Synthesis, photophysical, bioimaging potential and *in vitro toxicity* studies of naphthalimide imidazole boron complexes

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General Information

Vacuum line techniques were used for handlings air and moisture sensitive compounds. All reagents and metal precursors used for the reactions were purchased from spectrochem, Alfa-aesar and Sigma-Aldrich otherwise mentioned. The 2-butyl-6-hydroxy-1,3-dioxo-2,3-dihydro-1H-benzo[de]isoquinoline-5-carbaldehyde was synthesized by adopting the literature procedure. Acetic acid, dichloromethane (DCM), tetrahydrofuran (THF), and toluene were purchased from Spectrochem India. Toluene and THF were distilled from Na/benzophenone prior to use. Chlorinated solvents were distilled from CaH_2. ^{1}H NMR (400 MHz, 700 MHz), ^{13}C NMR (100 MHz, 176 MHz), ^{11}B NMR (128 MHz), ^{19}F NMR (376 MHz) spectra were recorded on a Bruker ARX 400 and 700 spectrometers operating at 400 MHz and 700 MHz respectively. All ^{1}H and ^{13}C NMR spectra were referenced internally to residual solvent signals namely chloroform (δ = 7.26 ^{1}H; δ = 77.16 ^{13}C in ppm), ^{11}B NMR spectra were referenced externally to $BF_3{\cdot}OEt_2$ in $CDCl_3$ (δ= 0), and ^{19}F NMR was recorded with reference to α,α,α-trifluorotoluene. All NMR spectra were recorded at ambient temperature. Chemical shifts in all the NMR spectra are reported in ppm (δ) with the multiplicities represented by singlet (s), doublet (d), triplet (t), quartet (q), muliplet (m), doublet of doublet (dd) and broad (br). Coupling constants (*J*) are reported in Hertz. Melting points for the solid compounds were measured on a Fischer John's melting point apparatus and mentioned as obtained. ESI-MS spectra were obtained from Bruker, microTOF-QII mass spectrometer. Elemental analyses were performed in a Euro Vector EA 3000 CHNS analyzer. Distilled and degassed solvents used for photo physical properties. UV-Visible spectral measurements were performed using Jasco Lambda 750 UV/Visible spectrometer. All the fluorescence spectral measurements, absolute fluorescence quantum yields in solution and solid-state were performed with Edinburg

fluorescence FS5 spectrophotometer and the instrumental response corrected for each experiment. Integrating sphere method was used for calculating the quantum yields.

Single crystal X-ray diffraction data were collected on Rigaku diffractometer at 293 K, 293 K and 130 K for complexes **1-3** respectively using Cu-Kα radiation (λ = 1.54184). SHELXT program was used for solving the crystal structures and simultaneous refinement was done[1] with least-squares minimization using SHELXL incorporated in Olex2[2]. In order to refine non-hydrogen atoms anisotropic displacement coefficients were used and the hydrogen atoms were placed at calculated positions and were refined as riding atoms. CCDC number 2267326-2267328.

Stock solution preparation: 3.82 mg of the compound was dissolved in 250 microlitres of DMSO to make a stock solution of 25 mM. 1 microlitre of this stock solution was diluted with 999 microlitres of DMEM (Cell culture medium) to yield a working concentration of 25 micromolar. 100 microlitre of this working concentration solution was added to each well for 25 micromolar concentration treatment so that the final DMSO concentration was 0.1%. Similarly, for the control well, 1 microlitre of DMSO was diluted with 999 microlitres of DMEM, and 100 microlitres of this solution were added to each well of the vehicle-treated lane so that the final DMSO concentration was 0.1%.

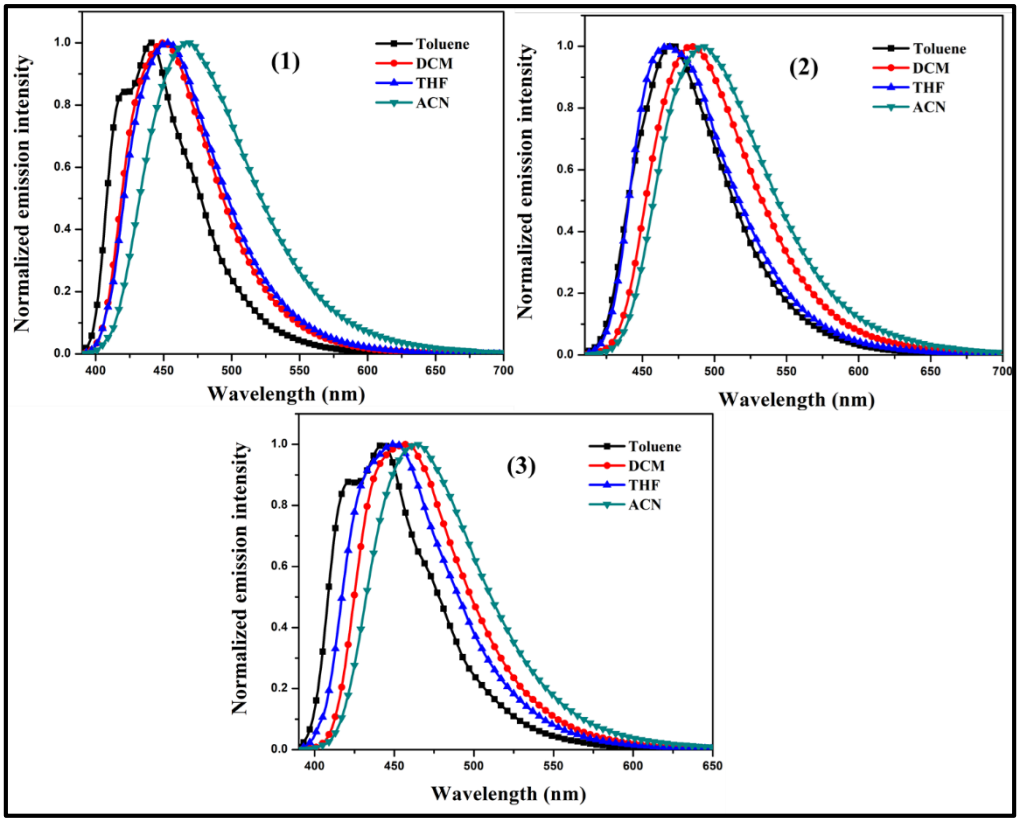
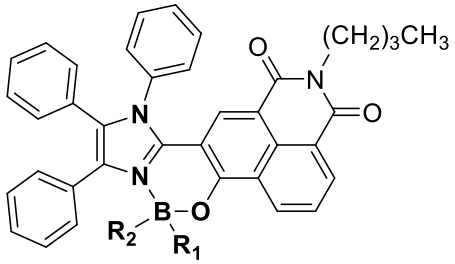


Figure S1: Normalized fluorescence spectra of the boron complexes **1-3** with increasing solvent polarity at concentration of 20 µM.

