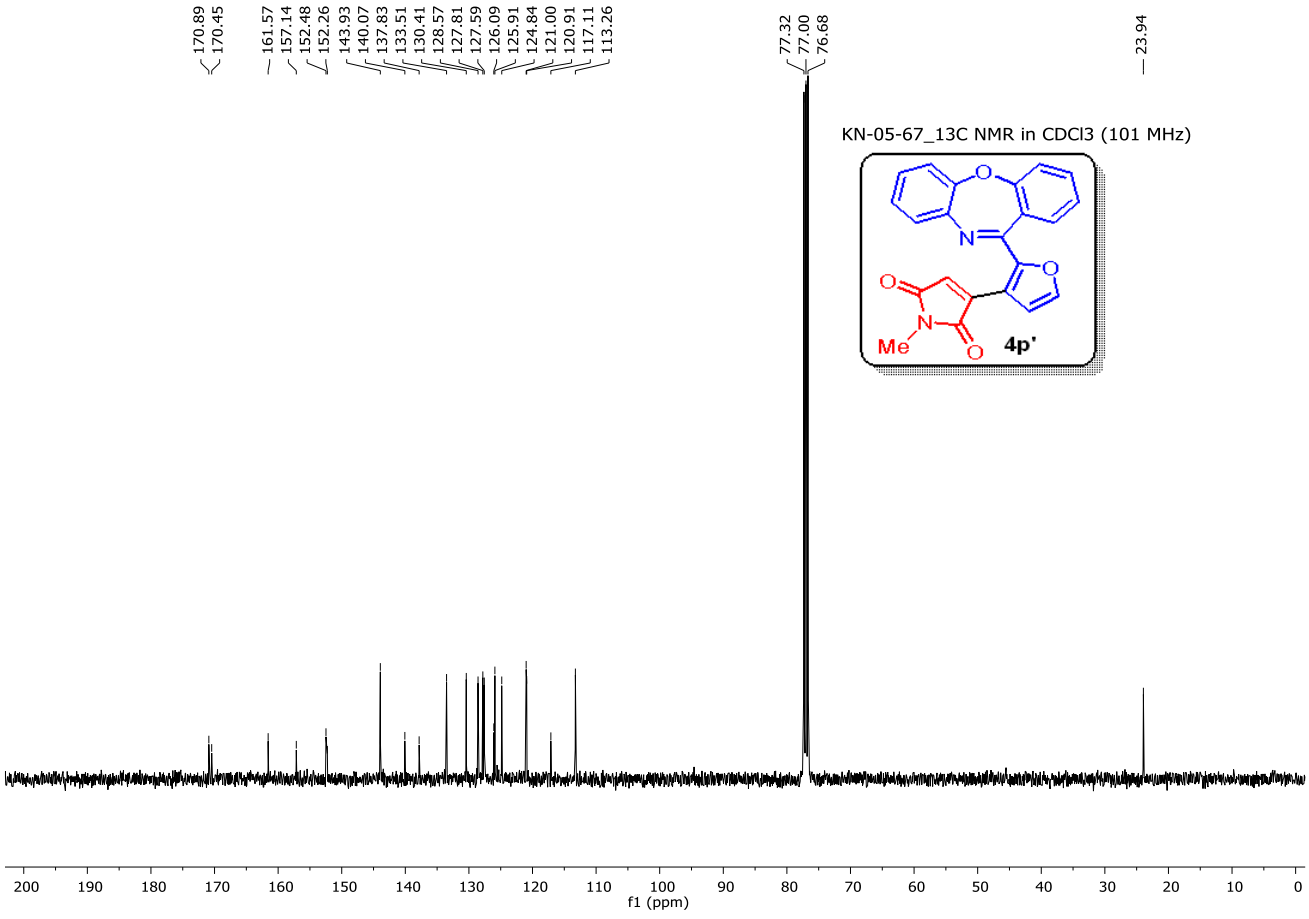
$^{13}C\{^{1}H\}$ NMR of 3x′ (101 MHz, $CDCl_3$):



