Supporting Information

Iodine(III)-promoted regioselective and efficient synthesis of β-triazolyl BODIPYs for the selective recognition of nickel ion and bovine serum albumin

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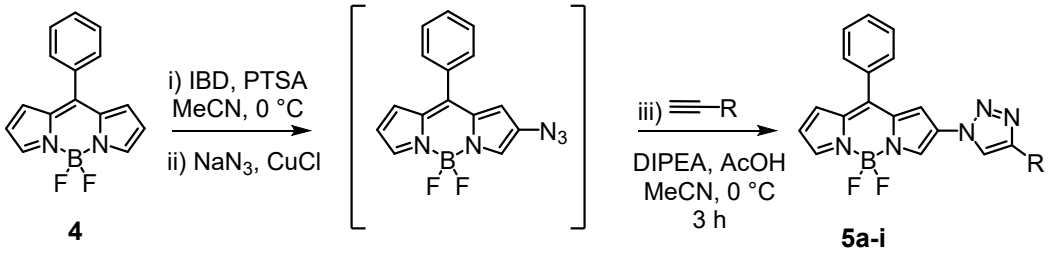
I. Experimental section

(a) Materials and methods

The reagents and solvents were procured from commercial sources and used as such unless otherwise mentioned. Dichloromethane (DCM) was freshly distilled over in presence of calcium hydride prior to use and hexane was distilled prior to use to remove any higher boiling fractions. TLC plates (60 F_{254}) and Silica gel (100 -200 mesh) were procured from Merck. Melting points (mps) were recorded on E-Z melting apparatus. NMR spectra were measured on a Brucker Advance II (400 MHz for ^{1}H and 100 MHz for ^{13}C) instrument using solvents DMSO-d_6 and $CDCl_3$. HRMS spectra were obtained on a 6200 series TOF (Q-TOF, B.06.01 (B6172 SP1). Spectroscopic grade solvents obtained from Sigma-Aldrich were used to make 3~5×10^{-6} M concentrations of the compounds necessary for solvent-dependent spectroscopic measurements.

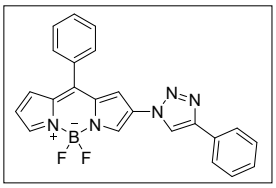
(b) General procedure for one-pot synthesis of triazolyl-tethered BODIPYs5a-i:



To a stirred solution of IBD(0.56 mmol, 1.5 eq.) in MeCN (3mL) was added PTSA (0.56 mmol, 1.5 eq.) and stirred the resulting suspension for 20 min at 0 ^{o}C. Then, prepared solution of BODIPY **4** (0.37 mmol, 1 eq.) in MeCN (1mL) was added and the resulting mixture was allowed to stir at same temperature (progress of the reaction was monitored by TLC). After the full conversion of **4,** NaN_3 (0.559 mmol, 1.5 eq.) was added, then immediately CuCl (0.1 mmol) and stirred the reaction mixture for 30 min. Finally, appropriate alkyne (0.74 mmol, 2 eq.), DIPEA (0.74 mmol, 2 eq.) and AcOH (0.74 mmol, 2 eq.) were added and stirring the reaction contents for 3 h. The reaction mixture was extracted with DCM (3 × 100 mL) and the combinedorganic layer was dried over anhydrous sodium sulfate, filtered and evaporated. The residue was purified by silica (100-200 mesh) column chromatographyusing chloroform: hexane (7:3) as the elute solvent.

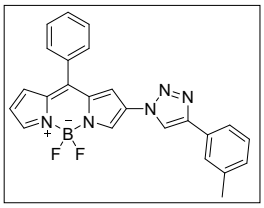
II. Characterization data of the synthesized compounds

5,5-difluoro-10-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (5a).



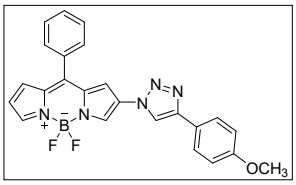
Dark reddish colour; Yield 77%; Mp: 257-258 ^{o}C;^{1}H NMR (400 MHz, DMSO-d_6) δ 9.26 (s, 1H), 8.63 (s, 1H), 8.45 (s, 1H), 7.88 (dd, *J* = 6.8, 1.2 Hz, 2H), 7.80-7.74 (m, 3H), 7.69 (t,*J* = 7.6 Hz, 2H), 7.50 (t,*J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.35 (s, 1H), 7.23 (d, *J* = 4.0 Hz, 1H), 6.86 (dd, *J* = 4.3, 1.6Hz,1H);^{13}C NMR (100 MHz, DMSO-d_6) *δ* 149.5, 148.4, 147.3, 136.0, 134.8, 133.1, 133.0, 132.6, 132.0, 131.2, 130.7, 130.5, 129.5, 129.4, 128.7, 125.7, 121.7, 120.4, 118.0; HRMS (ESI) m/z calcd for $C_{23}H_{17}BF_2N_5$ $[M+H]^+$ 412.1544; found 412.1499.

5,5-difluoro-10-phenyl-2-(4-(p-tolyl)-1*H*-1,2,3-triazol-1-yl)-5*H*-5λ⁴,6λ⁴-dipyrrolo[1,2-:2',1'-f][1,3,2]diazaborinine (5b).



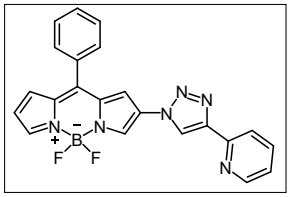
Reddish colour; Yield 65%; Mp: 217-218 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.19 (s, 1H), 8.62 (s, 1H), 8.44 (s, 1H), 7.79-7.76 (m, 5H), 7.68 (m, 2H), 7.33 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 4.0 Hz, 1H), 6.85 (dd, *J* = 4.4, 1.5 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.4, 148.4, 147.4, 138.1, 136.0, 135.0, 133.1, 133.0, 132.6, 132.0, 131.2, 131.0, 130.0, 129.4, 127.8, 125.6, 121.7, 119.9, 117.9, 21.3; HRMS (ESI) *m/z* calcd for $C_{24}H_{19}BF_2N_5$ $[M+H]^+$426.1700; found 426.1695.

5,5-difluoro-2-(4-(4-methoxyphenyl)-1H-1,2,3-triazol-1-yl)-10-phenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (5c).



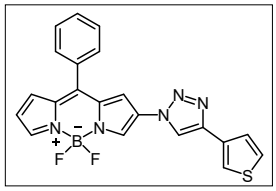
Gray colour; Yield 69%; Mp: 145-146 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.26 (s, 1H), 8.59 (s, 1H), 8.39 (s, 1H), 7.90 (d, *J* = 6.5 Hz, 2H), 7.79 (d, *J* = 7.4 Hz, 2H), 7.51 (q, 2H), 7.41 (brs, 2H), 7.27 (br s, 2H), 7.25 (s, 2H), 6.86 (d, *J* = 1.2 Hz, 1H), 3.94 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 162.9, 148.5, 148.3, 147.4, 135.8, 134.5, 133.5, 132.5, 132.3, 130.6, 129.5, 128.8, 125.7, 125.5, 121.3, 120.4, 118.0, 115.1, 56.1; HRMS (ESI) *m/z* calcd for $C_{24}H_{19}BF_2N_5O$ $[M+H]^+$ 442.1650; found 442.1637.

5,5-difluoro-10-phenyl-2-(4-(pyridin-2-yl)-1H-1,2,3-triazol-1-yl)-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (5d).



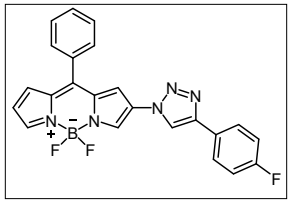
Reddish colour; Yield 72%; Mp: 276-277 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.34 (s, 1H), 8.69 (s, 1H), 8.64 (d, *J* = 4.4 Hz, 1H), 8.43 (s, 1H), 8.09 (d, *J* = 8 Hz, 1H), 7.94 (td, *J* = 7.6 Hz, 1H), 7.79-7.66 (m, 5H), 7.68 (t, *J* = 7.4 Hz, 2H), 7.48 (s, 1H), 7.41-7.38 (m, 1H), 7.22 (d, *J* = 3.6 Hz, 1H), 6.86 (d, *J* = 3.8 Hz, 1H); ^{13}CNMR (100 MHz, DMSO-d_6) δ 150.2, 149.9, 149.4, 148.5, 148.3, 137.8, 136.0, 134.8, 133.3, 133.0, 132.6 , 132.0, 131.3, 130.6, 129.4, 123.8, 122.1, 121.7, 120.2, 118.5; HRMS (ESI) *m/z* calcd for $C_{22}H_{16}BF_2N_6$ $[M+H]^+$ 413.1496; found 413.1497.

5,5-difluoro-10-phenyl-2-(4-(thiophen-3-yl)-1H-1,2,3-triazol-1-yl)-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (5e).



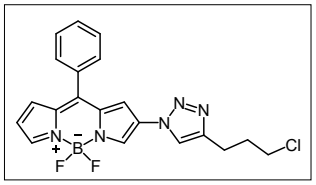
Dark reddish colour; Yield 62%; Mp: <300 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.09 (s, 1H), 8.60 (s, 1H), 8.44 (s, 1H), 7.89 (dd, *J* = 2.8 Hz, 1H), 7.79-7.74 (m, 3H), 7.71-7.66 (m, 3H), 7.50 (dd, *J* = 4.8 Hz, 1H), 7.32 (s, 1H), 7.22 (d, *J* = 4.4 Hz, 1H), 6.85 (dd, *J* = 4.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.5, 148.4, 143.9, 136.1, 134.8, 133.1, 133.0, 132.6, 132.0, 131.8, 131.2, 129.4, 128.0, 126.1, 122.0, 121.7, 120.1, 118.0; HRMS (ESI) *m/z* calcd for $C_{21}H_{15}BF_2N_5S$ $[M+H]^+$ 418.1108; found 418.1115.

5,5-difluoro-2-(4-(4-fluorophenyl)-1H-1,2,3-triazol-1-yl)-10-phenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (5f).



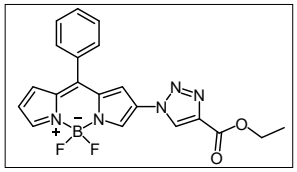
Reddish colour; Yield 60%; Mp: 237-238 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.23 (s, 1H), 8.61 (s, 1H), 8.45 (s, 1H), 7.92-7.88 (m, 2H), 7.80-7.74 (m, 3H), 7.68 (t, *J* = 7.4 Hz, 2H), 7.37-7.32 (m, 3H), 7.22 (d, *J* = 4.4 Hz, 1H), 6.86 (dd, *J* = 4.2 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.7, 161.2, 149.6, 148.4, 146.5, 136.1, 135.0, 133.0, 132.6, 132.0, 131.2, 129.4, 127.8, 127.7, 127.1, 125.7, 121.8, 120.3, 118.0, 116.7, 116.4;^{19}F NMR (376 MHz, DMSO-d_6) δ -113.42 (m, 1F), -141.83 (q, J = 57.0 Hz, 2F);HRMS (ESI) *m/z* calcd for $C_{23}H_{16}BF_3N_5$ $[M+H]^+$ 430.1451; found 430.1448.

2-(4-(3-chloropropyl)-1H-1,2,3-triazol-1-yl)-5,5-difluoro-10-phenyl-5H-5λ⁴,6λ⁴-dipyrrolo [1,2-c:2',1'-f][1,3,2]diazaborinine (5g).



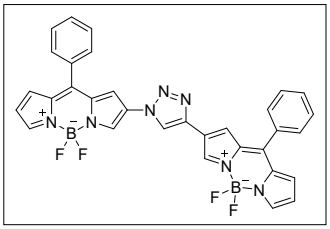
Dark reddish colour; Yield 55%; Mp: 158-159 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 (br s, 2H), 8.41 (s, 1H), 7.76-7.65 (m, 5H), 7.29 (s, 1H), 7.20 (br s, 1H), 6.84 (br s, 1H), 3.73-3.70 (t, *J* = 6.1 Hz, 2H), 2.83 (t, *J* = 7.0 Hz, 2H), 2.13-2.06 (t, *J* = 6.7 Hz2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.1, 148.4, 146.8, 135.9, 134.6, 133.2, 133.0, 132.6, 132.0, 131.0, 121.6, 121.3, 118.0, 45.0, 32.0, 22.7; HRMS (ESI) *m/z* calcd for $C_{20}H_{18}BClF_2N_5$ $[M+H]^+$ 412.1310; found 412.1318.

Ethyl 1-(5,5-difluoro-10-phenyl-5H-5λ⁴,6λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diaza-borinin-2-yl)-1H-1,2,3-triazole-4-carboxylate (5h).



Dark reddish colour; Yield 59%; Mp: 241-243 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.45 (s, 1H), 8.65 (s, 1H), 8.45 (s, 1H), 7.77-7.65 (m, 5H), 7.45 (s, 1H), 7.24 (d, *J* = 3.2 Hz,1H), 6.87 (d, *J* = 3.6 Hz, 1H), 4.35 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.4, 150.0, 139.8, 136.2, 135.1, 133.1, 132.9, 132.0, 131.2, 129.4, 127.8, 61.2, 14.6;HRMS (ESI) *m/z* calcd for $C_{20}H_{17}BF_2N_5O_2$ $[M+H]^+$ 408.1442; found 408.1450.

