Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Silver-mediated direct C−H amination of BODIPYs for screening endoplasmic reticulum-targeting reagents

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I. General remarks

NMR spectra were obtained on a Bruker AV II-400 MHz or a Varian Inova 400 MHz spectrometer. The ^{1}H NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or DMSO-d_6 as the internal reference ($CDCl_3$: δ = 7.26 ppm; DMSO-d_6: δ = 2.50 ppm). The ^{13}C NMR (100 MHz) chemical shifts were given using $CDCl_3$ or DMSO-d_6 as the internal standard ($CDCl_3$: δ = 77.16 ppm; DMSO-d_6: δ = 39.52 ppm). High resolution mass spectra (HR-MS) were obtained with a Waters-Q-TOF-Premier (ESI^+). X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single crystal diffractometer. Melting points were determined with XRC-1 and are uncorrected. Absorption spectra were obtained on a HITACHI U-2910 spectrometer. Fluorescence spectra and absolute quantum yields were collected on a Horiba Jobin Yvon-Edison Fluoromax-4 fluorescence spectrometer with a calibrated integrating sphere system. To reduce the fluctuation in the excitation intensity, the lamp was kept on for 1 h prior to the experiment. The confocal living cell imaging was performed on a Leica TCS SP8 confocal fluorescent microscope.

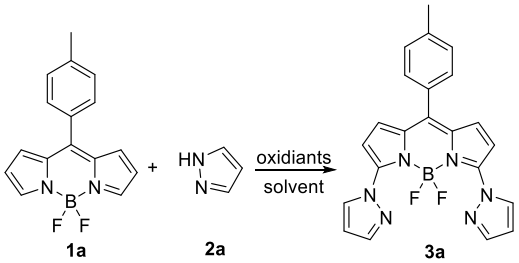
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. 8-(*p*-Tolyl)-4,4-difluoro-4-bora-*3a*,*4a*-diaza-*s*-indacene (8-(*p*-tolyl)-BODIPY)[1] (**1a**), 8-phenyl-4,4-difluoro-4-bora-*3a*,*4a*-diaza-*s*-indacene (8-phenyl-BODIPY)[1] (**1b**), 8-(*p*-cyano-phenyl)-4,4-difluoro-4-bora-*3a*,*4a*-diaza-*s*-indacene (8-(p-cyano-phenyl)-BODIPY)[2] (**1c**), 8-(3,5-*bis*(trifluoromethyl)phenyl)-4,4-difluoro-4-bora-*3a*,*4a*-diaza-*s*-indacene (8-(3,5-*bis*(trifluoromethyl)phenyl)-BODIPY)[3] (**1d**), 8-(thiophen-2-yl)-4,4-difluoro-4-bora-*3a*,*4a*-diaza-*s*-indacene (8-(thiophen-2-yl)-BODIPY)[4] (**1e**), 2-bromo-8-(*p*-Tolyl)-4,4-difluoro-4-bora-*3a*,*4a*-diaza-*s*-indacene (2-bromo-8-(*p*-tolyl)-BODIPY)[1] (**1g**), 4,4-difluoro-4-bora-*3a*,*4a*-diaza-*s*-indacene (BODIPY)[5] (**1h**) and 8-(4-nitrophenyl)-4,4-difluoro-4-bora-*3a*,*4a*-diaza-*s*-indacene (8-(4-nitrophenyl)-BODIPY)[1] (**1i**) were prepared according to the literatures.

II. Synthesis and compounds characterization

(1) Optimization of direct C–H amination

A dried Schlenk tube with a magnetic stir bar was charged with 8-(*p*-tolyl)-BODIPY (**1a,** 0.05 mmol), pyrazole (**2a**, 0.20 mmol, 4.0 equiv) and additives. The system was evacuated thrice and back filled with N_2. Next, the solvent was added *via* a syringe and the rubber septum was replaced with a polytetrafluoroethylene stopper under N_2. Then the reaction mixture was stirred at the indicated temperature for 2-24 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.

Table S1. Optimization of the direct C–H amination of BODIPY with pyrazole[a]



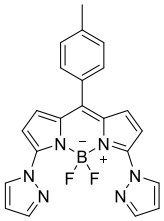
Entry	**1a**	**2a**	oxidants	Solvent	Temp. (℃)	Time (h)	Yield[b] (%)
1	0.05 mol	0.2 mol	Ag_2O	DMSO	120	12	67
2	0.05 mol	0.2 mol	MnO_2	DMSO	120	12	48
3	0.05 mol	0.2 mol	BQ	DMSO	120	12	trace
4	0.05 mol	0.2 mol	AgOAc	DMSO	120	12	80
5	0.05 mol	0.2 mol	$Cu(OAc)_2$	DMSO	120	12	trace
6	0.05 mol	0.2 mol	$K_2S_2O_8$	DMSO	120	12	trace
7[c]	0.05 mol	0.2 mol	O_2	DMSO	120	12	none
8	0.05 mol	0.2 mol	$PhI(OAc)_2$	DMSO	120	12	none
9[d]	0.05 mol	0.2 mol	$AgOAc/O_2$	DMSO	120	12	13
10[e]	0.05 mol	0.2 mol	$AgOAc/MnO_2$	DMSO	120	12	48

11[f]	0.05 mol	0.2 mol	AgOAc/K_2CO_3	DMSO	120	12	N.D.
12[f]	0.05 mol	0.2 mol	AgOAc/PivOH	DMSO	120	12	60
13[f]	0.05 mol	0.2 mol	Ag_2CO_3/ Phenanthroline	DMSO	120	12	58
14[f]	0.05 mol	0.2 mol	AgOAc/PPh_3	DMSO	120	12	60
15	0.05 mol	0.2 mol	AgOAc	DCE	120	12	N.D.
16	0.05 mol	0.2 mol	AgOAc	DMF	120	12	24
17	0.05 mol	0.2 mol	AgOAc	MeCN	120	12	20
18	0.05 mol	0.2 mol	AgOAc	Toluene	120	12	N.D.
19	0.05 mol	0.2 mol	AgOAc	THF	120	12	N.D.
20	0.05 mol	0.2 mol	AgOAc	Dioxane	120	12	N.D.
21	0.05 mol	0.2 mol	AgOAc	2-Methyl-2-butanol	120	12	N.D.
22	0.05 mol	0.2 mol	AgOAc	DMSO/ MeCN(1:1)	120	12	62
23	0.05 mol	0.2 mol	AgOAc	DMSO/ MeCN(1:10)	120	12	67
24	0.05 mol	0.2 mol	AgOAc	DMSO/ MeCN(10:1)	120	12	67
25	0.05 mol	0.05 mol	AgOAc	DMSO	120	12	42
26	0.05 mol	0.1 mol	AgOAc	DMSO	120	12	64
27	0.05 mol	0.4 mol	AgOAc	DMSO	120	12	81
28	0.05 mol	0.2 mol	AgOAc	DMSO	120	2	59
29	0.05 mol	0.2 mol	AgOAc	DMSO	120	6	71
30	0.05 mol	0.2 mol	AgOAc	DMSO	120	12	81
31	0.05 mol	0.2 mol	AgOAc	DMSO	120	24	55
32[g]	0.05mol	0.2mol	AgOAc	DMSO	120	12	75
33[h]	0.05mol	0.2mol	AgOAc	DMSO	120	12	40
34[i]	0.05mol	0.2mol	AgOAc	DMSO	120	12	72
35	0.05 mol	0.2 mol	AgOAc	DMSO	rt	12	71
36	0.05 mol	0.2 mol	AgOAc	DMSO	60	12	69
37	**0.05 mol**	**0.2 mol**	**AgOAc**	**DMSO**	**80**	**12**	**88**
38	0.05 mol	0.2 mol	AgOAc	DMSO	100	12	72
39	0.05 mol	0.2 mol	AgOAc	DMSO	140	12	55

[a]Reaction conditions: 8-(*p*-Tolyl)-BODIPY (**1a**, 0.05 mmol), pyrazole (**2a**, 4.0 equiv), oxidant (4.0 equiv) and solvent (1.0 mL) at 120 ℃ for 12 h under N_2 atmosphere. [b]Isolated yields. [c]Under O_2 atmosphere. [d]AgOAc (20 mol%) and under O_2 atmosphere. [e]AgOAc (20 mol%) and MnO_2 (4.0 equiv). [f]AgOAc (4.0 equiv) and additives (2.0 equiv). [g]AgOAc (3.0 equiv). [h]AgOAc (2.0 equiv). [i]AgOAc (3.0 equiv) and in the dark condition. PivOH = pivalic acid, BQ = 1,4-benzoquinone, DMSO = dimethylsulfoxide, DMF = *N*,*N*-dimethylformamide, DCE = 1,2-dichloroethane, THF = tetrahydrofuran, and N.D. = no detection.

(2) General procedure for direct C–H amination of BODIPYs

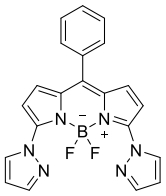
A dried Schlenk tube with a magnetic stir bar was charged with BODIPY (0.05 mmol), amine (0.20 mmol, 4.0 equiv) and AgOAc (4.0 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent DMSO was added *via* a syringe and the rubber septum was replaced with a polytetrafluoroethylene stopper under N_2. Then the reaction mixture was stirred at the 80 ℃ for 12 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.



3,5-Di(1*H*-pyrazol-1-yl)-8-(*p*-tolyl)-BODIPY (3a)

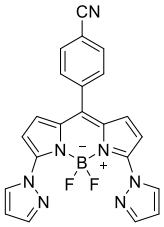
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a**, 14.1 mg, 0.05 mmol), pyrazole (**2a**, 13.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20/1/1, v/v) afforded the product **3a** (18.2 mg) in 88% yield as a brown solid with a greenish metallic lustre. M.p.: 200-202 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.48 (s, 3H), 6.53-6.54 (m, 2H), 6.92 (d, *J* = 4.4 Hz, 2H), 6.97 (d, *J* = 4.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 1.6 Hz, 2H), 8.80 (d, *J* = 2.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 109.1, 113.4, 129.3, 130.6-130.8 (m), 131.2, 132.1, 132.2, 132.3,

132.4, 141.0, 143.3, 150.7. HRMS (ESI$^+$): calcd. for $C_{22}H_{18}BF_2N_6$ $[M+H]^+$: 415.1649, found: 415.1649.



3,5-Di(1*H*-pyrazol-1-yl)-8-phenyl-BODIPY (3b)

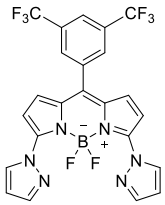
Following the general procedure, the mixture of 8-phenyl-BODIPY (**1b**, 13.4 mg, 0.05 mmol), pyrazole (**2a**, 13.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20/1/1, v/v) afforded the product **3b** (16.1 mg) in 80% yield as a brown solid with a greenish metallic lustre. M.p.: 202-204 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.55 (dd, J = 2.8 Hz, 1.6 Hz, 2H), 6.90 (d, J = 4.8 Hz, 2H), 6.99 (d, J = 3.6 Hz, 2H), 7.53-7.57 (m, 5H), 7.81 (d, J = 1.6 Hz, 2H), 8.82 (d, J = 2.8, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 109.2, 113.6, 128.6, 130.5, 130.7, 131.2, 132.1, 132.2, 132.3, 133.6, 143.3, 150.9. HRMS (ESI$^+$): calcd. for $C_{21}H_{16}BF_2N_6$ $[M+H]^+$: 401.1492, found: 401.1488.



3,5-Di(1*H*-pyrazol-1-yl)-8-(*p*-cyano-phenyl)-BODIPY (3c)

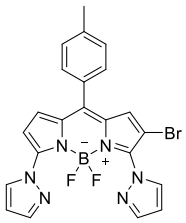
Following the general procedure, the mixture of 8-(*p*-cyano-phenyl)-BODIPY (**1c,** 14.6 mg, 0.05 mmol), pyrazole (**2a**, 13.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20/1/1, v/v) afforded the product **3c** (19.1 mg) in 90% yield as a golden solid with a golden metallic lustre. M.p.: 234-236 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 6.57 (dd, J = 2.8 Hz, 1.6 Hz, 2H), 6.79 (d, J = 4.4 Hz, 2H), 7.03 (d, J = 4.4 Hz, 2H), 7.67-7.70 (m, 2H), 7.82 (d, J = 1.6 Hz, 2H), 7.84-7.86 (m, 2H), 8.82 (d, J = 2.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 109.6, 114.2, 114.4, 118.1, 130.5, 131.3, 132.0, 132.1, 132.2, 132.4,

138.1, 143.7, 151.6. HRMS (ESI$^+$): calcd. for $C_{22}H_{15}BF_2N_7$ [M+H]$^+$: 426.1445, found: 426.1459.



3,5-Di(1*H*-pyrazol-1-yl)-8-(3,5-*bis*(trifluoromethyl)phenyl)-BODIPY (3d)

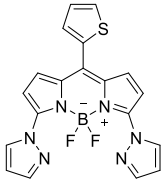
Following the general procedure, the mixture of 8-(3,5-*bis*(trifluoromethyl)phenyl)-BODIPY (**1d,** 20.2 mg, 0.05 mmol), pyrazole (**2a**, 13.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/10, v/v) afforded the product **3d** (21.4 mg) in 80% yield as a golden solid with a golden metallic lustre. M.p.: 206-208 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 6.58 (dd, J = 2.8 Hz, 1.6 Hz, 2H), 6.75 (d, J = 4.4 Hz, 2H), 7.07 (d, J = 4.0 Hz, 2H), 7.83 (d, J = 1.6 Hz, 2H), 8.03 (s, 2H), 8.11 (s, 1H), 8.83 (d, J = 2.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 109.8, 114.6, 123.0 (q, $J_{C\text{-}F}$ = 273.0 Hz), 124.1-124.2 (m), 130.3, 130.45-130.48 (m), 132.0, 132.1, 132.2, 132.3, 132.4 (q, $J_{C\text{-}F}$ = 34.0 Hz), 135.7, 137.9, 143.9, 151.9. HRMS (ESI$^+$): calcd. for $C_{23}H_{13}BF_8N_6Na$ [M+Na]$^+$: 559.1059, found: 559.1061.



2-Bromo-3,5-di(1*H*-pyrazol-1-yl)-8-(*p*-tolyl)-BODIPY (3e)

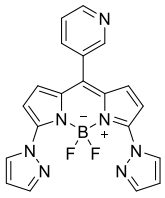
Following the general procedure, the mixture of 2-bromo-8-(*p*-tolyl)-BODIPY (**1g**, 18.0 mg, 0.05 mmol), pyrazole (**2a**, 13.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 5/1/1, v/v) afforded the product **3e** (18.7 mg) in 76% yield as a amaranthine powder. M.p.: 214-216 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 2.49 (s, 3H), 6.50 (dd, J = 2.8 Hz, 1.6

Hz, 1H), 6.54 (dd, *J* = 2.4 Hz, 2.0 Hz, 1H), 6.82 (s, 1H), 7.11 (d, *J* = 4.8 Hz, 1H), 7.21 (d, *J* = 4.8 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.44-7.46 (m, 2H), 7.80 (d, *J* = 1.6 Hz, 1H), 7.88-7.89 (m, 1H), 7.99 (d, *J* = 2.4 Hz, 1H), 8.80 (d, *J* = 2.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 107.1, 110.8, 116.7, 127.0, 129.6, 130.1, 130.7, 132.8, 132.9, 133.1, 133.38, 133.42, 134.8, 135.4, 141.6, 142.2, 142.5, 143.6, 144.7. HRMS (ESI^+): calcd. for $C_{22}H_{17}BBrF_2N_6$ $[M+H]^+$: 493.0754, 495.0733, found: 493.0756, 495.0737.



3,5-Di(1*H*-pyrazol-1-yl)-8-(thiophen-2-yl)-BODIPY (3f)

Following the general procedure, the mixture of 8-(thiophen-2-yl)-BODIPY (**1e,** 13.7 mg, 0.05 mmol), pyrazole (**2a**, 13.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/10, v/v) afforded the product **3f** (16.2 mg) in 80% yield as a brown solid with a greenish metallic lustre. M.p.: 170-172 ℃. ^{1}H NMR (400 MHz, DMSO-*d*6) δ = 6.72 (dd, *J* = 2.4 Hz, 1.6 Hz, 2H), 7.03 (d, *J* = 4.8 Hz, 2H), 7.39-7.41 (m, 3H), 7.77 (d, *J* = 3.6 Hz, 1H), 7.98 (d, *J* = 1.6 Hz, 2H), 8.13 (d, *J* = 4.8 Hz, 1H), 8.61 (d, *J* = 2.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-*d*6) δ = 109.7, 113.8, 128.7, 131.0, 131.7, 131.8, 131.9, 132.6, 133.8, 135.6, 143.7, 149.9. HRMS (ESI^+): calcd. for $C_{19}H_{13}BF_2N_6NaS$ $[M+Na]^+$: 429.0876, found: 429.0874.



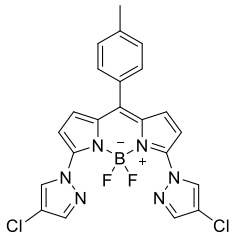
3,5-Di(1*H*-pyrazol-1-yl)-8-(pyridin-3-yl)-BODIPY (3g)

Following the general procedure, the mixture of 8-(pyridin-3-yl)-BODIPY (**1f,** 13.4 mg, 0.05 mmol), pyrazole (**2a**, 13.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column

chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 5/1/5, v/v) afforded the product **3g** (18.6 mg) in 93% yield as a black powder. M.p.: 165-167 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 6.56 (dd, J = 2.4 Hz, 1.6 Hz, 2H), 6.85 (d, J = 4.4 Hz, 2H), 7.04 (d, J = 4.4 Hz, 2H), 7.52 (dd, J = 7.6 Hz, 4.4 Hz, 2H), 7.82 (d, J = 1.6 Hz, 2H), 7.88-7.91 (m, 1H), 8.81-8.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 109.5, 114.1, 123.4, 129.8, 130.6, 132.1, 132.2, 132.3, 132.4, 137.9, 143.6, 150.4, 151.5. HRMS (ESI^+): calcd. for $C_{20}H_{14}BF_2N_7Na$ $[M+Na]^+$: 424.1264, found: 424.1265.

3,5-Di(1*H*-pyrazol-1-yl)-8-(*p*-tolyl)-BODIPY (3h)

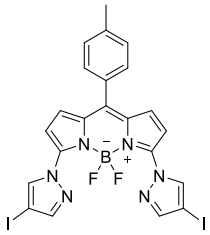
Following the general procedure, the mixture of BODIPY (**1h**, 9.6 mg, 0.05 mmol), pyrazole (**2a**, 13.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 4/1/1, v/v) afforded the product **3h** (6.3 mg) in 39% yield as a brown solid with a greenish metallic lustre. M.p.: 171-173 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 6.73 (dd, J = 2.8 Hz, 1.6 Hz, 2H), 7.00 (d, J = 4.4 Hz, 2H), 7.53 (d, J = 4.4 Hz, 2H), 7.91 (s, 1H), 7.98 (d, J = 1.6 Hz, 2H), 8.64 (d, J = 2.8 Hz, 2H).^{13}C NMR (100 MHz, DMSO-d_6) δ = 109.9, 113.2, 129.4, 131.3, 131.4, 131.5, 132.2, 132.3, 143.8, 150.0. HRMS (ESI^+): calcd. for $C_{15}H_{11}BF_2N_6Na^+$ $[M+Na]^+$: 347.0999, found: 347.0996.



3,5-Di(4-chloro-1*H*-pyrazole-1-yl)-8-(*p*-tolyl)-BODIPY (3i)

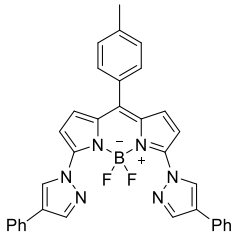
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), 4-chloro-1*H*-pyrazole (**2b**, 20.4 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20/1/1,

v/v) afforded the product **3i** (22.17 mg) in 92% yield as a golden solid with a greenish metallic lustre. M.p.: 222-224 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 2.48 (s, 3H), 6.94 (s, 4H), 7.34 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.73 (s, 2H), 8.74 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 113.3, 114.3, 129.4, 129.6, 130.5, 130.7, 131.4, 132.6, 141.3, 142.0, 144.5, 150.2. HRMS (ESI^+): calcd. for $C_{22}H_{16}BCl_2F_2N_6$ $[M+H]^+$: 483.0869, 485.0840 found: 483.0874, 485.0851.



3,5-Di(4-iodo-1*H*-pyrazole-1-yl)-8-(*p*-tolyl)-BODIPY (3j)

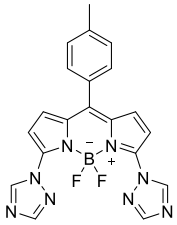
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), 4-iodo-1H-pyrazole (**2c**, 38.8 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20/1/1, v/v) afforded the product **3j** (27.3 mg) in 82% yield as a brown solid with a greenish metallic lustre. M.p.: 228-230 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 2.48 (s, 3H), 6.92-6.95 (m, 4H), 7.34 (d, J = 7.6 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.79 (s, 2H), 8.76 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 61.7, 113.4, 129.4, 130.5, 130.7, 131.4, 132.6, 135.7-136.1 (m), 141.3, 144.5, 148.1, 149.6. HRMS (ESI^+): calcd. for $C_{22}H_{15}BF_2I_2N_6Na$ $[M+Na]^+$: 688.9401, found: 688.9402.



3,5-Di(4-phenyl-1*H*-pyrazol-1-yl)-8-(*p*-tolyl)-BODIPY (3k)

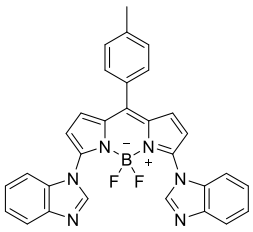
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), 4-phenyl-1H-pyrazol (**2d**, 28.8 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20/1/1,

v/v) afforded the product **3k** (16.1 mg) in 57% yield as a black solid with a greenish metallic lustre. M.p.: > 250 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 2.49 (s, 3H), 6.95 (d, J = 4.4 Hz, 2H), 7.05 (d, J = 4.8 Hz, 2H), 7.31-7.36 (m, 4H), 7.41-7.48 (m, 6H), 7.63-7.65 (m, 4H), 8.11 (s, 2H), 9.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.6, 113.2, 126.1, 126.2, 127.5, 128.1, 129.2, 129.3, 130.76, 130.80, 131.1, 131.5, 141.0, 141.3, 150.4 . HRMS (ESI$^+$): calcd. for $C_{34}H_{25}BF_2N_6Na$ $[M+Na]^+$: 589.2094, found: 589.2097.



3,5-Di(1*H*-1,2,4-triazol-1-yl)-8-(*p*-tolyl)-BODIPY (3l)

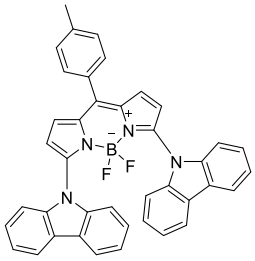
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), 1,2,4-triazol (**2e**, 27.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20/1/1, v/v) afforded the product **3l** (11.4 mg) in 55% yield as a brown solid with a greenish metallic lustre. M.p.: 229-231 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 2.50 (s, 3H), 6.96 (d, J = 4.4 Hz, 2H), 7.05 (d, J = 4.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 8.15 (s, 2H), 9.31 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.7, 114.0, 129.6, 130.0, 130.8, 132.5, 142.1, 145.2, 145.3, 147.3, 153.1. HRMS (ESI$^+$): calcd. for $C_{20}H_{16}BF_2N_8$ $[M+H]^+$: 417.1554, found: 417.1554.



