One-Pot Strategy for Symmetrical and Unsymmetrical BOIMPY Fluorophores

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Supporting Information

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1. Photophysical Data

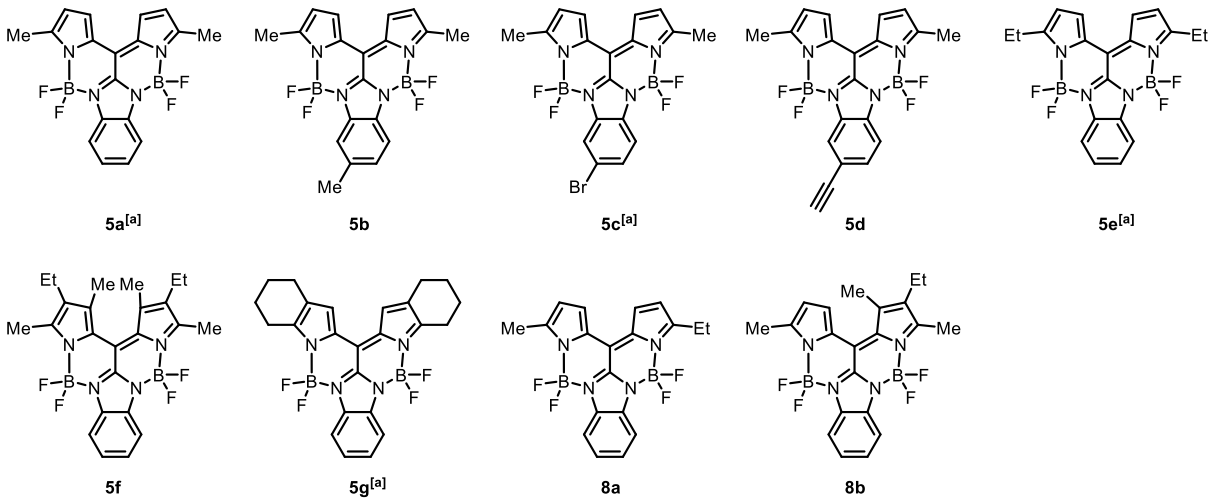

Figure S1. Compound overview. [a] Compounds are known from literature.[1]

Table S1. Photophysical data.

	λ^{A}_{max} [nm]	λ^{F}_{max} [nm]	ε [10^3 $M^{-1}cm^{-1}$] [b]	$\Delta\tilde{\nu}$[cm^{-1}] [c]	Φ_F (rt) [d]	τ_F [ns] [e]
5a	596 (594)	605 (602)	72.3 (70.5)	250 (224)	0.72 (0.71)	6.68
5b	596 (594)	605 (603)	80.1 (74.5)	250 (251)	0.73 (0.73)	6.58
5c	600 (598)	609 (607)	81.0 (75.5)	246 (248)	0.57 (0.55)	6.42
5d	600 (598)	609 (608)	75.9 (70.9)	246 (275)	0.72 (0.63)	6.47
5e	599 (596)	609 (606)	82.4 (80.5)	274 (277)	0.73 (0.67)	6.49
5f	589 (586)	618 (612)	60.3 (54.0)	797 (725)	0.08 (0.08)	1.12
5g	622 (619)	629 (625)	115.5 (103.8)	179 (155)	0.64 (0.58)	5.81
8a	597 (595)	607 (604)	77.3 (74.8)	276 (250)	0.70 (0.68)	6.50
8b	584 (581)	605 (603)	66.6 (62.2)	594 (628)	0.10 (0.09)	1.04

[a] First value in DCM, second value in THF (brackets), λ^{A}_{max} = absorption wavelength, λ^{F}_{max} = fluorescence wavelength. [b] Attenuation coefficient. [c] Stokes' shift. [d] Absolute fluorescence quantum yield. [e] Fluorescence lifetime, experimentally determined.

2. Spectroscopic Data

Due to bad solubility in most NMR solvents but DMSO, the ^{1}H- and ^{13}C-NMR spectra are given in DMSO-d_6. Problematic though is the fact that DMSO mediates a slow decarboxylation of benzimidazole carboxylic acids. Therefore, we firstly provide the ^{1}H-NMR spectrum measured in CD_3OD (Figure S2) to verify the purity of **1d** and secondly the ^{1}H- and ^{13}C-NMR spectra for the respective NMR shifts.

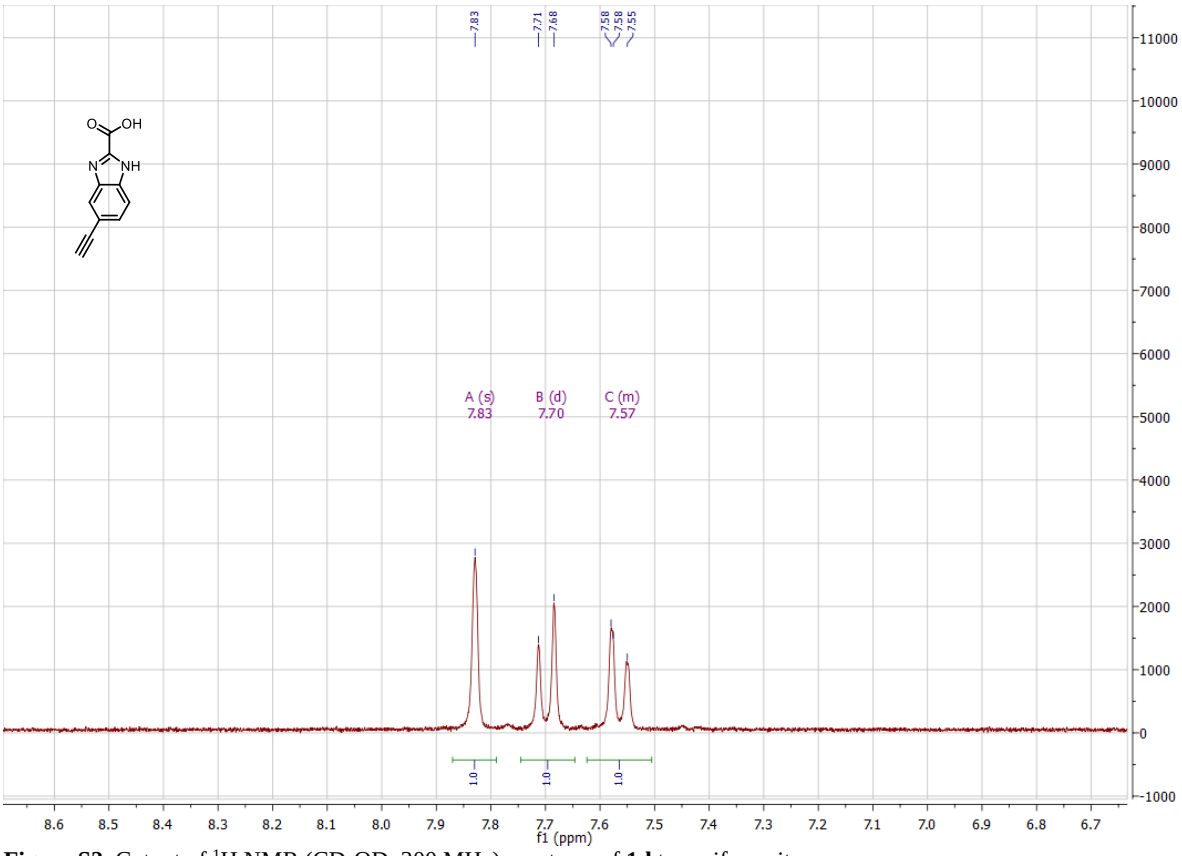

Figure S2. Cutout of ^{1}H NMR (CD_3OD, 300 MHz) spectrum of **1d** to verify purity.

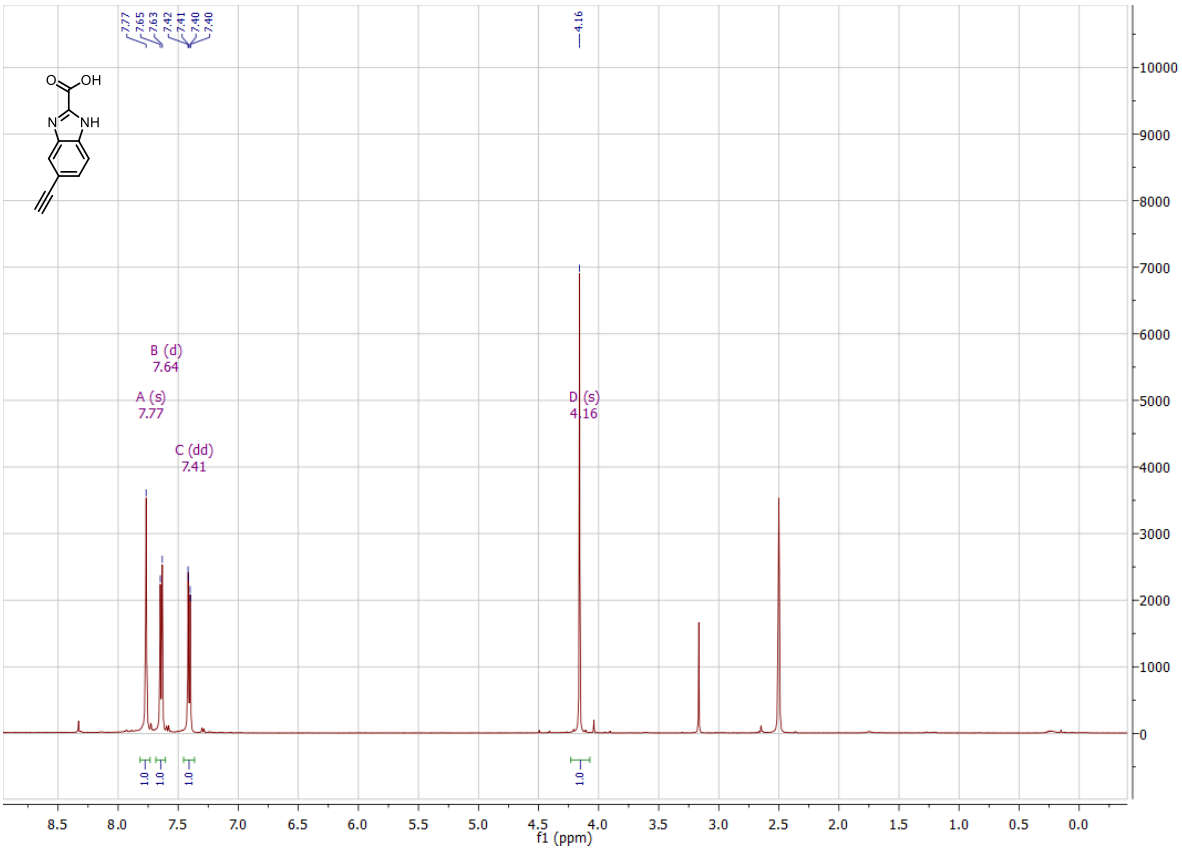

Figure S3. ^{1}H NMR (DMSO-d_6, 500 MHz) spectrum of **1d** containing decomposition by-product induced by DMSO.

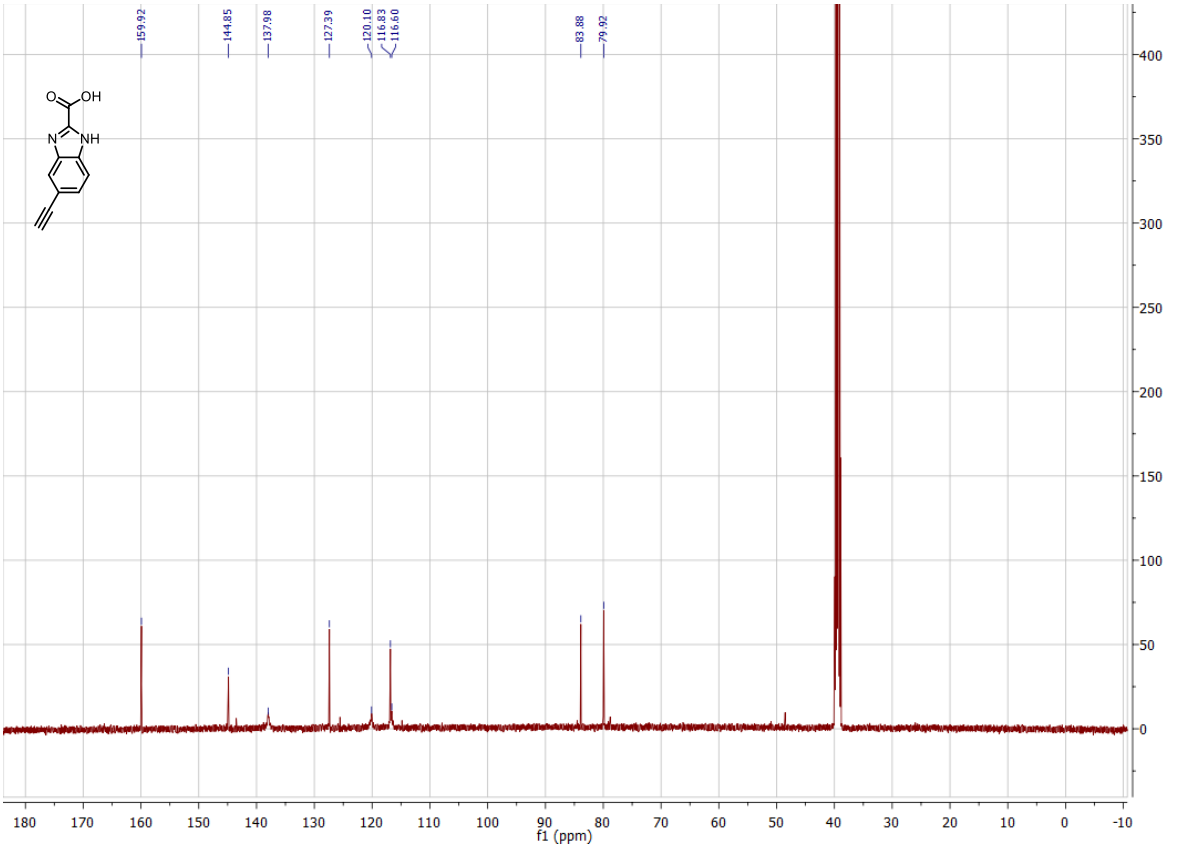

Figure S4. ^{13}C{^{1}H} NMR (DMSO-d_6, 125 MHz) spectrum of **1d** containing decomposition by-product induced by DMSO.

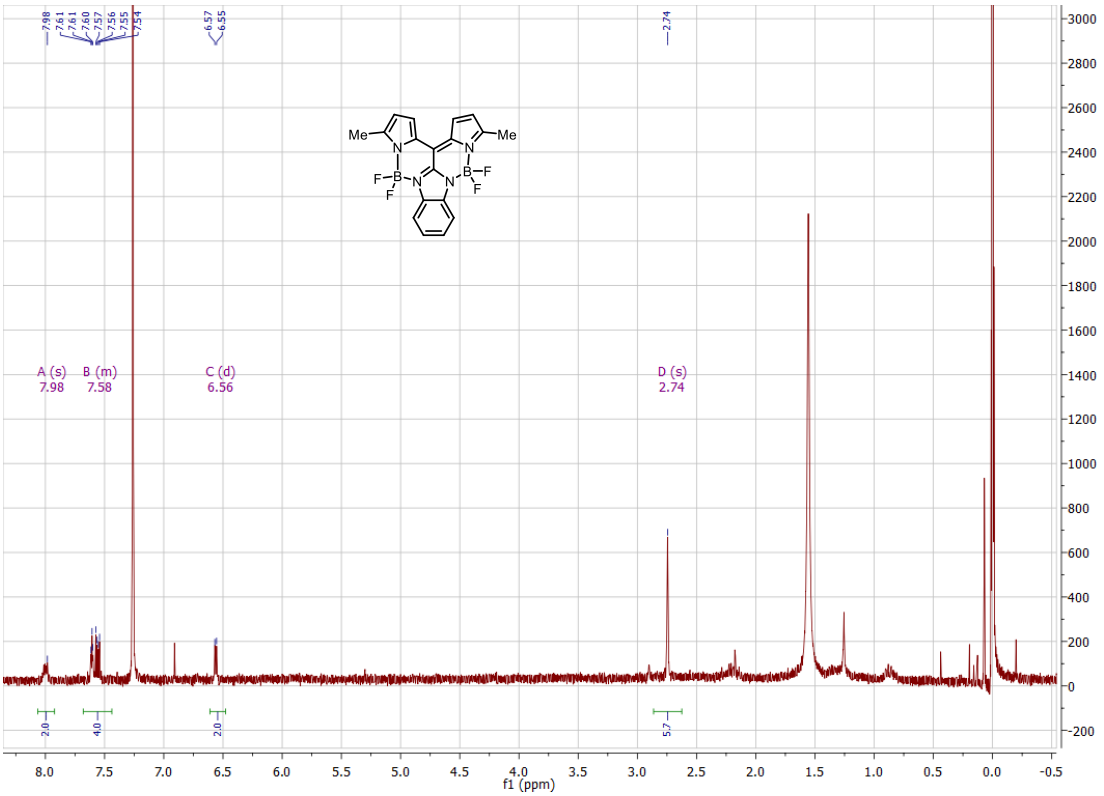

Figure S5. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5a**. Solubility is very low. Analytic data is in agreement with the literature.[1]

