Supporting Information

Metal-Free and Regioselective Synthesis of Substituted and Fused Chromenopyrrole Scaffolds *via* the Divergent Reactivity of α-Azido Ketones in Water

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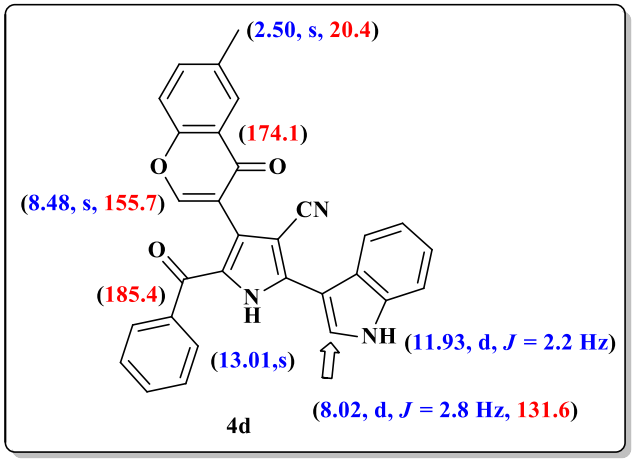
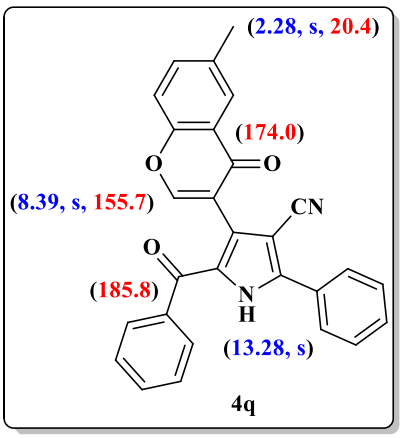
I. A brief discussion of the spectral characterization of compounds 4d, 4q, 8a, 10a, 12b, 15a, 17b and 18a

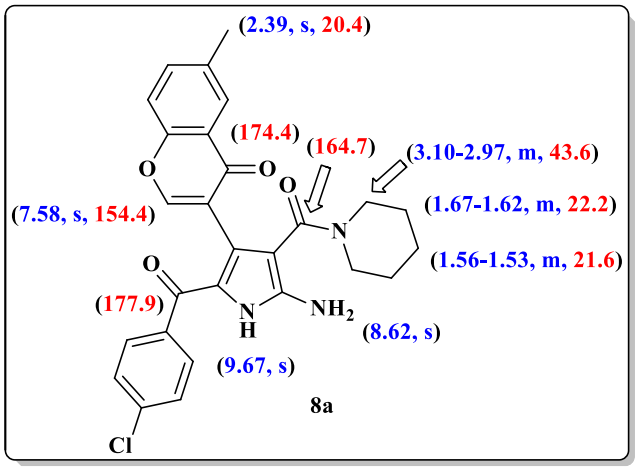


In the ^{1}H NMR spectra of a compound **4d,** a peak that appears at 13.01ppm for one proton belongs to the pyrrole –NH, a doublet that appears at 11.93 ppm with the coupling constant of 2.2 Hz for one proton belongs to the indole –NH, a singlet appears at 8.48 ppm for one proton belongs to the –CH of chromone ring, a doublet appears at 8.02 ppm with the coupling constant of 2.8 Hz for one proton belongs to –CH of indole ring and a peak appears as a singlet at 2.50 ppm for three protons belongs to the –CH_3 of chromone ring. Similarly in ^{13}C NMR spectra of a compound **4d**, a peak appears at 185.4 ppm belongs to the carbonyl carbon of benzoyl group, a peak appears at 174.1 ppm belongs to the carbonyl carbon of chromone ring, a peak appears at 155.7 ppm belongs to the –CH carbon of chromone ring and a peak that appears at 20.4 ppm belongs to the –CH_3 of chromone ring. Further, the structure of **4d** was confirmed by high resolution mass (HRMS-ESI) spectra of the molecular ion peak $[M + H]^+$ appears at 470.1533 indicate that the confirmation of product formation.

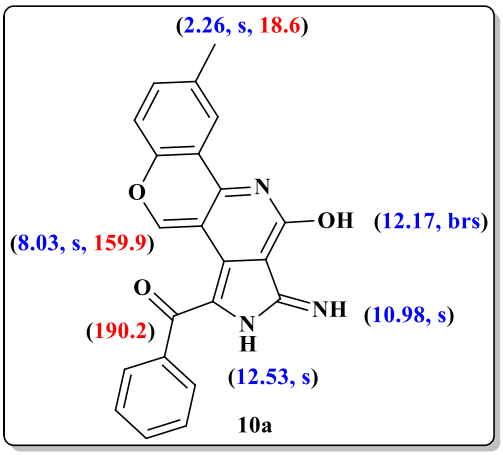


In the ^{1}H NMR spectra of a compound **4q,** a peak that appears at 13.28 ppm for one proton belongs to the pyrrole –NH, a singlet appears at 8.39 ppm for one proton belongs to the –CH of chromone ring and a peak appears as a singlet at 2.28 ppm for three protons that belongs

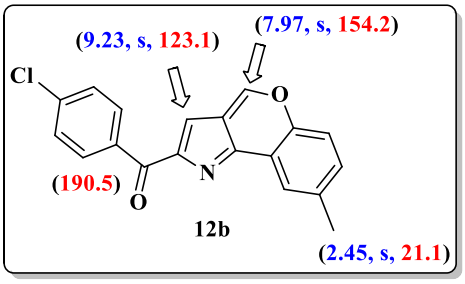
to the –CH_3 of chromone ring. Similarly in ^{13}C NMR spectra of a compound **4q**, a peak appears at 185.8 ppm belongs to the carbonyl carbon of benzoyl group, a peak appears at 174.0 ppm belongs to the carbonyl carbon of chromone ring, a peak appears at 155.7 ppm belongs to the –CH carbon of chromone ring and a peak that appears at 20.4 ppm belongs to the –CH_3 of chromone ring. Further, the structure of **4q** was confirmed by high resolution mass (HRMS-ESI) spectra of the molecular ion peak $[M + H]^+$ appears at 431.1396 indicate that the confirmation of product formation.



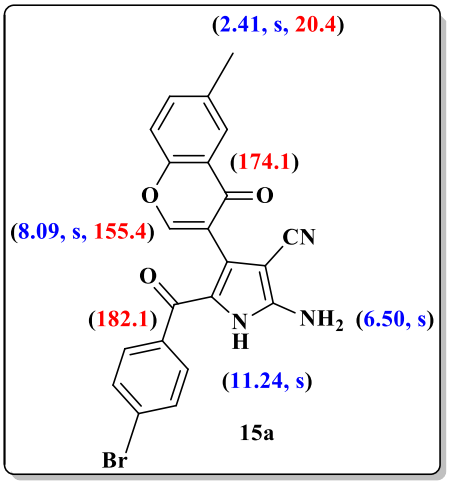
In the ^1H NMR spectra of a compound **8a,** a singlet appears at 9.67 ppm for one proton belongs to the pyrrole –NH, a broad singlet appears at 8.62 ppm for two protons belongs to the –NH_2 of pyrrole, a singlet appears at 7.58 ppm for one proton belongs to the –CH of chromone ring, a multiplet appears at 3.10 – 2.97 ppm for four protons belong to –CH_2 of piperidine ring (Adjacent to ring nitrogen), a singlet appears at 2.39 ppm belongs to the –CH_3 protons from chromone ring, a multiplet appears at 1.67 – 1.62 ppm for four protons belong to –CH_2 protons of piperidine ring and a multiplet appears at 1.56 - 1.53 ppm for two protons belong to –CH_2 protons of the piperidine ring. Similarly in ^{13}C NMR spectra of a compound **8a,** a peak appears at 177.9 ppm belongs to the carbonyl carbon of benzoyl group, a peak appears at 174.4 ppm belongs to the carbonyl carbon of chromone ring, a peak appears at 164.7 ppm belongs to the carbonyl group attached with piperidine ring, a peak appears at 154.4 ppm belongs to the –CH of chromone ring, a peak appears at 43.6 belong to two aliphatic –CH_2 of piperidine ring (Adjacent to ring nitrogen), a peak appears at 22.2 ppm belong to two aliphatic –CH_2 of piperidine ring, a peak appears at 21.6 ppm belong to one aliphatic –CH_2 of piperidine ring and a peak appears at 20.4 ppm belongs to the –CH_3 of chromone ring. Further, the structure of **8a** was confirmed by high resolution mass (HRMS-ESI) spectra of the molecular ion peak $[M + H]^+$ appears at 490.1516 indicate that the confirmation of product formation.



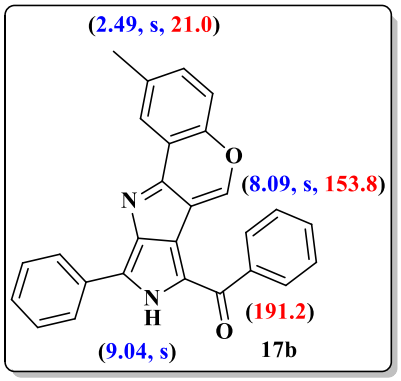
In the ^{1}H NMR spectra of a compound **10a,** a singlet appears at 12.53 ppm for one proton belongs to the pyrrole –NH, a broad singlet appears at 12.17 ppm for one proton belongs to the –OH of the pyridine ring, a singlet appears at 10.98 ppm for one proton belongs to the imine –NH of pyrrole ring and a peak appears at 2.26 ppm for three protons belongs to the–CH_3 of chromone ring. Similarly in ^{13}C NMR spectra of a compound **10a,** a peak appears at 190.2 ppm belongs to the carbonyl carbon of benzoyl group. A peak appears at 159.9 ppm belongs to the –CH of chromone ring and a peak appears at 18.6 ppm belongs to the –CH_3 of chromone ring.



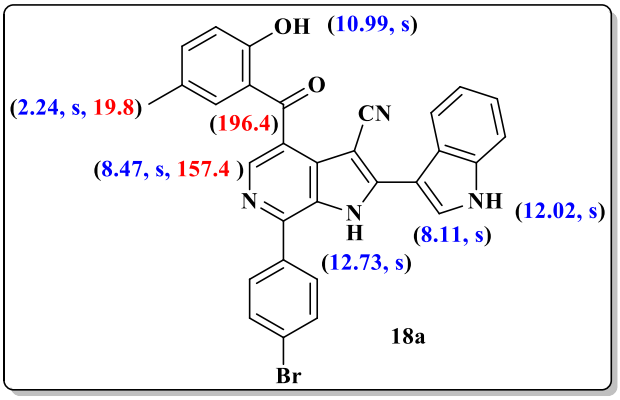
In the ^{1}H NMR spectra of a compound **12b,** a singlet appears at 9.23 ppm for one proton belongs to the –CH of pyrrole ring, a singlet appears at 7.97 ppm for one proton belongs to the –CH of chromone ring and a peak appears at 2.45 ppm for three protons belongs to the –CH_3 of chromone ring. Similarly in ^{13}C NMR spectra of a compound **12b,** a peak appears at 190.5 ppm belongs to the carbonyl carbon of benzoyl group, a peak appears at 154.2 ppm belongs to the –CH of chromone ring, a peak appears at 123.1 ppm belongs to the –CH of pyrrole ring and a peak appears at the 21.1 ppm belongs to the –CH_3 of chromone ring. Further, the structure of **12b** was confirmed by high resolution mass (HRMS-ESI) spectra of the molecular ion peak $[M - H+H_2O]^+$ appears at 338.0599 indicate that the confirmation of product formation.



In the ^{1}H NMR spectra of a compound **15a,** a singlet appears at 11.24 ppm for one proton belongs to the pyrrole –NH, a singlet appears at 8.09 ppm for one proton belongs to the –CH of chromone ring. A peak appears at 6.50 ppm for two protons belongs to the –NH_2 of pyrrole ring and a peak appears at 2.41 ppm for three protons belongs to the –CH_3 of chromone ring. Similarly in ^{13}C NMR spectra of a compound **15a,** a peak appears at 182.1 ppm belongs to the carbonyl carbon of benzoyl group, a peak appears at 174.1 ppm belongs to the carbonyl group of chromone ring, a singlet appears at 155.4 ppm belongs to the –CH of chromone ring and a peak appears at the 20.4 ppm belongs to the –CH_3 of chromone ring.

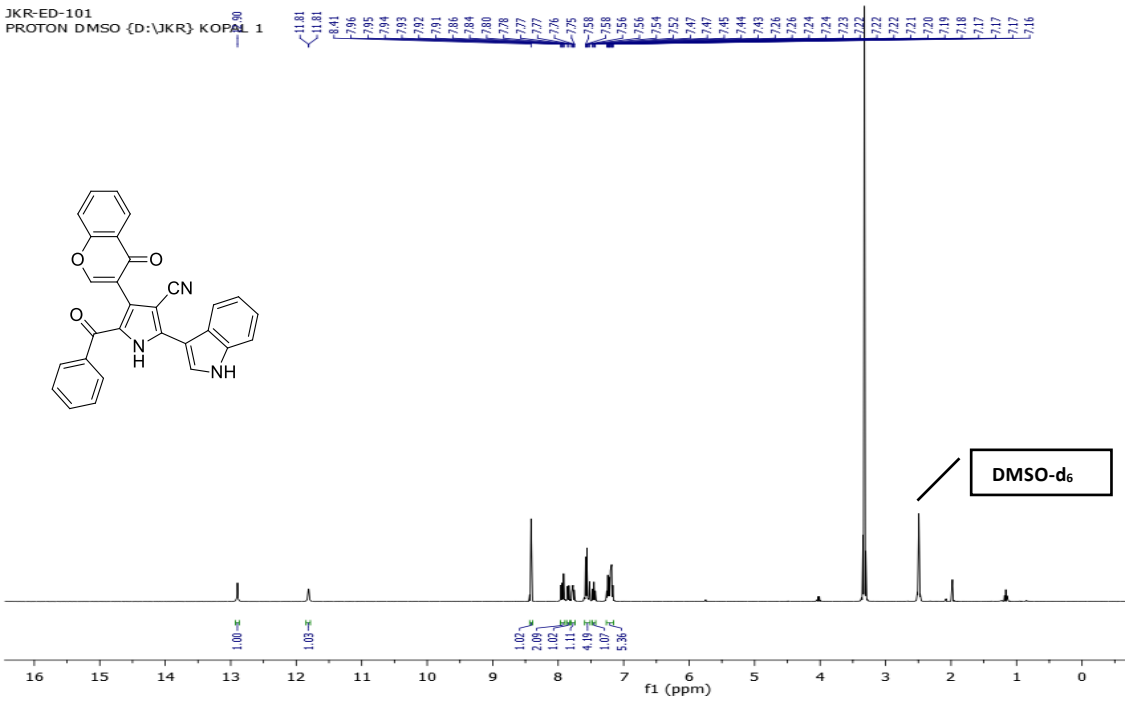


In the ^{1}H NMR spectra of a compound **17b,** a singlet appears at 9.04 ppm for one proton belongs to the pyrrole ring –NH, a singlet appears at 8.09 ppm for one proton belongs to the –CH of chromone ring and a singlet appears at 2.49 ppm for three protons belongs to the –CH_3 of chromone ring. Similarly in ^{13}C NMR spectra of a compound **15a,** a peak appears at 191.2 ppm belongs to the carbonyl carbon of benzoyl group, a peak appears at 153.8 ppm belongs to the –CH of chromone ring and a peak appears at the 21.0 ppm belongs to the –CH_3 of chromone ring. In addition, the DEPT 135 spectrum also confirms that the presence of ten aromatic –CH and one aliphatic –CH_3 in the positive phase. Further, the structure of **12b** was confirmed by high resolution mass (HRMS-ESI) spectra of the molecular ion peak $[M+H_2O]^+$ appears at 420.1224 indicate that the confirmation of product formation.

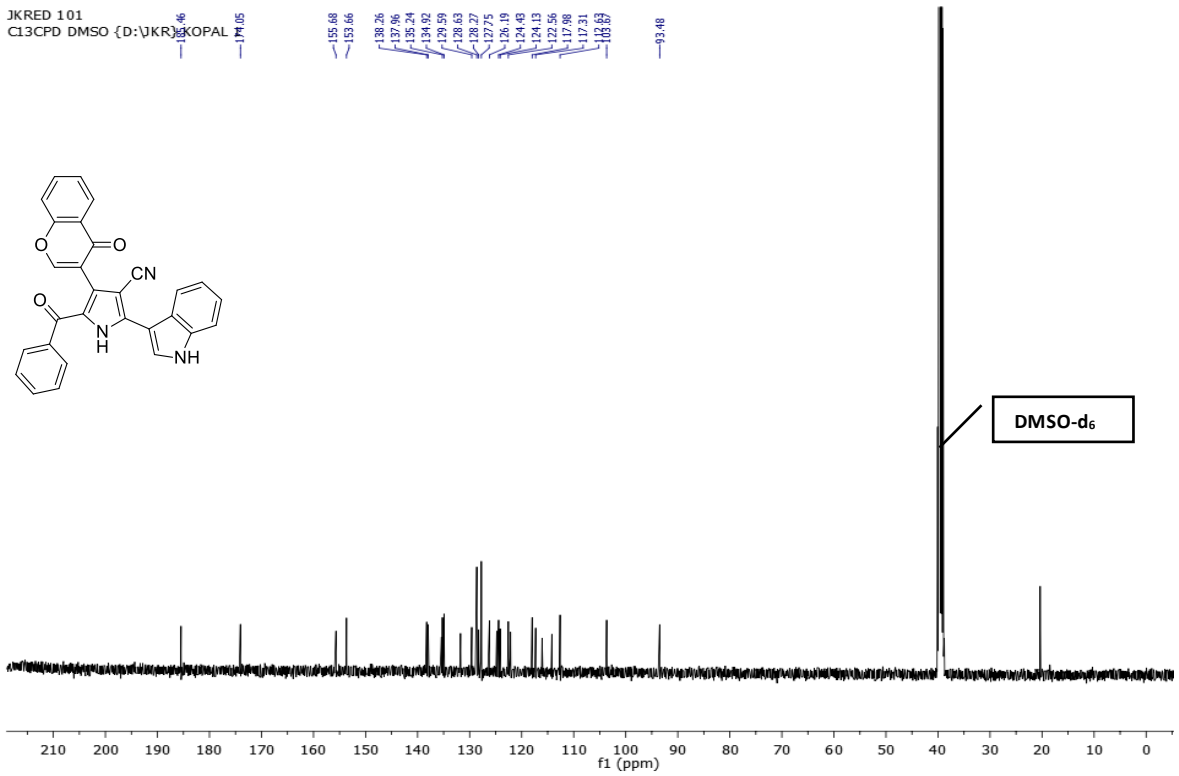


In the ^{1}H NMR spectra of a compound **18a,** a singlet appears at 12.73 ppm for one proton belongs to the –NH of the pyrrole ring, a singlet appears at 12.02 ppm for one proton belongs to the –NH of the indole ring. A peak appears 10.99 ppm for one proton belongs to the –OH of the benzene ring, a singlet appears at 8.47 ppm for one proton belongs to the –CH of the pyridine ring, a peak appears at 8.11 ppm as a singlet for one proton belongs to the –CH of the indole ring, a singlet appears at 2.24 ppm for three protons belongs to the $–CH_3$ of the benzene ring. Similarly in ^{13}C NMR spectra of a compound **18a,** a peak appears at 196.4 ppm belongs to the carbonyl carbon of the benzoyl group, a peak appears at 157.4 ppm belongs to the –CH carbon of the pyridine ring and a peak appears at the 19.8 ppm belongs to the $–CH_3$ of the benzene ring. In addition, the DEPT 135 spectrum also confirms that the presence of eleven aromatic –CH and one aliphatic $–CH_3$ in the positive phase. Further, the structure of **18a** was confirmed by high resolution mass (HRMS-ESI) spectra of the molecular ion peak $[M+H]^+$ appears at 547.0778 indicate that the confirmation of product formation.

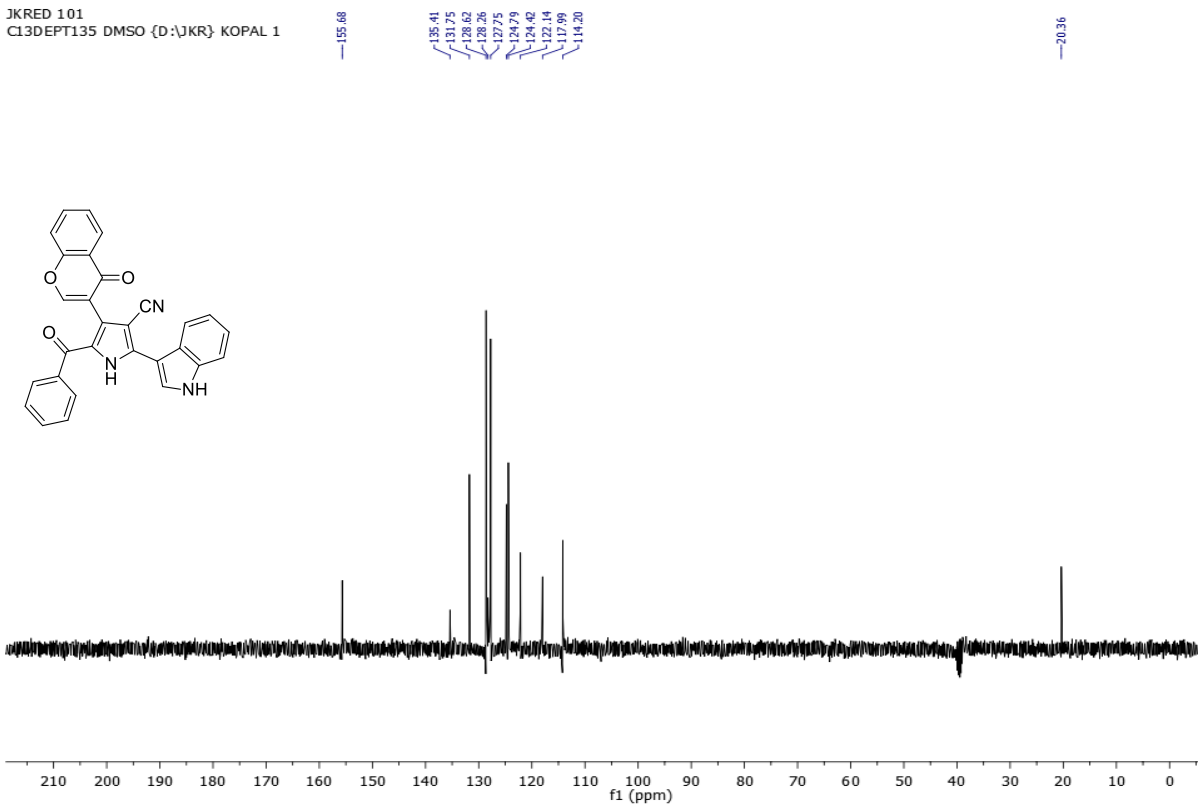
I. ^{1}H NMR, ^{13}C {^{1}H} NMR and HRMS (ESI) spectrum



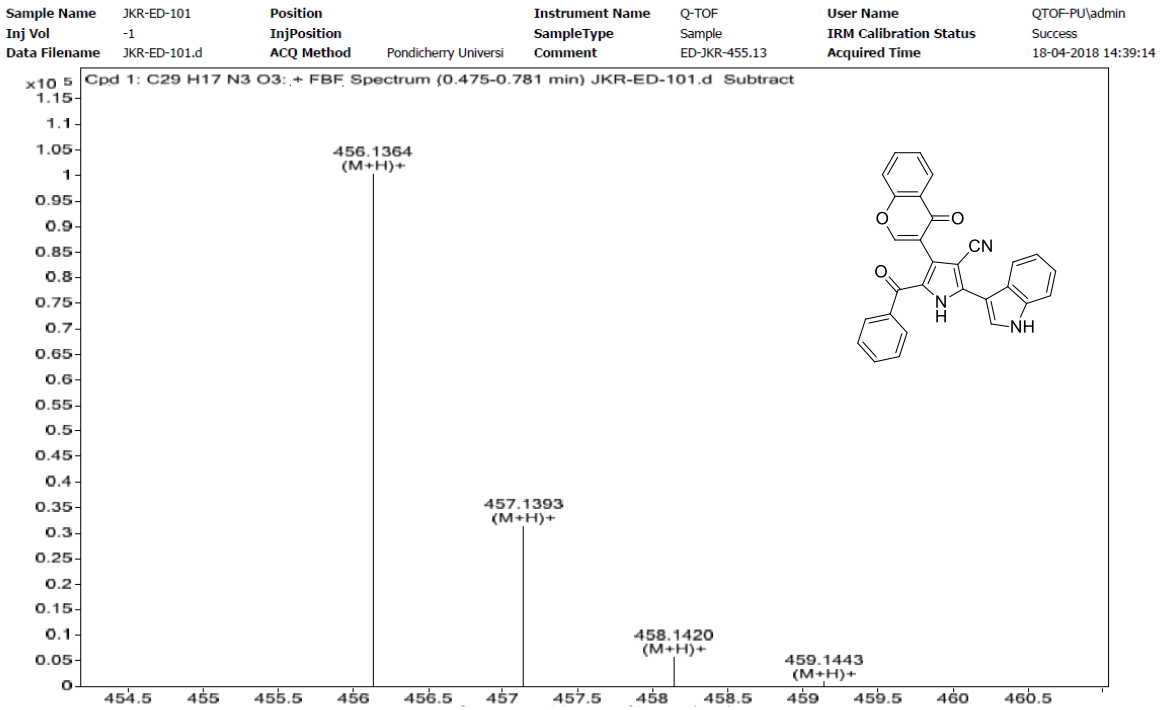
^{1}H NMR spectrum of **4a** (400 MHz, DMSO-d_6)



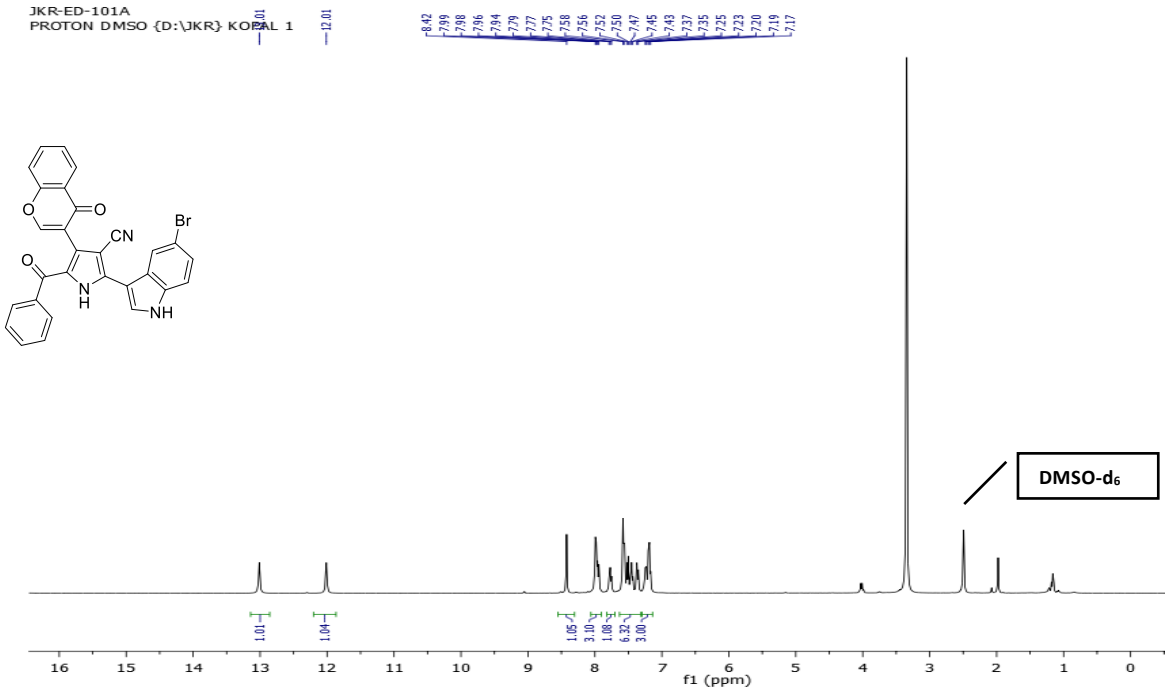
^{13}C{^{1}H} NMR spectrum of **4a** (100 MHz, DMSO-d_6)



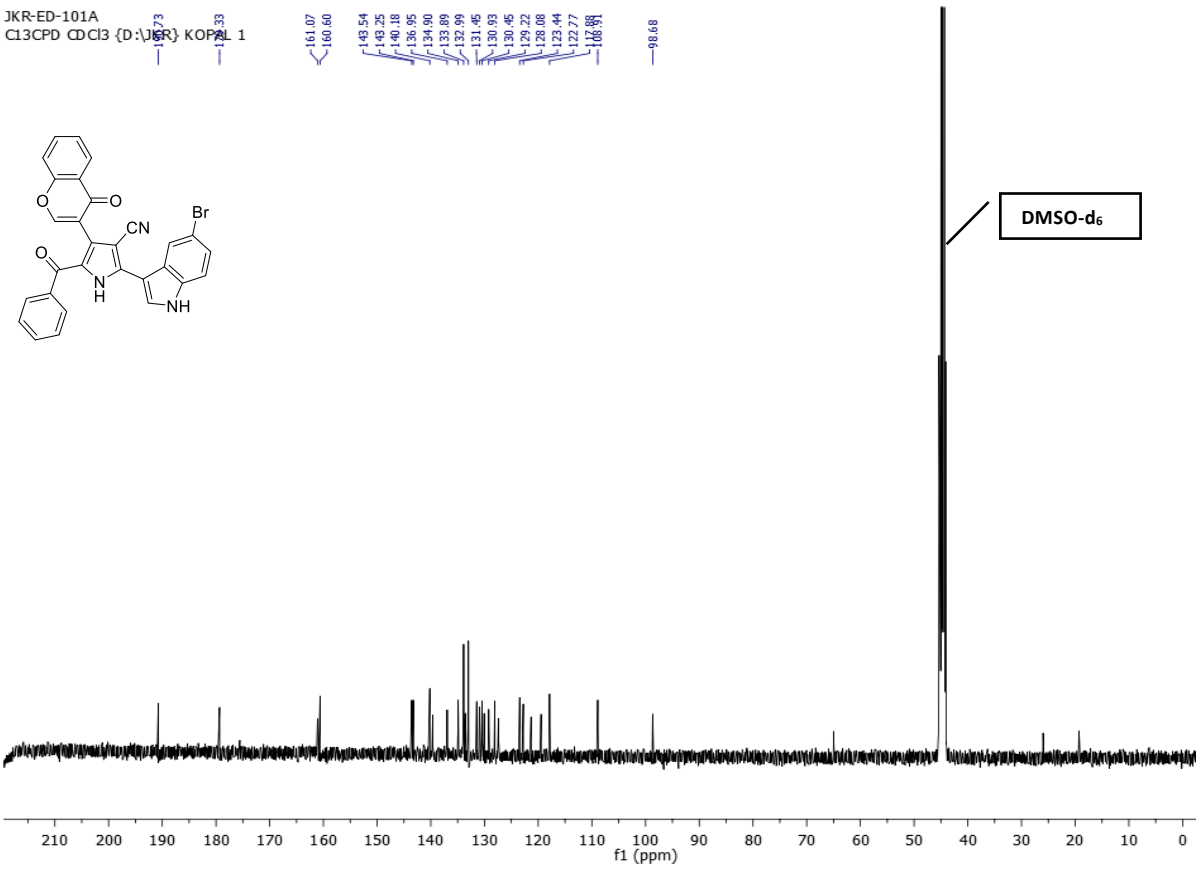
DEPT 135 NMR spectrum of **4a** (100 MHz, DMSO-d_6)



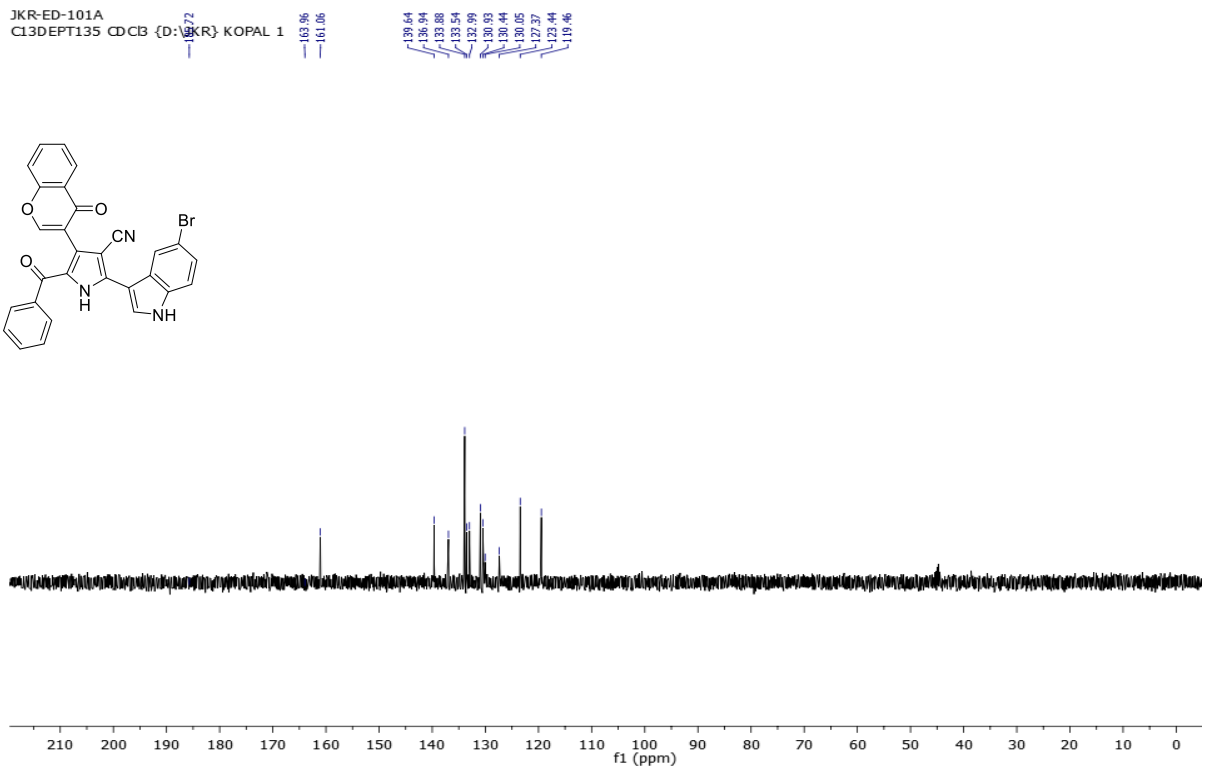
HRMS (ESI) spectrum of **4a**



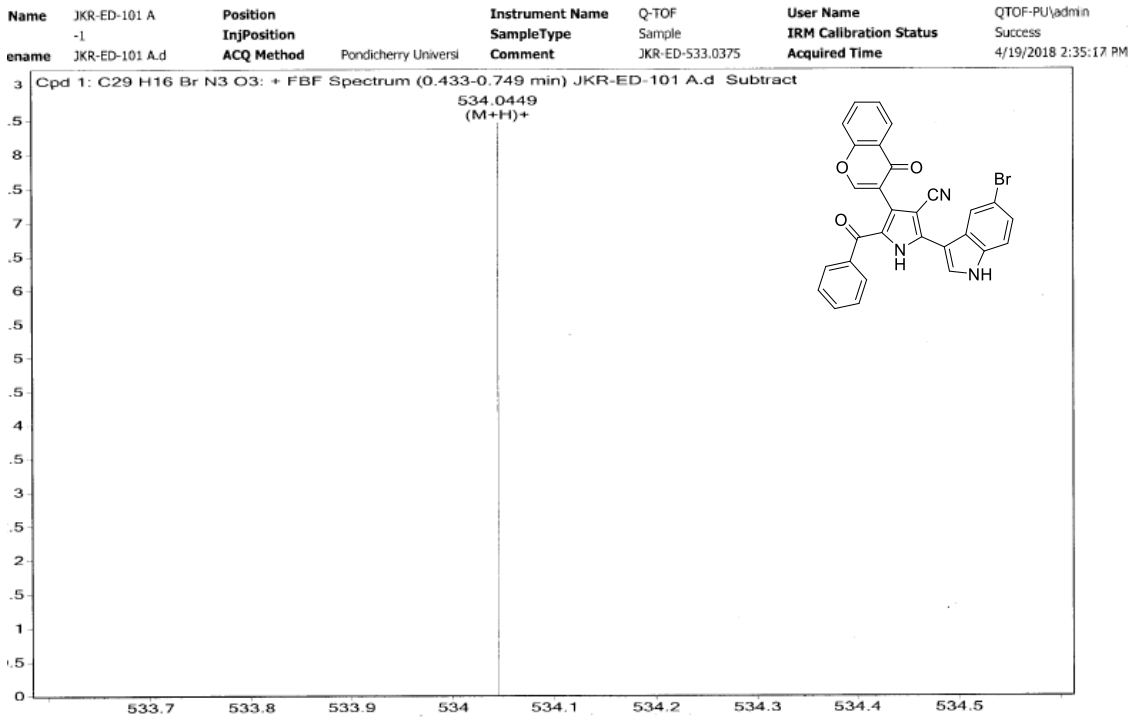
^{1}H NMR spectrum of **4b** (400 MHz, DMSO-d_6)



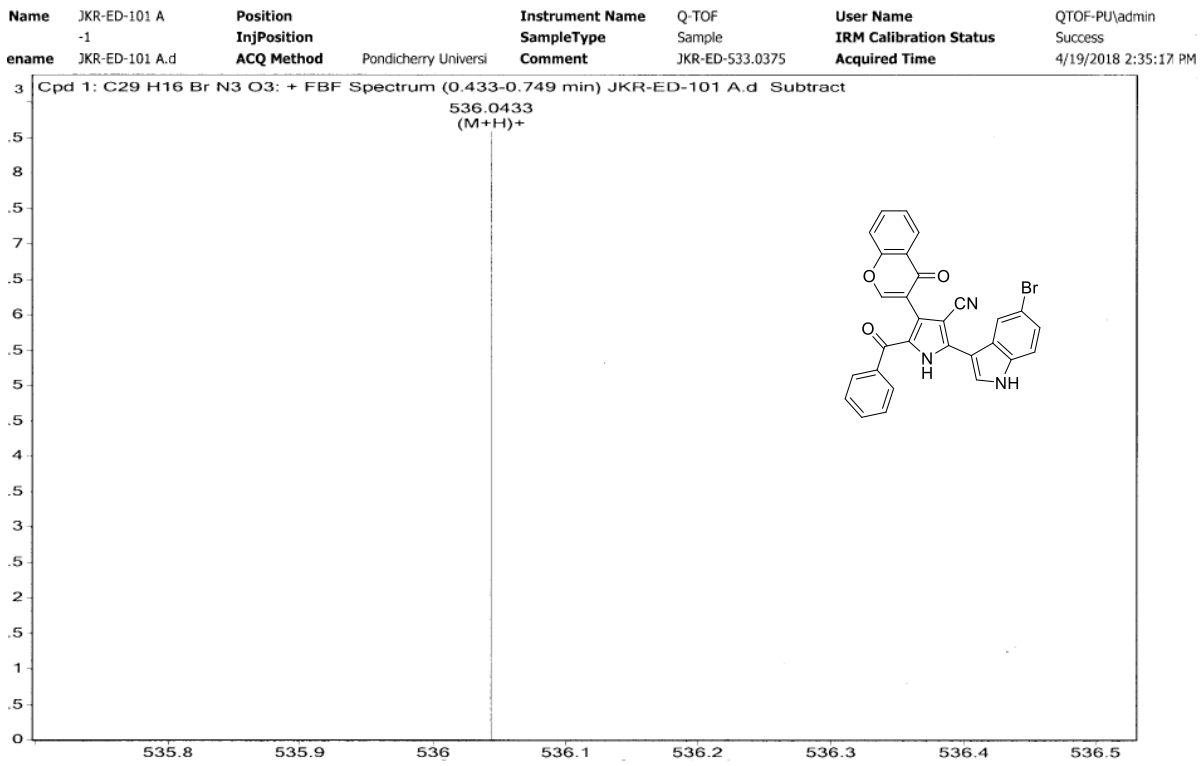
^{13}C{^{1}H} NMR spectrum of **4b** (100 MHz, DMSO-d_6)



DEPT 135 NMR spectrum of **4b** (100 MHz, DMSO-d_6)



HRMS (ESI) spectrum of **4b** (^{79}Br isotope)



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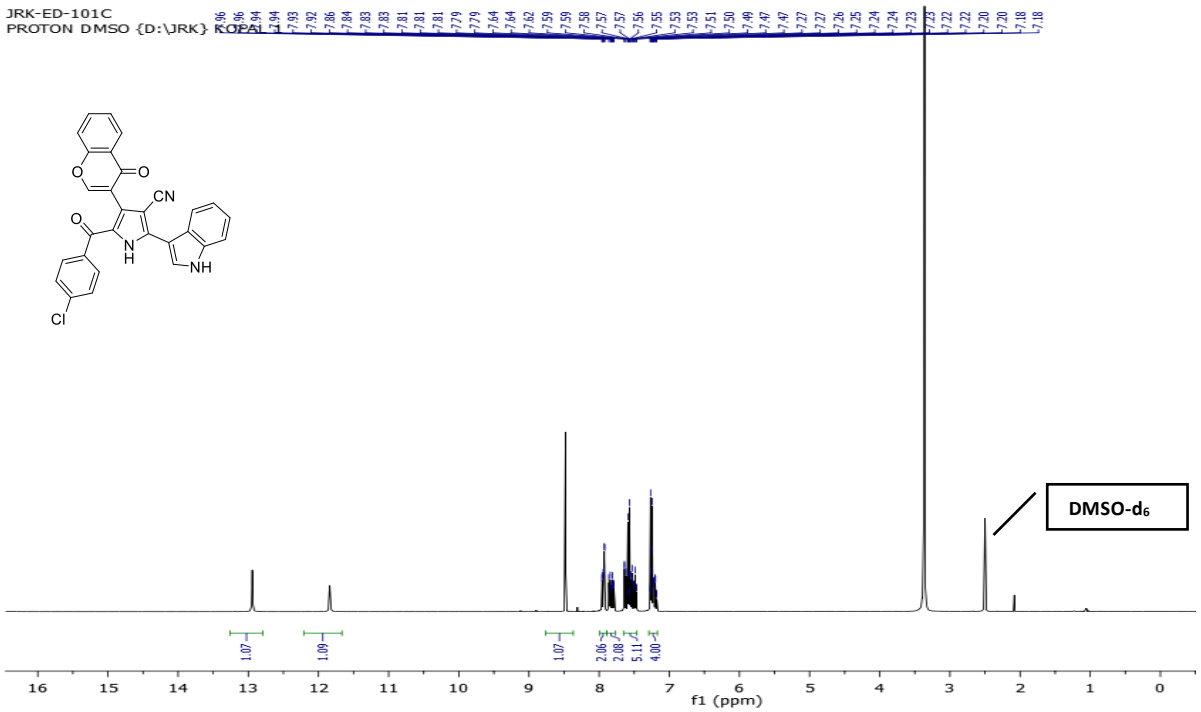
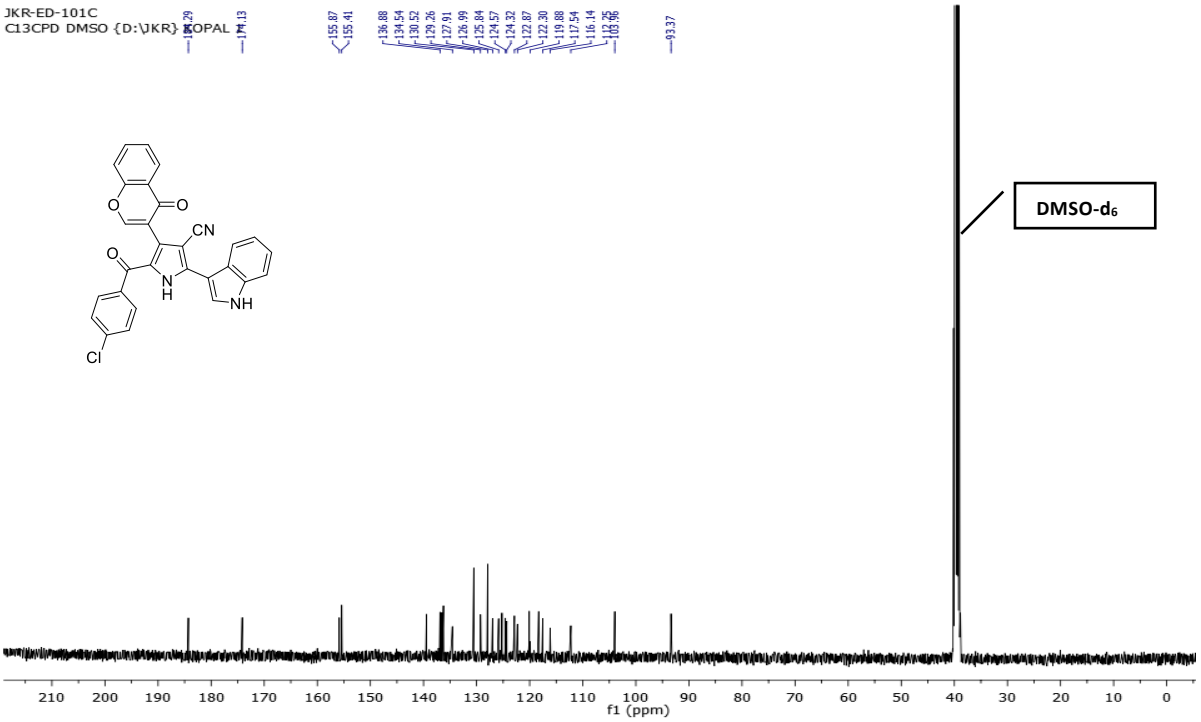
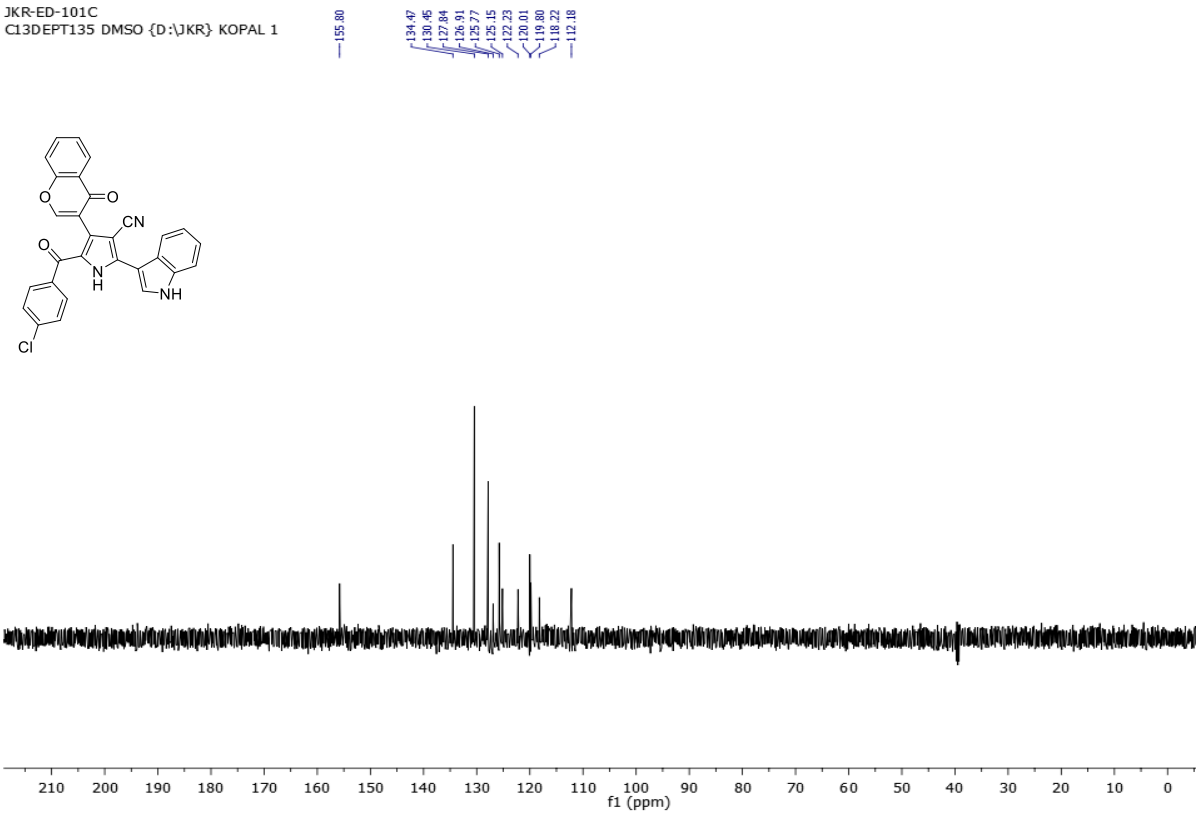


^{1}H NMR spectrum of **4c** (400 MHz, DMSO-d_6)



^{13}C{^{1}H} NMR spectrum of **4c** (100 MHz, DMSO-d_6)



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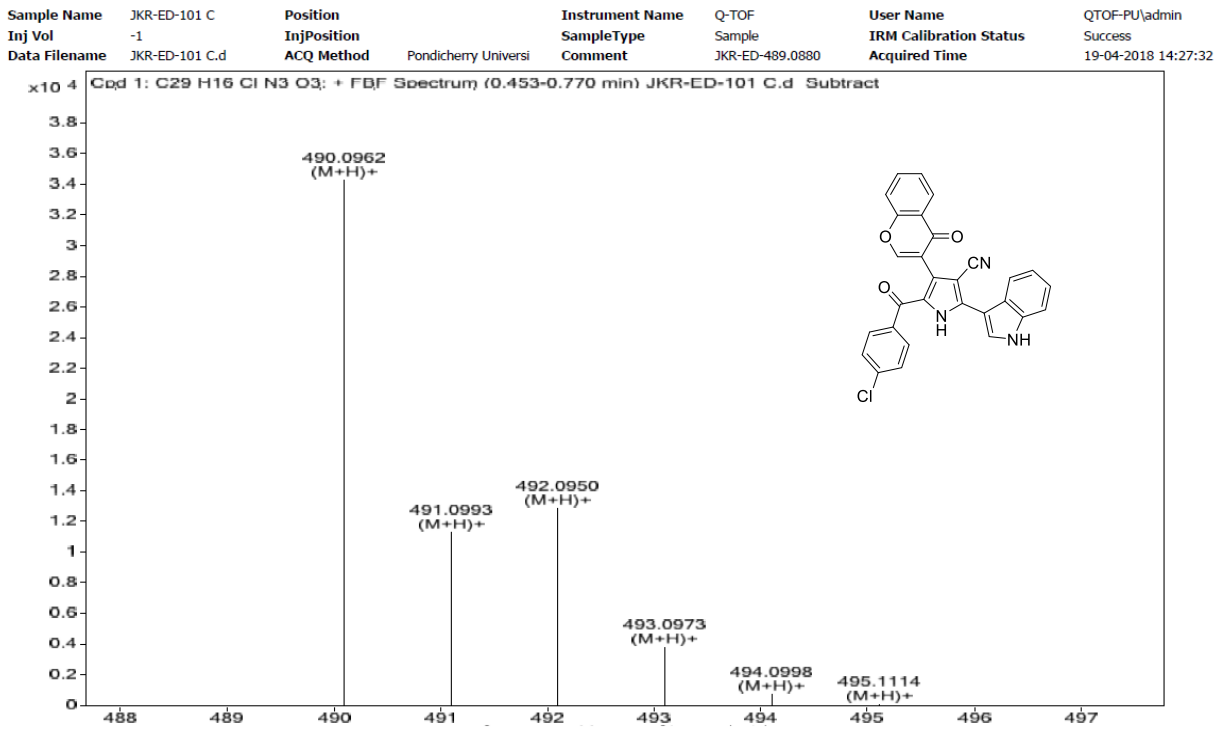
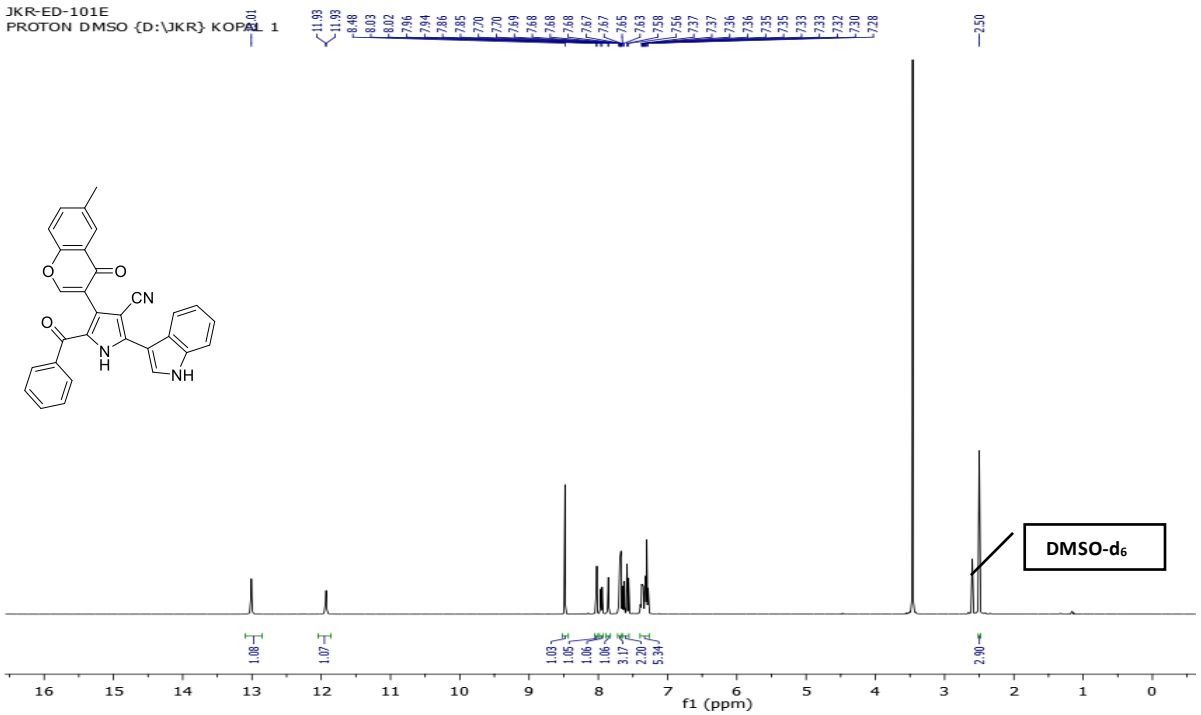


HRMS (ESI) spectrum of **4c**



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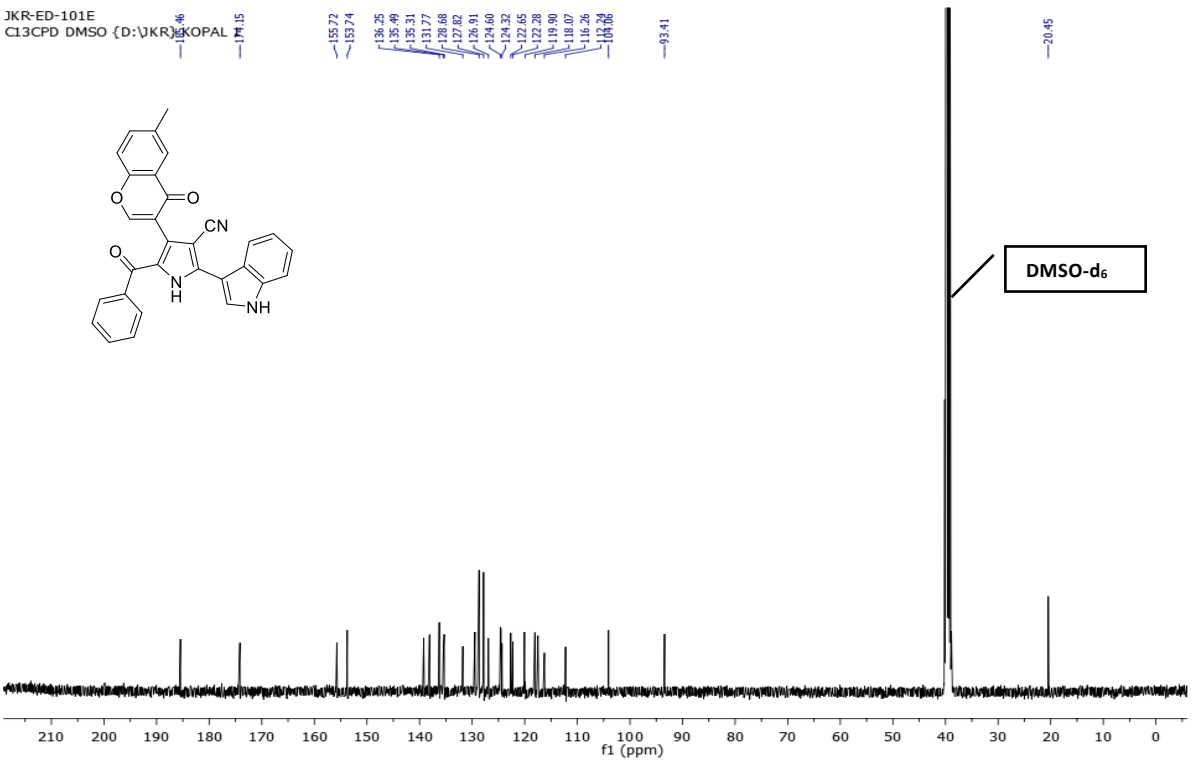

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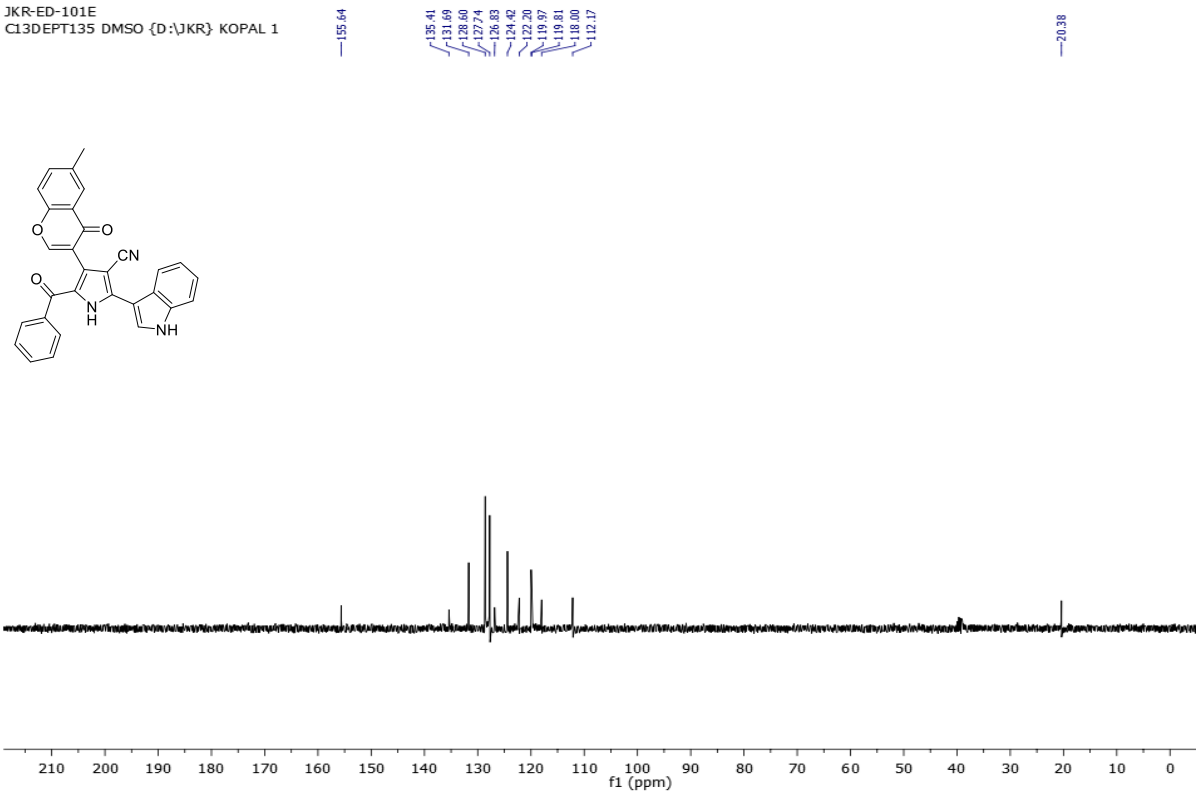

