Supporting Information for

9-Borafluoren-9-yl and diphenylboron tetracoordinate complexes of F- and Cl-substituted 8-quinolinolato ligands: synthesis, molecular and electronic structures, fluorescence and application in OLED devices

Carina B. Fialho,[a] Tiago F. C. Cruz,[a] Ana I. Rodrigues,[a] Maria José Calhorda,[b] Luís F. Vieira Ferreira,[c] Piotr Pander,[d,e,f] Fernando B. Dias,[f] Jorge Morgado,[g,h] António L. Maçanita,[a] Pedro T. Gomes*[a]

[a] *Centro de Química Estrutural, Departamento de Engenharia Química, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.*
E-mail: pedro.t.gomes@tecnico.ulisboa.pt

[b] *BioISI – Instituto de Biossistemas e Ciências Integrativas, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.*

[c] *BSIRG – Biospectroscopy and Interfaces Research Group, IBB-Institute for Bioengineering and Biosciences, Instituto SuperiorTécnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal*

[d] *Faculty of Chemistry, Silesian University of Technology, Strzody 9, 44-100 Gliwice, Poland*

[e] *Centre for Organic and Nanohybrid Electronics, Silesian University of Technology, Konarskiego 22B, 44-100 Gliwice, Poland*

[f] *Department of Physics, Durham University, South Road, Durham DH1 3LE, U.K.*

[g] *Instituto de Telecomunicações, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.*

[h] *Department of Bioengineering, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal.*

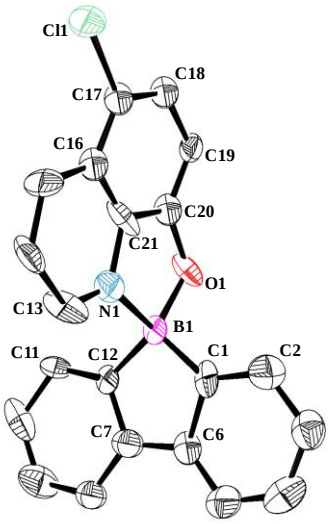
Table of Contents

Crystallographic and molecular structure data of boron complexes 3b, 3c, 3d, 4b and 4d

Table S1 Crystallographic data for boron complexes **3b**, **3c**, **3d, 4b** and **4d**.

	3b	**3c**	**3d**	**4b**	**4d**
Formula	$C_{42}H_{26}B_2F_2N_2O_2$	$C_{21}H_{13}BClNO$	$C_{21}H_{12}BCl_2NO$	$C_{42}H_{30}B_2FN_2O_3$	$C_{21}H_{14}BCl_2NO$
M (g mol^{-1})	650.27	341.58	376.03	651.30	378.04
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
T (K)	150(2)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/n$
a (Å)	11.2348(6)	15.228(16)	9.903(2)	10.8807(6)	8.9037(7)
b (Å)	14.9120(8)	7.863(8)	13.273(2)	28.8313(15)	17.9932(13)
c (Å)	18.6487(10)	13.804(14)	13.425(3)	11.2931(6)	11.0787(8)
α (º)	90	90	90	90	90
β (º)	92.236(2)	96.17(3)	103.851(5)	114.236(2)	102.586(4)
γ (º)	90	90	90	90	90
V (Å^3)	3121.9(3)	1643(3)	1713.4(6)	3230.5(3)	1732.2(2)
Z	4	4	4	8	4
ρ_{calc} (g cm^{-3})	1.384	1.381	1.458	1.339	1.450
Crystal size (mm)	0.10×0.08×0.08	0.20×0.15×0.15	0.20×0.10×0.10	0.12×0.10×0.07	0.10×0.10×0.05
θ_{max} (º)	30.173	25.721	25.821	27.269	25.791
Total data	187527	3366	7789	198612	9992
Unique data	9198	2040	3145	7197	3247
R_{int}	0.2476	0.1729	0.0566	0.084	0.0468
R [I > 2σ(I)]	0.1694	0.0854	0.0466	0.0606	0.0385
wR	0.2149	0.1361	0.0744	0.0730	0.0671
Goodness of fit	1.149	0.797	0.921	1.122	0.863
ρ_{min}, ρ_{max}	-0.433, 1.084	-0.261, 0.251	-0.284, 0.263	-0.274, 0.741	-0.256, 0.217

X-ray diffraction structures of complexes 3c



3c

Figure S1 Perspective views of the molecular structures of complex **3c**. The calculated hydrogen atoms were omitted for clarity and the ellipsoids were drawn at the 50% probability level.

Selected bond lengths and angles for complexes 3b, 3c, 3d, 4b and 4d

Table S2 Selected experimental and calculated (DFT) bond lengths (Å) and angles (º) for complexes **3b**, **3c** and **3d**. Atoms X1/X2 refer to the halogen atoms in 5 and 7 positions of the 8-hydroxyquinolinate, respectively.

	3b (molecule 1)	**3b** (molecule 2)	**3b** (DFT)	**3c**	**3d**	**3d** (DFT)
Lengths (Å)						
B(1)-O(1)	1.557(8)	1.517(7)	1.513	1.526(12)	1.527(4)	1.518
B(1)-C(12)	1.615(8)	1.605(8)	1.612	1.654(14)	1.599(4)	1.608
B(1)-C(1)	1.570(9)	1.611(8)	1.612	1.600(16)	1.606(4)	1.609
B(1)-N(1)	1.592(8)	1.611(7)	1.612	1.608(13)	1.613(4)	1.609
C(1)-C(2)	1.390(9)	1.395(8)	1.387	1.380(13)	1.385(4)	1.386
C(1)-C(6)	1.392(9)	1.407(8)	1.407	1.439(12)	1.402(4)	1.407
C(6)-C(7)	1.488(8)	1.483(8)	1.476	1.458(14)	1.480(4)	1.476
C(7)-C(12)	1.407(8)	1.416(7)	1.405	1.391(12)	1.403(4)	1.406
C(11)-C(12)	1.377(8)	1.389(8)	1.387	1.385(13)	1.390(4)	1.396
C(13)-N(1)	1.298(7)	1.332(6)	1.320	1.312(11)	1.322(3)	1.320
C(16)-C(21)	1.373(8)	1.394(7)	1.399	1.382(12)	1.395(4)	1.398
C(16)-C(17)	1.366(9)	1.428(9)	1.409	1.441(13)	1.411(4)	1.416
C(17)-C(18)	1.370(8)	1.328(12)	1.367	1.361(13)	1.368(4)	1.372
C(17)-X(1)	1.426(7)	1.351(8)	1.358	1.744(10)	1.726(3)	1.738
C(18)-C(19)	1.404(8)	1.396(12)	1.416	1.419(13)	1.412(4)	1.413
C(19)-C(20)	1.382(7)	1.374(8)	1.374	1.379(12)	1.367(4)	1.376
C(19)-X(2)	-	-	-	-	1.727(3)	1.730
C(20)-O(1)	1.313(7)	1.340(7)	1.334	1.358(11)	1.327(3)	1.323
C(20)-C(21)	1.442(7)	1.395(7)	1.405	1.402(13)	1.400(4)	1.405
C(21)-N(1)	1.364(7)	1.346(6)	1.348	1.388(11)	1.359(3)	1.350
Angles (º)						
O(1)-B(1)-C(12)	113.9(5)	117.7(4)	116.1	119.7(9)	113.1(2)	115.5
O(1)-B(1)-C(1)	113.4(5)	116.6(5)	116.7	114.3(9)	113.2(2)	116.3
C(12)-B(1)-C(1)	102.2(5)	100.9(4)	100.4	101.5(8)	100.8(2)	100.7
O(1)-B(1)-N(1)	98.9(4)	98.8(4)	99.4	99.9(8)	99.3(2)	99.2
C(12)-B(1)-N(1)	113.8(5)	111.2(4)	112.6	108.5(8)	117.1(2)	112.8
C(1)-B(1)-N(1)	115.3(5)	112.0(4)	112.2	113.3(9)	114.1(2)	113.0
C(2)-C(1)-C(6)	118.5(6)	119.1(5)		118.7(10)	118.4(3)	
C(2)-C(1)-B(1)	132.4(6)	132.0(5)		133.6(9)	132.6(3)	
C(6)-C(1)-B(1)	109.0(5)	108.9(5)		107.6(9)	108.9(2)	
C(1)-C(6)-C(7)	110.5(5)	110.5(5)		110.8(9)	110.3(2)	
C(11)-C(12)-C(7)	118.3(5)	119.1(5)		121.6(9)	117.9(3)	
C(11)-C(12)-B(1)	134.9(5)	132.4(5)		131.8(9)	133.2(3)	
C(7)-C(12)-B(1)	106.7(5)	108.5(5)		106.6(9)	108.7(2)	
C(21)-C(16)-C(17)	114.5(6)	113.0(6)		112.7(9)	114.4(2)	
C(18)-C(17)-C(16)	122.3(6)	122.2(7)		120.9(9)	121.5(3)	
C(18)-C(17)-X(1)	120.8(6)	121.9(7)		121.6(8)	119.7(2)	
C(16)-C(17)-X(1)	116.8(5)	115.9(7)		117.6(8)	118.8(2)	
C(17)-C(18)-C(19)	124.0(6)	123.3(6)		124.1(10)	121.3(3)	
C(20)-C(19)-C(18)	115.9(5)	117.6(7)		116.6(10)	119.9(2)	
C(20)-C(19)-X(2)	-	-		-	120.6(2)	
C(18)-C(19)-X(2)	-	-		-	119.4(2)	
O(1)-C(20)-C(19)	129.1(5)	129.7(6)		127.5(10)	130.0(2)	
O(1)-C(20)-C(21)	113.1(5)	112.0(4)		114.2(8)	113.2(2)	
C(19)-C(20)-C(21)	117.8(5)	118.3(6)		118.1(9)	116.8(2)	
N(1)-C(21)-C(16)	126.0(5)	123.7(5)		124.1(9)	123.8(2)	
N(1)-C(21)-C(20)	108.5(5)	110.8(5)		108.5(9)	110.1(2)	
C(16)-C(21)-C(20)	125.5(5)	125.4(5)		127.5(9)	126.1(2)	
C(13)-N(1)-C(21)	119.7(5)	119.5(5)		117.8(9)	119.3(2)	
C(13)-N(1)-B(1)	130.7(5)	132.6(4)		133.7(9)	133.3(2)	
C(21)-N(1)-B(1)	109.5(5)	107.9(4)		108.4(8)	107.4(2)	
C(20)-O(1)-B(1)	110.0(4)	110.5(4)		108.9(7)	109.7(2)	

Table S3 Selected experimental and calculated (DFT) bond lengths (Å) and angles (º) for complexes **4b** and **4d**. Atoms X1/X2 refer to the halogen atoms in 5 and 7 positions of the 8-hydroxyquinolinate.

	4b (molecule 1)	**4b** (molecule 2)	**4d**	**4d** (DFT)
Lengths (Å)				
B(1)-O(1)	1.538(3)	1.530(3)	1.544(3)	1.532
B(1)-C(12)	1.619(3)	1.606(3)	1.595(4)	1.609
B(1)-C(1)	1.599(3)	1.612(3)	1.597(4)	1.607
B(1)-N(1)	1.628(3)	1.631(3)	1.623(3)	1.623
C(1)-C(2)	1.401(3)	1.399(3)	1.393(3)	1.397
C(1)-C(6)	1.402(3)	1.403(3)	1.396(3)	1.399
C(7)-C(12)	1.396(3)	1.401(3)	1.399(3)	1.399
C(11)-C(12)	1.395(3)	1.402(3)	1.397(3)	1.398
C(13)-N(1)	1.320(3)	1.324(3)	1.319(3)	1.320
C(16)-C(21)	1.400(3)	1.398(3)	1.396(3)	1.399
C(16)-C(17)	1.399(3)	1.415(3)	1.418(3)	1.416
C(17)-C(18)	1.366(3)	1.358(4)	1.368(3)	1.373
C(17)-X(1)	1.367(3)	1.363(3)	1.732(2)	1.738
C(18)-C(19)	1.420(3)	1.420(3)	1.407(3)	1.412
C(19)-C(20)	1.372(3)	1.377(3)	1.372(3)	1.377
C(19)-X(2)	-	-	1.726(2)	1.731
C(20)-O(1)	1.330(3)	1.340(2)	1.326(3)	1.320
C(20)-C(21)	1.420(3)	1.412(3)	1.402(3)	1.406
C(21)-N(1)	1.350(3)	1.353(2)	1.356(3)	1.349
Angles (º)				
O(1)-B(1)-C(12)	107.96(16)	111.12(16)	108.9(2)	110.8
O(1)-B(1)-C(1)	111.32(16)	110.29(15)	111.3(2)	111.0
C(12)-B(1)-C(1)	117.08(17)	117.21(16)	116.7(2)	115.5
O(1)-B(1)-N(1)	98.40(15)	98.66(14)	98.4(2)	98.5
C(12)-B(1)-N(1)	109.03(16)	108.42(15)	111.6(2)	110.5
C(1)-B(1)-N(1)	111.39(16)	109.52(15)	108.4(2)	109.1
C(2)-C(1)-C(6)	117.09(18)	116.52(19)	116.7(2)	
C(2)-C(1)-B(1)	120.61(18)	123.24(18)	122.0(2)	
C(6)-C(1)-B(1)	122.30(18)	120.08(18)	121.3(2)	
C(11)-C(12)-C(7)	116.56(18)	116.97(18)	116.3(2)	
C(11)-C(12)-B(1)	122.65(18)	120.62(17)	125.1(2)	
C(7)-C(12)-B(1)	120.08(17)	122.38(17)	118.6(2)	
C(21)-C(16)-C(17)	114.6(2)	113.7(2)	114.5(2)	
C(18)-C(17)-C(16)	121.9(2)	122.5(2)	121.2(2)	
C(18)-C(17)-X(1)	121.3(2)	120.4(2)	120.8(2)	
C(16)-C(17)-X(1)	116.8(2)	117.1(2)	118.0(2)	
C(17)-C(18)-C(19)	122.6(2)	122.0(2)	121.5(2)	
C(20)-C(19)-C(18)	117.7(2)	118.3(2)	120.2(2)	
C(20)-C(19)-X(2)	-	-	120.0(2)	
C(18)-C(19)-X(2)	-	-	119.8(2)	
O(1)-C(20)-C(19)	129.6(2)	129.8(2)	130.0(2)	
O(1)-C(20)-C(21)	112.00(18)	112.31(17)	113.4(2)	
C(19)-C(20)-C(21)	118.4(2)	117.9(2)	116.6(2)	
N(1)-C(21)-C(16)	124.47(18)	123.65(19)	123.9(2)	
N(1)-C(21)-C(20)	110.76(17)	110.70(17)	110.2(2)	
C(16)-C(21)-C(20)	124.77(19)	125.64(19)	125.9(2)	
C(13)-N(1)-C(21)	119.18(18)	119.49(17)	119.3(2)	
C(13)-N(1)-B(1)	133.13(18)	132.76(16)	132.7(2)	
C(21)-N(1)-B(1)	107.52(16)	107.74(15)	108.0(2)	
C(20)-O(1)-B(1)	110.35(15)	110.55(15)	109.9(2)	

NMR spectra

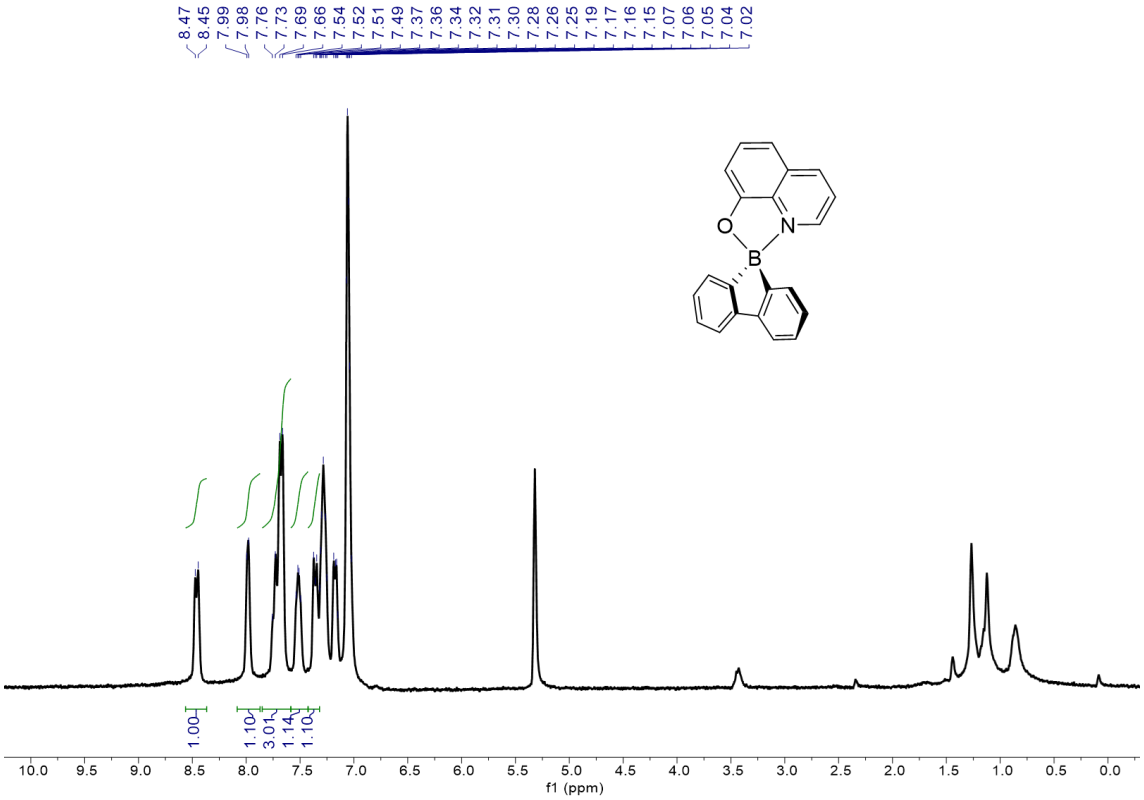


Figure S2 ^{1}H NMR (CD_2Cl_2, 300 MHz) spectrum of complex **3a**.