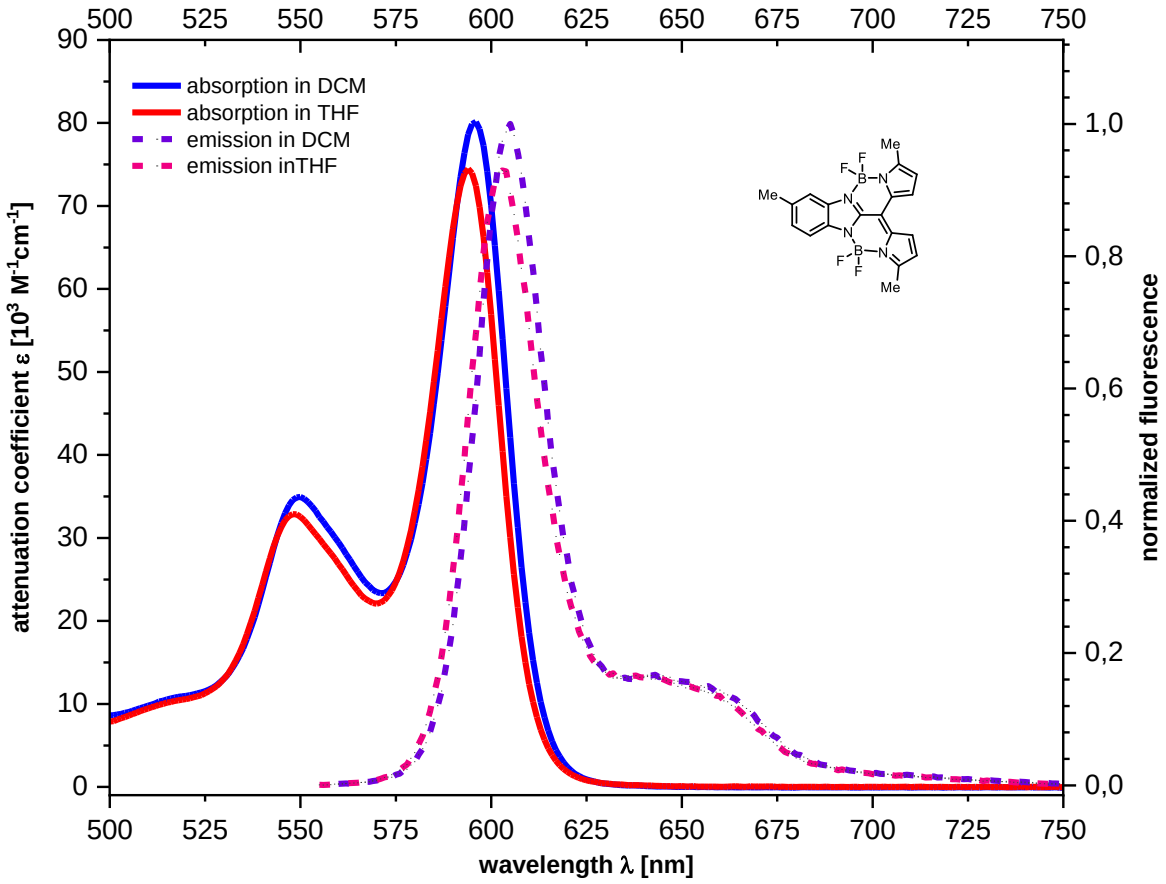

Figure S6. UV-Vis and normalized fluorescence spectra of **5b** in DCM and THF at room temperature.

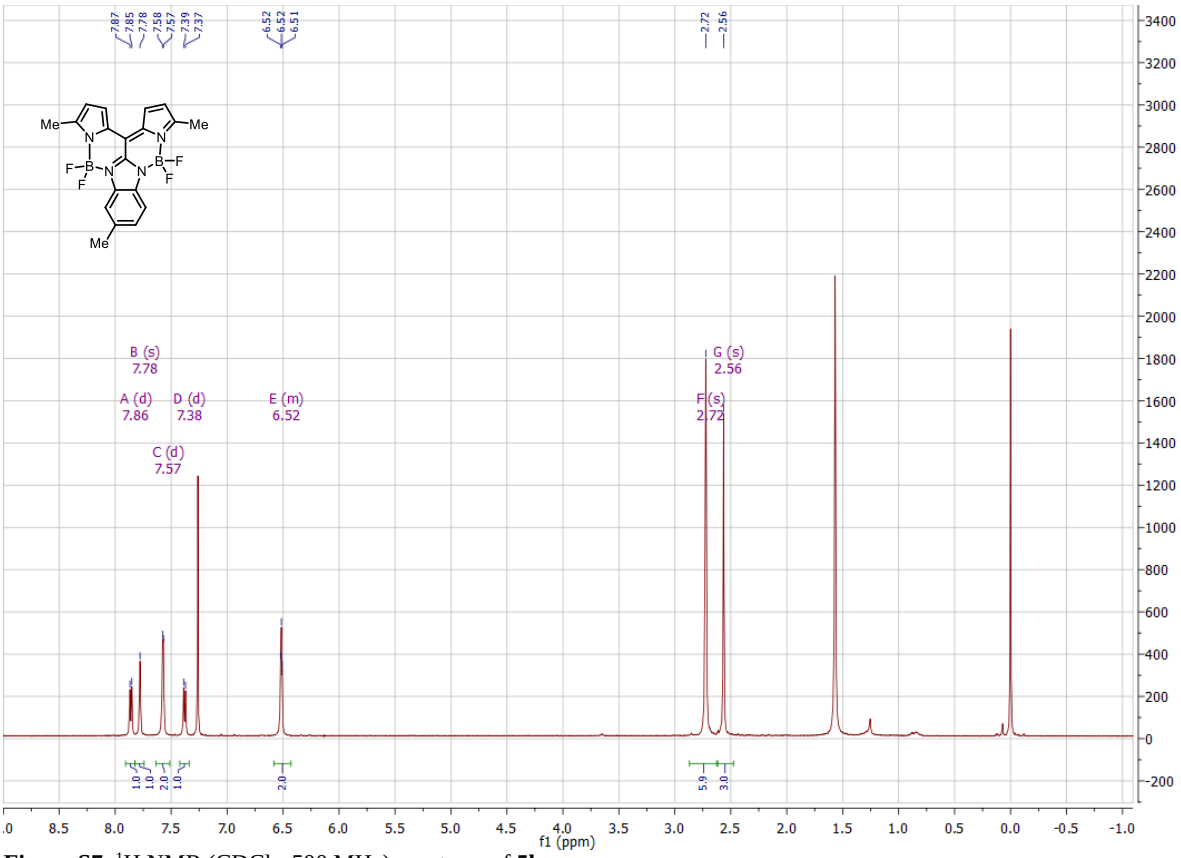

Figure S7. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **5b**.

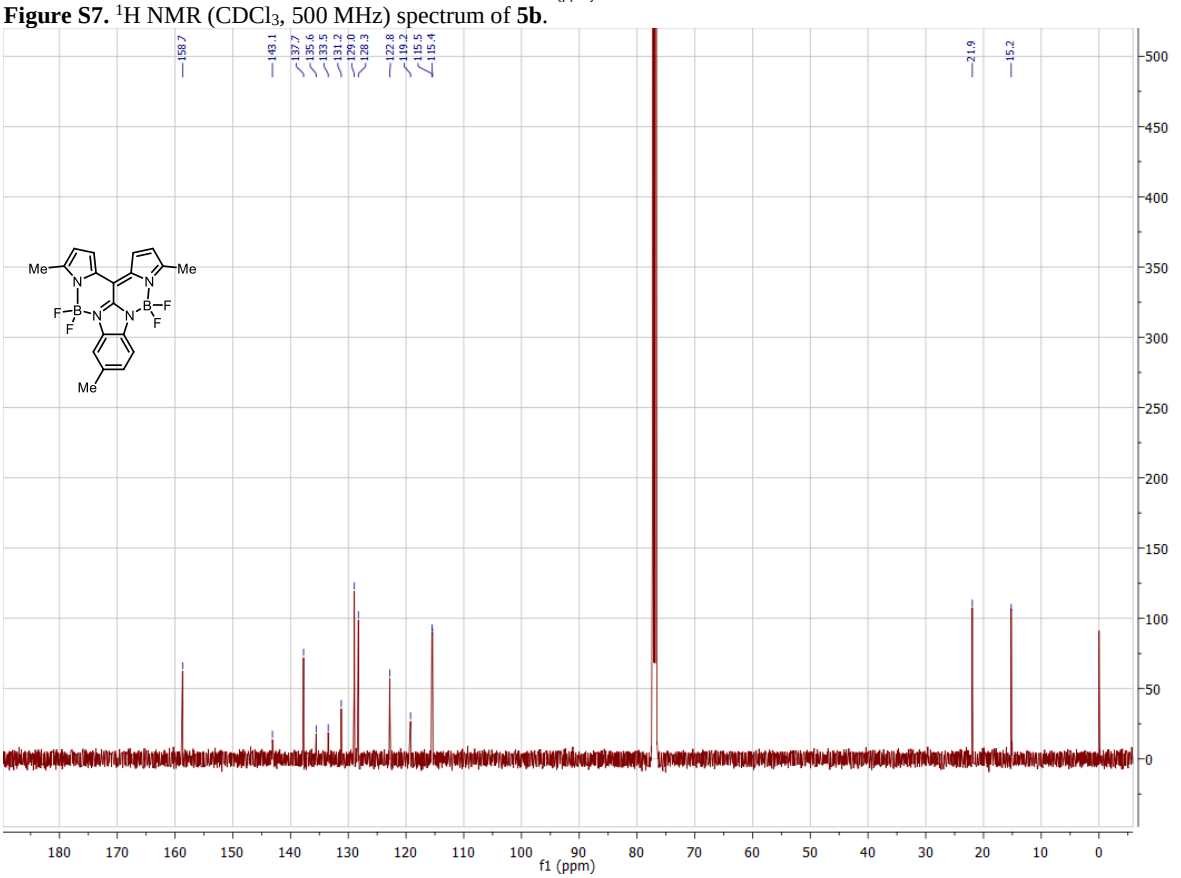

Figure S8. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectrum of **5b**.

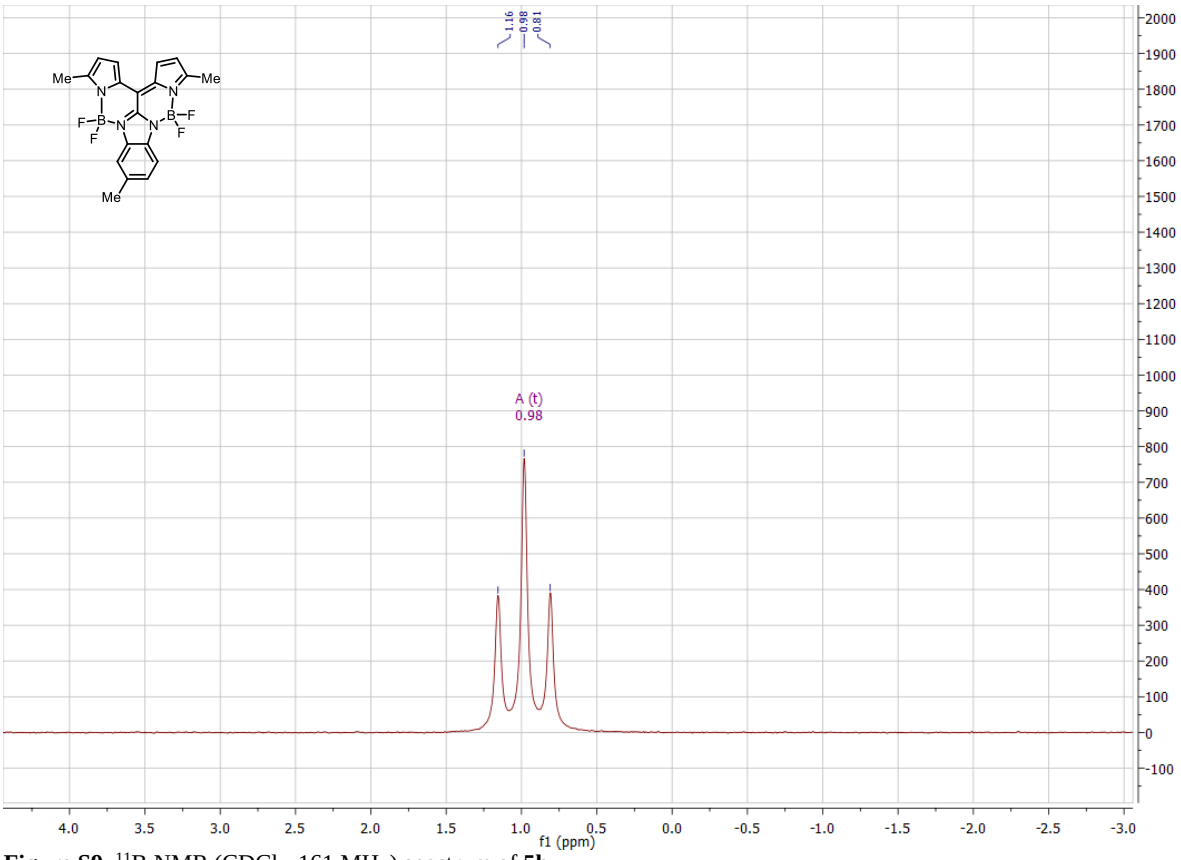

Figure S9. ^{11}B NMR ($CDCl_3$, 161 MHz) spectrum of **5b**.

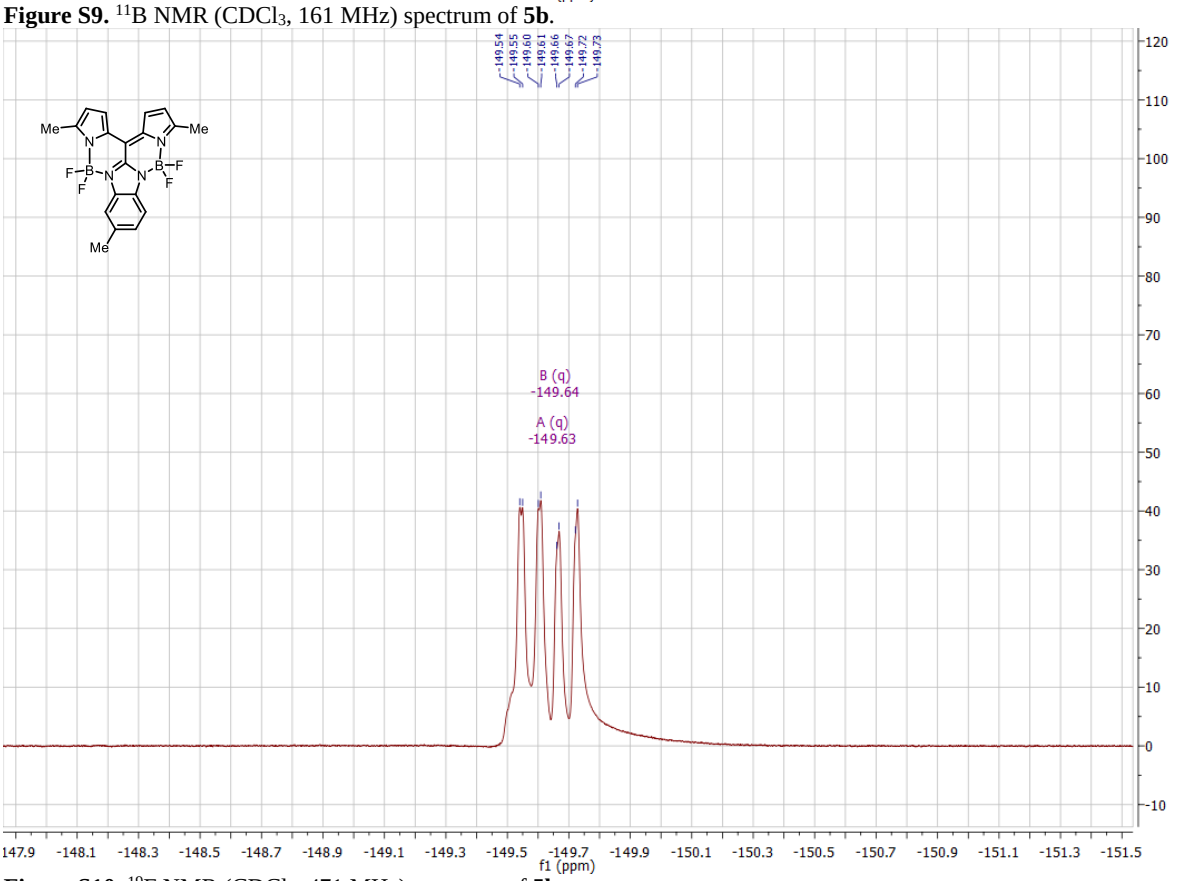

Figure S10. ^{19}F NMR ($CDCl_3$, 471 MHz) spectrum of **5b**.