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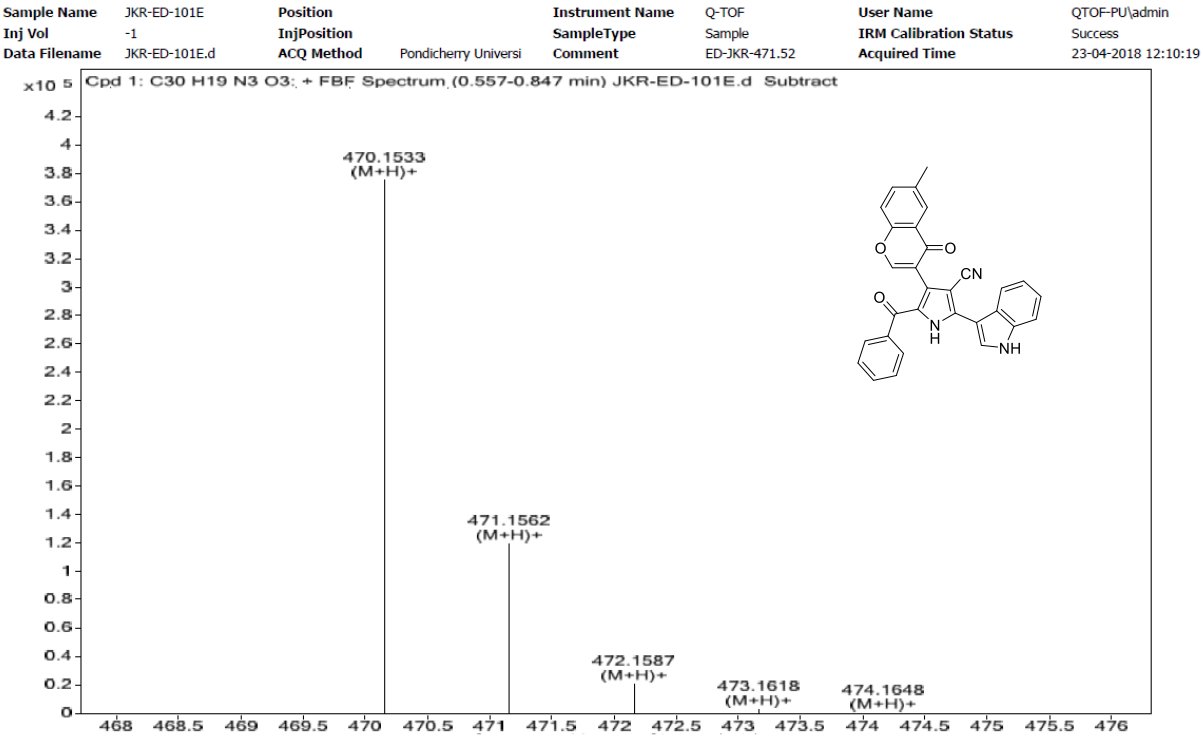
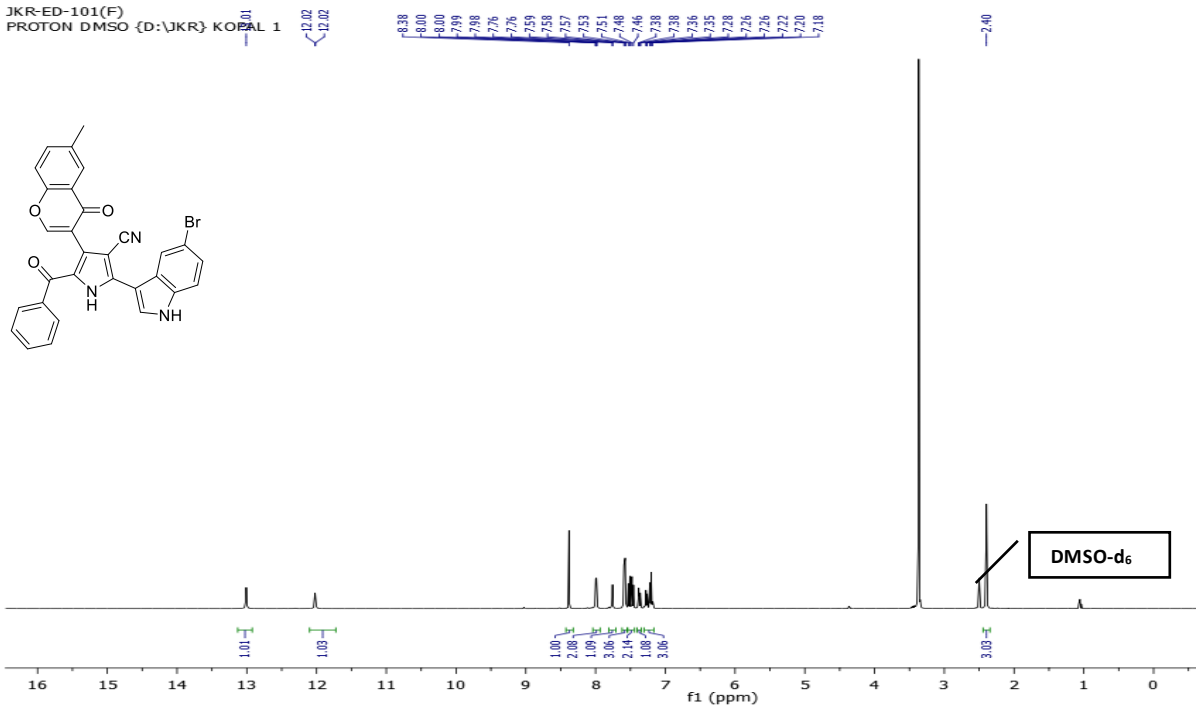
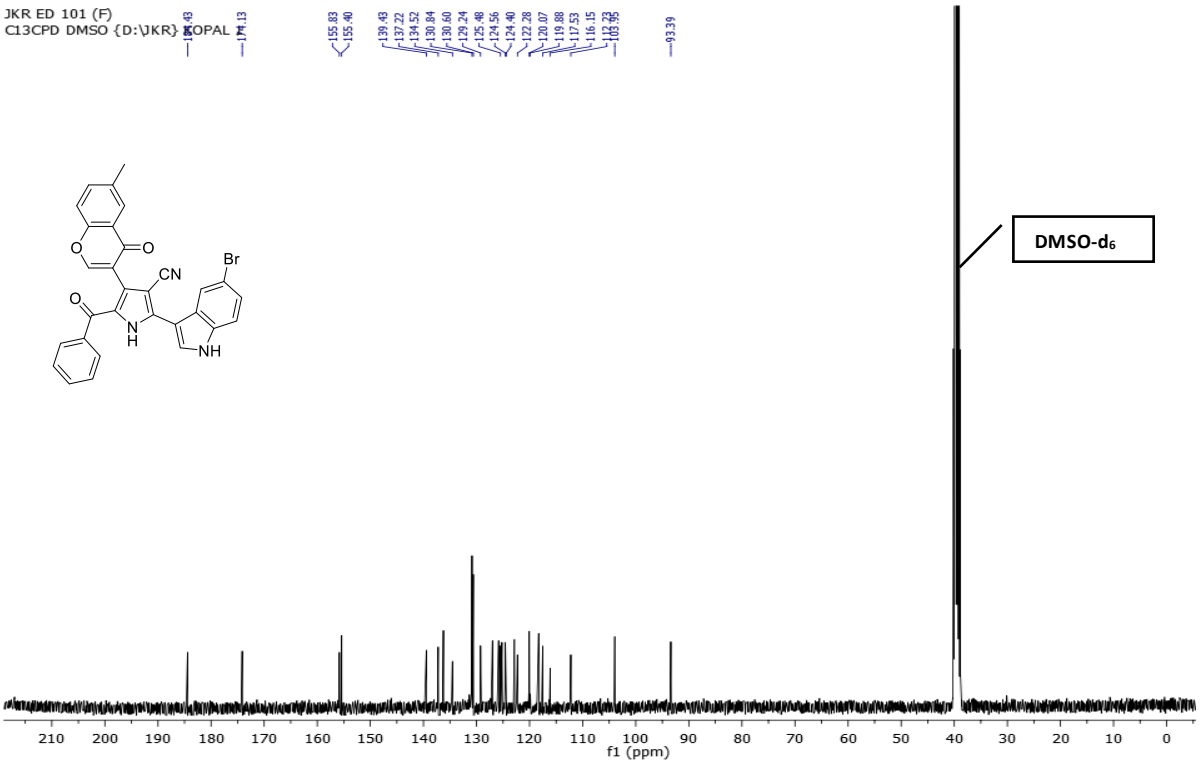


HRMS (ESI) spectrum of **4d**



^{1}H NMR spectrum of **4e** (400 MHz, DMSO-d_6)



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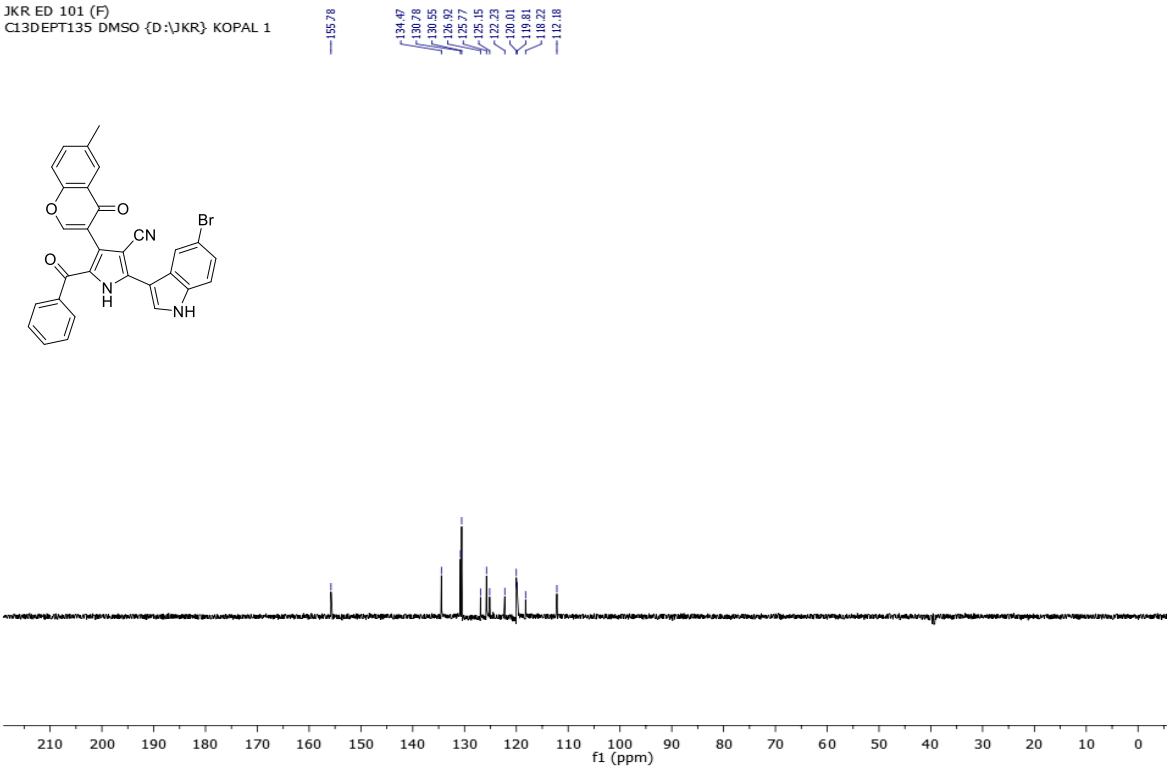

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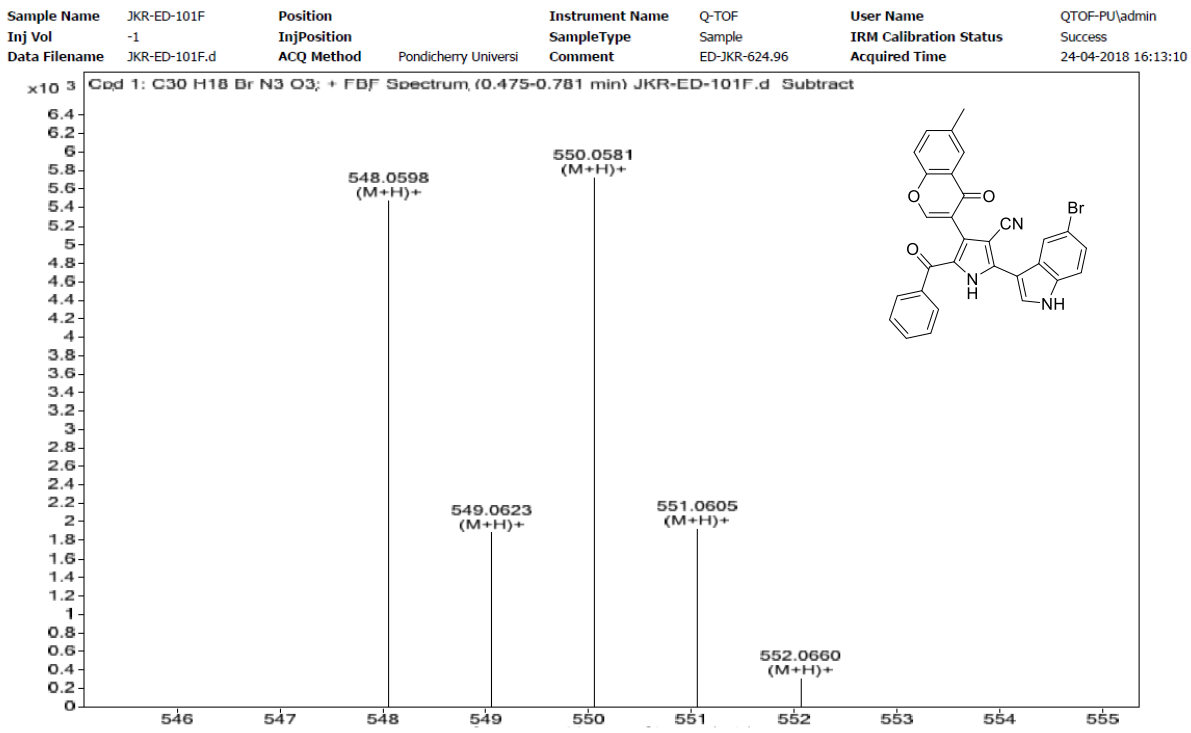
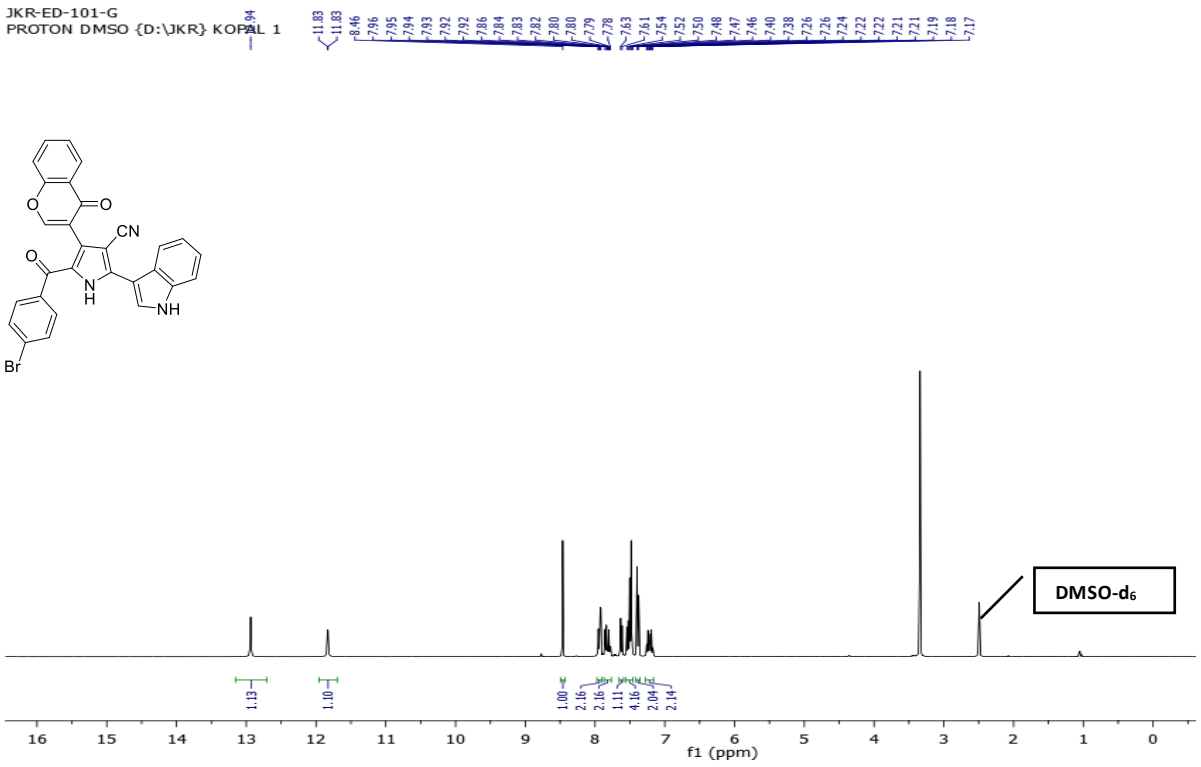
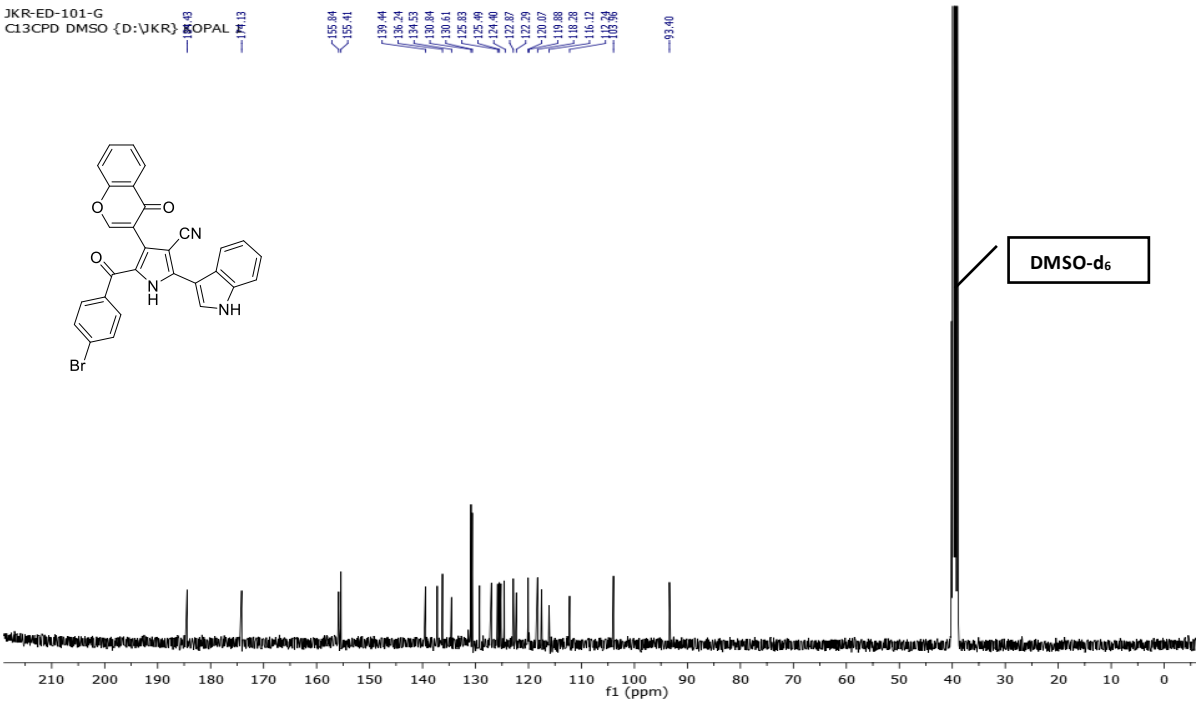


HRMS (ESI) spectrum of **4e**



^{1}H NMR spectrum of **4f** (400 MHz, DMSO-d_6)



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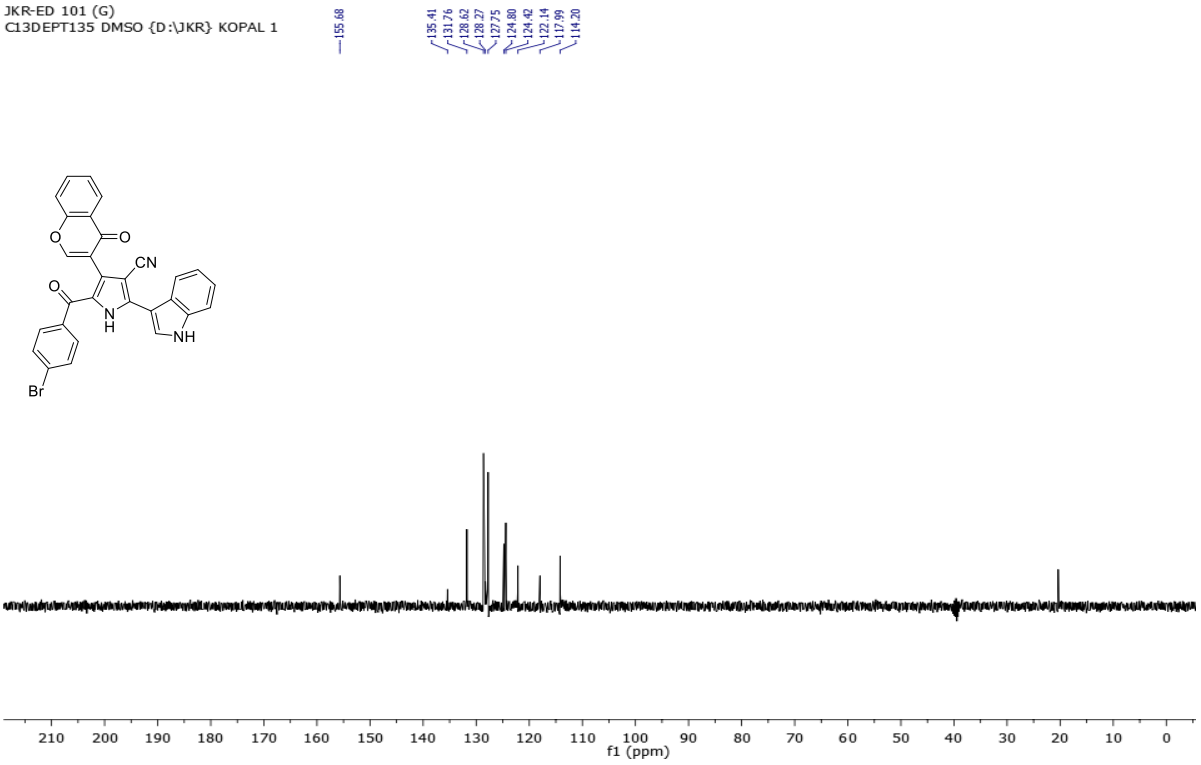

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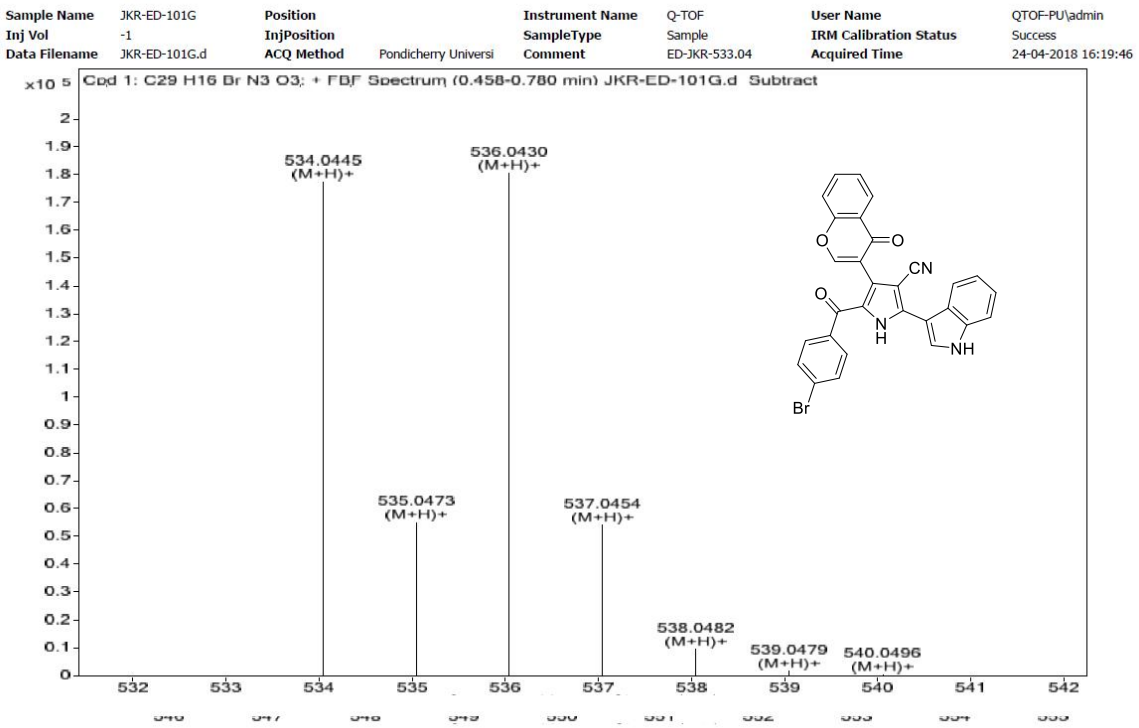
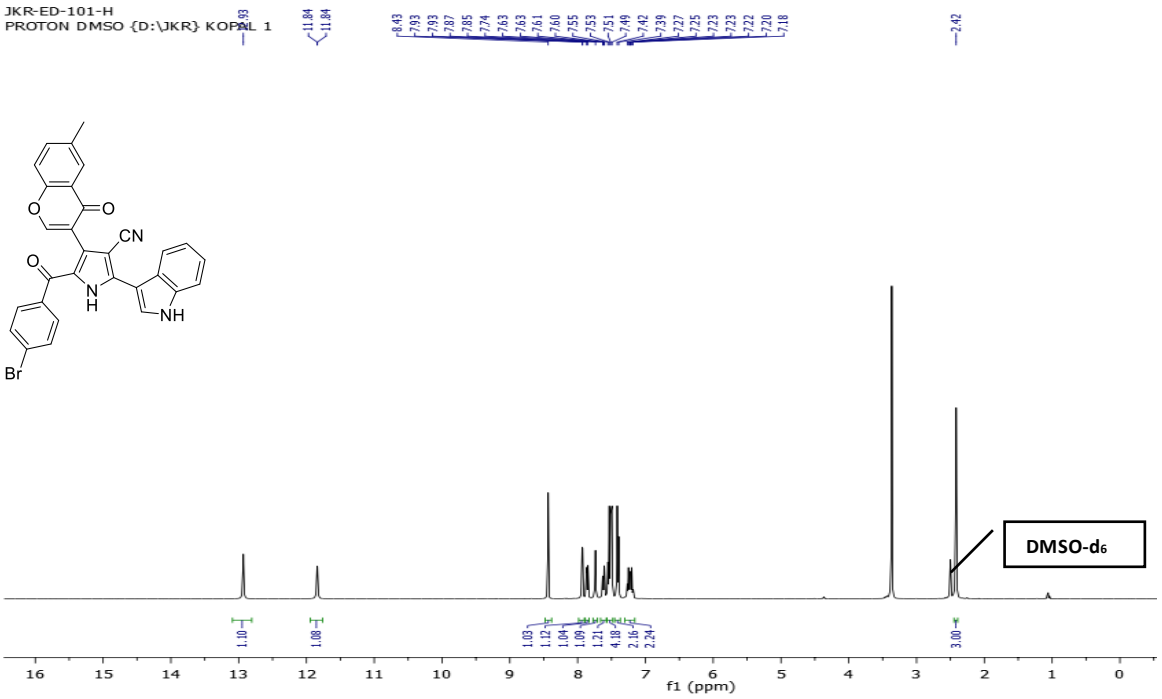


HRMS (ESI) spectrum of **4f**



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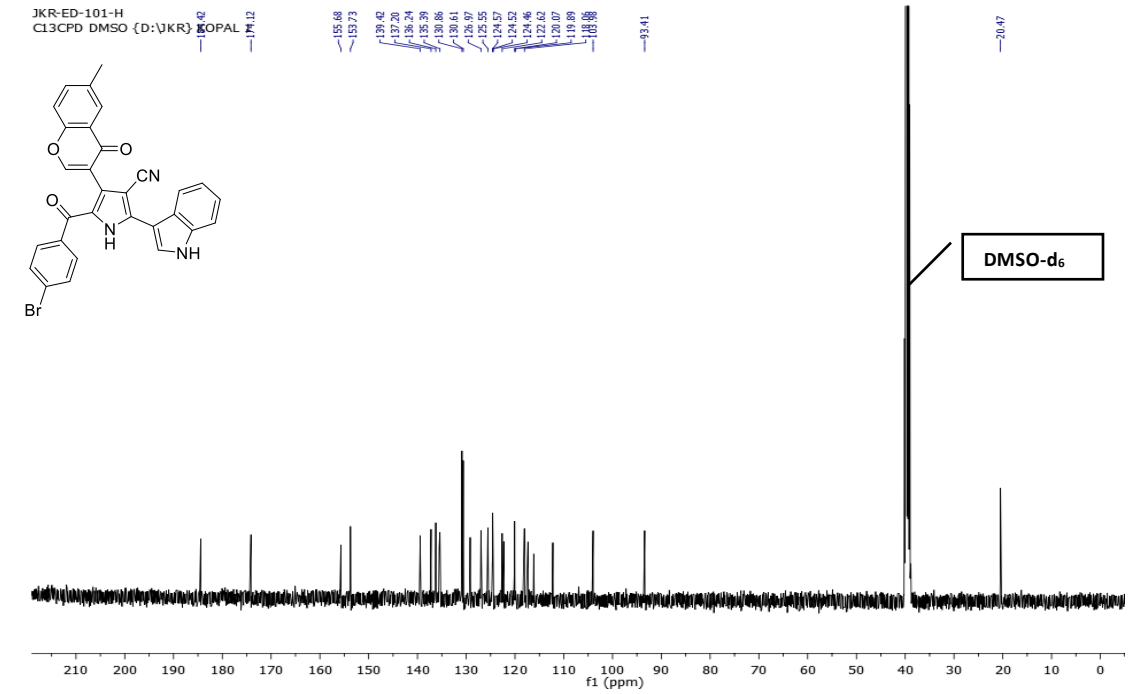

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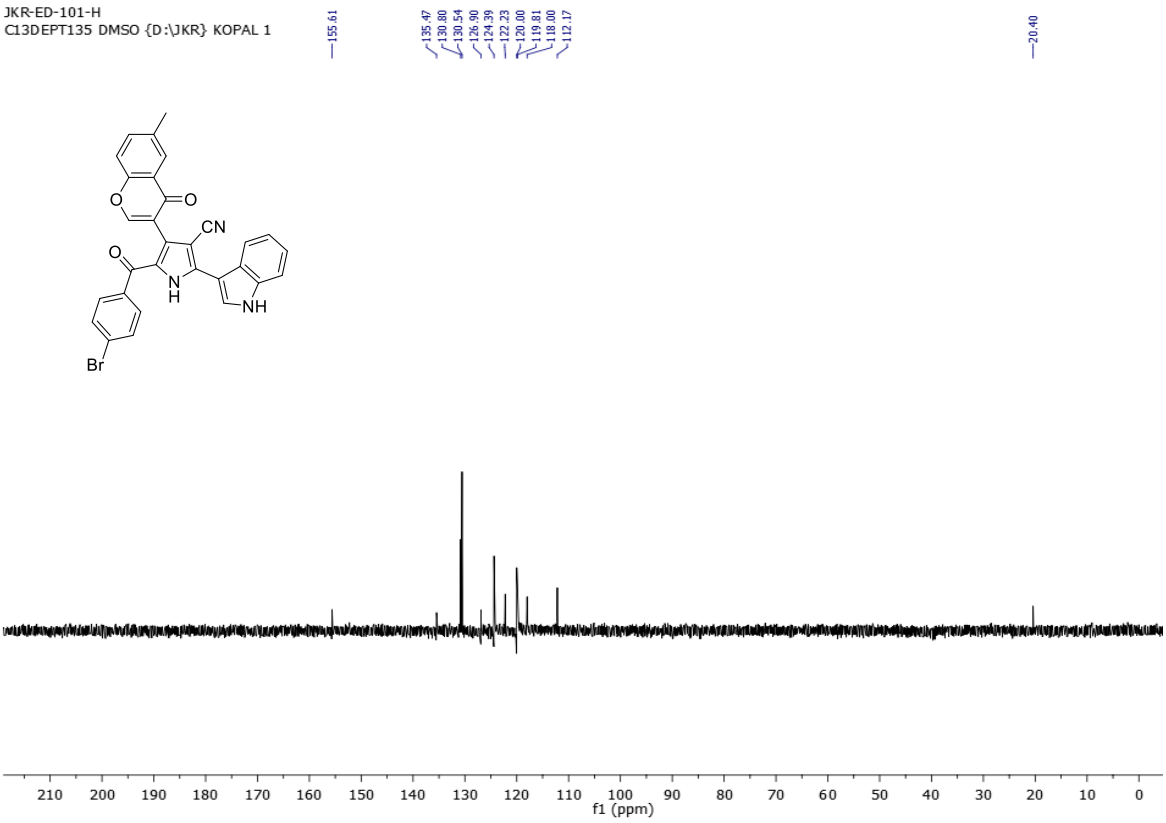

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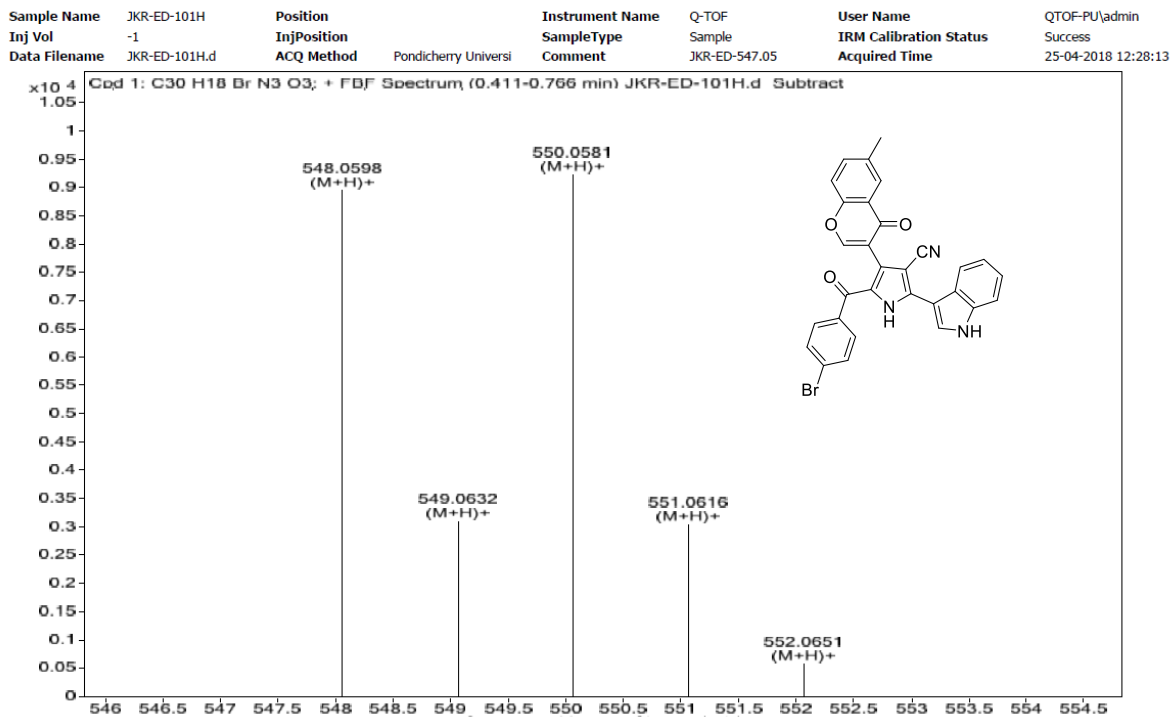
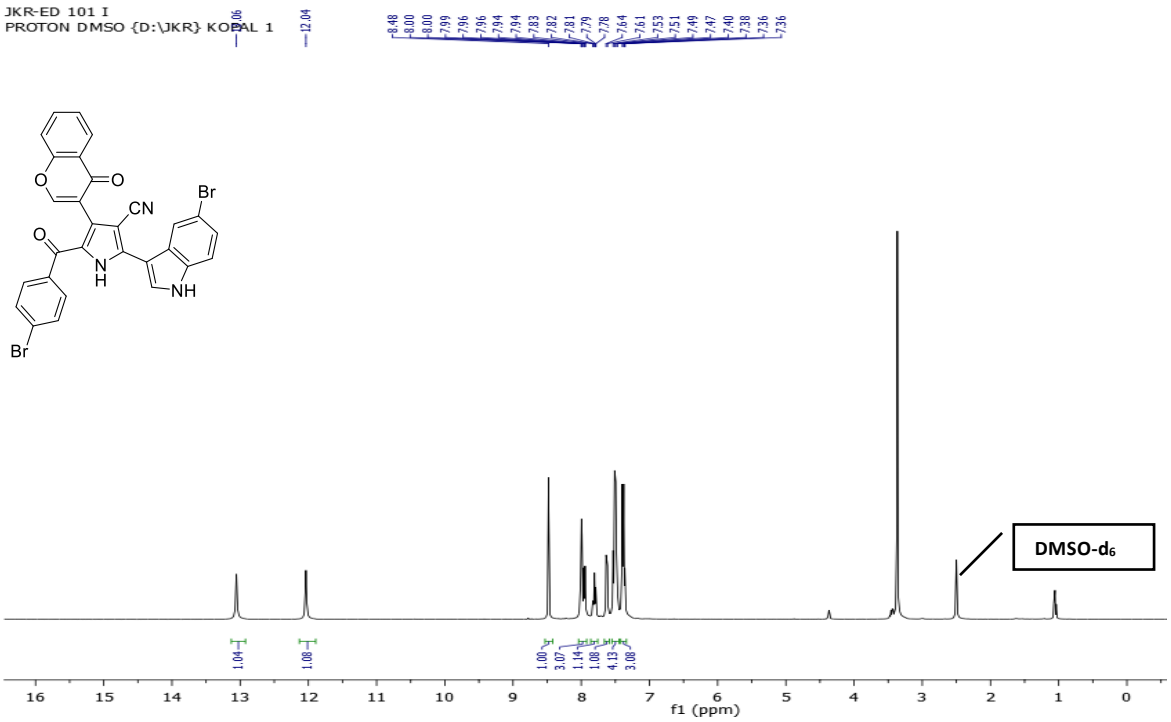
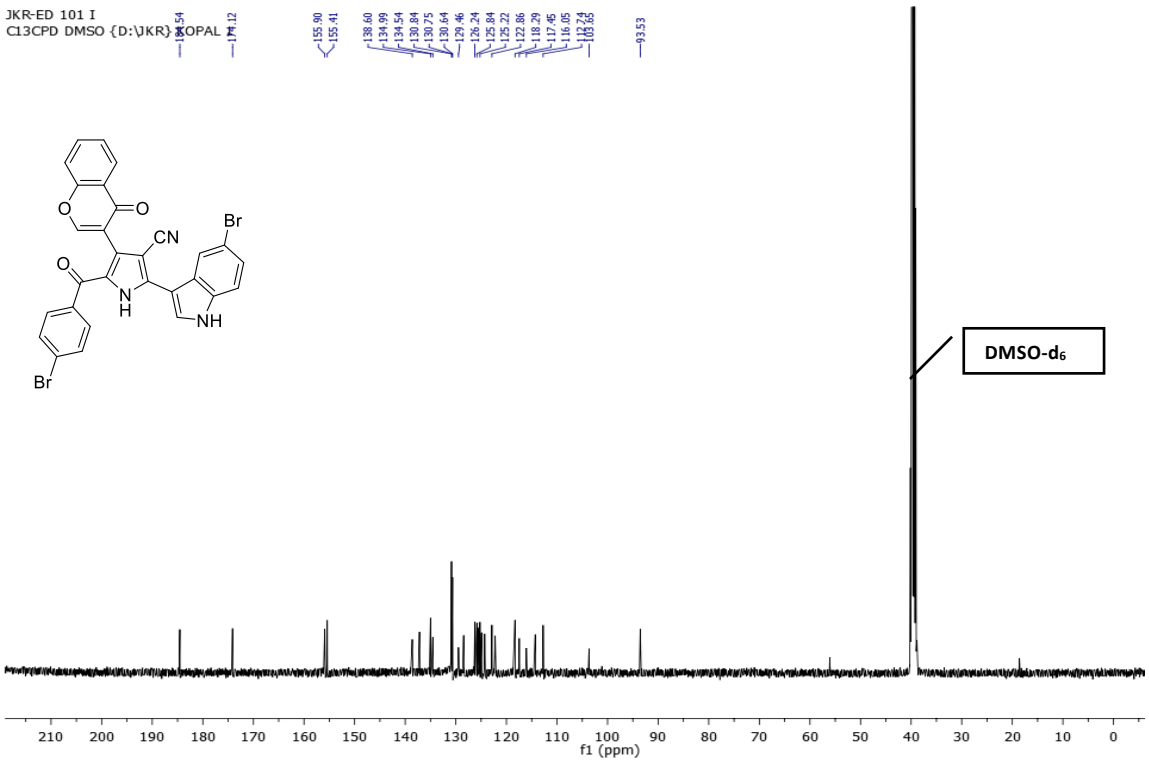


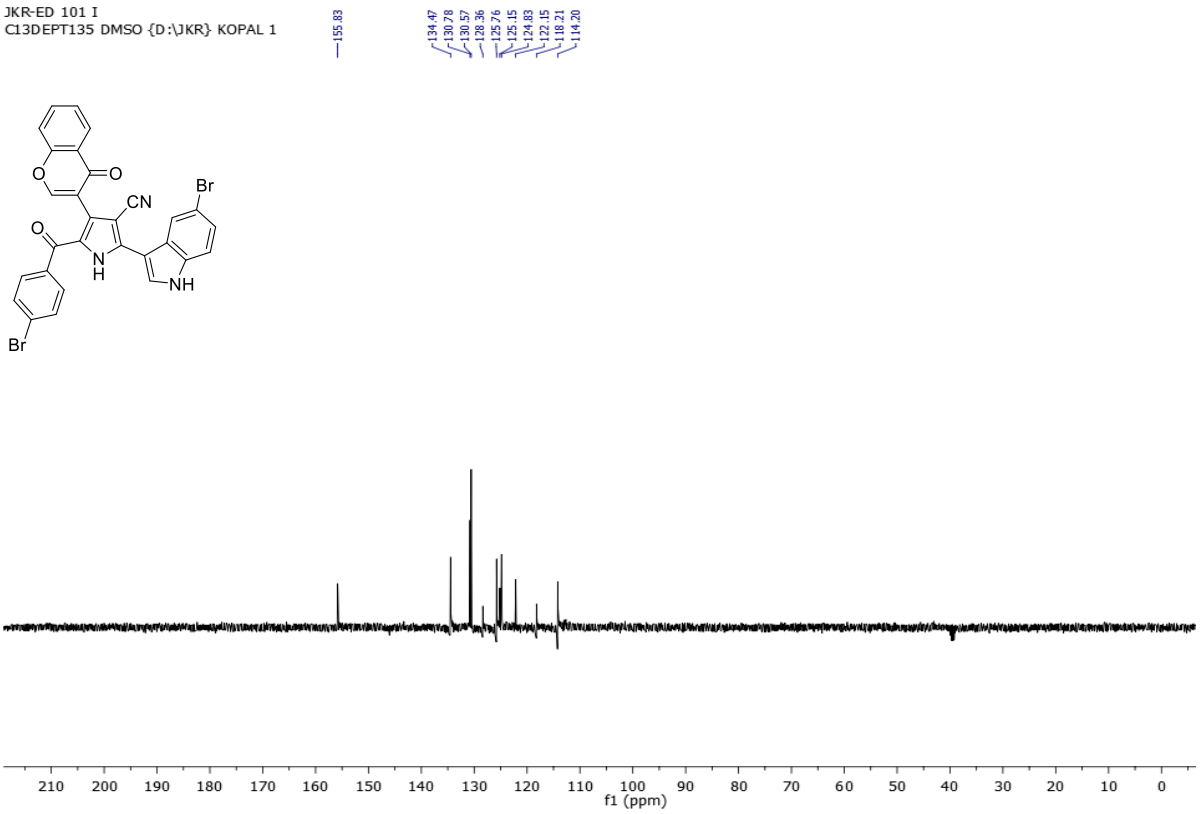
HRMS (ESI) spectrum of **4g**



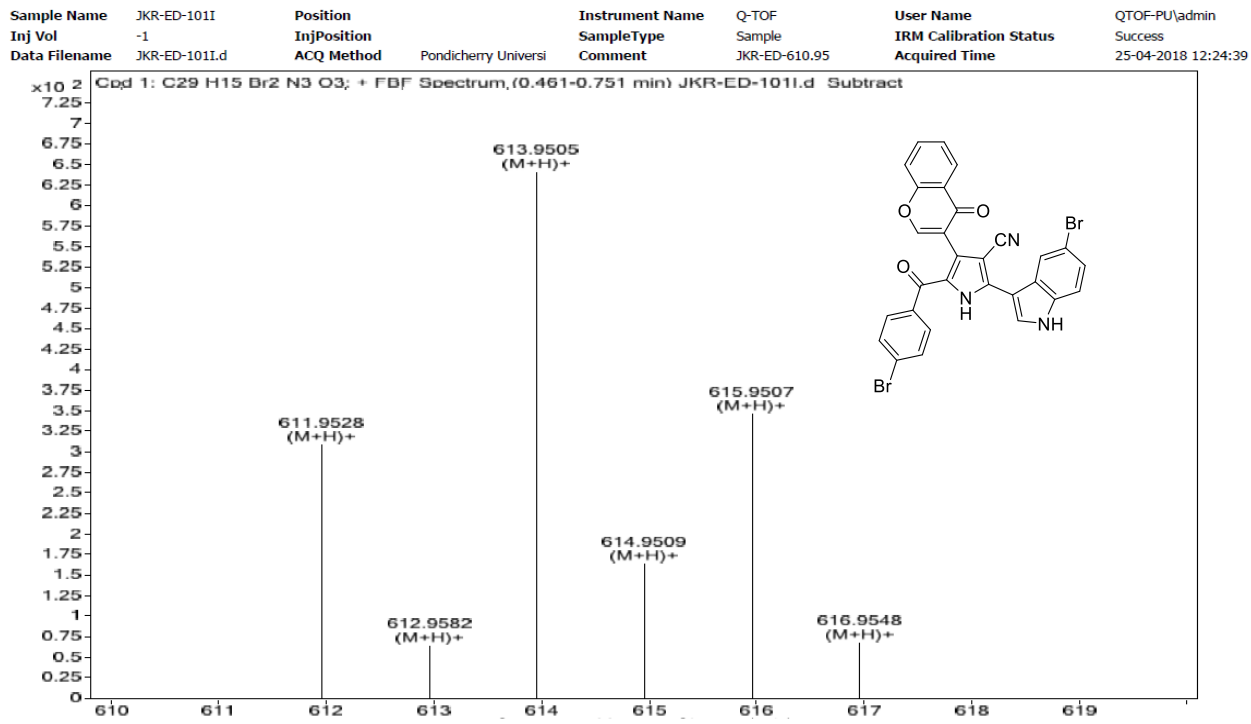
^{1}H NMR spectrum of **4h** (400 MHz, DMSO-d_6)



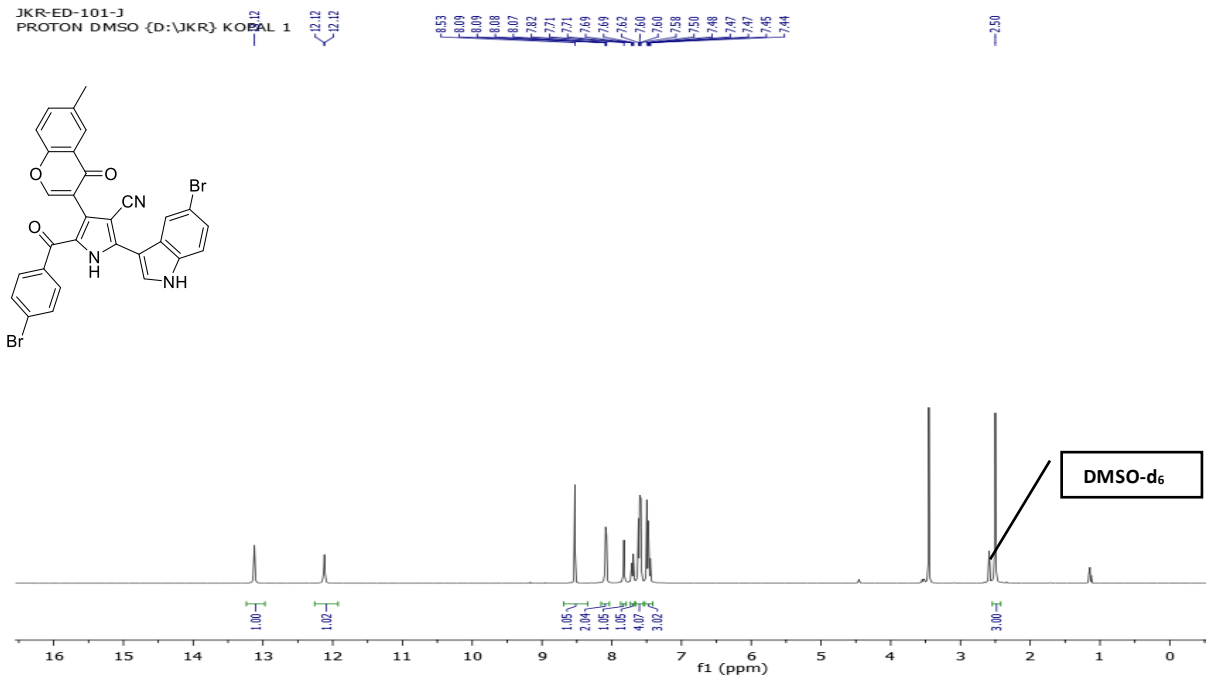
^{13}C{^{1}H} NMR spectrum of **4h** (100 MHz, DMSO-d_6)



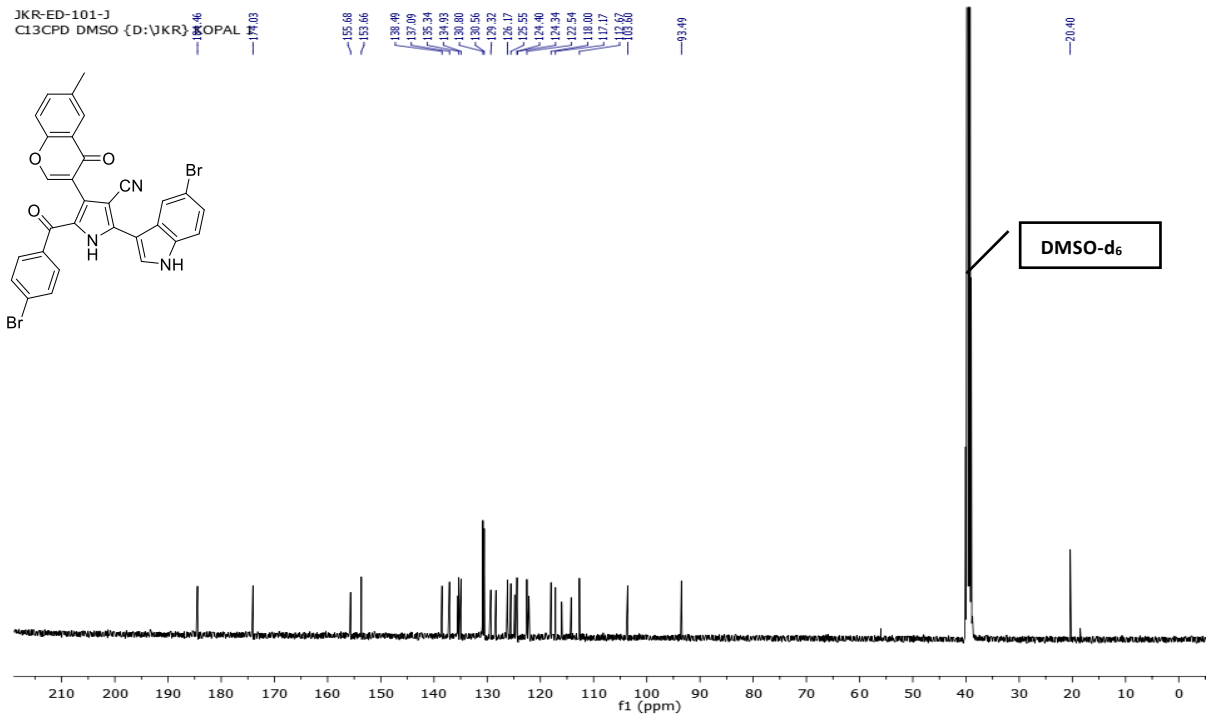
DEPT 135 NMR spectrum of **4h** (100 MHz, DMSO-d_6)



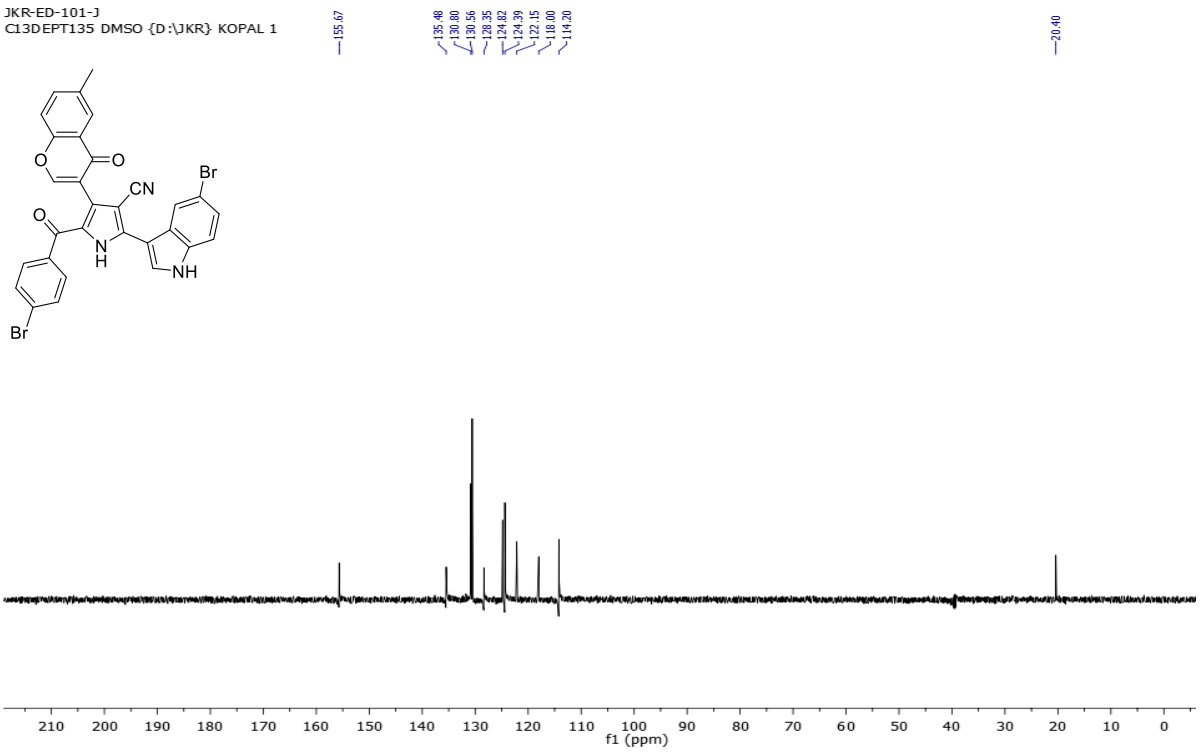
HRMS (ESI) spectrum of **4h**



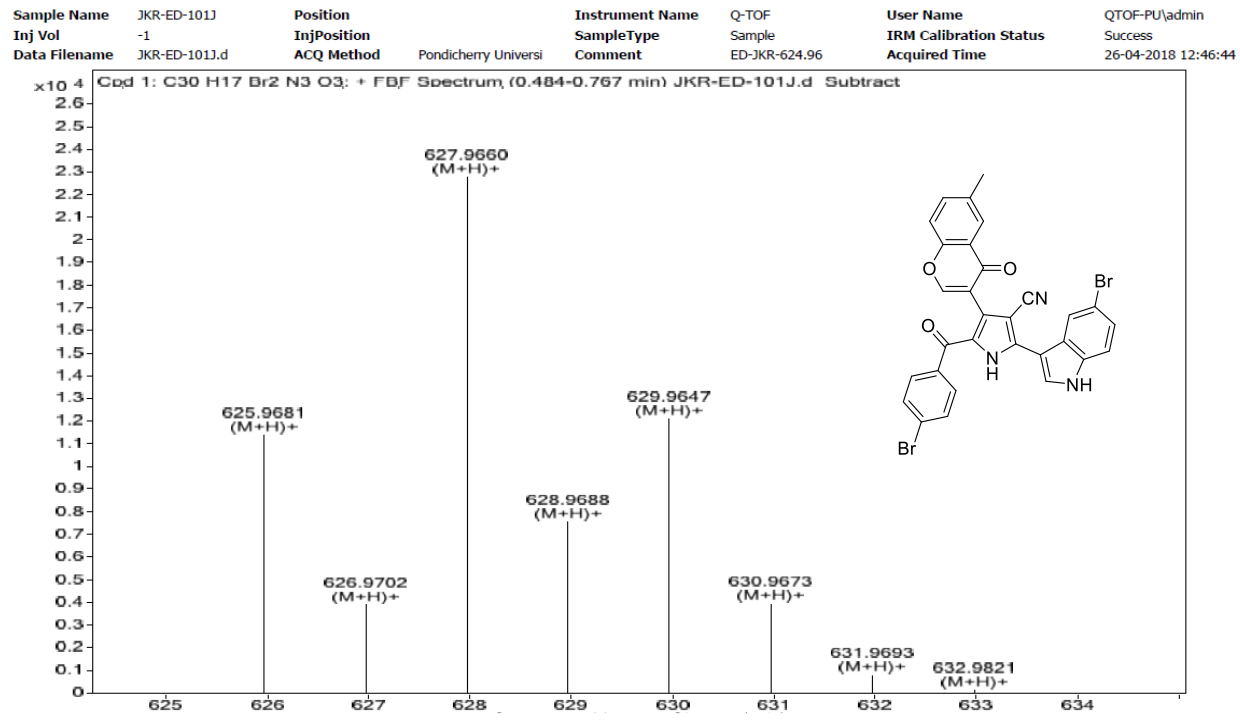
^{1}H NMR spectrum of **4i** (400 MHz, DMSO-d_6)



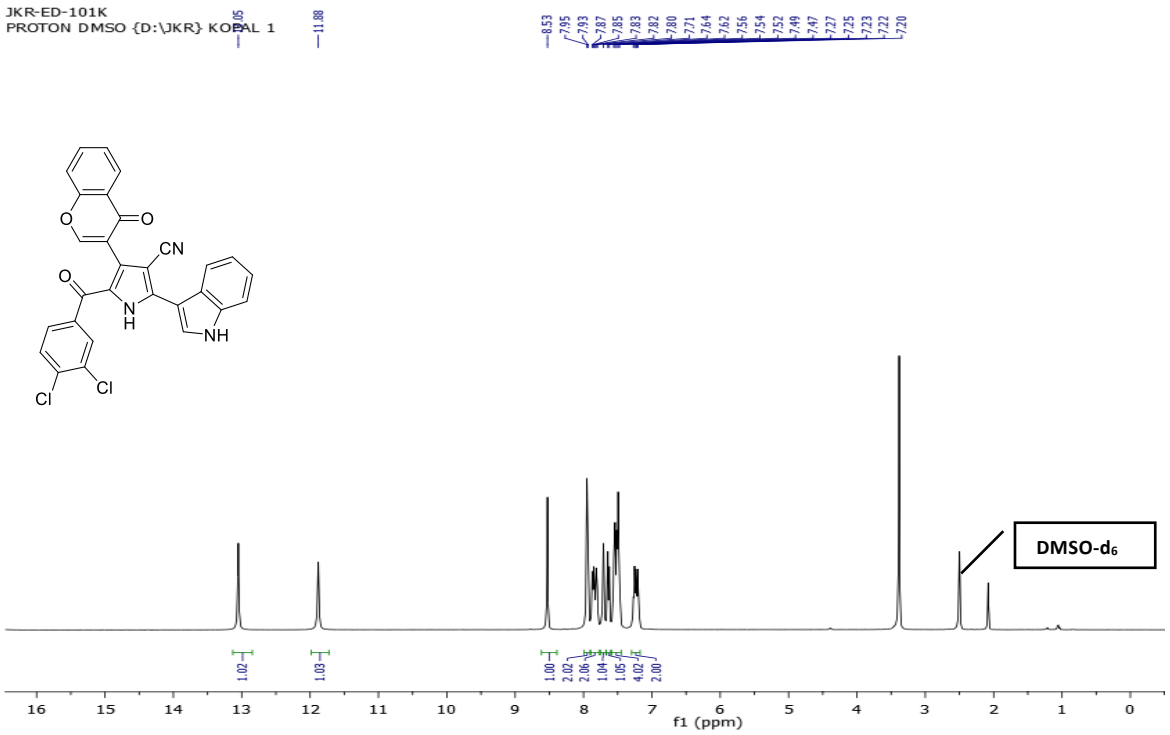
^{13}C{^{1}H} NMR spectrum of **4i** (100 MHz, DMSO-d_6)



