Electronic Supplementary Material (ESI) for MedChemComm.

Electronic Supplementary Information for:

Photophysical properties and application in live cell imaging of B,B-fluoro-perfluoroalkyl BODIPYs

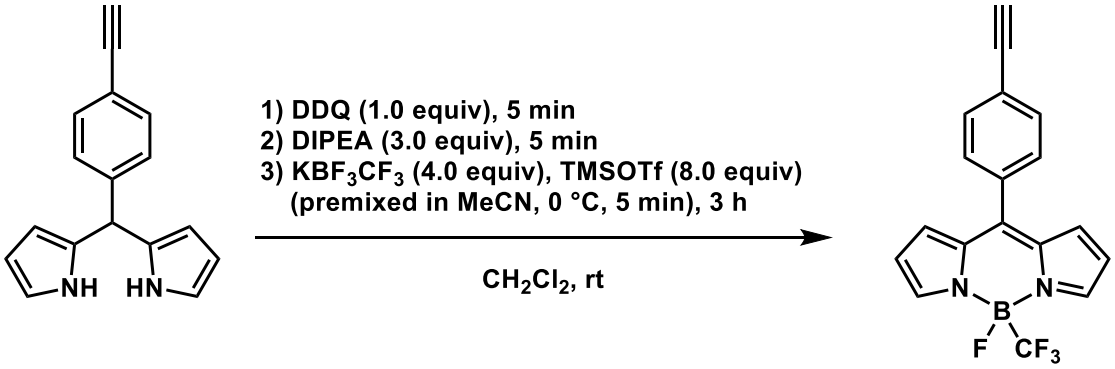
Atsuhiko Taniguchi,[a,b] Taka Sawazaki,[a] Yusuke Shimizu,[a] Youhei Sohma*[a], and Motomu Kanai*[a]

[a]Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan. E-mail: ysohma@mol.f.u-tokyo.ac.jp; kanai@mol.f.u-tokyo.ac.jp

[b]Present address: Department of Medicinal Chemistry, School of Pharmacy, Tokyo University of Pharmacy and Life Sciences, 1432-1 Horinouchi, Hachioji, Tokyo 192-0392, Japan.

Synthesis of compound **4**

DDQ (175.2 mg, 0.77 mmol) was added to 5–(4–ethynylphenyl)dipyrromethane[S1] (190.0 mmol, 0.77 mmol) in CH_2Cl_2 (10 mL) chilled in an ice bath. The mixture was stirred at 0 °C for 5 min, and then *N,N*–diisopropylethylamine (403 µL, 2.3 mmol) was added. After stirring at 0 °C for 5 min, an acetonitrile solution (2 mL) of potassium trifluoro(trifluoromethyl)borate (543.2 mg, 3.1 mmol) and trimethylsilyl trifluoromethanesulfonate (1.1 mL, 6.1 mmol), premixed at room temperature for 5 min, was added and then the mixture was stirred at room temperature for 3 hours. The mixture was washed with water, dried over Na_2SO_4, filtrated, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with hexane/CH_2Cl_2 to afford the title compound (36.9 mg, 14%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.99 (brs, 2H), 7.66 (d, *J* =8.6 Hz, 2H), 7.56 (d, *J* =8.6 Hz, 2H), 6.99 (d, *J* =4.0 Hz, 2H), 6.62 (dd, *J* =4.0, 1.7 Hz, 2H), 3.27 (s, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 146.77, 145.89, 134.37, 133.88, 132.33, 131.93, 130.59, 125.22, 119.35, 82.60, 80.19; ^{19}F NMR ($CDCl_3$, 370 MHz): δ –77.85 (s, 3F), –175.00 (m, 1F); ^{11}B NMR ($CDCl_3$, 126 Hz): δ –3.05; HRMS (ESI$^+$): m/z calcd for $C_{18}H_{11}BF_4N_2Na^+$ [M+Na]$^+$: 365.0849. Found 365.0848.



4

[S1] P. D. Rao, et al., *J. Org. Chem*., 2000, **65**, 7323.

Table S1 Photophysical properties of BODIPYs **1**–**3**

solvent	BODIPY	λ_{abs} (nm)	logε ($M^{-1}cm^{-1}$)	λ_{em} (nm)	ϕ^{d}
cyclohexane	**1**[a]	508	4.96	514	1
	2	509	5.08	513	0.99
	3	510	4.84	514	1
toluene	**1**[a]	511	4.89	519	0.82
	2	509	5.06	515	0.72
	3	510	4.94	516	0.75
chloroform	**1**[a]	508	4.95	516	0.9
	2	508	5.06	514	0.7
	3	509	4.87	515	0.75
methanol	**1**[b]	504	4.91	509	0.80
	2[c]	502	4.95	509	0.83
	3	503	4.94	509	0.82
DMF	**1**[a]	503	4.88	512	0.99
	2	503	5.16	510	0.95
	3	504	4.8	511	0.97

[a]N. A. Bumagina, et al., *Spectrochim. Acta, Part A*, 2017, **173**, 228; [b]ref 14; [c]ref 3; [d]calculated using fluorescein (0.86 in 0.1 N NaOH solution).

Table S2 Crystallographic data for **2**

	2
CCDC	1889593
formula	$C_{14}H_{15}BF_4N_2$
formula weight	298.13
crystal color, habit	red, block
crystal system	Monoclinic
space group	$P12_1/n1$
Lattice Parameters	a = 7.87143(14) Å
	b = 10.70505(19) Å
	c = 17.4437(3) Å
	α = 90.00 °
	β = 104.4010(10) °
	γ = 90.00 °
	V = 1423.69(4) $Å^3$
Z value	4
D_{calc}	1.386 g/cm^3
F_{000}	612
μ(CuKα)	10.25 cm^{-1}
no. observations	2606
no. parameters	190
*R*1 ((I>2.00σ(I))	0.0498
*wR*2 (all reflections)	0.1218
GOF on F^2	0.992
R_{int}	0.0707

(1) Least Squares function minimized:

$\Sigma w(Fo^2–Fc^2)^2$ where w = Least Squares weights.