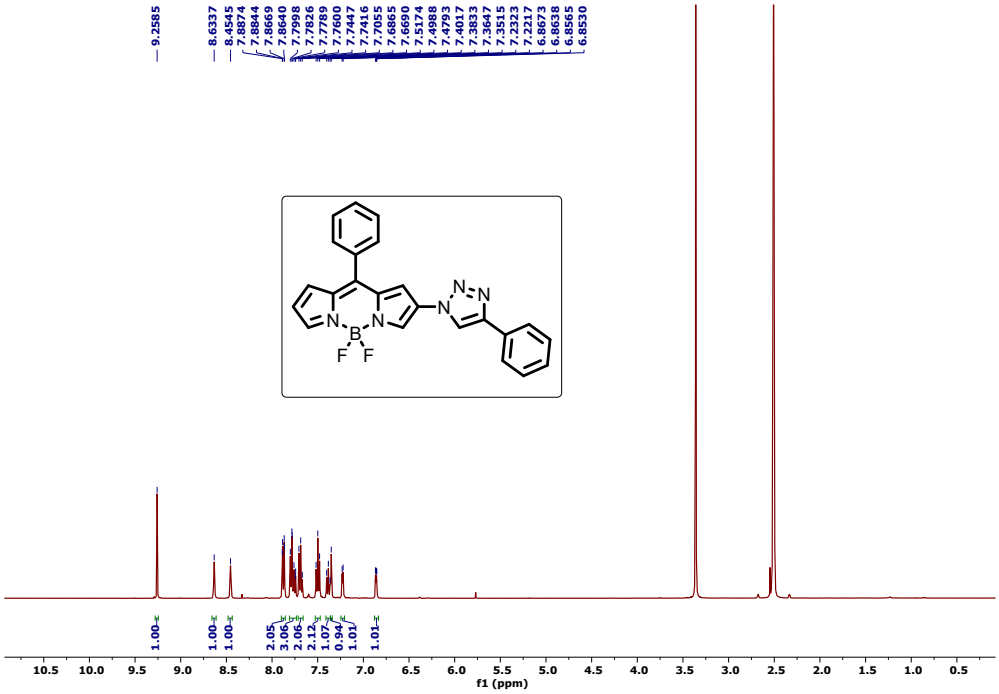
2-(4-(5,5-difluoro-10-phenyl-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-2-yl)-1H-1,2,3-triazol-1-yl)-5,5-difluoro-10-phenyl-5H-5λ⁴,6λ4-dipyrrolo[1,2-c:2',1'f][1,3,2] diaza-borinine (5i).



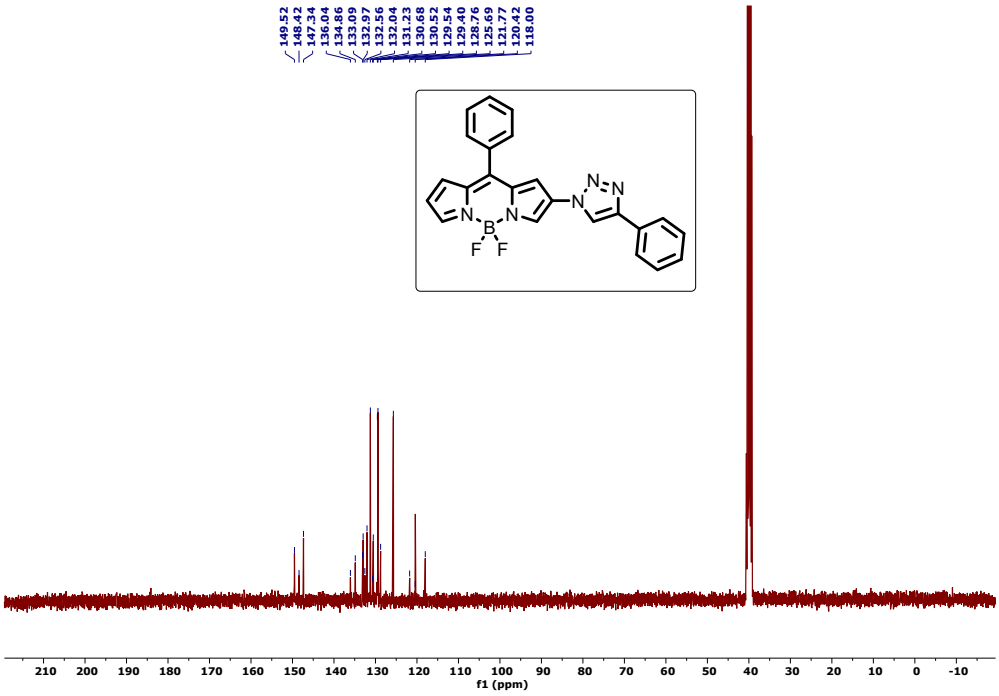
Dark brown colour; Yield45%; Mp: 178-179 ^{o}C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.16 (s, 1H), 8.54 (s, 1H), 8.42 (s, 1H), 8.24 (s, 1H), 8.00 (s, 1H), 7.77-7.64 (m, 10H), 7.25 (s, 1H), 7.20 (d, *J* = 3.2 Hz, 1H), 7.13 (s, 1H), 7.0 (d, *J* = 3.6 Hz, 1H), 6.84 (d, *J* = 2.9 Hz, 1H), 6.71 (d, *J* = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 146.8, 146.6, 141.7, 141.2, 136.2, 135.8, 133.9, 132.0,131.4, 131.3, 131.2, 130.9, 129.4, 129.2, 124.0, 123.2, 120.2, 119.7;^{19}F NMR (376 MHz, DMSO-d_6) δ-141.81 (q, J = 62.0 Hz, 4F).HRMS (ESI) *m/z* calcd for $C_{32}H_{23}BF_2N_7$ $[M+H-BF_2]^+$554.2076; found 554.2032.