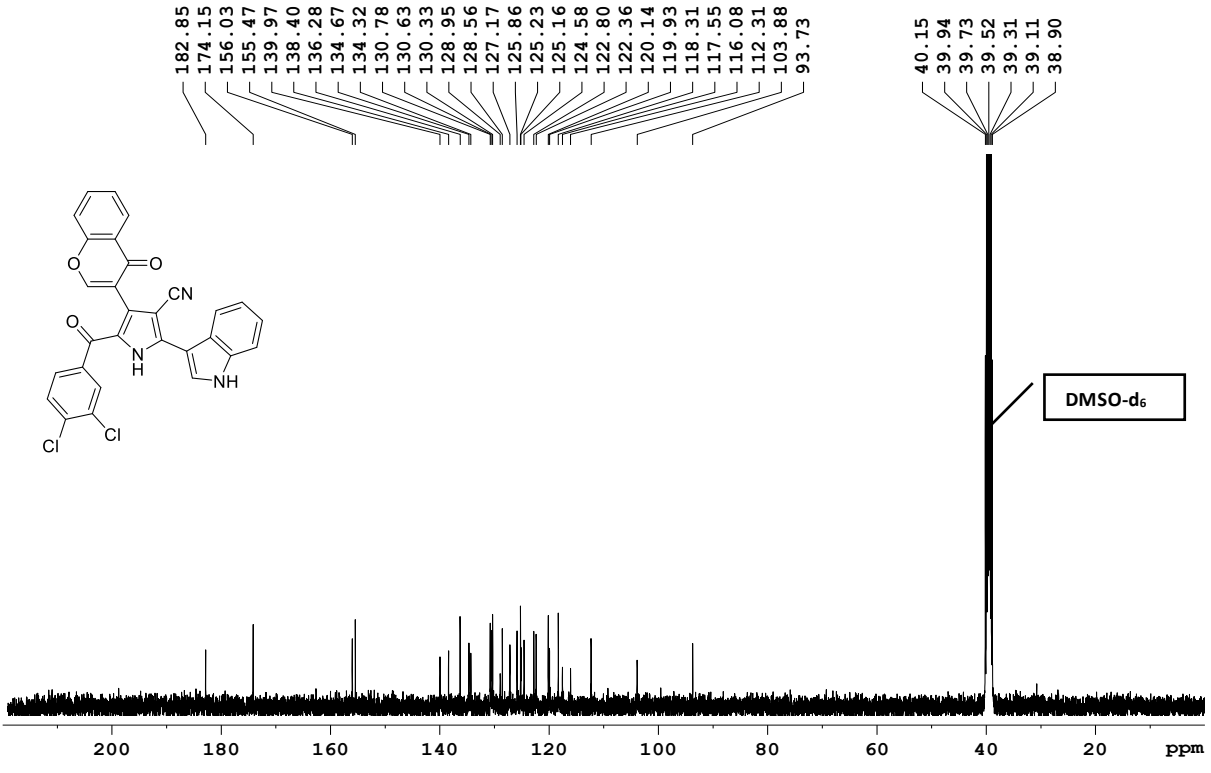
DEPT 135 NMR spectrum of **4i** (100 MHz, DMSO-d_6)



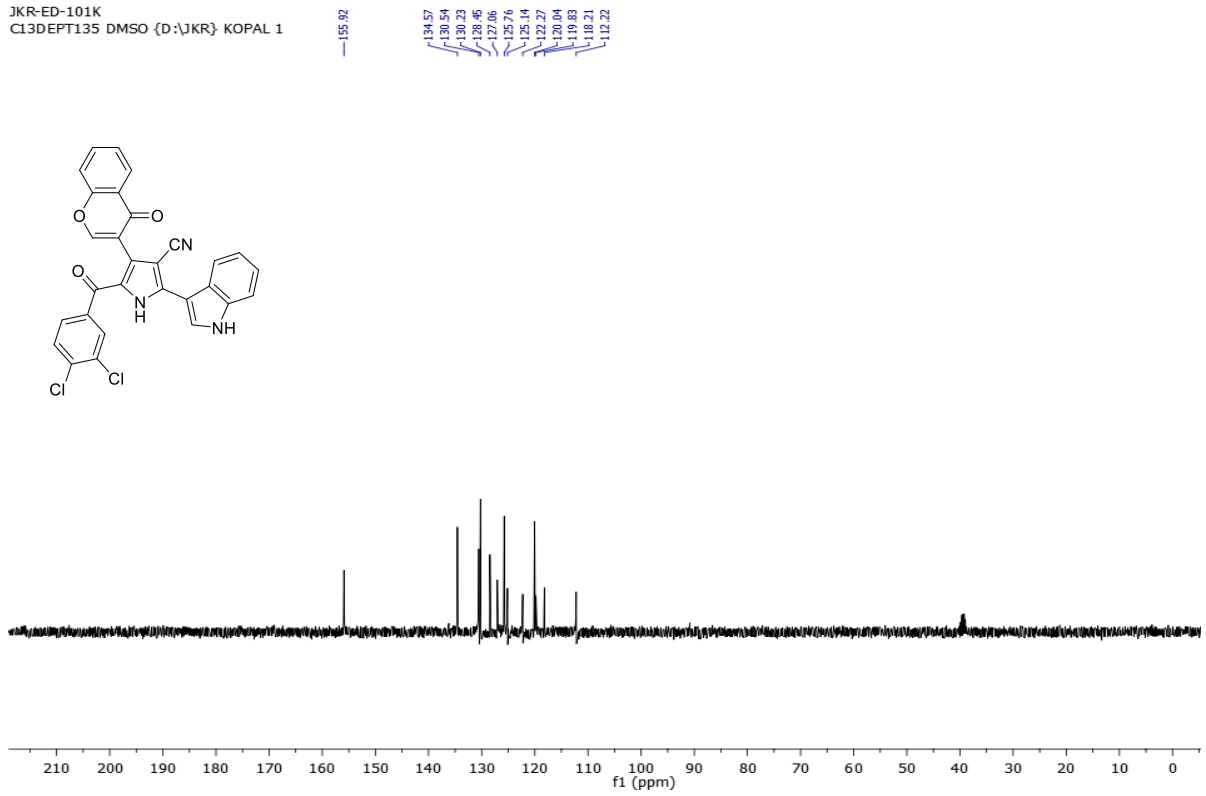
HRMS (ESI) spectrum of **4i**



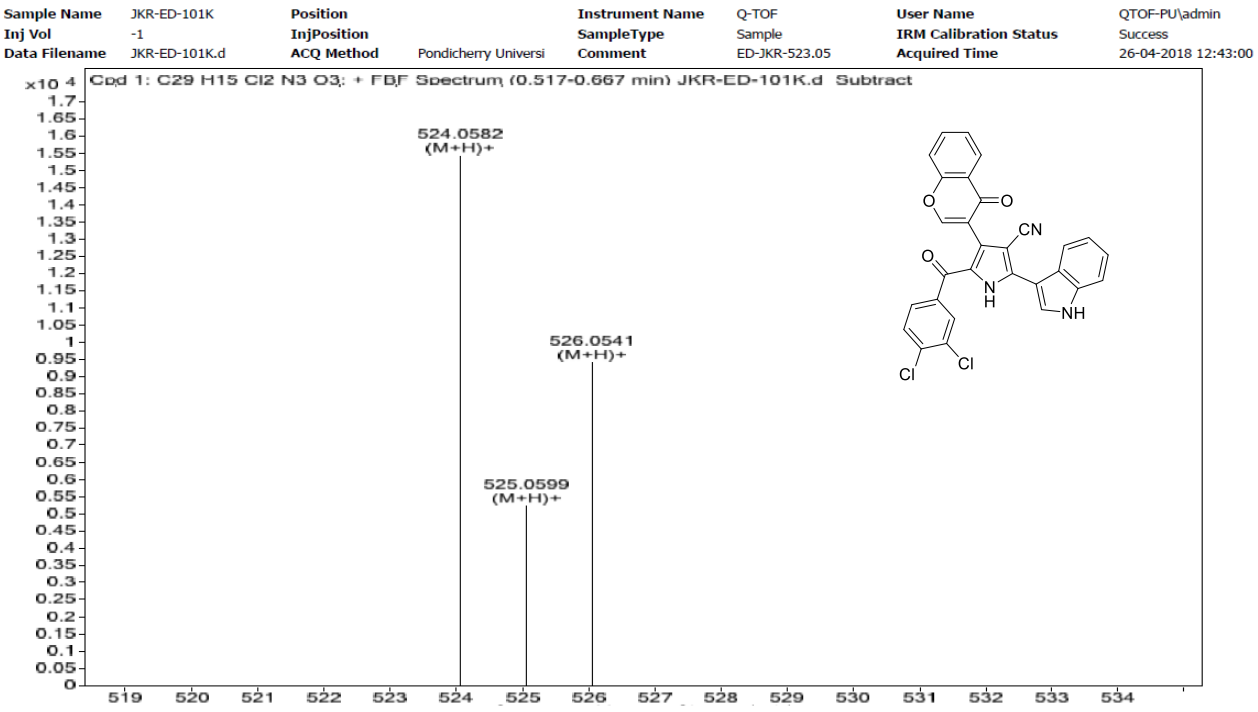
^{1}H NMR spectrum of **4j** (400 MHz, DMSO-d_6)



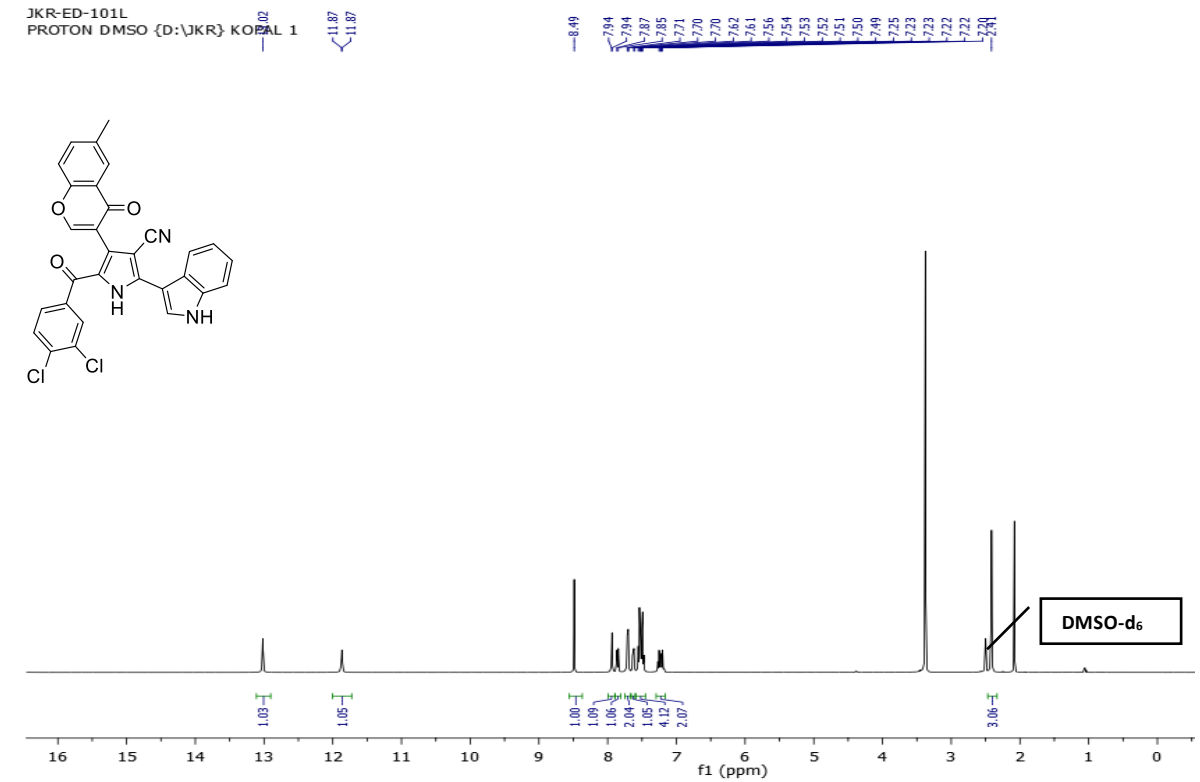
^{13}C{^{1}H} NMR spectrum of **4j** (100 MHz, DMSO-d_6)



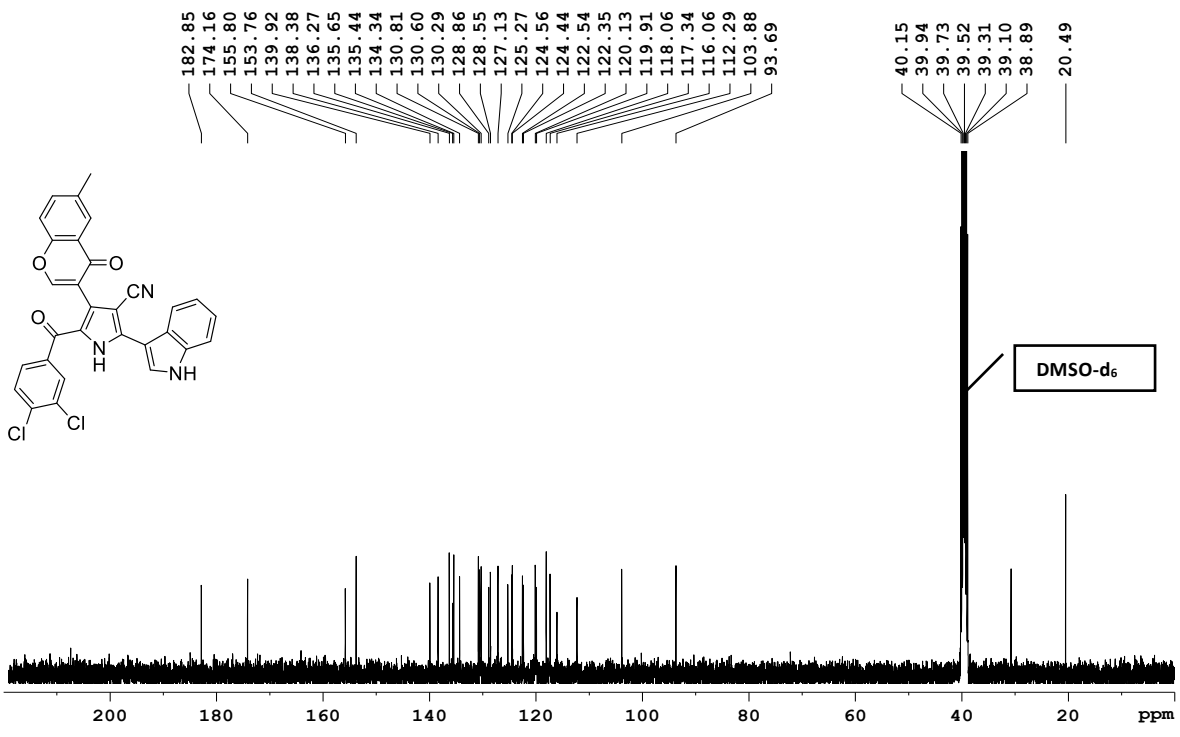
DEPT 135 NMR spectrum of **4j** (100 MHz, DMSO-d_6)



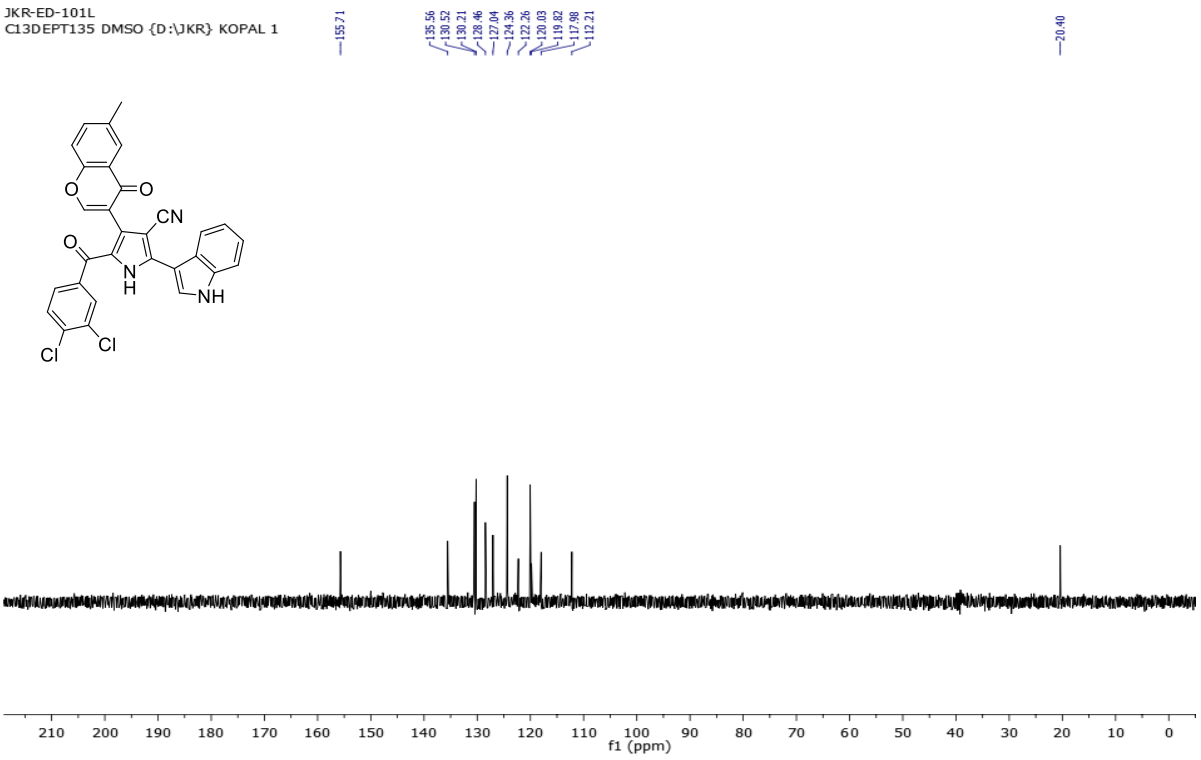
HRMS (ESI) spectrum of **4j**



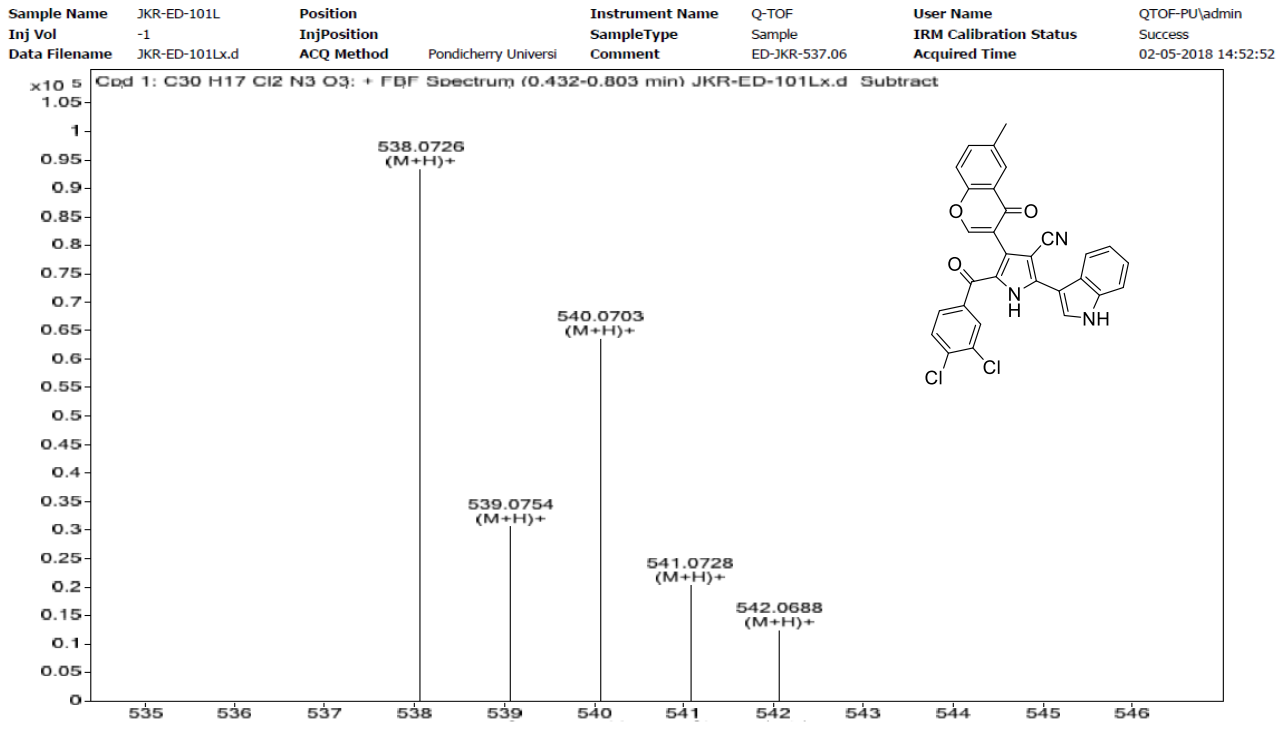
^{1}H NMR spectrum of **4k** (400 MHz, DMSO-d_6)



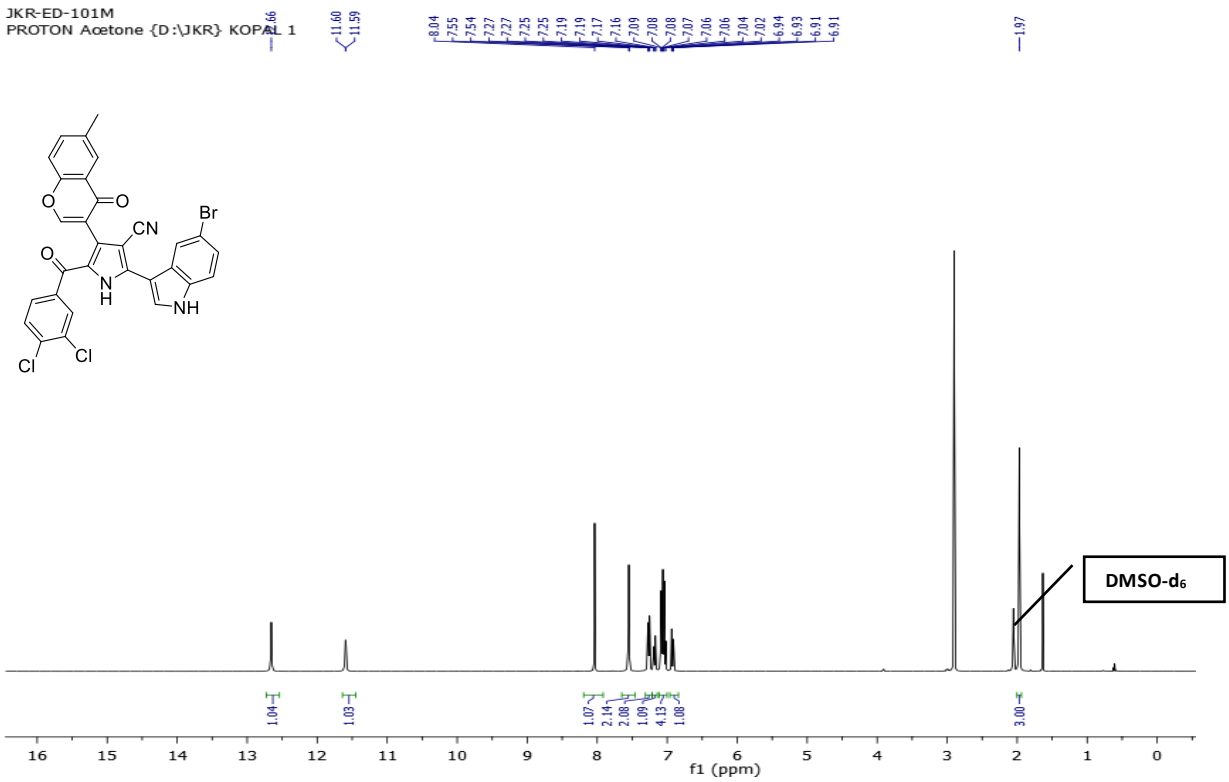
^{13}C{^{1}H} NMR spectrum of **4k** (100 MHz, DMSO-d_6)



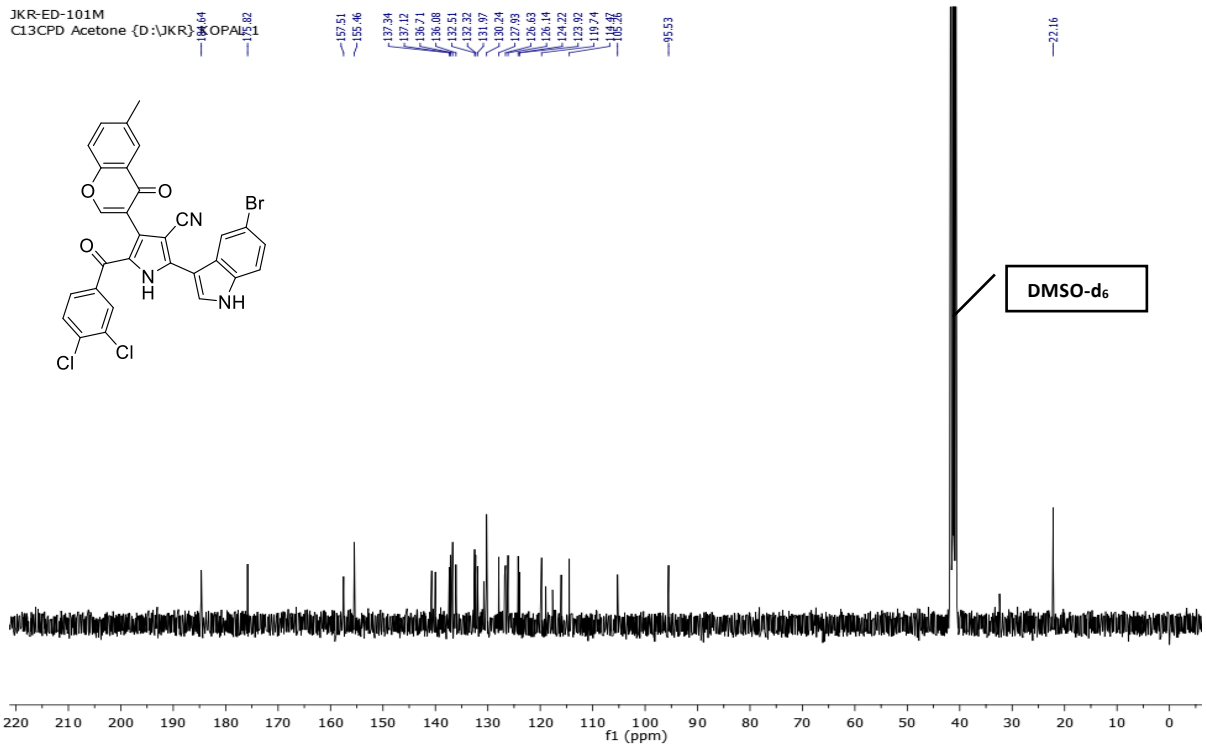
DEPT 135 NMR spectrum of **4k** (100 MHz, DMSO-d_6)



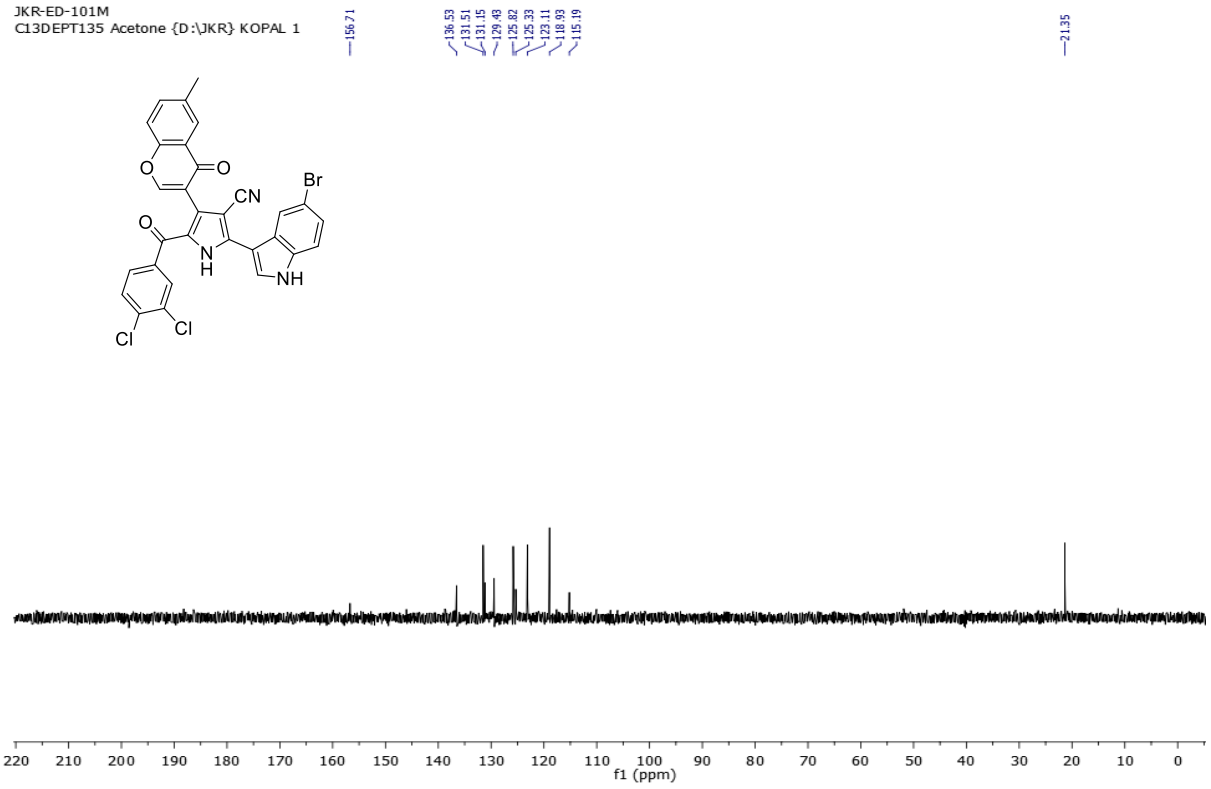
HRMS (ESI) spectrum of **4k**



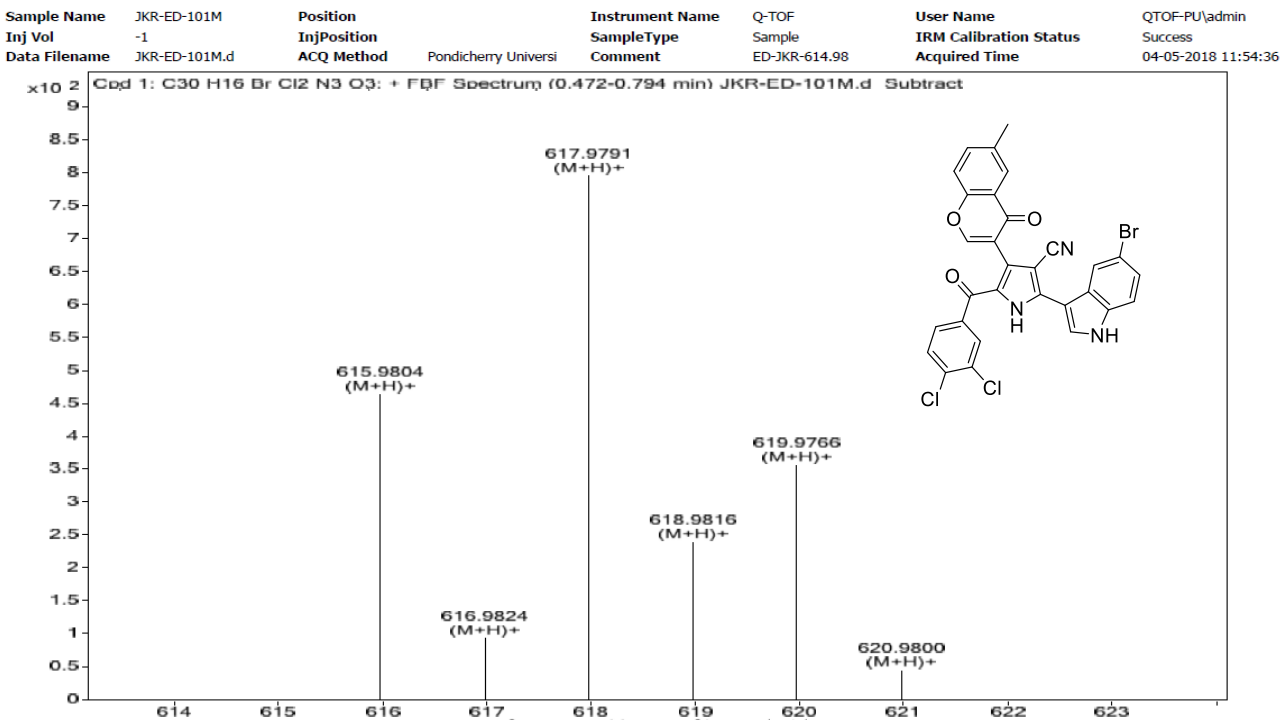
^{1}H NMR spectrum of **4l** (400 MHz, DMSO-d_6)



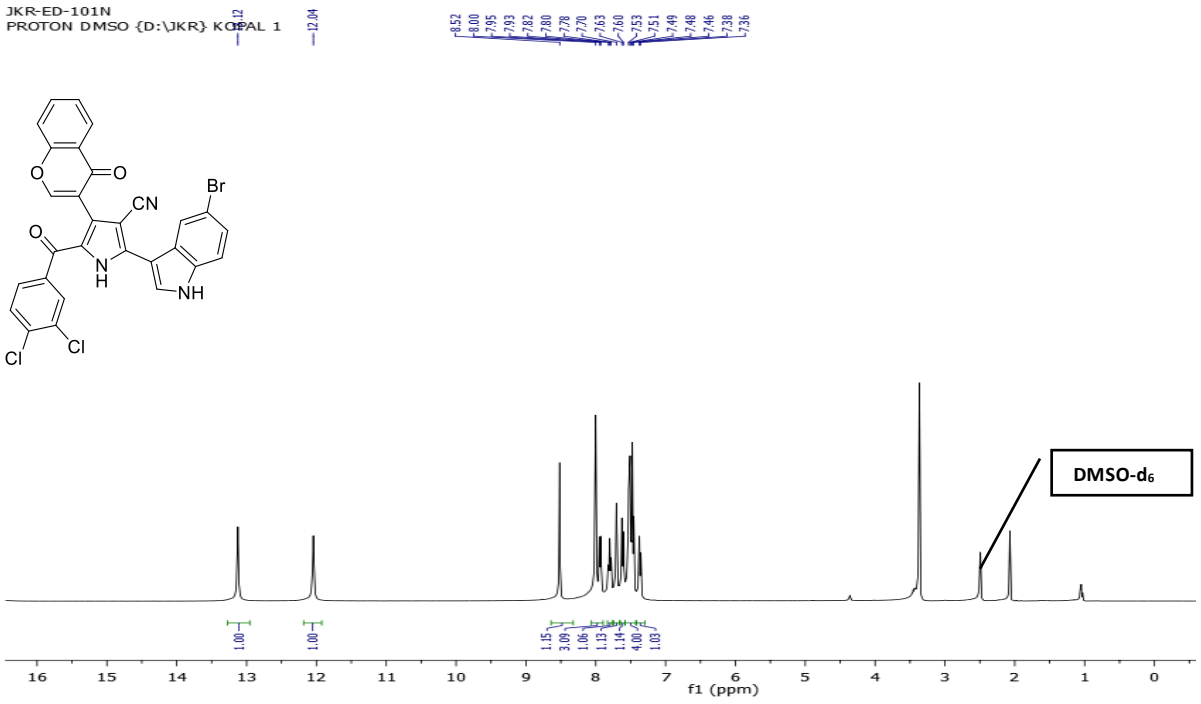
^{13}C{^{1}H} NMR spectrum of **4l** (100 MHz, DMSO-d_6)



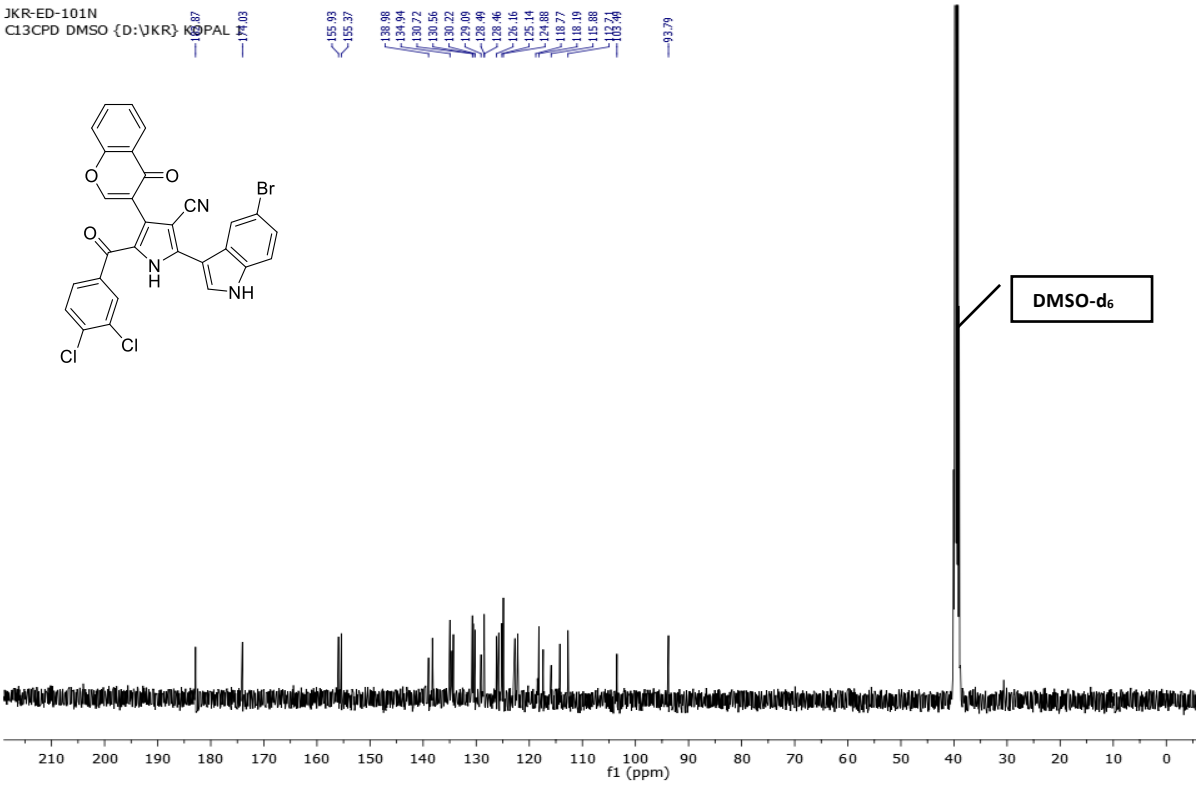
DEPT 135 NMR spectrum of **4l** (100 MHz, DMSO-d_6)



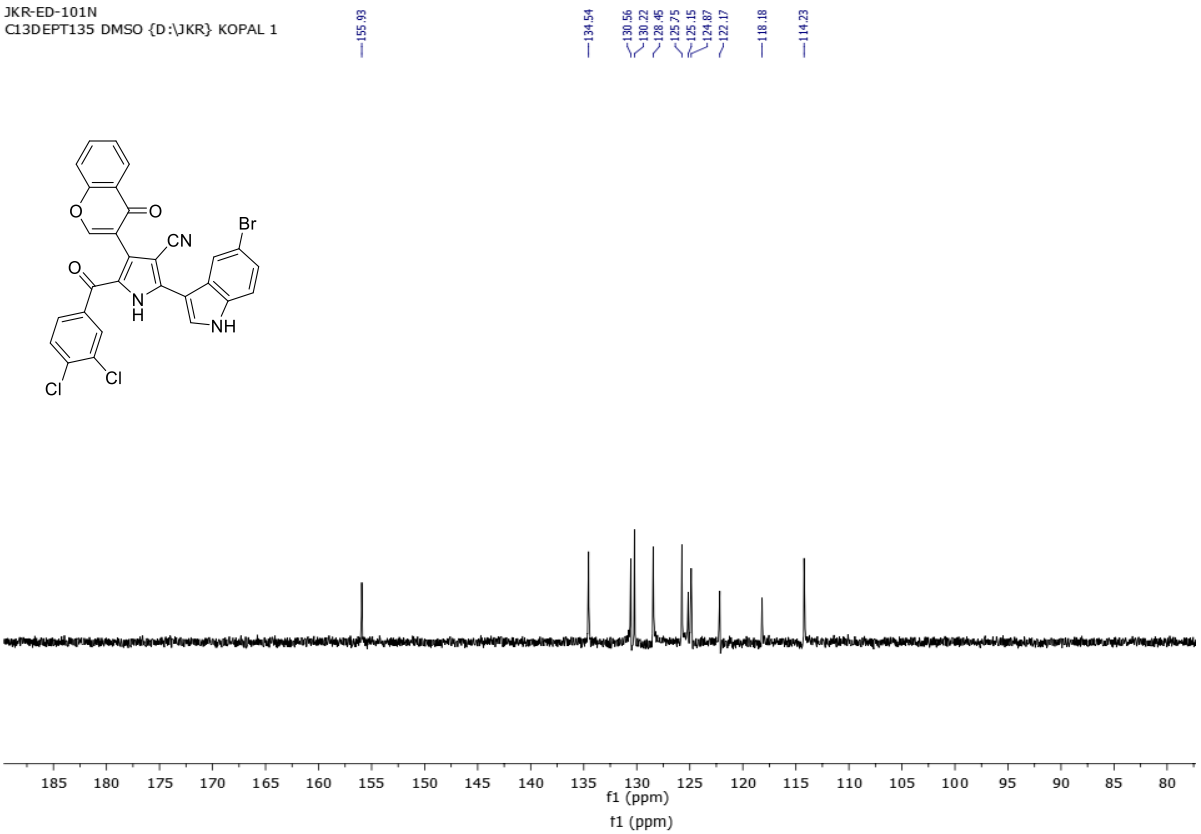
HRMS (ESI) spectrum of **4l**



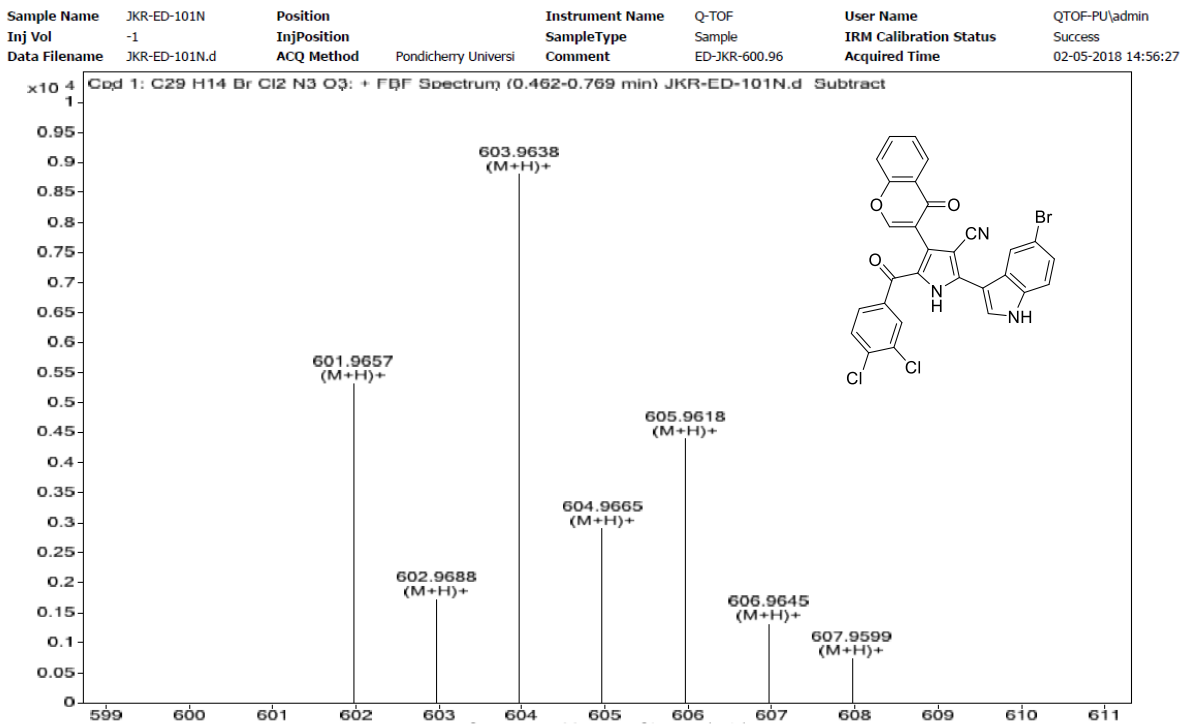
^{1}H NMR spectrum of **4m** (400 MHz, DMSO-d_6)



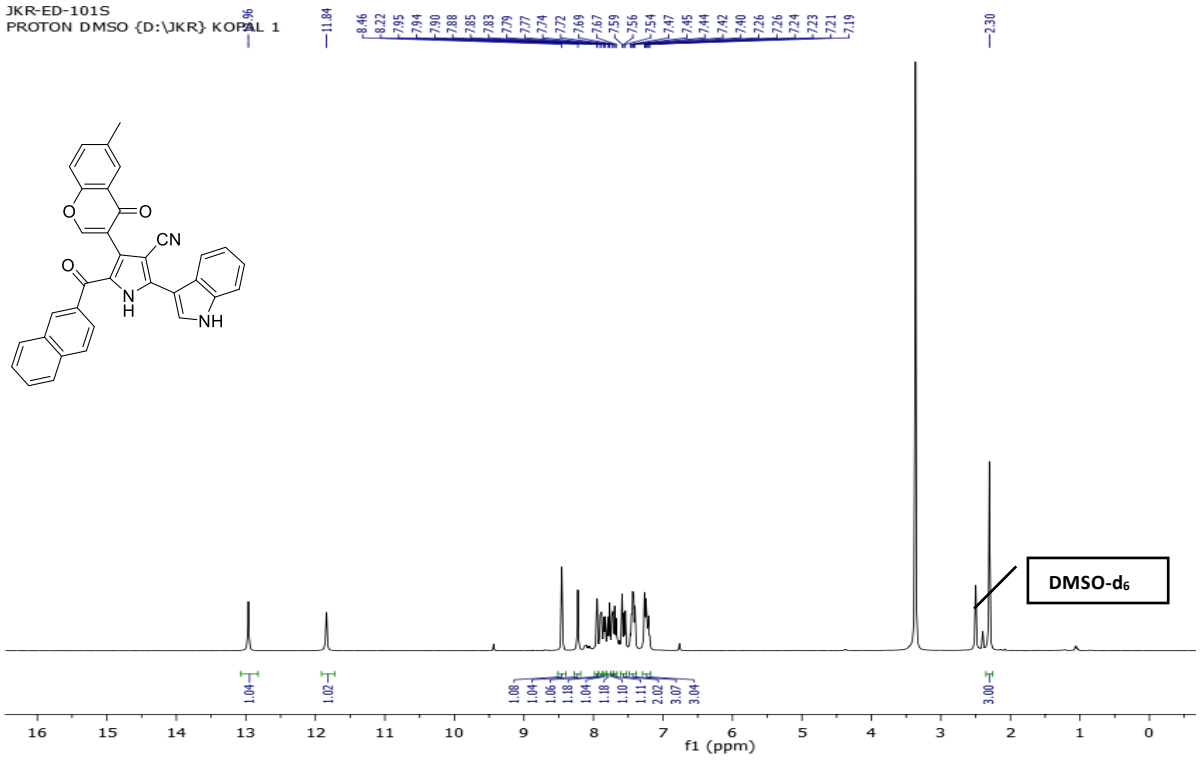
^{13}C{^{1}H} NMR spectrum of **4m** (100 MHz, DMSO-d_6)



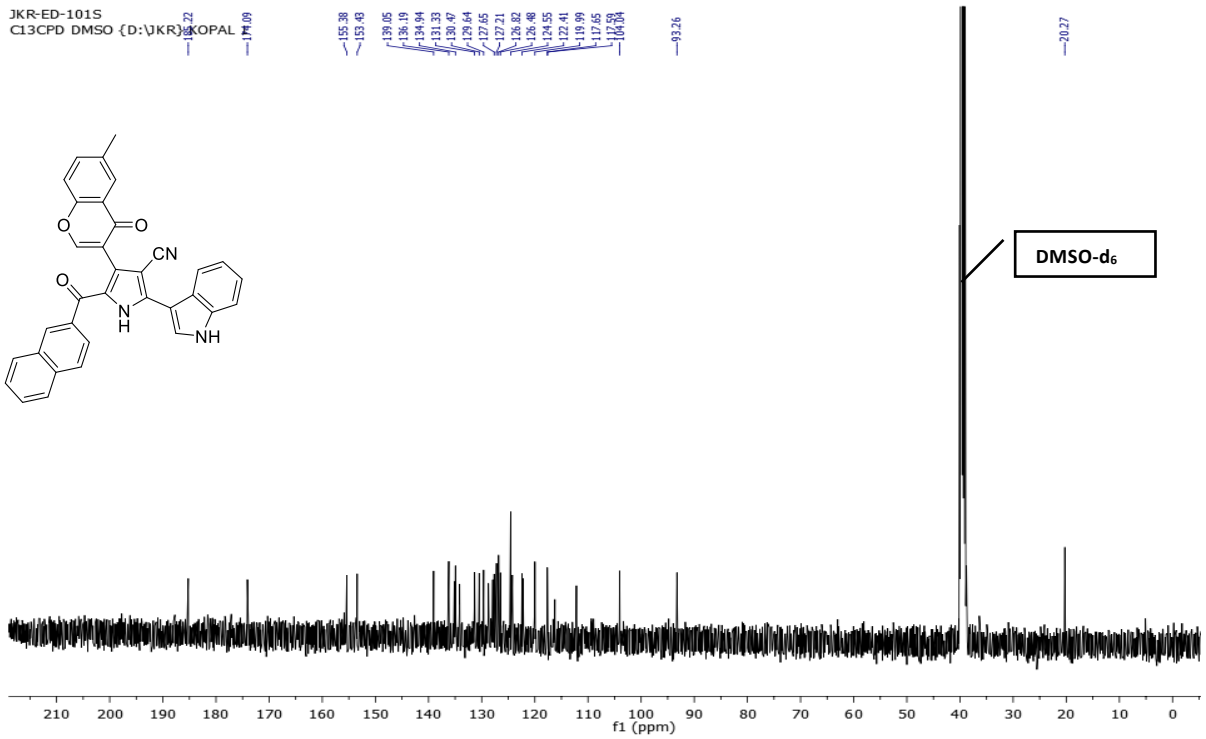
DEPT 135 NMR spectrum of **4m** (100 MHz, DMSO-d_6)



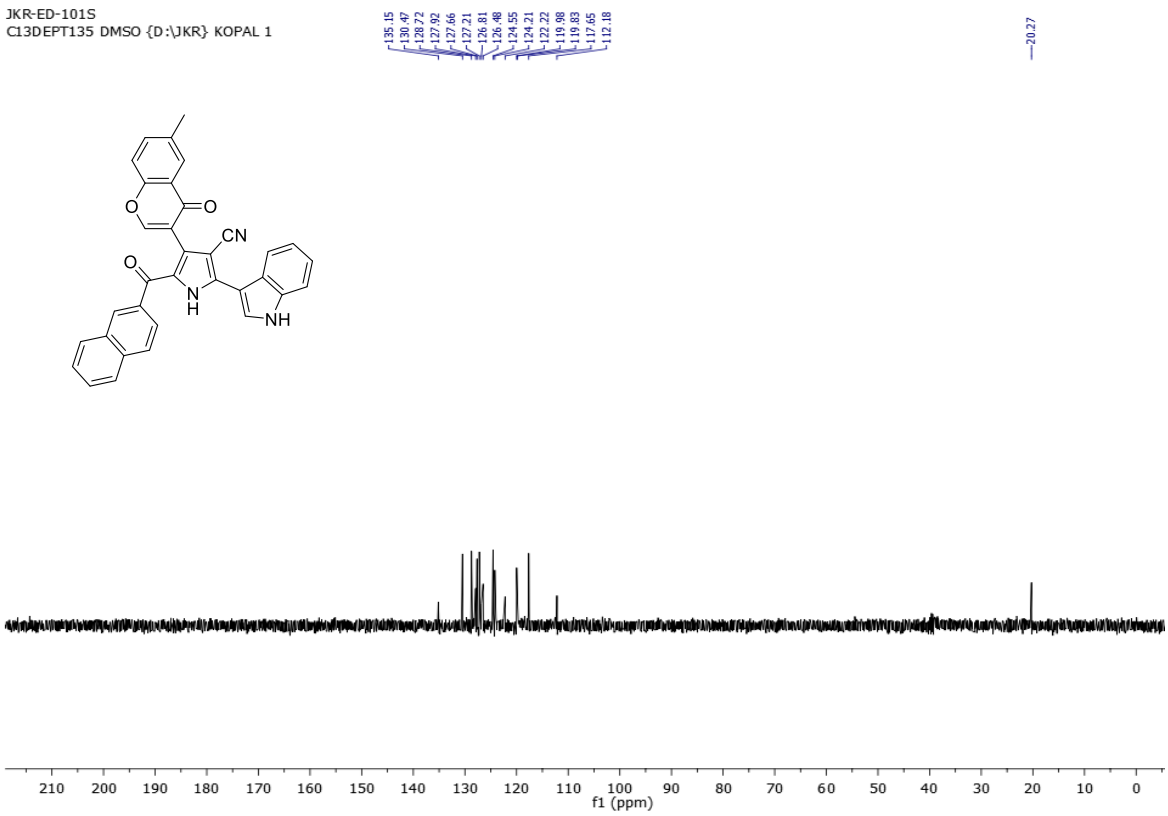
HRMS (ESI) spectrum of **4m**



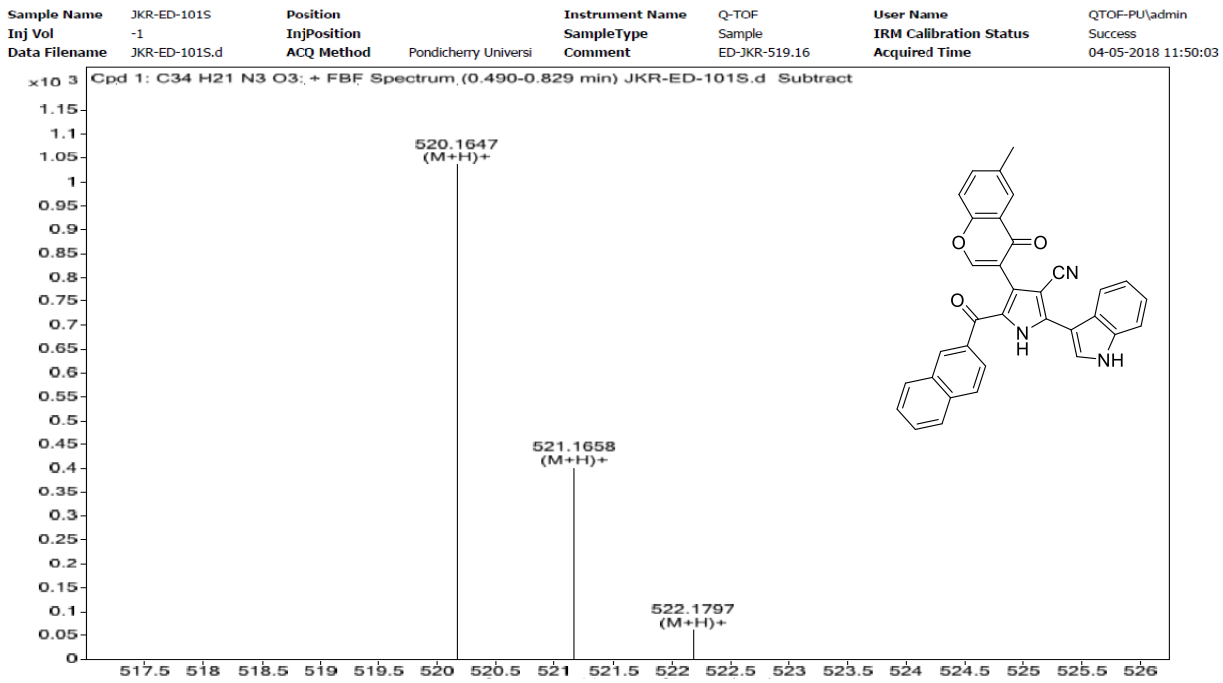
^{1}H NMR spectrum of **4n** (400 MHz, DMSO-d_6)



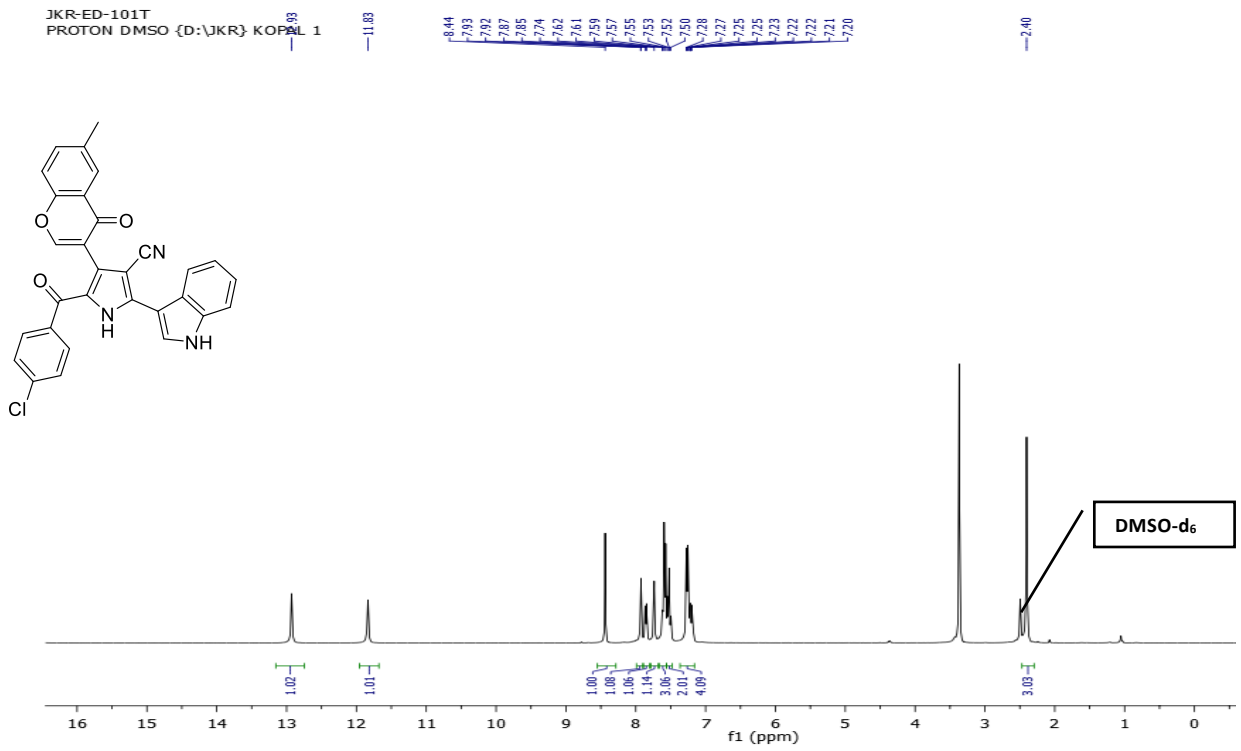
^{13}C{^{1}H} NMR spectrum of **4n** (100 MHz, DMSO-d_6)



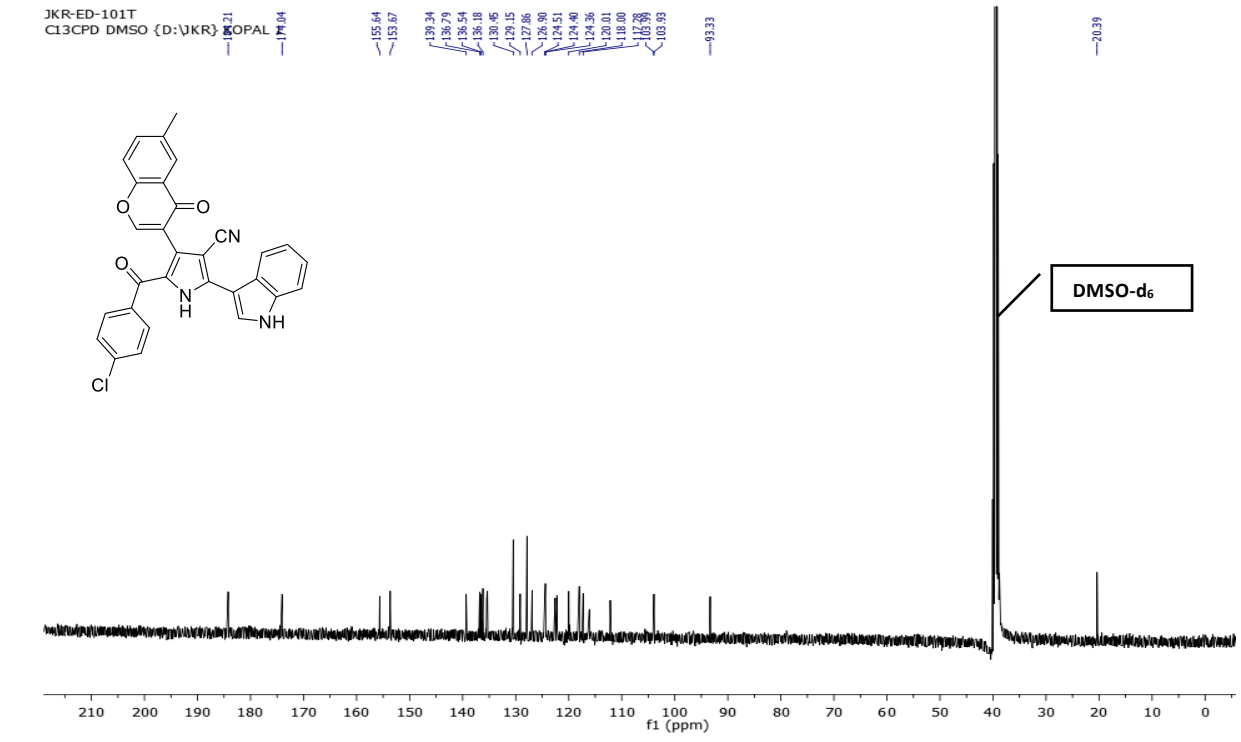
DEPT 135 NMR spectrum of **4n** (100 MHz, DMSO-d_6)



