Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Info

Blue-luminescent 5-(3-indolyl)oxazoles via microwave-assisted three-component coupling-cycloisomerization-Fischer indole synthesis

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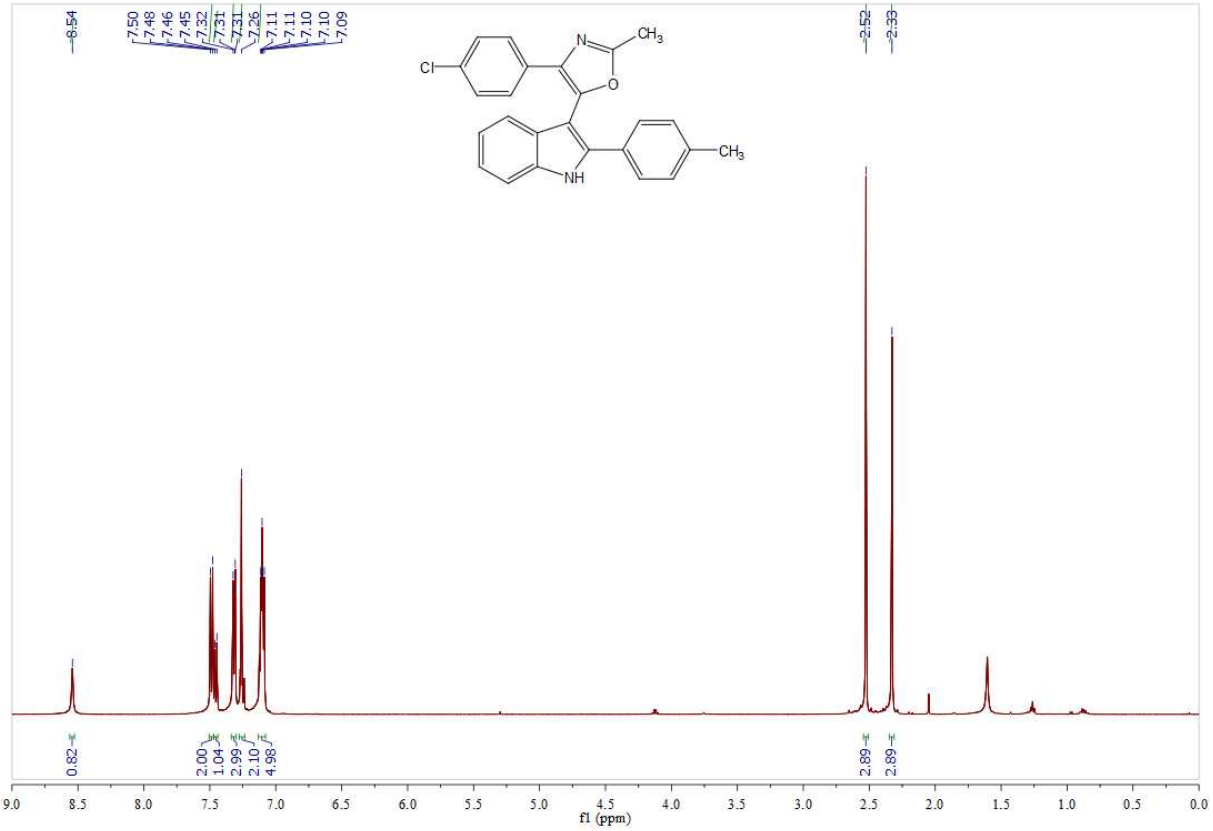
General considerations

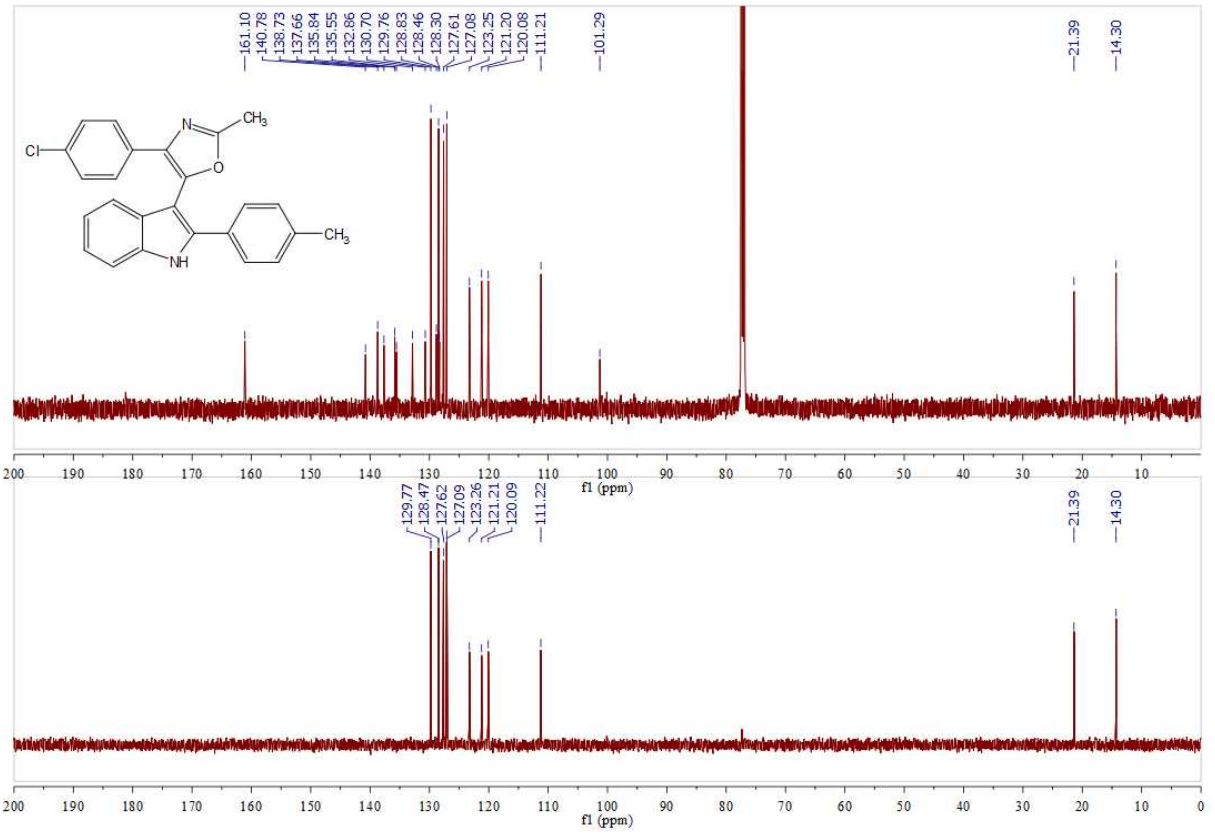
Tetrahydrofuran was dried using *MBraun* system MB-SPS-800, and triethylamine was refluxed under nitrogen over sodium, distilled and stored in a Schlenk flask over potassium hydroxide pellets under nitrogen atmosphere. Dielectric heating was performed with Discover Labmate microwave reactor by CEM (Kamp-Lintfort, Germany). Melting points were determined on a digital melting point apparatus and temperatures and are uncorrected. ^{1}H NMR, ^{13}C NMR and 135-DEPT spectra were recorded on a Bruker Avance DRX500 spectrometer. $CDCl_3$ and DMSO-d_6 were used as deuterated solvents. the solvents were locked as internal standards ($CDCl_3$: ^{1}H δ 7.26, ^{13}C δ 77.16; DMSO-d_6: ^{1}H δ 2.50, ^{13}C δ 39.52). The multiplicities of signals were abbreviated as follows: s: singlet; d: doublet; t: triplet; dd: doublet of doublets; ddd: doublet of doublets of doublets; dt: doublet of triplets; td: triplet of doublets; tt: triplet of triplets; m: multiplet and br: broad signal. The type of carbon atoms was determined on the basis of 135-DEPT NMR spectra. Infrared spectra were recorded on a Vector 22 spectrophotometer (Bruker). The intensity of signals is abbreviated as follows: s (strong), m (medium) and w (weak). Flash column chromatography was performed on 60 M (mesh 230-400) silica gel (Merck or Macherey-Nagel). For thin-layer chromatography (TLC), silica gel plates (Merck; 60 F_{154}) were used. The spots were detected with UV light at 254 nm and using aqueous potassium permanganate solution. Ultimate analysis was taken on a Perkin Elmar CHN-Analyzer 2400. Mass spectra were recorded by MALDI (Bruker Ultraflex). The UV/Vis Spectra were recorded on a Perkin Elmer Models Lambda 19 and the Emission spectra were recorded on a Perkin Elmer LS55 spectrometer.

Spectroscopic Data of 5-(3-Iindolyl)oxazoles 4

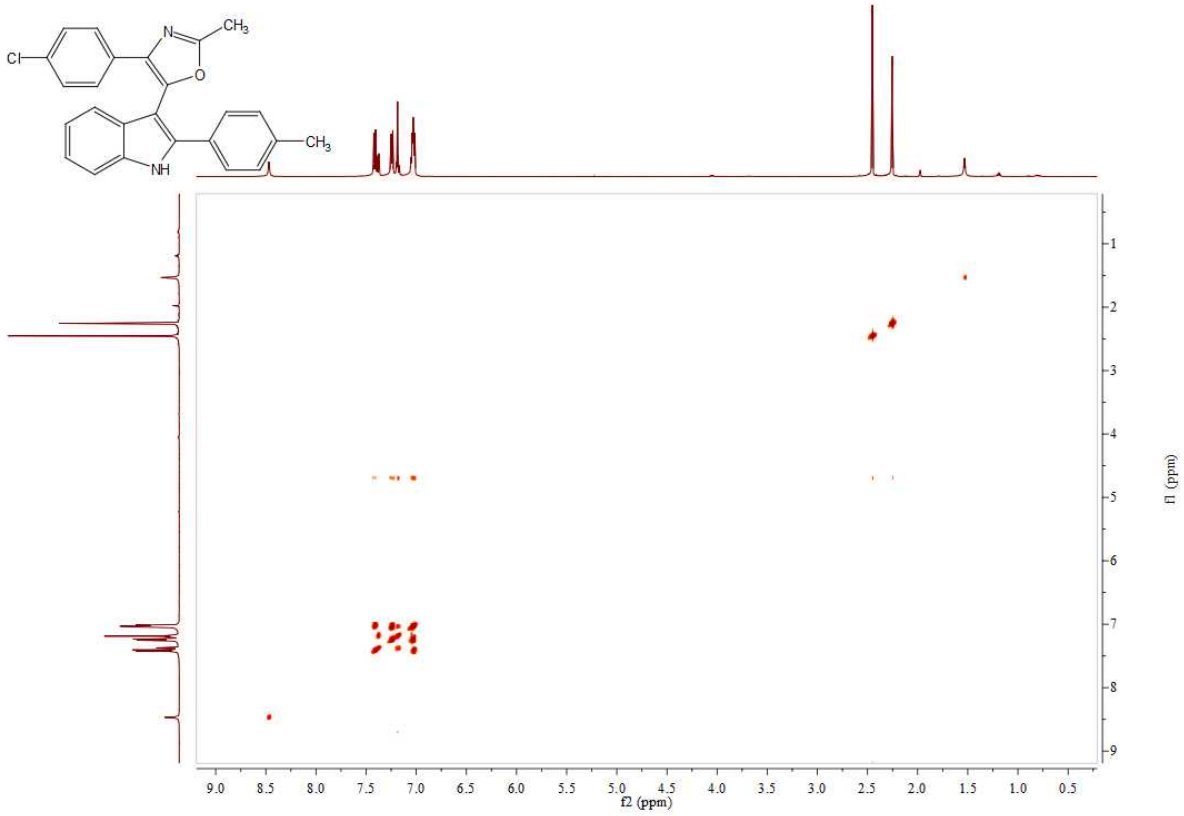
4-(4-Chlorophenyl)-2-methyl-5-(2-*p*-tolyl-1*H*-indol-3-yl)oxazole (4a)



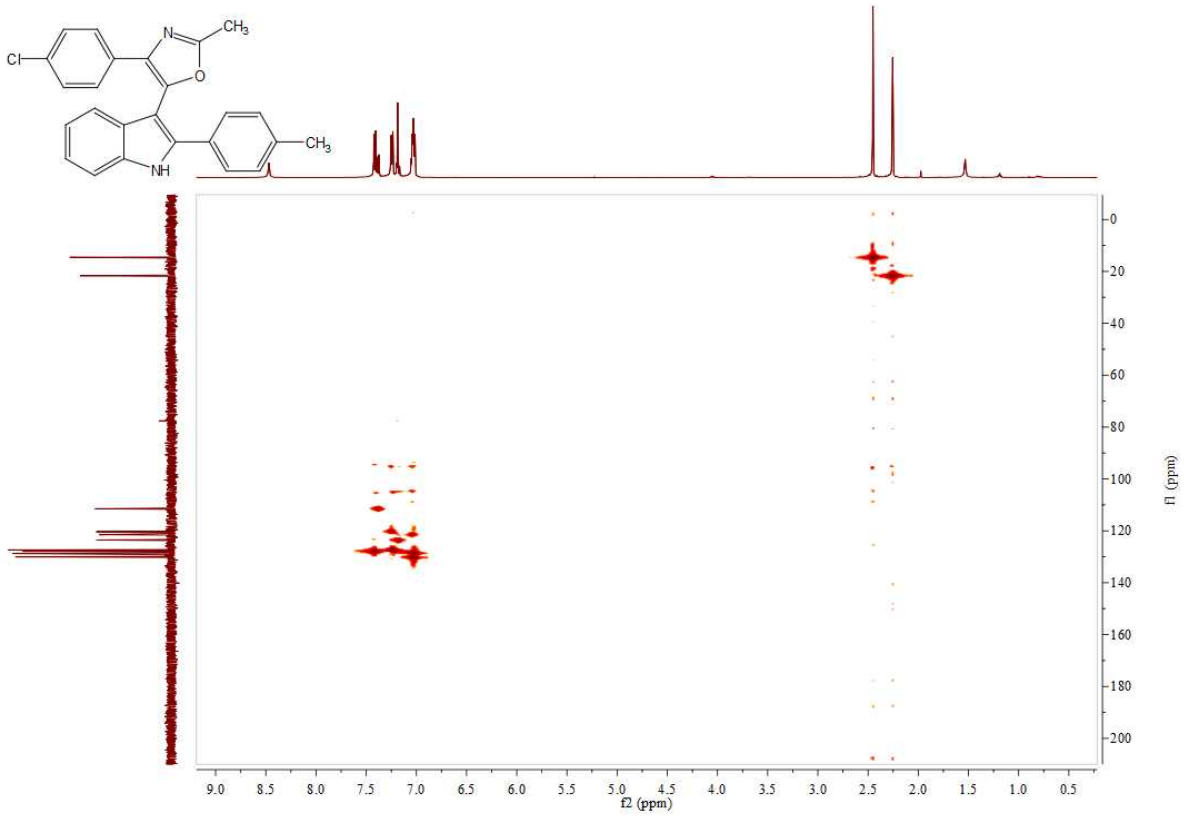
^{1}H NMR of **4a** in $CDCl_3$ at 296 K (δ in ppm).



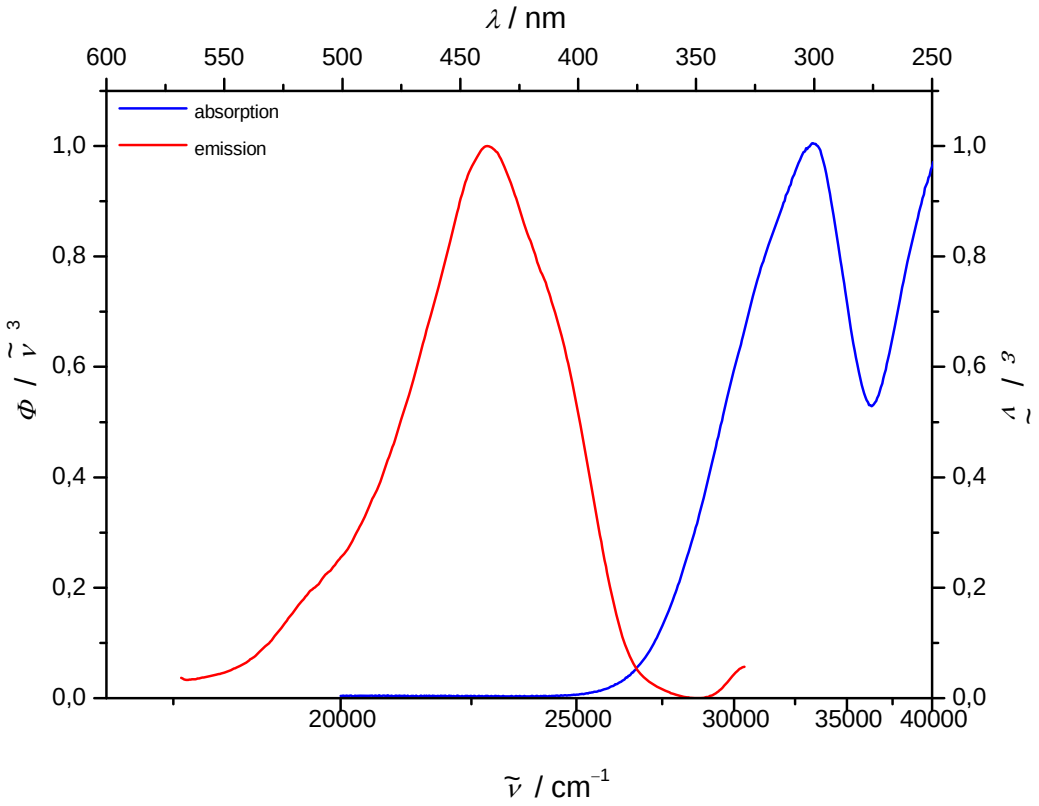
^{13}C NMR and 135-DEPT Spectra of **4a** in $CDCl_3$ at 296 K (δ in ppm).



H,H-COSY NMR of **4a** in $CDCl_3$ at 296 K (δ in ppm).

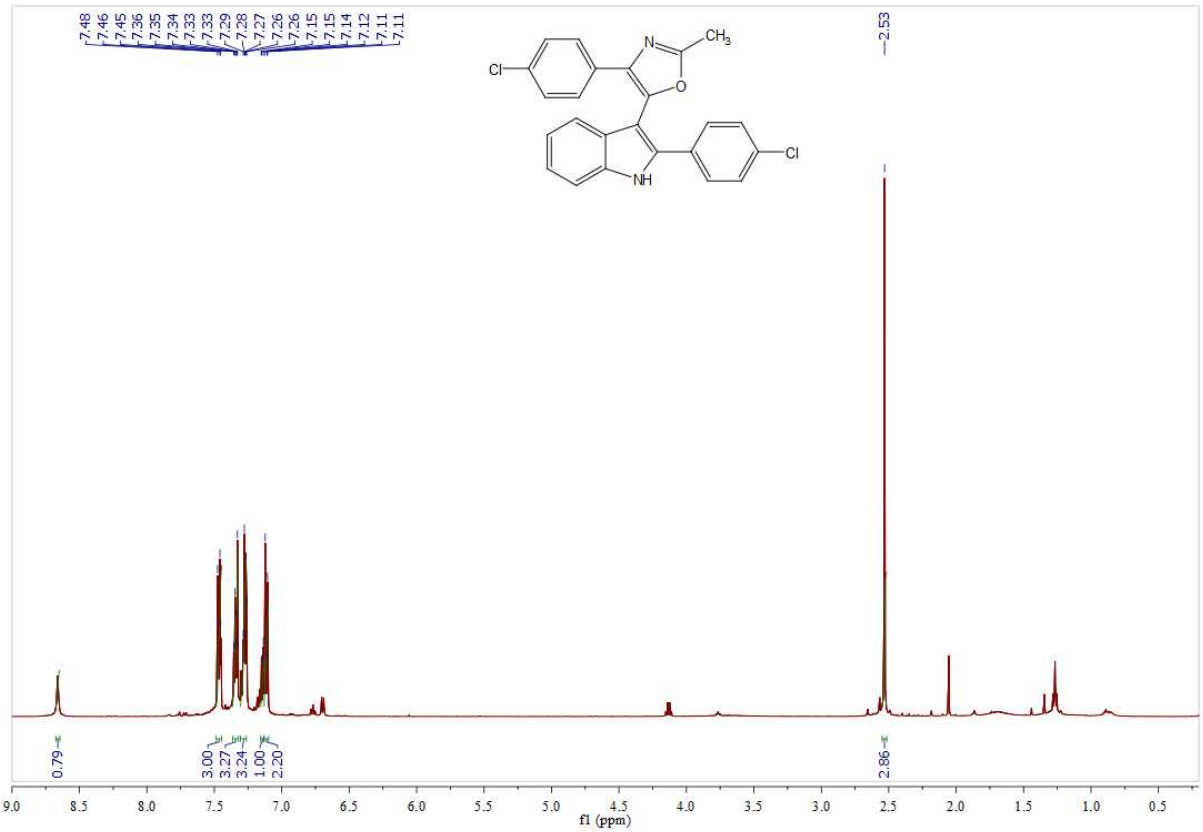


C,H-COSY NMR of **4a** in $CDCl_3$ at 296 K (δ in ppm).

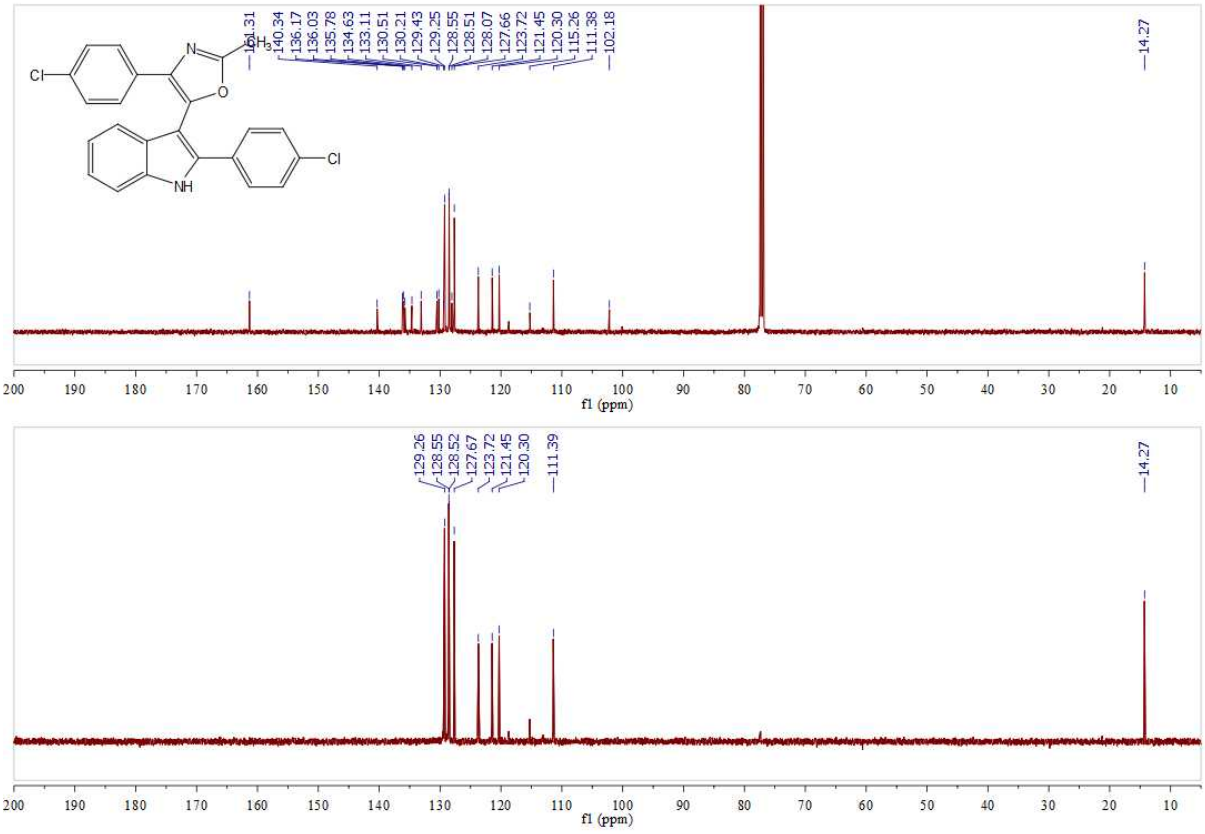


Normalized UV/Vis and fluorescence spectra of **4a** (recorded in EtOH at 298 K).

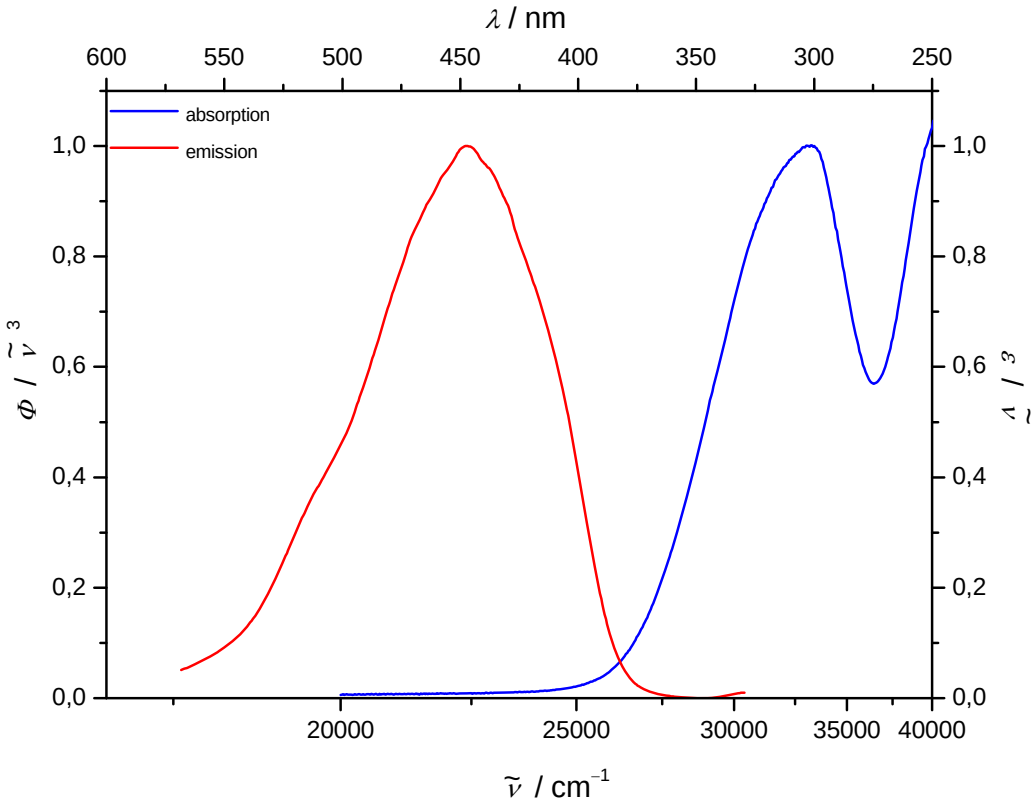
4-(4-Chlorophenyl)-5-(2-(4-chlorophenyl)-1*H*-indol-3-yl)-2-methyloxazole (4b)



^{1}H NMR of **4b** in $CDCl_3$ at 296 K (δ in ppm).

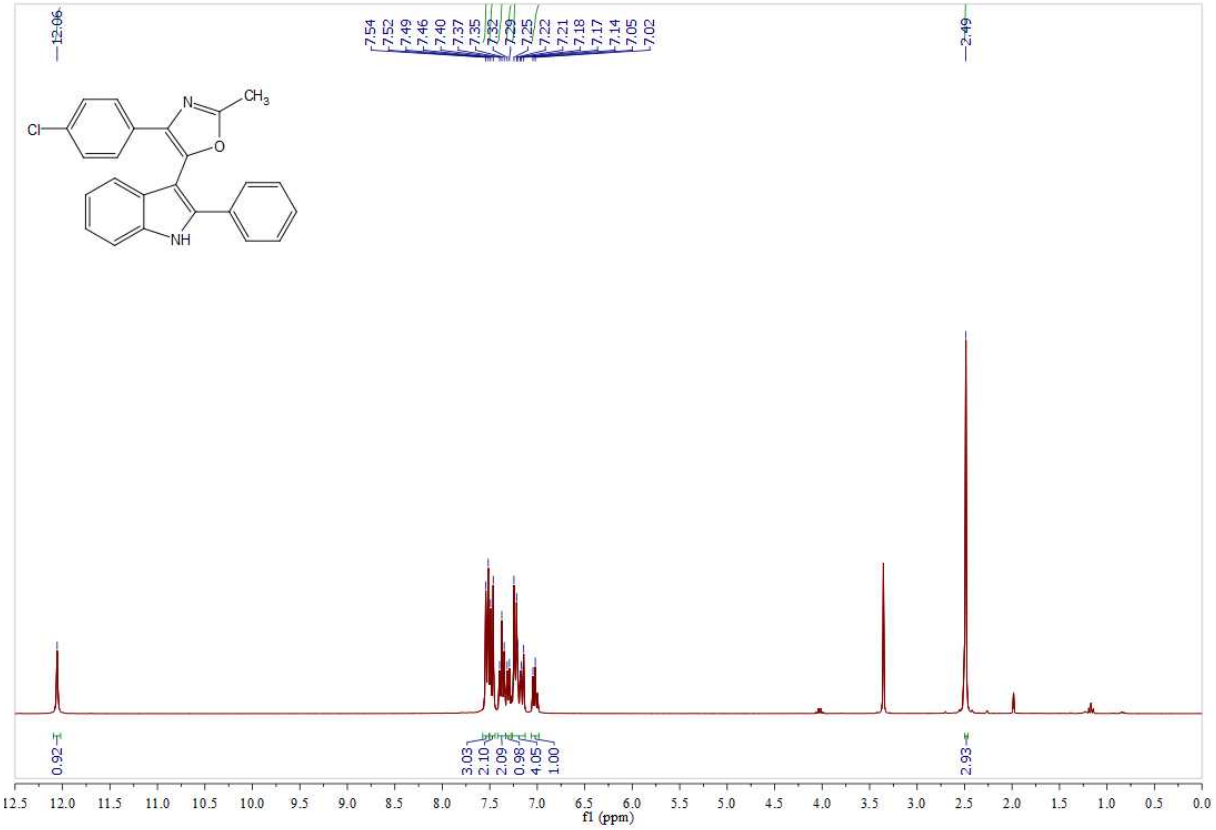


^{13}C NMR and 135-DEPT Spectra of **4b** in $CDCl_3$ at 296 K (δ in ppm).