3,5-Di(1*H*-benzo[*d*]imidazol-1-yl)-8-(*p*-tolyl)-BODIPY (3m)

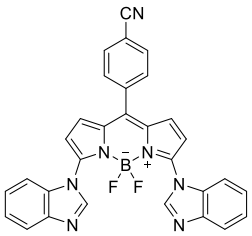
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), benzimidazole (**2f**, 23.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column

chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 20/1/1, v/v) afforded the product **3m** (21.3 mg) in 83% yield as a black solid with a red metallic lustre. M.p.: > 250 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 2.53 (s, 3H), 6.75 (d, *J* = 4.4 Hz, 2H), 7.15 (d, *J* = 4.4 Hz, 2H), 7.30-7.36 (m, 4H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.46-7.49 (m, 2H). 7.55 (d, *J* = 8.0 Hz, 2H), 7.85-7.87 (m, 2H), 8.60 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.7, 111.2, 114.3, 121.2, 123.9, 124.4, 129.7, 130.1, 132.4, 133.0, 133.9, 142.1, 143.4, 143.5, 143.6, 143.8, 146.3, 146.5. HRMS (ESI^+): calcd. for $C_{30}H_{21}BF_2N_6Na$ $[M+Na]^+$: 537.1781, found: 537.1780.



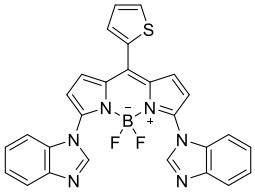
3,5-Di(9*H*-carbazole-9-yl)-8-(*p*-tolyl)-BODIPY (3n)

Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), carbazole (**2g**, 33.4 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane/Et_3N = 60/4/4/1, v/v) afforded the product **3n** (23.9 mg) in 78% yield as a black powder. M.p.: > 250 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 2.55 (s, 3H), 6.49 (d, *J* = 4.4 Hz, 2H), 7.18-7.22 (m, 6H), 7.30-7.36 (m, 8H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.7, 111.7, 117.4, 120.1, 121.1, 124.4, 126.2, 129.6, 130.5, 131.2, 132.2, 133.9, 141.9, 142.0, 146.8, 150.2. HRMS (ESI^+): calcd. for $C_{40}H_{27}BF_2N_4Na$ $[M+Na]^+$: 635.2189, found: 635.2190.



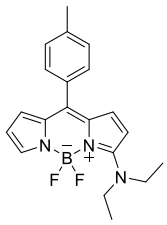
3,5-Di(1*H*-benzo[*d*]imidazol-1-yl)-8-(*p*-cyano-phenyl)-BODIPY (3o)

Following the general procedure, the mixture of 8-(*p*-cyano-phenyl)-BODIPY (**1c,** 14.6 mg, 0.05 mmol), benzimidazole (**2f**, 23.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 2/1/2, v/v) afforded the product **3o** (15.7 mg) in 60% yield as a red powder. M.p.: > 250 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 6.81 (d, J = 4.4 Hz, 2H), 7.02 (d, J = 4.8 Hz, 2H), 7.32-7.39 (m, 4H), 7.46-7.48 (m, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.87 (dd, J = 6.0 Hz, 2.4 Hz, 2H), 7.93 (d, J = 8.4 Hz, 2H), 8.62 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 111.2, 114.97, 115.03, 117.9, 121.3, 124.2, 124.7, 131.3, 131.9, 132.55, 132.64, 133.7, 137.3, 142.2, 143.3, 143.9, 147.6. HRMS (ESI^+): calcd. for $C_{30}H_{19}BF_2N_7$ $[M+H]^+$: 526.1758, found: 526.1761.



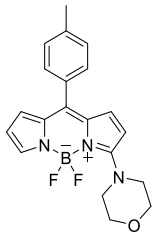
3,5-Di(1*H*-benzo[*d*]imidazol-1-yl)-8-(thiophen-2-yl)-BODIPY (3p)

Following the general procedure, the mixture of 8-(thiophen-2-yl)-BODIPY (**1e,** 13.7 mg, 0.05 mmol), benzimidazole (**2f**, 23.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 2/1/2, v/v) afforded the product **3p** (5.1 mg) in 20% yield as a black powder. M.p.: 242-244 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 7.13 (d, J = 4.4 Hz, 2H), 7.33-7.39 (m, 4H), 7.50-7.53 (m, 3H), 7.68 (d, J = 2.0 Hz, 2H), 7.76-7.79 (m, 2H), 7.96 (s, 1H), 8.30 (d, J = 4.4 Hz, 1H), 8.42 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 111.4, 115.9, 120.1, 123.5, 124.4, 129.5, 131.7, 132.6, 133.2, 133.8, 134.8, 135.4, 138.6, 142.9, 143.7, 145.8. HRMS (ESI^+): calcd. for $C_{27}H_{18}BF_2N_6S$ $[M+H]^+$: 507.1369, found: 507.1367.



3-(Diethylamino)-8-(*p*-tolyl)-BODIPY (4a)

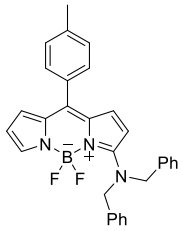
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), diethylamine (**2h**, 17.4 μL, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/10, v/v) afforded the product **4a** (16.2 mg) in 92% yield as a orange powder. M.p.: 110-112 ℃. ^{1}H NMR (400MHz, $CDCl_3$) δ = 1.36 (t, J = 7.2 Hz, 6H), 2.43 (s, 3H), 3.83 (q, J = 6.8 Hz, 4H), 6.20 (d, J = 5.2 Hz, 1H), 6.32 (d, J = 1.6 Hz, 2H), 6.90 (d, J = 5.6 Hz, 1H), 7.23-7.25 (m, 2H), 7.34-7.36 (m, 2H), 7.43 (t, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.9, 21.5, 47.0, 113.3, 113.9, 117.7, 128.9, 130.4, 130.5, 131.4, 131.9, 132.6, 135.8, 135.9, 138.9, 162.1. HRMS (ESI^+): calcd. for $C_{20}H_{22}BF_2N_3Na$ $[M+Na]^+$: 376.1767, found: 376.1747.



3-(4-Morpholino)-8-(*p*-tolyl)-BODIPY (4b)

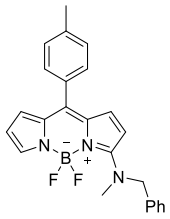
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), morpholine (**2i**, 17.4 μL, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/10, v/v) afforded the product **4b** (18.1 mg) in 99% yield as a orange powder. M.p.: 183-185 ℃. ^{1}H NMR (400MHz, DMSO-d_6) δ = 2.40 (s, 3H), 3.77 (t, J = 4.8 Hz, 4H), 4.00 (t, J = 4.4 Hz, 4H), 6.21 (dd, J = 3.6 Hz, 0.8 Hz, 1H), 6.28 (dd, J = 3.6 Hz, 2.4 Hz, 1H), 6.82 (d, J = 5.2 Hz, 1H), 6.98 (d, J = 5.2 Hz, 1H), 7.30 (dd, J = 2.4 Hz, 1.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100

MHz, DMSO-d_6) δ = 20.9, 50.4, 66.2, 113.1, 115.8, 116.8, 129.0, 129.7, 130.1, 130.2, 130.9, 131.6, 134.9, 135.5, 138.7, 161.8. HRMS (ESI^+): calcd. for $C_{20}H_{21}BF_2N_3O$ $[M+H]^+$: 368.1740, found: 368.1710.



3-(*N*,*N*-dibenzylamino)-8-(*p*-tolyl)-BODIPY (4c)

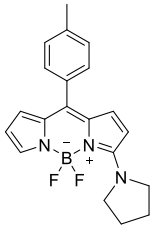
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), dibenzylamine (**2j**, 38.4 μL, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/10, v/v) afforded the product **4c** (23.8 mg) in 99% yield as a orange crystal. M.p.: 131-133 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 2.40 (s, 3H), 5.05 (s, 4H), 6.25 (dd, J = 4.0 Hz, 1.2 Hz, 1H), 6.30 (dd, J = 3.6 Hz, 2.4 Hz, 1H), 6.70 (d, J = 5.6 Hz, 1H), 6.98 (d, J = 5.2 Hz, 1H), 7.27-7.34 (m, 9H), 7.36-7.41 (m, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 20.9, 54.9, 113.5, 116.6, 117.6, 127.0, 127.6, 128.8, 129.0, 130.2, 130.4, 131.0, 131.2, 131.5, 134.9, 135.9, 136.5, 138.8, 163.8. HRMS (ESI^+): calcd. for $C_{30}H_{26}BF_2N_3Na$ $[M+Na]^+$: 500.2080, found: 500.2076.



3-(*N*-benzyl-*N*-methylamino)-8-(*p*-tolyl)-BODIPY (4d)

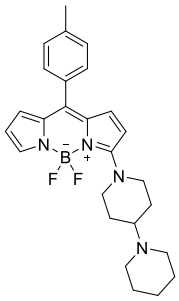
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), *N*-methylbenzylamine (**2k**, 25.8 μL, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/1, v/v) afforded the product **4d** (20.0 mg) in 99% yield as a orange powder. M.p.: 100-102 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 2.40 (s, 3H), 3.48 (s, 3H), 5.02 (s,

2H), 6.21 (d, *J* = 3.2 Hz, 1H), 6.29 (dd, *J* = 3.6 Hz, 2.4 Hz, 1H), 6.76 (d, *J* = 5.2 Hz, 1H), 6.97 (d, *J* = 5.2 Hz, 1H), 7.27 (d, *J* = 7.2 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 4H), 7.37-7.42 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 20.9, 58.2, 113.0, 116.4, 116.5, 126.8, 127.6, 128.8, 129.0, 129.5, 130.0, 130.1, 130.9, 131.6, 135.1, 135.6, 136.3, 138.6, 163.6. HRMS (ESI$^+$): calcd. for $C_{24}H_{22}BF_2N_3Na$ $[M+Na]^+$: 424.1767, found: 424.1750.



3-(Pyrrolidin-1-yl)-8-(*p*-tolyl)-BODIPY (4e)

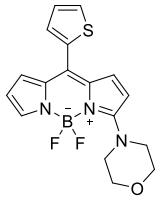
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg, 0.05 mmol), tetrahydro pyrrole (**2l**, 16.4 μL, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/10, v/v) afforded the product **4e** (13.1 mg) in 75% yield as a black powder. M.p.: > 250 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 2.00 (s, 4H), 2.40 (s, 3H), 3.89 (s, 4H), 6.17 (d, *J* = 3.2 Hz, 1H), 6.26 (dd, J = 3.6 Hz, 2.4 Hz, 1H), 6.60 (d, *J* = 5.2 Hz, 1H), 6.97 (d, *J* = 5.2 Hz, 1H), 7.27 (dd, *J* = 2.4 Hz, 1.6 Hz, 1H), 7.31-7.38 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 21.5, 25.8, 51.5, 113.1, 114.5, 117.6, 128.9, 130.1, 130.5, 131.3, 132.0, 132.5, 135.5, 135.6, 138.8, 160.4. HRMS (ESI$^+$): calcd. for $C_{20}H_{21}BF_2N_3$ $[M+H]^+$: 352.1791, found: 352.1789.



3-[(1,4'-Bipiperidin)-1'-yl]-8-(*p*-tolyl)-BODIPY (4f)

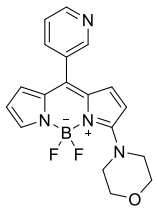
Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a,** 14.1 mg,

0.05 mmol), 4-piperidinopiperidine (**2m**, 16.4 μL, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (MeOH/dichloromethane = 1/30, v/v) afforded the product **4f** (22.3 mg) in 99% yield as a orange powder. M.p.: 174-176 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 1.37 (d, J = 4.8 Hz, 2H), 1.47 (d, J = 4.8 Hz, 4H), 1.54-1.61 (m, 2H), 1.87 (d, J = 10.8 Hz, 2H), 2.39 (s, 3H), 2.43-2.45 (m, 4H), 2.61 (t, J = 11.2 Hz, 1H), 3.29 (d, J = 12.0 Hz, 2H), 4.62 (d, J = 12.8 Hz, 2H), 6.17-6.18 (m, 1H), 6.26-6.27 (m, 1H), 6.82 (d, J = 5.6 Hz, 1H), 6.94 (d, J = 5.2 Hz, 1H), 7.28 (dd, J = 2.0 Hz, 1.2 Hz, 1H), 7.31-7.37 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 20.9, 24.6, 26.1, 28.3, 49.7, 49.8, 60.7, 112.9, 116.1, 116.3, 129.0, 129.2, 130.1, 131.0, 131.7, 135.1, 135.6, 138.6, 161.6. HRMS (ESI$^+$): calcd. for $C_{26}H_{32}BF_2N_4$ $[M+H]^+$: 449.2683, found: 449.2681.



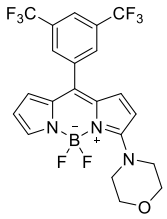
3-(4-Morpholino)-8-(thiophen-2-yl)-BODIPY (4g)

Following the general procedure, the mixture of 8-(thiophen-2-yl)-BODIPY (**1e,** 13.7 mg, 0.05 mmol), morpholine (**2i**, 17.4 μL, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/10, v/v) afforded the product **4g** (15.2 mg) in 85% yield as a red crystal. M.p.: 134-136 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.88-3.91 (m, 4H), 3.95-3.98 (m, 4H), 6.26 (d, J = 5.2 Hz, 1H), 6.38 (dd, J = 4.0 Hz, 2.4 Hz, 1H), 6.72 (d, J = 4.0 Hz, 1H), 7.15 (dd, J = 5.2 Hz, 3.6 Hz, 1H), 7.22 (d, J = 5.2 Hz, 1H), 7.30 (dd, J = 3.2 Hz, 1.2 Hz, 1H), 7.45 (dd, J = 2.4 Hz, 1.2 Hz, 1H), 7.50 (dd, J = 5.2 Hz, 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.7, 50.76, 50.82, 66.9, 113.0, 114.0, 119.6, 126.0, 127.3, 128.1, 130.4, 131.5, 132.0, 135.5, 135.7, 136.0, 162.3. HRMS (ESI$^+$): calcd. for $C_{17}H_{16}BF_2N_3NaOS$ $[M+Na]^+$: 382.0967, found: 382.0973.



3-(4-Morpholino)-8-(pyridin-3-yl)-BODIPY (4h)

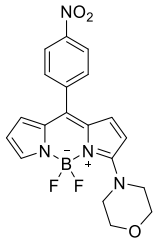
Following the general procedure, the mixture of 8-(pyridin-3-yl)-BODIPY (**1f,** 13.4 mg, 0.05 mmol), morpholine (**2i**, 17.4 μL, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane/Et_3N = 5/1/5/1, v/v) afforded the product **4h** (17.5 mg) in 99% yield as a orange crystal. M.p.: 172-174 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 3.89-3.91 (m, 4H), 3.98-4.01 (m, 4H), 6.30 (d, J = 5.2 Hz, 1H), 6.33-6.38 (m, 2H), 6.85 (d, J = 5.2 Hz, 1H), 7.40-7.44 (m, 1H), 7.47 (d, J = 0.8 Hz, 1H), 7.80-7.83 (m, 1H), 8.69-8.73 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.6, 50.65, 50.70, 66.8, 113.7, 114.1, 118.8, 123.1, 128.9, 131.0, 131.4, 132.0, 135.1, 135.3, 137.6, 150.2, 150.4, 162.2. HRMS (ESI^+): calcd. for $C_{18}H_{18}BF_2N_4O$ $[M+H]^+$: 355.1536, found: 355.1535.



3-(4-Morpholino)-8-(3,5-bis(trifluoromethyl)phenyl)-BODIPY (4i)

Following the general procedure, the mixture of 8-(3,5-bis(trifluoromethyl)phenyl)-BODIPY (**1d**, 20.2 mg, 0.05 mmol), morpholine (**2i**, 17.4 μL, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/10, v/v) afforded the product **4i** (19.5 mg) in 80% yield as a orange crystal. M.p.: 228-231 ℃. 1H NMR (400 MHz, $CDCl_3$) δ = 3.89-3.92 (m, 4H), 4.01-4.03 (m, 4H), 6.26 (d, J = 3.6 Hz, 1H), 6.35 (d, J = 5.2 Hz, 1H), 6.39 (dd, J = 3.6 Hz, 2.4 Hz, 1H), 6.77 (d, J = 5.2 Hz, 1H), 7.49 (dd, J = 2.0 Hz, 1.2 Hz, 1H), 7.94 (s, 2H), 8.00 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 50.9, 66.9,

114.5, 114.6, 118.7, 123.2 (q, $J_{C\text{-}F}$ = 273.0 Hz), 128.8, 129.9-130.1 (m), 130.47-130.50 (m), 131.0, 132.0 (q, J = 33.7 Hz), 131.0, 132.5, 134.8, 135.4, 137.3, 162.4. HRMS (ESI^+): calcd. for $C_{21}H_{17}BF_8N_3O$ $[M+H]^+$: 490.1331, found: 490.1316.



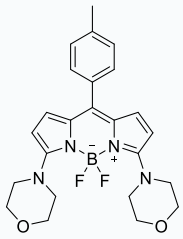
3-(4-Morpholino)-8-(4-nitrophenyl)BODIPY (4j)

Following the general procedure, the mixture of 8-(4-nitrophenyl)BODIPY (**1i**, 15.7 mg, 0.05 mmol), morpholine (**2i**, 17.4 μL, 0.10 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 1/1/1, v/v) afforded the product **4j** (17.2 mg) in 86% yield as a orange powder. M.p.: > 250 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.79 (t, J = 4.4 Hz, 4H), 4.05 (t, J = 4.4 Hz, 4H), 6.19 (d, J = 2.8 Hz, 1H), 6.30 (dd, J = 3.6 Hz, 2.4 Hz, 1H), 6.94 (d, J = 5.6 Hz, 1H), 7.03 (d, J = 5.6 Hz, 1H), 7.33 (dd, J = 2.4 Hz, 1.2 Hz, 1H), 7.75-7.79 (m, 2H), 8.33-8.37 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 50.7, 66.3, 113.4, 116.3, 117.3, 123.6, 127.0, 129.8, 130.1, 131.7, 141.2, 147.7, 162.1. HRMS (ESI^+): calcd. for $C_{19}H_{17}BF_2N_4NaO_3^+$ $[M+Na]^+$: 421.1254, found: 421.1254.

(3) **The procedure for double-amination of BODIPYs with morpholine**

A dried Schlenk tube with a magnetic stir bar was charged with BODIPY (0.1 mmol), morpholine (0.40 mmol, 4.0 equiv) and AgOAc (4.0 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent DMSO was added *via* a syringe and the rubber septum was replaced with a polytetrafluoroethylene stopper under N_2. Then the reaction mixture was stirred at the 80 ℃ for 12 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on

silica gel (100-200 mesh) to provide the desired products.

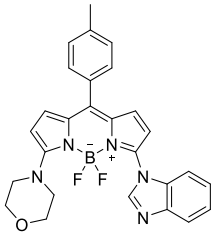


3,5-Di(4-morpholino)-8-(*p*-tolyl)-BODIPY (3q)

Following the general procedure, the mixture of 8-(*p*-tolyl)-BODIPY (**1a**, 28.2 mg, 0.10 mmol), morpholine (**2i**, 34.8 μL, 0.20 mmol), AgOAc (66.8 mg, 4.0 equiv), DMSO (1.0 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 10/1/10, v/v) afforded the product **3q** (8.1 mg) in 18% yield as a black powder. M.p.: 215-217 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 2.39 (s, 3H), 3.49 (t, J = 4.8 Hz, 8H), 3.72 (t, J = 4.8 Hz, 8H), 6.25 (d, J = 4.8 Hz, 2H), 6.52 (d, J = 4.8 Hz, 2H), 7.29-7.34 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 21.0, 51.2, 66.1, 108.1, 127.2, 128.9, 130.3, 130.5, 131.4, 131.5, 138.7, 159.2. HRMS (ESI$^+$): calcd. for $C_{24}H_{27}BF_2N_4NaO_2$ $[M+Na]^+$: 475.2087, found: 475.2085.

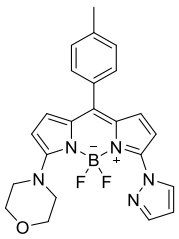
(4) The procedure for amination of 3-(4-morpholino)-8-(*p*-tolyl)-BODIPY with 2a or 2f

A dried Schlenk tube with a magnetic stir bar was charged with 3-(4-morpholino)-8-(*p*-tolyl)-BODIPY (**4b**, 0.05 mmol), **2a** or **2f** (0.20 mmol, 4.0 equiv) and AgOAc (33.4 mg, 4.0 equiv). The system was evacuated thrice and back filled with N_2. Next, the solvent DMSO/H_2O/HOAc was added sequence *via* a syringe and the rubber septum was replaced with a polytetrafluoroethylene stopper under N_2. Then the reaction mixture was stirred at the 80 ℃ for 12 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with 20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.



3-(1*H*-Benzo[*d*]imidazol-1-yl)-5-(4-morpholino)-8-(*p*-tolyl)-BODIPY (5a)

Following the general procedure, the mixture of 3-(4-morpholino)-8-(*p*-tolyl)-BODIPY (**4b**, 17.9 mg, 0.05 mmol), benzimidazole (**2f**, 23.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (0.5 mL)/H_2O (0.5 mL)/HOAc (0.5 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 1/1/1, v/v) afforded the product **5a** (6.0 mg) in 25% yield as a black solid. M.p.: > 250 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 2.42 (s, 3H), 3.66-3.68 (m, 4H), 3.86-3.88 (m, 4H), 6.35 (d, J = 4.0 Hz, 1H), 6.46 (d, J = 4.0 Hz, 1H), 6.93 (d, J = 5.6 Hz, 1H), 7.04 (d, J = 5.6 Hz, 1H), 7.25-7.31 (m, 3H), 7.37 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.71-7.75 (m, 1H), 8.31 (s, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 21.0, 50.6, 66.1, 110.7, 110.9, 115.8, 117.5, 119.5, 122.2, 123.3, 128.8, 129.2, 130.1, 130.3, 130.9, 132.2, 135.7, 135.8, 138.9, 142.5, 144.9, 162.1. HRMS (ESI$^+$): calcd. for $C_{27}H_{25}BF_2N_5O$ $[M+H]^+$: 484.2115, found: 484.2123.