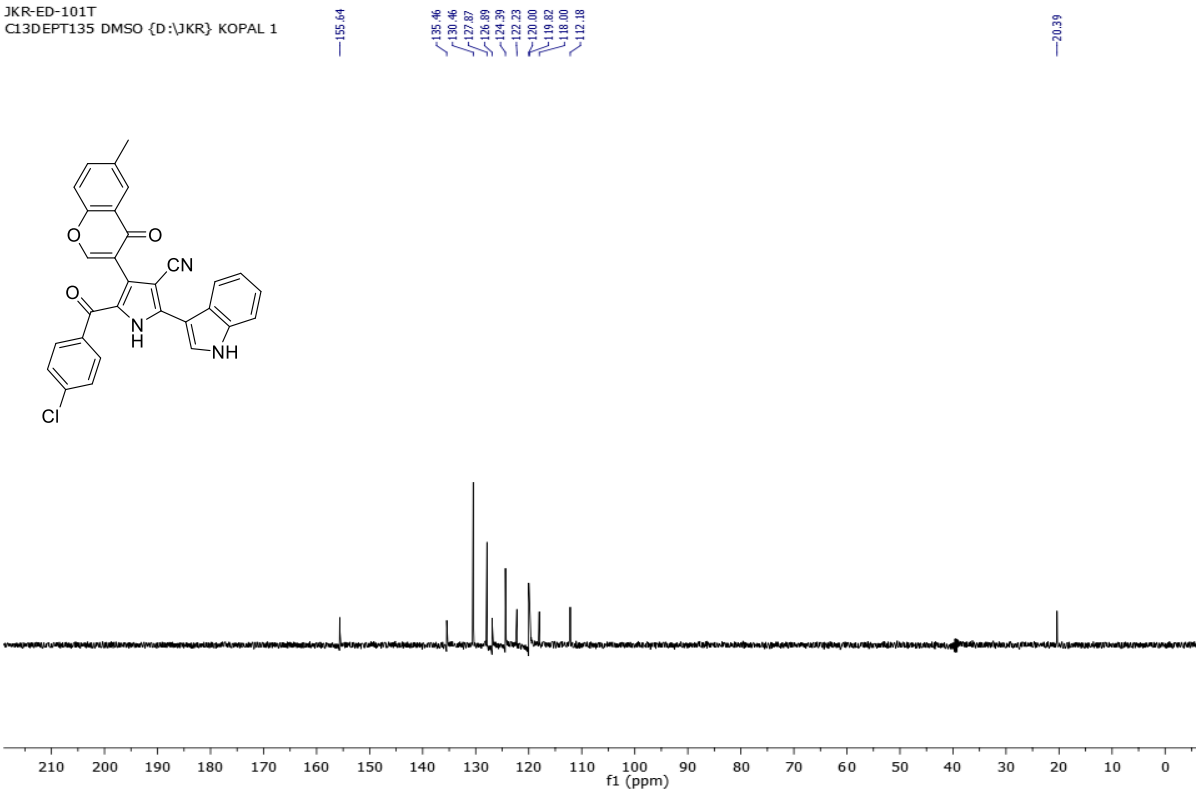
HRMS (ESI) spectrum of **4n**



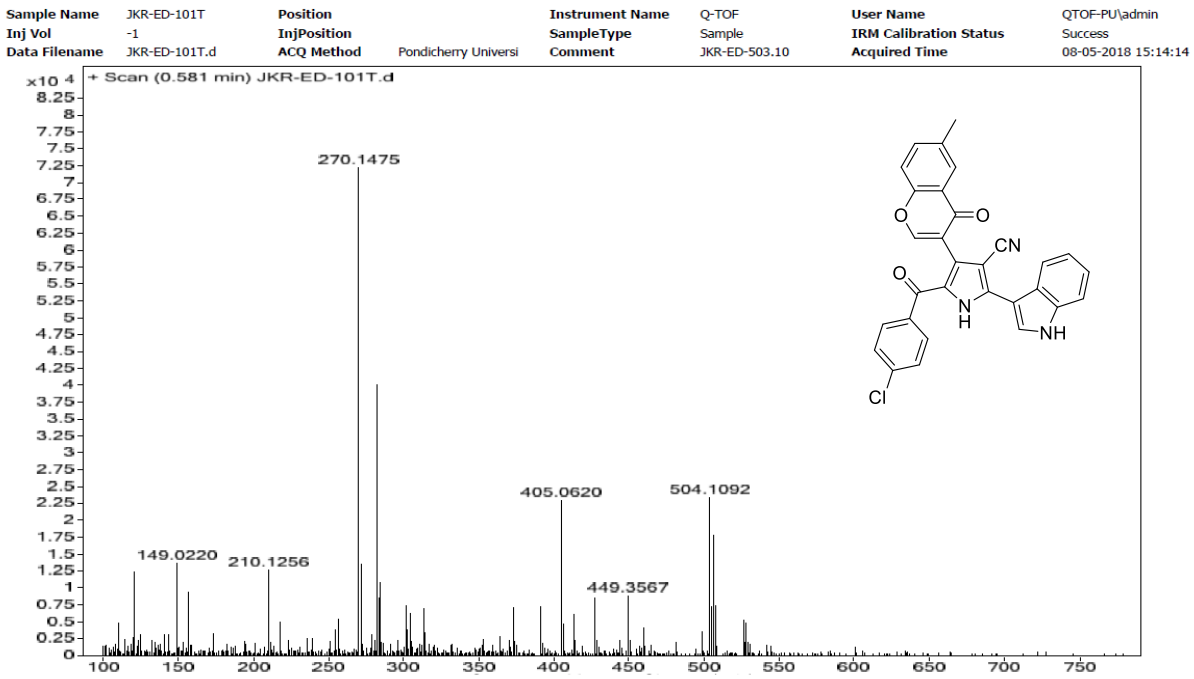
^{1}H NMR spectrum of **4o** (400 MHz, DMSO-d_6)



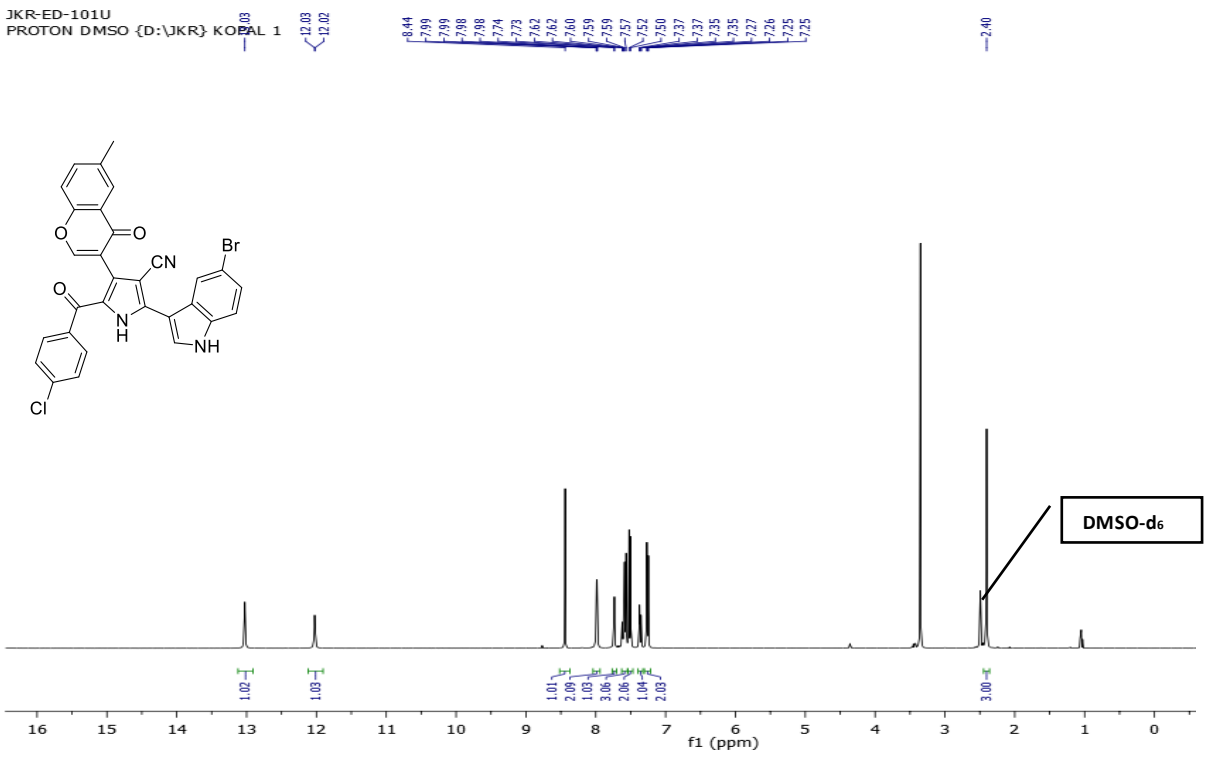
^{13}C{^{1}H} NMR spectrum of **4o** (100 MHz, DMSO-d_6)



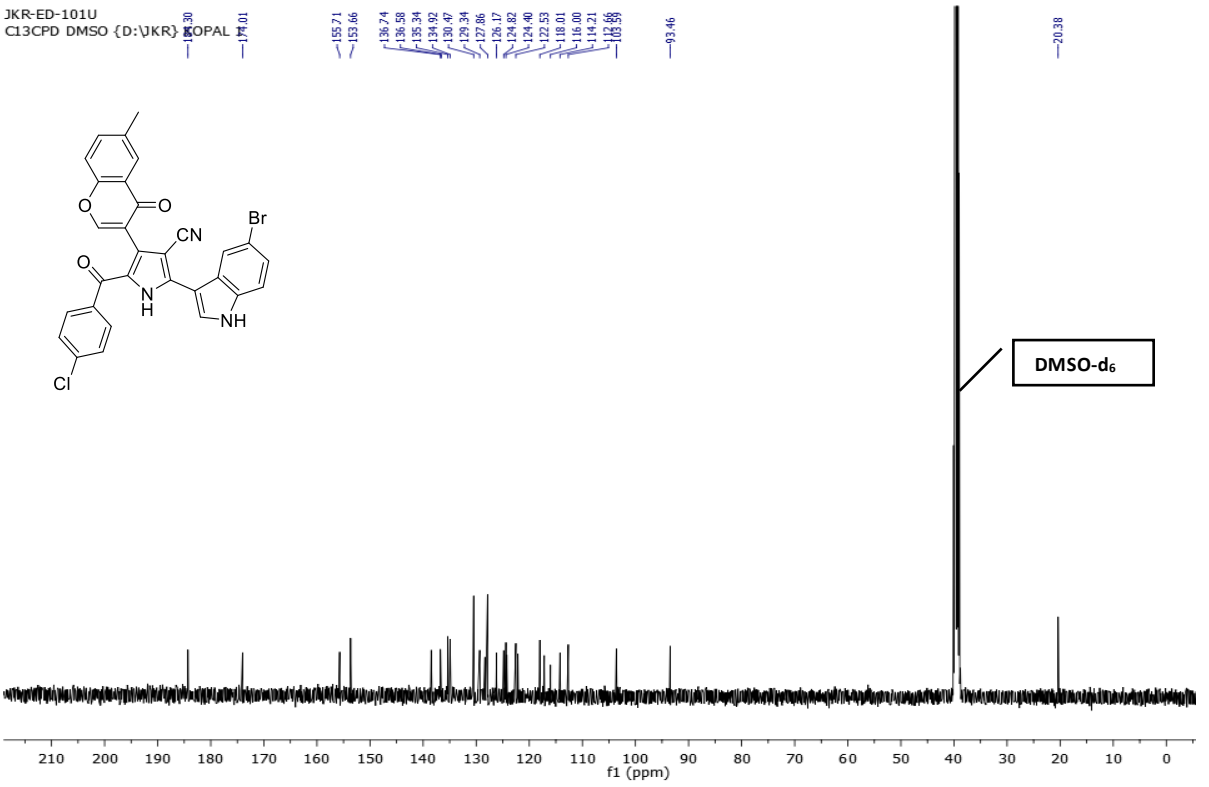
DEPT 135 NMR spectrum of **4o** (100 MHz, DMSO-d_6)



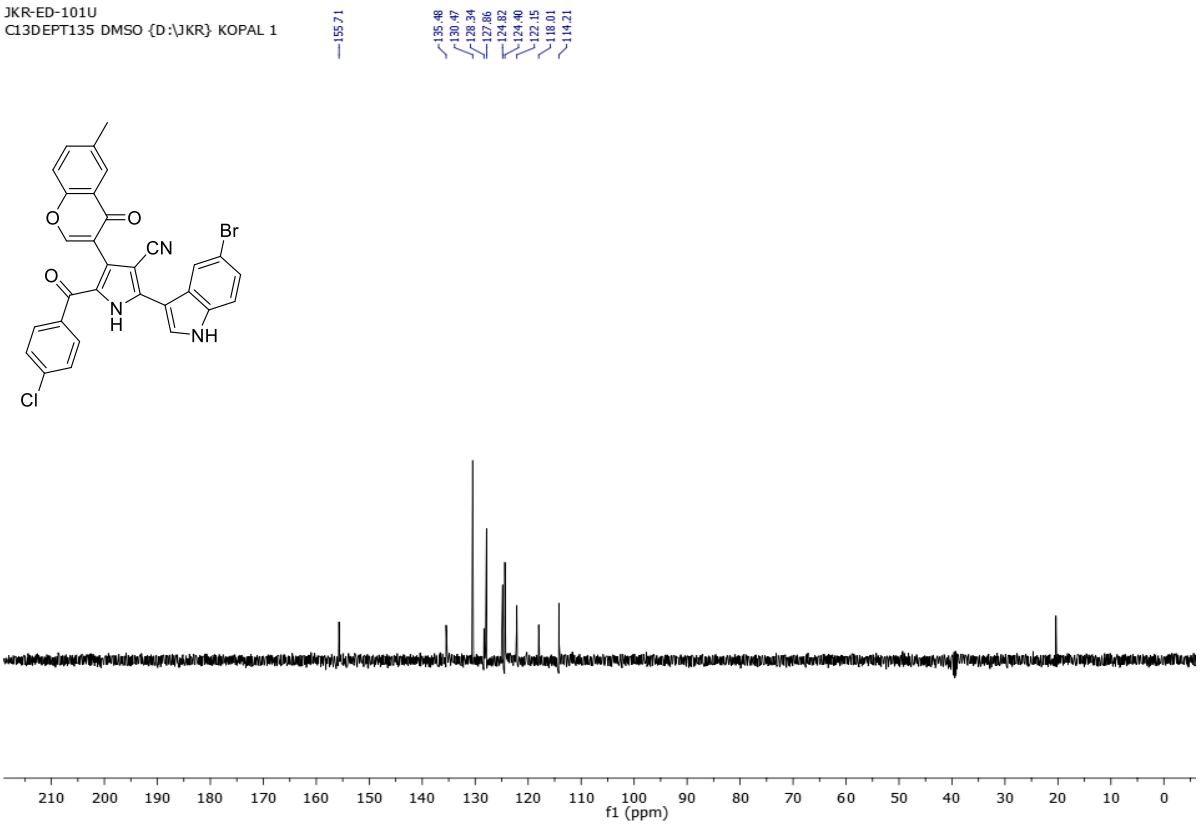
HRMS (ESI) spectrum of **4o**



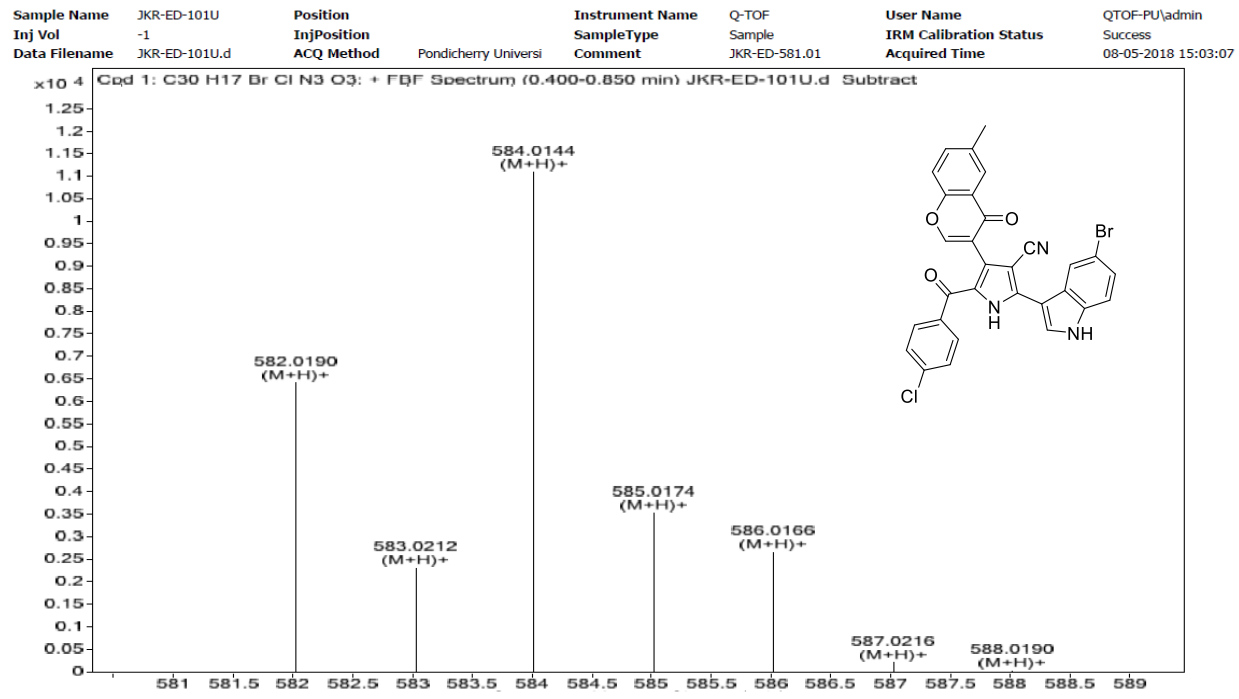
^{1}H NMR spectrum of **4p** (400 MHz, DMSO-d_6)



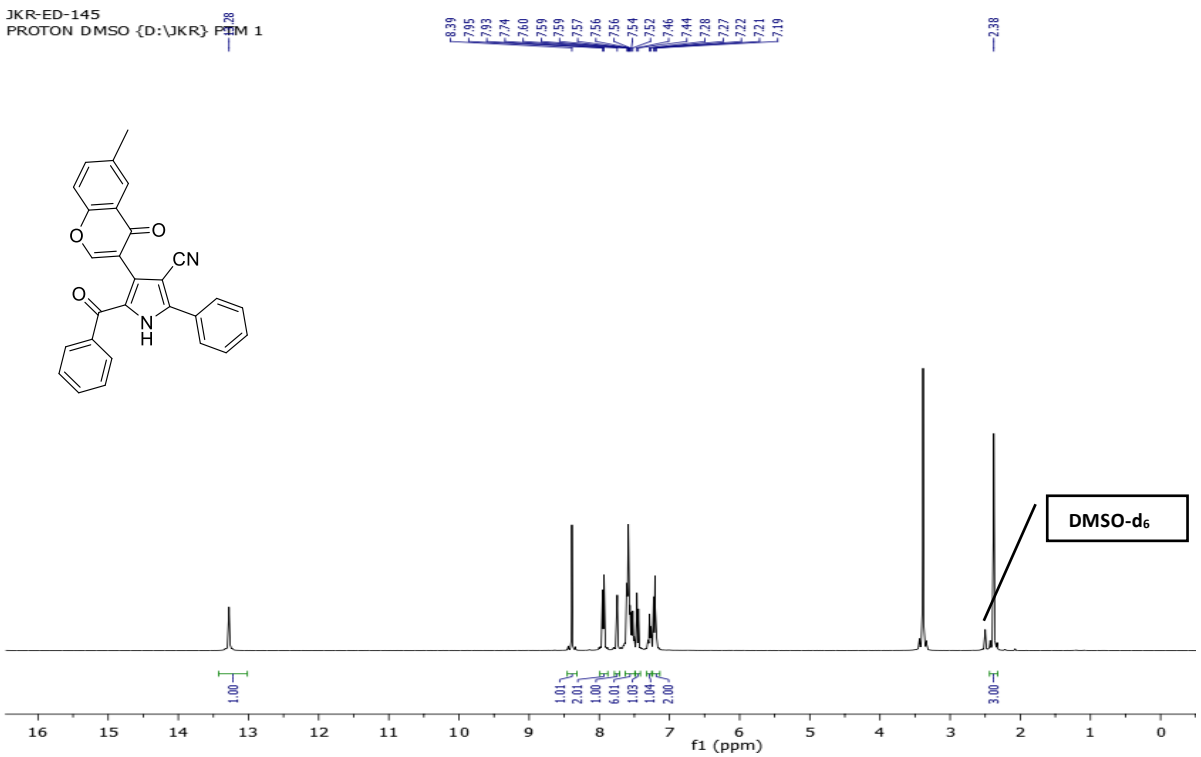
^{13}C{^{1}H} NMR spectrum of **4p** (100 MHz, DMSO-d_6)



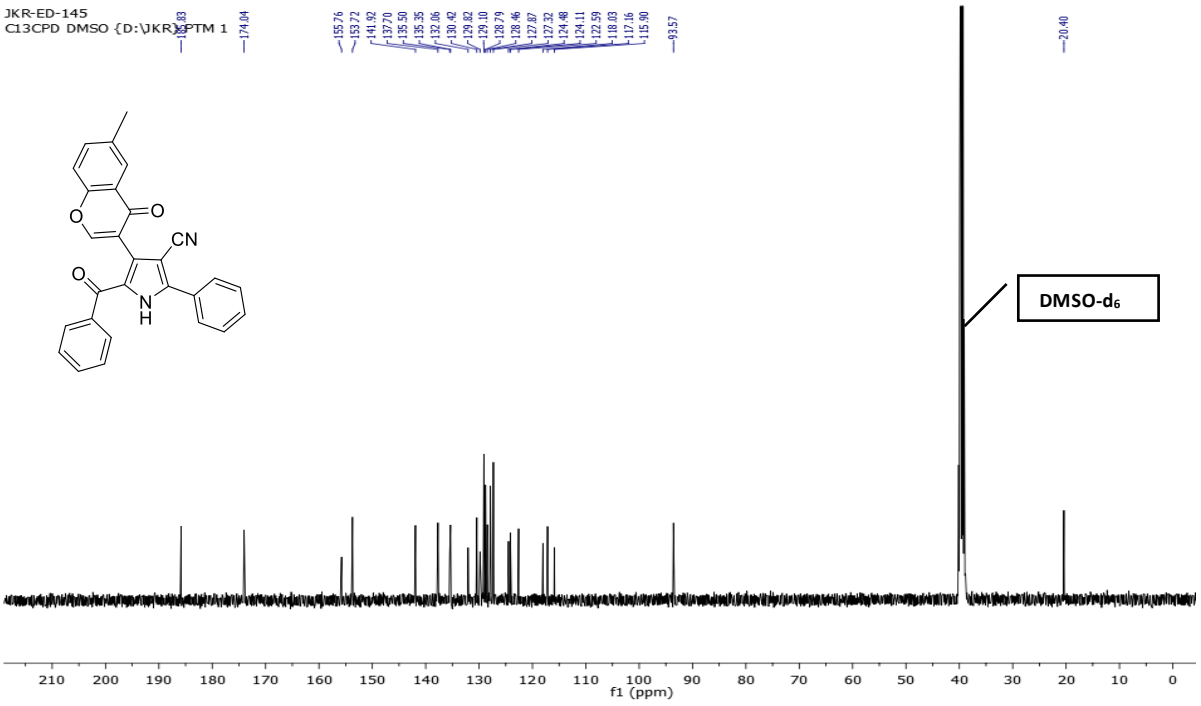
DEPT 135 NMR spectrum of **4p** (100 MHz, DMSO-d_6)



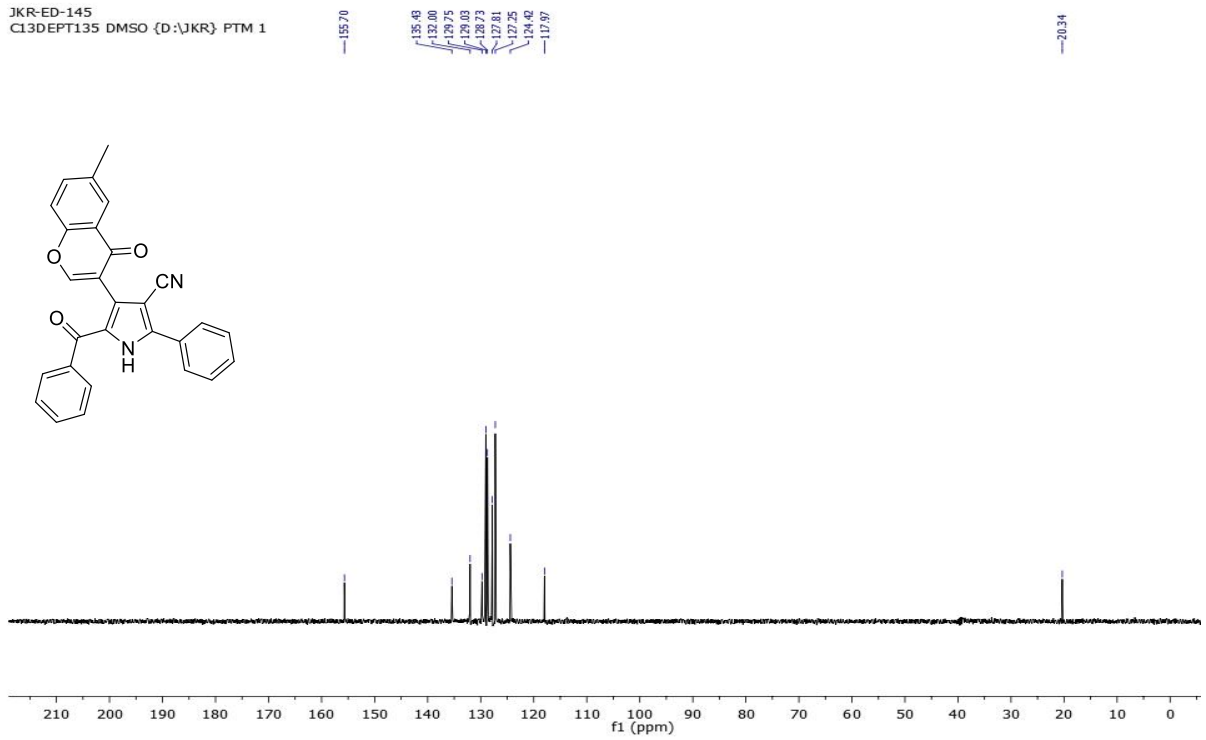
HRMS (ESI) spectrum of **4p**



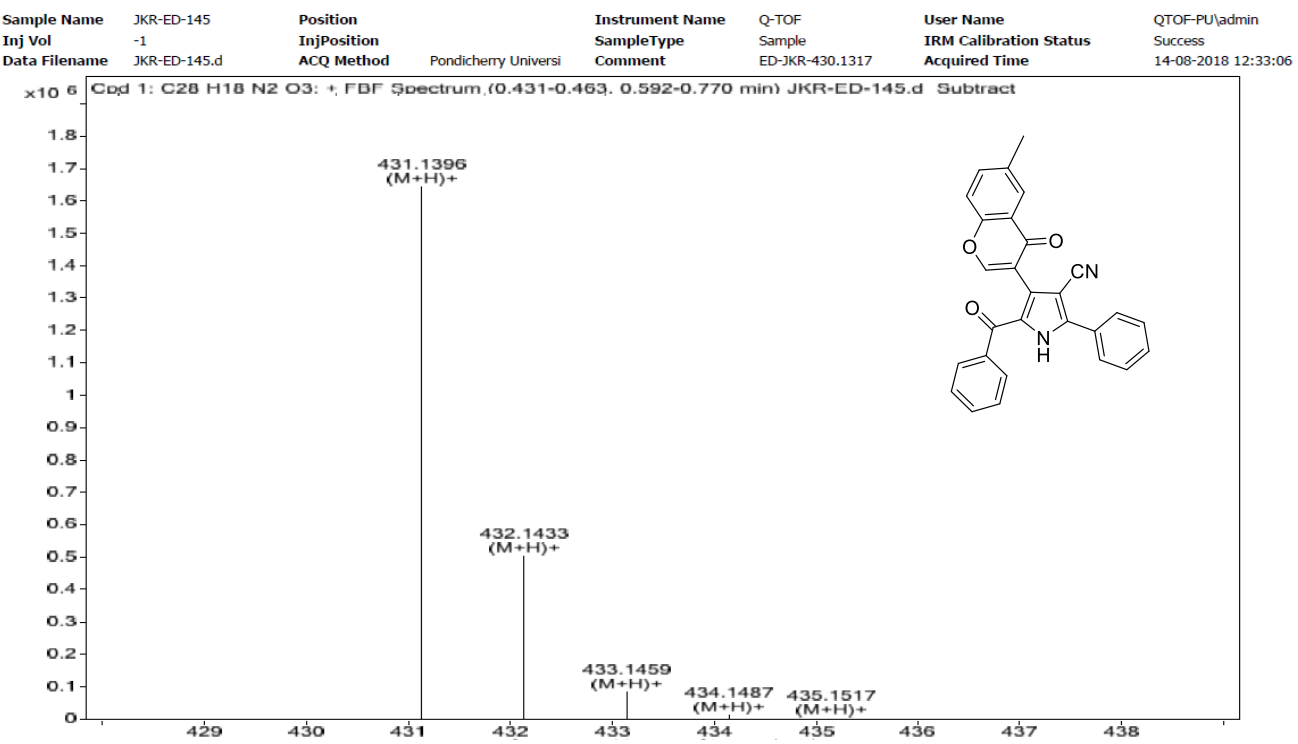
^{1}H NMR spectrum of **4q** (400 MHz, DMSO-d_6)



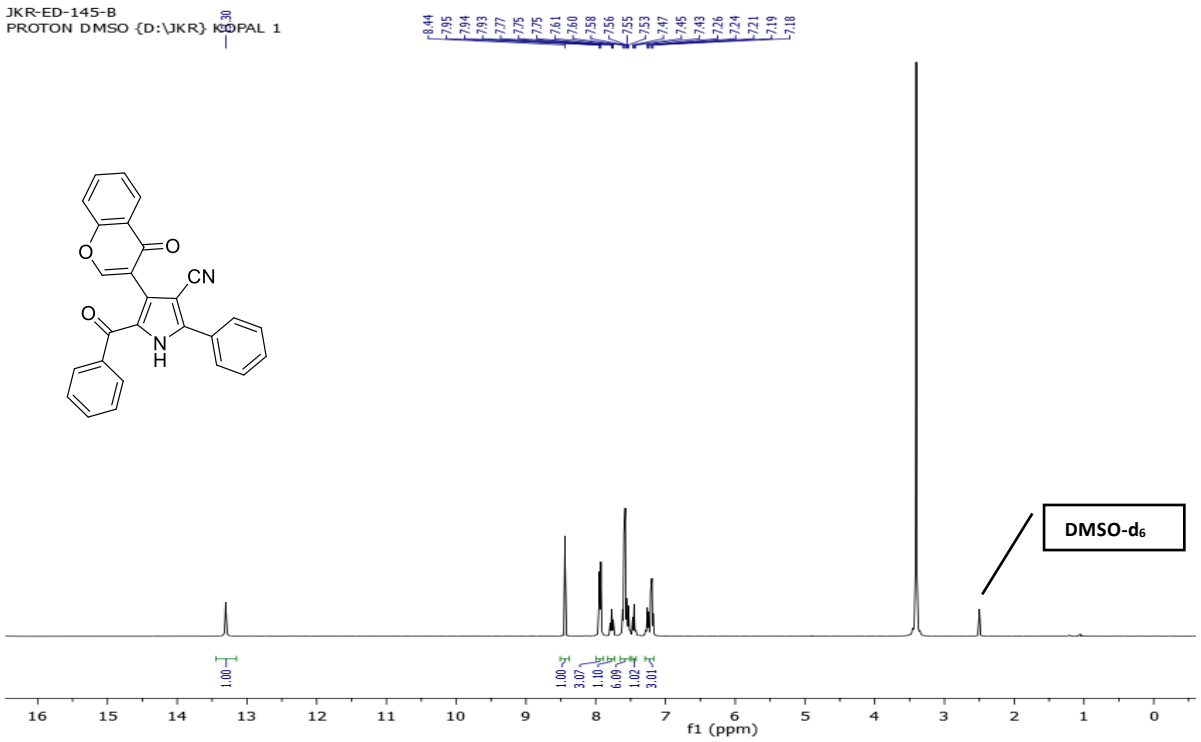
^{13}C{^{1}H} NMR spectrum of **4q** (100 MHz, DMSO-d_6)



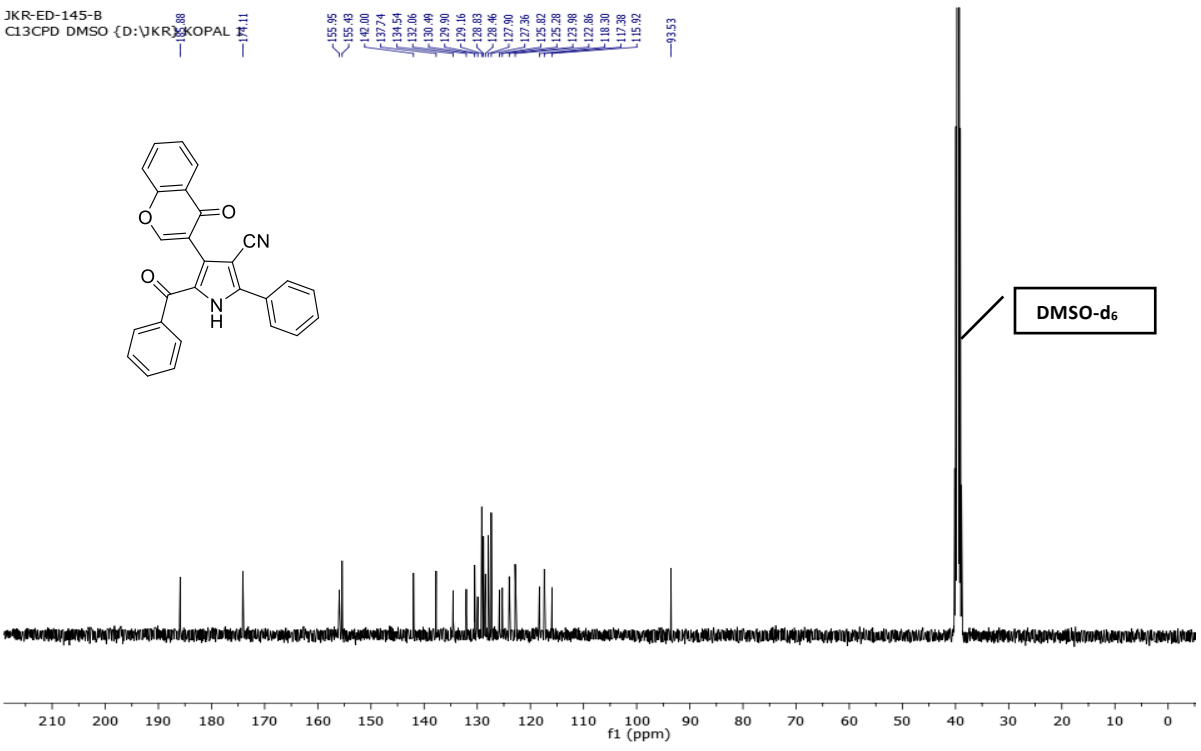
DEPT 135 NMR spectrum of **4q** (100 MHz, DMSO-d_6)



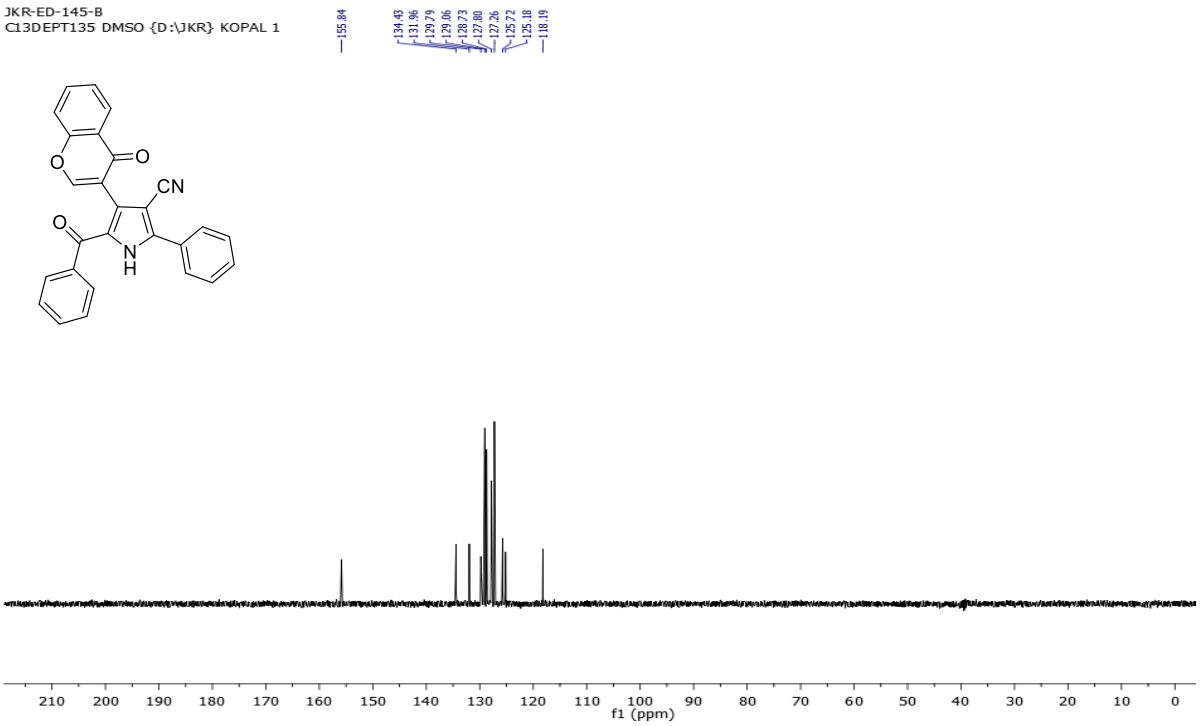
HRMS (ESI) spectrum of **4q**



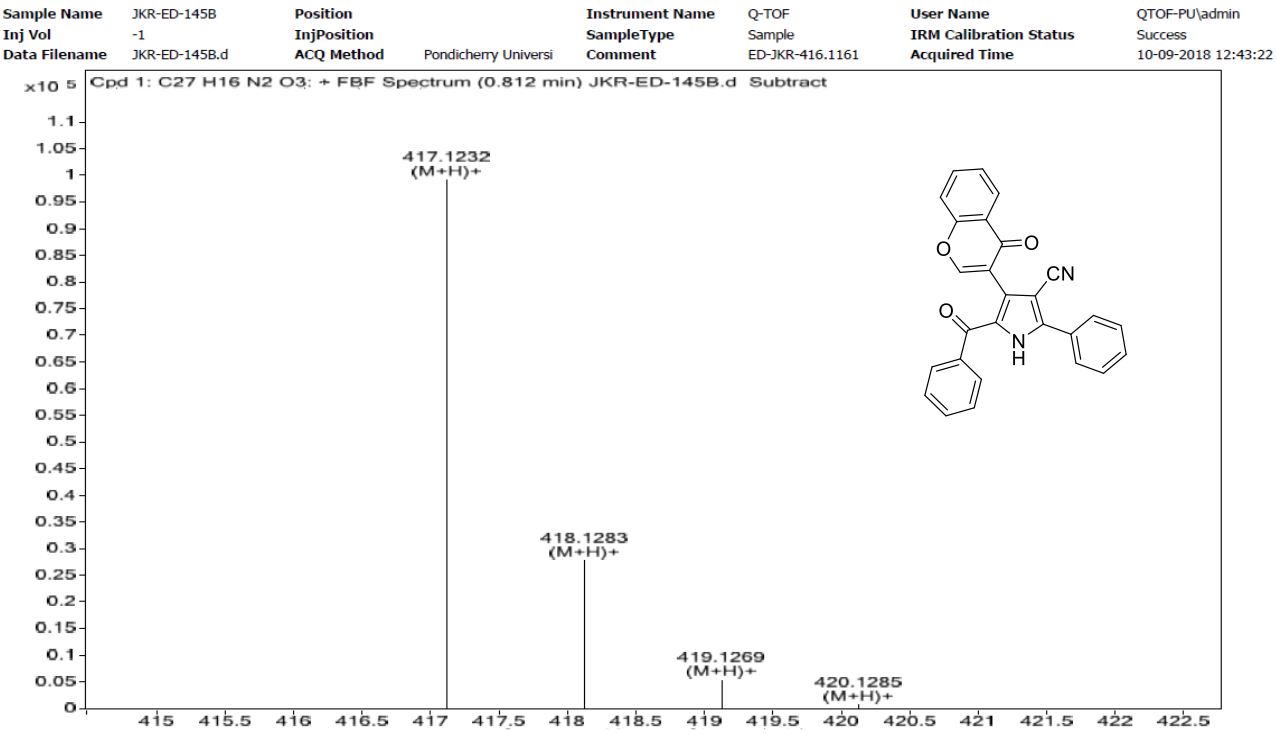
^{1}H NMR spectrum of **4r** (400 MHz, DMSO-d_6)



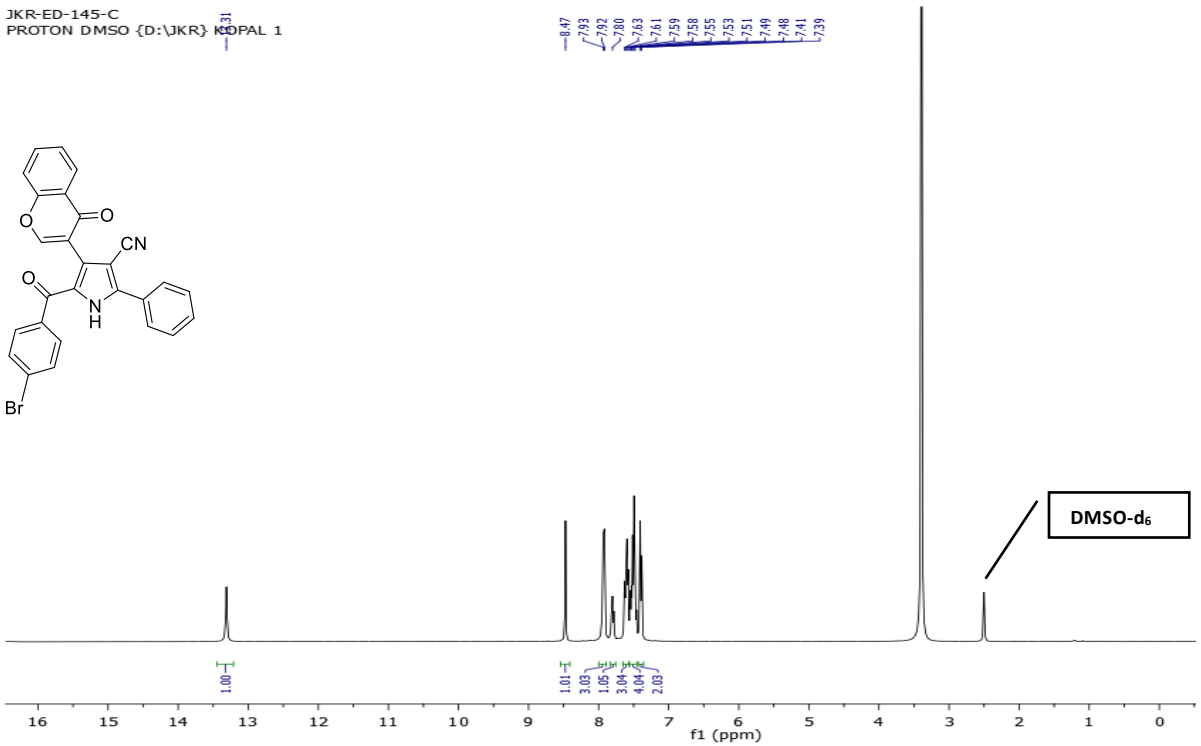
^{13}C{^{1}H} NMR spectrum of **4r** (100 MHz, DMSO-d_6)



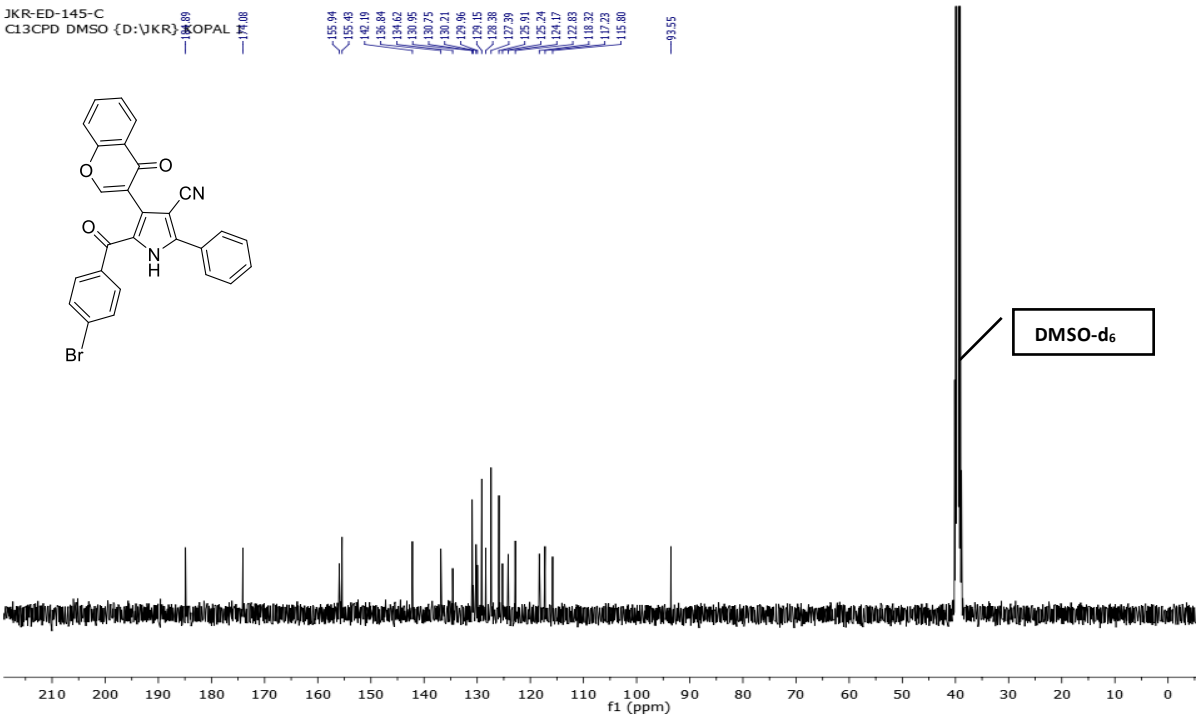
DEPT 135 NMR spectrum of **4r** (100 MHz, DMSO-d_6)



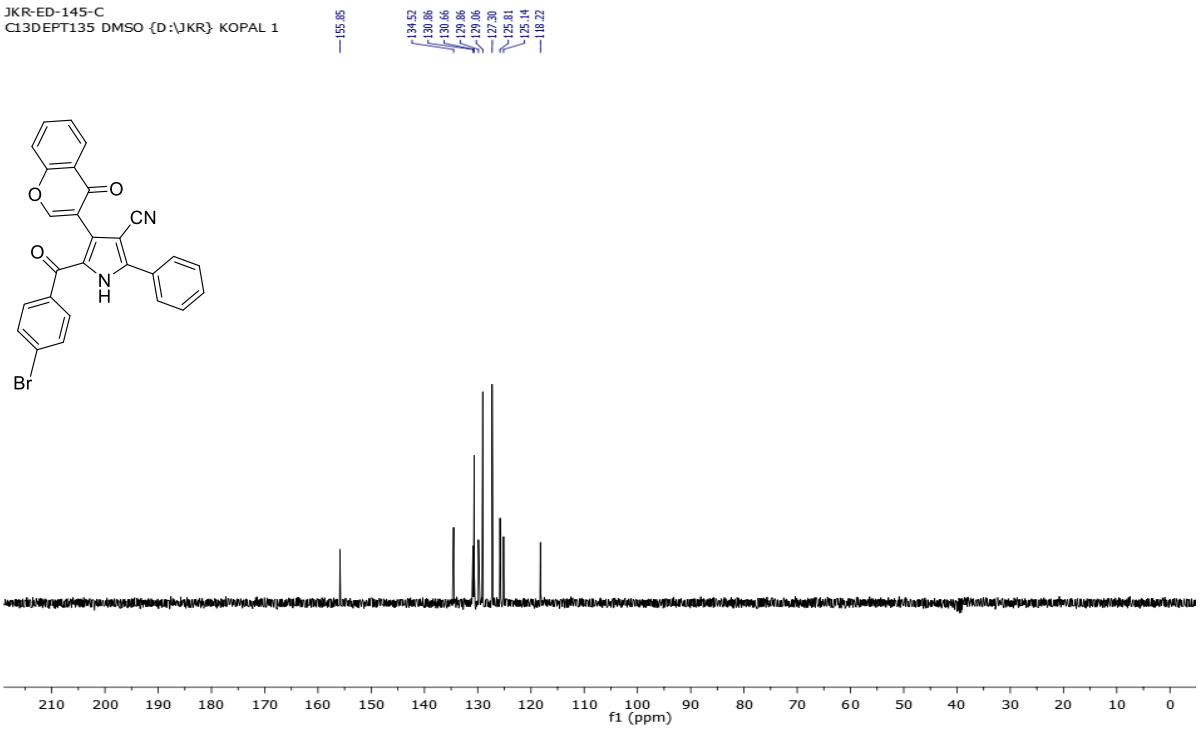
HRMS (ESI) spectrum of **4r**



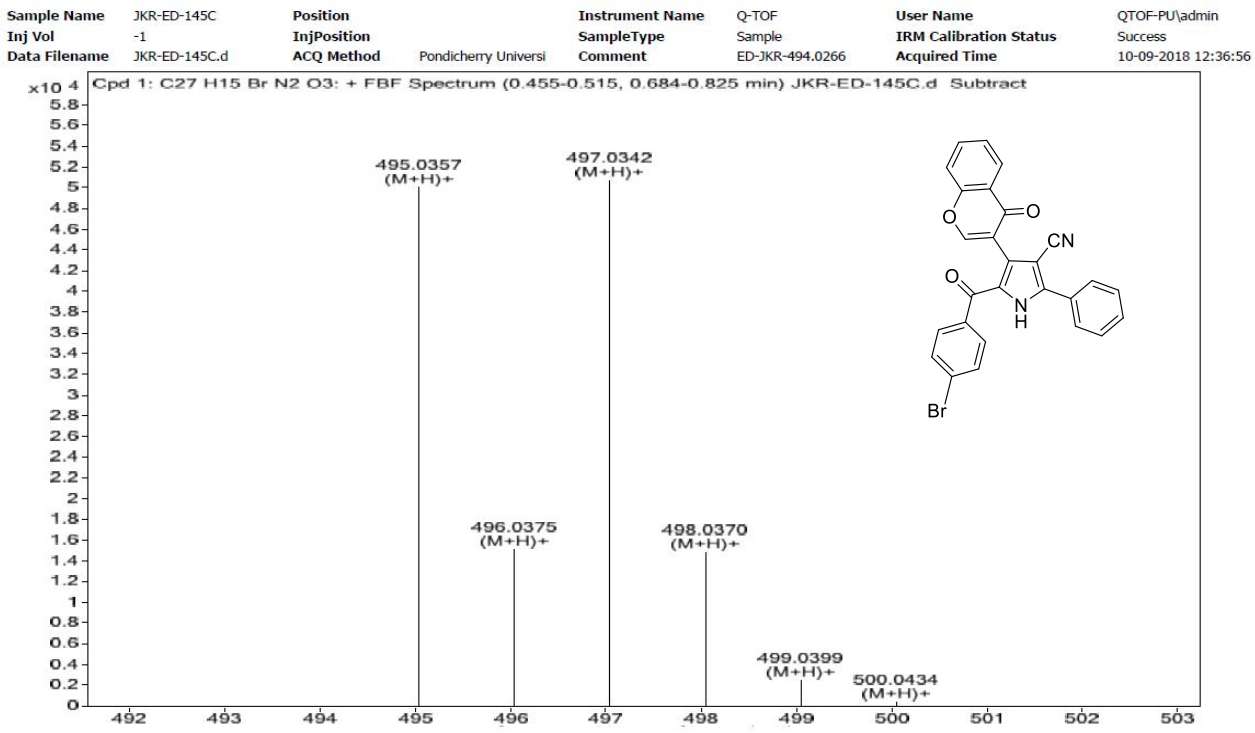
^{1}H NMR spectrum of **4s** (400 MHz, DMSO-d_6)



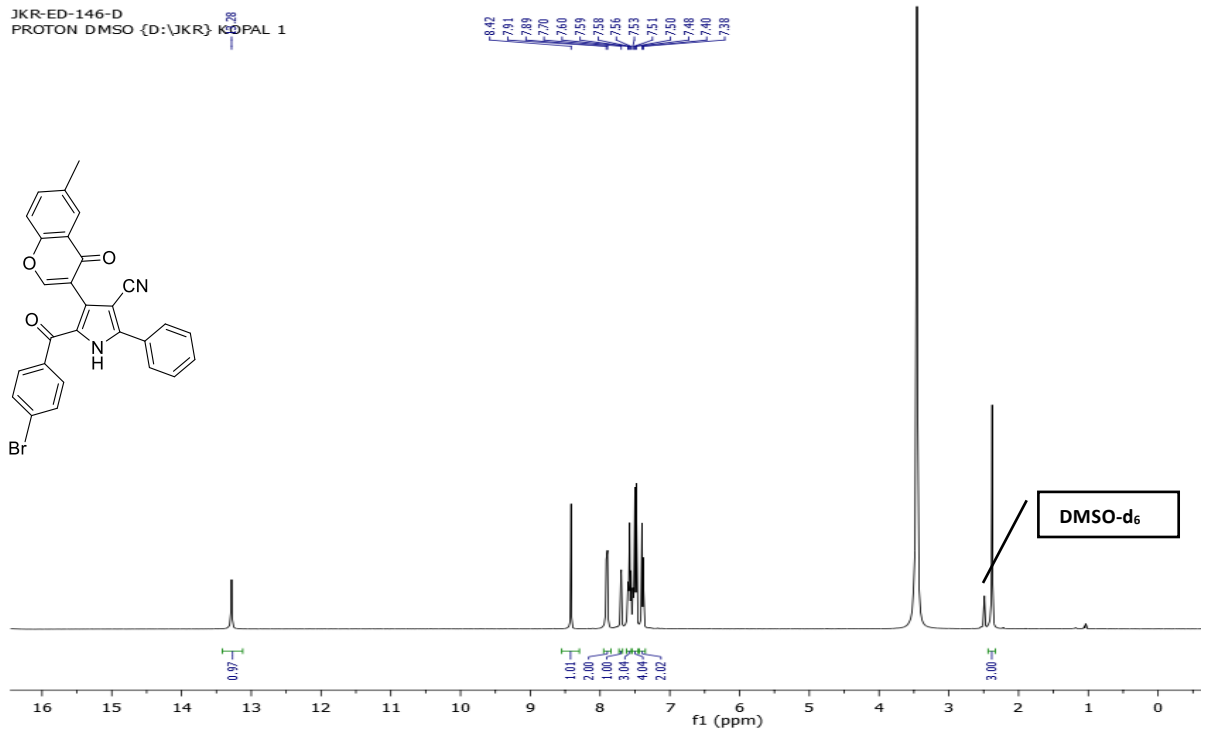
^{13}C{^{1}H} NMR spectrum of **4s** (100 MHz, DMSO-d_6)



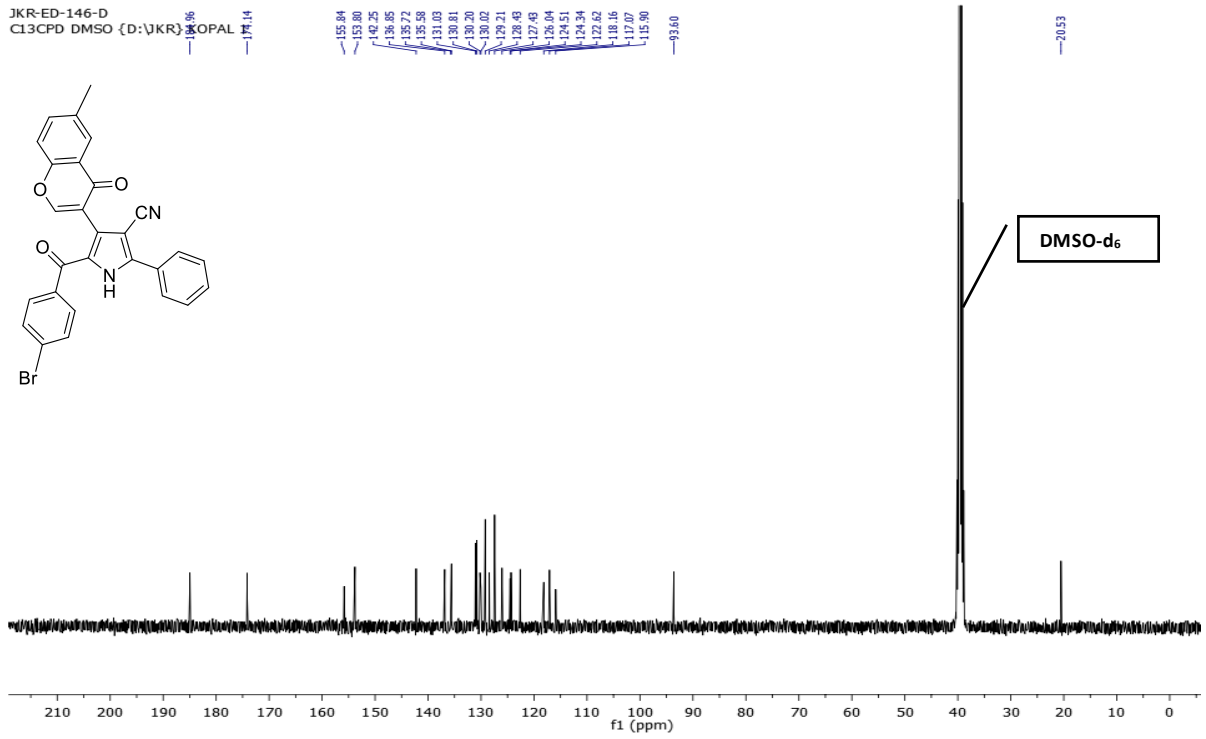
DEPT 135 NMR spectrum of **4s** (100 MHz, DMSO-d_6)



