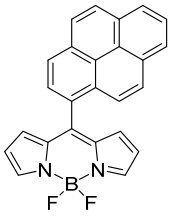
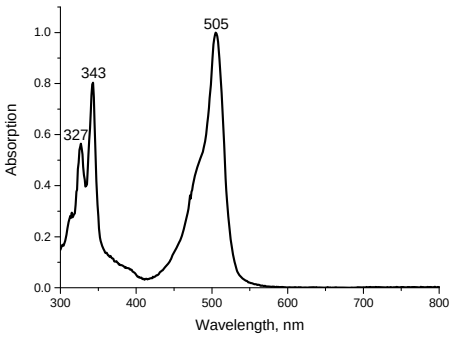
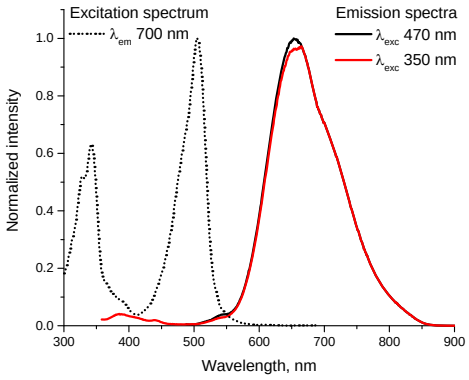
Content: Page

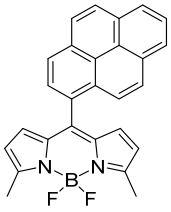
A. Optical spectra

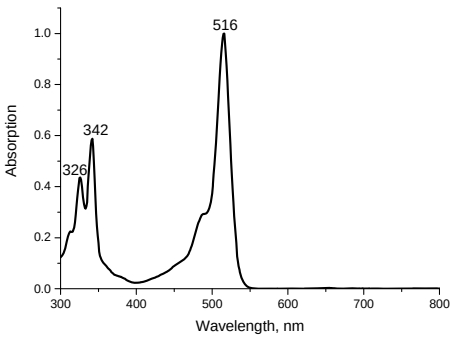
Table S1. Absorption, emission and excitation spectra of the dyads in dichloromethane.