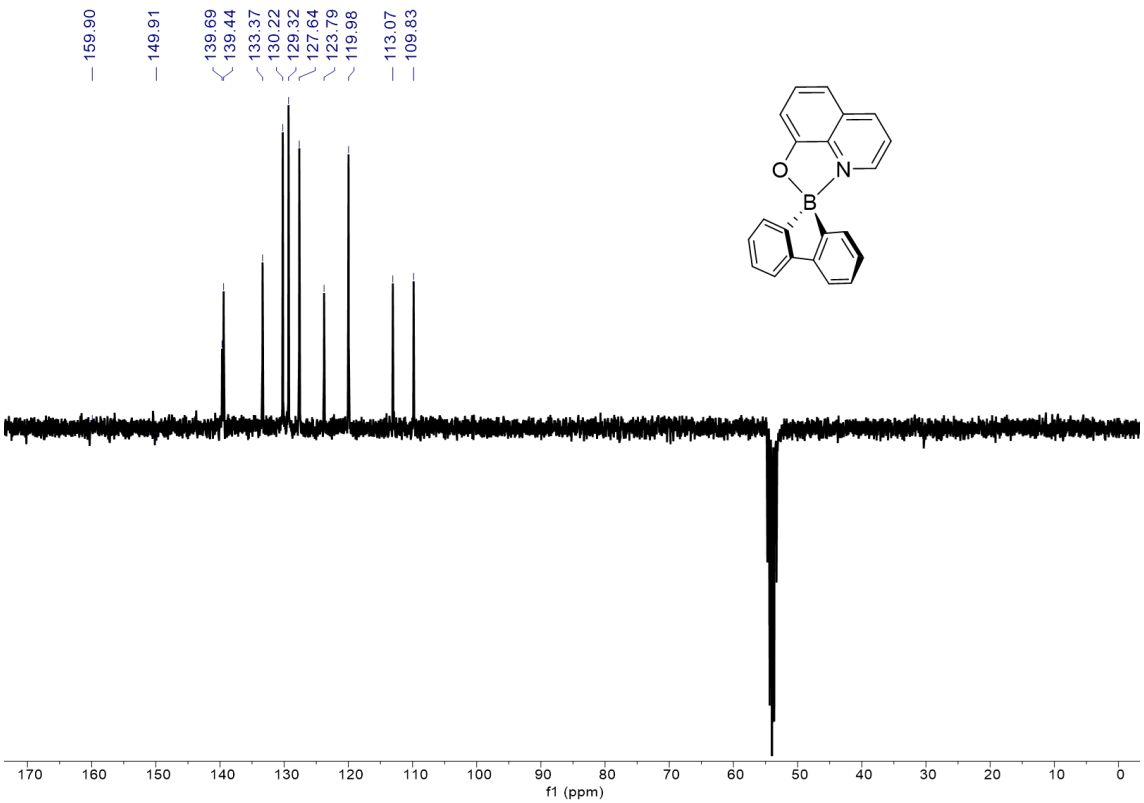


Figure S3 ^{13}C APT NMR (CD_2Cl_2, 75 MHz) spectrum of complex **3a**.

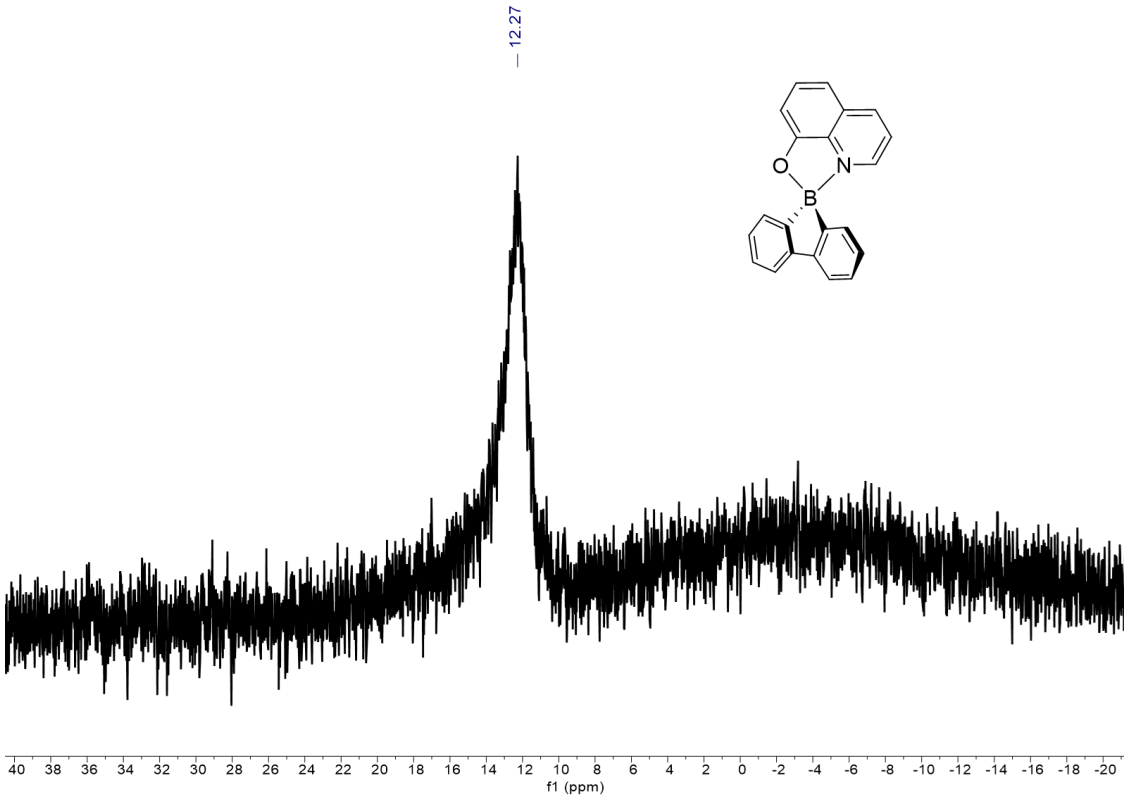


Figure S4 ^{11}B NMR (CD_2Cl_2, 96 MHz) spectrum of complex **3a**.

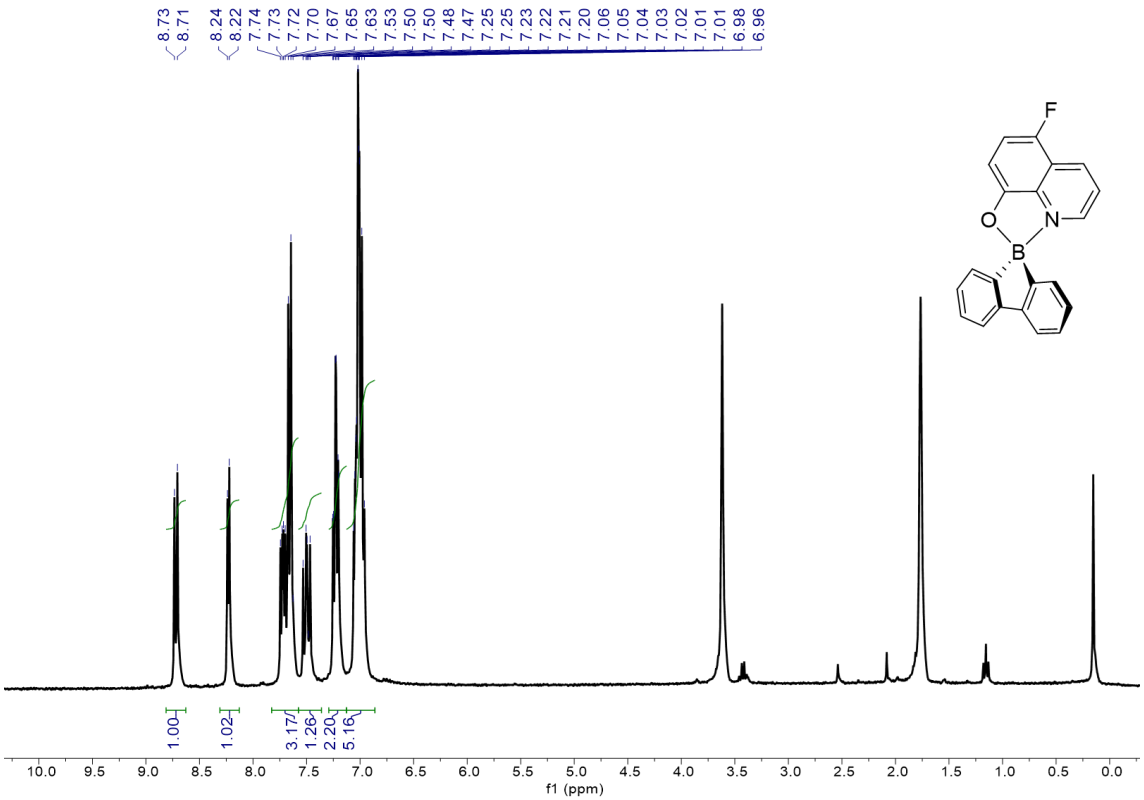


Figure S5 ^{1}H NMR (THF-d_8, 300 MHz) spectrum of complex **3b**.

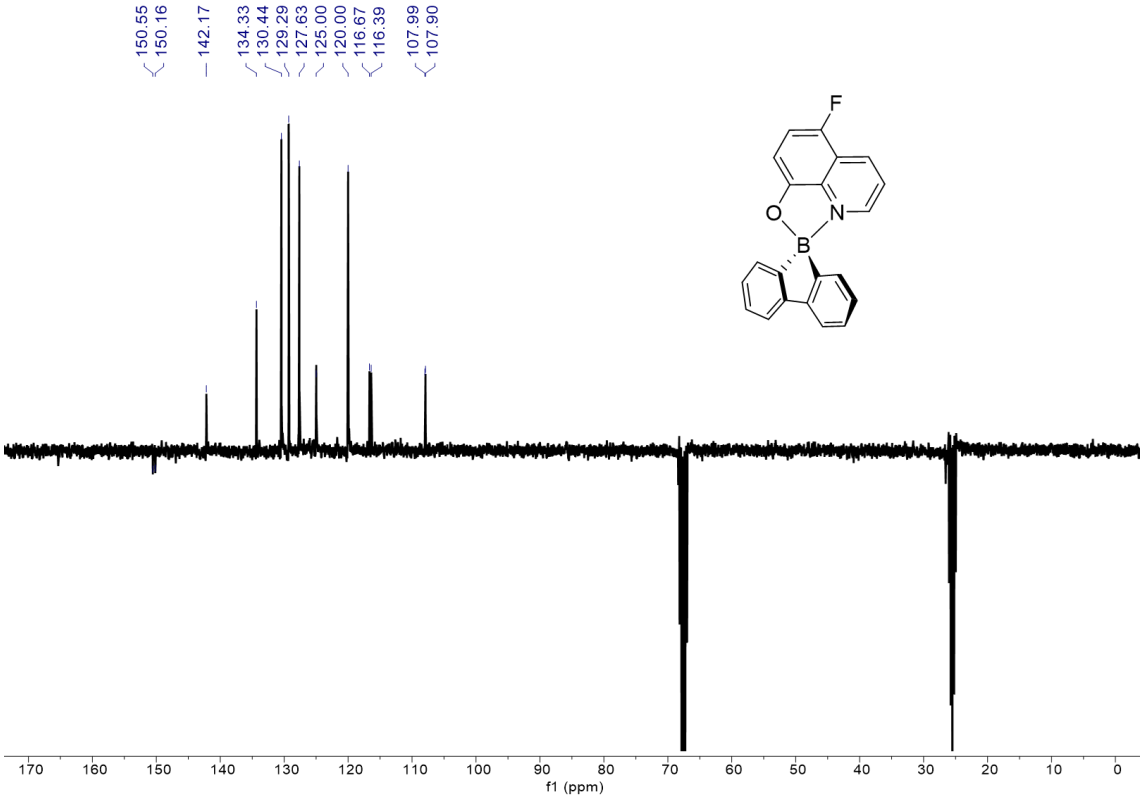


Figure S6 ^{13}C APT NMR (THF-d_8, 75 MHz) spectrum of complex **3b**.

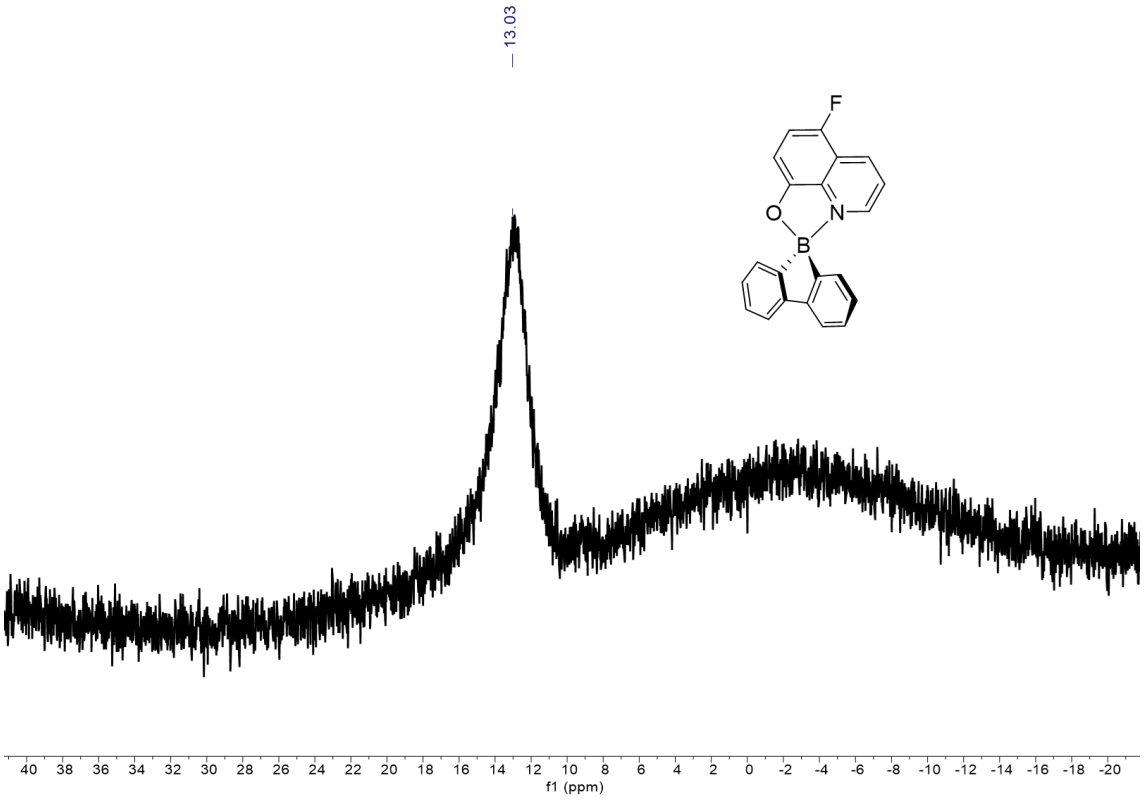


Figure S7 ^{11}B NMR (THF-d_8, 96 MHz) spectrum of complex **3b**.

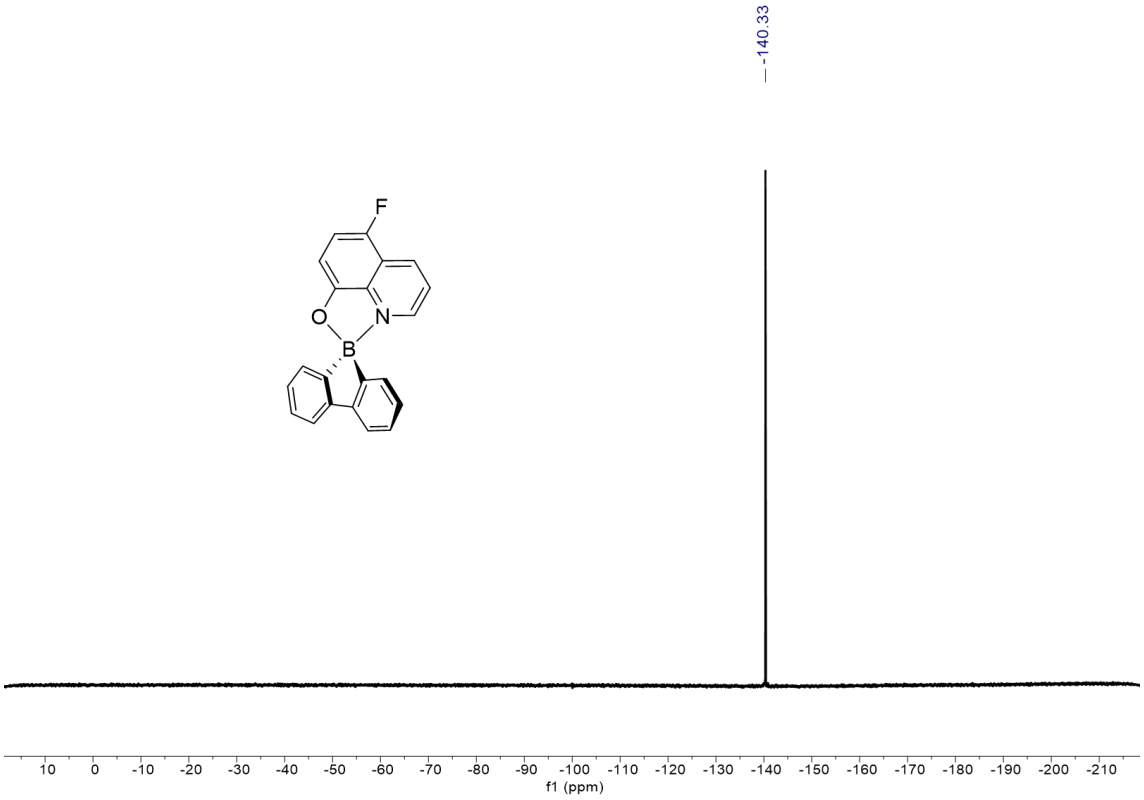


Figure S8 $^{19}F\{^{1}H\}$ NMR (THF-d_8, 282 MHz) spectrum of complex **3b**.