Actual spectra (^{1}H,^{13}C NMR and HRMS) of the synthesized compounds

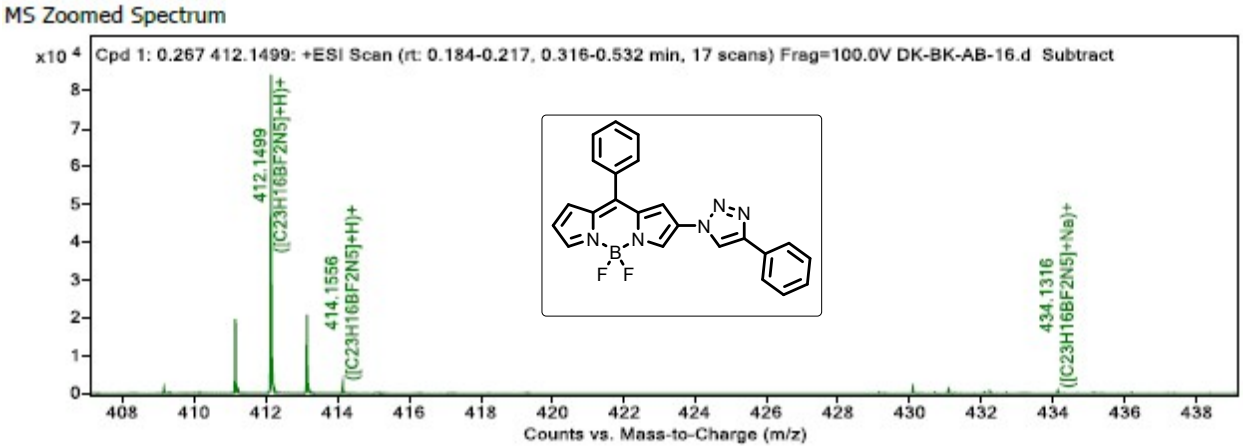
^{1}H NMR spectrum of 5a



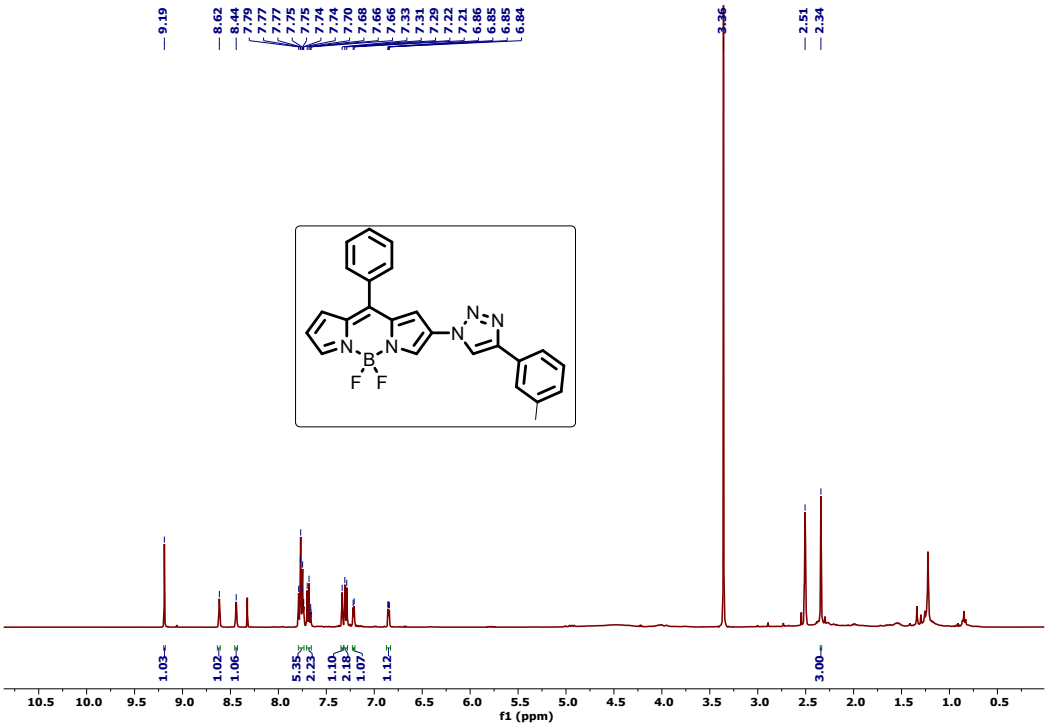
^{13}C NMR spectrum of 5a



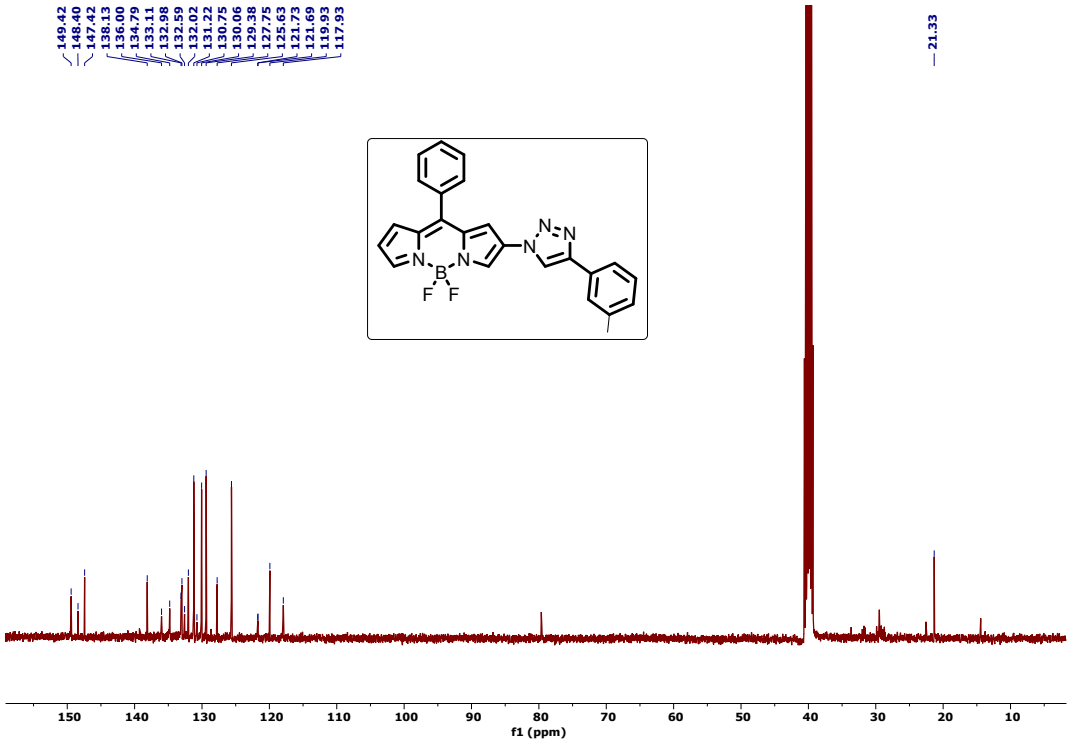
HRMS spectrum of 5a



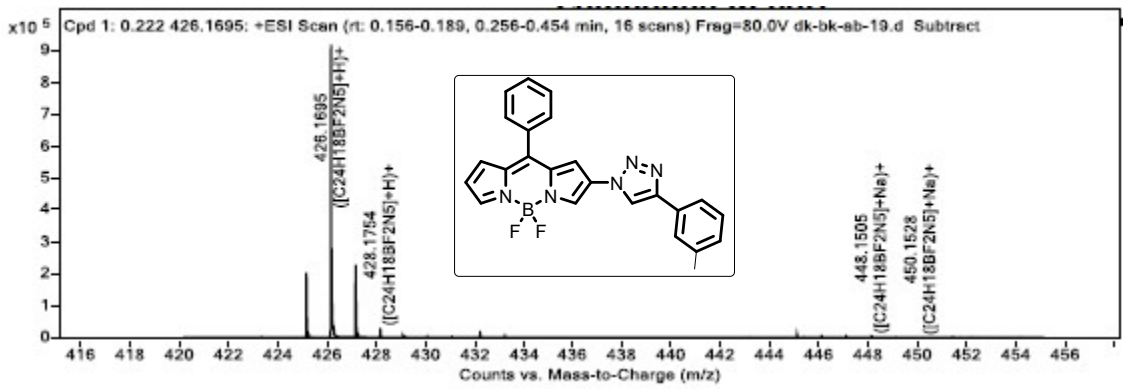
^{1}H NMR spectrum of 5b



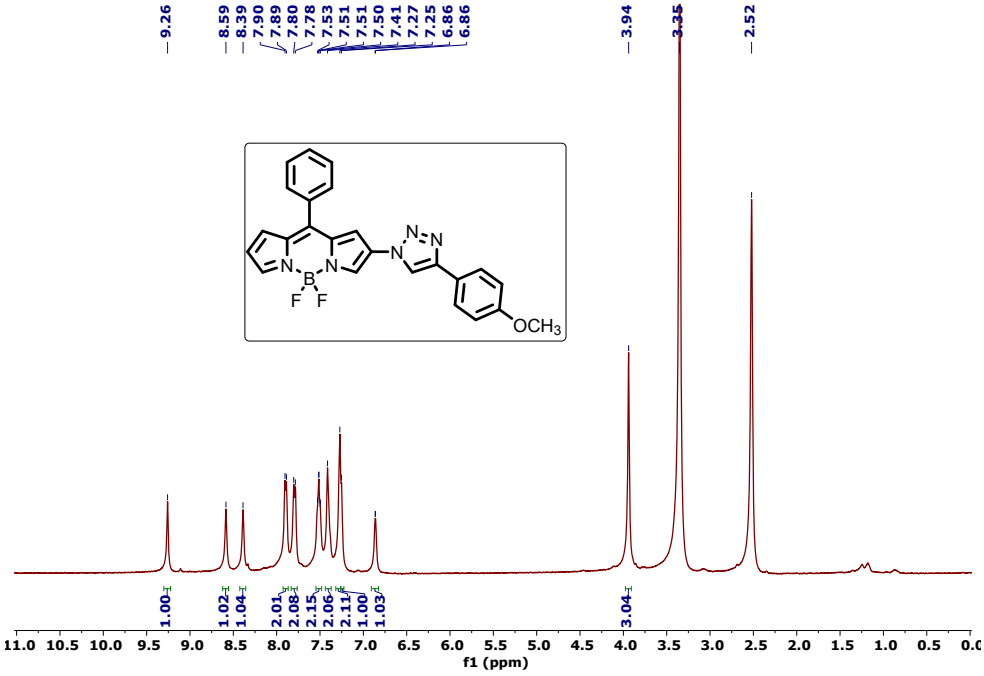
^{13}C NMR spectrum of 5b



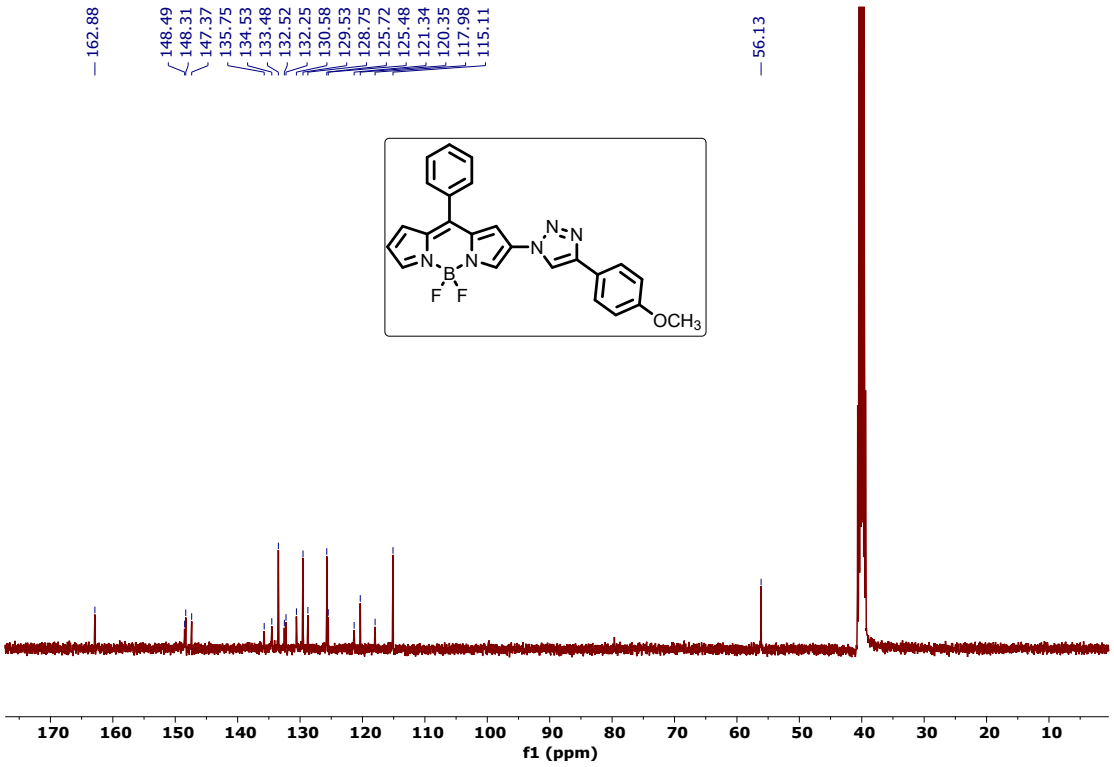
HRMS spectrum of 5b



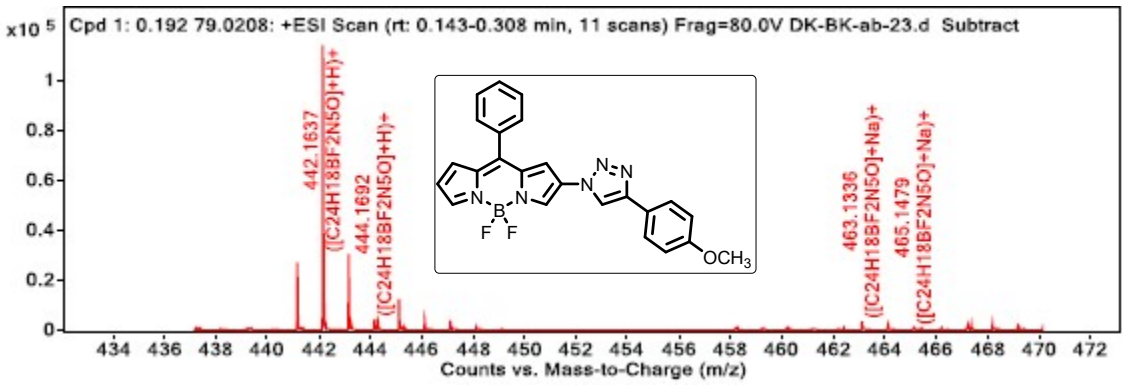
^{1}H NMR spectrum of 5c



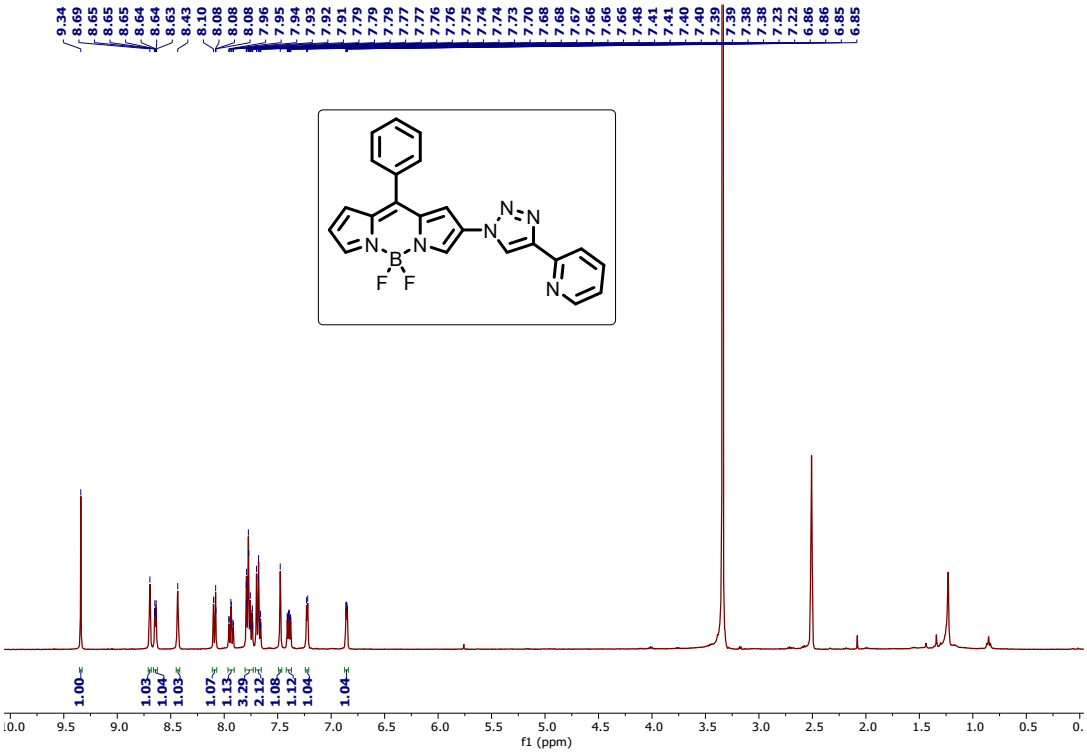
^{13}C NMR spectrum of 5c



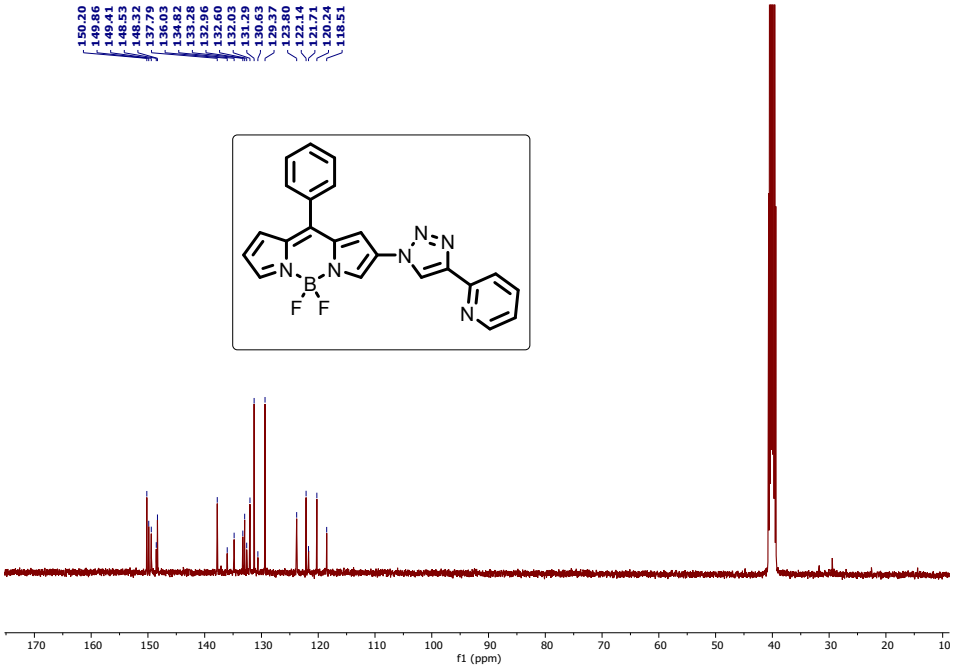
HRMS spectrum of 5c



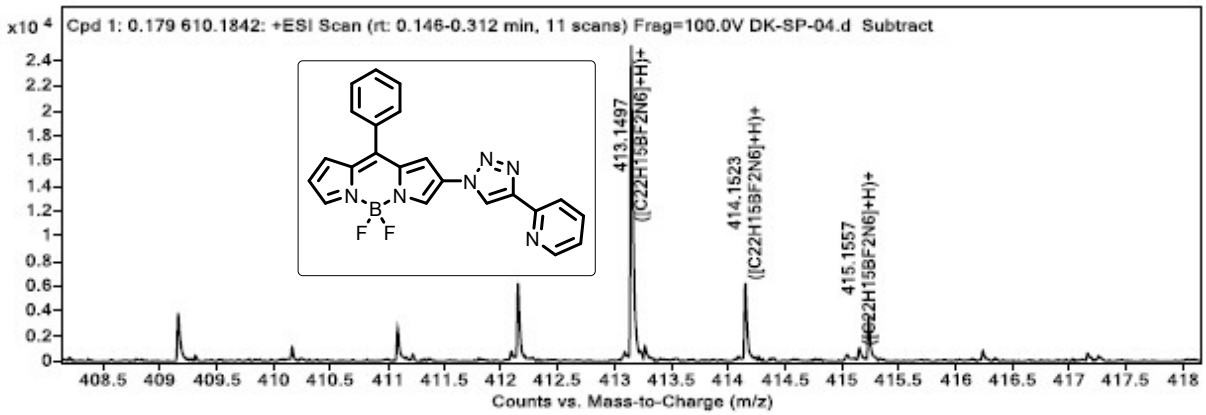
^{1}H NMR spectrum of 5d



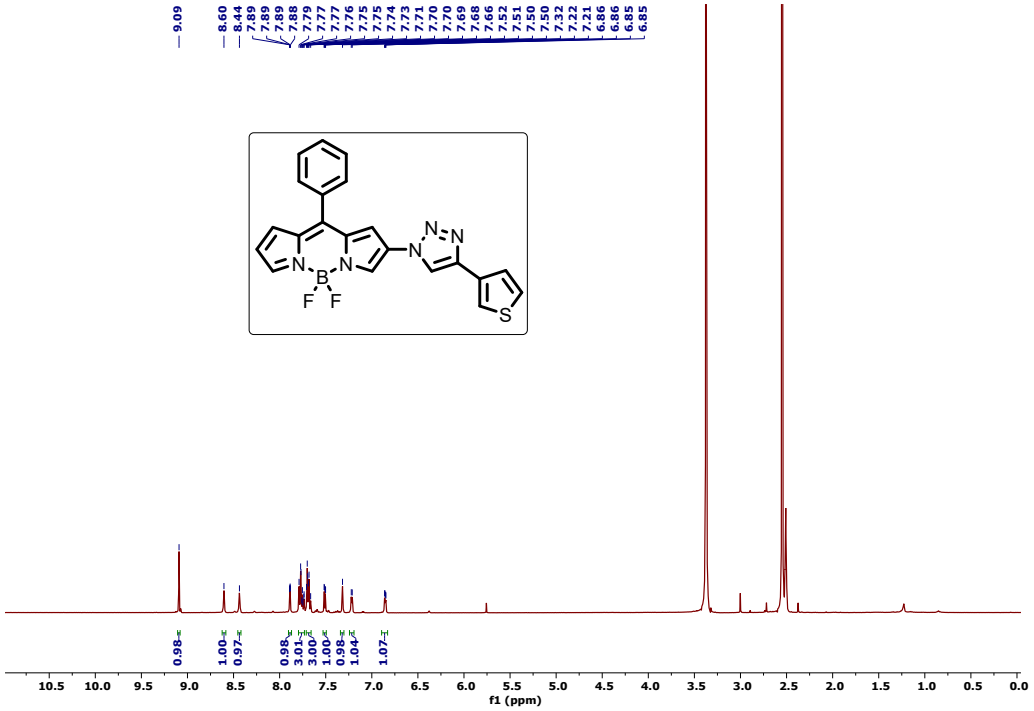
^{13}C NMR spectrum of 5d