(2) Standard deviation of an observation of unit weight:

$[\Sigma w(Fo^2–Fc^2)^2/(No\_Nv)]^{1/2}$ where: No = number of observations

Nv = number of variables

(3) Least squares weights:

$w=1/[\sigma^2(Fo^2) + (0.0650P)^2 + 1.0000P]$ where $P = (F_o^2 + 2Fc^2)/3$

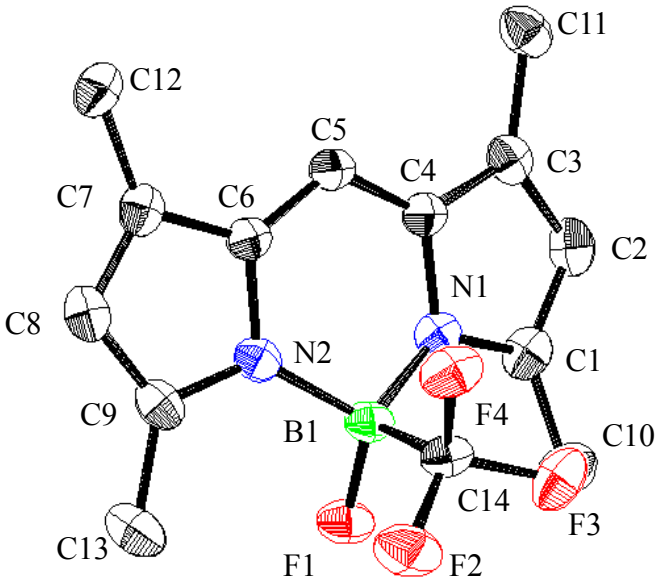


Table S3 Selected bond lengths [Å]

atom	atom	distance	atom	atom	distance
F1	B1	1.389(2)	C2	C3	1.379(3)
F2	C14	1.358(2)	C3	C4	1.414(3
F3	C14	1.355(2)	C3	C11	1.497(3)
F4	C14	1.355(2)	C4	C5	1.385(2)
N1	C1	1.356(2)	C5	C6	1.383(3)
N1	C4	1.400(2)	C6	C7	1.417(2)
N1	B1	1.545(2)	C7	C8	1.380(3)
N2	C9	1.354(2)	C7	C12	1.496(3)
N2	C6	1.398(2)	C8	C9	1.401(3)
N2	B1	1.553(2)	C9	C13	1.491(3)
C1	C2	1.398(3)	C14	B1	1.647(3)
C1	C10	1.494(3)			

Table S4 Selected angles [°]

atom	atom	atom	angle	atom	atom	atom	angle
C1	N1	C4	107.26(15)	C8	C7	C6	105.93(16)
C1	N1	B1	129.37(15)	C8	C7	C12	128.38(17)
C4	N1	B1	122.94(14)	C6	C7	C12	125.67(17)
C9	N2	C6	107.58(15)	C7	C8	C9	108.79(16)
C9	N2	B1	129.64(15)	N2	C9	C8	109.02(17)
C6	N2	B1	122.45(14)	N2	C9	C13	123.77(17)
N1	C1	C2	109.17(16)	C8	C9	C13	127.20(18)
N1	C1	C10	123.79(18)	F3	C14	F4	104.66(14)
C2	C1	C10	126.99(18)	F3	C14	F2	104.21(15)
C3	C2	C1	108.81(16)	F4	C14	F2	104.66(15)
C2	C3	C4	105.97(16)	F3	C14	B1	114.35(15)
C2	C3	C11	128.09(17)	F4	C14	B1	113.78(15)
C4	C3	C11	125.94(17)	F2	C14	B1	114.07(14)
C5	C4	N1	120.04(16)	F1	B1	N1	111.30(15)
C5	C4	C3	130.91(16)	F1	B1	N2	112.34(15)
N1	C4	C3	108.79(15)	N1	B1	N2	107.15(14)
C6	C5	C4	122.24(16)	F1	B1	C14	108.27(15)
C5	C6	N2	120.54(15)	N1	B1	C14	108.96(15)
C5	C6	C7	130.43(16)	N2	B1	C14	108.75(14)
N2	C6	C7	108.68(16)				

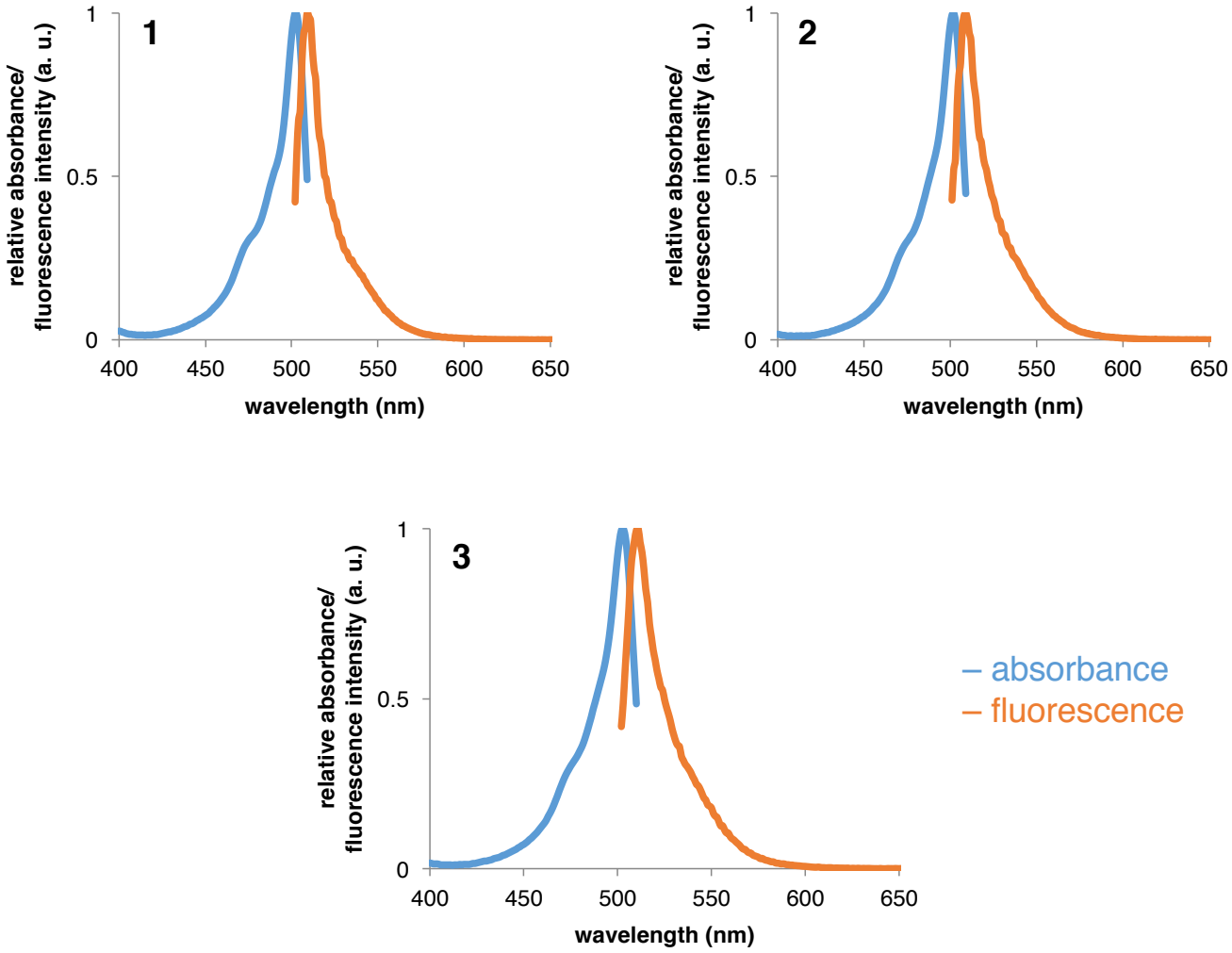


Fig. S1 Absorbance and fluorescence spectra of **1**–**3**.

