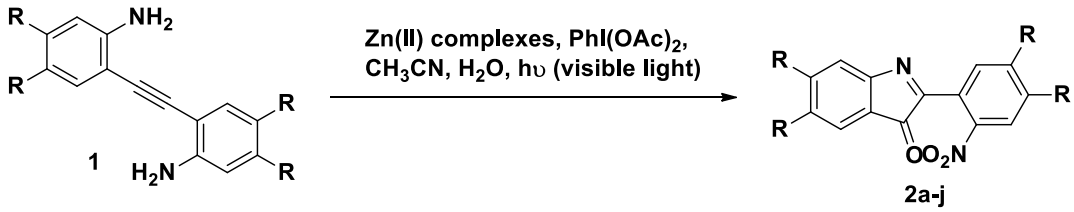
Supplementary Information

Photooxidation of 2,2'-(ethyne-1,2-diyl)dianilines; An Enhanced Photocatalytic Properties of New Salophen based Zn (II) Complexes

Photooxidation of 2,2'-(ethyne-1,2-diyl)dianilines



Scheme S1. Synthesis process for 2-(2-nitrophenyl)-3H-indol-3-one and its derivatives

Synthetic rout for the photooxidation reactions using 2,2'-(ethyne-1,2-diyl)dianiline and its derivatives is depicted in scheme 3 and are carried out with the following procedure;

Synthesis of 2-(2-nitrophenyl)-3H-indol-3-one and its derivatives (2a- 2j)

The quartz tube charged with 2,2'-(ethyne-1,2-diyl)dianiline (10 mmol) in 20 mL of water and CH_3CN (1:1) mixture, stirred for 15 minutes. Then (0.02 mmol**)** Zn (II) complex **([Zn(CPAMN) / [Zn(FPAMN)] / [Zn(MPAMN)])** with an oxidant (Diacetoxyiodo)benzene (1:2) was added to the reaction mass and examined under visible light irradiation (500wattstungsten visible light). After 24 hours, TLC (in 50:50 dichloromethane-hexane) exhibited a new mark at R_f 0.54 which indicates the product is formed. Then the light was turned off, and the reaction mixture temperature was reduced to room temperature and thinned with dichloromethane and separated the OL. The $MgSO_4$ was added to OL, filtered and the solvent was evaporated under vacuum. Then the crude compounds were purified by flash chromatography on silica gel using 10:90 methanol-dichloromethane as eluent.

Analytical data:

2-(2-nitrophenyl)-3H-indol-3-one (compound 2a):

The purification of the crude material by column chromatography gave a pure product with 84 % yield. M.P: 209 -211 ^oC (recrystallized from methanol); ^1H-NMR (400 MHz, $CDCl_3$), ∂ (ppm):

8.604 (m, 1H, Ar-*H*), 8.252 (m, 1H, Ar-*H*), 8.163 (m, 1H, Ar-*H*), 8.064 (m, 1H, Ar-*H*), and 7.794 – 7.662 (m, 4H, Ar-*H*); HRMS cald. For $C_{14}H_8N_2O_3^+$: 253.0529 (M^++1) found: 252.0535 (M^+).

2-(4,5-dimethyl-2-nitrophenyl)-5,6-dimethyl-3H-indol-3-one (compound 2b)

The purification of the crude material by column chromatography gave a pure product with 90 % yield. M.P: 234 -236 ^oC (recrystallized from ethanol); ^{1}H-NMR (400 MHz, $CDCl_3$), ∂ (ppm): 8.164 (s, 1H, Ar-*H*), 7.956 (s, 1H, Ar-*H*), 7.684 (s, 1H, Ar-*H*), 7.668 (s, 1H, Ar-*H*), 2.546 (s, 3H, C*H*$_3$), and 2.464 (s, 3H, C*H*$_3$); HRMS cald. For $C_{18}H_{16}N_2O_3^+$: 308.1161 $[M]^+$ found: 309.1157 $[M+1]^+$.

5,6-dichloro-2-(4,5-dichloro-2-nitrophenyl)-3H-indol-3-one (compound 2c):

The purification of the crude material by column chromatography gave a pure product with 79 % yield. M.P: 256 -258 ^oC; ^{1}H-NMR (400 MHz, $CDCl_3$), ∂ (ppm): 8.794 (s, 1H, Ar-*H*), 8.164 (s, 1H, Ar-*H*), 7.846 (s, 1H, Ar-*H*), and 7.578 (s, 1H, Ar-*H*); HRMS cald. For $C_{14}H_4Cl_4N_2O_3^+$: 387.8976 $[M]^+$ found: 388.8982 $[M+1]^+$.

5,6-difluoro-2-(4,5-difluoro-2-nitrophenyl)-3H-indol-3-one (compound 2d):

The purification of the crude material by column chromatography gave a pure product with 81 % yield. M.P: 262 -264 ^oC; ^{1}H-NMR (400 MHz, d_6-DMSO), ∂ (ppm): 8.186 (m, 1H, Ar-*H*), 8.062 (m, 1H, Ar-*H*), 7.586 (m, 1H, Ar-*H*), and 7.464 (m, 1H, Ar-*H*); HRMS cald. For $C_{14}H_4F_4N_2O_3^+$: 324.0158 $[M]^+$ found: 325.0151 $[M+1]^+$.

5-fluoro-2-(5-fluoro-4-methoxy-2-nitrophenyl)-6-methoxy-3H-indol-3-one (compound 2e):

The purification of the crude material by column chromatography gave a pure product with 85 % yield. M.P: 222 - 224 ^oC; ^{1}H-NMR (400 MHz, *CDCl*$_3$), ∂ (ppm): 8.194 (m, 1H, Ar-*H*), 7.754 (m, 1H, Ar-*H*), 7.598 (m, 1H, Ar-*H*), 7.312 (m, 1H, Ar-*H*), and 4.128 (s, 6H, Ar-OC*H*$_3$); HRMS cald. For $C_{16}H_{10}F_2N_2O_5^+$: 348.0558 $[M]^+$ found: 349.0549 $[(M+1)]^+$.

5-chloro-2-(5-chloro-4-methoxy-2-nitrophenyl)-6-methoxy-3H-indol-3-one (compound 2f):

The purification of the crude material by column chromatography gave a pure product with 86 % yield. M.P: 261 -263 ^oC; ^{1}H-NMR (400 MHz, *CDCl*$_3$), ∂ (ppm): 8.228 (s, 1H Ar-*H*), 8.042 (s, 1H, Ar-*H*), 7.884 (s, 1H, Ar-*H*), 7.586 (s, H, Ar-*H*), and 4.168 (s, 6H, Ar-OC*H*$_3$); HRMS cald. For $C_{16}H_{10}Cl_2N_2O_5^+$: 379.9967 $[M]^+$ found: 380.9963 $[(M+1)]^+$.

2-(4,5-dicyano-2-nitrophenyl)-3-oxo-3H-indole-5,6-dicarbonitrile (compound 2g):

The purification of the crude material by column chromatography gave a pure product with 69 % yield. M.P: 208 -210 ^{o}C; ^{1}H-NMR (400 MHz, *d_6-DMSO*), ∂ (ppm): 9.158 (s, 1H, Ar-*H*), 8.636 (s, 1H, Ar-*H*), 8.366 (s, 1H, Ar-*H*) and 7.962 (s, 1H, Ar-*H*); HRMS cald. For $C_{18}H_4N_6O_3^+$: 352.0345 $[M]^+$ found: 353.0339 $[M+1]^+$.

2-(5-cyano-2-nitrophenyl)-3-oxo-3H-indole-5-carbonitrile (compound 2h):

The purification of the crude material by column chromatography gave a pure product with 74 % yield. M.P: 202 – 204 ^{o}C; ^{1}H-NMR (400 MHz, *$CDCl_3$*), ∂ (ppm): 8.364 (s, 1H, Ar-*H*), 8.194 (s, 1H, Ar-*H*), 8.127 (d, 1H, J = 12 Hz, Ar-*H*), 7.937 (d, 1H, J = 11 Hz, Ar-*H*), 7.812 (d, 1H, J = 16 Hz, Ar-*H*), and 7.784 (d, 1H, J = 14 Hz, Ar-*H*); HRMS cald. For $C_{16}H_6N_4O_3^+$: 302.0440 $[M]^+$ found: 303.0436 $[M+1]^+$.

6-chloro-2-(4-chloro-5-methyl-2-nitrophenyl)-5-methyl-3H-indol-3-one (compound 2i):

The purification of the crude material by column chromatography gave a pure product with 87 % yield. M.P: 218 – 220 ^{o}C; ^{1}H-NMR (400 MHz, *$CDCl_3$*), ∂ (ppm): 7.996 (s, 1H, Ar-*H*), 7.792 (s, 1H, Ar-*H*), 7.552 (s, 1H, Ar-*H*), 7.205 (s, 1H, Ar-*H*), and 2.548 (s, 6H, C*H_3*); HRMS cald. For $C_{16}H_{10}Cl_2N_2O_3^+$: 348.0068 $[M]^+$ found: 349.0063 $[M+1]^+$.

2-(2-nitro-4,5-bis(trifluoromethyl)phenyl)-5,6-bis(trifluoromethyl)-3H-indol-3-one (compound 2j)

The purification of the crude material by column chromatography gave a pure product with 64 % yield. M.P: 286 - 288 ^{o}C; ^{1}H-NMR (400 MHz, *d_6*-DMSO), ∂ (ppm): 8.386 (s, 1H, Ar-*H*), 8.188 (s, 1H, Ar-*H*), 7.882 (s, 1H, Ar-*H*), and 7.786 (s, 1H, Ar-*H*),; HRMS cald. For $C_{18}H_4F_{12}N_2O_3^+$: 524.0030 $[M]^{+,}$ found: 525.0027 $[M+1]^+$.

Table S1. Analytical and Physicochemical data of Zn(II) complexes

Compound	% Yield	M.P/ D.P. (^{o}C)	%C (calcd)	%H (calcd)	%X (calcd)	%N (calcd)	% Zn (calcd)	Λ_m ohm^{-1} mol^{-1} cm^2 (DMF)
CPAMN $C_{28}H_{19}ClN_2O_2$	90	256	74.52 (74.58)	4.22 (4.25)	7.83 (Cl) (7.86)	6.15 (6.21)	--	---

FPAMN $C_{28}H_{19}FN_2O_2$	88	238	77.34 (77.41)	4.38 (4.41)	4.33 (F) (4.37)	6.39 (6.45)	--	--
MPAMN $C_{29}H_{22}N_2O_3$	85	218	77.97 (78.01)	4.93 (4.97)	6.21 (6.27)	6.21 (6.27)	--	--
[Zn(CPAMN)] $C_{28}H_{17}ClN_2O_2Zn$	64	363	65.34 (65.39)	3.29 (3.33)	6.85 (Cl) (6.89)	5.39 (5.45)	12.67 (12.71)	12.49
[Zn(FPAMN)] $C_{28}H_{17}FN_2O_2Zn$	71	349	67.51 (67.55)	3.41 (3.44)	3.78 (F) (3.82)	5.59 (5.63)	13.08 (13.13)	15.04
[Zn(MPAMN)] $C_{29}H_{20}N_2O_3Zn$	75	359	68.28 (68.31)	3.92 (3.95)	---	5.46 (5.49)	12.78 (12.82)	16.19