Table S1: Crystallographic information and refinement parameters for complexes **1-3**

Crystal data and structure refinement parameters			
	1	**2**	**3**
Empirical formula	$C_{37}H_{28}BF_2N_3O_3.CHCl_3$	$C_{49}H_{38}BN_3O_3.(CHCl_3)_2$	$C_{49}H_{28}BF_{10}N_3O_3.(CHCl_3)_2$
Formula weight	730.80	966.37	1146.29
Temperature/K	293(2)	293(2)	130(20)
crystal system	Triclinic	Triclinic	Triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a [*Å*]	11.5584(4)	10.7782(2)	10.8114(3)
b [*Å*]	12.9493(5)	11.7248(2)	12.1669(3)
c [*Å*]	13.6334(5)	20.6634(2)	20.5830(4)
α[˚]	100.768(3)	84.1410(10)	84.284(2)
β[˚]	97.117(3)	86.9470(10)	86.457(2)
γ[˚]	113.238(3)	65.911(2)	63.952(3)
Volume /Å^3	1797.32(12)	2371.22(7)	2419.91(12)
Z	2	2	2
ρ_{calc}[g cm^{-3}]	1.350	1.353	1.573
μ (CuK$_\alpha$) [mm^{-1}]	2.740	3.671	4.008
F (000)	752.0	996.0	1156.0
Crystal size [mm]^3	0.15 × 0.13 × 0.09	0.16 × 0.13 × 0.11	0.15 × 0.12 × 0.11
θ range [º]	3.382- 65.0	4.146-68.244	4.057-66.987
Index ranges	-13 ≤ h ≤ 13, -15 ≤ k ≤ 15, -16 ≤ l ≤ 15	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -24 ≤ l ≤ 19	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -24 ≤ l ≤ 18
reflections collected	23597	32740	29208
Independent reflns	6104 [R_{int} = 0.0685]	8654 [R_{int} = 0.0536]	8632 [R_{int} = 0.2132]
data/restraints/parameters	6104/105/491	8654/138/652	8632/63/705
Goodness-of-fit on F^2	1.057	1.090	1.519
Final R indexes [I>=2σ (I)]	R_1 = 0.0648,wR_2 = 0.2024	R_1 = 0.0609,wR_2 = 0.1852	R_1 = 0.1420,wR_2 = 0.3507
R indexes [all data]	R_1 = 0.0721,wR_2 = 0.2099	R_1 = 0.0661,wR_2 = 0.1902	R_1 = 0.1653,wR_2 = 0.3699
Largest diff.peak/hole/e Å^{-3}	0.45/-0.40	0.57/-0.46	1.34/-0.88

Table S2: List of selected bond lengths [Å] and bond angles [°] for complexes **1-3**.



R_1 =F_1 or C_1

R_2 =F_2 or C_2

	1		**2**		**3**
Bond lengths [Å]					
B-F_1	1.369 (3)	B-O	1.513 (3)	B-O	1.482(6)
B-F_2	1.369 (3)	B-N	1.608 (3)	B-N	1.577 (5)
B-O	1.449 (3)	B-C_1	1.609(3)	B-C_1	1.639 (7)
B-N	1.571 (2)	B-C_2	1.614 (3)	B-C_2	1.636 (7)
Bond angles [°]					
F_2-B-F_1	111.5 (2)	C_1-B1-C_2	117.4 (2)	N-B-O	107.4 (3)
O-B-F_1	109.2 (2)	O-B-C_2	108.9 (2)	C_1-B-C_2	116.4 (3)
O-B-F_2	109.9(2)	O-B-C_1	106.1 (2)	O-B-C_2	105.2 (4)
N-B-F_1	108.9 (2)	N-B-C_1	108.9 (2)	O-B-C_1	106.8 (4)
N-B-F_2	109.0 (2)	N-B-C_2	110.1 (2)	N-B-C_1	112.6 (4)
N-B-O	108.5 (2)	O-B-N	104.4 (2)	N-B-C_2	107.8 (3)

Table S3. Photophysical data for imidazole boron complexes **1-3** and **L**.

	Solvent	λ_{max}[a] (nm)	ε_{max} ($M^{-1}cm^{-1}$ X 10^3)	λ_{em}[a,b] (nm)	Φ_F[c] (%)	Stokes shift (cm^{-1})
1	Toluene	321, 367	45.2, 14.7	421, 441	45	4572
	CH_2Cl_2	319, 365	46.2, 14.8	450	56	5175
	THF	319, 364	46.1, 14.6	453	65	5397
	CH_3CN	315, 362	49.4, 13.3	468	66	6256
	TLF	319, 365		502	37	7476
2	Toluene	325, 364	42.2, 9.7	471	64	6241
	CH_2Cl_2	325, 375	45.2, 16.2	485	87	6048
	THF	323, 372	42.0, 13.3	472	86	5695
	CH_3CN	321, 369	41.5, 9.7	495	78	6898
	TLF	325, 356, 375		493	58	6383
3	Toluene	322, 371	42.1, 14.4	428, 448	31	4633
	CH_2Cl_2	322, 371	42.6, 14.3	458	56	5120
	THF	320, 369	44.9, 14.7	455	43	5122
	CH_3CN	319, 369	44.3, 13.4	467	69	5687
	TLF	322, 371		454	31	4928
L	Toluene	325, 393	34.9, 5.5	472	24	4259
	CH_2Cl_2	325, 395	41.5, 7.9	495	47	5114
	THF	323, 390	36.29, 5.5	496	35	5480
	CH_3CN	321,391	53.0, 5.3	512	47	6044