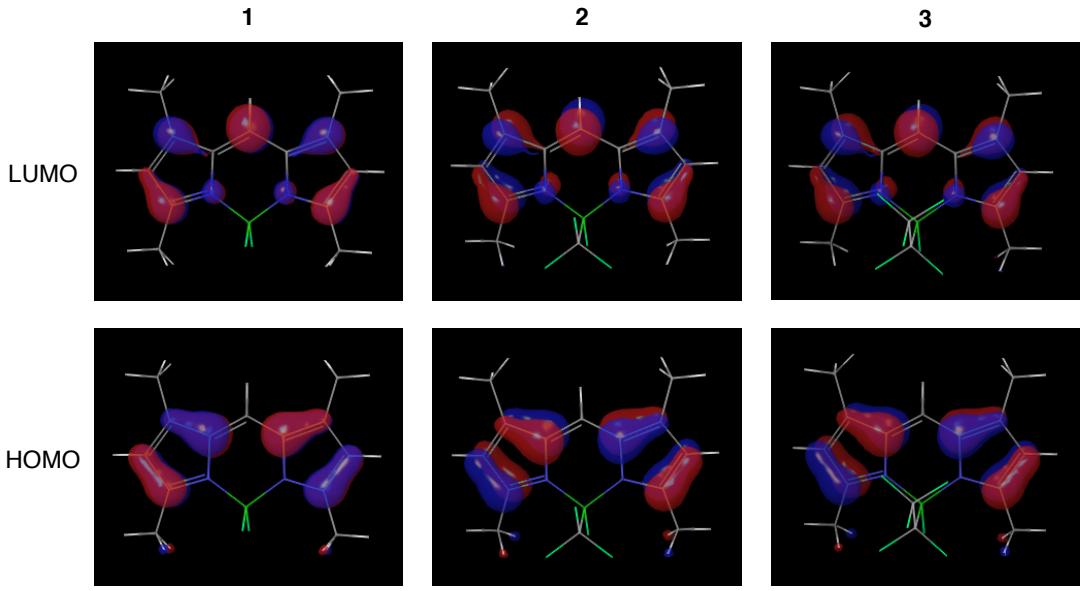


Fig. S2 HOMO and LUMO distributions of **1**–**3**.

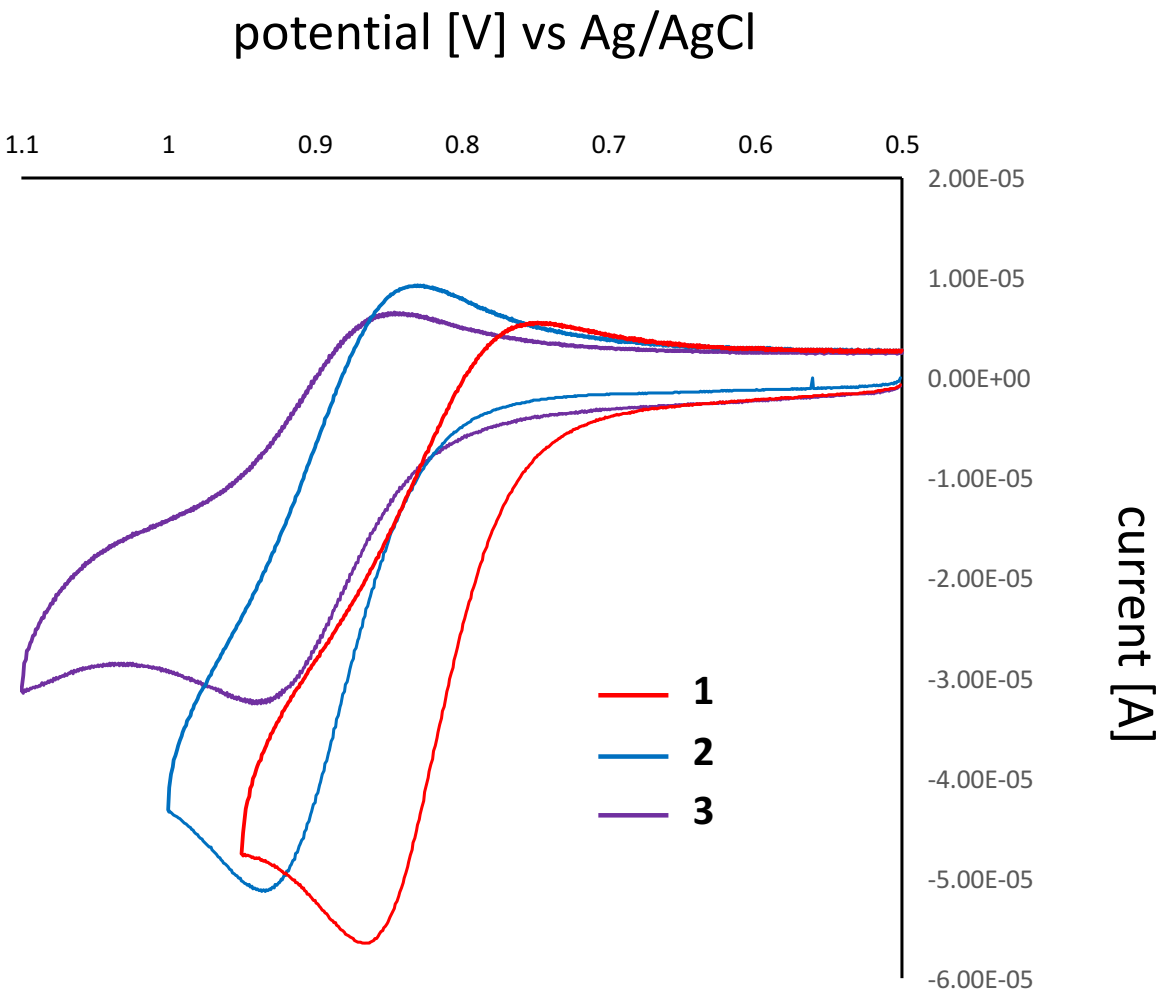
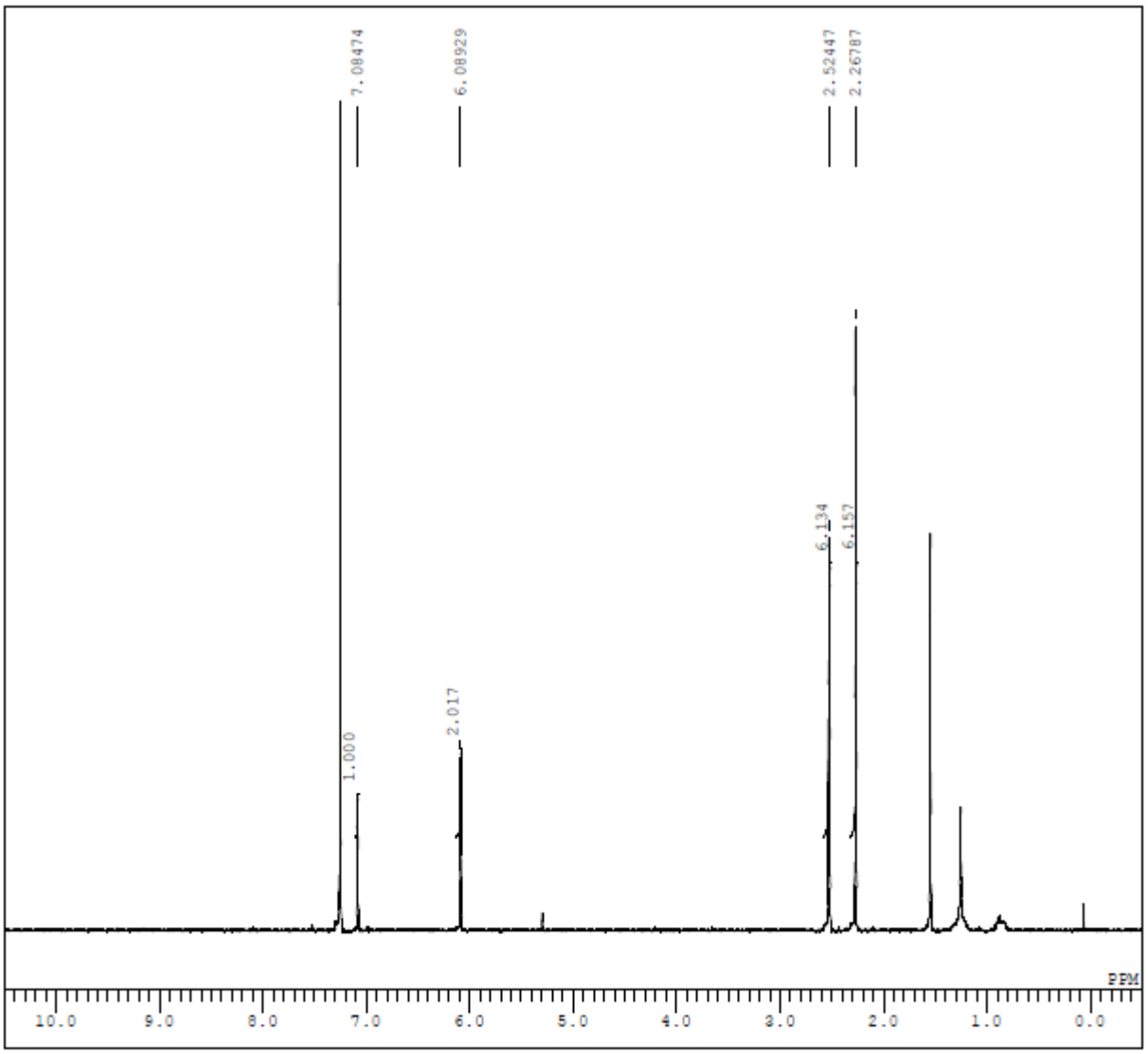
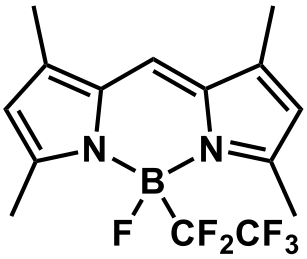


