Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
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Synthesis, properties and reactivity of BCl_2 aza-BODIPY complexes and salts of the aza-dipyrrinato scaffold

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Supplementary Information

Contents

Supporting Experimental Data

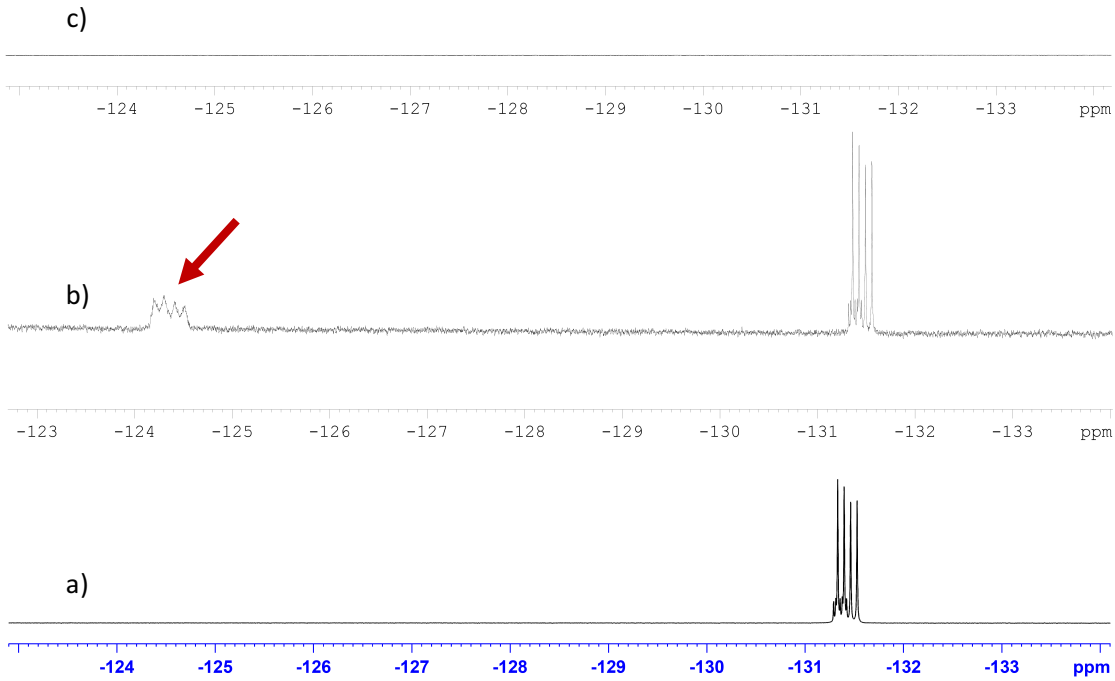


Figure S1. ^{19}F NMR spectra of **2** treated with a) 0 equiv BCl_3, b) 0.5 equiv BCl_3 and c) 1 equiv BCl_3. Note the appearance of a new signal around -124 ppm that suggests the presence of an F-B-Cl BODIPY intermediate in the halogen exchange of **2** to **3**.

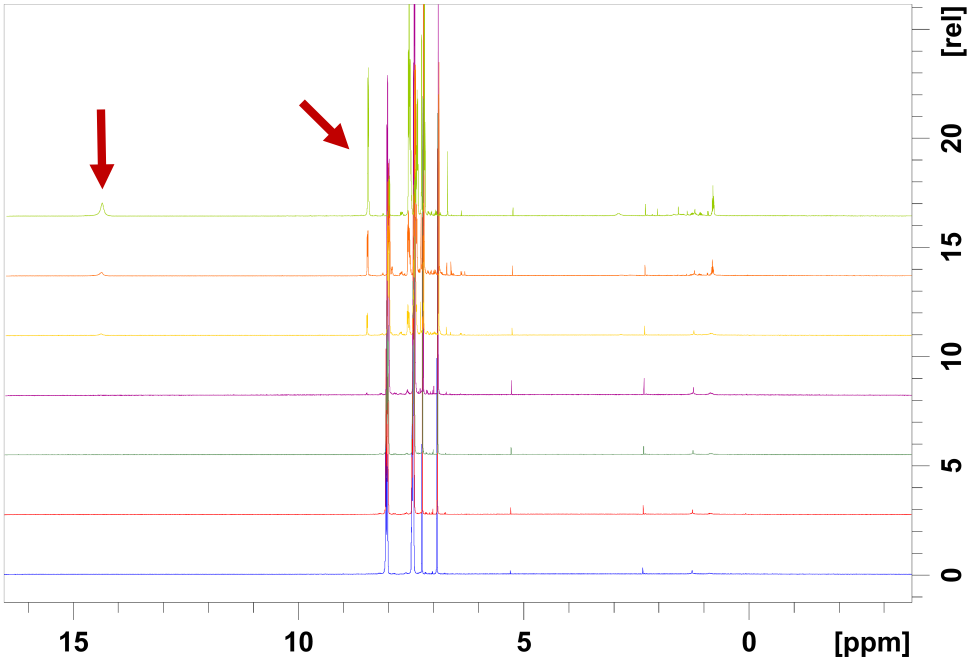


Figure S2. ^{1}H NMR spectra tracking the decomposition of **3** when exposed to ambient atmosphere. Bottom to top: before opening; immediately after opening; 30 min; 1 hour; 2 hours; 12 hours; 3 days. Note the appearance of signals at 14.4 and 8.5 ppm as decomposition progresses.

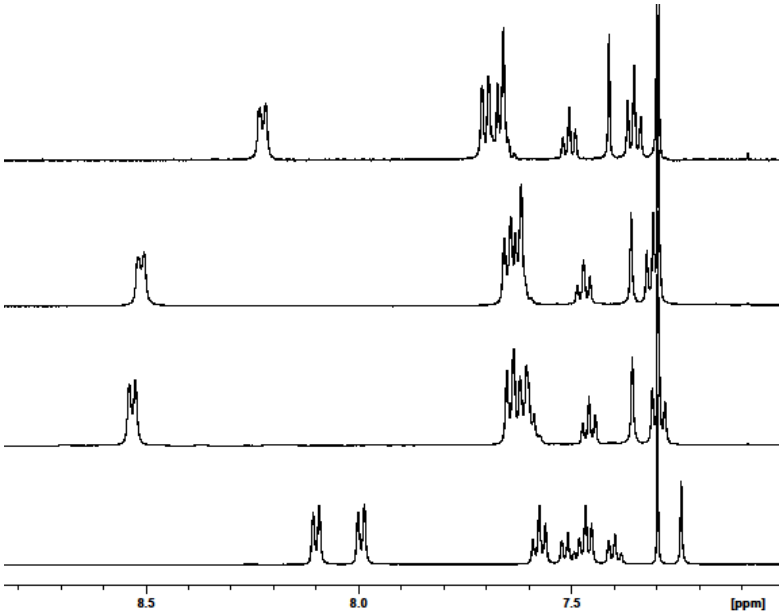
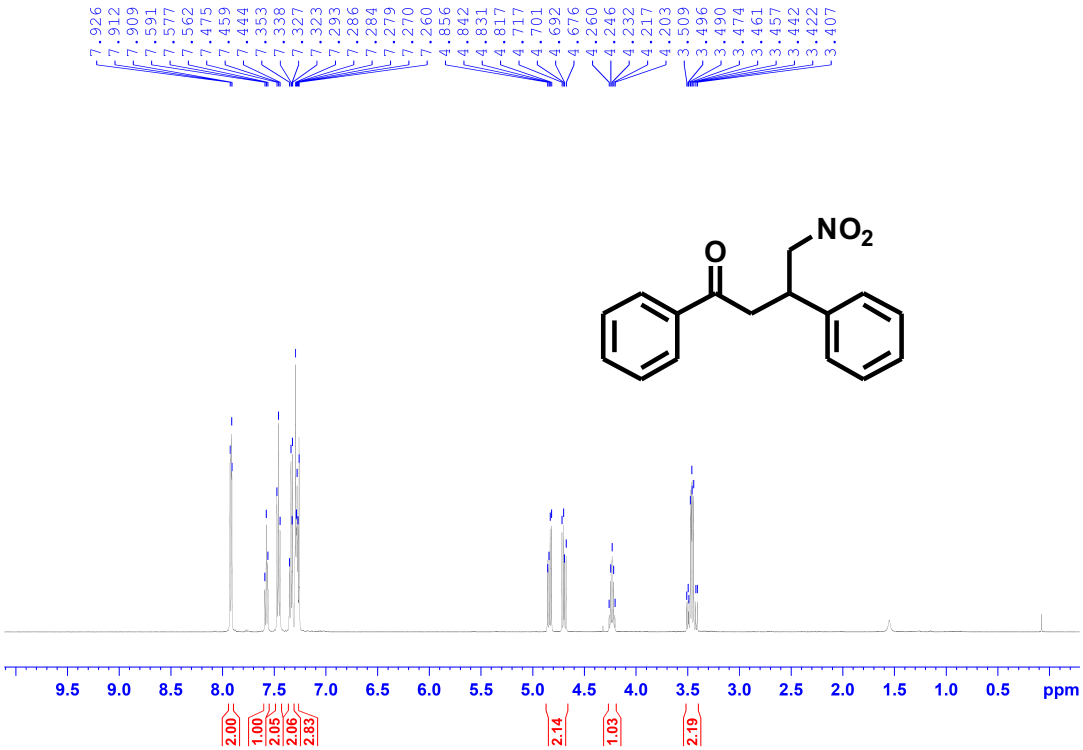


Figure S3. ^{1}H NMR (aromatic region) of **1** and its salts. Bottom to top: **1**, **1HCl**, **1HBr**, and **1HBF$_4$**. Note the simplification of signal patterns upon protonation (i.e. **1** cf. **1HX**).

Nuclear Magnetic Resonance Spectra

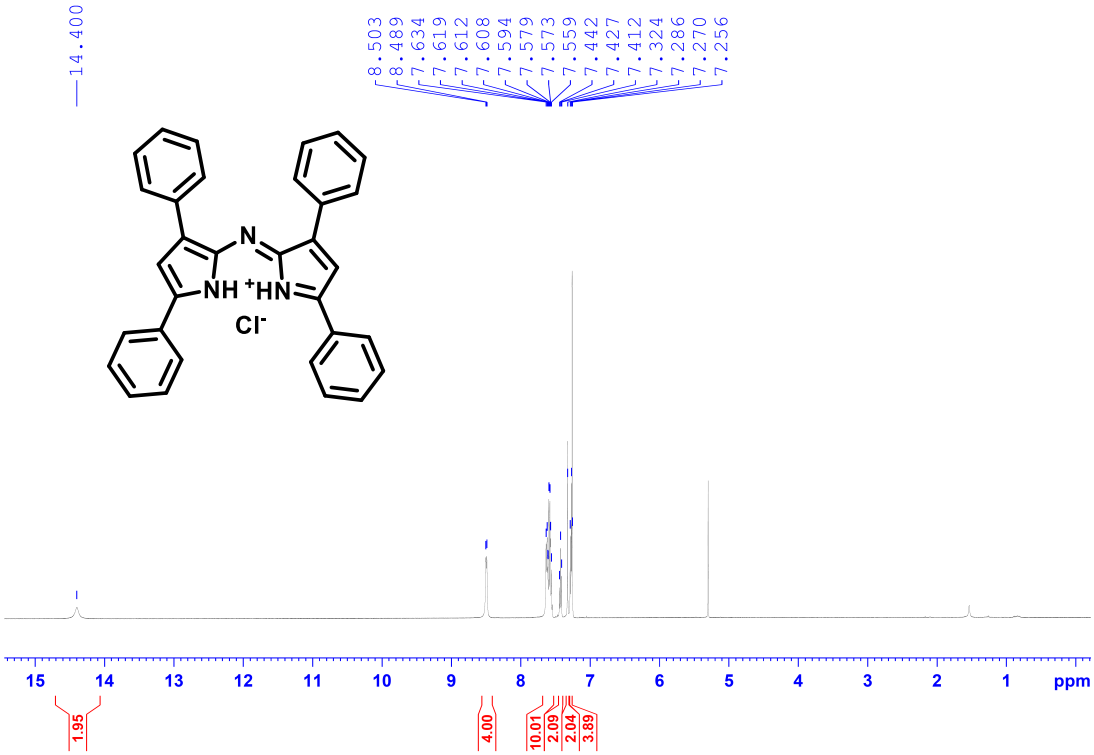
4-Nitro-1,3-diphenyl-1-butanone

^{1}H NMR ($CDCl_3$, 500 MHz)

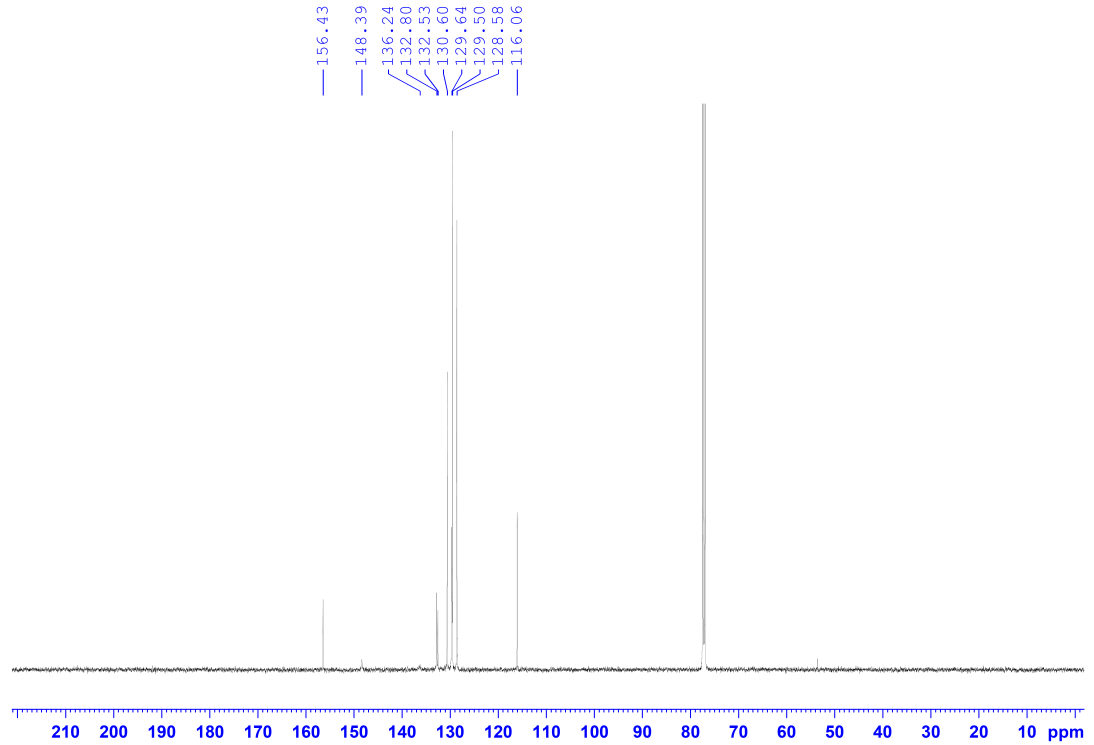


N-(3,5-Diphenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine hydrochloride (1HCl)