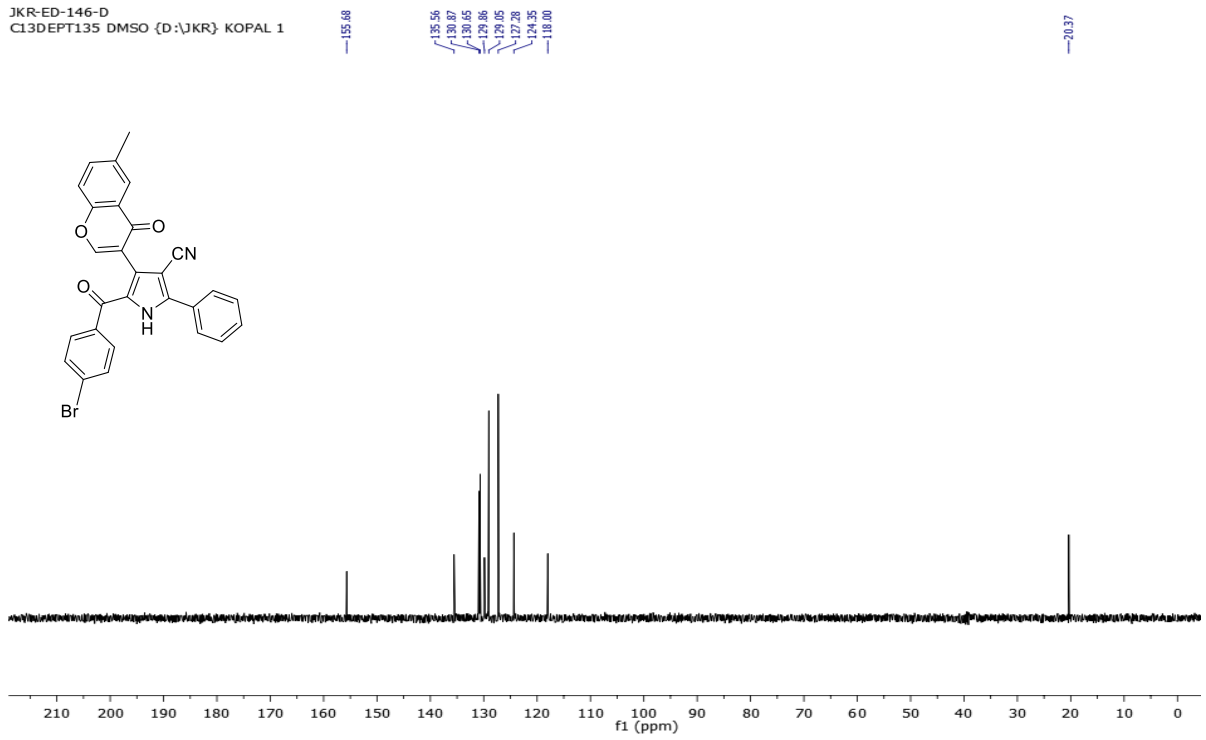
HRMS (ESI) spectrum of **4s**



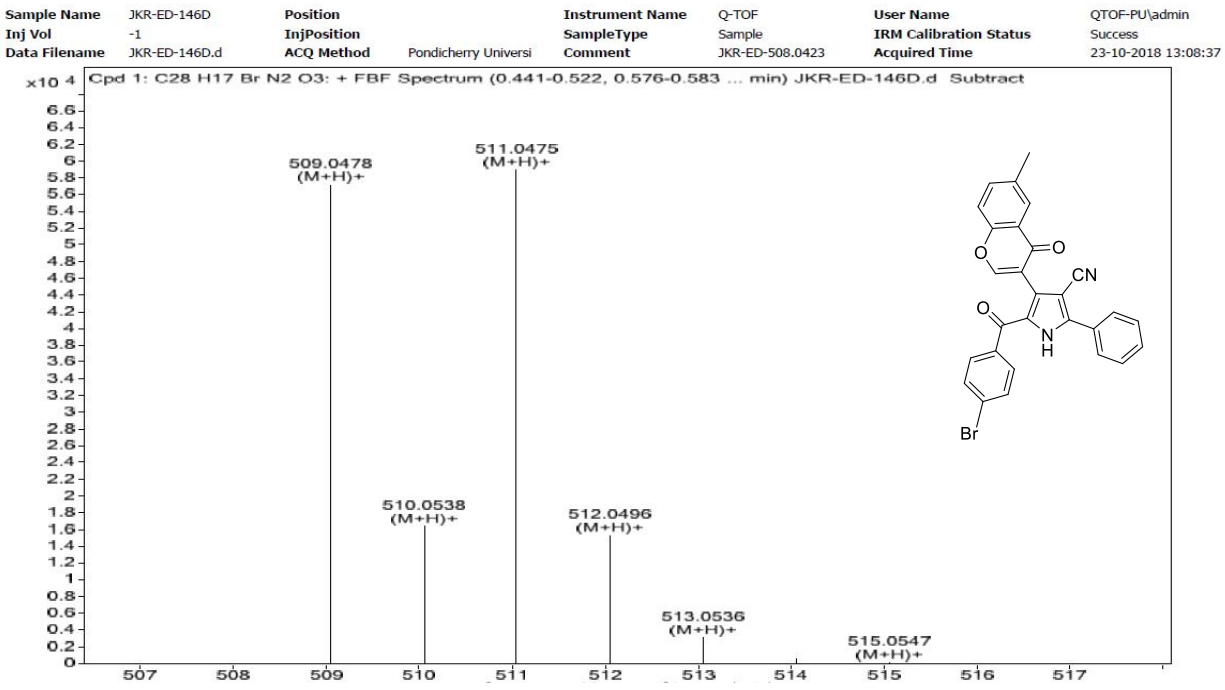
^{1}H NMR spectrum of **4t** (400 MHz, DMSO-d_6)



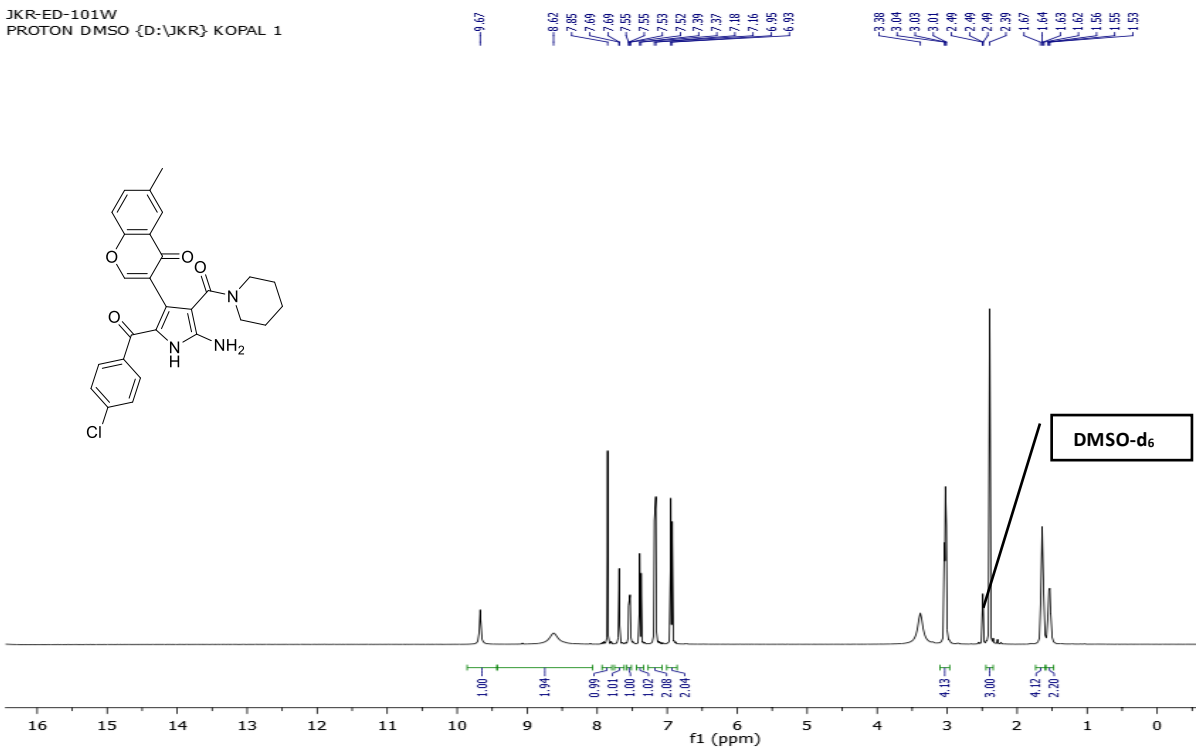
^{13}C{^{1}H} NMR spectrum of **4t** (100 MHz, DMSO-d_6)



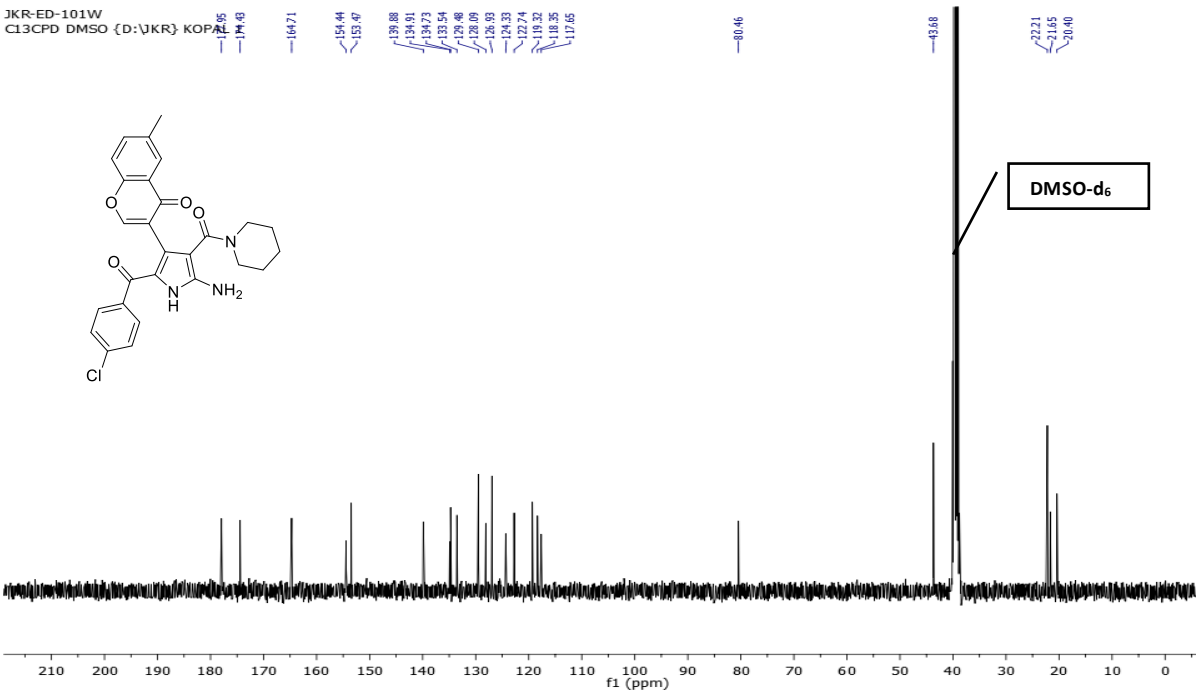
DEPT 135 NMR spectrum of **4t** (100 MHz, DMSO-d_6)



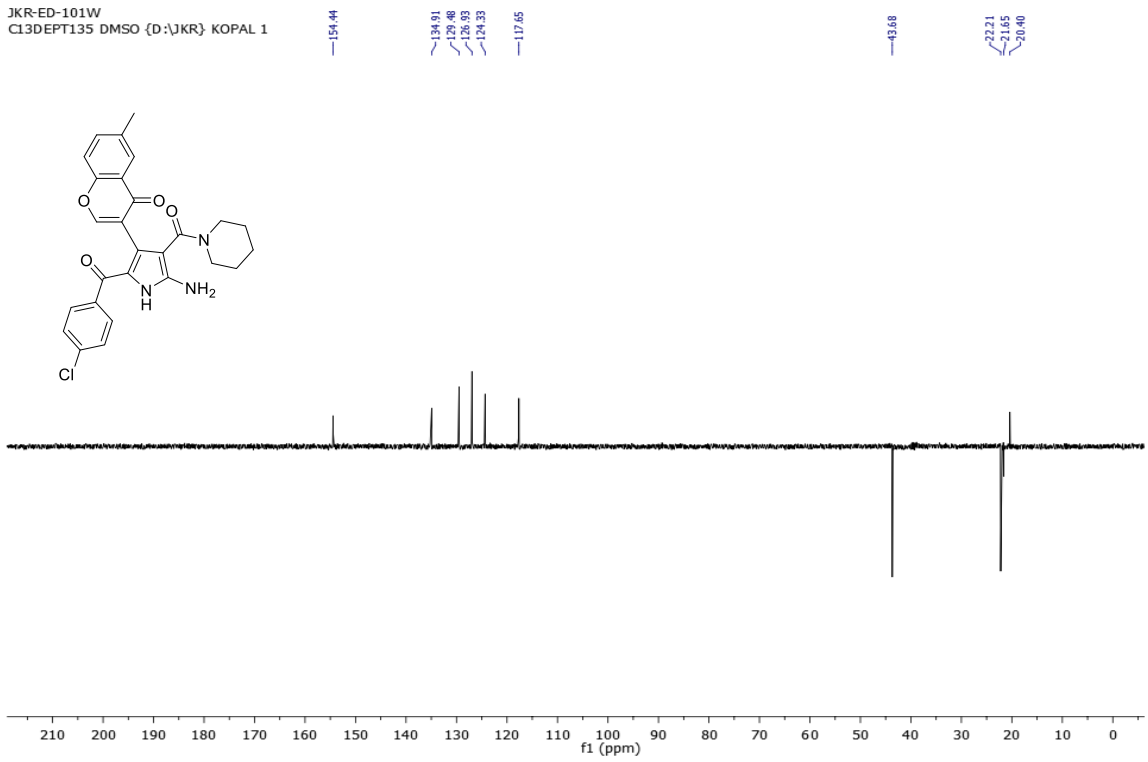
HRMS (ESI) spectrum of **4t**



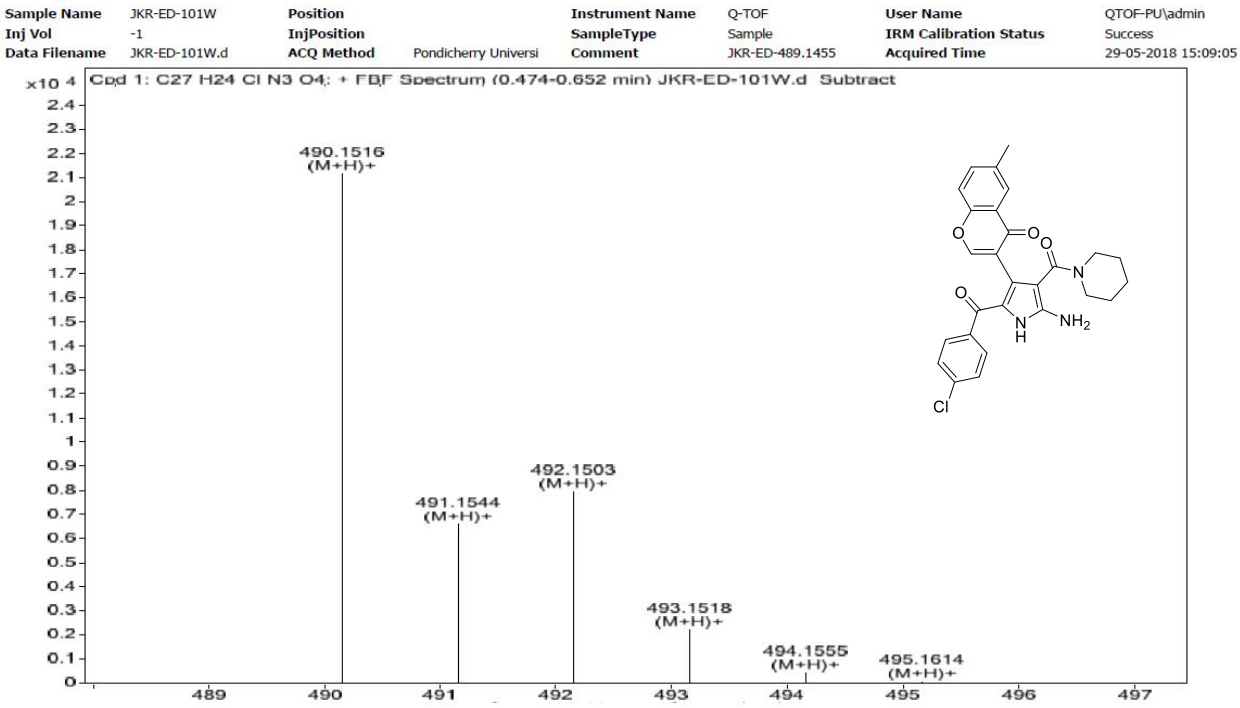
^{1}H NMR spectrum of **8a** (400 MHz, DMSO-d_6)



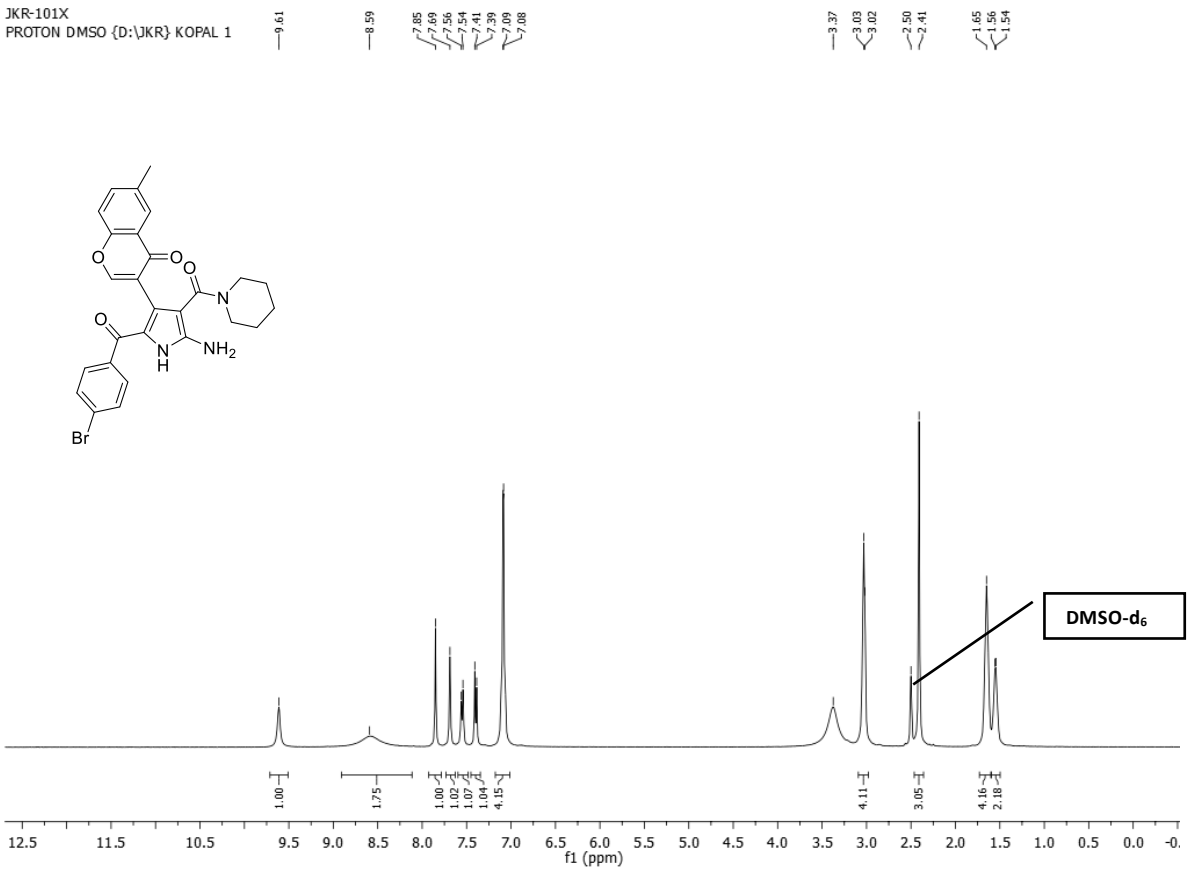
^{13}C{^{1}H} NMR spectrum of **8a** (100 MHz, DMSO-d_6)



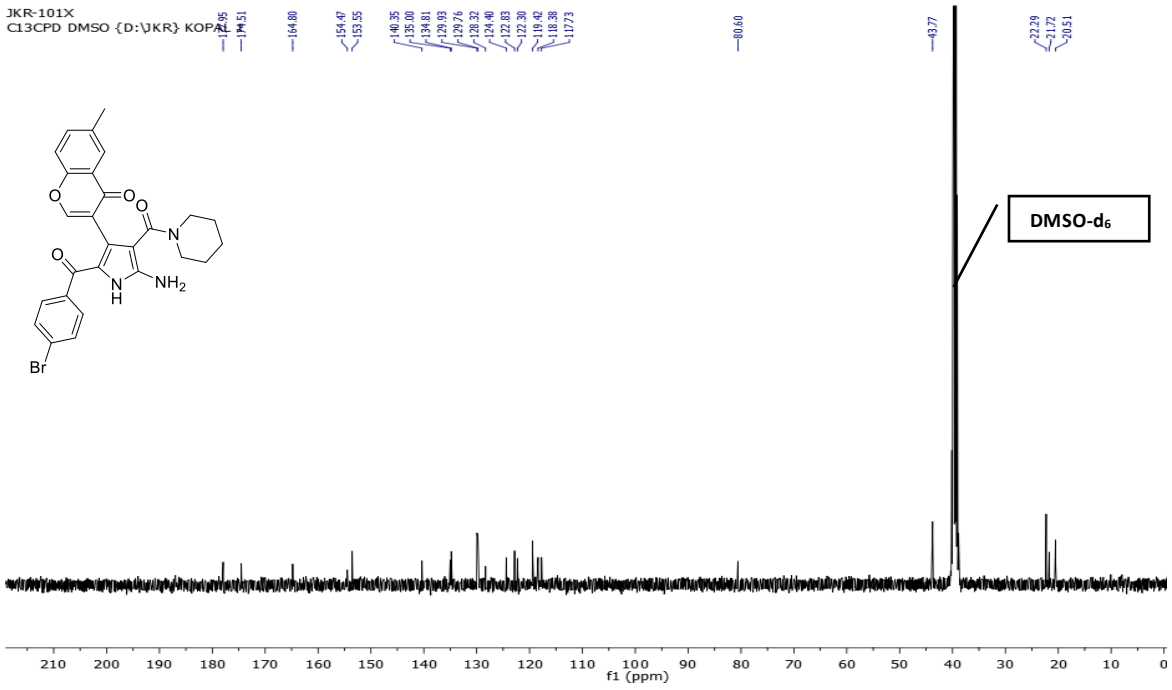
DEPT 135 NMR spectrum of **8a** (100 MHz, DMSO-d_6)



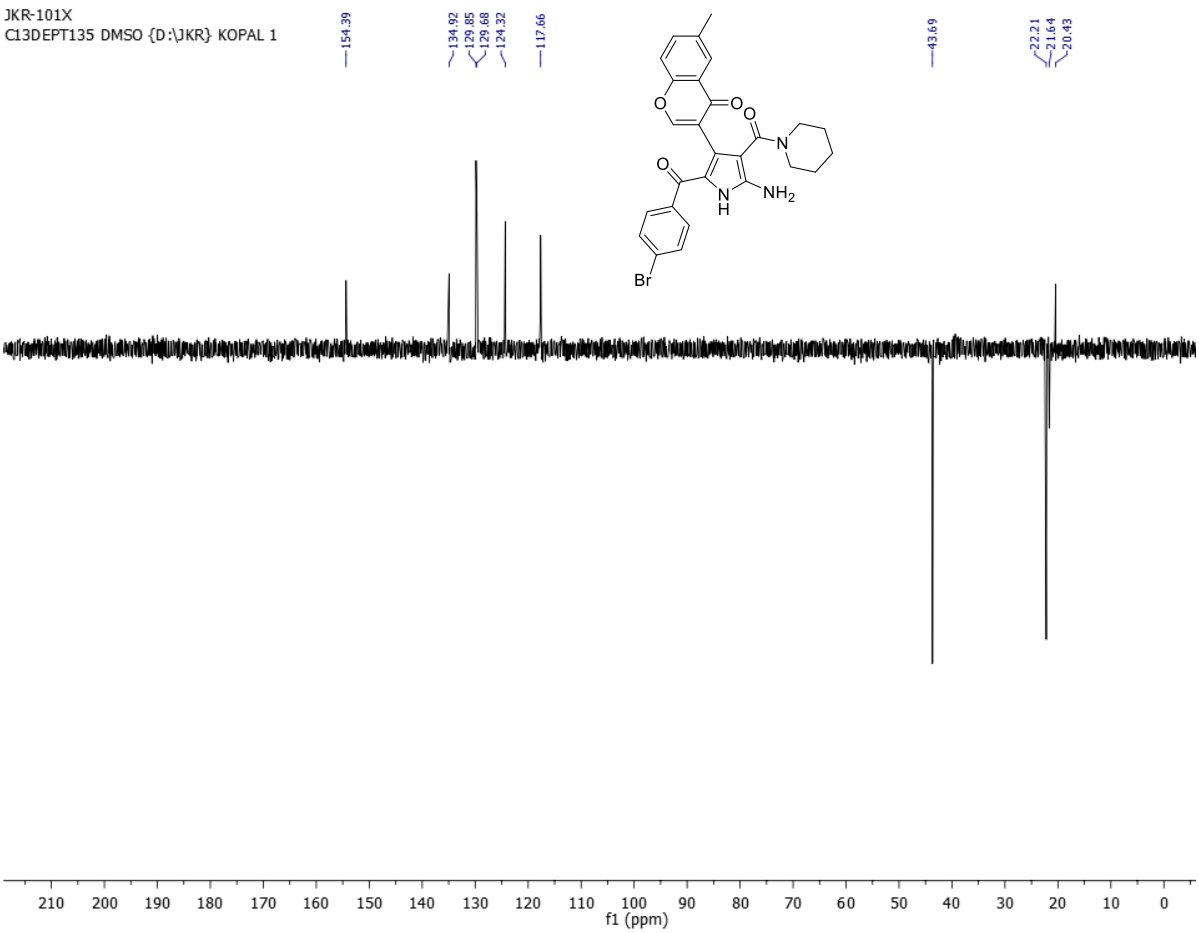
HRMS (ESI) spectrum of **8a**



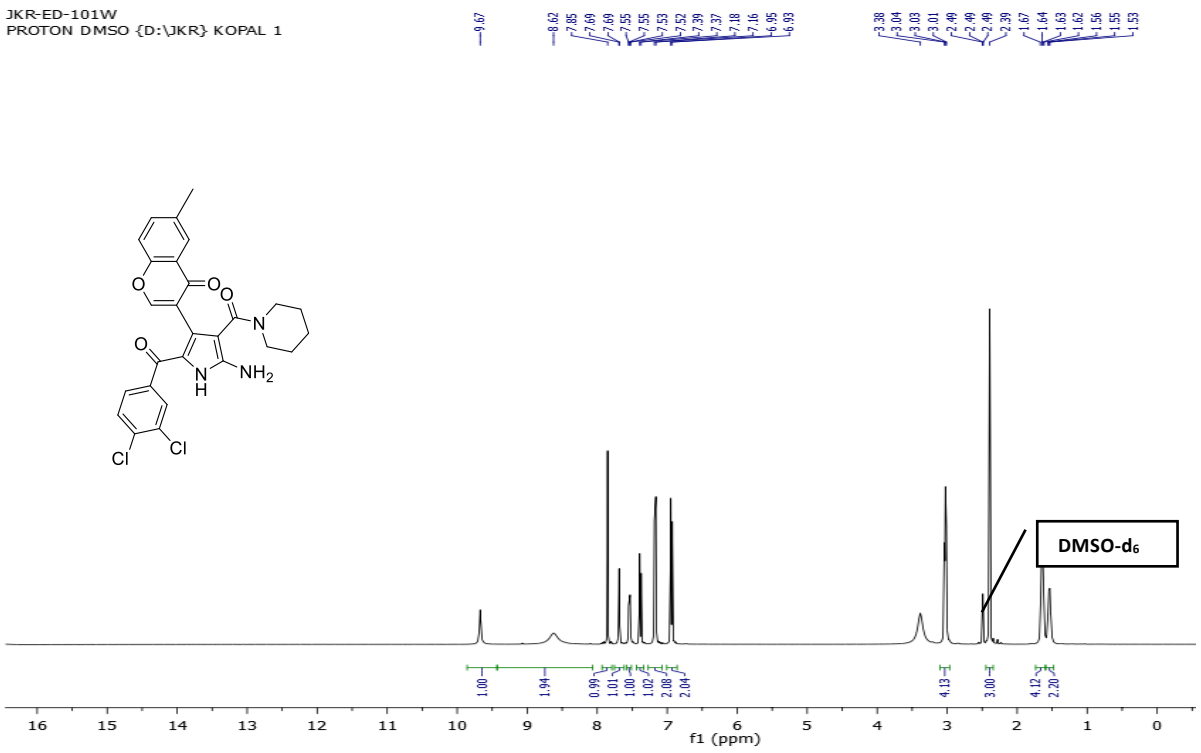
^{1}H NMR spectrum of **8b** (400 MHz, DMSO-d_6)



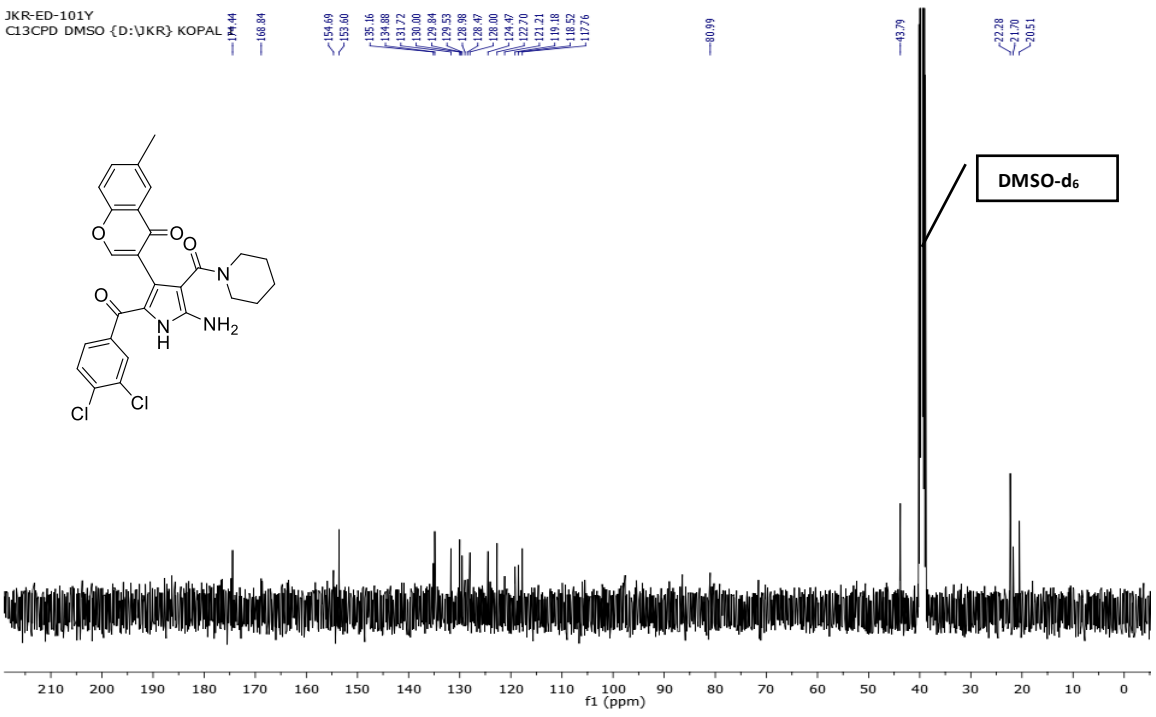
^{13}C{^{1}H} NMR spectrum of **8b** (100 MHz, DMSO-d_6)



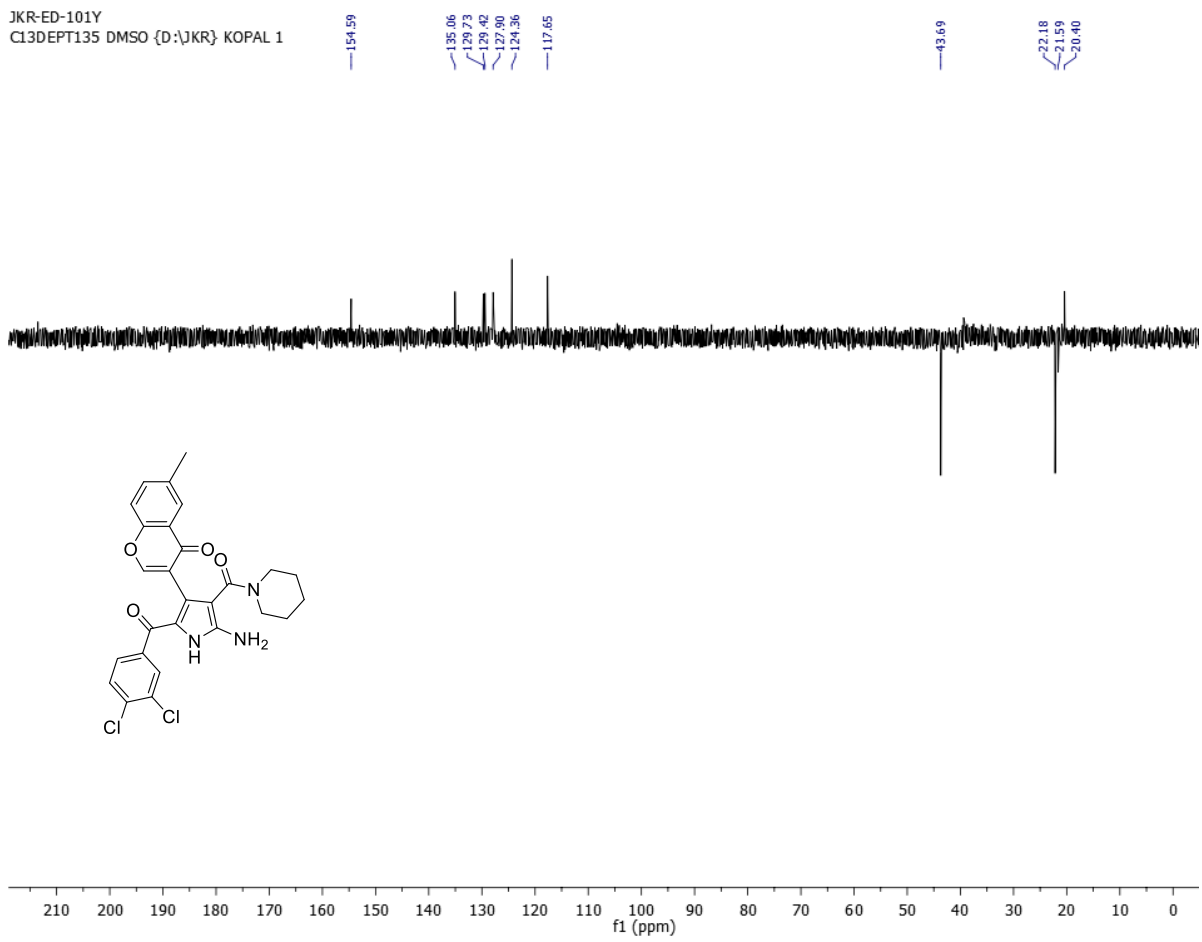
DEPT 135 NMR spectrum of **8b** (100 MHz, DMSO-d_6)



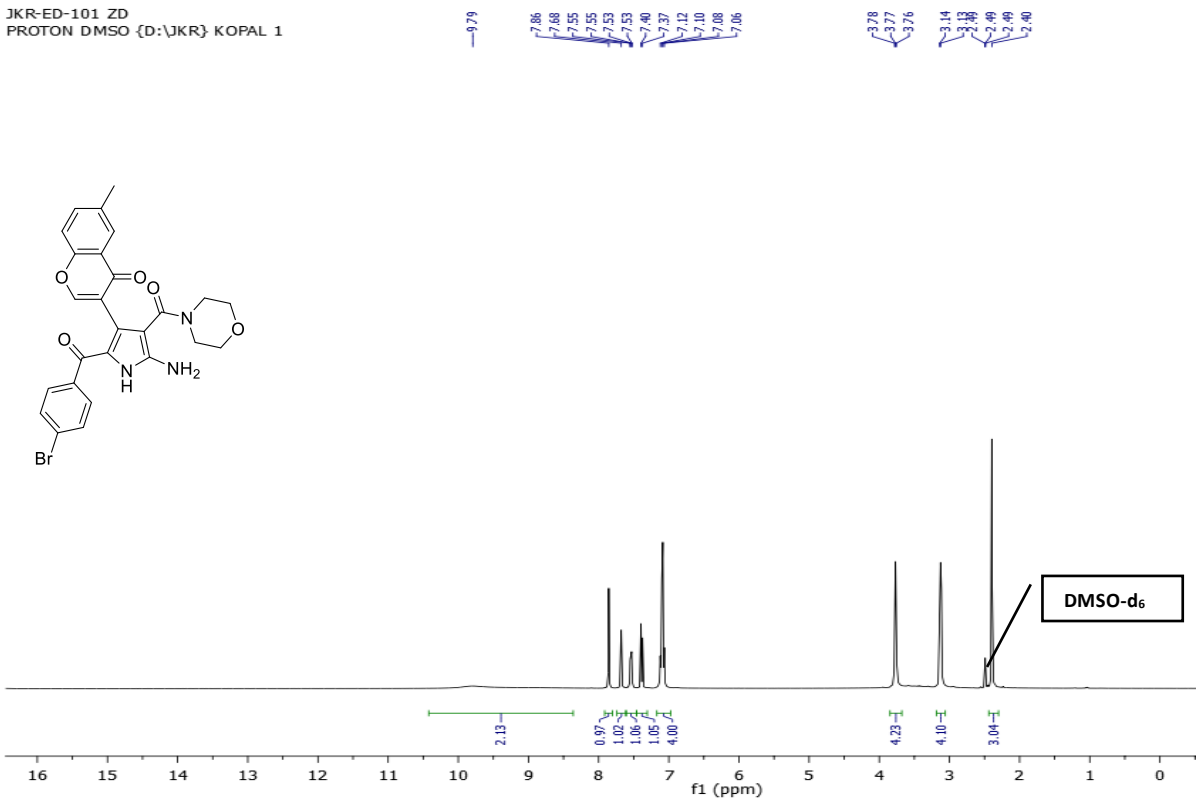
^{1}H NMR spectrum of **8c** (400 MHz, DMSO-d_6)



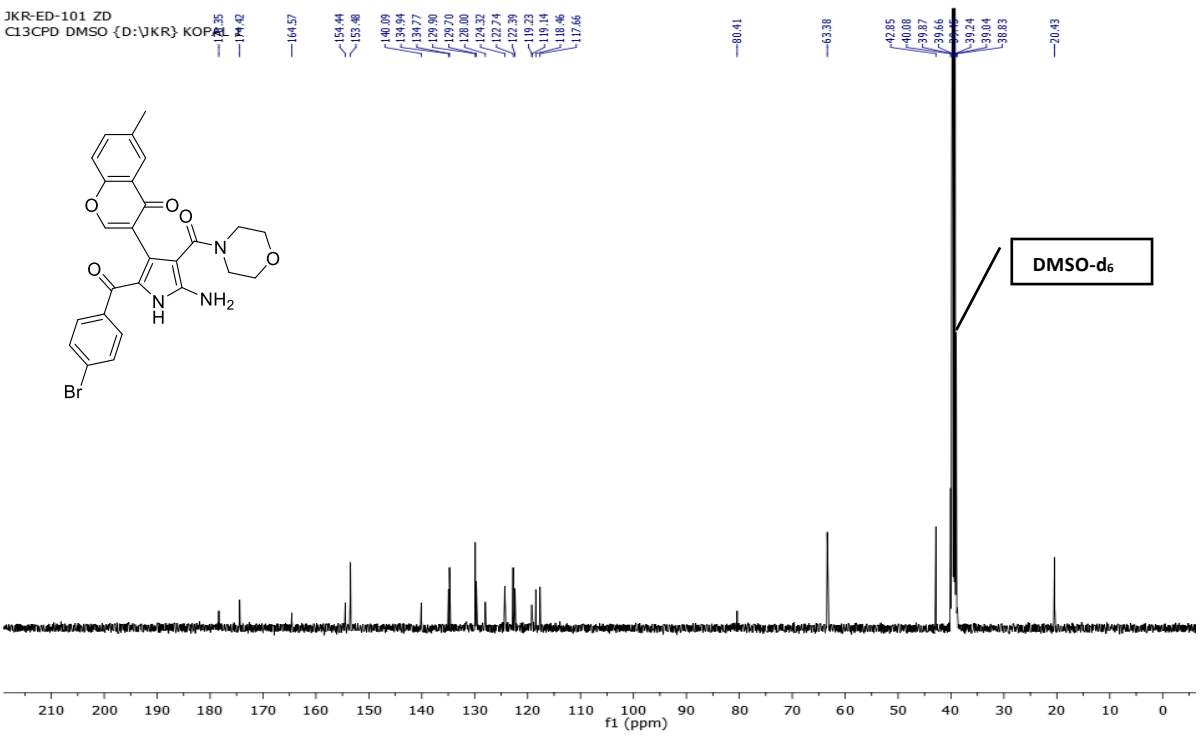
^{13}C{^{1}H} NMR spectrum of **8c** (100 MHz, DMSO-d_6)



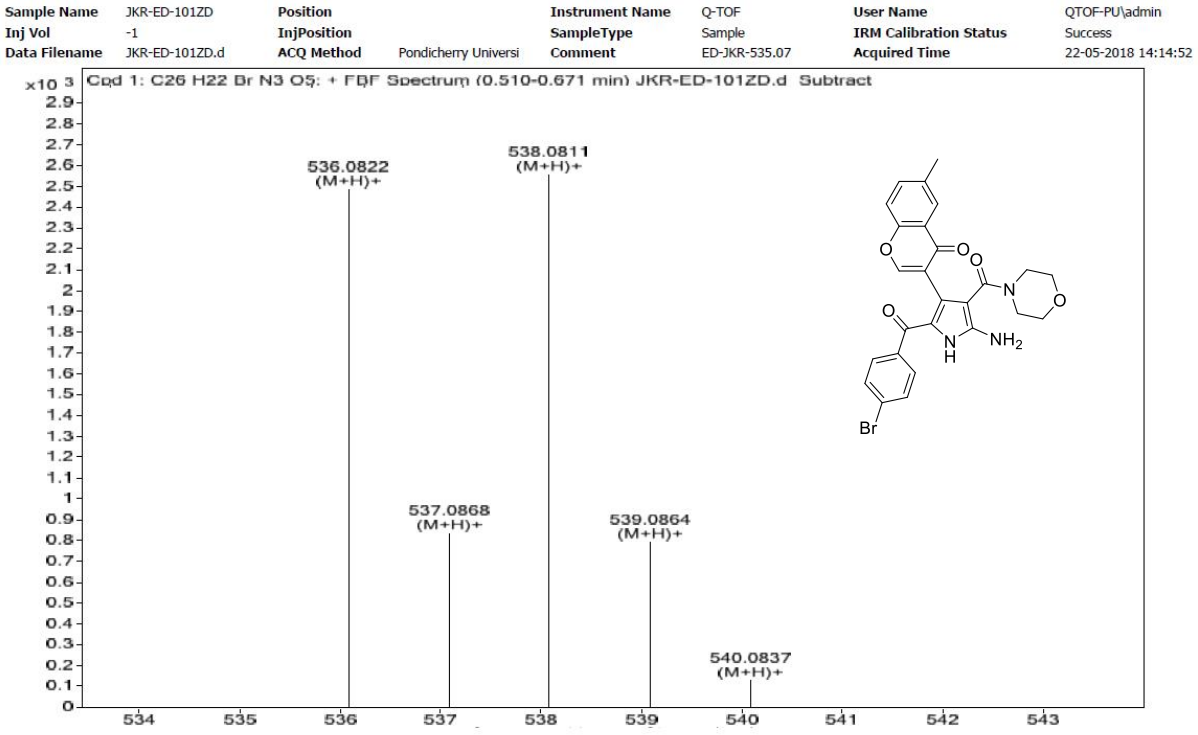
DEPT 135 NMR spectrum of **8c** (100 MHz, DMSO-d_6)



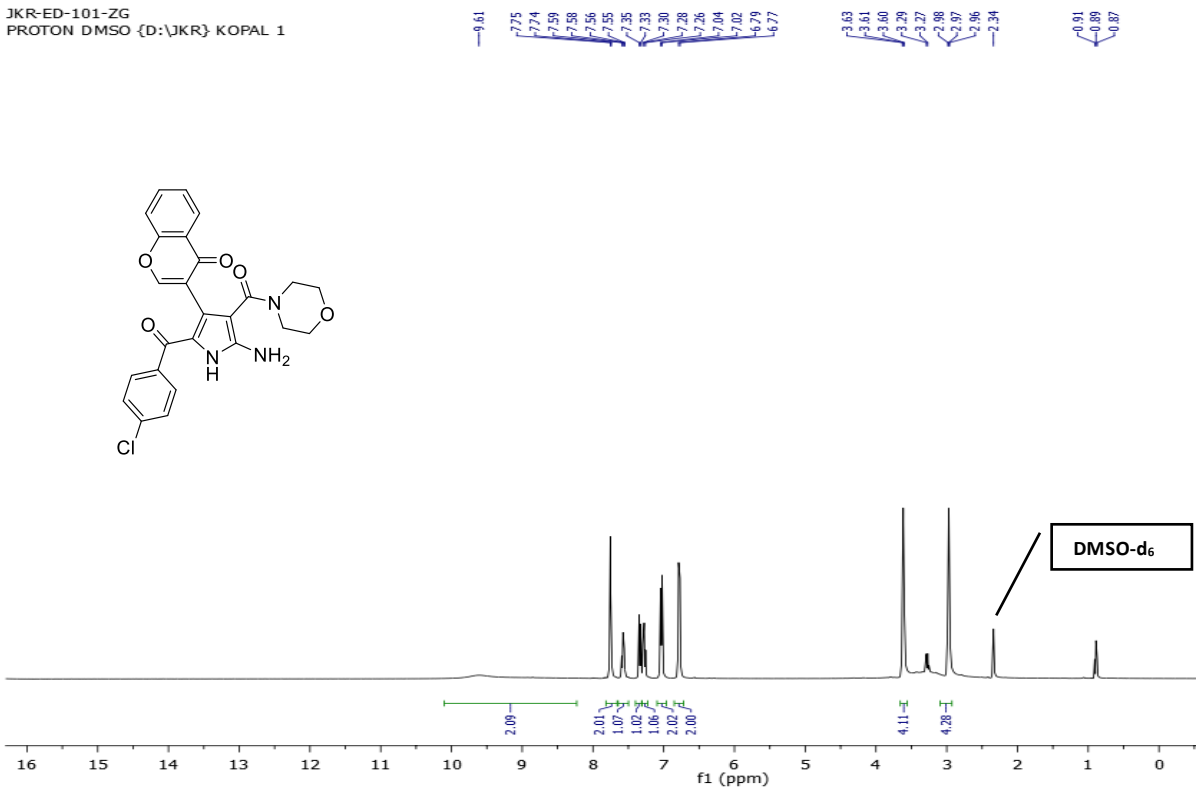
^{1}H NMR spectrum of **8d** (400 MHz, DMSO-d_6)



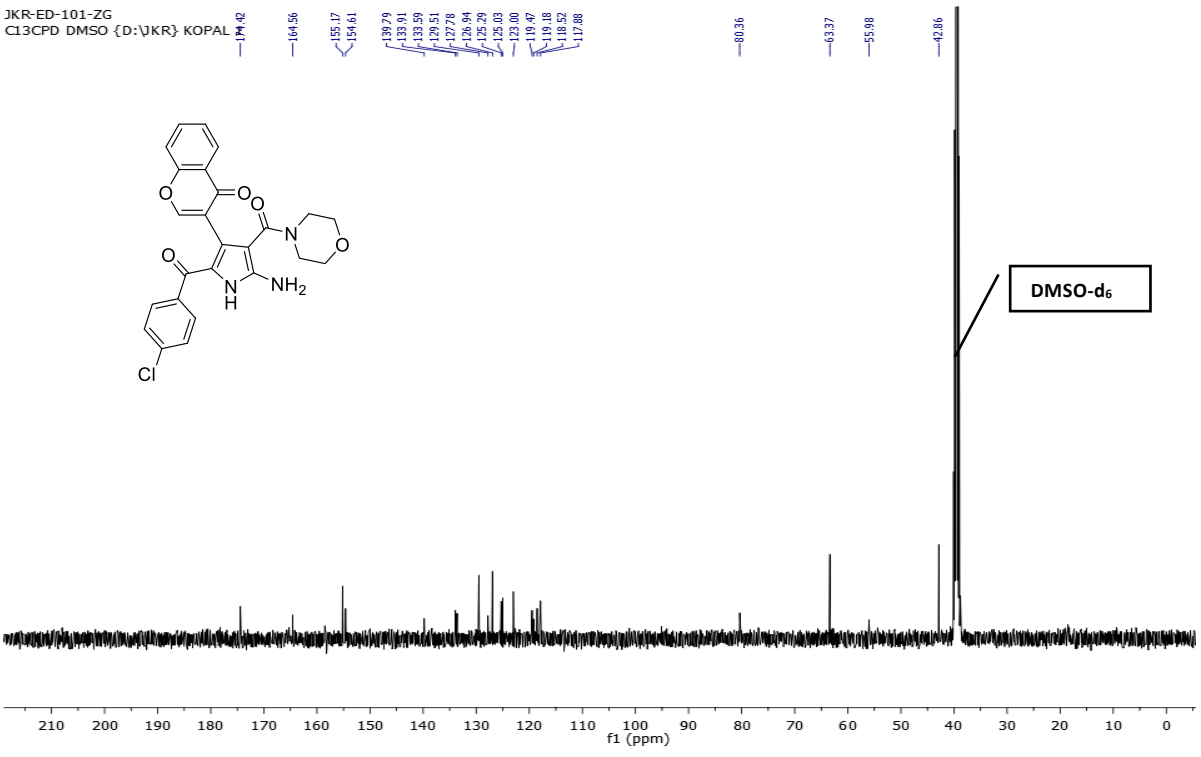
^{13}C{^{1}H} NMR spectrum of **8d** (100 MHz, DMSO-d_6)



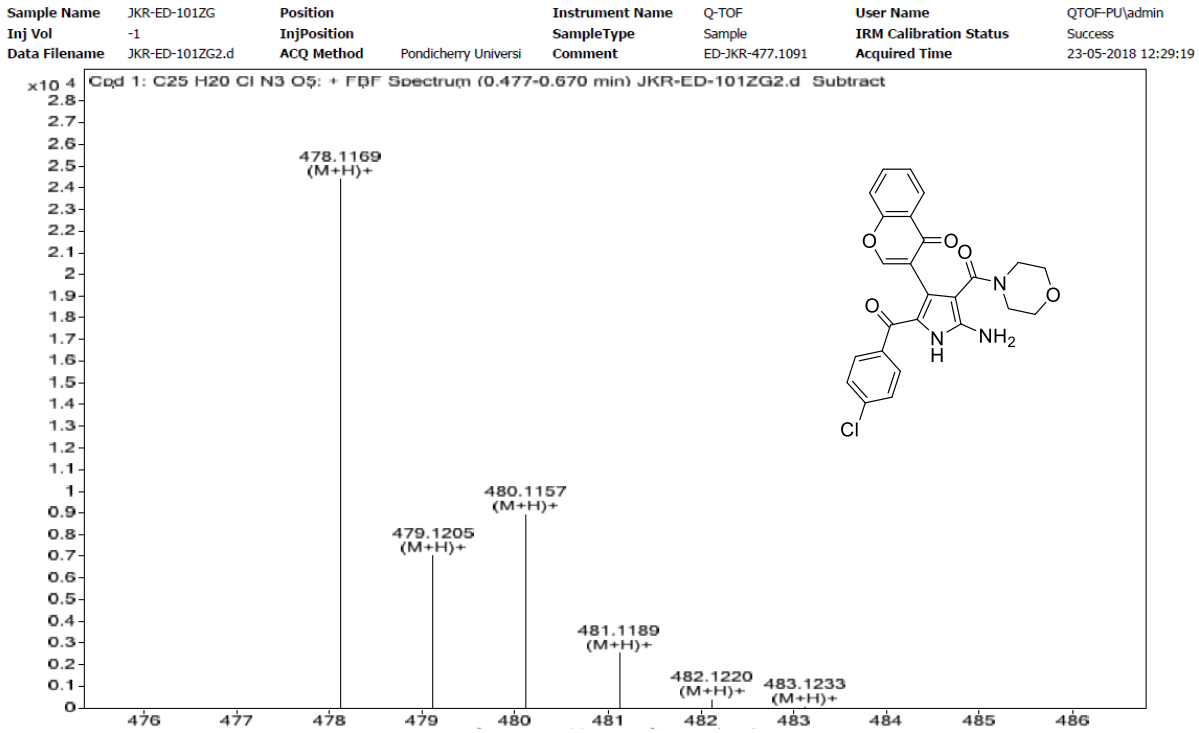
HRMS (ESI) spectrum of **8d**



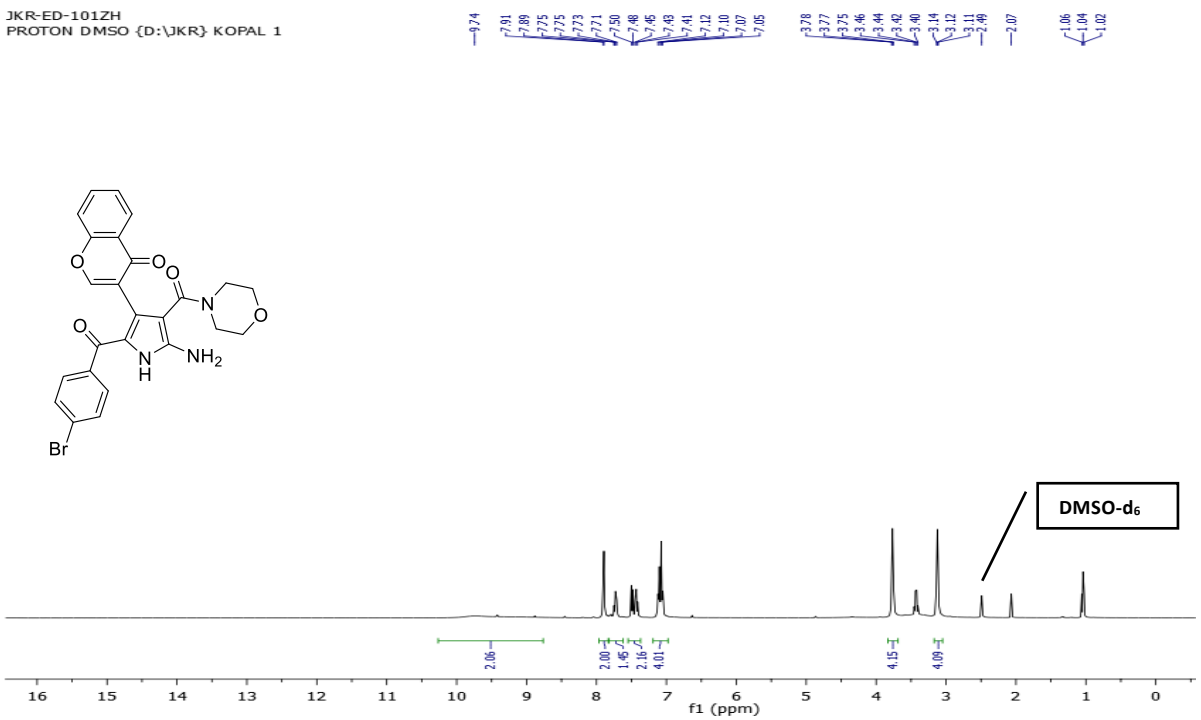
^{1}H NMR spectrum of **8e** (400 MHz, DMSO-d_6)



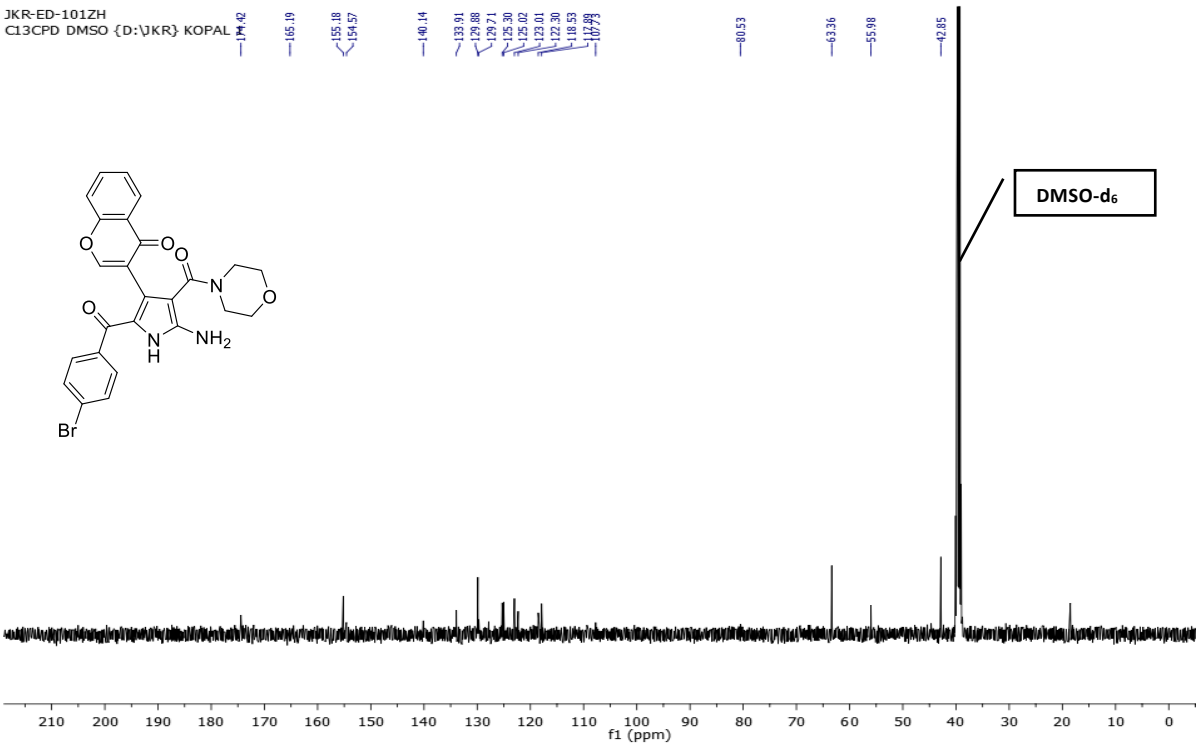
^{13}C{^{1}H} NMR spectrum of **8e** (100 MHz, DMSO-d_6)



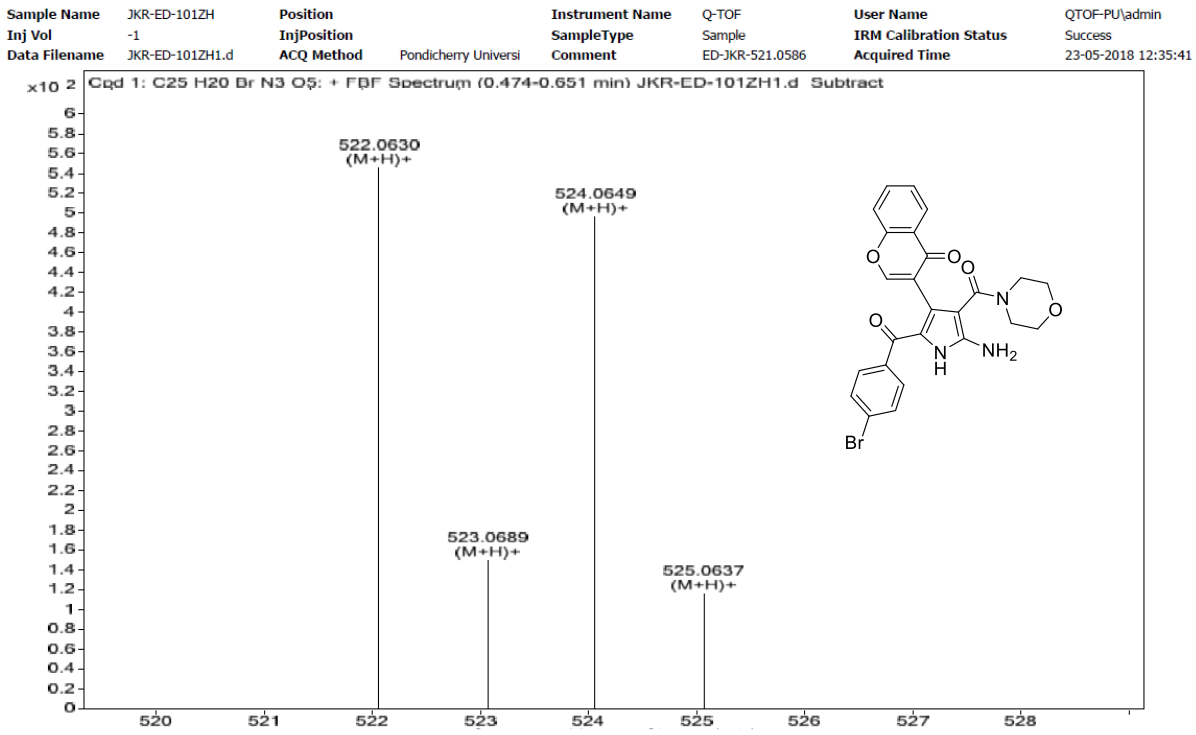
HRMS (ESI) spectrum of **8e**



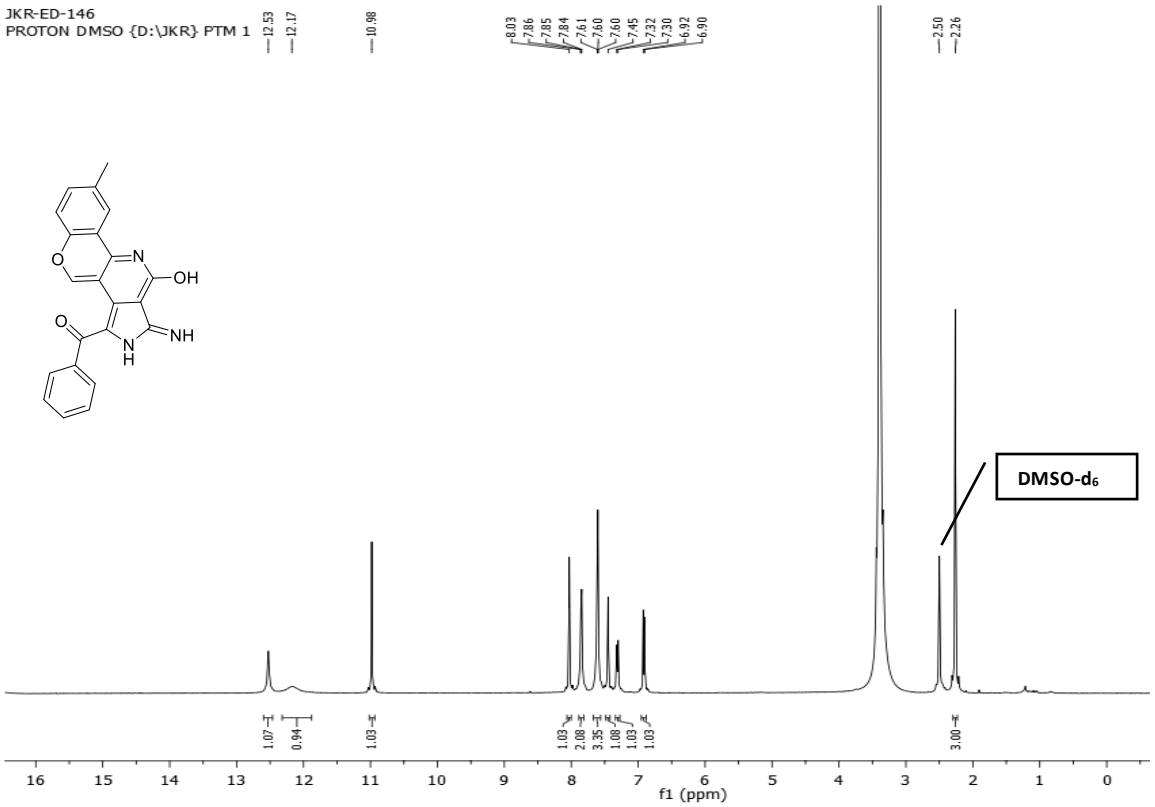
^{1}H NMR spectrum of **8f** (400 MHz, DMSO-d_6)