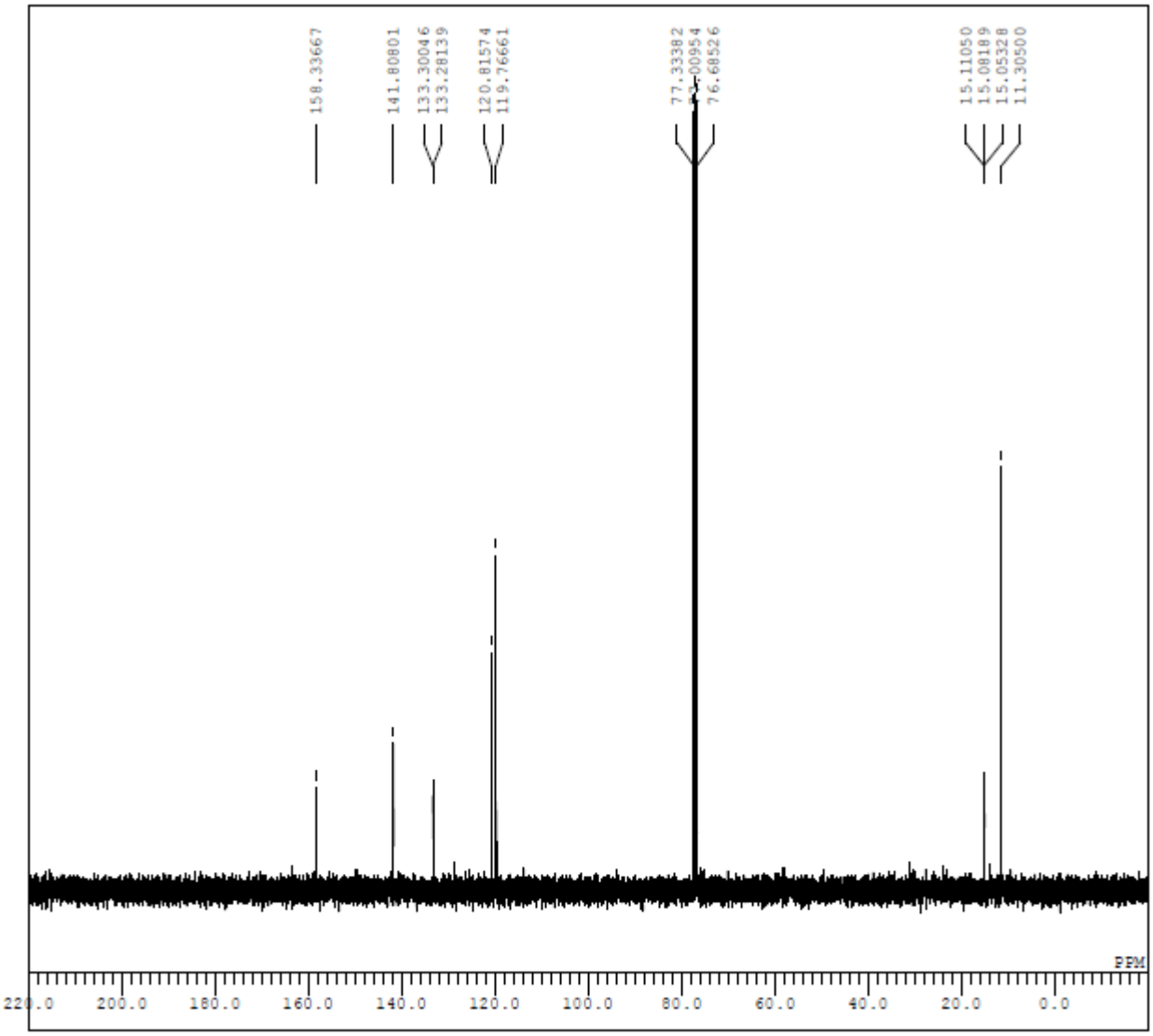
Fig. S3 Cyclic voltammograms of **1**–**3**.