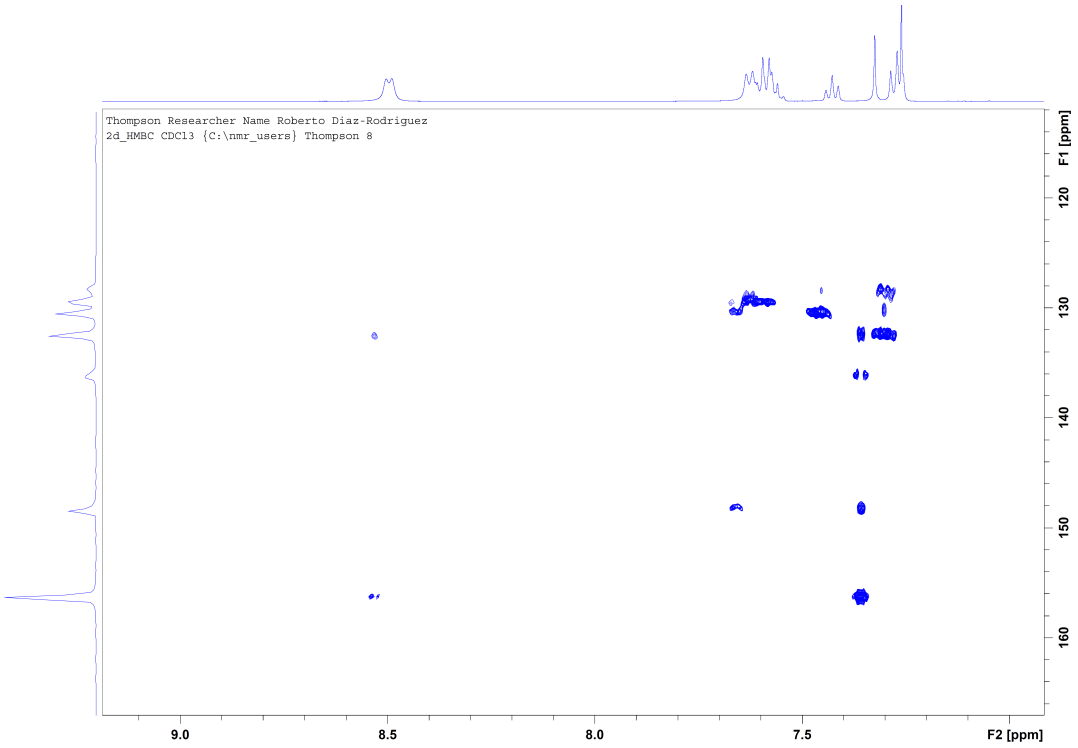
^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz); two signals not observed

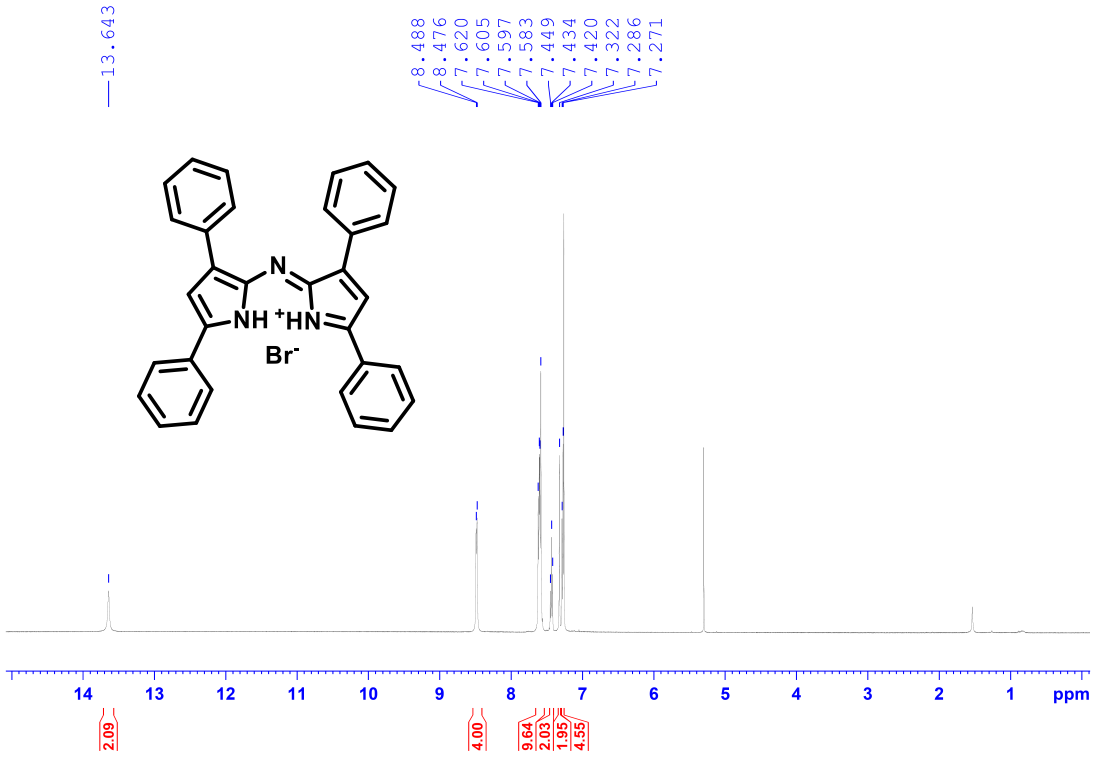


2D HMBC NMR ($CDCl_3$, 126/500 MHz); internal projection in F1 shown

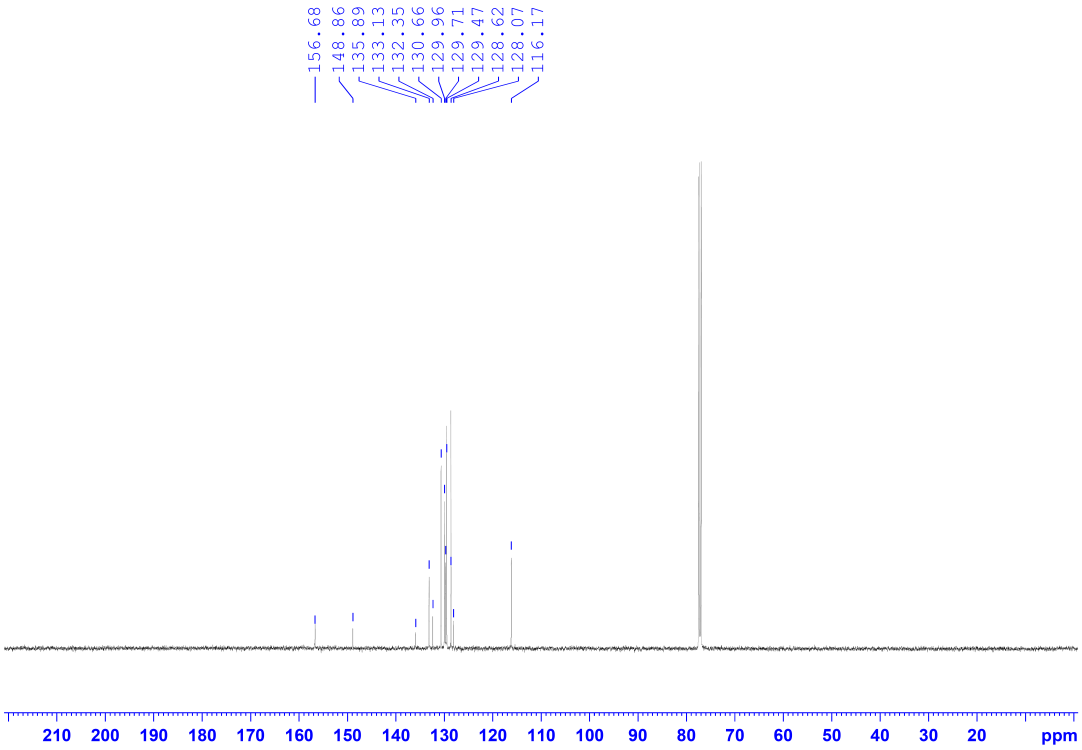


_N_-(3,5-Diphenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine hydrobromide (1HBr)

^{1}H NMR ($CDCl_3$, 500 MHz)

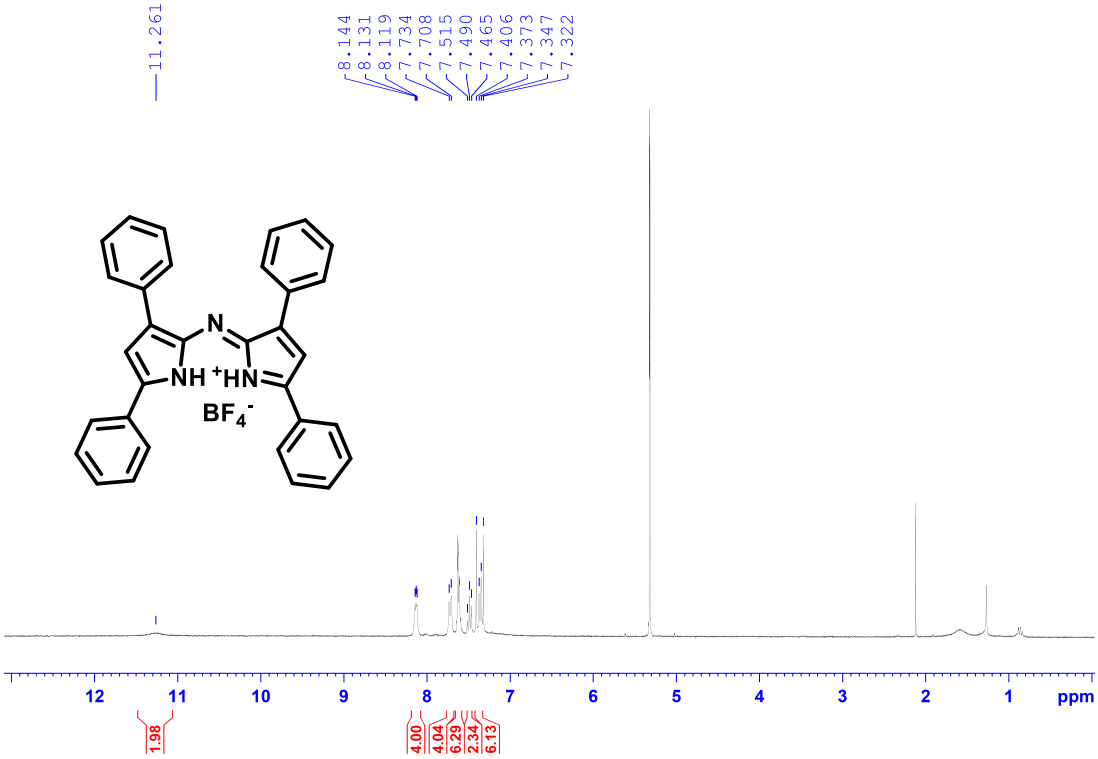


^{13}C NMR ($CDCl_3$, 126 MHz)

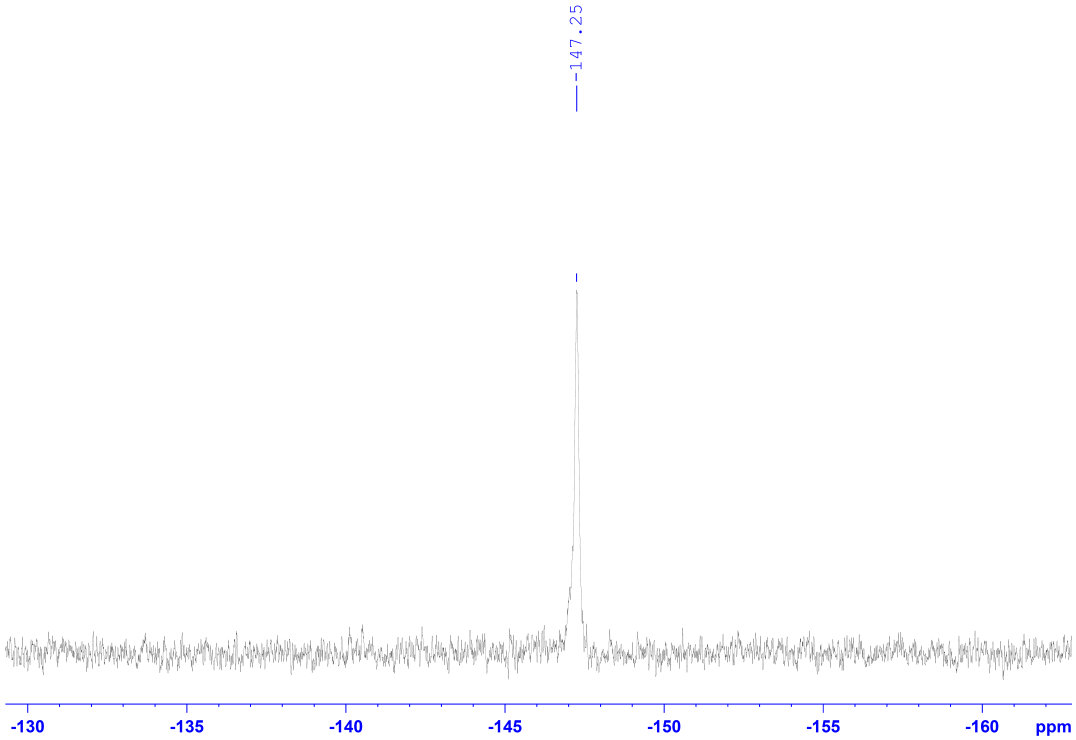


_N_-(3,5-Diphenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine hydrofluoroborate (1HBF$_4$)