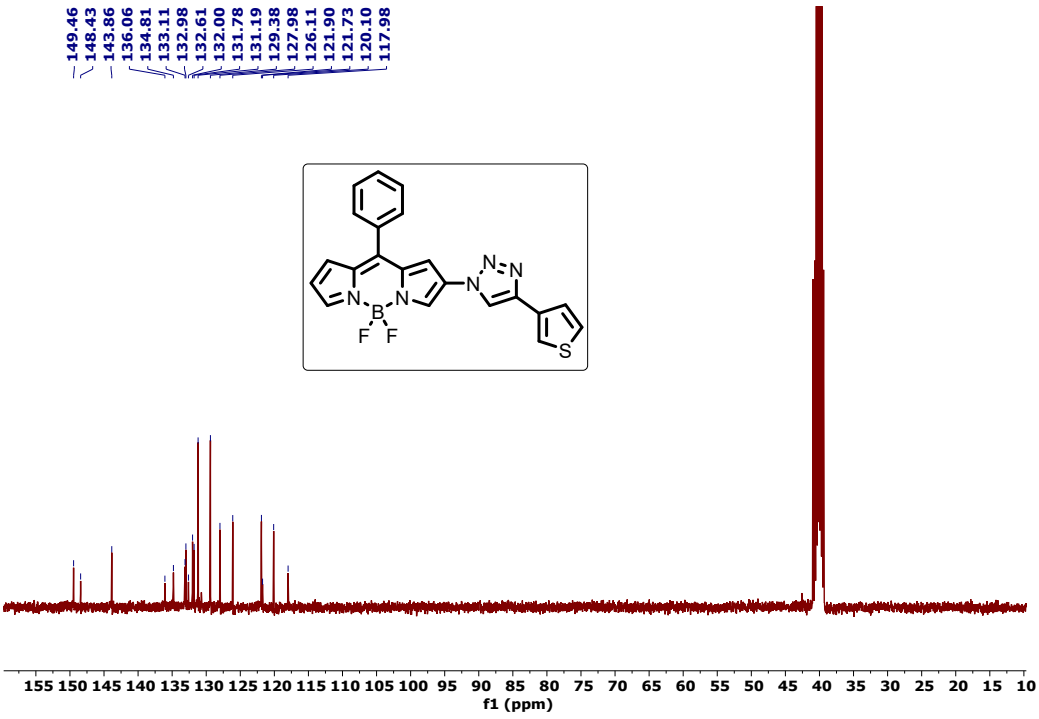
HRMS spectrum of 5d



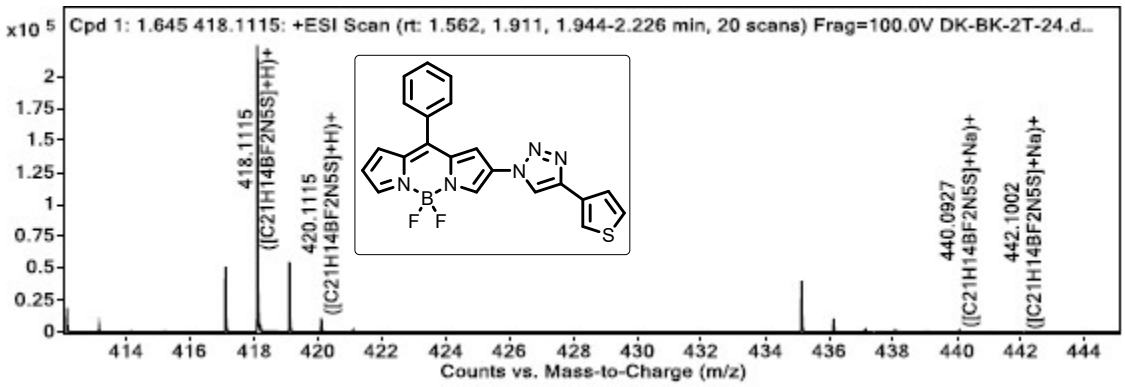
^{1}H NMR spectrum of 5e



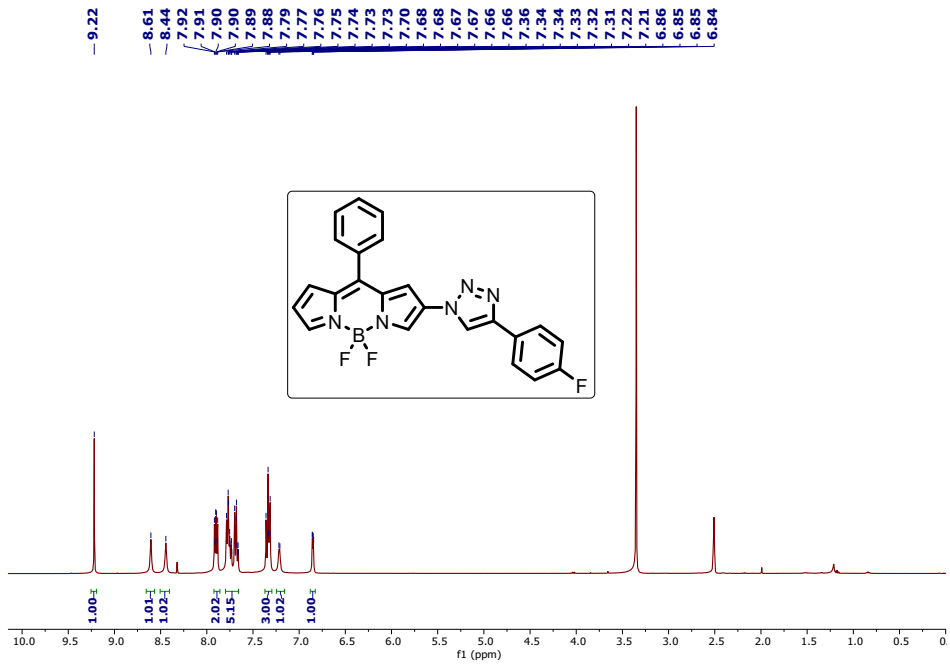
^{13}CNMR spectrum of 5e



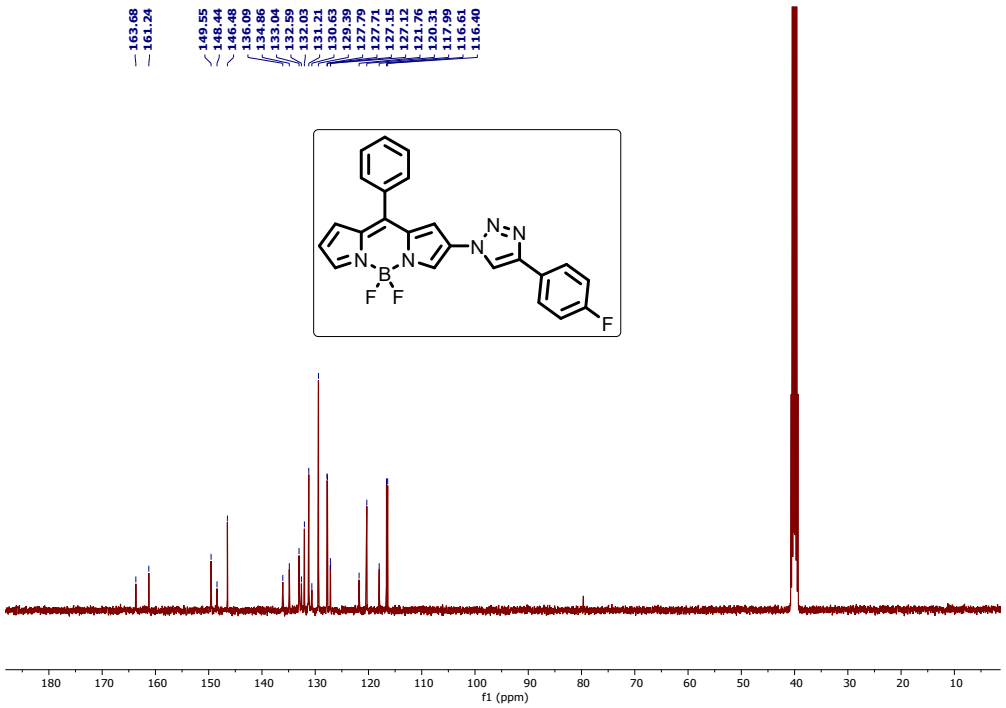
HRMS spectrum of 5e



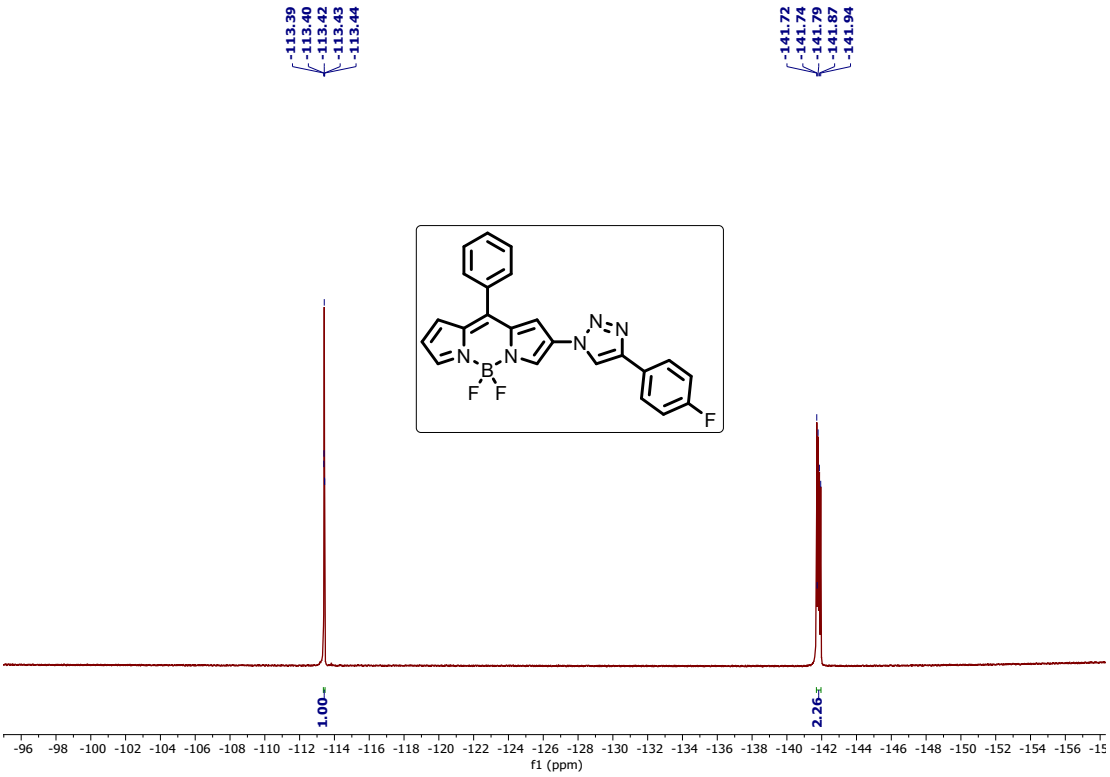
^{1}H NMR spectrum of 5f



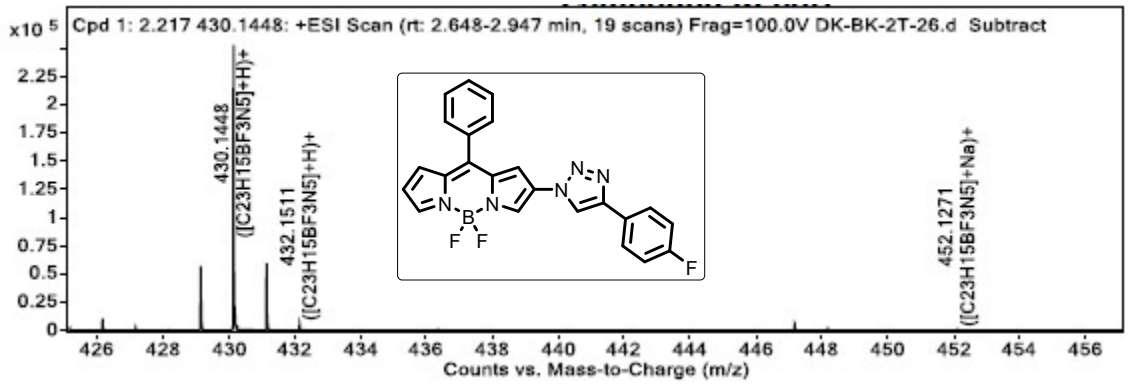
^{13}C NMR spectrum of 5f



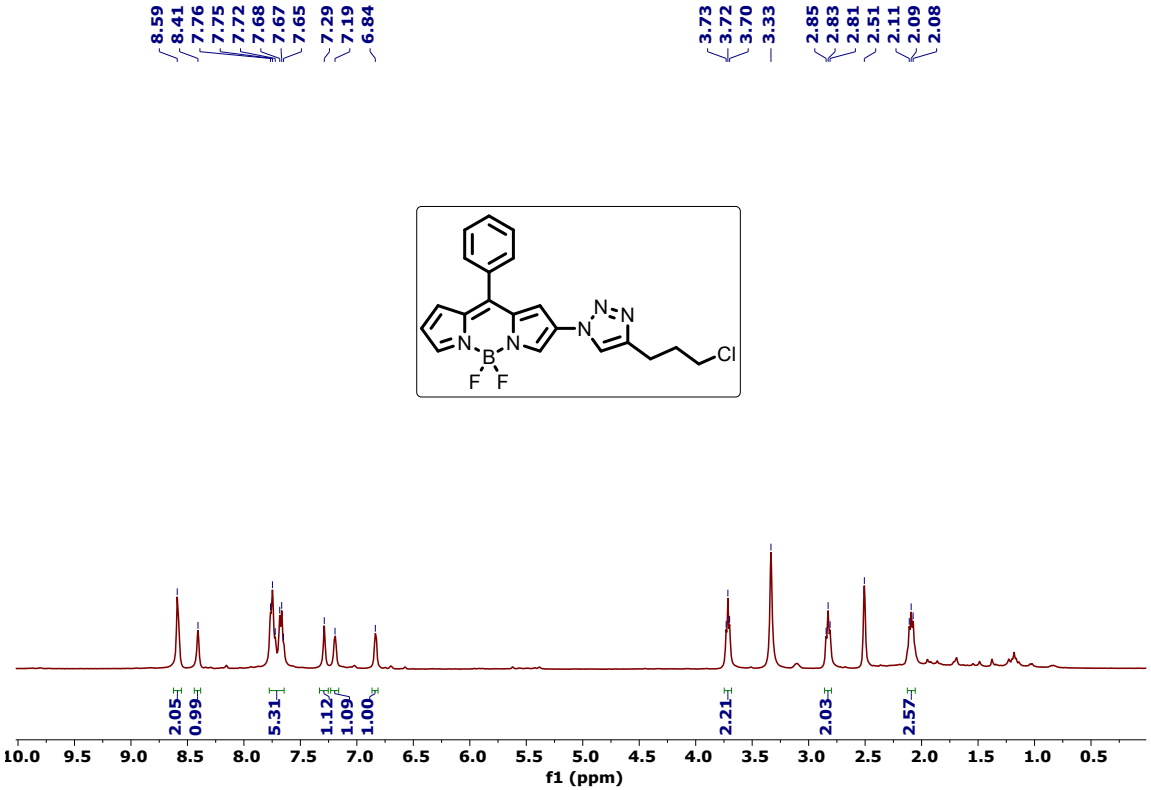
^{19}F NMR spectrum of 5f



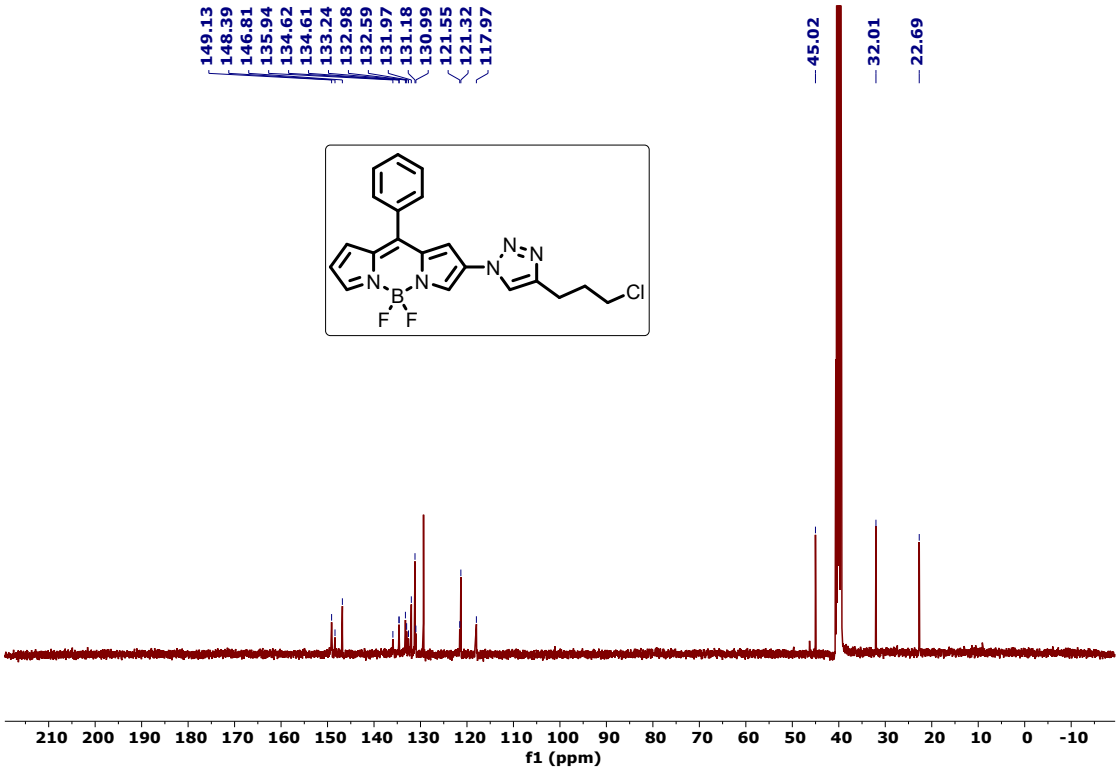
HRMS spectrum of 5f



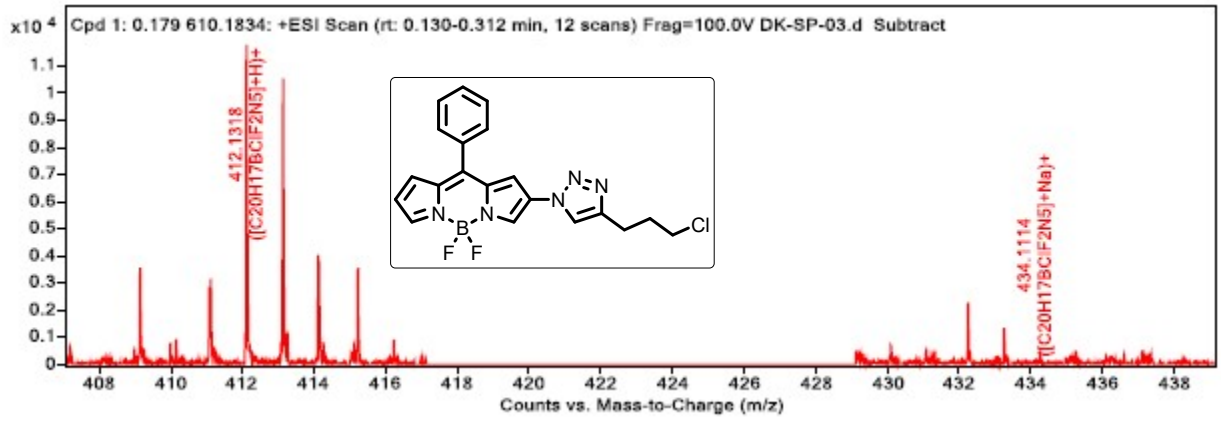
^{1}H NMR spectrum of 5g



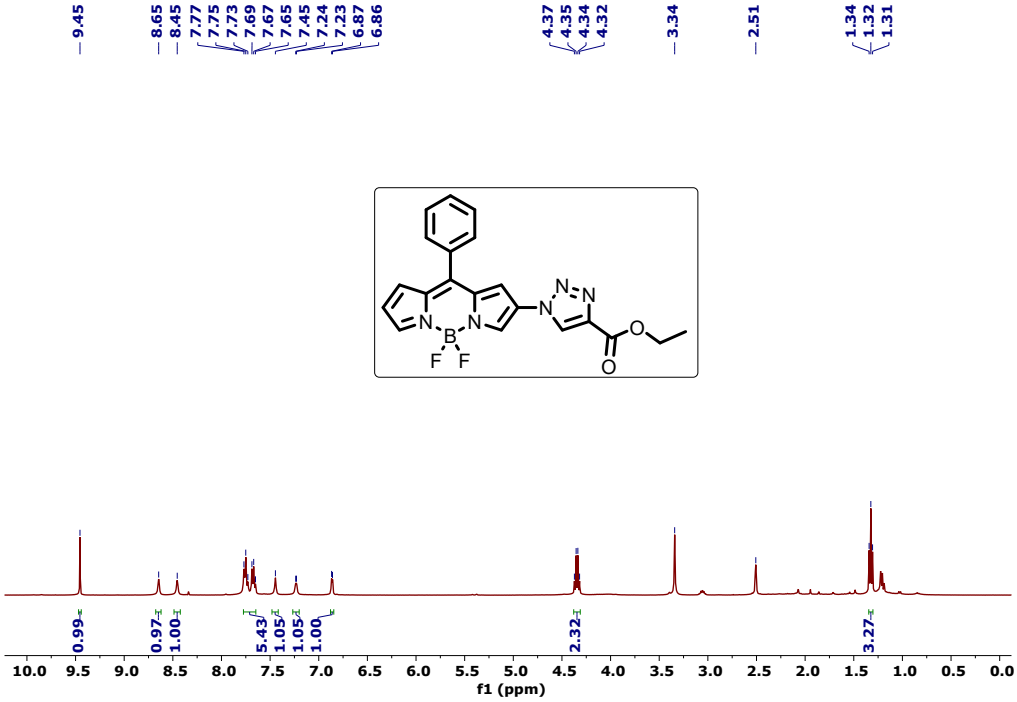
^{13}C NMR spectrum of 5g



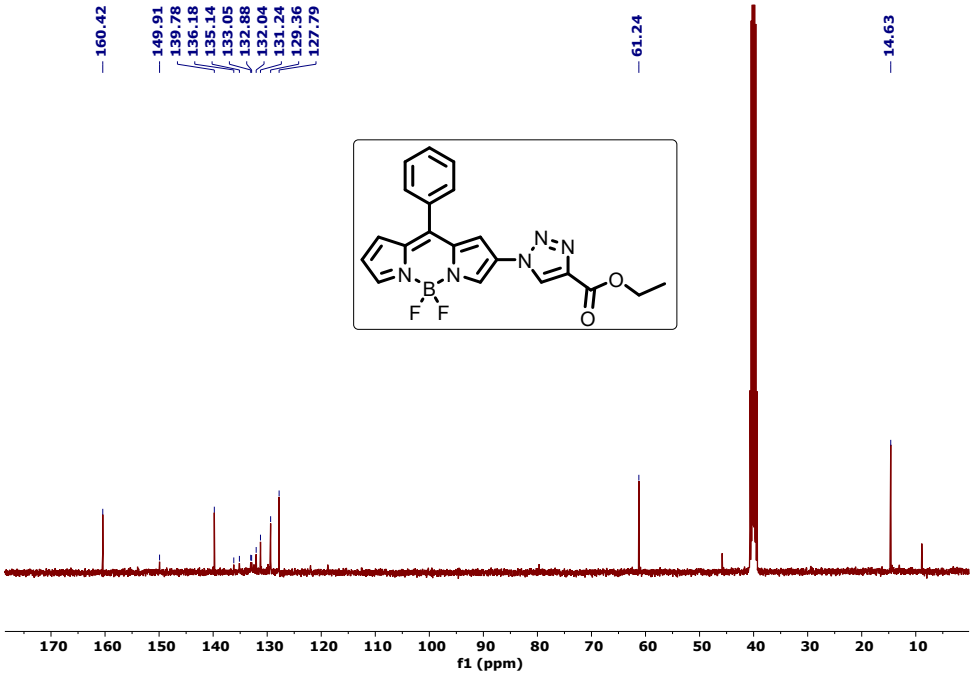
HRMS spectrum of 5g



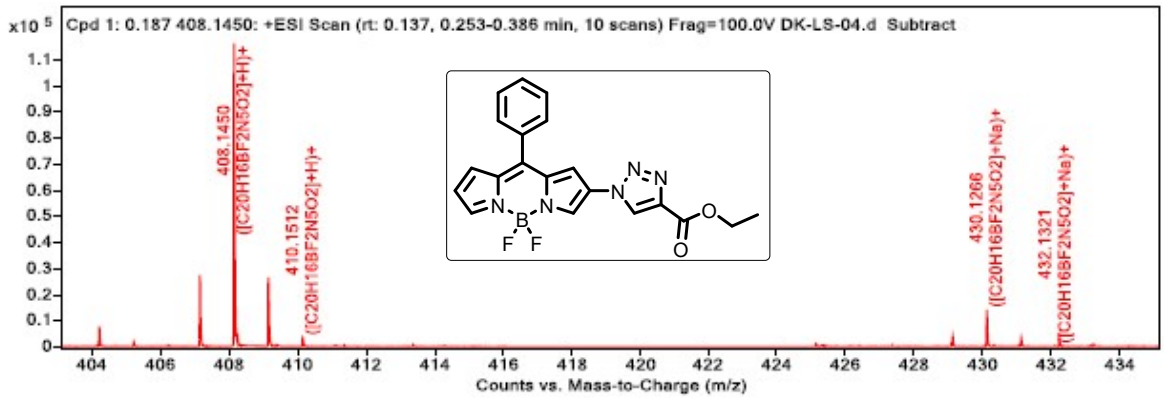
^{1}H NMR spectrum of 5h



