Supporting Information

Triazolylidene metal complexes tagged with a Bodipy chromophore: synthesis and monitoring of ligand exchange reactions

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1. Crystal structure determinations

Table 1S. Crystal data and structure refinement for compound **3**.

CCDC No.	1499694
Empirical formula	$C_{32}\ H_{40}\ B\ N_5\ O_3\ F_5\ S\ Cl_3$
Molecular formula	$[C_{30}\ H_{39}\ B\ N_5\ F_2]^+[C\ O_3\ F_3\ S]^-$ x C H Cl_3
Formula weight	786.91
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
Unit cell dimensions	a = 7.9707(2) Å
	b = 25.7264(4) Å β = 99.950(2)°.
	c = 17.9969(4) Å
Volume	3634.89(13) $Å^3$
Z	4
Density (calculated)	1.438 Mg/m^3
Absorption coefficient	3.401 mm^{-1}
F(000)	1632
Crystal size	0.2367 x 0.0402 x 0.0262 mm^3
Theta range for data collection	3.03 to 76.93°.
Index ranges	–7<=h<=9, –32<=k<=32, –20<=l<=22
Reflections collected	31133
Independent reflections	7529 [R(int) = 0.0524]
Completeness to theta = 76.00°	98.9 %
Absorption correction	Analytical
Max. and min. transmission	0.925 and 0.657
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	7529 / 0 / 459
Goodness–of–fit on F^2	1.026
Final R indices [I>2sigma(I)]	R1 = 0.0384, wR2 = 0.0922
R indices (all data)	R1 = 0.0509, wR2 = 0.1004
Largest diff. peak and hole	0.330 and –0.436 e.$Å^{-3}$

Table S2. Crystal data and structure refinement for compound **4**.

CCDC No.	1499696
Empirical formula	$C_{60}\ H_{74}\ B_2\ N_{10}\ F_4\ Cl_2\ Pd_2$
Formula weight	1316.61
Temperature	100(2) K
Wavelength	1.54184 Å
Crystal system	Monoclinic
Space group	$P2_1/c$ (#14)
Unit cell dimensions	a = 14.9355(2) Å
	b = 31.1889(3) Å β = 91.436(1)°.
	c = 14.9548(2) Å
Volume	6964.08(15) $Å^3$
Z	4
Density (calculated)	1.256 Mg/m^3
Absorption coefficient	5.292 mm^{-1}
F(000)	2704
Crystal size	0.1810 x 0.0725 x 0.0279 mm^3
Theta range for data collection	2.83 to 76.96°.
Index ranges	–18<=h<=18, –39<=k<=39, –17<=l<=18
Reflections collected	79312
Independent reflections	14485 [R(int) = 0.0778]
Completeness to theta = 76.96°	98.5 %
Absorption correction	Analytical
Max. and min. transmission	0.867 and 0.581
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	14485 / 0 / 731
Goodness–of–fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1404
R indices (all data)	R1 = 0.0671, wR2 = 0.1526
Largest diff. peak and hole	1.892 and –1.539 $e.Å^{-3}$

Table S3. Crystal data and structure refinement for compound **6**.

CCDC No.	1499697	
Empirical formula	C_{44} H_{48} B N_6 F_2 Cl_3 Pd	
Molecular formula	C_{43} H_{46} B N_6 F_2 Cl Pd x C H_2 Cl_2 [a)]	
Formula weight	922.44	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P–1 (#2)	
Unit cell dimensions	a = 9.98924(6) Å	α = 80.4957(8)°.
	b = 14.8914(2) Å	β = 74.8522(6)°.
	c = 15.0029(2) Å	γ = 87.4126(7)°.
Volume	2124.62(4) $Å^3$	
Z	2	
Density (calculated)	1.442 Mg/m^3	
Absorption coefficient	5.646 mm^{-1}	
F(000)	948	
Crystal size	0.2397 x 0.1304 x 0.0818 mm^3	
Theta range for data collection	3.01 to 76.87°.	
Index ranges	–12<=h<=12, –18<=k<=18, –18<=l<=18	
Reflections collected	85160	
Independent reflections	8910 [R(int) = 0.0434]	
Completeness to theta = 76.87°	99.3 %	
Absorption correction	Analytical	
Max. and min. transmission	0.723 and 0.416	
Refinement method	Full–matrix least–squares on F^2	
Data / restraints / parameters	8910 / 0 / 496	
Goodness–of–fit on F^2	1.072	
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0737	
R indices (all data)	R1 = 0.0292, wR2 = 0.0743	
Largest diff. peak and hole	0.529 and –0.584 $e.Å^{-3}$	

[a)] The solvent could not be refined in terms of atomic sites. Platon SQUEEZE was used to compensate for the spread electron density.

Table S4. Crystal data and structure refinement for compound **8b**.

CCDC No.	1499695
Empirical formula	$C_{32}\ H_{34}\ B\ N_6\ O_3\ F_5\ S$
Molecular formula	$[C_{31}\ H_{34}\ B\ N_6\ F_2]^+[C\ O_3\ F_3\ S]^-$
Formula weight	688.52
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$ (#4)
Unit cell dimensions	a = 7.57530(9) Å
	b = 12.1883(2) Å β = 96.031(1)°.
	c = 17.3804(2) Å
Volume	1595.85(4) $Å^3$
Z	2
Density (calculated)	1.433 Mg/m^3
Absorption coefficient	0.176 mm^{-1}
F(000)	716
Crystal size	0.2313 x 0.1317 x 0.0738 mm^3
Theta range for data collection	2.83 to 29.61°.
Index ranges	–10<=h<=10, –16<=k<=16, –23<=l<=22
Reflections collected	35441
Independent reflections	7929 [R(int) = 0.0298]
Completeness to theta = 28.00°	99.1 %
Absorption correction	Analytical
Max. and min. transmission	0.988 and 0.972
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	7929 / 1 / 440
Goodness–of–fit on F^2	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.0858
R indices (all data)	R1 = 0.0372, wR2 = 0.0878
Absolute structure parameter	0.01(5)
Largest diff. peak and hole	0.384 and –0.351 $e.Å^{-3}$

2. Comparison of ^{1}H NMR spectra

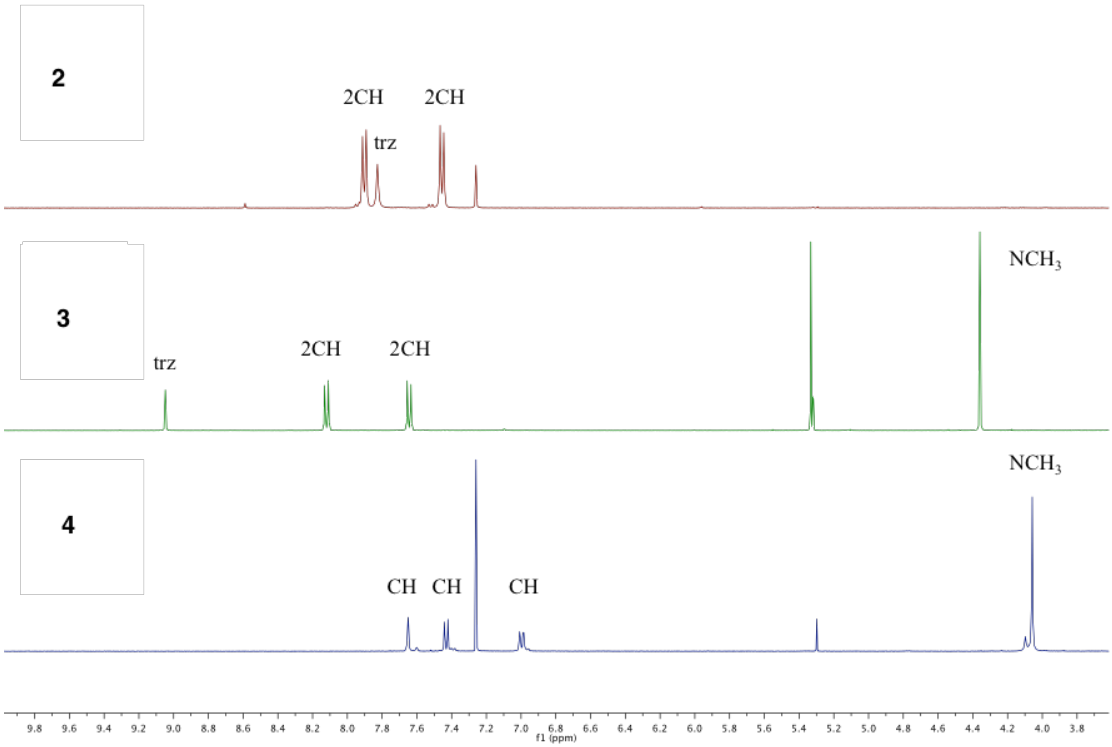

Figure S1. Comparison of the low-field section of the ^{1}H NMR spectra of compounds **2**, **3**, and **4**.

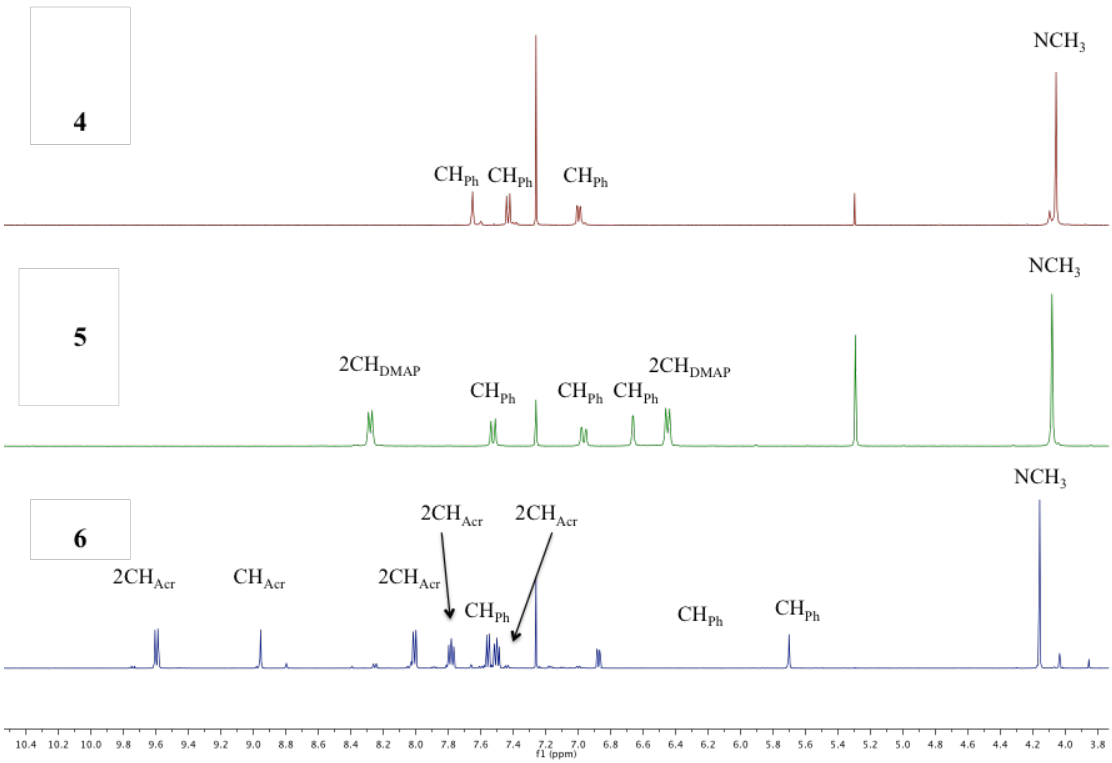

Figure S2. Comparison of ^{1}H NMR spectra of compounds **4**, **5** and **6** in the low field region.

