Supporting Information

Iodine-Catalyzed Oxidative Annulation: Facile Synthesis of Pyrazolooxepanopyrazolones via Methyl azaarenes sp^3 C-H Functionalization

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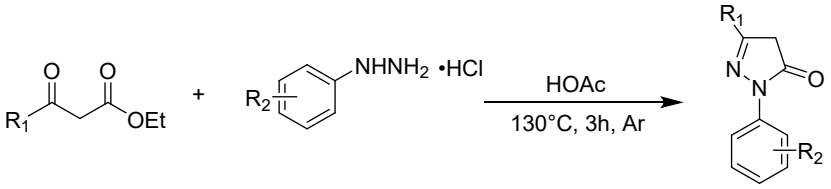
1. General information

Materials and General Experimental: Methyl quinolines were purchased from Beijing Innochem Science&Technology Co. Ltd. 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one were purchased from Shanghai Shaoyuan Co. Ltd. Unless stated otherwise, all solvents and commercially available reagents were obtained from commercial suppliers and used without further purification. In addition, petroleum ether (b.p. 60-90 ^{o}C), which was used for Column chromatography, was distilled prior to use. Non-commercial starting materials were prepared as described below or according to literature procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel HF254 glass plates. Column chromatography was performed using silica gel (200-300 mesh).

Instrumentation: Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 400 MHz spectrometer at ambient temperature using the non or partly deuterated solvent as internal standard (^{1}H: δ 7.26 ppm and ^{13}C{1H}: δ 77.0 ppm for $CDCl_3$). Chemical shifts (δ) are reported in ppm, relative to the internal standard of tetramethylsilane (TMS). The coupling constants (*J*) are quoted in hertz (Hz). Resonances are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or combinations thereof. High resolution mass spectra were obtained on Thermo Scientific Q-Exactive (ESI mode). Melting points were determined using SGW X-4 apparatus and not corrected.

2. General Procedure

2.1 General Procedure for the Synthesis of 5-alkyl-2-aryl-2,4-dihydro-3*H*-pyrazol-3-ones.



A 25 mL pressure vial with branch was charged with *α*-keto esters (3.0 mmol), Phenylhydrazine hydrochloride (3.0 mmol, 1.0 equiv.) and HOAc (5.0 mL). The vial was sealed and performed gas exchange 3 times. Then, the resulting mixture was stirred at 130 °C for 4 h under argon atmosphere. After the reaction was completed (monitored by TLC), and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The mixture was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding products (all substrates were prepared according to literature methods).[1]

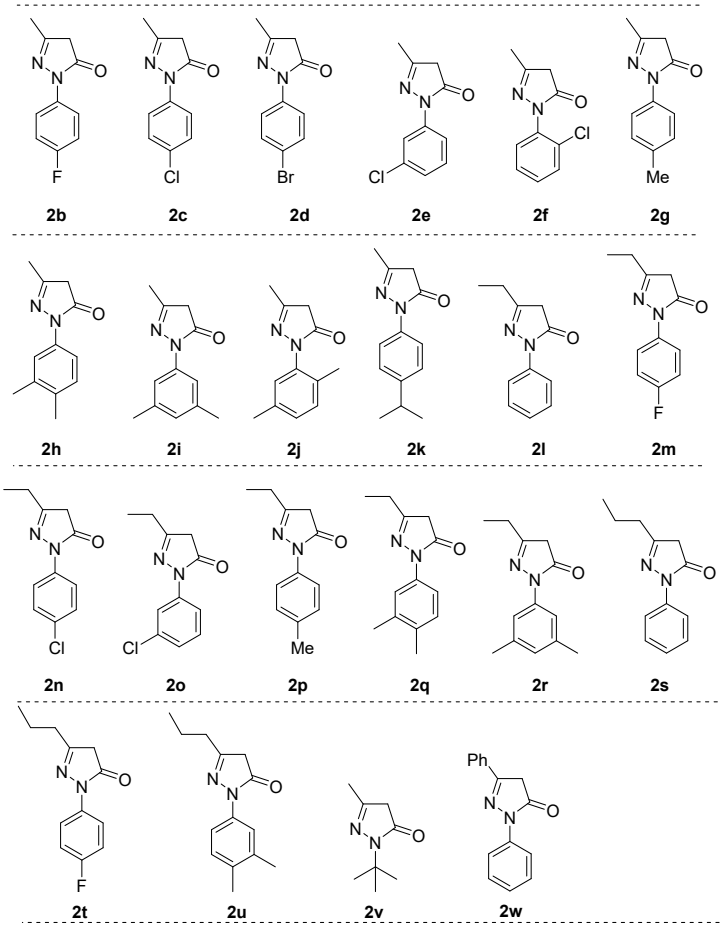
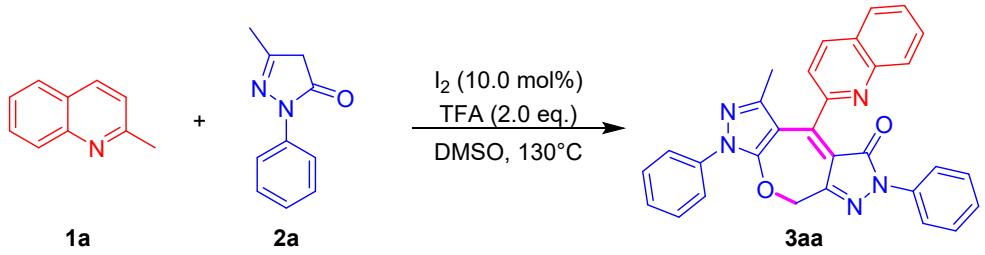


Table S1. The scope of 5-alkyl-2-aryl-2,4-dihydro-3*H*-pyrazol-3-ones

[1]. Y.-Y. Huang, H.-C. Lin, K.-M. Cheng, *et al*. *Tetrahedron,* **2009***, 65,* 9592-9597.

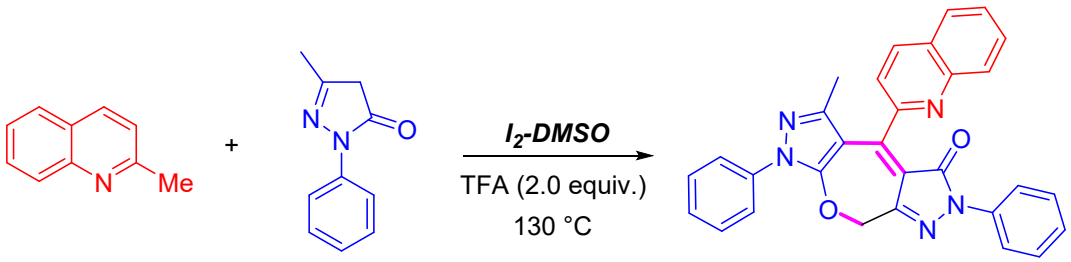
2.2 General Procedure for the Synthesis of 2,7-diaryl-4-azaaryl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-ones (3aa as an example).



1a **2a** **3aa**

A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (43.0 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 3 h under an air atmosphere. And then added 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (104.5 mg, 0.6 mmol, 2.0 equiv.) for additional 6h. After the reaction was completed (monitored by TLC), and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3aa** as a yellow solid (120 mg, 83% yield).

3. Scale-up of the reaction.



1a (**5.0 mmol**) (716 mg) **2a** (**2.0 equiv.**) (1.742 g) **3aa**

I_2 (**10.0 mol%**), Yield (**3aa**) = **73%**, **1.772g**

I_2 (**5.0 mol%**), Yield (**3aa**) = **61%**, **1.475g**

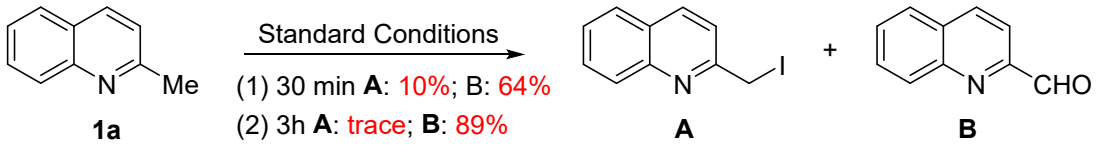
3.1 A 100 mL pressure vial was charged with 2-methylquinoline (**1a**) (716 mg, 5.0 mmol, 1.0 equiv.), I_2 (127 mg, 0.5 mmol, 0.1 equiv.), TFA (1142 mg, 10.0 mmol, 2.0 equiv.) and DMSO (30 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 3 h under an air atmosphere. And then added 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (1742 mg, 10.0 mmol, 2.0 equiv.) for additional 6h. After the reaction was completed (monitored by TLC), and added 120 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 5 times (5 × 80 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w),

dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3aa** as a yellow solid (1.772 g, 73% yield).

3.2 A 100 mL pressure vial was charged with 2-methylquinoline (**1a**) (716 mg, 5.0 mmol, 1.0 equiv.), I_2 (64 mg, 0.25 mmol, 0.05 equiv.), TFA (1142 mg, 10.0 mmol, 2.0 equiv.) and DMSO (30 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 3 h under an air atmosphere. And then added 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (1742 mg, 10.0 mmol, 2.0 equiv.) for additional 6h. After the reaction was completed (monitored by TLC), and added 120 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 5 times (5 × 80 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3aa** as a yellow solid (1.475 g, 61% yield).

4. Mechanism investigation

4.1 Control experiments (a):



Procedure and Results:

(1): A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (43.0 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for **30 min** under an air atmosphere. After the reaction was completed (monitored by TLC), and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **A** as a yellow solid (8 mg, 10% yield, detected by TLC-MS (APCI)) and **B** as a brown solid (30 mg, 64% yield).

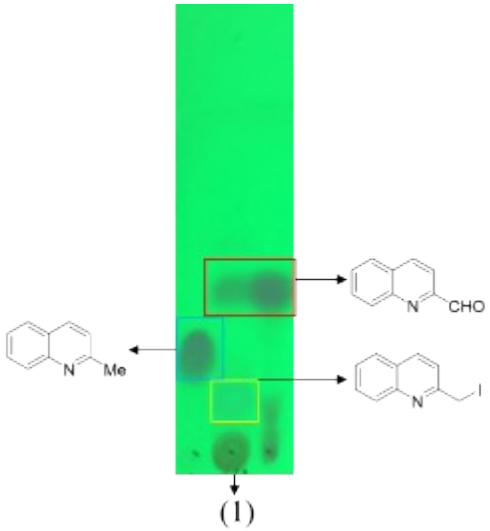


Figure S1. The TLC results for the control experiments **a (1)**

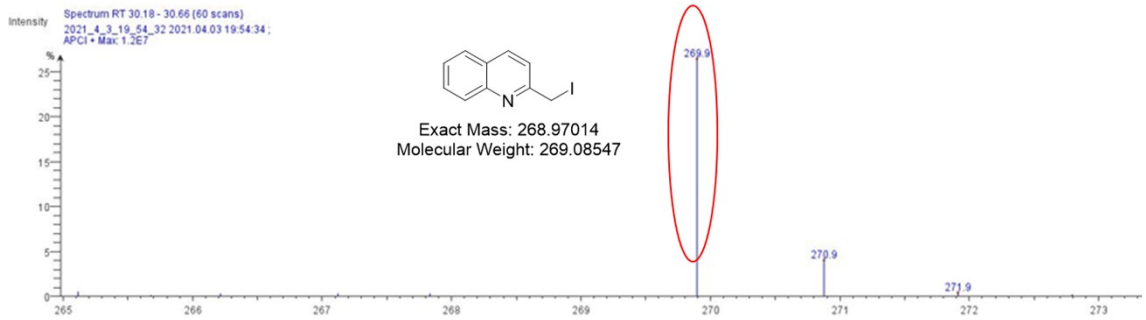


Figure S2. The MS (APCI) results for the control experiments **a (1)**

(2): A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (43.0 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for **3h** under an air atmosphere. After the reaction was completed (monitored by TLC), and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **B** as a brown solid (42 mg, 89% yield).

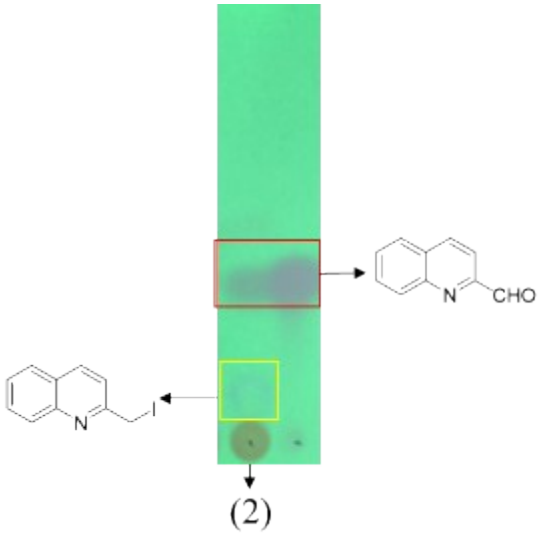
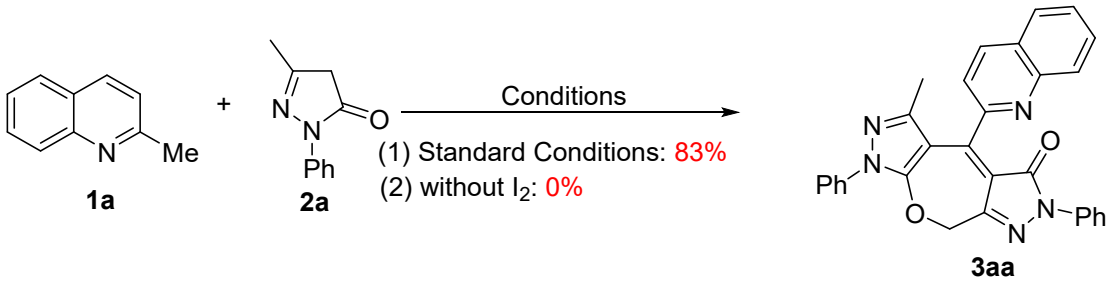


Figure S3. The TLC results for the control experiments **a (2)**

4.2 Control experiments (b):



Procedure and Results:

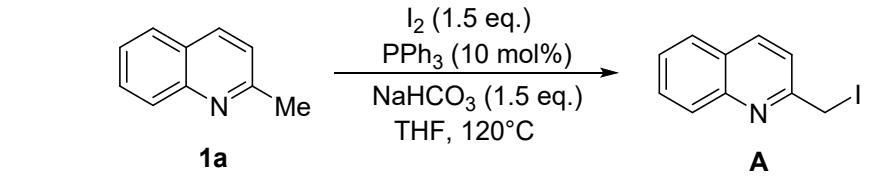
(1): A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (43.0 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 3 h under an air atmosphere. And then added 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (104.5 mg, 0.6 mmol, 2.0 equiv.) for additional 6h. After the reaction was completed (monitored by TLC), and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3aa** as a yellow solid (120 mg, 83% yield).

(2): A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (43.0 mg, 0.30 mmol, 1.0 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial

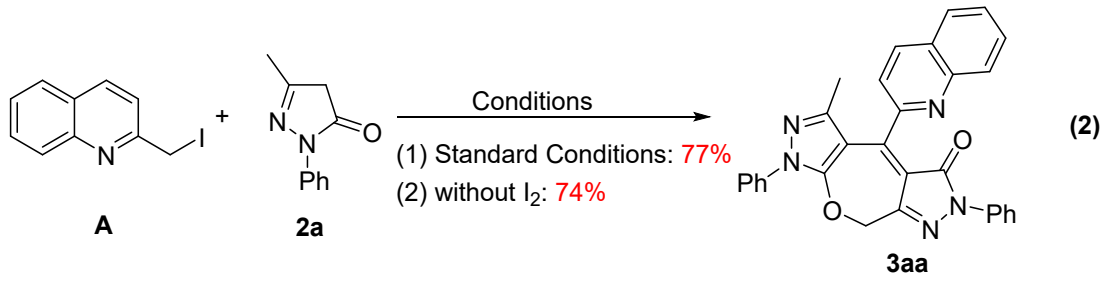
was sealed and the resulting mixture was stirred at 130 °C for 3 h under an air atmosphere. And then added 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (104.5 mg, 0.6 mmol, 2.0 equiv.) for additional 6h. After the reaction was finished, we monitored it by TLC. The TLC result showed that no product was formed.

4.3 Control experiments (c):

In order to show that compound **A** is a possible intermediate in this reaction, we synthesized it using the reported method,[2] and then placed it under two different conditions for reaction.



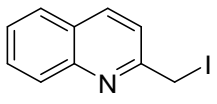
(1)



(2)

Procedure and Results:

(1): An oven-dried pressure tube was charged with 2-methylquinoline (**1a**) (0.3 mmol), I_2 (0.45 mmol), $NaHCO_3$ (0.45 mmol) , PPh_3 (0.03 mmol) and 2 mL of THF. The mixture was stirred at 120 °C for 1.5 h under nitrogen atmosphere. After cooling to room temperature, the mixture was diluted with ethyl acetate and washed with saturated sodium thiosulfate. Then extracted with ethyl acetate and dried with anhydrous sodium sulfate. The solvent was evaporated in vacuo and the residues were purified by column charomatography to afford the desired product **A** as a yellow solid (55 mg, 68% yield).



2-(iodomethyl)quinoline (A)

Yellow solid; melting point: 58-64 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.03 (m, 2 H), 7.77 (d, J = 8.0 Hz, 1 H), 7.72-7.68 (m, 2 H), 7.54-7.49 (m, 2 H), 4.67 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 147.5, 137.1, 129.8, 129.0, 127.4, 127.0, 126.7, 4 121.0, 6.84. IR (film, cm^{-1}): 3054, 2918, 2752, 1643, 1541, 1505, 1458, 1220, 1150, 769, 572. HRMS (ESI): m/z calcd for $C_{10}H_9IN$ [M+H]+ 269.9774, found 269.9771.(as reported in the previous literature).

[2] X.-B. Pang, L.-K. Xiang, J.-X. Ma, *et al*. *RSC Adv.*, **2016**, 6, 111713-111717.

(2)-1: A 25 mL pressure vial was charged with 2-(iodomethyl)quinoline (**A**) (80.7 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 3 h under an air atmosphere. And then added 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (104.5 mg, 0.6 mmol, 2.0 equiv.) for additional 6h. After the reaction was completed (monitored by TLC), and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3aa** as a yellow solid (112 mg, 77% yield).

(2)-2: A 25 mL pressure vial was charged with 2-(iodomethyl)quinoline (**A**) (80.7 mg, 0.30 mmol, 1.0 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 3 h under an air atmosphere. And then added 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (104.5 mg, 0.6 mmol, 2.0 equiv.) for additional 6h. After the reaction was completed (monitored by TLC), and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3aa** as a yellow solid (107 mg, 74% yield).

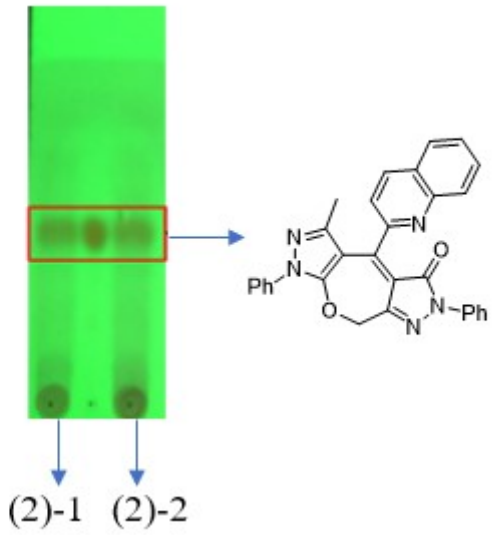
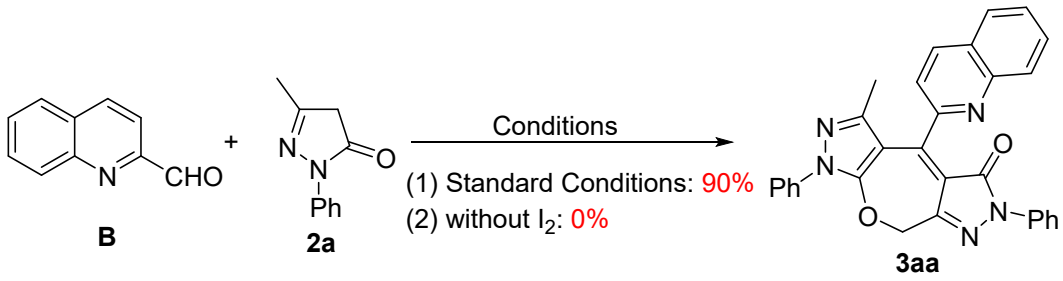


Figure S4. The TLC results for the control experiments **c (2)**



(3)

Procedure and Results:

(1): A 25 mL pressure vial was charged with quinoline-2-carbaldehyde (**B**) (47.2 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 3 h under an air atmosphere. And then added 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (104.5 mg, 0.6 mmol, 2.0 equiv.) for additional 6h. After the reaction was completed (monitored by TLC), and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3aa** as a yellow solid (131 mg, 90% yield).

(2): A 25 mL pressure vial was charged with quinoline-2-carbaldehyde (**B**) (47.2 mg, 0.30 mmol, 1.0 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 3 h under an air atmosphere. And then added 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (104.5 mg, 0.6 mmol, 2.0 equiv.) for additional 6h. After the reaction was finished, we monitored it by TLC. The TLC result showed that no product was formed.

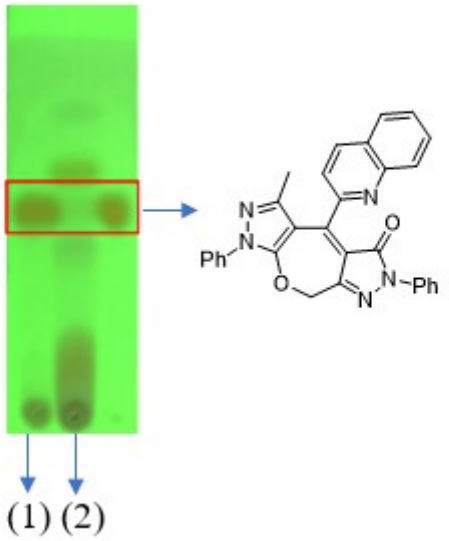
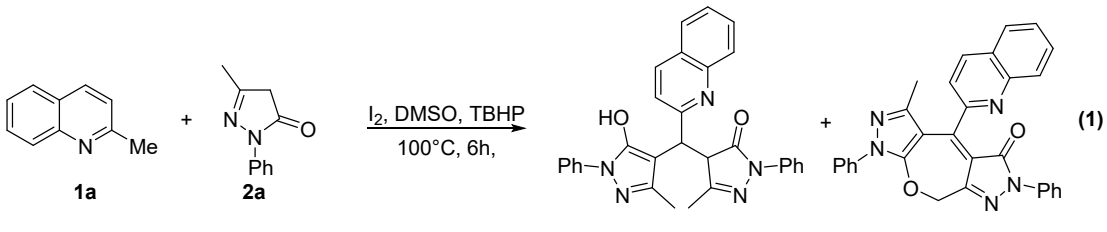
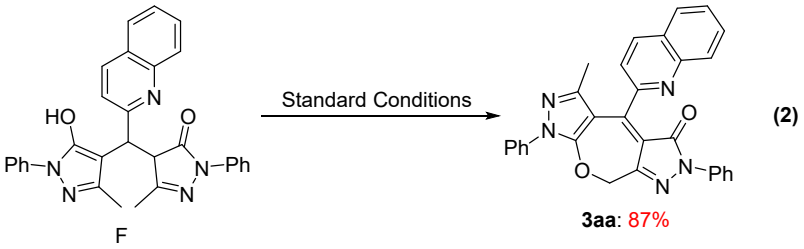


Figure S5. The TLC results for the control experiments **c (3)**

4.4 Control experiments (d):

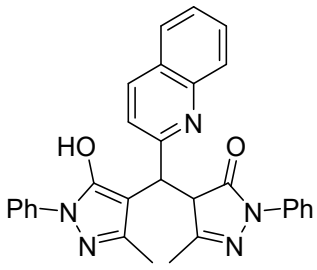




Procedure and Results:

(1): A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (43.0 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TBHP (27.0 mg, 0.3 mmol, 1.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 6 h under an air atmosphere. After the reaction was completed (monitored by TLC), and added 50 mL water, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **F** as a grey solid (29 mg, 20% yield).

(2): A 25 mL pressure vial was charged with compound **F** (146.3 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 6h under an air atmosphere. After the reaction was completed (monitored by TLC), and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3aa** as a yellow solid (126 mg, 87% yield).



4-((5-Hydroxy-3-methyl-1-phenyl-1*H*-pyrazol-4-yl)(quinolin-2-yl)methyl)-5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one. (F)

Grey solid, 29 mg, 20%, m.p. 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.4 Hz, 1H), 8.04 – 7.83 (m, 6H), 7.76 (t, J = 7.8 Hz, 1H), 7.59 (t, J = 7.5 Hz, 1H), 7.52 – 7.41 (m, 4H), 7.35 (d, J = 8.4 Hz, 1H), 7.28 (t, J = 7.4 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 4.25 (d, J = 13.0 Hz, 1H), 3.39 – 3.14 (m, 1H), 2.00 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (120 MHz, $CDCl_3$) δ 173.5, 162.9, 155.3, 146.8, 144.4, 138.8, 138.0, 131.2, 129.0, 128.7, 127.9, 127.7, 127.4, 126.2, 125.7, 125.3, 124.4, 122.3, 118.9, 57.5, 38.6, 14.1, 13.1. HRMS (ESI) m/z calculated for $[C_{30}H_{25}N_5O_2+H]^+$ 488.2081, found 488.2072.

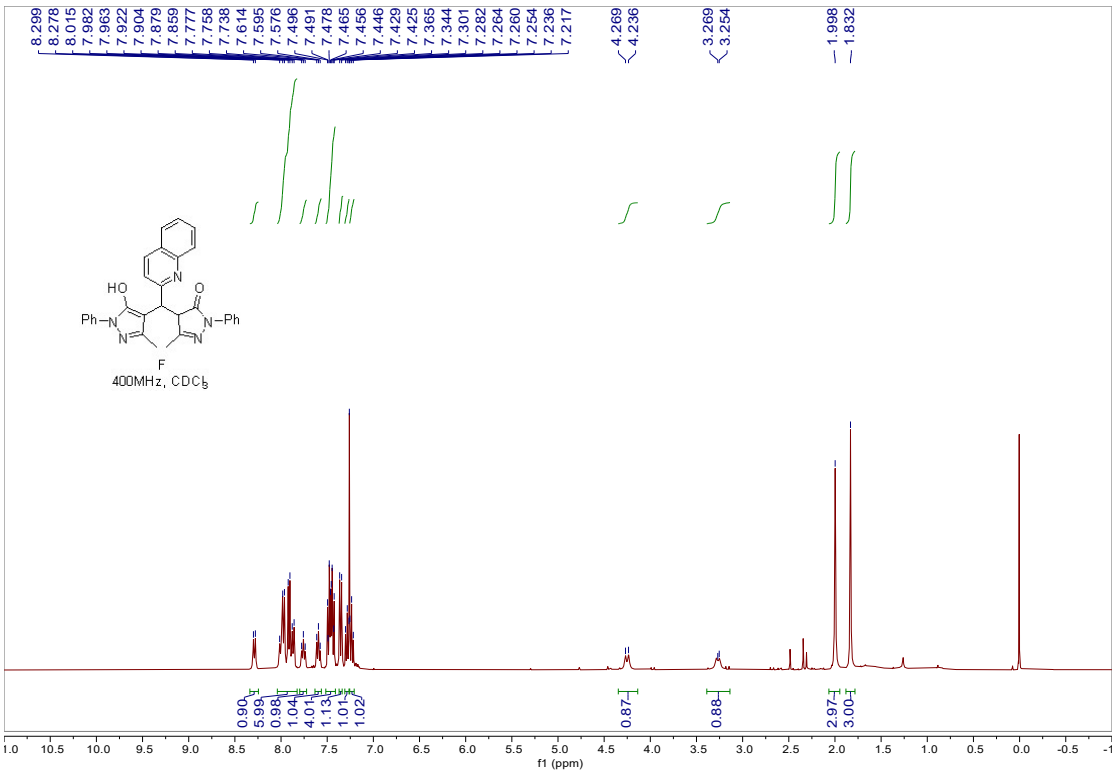


Figure S6. ^{1}H-NMR result of the compound **F**

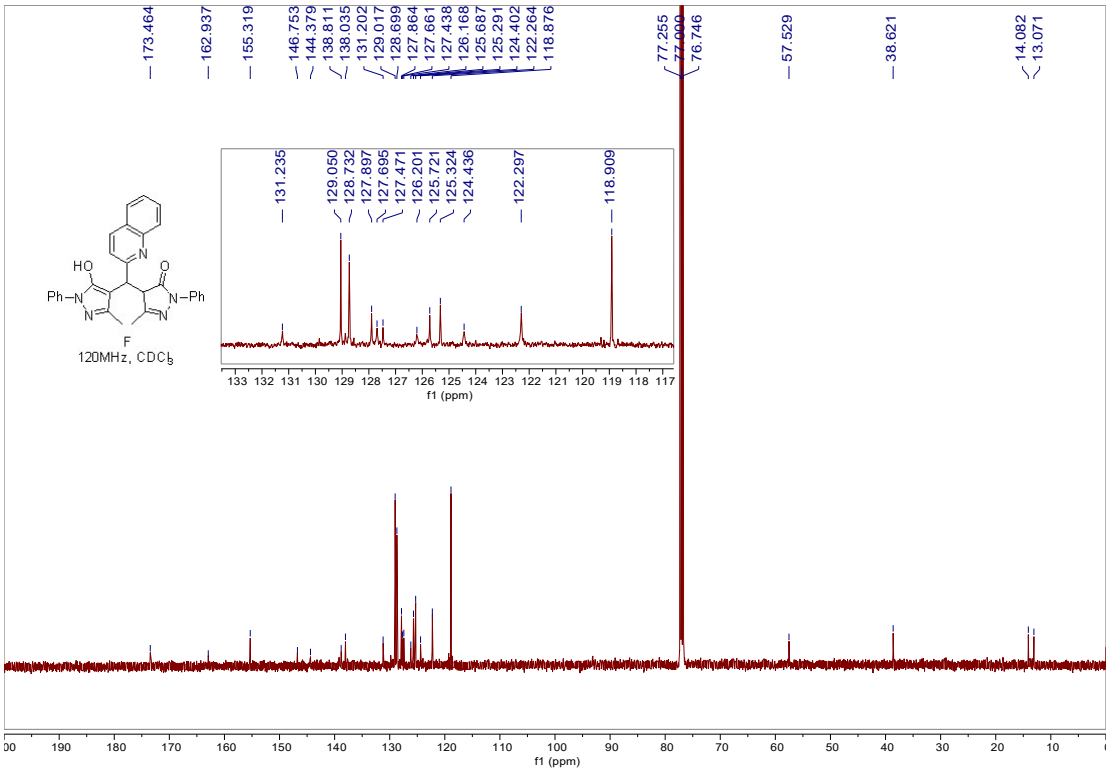


Figure S7. ^{13}C-NMR result of the compound **F**

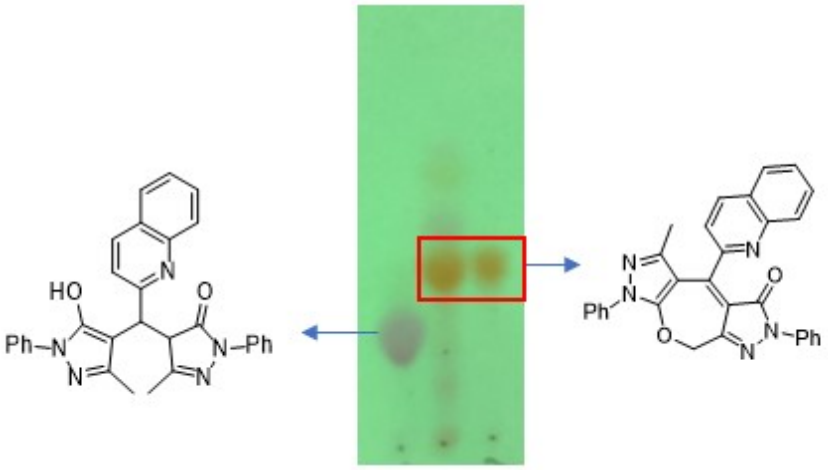
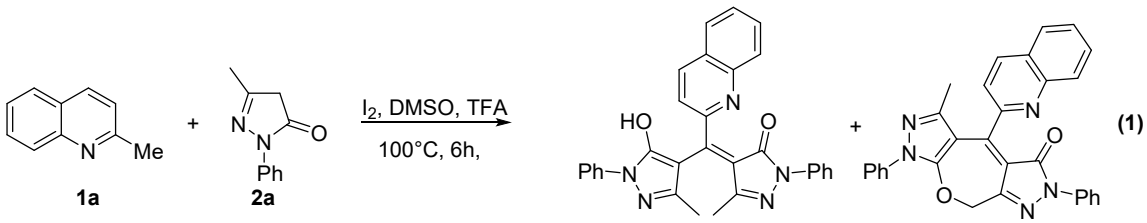


Figure S8. The TLC results for the control experiments **d (2)**

4.5 Control experiments (e):



F': detected by TLC-MS (APCI); **3aa**: 37%

Procedure and Results:

(1): A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (43.0 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (104.5 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 100 °C for 6 h under an air atmosphere. After the reaction was finished, and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under

reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3aa** as a yellow solid (54 mg, 37% yield).

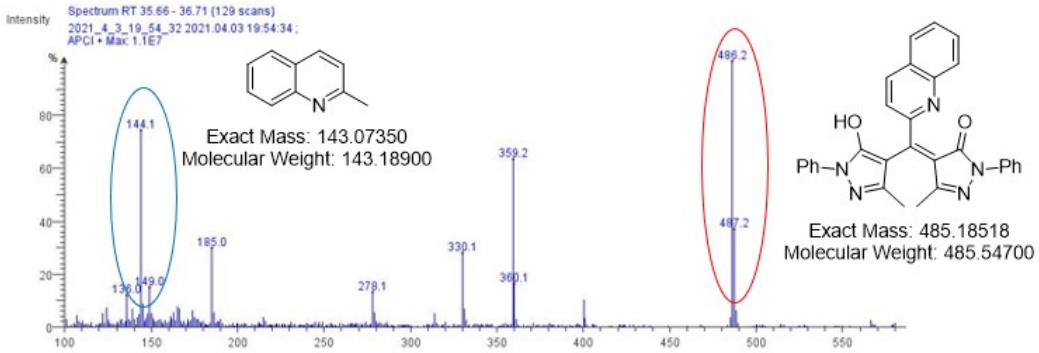
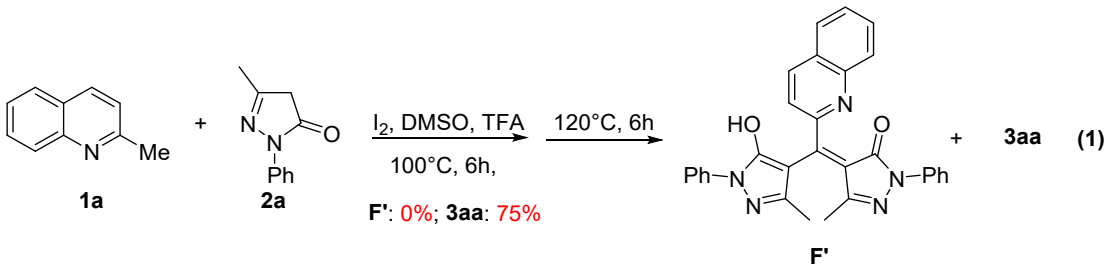


Figure S9. The MS (APCI) results for the control experiments **e (1)**

4.6 Control experiments (f):



(2): A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (43.0 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.), 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) (104.5 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 100 °C for 6 h under an air atmosphere. Then increased the temperature to 130 °C and continue to react for 6 hours After the reaction was finished, and added 50 mL water and an appropriate amount of 10% NaOH solution (w/w) to the mixture, then extracted with EtOAc 3 times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to yield the corresponding product **3aa** as a yellow solid (109 mg, 75% yield).

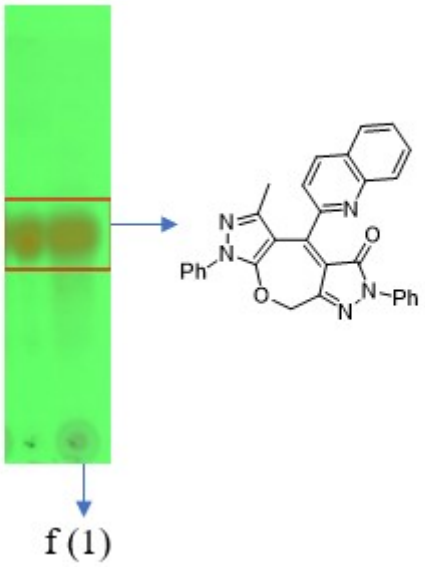
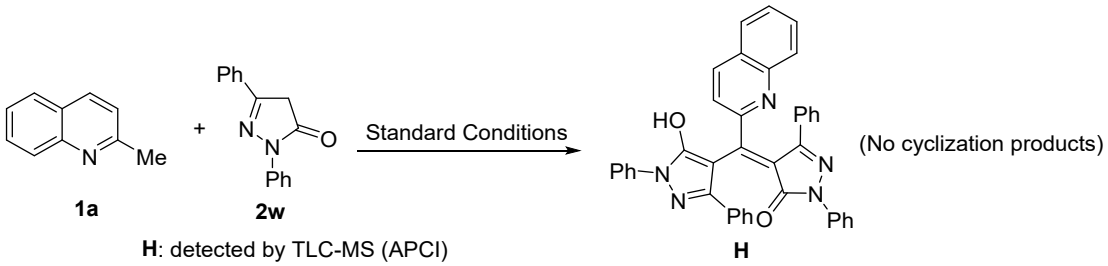


Figure S10. The TLC results for the control experiments **f (1)**

4.7 Control experiments (g):



Procedure and Results:

A 25 mL pressure vial was charged with 2-methylquinoline (**1a**) (43.0 mg, 0.30 mmol, 1.0 equiv.), I_2 (7.6 mg, 0.03 mmol, 0.1 equiv.), TFA (68.4 mg, 0.6 mmol, 2.0 equiv.) and DMSO (2.0 mL). The vial was sealed and the resulting mixture was stirred at 130 °C for 3 h under an air atmosphere. and then added 2,5-diphenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2w**) (141.8 mg, 0.6 mmol, 2.0 equiv.) for additional 6h. Then detected by TLC-MS (APCI).

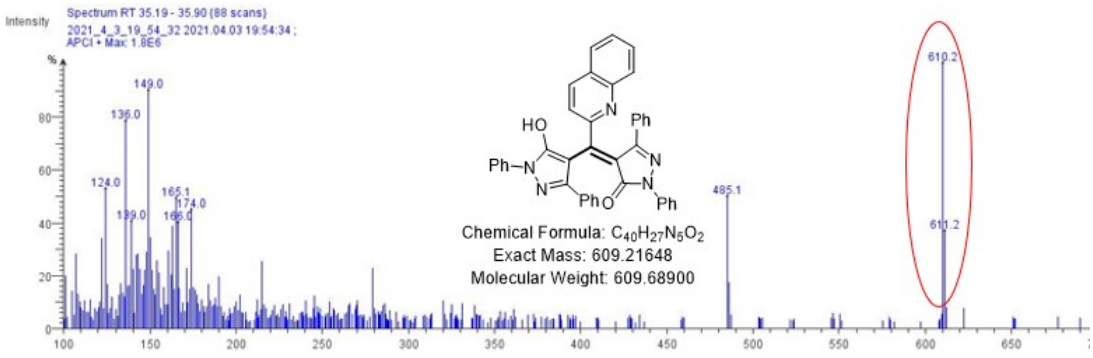


Figure S11. The MS (APCI) results for the control experiments **g**

5. Molecular structure and crystallographic data

Table S2 Crystal data and structure refinement for compound 3va

Identification code	CCDC: 2129039
Empirical formula	$C_{26}H_{19}N_5O_2$
Formula weight	433.46
Temperature/K	296(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.8332(17)
b/Å	13.452(2)
c/Å	16.081(3)
α/°	90
β/°	100.629(3)
γ/°	90
Volume/Å^3	2090.6(6)
Z	4
ρ_{calc}g/cm^3	1.377
μ/mm^{-1}	0.091
F(000)	904.0
Crystal size/mm^3	0.18 × 0.16 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.976 to 54.96
Index ranges	-12 ≤ h ≤ 12, -17 ≤ k ≤ 16, -19 ≤ l ≤ 20
Reflections collected	12761
Independent reflections	4771 [R_{int} = 0.0337, R_{sigma} = 0.0402]
Data/restraints/parameters	4771/0/299
Goodness-of-fit on F^2	1.010
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1333
Final R indexes [all data]	R_1 = 0.0643, wR_2 = 0.1509
Largest diff. peak/hole / e Å^{-3}	0.21/-0.25

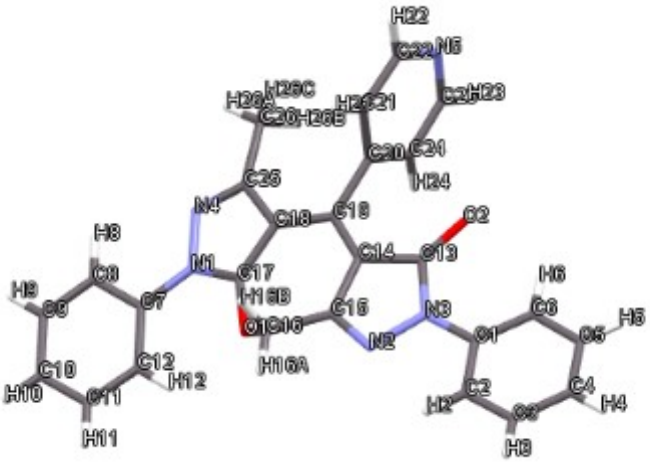
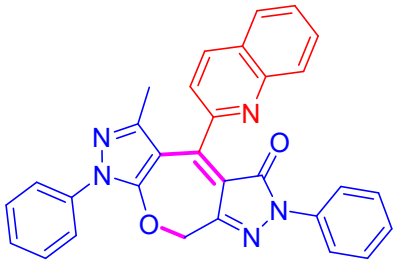


Figure S12. X-ray crystal structure of compound **3va.**

6 Characterization data for products

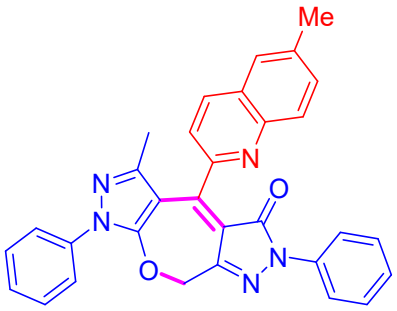
5-Methyl-2,7-diphenyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3aa)



3aa

Yellow solid, 120 mg, 83%, m.p. 234-236 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.81 – 7.75 (m, 3H), 7.70 (dd, J = 8.6, 1.2 Hz, 2H), 7.63 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.44 – 7.38 (m, 1H), 7.33 – 7.28 (m, 2H), 7.11 (t, J = 7.4 Hz, 1H), 5.29 (s, 2H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 155.0, 154.6, 151.1, 151.0, 148.2, 145.1, 138.2, 136.8, 136.7, 130.1, 129.6, 129.2, 128.6, 128.0, 127.7, 127.4, 124.9, 123.0, 121.1, 119.0, 106.8, 70.3, 15.1. HRMS (ESI) m/z calculated for $[C_{30}H_{21}N_5O_2+H]^+$: 484.1768, found: 484.1759.

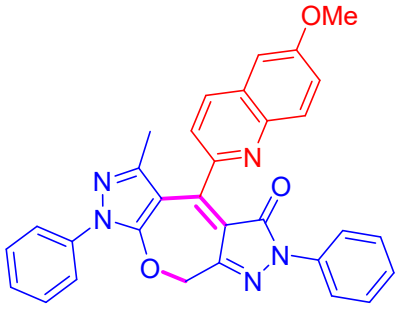
5-Methyl-4-(6-methylquinolin-2-yl)-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3ba)



3ba

Orange solid, 89 mg, 60%, m.p. 228-230 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.5 Hz, 1H), 8.05 (d, J = 8.6 Hz, 1H), 7.81 – 7.77 (m, 2H), 7.71 – 7.67 (m, 3H), 7.60 (dd, J = 8.6, 2.0 Hz, 1H), 7.56 – 7.48 (m, 3H), 7.43 – 7.40 (m, 1H), 7.33 – 7.27 (m, 2H), 7.14 – 7.08 (m, 1H), 5.29 (d, J = 2.6 Hz, 2H), 2.58 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 155.0, 153.6, 151.2, 146.8, 145.1, 138.3, 137.4, 136.8, 136.1, 132.4, 129.3, 129.2, 128.9, 128.6, 128.0, 127.8, 126.8, 124.9, 123.0, 121.1, 119.0, 106.9, 70.4, 21.7, 15.1. HRMS (ESI) m/z calculated for $[C_{31}H_{23}N_5O_2+H]^+$: 498.1924, found: 498.1915.

4-(6-Methoxyquinolin-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3ca)

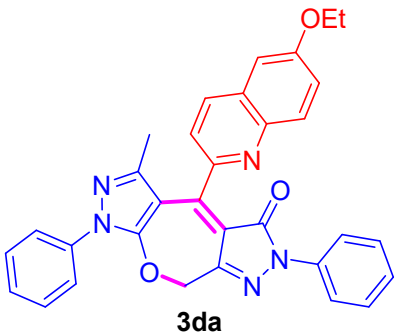


3ca

Orange solid, 99 mg, 64%, m.p. 236-238 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.7 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.83 – 7.77 (m, 2H), 7.72 – 7.67 (m, 2H), 7.52 (dd, J = 16.5, 8.4 Hz, 3H), 7.45 – 7.38 (m, 2H), 7.34 – 7.27 (m, 2H), 7.18 (d, J = 2.8 Hz, 1H), 7.14 – 7.08 (m, 1H), 5.28 (s, 2H), 3.97 (s, 3H), 1.38 (s, 3H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 158.5, 155.0, 151.9, 151.3, 151.2, 145.1, 144.3, 138.3, 136.8,

135.4, 131.1, 129.2, 128.9, 128.6, 128.0, 124.9, 123.0, 122.9, 121.4, 119.0, 107.0, 105.5, 70.4, 55.7, 15.1. HRMS (ESI) m/z calculated for $[C_{31}H_{23}N_5O_3+H]^+$: 514.1874, found: 514.1867.

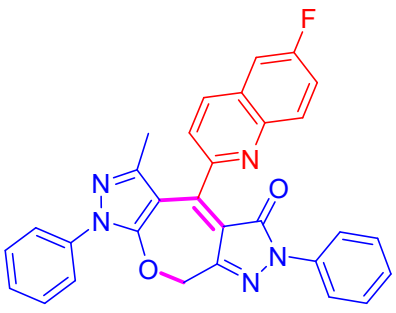
4-(6-Ethoxyquinolin-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3da)



3da

Yellow solid, 92 mg, 58%, m.p. 255-257 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.5 Hz, 1H), 8.04 (d, J = 9.2 Hz, 1H), 7.80 (dd, J = 8.8, 1.2 Hz, 2H), 7.69 (dd, J = 8.6, 1.3 Hz, 2H), 7.55 – 7.48 (m, 3H), 7.43 – 7.37 (m, 2H), 7.34 – 7.28 (m, 2H), 7.16 (d, J = 2.7 Hz, 1H), 7.11 (t, J = 7.4 Hz, 1H), 5.28 (s, 2H), 4.19 (q, J = 7.0 Hz, 2H), 1.52 (t, J = 7.0 Hz, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 157.8, 155.0, 151.7, 151.4, 151.3, 145.1, 144.2, 138.3, 136.8, 135.4, 131.0, 129.2, 129.0, 128.6, 128.0, 124.9, 123.2, 123.0, 121.4, 119.0, 107.0, 106.2, 70.4, 63.9, 15.1, 14.7. HRMS (ESI) m/z calculated for $[C_{32}H_{25}N_5O_3+H]^+$: 528.2030, found: 528.2025.