Table S2. Thermal data of Zn (II) complexes

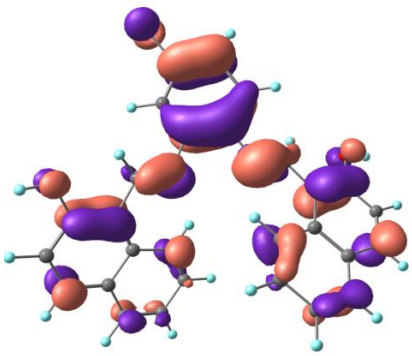
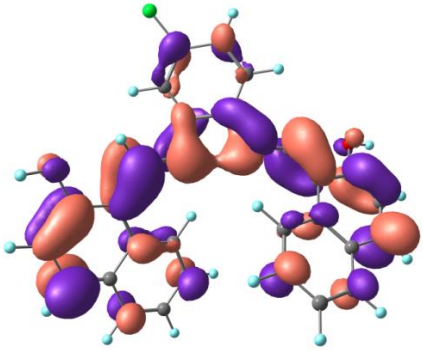
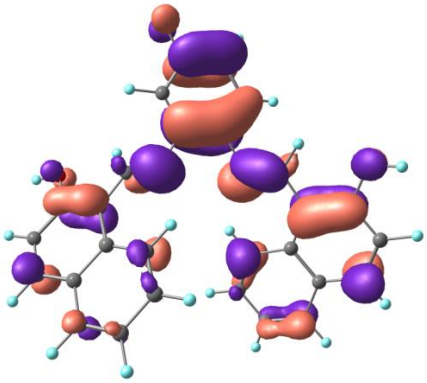
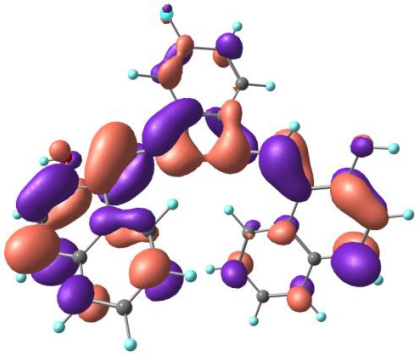
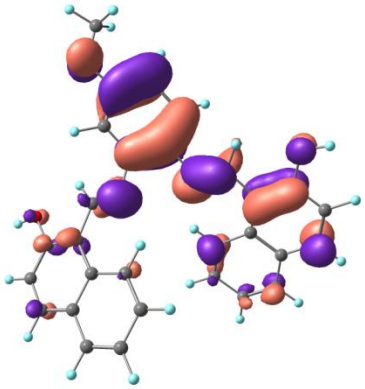
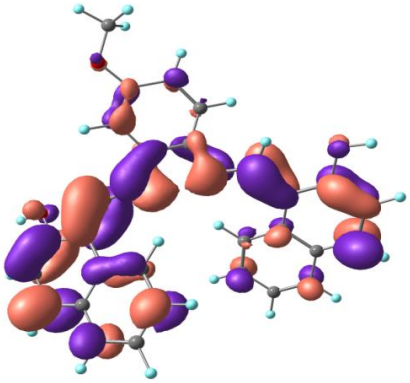
S.No.	Complex	Thermal Process	Temperature Range, ^{0}C	Pyrolysis product, %	
				Found	Calcd
1	[Zn(CPAMN)]	[Zn(CPAMN)]→ [ZnO]	268.15 – 677.82	83.58	84.12
2	[Zn(FPAMN)]	[Zn(FPAMN)]→ [ZnO]	276.28 – 682.45	83.06	83.59
3	[Zn(MPAMN)]	[Zn(MPAMN)] → [ZnO]	256.82 – 658.68	83.63	83.98

Table S3. Electronic excitations (λ_{CAL}in nm) oscillator strength (*f*) major transitions (MT) and % weight (%Ci) of ligands and complexes at TD-B3LYP/6-31G (d, p) method.

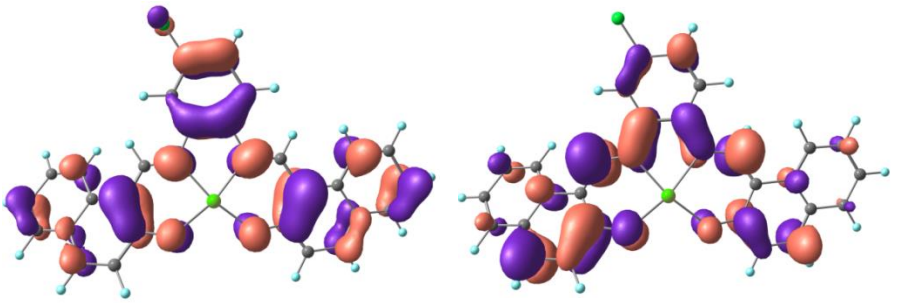
NAME	λ_{CAL}(nm)	*f*	MT	%Ci
CPAMN	437	0.226	H→L	93

FPAMN	442	0.215	H→L	93
MPAMN	455	0.183	H→L	95
[Zn(CPAMN)]	453	0.410	H→L	99
[Zn(FPAMN)]	456	0.367	H→L	98
[Zn(MPAMN)]	459	0.316	H→L	99

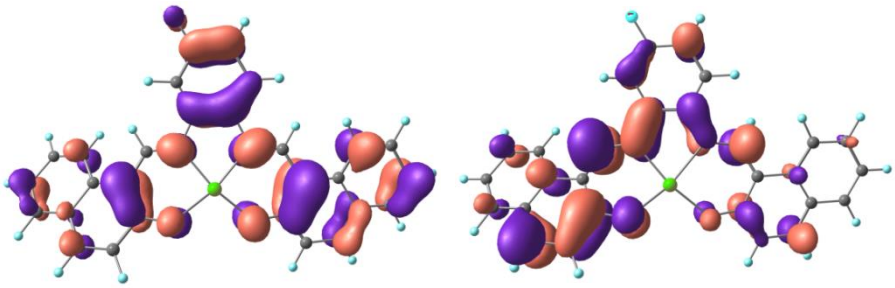
Table S4. Molecular orbitals pictures of HOMO LUMO for ligands and Zn (II) complexes:

NAME	HOMO	LUMO
CPAMN		
FPAMN		
MPAMN		

[Zn(CPAMN)]



[Zn(FPAMN)]



[Zn(MPAMN)]

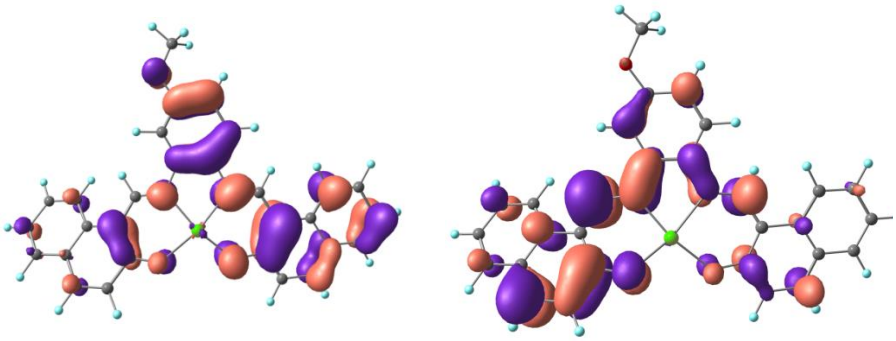


Table S5. Calculated HOMO, LUMO energies and HLG (in eV) of ligands and complexes

Name	E_{HOMO} (eV)	E_{LUMO} (eV)	HLG
CPAMN	-5.25	-1.87	3.38
FPAMN	-5.16	-1.81	3.35
MPAMN	-4.91	-1.66	3.25
[Zn(CPAMN)]	-5.35	-2.17	3.18
[Zn(FPAMN)]	-5.29	-2.12	3.17
[Zn(MPAMN)]	-5.10	-1.95	3.15