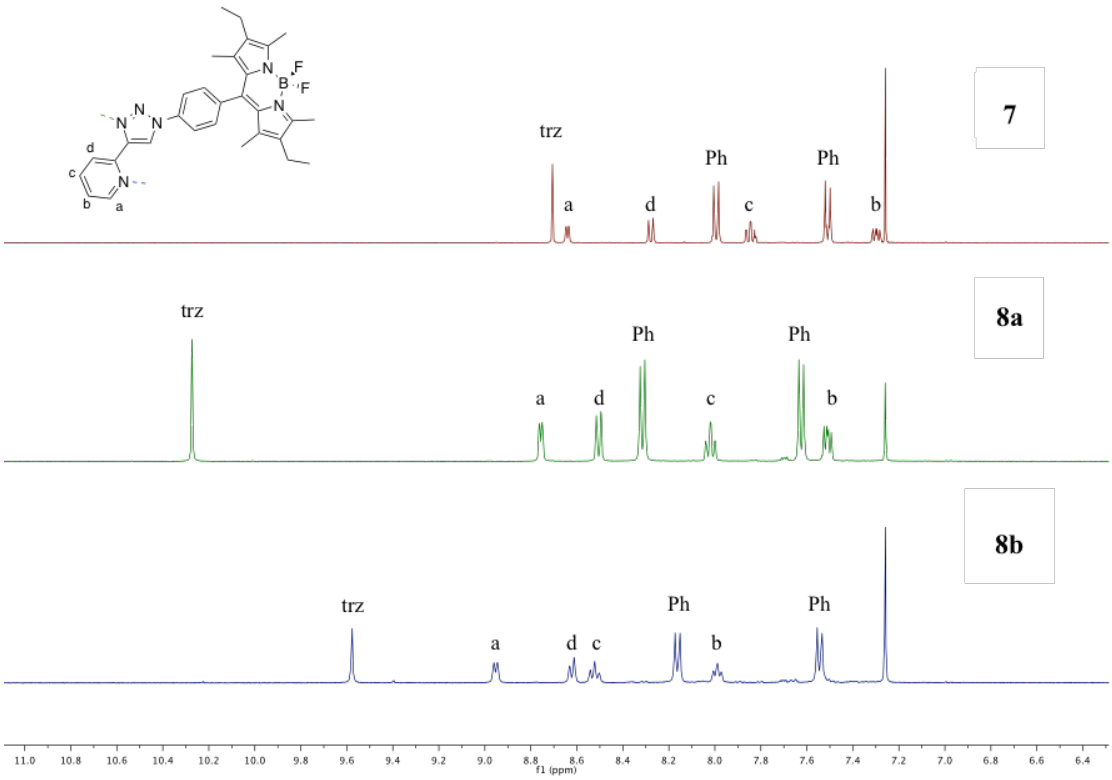

Figure S3. Comparison of the ^{1}H NMR spectra of compounds **7**, **8a** and **8b** in $CDCl_3$ of the aromatic region.

3. Stern-Volmer plots for complex 5 and decay measurements

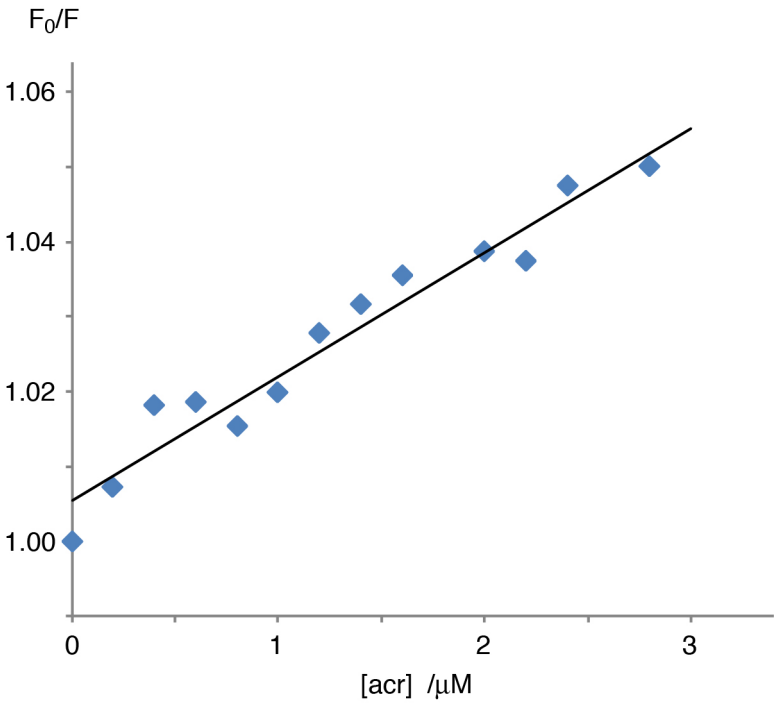

Figure S4. Stern-Volmer plot of complex **5** (slop is 16,500 and linear regression is 0.945).

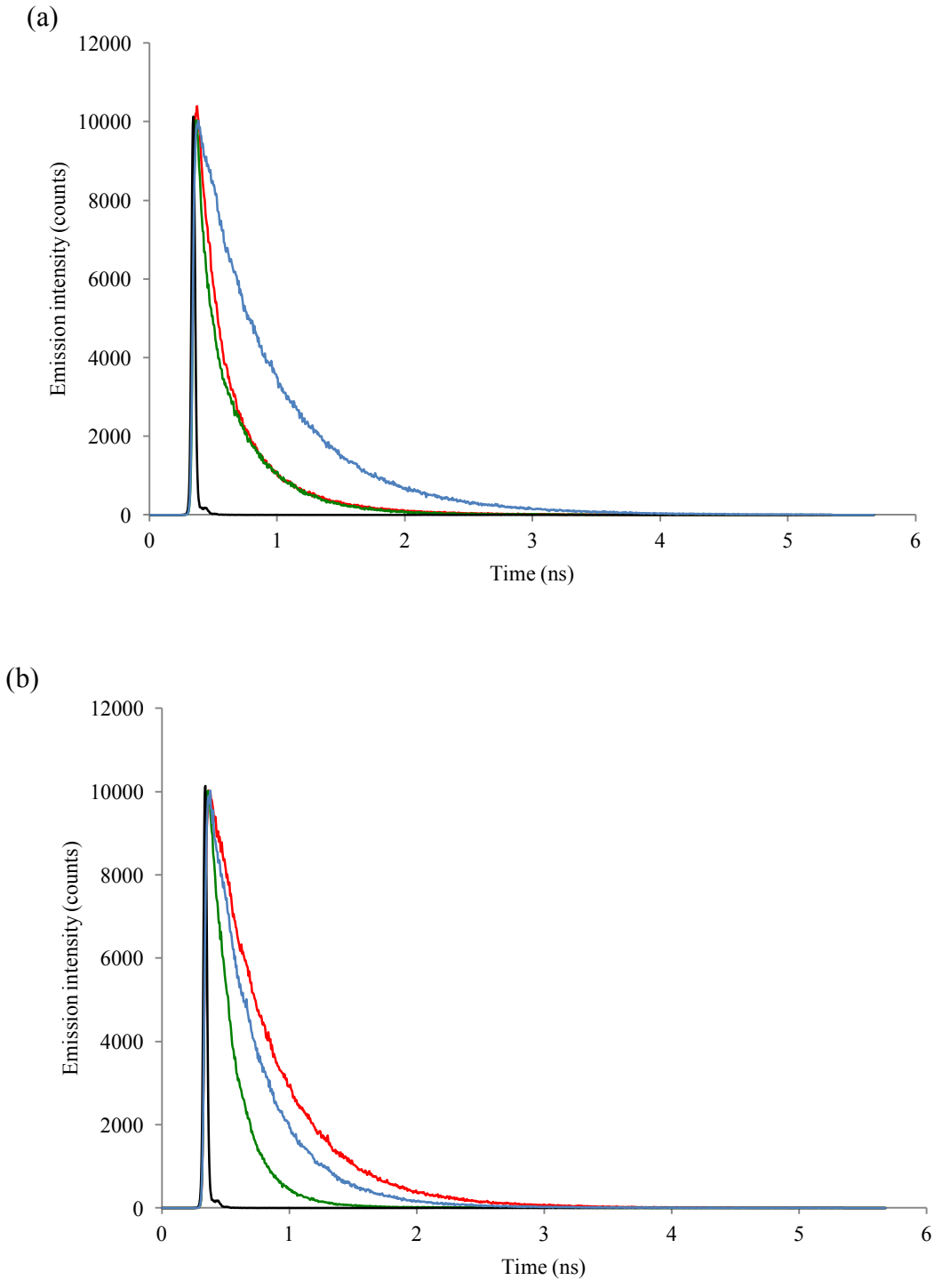

Figure S5. Photoluminescence decays measured for butyl (a) and pyridine (b) derived triazols **2** and **7** (red lines), triazolium salts **3** and **8a** (green lines), and triazolylidene complexes **4** and **9** (blue lines); instrument response function (black line).

4. NMR spectra of all new compounds

In some NMR spectra residual solvents from synthetic or purification procedures are present as well as in some cases signals from H grease (δ_H = 1.25, 0.85; δ_C = 29.7 in $CDCl_3$) despite major efforts to remove them with several pentane washes. In all cases, such residual signals were assigned according literature: Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stolts, B. M.; Bercaw, J. E.; Goldberg, K. I.; *Organometallics* **2010**, *29*, 2176.