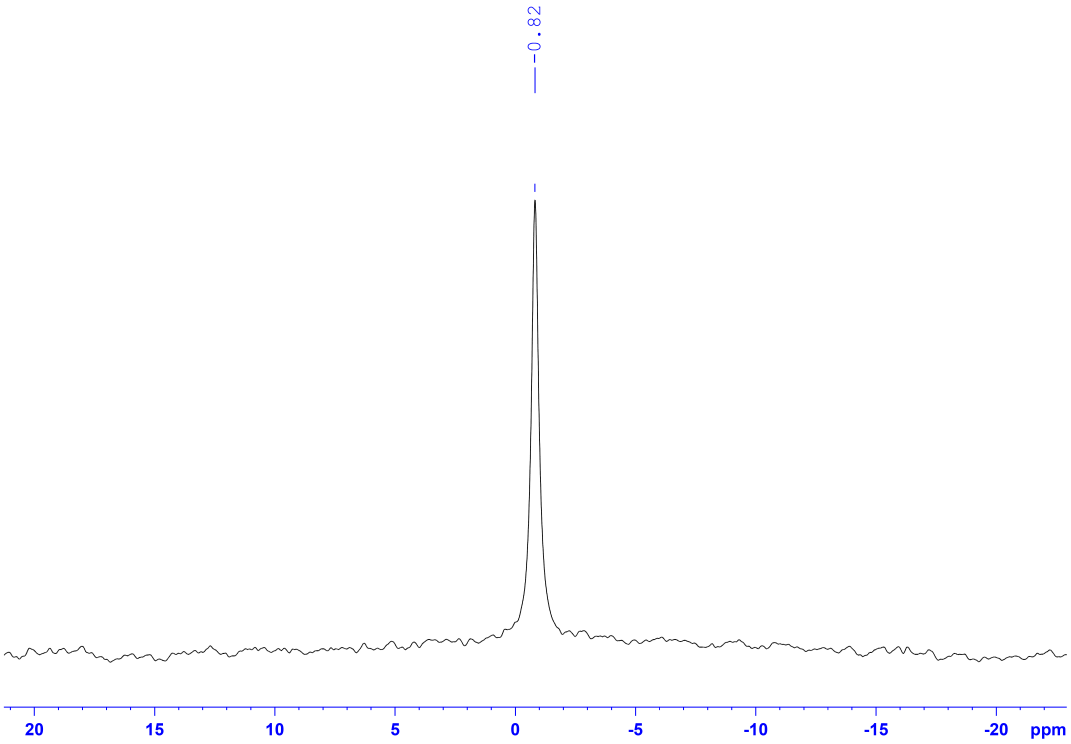
^{1}H NMR (CD_2Cl_2, 300 MHz)



^{19}F NMR (CD_2Cl_2, 282 MHz)

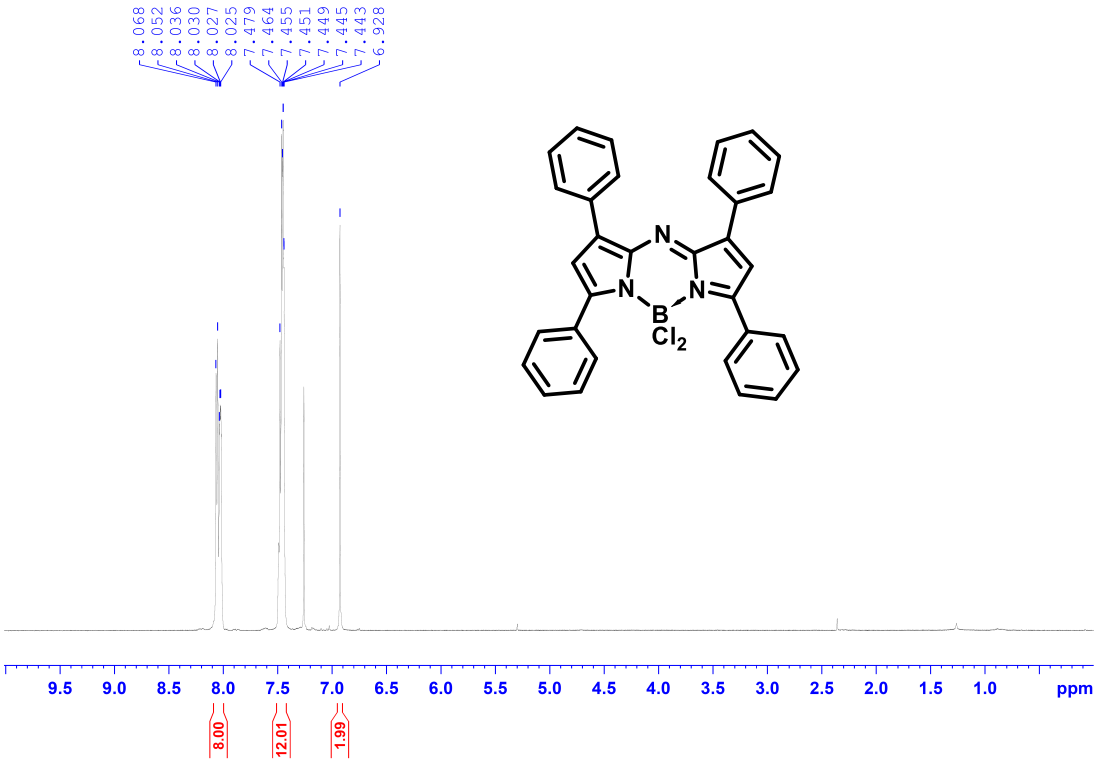


^{11}B NMR (CD_2Cl_2, 96 MHz)

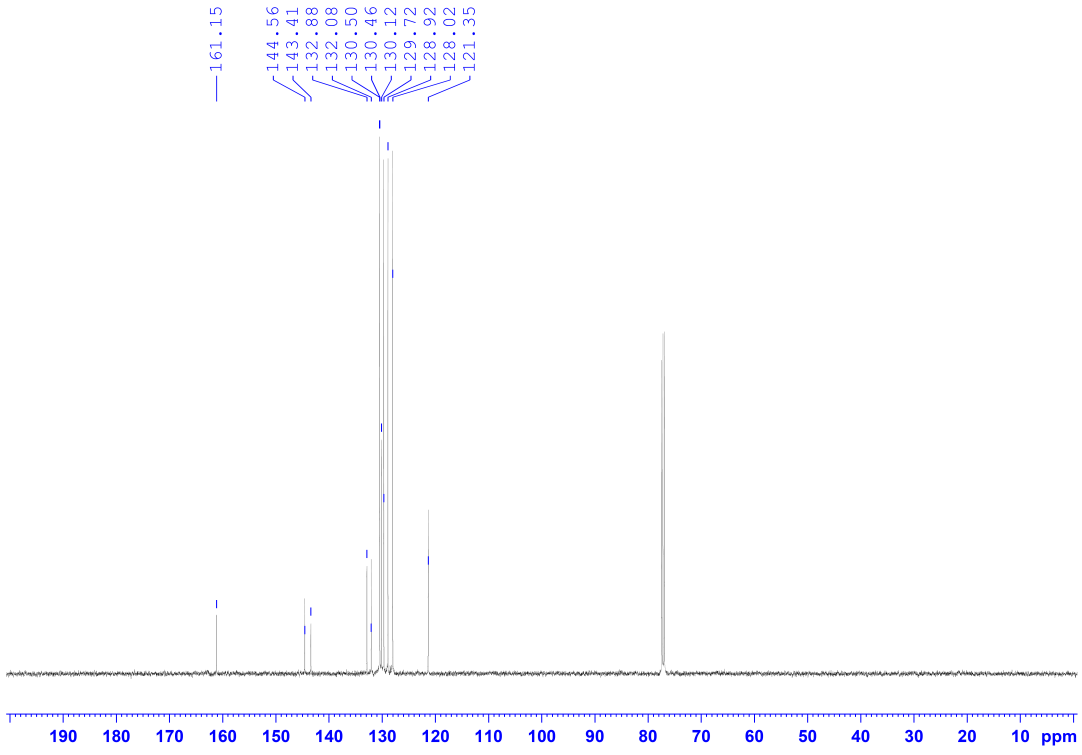


4,4-Dichloro-1,3,5,7-tetraphenyl-4-bora-3a,4a,8-triaza-s-indacene (3)

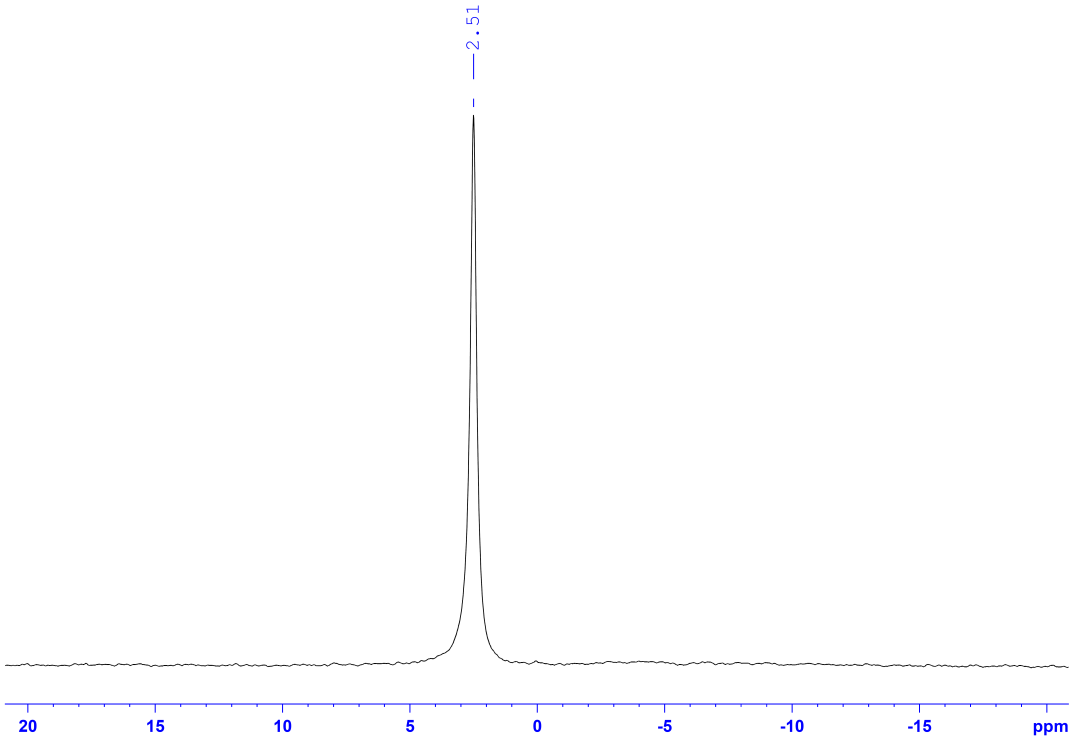
^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz)

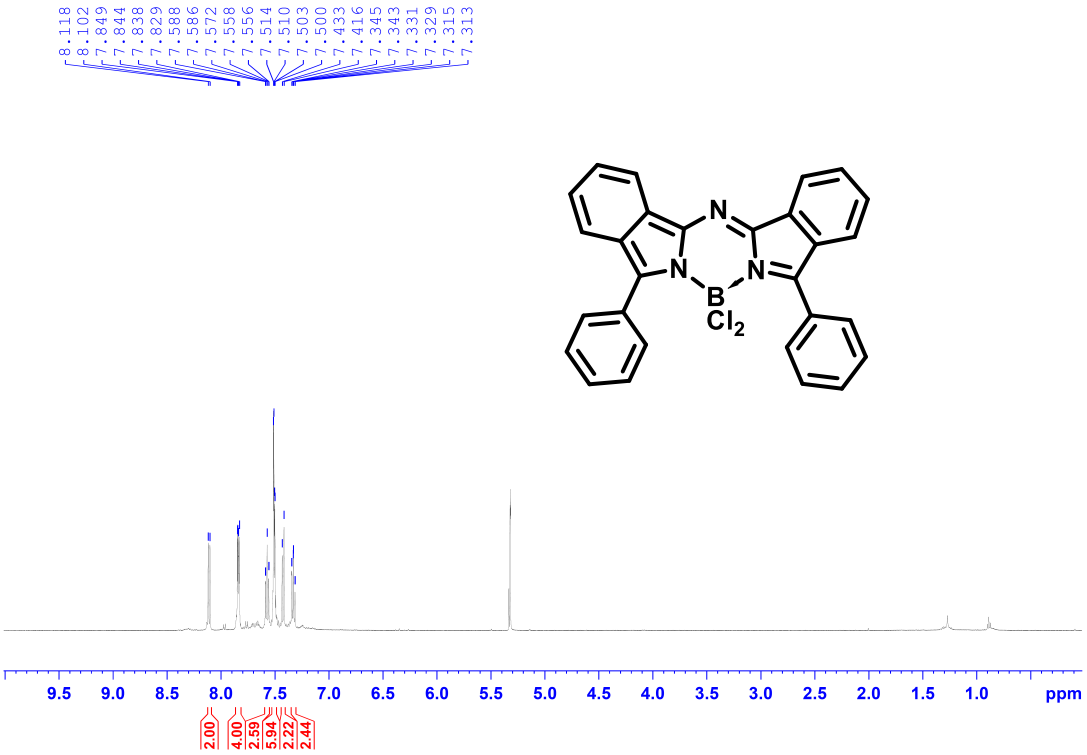


^{11}B NMR ($CDCl_3$, 160 MHz)