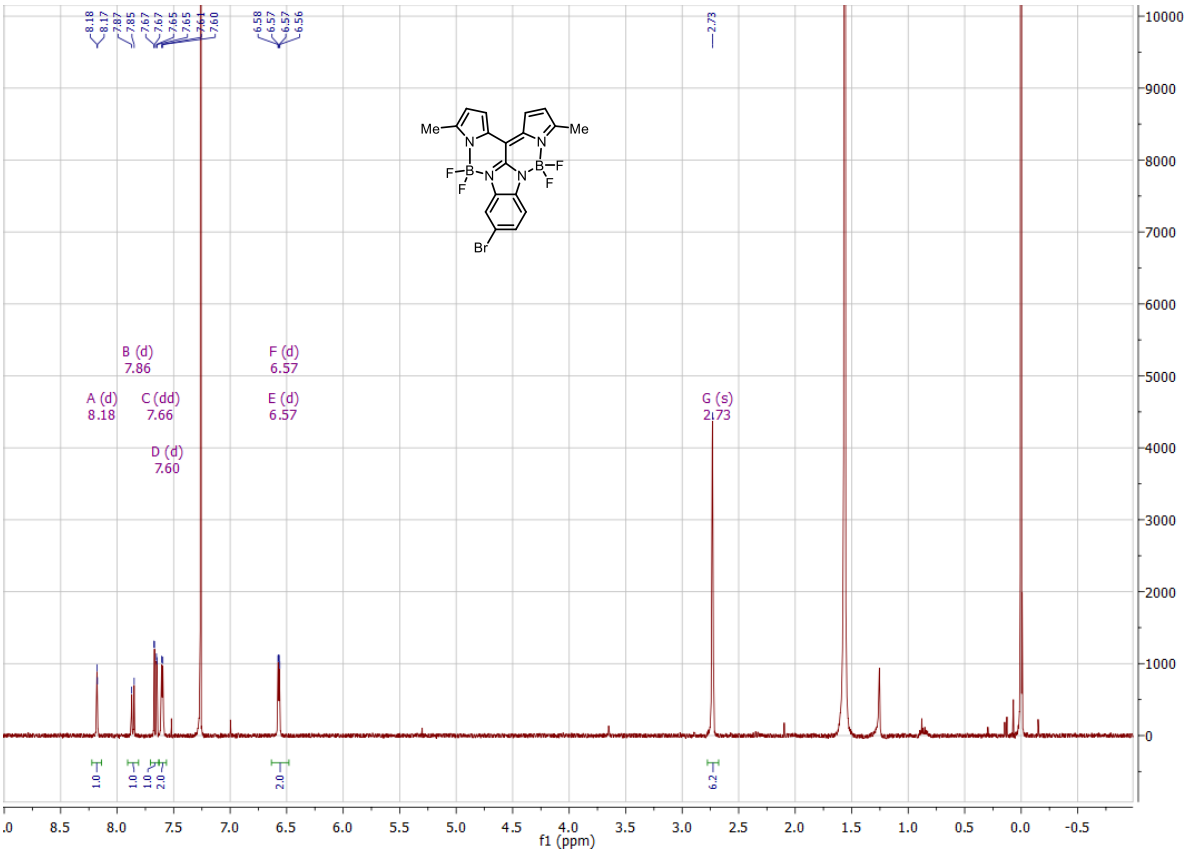

Figure S11. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **5c**. Analytic data is in agreement with the literature.[1]

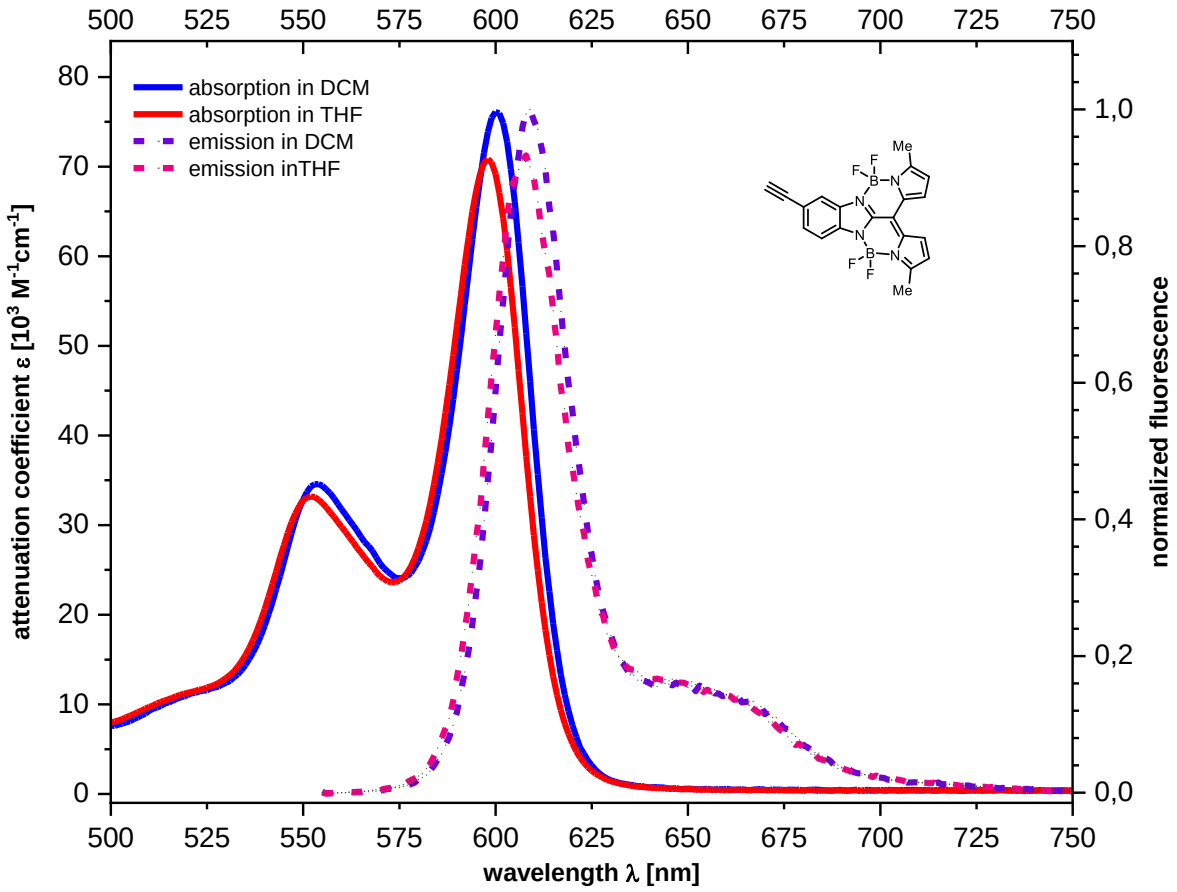

Figure S12. UV-Vis and normalized fluorescence spectra of **5d** in DCM and THF at room temperature.

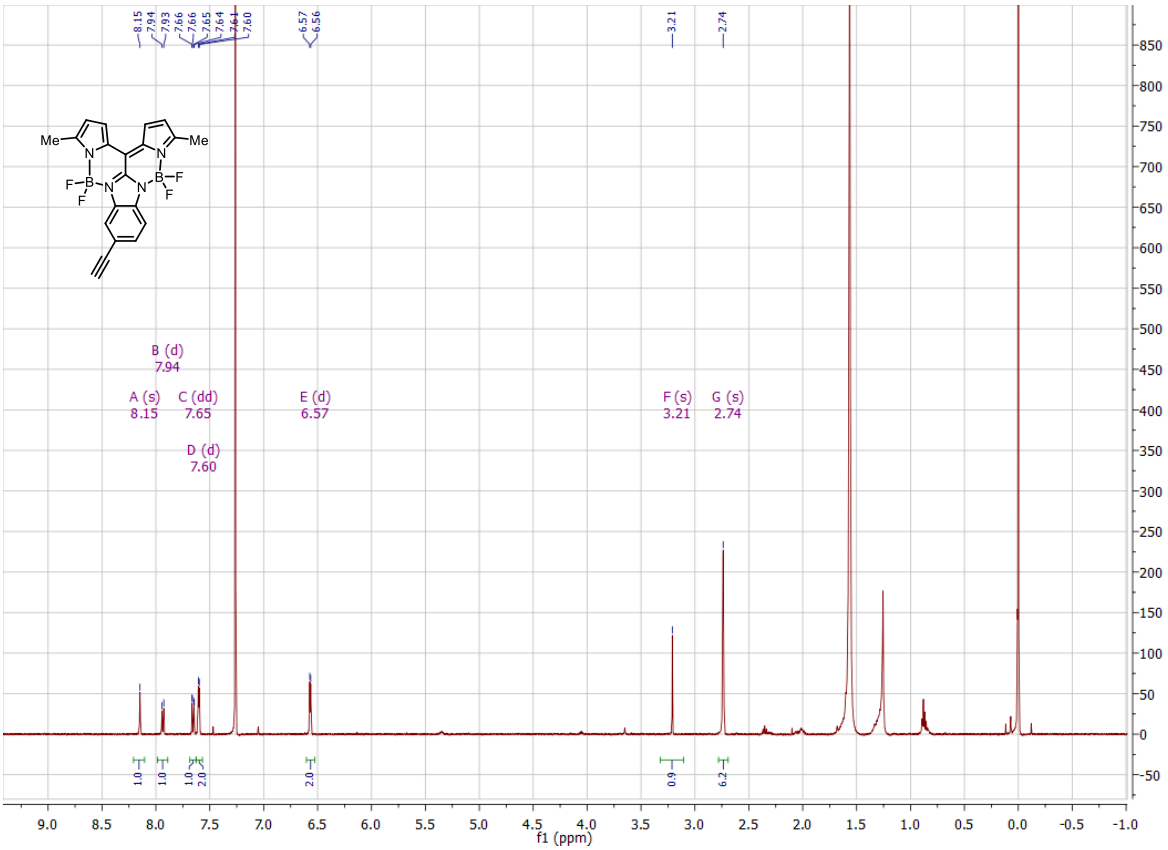

Figure S13. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **5d**.

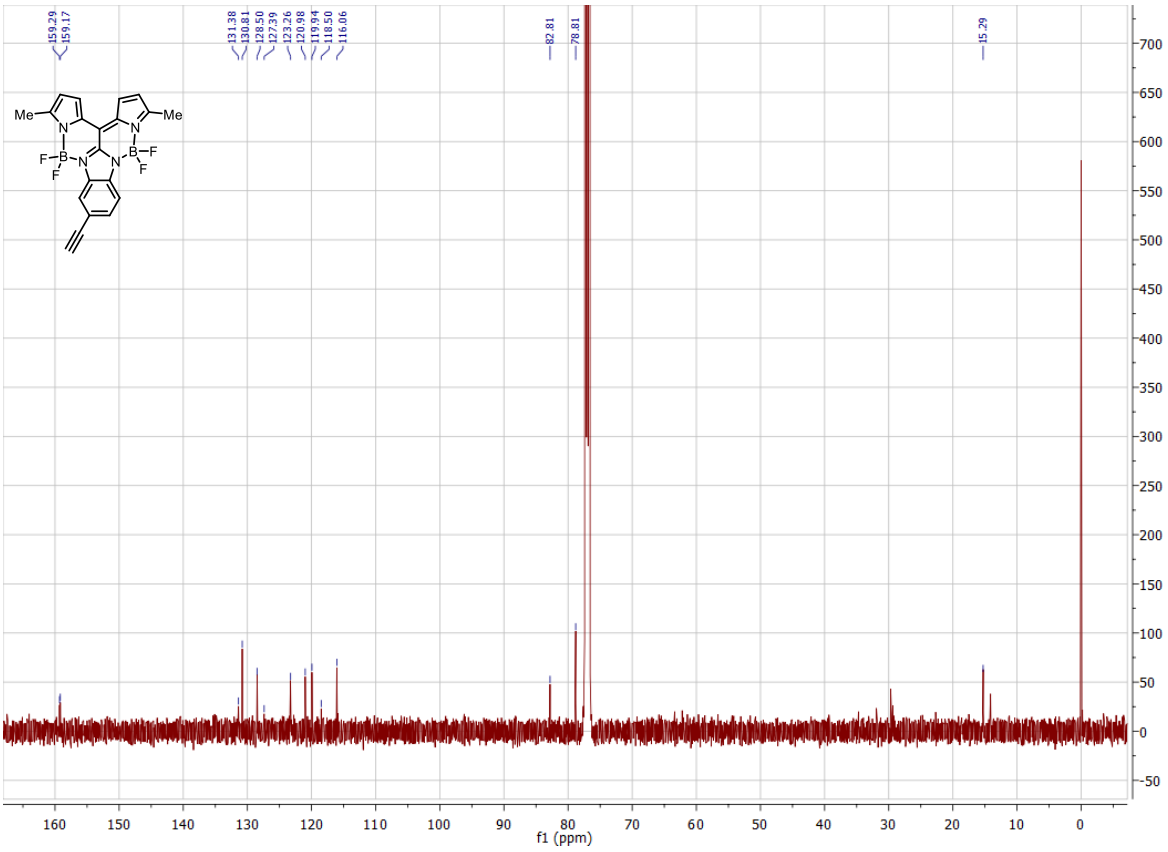

Figure S14. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectrum of **5d**.

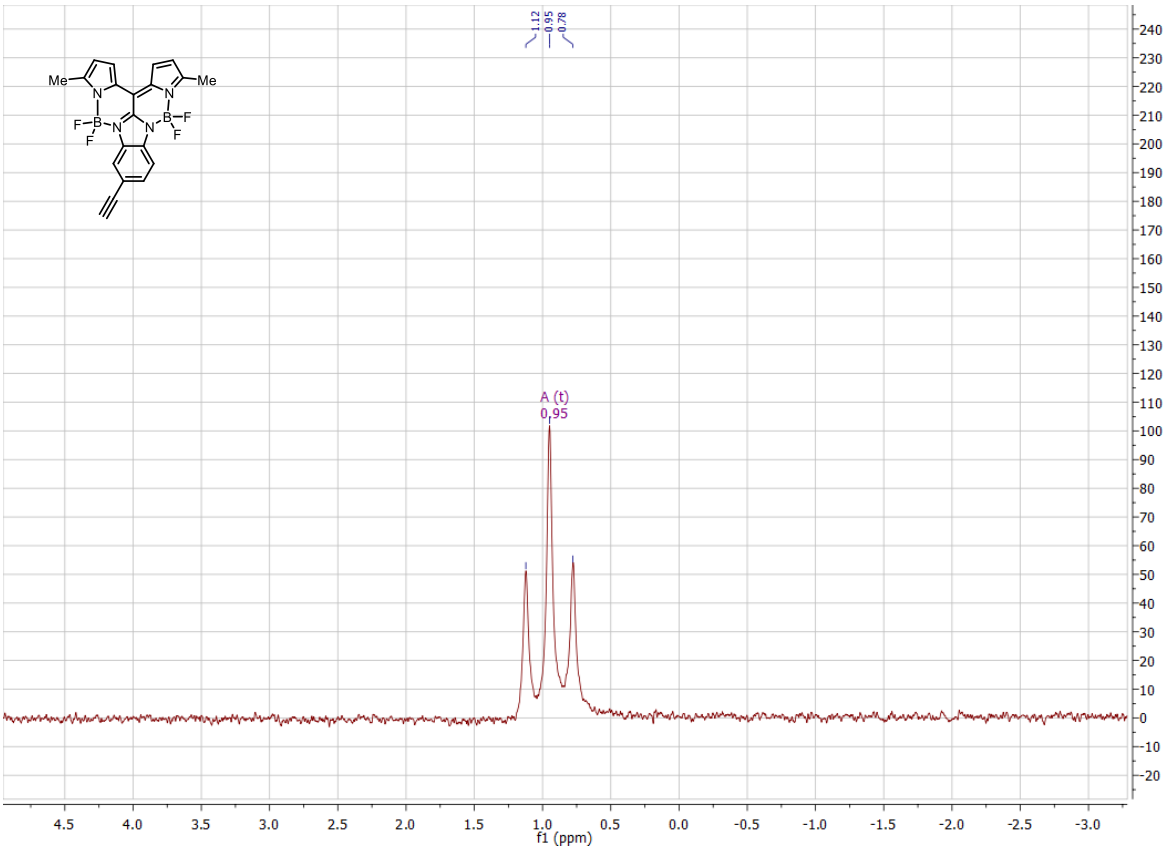

Figure S15. ^{11}B NMR ($CDCl_3$, 161 MHz) spectrum of **5d**.

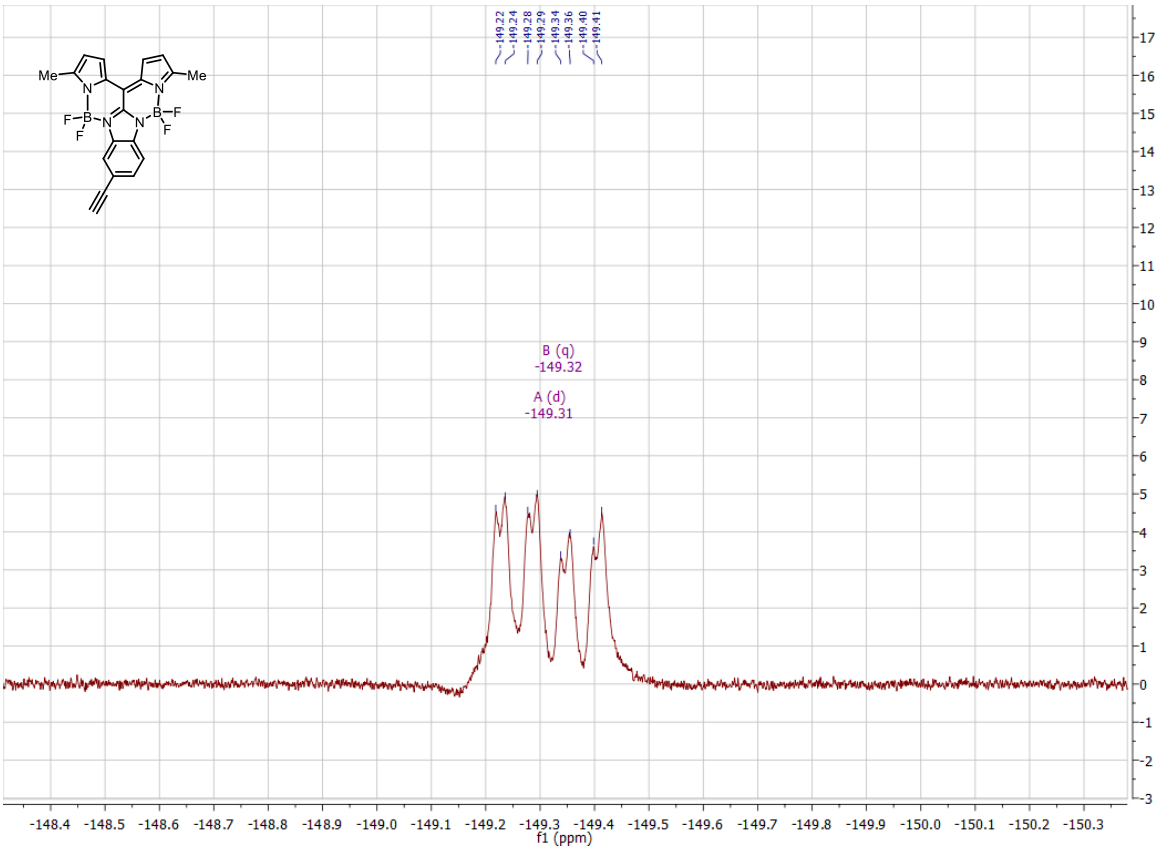

Figure S16. ^{19}F NMR ($CDCl_3$, 471 MHz) spectrum of **5d**.