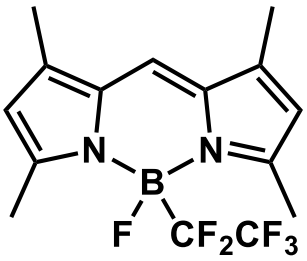
NMR spectrum



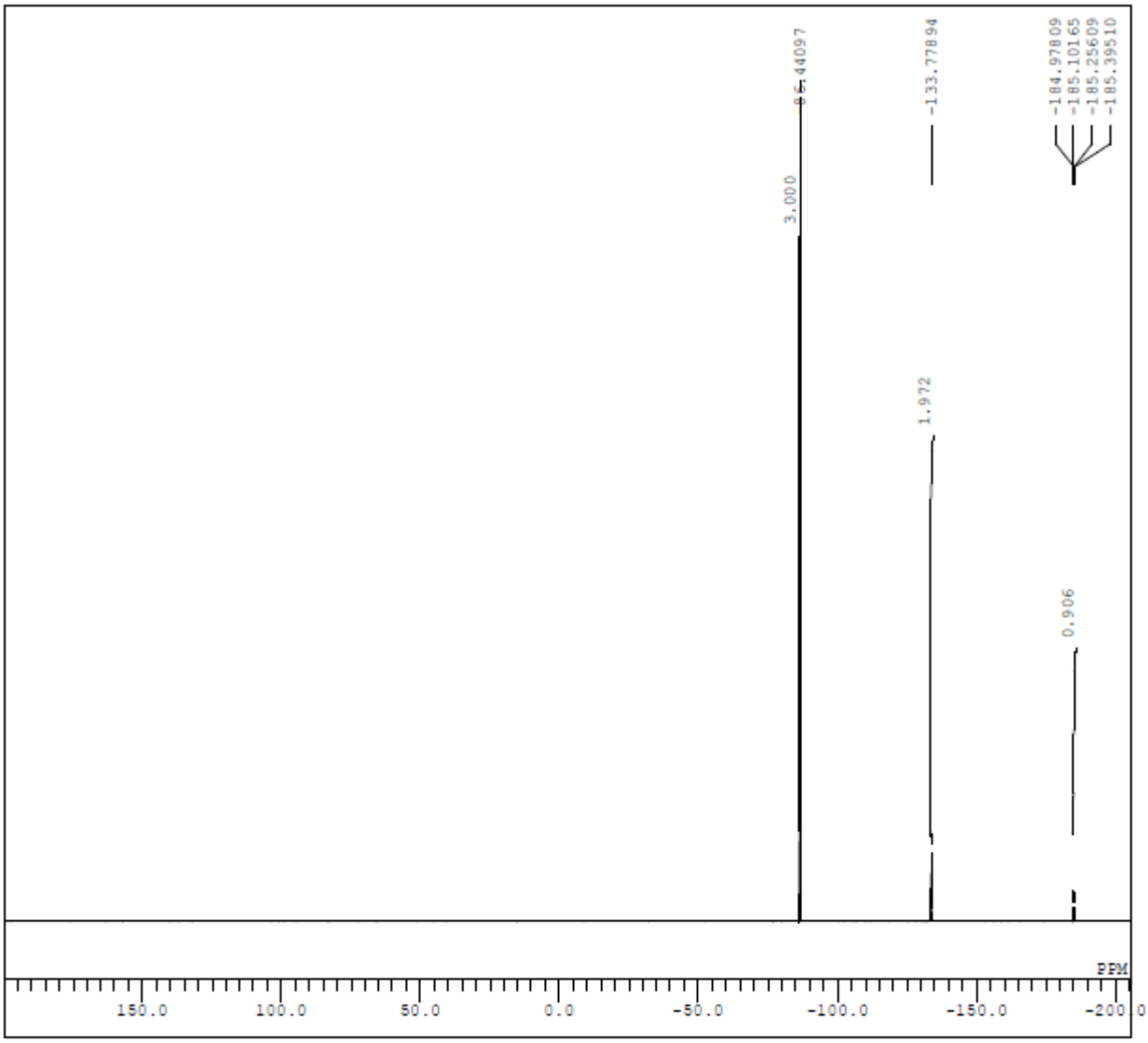


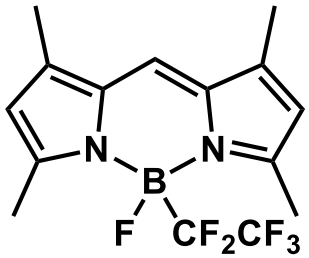
^{1}H NMR spectrum



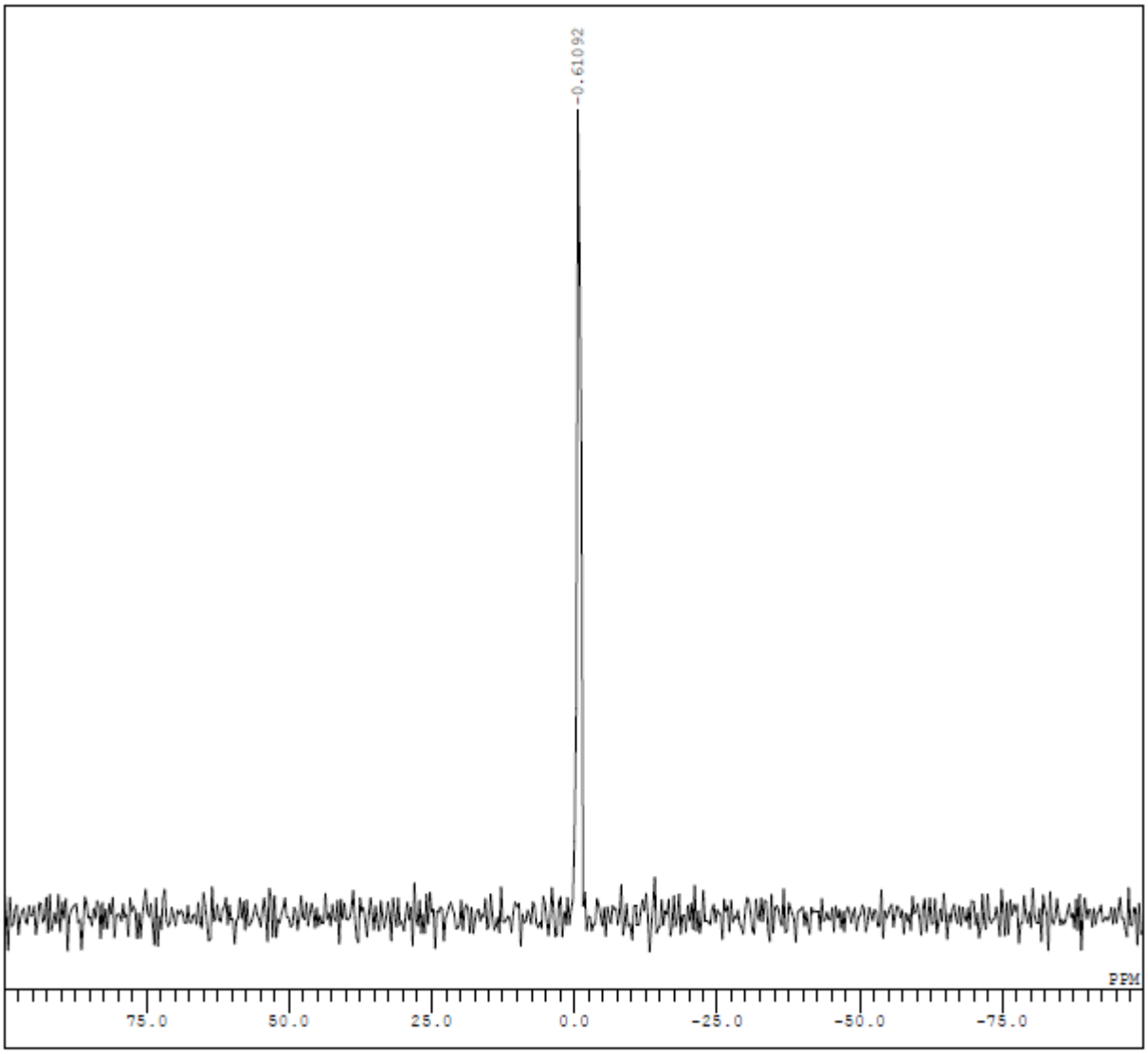