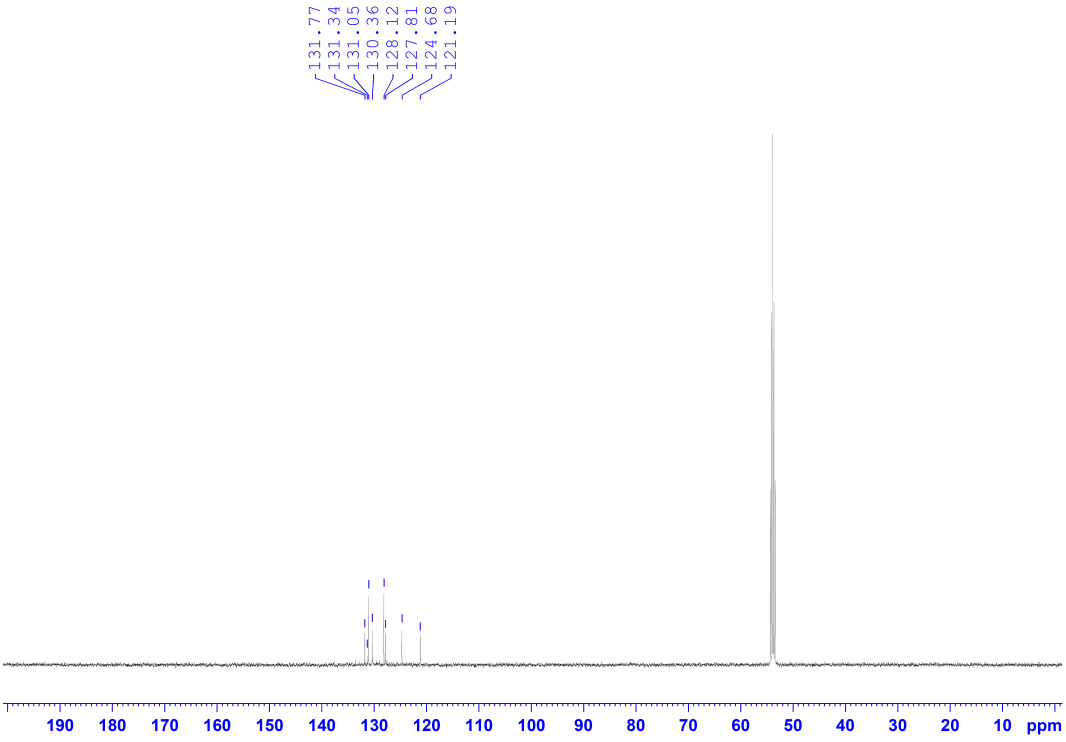


N,N-Dichloroboryl-[N-(3-phenyl-2H-isoindol-1-yl)-N-(3-phenyl-1H-isoindol-1-ylidene)amine] (6)

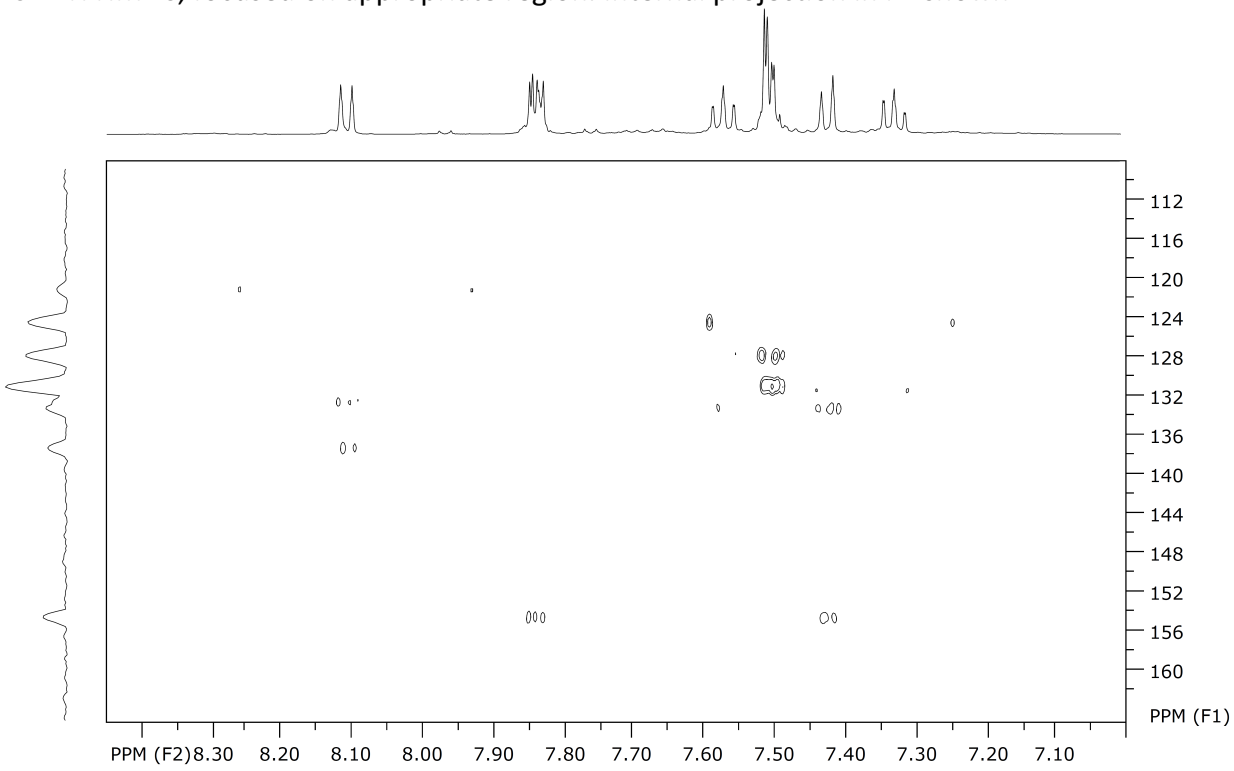
^{1}H NMR (CD_2Cl_2, 500 MHz)



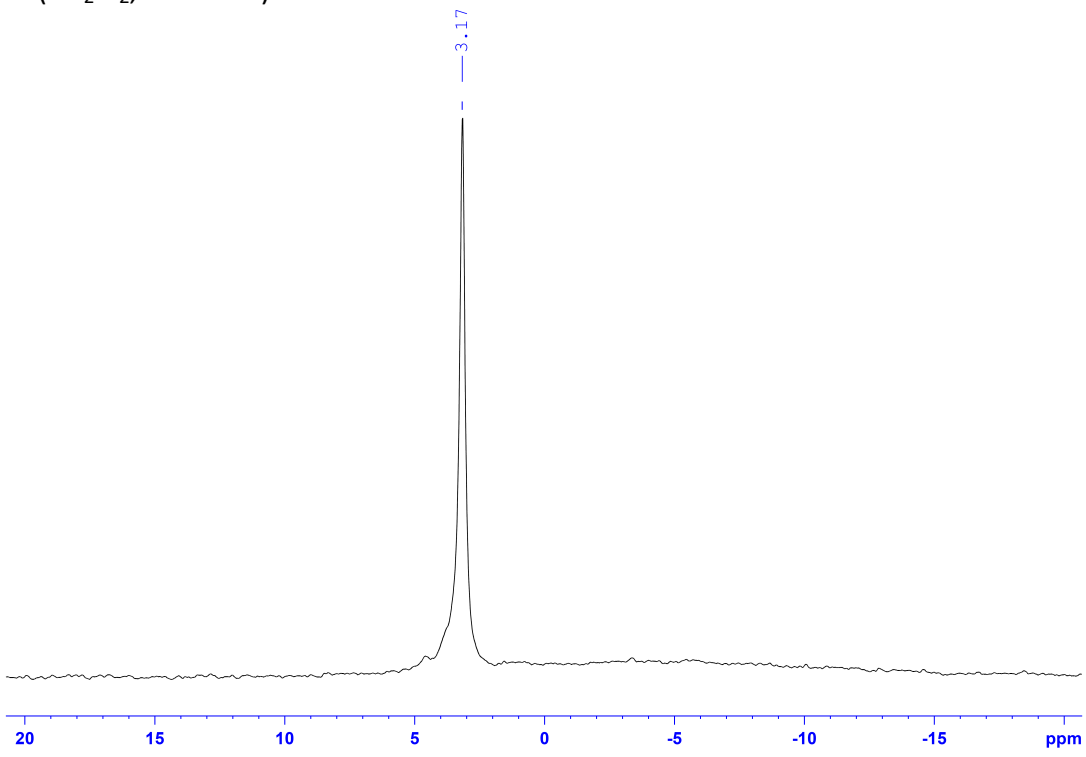
^{13}C NMR (CD_2Cl_2, 126 MHz); several signals do not appear on 1D spectrum



^{13}C – ^{1}H HMBC; focused on appropriate region. Internal projection in F1 shown

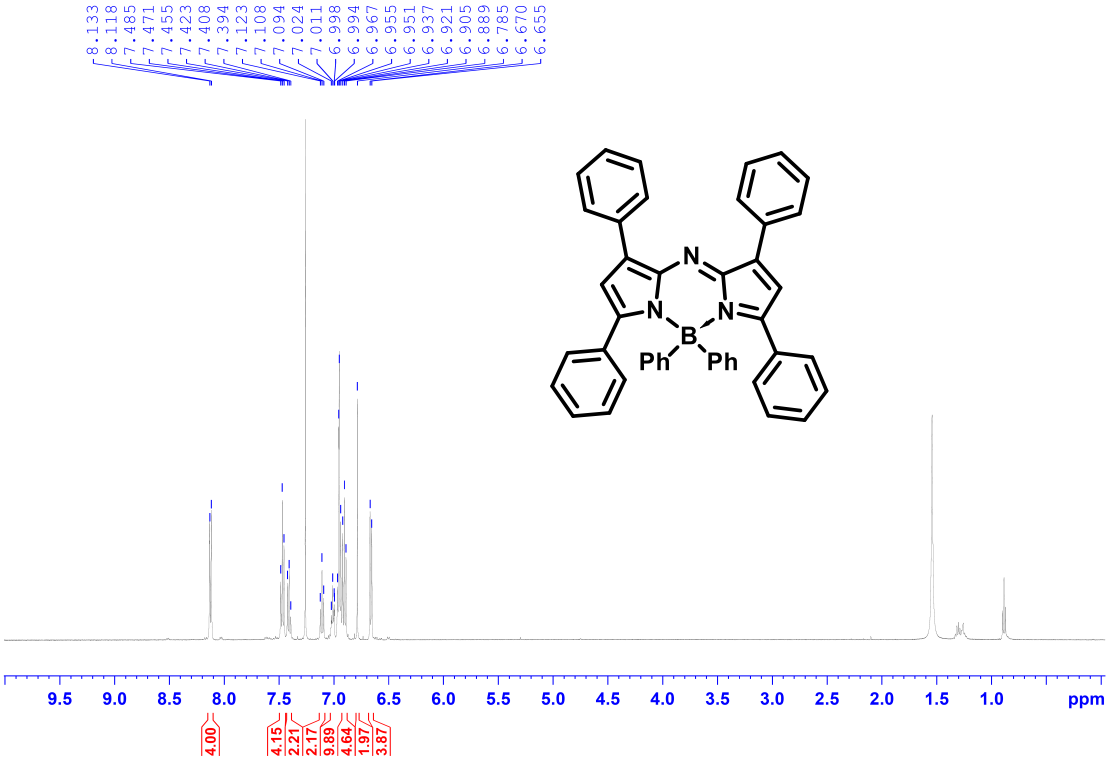


^{11}B NMR (CD_2Cl_2, 160 MHz)

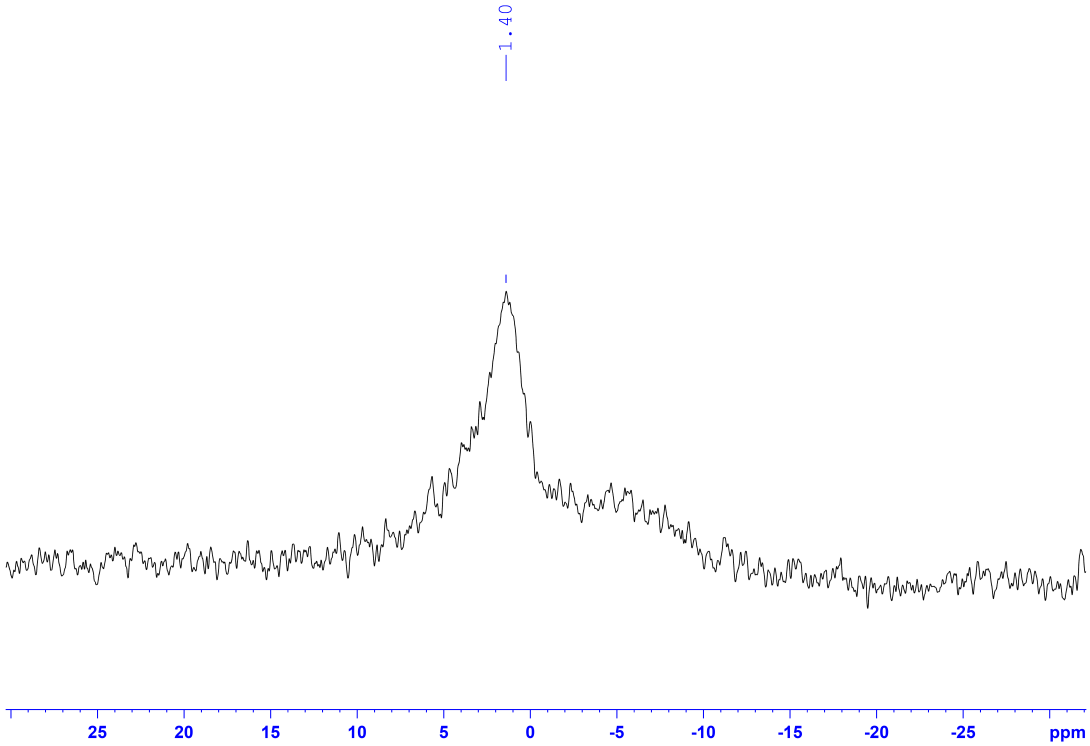


4,4-Diphenyl-1,3,5,7-tetraphenyl-4-bora-3a,4a,8-triaza-s-indacene (7a)

^{1}H NMR ($CDCl_3$, 500 MHz)

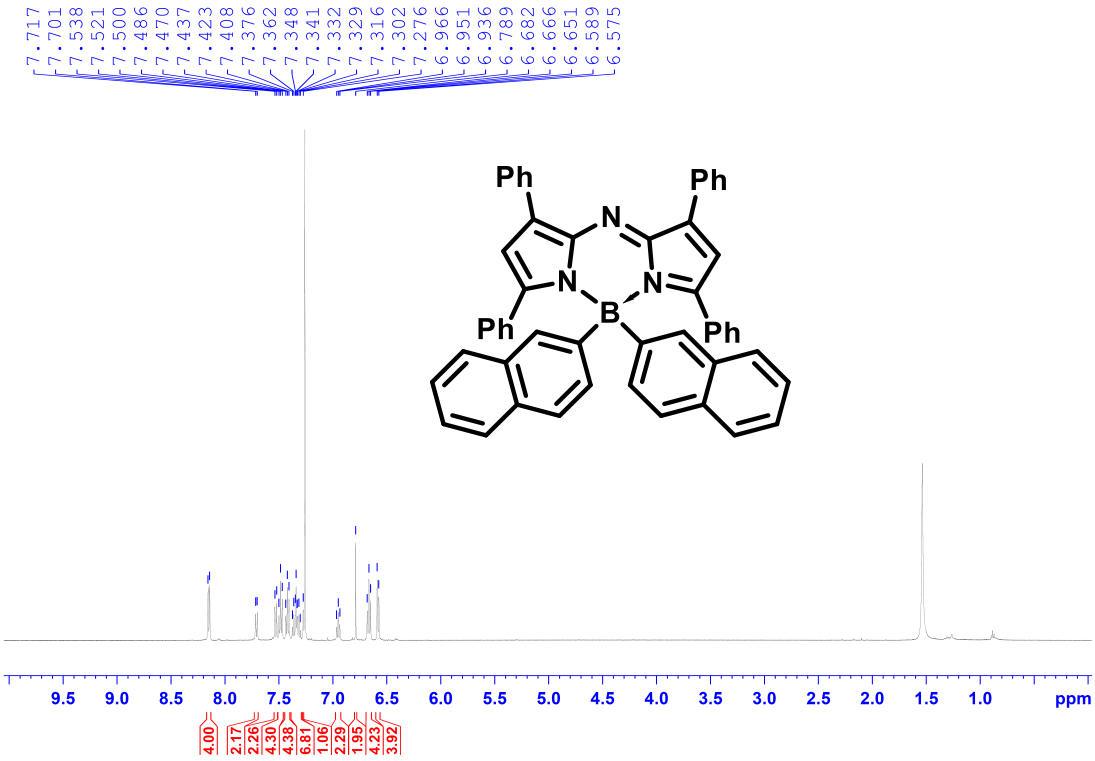


^{11}B NMR ($CDCl_3$, 160 MHz)