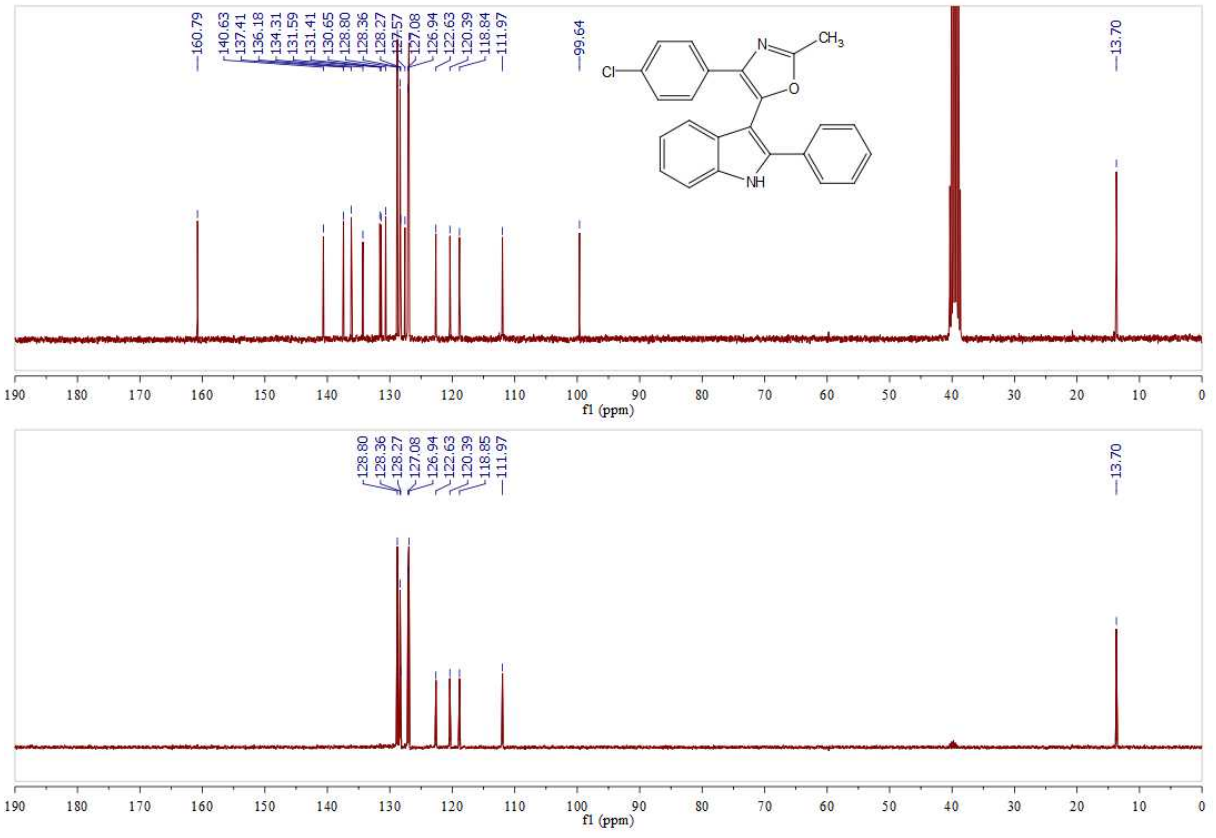


Normalized UV/Vis and fluorescence spectra of **4b** (recorded in EtOH at 298 K).

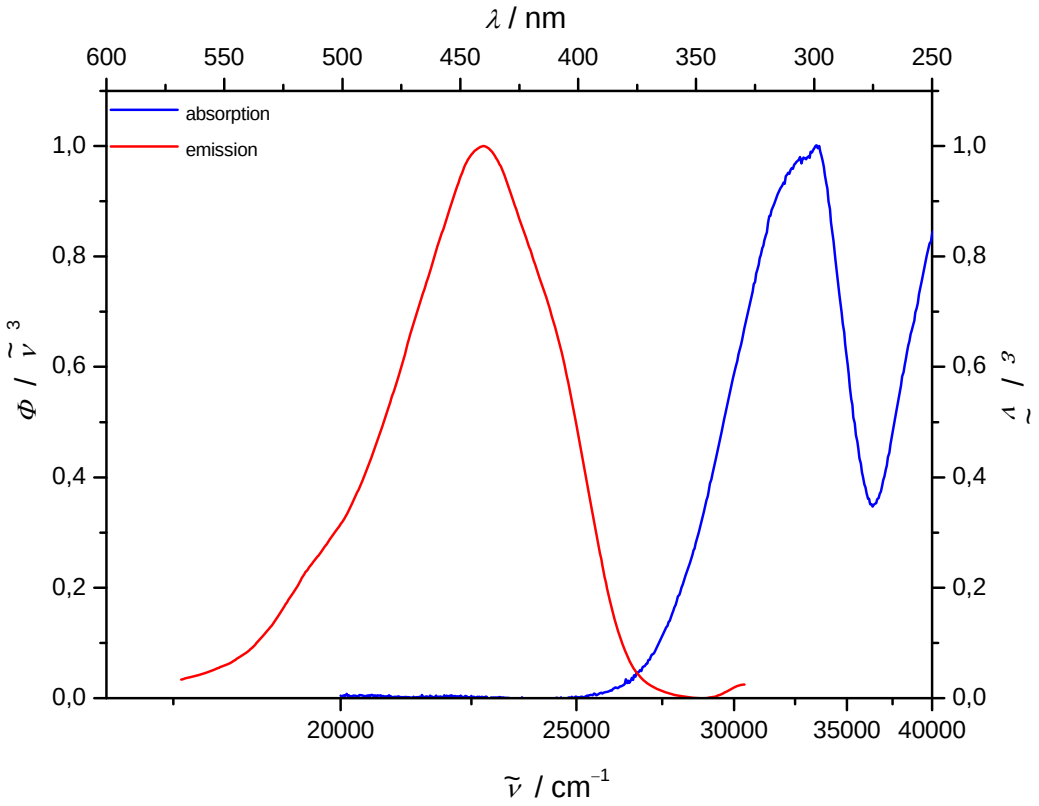
4-(4-Chlorophenyl)-2-methyl-5-(2-phenyl-1*H*-indol-3-yl)oxazole (4c)



^{1}H NMR of **4c** in DMSO-d^{6} at 296 K (δ in ppm).

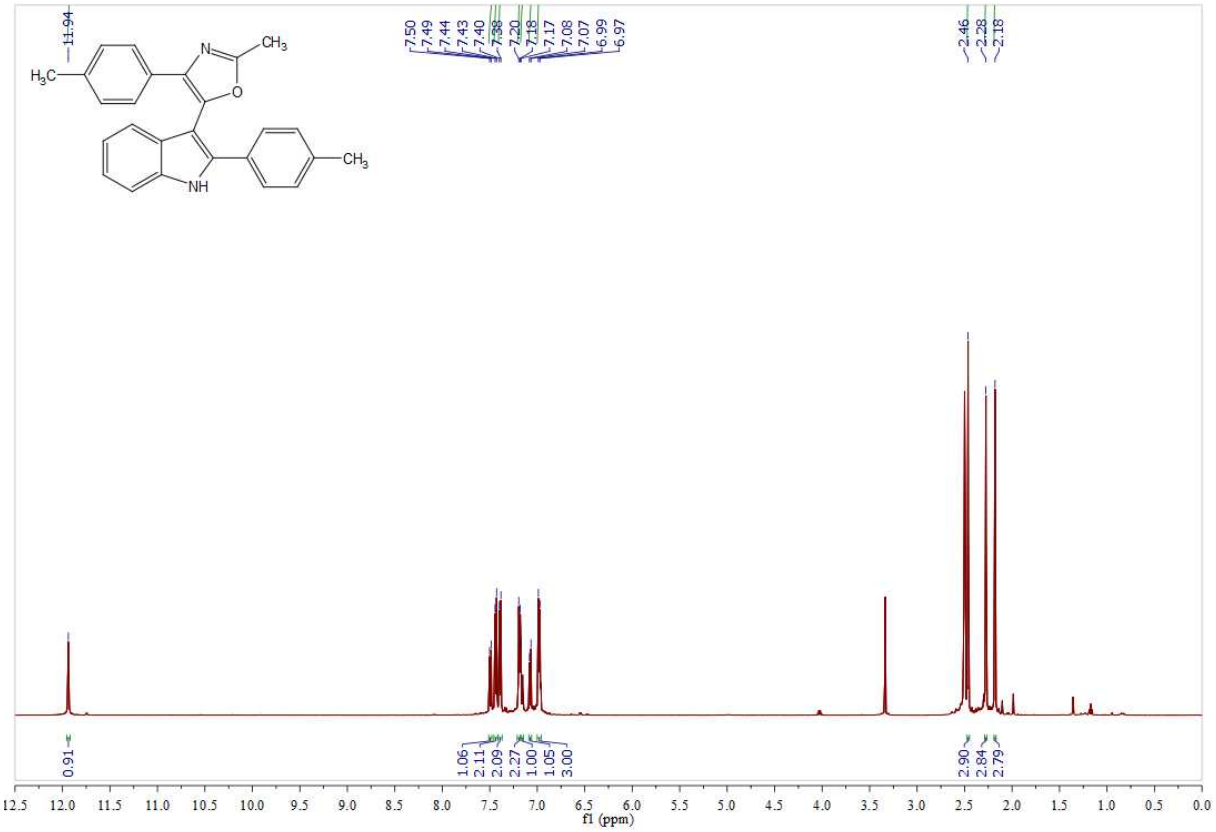


^{13}C NMR and 135-DEPT Spectra of **4c** in DMSO-d^{6} at 296 K (δ in ppm).

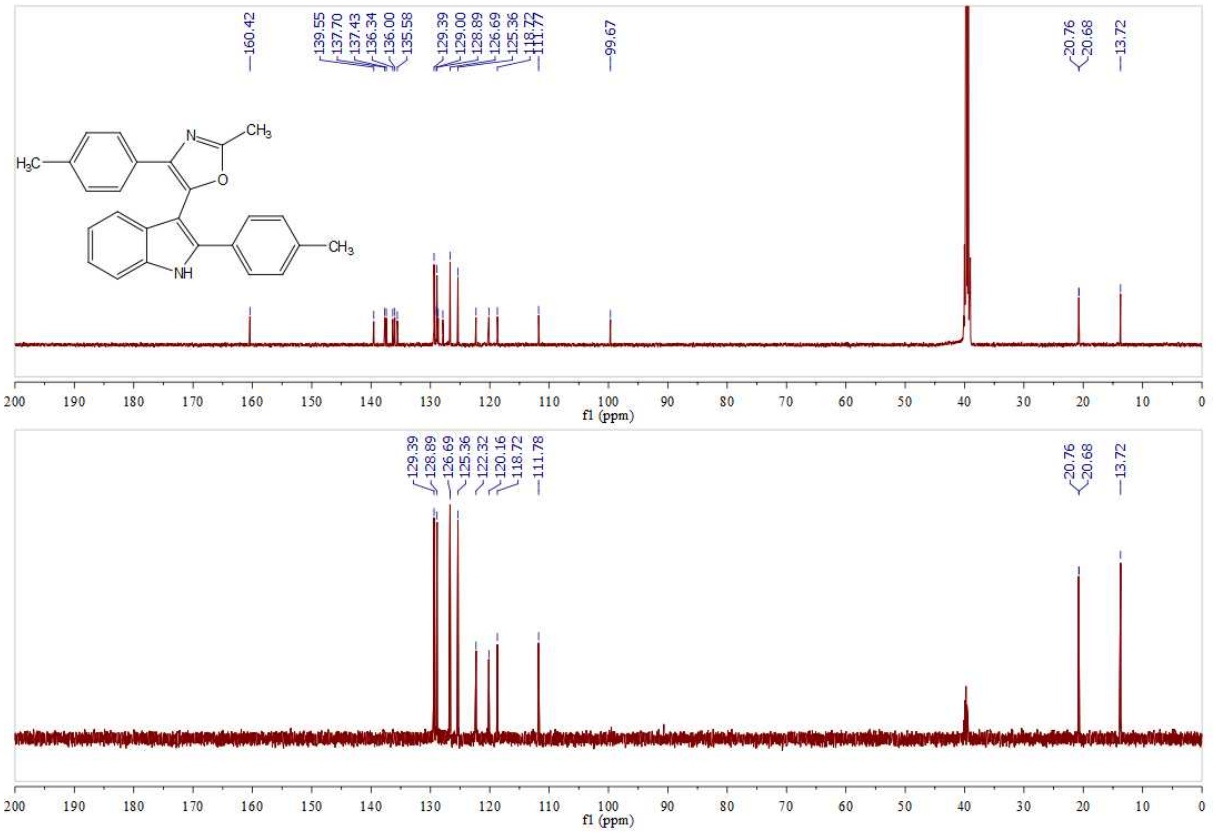


Normalized UV/Vis and fluorescence spectra of **4c** (recorded in EtOH at 298 K).

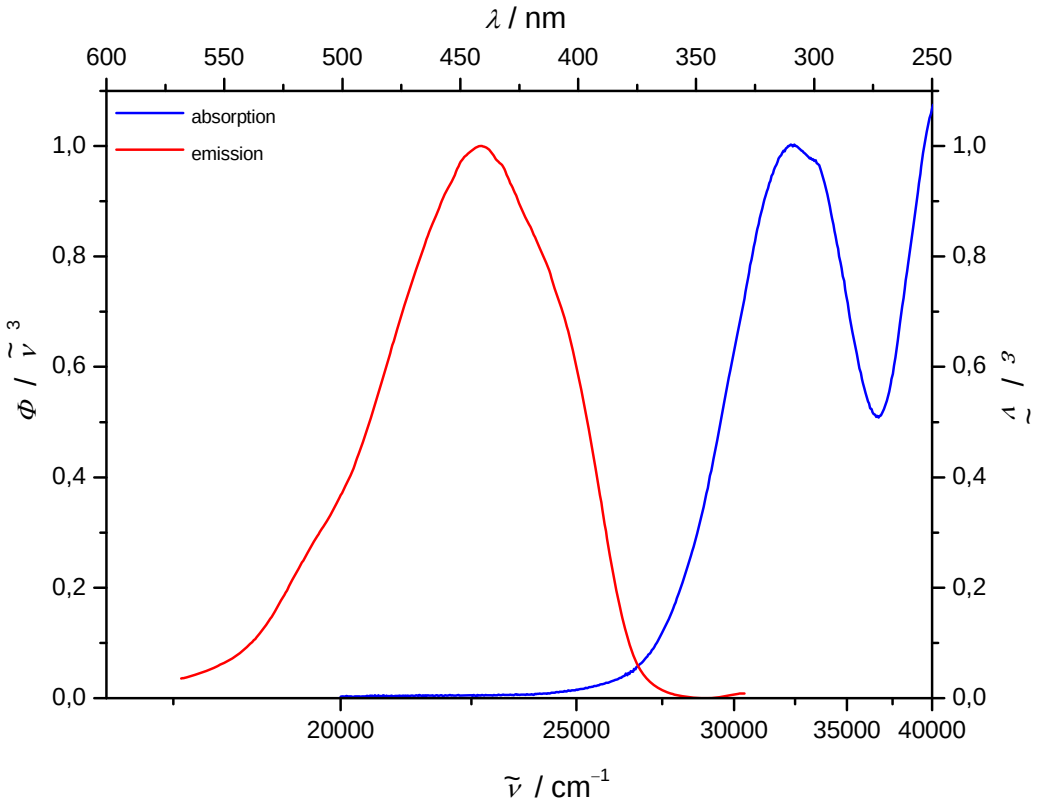
2-Methyl-4-*p*-tolyl-5-(2-p-tolyl-1*H*-indol-3-yl)oxazole (4d)



^{1}H NMR of **4d** in DMSO-d^{6} at 296 K (δ in ppm).

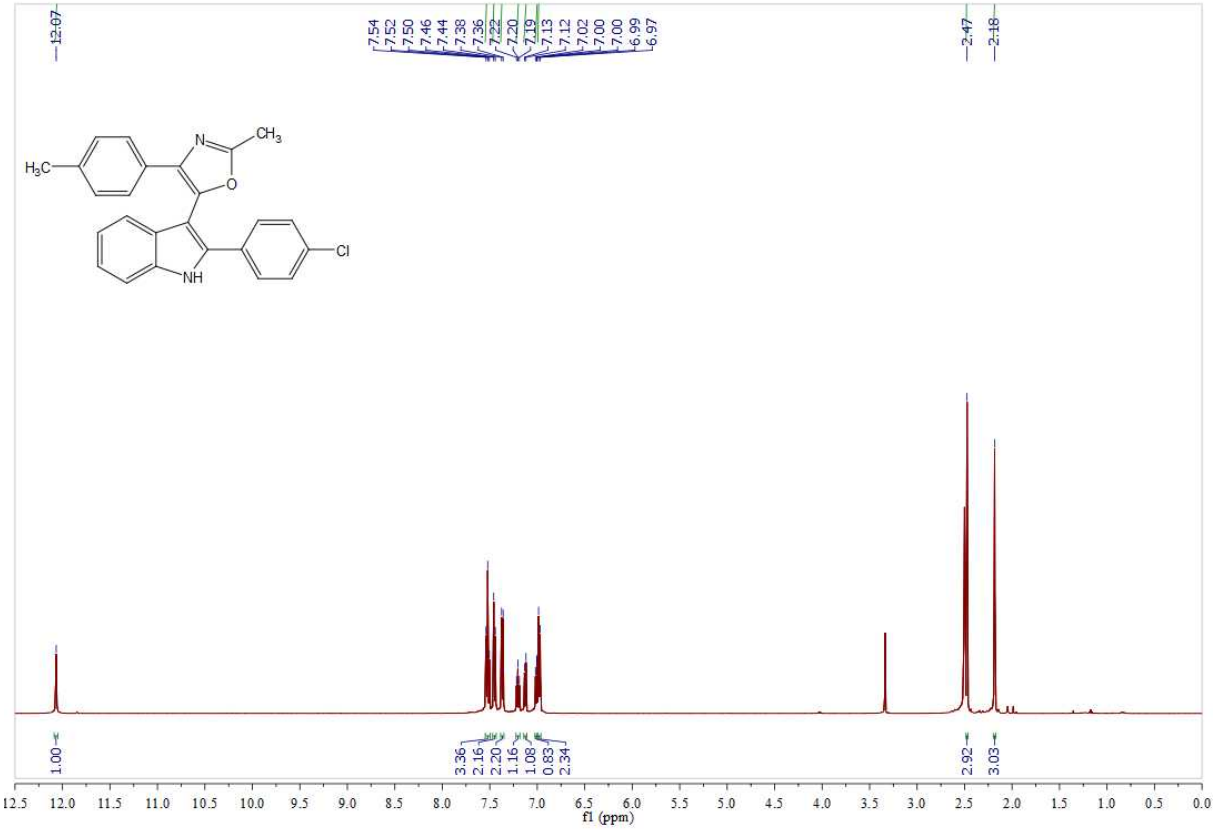


^{13}C NMR and 135-DEPT Spectra of **4d** in DMSO-d^{6} at 296 K (δ in ppm).

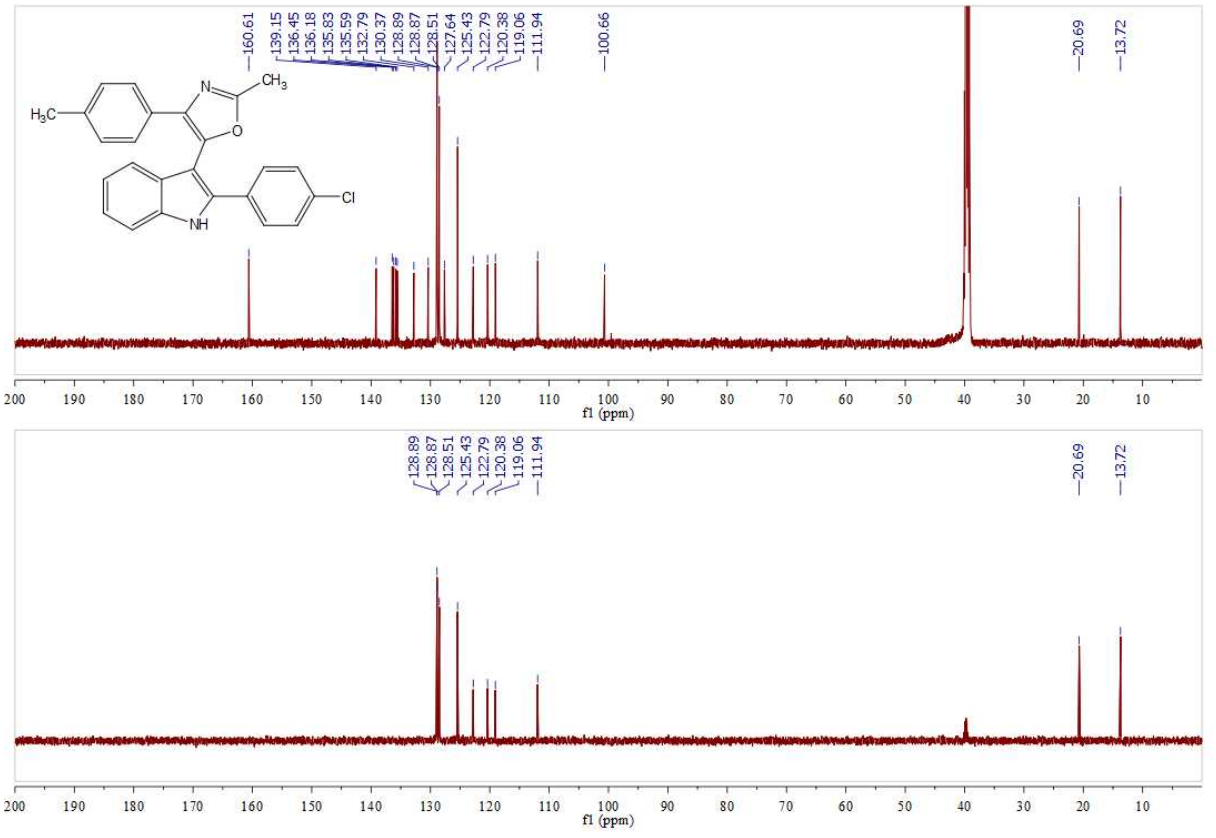


Normalized UV/Vis and fluorescence spectra of **4d** (recorded in EtOH at 298 K).

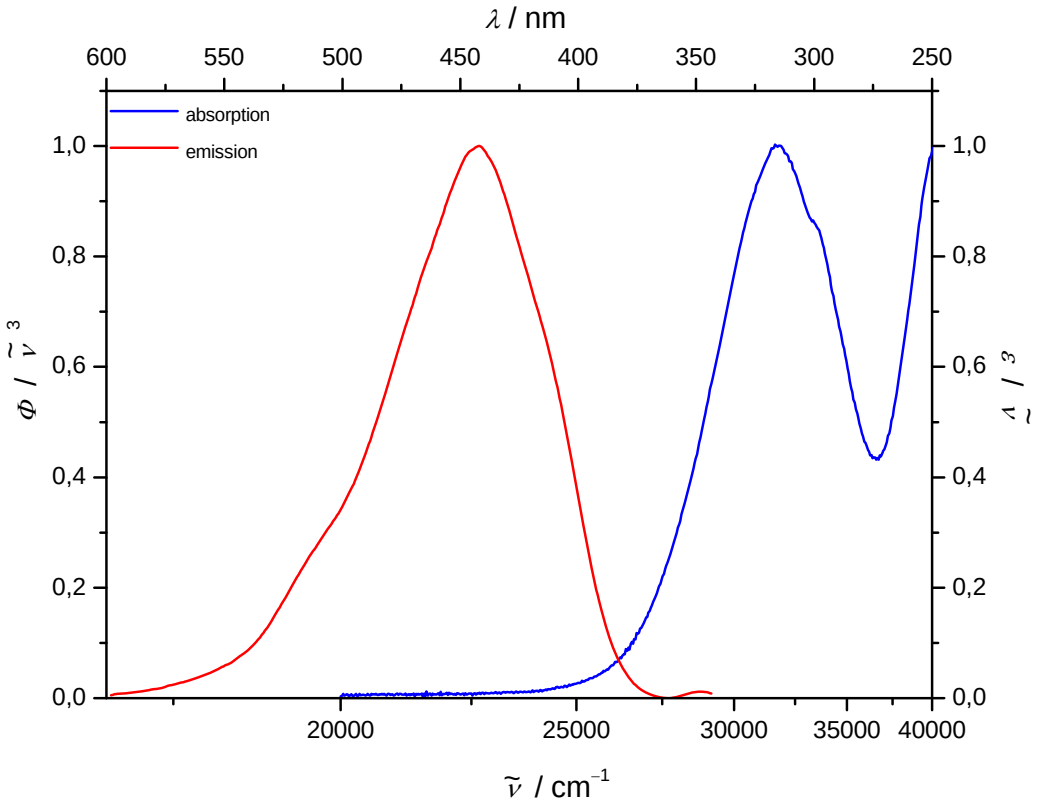
5-(2-(4-Chlorophenyl)-1*H*-indol-3-yl)-2-methyl-4-*p*-tolyloxazole (4e)



^{1}H NMR of **4e** in DMSO-d^6 at 296 K (δ in ppm).

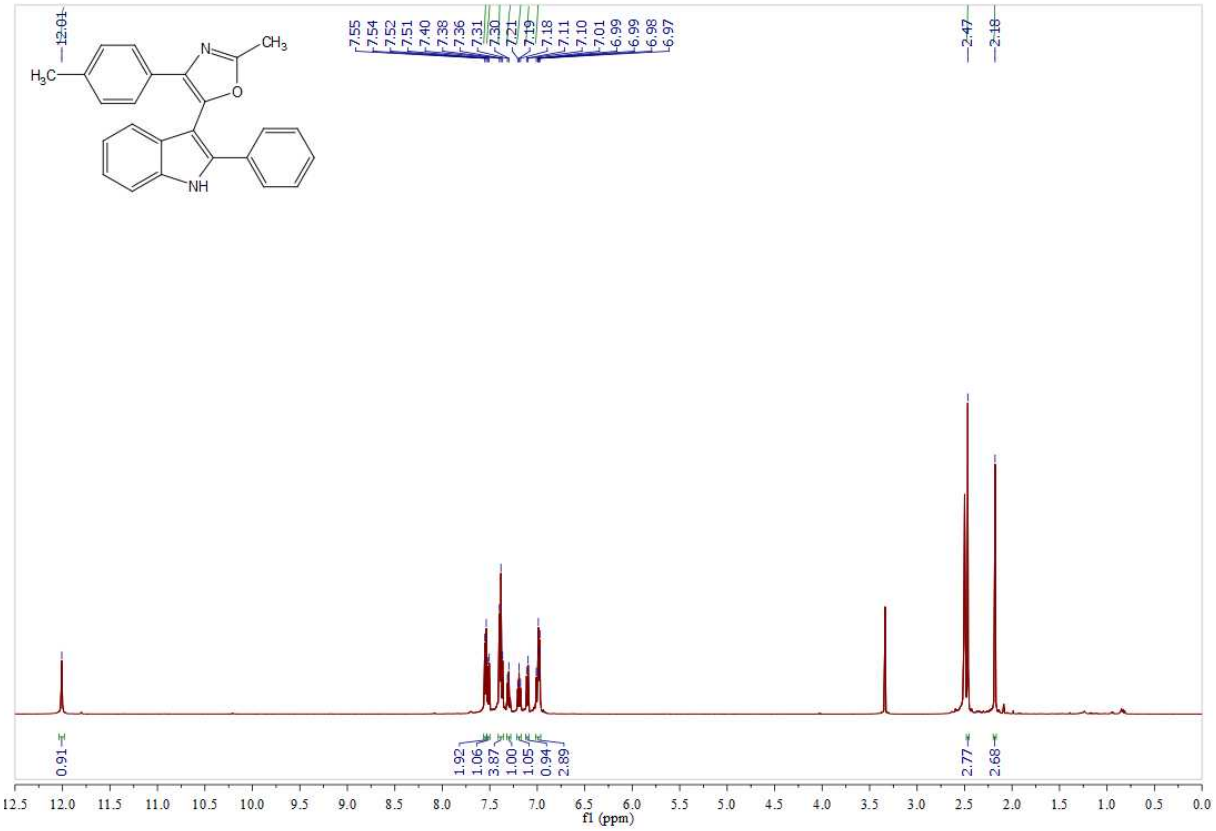


^{13}C NMR and 135-DEPT Spectra of **4e** in DMSO-d^{6} at 296 K (δ in ppm).

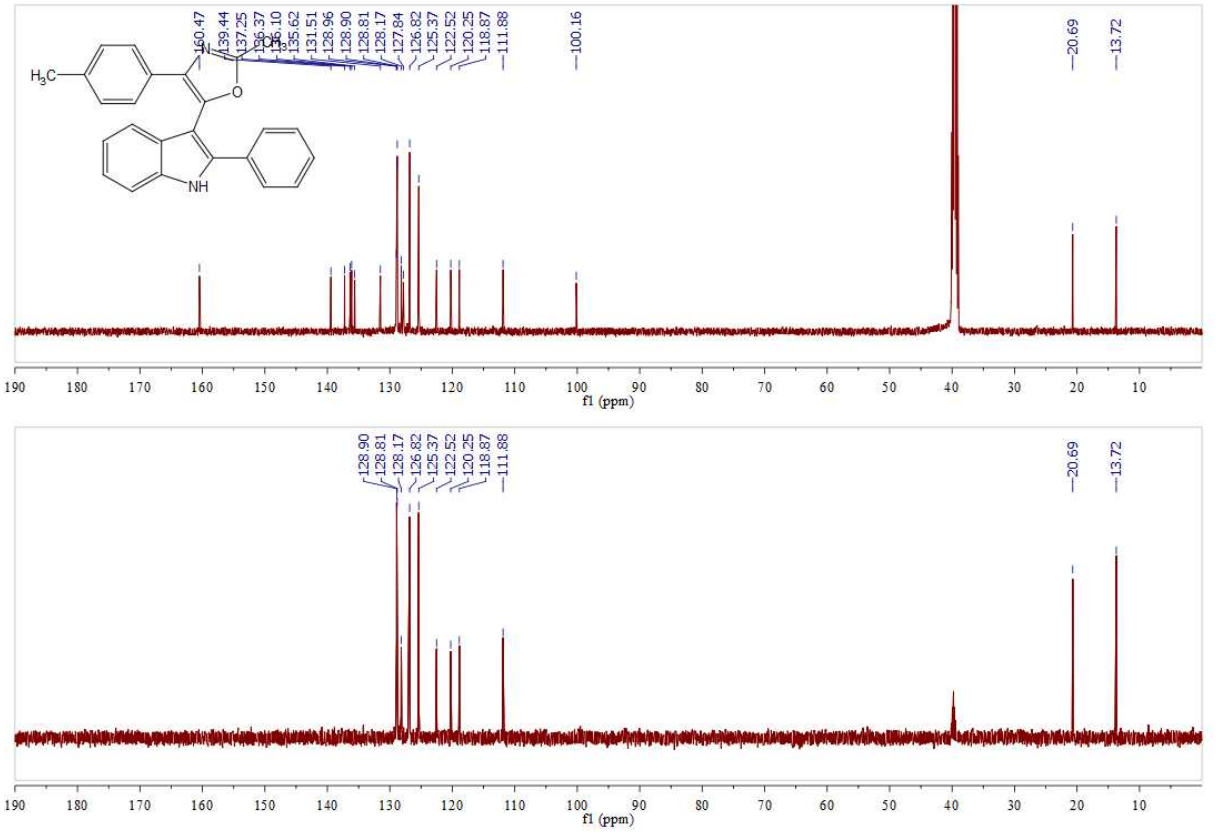


Normalized UV/Vis and fluorescence spectra of **4e** (recorded in EtOH at 298 K).