IICT - HYDERABAD

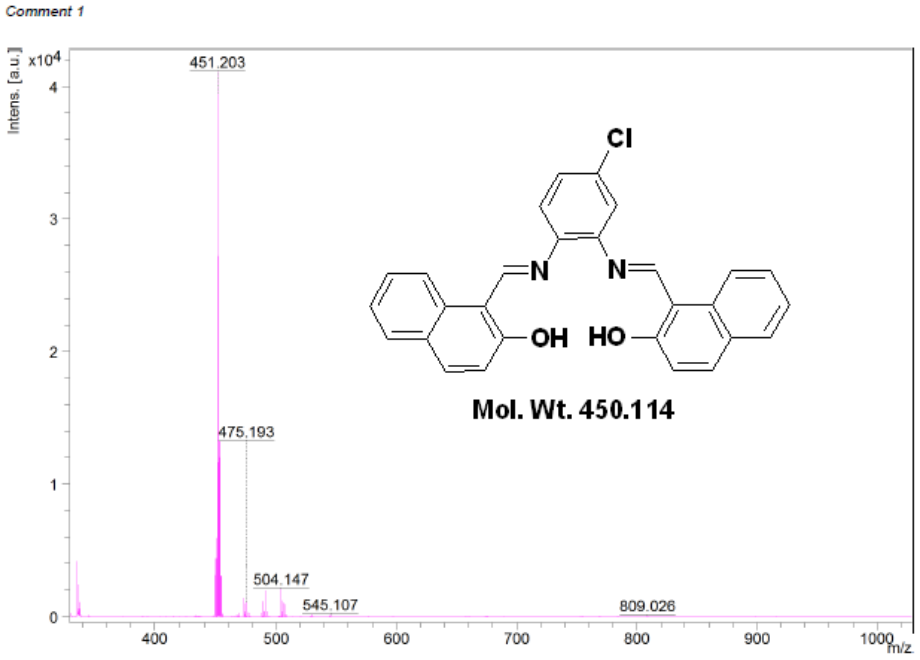


Figure S1. Maldi mass spectrum of CPAMN ligand

IICT - HYDERABAD

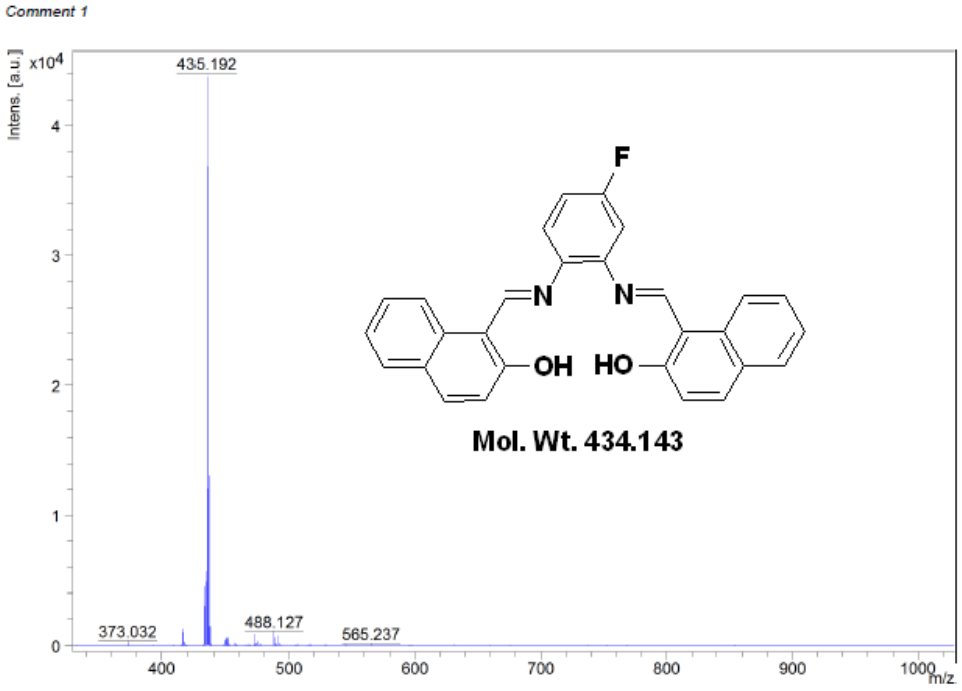


Figure S2. Maldi mass spectrum of FPAMN ligand

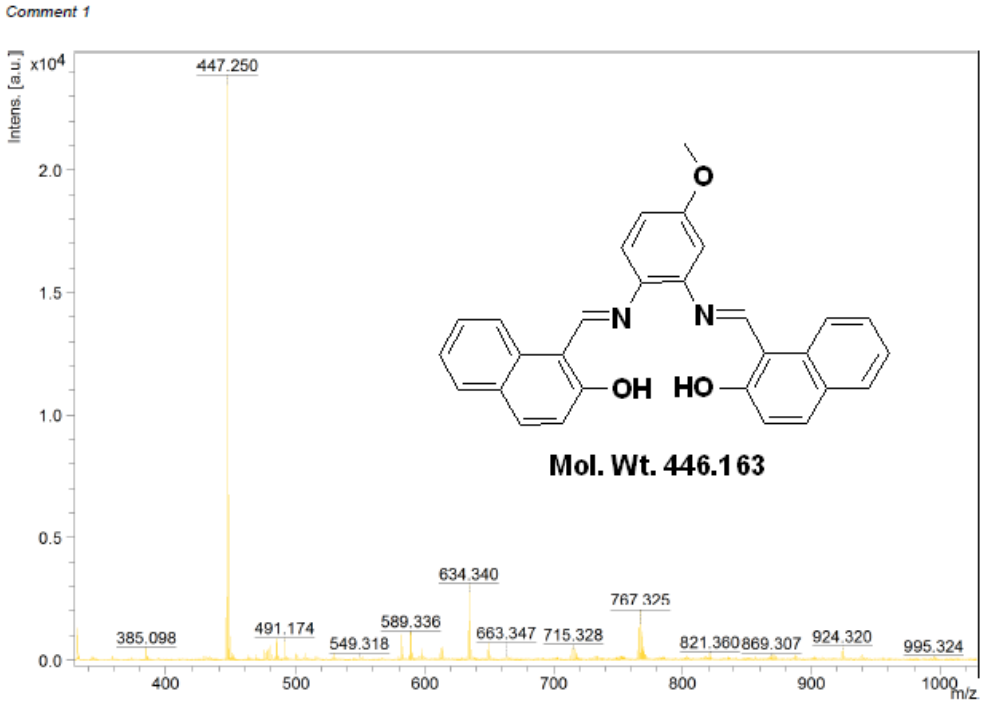


Figure S3. Maldi mass spectrum of MPAMN ligand

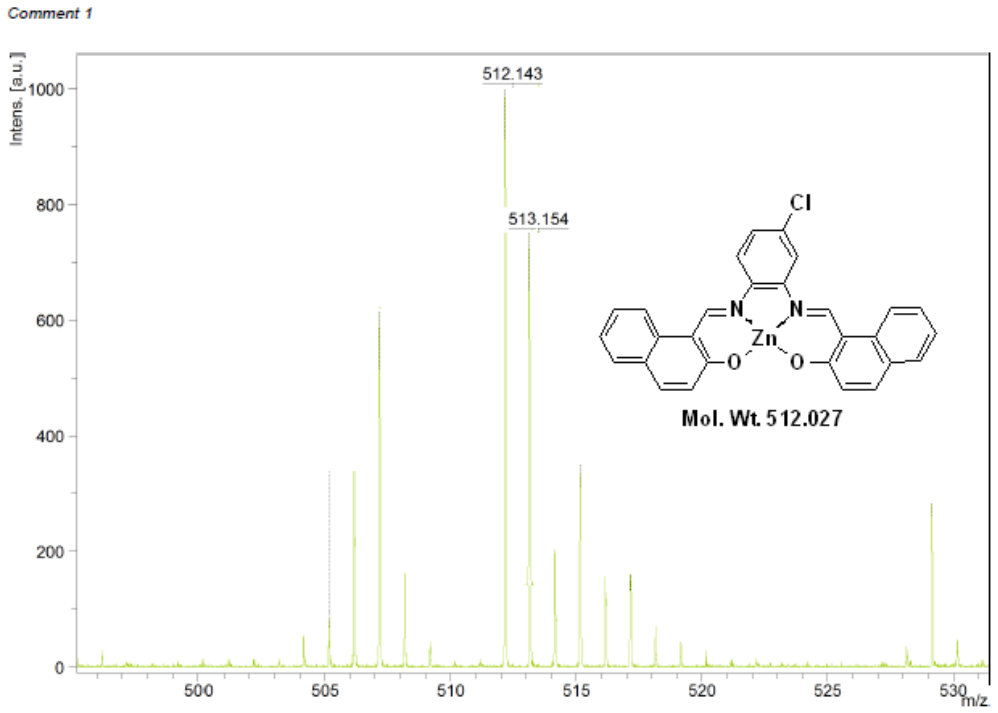


Figure S4. Maldi mass spectrum of [Zn(CPAMN)] complex

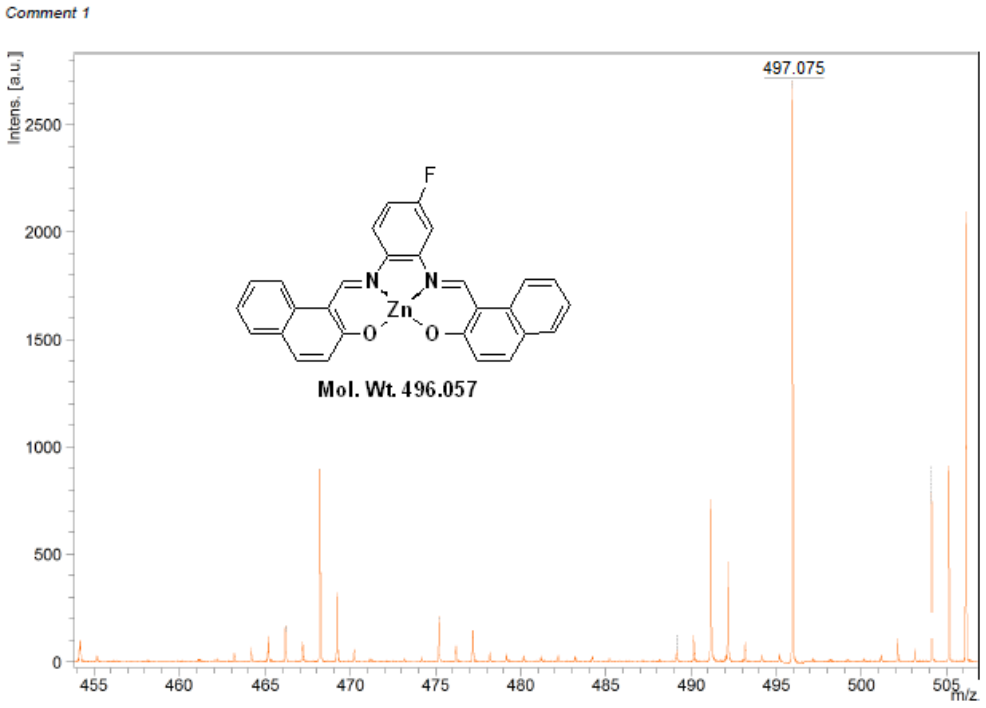


Figure S5. Maldi mass spectrum of [Zn(FPAMN)] complex

RS-PN-18-0007

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Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron_HiRes, Power: 80, Blanked, P.Ext. @ 1000 (bin 65)
%Int. 5.3 mV[sum= 265 mV] Profiles 1-50 Smooth Gauss 7