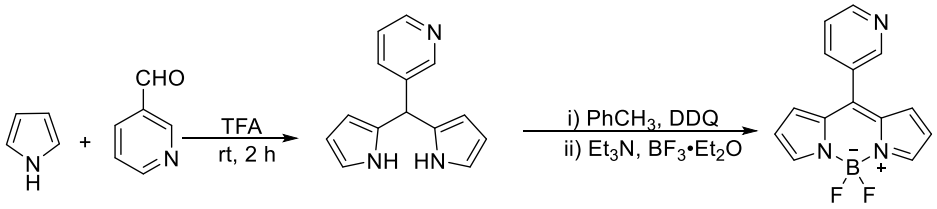


3-(1*H*-Pyrazol-1-yl)-5-(4-morpholino)-8-(*p*-tolyl)-BODIPY (5b)

Following the general procedure, the mixture of 3-(4-morpholino)-8-(*p*-tolyl)-BODIPY (**4b**, 17.9 mg, 0.05 mmol), pyrazole (**2a**, 13.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv), DMSO (0.5 mL)/H_2O (0.5 mL)/HOAc (0.5 mL) was stirred at 80 ℃ for 12 h. Purification *via* column chromatography on silica gel (petroleum ether/ethyl acetate/dichloromethane = 5/1/5, v/v) afforded the product **5b** (6.9 mg) in 32% yield as a brown solid with a greenish metallic lustre. M.p.: 195-197 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ = 2.41 (s, 3H), 3.74 (t, J = 4.8

Hz, 4H), 3.95 (t, J = 4.8 Hz, 4H), 6.25 (d, J = 3.6 Hz, 1H), 6.38 (d, J = 4.0 Hz, 1H), 6.48 (dd, J = 2.8 Hz, 2.0 Hz, 1H), 6.88 (d, J = 5.6 Hz, 1H), 6.98 (d, J = 5.2 Hz, 1H), 7.34-7.40 (m, 4H), 7.68 (d, J = 2.0 Hz, 1H), 8.17 (d, J = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ = 21.0, 50.6, 66.2, 106.5, 109.0, 116.8, 129.1, 129.4, 131.1, 131.7, 131.8, 131.9, 134.7, 135.3, 138.8, 139.4, 140.5, 161.9. HRMS (ESI$^+$): calcd. for $C_{23}H_{23}BF_2N_5O$ $[M+H]^+$: 434.1958, found: 434.1933.

(5) Synthesis of 8-(pyridin-3-yl)-BODIPY (1f) substrates



A 250 mL flask was charged with pyrrole (1.2 mol) and 3-pyridinecarboxaldehyde (60 mmol), stirred at room temperature for 10 min under N_2 atmosphere without the light, and then, trifluoroacetic acid (1.5 mL) was added. The mixture was stirred for 4 h. Upon completion of the reaction by TLC assay, the dilute NaOH (0.1 mol/L) was added to quench the reaction. The product was extracted with ethyl acetate, dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified *via* silica gel column chromatography (petroleum ether/dichloromethane = 1/1, v/v) to give the corresponding dipyrromethanes.

Then a 250 mL flask was charged with the corresponding dipyrromethanes (30 mmol), DDQ (1.2 equiv) and toluene (120 mL). The mixture was stirred for 3 h at room temperature under N_2 atmosphere. And then Et_3N (30 mL) and $BF_3{\cdot}Et_2O$ (28 mL) was added to the reaction. The mixture was stirred for another 11 h. The product was extracted with ethyl acetate, dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified *via* silica gel column chromatography (petroleum ether/dichloromethane = 1/1, v/v) to give the 8-(pyridin-3-yl)-BODIPY Yield: (5 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.58 (s, 2H), 6.90 (s, 2H), 7.48-7.53 (m, 1H), 7.88-7.92 (m, 1H), 7.98 (s, 2H), 8.81-8.84 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 119.3, 123.4, 130.0, 131.4, 135.0, 137.7, 143.3,

145.2, 150.2, 151.8. HRMS (ESI$^+$): calcd. for $C_{14}H_{11}BF_2N_3$ $[M+H]^+$: 270.1014, found: 270.1007.

III. Single crystal X-ray structures of 3m and 4b

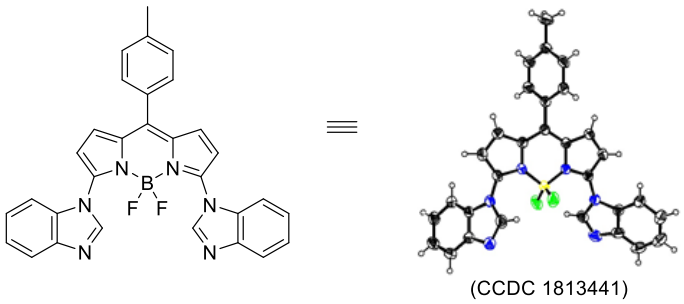


Fig. S1 ORTEP diagram of **3m**.

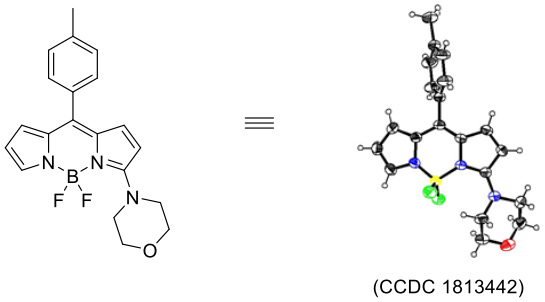


Fig. S2 ORTEP diagram of **4b**.

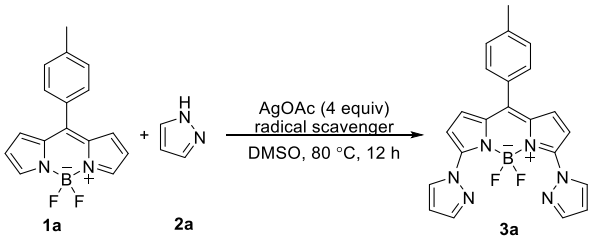
IV. Mechanistic study

General procedure for direct C–H amination of BODIPYs in the presence of radical scavenger

A dried Schlenk tube with a magnetic stir bar was charged with 8-(*p*-tolyl)-BODIPY (**1a**, 14.1 mg, 0.05 mmol), pyrazole (**2a**, 13.6 mg, 0.20 mmol), AgOAc (33.4 mg, 4.0 equiv) and the radical scavenger. The system was evacuated thrice and back filled with N_2. Next, the solvent DMSO was added *via* a syringe and the rubber septum was replaced with a polytetrafluoroethylene stopper under N_2. Then the reaction mixture was stirred at the 80 ℃ for 12 h in an oil bath. After the reaction mixture was cooled to ambient temperature, the solvent was removed under reduced pressure. The residue was dissolved in 10 mL of CH_2Cl_2, filtered through a celite pad, and then washed with

20-30 mL of CH_2Cl_2. The combined filtrates were concentrated and purified *via* column chromatography on silica gel (100-200 mesh) to provide the desired products.

Table S2. Direct C–H amination of BODIPYs in the presence of radical scavenger[a]



Entry	Radical Scavenger	Equivalent	Yield (%)[b]
1	TEMPO	2	37
2	TEMPO	1	58
3	TEMPO	0.5	68
4	BHT	2	19
5	BHT	1	39
6	BHT	0.5	50
7	ascorbic acid	2	0
8	ascorbic acid	1	0
9	ascorbic acid	0.5	14

[a]Reaction conditions: 8-(*p*-Tolyl)-BODIPY (**1a**, 0.05 mmol), pyrazole (**2a**, 4.0 equiv), AgOAc (4.0 equiv) and solvent (1.0 mL) at 80 ℃ for 12 h under N_2. [b]Isolated yields. TEMPO = 2,2,6,6-tetramethyl-1-piperidinyloxy; BHT = 2,6-*di*-tert-butyl-4-methylphenol.

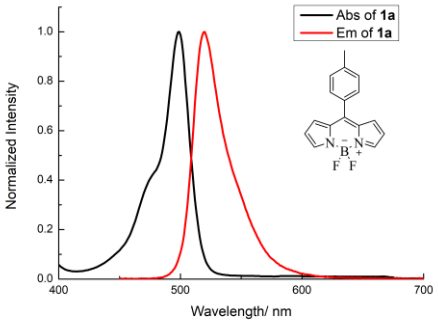
V. Photophysical data of BODIPYs

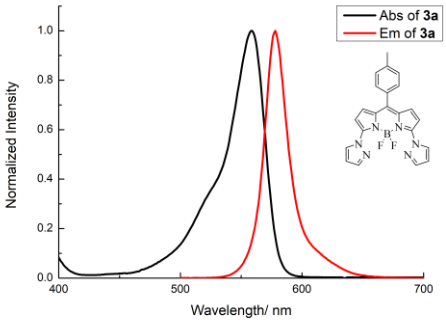
Table S3. Absorption maxima, emission maxima, Stokes shifts and fluorescence quantum yields of BODIPYs

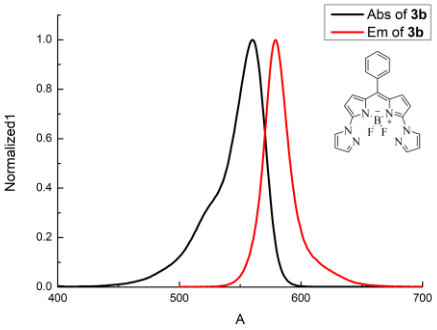
Compd.	λ_{abs} (nm)[a] in CH_2Cl_2	λ_{em} (nm)[b] in CH_2Cl_2	(Φ_f)[c] in CH_2Cl_2	Stokes Shift (nm)
1a	499	520	0.01	21
3a	559	578	0.60	19
3b	560	579	0.64	19
3c	568	591	0.18	23
3d	571	587	0.44	16
3e	540	577	0.30	37
3f	571	591	0.03	20
3g	565	585	0.68	20

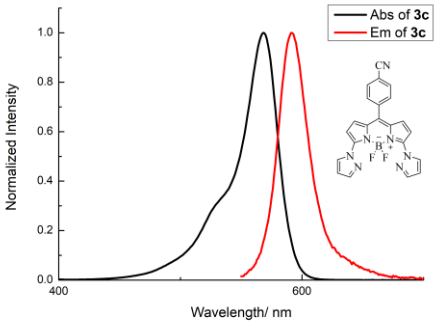
3h	562	578	0.81	16
3i	562	579	0.76	17
3j	565	585	0.72	20
3k	584	606	0.80	22
3l	540	559	0.69	19
3m	546	576	0.20	30
3n	564	636	< 0.01	72
3o	561	592	0.07	31
3p	559	590	0.01	31
3q	570	604	< 0.01	34
4a	473	552	< 0.01	79
4b	488	547	< 0.01	59
4c	501	548	< 0.01	47
4d	489	548	< 0.01	59
4e	473	541	< 0.01	68
4f	481	554	< 0.01	73
4g	496	564	< 0.01	68
4h	487	557	< 0.01	70
4i	491	562	< 0.01	71
4j	496	570	< 0.01	74
5a	484	564	0.01	80
5b	502	581	< 0.01	79

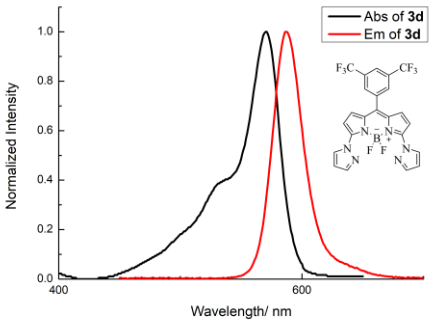
[a]Absorption maximum in CH_2Cl_2 at 1×10^{-5} mol/L. [b]Emission maximum in CH_2Cl_2 at 1×10^{-5} mol/L. [c]Absolute quantum yield determined in CH_2Cl_2 at 1×10^{-5} mol/L with an integrating sphere system.

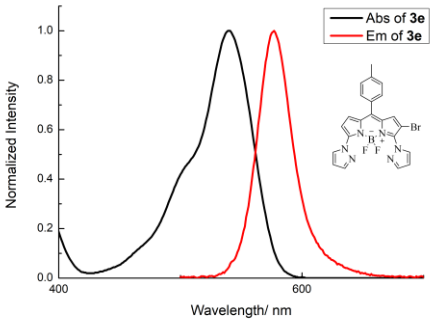


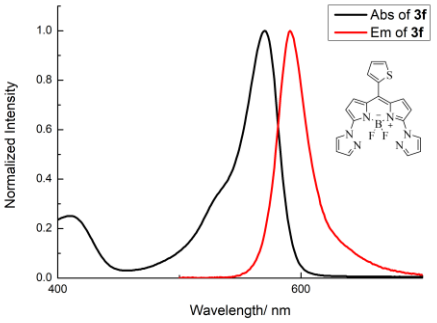

Abs of 3a
Em of 3a
Normalized Intensity
Wavelength/ nm

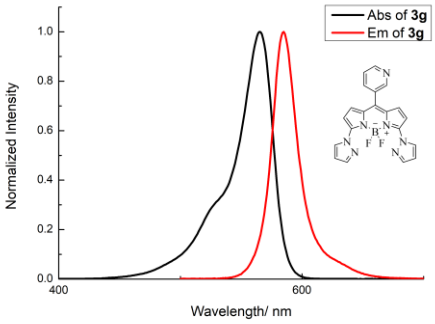

Abs of 3b
Em of 3b
Normalized1
A

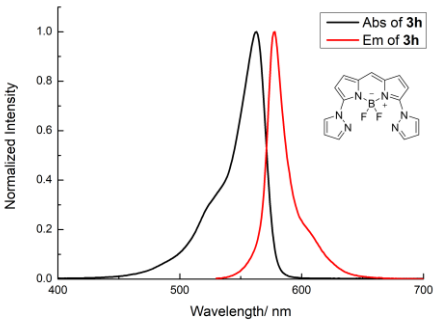

Abs of 3c
Em of 3c
CN
Normalized Intensity
Wavelength/ nm

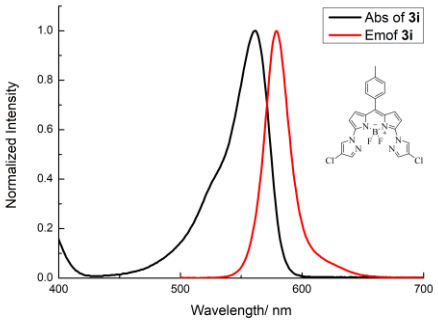

Abs of 3d
Em of 3d
F3C
CF3
Normalized Intensity
Wavelength/ nm

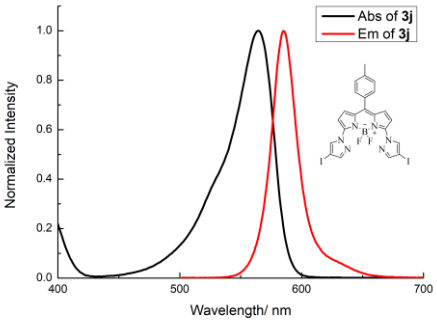

Abs of 3e
Em of 3e
Br
Normalized Intensity
Wavelength/ nm

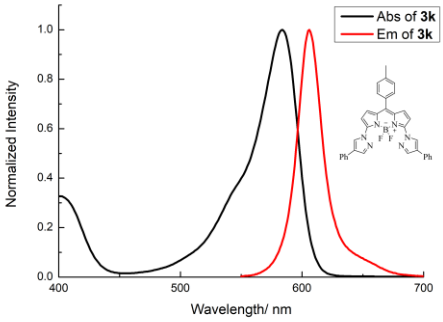

Abs of 3f
Em of 3f
S
Normalized Intensity
Wavelength/ nm

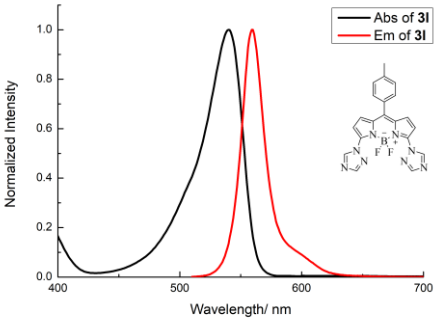

Abs of 3g
Em of 3g
N
Normalized Intensity
Wavelength/ nm

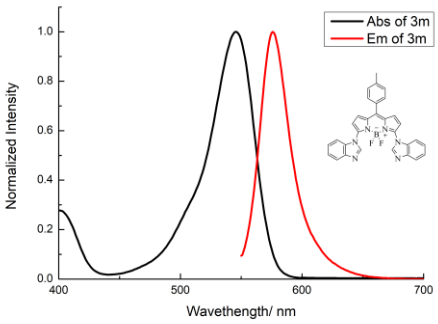

Abs of 3h
Em of 3h
Normalized Intensity
Wavelength/ nm

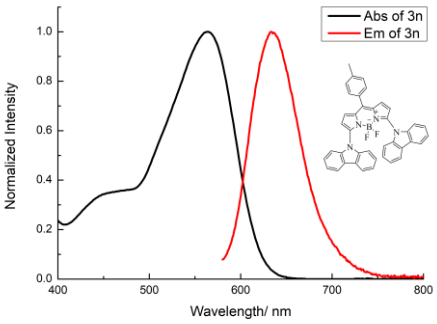

Abs of 3i
Emof 3i
Normalized Intensity
Wavelength/ nm

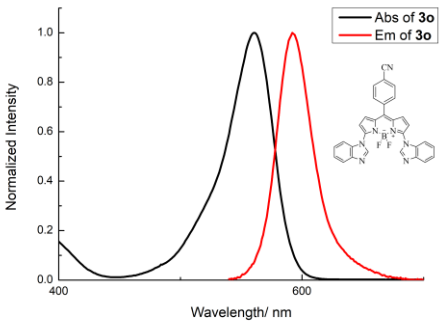

Abs of 3j
Em of 3j
Normalized Intensity
Wavelength/ nm

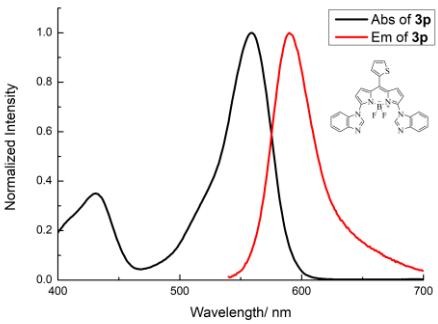

Abs of 3k
Em of 3k
Normalized Intensity
Wavelength/ nm

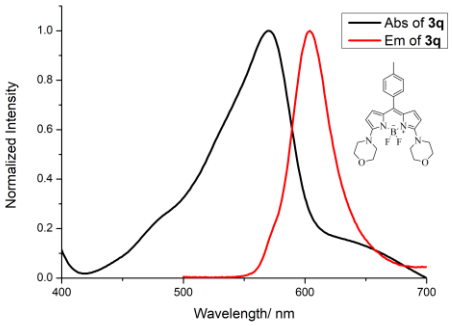

Abs of 3l
Em of 3l
Normalized Intensity
Wavelength/ nm

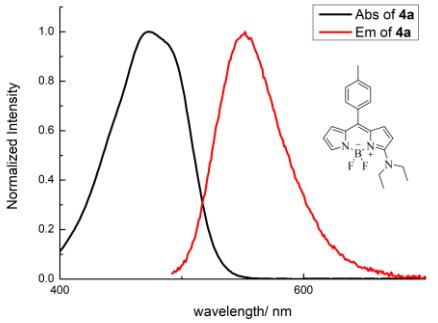

Abs of 3m
Em of 3m
Normalized Intensity
Wavethength/ nm

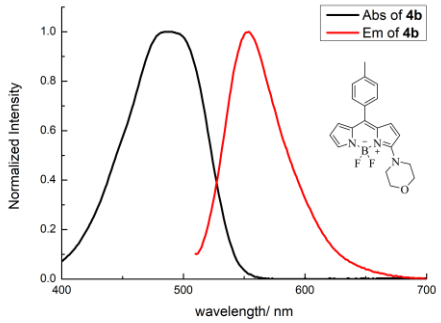

Abs of 3n
Em of 3n
Normalized Intensity
Wavelength/ nm

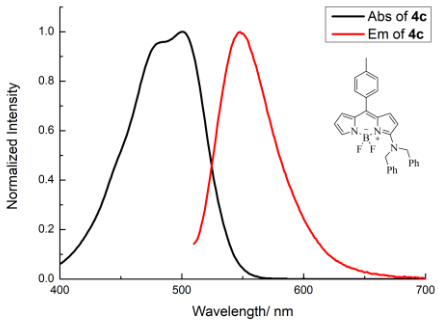

Abs of 3o
Em of 3o
Normalized Intensity
Wavelength/ nm

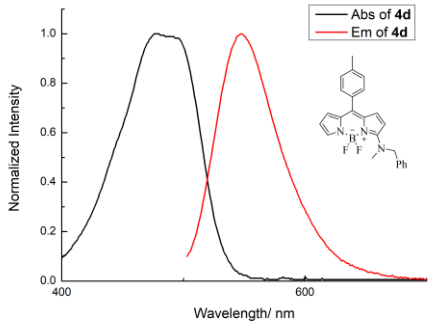

Abs of 3p
Em of 3p
Normalized Intensity
Wavelength/ nm

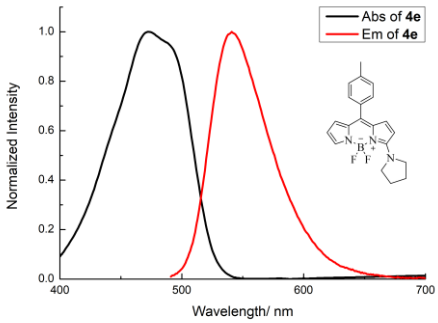

Abs of 3q
Em of 3q
Normalized Intensity
Wavelength/ nm

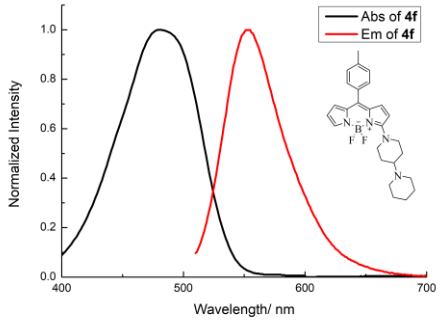

Abs of 4a
Em of 4a
Normalized Intensity
wavelength/ nm

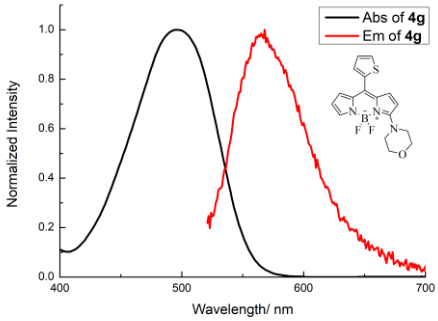

Abs of 4b
Em of 4b
Normalized Intensity
wavelength/ nm


Abs of 4c
Em of 4c
Normalized Intensity
Wavelength/ nm


Abs of 4d
Em of 4d
Normalized Intensity
Wavelength/ nm


Abs of 4e
Em of 4e
Normalized Intensity
Wavelength/ nm


Abs of 4f
Em of 4f
Normalized Intensity
Wavelength/ nm


Abs of 4g
Em of 4g
Normalized Intensity
Wavelength/ nm

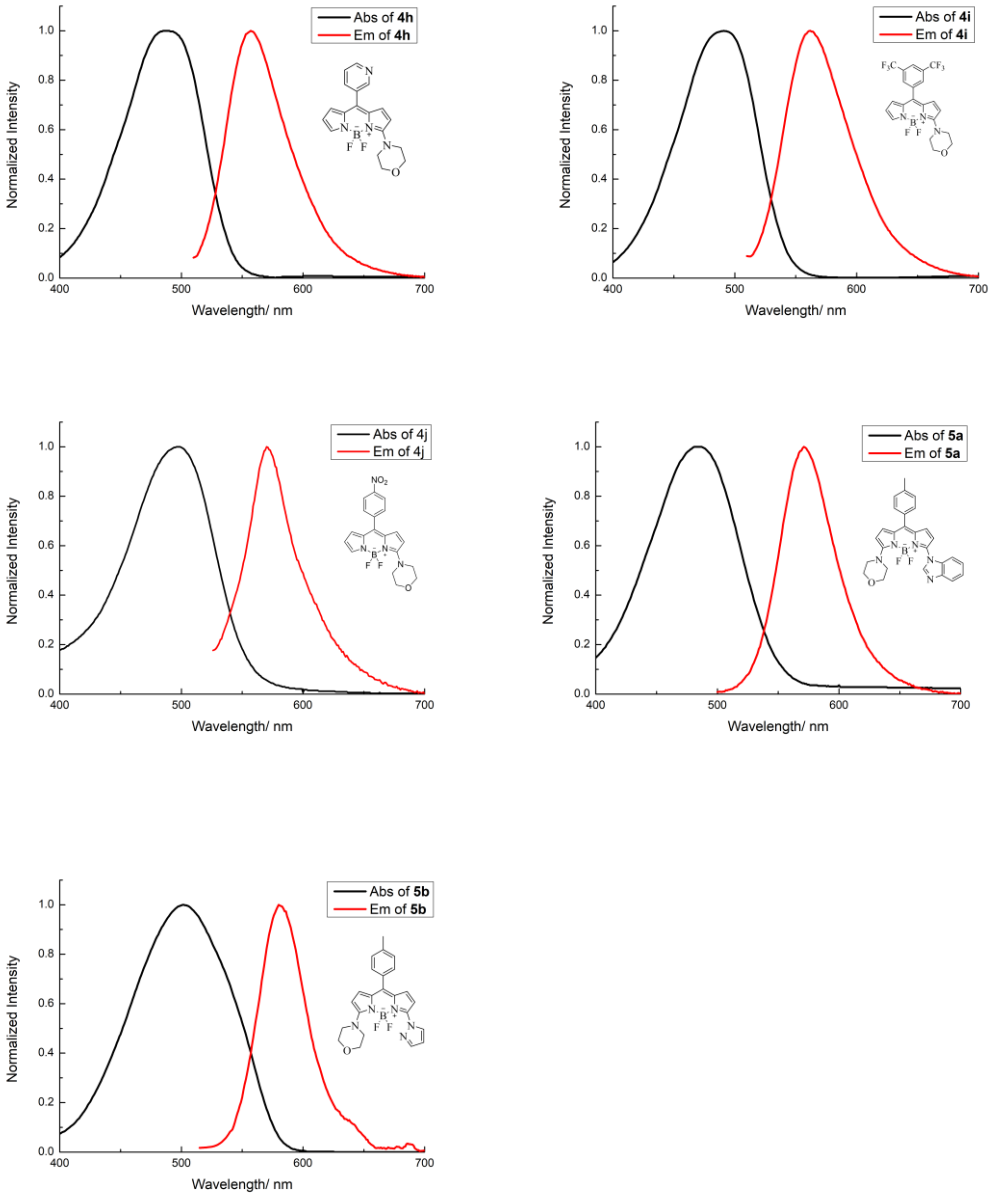


Fig. S3 Normalized UV-*vis*-NIR absorption spectra (black lines) and fluorescence emission spectra (red lines) of BODIPYs in CH_2Cl_2 (1×10^{-5} mol/L).