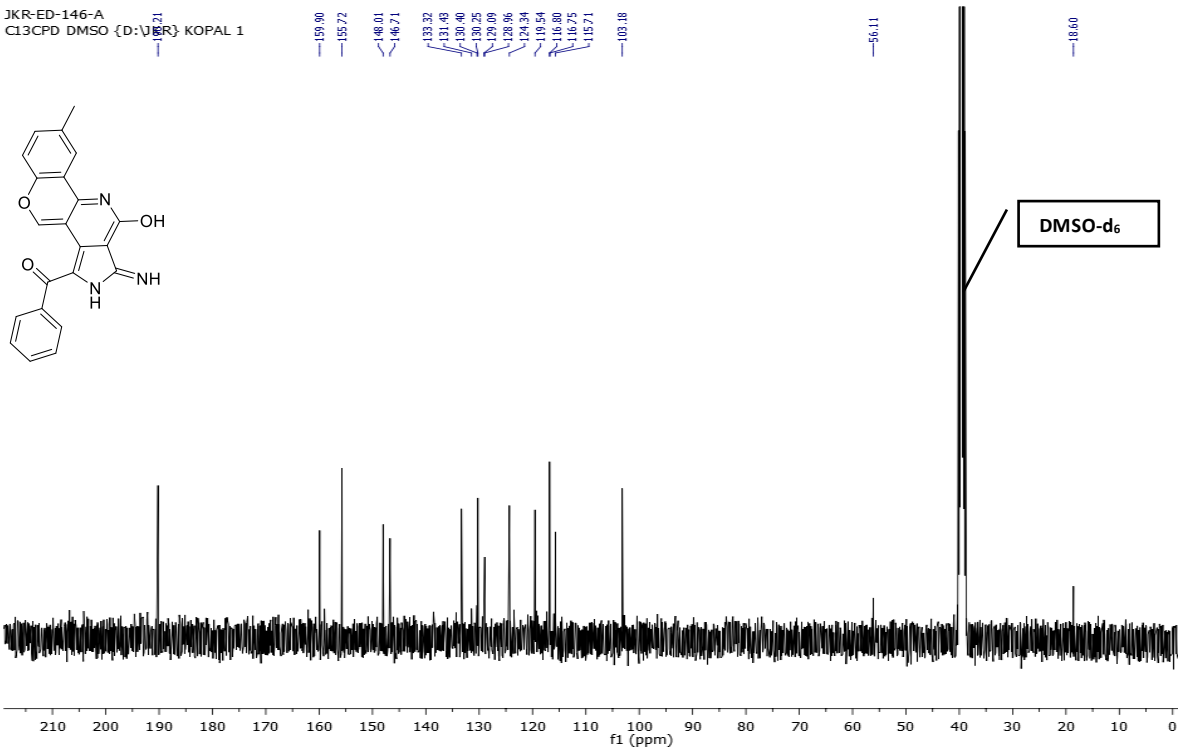
^{13}C{^{1}H} NMR spectrum of **8f** (100 MHz, DMSO-d_6)



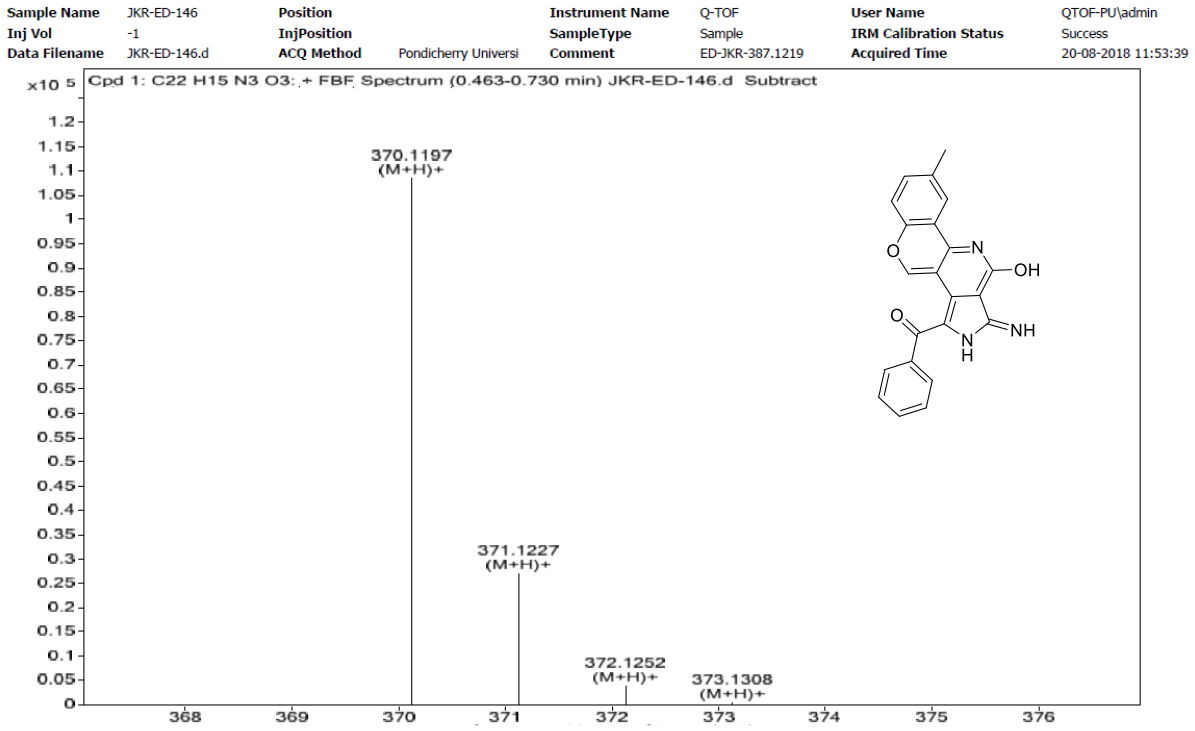
HRMS (ESI) spectrum of **8f**



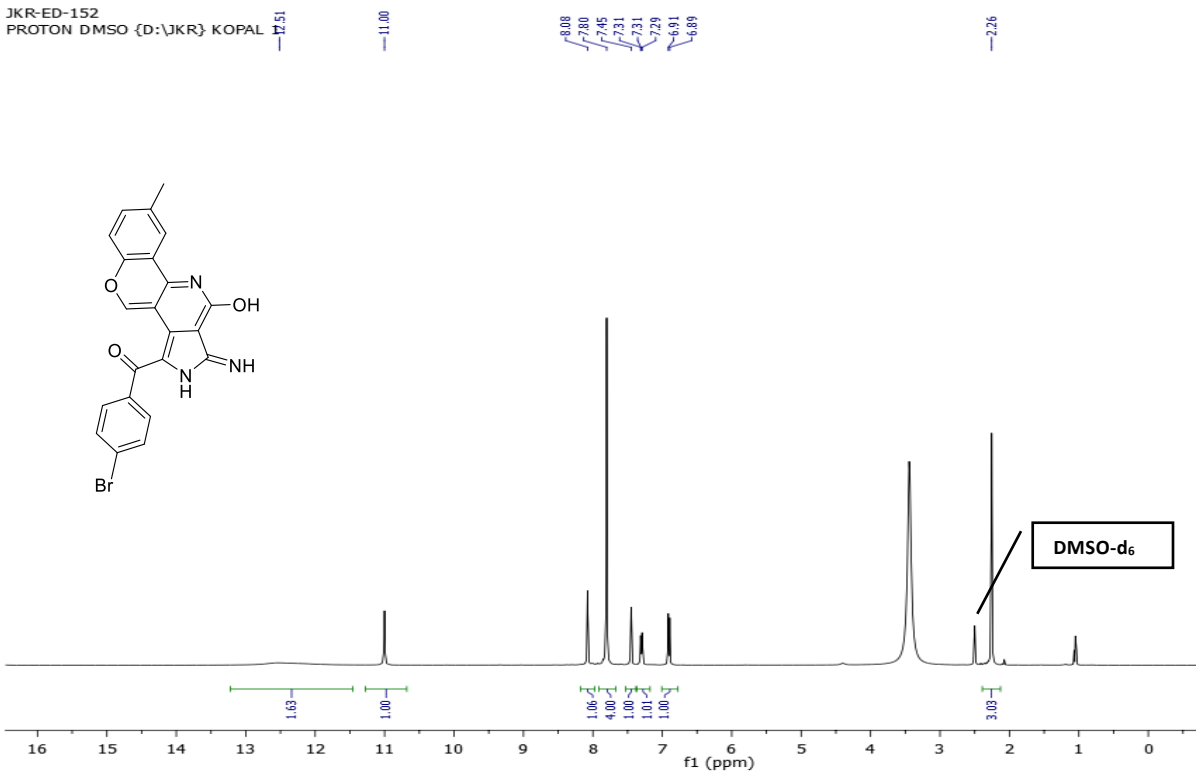
^{1}H NMR spectrum of **10a** (400 MHz, DMSO-d_6)



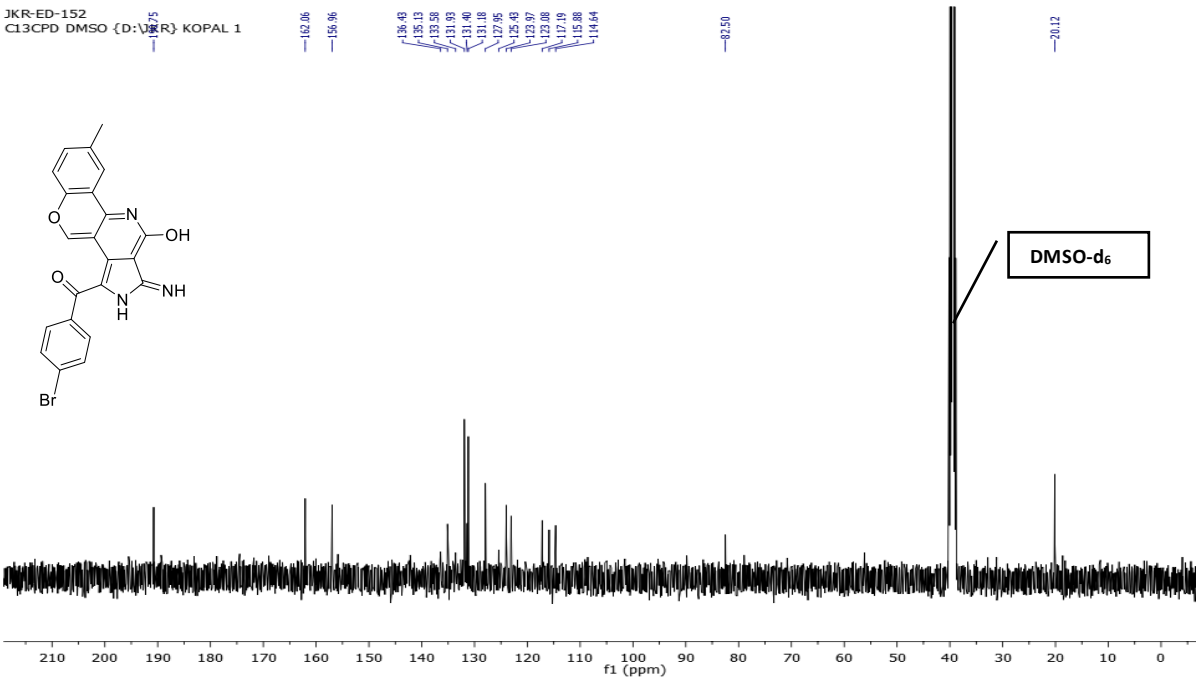
^{13}C{^{1}H} NMR spectrum of **10a** (100 MHz, DMSO-d_6)



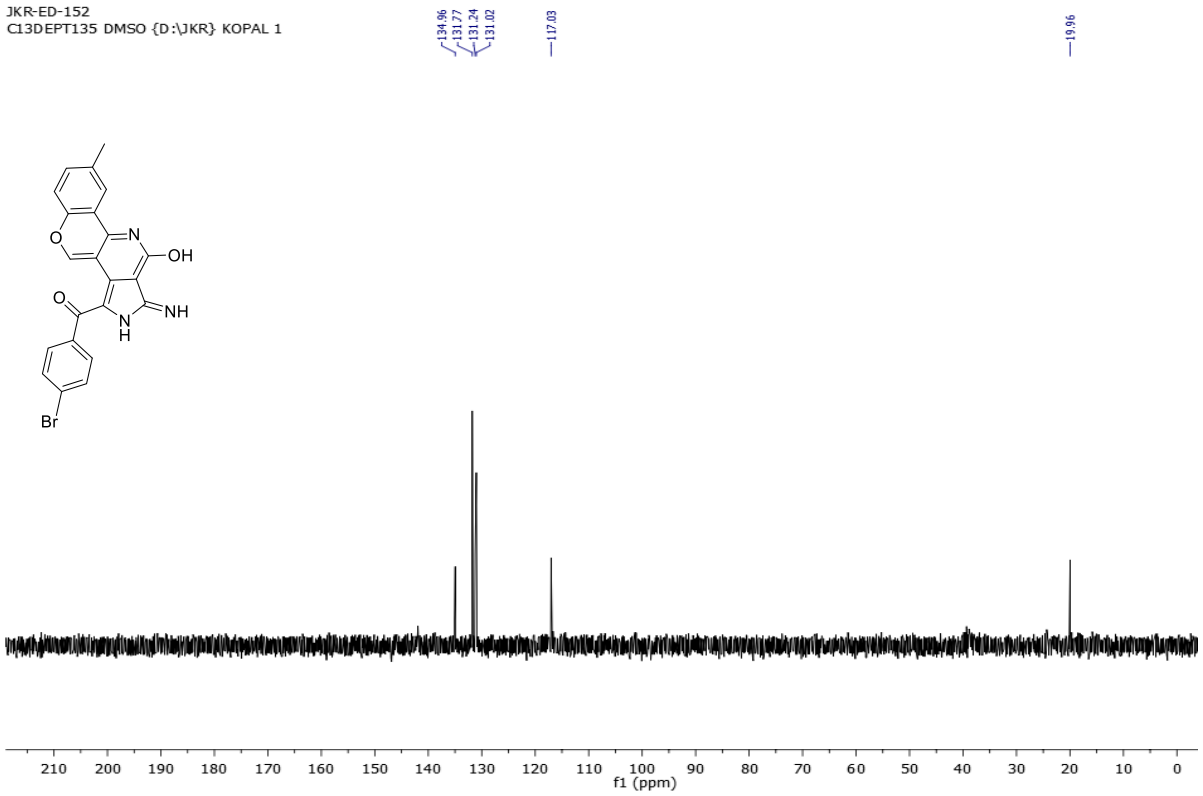
HRMS (ESI) spectrum of **10a**



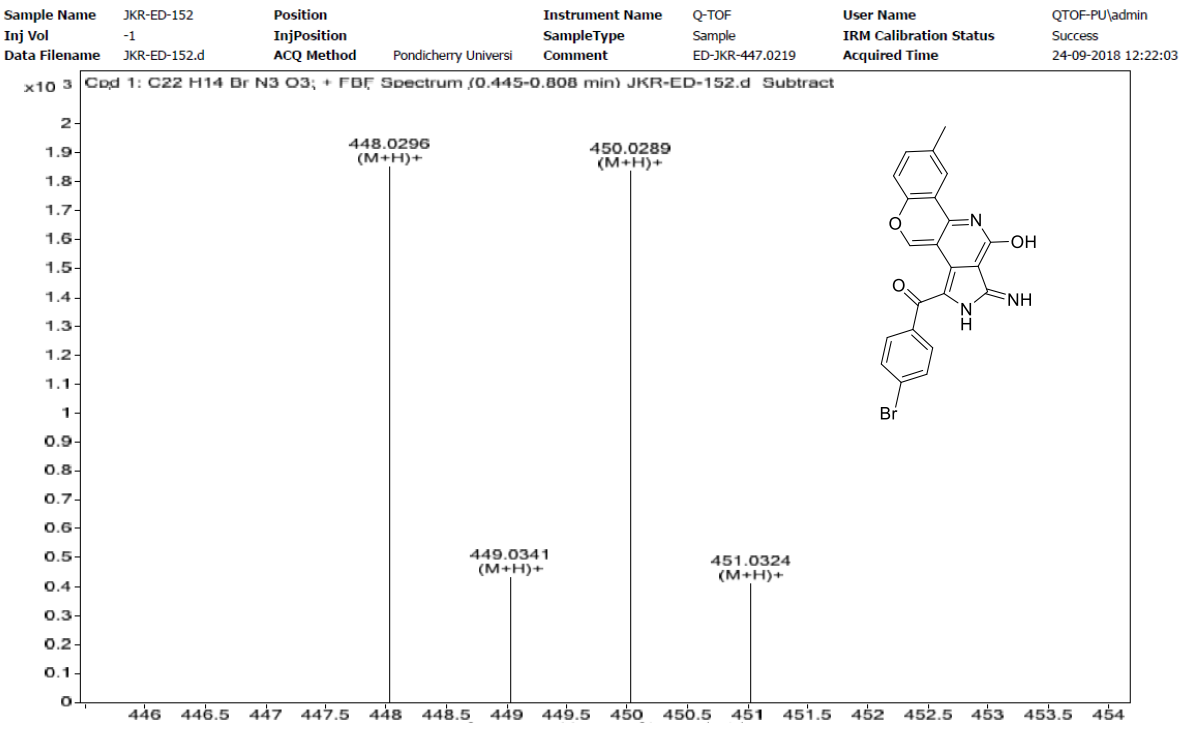
^{1}H NMR spectrum of **10b** (400 MHz, DMSO-d_6)



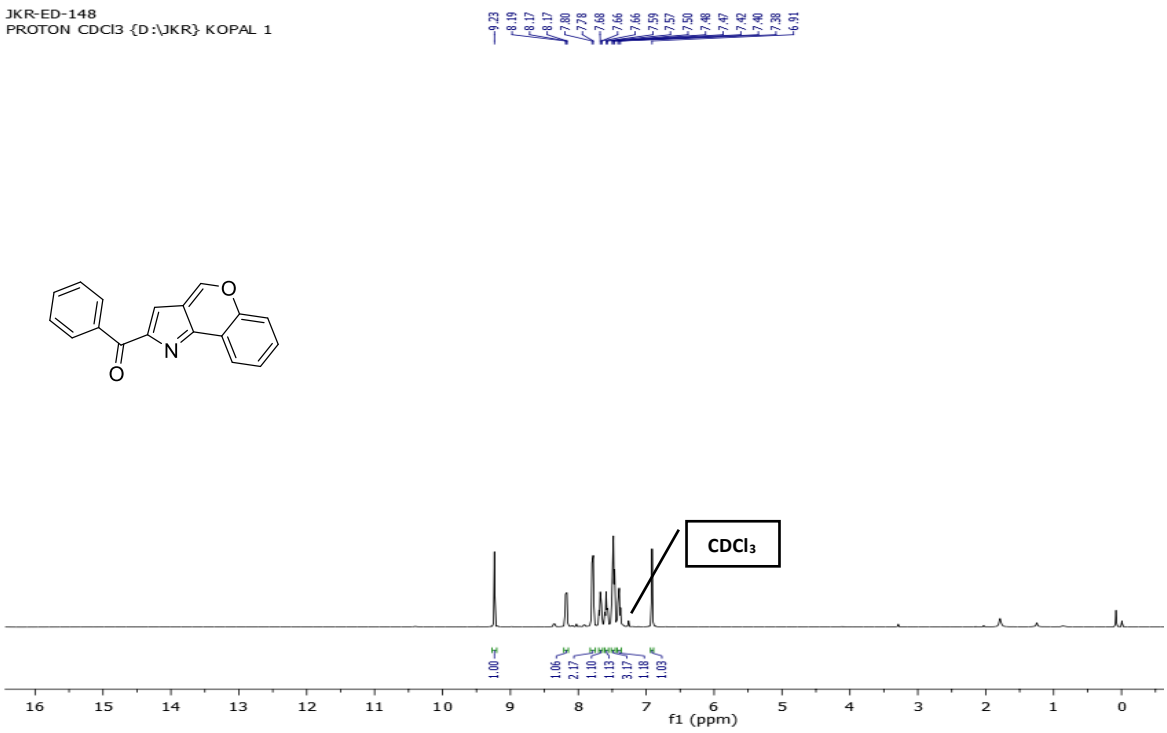
^{13}C{^{1}H} NMR spectrum of **10b** (100 MHz, DMSO-d_6)



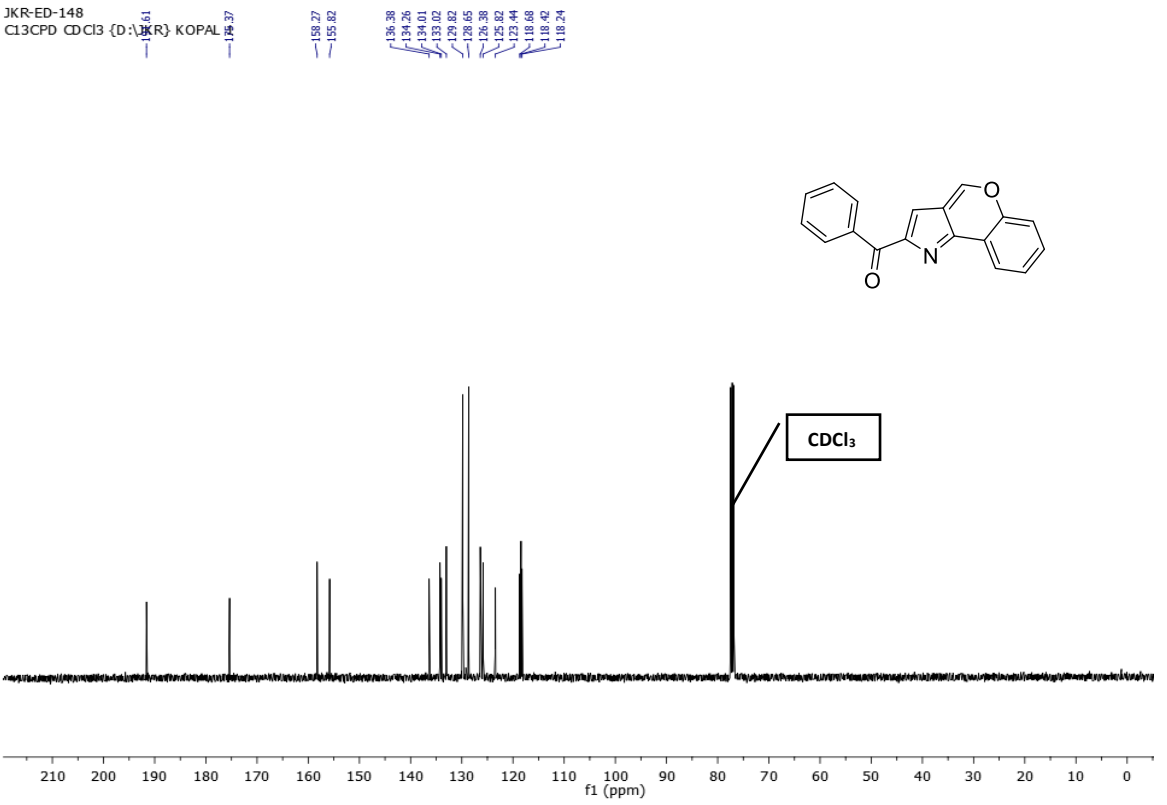
DEPT 135 NMR spectrum of **10b** (100 MHz, DMSO-d_6)



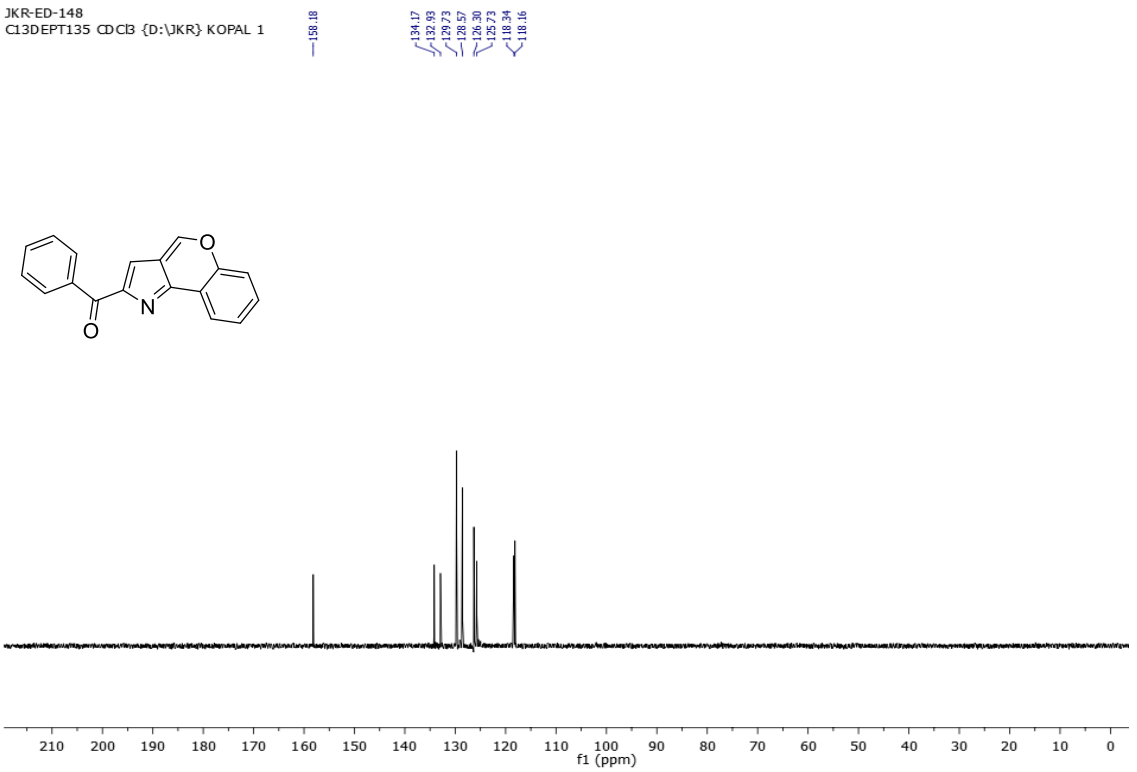
HRMS (ESI) spectrum of **10b**



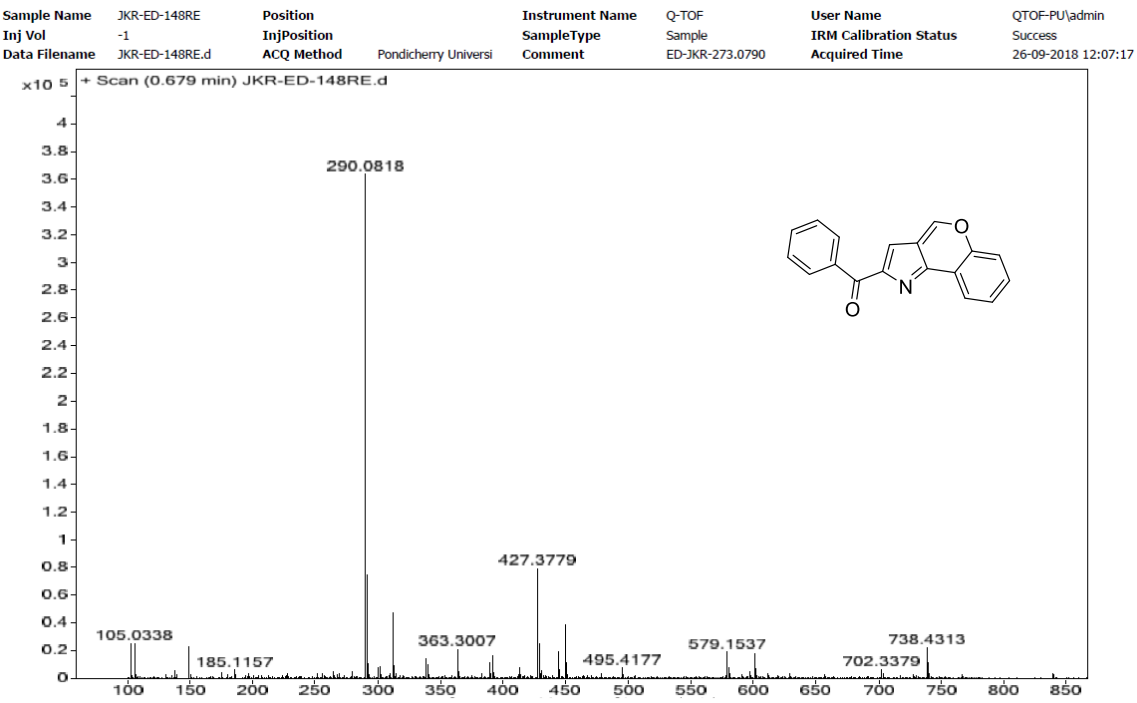
^{1}H NMR spectrum of **12a** (400 MHz, $CDCl_3$)



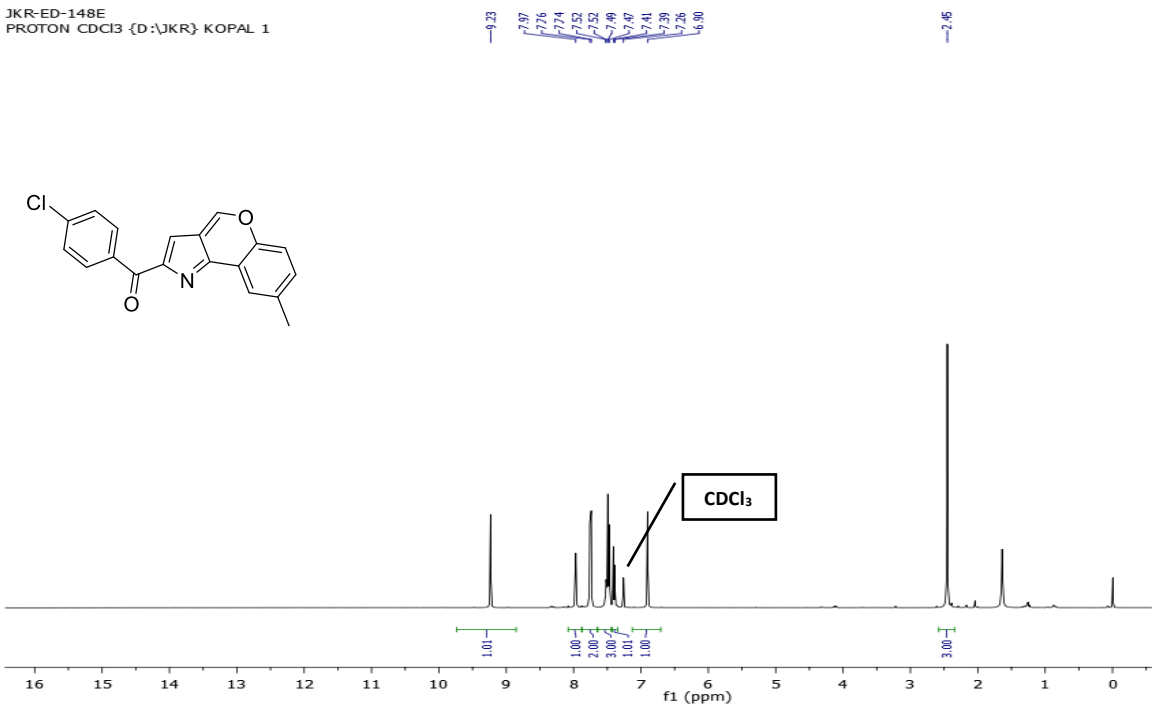
^{13}C{^{1}H} NMR spectrum of **12a** (100 MHz, $CDCl_3$)



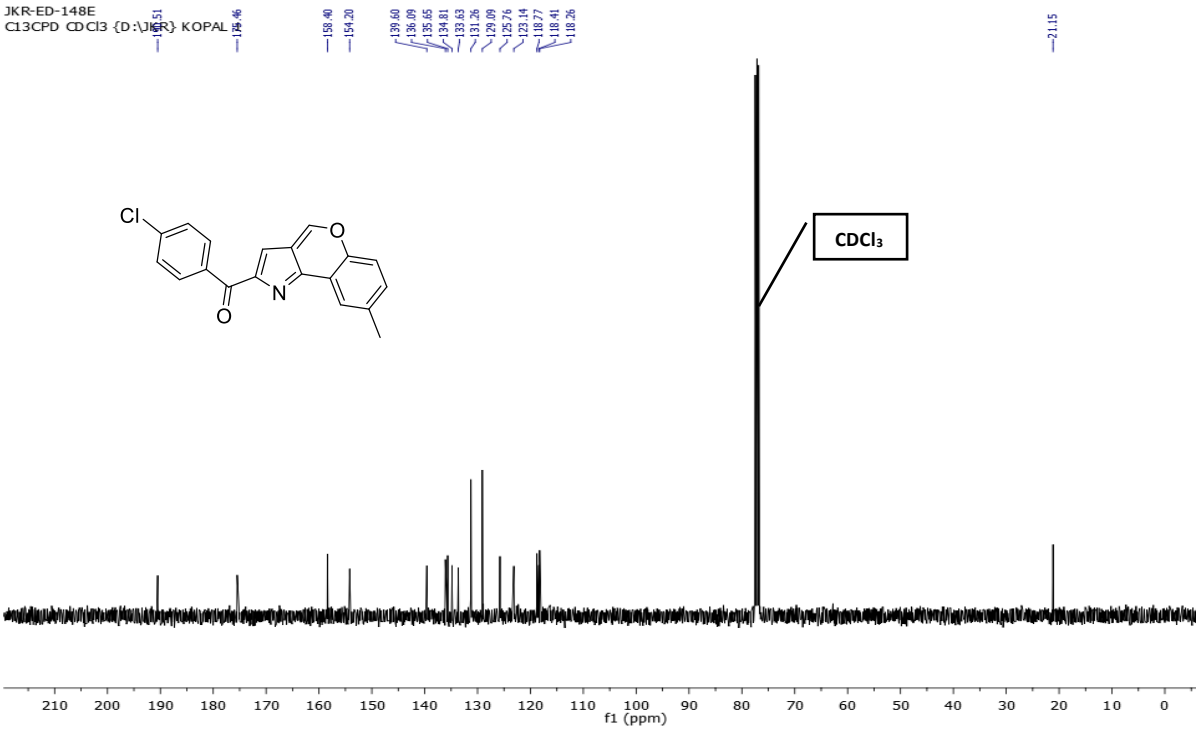
DEPT 135 NMR spectrum of **12a** (100 MHz, $CDCl_3$)



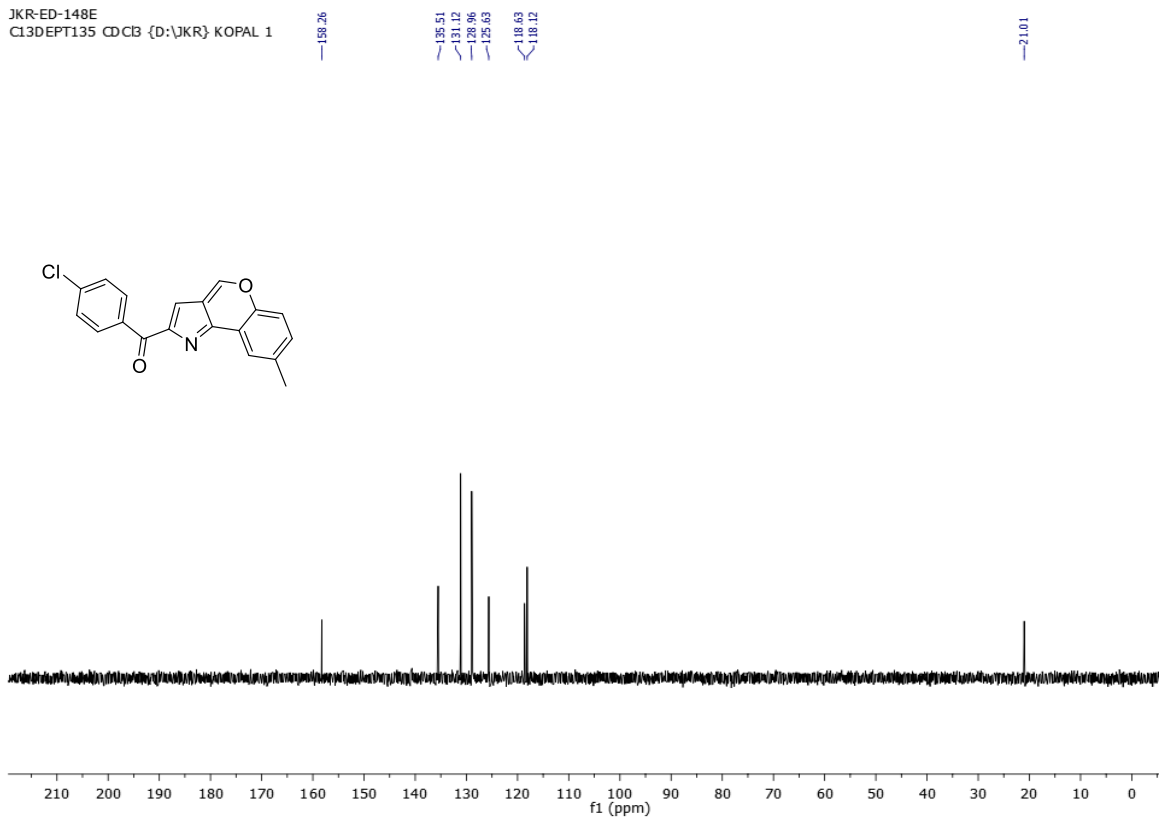
HRMS (ESI) spectrum of **12a**



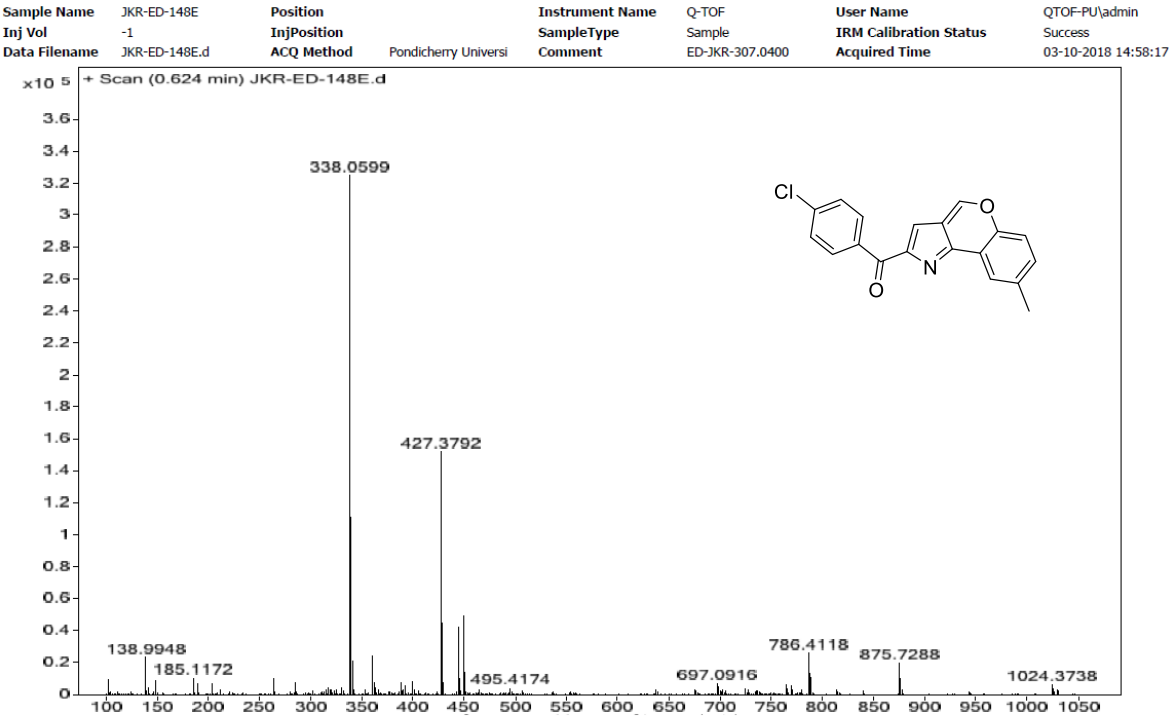
^{1}H NMR spectrum of **12b** (400 MHz, $CDCl_3$)



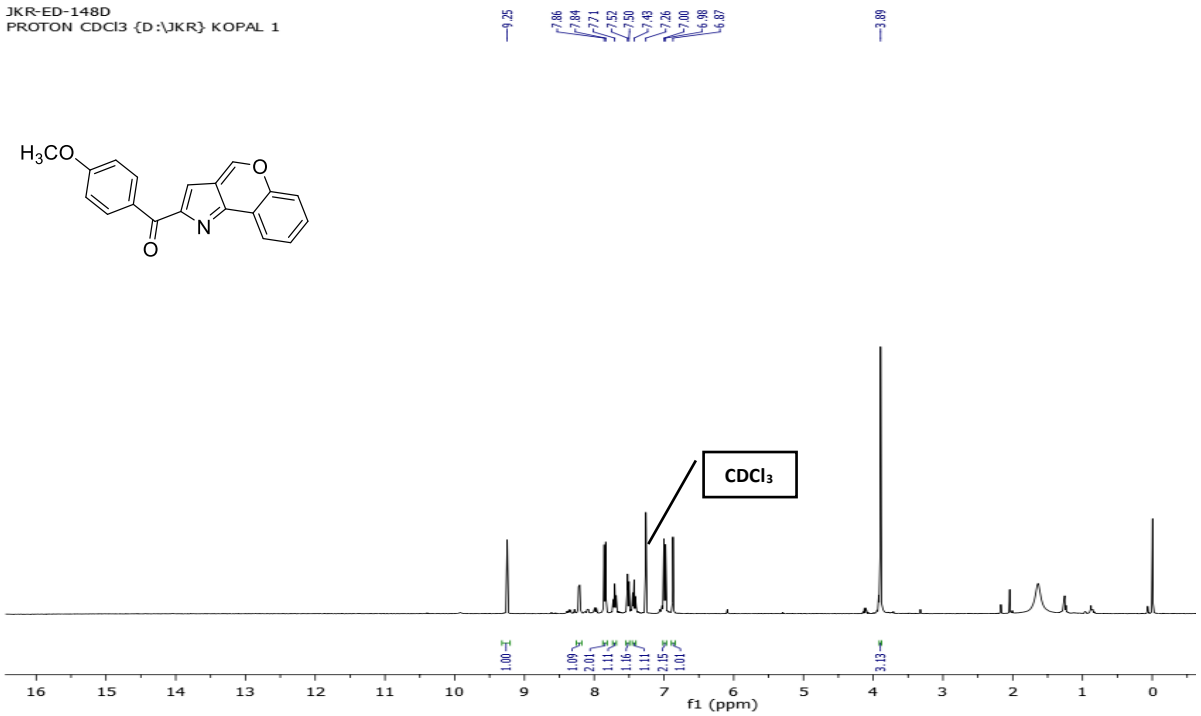
^{13}C{^{1}H} NMR spectrum of **12b** (100 MHz, $CDCl_3$)



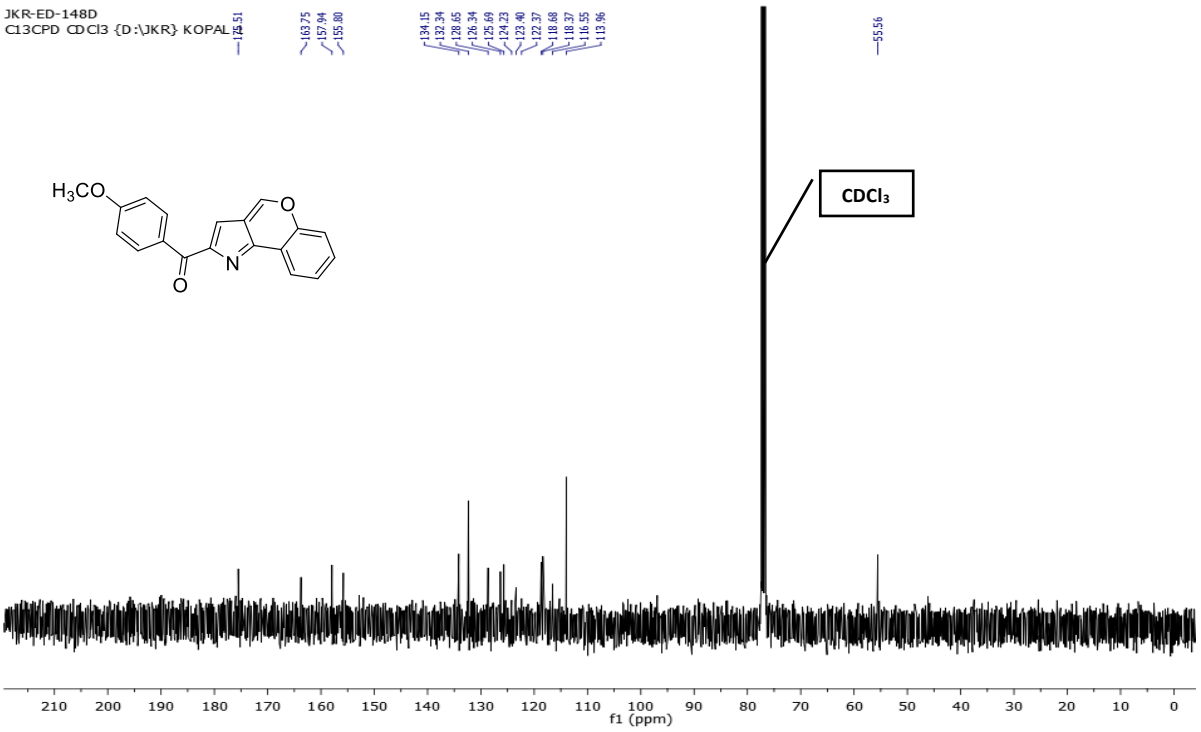
DEPT 135 NMR spectrum of **12b** (100 MHz, $CDCl_3$)



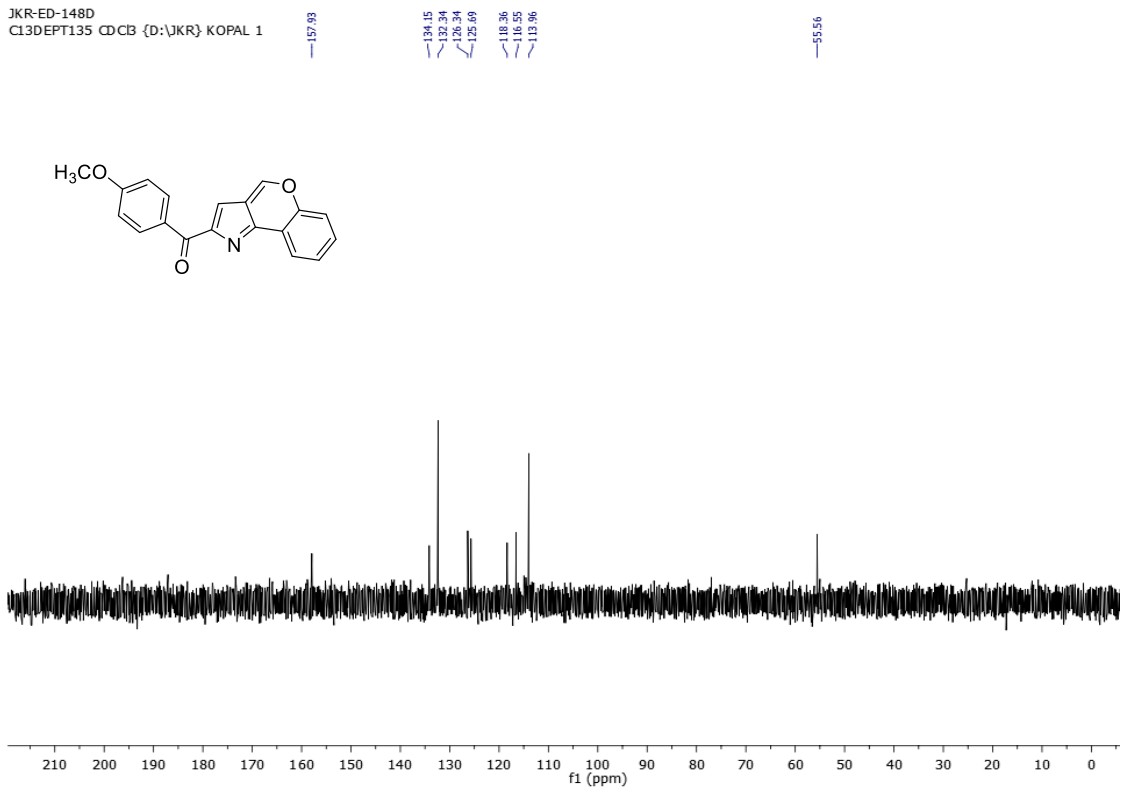
HRMS (ESI) spectrum of **12b**



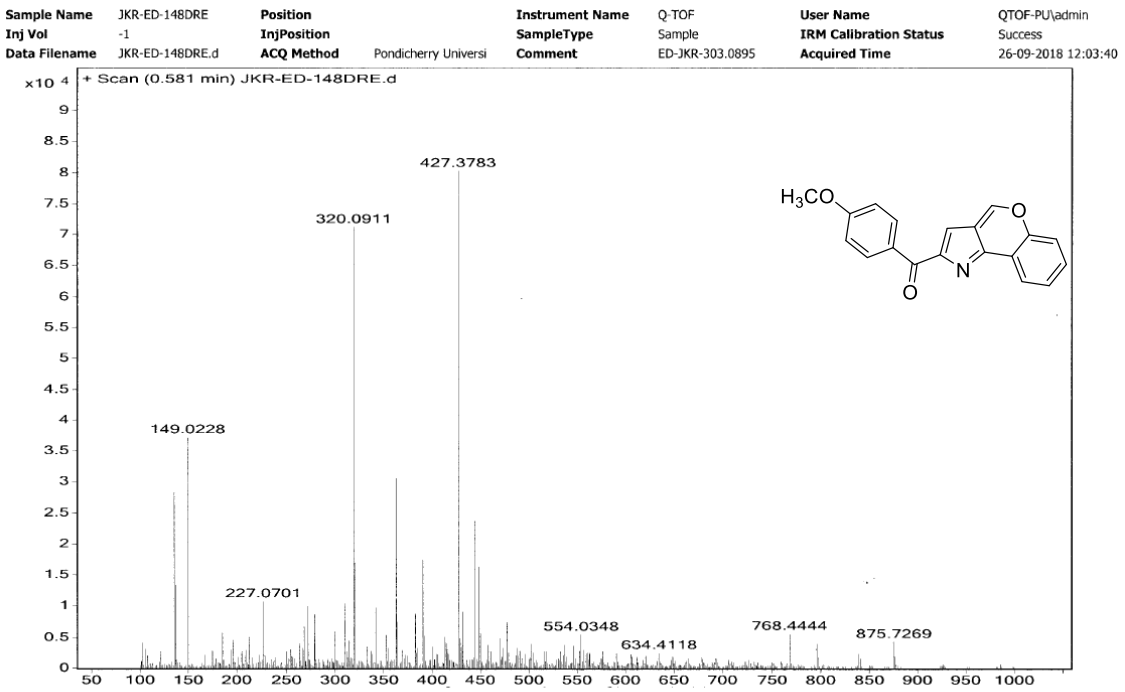
^{1}H NMR spectrum of **12c** (400 MHz, $CDCl_3$)



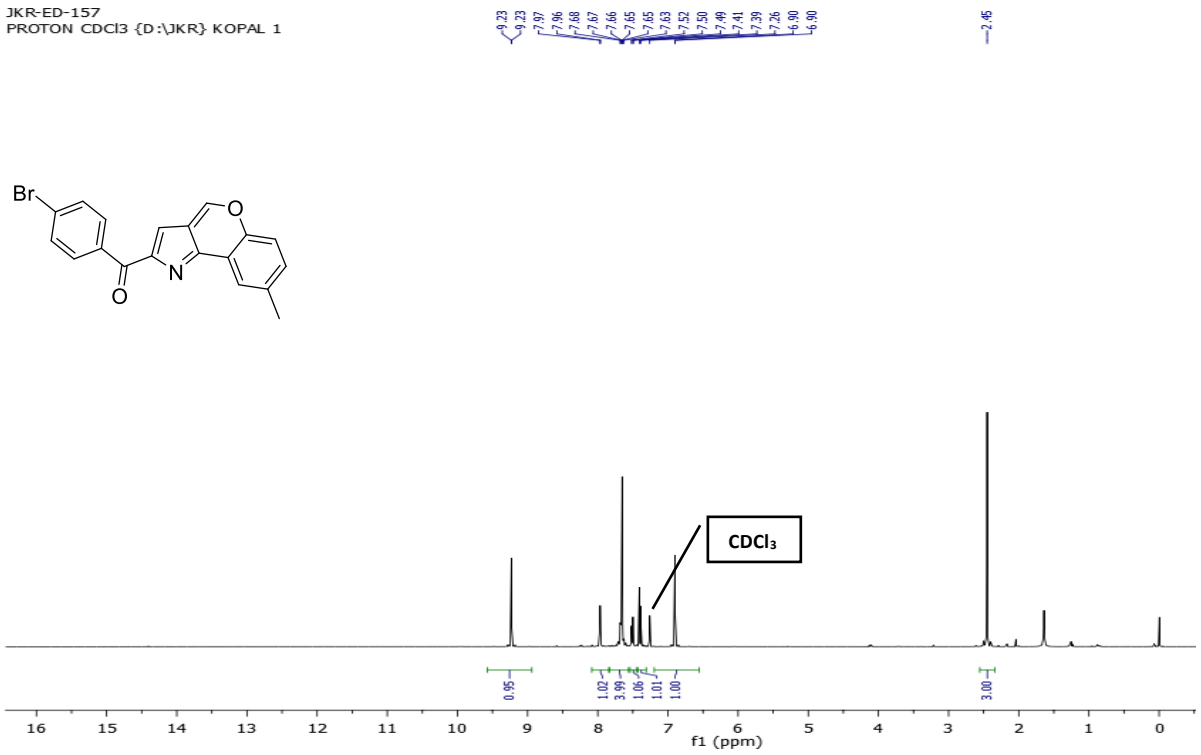
^{13}C{^{1}H} NMR spectrum of **12c** (100 MHz, $CDCl_3$)



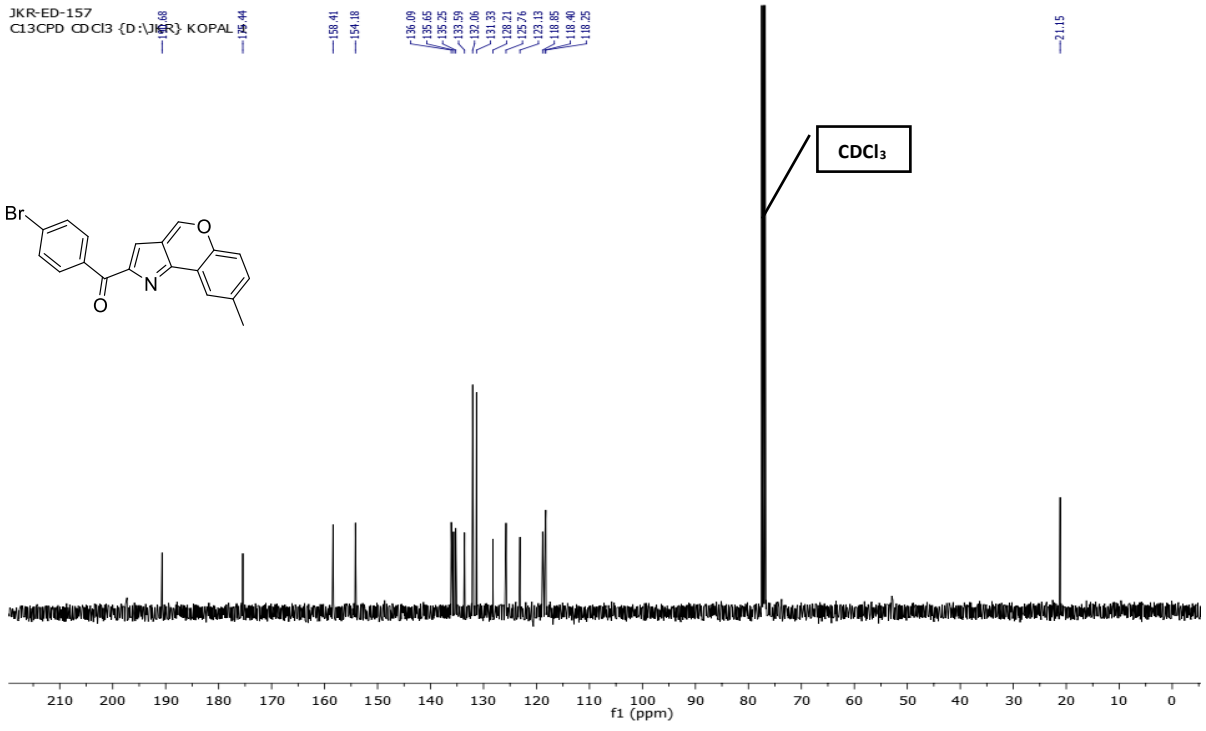
DEPT 135 NMR spectrum of **12c** (100 MHz, $CDCl_3$)