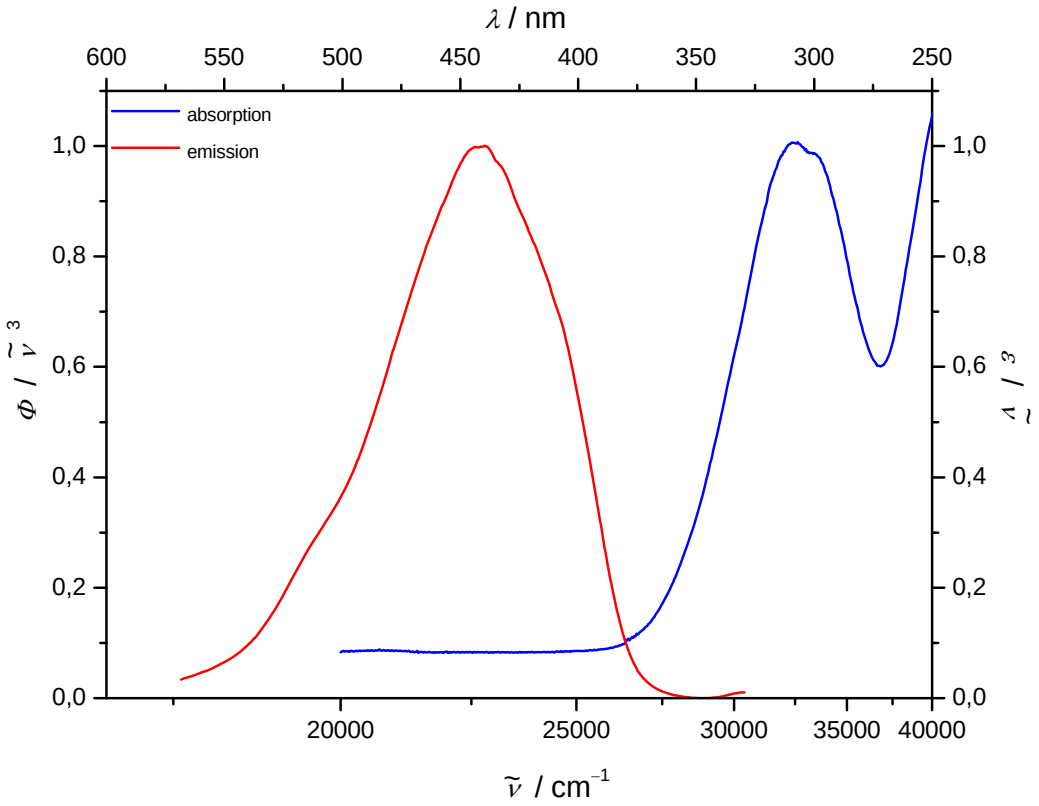
2-Methyl-5-(2-phenyl-1*H*-indol-3-yl)-4-*p*-tolyloxazole (4f)



^{1}H NMR of **4f** in DMSO-d^6 at 296 K (δ in ppm).

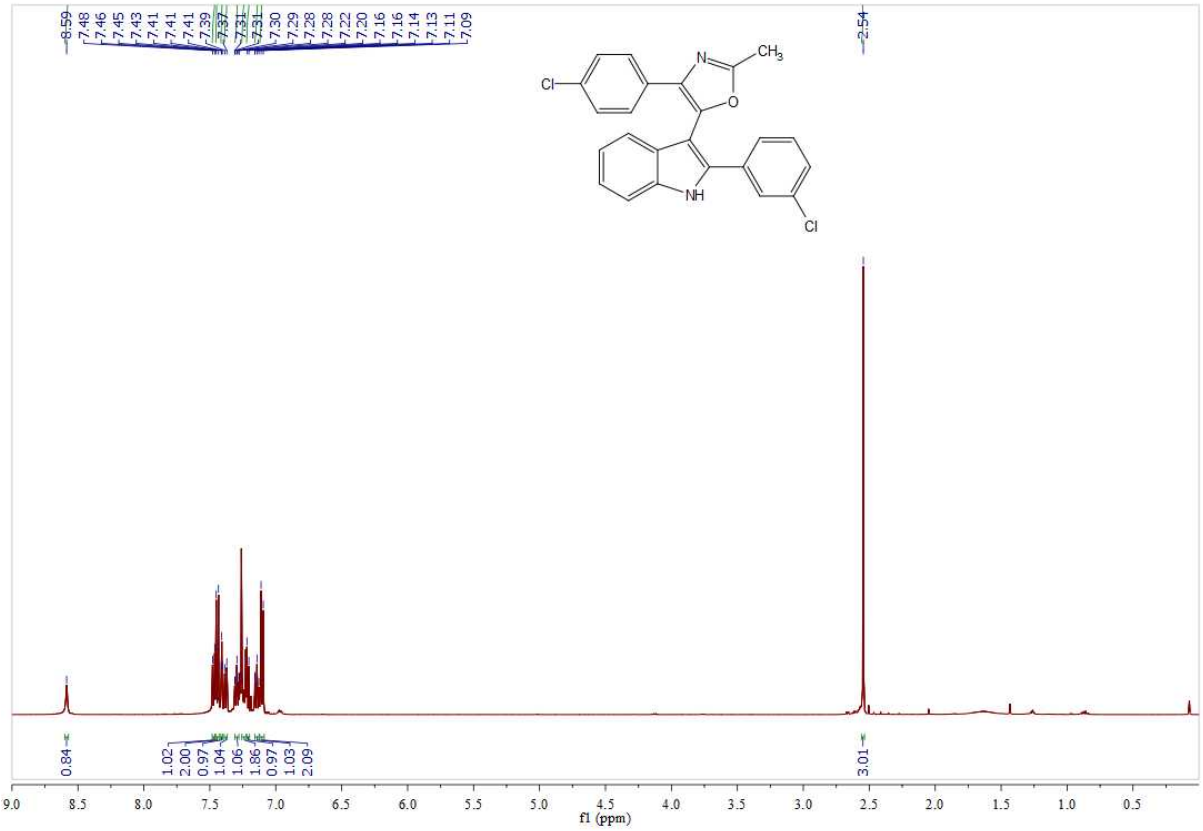


^{13}C NMR and 135-DEPT Spectra of **4f** in DMSO-d^{6} at 296 K (δ in ppm).

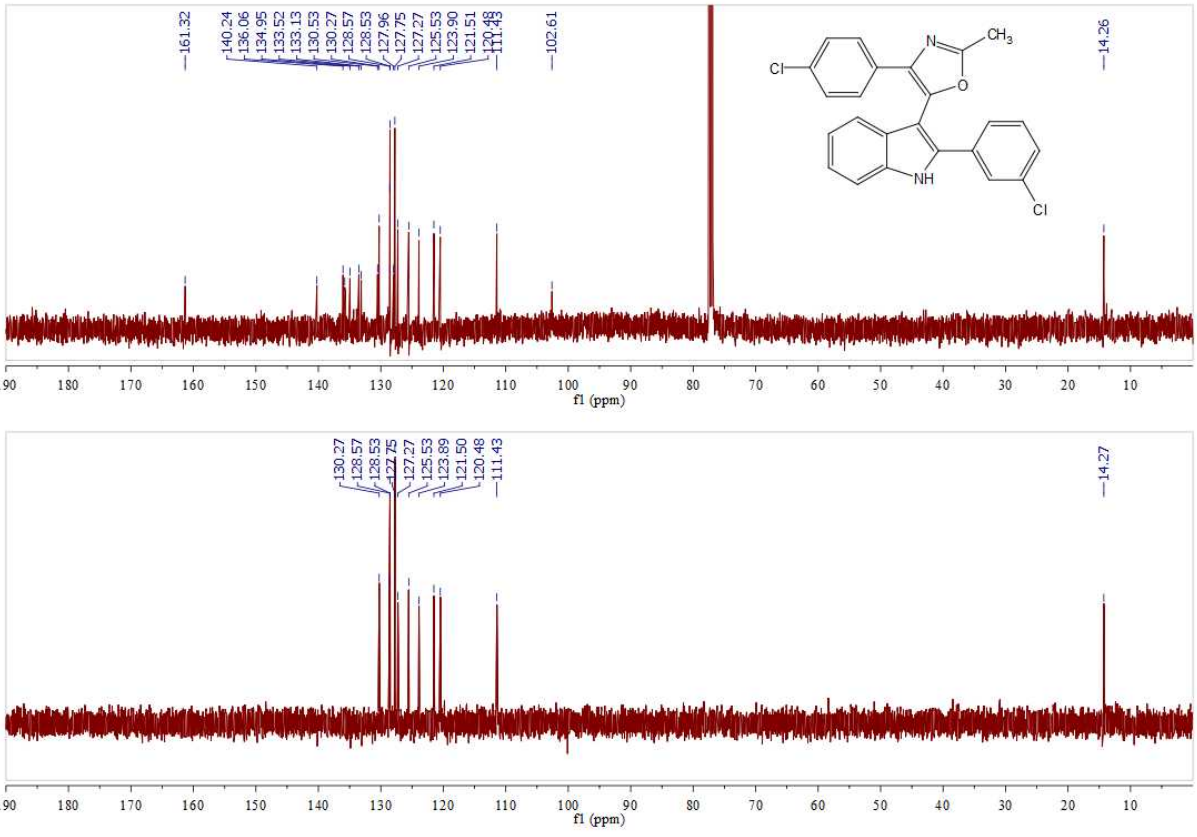


Normalized UV/Vis and fluorescence spectra of **4f** (recorded in EtOH at 298 K).

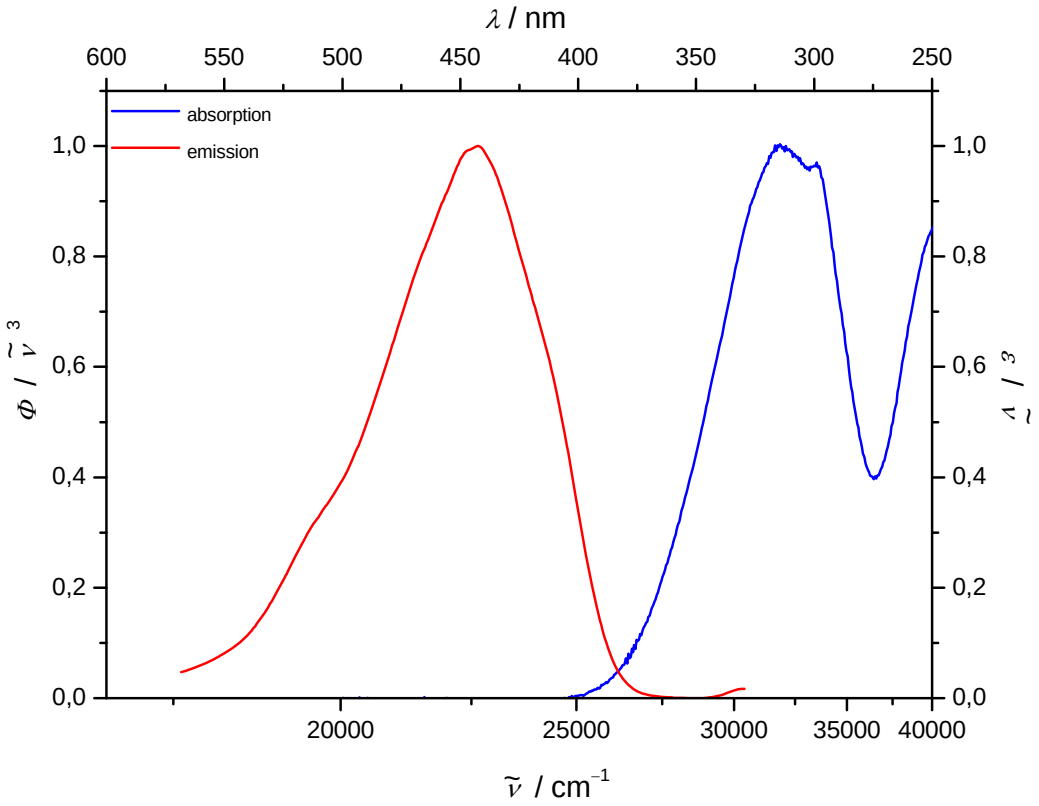
4-(4-Chlorophenyl)-5-(2-(3-chlorophenyl)-1*H*-indol-3-yl)-2-methyloxazole (4g)



^{1}H NMR of **4g** in $CDCl_3$ at 296 K (δ in ppm).

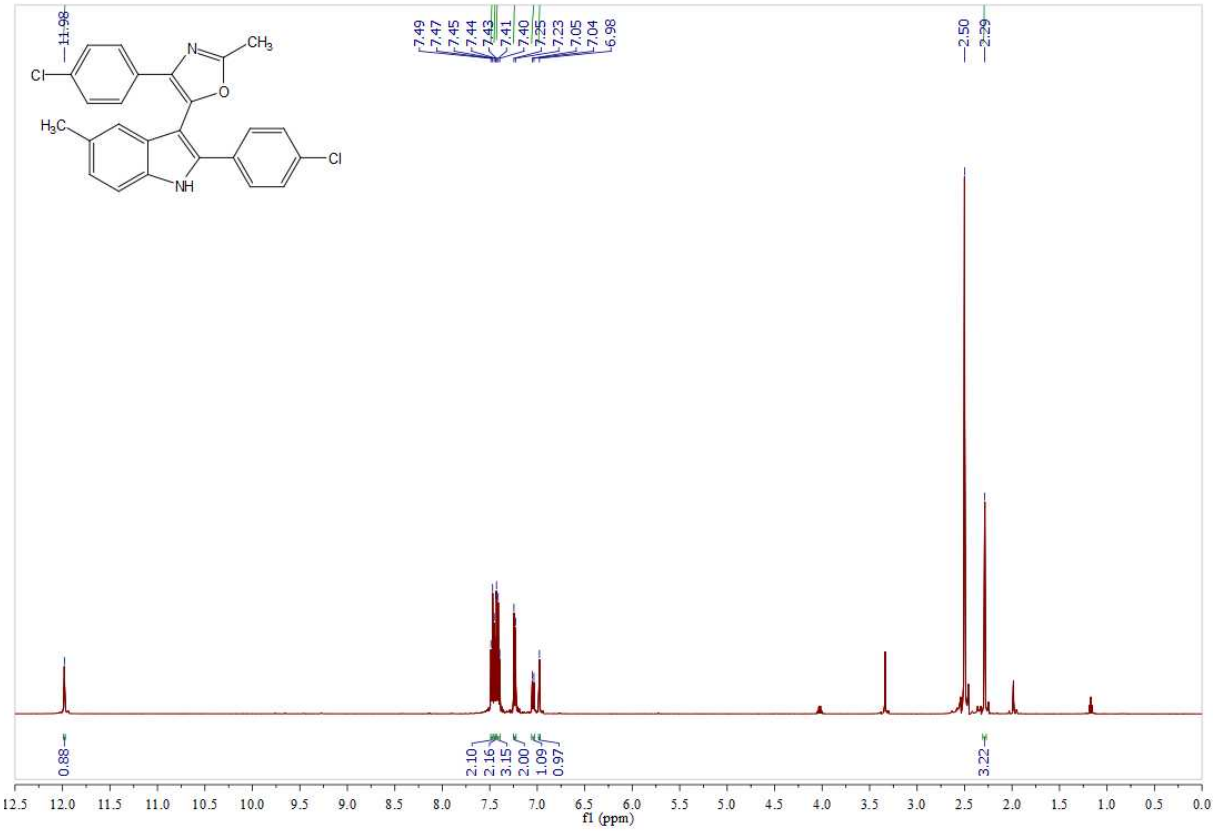


^{13}C NMR and 135-DEPT Spectra of **4g** in $CDCl_3$ at 296 K (δ in ppm).

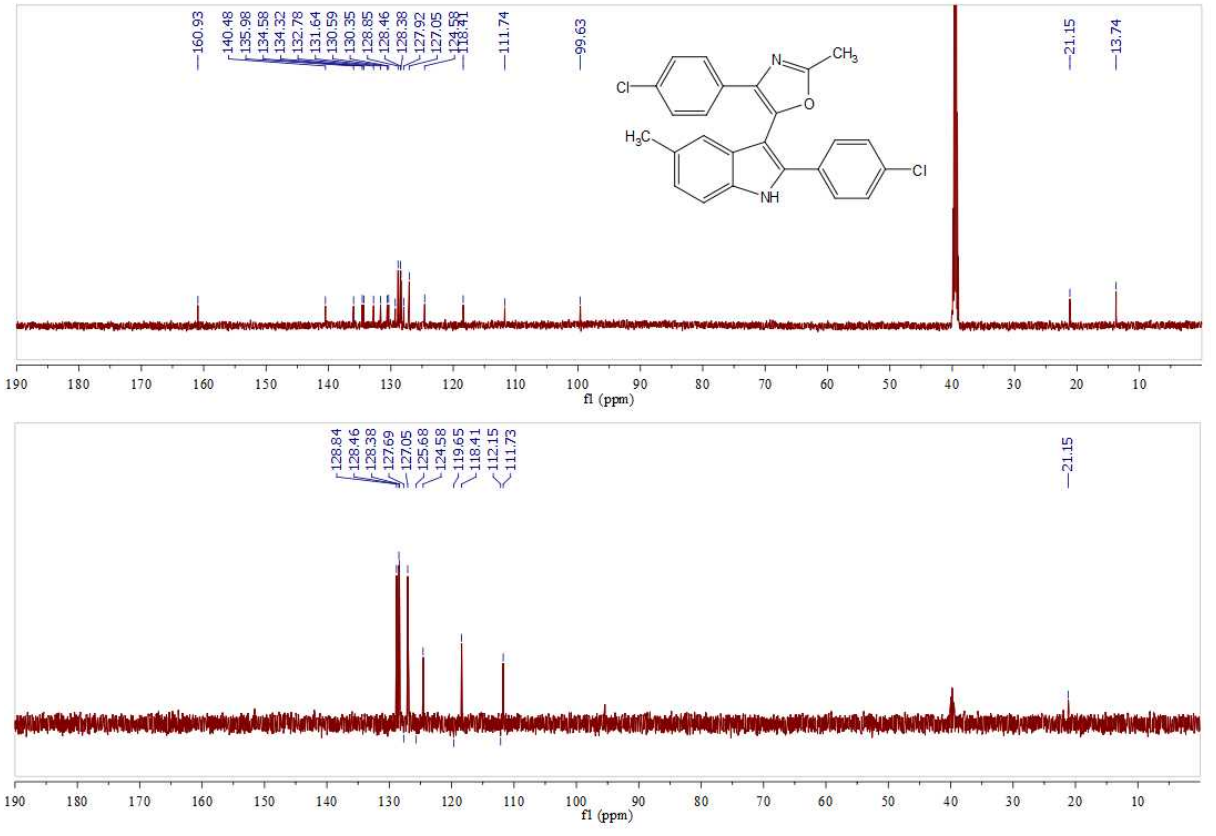


Normalized UV/Vis and fluorescence spectra of **4g** (recorded in EtOH at 298 K).

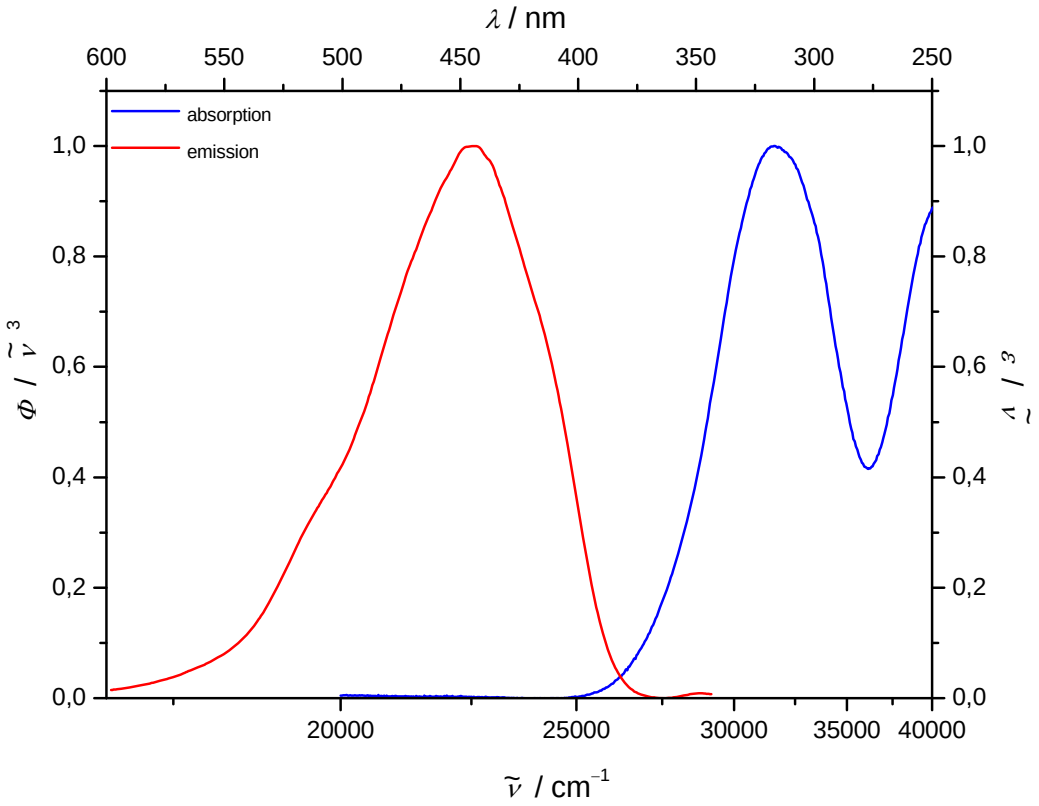
4-(4-Chlorophenyl)-5-(2-(4-chlorophenyl)-5-methyl-1*H*-indol-3-yl)-2-methyloxazole (4h)



^{1}H NMR of **4h** in DMSO-d^{6} at 296 K (δ in ppm).

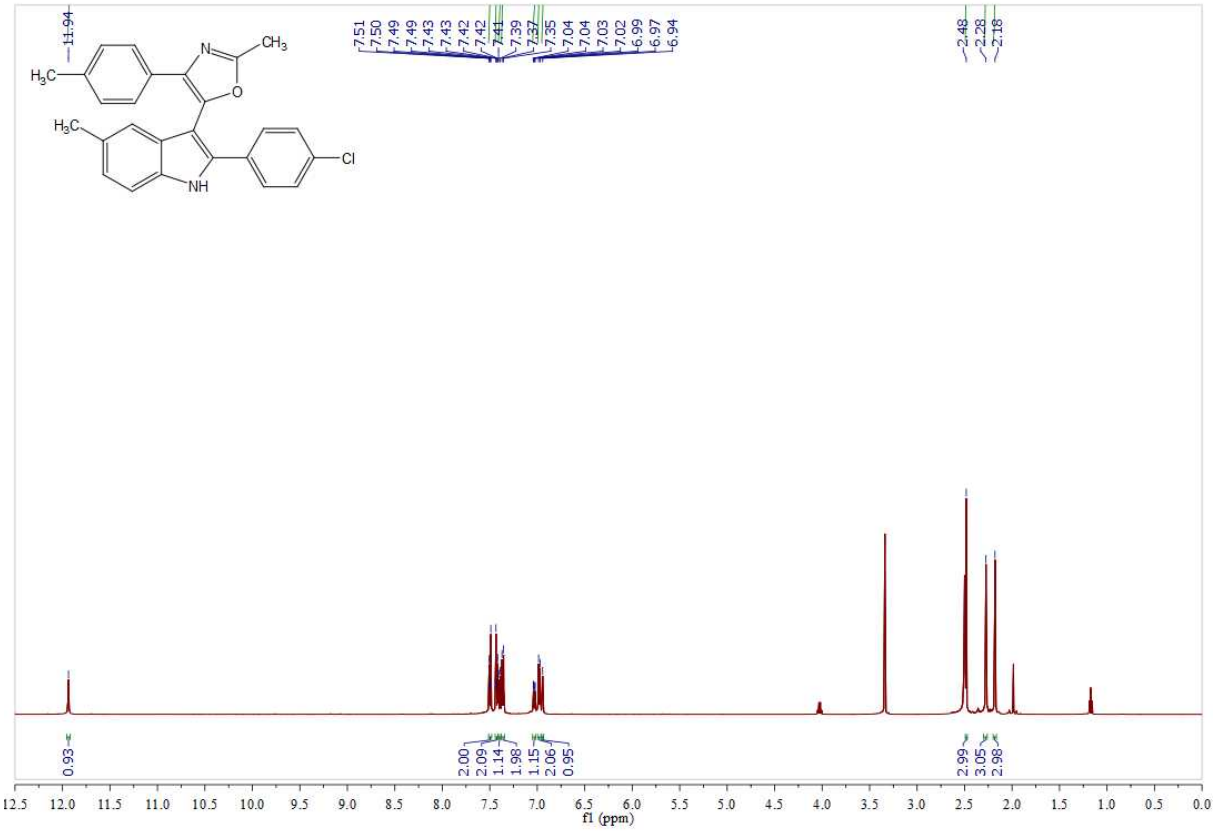


^{13}C NMR and 135-DEPT Spectra of **4h** in DMSO-d^{6} at 296 K (δ in ppm).

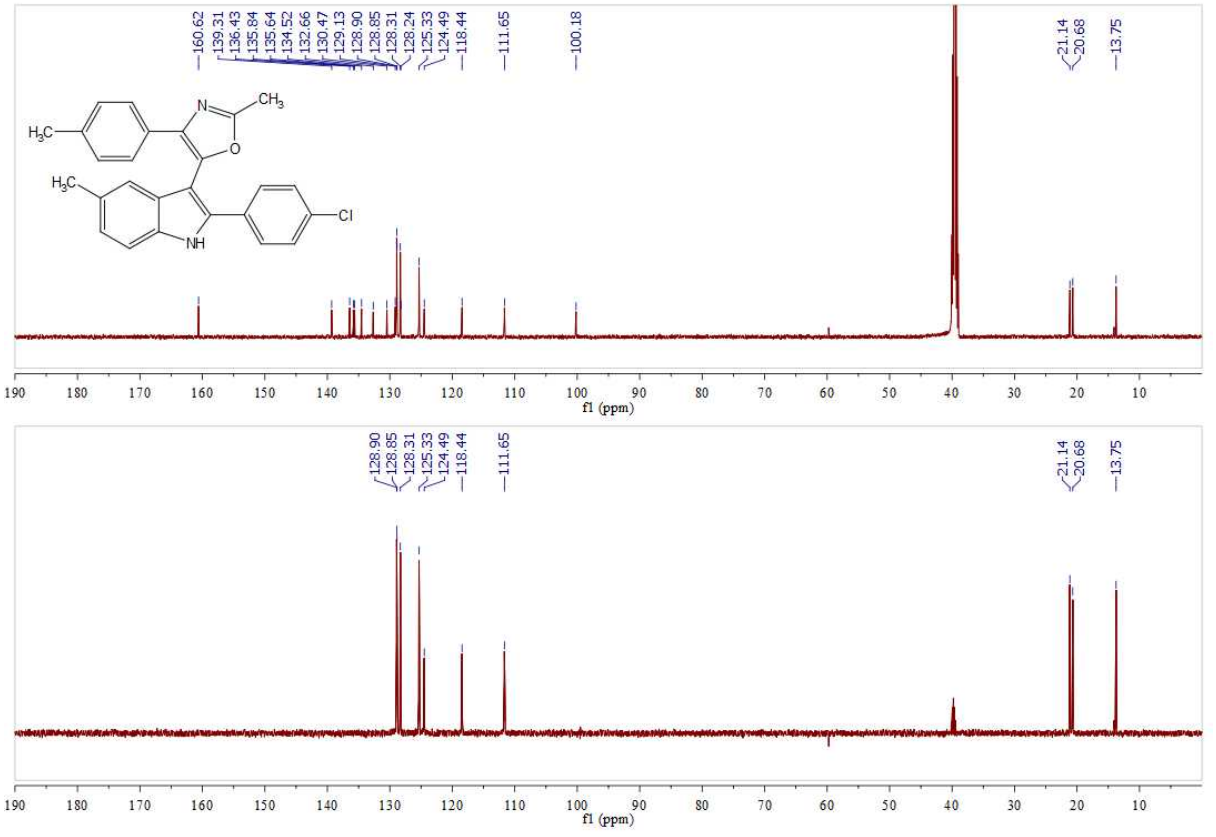


Normalized UV/Vis and fluorescence spectra of **4h** (recorded in EtOH at 298 K).

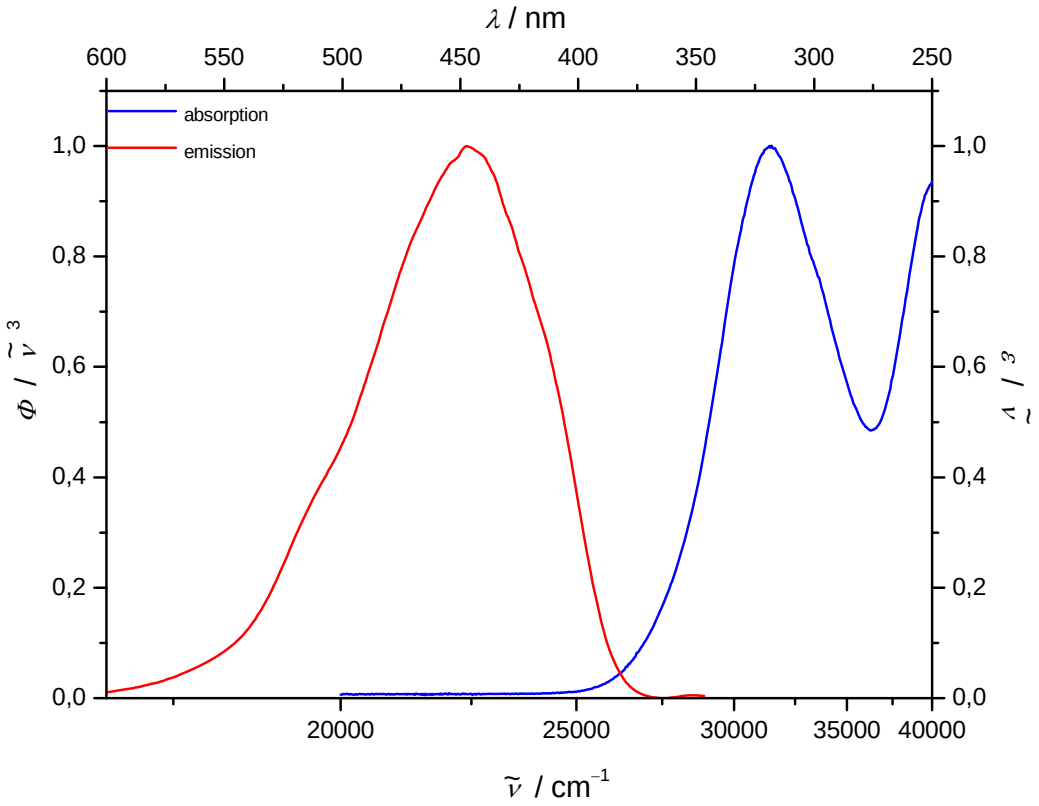
5-(2-(4-Chlorophenyl)-5-methyl-1*H*-indol-3-yl)-2-methyl-4-*p*-tolyloxazole (4i)



^{1}H NMR of **4i** in DMSO-d^6 at 296 K (δ in ppm).