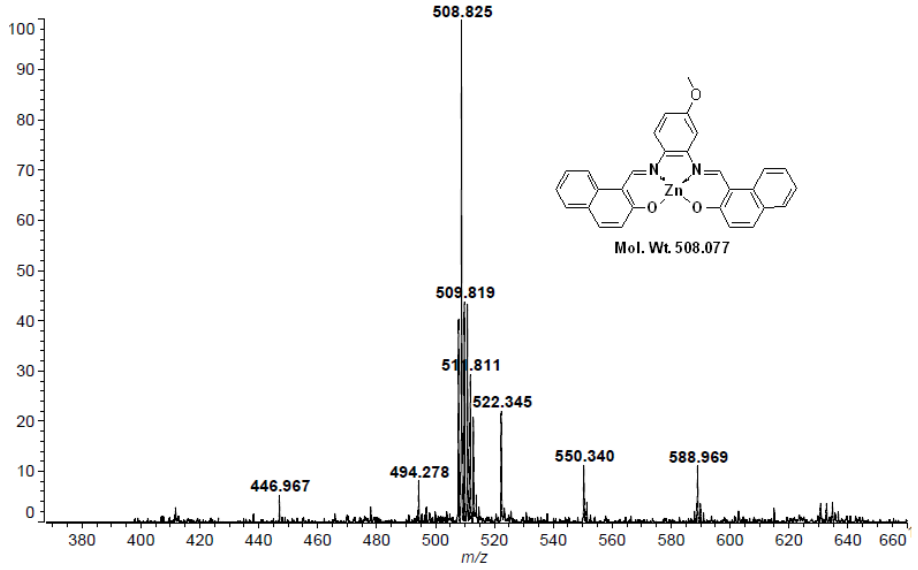

Figure S6. Maldi mass spectrum of [Zn(MPAMN)] complex

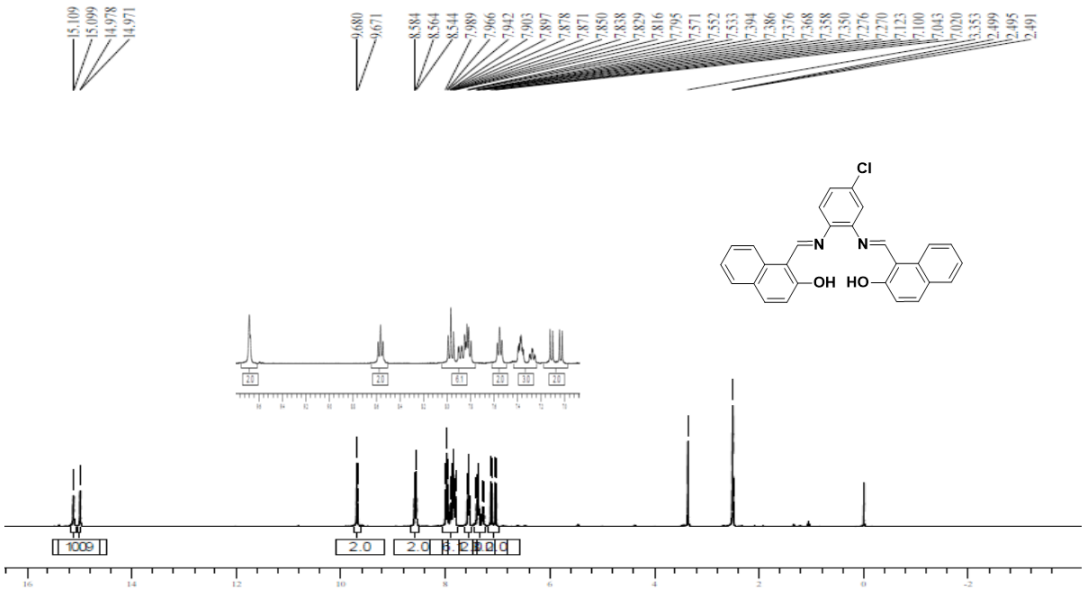

Figure S7. ^{1}H-NMR spectral pattern of CPAMN ligand

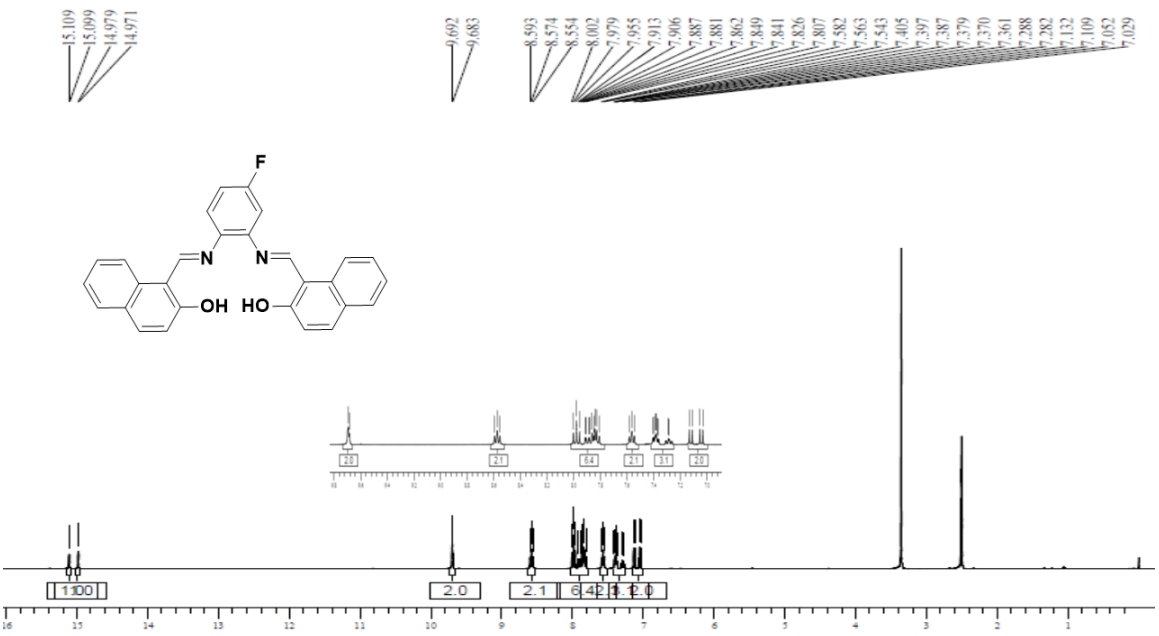

Figure S8. [1]H-NMR spectral pattern of FPAMN ligand

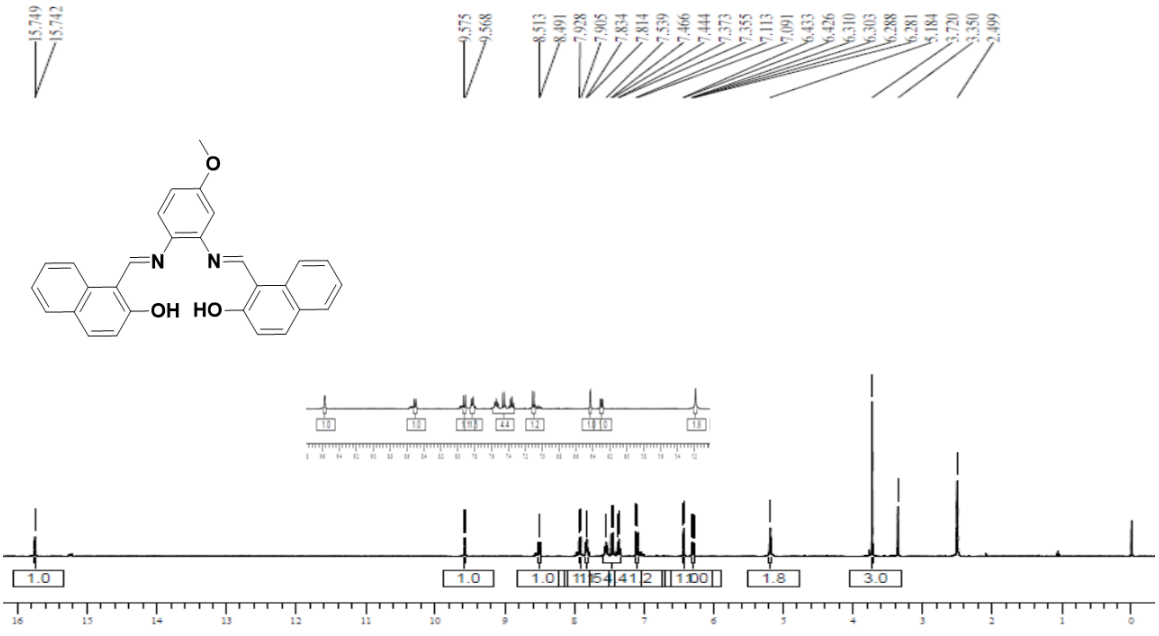

Figure S9. [1]H-NMR spectral pattern of MPAMN ligand

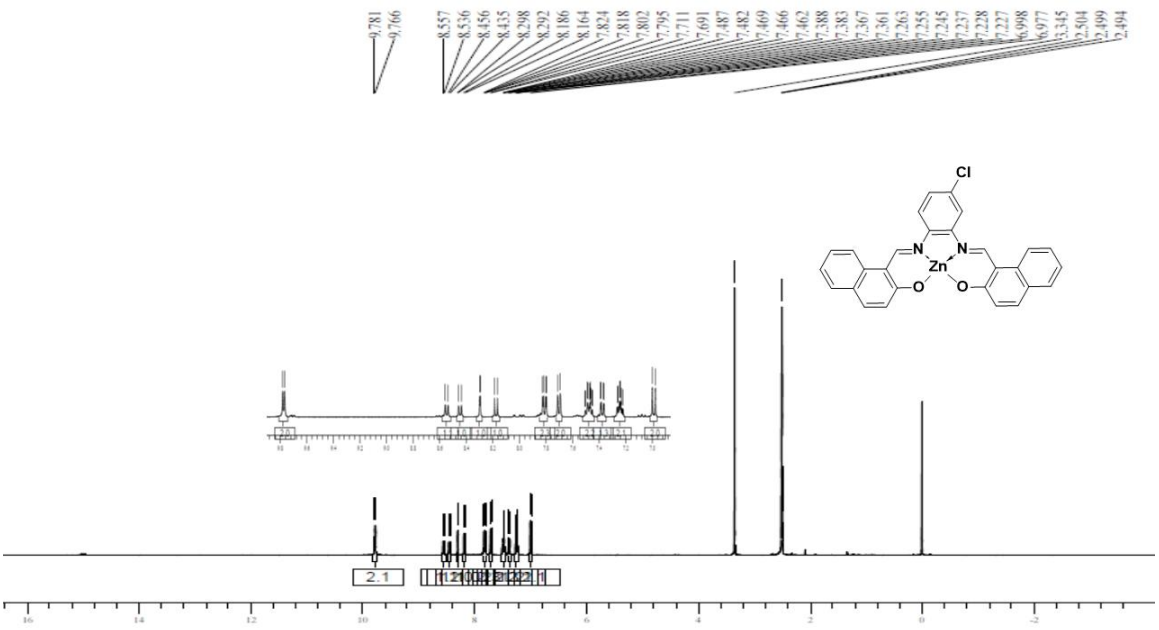

Figure S10. ^{1}H-NMR spectral pattern of [Zn(CPAMN)] complex