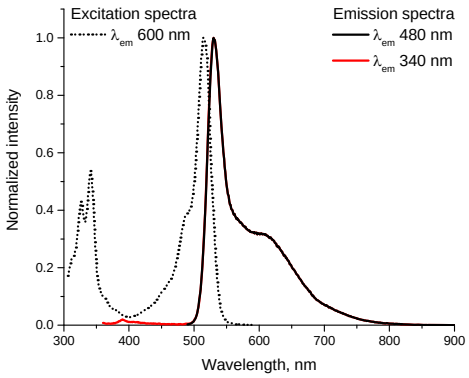


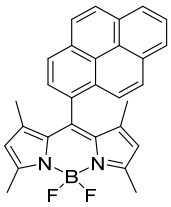


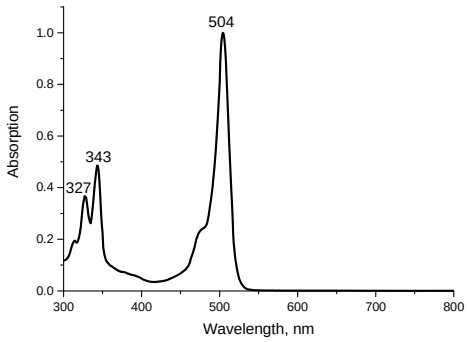


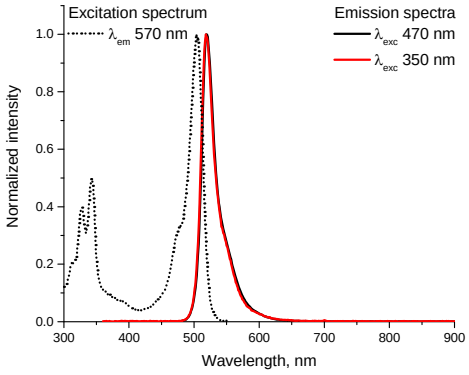


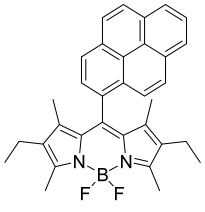


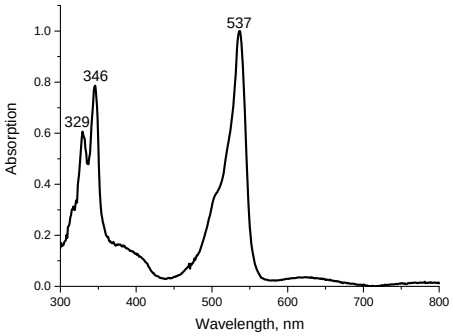


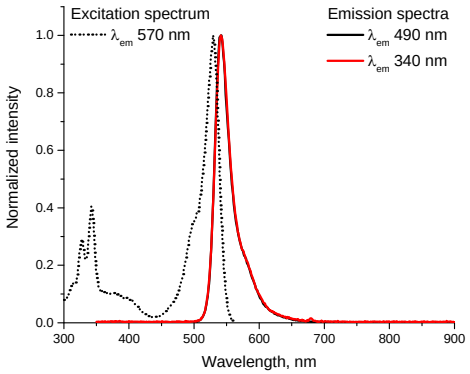


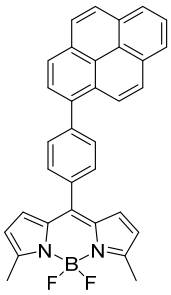


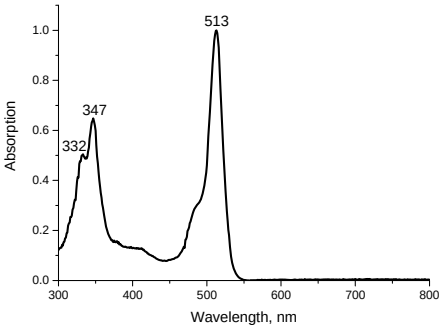


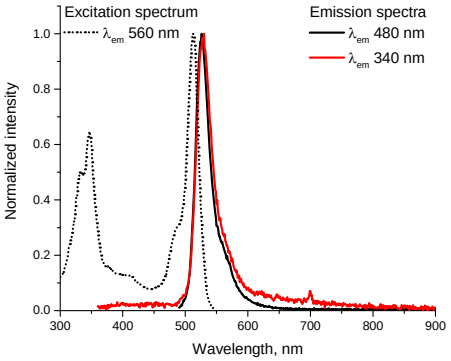


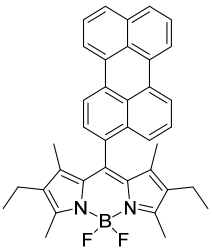

Absorption
Wavelength, nm
346
329
537

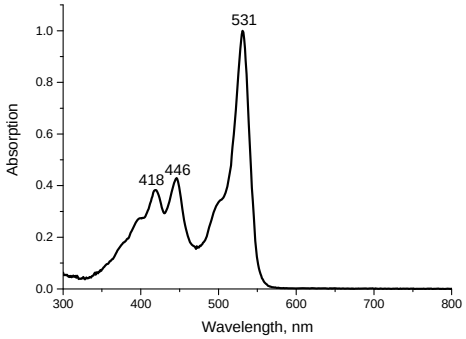

Excitation spectrum
λem 570 nm
Emission spectra
λem 490 nm
λem 340 nm
Normalized intensity
Wavelength, nm

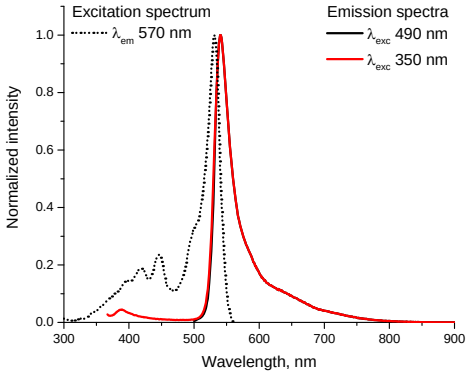



Absorption
Wavelength, nm
513
347
332


Excitation spectrum
λem 560 nm
Emission spectra
λem 480 nm
λem 340 nm
Normalized intensity
Wavelength, nm




Absorption
Wavelength, nm
531
418
446


Excitation spectrum
λem 570 nm
Emission spectra
λexc 490 nm
λexc 350 nm
Normalized intensity
Wavelength, nm

B. X-ray Crystallography Data

Table S2: Details of XRD data refinement

Compound	**BPyrD1 (KJF161)**	**BPyrD3 (KJF158)**	**BPyrD4 (KJF183)**	**BPerD (KJF162)**
Empirical formula	$C_{25}H_{15}BF_2N_2$	$C_{29}H_{23}BF_2N_2$	$C_{33}H_{31}BF_2N_2$	$C_{37}H_{33}BF_2N_2$
Formula weight	392.20	448.30	504.41	554.46
Temperature/K	100.01	99.99	99.99	100.01
Crystal system	monoclinic	orthorhombic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_12_12_1$	Cc	$P2_1/n$
a/Å	17.082(17)	8.5915(4)	7.8654(2)	7.8092(3)
b/Å	8.600(12)	11.3514(6)	44.0642(11)	30.8205(11)
c/Å	13.632(14)	23.2887(11)	14.9251(4)	23.4106(9)
α/°	90	90	90	90
β/°	112.854(15)	90	91.213(2)	95.314(2)
γ/°	90	90	90	90
Volume/Å³	1845(4)	2271.24(19)	5171.6(2)	5610.3(4)
Z	4	4	8	8
D_{calc} *g/cm³*	1.412	1.311	1.296	1.313
μ/mm⁻¹	0.097	0.087	0.676	0.675
F(000)	808.0	936.0	2128.0	2336.0
Crystal size/mm³	0.37 × 0.27 × 0.03	0.6 × 0.1 × 0.07	0.5 × 0.2 × 0.06	0.26 × 0.09 × 0.03
Radiation	MoKα	MoKα	CuKα	CuKα
Wavelength/Å	λ = 0.71073	λ = 0.71073	λ = 1.54178	λ = 1.54178
2θ/°	5.176 to 59.246	3.498 to 62.28	4.01 to 135.99	4.752 to 136.504
Reflections collected	19468	92743	60945	48297
Independent reflections	5178	7314	9342	10233
R_{int}	0.0330	0.0651	0.0505	0.0685
R_{sigma}	0.0328	0.0303	0.0311	0.0577
Restraints	0	78	2	13
Parameters	271	309	698	689
GooF	1.033	1.022	1.045	1.042
R_1 *[I>=2σ (I)]*	0.0413	0.0408	0.0392	0.0949
wR_2 *[I>=2σ (I)]*	0.1034	0.0916	0.1050	0.2548
R_1 *[all data]*	0.0648	0.0536	0.0407	0.1172
wR_2 *[all data]*	0.1142	0.0981	0.1063	0.2740
Largest peak/e Å⁻³	0.40	0.33	0.22	0.85
Deepest hole/e Å⁻³	-0.21	-0.65	-0.21	-0.50
Flack parameter	--	-0.06(18)	0.23(13)	--

Crystal Data for BPyrD1: $C_{25}H_{15}BF_2N_2$ (M =392.20 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 17.082(17) Å, b = 8.600(12) Å, c = 13.632(14) Å, β = 112.854(15)°, V = 1845(4) Å^3, Z = 4, T = 100.01 K, μ(MoK_α) = 0.097 mm^{-1}, D_{calc} = 1.412 g/cm^3, 19468 reflections measured (5.176° ≤ 2θ ≤ 59.246°), 5178 unique (R_{int} = 0.0330, R_{sigma} = 0.0328) which were used in all calculations. The final R_1 was 0.0413 (I > 2σ(I)) and wR_2 was 0.1142 (all data).