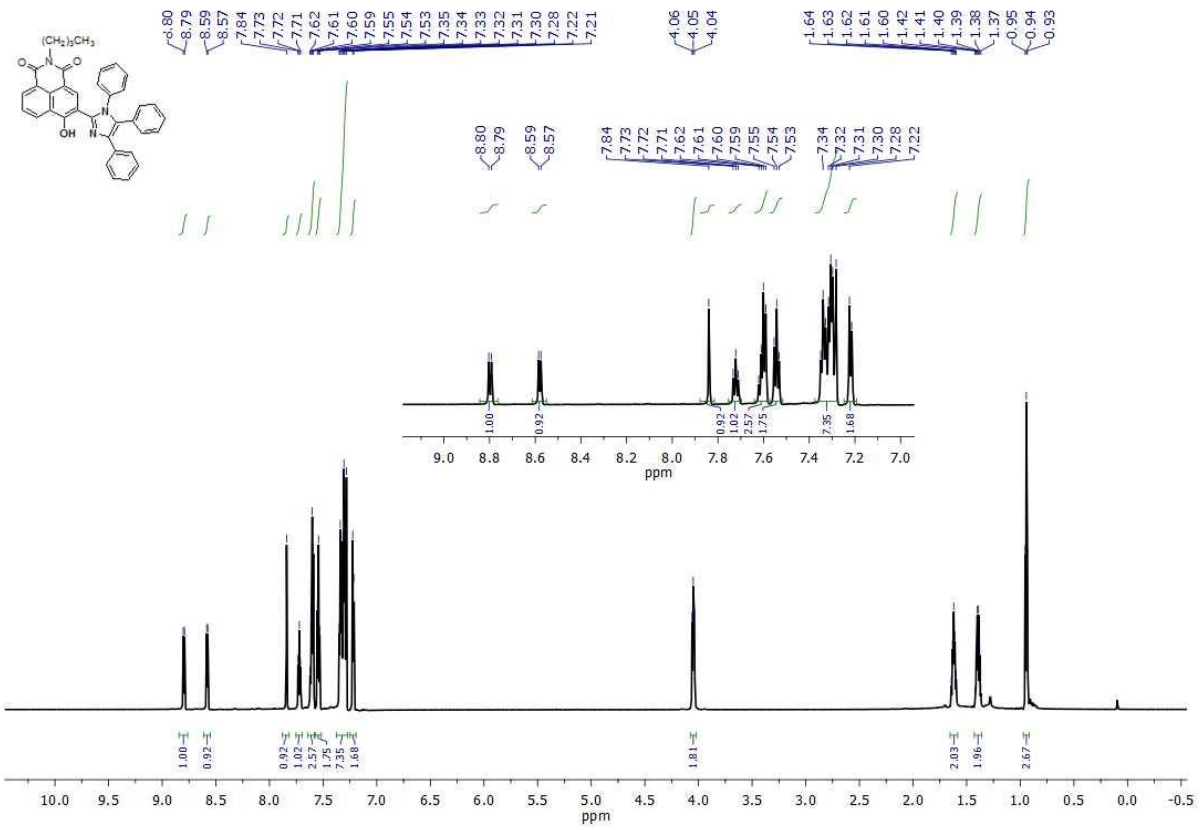


Figure S2: ^{1}H NMR spectrum of ligand (**L**)

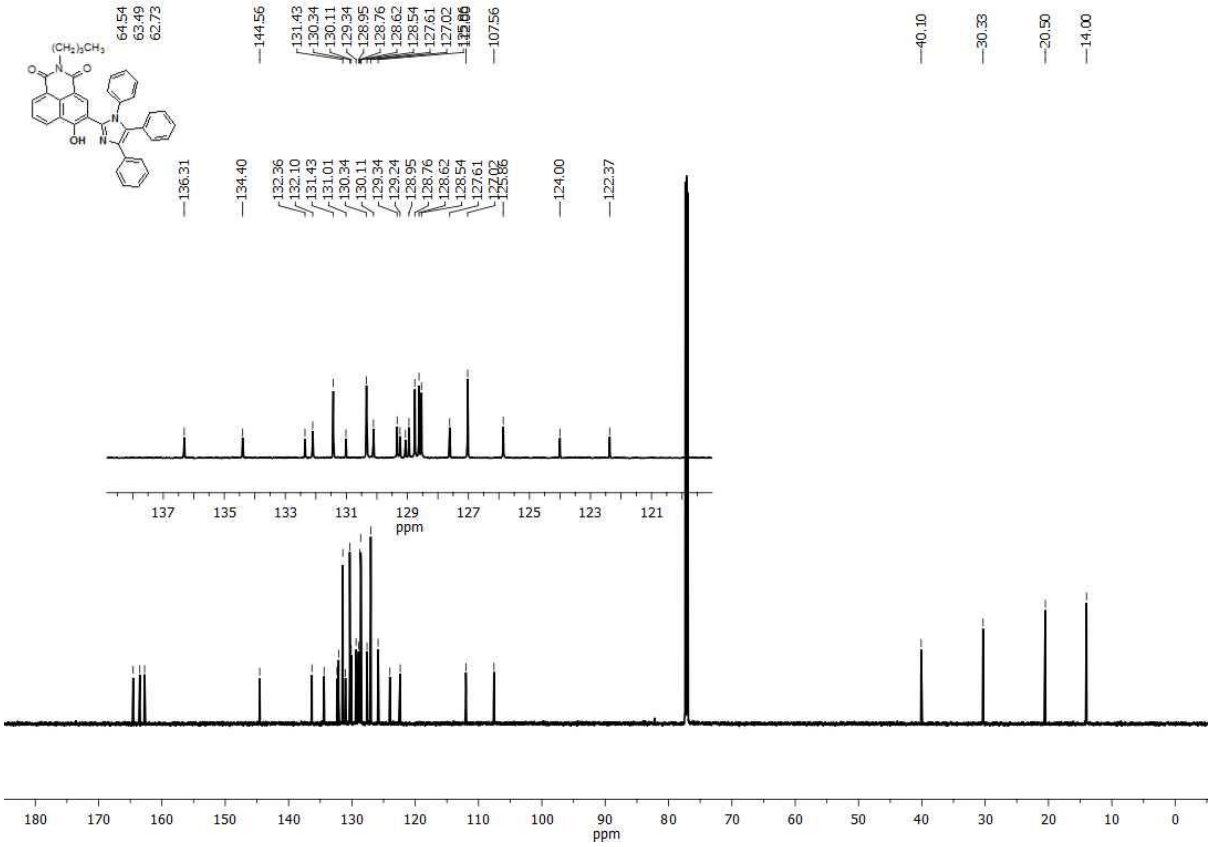


Figure S3: ^{13}C NMR spectrum of ligand (**L**)

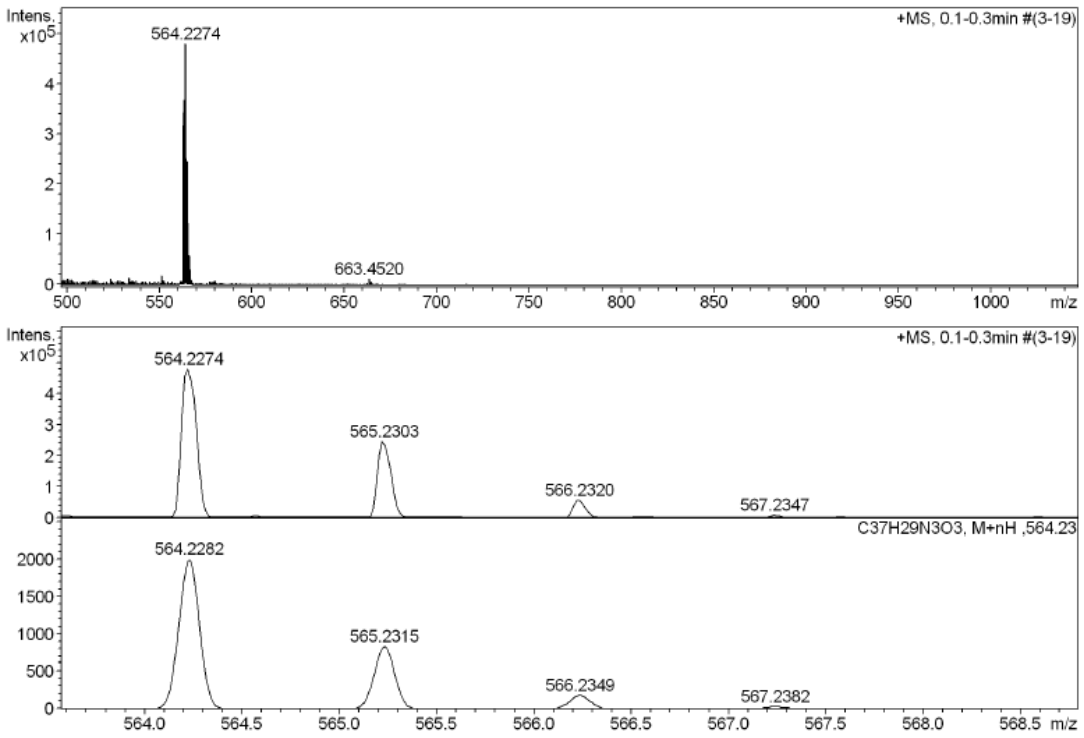


Figure S4: HR-MS of ligand (**L**)