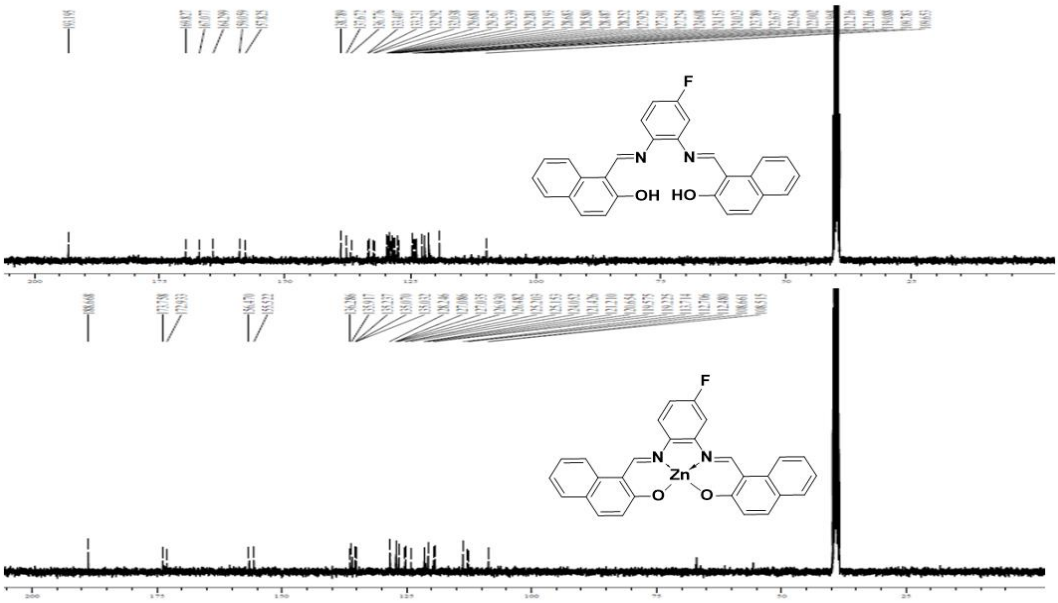

Figure S11. ^{13}C-NMR spectral pattern of FPAMN ligand and [Zn(FPAMN)] complex

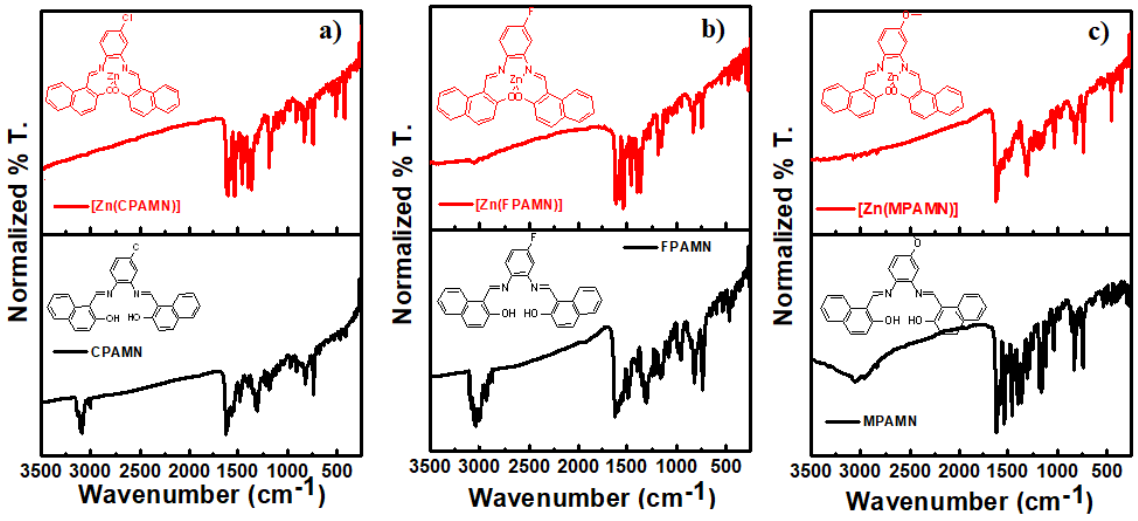

Figure S12. IR spectral images of ligands and Zn (II) complexes

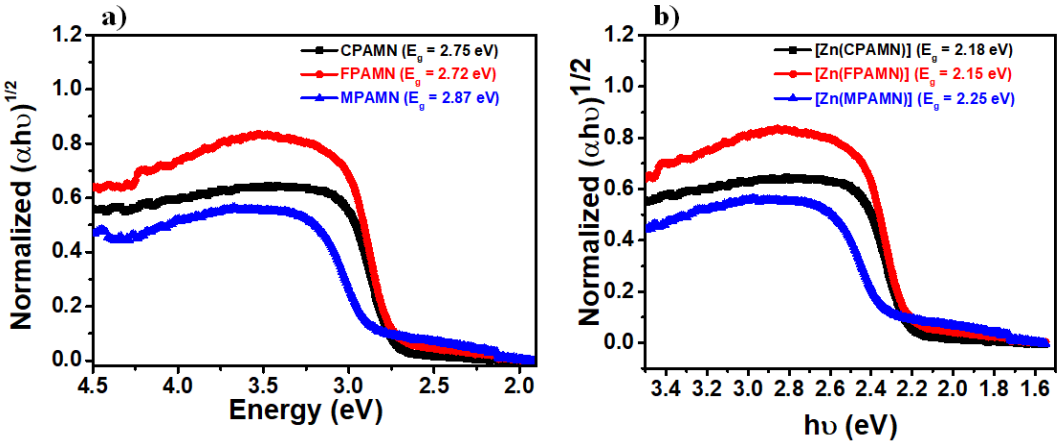

Figure S13. UV-vis-DRS spectra of ligands and Zn (II) complexes

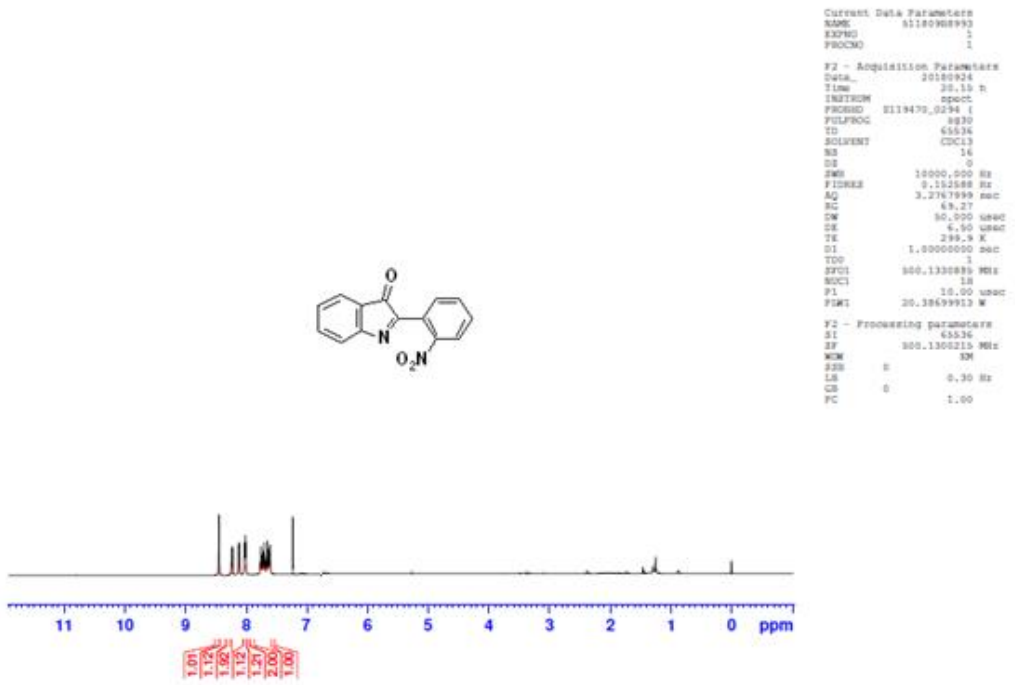

Figure S14. ^{1}H-NMR Spectrum of Compound 2a

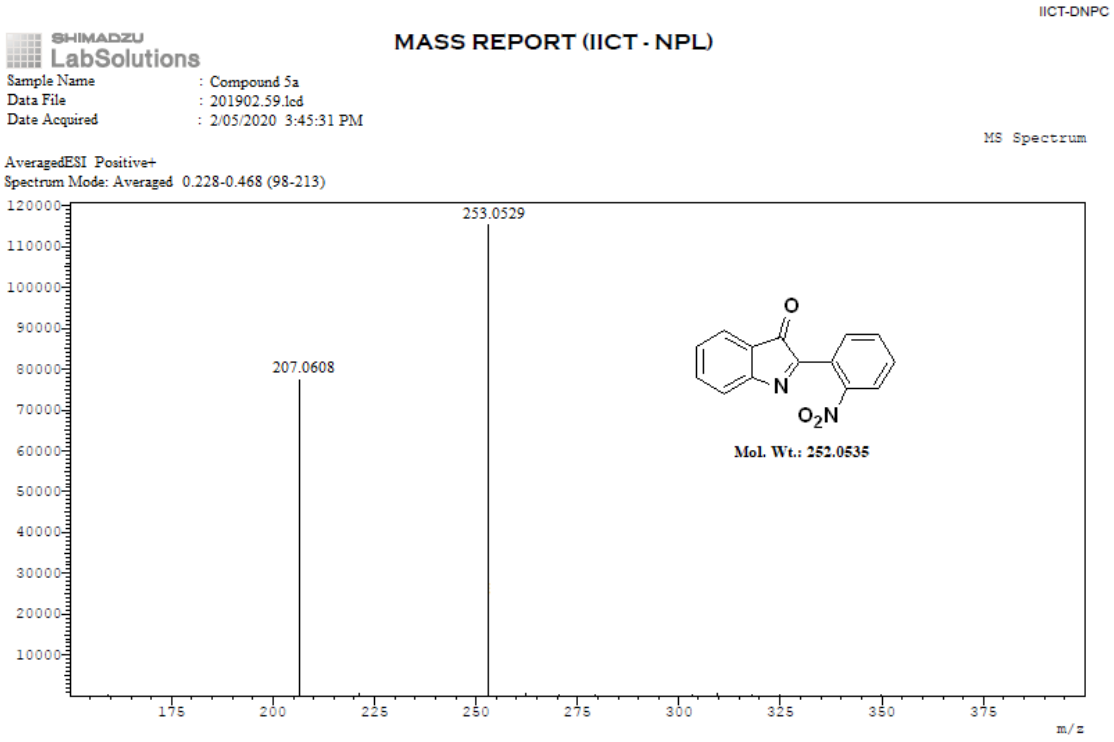

Figure S15 Mass Spectrum of Compound 2a

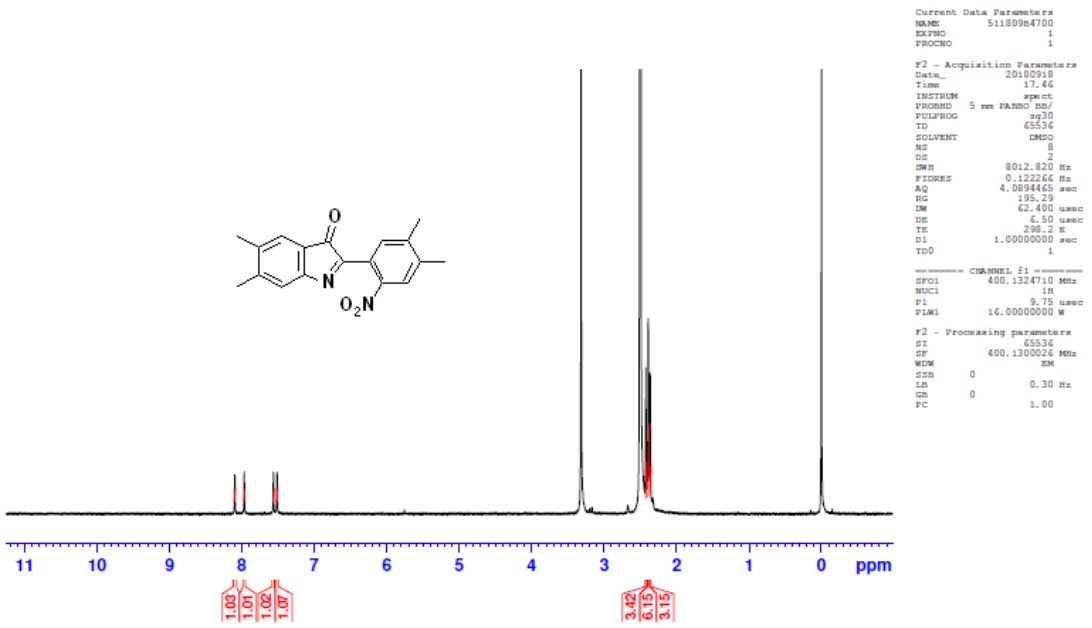