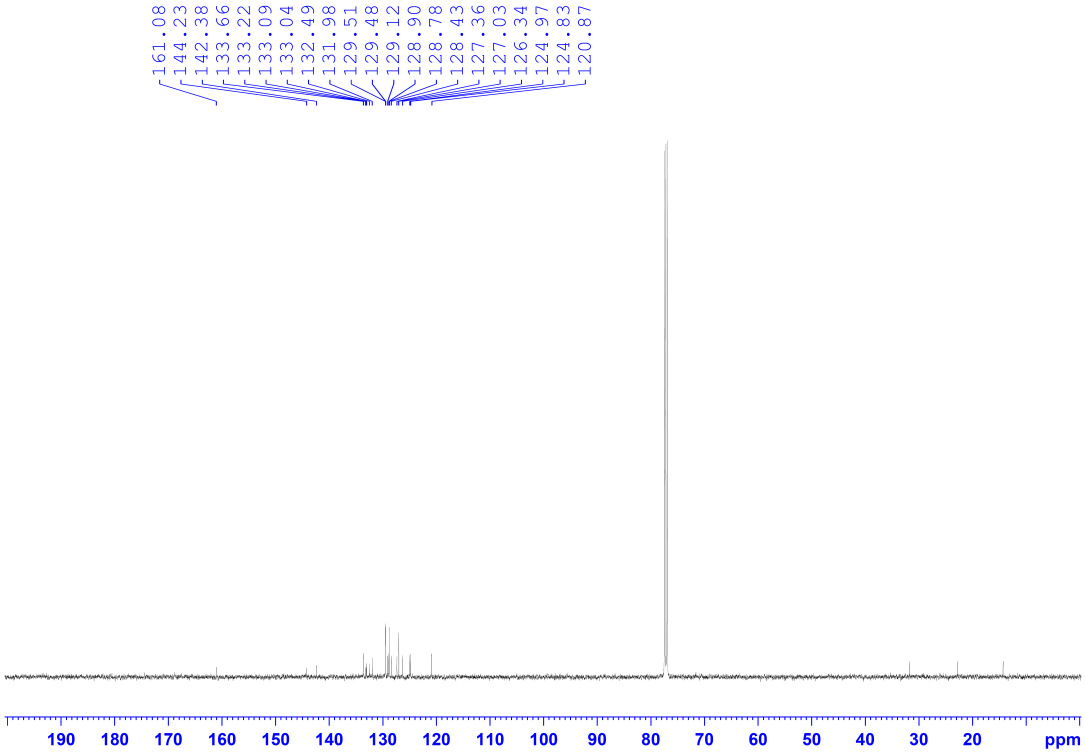


4,4-Dinaphthyl-1,3,5,7-tetraphenyl-4-bora-3a,4a,8-triaza-s-indacene (7b)

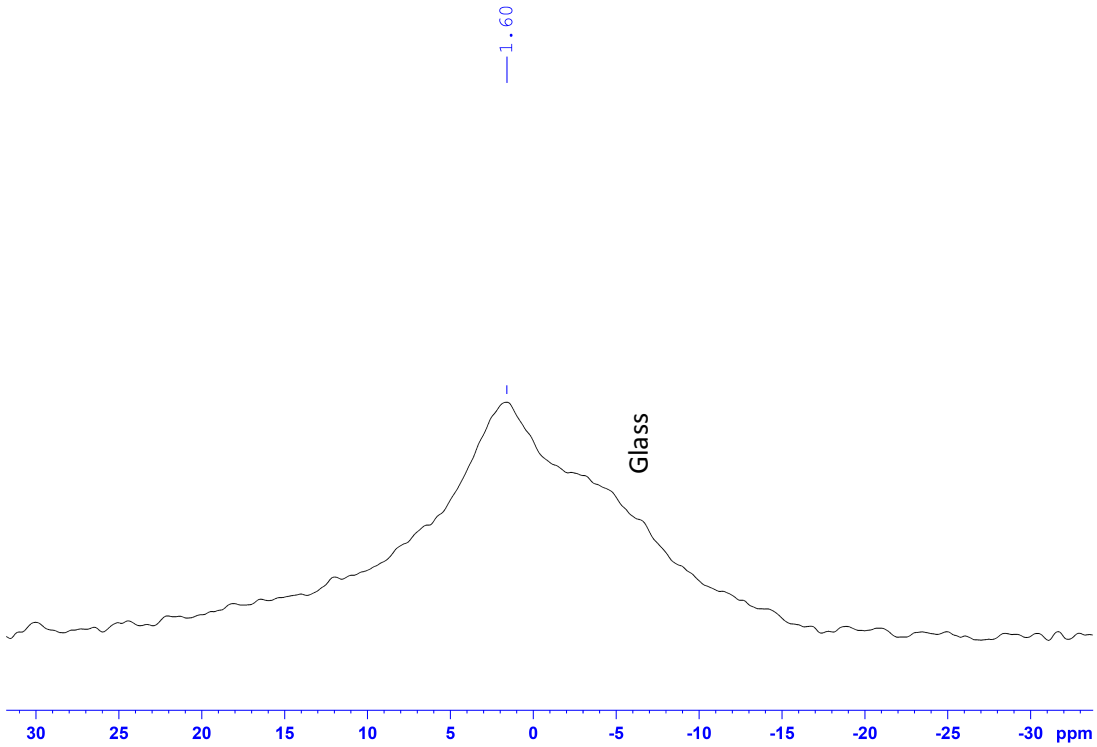
^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz)

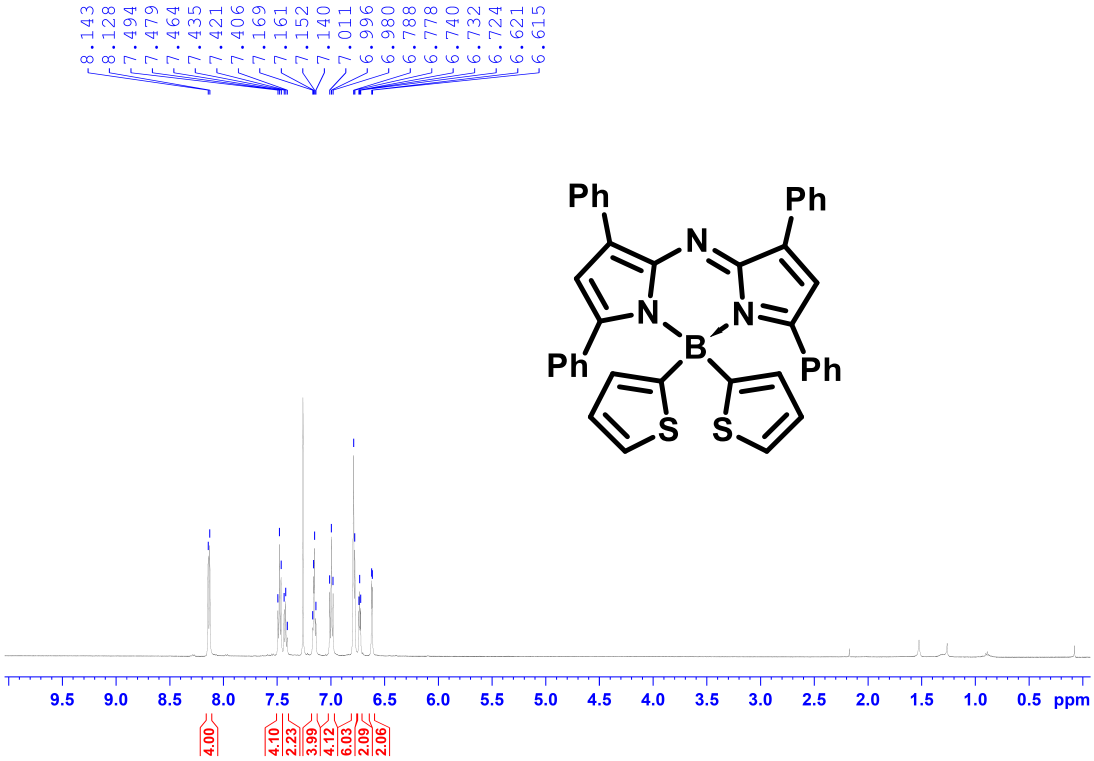


^{11}B NMR ($CDCl_3$, 160 MHz); S/N is poor due to quadrupolar broadening

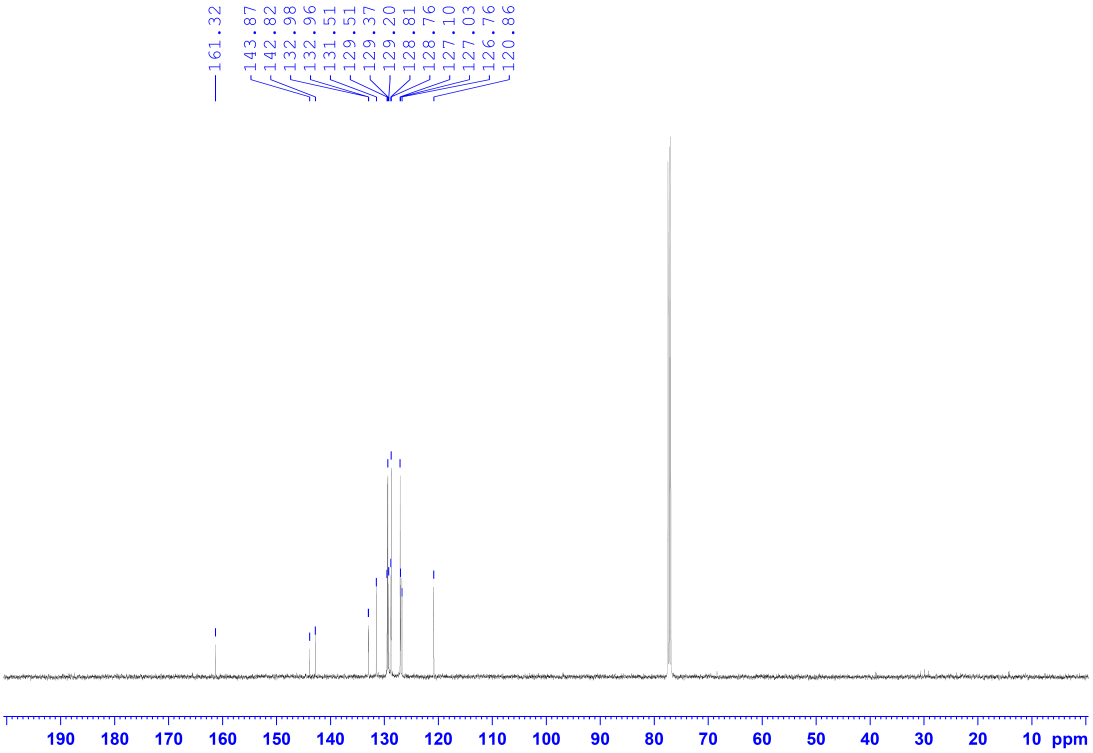


4,4-Dithienyl-1,3,5,7-tetraphenyl-4-bora-3a,4a,8-triaza-s-indacene (7c)

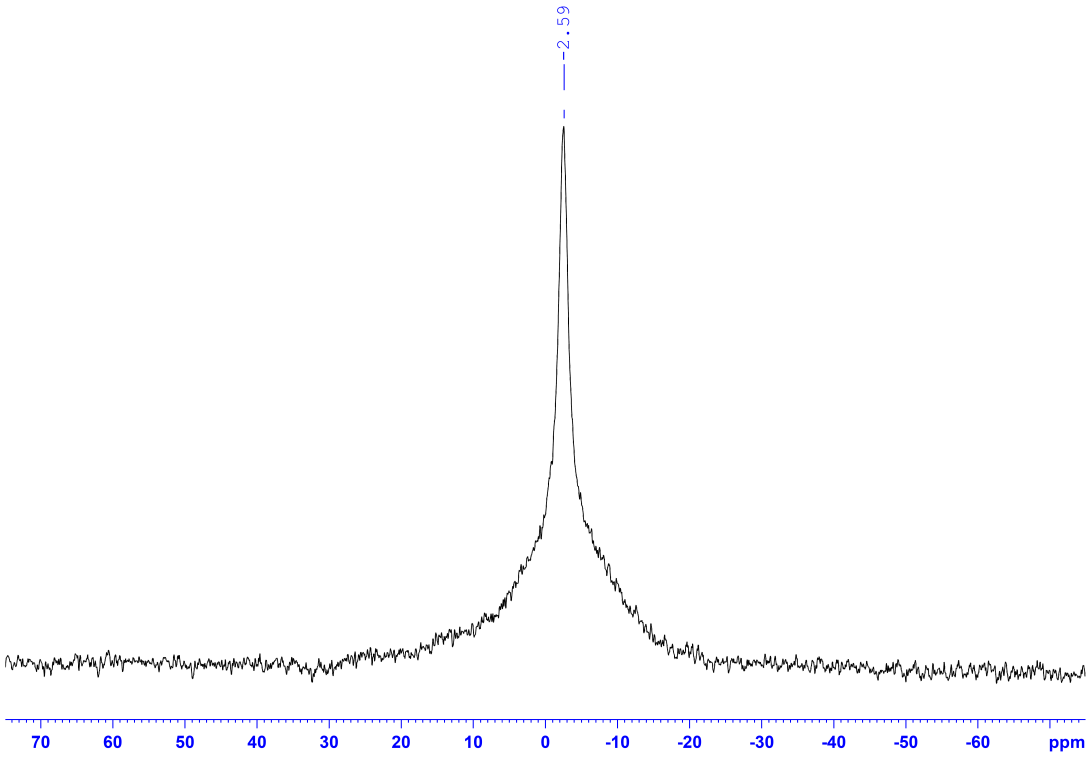
^{1}H NMR ($CDCl_3$, 500 MHz)