VI. Cell imaging experiments and cytotoxicity assays

i) Cell culture

HepG2 cells were hatched in DMEM (Dublecco's modified Eagle's Medium) supplemented with 10% (v/v) FBS (fetal bovine serum), 100 kU/L of penicillin, and 100 mg/L of streptomycin at 37 ℃ in a humidified atmosphere containing 5% CO_2.

ii) Confocal imaging experiments

For Confocal fluorescence images experiments, HepG2 cells were incubated with 2.5 μM of **3** or **4** in PBS (phosphate buffered solution) containing 1% DMSO for 15 min at 37 ℃. After incubation HepG2 cells were washed twice with PBS. The cells were observed with a Leica TCS SP8 confocal laser scanning microscope.

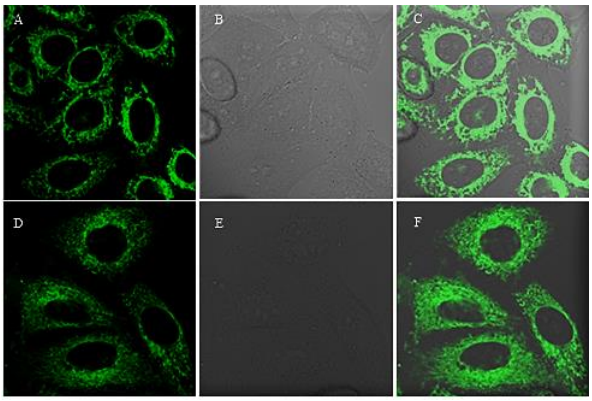


Fig. S4 (A) Fluorescence images of HepG2 cells stained with **3m**; (B) Bright-field image of HepG2 cells stained with **3m**; (C) Merged image of A and B; (D) Fluorescence images of HepG2 cells stained with **4b**; (E) Bright-field image of HepG2 cells stained with **4b**; (F) Merged image of D and E. HepG2 cells cultured with **3m** (2.5 μM, λ_{ex} = 543 nm, λ_{em} = 550-650 nm) and **4b** (2.5 μM, λ_{ex} = 488 nm, λ_{em} = 450-550 nm) in PBS containing 1% DMSO.

For subcellular co-localization experiments, live cells were incubated with 2.5 μM of **3m**, **3o**, **3p**, **3q** or **4b** in a PBS containing 1% DMSO for 15 min at 37 ℃. After incubated live cells were washed twice with PBS and 1 μM ER-Tracker™ Red or ER-Tracker™ Green was added and incubated for an additional 30 min before imaging. The cells were observed with a Leica TCS SP8 confocal laser scanning microscope.

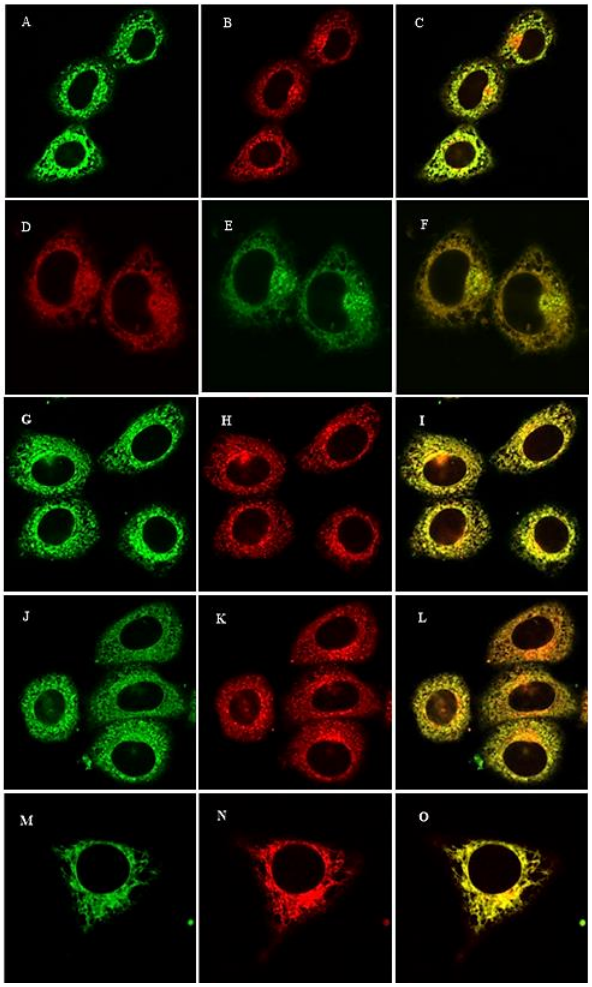


Fig. S5 Fluorescent images of HepG2 cells: (A) Stained with ER Tracker™ Green (λ_{ex} = 488 nm, λ_{em} = 450-550 nm); (B) Stained with **3m** (λ_{ex} =543 nm, λ_{em} = 550-650 nm); (C) Merged image of A and B; (D) Stained with ER Tracker™ Red (λ_{ex} = 543 nm, λ_{em} = 550-650 nm); (E) Stained with **4b** (λ_{ex} = 488 nm, λ_{em} = 450-550 nm); (F) Merged image of D and E. (G) Stained with ER Tracker™ Green (λ_{ex} = 488 nm, λ_{em} = 450-550 nm); (H) Stained with **3o** (λ_{ex} =543 nm, λ_{em} = 550-650 nm); (I) Merged image of G and H; (J) Stained with ER Tracker™ Green (λ_{ex} = 488 nm, λ_{em} = 450-550 nm); (K) Stained with **3p** (λ_{ex} = 543 nm, λ_{em} = 550-650 nm); (L) Merged image of J and K. (M) Stained with ER Tracker™ Green (λ_{ex} = 488 nm, λ_{em} = 450-550 nm); (N) Stained with **3q** (λ_{ex} =543 nm, λ_{em} = 550-650 nm); (O) Merged image of M and N.

ii) Cytotoxicity assays

Cell counting Kit-8 (CCK-8) assays were performed to evaluate the cytotoxicity effect of **3m**, **3o**, **3p**, **3q** and **4b**. HepG2 cells were incubated in a 96-well culture plates at a volume of 100 μL (1×10^4 cells/mL) for a stationary culture. This media were changed into fresh media with a final volume of 200 μL containing sample in the 2-fold down dilution series and then incubated for 24 h. Then 10 μL of CCK-8 solution was added to each well, incubated for an additional 1 h and then absorbance

readings at a wavelength of 490 nm were taken on a spectrophotometer (Molecular Devices, Sunnyvale, USA). The cell viability was calculated by the following formula: (mean optical density(OD) in treated wells/mean OD in control wells)×100%.

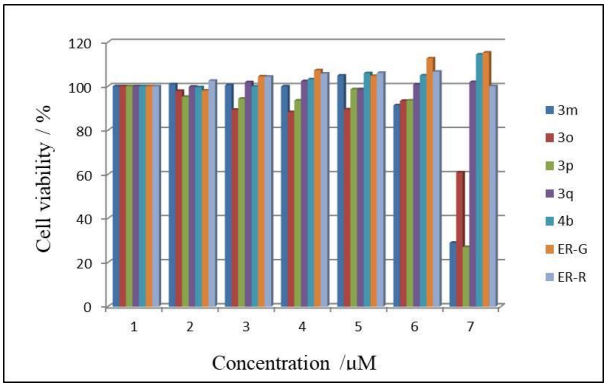


Fig. S6 Cell viability values (%) estimated by CCK8 assays on HepG2 cells, which were cultured in the presence of 0.25-8 μM of **3m**, **3o**, **3p**, **3q**, **4b**, ER Tracker™ Red or ER Tracker™ Green for 24 h at 37 ℃.

VII. References

1. D. Prasannan, D. Raghav, S. Sujatha, H. Hareendrakrishnakumar, K. Rathinasamy and C. Arunkumar, *RSC Adv*., 2016, **6**, 80808.

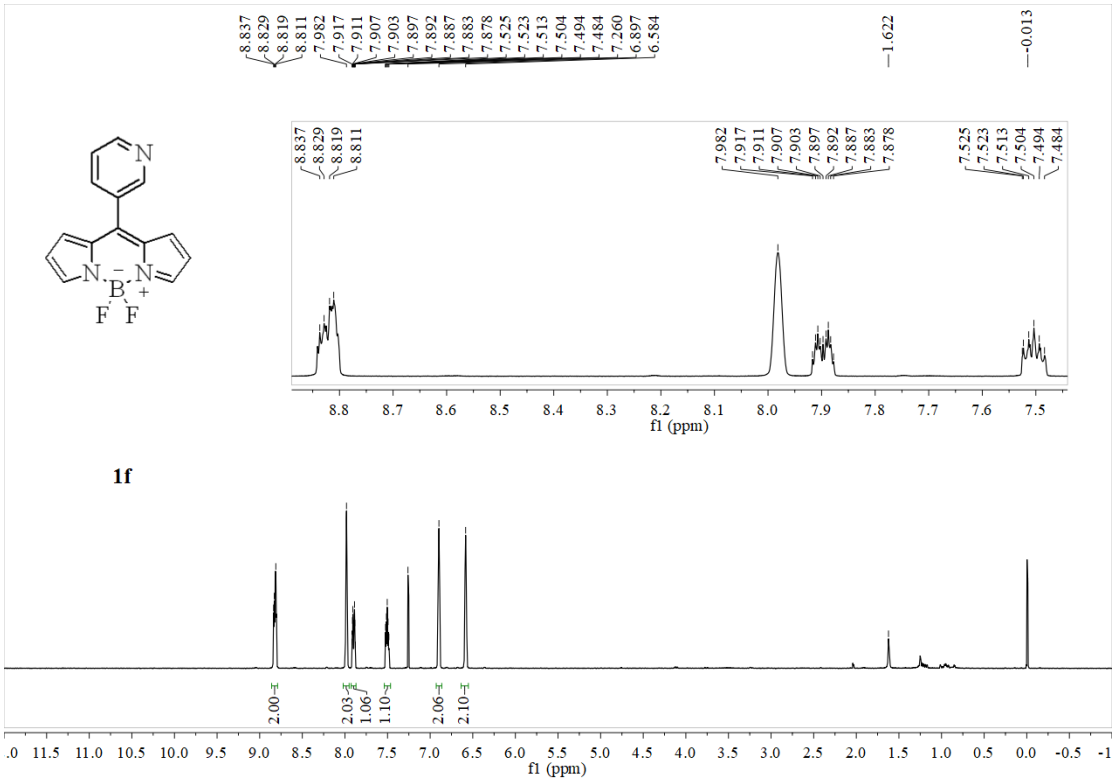
2. X. Zhang, F. Xu, P. Guo and X. Qian, *New J. Chem*., 2012, **36**, 1621.

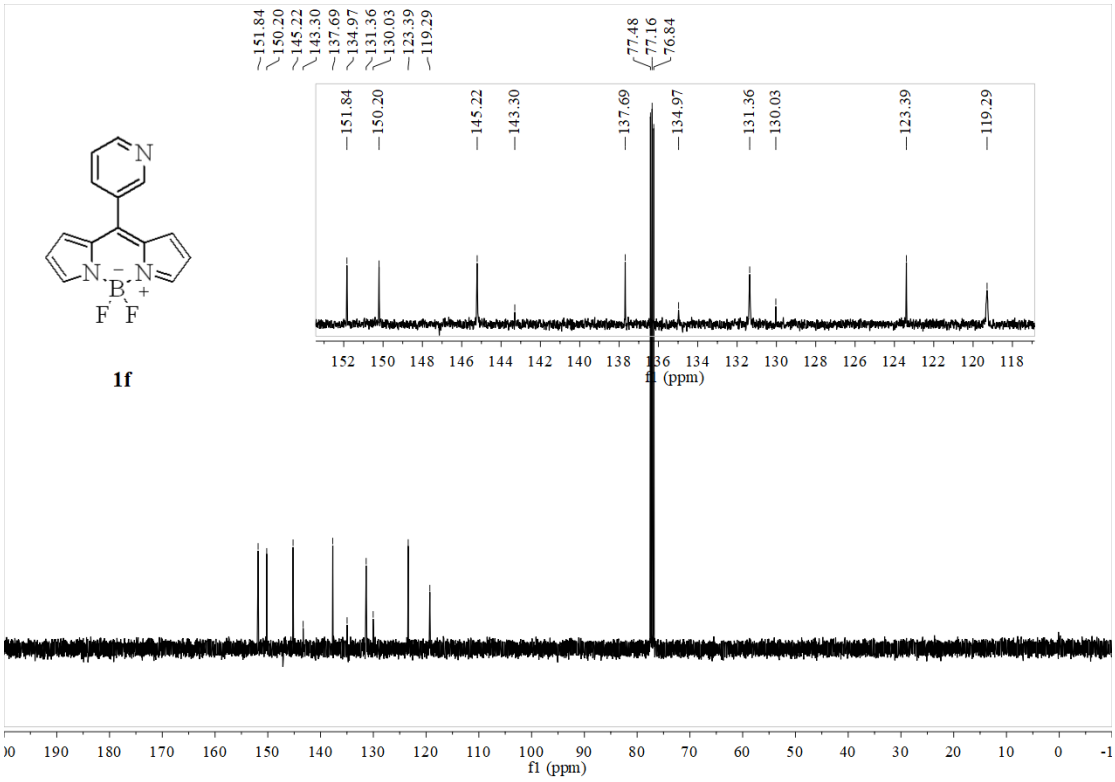
3. M. Hecht, T. Fischer, P. Dietrich, W. Kraus, A. B. Descalzo, W. E. S. Unger and K. Rurack, *ChemistryOpen*, 2013, **2**, 25.

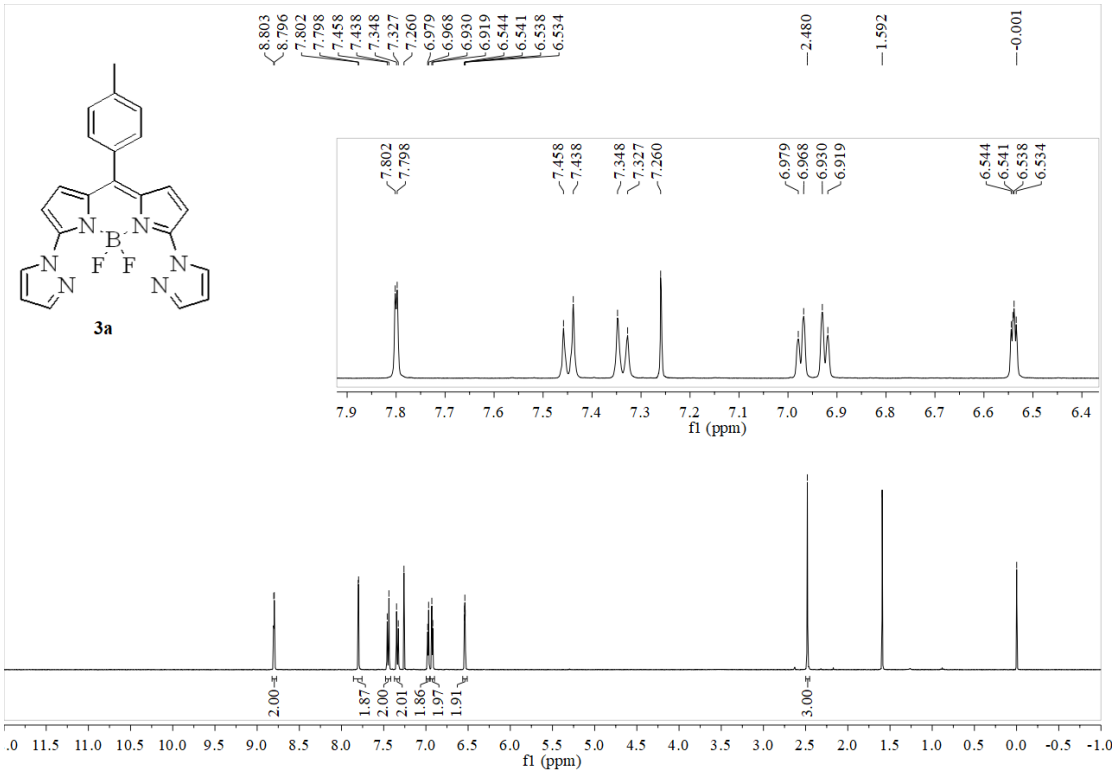
4. J. Songkhao, R. Banerjee, S. Debnath, S. Narasimhan, N. Wannaprom, P. Vanalabhpatana, N. Seriani, R. Gebauer and P. Thamyongkit, *Dyes and Pigments*, 2017, **142**, 558.

5. B. R. Groves, S. M. Crawford, T. Lundrigan, C. F. Matta, S. Sowlati and A. Thompson, *Chem. Commun.*, 2013, **49**, 816.

