Electronic Supporting Information

Iron-iodine co-catalysis towards tandem C−N/C−C bond formation: one-pot regioselective synthesis of 2-amino-3-alkylindoles

Yingying Zhang,[a] Yating Huang,[a] Kewei Yu,[a] Xiaoxiang Zhang,[a] Wenhua Yu,[a] Jiale Tang,[a] Yiran Tian,[a] Wanxing Wei,[a] Zhuan Zhang,*[,a,b] and Taoyuan Liang*[,a,b]

[a] *School of Chemistry and Chemical Engineering, Guangxi University, Nanning, Guangxi 530004, P. R. China.*

[b] *Guangxi Key Laboratory of Electrochemical Energy Materials, Nanning, Guangxi 530004, P. R. China*

*E-mail: zhuan.zhang@gxu.edu.cn (Z. Zhang), taoyuanliang@gxu.edu.cn (T. Liang)

Table of contents

1. General information. S2

2. Substrates preparation. S3-S4

3. Optimization of reaction conditions. S4-S6

4. Typical procedure for the synthesis of **4aaa**. S6-S7

5. Synthetic utility. S7-S8

6. Control experiments. S8-S9

7. Single crystal X-ray diffraction of **4aaa**. S9-S15

8. References. S15

9. Analytical data of the obtained compounds. S16-S32

10. NMR spectra of the obtained compounds. S33-S73

1. General information.

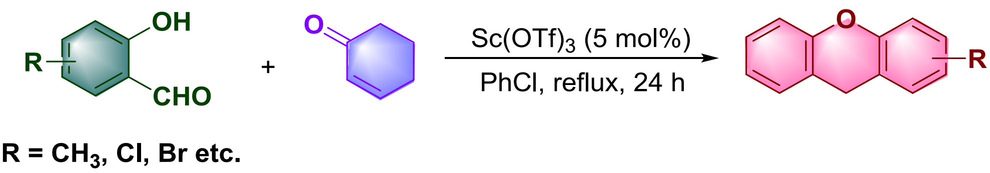
All the obtained products were characterized by melting points (m.p.), ^{1}H-NMR, ^{13}C-NMR. Melting points were measured on an Electrothemal SGW-X4 microscopy digital melting point apparatus and are uncorrected; ^{1}H-NMR and ^{13}C-NMR spectra were obtained on Bruker-400/500 and referenced to 7.26 ppm for chloroform solvent with TMS as internal standard (0 ppm). Chemical shifts were reported in parts per million (ppm, δ) downfield from tetramethylsilane. Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), multiplet (m); TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization effected at 254 nm; Unless otherwise stated, all the reagents were purchased from commercial sources, used without further purification.

All the reagents were purchased from Bide Pharmatech Ltd. and Energy Chemical. All solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification. All reactions were heated by metal sand bath (WATTCAS, LAB-500, https://wwwwattcas.com). Column chromatography was performed on silica gel or netural alumina (200-300 mesh). Reactions were monitored by using thin layer chromatography (TLC) (Qingdao Jiyida silica gel reagent factory GF254)

Figure S1. Metal sand bath (WATTCAS, LAB-500)

2. Substrates preparation.

General Procedure for the preparation of substituted xanthenes (2b-2i)[1]:



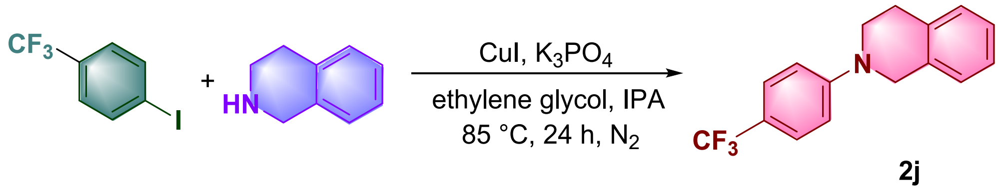
Salicylaldehyde derivatives (1.1 mmol) and 2-cyclohexene-1-one (1.0 mmol) was quickly added to a suspension of scandium (III) triflate (0.05 mmol) in chlorobenzene (4.0 mL). The reaction mixture was refluxed for 24 hours and allowed to cool to room temperature. DCM (20.0 mL) and saturated aqueous $NaHCO_3$ (20.0 mL) were added to the reaction mixture and the two layers separated. The aqueous phase was extracted with DCM (3×20.0 mL) and the combined organic layers were dried over $MgSO_4$, filtered and solvent was removed by rotary evaporator. The crude xanthene products **2** was purified by column chromatography on silica gel using eluent mixtures of hexane and ethyl acetate.

General Procedure for the preparation of *N*-substituted indole derivatives (1a-1d, 1f-1r)[2]:

Procedure for 5-chloro-1-methyl-1*H*-indole (**1k**): To a suspended solution of NaH (0.55 g, 65% dispersion in mineral oil, 15.0 mmol) in DMF (5.0 mL), 5-chloro-1*H*-indole (1.51 g, 10.0 mmol) in DMF (5.0 mL) was added dropwise at 0 °C. The heterogeneous mixture was stirred at 0 °C for 15 min and 1 h at room temperature. The mixture was then cooled to 0 °C, treated with iodomethane (0.83 mL, 13.0 mmol), and allowed to warm to room temperature. After 30 min, the reaction mixture was cooled to 0 °C, quenched with saturated NH_4Cl (20.0 mL), and extracted with ether (3 × 20.0 mL). The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The resulting oil was purified by column chromatography on silica gel (petroleum ether) afforded **1k** as a yellow oil. Similarly, the other *N*-substituted indole derivatives were prepared from their corresponding indoles and halides.

General procedure for the synthesis of 2-(4-(trifluoromethyl)phenyl)-1,2,3,4-

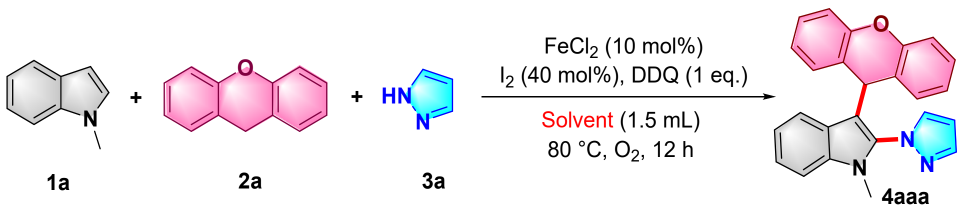
tetrahydroisoquinoline (2j)[3]:



Copper(I) iodide (200 mg, 1.0 mmol) and potassium phosphate (4.25 g, 20.0 mmol) were added to an over-dried 50 mL three-neck flask. The flask was evacuated and back filled with Ar. 2-Propanol (10.0 mL), ethylene glycol (1.11 mL), 1,2,3,4-tetrahydroisoquinoline (2.0 mL, 15 mmol) and 1-iodo-4-(trifluoromethyl)benzene (10.0 mmol) were added successively by syringe at roomtemperature. The reaction mixture was heated at 85 °C and kept for 24 h and then allowed to cool to room temperature. Diethyl ether (20 mL) and water (20 mL) were then added to the reaction mixture. The organic layer was extracted with diethyl ether (2 × 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed and the residue was purified by column chromatography on silica gel using ethylacetate/petroleum ether (1:20) as an eluent to afford the desired product **2j**.

3. Optimization of reaction conditions.

Table S1. Screening of solvent. [a]

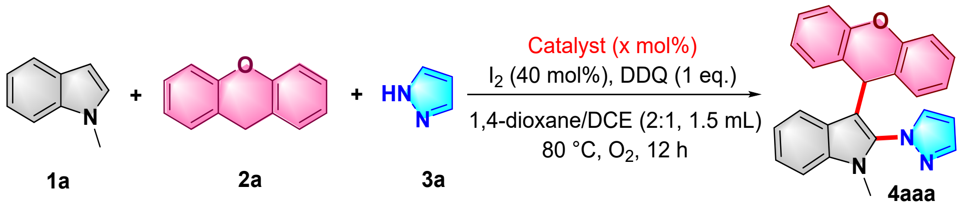


Entry	Catalyst	Solvent[b]	Oxidant	Yield(%)[c]
1	$FeCl_2$	CH_3CN	DDQ	46
2	$FeCl_2$	DCE	DDQ	58
3	$FeCl_2$	DMF	DDQ	trace
4	$FeCl_2$	toluene	DDQ	53
5	$FeCl_2$	1,4-dioxane	DDQ	77
6	**$FeCl_2$**	**1,4-dioxane/DCE**	**DDQ**	**89**
7	$FeCl_2$	1,4-dioxane/CH_3CN	DDQ	57

8	$FeCl_2$	1,4-dioxane/toluene	DDQ	44
9	$FeCl_2$	1,4-dioxane/DCE	DDQ	(46, 60)[d]

[a]Conditions: unless otherwise stated, all the reactions were performed with **1a** (0.25 mmol), **2a** (0.25 mmol) and **3a** (0.75 mmol), $FeCl_2$ (10 mol%), DDQ (1.0 eq), iodine (40 mol%), 1,4-dioxane/DCE (v/v = 2:1, 1.5 mL) at 80 °C under O_2 for 12 h; [b](v/v = 2:1); [c]Isolated yield; [d]1,4-dioxane/DCE (v/v = 1:1) and (v/v = 1:2).

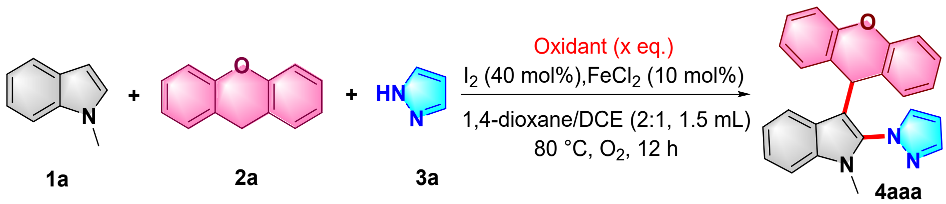
Table S2. Screening of catalyst.[a]



Entry	Catalyst[c]	Solvent	Oxidant	Yield(%)[b]
1	$FeCl_3$	1,4-dioxane/DCE	DDQ	75
2	$CuCl_2$	1,4-dioxane/DCE	DDQ	61
3	$ZnCl_2$	1,4-dioxane/DCE	DDQ	61
4	$Fe(OTf)_3$	1,4-dioxane/DCE	DDQ	59
5	None	1,4-dioxane/DCE	DDQ	61
6	$FeCl_2$	1,4-dioxane/DCE	DDQ	(71, 68)[d]

[a]Conditions: unless otherwise stated, all the reactions were performed with **1a** (0.25 mmol), **2a** (0.25 mmol) and **3a** (0.75 mmol), $FeCl_2$ (10 mol%), DDQ (1.0 eq), iodine (40 mol%), 1,4-dioxane/DCE (v/v = 2:1, 1.5 mL) at 80 °C under O_2 for 12 h; [b]Isolated yield; [c]catalyst (10 mol%); [d]5 mol% and 20 mol% of $FeCl_2$ were used, respectively.

Table S3. Screening of oxidant.[a]

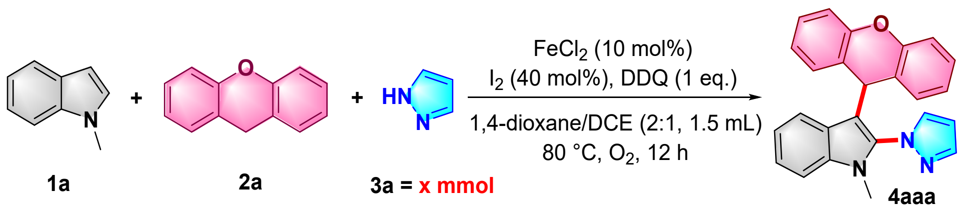


Entry	Catalyst	Solvent	Oxidant	Yield(%)[b]
1	$FeCl_2$	1,4-dioxane/DCE	TBHP	46
2	$FeCl_2$	1,4-dioxane/DCE	$K_2S_2O_8$	35
3	$FeCl_2$	1,4-dioxane/DCE	DTBP	19
4	$FeCl_2$	1,4-dioxane/DCE	NFSI	ND
5	$FeCl_2$	1,4-dioxane/DCE	DDQ	(44, 25)[c]

[a]Conditions: unless otherwise stated, all the reactions were performed with **1a** (0.25 mmol), **2a** (0.25 mmol) and **3a**

(0.75 mmol), $FeCl_2$ (10 mol%), DDQ (1.0 eq), iodine (40 mol%), 1,4-dioxane/DCE (v/v = 2:1, 1.5 mL) at 80 °C under O_2 for 12 h; [b]Isolated yield; [c]0.5 equiv and 1.5 equiv of DDQ were used, respectively.

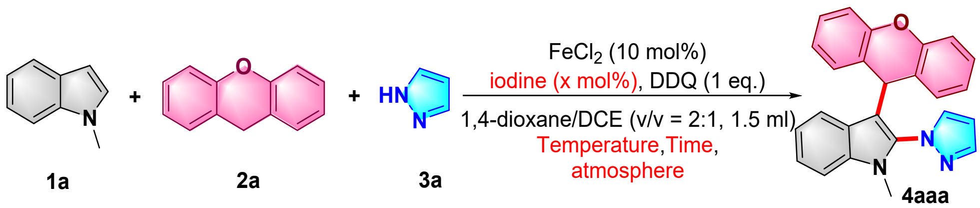
Table S4. The effect of usage amount of 3a. [a]



Entry	Usage amount of 3a	Yield(%)[b]
1	0.25 mmol	30
2	0.375 mmol	45
3	0.50mmol	51

[a]Conditions: unless otherwise stated, all the reactions were performed with **1a** (0.25 mmol), **2a** (0.25 mmol) and **3a** (0.75 mmol), $FeCl_2$ (10 mol%), DDQ (1.0 eq), iodine (40 mol%), 1,4-dioxane/DCE (v/v = 2:1, 1.5 mL) at 80 °C under O_2 for 12 h; [b]Isolated yield.

Table S5. Others supplementary screening. [a]



Entry	Catalyst	Solvent	Oxidant	Yield(%)[b]
1	$FeCl_2$	1,4-dioxane/DCE	DDQ	(66, ND)[c]
2	$FeCl_2$	1,4-dioxane/DCE	DDQ	(61, 64)[d]
3	$FeCl_2$	1,4-dioxane/DCE	DDQ	34[e]
4	$FeCl_2$	1,4-dioxane/DCE	DDQ	(55, 37)[f]

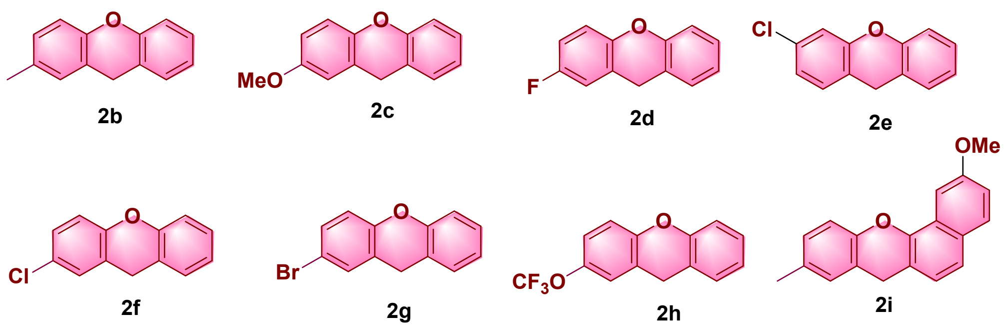
[a]Conditions: unless otherwise stated, all the reactions were performed with **1a** (0.25 mmol), **2a** (0.25 mmol) and **3a** (0.75 mmol), $FeCl_2$ (10 mol%), DDQ (1.0 eq), iodine (40 mol%), 1,4-dioxane/DCE (v/v = 2:1, 1.5 mL) at 80 °C under O_2 for 12 h; [b]Isolated yield; [c]20 mol% of I_2 was used, 40 mol% of NaI was used; [d]for 9 h and 24 h; [e]at 60 °C; [f]under air and argon atmosphere conditions, respectively.

4. Typical procedure for the synthesis of 4aaa.

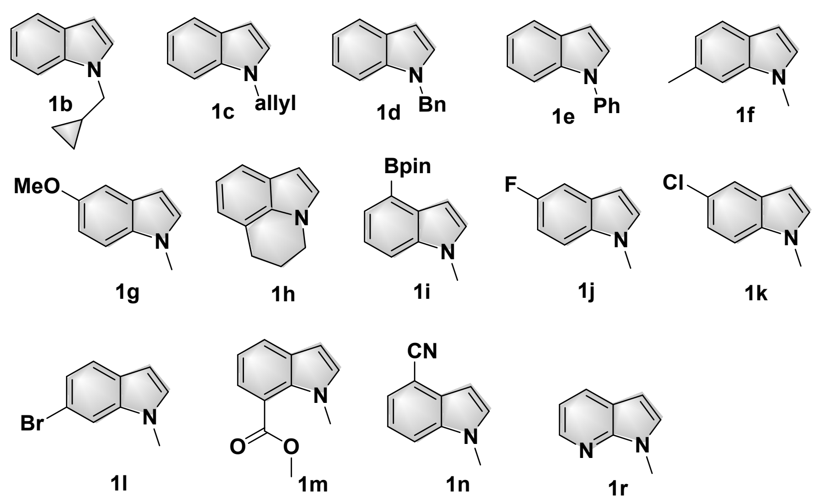
The mixture of 1-methyl-1*H*-indole **1a** (33.0 mg, 0.25 mmol), 9*H*-xanthene **2a** (45.0

mg, 0.25 mmol), pyrazole **3a** (51.0 mg, 0.75 mmol), DDQ (56.0 mg, 0.25 mmol), $FeCl_2$ (3.0 mg, 10 mol%), iodine (25.0 mg, 40 mol%) in 1,4-dioxane/DCE (v/v = 2:1, 1.5 mL) was stirred at 80 °C under O_2 for 12 h. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/ethyl acetate (20 :1) as the eluent to give **4aaa** as a yellow solid (84.0 mg, 89% yield).

Scheme S1. **Substrates employed of xanthene.**

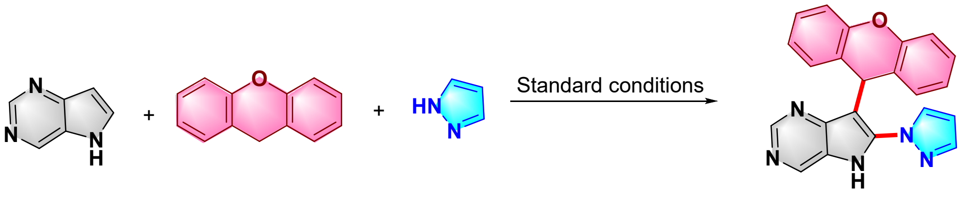


Scheme S2. **Substrates employed of indoles.**



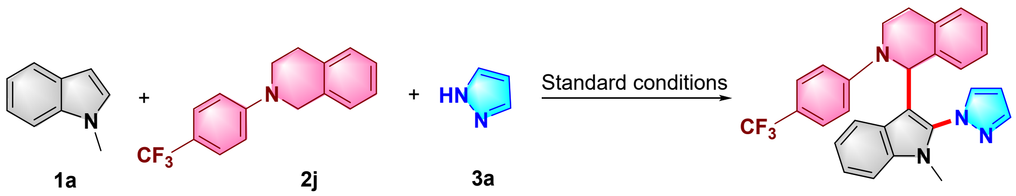
5. Synthetic utility.

The mixture of 5*H*-pyrrolo[3,2-*d*]pyrimidine (29.0 mg), 9*H*-xanthene (45.0 mg, 0.25 mmol) and 1*H*-pyrazole (51.0 mg, 0.75 mmol), DDQ (56.0 mg, 0.25 mmol), $FeCl_2$ (3.0 mg, 5 mol%) and I_2 (25.0 mg, 40 mol%) in 1,4-dioxane/DCE (v/v = 2:1) was stirred at 80 °C for 12 h under O_2. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/ethyl acetate (v/v = 20:1) as the eluent to give **4saa** as yellow solid. [a]Yield of standard conditions deviation: 2.0 equiv of xanthene **2a** was used.



1s **2a** **3a** **4saa**, 17% (39%)[a]

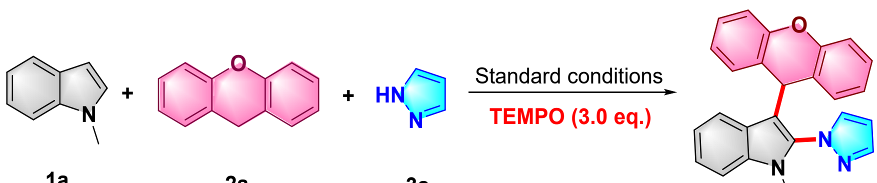
The mixture of 1-methyl-1*H*-indole (33.0 mg), 2-(4-(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (69.0 mg, 0.25 mmol) and 1*H*-pyrazole (51.0 mg, 0.75 mmol), DDQ (56.0 mg, 0.25 mmol), $FeCl_2$ (3.0 mg, 5 mol%) and I_2 (25.0 mg, 40 mol%) in 1,4-dioxane/DCE (v/v = 2:1) was stirred at 80 °C for 12 h under O_2. The resulting mixture was concentrated by removing the solvent under vacuum, and the residue was purified by preparative TLC on silica gel by using petroleum ether/ethyl acetate (v/v = 20:1) as the eluent to give **4aja** as yellow solid. [a]Yield of standard conditions deviation: DDQ was replaced by 2.0 equivalent of TBHP (49.5 mg, 0.50 mmol) and the solvent was raplaced by 1.5 mL of 1,4-dioxane, respectively.



1a **2j** **3a** **4aja**, 13% (42%)[a]

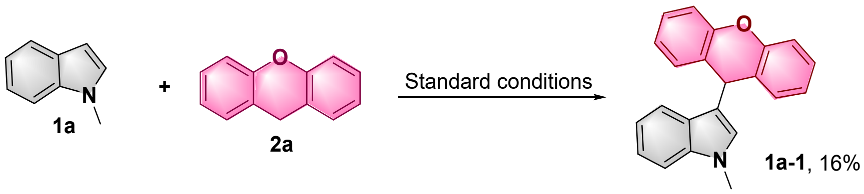
6. Control experiments.

(1) Under the optimized reaction conditions, the model reaction was carried out by introducing 3.0 equivalent of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy). And no **4aaa** was detected.

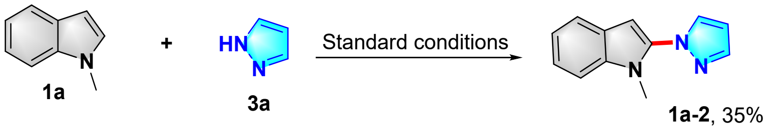


1a **2a** **3a** **4aaa**, 0%

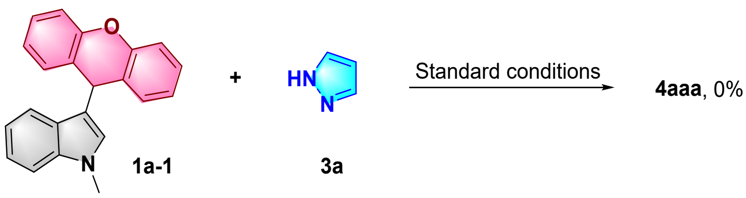
(2) Under the optimized reaction conditions, the reaction of **1a** (33.0 mg, 0.25 mmol) and **2a** (45.0 mg, 0.25 mmol) was carried. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (v/v = 20:1) to give product **1a-1** as yellow solid (13.0 mg, 16% yield) and product **1a-1** as yellow solid.



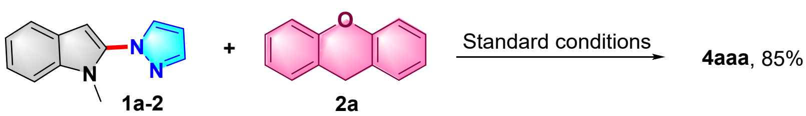
(3) Under the optimized reaction conditions, the reaction of **1a** (33.0 mg, 0.25 mmol) and **3a** (51.0 mg, 0.75 mmol) was carried. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (v/v = 20:1) to give product **1a-2** as white solid (17.0 mg, 35% yield).



(4) Under the optimized reaction conditions, the reaction of **1a-1** (77.7 mg, 0.25 mmol) and **3a** (51.0 mg, 0.75 mmol) was carried out. And no **4aaa** was detected.



(5) Under the optimized reaction conditions, the reaction of **1a-2** (49.0 mg, 0.25 mmol) and **2a** (45.0 mg, 0.25 mmol) was carried. Then, the reaction mixture was purified by preparative TLC on silica eluting with petroleum ether/ethyl acetate (v/v = 20:1) to give product **4aaa** as yellow solid (80.5 mg, 85% yield).



7. Single crystal X-ray diffraction of 4aaa.

White block-like single crystals of **4aaa** were grown by layering a dichlormethane solution with methanol at ambient temperature. X-Ray diffraction data of one these crystals were collected on a R-AXIS SPIDER diffractometer. The measurements were performed with Mo-Kα radiation (λ = 0.71073 Å). Data were collected at 298(2) K, using the *ω*- and *φ*- scans to a maximum θ value of 28.327°. The data were refined by full-matrix least-squares techniques on F^2 with SHELXL-2018/3. And the structures were solved by direct methods SHELXL-2018/3. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included at geometrically idealized positions. And an ORTEP representation of the structure is shown below.

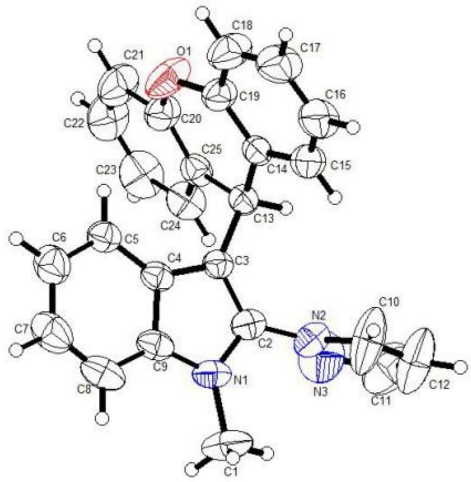


Figure S2. ORTEP drawing of **4aaa** with the numbering scheme.

Table S2. Crystal data and structure refinement for **4aaa**.

Identification code	4aaa	
Empirical formula	$C_{25}H_{19}N_3O_1$	
Formula weight	377.43	
Temperature	298 K	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 18.6523(15) Å	□= 90°.
	b = 8.3706(5) Å	□= 104.543(8)°.
	c = 25.8377(19) Å	□ = 90°.
Volume	3904.8(5) Å^3	
Z	8	
ρ_{calc}g	1.284 cm^3	
μ	0.080 mm^{-1}	
F(000)	1584.0	

Crystal size	0.3 × 0.2 × 0.1 mm^3
Radiation	MoKα (λ = 0.71073)
2^Θ range for data collection	7.632 to 58.912
Index ranges	-24≤h≤24, -11≤k≤10, -33≤l≤35
Reflections collected	14957
Independent reflections	4646 [Rint = 0.0286, Rsigma = 0.0308]
Data / restraints / parameters	4646/0/264
Goodness-of-fit on F^2	1.032
Final R indices [I>=2^σ (I)]	R1 = 0.0580, wR2 = 0.1369
Final R indices (all data)	R1 = 0.0863, wR2 = 0.1555
Largest diff. peak and hole	0.20/-0.18 $Å^{-3}$

Table S3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for **4aaa**. U(eq) is defined as 1/3 of of the trace of the orthogonalised U^{ij} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
O1	9149.4(8)	6735.4(17)	4794.8(7)	78.0(5)
N1	7104.1(8)	10054.3(17)	2924.0(6)	49.5(4)
N2	6269.5(8)	9299.8(18)	3456.6(6)	51.0(4)
N3	5777.3(12)	8128(3)	3288.8(10)	90.5(7)
C1	6553.8(13)	10784(3)	2488.8(9)	82.3(7)
C2	6980.9(9)	9288.6(19)	3366.3(7)	43.7(4)
C3	7613.8(9)	8665.0(18)	3678.3(6)	38.3(4)
C4	8182.4(9)	9068.0(18)	3418.5(6)	39.8(4)
C5	8944.4(10)	8811(2)	3533.2(7)	48.6(4)
C6	9335.8(11)	9398(3)	3190.0(8)	63.2(5)
C7	8990.2(13)	10263(3)	2735.8(9)	70.5(6)
C8	8249.8(13)	10546(2)	2612.2(8)	63.1(6)
C9	7844.7(10)	9935(2)	2951.9(6)	45.8(4)
C10	5991.3(14)	10458(3)	3697.3(15)	103.9(11)
C11	5290.1(17)	10030(4)	3674.7(17)	115.7(12)
C12	5178.7(14)	8619(4)	3438.7(14)	100.5(10)
C13	7689.3(9)	7759.7(19)	4195.7(6)	40.1(4)
C14	8161.0(9)	8663.6(19)	4663.1(6)	40.4(4)
C15	7921.9(12)	10084(2)	4833.7(7)	57.3(5)
C16	8361.0(14)	10966(3)	5239.7(8)	71.4(6)

C17	9053.1(14)	10436(3)	5488.3(9)	75.7(7)
C18	9300.2(13)	9020(3)	5335.1(9)	74.7(7)
C19	8853.0(10)	8145(2)	4927.4(7)	52.6(5)
C20	8688.0(11)	5681(2)	4458.1(8)	53.5(5)
C21	8977.2(13)	4165(2)	4425.9(10)	71.6(6)
C22	8569.9(14)	3068(3)	4089.3(10)	75.4(7)
C23	7880.4(15)	3448(2)	3789.4(10)	73.9(7)
C24	7592.8(12)	4950(2)	3828.3(8)	58.5(5)
C25	7998.2(10)	6098.2(19)	4161.1(7)	42.6(4)

Table S4. Anisotropic Displacement Parameters (Å^2×10^3) for **4aaa**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	61.6(9)	62.2(9)	93.4(11)	-24.6(8)	-12.0(8)	24.1(7)
N1	57.3(9)	44.1(8)	39.8(8)	6.0(6)	-1.4(6)	3.2(7)
N2	42.1(8)	45.6(8)	60.3(9)	-5.2(7)	3.6(7)	3.9(6)
N3	75.0(13)	86.0(15)	110.5(17)	-22.2(13)	23.1(12)	-24.2(11)
C1	75.9(15)	86.4(17)	68.3(14)	29.7(13)	-12.5(12)	9.2(13)
C2	47.2(9)	36.9(8)	42.5(9)	-3.0(7)	3.1(7)	1.8(7)
C3	45.0(8)	34.3(8)	34.0(8)	-2.6(7)	6.9(6)	2.6(7)
C4	49.8(9)	35.5(8)	32.2(7)	-3.8(7)	6.9(7)	-1.9(7)
C5	48.4(9)	54.8(10)	41.5(9)	-0.7(8)	9.2(7)	-0.6(8)
C6	53.6(11)	80.2(14)	58.6(12)	-0.9(11)	19.1(9)	-10.5(10)
C7	74.7(15)	84.9(16)	56.5(12)	4.4(12)	25.4(11)	-22.7(12)
C8	86.6(15)	59.1(12)	42.0(10)	8.5(9)	13.1(10)	-13.2(11)
C9	58.7(11)	39.4(9)	35.4(8)	-1.8(7)	4.6(7)	-3.5(8)
C10	72.8(16)	65.5(15)	189(3)	-46.6(18)	62.5(19)	-1.3(12)
C11	81.3(19)	86(2)	199(4)	-9(2)	71(2)	21.9(16)
C12	54.6(14)	103(2)	140(3)	6(2)	16.8(16)	-10.3(14)
C13	42.6(8)	42.2(8)	37.4(8)	3.6(7)	13.8(7)	3.0(7)
C14	49.4(9)	40.8(8)	33.2(8)	3.0(7)	14.4(7)	6.6(7)
C15	68.3(12)	55.6(11)	45.9(10)	-3.8(9)	10.7(9)	18.5(9)
C16	96.9(17)	59.7(12)	54.3(12)	-17.5(10)	12.6(12)	18.3(12)
C17	90.7(17)	72.4(15)	52.8(12)	-19.7(11)	-2.8(11)	6.8(13)
C18	67.5(13)	74.5(15)	67.2(13)	-15.6(12)	-11.2(11)	15.8(11)

C19	56.3(11)	49.3(10)	47.8(10)	-5.4(8)	4.6(8)	11.1(8)
C20	59.4(11)	42.3(9)	57.7(11)	-2.0(9)	12.4(9)	8.9(8)
C21	74.7(14)	50.1(11)	87.4(16)	-2.8(11)	15.8(12)	18.8(11)
C22	94.6(18)	40.8(11)	95.5(18)	-6.4(11)	32.5(15)	7.6(11)
C23	96.3(18)	45.4(11)	82.4(16)	-16.3(11)	26.7(14)	-14.6(11)
C24	69.5(13)	49.6(10)	56.4(11)	-2.6(9)	15.8(10)	-5.8(9)
C25	54.6(10)	36.9(8)	39.7(8)	3.9(7)	17.9(7)	-0.2(7)

Table S5. Bond Angles for **4aaa**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C20	O1	C19	118.55(14)	C12	C11	C10	107.3(2)
C2	N1	C1	127.18(18)	C11	C12	N3	111.3(2)
C9	N1	C1	125.39(17)	C3	C13	C25	111.08(13)
C9	N1	C2	107.36(13)	C14	C13	C3	111.27(13)
N3	N2	C2	122.77(16)	C14	C13	C25	110.72(13)
C10	N2	N3	111.73(19)	C15	C14	C13	121.20(15)
C10	N2	C2	125.47(17)	C19	C14	C13	121.83(15)
C12	N3	N2	103.7(2)	C19	C14	C15	116.94(16)
N1	C2	N2	119.72(15)	C16	C15	C14	121.92(18)
C3	C2	N1	111.73(15)	C17	C16	C15	119.84(19)
C3	C2	N2	128.47(16)	C16	C17	C18	119.6(2)
C2	C3	C4	105.52(14)	C17	C18	C19	119.9(2)
C2	C3	C13	126.33(15)	C14	C19	O1	122.16(16)
C4	C3	C13	128.14(14)	C14	C19	C18	121.72(17)
C5	C4	C3	134.45(15)	C18	C19	O1	116.11(17)
C5	C4	C9	118.24(16)	O1	C20	C21	115.62(17)
C9	C4	C3	107.30(15)	C25	C20	O1	122.73(16)
C6	C5	C4	119.12(17)	C25	C20	C21	121.63(19)
C5	C6	C7	121.5(2)	C22	C21	C20	119.5(2)
C8	C7	C6	121.18(19)	C21	C22	C23	120.2(2)
C7	C8	C9	117.93(19)	C22	C23	C24	120.0(2)
N1	C9	C4	108.08(15)	C23	C24	C25	121.1(2)
N1	C9	C8	129.83(17)	C20	C25	C13	121.26(15)
C8	C9	C4	122.06(18)	C20	C25	C24	117.54(16)
N2	C10	C11	106.0(2)	C24	C25	C13	121.20(16)

Table S6. Bond Lengths for **4aaa**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C19	1.382(2)	C8	C9	1.392(3)
O1	C20	1.379(2)	C10	C11	1.343(4)
N1	C1	1.453(2)	C11	C12	1.321(4)
N1	C2	1.379(2)	C13	C14	1.507(2)
N1	C9	1.369(2)	C13	C25	1.517(2)
N2	N3	1.339(2)	C14	C15	1.380(2)
N2	C2	1.404(2)	C14	C19	1.371(2)
N2	C10	1.326(3)	C15	C16	1.373(3)
N3	C12	1.335(3)	C16	C17	1.363(3)
C2	C3	1.356(2)	C17	C18	1.366(3)
C3	C4	1.431(2)	C18	C19	1.379(3)
C3	C13	1.512(2)	C20	C21	1.389(3)
C4	C5	1.394(2)	C20	C25	1.368(3)
C4	C9	1.412(2)	C21	C22	1.359(3)
C5	C6	1.373(3)	C22	C23	1.362(3)
C6	C7	1.392(3)	C23	C24	1.381(3)
C7	C8	1.358(3)	C24	C25	1.381(3)

Table S7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **4aaa**.