4-(6-Fluoroquinolin-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3ea)

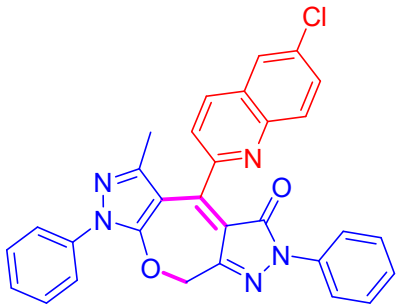


3ea

Brown solid, 114 mg, 76%, m.p. 202-204 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 9.4 Hz, 1H), 8.21 (dd, J = 10.0, 5.2 Hz, 1H), 7.77 (dd, J = 8.7, 1.2 Hz, 2H), 7.69 (dd,

J = 8.5, 1.2 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 1H), 7.59 – 7.56 (m, 1H), 7.54 (d, *J* = 5.3 Hz, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 5.30 (s, 2H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 162.3, 159.8, 155.1, 153.8, 150.9, 145.0, 138.1, 136.7, 131.9, 129.2, 128.7, 128.5, 128.1, 125.0, 123.0, 122.0, 120.5, 119.1, 111.3, 111.0, 106.6, 70.3, 14.6. HRMS (ESI) m/z calculated for $[C_{30}H_{20}FN_5O_2+H]^+$: 502.1674, found: 502.1665.

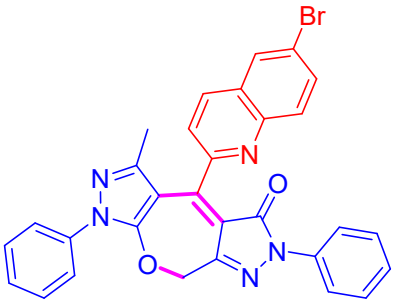
4-(6-Chloroquinolin-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*'] dipyrazol-3(7*H*)-one (3fa)



3fa

Orange solid, 135 mg, 87%, m.p. 208-210 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.9 Hz, 1H), 8.15 (d, *J* = 9.1 Hz, 1H), 7.94 (d, *J* = 2.3 Hz, 1H), 7.77 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.73 (dd, *J* = 9.0, 2.3 Hz, 1H), 7.71 – 7.68 (m, 2H), 7.62 (d, *J* = 8.4 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.44 – 7.39 (m, 1H), 7.33 – 7.28 (m, 2H), 7.15 – 7.10 (m, 1H), 5.30 (s, 2H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 155.1, 154.7, 150.6, 144.9, 138.1, 136.7, 136.4, 133.6, 131.5, 130.8, 129.2, 128.7, 128.3, 128.1, 126.7, 125.1, 123.0, 122.1, 119.3, 106.7, 99.9, 70.3, 15.1. HRMS (ESI) m/z calculated for $[C_{30}H_{20}ClN_5O_2+H]^+$: 518.1378, found: 518.1370.

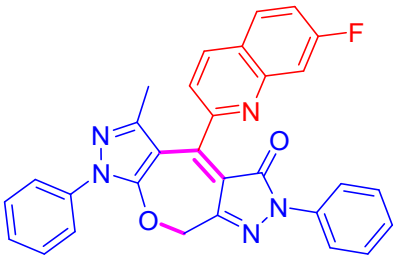
4-(6-Bromoquinolin-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*'] dipyrazol-3(7*H*)-one (3ga)



3ga

Yellow solid, 106 mg, 63%, m.p. 216-218 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 7.8 Hz, 1H), 8.13 – 8.07 (m, 2H), 7.86 (dd, J = 9.0, 2.2 Hz, 1H), 7.77 (dd, J = 8.8, 1.2 Hz, 2H), 7.69 (dd, J = 8.6, 1.2 Hz, 2H), 7.62 (d, J = 8.4 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H), 5.31 (s, 2H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 155.1, 154.8, 150.8, 145.0, 143.2, 138.1, 136.7, 134.1, 130.9, 130.1, 129.2, 128.8, 128.7, 128.2, 125.1, 123.0, 122.1, 121.8, 119.2, 119.1, 106.5, 70.3, 15.1. HRMS (ESI) m/z calculated for $[C_{30}H_{20}BrN_5O_2+H]^+$: 562.0873, found: 562.0866.

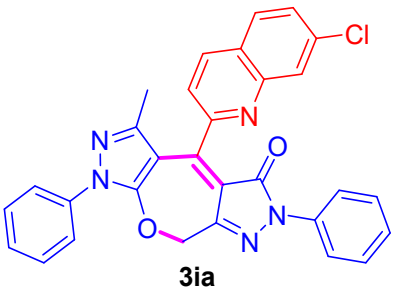
4-(7-Fluoroquinolin-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7H)-one (3ha)



3ha

Brown solid, 105 mg, 70%, m.p. 200-202 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, J = 8.4 Hz, 1H), 7.95 (dd, J = 9.0, 5.9 Hz, 1H), 7.84 (dd, J = 9.9, 2.5 Hz, 1H), 7.77 (dd, J = 8.7, 1.1 Hz, 2H), 7.70 (dd, J = 8.7, 1.2 Hz, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.54 – 7.49 (m, 2H), 7.45 – 7.40 (m, 2H), 7.33 – 7.28 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H), 5.30 (s, 2H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 162.2, 155.6, 155.1, 150.9, 145.0, 138.1, 137.1, 136.7, 130.2, 130.1, 129.2, 128.7, 128.1, 125.0, 124.8, 123.0, 120.5, 119.1, 118.3, 118.1, 106.5, 99.9, 70.3, 15.1. HRMS (ESI) m/z calculated for $[C_{30}H_{20}FN_5O_2+H]^+$: 502. 1674, found: 502.1663.

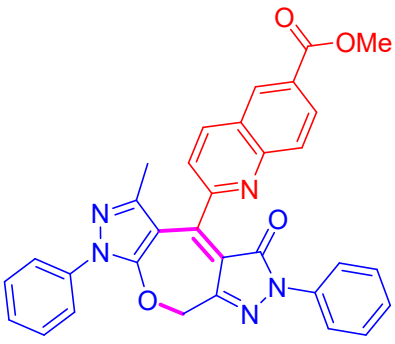
4-(7-Chloroquinolin-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3ia)



3ia

Brown solid, 113 mg, 73%, m.p. 228-230 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 7.6 Hz, 1H), 8.22 (d, J = 2.1 Hz, 1H), 7.89 (d, J = 8.7 Hz, 1H), 7.77 (dd, J = 8.7, 1.1 Hz, 2H), 7.70 (dd, J = 8.5, 1.2 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.52 (t, J = 7.7 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H), 5.31 (s, 2H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 158.1, 155.6, 155.1, 150.8, 145.0, 138.1, 137.2, 136.7, 129.3, 129.2, 128.8, 128.7, 128.3, 126.1, 125.1, 123.0, 121.3, 119.3, 119.1, 106.5, 70.3, 15.1. HRMS (ESI) m/z calculated for $[C_{30}H_{20}ClN_5O_2+H]^+$: 518.1378, found: 518.1371.

Methyl-2-(5-methyl-3-oxo-2,7-diphenyl-2,3,7,9-tetrahydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-4-yl)quinoline-6-carboxylate (3ja)

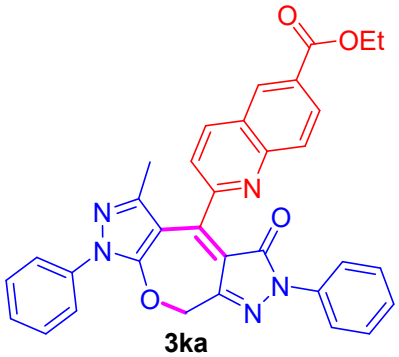


3ja

Orange solid, 89 mg, 55%, m.p. 267-269 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 1.9 Hz, 1H), 8.45 (d, J = 8.5 Hz, 1H), 8.36 (dd, J = 8.8, 1.9 Hz, 1H), 8.20 (d, J = 9.6 Hz, 1H), 7.77 (dd, J = 8.7, 1.2 Hz, 2H), 7.69 (d, J = 7.3 Hz, 2H), 7.65 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H), 5.31 (s, 2H), 4.02 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

166.4, 162.5, 157.0, 155.1, 150.8, 150.3, 149.9, 145.0, 138.1, 136.6, 131.1, 129.9, 129.7, 129.2, 128.9, 128.7, 128.1, 126.9, 125.1, 123.0, 121.9, 119.0, 106.5, 70.3, 52.5, 14.2. HRMS (ESI) m/z calculated for $[C_{32}H_{23}N_5O_4+H]^+$: 542.1823, found: 542.1814.

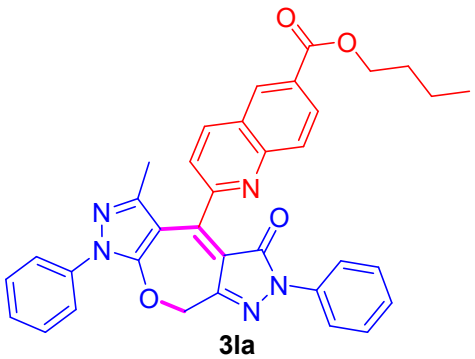
Ethyl-2-(5-methyl-3-oxo-2,7-diphenyl-2,3,7,9-tetrahydrooxepino[2,3-*c*:6,5-*c*']dipy-razol-4-yl)quinoline-6-carboxylate (3ka)



3ka

Orange solid, 85 mg, 51%, m.p. 253-255 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 1.9 Hz, 1H), 8.45 (d, J = 8.5 Hz, 1H), 8.37 (dd, J = 8.8, 2.0 Hz, 1H), 8.20 (d, J = 8.6 Hz, 1H), 7.77 (d, J = 8.3 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.34 – 7.28 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H), 5.30 (s, 2H), 4.48 (q, J = 7.2 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 162.5, 156.9, 155.1, 150.8, 150.3, 149.9, 145.0, 138.1, 138.0, 136.7, 131.0, 129.9, 129.7, 129.2, 128.7, 128.1, 126.9, 125.0, 123.0, 121.9, 119.0, 106.5, 70.3, 61.5, 15.1, 14.3. HRMS (ESI) m/z calculated for $[C_{33}H_{25}N_5O_4+H]^+$: 556.1979, found: 556.1970.

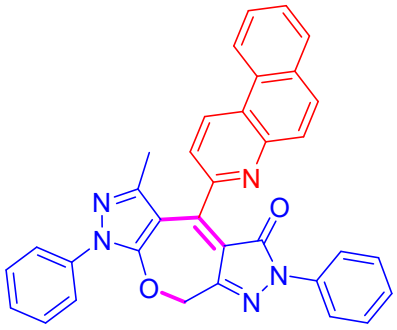
Butyl-2-(5-methyl-3-oxo-2,7-diphenyl-2,3,7,9-tetrahydrooxepino[2,3-*c*:6,5-*c*']dipy-razol-4-yl)quinoline-6-carboxylate (3la)



3la

Orange solid, 91 mg, 52%, m.p. 175-177 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, J = 1.9 Hz, 1H), 8.46 (d, J = 7.7 Hz, 1H), 8.37 (dd, J = 8.8, 1.9 Hz, 1H), 8.20 (d, J = 8.8 Hz, 1H), 7.77 (d, J = 8.6 Hz, 2H), 7.69 (d, J = 7.3 Hz, 2H), 7.65 (d, J = 8.4 Hz, 1H), 7.51 (t, J = 7.8 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.12 (t, J = 7.4 Hz, 1H), 5.30 (d, J = 3.0 Hz, 2H), 4.43 (t, J = 6.6 Hz, 2H), 1.87 – 1.78 (m, 2H), 1.57 – 1.50 (m, 2H), 1.36 (s, 3H), 1.02 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 162.5, 156.9, 155.1, 150.8, 150.3, 149.9, 145.0, 138.1, 138.0, 136.7, 131.0, 129.9, 129.7, 129.3, 129.2, 128.7, 128.1, 126.9, 125.0, 123.0, 121.9, 119.0, 105.8, 70.3, 65.3, 30.8, 19.3, 15.1, 13.8. HRMS (ESI) m/z calculated for $[C_{35}H_{29}N_5O_4+H]^+$: 584.2292, found: 584.2286.

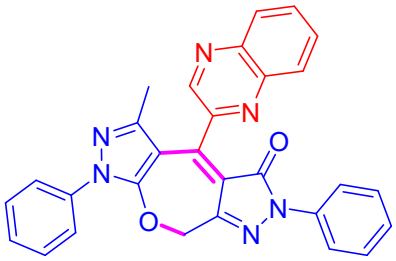
4-(Benzo[*f*]quinolin-3-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*'] dipyrazol-3(7*H*)-one (3ma)



3ma

Brown solid, 125 mg, 78%, m.p. 234-236 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (d, J = 8.6 Hz, 1H), 8.70 (d, J = 7.5 Hz, 1H), 8.06 (s, 2H), 8.00 – 7.94 (m, 1H), 7.81 (dd, J = 8.8, 1.1 Hz, 2H), 7.78 (d, J = 8.5 Hz, 1H), 7.76 – 7.73 (m, 1H), 7.73 – 7.68 (m, 3H), 7.54 – 7.48 (m, 2H), 7.43 – 7.38 (m, 1H), 7.33 – 7.27 (m, 2H), 7.13 – 7.08 (m, 1H), 5.36 – 5.26 (m, 2H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 155.0, 153.8, 151.2, 151.0, 148.3, 145.1, 138.2, 136.7, 132.0, 131.6, 131.5, 129.5, 129.2, 128.8, 128.7, 128.6, 128.0, 127.6, 127.3, 125.2, 124.9, 122.9, 122.6, 121.3, 119.1, 119.0, 118.8, 106.9, , 70.3, 15.1. HRMS (ESI) m/z calculated for $[C_{34}H_{23}N_5O_2+H]^+$: 534.1924, found: 534.1919.

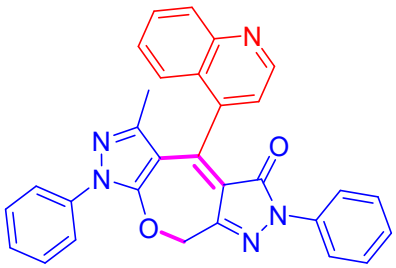
5-Methyl-2,7-diphenyl-4-(quinoxalin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyr-azol-3(7*H*)-one (3na)



3na

Brown solid, 109 mg, 75%, m.p. 209-211 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.24 (dd, J = 8.1, 1.8 Hz, 1H), 8.19 – 8.13 (m, 1H), 7.90 – 7.80 (m, 2H), 7.77 (d, J = 7.6 Hz, 2H), 7.70 (d, J = 7.4 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.42 (t, J = 7.4 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.13 (t, J = 7.4 Hz, 1H), 5.31 (d, J = 10.0 Hz, 2H), 1.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.6, 155.0, 150.5, 150.1, 147.5, 144.7, 144.4, 142.1, 141.9, 138.0, 136.6, 130.8, 130.7, 129.7, 129.5, 129.2, 128.7, 128.2, 125.2, 123.0, 119.8, 119.0, 70.3, 15.8. HRMS (ESI) m/z calculated for $[C_{29}H_{20}N_6O_2+H]^+$: 485.1720, found: 485.1713.

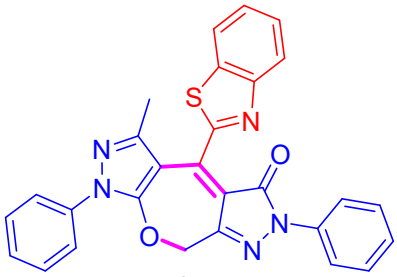
5-Methyl-2,7-diphenyl-4-(quinolin-4-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3oa)



3oa

Orange solid, 83 mg, 57%, m.p. 242-244 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, J = 4.4 Hz, 1H), 8.23 (d, J = 8.2 Hz, 1H), 7.77 (dd, J = 2.7, 1.3 Hz, 1H), 7.76 – 7.74 (m, 2H), 7.74 – 7.72 (m, 2H), 7.71 (d, J = 1.1 Hz, 1H), 7.52 (t, J = 7.8 Hz, 3H), 7.42 (t, J = 7.4 Hz, 1H), 7.38 (d, J = 4.4 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.10 (t, J = 7.4 Hz, 1H), 5.35 (d, J = 2.8 Hz, 2H), 1.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 154.3, 150.7, 150.1, 148.7, 148.1, 144.3, 142.5, 138.0, 136.6, 130.4, 130.0, 129.2, 128.6, 128.1, 127.6, 125.8, 125.0, 123.9, 122.9, 119.6, 119.4, 118.9, 106.6, 70.3, 15.0. HRMS (ESI) m/z calculated for $[C_{30}H_{21}N_5O_2+H]^+$: 484.1768, found: 484.1759.

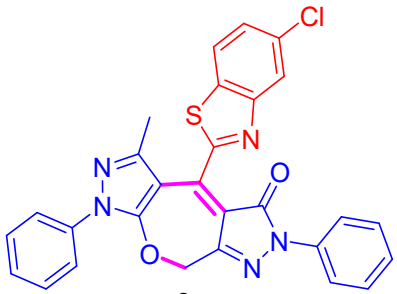
4-(Benzo[*d*]thiazol-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']-dipyrazol-3(7*H*)-one (3pa)



3pa

Orange solid, 63 mg, 43%, m.p. 228-230 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (ddd, J = 8.2, 1.3, 0.7 Hz, 1H), 8.01 (ddd, J = 8.0, 1.3, 0.7 Hz, 1H), 7.81 (dd, J = 8.8, 1.1 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.60 – 7.55 (m, 1H), 7.54 – 7.48 (m, 3H), 7.44 – 7.40 (m, 1H), 7.35 – 7.30 (m, 2H), 7.16 – 7.11 (m, 1H), 5.28 (s, 2H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 161.2, 154.7, 153.2, 151.0, 144.3, 143.2, 138.0, 136.6, 136.1, 129.2, 128.7, 128.2, 126.5, 126.1, 125.1, 124.2, 123.0, 122.2, 120.5, 119.0, 106.2, 70.3, 14.6. HRMS (ESI) m/z calculated for $[C_{28}H_{19}N_5O_2S+H]^+$: 490.1332, found: 490.1326.

4-(5-Chlorobenzo[*d*]thiazol-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3qa)

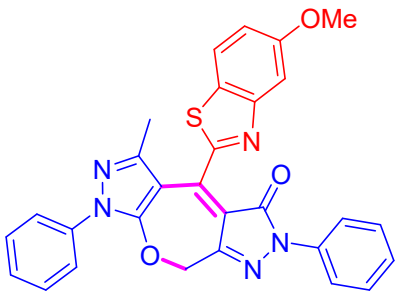


3qa

Orange solid, 123 mg, 78%, m.p. 232-234 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 1.9 Hz, 1H), 7.92 (d, J = 8.6 Hz, 1H), 7.80 (dd, J = 8.5, 1.4 Hz, 2H), 7.71 – 7.67 (m, 2H), 7.54 – 7.46 (m, 3H), 7.45 – 7.39 (m, 1H), 7.36 – 7.30 (m, 2H), 7.17 – 7.11 (m, 1H), 5.26 (s, 2H), 1.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 161.7, 154.7, 153.9, 150.7, 144.2, 142.3, 137.9, 136.5, 134.3, 132.7, 129.2, 128.7, 128.2, 126.7,

125.2, 123.9, 122.9, 120.5, 119.0, 106.0, 70.2, 14.6. HRMS (ESI) m/z calculated for $[C_{28}H_{18}ClN_5O_2S+H]^+$: 524.0942, found: 524.0933.

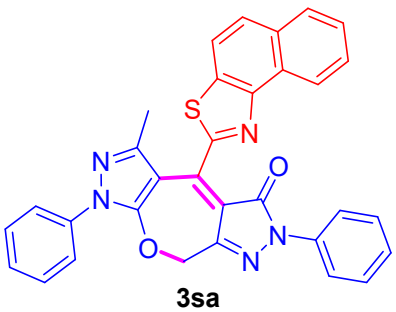
4-(5-Methoxybenzo[*d*]thiazol-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3ra)



3ra

Orange solid, 131 mg, 84%, m.p. 214-216 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 3H), 7.72 – 7.67 (m, 2H), 7.65 (d, J = 2.5 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.44 – 7.38 (m, 1H), 7.35 – 7.29 (m, 2H), 7.17 – 7.11 (m, 2H), 5.26 (s, 2H), 3.92 (s, 3H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 161.8, 159.2, 154.6, 154.5, 151.0, 144.3, 143.1, 138.0, 136.6, 129.2, 128.6, 128.1, 127.9, 125.1, 122.9, 122.3, 120.4, 119.0, 116.6, 106.2, 70.2, 55.6, 14.6. HRMS (ESI) m/z calculated for $[C_{29}H_{21}N_5O_3S+H]^+$: 520.1438. found: 520.1430.

5-Methyl-4-(naphtho[1,2-*d*]thiazol-2-yl)-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3sa)

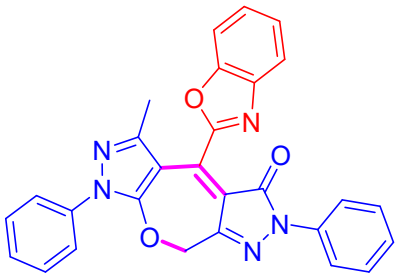


3sa

Orange solid, 128 mg, 79%, m. p. 228-230 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, J = 8.2 Hz, 1H), 8.03 – 7.98 (m, 2H), 7.92 (d, J = 8.8 Hz, 1H), 7.82 (dd, J = 8.7, 1.2 Hz, 2H), 7.74 – 7.70 (m, 2H), 7.69 – 7.60 (m, 2H), 7.55 – 7.49 (m, 2H), 7.45 – 7.39 (m, 1H), 7.35 – 7.29 (m, 2H), 7.16 – 7.10 (m, 1H), 5.30 (s, 2H), 1.65 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9, 159.7, 154.7, 151.2, 149.9, 144.3, 143.5, 138.1, 136.6,

133.3, 132.1, 129.2, 129.0, 128.7, 128.2, 128.1, 127.2, 127.0, 126.4, 125.1, 124.0, 123.0, 120.7, 119.1, 119.0, 106.6, 70.3, 14.8. HRMS (ESI) m/z calculated for $[C_{32}H_{21}N_5O_2S+H]^+$: 540.1489. found: 540.1481.

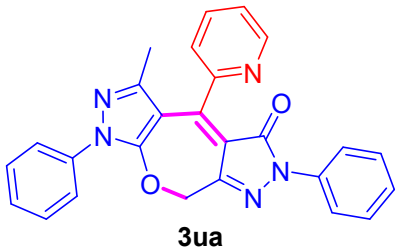
4-(Benzo[*d*]oxazol-2-yl)-5-methyl-2,7-diphenyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipy-razol-3(7*H*)-one (3ta)



3ta

Orange solid, 84 mg, 59%, m.p. 242-244 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 1H), 7.82 (d, J = 1.4 Hz, 2H), 7.71 – 7.66 (m, 3H), 7.54 – 7.49 (m, 2H), 7.48 – 7.44 (m, 2H), 7.44 – 7.39 (m, 1H), 7.36 – 7.30 (m, 2H), 7.17 – 7.12 (m, 1H), 5.28 (s, 2H), 1.72 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 156.5, 154.9, 150.8, 150.5, 144.4, 141.0, 137.9, 136.5, 135.4, 129.2, 128.7, 128.2, 126.2, 125.2, 125.1, 122.9, 122.2, 121.0, 119.0, 111.2, 105.8, 70.1, 13.8. HRMS (ESI) m/z calculated for $[C_{28}H_{19}N_5O_3+H]^+$: 474.1561. found: 474.1553.

5-Methyl-2,7-diphenyl-4-(pyridin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3ua)

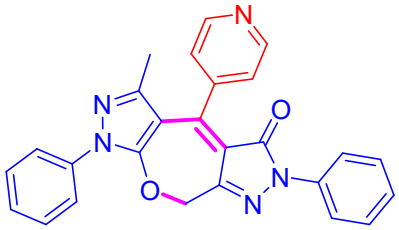


3ua

Orange solid, 60 mg, 46%, m.p. 206-208 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 4.9 Hz, 1H), 7.90 – 7.80 (m, 3H), 7.72 – 7.64 (m, 2H), 7.50 (td, J = 7.7, 1.5 Hz, 3H), 7.47 – 7.43 (m, 1H), 7.42 – 7.37 (m, 1H), 7.35 – 7.29 (m, 2H), 7.15 – 7.10 (m, 1H), 5.24 (s, 2H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 154.9, 154.0, 150.9,

150.7, 150.1, 145.0, 138.2, 136.6, 129.1, 128.6, 128.0, 124.9, 123.9, 123.6, 122.9, 119.0, 118.9, 106.7, 70.3, 14.8. HRMS (ESI) m/z calculated for $[C_{26}H_{19}N_5O_2+H]^+$: 434.1611. found: 434.1604.

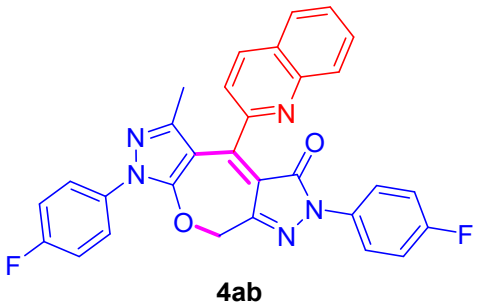
5-Methyl-2,7-diphenyl-4-(pyridin-4-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (3va)



3va

Orange solid, 48 mg, 37%, m.p. 220-222 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 6.0 Hz, 2H), 7.82 (dd, J = 8.7, 1.2 Hz, 2H), 7.72 – 7.67 (m, 2H), 7.54 – 7.48 (m, 2H), 7.45 – 7.39 (m, 1H), 7.36 – 7.31 (m, 2H), 7.31 – 7.28 (m, 2H), 7.16 – 7.11 (m, 1H), 5.23 (s, 2H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 1162.2, 154.4, 150.6, 150.3, 149.9, 144.5, 143.8, 138.1, 136.6, 129.2, 128.7, 128.1, 125.0, 122.9, 122.4, 118.9, 118.3, 106.3, 70.4, 15.6. HRMS (ESI) m/z calculated for $[C_{26}H_{19}N_5O_2+H]^+$: 434.1611. found: 434.1604.

2,7-Bis(4-fluorophenyl)-5-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4ab)

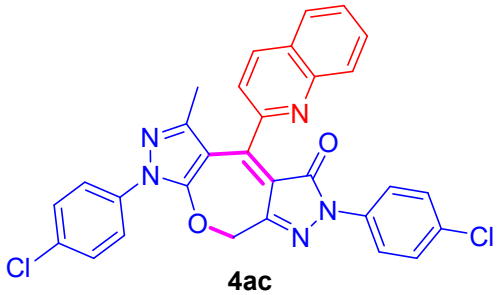


4ab

Orange solid, 115 mg, 74%, m.p. 240-242 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 7.2 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.77 – 7.73 (m, 2H), 7.70 – 7.61 (m, 3H), 7.57 (d, J = 8.5 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.02 – 6.95 (m, 2H), 5.28 (d, J = 3.0 Hz, 2H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$)

δ 163.1, 162.4, 161.1, 160.6, 158.7, 154.9, 154.4, 151.2, 148.2, 145.0, 136.9, 134.3, 132.8, 130.5, 130.2, 129.6, 128.1, 127.7, 127.5, 124.9, 124.8, 121.0, 120.8, 120.7, 118.9, 116.0, 115.4, 115.2, 106.7, 70.3, 15.0. HRMS (ESI) m/z calculated for $[C_{30}H_{19}F_2N_5O_2+H]^+$: 520.1580 found: 520.1571.

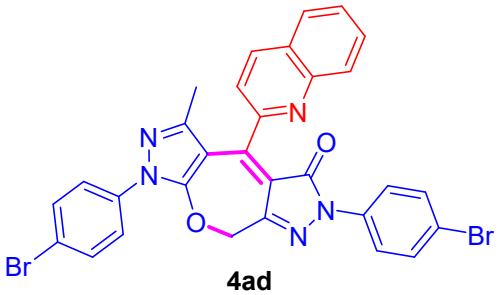
2,7-Bis(4-chlorophenyl)-5-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4ac)



4ac

Orange solid, 109 mg, 66%, m.p. 232-234 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.4 Hz, 1H), 8.15 (d, J = 8.5 Hz, 1H), 7.95 – 7.91 (m, 1H), 7.81 – 7.75 (m, 3H), 7.68 – 7.63 (m, 3H), 7.56 (d, J = 8.4 Hz, 1H), 7.47 (d, J = 8.9 Hz, 2H), 7.26 (s, 1H), 7.24 (s, 1H), 5.29 (d, J = 3.5 Hz, 2H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 155.0, 154.3, 151.4, 151.2, 148.2, 145.2, 136.9, 135.2, 133.7, 130.2, 130.0, 129.6, 129.3, 128.7, 128.1, 127.7, 127.5, 123.9, 120.9, 119.9, 118.9, 106.9, 70.3, 15.0. HRMS (ESI) m/z calculated for $[C_{30}H_{19}Cl_2N_5O_2+H]^+$: 552.0989 found: 552.0981.

2,7-Bis(4-bromophenyl)-5-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4ad)

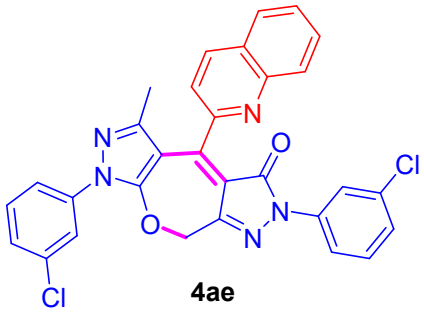


4ad

Orange solid, 150 mg, 78%, m.p. 225-227 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.5 Hz, 1H), 8.15 (d, J = 8.4 Hz, 1H), 7.94 (d, J = 8.2 Hz, 1H), 7.78 (t, J = 7.7 Hz, 1H), 7.73 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 7.0 Hz, 1H), 7.61 (d, J = 4.2 Hz, 4H), 7.56

(d, J = 8.4 Hz, 1H), 7.40 (d, J = 9.1 Hz, 2H), 5.28 (d, J = 5.1 Hz, 2H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 155.0, 154.2, 151.4, 151.2, 148.1, 145.2, 137.3, 136.9, 135.7, 132.3, 131.6, 130.3, 129.6, 128.1, 127.7, 127.5, 124.2, 121.7, 120.9, 120.2, 118.9, 117.7, 106.9, 70.3, 15.1. HRMS (ESI) m/z calculated for $[C_{30}H_{19}Br_2N_5O_2+H]^+$: 639.9978 found: 639.9966.

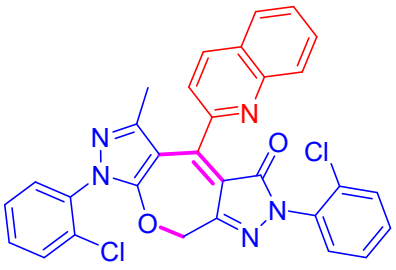
2,7-Bis(3-chlorophenyl)-5-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4ae)



4ae

Orange solid, 113 mg, 68%, m.p. 236-238 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 7.6 Hz, 1H), 8.16 (d, J = 7.4 Hz, 1H), 7.94 (d, J = 6.3 Hz, 1H), 7.90 (t, J = 2.0 Hz, 1H), 7.81 – 7.72 (m, 3H), 7.67 – 7.61 (m, 2H), 7.57 (d, J = 8.4 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.39 – 7.34 (m, 1H), 7.21 (t, J = 8.2 Hz, 1H), 7.08 (ddd, J = 8.0, 2.1, 1.0 Hz, 1H), 5.30 (d, J = 3.8 Hz, 2H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 155.1, 154.2, 151.4, 151.1, 148.1, 145.3, 139.2, 137.6, 136.9, 134.9, 134.4, 130.3, 130.2, 129.6, 128.0, 127.7, 127.5, 124.7, 122.8, 120.9, 120.6, 119.0, 118.5, 116.5, 106.9, 70.3, 15.0. HRMS (ESI) m/z calculated for $[C_{30}H_{19}Cl_2N_5O_2+H]^+$: 552.0989 found: 552.0979.

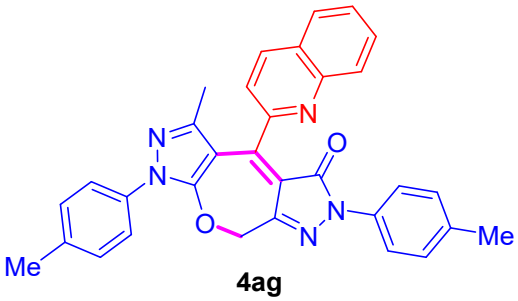
2,7-Bis(2-chlorophenyl)-5-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4af)



4af

Yellow solid, 113 mg, 68%, m.p. 254-256 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 7.7 Hz, 1H), 8.16 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 7.1 Hz, 1H), 7.76 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.64 – 7.57 (m, 3H), 7.50 – 7.44 (m, 3H), 7.41 (dd, J = 6.1, 3.4 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.26 – 7.21 (m, 2H), 5.32 (s, 2H), 1.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 156.3, 154.3, 151.6, 151.1, 148.1, 145.1, 136.8, 134.5, 134.1, 131.9, 131.3, 131.0, 130.3, 130.0, 129.5, 129.4, 129.3, 129.1, 127.9, 127.7, 127.3, 127.1, 120.9, 117.9, 105.7, 70.0, 15.2. HRMS (ESI) m/z calculated for $[C_{30}H_{19}Cl_2N_5O_2+H]^+$: 552.0989 found: 552.0981.

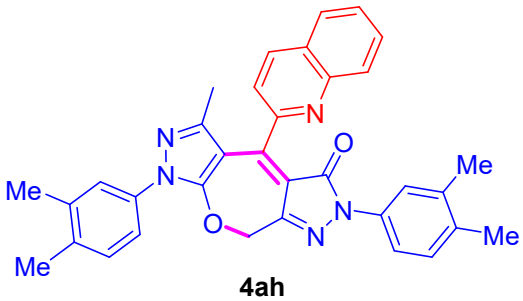
5-Methyl-4-(quinolin-2-yl)-2,7-di-*p*-tolyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4ag)



4ag

Brown solid, 124 mg, 81%, m.p. 214-216 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.66 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 7.0 Hz, 1H), 7.58 (d, J = 10.8 Hz, 2H), 7.54 (s, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.5 Hz, 2H), 5.28 (d, J = 7.7 Hz, 2H), 2.42 (s, 3H), 2.28 (s, 3H), 1.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 154.9, 154.6, 150.9, 144.9, 138.1, 136.9, 135.8, 134.5, 134.3, 130.2, 129.7, 129.1, 128.0, 127.7, 127.4, 122.9, 122.6, 121.1, 119.0, 106.6, 70.2, 21.1, 20.9, 15.0. HRMS (ESI) m/z calculated for $[C_{32}H_{25}N_5O_2+H]^+$: 512.2081 found: 512.2072.

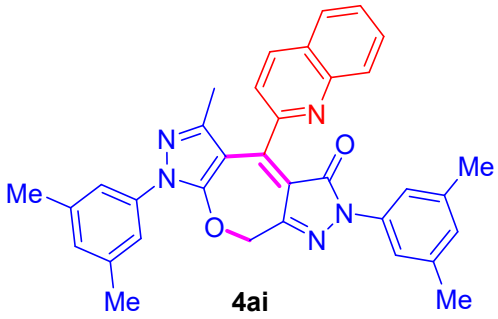
2,7-Bis(3,4-dimethylphenyl)-5-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4ah)



4ah

Orange solid, 118 mg, 73%, m.p. 246-248 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 9.5 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.77 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.60 – 7.55 (m, 2H), 7.49 (dd, J = 8.3, 2.3 Hz, 1H), 7.44 (d, J = 2.3 Hz, 1H), 7.38 (dd, J = 8.1, 2.4 Hz, 1H), 7.24 (s, 1H), 7.05 (d, J = 8.3 Hz, 1H), 5.26 (d, J = 3.5 Hz, 2H), 2.33 (d, J = 6.0 Hz, 6H), 2.20 (d, J = 3.7 Hz, 6H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 154.9, 154.8, 150.8, 148.2, 144.9, 137.8, 136.9, 136.8, 136.1, 134.4, 133.3, 130.1, 129.7, 129.6, 128.0, 127.7, 127.3, 124.1, 121.1, 120.5, 120.2, 119.0, 116.6, 106.6, 70.3, 19.9, 19.8, 19.5, 19.2, 15.0. HRMS (ESI) m/z calculated for $[C_{34}H_{29}N_5O_2+H]^+$ 540.2394, found: 540.2385.

2,7-Bis(3,5-dimethylphenyl)-5-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4ai)

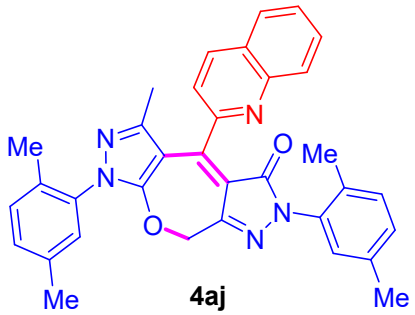


4ai

Orange solid, 110 mg, 68%, m.p. 268-270 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 9.4 Hz, 1H), 8.17 (d, J = 9.5 Hz, 1H), 7.93 (dd, J = 8.0, 1.4 Hz, 1H), 7.78 (ddd, J = 8.5, 7.0, 1.5 Hz, 1H), 7.63 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.43 (s, 2H), 7.27 (s, 2H), 7.05 (s, 1H), 6.76 (s, 1H), 5.27 (d, J = 4.6 Hz, 2H), 2.40 (d, J = 0.7 Hz, 6H), 2.26 (d, J = 0.7 Hz, 6H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 155.0, 154.7, 150.9, 148.2, 145.0, 139.1, 138.3, 138.1, 136.8, 136.5, 130.1, 129.8, 129.7, 128.0, 127.7, 127.4, 126.7, 121.1, 120.9, 119.0, 116.8, 106.7, 70.3, 21.4,

21.3, 15.0. HRMS (ESI) m/z calculated for $[C_{34}H_{29}N_5O_2+H]^+$ 540.2394, found: 540.2383.

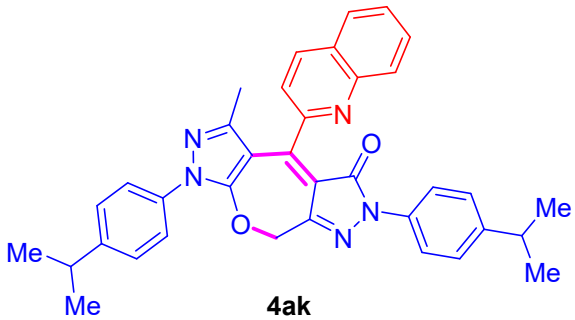
2,7-Bis(2,5-dimethylphenyl)-5-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4aj)



4aj

Orange solid, 107 mg, 66%, m.p. 219-221 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.0 Hz, 1H), 8.17 (d, J = 9.2 Hz, 1H), 7.89 (dd, J = 8.2, 1.0 Hz, 1H), 7.76 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.22 (dd, J = 8.6, 7.1 Hz, 2H), 7.13 (s, 1H), 7.06 (d, J = 7.8 Hz, 1H), 7.03 (s, 1H), 6.98 (dd, J = 7.8, 1.4 Hz, 1H), 5.20 (s, 2H), 2.38 (s, 3H), 2.23 (d, J = 5.0 Hz, 6H), 2.15 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 155.8, 154.7, 151.0, 150.9, 148.1, 144.6, 136.8, 136.7, 136.0, 135.6, 135.2, 132.1, 131.9, 130.9, 130.7, 130.0, 129.6, 129.1, 127.9, 127.7, 127.3, 127.2, 121.0, 118.1, 105.4, 70.0, 20.7, 17.9, 17.3, 15.2. HRMS (ESI) m/z calculated for $[C_{34}H_{29}N_5O_2+H]^+$ 540.2394, found: 540.2384.

2,7-Bis(4-isopropylphenyl)-5-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4ak)

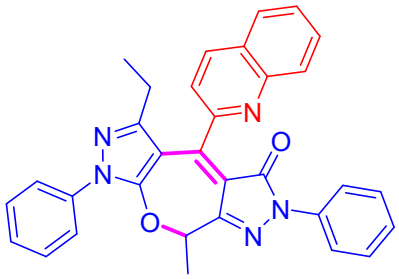


4ak

Red solid, 109mg, 64%, m.p. 273-275 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.5 Hz, 1H), 8.16 (d, J = 9.4 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.81 – 7.73 (m, 1H), 7.70 – 7.56 (m, 6H), 7.36 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.7 Hz, 2H), 5.30 – 5.25 (m,

2H), 2.99 (p, J = 6.9 Hz, 1H), 2.85 (p, J = 6.9 Hz, 1H), 1.35 (s, 3H), 1.30 (d, J = 6.9 Hz, 6H), 1.19 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 154.9, 154.7, 150.9, 149.0, 148.1, 145.7, 144.9, 136.7, 136.0, 134.5, 130.0, 129.6, 128.0, 127.7, 127.3, 127.1, 126.5, 123.0, 121.1, 119.3, 118.9, 106.6, 70.3, 33.8, 33.6, 23.9, 15.1. HRMS (ESI) m/z calculated for $[C_{36}H_{33}N_5O_2+H]^+$ 568.2707, found: 568.2697.

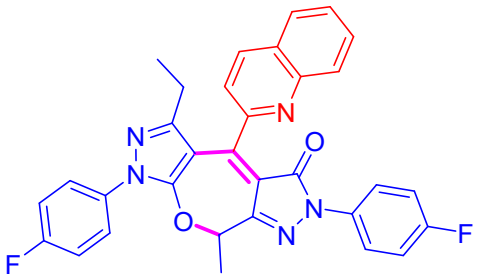
5-Ethyl-9-methyl-2,7-diphenyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*'] dipyrazol-3(7*H*)-one（4al）



4al

Yellow solid, 104 mg, 68%, m.p. 229-231 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.3 Hz, 1H), 7.93 (dd, J = 8.2, 1.1 Hz, 1H), 7.80 (d, J = 7.9 Hz, 2H), 7.76 (d, J = 8.2 Hz, 3H), 7.63 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.43 – 7.36 (m, 1H), 7.29 (t, J = 8.0 Hz, 2H), 7.10 (t, J = 7.4 Hz, 1H), 5.39 (d, J = 5.9 Hz, 1H), 1.89 (d, J = 6.6 Hz, 3H), 1.62 (dq, J = 14.9, 7.5 Hz, 2H), 0.88 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 155.6, 155.0, 148.2, 138.3, 137.1, 130.0, 129.7, 129.1, 128.6, 128.0, 127.7, 127.2, 124.8, 122.8, 119.1, 77.8, 22.0, 16.9, 12.3. HRMS (ESI) m/z calculated for $[C_{32}H_{25}N_5O_2+H]^+$ 512.2081, found: 512.2073.

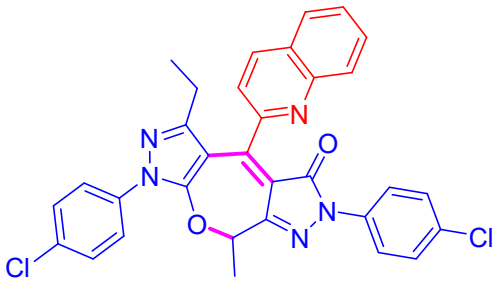
5-Ethyl-2,7-bis(4-fluorophenyl)-9-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2, 3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one（4am）



4am

Orange solid, 89 mg, 54%, m.p. 189-191 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.82 – 7.68 (m, 5H), 7.63 (ddd, J = 8.1, 6.8, 1.2 Hz, 2H), 7.23 – 7.15 (m, 2H), 6.98 (t, J = 8.7 Hz, 2H), 5.38 (s, 1H), 1.87 (d, J = 6.6 Hz, 3H), 1.66 – 1.43 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 62.9, 162.7, 161.0, 160.5, 158.6, 155.7, 154.7, 148.1, 136.8, 136.4, 134.4, 133.2, 133.1, 130.1, 129.6, 128.1, 127.7, 127.3, 124.6, 124.5, 120.8, 120.7, 116.2, 115.9, 115.3, 115.1, 77.8, 21.9, 16.8, 12.2.HRMS (ESI) m/z calculated for $[C_{32}H_{23}F_2N_5O_2+H]^+$ 548.1893, found: 548.1882.

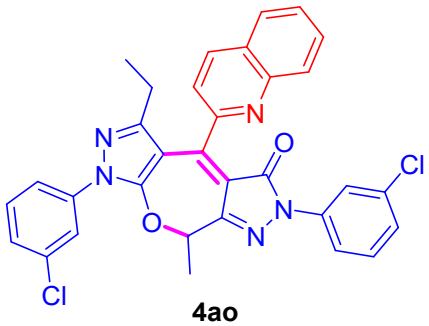
2,7-Bis(4-chlorophenyl)-5-ethyl-9-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one（4an）



4an

Orange solid, 89 mg, 51%, m.p. 238-240 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 8.3 Hz, 1H), 8.16 (d, J = 8.3 Hz, 1H), 7.97 – 7.91 (m, 1H), 7.78 (t, J = 7.6 Hz, 3H), 7.72 (d, J = 8.7 Hz, 2H), 7.64 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 7.48 (d, J = 8.9 Hz, 3H), 7.24 (d, J = 8.9 Hz, 2H), 5.38 (s, 1H), 1.89 (d, J = 6.5 Hz, 3H), 1.60 (dq, J = 14.9, 7.5 Hz, 2H), 0.87 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 159.6, 155.8, 154.6, 153.8, 149.4, 148.3, 136.8, 136.4, 135.5, 133.4, 130.2, 129.8, 129.6, 129.3, 128.6, 128.1, 127.6, 127.4, 123.7, 121.4, 120.5, 119.9, 77.9,, 22.0, 16.8, 12.1. HRMS (ESI) m/z calculated for $[C_{32}H_{23}Cl_2N_5O_2+H]^+$ 580.1302, found: 580.1290.

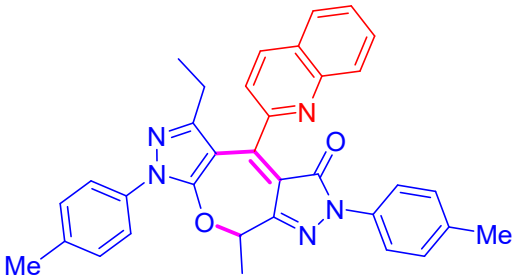
2,7-Bis(3-chlorophenyl)-5-ethyl-9-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one（4ao）



4ao

Orange solid, 104 mg, 60%, m.p. 211-213 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.97 – 7.92 (m, 1H), 7.89 (s, 1H), 7.79 (dd, J = 17.2, 9.7 Hz, 3H), 7.70 (d, J = 8.1 Hz, 1H), 7.64 (ddd, J = 8.1, 7.0, 1.1 Hz, 2H), 7.44 (t, J = 8.1 Hz, 1H), 7.36 (ddd, J = 8.1, 1.9, 1.1 Hz, 1H), 7.20 (t, J = 8.2 Hz, 1H), 7.11 – 7.04 (m, 1H), 5.40 (s, 1H), 1.92 (d, J = 6.5 Hz, 3H), 1.65 – 1.44 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 155.9, 154.6, 148.4, 139.3, 138.0, 134.9, 134.4, 130.1, 129.7, 129.6, 128.1, 127.7, 127.4, 124.7, 122.7, 120.4, 118.6, 116.6, 78.1, 22.0, 16.8, 12.1. HRMS (ESI) m/z calculated for $[C_{32}H_{23}Cl_2N_5O_2+H]^+$ 580.1302, found: 580.1290.

5-Ethyl-9-methyl-4-(quinolin-2-yl)-2,7-di-*p*-tolyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*'] dipyrazol-3(7*H*)-one (4ap)

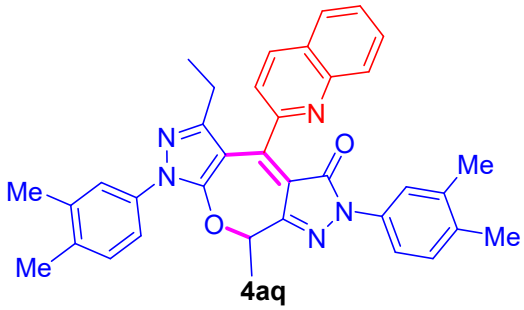


4ap

Orange solid, 104 mg, 64%, m.p. 259-261 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 1H), 8.17 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 6.8 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.70 – 7.49 (m, 6H), 7.30 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.3 Hz, 2H), 5.33 (d, J = 32.2 Hz, 1H), 2.42 (s, 3H), 2.28 (s, 3H), 1.87 (d, J = 6.6 Hz, 3H), 1.67 – 1.43 (m, 2H), 0.87 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 155.4, 155.1, 148.0, 137.8, 135.9, 134.6, 134.3, 129.9, 129.7, 129.1, 128.0, 127.7, 127.2, 122.7, 119.1, 76.7, 21.9,

21.1, 20.9, 16.9, 12.4. HRMS (ESI) m/z calculated for $[C_{34}H_{29}N_5O_2+H]^+$ 540.2394, found: 540.2383.