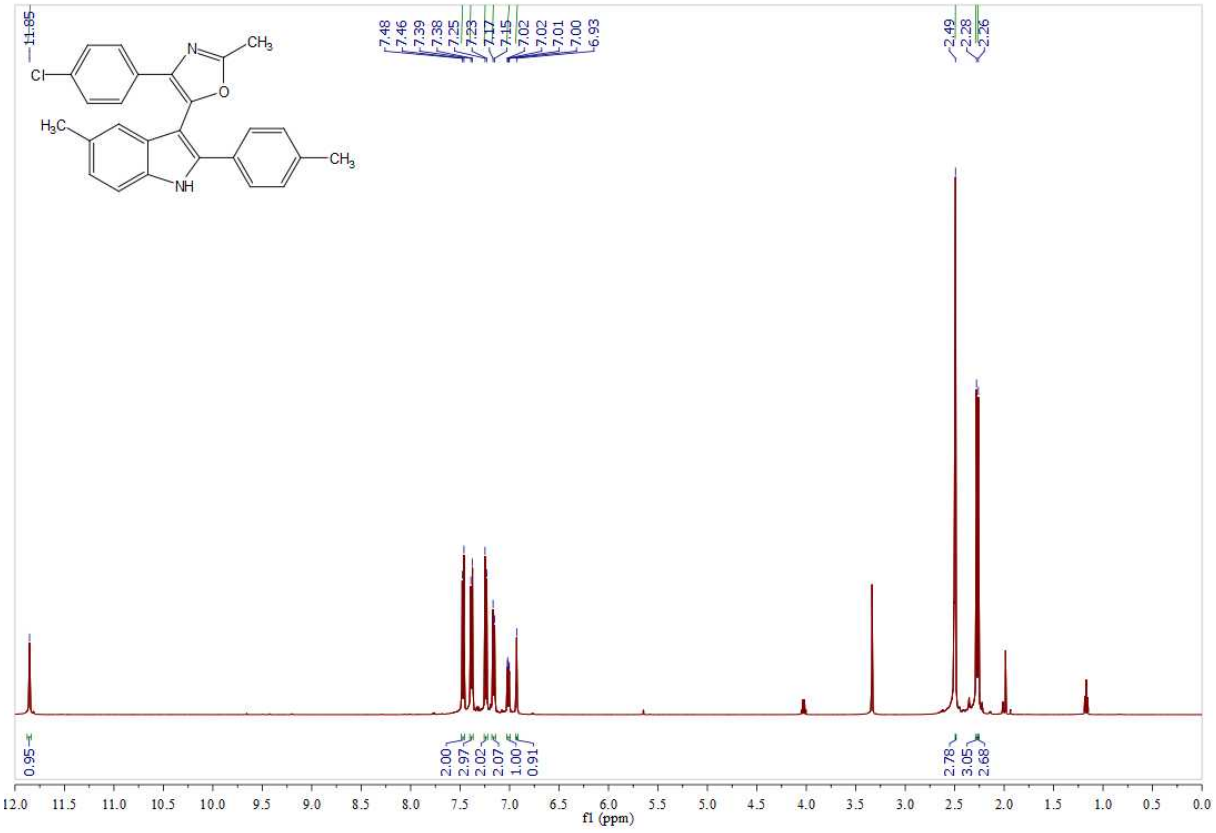


^{13}C NMR and 135-DEPT Spectra of **4i** in DMSO-d^{6} at 296 K (δ in ppm).

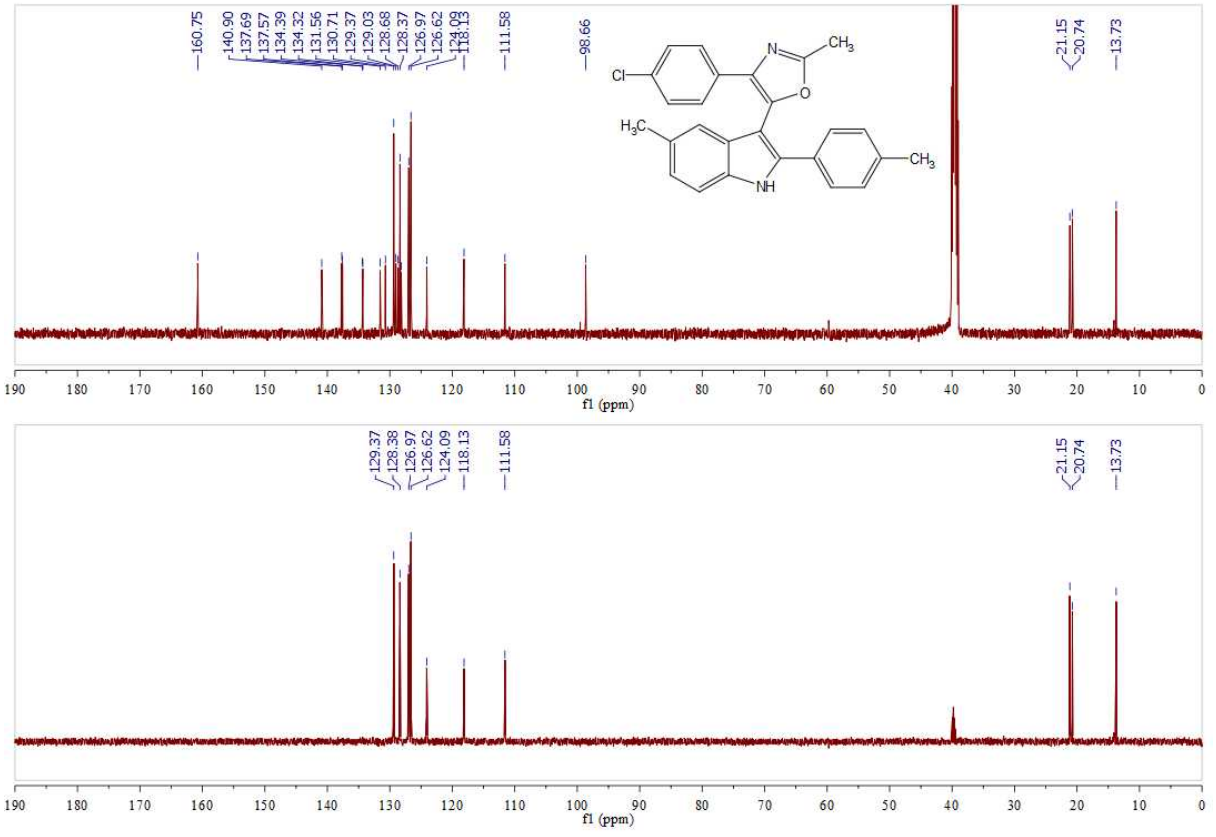


Normalized UV/Vis and fluorescence spectra of **4i** (recorded in EtOH at 298 K).

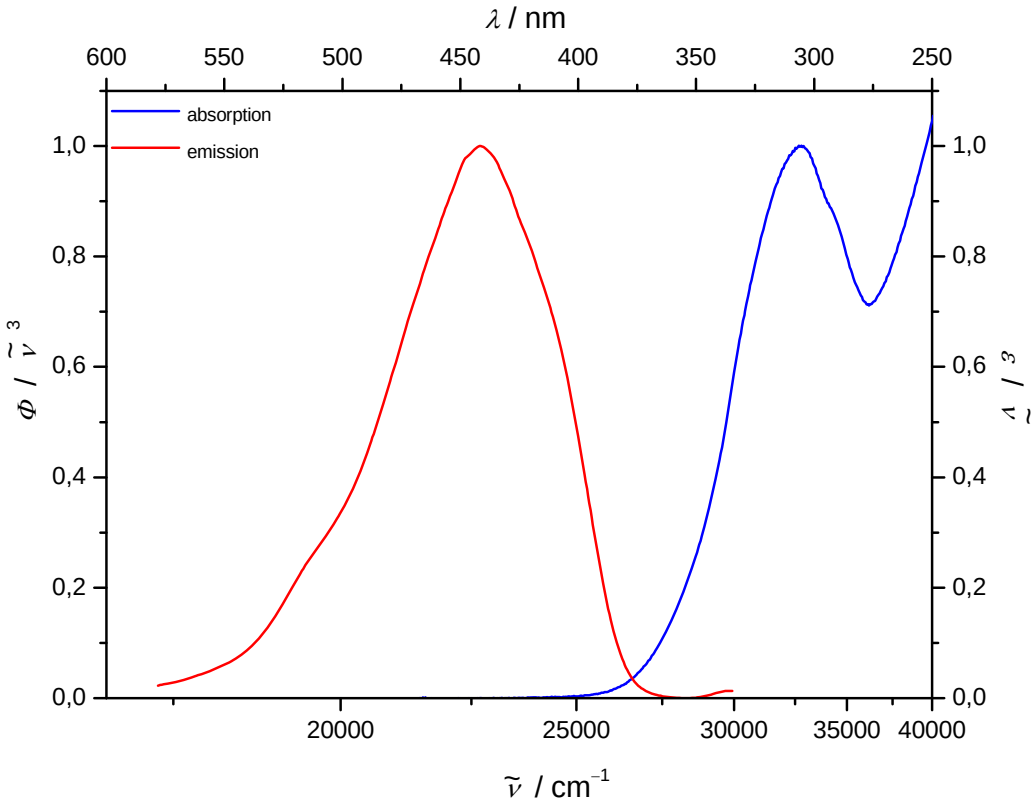
4-(4-Chlorophenyl)-2-methyl-5-(5-methyl-2-*p*-tolyl-1*H*-indol-3-yl)oxazole (4j)



^{1}H NMR of **4j** in DMSO-d^6 at 296 K (δ in ppm).

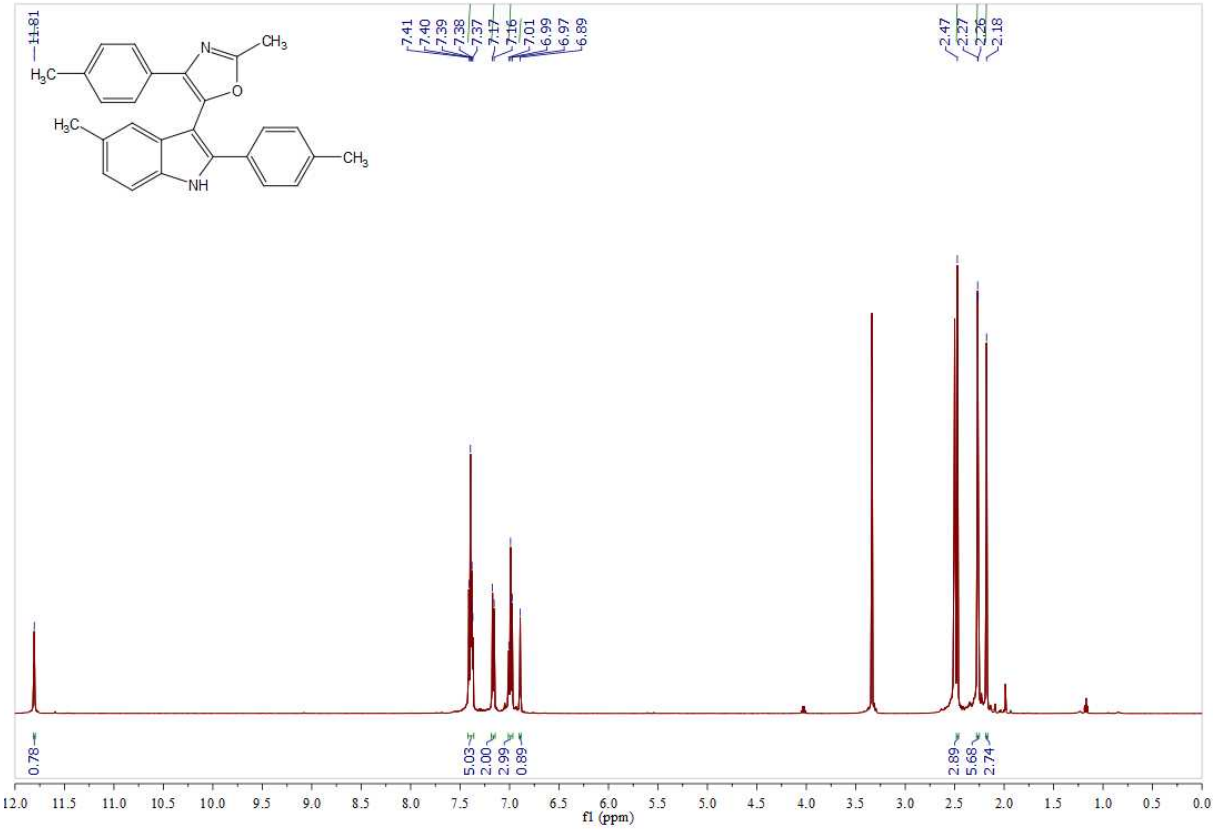


^{13}C NMR and 135-DEPT Spectra of **4j** in DMSO-d^{6} at 296 K (δ in ppm).

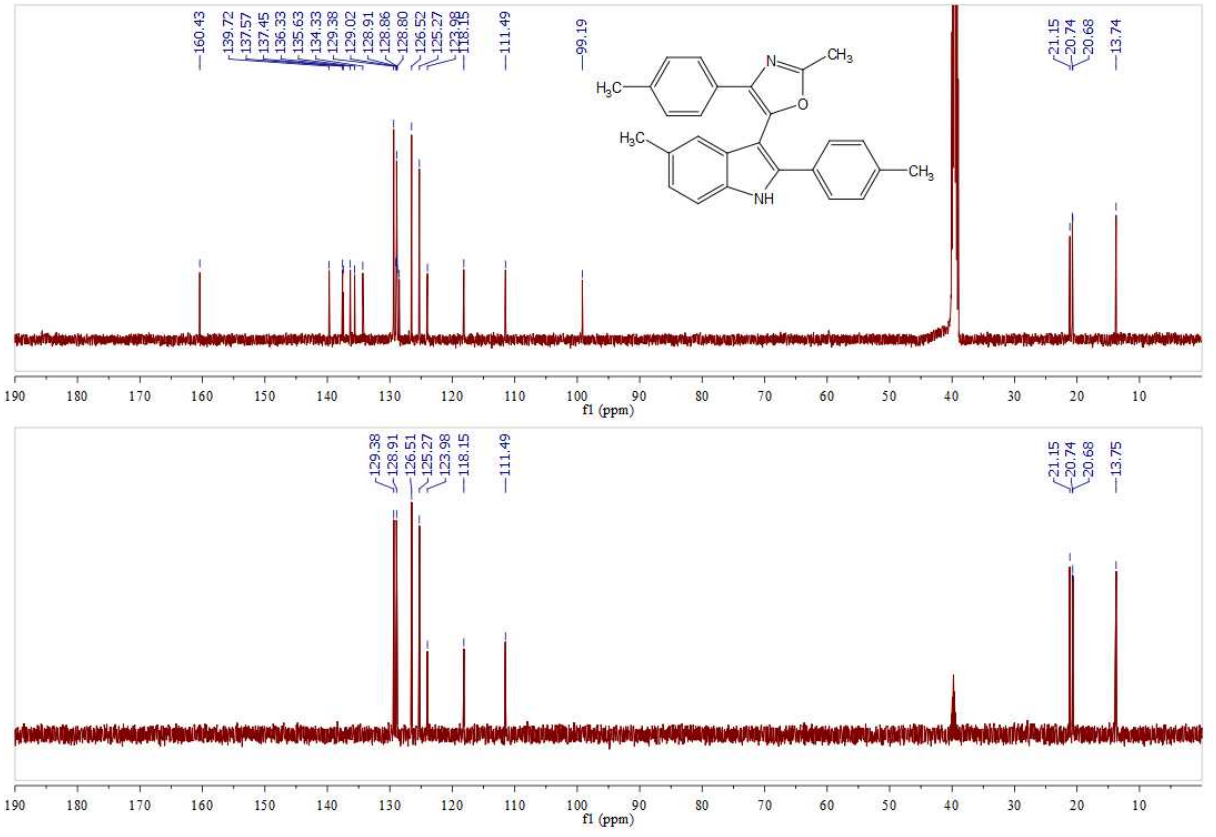


Normalized UV/Vis and fluorescence spectra of **4j** (recorded in EtOH at 298 K).

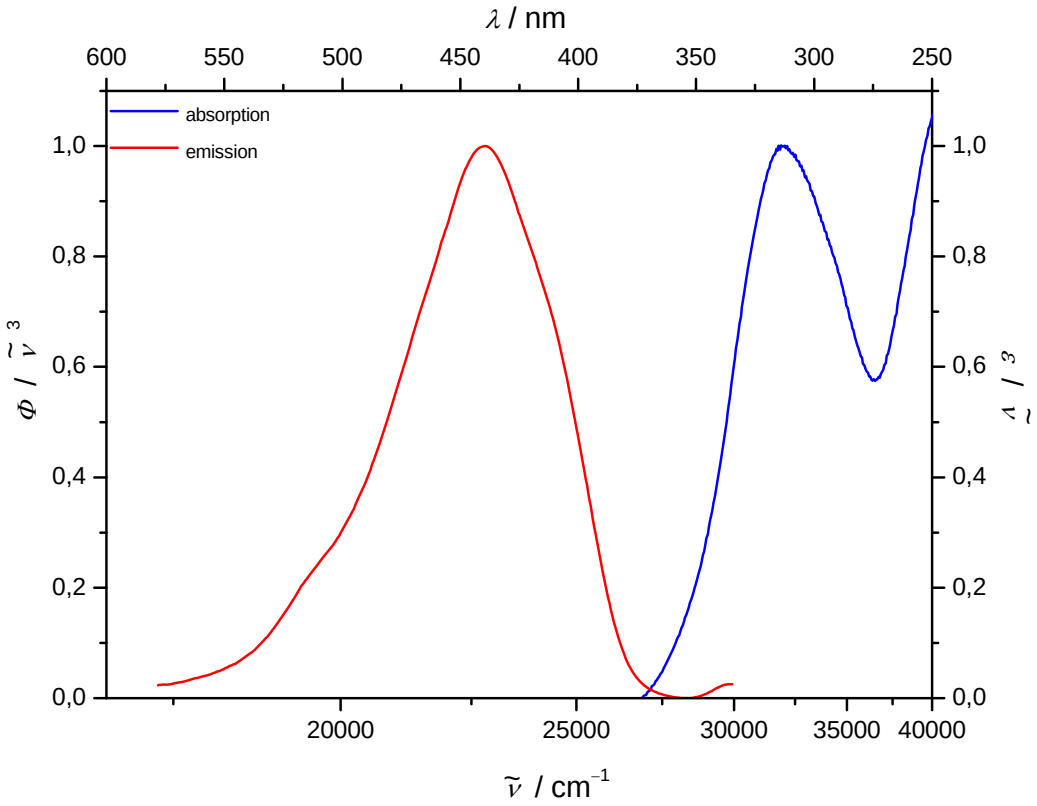
2-Methyl-5-(5-methyl-2-*p*-tolyl-1*H*-indol-3-yl)-4-*p*-tolyloxazole (4k)



^{1}H NMR of **4k** in DMSO-d^6 at 296 K (δ in ppm).

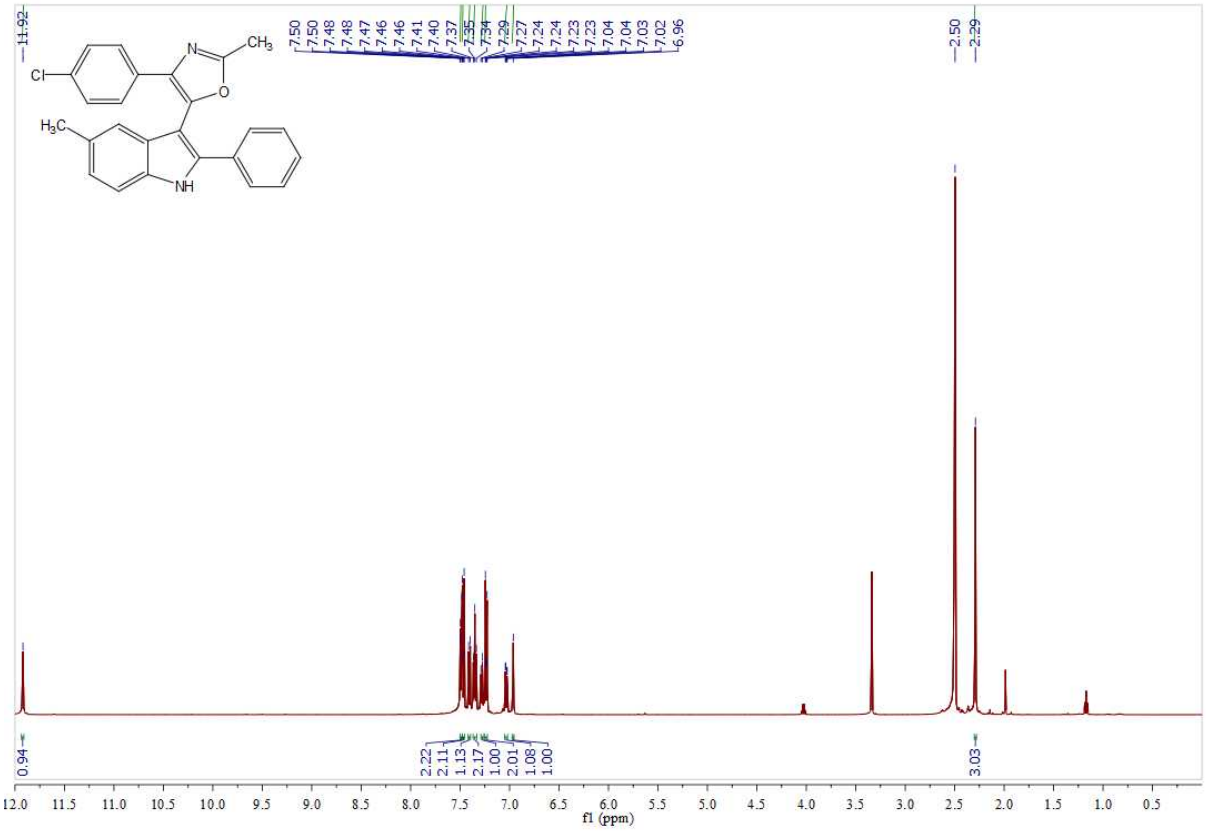


^{13}C NMR and 135-DEPT Spectra of **4k** in DMSO-d^{6} at 296 K (δ in ppm).

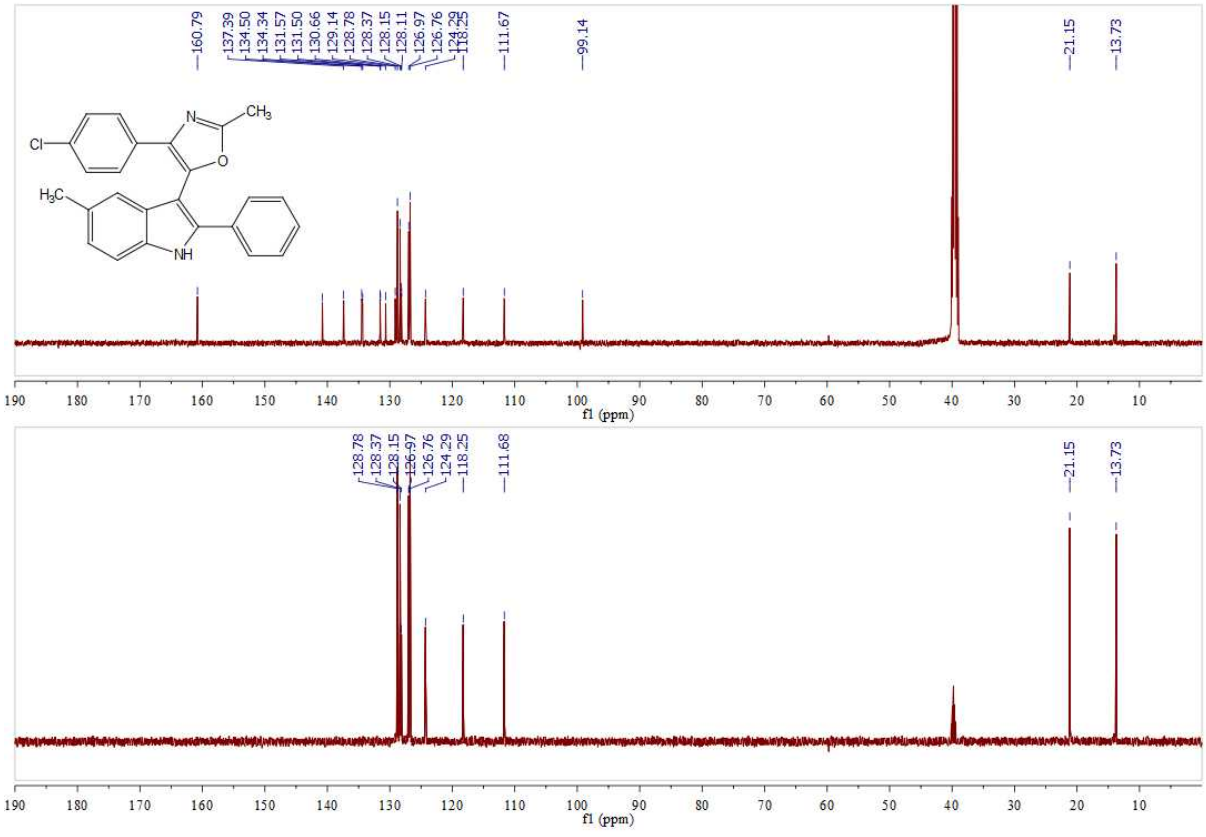


Normalized UV/Vis and fluorescence spectra of **4k** (recorded in EtOH at 298 K).

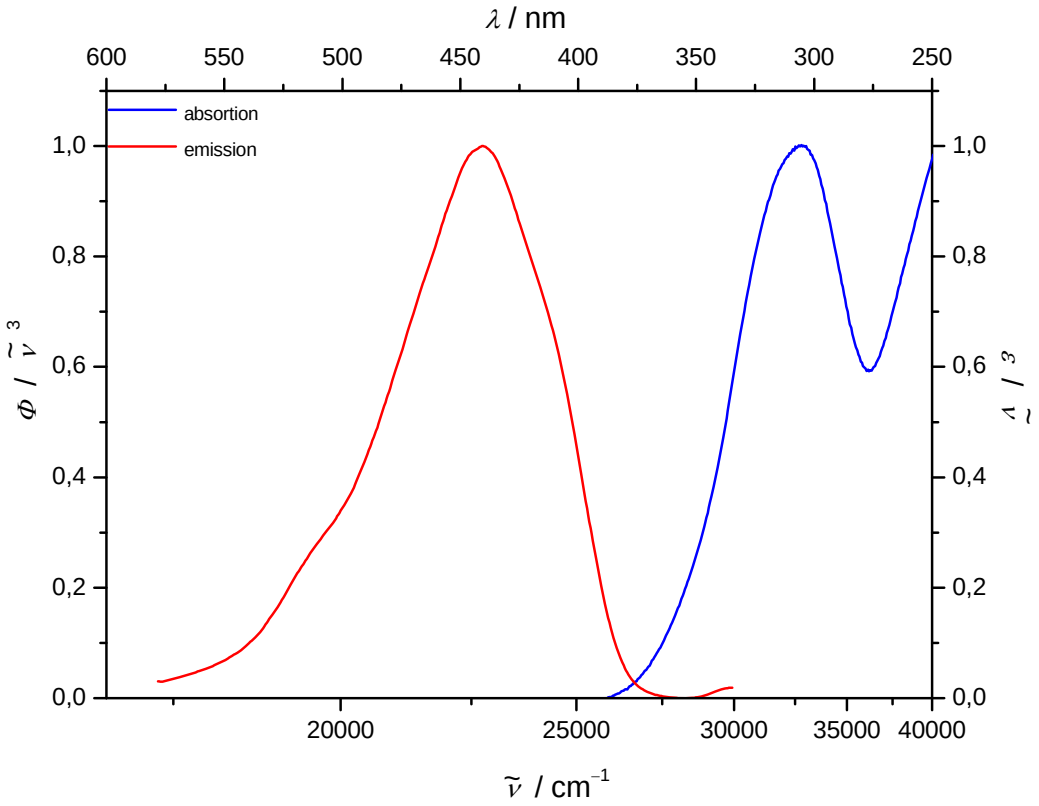
4-(4-Chlorophenyl)-2-methyl-5-(5-methyl-2-phenyl-1*H*-indol-3-yl)oxazole (4l)



^{1}H NMR of **4l** in DMSO-d^6 at 296 K (δ in ppm).

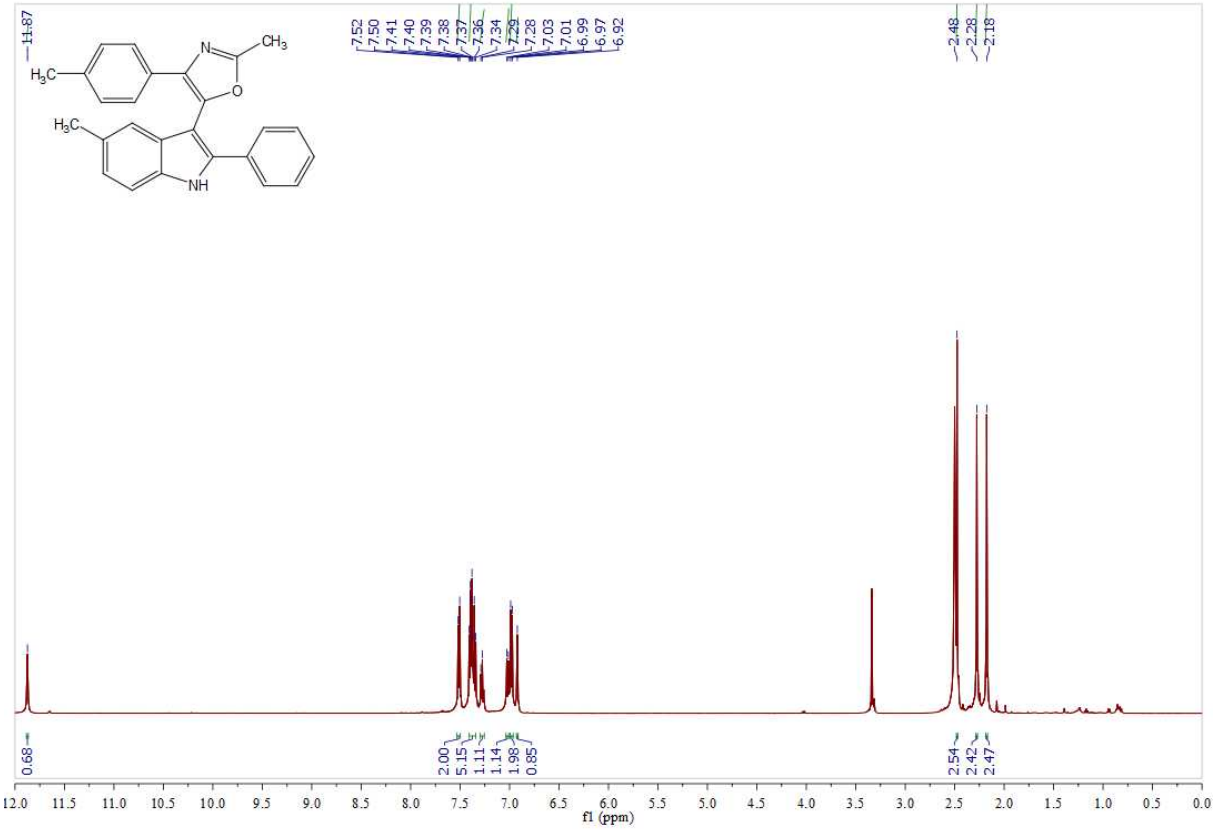


^{13}C NMR and 135-DEPT Spectra of **4l** in DMSO-d^{6} at 296 K (δ in ppm).