Atom	*x*	*y*	*z*	U(eq)
H1A	6581.04	10309.39	2155.97	123
H1B	6647.79	11909.65	2479.82	123
H1C	6068.83	10614	2543	123
H5	9184.61	8249.86	3838.14	58
H6	9842.95	9212.86	3262.65	76
H7	9271.33	10653	2513.01	85
H8	8020.62	11131.61	2309.96	76
H10	6232.54	11380.07	3850.47	125
H11	4946.71	10617.04	3801.69	139
H12	4739.91	8042.32	3383.97	121
H13	7193.52	7644.75	4255.66	48
H15	7449.61	10453.86	4668.95	69
H16	8186.86	11922.7	5344.82	86
H17	9355.11	11035.81	5760.54	91
H18	9769.59	8646.32	5505.76	90
H21	9446.19	3903.57	4633.32	86
H22	8762.36	2054.12	4063.59	90

H23	7603.4	2695.54	3558.41	89
H24	7118.05	5193.2	3627	70

8. Reference.

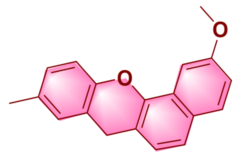
1 E. Böβ, T. Hillringhaus, J. Nitsch and M. Klussmann, Lewis Acid-Catalysed One Pot Synthesis of Substituted Xanthenes. *Org. Biomol. Chem.*, 2011, **9**, 1744−1748.

2 J. Rodriguez, D. Vesseur, A. Tabey, S. Mallet-Ladeira, K. Miqueu and D. Bourissou, Au(I)/Au(III) Catalytic Allylation Involving π-Allyl Au(III) Complexes. *ACS Catal.*, 2022, **12**, 993−1003.

3 Y. Kong, J-K. Kim, Y. Li, J. Zhang, M. Huang and Y. Wu, An oxidant- and catalyst-free electrooxidative cross-coupling approach to 3-tetrahydroisoquinoline substituted coumarins. *Green Chem.*, 2021, **23**, 274−1279.

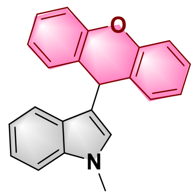
9. Analytic data of the obtained compounds.

(1) 2-methoxy-9-methyl-7*H*-benzo[*c*]xanthene (2i)



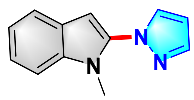
Yellow solid; m.p.: 80-83 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 8.9 Hz, 1H), 7.64 (d, *J* = 2.6 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.16 – 7.12 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 10.1 Hz, 2H), 4.15 (s, 2H), 4.01 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.00, 149.87, 145.98, 132.64, 129.49, 129.27, 128.93, 128.31, 125.33, 124.40, 122.11, 120.24, 118.64, 116.43, 114.94, 100.02, 55.57, 28.36, 20.85. HRMS (ESI): Calcd. for $C_{19}H_{16}O_2$ $[M+H]^+$: 277.1223; found: 277.1220.

(2) methyl-3-(9*H*-xanthen-9-yl)-1*H*-indole (1a-1)



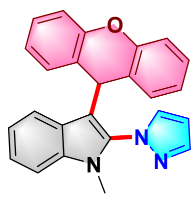
Known compounds, yellow solid, ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.42 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 2H), 7.23 – 7.13 (m, 7H), 7.18 – 7.12 (m, 6H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.96 – 6.90 (m, 2H), 6.90 (s, 1H), 5.54 (s, 1H), 3.74 (s, 3H).

(3) 1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (1a-2)



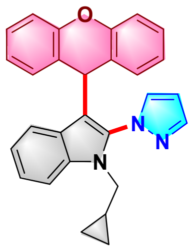
Known compounds, white solid, ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 1.2 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.64 (d, *J* = 6.9 Hz, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.31 (t, *J* = 7.1 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.53 (s, 1H), 6.49 – 6.47 (m, 1H), 3.69 (s, 3H).

(4) 1-methyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4aaa)



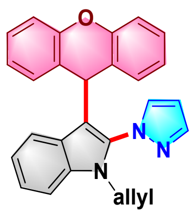
Yellow solid, (84.0 mg, 89% yield); m.p.: 226-228 °C; ^{1}HNMR (500 MHz, Chloroform-d) δ 7.86 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 2.4 Hz, 1H), 7.33 (d, *J* = 8.9 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.20 – 7.16 (m, 2H), 7.13 – 7.08 (m, 4H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.95 – 6.90 (m, 2H), 6.52 (t, *J* = 2.2 Hz, 1H), 5.37 (s, 1H), 3.53 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.16, 142.30, 135.30, 133.18, 132.99, 129.63, 127.95, 124.20, 123.26, 123.15, 120.73, 120.32, 116.35, 113.98, 109.71, 107.23, 33.64, 29.35. HRMS (ESI): Calcd. for $C_{25}H_{18}N_3O$ [M+H]$^+$: 378.1601; found: 378.1597

(5)1-(cyclopropylmethyl)-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4baa)



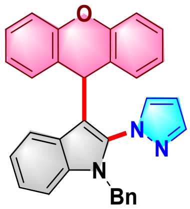
Yellow solid, (75.0 mg, 72% yield); m.p.: 192-194 °C; ^{1}HNMR (500 MHz, Chloroform-d) δ 7.86 (d, *J* = 1.9 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.21 – 7.17 (m, 2H), 7.15 – 7.10 (m, 4H), 7.00 – 6.96 (m, 1H), 6.96 – 6.92 (m, 2H), 6.52 (t, *J* = 2.2 Hz, 1H), 5.33 (s, 1H), 3.88 (d, *J* = 6.8 Hz, 2H), 1.21 – 1.09 (m, 1H), 0.48 (q, *J* = 5.9 Hz, 2H), 0.14 (q, *J* = 5.9 Hz, 2H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.19, 142.19, 134.89, 133.50, 132.63, 129.62, 127.92, 124.24, 123.29, 123.20, 123.16, 120.80, 120.19, 116.34, 114.11, 110.22, 107.14, 47.81, 33.68, 11.39, 4.22. HRMS (ESI): Calcd. for $C_{28}H_{22}N_3O$ [M+H]$^+$: 418.1914 ; found: 418.1911.

(6) 1-allyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4caa)



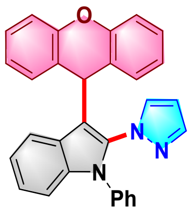
Yellow solid, (40.0 mg, 40% yield); m.p.: 169-171 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 1.9 Hz, 1H), 7.67 (d, *J* = 2.4 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H), 7.12 – 7.05 (m, 4H), 6.98 – 6.93 (m, 1H), 6.93 – 6.89 (m, 2H), 6.48 (t, *J* = 2.2 Hz, 1H), 5.90 (ddt, *J* = 17.2, 10.3, 5.1 Hz, 1H), 5.33 (s, 1H), 5.12 (d, *J* = 10.3 Hz, 1H), 4.92 (d, *J* = 17.1 Hz, 1H), 4.52 (dt, *J* = 5.0, 1.6 Hz, 2H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.21, 142.30, 134.84, 133.45, 133.36, 132.66, 129.62, 127.98, 124.33, 123.38, 123.32, 123.11, 120.92, 120.45, 116.92, 116.39, 114.41, 110.29, 107.16, 45.58, 33.66. HRMS (ESI): Calcd. for $C_{27}H_{21}N_3O$ $[M+H]^+$: 404.1757; found: 404.1752.

(7) 1-benzyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4daa)



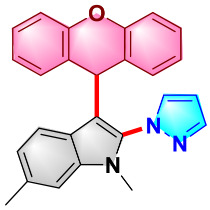
Yellow solid, (42.0 mg, 37% yield); m.p.: 214-215 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.86 (t, J = 1.6 Hz, 1H), 7.53 (t, J = 2.0 Hz, 1H), 7.32 – 7.26 (m, 5H), 7.21 (q, J = 8.3 Hz, 3H), 7.17 – 7.12 (m, 4H), 7.08 – 7.04 (m, 2H), 6.98 (q, J = 7.6 Hz, 3H), 6.44 (t, J = 2.2 Hz, 1H), 5.38 (s, 1H), 5.19 (s, 2H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.24, 142.36, 137.41, 135.15, 133.40, 132.96, 129.61, 128.84, 128.02, 127.61, 126.61, 124.40, 123.54, 123.36, 123.08, 120.95, 120.55, 116.42, 114.59, 110.49, 107.24, 46.81, 33.70. HRMS (ESI): Calcd. for $C_{31}H_{23}N_3O$ $[M+H]^+$: 454.1914; found: 454.1908.

(8) 1-phenyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4eaa)



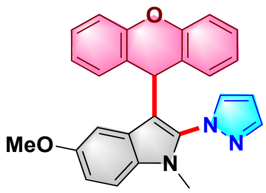
Yellow solid, (74.0 mg, 67% yield); m.p.: 199-201 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.72 (d, J = 1.8 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.36 – 7.31 (m, 1H), 7.31 – 7.27 (m, 4H), 7.23 (d, J = 7.6 Hz, 2H), 7.22 – 7.16 (m, 3H), 7.15 – 7.13 (m, 2H), 7.00 – 6.94 (m, 3H), 6.34 (t, J = 2.2 Hz, 1H), 5.46 (s, 1H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.24, 141.81, 136.26, 135.72, 133.21, 132.51, 129.97, 129.43, 128.07, 127.77, 126.79, 124.43, 123.85, 123.37, 122.90, 121.16, 120.84, 116.48, 116.44, 110.92, 107.32, 33.70. HRMS (ESI): Calcd. for $C_{30}H_{21}N_3O$ $[M+H]^+$: 440.1757; found: 440.1755.

(9) 1,6-dimethyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4faa)



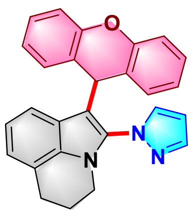
Yellow solid, (67.0 mg, 68% yield); m.p.: 195-197 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 1.8 Hz, 1H), 7.70 (d, *J* = 2.4 Hz, 1H), 7.21 – 7.16 (m, 2H), 7.15 – 7.08 (m, 6H), 6.93 (td, *J* = 7.4, 1.4 Hz, 2H), 6.82 (d, *J* = 6.7 Hz, 1H), 6.51 (t, *J* = 2.1 Hz, 1H), 5.33 (s, 1H), 3.51 (s, 3H), 2.46 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.18, 142.23, 135.71, 133.24, 133.21, 132.49, 129.61, 127.90, 123.27, 123.25, 122.10, 121.95, 120.41, 116.31, 113.78, 109.66, 107.14, 33.66, 29.26, 22.05. HRMS (ESI): Calcd. for $C_{26}H_{21}N_3O$ $[M+H]^+$: 392.1757; found: 392.1751.

(10) 5-methoxy-1-methyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4gaa)



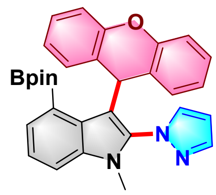
Yellow solid, (62.0 mg, 61% yield); m.p.: 230-232 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 1.9 Hz, 1H), 7.67 (d, *J* = 2.4 Hz, 1H), 7.19 (d, *J* = 8.9 Hz, 2H), 7.16 (td, *J* = 7.7, 1.0 Hz, 3H), 7.09 (dd, *J* = 8.1, 1.3 Hz, 4H), 6.92 (td, *J* = 7.4, 1.3 Hz, 3H), 6.88 (dd, *J* = 8.9, 2.5 Hz, 2H), 6.69 (d, *J* = 2.5 Hz, 1H), 6.50 (t, *J* = 2.2 Hz, 1H), 5.30 (s, 1H), 3.63 (s, 3H), 3.48 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 154.25, 151.27, 142.25, 133.18, 132.99, 130.52, 129.73, 127.97, 124.58, 123.35, 123.12, 116.29, 114.01, 113.43, 110.57, 107.22, 102.24, 55.69, 33.71, 29.48. HRMS (ESI): Calcd. for $C_{26}H_{21}N_3O_2$ $[M+H]^+$: 408.1706; found: 408.1701.

(11) 2-(1*H*-pyrazol-1-yl)-1-(9*H*-xanthen-9-yl)-5,6-dihydro-4*H*-pyrrolo[3,2,1-*ij*]quinoline (4haa)



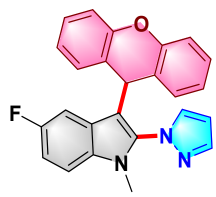
Yellow solid, (49.5 mg, 49% yield); m.p.: 155-157 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 1.8 Hz, 1H), 7.70 (d, *J* = 2.3 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.14 – 7.07 (m, 4H), 7.03 (d, *J* = 7.1 Hz, 1H), 6.97 – 6.89 (m, 3H), 6.91 – 6.84 (m, 1H), 6.50 (t, *J* = 2.1 Hz, 1H), 5.41 (s, 1H), 3.99 – 3.93 (m, 2H), 2.99 (t, *J* = 6.1 Hz, 2H), 2.24 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.25, 142.10, 132.70, 132.39, 131.62, 129.65, 127.87, 123.42, 123.26, 122.36, 121.93, 120.31, 120.12, 118.06, 116.32, 113.05, 107.09, 41.62, 33.75, 24.83, 22.57. HRMS (ESI): Calcd. for $C_{27}H_{21}N_3O$ $[M+H]^+$: 404.1757; found: 404.1752.

(12) 1-methyl-2-(1*H*-pyrazol-1-yl)-4-(4,4,5,5-tetramethyl-1,3-dioxolan-2-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4iaa)



Yellow solid, (76.0 mg, 60% yield); m.p.: 192-194 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.83 (d, *J* = 6.0 Hz, 1H), 7.48 (d, *J* = 7.0 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.17 (d, *J* = 7.4 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 3H), 6.91 – 6.85 (m, 5H), 6.90 – 6.83 (m, 5H), 6.55 (d, *J* = 2.5 Hz, 1H), 6.09 (t, *J* = 2.1 Hz, 1H), 3.31 (s, 3H), 1.33 (s, 13H). ^{13}CNMR (125MHz, $CDCl_3$) δ 150.22, 141.21, 134.13, 133.80, 132.98, 130.05, 129.68, 129.41, 127.25, 124.29, 122.63, 122.20, 118.38, 115.78, 112.67, 106.08, 84.17, 32.04, 29.02, 24.89. HRMS (ESI): Calcd. for $C_{31}H_{30}BN_3O_3$ $[M+H]^+$: 503.2489; found: 504.2449.

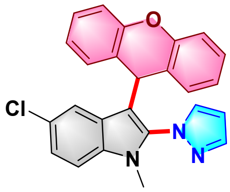
(13) 5-fluoro-1-methyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4jaa)



Yellow solid, (57.0 mg, 58% yield), m.p.: 239-241 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 1.8 Hz, 1H), 7.70 (d, *J* = 2.3 Hz, 1H), 7.22 (dd, *J* = 8.9, 4.2 Hz, 1H), 7.22 – 7.14 (m, 2H), 7.11 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.97 (td, *J* = 9.0, 2.5 Hz, 2H), 6.92 (td, *J* = 7.4, 1.3 Hz, 2H), 6.86 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.52 (t, *J* = 2.1 Hz, 1H), 5.30 (s, 1H), 3.51 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$)

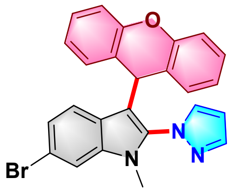
δ 157.88 (d, J = 233.7 Hz), 151.18, 142.46, 134.13, 133.10, 131.93, 129.50, 128.13,124.38 (d, J = 10 Hz), 123.34, 122.75, 116.54, 114.18 (d, J = 5 Hz), 111.95 (d, J = 26.2 Hz), 110.66 (d, J = 10 Hz), 107.43, 105.68 (d, J = 23.7 Hz), 33.61, 29.62. ^{19}FNMR (470 MHz, $CDCl_3$) δ -122.65. HRMS (ESI): Calcd. for $C_{25}H_{18}FN_3O$ $[M+H]^+$: 396.1507; found: 396.1504.

(14) 5-chloro-1-methyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4kaa)



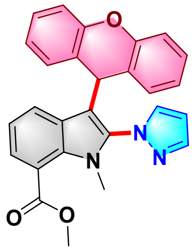
Yellow solid, (70.0 mg, 68% yield), m.p.: 252-254 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.83 (d, J = 1.9 Hz, 1H), 7.64 (d, J = 2.4 Hz, 1H), 7.26 – 7.16 (m, 3H), 7.22 – 7.15 (m, 1H), 7.10 (dd, J = 8.2, 1.3 Hz, 2H), 7.03 (dt, J = 7.8, 1.4 Hz, 2H), 6.92 (td, J = 7.4, 1.3 Hz, 2H), 6.49 (t, J = 2.2 Hz, 1H), 5.32 (s, 1H), 3.50 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.15, 142.49, 134.09, 133.69, 133.09, 129.39, 128.18, 126.01, 125.17, 123.83, 123.35, 122.71, 120.04, 116.57, 113.65, 110.96, 107.43, 33.53, 29.60. HRMS (ESI): Calcd. for $C_{25}H_{18}ClN_3O$ $[M+H]^+$: 412.1211; found: 412.1205.

(15) 6-bromo-1-methyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4laa)



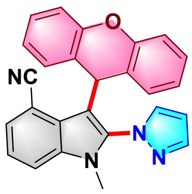
Yellow solid, (70.0 mg, 61% yield), m.p.: 222-224 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.87 (d, J = 1.9 Hz, 1H), 7.71 (d, J = 2.4 Hz, 1H), 7.48 (d, J = 1.5 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.12 – 7.08 (m, 2H), 7.07 (s, 1H), 7.06 – 7.03 (m, 3H), 6.92 (td, J = 7.4, 1.3 Hz, 2H), 6.53 (t, J = 2.2 Hz, 1H), 5.32 (s, 1H), 3.49 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.12, 142.55, 136.11, 133.31, 133.14, 129.49, 128.14, 123.74, 123.36, 122.97, 122.80, 122.08, 117.06, 116.48, 114.32, 112.84, 107.49, 33.57, 29.53. HRMS (ESI): Calcd. for $C_{25}H_{18}BrN_3O[M+H]^+$: 456.0706; found: 456.0700.

(16) methyl 1-methyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole-7-carboxylate (4maa)



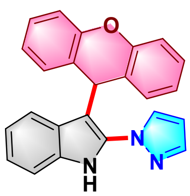
Yellow solid, (30.5 mg, 28% yield), m.p.: 202-204 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 1.7 Hz, 1H), 7.74 (d, *J* = 2.4 Hz, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.08 (dd, *J* = 14.9, 7.8 Hz, 4H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 2H), 6.54 (t, *J* = 2.2 Hz, 1H), 5.35 (s, 1H), 3.96 (s, 3H), 3.49 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 167.97, 151.08, 142.53, 135.11, 133.35, 133.14, 129.64, 128.12, 126.44, 126.35, 125.04, 123.33, 122.78, 119.56, 116.65, 116.43, 114.83, 107.62, 52.39, 33.56, 33.04. HRMS (ESI): Calcd. for $C_{27}H_{21}N_3O_3$ $[M+H]^+$: 436.1655; found: 436.1652.

(17) 1-methyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole-4-carbonitrile (4naa)



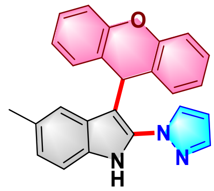
Yellow solid, (40.0 mg, 40% yield), m.p.: 126-128 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 1.6 Hz, 1H), 7.57 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.44 (ddd, *J* = 8.7, 7.1, 1.7 Hz, 2H), 7.35 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.25 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.23 – 7.19 (m, 3H), 7.07 (td, *J* = 7.5, 1.3 Hz, 2H), 6.93 (d, *J* = 2.2 Hz, 1H), 6.47 (s, 1H), 6.14 (t, *J* = 2.1 Hz, 1H), 3.81 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 152.35, 140.16, 138.28, 132.95, 130.47, 129.99, 129.00, 127.83, 124.48, 123.85, 123.13, 121.57, 117.60, 117.20, 114.47, 104.87, 103.79, 64.44, 33.37. HRMS (ESI): Calcd. for $C_{26}H_{18}N_4O$ $[M+H]^+$: 403.1553; found: 403.1547.

(18) 2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4oaa)



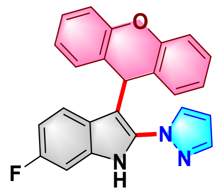
Brownish solid, (36.0 mg, 40% yield), m.p.: 142-144 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 9.84 (s, 1H), 7.77 (d, *J* = 1.9 Hz, 1H), 7.73 (d, *J* = 2.5 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.17 (m, 4H), 7.15 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.01 (dt, *J* = 7.8, 1.4 Hz, 2H), 6.96 (t, *J* = 7.1 Hz, 1H), 6.91 – 6.87 (m, 2H), 6.40 (t, *J* = 2.2 Hz, 1H), 5.79 (s, 1H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.47, 151.00, 141.57, 133.82, 132.74, 130.66, 129.05, 128.13, 126.39, 123.39, 123.19, 123.05, 120.44, 120.43, 116.44, 111.36, 107.55, 107.14, 33.38. HRMS (ESI): Calcd. for $C_{24}H_{17}N_3O$ $[M+H]^+$: 364.1444; found: 364.1440.

(19) 5-methyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4paa)



Brownish solid, (43.5 mg, 46% yield), m.p.: 194-196 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 9.64 (s, 1H), 7.73 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 2.5 Hz, 1H), 7.25 – 7.19 (m, 3H), 7.16 (m, 2H), 7.01 (ddd, *J* = 7.8, 6.3, 1.6 Hz, 4H), 6.90 (td, *J* = 7.4, 1.4 Hz, 2H), 6.35 (t, *J* = 2.2 Hz, 1H), 5.76 (s, 1H), 2.28 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.51, 141.45, 132.86, 132.03, 132.01, 130.63, 130.60, 129.71, 128.96, 128.09, 126.79, 124.75, 123.40, 123.29, 119.90, 116.41, 111.05, 111.03, 107.41, 106.29, 33.34, 21.67. HRMS (ESI): Calcd. for $C_{25}H_{19}N_3O$ $[M+H]^+$: 378.1601; found: 378.1597.

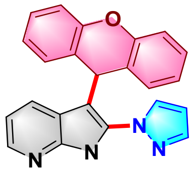
(20) 6-fluoro-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4qaa)



Brownish solid, (61.0 mg, 64% yield), m.p.: 171-173 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 10.17 – 9.98 (m, 1H), 7.77 (d, *J* = 1.9 Hz, 1H), 7.74 (d, *J* = 2.6 Hz, 1H), 7.22 (t, *J* = 6.8 Hz, 2H), 7.15 (d, *J* = 7.0 Hz, 2H), 7.06 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.00 (dd, *J* = 9.3, 2.3 Hz, 1H), 6.97 (d, *J* = 7.7 Hz, 2H), 6.92 (td, *J* = 7.4, 1.3 Hz, 2H), 6.70 (td, *J* = 9.2, 2.4 Hz, 1H), 6.42 (t, *J* = 2.2 Hz, 1H), 5.72 (s, 1H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 160.41 (d, *J* = 238.8 Hz), 151.44, 141.70, 133.92 (d, *J* = 12.5 Hz), 132.82 (d, *J* = 2.5 Hz), 130.75, 128.94, 128.31, 123.48, 122.90, 122.66, 121.47 (d, *J* = 10 Hz), 116.57, 109.33 (d, *J* = 23.7 Hz), 107.65, 107.50, 97.82 (d, *J* = 26.2Hz), 33.39. ^{19}FNMR

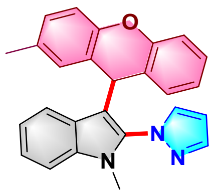
(470 MHz, $CDCl_3$) δ -118.98. HRMS (ESI): Calcd. for $C_{24}H_{16}N_4O$ $[M+H]^+$: 382.1350; found: 382.1348.

(21) 1-methyl-2-(1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-pyrrolo[2,3-b]pyridine (4raa)



Yellow solid, (52.0 mg, 55% yield), m.p.: 173-175 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 8.32 (dd, *J* = 4.7, 1.6 Hz, 1H), 7.90 (d, *J* = 1.9 Hz, 1H), 7.78 (d, *J* = 2.5 Hz, 1H), 7.47 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.11 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.06 (d, *J* = 7.6 Hz, 2H), 6.93 (td, *J* = 7.4, 1.3 Hz, 2H), 6.89 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.57 (t, *J* = 2.2 Hz, 1H), 5.34 (s, 1H), 3.65 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.14, 146.22, 144.56, 142.63, 133.01, 132.99, 129.63, 129.01, 128.22, 123.43, 122.79, 117.30, 116.72, 116.54, 112.95, 107.67, 33.60, 28.13. HRMS (ESI): Calcd. for $C_{24}H_{18}N_4O$ $[M+H]^+$: 379.1553; found: 379.1551.

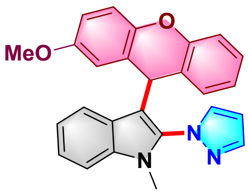
(22) 1-methyl-3-(2-methyl-9*H*-xanthen-9-yl)-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4aba)



Yellow solid, (73.0 mg, 75% yield), m.p.: 195-197 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.8 Hz, 1H), 7.72 (d, *J* = 2.3 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.19 – 7.14 (m, 1H), 7.12 – 7.08 (m, 2H), 7.03 (d, *J* = 8.3 Hz, 1H), 7.01 – 6.97 (m, 2H), 6.93 – 6.89 (m, 2H), 6.53 (t, *J* = 2.2 Hz, 1H), 5.34 (s, 1H), 3.54 (s, 3H), 2.19 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.27, 149.08, 142.27, 135.27, 133.19, 132.81, 132.49, 129.78, 129.67, 128.70, 127.85, 124.26, 123.21, 123.15, 123.05, 122.65, 120.76, 120.28, 116.29, 116.08, 114.24, 109.67, 107.21, 33.68, 29.35, 20.86. HRMS (ESI): Calcd. for $C_{26}H_{21}N_3O$ $[M+H]^+$: 392.1757; found: 392.1751.

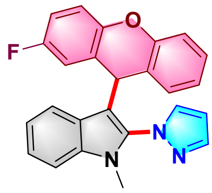
(23) 3-(2-methoxy-9*H*-xanthen-9-yl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole

(4aca)



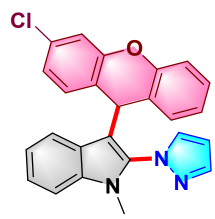
Yellow solid, (51.0 mg, 50% yield), m.p.: 155-157 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.8 Hz, 1H), 7.72 (d, *J* = 2.4 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.20 – 7.15 (m, 1H), 7.09 (dd, *J* = 7.9, 5.3 Hz, 2H), 7.06 (d, *J* = 8.9 Hz, 1H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.74 (dd, *J* = 8.9, 3.0 Hz, 1H), 6.67 (d, *J* = 2.4 Hz, 1H), 6.53 (t, *J* = 2.2 Hz, 1H), 5.33 (s, 1H), 3.53 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 155.35, 151.40, 145.30, 142.28, 135.28, 133.16, 132.82, 129.65, 127.91, 124.18, 123.92, 123.25, 123.00, 122.55, 120.71, 120.32, 117.01, 116.27, 114.25, 114.01, 113.67, 109.69, 107.26, 55.65, 34.08, 29.34. HRMS (ESI): Calcd. for $C_{26}H_{21}N_3O$ $[M+H]^+$: 408.1706; found: 408.1704.

(24) 3-(2-fluoro-9*H*-xanthen-9-yl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4ada)



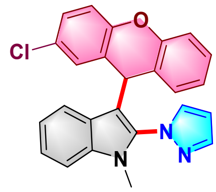
Yellow solid, (66.0 mg, 67% yield), m.p.: 219-221 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.9 Hz, 1H), 7.70 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 7.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.21 – 7.16 (m, 1H), 7.12 – 7.05 (m, 3H), 7.00 (t, *J* = 8.1 Hz, 1H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.88 (td, *J* = 8.4, 3.1 Hz, 1H), 6.84 – 6.80 (m, 1H), 6.54 (t, *J* = 2.2 Hz, 1H), 5.33 (s, 1H), 3.54 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 158.57 (d, *J* = 240.0 Hz), 151.07, 147.29 (d, *J* = 2.5 Hz), 142.38, 135.32, 133.10, 133.07, 129.58, 128.12, 124.70 (d, *J* = 7.5 Hz), 124.00, 123.42, 123.41, 122.16, 120.55, 120.46, 117.50 (d, *J* = 7.5 Hz), 116.32, 115.58 (d, *J* = 23.7 Hz), 114.95 (d, *J* = 25 Hz), 113.42, 109.84, 107.39, 33.94, 29.37. ^{19}FNMR (470 MHz, $CDCl_3$) δ -120.14. HRMS (ESI): Calcd. for $C_{25}H_{18}FN_3O$ $[M+H]^+$: 396.1506; found: 396.1505.

