

Supporting Information

Synthesis of Indene-fused Spiro-Dibenz(ox)azepines via Rh(III)-Catalyzed Cascade Regioselective C–H Activation/Annulation

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General Information:

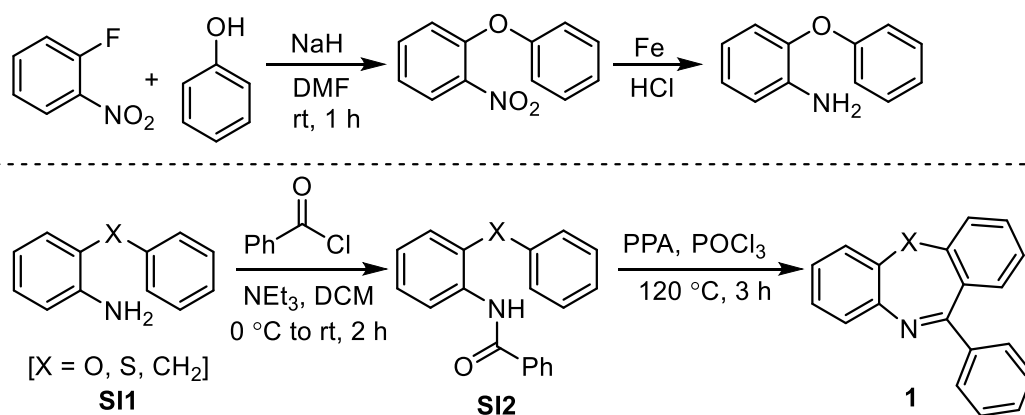
All reactions were carried out in oven-dried reaction vessels under air atmosphere unless otherwise mentioned. TLC analysis was performed on silica gel TLC plates. Column chromatography was done using 230–400 mesh silica gel by applying pressure through an air pump. ^1H and ^{13}C NMR spectra were recorded on 400 MHz spectrometer and are reported as chemical shifts (δ) 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. HRMS (m/z) was recorded using ESI (Q-Tof, positive ion) and Orbitrap (positive ion) mass spectrometry. Melting points were determined in a capillary melting point apparatus and are uncorrected. Single-crystal X-ray diffraction data were collected on Bruker D8 Venture with microfocus optics using Cu K α radiation. The CIF files were submitted to **CCDC (2226411-2226415 and 2242551)** and can be obtained at <https://summary.ccdc.cam.ac.uk/structure-summary-form>. Dibenzoxazepines¹ and alkynones² were prepared following literature methods. Single crystals of the spirocyclized compounds were obtained by taking 5-10 mg of the sample in 5 mL vials using a bi-solvent system applying the solvent diffusion technique. The choice of solvent systems and method for crystal growth for each compound (**3a**, **3o**, **3x**, **4o**, **4v**, **Rh-1b**) are provided in the characterization data section.

1. General Procedure for the Preparation of Staring Materials:

(a) Preparation of Directing Group:

The corresponding heterocyclic dibenzo-azepine were synthesized in 2 steps from the substituted anilines **SI1** by following a general literature procedure.^[1a-b]

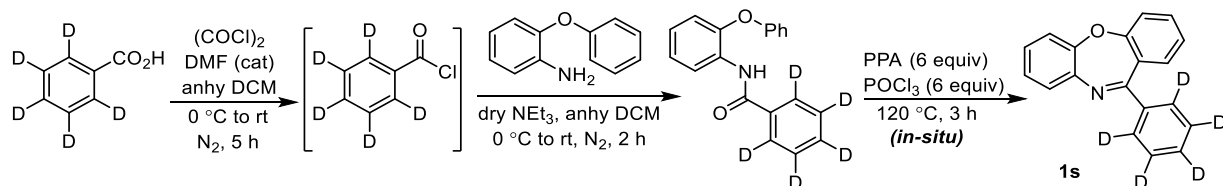
Schematic representation for the preparation of dibenzo-azepine:



Prepared or commercially available aniline derivatives **SI1** (1.0 equiv, 10.8 mmol) were dissolved in 30 mL of CH₂Cl₂ and cooled to 0 °C. The corresponding acetyl chloride (1.05 equiv) was added slowly to the solution followed by the addition of dry Et₃N (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 Na₂SO₄ and concentrated in vacuo. The residue was purified by column chromatography over SiO₂ using mixtures of EtOAc and petroleum ether (2% to 5% EtOAc/petroleum ether) to obtain the products **SI2**. In many cases, these derivatives were used in the synthetic protocol without any further purification. Thus, compounds **SI2** (1.0 equiv, 11.4 mmol) were added to a mixture of polyphosphoric acid (PPA) (6.0 equiv) and phosphorus oxychloride (POCl₃) (6.0 equiv). The reaction mixture was heated at 120 °C and the dense solution was stirred for 3 h. The reaction mixture was allowed to cool down to room temperature. CH₂Cl₂ was added to the original dense solution and the new solution was slowly poured into ice water. The aqueous solution was neutralized with an ammonia solution (30%), extracted with CH₂Cl₂ (30 mL). The organic solution was washed with brine (2 x 30 mL) and dried over anhydrous Na₂SO₄, concentrated under vacuum. The crude mixture was purified by column chromatography over SiO₂ eluting with mixtures of EtOAc and petroleum ether (1:19) to give the desired products.

(b) Preparation of Deuterated Dibenzoxazepine:

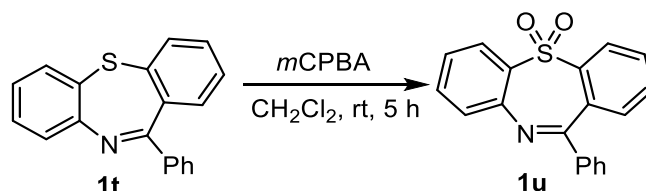
Schematic representation for the preparation of deuterated dibenzoxazepine:



A 25 mL two-necked round-bottom flask was charged with benzoic acid-2,3,4,5,6-*d*₅ (1.0 equiv, 3.93 mmol), dry DCM (8 mL) and catalytic amount of DMF (4 drops). The reaction mixture was cooled to 0 °C and stirred for 5 minutes under N₂. Then oxalyl chloride (1.2 equiv) was added dropwise to the reaction mixture and stirred at room temperature for 5 h. The resulting mixture was concentrated under reduced pressure to afford deuterated acid chloride quantitatively which was used directly without further purification for the next step. Swiftly the corresponding deuterated acid chloride was dissolved in dry DCM (10 mL) at 0 °C under N₂ and 2-phenoxy aniline (1.0 equiv, 3.56 mmol) was added into the solution followed by the addition of dry Et₃N (1.0 mL) and stirred at room temperature for 2 h. After checking TLC, the crude product was used directly without further purification for the final cyclization step in presence of PPA (6.0 equiv) and POCl₃ (6.0 equiv) at 120 °C for 3 h as mentioned above in details. Purification by column chromatography over SiO₂ eluting with mixtures of EtOAc and petroleum ether (1:19) afforded 11-(phenyl-*d*₅)dibenzo[*b,f*][1,4]oxazepine (**1s**, 951 mg, pale-yellow solid, yield = 86%).

¹H NMR (400 MHz, CDCl₃) δ 7.52-7.47 (m, 1H), 7.46-7.44 (m, 1H), 7.28 (app d, *J* = 8 Hz, 1H), 7.23-7.19 (comp, 4H), 7.17-7.13 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃) 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 C₁₉H₉D₅NO [M + H]⁺ 277.1389, found 277.1386.

(c) Oxidation of Benzothiazepine Directing Group:



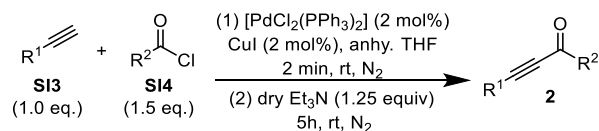
Following a literature procedure^[1b] 11-phenyldibenzo[*b,f*][1,4]thiazepine, **1t** (1.0 equiv, 1.0 mmol) was dissolved in CH₂Cl₂ (15 mL) and 3-chloroperbenzoic acid (55-75% wt.) (3.0 equiv) was added. After 5 hours stirring at room temperature the mixture was diluted with CH₂Cl₂ and washed with saturated aq. NaHCO₃ (3 x 30 mL). The organic phase was dried over Na₂SO₄, filtered and evaporated to dryness. Purification by column chromatography over SiO₂ eluting with mixtures

of EtOAc and petroleum ether (1:9) afforded 11-phenyldibenzo[*b,f*][1,4]thiazepine 5,5-dioxide (**1u**, 220 mg, yield = 69%).

(d) Preparation of Ynones as Coupling Partner:

The corresponding ynones was synthesized by following the general known literature.^[2]

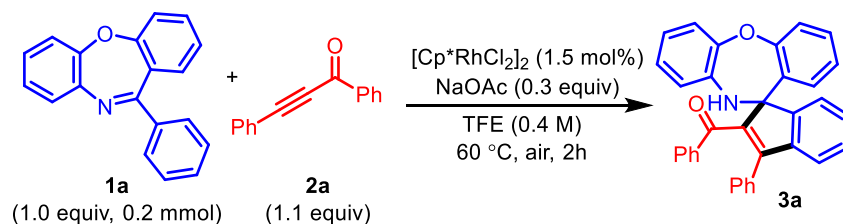
Schematic representation for the preparation of alkynone:



To a dry, 25 ml two-neck flask was added alkyne (1.0 equiv), acid chloride (1.5 equiv), PdCl₂(PPh₃)₂ (0.02 equiv) and CuI (0.02 equiv). The flask was filled with N₂ for three times by evacuating air. Then dry THF (5 mL) was added to the flask by syringe. After stirring at room temperature for 2 min, dry Et₃N (1.25 equiv) was added. The reaction mixture was stirred for 5 hours then diluted by EtOAc (3 x 30 mL) and washed with brine (3 x 30 mL). The organic layer was collected and dried over anhydrous Na₂SO₄, concentrated under vacuum and purified by column chromatography over SiO₂ with mixtures of EtOAc and petroleum ether (2% to 5% EtOAc/petroleum ether) to afford corresponding ynones.

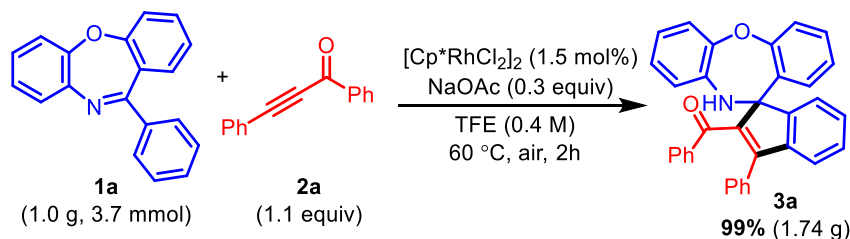
2. General Procedure for Spirocyclization:

(a) Mili-gram scale (0.2 mmol Scale):



In a dried 5 mL screw-capped reaction vial, 11-phenyldibenzo[*b,f*][1,4]oxazepane (**1a**) (54.3 mg, 0.2 mmol, 1.0 equiv), 1,3-diphenylprop-2-yn-1-one (**2a**) (45.4 mg, 0.22 mmol, 1.1 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (1.85 mg, 0.003 mmol, 0.015 equiv), and NaOAc (4.92 mg, 0.06 mmol, 0.3 equiv) were taken and 0.5 mL (0.4 M) of TFE was added. The vial was closed with a teflon-lined cap and kept on stirring in a preheated hot-plate at 60 °C. After 2 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite and concentrated under vacuo. The crude reaction mixture was directly purified by column chromatography on silica gel using pet ether/ethyl acetate (4:1) as eluent to obtain phenyl(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (**3a**) (95.5 mg, yield = 99%).

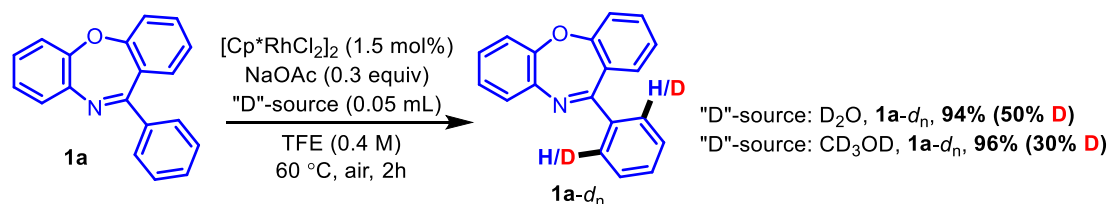
(b) Gram scale:



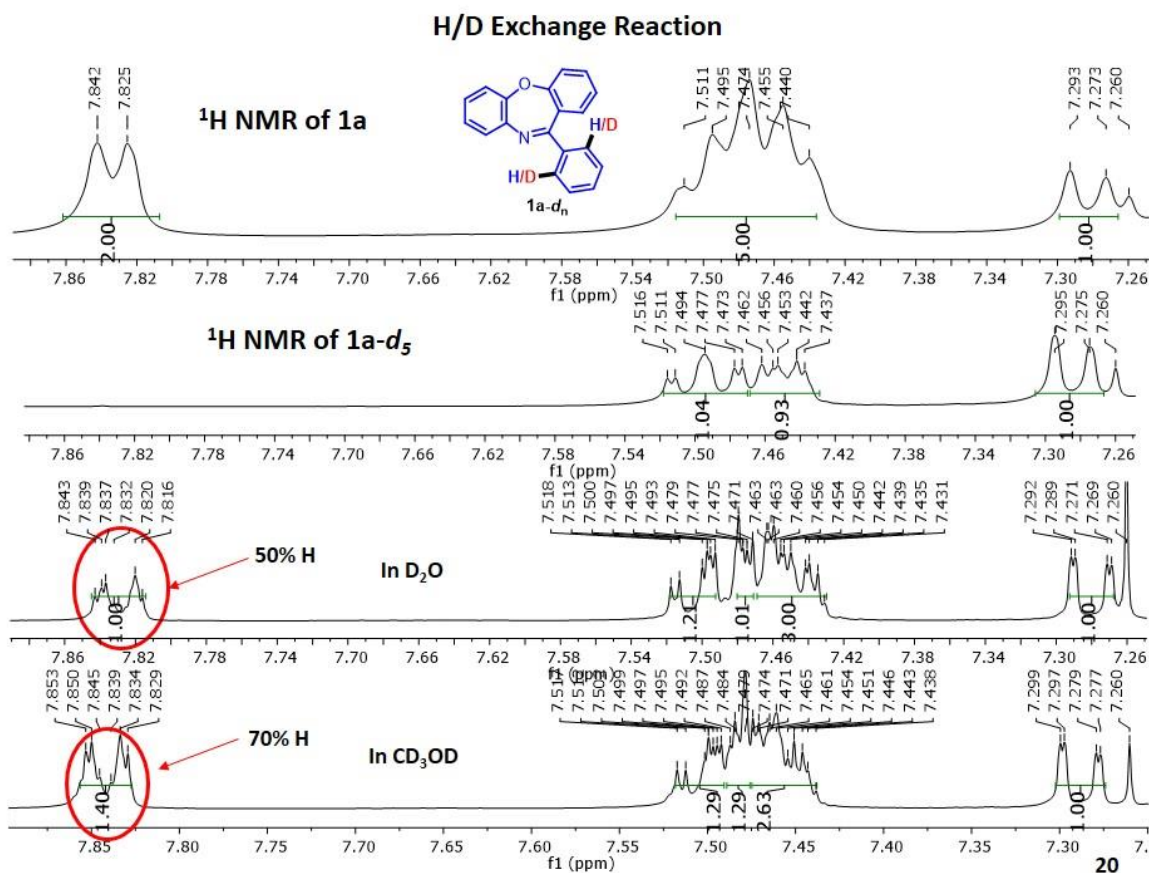
To a dried 25 mL round bottom flask, 11-phenyldibenzo[*b,f*][1,4]oxazepane (**1a**) (1.0 g, 3.7 mmol, 1.0 equiv), 1,3-diphenylprop-2-yn-1-one (**2a**) (836.3 mg, 4.1 mmol, 1.1 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (34.2 mg, 0.055 mmol, 0.015 equiv), and NaOAc (90.7 mg, 1.1 mmol, 0.3 equiv) were taken and 9.2 mL (0.4 M) of TFE was added. The mouth of the round bottom flask was closed with a glass stopper and kept on stirring in a preheated oil bath at 60 °C. After 2 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite and concentrated under vacuo. The crude reaction mixture was directly purified by column chromatography on silica gel using pet ether/ethyl acetate (4:1) as eluent to obtain phenyl(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (**3a**) (1.74 g, yield = 99%).

3. Mechanistic Experiments:

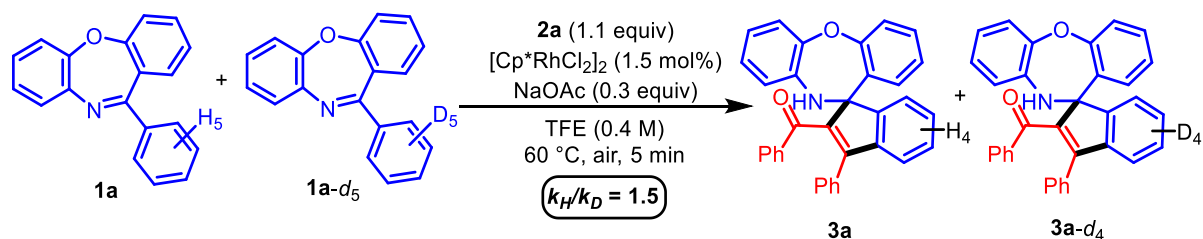
(a) Procedure for H/D Exchange Experiment:



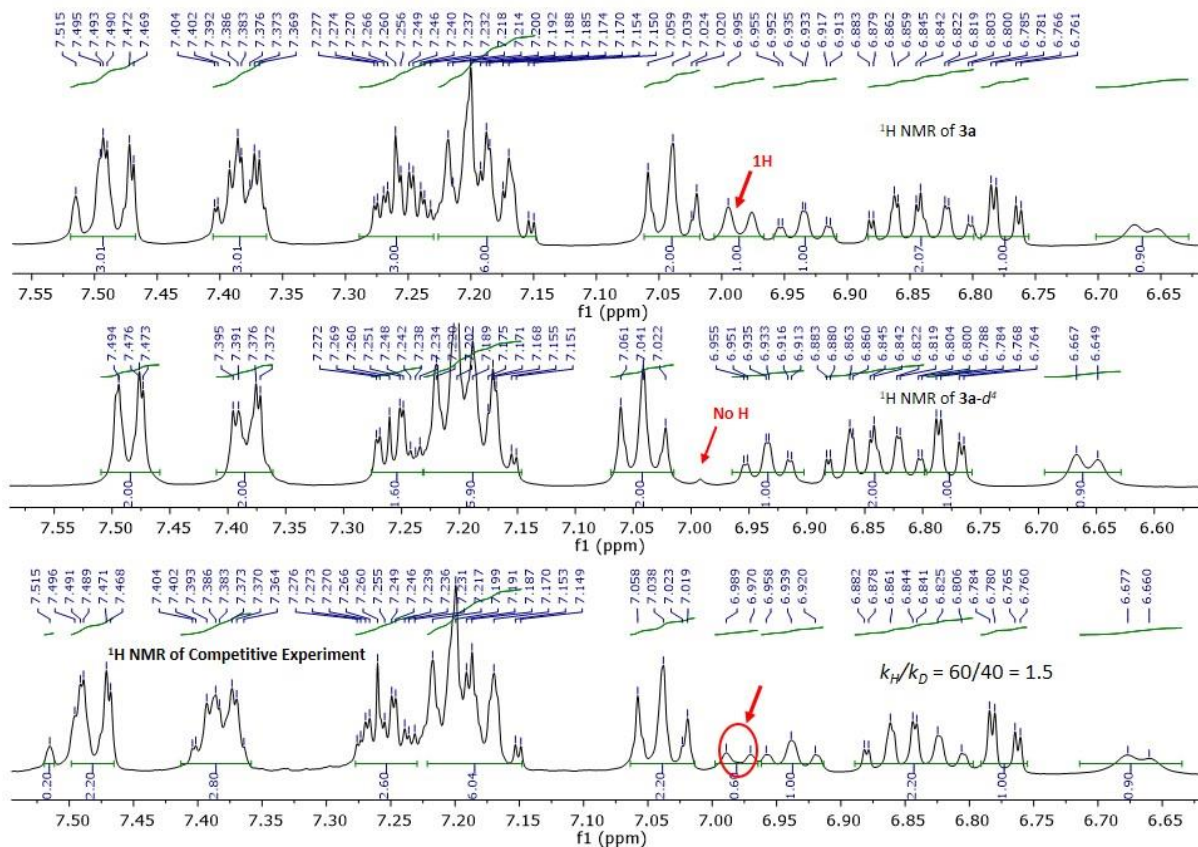
A dried 5 mL screw-capped reaction vial was charged with 11-phenyldibenzo[*b,f*][1,4]oxazepane (**1a**) (54.3 mg, 0.2 mmol, 1.0 equiv), [Cp*RhCl₂]₂ (1.85 mg, 0.003 mmol, 0.015 equiv), and NaOAc (4.92 mg, 0.06 mmol, 0.3 equiv) were taken and 0.5 mL (0.4 M) of TFE was added. To it, 0.05 mL (3.0 mmol, 15.0 equiv) of D₂O or 0.05 mL of CD₃OD as D-source (excess) was added. The vial was closed with a teflon-lined cap and stirred in a preheated hot-plate. After 2 h, the reactions were stopped and cooled to room temperature. The reaction mixture were filtered through a short pad of celite and concentrated under vacuo. The starting material (**1a-d_n**) was recovered by purifying through column chromatography on silica gel using pet ether/ethyl acetate (19:1) as eluent. The deuterium incorporation was determined by ¹H NMR spectroscopy.



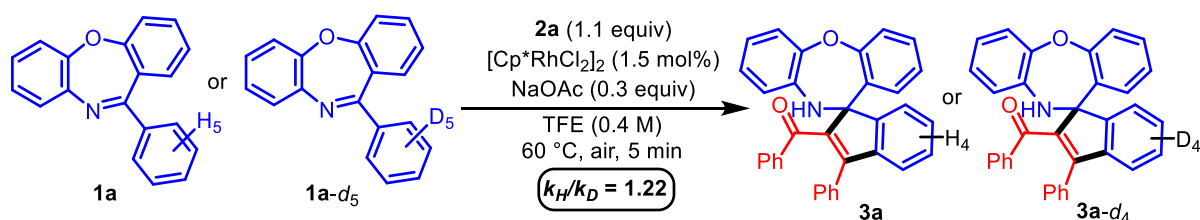
(b) Procedure for Competitive Experiments between Dibenzoxazepines and alkyne:



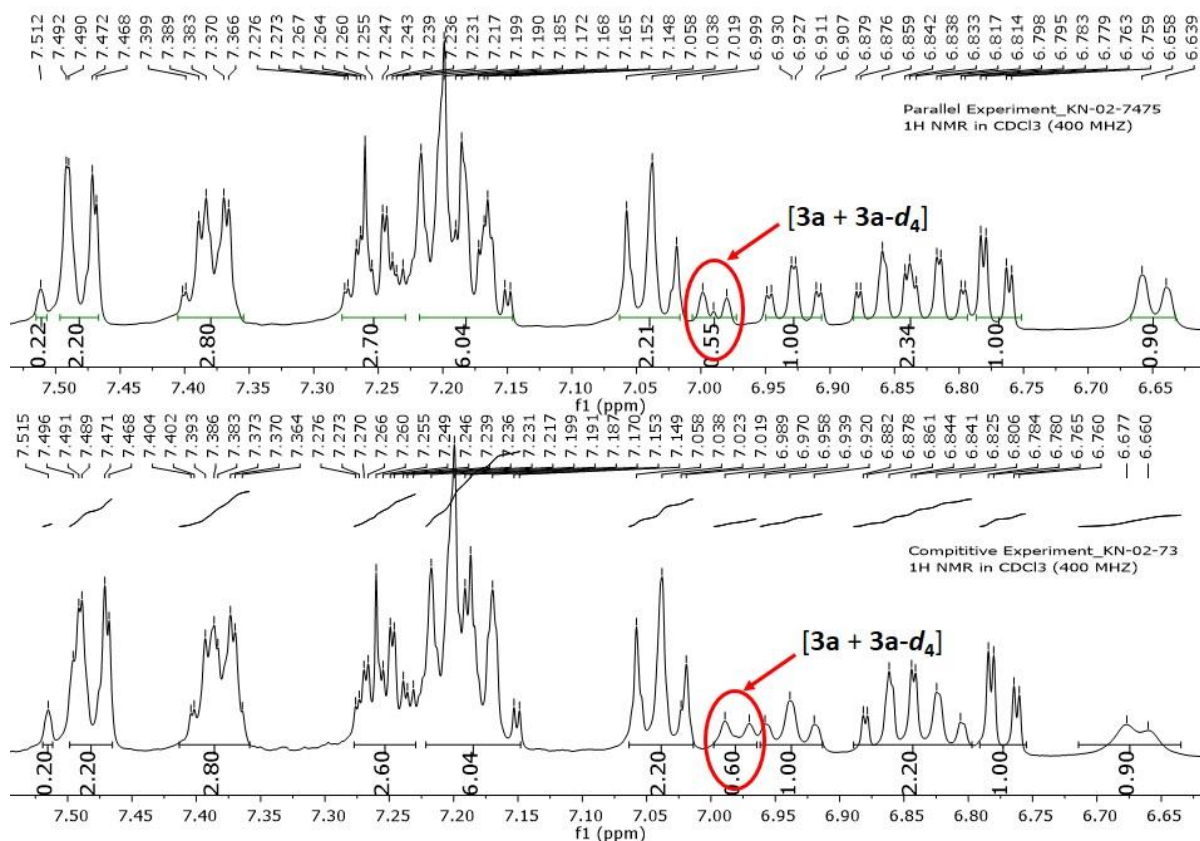
Competitive Experiment between 11-phenyldibenzo[*b,f*][1,4]oxazepane (**1a**) and 11-(phenyl-*d*₅)dibenzo[*b,f*][1,4]oxazepane (**1a-d₅**). In a dried 5 mL screw-capped reaction vial, 11-phenyldibenzo[*b,f*][1,4]oxazepane (**1a**) (27.1 mg, 0.1 mmol, 1.0 equiv), 11-(phenyl-*d*₅)dibenzo[*b,f*][1,4]oxazepane (**1a-d₅**) (27.6 mg, 0.1 mmol, 1.0 equiv), 1,3-diphenylprop-2-yn-1-one (**2a**) (45.4 mg, 0.22 mmol, 1.1 equiv), [Cp**RhCl*₂]₂ (1.85 mg, 0.003 mmol, 0.015 equiv), and NaOAc (4.92 mg, 0.06 mmol, 0.3 equiv) were taken and 0.5 mL (0.4 M) of TFE was added. The vial was closed with a teflon-lined cap and stirred in a preheated hot-plate. After 5 min, the reaction was quickly quenched by adding ethyl acetate keeping in an ice bath. The reaction mixture was filtered through a short pad of celite and concentrated under vacuo. The crude reaction mixture was directly purified by column chromatography on silica gel using petroleum ether/ethyl acetate (19:1 then 9:1) as eluent. The ratio of **3a** and **3a-d₄** was determined by ¹H NMR spectroscopy. No primary kinetic isotopic effect was found as $k_H/k_D \approx 0.60/0.40 \approx 1.5$.



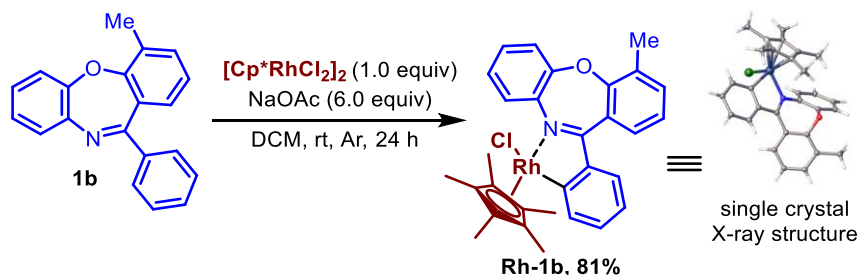
(c) Procedure for parallel experiment between **1a and **1a-d₅**:**



Two separate dried 5 mL screw-capped reaction vial were charged with **1a** (27.1 mg, 0.1 mmol) and **1a-d₅** (27.6 mg, 0.1 mmol). 1,3-diphenylprop-2-yn-1-one (**2a**) (45.4 mg, 0.22 mmol, 1.1 equiv), [Cp**RhCl*₂]₂ (1.85 mg, 0.003 mmol, 0.015 equiv), and NaOAc (4.92 mg, 0.06 mmol, 0.3 equiv) were taken and 0.5 mL (0.4 M) of TFE was added. The vial was closed with a teflon-lined cap and stirred in a preheated hot-plate. After 5 min, the reaction was quickly quenched by adding ethyl acetate keeping in an ice bath. The reaction mixture was filtered through a short pad of celite, both the reaction mixtures were combined and concentrated under vacuo. The crude reaction mixture was directly purified by column chromatography on silica gel using petroleum ether/ethyl acetate (19:1 then 9:1) as eluent. The ratio of **3a** and **3a-d₄** was determined by ¹H NMR spectroscopy. No primary kinetic isotopic effect was found as $k_H/k_D \approx 0.55/0.45 \approx 1.22$.



(d) General Procedure for the Preparation of the Rhodacycle Complexes:

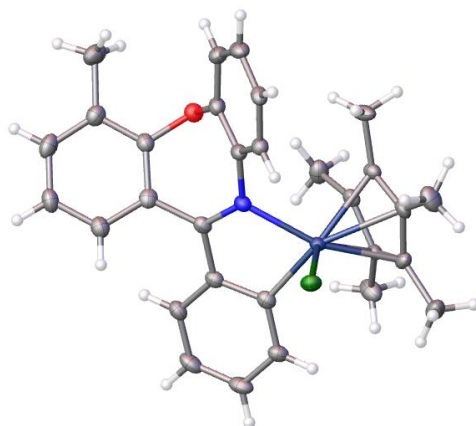


Following an analogous literature procedure,^[3] a mixture of $[\text{Cp}^*\text{RhCl}_2]_2$ (25.0 mg, 0.04 mmol, 1 equiv), 4-methyl-11-phenyldibenzo[*b,f*][1,4]oxazepine (**1b**) (25.1 mg, 0.088 mmol, 2.2 equiv), and NaOAc (20.0 mg, 0.24 mmol, 6.0 equiv) in 10.0 mL of dry DCM was allowed to stir under argon atmosphere at room temperature (approximately 28 °C) overnight. After completion of the reaction, the reaction mixture was passed through a short pad of celite and concentrated under vacuo, followed by washing with hexane and finally vacuum-dried to give the cyclometalated compound **Rh-1b** as a reddish-brown solid (36.1 mg, 81% yield).

Yield 81% (36.1 mg); Reddish-brown solid; **mp**: 256-258 °C (decomp.) (Crystallization from CHCl_3 and hexane using solvent diffusion method); **¹H NMR** (400 MHz, CDCl_3) δ 8.62-8.59 (m, 1H), 7.90 (app dd, $J = 7.7, 1.0$ Hz, 1H),

7.46 (app dd, $J = 7.8, 1.3$ Hz, 1H), 7.41-7.39 (m, 1H), 7.35-7.33 (m, 1H), 7.29-7.27 (m, 1H), 7.24-7.19 (comp, 3H), 7.15-7.11 (m, 1H), 7.04-6.99 (m, 1H), 2.54 (s, 3H), 1.38 (s, 15H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 142.6, 140.6, 136.8, 134.0, 133.2, 131.1, 130.7, 130.1, 129.7, 128.2, 127.8, 127.4, 126.2, 124.1, 122.0, 121.6, 121.5, 119.7, 97.0, 97.0, 16.2, 8.8; HRMS (ESI, m/z) calcd for $\text{C}_{30}\text{H}_{29}\text{NORh}$ $[\text{M} - \text{Cl}]^+$ 522.1304, found 522.1304.

Figure S1. X-ray crystal structure of **Rh-1b** (ellipsoid contour at 50% probability level)

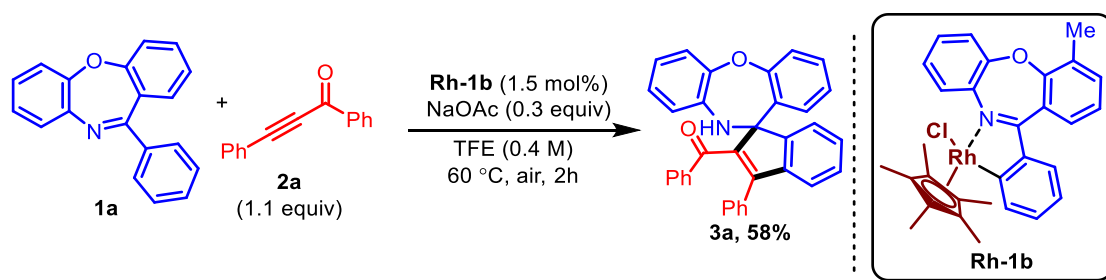


Crystal data and structure refinement for Rh-1b, CCDC No. 2226413

Empirical formula	$\text{C}_{30}\text{H}_{29}\text{ClNORh}$
Formula weight	557.90
Temperature/K	100.0
Crystal system	orthorhombic
Space group	Pbca
$a/\text{\AA}$	15.3583(10)
$b/\text{\AA}$	13.3106(9)
$c/\text{\AA}$	23.5375(16)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	4811.7(6)
Z	8
$\rho_{\text{calc}}/\text{g/cm}^3$	1.540
μ/mm^{-1}	6.939
F(000)	2288.0
Crystal size/ mm^3	$0.2 \times 0.2 \times 0.1$
Radiation	Cu $\text{K}\alpha$ ($\lambda = 1.54178$)
2Θ range for data collection/ $^\circ$	7.512 to 132.792

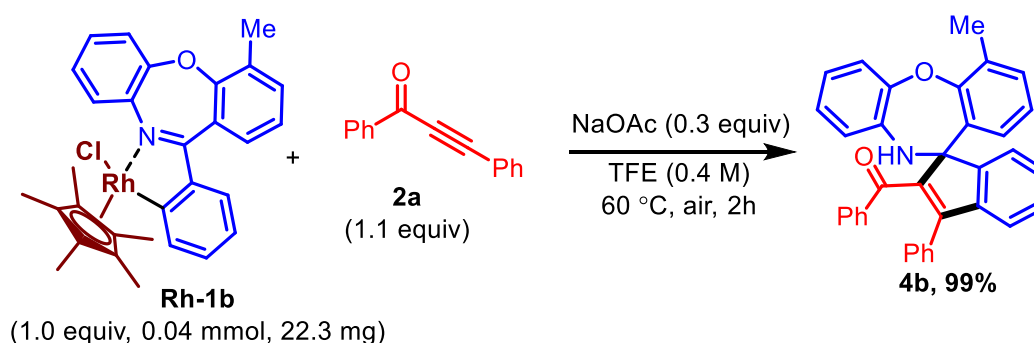
Index ranges	$-18 \leq h \leq 18, -15 \leq k \leq 15, -27 \leq l \leq 27$
Reflections collected	86084
Independent reflections	4211 [$R_{\text{int}} = 0.0890, R_{\text{sigma}} = 0.0310$]
Data/restraints/parameters	4211/0/314
Goodness-of-fit on F^2	1.133
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0421, wR_2 = 0.1006$
Final R indexes [all data]	$R_1 = 0.0432, wR_2 = 0.1014$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.73/-0.88

(e) Procedure for the Treatment of the Rhodacycle Complex Rh-1b as Catalyst:



In a dried 5 mL screw-capped reaction vial, 11-phenyldibenzo[*b,f*][1,4]oxazepane (**1a**) (54.3 mg, 0.2 mmol, 1.0 equiv), 1,3-diphenylprop-2-yn-1-one (**2a**) (45.4 mg, 0.22 mmol, 1.1 equiv), Catalyst (**Rh-1b**) (1.67 mg, 0.003 mmol, 0.015 equiv), and NaOAc (4.92 mg, 0.06 mmol, 0.3 equiv) were taken and 0.5 mL (0.4 M) of TFE was added. The vial was closed with a screw cap and kept on stirring in a preheated hot-plate at 60 °C. After 2 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite and concentrated under vacuo. The crude reaction mixture was directly purified by column chromatography on silica gel using pet ether/ethyl acetate (4:1) as eluent to obtain phenyl(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (**3a**) (56 mg, yield = 58%).

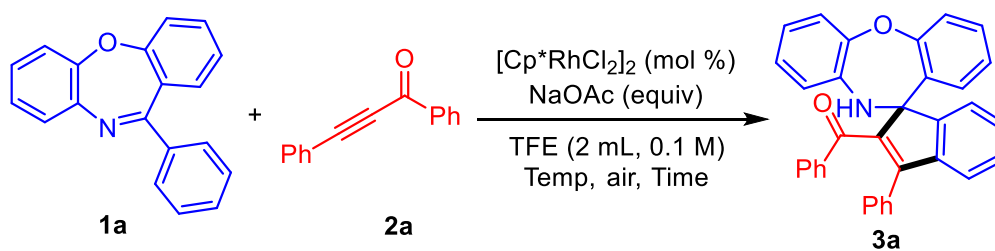
(f) Procedure for the Treatment of the Rhodacycle Complex Rh-1b as Substrate:



In a dried 5 mL screw-capped reaction vial, Catalyst (**Rh-1b**) (22.3 mg, 0.04 mmol, 1.0 equiv), 1,3-diphenylprop-2-yn-1-one (**2a**) (9.1 mg, 0.044 mmol, 1.1 equiv) and NaOAc (0.98 mg, 0.012 mmol, 0.3 equiv) were taken and 0.1 mL (0.4 M) of TFE was added. The vial was closed with a screw cap and kept on stirring in a preheated hot-plate at 60 °C. After 2 h, the reaction was stopped and cooled to room temperature. The reaction mixture was filtered through a short pad of celite and concentrated under vacuo. The crude reaction mixture was directly purified by column chromatography on silica gel using pet ether/ethyl acetate (9:1) as eluent to obtain (4-methyl-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (**4b**) (19.5 mg, yield = 99%).

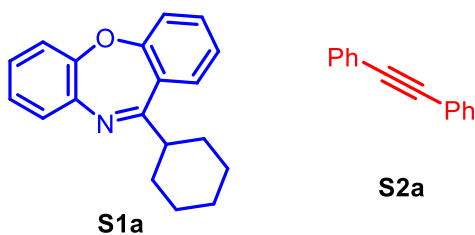
References:

1. (a) Zhang *et al.*, *Chem. Commun.*, 2011, **47**, 7845–7847; (b) Vidal-Ferran *et al.*, *Chem. Eur. J.*, 2016, **22**, 10607–10613.
2. Sun *et al.*, *Org. Biomol. Chem.*, 2020, **18**, 1073–1077.
3. Xiao *et al.*, *Chem. Commun.*, 2018, **54**, 11805-11808.

Table S1. Additional Optimization of Reaction Conditions^a

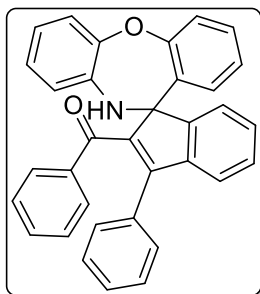
Entry	$[\text{Cp}^*\text{RhCl}_2]_2$ (mol %)	NaOAc (equiv)	Temp (°C)	Time (h)	Yield (%) of 3a ^b
1	1	1.0	60	2	92
2	3	1.0	60	2	99
3	1.5	0.15	60	2	94
4	1.5	0.5	60	2	99
5 ^c	5	1.0	60	2	99
6 ^c	5	1.0	40	2	97
7 ^c	5	1.0	60	1	92
8 ^d	1.5	0.3	60	2	99

^aReaction conditions: **1a** (1.0 equiv, 0.2 mmol), **2a** (1.1 equiv), $[\text{Cp}^*\text{RhCl}_2]_2$ (mol %), NaOAc (equiv), 2.0 mL TFE (0.1 M), under air. ^bIsolated yield. ^cunder N_2 . ^d1.0 mL TFE (0.1 M). TFE = 2,2,2-trifluoroethanol.

Table S2. Unsuccessful Substrate and Coupling Partner

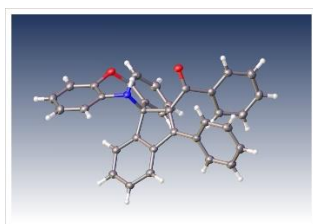
Characterization of Spirocyclized Products:

phenyl(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (**3a**):



Yield 99% (95.5 mg); Yellow solid; **R_f** 0.38 (pet ether/ethyl acetate = 9:1); **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 80-82 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.52-7.50 (comp, 2H), 7.48-7.47 (m, 1H), 7.40-7.36 (comp, 3H), 7.28-7.24 (comp, 2H), 7.23-7.17 (comp, 5H), 7.16 (comp, 2H), 7.07-7.02 (comp, 2H), 7.00 (app d, *J* = 7.4 Hz, 1H), 6.96-6.91 (m, 1H), 6.86 (m, 1H), 6.84-6.77 (comp, 2H), 6.67-6.65 (m, 1H), 4.50 (br s, 1 N-H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 194.8, 156.4, 152.1, 152.0, 147.3, 146.6, 141.0, 138.1, 137.5, 132.9, 132.0, 129.1, 129.0, 128.8, 128.7, 128.6, 128.5, 128.5, 128.3, 127.6, 127.4, 124.6, 124.4, 123.8, 123.7, 123.4, 122.9, 122.0, 120.9, 76.0; **HRMS** (ESI, *m/z*) calcd for C₃₄H₂₄NO₂ [M + H]⁺ 478.1807, found 478.1807.

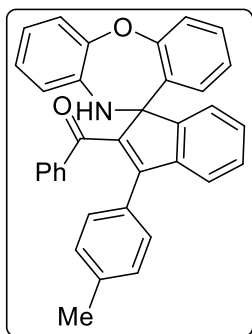
Figure S2. X-ray crystal structure of **3a** (ellipsoid contour at 50% probability level)



Crystal data and structure refinement for **3a**, CCDC No. 2242551

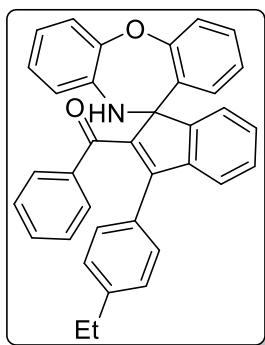
Identification code	KN_01_133	$\rho_{\text{calc}}/\text{cm}^3$	1.306
Empirical formula	C ₃₄ H ₂₃ NO ₂	μ/mm^{-1}	0.634
Formula weight	477.53	F(000)	500.0
Temperature/K	100.00	Crystal size/mm ³	0.35 × 0.2 × 0.02
Crystal system	Triclinic	Radiation	CuK α (λ = 1.54178)
Space group	P-1	2 θ range for data collection/°	7.382 to 130.13
<i>a</i> /Å	8.8451(2)	Index ranges	-10 ≤ <i>h</i> ≤ 10, -14 ≤ <i>k</i> ≤ 14, -15 ≤ <i>l</i> ≤ 15
<i>b</i> /Å	11.9809(3)	Reflections collected	47267
<i>c</i> /Å	13.3608(3)	Independent reflections	4121 [R _{int} = 0.0728, R _{sigma} = 0.0348]
α /°	65.2590(10)	Data/restraints/parameters	4121/0/335
β /°	74.7890(10)	Goodness-of-fit on F ²	1.057
γ /°	73.1520(10)	Final R indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	R ₁ = 0.0508, wR ₂ = 0.1333
Volume/Å ³	1214.40(5)	Final R indexes [all data]	R ₁ = 0.0529, wR ₂ = 0.1354
Z	2	Largest diff. peak/hole / e Å ⁻³	0.72/-0.76

phenyl(3'-(*p*-tolyl)-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3b):



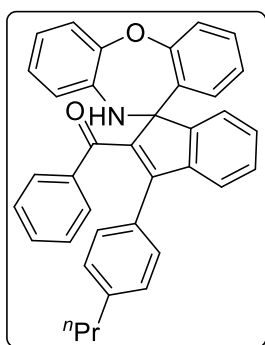
Yield 97% (95.4 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 196-198 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.51 (comp, 2H), 7.48-7.47 (m, 1H), 7.38 (app td, *J* = 7.6, 0.9 Hz, 1H), 7.28-7.26 (comp, 3H), 7.24 (app dd, *J* = 2.9, 1.1 Hz, 1H), 7.22-7.19 (m, 1H), 7.18-7.14 (comp, 2H), 7.07-7.01 (m, 4H), 6.98-6.91(comp, 2H), 6.87-6.79 (comp, 2H), 6.77 (app dd, *J* = 7.9, 1.6 Hz, 1H), 6.64 (app d, *J* = 6.7 Hz, 1H), 4.42 (br s, 1 N-H), 2.25 (s, 3H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 195.0, 156.4, 152.1, 141.2, 138.7, 137.6, 131.9, 129.9, 129.1 (x 2), 129.0 (x 2), 129.0 (x 2), 128.8, 128.6, 128.5, 128.4, 127.6 (x 2), 127.5, 124.6, 124.4, 123.8, 123.7, 123.4, 122.9, 122.0, 120.9, 75.9, 21.2; **HRMS** (ESI, *m/z*) calcd for C₃₅H₂₆NO₂ [M + H]⁺ 492.1964, found 492.1964.

(3'-(4-ethylphenyl)-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (3c):



Yield 96% (96.7 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 168-170 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.53 (app d, *J* = 7.5 Hz, 1H), 7.48-7.46 (comp, 2H), 7.38 (app td, *J* = 7.5, 1.1 Hz, 1H), 7.30-7.26 (comp, 2H), 7.25-7.24 (m, 1H), 7.22-7.14 (comp, 3H), 7.05-7.01 (comp, 4H), 6.97-6.92 (comp, 2H), 6.87-6.84 (m, 1H), 6.84-6.80 (m, 1H), 6.77 (app dd, *J* = 7.9, 1.7 Hz, 1H), 6.65 (app d, *J* = 7.3 Hz, 1H), 4.45 (br s, 1 N-H), 2.54 (q, *J* = 7.6 Hz, 3H), 1.13 (t, *J* = 7.6 Hz, 2H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 194.9, 156.3, 152.3, 152.0, 152.0, 147.2, 146.8, 145.0, 141.2, 138.1, 137.6, 131.8, 130.1, 129.1, 129.1, 128.8, 128.6, 128.5, 128.4, 127.8, 127.5, 124.6, 124.4, 124.0, 123.8, 123.4, 123.0, 122.0, 120.8, 75.8, 28.6, 15.3; **HRMS** (ESI, *m/z*) calcd for C₃₆H₂₈NO₂ [M + H]⁺ 506.2120, found 506.2125.

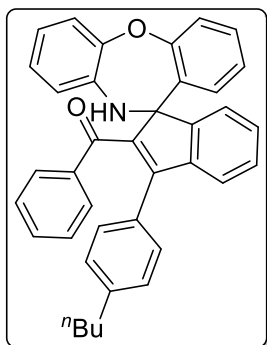
phenyl(3'-(4-propylphenyl)-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3d):



Yield 96% (99.6 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 160-162 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.54 (app d, *J* = 7.5 Hz, 1H), 7.48-7.45 (comp, 2H), 7.38 (app td, *J* = 7.5, 1.0 Hz, 1H), 7.29-7.26 (comp, 3H), 7.23 (app dd, *J* = 7.5, 1.0 Hz, 1H), 7.20-7.14 (comp, 3H), 7.04-6.99 (comp, 4H), 6.97-6.92 (comp, 2H), 6.87-6.81 (comp, 2H), 6.77 (app dd, *J* = 7.9, 1.7 Hz, 1H), 6.66 (app d, *J* = 7.5 Hz, 1H), 4.47 (br s, 1 N-H), 2.48

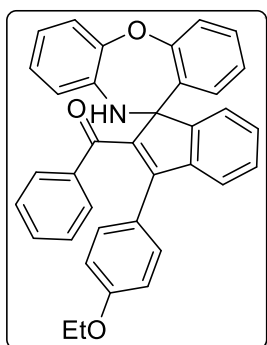
(t, $J = 7.5$ Hz, 2H), 1.53 (m, 2H), 0.82 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.9, 156.3, 152.4, 152.0, 147.5, 146.6, 143.4, 141.1, 138.1, 137.7, 131.7, 130.2, 129.1 (x 2), 129.0, 128.8, 128.5, 128.5, 128.4 (x 2), 127.4, 124.6, 124.4, 124.2, 123.9, 123.4, 123.0, 122.0, 120.8, 75.8, 37.6, 24.2, 13.5; HRMS (ESI, m/z) calcd for $\text{C}_{37}\text{H}_{30}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 520.2277, found 520.2281.

(3'-(4-butylphenyl)-10H-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (3e):



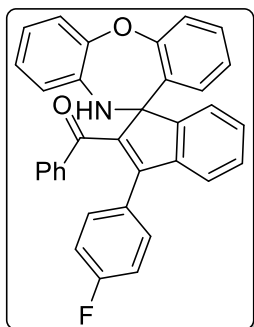
Yield 98% (104.0 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 122-124 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (app d, $J = 7.6$ Hz, 1H), 7.47-7.44 (comp, 2H), 7.38 (app td, $J = 7.6, 1.0$ Hz, 1H), 7.27-7.26 (comp, 3H), 7.24-7.14 (comp, 4H), 7.04-6.99 (comp, 4H), 6.97-6.93 (comp, 2H), 6.87-6.81 (comp, 2H), 6.76 (app dd, $J = 7.9, 1.7$ Hz, 1H), 6.69 (app s, 1H), 4.48 (br s, 1 N-H), 2.50 (t, $J = 7.5$ Hz, 2H), 1.52-1.44 (m, 2H), 1.26-1.16 (m, 2H), 0.89 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.9, 156.3, 152.5, 152.0, 151.9, 143.7, 141.2, 141.0, 138.0, 137.7, 131.7, 130.1, 129.1 (x 2), 129.0, 128.8, 128.6, 128.5, 128.4, 127.4, 124.6, 124.5, 124.2, 124.0, 124.0, 123.4, 123.1, 122.0, 120.8, 75.8, 35.3, 33.2, 22.0, 13.9; HRMS (ESI, m/z) calcd for $\text{C}_{38}\text{H}_{32}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 534.2433, found 534.2412.

(3'-(4-ethoxyphenyl)-10H-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (3f):



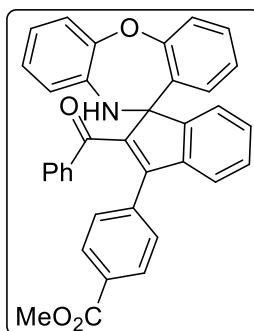
Yield 93% (97.0 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 192-194 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (app d, $J = 7.5$ Hz, 1H), 7.50-7.47 (comp, 2H), 7.38 (app td, $J = 7.5, 1.0$ Hz, 1H), 7.31-7.28 (comp, 2H), 7.27-7.22 (comp, 2H), 7.20-7.13 (comp, 2H), 7.07-7.04 (comp, 2H), 6.96-6.92 (comp, 2H), 6.86-6.81 (comp, 2H), 6.77-6.70 (comp, 3H), 6.64 (app d, $J = 7.5$ Hz, 1H), 4.44 (br s, 1 N-H), 3.94 (q, $J = 7.0$ Hz, 2H), 1.36 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.0, 159.3, 156.3, 152.4, 141.2, 137.6, 131.9, 130.5 (x 2), 129.1 (x 2), 128.8, 128.6, 128.5, 128.4, 127.6 (x 2), 127.5, 125.0, 123.9 (x 2), 124.6, 124.5, 124.1, 123.4, 123.0, 122.0, 120.8, 114.4, 75.8, 63.4, 14.7; HRMS (ESI, m/z) calcd for $\text{C}_{36}\text{H}_{28}\text{NO}_3$ $[\text{M} + \text{H}]^+$ 522.2069, found 522.2087.

(3'-(4-fluorophenyl)-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (3g):



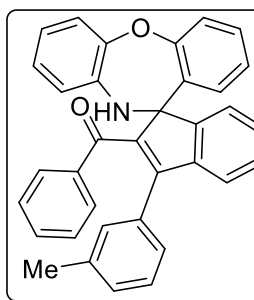
Yield 99% (98.1 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 172-174 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.47-7.44 (m, 3H), 7.41-7.34 (m, 3H), 7.28 (app dd, *J* = 7.5, 1.2 Hz, 1H), 7.26-7.22 (m, 2H), 7.19-7.15 (m, 2H), 7.08-7.04 (app t, 2H), 6.98 (app d, *J* = 7.4 Hz, 1H), 6.94-6.89 (m, 3H), 6.88-6.80 (m, 2H), 6.74 (app dd, *J* = 7.9, 1.6 Hz, 1H), 6.65 (app d, *J* = 6.8 Hz, 1H), 4.47 (br s, 1 N-H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 194.8, 164.0, 161.5, 156.5, 152.0, 151.6, 140.9, 137.4, 132.2, 130.9, 130.8, 129.1 (x 2), 128.9 (d, *J* = 3.2 Hz), 128.8, 128.6 (d, *J* = 3.1 Hz) (x 2), 127.7 (x 2), 127.3, 124.7, 124.5, 123.8, 123.5, 122.7, 122.0, 120.9, 115.6, 115.4, 75.9; **¹⁹F NMR** (376 MHz, CDCl₃) δ -111.75; **HRMS** (ESI, *m/z*) calcd for C₃₄H₂₃FNO₂ [M + H]⁺ 496.1713, found 496.1715.

methyl 4-(2'-(benzoyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-3'-yl)benzoate (3h):



Yield 66% (70.7 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 88-90 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.90-7.88 (comp, 2H), 7.47-7.45 (comp, 4H), 7.43-7.42 (m, 1H), 7.40-7.38 (m, 1H), 7.29 (app td, *J* = 7.4, 1.4 Hz, 1H), 7.24 (app dd, *J* = 8.2, 1.3 Hz, 1H), 7.21-7.18 (comp, 2H), 7.16-7.14 (comp, 1H), 7.06-7.02 (comp, 3H), 6.94-6.86 (comp, 2H), 6.84-6.80 (m, 1H), 6.76 (app dd, *J* = 7.9, 1.6 Hz, 1H), 6.66 (app d, *J* = 5.8 Hz, 1H), 4.47 (br s, 1 N-H), 3.88 (s, 3H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 194.6, 166.4, 156.5, 151.6, 151.4, 140.6, 137.6, 137.2, 132.4, 130.0, 129.6 (x 2), 129.0 (x 4), 128.9, 128.8, 128.7, 128.6, 127.7 (x 2), 127.1, 124.8, 124.5, 123.6 (x 2), 122.6, 122.0, 120.9, 76.1, 52.2; **HRMS** (ESI, *m/z*) calcd for C₃₆H₂₆NO₄ [M + H]⁺ 536.1862, found 536.1856.

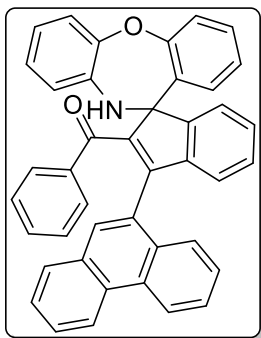
phenyl(3'-(*m*-tolyl)-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3i):



Yield 92% (90.4 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 86-88 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.52 (app d, *J* = 7.6 Hz, 1H), 7.49-7.47 (comp, 2H), 7.38 (app td, *J* = 7.5, 1.0 Hz, 1H), 7.28-7.11 (comp, 8H), 7.06-7.03 (comp, 2H), 6.98 (app t, *J* = 7.4 Hz, 2H), 6.93 (app dd, *J* = 7.8, 1.5 Hz, 1H), 6.89-6.81 (comp, 2H), 6.78 (app dd, *J* = 7.9, 1.7 Hz, 1H), 6.67-6.65 (m, 1H), 4.46 (br s, 1 N-H), 2.20 (s, 3H); **¹³C{¹H} NMR** (100 MHz,

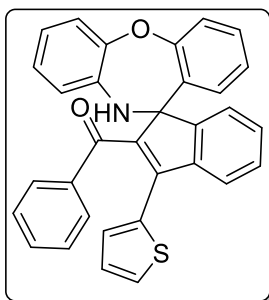
CDCl₃) δ 194.8 , 156.4 , 152.3 , 152.0 , 147.2 , 147.0 , 141.1 , 138.1 , 138.0 , 137.7 , 132.7 , 131.8 , 123.0 , 129.4 , 129.0 (x 2), 128.8 , 128.6 , 128.5 (x 2), 128.2 , 127.4 (x 2), 125.9 , 124.6 , 124.4 , 124.0 , 123.8 , 123.4 , 123.0 , 122.0 , 120.8 , 75.8 , 21.1; **HRMS** (ESI, m/z) calcd for C₃₅H₂₆NO₂ [M + H]⁺ 492.1964, found 492.1962.

(3'-(phenanthren-9-yl)-10H-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (3j):



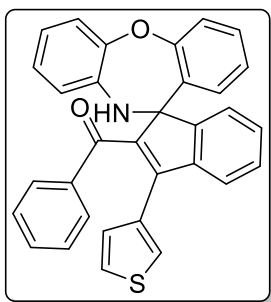
Yield 75% (86.3 mg, stereoisomeric ratio = 5:2); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 262-264 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.65-8.60 (m, 1H), 8.55 (app d, *J* = 8.3 Hz, 1H), 7.80-7.75 (m, 1H), 7.73-7.68 (m, 1H), 7.66-7.64 (m, 1H), 7.62-7.58 (m, 1H), 7.56-7.50 (comp, 2H), 7.38-7.35 (m, 1H), 7.29-7.19 (comp, 7H), 7.13-7.10 (m, 1H), 7.06-6.91 (comp, 4H), 6.86-6.76 (comp, 3H), 6.66-6.60 (comp, 2H), 4.48 (br s, 1 N-H); **Combined ¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 195.4 , 194.3 , 157.1 , 156.2 , 152.2 , 141.9 , 138.2 , 137.9 , 131.4 , 131.4 , 130.9 , 130.4 , 130.3 , 130.3 , 130.2 , 129.7 , 129.1 , 128.9 , 128.8 , 128.7 , 128.6 , 128.1 , 128.1 , 128.0 , 127.4 , 127.2 , 127.1 , 127.0 , 126.8 , 126.6 , 126.6 (x 2) , 126.5 , 124.8 , 124.7 , 124.6 , 124.4 , 124.1 , 124.0 , 123.8 , 123.8 , 123.4 , 123.0 , 122.3 , 122.3 , 122.1 , 121.0 , 120.9 , 76.1 , 75.7; **HRMS** (ESI, m/z) calcd for C₄₂H₂₈NO₂ [M + H]⁺ 578.2120, found 578.2122.

phenyl(3'-(thiophen-2-yl)-10H-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3k):



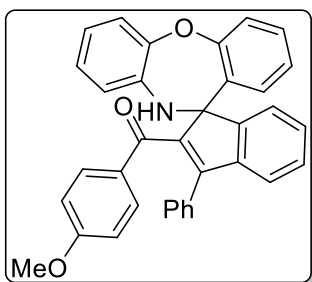
Yield 74% (71.8 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 172 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.79 (app d, *J* = 7.6 Hz, 1H), 7.58-7.56 (comp, 2H), 7.44 (app td, *J* = 7.6, 1.1 Hz, 1H), 7.31-7.27 (comp, 3H), 7.22-7.16 (comp, 2H), 7.15-7.11 (comp, 4H), 7.04 (app d, *J* = 7.4 Hz, 1H), 6.91-6.84 (comp, 3H), 6.81-6.75 (comp, 2H), 6.60-6.57 (m, 1H), 4.31 (br s, 1 N-H); **¹³C{¹H} NMR** δ 194.9 , 156.5 , 151.3 , 151.3 , 147.7 , 140.4 , 138.1 , 137.8 , 137.3 , 133.5 , 132.3 , 129.4 , 128.9 (x 2) , 128.8 , 128.7 , 128.5 , 127.8 , 127.5 , 127.4 , 127.1 , 124.6 , 124.5 , 123.5 , 123.3 , 123.2 , 122.8 , 121.9 , 120.9 , 76.0; **HRMS** (ESI, m/z) calcd for C₃₂H₂₂NO₂S [M + H]⁺ 484.1371, found 484.1353.

phenyl(3'-(thiophen-3-yl)-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3l):



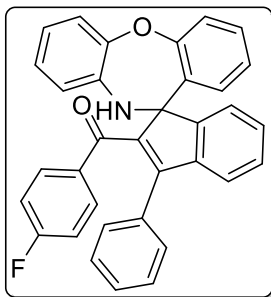
Yield 97% (93.7 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 180 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.59 (app d, *J* = 7.5 Hz, 1H), 7.53-7.51 (comp, 2H), 7.41 (app td, *J* = 7.6, 1.1 Hz, 1H), 7.36 (app dd, *J* = 2.9, 1.3 Hz, 1H), 7.30-7.24 (comp, 2H), 7.19-7.18 (m, 1H), 7.17-7.14 (comp, 2H), 7.13-7.09 (comp, 3H), 7.00 (app d, *J* = 7.5 Hz, 1H), 6.91 (app td, *J* = 7.7, 1.5 Hz, 1H), 6.87-6.79 (comp, 2H), 6.76 (app dd, *J* = 7.9, 1.6 Hz, 1H), 6.62 (app d, *J* = 7.3 Hz, 1H), 4.44 (br s, 1 N-H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 195.0, 156.4, 151.8, 151.5, 146.9, 140.9, 137.9, 137.4, 133.2, 132.1, 129.0 (x 2), 128.8, 128.7, 128.7, 128.5, 127.9, 127.7 (x 2), 127.4, 126.0, 126.0, 124.6, 124.5, 123.7, 123.5, 122.8, 122.0, 120.9, 75.8; **HRMS** (ESI, *m/z*) calcd for C₃₂H₂₂NO₂S [M + H]⁺ 484.1371, found 484.1379.