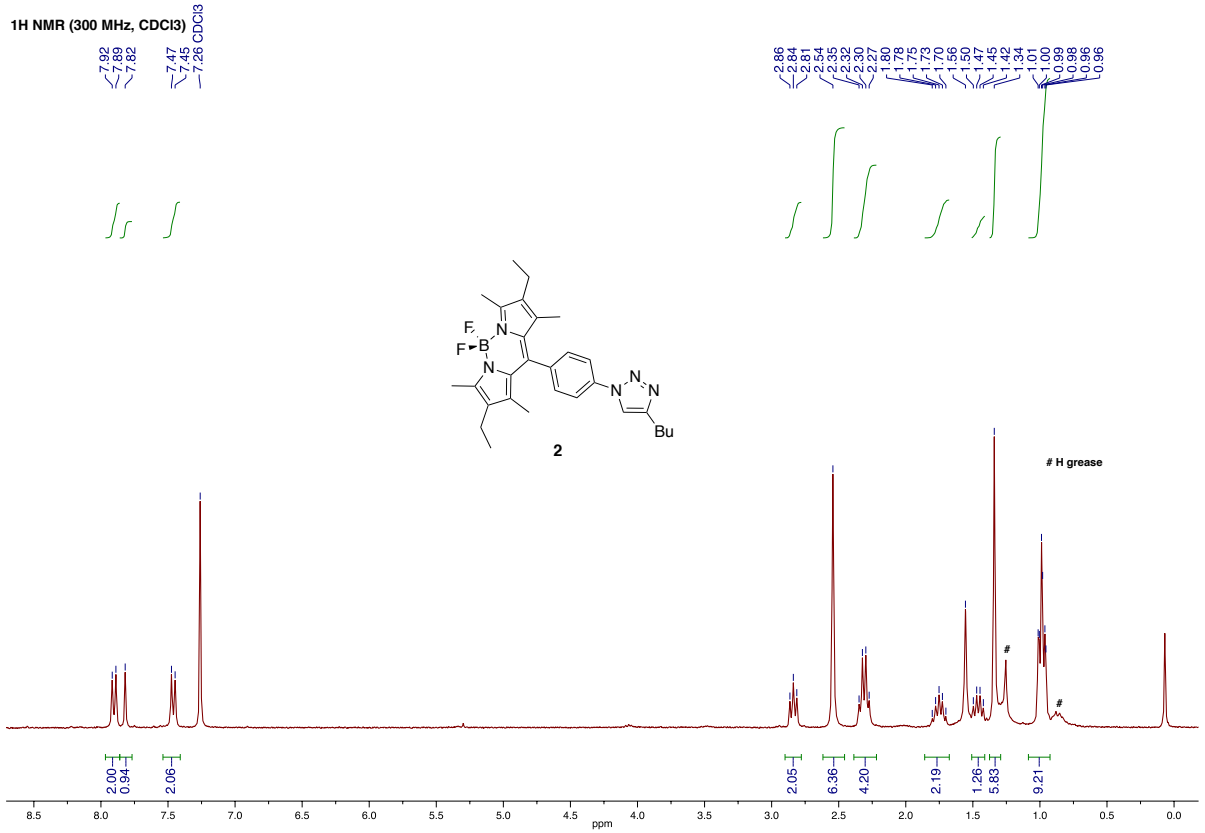

Figure S6. ^{1}H NMR spectrum of compound **2**.

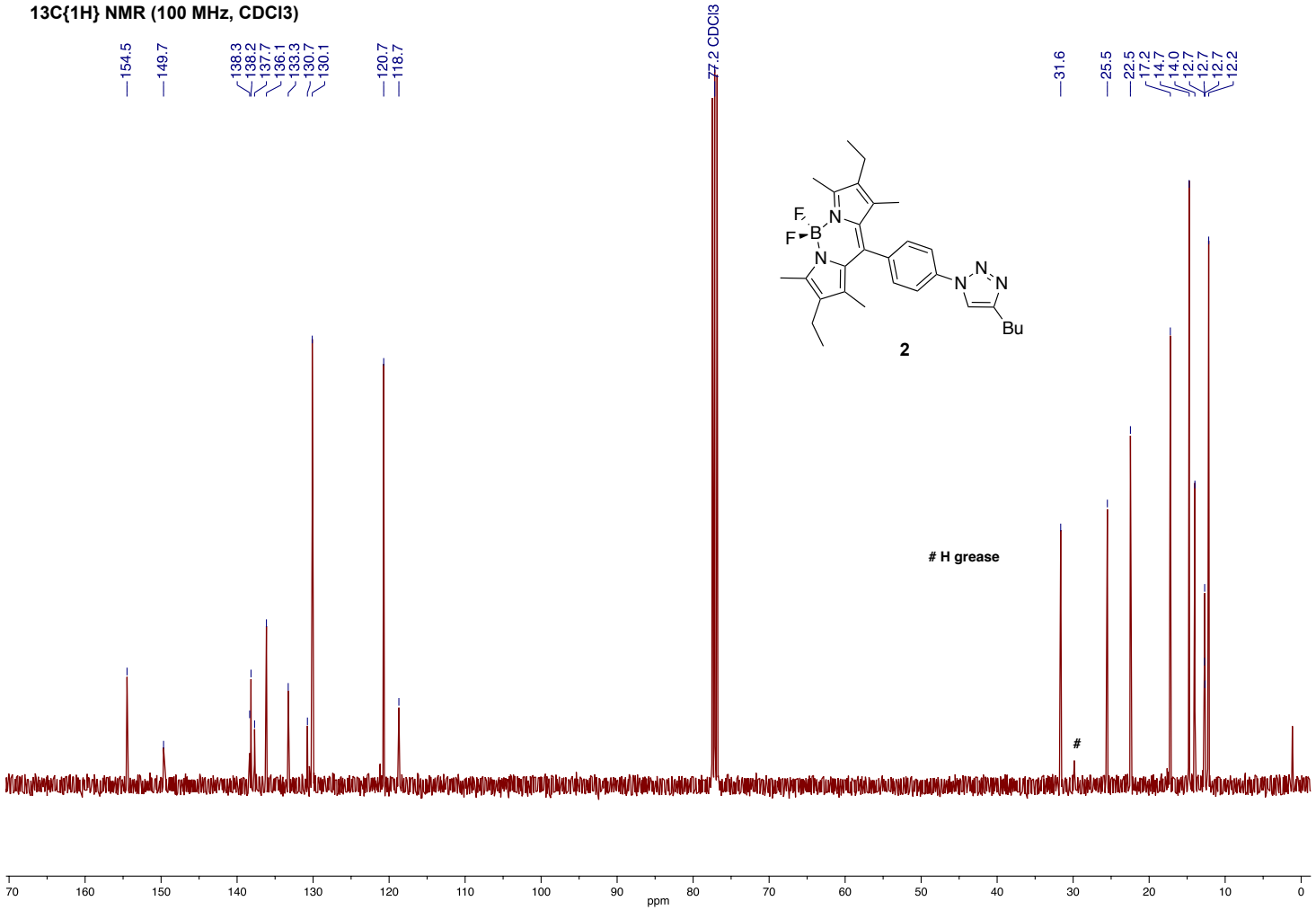

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of compound **2**.

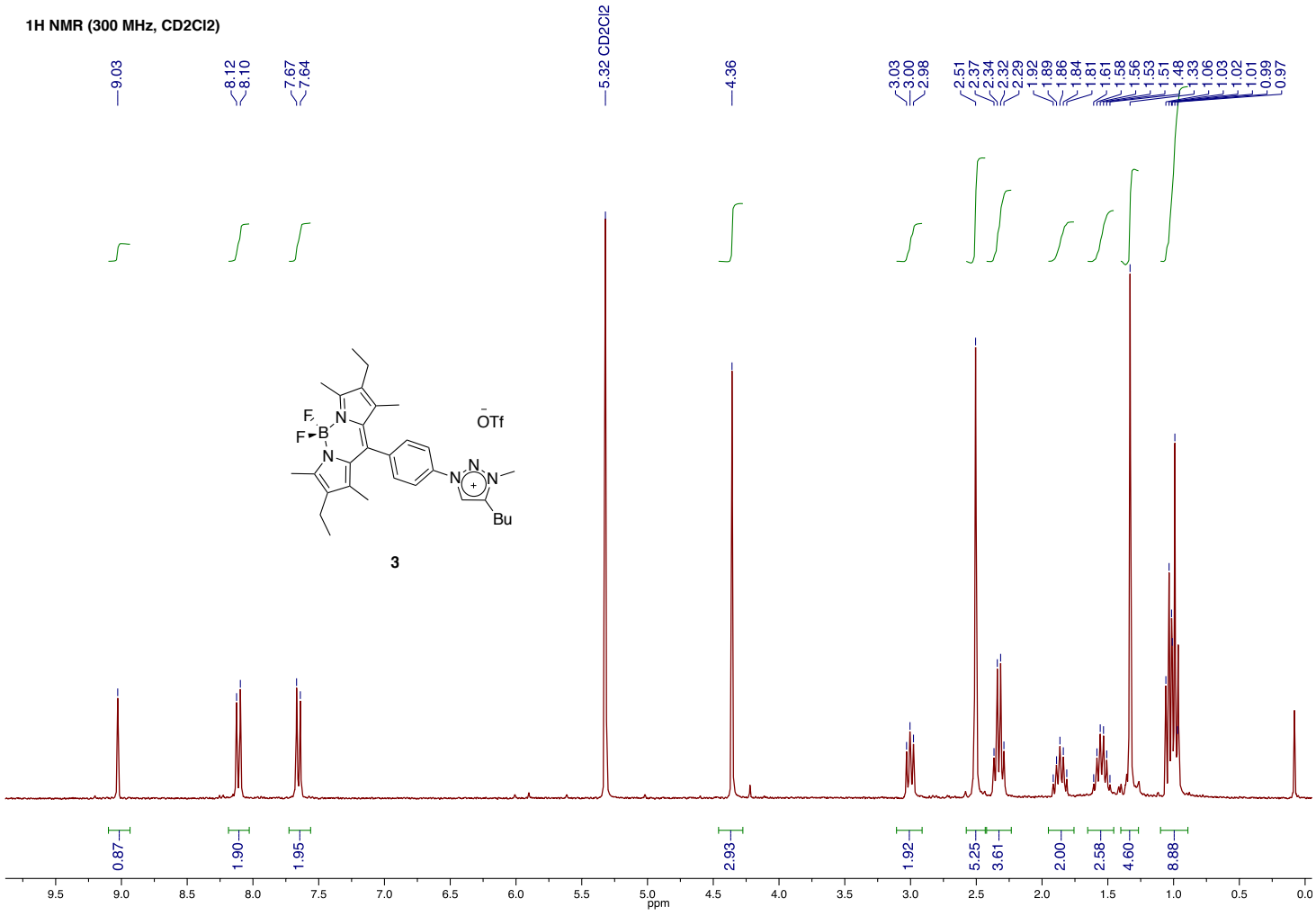

Figure S8. [1]H NMR spectrum of compound **3**.