(25) 3-(3-chloro-9*H*-xanthen-9-yl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4aea)



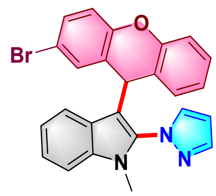
Yellow solid, (39.0 mg, 38% yield), m.p.: 201-203 °C; [1]HNMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 1.8 Hz, 1H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 7.1 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.18 (t, *J* = 6.8 Hz, 1H), 7.11 (d, *J* = 2.1 Hz, 1H), 7.10 – 7.06 (m, 2H), 7.00 (dd, *J* = 17.2, 8.1 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.88 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.52 (t, *J* = 2.2 Hz, 1H), 5.30 (s, 1H), 3.52 (s, 3H). [13]CNMR (125 MHz, $CDCl_3$) δ 151.58, 150.74, 142.38, 135.29, 133.12, 133.03, 133.02, 130.72, 129.61, 128.14, 124.03, 123.68, 123.51, 123.43, 122.78, 121.82, 120.52, 120.48, 116.59, 116.42, 113.68, 109.83, 107.37, 33.29, 29.37. HRMS (ESI): Calcd. for $C_{25}H_{18}ClN_3O$ $[M+H]^+$: 412.1211; found: 412.1206.

(26) 3-(2-chloro-9*H*-xanthen-9-yl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4afa)



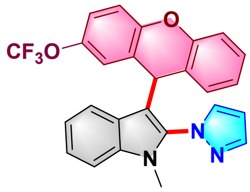
Yellow solid, (51.0 mg, 50% yield), m.p.: 208-210 °C; [1]HNMR (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.9 Hz, 1H), 7.69 (d, *J* = 2.5 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 1.3 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.17 (td, *J* = 7.9, 7.5, 1.6 Hz, 1H), 7.11 (s, 1H), 7.10 – 7.06 (m, 3H), 7.04 (d, *J* = 8.7 Hz, 1H), 6.99 (s, 1H), 6.92 (d, *J* = 1.3 Hz, 1H), 6.53 (t, *J* = 2.1 Hz, 1H), 5.31 (s, 1H), 3.53 (s, 3H). [13]CNMR (125 MHz, $CDCl_3$) δ 150.78, 149.80, 142.39, 135.29, 133.11, 129.70, 129.28, 128.15, 128.13, 127.94, 124.86, 124.02, 123.59, 123.41, 122.42, 120.49, 120.45, 117.81, 116.35, 113.59, 109.87, 107.41, 33.65, 29.39. HRMS (ESI): Calcd. for $C_{25}H_{18}ClN_3O$ $[M+H]^+$: 412.1211; found: 412.1207.

(27) 3-(2-bromo-9*H*-xanthen-9-yl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4aga)



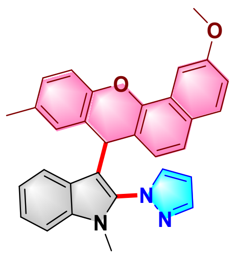
Yellow solid, (65.0 mg, 57% yield), m.p.: 200-202 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 1.9 Hz, 1H), 7.68 (d, *J* = 2.5 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.28 (s, 1H), 7.25 (d, *J* = 5.5 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 7.21 (d, *J* = 1.4 Hz, 1H), 7.19 – 7.15 (m, 1H), 7.08 (dt, *J* = 7.8, 1.6 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.53 (t, *J* = 2.2 Hz, 1H), 5.32 (s, 1H), 3.53 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 150.72, 150.33, 142.39, 135.28, 133.11, 132.23, 131.03, 129.73, 128.16, 125.37, 124.03, 123.62, 123.42, 122.48, 120.51, 120.43, 118.25, 116.36, 115.42, 113.64, 109.88, 107.42, 33.58, 29.40. HRMS (ESI): Calcd. for $C_{25}H_{18}BrN_3O$ $[M+H]^+$: 456.0706; found: 456.0700.

(28) 1-methyl-2-(1*H*-pyrazol-1-yl)-3-(2-(trifluoromethyl)-9*H*-xanthen-9-yl)-1*H*-indole (4aha)



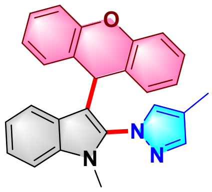
Yellow solid, (50.0 mg, 43% yield), m.p.: 221-223 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 1.9 Hz, 1H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.26 (d, *J* = 15.3 Hz, 1H), 7.19 (dd, *J* = 15.2, 7.4 Hz, 2H), 7.13 – 7.00 (m, 4H), 6.99 (t, *J* = 7.9 Hz, 2H), 6.94 (dd, *J* = 13.5, 7.5 Hz, 2H), 6.52 (t, *J* = 2.2 Hz, 1H), 5.33 (s, 1H), 3.53 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 150.88, 149.71, 144.52 (q, *J* = 3.7，1.2 Hz), 142.41, 135.32, 133.16, 133.03, 129.60, 128.22, 124.76, 124.00, 123.73, 123.45, 122.30, 121.57, 120.85, 120.51, 120.48, 119.53, 117.50, 116.38, 113.20, 109.90, 107.45, 33.85, 29.42. ^{19}FNMR (470 MHz, $CDCl_3$) δ -58.13. HRMS (ESI): Calcd. for $C_{26}H_{18}F_3N_3O$ $[M+H]^+$: 462.1423; found: 462.1416.

(29) 3-(2-methoxy-10-methyl-12*H*-benzo[a]xanthen-12-yl)-1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indole (4aia)



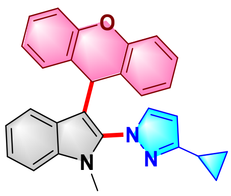
Yellow solid, (12.0 mg, 10% yield), m.p.: 226-228 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 1.9 Hz, 1H), 7.75 (dd, *J* = 4.2, 2.5 Hz, 2H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.31 – 7.27 (m, 3H), 7.20 (t, *J* = 8.0 Hz, 2H), 7.14 (dd, *J* = 8.9, 2.6 Hz, 1H), 7.01 (d, *J* = 8.6 Hz, 2H), 6.94 (s, 1H), 6.92 (t, *J* = 8.1 Hz, 1H), 6.52 (t, *J* = 2.2 Hz, 1H), 5.43 (s, 1H), 4.05 (s, 3H), 3.52 (s, 3H), 2.21 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 157.99, 148.94, 145.08, 142.29, 135.26, 133.30, 132.79, 132.55, 130.06, 129.23, 128.90, 128.68, 125.10, 124.63, 124.43, 123.21, 122.60, 122.28, 120.67, 120.30, 118.70, 117.30, 116.23, 114.92, 109.65, 107.25, 100.41, 55.59, 34.07, 29.35, 20.93. HRMS (ESI): Calcd. for $C_{31}H_{25}N_3O_2$ $[M+H]^+$: 472.2019; found: 472.2015.

(30) 1-methyl-2-(4-methyl-1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4aab)



Yellow solid, (68.5 mg, 70% yield), m.p.: 194-196 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.66 (s, 1H), 7.44 (s, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.19 – 7.15 (m, 2H), 7.12 – 7.07 (m, 4H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.92 (td, *J* = 7.4, 1.3 Hz, 2H), 5.37 (s, 1H), 3.54 (s, 3H), 2.19 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.20, 143.15, 135.27, 133.44, 131.50, 129.67, 127.90, 124.18, 123.26, 123.12, 120.73, 120.22, 117.68, 116.29, 113.64, 109.68, 33.64, 29.37, 8.96. HRMS (ESI): Calcd. for $C_{26}H_{21}N_3O$ $[M+H]^+$: 392.1757; found: 392.1750.

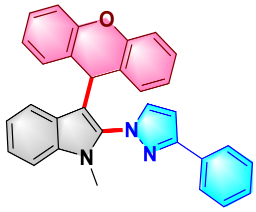
(31) 2-(3-cyclopropyl-1*H*-pyrazol-1-yl)-1-methyl-3-(9*H*-xanthen-9-yl)-1*H*-indole (4aac)



Yellow solid, (53.0 mg, 51% yield), m.p.: 121-123 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.49 (d, *J* = 2.4 Hz, 1H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.23 (dd, *J* = 13.9, 8.1 Hz, 2H), 7.18 – 7.15 (m, 2H), 7.10 – 7.06 (m, 4H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.92 – 6.89 (m, 2H), 6.13 (d, *J* = 2.4 Hz, 1H), 5.38 (s, 1H), 3.54 (s, 3H), 2.02 (ddd, *J* = 13.4, 8.5, 5.0 Hz, 1H), 1.01 – 0.97 (m, 2H), 0.85 – 0.81 (m, 2H). ^{13}CNMR (125 MHz, $CDCl_3$)

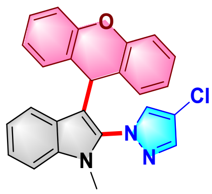
δ 158.03, 151.17, 135.23, 133.63, 133.29, 129.68, 127.88, 124.33, 123.31, 123.21, 123.11, 120.58, 120.21, 116.31, 113.78, 109.67, 103.91, 33.61, 29.42, 9.38, 8.47. HRMS (ESI): Calcd. for $C_{28}H_{23}N_3O$ $[M+H]^+$: 418.1914; found: 418.1908.

(32) 1-methyl-2-(3-phenyl-1*H*-pyrazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4aad)



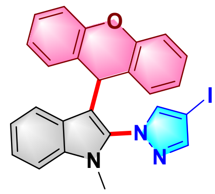
Yellow solid, (57.0 mg, 50% yield), m.p.: 253-254 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 6.9 Hz, 2H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.32 (dd, *J* = 12.4, 8.1 Hz, 2H), 7.27 – 7.24 (m, 1H), 7.16 (t, *J* = 7.8 Hz, 4H), 7.08 (d, *J* = 6.9 Hz, 2H), 7.00 (t, *J* = 7.0 Hz, 1H), 6.95 – 6.89 (m, 2H), 6.79 (d, *J* = 2.4 Hz, 1H), 5.49 (s, 1H), 3.60 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 154.14, 151.16, 135.31, 134.44, 133.04, 132.89, 129.71, 128.83, 128.44, 127.95, 126.17, 124.38, 123.30, 123.25, 123.21, 120.64, 120.38, 116.38, 114.27, 109.77, 104.64, 33.68, 29.52. HRMS (ESI): Calcd. for $C_{31}H_{23}N_3O$ $[M+H]^+$: 454.1914; found: 454.1908.

(33) 2-(4-chloro-1*H*-pyrazol-1-yl)-1-methyl-3-(9*H*-xanthen-9-yl)-1*H*-indole (4aae)



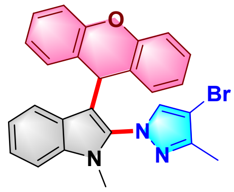
Yellow solid, (36.0 mg, 35% yield), m.p.: 164-166 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.54 (s, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 7.28 (m, 1H), 7.20 – 7.15 (m, 2H), 7.09 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.05 (d, *J* = 7.7 Hz, 2H), 7.03 – 7.00 (m, 1H), 6.93 – 6.89 (m, 2H), 5.40 (s, 1H), 3.52 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.08, 140.89, 135.19, 132.17, 130.84, 129.55, 128.10, 124.20, 123.66, 123.30, 122.86, 120.72, 120.60, 116.45, 114.94, 112.09, 109.83, 33.55, 29.38. HRMS (ESI): Calcd. for $C_{25}H_{18}ClN_3O$ $[M+H]^+$: 412.1211; found: 412.1207.

(34) 2-(4-iodo-1*H*-pyrazol-1-yl)-1-methyl-3-(9*H*-xanthen-9-yl)-1*H*-indole (4aaf)



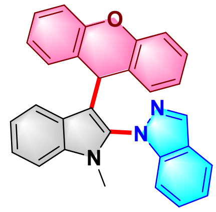
Yellow solid (35.0 mg, 28% yield), m.p.: 198-200 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.55 (s, 1H), 7.34 (dd, *J* = 13.7, 8.1 Hz, 2H), 7.28 (d, *J* = 7.1 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.10 (d, *J* = 6.9 Hz, 2H), 7.06 – 7.02 (m, 3H), 6.93 – 6.89 (m, 2H), 5.42 (s, 1H), 3.50 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.00, 147.23, 137.26, 135.16, 131.95, 129.56, 128.08, 124.27, 123.62, 123.28, 122.85, 120.64, 120.58, 116.44, 114.99, 109.82, 58.66, 33.49, 29.39. HRMS (ESI): Calcd. for $C_{25}H_{18}IN_3O$ $[M+H]^+$: 504.0567; found: 504.0562.

(35) 2-(4-bromo-3-methyl-1*H*-pyrazol-1-yl)-1-methyl-3-(9*H*-xanthen-9-yl)-1*H*-indole (4aag)



Yellow solid, (53.0 mg, 45% yield), m.p.: 140-142 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.46 (s, 1H), 7.34 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.26 (d, *J* = 1.2 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.09 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 8.1 Hz, 1H), 6.93 – 6.89 (m, 2H), 5.44 (s, 1H), 3.53 (s, 3H), 2.32 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.04, 150.48, 135.13, 133.26, 132.46, 129.58, 127.97, 127.95, 124.31, 123.48, 123.24, 123.00, 120.58, 120.48, 116.36, 114.84, 109.78, 96.28, 33.48, 29.38, 12.22. HRMS (ESI): Calcd. for $C_{26}H_{20}BrN_3O$ $[M+H]^+$: 470.0862; found: 470.0860.

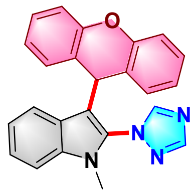
(36) 1-(1-methyl-3-(9*H*-xanthen-9-yl)-1*H*-indol-2-yl)-1*H*-indazole (4aah)



Yellow solid, (13.0 mg, 12% yield), m.p.: 202-204 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.2 Hz, 1H), 7.37 –

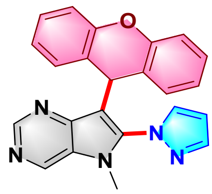
7.33 (m, 2H), 7.32 – 7.26 (m, 4H), 7.17 – 7.13 (m, 1H), 7.13 – 7.09 (m, 1H), 7.06 (d, *J* = 6.9 Hz, 1H), 7.01 – 6.96 (m, 3H), 6.94 – 6.91 (m, 1H), 6.89 – 6.85 (m, 1H), 5.23 (s, 1H), 3.39 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.40, 150.97, 142.70, 137.08, 135.70, 130.84, 130.14, 129.60, 128.06, 127.92, 127.80, 124.46, 124.33, 123.39, 123.30, 123.28, 123.11, 122.95, 122.10, 121.52, 120.89, 120.26, 116.67, 116.44, 116.18, 109.76, 109.73, 33.93, 29.30. HRMS (ESI): Calcd. for $C_{29}H_{21}N_3O$ $[M+H]^+$: 428.1757; found: 428.1752.

(37) 1-methyl-2-(1*H*-1,2,4-triazol-1-yl)-3-(9*H*-xanthen-9-yl)-1*H*-indole (4aai)



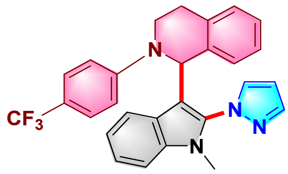
Yellow solid, (37.0 mg, 39% yield), m.p.: 205-208 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 8.10 (s, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 7.32 (t, *J* = 7.0 Hz, 1H), 7.20 – 7.15 (m, 2H), 7.09 (ddd, *J* = 12.1, 8.1, 1.3 Hz, 3H), 7.06 – 7.03 (m, 2H), 6.92 (td, *J* = 7.4, 1.3 Hz, 2H), 5.43 (s, 1H), 3.49 (s, 3H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 153.41, 150.84, 146.38, 135.35, 129.39, 128.48, 128.25, 124.44, 124.04, 123.32, 122.57, 120.87, 120.52, 116.60, 116.11, 109.92, 33.42, 29.39. HRMS (ESI): Calcd. for $C_{24}H_{18}N_4O$ $[M+H]^+$: 379.1553; found: 379.1548.

(38) 6-(1*H*-pyrazol-1-yl)-7-(9*H*-xanthen-9-yl)-5*H*-pyrrolo[3,2-*d*]pyrimidine (4saa)



Yellow solid, (26.0 mg, 34% yield), m.p.: 102-105 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 8.86 (s, 1H), 8.73 (d, *J* = 2.7 Hz, 1H), 7.81 (d, *J* = 1.6 Hz, 1H), 7.41 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.14 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.02 (d, *J* = 2.8 Hz, 1H), 7.00 (td, *J* = 7.4, 1.4 Hz, 2H), 6.52 (dd, *J* = 2.7, 1.7 Hz, 1H), 5.95 (s, 1H).^{13}CNMR (125 MHz, $CDCl_3$) δ 151.47, 150.36, 149.88, 143.58, 141.71, 130.54, 129.87, 128.02, 127.83, 124.68, 123.46, 123.42, 116.64, 116.02, 108.23, 33.55. HRMS (ESI): Calcd. for $C_{22}H_{15}N_5O$ $[M+H]^+$: 366.1349; found: 366.1347.

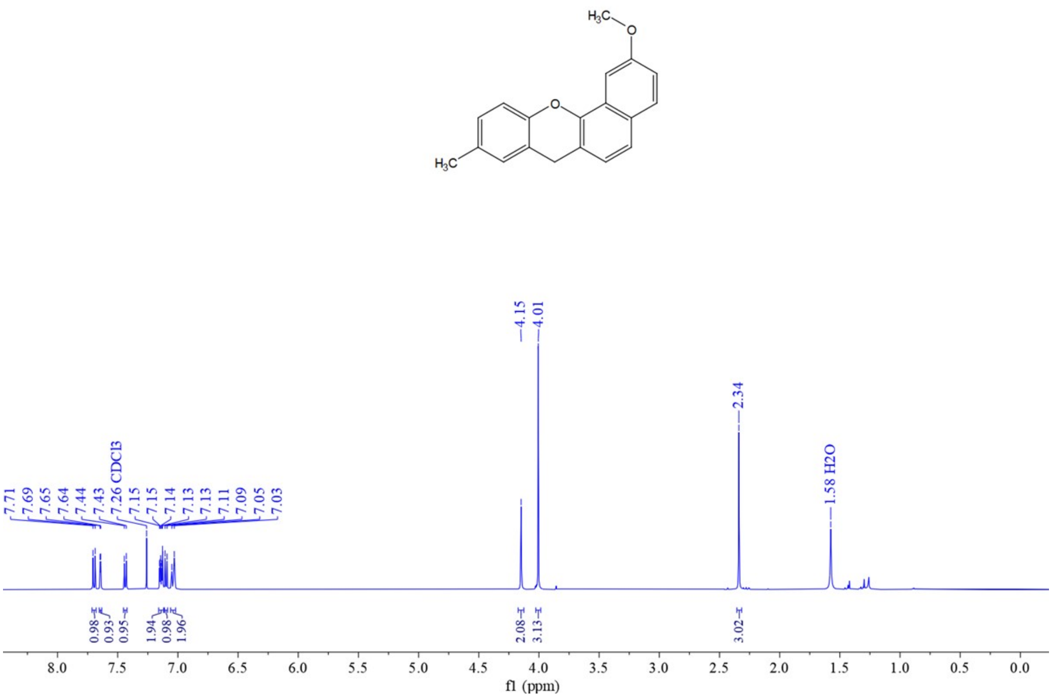
(39)1-(1-methyl-2-(1*H*-pyrazol-1-yl)-1*H*-indol-3-yl)-2-(4(trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (4aja)



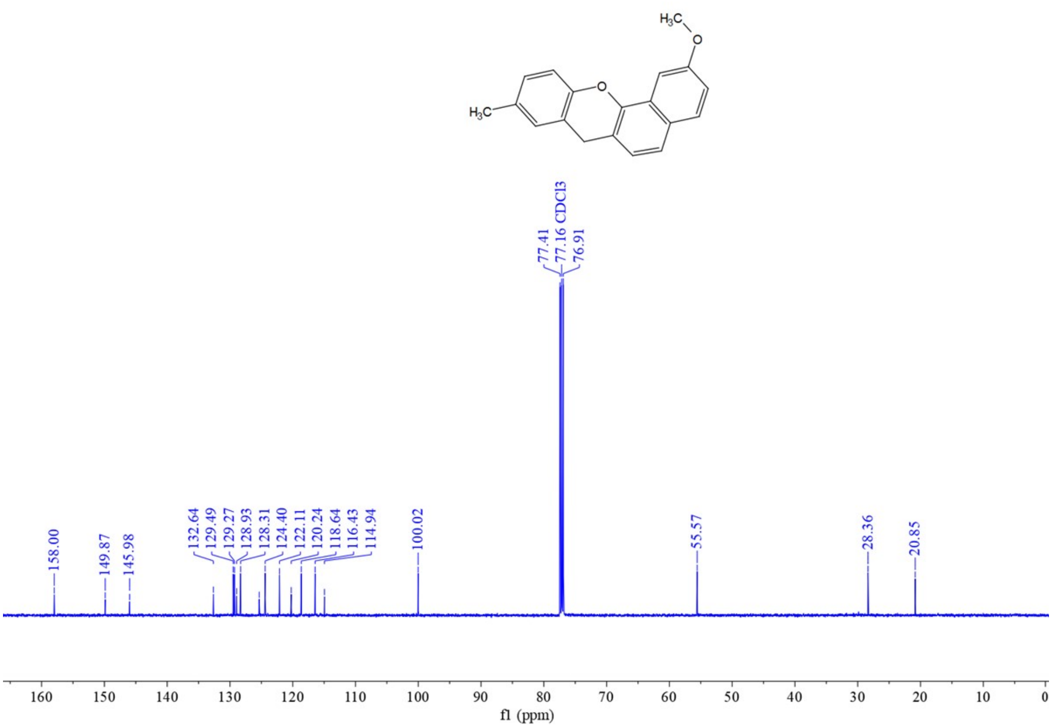
Yellow solid, (16.0 mg, 13% yield), m.p.: 83-85 °C; ^{1}HNMR (500 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.34 – 7.27 (m, 2H), 7.27 – 7.21 (m, 2H), 7.16 (m, 2H), 7.09 (dt, *J* = 15.4, 8.3 Hz, 3H), 6.79 (d, *J* = 8.5 Hz, 2H), 6.37 (t, *J* = 2.3 Hz, 1H), 6.20 (s, 1H), 3.79 – 3.65 (m, 2H), 3.40 (s, 3H), 3.06 (dt, *J* = 15.5, 7.0 Hz, 1H), 2.87 (dt, *J* = 16.3, 4.5 Hz, 1H). ^{13}CNMR (125 MHz, $CDCl_3$) δ 151.80, 141.98, 136.53, 134.93, 134.67, 133.48, 133.14, 128.66, 127.99, 126.97, 126.47, 126.44, 126.41, 126.39, 125.43, 124.97 (d, *J* = 268.7), 123.10, 120.66, 120.51, 119.60 (q, *J* = 32.7), 115.02, 111.65, 109.83, 107.13, 55.08, 43.30, 29.23, 27.22. ^{19}FNMR (470 MHz, $CDCl_3$) δ -61.07. HRMS (ESI): Calcd. for $C_{28}H_{23}F_3N_4$ [M+H]+: 473.1947; found: 473.1944.

10. NMR spectra of the obtained compounds.

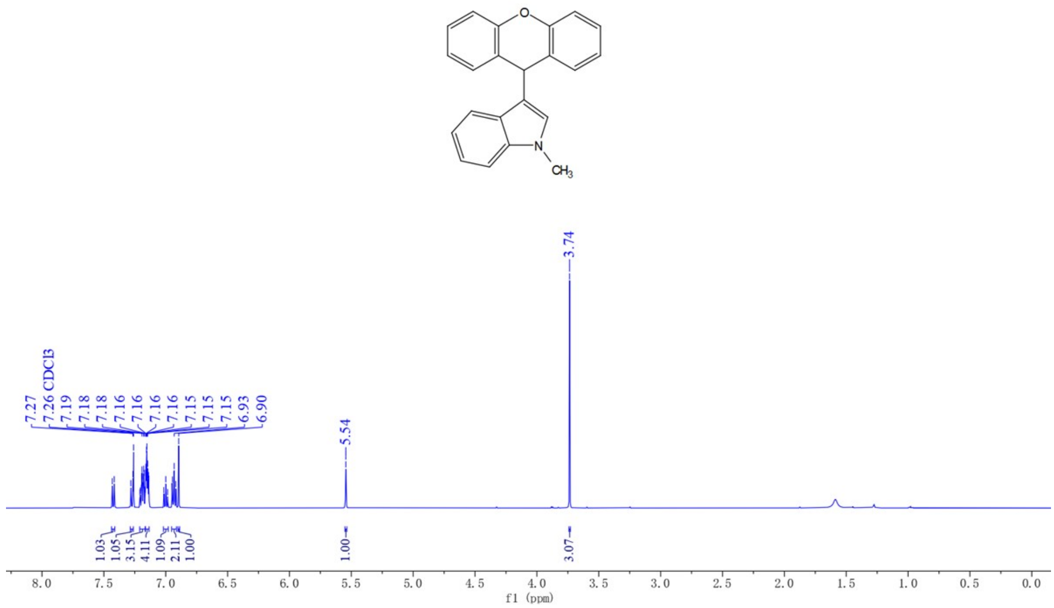
(1) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 2i



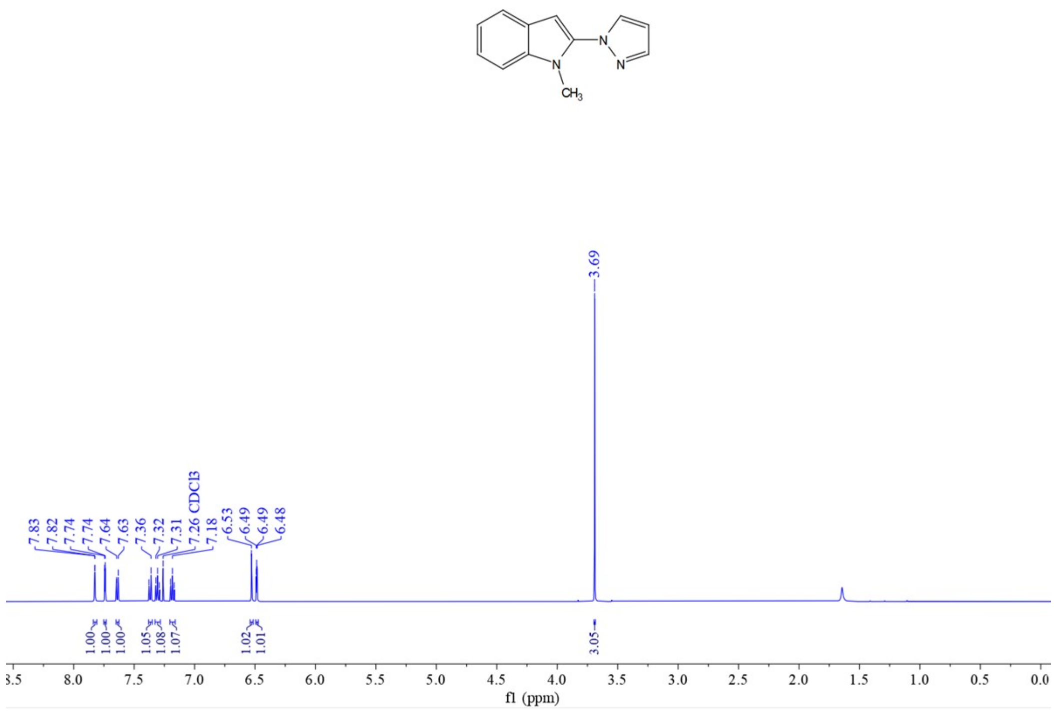
(2) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 2i



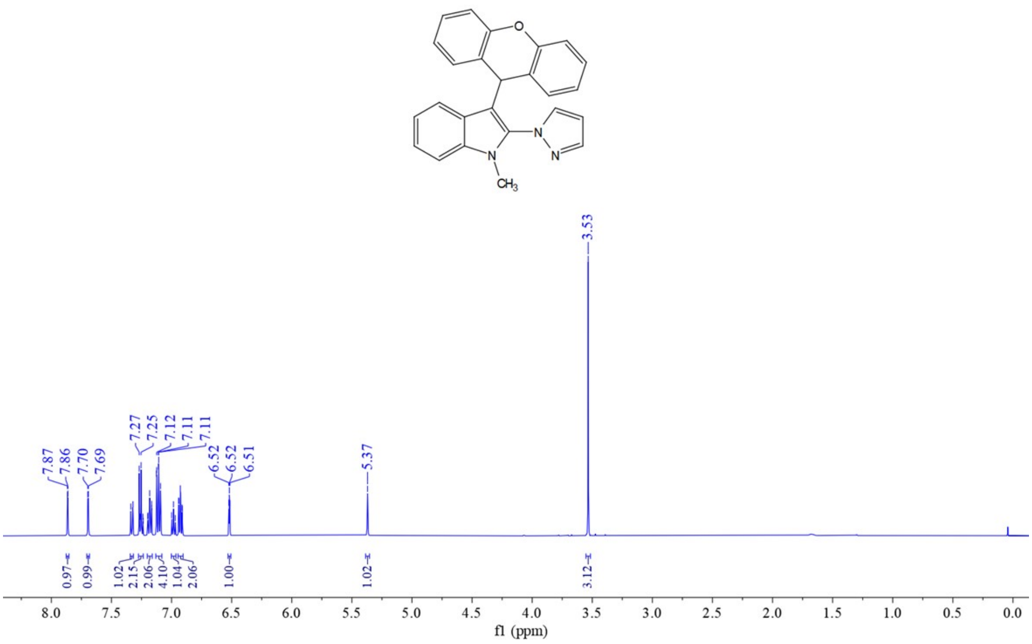
(3) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 2a-1



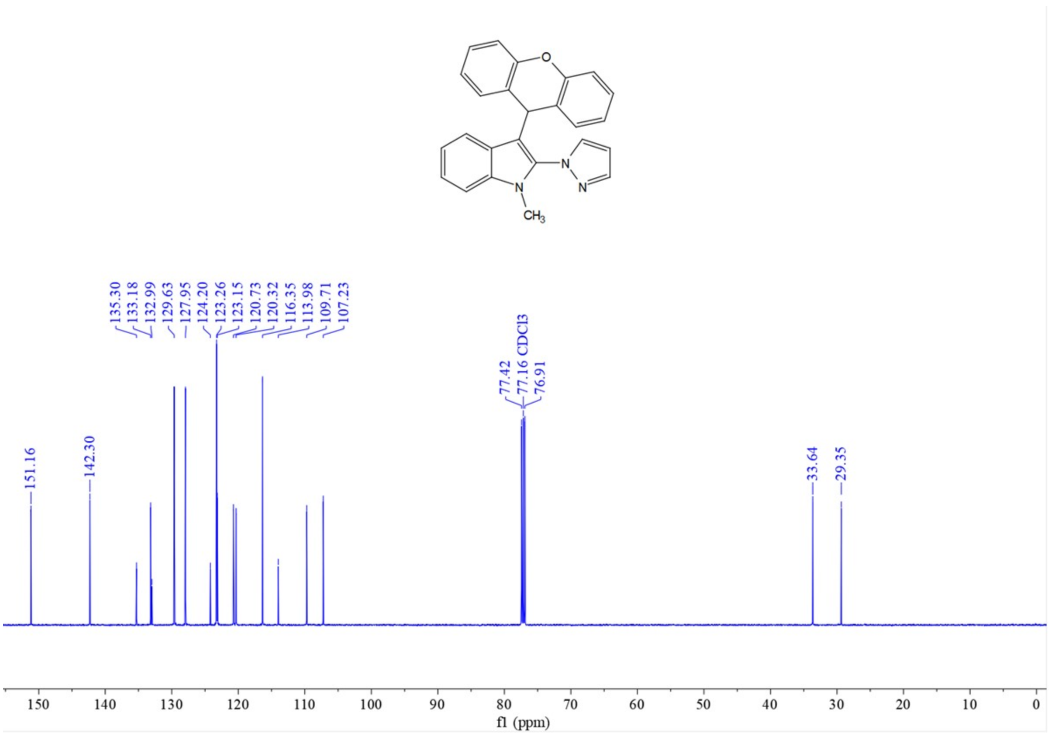
(4) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 2a-2