(4-methoxyphenyl)(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3m):



Yield 98% (99.5 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 202-204 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.51-7.48 (comp, 3H), 7.42-7.39 (comp, 2H), 7.39-7.35 (m, 1H), 7.27-7.21 (comp, 5H), 7.18-7.14 (m, 2H), 7.02 (app d, *J* = 7.4 Hz, 1H), 6.92-6.88 (m, 1H), 6.87-6.83 (m, 1H), 6.82-6.77 (m, 1H), 6.61 (app dd, *J* = 7.7, 1.6 Hz, 1H), 6.56-6.52 (comp, 2H), 4.38 (br s, 1 N-H), 3.71 (s, 3H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 193.4, 162.8, 156.5, 151.8, 151.7, 147.7, 144.9, 141.1, 138.1, 133.0, 131.5, 130.5, 128.9 (x 3), 128.6, 128.5, 128.4, 128.2, 127.4, 124.6, 124.4, 123.5, 123.4 (x 2), 122.6, 122.0, 120.8, 112.9, 76.0, 55.2; **HRMS** (ESI, *m/z*) calcd for C₃₅H₂₆NO₃ [M + H]⁺ 508.1913, found 508.1911.

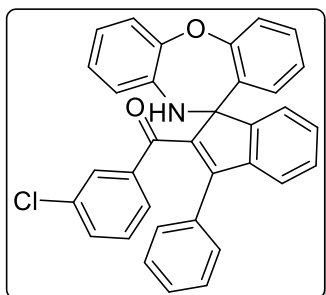
(4-fluorophenyl)(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3n):



Yield 98% (97.1 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 114-116 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.52-7.46 (comp, 3H), 7.41 (app dd, *J* = 7.4, 1.0 Hz, 1H), 7.39-7.36 (comp, 2H), 7.29-7.25 (comp, 2H), 7.24-7.23 (comp, 3H), 7.20-7.16 (comp, 2H), 7.00-6.93 (comp, 2H), 6.88-6.86 (m, 1H), 6.85-6.82 (m, 1H), 6.75-6.68 (comp, 4H), 4.45 (br s, 1 N-H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 193.3, 166.2, 163.9, 163.7, 156.4, 151.9, 141.1 (x 2), 133.8 (d, *J* = 2.5 Hz), 132.7, 131.7, 131.6, 129.0 (x 2), 128.9 (x 2), 128.7,

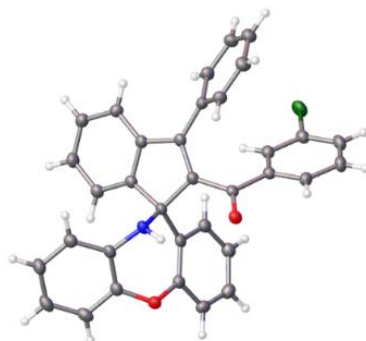
128.6 , 128.4 (x 2), 124.7 , 124.6 , 123.7 (d, $J = 3.6$ Hz), 123.6 , 123.0 , 122.0 , 120.9 , 114.8 , 114.6 , 76.0; ^{19}F NMR (376 MHz, CDCl_3) δ -106.27; HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{23}\text{FNO}_2$ $[\text{M} + \text{H}]^+$ 496.1713, found 496.1692.

(3-chlorophenyl)(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3o):



Yield 97% (99.3 mg); **Yellow solid; eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 178-180 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.50 (app d, $J = 7.5$ Hz, 1H), 7.41 (app dd, $J = 7.5, 1.0$ Hz, 1H), 7.38-7.36 (comp, 2H), 7.35-7.30 (comp, 3H), 7.29-7.20 (comp, 5H), 7.19-7.14 (comp, 3H), 7.02 (app d, $J = 7.4$ Hz, 1H), 6.98 (app d, $J = 7.9$ Hz, 1H), 6.96-6.92 (m, 1H), 6.89-6.80 (comp, 2H), 6.72 (app dd, $J = 7.9, 1.6$ Hz, 1H), 6.67 (app d, $J = 7.2$ Hz, 1H), 4.40 (s, 1 N-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) 193.2 , 156.4 , 151.9 , 151.8 , 140.9 , 139.1 , 138.0 , 133.6 , 132.7 , 131.8 , 129.2 , 129.0 , 128.9 (x 3) , 128.8 , 128.8 , 128.7 , 128.6 , 128.5 (x 2), 127.2 , 127.0 , 124.7 , 124.5 , 123.8 , 123.7 , 123.5 , 123.1 , 122.0 , 120.9 , 75.9; HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{23}\text{ClNO}_2$ $[\text{M} + \text{H}]^+$ 512.1417, found 512.1423.

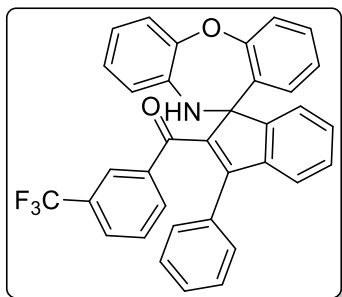
Figure S3. X-ray crystal structure of **3o** (ellipsoid contour at 50% probability level)



Crystal data and structure refinement for 3o, CCDC No. 2226411

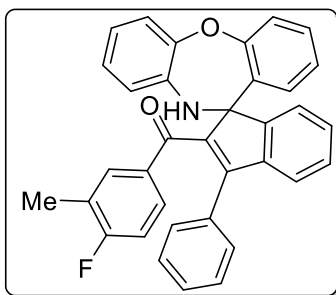
Empirical formula	C ₃₄ H ₂₂ ClNO ₂	$\rho_{\text{calc}}/\text{cm}^3$	1.376
Formula weight	511.97	μ/mm^{-1}	1.634
Temperature/K	100.0	F(000)	532.0
Crystal system	triclinic	Crystal size/mm ³	0.4 × 0.25 × 0.2
Space group	P-1	Radiation	Cu K α ($\lambda = 1.54178$)
a/Å	8.8279(9)	2 θ range for data collection/°	7.16 to 130.208
b/Å	11.8609(12)	Index ranges	-9 ≤ h ≤ 10, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15
c/Å	13.5405(13)	Reflections collected	18829
α /°	68.435(4)	Independent reflections	4176 [R _{int} = 0.0620, R _{sigma} = 0.0473]
β /°	73.562(3)	Data/restraints/parameters	4176/0/343
γ /°	72.877(4)	Goodness-of-fit on F ²	1.023
Volume/Å ³	1235.5(2)	Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0578, wR ₂ = 0.2117
Z	2	Final R indexes [all data]	R ₁ = 0.0661, wR ₂ = 0.2241
		Largest diff. peak/hole / e Å ⁻³	0.47/-1.15

(3'-phenyl-10H-spiro[dibenzo[b,f][1,4]oxazepine-11,1'-inden]-2'-yl)(3-(trifluoromethyl)phenyl)methanone (3p):



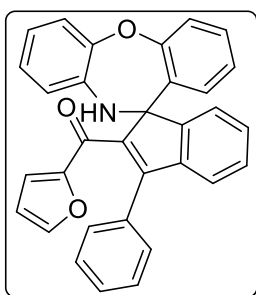
Yield 97% (105.8 mg); **Yellow solid**; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 188-190 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.65 (app d, $J = 7.9$ Hz, 1H), 7.62 (app s, 1H), 7.51 (app d, $J = 7.6$ Hz, 1H), 7.44-7.39 (comp, 3H), 7.34-7.31 (comp, 3H), 7.29 (app dd, $J = 6.4, 1.1$ Hz, 1H), 7.24-7.15 (comp, 6H), 7.05 (d, $J = 7.4$ Hz, 1H), 6.92 (m, 1H), 6.86 (app td, $J = 7.7, 7.2, 1.3$ Hz, 1H), 6.79 (app td, 1H), 6.72 (app dd, $J = 7.9, 1.5$ Hz, 1H), 6.66 (app d, $J = 7.3$ Hz, 1H), 4.43 (br s, 1 N-H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 193.2, 156.4, 151.9, 140.9, 138.0, 132.5, 131.8, 130.0, 129.7, 129.0 (x 2), 129.0 (x 2), 128.8 (x 2), 128.5 (x 2), 128.5, 128.3, 128.2, 128.2, 127.1, 126.2 (q, $J = 3.7$ Hz), 124.8, 124.5, 124.0, 123.7, 123.5, 123.2, 122.0, 120.9, 76.0; **¹⁹F NMR** (376 MHz, CDCl₃) δ -62.76; **HRMS** (ESI, m/z) calcd for C₃₅H₂₃F₃NO₂ [M + H]⁺ 546.1681, found 546.1671.

(4-fluoro-3-methylphenyl)(3'-phenyl-10H-spiro[dibenzo[b,f][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3q):



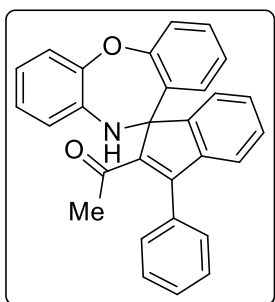
Yield 95% (96.8 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 142-144 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (app d, $J = 7.5$ Hz, 1H), 7.41-7.37 (comp, 3H), 7.33-7.27 (comp, 3H), 7.27-7.22 (comp, 4H), 7.20-7.14 (comp, 2H), 7.03 (app d, $J = 7.4$ Hz, 1H), 6.92 (app td, $J = 7.7, 1.5$ Hz, 1H), 6.88-6.81 (comp, 2H), 6.75 (app dd, $J = 7.9, 1.6$ Hz, 1H), 6.68-6.63 (comp, 2H), 4.41 (br s, 1 N-H), 2.04 (d, $J = 1.5$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 193.4, 164.8, 162.2, 156.5, 151.7, 147.4, 146.3, 141.0, 138.0, 133.5 (d, $J = 2.8$ Hz), 133.0, 133.0 (d, $J = 3.1$ Hz), 129.0, 129.0, 128.9, 128.8, 128.7 (d, $J = 2.2$ Hz), 128.6, 128.5, 128.4, 124.6, 124.4, 124.2, 124.0, 123.6, 123.4, 122.8, 122.0, 120.9, 114.4, 114.2, 75.9, 14.2 (d, $J = 3.3$ Hz); $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -110.54; **HRMS** (ESI, m/z) calcd for $\text{C}_{35}\text{H}_{25}\text{FNO}_2$ [$\text{M} + \text{H}$] $^+$ 510.1869, found 510.1872.

furan-2-yl(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3r):



Yield 99% (97.7 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 162-164 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.50 (app d, $J = 7.5$ Hz, 1H), 7.48-7.46 (comp, 2H), 7.38 (app dd, $J = 7.5, 1.1$ Hz, 1H), 7.35-7.27 (comp, 5H), 7.24 (app dd, $J = 7.5, 1.1$ Hz, 1H), 7.22-7.16 (comp, 2H), 7.13 (app dd, $J = 1.6, 0.7$ Hz, 1H), 6.99-6.93 (comp, 2H), 6.86-6.82 (comp, 2H), 6.78 (app dd, $J = 7.9, 1.8$ Hz, 1H), 6.67 (app dd, $J = 3.6, 0.7$ Hz, 1H), 6.15 (app dd, $J = 3.6, 1.7$ Hz, 1H), 4.34 (br s, 1 N-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 181.7, 156.2, 152.9, 151.9, 151.7, 146.7, 146.6, 145.7, 140.8, 138.1, 133.2, 128.9, 128.7, 128.6, 128.6 (x 2), 128.5, 128.5, 126.8, 124.5, 124.7, 123.6, 123.3, 123.2, 122.8, 122.0, 120.9, 118.3, 111.8, 76.0; **HRMS** (ESI, m/z) calcd for $\text{C}_{32}\text{H}_{22}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$ 468.1600, found 468.1582.

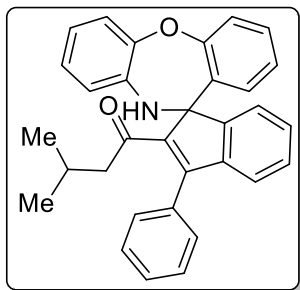
1-(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)ethan-1-one (3s):



Yield 97% (83.1 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 164-166 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.56-7.54 (m, 1H), 7.53-7.52 (comp, 3H), 7.50-7.47 (m, 1H), 7.37-7.32 (comp, 2H), 7.28-7.22 (comp, 2H), 7.20-7.16 (m, 1H), 7.13-7.08 (comp, 2H), 7.02 (app td, $J = 7.5, 1.5$ Hz, 1H), 6.84 (app td, $J = 7.6, 1.3$ Hz, 1H), 6.72 (app d, $J = 7.5$ Hz, 1H), 6.67 (app dd, $J = 7.9, 1.6$ Hz, 1H), 6.47 (app d, $J = 7.5$ Hz, 1H), 4.141 (br s, 1 N-H), 2.012 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 197.2, 155.5, 153.4, 152.0, 151.6, 147.2, 141.5, 138.3, 133.7, 129.1, 128.9, 128.7, 128.5, 128.5 (x 2), 128.3,

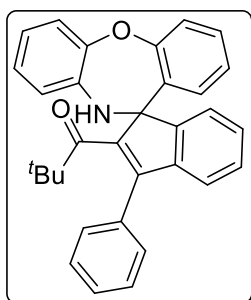
126.9, 124.9, 124.8, 124.6, 124.1, 123.9, 123.7, 122.3, 121.0, 74.1, 30.8; **HRMS** (ESI, m/z) calcd for C₂₉H₂₂NO₂ [M + H]⁺ 416.1651, found 416.1653.

3-methyl-1-(3'-phenyl-10H-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)butan-1-one (3t):



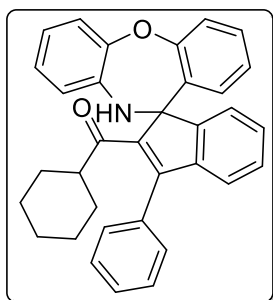
Yield 80% (73.2 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 136 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.54-7.45 (comp, 5H), 7.32 (comp, 2H), 7.25-7.20 (comp, 2H), 7.18-7.14 (m, 1H), 7.12-7.05 (comp, 2H), 7.01 (app td, *J* = 7.5, 1.5 Hz, 1H), 6.84-6.80 (m, 1H), 6.73 (app d, *J* = 7.6 Hz, 1H), 6.64 (app dd, *J* = 7.9, 1.6 Hz, 1H), 6.43 (app d, *J* = 7.5 Hz, 1H), 2.27 (dd, *J* = 16.5, 6.8 Hz, 1H), 2.10 (dd, *J* = 16.5, 6.8 Hz, 1H), 1.88 (dt, *J* = 13.3, 6.7 Hz, 1H), 0.60 (d, *J* = 6.6 Hz, 3H), 0.53 (d, *J* = 6.6 Hz, 3H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 200.3, 155.6, 153.7, 151.8, 150.3, 147.7, 141.6, 138.3, 133.7, 128.8 (x 2), 128.6 (x2), 128.5 (x 2), 128.4, 128.2, 126.9, 125.3, 124.8, 124.6, 124.1, 123.6, 122.1, 120.9, 74.2, 51.3, 24.1, 22.3, 22.2; **HRMS** (ESI, m/z) calcd for C₃₂H₂₈NO₂ [M + H]⁺ 458.2120, found 458.2112.

2,2-dimethyl-1-(3'-phenyl-10H-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)propan-1-one (3u):



Yield 97% (88.8 mg); White solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 176 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.50-7.41 (comp, 5H), 7.36 (app d, *J* = 7.4 Hz, 1H), 7.31-7.27 (comp, 2H), 7.26-7.18 (comp, 2H), 7.10 (app td, *J* = 7.4, 1.1 Hz, 1H), 7.05-6.99 (comp, 2H), 6.92-6.88 (m, 1H), 6.76 (comp, 2H), 6.65 (app d, *J* = 7.5 Hz, 1H), 3.91 (br s, 1 N-H), 0.77 (s, 9H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 213.5, 156.5, 152.6, 141.1, 133.8, 130.5, 128.9 (x 5), 128.8 (x 4), 128.2, 127.3, 126.1, 125.0, 123.7, 123.6, 123.5, 122.0, 121.7, 120.9, 76.2, 44.7, 26.9; **HRMS** (ESI, m/z) calcd for C₃₂H₂₈NO₂ [M + H]⁺ 458.2120, found 458.2119.

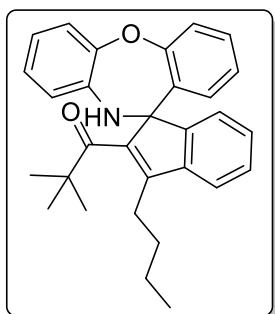
cyclohexyl(3'-phenyl-10H-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3v):



Yield 88% (84.8 mg); Greenish-yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 74-76 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.52-7.48 (comp, 5H), 7.35 (app dd, *J* = 8.2, 1.2 Hz, 1H), 7.32 (app dd, *J* = 7.9, 1.4 Hz, 1H), 7.28-7.22 (comp, 2H), 7.19-7.15 (m, 1H), 7.11-7.07 (comp, 2H), 7.04-7.00 (m, 1H), 6.85-6.81 (m, 1H), 6.72 (app d, *J* = 7.4 Hz, 1H), 6.67 (app dd, *J* = 7.9, 1.6 Hz, 1H), 6.48 (app d, *J* = 16.0 Hz, 1H), 4.14 (br s, 1 N-H), 2.57 (tt, *J* = 11.5,

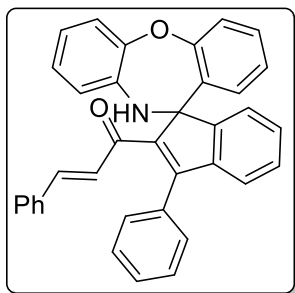
3.0 Hz, 1H), 1.56-1.43 (m, 4H), 1.30-1.26 (m, 1H), 1.14-1.03 (m, 2H), 1.01-0.92 (m, 1H), 0.89-0.79 (m, 1H), 0.73-0.61 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 204.0, 155.6, 153.8, 152.2, 150.7, 147.4 (x 2), 141.6, 138.5, 133.9, 129.1, 128.8, 128.8, 128.6, 128.4, 128.4, 128.2, 126.9, 125.2, 124.8, 124.5, 124.1, 123.5, 122.2, 121.0, 74.4, 48.6, 28.7, 28.3, 25.8, 25.7, 25.6; **HRMS** (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{30}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 484.2277, found 484.2261.

1-(3'-butyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)-2,2-dimethylpropan-1-one (3w):



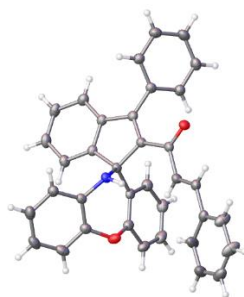
Yield 86% (76 mg); Yellowish gel; **eluent composition** petroleum ether/ethyl acetate = 99:1 to 19:1; ^1H NMR (400 MHz, CDCl_3) δ 7.34 (d, $J = 7.4$ Hz, 1H), 7.29-7.19 (comp, 3H), 7.17-7.13 (m, 1H), 7.02-6.97 (comp, 3H), 6.87-6.83 (m, 1H), 6.68-6.62 (comp, 2H), 6.45 (d, $J = 7.5$ Hz, 1H), 3.54 (br s, 1 N-H), 2.53-2.41 (comp, 2H), 1.73-1.65 (comp, 2H), 1.50-1.40 (comp, 2H), 1.09 (s, 9H), 0.97 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 213.1, 155.8, 152.6, 152.3, 150.4, 142.4, 141.1, 138.4, 133.1, 130.8, 128.6, 127.9, 126.9, 125.8, 124.9, 123.4, 123.4, 123.2, 121.8, 120.9, 120.8, 75.7, 44.5, 30.6, 27.5, 26.6, 23.2, 13.9; **HRMS** (ESI, m/z) calcd for $\text{C}_{30}\text{H}_{32}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 438.2433, found 438.2436.

(*E*)-3-phenyl-1-(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)prop-2-en-1-one (3x):



Yield 97% (97.7 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 150-152 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.61-7.50 (comp, 5H), 7.39-7.37 (m, 1H), 7.36-7.32 (comp, 3H), 7.31-7.27 (comp, 2H), 7.25-7.23 (m, 1H), 7.18-7.13 (comp, 4H), 7.08 (app td, $J = 7.5, 1.2$ Hz, 1H), 7.01 (app td, $J = 7.5, 1.3$ Hz, 1H), 6.92 (app d, $J = 15.7$ Hz, 1H), 6.83 (app td, $J = 7.6, 7.2, 1.3$ Hz, 1H), 6.75 (app d, $J = 5.4$ Hz, 1H), 6.70 (app dd, $J = 7.9, 1.6$ Hz, 1H), 6.61 (app d, $J = 7.5$ Hz, 1H), 4.30 (br s, 1 N-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 188.0, 155.6, 153.5, 141.6, 141.4, 135.1, 133.8, 129.9, 129.2, 129.0, 128.9 (x 2), 128.7 (x 2), 128.6, 128.6 (x 3), 128.4, 128.2 (x 2), 127.2, 125.8, 125.1, 124.8, 124.3, 123.8, 123.7, 122.2, 121.0, 74.4; **HRMS** (ESI, m/z) calcd for $\text{C}_{36}\text{H}_{26}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 504.1964, found 504.1940.

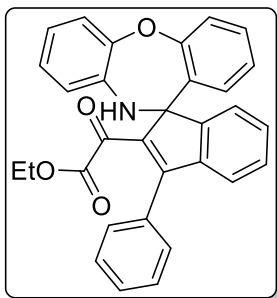
Figure S4. X-ray crystal structure of **3x** (ellipsoid contour at 50% probability level)



Crystal data and structure refinement for 3x, CCDC No. 2226412

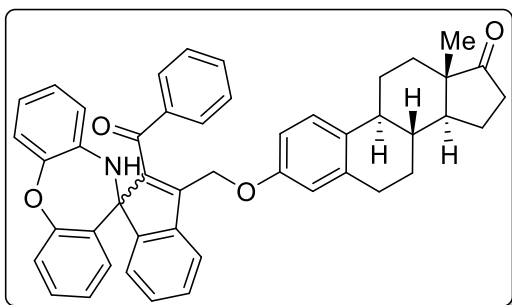
Empirical formula	C ₃₆ H ₂₅ NO ₂
Formula weight	503.57
Temperature/K	101.0
Crystal system	triclinic
Space group	P-1
a/Å	10.6943(5)
b/Å	11.3031(6)
c/Å	12.5505(6)
α/°	70.5720(10)
β/°	89.8510(10)
γ/°	66.3090(10)
Volume/Å ³	1294.96(11)
Z	2
ρ _{calc} /cm ³	1.291
μ/mm ⁻¹	0.623
F(000)	528.0
Crystal size/mm ³	0.6 × 0.25 × 0.2
Radiation	Cu Kα (λ = 1.54178)
2θ range for data collection/°	9.814 to 136.382
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	55903
Independent reflections	4562 [R _{int} = 0.0461, R _{sigma} = 0.0253]
Data/restraints/parameters	4562/0/352
Goodness-of-fit on F ²	1.038
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0492, wR ₂ = 0.1218
Final R indexes [all data]	R ₁ = 0.0495, wR ₂ = 0.1221
Largest diff. peak/hole / e Å ⁻³	0.71/-0.71

ethyl 2-oxo-2-(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)acetate (3y):



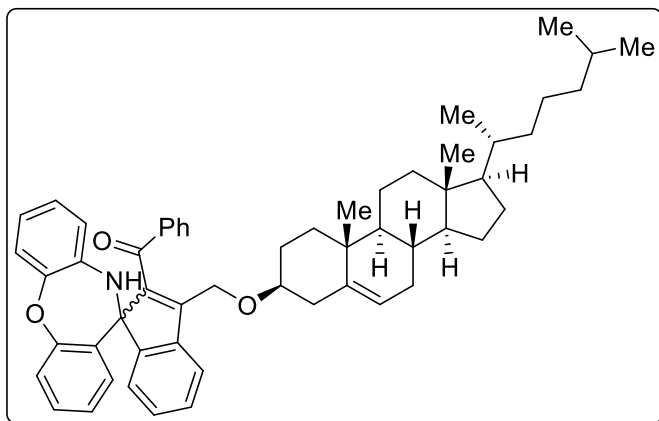
Yield 81% (76.7 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 82-84 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.56-7.52 (comp, 5H), 7.40 (app d, *J* = 7.5 Hz, 1H), 7.36 (app dd, *J* = 3.6, 1.1 Hz, 1H), 7.34 (app dd, *J* = 2.8, 1.1 Hz, 1H), 7.32-7.29 (m, 1H), 7.24 (app td, *J* = 7.5, 1.2 Hz, 1H), 7.20-7.16 (m, 1H), 7.06 (app td, *J* = 7.7, 1.6 Hz, 1H), 6.97 (app td, *J* = 7.5, 1.5 Hz, 1H), 6.86 (app d, *J* = 7.5 Hz, 1H), 6.84-6.80 (m, 1H), 6.74 (app dd, *J* = 7.7, 1.5 Hz, 1H), 6.67 (app dd, *J* = 7.9, 1.6 Hz, 1H), 3.60 (q, *J* = 7.2 Hz, 2H), 1.03 (t, *J* = 7.2 Hz, 3H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 184.0, 163.1, 156.4, 155.6, 152.9, 152.8, 143.1, 140.2, 138.1, 132.0, 131.2, 130.3, 129.9, 129.1, 128.7, 128.6, 128.0, 126.5, 124.7, 124.7, 124.2, 124.2 (x 2), 123.5, 122.2, 121.0, 74.4, 61.7, 13.5; **HRMS** (ESI, *m/z*) calcd for C₃₁H₂₄NO₄ [M + H]⁺ 474.1705, found 474.1716.

(8*R*,9*S*,13*S*,14*S*)-3-((2'-benzoyl-10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,1'-inden]-3'-yl)methoxy)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (3z):



Combined yield 73% (100.4 mg, dr 100:97 calculated from ¹H-NMR); Inseparable diastereomeric mixture; Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 4:1; **mp** 120-122 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.68-7.64 (comp, 6H), 7.43-7.39 (comp, 4H), 7.29-7.23 (comp, 9H), 7.16-7.12 (comp, 6H), 7.06-7.02 (comp, 4H), 6.87-6.84 (comp, 2H), 6.82-6.77 (comp, 4H), 6.63-6.59 (comp, 6H), 6.54-6.53 (comp, 2H), 4.89-4.82 (m, 4H), 4.24 (br s, 1.30 N-H), 2.87-2.74 (m, 4H), 2.54-2.47 (m, 2H), 2.40-2.34 (m, 2H), 2.24-2.04 (m, 7H), 2.01-1.93 (m, 4H), 1.67-1.57 (m, 4H), 1.54-1.50 (m, 4H), 1.47-1.34 (m, 4H), 0.91 (s, 3H), 0.90 (s, 2.92H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 220.8, 194.4, 156.5, 156.1, 150.7, 140.3, 138.3, 137.8, 132.8, 132.7, 129.0, 128.9 (x 2), 128.7, 128.5, 128.1 (x 2), 126.8, 126.3 (x 2), 124.5, 124.3, 123.4, 123.0, 122.9, 121.8, 120.9 (x 2), 114.7, 114.7, 112.6, 112.5, 76.2, 63.1, 50.4, 48.0, 44.0, 38.3, 35.83, 31.5, 29.5, 26.4, 25.8, 21.6, 13.8; **HRMS** (ESI, *m/z*) calcd for C₄₇H₄₂NO₄ [M + H]⁺ 684.3114, found 684.3115.

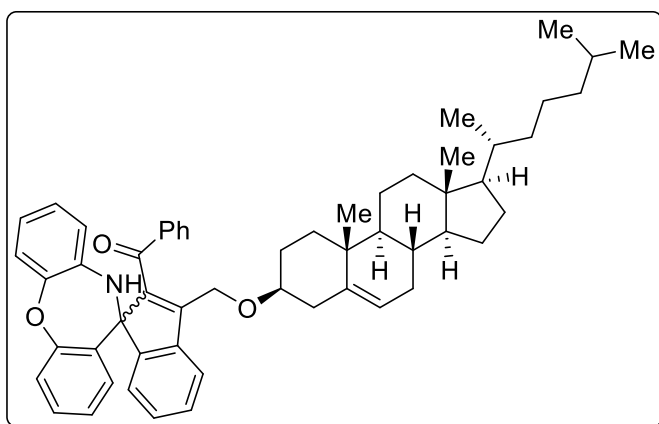
(3'-((((3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)methyl)-10*H*-spiro[dibenzo[*b*,*f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (3za):



Yield of isolated diastereomer (3za) 33% (53 mg); Yellowish gel; **eluent composition**

petroleum ether/ethyl acetate = 49:1 to 19:1; **¹H NMR of 3za** (400 MHz, CDCl₃) δ 7.73-7.71 (comp, 2H), 7.64 (app d, *J* = 7.5 Hz, 1H), 7.48-7.44 (m, 1H), 7.42-7.38 (m, 1H), 7.33-7.29 (comp, 2H), 7.25-7.22 (m, 1H), 7.19-7.12 (m, 2H),

7.08 (app d, *J* = 7.8 Hz, 1H), 6.97-6.94 (m, 1H), 6.88- 6.76 (comp, 3H), 6.67-6.65 (m, 1H), 6.59-6.57 (m, 1H), 5.25-5.24 (m, 1H), 4.34 (s, 2H), 3.10-3.01 (m, 1H), 2.21-2.13 (m, 1H), 2.09 (d, *J* = 11.8 Hz, 1H), 2.04-1.87 (comp, 4H), 1.86-1.70 (comp, 5H), 1.58-1.42 (comp, 10H), 1.39 (s, 2H), 1.36-1.32 (comp, 4H), 1.26-1.24 (comp, 2H), 1.23-1.21 (comp, 2H), 1.15 (d, *J* = 9.7 Hz, 2H), 1.13-1.07 (comp, 6H), 1.05-0.98 (comp, 4H), 0.95 (s, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 1.7 Hz, 3H), 0.86 (d, *J* = 1.7 Hz, 3H), 0.67 (s, 3H); **¹³C{¹H} NMR of 3za** (100 MHz, CDCl₃) δ 194.5 , 156.4 , 140.8 , 140.6 , 140.5 , 138.5 , 132.7 , 129.1 , 128.9 , 128.8 , 128.8 , 128.6 , 128.4 , 128.2 , 128.0 , 124.5 , 124.2 , 123.4 , 123.2 , 121.8 (x 3), 120.9 , 79.6 , 79.5 , 76.2 , 62.7, 56.7 , 56.1 , 50.1 , 42.3 , 39.8 , 39.5 , 38.8 , 38.6 , 37.1 , 37.1 , 36.8 , 36.6 , 36.2 , 35.8 , 31.9 , 31.8 , 28.2 , 28.1 , 28.0 (x 2) , 24.7 , 24.3 , 23.8 , 23.3 , 22.8 , 22.6 , 21.0 , 19.3 , 18.7 , 11.8; **HRMS** (ESI, *m/z*) calcd for C₅₆H₆₆NO₃ [M + H]⁺ 800.5037, found 800.5016.



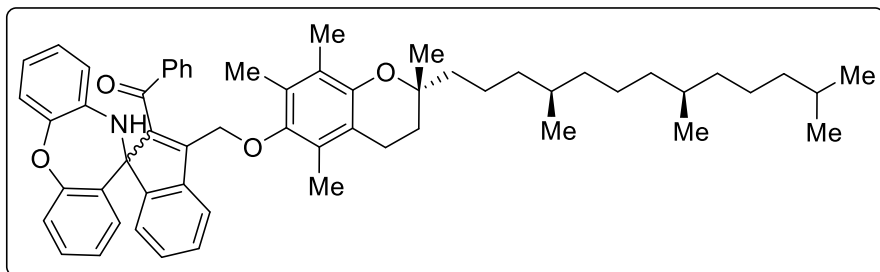
Yield of other isolated diastereomer (3za') 20% (32.2 mg); Yellowish gel; **eluent composition**

petroleum ether/ethyl acetate = 49:1 to 19:1; **¹H NMR of 3za'** (400 MHz, CDCl₃) δ 8.05 (app d, *J* = 7.6 Hz, 2H), 7.63-7.57 (m, 1H), 7.52-7.48 (comp, 2H), 7.34 (app d, *J* = 7.9 Hz, 1H), 7.29 (dd, *J* = 7.1, 2.1 Hz,

1H), 7.25-7.17 (comp, 3H), 7.13 (app d, *J* = 7.3 Hz, 1H), 7.08-6.98 (comp, 3H), 6.96-6.91 (m, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 5.10 (dd, *J* = 19.0, 5.1 Hz, 1H), 4.38 (d, *J* = 15.2 Hz, 1H), 3.99 (d, *J* = 15.2 Hz, 1H), 2.82-2.74 (m, 1H), 1.99-1.67 (comp, 7H), 1.65-1.47 (comp, 8H), 1.46-1.30 (comp, 11H), 1.26-1.21 (comp, 4H), 1.17-0.92 (comp, 14H), 0.91-0.84 (comp, 14H), 0.79 (s, 3H), 0.63 (s, 3H). **¹³C NMR** (100 MHz, CDCl₃) δ 194.8 , 155.9 (x 2) , 151.7 , 140.8 , 140.6 (x 2) , 137.7 , 137.6 , 133.4 , 129.2 , 129.1 , 128.8 , 128.6 , 128.4 , 126.6 , 125.9 , 125.1 , 123.9 , 123.7 , 123.2 , 122.2 , 121.4 , 121.3 , 121.2 , 121.1 , 79.2 , 74.6 , 74.6 , 63.0 , 56.7 , 56.1 , 50.0 , 42.3 , 39.7 , 39.5 , 37.8 (x 2)

, 36.9 , 36.6 (x 2) , 36.2 , 35.8 , 31.8 (x 2) , 29.7 , 28.2 , 28.0 , 27.2 , 27.1 , 24.7 , 24.2 , 23.8 (x 2) , 22.5 , 21.0 , 19.2 , 18.7 , 11.8.

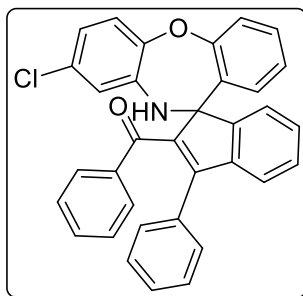
phenyl(3'-((((S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)-10H-spiro[dibenzo[b,f][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (3zb):



Combined yield 90% (152 mg, dr 100:2; calculated from $^1\text{H-NMR}$); Inseparable diastereomeric mixture;

Yellowish gel; **eluent composition** petroleum ether/ethyl acetate = 19:1 to 9:1; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 (d, $J = 7.5$ Hz, 1H), 7.56-7.54 (m, 2H), 7.45 (app td, $J = 7.6, 1.3$ Hz, 1H), 7.38-7.35 (m, 1H), 7.31-7.27 (m, 1H), 7.20-7.14 (comp, 3H), 7.11-7.02 (comp, 3H), 6.91-6.84 (comp, 3H), 6.78 (dd, $J = 8.0, 1.7$ Hz, 1H), 6.70-6.63 (m, 1H), 4.71 (d, $J = 13.1$ Hz, 1H), 4.61 (d, $J = 13.1$ Hz, 1H), 2.57 (t, $J = 7.2$ Hz, 0.06H), 2.48 (t, $J = 6.9$ Hz, 2H), 2.02 (s, 3H), 2.01 (s, 3H), 1.97 (s, 3H), 1.78-1.68 (comp, 2H), 1.54-1.50 (comp, 2H), 1.42-1.34 (comp, 4H), 1.28-1.23 (comp, 7H), 1.20 (s, 3H), 1.16-1.13 (comp, 3H), 1.11-1.04 (comp, 5H), 0.88 (s, 3H), 0.86 (s, 3H), 0.85 (s, 3H), 0.84 (s, 3H), 0.72 (s, 0.05H), 0.71 (s, 0.05H), 0.70 (s, 0.04H), 0.68 (s, 0.05H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.0 , 156.9 , 156.9 , 150.5 , 149.9 , 148.1 , 148.0 , 140.9 , 140.8 , 138.3 , 132.4 , 129.2 , 129.1 , 128.9 , 128.7 , 128.2 , 127.9 , 127.7 , 127.1 , 125.8 , 124.6 , 124.3 , 123.7 , 123.0 , 122.9 , 122.3 , 121.8 , 121.0 , 117.6 , 76.0 , 74.8 , 67.8 , 40.1 , 40.0 , 39.4 , 37.5 , 37.4 , 37.4 , 37.3 , 37.3 , 32.8 , 32.7 , 31.2 , 31.1 , 28.0 , 24.8 , 24.4 , 23.8 , 22.7 , 22.6 , 21.0 , 20.6 , 19.7 , 19.7 , 19.6 , 19.6 , 19.6 , 13.0 , 12.1 , 11.7; **HRMS** (ESI, m/z) calcd for $\text{C}_{58}\text{H}_{70}\text{NO}_4$ $[\text{M} + \text{H}]^+$ 844.5299, found 844.5270.

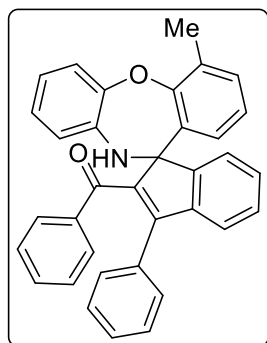
(8-chloro-3'-phenyl-10H-spiro[dibenzo[b,f][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4a):



Yield 98% (100.8 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 216-218 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.51-7.48 (comp, 3H), 7.41 (app td, $J = 7.6, 1.1$ Hz, 1H), 7.36-7.31 (comp, 3H), 7.25-7.22 (comp, 2H), 7.20-7.16 (comp, 5H), 7.08-7.03 (comp, 3H), 6.91-6.87 (m, 1H), 6.81-6.77 (comp, 2H), 6.59 (app d, $J = 2.4$ Hz, 1H), 4.38 (br s, 1 N-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.8 , 156.3 , 151.2 , 149.2 , 147.1 , 146.1 , 141.0 , 139.1 , 137.2 , 132.7 , 132.3 , 129.2 , 129.1 , 129.0 , 128.9 (x 2), 128.8 , 128.7 , 128.5 , 128.4 ,

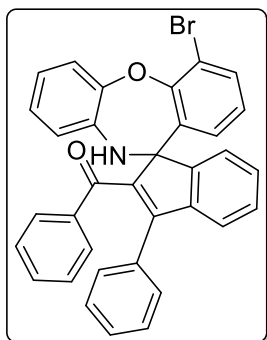
127.7 , 127.5 , 124.5 , 123.8 , 122.9 , 122.6 , 122.3 , 122.0 , 121.8 , 75.8; **HRMS** (ESI, m/z) calcd for C₃₄H₂₃ClNO₂ [M + H]⁺ 512.1417, found 512.1428.

(4-methyl-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4b):



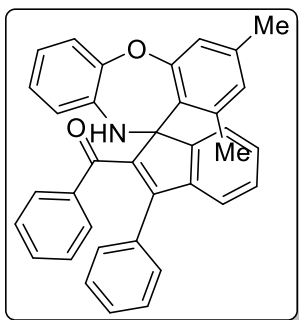
Yield 99% (98.0 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 84-86 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.49-7.47 (comp, 3H), 7.40-7.37 (comp, 3H), 7.29 (td, *J* = 7.5, 1.1 Hz, 1H), 7.25-7.19 (comp, 4H), 7.14 (app dd, *J* = 7.5, 2.0 Hz, 1H), 7.11 (app d, *J* = 7.6 Hz, 1H), 7.07-7.03 (comp, 3H), 6.91-6.83 (comp, 2H), 6.79-6.75 (m, 1H), 6.68-6.65 (comp, 2H), 4.55 (br s, 1 N-H), 2.41 (s, 3H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 195.2 , 155.3 , 151.6 , 150.7 , 147.5 , 145.6 , 141.1 , 138.5 , 137.6 , 132.9 , 131.9 , 130.7 , 130.3 , 129.1 (x 2), 129.0 , 128.6 , 128.3 (x 2), 127.8 , 127.5 , 126.2 , 124.6 , 124.5 , 123.2 , 122.8 , 122.8 , 122.7 , 121.4 , 75.9 , 17.3; **HRMS** (ESI, m/z) calcd for C₃₅H₂₆NO₂ [M + H]⁺ 492.1964, found 492.1965.

(4-bromo-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4c):



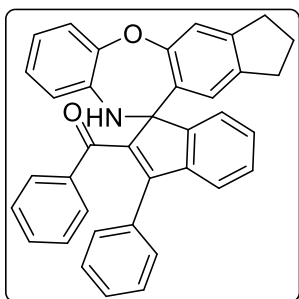
Yield 96% (106.8 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 192-194 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.49 (comp, 2H), 7.47-7.44 (comp, 2H), 7.42-7.38 (comp, 2H), 7.37-7.35 (comp, 2H), 7.28 (app dd, *J* = 7.6, 1.2 Hz, 1H), 7.25-7.24 (m, 1H), 7.23-7.19 (comp, 3H), 7.07-7.00 (comp, 3H), 6.94 (app td, *J* = 7.7, 1.5 Hz, 1H), 6.85 (app td, *J* = 7.6, 1.6 Hz, 1H), 6.76-6.70 (comp, 2H), 6.65 (app d, *J* = 7.2 Hz, 1H), 4.48 (br s, 1 N-H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 194.7 , 153.0 , 151.6 , 151.4 , 146.9 , 140.9 , 138.0 , 137.4 , 132.7 , 132.6 , 132.1 , 130.1 , 129.1 (x 2), 129.0 , 128.8 , 128.8 , 128.7 , 128.4 , 128.0 , 127.6 , 125.0 , 124.6 , 124.3 , 123.5 , 123.4 , 123.0 , 121.7 , 116.8 , 75.8; **HRMS** (ESI, m/z) calcd for C₃₄H₂₃BrNO₂ [M + H]⁺ 556.0912, found 556.0920.

(1,3-dimethyl-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4d):



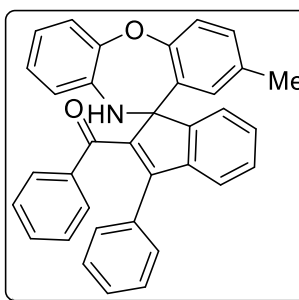
Yield 46% (24 h, 46.3 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 88-90 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.55 (app d, $J = 7.6$ Hz, 1H), 7.53-7.49 (comp, 2H), 7.38-7.35 (comp, 3H), 7.26-7.19 (comp, 5H), 7.17-7.15 (m, 1H), 7.11-7.09 (m, 1H), 7.05-7.02 (comp, 3H), 6.86 (app t, $J = 7.2$ Hz, 1H), 6.61 (app d, 1H), 6.57 (app s, 1H), 6.51 (app d, $J = 7.4$ Hz, 1H), 4.65 (br s, 1 N-H), 2.26 (s, 3H), 1.71 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ **NMR** (100 MHz, CDCl_3) δ 194.1, 157.5, 155.8, 138.2, 138.0, 137.5, 133.1, 133.1, 131.8, 129.2 (x 3), 129.2 (x 3), 128.9, 128.8, 128.3 (x 3), 127.5 (x 3), 126.5, 124.2, 124.1, 124.0, 121.1, 119.9, 76.0, 20.5, 20.2; **HRMS** (ESI, m/z) calcd for $\text{C}_{36}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 506.2120, found 506.2120.

phenyl(3'-phenyl-2,3-dihydro-1H,10H-spiro[benzo[b]indeno[5,6-f][1,4]oxazepine-11,1'-inden]-2'-yl)methanone (4e):



Yield 96% (99.3 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 210-212 °C (crystallization from DCM/hexane bilayer mixture using solvent evaporation method); $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53-7.48 (comp, 3H), 7.40-7.36 (comp, 3H), 7.28 (app dd, $J = 7.5, 1.1$ Hz, 1H), 7.25-7.22 (comp, 2H), 7.20-7.18 (comp, 2H), 7.12 (app dd, $J = 7.8, 1.4$ Hz, 1H), 7.09 (app s, 1H), 7.07-7.03 (comp, 3H), 6.90-6.86 (m, 1H), 6.84-6.80 (m, 1H), 6.62 (app d, $J = 7.6$ Hz, 1H), 6.59 (app s, 1H), 4.51 (br s, 1 N-H), 2.82 (t, $J = 7.4$ Hz, 2H), 2.70-2.58 (m, 2H), 2.03-1.92 (m, 2H); $^{13}\text{C}\{^1\text{H}\}$ **NMR** (100 MHz, CDCl_3) δ 195.1, 155.6, 152.0, 151.8, 147.6, 145.8, 145.4, 141.1, 139.4, 138.3, 137.7, 133.0, 131.9, 129.2, 129.1, 128.6, 128.4, 128.3 (x 2), 127.5, 125.0, 124.6, 124.4, 123.6, 123.3, 123.1, 122.8, 120.8, 117.6, 76.0, 32.6, 32.1, 25.6; **HRMS** (ESI, m/z) calcd for $\text{C}_{37}\text{H}_{28}\text{NO}_2$ $[\text{M} + \text{H}]^+$ 518.2120, found 518.2114.

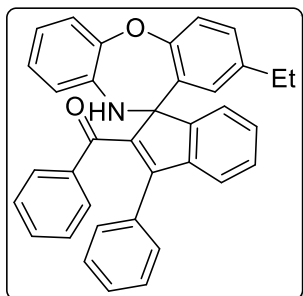
(2-methyl-3'-phenyl-10H-spiro[dibenzo[b,f][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4f):



Yield 97% (95.1 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 188-190 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.53-7.50 (comp, 3H), 7.42-7.37 (comp, 3H), 7.28-7.19 (comp, 5H), 7.17-7.16 (m, 1H), 7.15-7.14 (m, 1H), 7.07-7.03 (comp, 2H), 7.00-6.90 (comp, 3H), 6.83 (app td, $J = 7.6, 1.4$ Hz, 1H), 6.64 (app d, $J = 7.2$ Hz, 1H), 6.56 (d, $J = 1.6$ Hz, 1H), 4.51 (br s, 1 N-H), 2.09 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ **NMR** (100 MHz, CDCl_3) δ 195.0, 154.6, 152.4, 152.0, 147.3, 146.7, 141.2, 138.2, 137.7, 133.1, 132.8, 132.1, 129.6, 129.3, 129.2, 128.9, 128.8, 128.6, 128.6, 128.5, 127.7, 127.1

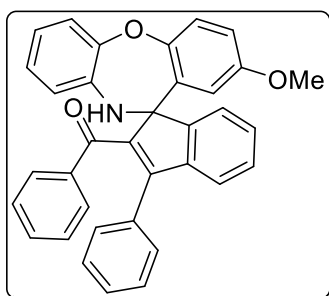
, 124.8 , 124.5 , 124.1 , 123.8 , 123.0 , 121.9 , 120.9 , 76.0, 20.8; **HRMS** (ESI, m/z) calcd for C₃₅H₂₆NO₂ [M + H]⁺ 492.1964, found 492.1973.

(2-ethyl-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4g):



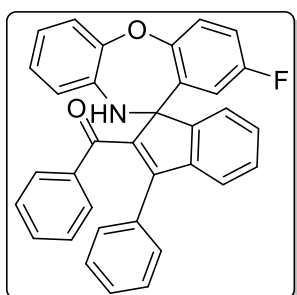
Yield 97% (95.1 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 158-160 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.53-7.50 (comp, 3H), 7.42-7.37 (comp, 3H), 7.28-7.16 (comp, 7H), 7.07-7.03 (comp, 2H), 7.00-6.98 (comp, 2H), 6.96-6.92 (m, 1H), 6.87-6.83 (m, 1H), 6.66 (app d, *J* = 7.6 Hz, 1H), 6.59 (app d, *J* = 2.0 Hz, 1H), 4.62 (br, 1 N-H), 2.39 (q, *J* = 7.5 Hz, 2H), 1.02 (t, *J* = 7.6 Hz, 3H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 195.2 , 154.8 , 152.6 , 152.0 , 147.3 , 146.8 , 141.2 , 139.2 , 138.3 , 137.8 , 133.1 , 132.1 , 129.3 , 129.2 , 128.8 , 128.6 , 128.5 , 128.5 , 128.3 , 127.9 , 127.7 , 127.2 , 124.8 , 124.5 , 124.3 , 123.8 , 123.0 , 121.9 , 120.9 , 76.0 , 28.1 , 15.6; **HRMS** (ESI, m/z) calcd for C₃₆H₂₈NO₂ [M + H]⁺ 506.2120, found 506.2022.

(2-methoxy-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4h):



Yield 92% (92.9 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 196-198 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.53-7.48 (comp, 3H), 7.40-7.36 (comp, 3H), 7.28 (app dd, *J* = 7.5, 1.0 Hz, 1H), 7.24-7.18 (comp, 5H), 7.15 (app dd, *J* = 7.9, 1.4 Hz, 1H), 7.07-7.04 (comp, 3H), 6.91 (app td, *J* = 7.7, 1.5 Hz, 1H), 6.83 (app td, *J* = 7.6, 1.4 Hz, 1H), 6.72 (app dd, *J* = 8.9, 3.1 Hz, 1H), 6.64 (app d, *J* = 7.4 Hz, 1H), 6.33 (app d, *J* = 3.2 Hz, 1H), 4.54 (br s, 1 N-H), 3.57 (s, 3H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 194.8 , 155.2 , 152.0 , 151.5 , 150.8 , 147.0 , 146.6 , 141.0 , 138.1 , 137.6 , 132.9 , 132.0 , 129.1 , 129.0 , 128.8 , 128.7 , 128.6 , 128.5 , 128.3 , 127.5 , 124.6 , 124.4 , 123.6 , 123.4 , 122.9 , 122.6 , 120.7 , 114.0 , 113.4 , 75.7 , 55.3; **HRMS** (ESI, m/z) calcd for C₃₅H₂₆NO₃ [M + H]⁺ 508.1913, found 508.1918.

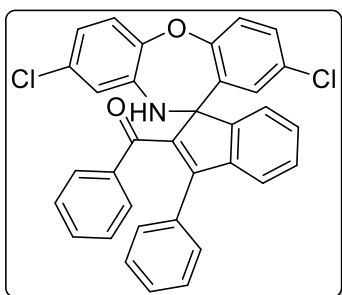
(2-fluoro-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4i):



Yield 98% (96.9 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 88-90 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.53-7.51 (comp, 2H), 7.49-7.48 (m, 1H), 7.41 (app dd, *J* = 7.5, 1.1 Hz, 1H), 7.39-7.38 (m, 1H), 7.37-7.36 (m, 1H), 7.30-7.26 (m, 1H), 7.24-7.19 (comp, 5H), 7.17 (app dd, *J* = 7.9, 1.6 Hz, 1H), 7.08-7.04 (comp, 2H), 7.00 (app d, *J* = 7.6 Hz, 1H), 6.94 (app td, *J* = 7.7, 1.5

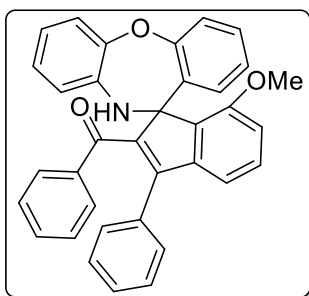
Hz, 1H), 6.89-6.85 (m, 1H), 6.84-6.80 (m, 1H), 6.66-6.64 (m, 1H), 6.45 (app dd, $J = 9.9, 3.1$ Hz, 1H), 4.44 (br s, 1 N-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.6, 159.6, 157.2, 152.6 (d, $J = 2.1$ Hz), 152.1, 151.3, 147.1, 146.7, 140.9, 137.9, 137.4, 132.6, 132.1, 129.4 (d, $J = 6.9$ Hz), 129.1, 129.0, 128.8, 128.7, 128.4, 127.6, 124.6, 124.5, 123.9, 123.3, 123.2, 123.1, 120.8, 115.4 (d, $J = 23.2$ Hz), 114.7 (d, $J = 24.5$ Hz), 75.6; ^{19}F NMR (376 MHz, CDCl_3) δ -119.76; HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{23}\text{FNO}_2$ [$\text{M} + \text{H}$] $^+$ 496.1713, found 496.1735.

(2,8-dichloro-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4j):



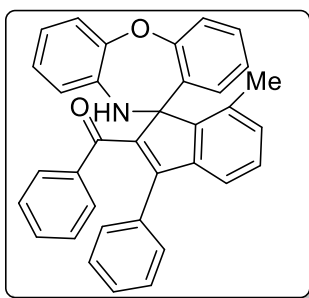
Yield 59% (64.4 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 202-204 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (app d, $J = 7.6$ Hz, 1H), 7.49-7.42 (comp, 3H), 7.37-7.33 (comp, 3H), 7.25-7.20 (comp, 4H), 7.18-7.12 (comp, 3H), 7.11-7.09 (m, 1H), 7.07-7.05 (m, 1H), 7.04 (app d, $J = 7.2$ Hz, 1H), 6.83 (app dd, $J = 8.5, 2.4$ Hz, 1H), 6.69 (app d, $J = 2.0$ Hz, 1H), 6.61 (app d, $J = 2.4$ Hz, 1H), 4.47 (br s, 1 N-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.5, 154.8, 150.6, 149.1, 146.7, 146.5, 140.8, 138.8, 137.0, 132.5, 132.4, 129.3, 129.3, 129.2, 129.0, 128.9 (x 4), 128.9, 128.6, 128.4, 128.1, 127.7, 124.4, 123.2, 123.0, 122.7, 121.8, 75.4; HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{22}\text{Cl}_2\text{NO}_2$ [$\text{M} + \text{H}$] $^+$ 546.1028, found 546.1023.

(7'-methoxy-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4k):



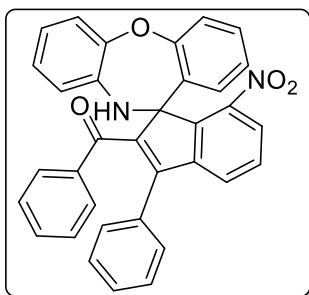
Yield 99% (100.8 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 234-236 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.52-7.49 (m, 2H), 7.40 (app d, $J = 8.0$ Hz, 1H), 7.37-7.34 (comp, 2H), 7.22-7.16 (comp, 6H), 7.10-7.02 (comp, 4H), 6.90-6.85 (comp, 2H), 6.81-6.76 (comp, 2H), 6.74-6.70 (m, 1H), 6.63-6.61 (m, 1H), 4.60 (br s, 1 N-H), 3.47 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.7, 156.8, 155.4, 150.7, 148.6, 143.2, 138.9, 137.4, 136.8, 133.0, 132.0, 130.6, 129.2, 128.9, 128.6, 128.4, 128.2 (x 2), 127.4 (x 2), 127.1, 124.2, 123.5, 122.4, 122.0, 121.6, 120.6, 115.2, 112.0, 76.0, 55.5; HRMS (ESI, m/z) calcd for $\text{C}_{35}\text{H}_{26}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$ 508.1913, found 508.1904.

(7'-methyl-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4l):



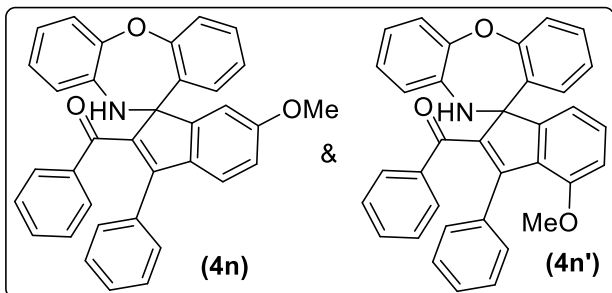
Yield 98% (96.3 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 184-186 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.39-7.37 (comp, 2H), 7.33-7.29 (comp, 4H), 7.22-7.14 (comp, 7H), 7.06-7.04 (m, 1H), 7.01-6.97 (comp, 2H), 6.88-6.84 (m, 1H), 6.74-6.71 (comp, 2H), 6.52-6.48 (m, 1H), 6.44-6.42 (m, 1H), 4.04 (br s, 1 N-H), 2.27 (s, 3H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 194.4 , 156.0 , 150.1 , 149.10, 148.8 , 145.1 , 141.4 , 138.0 , 137.1 , 135.9 , 133.1 , 131.8 , 131.1 , 129.1 , 129.0 , 128.8 , 128.6 , 128.4 , 128.3 , 127.9 , 127.3 , 125.8 , 124.1 , 123.3 , 122.8 , 121.7 , 121.6, 120.7 , 120.0 , 76.8 , 18.0; **HRMS** (ESI, m/z) calcd for C₃₅H₂₆NO₂ [M + H]⁺ 492.1964, found 492.1963.

(7'-nitro-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4m):



Yield 90% (94.1 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 186-188 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.98 (app d, *J* = 8.0 Hz, 1H), 7.74 (app d, *J* = 7.6 Hz, 1H), 7.60 (m, 1H), 7.41-7.39 (comp, 2H), 7.33-7.29 (comp, 2H), 7.23-7.18 (comp, 6H), 7.09-7.07 (m, 1H), 7.04-7.00 (comp, 2H), 6.90-6.86 (m, 1H), 6.84-6.80 (m, 1H), 6.69- 6.67 (m, 1H), 6.59-6.52 (comp, 2H), 4.80 (br s, 1 N-H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 193.3 , 156.2 , 152.0 , 150.3 , 145.7 , 145.2 , 144.0 , 141.9 , 137.1 , 136.6 , 132.4 , 131.9 , 130.6 , 129.2 , 129.1 , 129.0 , 128.7 (x 2) , 128.6 , 127.5 , 127.2 , 126.6 , 125.9 , 124.3 , 123.9 , 123.9 , 123.6 , 122.2 , 120.8 , 77.7; **HRMS** (ESI, m/z) calcd for C₃₄H₂₃N₂O₄ [M + H]⁺ 523.1658, found 523.1643.

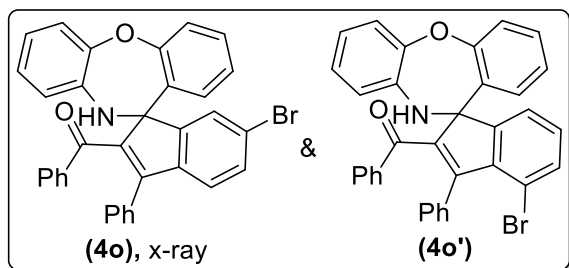
(6'-methoxy-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4n) and (4'-methoxy-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4n'):



Combined Yield 99% (109.3 mg, regioisomeric ratio of **4n** : **4n'** = 1.2:1); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 76-78 °C; **Combined ¹H NMR** (400 MHz, CDCl₃) δ 7.46-7.43 (comp, 4H), 7.41 (app d, *J* = 8.4 Hz, 1H), 7.37-7.34 (comp, 3H), 7.30 (app dd, *J* = 8.2, 1.2 Hz, 1H), 7.24-7.22 (comp, 3H), 7.20-7.19 (comp, 3H), 7.18-7.16 (comp, 4H), 7.16-7.14 (comp, 2H), 7.11-7.08 (comp, 3H), 7.04-7.02 (comp, 3H), 7.01-6.97 (comp, 2H), 6.92-6.89 (comp, 3H), 6.88-6.86 (comp, 3H), 6.85-6.84 (m, 1H), 6.82-6.78

(comp, 2H), 6.74 (app d, $J = 6.9$ Hz, 1H), 6.66-6.62 (comp, 2H), 6.44 (app d, $J = 2.1$ Hz, 1H), 4.60 (br s, 1 N-H), 4.36 (br s, 1 N-H), 3.66 (s, 3H), 3.64 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.0, 194.3, 160.6, 156.2, 156.0, 155.7, 154.1, 154.1, 154.1, 153.1, 151.8, 148.6, 148.6, 147.6, 147.5, 146.3, 146.3, 145.1, 145.0, 138.0, 137.9, 137.6, 134.5, 133.4, 133.1, 131.7, 131.6, 130.2, 129.6, 129.2, 129.0 (x 3), 128.9, 128.8, 128.7, 128.6, 128.5, 128.2, 127.9, 127.7, 127.7, 127.4, 127.4, 126.9, 125.0, 124.4, 124.1, 123.6, 123.4, 122.0, 121.9, 120.9, 120.8, 117.2, 114.6, 112.0, 110.3, 75.6, 75.4, 55.4, 55.3; HRMS (ESI, m/z) calcd for $\text{C}_{35}\text{H}_{26}\text{NO}_3$ [$\text{M} + \text{H}$] $^+$ 508.1913, found 508.1915.