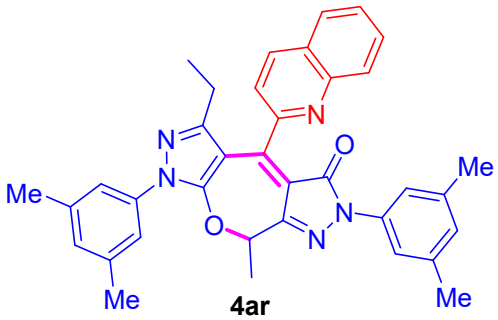
2,7-Bis(3,4-dimethylphenyl)-5-ethyl-9-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4aq)



4aq

Orange solid, 111 mg, 65% m.p. 220-222 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 8.4 Hz, 1H), 8.18 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 8.2, 1.1 Hz, 1H), 7.81 – 7.72 (m, 1H), 7.65 – 7.53 (m, 3H), 7.50 (s, 2H), 7.44 (d, J = 8.1 Hz, 1H), 7.24 (s, 1H), 7.05 (d, J = 8.3 Hz, 1H), 5.37 (s, 1H), 2.34 (d, J = 9.7 Hz, 6H), 2.20 (d, J = 6.3 Hz, 6H), 1.88 (d, J = 6.6 Hz, 3H), 1.55 (ddt, J = 48.1, 15.6, 7.7 Hz, 2H), 0.87 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 155.3, 155.1, 148.0, 137.6, 136.7, 136.5, 136.2, 134.8, 133.1, 130.0, 129.9, 129.7, 129.5, 128.0, 127.6, 127.1, 123.9, 120.2, 116.7, 77.6, 21.9, 19.9, 19.8, 19.4, 19.1, 16.9, 12.5. HRMS (ESI) m/z calculated for $[C_{36}H_{33}N_5O_2+H]^+$ 568.2707, found: 568.2697.

2,7-Bis(3,5-dimethylphenyl)-5-ethyl-9-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4ar)

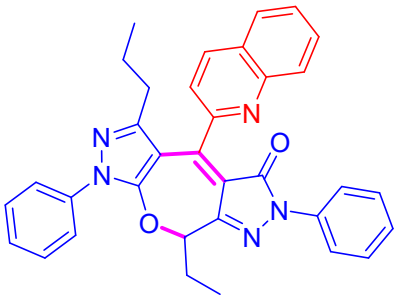


4ar

Orange solid, 102 mg, 60%, m.p. 239-241 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.2 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.93 (dd, J = 8.2, 1.1 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.62 (ddd, J = 8.1, 6.9, 1.2 Hz, 2H), 7.42 (s, 2H), 7.33 (s, 2H), 7.03 (s, 1H), 6.75

(s, 1H), 5.44 – 5.30 (m, 1H), 2.41 (s, 6H), 2.26 (s, 6H), 1.88 (d, J = 6.5 Hz, 3H), 1.62 – 1.54 (m, 1H), 1.46 (dt, J = 15.4, 7.3 Hz, 1H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9, 155.4, 155.1, 148.1, 138.9, 138.2, 138.2, 136.8, 130.0, 129.7, 129.5, 128.0, 127.7, 127.2, 126.6, 120.7, 116.9, 77.7, 21.9, 21.4, 16.9, 12.5. HRMS (ESI) m/z calculated for $[C_{36}H_{33}N_5O_2+H]^+$ 568.2707, found: 568.2694.

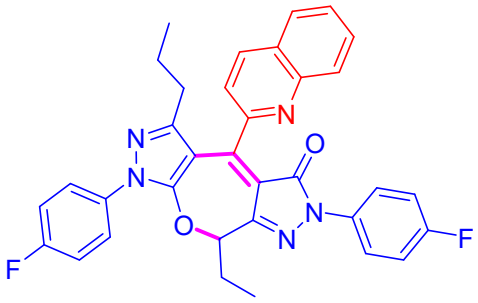
9-Ethyl-2,7-diphenyl-5-propyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*'] dipyrazol-3(7*H*)-one（4as）



4as

Yellow solid, 104 mg, 64%, m.p. 186-188 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 1H), 8.20 – 8.14 (m, 1H), 7.93 (dd, J = 8.2, 1.1 Hz, 1H), 7.82 – 7.78 (m, 2H), 7.78 – 7.72 (m, 3H), 7.62 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H), 7.57 (s, 1H), 7.53 – 7.48 (m, 2H), 7.42 – 7.37 (m, 1H), 7.32 – 7.27 (m, 2H), 7.13 – 7.07 (m, 1H), 5.14 (s, 1H), 2.24 (dd, J = 63.3, 7.1 Hz, 2H), 1.64 (d, J = 28.1 Hz, 1H), 1.46 (s, 1H), 1.36 (d, J = 18.7 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H), 0.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.8, 154.8, 154.6, 147.4, 138.3, 136.9, 130.0, 129.6, 129.0, 128.5, 127.9, 127.6, 127.2, 124.7, 123.1, 119.0, 83.0, 30.6, 24.1, 22.3, 13.5, 9.9. HRMS (ESI) m/z calculated for $[C_{34}H_{29}N_5O_2+H]^+$ 540.2394, found: 540.2383.

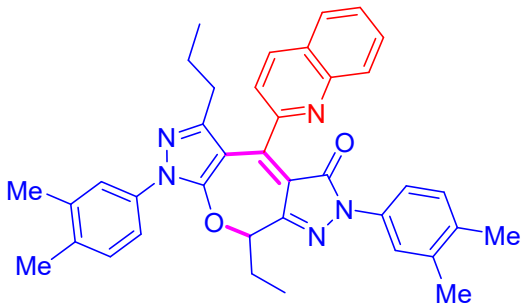
9-Ethyl-2,7-bis(4-fluorophenyl)-5-propyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2, 3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one（4at）



4at

Orange solid, 109 mg, 63%, m.p. 174-176 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.4 Hz, 1H), 8.16 (d, J = 8.5 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.79 – 7.68 (m, 5H), 7.66 – 7.60 (m, 1H), 7.55 (s, 1H), 7.23 – 7.16 (m, 2H), 7.01 – 6.94 (m, 2H), 5.17 – 5.07 (m, 1H), 2.22 (d, J = 61.7 Hz, 2H), 1.59 (s, 1H), 1.43 (s, 1H), 1.29 (d, J = 21.5 Hz, 2H), 1.02 (t, J = 7.4 Hz, 3H), 0.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 162.7, 161.0, 160.6, 158.6, 154.8, 154.6, 147.4, 134.5, 134.4, 133.0, 130.1, 129.6, 128.0, 127.6, 127.3, 125.0, 124.9, 120.8, 120.7, 116.1, 115.9, 115.4, 115.1, 83.1, 30.6, 24.1, 22.2, 13.5, 9.9. HRMS (ESI) m/z calculated for $[C_{34}H_{27}F_2N_5O_2+H]^+$ 576.2206, found: 576.2192.

2,7-Bis(3,4-dimethylphenyl)-9-ethyl-5-propyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4au)

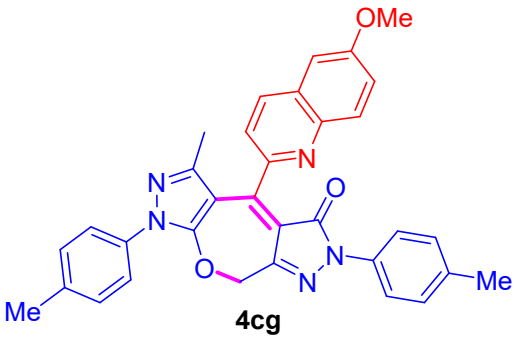


4au

Orange solid, 100 mg, 56%, m.p. 174-176 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.27 (m, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.95 – 7.89 (m, 1H), 7.76 (ddd, J = 8.4, 6.9, 1.4 Hz, 1H), 7.64 – 7.54 (m, 3H), 7.49 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.2 Hz, 1H), 7.04 (d, J = 8.3 Hz, 1H), 5.28 (s, 3H), 5.13 (d, J = 7.7 Hz, 1H), 2.33 (d, J = 7.2 Hz, 6H), 2.19 (d, J = 5.5 Hz, 6H), 1.47 – 1.23 (m, 4H), 1.09 – 0.96 (m, 3H), 0.33 (q, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7, 155.0, 154.3, 147.2,

137.5, 136.7, 136.5, 136.2, 134.6, 133.0, 129.9, 129.6, 129.5, 127.9, 127.6, 127.1, 124.1, 120.5, 120.2, 116.7, 82.8, 53.4, 24.1, 22.4, 19.8, 19.4, 19.1, 13.5, 9.9. HRMS (ESI) m/z calculated for $[C_{38}H_{37}N_5O_2+H]^+$ 596.3020, found: 596.3009.

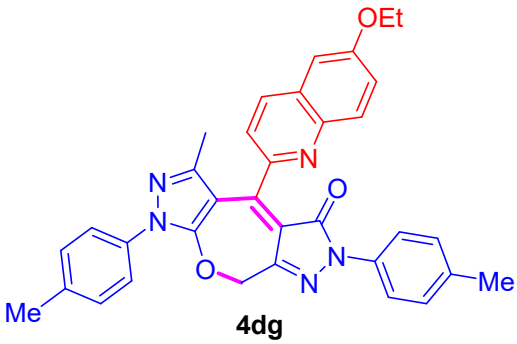
4-(6-Methoxyquinolin-2-yl)-5-methyl-2,7-di-*p*-tolyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4cg)



4cg

Brown solid, 91 mg, 56%, m.p. 220-222 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 7.7 Hz, 1H), 8.05 (d, J = 9.2 Hz, 1H), 7.69 – 7.65 (m, 2H), 7.54 (t, J = 8.7 Hz, 3H), 7.41 (dd, J = 9.2, 2.8 Hz, 1H), 7.30 (d, J = 7.9 Hz, 2H), 7.17 (d, J = 2.7 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 5.27 (d, J = 13.0 Hz, 2H), 3.96 (s, 3H), 2.42 (s, 3H), 2.29 (s, 3H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5, 158.5, 154.8, 152.0, 151.2, 151.0, 144.9, 144.3, 138.1, 135.9, 135.4, 134.4, 134.3, 131.1, 129.7, 129.1, 128.9, 122.9, 122.8, 121.5, 119.0, 118.9, 106.8, 105.4, 70.3, 55.6, 21.1, 20.9, 15.0. HRMS (ESI) m/z calculated for $[C_{33}H_{27}N_5O_3+H]^+$ 542.2187, found: 542.2181.

4-(6-Ethoxyquinolin-2-yl)-5-methyl-2,7-di-*p*-tolyl-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4dg)

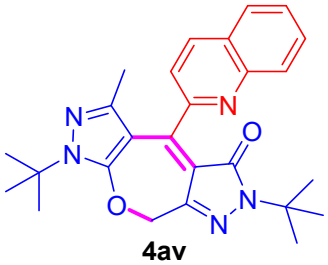


4dg

Brown solid, 97 mg, 58%, m.p. 214-216 ℃, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.3 Hz, 1H), 8.09 (s, 1H), 7.66 (d, J = 8.5 Hz, 2H), 7.54 (dd, J = 8.3, 6.3 Hz, 3H),

7.43 (dd, J = 9.3, 2.3 Hz, 1H), 7.30 (d, J = 8.2 Hz, 2H), 7.17 (d, J = 2.6 Hz, 1H), 7.10 (d, J = 8.3 Hz, 2H), 5.26 (s, 2H), 4.20 (q, J = 7.0 Hz, 2H), 2.42 (s, 3H), 2.29 (s, 3H), 1.52 (t, J = 7.0 Hz, 3H), 1.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 154.8, 144.9, 138.1, 135.8, 134.5, 134.3, 129.7, 129.1, 122.9, 121.5, 119.1, 106.1, 70.3, 64.0, 27.7, 27.7, 21.1, 20.9, 15.1, 14.7. HRMS (ESI) m/z calculated for $[C_{34}H_{29}N_5O_3+H]^+$ 556.2343, found: 556.2336.

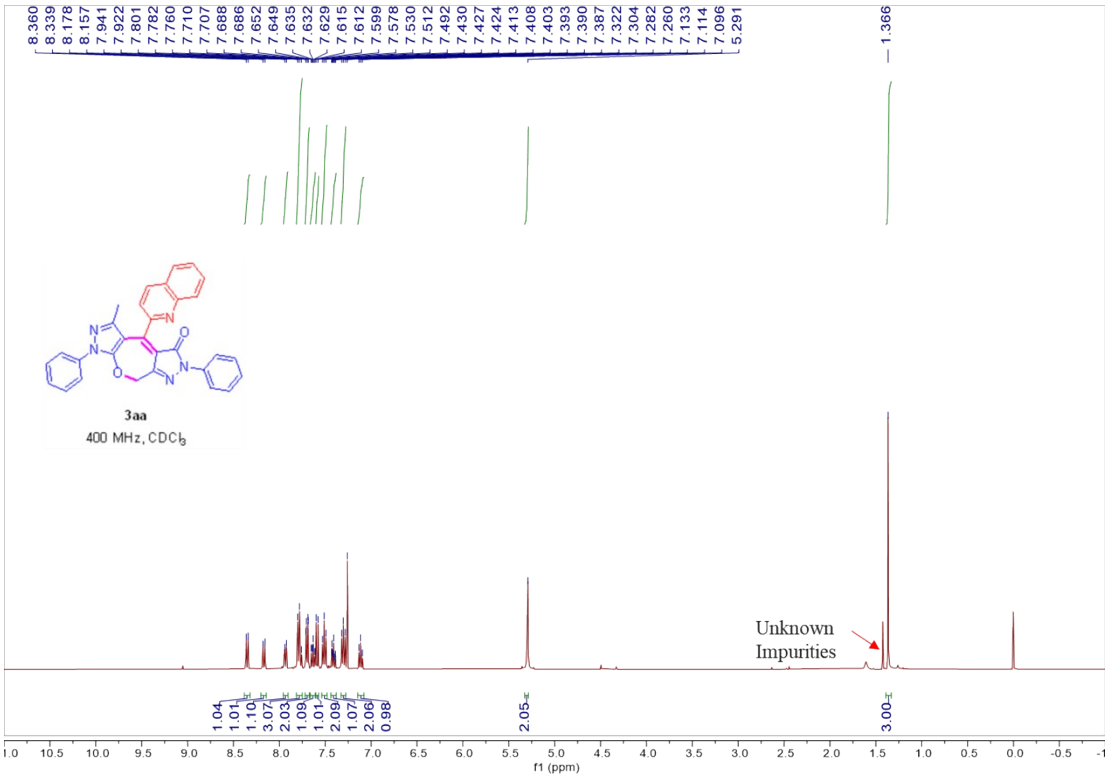
2,7-Di-*tert*-butyl-5-methyl-4-(quinolin-2-yl)-2,9-dihydrooxepino[2,3-*c*:6,5-*c*']dipyrazol-3(7*H*)-one (4av)

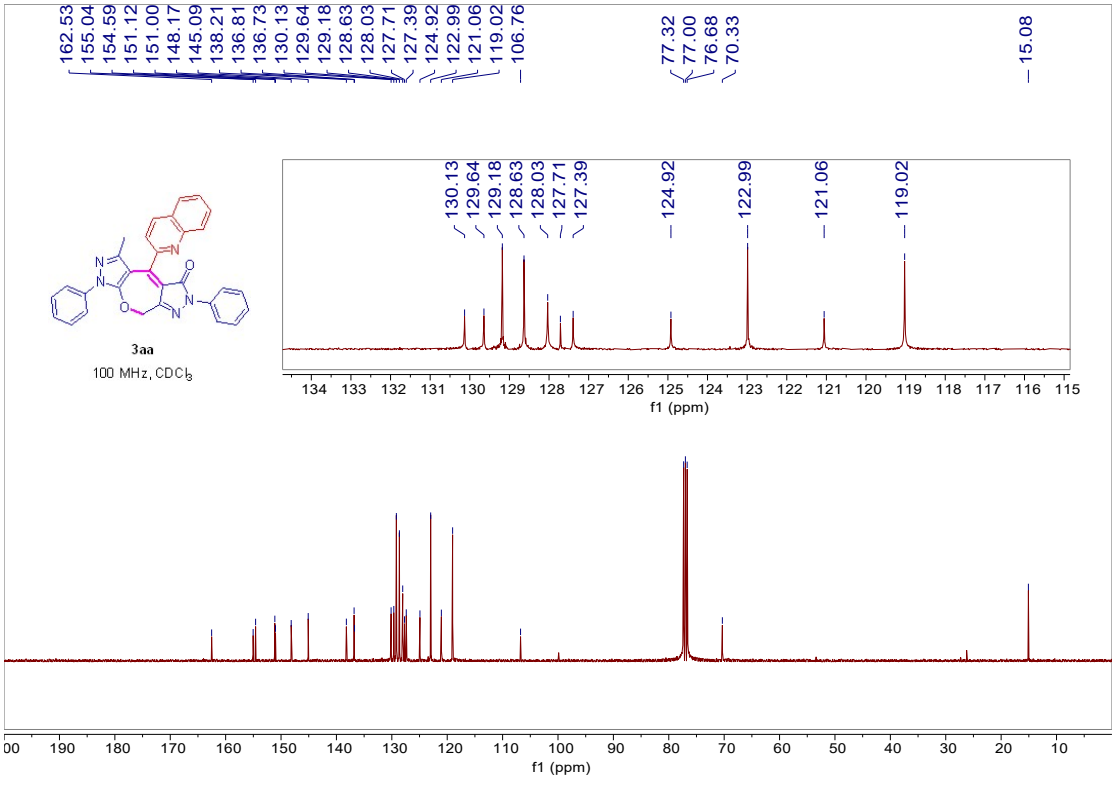


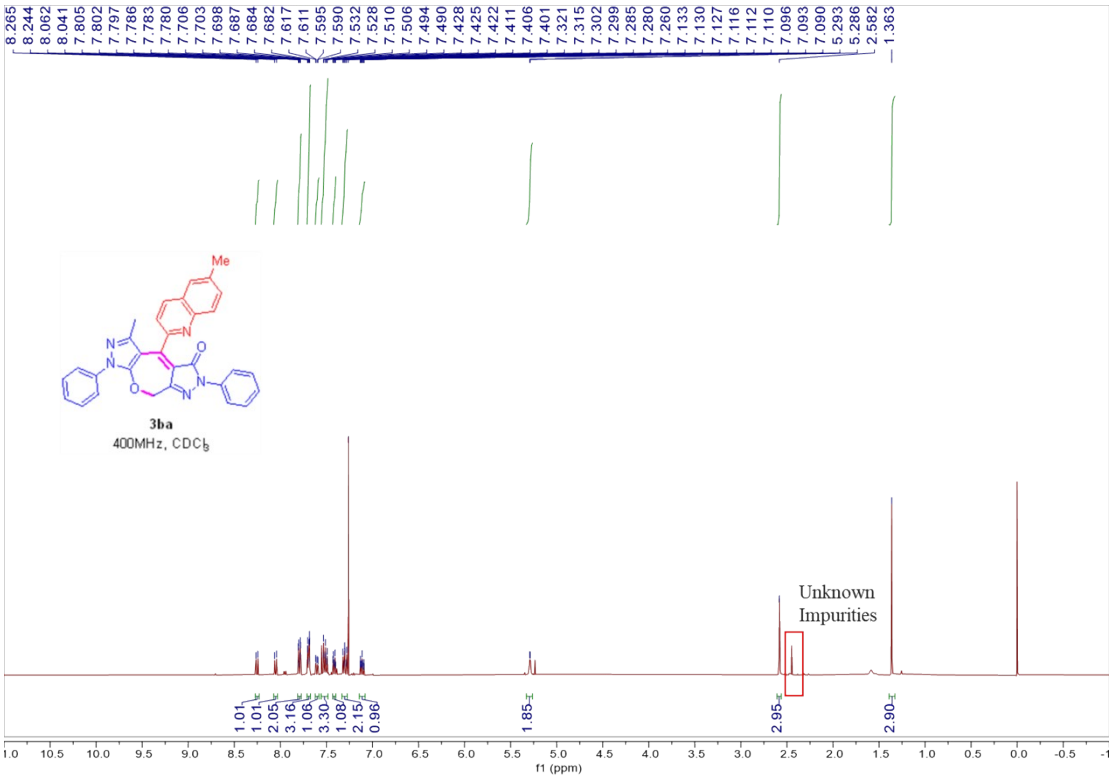
4av

Orange solid, 63 mg, 47%, m.p. 178-180 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 8.5 Hz, 1H), 8.12 (d, J = 8.5 Hz, 1H), 7.87 (d, J = 6.7 Hz, 1H), 7.72 (ddd, J = 8.5, 6.9, 1.5 Hz, 1H), 7.57 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 7.48 (d, J = 8.4 Hz, 1H), 5.07 (d, J = 3.1 Hz, 2H), 1.61 (s, 9H), 1.43 (s, 9H), 1.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.0, 155.6, 155.5, 147.7, 142.3, 136.5, 129.8, 129.6, 128.0, 127.6, 127.0, 121.3, 119.5, 106.6, 69.6, 60.0, 57.4, 53.4, 28.9, 28.4, 14.9. HRMS (ESI) m/z calculated for $[C_{26}H_{29}N_5O_2+H]^+$ 444.2394, found: 444.2387.

7. ^{1}H-NMR and ^{13}C-NMR Spectra of Products



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8.244
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8.041
7.805
7.802
7.797
7.786
7.783
7.780
7.706
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7.687
7.684
7.682
7.617
7.611
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7.425
7.422
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7.406
7.401
7.321
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7.299
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7.280
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7.130
7.127
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7.112
7.110
7.096
7.093
7.090
5.293
5.286
2.582
1.363
Me
3ba
400MHz, CDCl3
Unknown
Impurities
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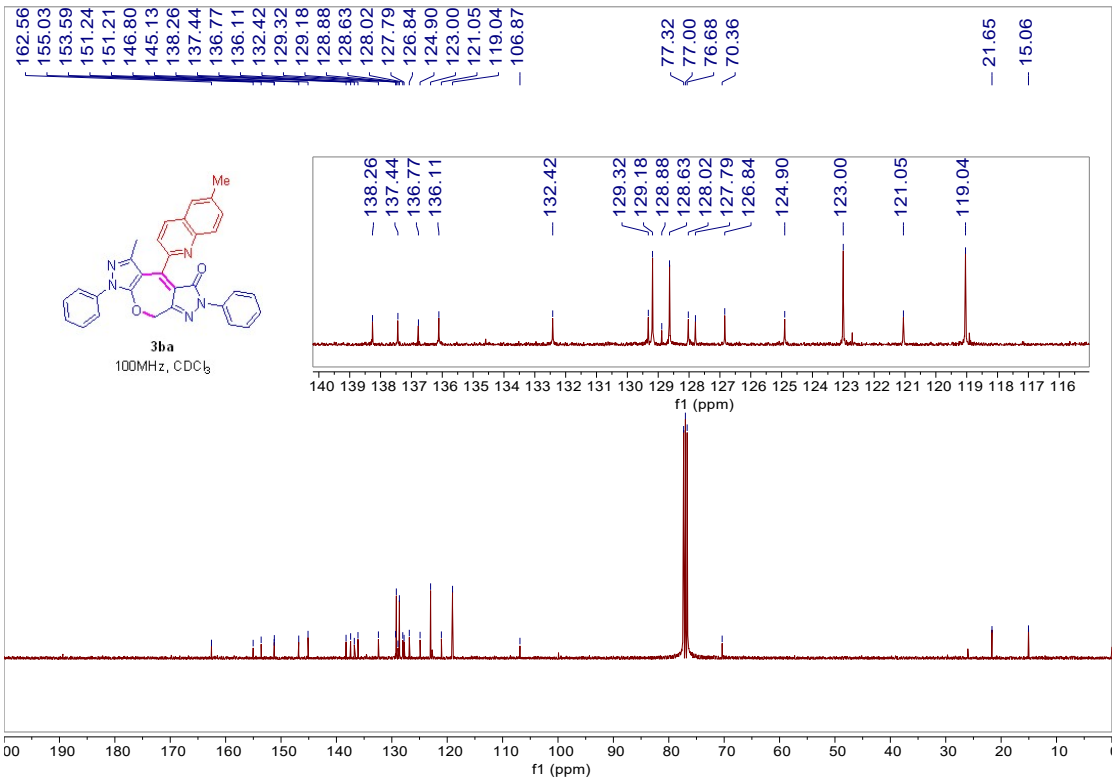
1.06
3.30
1.08
2.15
0.96
1.85
2.95
2.90
f1 (ppm)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155.03
153.59
151.24
151.21
146.80
145.13
138.26
137.44
136.77
136.11
132.42
129.32
129.18
128.88
128.63
128.02
127.79
126.84
124.90
123.00
121.05
119.04
106.87
77.32
77.00
76.68
70.36
21.65
15.06
Me
3ba
100MHz, CDCl3
138.26
137.44
136.77
136.11
132.42
129.32
129.18
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128.02
127.79
126.84
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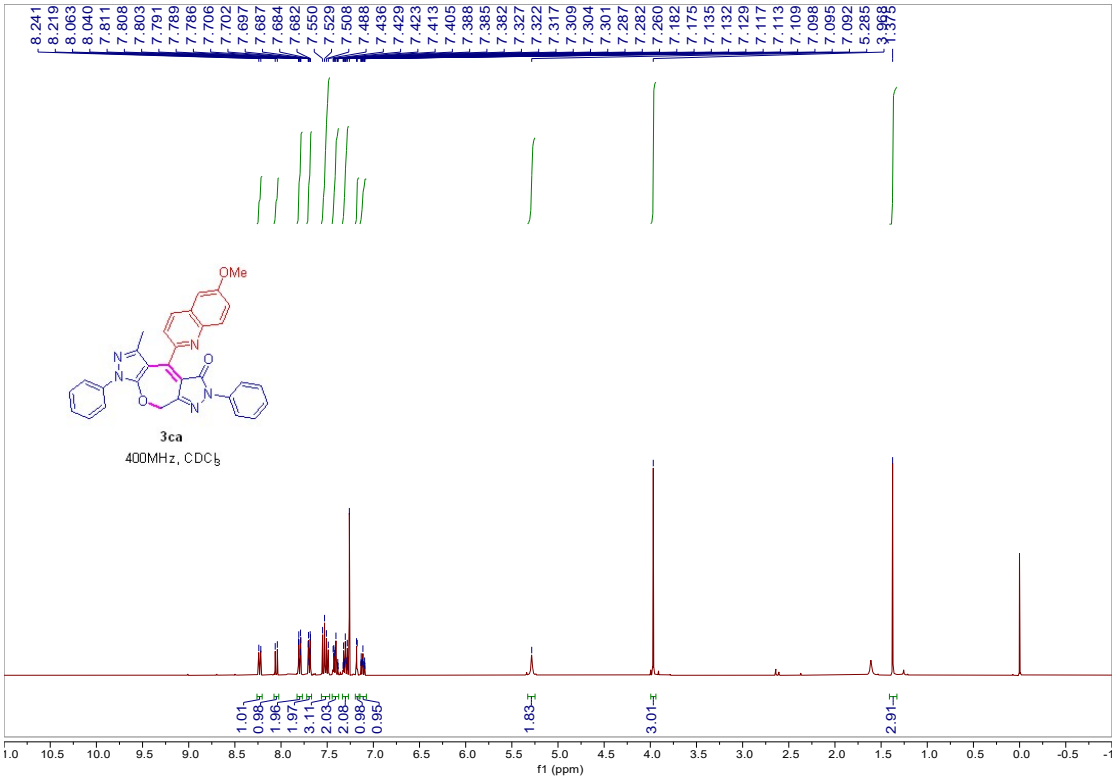
121.05
119.04
f1 (ppm)
f1 (ppm)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7.697
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7.684
7.682
7.550
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7.488
7.436
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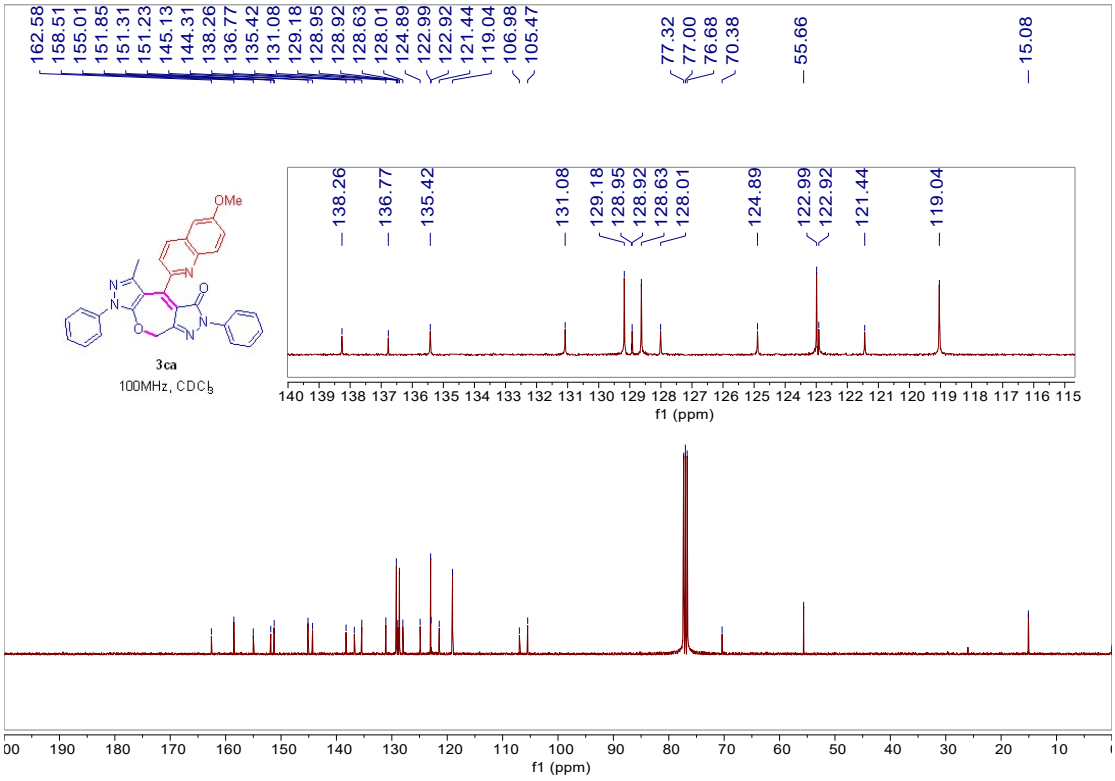
7.413
7.405
7.388
7.385
7.382
7.327
7.322
7.317
7.309
7.304
7.301
7.287
7.282
7.260
7.182
7.175
7.135
7.132
7.129
7.117
7.113
7.109
7.098
7.095
7.092
5.285
3.968
3.975
OMe
3ca
400MHz, CDCl3
1.01
0.98
1.96
1.97
3.11
2.03
2.08
0.98
0.95
1.83
3.01
2.91
f1 (ppm)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128.95
128.92
128.63
128.01
124.89
122.99
122.92
121.44
119.04
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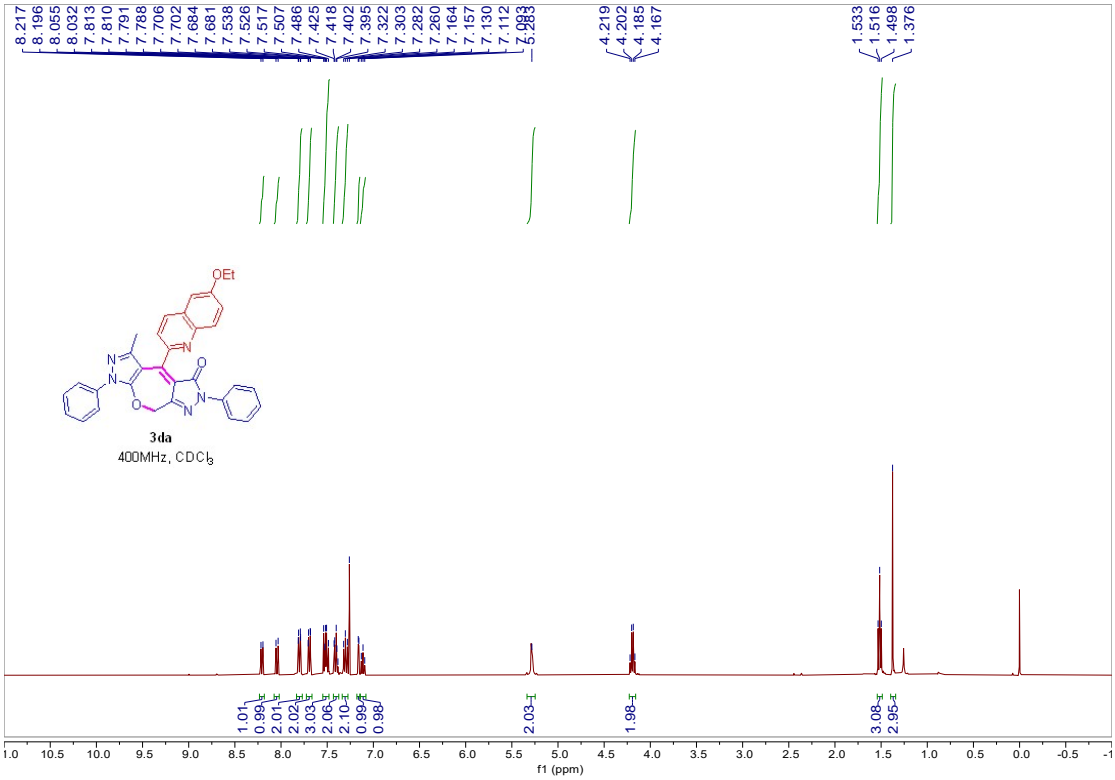
77.00
76.68
70.38
55.66
15.08
OMe
3ca
100MHz, CDCl3
f1 (ppm)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7.702
7.684
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7.517
7.507
7.486
7.425
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7.322
7.303
7.282
7.260
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7.157
7.130
7.112
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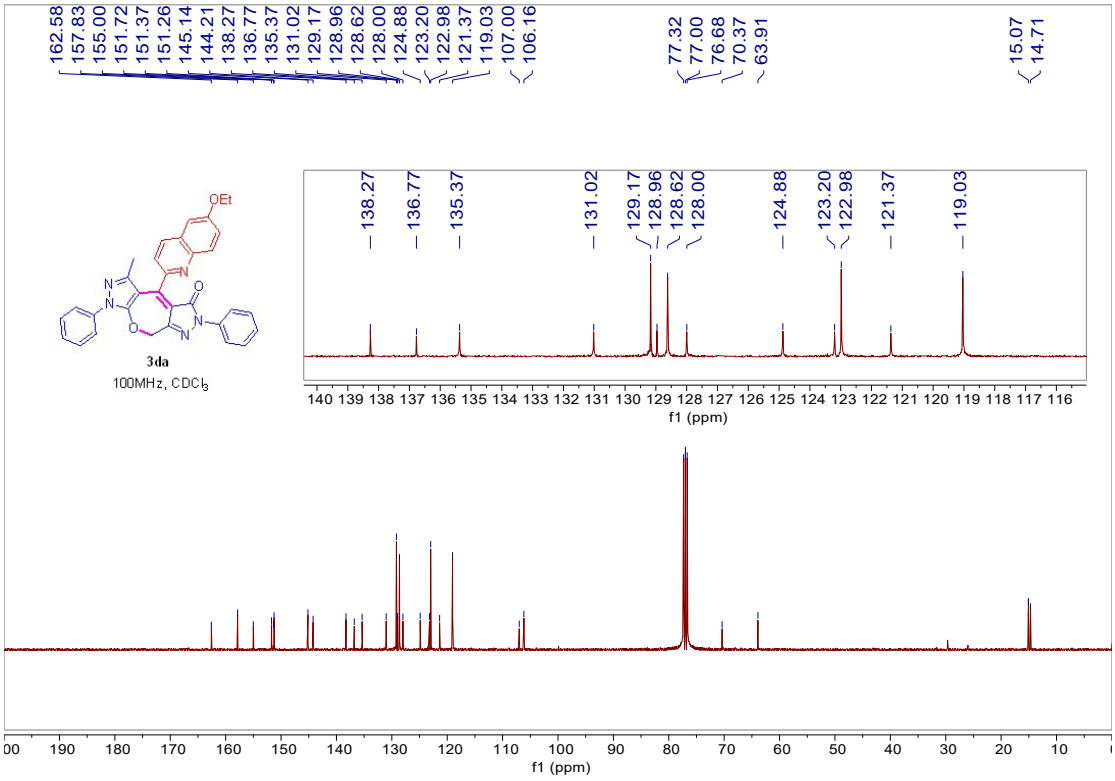
4.219
4.202
4.185
4.167
1.533
1.516
1.498
1.376
OEt
3da
400MHz, CDCl3
1.01
0.99
2.01
2.02
3.03
2.06
2.10
0.99
0.98
2.03
1.98
3.08
2.95
f1 (ppm)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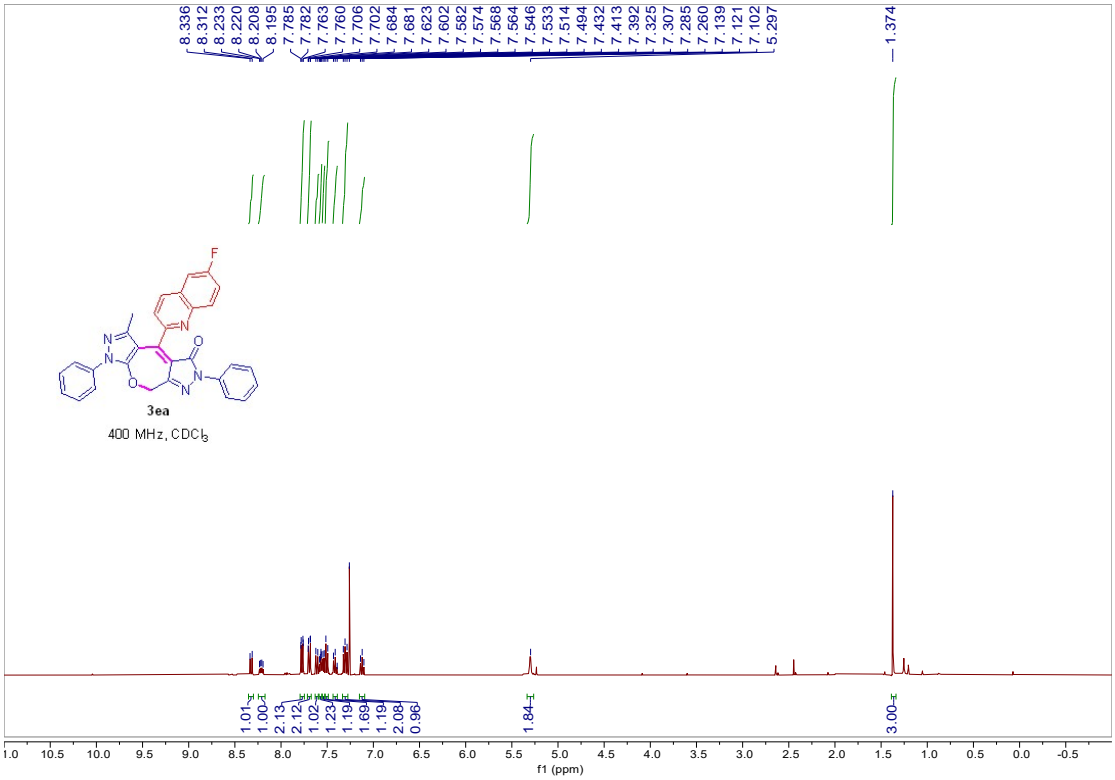
151.26
145.14
144.21
138.27
136.77
135.37
131.02
129.17
128.96
128.62
128.00
124.88
123.20
122.98
121.37
119.03
107.00
106.16
77.32
77.00
76.68
70.37
63.91
15.07
14.71
OEt
3da
100MHz, CDCl3
f1 (ppm)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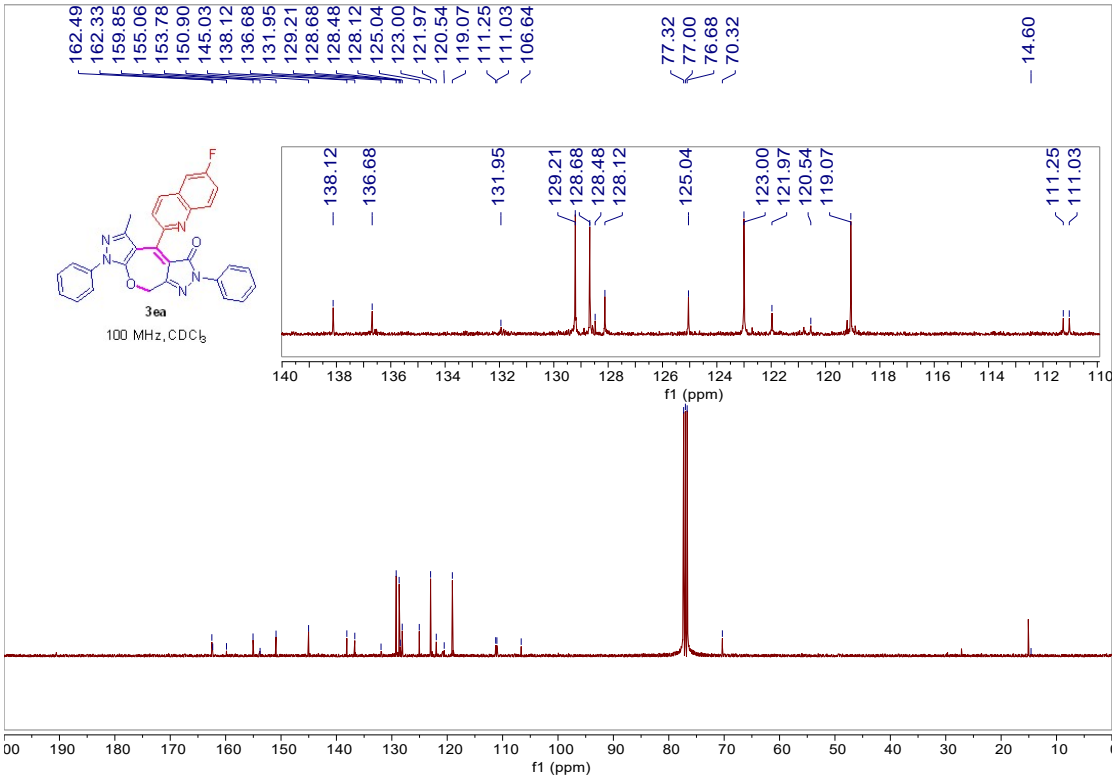
8.312
8.233
8.220
8.208
8.195
7.785
7.782
7.763
7.760
7.706
7.702
7.684
7.681
7.623
7.602
7.582
7.574
7.568
7.564
7.546
7.533
7.514
7.494
7.432
7.413
7.392
7.325
7.307
7.285
7.260
7.139
7.121
7.102
5.297
1.374
F
N
N
O
O
N
3ea
400 MHz, CDCl3
1.01
1.00
2.13
2.12
1.02
1.23
1.19
1.69
1.19
2.08
0.96
1.84
3.00
f1 (ppm)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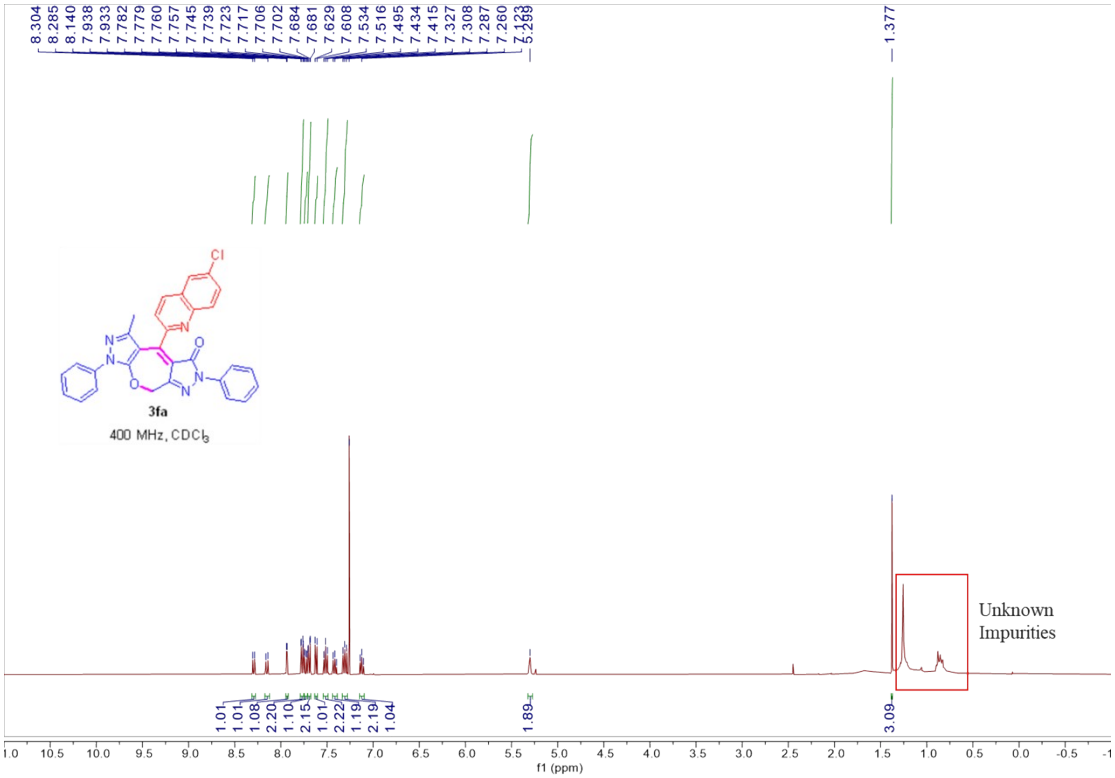
162.33
159.85
155.06
153.78
150.90
145.03
138.12
136.68
131.95
129.21
128.68
128.48
128.12
125.04
123.00
121.97
120.54
119.07
111.25
111.03
106.64
77.32
77.00
76.68
70.32
14.60
F
N
N
O
O
N
3ea
100 MHz, CDCl3
f1 (ppm)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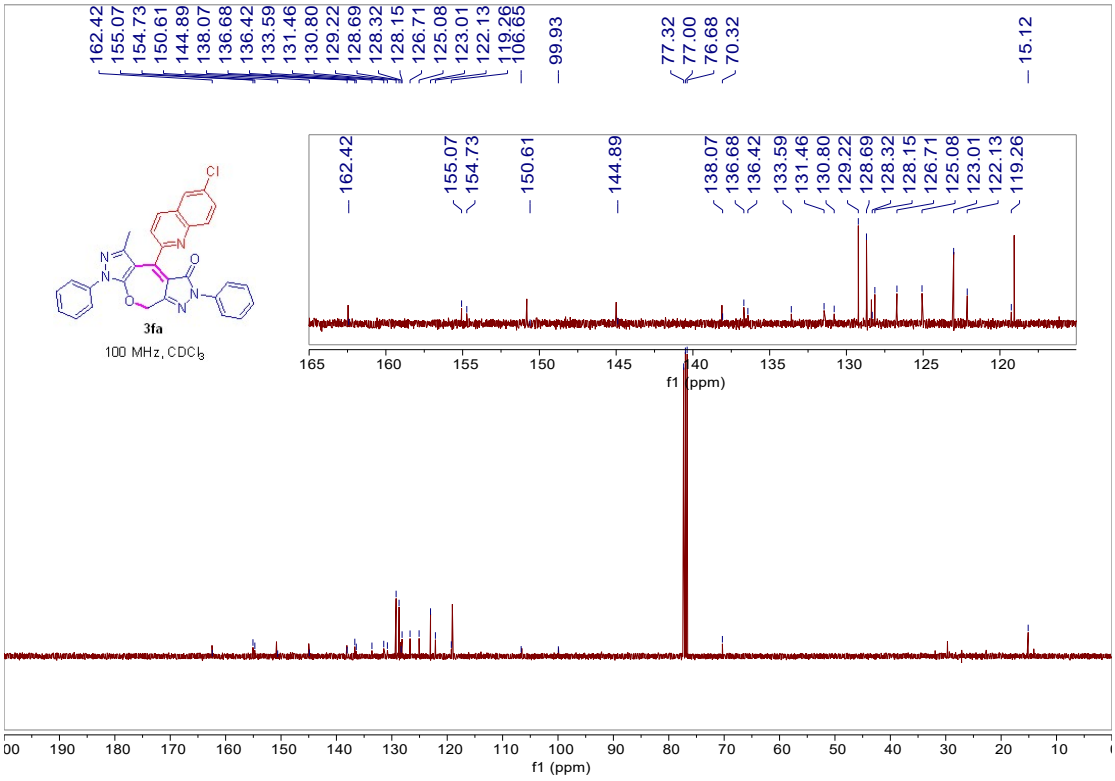
7.782
7.779
7.760
7.757
7.745
7.739
7.723
7.717
7.706
7.702
7.684
7.681
7.629
7.608
7.534
7.516
7.495
7.434
7.415
7.327
7.308
7.287
7.260
5.293
1.377
Cl
3fa
400 MHz, CDCl3
Unknown
Impurities
1.01
1.01
1.08
2.20
2.15
1.10
1.01
2.22
1.19
2.19
1.04
1.89
3.09
f1 (ppm)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155.07
154.73
150.61
144.89
138.07
136.68
136.42
133.59
131.46
130.80
129.22
128.69
128.32
128.15
126.71
125.08
123.01
122.13
119.26
106.65
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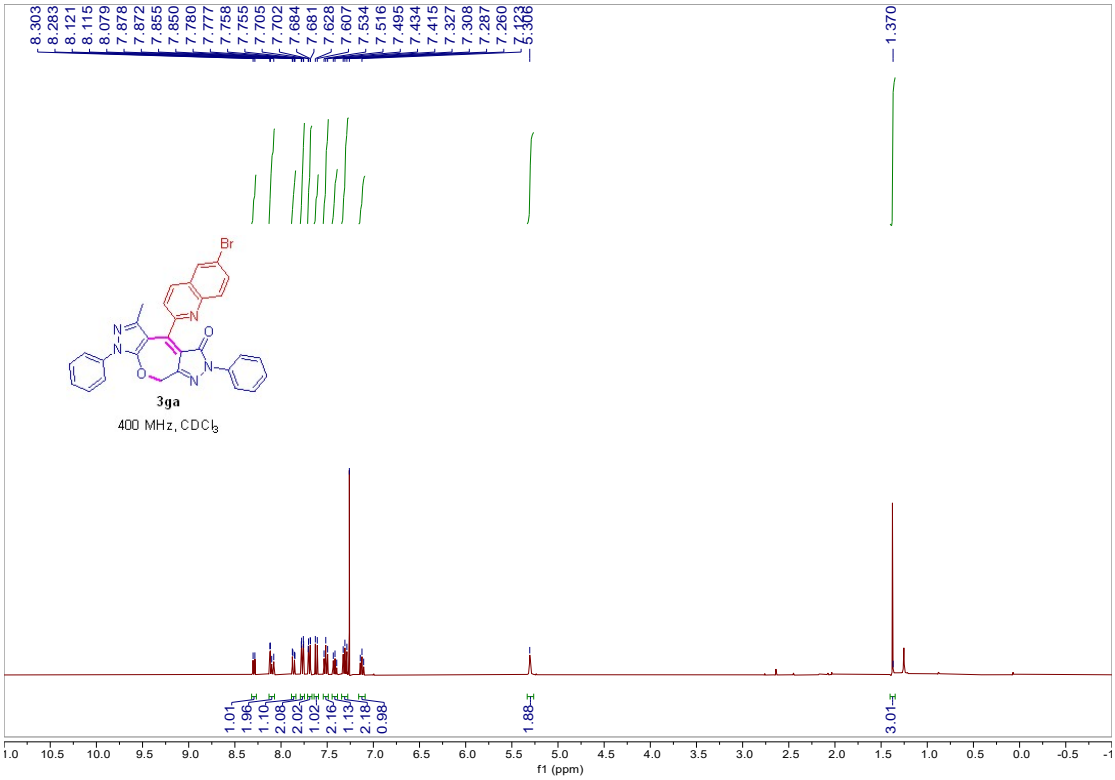
77.32
77.00
76.68
70.32
15.12
Cl
3fa
100 MHz, CDCl3
f1 (ppm)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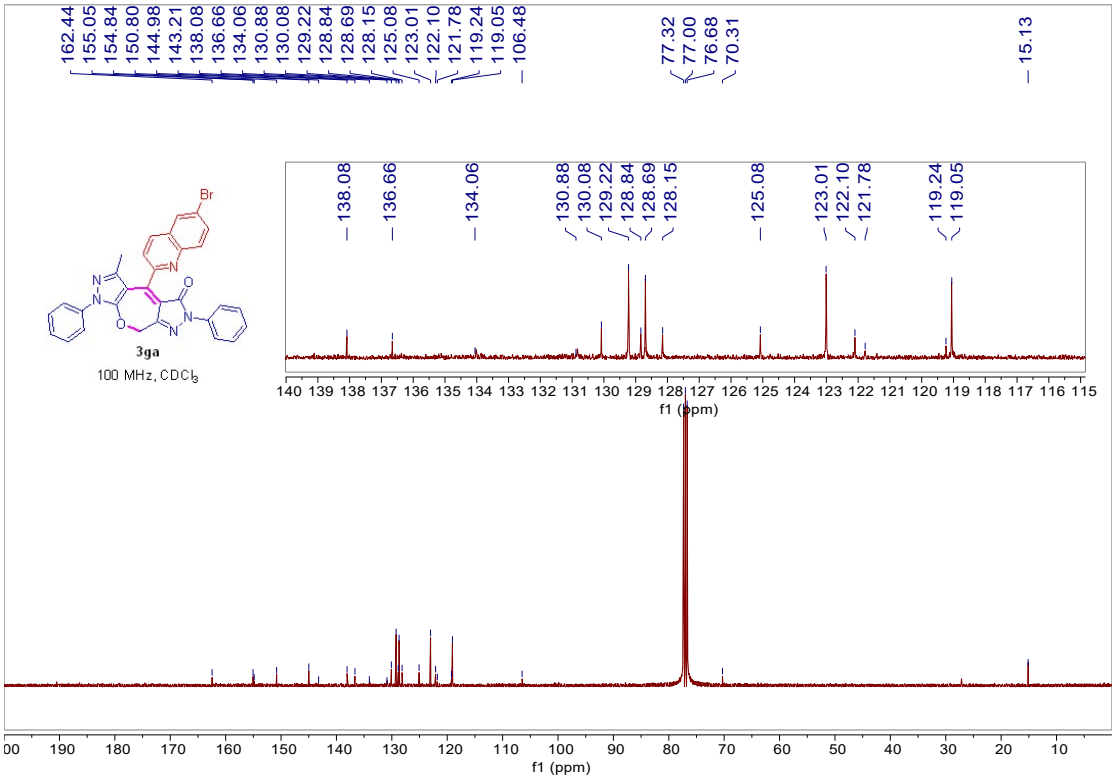
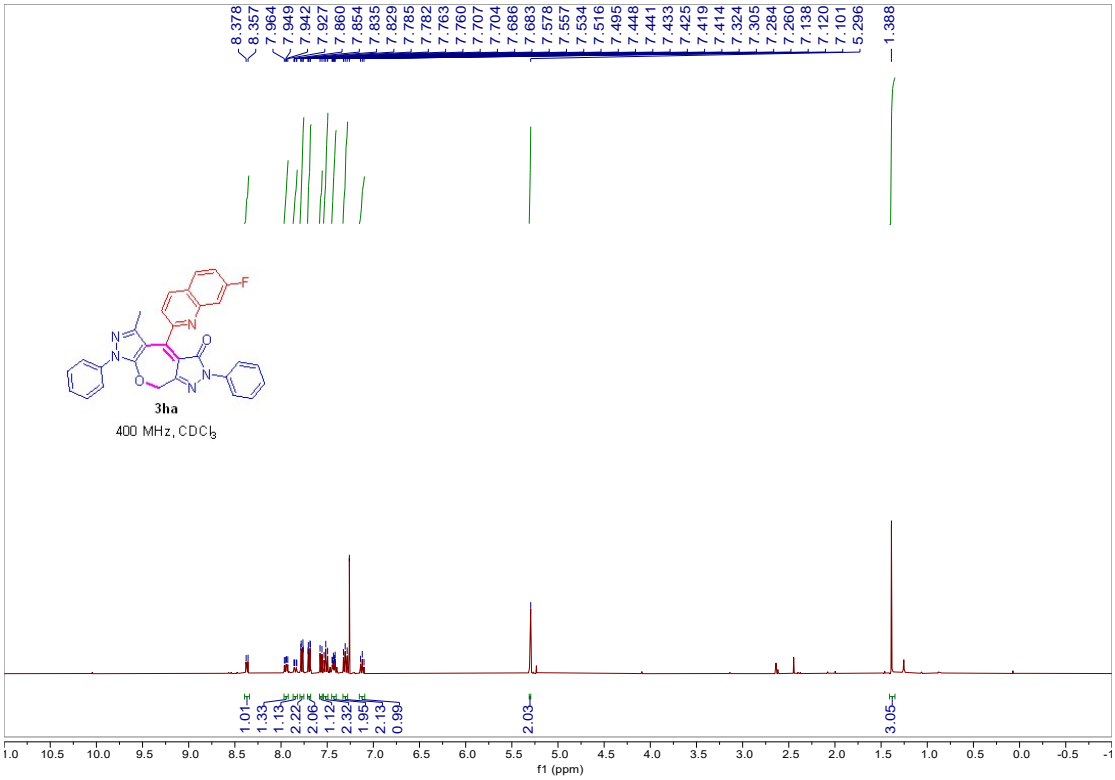
8.283
8.121
8.115
8.079
7.878
7.872
7.855
7.850
7.780
7.777
7.758
7.755
7.705
7.702
7.684
7.681
7.628
7.607
7.534
7.516
7.495
7.434
7.415
7.327
7.308
7.287
7.260
7.123
5.308
1.370
Br
N
N
O
O
N
N
3ga
400 MHz, CDCl3
1.01
1.96
1.10
2.08
2.02
1.02
2.16
1.13
2.18
0.98
1.88
3.01
f1 (ppm)