Crystal Data for BPyrD3: $C_{29}H_{23}BF_2N_2$ (M =448.30 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 8.5915(4) Å, b = 11.3514(6) Å, c = 23.2887(11) Å, V = 2271.24(19) Å^3, Z = 4, T = 99.99 K, μ(MoK_α) = 0.087 mm^{-1}, D_{calc} = 1.311 g/cm^3, 92743 reflections measured (3.498° ≤ 2θ ≤ 62.28°), 7314 unique (R_{int} = 0.0651, R_{sigma} = 0.0303) which were used in all calculations. The final R_1 was 0.0408 (I > 2σ(I)) and wR_2 was 0.0981 (all data). The methyl groups at the α-positions (C3 and C5) and the β-positions (C1 and C7) were modelled in two positions using restraints (ISOR, SADI, and DFIX) and constraint (EDAP) in a 90:10 % occupancy.

Crystal Data for BPyrD4: $C_{33}H_{31}BF_2N_2$ (M =504.41 g/mol): monoclinic, space group Cc (no. 9), a = 7.8654(2) Å, b = 44.0642(11) Å, c = 14.9251(4) Å, β = 91.213(2)°, V = 5171.6(2) Å^3, Z = 8, T = 99.99 K, μ(CuK_α) = 0.676 mm^{-1}, D_{calc} = 1.296 g/cm^3, 60945 reflections measured (4.01° ≤ 2θ ≤ 135.99°), 9342 unique (R_{int} = 0.0505, R_{sigma} = 0.0311) which were used in all calculations. The final R_1 was 0.0392 (I > 2σ(I)) and wR_2 was 0.1063 (all data). Two individual data collections on one crystal were merged together to get complete data for this structure. The overall structure was refined as a two-component inversion twin.

Crystal Data for BPerD: $C_{37}H_{33}BF_2N_2$ (M =554.46 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 7.8092(3) Å, b = 30.8205(11) Å, c = 23.4106(9) Å, β = 95.314(2)°, V = 5610.3(4) Å^3, Z = 8, T = 100.01 K, μ(CuK_α) = 0.675 mm^{-1}, D_{calc} = 1.313 g/cm^3, 48297 reflections measured (4.752° ≤ 2θ ≤ 136.504°), 10233 unique (R_{int} = 0.0685, R_{sigma} = 0.0577) which were used in all calculations. The final R_1 was 0.0949 (I > 2σ(I)) and wR_2 was 0.2740 (all data). The perylene unit to the second residue was modelled over two positions to using restraints (ISOR and SADI) and constraints (EADP) in a 50:50 % occupancy. The boron difluoride moiety of residue two was modelled over two positions in a 87:13 % occupancy.

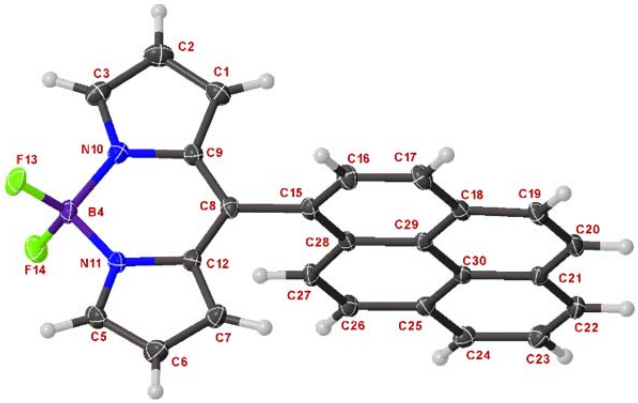


Figure S1: Molecular structure of **BPyrD1** (thermal displacement 50%).

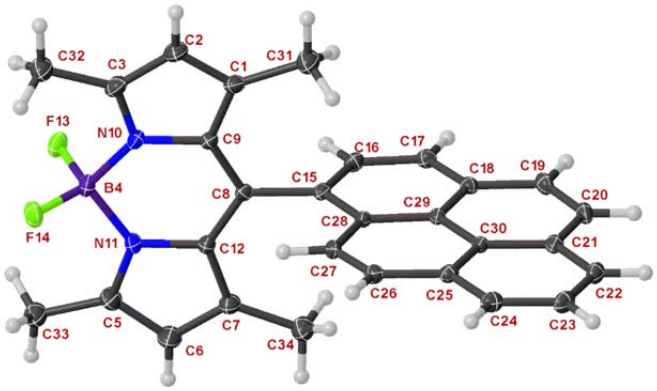


Figure S2: Molecular structure of **BPyrD3** (thermal displacement 50%).

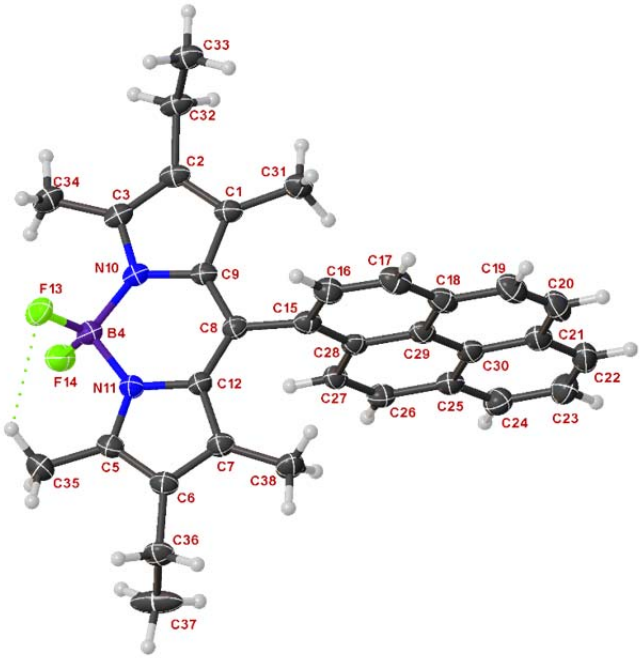


Figure S3: Molecular structure of **BPyrD4** (thermal displacement 50%).