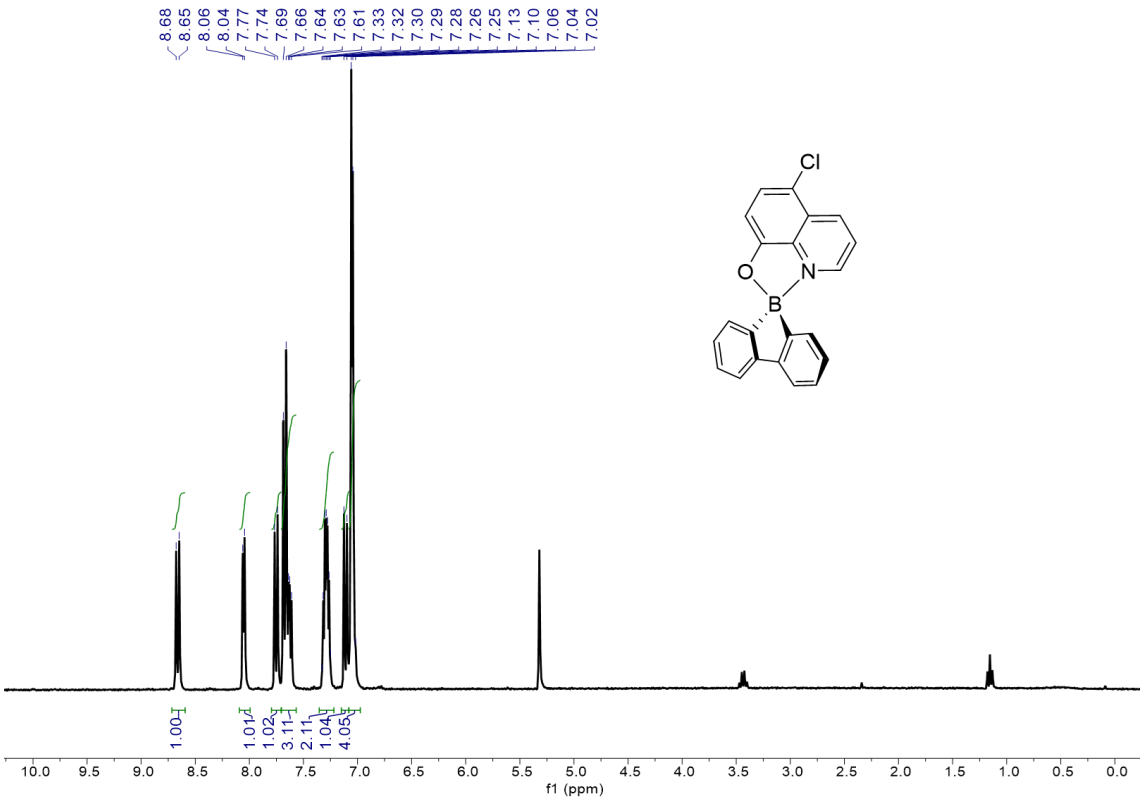


Figure S9 ^{1}H NMR (CD_2Cl_2, 300 MHz) spectrum of complex **3c**.

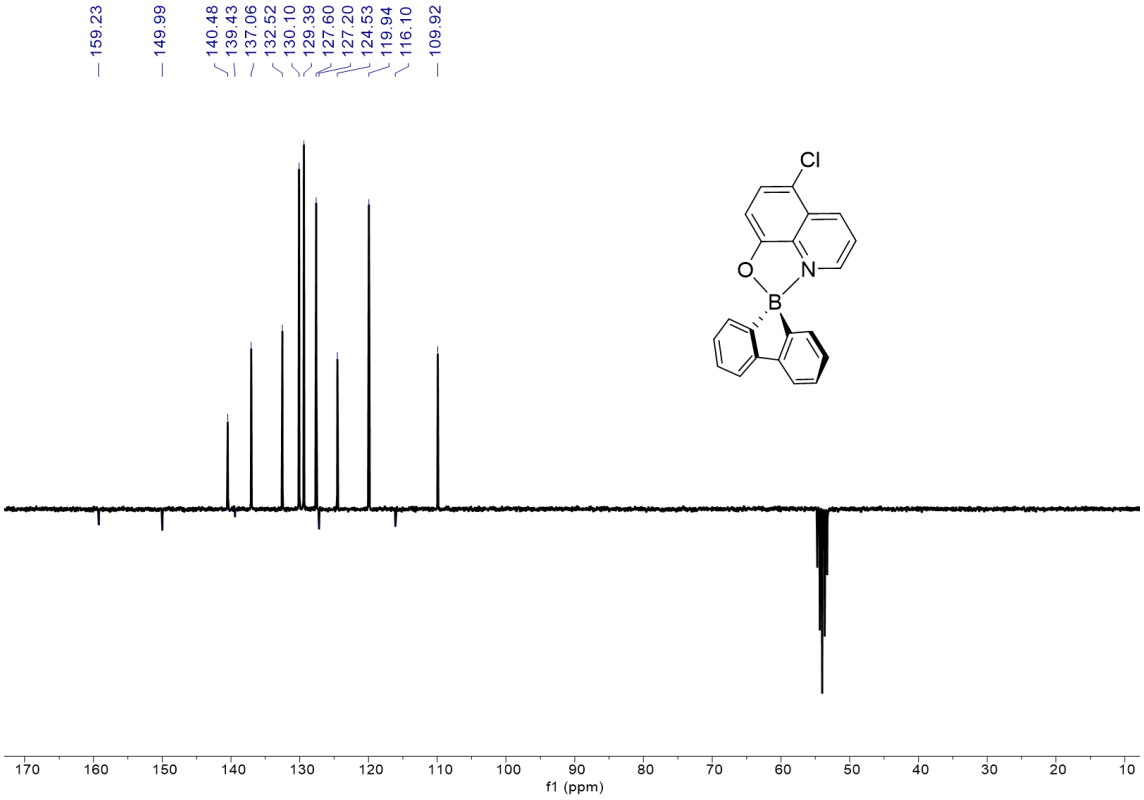


Figure S10 ^{13}C APT NMR (CD_2Cl_2, 75 MHz) spectrum of complex **3c**.

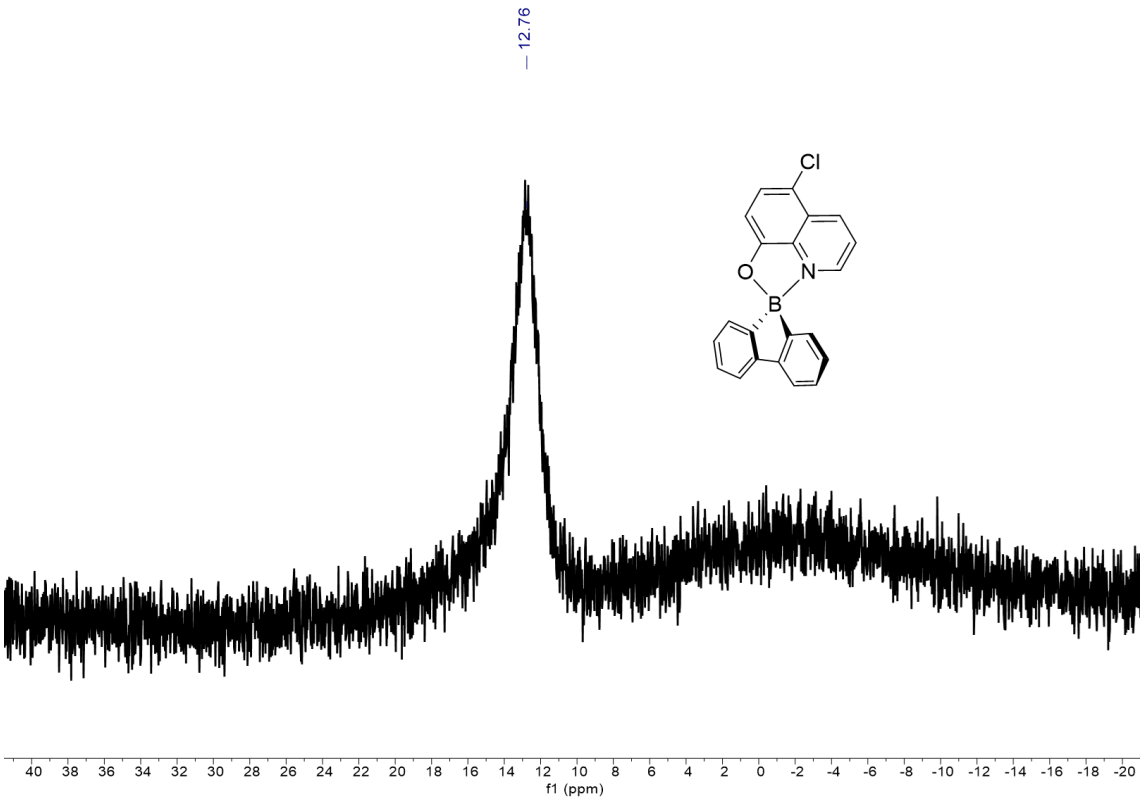


Figure S11 ^{11}B NMR (CD_2Cl_2, 96 MHz) spectrum of complex **3c**.

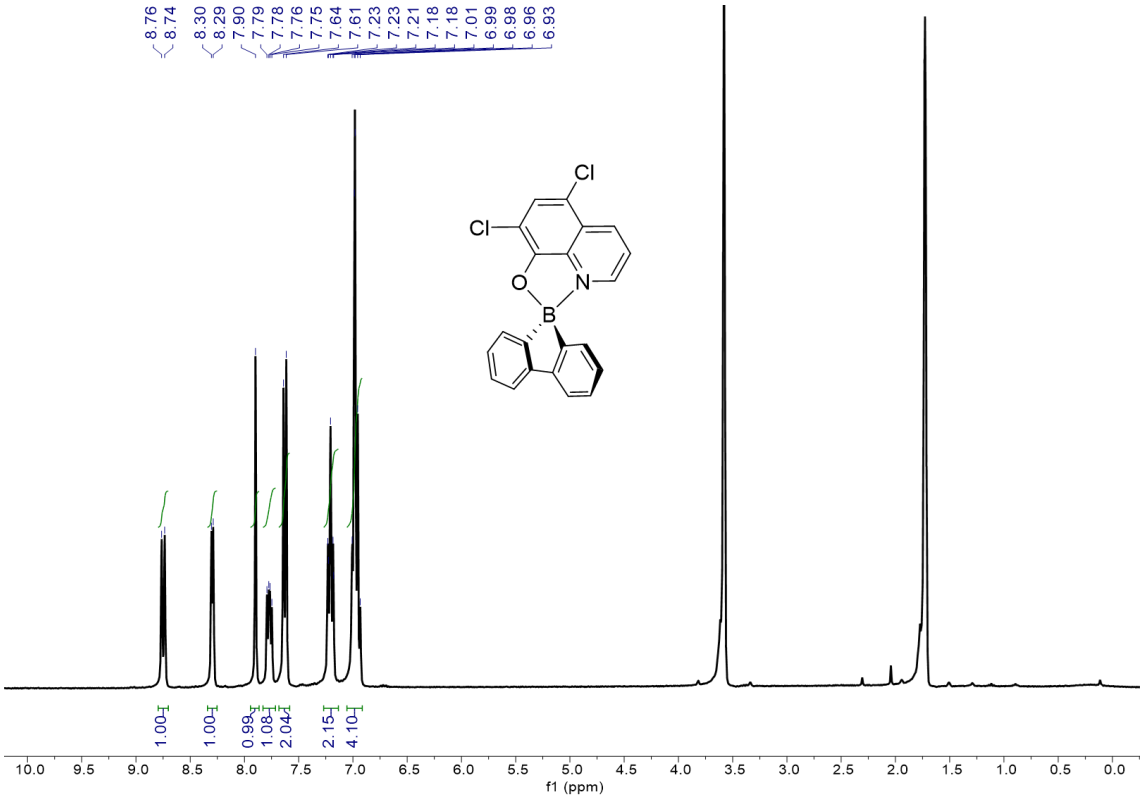


Figure S13 ^{1}H NMR (THF-d_8, 300 MHz) spectrum of complex **3d**.

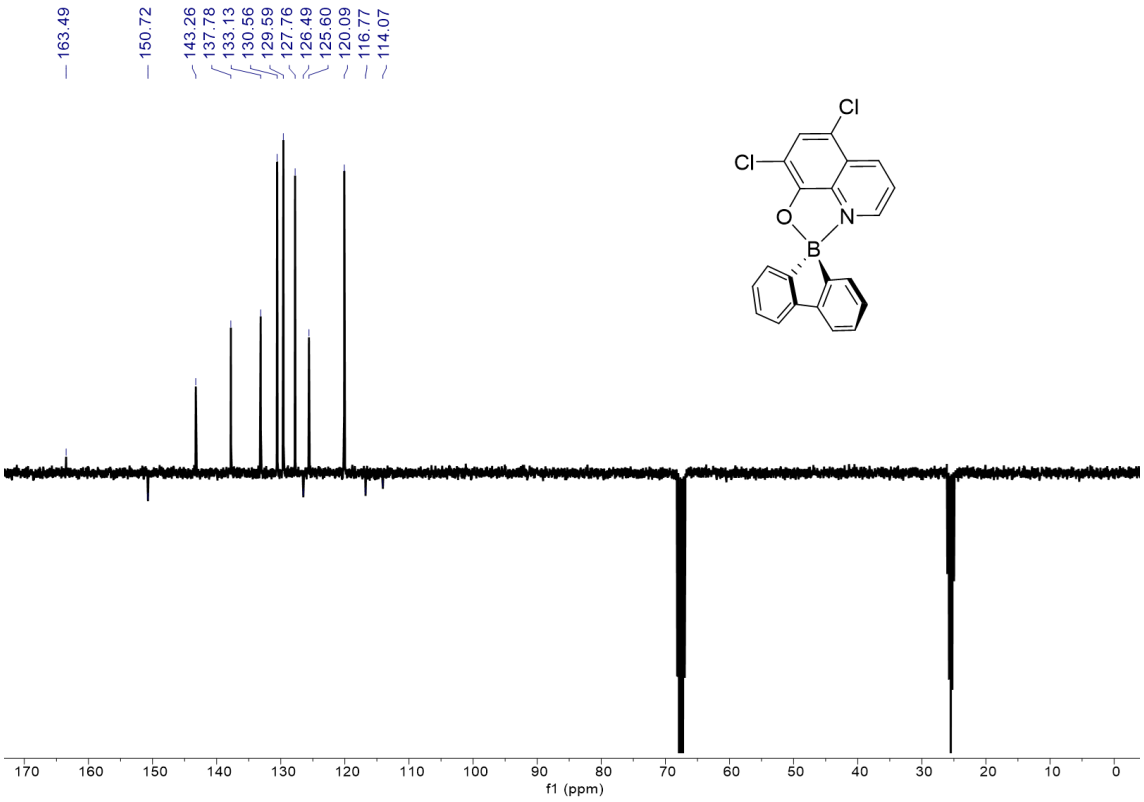


Figure S13 ^{13}C APT NMR (THF-d_8, 75 MHz) spectrum of complex **3d**.