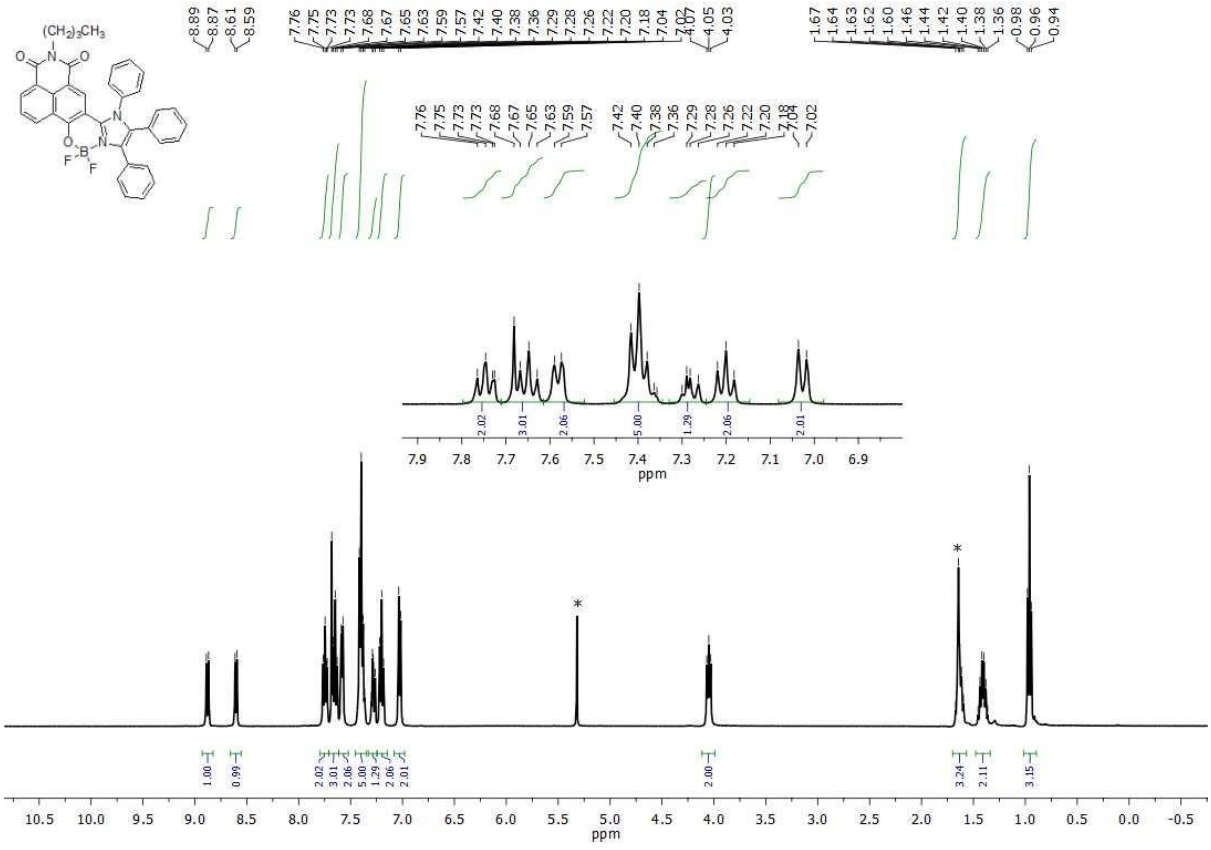


Figure S5: ^{1}H NMR spectrum of complex **1**

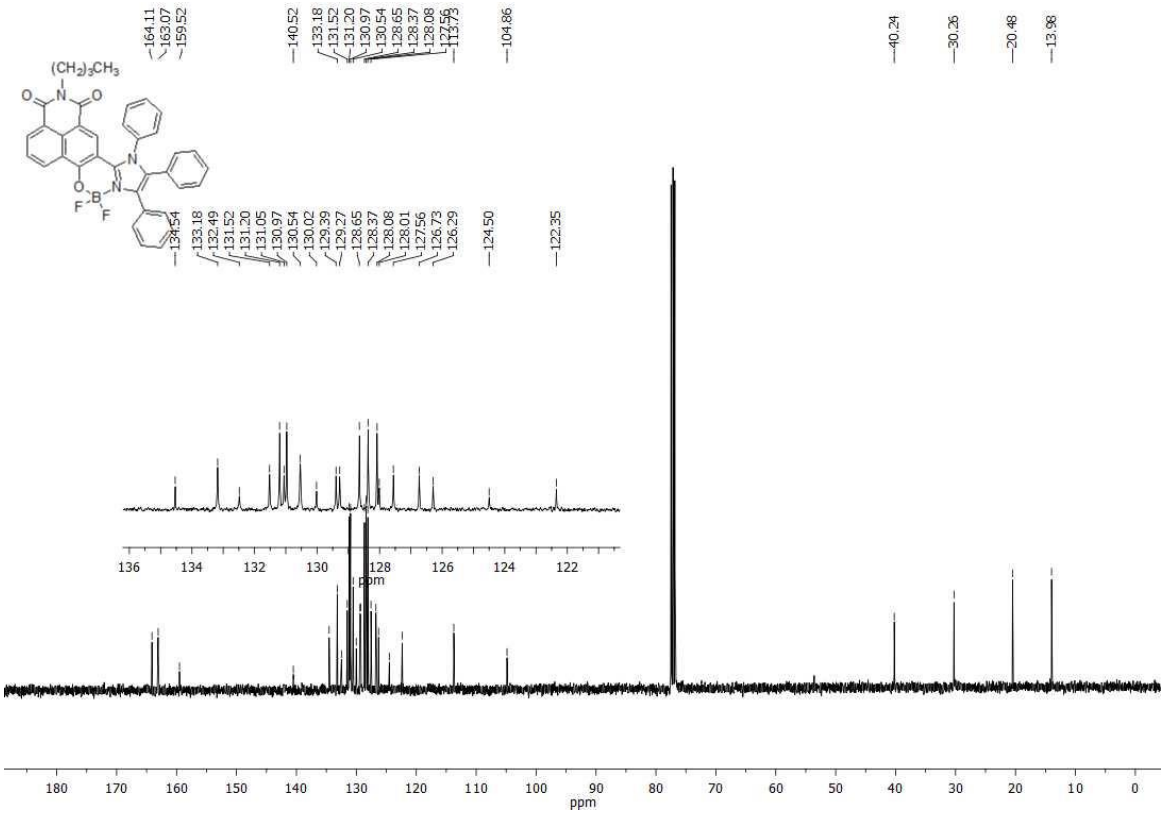


Figure S6: ^{13}C NMR spectrum of complex **1**

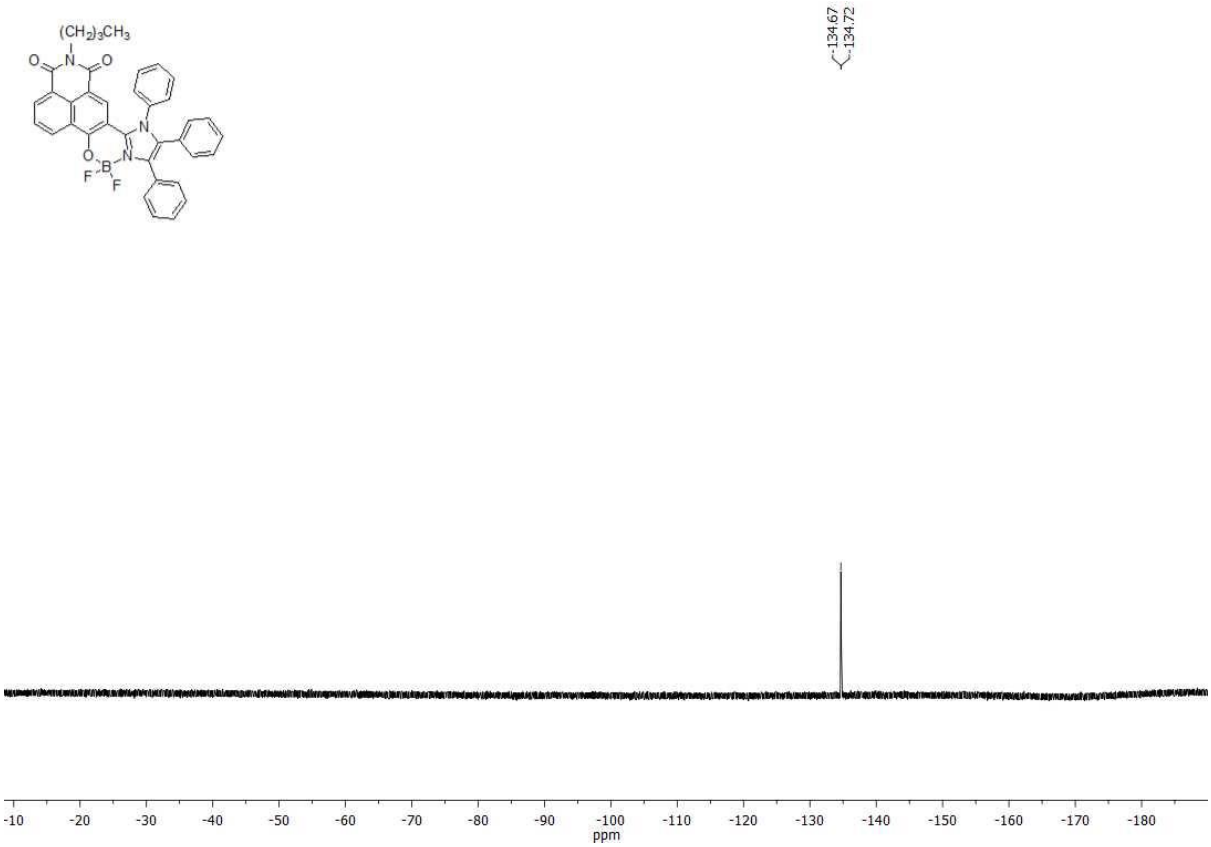