VIII. Copies of 1H and 13C NMR spectra



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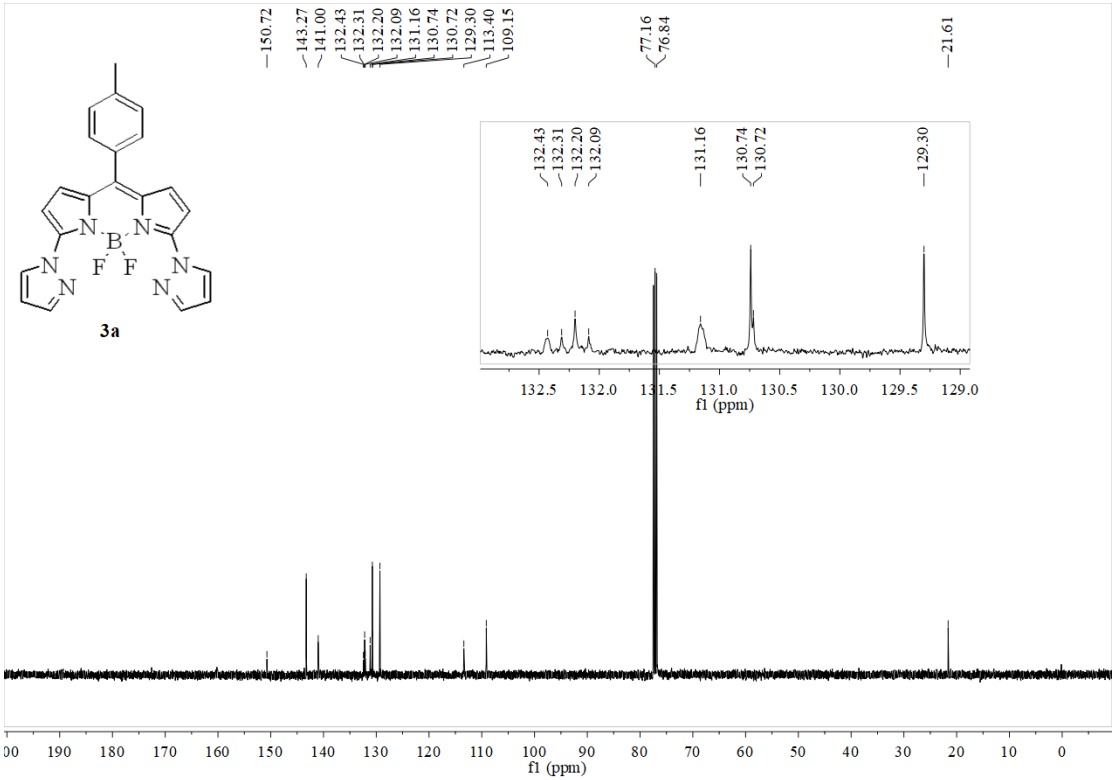
7.438
7.348
7.327
7.260
6.979
6.968
6.930
6.919
6.544
6.541
6.538
6.534
2.480
1.592
0.001
3a
f1 (ppm)
2.00
1.87
2.00
2.01
1.86
1.97
1.91
3.00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143.27
141.00
132.43
132.31
132.20
132.09
131.16
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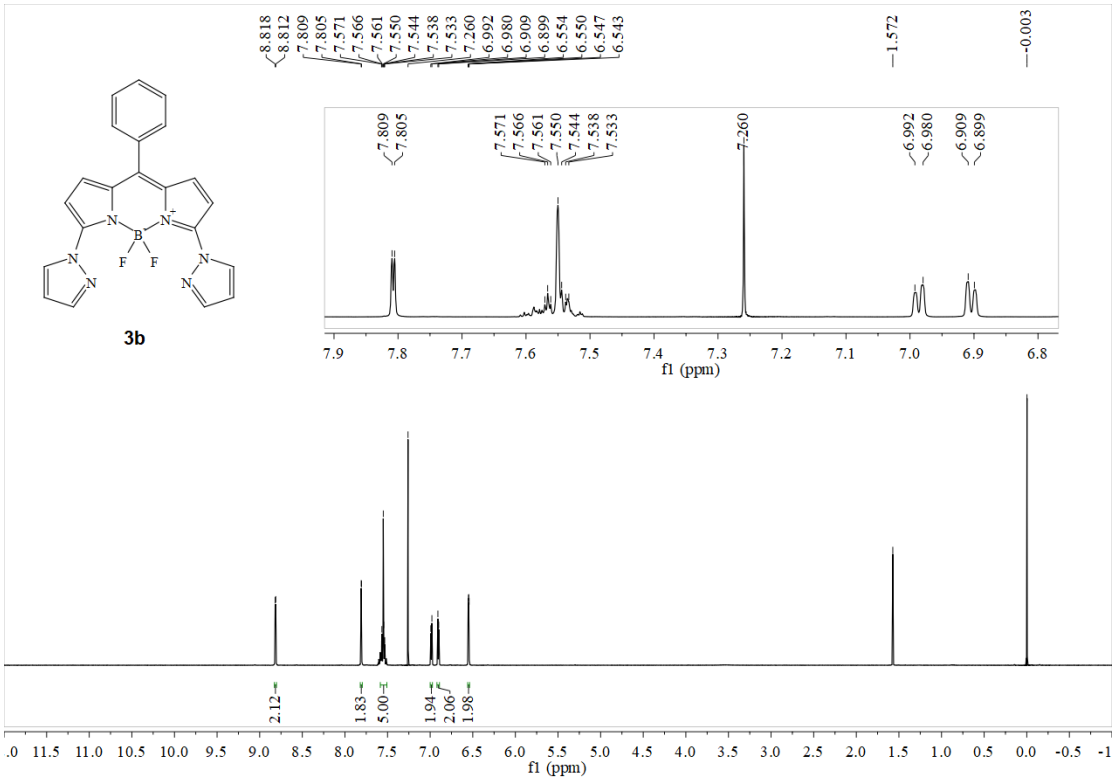
77.16
76.84
21.61
3a
f1 (ppm)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7.571
7.566
7.561
7.550
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7.538
7.533
7.260
6.992
6.980
6.909
6.899
6.554
6.550
6.547
6.543
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0.003
3b
f1 (ppm)
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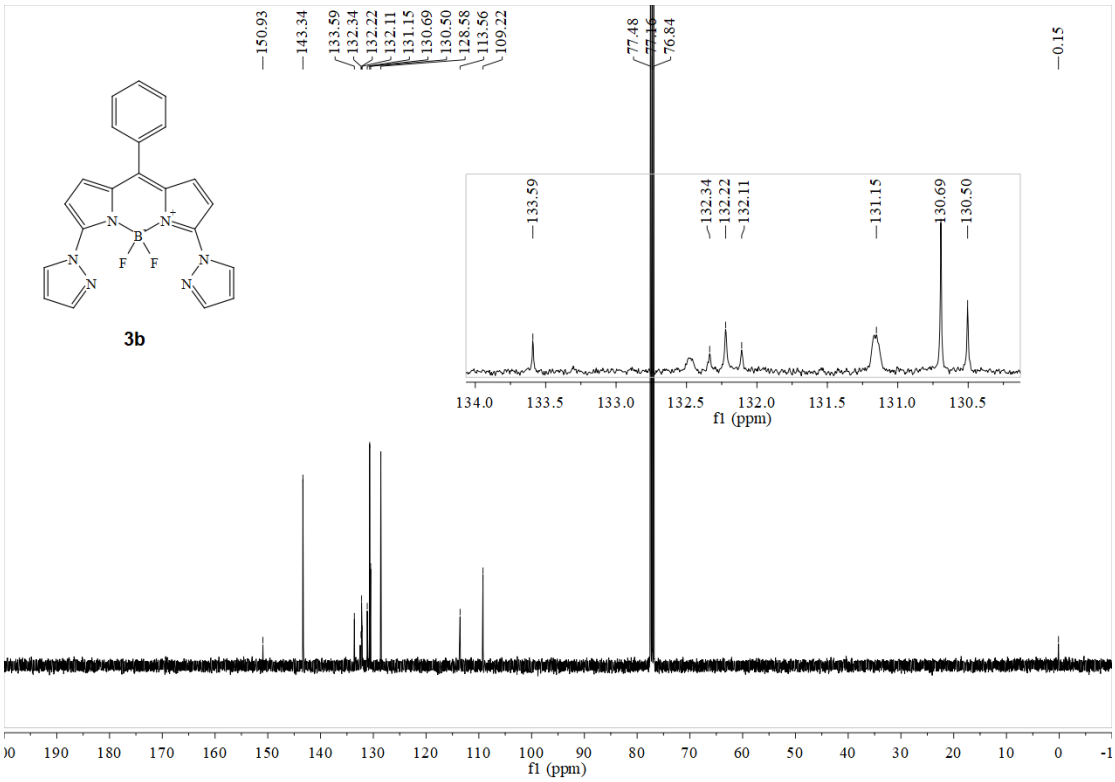
1.83
5.00
1.94
2.06
1.98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132.22
132.11
131.15
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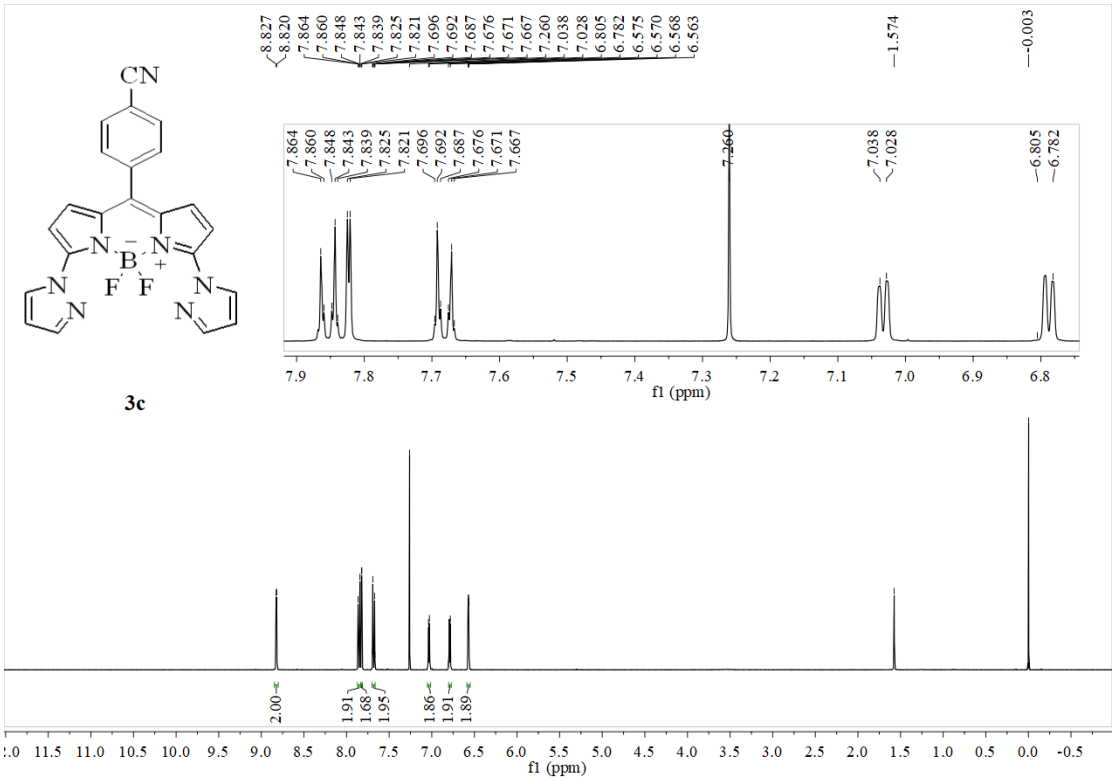
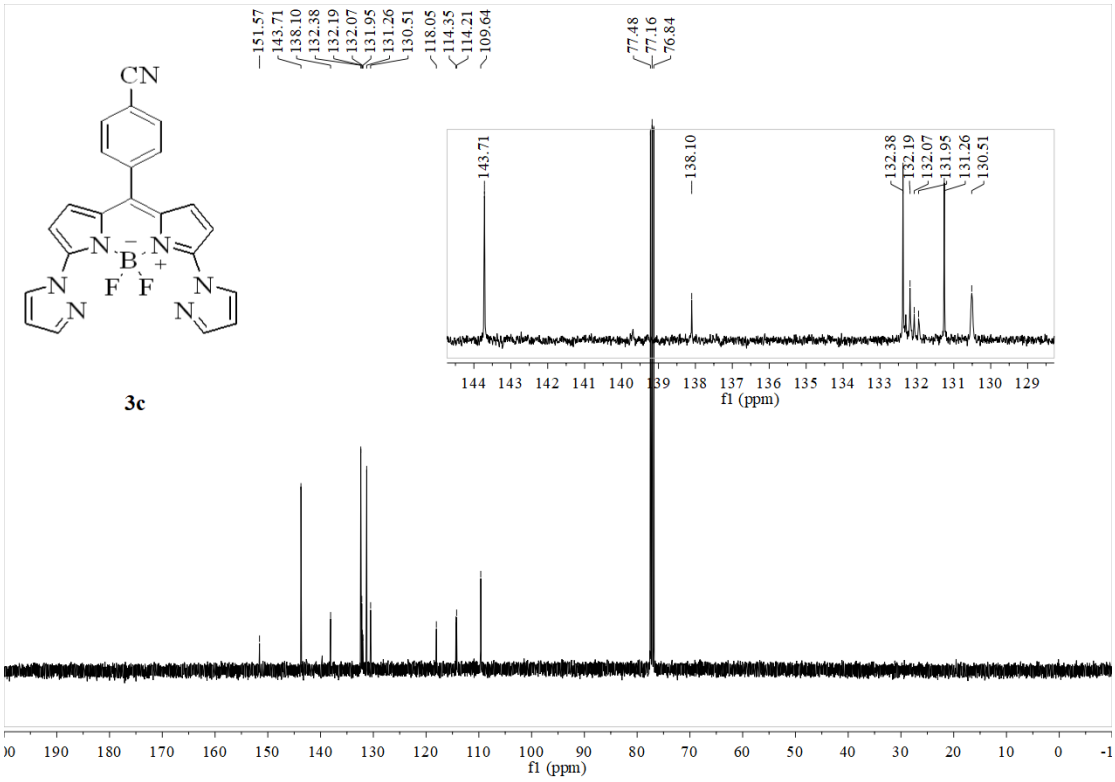
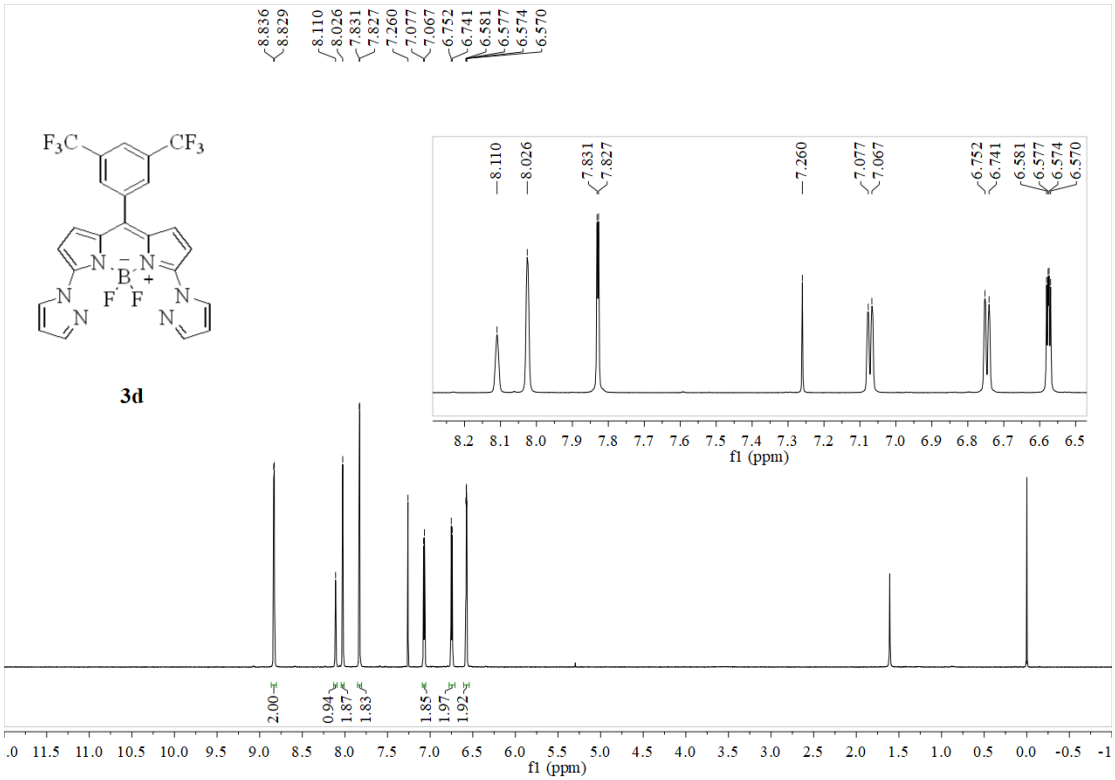
77.48
77.16
76.84
0.15
3b
f1 (ppm)


CN
3c
f1 (ppm)