162.44
155.05
154.84
150.80
144.98
143.21
138.08
136.66
134.06
130.88
130.08
129.22
128.84
128.69
128.15
125.08
123.01
122.10
121.78
119.24
119.05
106.48
77.32
77.00
76.68
70.31
15.13
Br
N
N
O
O
N
N
3ga
100 MHz, CDCl3
f1 (ppm)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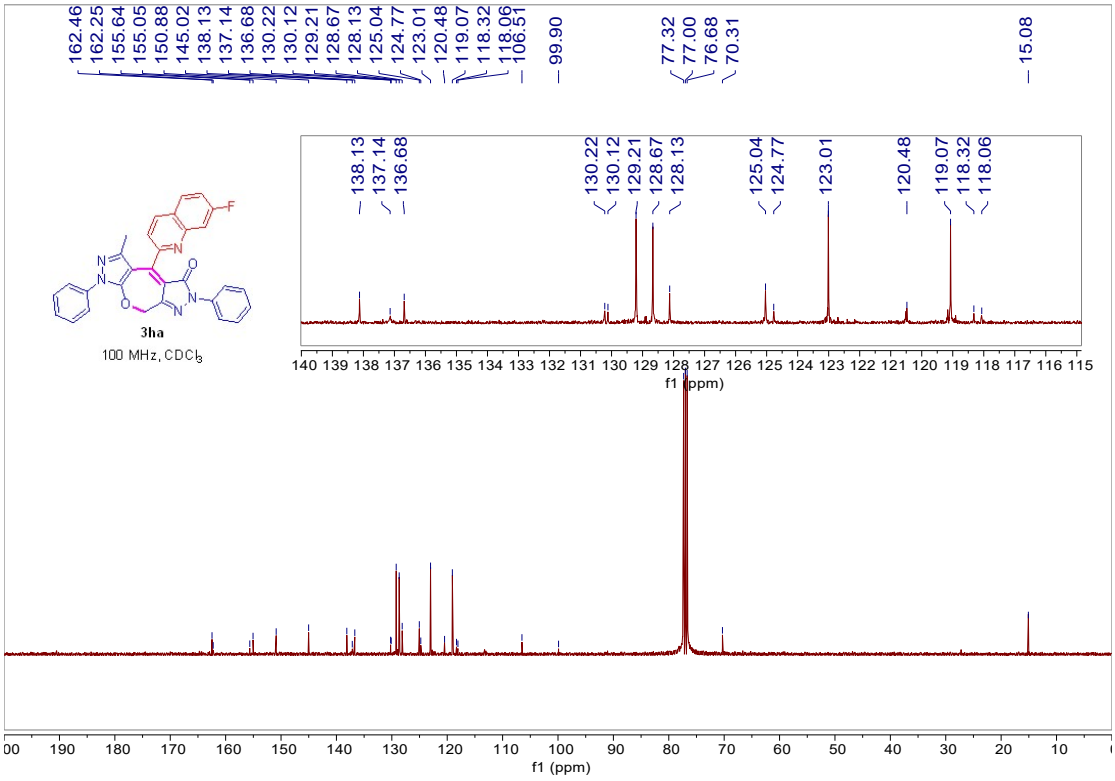
7.964
7.949
7.942
7.927
7.860
7.854
7.835
7.829
7.785
7.782
7.763
7.760
7.707
7.704
7.686
7.683
7.578
7.557
7.534
7.516
7.495
7.448
7.441
7.433
7.425
7.419
7.414
7.324
7.305
7.284
7.260
7.138
7.120
7.101
5.296
1.388
3ha
400 MHz, CDCl3
1.01
1.33
1.13
2.22
2.06
1.12
2.32
1.95
2.13
0.99
2.03
3.05
f1 (ppm)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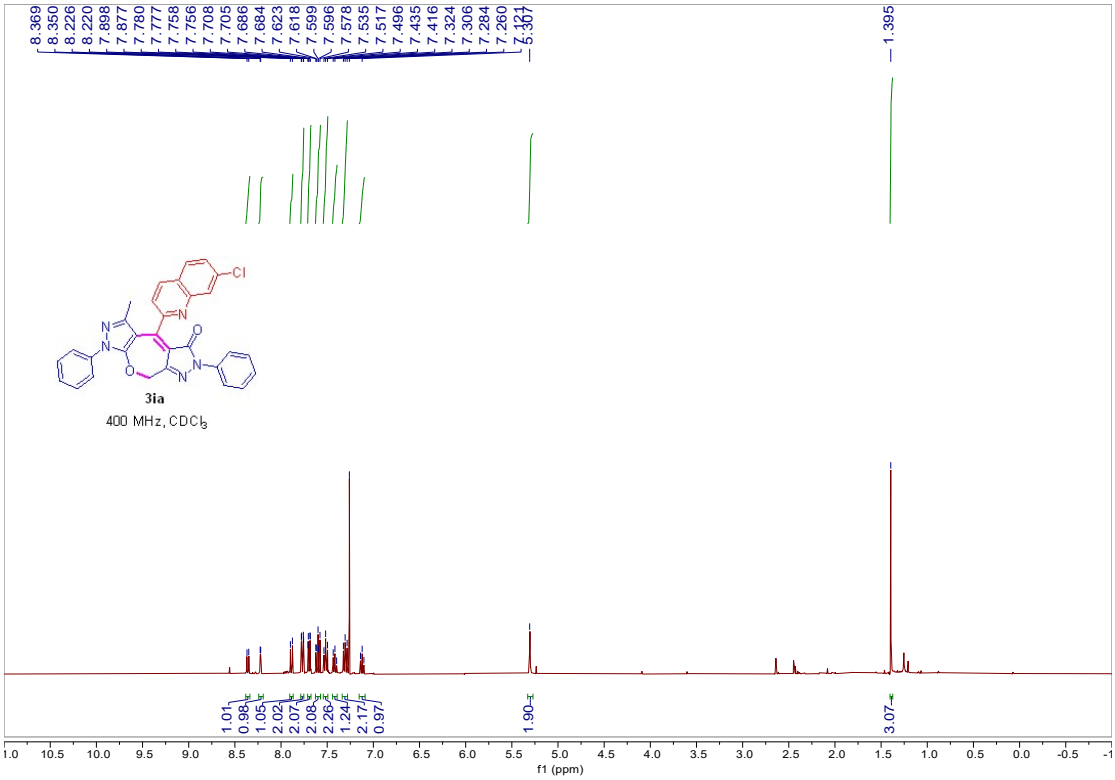
162.25
155.64
155.05
150.88
145.02
138.13
137.14
136.68
130.22
130.12
129.21
128.67
128.13
125.04
124.77
123.01
120.48
119.07
118.32
118.06
106.51
99.90
77.32
77.00
76.68
70.31
15.08
3ha
100 MHz, CDCl3
f1 (ppm)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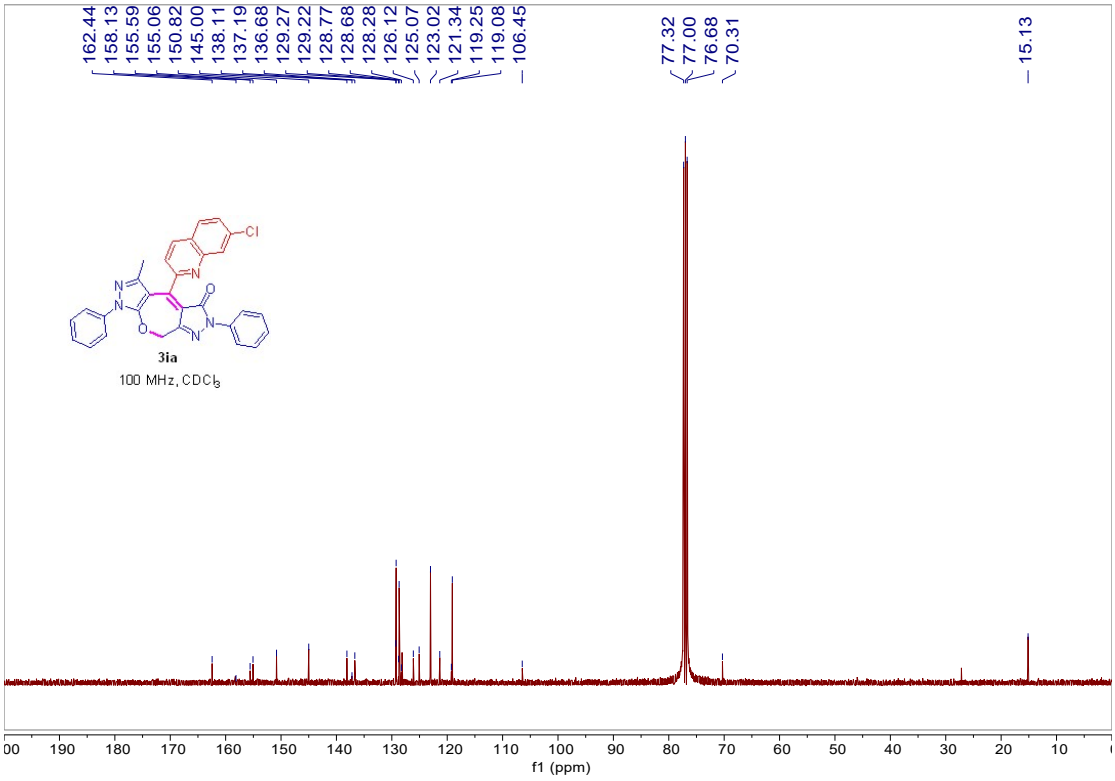
8.350
8.226
8.220
7.898
7.877
7.780
7.777
7.758
7.756
7.708
7.705
7.686
7.684
7.623
7.618
7.599
7.596
7.578
7.535
7.517
7.496
7.435
7.416
7.324
7.306
7.284
7.260
7.121
5.307
1.395
Cl
O
N
3ia
400 MHz, CDCl3
1.01
0.98
1.05
2.02
2.07
2.08
2.26
1.24
2.17
0.97
1.90
3.07
f1 (ppm)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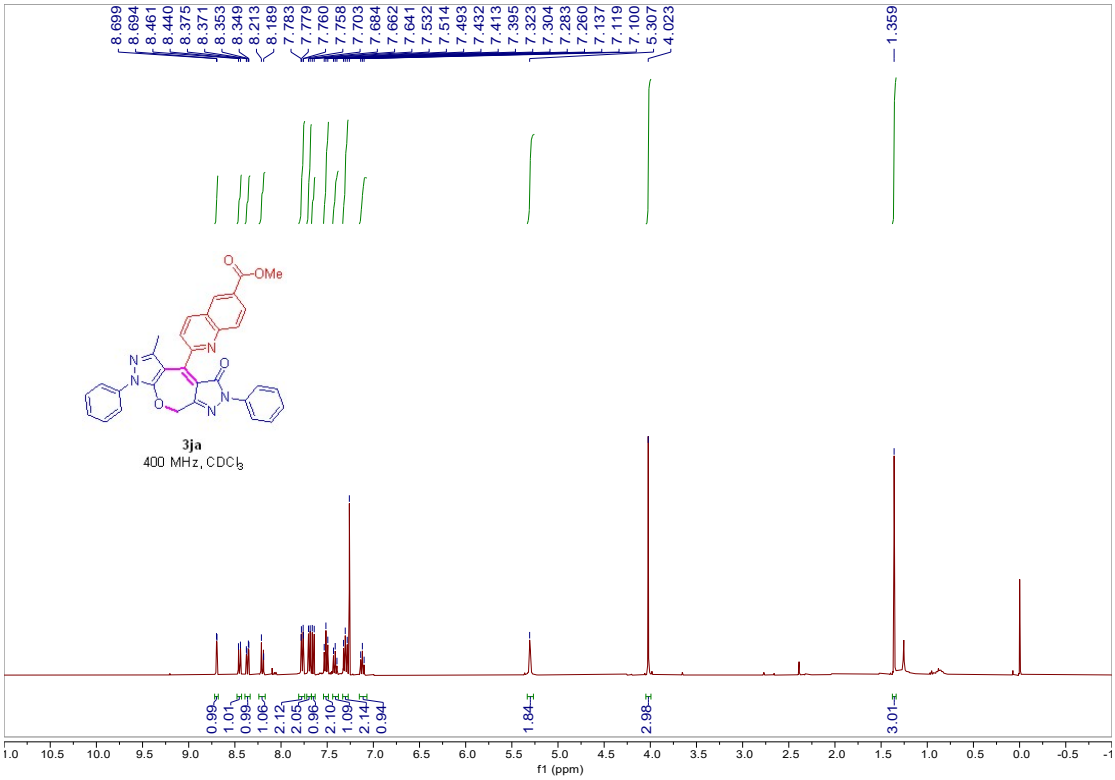
158.13
155.59
155.06
150.82
145.00
138.11
137.19
136.68
129.27
129.22
128.77
128.68
128.28
126.12
125.07
123.02
121.34
119.25
119.08
106.45
77.32
77.00
76.68
70.31
15.13
Cl
O
N
3ia
100 MHz, CDCl3
f1 (ppm)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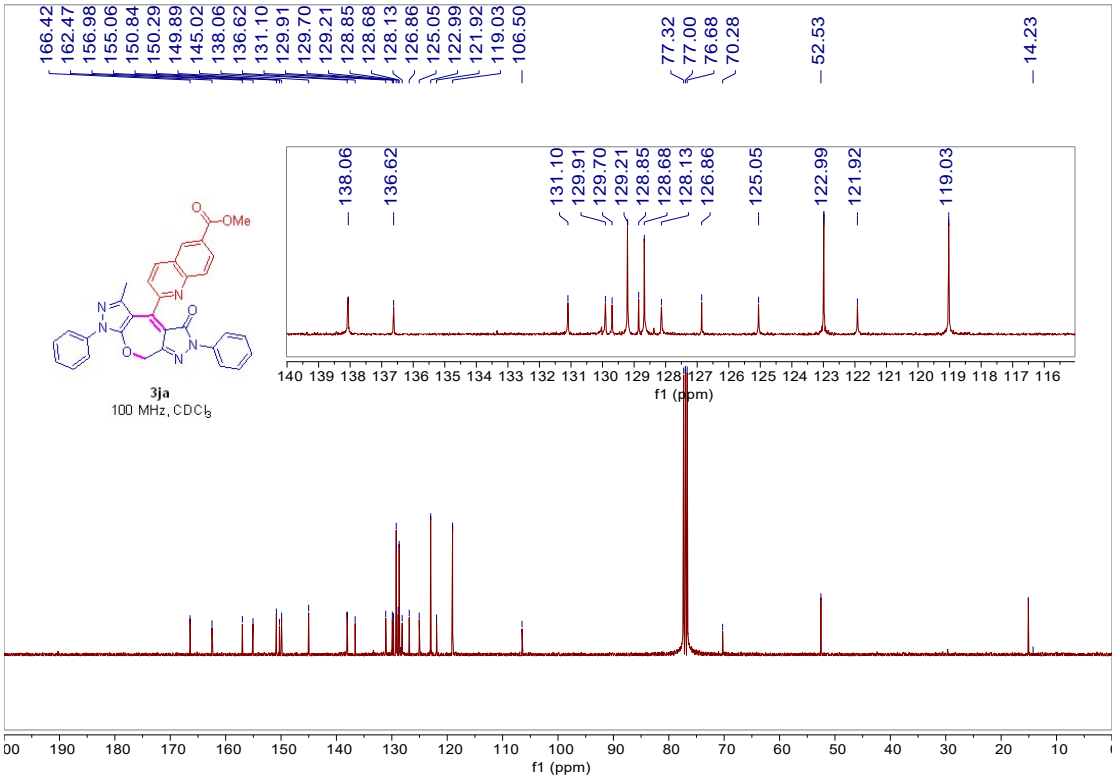
8.461
8.440
8.375
8.371
8.353
8.349
8.213
8.189
7.783
7.779
7.760
7.758
7.703
7.684
7.662
7.641
7.532
7.514
7.493
7.432
7.413
7.395
7.323
7.304
7.283
7.260
7.137
7.119
7.100
5.307
4.023
1.359
OMe
3ja
400 MHz, CDCl3
0.99
1.01
0.99
1.06
2.12
2.05
0.96
2.10
1.09
2.14
0.94
1.84
2.98
3.01
f1 (ppm)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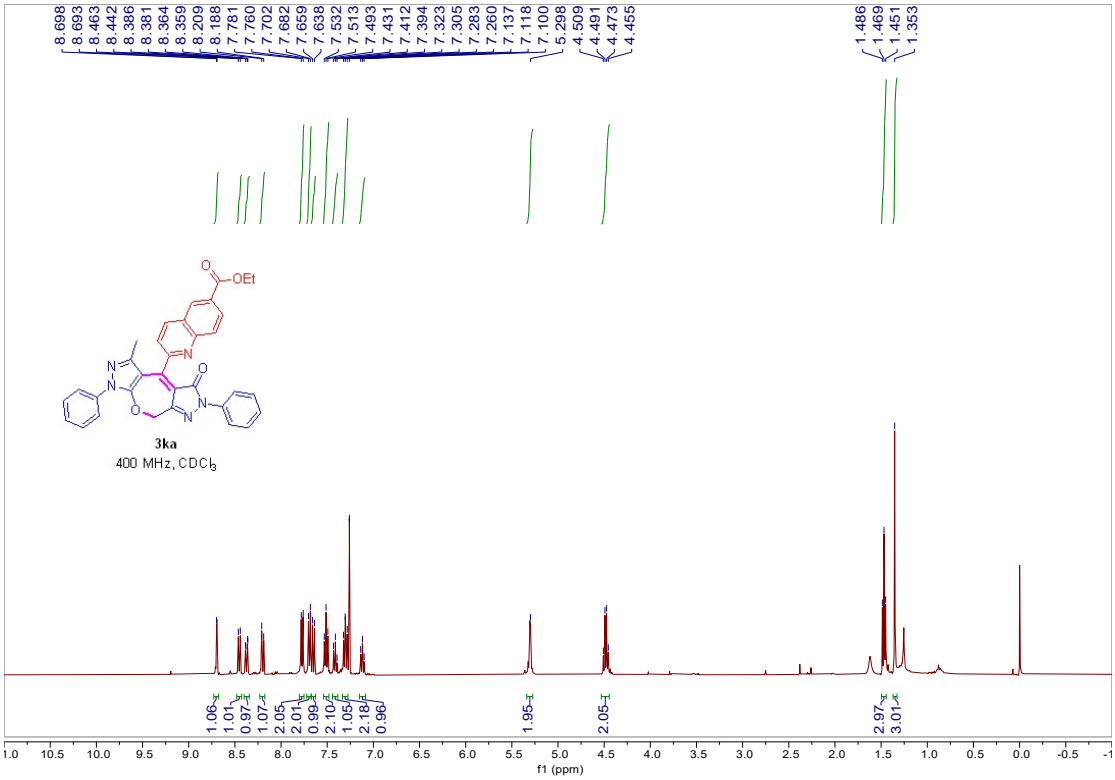
162.47
156.98
155.06
150.84
150.29
149.89
145.02
138.06
136.62
131.10
129.91
129.70
129.21
128.85
128.68
128.13
126.86
125.05
122.99
121.92
119.03
106.50
77.32
77.00
76.68
70.28
52.53
14.23
OMe
3ja
100 MHz, CDCl3
f1 (ppm)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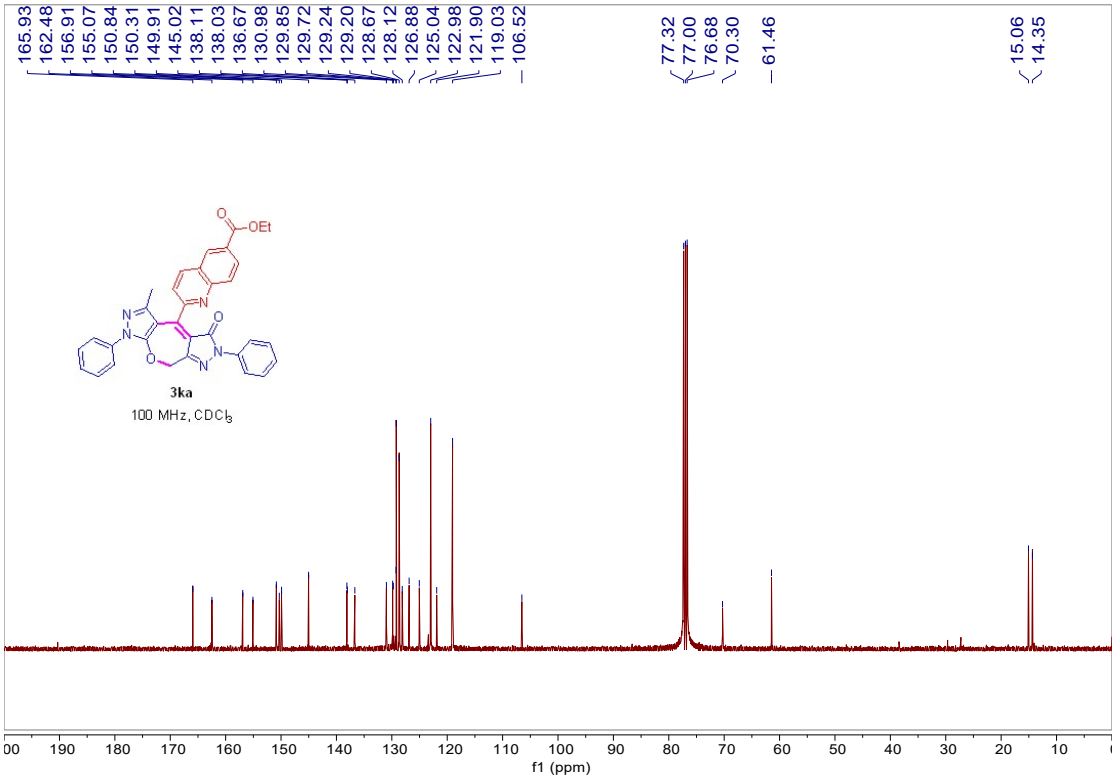
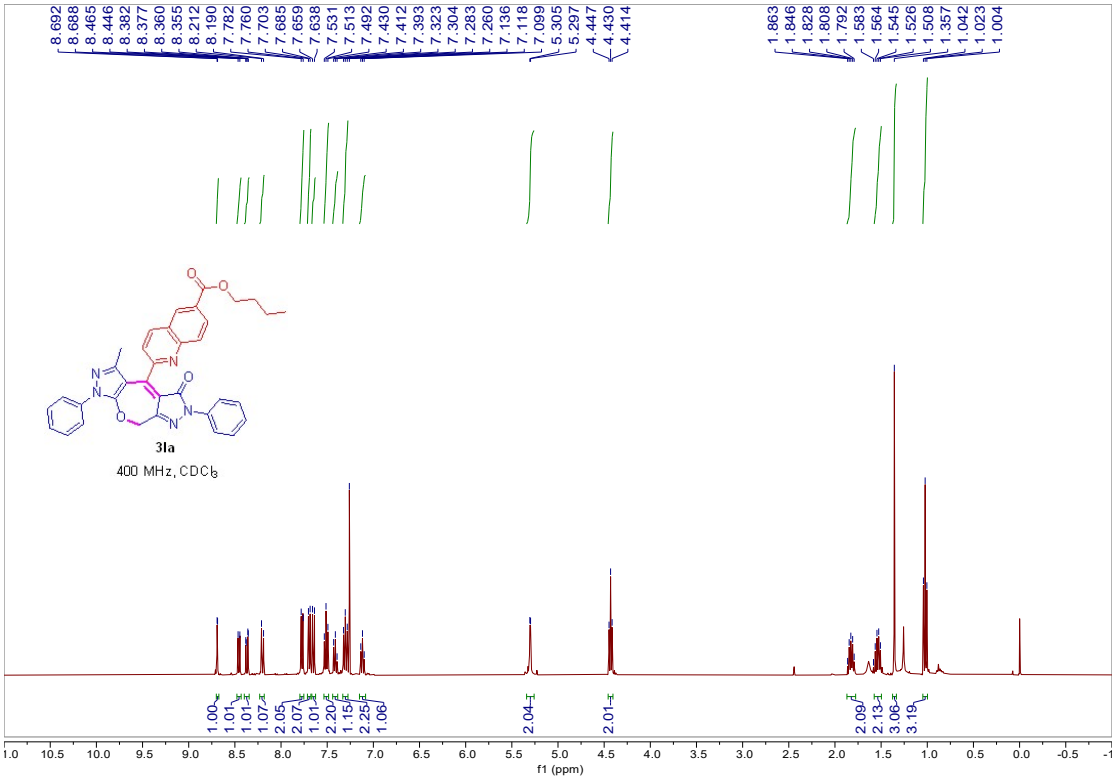
8.693
8.463
8.442
8.386
8.381
8.364
8.359
8.209
8.188
7.781
7.760
7.702
7.682
7.659
7.638
7.532
7.513
7.493
7.431
7.412
7.394
7.323
7.305
7.283
7.260
7.137
7.118
7.100
5.298
4.509
4.491
4.473
4.455
1.486
1.469
1.451
1.353
OEt
3ka
400 MHz, CDCl3
1.06
1.01
0.97
1.07
2.05
2.01
0.99
2.10
1.05
2.18
0.96
1.95
2.05
2.97
3.01
f1 (ppm)


165.93
162.48
156.91
155.07
150.84
150.31
149.91
145.02
138.11
138.03
136.67
130.98
129.85
129.72
129.24
129.20
128.67
128.12
126.88
125.04
122.98
121.90
119.03
106.52
77.32
77.00
76.68
70.30
61.46
15.06
14.35
OEt
3ka
100 MHz, CDCl3
f1 (ppm)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8.688
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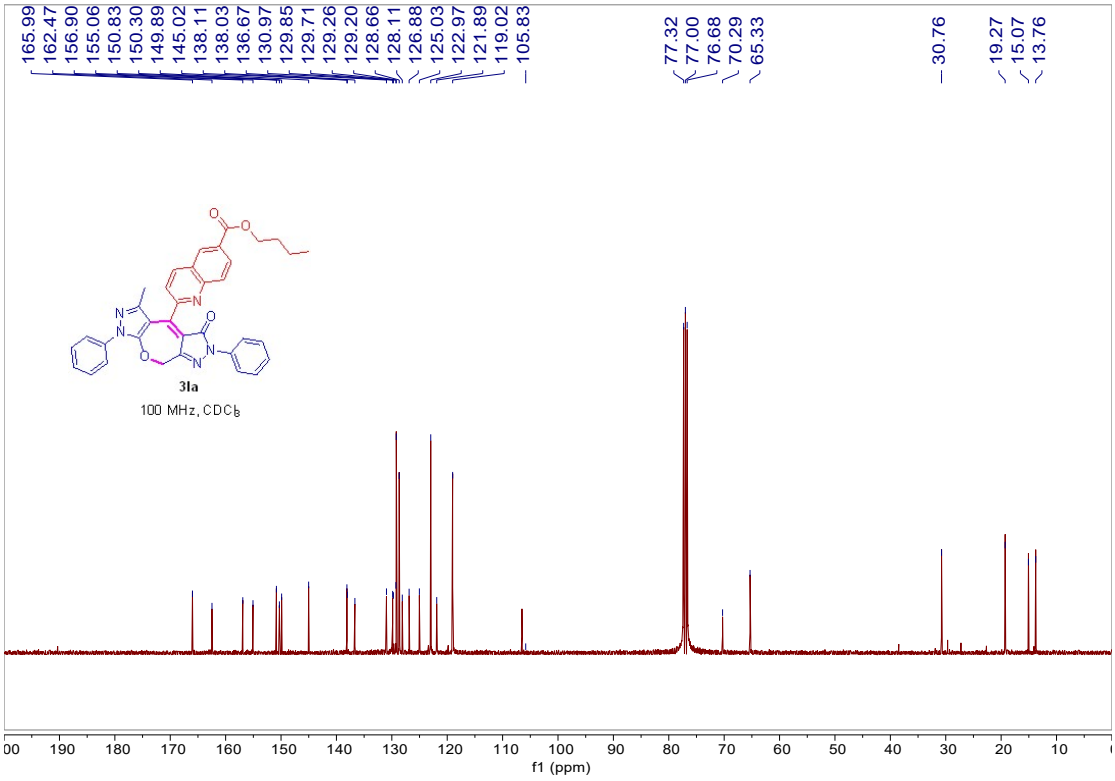
8.377
8.360
8.355
8.212
8.190
7.782
7.760
7.703
7.685
7.659
7.638
7.531
7.513
7.492
7.430
7.412
7.393
7.323
7.304
7.283
7.260
7.136
7.118
7.099
5.305
5.297
4.447
4.430
4.414
1.863
1.846
1.828
1.808
1.792
1.583
1.564
1.545
1.526
1.508
1.357
1.042
1.023
1.004
3la
400 MHz, CDCl3
1.00
1.01
1.01
1.07
2.05
2.07
1.01
2.20
1.15
2.25
1.06
2.04
2.01
2.09
2.13
3.06
3.19
f1 (ppm)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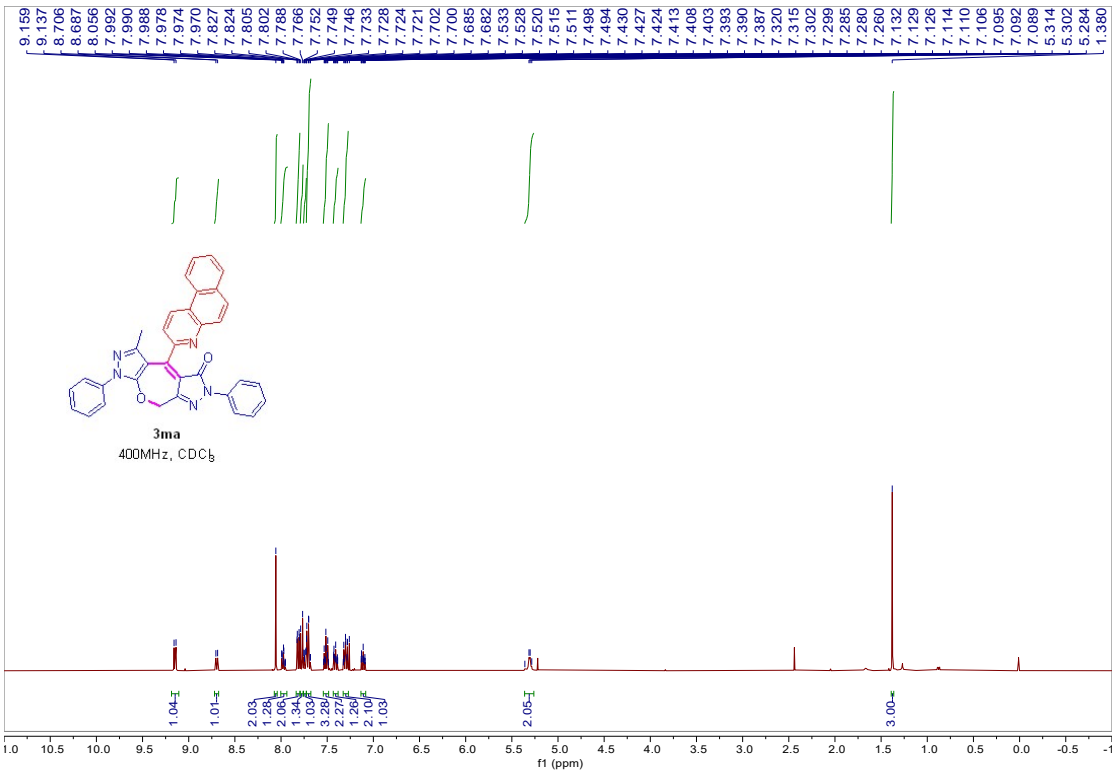
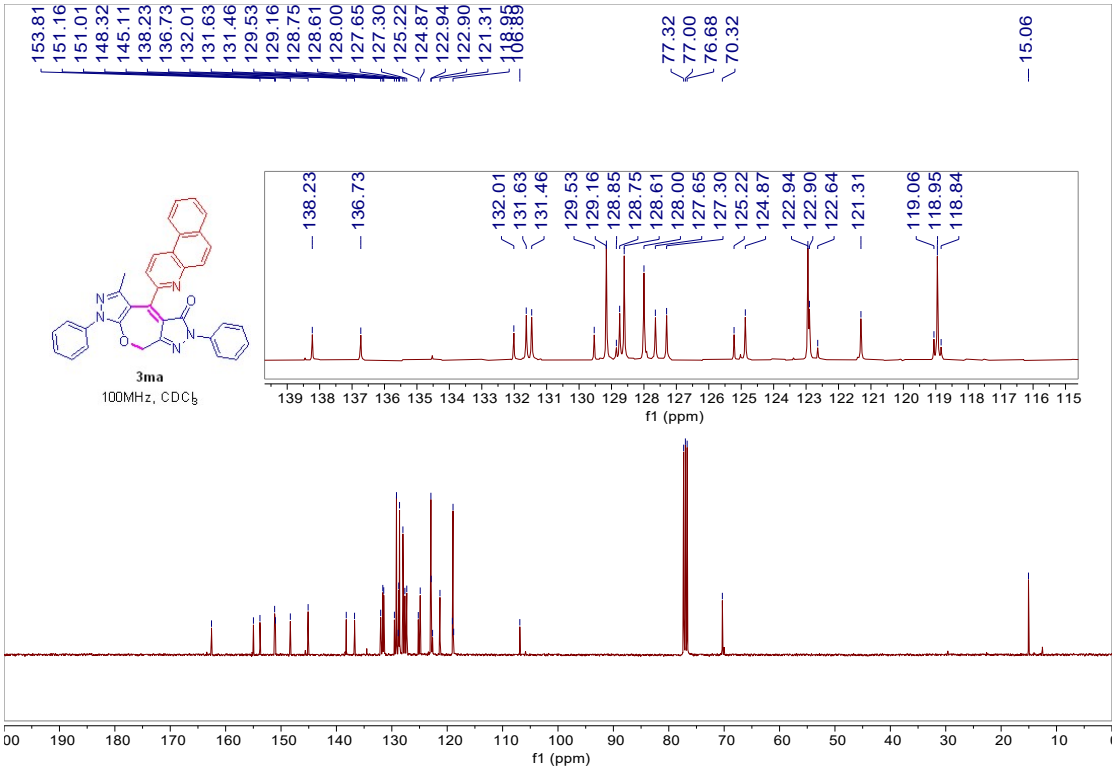
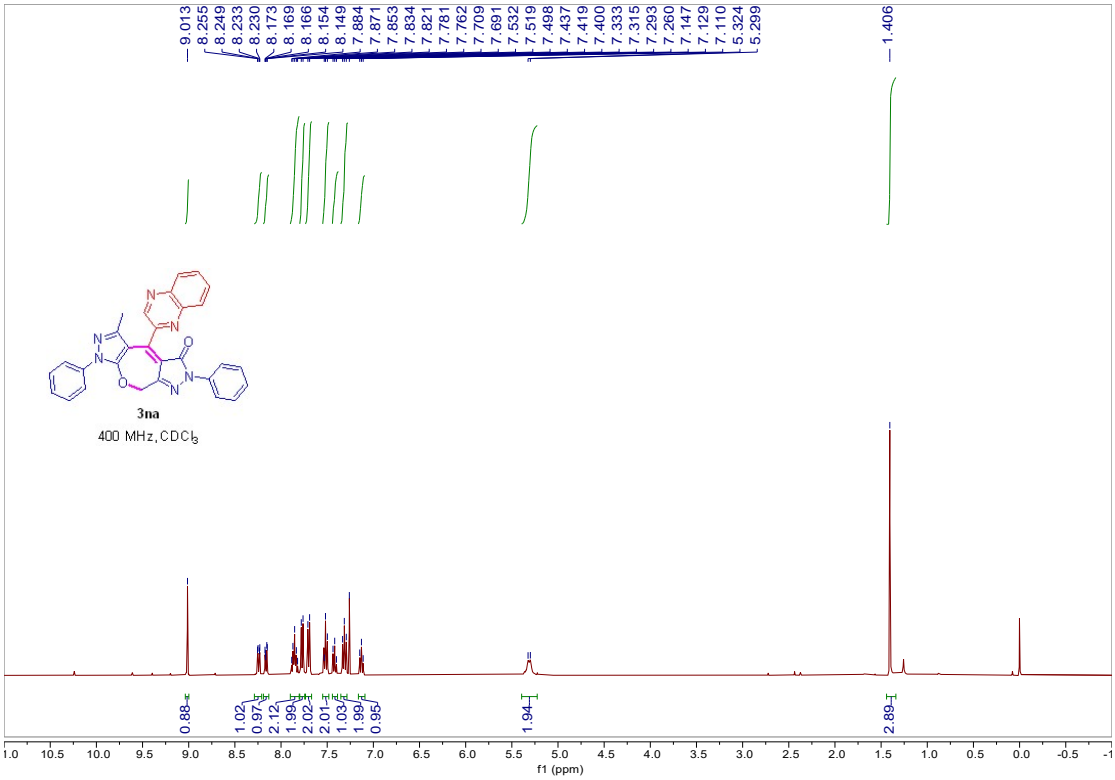
150.30
149.89
145.02
138.11
138.03
136.67
130.97
129.85
129.71
129.26
129.20
128.66
128.11
126.88
125.03
122.97
121.89
119.02
105.83
77.32
77.00
76.68
70.29
65.33
30.76
19.27
15.07
13.76
3la
100 MHz, CDCl3
f1 (ppm)


3ma
400MHz, CDCl3
f1 (ppm)