Figure S16. ^{1}H-NMR Spectrum of Compound 2b

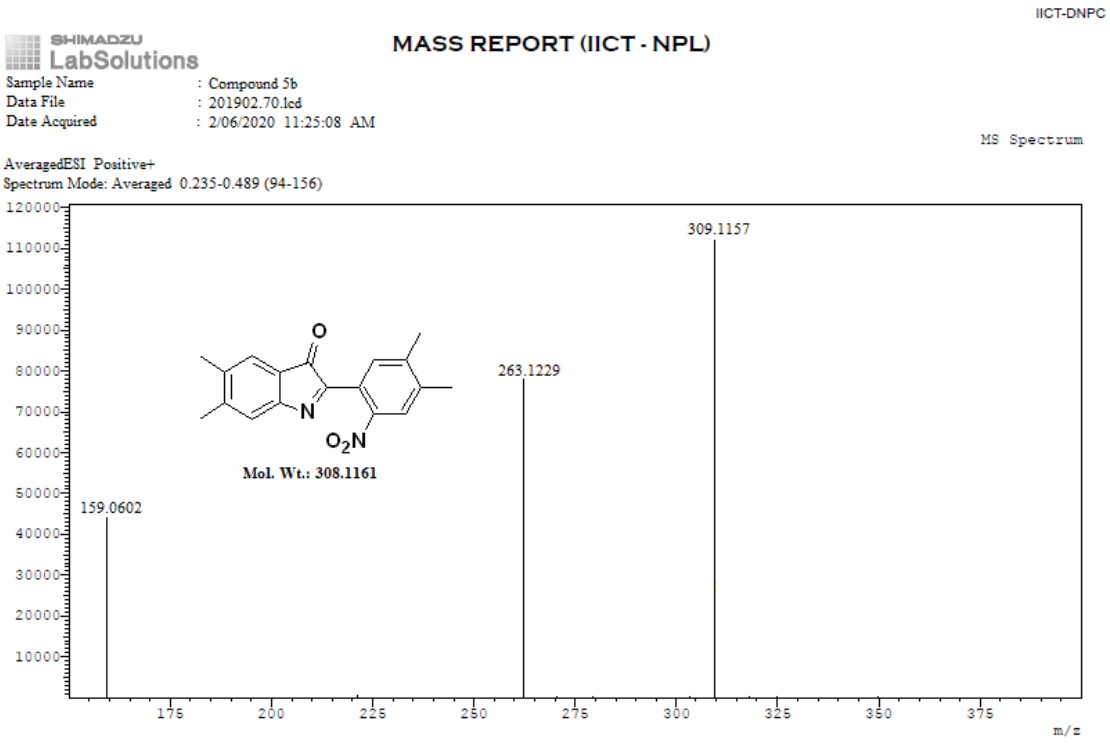

Figure S17. Mass Spectrum of Compound 2b

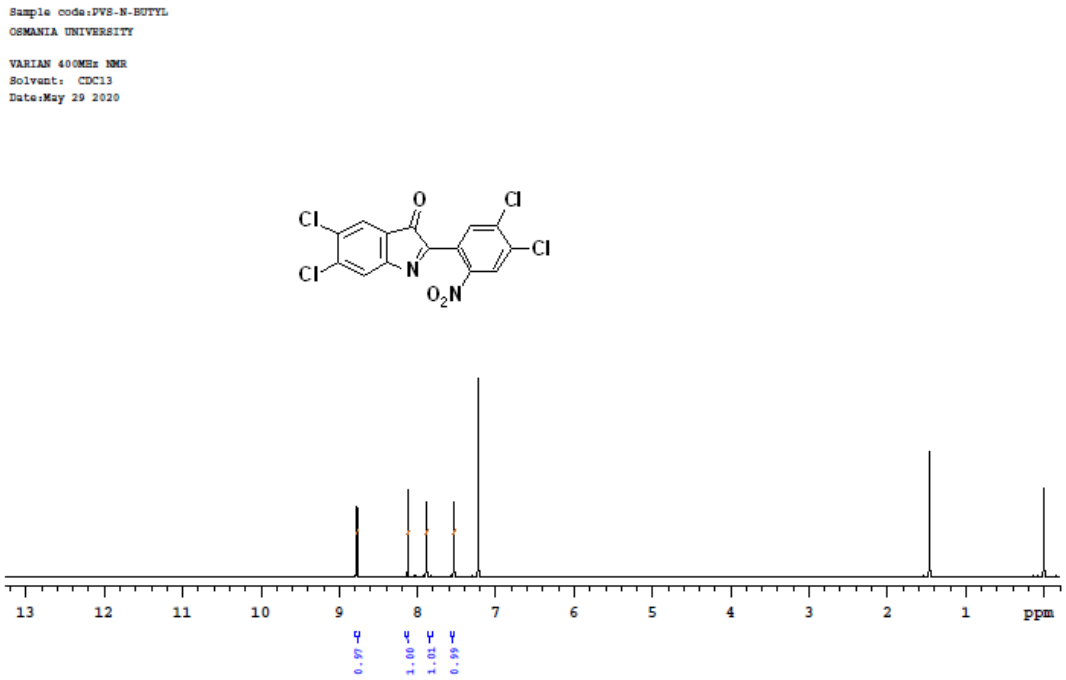

Figure S18. ^{1}H-NMR spectrum of compound 2c

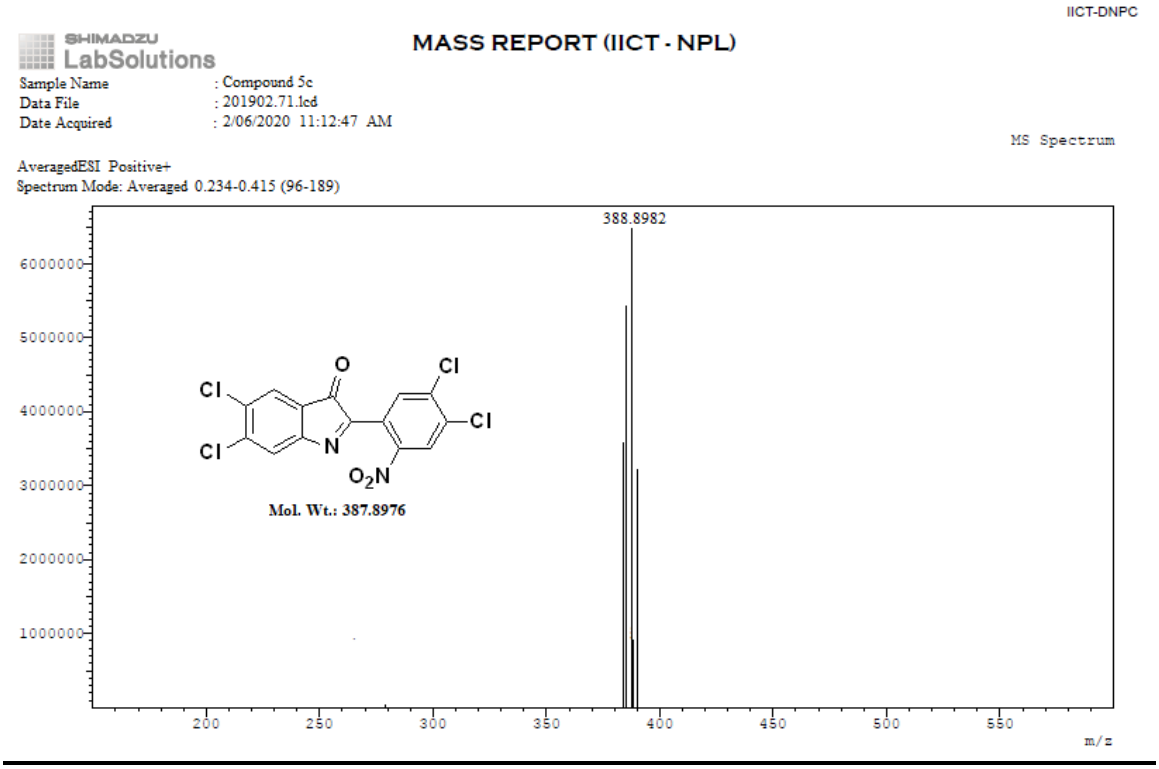

Figure S19. Mass spectrum of compound 2c

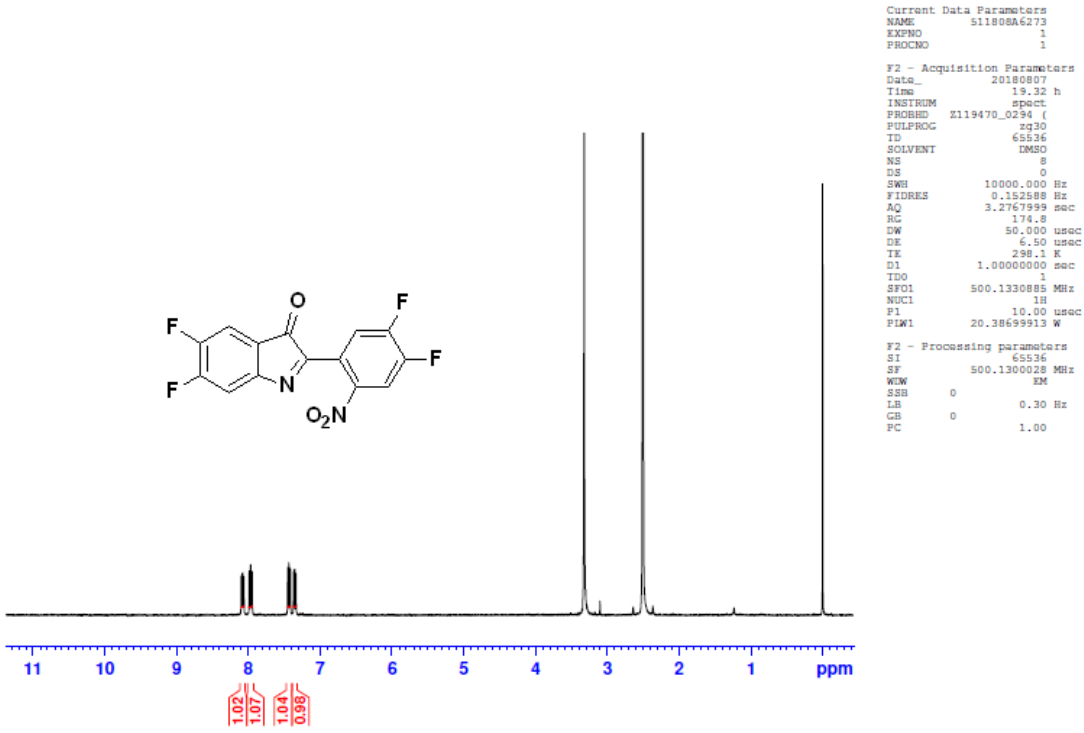

Figure S20. ^{1}H-NMR spectrum of compound 2d

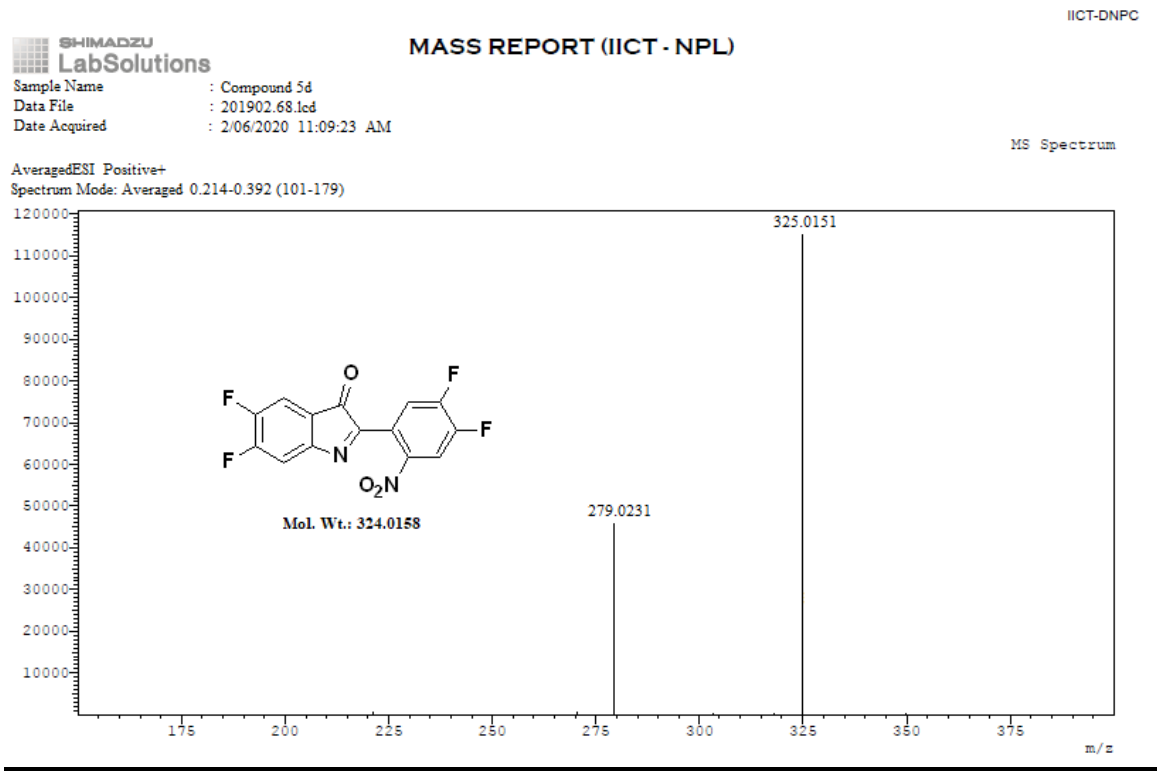

Figure S21. Mass spectrum of compound 2d