CN
3c
f1 (ppm)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7.827
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7.067
6.752
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6.581
6.577
6.574
6.570
F3C
CF3
3d
f1 (ppm)
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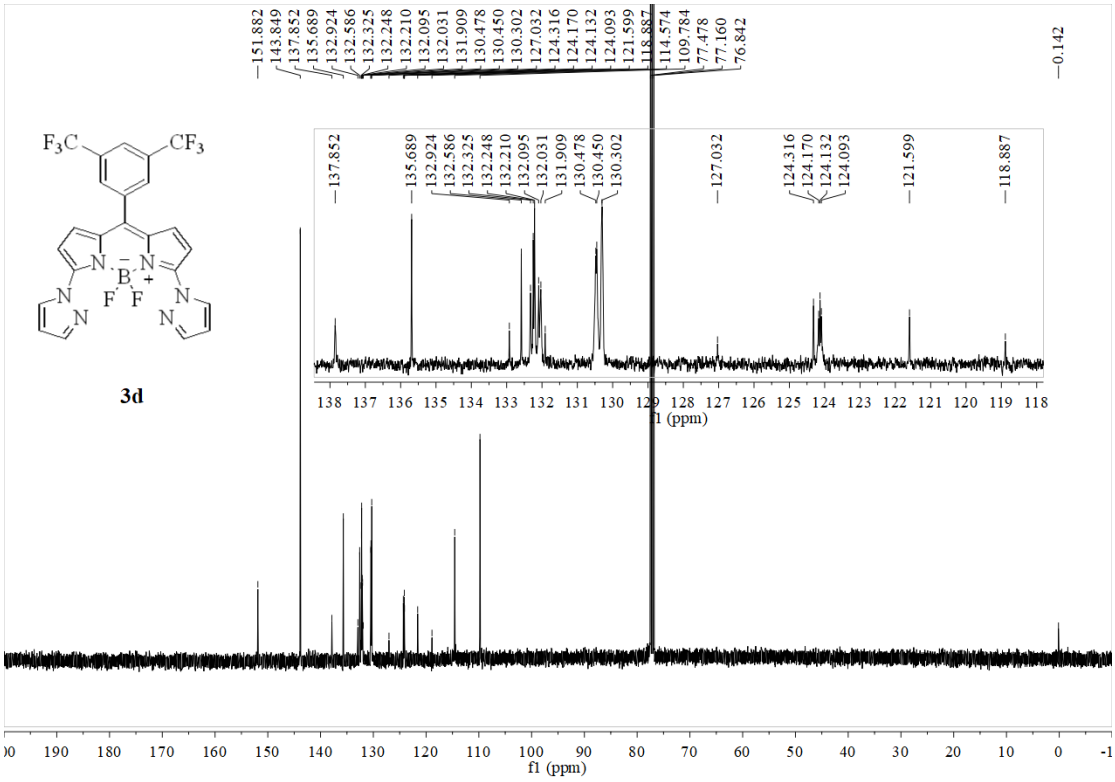
1.85
1.97
1.92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130.450
130.302
127.032
124.316
124.170
124.132
124.093
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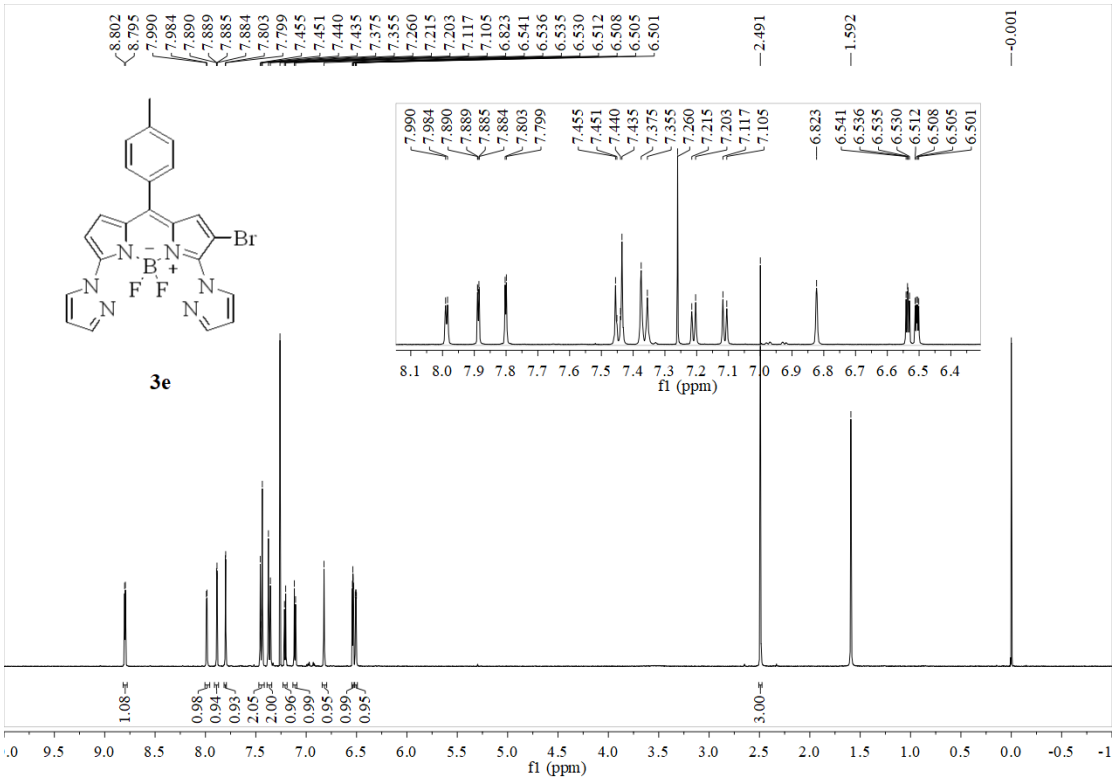
0.142
F3C
CF3
3d
f1 (ppm)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7.355
7.260
7.215
7.203
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7.105
6.823
6.541
6.536
6.535
6.530
6.512
6.508
6.505
6.501
2.491
1.592
0.001
Br
N
B
F
F
3e
f1 (ppm)
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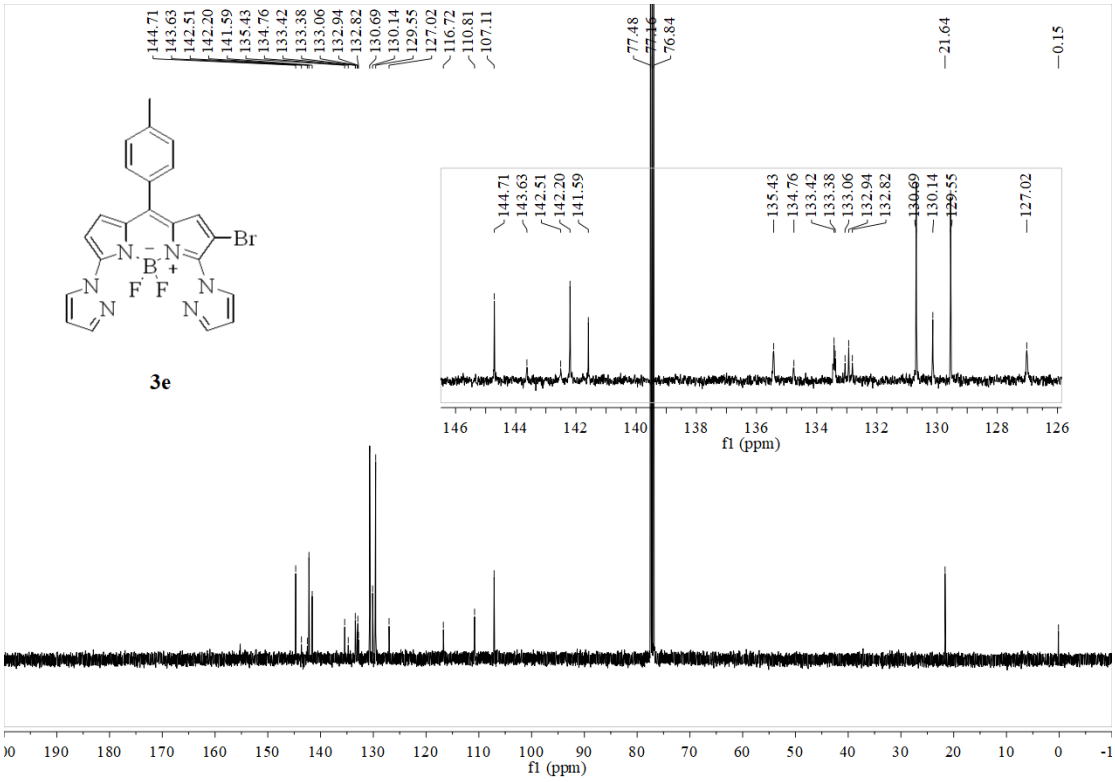
0.98
0.94
0.93
2.05
2.00
0.96
0.99
0.95
0.99
0.95
3.00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135.43
134.76
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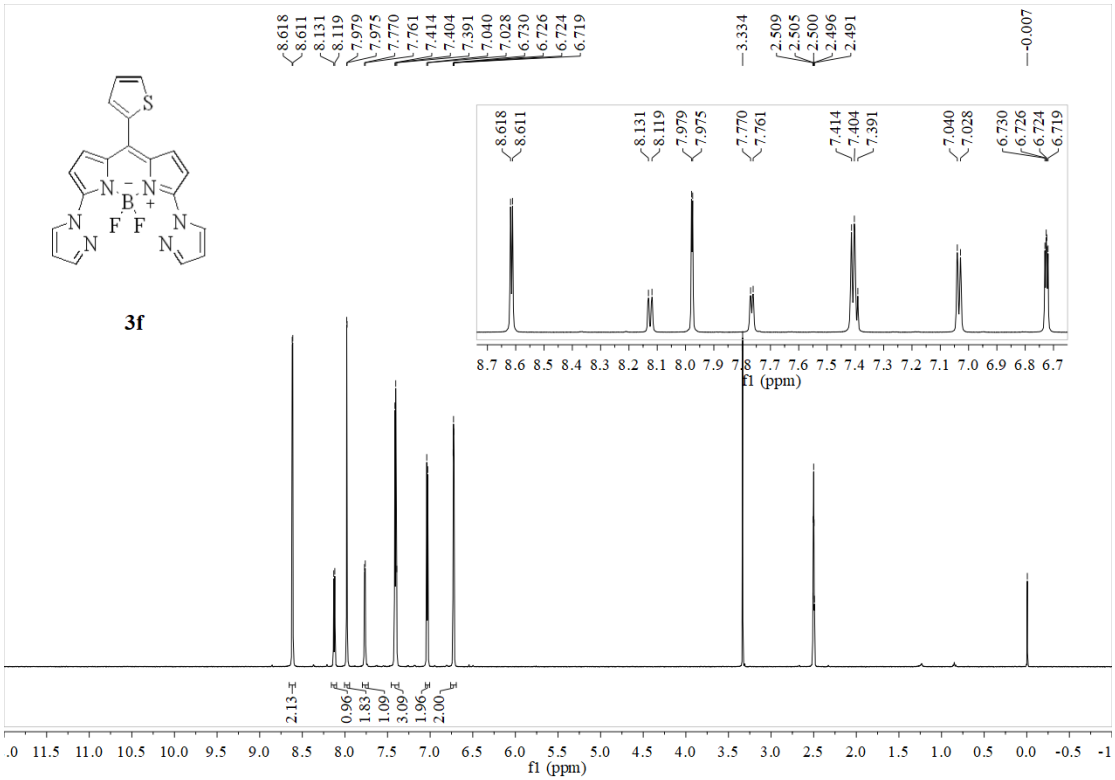
130.69
130.14
129.55
127.02
116.72
110.81
107.11
77.48
77.16
76.84
21.64
0.15
Br
N
B
F
F
3e
f1 (ppm)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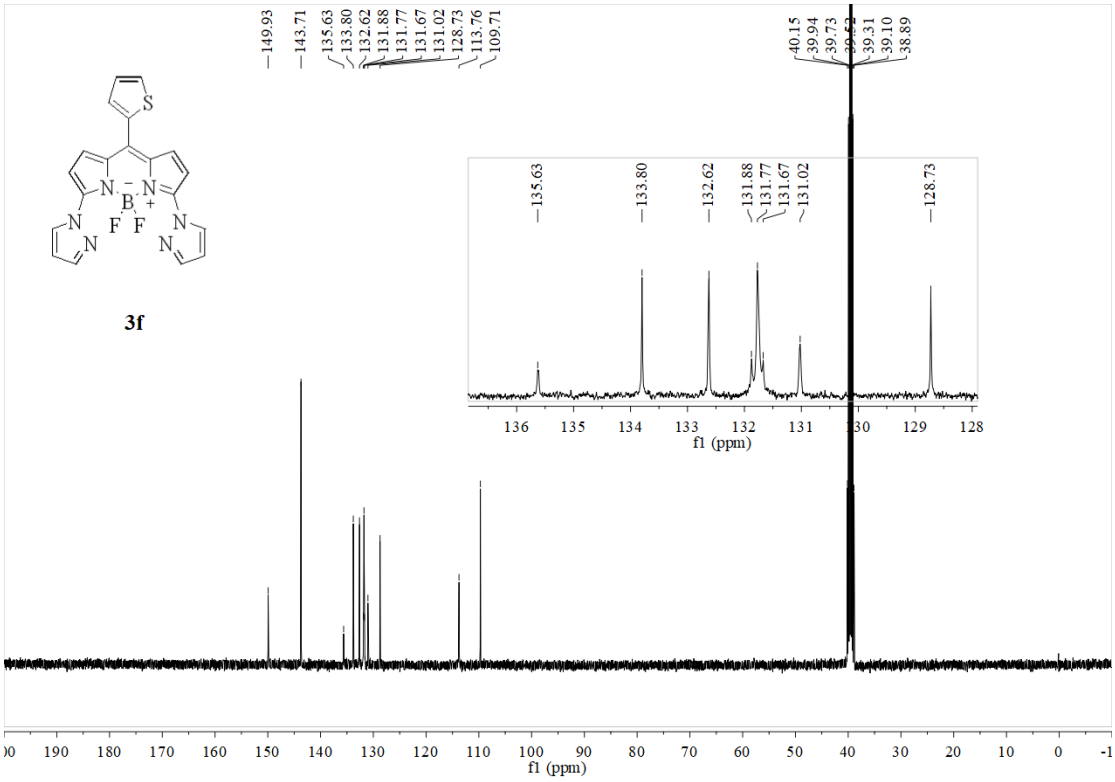
8.611
8.131
8.119
7.979
7.975
7.770
7.761
7.414
7.404
7.391
7.040
7.028
6.730
6.726
6.724
6.719
3.334
2.509
2.505
2.500
2.496
2.491
0.007
3f
2.13
0.96
1.83
1.09
3.09
1.96
2.00
f1 (ppm)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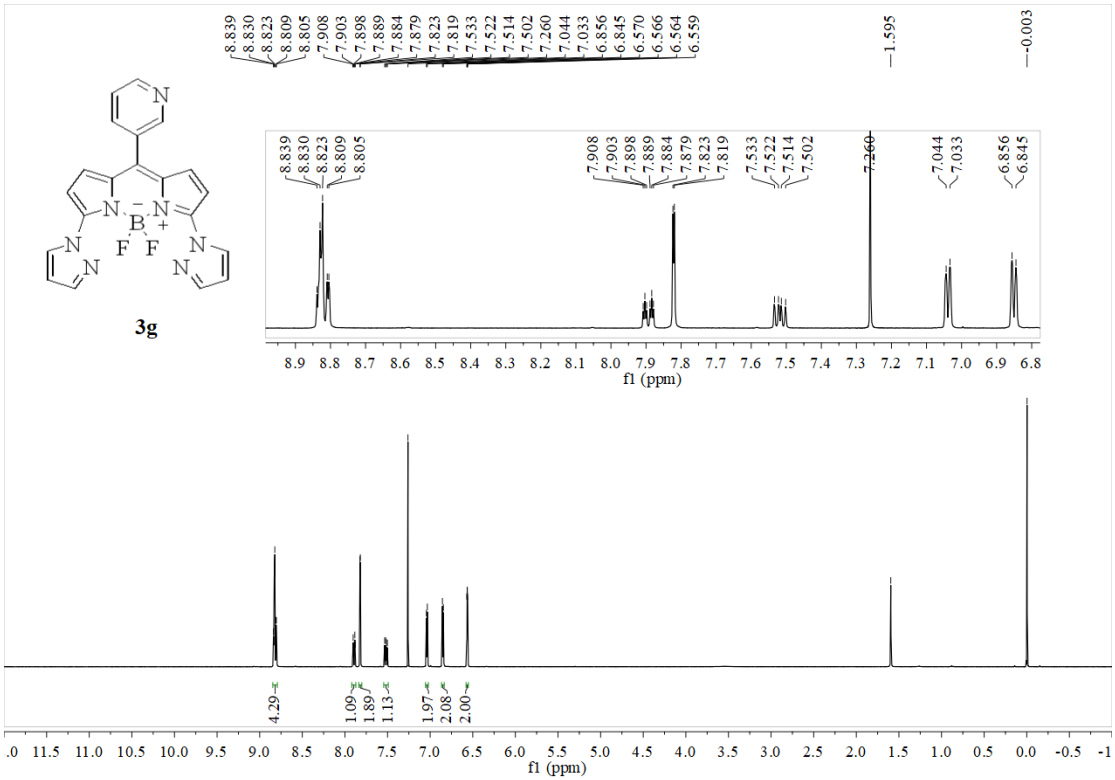
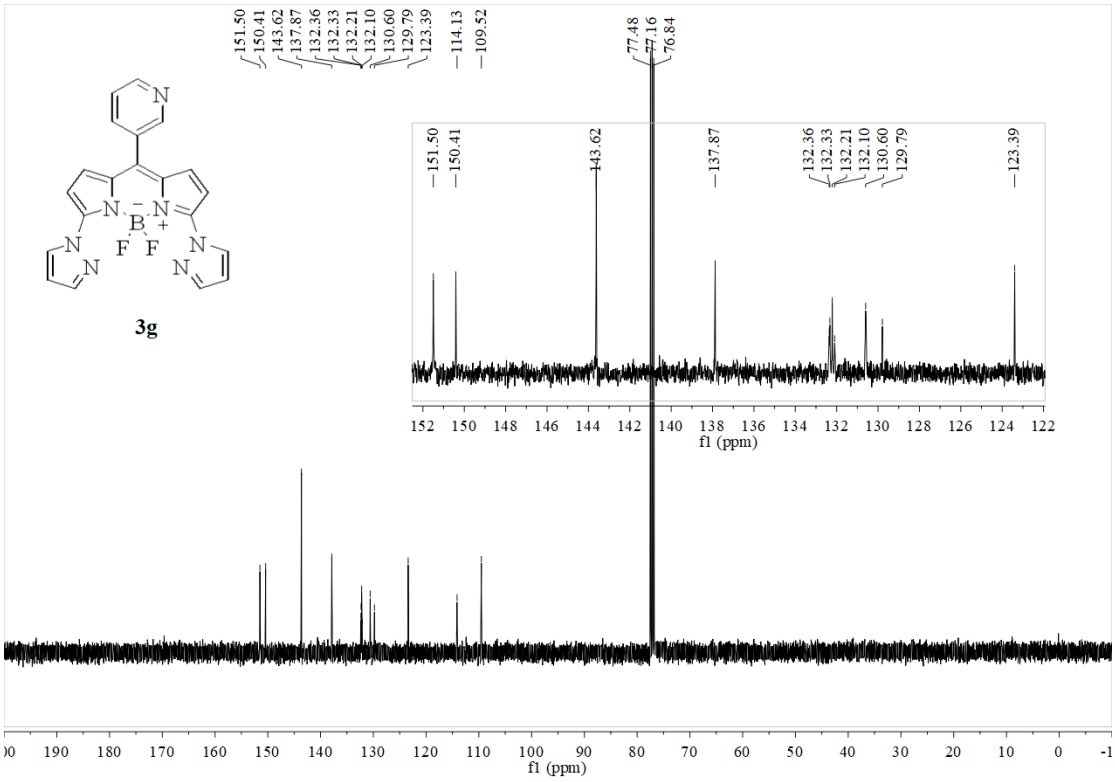
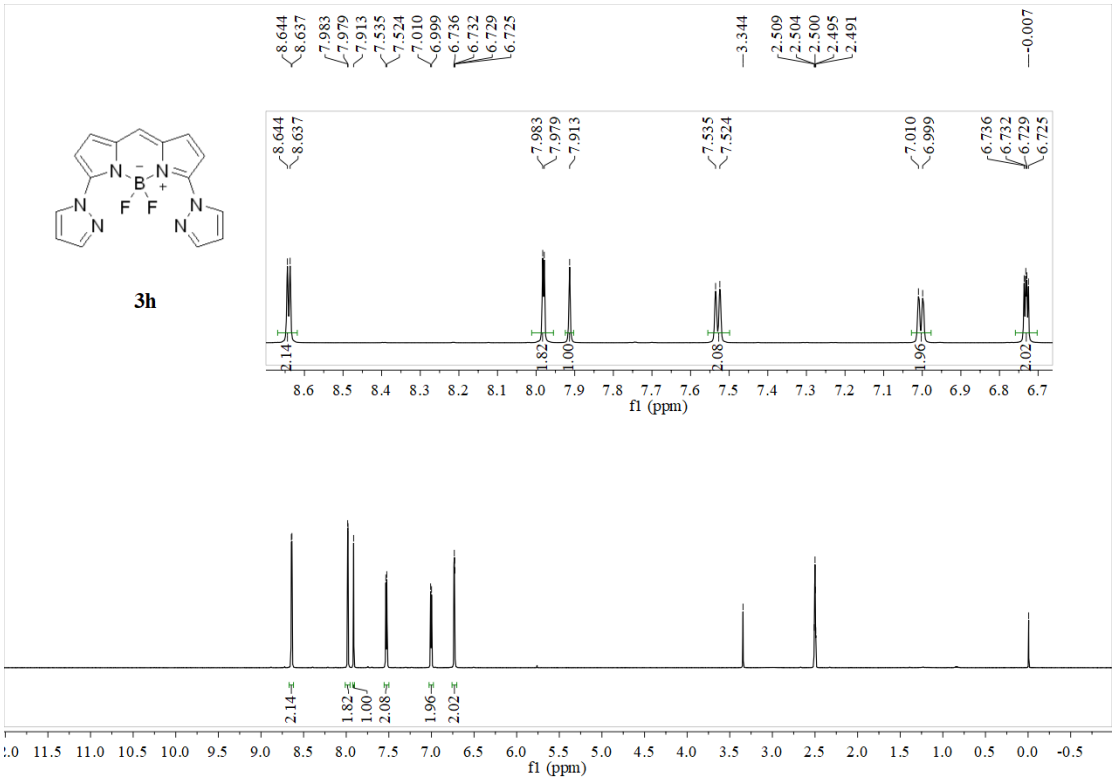
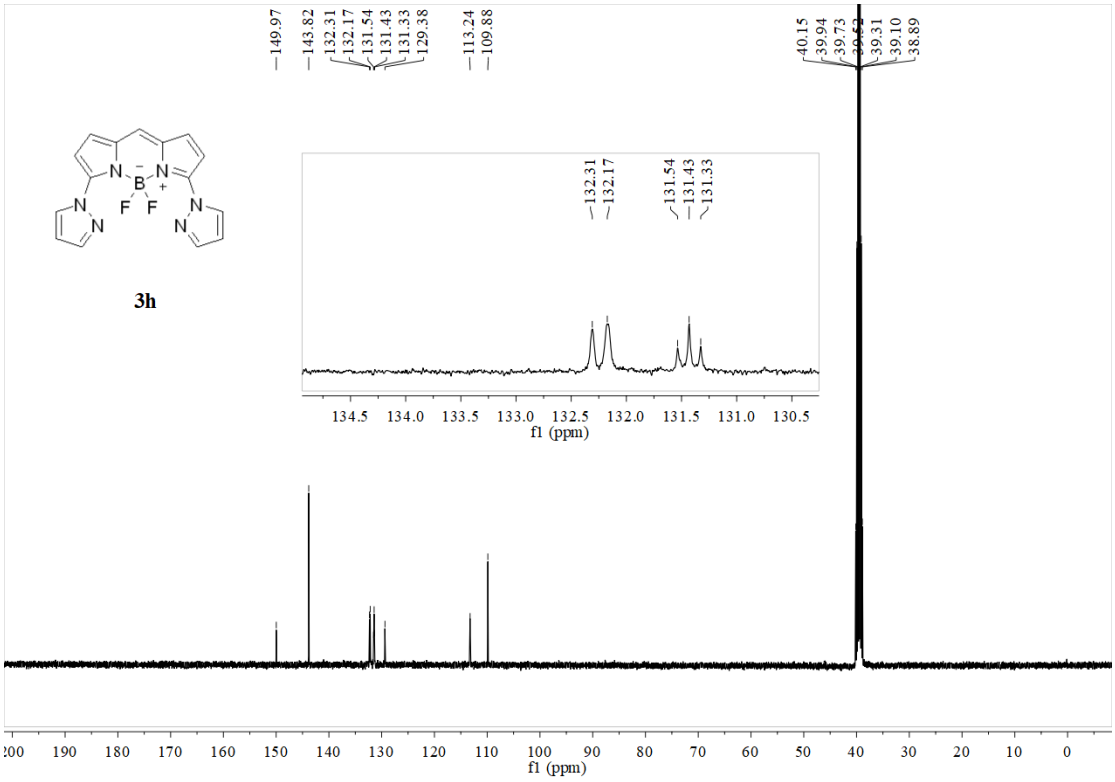
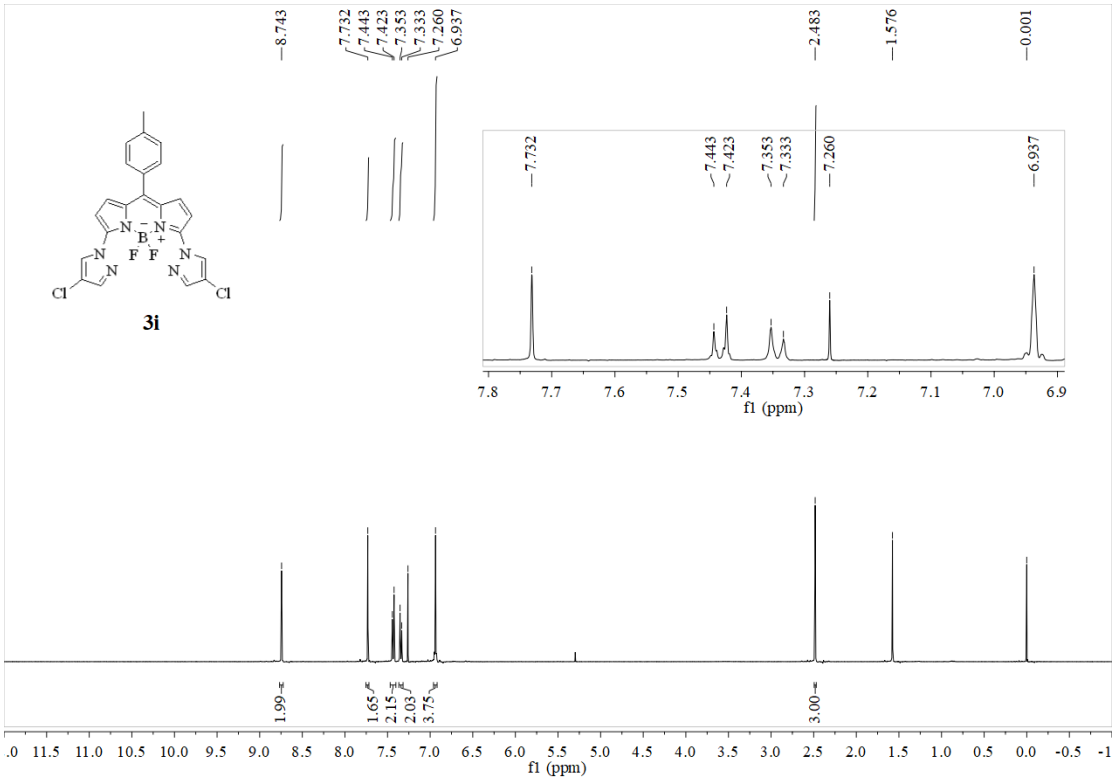
143.71
135.63
133.80
132.62
131.88
131.77
131.67
131.02
128.73
113.76
109.71
40.15
39.94
39.73
39.52
39.31
39.10
38.89
3f
f1 (ppm)


8.839
8.830
8.823
8.809
8.805
7.908
7.903
7.898
7.889
7.884
7.879
7.823
7.819
7.533
7.522
7.514
7.502
7.260
7.044
7.033
6.856
6.845
6.570
6.566
6.564
6.559
1.595
0.003
3g
f1 (ppm)
4.29
1.09
1.89
1.13
1.97
2.08
2.00
f1 (ppm)

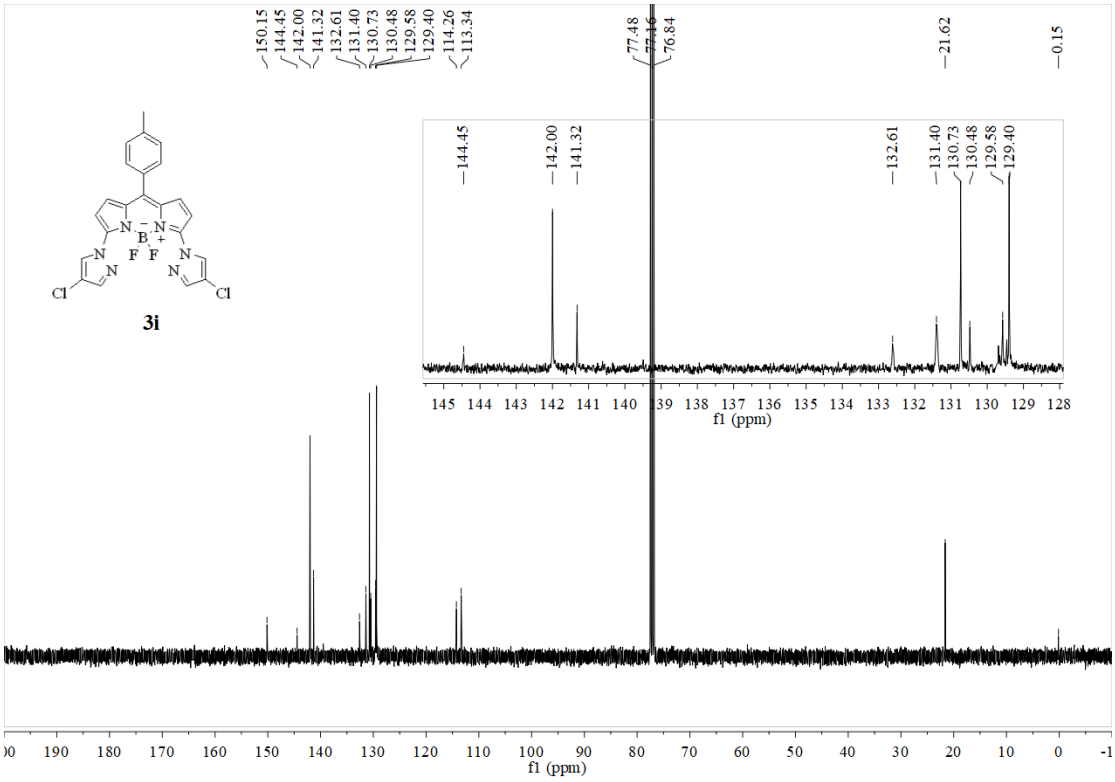

151.50
150.41
143.62
137.87
132.36
132.33
132.21
132.10
130.60
129.79
123.39
114.13
109.52
77.48
77.16
76.84
3g
f1 (ppm)
f1 (ppm)


8.644
8.637
7.983
7.979
7.913
7.535
7.524
7.010
6.999
6.736
6.732
6.729
6.725
3.344
2.509
2.504
2.500
2.495
2.491
0.007
3h
2.14
1.82
1.00
2.08
1.96
2.02
f1 (ppm)

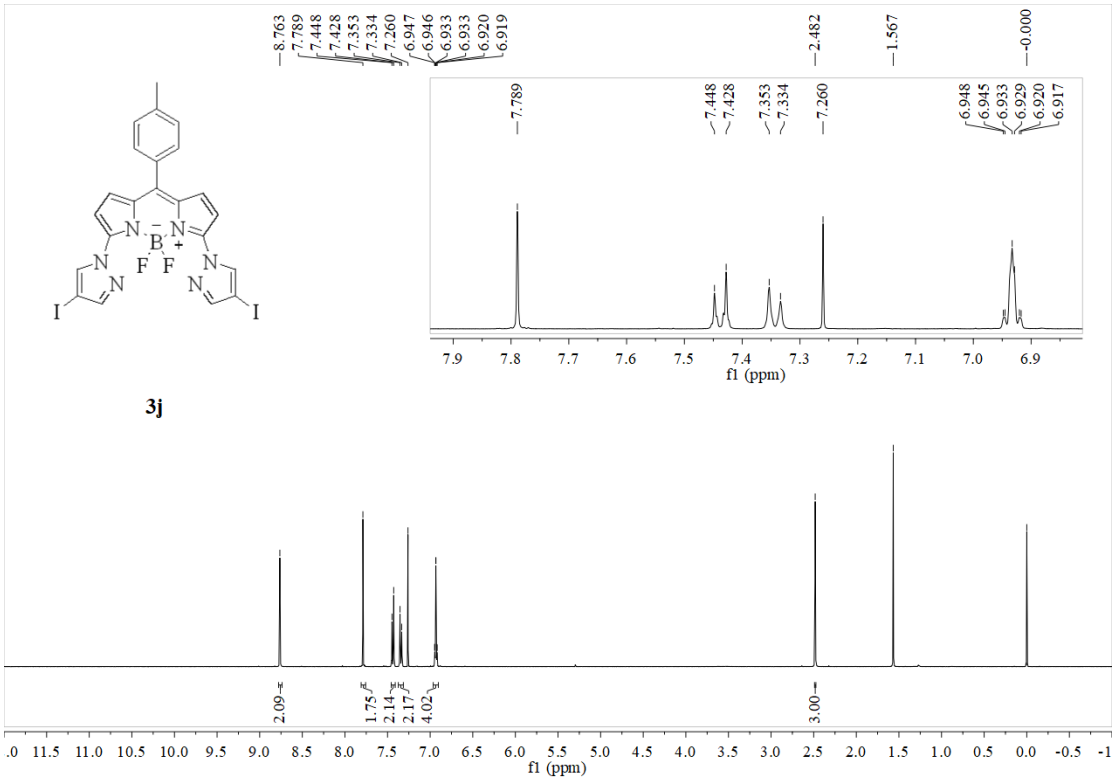

149.97
143.82
132.31
132.17
131.54
131.43
131.33
129.38
113.24
109.88
40.15
39.94
39.73
39.52
39.31
39.10
38.89
3h
f1 (ppm)