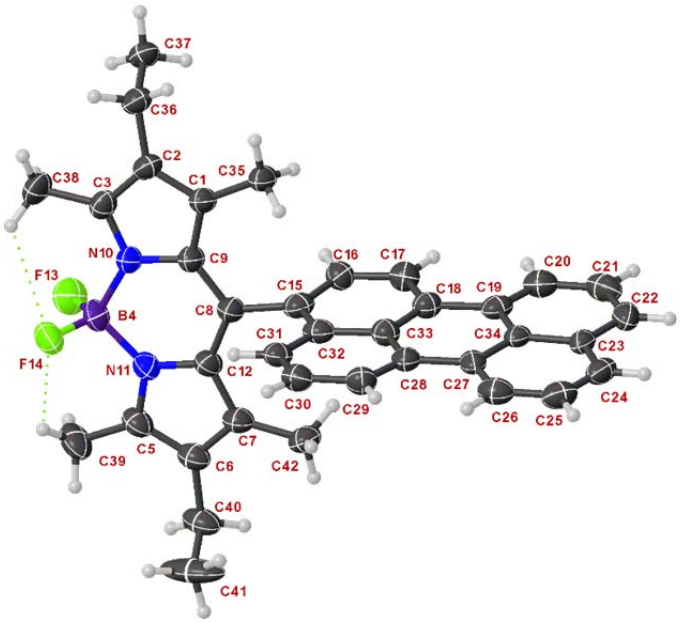


Figure S4: Molecular structure of **BPerD** (thermal displacement 50%).

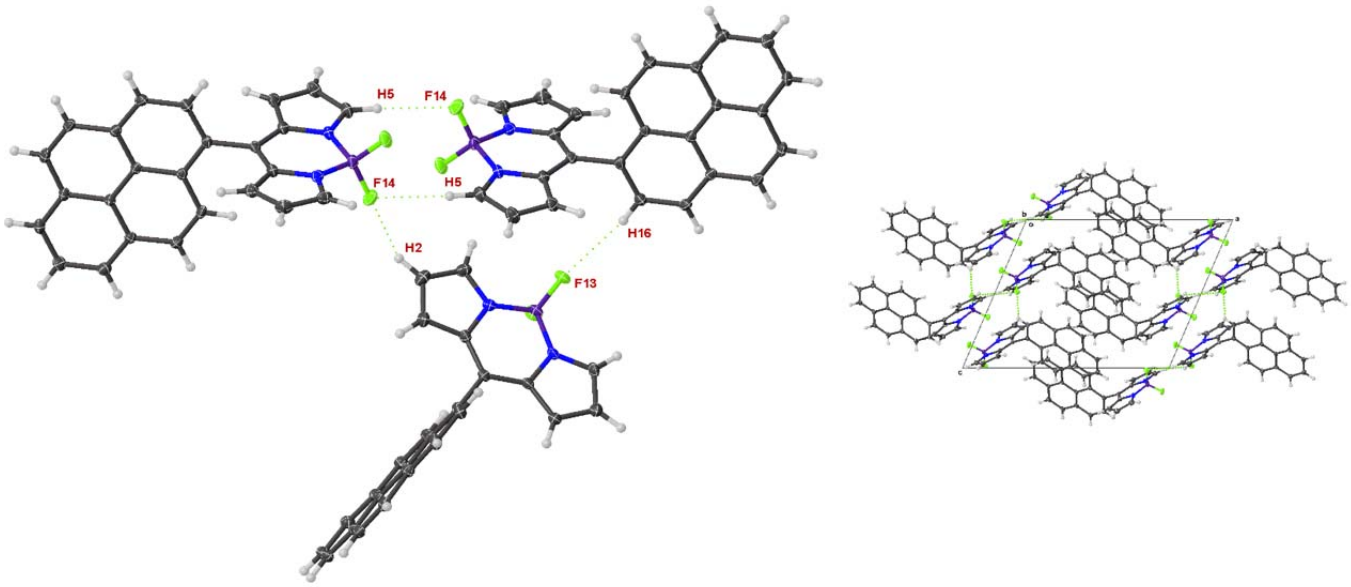


Figure S5: Left: Expanded structure of **BPyrD1** displaying the H···F close contacts present in the structure (thermal displacement 50%). Atoms involved in the H···F have been labelled. All other atom labels have been omitted for clarity. Right: Moiety packing of **BPyrD1** looking down the b-axis showing the repeating head-to-head interactions between individual molecules within the unit cell.

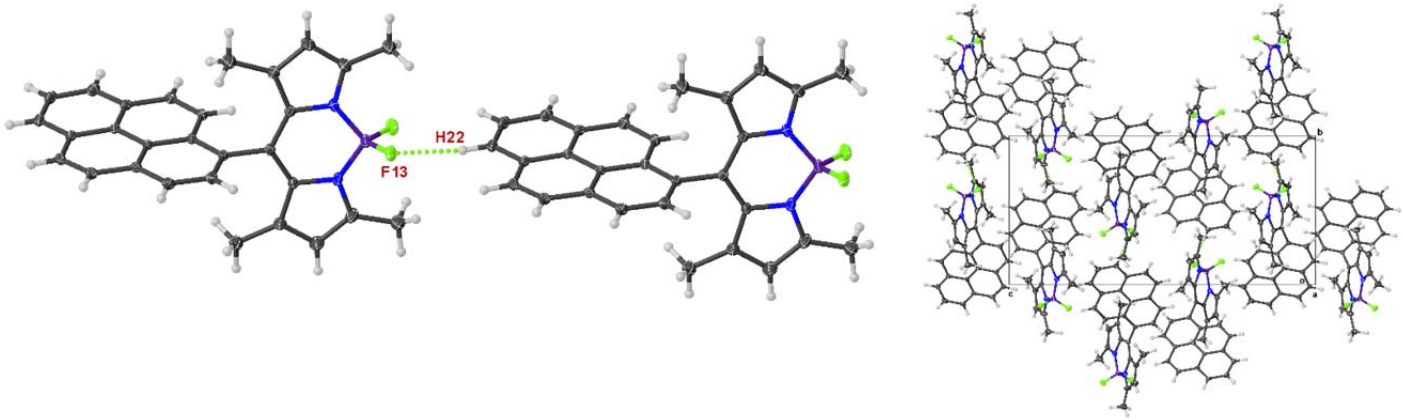


Figure S6: Left: Expanded structure of **BPyrD3** displaying the H···F close contacts present in the structure (thermal displacement 50%). Atoms involved in the H···F have been labelled. All other atom labels have been omitted for clarity. Right: Moiety packing of **BPyrD3** looking down the a-axis showing the repeating head-to-tail interactions between individual molecules within the unit cell.