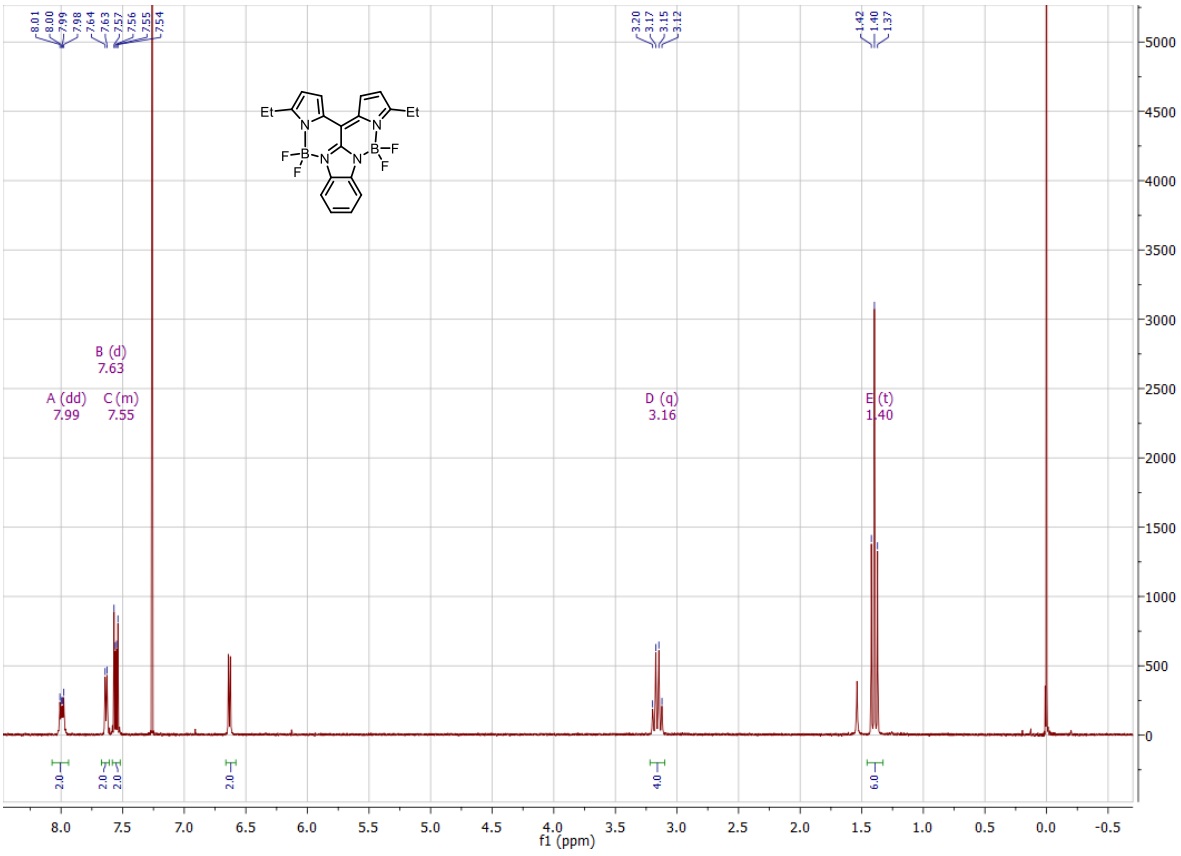

Figure S17. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5e**. Analytic data is in agreement with the literature.[1]

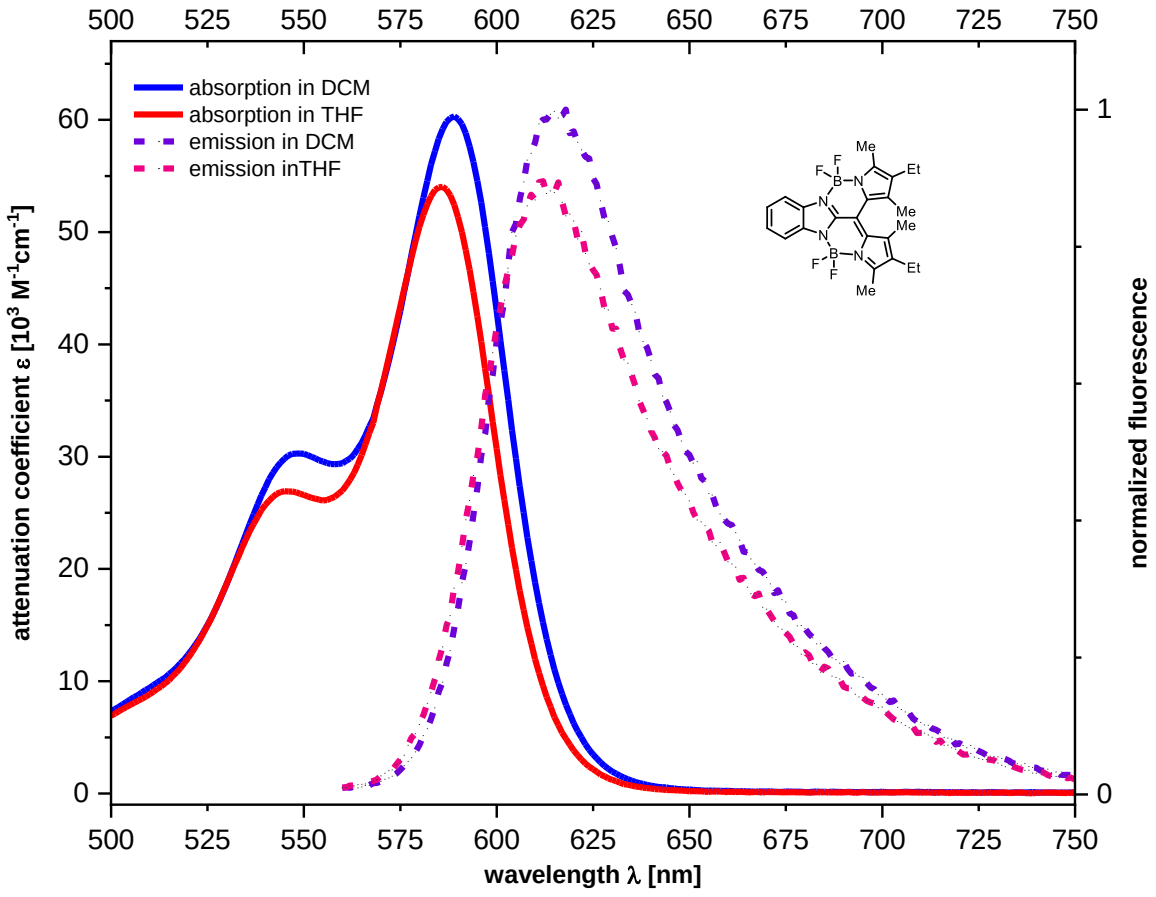

Figure S18. UV-Vis and normalized fluorescence spectra of **5f** in DCM and THF at room temperature.

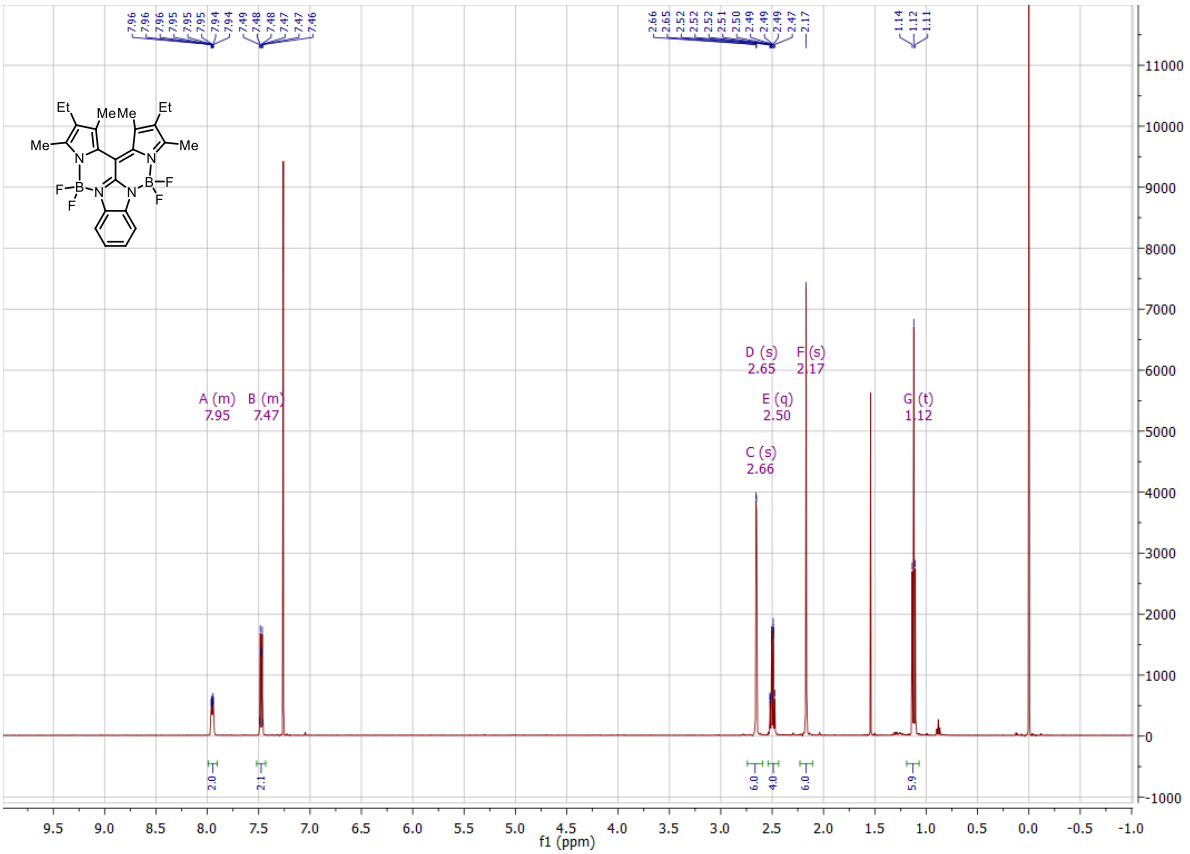

Figure S19. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **5f**.

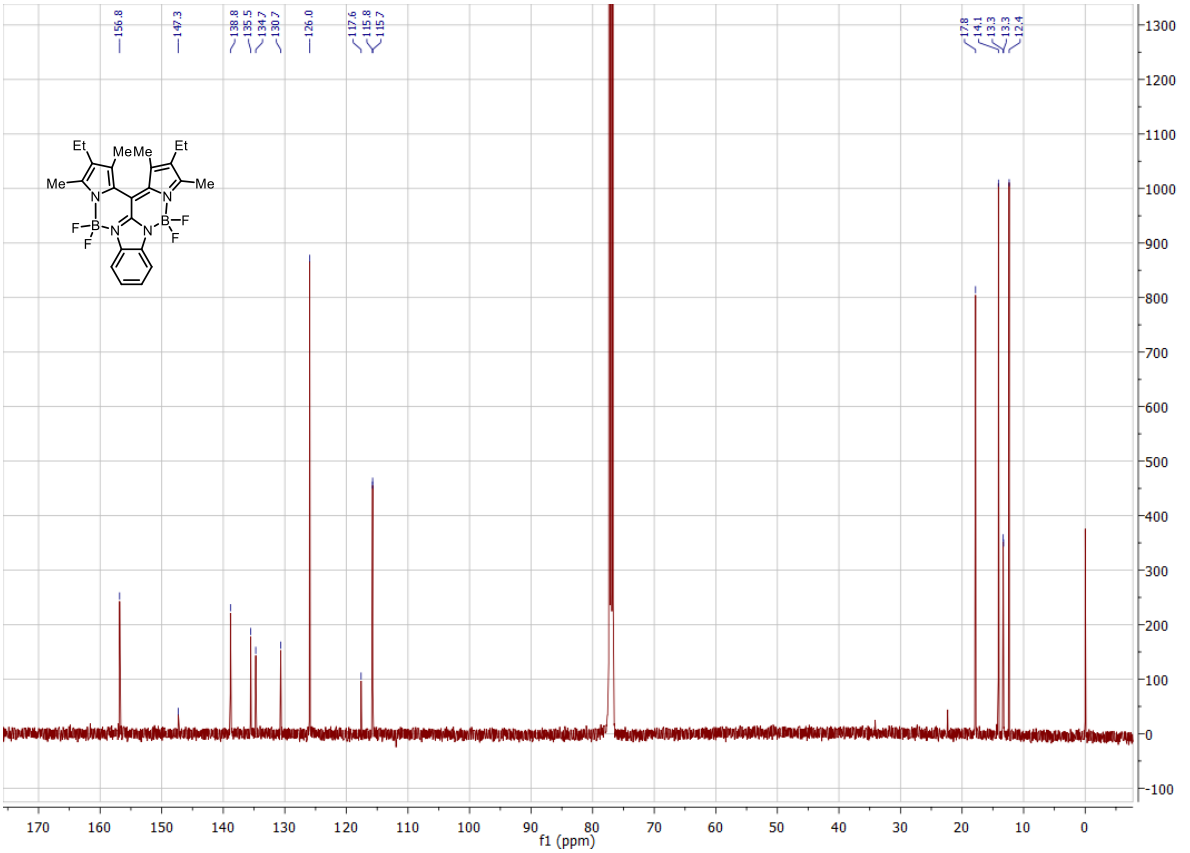

Figure S20. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectrum of **5f**.

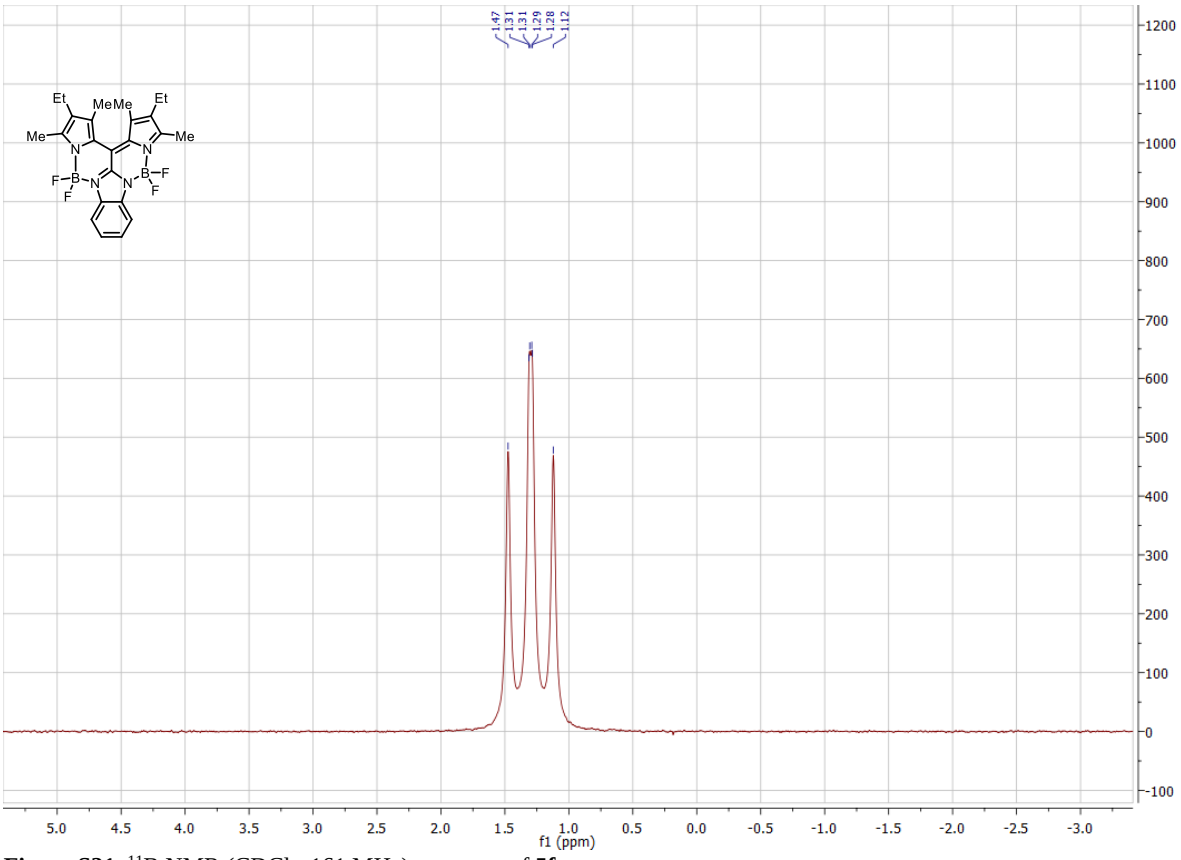

Figure S21. ^{11}B NMR ($CDCl_3$, 161 MHz) spectrum of **5f**.