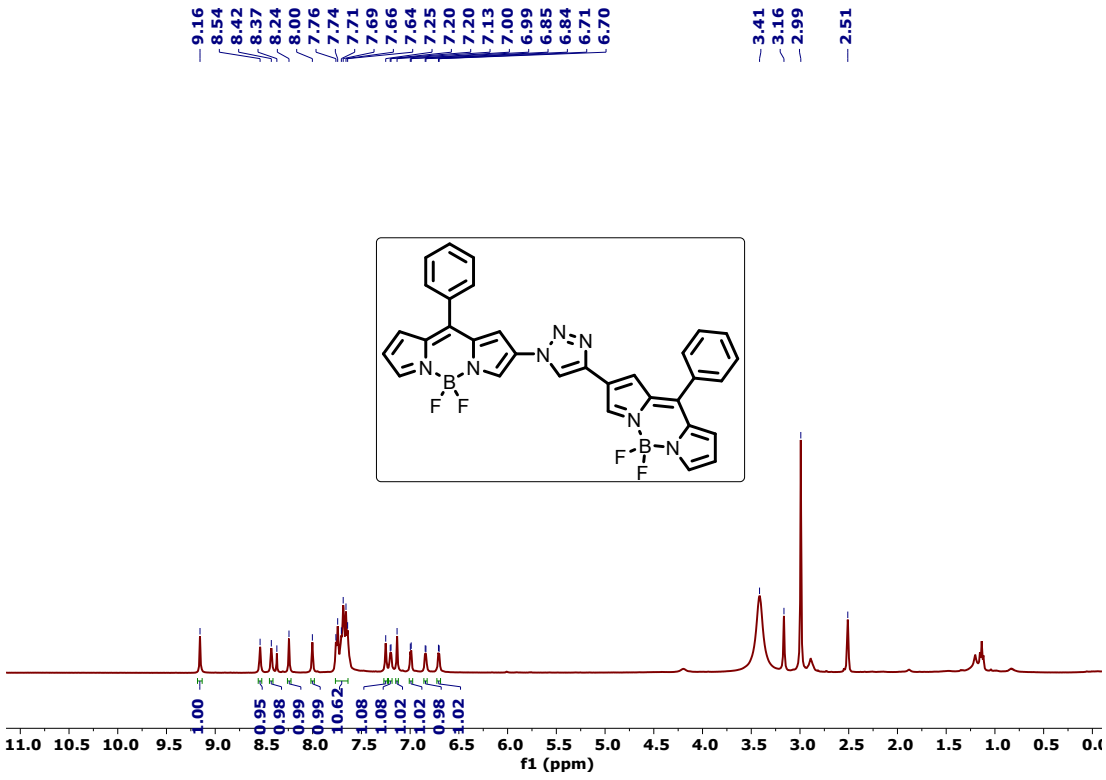
^{13}C NMR spectrum of 5h



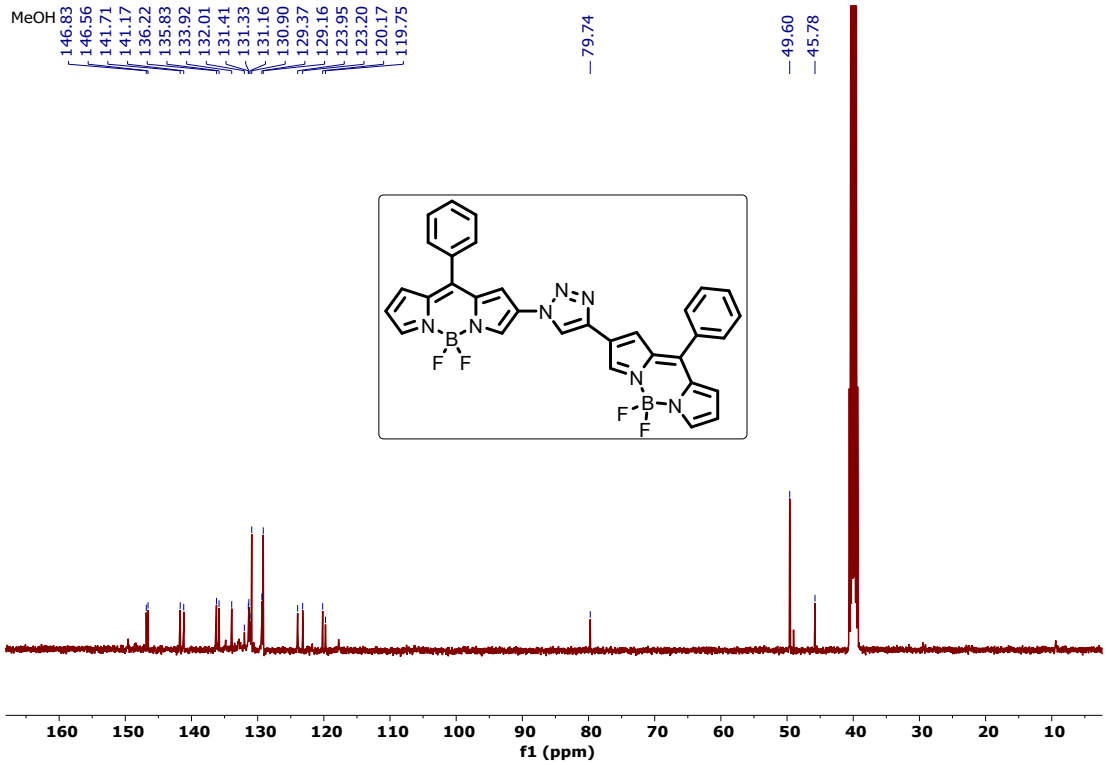
HRMS spectrum of 5h



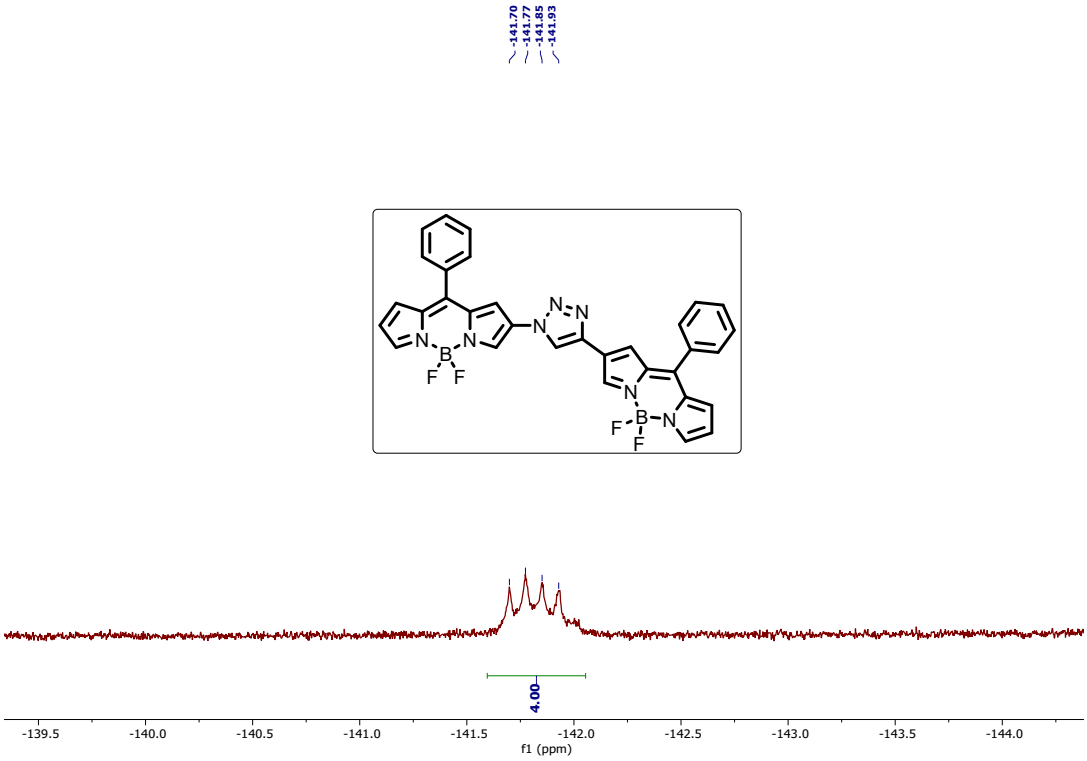
^{1}H NMR spectrum of 5i



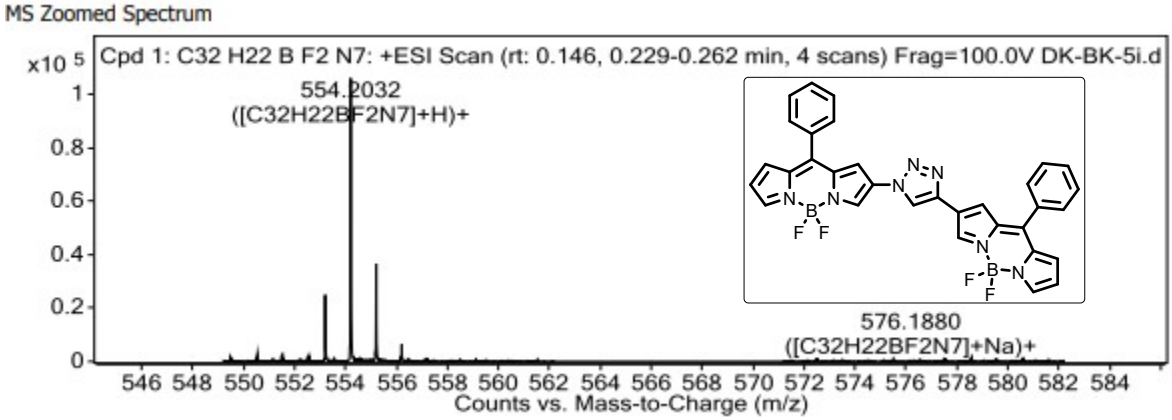
^{13}C NMR spectrum of 5i



^{19}F NMR spectrum of 5i



HRMS spectrum of 5i



III. X-ray crystallographic data

Single Crystal structure description of compound (5a):

The single crystal of compound (**5a**) $C_{24}H_{18}BClF_2N_5$ was crystalizedas a red block through the slow evaporation of $ClCH_2CH_2Cl$ solution at room temperature. The compound **5a** was crystallized in the $P\bar{1}$space group and the asymmetric unit contains one molecule of **5a**and half of molecule of dichloroethane (DCE). Crystal Data for $C_{24}H_{18}BClF_2N_5$ (*M* =460.69 g/mol): triclinic, space