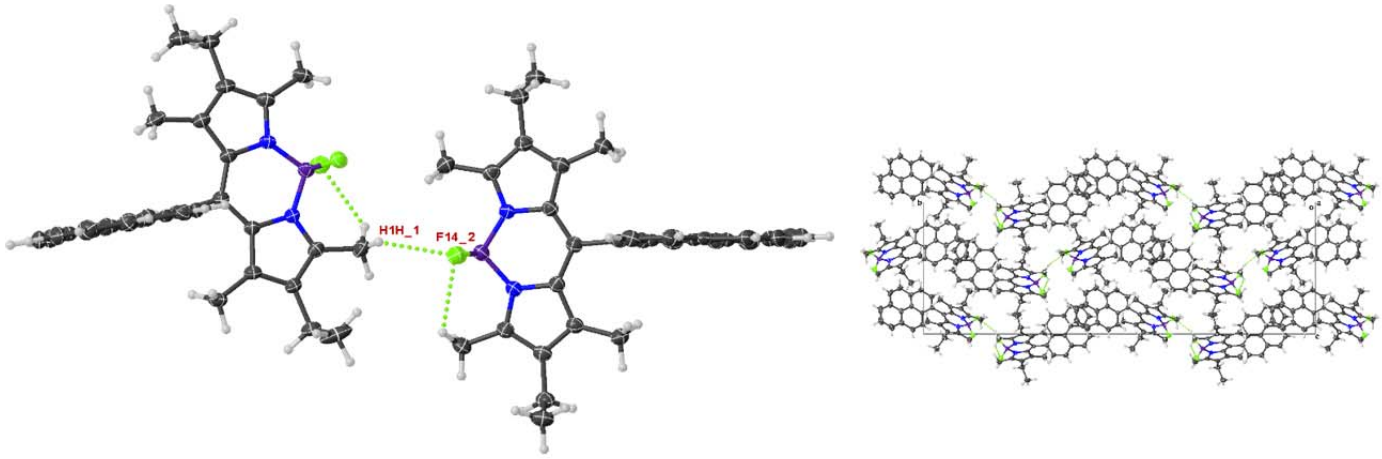


Figure S7: Left: Expanded structure of **BPyrD4** displaying the H···F close contacts present in the structure (thermal displacement 50%). Atoms involved in the H···F have been labelled. All other atom labels have been omitted for clarity. Right: Moiety packing of **BPyrD4** looking down the a-axis showing the repeating head-to-head interactions between individual molecules within the unit cell.

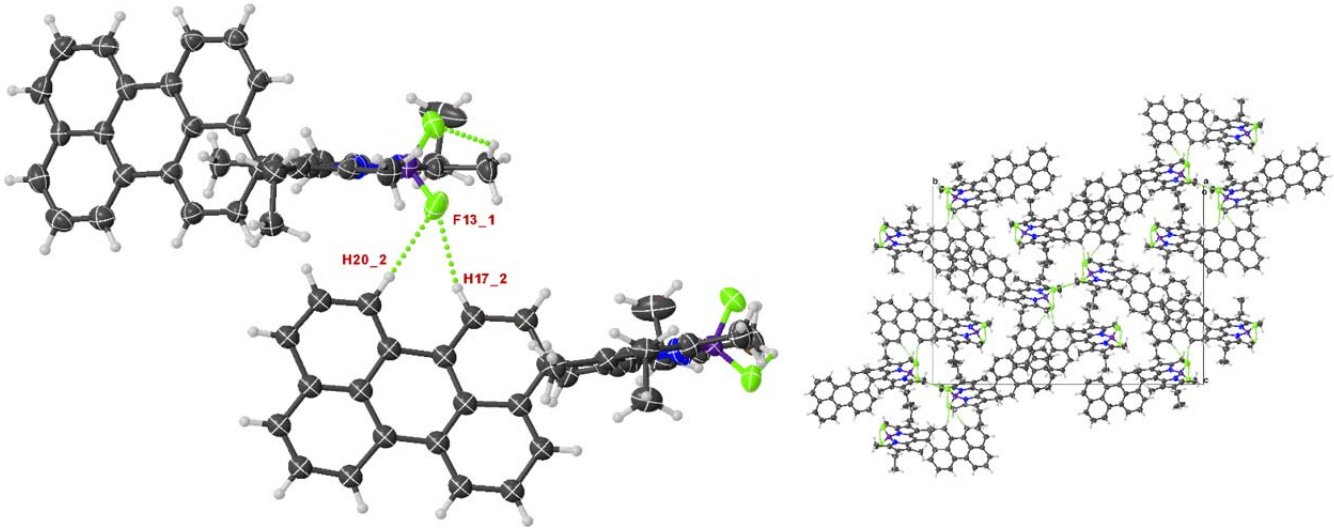


Figure S8: Left: Expanded structure of **BPerD** displaying the H···F close contacts present in the structure (thermal displacement 50%). Atoms involved in the H···F have been labelled. All other atom labels have been omitted for clarity. Right: Moiety packing of **BPerD** looking down the a-axis showing to exhibiting a mix of both head-to-head and head-to-tail interactions within the unit cell.