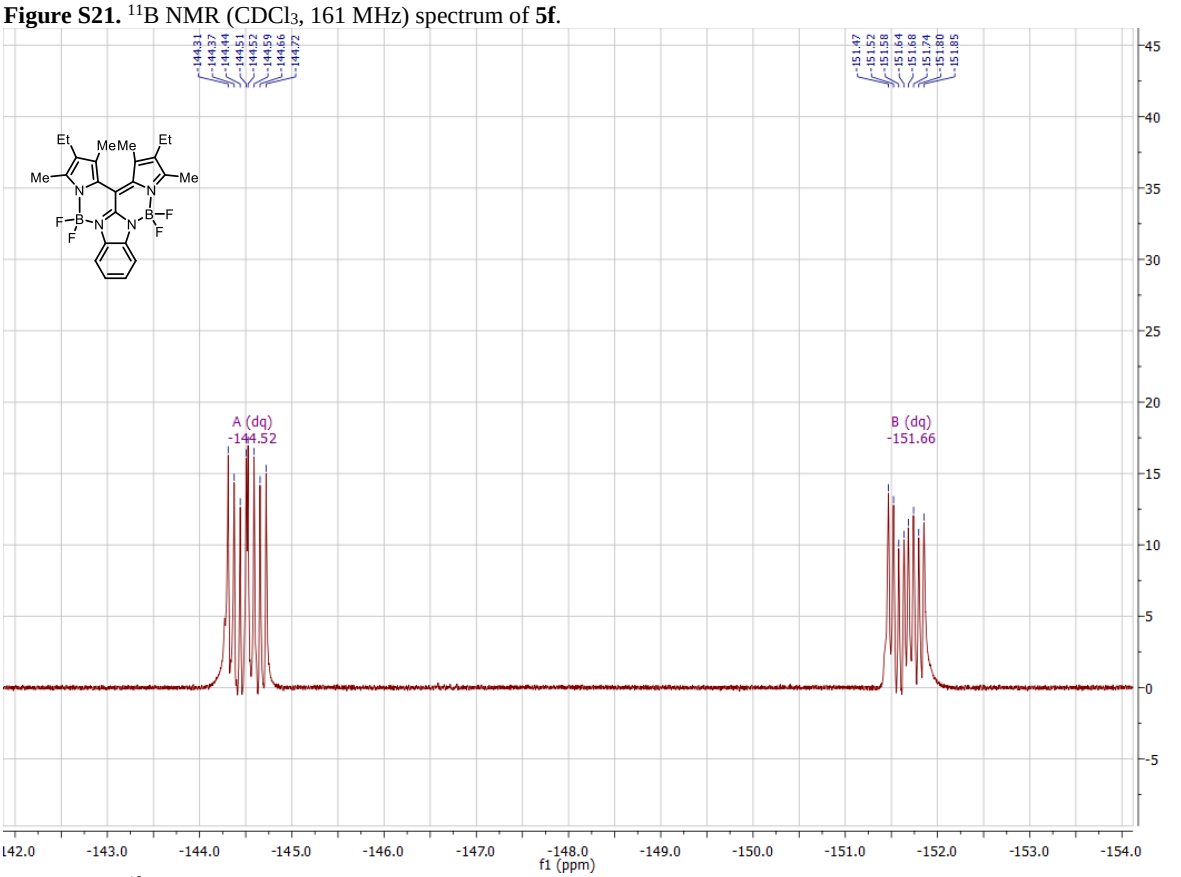

Figure S22. ^{19}F NMR ($CDCl_3$, 471 MHz) spectrum of **5f**.

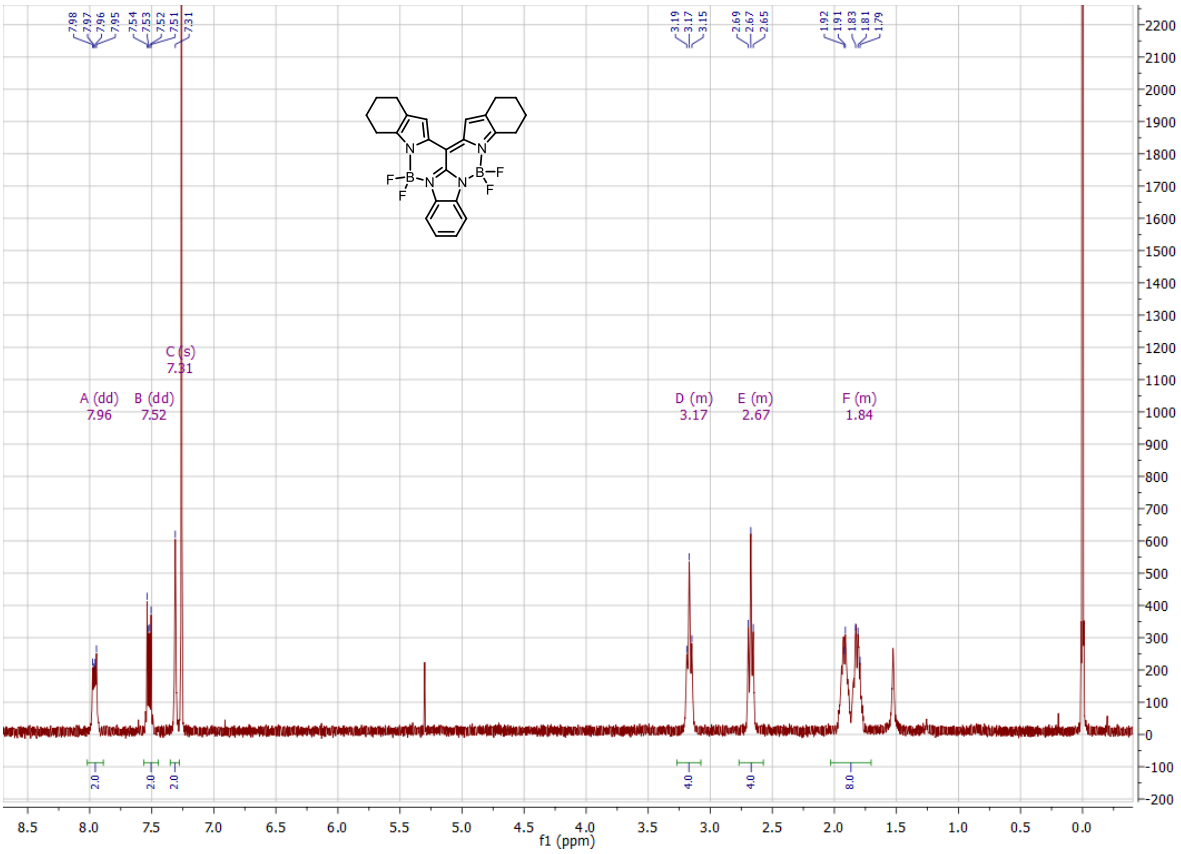

Figure S23. ^{1}H NMR ($CDCl_3$, 300 MHz) spectrum of **5g**. Analytic data is in agreement with the literature.[1]

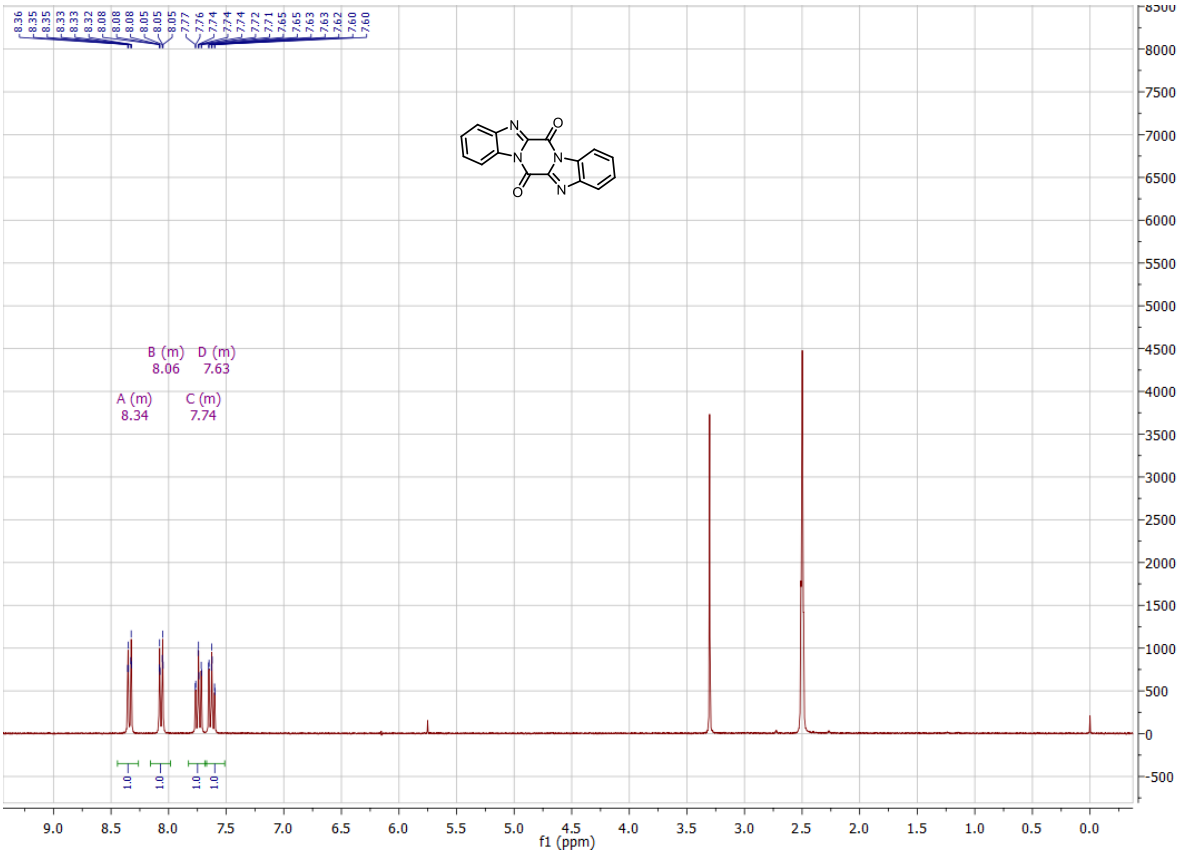

Figure 24. ^{1}H NMR (DMSO-d_6, 300 MHz) spectrum of **6a**. Analytic data is in agreement with the literature.[2]

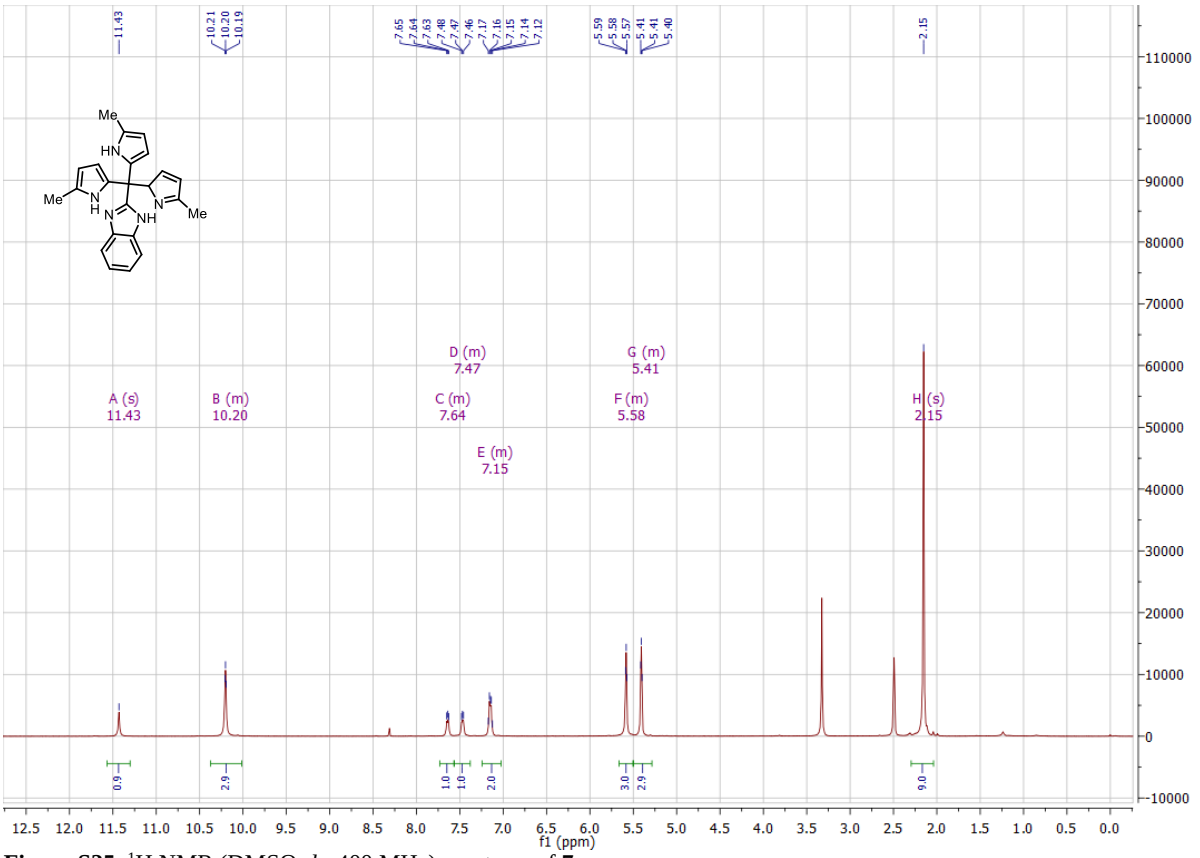

Figure S25. ^{1}H NMR (DMSO-d_6, 400 MHz) spectrum of **7a**.

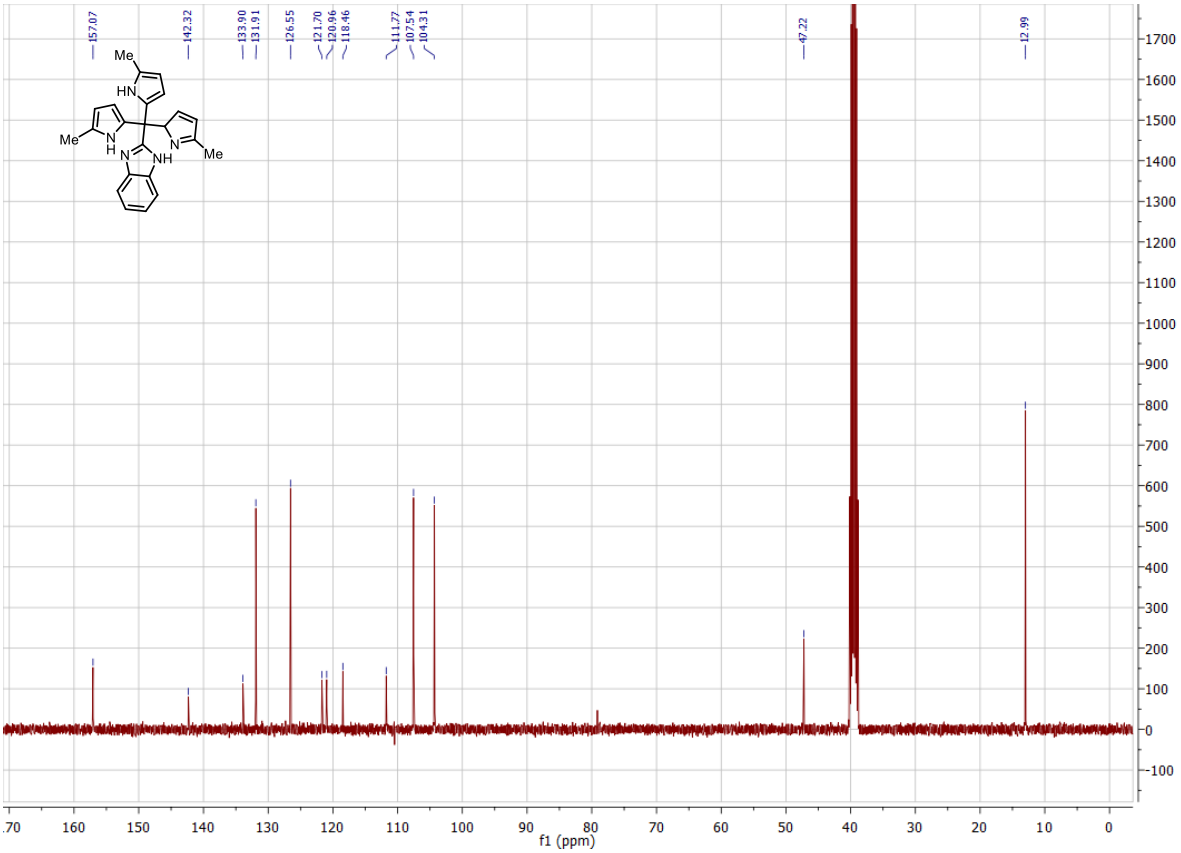

Figure S26. ^{13}C{^{1}H} NMR (DMSO-d_6, 100 MHz) spectrum of **7a**.