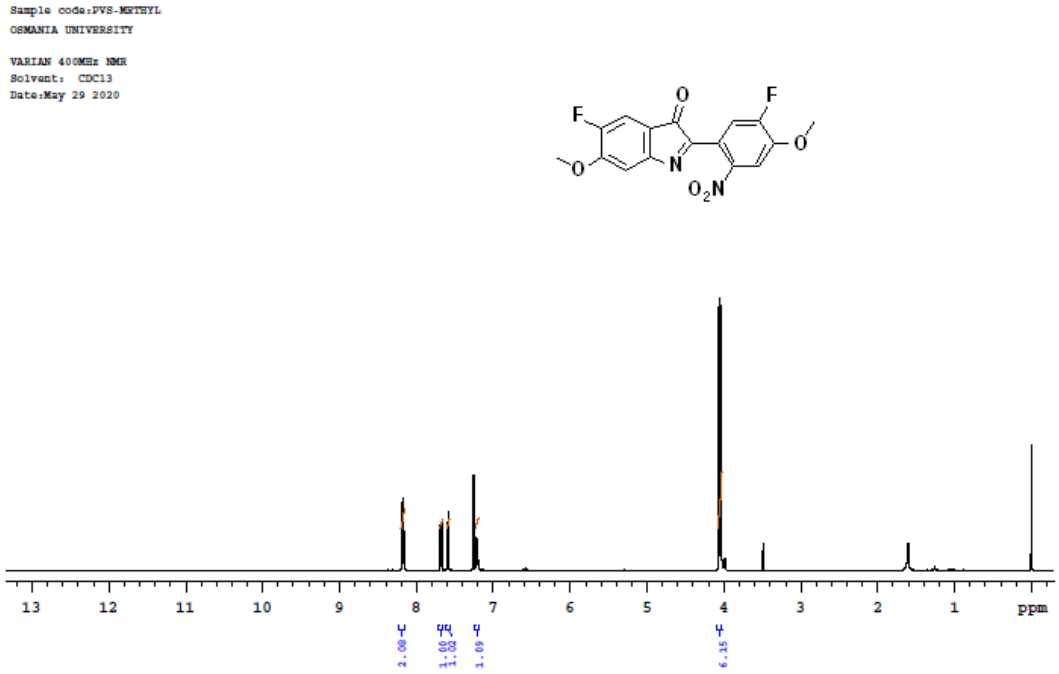

Figure S22. ^{1}H-NMR spectrum of compound 2e

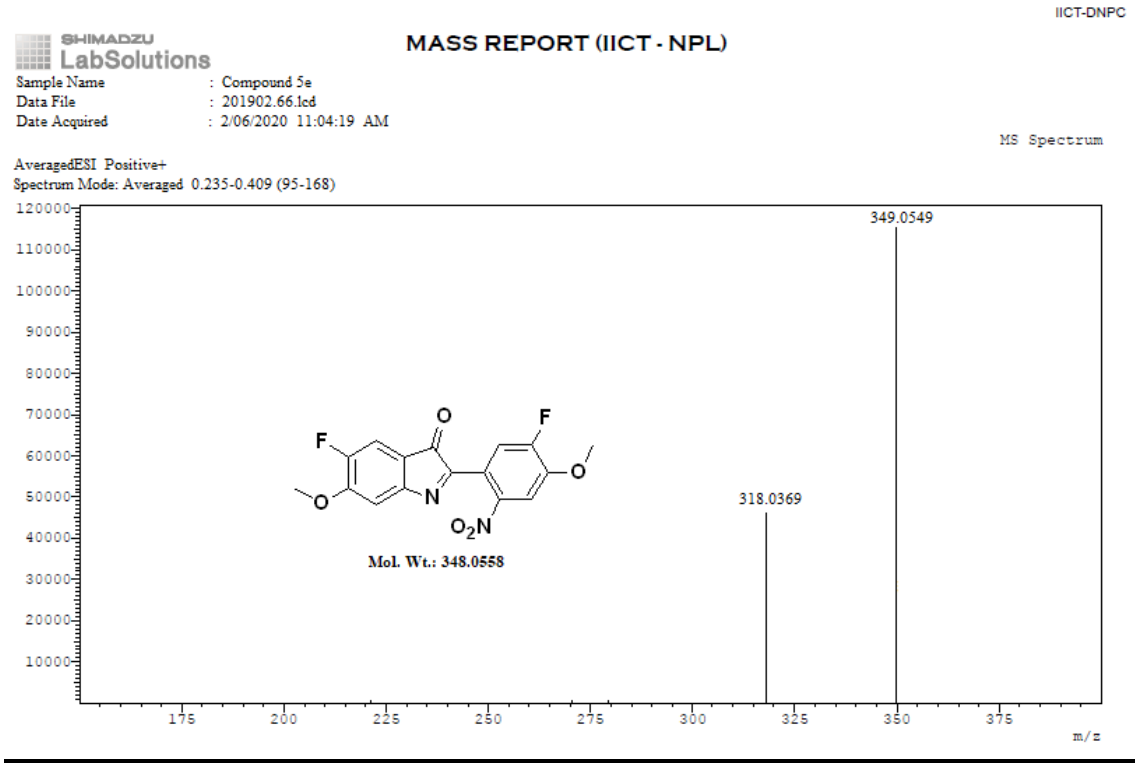

Figure S23. Mass spectrum of compound 2e

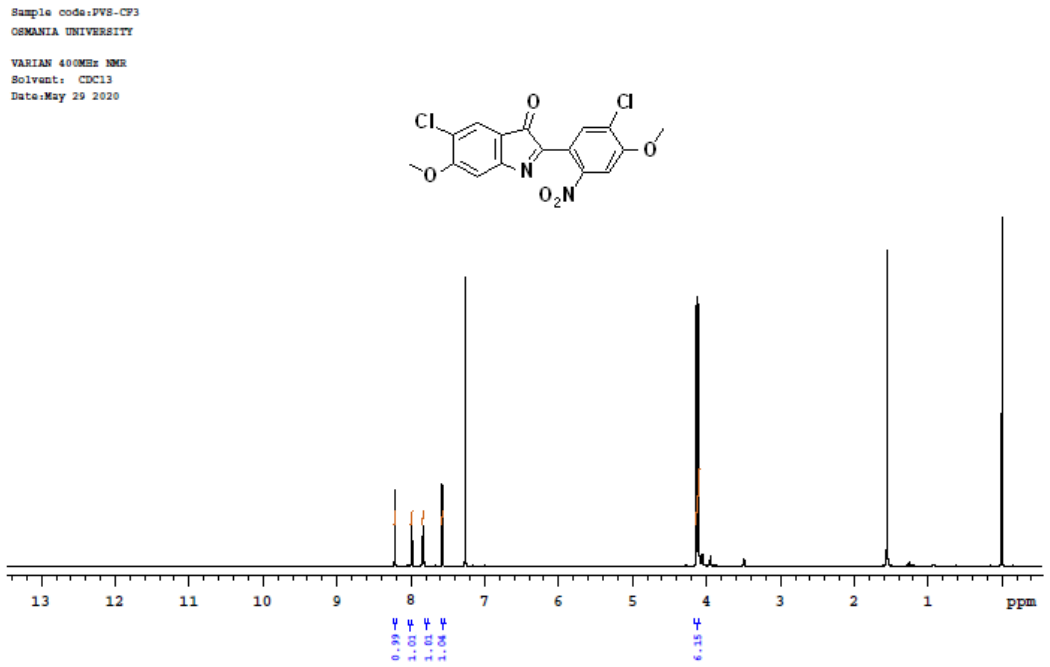

Figure S24. ^{1}H-NMR spectrum of compound 2f

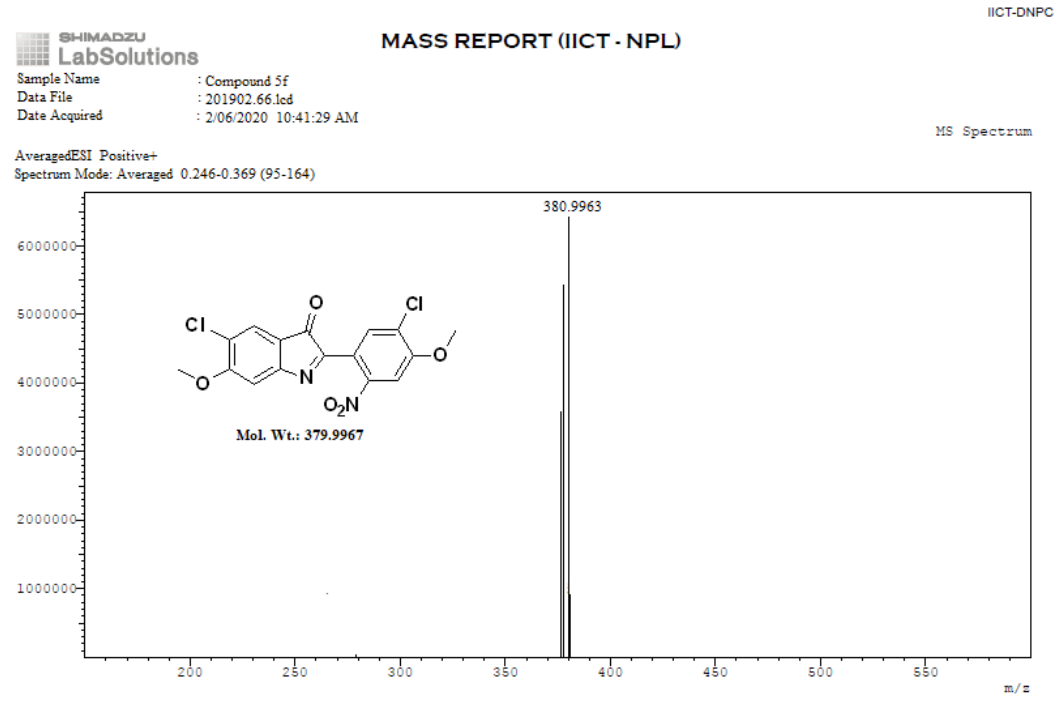

Figure S25. Mass spectrum of compound 2f

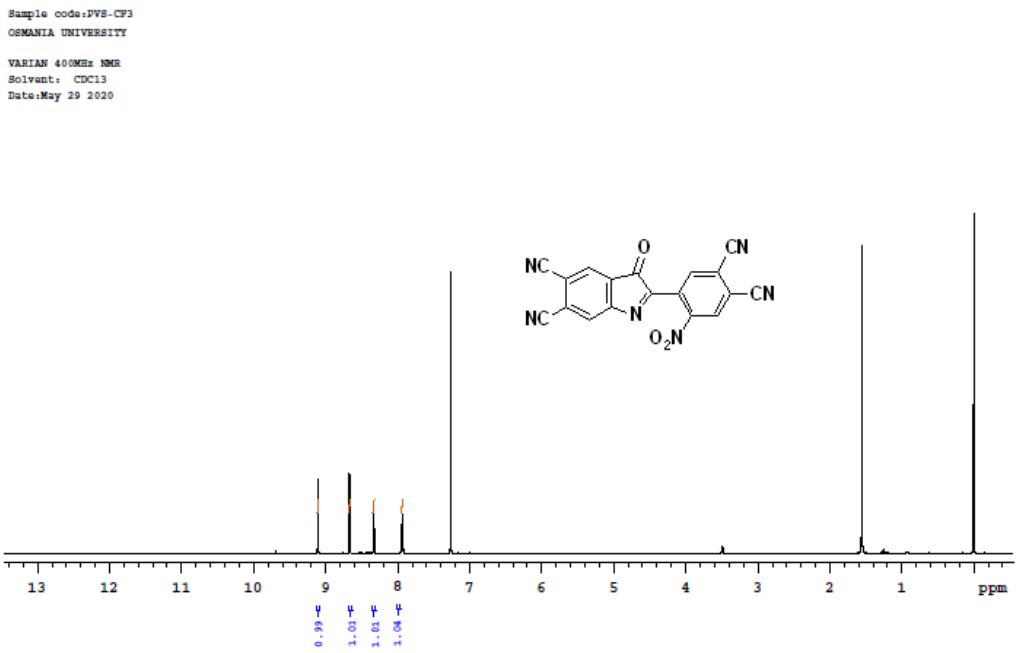

Figure S26. ^{1}H-NMR spectrum of compound 2g

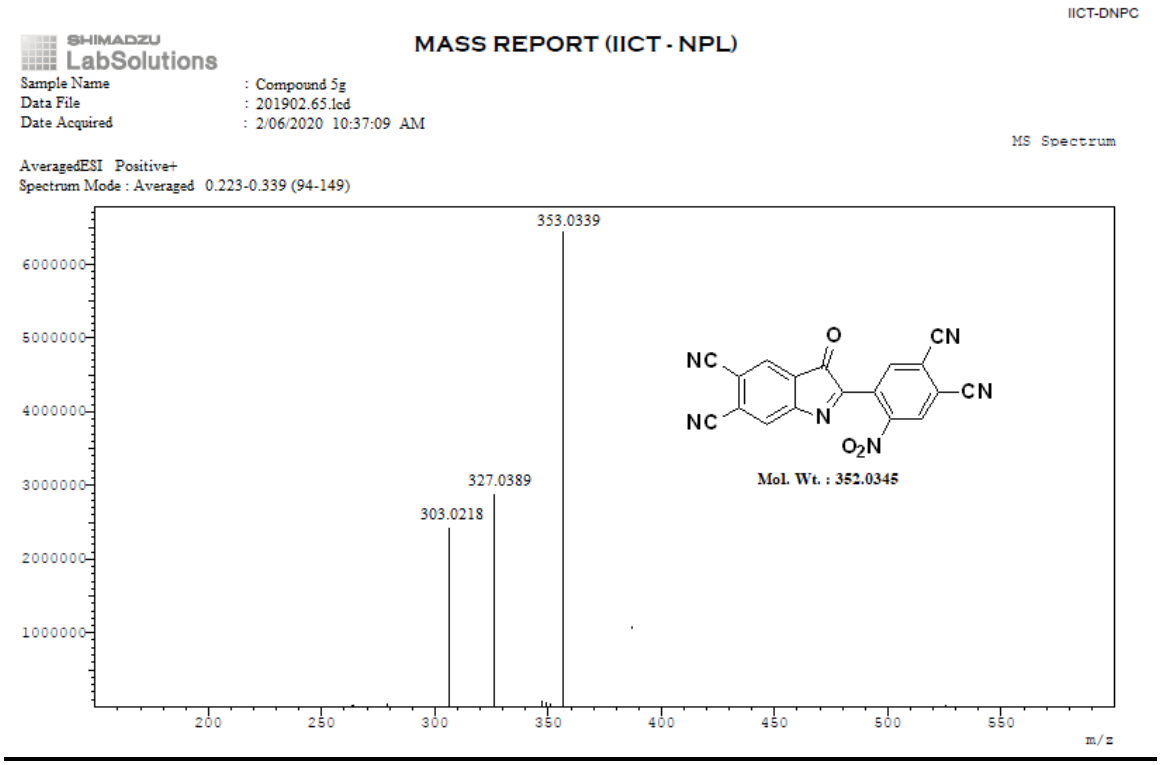

Figure S27. Mass spectrum of compound 2g