Figure S7: ^{19}F NMR spectrum complex **1**

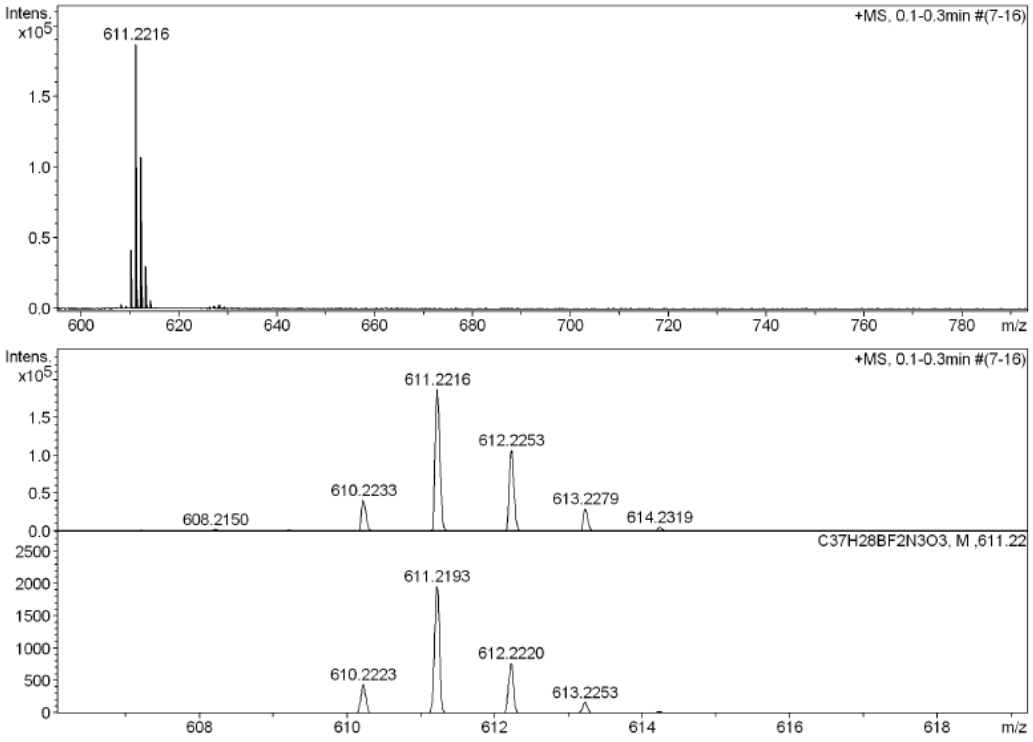


Figure S8: HR-MS of complex **1**

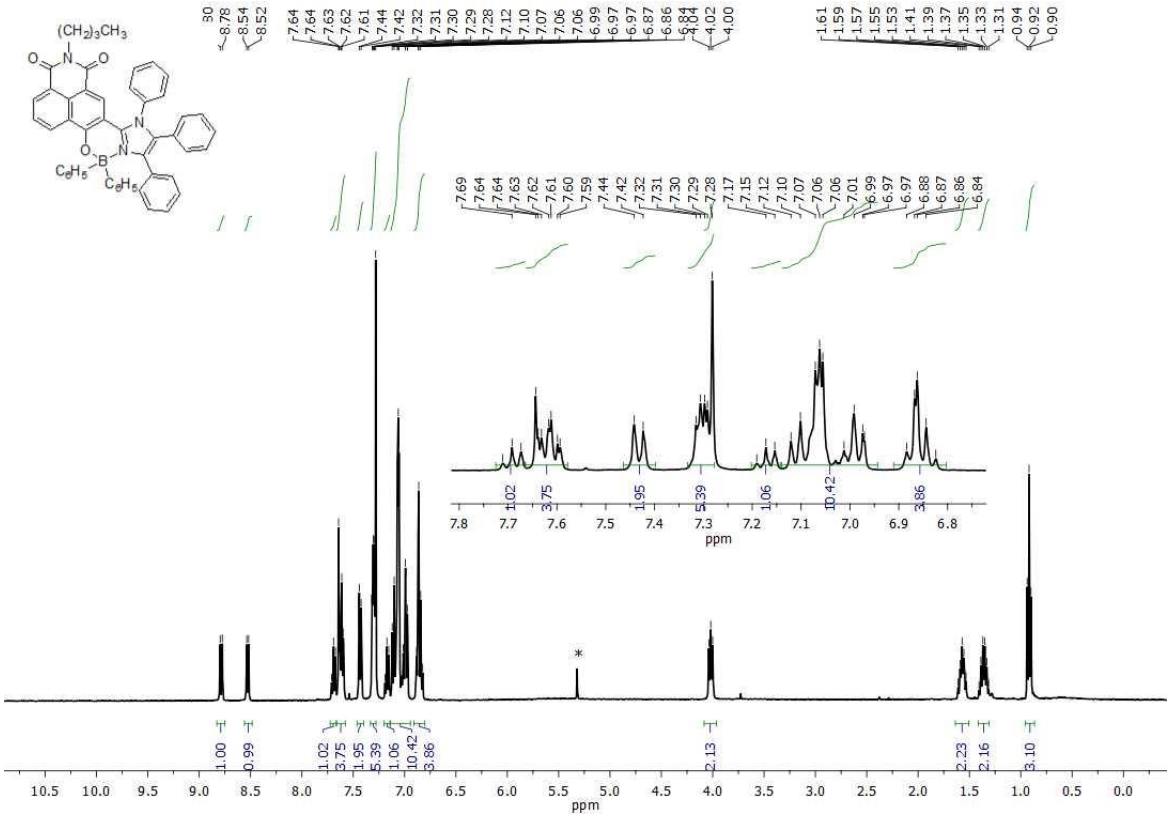


Figure S9: ^{1}H NMR spectrum of complex **2**

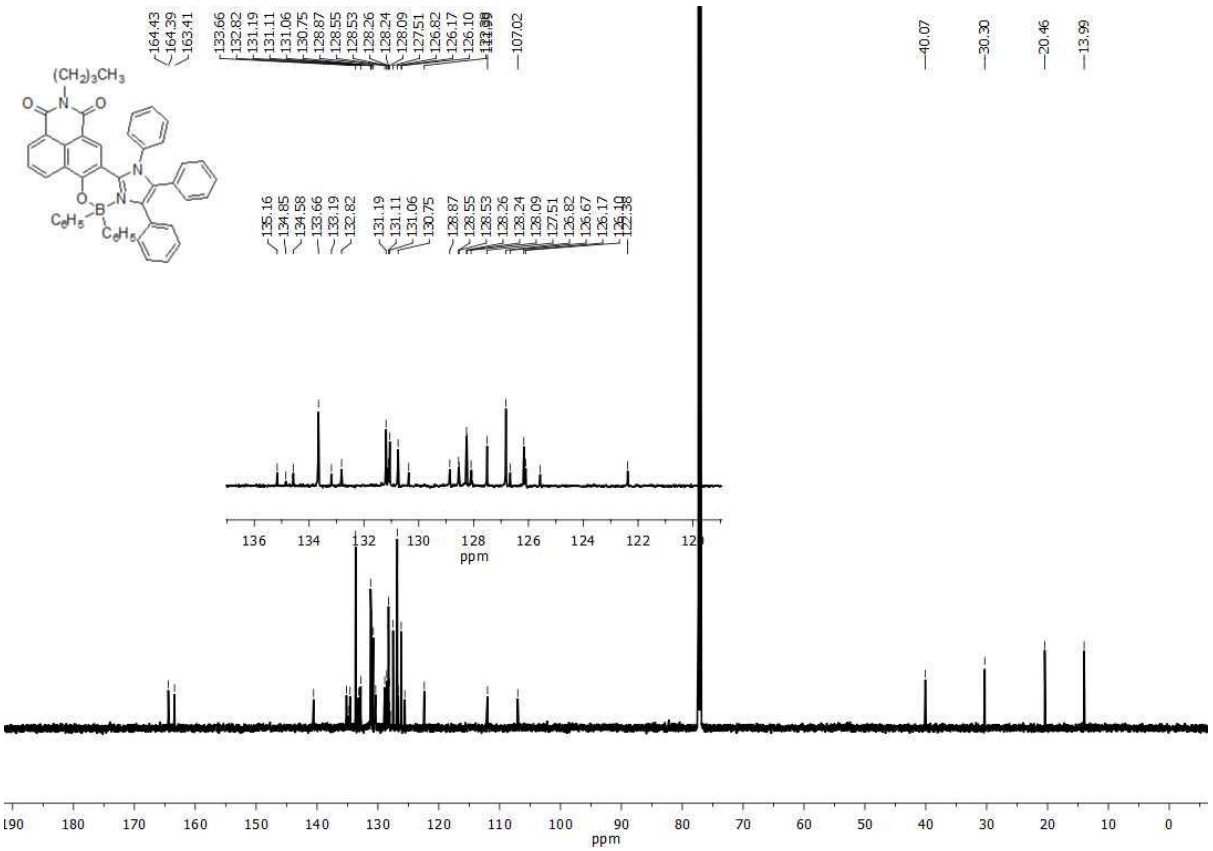