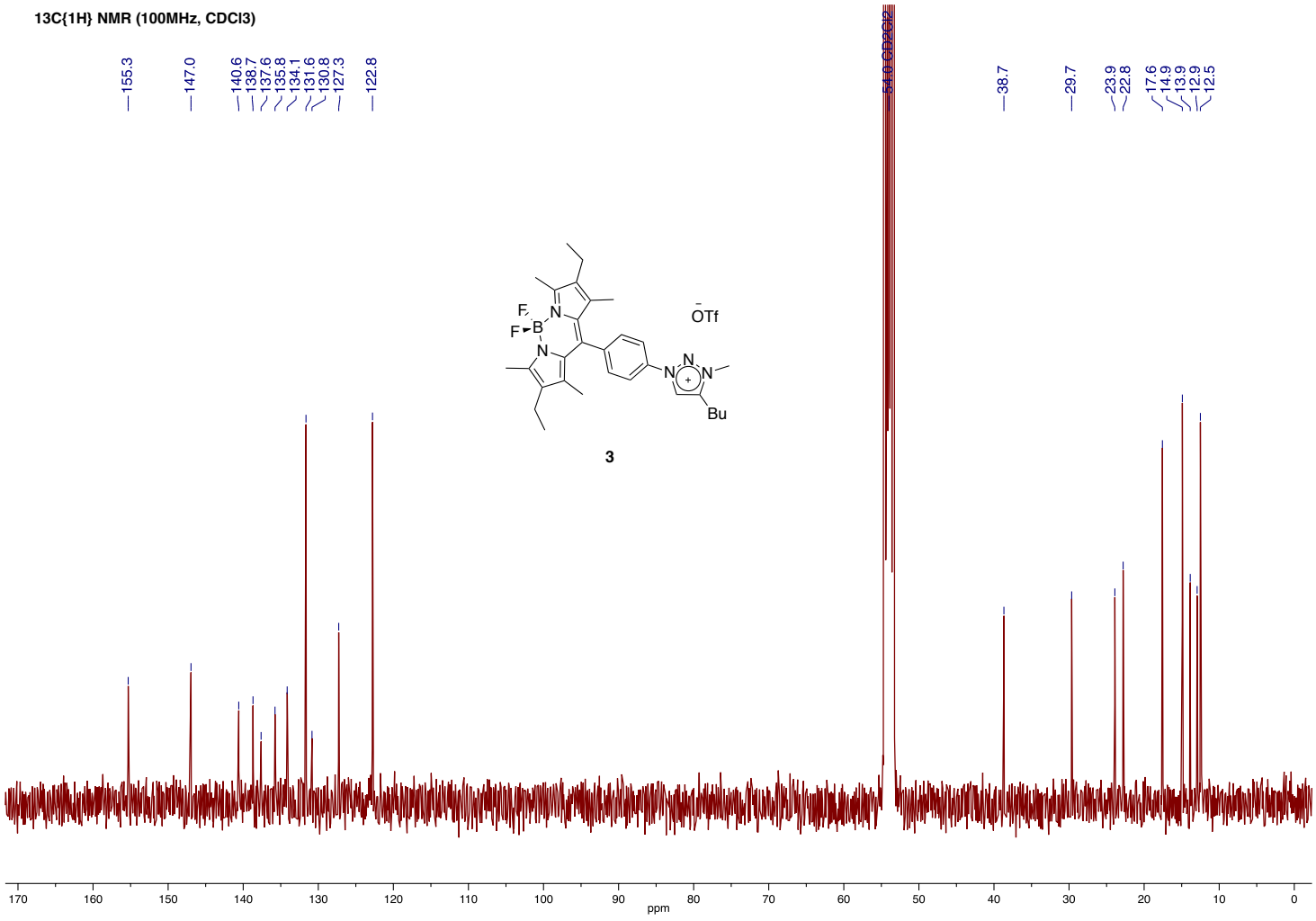

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of compound **3**.

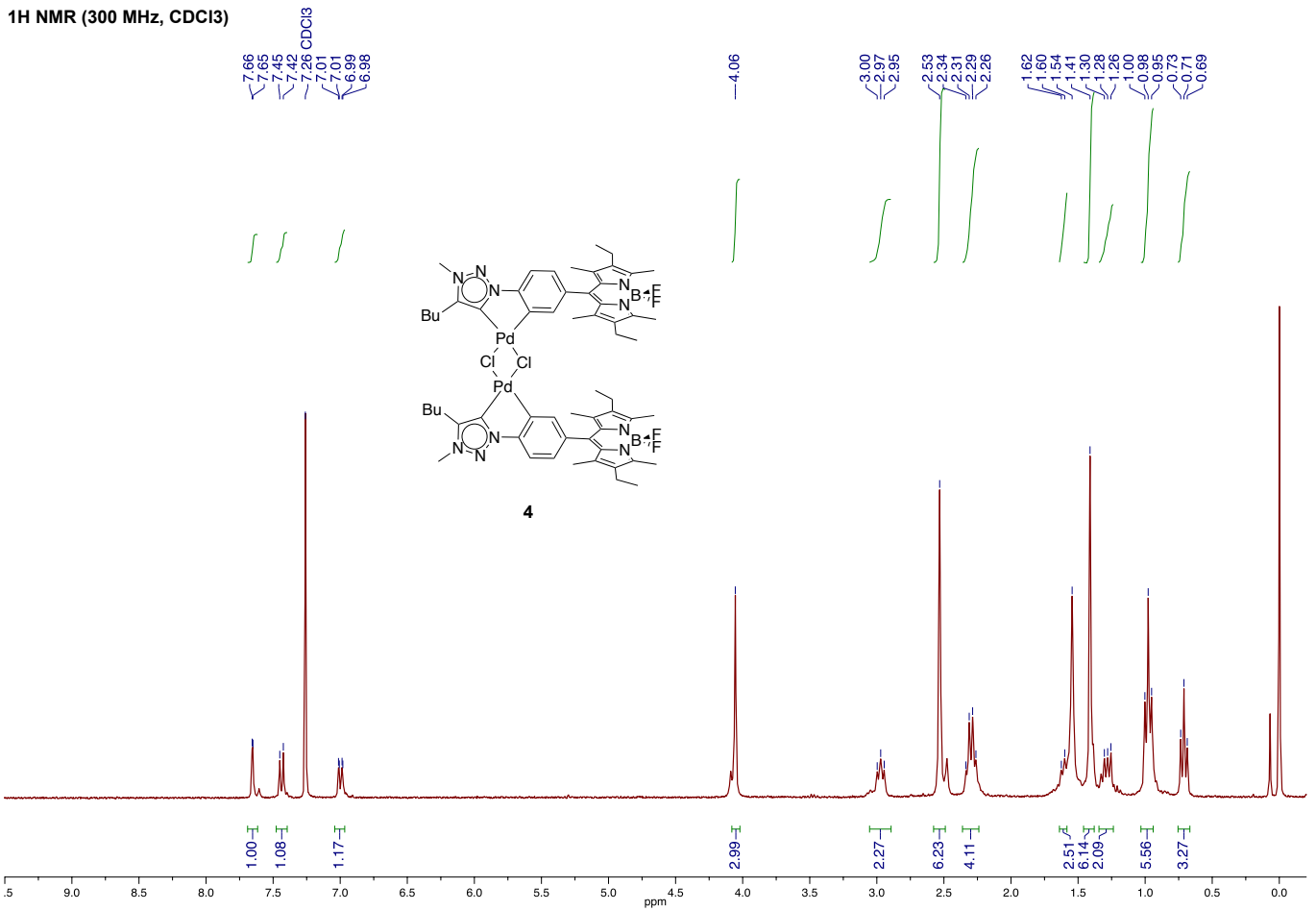

Figure S10. ^{1}H NMR spectrum of compound **4** (the spectrum also shows a smaller set of signals almost identical to those of **4** with just minor shifts (ca. 5% integration). This second component could not be separated and was even present when dissolving crystals of **4**, and was therefore tentatively attributed to the *anti* isomer (*i.e.* bodipy residues pointing in opposite directions).

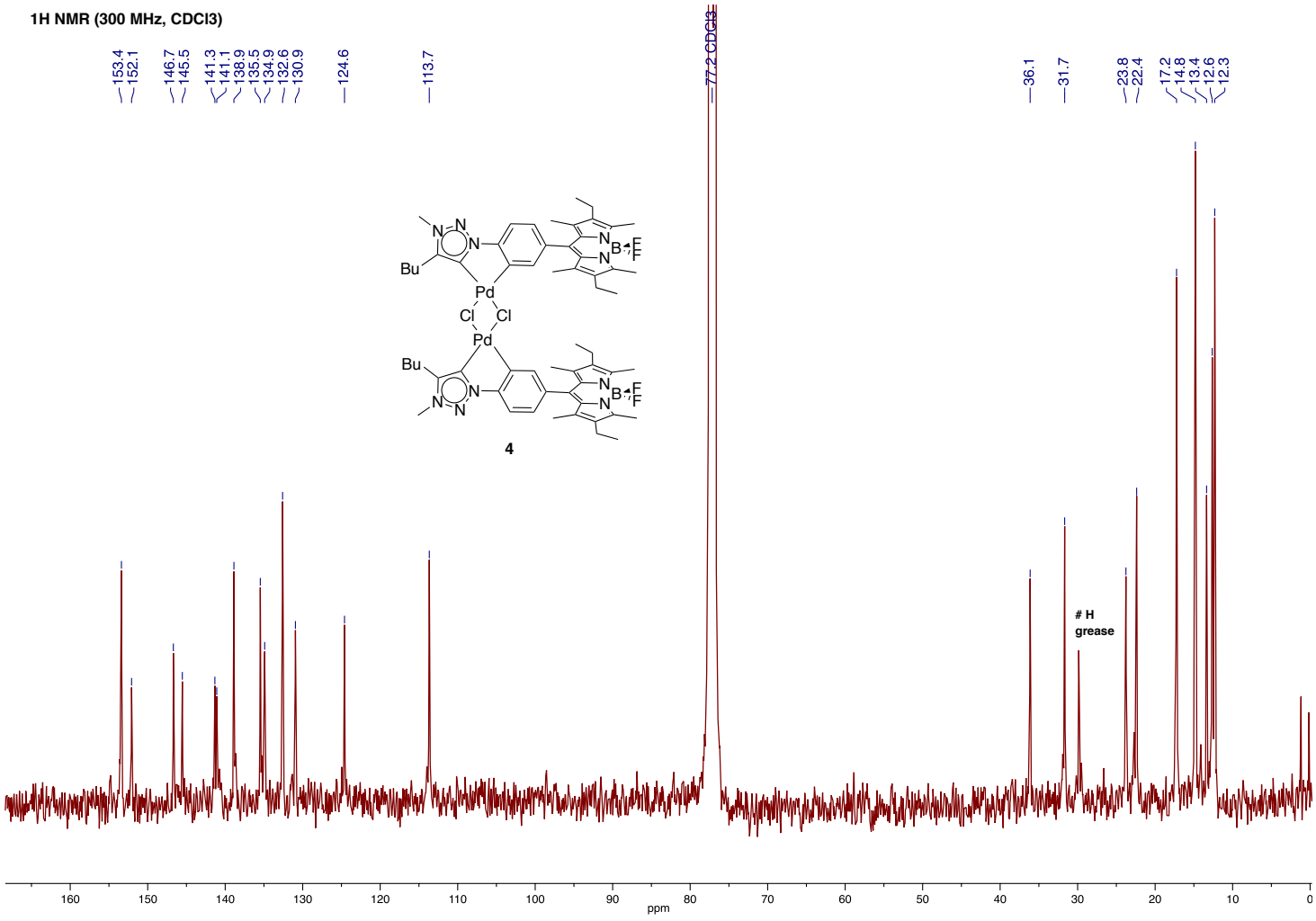

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of compound **4**.