^{13}C NMR ($CDCl_3$, 126 MHz)

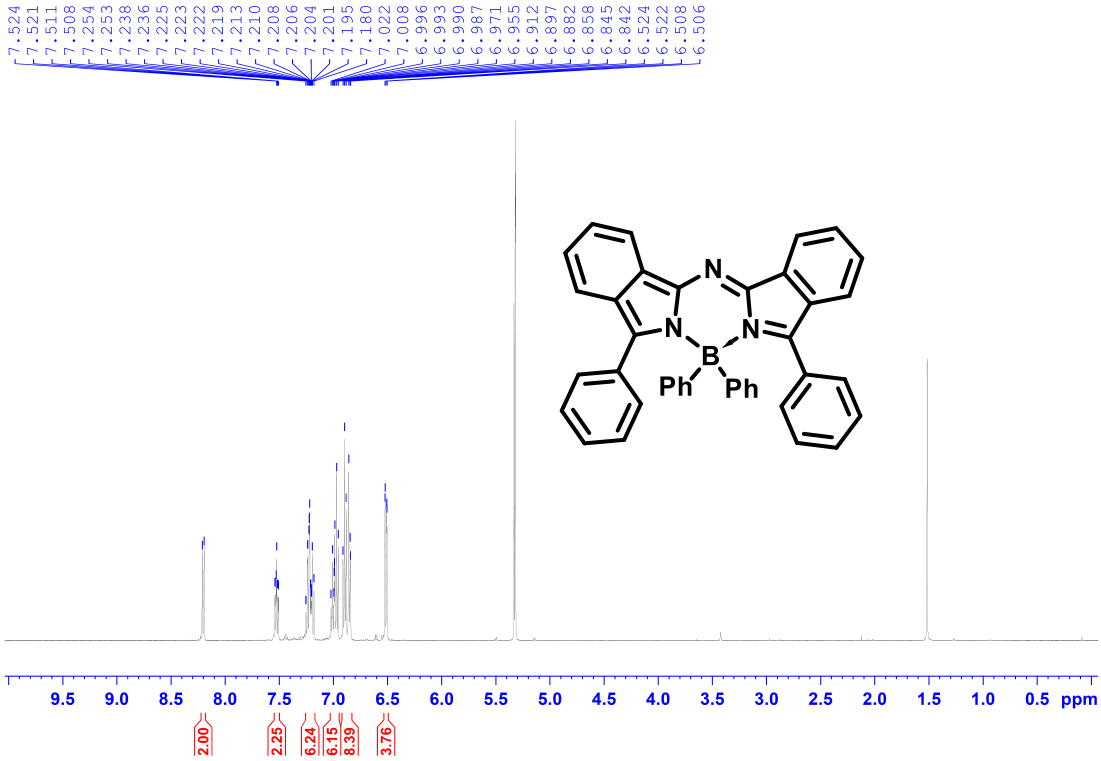


^{11}B NMR ($CDCl_3$, 160 MHz)

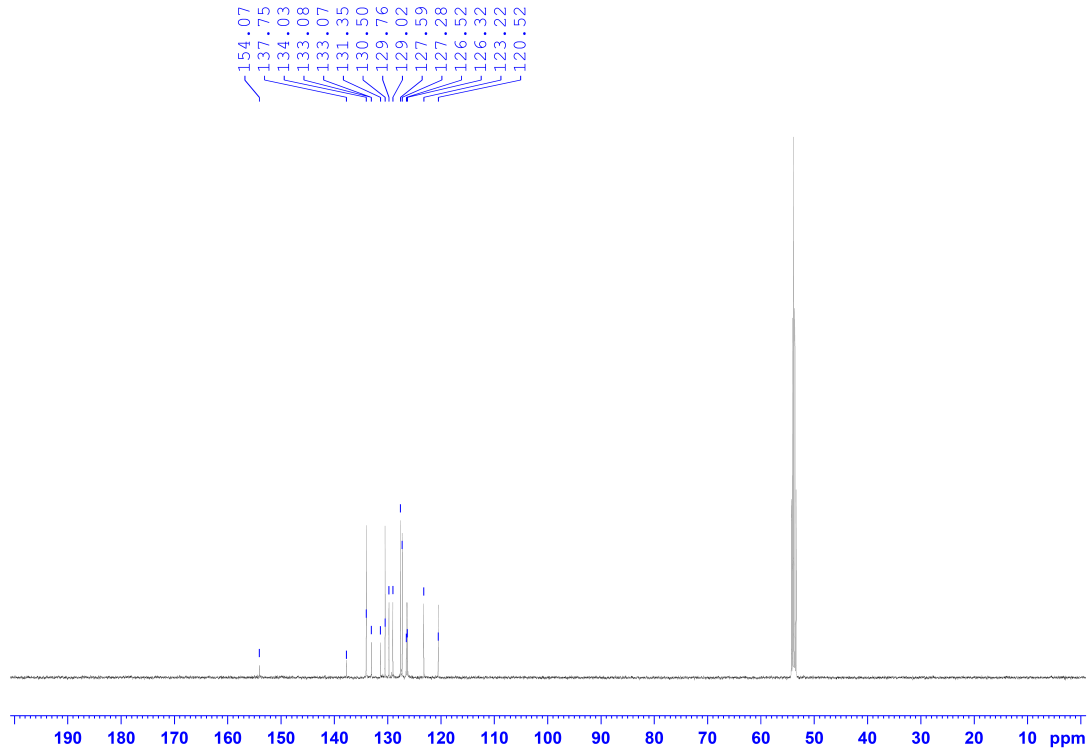


N,N-Diphenylboryl-[N-(3-phenyl-2H-isoindol-1-yl)-N-(3-phenyl-1H-isoindol-1-ylidene)amine] (8)

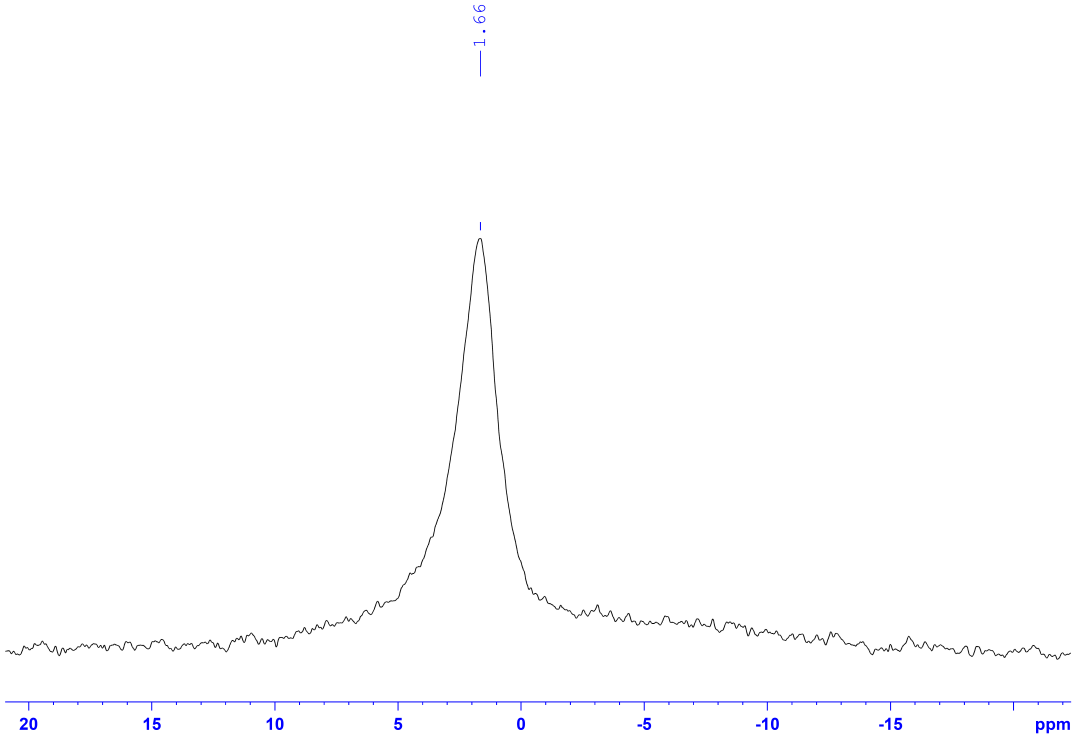
^{1}H NMR (CD_2Cl_2, 500 MHz)



^{13}C NMR (CD_2Cl_2, 126 MHz)



^{11}B NMR (CD_2Cl_2, 160 MHz)



Crystallographic Data

The crystals chosen for data collection were attached to the tip of a 200 µm MicroLoop with paratone-N oil. Measurements were made on a CCD-equipped diffractometer (30 mA, 50 kV) using monochromated Mo Kα radiation (λ = 0.71073 Å) at 125 K.[2] The initial orientations and unit cells were indexed using a least-squares analysis of a random set of reflections collected from three series of 0.5° ω-scans, 10 seconds per frame and 12 frames per series, that were well distributed in reciprocal space. For data collection, four ω-scan frame series were collected with 0.5° wide scans, 60 second frames and 366 frames per series at varying ϕ angles (ϕ = 0°, 90°, 180°, 270°). Compounds **1HCl** and **1HBF$_4$** required only 20 seconds per frame. The crystal to detector distance was set to 6 cm and a complete sphere of data was collected. Cell refinements and data reductions were performed with the Bruker SAINT[3] software, which corrects for beam inhomogeneity, possible crystal decay, Lorentz and polarisation effects. A multi-scan absorption correction was applied in each case (SADABS).[4] The structures were solved using SHELXT-2014[5, 6] and were refined using a full-matrix least-squares method on F^2 with SHELXL-2014.[5, 6] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon were included at geometrically idealised positions and were not refined. The isotropic thermal parameters of the hydrogen atoms were fixed at 1.2U_{eq} of the parent carbon atom or 1.5U_{eq} for methyl hydrogens. The H(N) hydrogen atoms, if present, were allowed to refine isotropically. If necessary, a weak restraint was placed on the N-H bond length.

In the final refinement of compound **1HBr** enhanced rigid body restraints were applied over the entire molecule, using the RIGU command in SHELXL,[5, 6] to make the orientations of the atomic displacement parameters more reasonable.

The crystal structures of compounds **1HCl**, **1HBr** and **1HBF$_4$** were all found to incorporate dichloromethane solvent from the crystallisation media. In the two former cases there was one half a solvent molecule in the asymmetric unit (or one molecule of solvent for each two cation/anion pairs) while in the latter case, one dichloromethane solvent molecule was found in the asymmetric unit (or one molecule of solvent for each cation/anion pair). In **1HBF$_4$** the solvent was not disordered and was well-behaved during the refinement. In **1HCl** and **1HBr** the solvent is disordered across the inversion centers of the unit cell. In **1HCl** it is well-behaved and did not have to be restrained during the refinement. In **1HBr** the C-Cl bond lengths were restrained to be approximately equal during the refinement.

All diagrams were prepared using the program Mercury CSD 3.7.[7] The data has been deposited with the Cambridge Crystallographic Data Centre. The deposition numbers for each compound are given in Table S1.

Table S1: Crystal data and structure refinement details.

Identification code	**1HCl**	**1HBr**	**1HBF4**	**6**	**8**
CCDC deposit number	1955378	1955377	1955376	1955379	1955380
Empirical formula	$C_{65}H_{50}Cl_4N_6$	$C_{65}H_{50}Br_2Cl_2N_6$	$C_{33}H_{26}BCl_2F_4N_3$	$C_{28}H_{18}BCl_2N_3$	$C_{46}H_{34}BN_3$
Formula weight	1056.91	1145.83	622.28	478.16	639.57
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
Unit cell dimensions (Å and º)	*a* = 9.4100(3)	*a* = 9.429(2)	*a* = 10.2647(3)	*a* = 9.965(2)	*a* = 10.9702(11)
	b = 10.4509(4)	*b* = 10.505(3)	*b* = 11.6265(4)	*b* = 10.359(3)	*b* = 12.8749(13)
	c = 13.6039(5)	*c* = 13.733(3)	*c* = 13.2263(4)	*c* = 11.761(3)	*c* = 13.9596(14)
	α = 73.214(2)	*α* = 72.898(3)	*α* = 74.145(2)	*α* = 79.445(3)	*α* = 67.6470(10)
	β = 87.718(2)	*β* = 88.384(3)	*β* = 82.775(2)	*β* = 86.088(3)	*β* = 67.7290(10)
	γ = 79.175(2)	*γ* = 80.368(3)	*γ* = 72.328(2)	*γ* = 67.630(3)	*γ* = 88.5480(10)
Volume ($Å^3$)	1257.90(8)	1281.5(5)	1445.18(8)	1103.7(5)	1671.1(3)
Z	1	1	2	2	2
Density (calculated, Mg/m^3)	1.395	1.485	1.430	1.439	1.271
Absorption coefficient (mm^{-1})	0.287	1.736	0.280	0.318	0.074
F(000)	550	586	640	492	672
Crystal size (mm^3)	0.300x0.225x0.100	0.250x0.060x0.030	0.275x0.175x0.075	0.400x0.100x0.050	0.400x0.350x0.300
Theta range of data (º)	1.564 to 28.944	1.552 to 26.400	1.602 to 27.811	1.761 to 28.812	1.721 to 28.886
Index ranges	-12/12, -14/13, -18/18	-11/11, -13/13, -17/17	-13/13, -15/15, -17/17	-12/12, -13/13, -15/15	-14/14, -17/17, -18/18
Reflections collected	22450	13954	25693	13301	20441
Independent reflections	6101	5211	6732	5269	8073
R(int)	0.0581	0.1076	0.0424	0.0535	0.0187
Completeness to 25.242º (%)	99.8	99.8	99.7	99.8	99.9
Max. and min. transmission	0.7458 and 0.6729	0.7453 and 0.6418	0.7456 and 0.7054	0.7458 and 0.6446	0.7458 and 0.7073
Data / restrains / parameters	6101 / 0 / 360	5211 / 297 / 360	6732 / 0 / 396	5269 / 0 / 307	8073 / 0 / 451
Goodness-of-fit on F^2	1.047	0.956	1.004	1.037	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0442	R1 = 0.0588	R1 = 0.0525	R1 = 0.0537	R1 = 0.0427
	wR2 = 0.1107	wR2 = 0.0867	wR2 = 0.1279	wR2 = 0.1184	wR2 = 0.1032
R indices (all data)	R1 = 0.0580	R1 = 0.1254	R1 = 0.0983	R1 = 0.1042	R1 = 0.0557
	wR2 = 0.1192	wR2 = 0.1048	wR2 = 0.1513	wR2 = 0.1383	wR2 = 0.1112
Largest diff. peak and hole ($e.Å^{-3}$)	0.332 and -0.341	0.415 and -0.605	0.455 and -0.462	0.459 and -0.364	0.304 and -0.187

N,N-Dichloroboryl-[N-(3-phenyl-2H-isoindol-1-yl)-N-(3-phenyl-1H-isoindol-1-ylidene)amine] (6)

Gold coloured, thin rectangular rods were grown via slow evaporation from dichloromethane under nitrogen atmosphere. The boron center is pseudo-tetrahedral (sum of angles 657.74°), and the relatively wide bite angle of 106.8(2)° agrees with bite angles typically observed in BODIPYs.[1] B-Cl bond lengths are long at ca. 1.8 Å, and substantially longer than the analogous *F*-aza-BODIPY (ca. 1.4 Å),[8] supporting the increased lability and facilitated nucleophilic substitution.