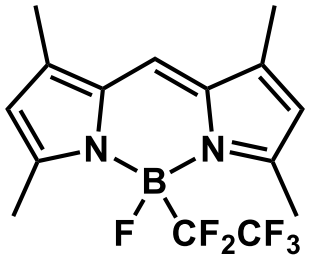
^{13}C NMR spectrum



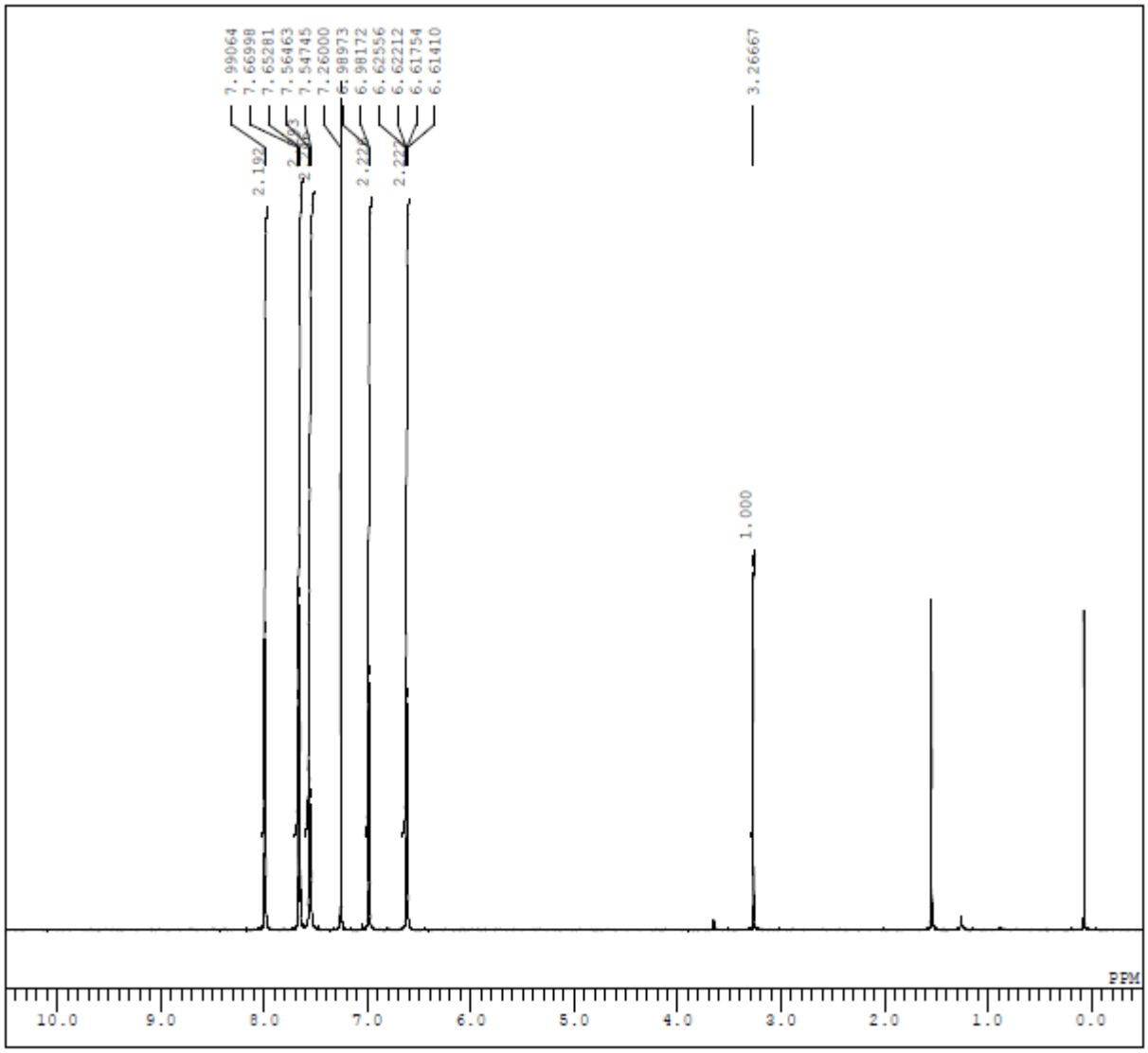


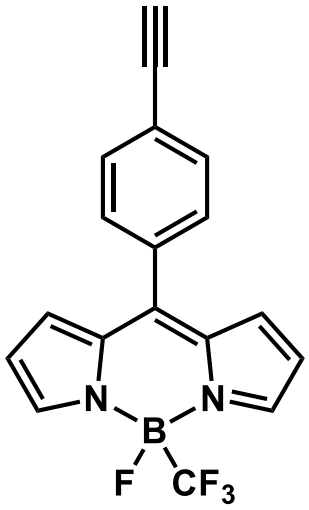
^{19}F NMR spectrum