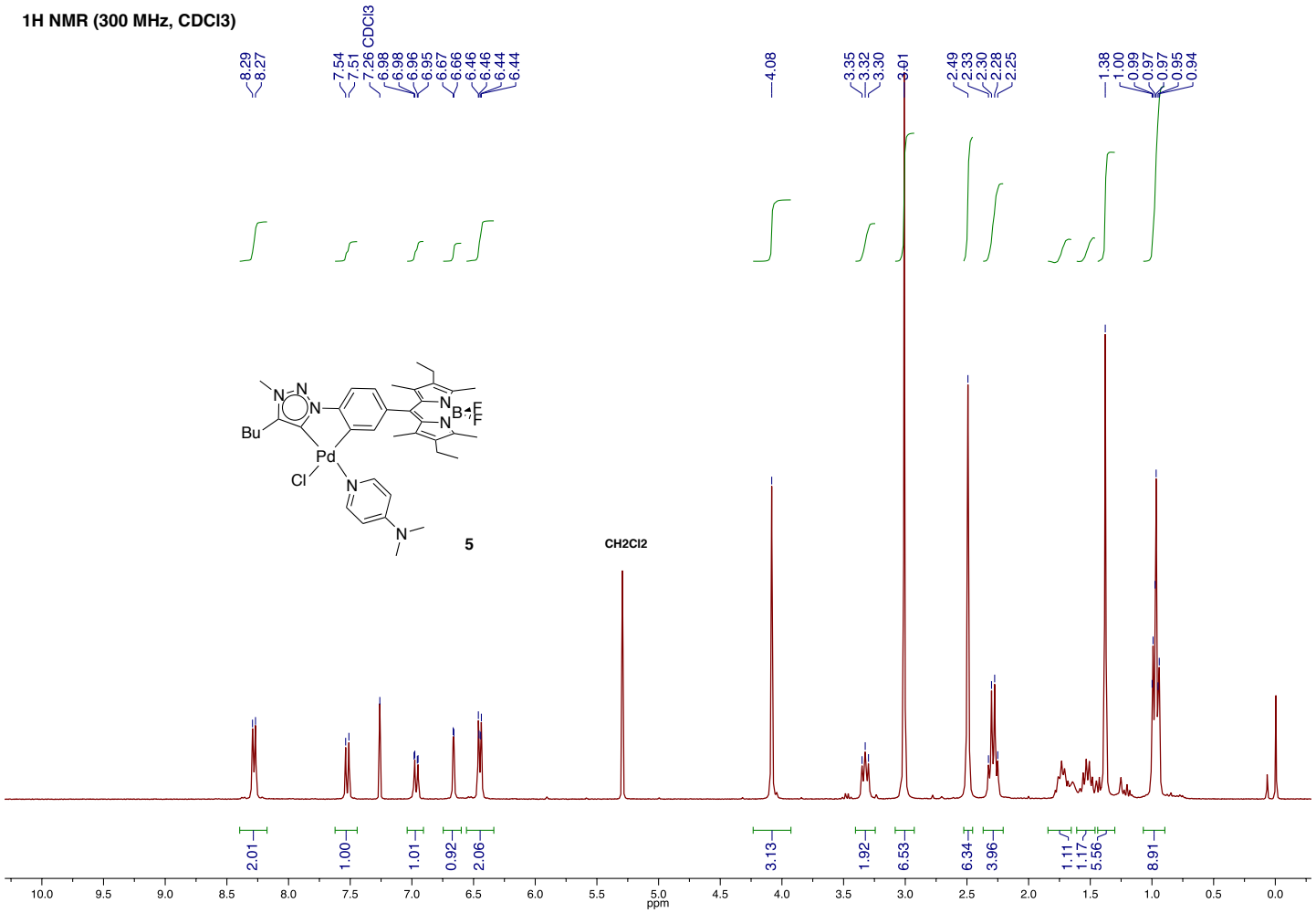

Figure S12. ^{1}H NMR spectrum of compound **5**.

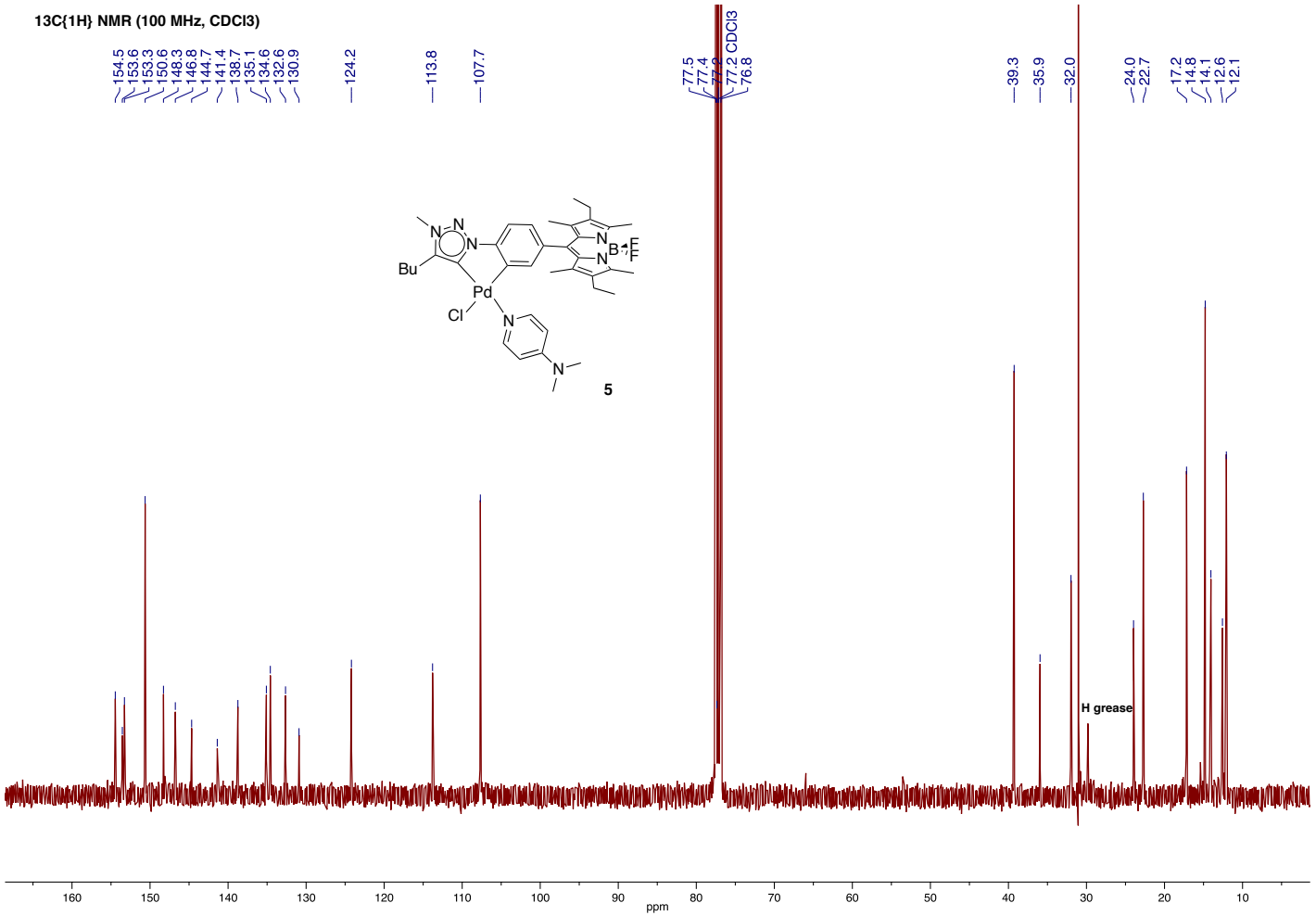

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of compound **5**.

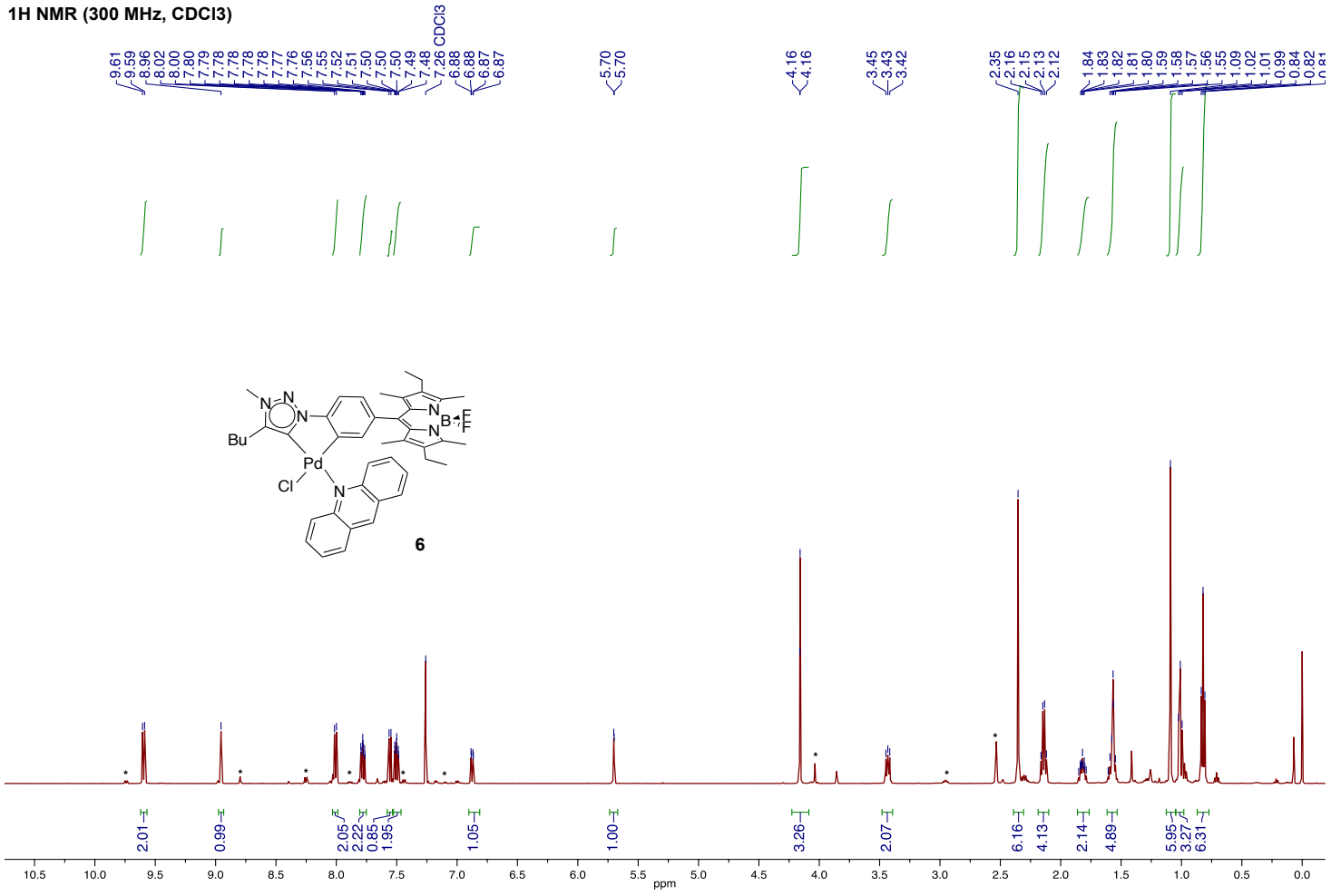

Figure S14. ^{1}H NMR spectrum of compound **6** (the signals marked with a * were attributed to minor portions of the isomer featuring the acridine *cis* to the triazolylidene ligand; signals of this minor isomer in the aliphatic region could not be unambiguously assigned and were thus not labeled).