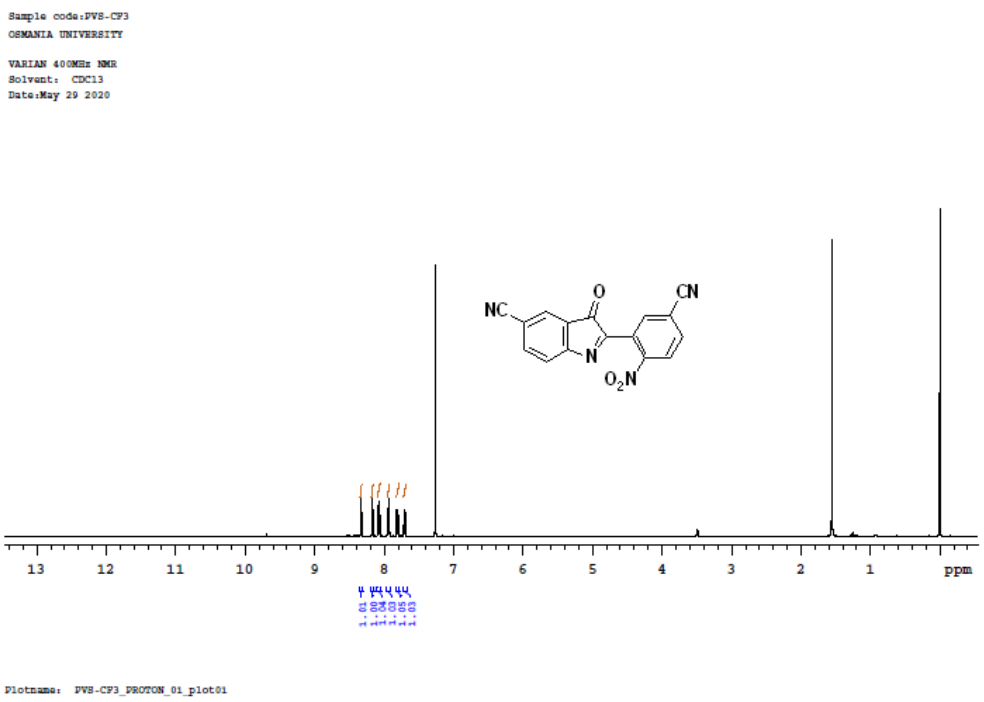

Figure S28. ^{1}H-NMR spectrum of compound 2h

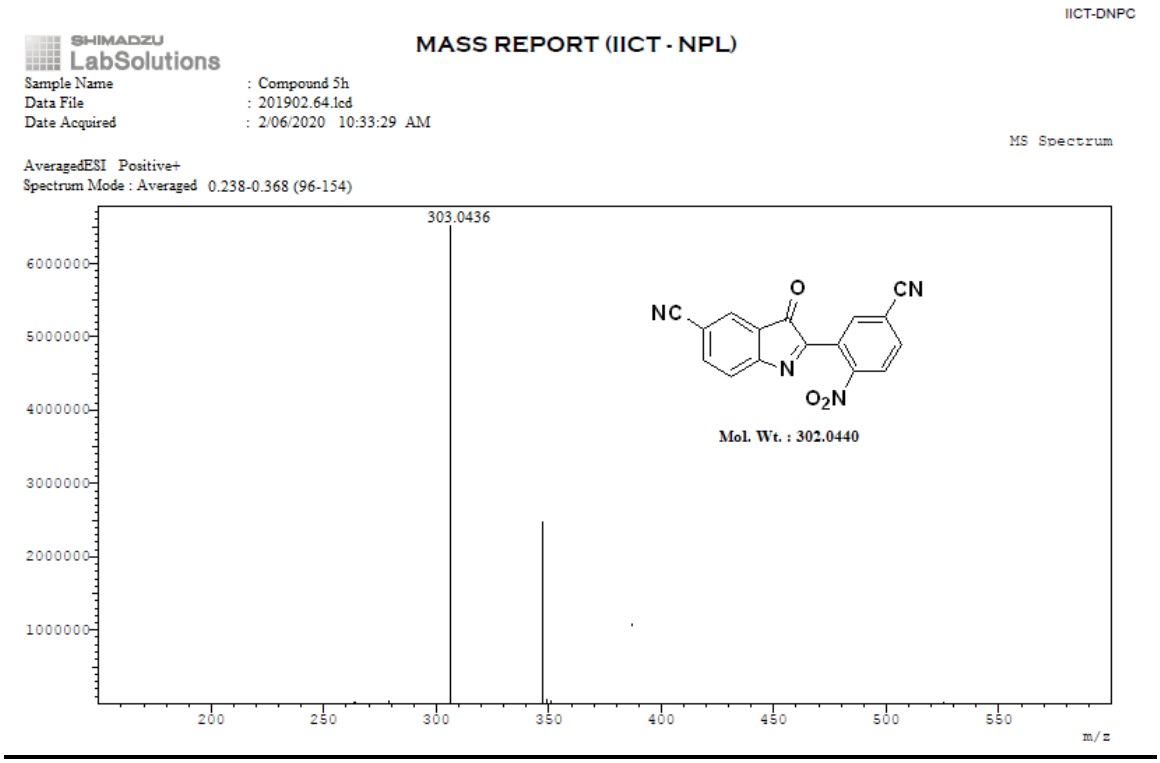

Figure S29. Mass spectrum of compound 2h

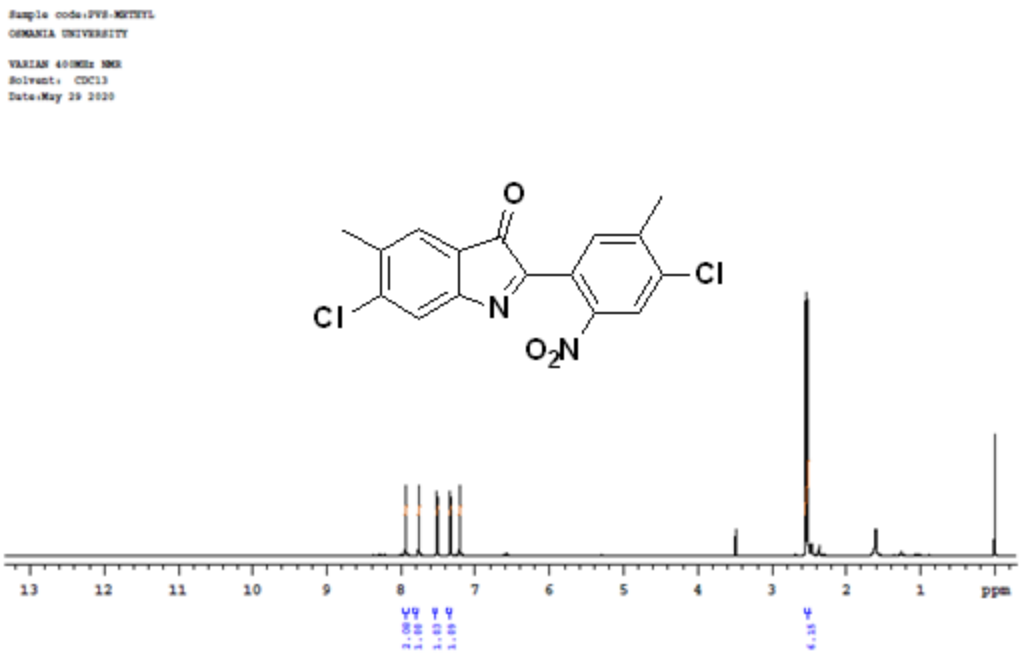

Figure S30. ^{1}H-NMR Spectrum of compound 2i

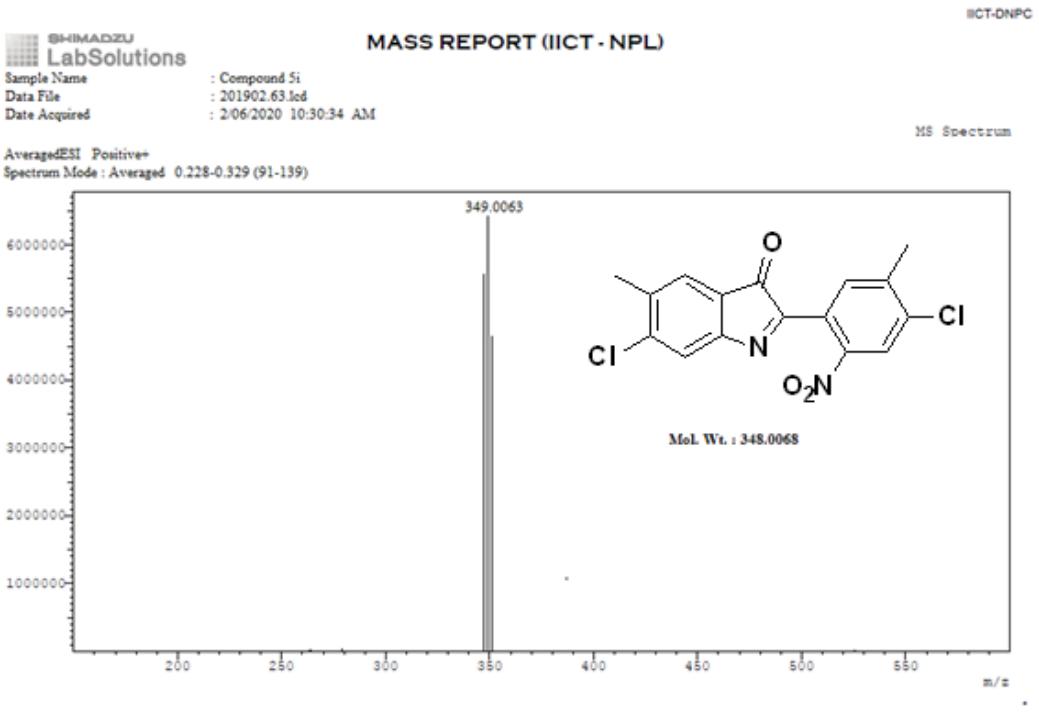

Figure S31. Mass Spectrum of compound 2i

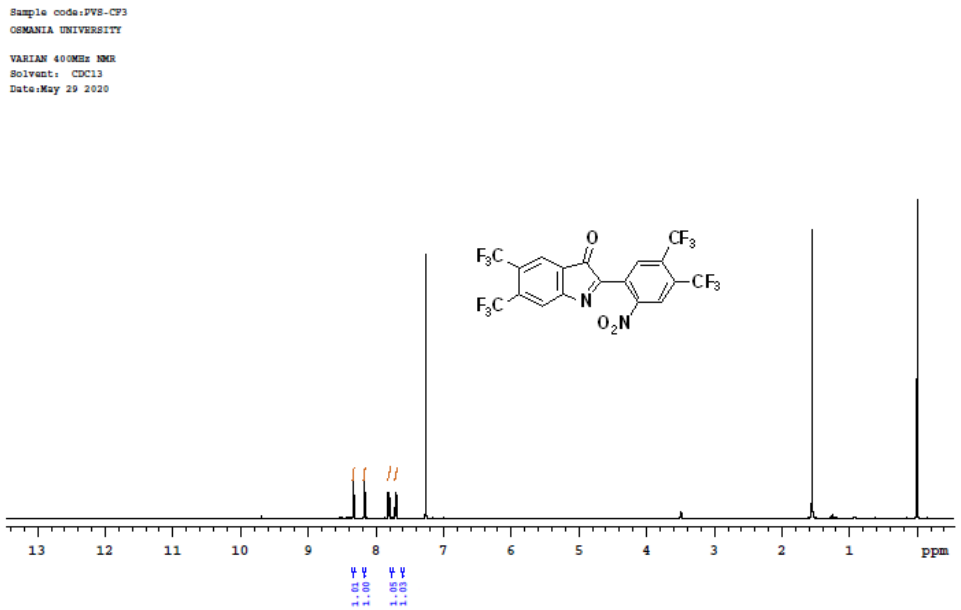

Figure S32. ^{1}H-NMR spectrum of compound 2j

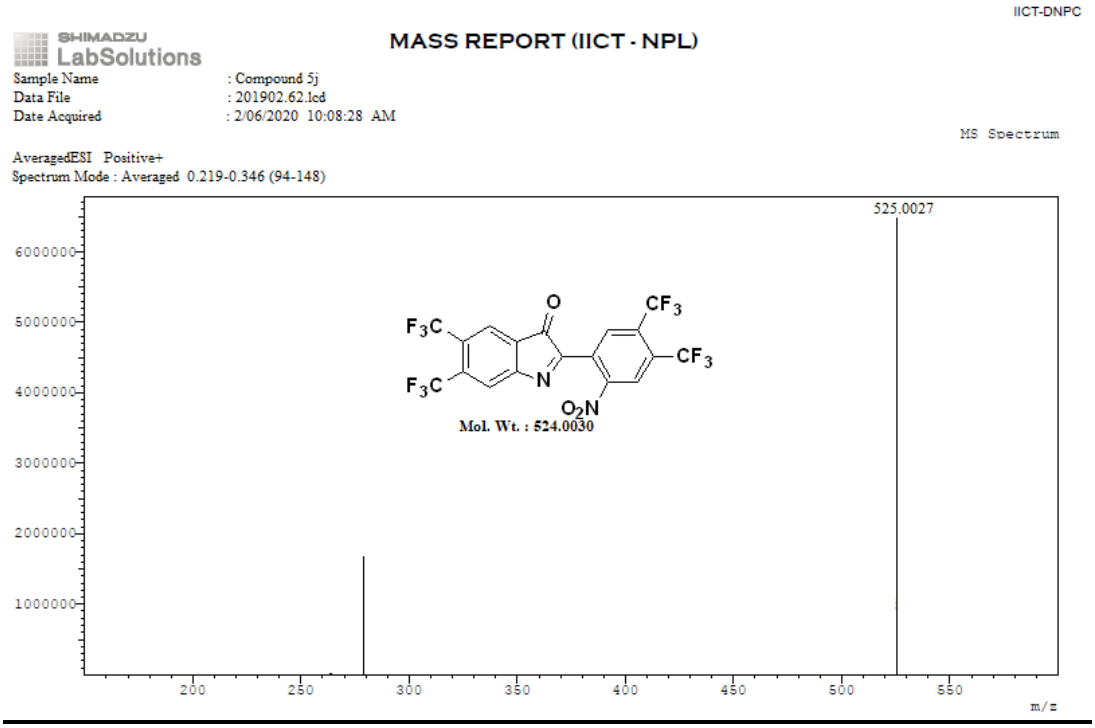

Figure S33. Mass spectrum of compound 2j