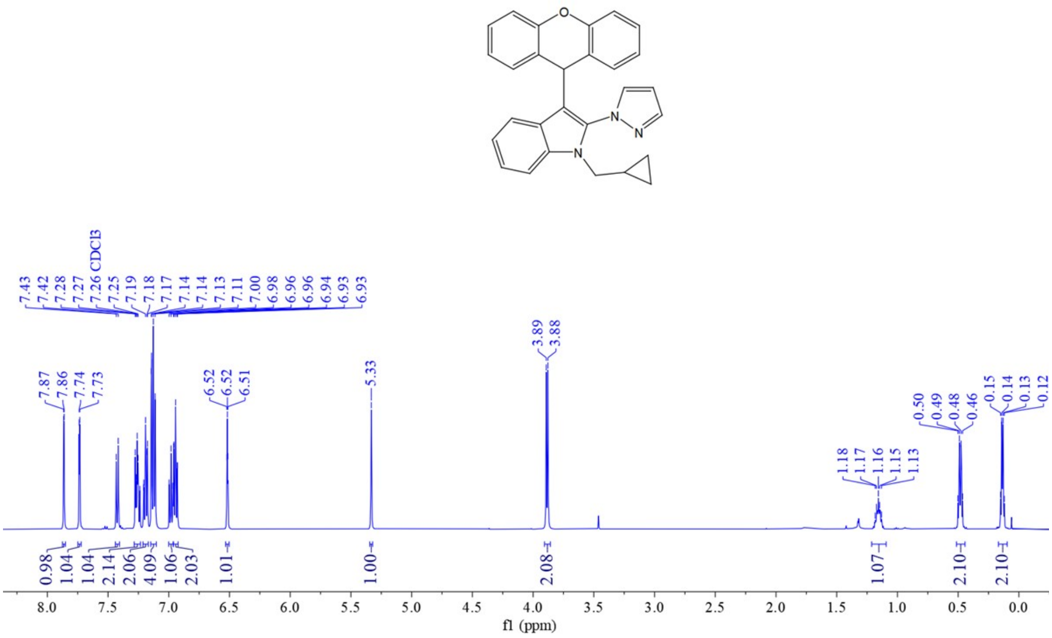
(5) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aaa



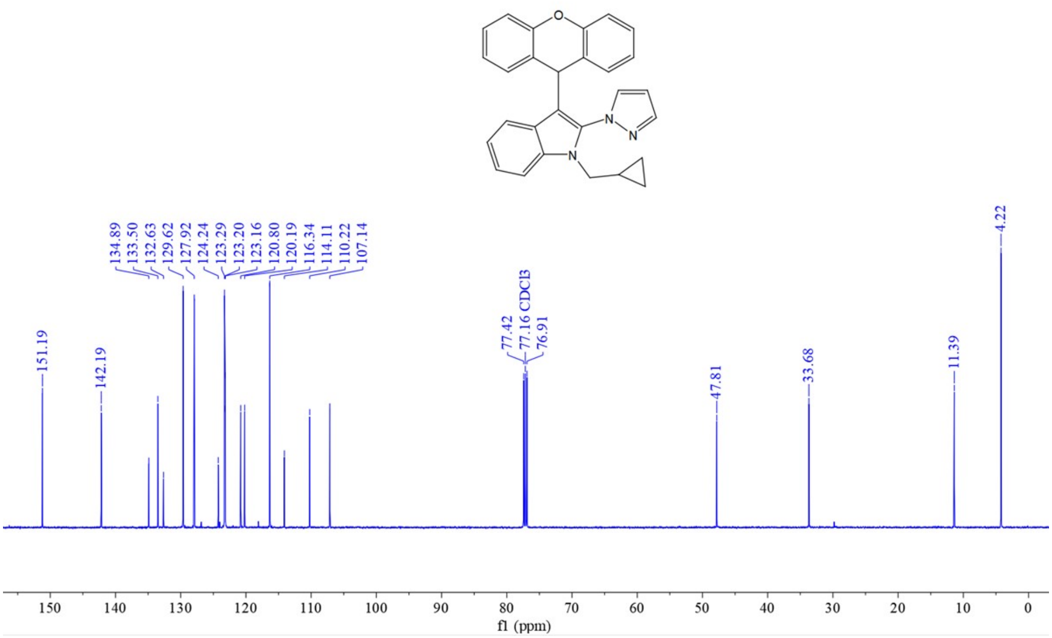
(6) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aaa



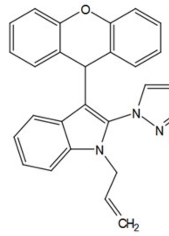
(7) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4baa

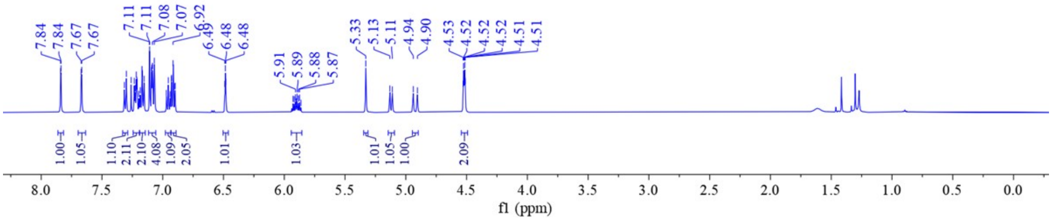


(8) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4baa

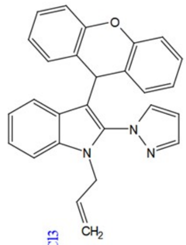


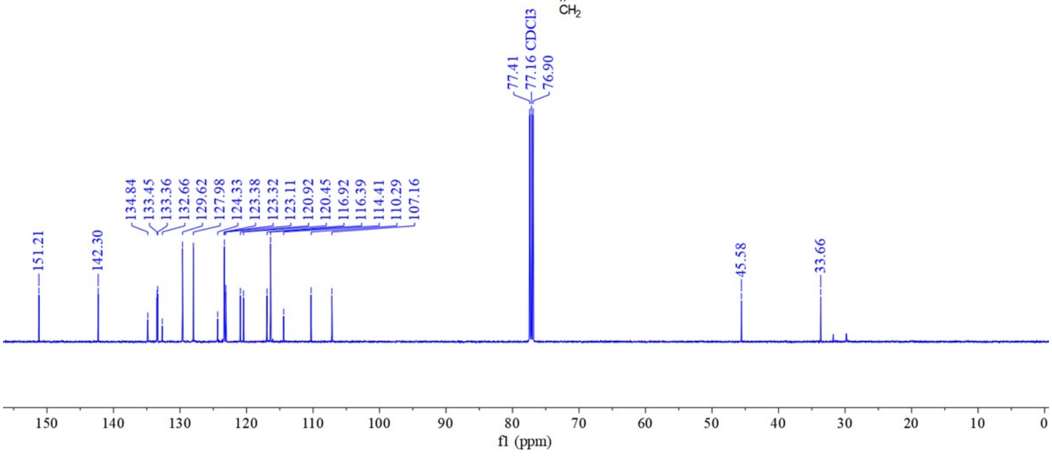
(9) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4caa



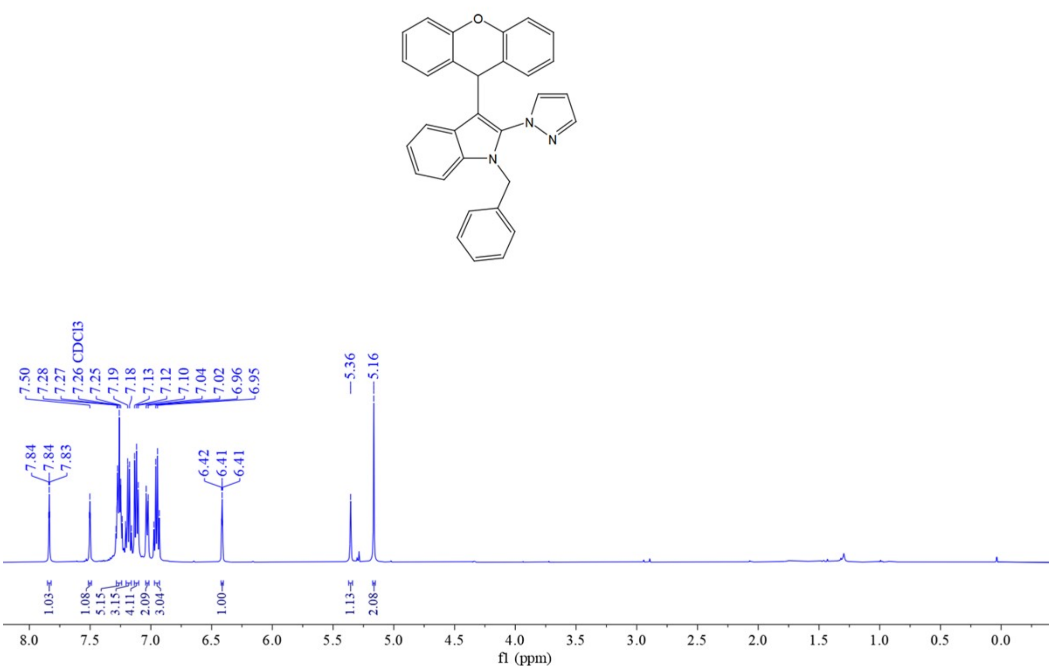


(10) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4caa

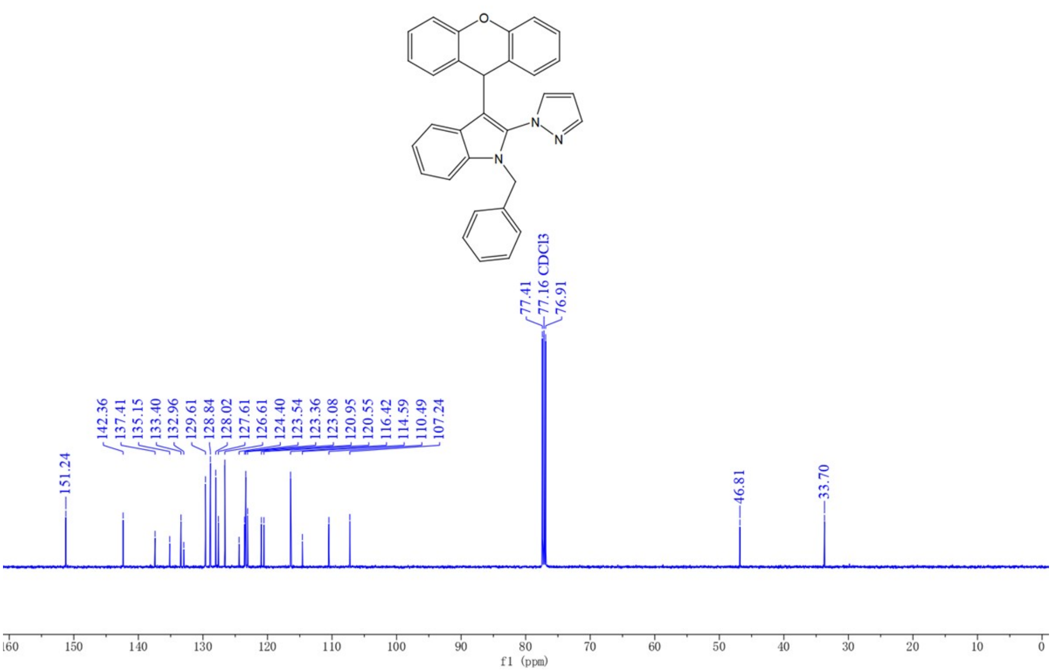




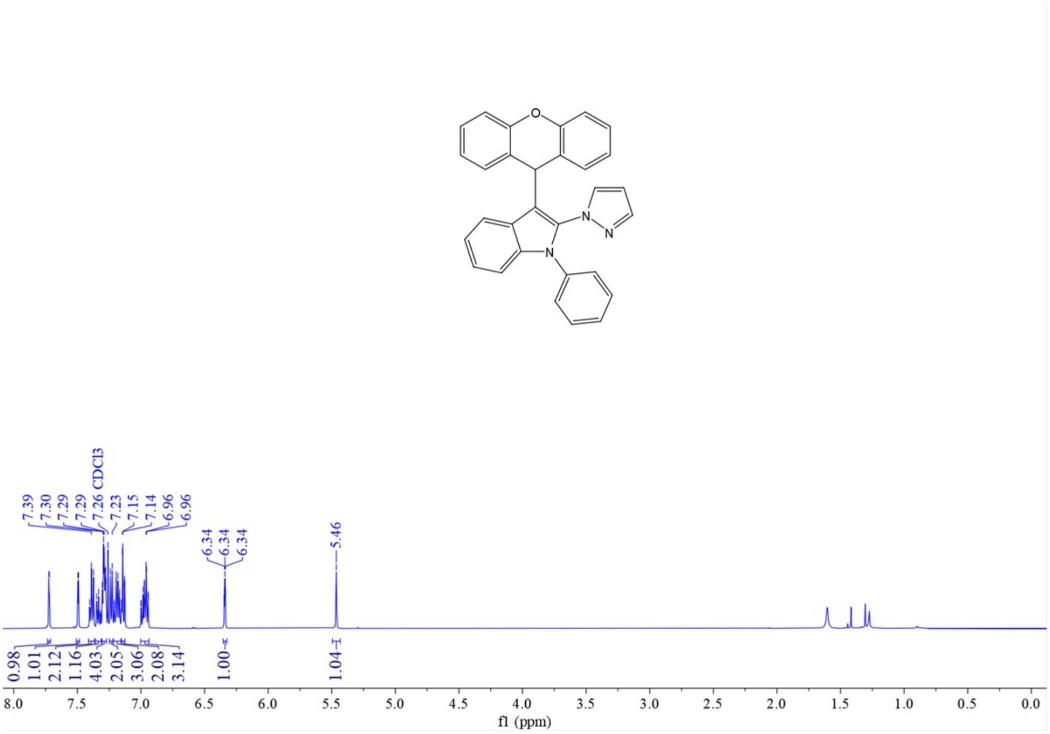
(11) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4daa



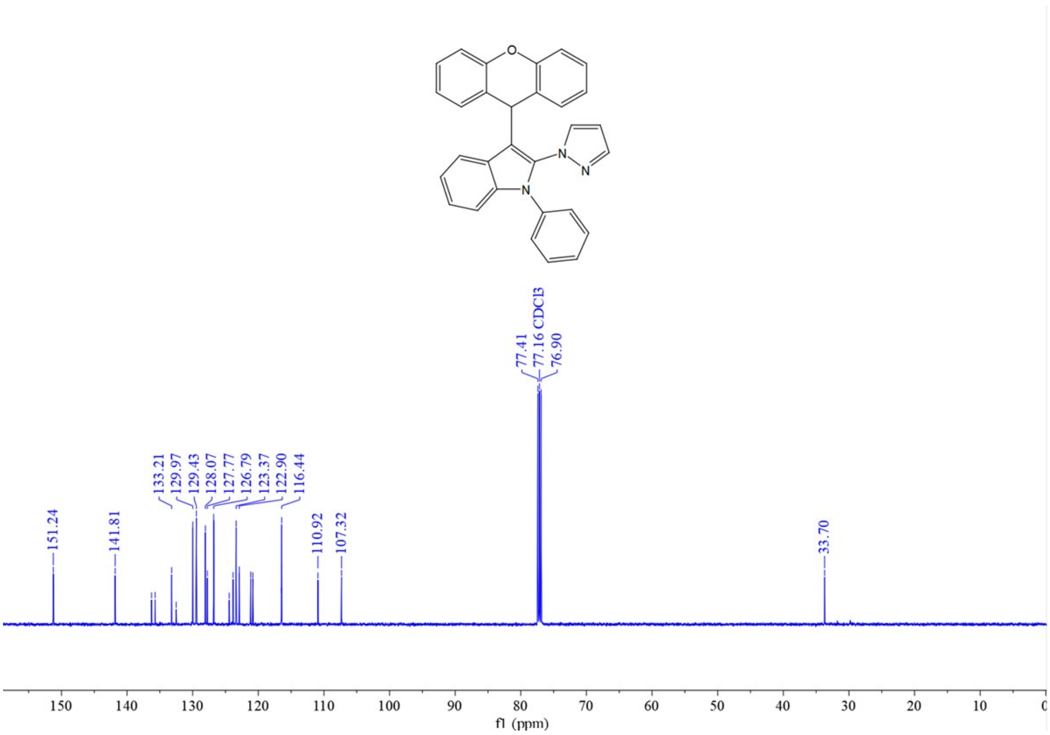
(12) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4daa



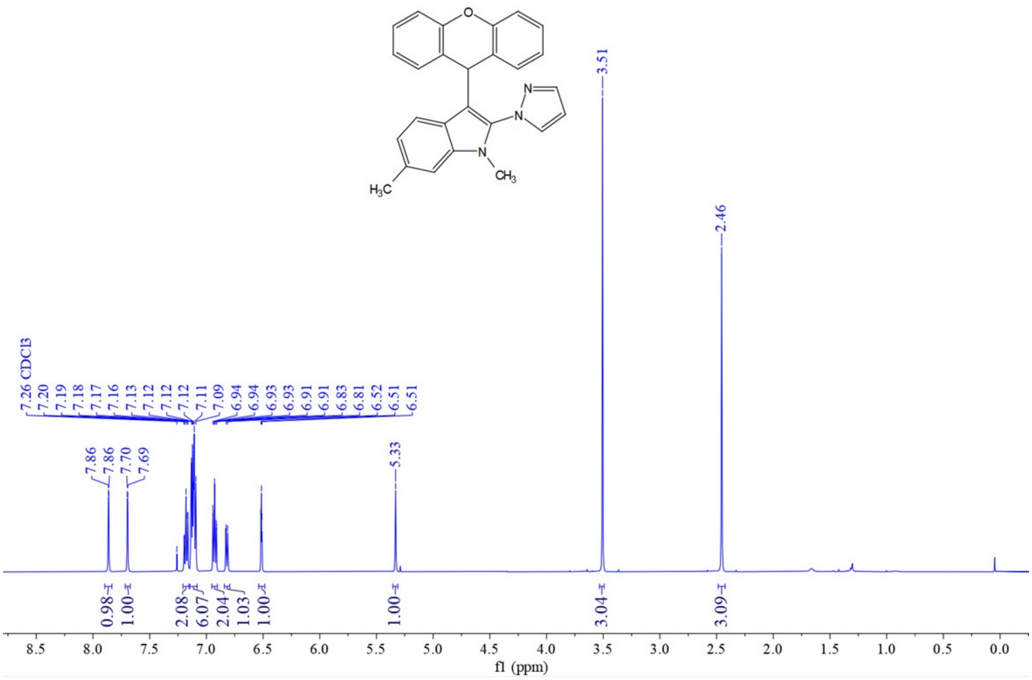
(13) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4eaa



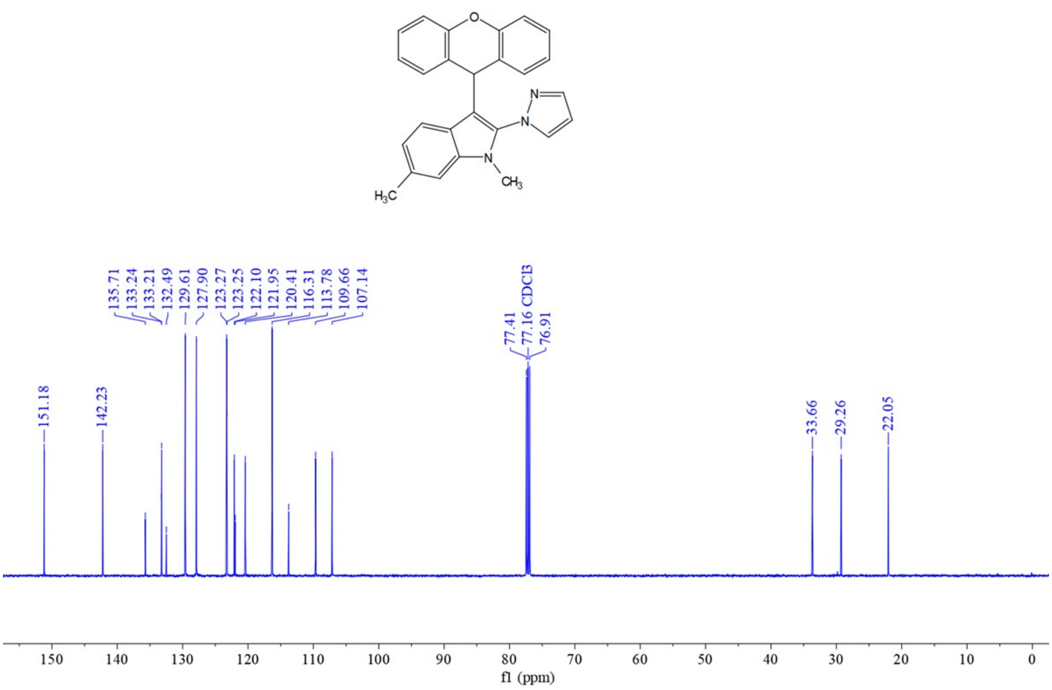
(14) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4eaa



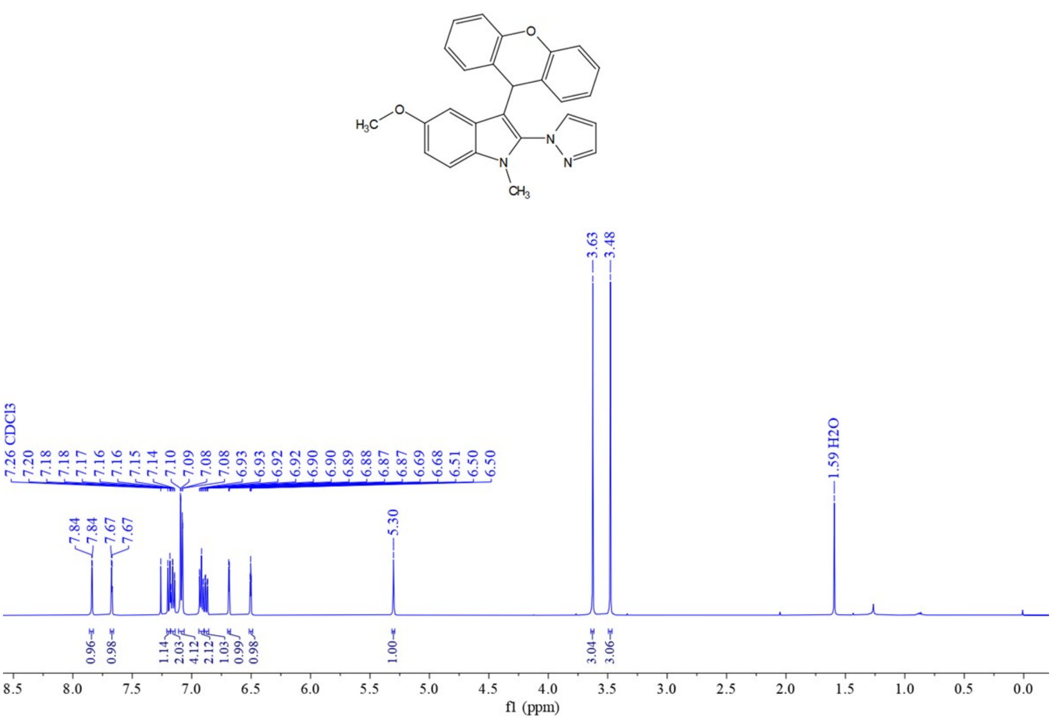
(15) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4faa



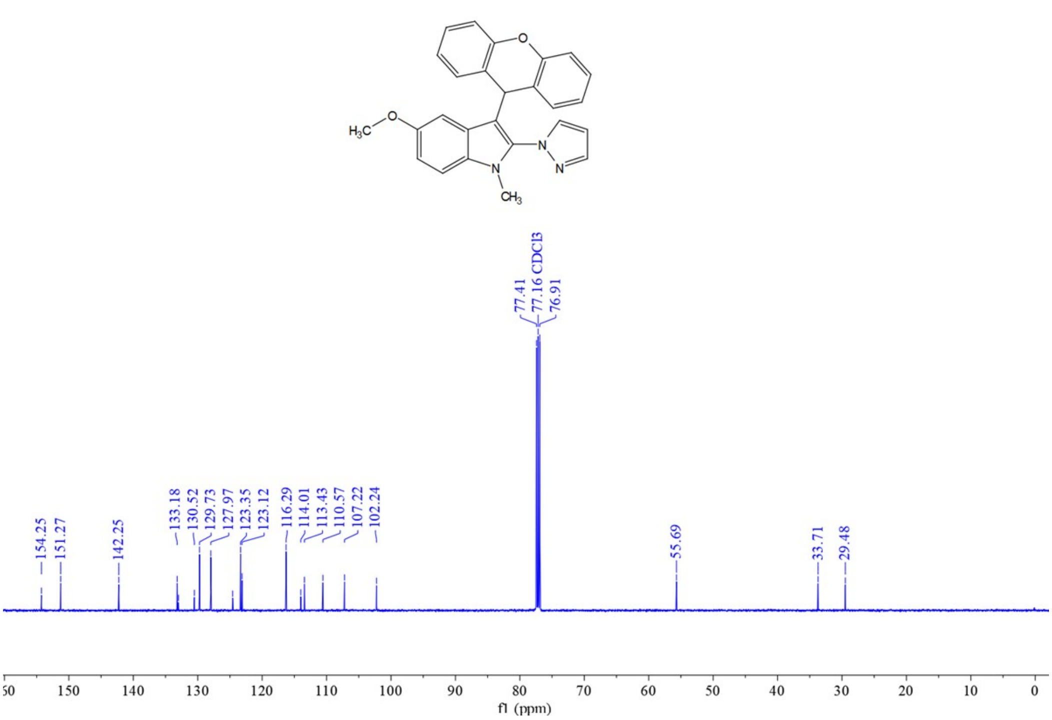
(16) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4faa



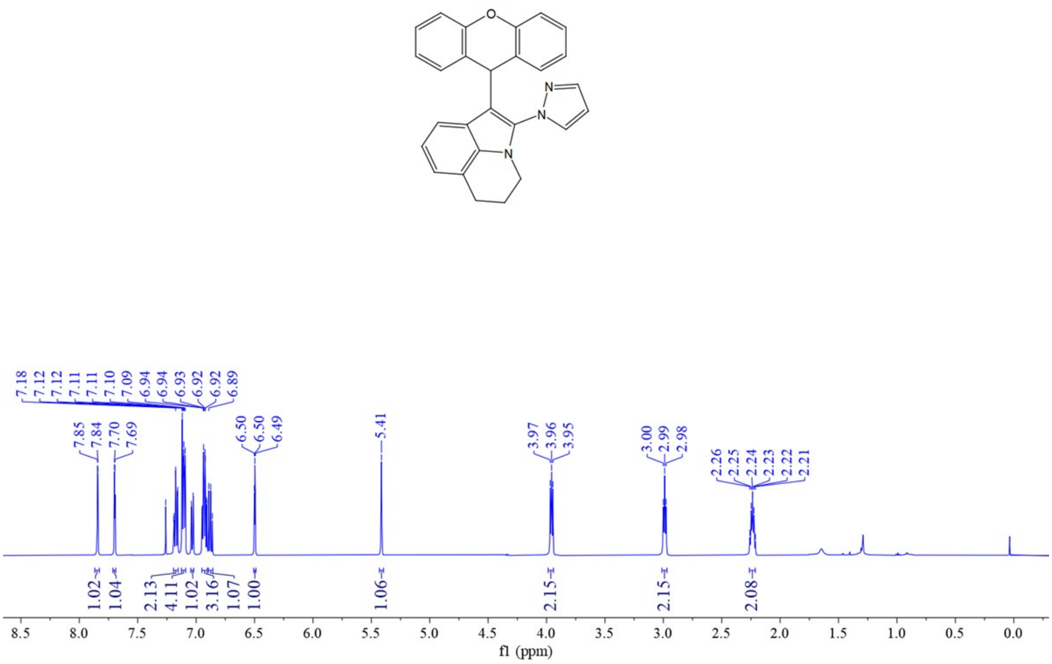
(17) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4gaa



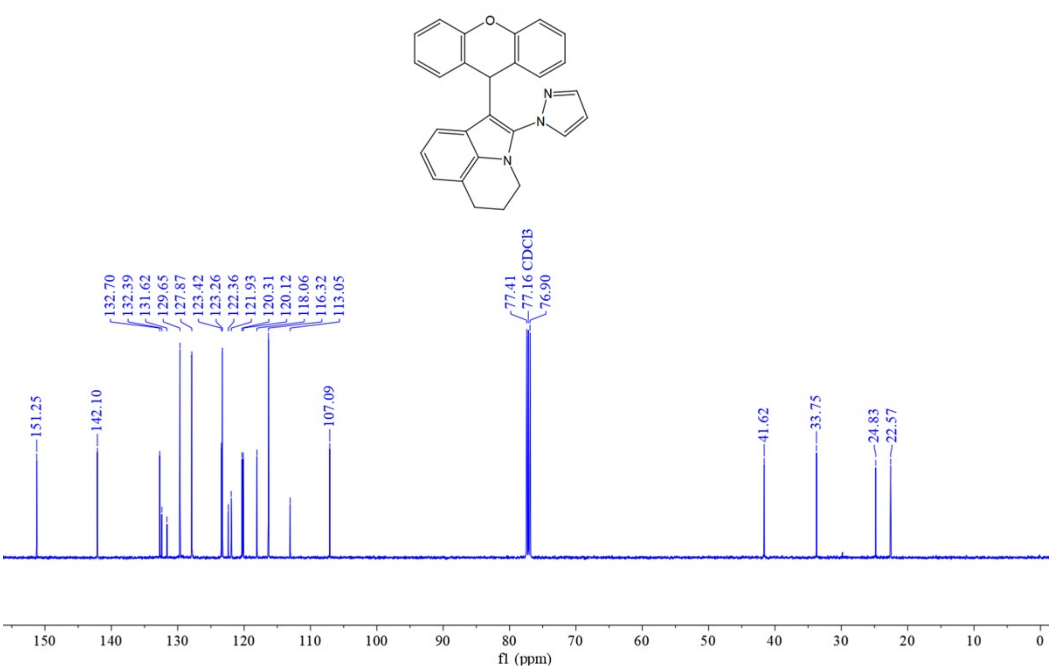
(18) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4gaa



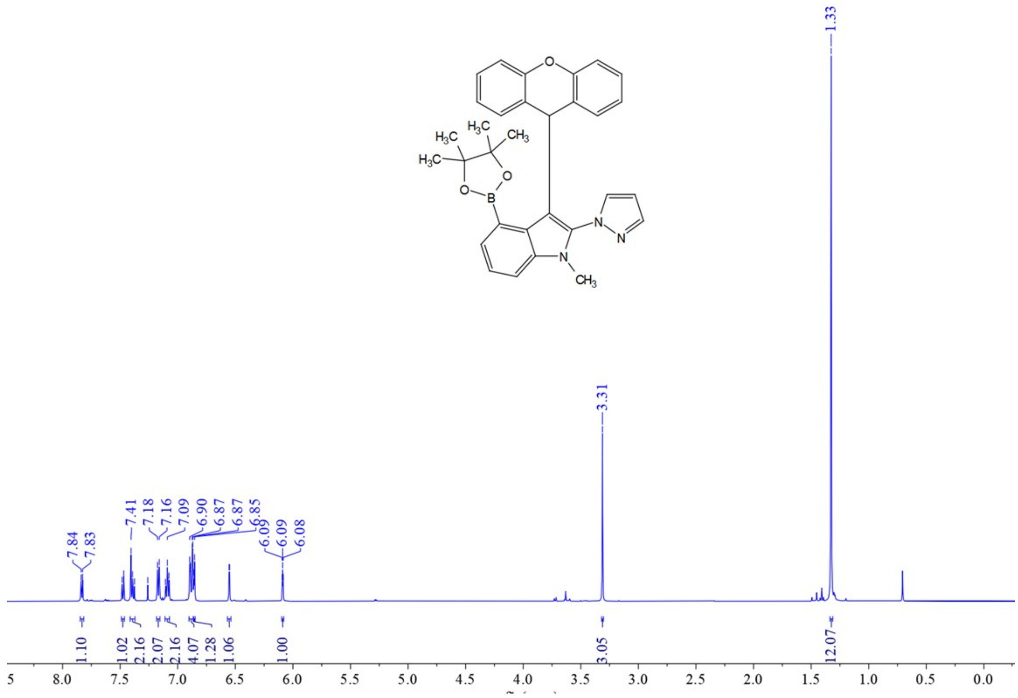
(19) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4haa