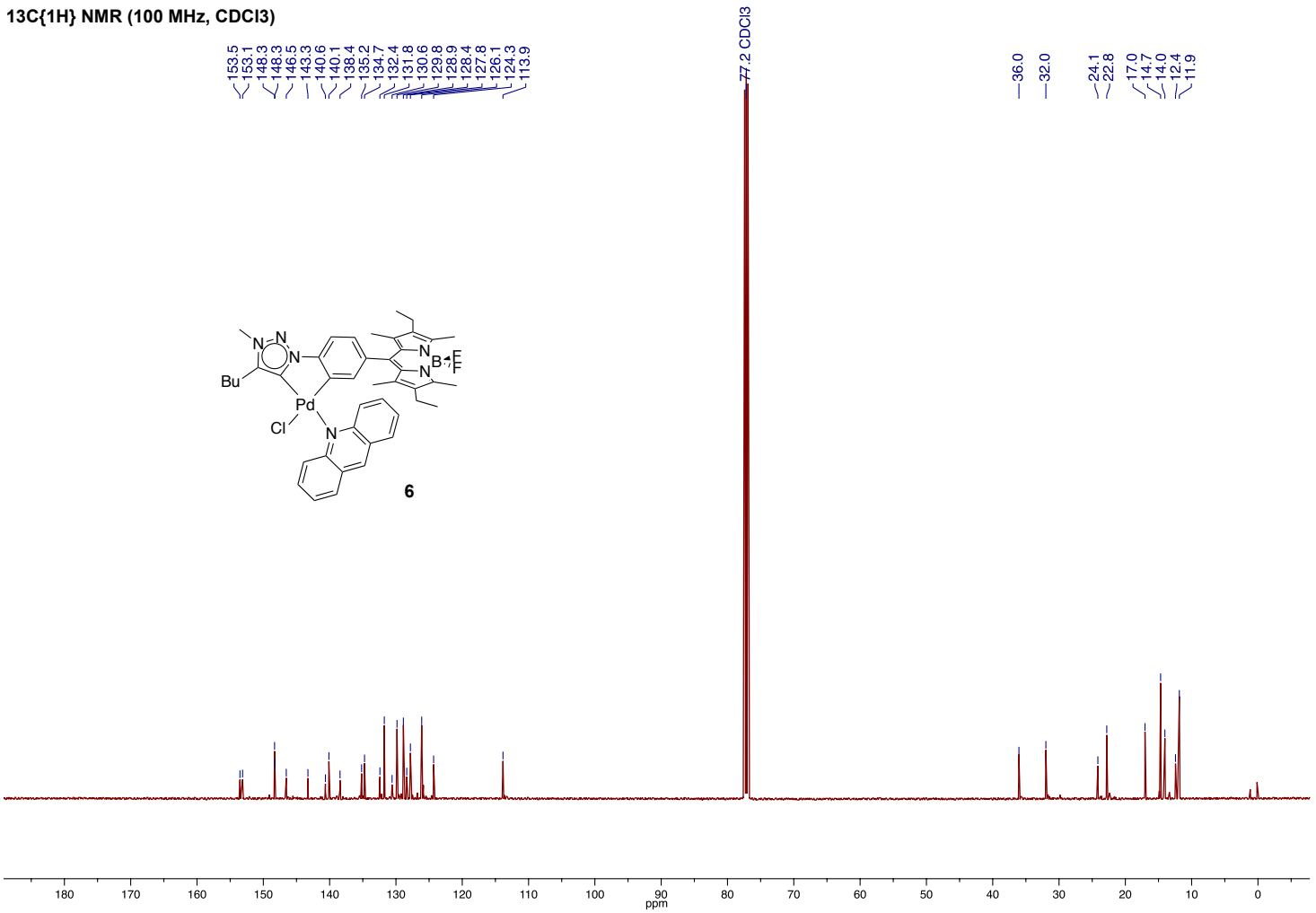

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of compound **6** (for minor signals, see comment to Fig. S14).

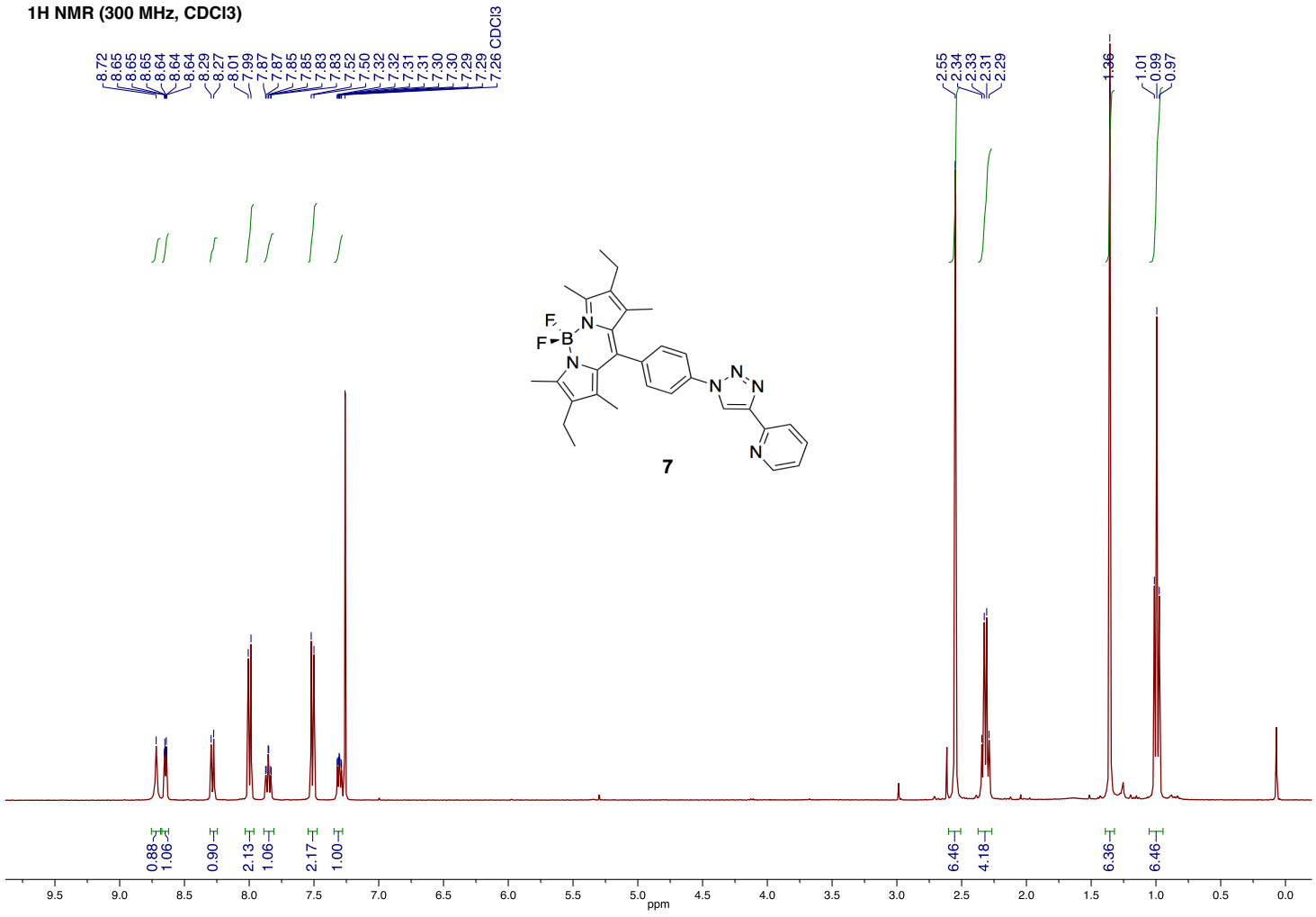

Figure S16. ^{1}H NMR spectrum of compound **7**.

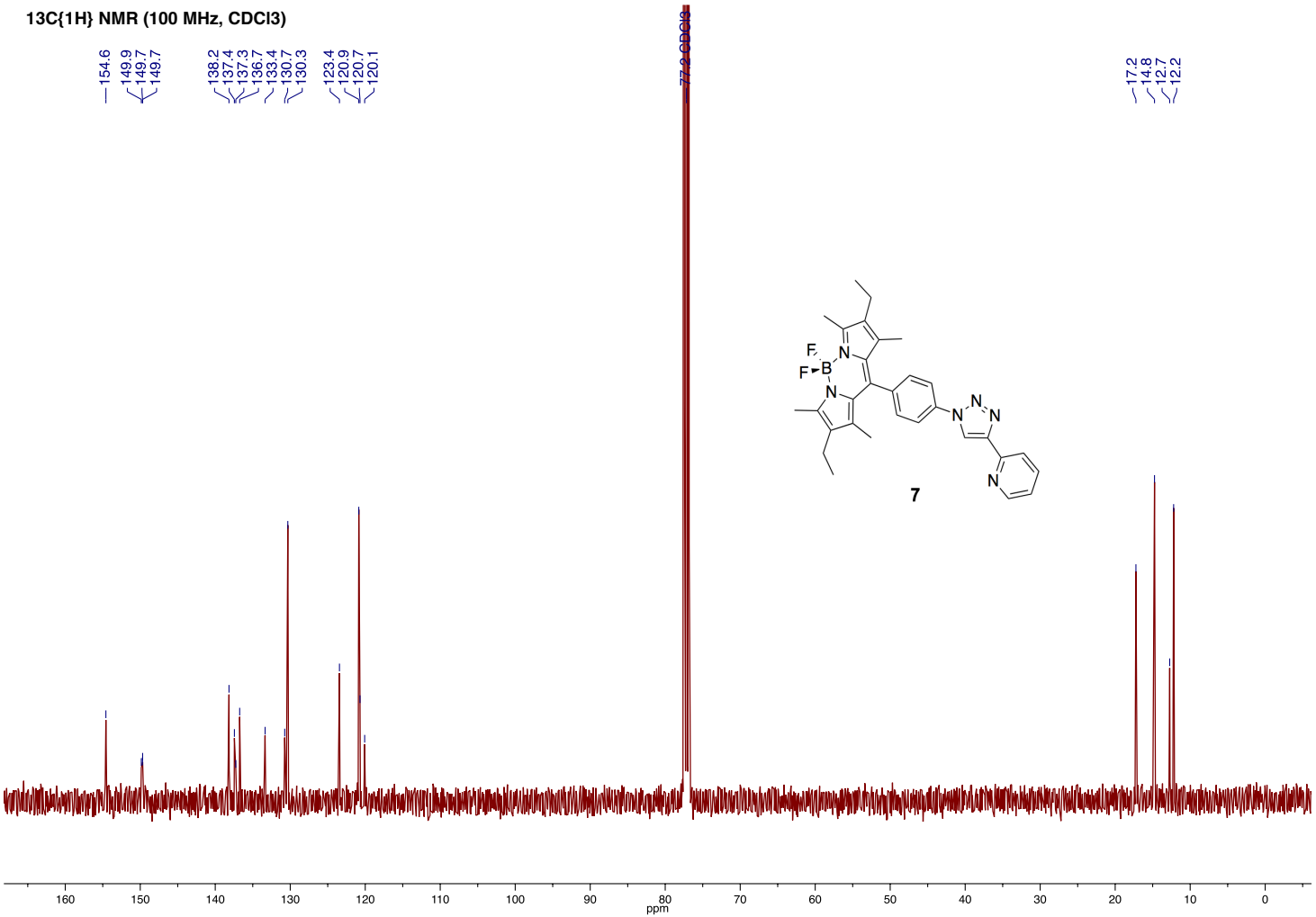

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of compound **7**.