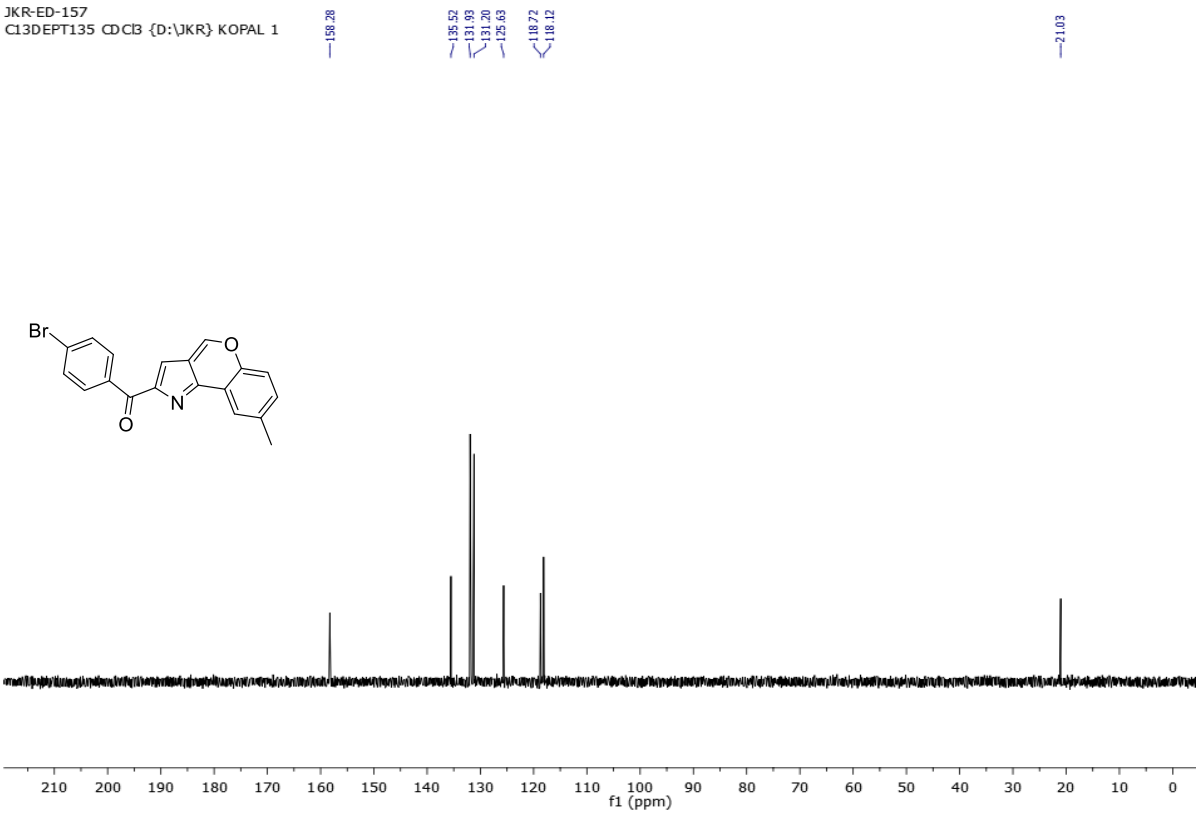
HRMS (ESI) spectrum of **12c**



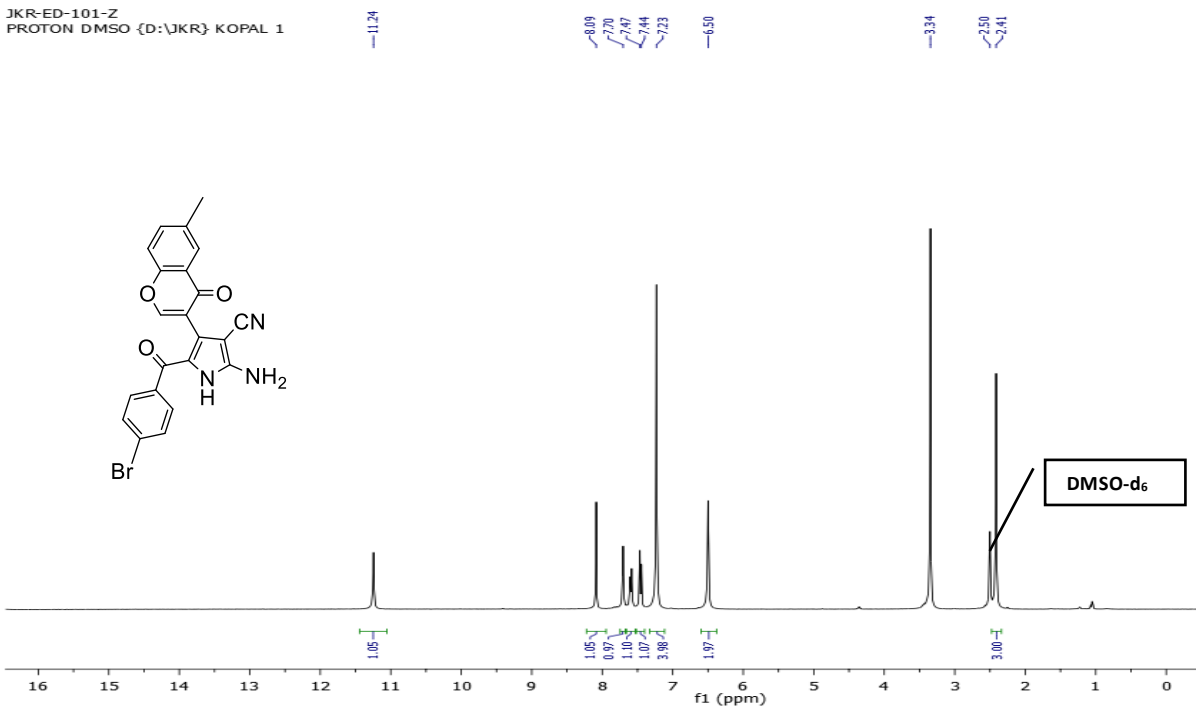
^{1}H NMR spectrum of **12d** (400 MHz, $CDCl_3$)



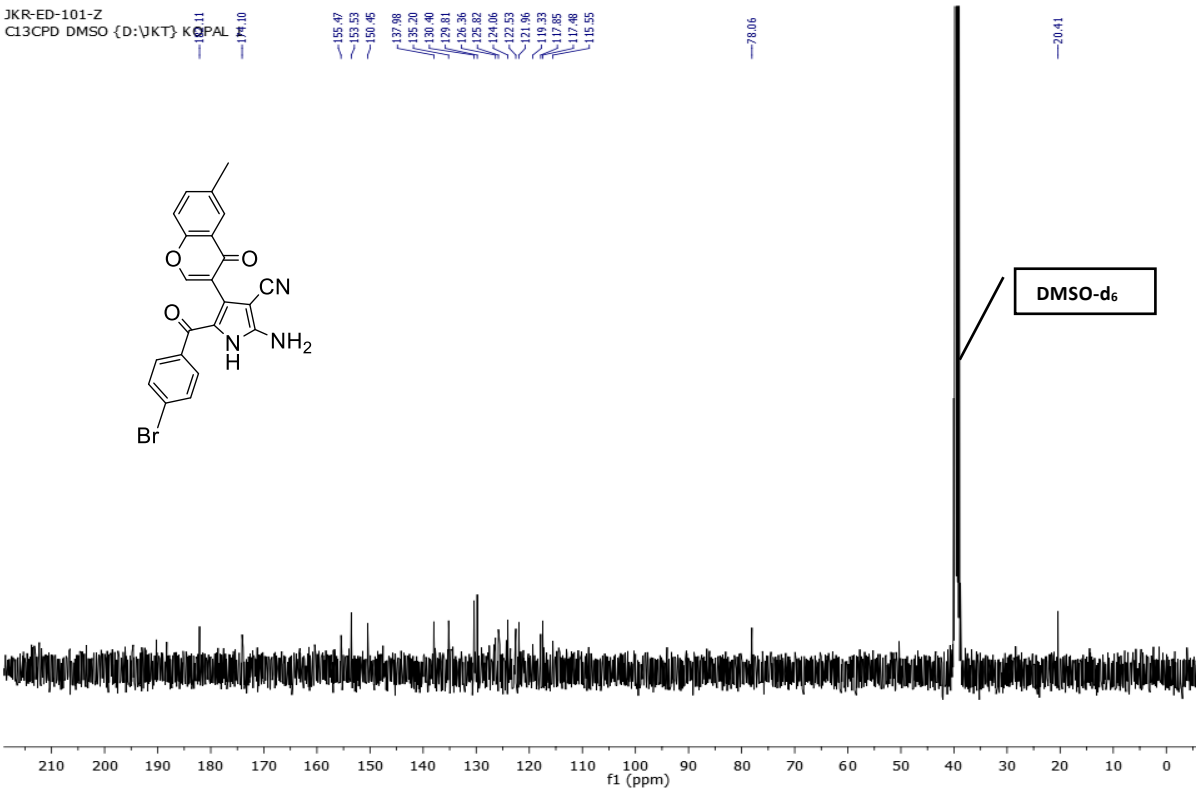
^{13}C{^{1}H} NMR spectrum of **12d** (100 MHz, $CDCl_3$)



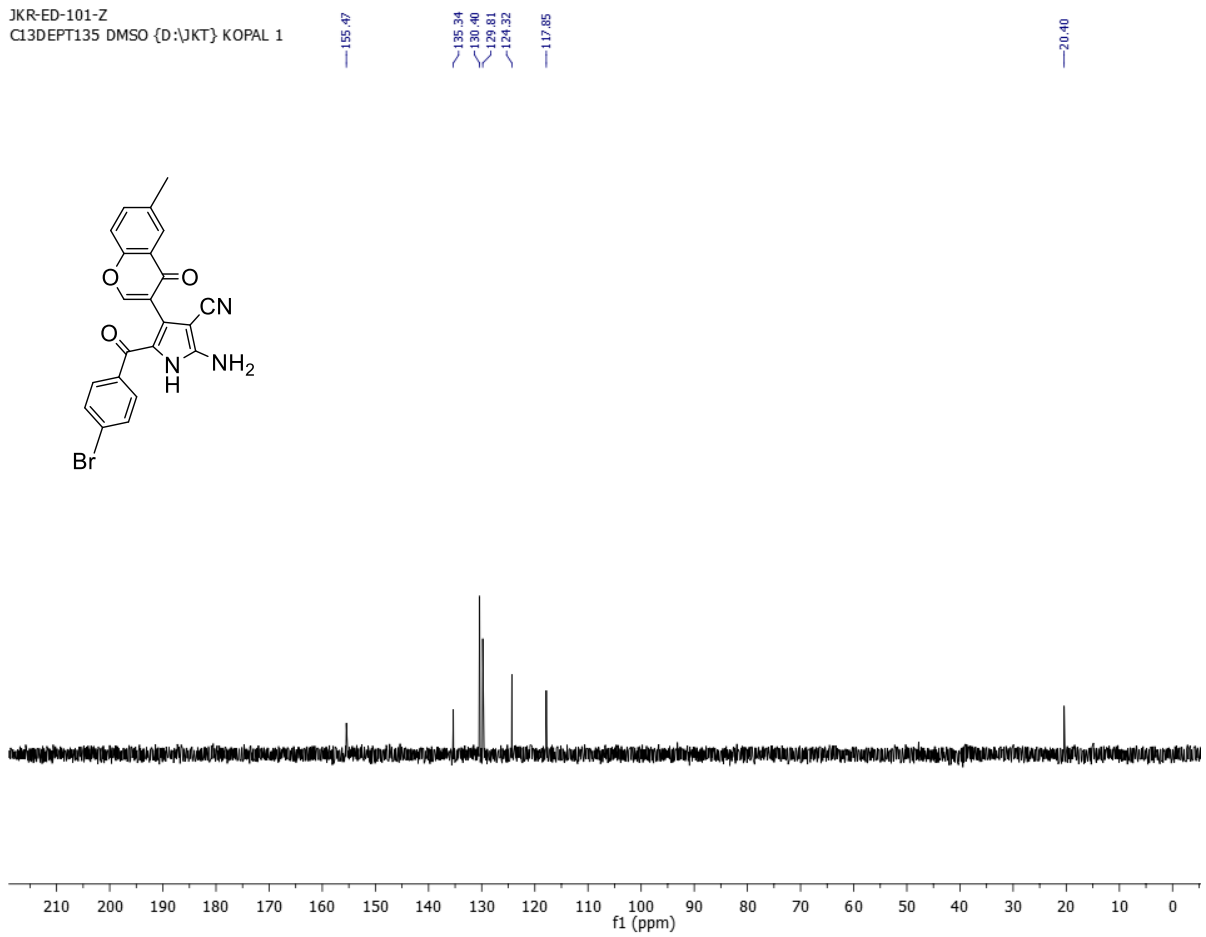
DEPT 135 NMR spectrum of **12d** (100 MHz, $CDCl_3$)



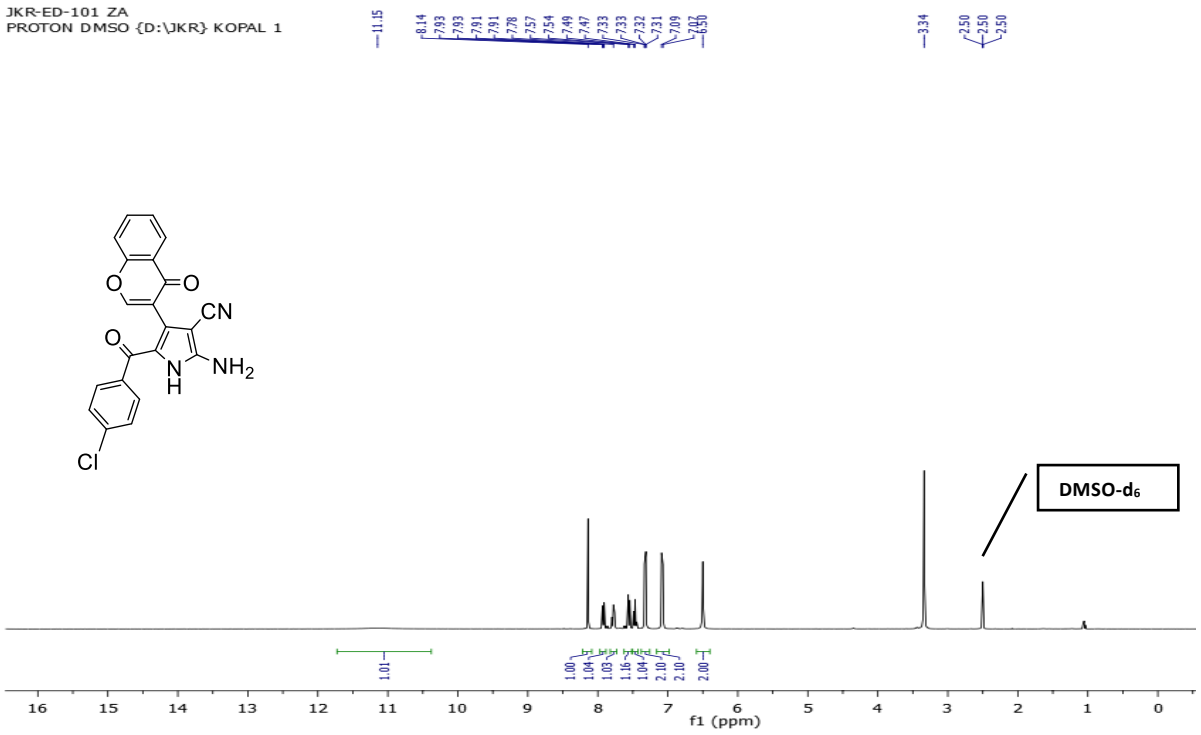
^{1}H NMR spectrum of **15a** (400 MHz, DMSO-*d*$_6$)



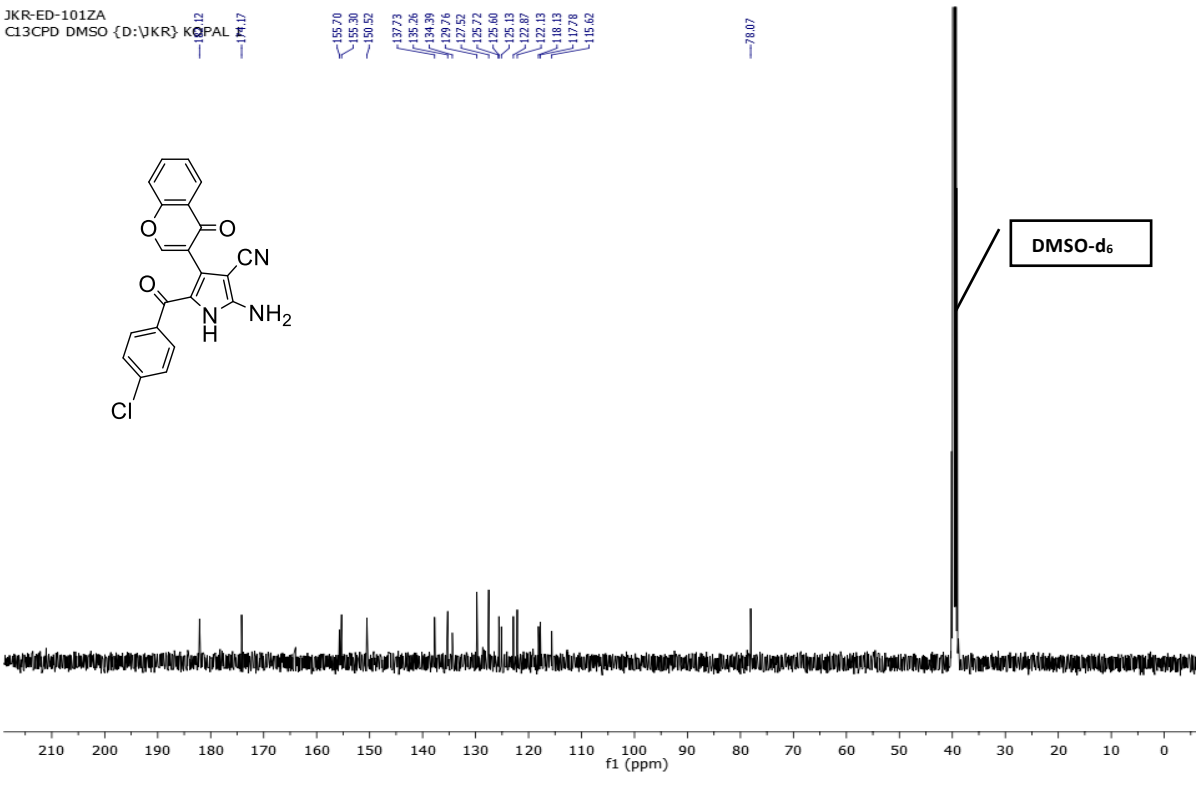
^{13}C{^{1}H} NMR spectrum of **15a** (100 MHz, DMSO-*d*$_6$)



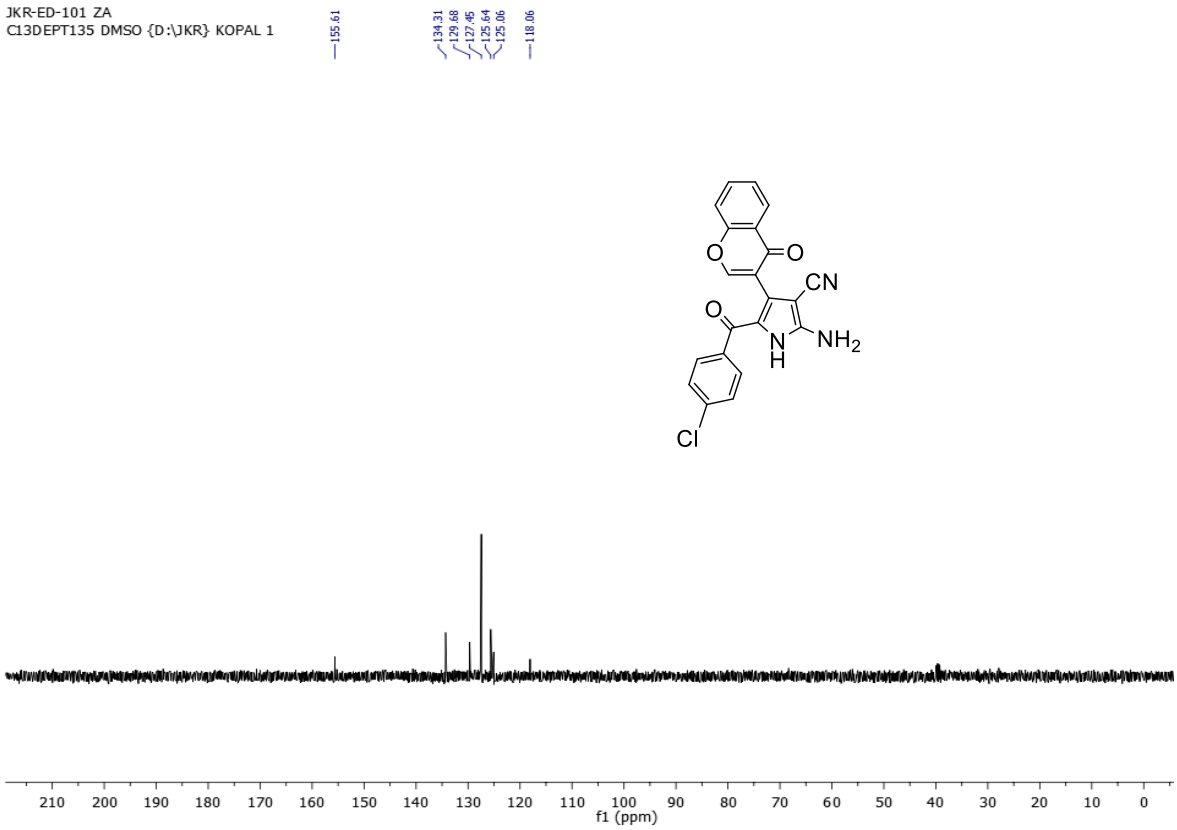
DEPT 135 NMR spectrum of **15a** (100 MHz, DMSO-d_6)



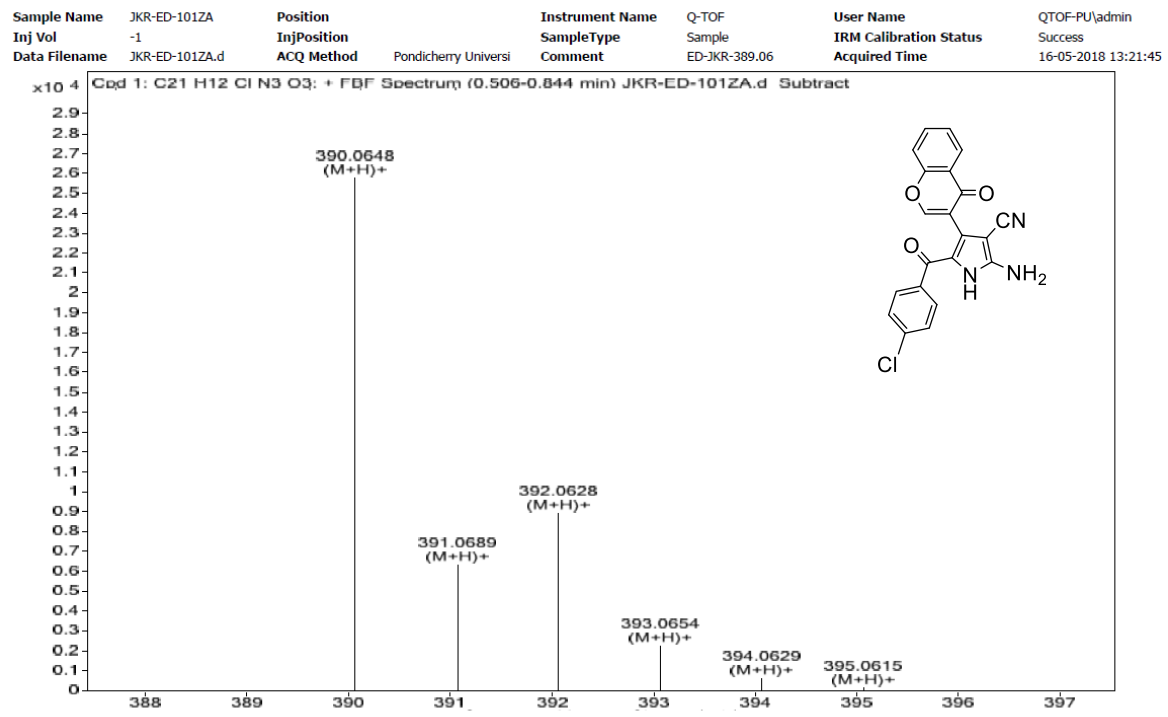
^{1}H NMR spectrum of **15b** (400 MHz, DMSO-d_6)



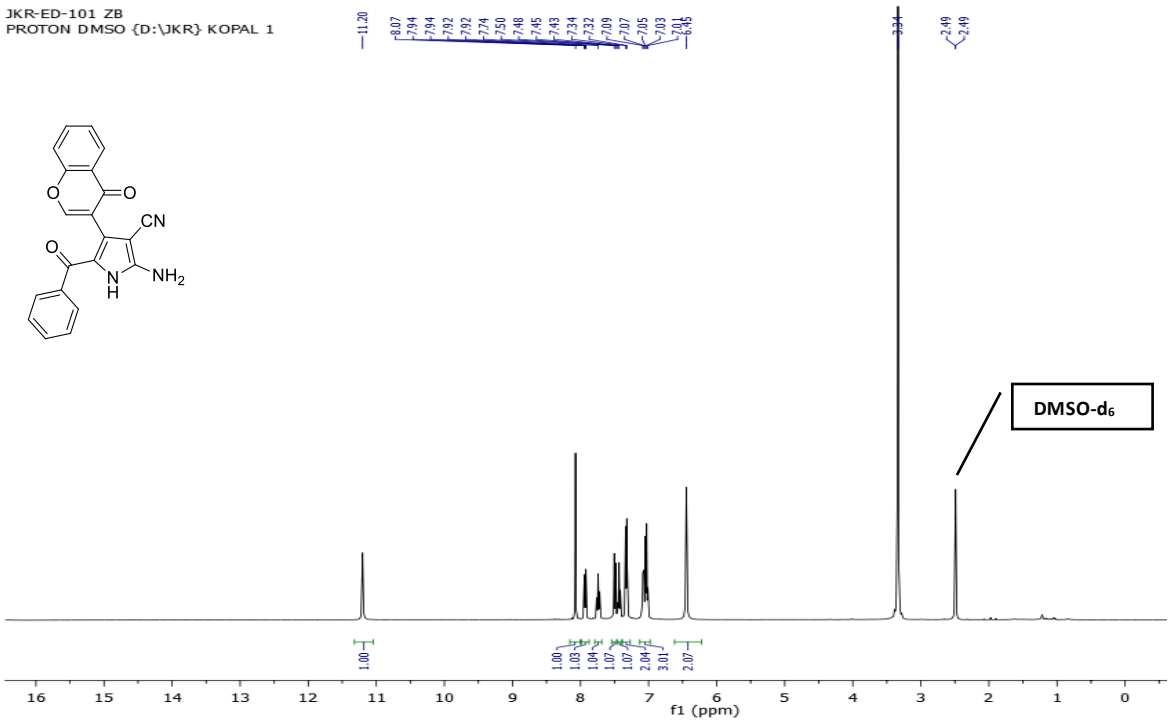
^{13}C{^{1}H} NMR spectrum of **15b** (100 MHz, DMSO-d_6)



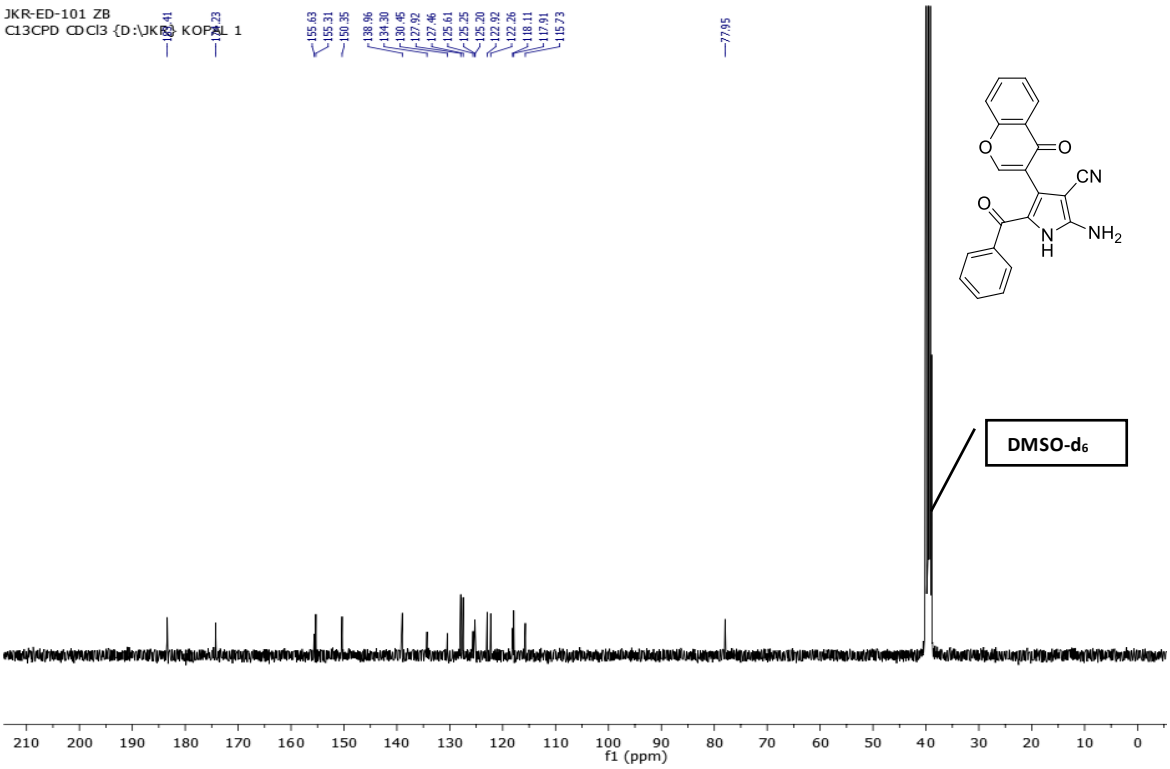
DEPT 135 NMR spectrum of **15b** (100 MHz, DMSO-d_6)



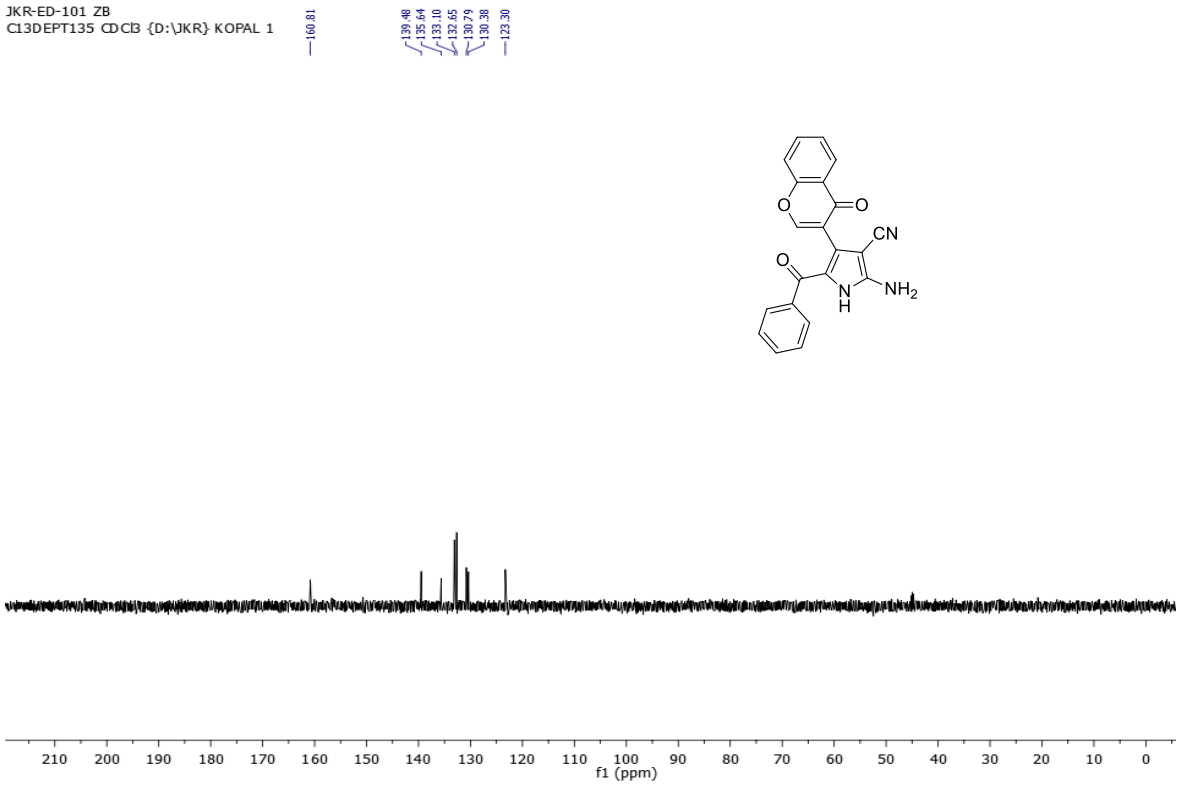
HRMS (ESI) spectrum of **15b**



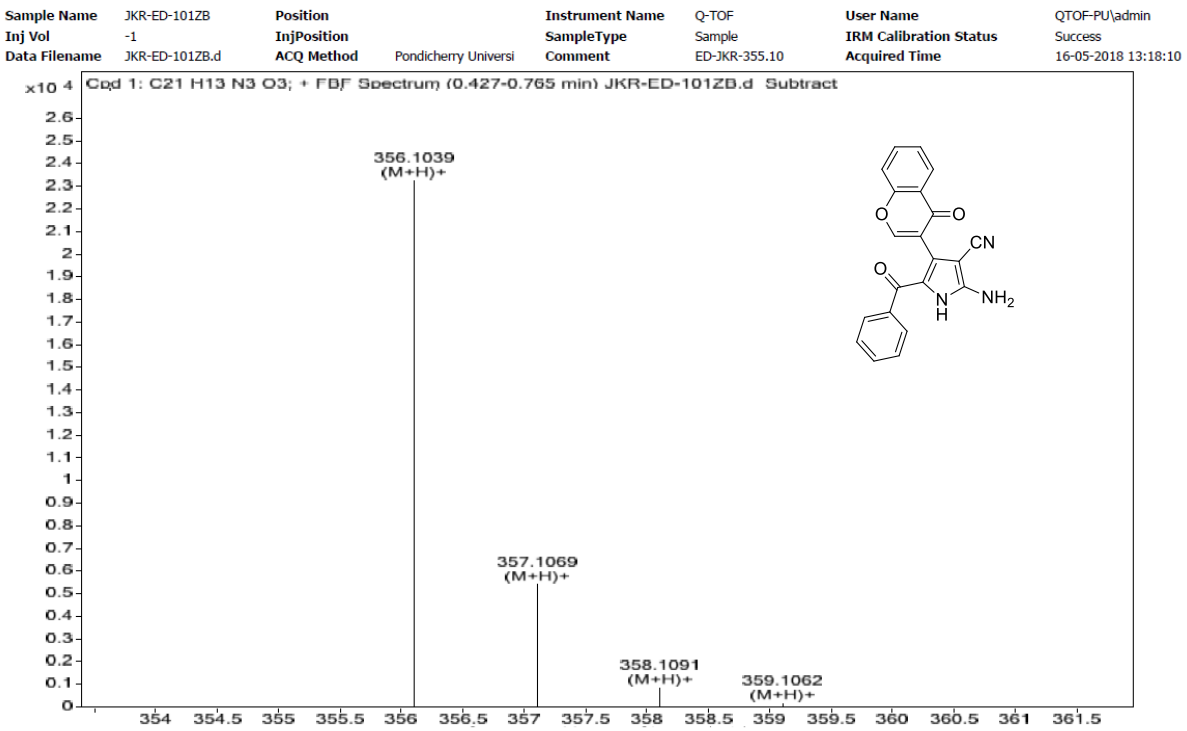
^{1}H NMR spectrum of **15c** (400 MHz, DMSO-d_6)



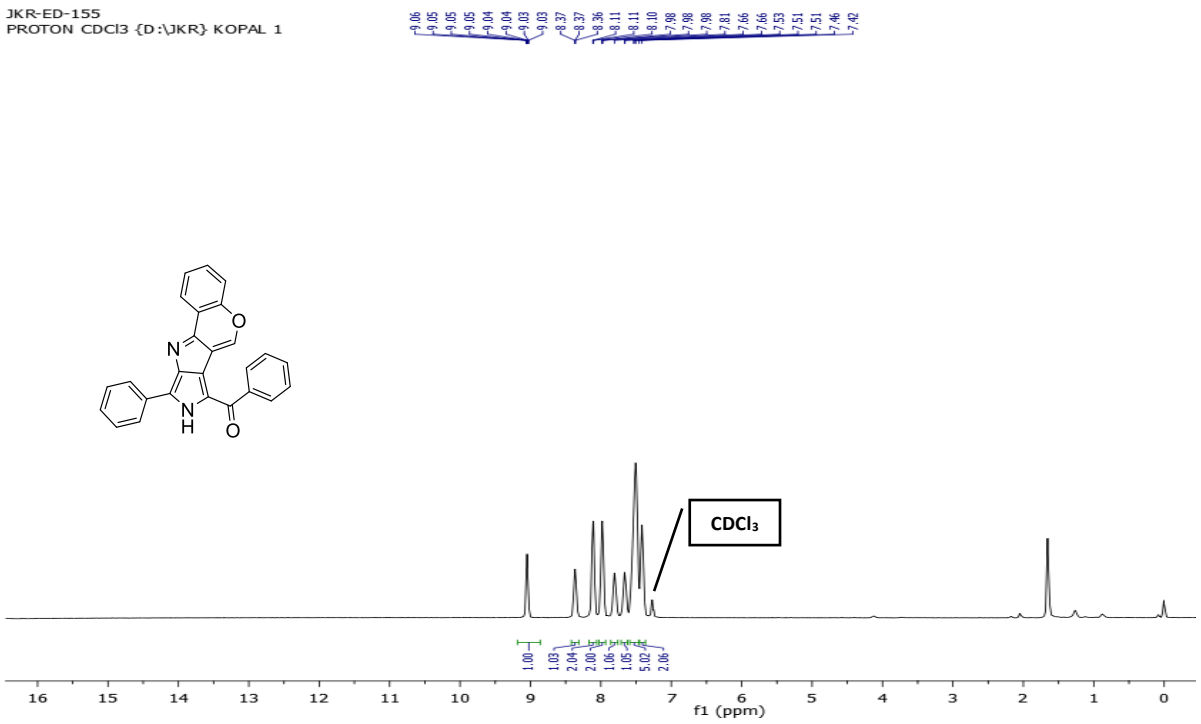
^{13}C{^{1}H} NMR spectrum of **15c** (100 MHz, DMSO-d_6)



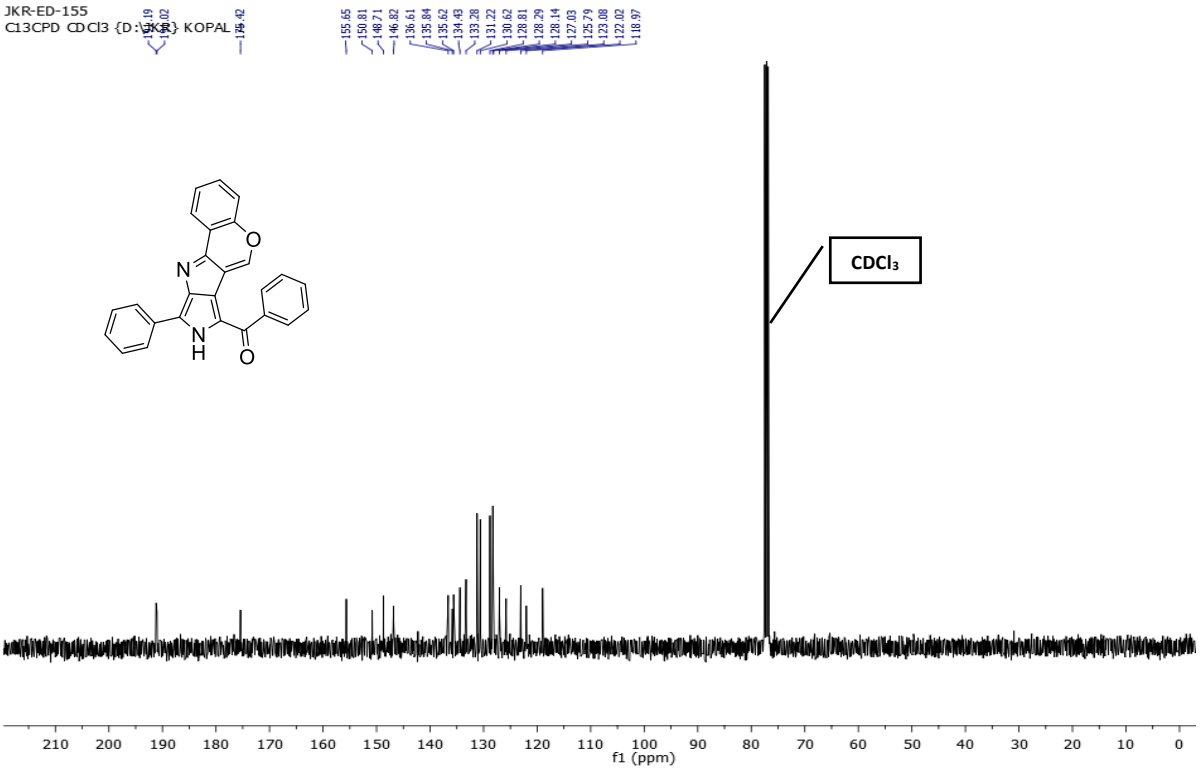
DEPT 135 NMR spectrum of **15c** (100 MHz, DMSO-d_6)



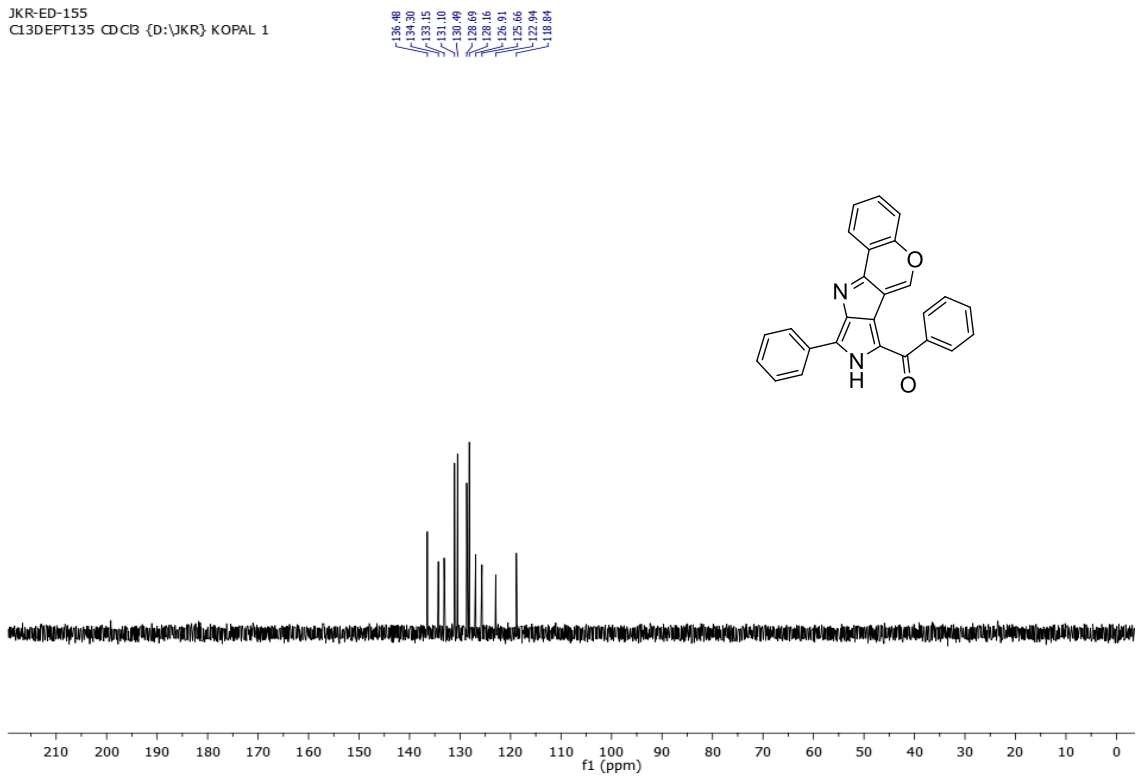
HRMS (ESI) spectrum of **15c**



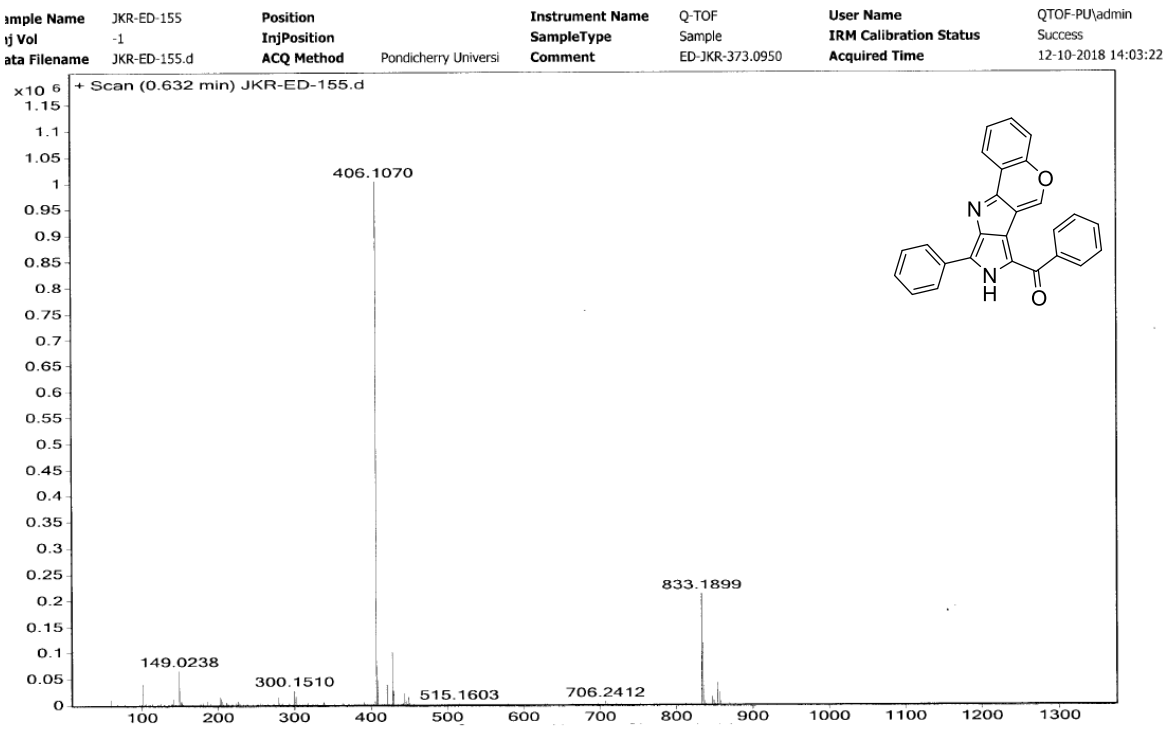
^{1}H NMR spectrum of **17a** (400 MHz, $CDCl_3$)



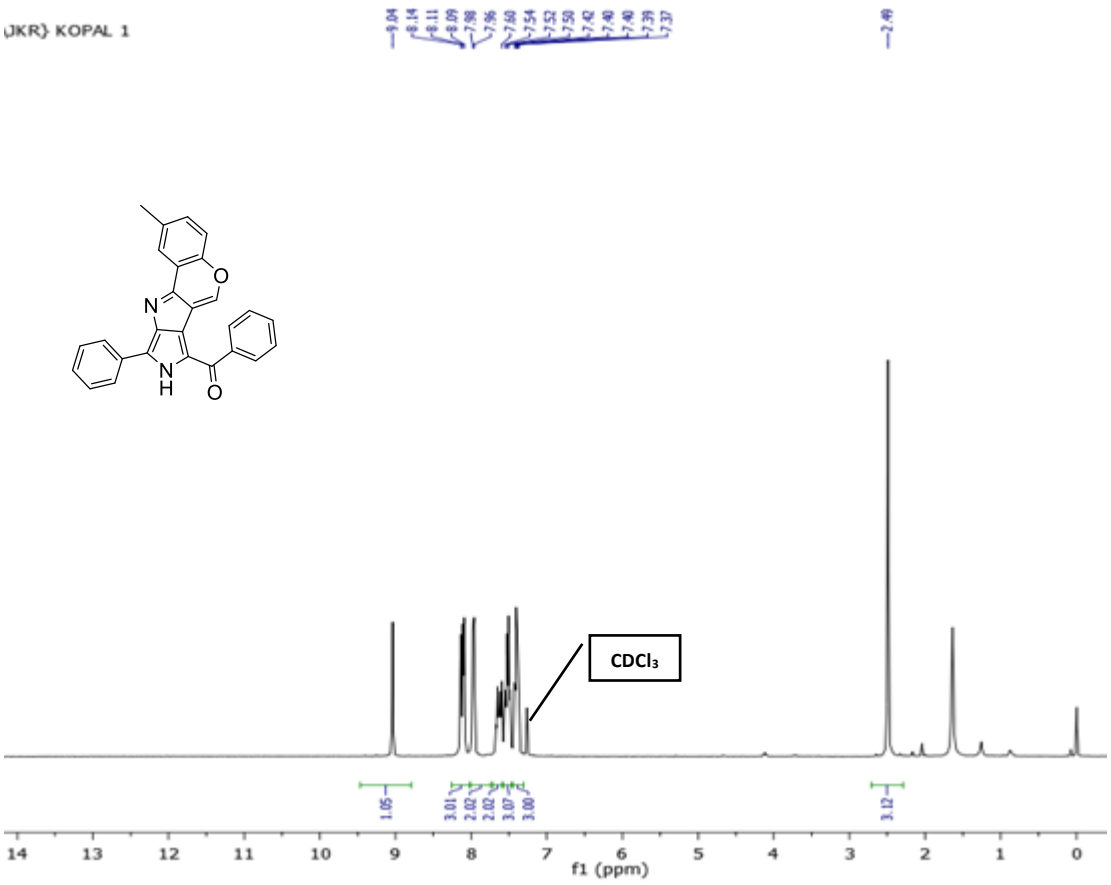
^{13}C{^{1}H} NMR spectrum of **17a** (100 MHz, $CDCl_3$)



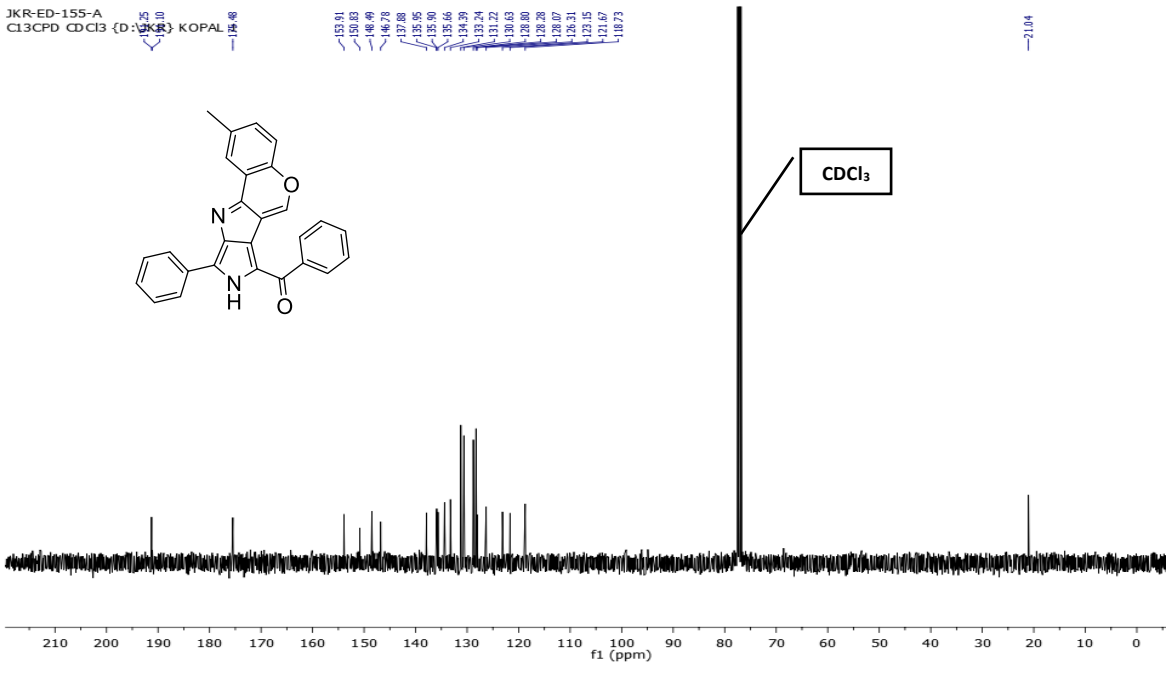
DEPT 135 NMR spectrum of **17a** (100 MHz, $CDCl_3$)



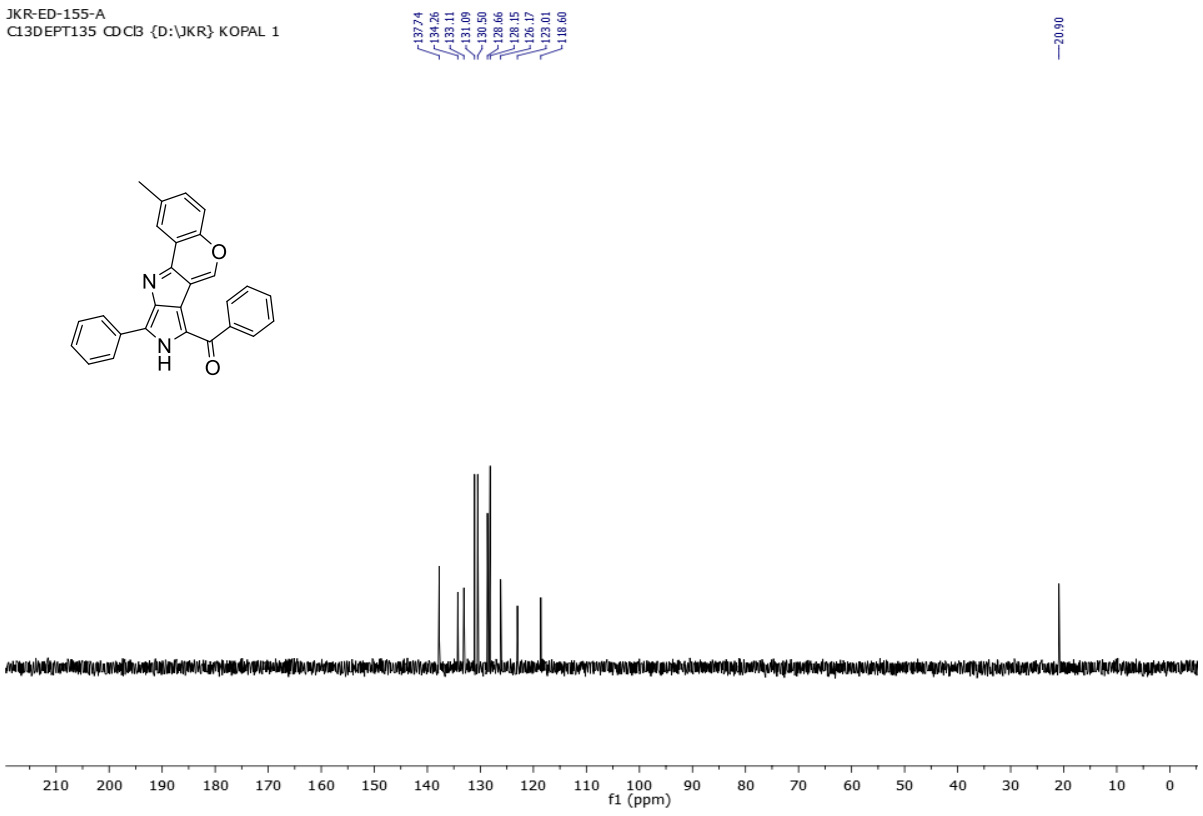
HRMS (ESI) spectrum of **17a**



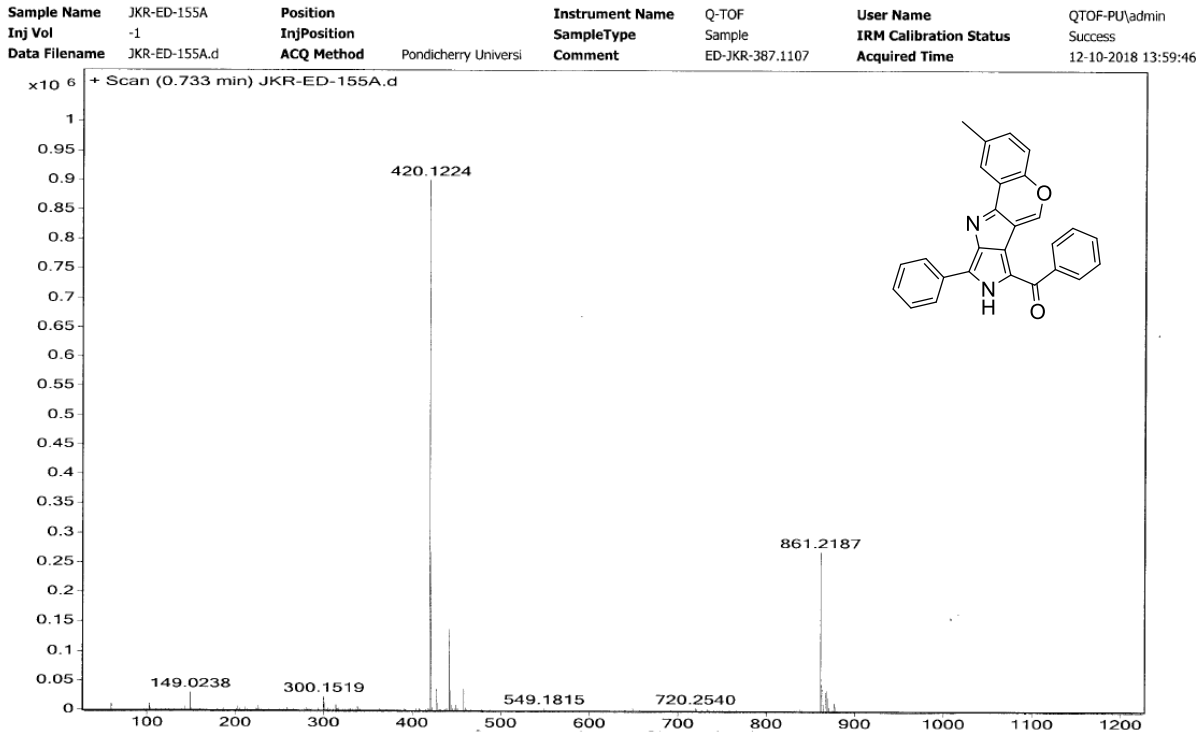
^{1}H NMR spectrum of **17b** (400 MHz, $CDCl_3$)



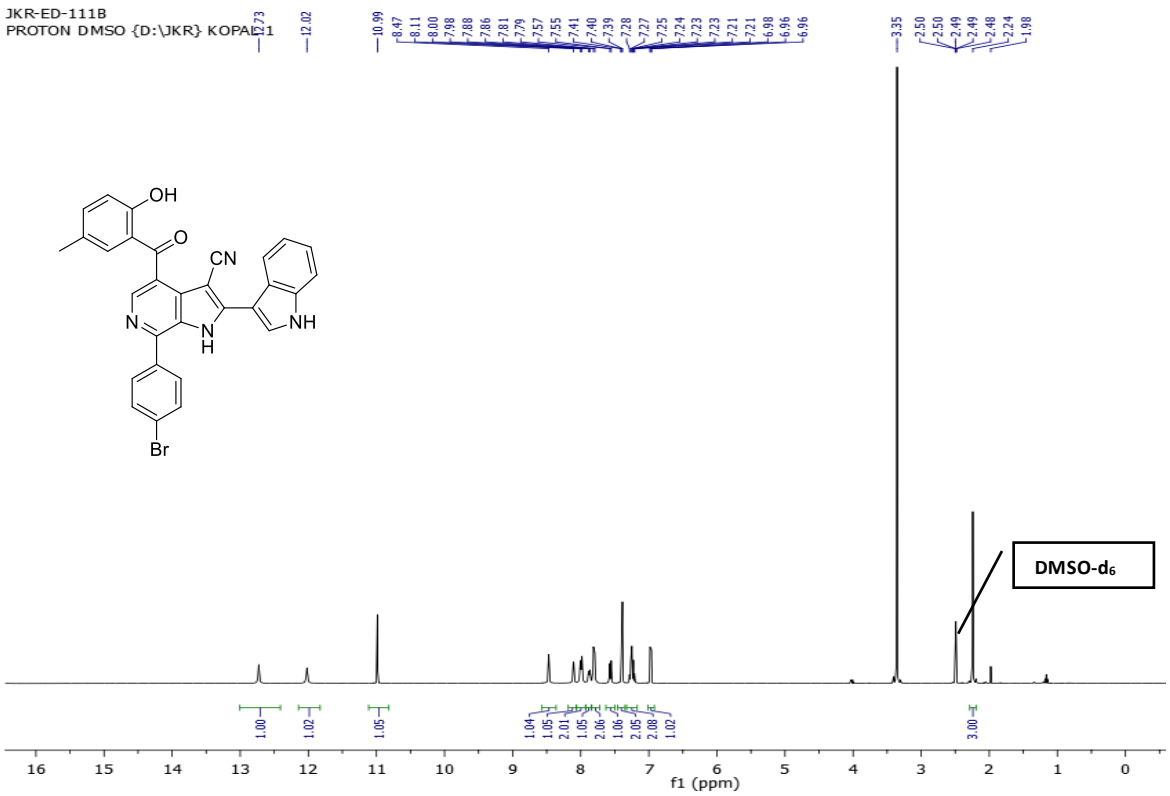
^{13}C{^{1}H} NMR spectrum of **17b** (100 MHz, $CDCl_3$)