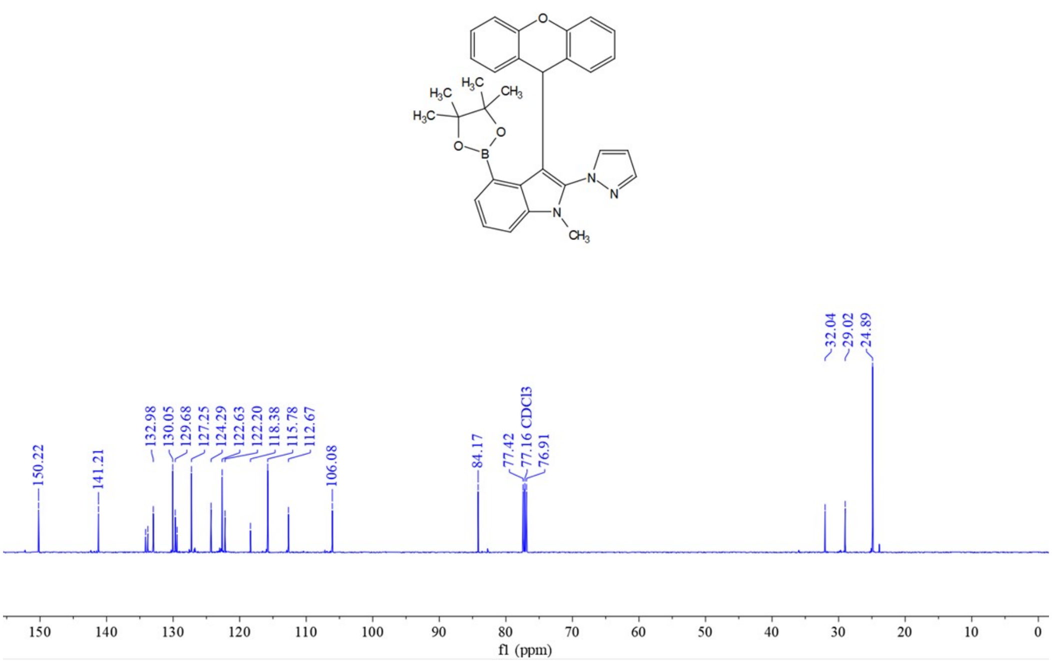
(20) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4haa



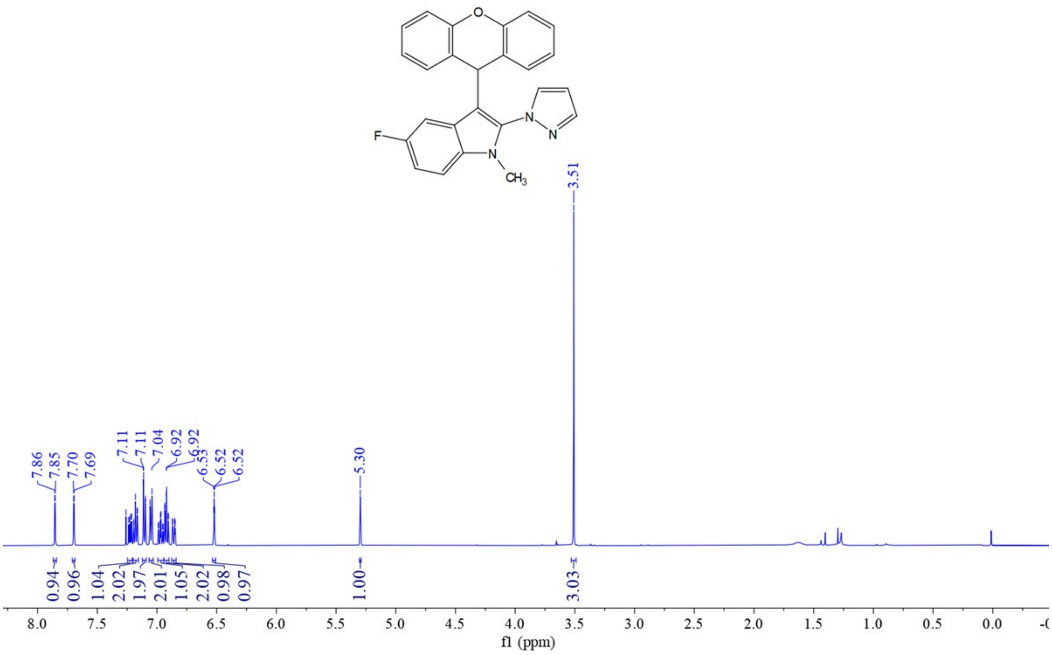
(21) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4iaa



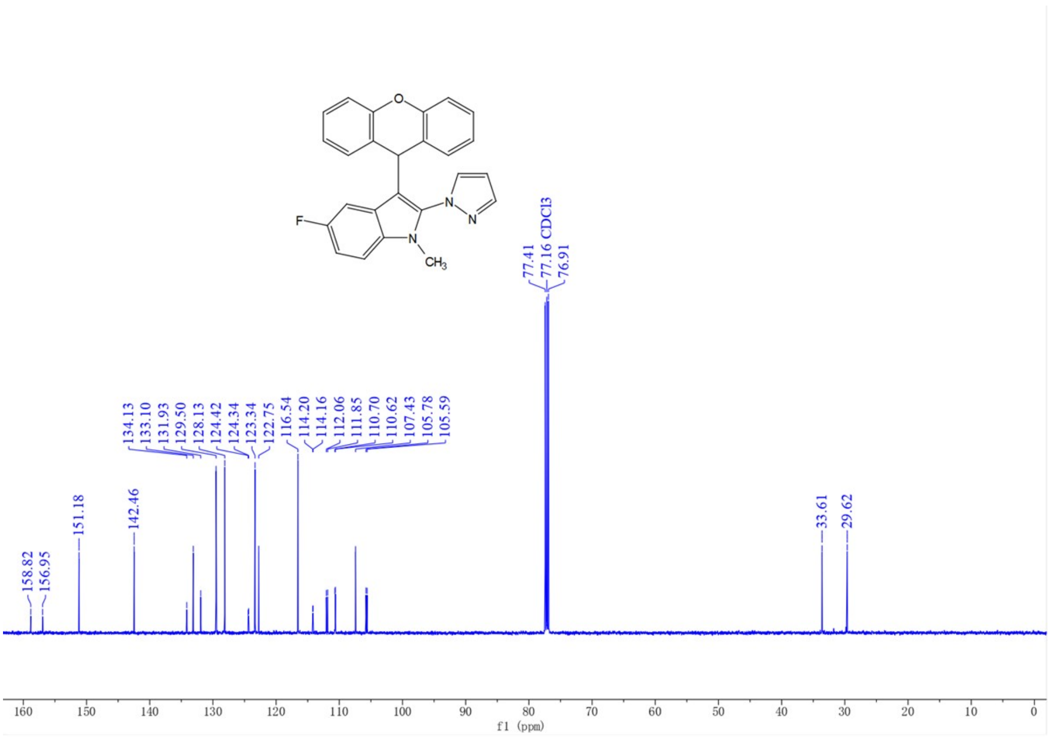
(22) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4iaa



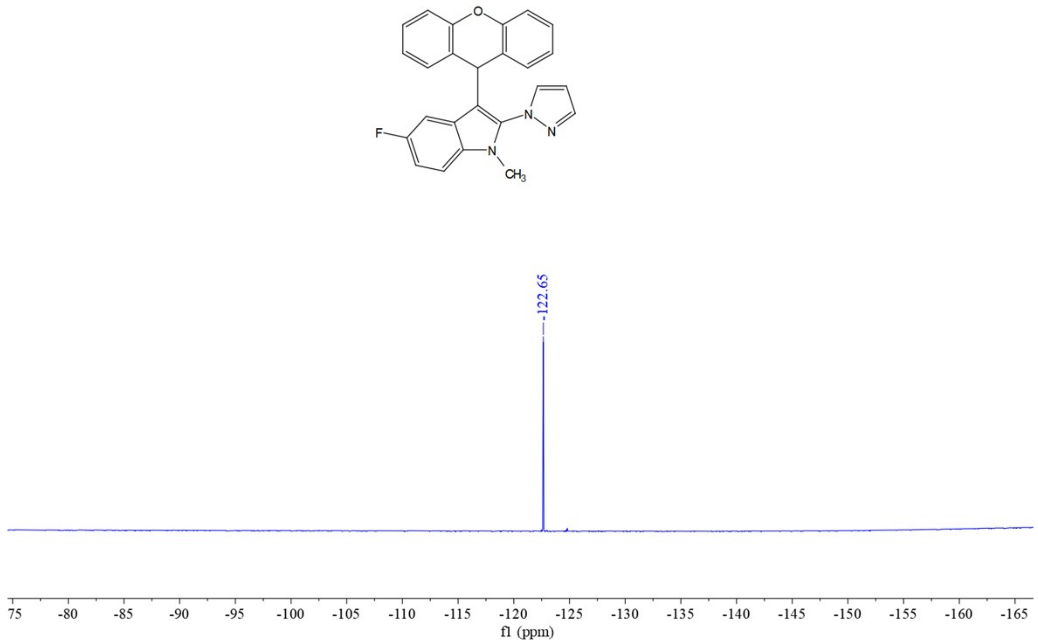
(23) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4jaa



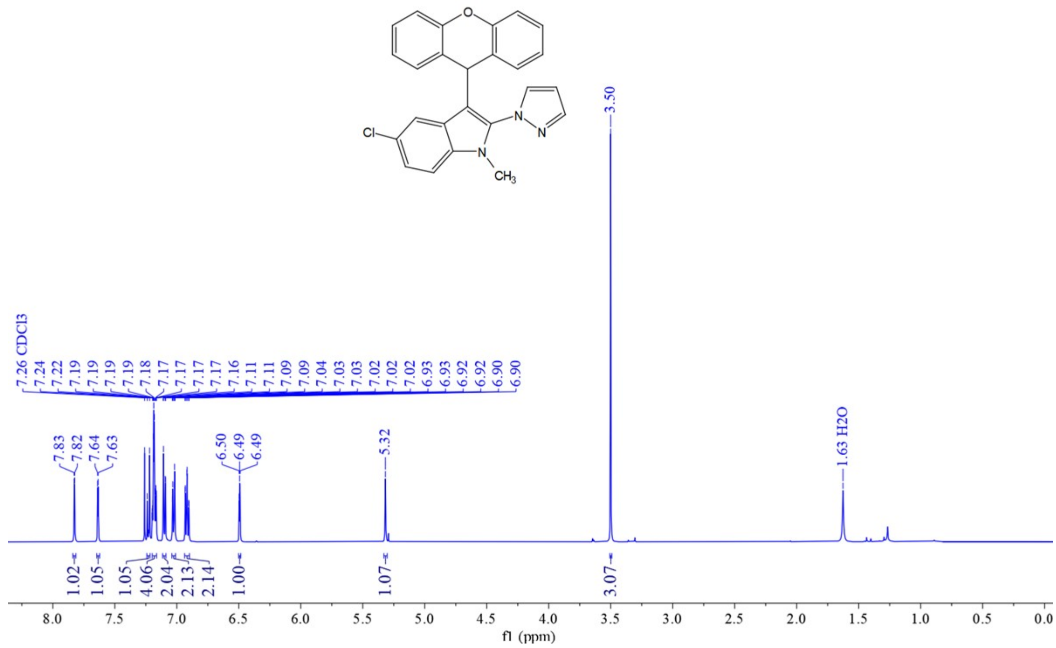
(24) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4jaa



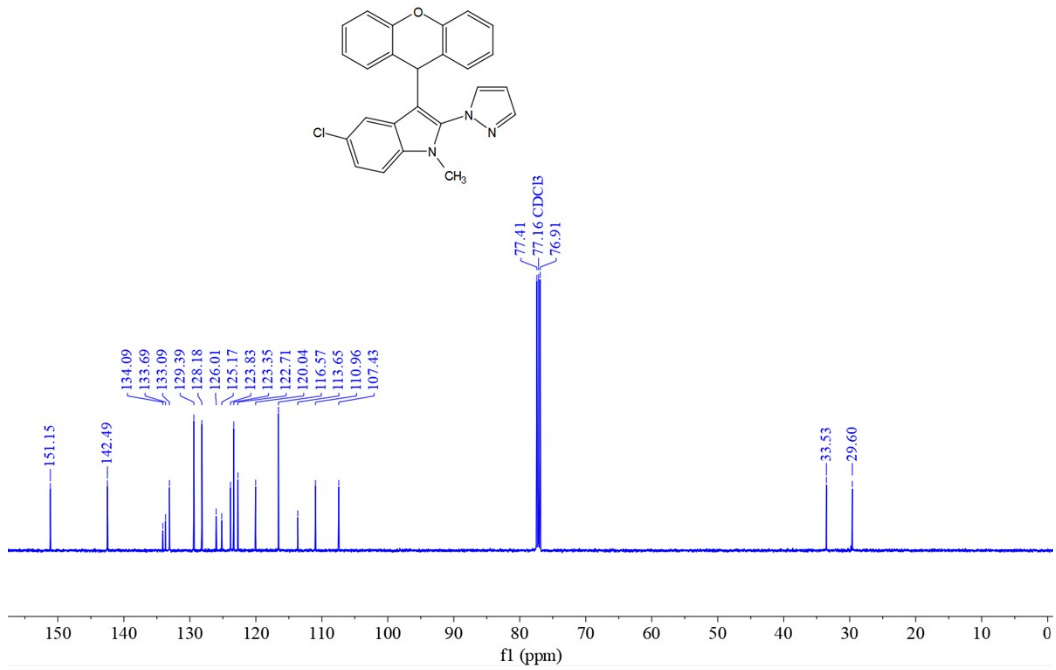
(25) ^{19}F-NMR (470 MHz, $CDCl_3$) spectrum of 4jaa



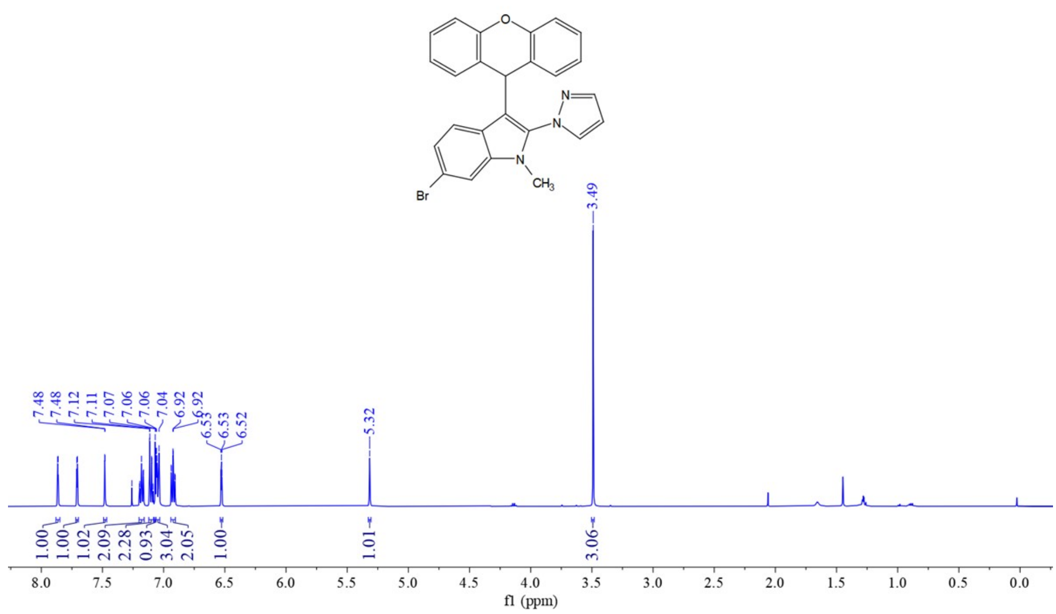
(26) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4kaa



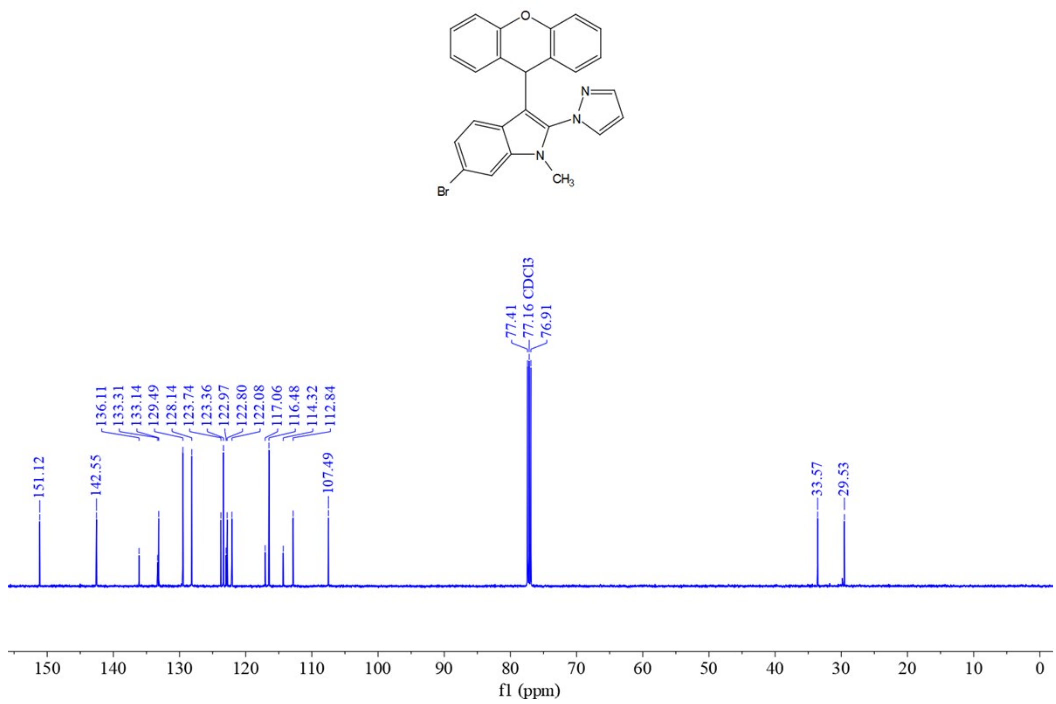
(27) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4kaa



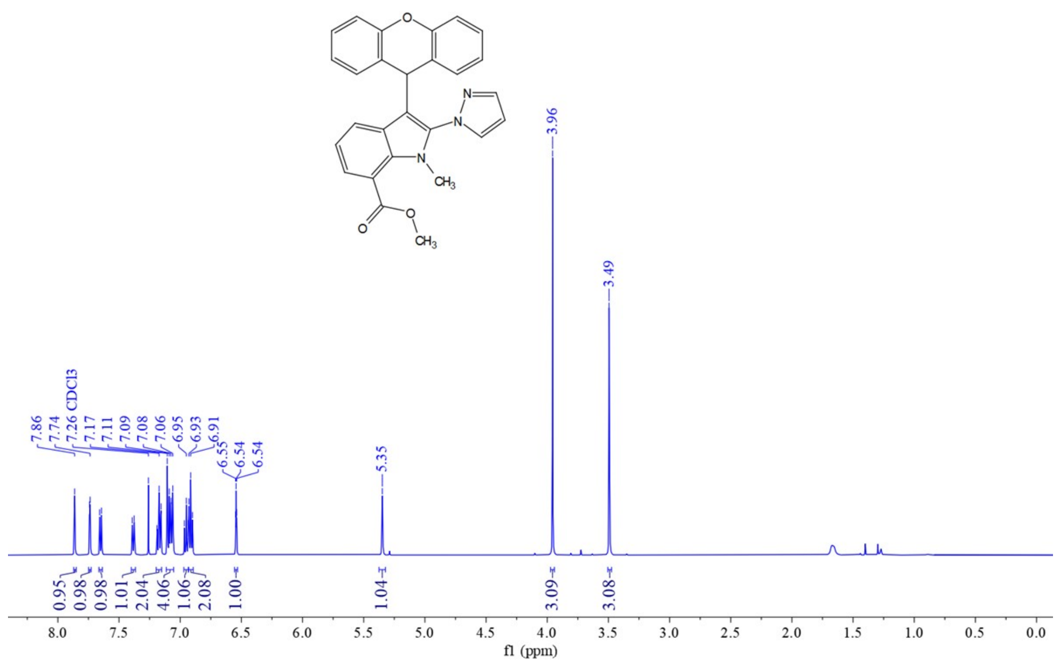
(28) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4laa



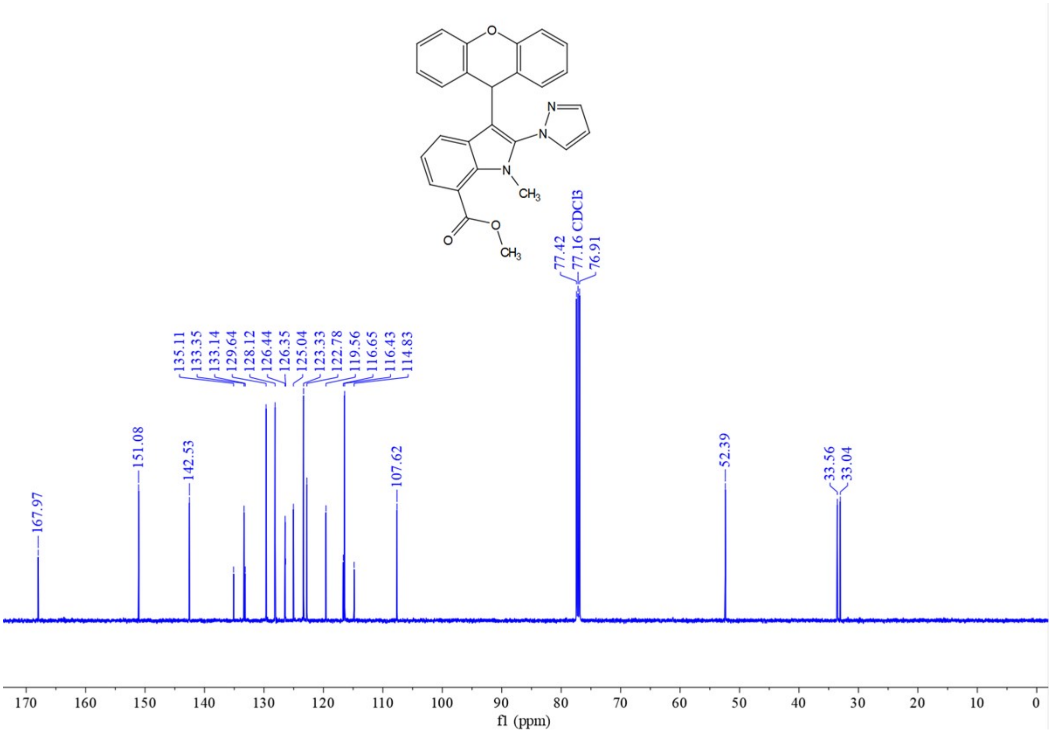
(29) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4laa



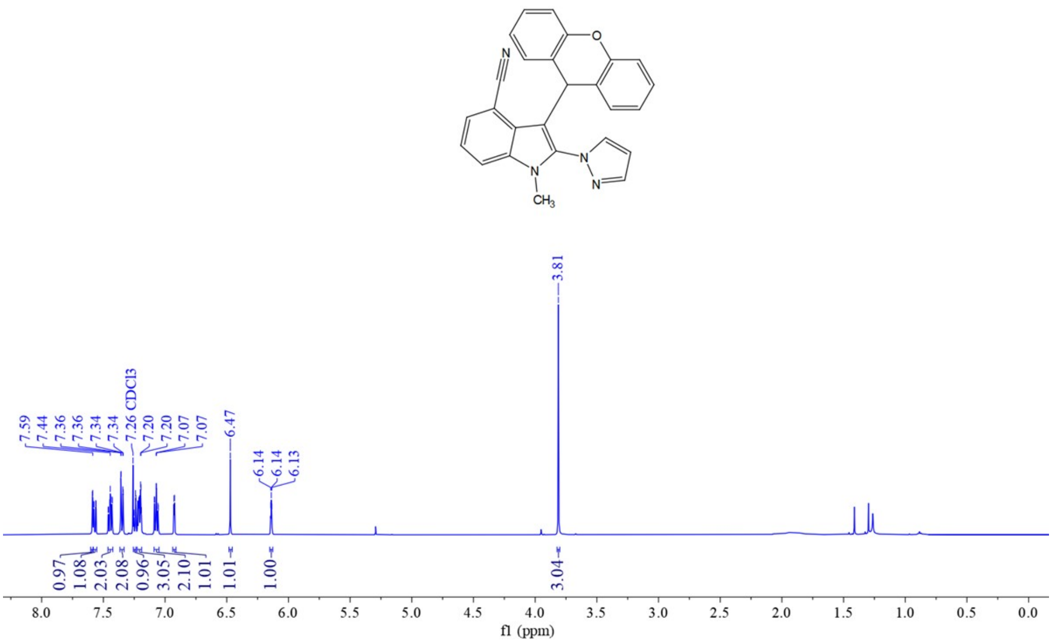
(30) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4maa



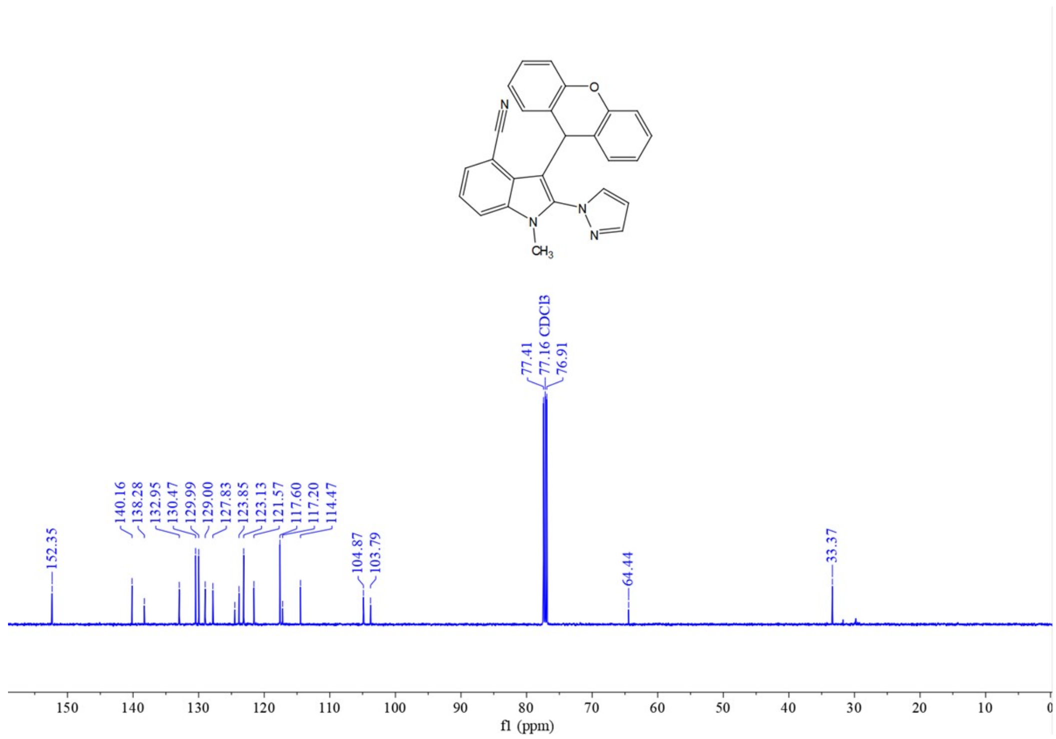
(31) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4maa



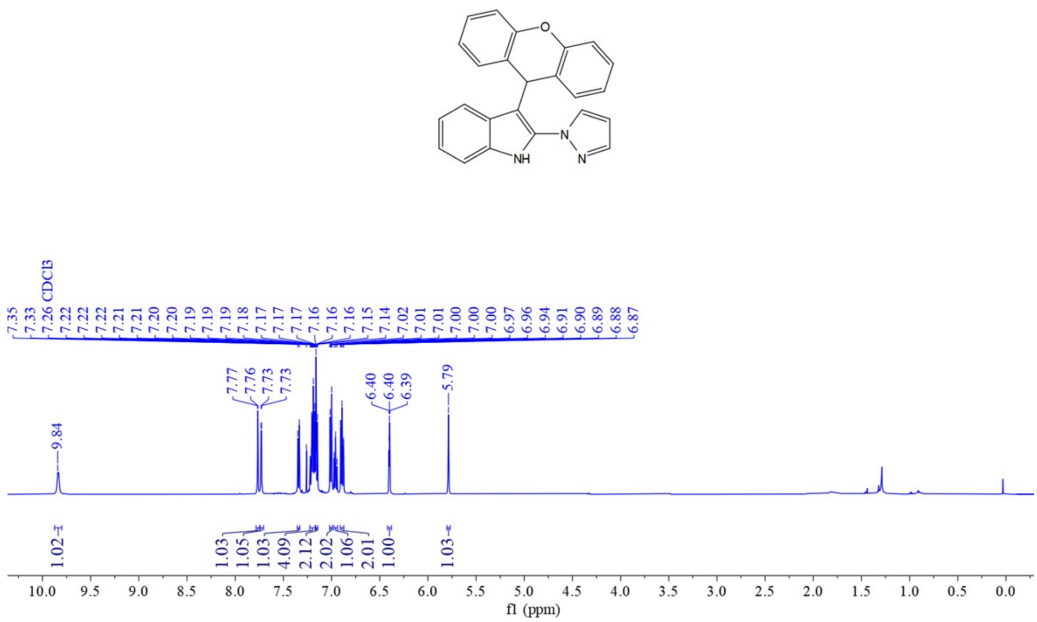
(32) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4naa



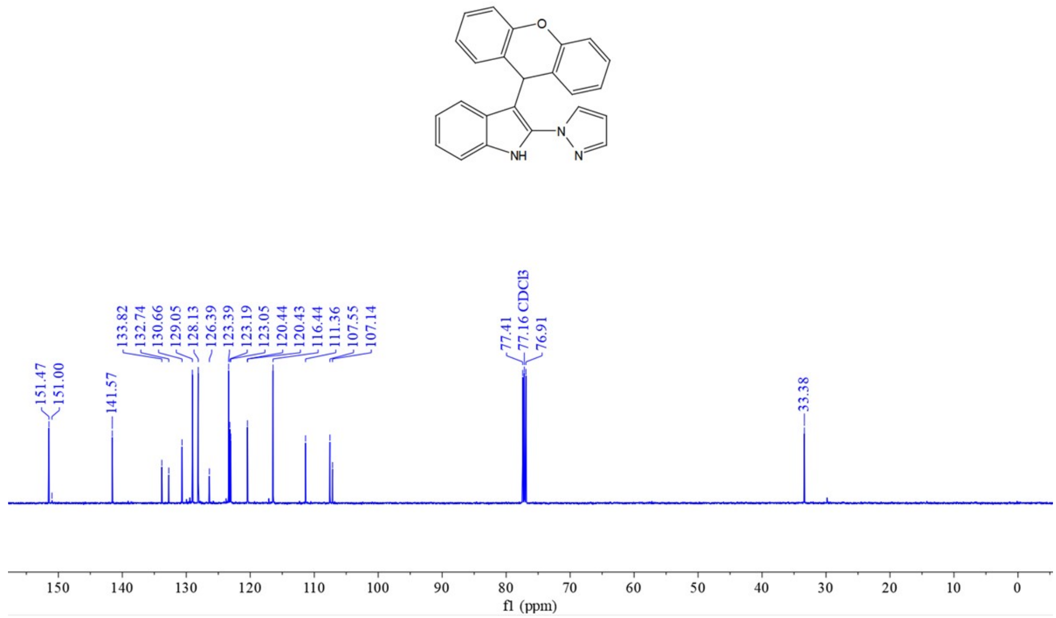
(33) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4naa



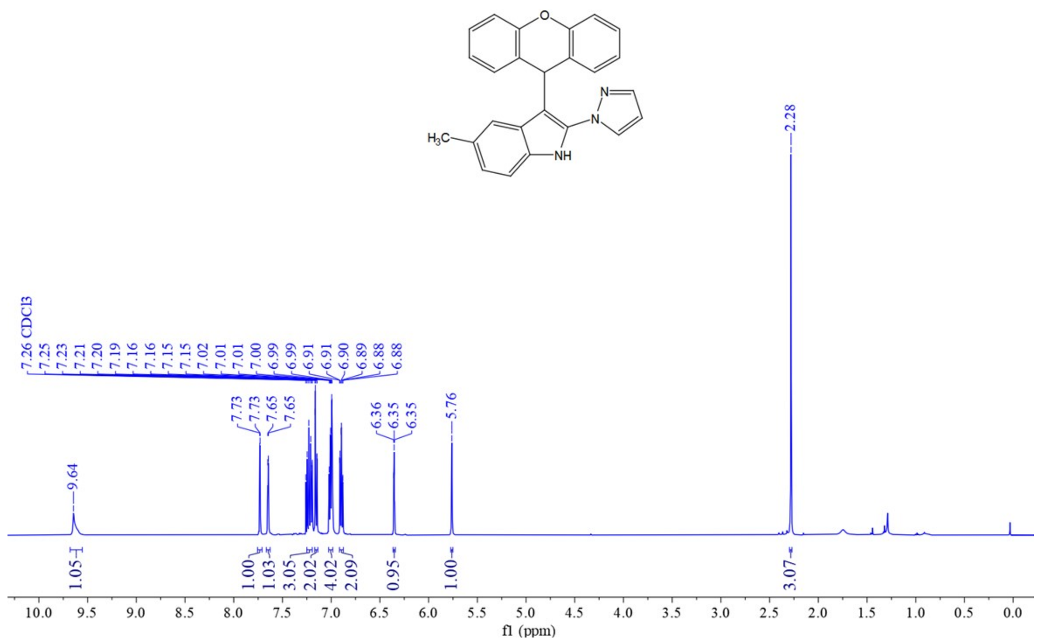
(34) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4oaa