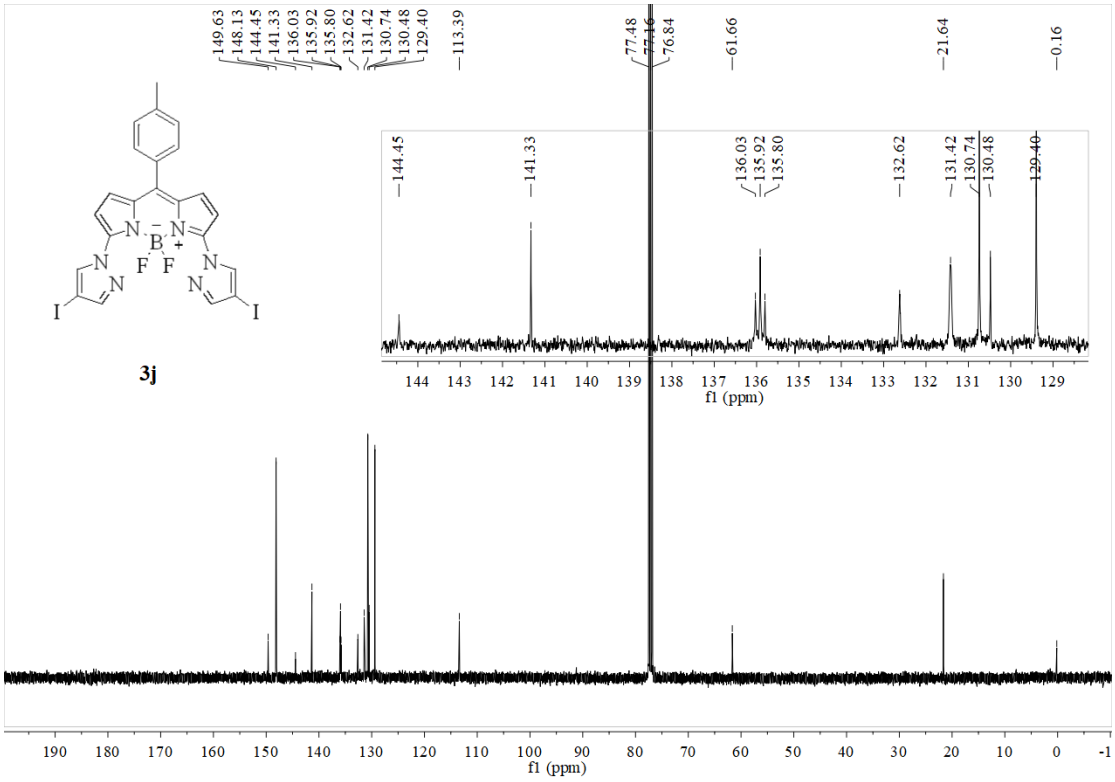

8.743
7.732
7.443
7.423
7.353
7.333
7.260
6.937
2.483
1.576
0.001
1.99
1.65
2.15
2.03
3.75
3.00
f1 (ppm)

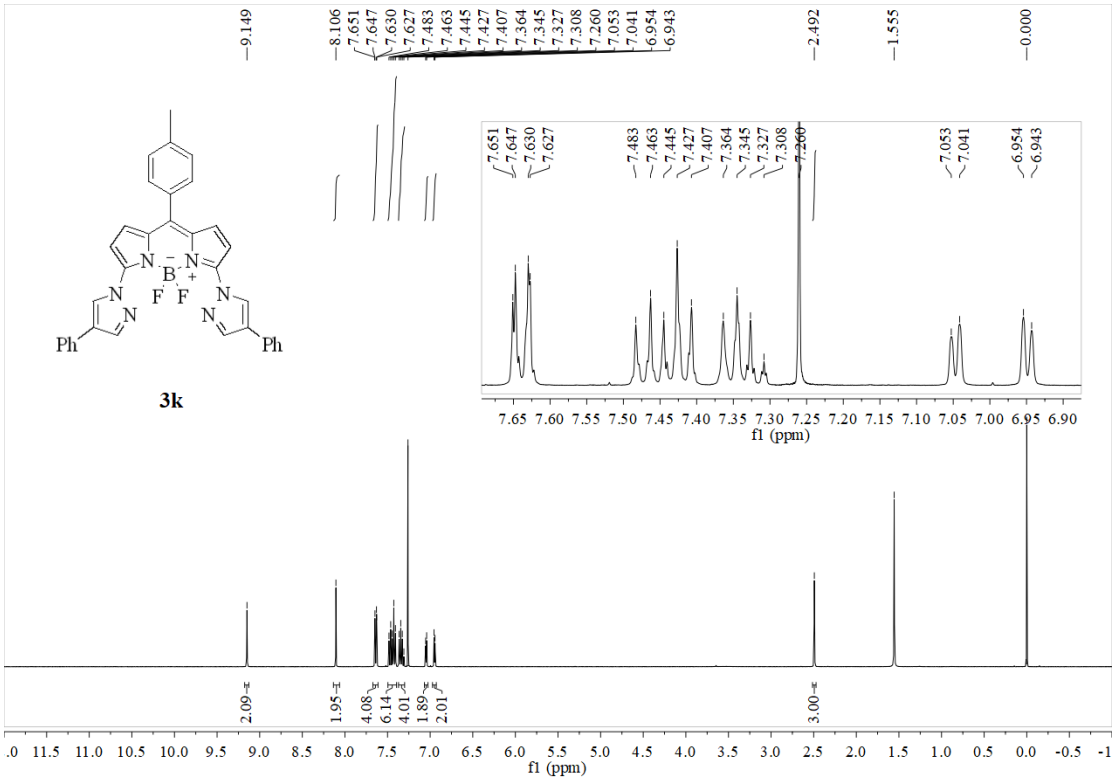
3i

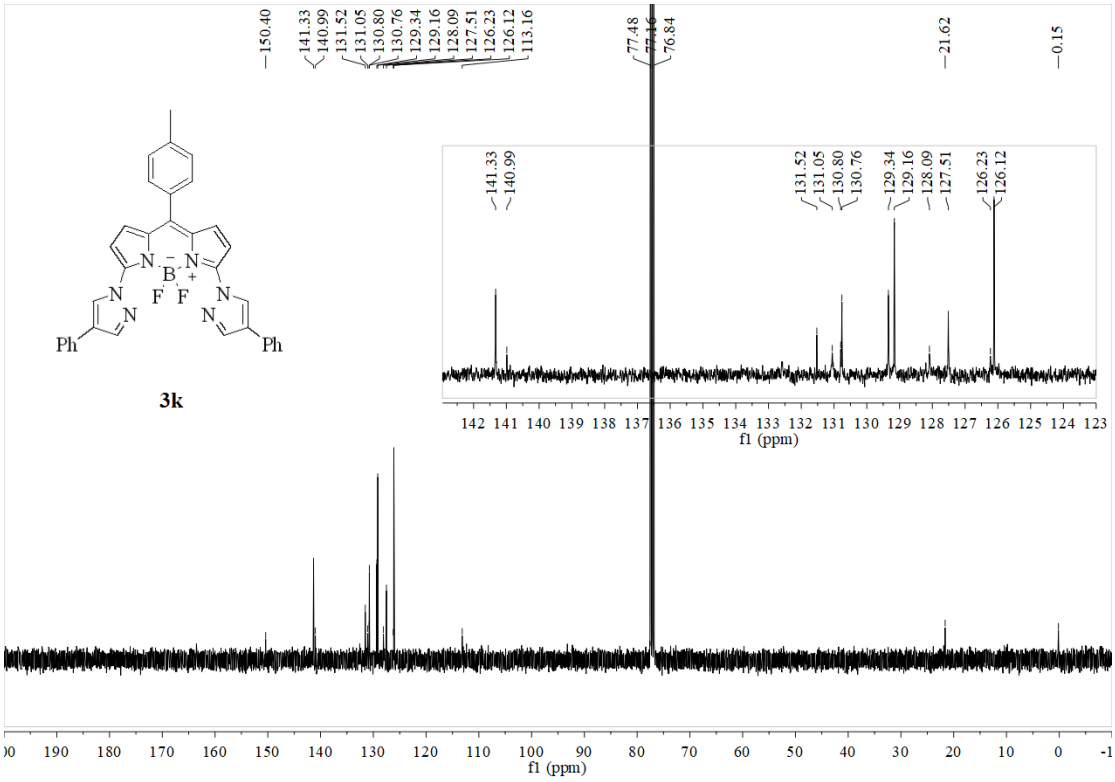

150.15
144.45
142.00
141.32
132.61
131.40
130.73
130.48
129.58
129.40
114.26
113.34
77.48
77.16
76.84
21.62
0.15
f1 (ppm)

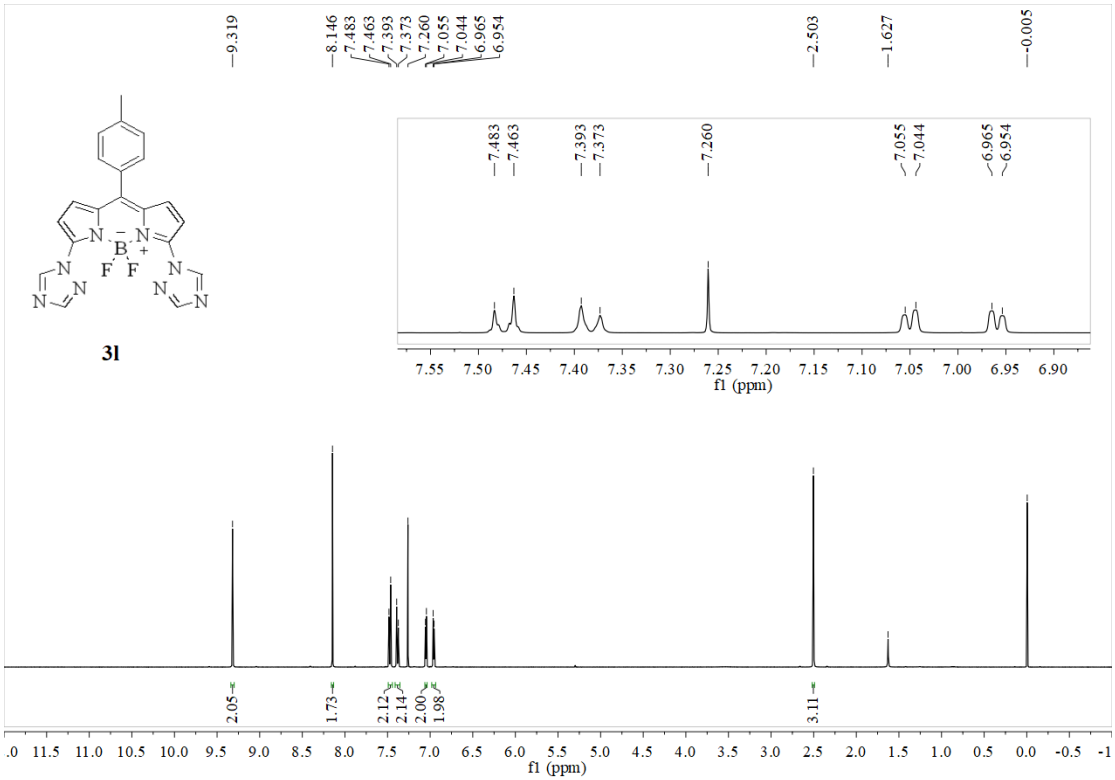
3i

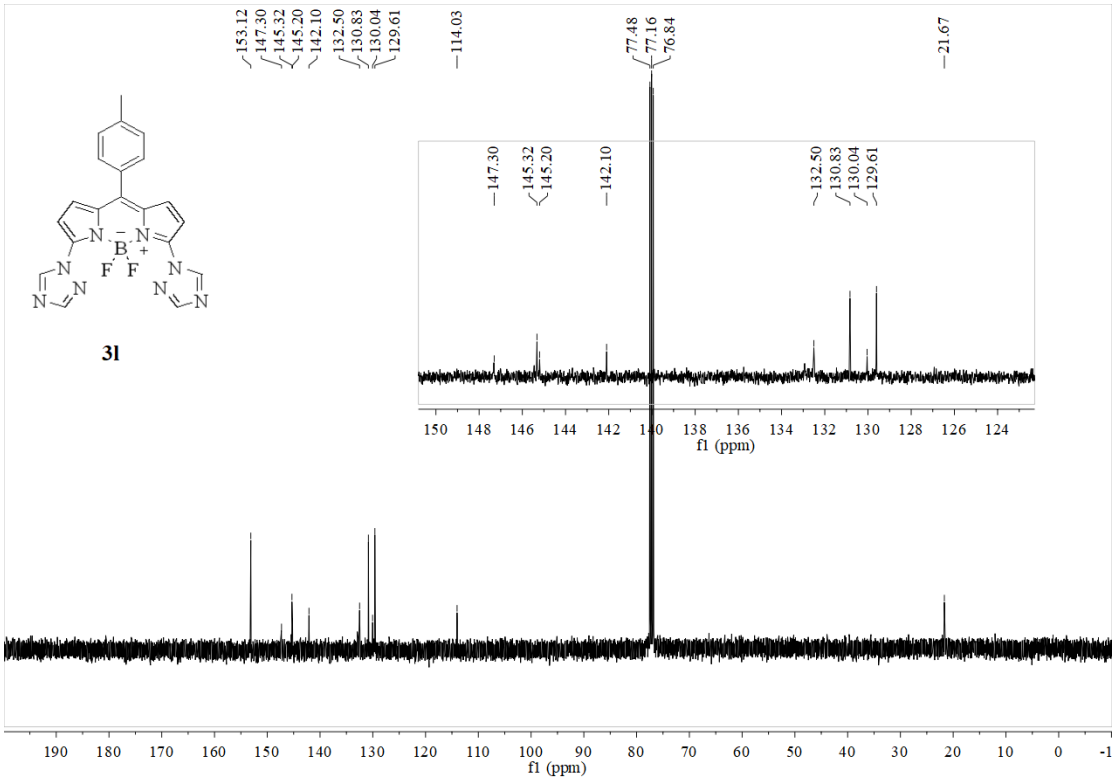

8.763
7.789
7.448
7.428
7.353
7.334
7.260
6.947
6.946
6.933
6.933
6.920
6.919
2.482
1.567
0.000
7.789
7.448
7.428
7.353
7.334
7.260
6.948
6.945
6.933
6.929
6.920
6.917
f1 (ppm)
3j
2.09
1.75
2.14
2.17
4.02
3.00
f1 (ppm)

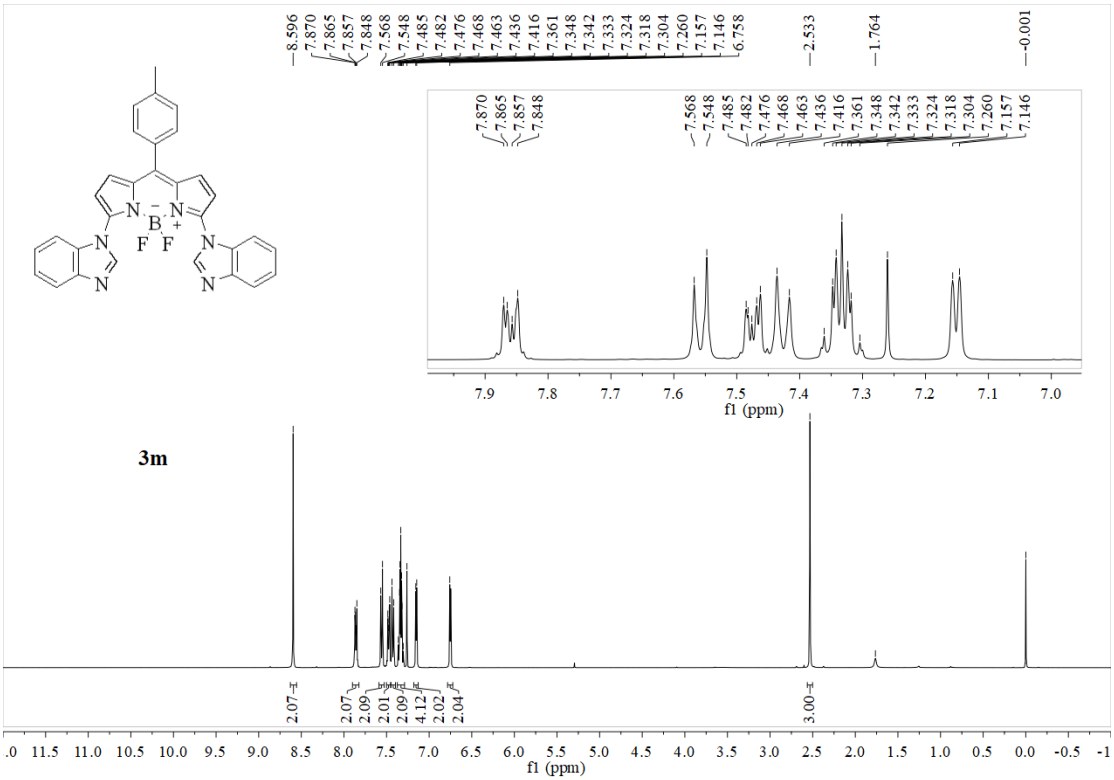

149.63
148.13
144.45
141.33
136.03
135.92
135.80
132.62
131.42
130.74
130.48
129.40
113.39
77.48
77.16
76.84
61.66
21.64
0.16
144.45
141.33
136.03
135.92
135.80
132.62
131.42
130.74
130.48
129.40
f1 (ppm)
3j
f1 (ppm)


9.149
8.106
7.651
7.647
7.630
7.627
7.483
7.463
7.445
7.427
7.407
7.364
7.345
7.327
7.308
7.260
7.053
7.041
6.954
6.943
2.492
1.555
0.000
Ph
Ph
3k
f1 (ppm)
2.09
1.95
4.08
6.14
4.01
1.89
2.01
3.00


150.40
141.33
140.99
131.52
131.05
130.80
130.76
129.34
129.16
128.09
127.51
126.23
126.12
113.16
77.48
77.16
76.84
21.62
0.15
Ph
Ph
3k
f1 (ppm)


9.319
8.146
7.483
7.463
7.393
7.373
7.260
7.055
7.044
6.965
6.954
2.503
1.627
0.005
3l
2.05
1.73
2.12
2.14
2.00
1.98
3.11
f1 (ppm)