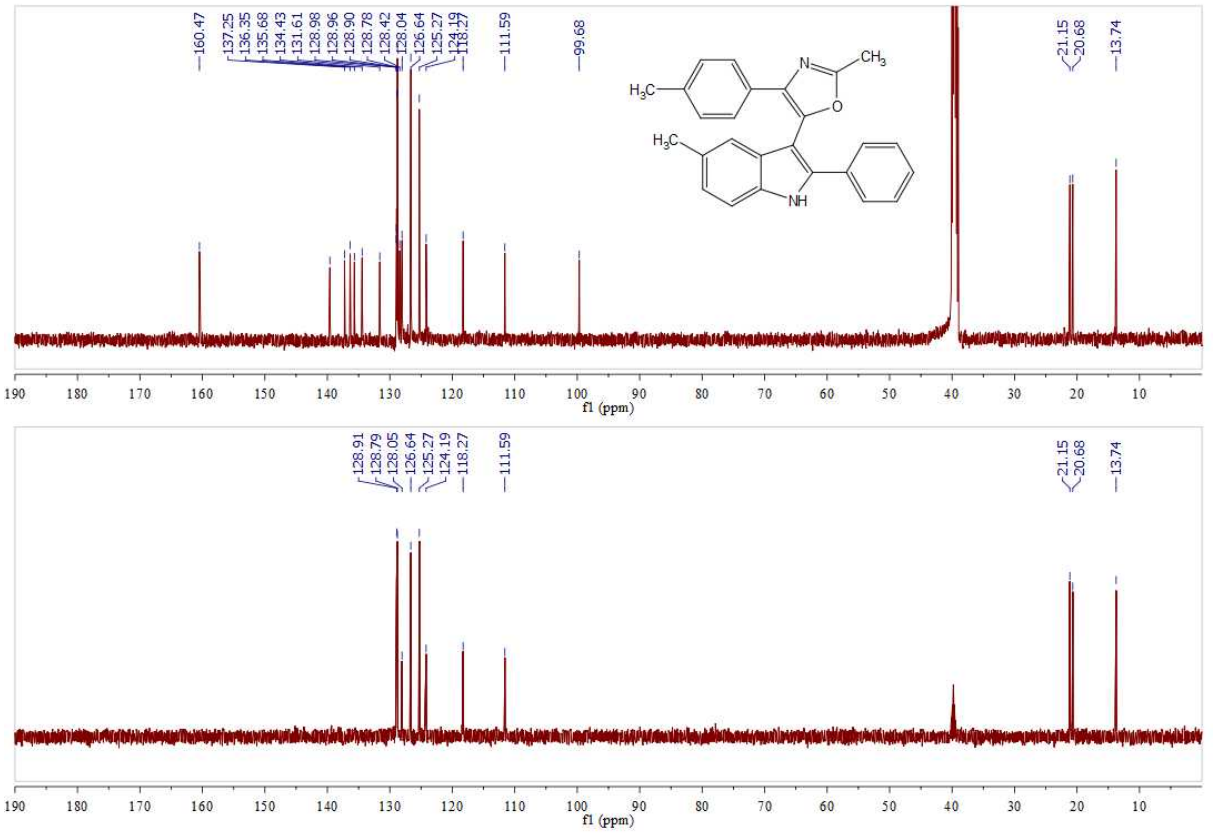


Normalized UV/Vis and fluorescence spectra of **4l** (recorded in EtOH at 298 K).

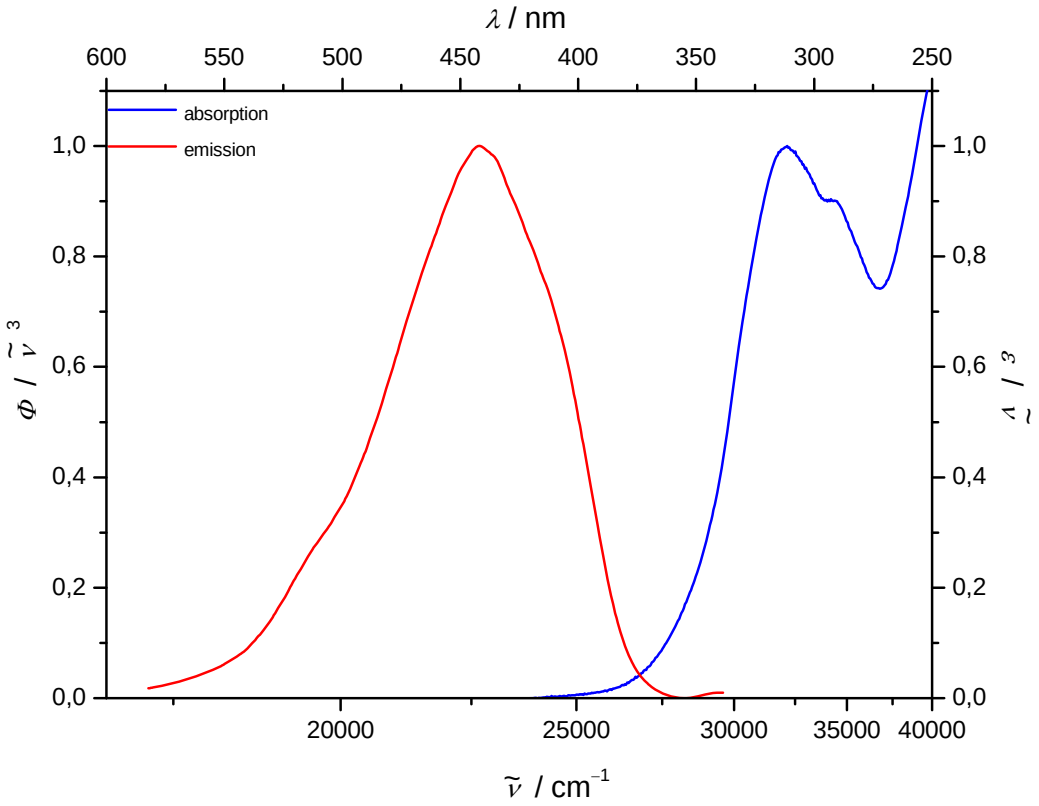
2-Methyl-5-(5-methyl-2-phenyl-1*H*-indol-3-yl)-4-*p*-tolyloxazole (4m)



^{1}H NMR of **4m** in DMSO-d^6 at 296 K (δ in ppm).

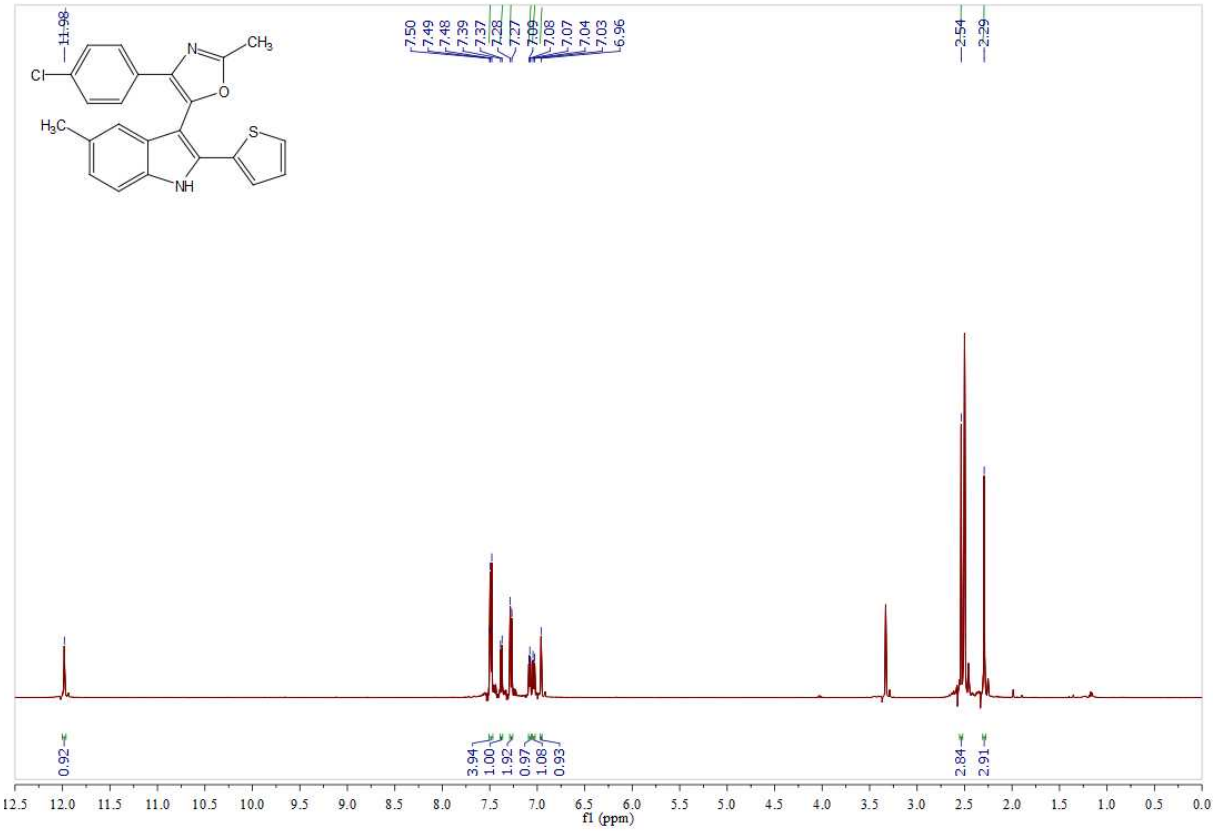


^{13}C NMR and 135-DEPT Spectra of **4m** in DMSO-d^{6} at 296 K (δ in ppm).

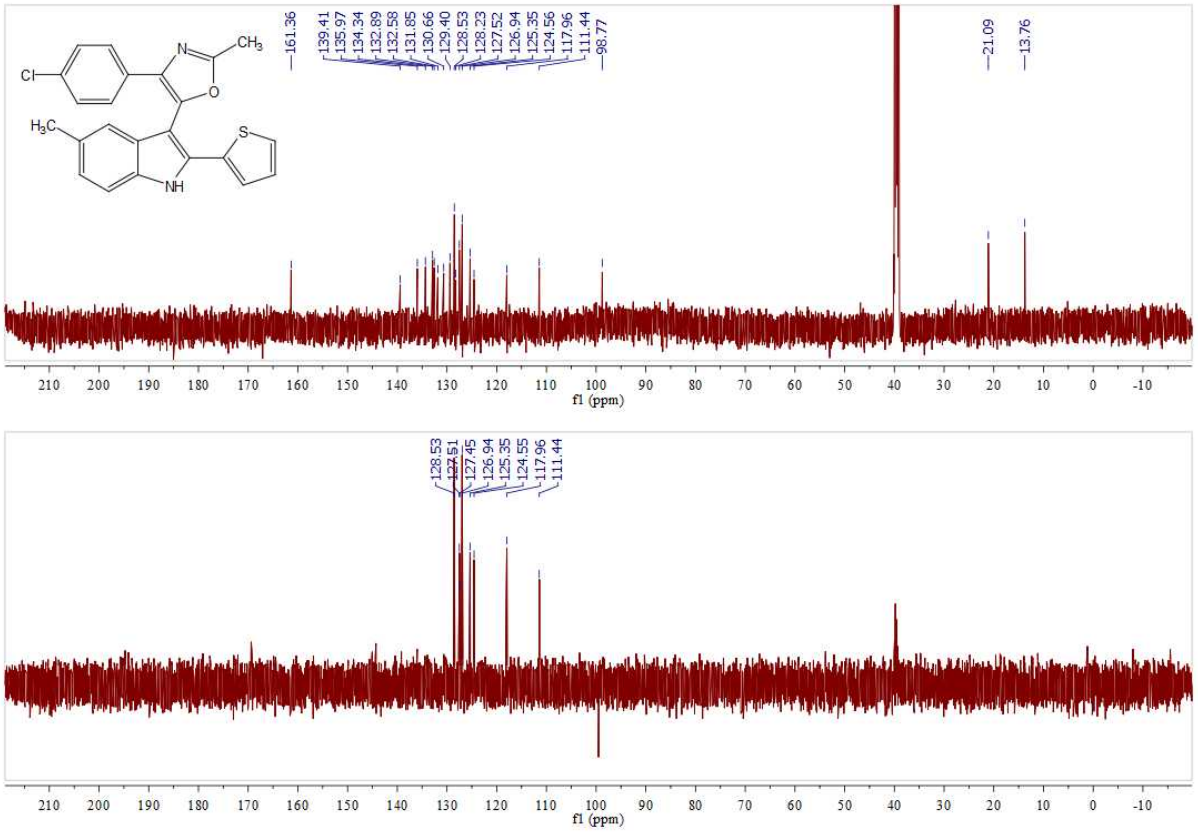


Normalized UV/Vis and fluorescence spectra of **4m** (recorded in EtOH at 298 K).

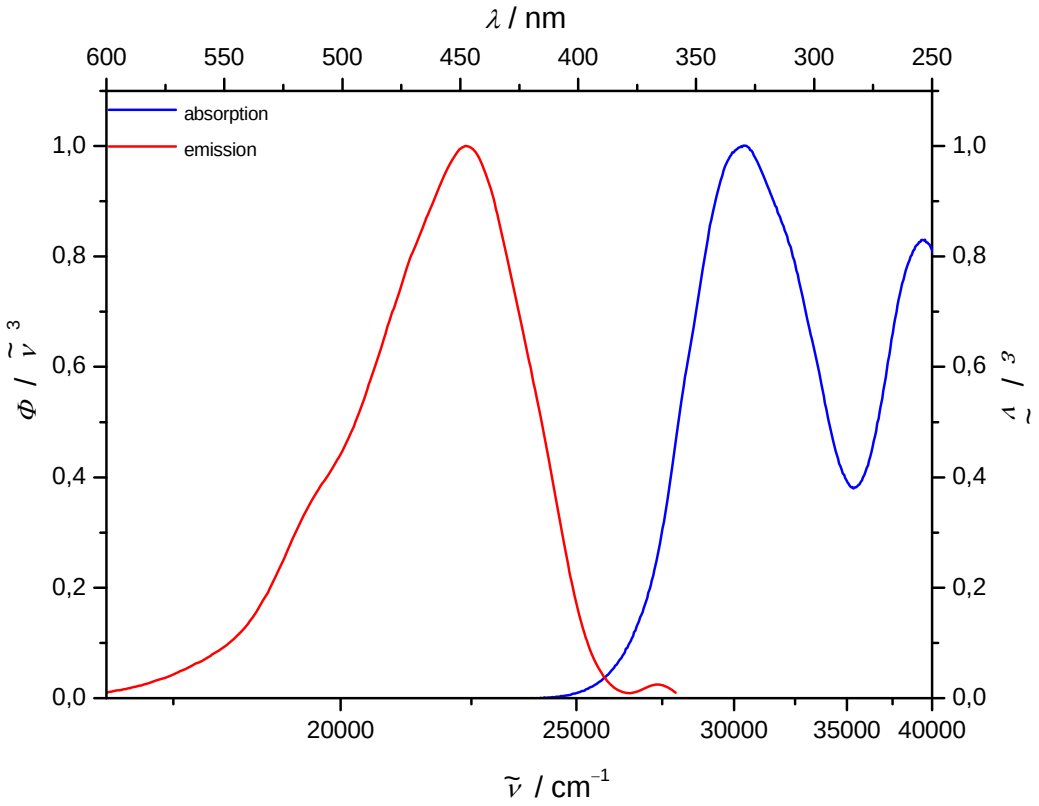
4-(4-Chlorophenyl)-2-methyl-5-(5-methyl-2-(thiophen-2-yl)-1*H*-indol-3-yl)oxazole (4n)



^{1}H NMR of **4n** in DMSO-d^6 at 296 K (δ in ppm).

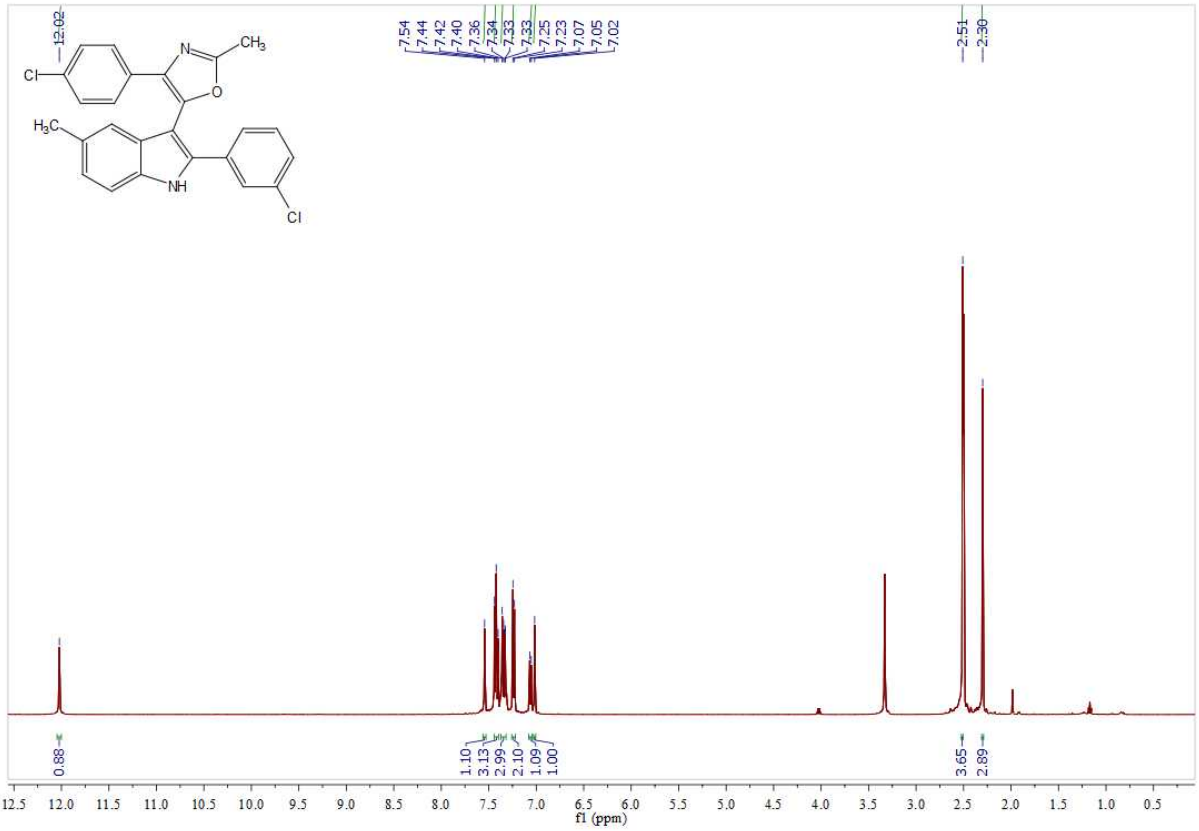


^{13}C NMR and 135-DEPT Spectra of **4n** in DMSO-d^{6} at 296 K (δ in ppm).

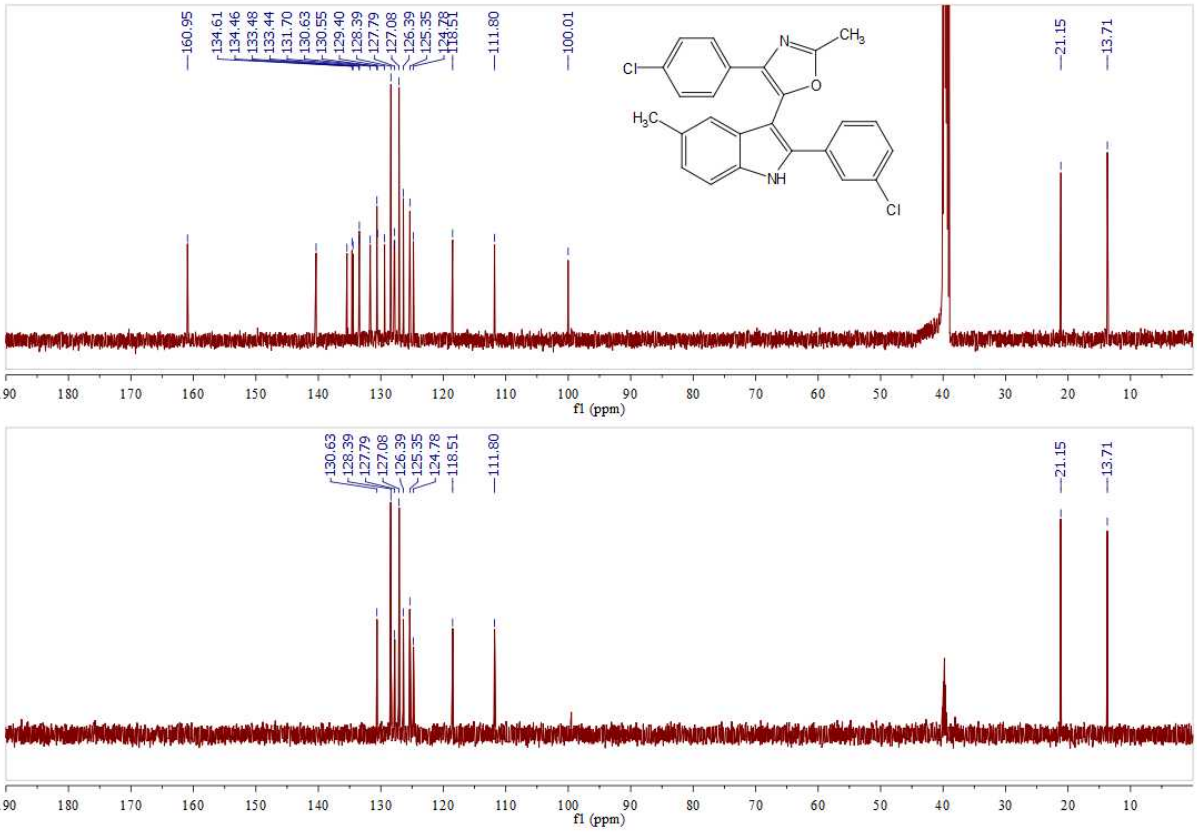


Normalized UV/Vis and fluorescence spectra of **4n** (recorded in EtOH at 298 K).

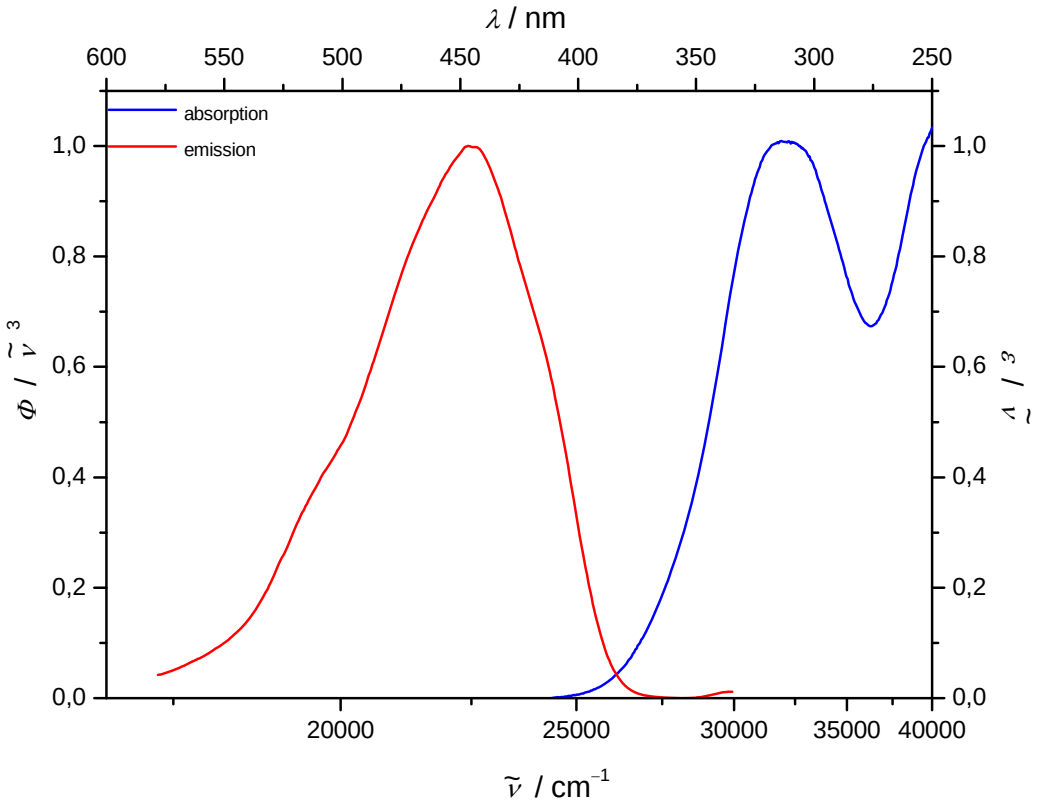
4-(4-Chlorophenyl)-5-(2-(3-chlorophenyl)-5-methyl-1*H*-indol-3-yl)-2-methyloxazole (4o)



^{1}H NMR of **4o** in DMSO-d^6 at 296 K (δ in ppm).

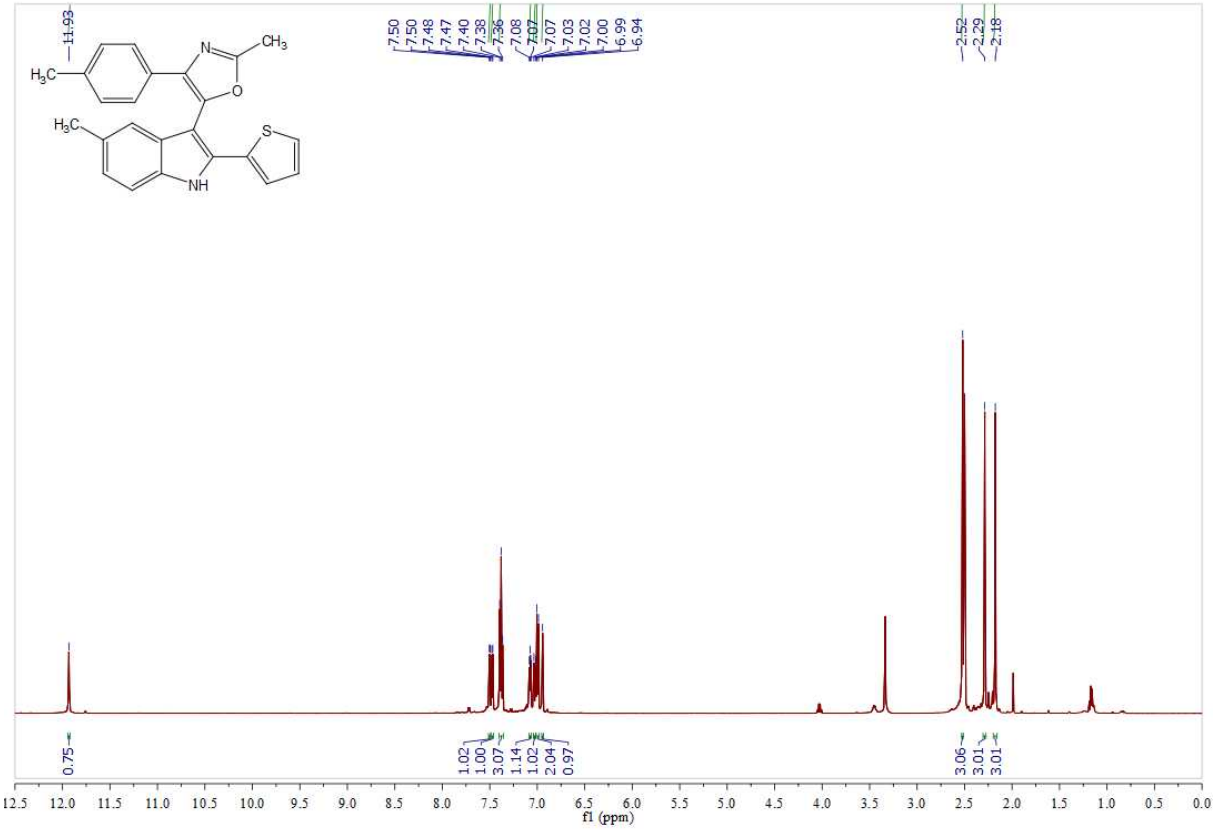


^{13}C NMR and 135-DEPT Spectra of **4o** in DMSO-d^{6} at 296 K (δ in ppm).

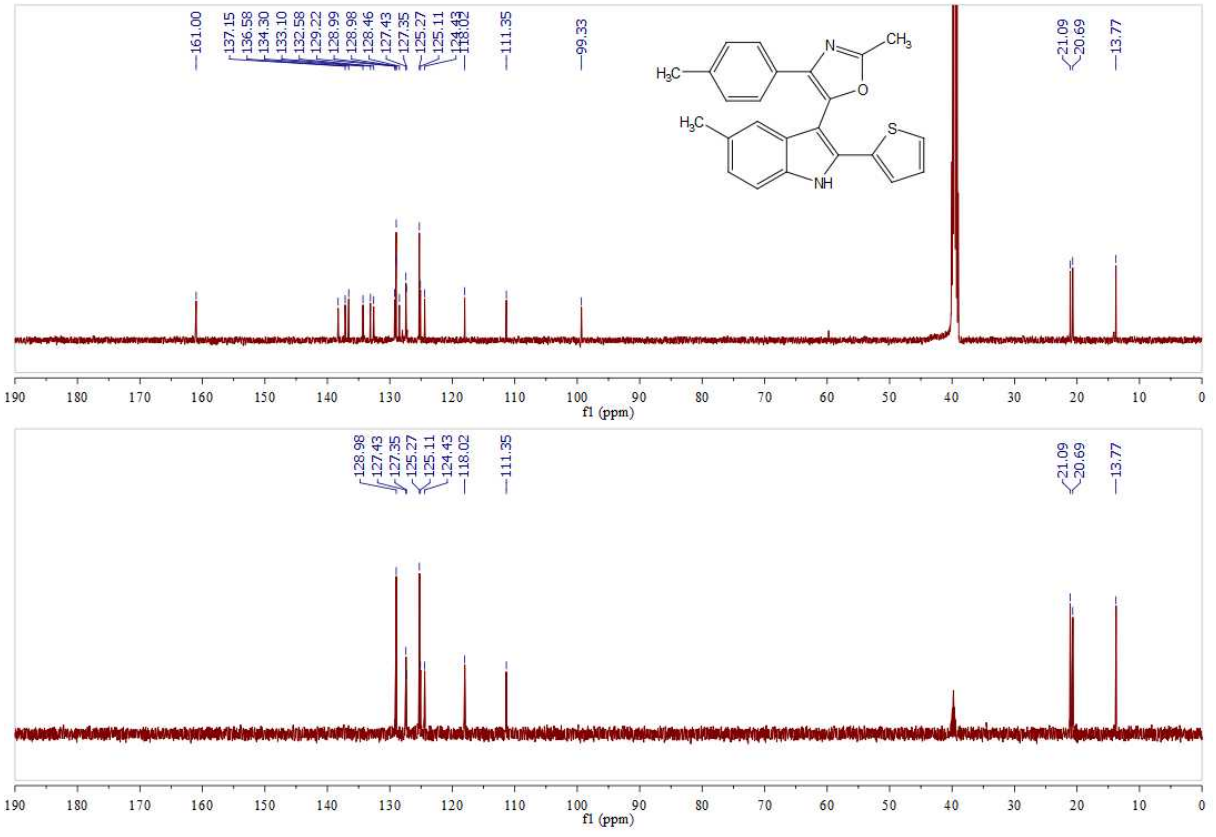


Normalized UV/Vis and fluorescence spectra of **4o** (recorded in EtOH at 298 K).