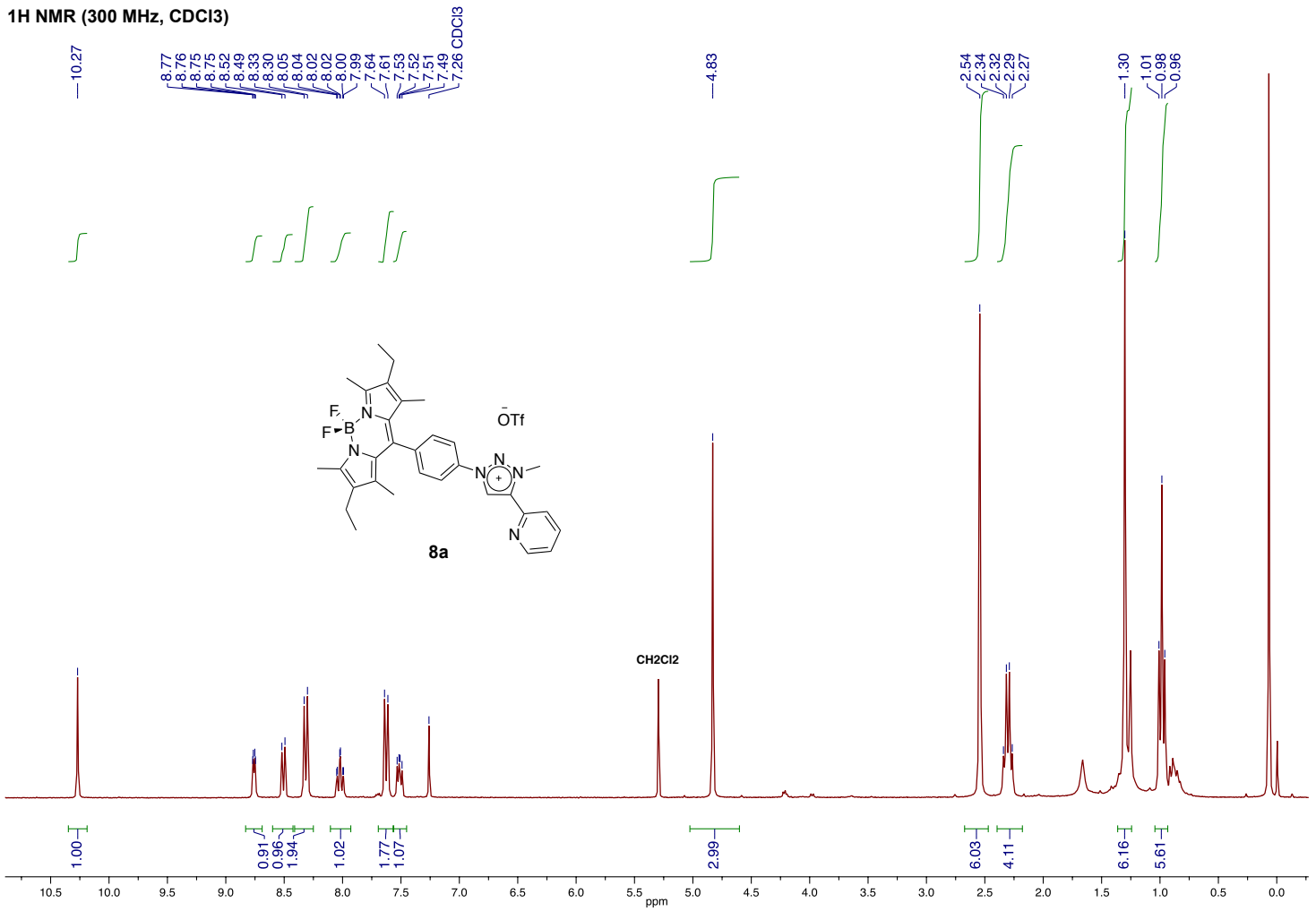

Figure S18. [1]H NMR spectrum of compound **8a**.

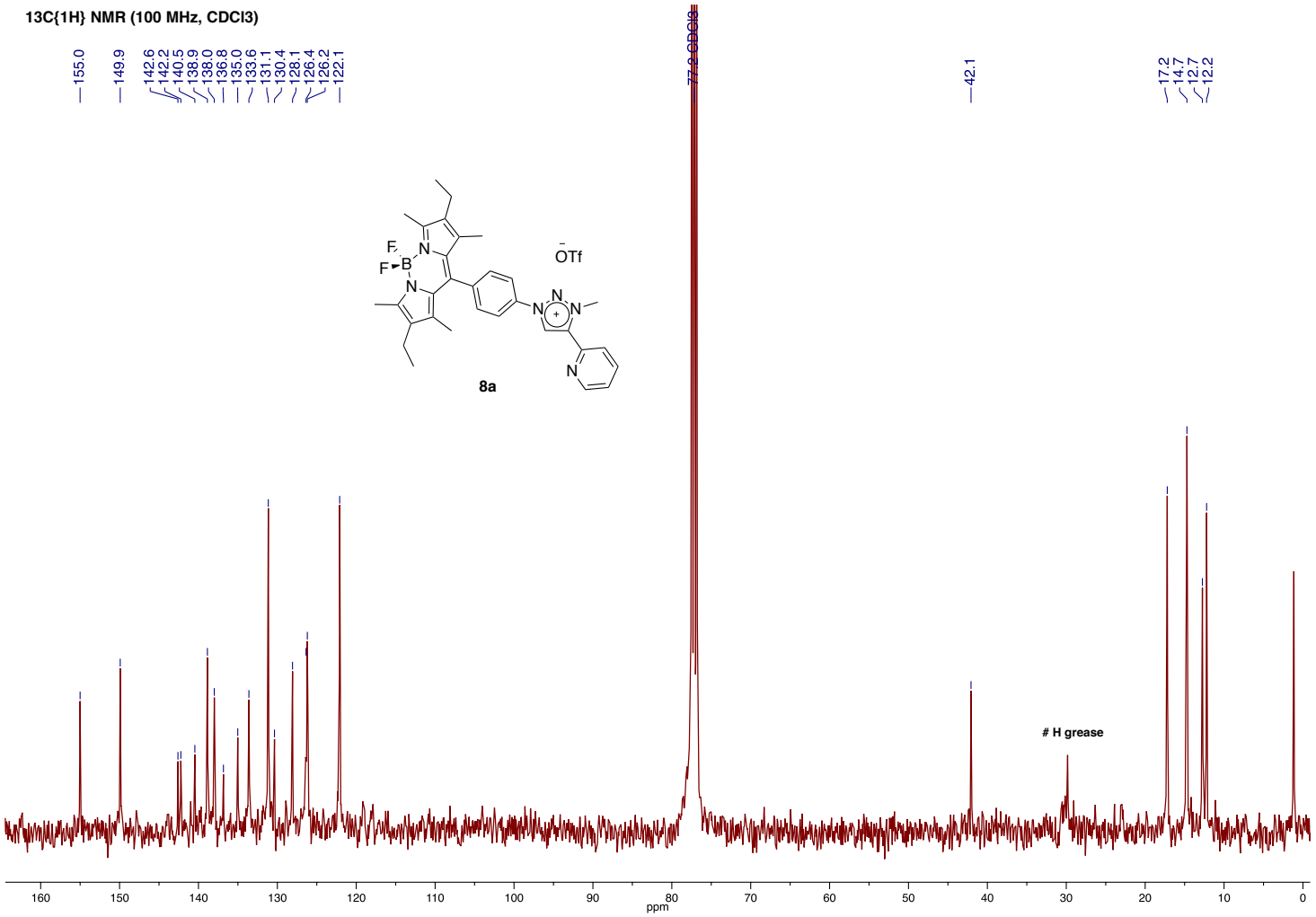

Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8a**.

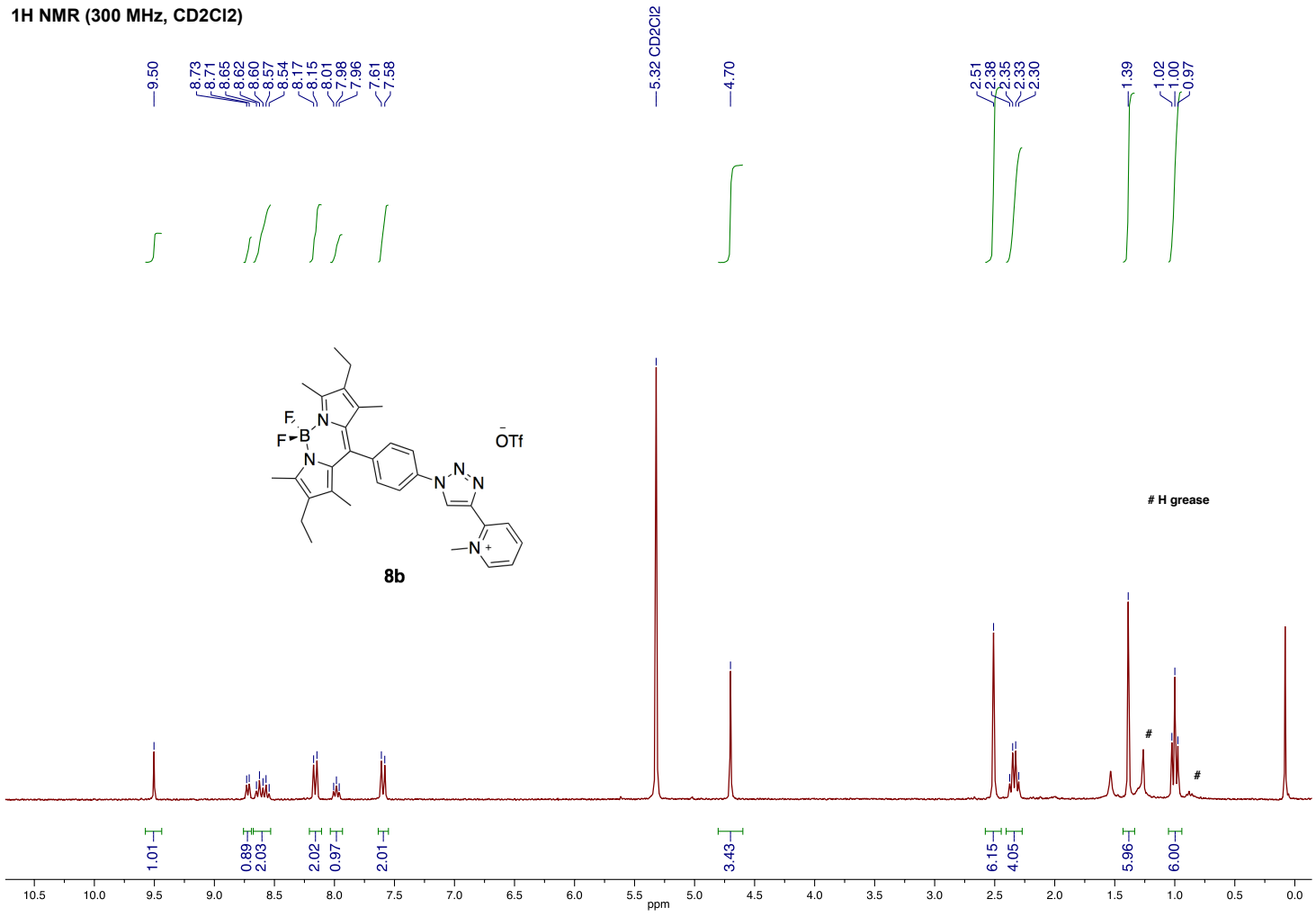

Figure S20. [1]H NMR spectrum of compound **8b**.