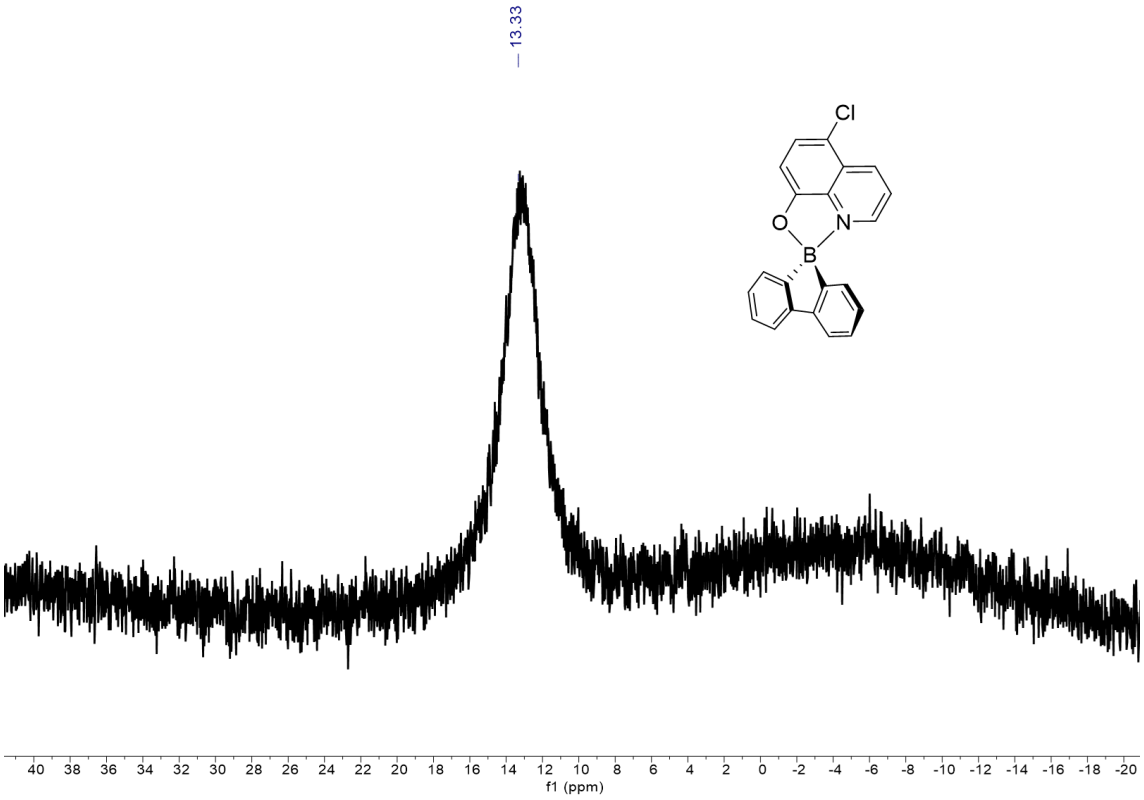


Figure S14 ^{11}B NMR (THF-d_8, 96 MHz) spectrum of complex **3d**.

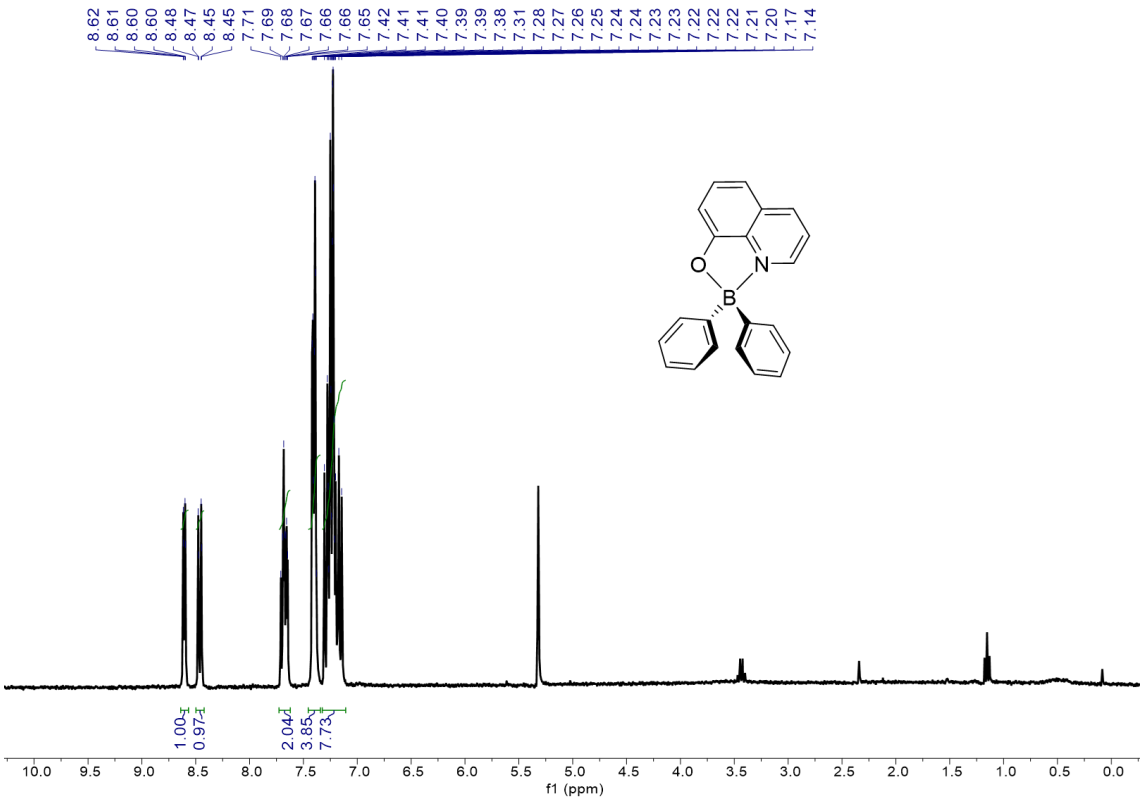


Figure S15 ^{1}H NMR (CD_2Cl_2, 300 MHz) spectrum of complex **4a**.

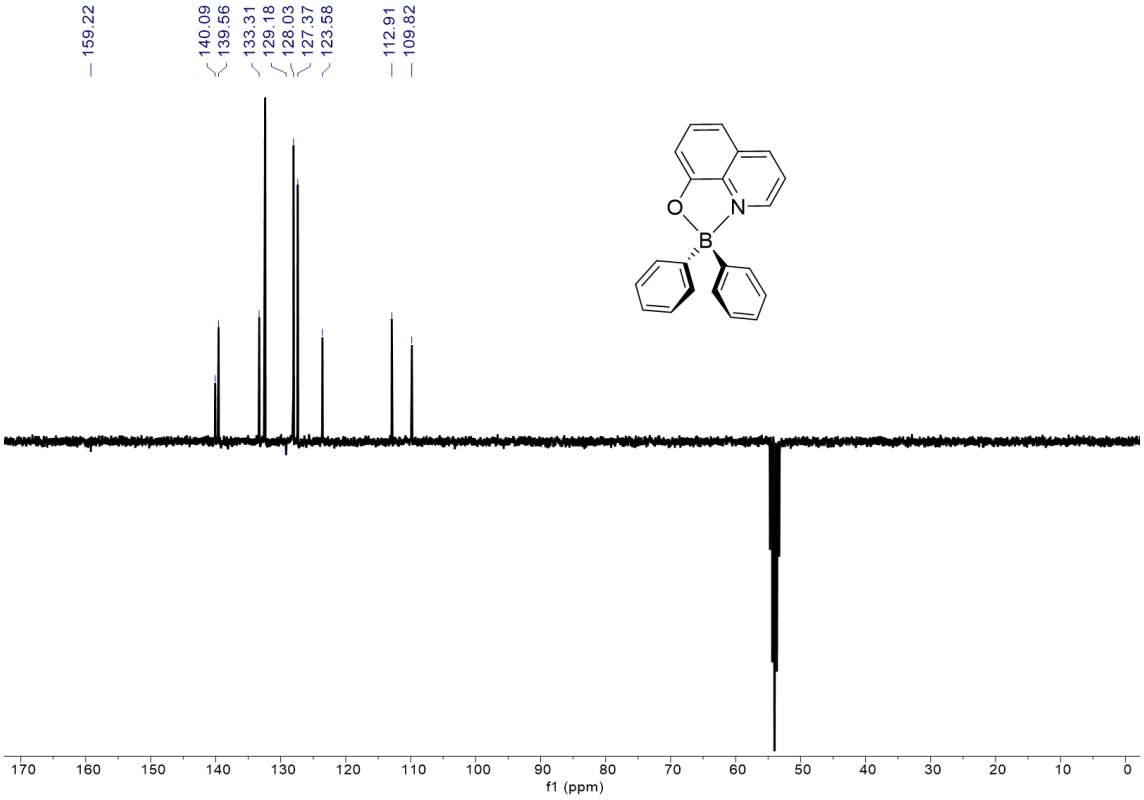


Figure S16 ^{13}C APT NMR (CD_2Cl_2, 75 MHz) spectrum of complex **4a**.

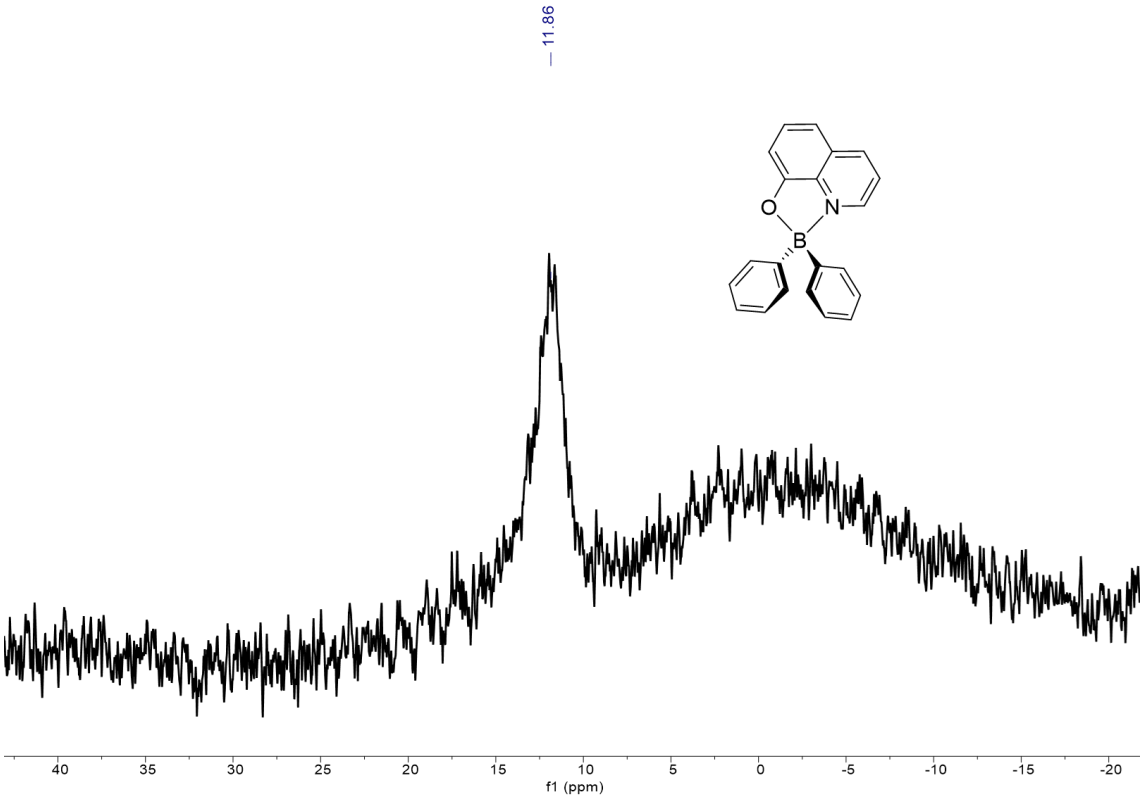


Figure S17 ^{11}B NMR (CD_2Cl_2, 96 MHz) spectrum of complex **4a**.

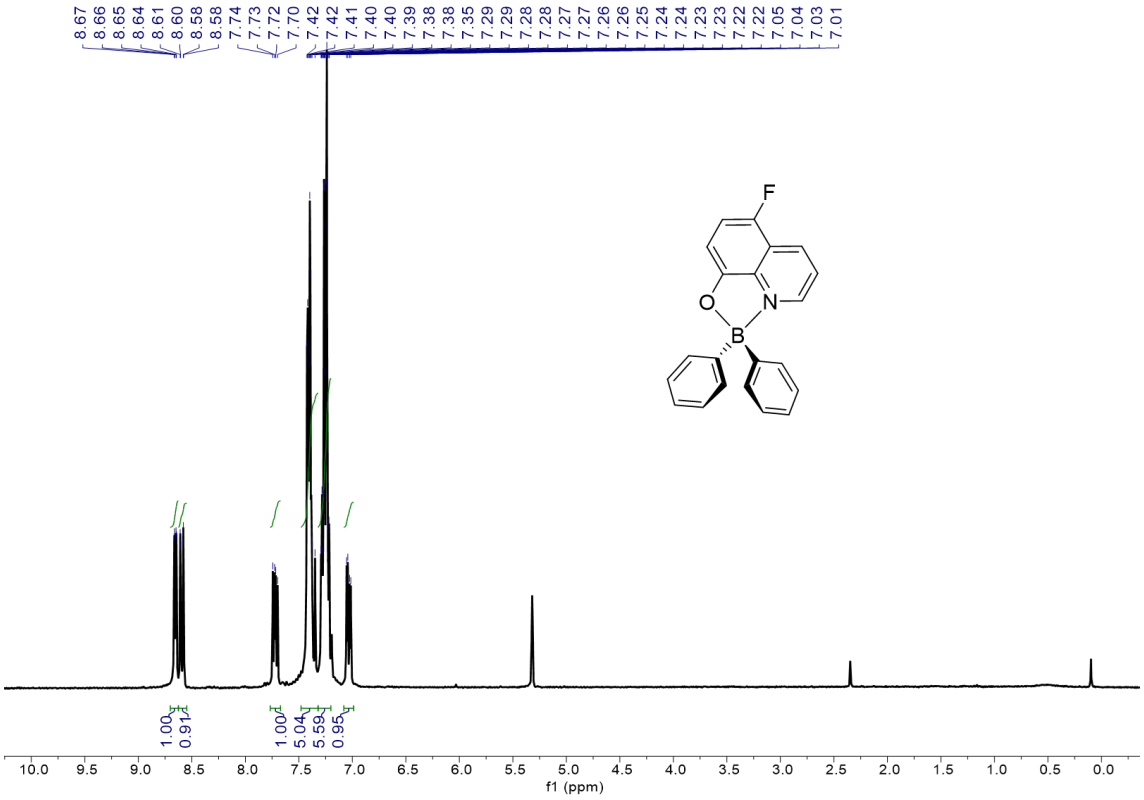


Figure S18 ^{1}H NMR (CD_2Cl_2, 300 MHz) spectrum of complex **4b**.

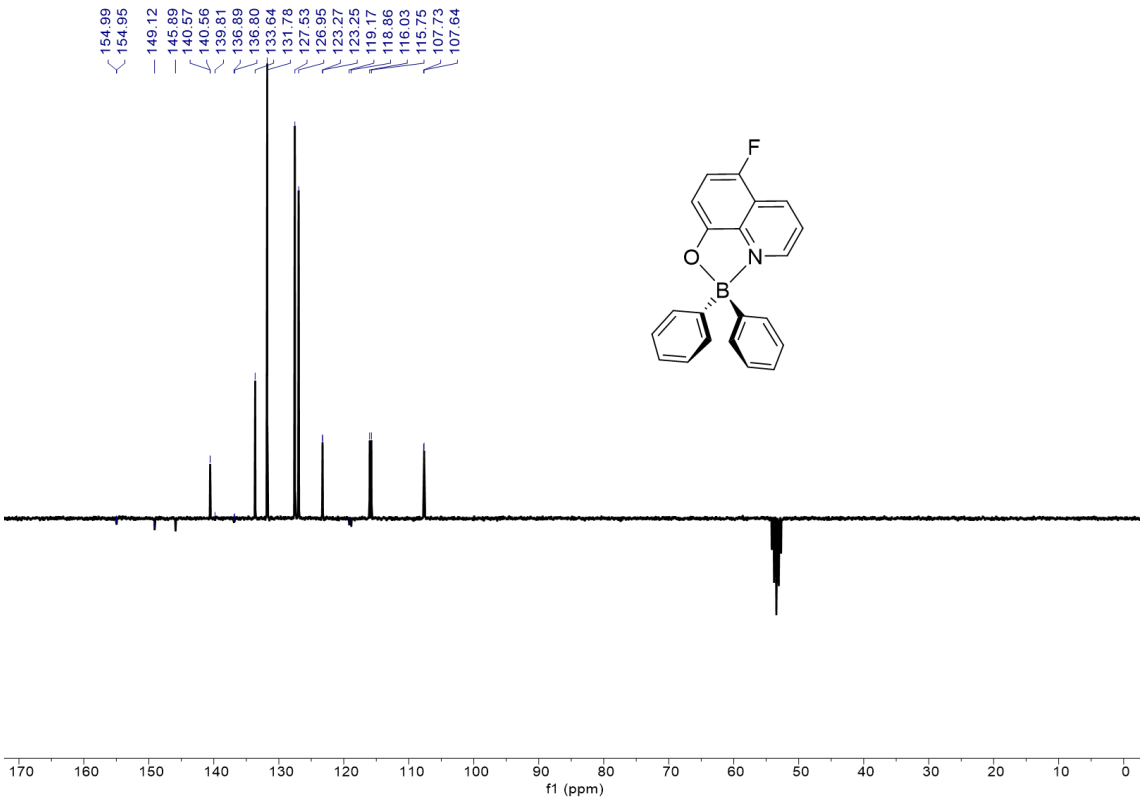


Figure S19 ^{13}C APT NMR (CD_2Cl_2, 75 MHz) spectrum of complex **4b**.