group P-1 (no. 2), *a* = 6.20900(10) Å, *b* = 11.20540(10) Å, *c* = 15.9859(2) Å, *α* = 104.6660(10)°, *β* = 100.0400(10)°, *γ* = 97.3940(10)°, *V* = 1041.91(2) Å^3, *Z* = 2, *T* = 93(2) K, μ(CuKα) = 1.979 mm^{-1}, *Dcalc* = 1.468 g/cm^3, 10418 reflections measured (8.294° ≤ 2Θ ≤ 159.546°), 4407 unique (R_{int} = 0.0271, R_{sigma} = 0.0344) which were used in all calculations. The final R_1 was 0.0397 (I > 2σ(I)) and wR_2 was 0.1107 (all data). The crystallographic details of the compound **5a** are deposited to the Cambridge Crystallographic (CCDC 2156138). The ORTEP diagram as crystal structure of (**5a**) is illustrated in Fig. S1.

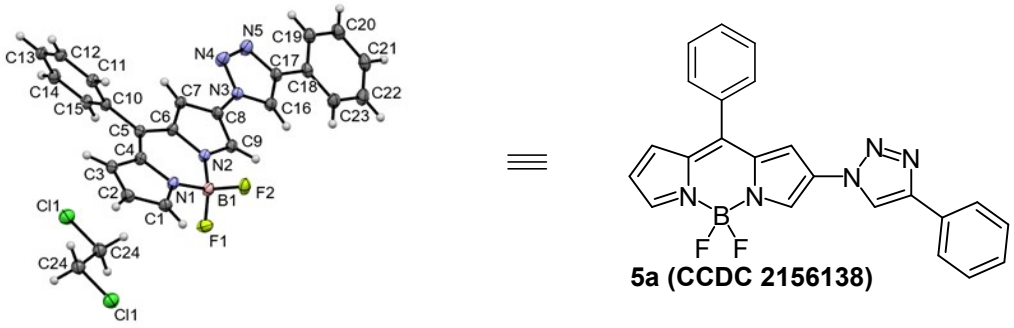


Fig. S1: TheORTEP diagram of compound (**5a**) (CCDC 2156138). (The thermal ellipsoid is drawn at the 50 % probability level.)