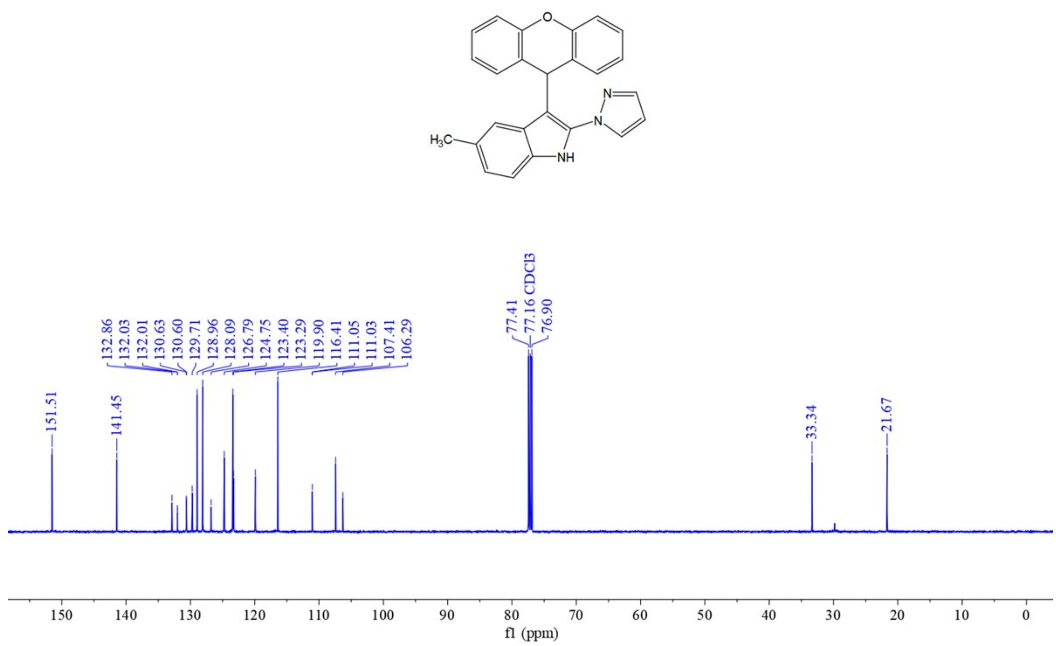
(35) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4oaa



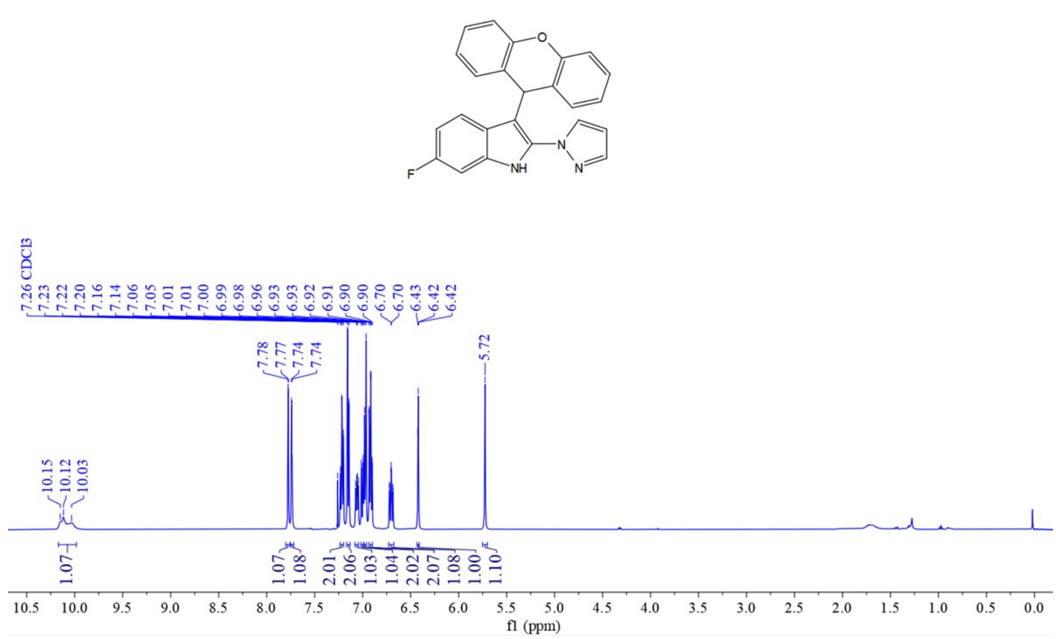
(36) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4paa



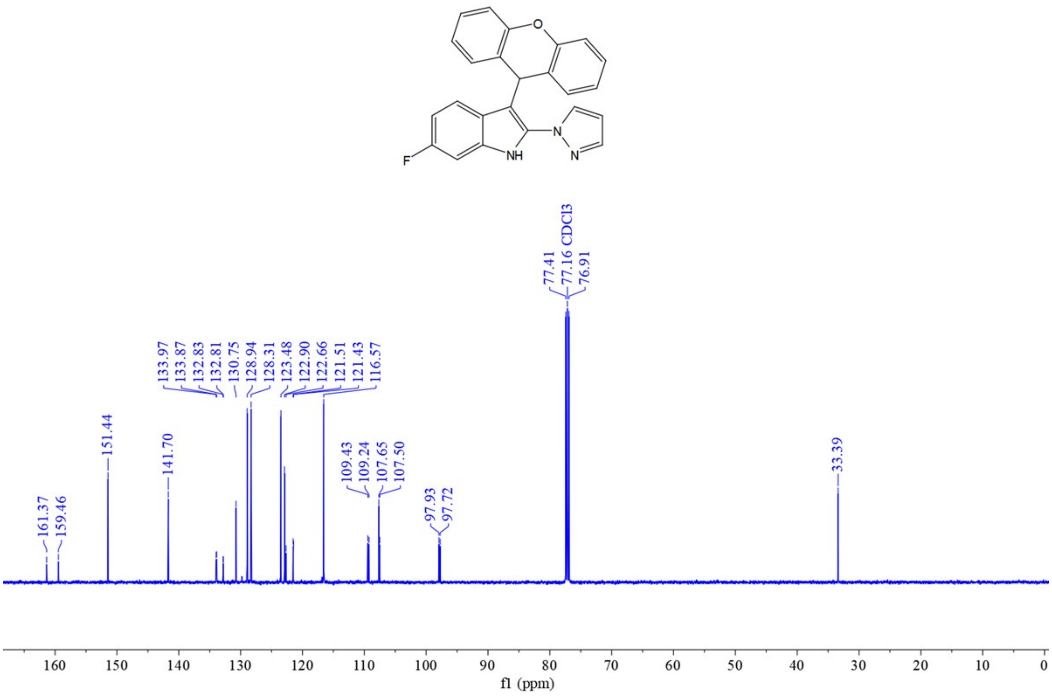
(37) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4paa



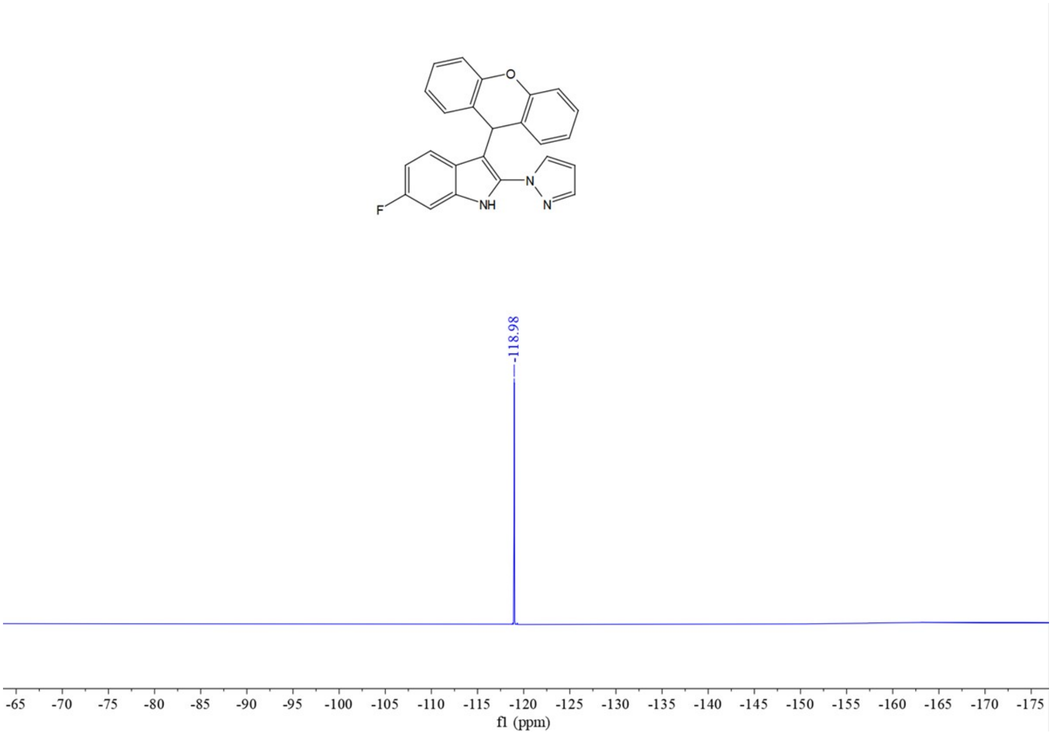
(38) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4qaa



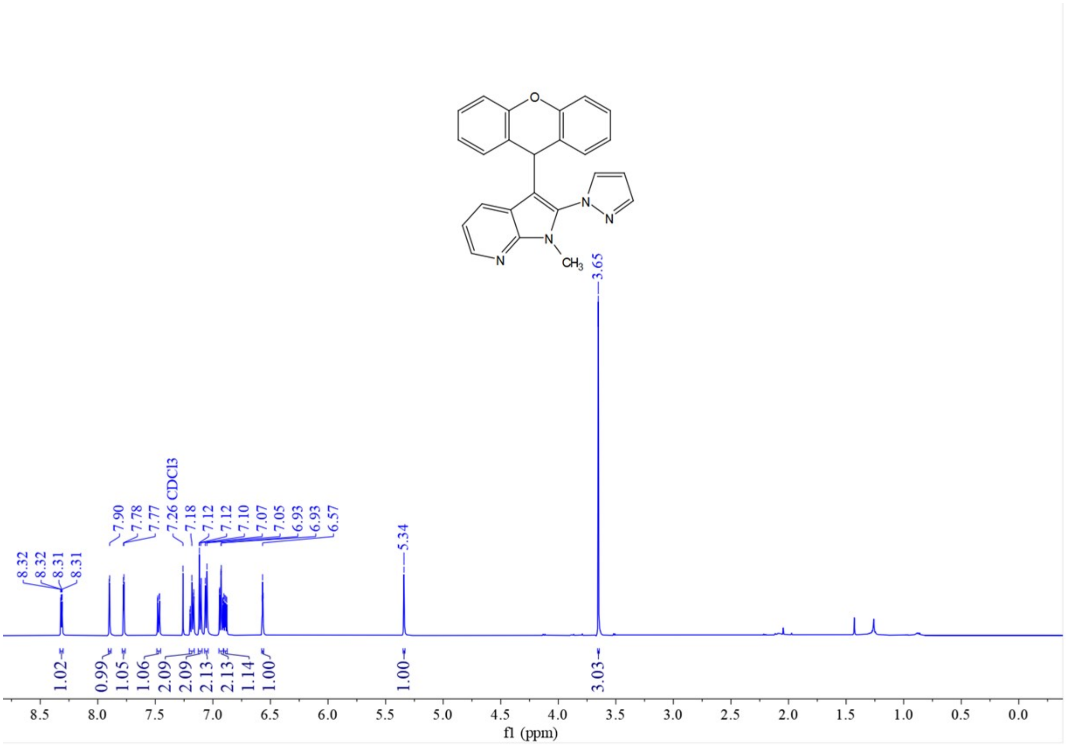
(39) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4qaa



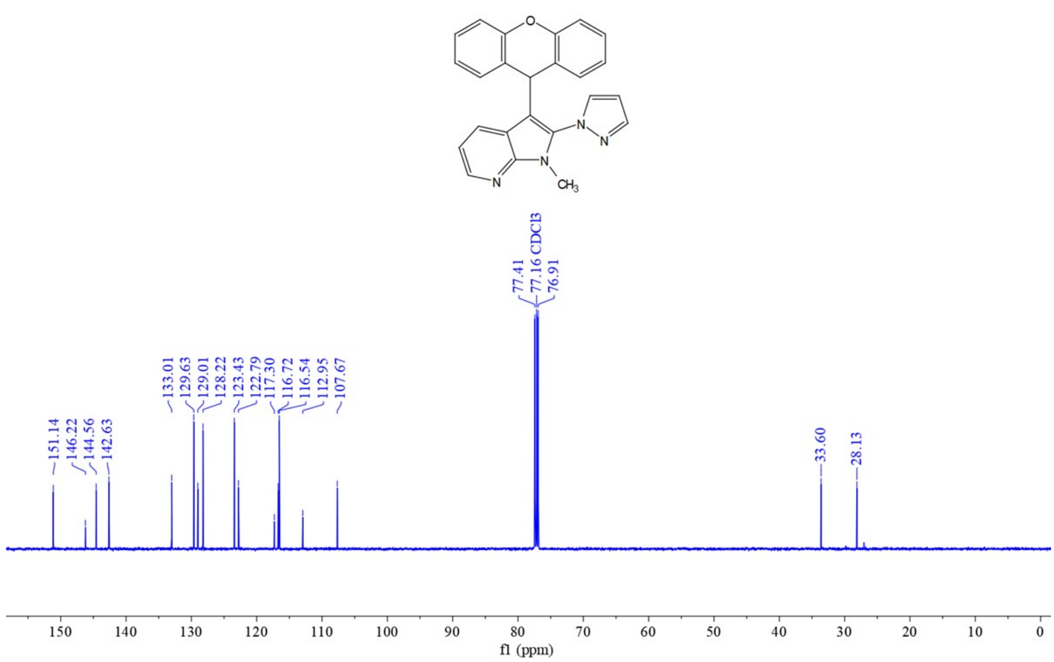
(40) ^{19}F-NMR (470 MHz, $CDCl_3$) spectrum of 4qaa



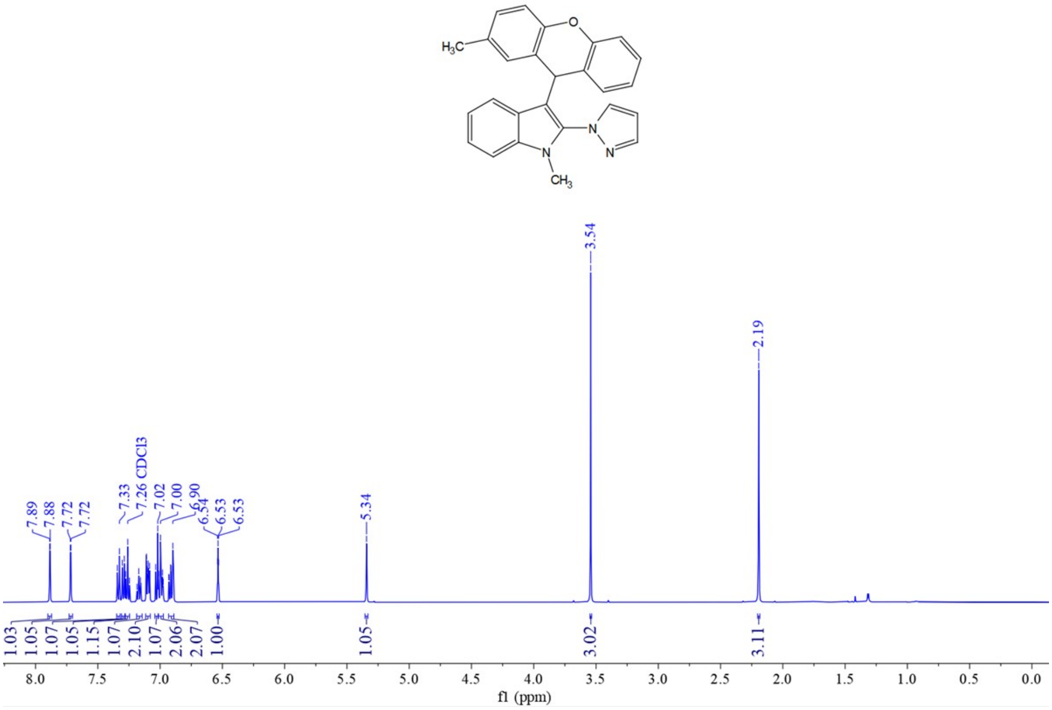
(41) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4raa



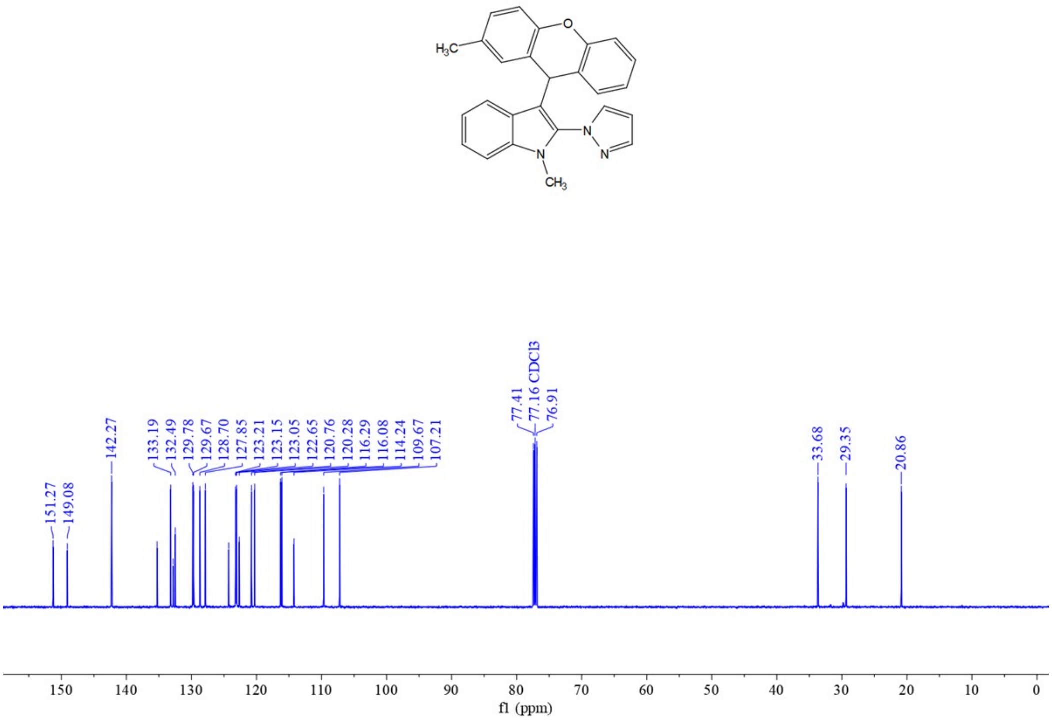
(42) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4raa



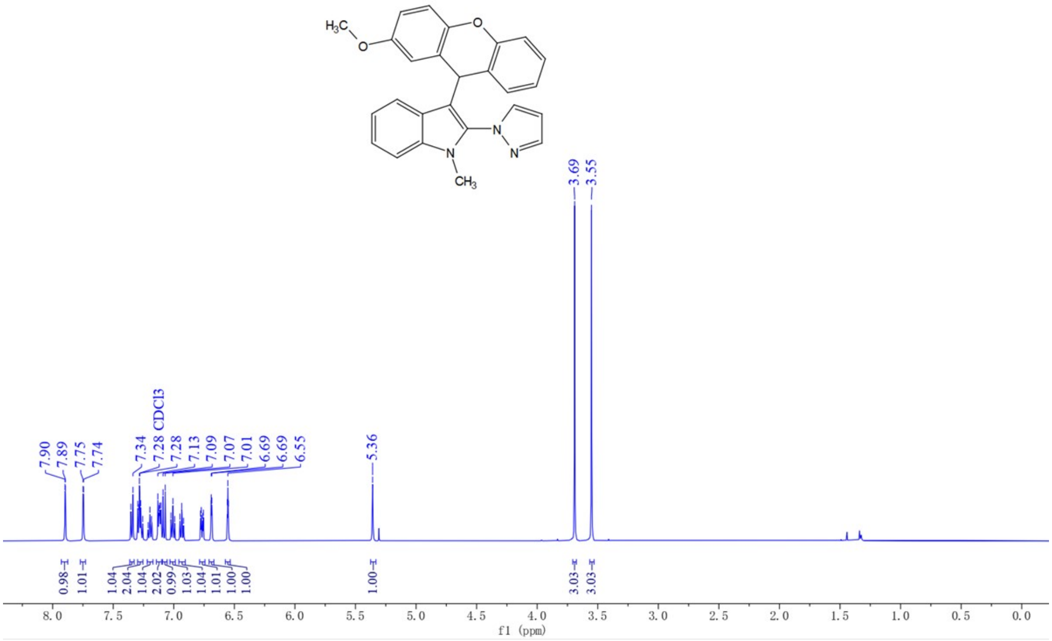
(43) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aba



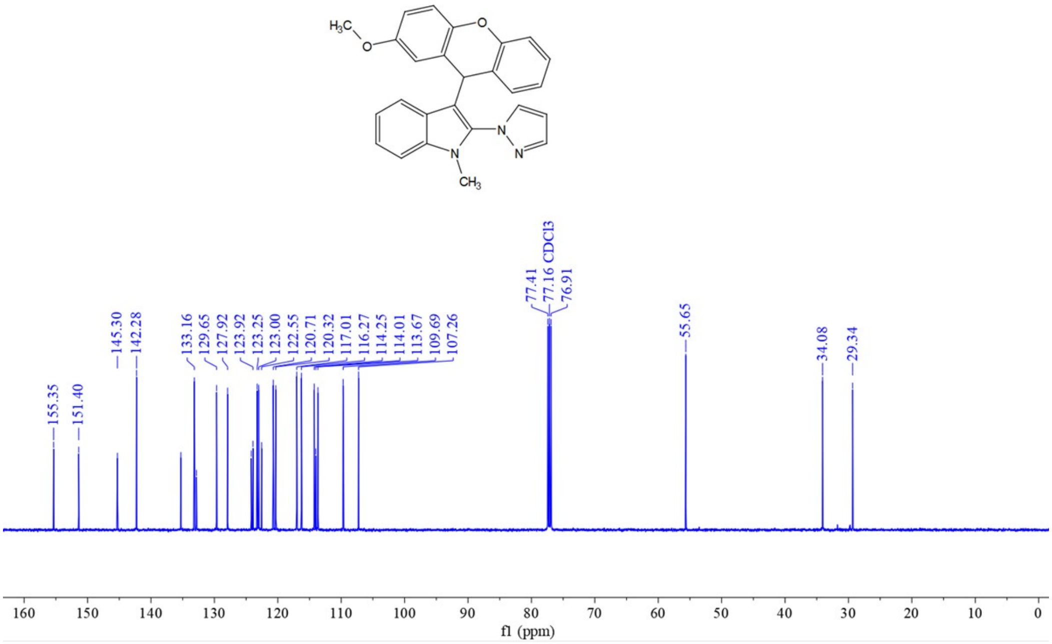
(44) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aba



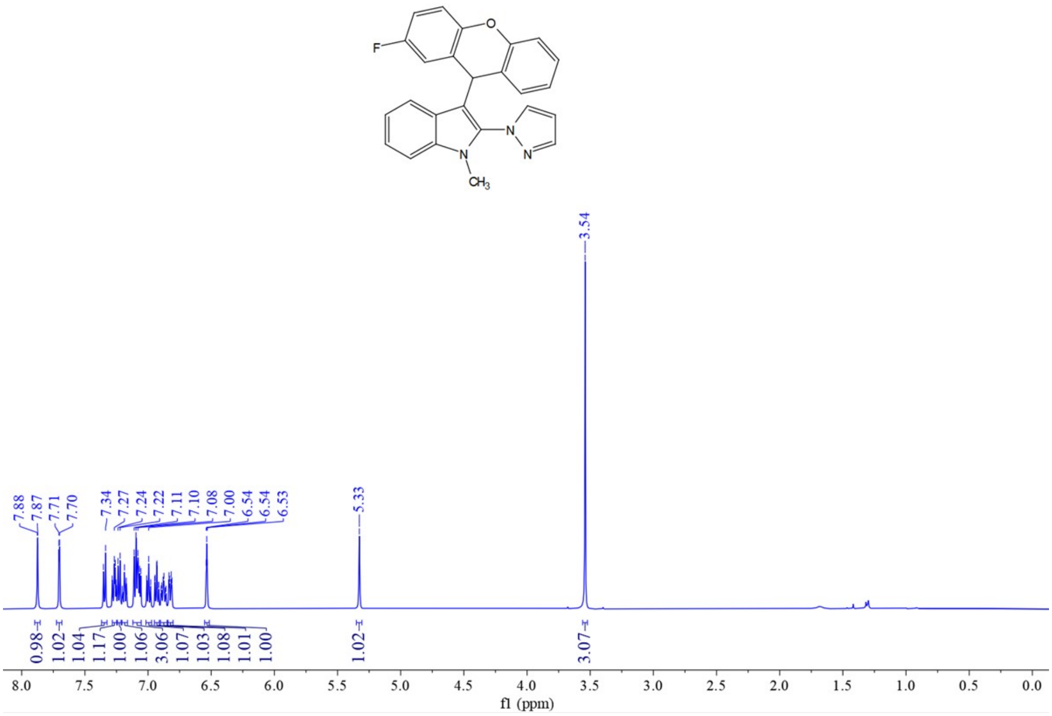
(45) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aca



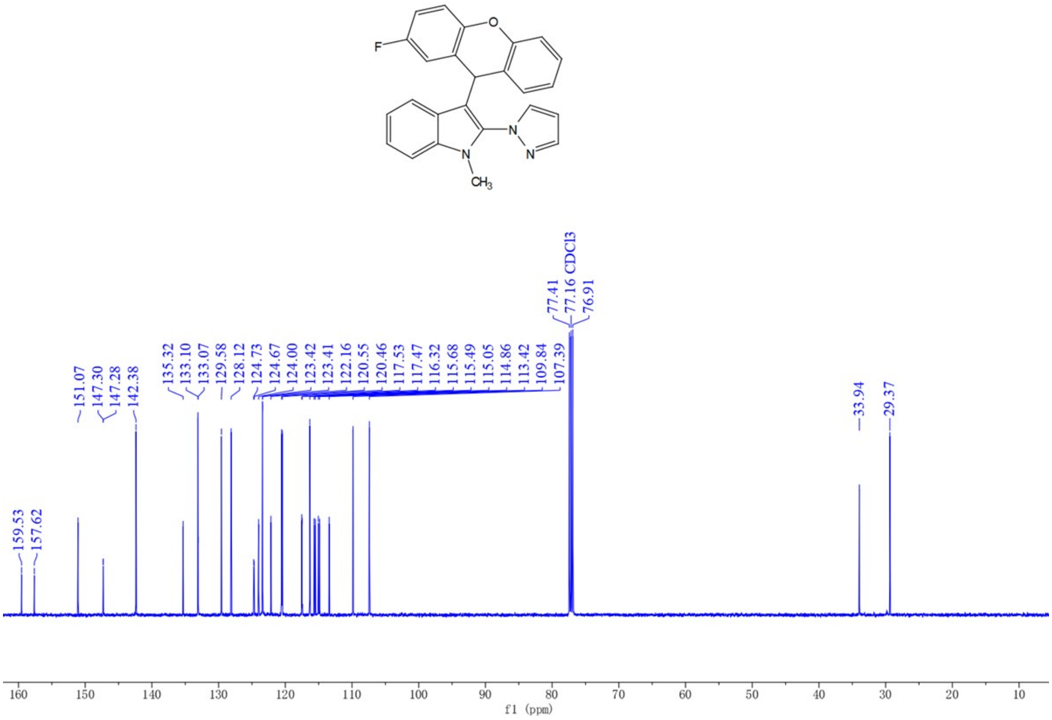
(46) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aca



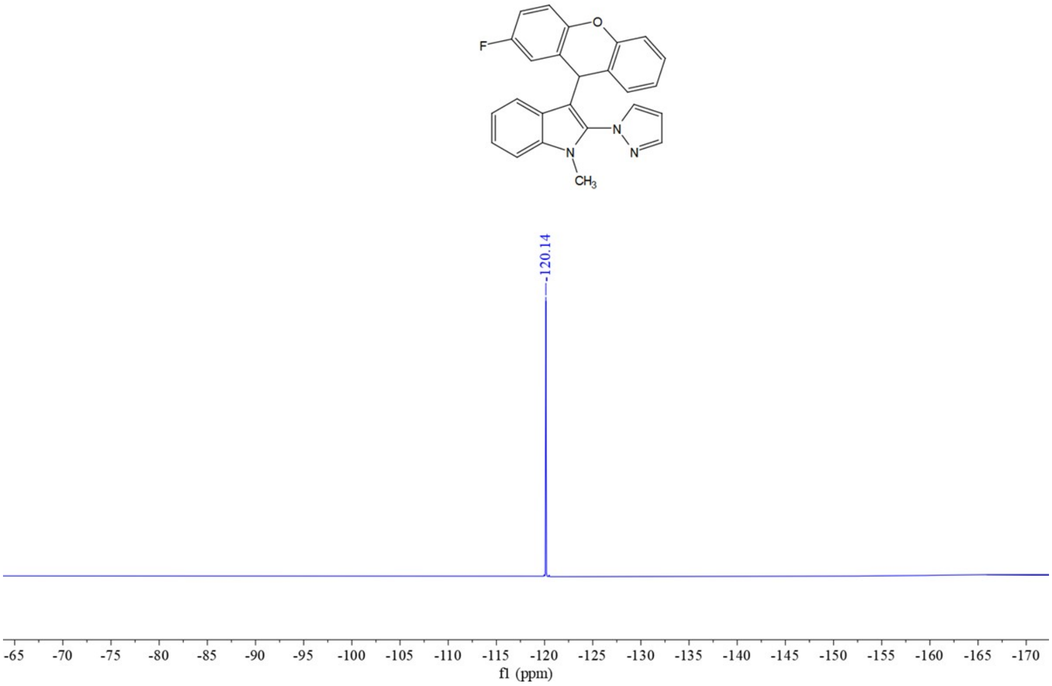
(47) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4ada



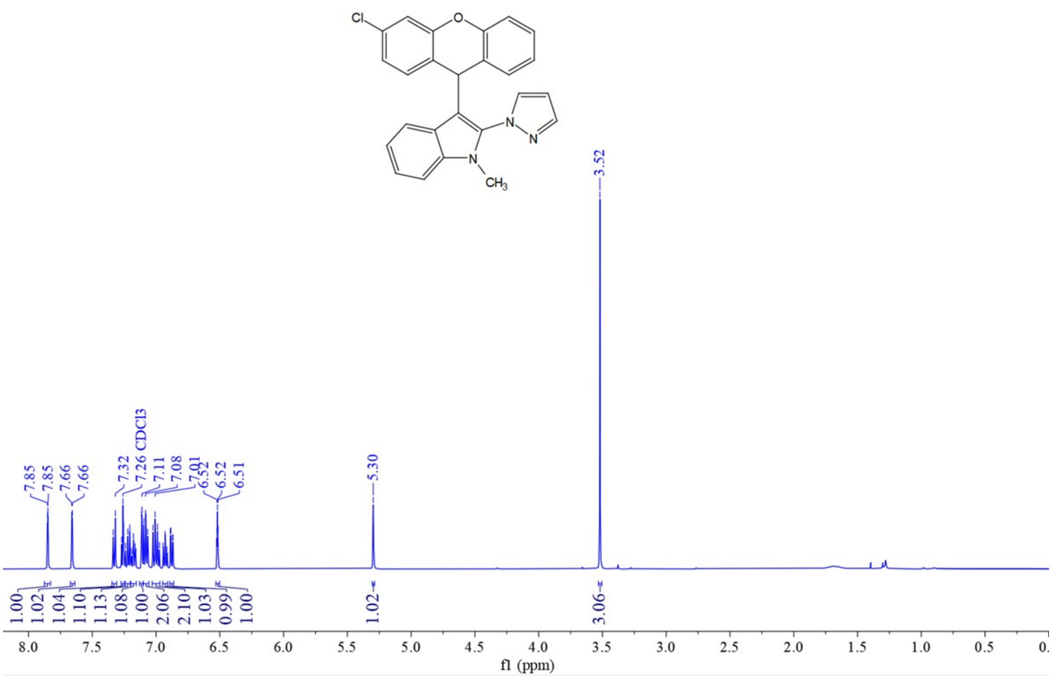
(48) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4ada