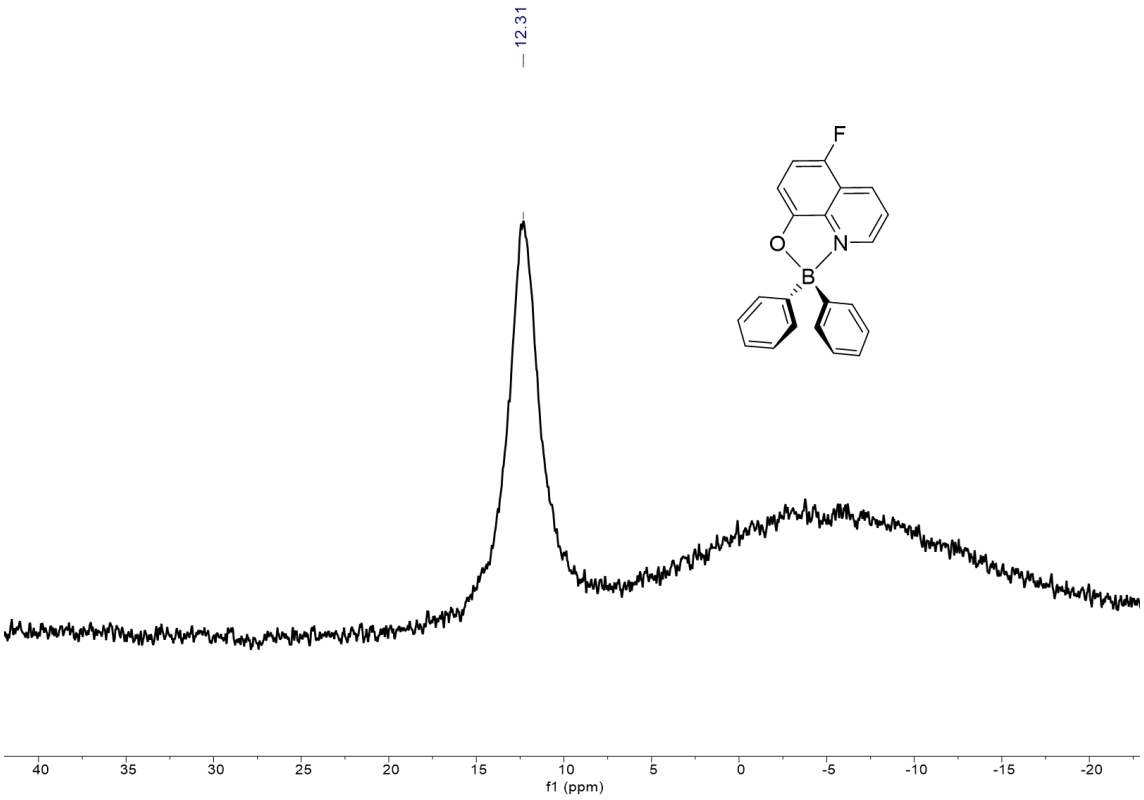


Figure S20 ^{11}B NMR (CD_2Cl_2, 96 MHz) spectrum of complex **4b**.

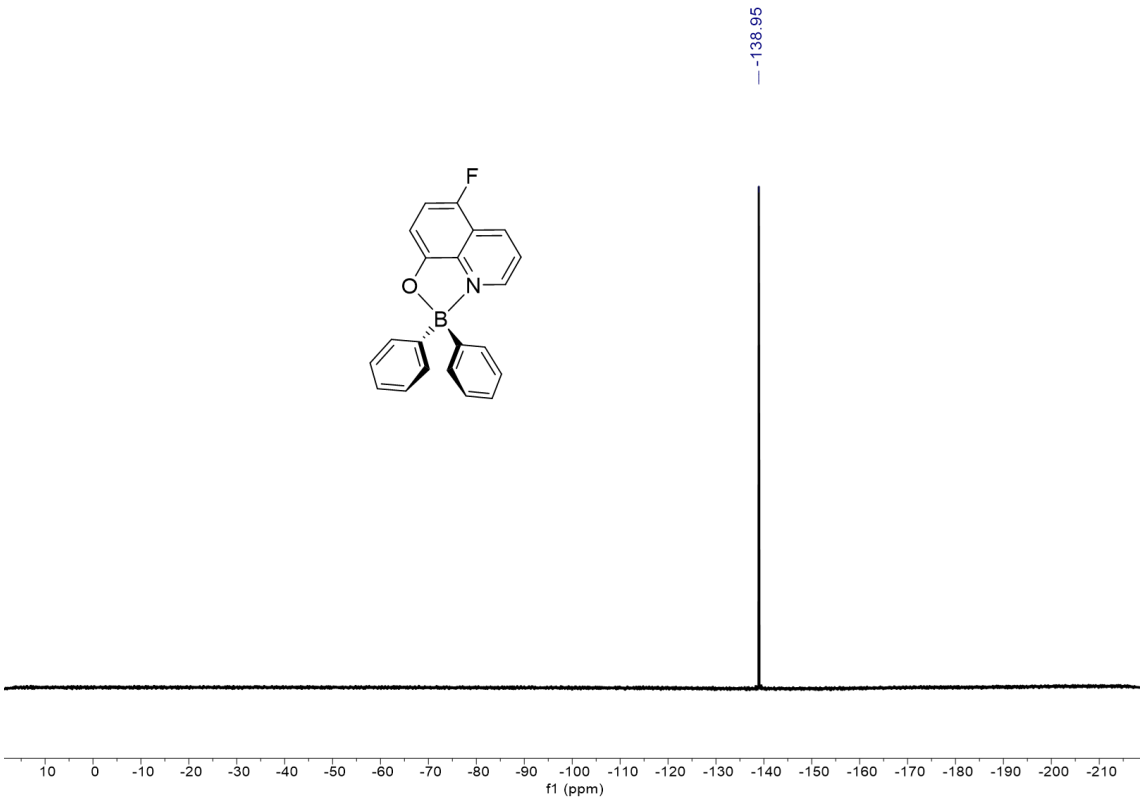


Figure S21 $^{19}F\{^1H\}$ NMR (CD_2Cl_2, 282 MHz) spectrum of complex **4b**.

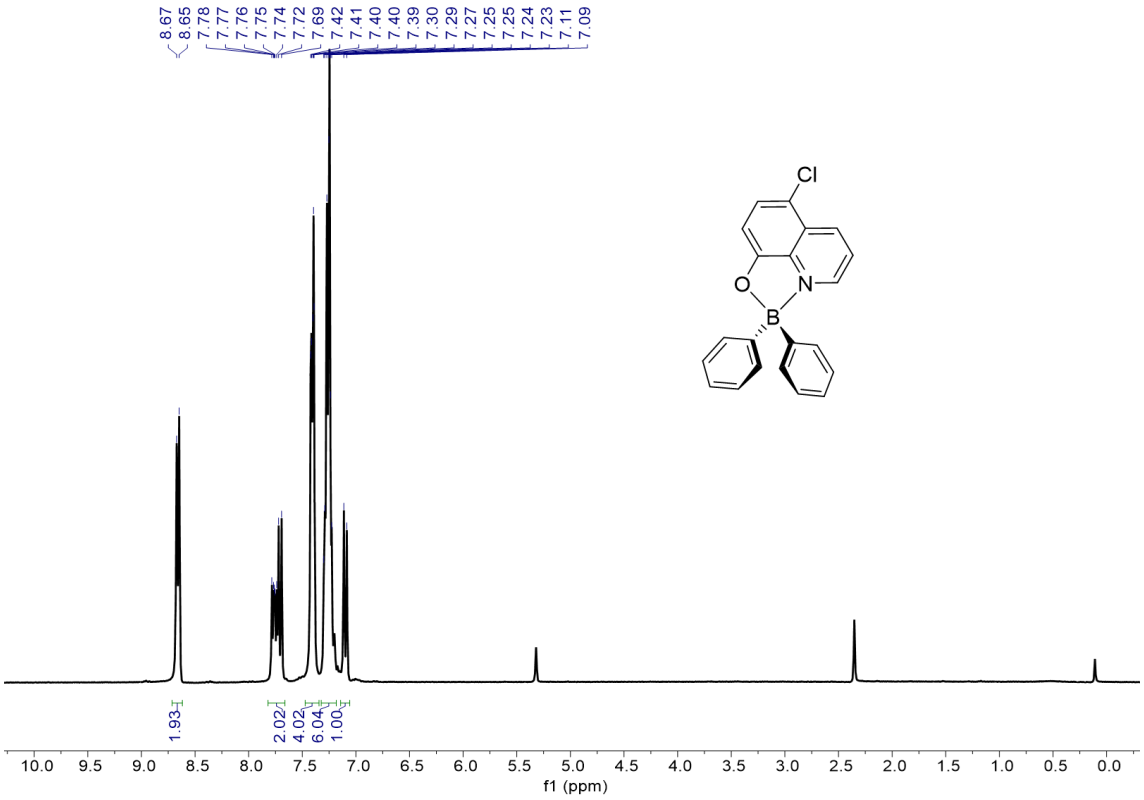


Figure S22 ^{1}H NMR (CD_2Cl_2, 300 MHz) spectrum of complex **4c**.

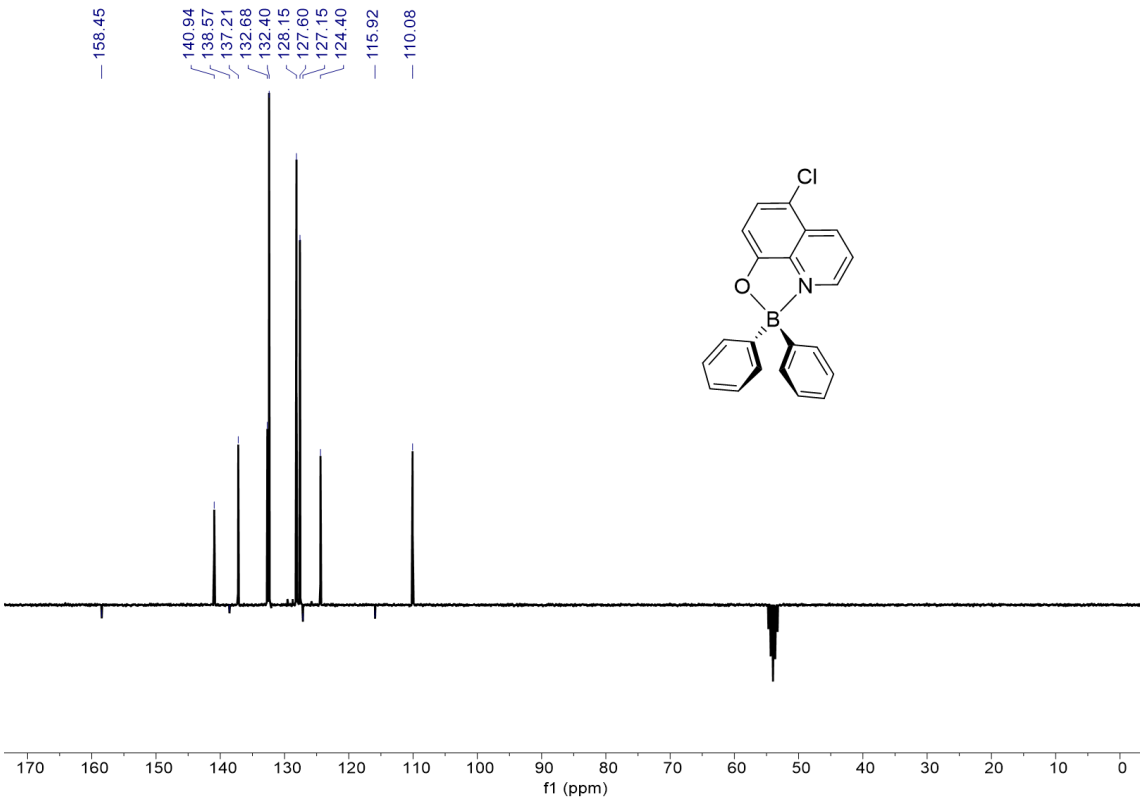


Figure S23 ^{13}C APT NMR (CD_2Cl_2, 75 MHz) spectrum of complex **4c**.

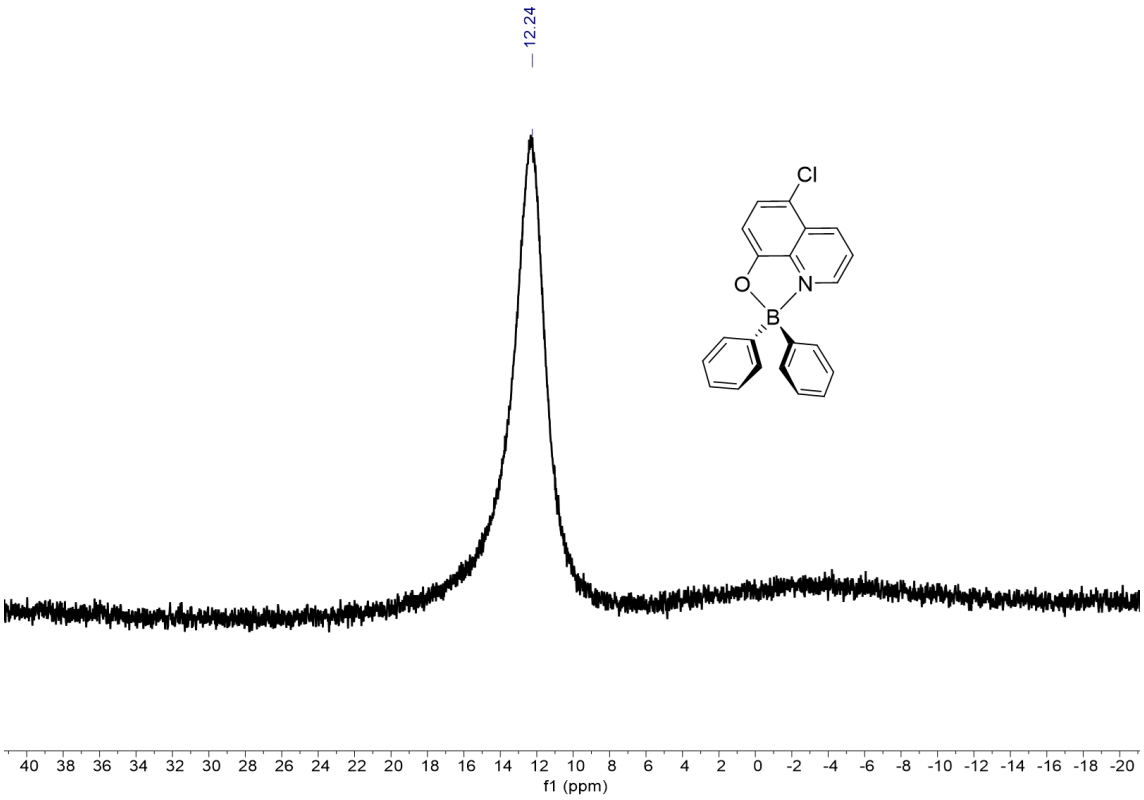


Figure S24 ^{11}B NMR (CD_2Cl_2, 96 MHz) spectrum of complex **4c**.

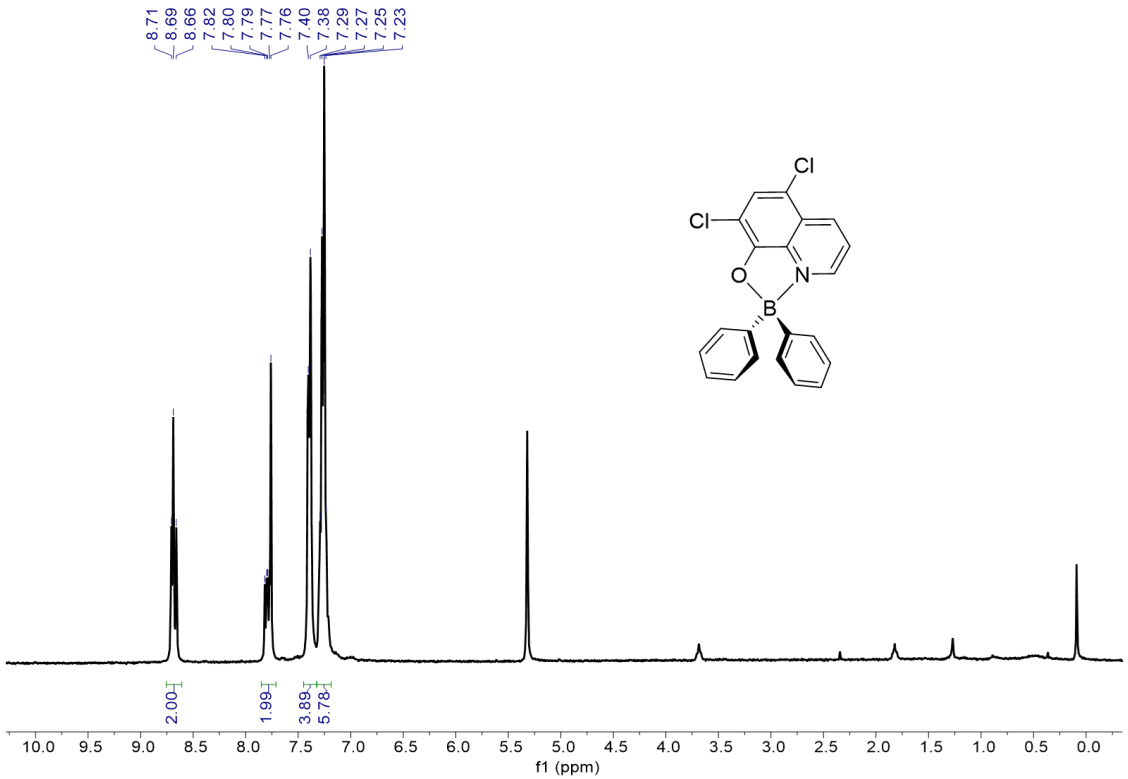


Figure S25 ^{1}H NMR (CD_2Cl_2, 300 MHz) spectrum of complex **4d**.