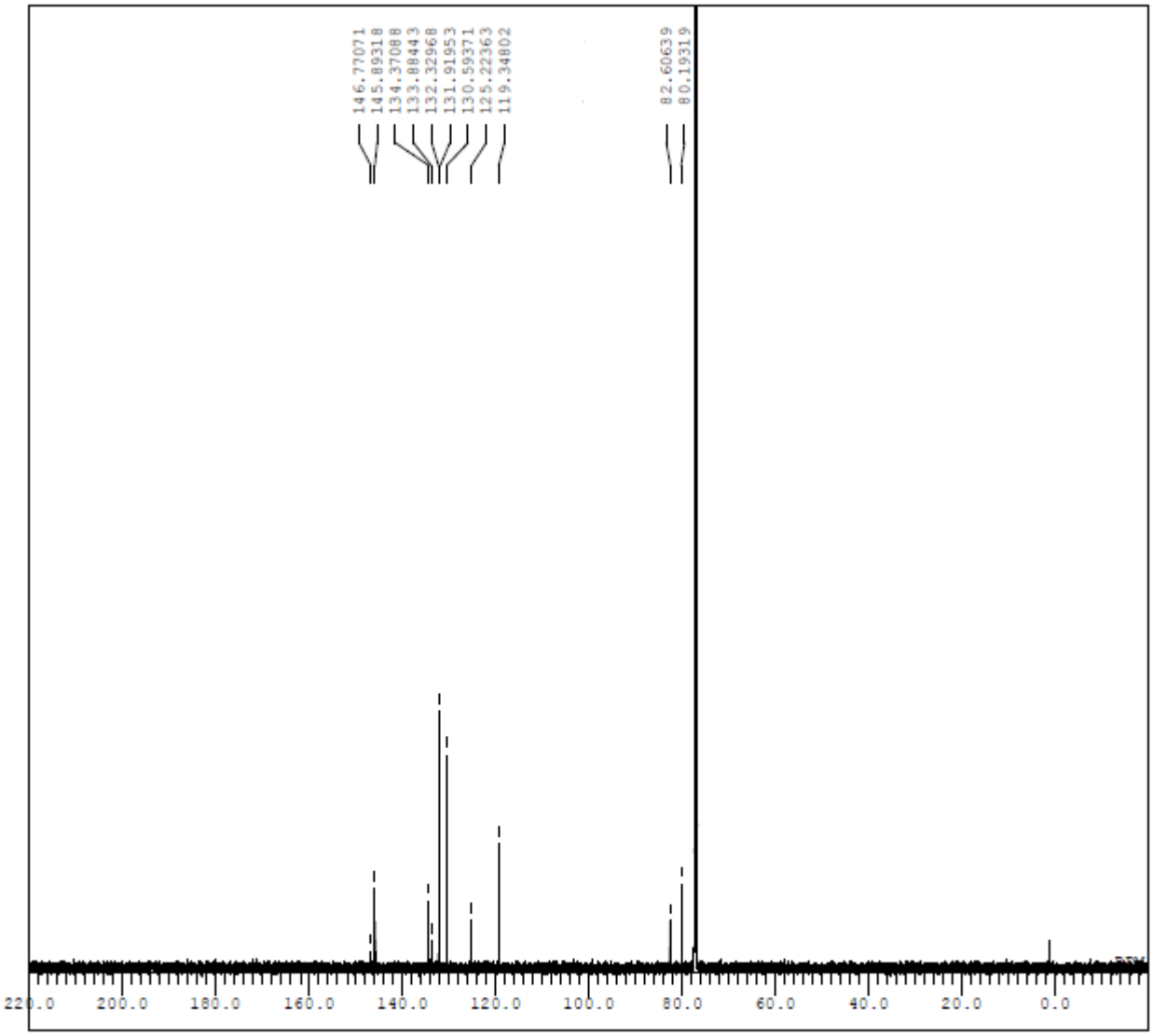


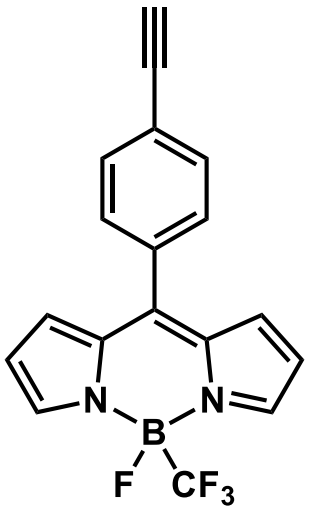
^{11}B NMR spectrum



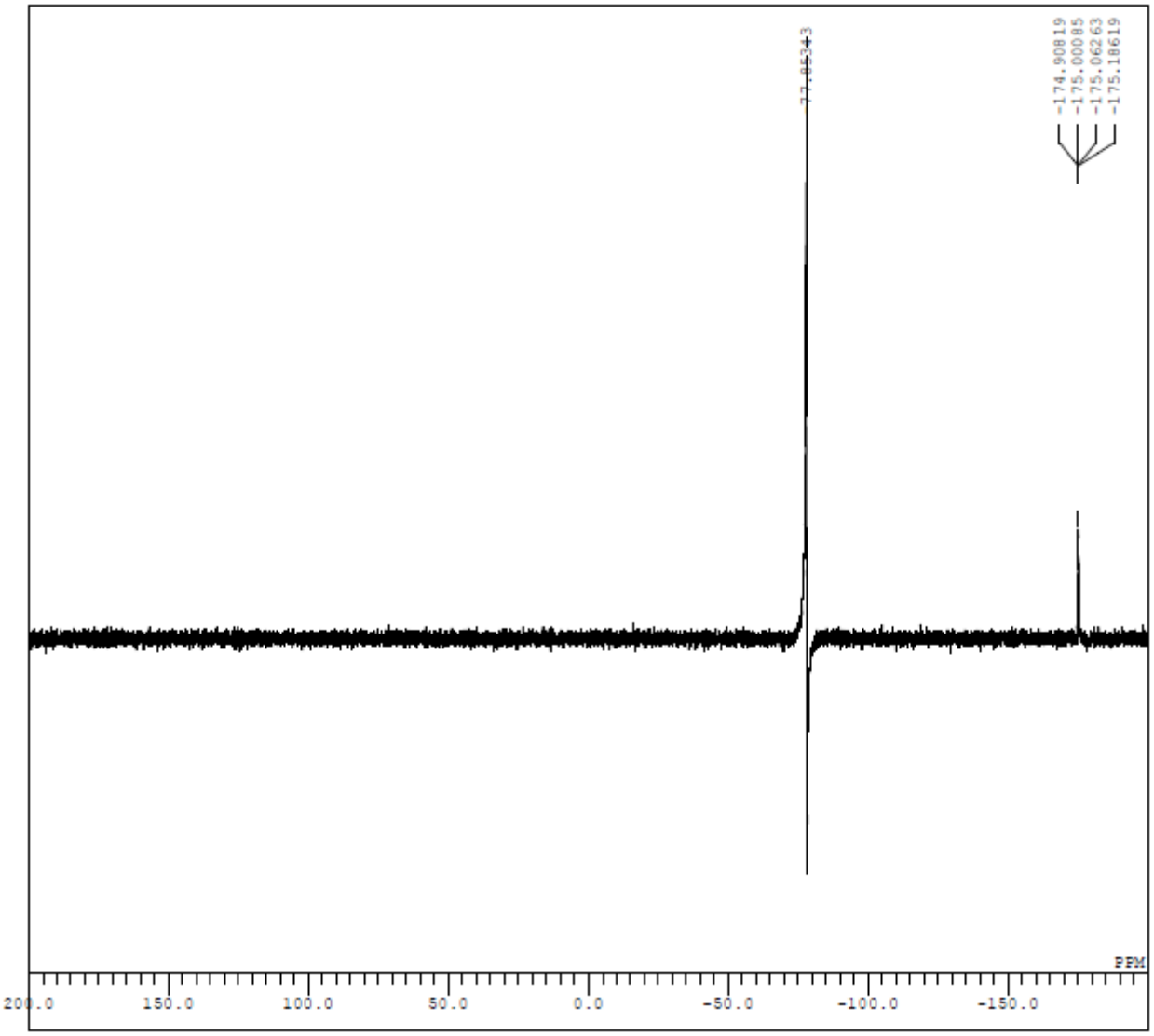


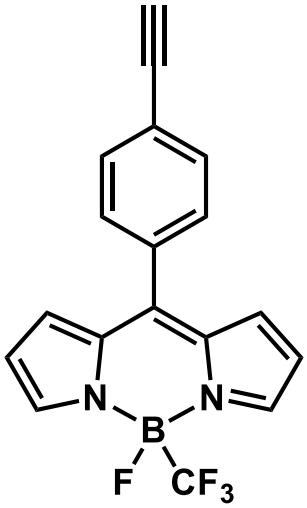