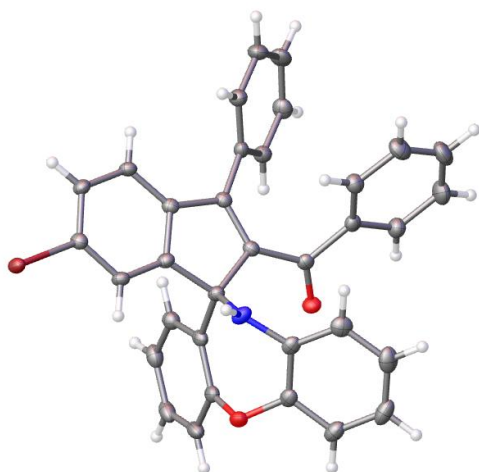
(6'-bromo-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4o) and (4'-bromo-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4o')



Combined Yield 93% (103.6 mg, regioisomeric ratio of **4o** : **4o'** = 5:1); **Yellow solid**; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 158-160 °C (crystallization from DCM/hexane bilayer mixture using solvent evaporation method); ^1H NMR

of 4o, after x-ray (400 MHz, CDCl_3) δ 7.51 (app dd, $J = 8.1, 1.8$ Hz, 1H), 7.47-7.44 (comp, 2H), 7.37-7.33 (comp, 3H), 7.28-7.24 (m, 1H), 7.23-7.17 (comp, 6H), 7.09-7.02 (comp, 3H), 6.97 (td, $J = 7.7, 1.5$ Hz, 1H), 6.91-6.88 (m, 1H), 6.87-6.84 (m, 1H), 6.78 (app dd, $J = 7.9, 1.6$ Hz, 1H), 6.67 (app d, $J = 7.5$ Hz, 1H), 4.52 (br s, 1 N-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.4, 156.4, 153.5, 152.4, 147.1, 146.1, 140.0, 137.6, 137.3, 132.4, 132.2, 131.7, 129.1, 129.0 (x 4), 128.6, 128.4, 128.0, 127.6, 126.6, 124.6, 124.2, 124.2, 123.6, 122.7, 122.2, 121.0, 75.8; HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{23}\text{BrNO}_2$ [$\text{M} + \text{H}$] $^+$ 556.0912, found 556.0933.

Figure S5. X-ray crystal structure of **4o** (ellipsoid contour at 50% probability level)

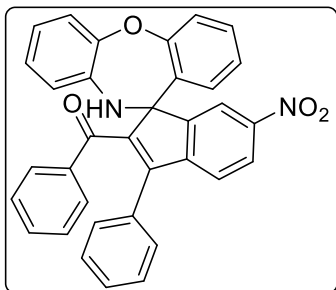


Crystal data and structure refinement for 4o, CCDC No. 2226415

Empirical formula	C ₃₄ H ₂₂ BrNO ₂
Formula weight	556.43
Temperature/K	100.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	11.7008(2)
b/Å	13.1668(3)
c/Å	17.7959(3)
α/°	90
β/°	106.2500(10)
γ/°	90
Volume/Å ³	2632.14(9)
Z	4
ρ _{calc} /cm ³	1.404
μ/mm ⁻¹	2.379
F(000)	1136.0
Crystal size/mm ³	0.35 × 0.25 × 0.2
Radiation	Cu Kα (λ = 1.54178)
2θ range for data collection/°	7.87 to 130.102
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	45439
Independent reflections	4432 [R _{int} = 0.0442, R _{sigma} = 0.0271]
Data/restraints/parameters	4432/0/343
Goodness-of-fit on F ²	1.069
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0325, wR ₂ = 0.0850
Final R indexes [all data]	R ₁ = 0.0328, wR ₂ = 0.0853

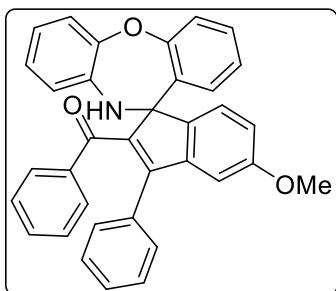
Largest diff. peak/hole / e Å⁻³ 0.61/-0.76

(6'-nitro-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4p):



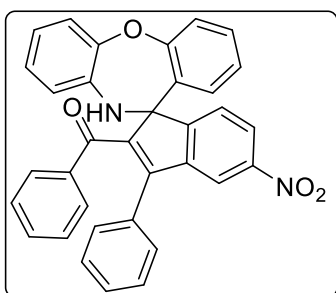
Yield 77% (80.5 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 226-228 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.28 (app dd, *J* = 8.4, 2.1 Hz, 1H), 7.76 (app d, *J* = 2.0 Hz, 1H), 7.63 (app d, *J* = 8.4 Hz, 1H), 7.51-7.48 (comp, 2H), 7.39-7.37 (comp, 2H), 7.29-7.24 (comp, 5H), 7.23-7.18 (comp, 2H), 7.10-7.06 (comp, 2H), 7.02-6.98 (m, 1H), 6.91-6.85 (comp, 2H), 6.77 (app dd, *J* = 7.9, 1.5 Hz, 1H), 6.65 (app d, *J* = 7.6 Hz, 1H), 4.60 (br s, 1 N-H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 194.2, 156.7, 155.9, 152.7, 152.3, 151.2, 147.6, 147.5, 144.3, 137.2, 136.7, 132.7, 131.7, 129.5, 129.4, 129.1, 128.8, 128.7, 128.3, 127.8, 125.4, 125.0, 124.7, 124.2, 123.8, 123.0, 122.5, 121.2, 119.8, 75.8; **HRMS** (ESI, *m/z*) calcd for C₃₄H₂₃N₂O₄ [M + H]⁺ 523.1658, found 523.1644.

(5'-methoxy-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4q):



Yield 92% (93.2 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 194-196 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.49-7.47 (comp, 2H), 7.38-7.36 (comp, 2H), 7.25-7.22 (comp, 2H), 7.21-7.18 (comp, 3H), 7.17-7.14 (comp, 2H), 7.06-7.02 (comp, 3H), 6.93 (app d, *J* = 8.2 Hz, 1H), 6.91-6.89 (m, 1H), 6.88-6.85 (m, 1H), 6.82-6.78 (comp, 3H), 6.65 (app d, *J* = 7.5 Hz, 1H), 4.45 (br s, 1 N-H), 3.82 (s, 3H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 194.7, 160.3, 156.4, 151.7, 148.5, 146.1, 144.0, 142.6, 138.1, 137.4, 132.8, 132.0, 129.1, 128.9, 128.8, 128.7, 128.6, 128.3, 127.8, 127.5, 125.3, 124.4, 123.6, 123.5, 123.4, 121.9, 120.8, 113.3, 108.9, 75.4, 55.6; **HRMS** (ESI, *m/z*) calcd for C₃₅H₂₆NO₃ [M + H]⁺ 508.1913, found 508.1911.

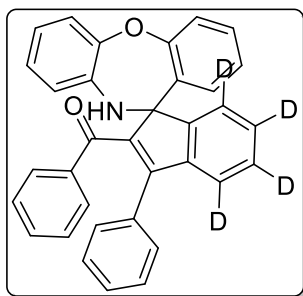
(5'-nitro-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4r):



Yield 95% (99.3 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 246-248 °C; **¹H NMR** (400 MHz, CDCl₃) δ 8.32 (app d, *J* = 2.0 Hz, 1H), 8.11 (app dd, *J* = 8.3, 2.1 Hz, 1H), 7.53-7.48 (comp, 2H), 7.43-7.38 (comp, 2H), 7.31-7.27 (comp, 4H), 7.25-7.18 (comp, 3H), 7.11-7.06 (comp, 2H), 7.01 (app d, *J* = 8.3 Hz, 2H), 6.92-6.89 (m, 1H), 6.89-6.86 (m, 1H), 6.76

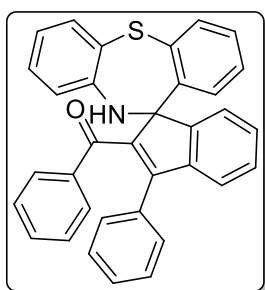
(app dd, $J = 7.9, 1.6$ Hz, 1H), 6.68 (app d, $J = 7.7$ Hz, 1H), 4.71 (br s, 1 N-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.1, 157.8, 156.3, 152.8, 148.7, 144.9, 142.8, 137.3, 136.9, 132.6, 131.6, 129.5, 129.3, 129.1, 128.8 (x 3), 128.6, 127.8, 125.4, 125.0, 124.9, 124.7, 124.5, 123.9, 123.8, 122.5, 121.1, 117.8, 75.7; HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{23}\text{N}_2\text{O}_4$ $[\text{M} + \text{H}]^+$ 523.1658, found 523.1649.

phenyl(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]oxazepine-11,1'-inden]-2'-yl-4',5',6',7'-*d*₄)methanone (4s):



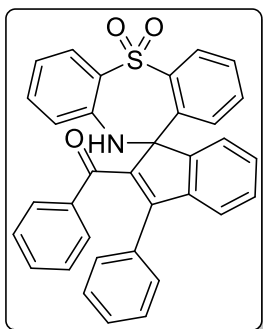
Yield 99% (95.7 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 150-152 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.47 (comp, 2H), 7.40-7.37 (comp, 2H), 7.27-7.23 (m, 1H), 7.22-7.15 (comp, 6H), 7.06-7.02 (comp, 2H), 6.96-6.91 (m, 1H), 6.88-6.80 (comp, 2H), 6.78 (app dd, $J = 7.9, 1.6$ Hz, 1H), 6.66 (app d, $J = 7.4$ Hz, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 194.8, 156.4, 152.1, 151.7, 147.2-147.1 (m), 147.0-146.8 (m), 141.0, 138.1-137.8 (m), 137.5, 132.9, 132.0, 129.1 (x 2), 129.0 (x 2), 128.8, 128.7, 128.7, 128.3 (x 2), 127.5 (x 2), 127.4, 124.5, 123.9, 123.8, 123.5, 122.0, 120.9, 75.9; HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{20}\text{D}_4\text{NO}_2$ $[\text{M} + \text{H}]^+$ 482.2058, found 482.2043.

phenyl(3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]thiazepine-11,1'-inden]-2'-yl)methanone (4t):



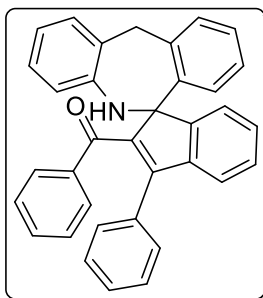
Yield 75% (74.0 mg); White solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 158-160 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.65-7.63 (m, 1H), 7.55 (app d, $J = 7.6$ Hz, 1H), 7.47 (app dd, $J = 7.8, 1.3$ Hz, 1H), 7.42-7.36 (comp, 5H), 7.21-7.14 (comp, 5H), 7.10-7.10 (comp, 2H), 7.02-6.98 (comp, 3H), 6.94-6.90 (m, 1H), 6.72 (app dd, $J = 7.9, 1.4$ Hz, 2H), 6.55 (app d, $J = 7.3$ Hz, 1H), 5.66 (br s, 1 N-H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) δ 195.2, 152.4, 148.4, 147.4, 147.0, 141.6, 137.9, 137.7, 136.1, 133.8, 132.9, 132.3, 131.7, 131.2, 129.8, 129.4, 129.0, 128.8, 128.7, 128.6, 128.2, 128.2 (x 2), 127.5, 127.0, 126.9, 125.6, 125.3, 123.3, 76.1; HRMS (ESI, m/z) calcd for $\text{C}_{34}\text{H}_{24}\text{NOS}$ $[\text{M} + \text{H}]^+$ 494.1579, found 494.1582.

(5,5-dioxido-3'-phenyl-10*H*-spiro[dibenzo[*b,f*][1,4]thiazepine-11,1'-inden]-2'-yl)(phenyl)methanone (4u):



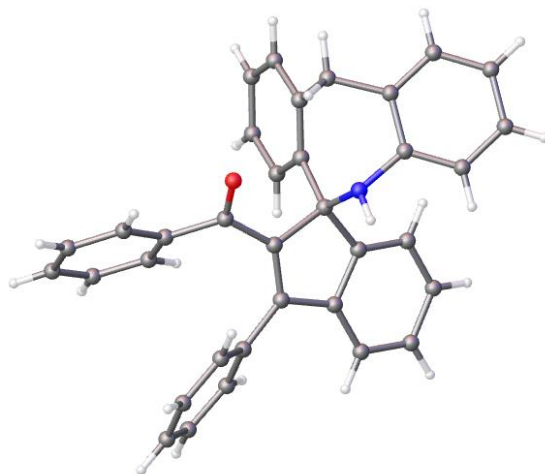
Yield 58% (60.6 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 254-256 °C (crystallization from EtOH/hexane mixture using solvent evaporation method); **¹H NMR** (400 MHz, CDCl₃) δ 8.37 (app dd, *J* = 7.9, 1.5 Hz, 1H), 8.06 (app dd, *J* = 7.7, 1.5 Hz, 1H), 7.54 (app d, *J* = 7.6 Hz, 1H), 7.47-7.45 (comp, 2H), 7.42-7.40 (m, 1H), 7.38-7.32 (comp, 4H), 7.30-7.26 (m, 1H), 7.24-7.12 (comp, 7H), 7.03 (comp, 2H), 6.91 (app dd, *J* = 7.9, 1.1 Hz, 1H), 6.73 (app d, *J* = 7.6 Hz, 1H), 5.35 (br s, 1 N-H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 193.4, 151.5, 149.7, 146.2, 143.4, 140.5, 139.6, 139.2, 139.0, 137.4, 134.0, 133.1, 132.6, 131.9, 129.3 (x 2), 129.2 (x 2), 129.1, 129.0, 129.0, 128.3, 127.6, 127.4, 127.2, 126.7, 125.4, 125.3, 123.5, 77.8; **HRMS** (ESI, *m/z*) calcd for C₃₄H₂₄NO₃S [M + H]⁺ 526.1477, found 526.1479.

phenyl(3'-phenyl-5,11-dihydrospiro[dibenzo[*b,e*]azepine-6,1'-inden]-2'-yl)methanone (4v):



Yield 96% (90.9 mg); Yellow solid; **eluent composition** petroleum ether/ethyl acetate = 9:1; **mp** 174-176 °C; **¹H NMR** (400 MHz, CDCl₃) δ 7.54-7.51 (comp, 3H), 7.43-7.40 (comp, 2H), 7.35 (app td, *J* = 7.5, 1.0 Hz, 1H), 7.28-7.25 (m, 1H), 7.24-7.19 (comp, 5H), 7.16 (app dd, *J* = 7.5, 0.9 Hz, 1H), 7.09-7.00 (comp, 5H), 6.96-6.92 (m, 1H), 6.68-6.64 (comp, 2H), 6.61 (app d, *J* = 7.5 Hz, 1H), 4.87 (d, *J* = 13.6 Hz, 1H), 3.89 (br s, 1 N-H), 3.63 (d, *J* = 13.7 Hz, 1H); **¹³C{¹H} NMR** (100 MHz, CDCl₃) δ 195.2, 154.0, 148.1, 146.9, 143.8, 140.6, 138.9, 138.0, 135.7, 133.1, 131.9, 129.9, 129.1, 129.0 (x 2), 128.8, 128.7, 128.3, 127.8, 127.7 (x 2), 127.6, 127.0, 126.7, 126.3, 124.5, 124.2, 123.7, 122.8, 77.1, 39.9; **HRMS** (ESI, *m/z*) calcd for C₃₅H₂₆NO [M + H]⁺ 476.2014, found 476.2015.

Figure S6. X-ray crystal structure of **4v** (ellipsoid contour at 50% probability level)

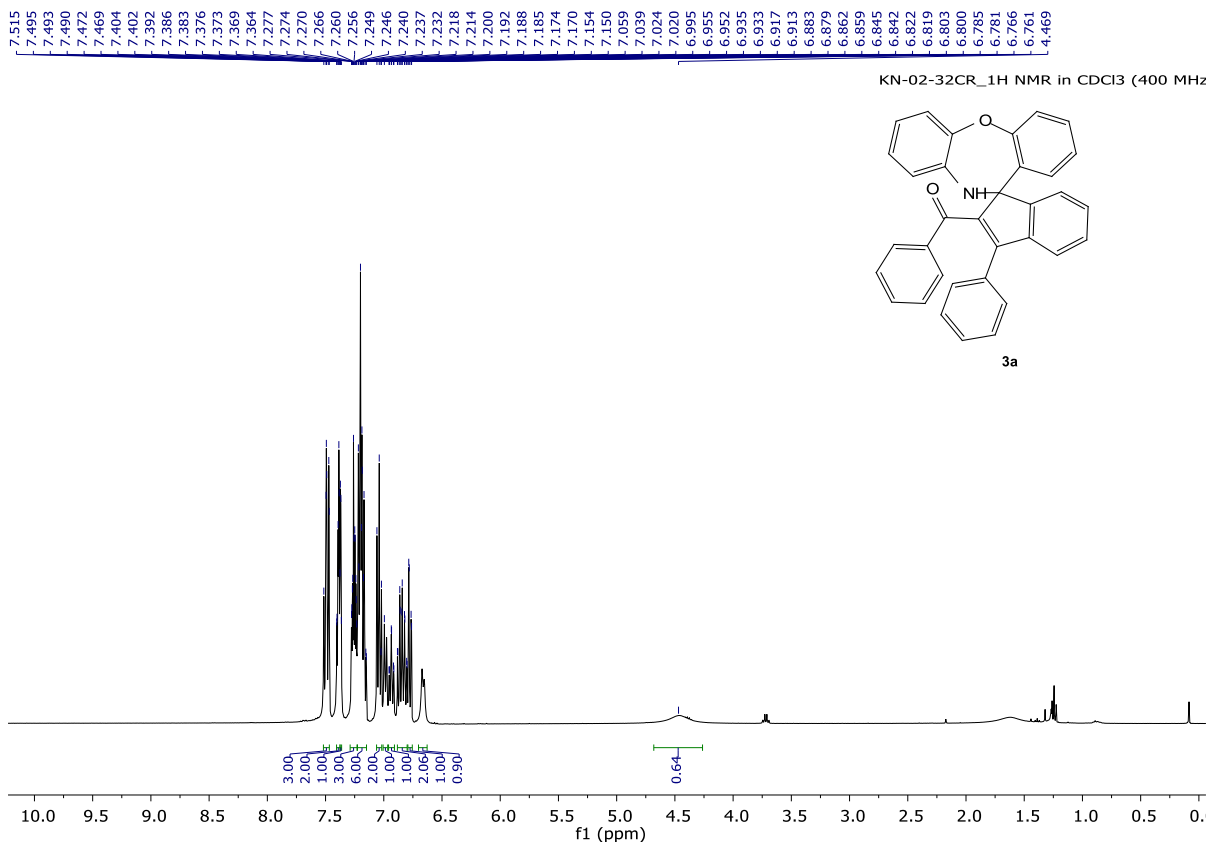


Crystal data and structure refinement for 4v, CCDC No. 2226414

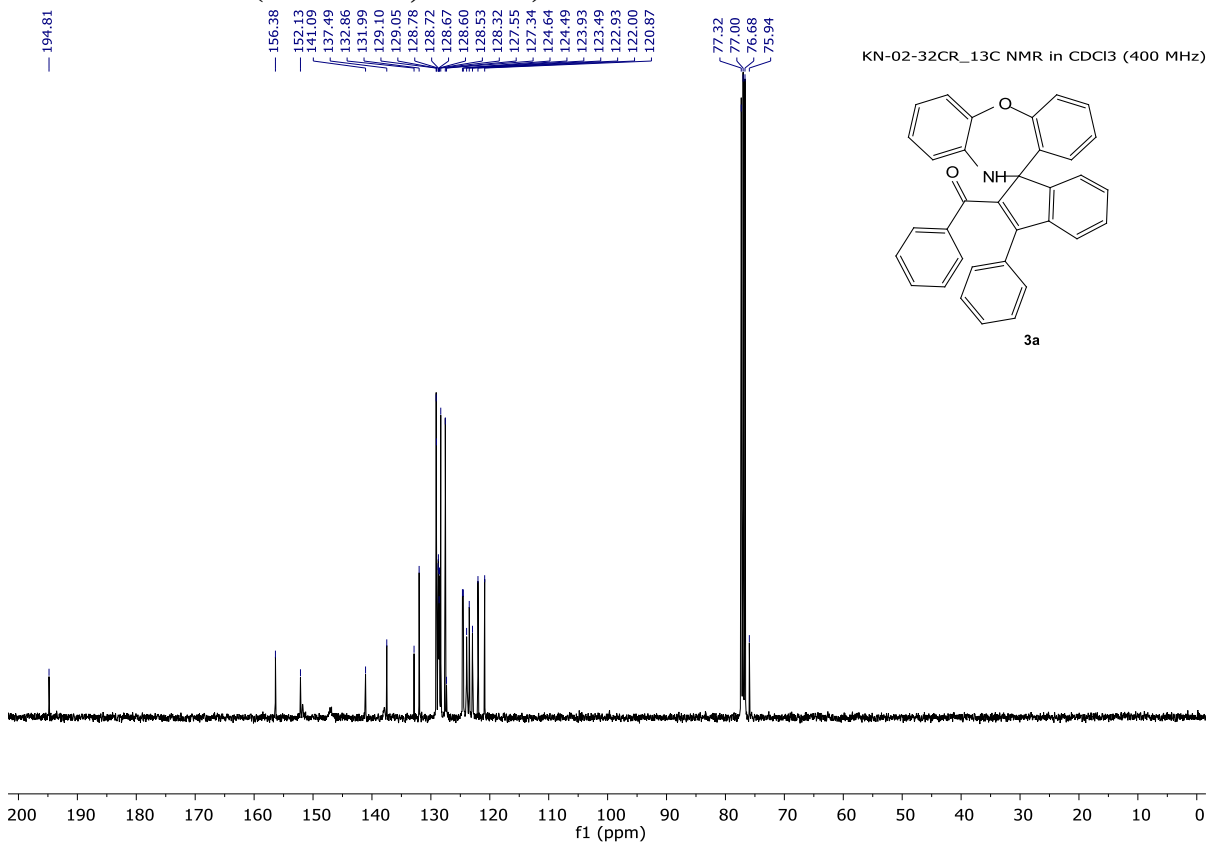
Empirical formula	C ₃₅ H ₂₅ NO
Formula weight	475.56
Temperature/K	100.0
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.8267(12)
b/Å	9.9692(11)
c/Å	24.995(3)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2448.6(5)
Z	4
ρ _{calc} /cm ³	1.290
μ/mm ⁻¹	0.595
F(000)	1000.0
Crystal size/mm ³	0.404 × 0.25 × 0.18
Radiation	Cu Kα (λ = 1.54178)
2θ range for data collection/°	9.55 to 127.28
Index ranges	-11 ≤ h ≤ 11, -11 ≤ k ≤ 11, -29 ≤ l ≤ 28
Reflections collected	45710
Independent reflections	3942 [R _{int} = 0.0576, R _{sigma} = 0.0339]
Data/restraints/parameters	3942/0/335
Goodness-of-fit on F ²	1.142
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0377, wR ₂ = 0.0928
Final R indexes [all data]	R ₁ = 0.0378, wR ₂ = 0.0929
Largest diff. peak/hole / e Å ⁻³	0.22/-0.25
Flack parameter	0.01(8)

¹H and ¹³C NMR of Spirocyclized Products:

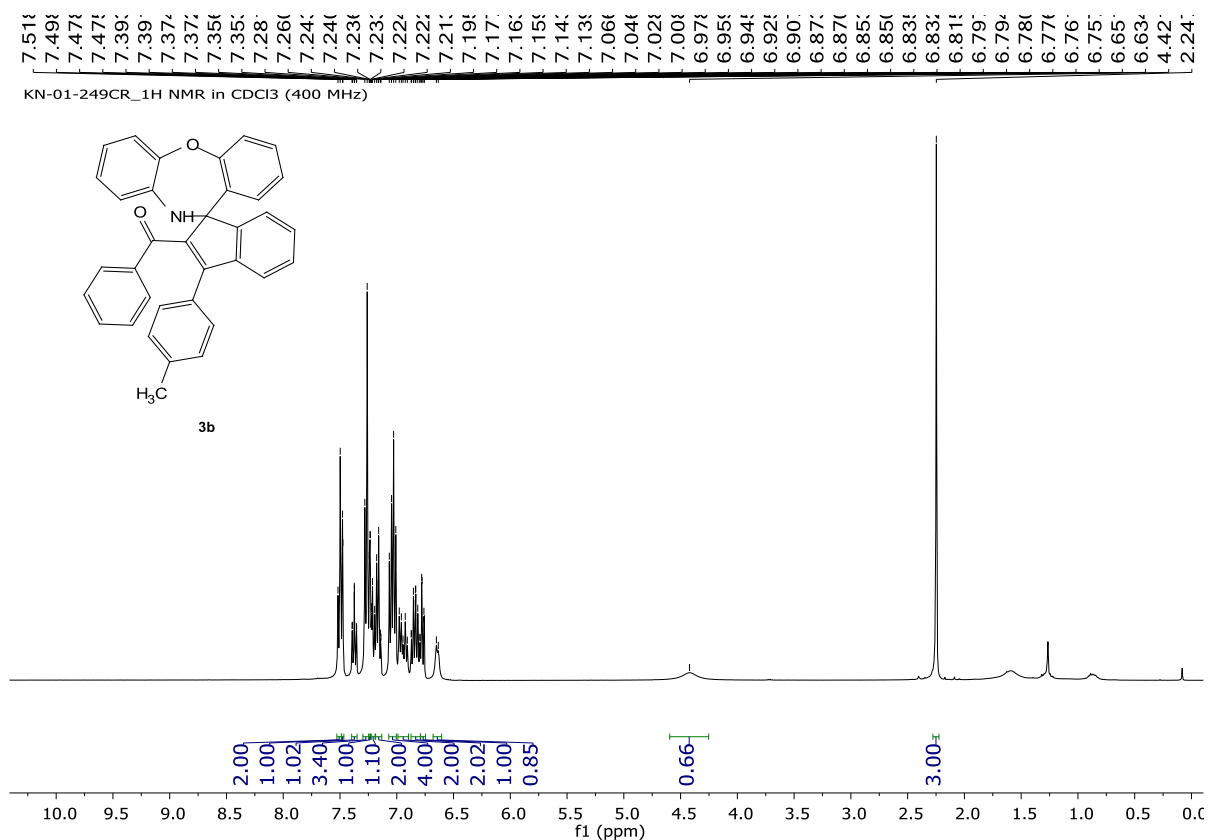
¹H NMR of 3a (400 MHz, CDCl₃):



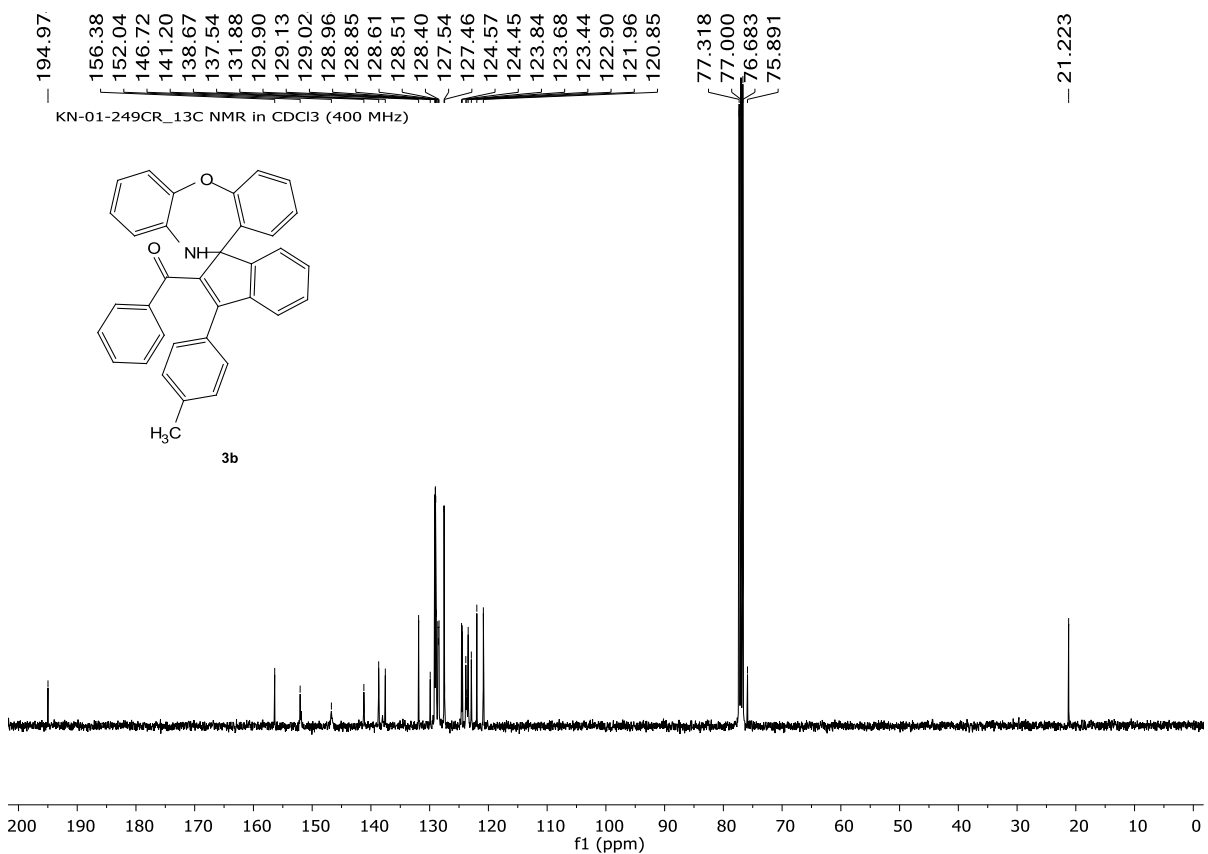
¹³C NMR of 3a (100 MHz, CDCl₃):



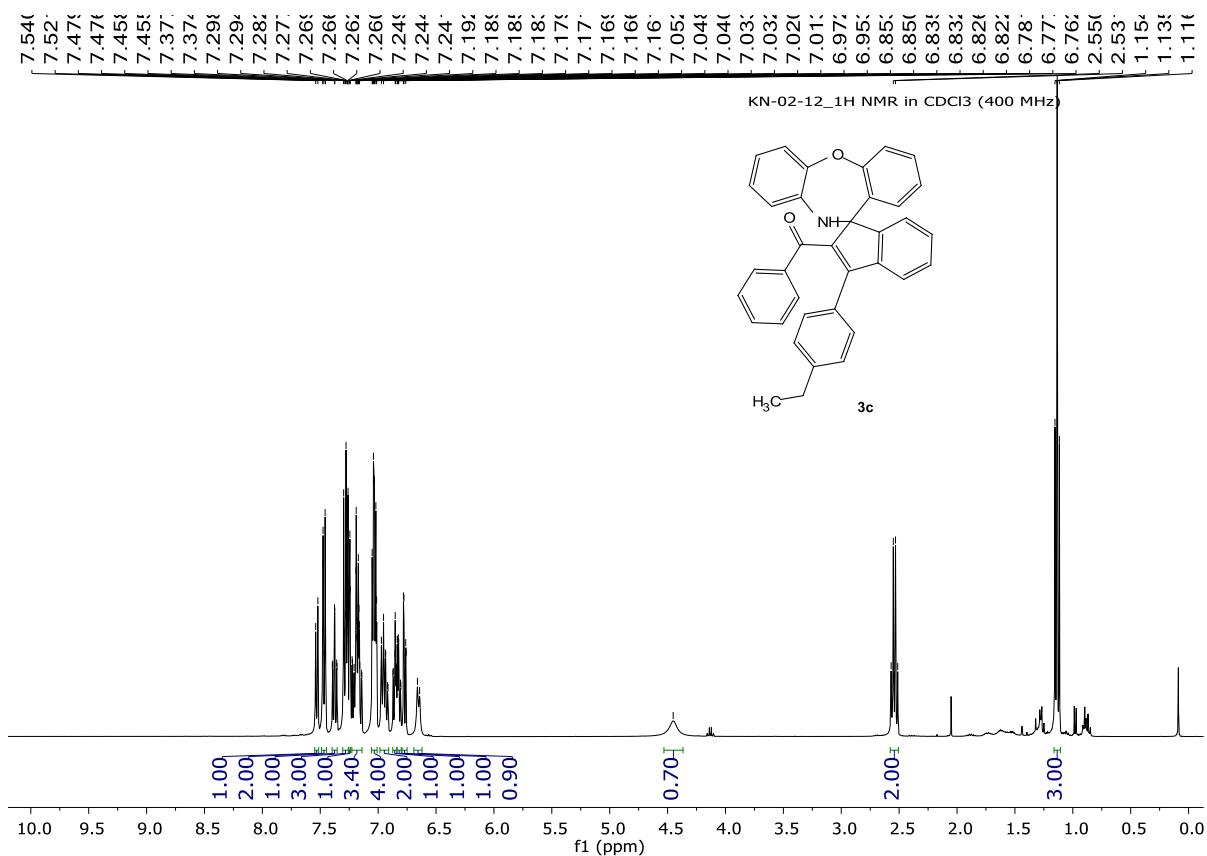
¹H NMR of 3b (400 MHz, CDCl₃):



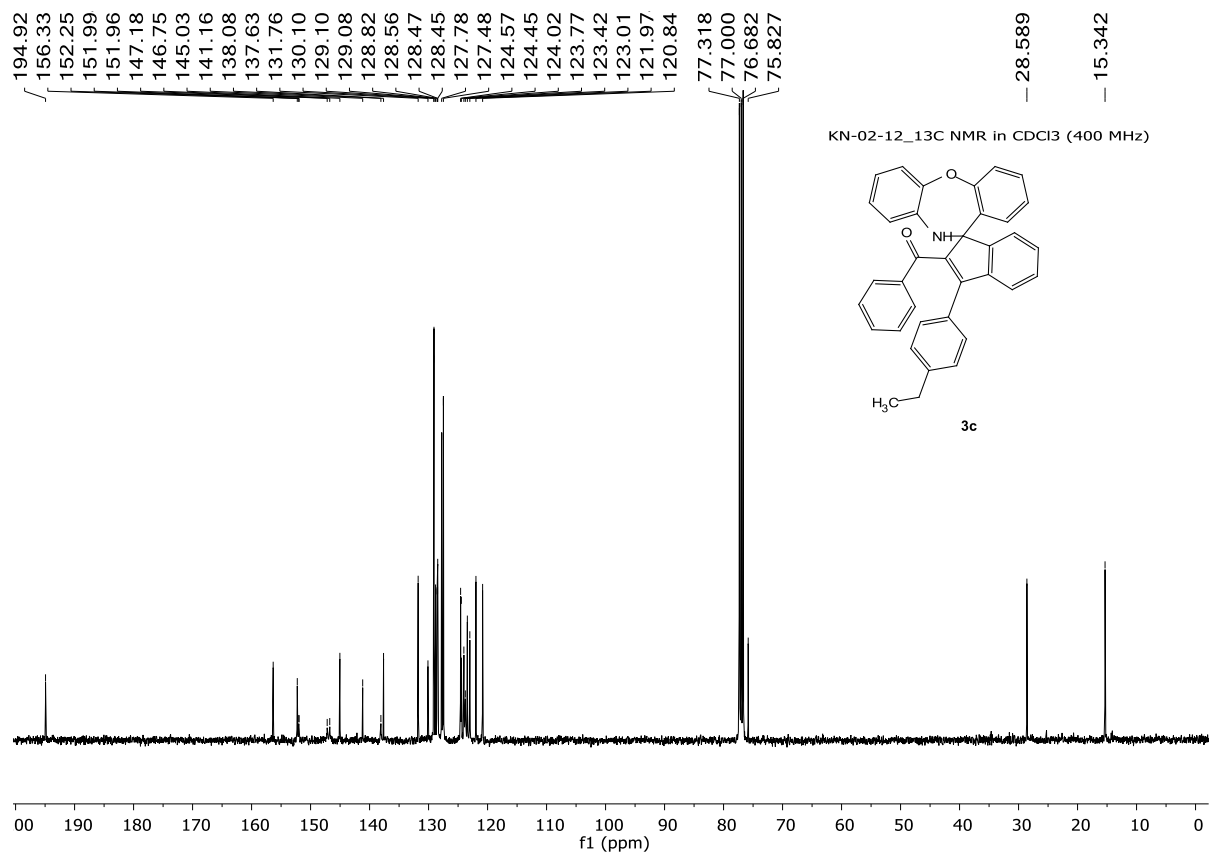
¹³C NMR of 3b (100 MHz, CDCl₃):



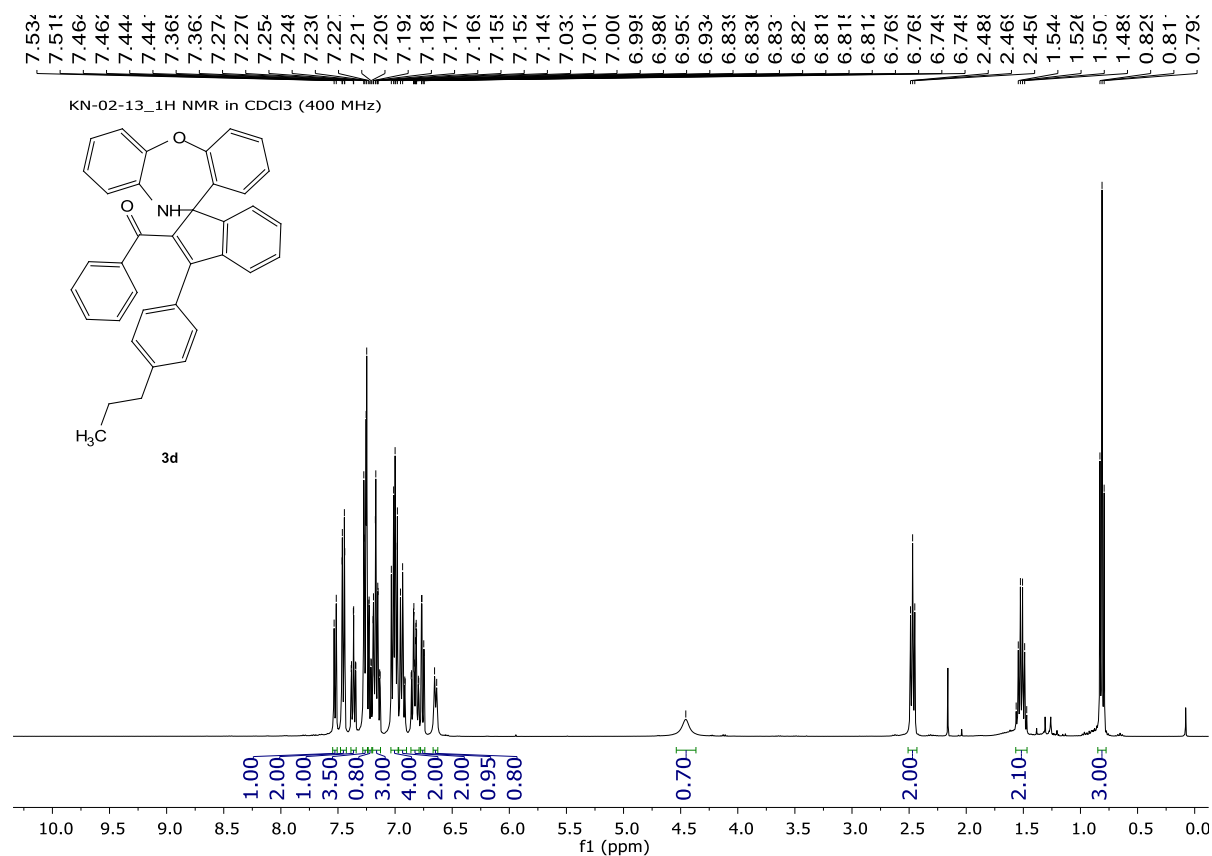
¹H NMR of 3c (400 MHz, CDCl₃):



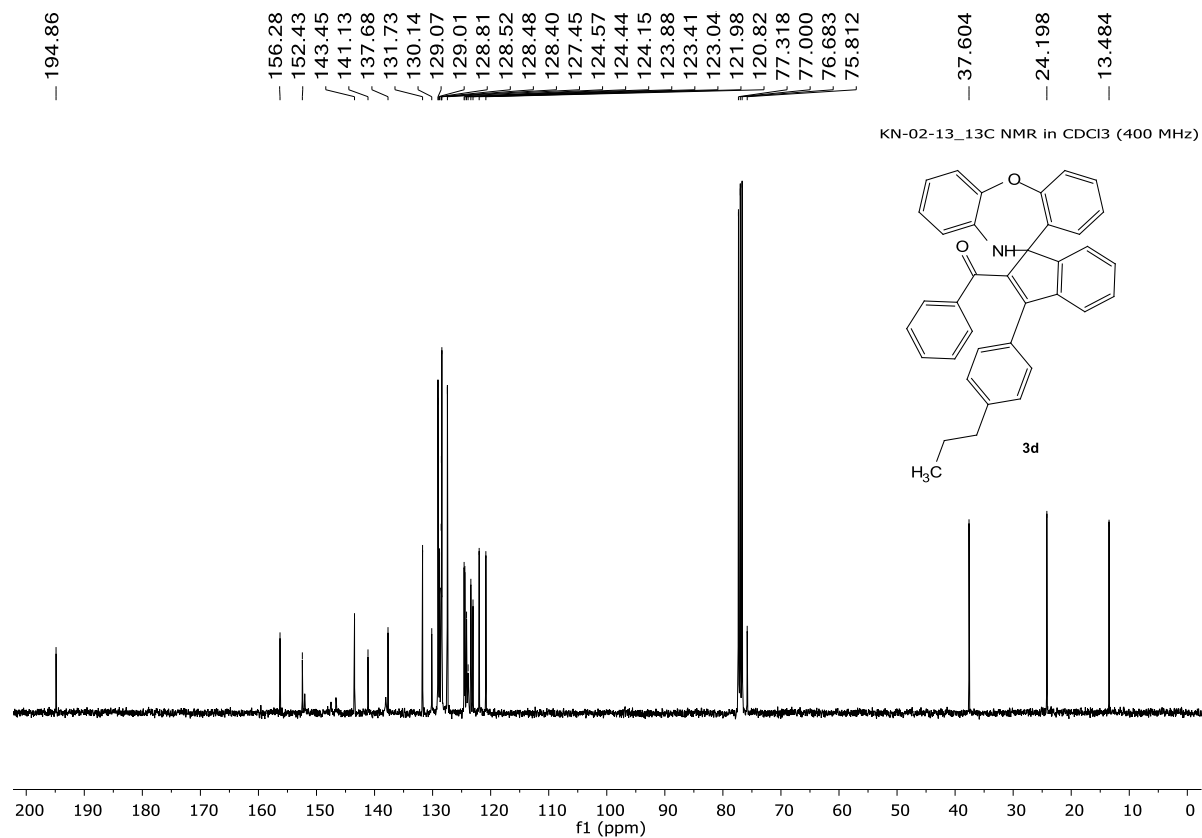
¹³C NMR of 3c (100 MHz, CDCl₃):



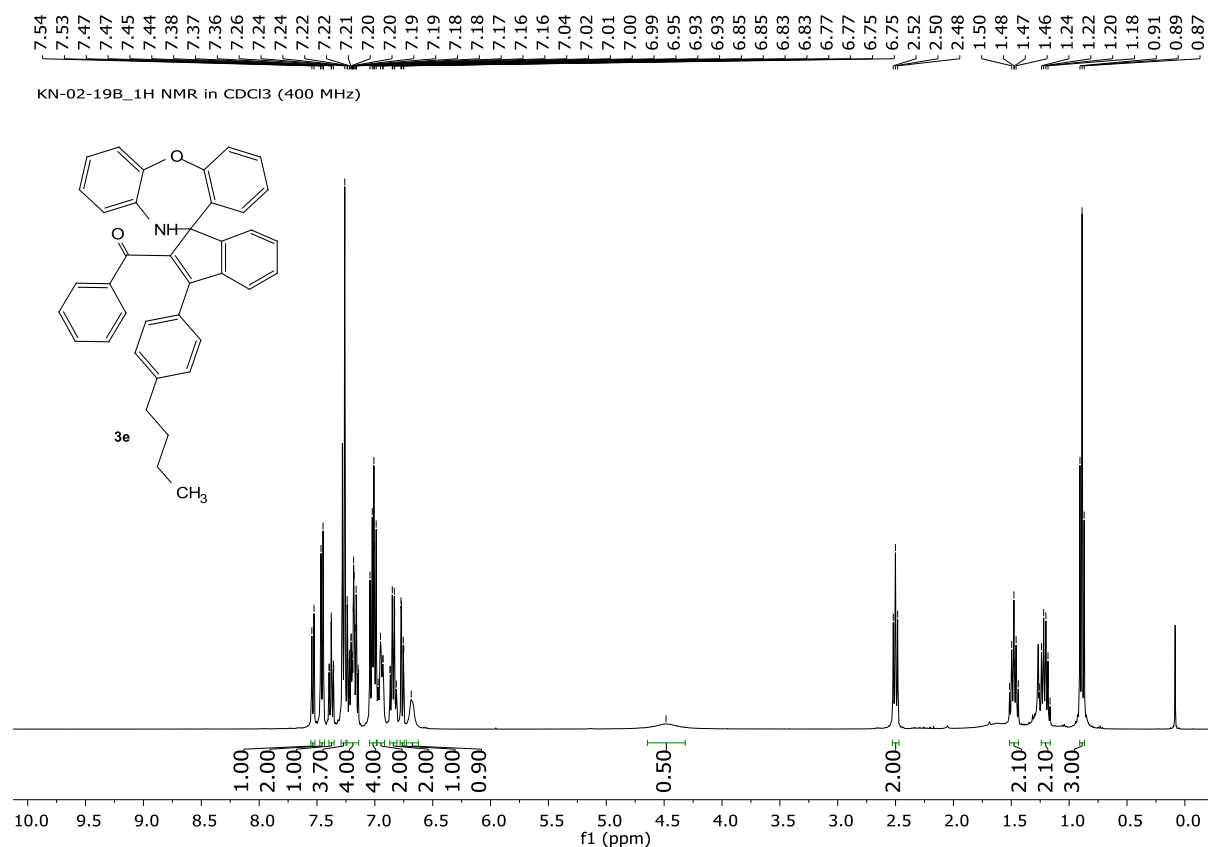
¹H NMR of 3d (400 MHz, CDCl₃):



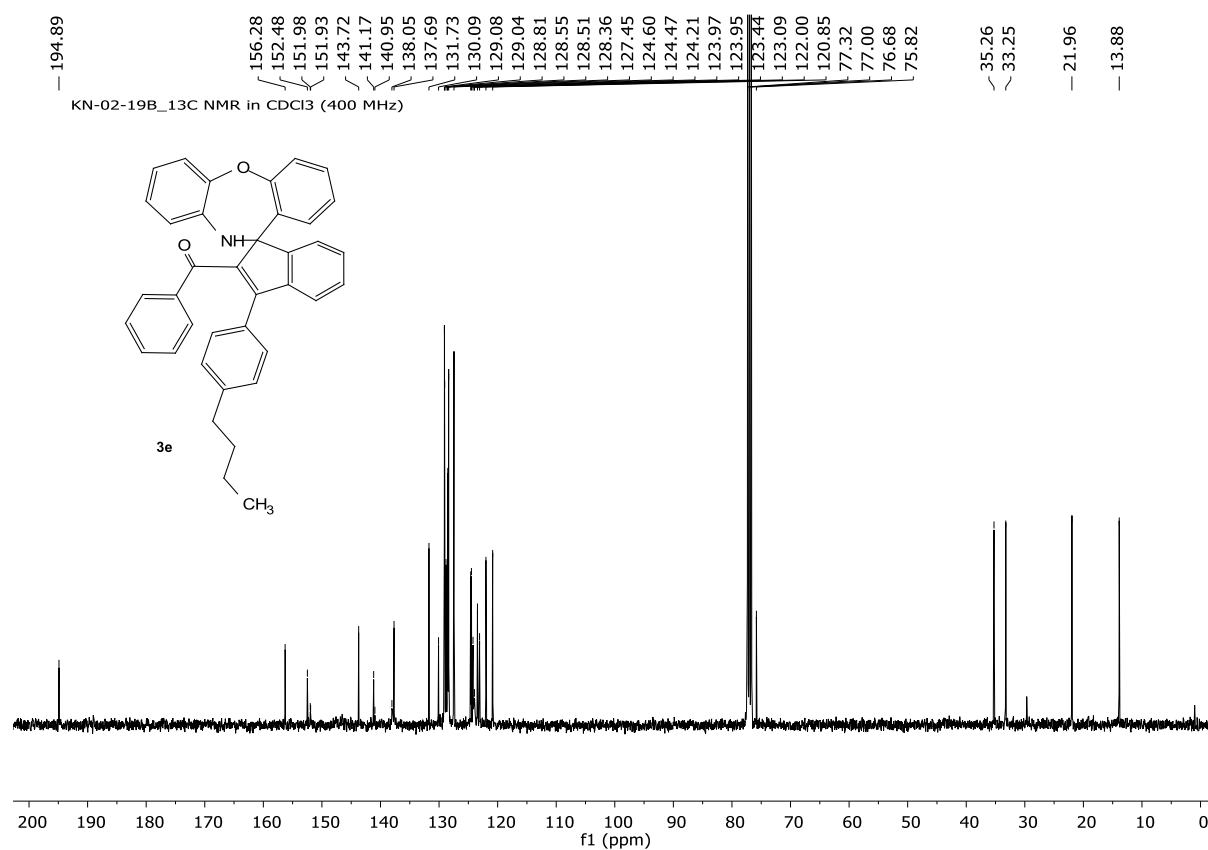
¹³C NMR of 3d (100 MHz, CDCl₃):



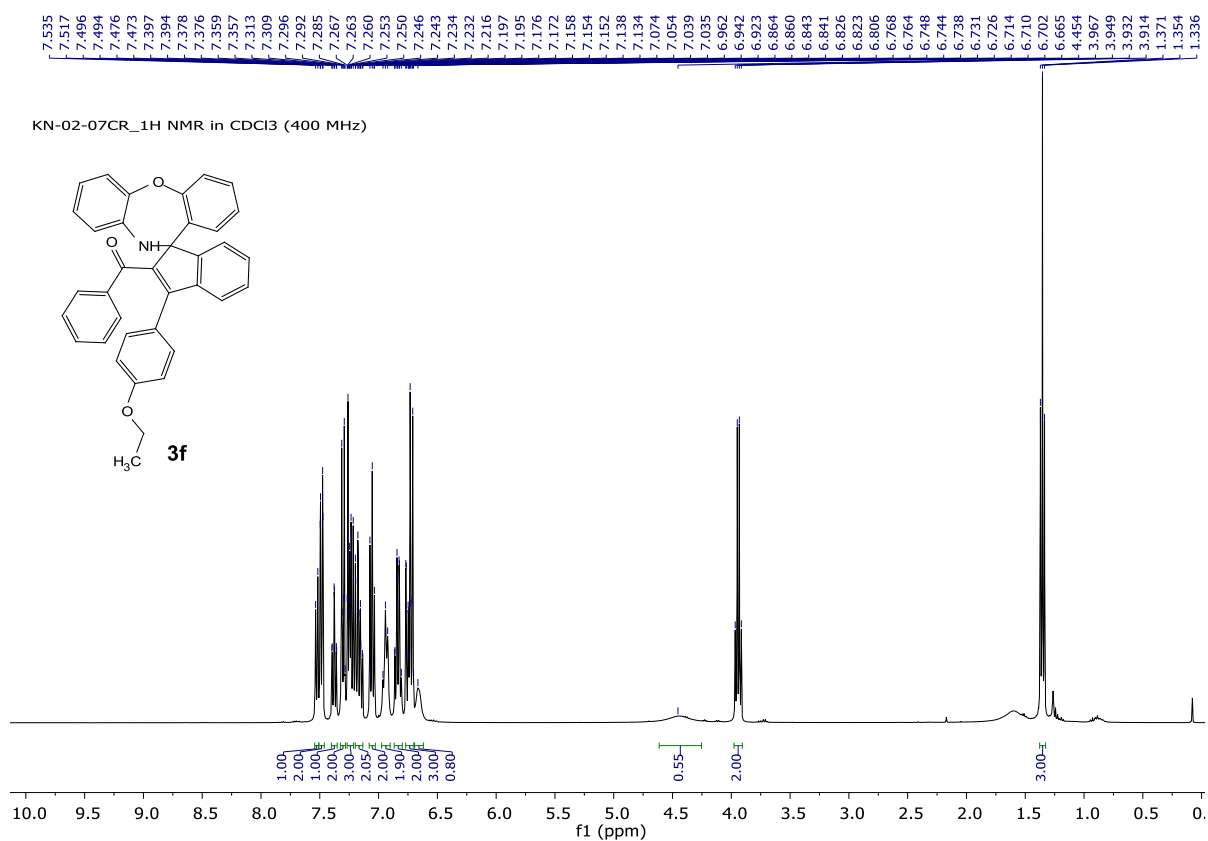
¹H NMR of 3e (400 MHz, CDCl₃):



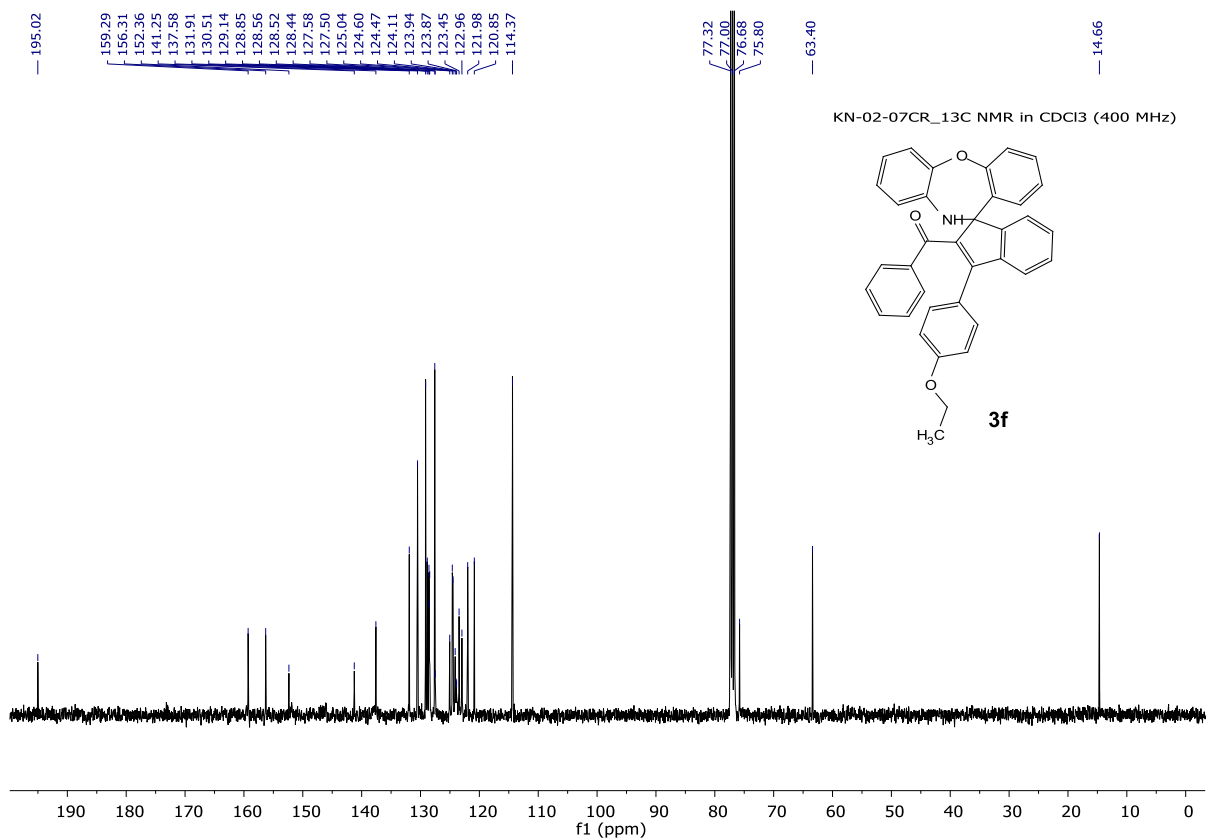
¹³C NMR of 3e (100 MHz, CDCl₃):



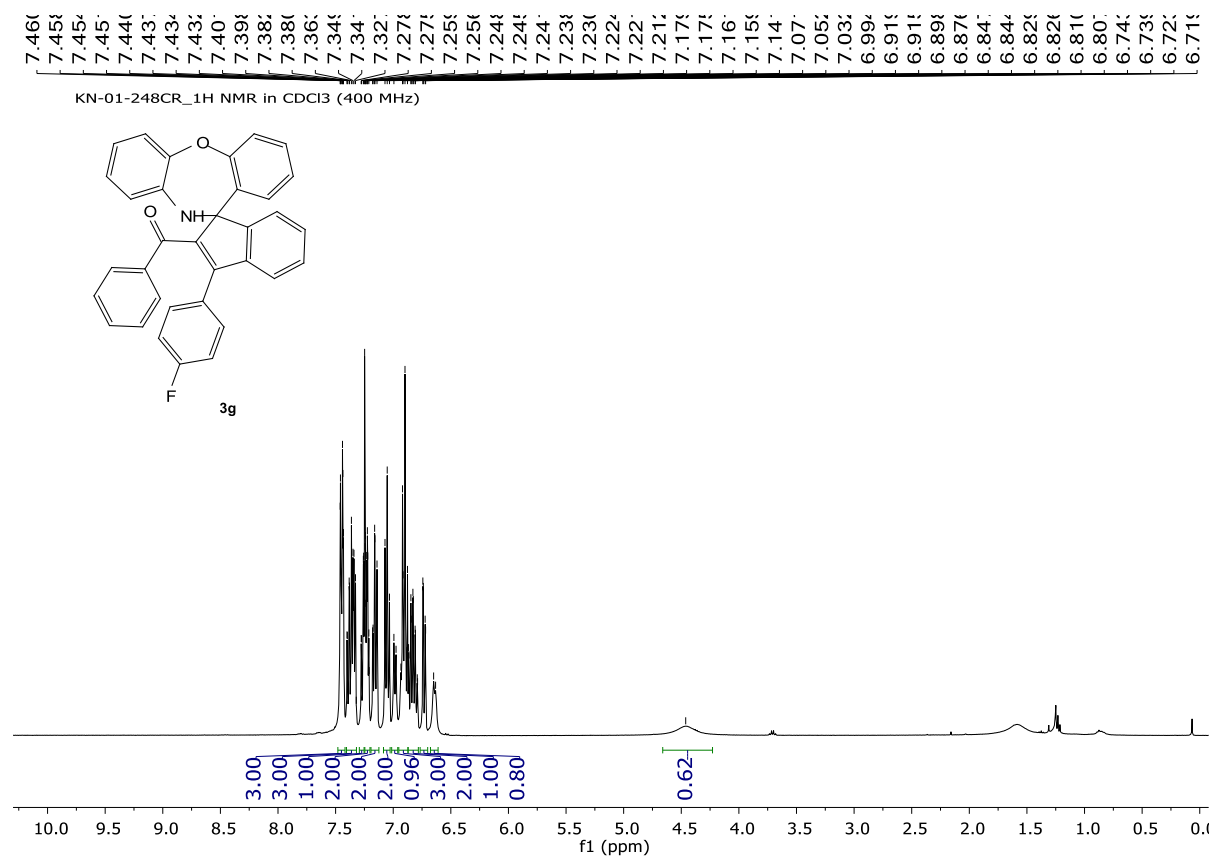
¹H NMR of 3f (400 MHz, CDCl₃):



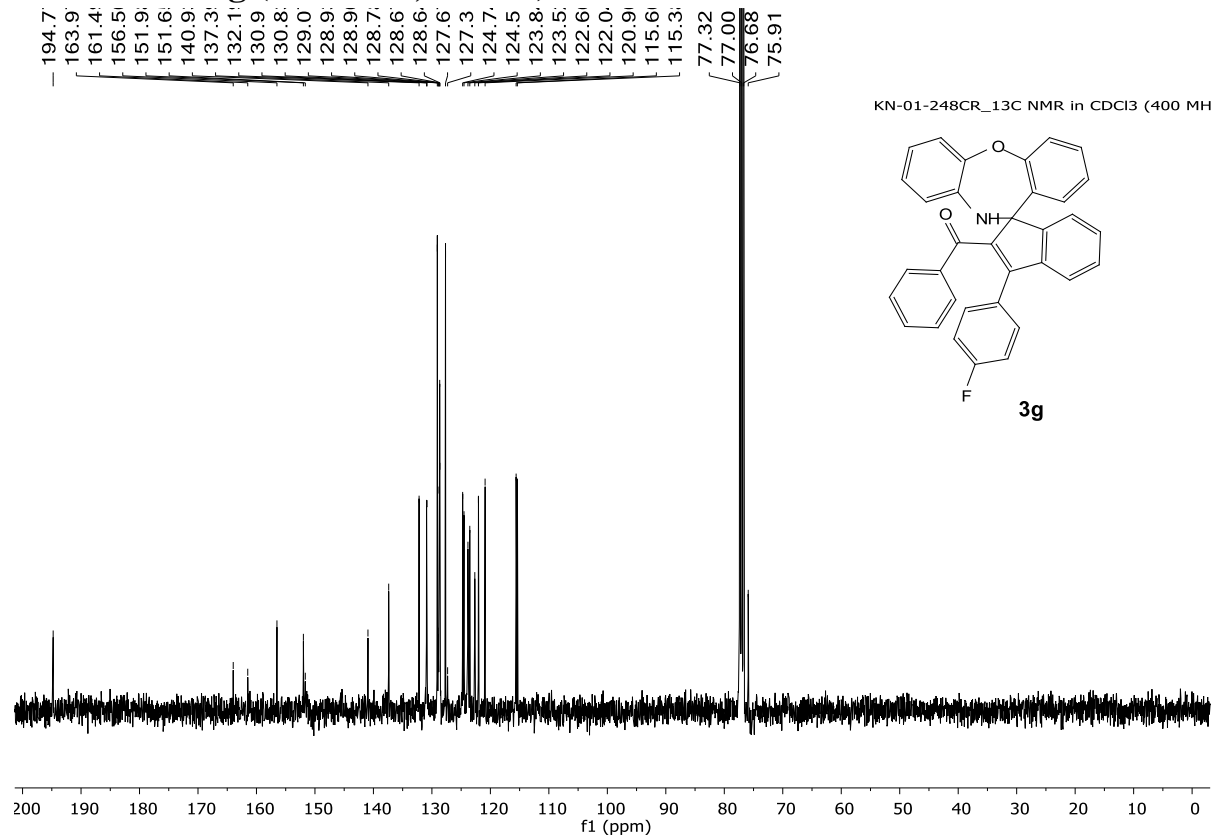
¹³C NMR of 3f (100 MHz, CDCl₃):