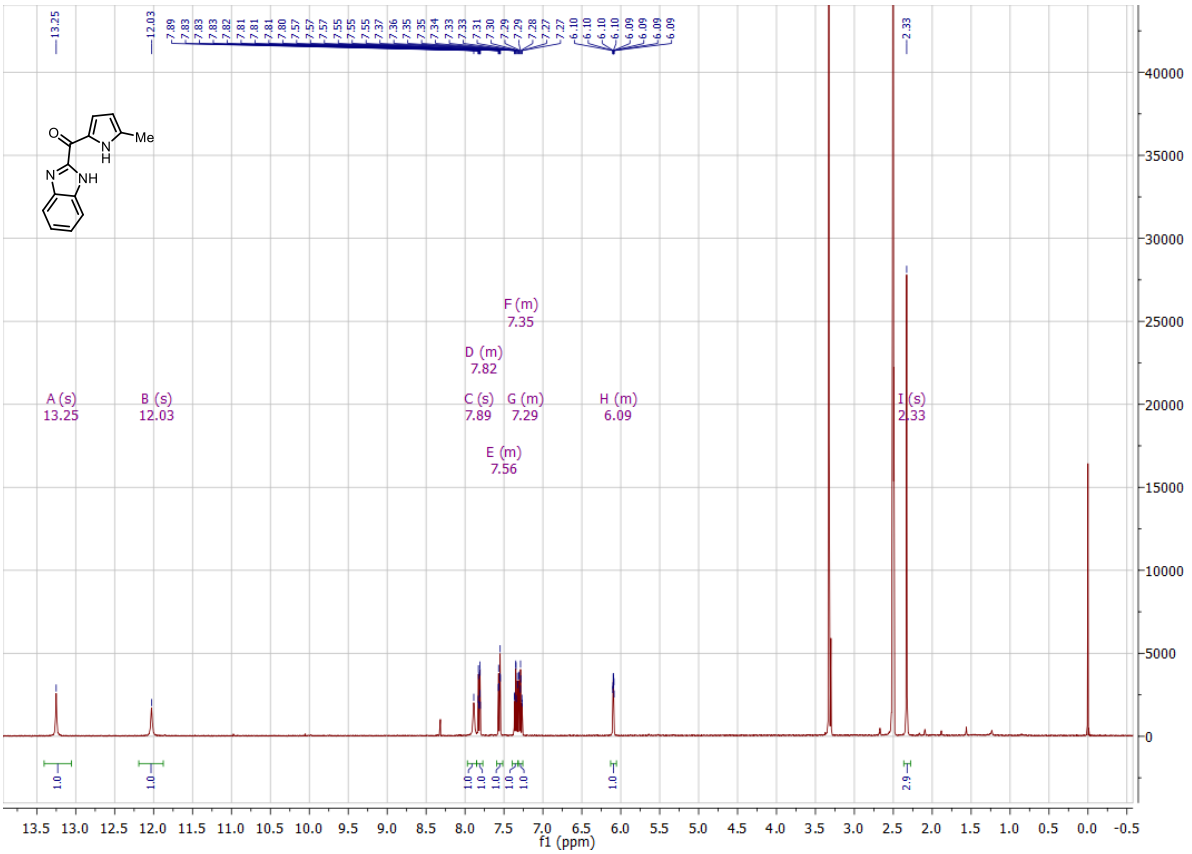

Figure S27. ^{1}H NMR (DMSO-*d*$_6$, 400 MHz) spectrum of **3a**.

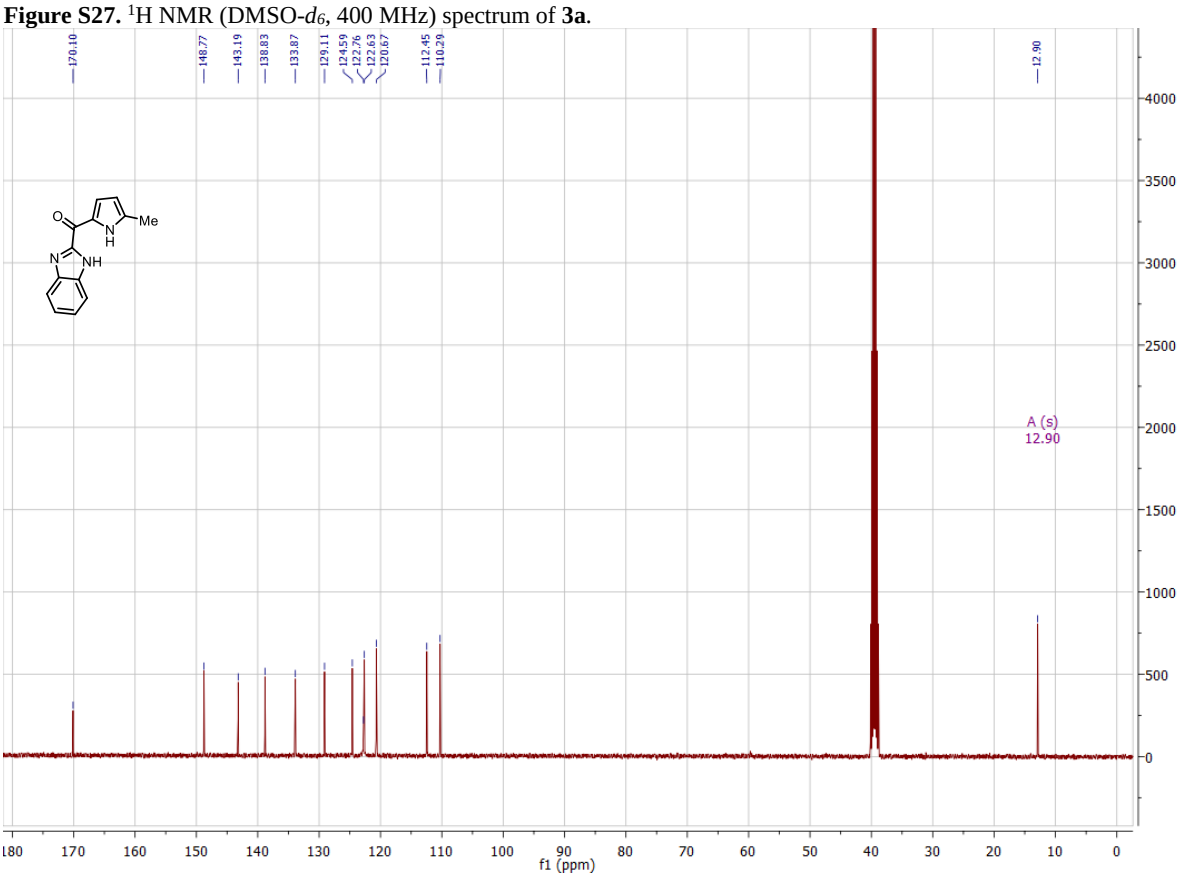

Figure S28. ^{13}C NMR (DMSO-*d*$_6$, 100 MHz) spectrum of **3a**.

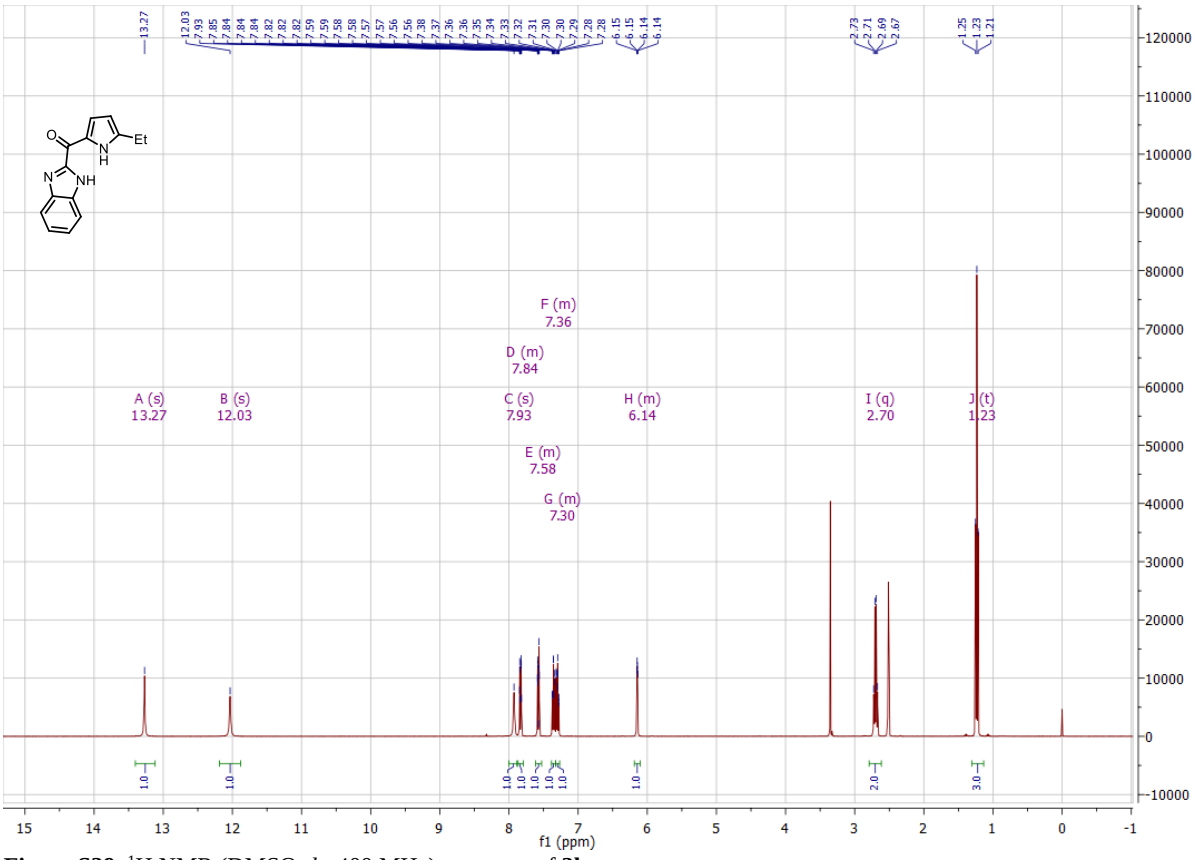

Figure S29. ^{1}H NMR (DMSO-*d*$_6$, 400 MHz) spectrum of **3b**.

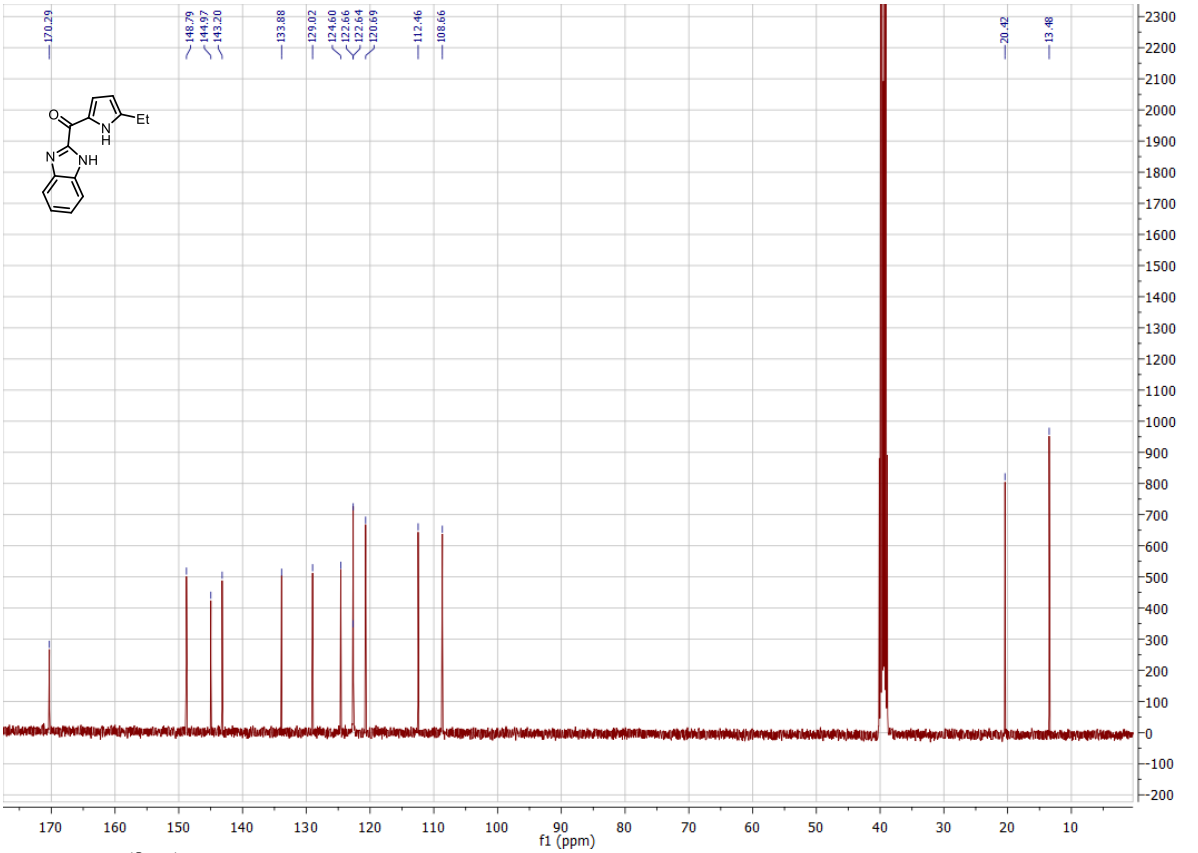

Figure S30. ^{13}C{^{1}H} NMR (DMSO-*d*$_6$, 100 MHz) spectrum of **3b**.

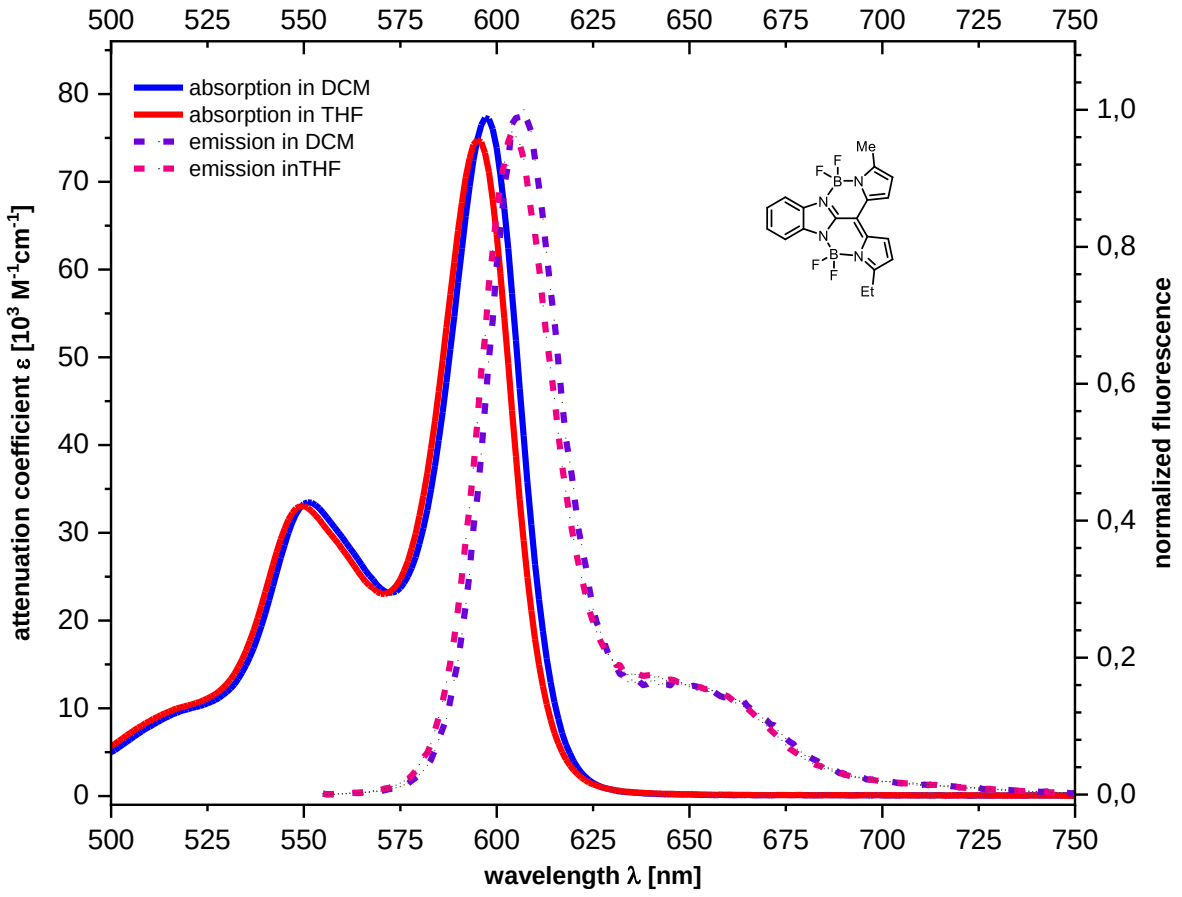

Figure S31. UV-Vis and normalized fluorescence spectra of **8a** in DCM and THF at room temperature.