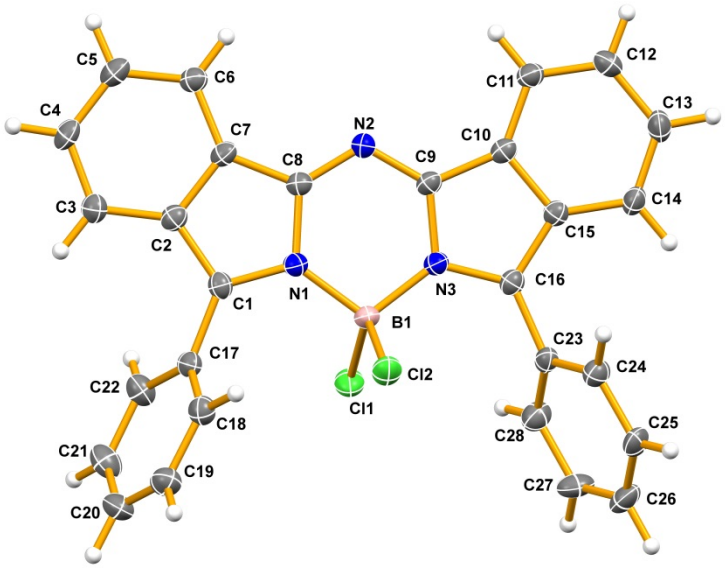


Figure S4. Structural diagram of **6**. Thermal ellipsoids are drawn at 50% probability.

Table S2. Selected bond lengths and angles around boron of **6**.

Bond	Length (Å)	Entry	Angle (°)
N1 – B1	1.549(4)	N1 – B1 – N3	106.8(2)
N3 – B1	1.553(4)	N1 – B1 – Cl2	111.69(19)
Cl1 – B1	1.848(3)	N3 – B1 – Cl2	107.95(18)
Cl2 – B1	1.847(3)	N1 – B1 – Cl1	107.89(18)
		N3 – B1 – Cl1	111.07(19)
		Cl2 – B1 – Cl1	111.34(16)

N,N-Diphenylboryl-[N-(3-phenyl-2H-isoindol-1-yl)-N-(3-phenyl-1H-isoindol-1-ylidene)amine] (8)

A dark green-black rough cube was cut from a thick rod (grown via slow evaporation from benzene) for data collection. The boron center is pseudo-tetrahedral (sum of angles 655.67°) with a somewhat wide bite angle in the expected range for BODIPYs,[1] but several degrees narrower than that of **6**. The C29 – B1 – C35 angle is wide (almost 120°), reasonably due to the steric demands of the phenyl substituents. The crystal is stabilised by π-stacking interactions (Figure S5), and thus crystallised easily from evaporating benzene.

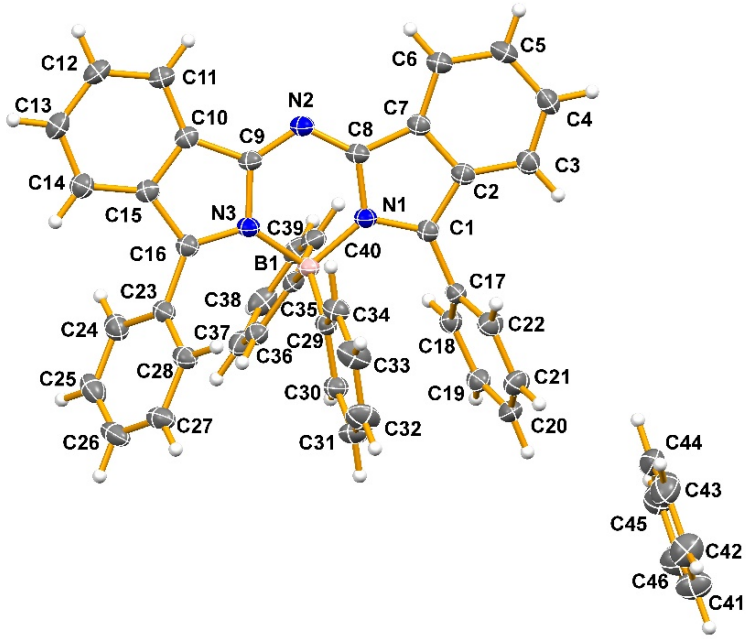


Figure S5a. Structural diagram of **8**, including one molecule of benzene solvation. Thermal ellipsoids are drawn at 50% probability.

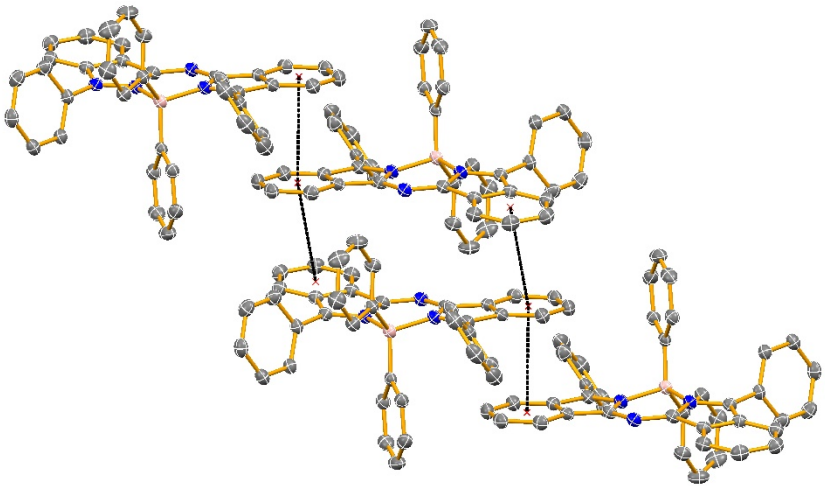


Figure S5b. Short ring stacking interactions within the crystal of **8**.

Table S3. Selected bond lengths and angles around boron of **8**.

Bond	Length (Å)	Entry	Angle (°)
N1 – B1	1.5935(16)	N1 – B1 – N3	103.24(9)
N3 – B1	1.6201(16)	N1 – B1 – C29	105.68(10)
C29 – B1	1.6152(18)	N3 – B1 – C29	111.30(9)
C35 – B1	1.6214(18)	N1 – B1 – C35	109.90(9)
		N3 – B1 – C35	105.77(9)
		C29 – B1 – C35	119.78(10)

N-(3,5-Diphenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine hydrochloride (1HCl)

A clear, green rectangular prism was cut from a larger needle for data collection. The structure was found to contain one half of a dichloromethane solvent molecule in the asymmetric unit (or one molecule of solvent for each two cation/anion pairs**).** The crystal structure shows that the α-phenyl rings are virtually completely coplanar with the dipyrrin core, while the β-phenyl rings are rotated slightly away from the plane of the core. This makes the overall structure of the compound appear very flat, leading to a sheet-like arrangement of constituents in the macroscopic lattice (Figure S7). The chloride ion is positioned centrally in the pocket defined by the pyrrolic nitrogen atoms and α-phenyl rings (Figure S6a), and so planarity is induced via hydrogen bonding between Cl1 and N2H and N3H (Table S4 and Figure S7b) as well as between C10-H10 and Cl1. A similar effect is observed frequently in α-aryl F-BODIPYs, where hydrogen bonding between the *ortho*-H of the α-phenyl and the fluorine atoms of the chelated BF_2 moiety prevents the rotation of these arenes. This consequently eliminates their contribution to non-radiative decay. Indeed, this effect is responsible for the moderate fluorescence quantum yield of **2** and similar *F*-aza-BODIPYs, where otherwise the free rotation of the four (or more) pendant arenes would lead to significant excited-state energy loss.

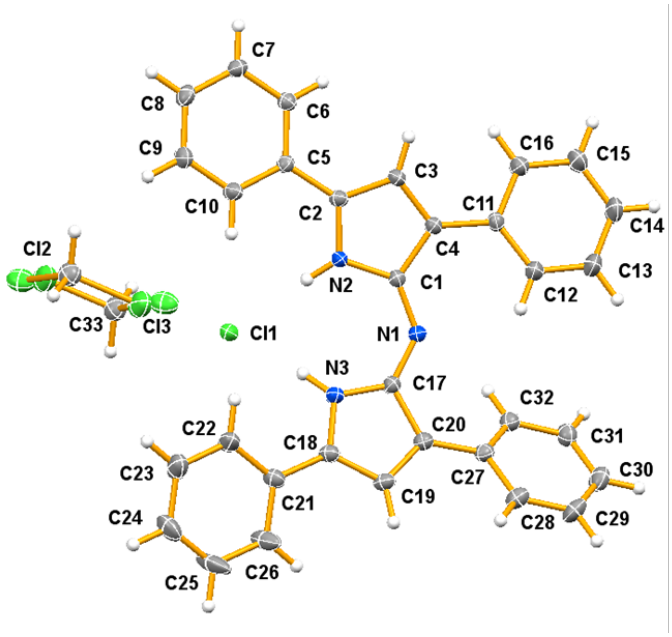


Figure S6a. Structural diagram of **1HCl**. Thermal ellipsoids are drawn at 50% probability.

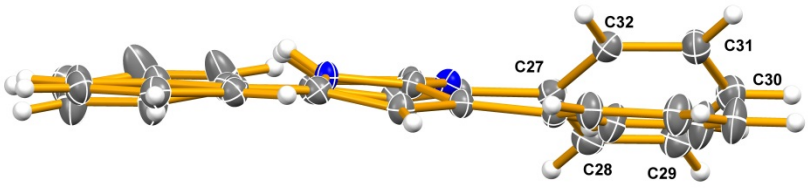


Figure S6b. Side-on view of **1HCl** highlighting co-planarity of α-phenyl rings with the dipyrrin core, while the β-phenyls are further out of plane.

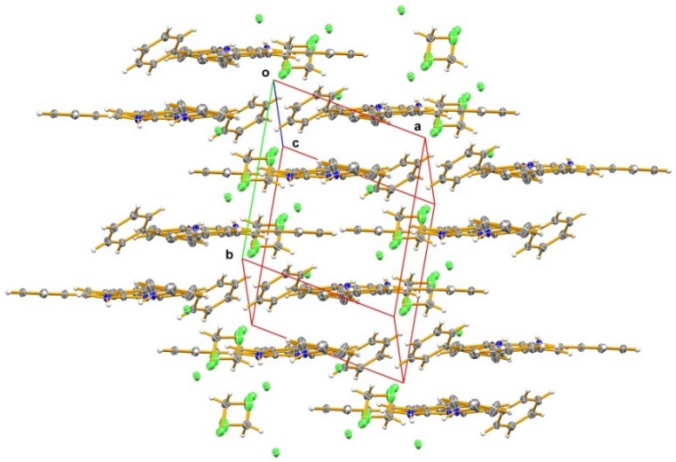


Figure S7a. Packing diagram of **1HCl** drawn to illustrate the packing of the cation layers.

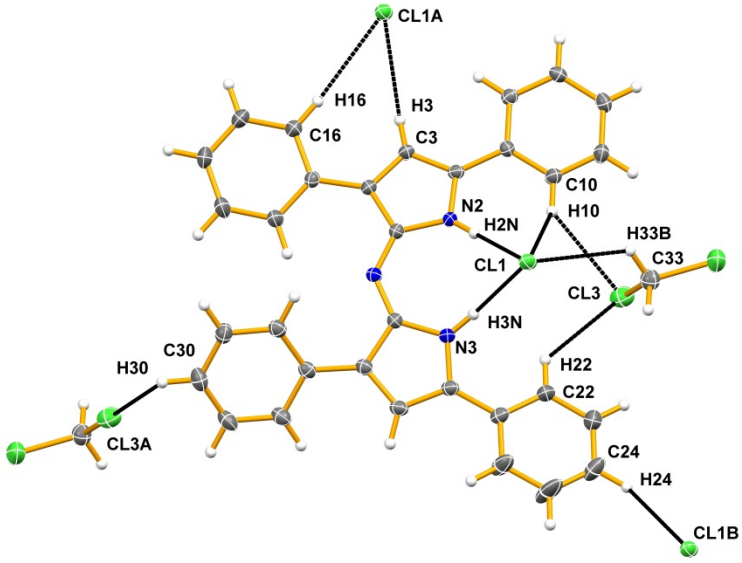


Figure S7b. Diagram of **1HCl** showing the N-H…Cl and C-H…Cl hydrogen bonds in the structure.

Table S4. N-H…Acceptor hydrogen bonds in the **3HX** compounds [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
1HCl				
N(2)-H(2N)...Cl(1)	0.87(2)	2.25(2)	3.1070(15)	169(2)
N(3)-H(3N)...Cl(1)	0.90(2)	2.22(2)	3.0888(15)	164(2)
1HBr				
N(2)-H(2N)...Br(1)	0.905(19)	2.37(2)	3.259(4)	169(5)
N(3)-H(3N)...Br(1)	0.915(19)	2.37(2)	3.240(4)	160(4)
1HBF$_4$				
N(2)-H(2N)...F(2)	0.84(2)	2.06(2)	2.862(2)	161(2)
N(3)-H(3N)...F(2)	0.92(2)	1.90(2)	2.811(2)	170(2)

N-(3,5-Diphenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine hydrobromide (1HBr)

A dark green, thin flat needle was cut down for the data collection. The structure was found to contain one half of a dichloromethane solvent molecule in the asymmetric unit (or one molecule of solvent for each two cation/anion pairs).