Figure S10: ^{13}C NMR spectrum of complex **2**

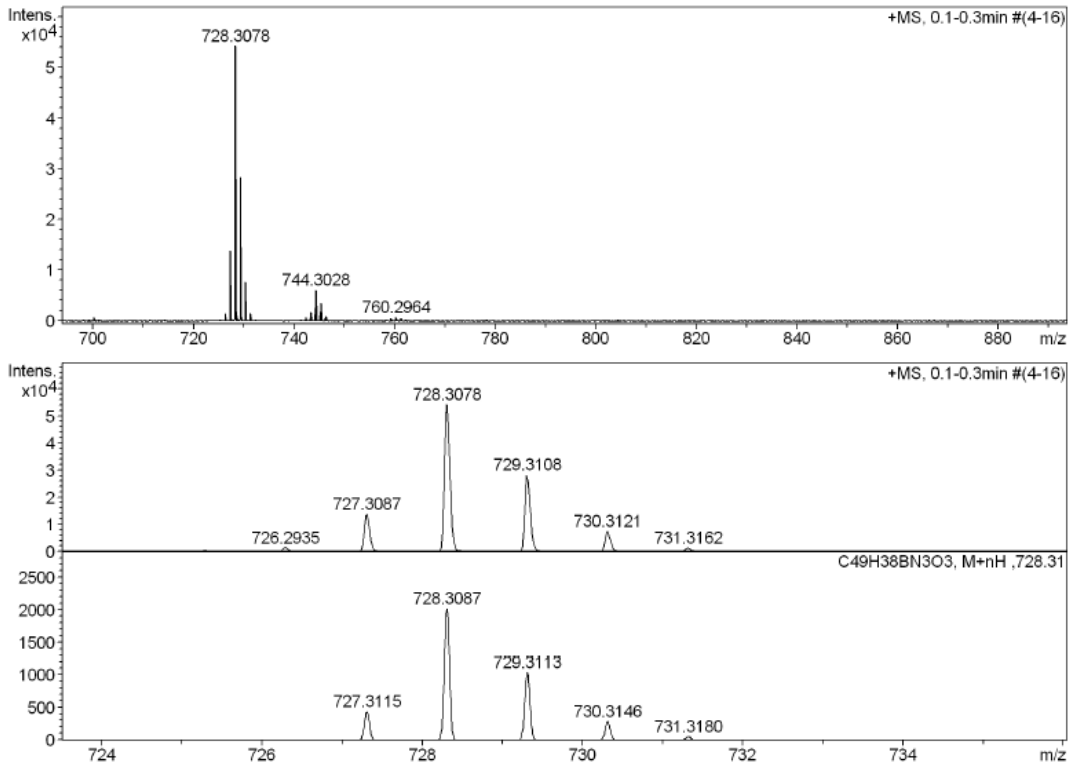


Figure S11: HR-MS of complex **2**

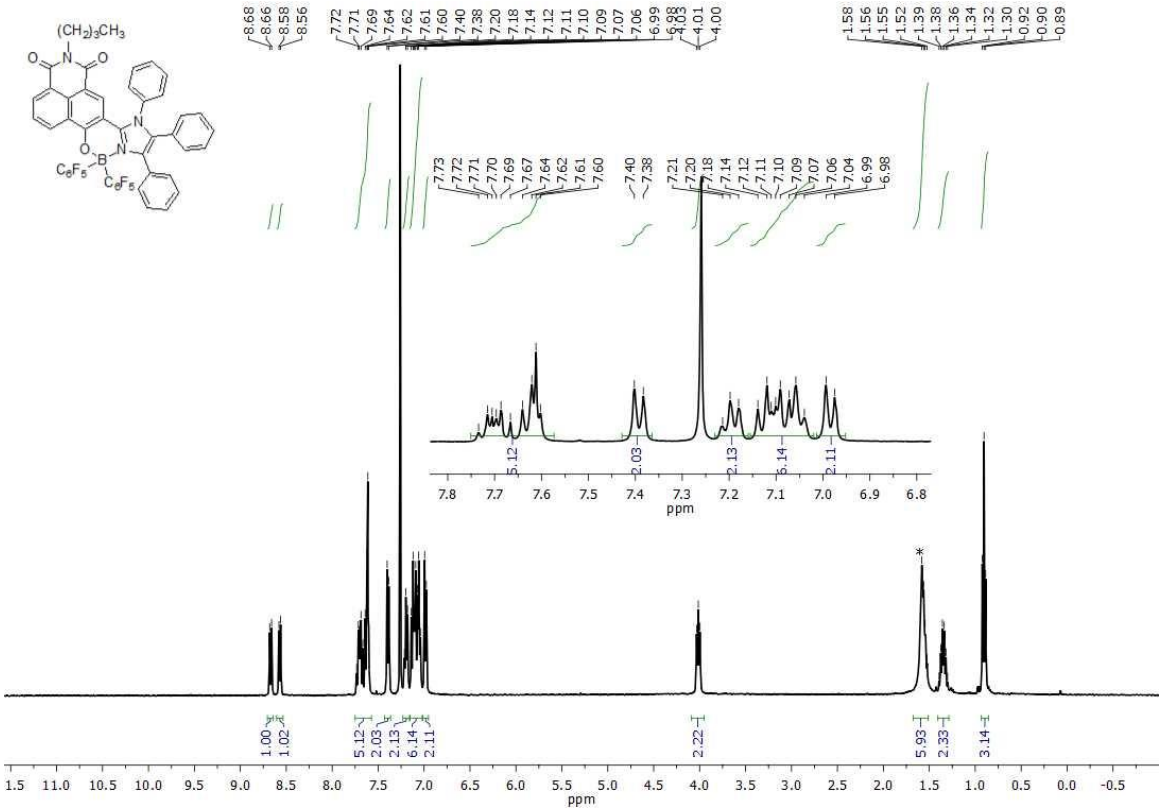


Figure S12: ^{1}H NMR spectrum of complex **3**