¹H NMR of 3g (400 MHz, CDCl₃):

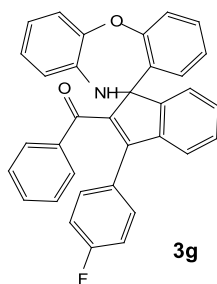


¹³C NMR of 3g (100 MHz, CDCl₃):

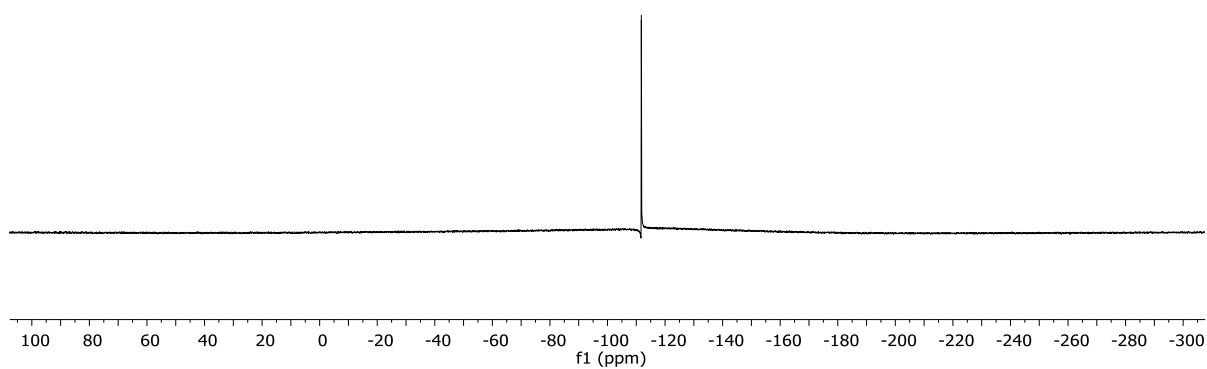


^{19}F NMR of 3g (376 MHz, CDCl_3):

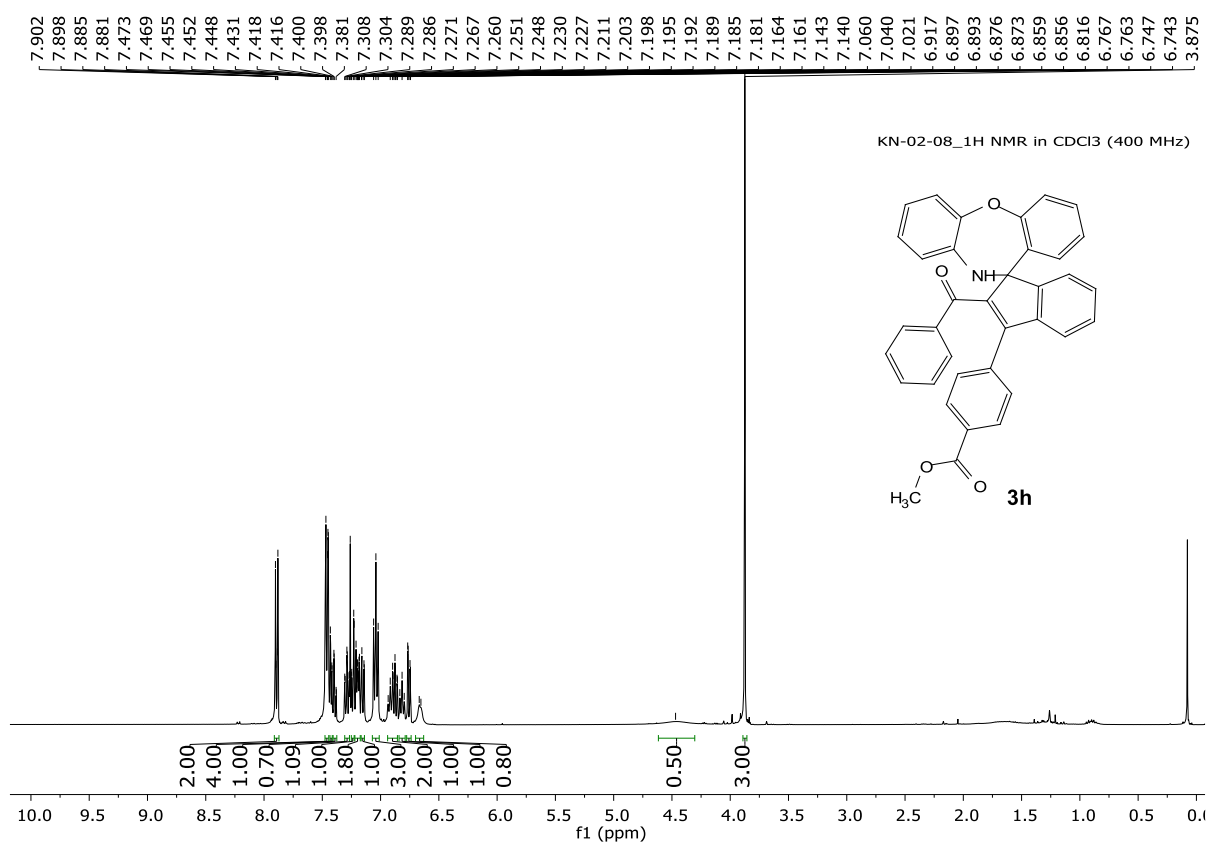
KN-01-248_19F NMR in CDCl_3 (400 MHz)



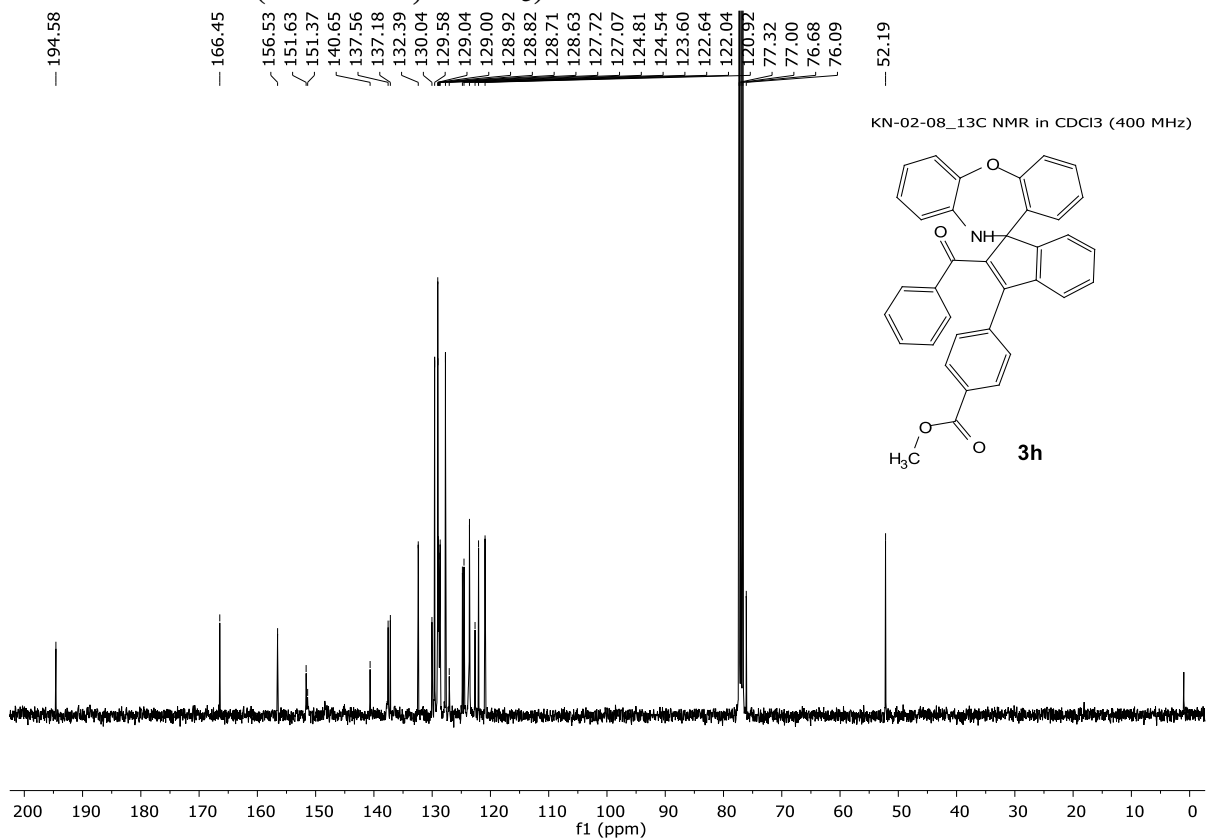
-111.75



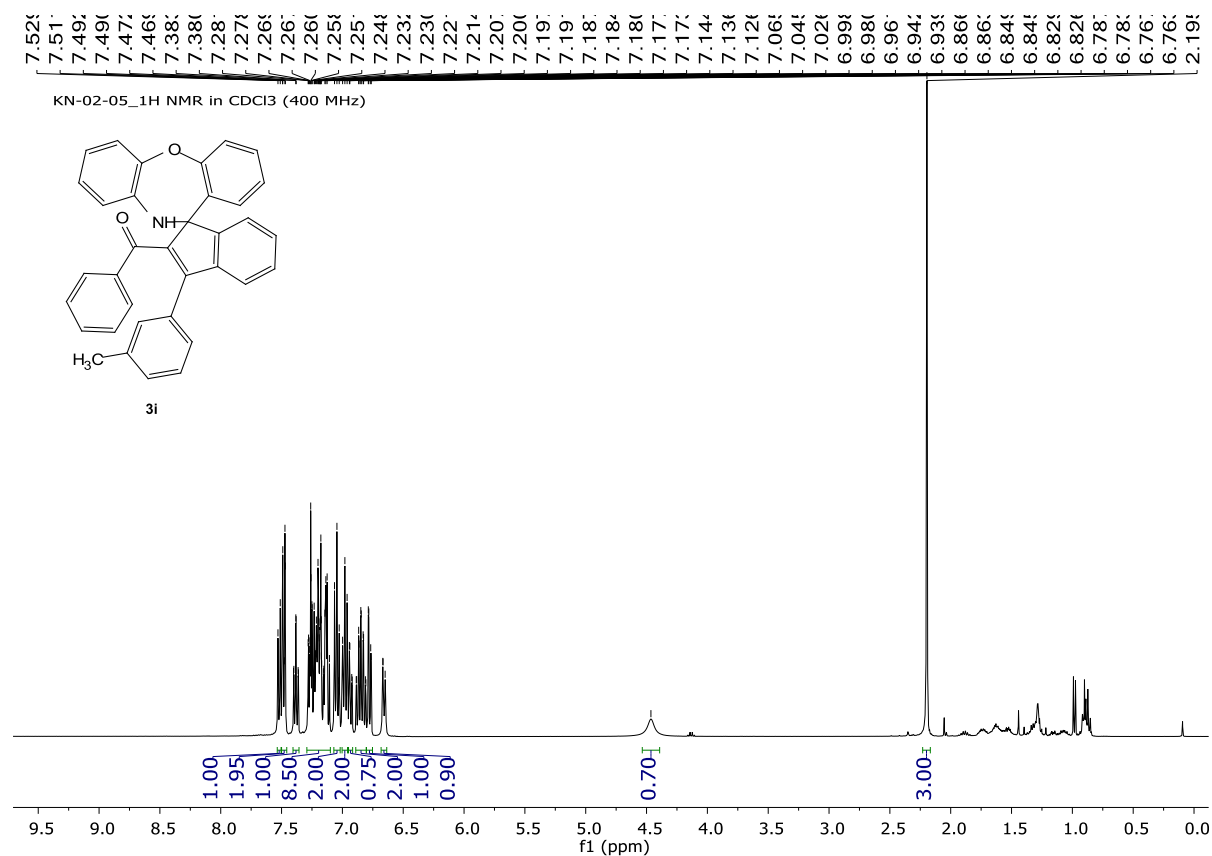
¹H NMR of 3h (400 MHz, CDCl₃):



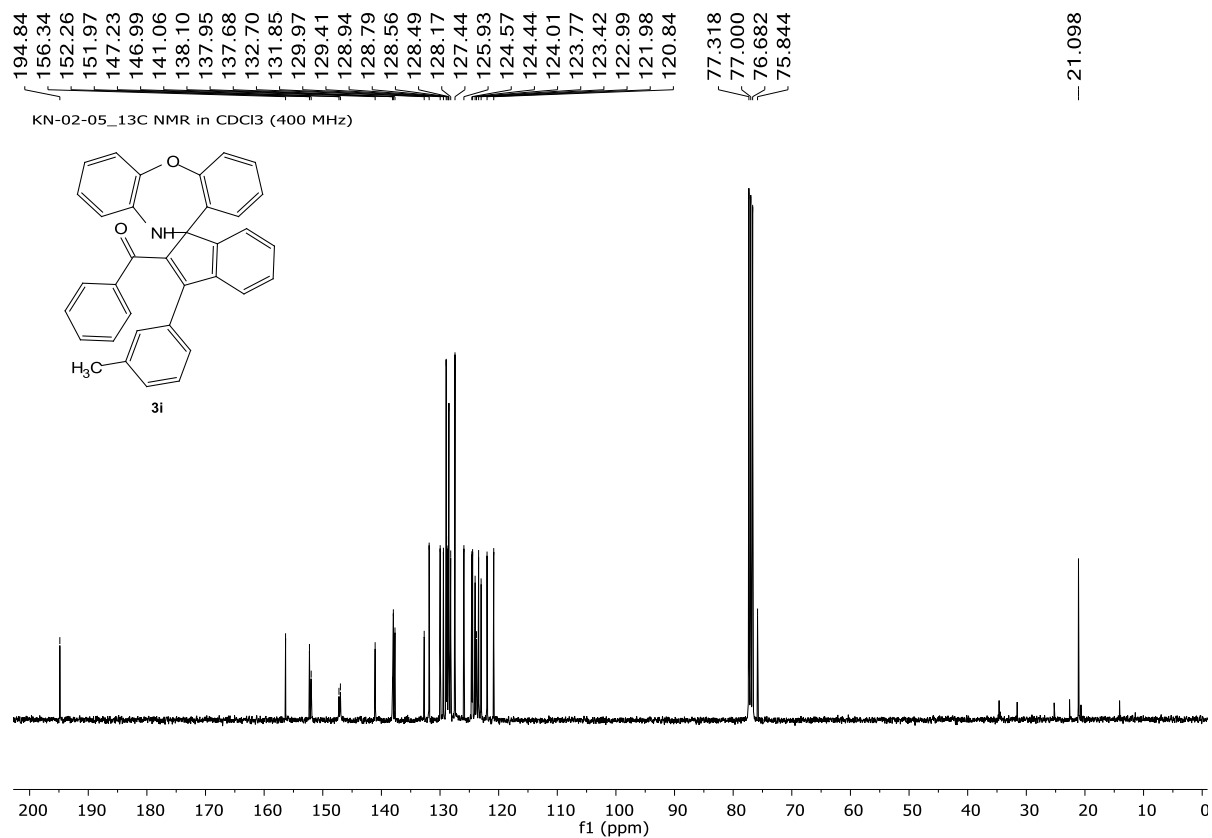
¹³C NMR of 3h (100 MHz, CDCl₃):



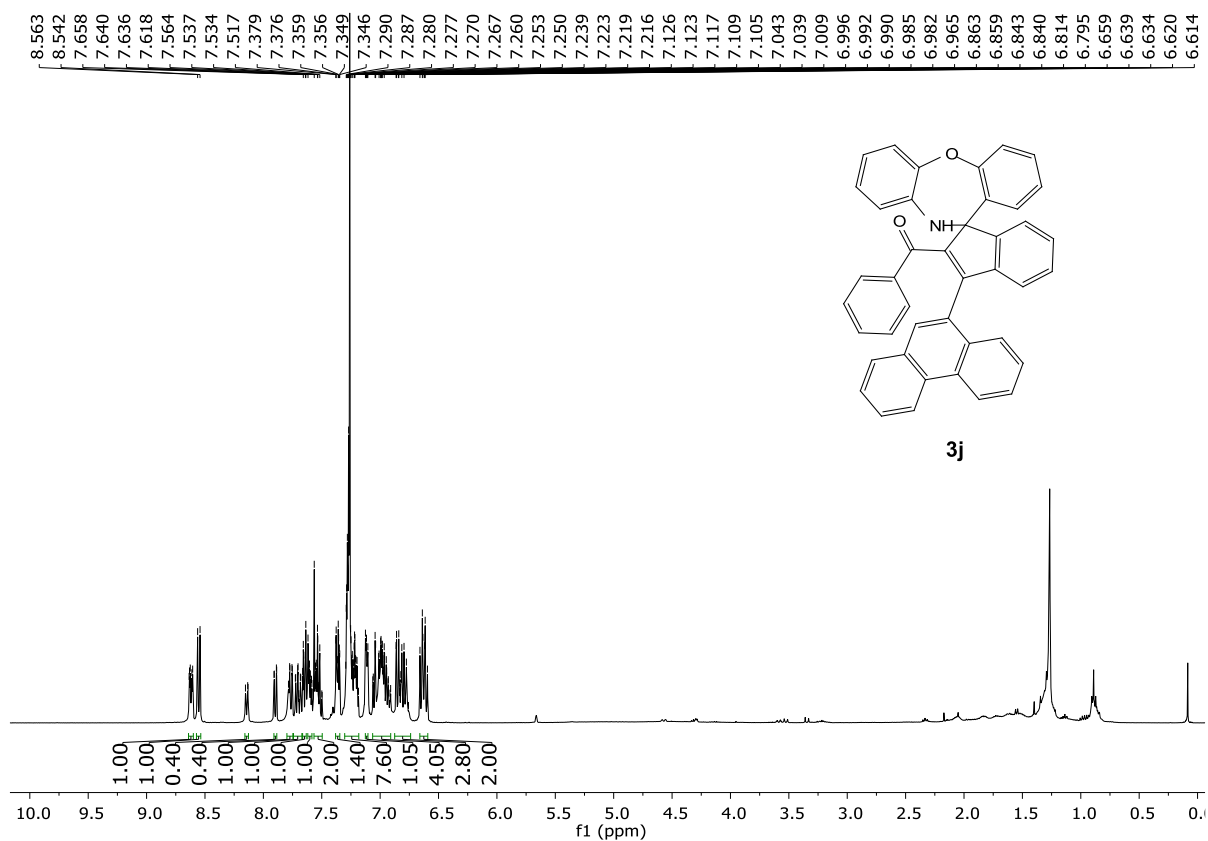
¹H NMR of 3i (400 MHz, CDCl₃):



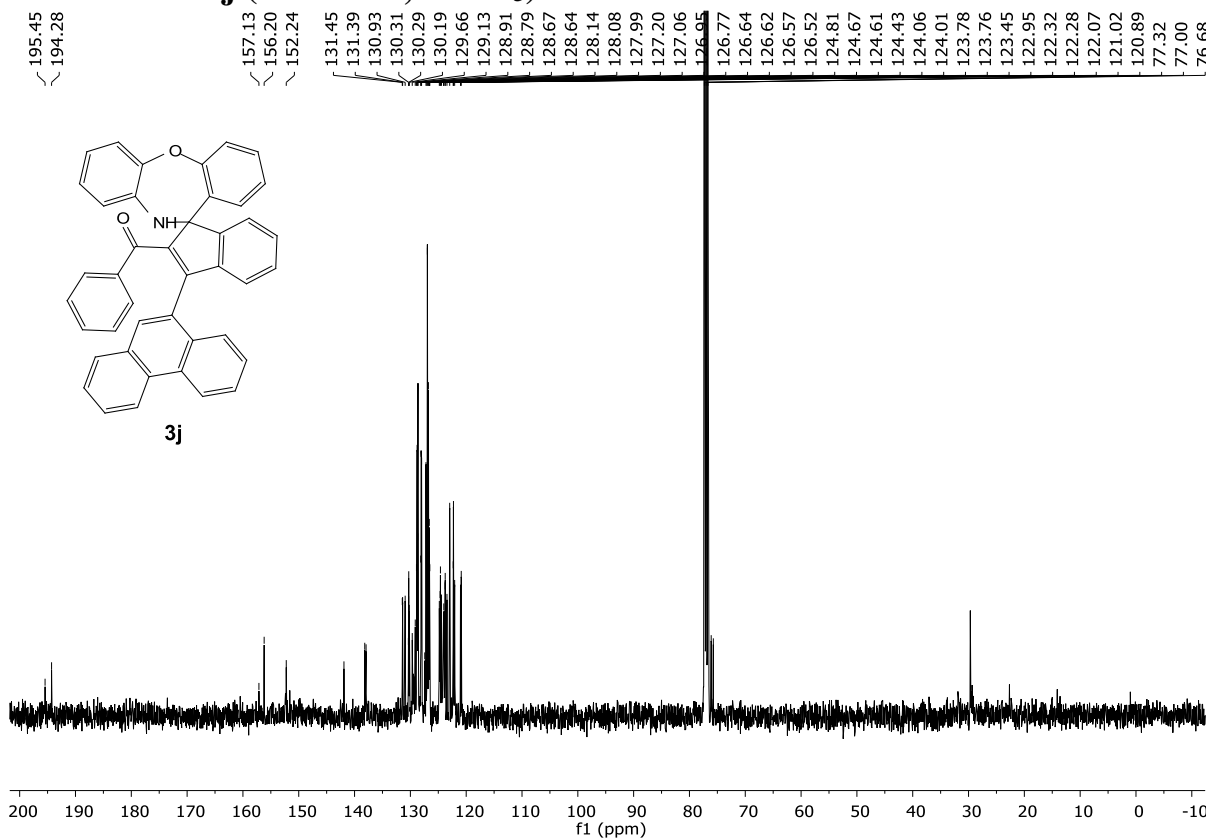
¹³C NMR of 3i (100 MHz, CDCl₃):



¹H NMR of 3j (400 MHz, CDCl₃):



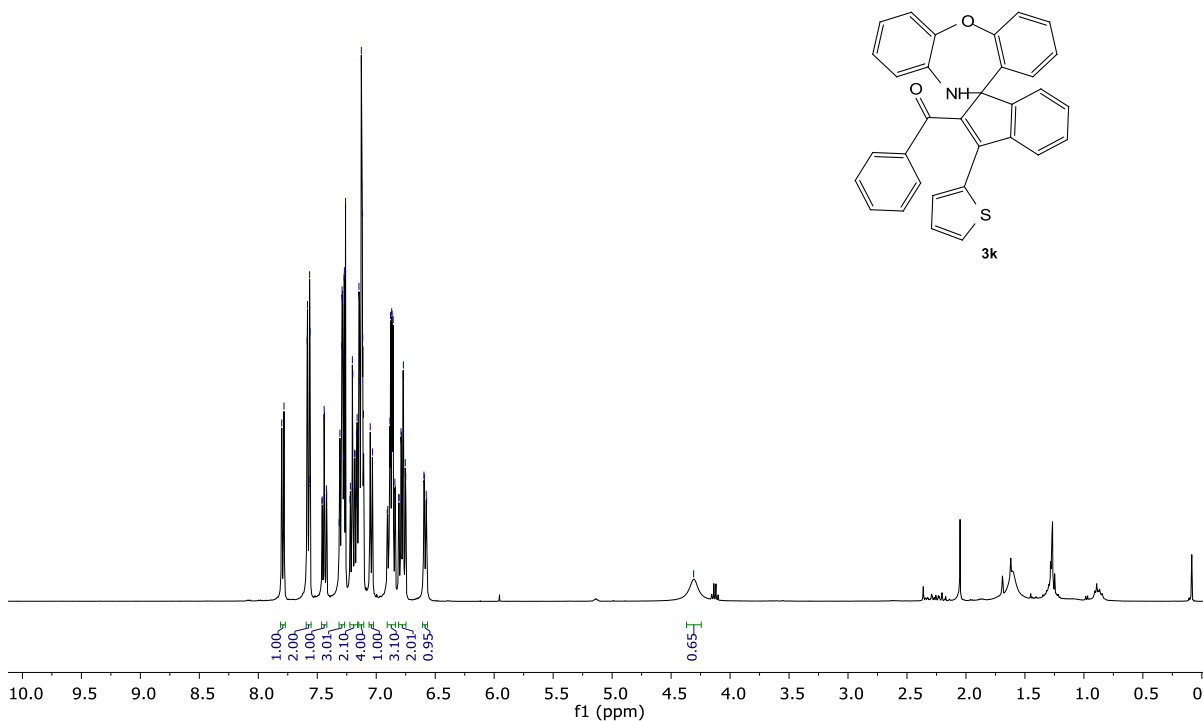
¹³C NMR of 3j (100 MHz, CDCl₃):



¹H NMR of 3k (400 MHz, CDCl₃):

7.801
7.782
7.585
7.583
7.569
7.565
7.562
7.461
7.458
7.442
7.439
7.423
7.420
7.314
7.311
7.308
7.306
7.292
7.290
7.287
7.286
7.282
7.277
7.272
7.270
7.260
7.223
7.219
7.202
7.199
7.183
7.179
7.166
7.162
7.159
7.146
7.142
7.138
7.127
7.124
7.118
7.115
7.108
7.051
7.032
6.902
6.900
6.887
6.884
6.878
6.875
6.869
6.866
6.856
6.842
6.838
6.809
6.806
6.790
6.787
6.773
6.770
6.754
6.750
6.595
6.592
6.576
6.573
4.309

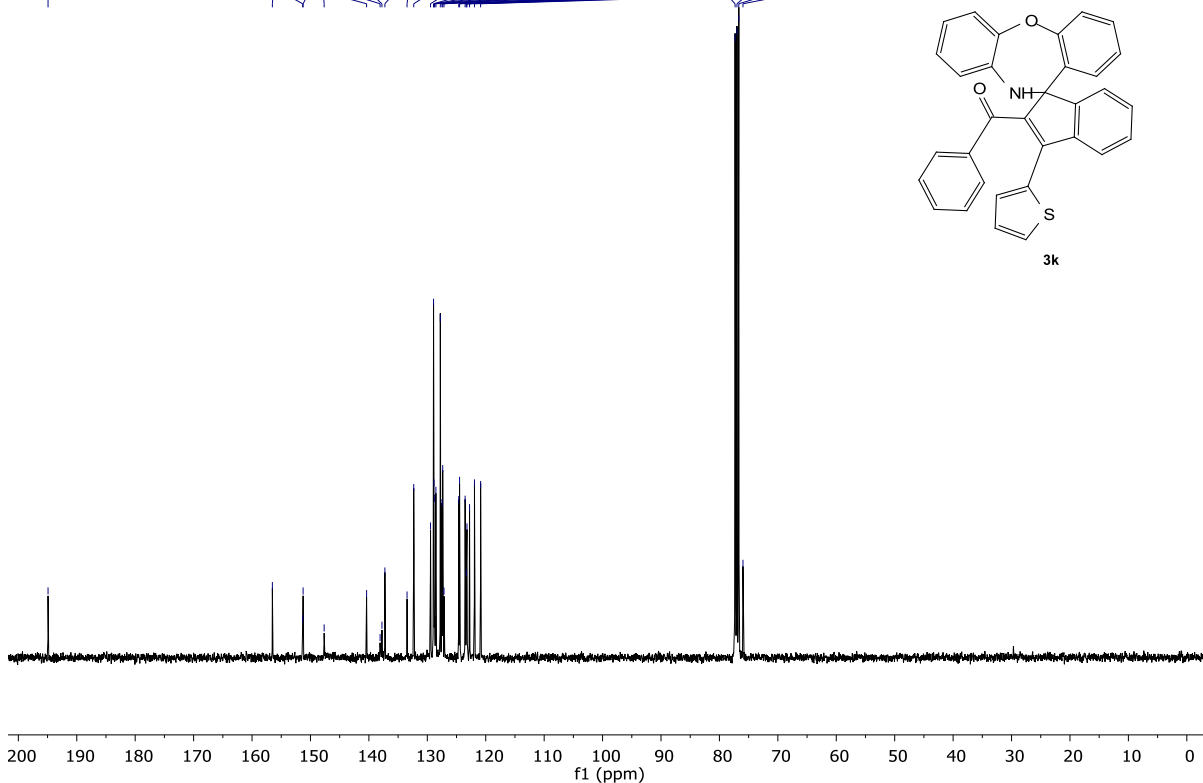
KN-02-59B_1H NMR in CDCl₃ (400 MHz)



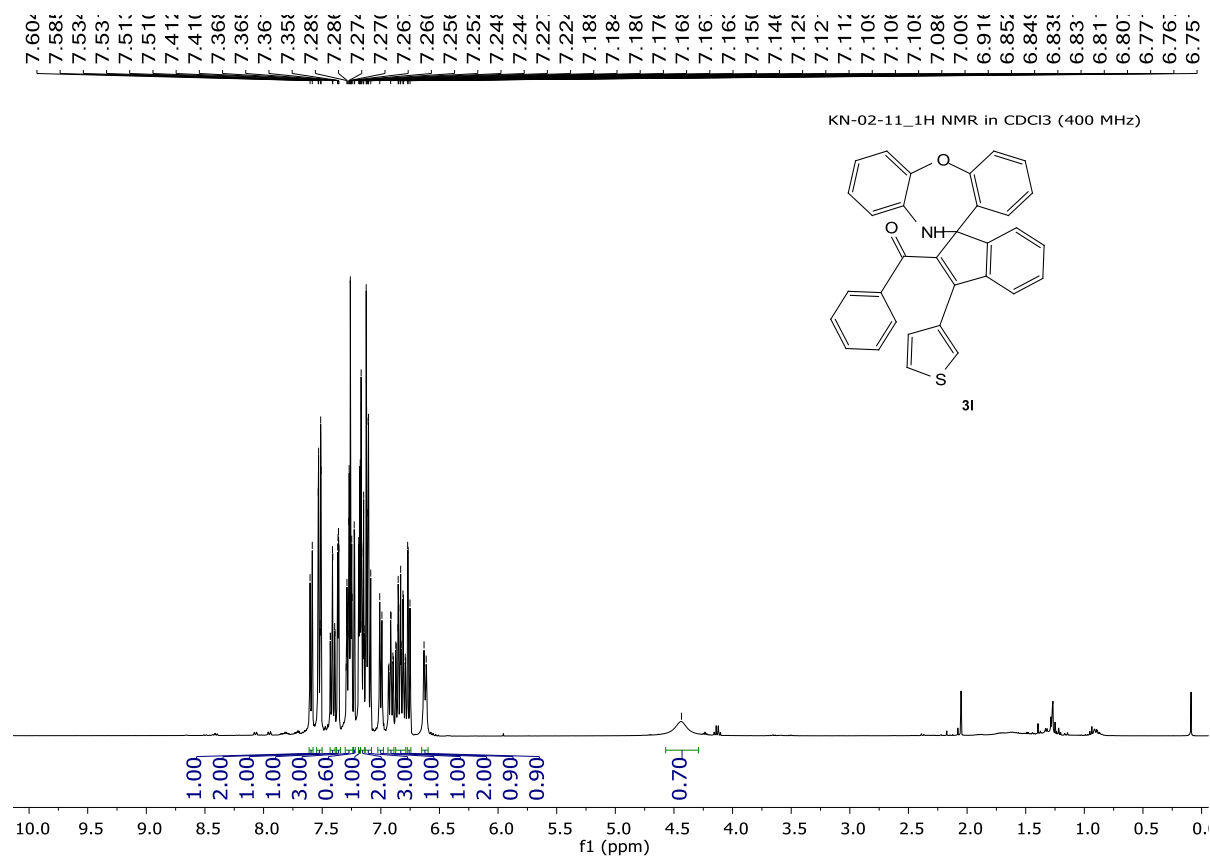
¹³C NMR of 3k (100 MHz, CDCl₃):

194.92
156.52
151.33
151.26
147.66
140.39
138.08
137.77
137.26
133.47
132.32
129.45
128.94
128.85
128.74
128.53
127.77
127.49
127.36
127.14
124.61
124.48
123.53
123.33
123.21
122.77
121.93
120.88
77.32
77.00
76.68
75.97

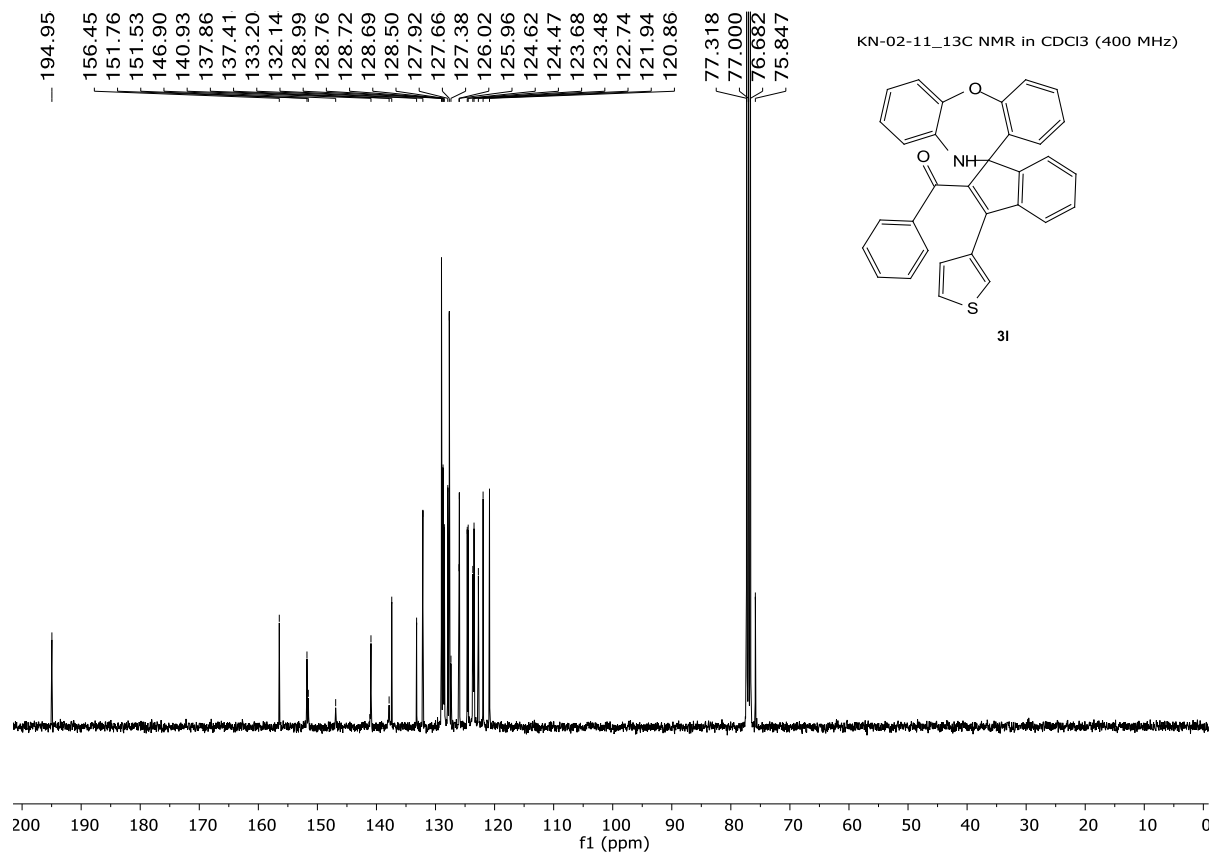
KN-02-59B_13C NMR in CDCl₃ (400 MHz)



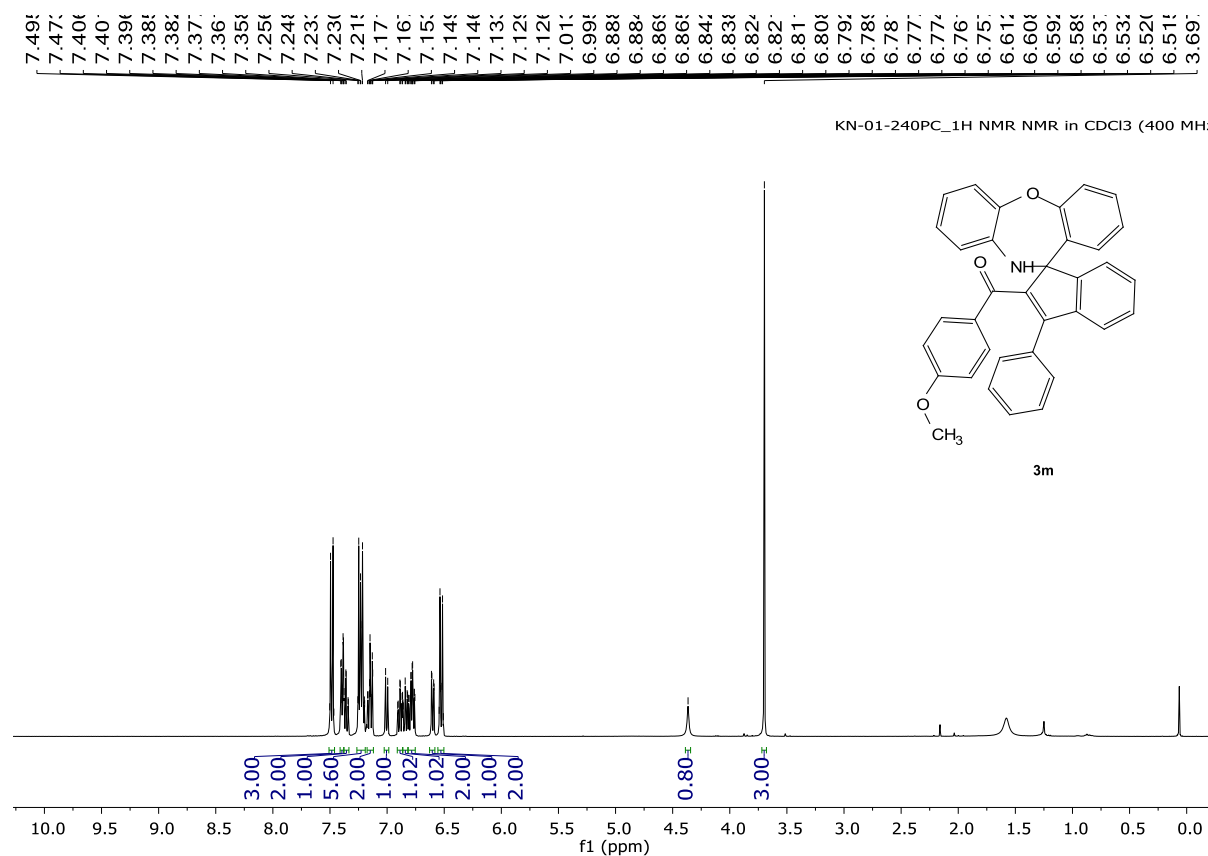
¹H NMR of 31 (400 MHz, CDCl₃):



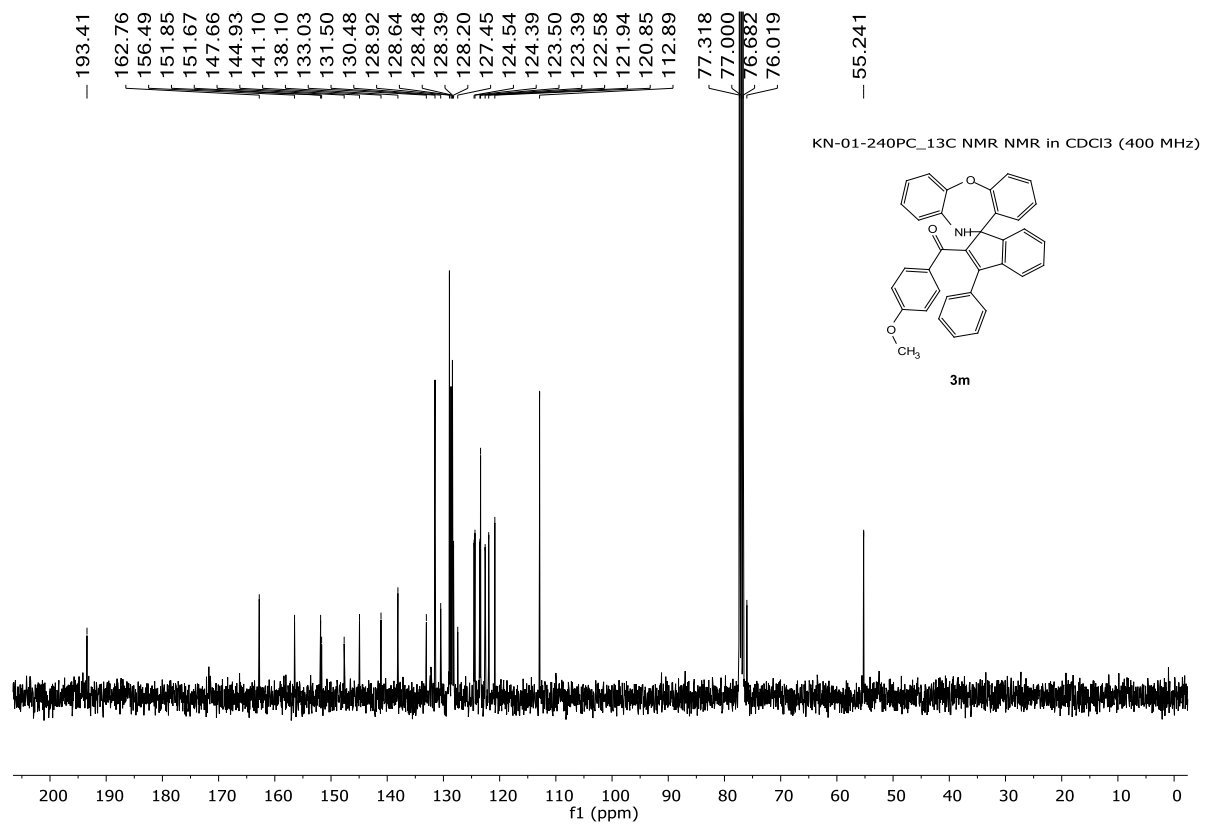
¹³C NMR of 31 (100 MHz, CDCl₃):



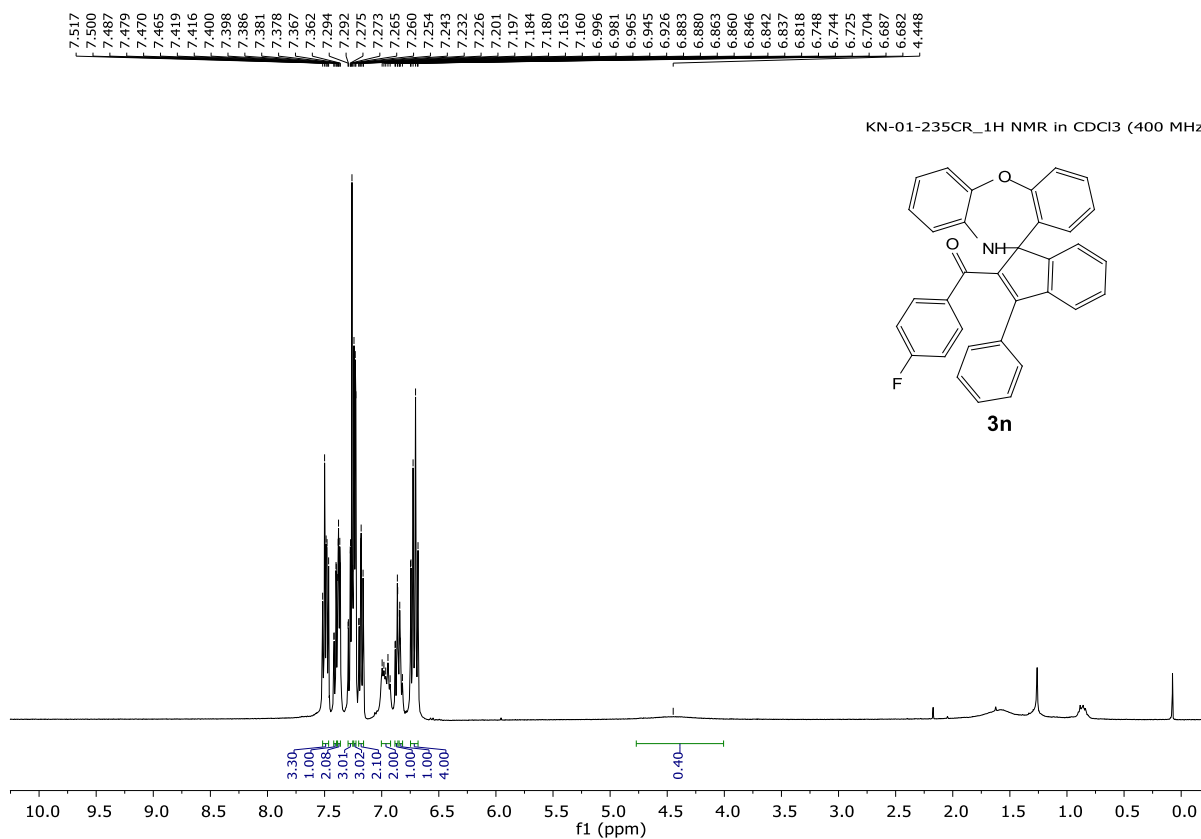
¹H NMR of 3m (400 MHz, CDCl₃):



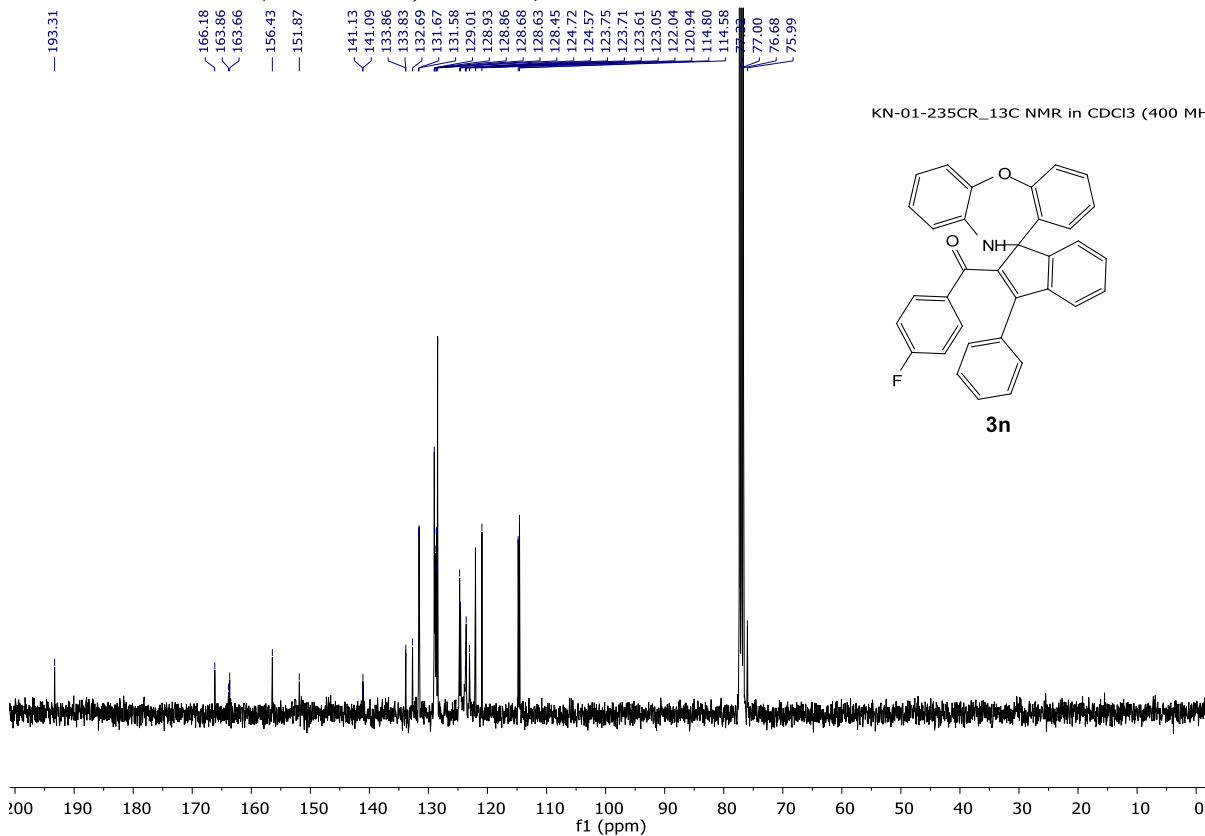
¹³C NMR of 3m (100 MHz, CDCl₃):



¹H NMR of 3n (400 MHz, CDCl₃):

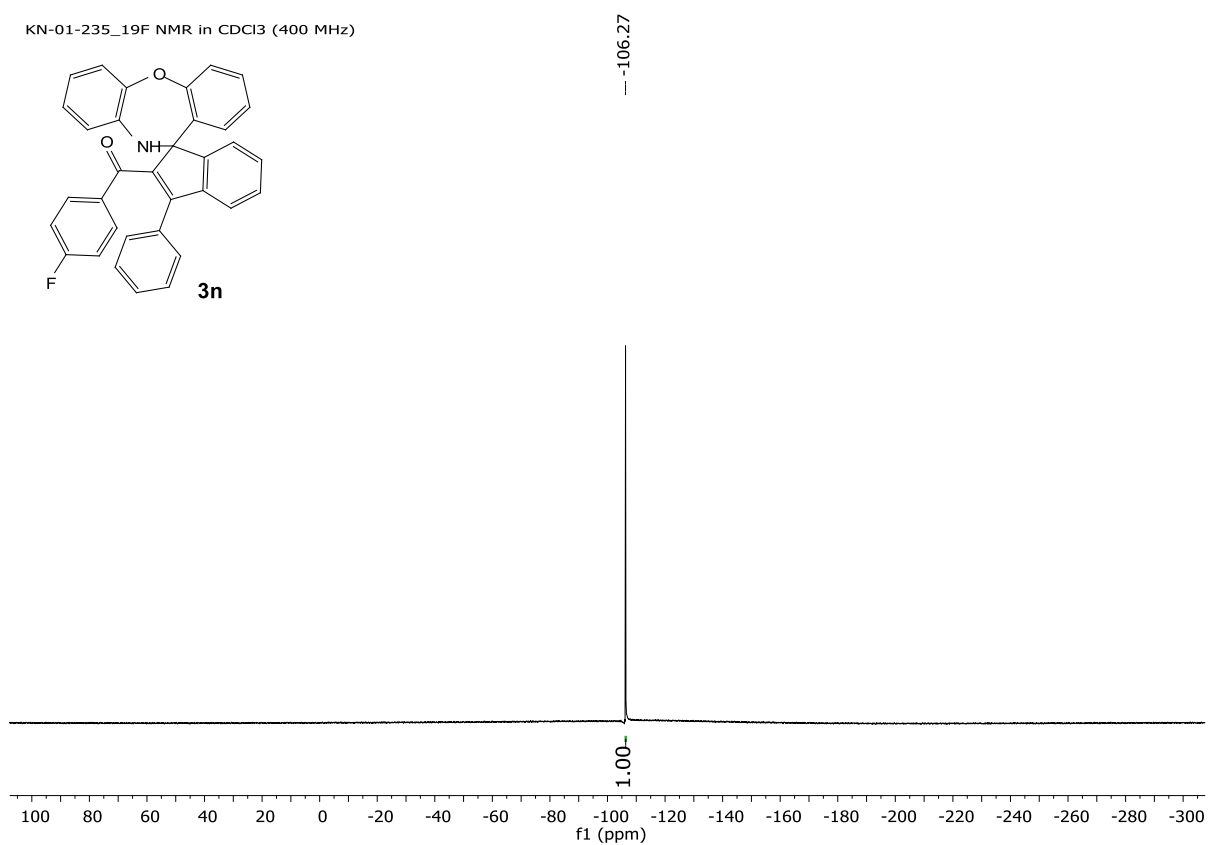
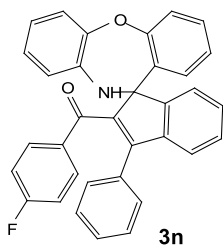


¹³C NMR of 3n (100 MHz, CDCl₃):

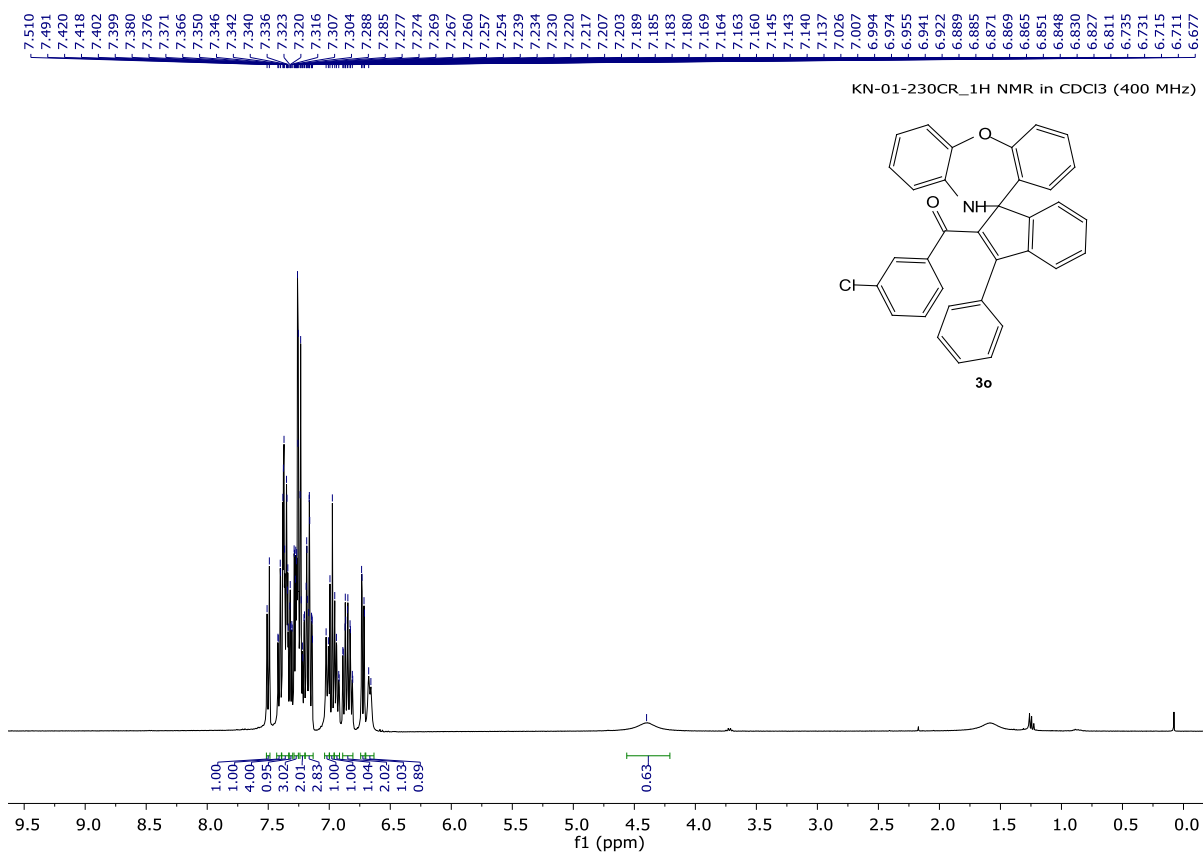


^{19}F NMR of **3n** (376 MHz, CDCl_3):

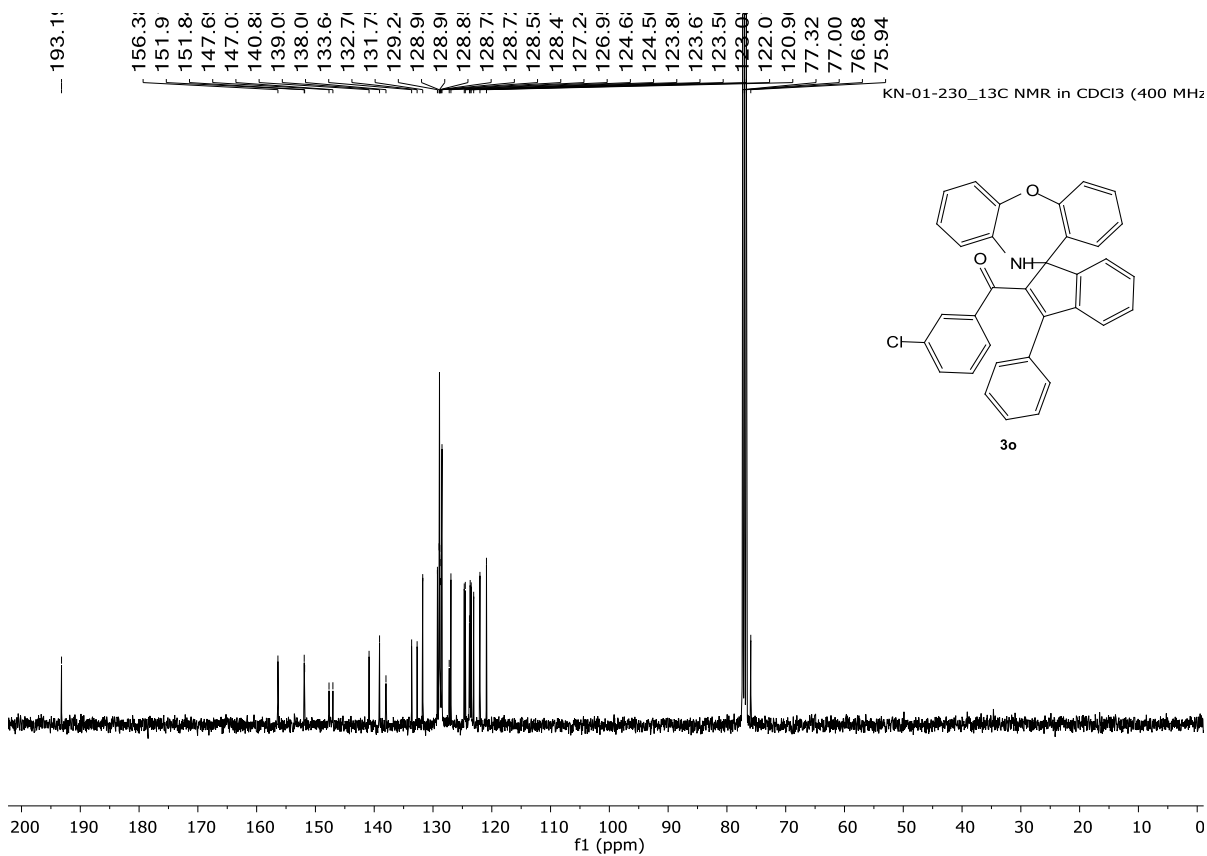
KN-01-235_19F NMR in CDCl_3 (400 MHz)