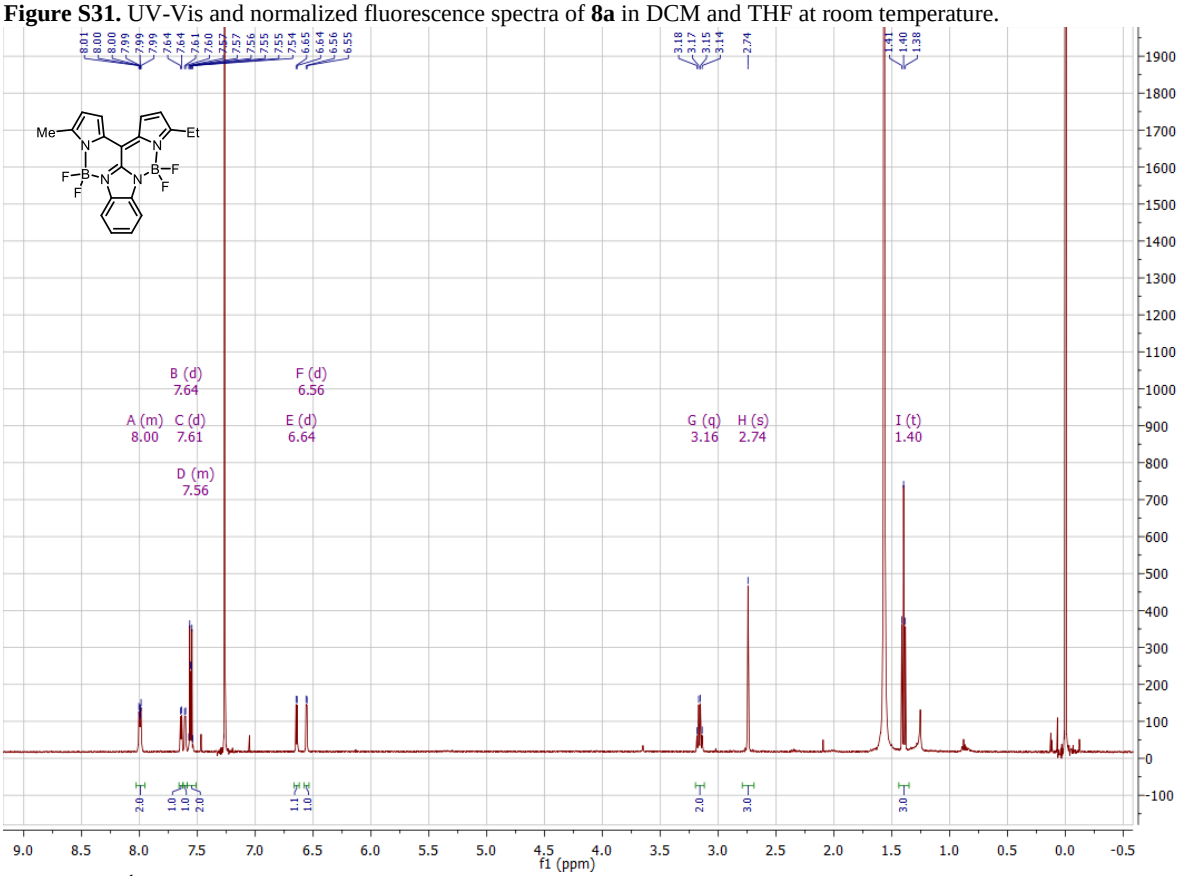

Figure S32. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **8a**.

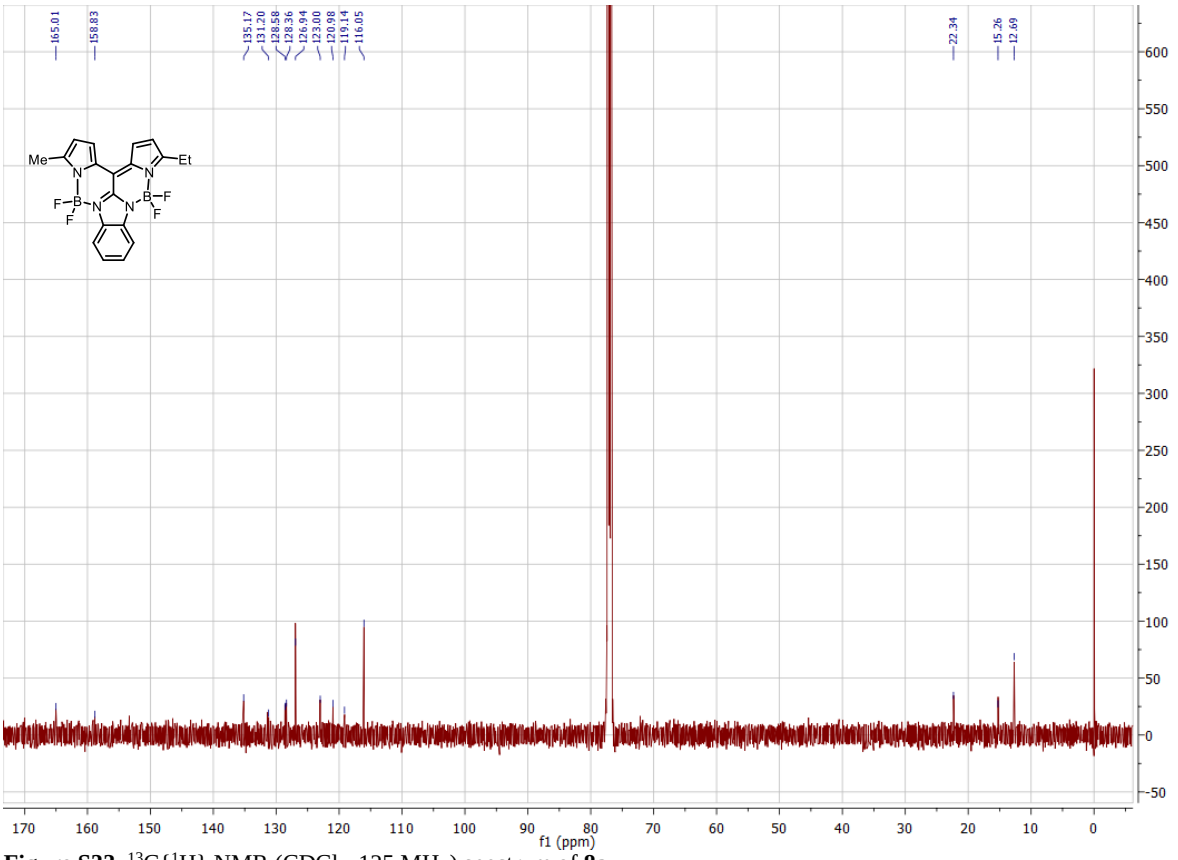

Figure S33. $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz) spectrum of **8a**.

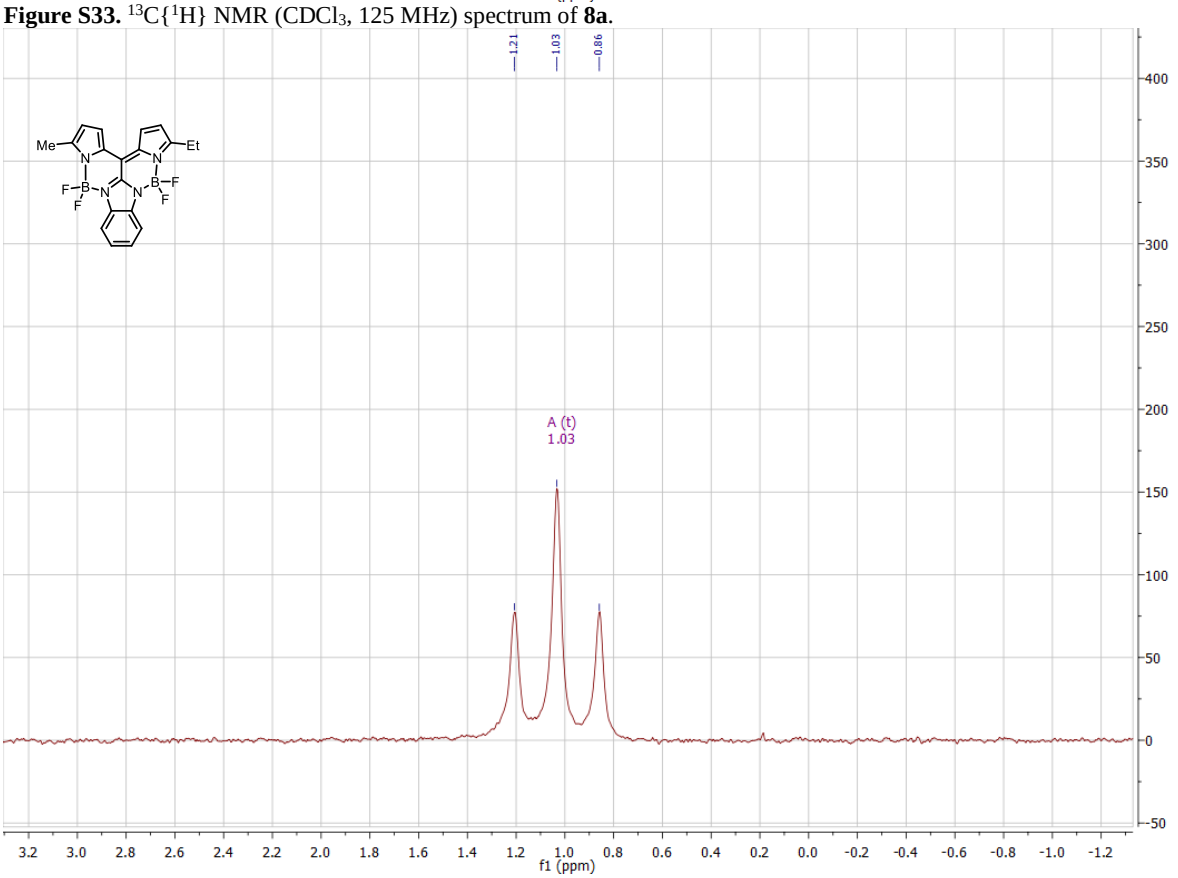

Figure S34. ^{11}B NMR ($CDCl_3$, 161 MHz) spectrum of **8a**.

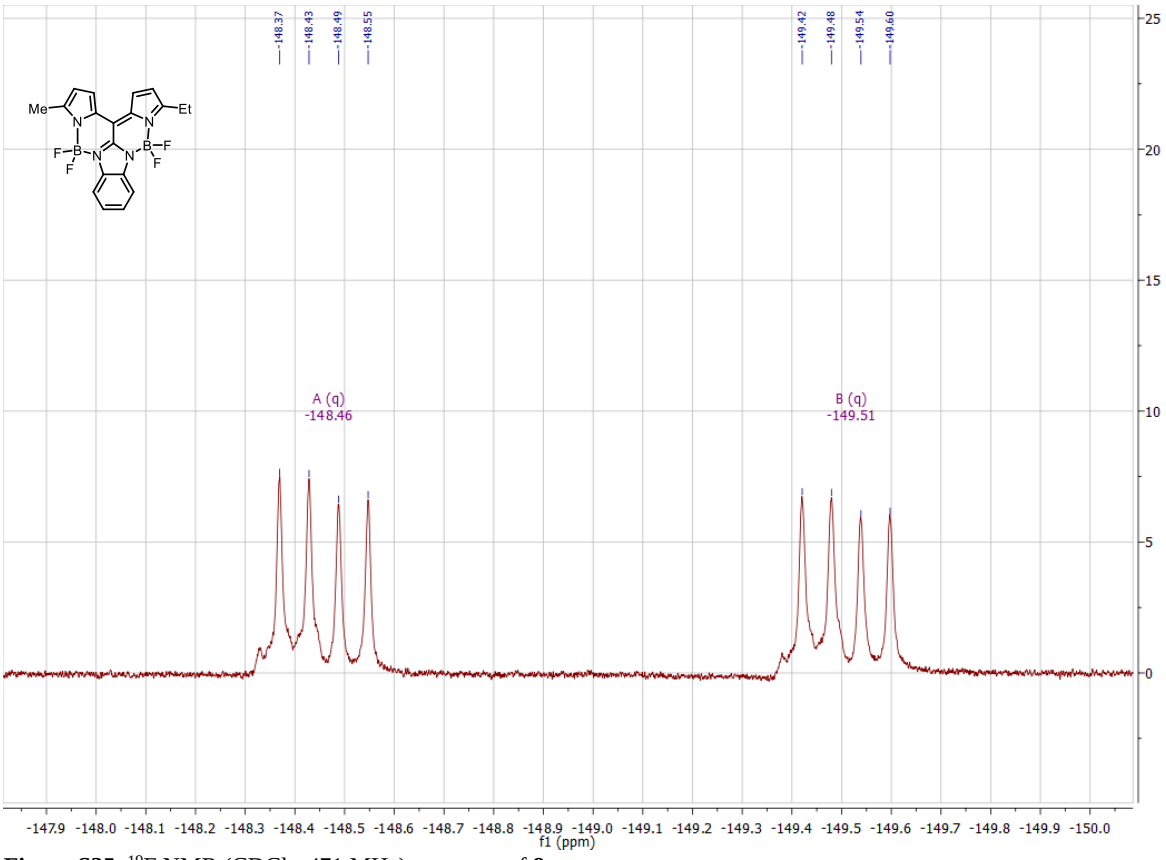

Figure S35. ^{19}F NMR ($CDCl_3$, 471 MHz) spectrum of **8a**.

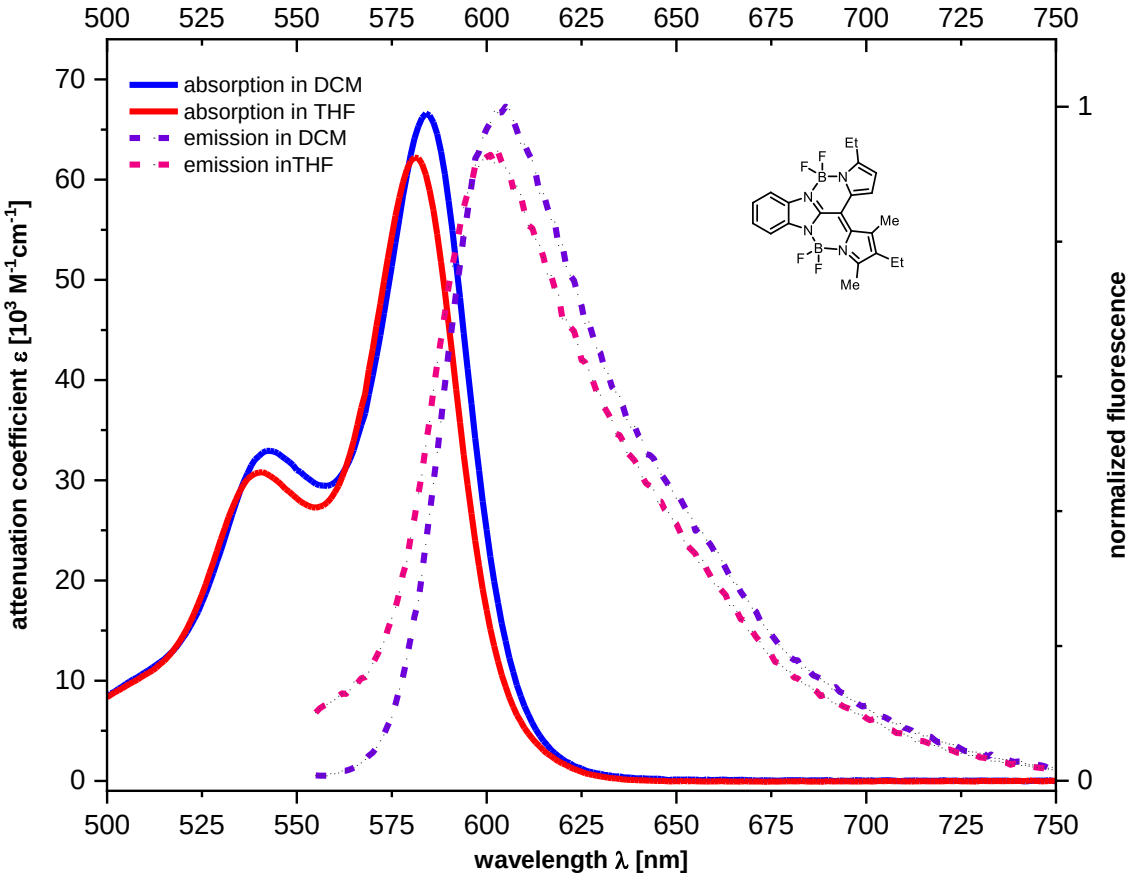

Figure S36. UV-Vis and normalized fluorescence spectra of **8b** in DCM and THF at room temperature.

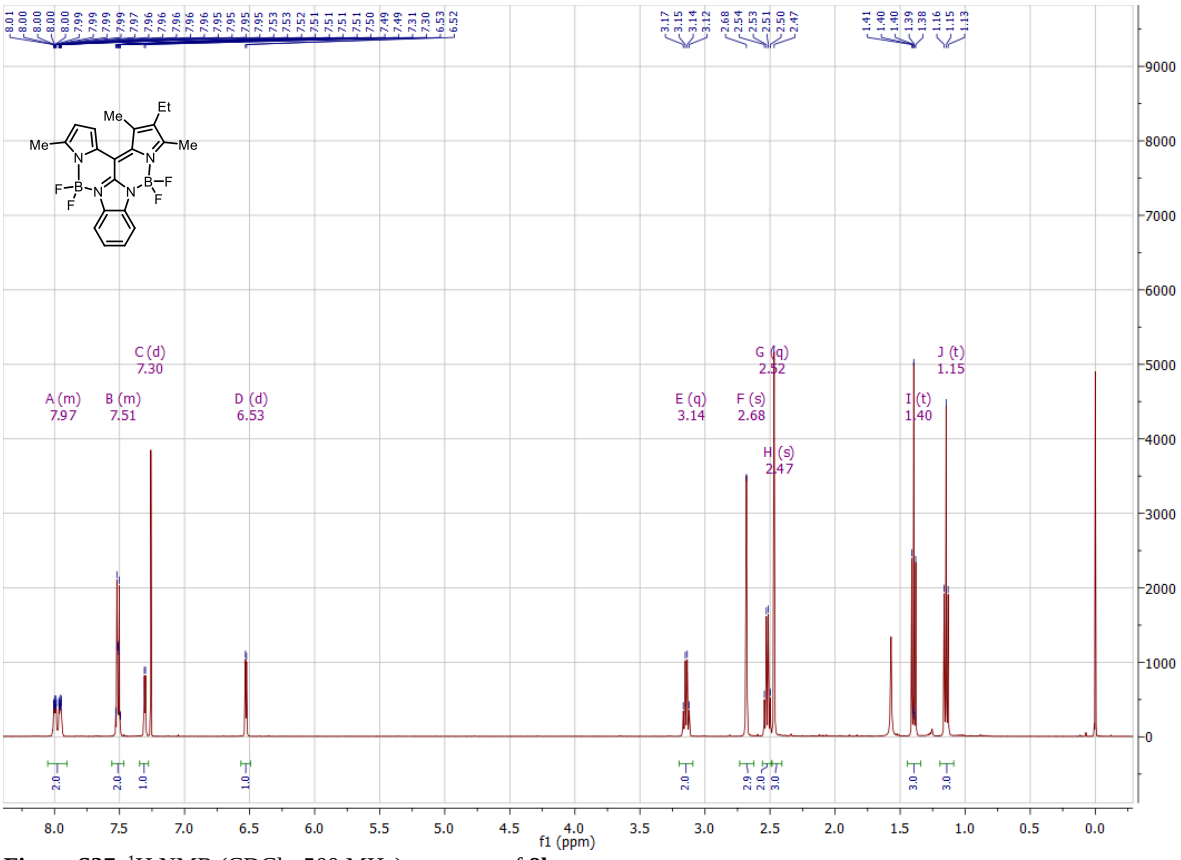

Figure S37. ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum of **8b**.