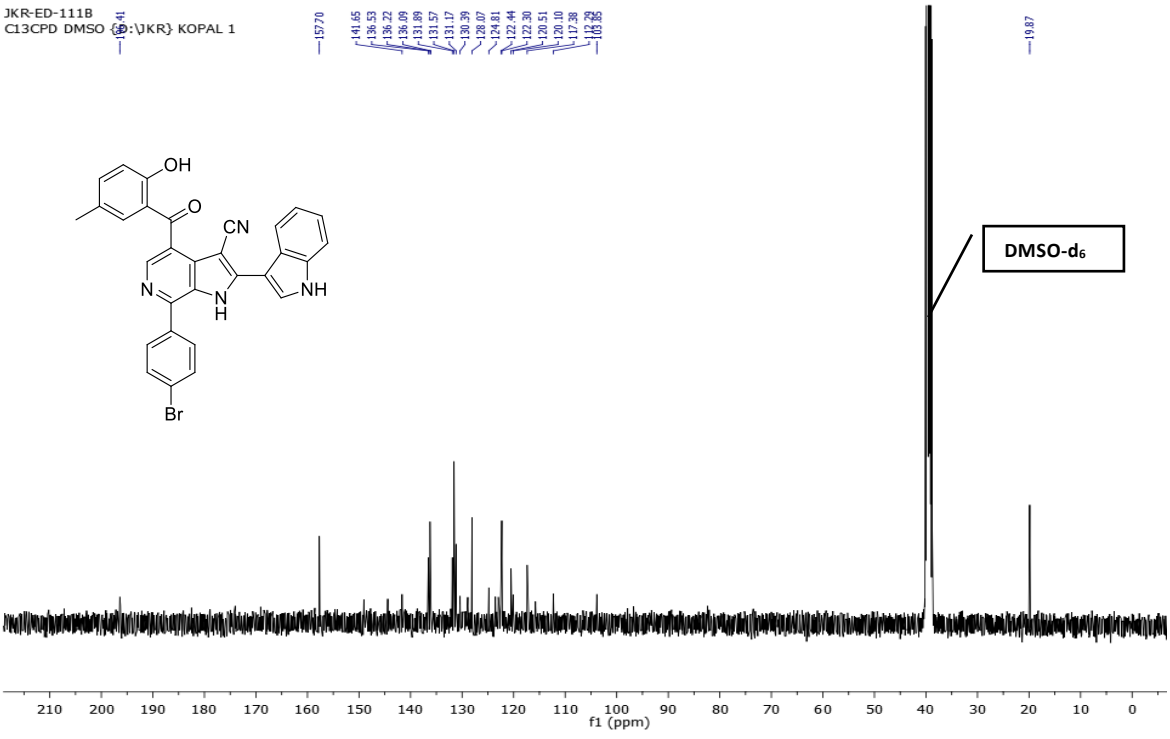
DEPT 135 NMR spectrum of **17b** (100 MHz, $CDCl_3$)



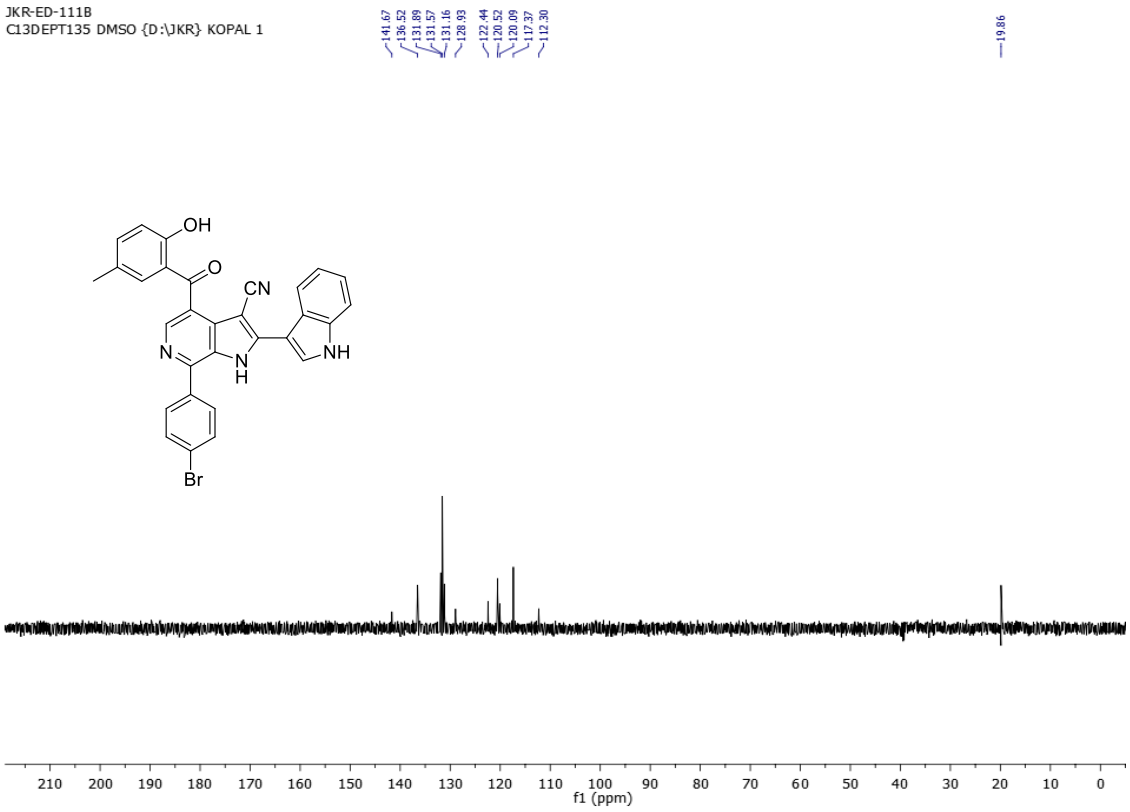
HRMS (ESI) spectrum of **17b**



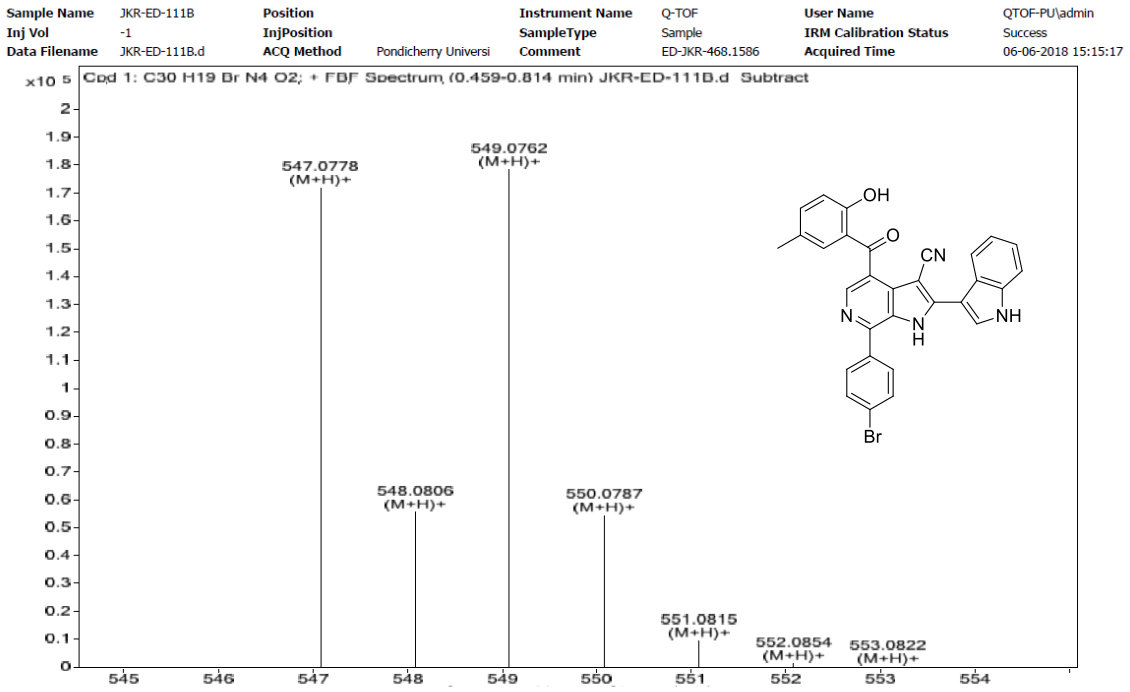
^{1}H NMR spectrum of **18a** (400 MHz, DMSO-d_6)



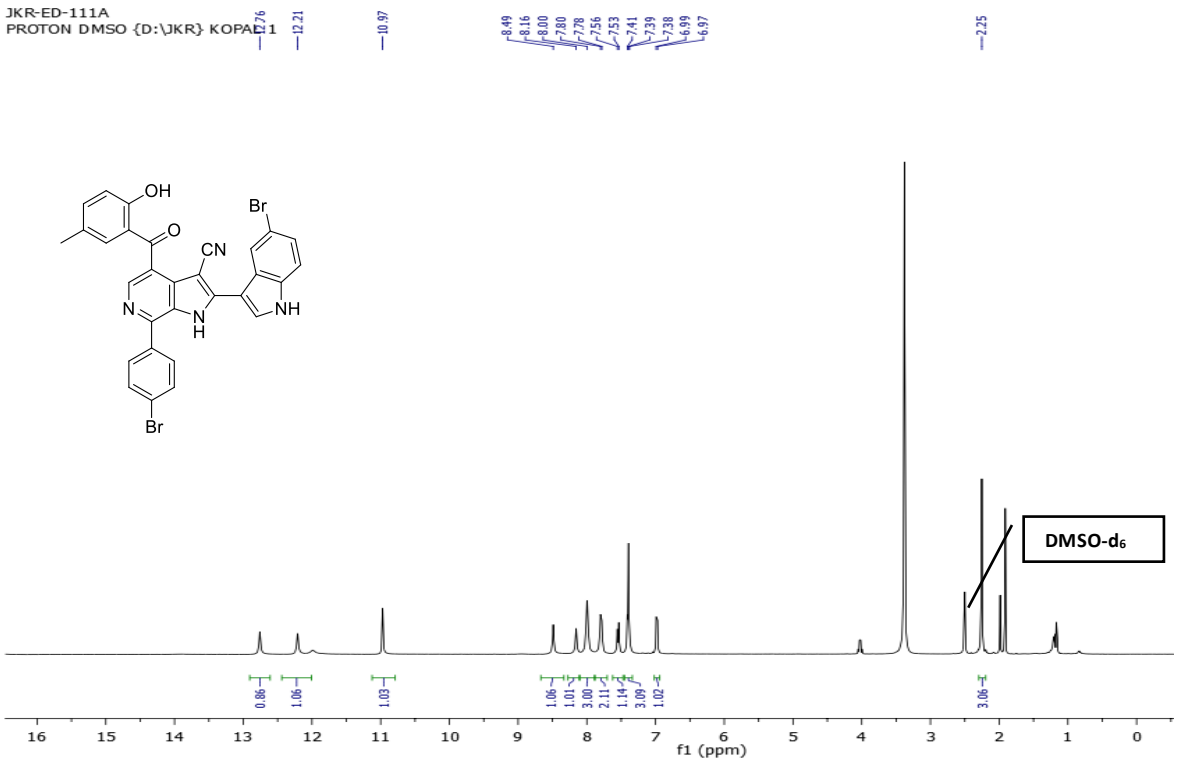
^{13}C{^{1}H} NMR spectrum of **18a** (100 MHz, DMSO-d_6)



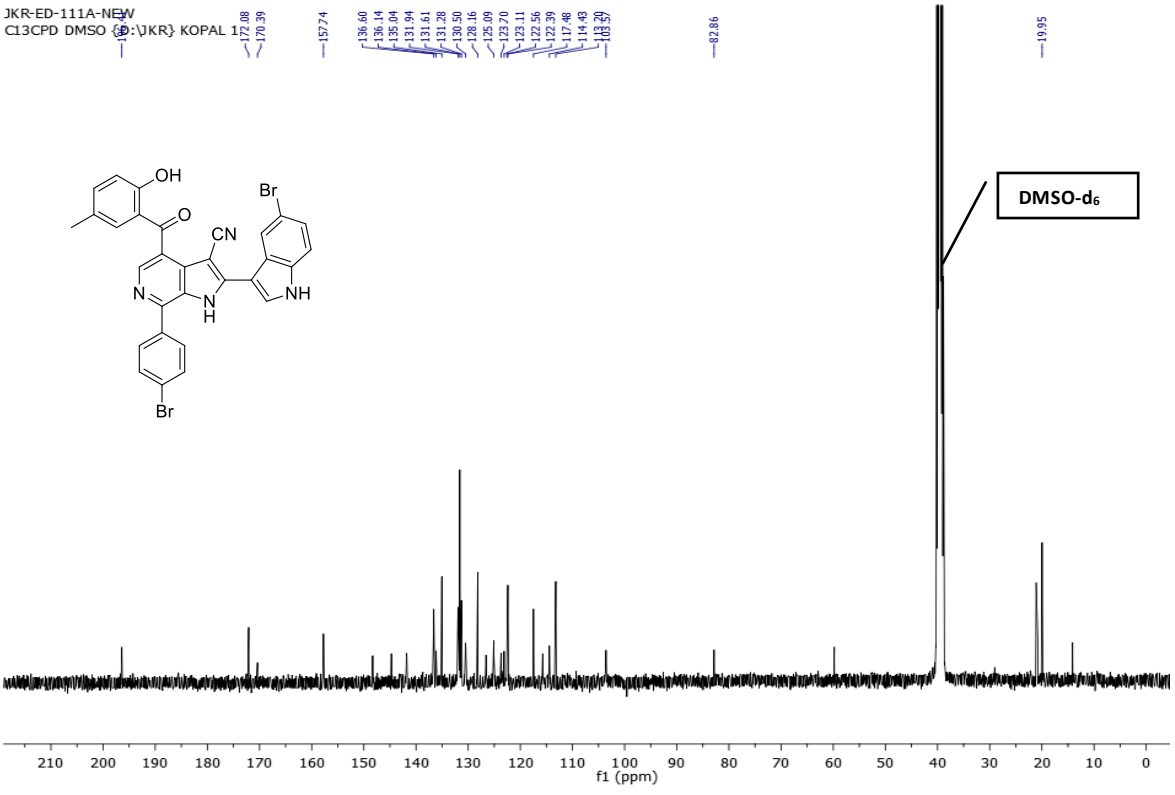
DEPT 135 NMR spectrum of **18a** (100 MHz, DMSO-d_6)



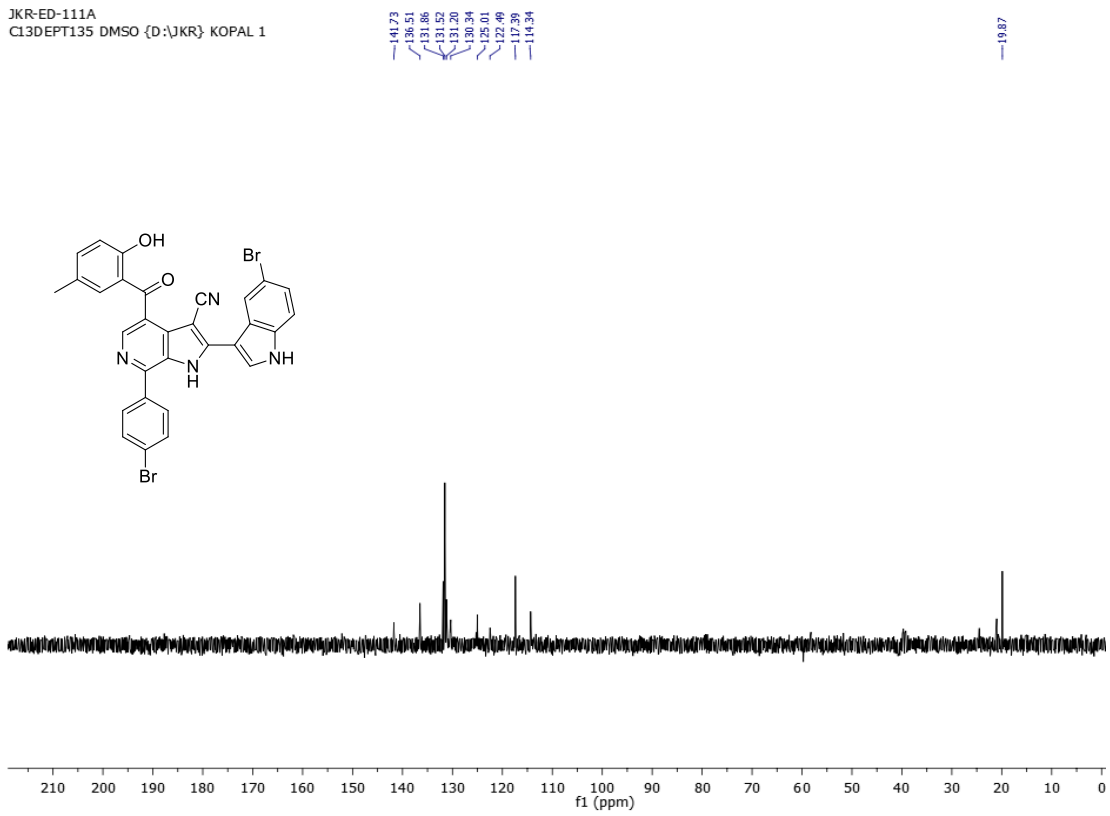
HRMS (ESI) spectrum of **18a**



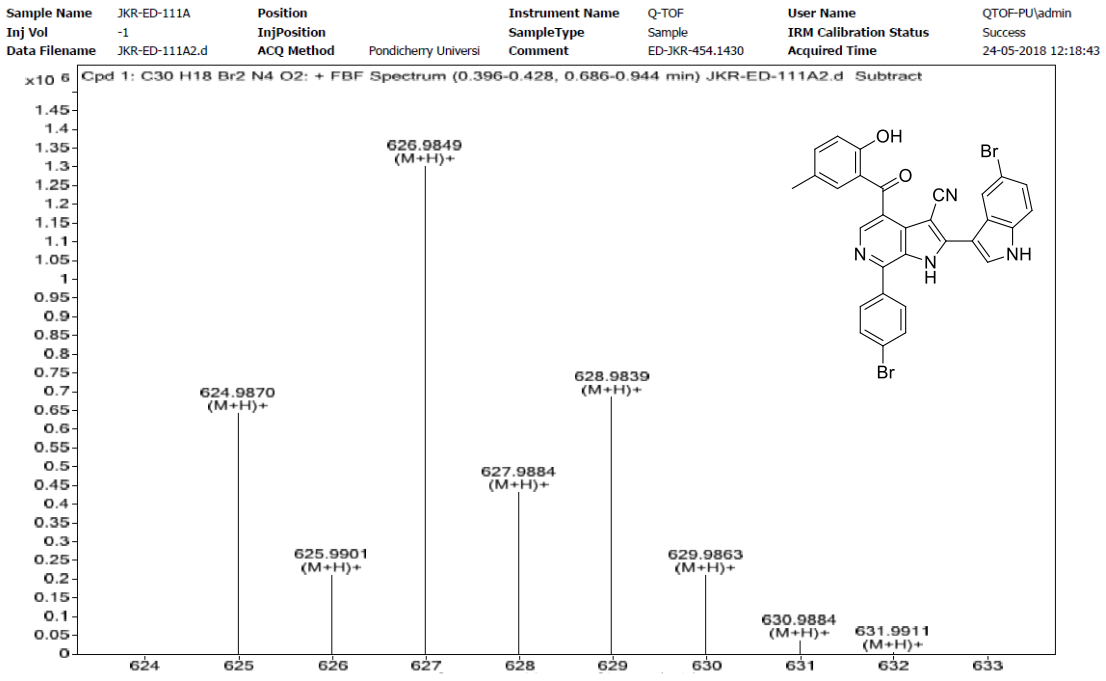
^{1}H NMR spectrum of **18b** (400 MHz, DMSO-d_6)



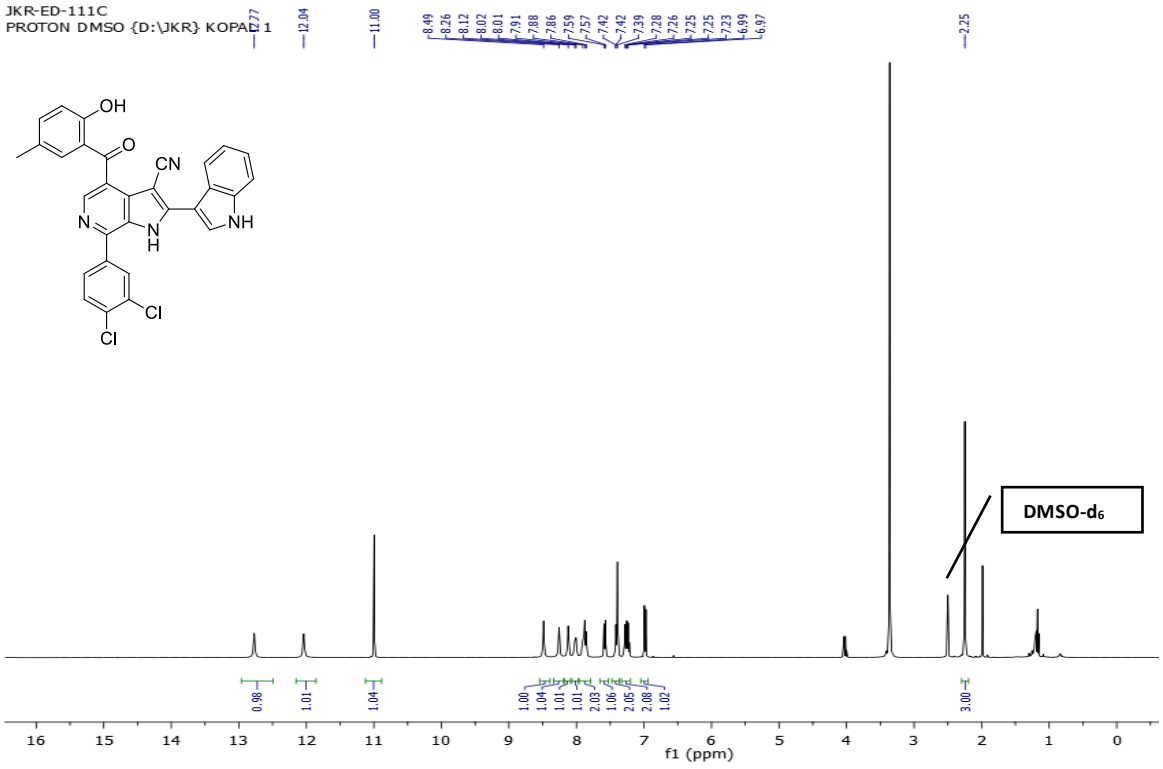
^{13}C{^{1}H} NMR spectrum of **18b** (100 MHz, DMSO-d_6)



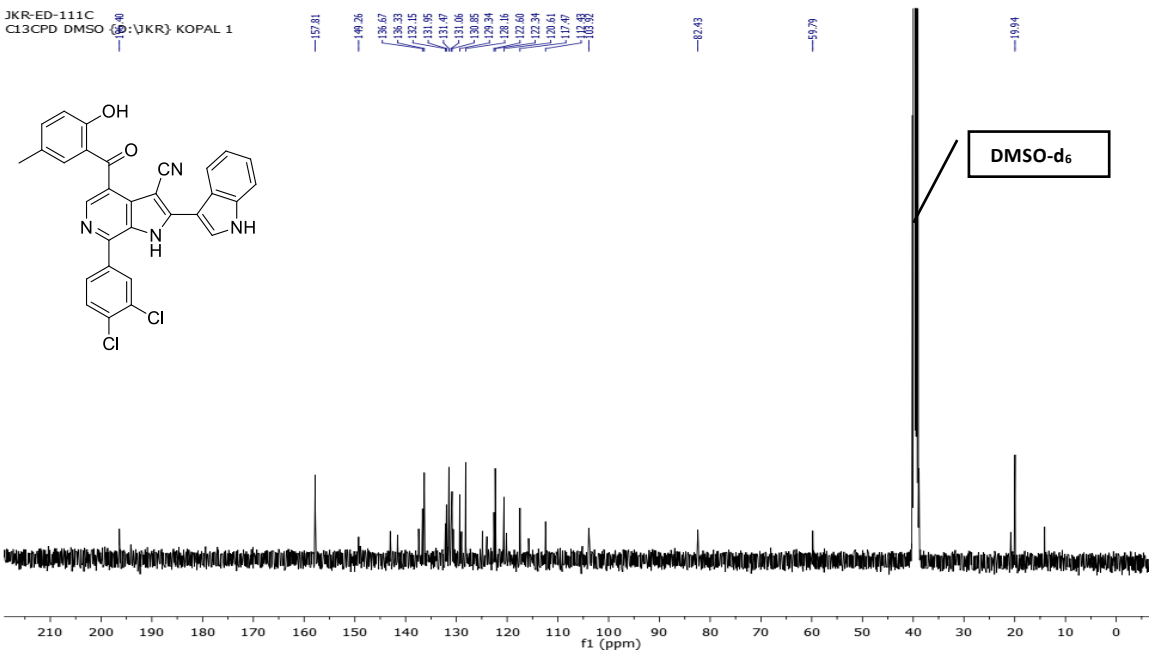
DEPT 135 NMR spectrum of **18b** (100 MHz, DMSO-d_6)



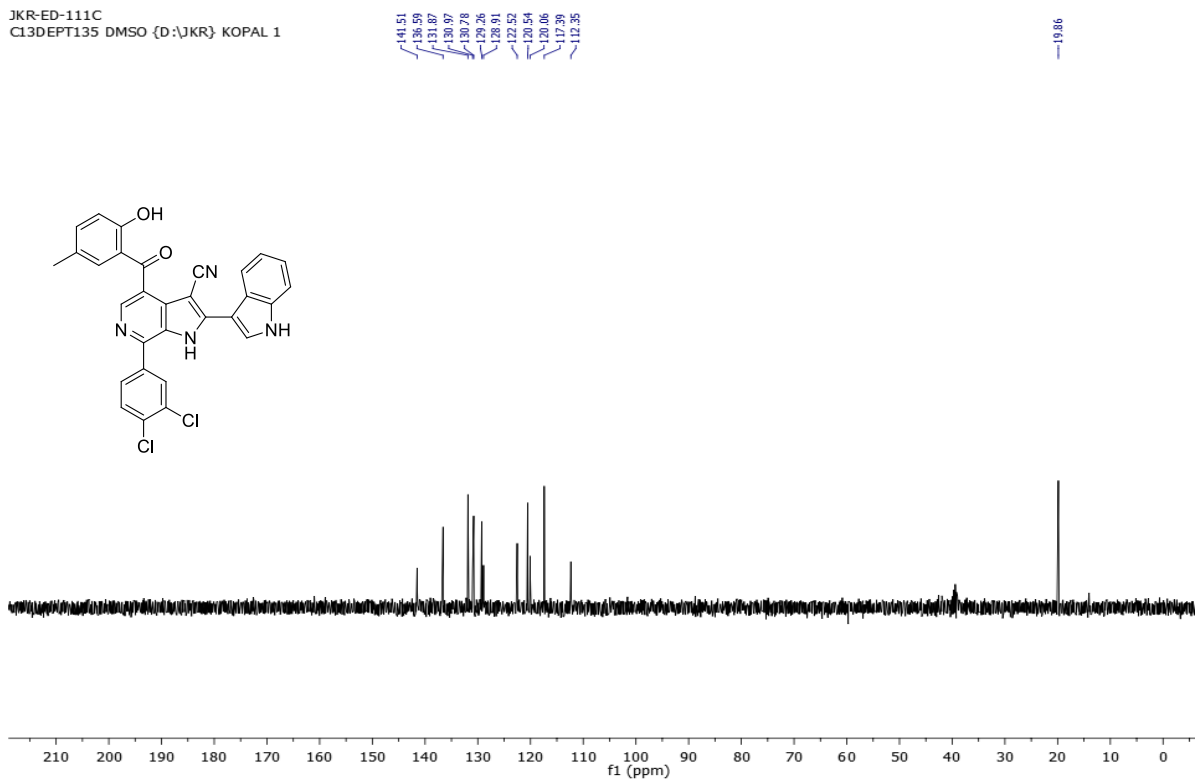
HRMS (ESI) spectrum of **18b**



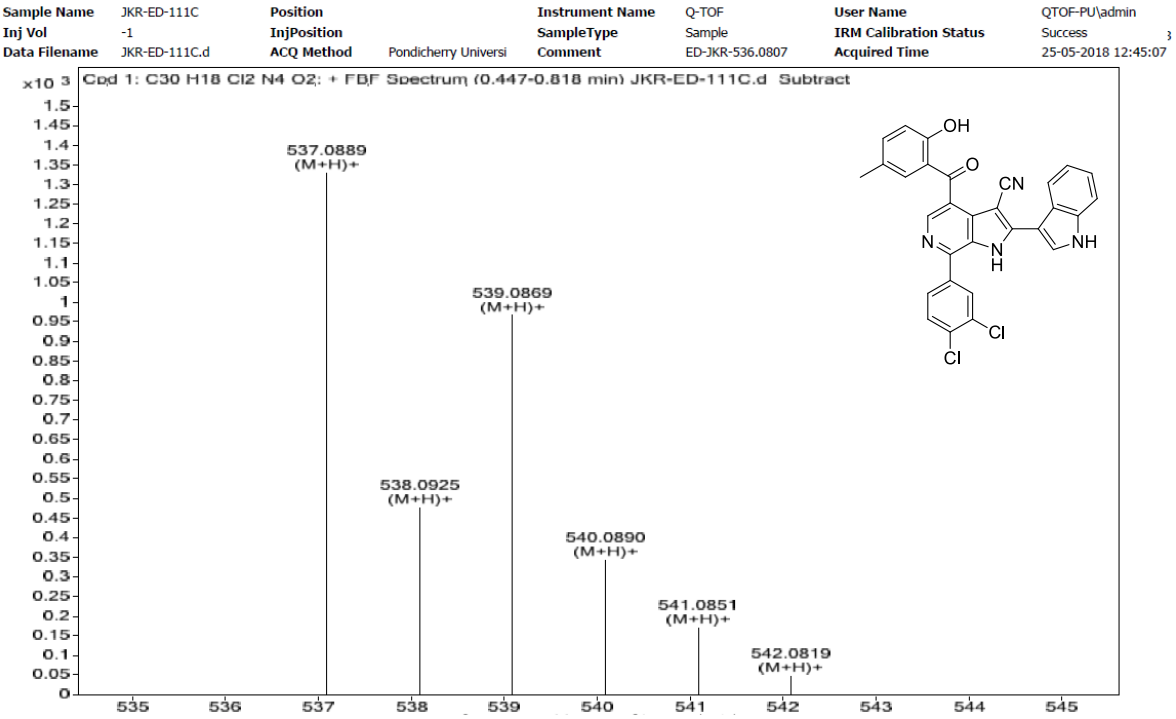
^{1}H NMR spectrum of **18c** (400 MHz, DMSO-*d*$_6$)



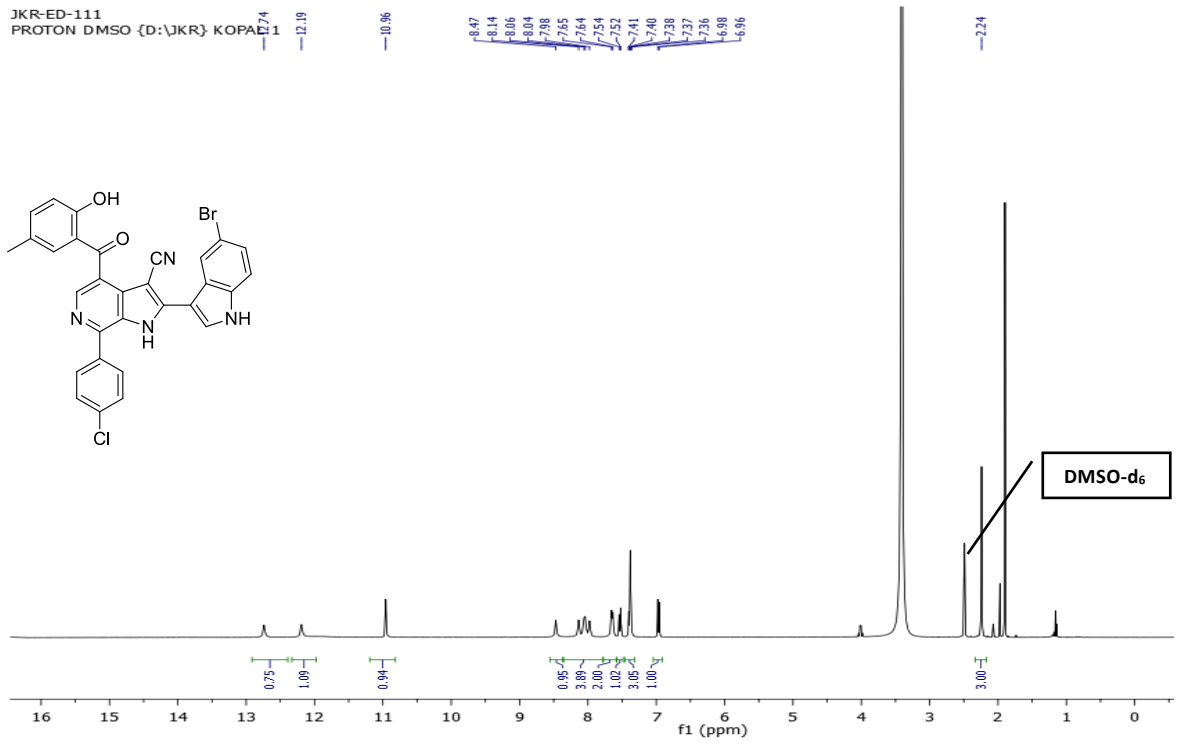
^{13}C{^{1}H} NMR spectrum of **18c** (100 MHz, DMSO-*d*$_6$)



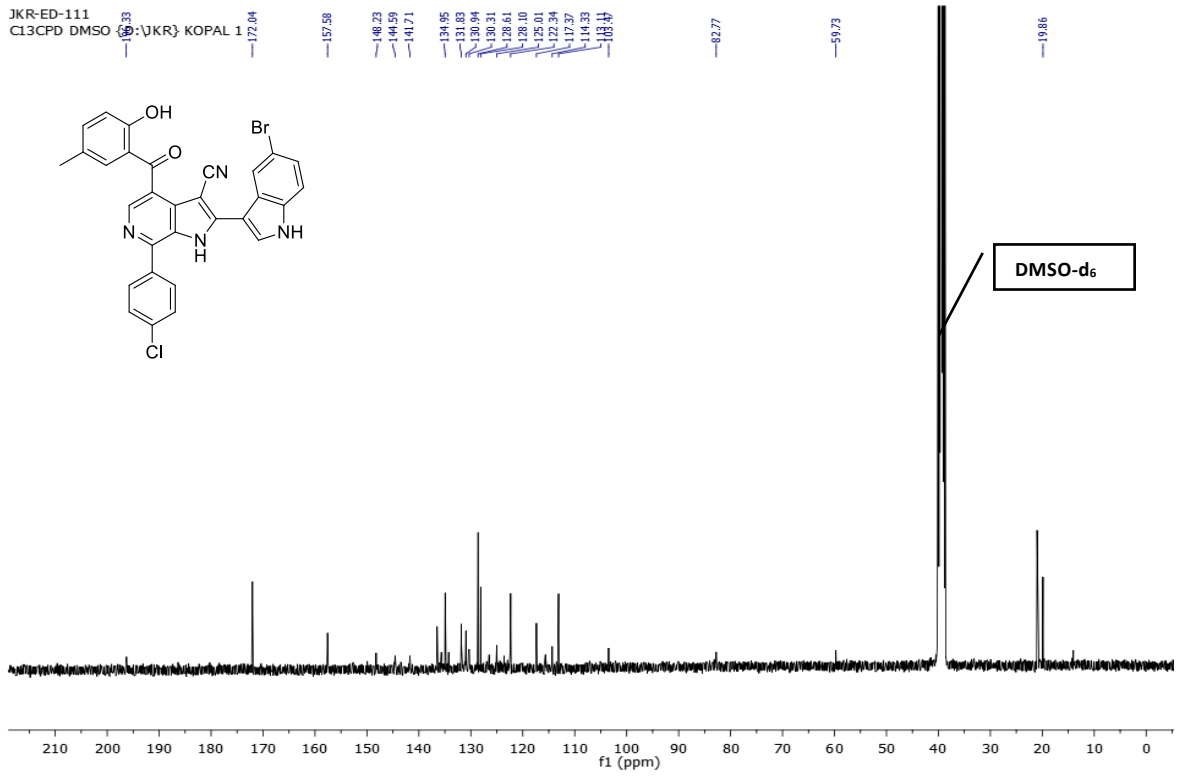
DEPT 135 NMR spectrum of **18c** (100 MHz, DMSO-d_6)



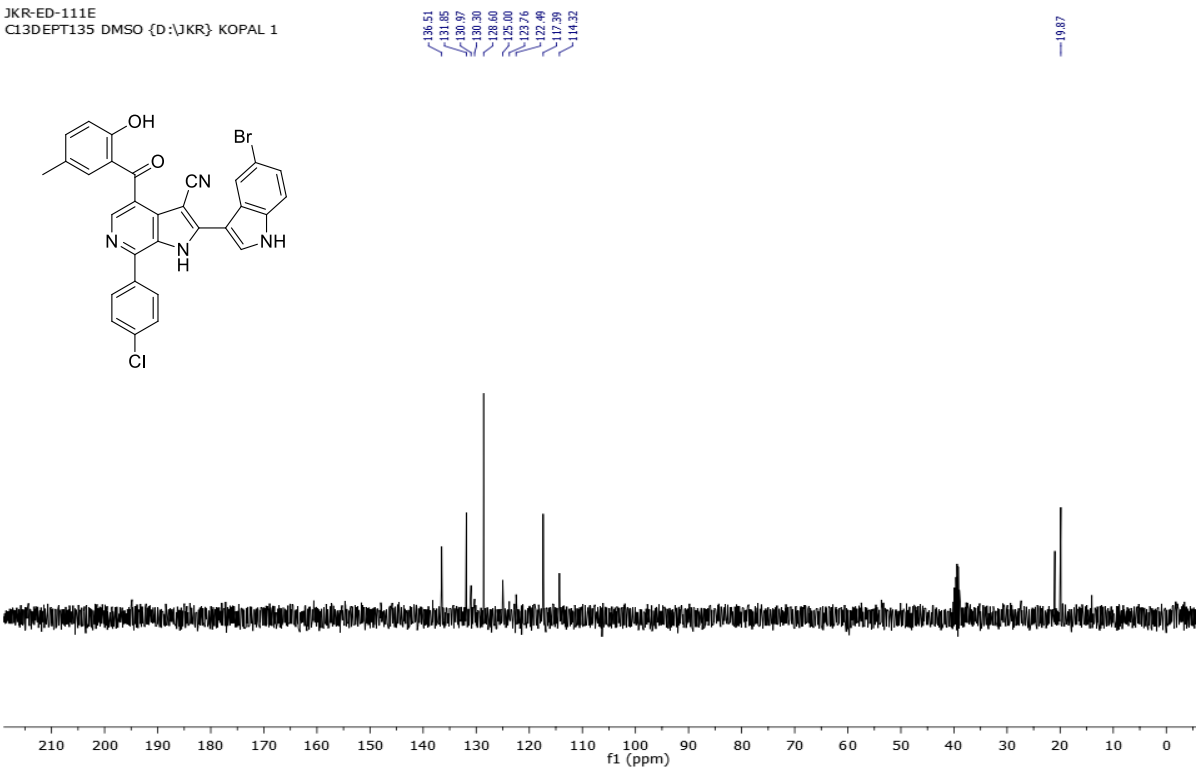
HRMS (ESI) spectrum of **18c**



^{1}H NMR spectrum of **18d** (400 MHz, DMSO-d_6)



^{13}C{^{1}H} NMR spectrum of **18d** (100 MHz, DMSO-d_6)



DEPT 135 NMR spectrum of **18d** (100 MHz, DMSO-d_6)

III. Experimental Details of X-ray analysis of Compound 4i

Single crystal of compound **4i** was prepared using DMSO solvent by a slow evaporation method. X-ray diffraction data were collected using Bruker AXS Kappa ApexII CCD diffractometer equipped with graphite monochromated MoKα (λ=0.71073Å) radiation. The single crystal of size ca. 0.25 x 0.22 x 0.18 mm was used for data collection. Data collection, data reduction and absorption correction were performed by APEX2, SAINT-plus and SADABS [v2014/5] programs[1]. The structure was solved by direct methods procedure using SHELXS-97 (Sheldrick, 2008) and refined by full-matrix least-squares procedure on F^2 using SHELXL-2014(Sheldrick, 2015) program[2]. All the non-hydrogen atoms were subjected to anisotropic refinement whereas the hydrogen atoms were refined isotropically. The H-atoms bound to the C-atoms were treated as riding atoms with Uiso(H) set to 1.5Ueq© and C–H distance of 0.96Å for CH_3 groups and Uiso(H) set to 1.2Ueq© and C–H distance of 0.93Å for aromatic CH. The H atoms bounded to amine nitrogen were refined to constrained distances with Uiso(H) = 1.2 Ueq(N), N—H distances of 0.90(1)Å. The final refinement converged to the R-value of 0.0531 for 3824 observed reflections. Crystallographic data **4i** have been deposited with the Cambridge Crystallographic Data Center, (39) CCDC 1881467. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk). Crystal structure determination was performed in the Department of Chemistry, Indian Institute of Technology Madras, Chennai – 600036, INDIA.

1. Bruker, **2014**, SADABS v2014/5, Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick, G. M. **2015**, *Acta Cryst.* C71, 3–8.

IV. ORTEP diagram of compound 4i

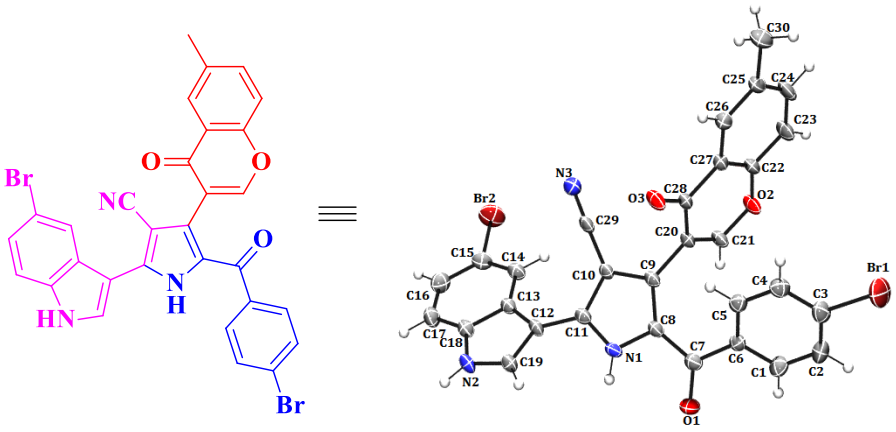


Figure S1. Molecular configuration and the atom numbering structure of **4i** crystal. Displacement ellipsoids are drawn at 30% probability level.

V. Table S1. Crystal data and structure refinement for 4i

Bond precision:	C-C = 0.0066 A		Wavelength = 0.71073
Cell:	a = 11.6878(4)	b = 12.5438(4)	c = 13.3312(4)
	alpha = 70.9079(14)	beta = 72.8568(15)	gamma = 81.4490(16)
Temperature:	296 K		
	Calculated		Reported
Volume	1761.95(10)		1761.95(10)
Space group	P -1		P -1
Hall group	-P 1		-P 1
Moiety formula	C30 H17 Br2 N3 O3, 2(C2 H6 O S)		C34 H29 Br2 N3 O5 S2
Sum formula	C34 H29 Br2 N3 O5 S2		C34 H29 Br2 N3 O5 S2
Mr	783.52		783.52
Dx,g cm-3	1.477		1.477
Z	2		2
Mu (mm-1)	2.463		2.463
F000	792.0		792.0
F000'	791.65		
h,k,lmax	13,14,15		13,14,15
Nref	6187		6171
Tmin,Tmax	0.546,0.642		0.578,0.666
Tmin'	0.535		

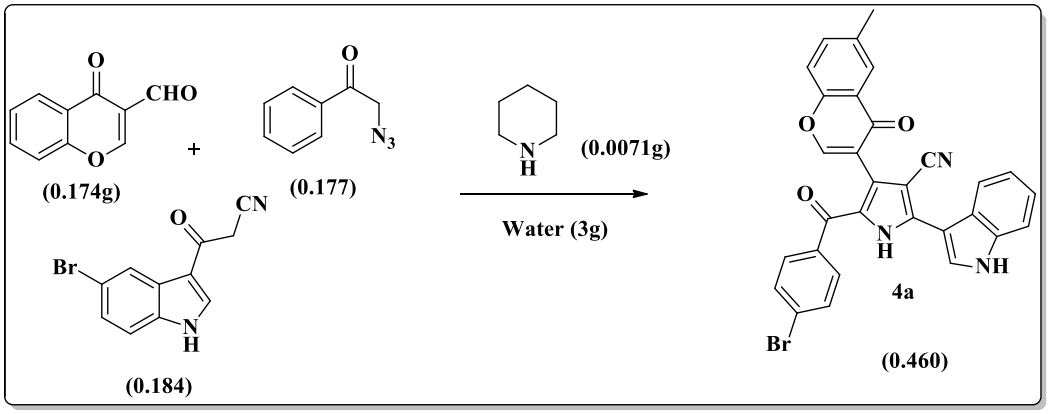
Correction method= # Reported T Limits: Tmin= 0.578 Tmax=0.666
AbsCorr = MULTI-SCAN

Data completeness = 0.997	Theta(max) = 25.000
R(reflections) = 0.0531(3824)	wR2(reflections) = 0.1477(6171)
S = 1.034	Npar = 428

VI. Green matrix Factors: Atom Economy and E-Factor Calculations

E-Factor and Atom Economy for each class of compounds

E- Factor for compound **4a**



$$\text{E-Factor} = \frac{\text{Weight of total starting material} - \text{Product weight}}{\text{Product weight}}$$

$$\text{E-Factor} = \frac{3.5427 - 0.46}{0.46}$$

$$\text{E-Factor} = 6.69$$

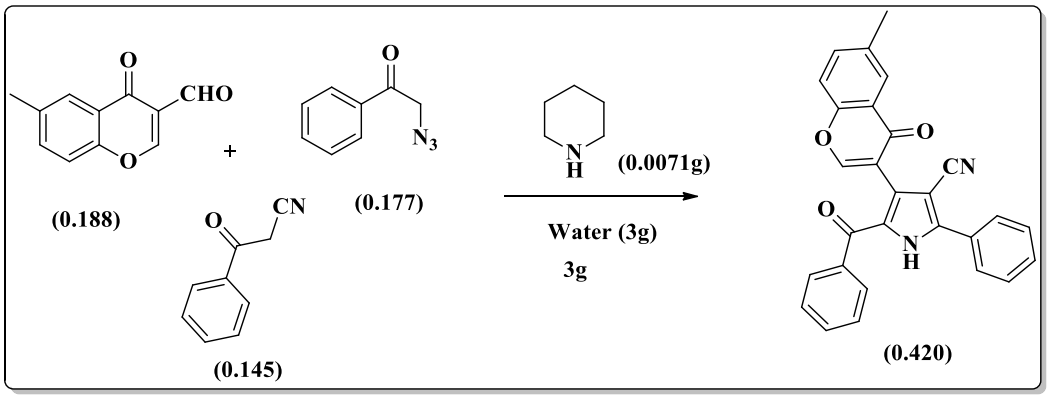
Atom economy for compound **4a**

$$\text{Atom Economy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in the reactant}}$$

$$\text{Atom Economy} = \frac{455 \text{ X } 100}{650}$$

$$\text{Atom Economy} = 70.03$$

E- Factor for compound **4q**



$$\text{E-Factor} = \frac{\text{Weight of total starting material} - \text{Product weight}}{\text{Product weight}}$$

$$\text{E-Factor} = \frac{3.5171 - 0.425}{0.425}$$

E-Factor = 7.27

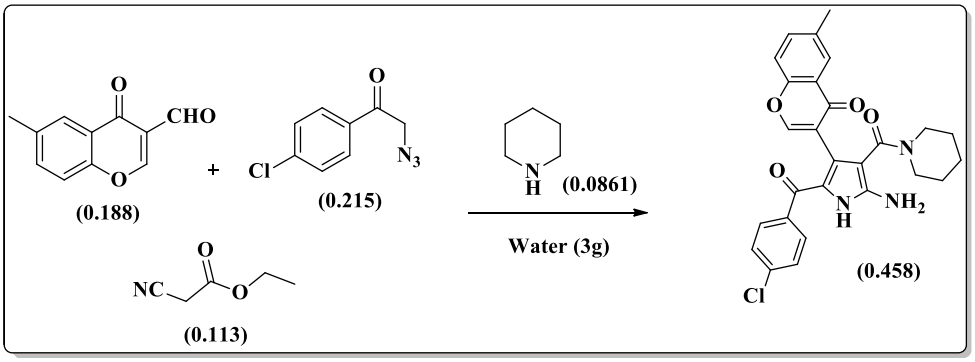
Atom economy for compound **4q**

$$\text{Atom Economy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in the reactant}}$$

$$\text{Atom Economy} = \frac{430 \text{ X } 100}{494}$$

Atom Economy = 87.04

E- Factor for compound **8a**



$$\text{E-Factor} = \frac{\text{Weight of total starting material} - \text{Product weight}}{\text{Product weight}}$$

$$\text{E-Factor} = \frac{3.602 - 0.458}{0.458}$$

$$\text{E-Factor} = 6.86$$

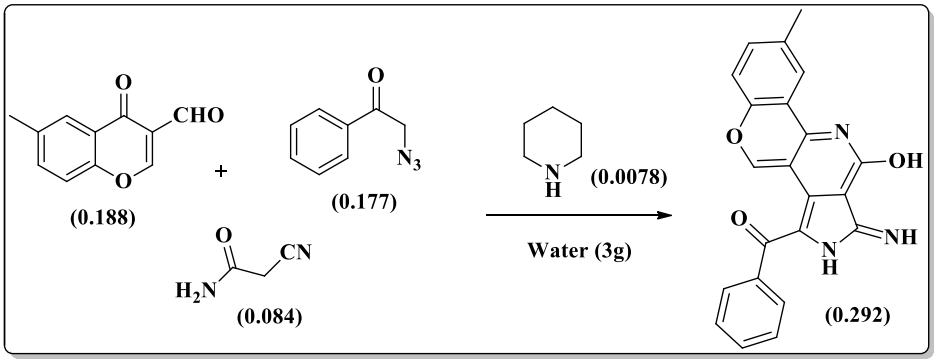
Atom economy for compound **8a**

$$\text{Atom Economy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in the reactant}}$$

$$\text{Atom Economy} = \frac{489 \text{ X } 100}{627}$$

$$\text{Atom Economy} = 78.13$$

E- Factor for compound **10a**



$$\text{E-Factor} = \frac{\text{Weight of total starting material} - \text{Product weight}}{\text{Product weight}}$$

$$\text{E-Factor} = \frac{3.456 - 0.292}{0.292}$$

$$\text{E-Factor} = 10.83$$

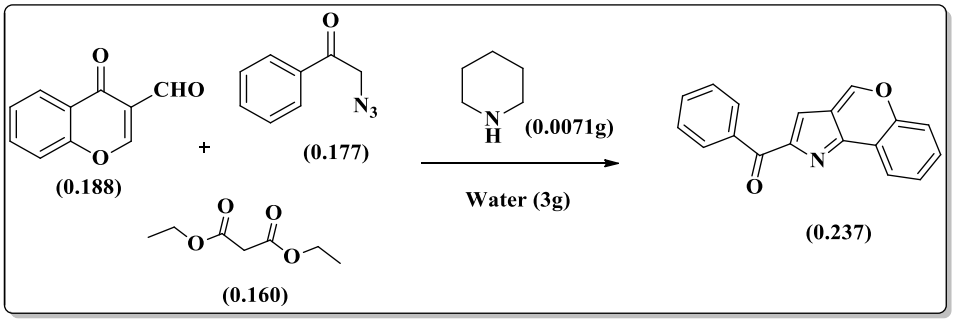
Atom economy for compound **10a**

$$\text{Atom Economy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in the reactant}}$$

$$\text{Atom Economy} = \frac{369 \text{ X } 100}{564}$$

$$\text{Atom Economy} = 65.49$$

E- Factor for compound **12a**



$$\text{E-Factor} = \frac{\text{Weight of total starting material} - \text{Product weight}}{\text{Product weight}}$$

$$\text{E-Factor} = \frac{3.53 - 0.237}{0.237}$$

$$\text{E-Factor} = 13.90$$

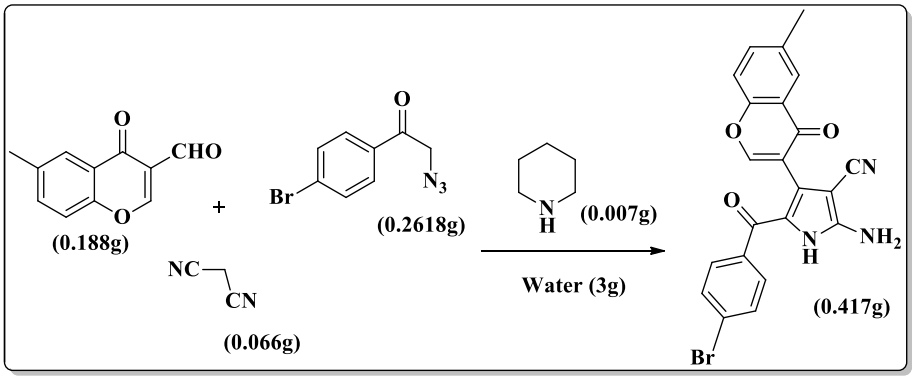
Atom economy for compound **12a**

$$\text{Atom Economy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in the reactant}}$$

$$\text{Atom Economy} = \frac{273 \text{ X } 100}{640}$$

$$\text{Atom Economy} = 42.70$$

E- Factor for compound **15a**



$$\text{E-Factor} = \frac{\text{Weight of total starting material} - \text{Product weight}}{\text{Product weight}}$$

$$\text{E-Factor} = \frac{3.523 - 0.417}{0.417}$$

$$\text{E-Factor} = 7.43$$

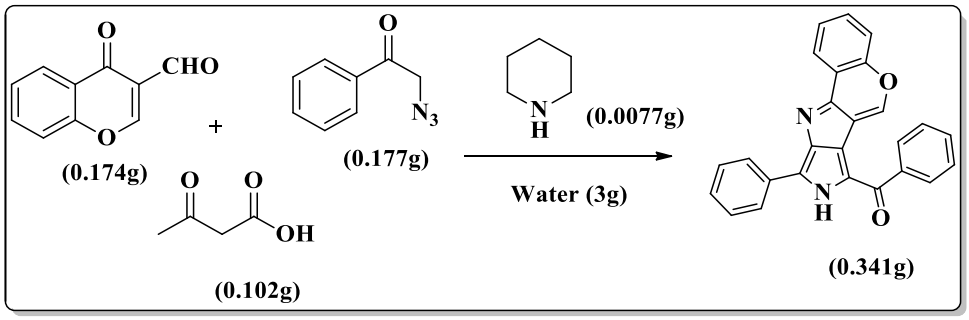
Atom economy for compound **15a**

$$\text{Atom Economy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in the reactant}}$$

$$\text{Atom Economy} = \frac{447 \text{ X } 100}{625}$$

$$\text{Atom Economy} = 71.52$$

E- Factor for compound **17a**



$$\text{E-Factor} = \frac{\text{Weight of total starting material} - \text{Product weight}}{\text{Product weight}}$$

$$\text{E-Factor} = \frac{3.489 - 0.341}{0.341}$$

$$\text{E-Factor} = 9.23$$

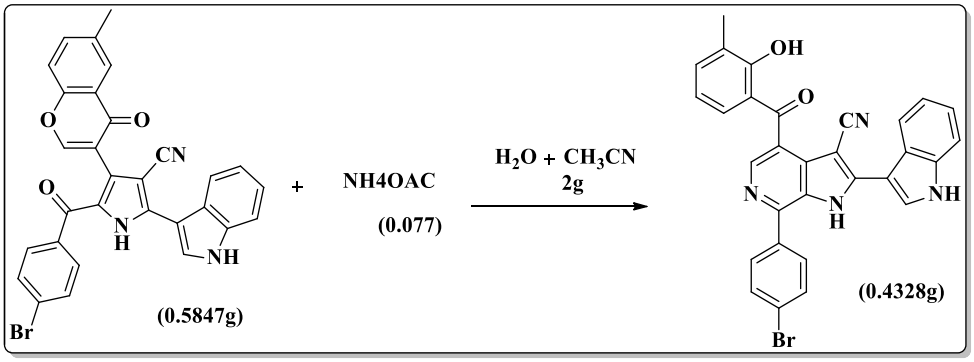
Atom economy for compound **17a**

$$\text{Atom Economy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in the reactant}}$$

$$\text{Atom Economy} = \frac{388 \quad X\ 100}{556}$$

$$\text{Atom Economy} = 69.80$$

E- Factor for compound **18a**



$$\text{E-Factor} = \frac{\text{Weight of total starting material} - \text{Product weight}}{\text{Product weight}}$$

$$\text{E-Factor} = \frac{2.624 - 0.4328}{0.4328}$$

$$\text{E-Factor} = 5.06$$

Atom economy for compound **18a**

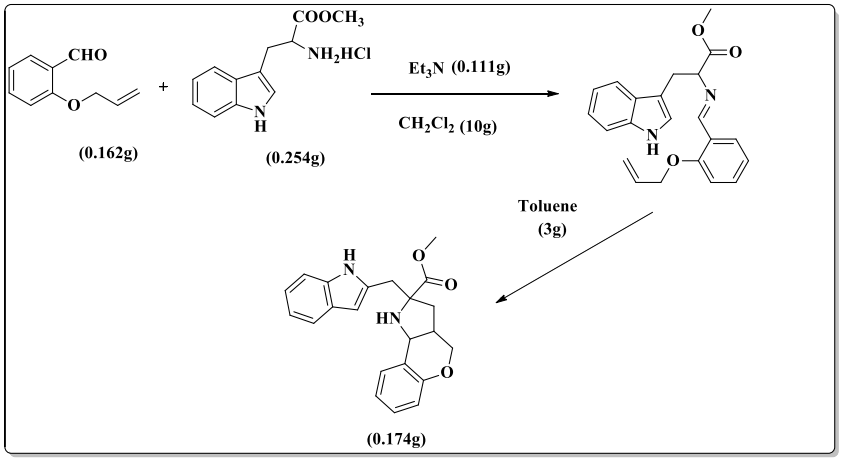
$$\text{Atom Economy} = \frac{\text{Mass of atoms in the desired product}}{\text{Mass of atoms in the reactant}}$$

$$\text{Atom Economy} = \frac{547 \text{ X } 100}{684}$$

$$\text{Atom Economy} = 80.03$$

Comparison of E- Factor and Atom Economy of our methodology with other similar reports compound

E- Factor for similarly reported compound



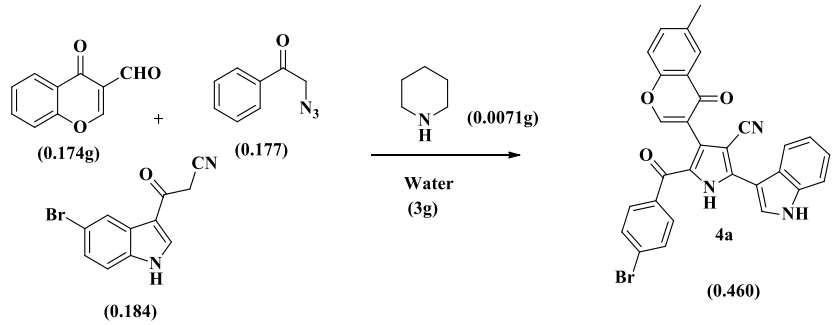
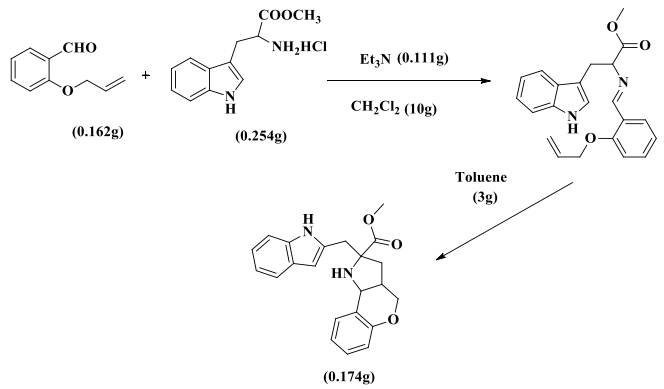
Ref: N. Arumugam R. Raghunathan, , A. I. Almansour, U. Karama, *Bioorg. Med. Chem. Lett*. **2012**, *22*, 1375–1379.

$$\text{E-Factor} = \frac{\text{Weight of total starting material} - \text{Product weight}}{\text{Product weight}}$$

$$\text{E-Factor} = \frac{13.527 - 0.174}{0.174}$$

$$\text{E-Factor} = 76.74$$

Comparison of E- Factor and Atom Economy

	E-Factor	Atom Economy
 **Our methodology**	6.69	70.03
 **Reported methodology**	76.74	50.2

Advantages of our methodology:

1) Higher atom economy
2) Low E factor
3) Remarkably eco-friendly solvent *viz* water used as reaction medium