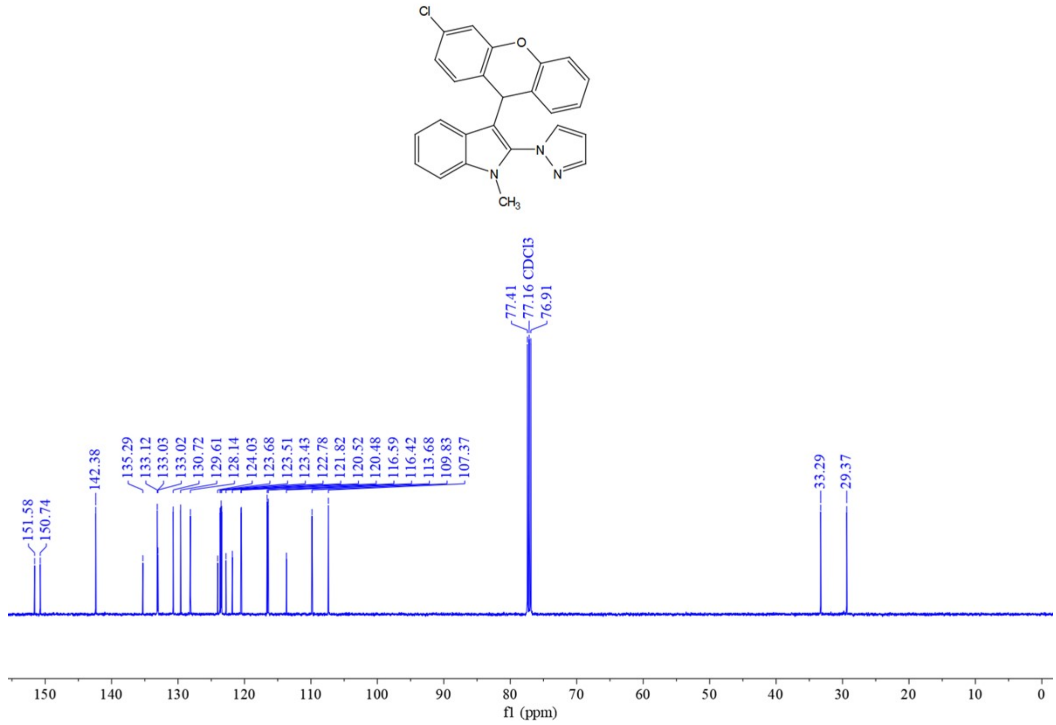
(49) ^{19}F-NMR (470 MHz, $CDCl_3$) spectrum of 4ada



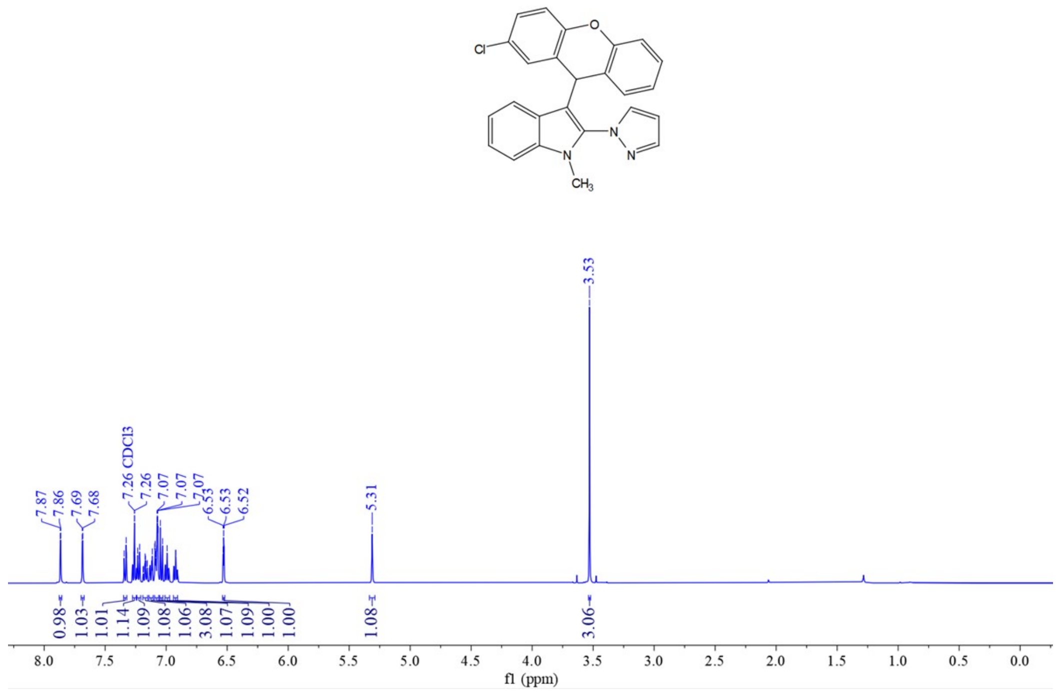
(50) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aea



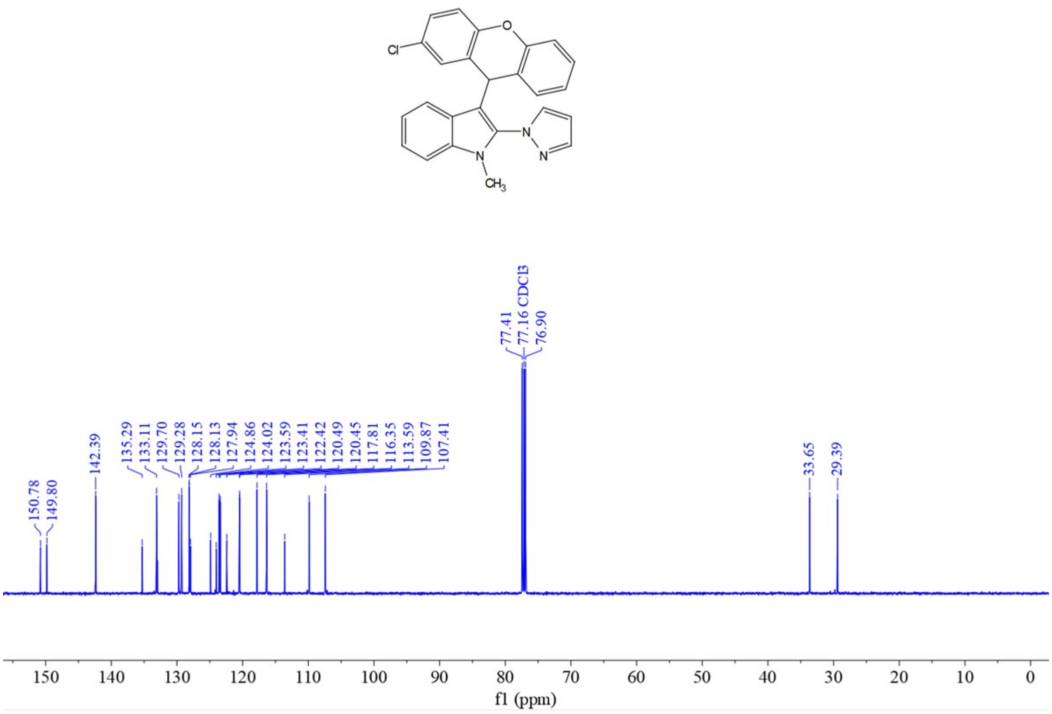
(51) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aea



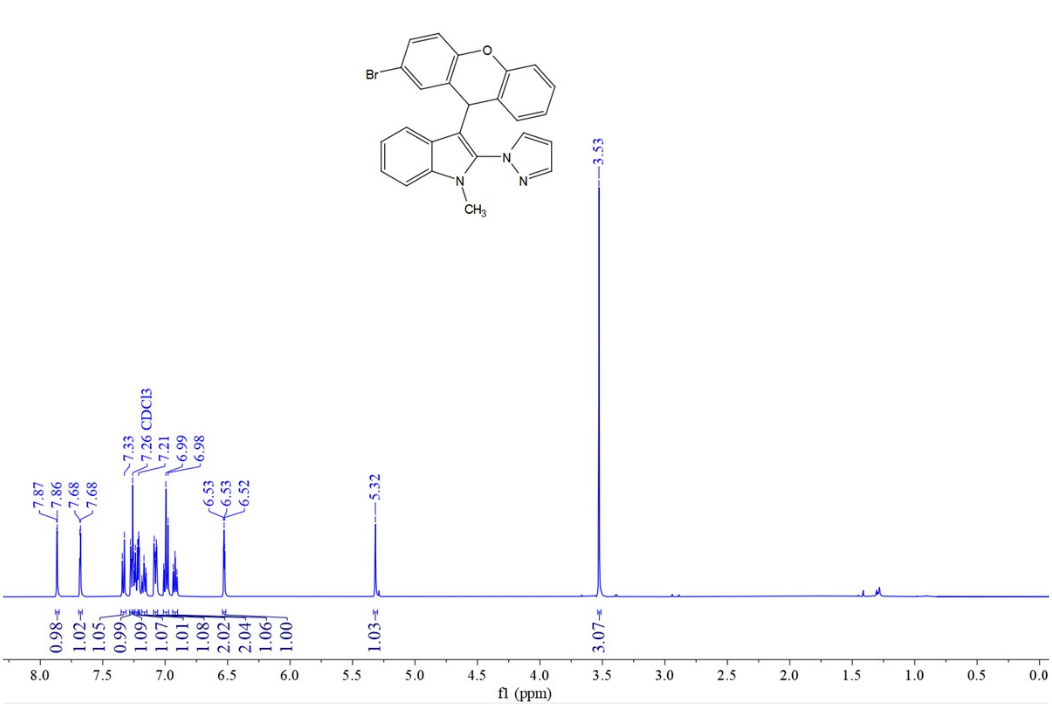
(52) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4afa



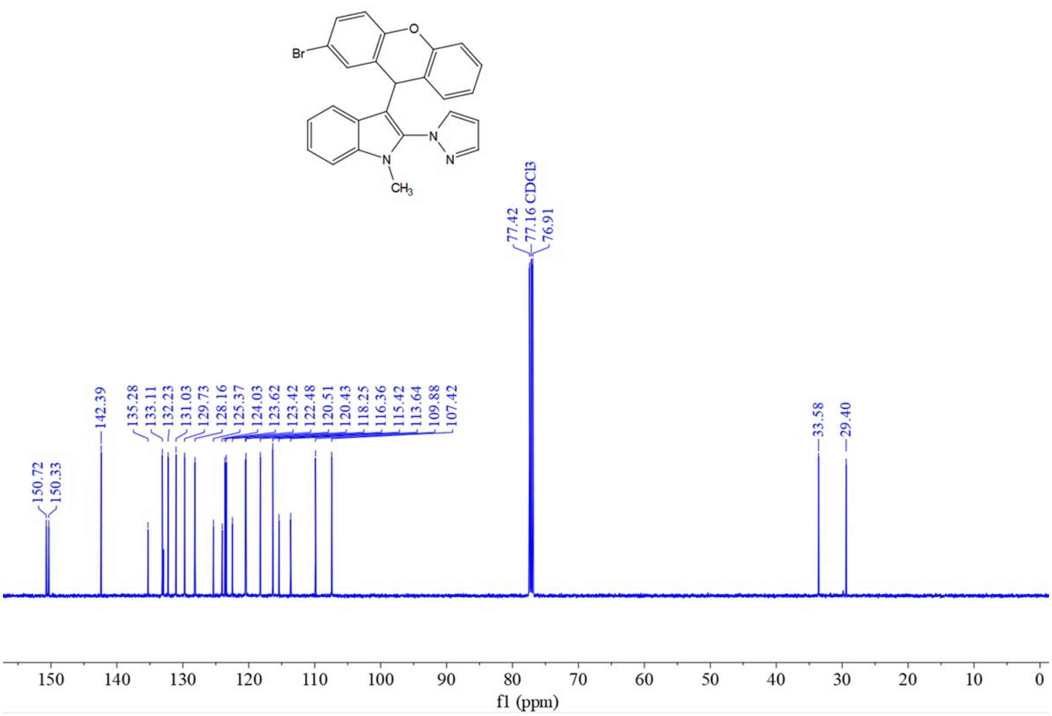
(53) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4afa



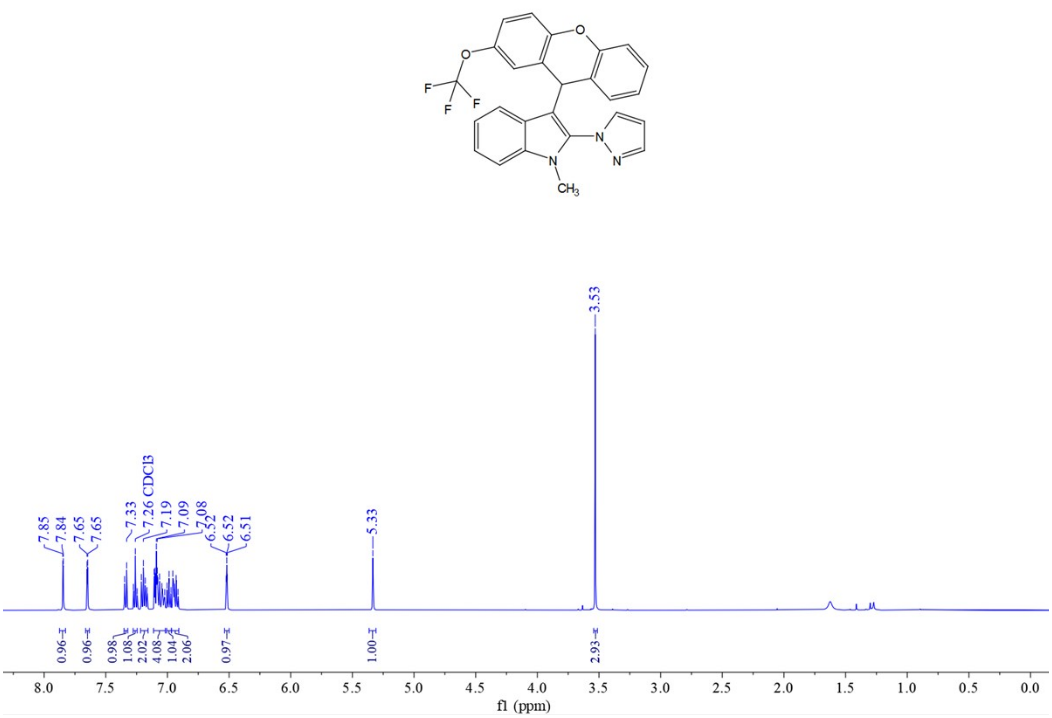
(54) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aga



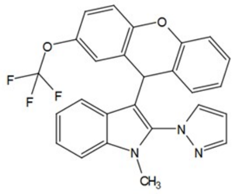
(55) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aga

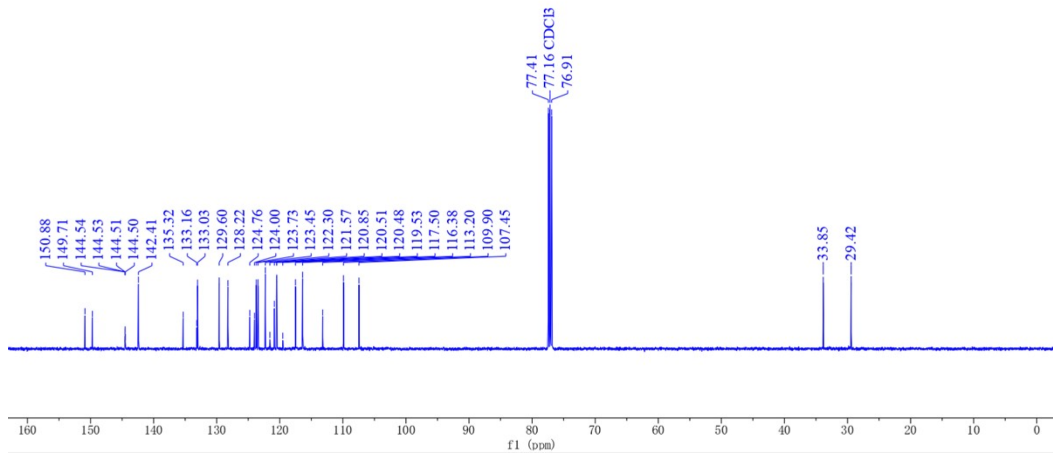


(56) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aha

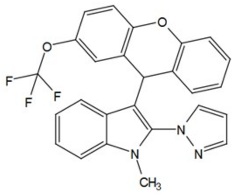


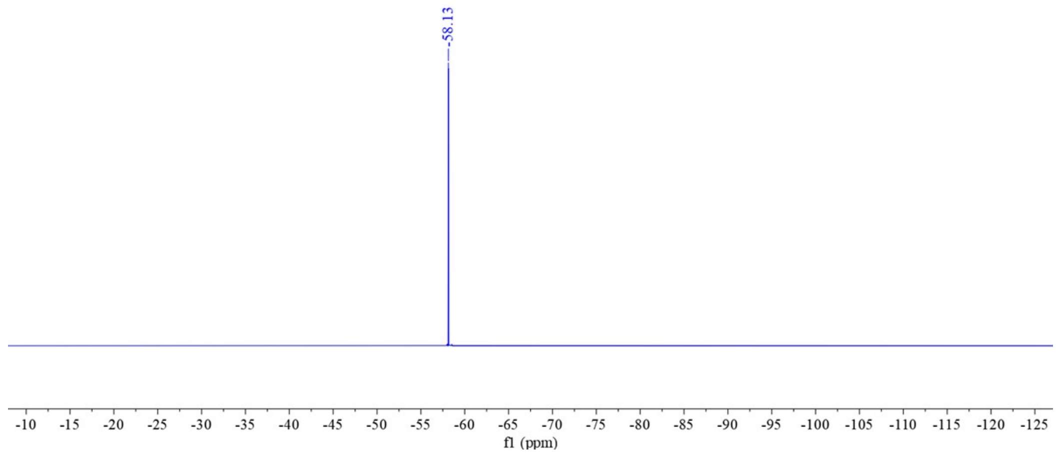
(57) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aha



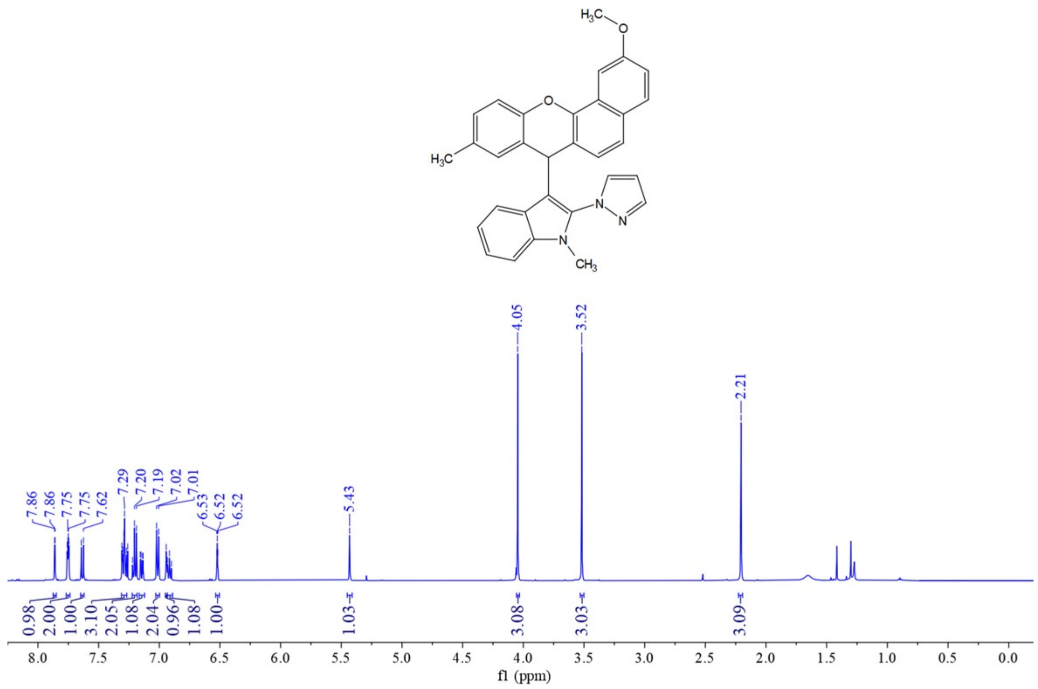


(58) ^{19}F-NMR (470 MHz, $CDCl_3$) spectrum of 4aha

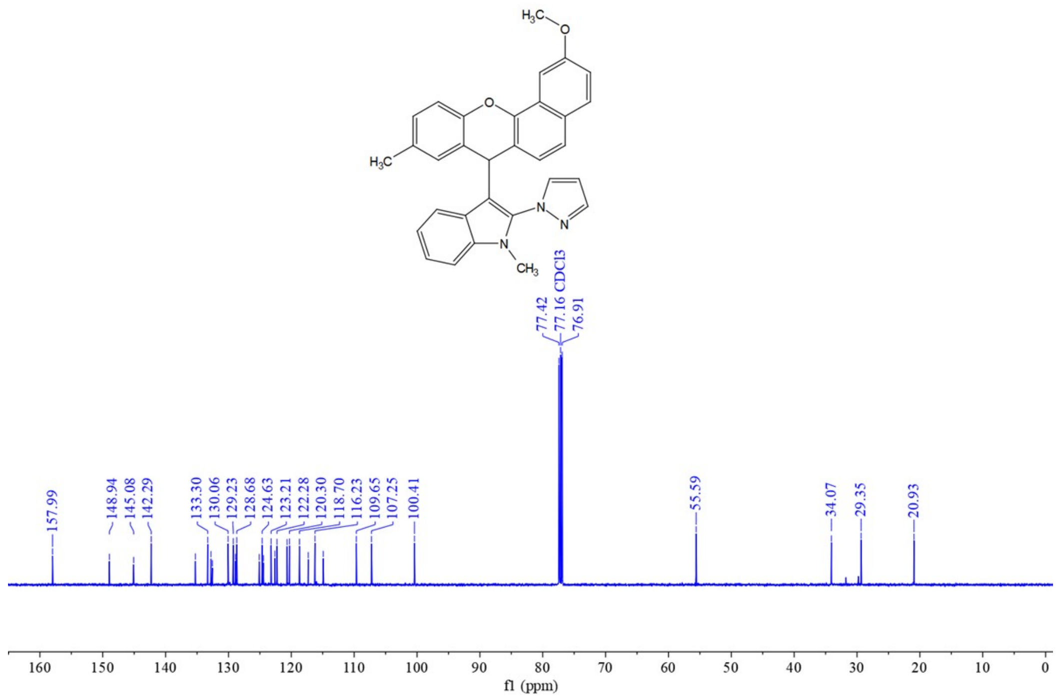




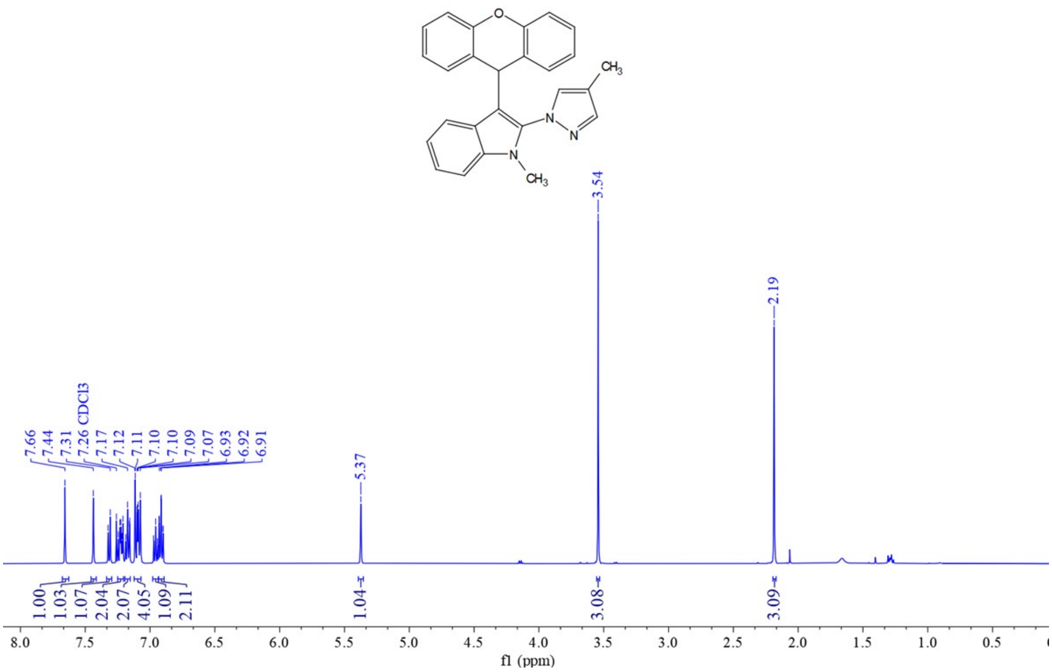
(59) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aia



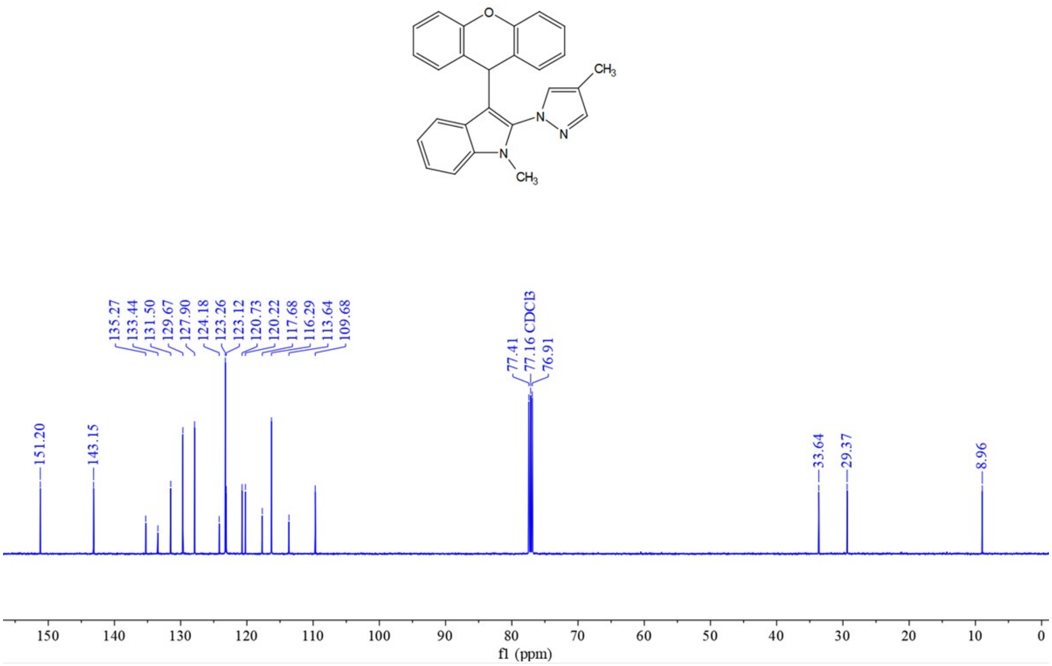
(60) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aia



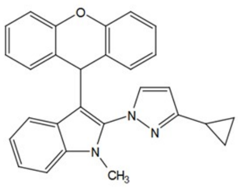
(61) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aab

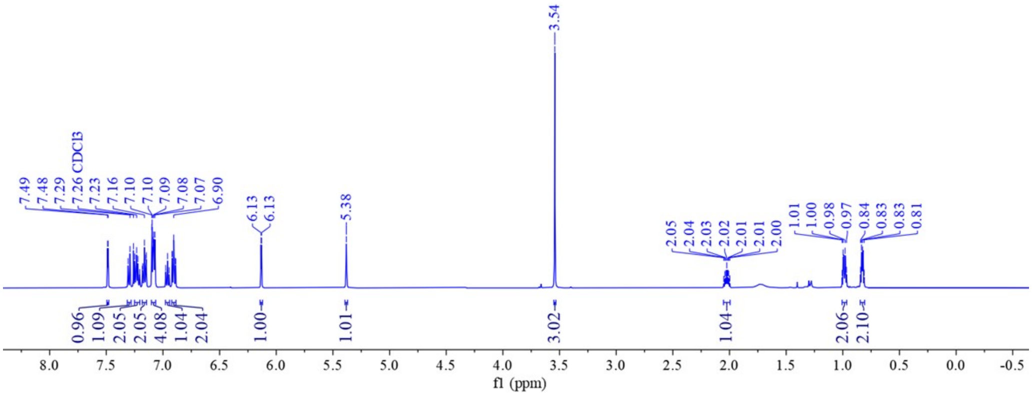


(62) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aab

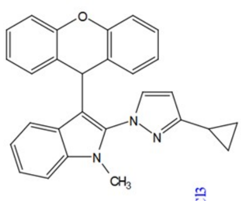


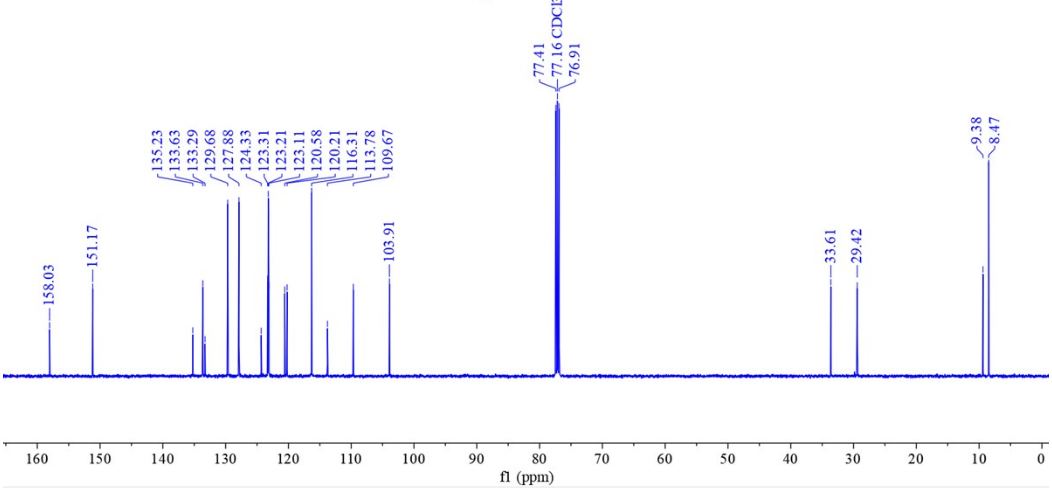
(63) ¹H-NMR (500 MHz, $CDCl_3$) spectrum of 4aac