3ma
100MHz, CDCl3
f1 (ppm)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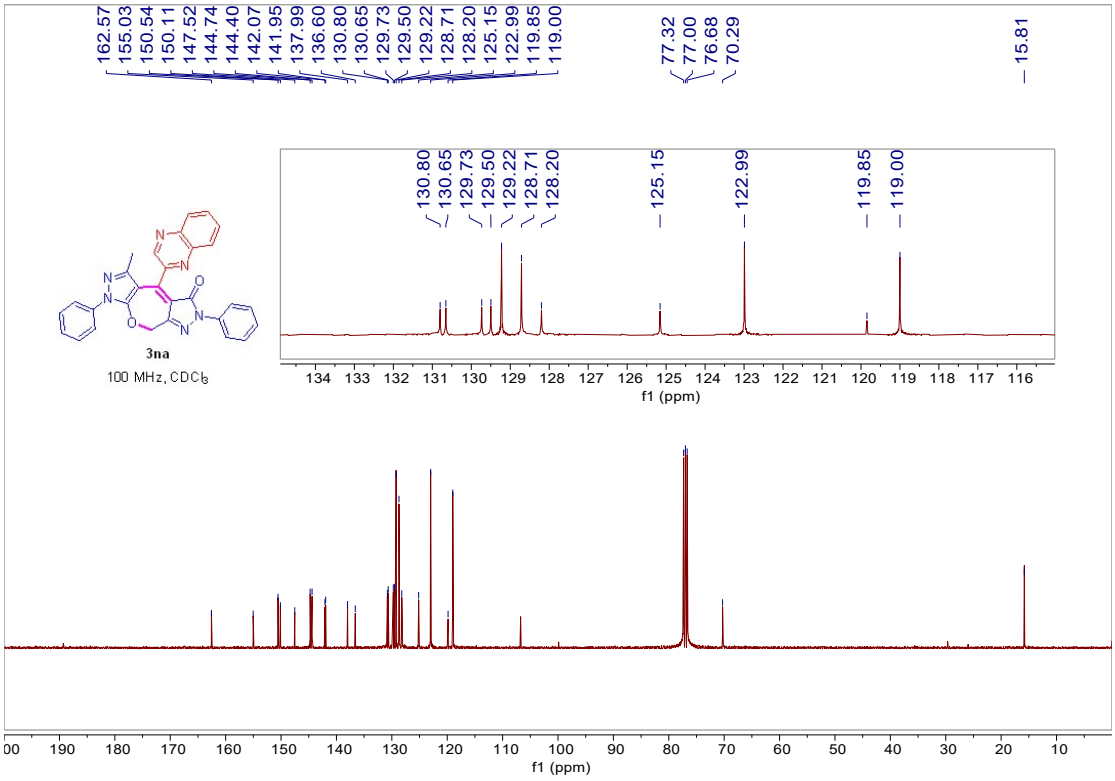
8.230
8.173
8.169
8.166
8.154
8.149
7.884
7.871
7.853
7.834
7.821
7.781
7.762
7.709
7.691
7.532
7.519
7.498
7.437
7.419
7.400
7.333
7.315
7.293
7.260
7.147
7.129
7.110
5.324
5.299
1.406
3na
400 MHz, CDCl3
0.88
1.02
0.97
2.12
1.99
2.02
2.01
1.03
1.99
0.95
1.94
2.89
f1 (ppm)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150.11
147.52
144.74
144.40
142.07
141.95
137.99
136.60
130.80
130.65
129.73
129.50
129.22
128.71
128.20
125.15
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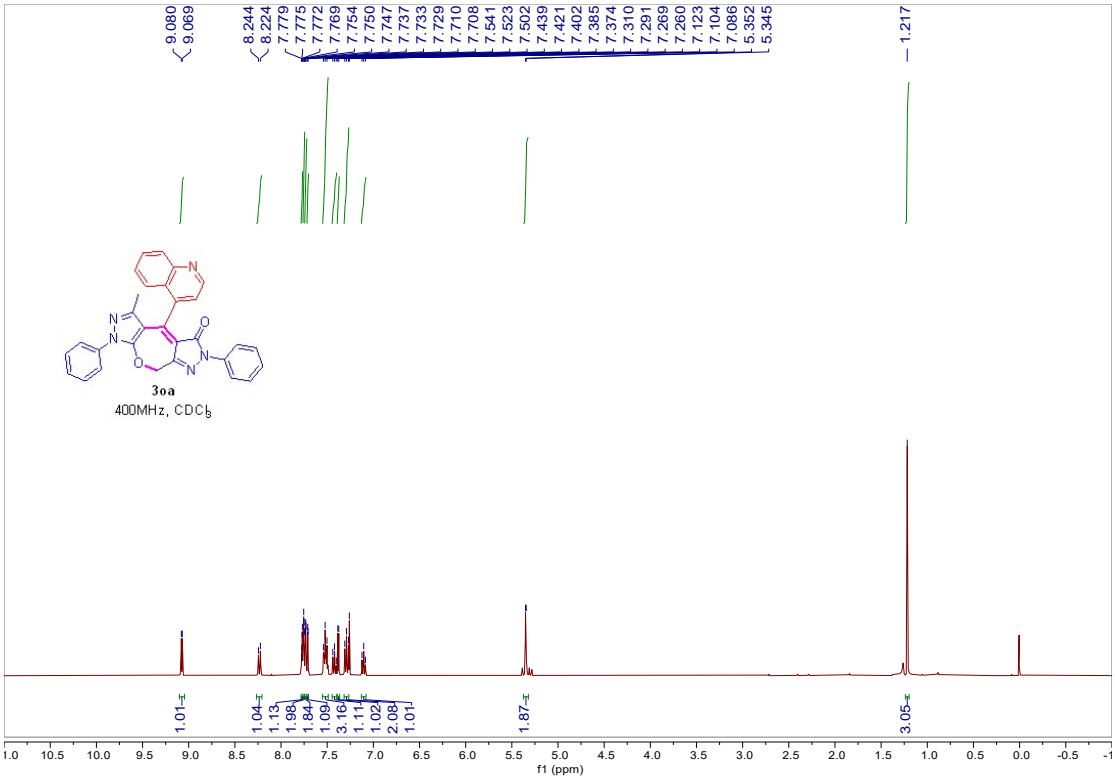
77.32
77.00
76.68
70.29
15.81
3na
100 MHz, CDCl3
f1 (ppm)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9.069
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8.224
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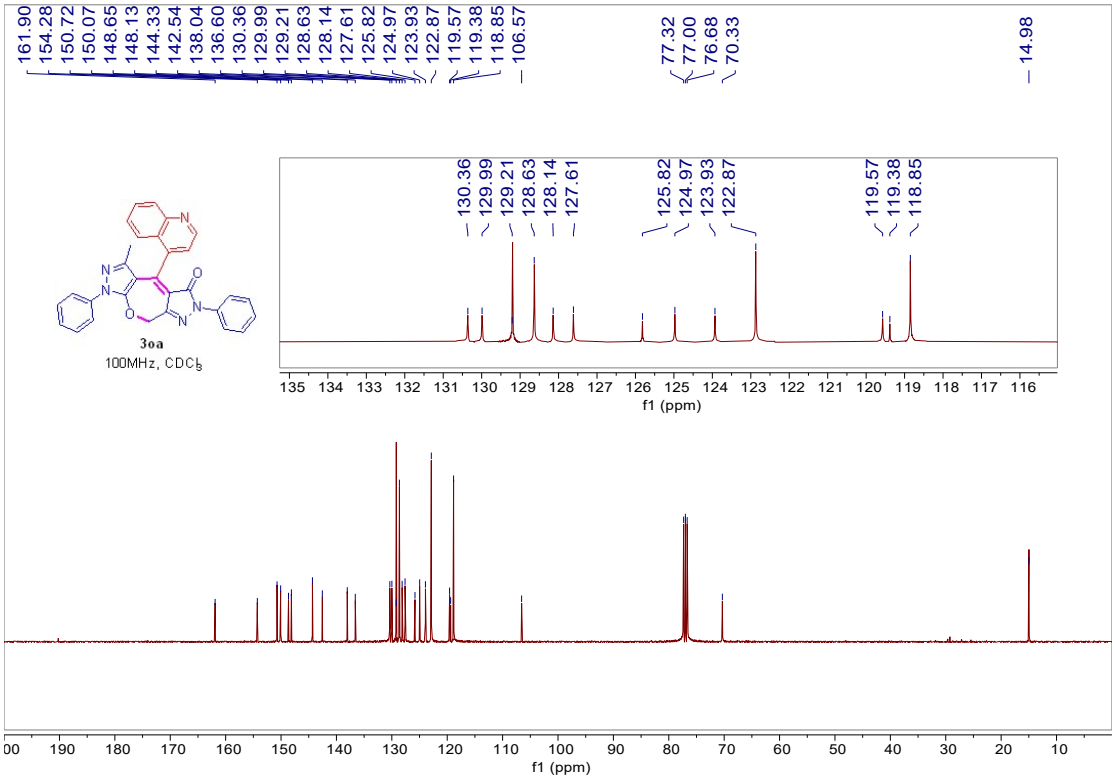
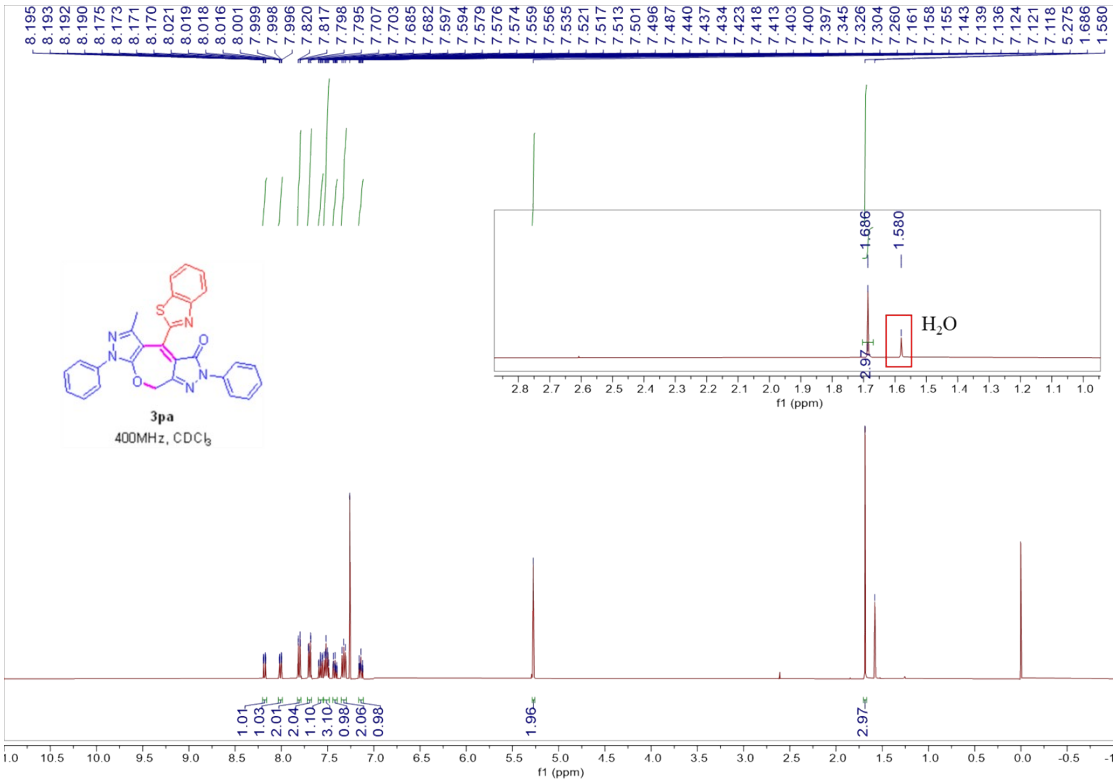
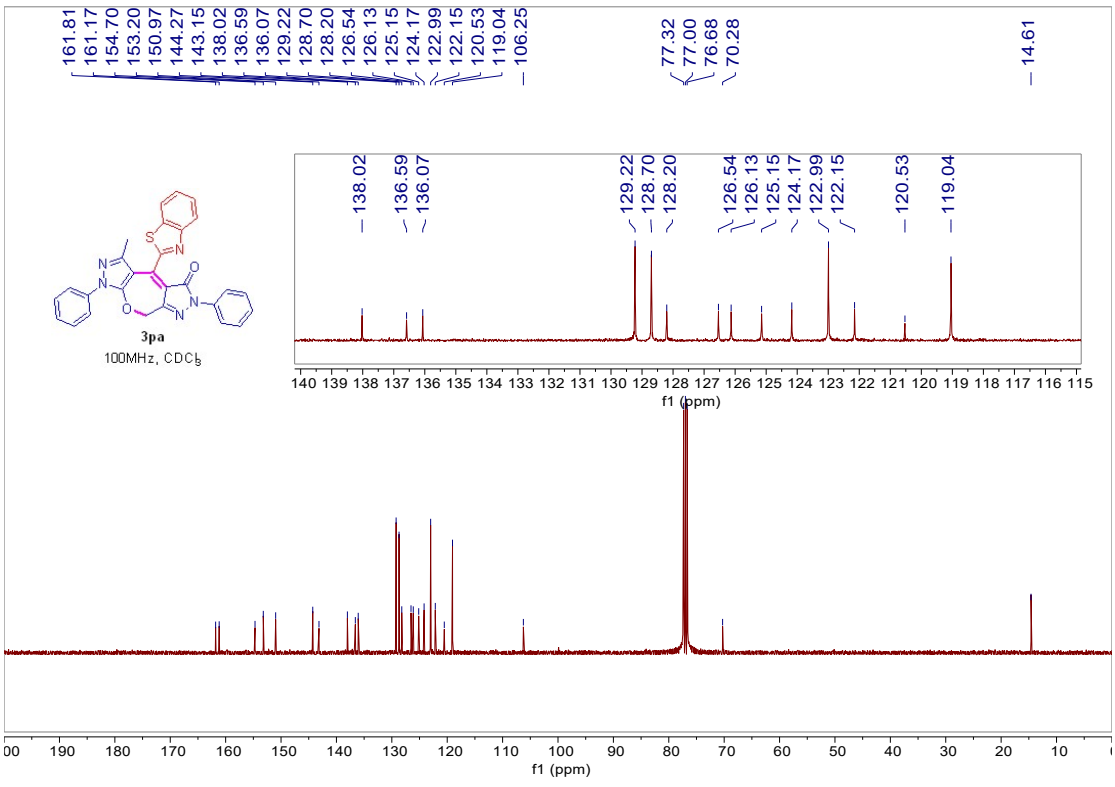
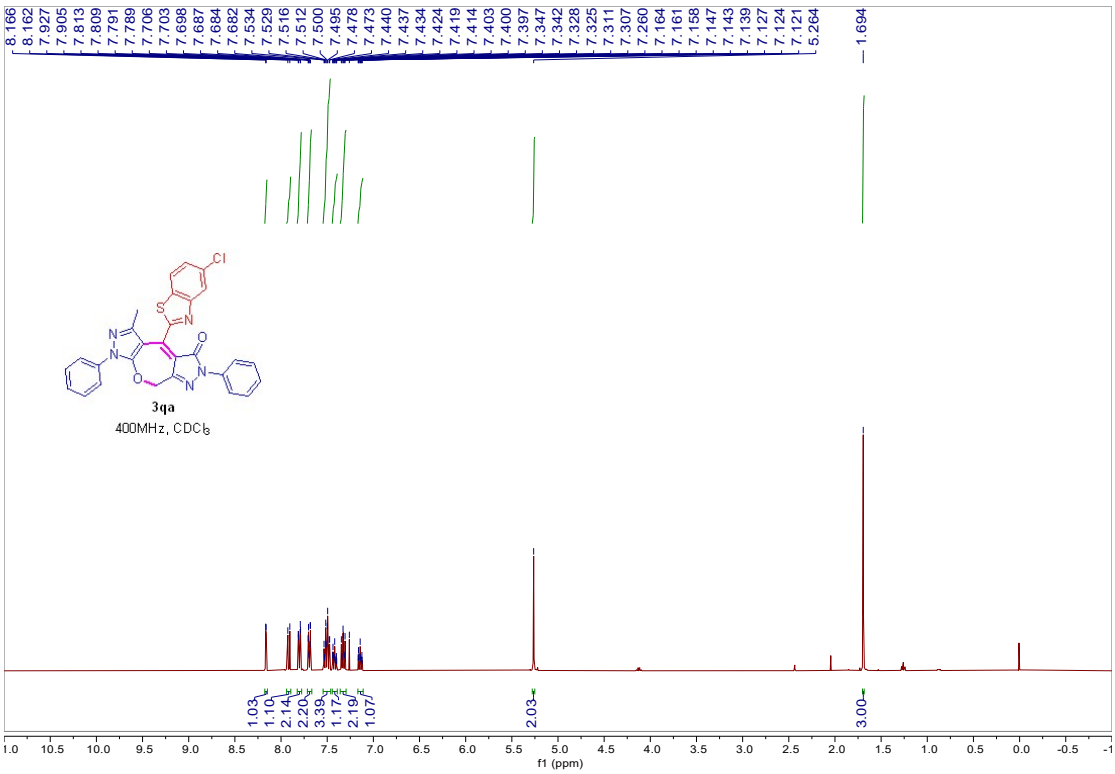
7.775
7.772
7.769
7.754
7.750
7.747
7.737
7.733
7.729
7.710
7.708
7.541
7.523
7.502
7.439
7.421
7.402
7.385
7.374
7.310
7.291
7.269
7.260
7.123
7.104
7.086
5.352
5.345
1.217
3oa
400MHz, CDCl3
1.01
1.04
1.13
1.98
1.84
1.09
3.16
1.11
1.02
2.08
1.01
1.87
3.05
f1 (ppm)


161.90
154.28
150.72
150.07
148.65
148.13
144.33
142.54
138.04
136.60
130.36
129.99
129.21
128.63
128.14
127.61
125.82
124.97
123.93
122.87
119.57
119.38
118.85
106.57
77.32
77.00
76.68
70.33
14.98
3oa
100MHz, CDCl3
f1 (ppm)


3pa
400MHz, CDCl3
H2O
f1 (ppm)


3pa
100MHz, CDCl3
f1 (ppm)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7.789
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7.703
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7.687
7.684
7.682
7.534
7.529
7.516
7.512
7.500
7.495
7.478
7.473
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7.437
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7.419
7.414
7.403
7.400
7.397
7.347
7.342
7.328
7.325
7.311
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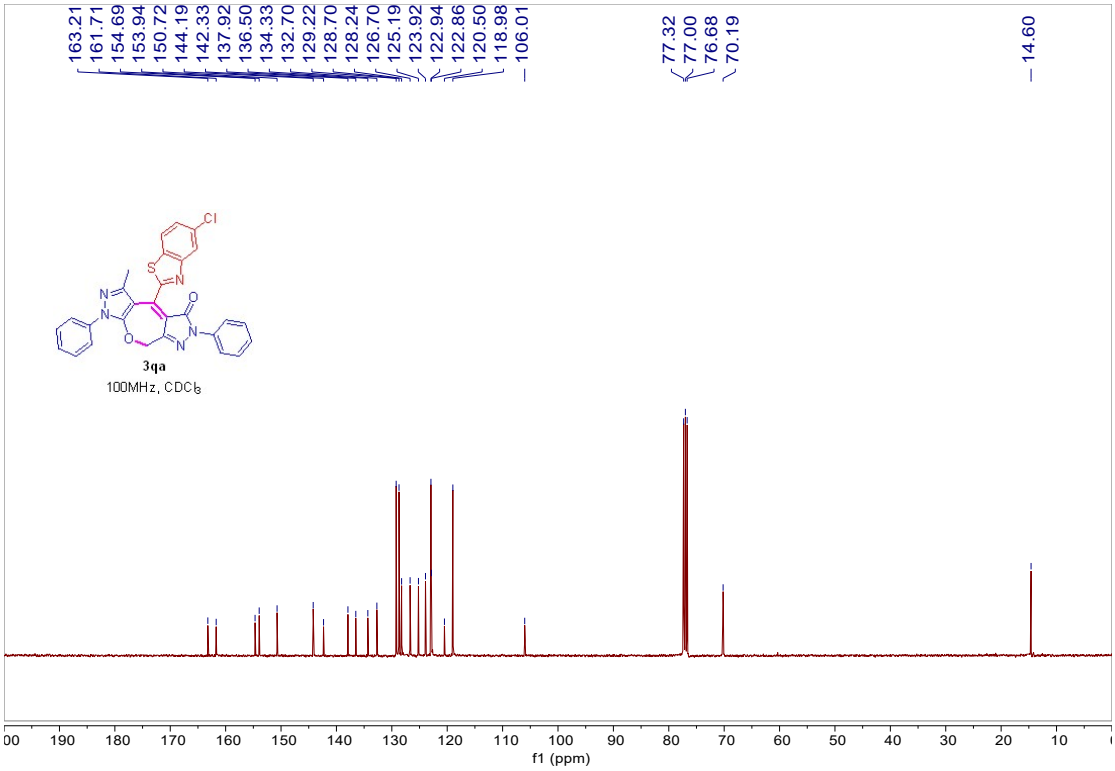
7.260
7.164
7.161
7.158
7.147
7.143
7.139
7.127
7.124
7.121
5.264
1.694
Cl
S
N
N
N
O
O
N
3qa
400MHz, CDCl3
1.03
1.10
2.14
2.20
3.39
1.17
2.19
1.07
2.03
3.00
f1 (ppm)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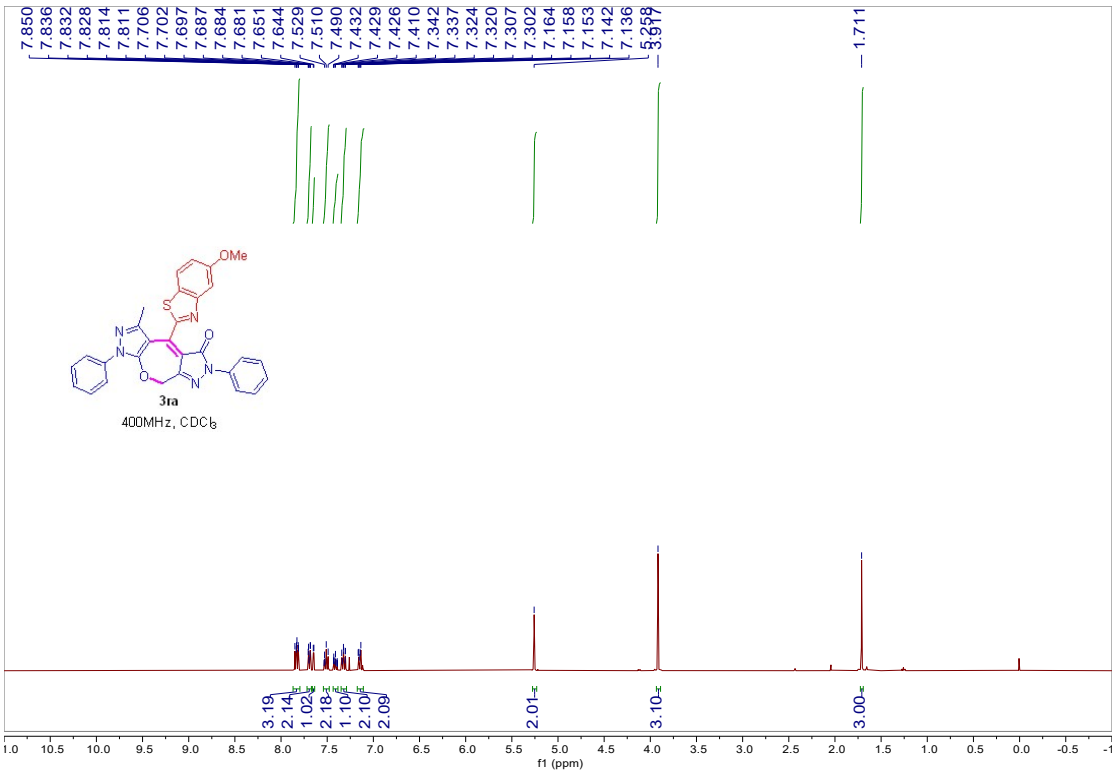
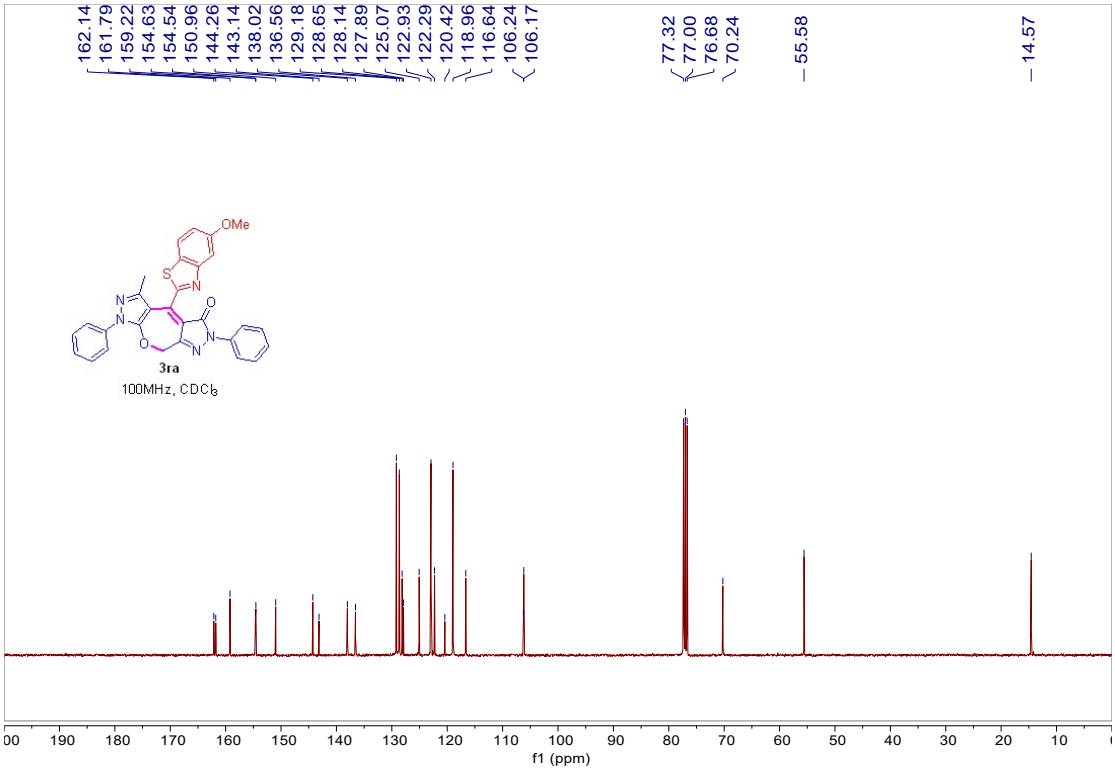
154.69
153.94
150.72
144.19
142.33
137.92
136.50
134.33
132.70
129.22
128.70
128.24
126.70
125.19
123.92
122.94
122.86
120.50
118.98
106.01
77.32
77.00
76.68
70.19
14.60
Cl
S
N
N
N
O
O
N
3qa
100MHz, CDCl3
f1 (ppm)


7.850
7.836
7.832
7.828
7.814
7.811
7.706
7.702
7.697
7.687
7.684
7.681
7.651
7.644
7.529
7.510
7.490
7.432
7.429
7.426
7.410
7.342
7.337
7.324
7.320
7.307
7.302
7.164
7.158
7.153
7.142
7.136
5.259
3.917
1.711
OMe
3ra
400MHz, CDCl3
3.19
2.14
1.02
2.18
1.10
2.10
2.09
2.01
3.10
3.00
f1 (ppm)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144.26
143.14
138.02
136.56
129.18
128.65
128.14
127.89
125.07
122.93
122.29
120.42
118.96
116.64
106.24
106.17
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77.00
76.68
70.24
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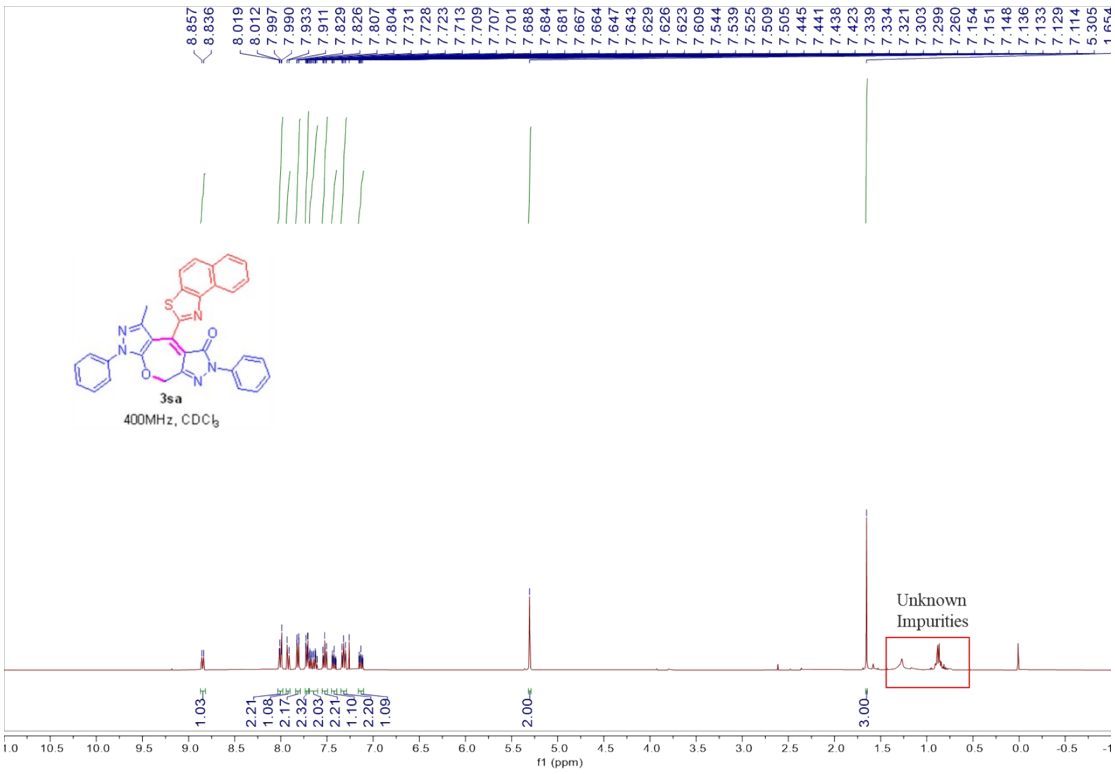
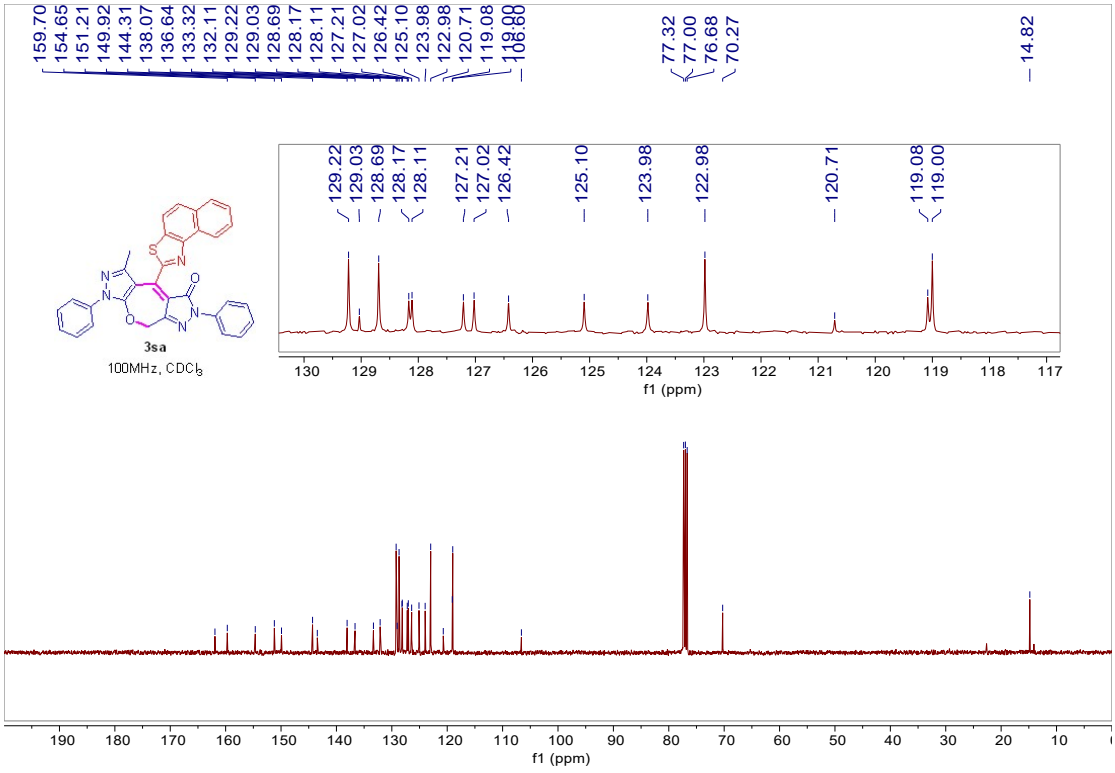
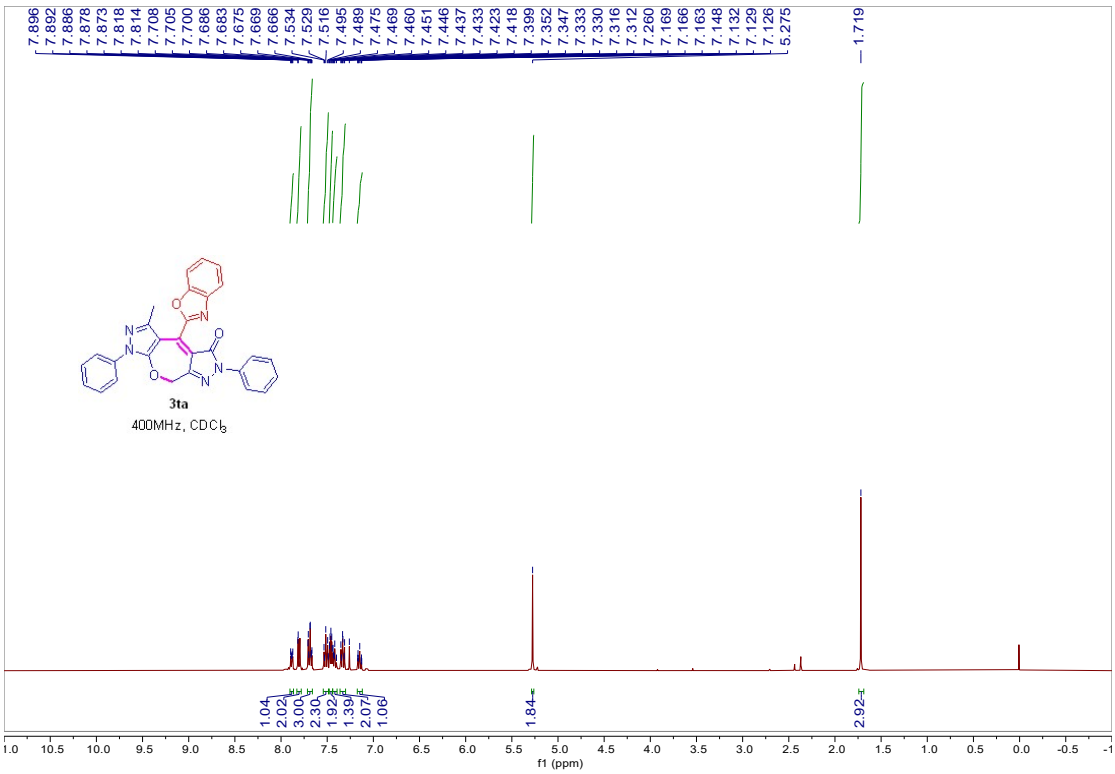
14.57
OMe
3ra
100MHz, CDCl3
f1 (ppm)


3sa
400MHz, CDCl3
Unknown
Impurities
f1 (ppm)


3sa
100MHz, CDCl3
f1 (ppm)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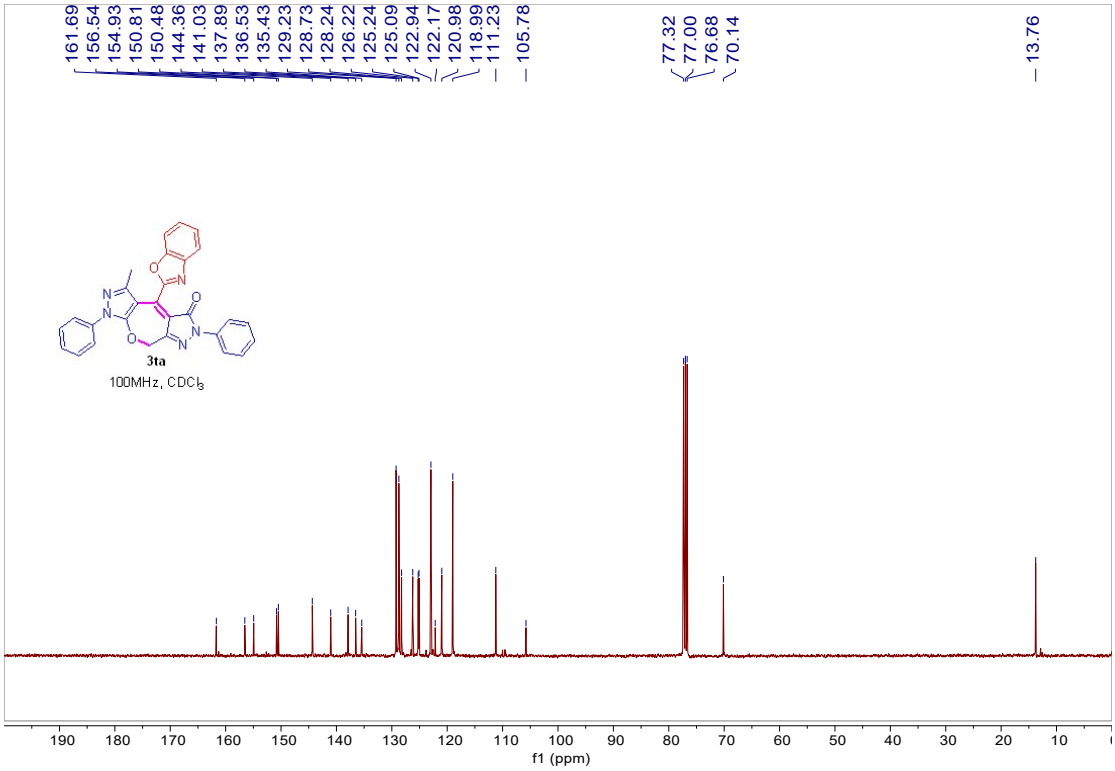
7.892
7.886
7.878
7.873
7.818
7.814
7.708
7.705
7.700
7.686
7.683
7.675
7.669
7.666
7.534
7.529
7.516
7.495
7.489
7.475
7.469
7.460
7.451
7.446
7.437
7.433
7.423
7.418
7.399
7.352
7.347
7.333
7.330
7.316
7.312
7.260
7.169
7.166
7.163
7.148
7.132
7.129
7.126
5.275
1.719
3ta
400MHz, CDCl3
1.04
2.02
3.00
2.30
1.92
1.39
2.07
1.06
1.84
2.92
f1 (ppm)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154.93
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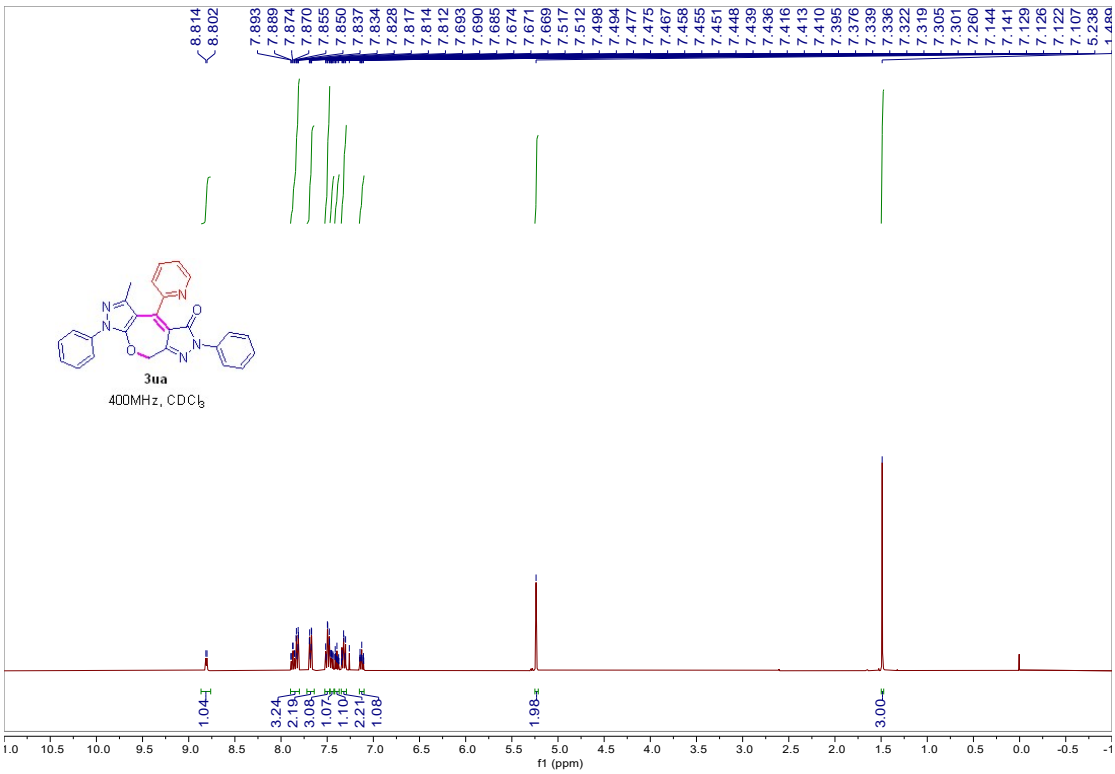
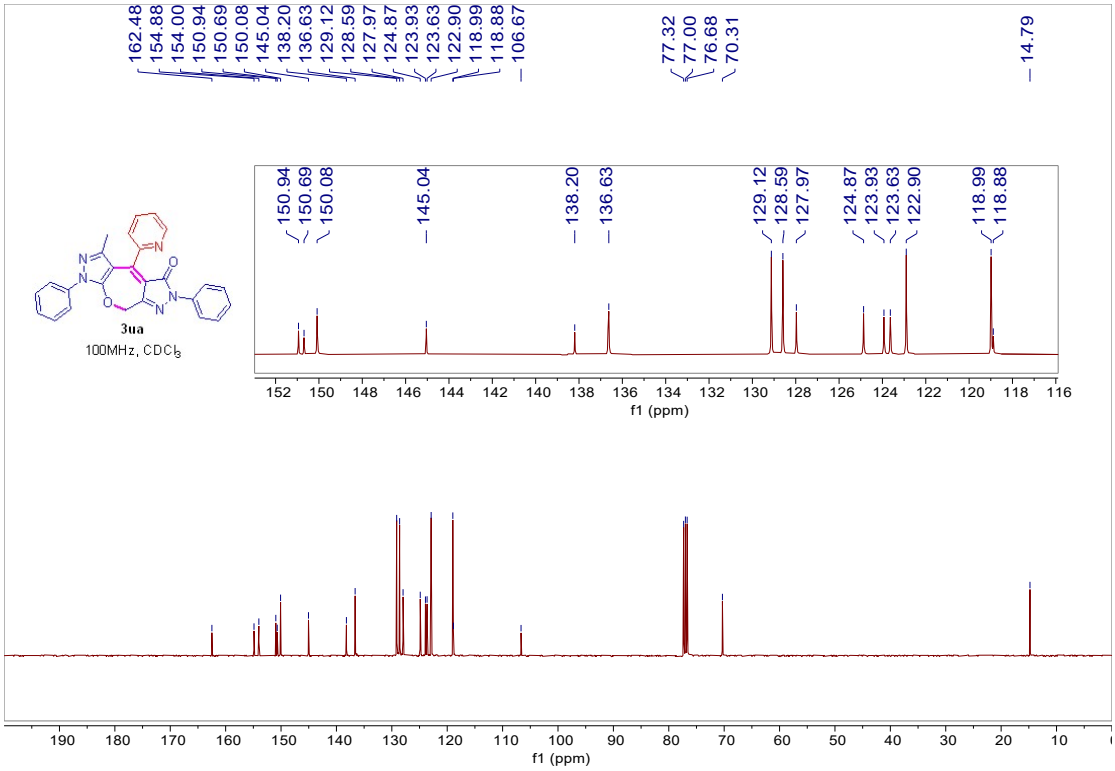
144.36
141.03
137.89
136.53
135.43
129.23
128.73
128.24
126.22
125.24
125.09
122.94
122.17
120.98
118.99
111.23
105.78
77.32
77.00
76.68
70.14
13.76
3ta
100MHz, CDCl3
f1 (ppm)


8.814
8.802
7.893
7.889
7.874
7.870
7.855
7.850
7.837
7.834
7.828
7.817
7.814
7.812
7.693
7.690
7.685
7.674
7.671
7.669
7.517
7.512
7.498
7.494
7.477
7.475
7.467
7.458
7.455
7.451
7.448
7.439
7.436
7.416
7.413
7.410
7.395
7.376
7.339
7.336
7.322
7.319
7.305
7.301
7.260
7.144
7.141
7.129
7.126
7.122
7.107
5.238
3ua
400MHz, CDCl3
1.04
3.24
2.19
3.08
1.07
1.10
2.21
1.08
1.98
3.00
f1 (ppm)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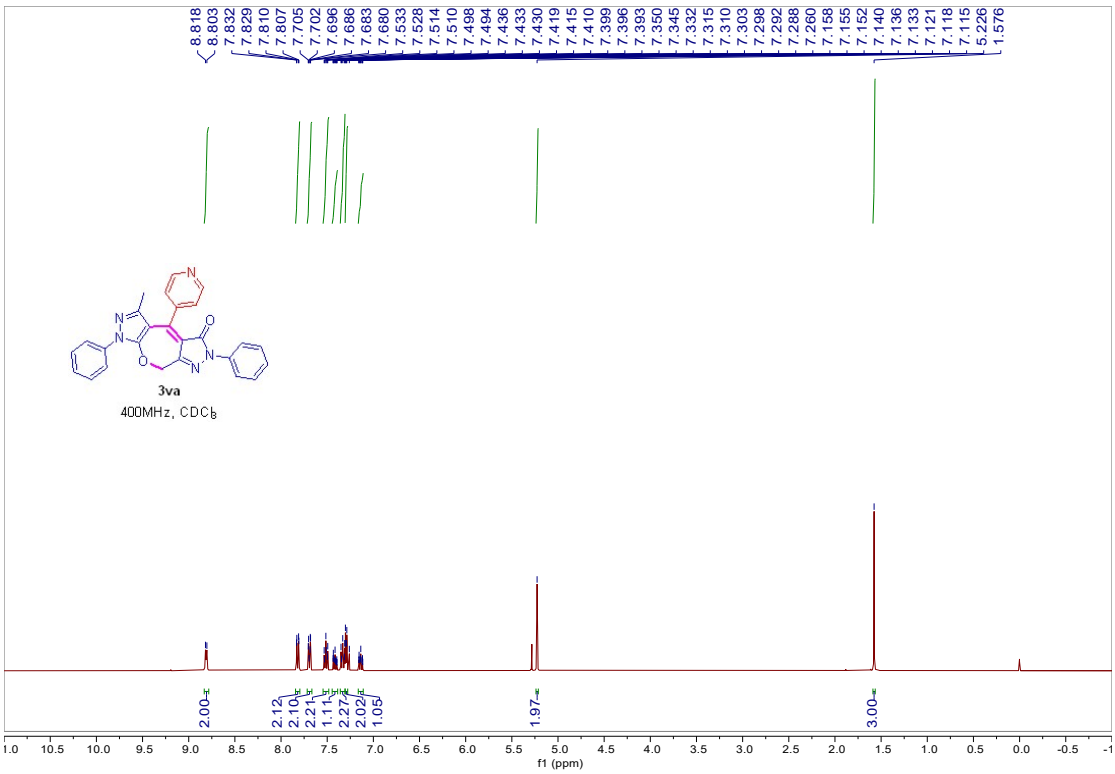
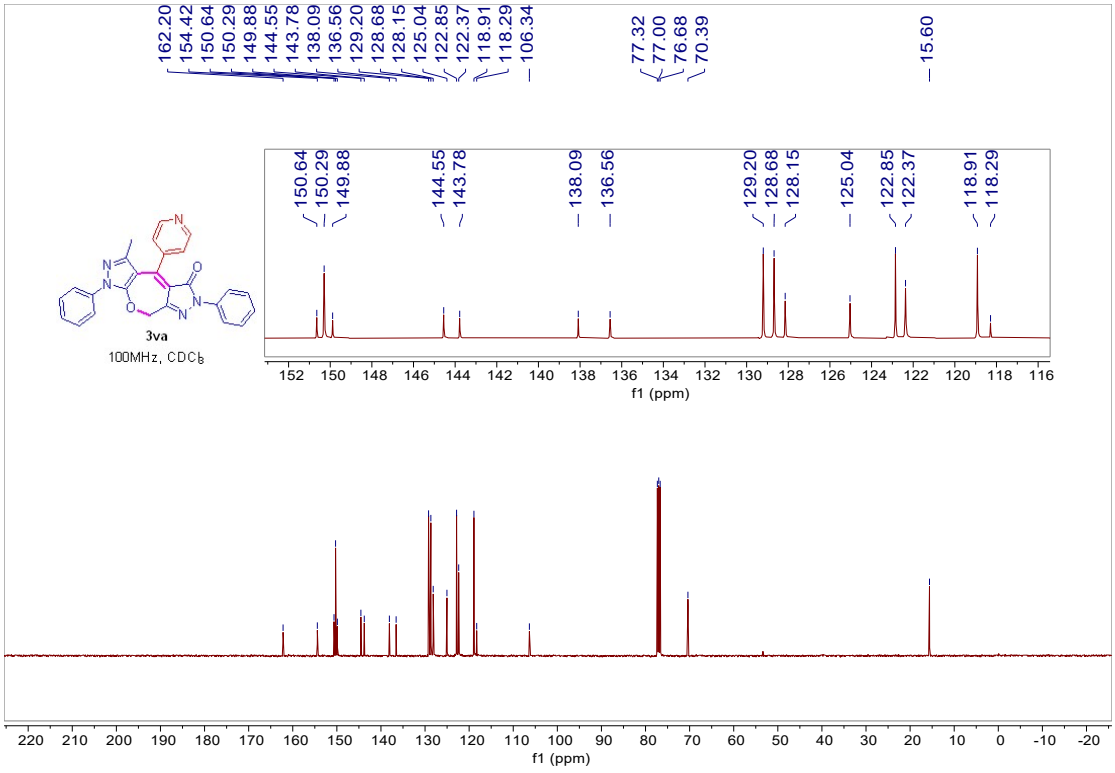
154.88
154.00
150.94
150.69
150.08
145.04
138.20
136.63
129.12
128.59
127.97
124.87
123.93
123.63
122.90
118.99
118.88
106.67
77.32
77.00
76.68
70.31
14.79
3ua
100MHz, CDCl3
f1 (ppm)