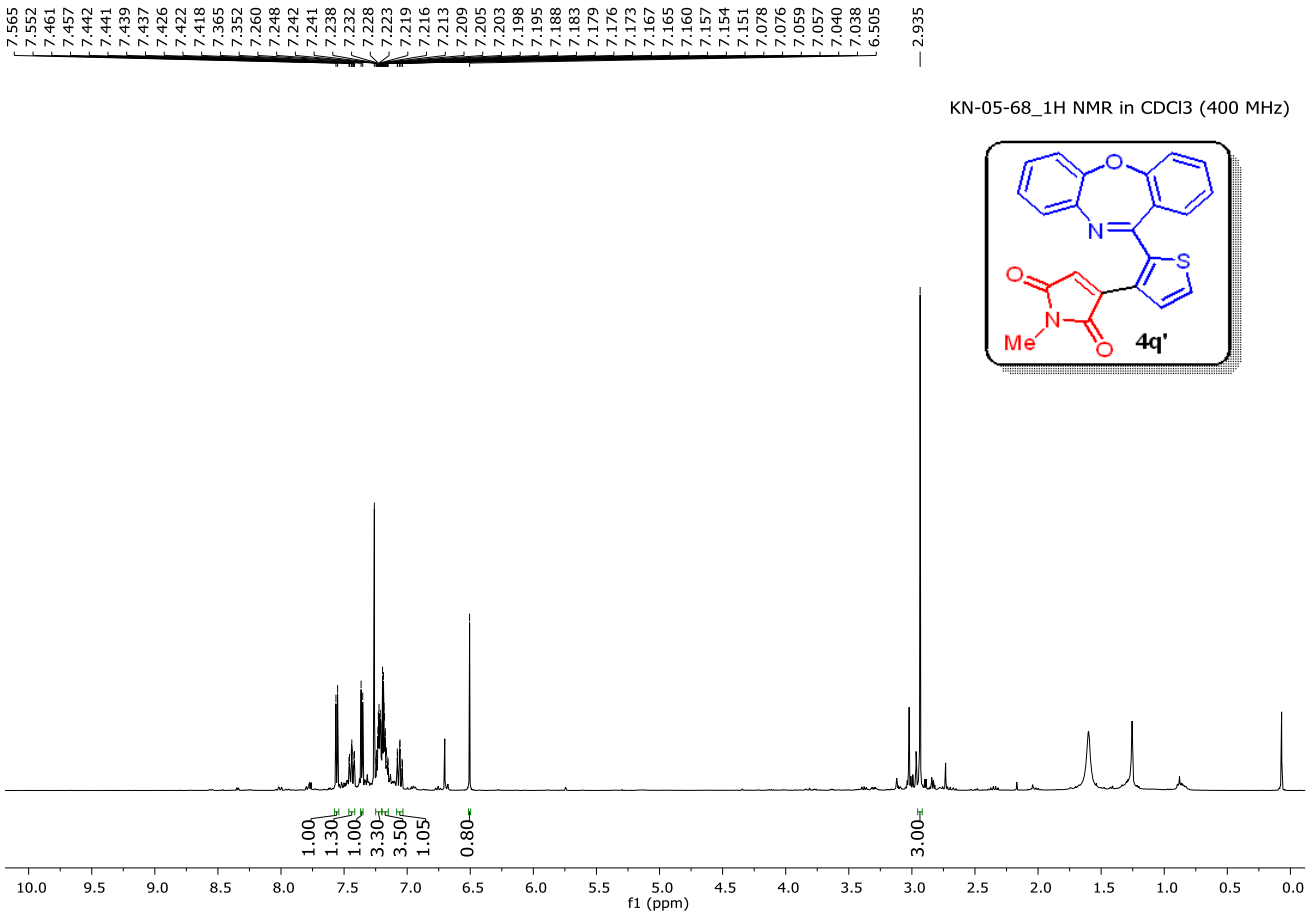
^{1}H NMR of 4p′ (400 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR of 4p′ (101 MHz, $CDCl_3$):



^{1}H NMR of 4q′ (400 MHz, $CDCl_3$):



^{13}C{^{1}H} NMR of 4q′ (101 MHz, $CDCl_3$):