Table S1 Crystal data and structure refinement for 5a (exp_582_DP_COMPOUND-1).

Identification code	**5a** (exp_582_DP_COMPOUND-1)
Empirical formula	$C_{24}H_{18}BClF_2N_5$
Formula weight	460.69
Temperature/K	93(2)
Crystal system	triclinic
Space group	P-1
a/Å	6.20900(10)
b/Å	11.20540(10)
c/Å	15.9859(2)
α/°	104.6660(10)
β/°	100.0400(10)
γ/°	97.3940(10)
Volume/Å^3	1041.91(2)
Z	2
ρ_{calc}g/cm^3	1.468
μ/mm^{-1}	1.979
F(000)	474.0
Crystal size/mm^3	0.2 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.294 to 159.546
Index ranges	-7 ≤ h ≤ 4, -14 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	10418
Independent reflections	4407 [R_{int} = 0.0271, R_{sigma} = 0.0344]
Data/restraints/parameters	4407/0/298
Goodness-of-fit on F^2	1.112
Final R indexes [I>=2σ (I)]	R_1 = 0.0397, wR_2 = 0.1095
Final R indexes [all data]	R_1 = 0.0412, wR_2 = 0.1107
Largest diff. peak/hole / e Å^{-3}	0.32/-0.39

Table S2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 5a (exp_582_DP_COMPOUND-1). U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl(1)	1386.0(7)	-938.4(4)	3919.6(3)	32.42(13)
F(1)	2997.1(15)	3444.0(9)	4892.0(6)	27.6(2)
F(2)	1336.5(15)	4817.8(8)	4293.1(6)	27.2(2)
N(2)	2890.1(19)	3291.4(11)	3347.6(8)	17.9(2)
N(1)	-514.1(19)	2645.3(11)	3849.6(8)	18.5(2)
N(3)	6975.6(19)	3858.7(11)	2084.6(8)	18.8(2)
N(4)	7065(2)	3294.6(13)	1236.1(9)	26.6(3)
N(5)	8856(2)	3876.0(13)	1082.4(9)	26.7(3)
C(6)	2193(2)	2261.4(13)	2602.9(9)	17.6(3)
C(7)	3641(2)	2333.6(13)	2024.6(9)	17.9(3)
C(4)	-1049(2)	1575.3(13)	3126.6(9)	17.9(3)
C(16)	8723(2)	4805.5(13)	2468.0(10)	20.6(3)
C(3)	-3017(2)	836.0(13)	3186.8(9)	19.1(3)
C(5)	270(2)	1379.1(13)	2498.6(9)	17.4(3)
C(11)	-2471(2)	-18.9(13)	1168.2(9)	19.4(3)
C(17)	9930(2)	4812.6(13)	1825.9(10)	19.9(3)
C(10)	-349(2)	263.3(13)	1719.2(9)	18.0(3)
C(9)	4723(2)	3988.1(13)	3253.1(9)	19.0(3)
C(18)	12027(2)	5618.2(13)	1861.8(10)	20.6(3)
C(1)	-2096(2)	2586.7(14)	4324.2(10)	20.8(3)
C(12)	-3040(2)	-1063.8(13)	436.2(9)	21.0(3)
C(2)	-3676(2)	1483.0(14)	3931.0(10)	20.8(3)
C(15)	1188(2)	-517.5(13)	1517.8(10)	20.7(3)
C(8)	5208(2)	3411.6(13)	2435.9(9)	18.5(3)
C(19)	12855(3)	5546.9(14)	1093.7(10)	23.5(3)
C(14)	607(2)	-1566.0(14)	785.6(10)	22.8(3)
C(20)	14864(3)	6290.7(15)	1132.9(11)	26.3(3)
C(23)	13239(3)	6443.9(14)	2660.6(11)	25.5(3)
C(13)	-1502(3)	-1838.7(13)	244.0(10)	22.2(3)
C(24)	1028(3)	236.4(15)	4857.9(11)	27.3(3)
C(22)	15252(3)	7188.5(15)	2697.1(12)	28.8(3)
C(21)	16067(3)	7110.4(15)	1931.4(12)	27.8(3)
B(1)	1716(3)	3599.7(15)	4136.0(11)	20.3(3)

Table S3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 5a (exp_582_DP_COMPOUND-1). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl(1)	38.8(2)	30.1(2)	30.4(2)	6.88(16)	13.24(16)	8.98(16)
F(1)	24.1(4)	35.7(5)	19.4(4)	5.6(4)	3.7(3)	-1.6(4)
F(2)	33.3(5)	16.6(4)	31.1(5)	0.3(3)	16.7(4)	2.1(3)
N(2)	17.4(5)	15.8(5)	18.6(6)	1.5(4)	5.2(4)	1.0(4)
N(1)	18.9(6)	16.8(6)	19.0(6)	2.1(5)	6.5(4)	2.8(4)
N(3)	19.6(6)	16.7(6)	19.8(6)	3.0(4)	7.9(4)	1.4(4)
N(4)	26.5(7)	26.0(7)	23.7(6)	-0.6(5)	12.8(5)	-3.4(5)
N(5)	25.3(6)	24.5(6)	26.8(7)	0.4(5)	12.2(5)	-3.1(5)
C(6)	17.6(6)	15.7(6)	18.2(6)	1.8(5)	4.6(5)	3.1(5)
C(7)	18.6(6)	16.6(6)	18.4(6)	3.0(5)	6.4(5)	3.6(5)
C(4)	16.4(6)	16.6(6)	19.2(7)	2.7(5)	3.6(5)	2.6(5)
C(16)	20.8(7)	18.3(7)	21.6(7)	3.2(5)	6.8(5)	1.3(5)
C(3)	17.3(6)	18.2(6)	20.9(7)	4.8(5)	3.7(5)	2.1(5)
C(5)	16.7(6)	16.7(6)	18.6(7)	4.4(5)	3.6(5)	3.7(5)
C(11)	17.5(6)	19.0(6)	21.1(7)	4.1(5)	5.6(5)	3.0(5)
C(17)	20.8(7)	15.8(6)	23.5(7)	4.6(5)	7.7(5)	3.4(5)
C(10)	17.6(6)	16.2(6)	19.3(7)	3.3(5)	5.9(5)	0.8(5)
C(9)	18.4(6)	16.9(6)	20.6(7)	3.3(5)	5.9(5)	1.3(5)
C(18)	20.4(7)	15.6(6)	28.0(8)	6.4(6)	9.7(6)	4.1(5)
C(1)	22.0(7)	20.7(7)	21.4(7)	5.1(5)	9.3(5)	5.0(5)
C(12)	20.5(7)	20.6(7)	19.3(7)	3.6(5)	3.3(5)	0.0(5)
C(2)	19.2(7)	22.1(7)	23.5(7)	7.3(6)	8.8(5)	4.4(5)
C(15)	18.0(6)	18.6(7)	24.4(7)	3.8(5)	5.2(5)	2.8(5)
C(8)	18.5(6)	16.8(6)	21.4(7)	5.2(5)	7.8(5)	2.8(5)
C(19)	24.1(7)	20.3(7)	27.4(8)	6.2(6)	9.7(6)	3.8(5)
C(14)	24.1(7)	18.2(7)	27.0(7)	3.6(6)	10.3(6)	5.5(5)
C(20)	26.5(8)	23.6(7)	32.8(8)	9.7(6)	14.8(6)	3.9(6)
C(23)	27.7(8)	20.6(7)	27.9(8)	4.8(6)	10.9(6)	0.8(6)
C(13)	27.9(7)	16.8(6)	20.1(7)	2.1(5)	7.1(6)	0.9(5)
C(24)	30.4(8)	22.7(7)	29.4(8)	8.0(6)	7.6(6)	4.6(6)
C(22)	27.2(8)	21.1(7)	34.0(9)	3.8(6)	7.1(6)	-2.3(6)
C(21)	23.0(7)	22.0(7)	39.8(9)	9.9(7)	11.6(6)	0.2(6)
B(1)	20.5(7)	18.7(7)	19.5(7)	0.9(6)	6.9(6)	0.8(6)

Table S4 Bond Lengths for 5a (exp_582_DP_COMPOUND-1).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl(1)	C(24)	1.7954(17)	C(16)	C(17)	1.373(2)
F(1)	B(1)	1.3895(19)	C(3)	C(2)	1.385(2)
F(2)	B(1)	1.3826(18)	C(5)	C(10)	1.4778(19)
N(2)	C(6)	1.3903(17)	C(11)	C(10)	1.3996(19)
N(2)	C(9)	1.3484(18)	C(11)	C(12)	1.386(2)
N(2)	B(1)	1.5506(19)	C(17)	C(18)	1.4695(19)
N(1)	C(4)	1.3948(18)	C(10)	C(15)	1.3995(19)
N(1)	C(1)	1.3465(18)	C(9)	C(8)	1.4052(19)
N(1)	B(1)	1.5557(19)	C(18)	C(19)	1.400(2)
N(3)	N(4)	1.3577(17)	C(18)	C(23)	1.393(2)
N(3)	C(16)	1.3495(18)	C(1)	C(2)	1.402(2)
N(3)	C(8)	1.4096(18)	C(12)	C(13)	1.393(2)
N(4)	N(5)	1.3084(18)	C(15)	C(14)	1.388(2)
N(5)	C(17)	1.3677(19)	C(19)	C(20)	1.390(2)
C(6)	C(7)	1.4064(19)	C(14)	C(13)	1.387(2)
C(6)	C(5)	1.4051(19)	C(20)	C(21)	1.389(2)
C(7)	C(8)	1.3821(19)	C(23)	C(22)	1.394(2)
C(4)	C(3)	1.4175(19)	C(24)	C(24)[1]	1.506(3)
C(4)	C(5)	1.3959(19)	C(22)	C(21)	1.391(2)

Table S5 Bond Angles for 5a (exp_582_DP_COMPOUND-1).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(6)	N(2)	B(1)	125.65(11)	C(15)	C(10)	C(5)	120.40(12)
C(9)	N(2)	C(6)	108.19(11)	C(15)	C(10)	C(11)	119.16(13)
C(9)	N(2)	B(1)	126.14(12)	N(2)	C(9)	C(8)	108.48(12)
C(4)	N(1)	B(1)	125.33(11)	C(19)	C(18)	C(17)	120.24(14)
C(1)	N(1)	C(4)	107.63(12)	C(23)	C(18)	C(17)	120.64(13)
C(1)	N(1)	B(1)	126.23(12)	C(23)	C(18)	C(19)	119.11(13)
N(4)	N(3)	C(8)	119.37(12)	N(1)	C(1)	C(2)	110.21(13)
C(16)	N(3)	N(4)	110.71(12)	C(11)	C(12)	C(13)	120.18(13)
C(16)	N(3)	C(8)	129.92(12)	C(3)	C(2)	C(1)	107.09(13)
N(5)	N(4)	N(3)	106.98(12)	C(14)	C(15)	C(10)	120.42(13)
N(4)	N(5)	C(17)	109.40(12)	C(7)	C(8)	N(3)	125.39(13)
N(2)	C(6)	C(7)	108.70(12)	C(7)	C(8)	C(9)	108.55(12)
N(2)	C(6)	C(5)	121.37(12)	C(9)	C(8)	N(3)	126.05(13)
C(5)	C(6)	C(7)	129.87(13)	C(20)	C(19)	C(18)	120.13(15)
C(8)	C(7)	C(6)	106.06(12)	C(13)	C(14)	C(15)	119.99(13)
N(1)	C(4)	C(3)	107.98(12)	C(21)	C(20)	C(19)	120.50(15)
N(1)	C(4)	C(5)	121.12(12)	C(18)	C(23)	C(22)	120.59(15)
C(5)	C(4)	C(3)	130.90(13)	C(14)	C(13)	C(12)	120.04(13)
N(3)	C(16)	C(17)	104.93(13)	C(24)[1]	C(24)	Cl(1)	108.77(15)
C(2)	C(3)	C(4)	107.06(12)	C(21)	C(22)	C(23)	119.98(15)
C(6)	C(5)	C(10)	119.62(12)	C(20)	C(21)	C(22)	119.69(14)
C(4)	C(5)	C(6)	119.60(13)	F(1)	B(1)	N(2)	110.65(12)
C(4)	C(5)	C(10)	120.78(12)	F(1)	B(1)	N(1)	109.67(12)
C(12)	C(11)	C(10)	120.20(13)	F(2)	B(1)	F(1)	110.06(12)
N(5)	C(17)	C(16)	107.98(13)	F(2)	B(1)	N(2)	109.74(12)
N(5)	C(17)	C(18)	122.07(13)	F(2)	B(1)	N(1)	110.97(12)
C(16)	C(17)	C(18)	129.94(14)	N(2)	B(1)	N(1)	105.67(11)
C(11)	C(10)	C(5)	120.43(12)				

Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 5a (exp_582_DP_COMPOUND-1).