C. NMR spectra

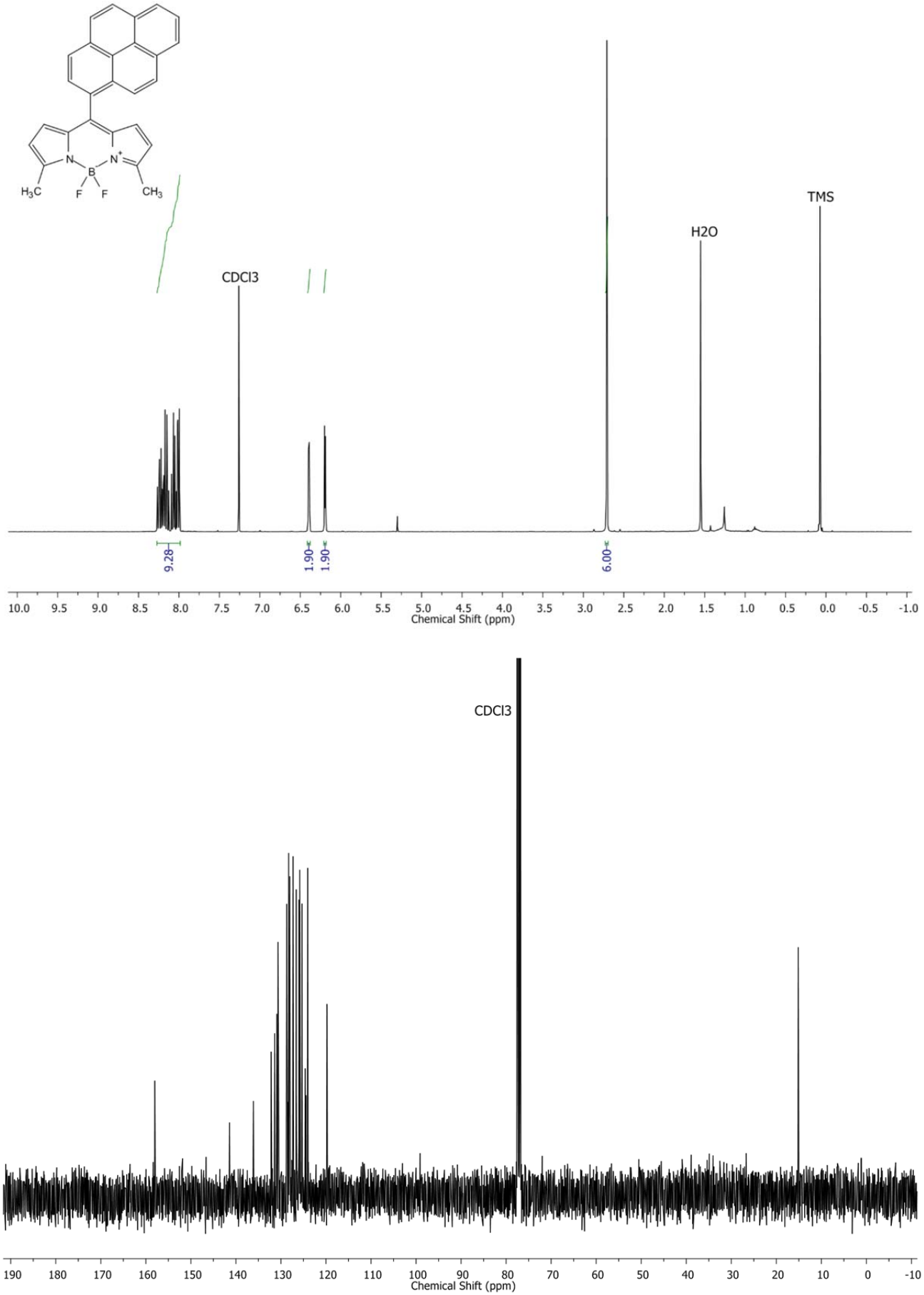
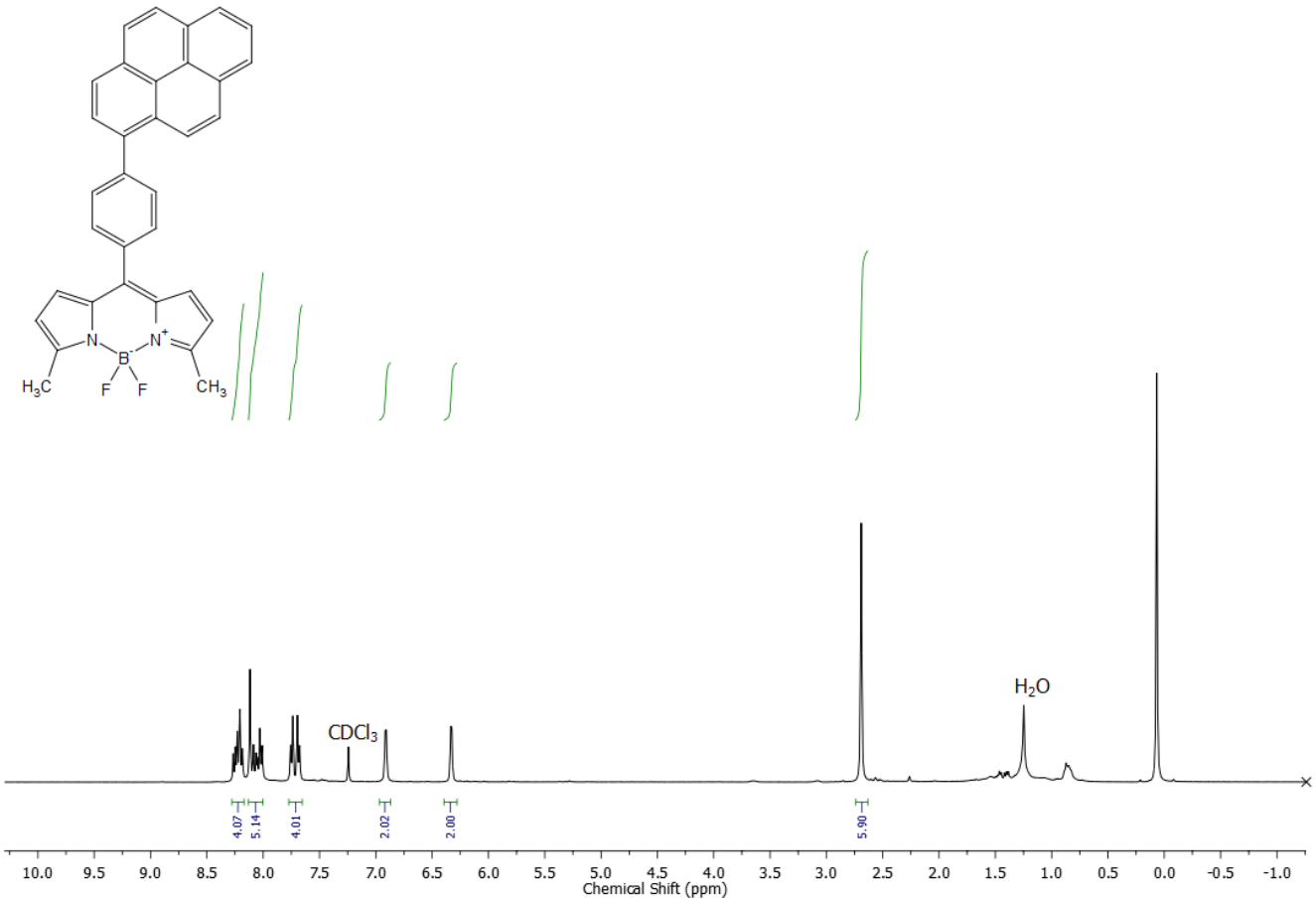


Figure S9: ^{1}H and ^{13}C NMR spectra of compound **BPyrD2**.