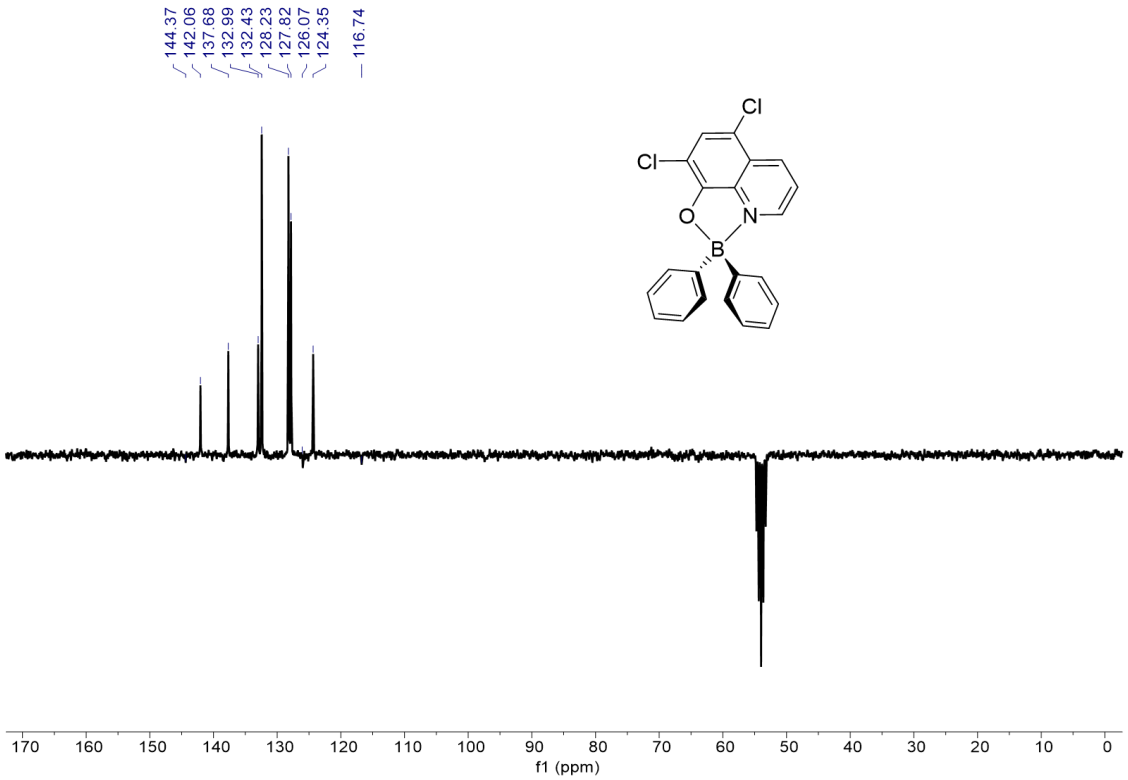


Figure S26 ^{13}C APT NMR (CD_2Cl_2, 75 MHz) spectrum of complex **4d**.

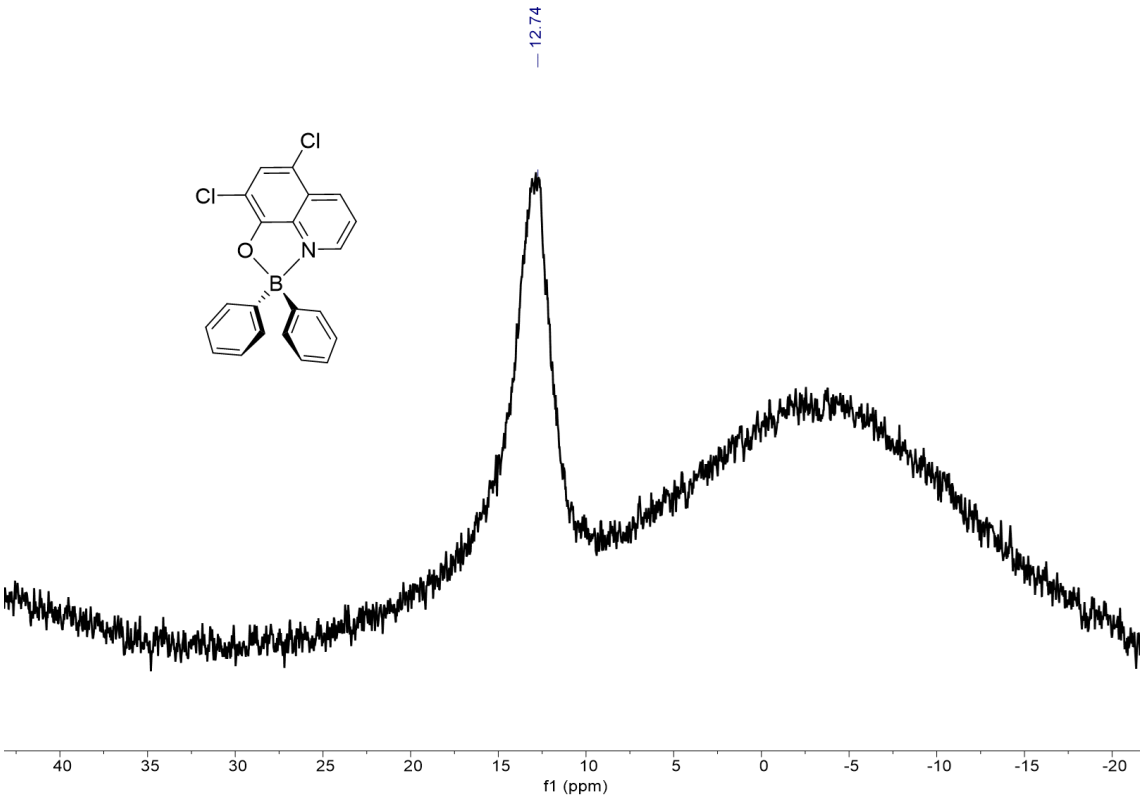
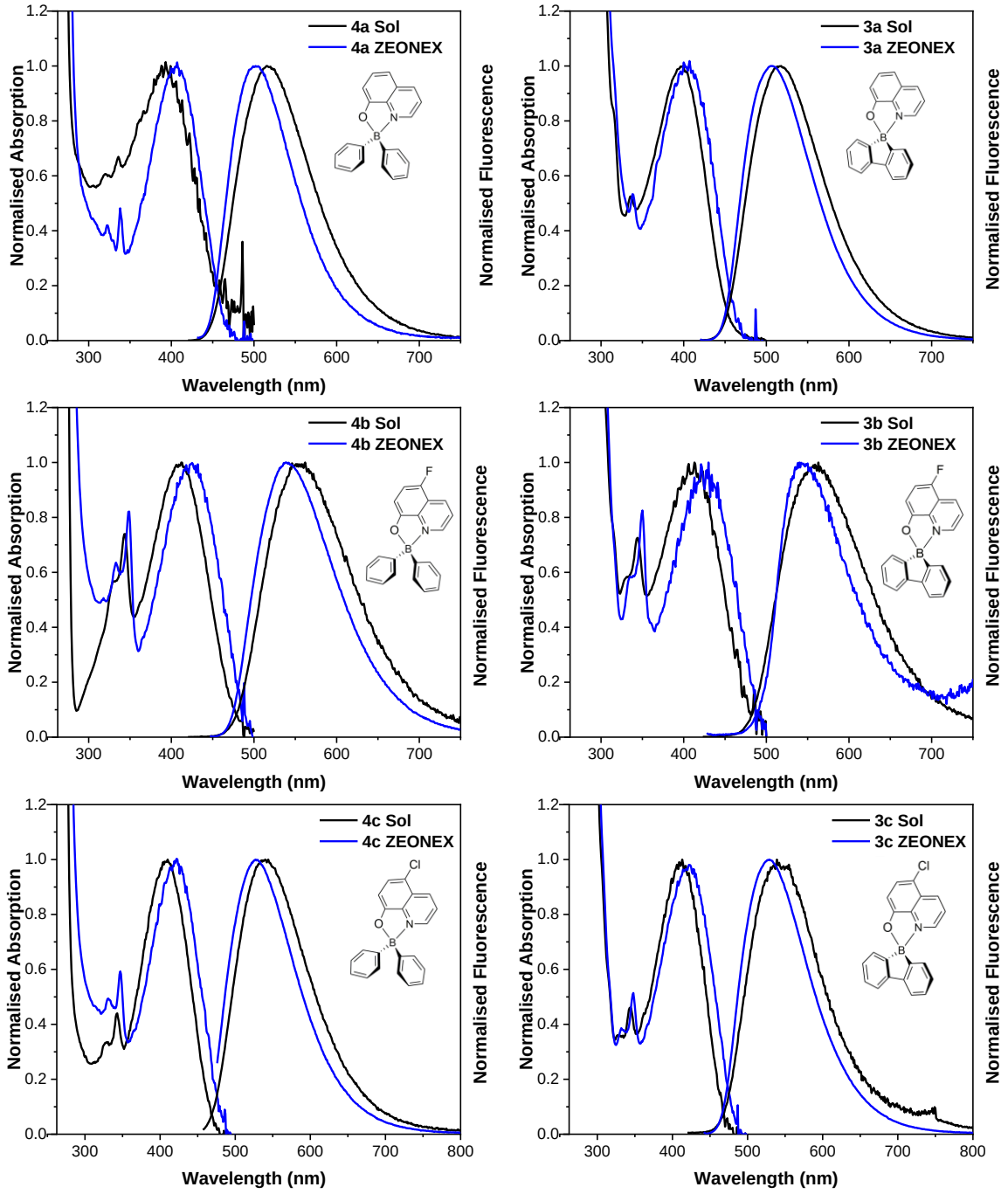


Figure S27 ^{11}B NMR (CD_2Cl_2, 96 MHz) spectrum of complex **4d**.

Absorption and emission spectra of complexes 3a-d and 4a-d in THF solution and in ZEONEX film



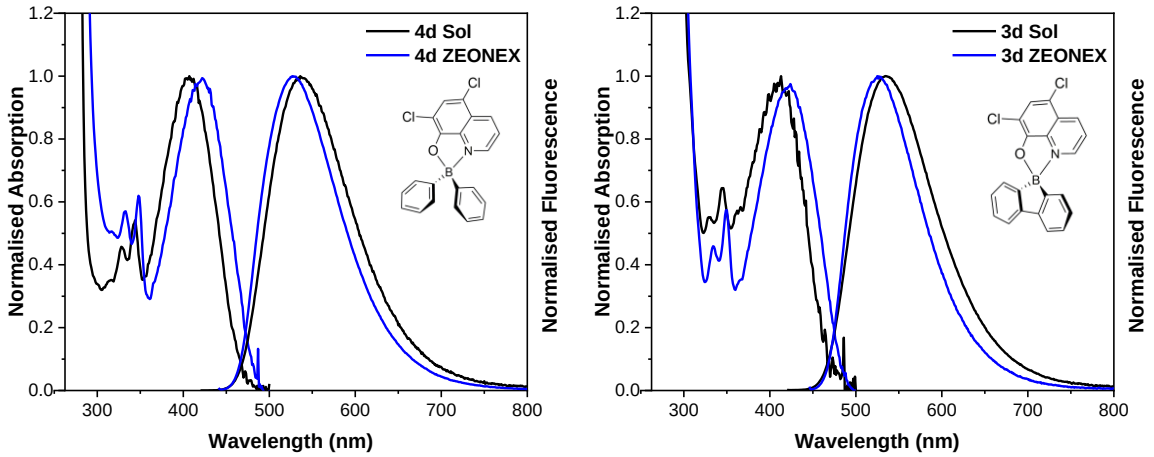


Figure S28 Normalised absorption and emission spectra of complexes **3a-d** and **4a-d** in THF solution ($OD_{max} < 0.2$ at λ_{abs}^{max}; $c < 8\times10^{-5}$ M) and in film (ZEONEX 480R, 1% wt), at 293 K.

Absorption and emission spectra of complexes 3a and 4a in solvents of different polarity

Table S4 Absorption and emission maxima of complexes **3a** and **4a** and corresponding Stokes shifts in solvents of different polarity (dielectric constant ε; dipole moment μ)**.**

			Complex **3a**			Complex **4a**		
Solvent	ε	μ	Stokes shift (cm^{-1})	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)	Stokes shift (cm^{-1})	λ_{abs}^{max} (nm)	λ_{em}^{max} (nm)
ZEONEX 480R	2.34	-	4929	405	506	4650	407	502
Toluene	2.379	0.31	5583	400	515	5507	400	513
Dichloromethane	9.08	1.14	5772	397	515	5888	394	513
THF	7.58	1.75	5809	397	516	6102	393	517
Acetonitrile	38.8	3.44	6579	388	521	6431	388	517

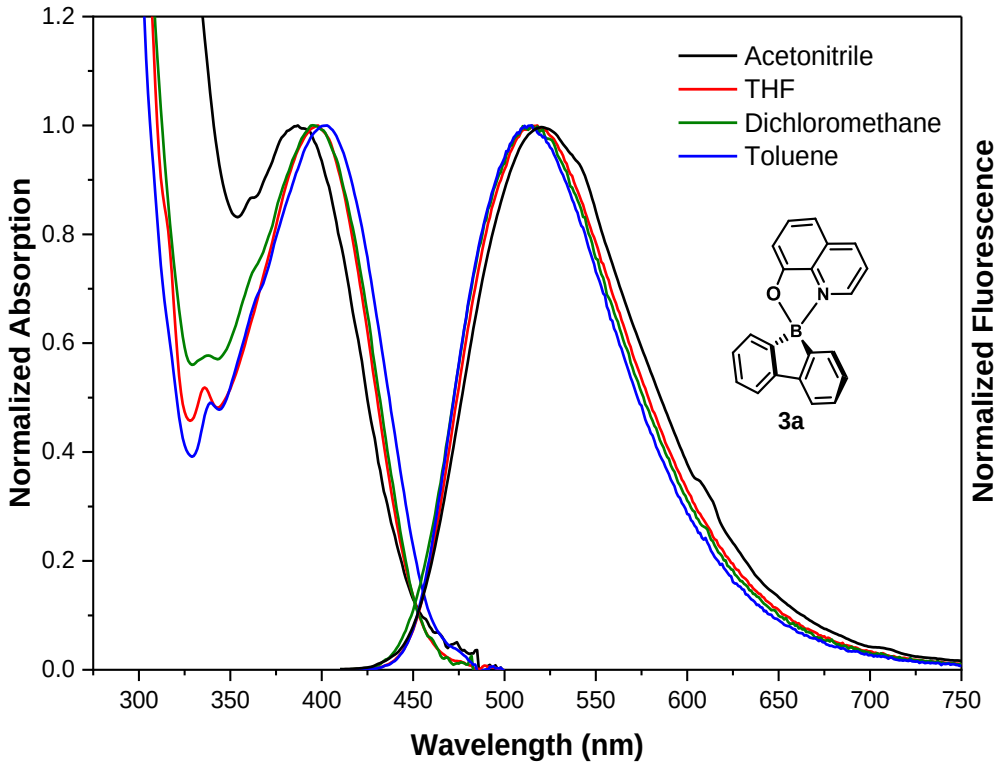


Figure S29 Normalised absorption and emission spectra of solutions of complex **3a** at 293 K. Solvents are indicated in the figure legend.

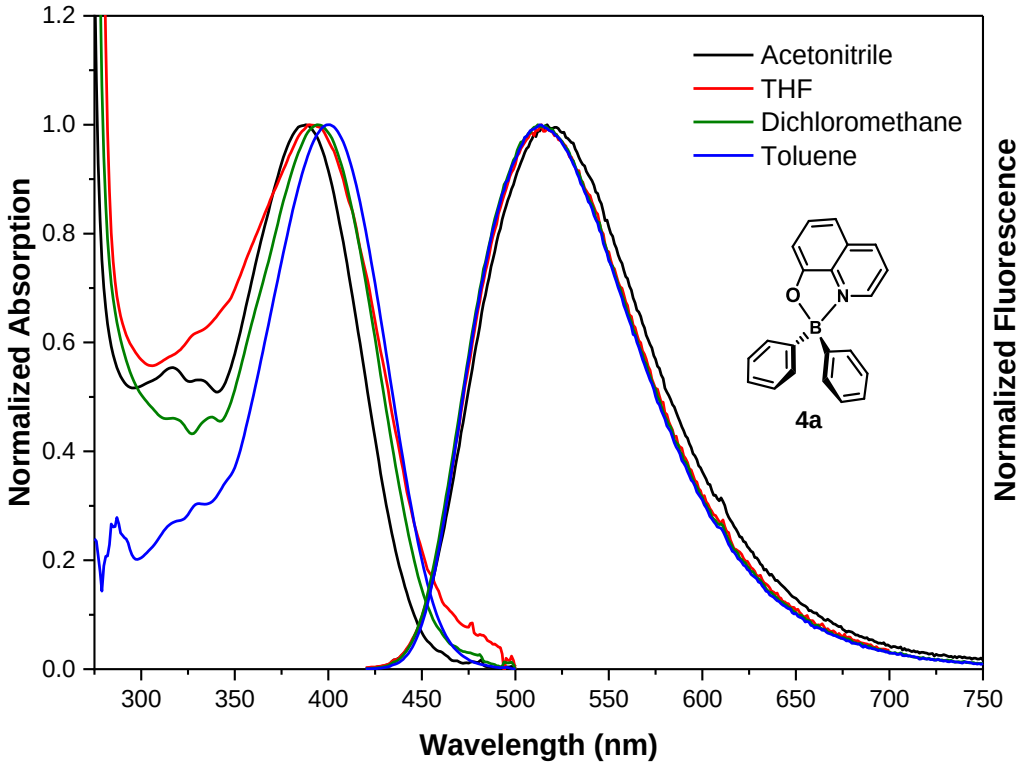


Figure S30 Normalised absorption and emission spectra of solutions of complex **4a** at 293 K. Solvents are indicated in the figure legend.