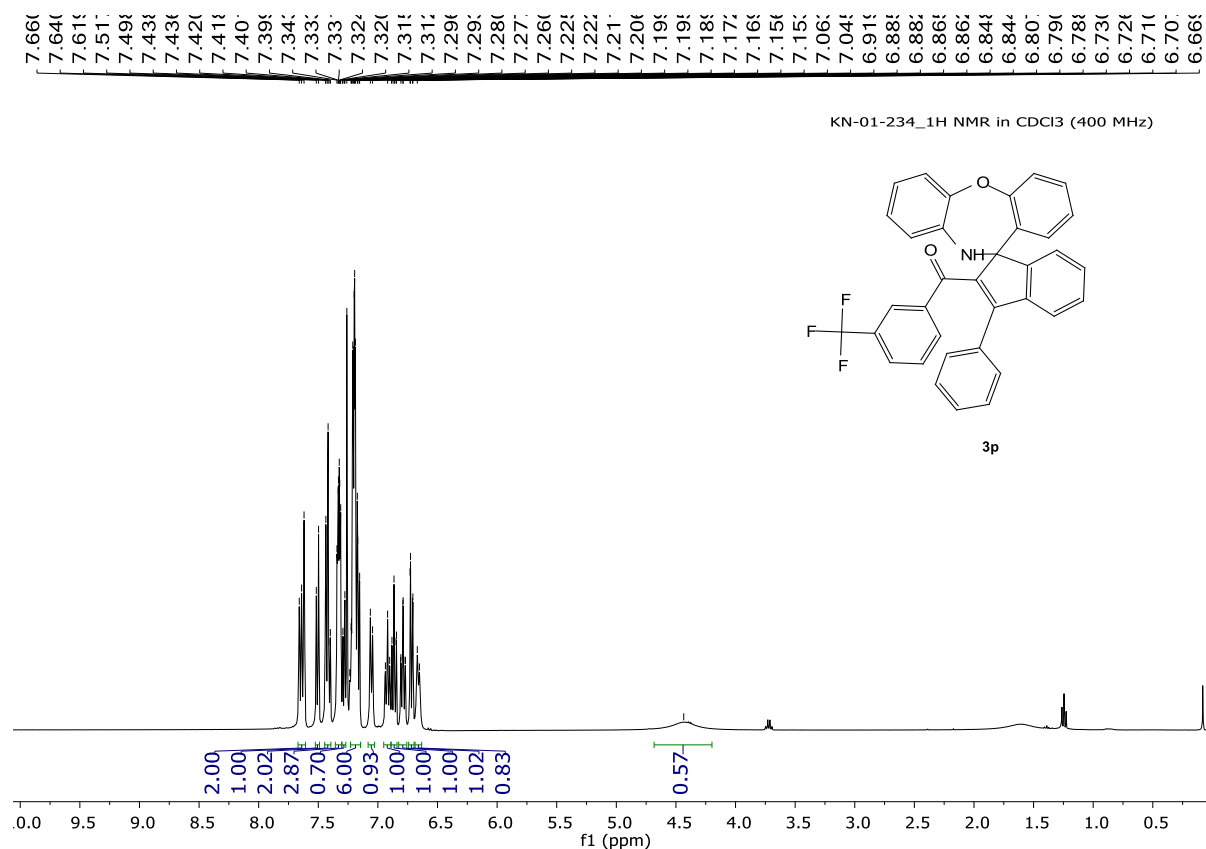
¹H NMR of 3o (400 MHz, CDCl₃):



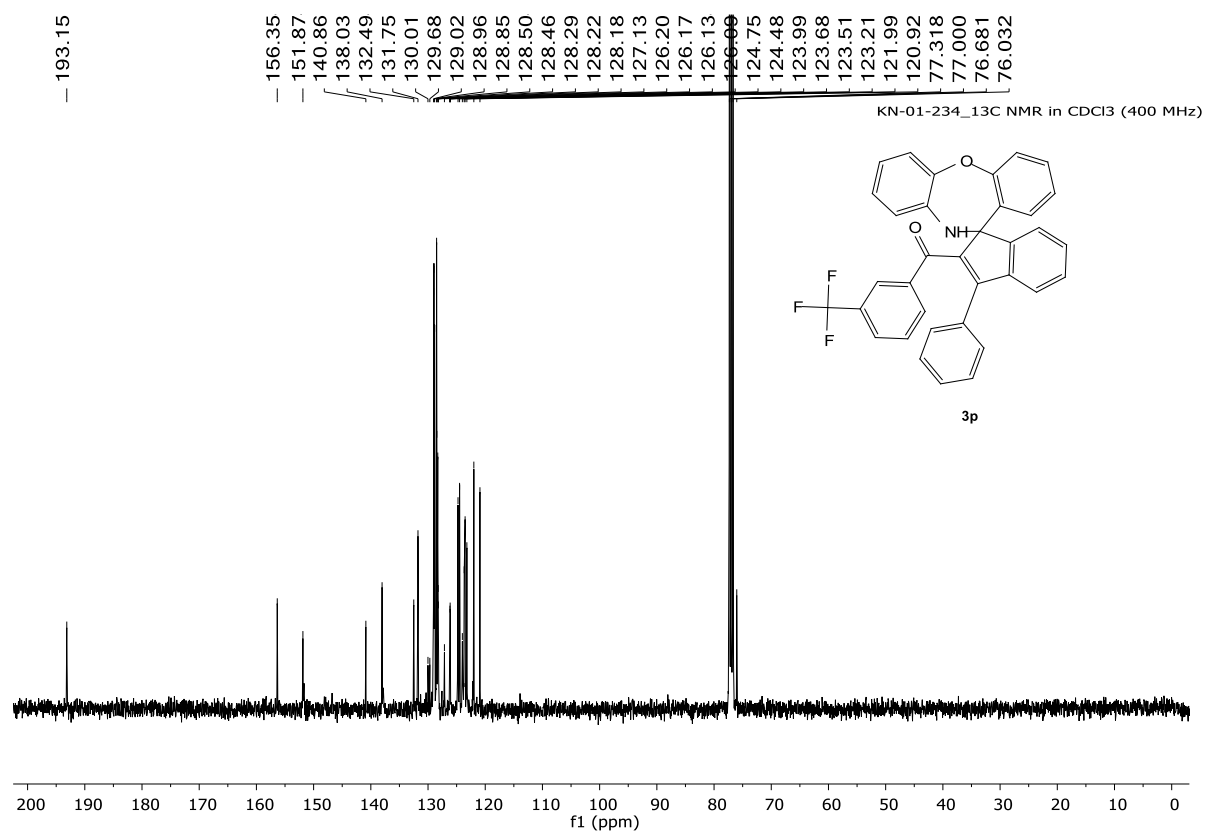
¹³C NMR of 3o (100 MHz, CDCl₃):



¹H NMR of 3p (400 MHz, CDCl₃):

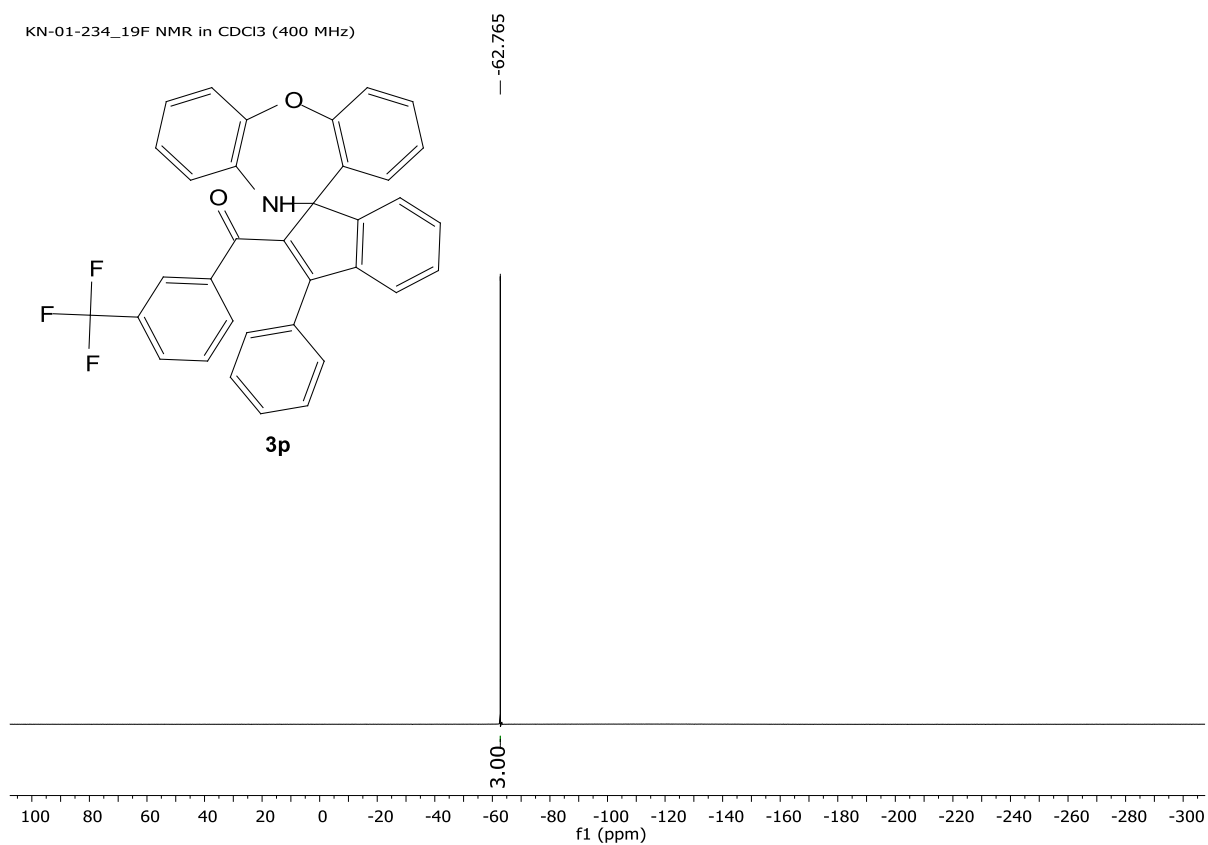


¹³C NMR of 3p (100 MHz, CDCl₃):

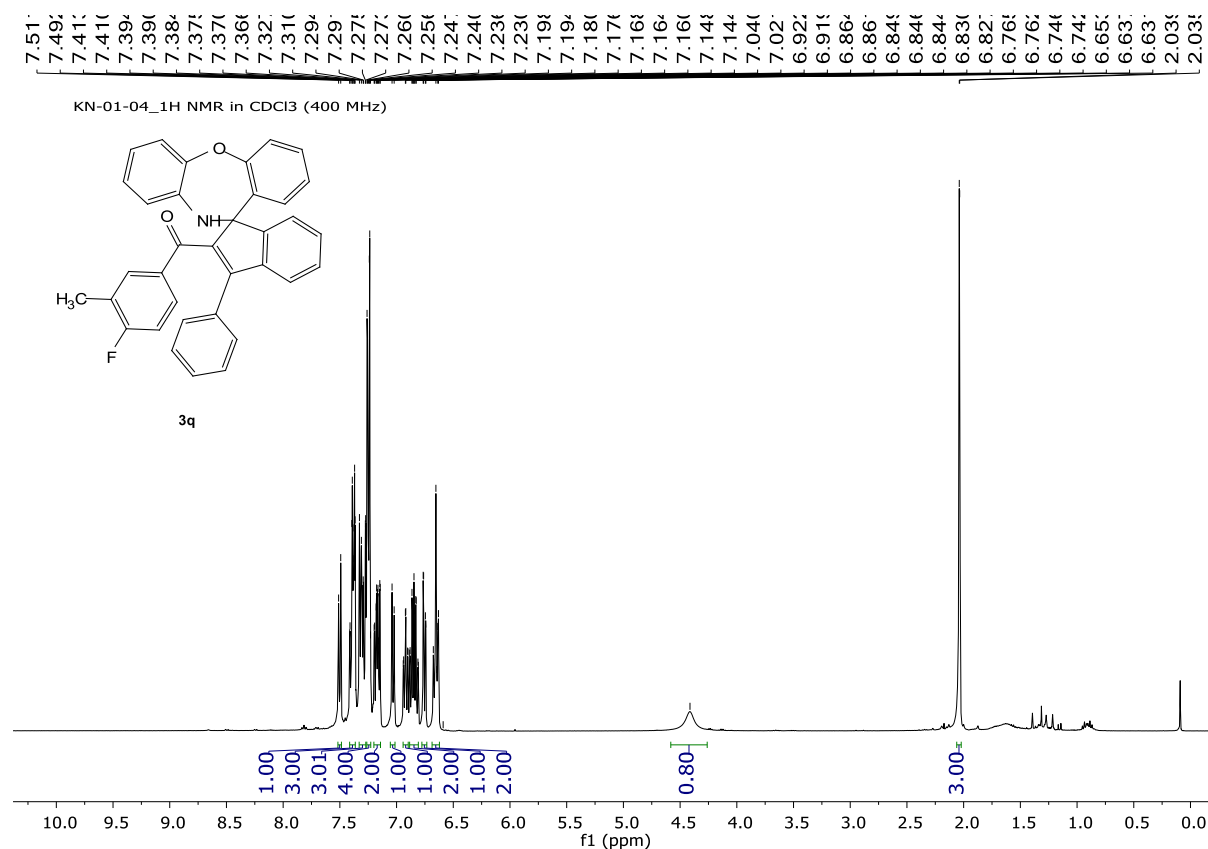


^{19}F NMR of **3p** (376 MHz, CDCl_3):

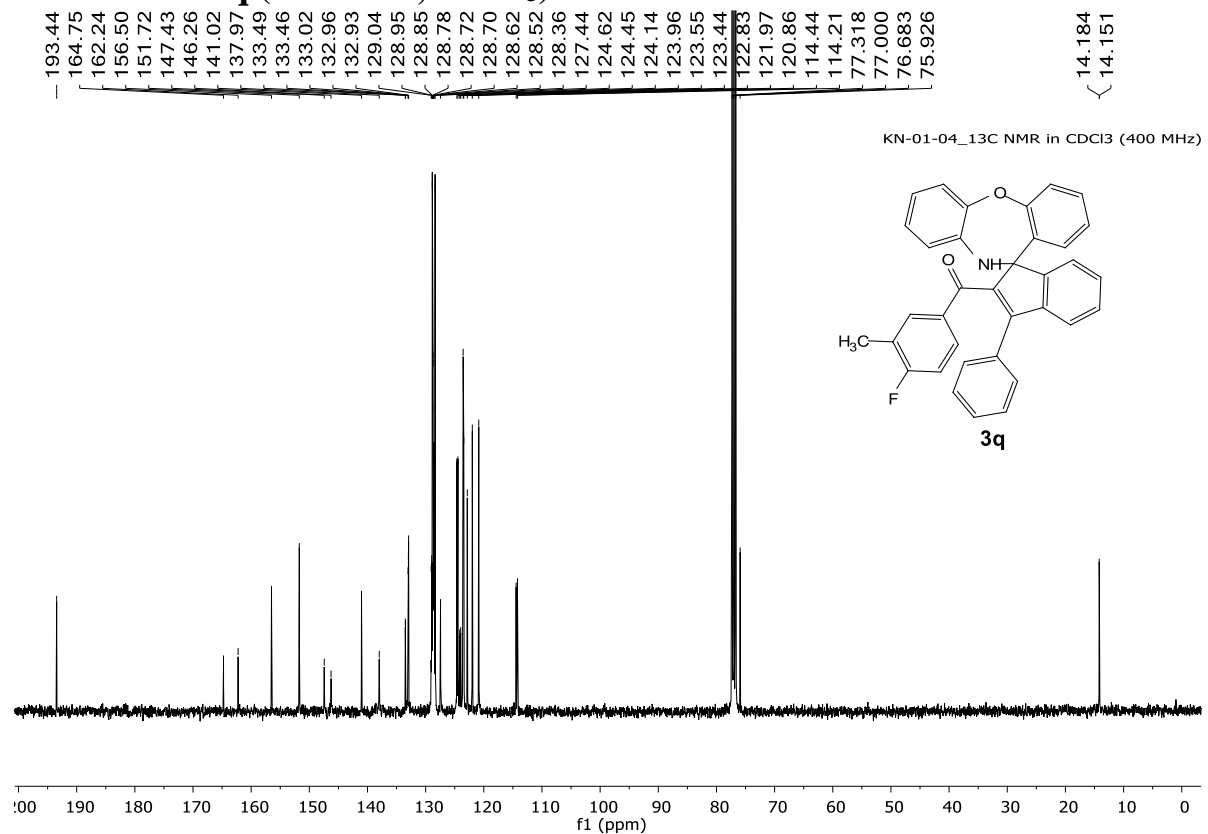
KN-01-234_19F NMR in CDCl_3 (400 MHz)



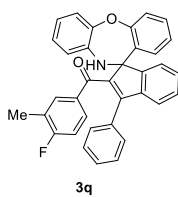
¹H NMR of 3q (400 MHz, CDCl₃):



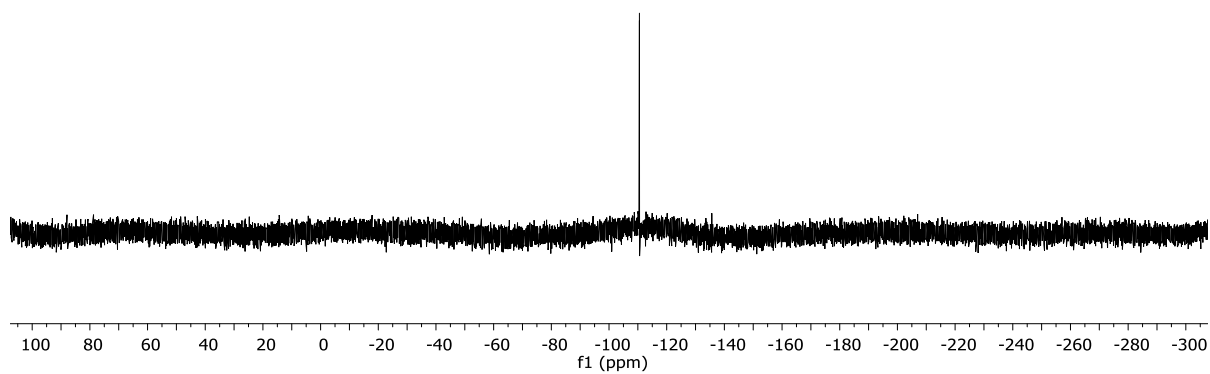
¹³C NMR of 3q (100 MHz, CDCl₃):



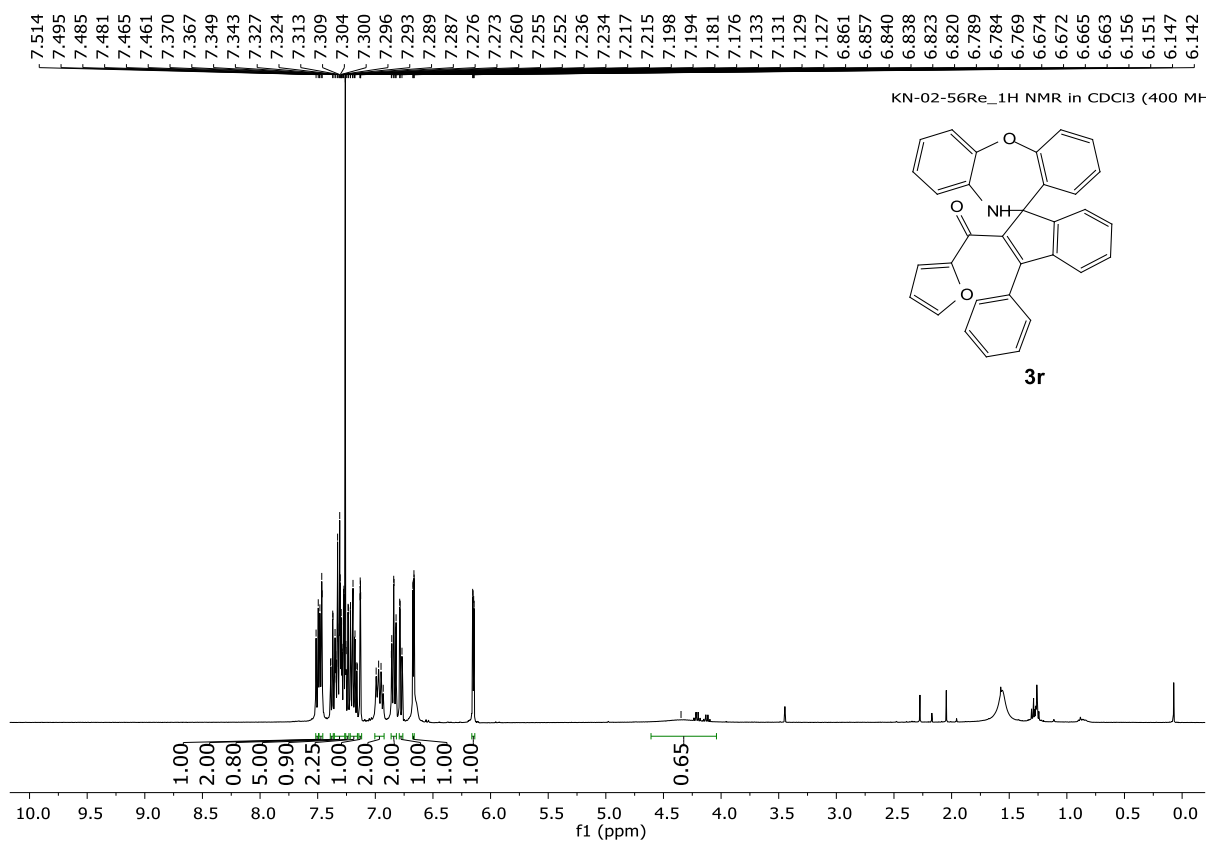
^{19}F NMR of 3q (376 MHz, CDCl_3):



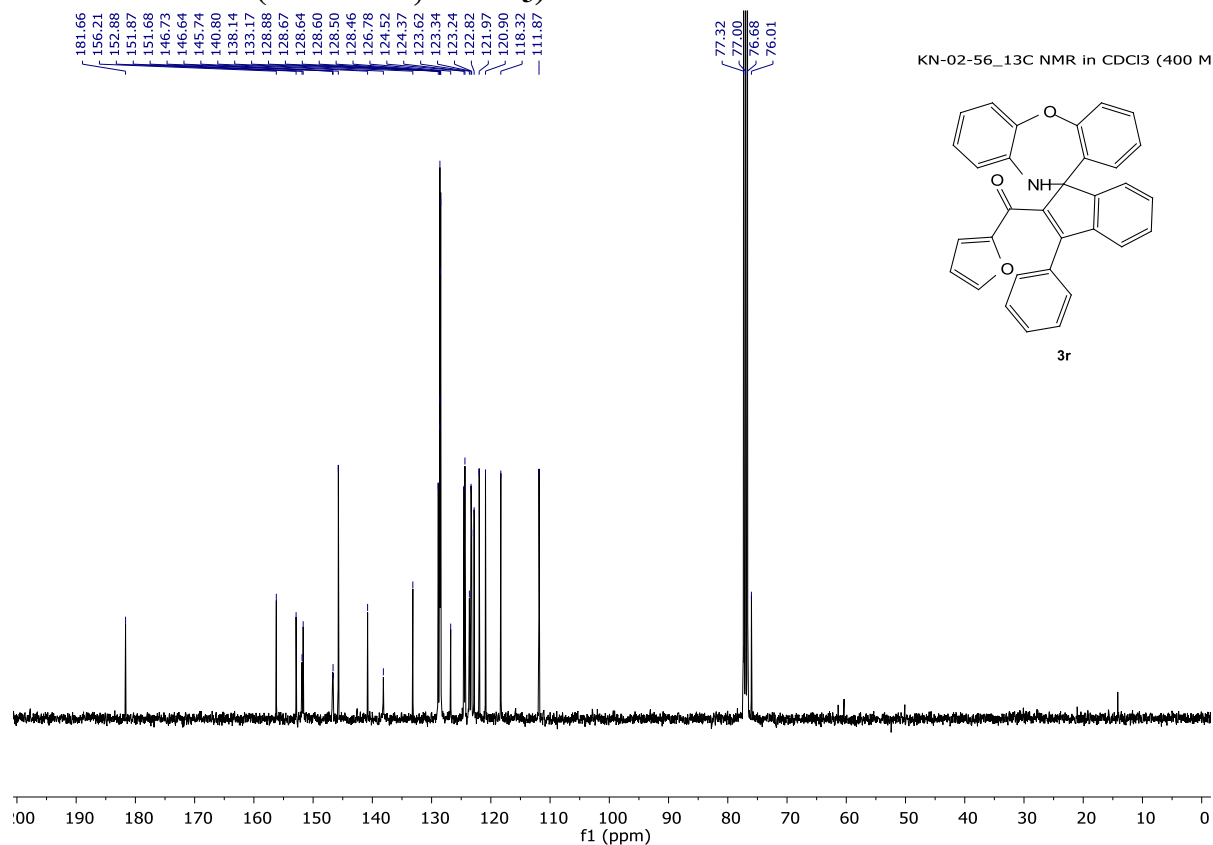
— -110.544



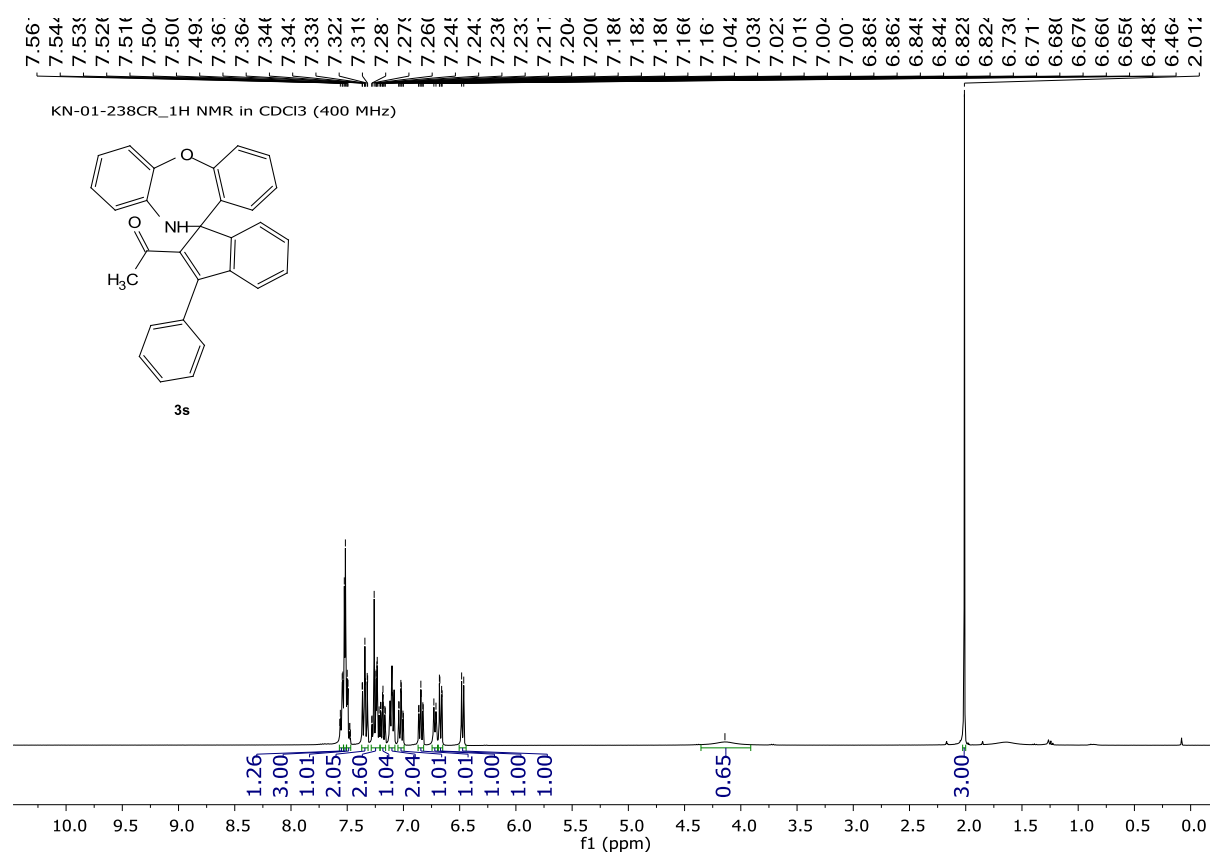
¹H NMR of 3r (400 MHz, CDCl₃):



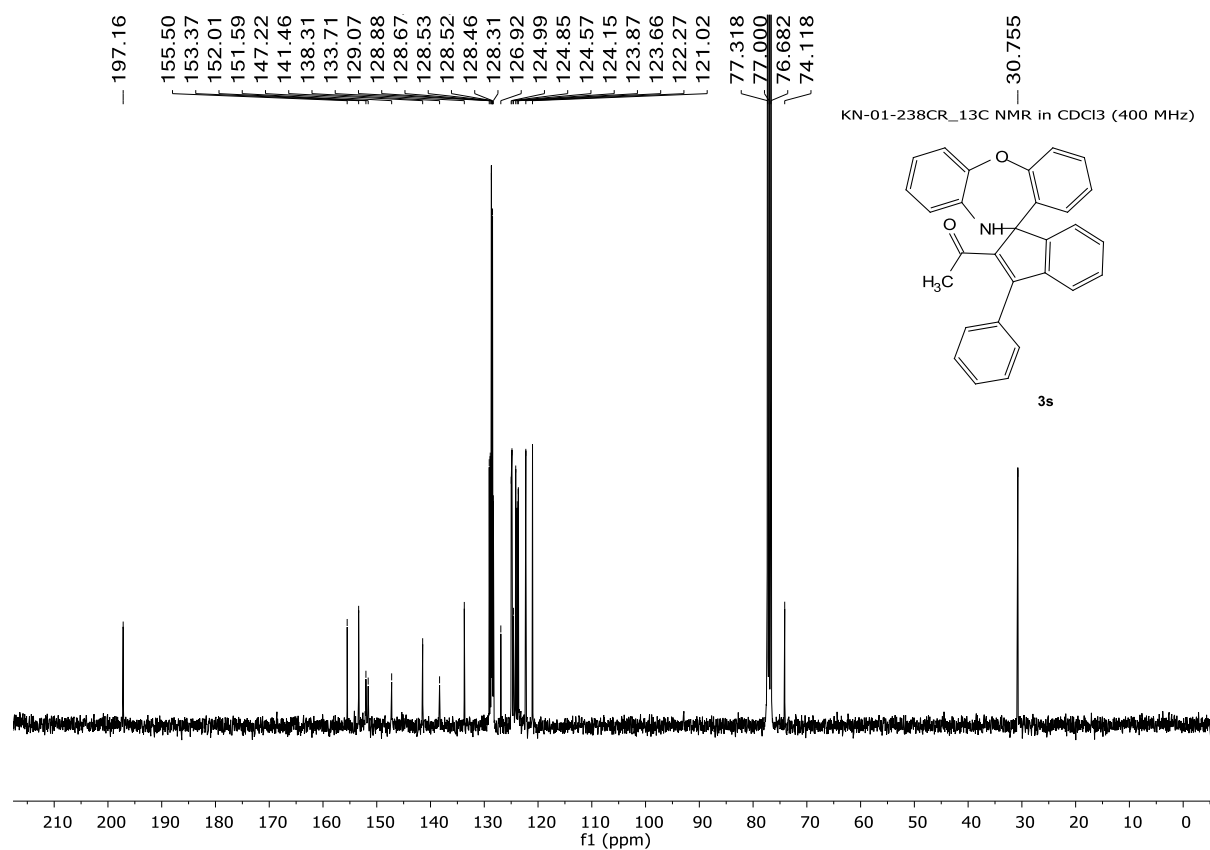
¹³C NMR of 3r (100 MHz, CDCl₃):



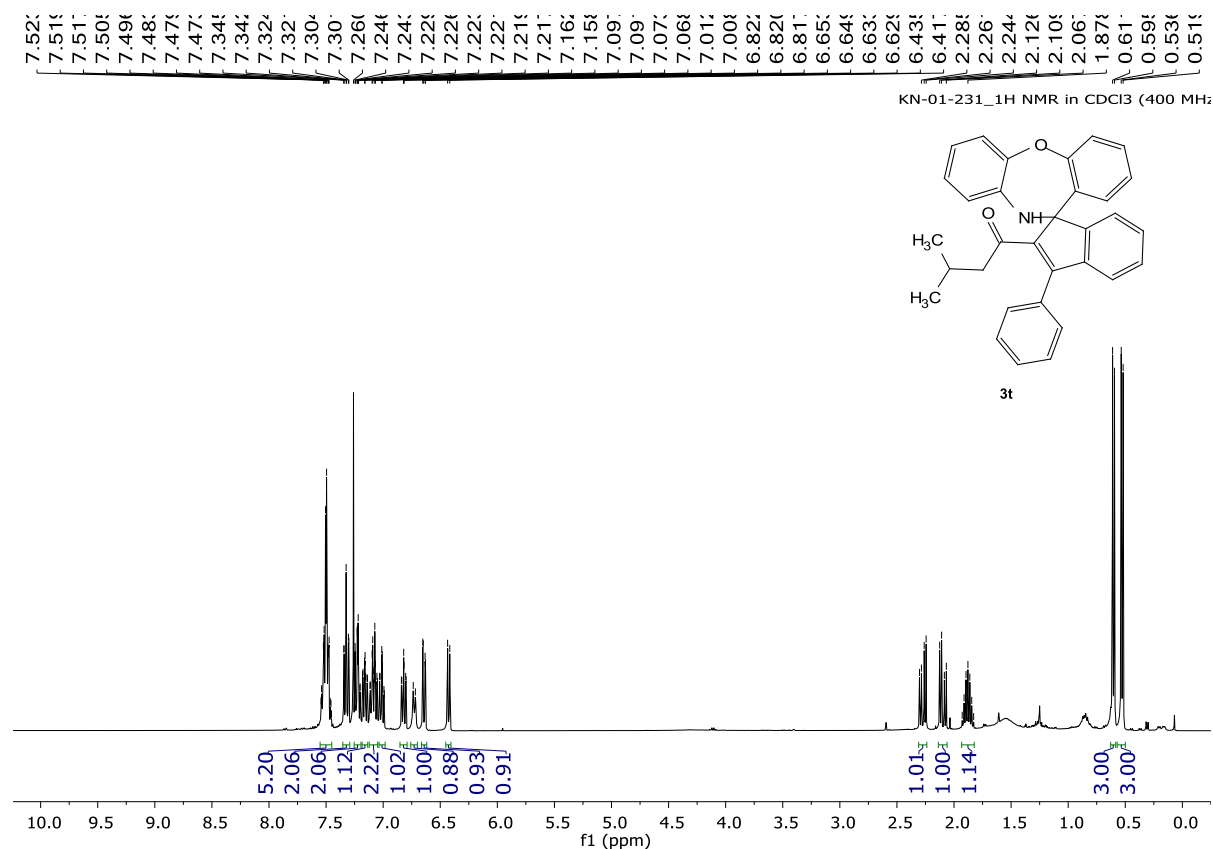
¹H NMR of 3s (400 MHz, CDCl₃):



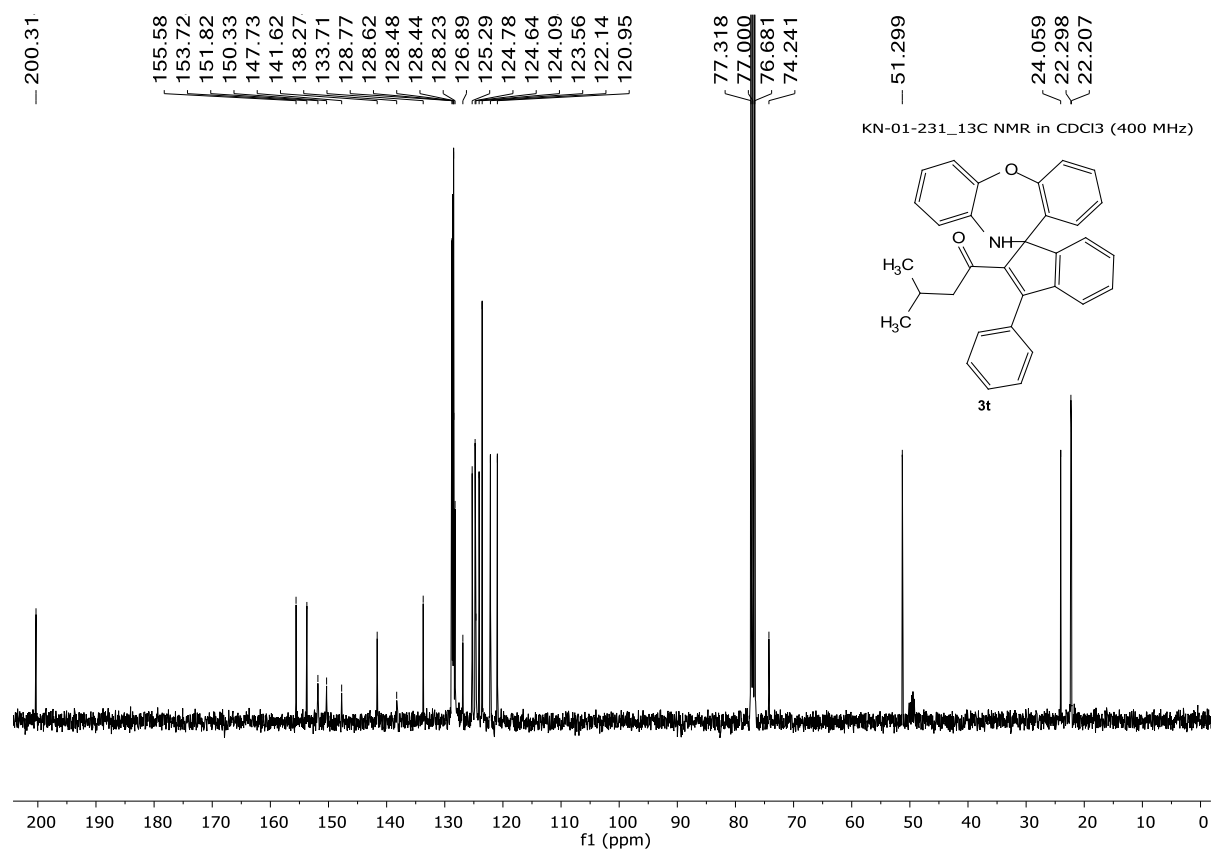
¹³C NMR of 3s (100 MHz, CDCl₃):



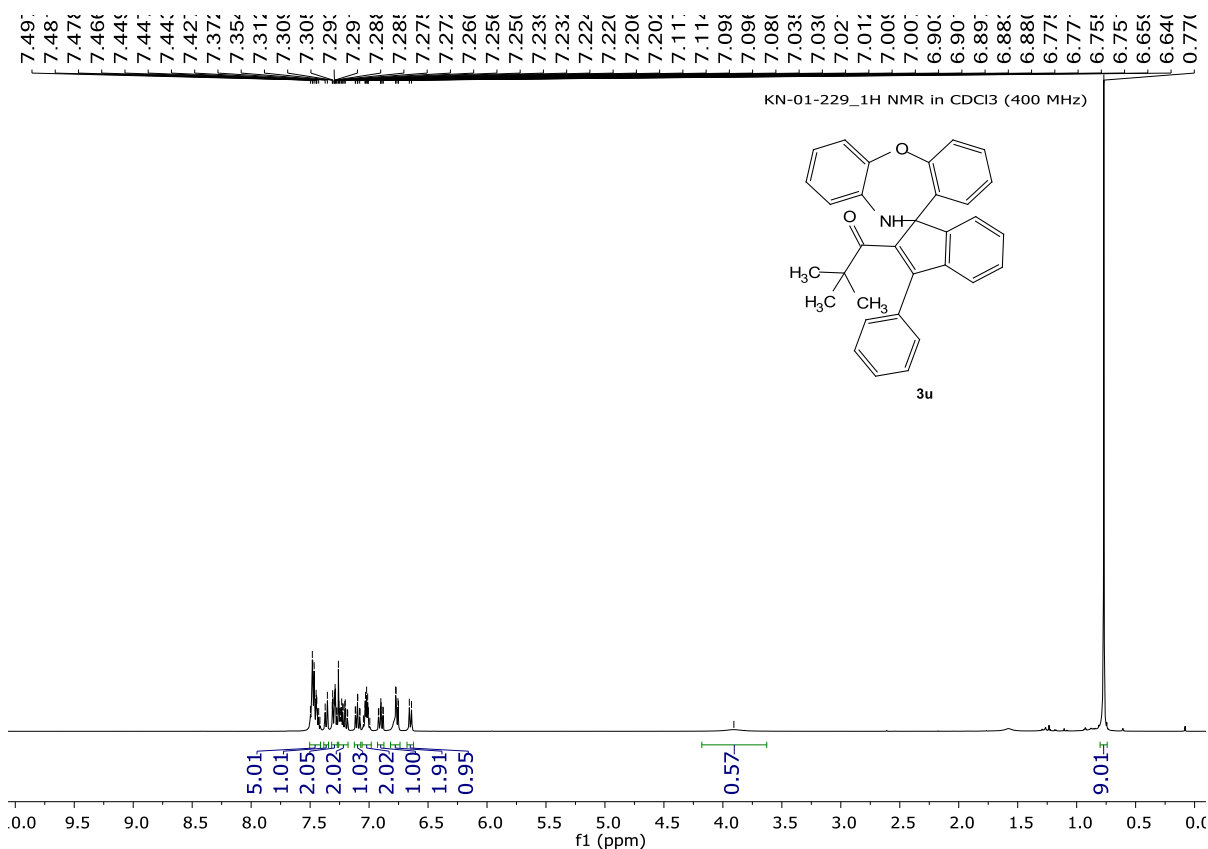
¹H NMR of 3t (400 MHz, CDCl₃):



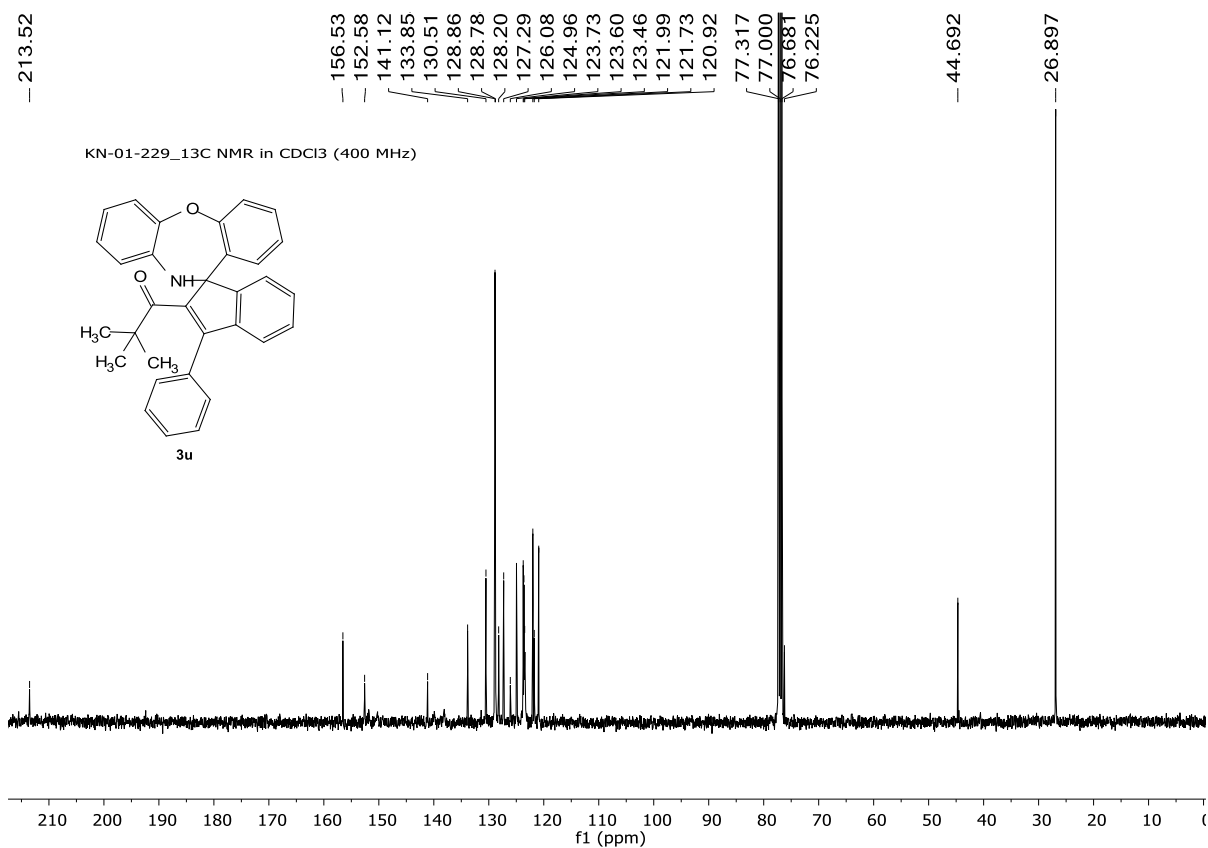
¹³C NMR of 3t (100 MHz, CDCl₃):



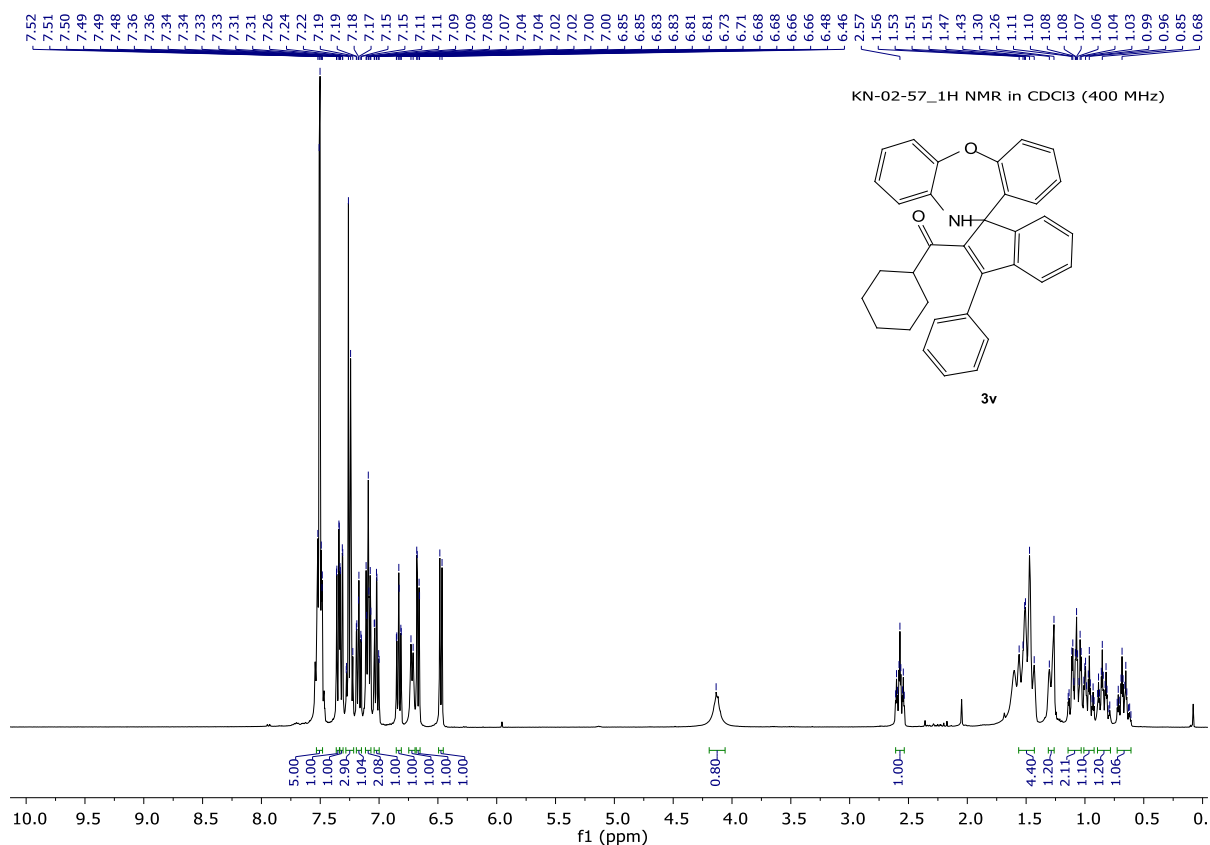
¹H NMR of 3u (400 MHz, CDCl₃):



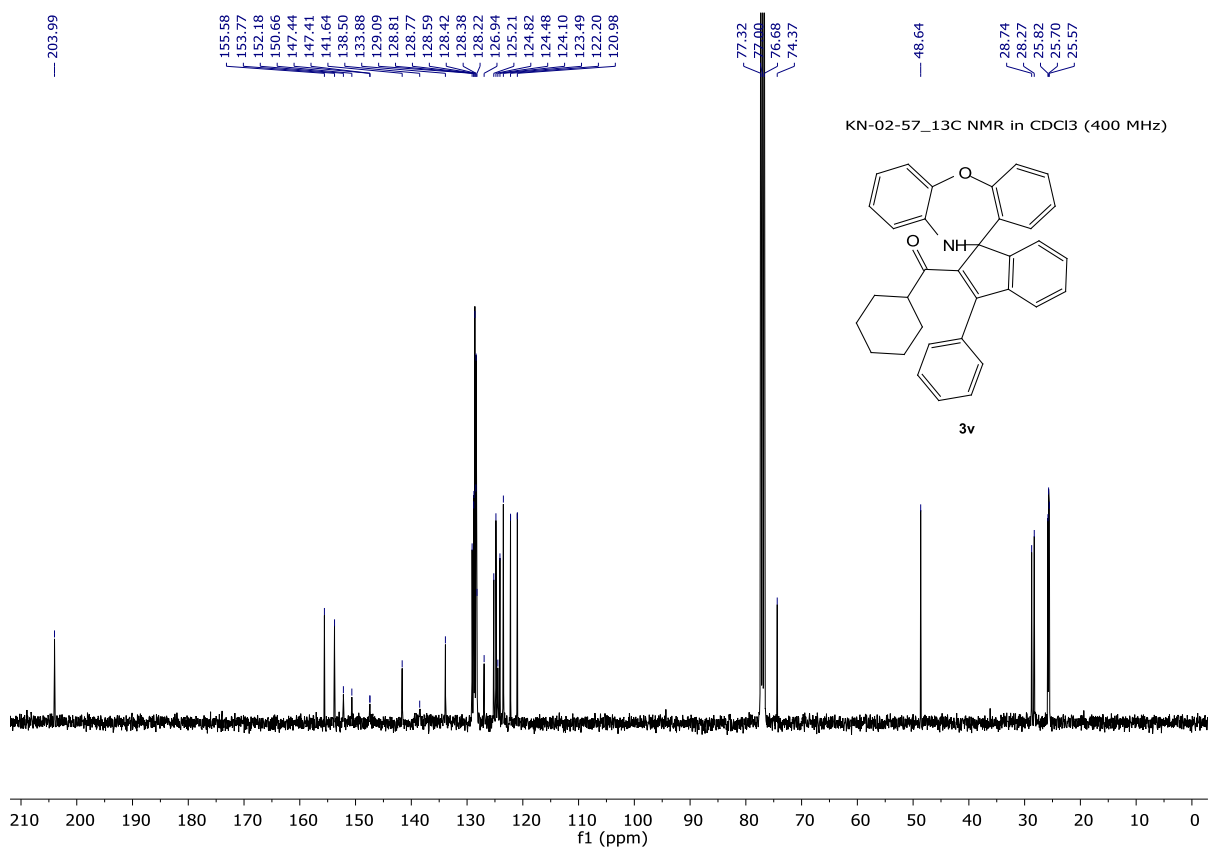
¹³C NMR of 3u (100 MHz, CDCl₃):



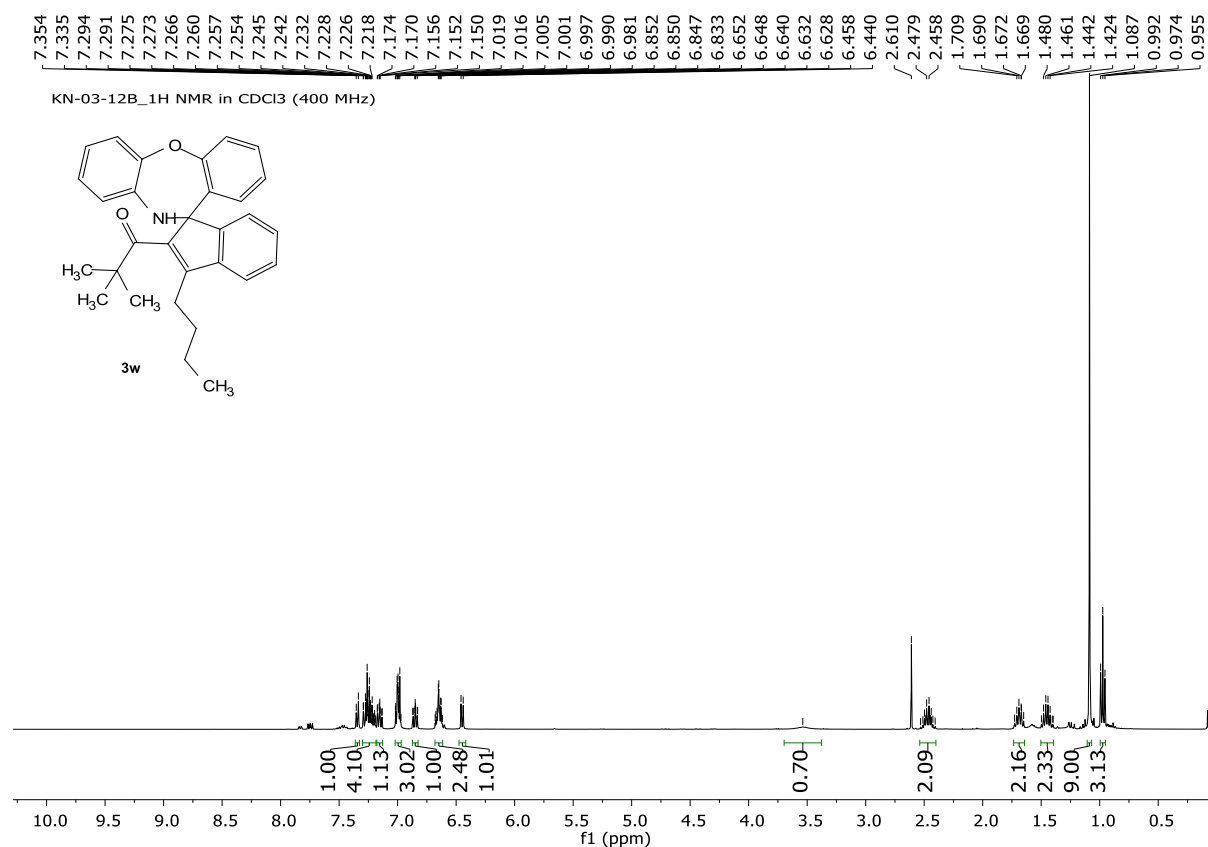
¹H NMR of 3v (400 MHz, CDCl₃):



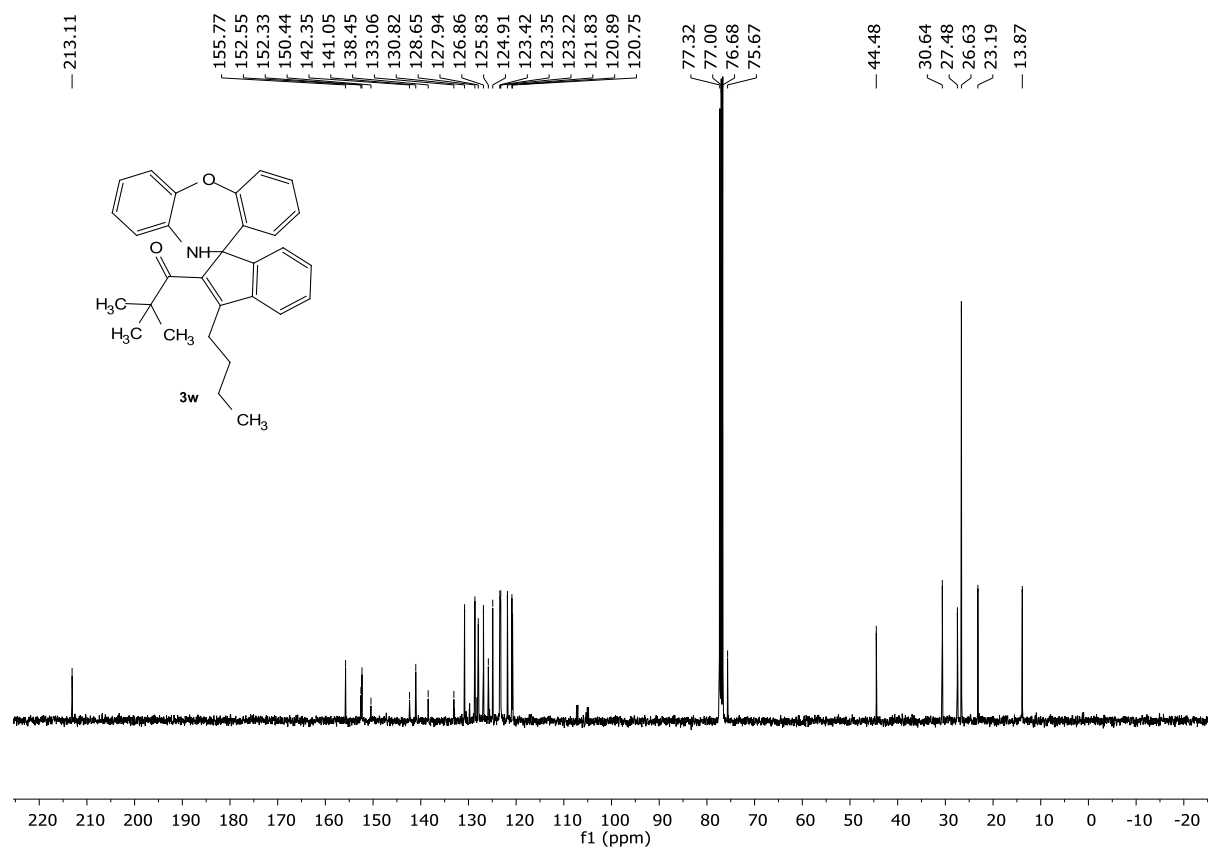
¹³C NMR of 3v (100 MHz, CDCl₃):



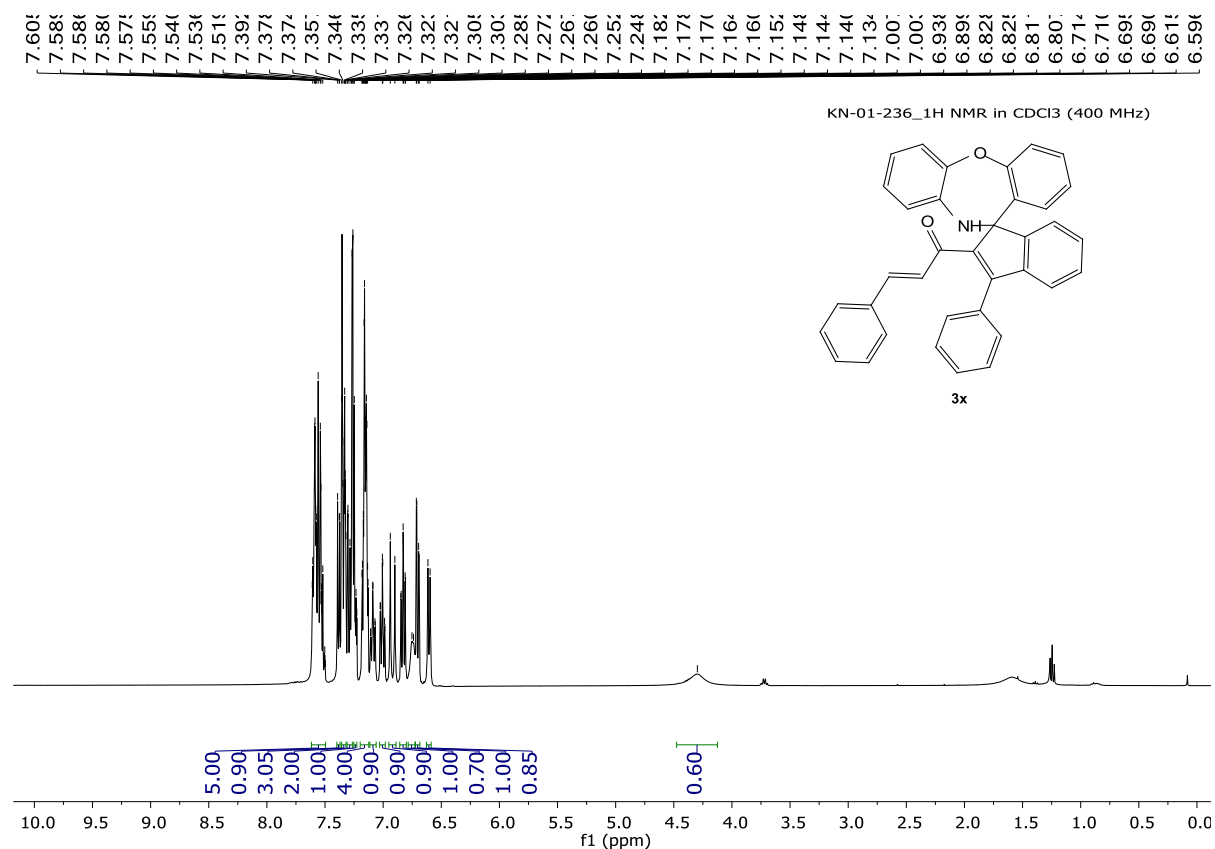
¹H NMR of 3w (400 MHz, CDCl₃):