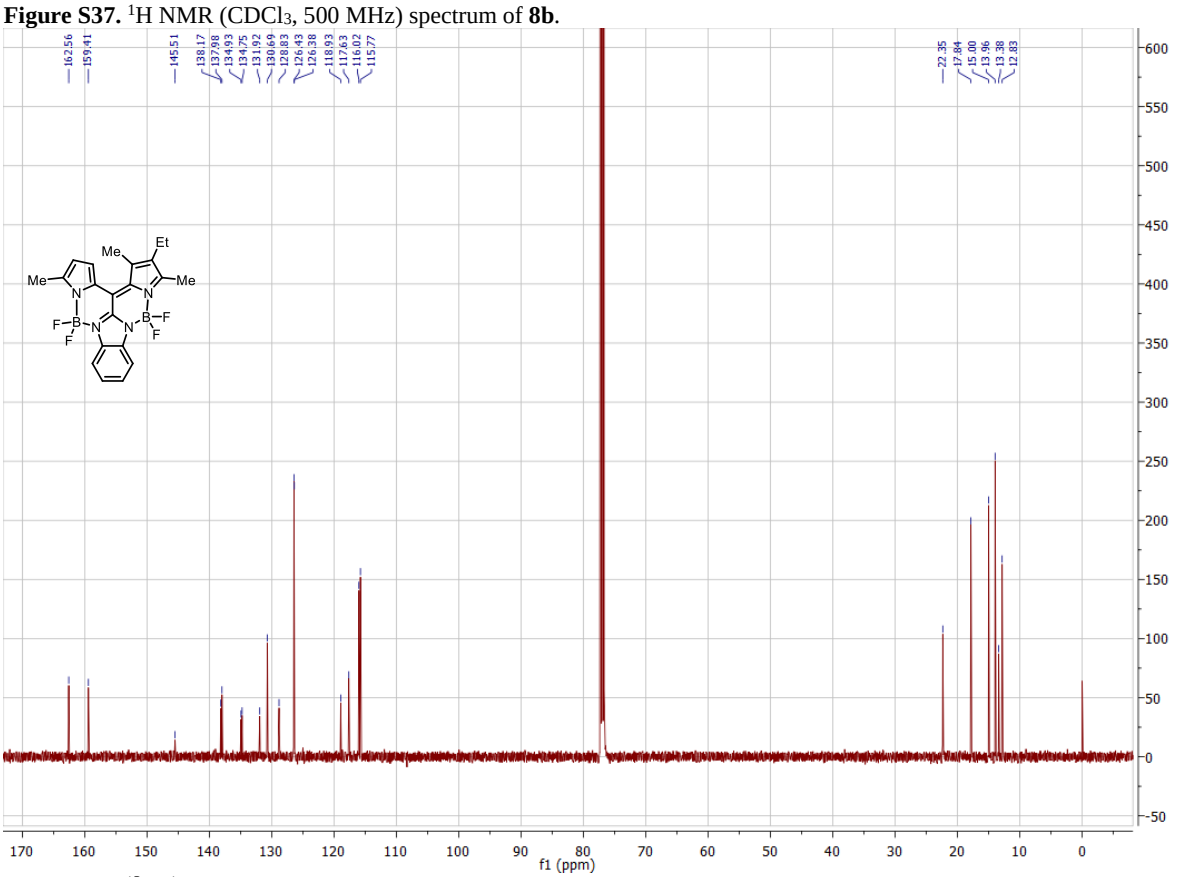

Figure S38. ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz) spectrum of **8b**.

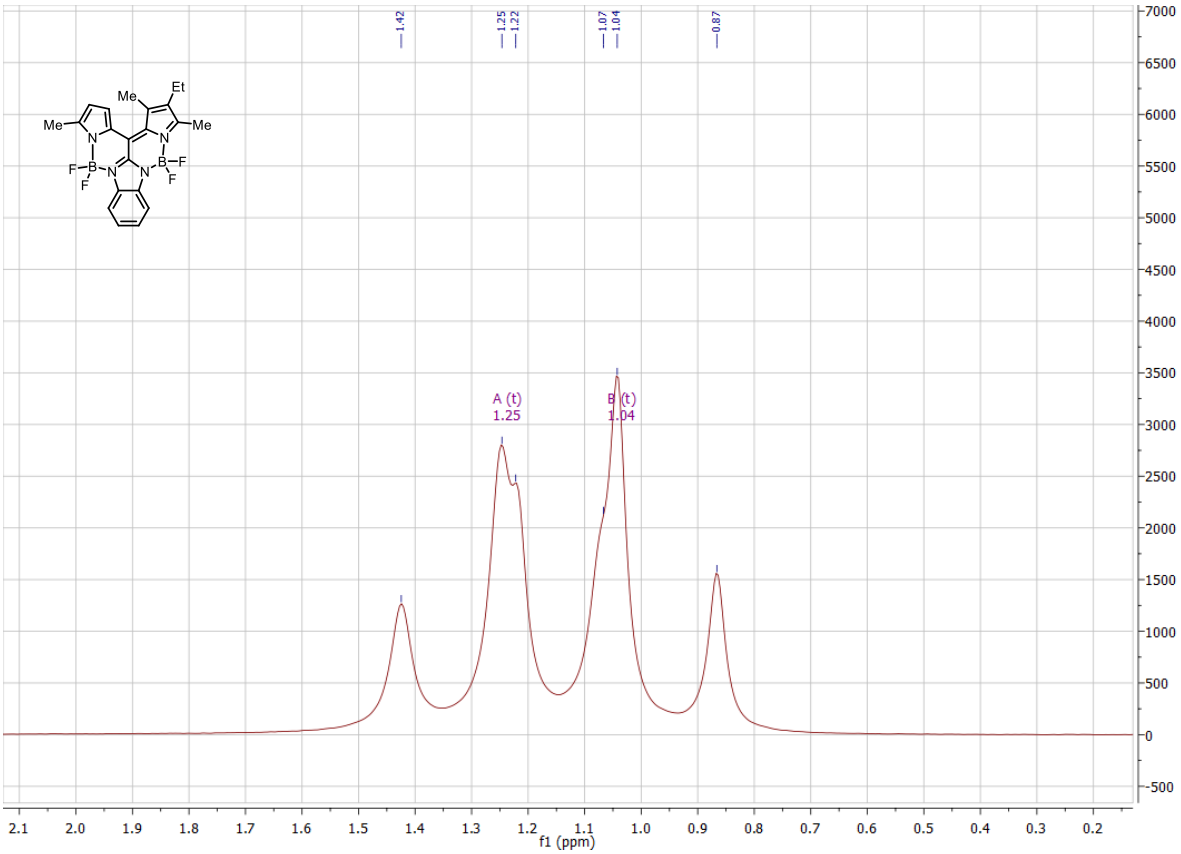

Figure S39. ^{11}B NMR ($CDCl_3$, 161 MHz) spectrum of **8b**.

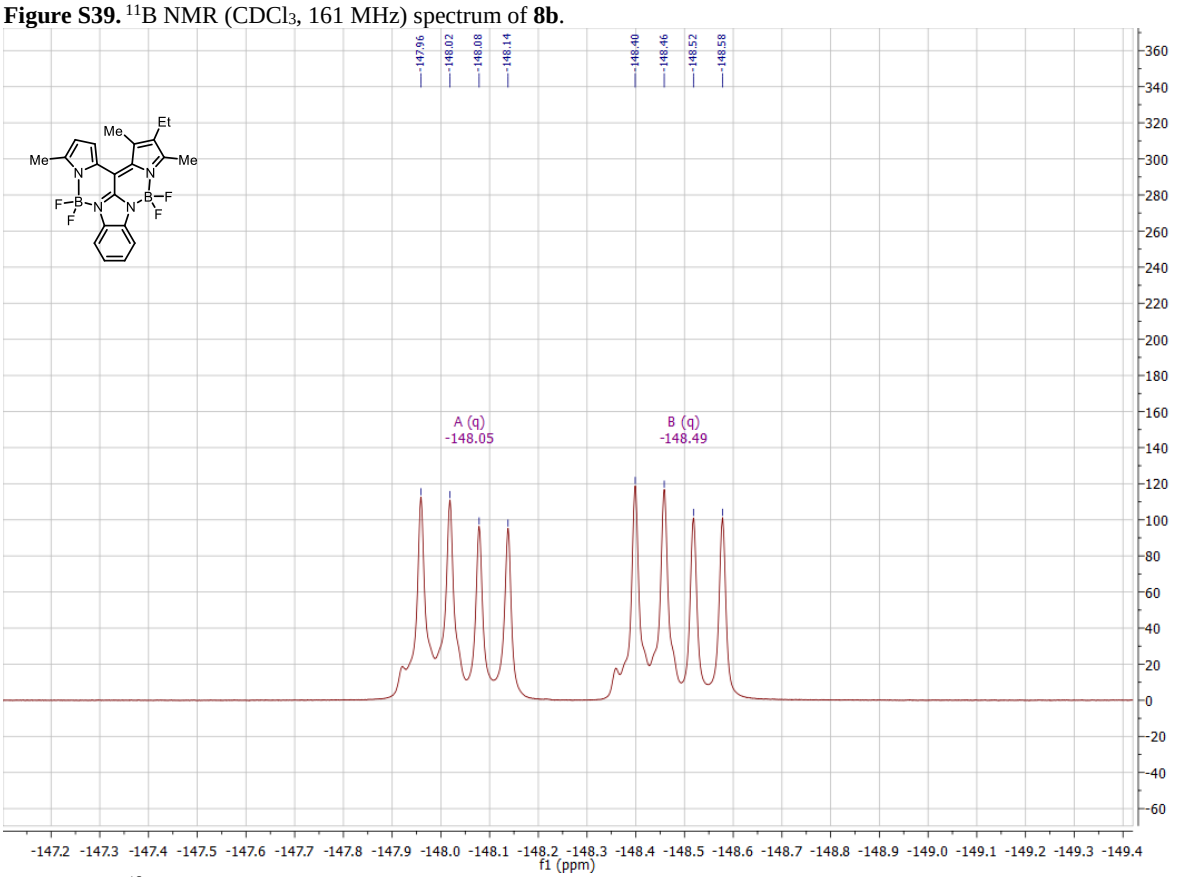

Figure S40. ^{19}F NMR ($CDCl_3$, 471 MHz) spectrum of **8b**.

3. X-Ray Crystallographic Results

Crystal Structure Determinations

Both compounds were recrystallized by evaporation of a solution in a mixture of chloroform and *n*-hexane at room temperature. Crystals were mounted in inert oil on nylon loops and transferred to the cold gas stream of a Rigaku/Oxford XtaLAB Synergy diffractometer. Intensity data were recorded using mirror-focussed Mo-*K*α radiation. Absorption corrections were implemented on the basis of multi-scans. The structures were refined anisotropically on F^2 using the program SHELXL-2018.[3] Hydrogen atoms were included using rigid methyl groups or a riding model starting from calculated positions.

Special features: The symmetry of compound **8a** is approximately that of space group *P*(-1), but this would involve disorder of the ethyl and methyl groups (by superposition); in *P*1, an unusual space group for compounds that are not pure enantiomers, the structure is ordered. The largest difference peak may correspond to a small extent of such a disorder. The structure was refined as a two-component inversion twin. The anomalous dispersion effects were however at best weak and the Flack parameter is almost indeterminate.

Crystallographic data are summarized in Table S2. Additionally, complete data have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC 2047141-2. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.

Table S2: Crystallographic data and structure refinement details for compounds **5f** and **8a**.

Compound	**5f**	**8a**
CCDC number	2047141	2047142
Formula	$C_{30}H_{26}B_2F_4N_4$	$C_{19}H_{16}B_2F_4N_4$
M_r	468.11	397.98
Cryst. size (mm)	0.2 x 0.15 x 0.08	0.2 x 0.15 x 0.08
Crystal system	triclinic	triclinic
Space group	*P*(-1)	*P*1
Temperature (°C)	-173	-173
a (Å)	8.9527(2)	7.8604(5)
b (Å)	11.4590(3)	10.9975(6)
c (Å)	12.3461(4)	11.8617(6)
α (°)	64.481(3)	63.403(5)
β (°)	82.718(2)	89.660(5)
γ (°)	77.051(2)	70.625(6)
V (Å^3)	1113.29	852.51
Z	2	2
D_x (Mg m^{-3})	1.396	1.550
λ (Å)	0.71073	0.71073
μ (mm^{-1})	0.11	0.12
Transmissions	0.949 – 1.000	0.792 – 1.000
F(000)	488	408
$2\theta_{max}$	71.8	66.2
Refl. measured	106038	78435
Refl. indep.	9822	12987
R_{int}	0.028	0.038
Parameters	313	528
Restraints	0	3
wR(F^2, all refl.)	0.104	0.112
R(*F*, >4σ(*F*))	0.035	0.042
Flack parameter	–	0.3(4)
S	1.06	1.03
Max. Δ*p* (e Å^{-3})	0.59, –0.25	0.63, –0.29

Thermal ellipsoid plots (at the 50% probability level):

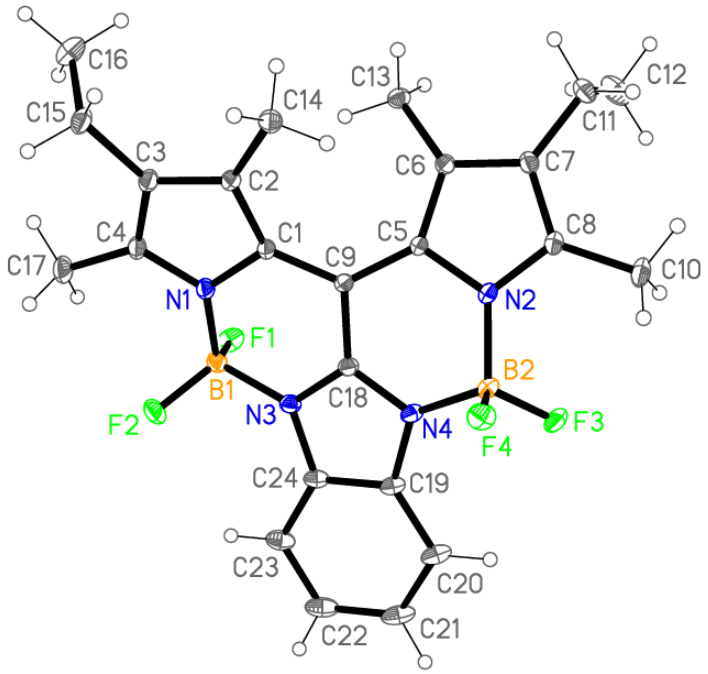

Figure S41. Structure of compound **5f** in the crystal.

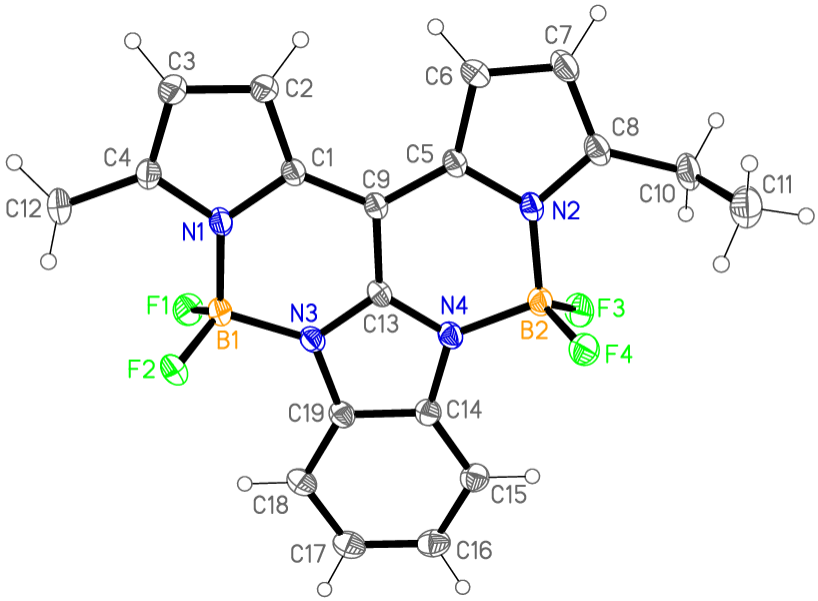

Figure S42. Structure of compound **8a** in the crystal. The asymmetric unit consists of two independent molecules, only one of which is shown.

4. References

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