Computational studies

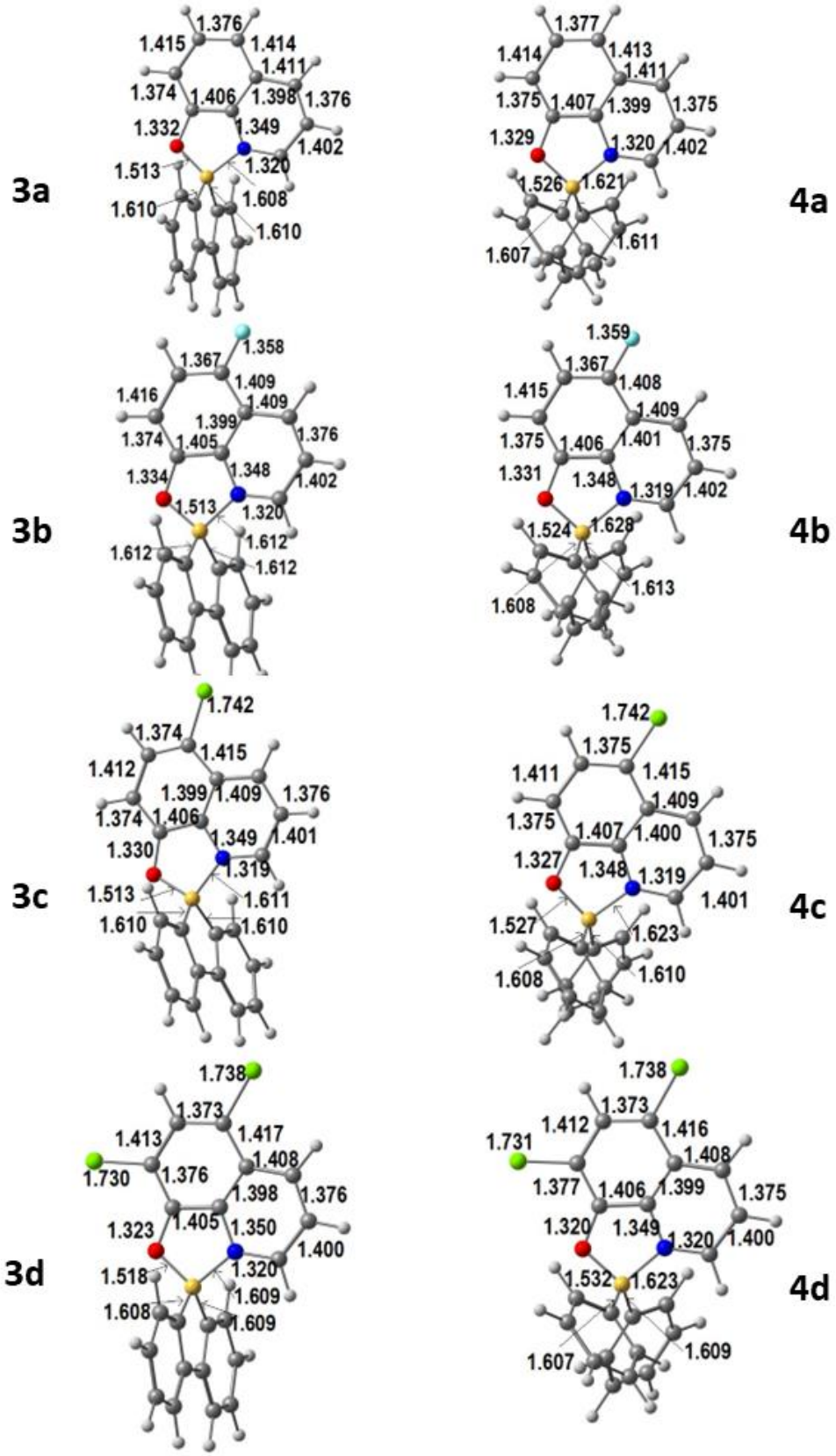


Figure S31 Optimised geometries of complexes **3a-3d** and **4a-4b** in the S_0 state (ground state) with relevant distances (Å).

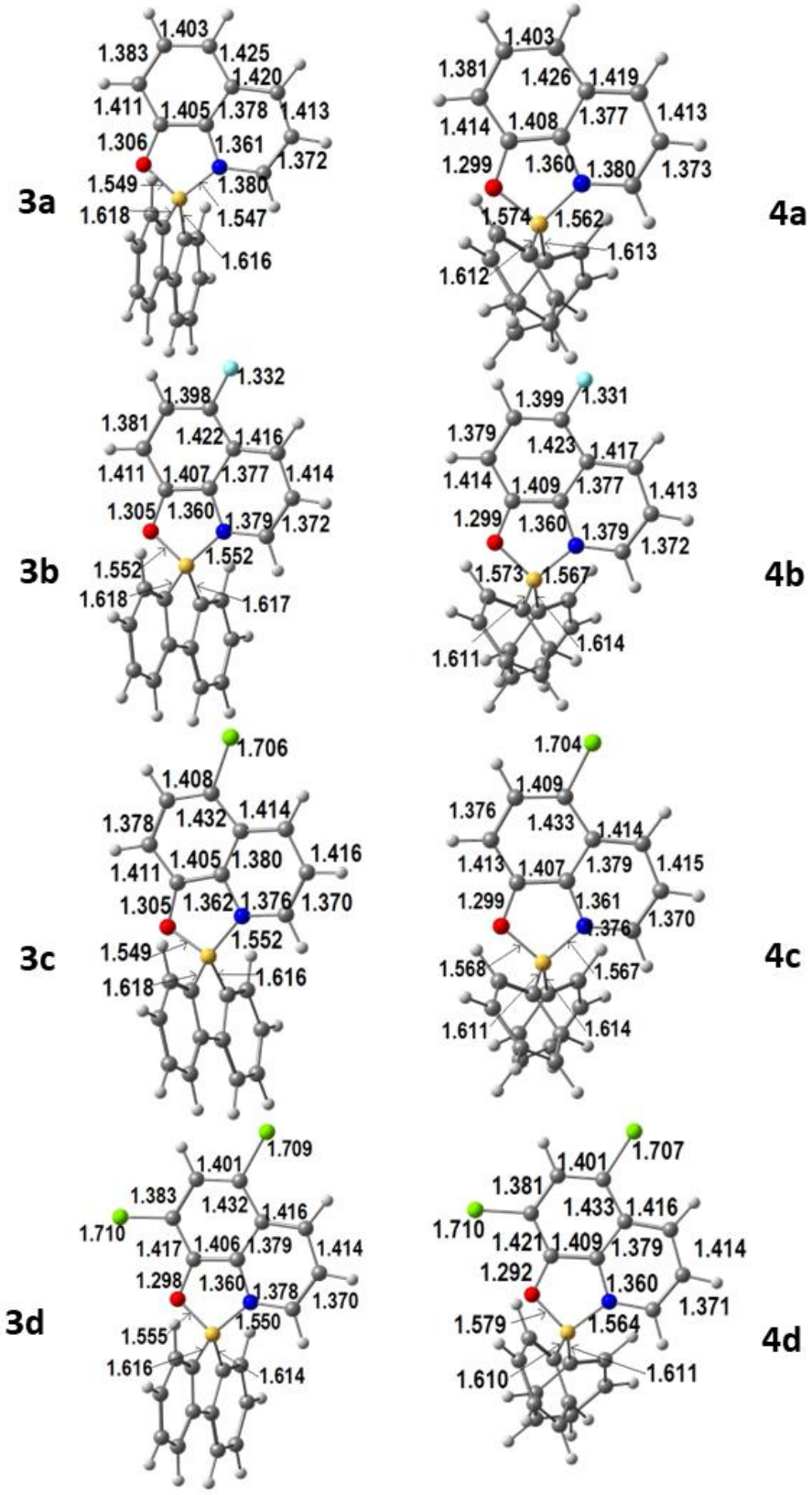


Figure S32 Optimised geometries of complexes **3a-3d** and **4a-4b** in the S_1 state (first singlet excited state) with relevant distances (Å).

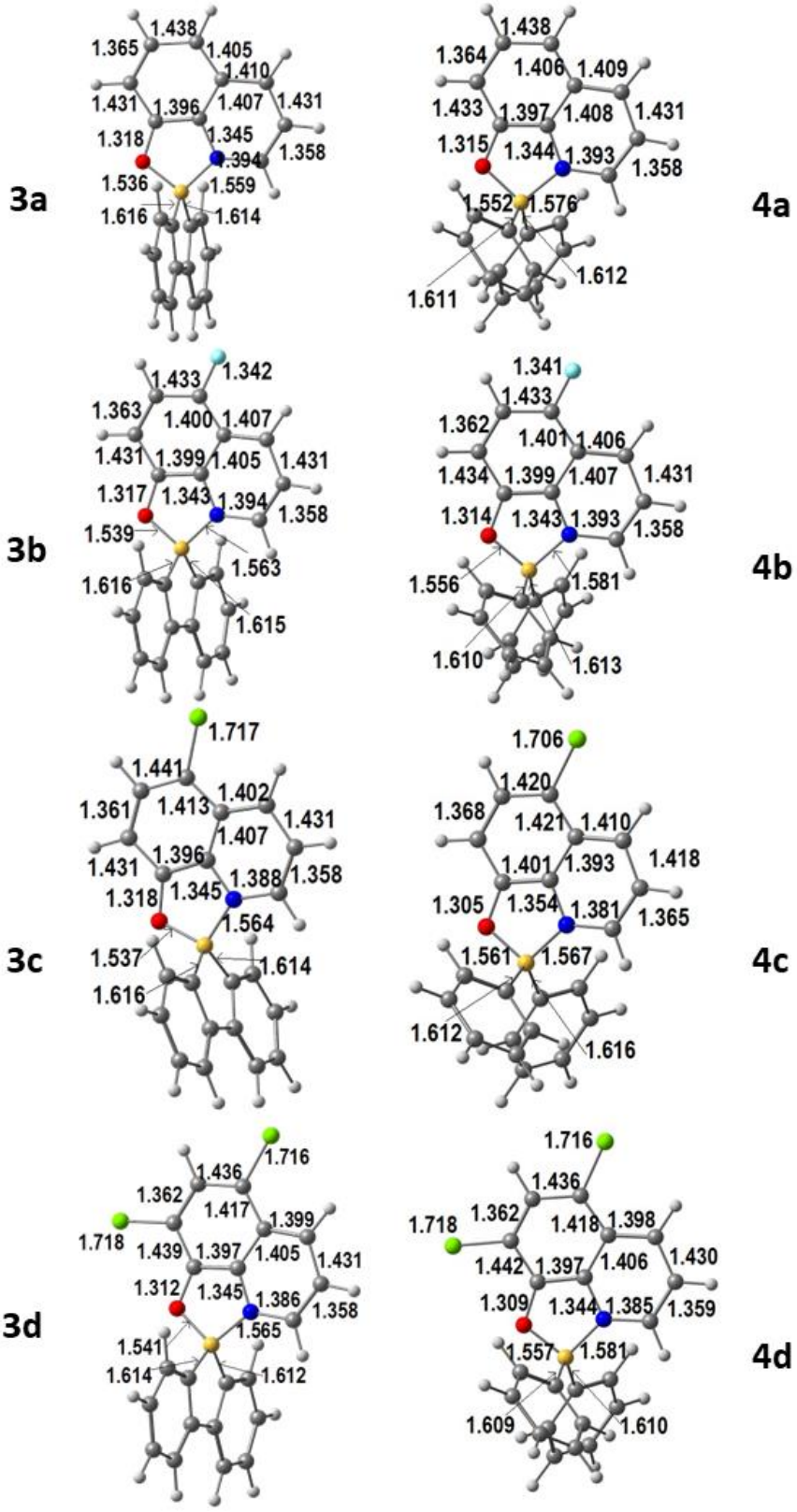


Figure S33 Optimised geometries of complexes **3a-3d** and **4a-4b** in the T_1 state (first triplet excited state) with relevant distances (Å).

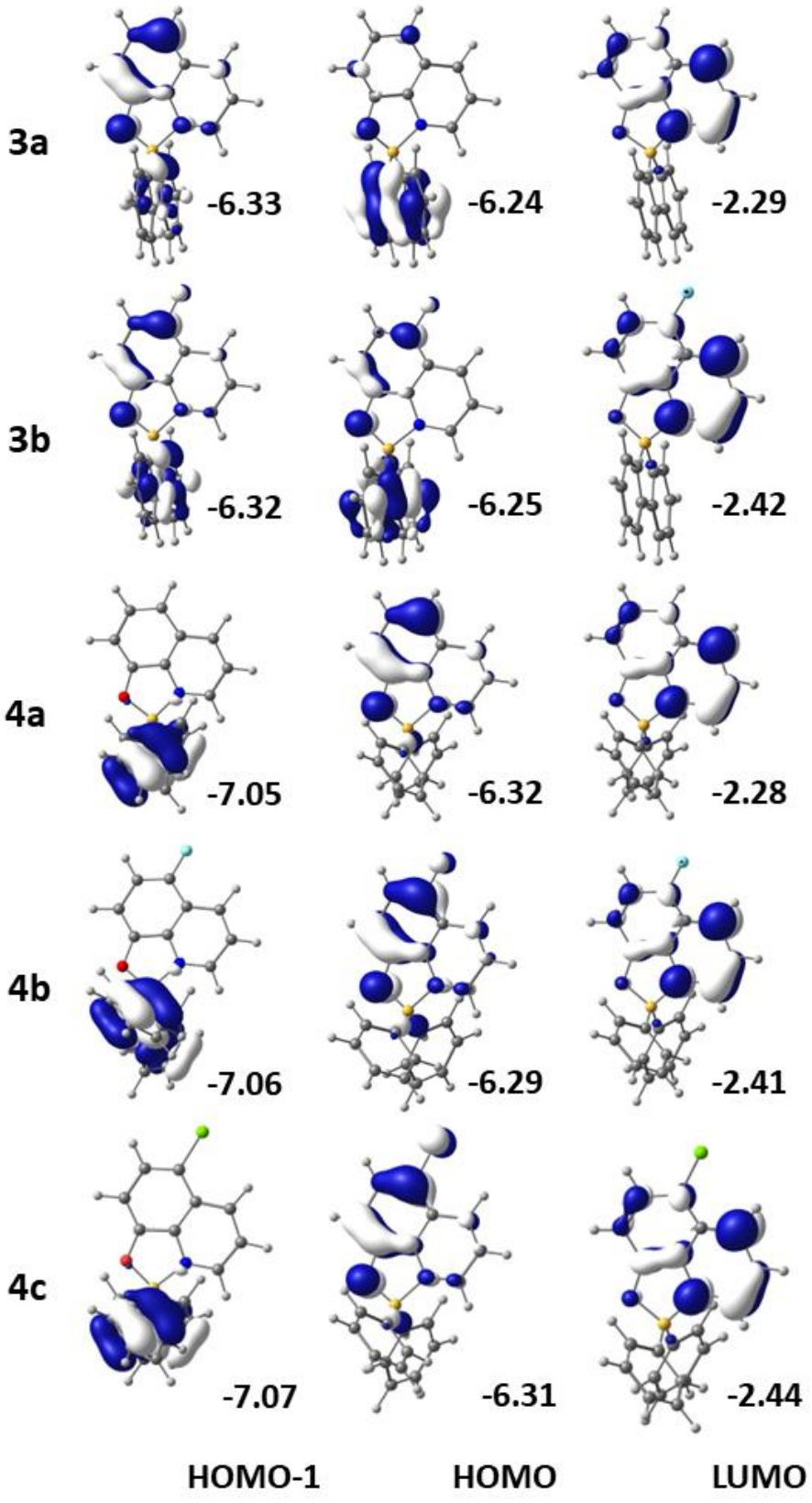


Figure S34 Frontier molecular orbitals (HOMO-1, HOMO and LUMO) of complexes **3a-3b** and **4a-4c**, with their energies in eV.

Table S5 Calculated HOMOs and LUMOs energies (eV) for complexes **3a-3d** and **4a-4d** using different methods.