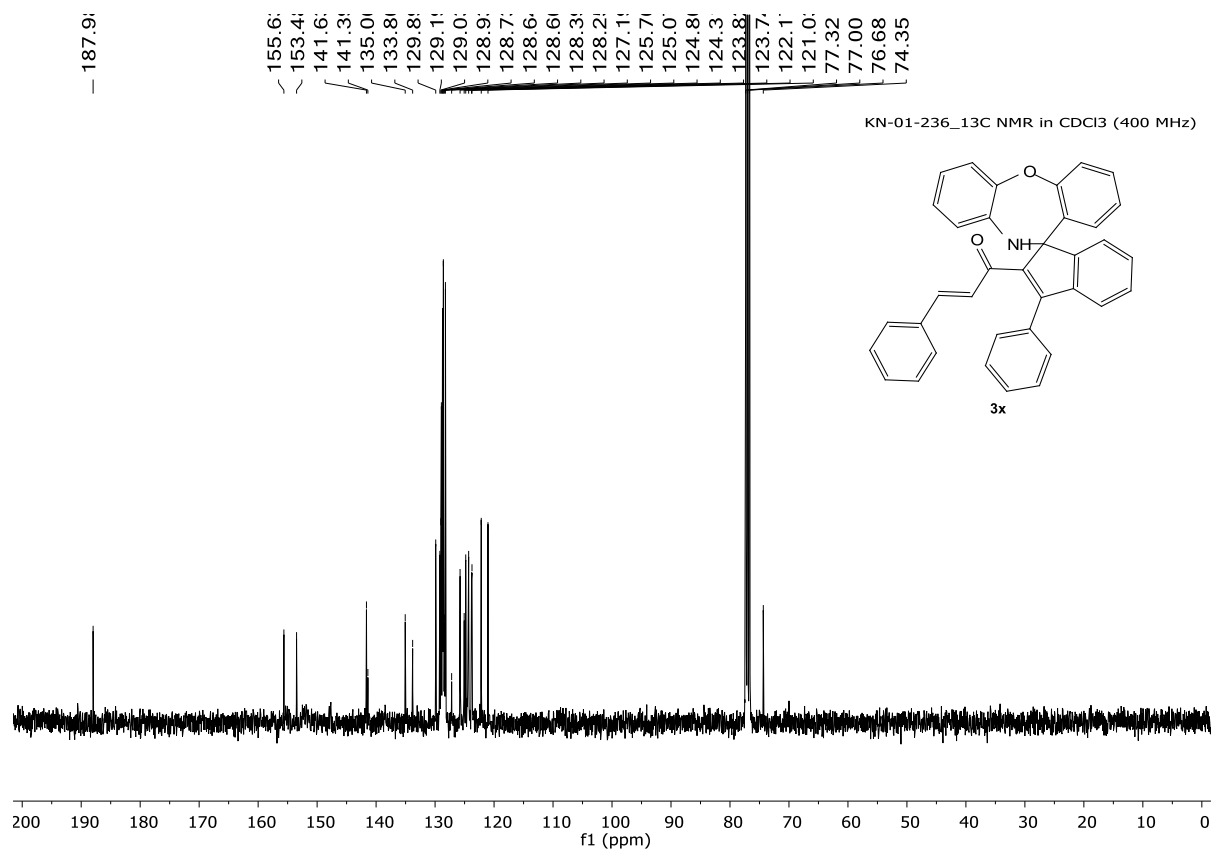
¹³C NMR of 3w (100 MHz, CDCl₃):



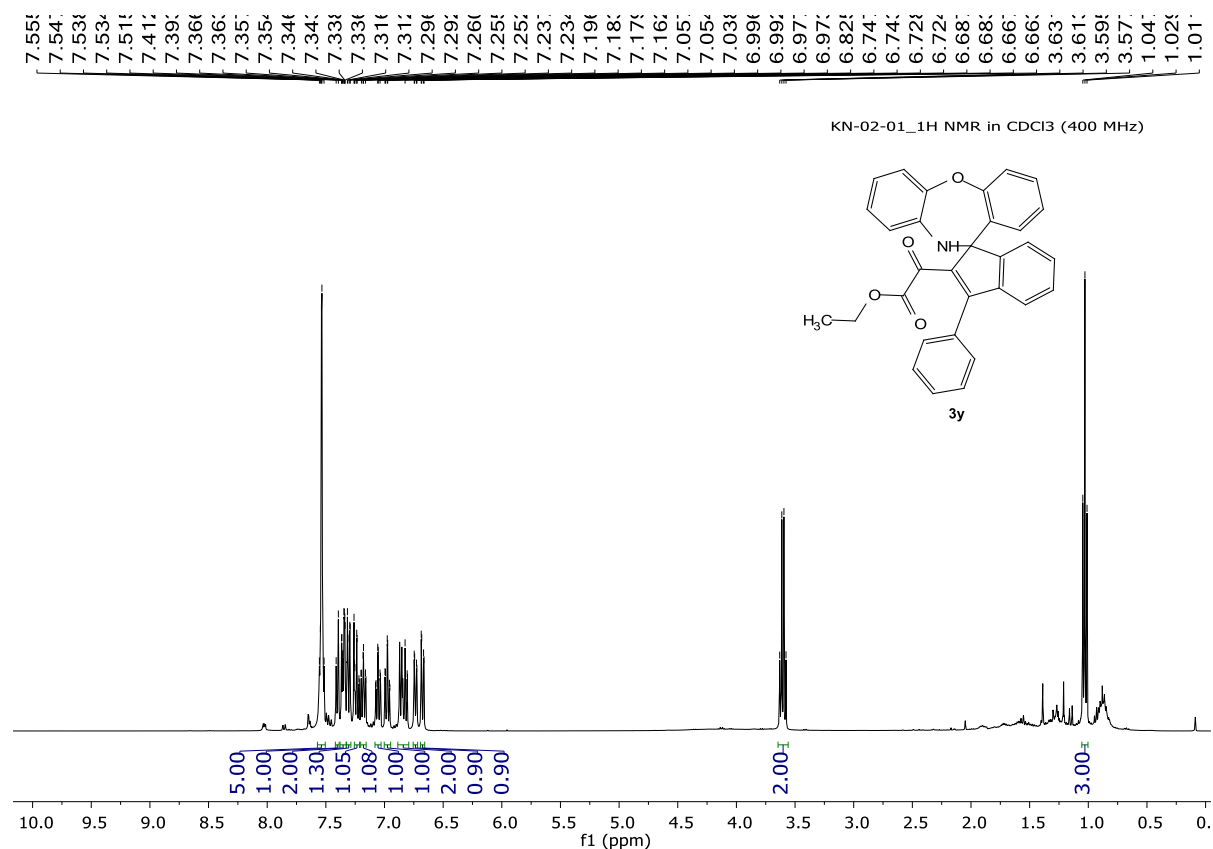
¹H NMR of 3x (400 MHz, CDCl₃):



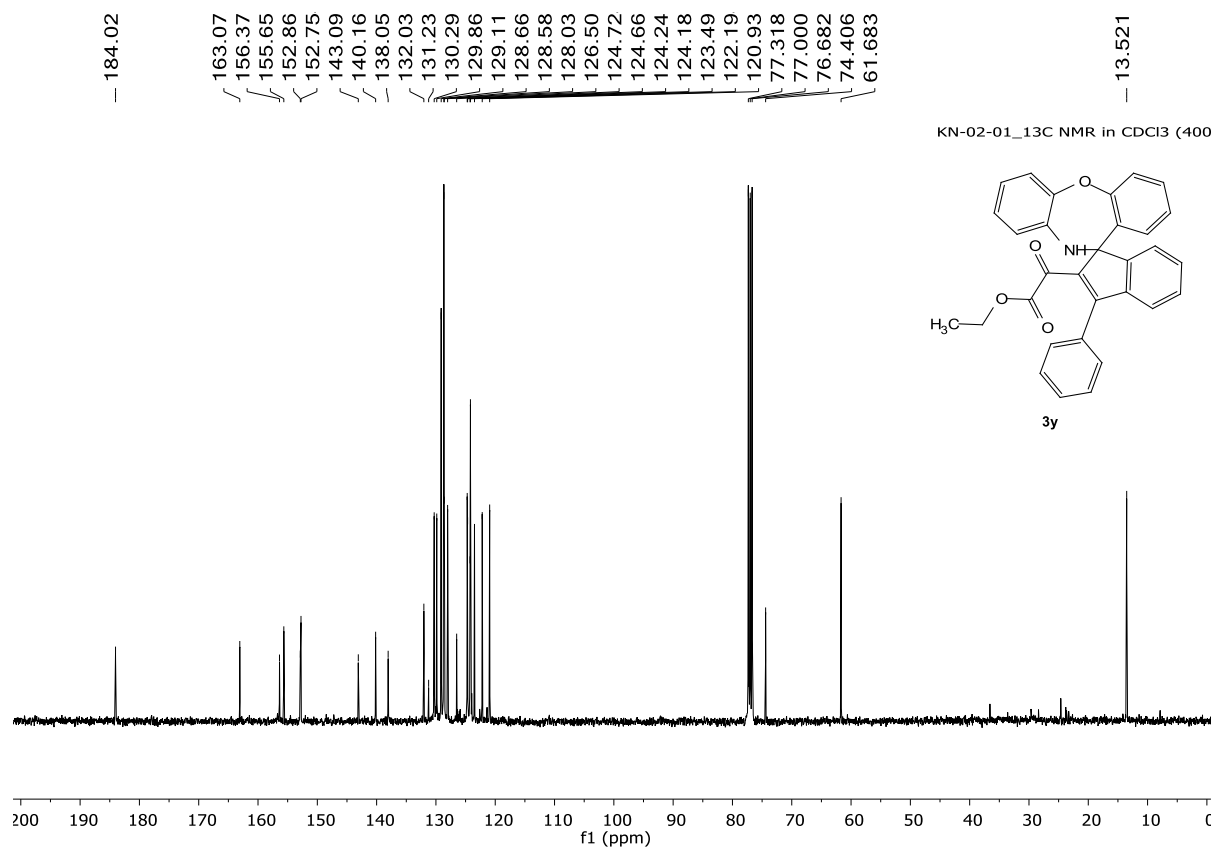
¹³C NMR of 3x (100 MHz, CDCl₃):



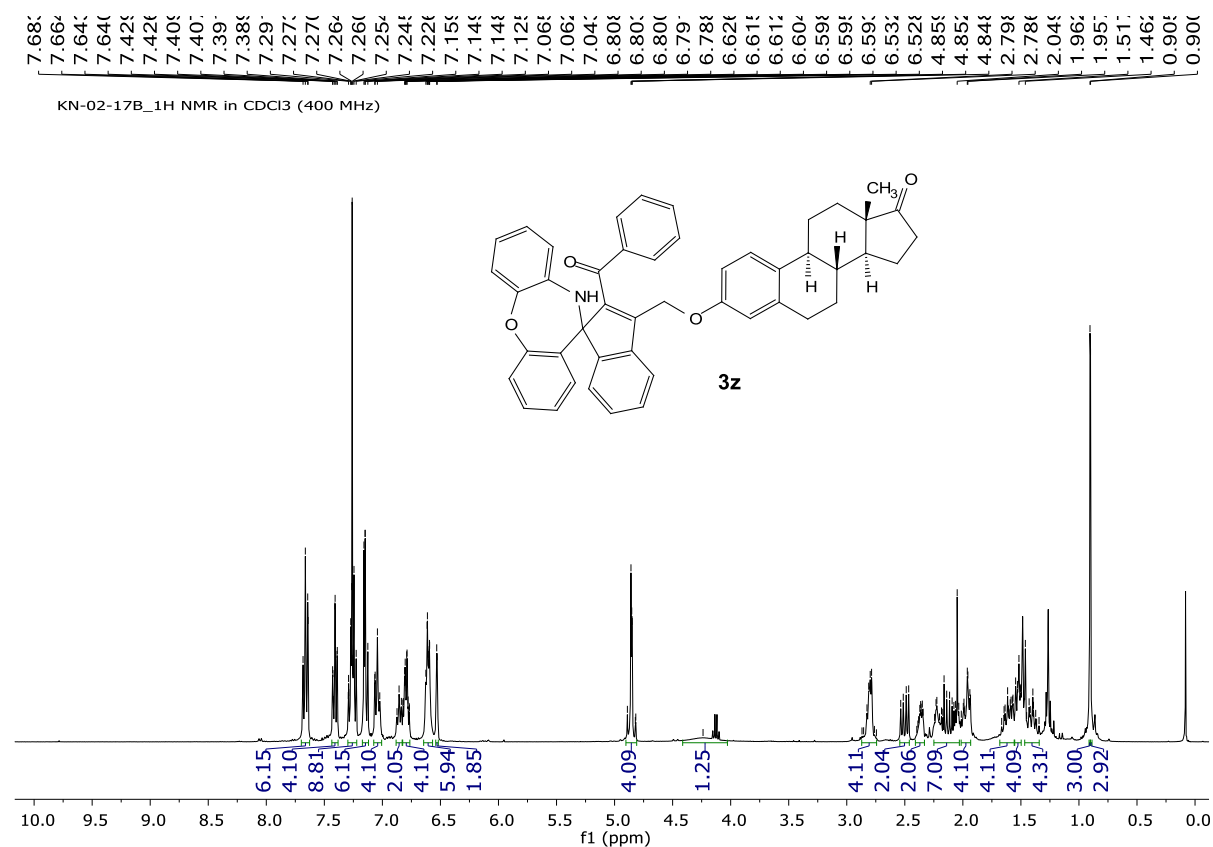
¹H NMR of 3y (400 MHz, CDCl₃):



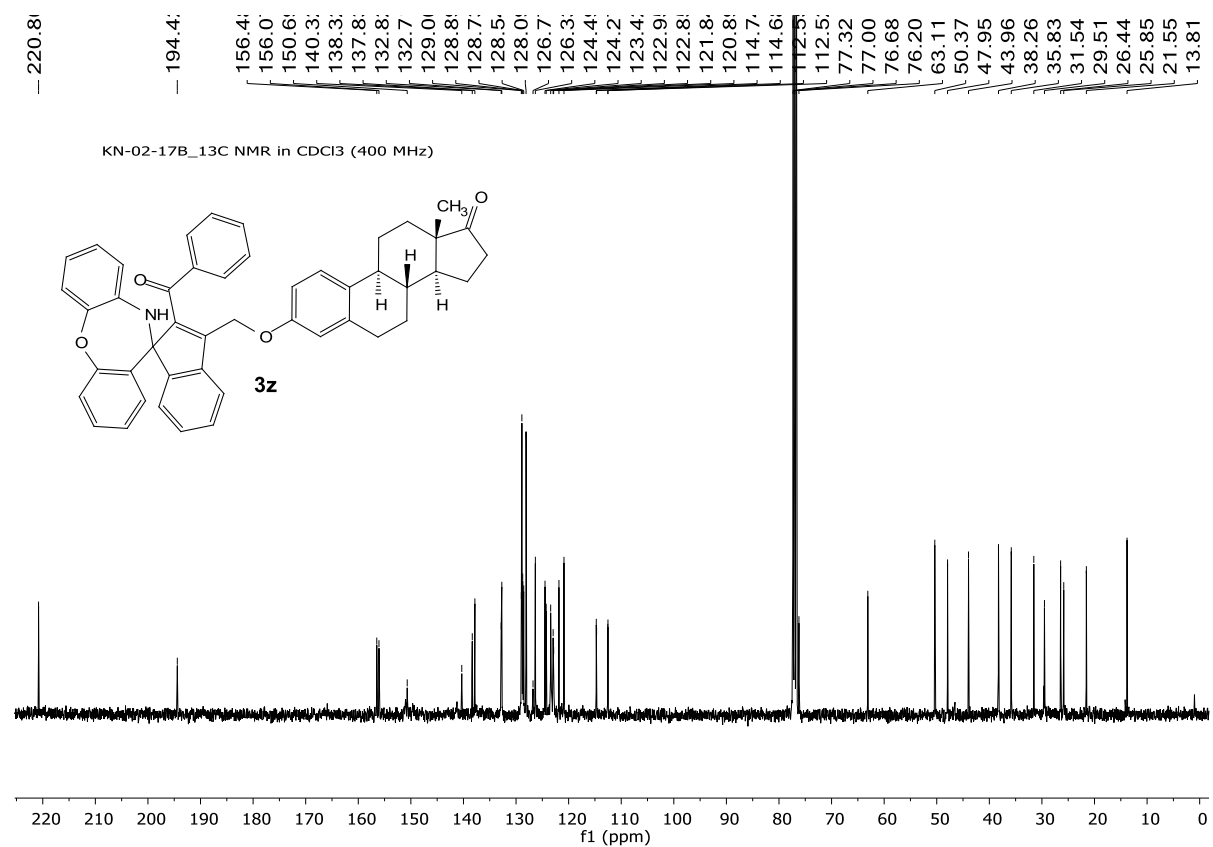
¹³C NMR of 3y (100 MHz, CDCl₃):



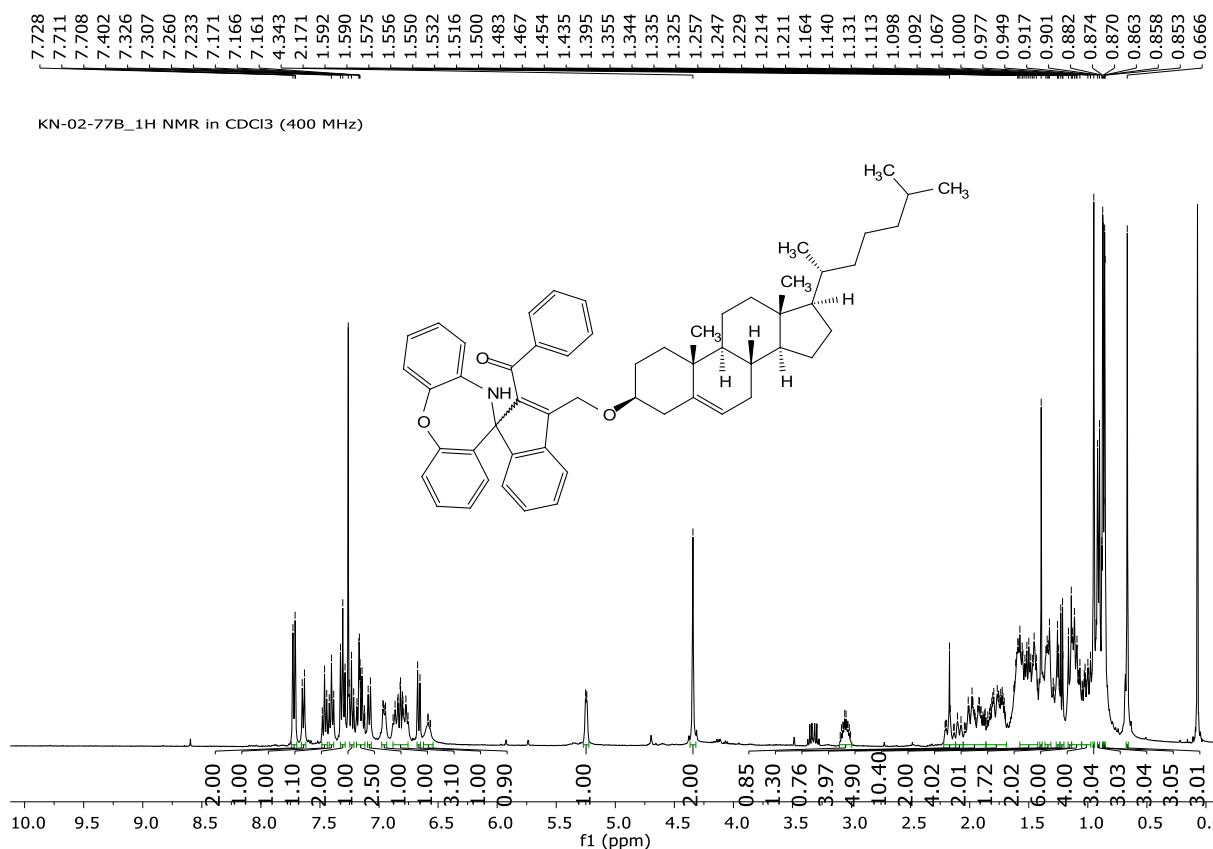
¹H NMR of 3z (400 MHz, CDCl₃):



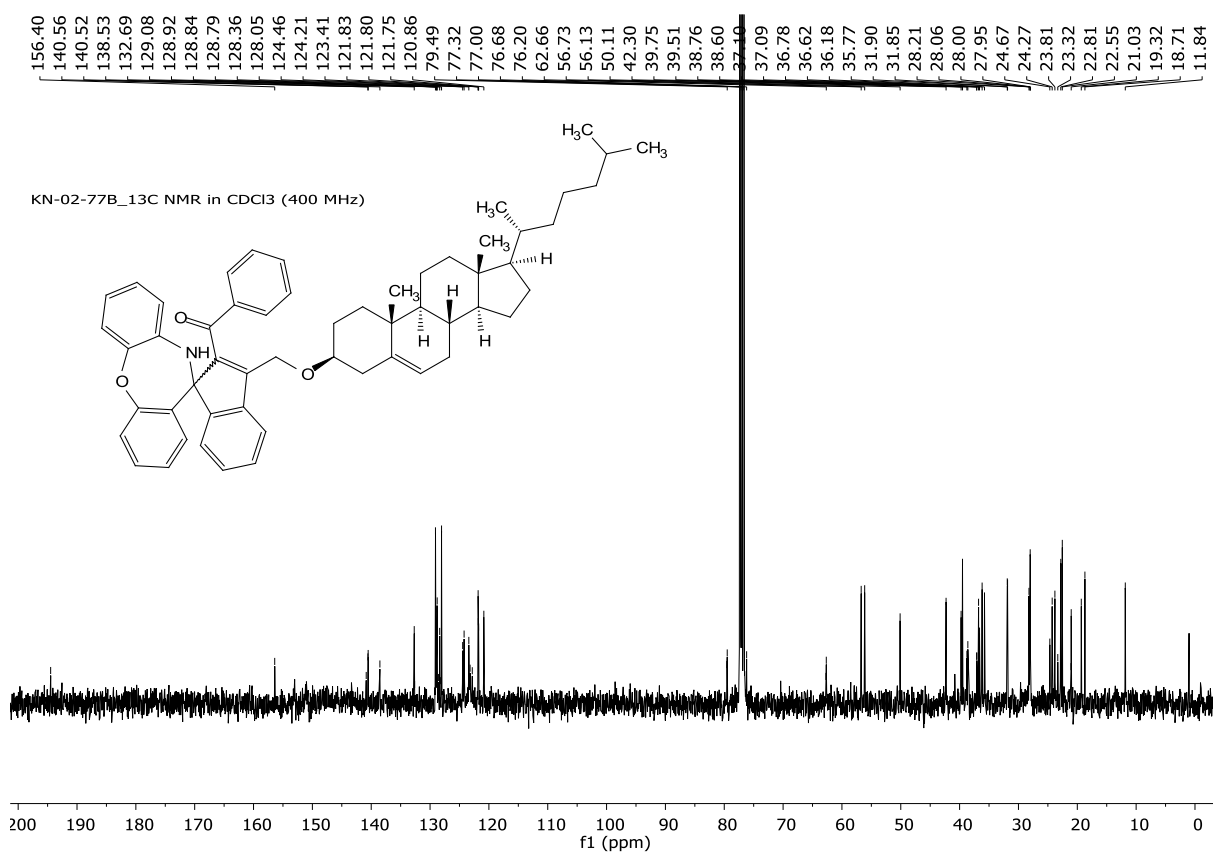
¹³C NMR of 3z (100 MHz, CDCl₃):



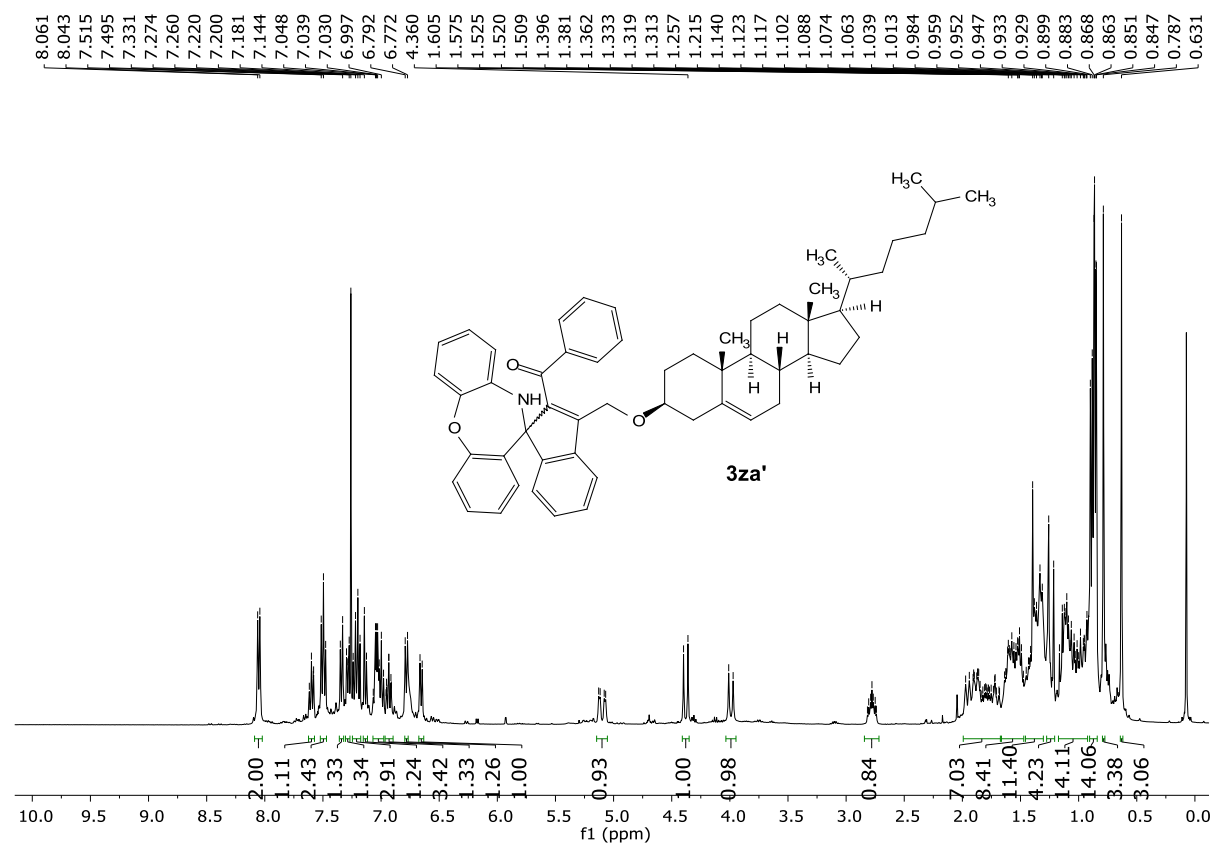
¹H NMR of 3a (400 MHz, CDCl₃):



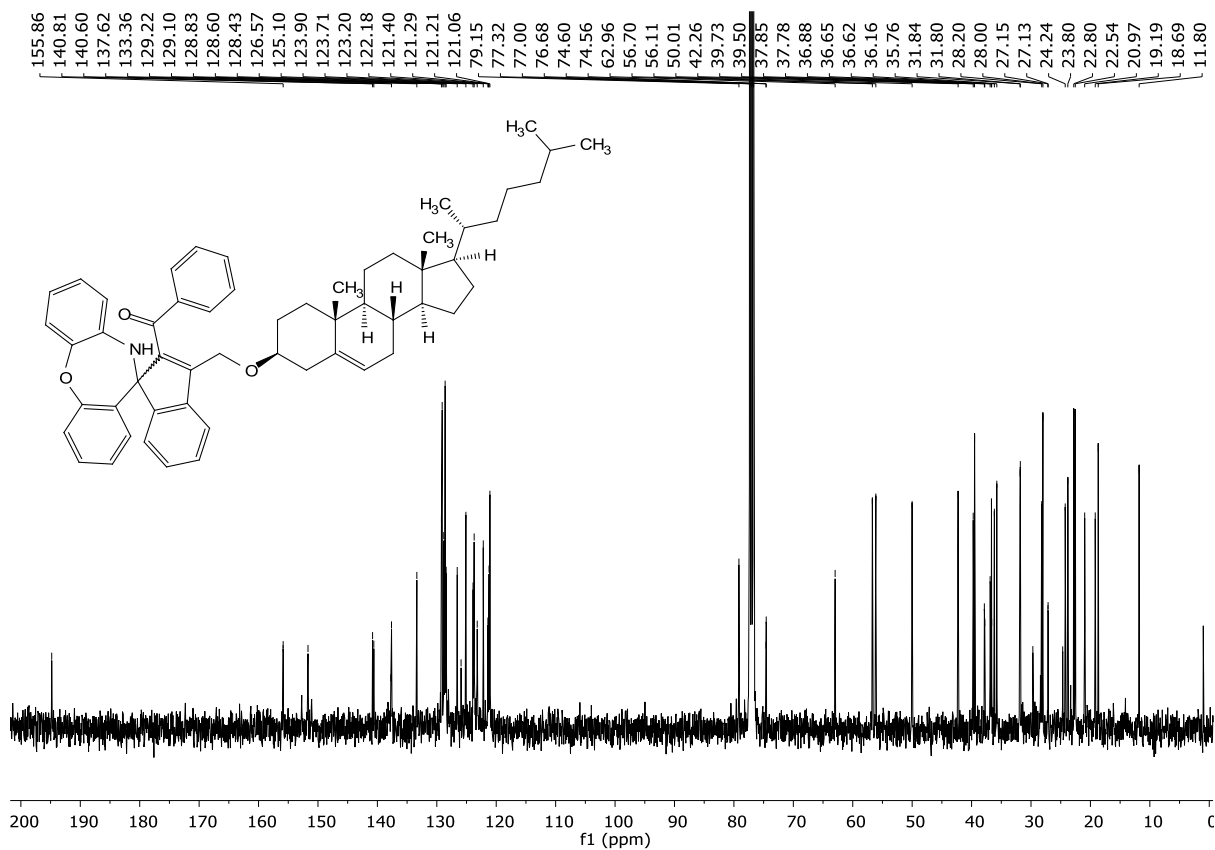
¹³C NMR of 3a (100 MHz, CDCl₃):



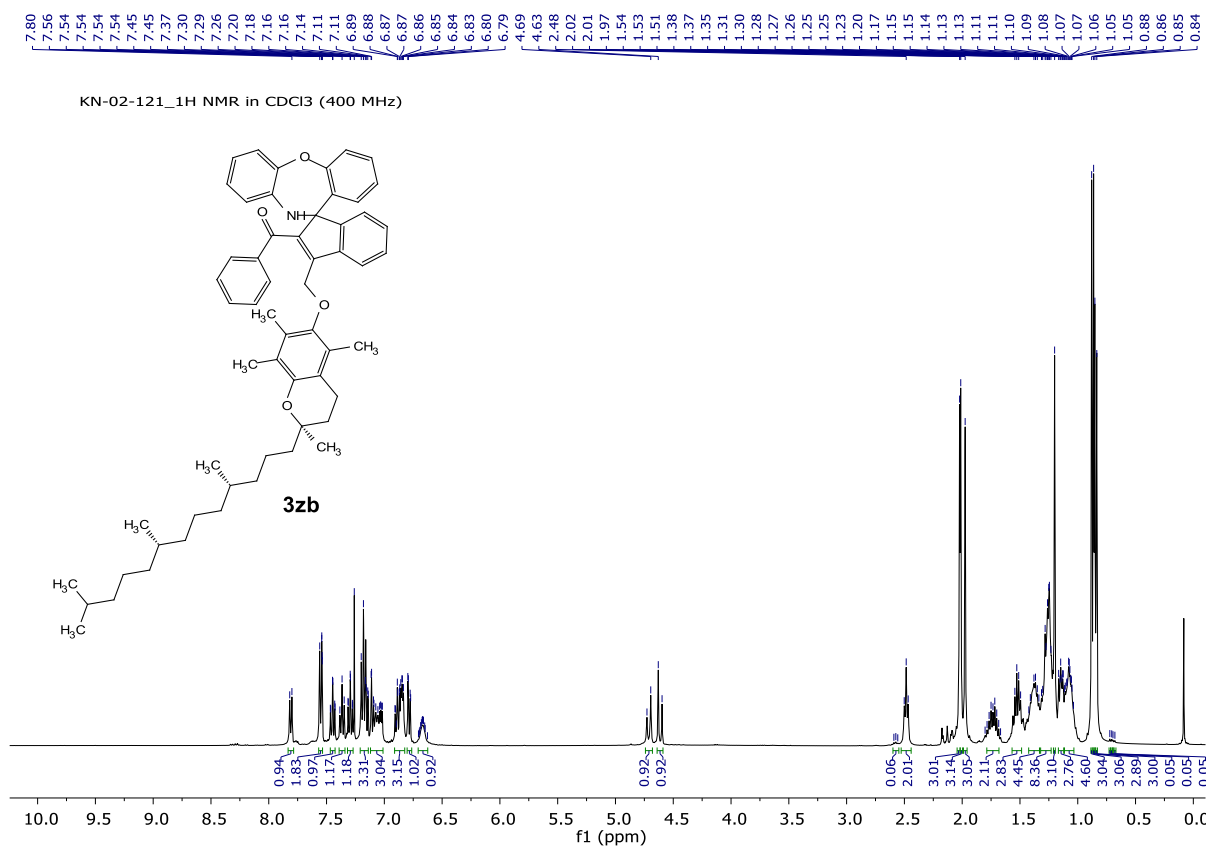
¹H NMR of 3za' (400 MHz, CDCl₃):



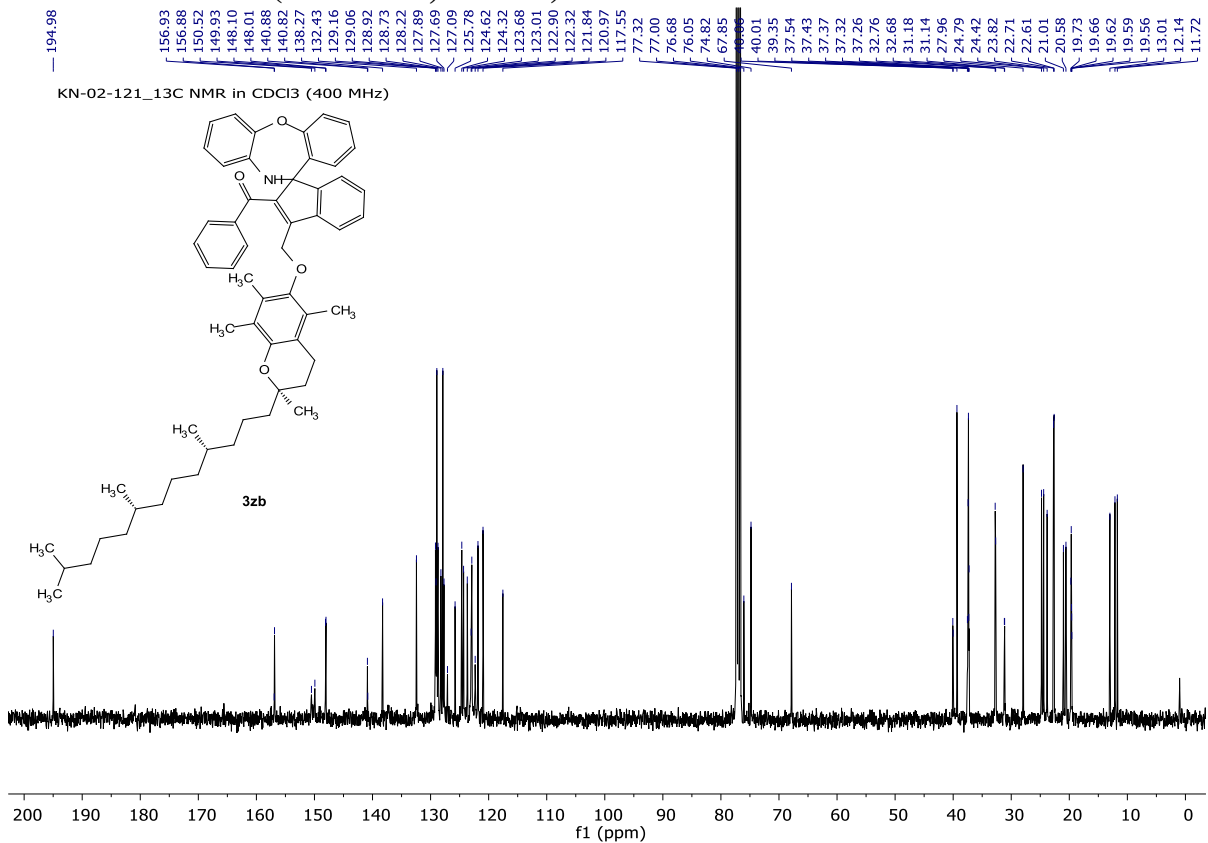
¹³C NMR of 3za' (100 MHz, CDCl₃):



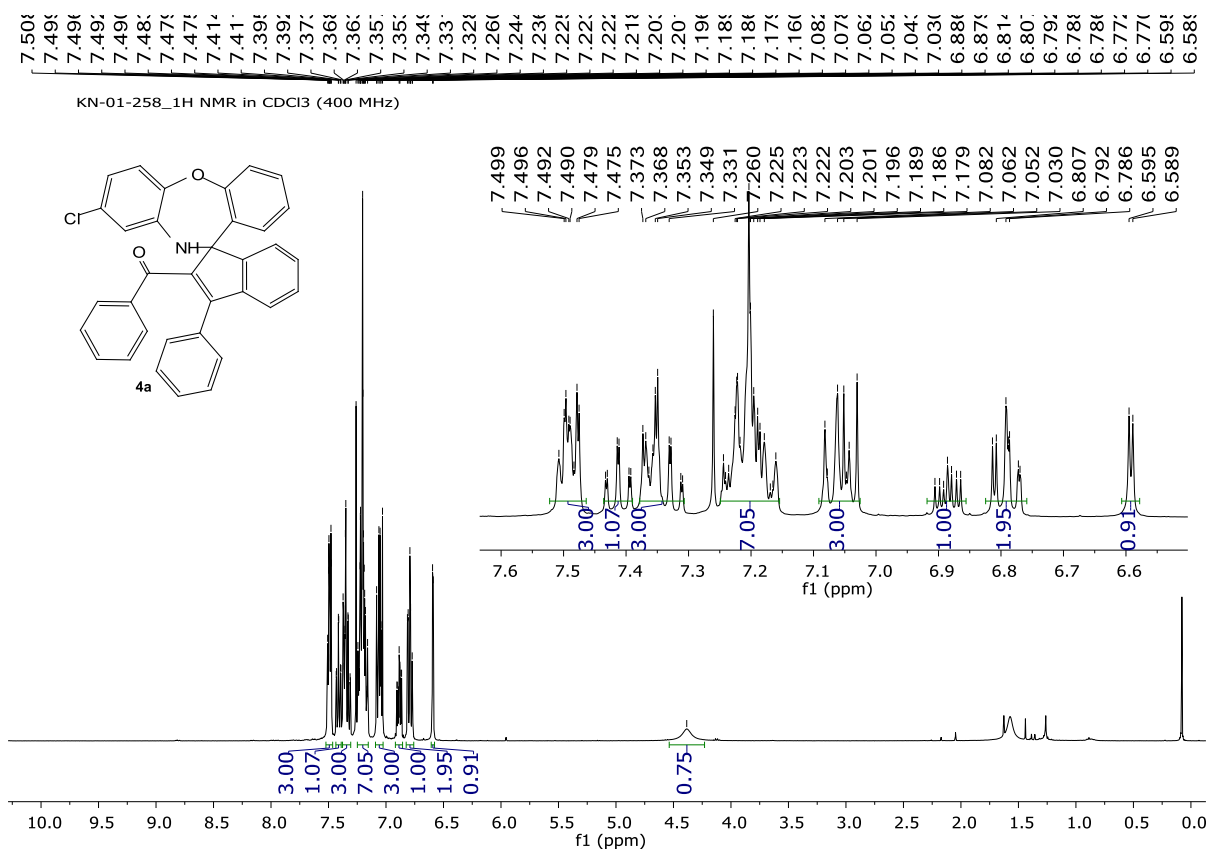
¹H NMR of 3zb (400 MHz, CDCl₃):



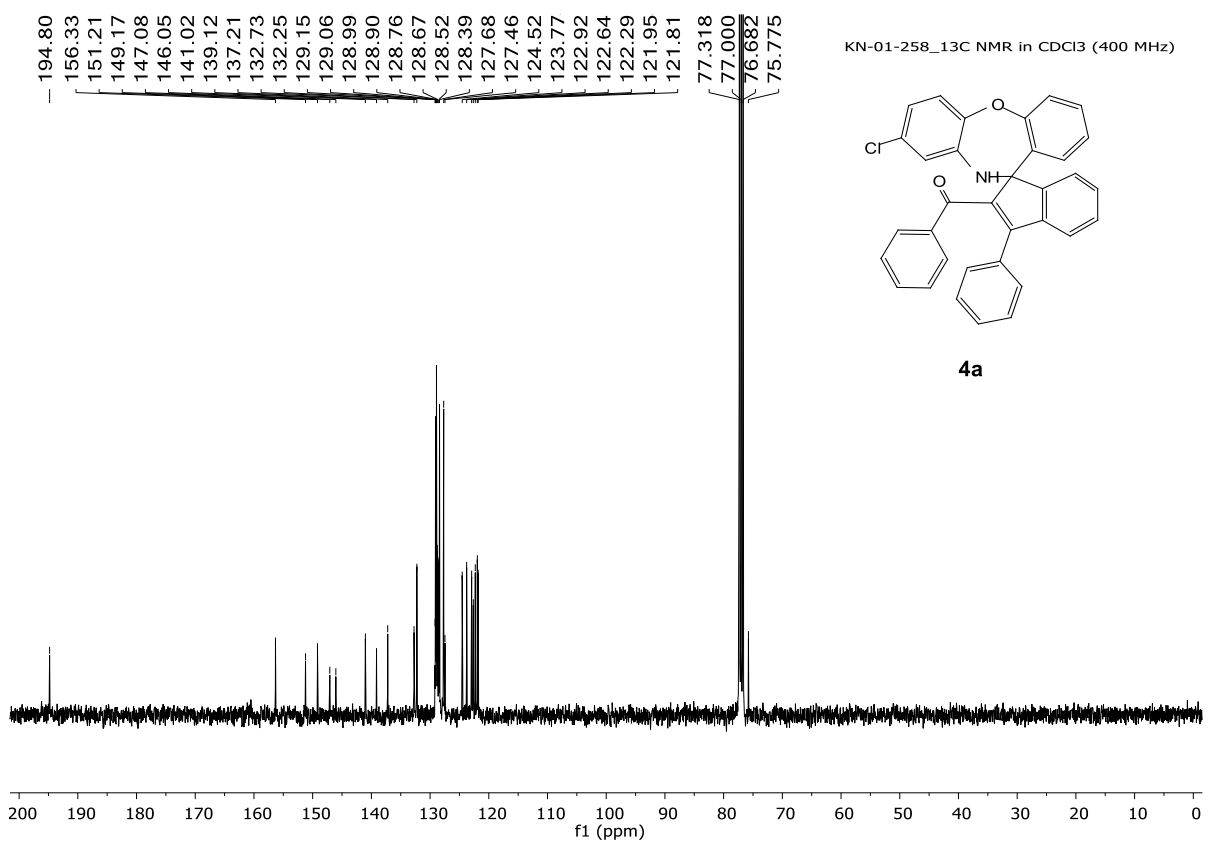
¹³C NMR of 3zb (100 MHz, CDCl₃):



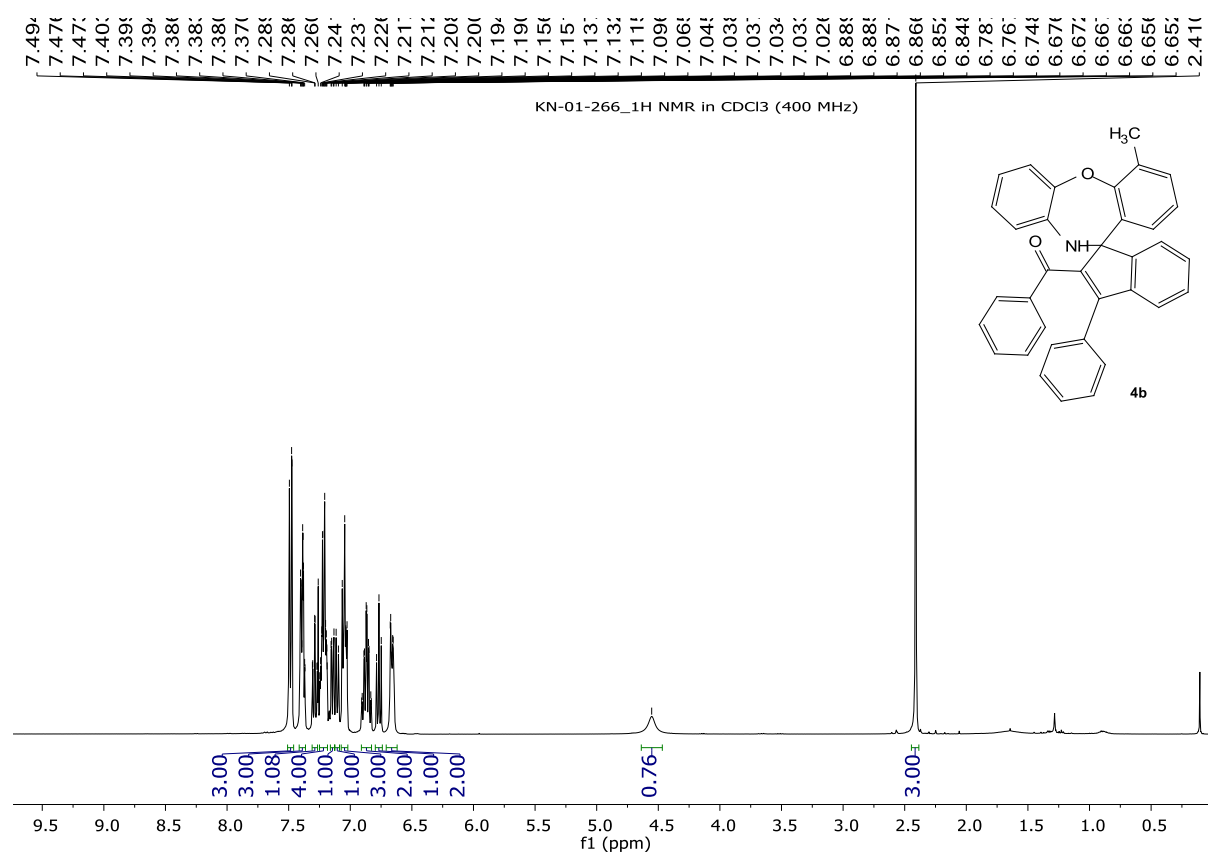
¹H NMR of 4a (400 MHz, CDCl₃):



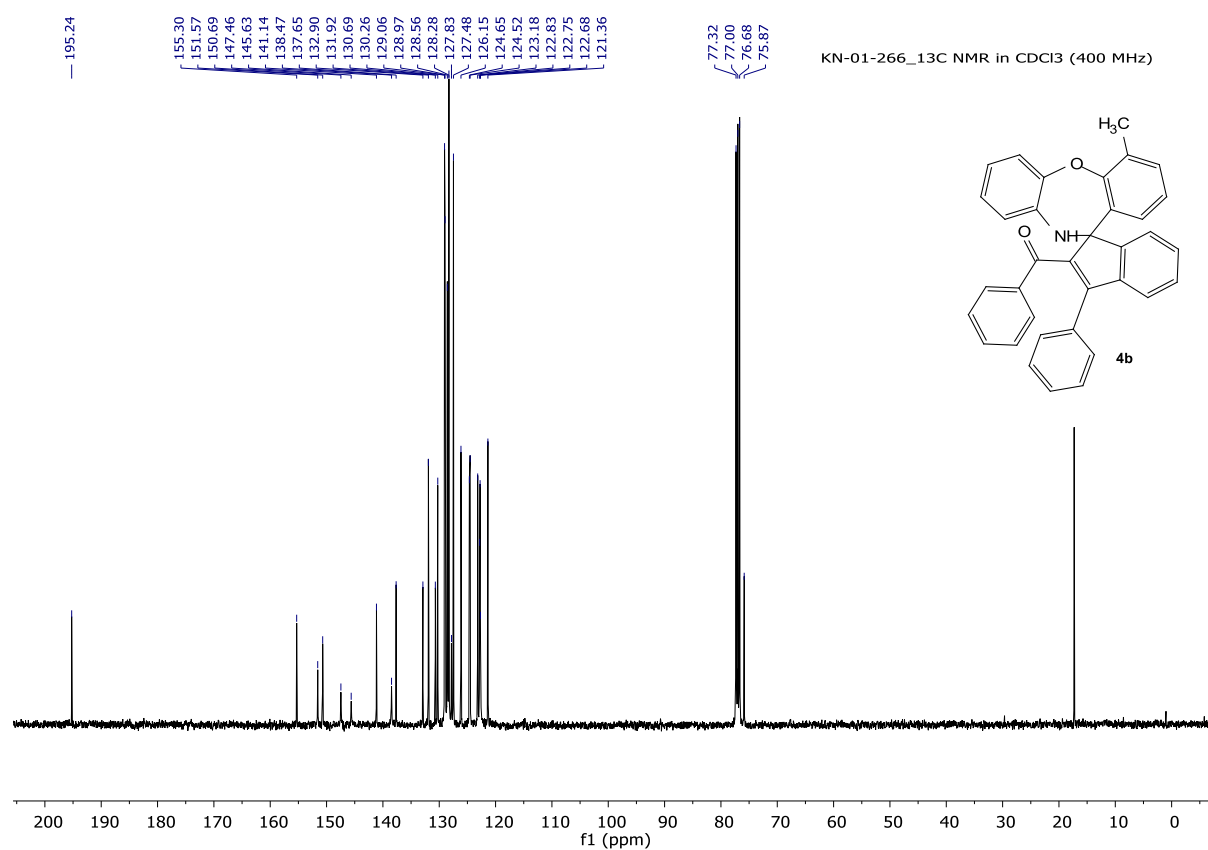
¹³C NMR of 4a (100 MHz, CDCl₃):



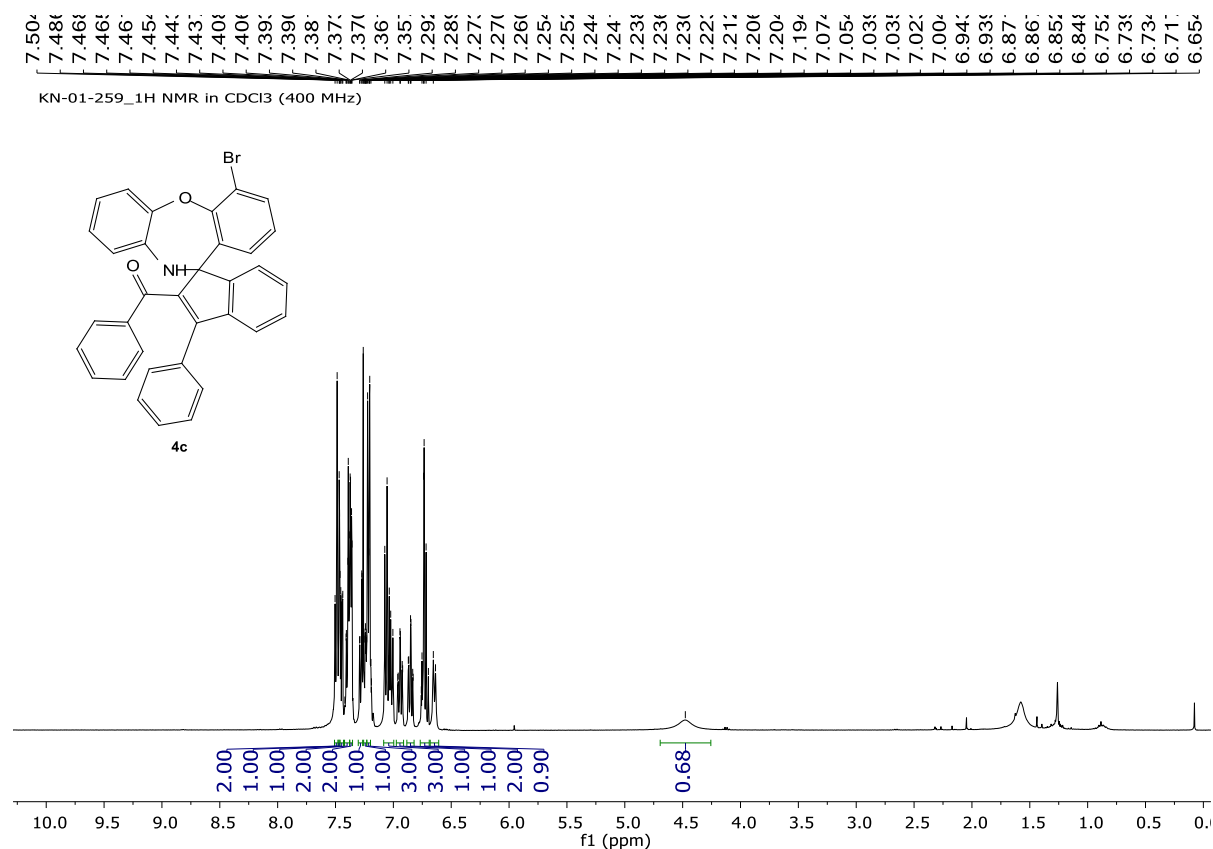
¹H NMR of 4b (400 MHz, CDCl₃):



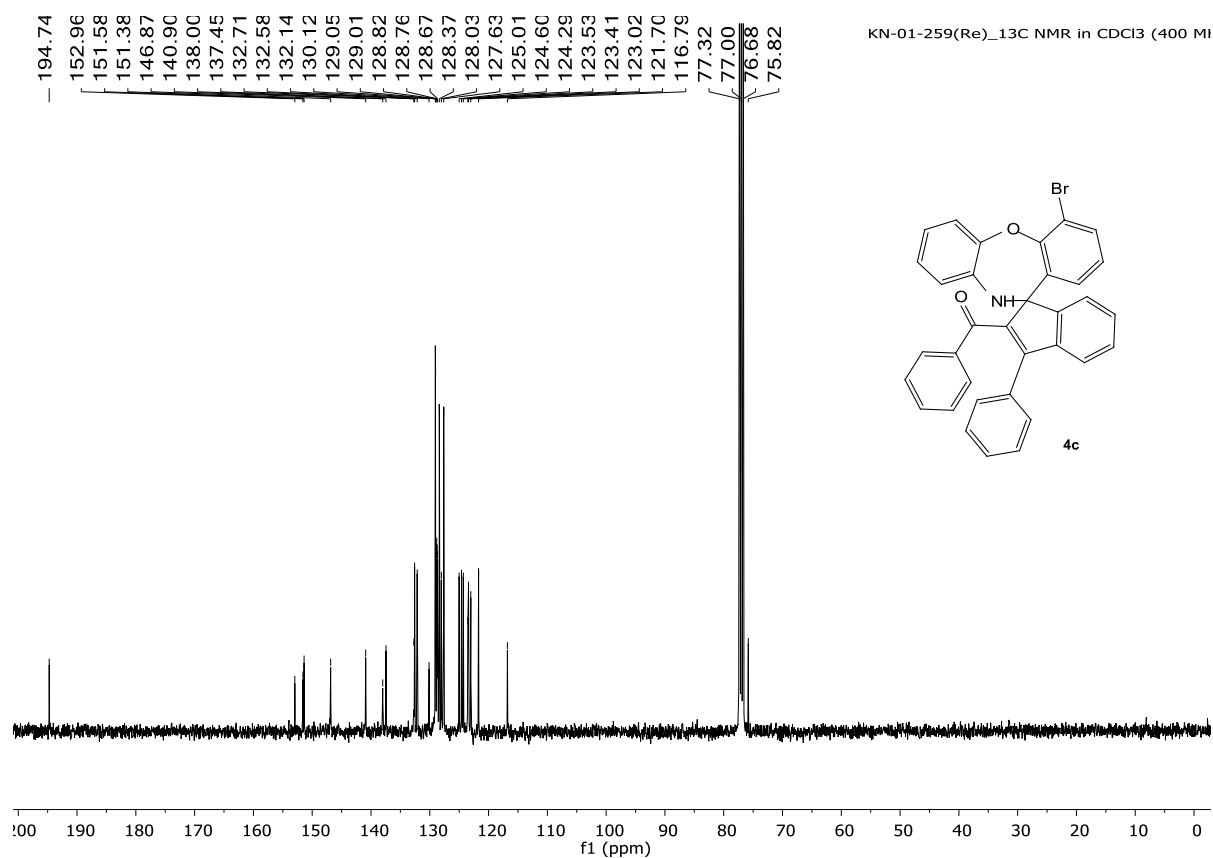
¹³C NMR of 4b (100 MHz, CDCl₃):



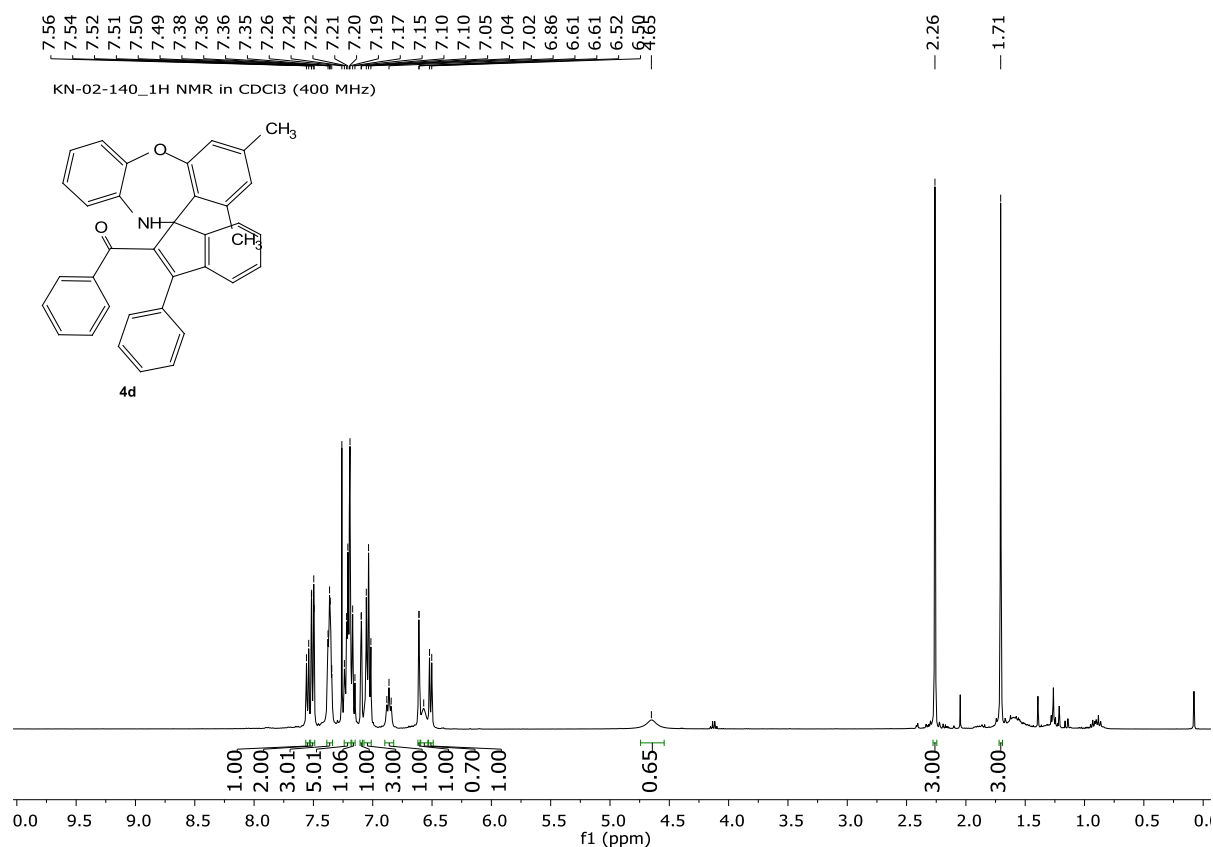
¹H NMR of 4c (400 MHz, CDCl₃):