8.818
8.803
7.832
7.829
7.810
7.807
7.705
7.702
7.696
7.686
7.683
7.680
7.533
7.528
7.514
7.510
7.498
7.494
7.436
7.433
7.430
7.419
7.415
7.410
7.399
7.396
7.393
7.350
7.345
7.332
7.315
7.310
7.303
7.298
7.292
7.288
7.260
7.158
7.155
7.152
7.140
7.136
7.133
7.121
7.118
7.115
5.226
1.576
3va
400MHz, CDCl3
2.00
2.12
2.10
2.21
1.11
2.27
2.02
1.05
1.97
3.00
f1 (ppm)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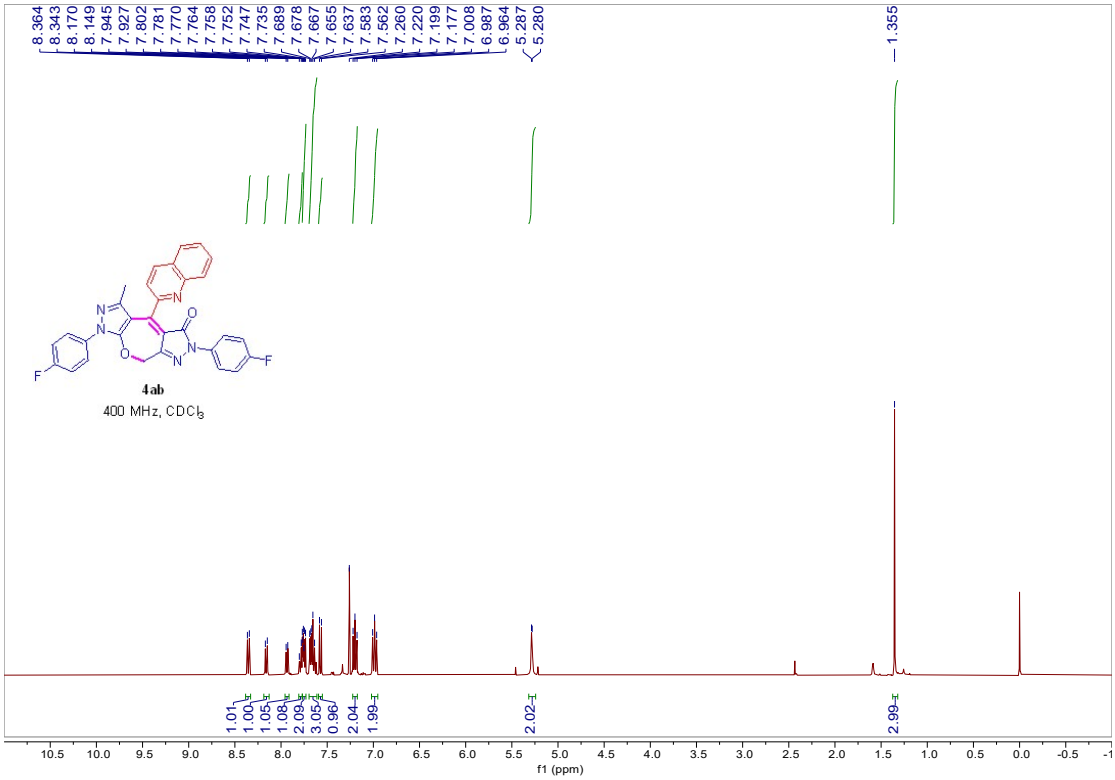
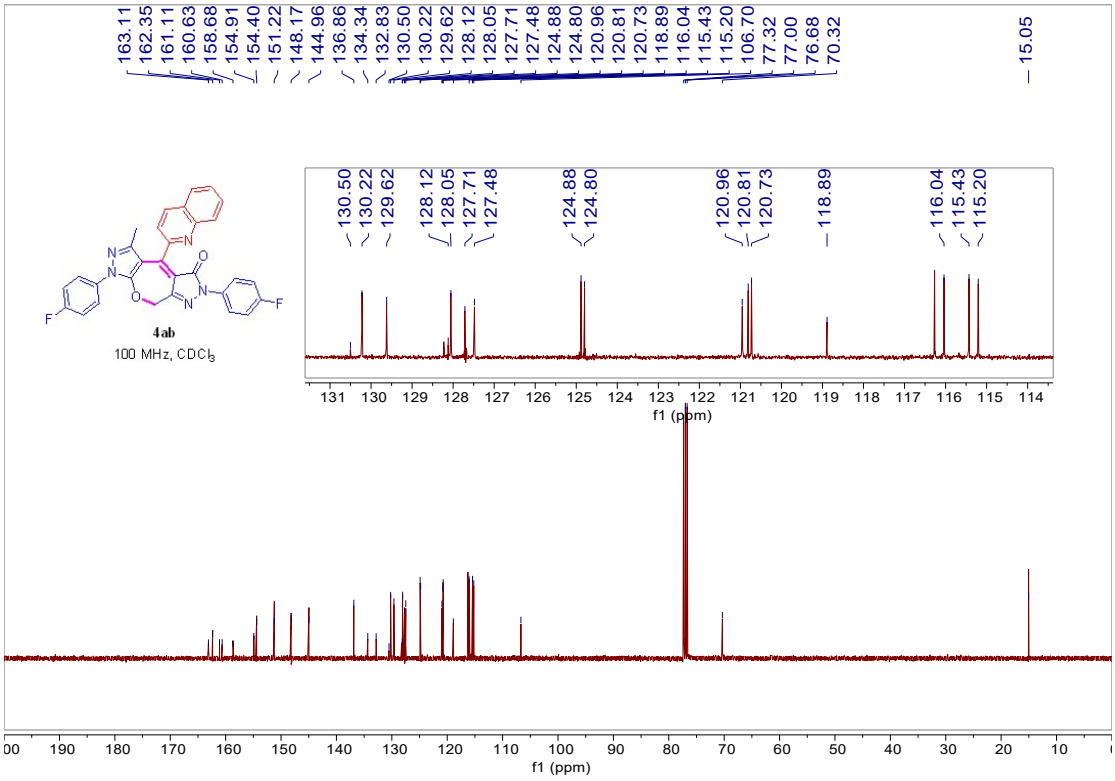
154.42
150.64
150.29
149.88
144.55
143.78
138.09
136.56
129.20
128.68
128.15
125.04
122.85
122.37
118.91
118.29
106.34
77.32
77.00
76.68
70.39
15.60
3va
100MHz, CDCl3
f1 (ppm)


8.364
8.343
8.170
8.149
7.945
7.927
7.802
7.781
7.770
7.764
7.758
7.752
7.747
7.735
7.689
7.678
7.667
7.655
7.637
7.583
7.562
7.260
7.220
7.199
7.177
7.008
6.987
6.964
5.287
5.280
1.355
4ab
400 MHz, CDCl3
1.01
1.00
1.05
1.08
2.09
3.05
0.96
2.04
1.99
2.02
2.99
f1 (ppm)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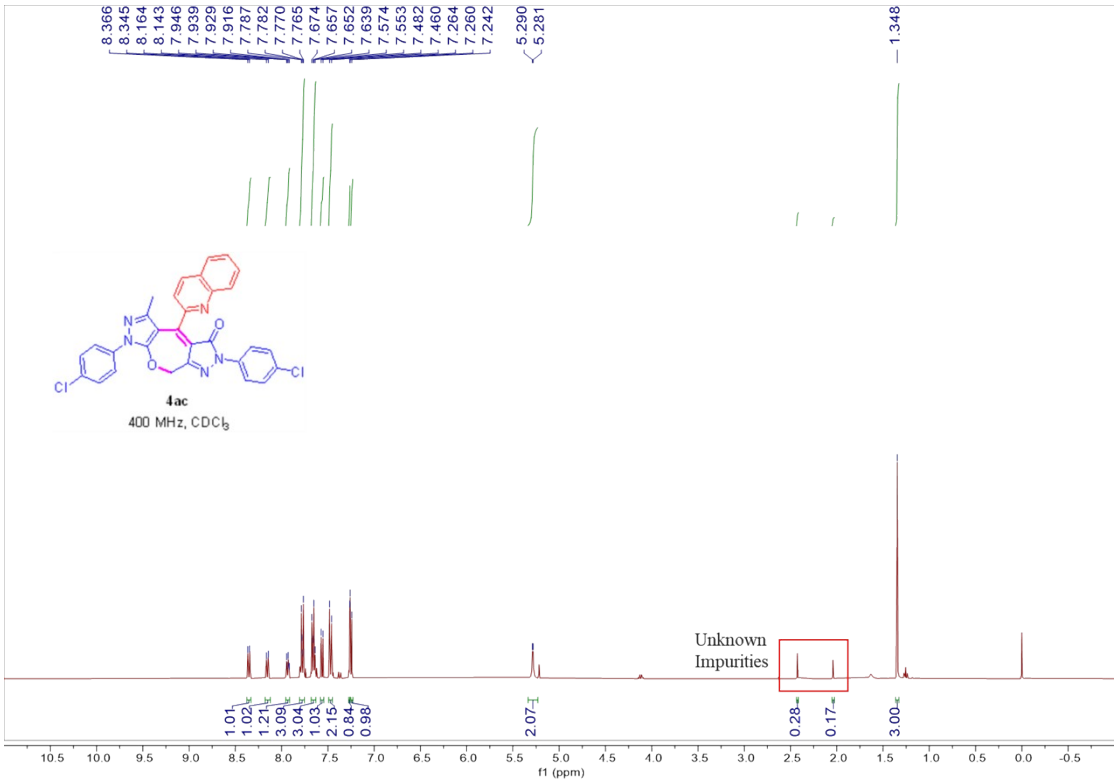
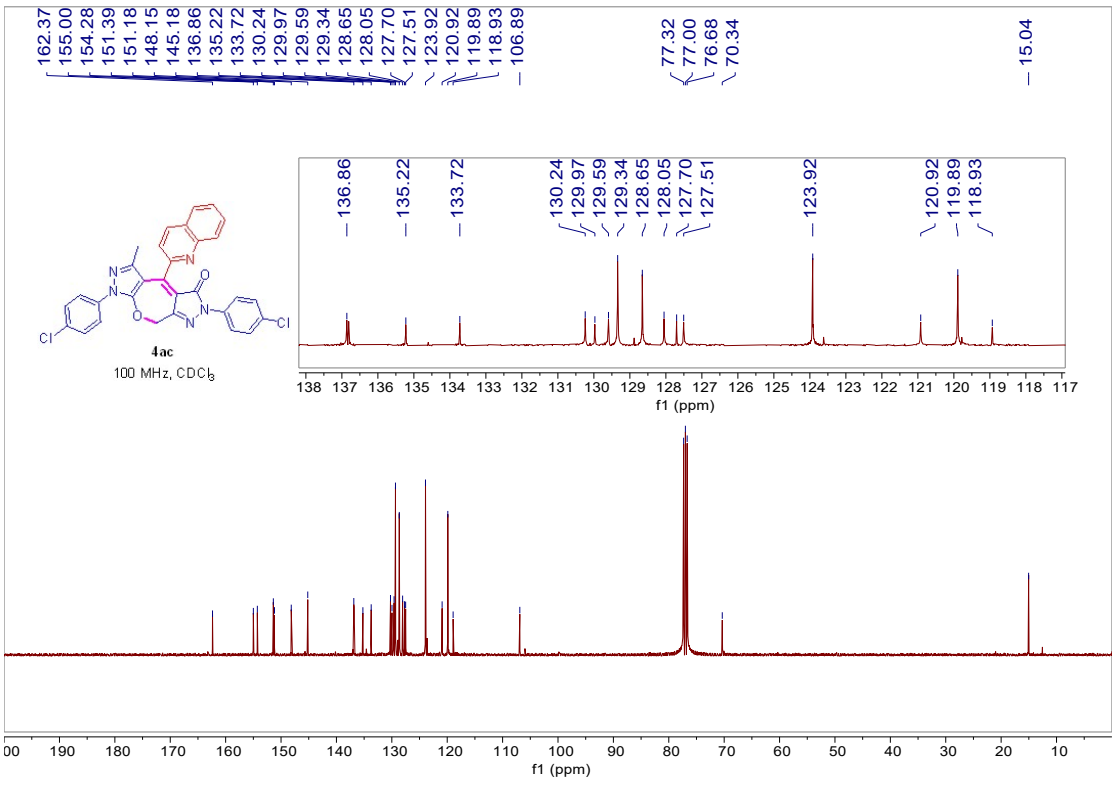
162.35
161.11
160.63
158.68
154.91
154.40
151.22
148.17
144.96
136.86
134.34
132.83
130.50
130.22
129.62
128.12
128.05
127.71
127.48
124.88
124.80
120.96
120.81
120.73
118.89
116.04
115.43
115.20
106.70
77.32
77.00
76.68
70.32
15.05
4ab
100 MHz, CDCl3
f1 (ppm)


8.366
8.345
8.164
8.143
7.946
7.939
7.929
7.916
7.787
7.782
7.770
7.765
7.674
7.657
7.652
7.639
7.574
7.553
7.482
7.460
7.264
7.260
7.242
5.290
5.281
1.348
4ac
400 MHz, CDCl3
Unknown
Impurities
1.01
1.02
1.21
3.09
3.04
1.03
2.15
0.84
0.98
2.07
0.28
0.17
3.00
f1 (ppm)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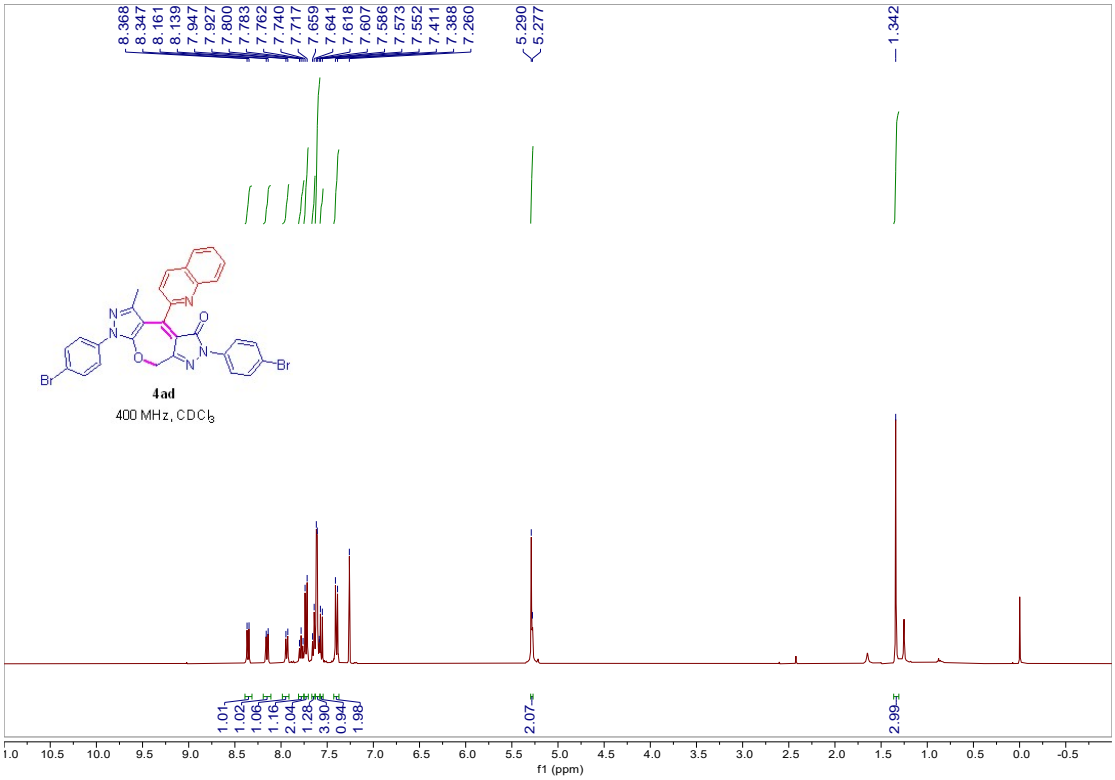
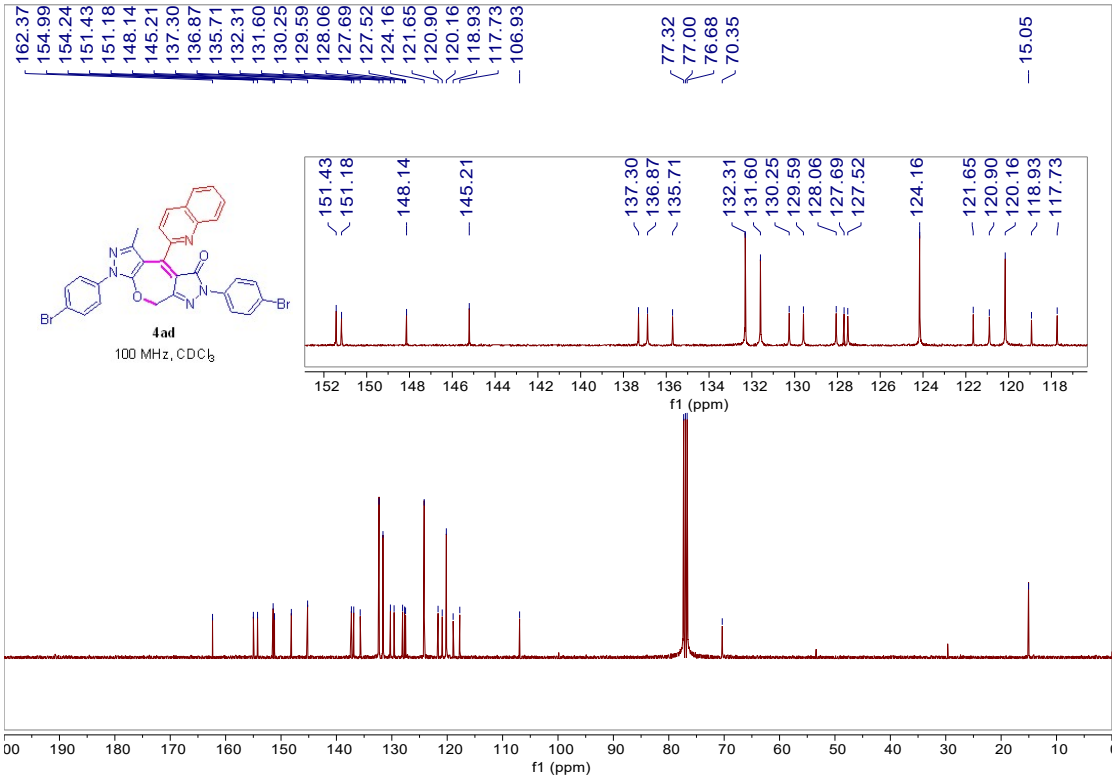
155.00
154.28
151.39
151.18
148.15
145.18
136.86
135.22
133.72
130.24
129.97
129.59
129.34
128.65
128.05
127.70
127.51
123.92
120.92
119.89
118.93
106.89
77.32
77.00
76.68
70.34
15.04
4ac
100 MHz, CDCl3
f1 (ppm)


8.368
8.347
8.161
8.139
7.947
7.927
7.800
7.783
7.762
7.740
7.717
7.659
7.641
7.618
7.607
7.586
7.573
7.552
7.411
7.388
7.260
5.290
5.277
1.342
4ad
400 MHz, CDCl3
1.01
1.02
1.06
1.16
2.04
1.28
3.90
0.94
1.98
2.07
2.99
f1 (ppm)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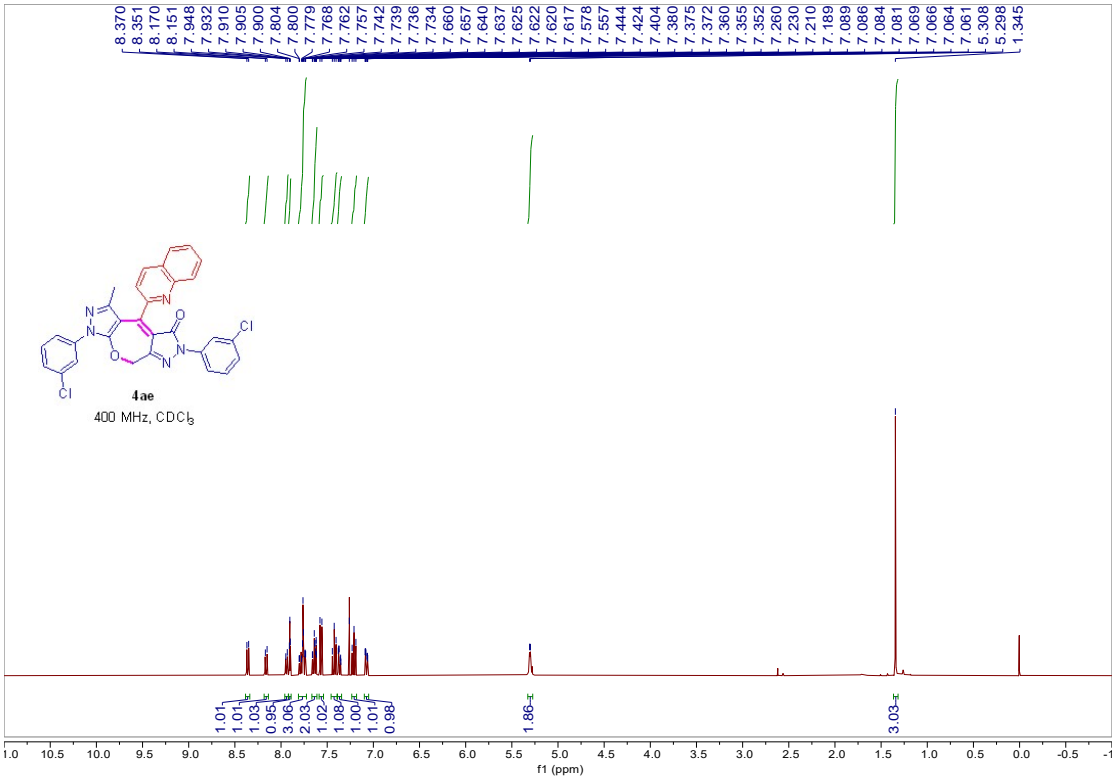
154.24
151.43
151.18
148.14
145.21
137.30
136.87
135.71
132.31
131.60
130.25
129.59
128.06
127.69
127.52
124.16
121.65
120.90
120.16
118.93
117.73
106.93
77.32
77.00
76.68
70.35
15.05
4ad
100 MHz, CDCl3
f1 (ppm)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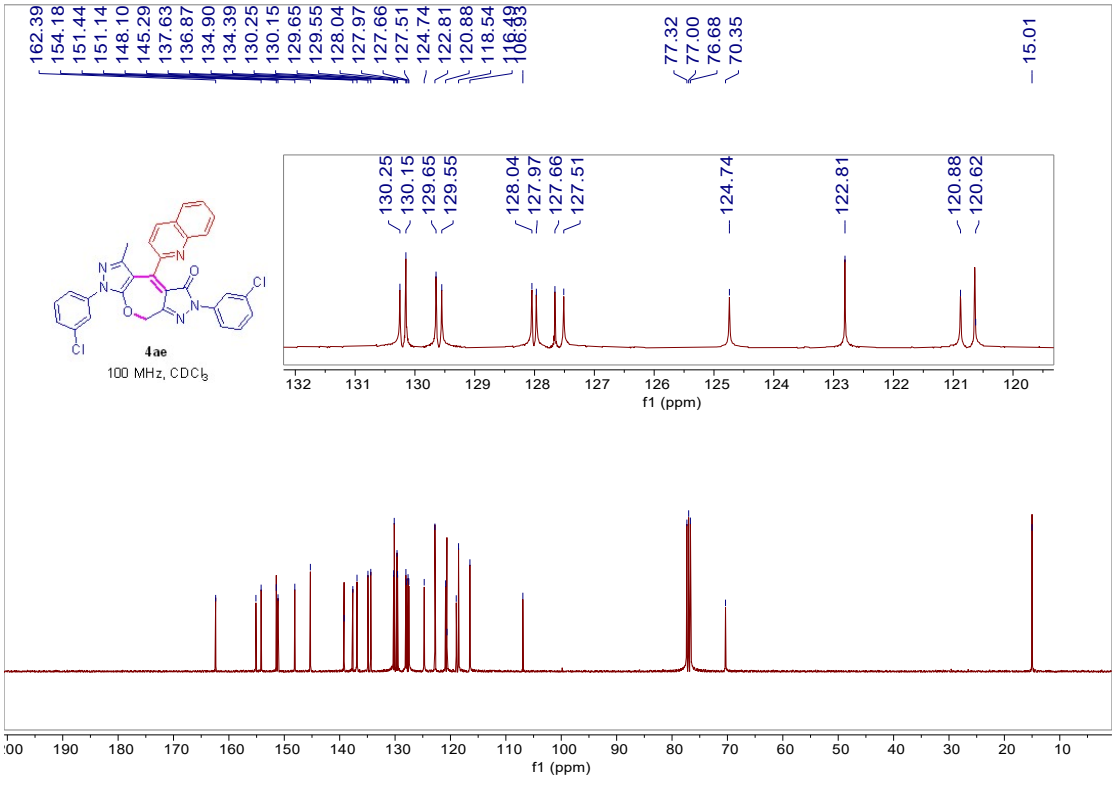
8.151
7.948
7.932
7.910
7.905
7.900
7.804
7.800
7.779
7.768
7.762
7.757
7.742
7.739
7.736
7.734
7.660
7.657
7.640
7.637
7.625
7.622
7.620
7.617
7.578
7.557
7.444
7.424
7.404
7.380
7.375
7.372
7.360
7.355
7.352
7.260
7.230
7.210
7.189
7.089
7.086
7.084
7.081
7.069
7.066
7.064
7.061
5.308
5.298
1.345
4ae
400 MHz, CDCl3
1.01
1.01
1.03
0.95
3.06
2.03
1.02
1.08
1.00
1.01
0.98
1.86
3.03
f1 (ppm)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151.44
151.14
148.10
145.29
137.63
136.87
134.90
134.39
130.25
130.15
129.65
129.55
128.04
127.97
127.66
127.51
124.74
122.81
120.88
118.54
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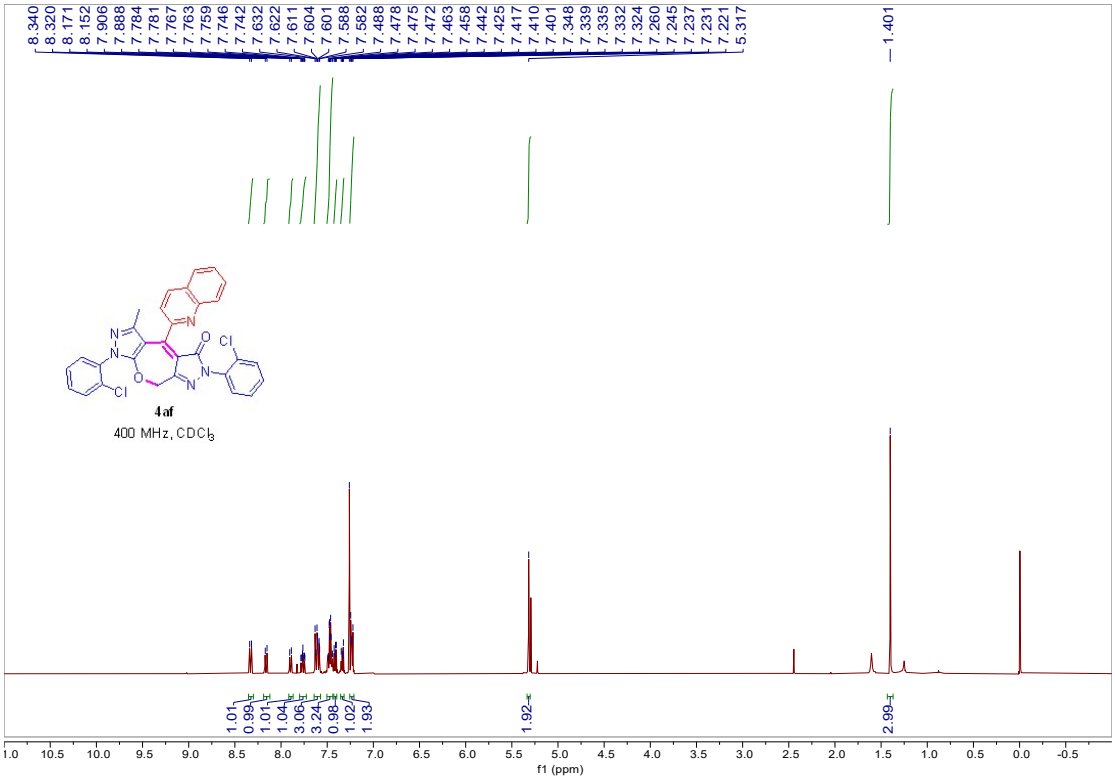
106.93
77.32
77.00
76.68
70.35
15.01
4ae
100 MHz, CDCl3
f1 (ppm)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8.152
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7.888
7.784
7.781
7.767
7.763
7.759
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7.742
7.632
7.622
7.611
7.604
7.601
7.588
7.582
7.488
7.478
7.475
7.472
7.463
7.458
7.442
7.425
7.417
7.410
7.401
7.348
7.339
7.335
7.332
7.324
7.260
7.245
7.237
7.231
7.221
5.317
1.401
4af
400 MHz, CDCl3
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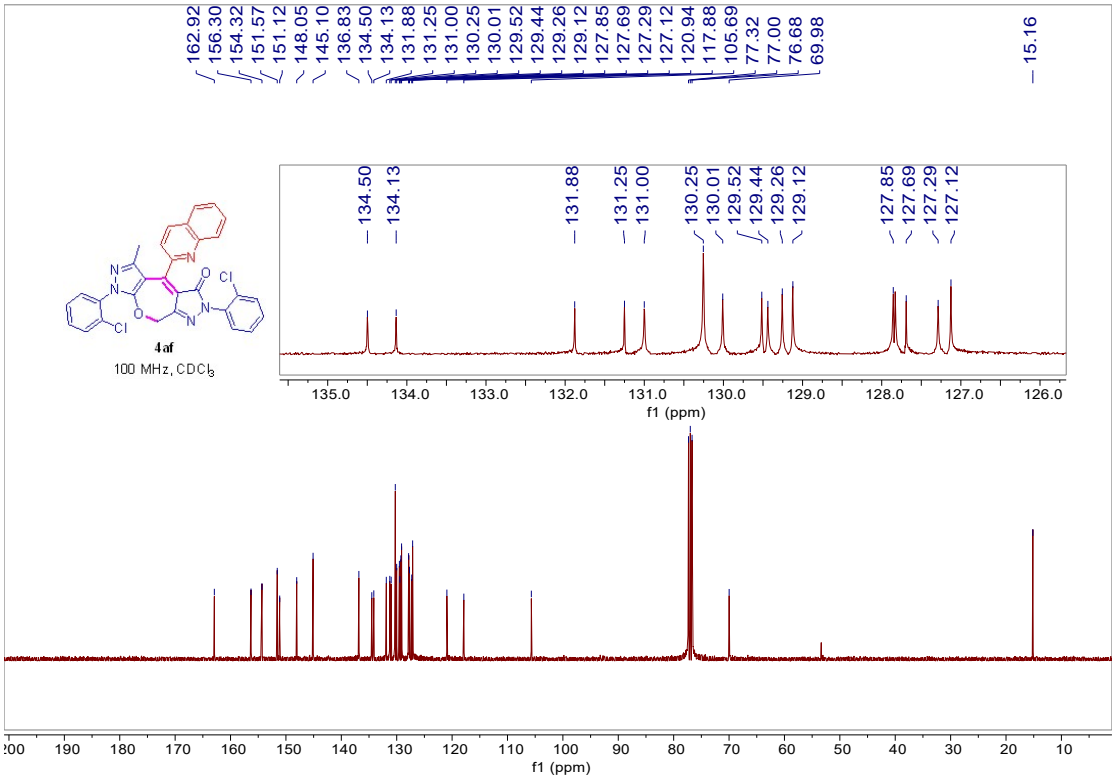
0.99
1.01
1.04
3.06
3.24
0.98
1.02
1.93
1.92
2.99
f1 (ppm)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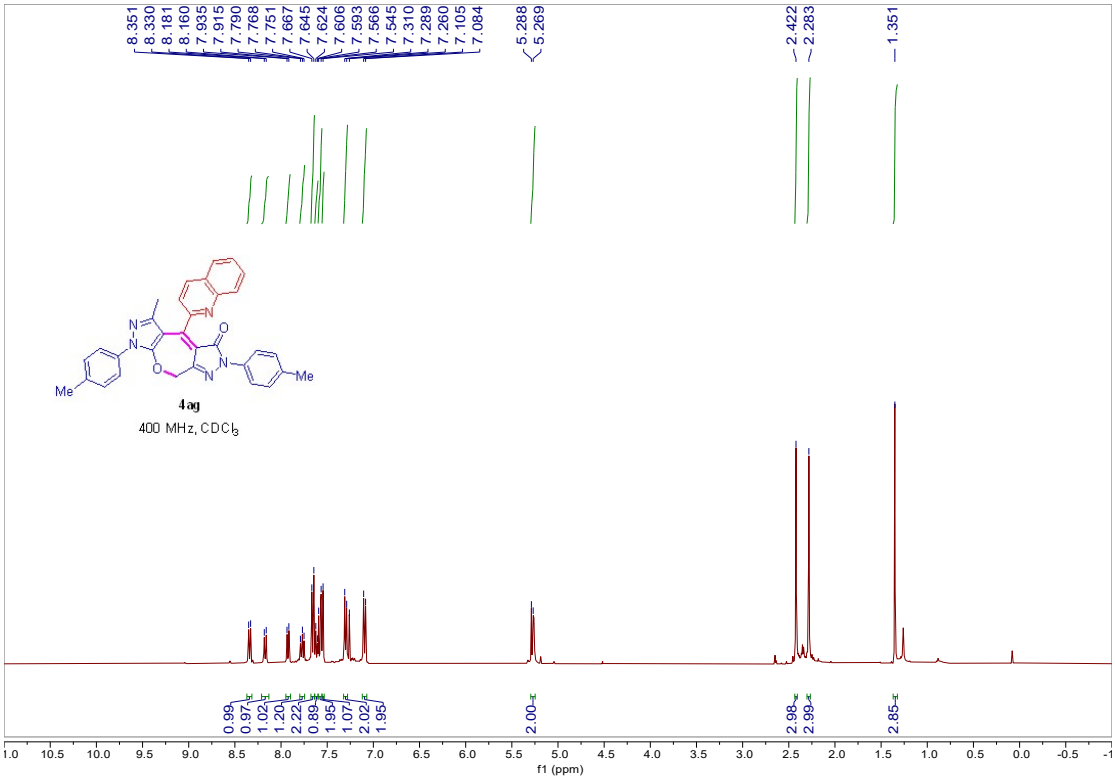
154.32
151.57
151.12
148.05
145.10
136.83
134.50
134.13
131.88
131.25
131.00
130.25
130.01
129.52
129.44
129.26
129.12
127.85
127.69
127.29
127.12
120.94
117.88
105.69
77.32
77.00
76.68
69.98
15.16
4af
100 MHz, CDCl3
f1 (ppm)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8.160
7.935
7.915
7.790
7.768
7.751
7.667
7.645
7.624
7.606
7.593
7.566
7.545
7.310
7.289
7.260
7.105
7.084
5.288
5.269
2.422
2.283
1.351
Me
Me
4ag
400 MHz, CDCl3
0.99
0.97
1.02
1.20
2.22
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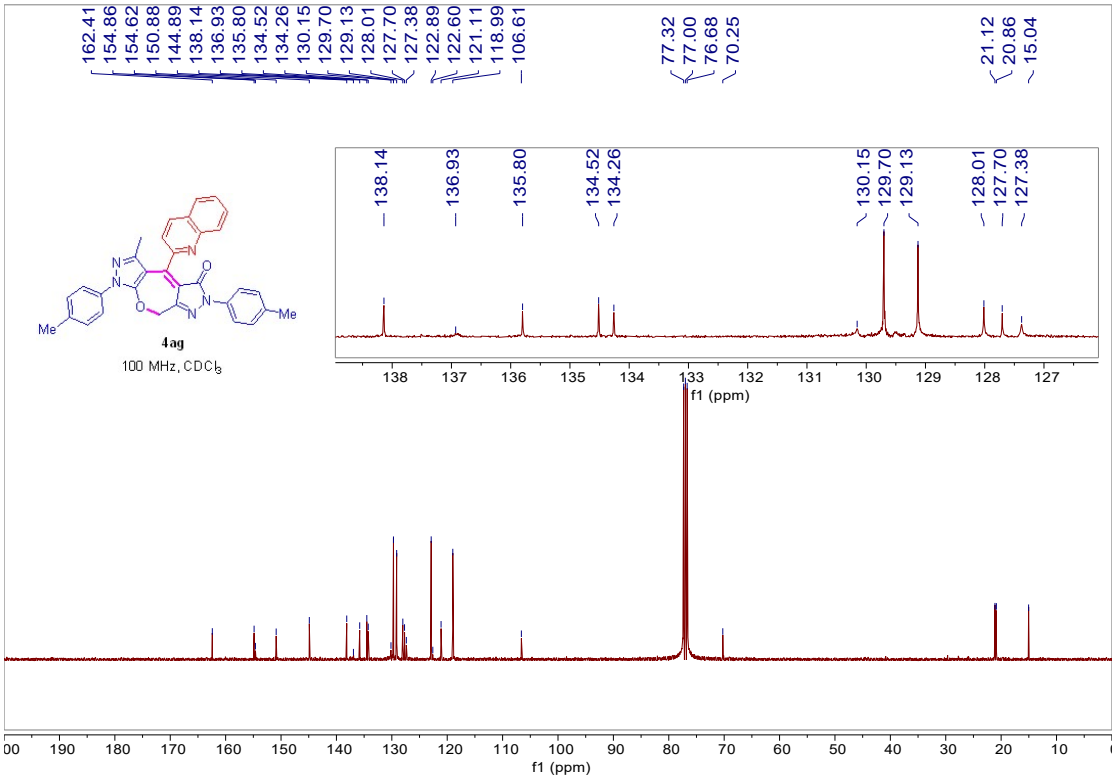
1.95
1.07
2.02
1.95
2.00
2.98
2.99
2.85
f1 (ppm)


162.41
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136.93
135.80
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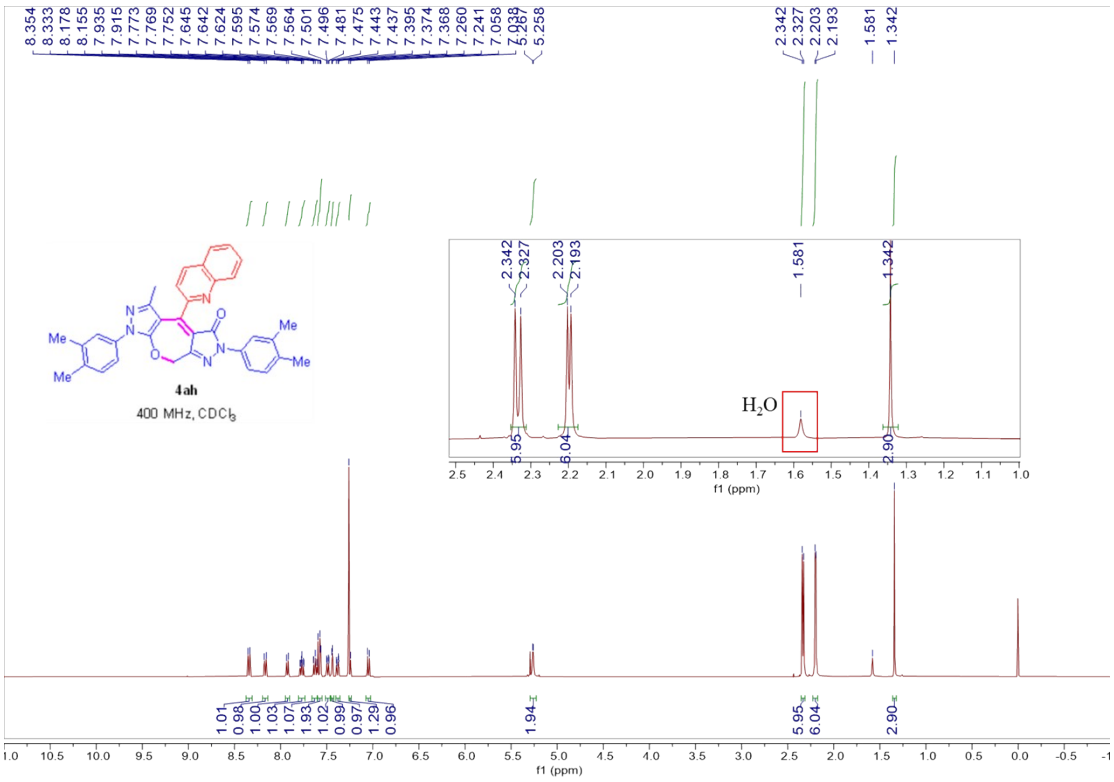
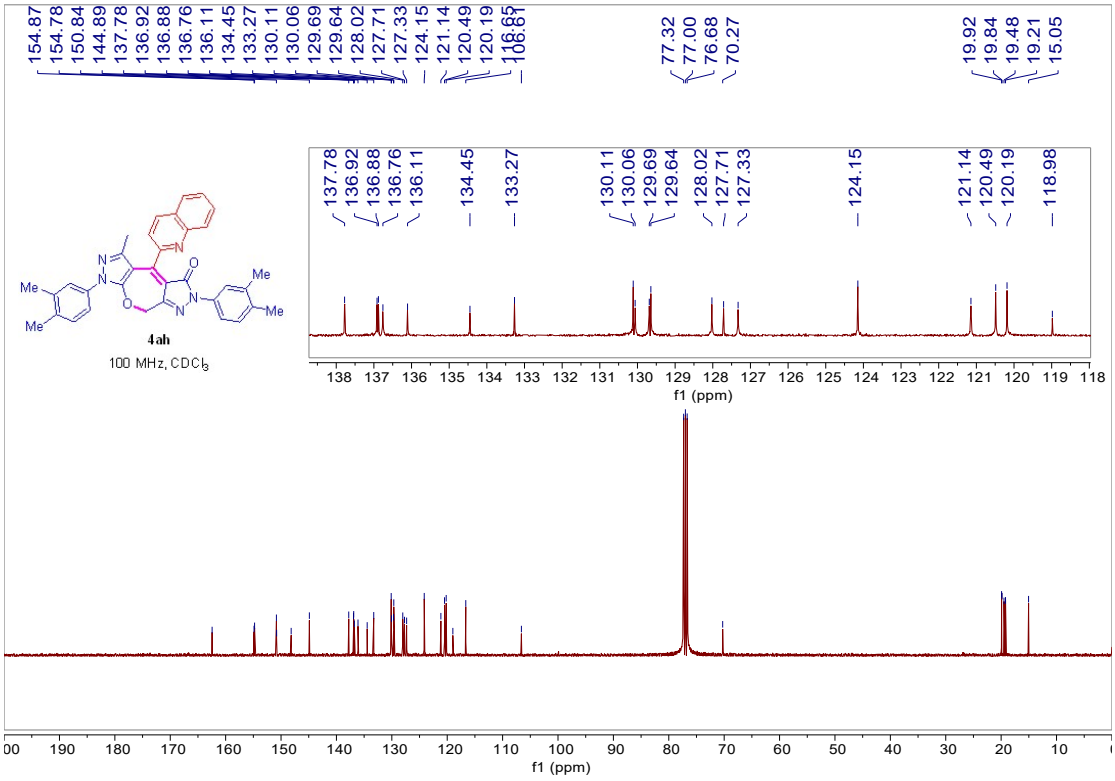
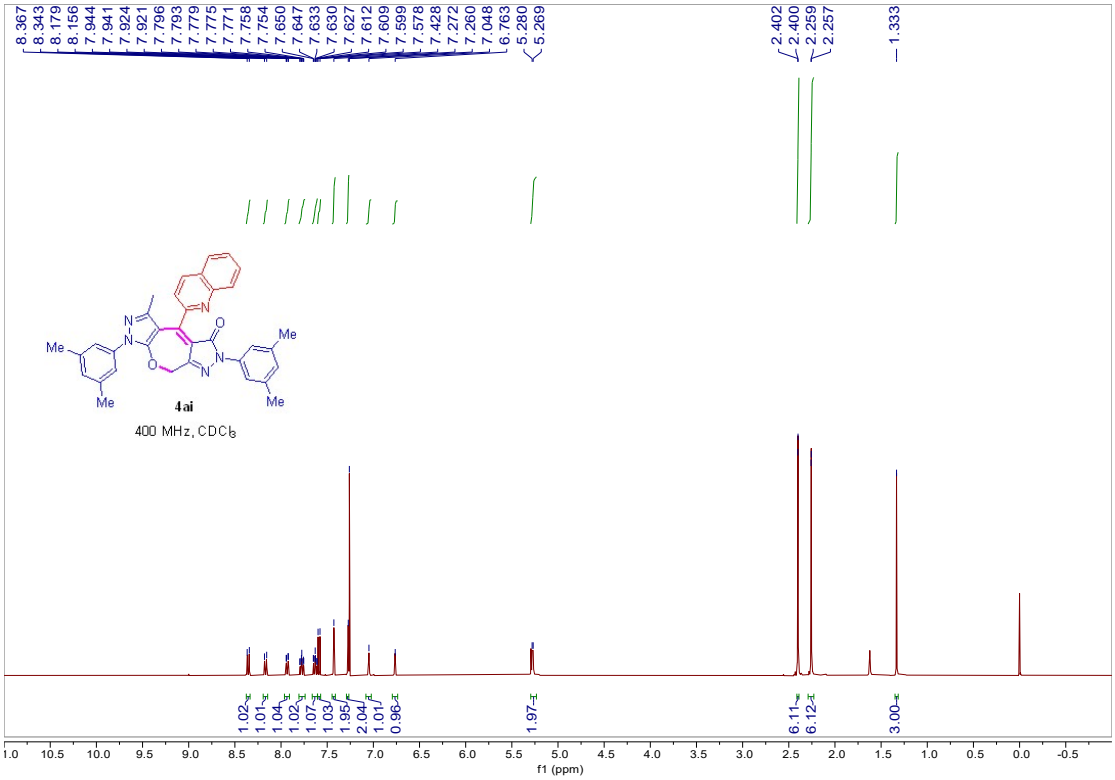
134.26
130.15
129.70
129.13
128.01
127.70
127.38
122.89
122.60
121.11
118.99
106.61
77.32
77.00
76.68
70.25
21.12
20.86
15.04
Me
Me
4ag
100 MHz, CDCl3
f1 (ppm)


4ah
400 MHz, CDCl3
H2O
f1 (ppm)