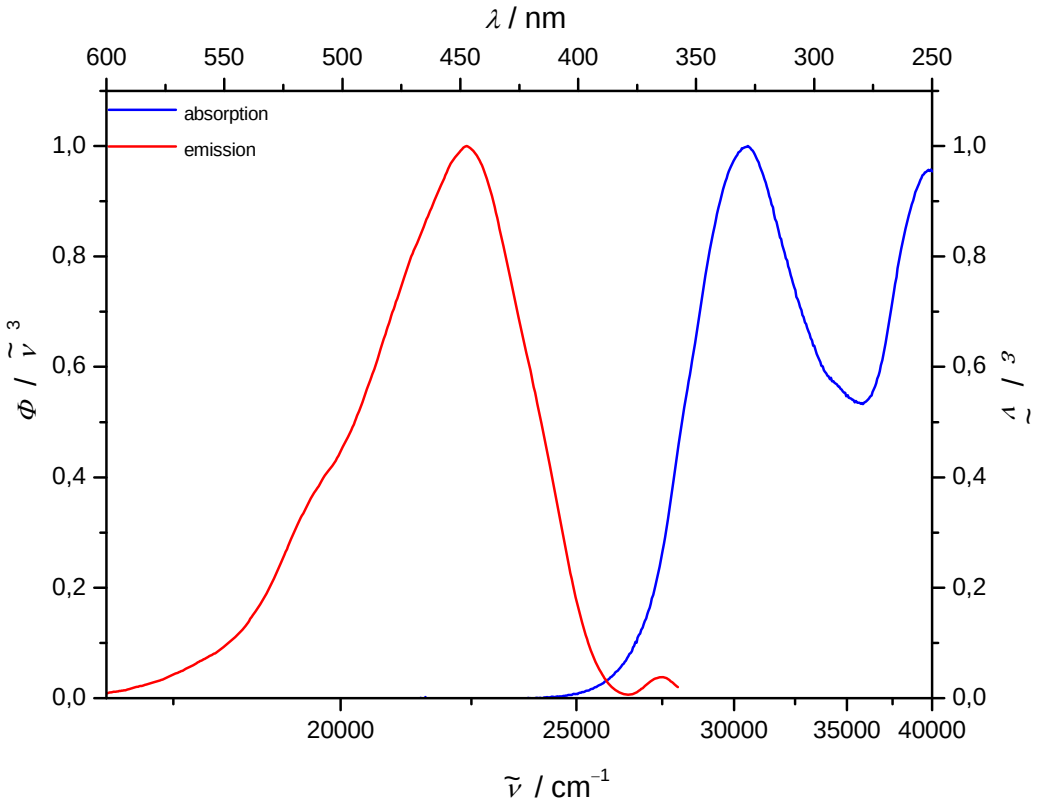
2-Methyl-5-(5-methyl-2-(thiophen-2-yl)-1*H*-indol-3-yl)-4-*p*-tolyloxazole (4p)



^{1}H NMR of **4p** in DMSO-d^6 at 296 K (δ in ppm).

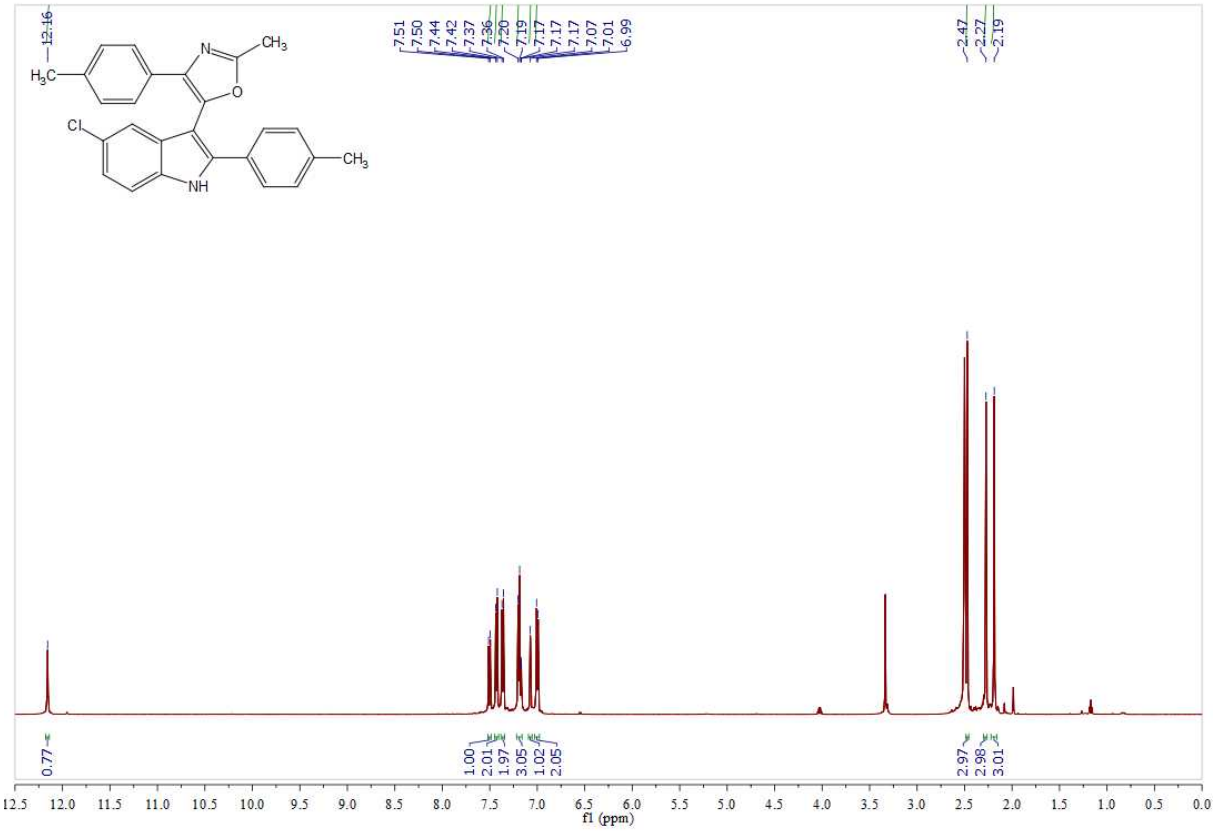


^{13}C NMR and 135-DEPT Spectra of **4p** in DMSO-d^{6} at 296 K (δ in ppm).

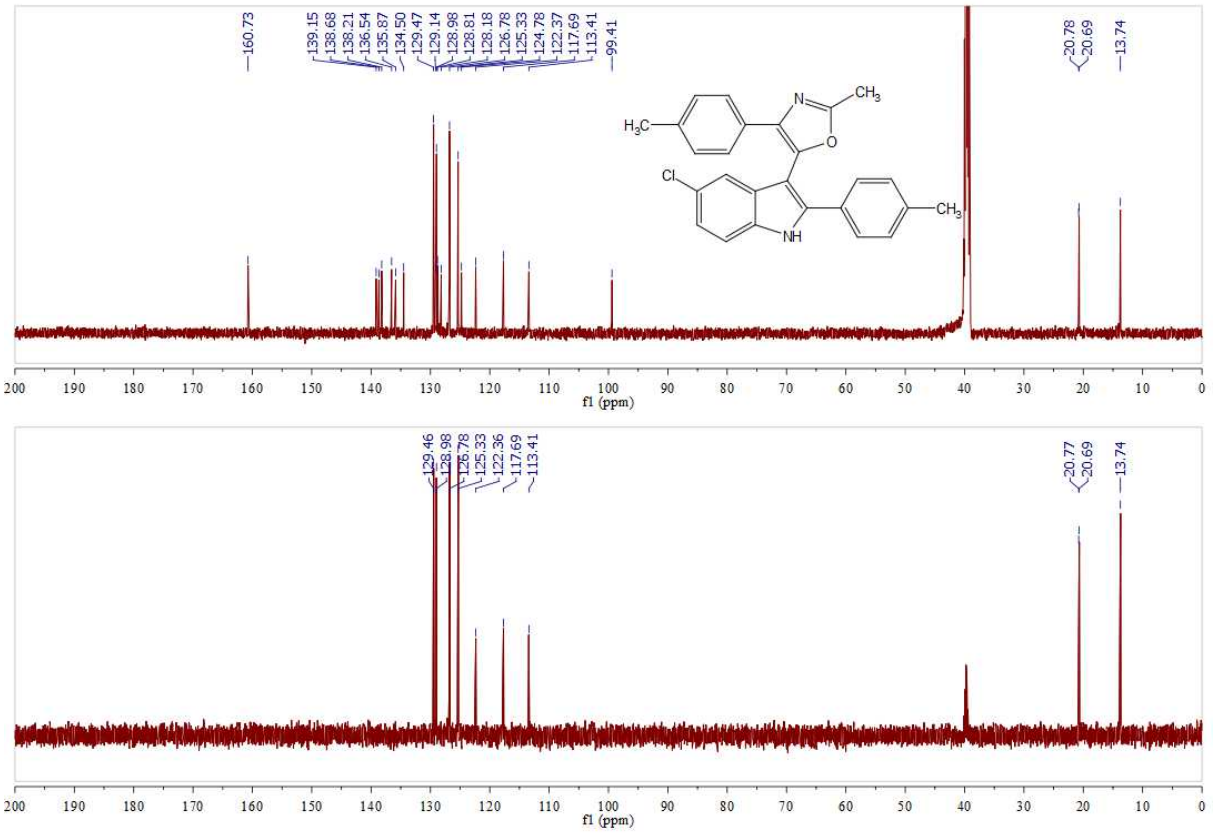


Normalized UV/Vis and fluorescence spectra of **4p** (recorded in EtOH at 298 K).

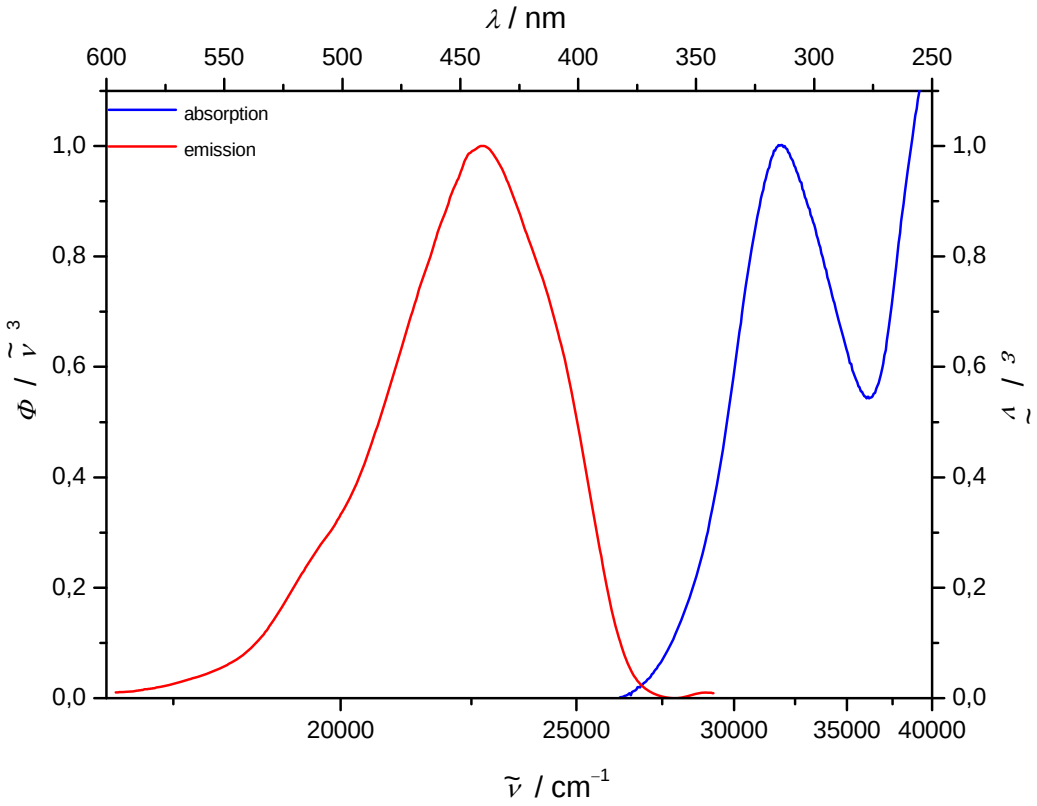
5-(5-Chloro-2-*p*-tolyl-1*H*-indol-3-yl)-2-methyl-4-*p*-tolyloxazole (4q)



^{1}H NMR of **4q** in DMSO-d^6 at 296 K (δ in ppm).

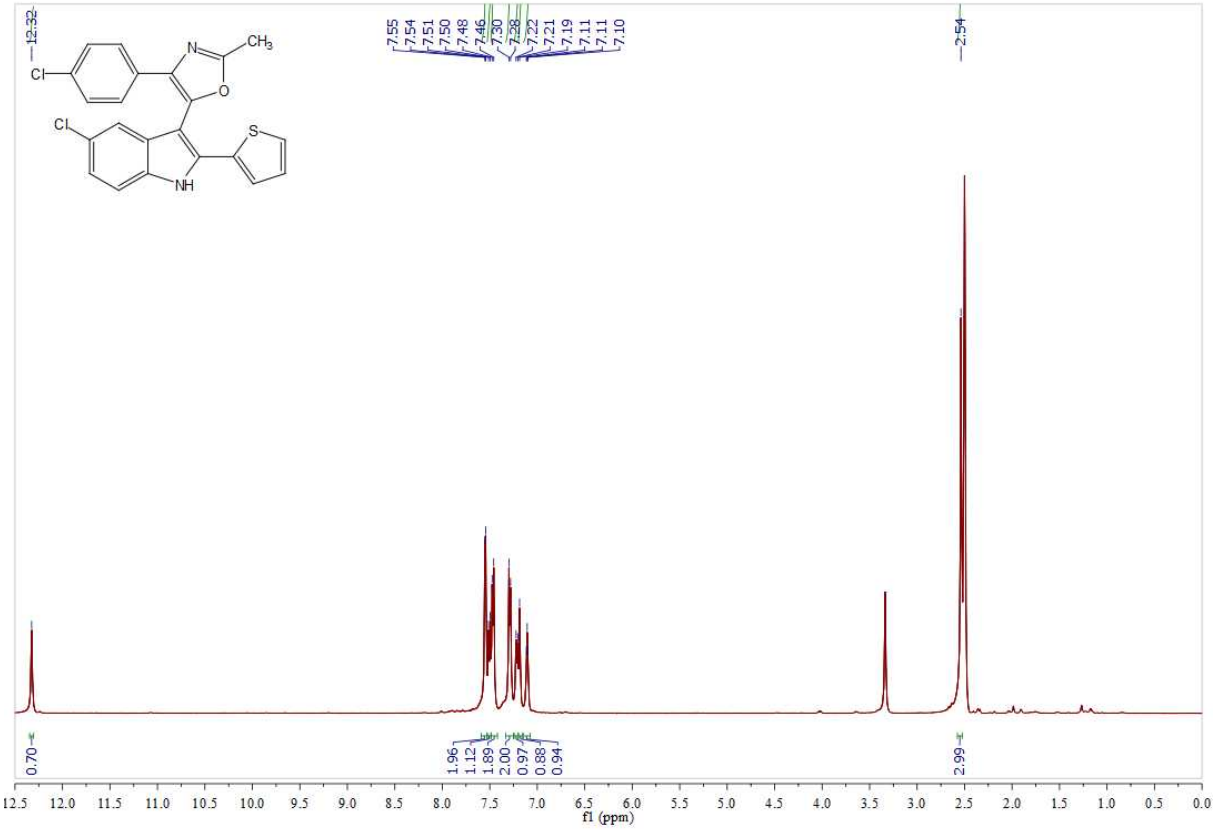


^{13}C NMR and 135-DEPT Spectra of **4q** in DMSO-d^{6} at 296 K (δ in ppm).

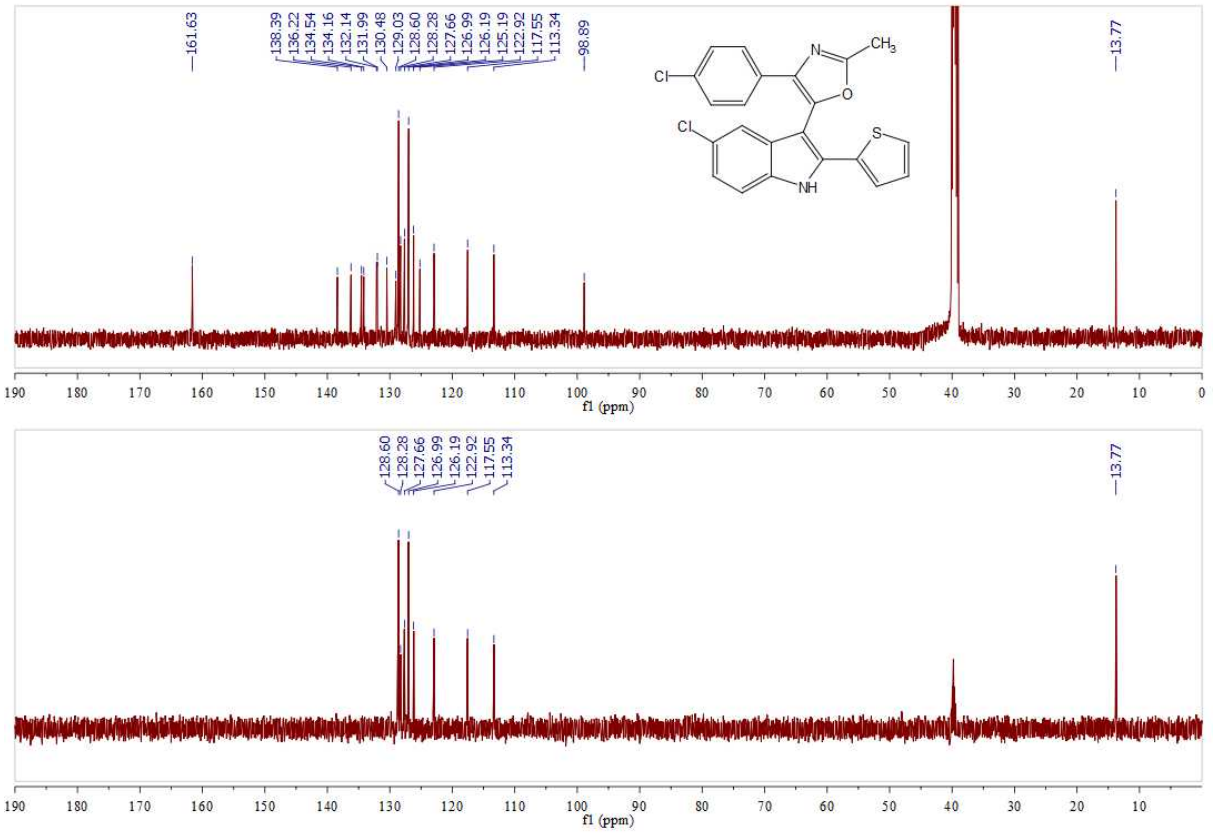


Normalized UV/Vis and fluorescence spectra of **4q** (recorded in EtOH at 298 K).

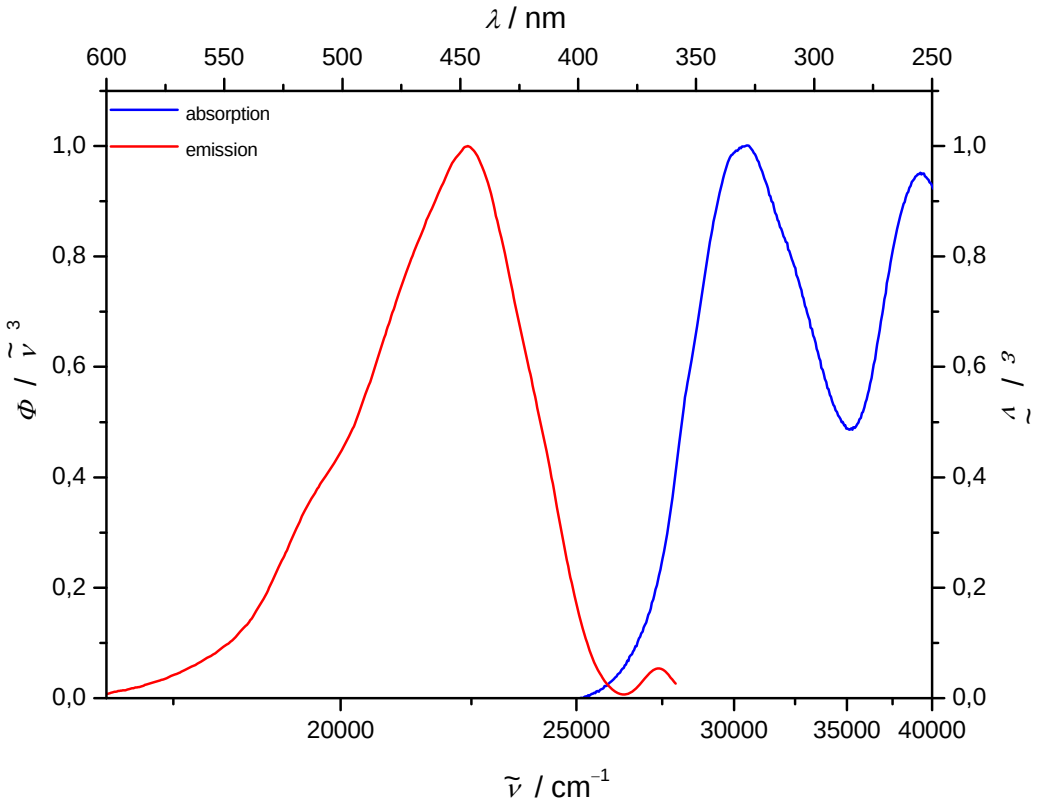
5-(5-Chloro-2-(thiophen-2-yl)-1*H*-indol-3-yl)-4-(4-chlorophenyl)-2-methyloxazole (4r)



^{1}H NMR of **4r** in DMSO-d^6 at 296 K (δ in ppm).

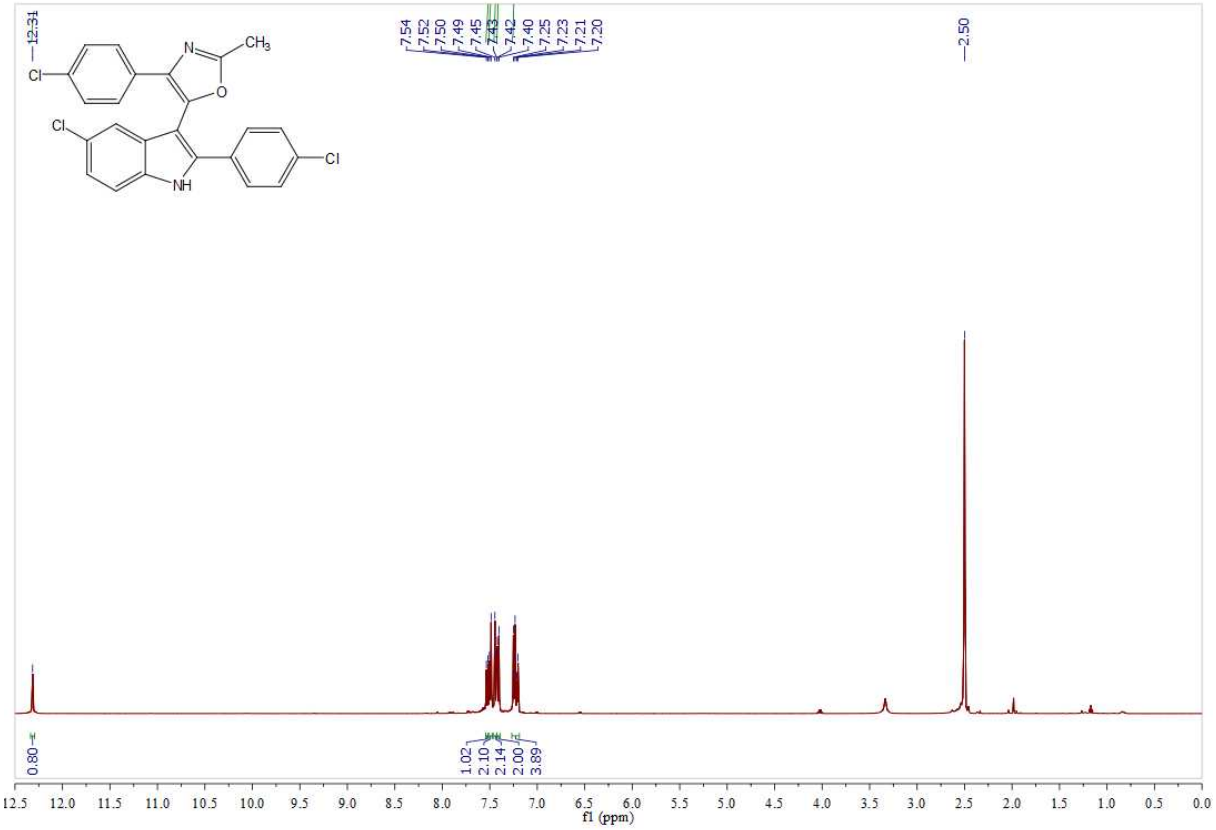


^{13}C NMR and 135-DEPT Spectra of **4r** in DMSO-d^{6} at 296 K (δ in ppm).

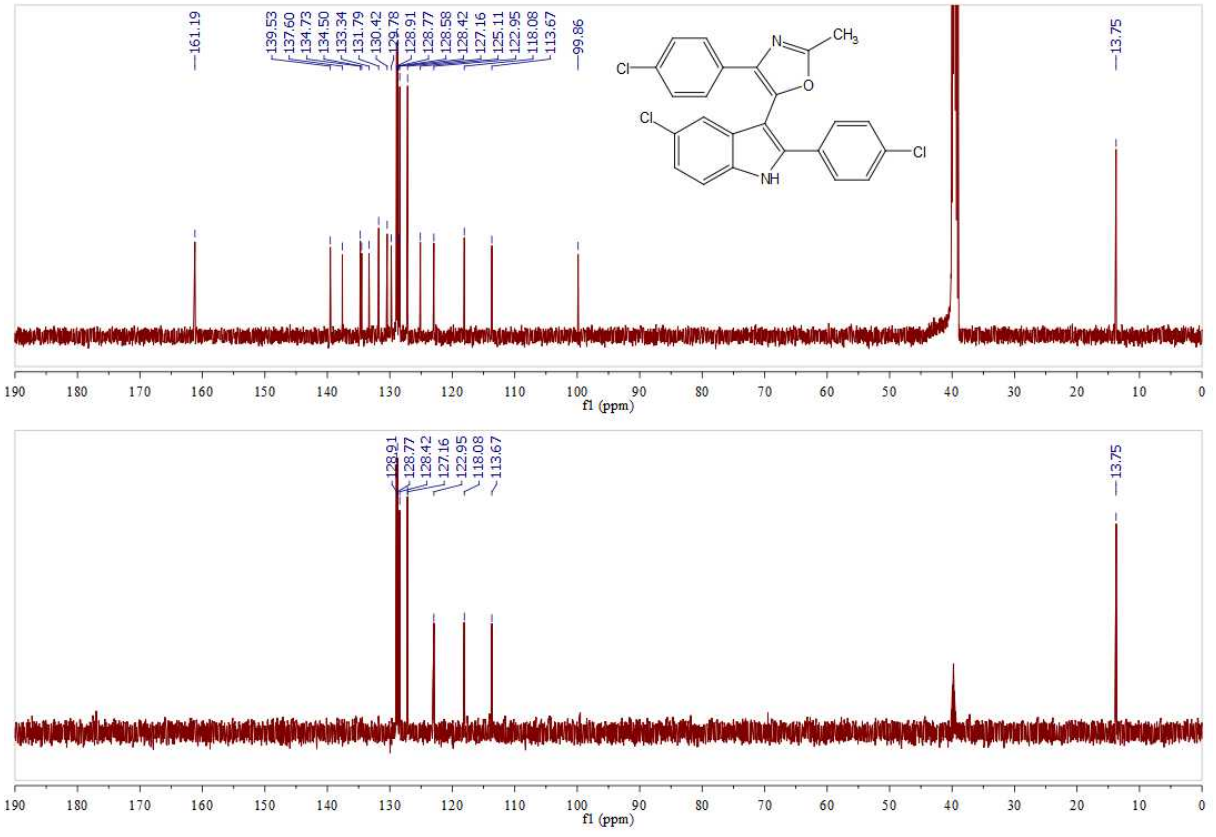


Normalized UV/Vis and fluorescence spectra of **4r** (recorded in EtOH at 298 K).

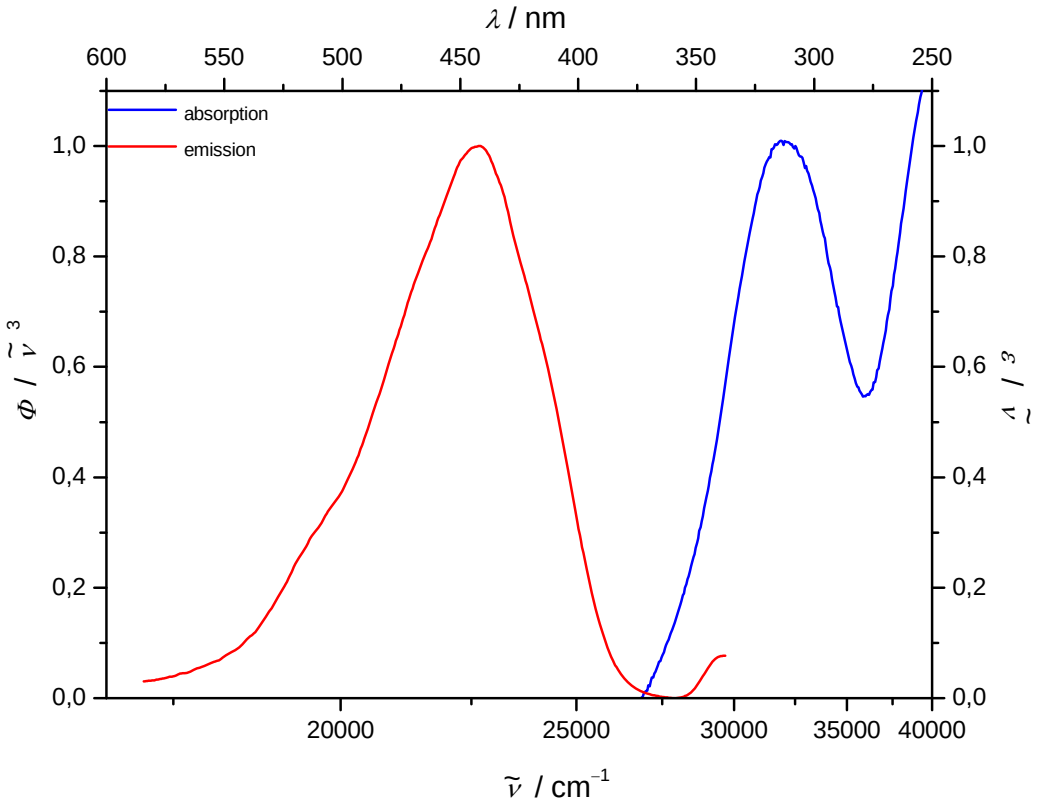
5-(5-Chloro-2-(4-chlorophenyl)-1*H*-indol-3-yl)-4-(4-chlorophenyl)-2-methyloxazole (4s)



^{1}H NMR of **4s** in DMSO-d^6 at 296 K (δ in ppm).