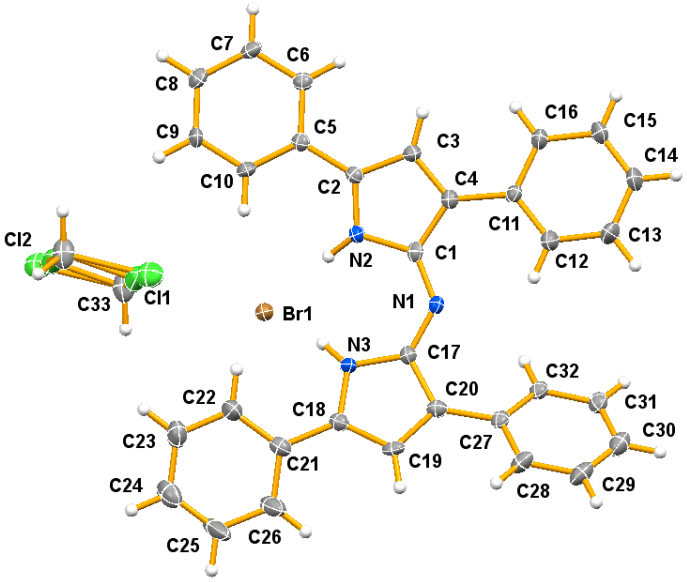


Figure S8. Structural diagram of **3HBr** including solvent. Thermal ellipsoids are drawn at 50% probability.

N-(3,5-Diphenyl-2H-pyrrol-2-ylidene)-3,5-diphenyl-1H-pyrrol-2-amine hydrofluoroborate (1HBF$_4$)

A dark green rectangular plate was chosen for the data collection. The structure was found to contain one dichloromethane solvent molecule in the asymmetric unit (or one molecule of solvent for each cation/anion pair).

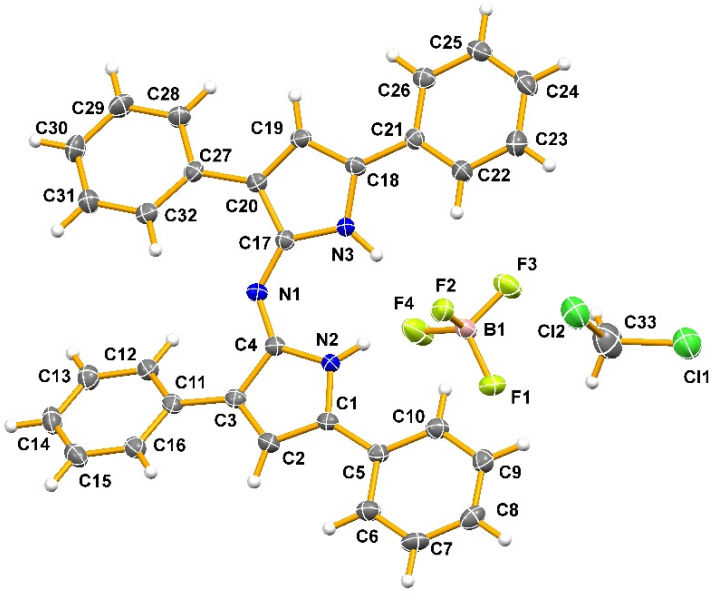


Figure S9. Structural diagram of **1HBF$_4$** including solvent. Thermal ellipsoids are drawn at 50% probability.

Photophysical Data

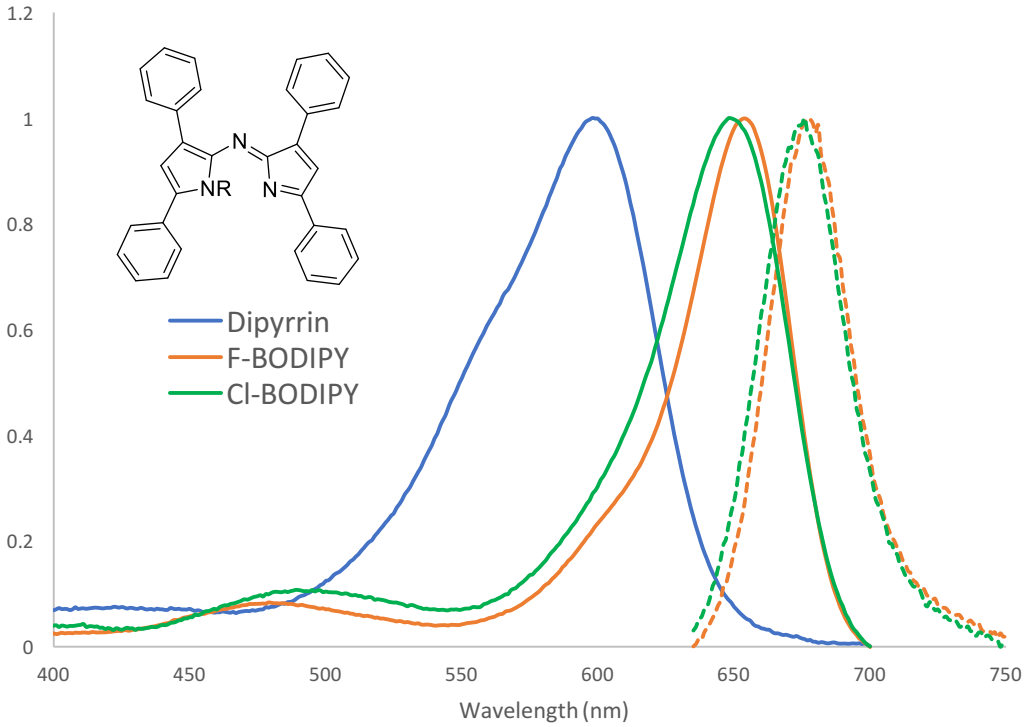


Figure S10. Plot of the normalised absorption (solid lines) and emission (dashed lines) spectra of **1**, **2** and **3**

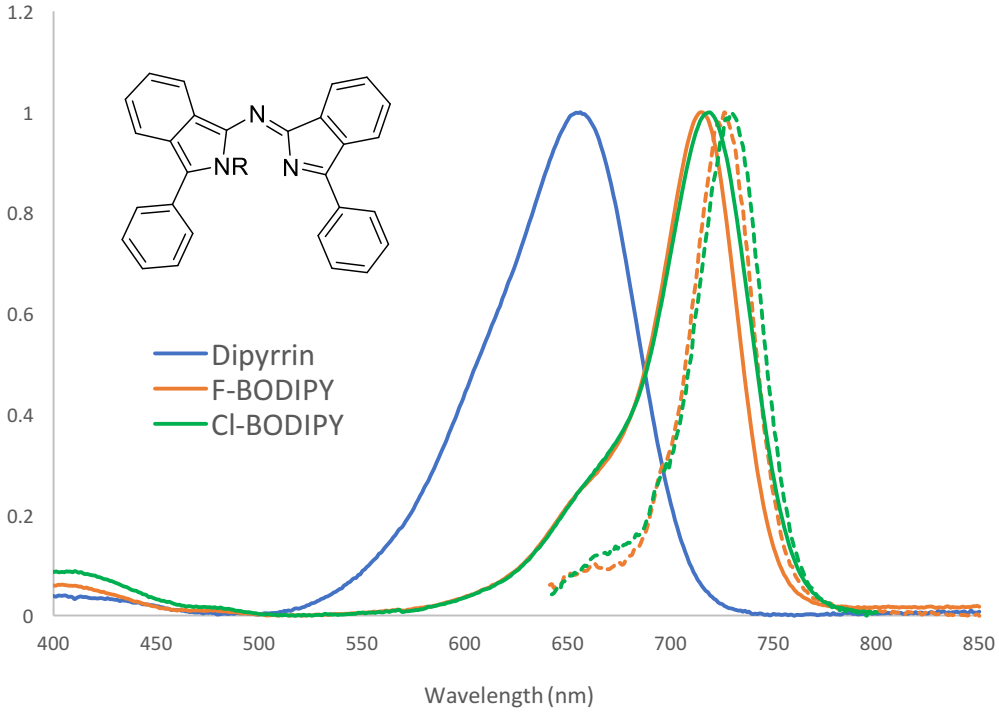


Figure S11. Plot of the normalised absorption (solid lines) and emission (dashed lines) spectra of **4**, **5** and **6**.

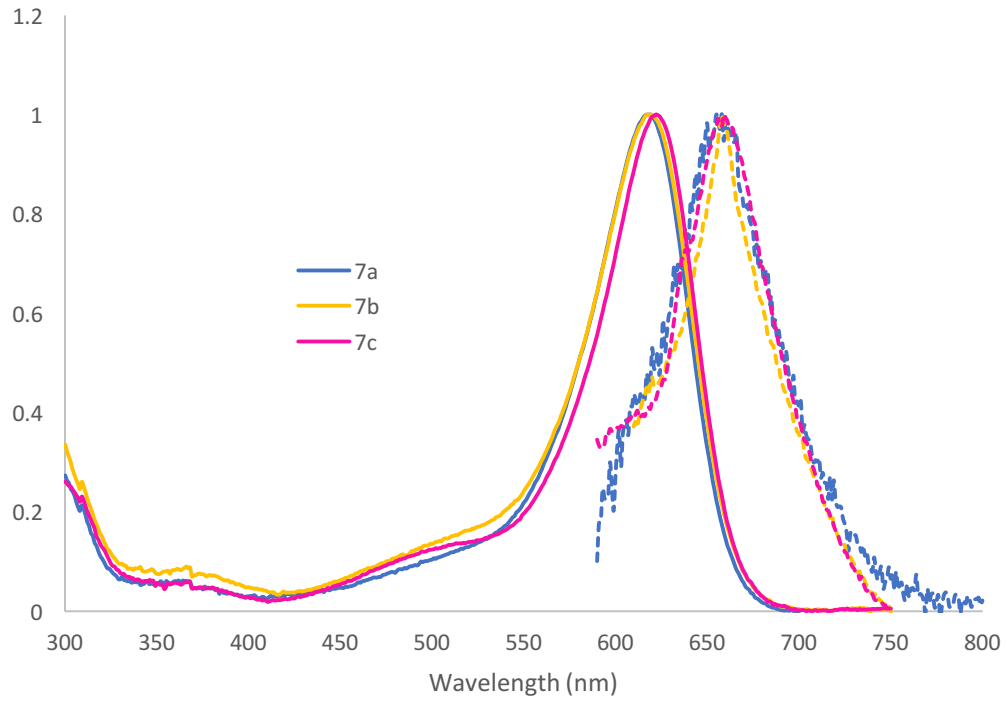


Figure S12. Plot of the normalised absorption (solid lines) and emission (dashed lines) spectra of aza-BODIPYs **7a-c**.

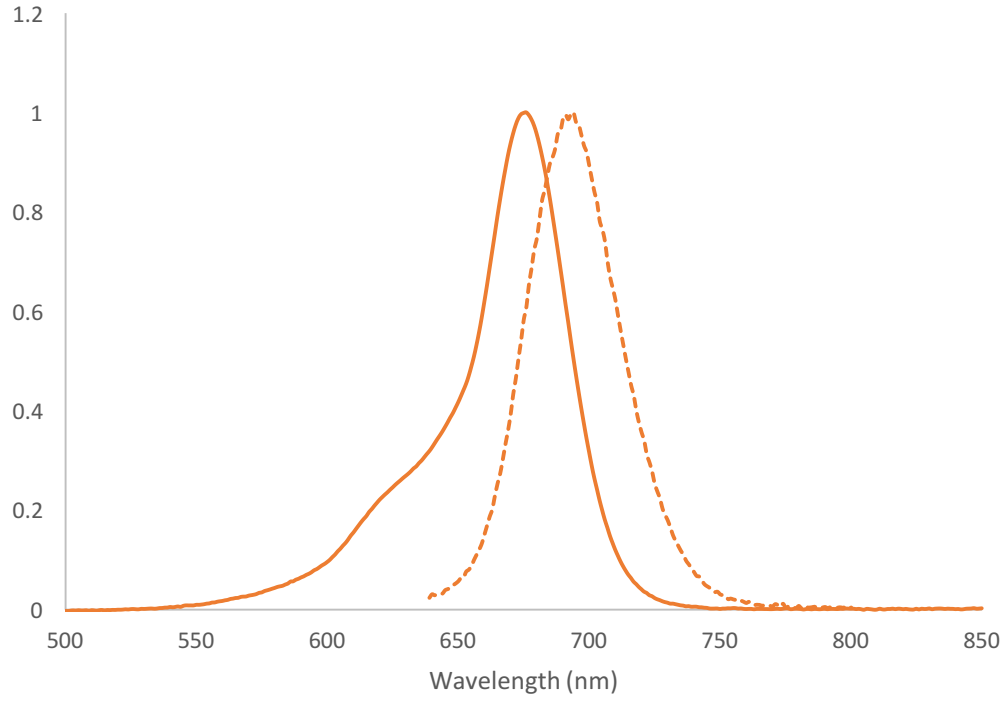


Figure S13. Plot of the normalised absorption (solid line) and emission (dashed line) spectra of **8**.

References

1. Gorman, A.; Killoran, J.; O'Shea, C.; Kenna, T.; Gallagher, W. M.; O'Shea, D. F., In vitro demonstration of the heavy-atom effect for photodynamic therapy, *J. Am. Chem. Soc.* **2004,** *126*, 10619-10631.
2. APEXII Bruker AXS Inc., Madison, Wisconsin, USA, 2008.
3. SAINT Bruker AXS Inc., Madison, Wisconsin, USA, 2008.
4. SADABS Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
5. Sheldrick, G. M., A short history of SHELX, *Acta Cryst.* **2008,** *A64*, 112-122.
6. Sheldrick, G. M., SHELXT - integrated space-group and crystal-structure determination, *Acta Cryst.* **2015,** *A71*, 3-8.
7. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A., Mercury CSD 2.0—new features for the visualization and investigation of crystal structures, *J. Appl. Cryst.* **2008,** *41*, 466-470.
8. Maligaspe, E.; Pundsack, T. J.; Albert, L. M.; Zatsikha, Y. V.; Solntsev, P. V.; Blank, D. A.; Nemykin, V. N., Synthesis and charge-transfer dynamics in a ferrocene-containing organoboryl aza-bodipy donor–acceptor triad with boron as the hub, *Inorg. Chem.* **2015,** *54*, 4167-4174.