Atom	*x*	*y*	*z*	U(eq)
H(7)	3559.97	1770.24	1476.68	22
H(16)	9040.79	5337.15	3041.69	25
H(3)	-3731.28	62.34	2799.56	23
H(11)	-3502.15	496.37	1293.69	23
H(9)	5529.92	4725.6	3660.14	23
H(1)	-2134.84	3191.13	4838.76	25
H(12)	-4452.25	-1248.28	72.21	25
H(2)	-4929.76	1232.69	4132.04	25
H(15)	2606.57	-333.04	1876.7	25
H(19)	12059.74	5000.86	556.02	28
H(14)	1631.17	-2085.26	658.2	27
H(20)	15405.67	6239.02	620.42	32
H(23)	12700.49	6498.82	3174.08	31
H(13)	-1888.47	-2539.28	-247.72	27
H(24A)	2316.49	409.12	5340.13	33
H(24B)	878.15	1007.93	4701.41	33
H(22)	16049.91	7737.32	3233.2	35
H(21)	17410.84	7604.73	1954.2	33

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
2.a Secondary CH2 refined with riding coordinates:
 C24(H24A,H24B)
2.b Aromatic/amide H refined with riding coordinates:
 C7(H7), C16(H16), C3(H3), C11(H11), C9(H9), C1(H1), C12(H12), C2(H2),
 C15(H15), C19(H19), C14(H14), C20(H20), C23(H23), C13(H13), C22(H22), C21(H21)
```

V. Photophysical Studies and related data

For making the aqueous solutions, purified water, collected from an Elix 10 water purification system (Millipore India Pvt. Ltd) was used. The absorption and steady-state fluorescence emission/excitation spectra (slit width 5 nm, λ_{em} = 520 nm)were collected in PerkinElmer Lambda25,Fluoromax-4 and Quanta master (QM-40) steady-state fluorescence apparatus supplied by Photon Technology International (PTI), respectively. The solvent-dependent photophysical studies were performed at room temperature (298 K) with 10 mm quartz cuvettes. Fluorescence quantum yields (ϕ_f) of the compound were calculated by comparing the total intensity under the whole fluorescence spectral range with that of a standard rhodamine 6G (ϕ_f= 0.93 in UV-grade methanol) (Eq. 1) following the procedure described elsewhere.[1, 2]

$$\phi_f^i = \phi_f^s \times \frac{F_i}{F_s} \times \frac{1 - 10^{-A_s}}{1 - 10^{-A_i}} \times \left(\frac{n_i}{n_s}\right)^2 \quad (1)$$

Where A_i and A_s are the optical densities of the sample and standard, respectively; and *n* is the refractive index of the solvent at 298 K. Fluorescence spectrometer (QM-40, PTI, USA) equipped with a TCSPC fluorescence lifetime detection unit (PM-3) was used for the measurements of time-resolved fluorescence decay. The decay traces obtained experimentally were expressed as a sum of exponentials (Eq. 2) and fitted with the iterative deconvolution method based on the Levenberg–Marquardt algorithm with reference to the instrument response function (IRF), collected at the excitation wavelength using a scattering solution.

$$I(t) = \sum_i \alpha_i \times \exp\left(\frac{t}{\tau_i}\right) \quad (2)$$

Where α_i denotes the amplitude of the i^{th} component associated with fluorescence lifetime τ_i such that $\Sigma\alpha_i$= 1.

Moreover, for the multi-exponential fluorescence decay function, the average fluorescence lifetime was expressed by the fractional contribution of individual decay components (f_i) to the steady-state intensity (Eq. 3).[2, 3]

$$\tau_{av} = \sum_i f_i = \frac{\sum_i \alpha_i \tau_i^2}{\sum_i \alpha_i \tau_i} \quad (3)$$

The radiative (k_r) and total non-radiative (Σk_{nr}) decay rate constants in each case were calculated with known quantum yield (φ_f) and average lifetime (τ_{av}) using the following relations (Eq. 4).

$$k_r = \frac{\phi_f}{\tau_{av}}; \quad \sum k_{nr} = \frac{(1-\phi_f)}{\tau_{av}} \quad (4)$$

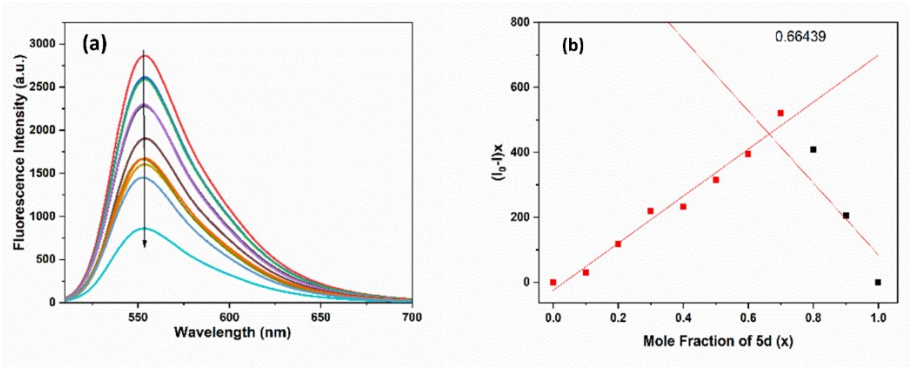


Fig. **S2**(a) Fluorescence intensity *vs*. wavelength different moleof **5d**-Ni^{2+}; (b) Job's plot of Ni^{2+} and varying the mole fraction of the **5d** in MeOH. Where the total concentration of **5d** and Ni^{2+} (10 µM), x is the mole fraction of the **5d** added ($x_{\mathbf{5d}}$ = [**5d**]/[**5d**] + [Ni^{2+}]), *I* is the fluorescence intensity of **5d** in the presence of Ni^{2+} and I_0 is the fluorescence intensity of **5d** in the absence of Ni^{2+} (λ_{ex} : 490 nm, λ_{em} : 554 nm, slit width : 2.5 nm).

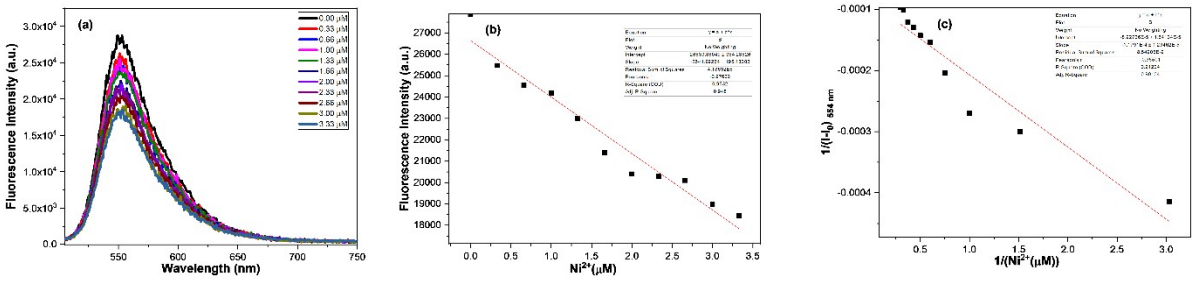


Fig.S3 (a) Fluorescence intensity *vs*. wavelength of different conc. of Ni^{2+} in **5d** (10 µM);(b) Calibration plot of of **5d**-Ni^{2+}; (c) Benesi-Hildebrand plot of the Ni^{2+} complex with **5d** in MeOH; (λ_{ex} : 490 nm, λ_{em} : 554 nm, slit width : 2.5 nm).

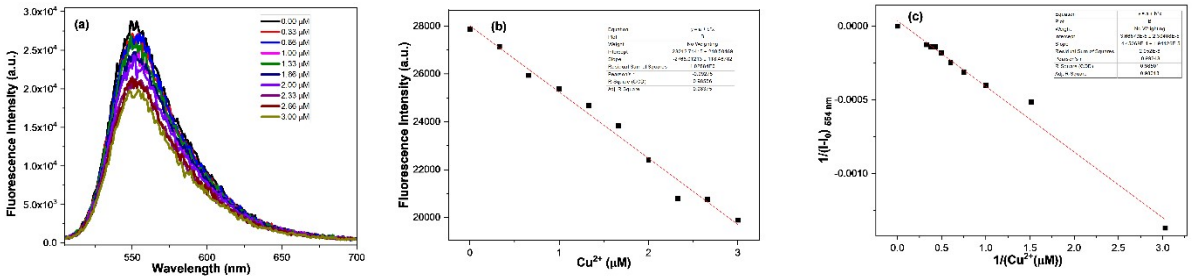


Fig.S4 (a) Fluorescence intensity *vs*. wavelength of different conc. of Cu^{2+}in **5d** (10 μM);(b) Calibration plot of **5d**-Cu^{2+}; (c) Benesi-Hildebrand plot of the Cu^{2+} complex with **5d** in MeOH; (λ_{ex} : 490 nm, λ_{em} : 554 nm, slit width : 2.5 nm).

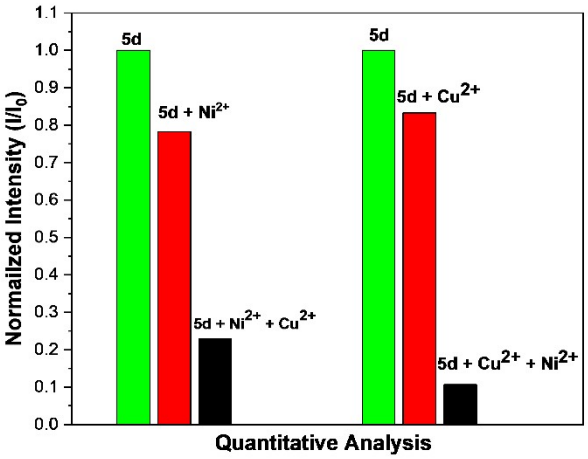


Fig. S5 Normalized fluorescence intensity of **5d** in the presence of Ni^{2+} and Cu^{2+} ions and vice-versa for competitive analysis

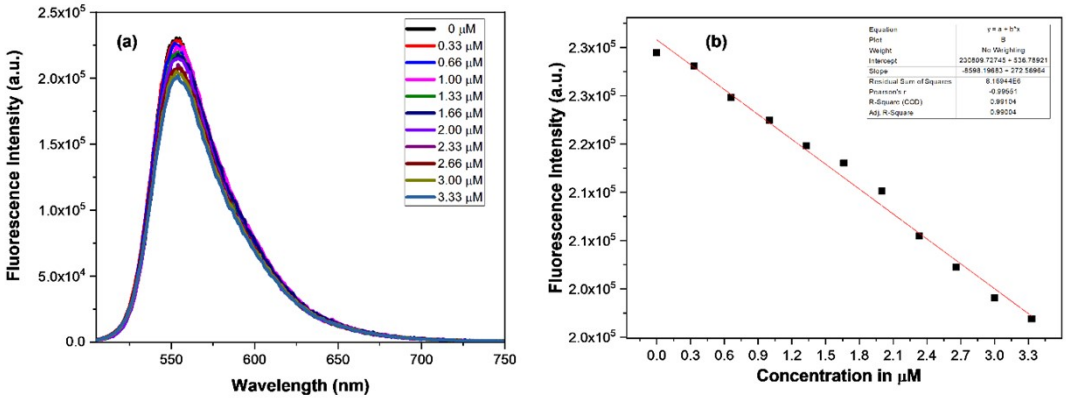


Fig. S6 (a) Fluorescence intensity *vs*. wavelength of different conc. of Ni^{2+} ion in Milli-Q water (b) Linear calibration curve

Table S7: Determination of Ni^{2+} in a water sample

Sample	Fluorescence Intensity (a.u.)	Amount of Ni^{2+} added (μM)	Amount of Ni^{2+} found (μM) ± 0.05	Relative Recovery,%
tap water	227050	-	0.39	-
tap water + Ni^{2+}	225450	0.33	0.51	154
tap water + Ni^{2+}	222490	0.66	0.82	124
tap water + Ni^{2+}	221370	1.00	0.90	90
tap water + Ni^{2+}	214620	1.33	2.17	163
tap water + Ni^{2+}	214320	1.66	2.13	128

Table S8: Fluorescence decay data of **5i** with the addition of increasing concentration of BSA

[BSA]/ μM	α_1	τ_1/ ns	α_2	τ_2/ ns	τ_{av}/ ns
0	77.93	0.68	22.07	3.77	2.57
1	76.24	0.77	23.76	3.96	2.73
5	72.22	0.73	27.78	4.09	3.02
10	81.3	0.99	18.7	4.35	2.68
20	73.72	0.79	26.28	4.36	3.15
30	80.67	0.97	19.33	4.31	2.69
35	83.88	1.00	16.12	4.37	2.54
40	83.16	1.01	16.84	4.44	2.62
45	82.09	0.99	17.91	4.36	2.64
50	83.53	1.01	16.47	4.44	2.60

Table S9. Spectroscopic parameters of **5i** with addition of increasing concentration of BSA

[BSA]/ μM	φ_f $/10^{-2}$	τ_{av}/ ns	κ_r/ ns^{-1}	$\Sigma\kappa_{nr}$/ ns^{-1}
0	3.70	2.57	0.01	0.37
1	5.08	2.73	0.02	0.35
5	8.66	3.02	0.03	0.30
10	10.31	2.68	0.04	0.33
20	12.20	3.15	0.04	0.28
30	13.17	2.69	0.05	0.32
35	13.95	2.54	0.05	0.34
40	14.27	2.62	0.05	0.33
45	14.31	2.64	0.05	0.32
50	13.60	2.60	0.05	0.33

V. References

1. P. Baruah, G. Basumatary, S. O. Yesylevskyy, K. Aguan, G. Bez and S. Mitra, *J. Biomol. Struct. Dyn.*, 2019, **37**, 1750-1765.
2. Q. Lai, Q. Liu, Y. He, K. Zhao, C. Wei, L. Wojtas, X. Shi and Z. Song, *Org. Biomol. Chem.*, 2018, **16**, 7801-7805.
3. M. A. Rohman, P. Baruah, A. Bhatta and S. Mitra, *J. Mol. Liq.*, 2019, **290**, 111210.