4ah
100 MHz, CDCl3
f1 (ppm)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8.179
8.156
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7.941
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7.921
7.796
7.793
7.779
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7.771
7.758
7.754
7.650
7.647
7.633
7.630
7.627
7.612
7.609
7.599
7.578
7.428
7.272
7.260
7.048
6.763
5.280
5.269
2.402
2.400
2.259
2.257
1.333
Me
Me
Me
Me
4ai
400 MHz, CDCl3
1.02
1.01
1.04
1.02
1.07
1.03
1.95
2.04
1.01
0.96
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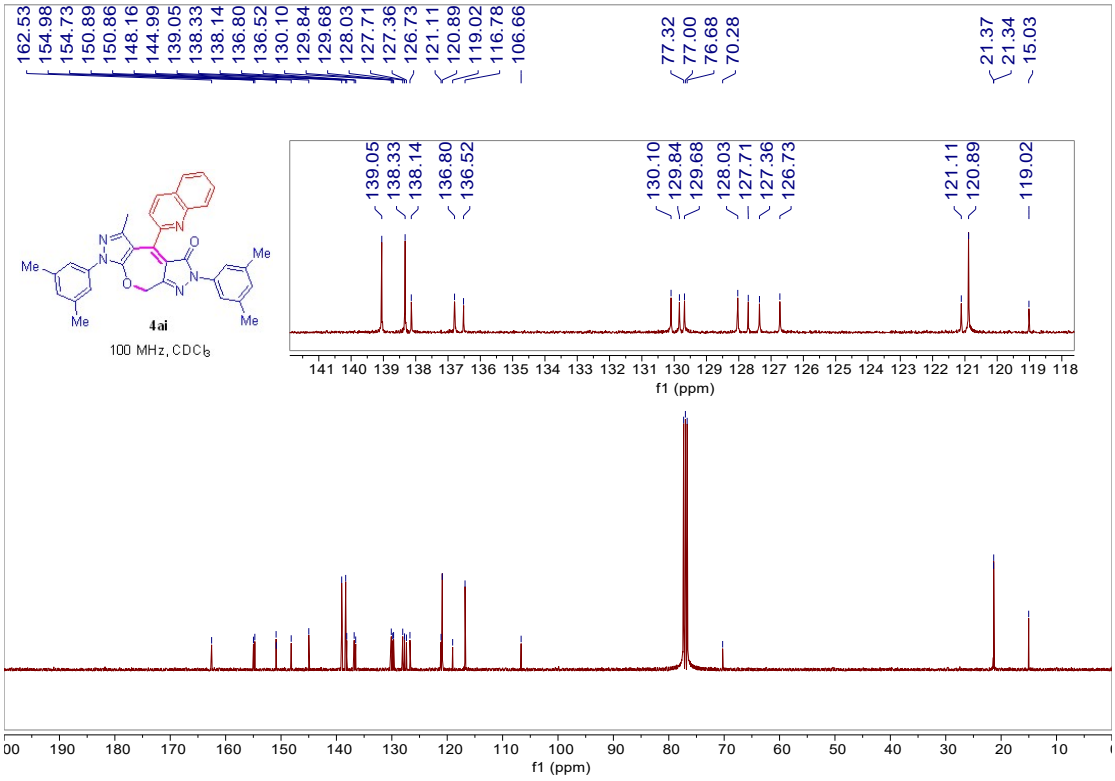
6.11
6.12
3.00
f1 (ppm)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139.05
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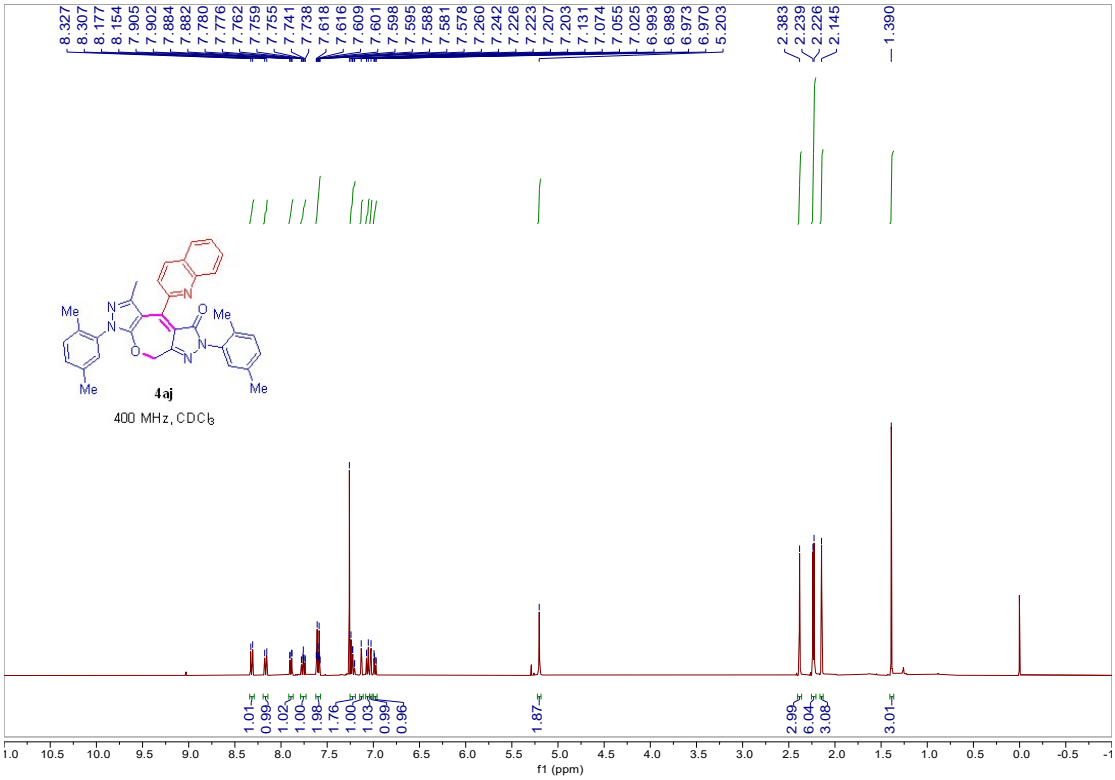
130.10
129.84
129.68
128.03
127.71
127.36
126.73
121.11
120.89
119.02
116.78
106.66
77.32
77.00
76.68
70.28
21.37
21.34
15.03
Me
Me
Me
Me
4ai
100 MHz, CDCl3
f1 (ppm)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7.776
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7.755
7.741
7.738
7.618
7.616
7.609
7.601
7.598
7.595
7.588
7.581
7.578
7.260
7.242
7.226
7.223
7.207
7.203
7.131
7.074
7.055
7.025
6.993
6.989
6.973
6.970
5.203
2.383
2.239
2.226
2.145
1.390
Me
Me
Me
Me
4aj
400 MHz, CDCl3
1.01
0.99
1.02
1.00
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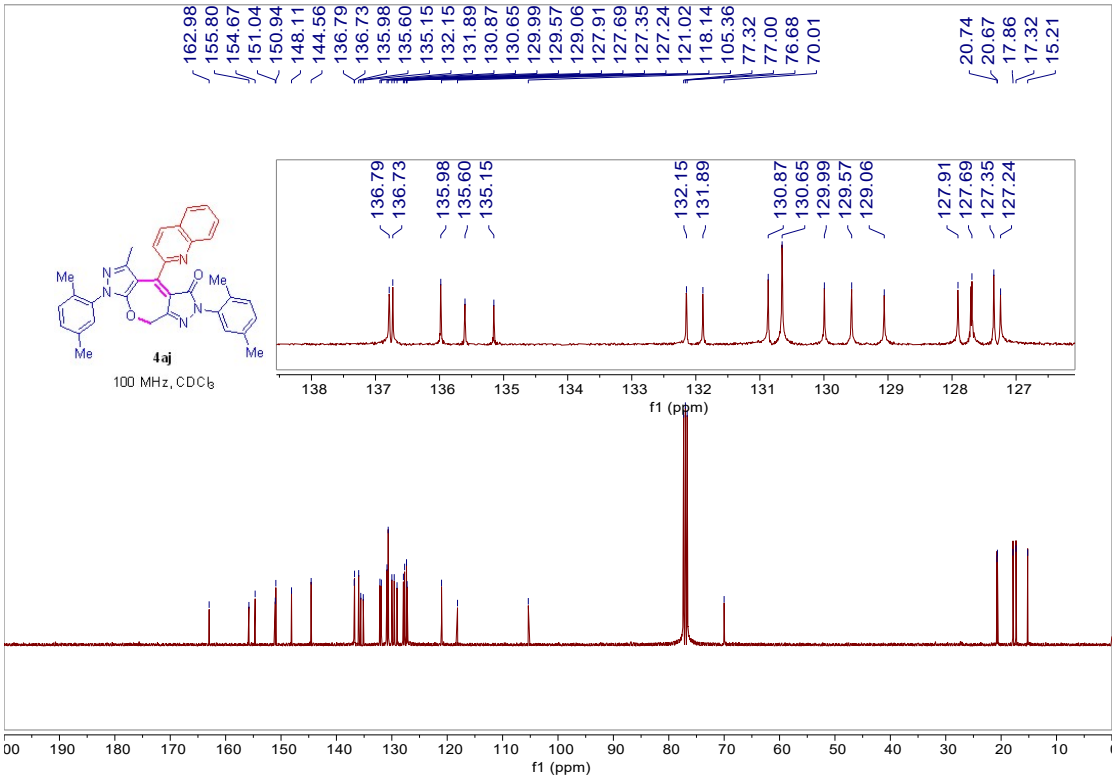
1.03
0.99
0.96
1.87
2.99
6.04
3.08
3.01
f1 (ppm)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136.79
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135.98
135.60
135.15
132.15
131.89
130.87
130.65
129.99
129.57
129.06
127.91
127.69
127.35
127.24
121.02
118.14
105.36
77.32
77.00
76.68
70.01
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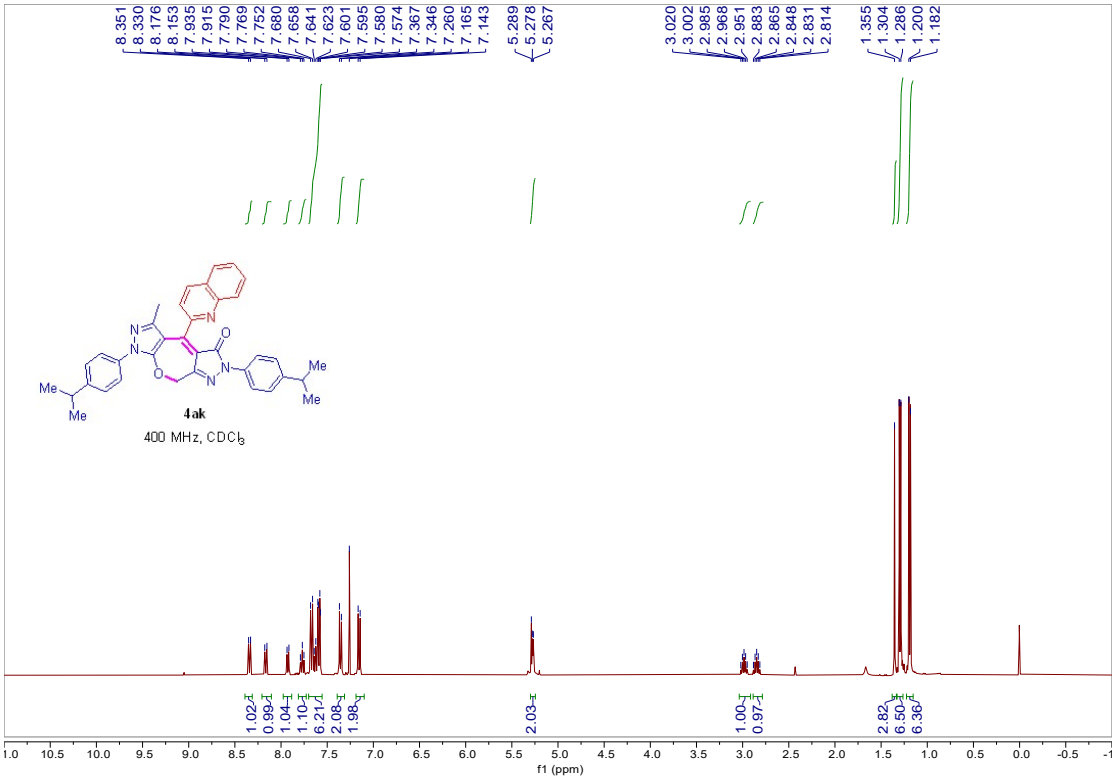
17.86
17.32
15.21
Me
Me
Me
Me
4aj
100 MHz, CDCl3
f1 (ppm)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8.153
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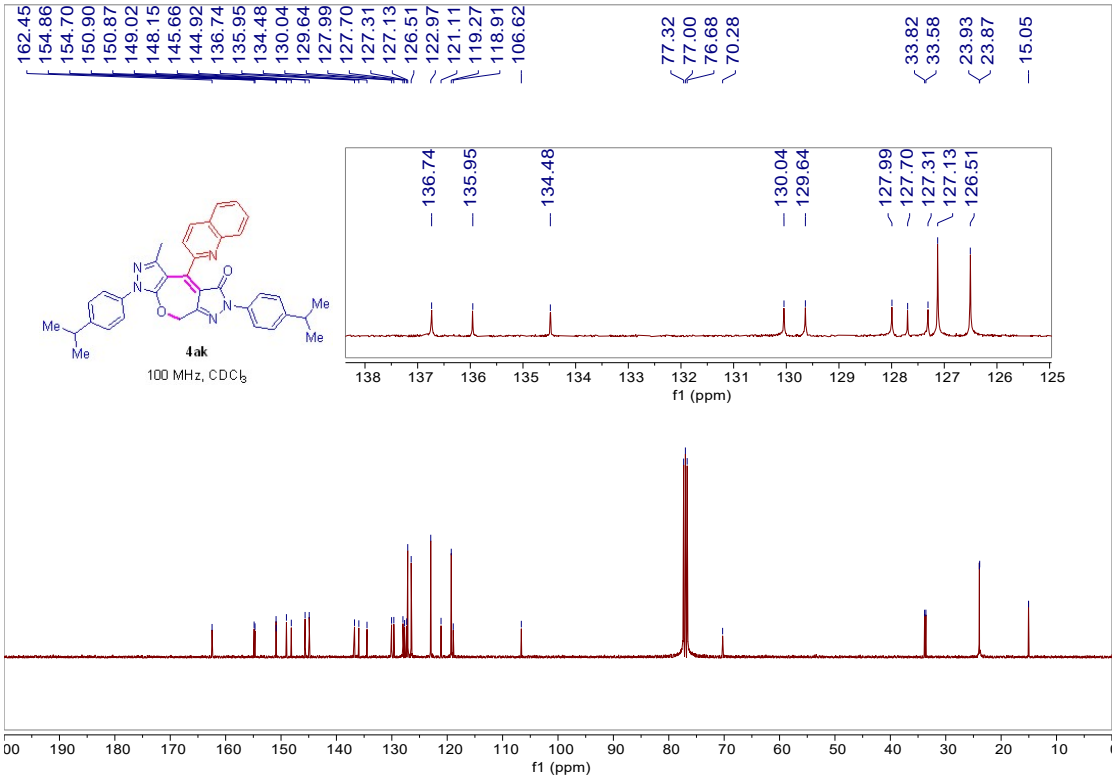
7.915
7.790
7.769
7.752
7.680
7.658
7.641
7.623
7.601
7.595
7.580
7.574
7.367
7.346
7.260
7.165
7.143
5.289
5.278
5.267
3.020
3.002
2.985
2.968
2.951
2.883
2.865
2.848
2.831
2.814
1.355
1.304
1.286
1.200
1.182
Me
Me
Me
Me
4ak
400 MHz, CDCl3
1.02
0.99
1.04
1.10
6.21
2.08
1.98
2.03
1.00
0.97
2.82
6.50
6.36
f1 (ppm)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145.66
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135.95
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129.64
127.99
127.70
127.31
127.13
126.51
122.97
121.11
119.27
118.91
106.62
77.32
77.00
76.68
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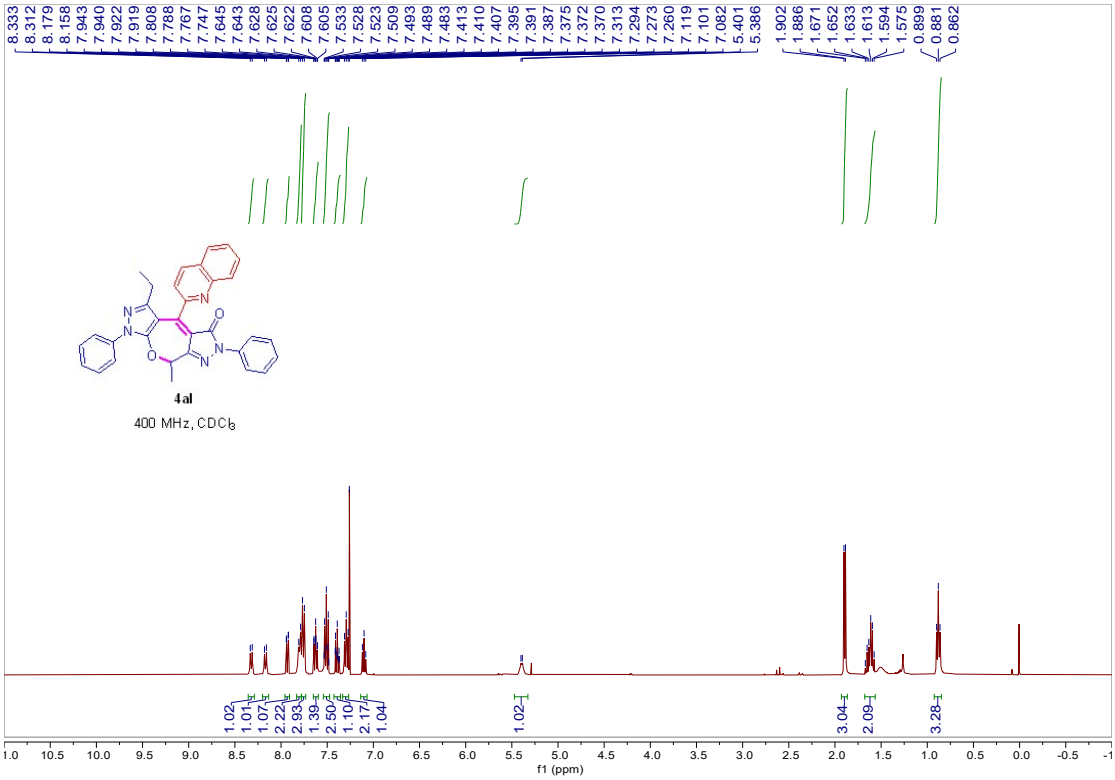
23.93
23.87
15.05
Me
Me
Me
Me
4ak
100 MHz, CDCl3
f1 (ppm)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7.767
7.747
7.645
7.643
7.628
7.625
7.622
7.608
7.605
7.533
7.528
7.523
7.509
7.493
7.489
7.483
7.413
7.410
7.407
7.395
7.391
7.387
7.375
7.372
7.370
7.313
7.294
7.273
7.260
7.119
7.101
7.082
5.401
5.386
1.902
1.886
1.671
1.652
1.633
1.613
1.594
1.575
0.899
0.881
0.862
4al
400 MHz, CDCl3
1.02
1.01
1.07
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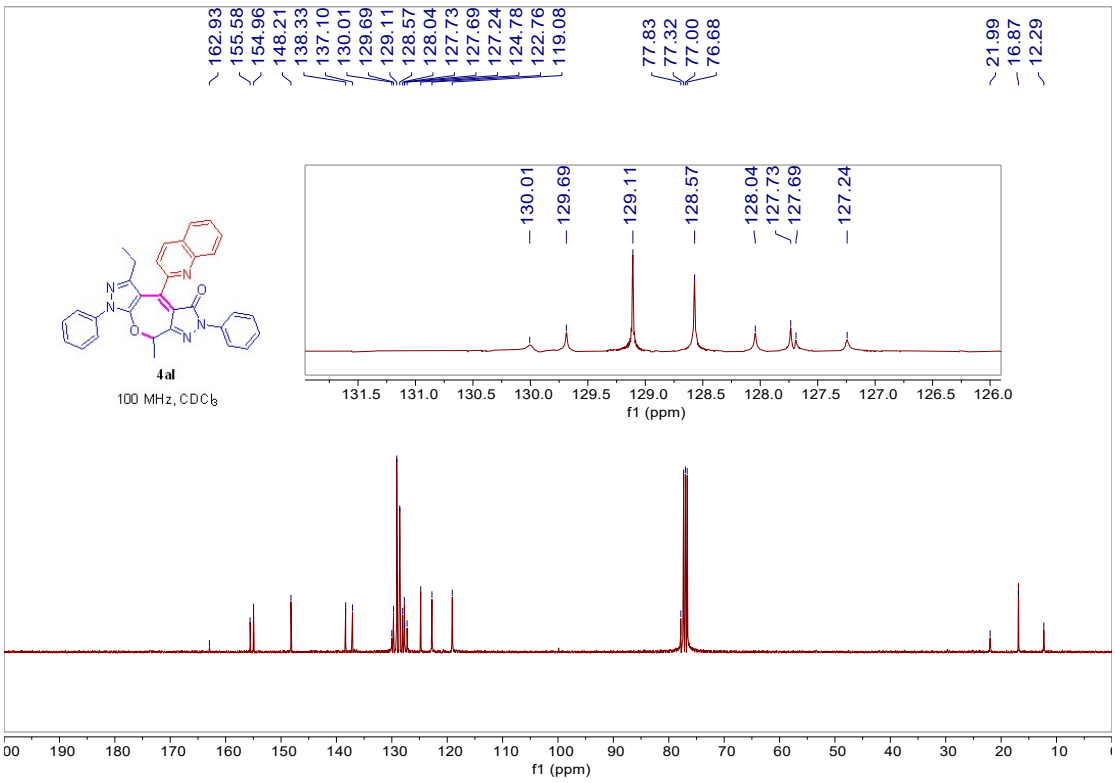
2.93
1.39
2.50
1.10
2.17
1.04
1.02
3.04
2.09
3.28
f1 (ppm)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154.96
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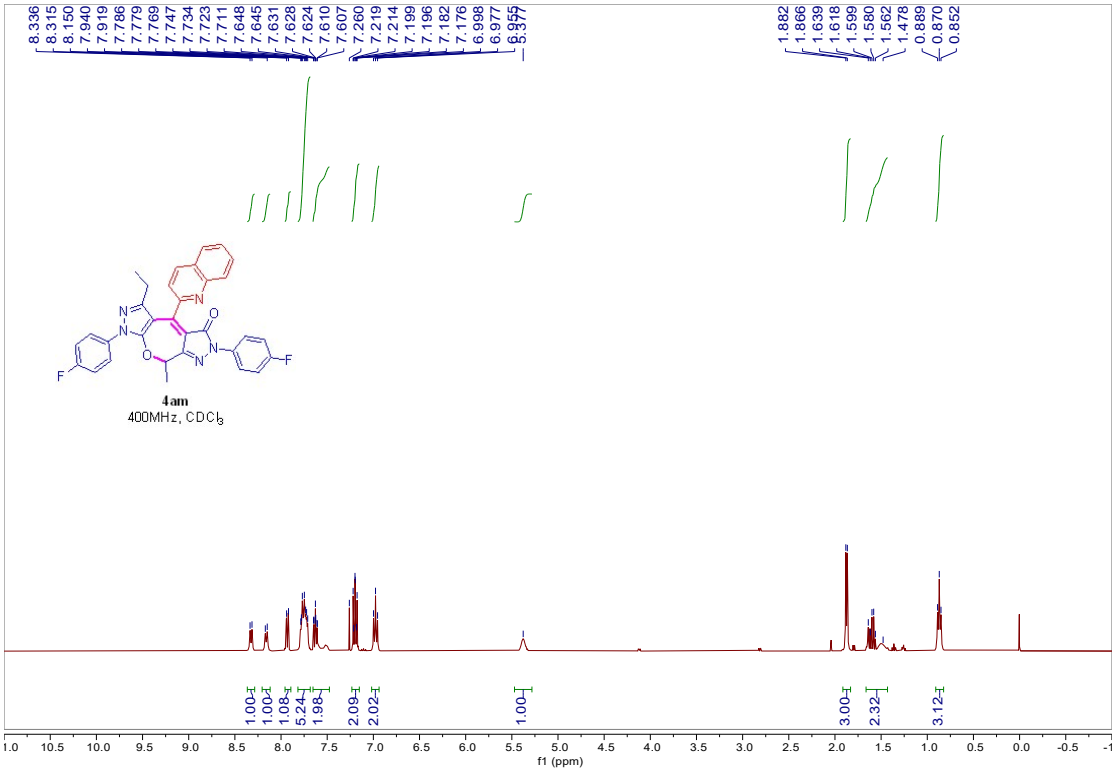
137.10
130.01
129.69
129.11
128.57
128.04
127.73
127.69
127.24
124.78
122.76
119.08
77.83
77.32
77.00
76.68
21.99
16.87
12.29
130.01
129.69
129.11
128.57
128.04
127.73
127.69
127.24
4al
100 MHz, CDCl3
f1 (ppm)
f1 (ppm)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7.769
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7.734
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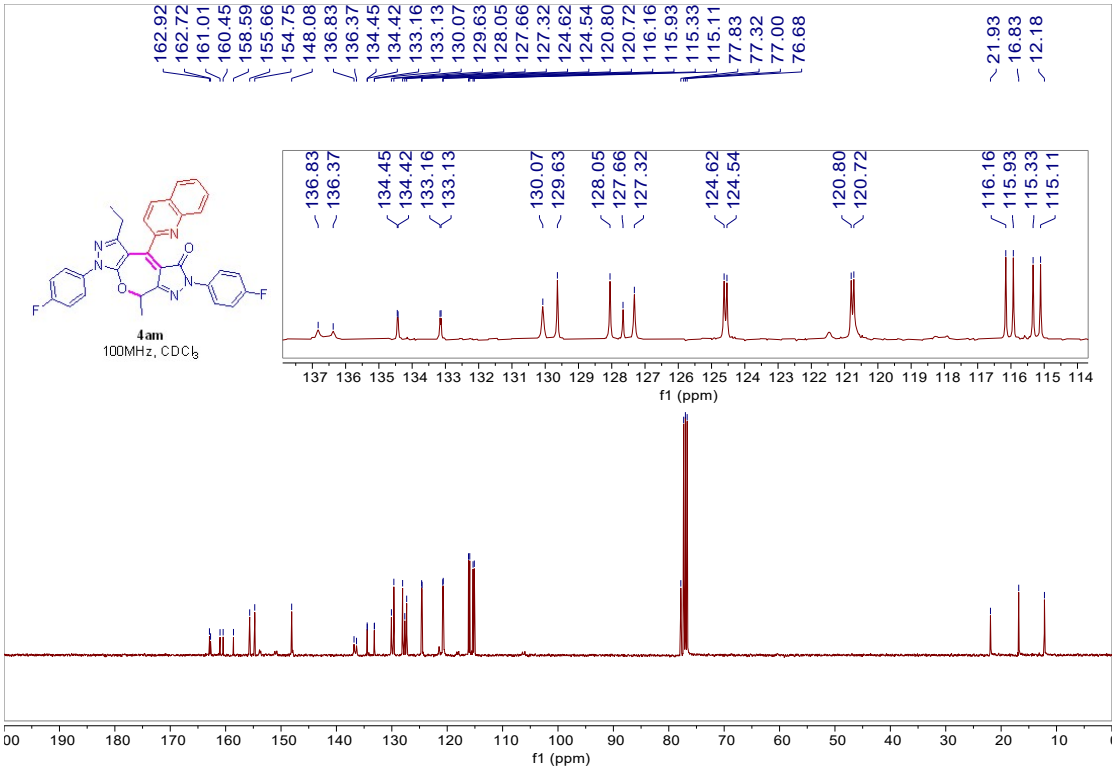
7.711
7.648
7.645
7.631
7.628
7.624
7.610
7.607
7.260
7.219
7.214
7.199
7.196
7.182
7.176
6.998
6.977
6.955
5.377
1.882
1.866
1.639
1.618
1.599
1.580
1.562
1.478
0.889
0.870
0.852
4am
400MHz, CDCl3
1.00
1.00
1.08
5.24
1.98
2.09
2.02
1.00
3.00
2.32
3.12
f1 (ppm)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160.45
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155.66
154.75
148.08
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136.37
134.45
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133.16
133.13
130.07
129.63
128.05
127.66
127.32
124.62
124.54
120.80
120.72
116.16
115.93
115.33
115.11
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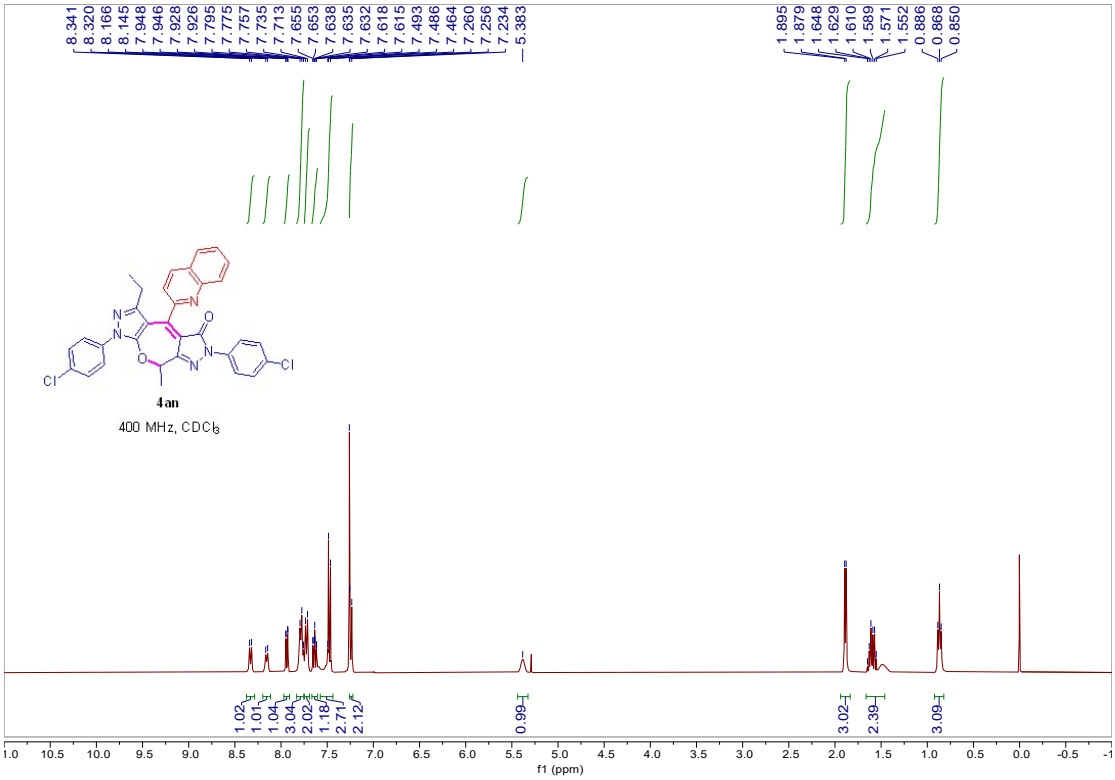
77.32
77.00
76.68
21.93
16.83
12.18
4am
100MHz, CDCl3
f1 (ppm)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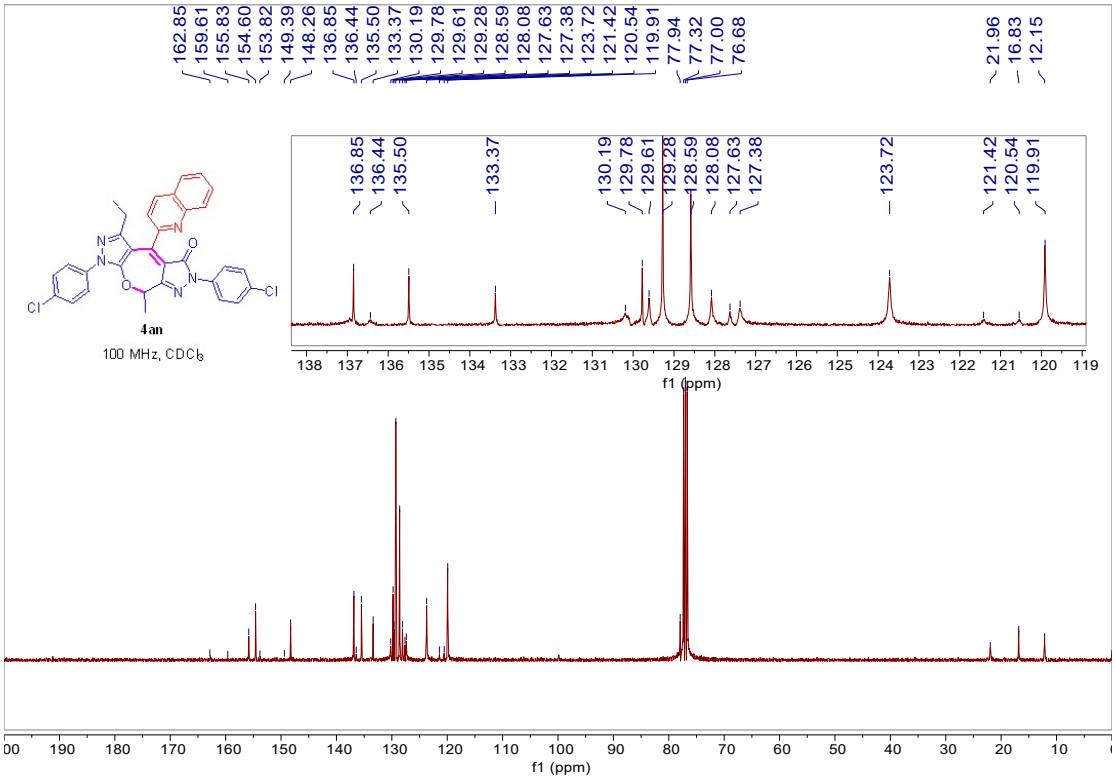
7.795
7.775
7.757
7.735
7.713
7.655
7.653
7.638
7.635
7.632
7.618
7.615
7.493
7.486
7.464
7.260
7.256
7.234
5.383
1.895
1.879
1.648
1.629
1.610
1.589
1.571
1.552
0.886
0.868
0.850
4an
400 MHz, CDCl3
1.02
1.01
1.04
3.04
2.02
1.18
2.71
2.12
0.99
3.02
2.39
3.09
f1 (ppm)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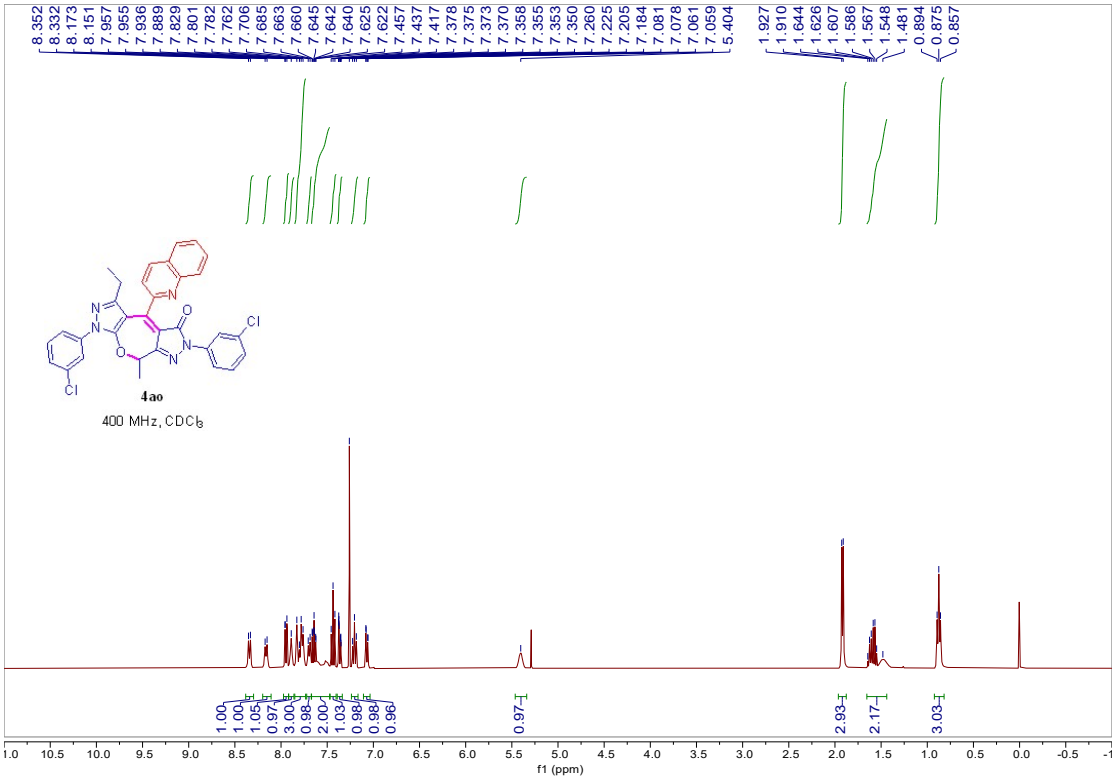
154.60
153.82
149.39
148.26
136.85
136.44
135.50
133.37
130.19
129.78
129.61
129.28
128.59
128.08
127.63
127.38
123.72
121.42
120.54
119.91
77.94
77.32
77.00
76.68
21.96
16.83
12.15
4an
100 MHz, CDCl3
f1 (ppm)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7.706
7.685
7.663
7.660
7.645
7.642
7.640
7.625
7.622
7.457
7.437
7.417
7.378
7.375
7.373
7.370
7.358
7.355
7.353
7.350
7.260
7.225
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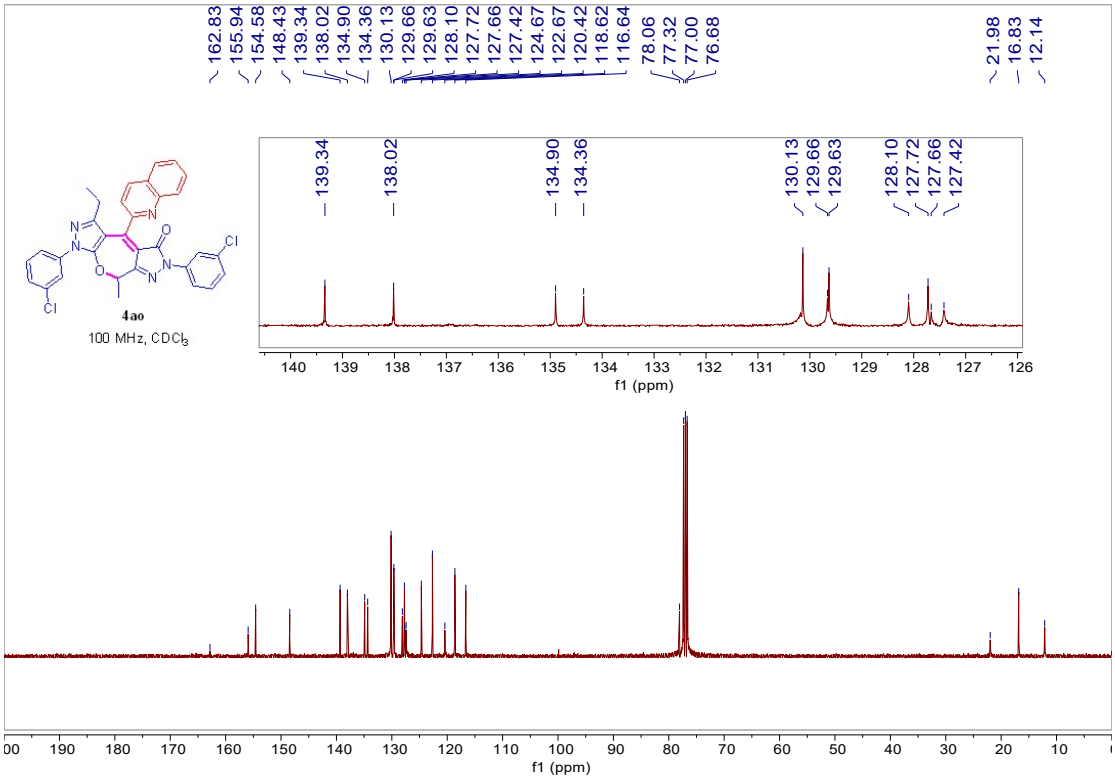
7.184
7.081
7.078
7.061
7.059
5.404
1.927
1.910
1.644
1.626
1.607
1.586
1.567
1.548
1.481
0.894
0.875
0.857
4ao
400 MHz, CDCl3
1.00
1.00
1.05
0.97
3.00
0.98
2.00
1.03
0.98
0.98
0.96
0.97
2.93
2.17
3.03
f1 (ppm)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134.90
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129.66
129.63
128.10
127.72
127.66
127.42
124.67
122.67
120.42
118.62
116.64
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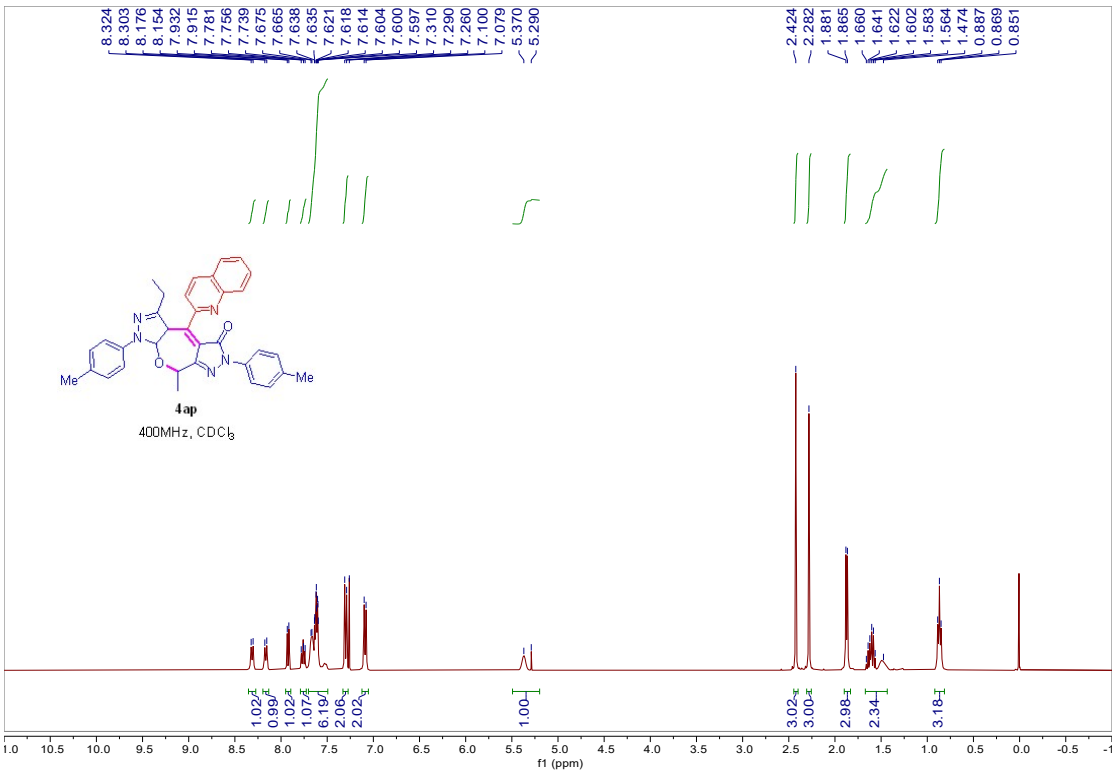
77.00
76.68
21.98
16.83
12.14
4ao
100 MHz, CDCl3
f1 (ppm)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7.675
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7.635
7.621
7.618
7.614
7.604
7.600
7.597
7.310
7.290
7.260
7.100
7.079
5.370
5.290
2.424
2.282
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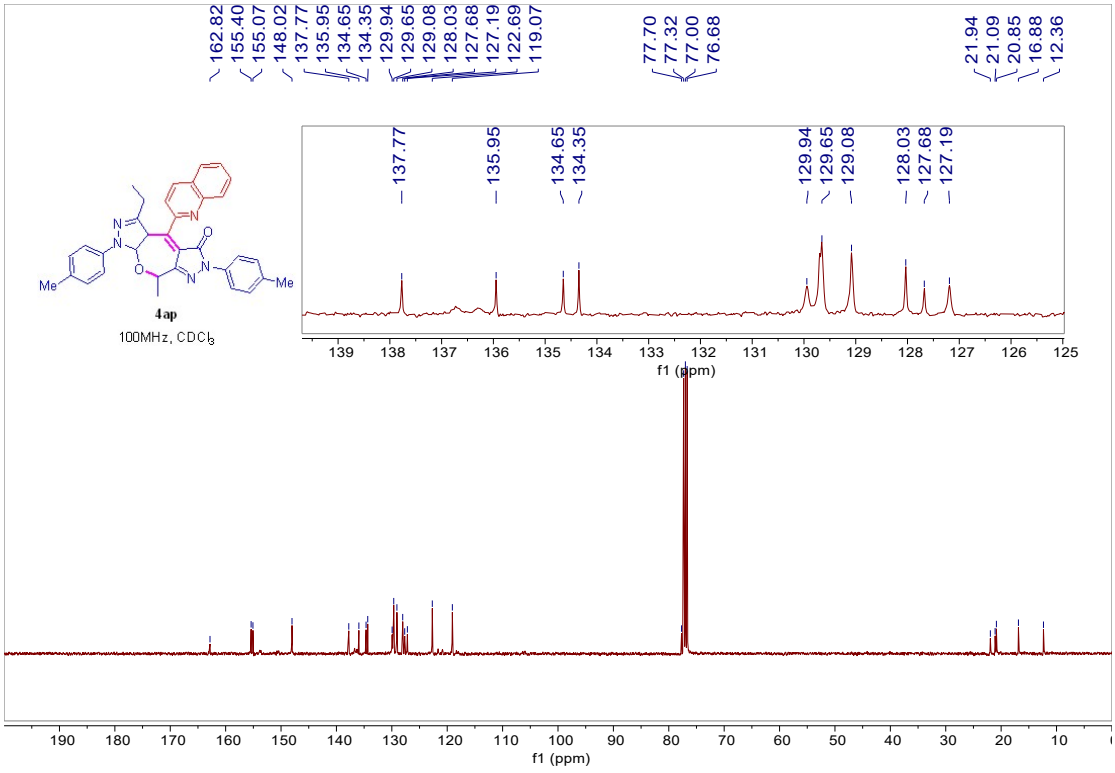
1.865
1.660
1.641
1.622
1.602
1.583
1.564
1.474
0.887
0.869
0.851
Me
Me
4ap
400MHz, CDCl3
1.02
0.99
1.02
1.07
6.19
2.06
2.02
1.00
3.02
3.00
2.98
2.34
3.18
f1 (ppm)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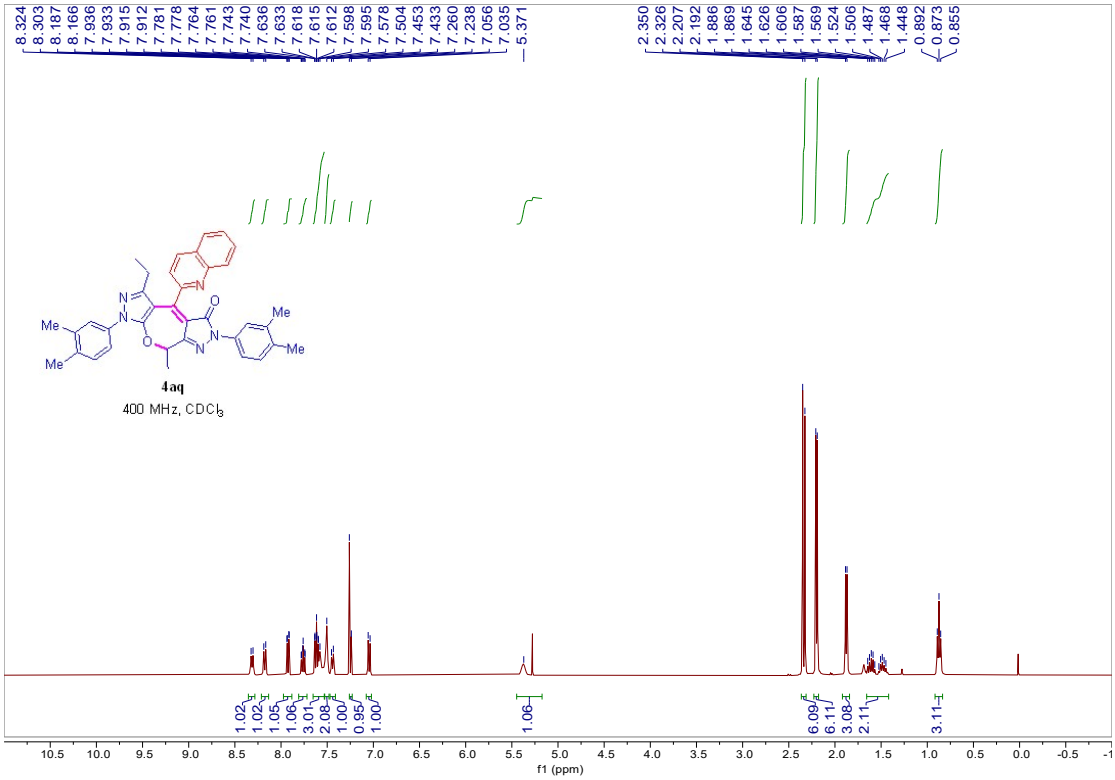
135.95
134.65
134.35
129.94
129.65
129.08
128.03
127.68
127.19
122.69
119.07
77.70
77.32
77.00
76.68
21.94
21.09
20.85
16.88
12.36
Me
Me
4ap
100MHz, CDCl3
f1 (ppm)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7.743
7.740
7.636
7.633
7.618
7.615
7.612
7.598
7.595
7.578
7.504
7.453
7.433
7.260
7.238
7.056
7.035
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2.350
2.326
2.207
2.192
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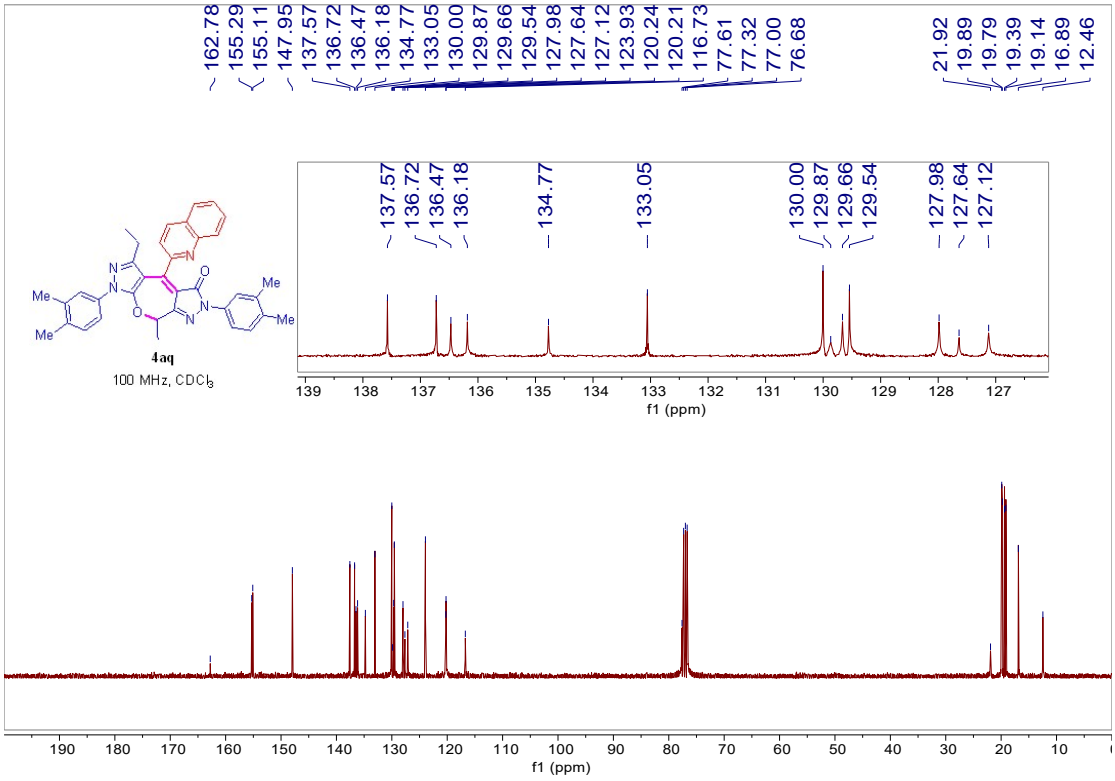
1.869
1.645
1.626
1.606
1.587
1.569
1.524
1.506
1.487
1.468
1.448
0.892
0.873
0.855
Me
Me
Me
Me
4aq
400 MHz, CDCl3
1.02
1.02
1.05
1.06
3.01
2.08
1.00
0.95
1.00
1.06
6.09
6.11
3.08
2.11
3.11
f1 (ppm)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136.18
134.77
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130.00
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129.66
129.54
127.98
127.64
127.12
123.93
120.24
120.21
116.73
77.61
77.32
77.00
76.68
21.92
19.89
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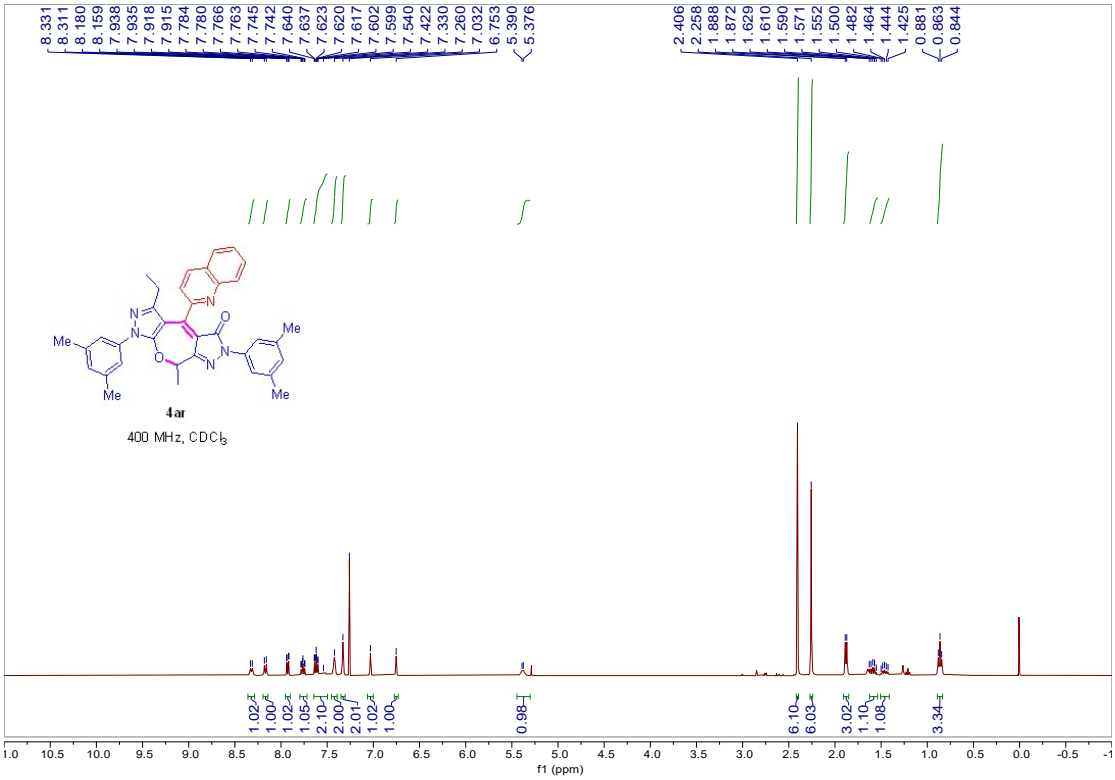
19.14
16.89
12.46
Me
Me
Me
Me
4aq
100 MHz, CDCl3
f1 (ppm)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7.780
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7.745
7.742
7.640
7.637
7.623
7.620
7.617
7.602
7.599
7.540
7.422
7.330
7.260
7.032
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5.376
2.406
2.258
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1.872
1.629
1.610
1.590
1.571
1.552
1.500
1.482
1.464
1.444
1.425
0.881
0.863
0.844
Me
Me
Me
Me
4ar
400 MHz, CDCl3
1.02
1.00
1.02
1.05
2.10
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1.02
1.00
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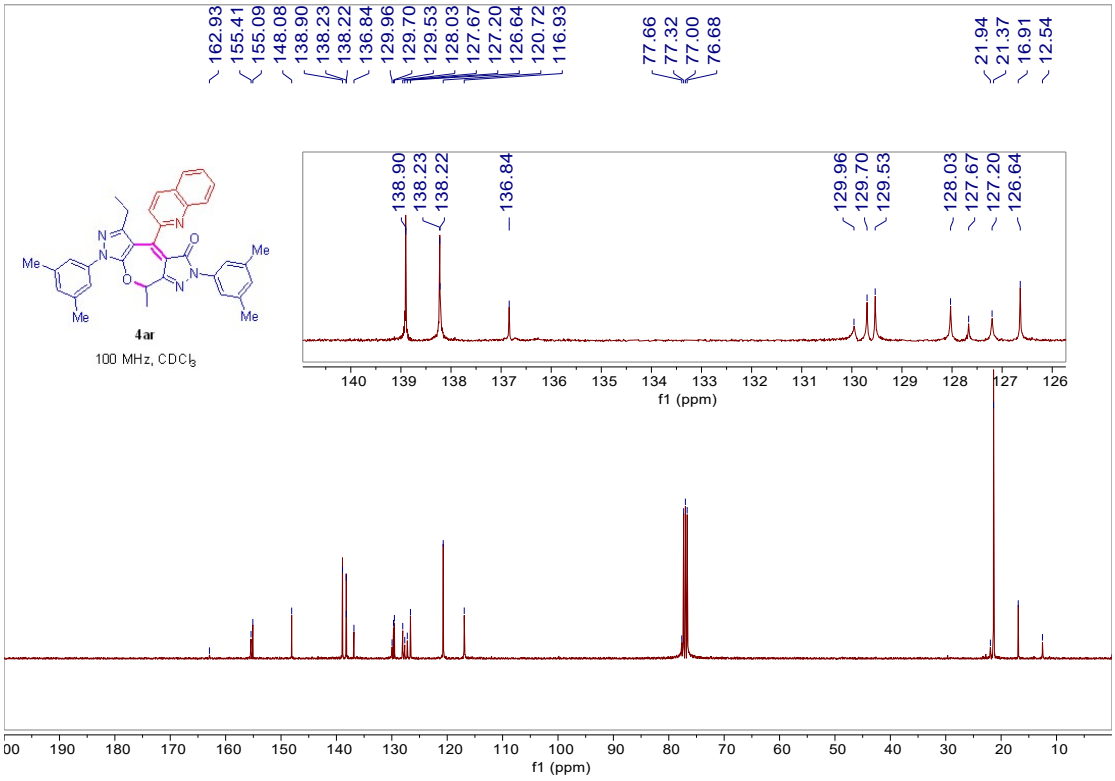
6.03
3.02
1.10
1.08
3.34
f1 (ppm)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136.84
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129.70
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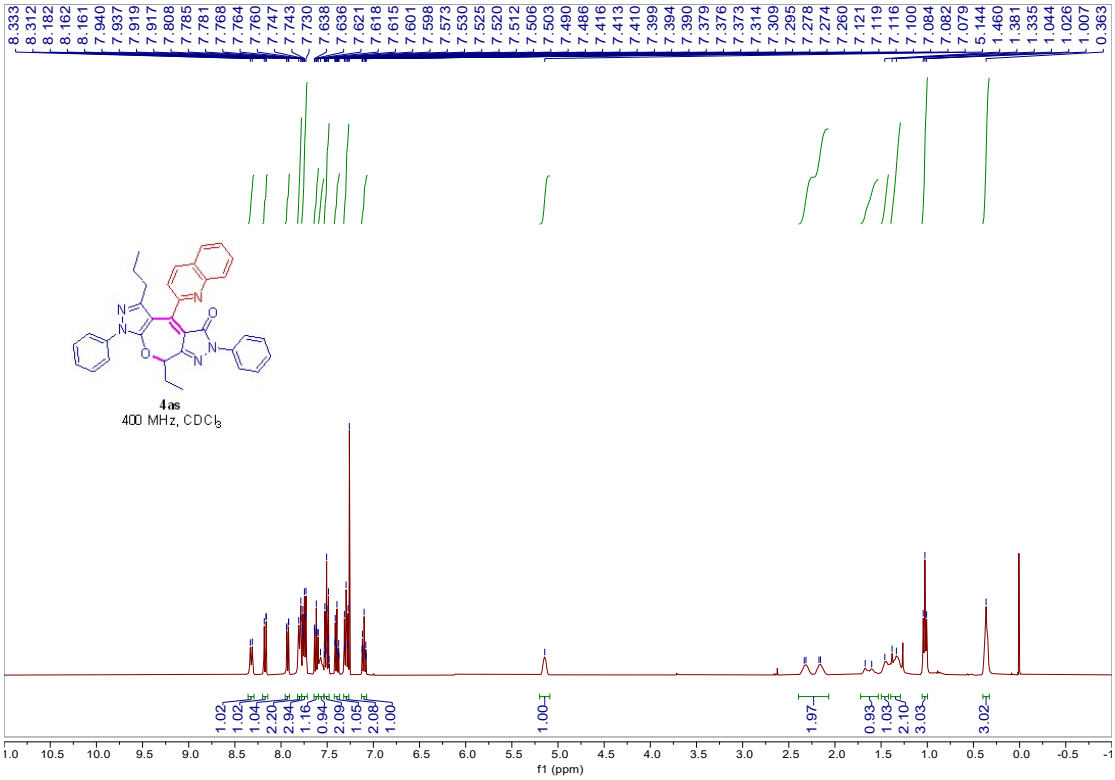
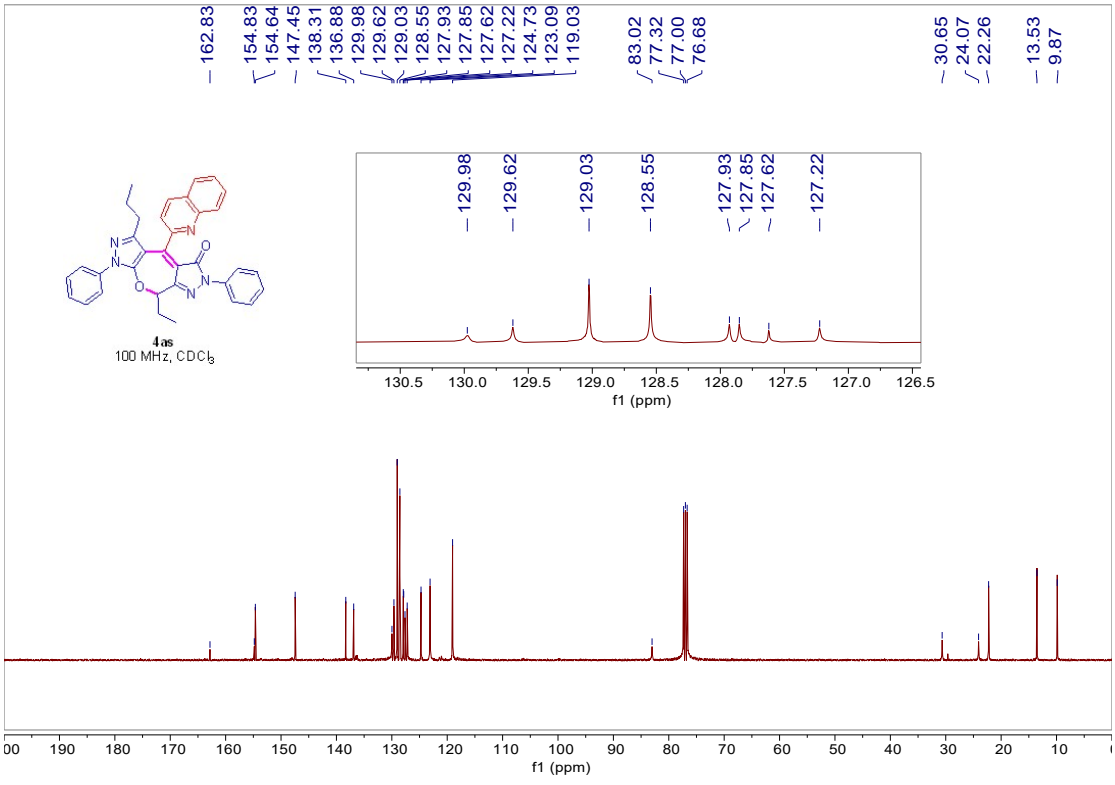
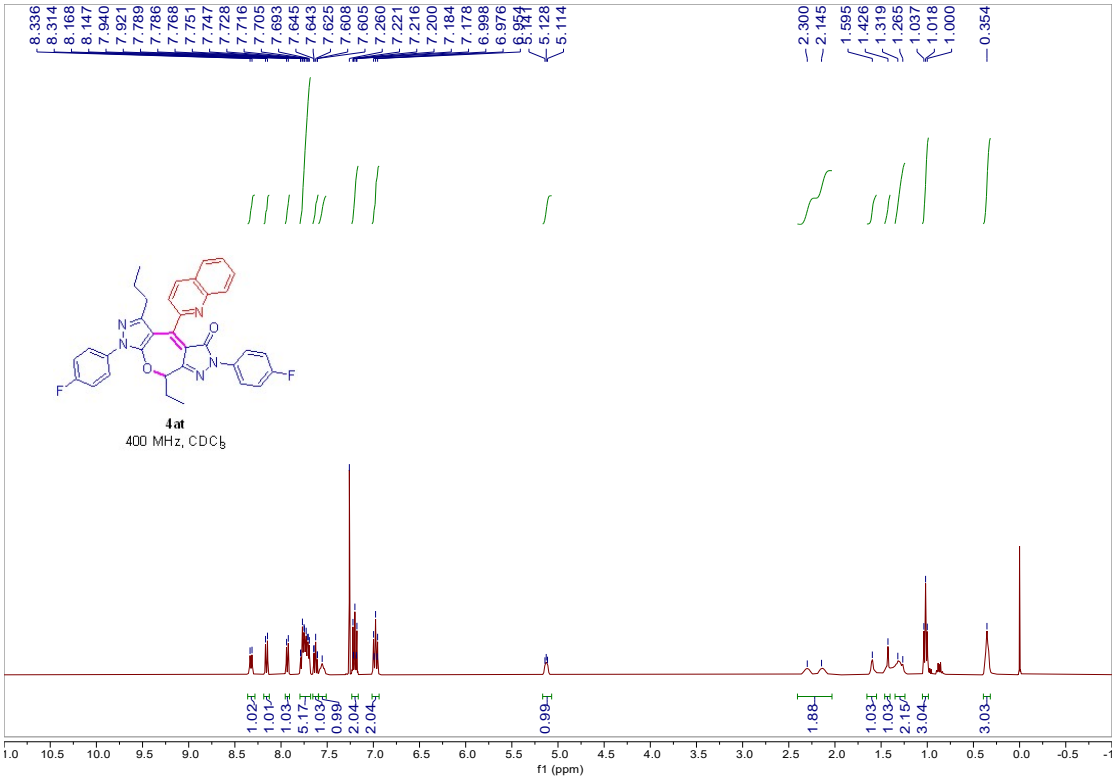
128.03
127.67
127.20
126.64
120.72
116.93
77.66
77.32
77.00
76.68
21.94
21.37
16.91
12.54
Me
Me
Me
Me
4ar
100 MHz, CDCl3
f1 (ppm)