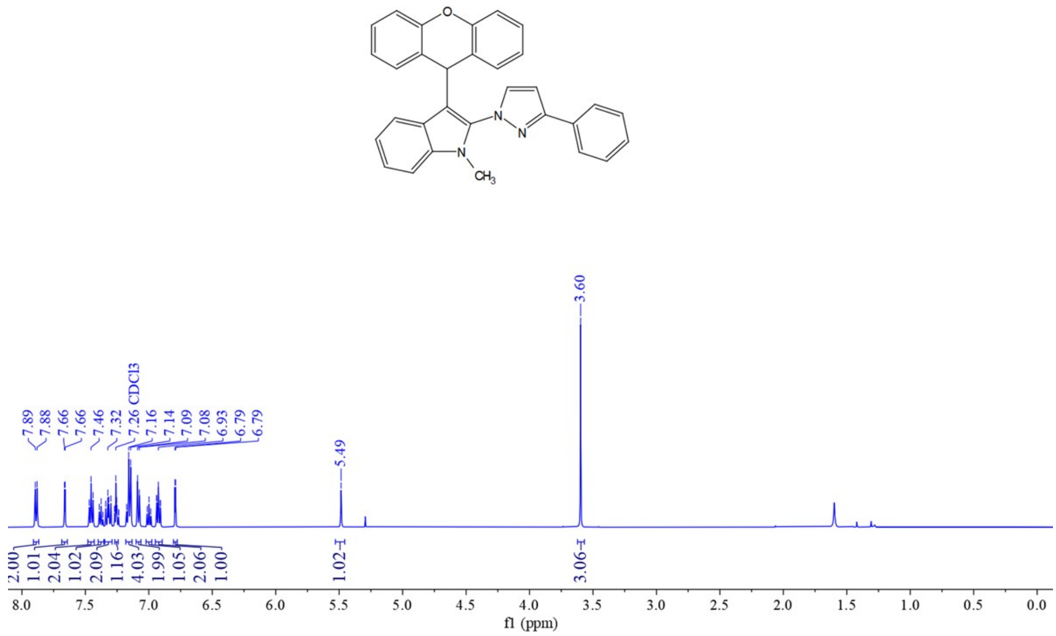


(64) ¹³C-NMR (125 MHz, $CDCl_3$) spectrum of 4aac

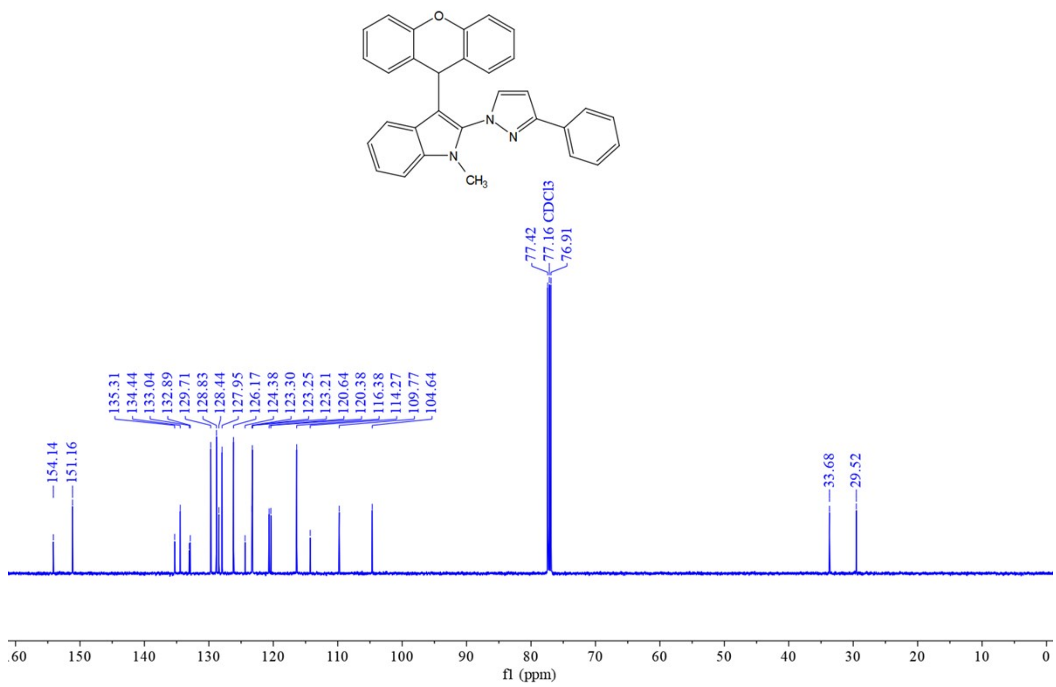




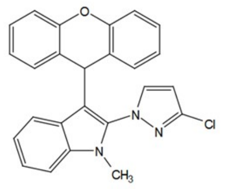
(65) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aad

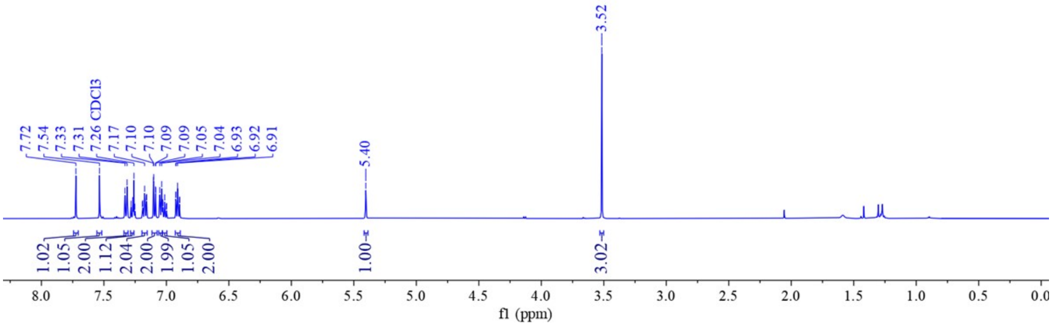


(66) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aad

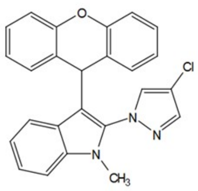


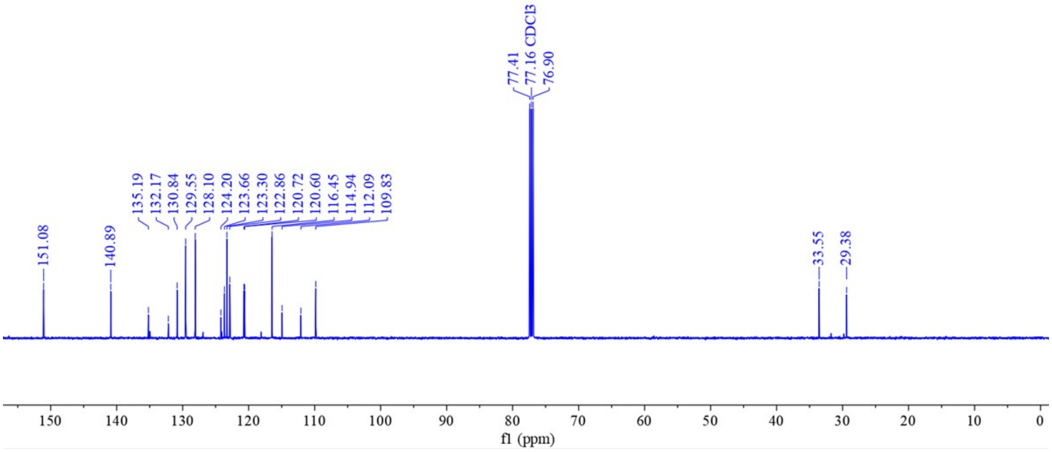
(67) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aae



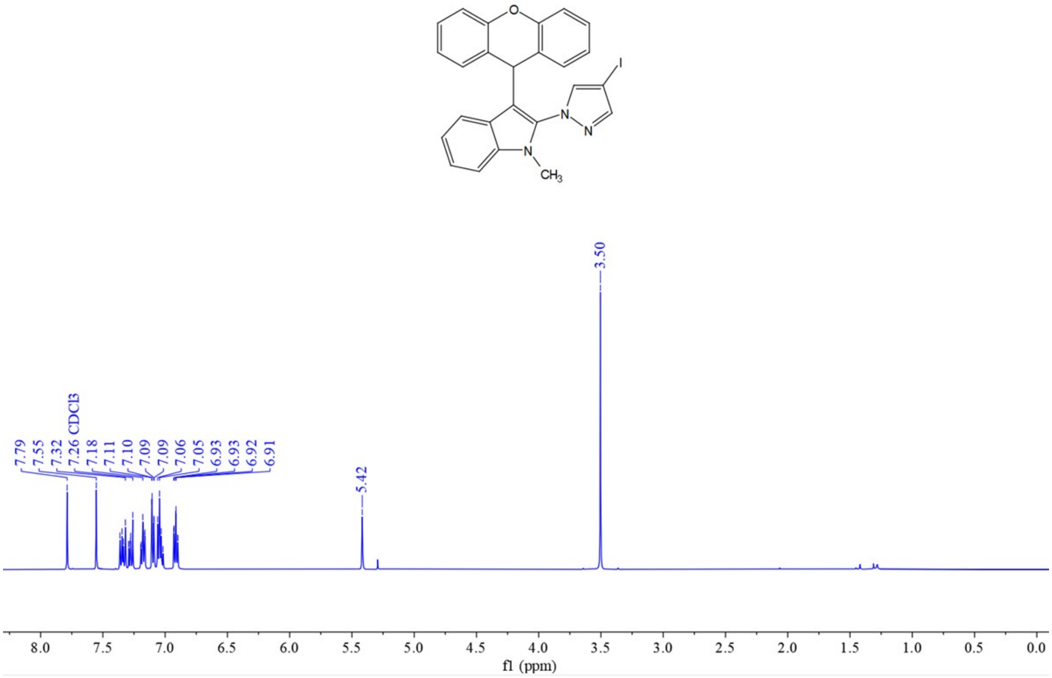


(68) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aae

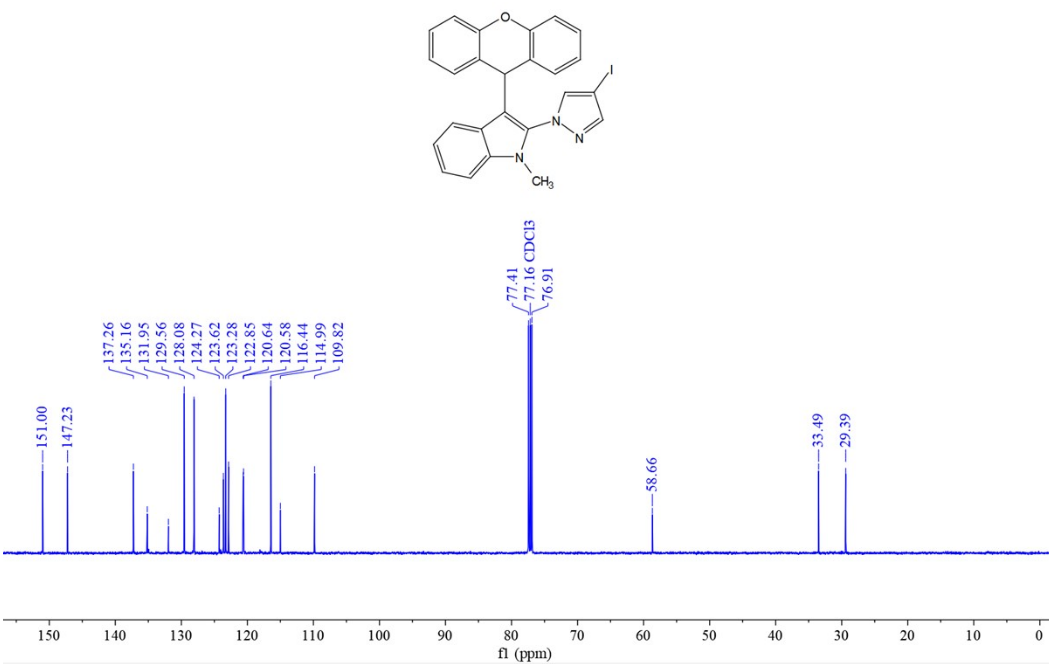




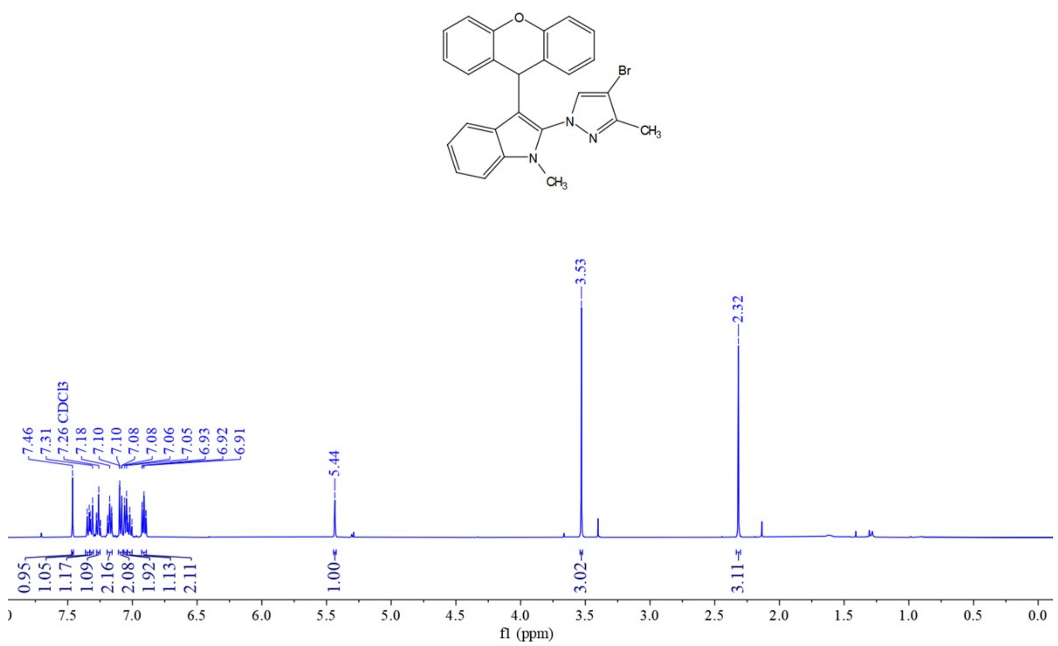
(69) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aaf



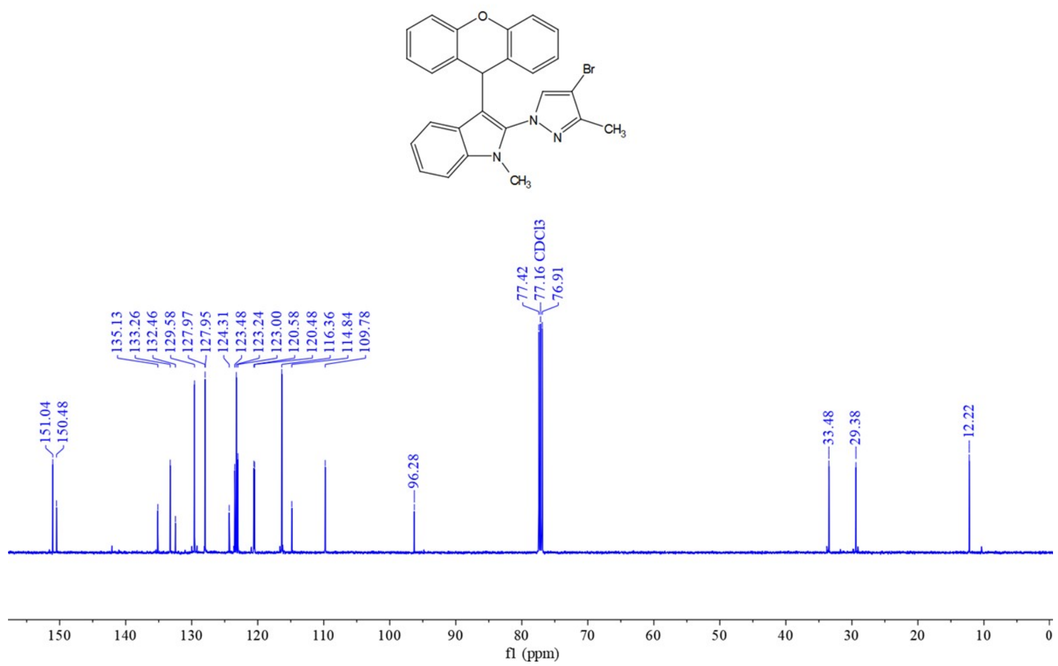
(70) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aaf



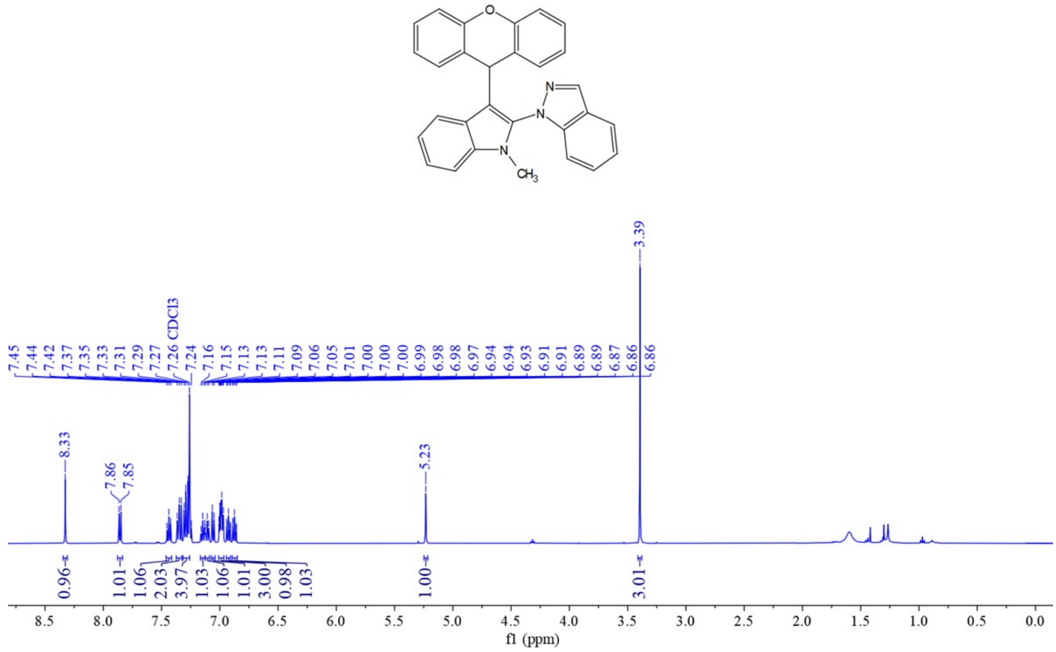
(71) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aag



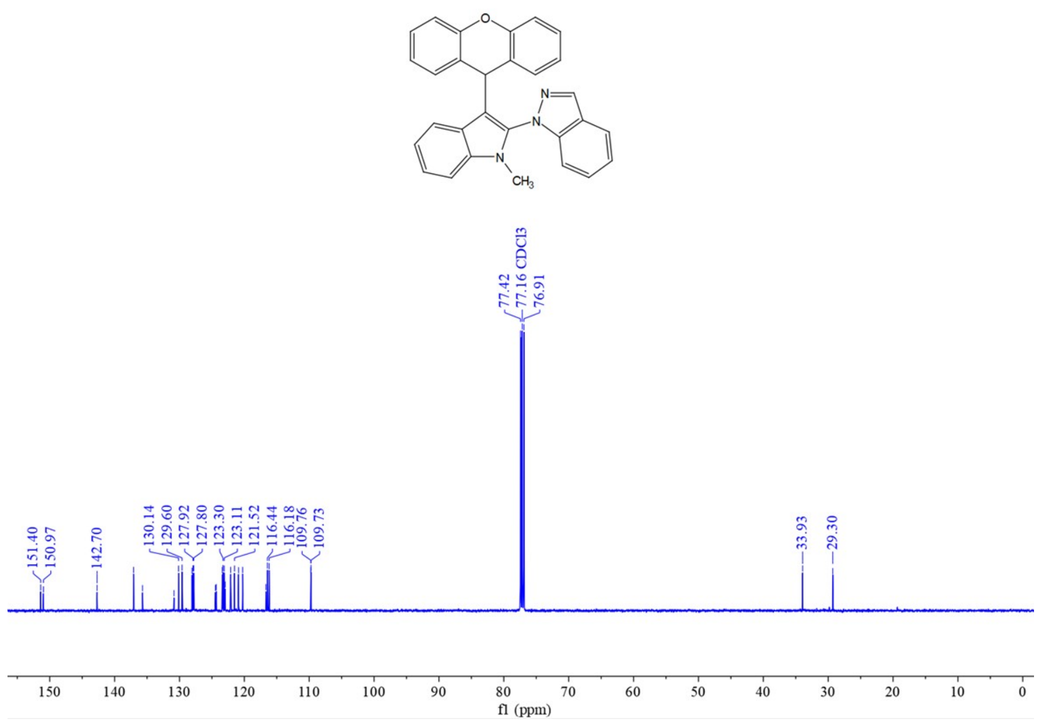
(72) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aag



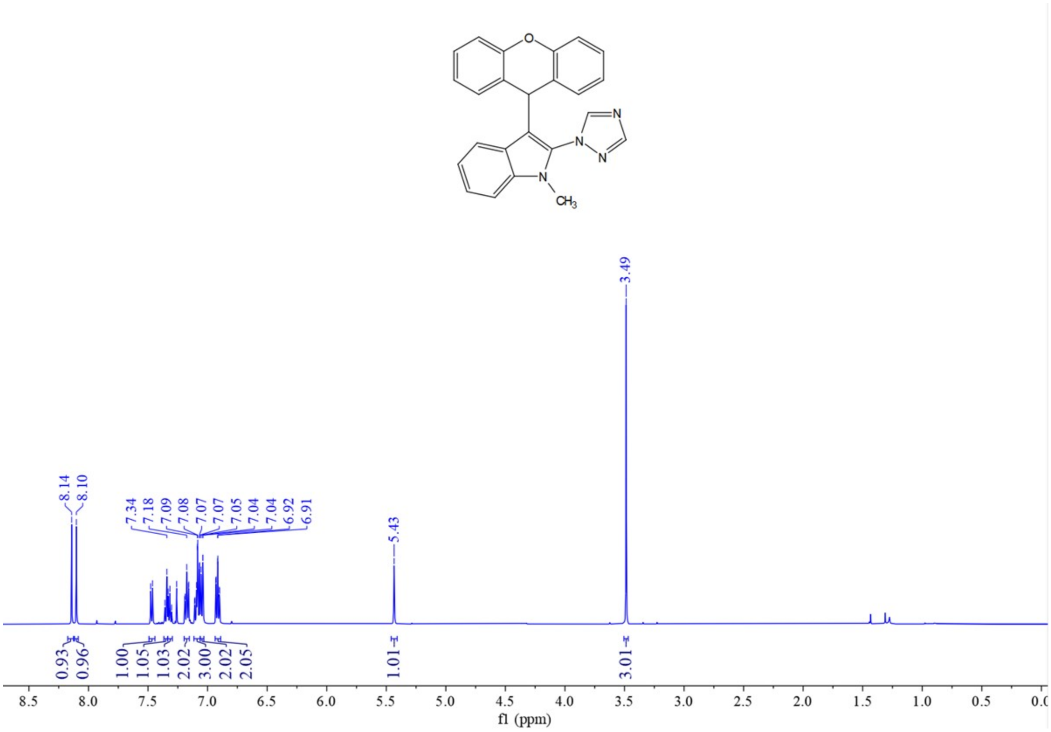
(73) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aah



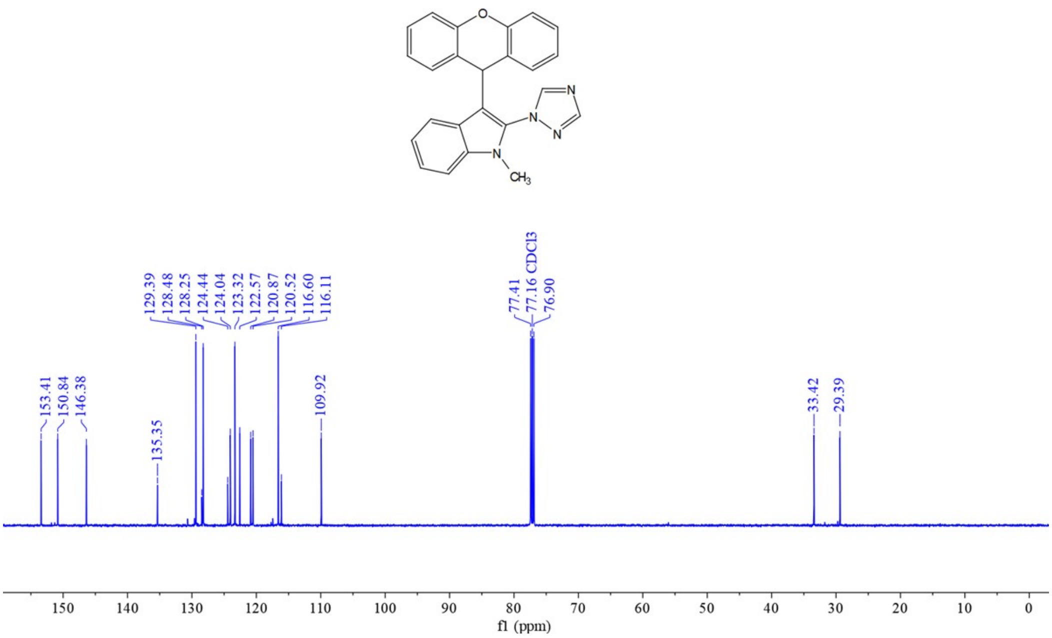
(74) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aah



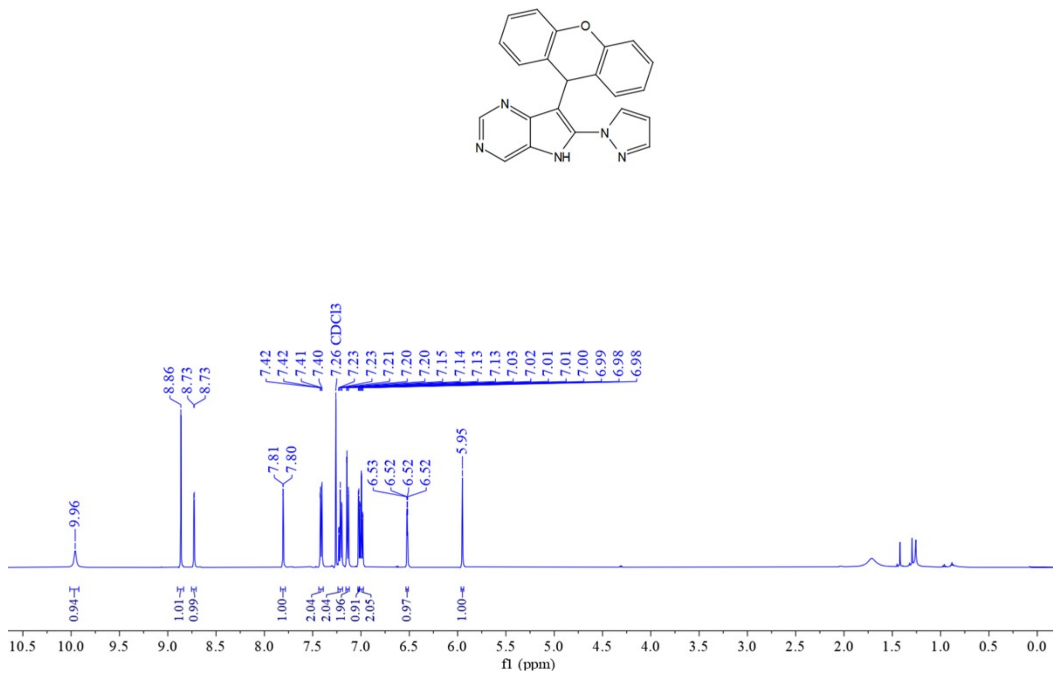
(75) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aai



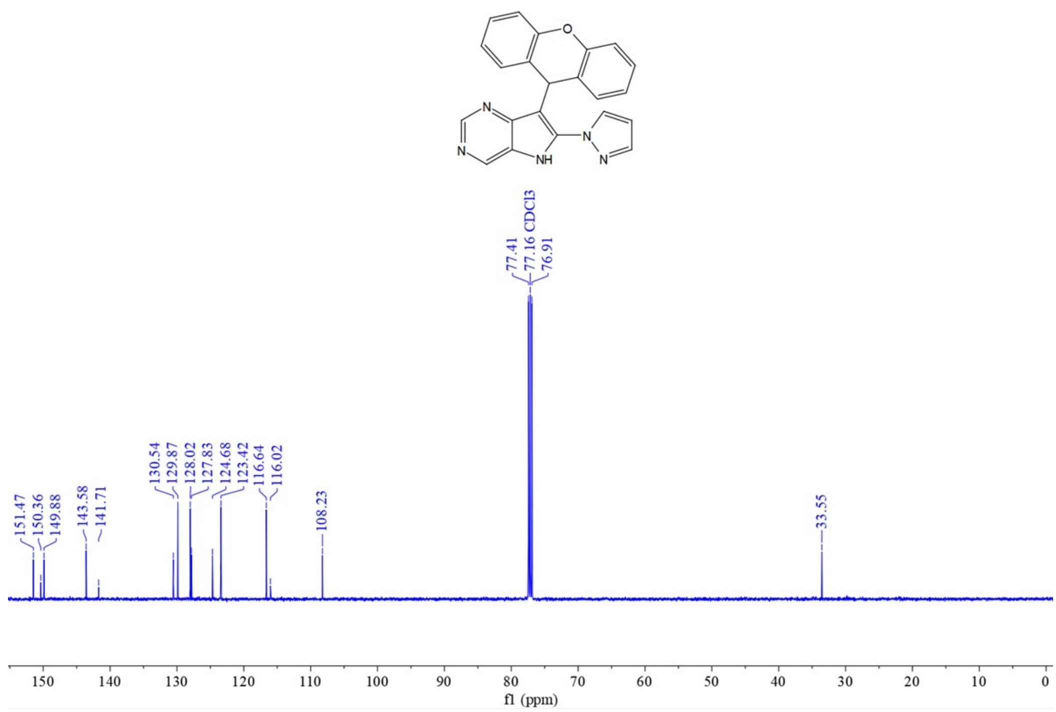
(76) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aai



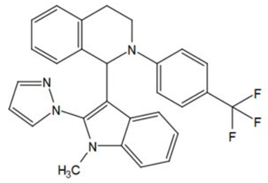
(77) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4saa

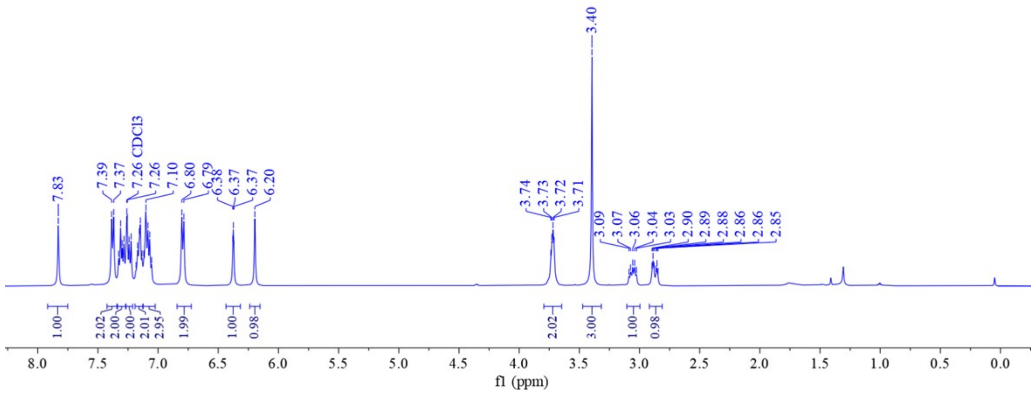


(78) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4saa

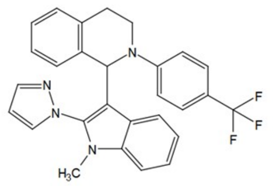


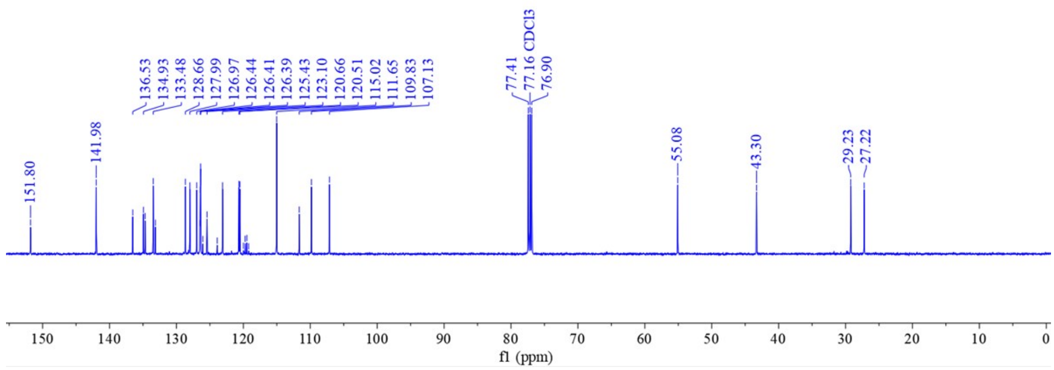
(79) ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of 4aja





(80) ^{13}C-NMR (125 MHz, $CDCl_3$) spectrum of 4aja





(81) ^{19}F-NMR (470 MHz, $CDCl_3$) spectrum of 4aja