H3C
F
F
CH3
CDCl3
H2O
4.07
5.14
4.01
2.02
2.00
5.90
Chemical Shift (ppm)

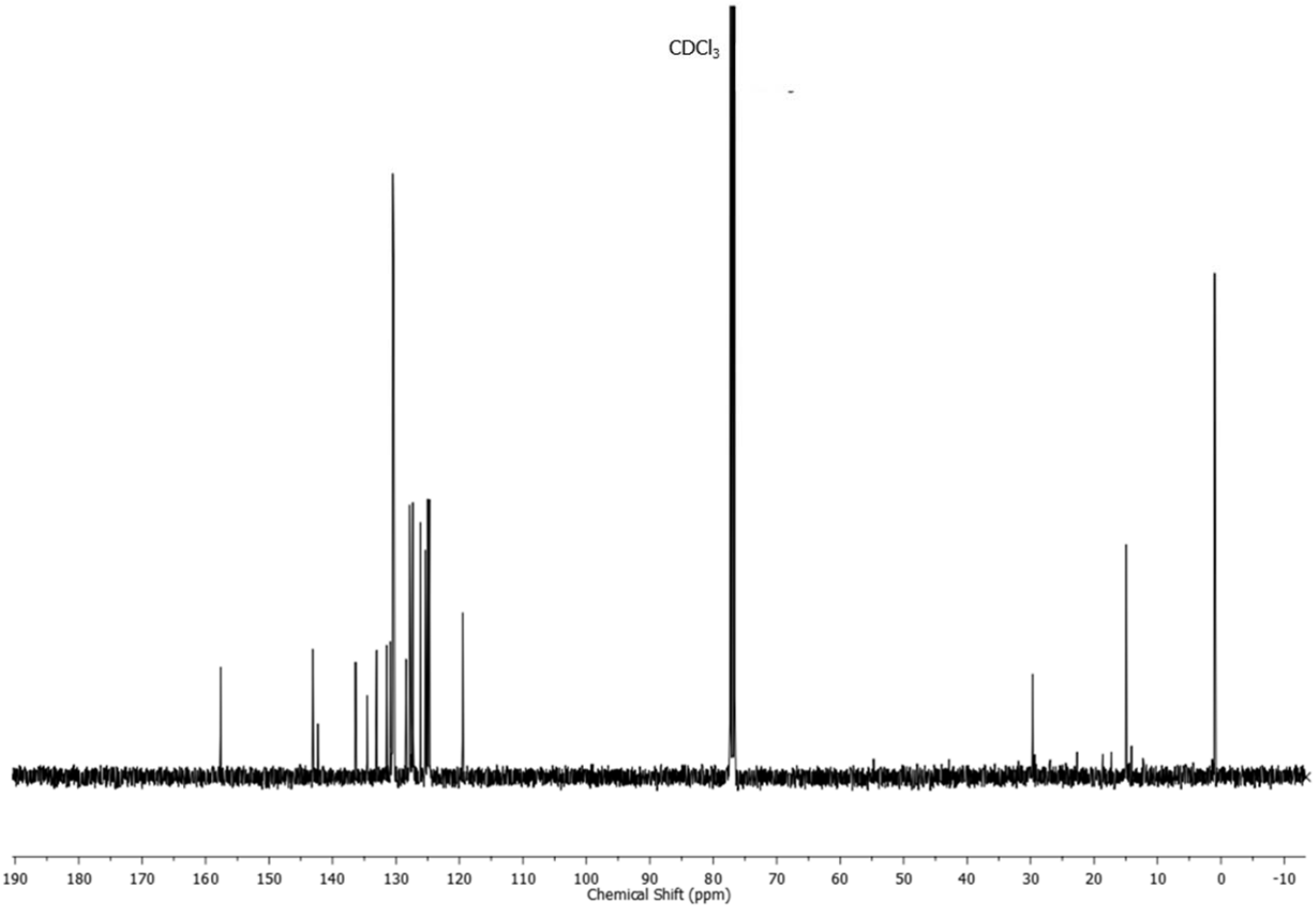
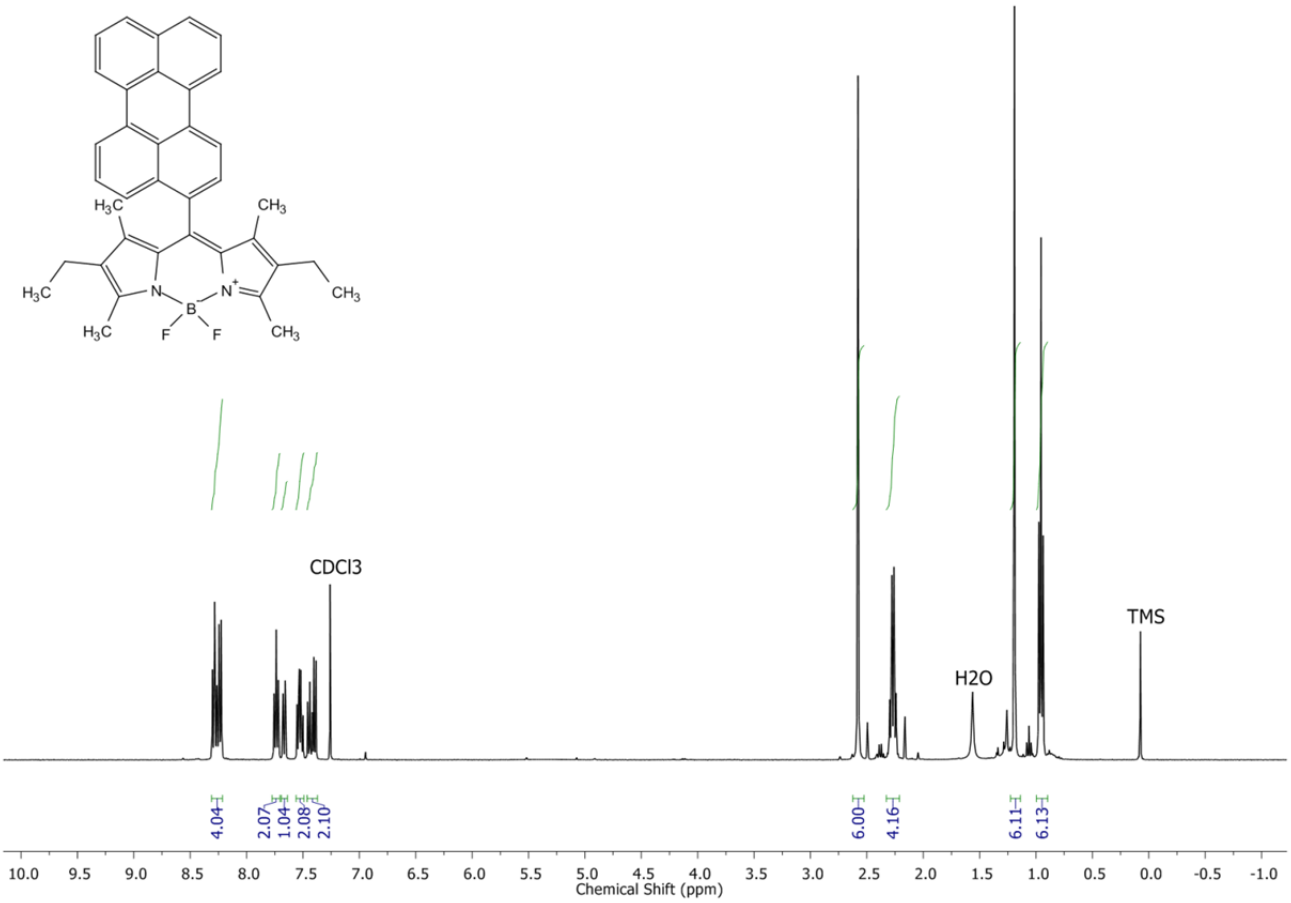