	GP		**THF**		**CH_2Cl_2**		**A**		**A/D3**		**B**		**B/D3**	
	HOMO	**LUMO**	**HOMO**	**LUMO**	**HOMO**	**LUMO**	**HOMO**	**LUMO**	**HOMO**	**LUMO**	**HOMO**	**LUMO**	**HOMO**	**LUMO**
3a	-0.2707	-0.0995	-0.2709	-0.0993	-0.2568	-0.1021	-0.2559	-0.1018	-0.2259	-0.1459	-0.2320	-0.1317	-0.2321	-0.1310
3b	-0.2709	-0.1049	-0.2710	-0.1046	-0.2564	-0.1080	-0.2565	-0.1076	-0.2285	-0.1531	-0.2304	-0.1410	-0.2301	-0.1402
3c	-0.2714	-0.1062	-0.2716	-0.1060	-0.2568	-0.1088	-0.2570	-0.1085	-0.2298	-0.1541	-0.2308	-0.1398	-0.2326	-0.1415
3d	-0.2728	-0.1102	-0.2730	-0.1101	-0.2580	-0.1128	-0.2581	-0.1126	-0.2326	-0.1606	-0.2353	-0.1458	-0.2349	-0.1449
4a	-0.2741	-0.0990	-0.2741	-0.0989	-0.2603	-0.1015	-0.2604	-0.1013	-0.2367	-0.1458	-0.2345	-0.1360	-0.2343	-0.1353
4b	-0.2729	-0.1043	-0.2729	-0.1042	-0.2602	-0.1071	-0.2603	-0.1068	-0.2358	-0.1529	-0.2314	-0.1408	-0.2311	-0.1401
4c	-0.2735	-0.1057	-0.2736	-0.1055	-0.2607	-0.1082	-0.2607	-0.1082	-0.2394	-0.1545	-0.2339	-0.1421	-0.2335	-0.1530
4d	-0.2765	-0.1096	-0.2766	-0.1095	-0.2640	-0.1120	-0.2642	-0.1119	-0.2436	-0.1603	-0.2366	-0.1454	-0.2362	-0.1446

A – PBE0, TZP (all electron), THF, SO
A/D3 – PBE0/D3, TZP (all electron), THF, SO
B – B3LYP, TZP (all electron), THF, SO
B/D3 – B3LYP/D3, TZP (all electron), THF, SO
GP – BP86 (small core, T2ZP)
THF – BP86 (small core, T2ZP), THF (single point)
CH_2Cl_2 – BP86 (small core, T2ZP), dichloromethane (single point)

Table S6. DFT calculated (THF and vacuum) and experimental (THF and ZEONEX 480R) values of wavelength maximum (λ_{abs}^{max}) of the absorption band of boron complexes **3a-3d** and **4a-4d**, and their dipole moments in S_0, non-relaxed S_1', and S_1 states.

Complex	R^1	R^2	λ_{abs}^{max} (nm)		λ_{abs}^{max} (nm)		μ (D)		
			THF		ZEONEX 480R	vacuum	S_0	S_1	S_1' [a]
			exp	calc	exp	calc	calc	calc	calc
4a	H	H	397	383	407	402	7.60	7.63	6.08
3a	H	H	397	378	405	398	8.10	8.81	5.98
4b	F	H	412	399	423	418	5.96	6.33	4.36
3b	F	H	413	401	424	418	6.42	6.82	4.30
4c	Cl	H	409	400	422	417	5.79	5.96	5.05
3c	Cl	H	413	399	422	414	6.23	6.44	4.95
4d	Cl	Cl	407	401	422	417	7.48	7.57	4.82
3d	Cl	Cl	411	400	422	423	7.86	8.04	4.70

[a] S_1' is the non-relaxed singlet excited state (calculated at the S_0 relaxed geometry).

Transient emission spectra of complexes 3b, 3c, 4b and 4c in solid films

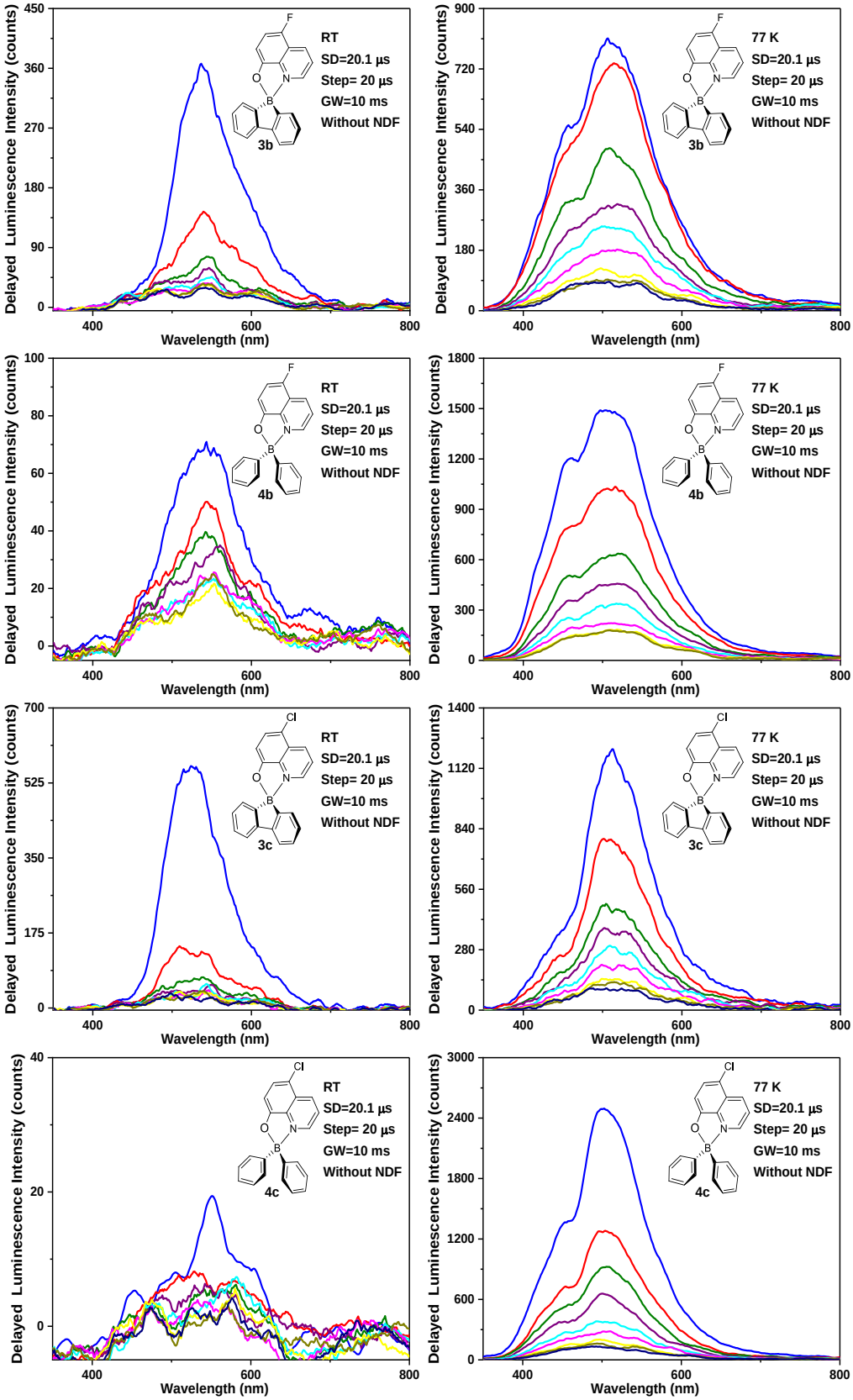


Figure S35 Transient emission spectra of complexes **3b**,**c** and **4b**,**c** in ZEONEX 480R films (1% wt) at room temperature (*ca.* 293 K) (left) and at 77 K (right). All spectra were recorded with a start delay (SD) of 20.1 µs (blue curve) and recorded every 20 µs (Step), with the use of a large gate width (GW=10 ms).

Electroluminescent devices

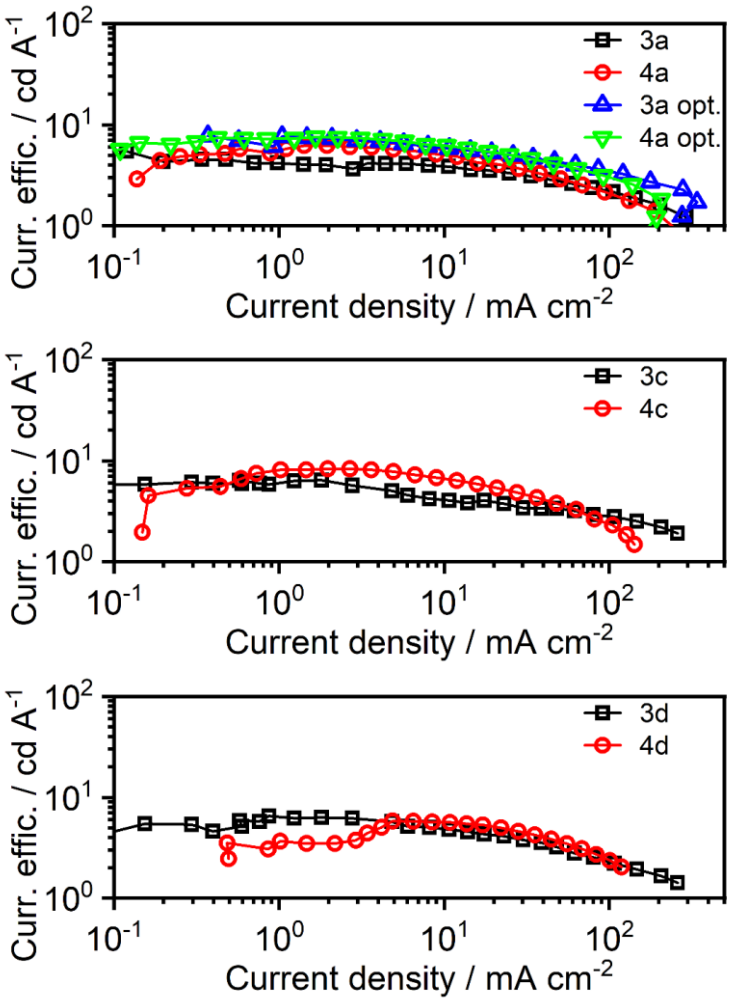


Figure S36 Characteristics of OLED devices: current efficiency *vs*. current density.

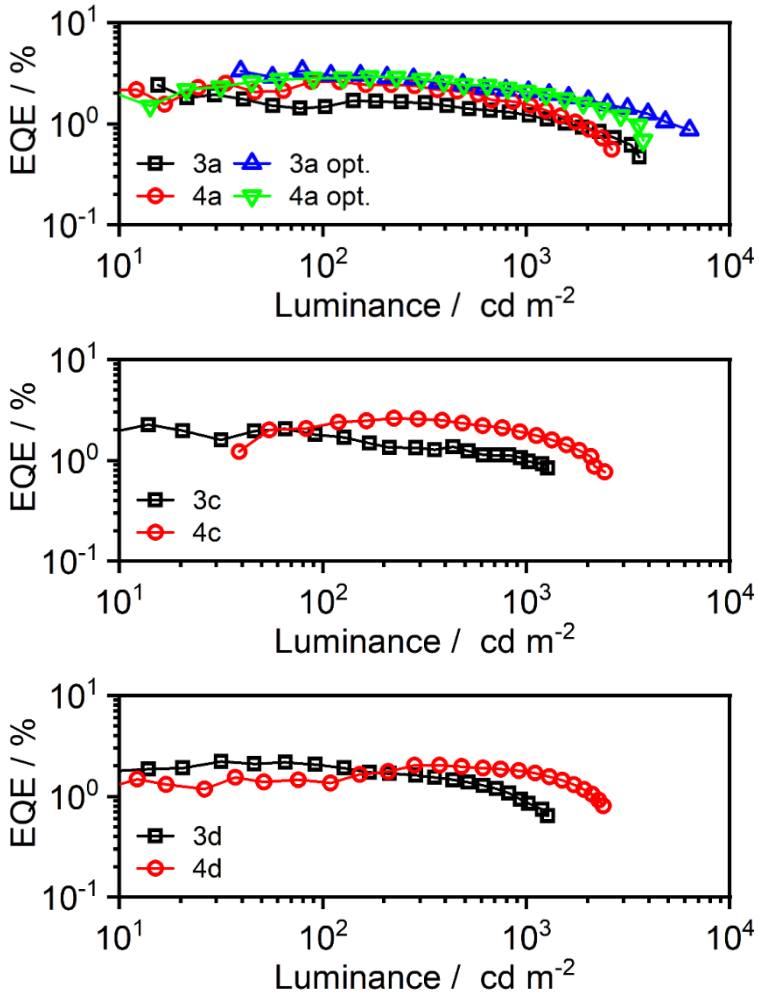


Figure S37 Characteristics of OLED devices: external quantum efficiency (EQE) *vs.* luminance.

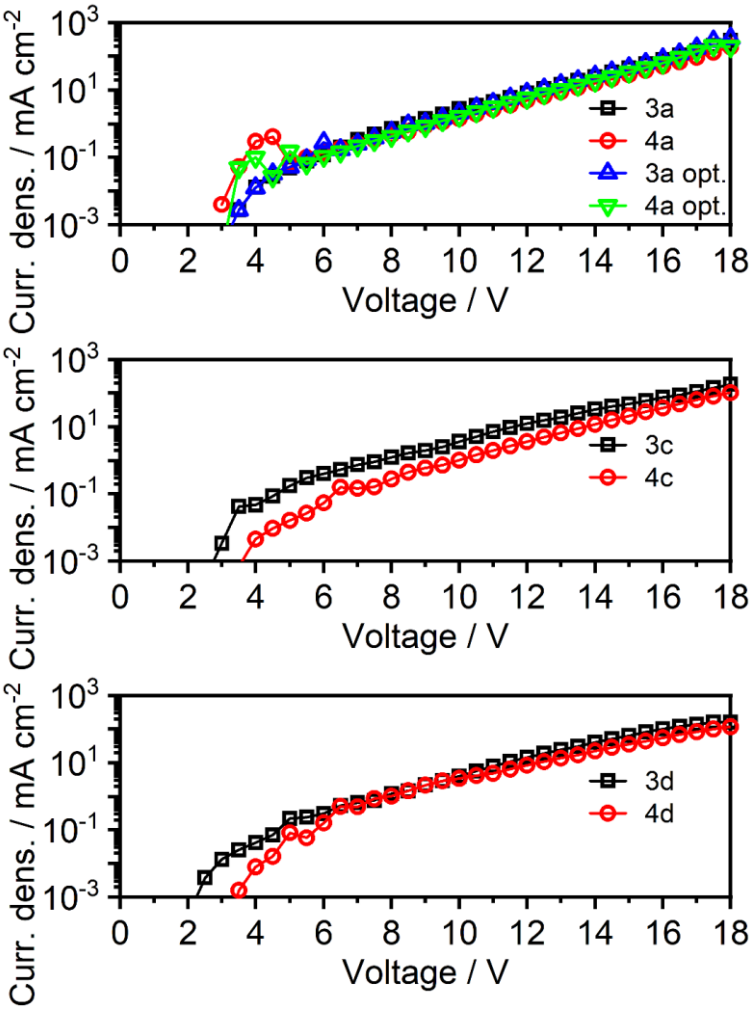


Figure S38 Characteristics of OLED devices: current density *vs.* voltage.

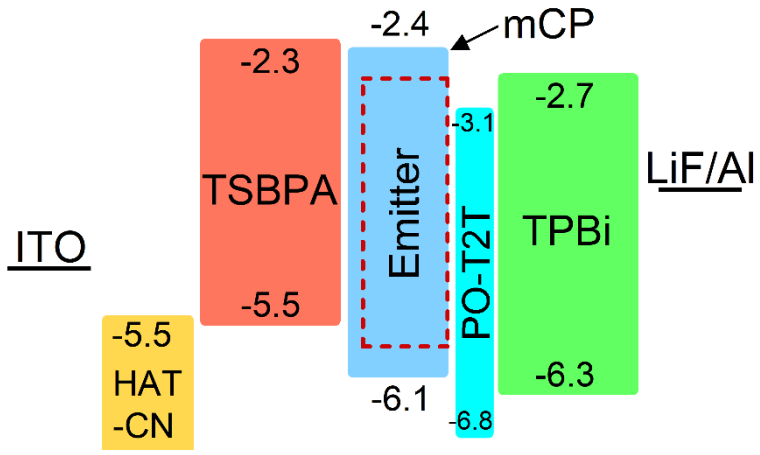


Figure S3839 Graphical representation of the architecture of OLEDs **3a**, **3c**, **3d**, **4a**, **4c**, and **4d**: ITO | HAT-CN (10 nm) | TSBPA (40 nm) | mCP (2 nm) | mCP co 10% **emitter** (20 nm) | PO-T2T (5 nm) | TPBi (40 nm) | LiF (0.8 nm) | Al (100 nm). Numerical values represent the HOMO (bottom) and LUMO (top) energy of the respective molecule.

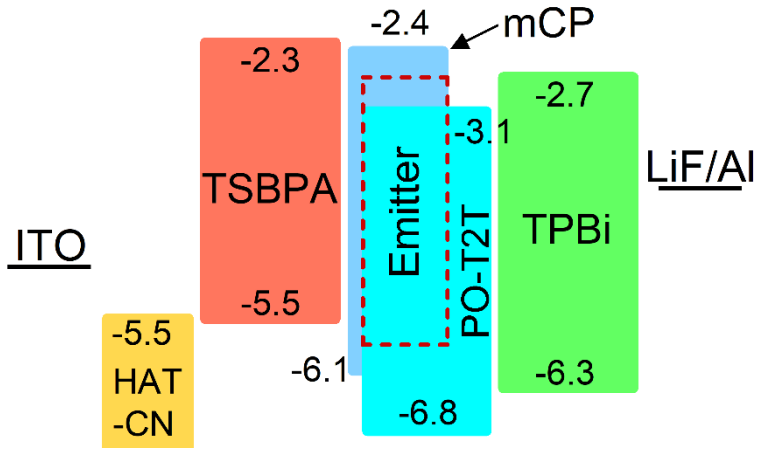


Figure S40 Graphical representation of the architecture of OLEDs **3a opt.** and **4a opt.**: ITO | HAT-CN (10 nm) | TSBPA (40 nm) | mCP (2 nm) | mCP:PO-T2T (80:20) co 10% **emitter** | PO-T2T (5 nm) | TPBi (40 nm) | LiF (0.8 nm) | Al (100 nm). Numerical values represent the HOMO (bottom) and LUMO (top) energy of the respective molecule.