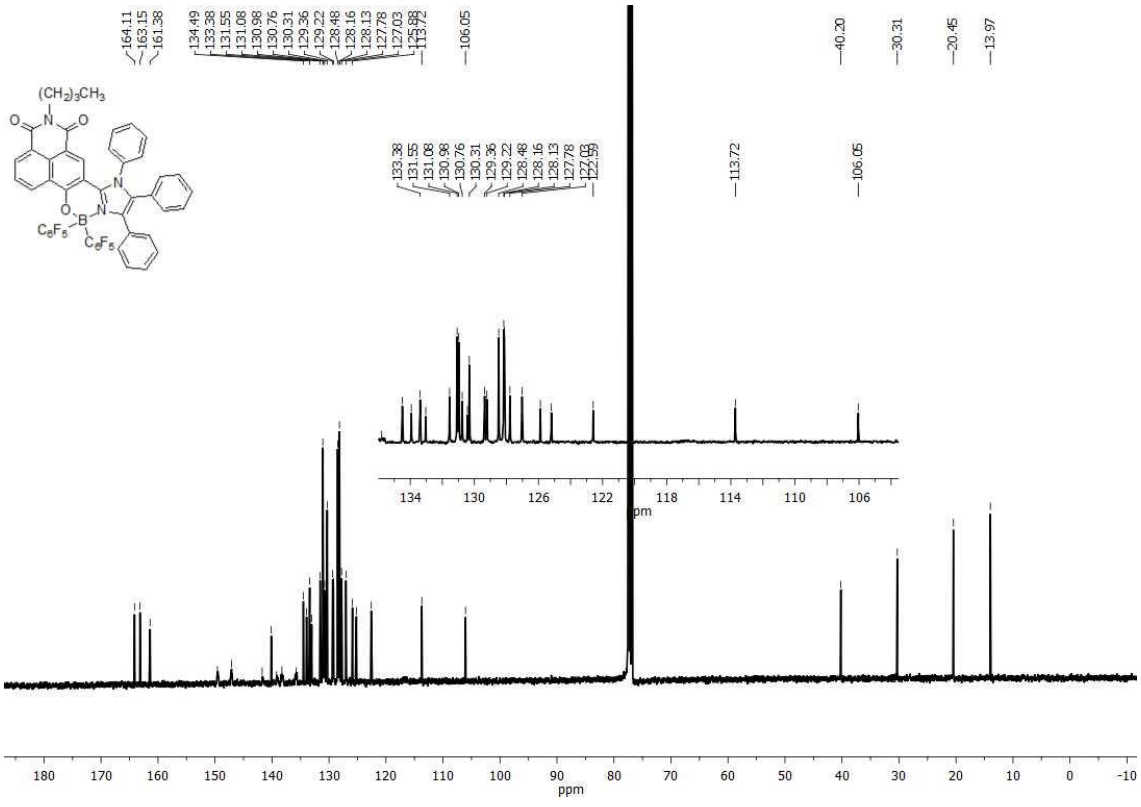


Figure S13: ^{13}C NMR spectrum of complex **3**

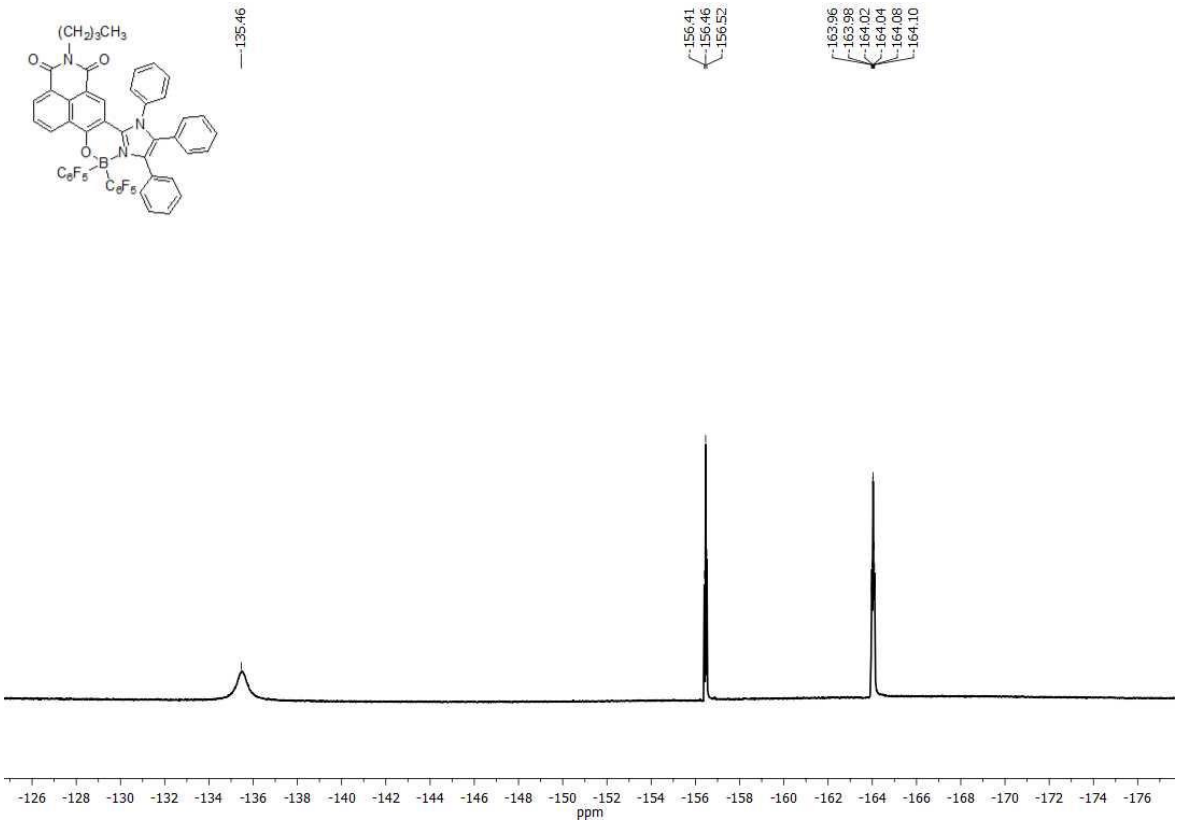


Figure S14: ^{19}F NMR spectrum of complex **3**

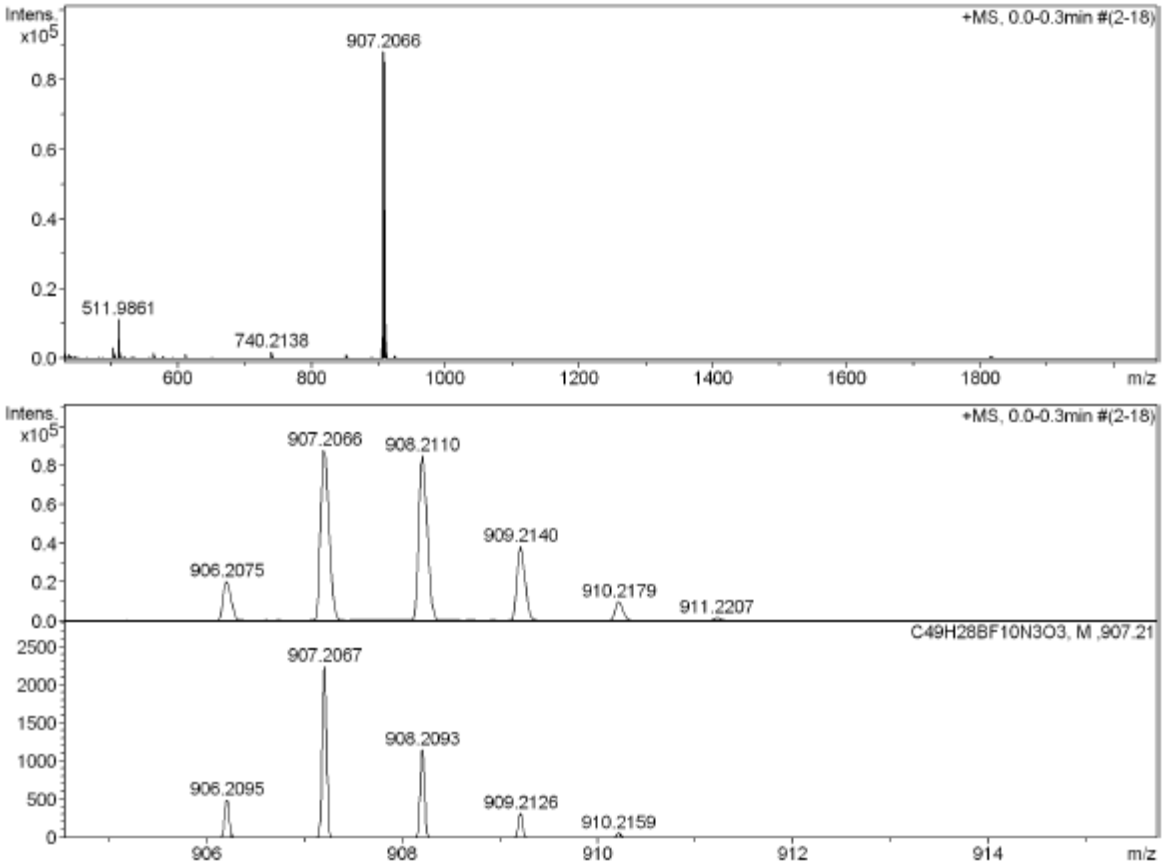


Figure S15: HR-MS of complex **3**

References:

(1) Sheldrick, G. M. *Acta Crystallogr. Sect. A: Found. Crystallogr*. **2008**, *64*, 112.
(2) Allen, A. J.; Hajdu, J.; McIntyre, G. J. *J. Appl. Crystallogr.* **2018**, *51*, 233.