4as
400 MHz, CDCl3
f1 (ppm)


4as
100 MHz, CDCl3
f1 (ppm)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7.940
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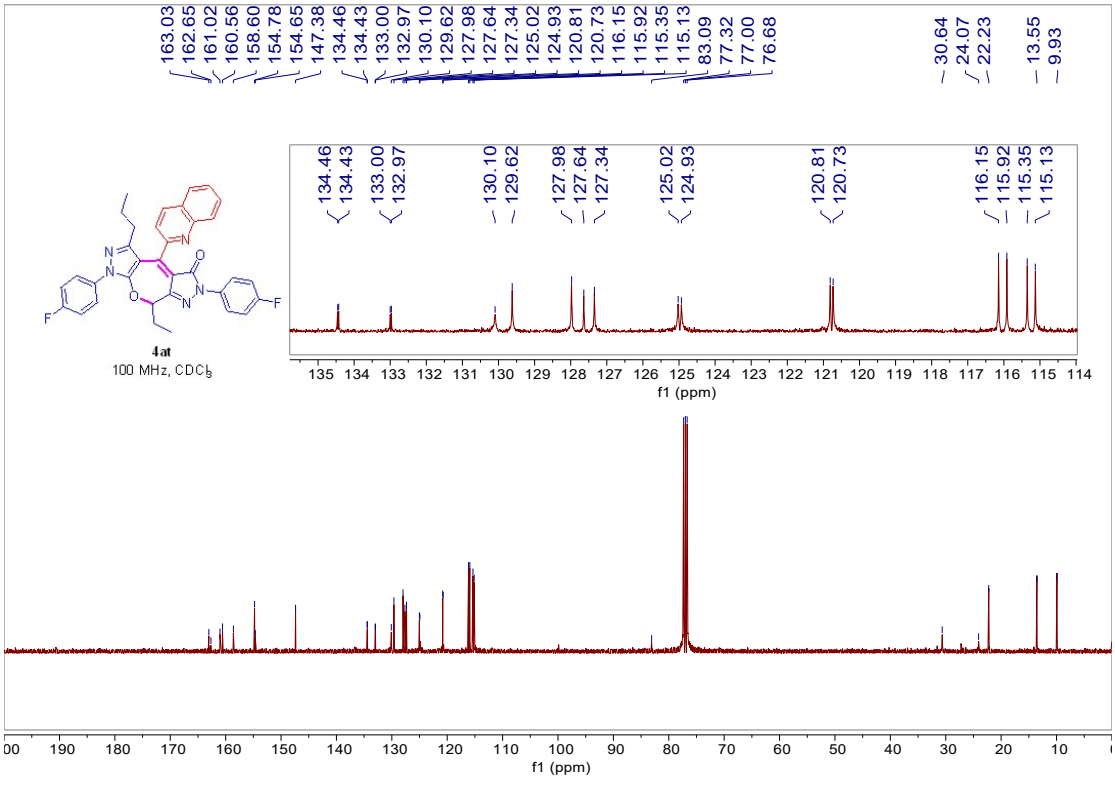
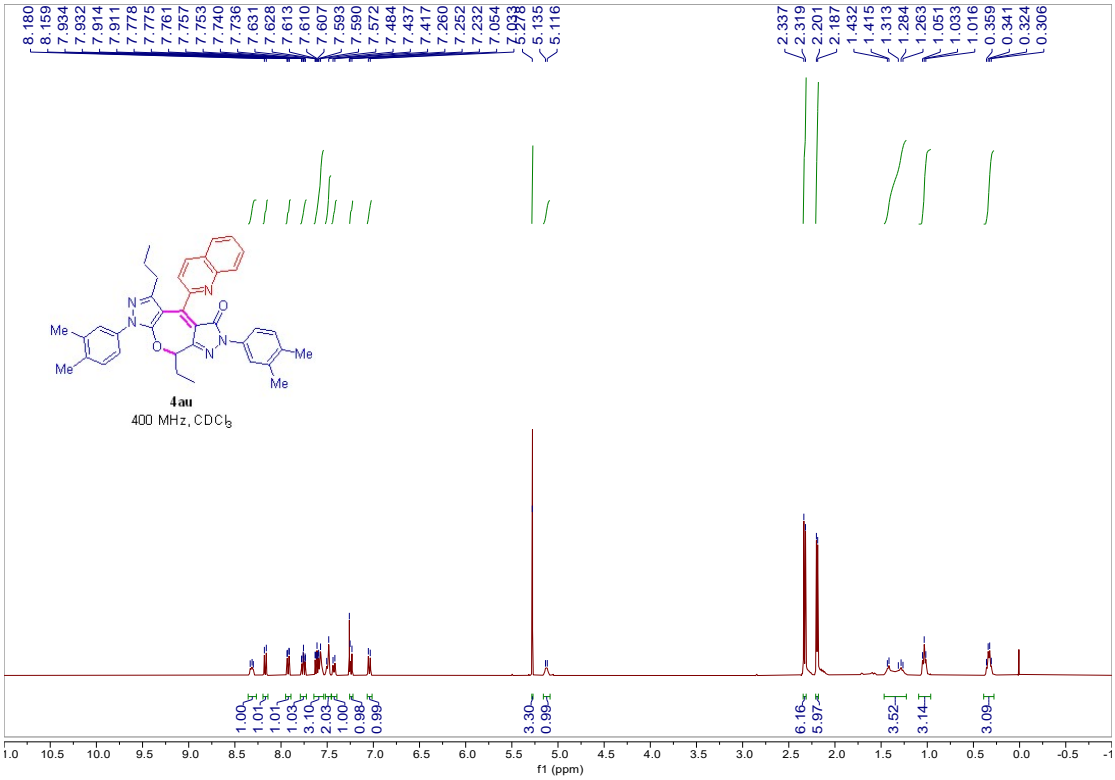
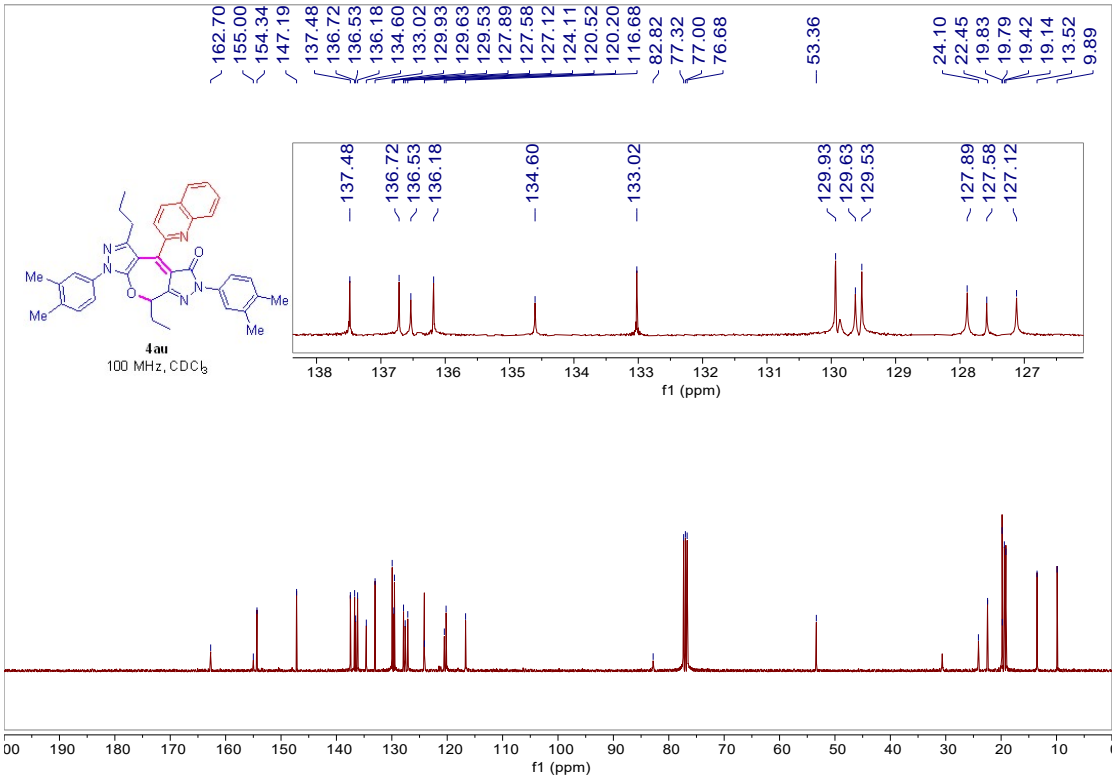
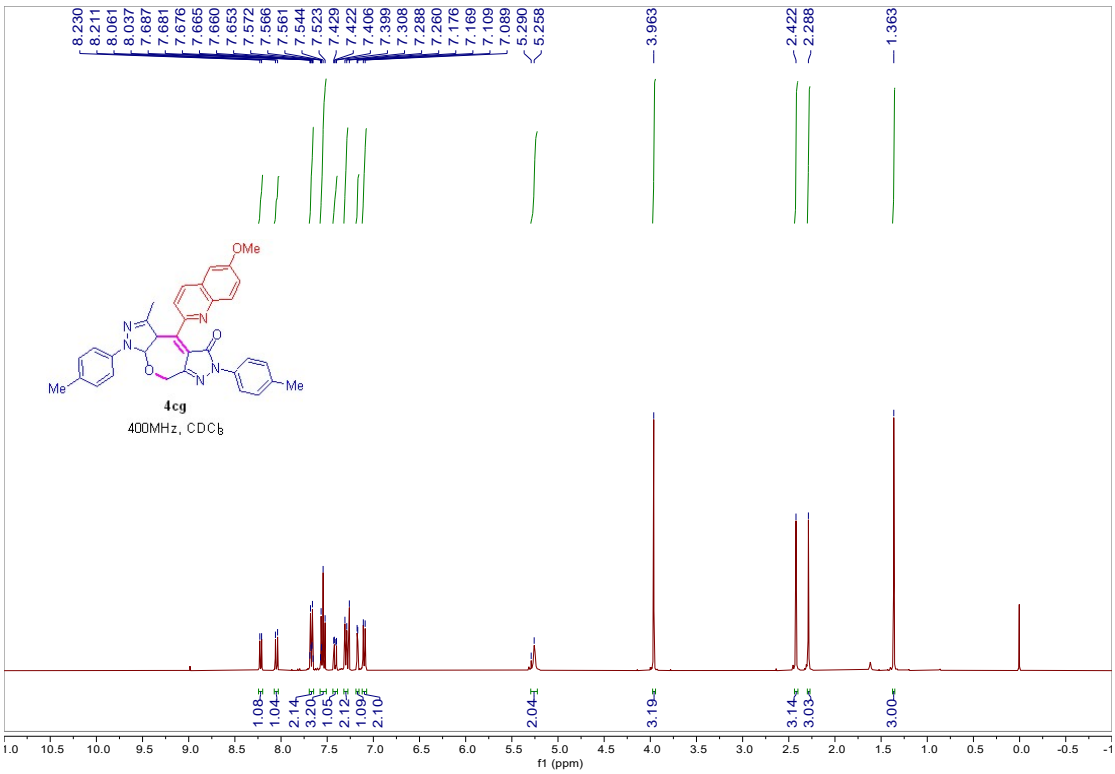
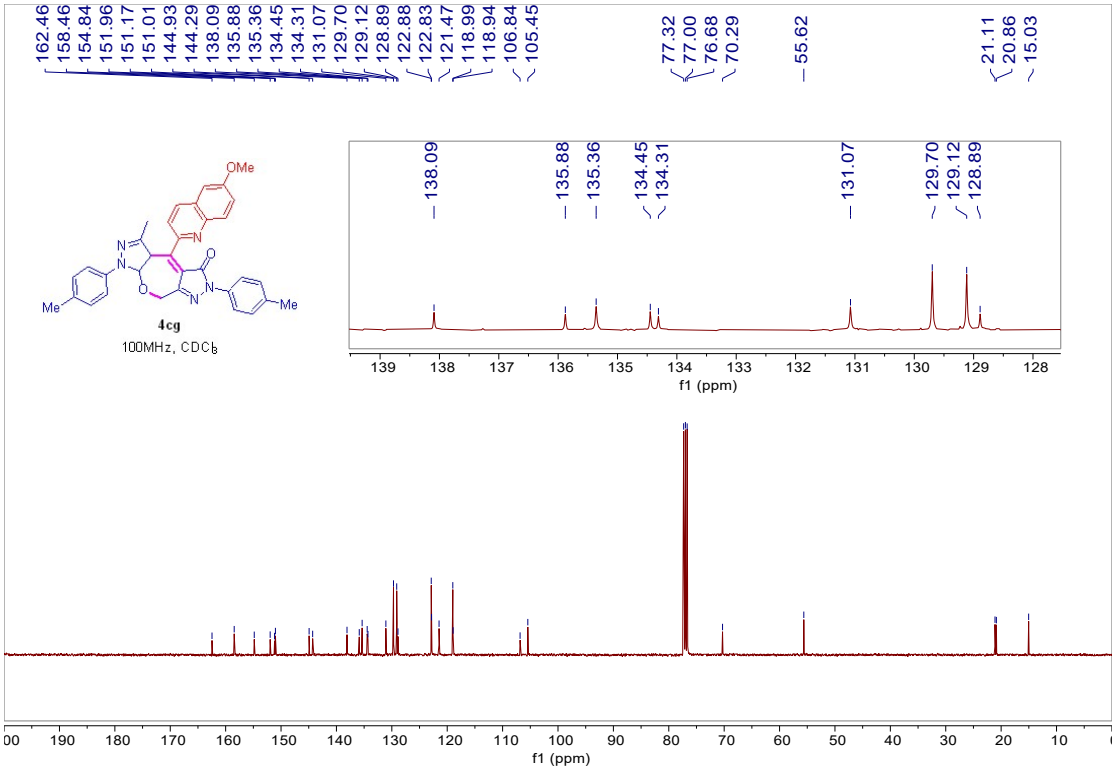
7.728
7.716
7.705
7.693
7.645
7.643
7.625
7.608
7.605
7.260
7.221
7.216
7.200
7.184
7.178
6.998
6.976
6.954
6.941
5.128
5.114
2.300
2.145
1.595
1.426
1.319
1.265
1.037
1.018
1.000
0.354
4at
400 MHz, CDCl3
1.02
1.01
1.03
5.17
1.03
0.99
2.04
2.04
0.99
1.88
1.03
1.03
2.15
3.04
3.03
f1 (ppm)

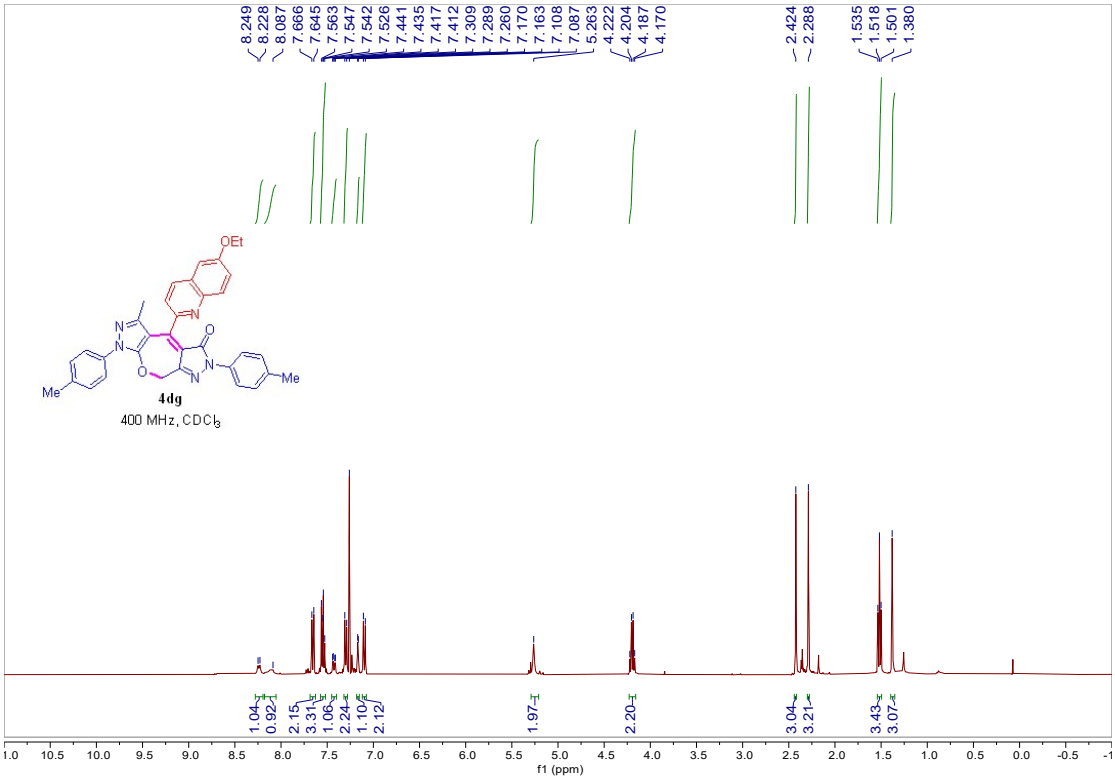

163.03
162.65
161.02
160.56
158.60
154.78
154.65
147.38
134.46
134.43
133.00
132.97
130.10
129.62
127.98
127.64
127.34
125.02
124.93
120.81
120.73
116.15
115.92
115.35
115.13
83.09
77.32
77.00
76.68
30.64
24.07
22.23
13.55
9.93
4at
100 MHz, CDCl3
f1 (ppm)

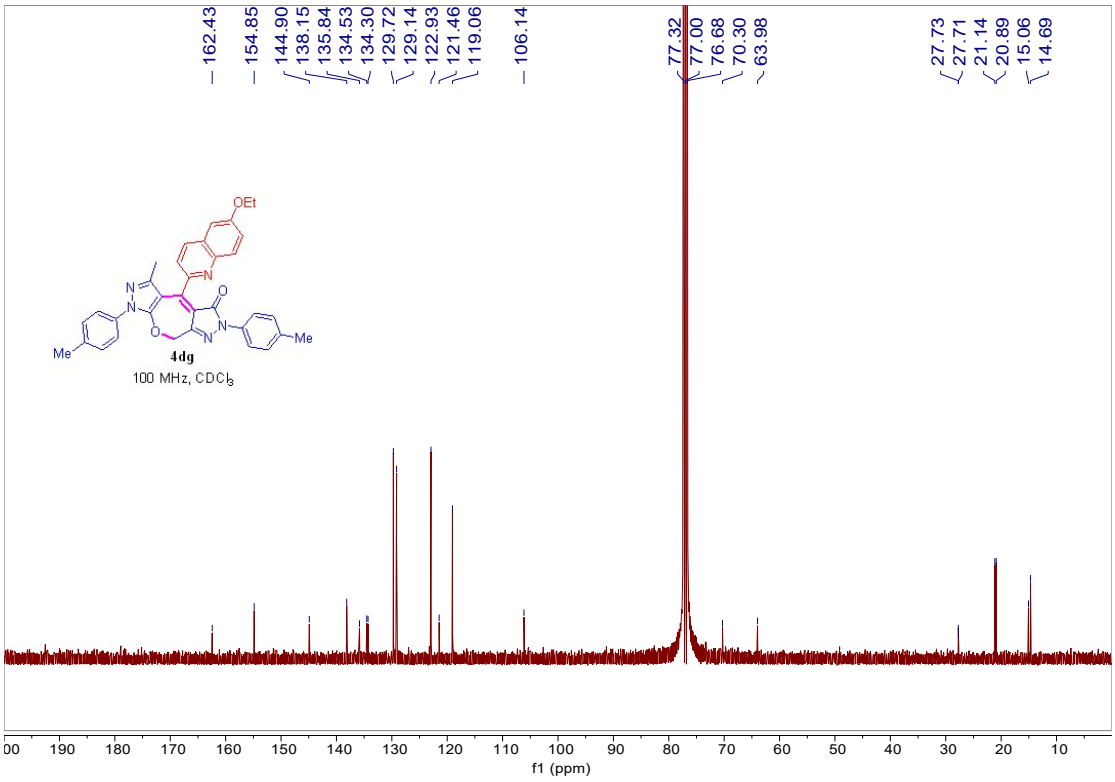

8.180
8.159
7.934
7.932
7.914
7.911
7.778
7.775
7.761
7.757
7.753
7.740
7.736
7.631
7.628
7.613
7.610
7.607
7.593
7.590
7.572
7.484
7.437
7.417
7.260
7.252
7.232
7.054
5.278
5.135
5.116
2.337
2.319
2.201
2.187
1.432
1.415
1.313
1.284
1.263
1.051
1.033
1.016
0.359
0.341
0.324
0.306
Me
Me
Me
Me
4au
400 MHz, CDCl3
1.00
1.01
1.01
1.03
3.10
2.03
1.00
0.98
0.99
3.30
0.99
6.16
5.97
3.52
3.14
3.09
f1 (ppm)

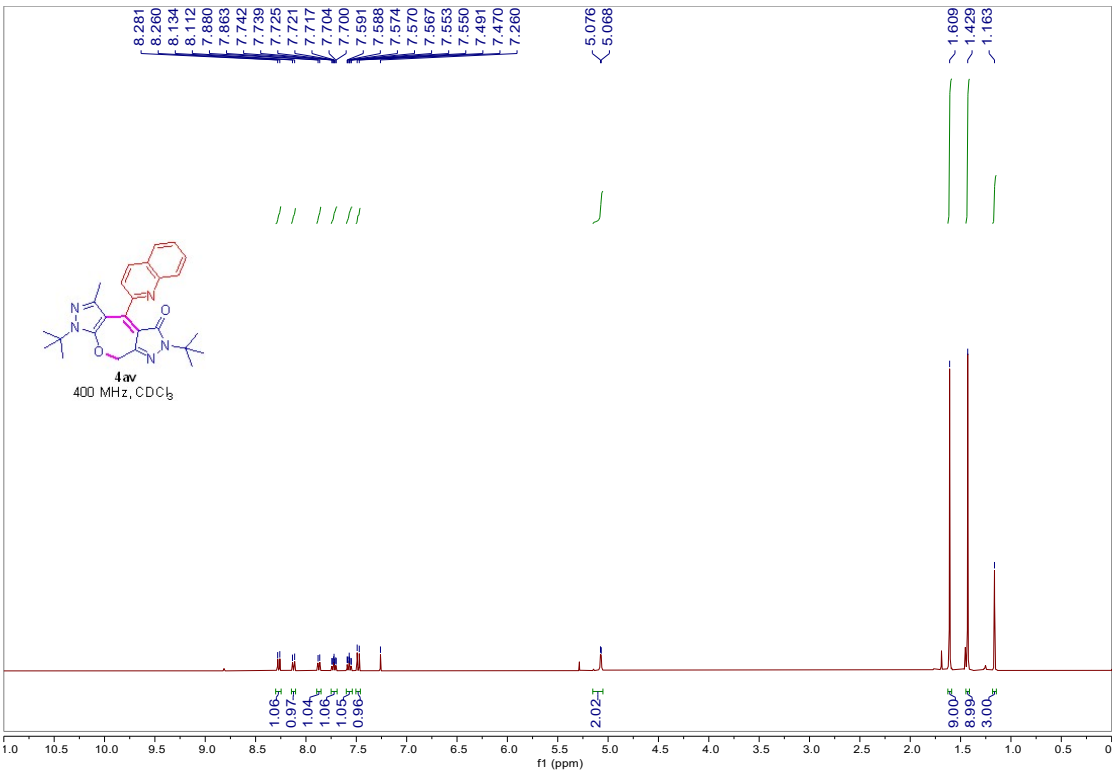

162.70
155.00
154.34
147.19
137.48
136.72
136.53
136.18
134.60
133.02
129.93
129.63
129.53
127.89
127.58
127.12
124.11
120.52
120.20
116.68
82.82
77.32
77.00
76.68
53.36
24.10
22.45
19.83
19.79
19.42
19.14
13.52
9.89
Me
Me
Me
Me
4au
100 MHz, CDCl3
f1 (ppm)
f1 (ppm)

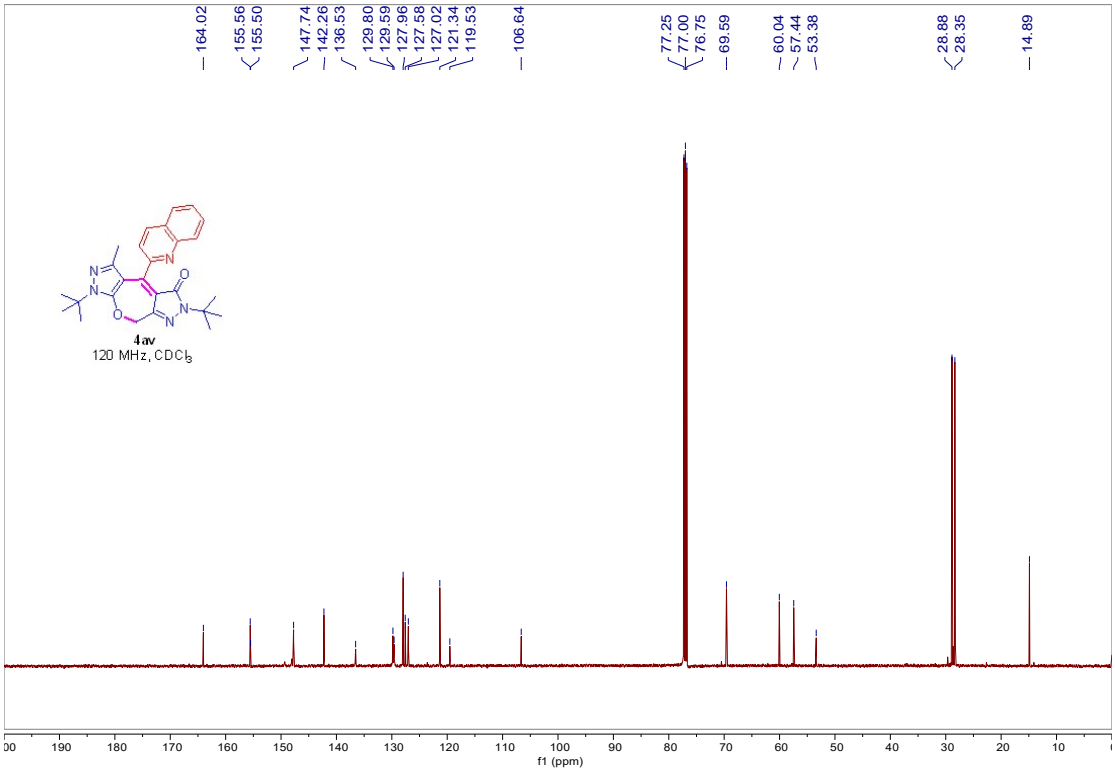

8.230
8.211
8.061
8.037
7.687
7.681
7.676
7.665
7.660
7.653
7.572
7.566
7.561
7.544
7.523
7.429
7.422
7.406
7.399
7.308
7.288
7.260
7.176
7.169
7.109
7.089
5.290
5.258
3.963
2.422
2.288
1.363
OMe
Me
Me
4cg
400MHz, CDCl3
1.08
1.04
2.14
3.20
1.05
2.12
1.09
2.10
2.04
3.19
3.14
3.03
3.00
f1 (ppm)


162.46
158.46
154.84
151.96
151.17
151.01
144.93
144.29
138.09
135.88
135.36
134.45
134.31
131.07
129.70
129.12
128.89
122.88
122.83
121.47
118.99
118.94
106.84
105.45
77.32
77.00
76.68
70.29
55.62
21.11
20.86
15.03
OMe
Me
Me
4cg
100MHz, CDCl3
138.09
135.88
135.36
134.45
134.31
131.07
129.70
129.12
128.89
f1 (ppm)


8.249
8.228
8.087
7.666
7.645
7.563
7.547
7.542
7.526
7.441
7.435
7.417
7.412
7.309
7.289
7.260
7.170
7.163
7.108
7.087
5.263
4.222
4.204
4.187
4.170
2.424
2.288
1.535
1.518
1.501
1.380
OEt
Me
Me
4dg
400 MHz, CDCl3
1.04
0.92
2.15
3.31
1.06
2.24
1.10
2.12
1.97
2.20
3.04
3.21
3.43
3.07
f1 (ppm)


162.43
154.85
144.90
138.15
135.84
134.53
134.30
129.72
129.14
122.93
121.46
119.06
106.14
77.32
77.00
76.68
70.30
63.98
27.73
27.71
21.14
20.89
15.06
14.69
OEt
Me
Me
4dg
100 MHz, CDCl3
f1 (ppm)


8.281
8.260
8.134
8.112
7.880
7.863
7.742
7.739
7.725
7.721
7.717
7.704
7.700
7.591
7.588
7.574
7.570
7.567
7.553
7.550
7.491
7.470
7.260
5.076
5.068
1.609
1.429
1.163
4av
400 MHz, CDCl3
1.06
0.97
1.04
1.06
1.05
0.96
2.02
9.00
8.99
3.00
f1 (ppm)


164.02
155.56
155.50
147.74
142.26
136.53
129.80
129.59
127.96
127.58
127.02
121.34
119.53
106.64
77.25
77.00
76.75
69.59
60.04
57.44
53.38
28.88
28.35
14.89
4av
120 MHz, CDCl3
f1 (ppm)