CDCl3
Chemical Shift (ppm)

Figure S12: ^{1}H and ^{13}C NMR spectra of compound **BPyrD5**.



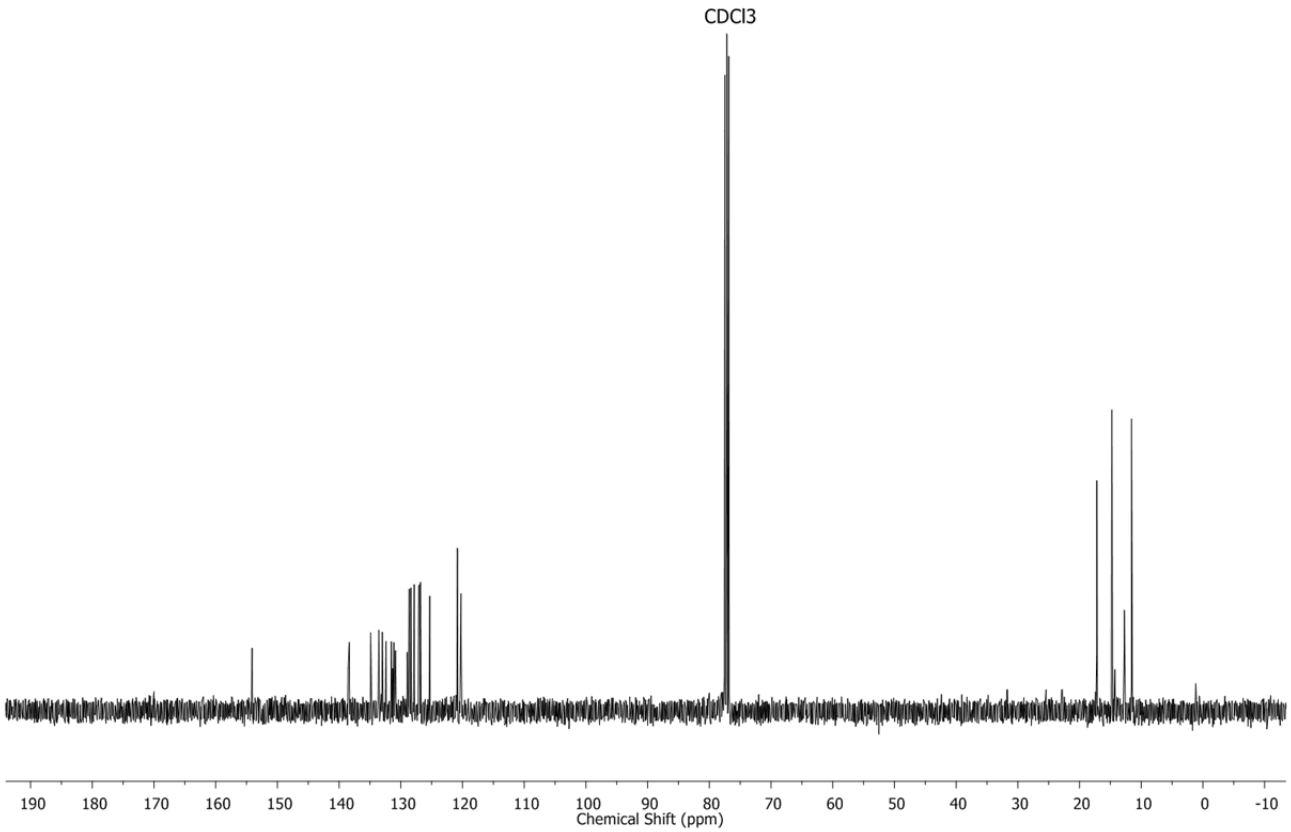


Figure S13: ^{1}H and ^{13}C NMR spectra of compound **BPerD**.