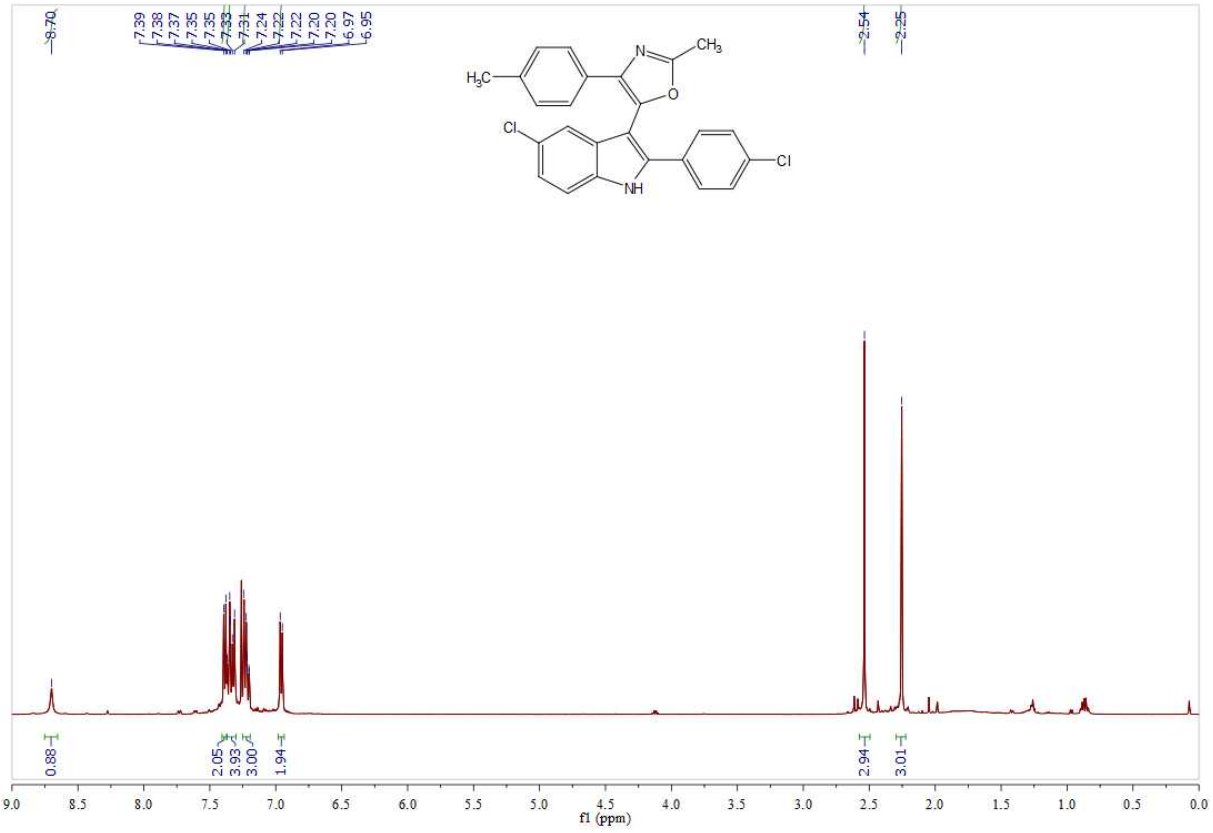


^{13}C NMR and 135-DEPT Spectra of **4s** in DMSO-d^{6} at 296 K (δ in ppm).

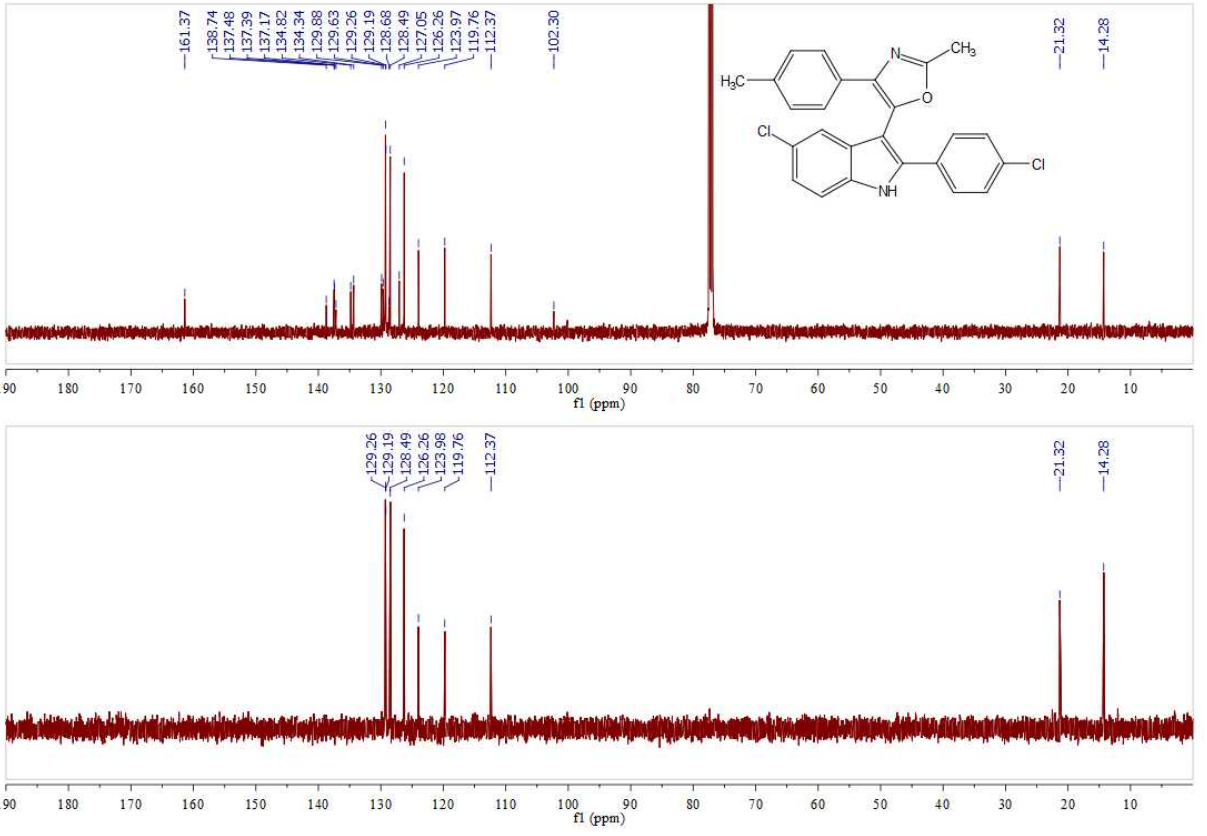


Normalized UV/Vis and fluorescence spectra of **4s** (recorded in EtOH at 298 K).

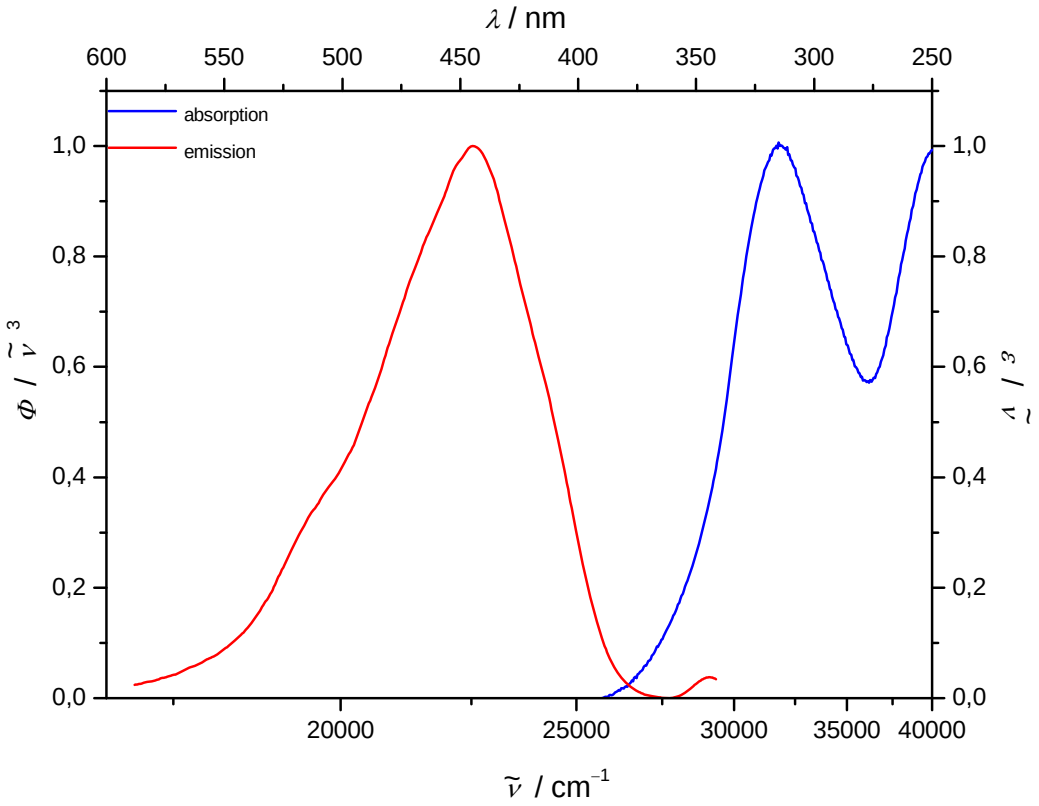
5-(5-Chloro-2-(4-chlorophenyl)-1*H*-indol-3-yl)-2-methyl-4-*p*-tolyloxazol (4t)



^{1}H NMR of **4t** in $CDCl_3$ at 296 K (δ in ppm).

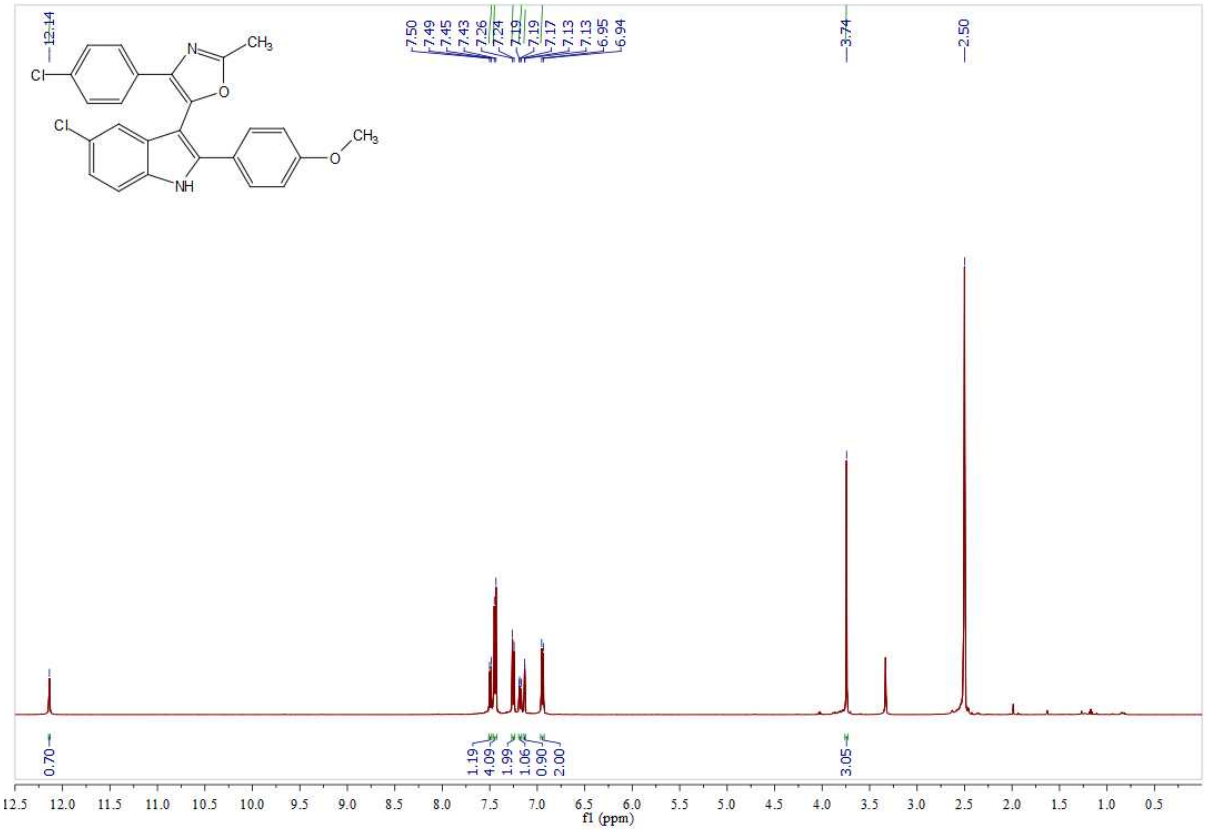


^{13}C NMR and 135-DEPT Spectra of **4t** in $CDCl_3$ at 296 K (δ in ppm).

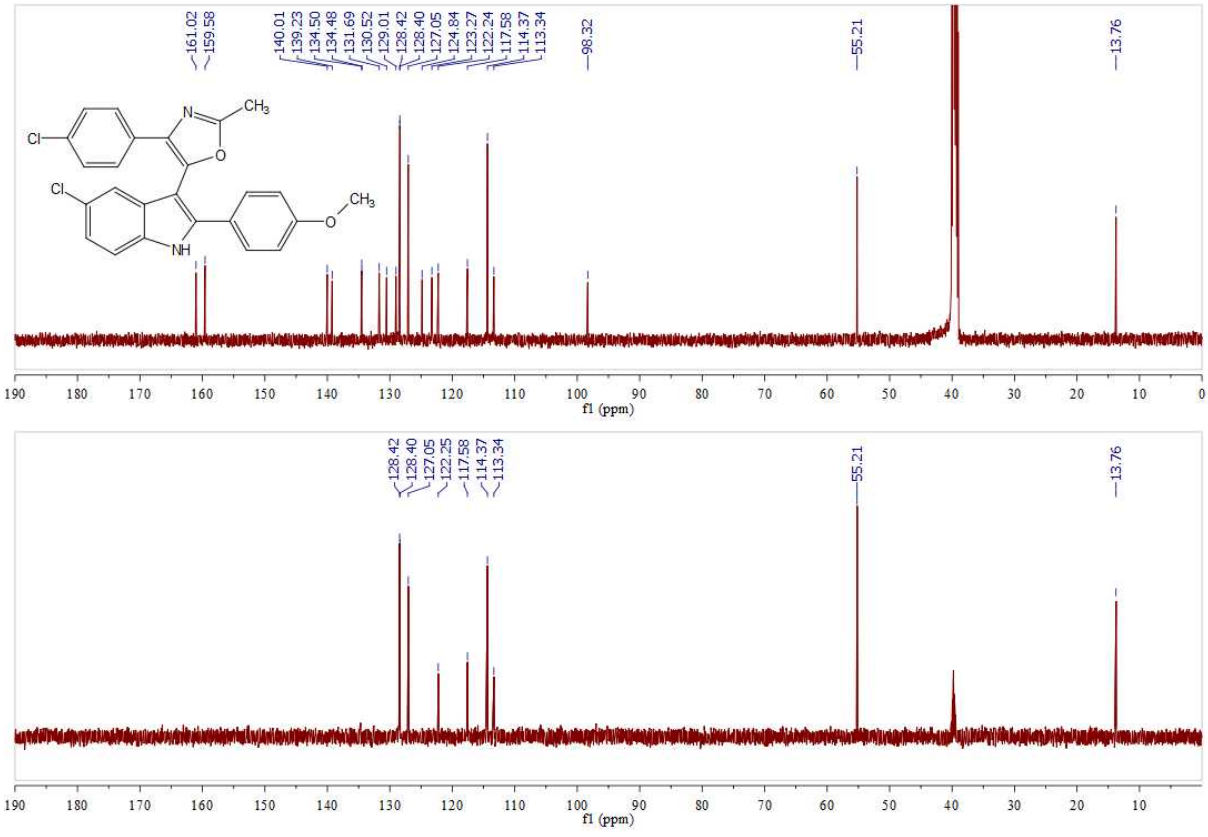


Normalized UV/Vis and fluorescence spectra of **4t** (recorded in EtOH at 298 K).

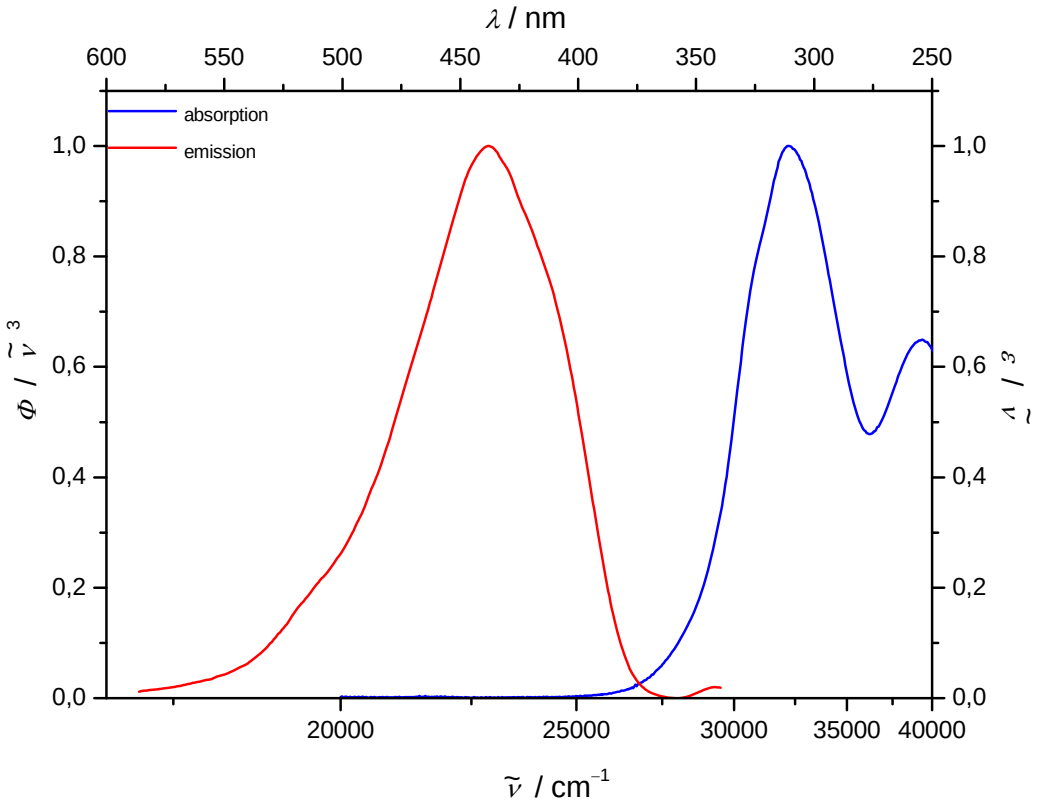
(5-Chloro-2-(4-methoxyphenyl)-1*H*-indol-3-yl)-2-methyl-4-*p*-tolyloxazole (4u)



^{1}H NMR of **4u** in DMSO-d^6 at 296 K (δ in ppm).

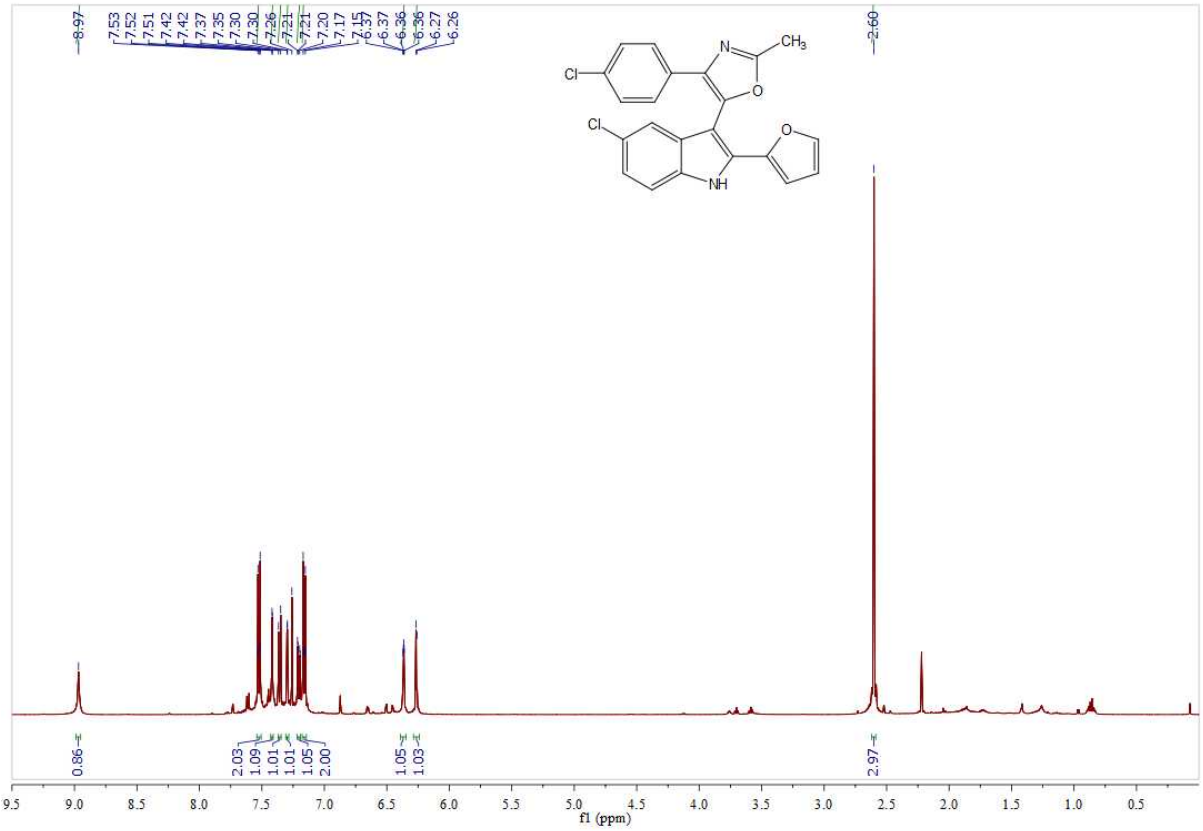


^{13}C NMR and 135-DEPT Spectra of **4u** in DMSO-d^{6} at 296 K (δ in ppm).

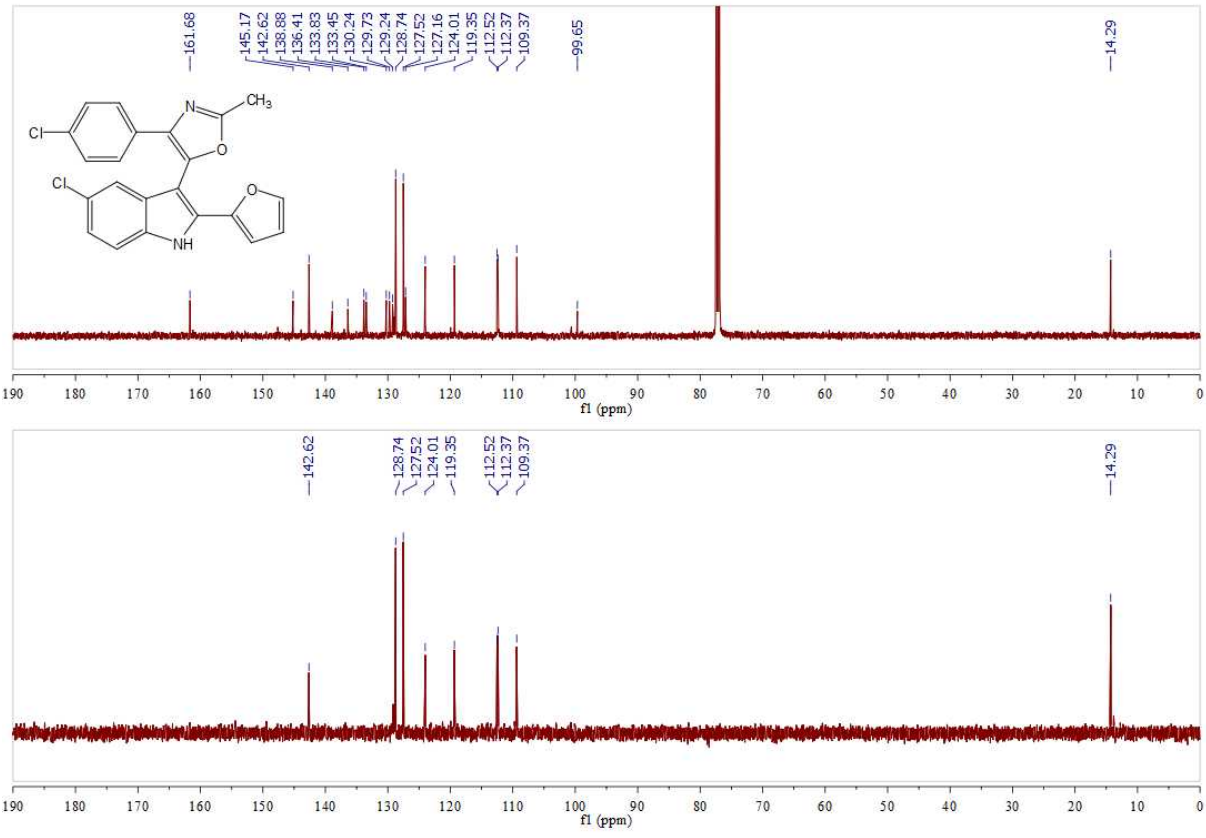


Normalized UV/Vis and fluorescence spectra of **4u** (recorded in EtOH at 298 K).

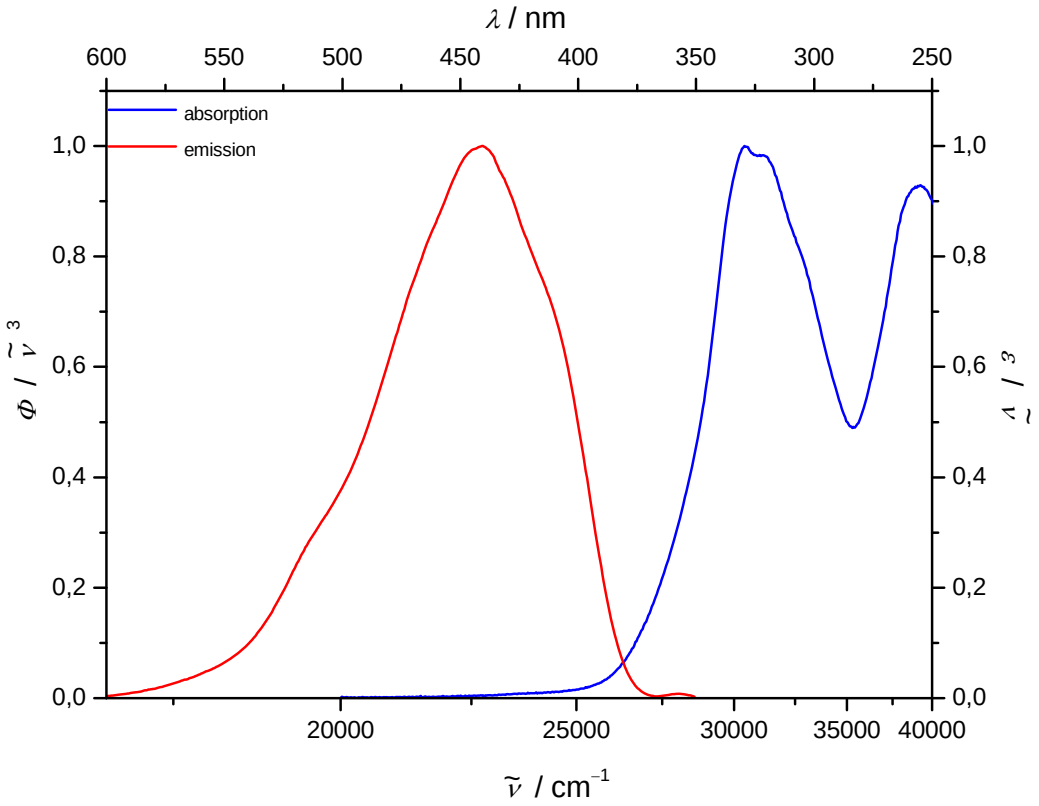
5-(5-Chloro-2-(furan-2-yl)-1*H*-indol-3-yl)-4-(4-chlorophenyl)-2-methyloxazole (4v)



^{1}H NMR of **4v** in $CDCl_3$ at 296 K (δ in ppm).

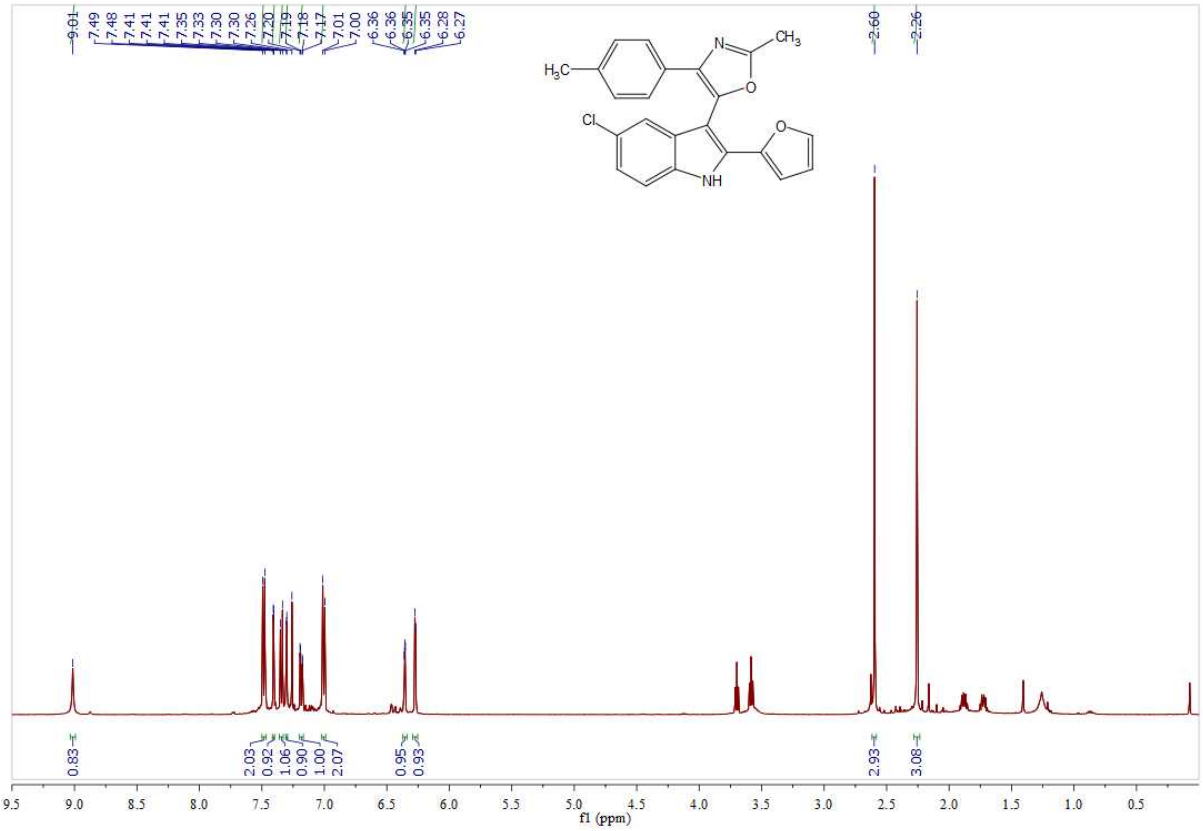


^{13}C NMR and 135-DEPT Spectra of **4v** in $CDCl_3$ at 296 K (δ in ppm).