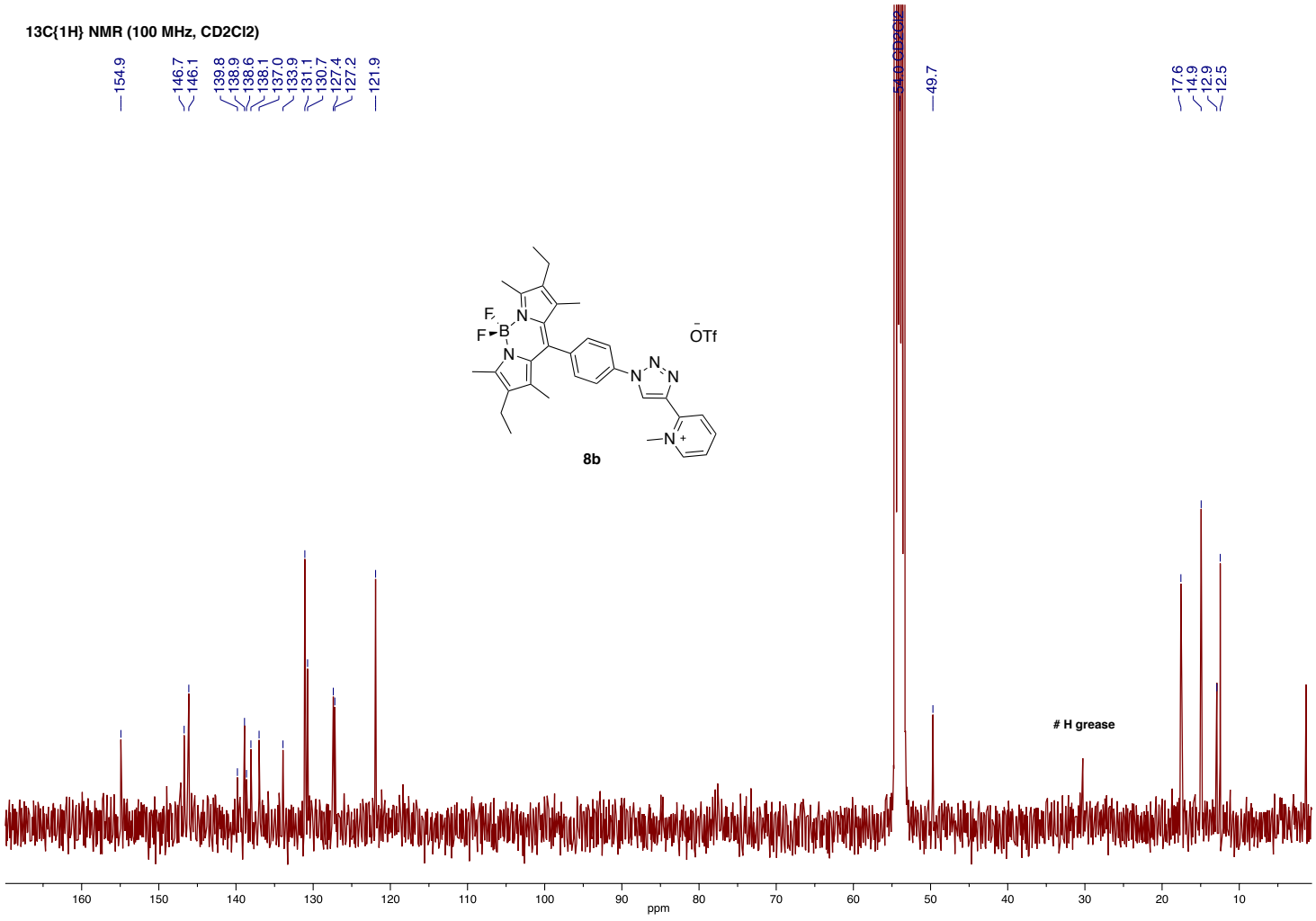

Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of compound **8b**.

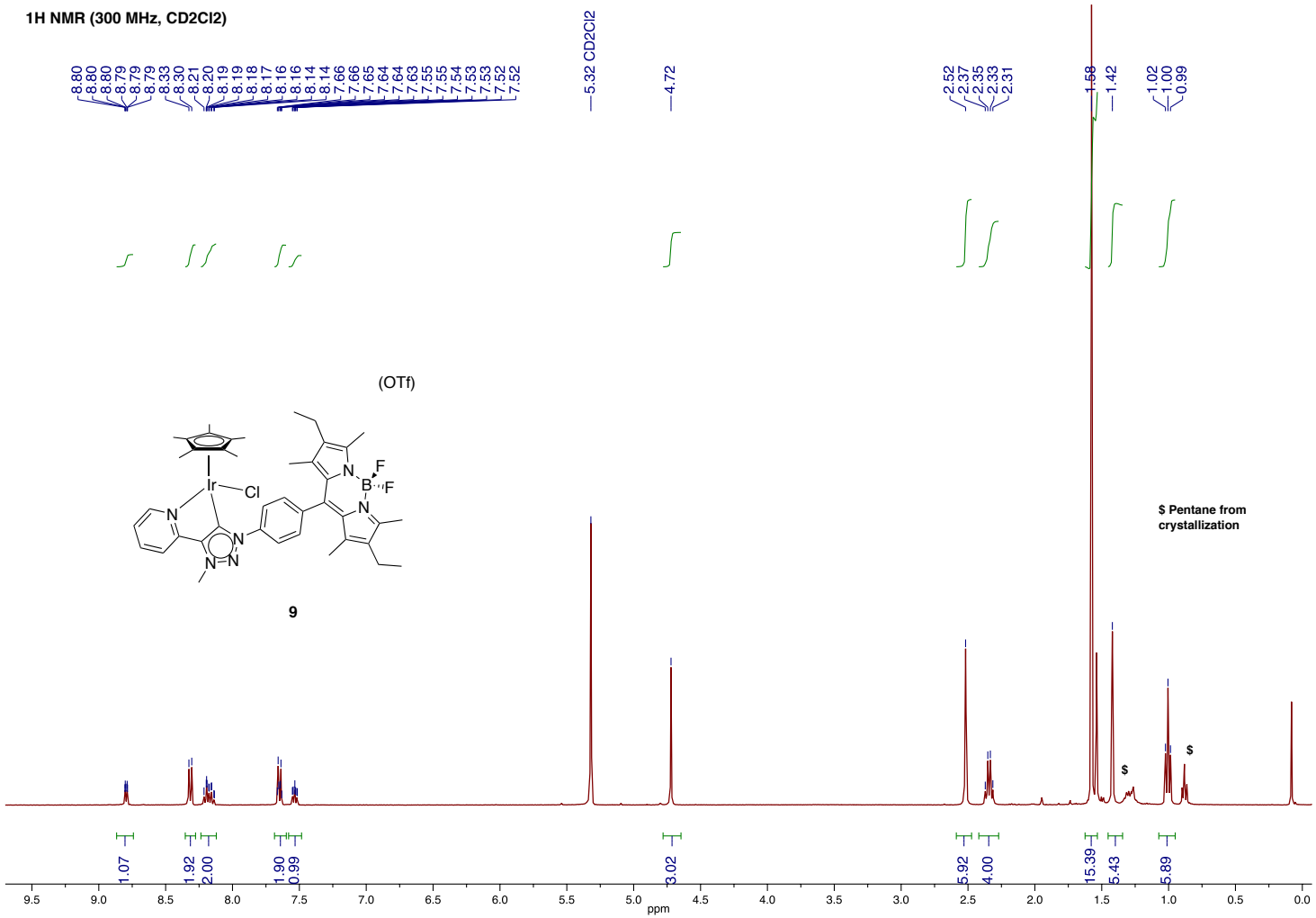

Figure S22. ^{1}H NMR spectrum of compound **9**.

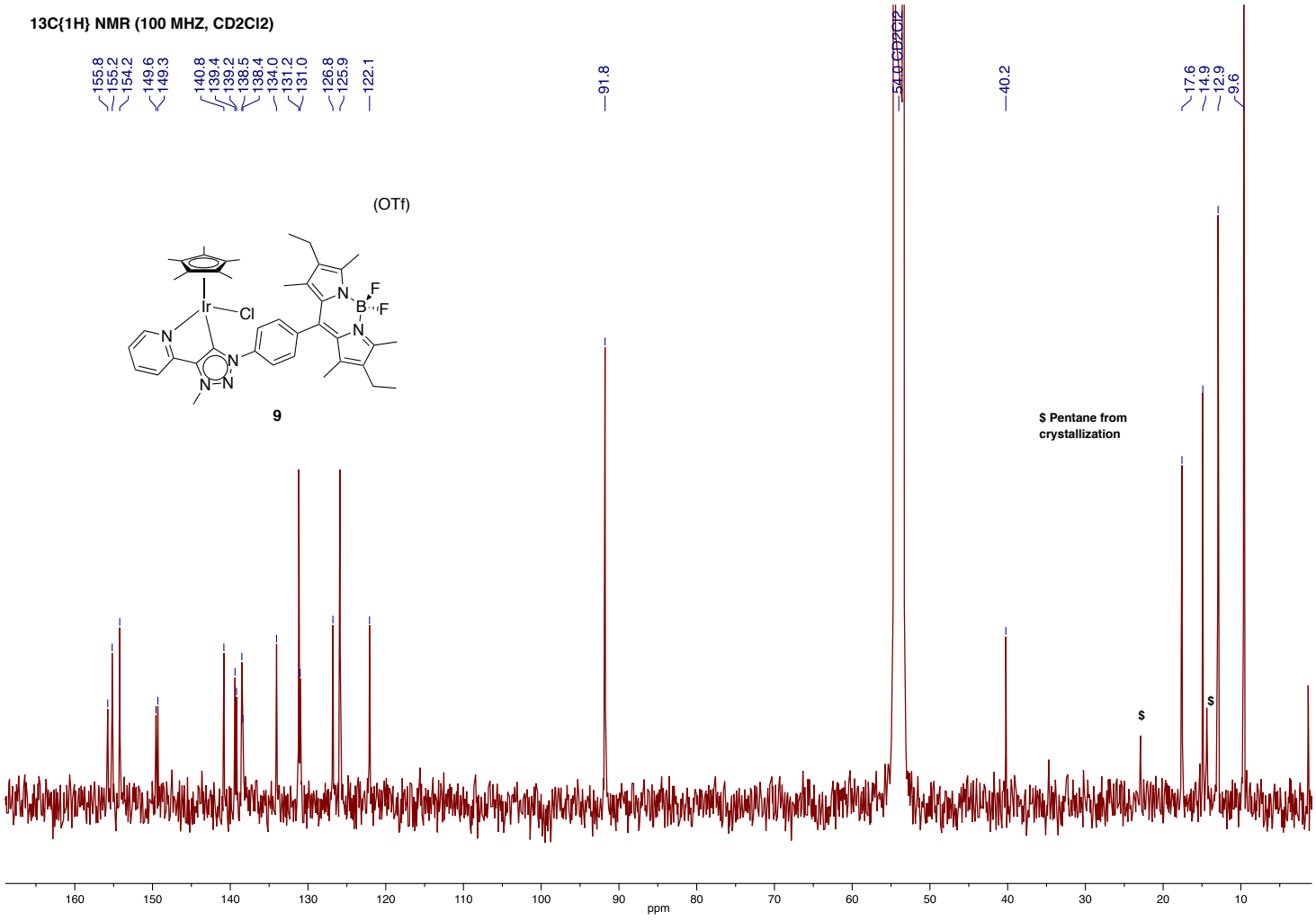

Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of compound **9**.