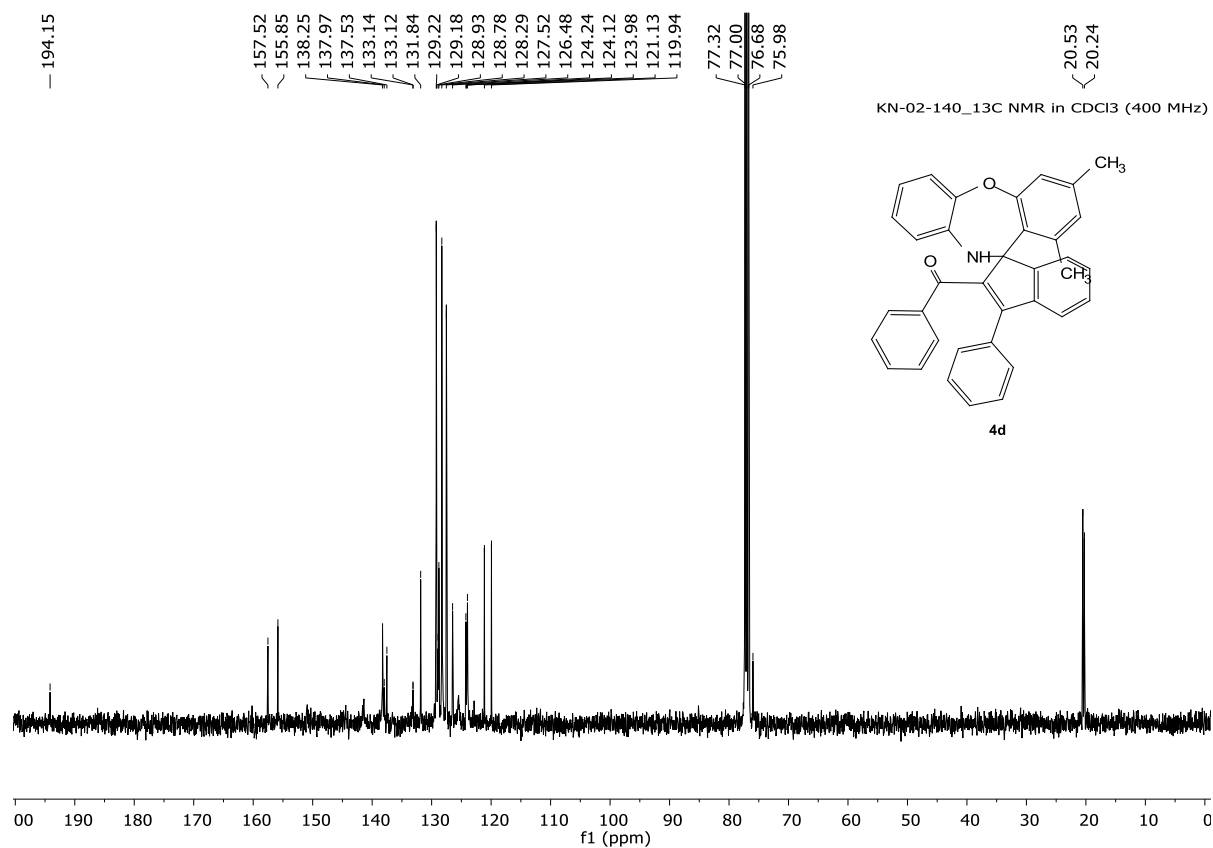
¹³C NMR of 4c (100 MHz, CDCl₃):



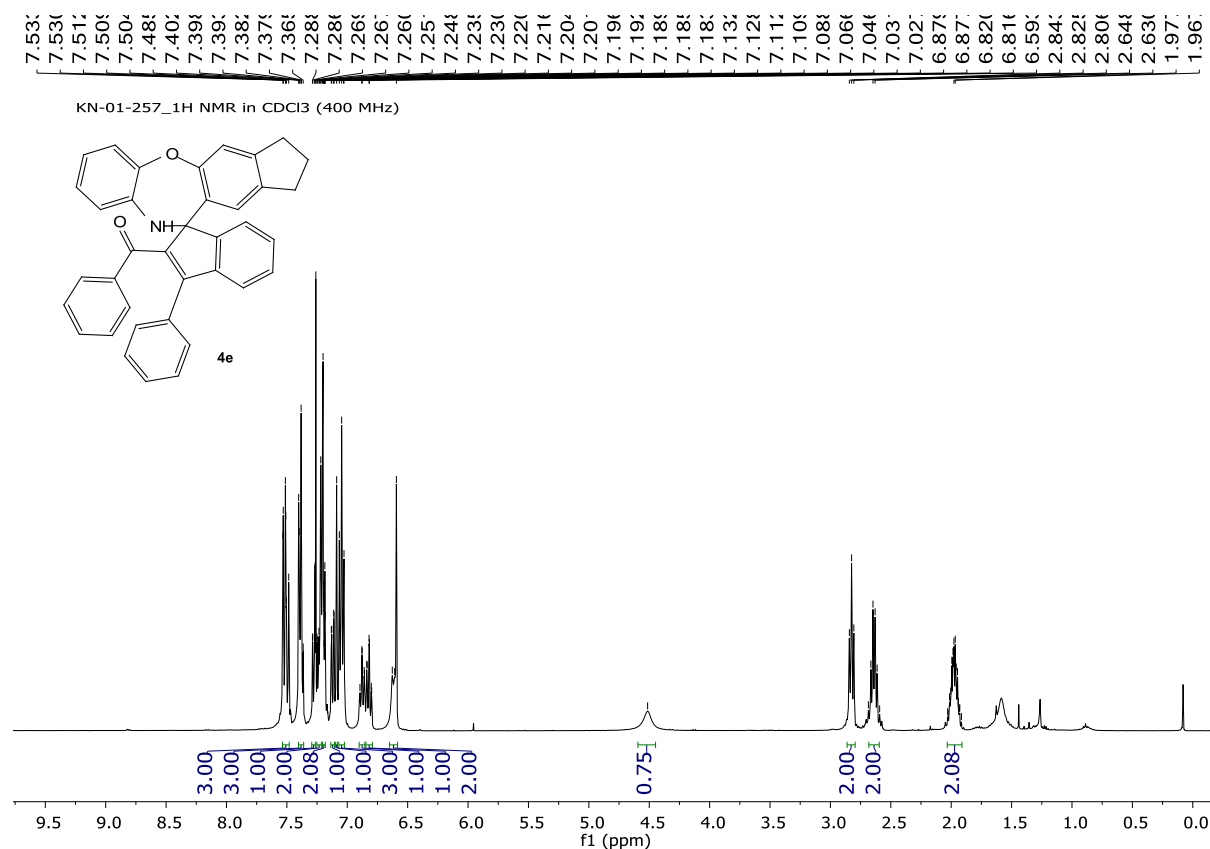
¹H NMR of 4d (400 MHz, CDCl₃):



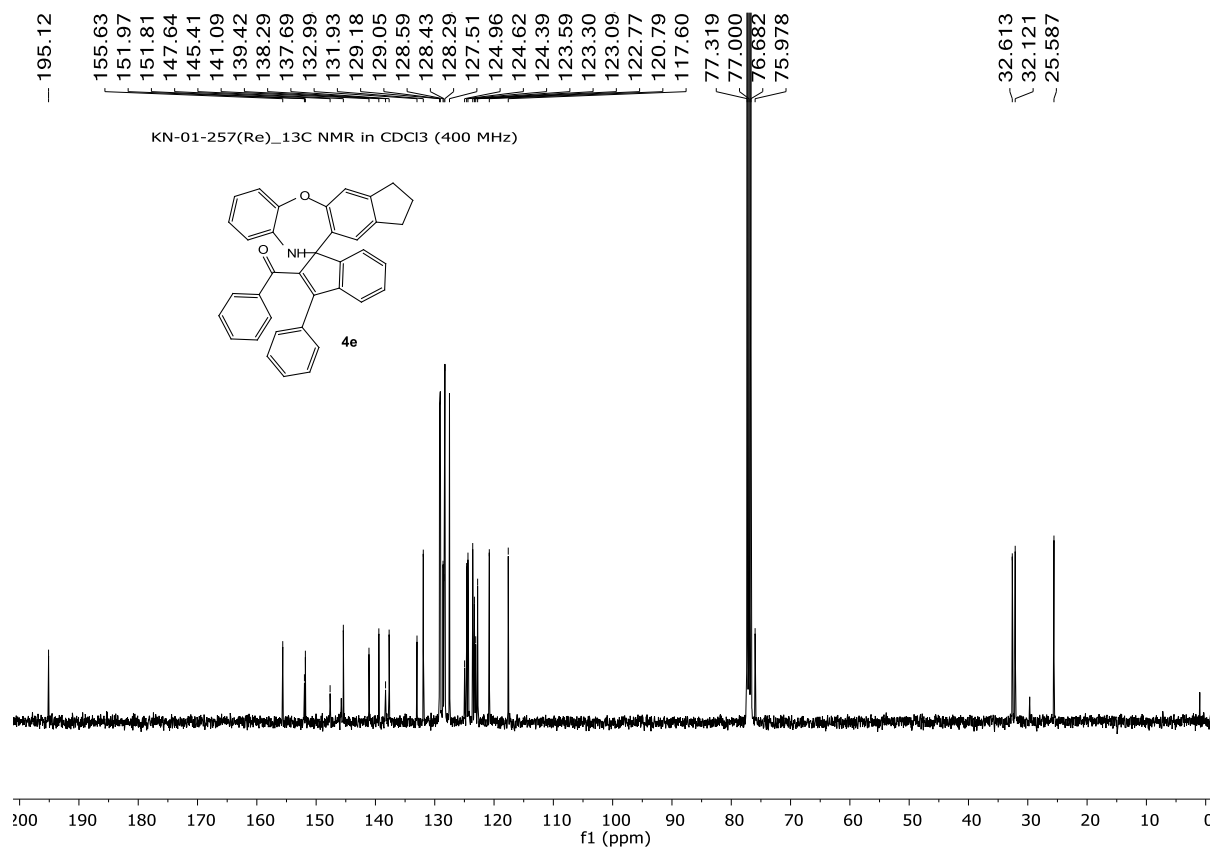
¹³C NMR of 4d (100 MHz, CDCl₃):



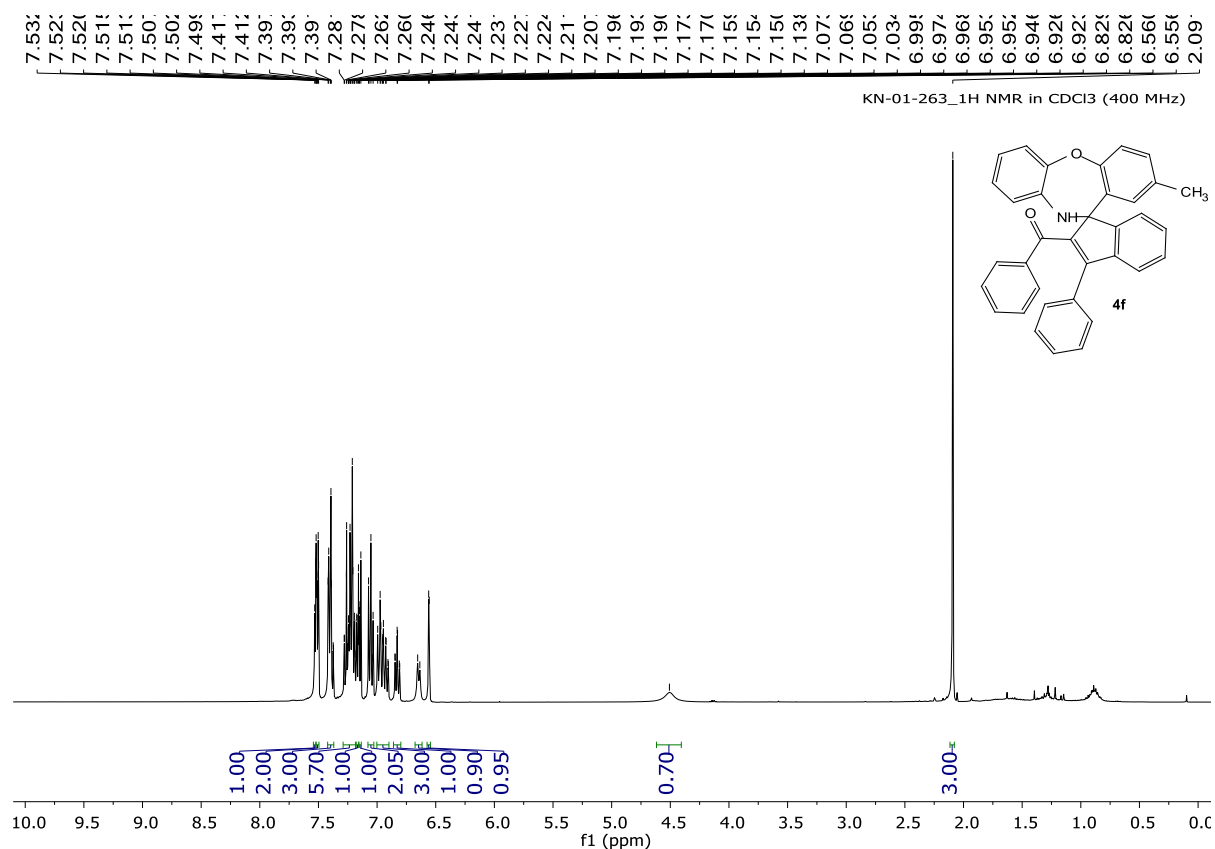
¹H NMR of 4e (400 MHz, CDCl₃):



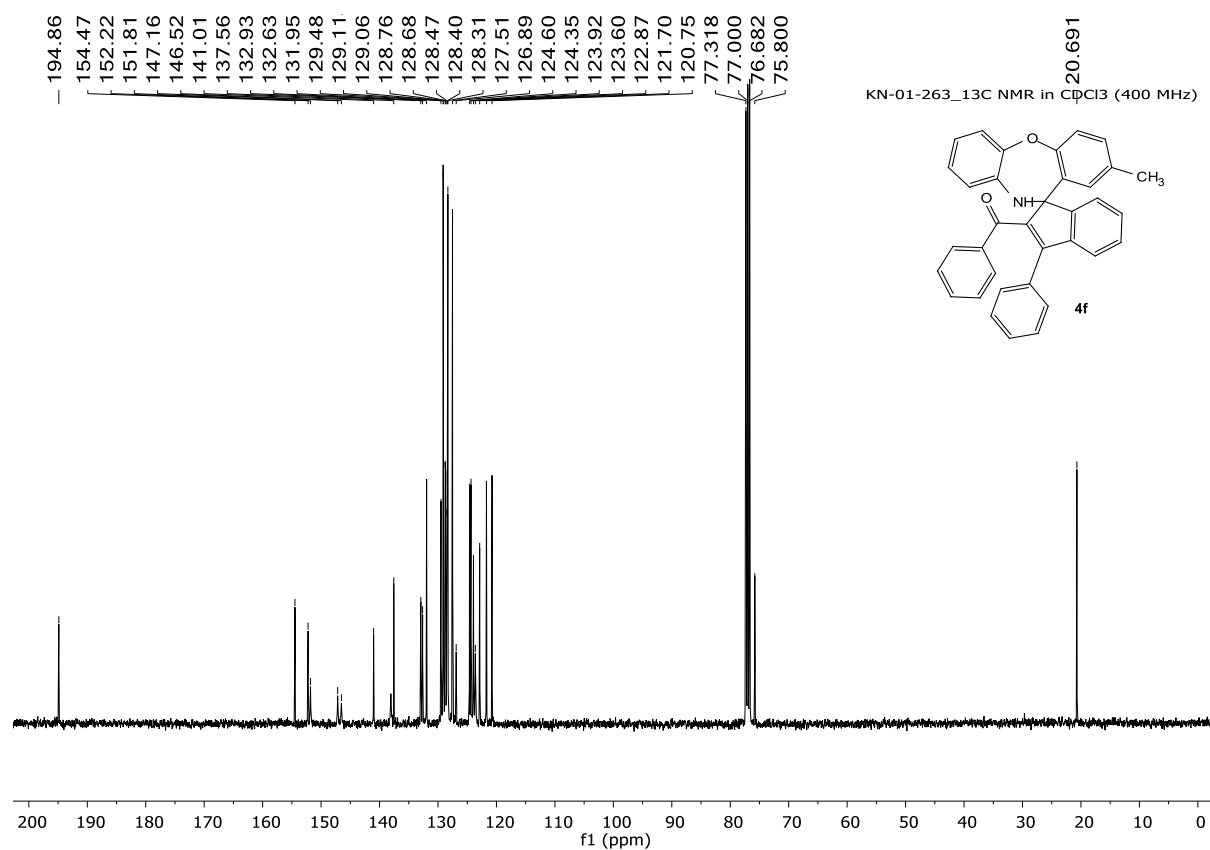
¹³C NMR of 4e (100 MHz, CDCl₃):



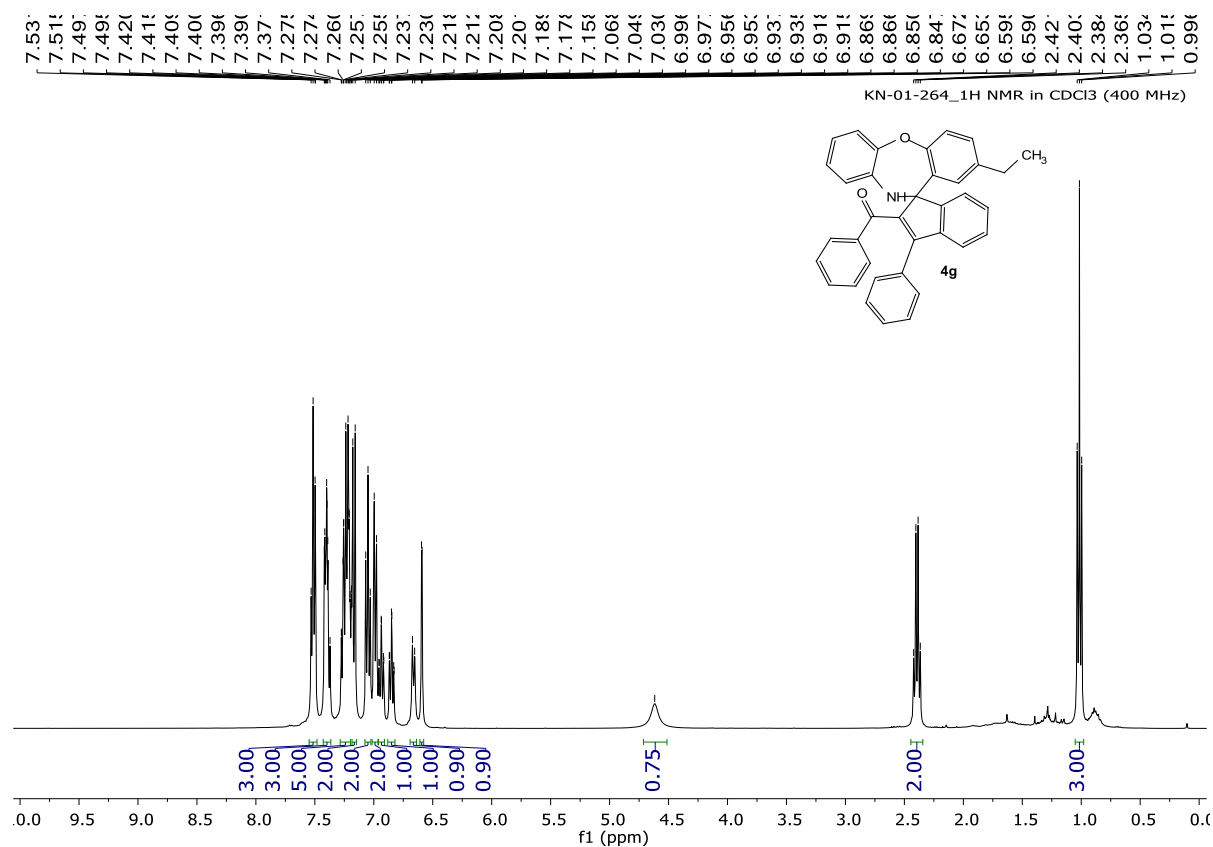
¹H NMR of 4f (400 MHz, CDCl₃):



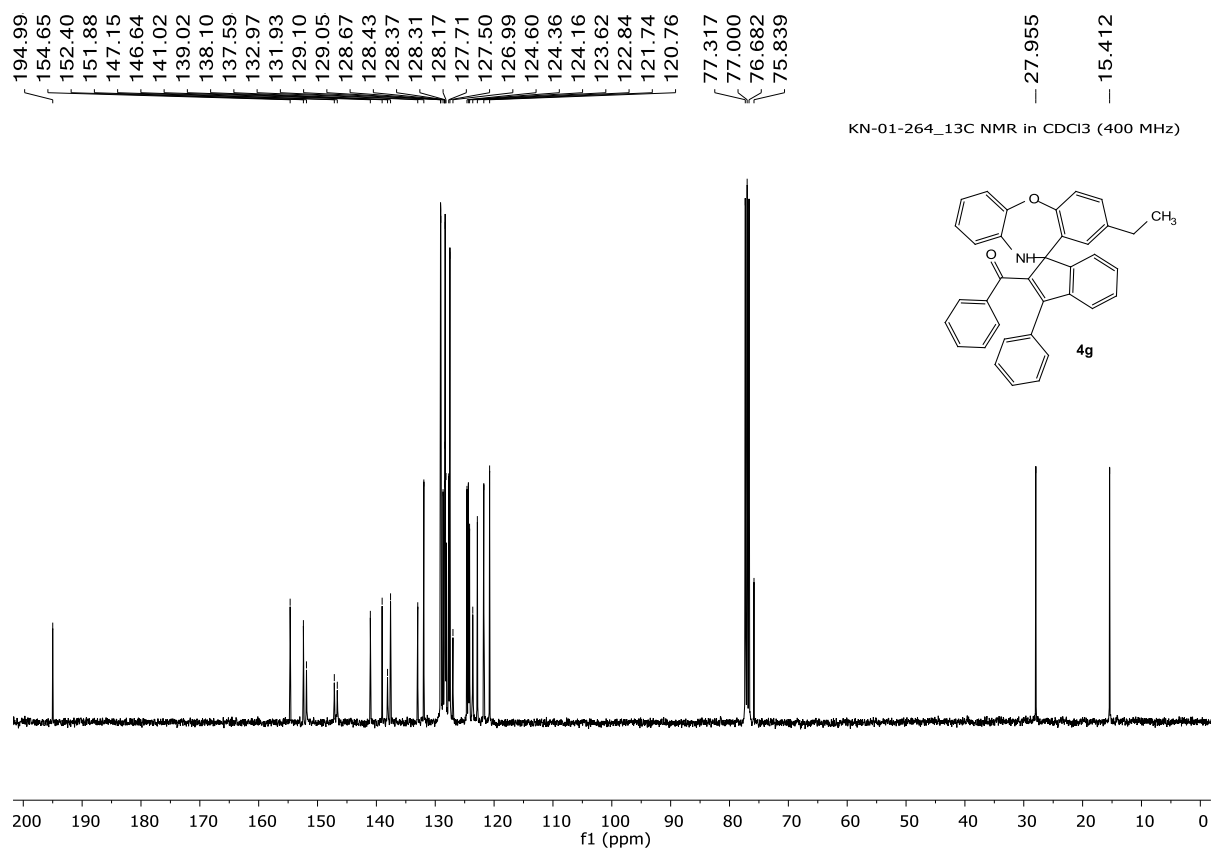
¹³C NMR of 4f (100 MHz, CDCl₃):



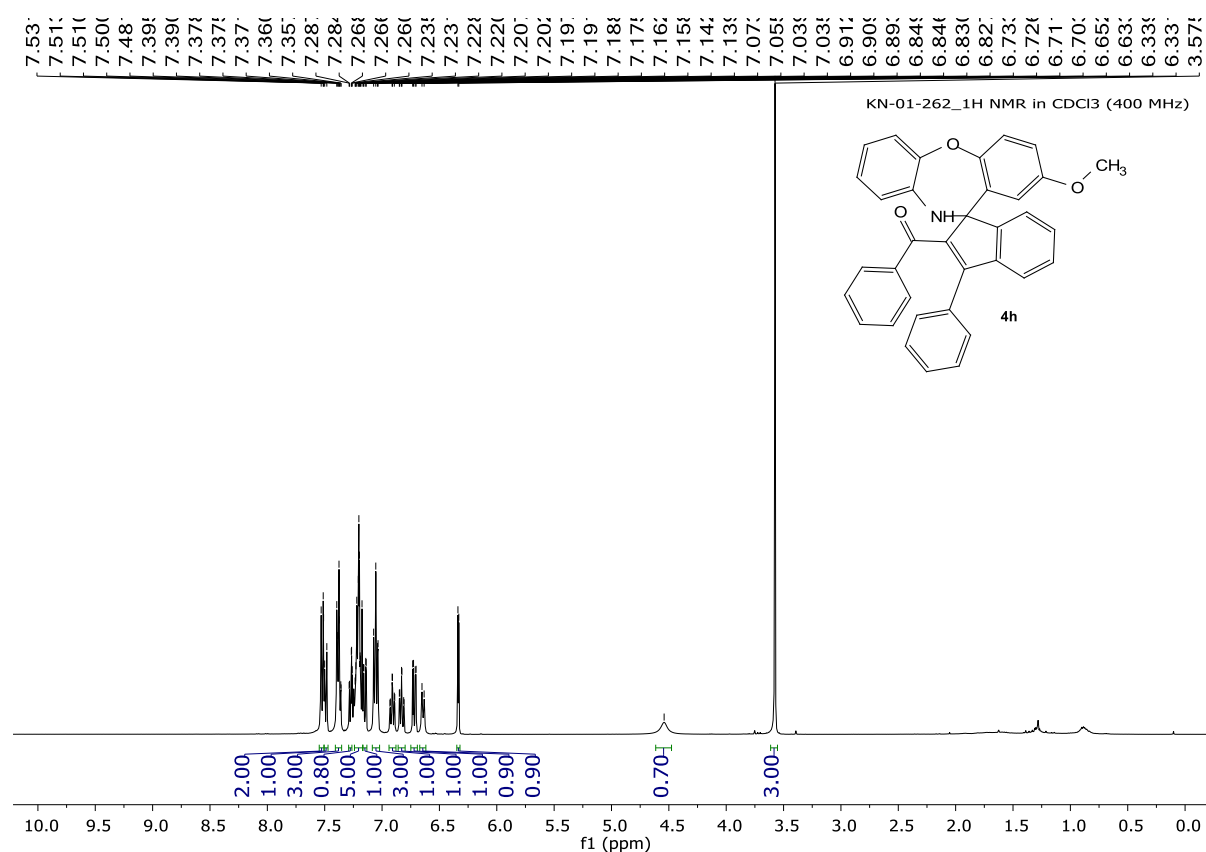
¹H NMR of 4g (400 MHz, CDCl₃):



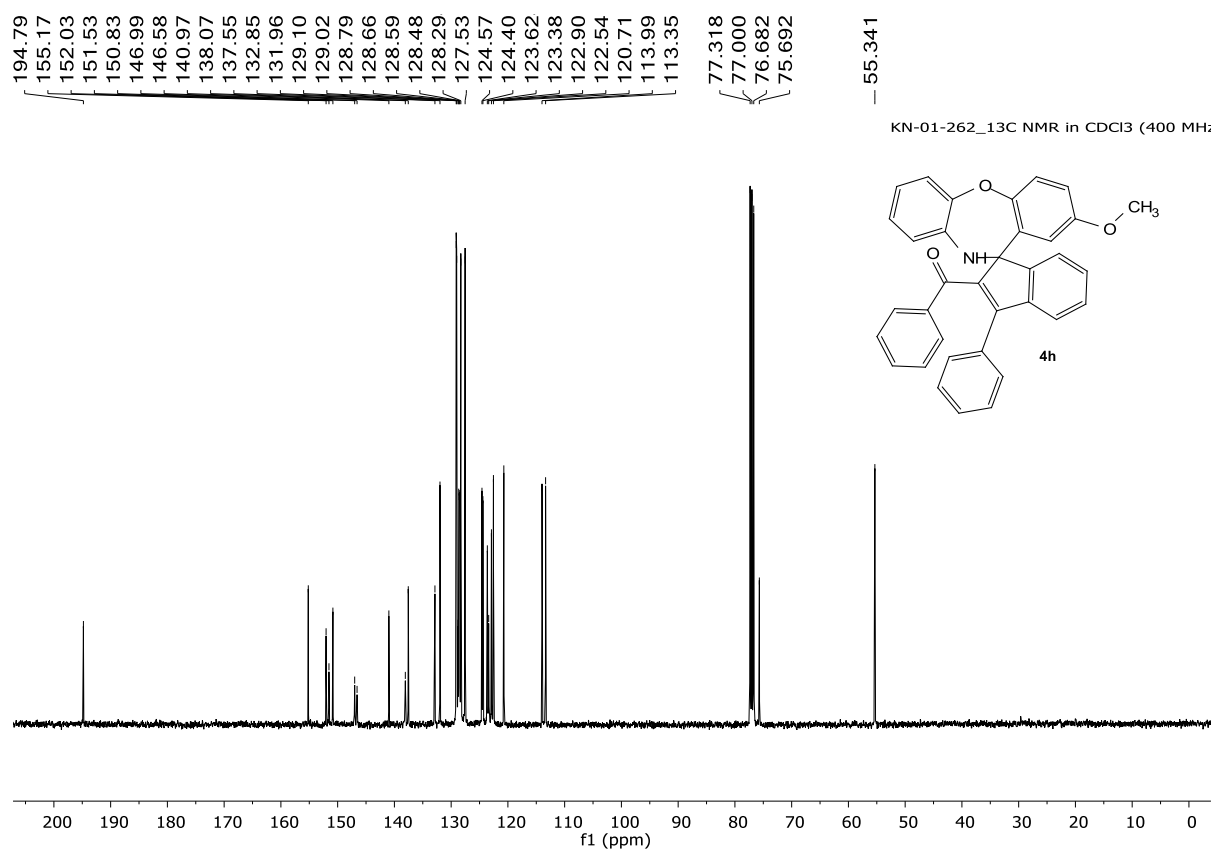
¹³C NMR of 4g (100 MHz, CDCl₃):



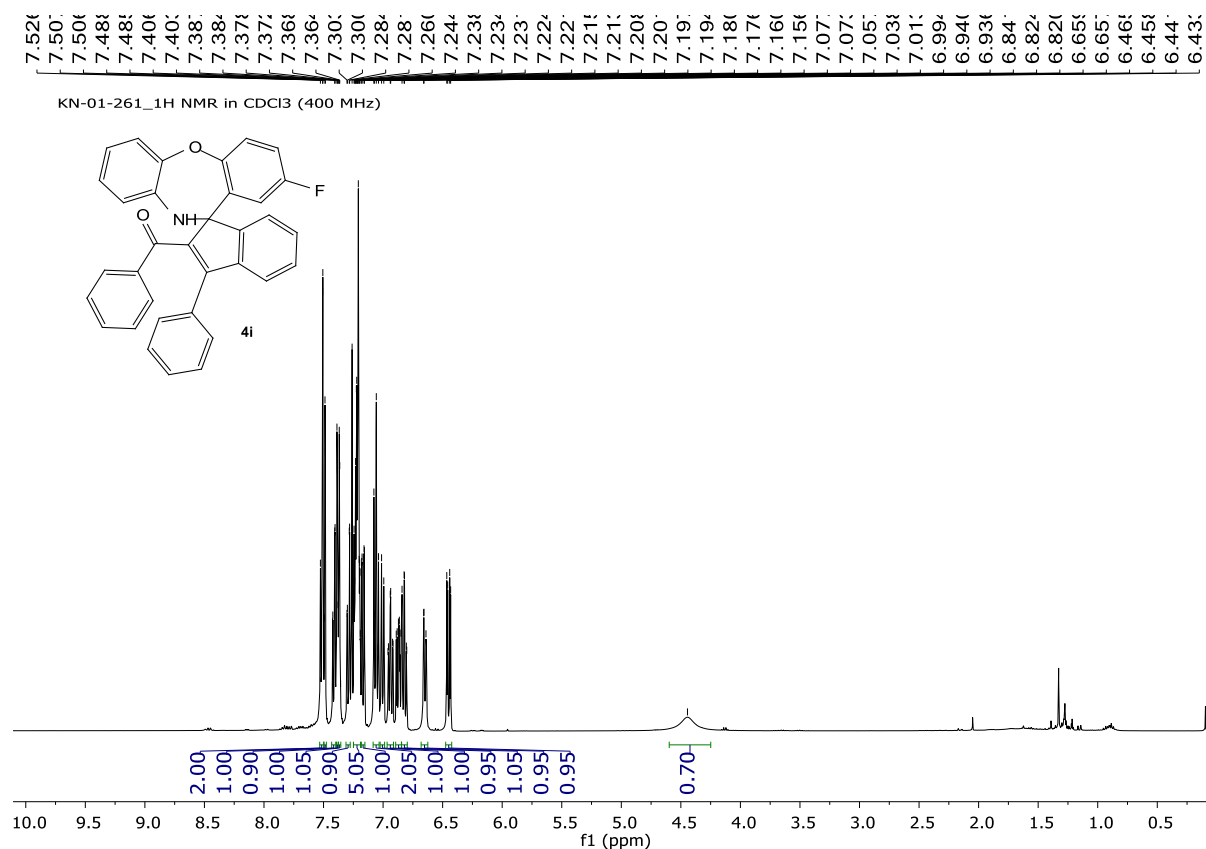
¹H NMR of 4h (400 MHz, CDCl₃):



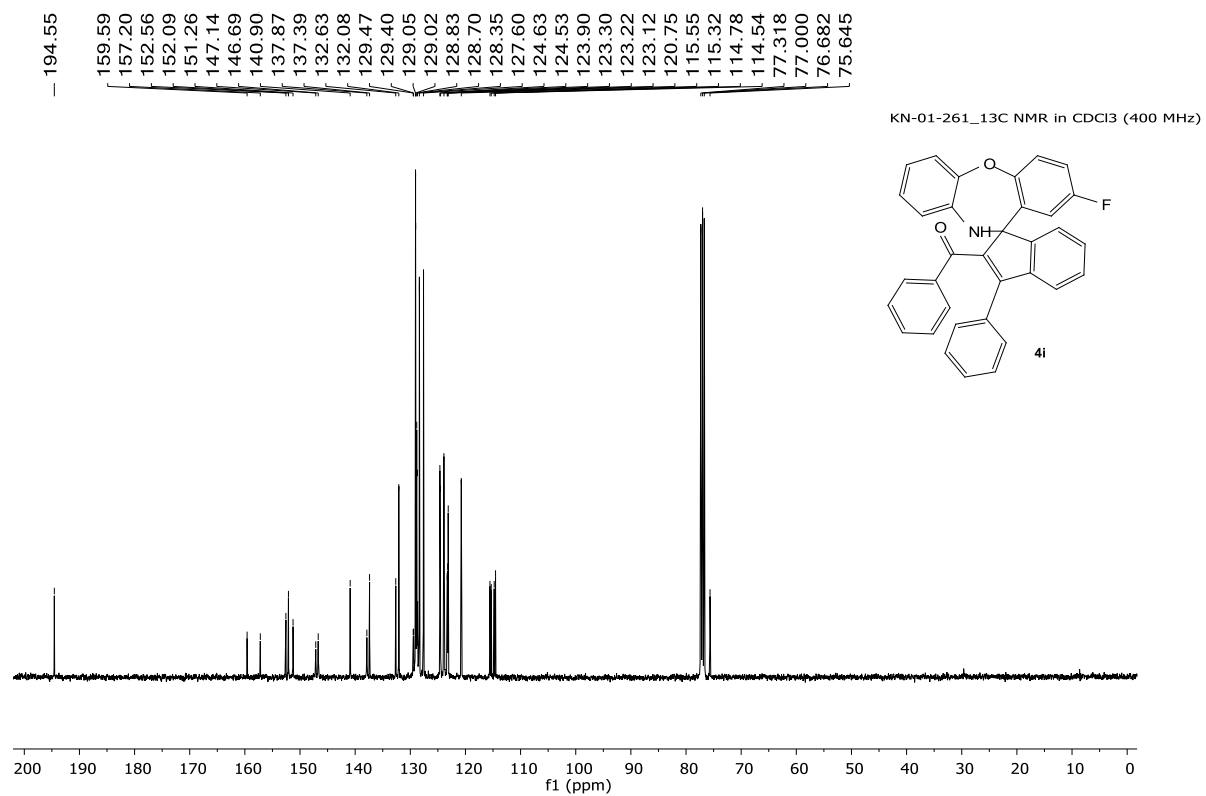
¹³C NMR of 4h (100 MHz, CDCl₃):



¹H NMR of 4i (400 MHz, CDCl₃):

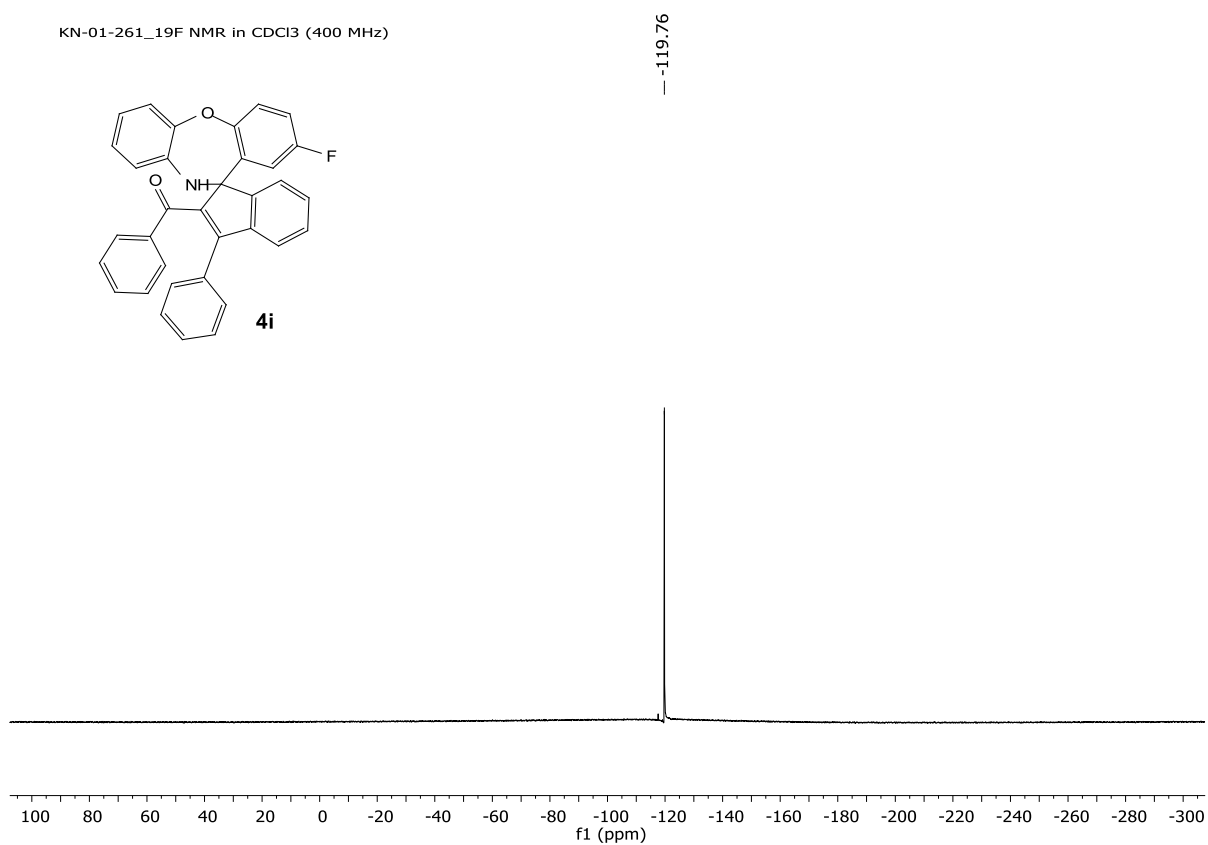
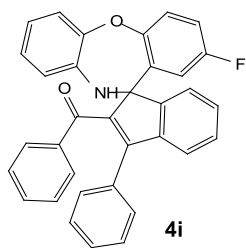


¹³C NMR of 4i (100 MHz, CDCl₃):

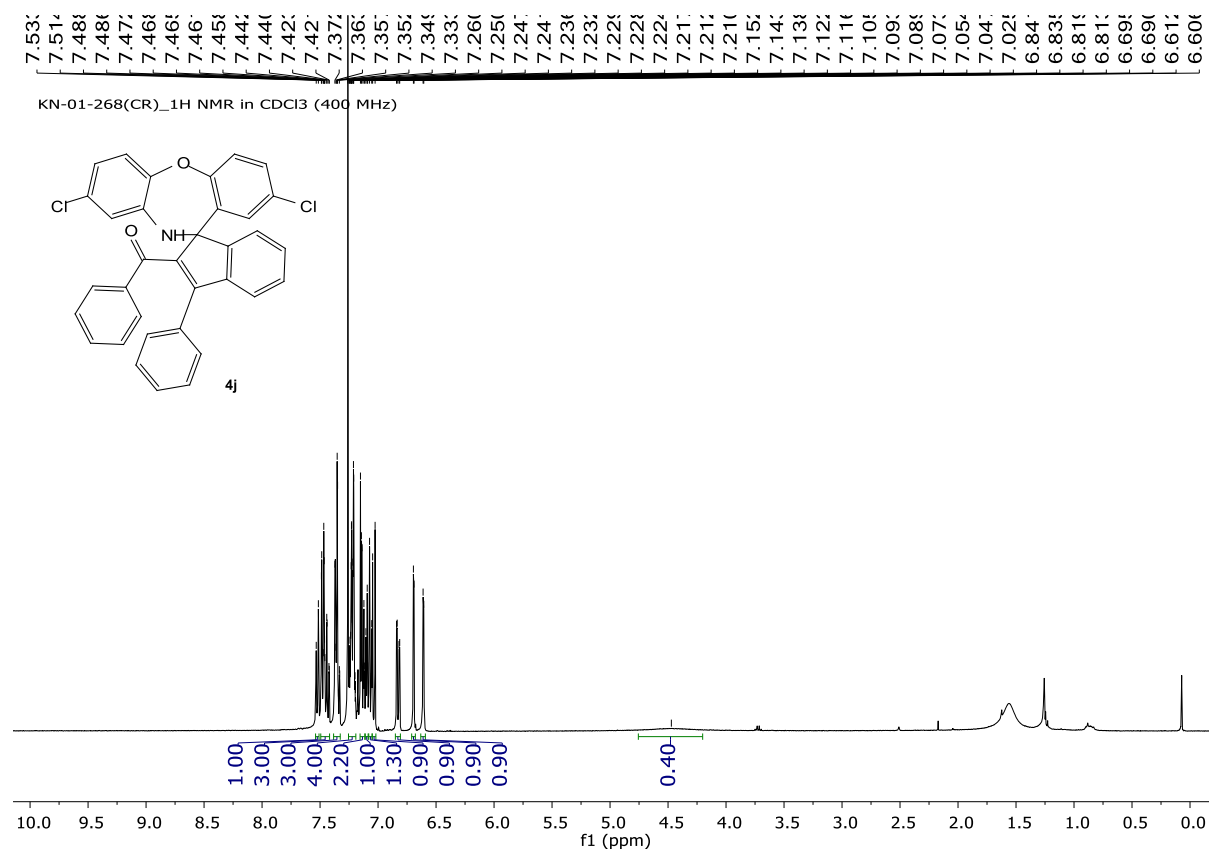


^{19}F NMR of 4i (376 MHz, CDCl_3):

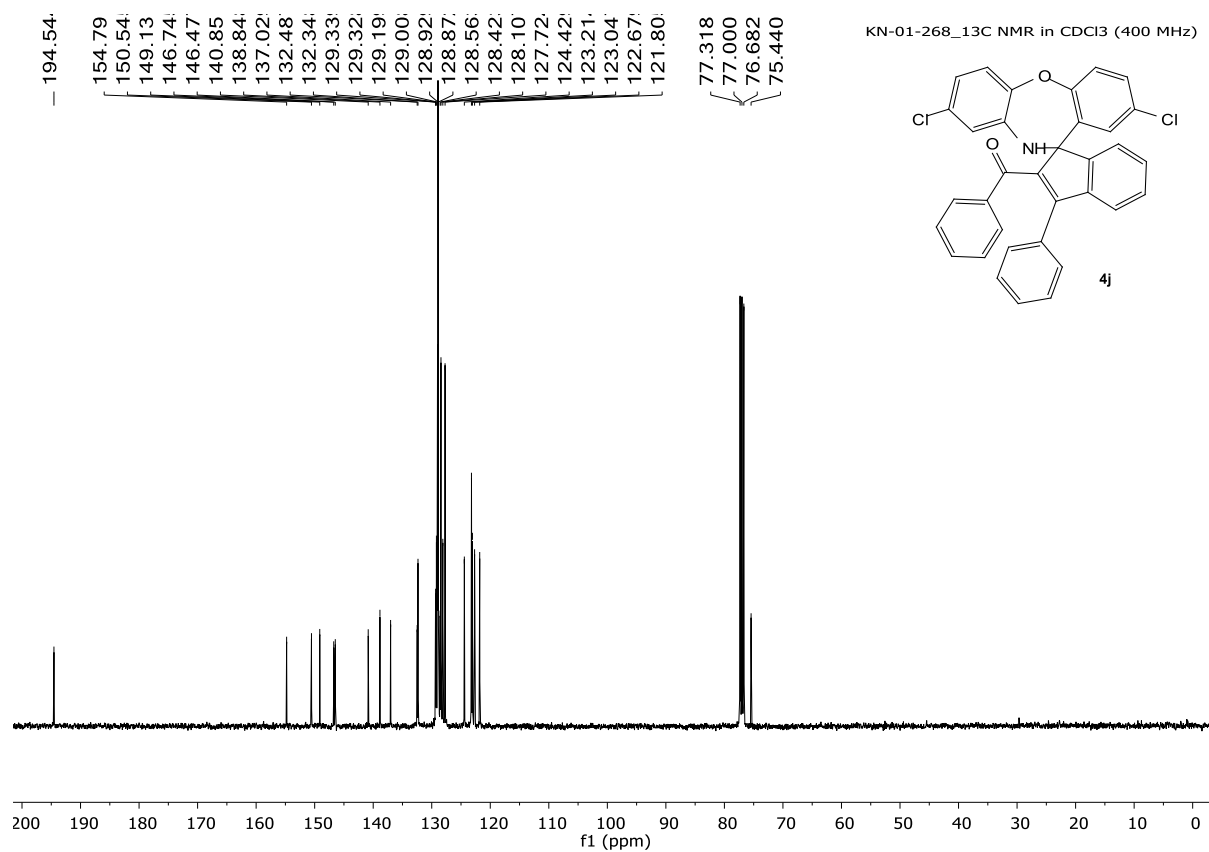
KN-01-261_19F NMR in CDCl_3 (400 MHz)



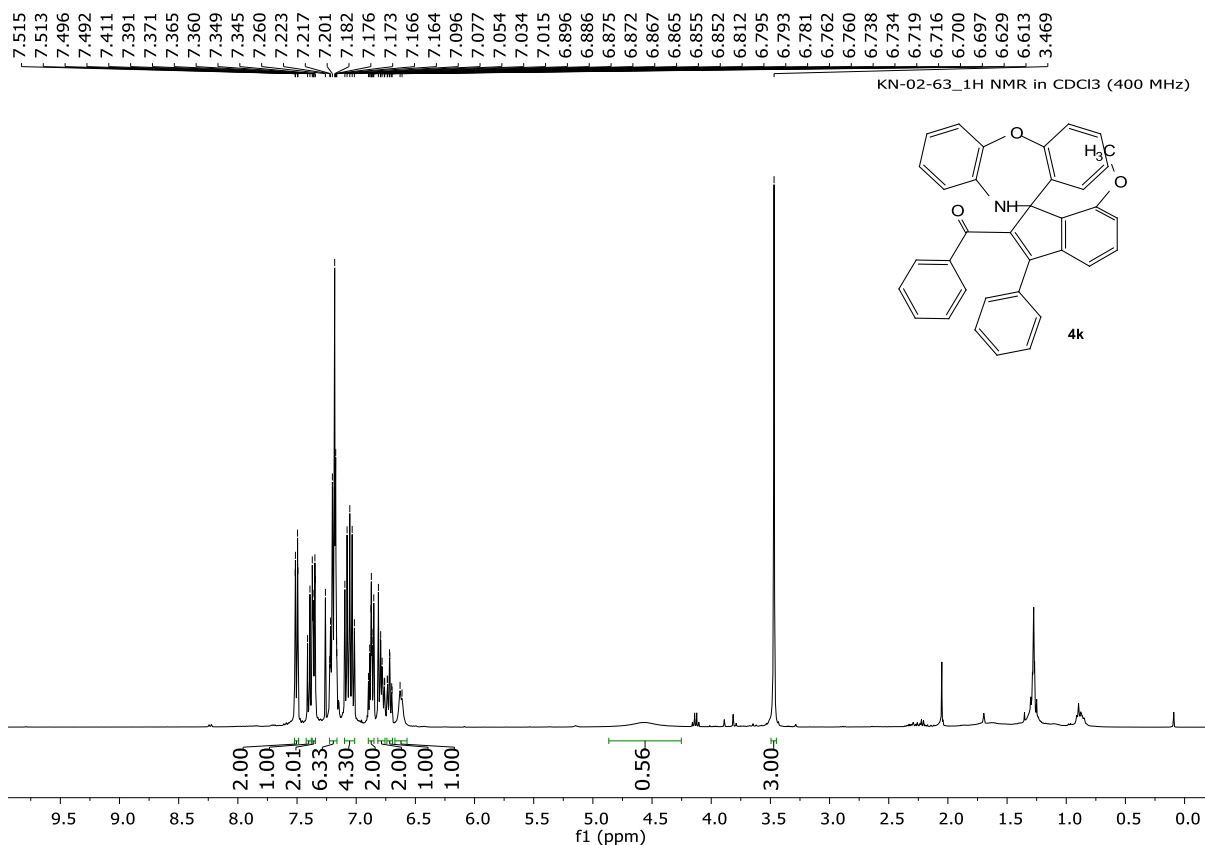
¹H NMR of 4j (400 MHz, CDCl₃):



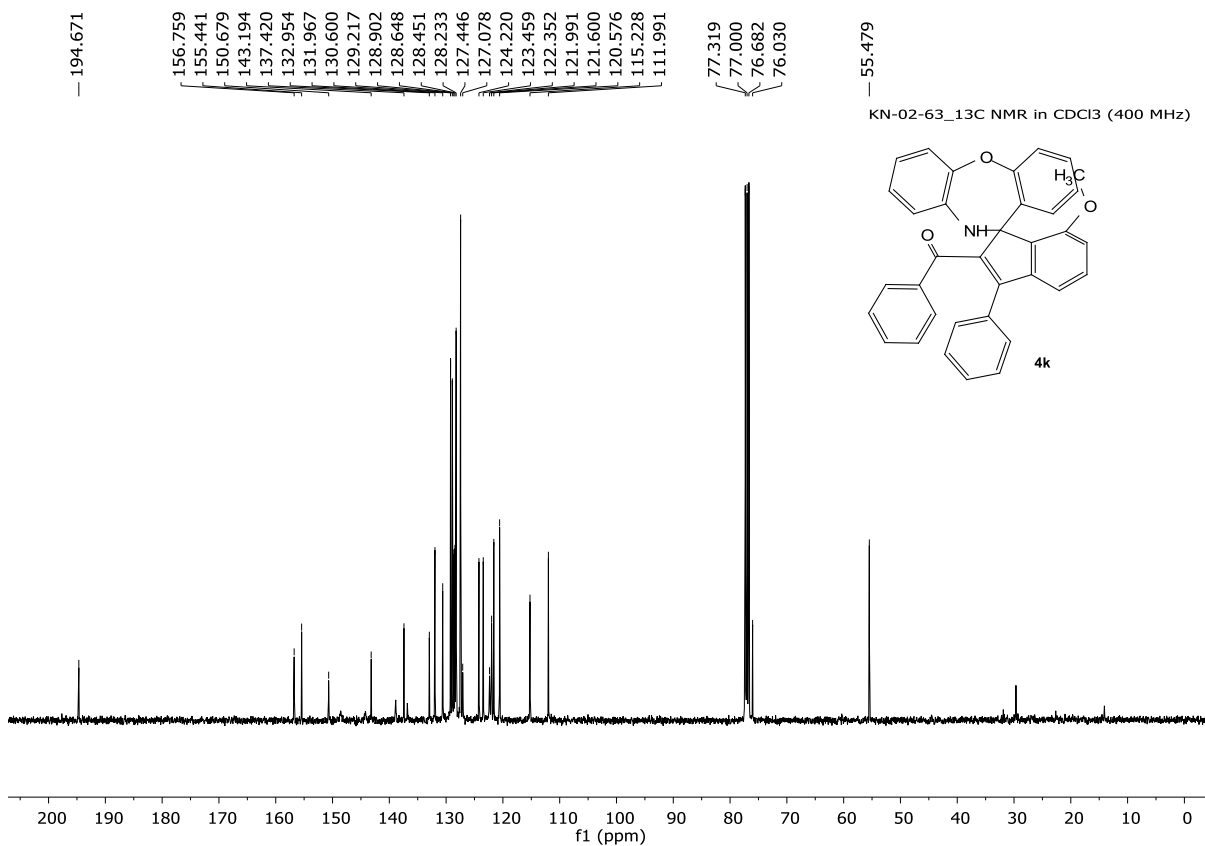
¹³C NMR of 4j (100 MHz, CDCl₃):



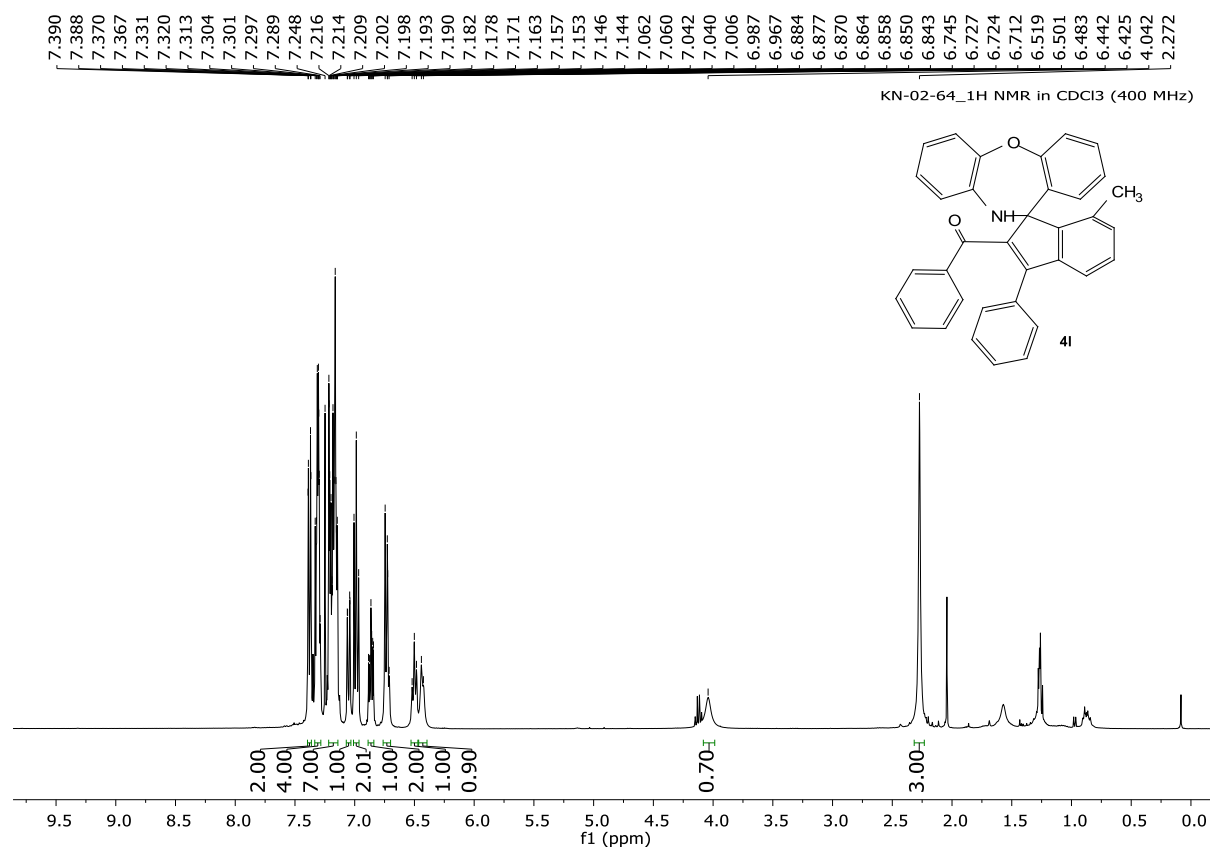
¹H NMR of 4k (400 MHz, CDCl₃):



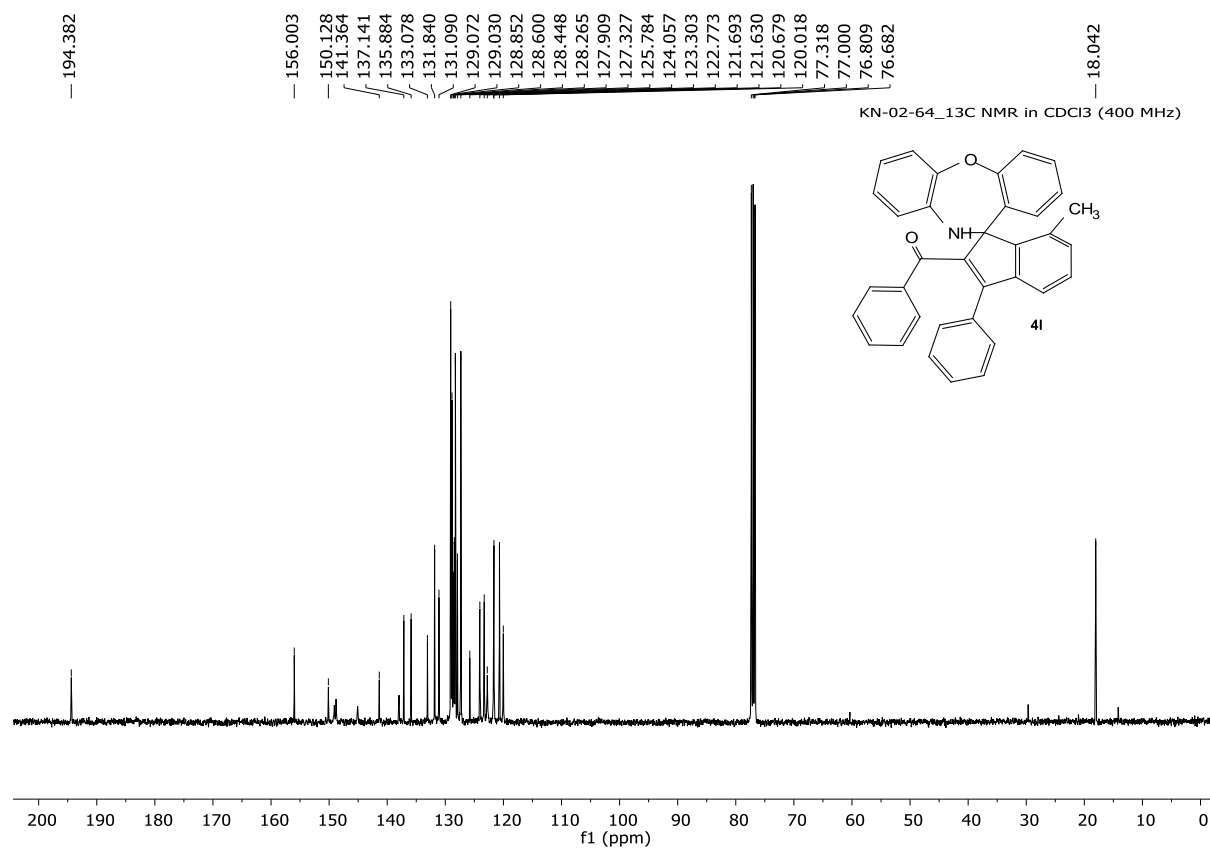
¹³C NMR of 4k (100 MHz, CDCl₃):



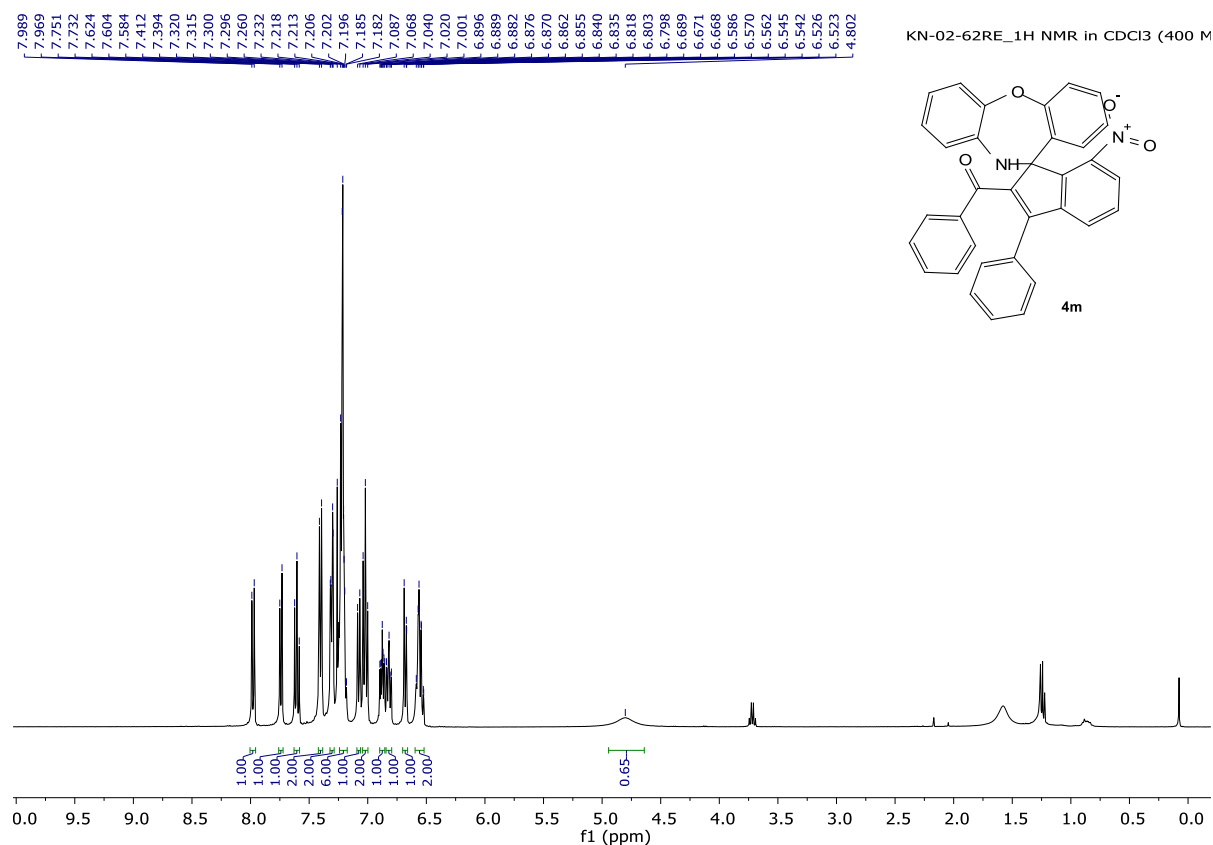
¹H NMR of 4l (400 MHz, CDCl₃):