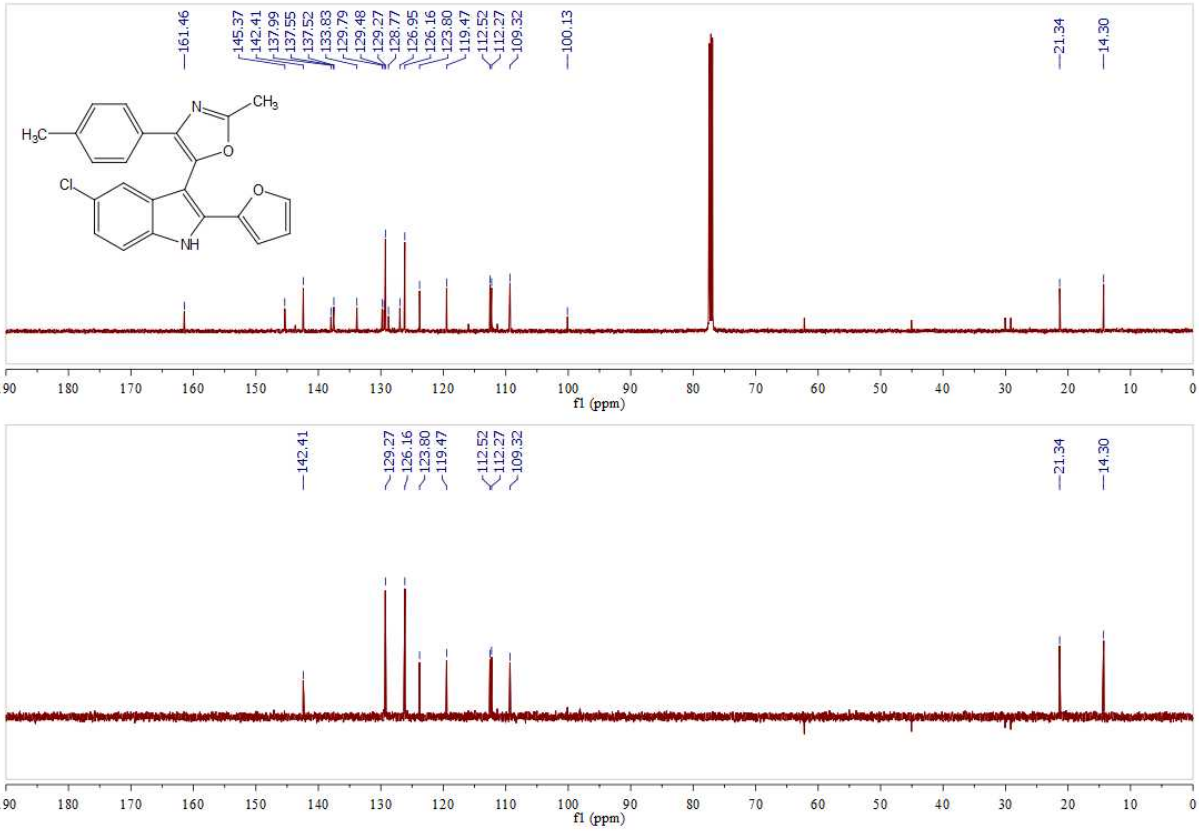


Normalized UV/Vis and fluorescence spectra of **4v** (recorded in EtOH at 298 K).

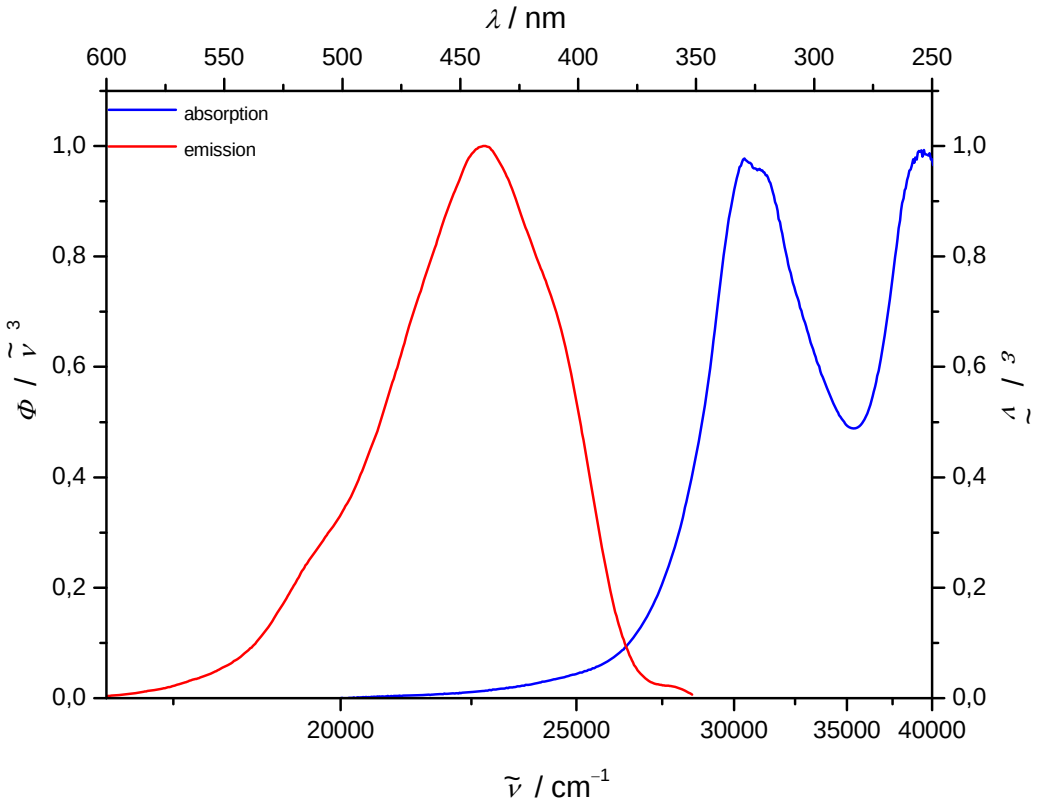
5-(5-Chloro-2-(furan-2-yl)-1*H*-indol-3-yl)-2-methyl-4-*p*-tolyloxazole (4w)



^{1}H NMR of **4w** in $CDCl_3$ at 296 K (δ in ppm).

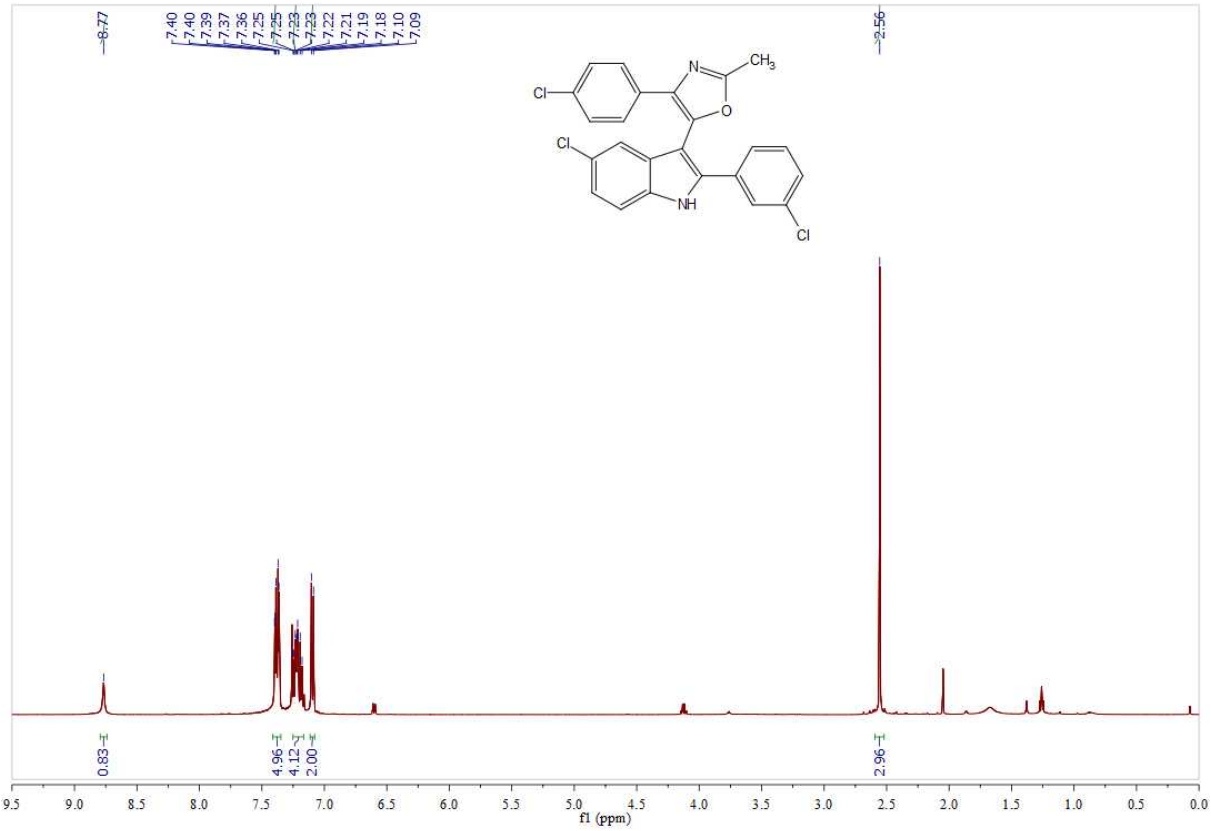


^{13}C NMR and 135-DEPT Spectra of **4w** in $CDCl_3$ at 296 K (δ in ppm).

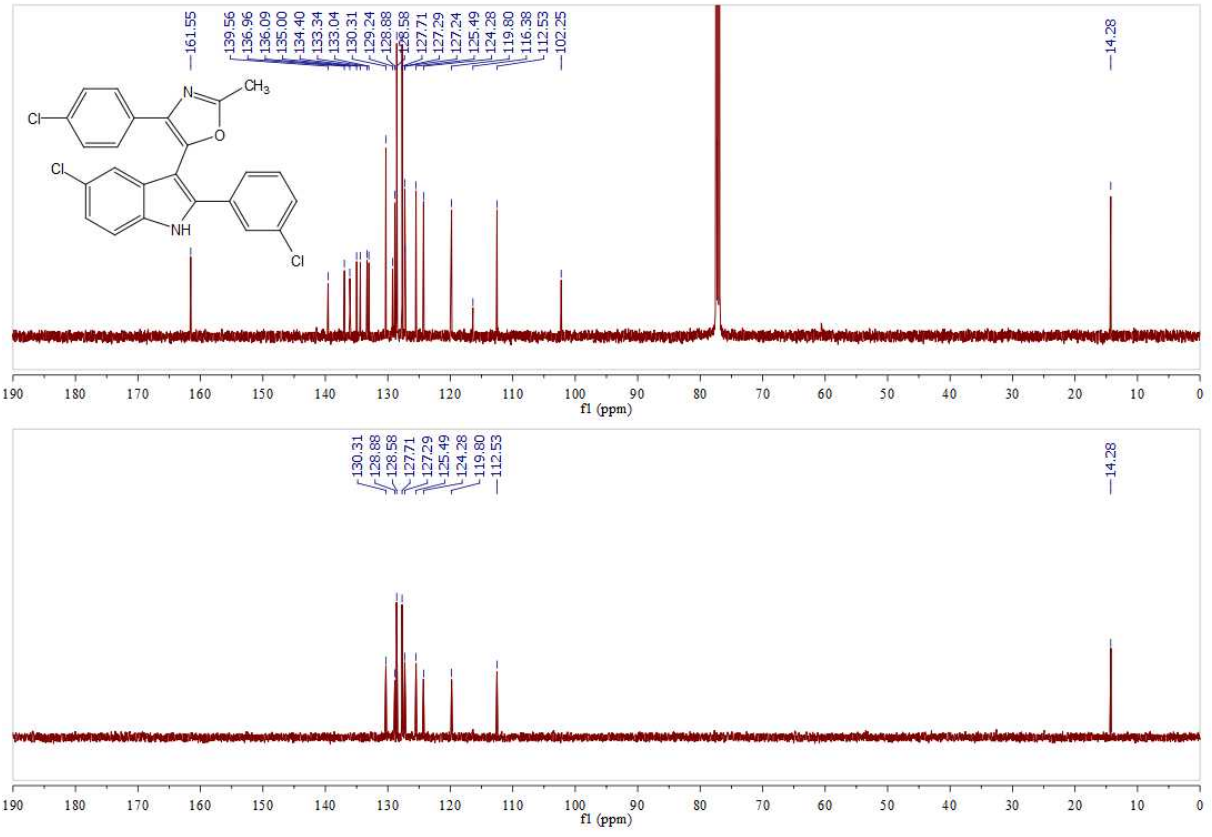


Normalized UV/Vis and fluorescence spectra of **4w** (recorded in EtOH at 298 K).

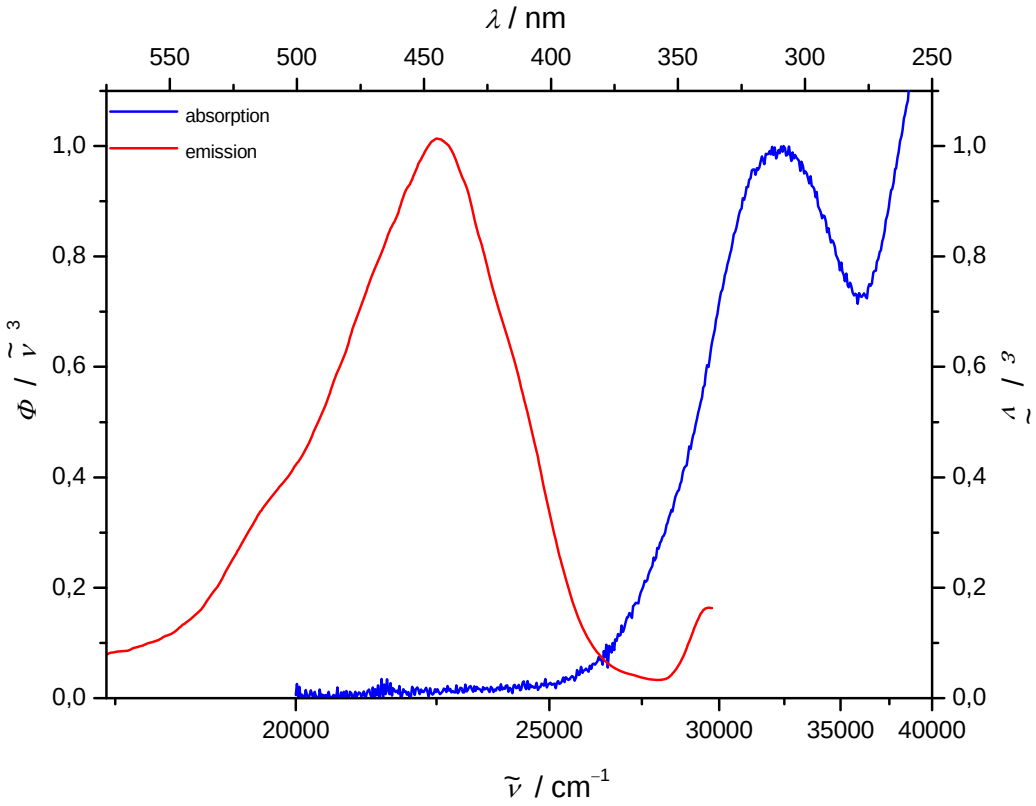
5-(5-Chloro-2-(3-chlorophenyl)-1*H*-indol-3-yl)-4-(4-chlorophenyl)-2-methyloxazole (4x)



^{1}H NMR of **4x** in $CDCl_3$ at 296 K (δ in ppm).

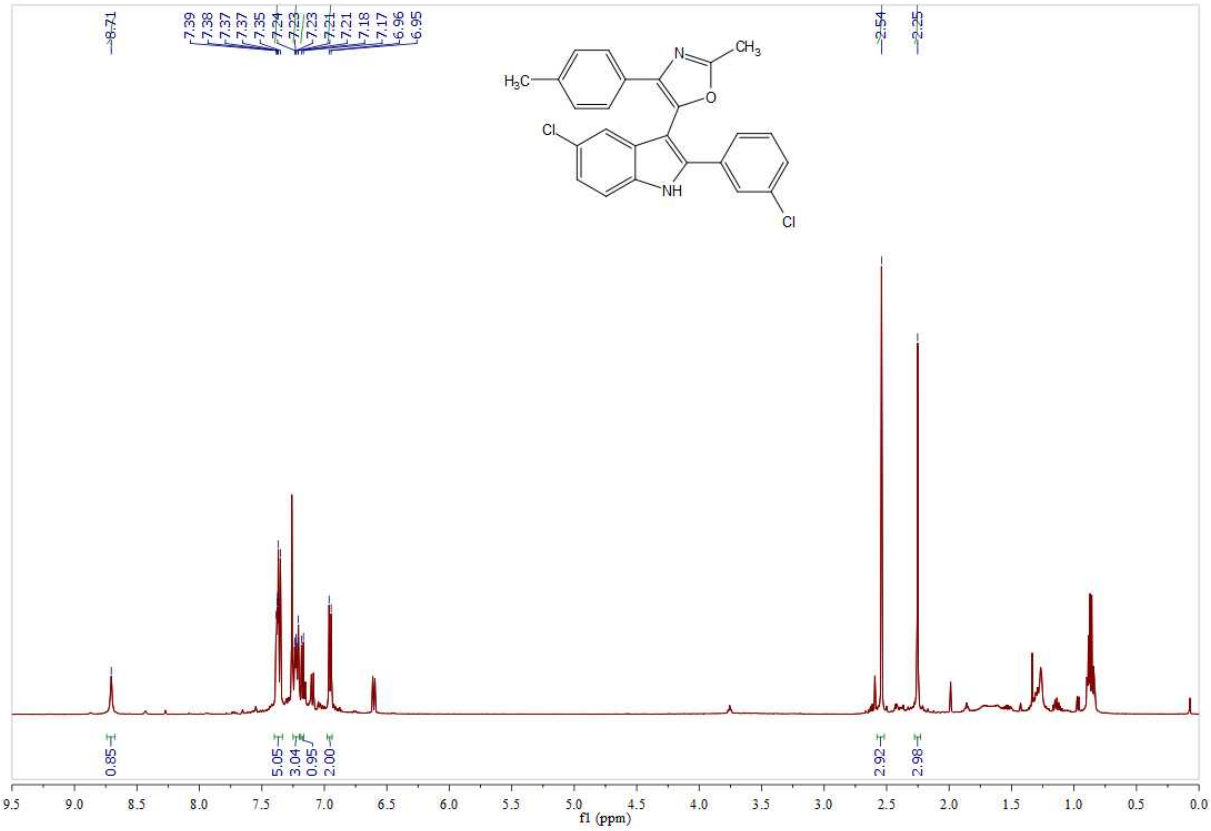


^{13}C NMR and 135-DEPT Spectra of **4x** in $CDCl_3$ at 296 K (δ in ppm).

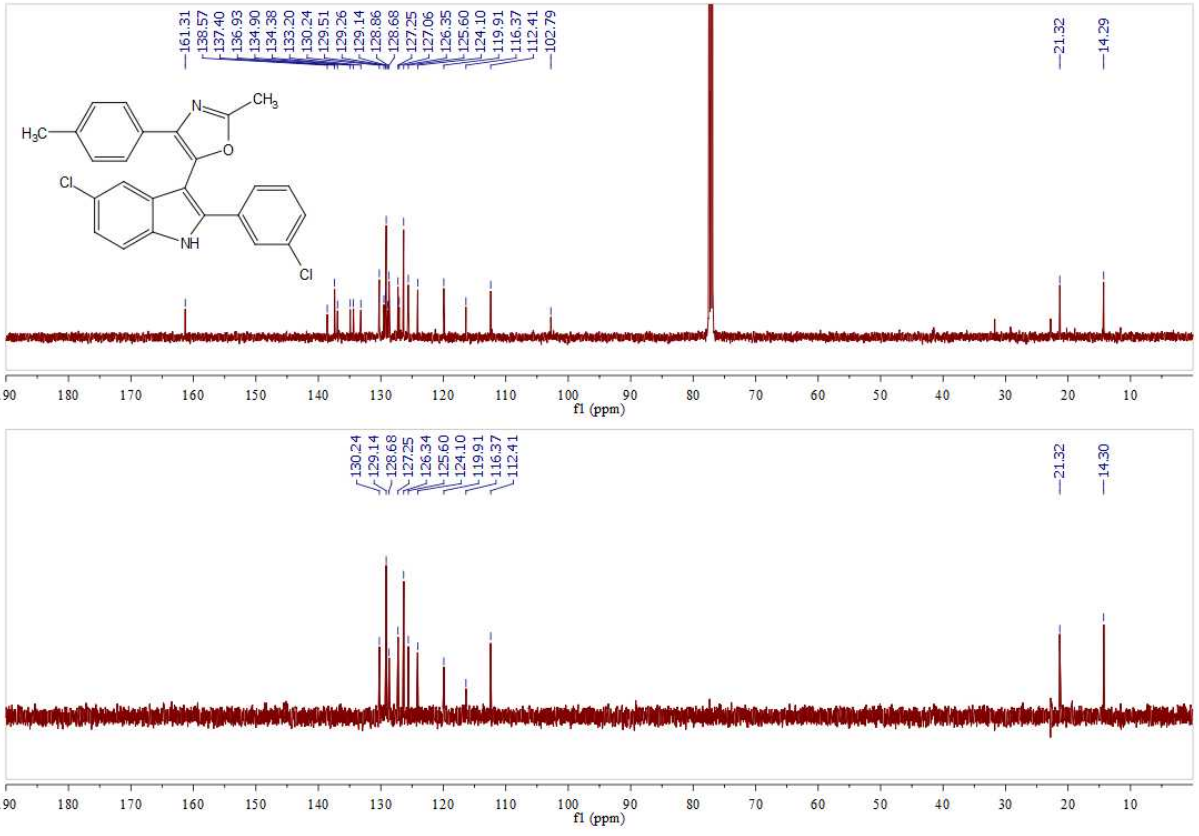


Normalized UV/Vis and fluorescence spectra of **4x** (recorded in EtOH at 298 K).

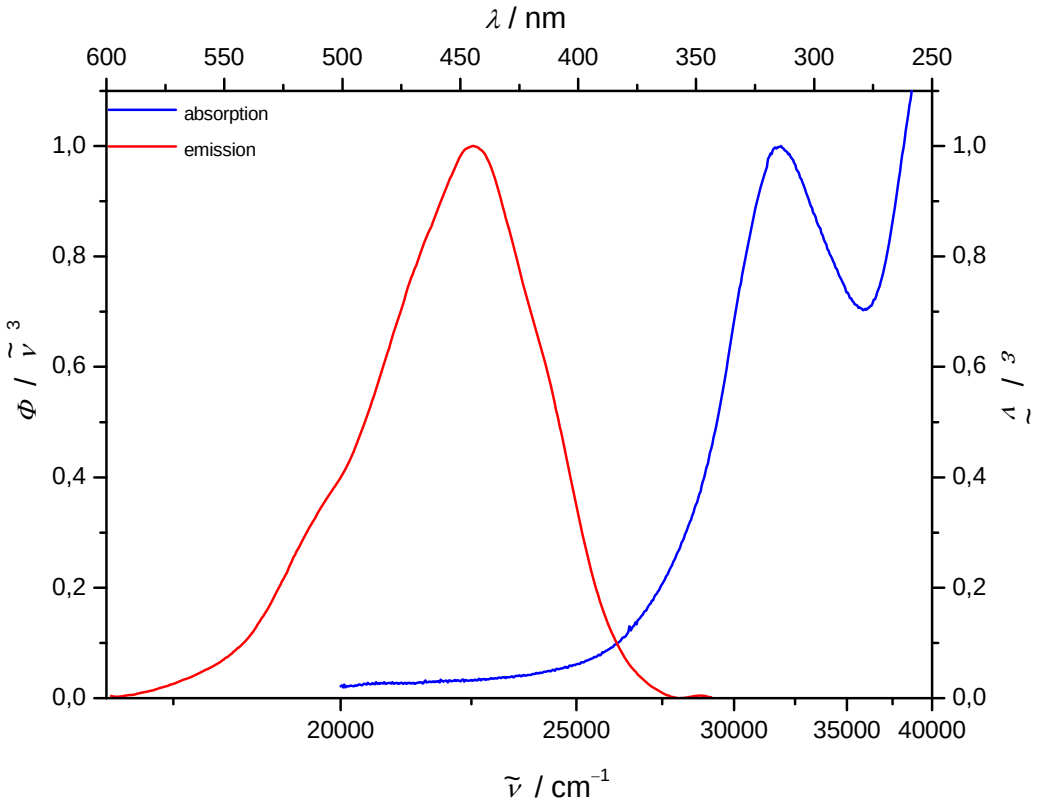
5-(5-Chloro-2-(3-chlorophenyl)-1*H*-indol-3-yl)-2-methyl-4-*p*-tolyloxazole (4y)



^{1}H NMR of **4y** in $CDCl_3$ at 296 K (δ in ppm).



^{13}C NMR and 135-DEPT Spectra of **4y** in $CDCl_3$ at 296 K (δ in ppm).



Normalized UV/Vis and fluorescence spectra of **4y** (recorded in EtOH at 298 K).

Computed xyz-Coordinates of Compound 4x:

The geometries of the indolyloxazoles were optimized in a DFT calculation with the B3LYPfunctional and the 6-311+G(2d,p) basis set in the programme package *Gaussian03*. Theminima structures were confirmed by analytical frequency analysis.Computational details of **4x**:

XYZ-coordinates:

C	-2.7064	-1.4373	-0.9233
C	-2.8839	-0.0840	-0.5996
C	-4.1843	0.4433	-0.5797
C	-5.2652	-0.3736	-0.8845
C	-5.0953	-1.7153	-1.2049
C	-3.8029	-2.2377	-1.2187
C	-1.7370	0.7837	-0.3098
N	-1.7492	2.1106	-0.6991
C	-0.5625	2.7180	-0.3468
C	0.2192	1.7514	0.3313
C	-0.5387	0.5235	0.3430
C	1.4708	2.1172	0.8496
C	1.8962	3.4174	0.6498
C	1.1268	4.3688	-0.0420
C	-0.1180	4.0254	-0.5463
Cl	3.4649	3.9146	1.2836
C	-0.1746	-0.7043	1.0319
O	-1.0670	-1.1745	1.9807
C	-0.4817	-2.2791	2.5101
N	0.6731	-2.5468	1.9988
C	0.8973	-1.5603	1.0351
C	-1.2195	-3.0117	3.5713
C	2.1155	-1.5967	0.2165
C	2.2618	-0.8409	-0.9563
C	3.4250	-0.9110	-1.7143

C	4.4569	-1.7472	-1.3028
C	4.3378	-2.5150	-0.1496
C	3.1707	-2.4384	0.6003
Cl	5.9324	-1.8382	-2.2588
Cl	-6.8871	0.3083	-0.8497
H	1.5127	5.3710	-0.1719
H	-0.7212	4.7575	-1.0707
H	2.0886	1.4071	1.3826
H	-2.4379	2.5041	-1.3198
H	-0.6240	-3.8648	3.8918
H	-2.1853	-3.3651	3.2001
H	-1.4112	-2.3630	4.4302
H	1.4607	-0.1946	-1.2903
H	3.5290	-0.3240	-2.6176
H	5.1480	-3.1642	0.1566
H	3.0596	-3.0371	1.4947
H	-4.3589	1.4729	-0.2948
H	-5.9522	-2.3334	-1.4379
H	-3.6539	-3.2802	-1.4744
H	-1.7074	-1.8523	-0.9598

Computed UV/vis Spectrum of Compound 4x by ZINDO-CI

The optimized structure was used in a ZINDO-CI calculation using the programme package *ArgusLab* 4.0.1 (M. A. Thompson, *ArgusLab 4.0*, Planaria Software LLC: Seattle, WA, USA, 2004.)

First three computed transitions of compound **4x**:

1) 344 nm, oscillator strength: 0.3153, orbitals involved: HOMO -> LUMO

2) 307 nm, oscillator strength: 0.072, HOMO-1 -> LUMO, HOMO-2 -> LUMO, and HOMO-1 -> LUMO+3

3) 296nm, oscillator strength: 0.3659, HOMO -> LUMO+1

References

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C. Zorn, M. Bowen, S. Majewski, J. Walker, R. Wojcik, C. Hurlbut, W. Moser, *Nucl. Instrum. Methods Phys. Res. A*, 1988, **273**, 108.

X-ray Structure Analysis of Compound 4x

Table 1. Crystal data and structure refinement for compound **4x** (OPUS901A).

Identification code	opus901a	
Empirical formula	C24 H15 Cl3 N2 O	
Formula weight	453.73	
Temperature	291(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.5836(5) Å	α= 90°.
	b = 16.6354(15) Å	β= 97.485(8)°.
	c = 16.7866(10) Å	γ = 90°.
Volume	2099.7(3) $Å^3$	
Z	4	
Density (calculated)	1.435 Mg/m^3	
Absorption coefficient	0.456 mm^{-1}	
F(000)	928	
Crystal size	0.27 x 0.10 x 0.08 mm^3	
Theta range for data collection	2.45 to 25.00°.	
Index ranges	-9<=h<=9, -19<=k<=17, -19<=l<=16	
Reflections collected	8681	
Independent reflections	3606 [R(int) = 0.0968]	
Completeness to theta = 25.00°	97.9 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3606 / 0 / 273	
Goodness-of-fit on F^2	0.936	
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.0501	
R indices (all data)	R1 = 0.1556, wR2 = 0.0623	
Largest diff. peak and hole	0.160 and -0.177 $e.Å^{-3}$	

Hydrogen bonds for compound **4x** (OPUS901A) [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1)...N(2)#1	0.86	2.27	3.084(6)	159.0

Symmetry transformations used to generate equivalent atoms: x,-y+1/2,z-1/2