^{1}H NMR spectrum



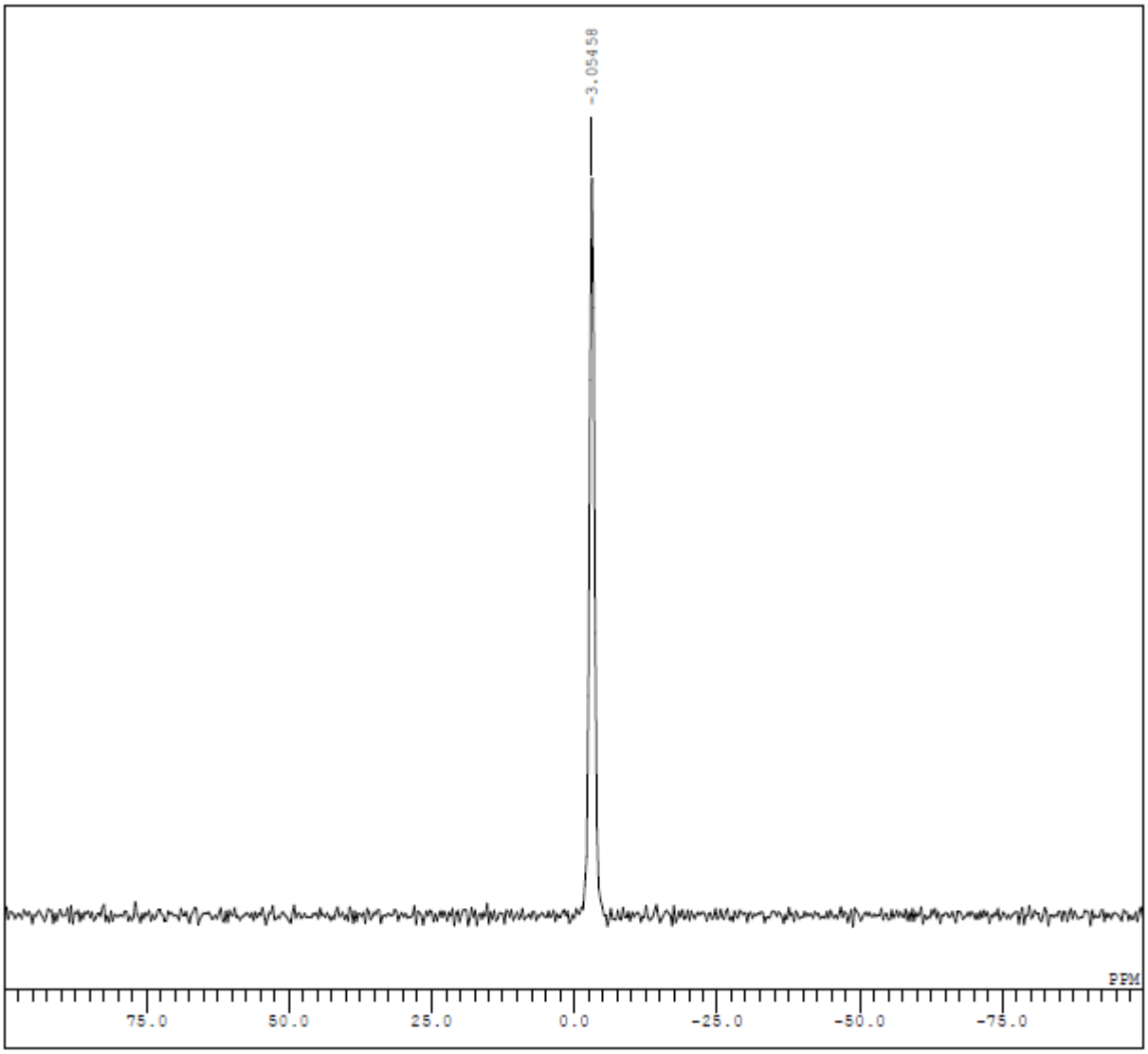


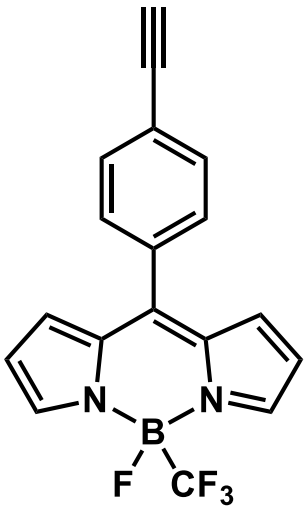
^{13}C NMR spectrum





^{19}F NMR spectrum





^{11}B NMR spectrum