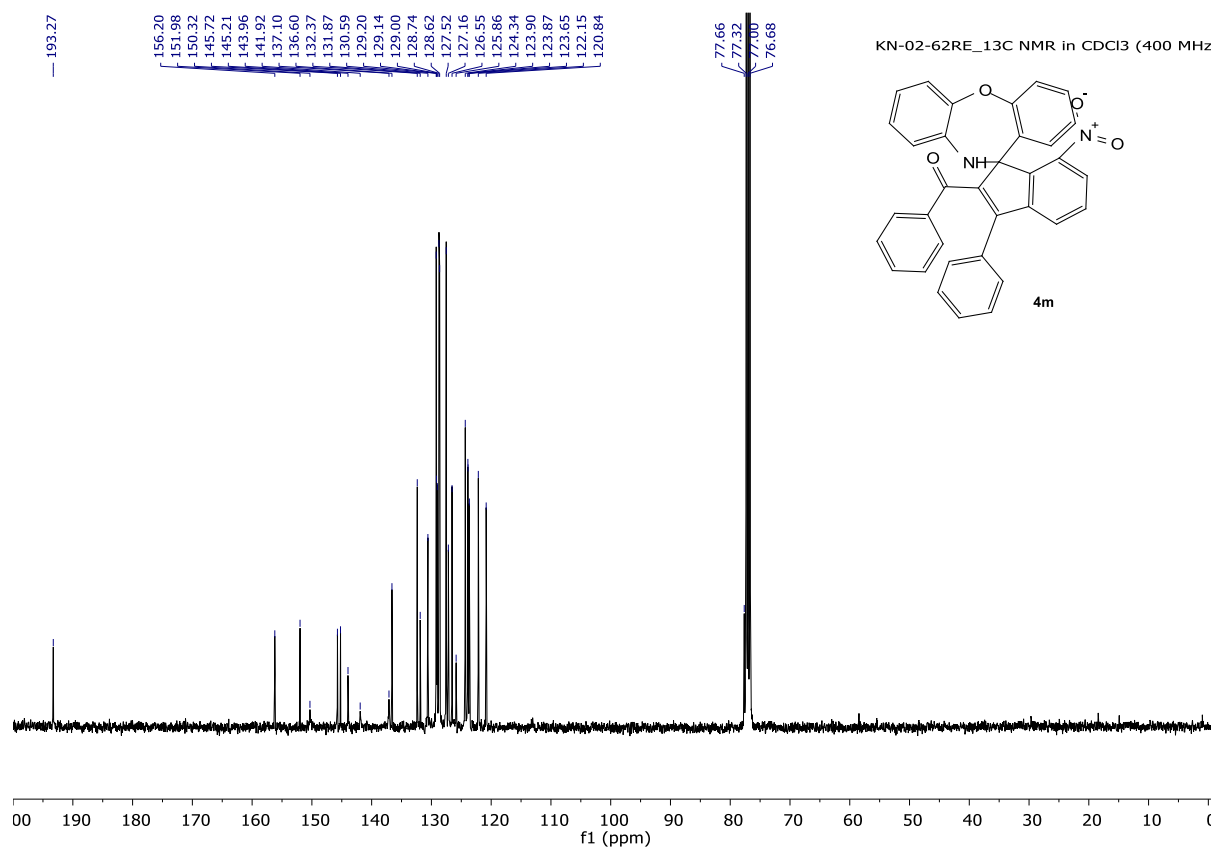
¹³C NMR of 4l (100 MHz, CDCl₃):



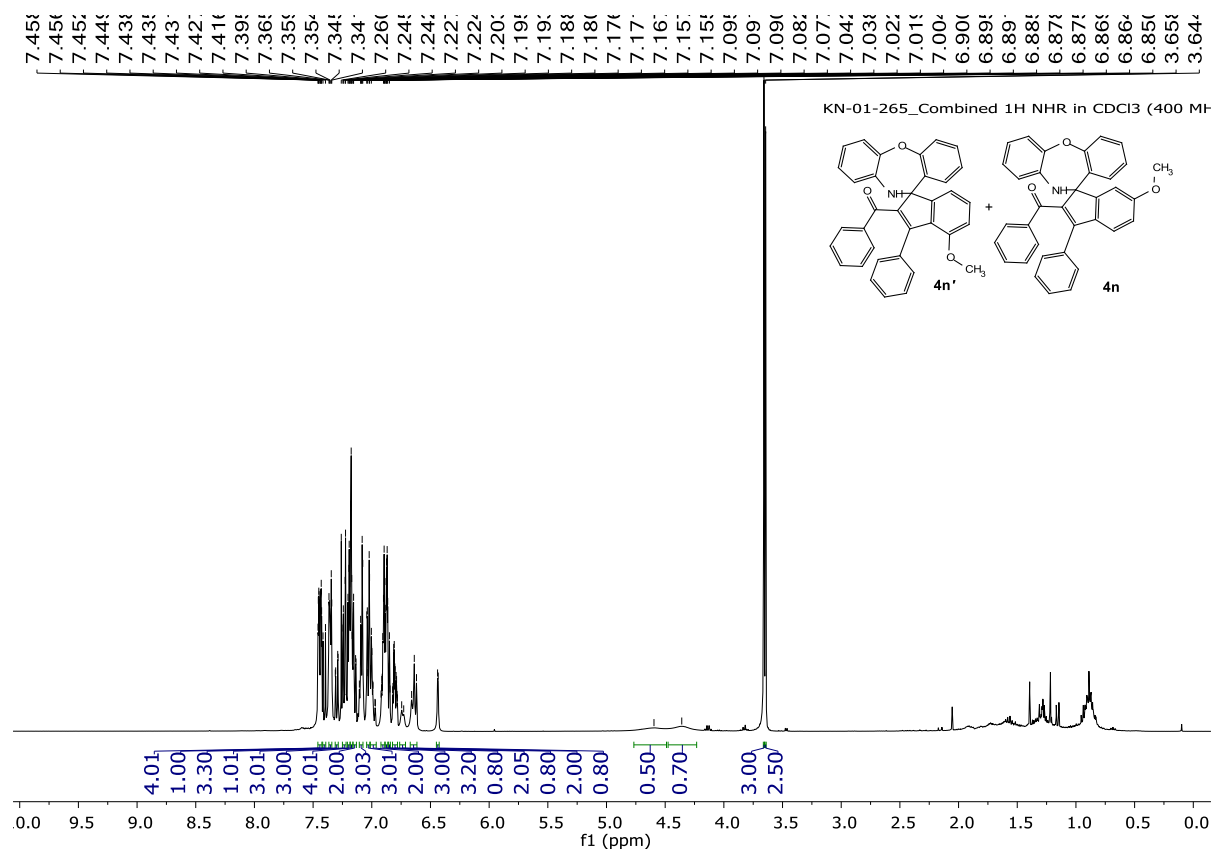
¹H NMR of 4m (400 MHz, CDCl₃):



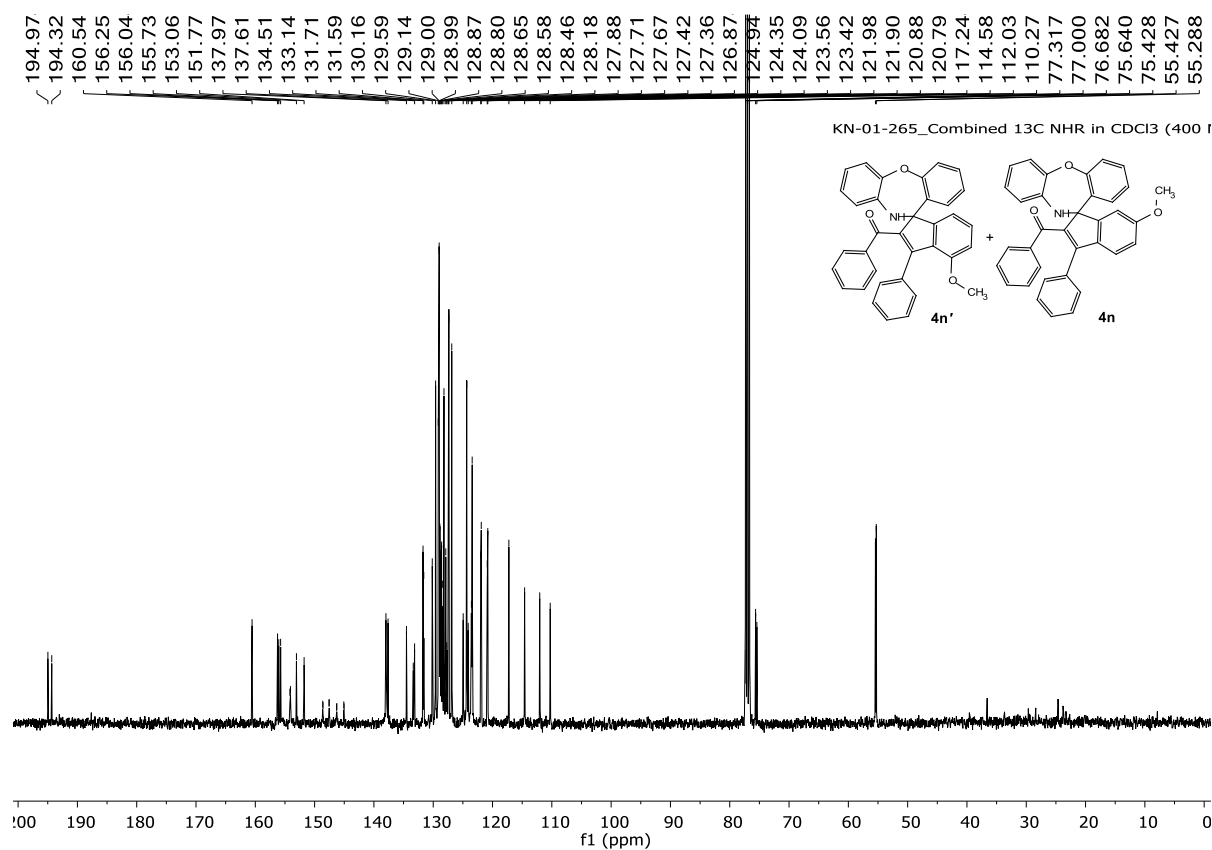
¹³C NMR of 4m (100 MHz, CDCl₃):



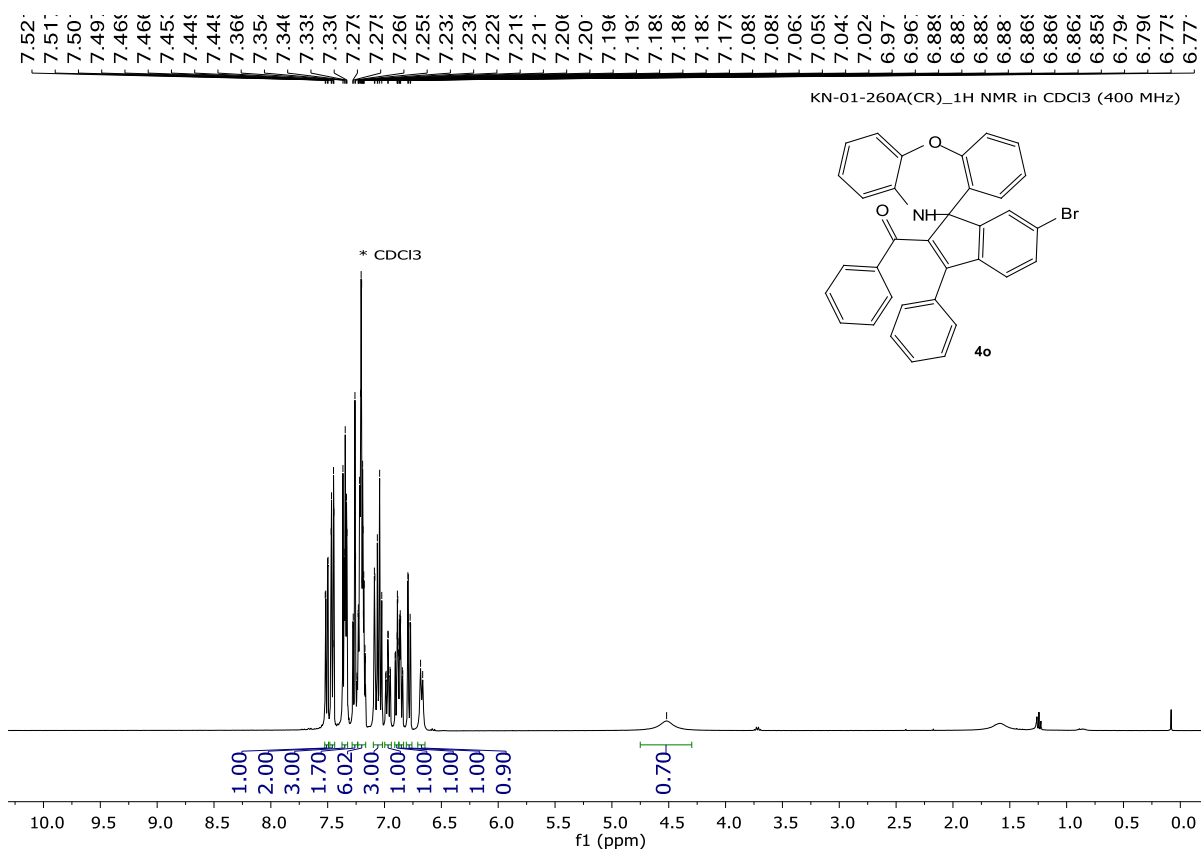
¹H NMR of 4n (400 MHz, CDCl₃):



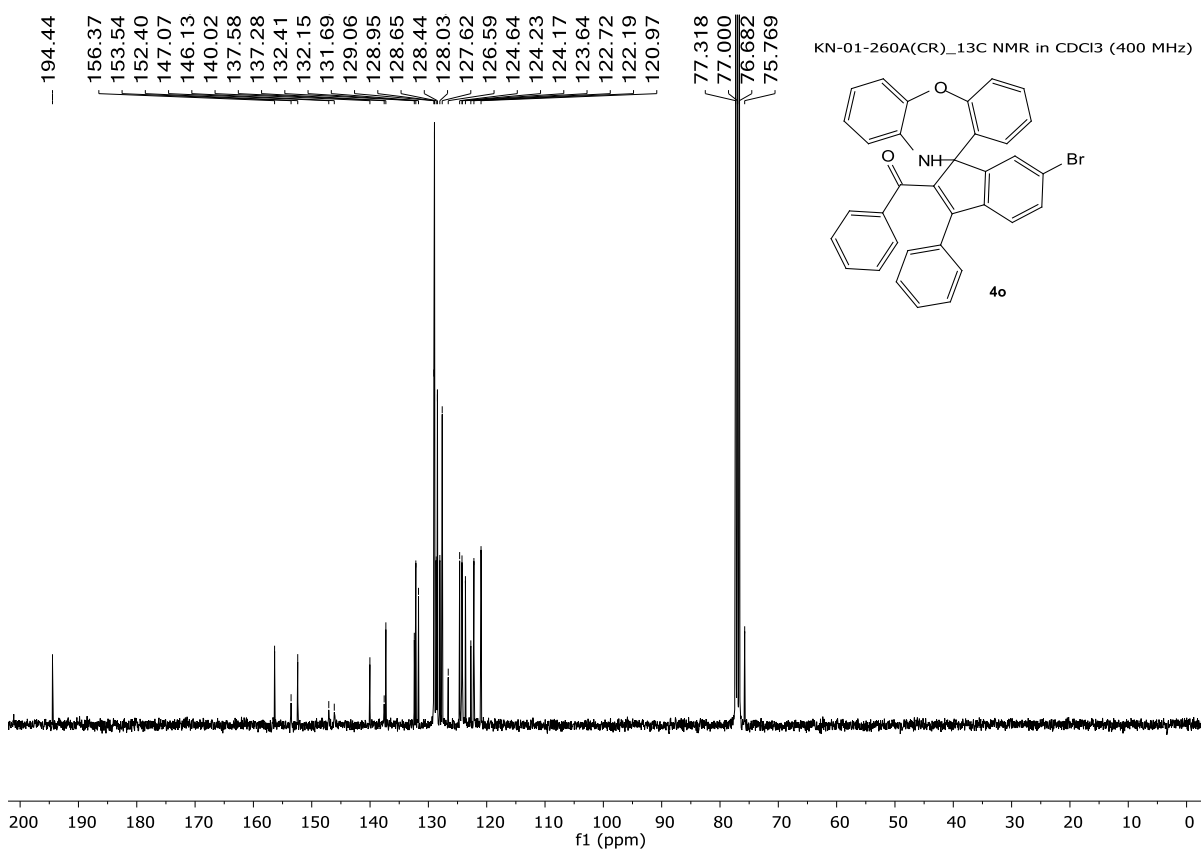
¹³C NMR of 4n (100 MHz, CDCl₃):



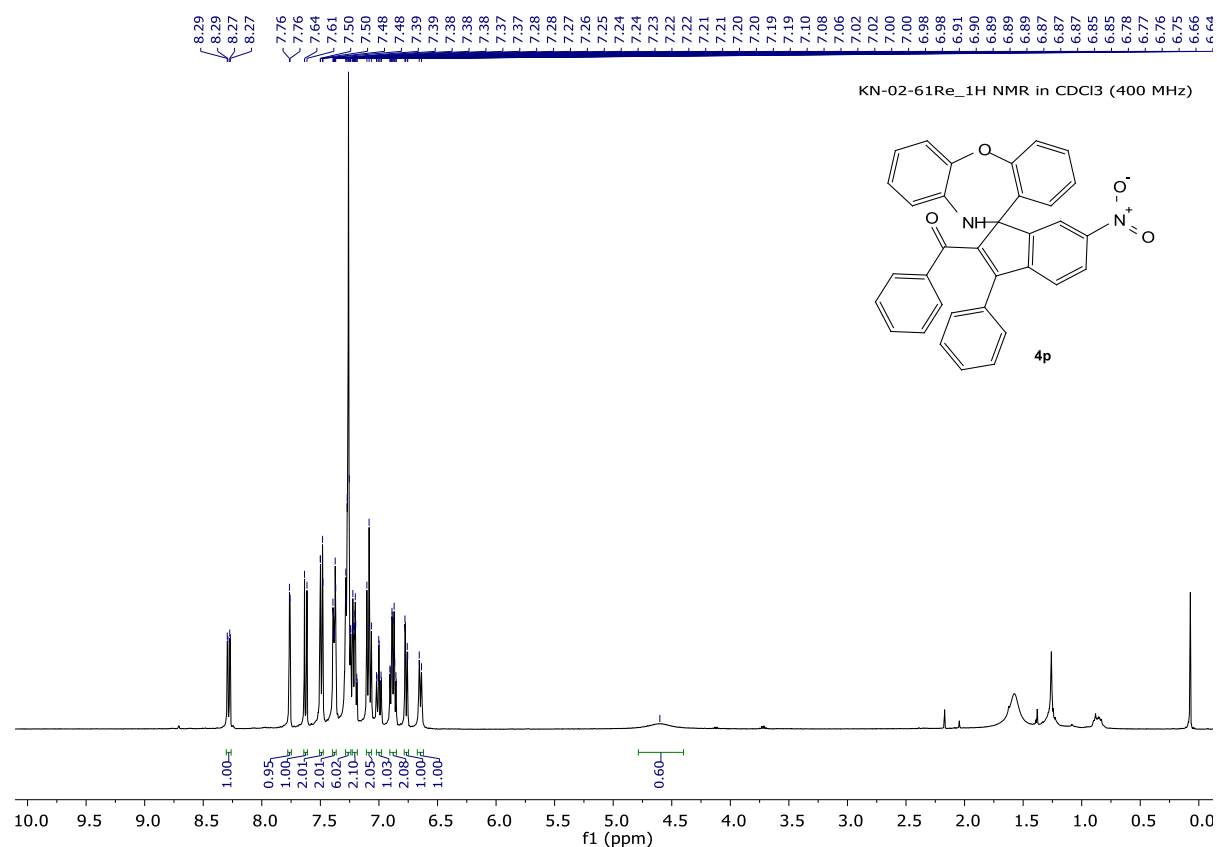
¹H NMR of 4o (400 MHz, CDCl₃):



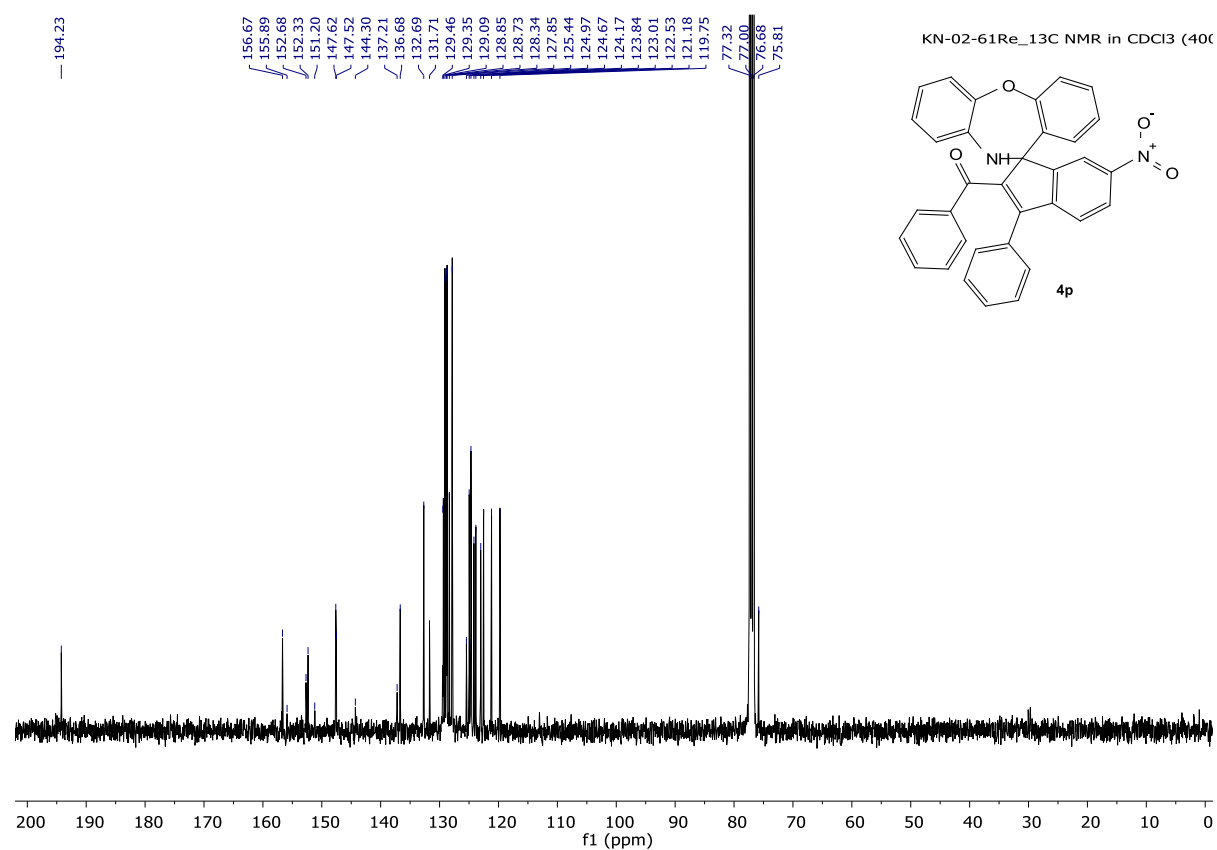
¹³C NMR of 4o (100 MHz, CDCl₃):



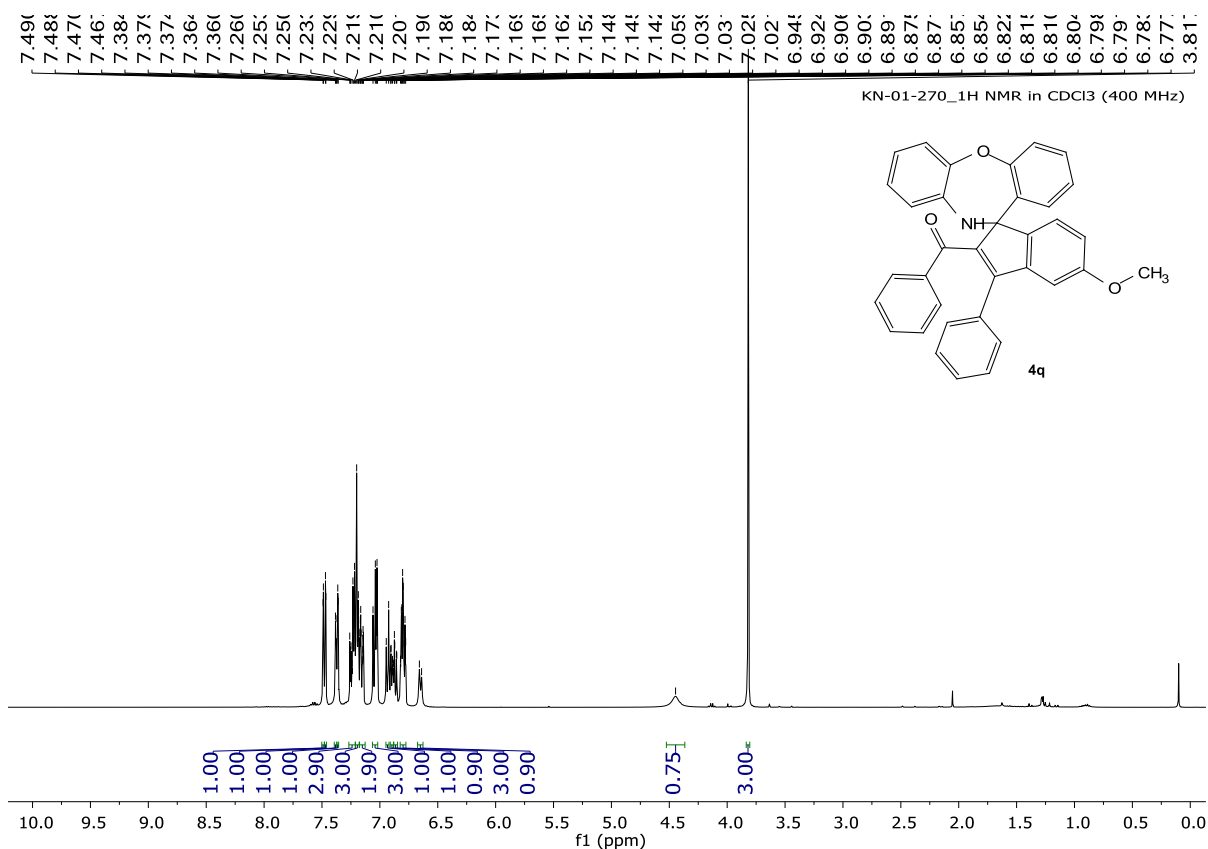
¹H NMR of 4p (400 MHz, CDCl₃):



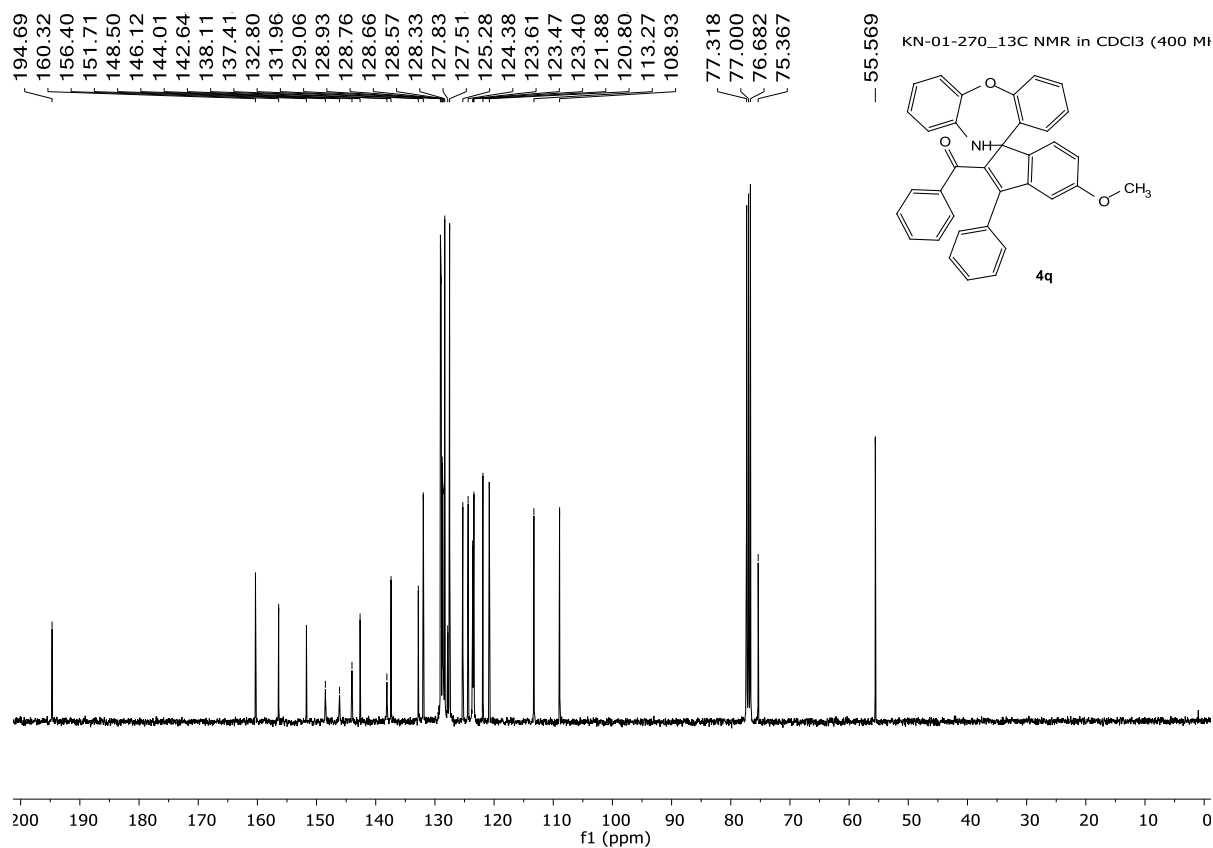
¹³C NMR of 4p (100 MHz, CDCl₃):



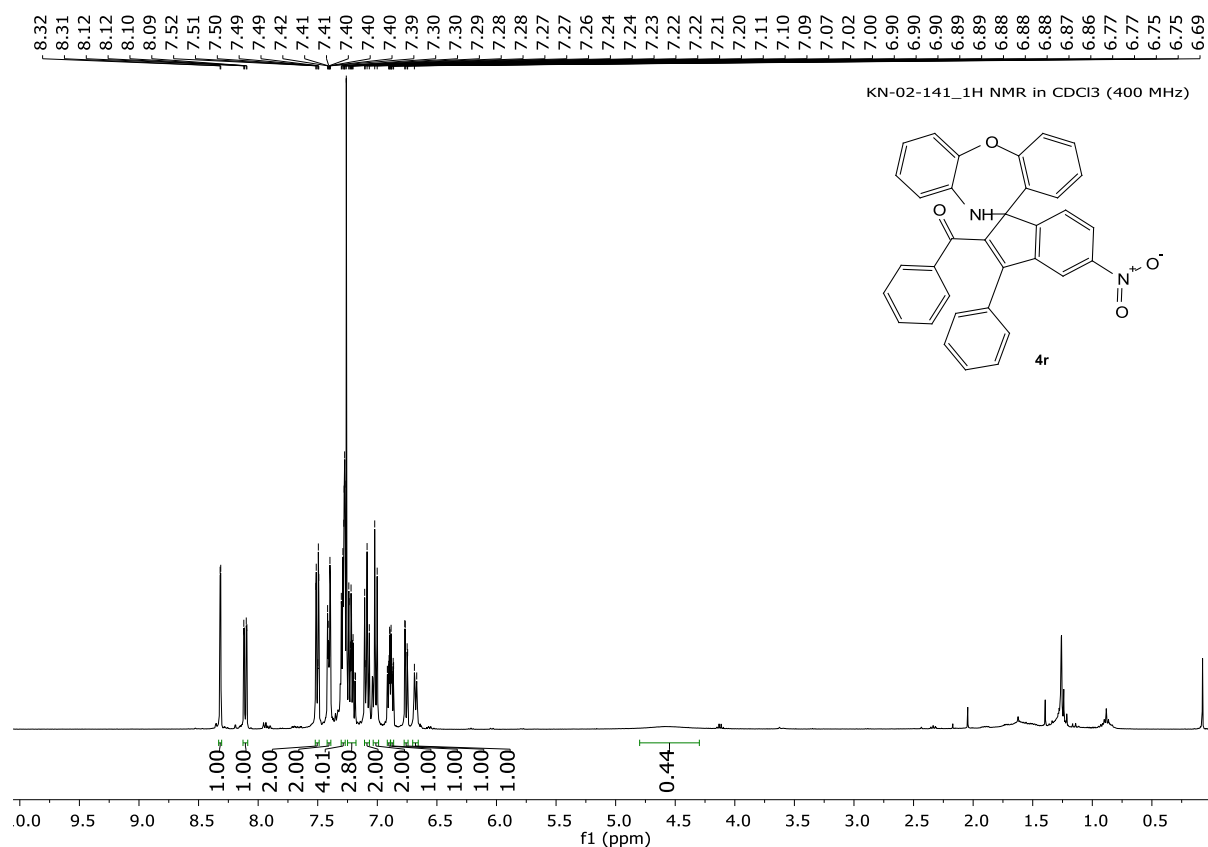
¹H NMR of 4q (400 MHz, CDCl₃):



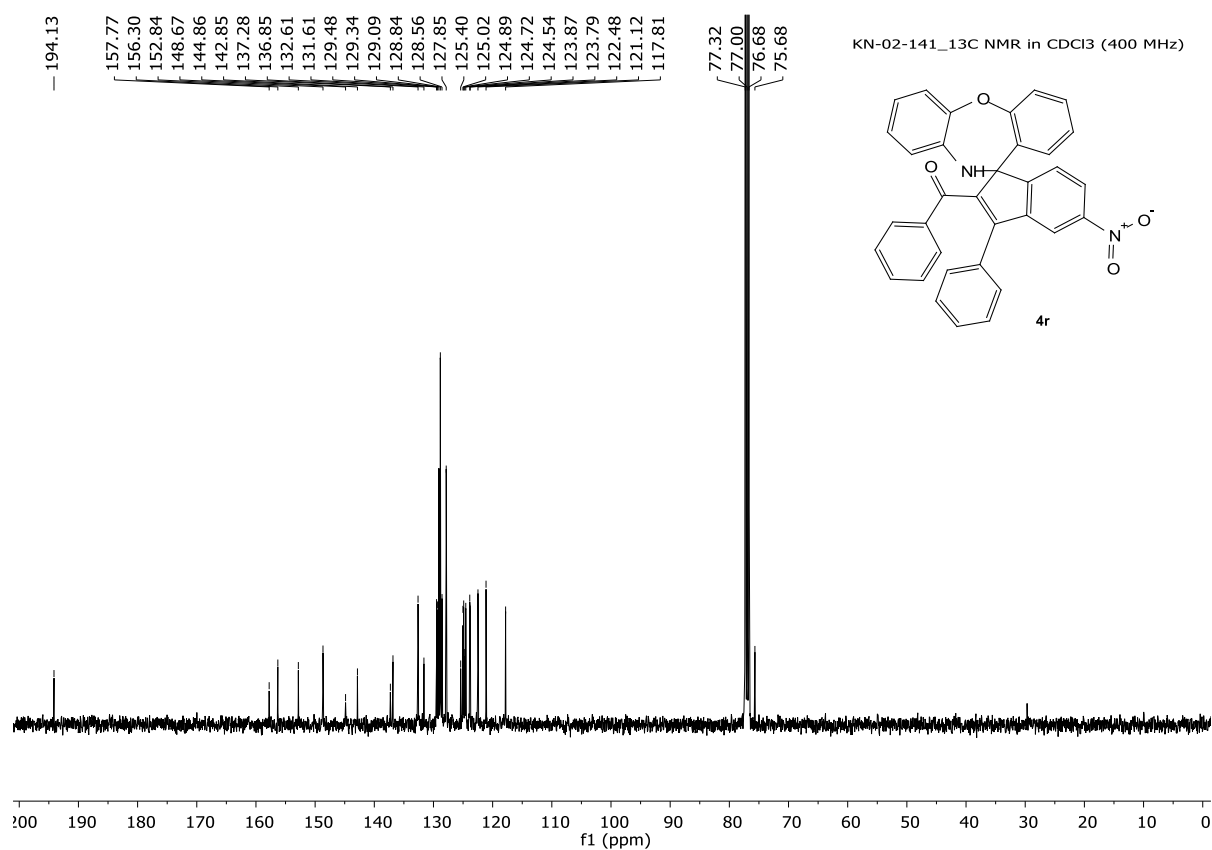
¹³C NMR of 4q (100 MHz, CDCl₃):



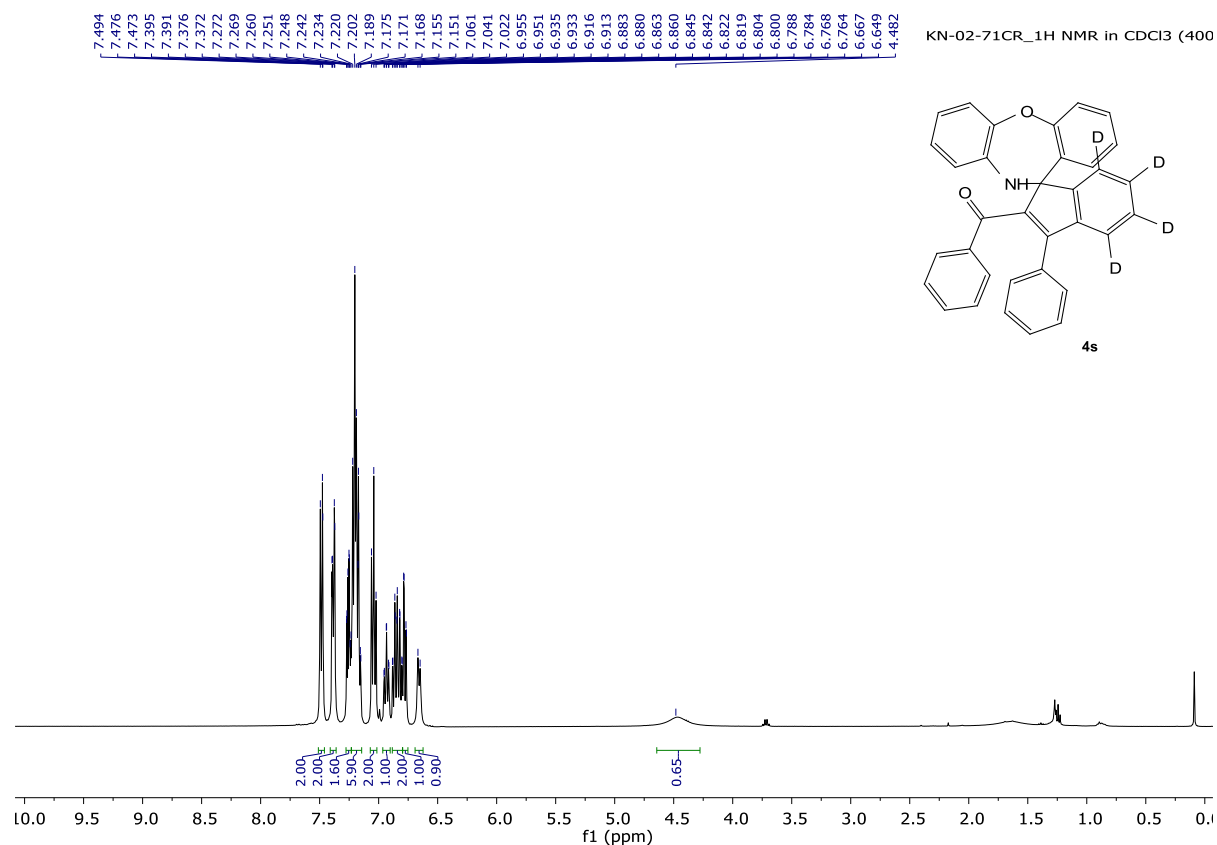
¹H NMR of 4r (400 MHz, CDCl₃):



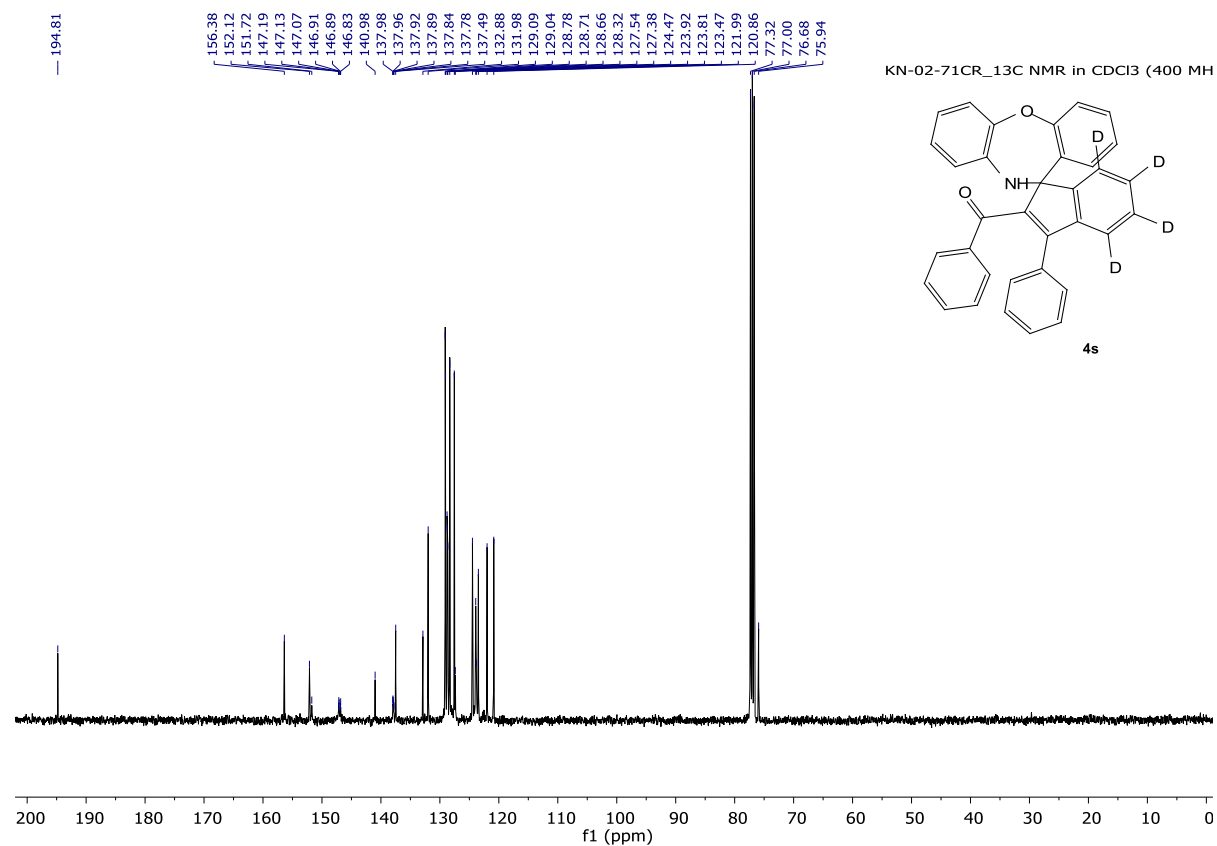
¹³C NMR of 4r (100 MHz, CDCl₃):



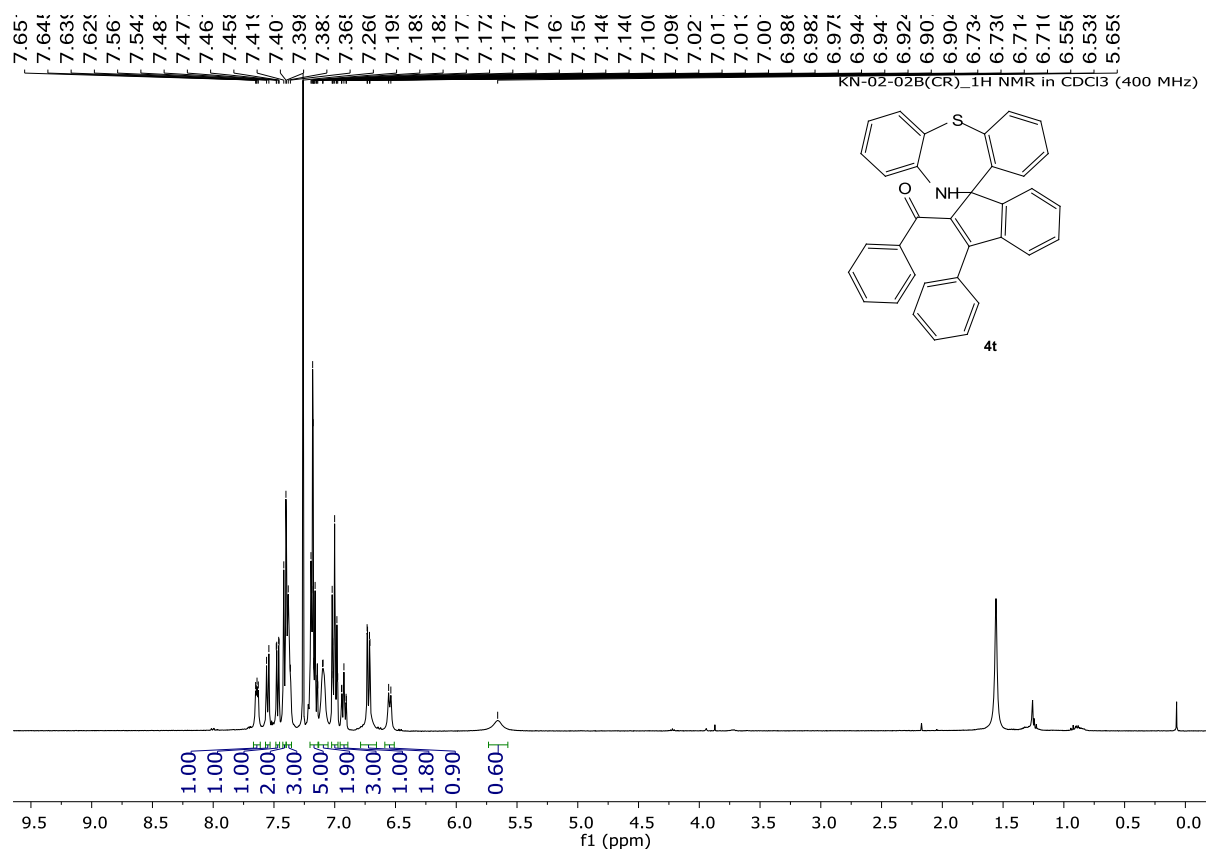
^1H NMR of 4s (400 MHz, CDCl_3):



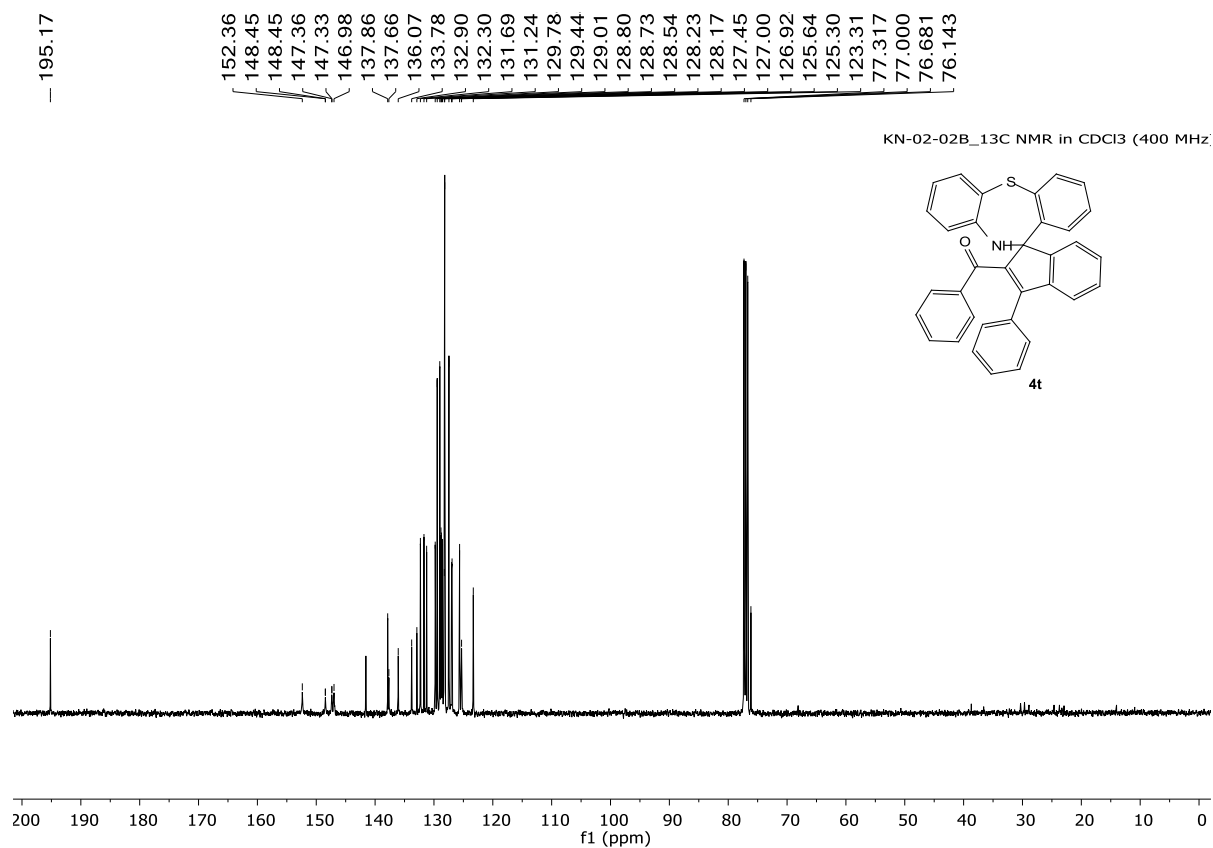
^{13}C NMR of 4s (100 MHz, CDCl_3):



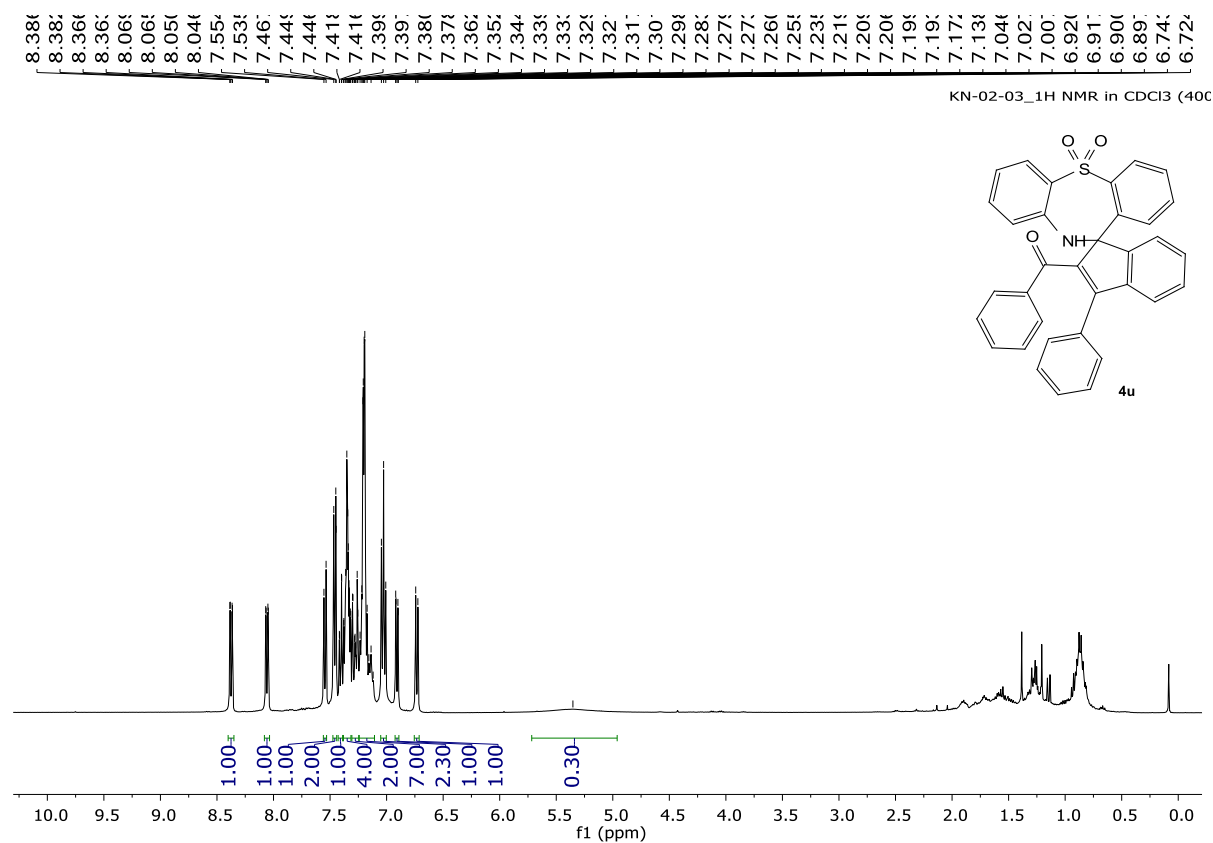
¹H NMR of 4t (400 MHz, CDCl₃):



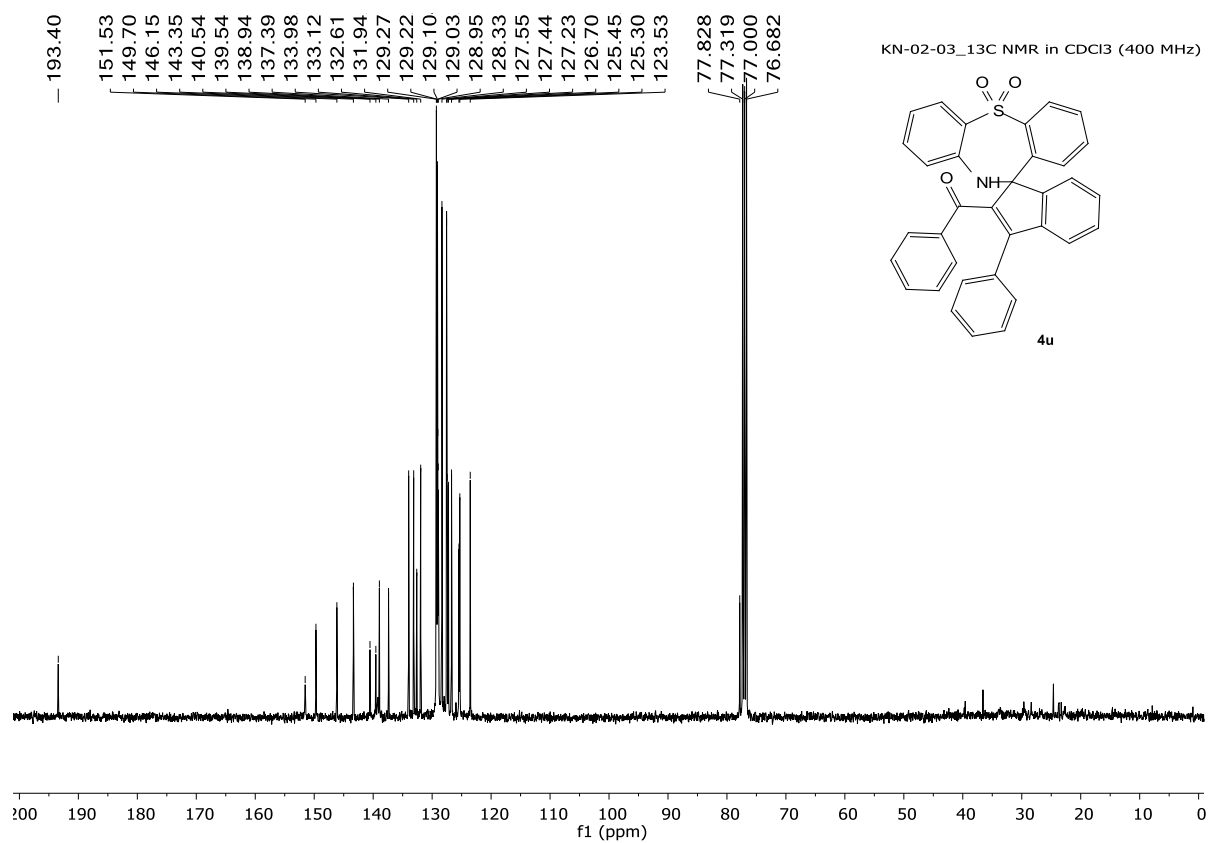
¹³C NMR of 4t (100 MHz, CDCl₃):



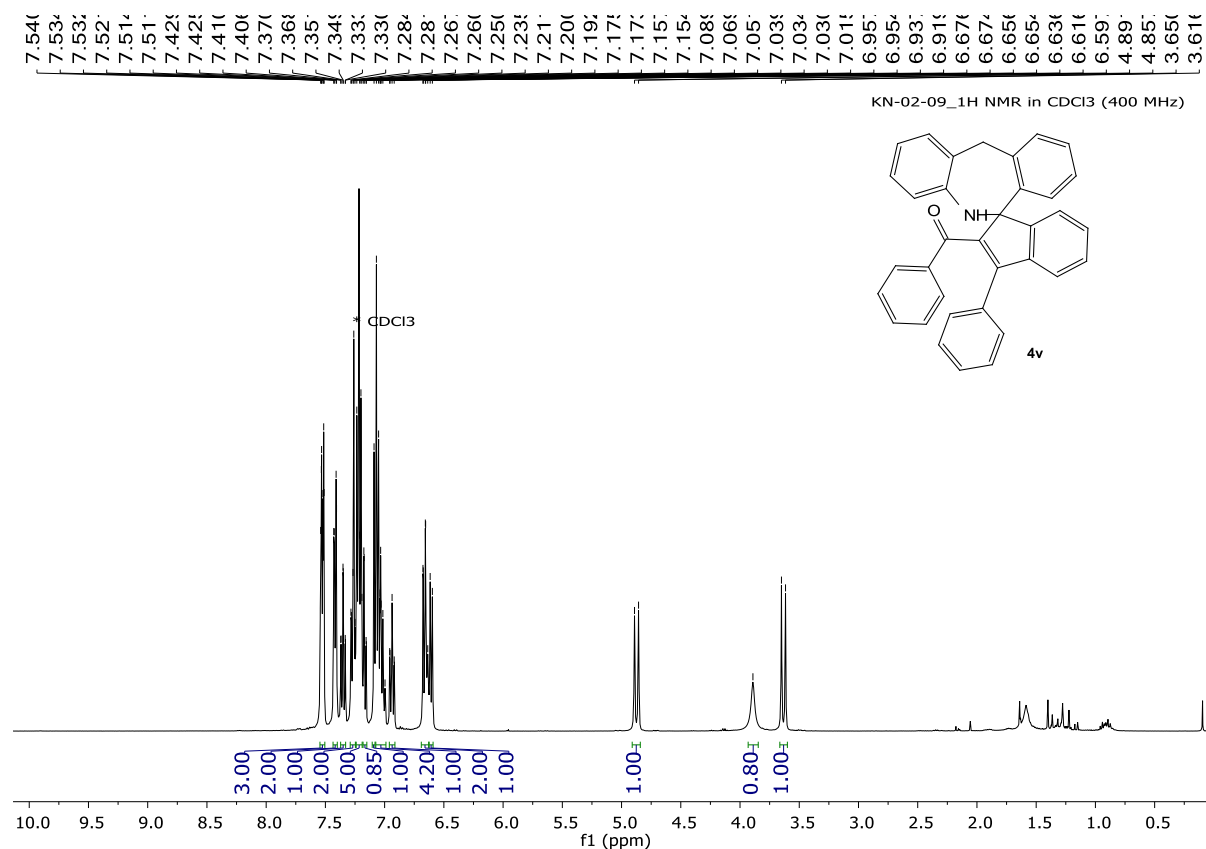
¹H NMR of 4u (400 MHz, CDCl₃):



¹³C NMR of 4u (100 MHz, CDCl₃):



¹H NMR of 4v (400 MHz, CDCl₃):



¹³C NMR of 4v (100 MHz, CDCl₃):