153.12
147.30
145.32
145.20
142.10
132.50
130.83
130.04
129.61
114.03
77.48
77.16
76.84
21.67
3l
f1 (ppm)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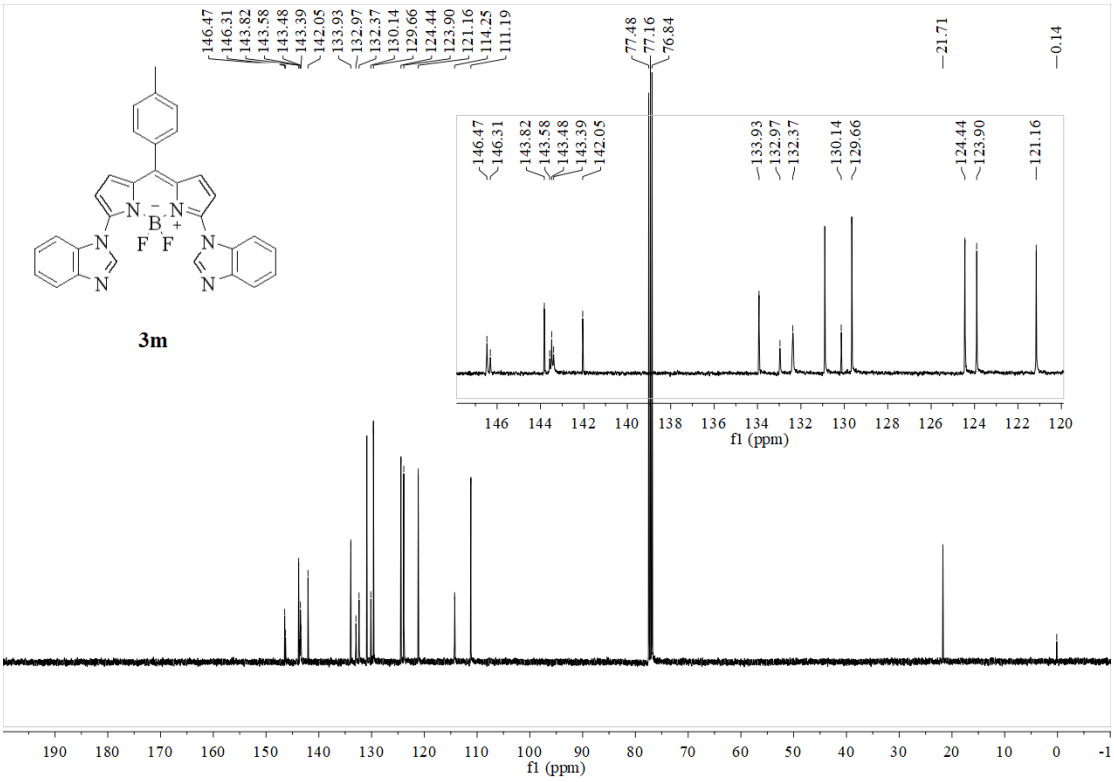
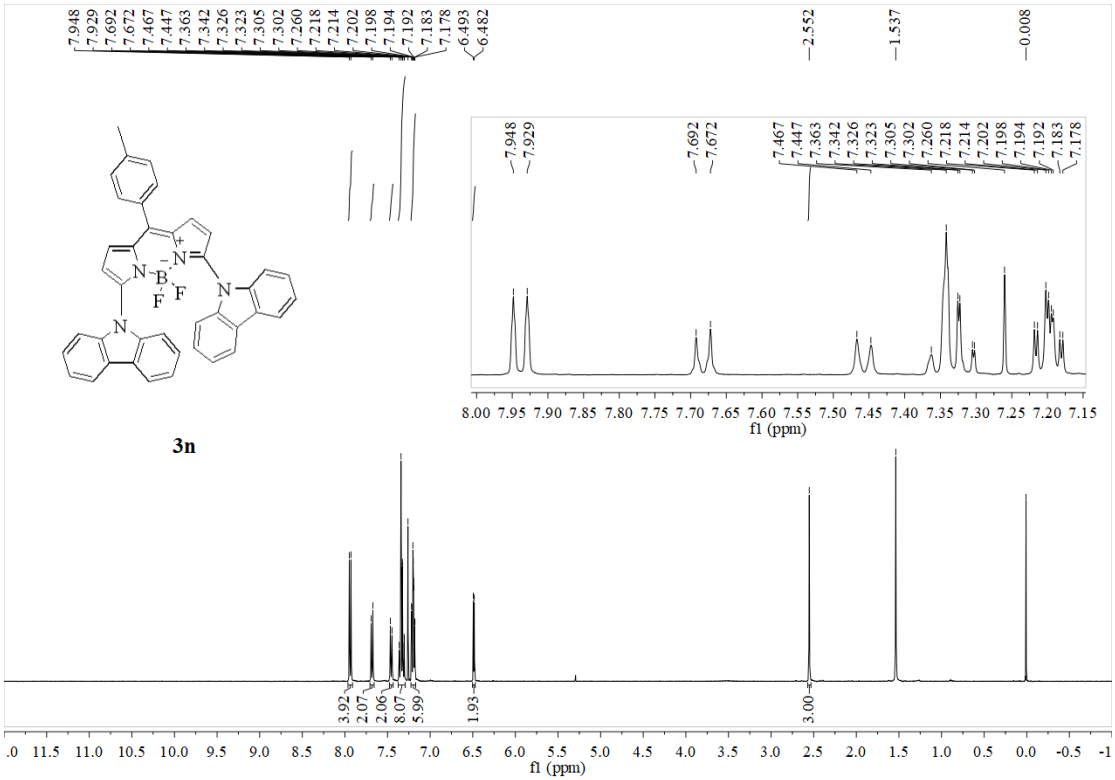
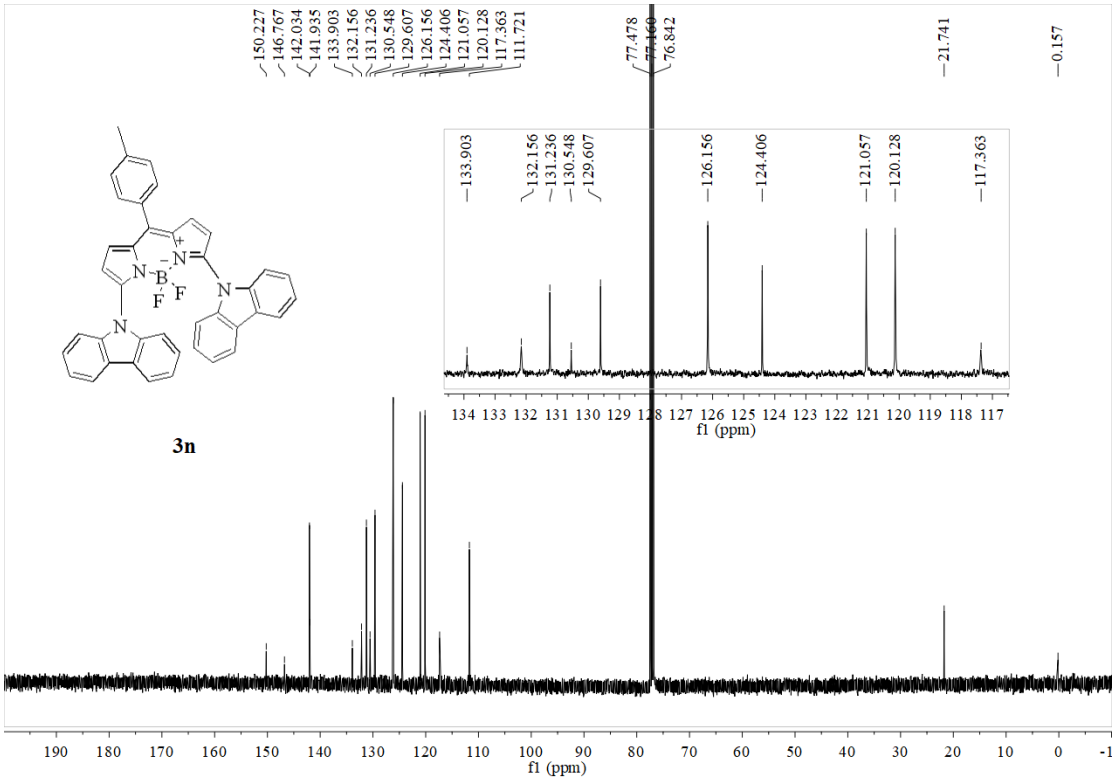
7.870
7.865
7.857
7.848
7.568
7.548
7.485
7.482
7.476
7.468
7.463
7.436
7.416
7.361
7.348
7.342
7.333
7.324
7.318
7.304
7.260
7.157
7.146
6.758
2.533
1.764
0.001
3m
f1 (ppm)
2.07
2.07
2.09
2.01
2.09
4.12
2.02
2.04
3.00


146.47
146.31
143.82
143.58
143.48
143.39
142.05
133.93
132.97
132.37
130.14
129.66
124.44
123.90
121.16
114.25
111.19
77.48
77.16
76.84
21.71
0.14
3m
f1 (ppm)


7.948
7.929
7.692
7.672
7.467
7.447
7.363
7.342
7.326
7.323
7.305
7.302
7.260
7.218
7.214
7.202
7.198
7.194
7.192
7.183
7.178
6.493
6.482
2.552
1.537
0.008
3n
3.92
2.07
2.06
8.07
5.99
1.93
3.00
fl (ppm)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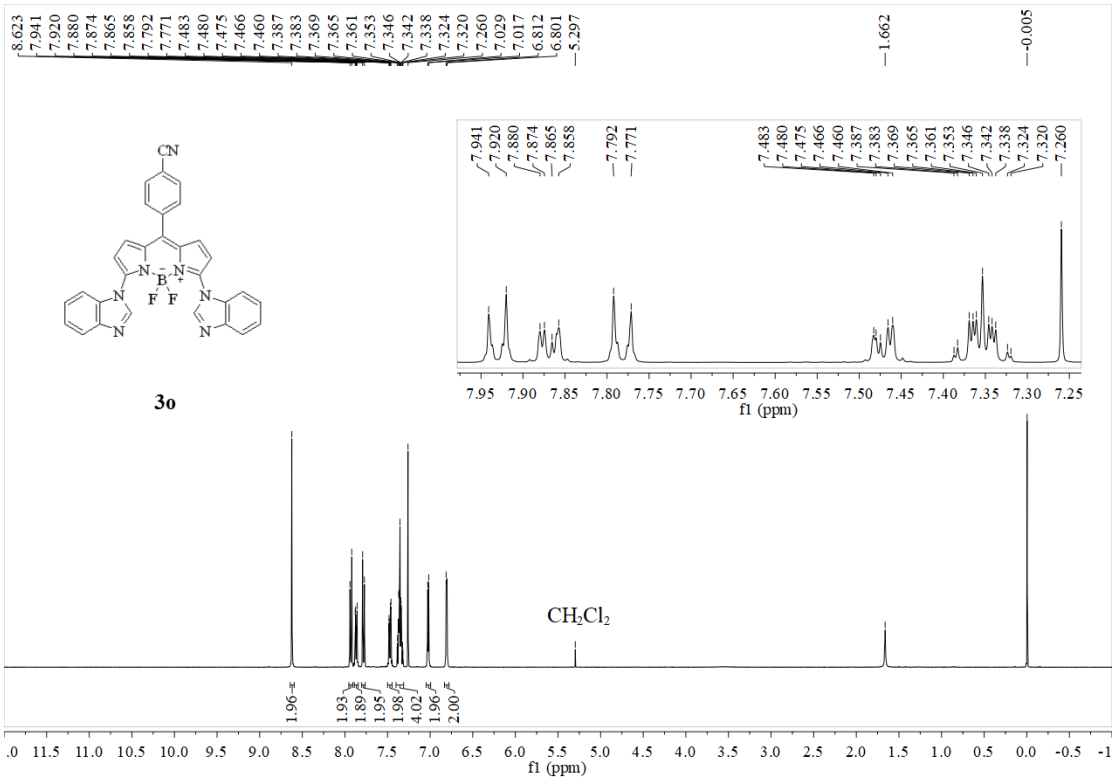
141.935
133.903
132.156
131.236
130.548
129.607
126.156
124.406
121.057
120.128
117.363
111.721
77.478
77.160
76.842
21.741
0.157
3n
fl (ppm)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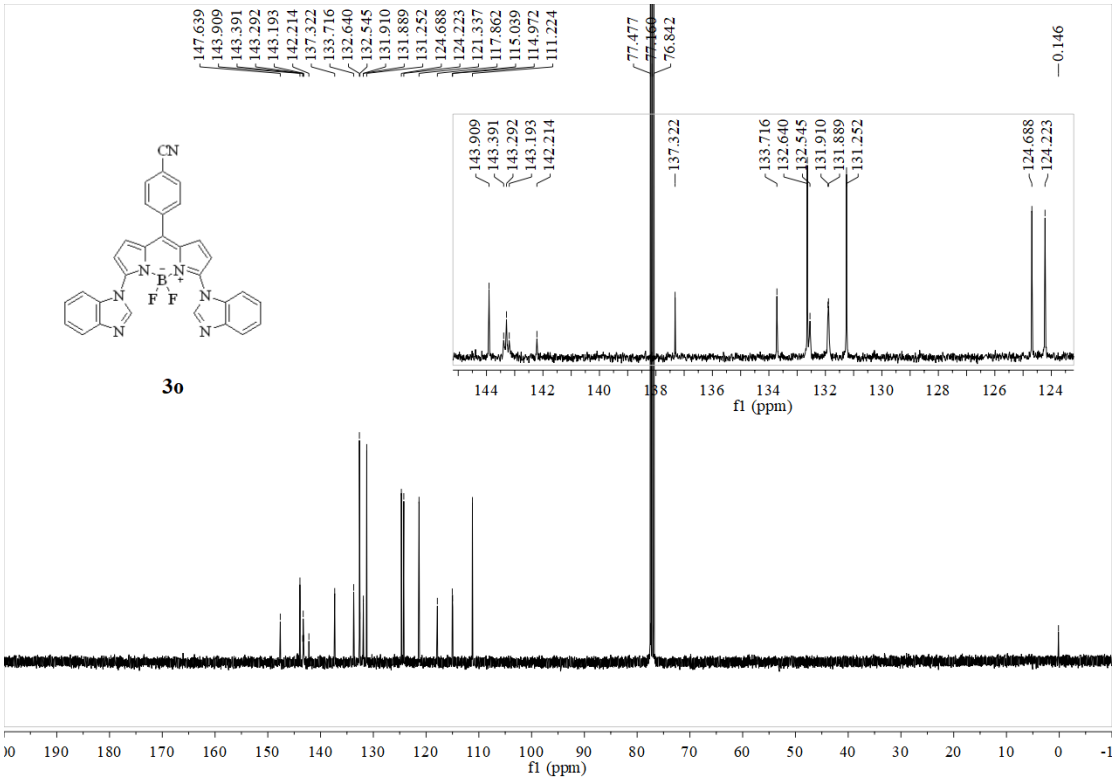
7.880
7.874
7.865
7.858
7.792
7.771
7.483
7.480
7.475
7.466
7.460
7.387
7.383
7.369
7.365
7.361
7.353
7.346
7.342
7.338
7.324
7.320
7.260
7.029
7.017
6.812
6.801
5.297
1.662
0.005
3o
CH2Cl2
1.96
1.93
1.89
1.95
1.98
4.02
1.96
2.00
f1 (ppm)


147.639
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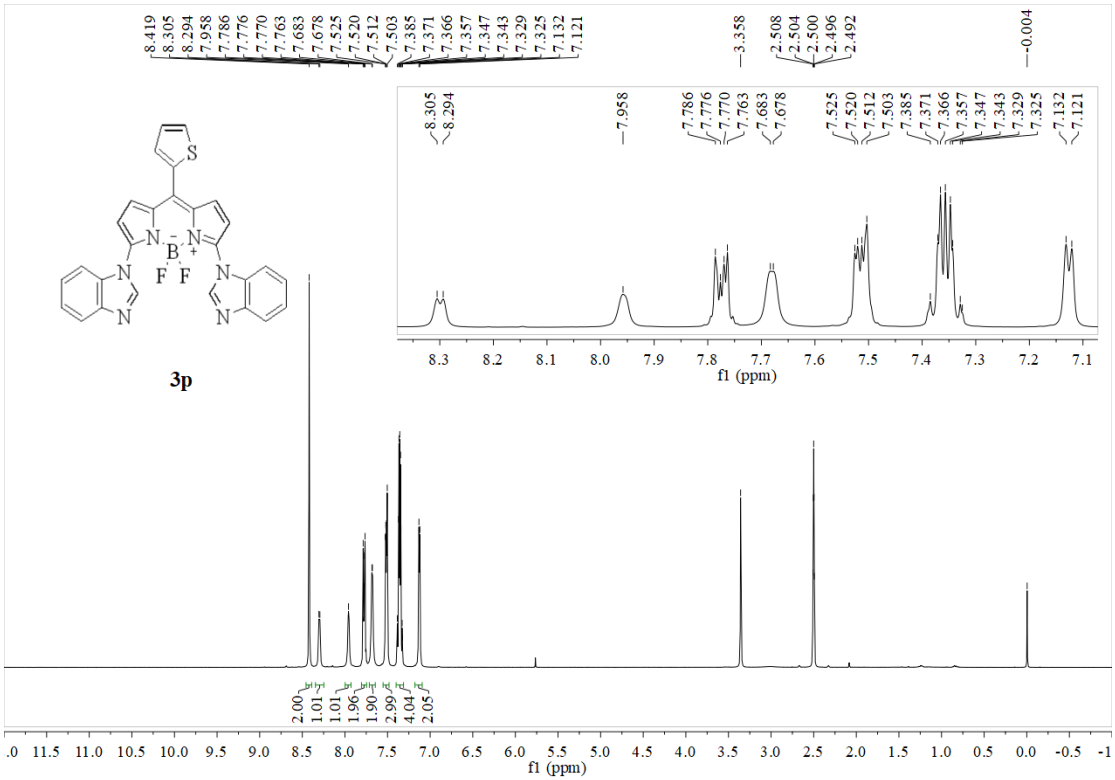
143.391
143.292
143.193
142.214
137.322
133.716
132.640
132.545
131.910
131.889
131.252
124.688
124.223
121.337
117.862
115.039
114.972
111.224
77.477
77.160
76.842
0.146
3o
f1 (ppm)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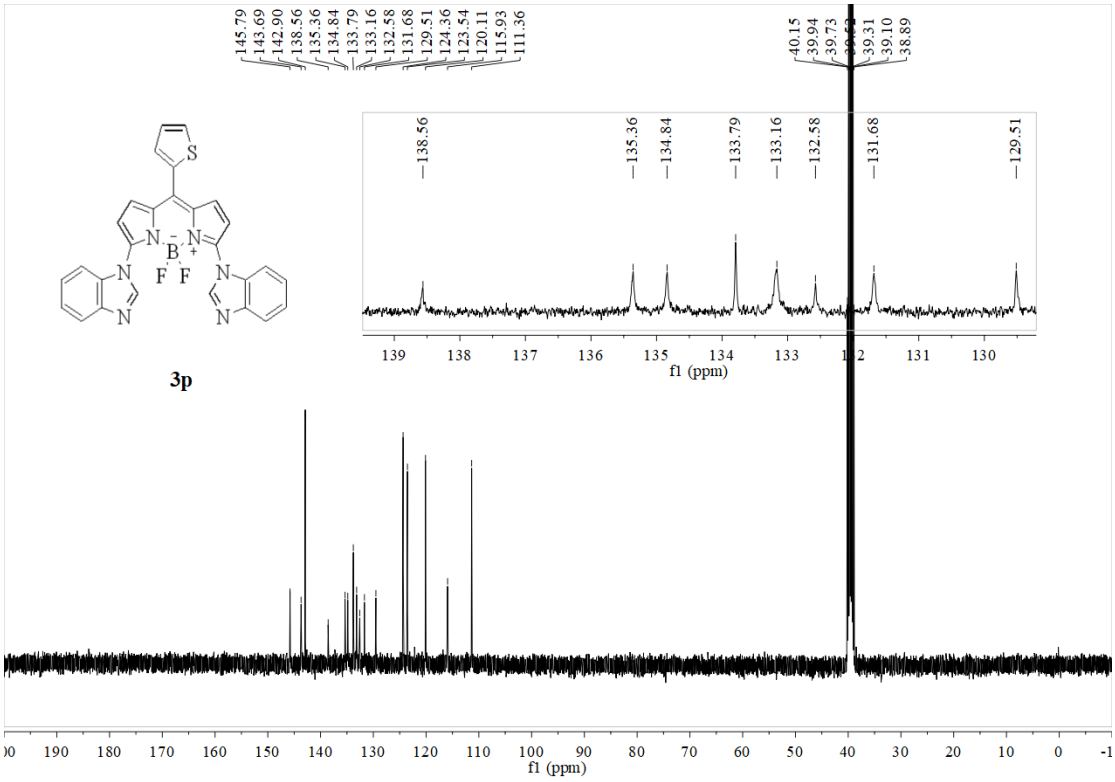
8.294
7.958
7.786
7.776
7.770
7.763
7.683
7.678
7.525
7.520
7.512
7.503
7.385
7.371
7.366
7.357
7.347
7.343
7.329
7.325
7.132
7.121
3.358
2.508
2.504
2.500
2.496
2.492
-0.004
2.00
1.01
1.01
1.96
1.90
2.99
4.04
2.05
f1 (ppm)

3p


145.79
143.69
142.90
138.56
135.36
134.84
133.79
133.16
132.58
131.68
129.51
124.36
123.54
120.11
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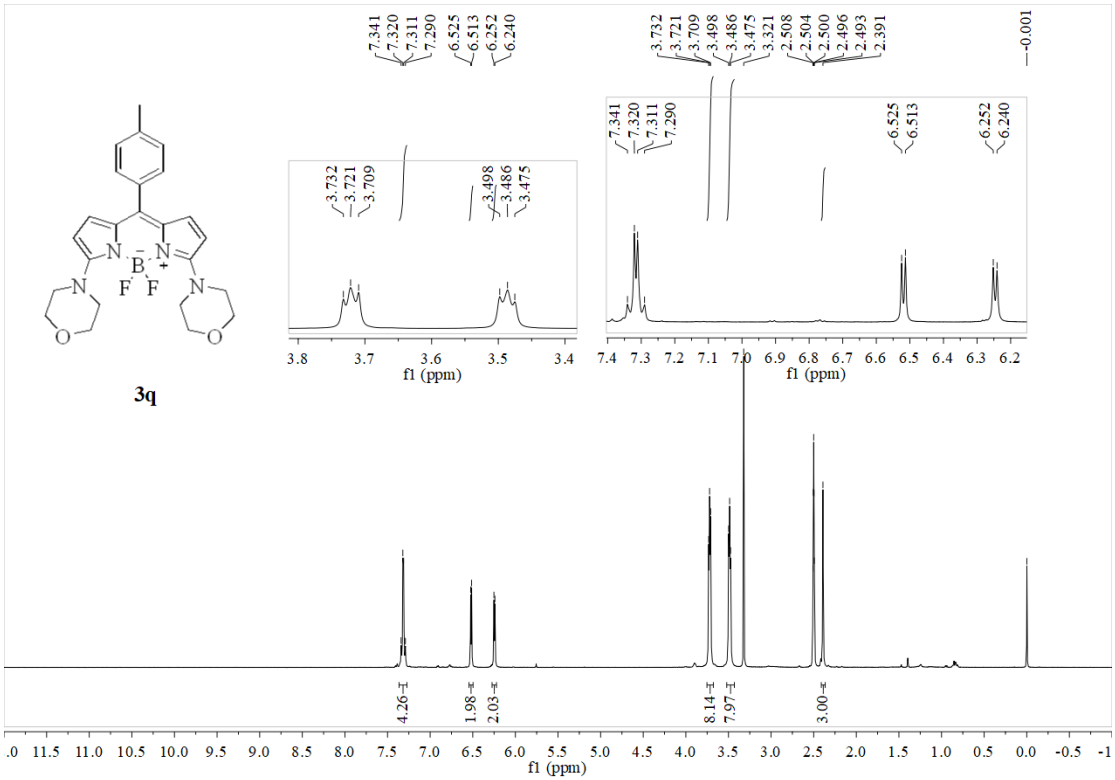
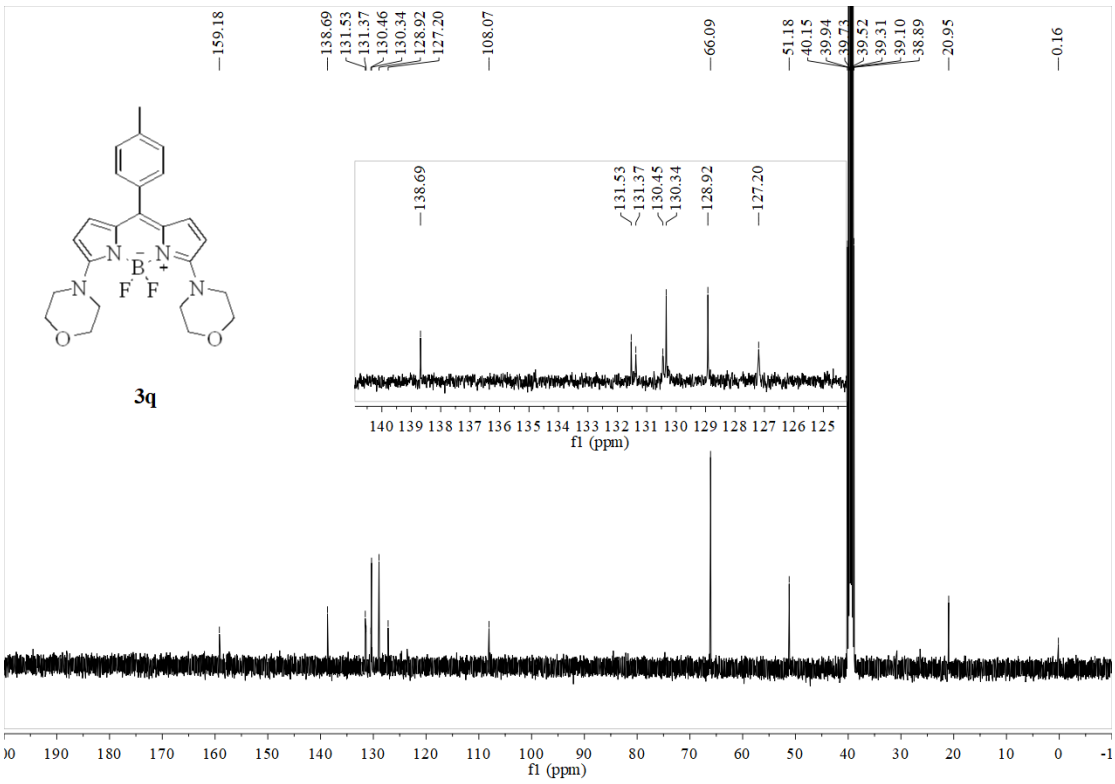
39.94
39.73
39.52
39.31
39.10
38.89
f1 (ppm)

3p


7.341
7.320
7.311
7.290
6.525
6.513
6.252
6.240
3.732
3.721
3.709
3.498
3.486
3.475
3.321
2.508
2.504
2.500
2.496
2.493
2.391
-0.001
4.26
1.98
2.03
8.14
7.97
3.00
f1 (ppm)

3q


159.18
138.69
131.53
131.37
130.46
130.34
128.92
127.20
108.07
66.09
51.18
40.15
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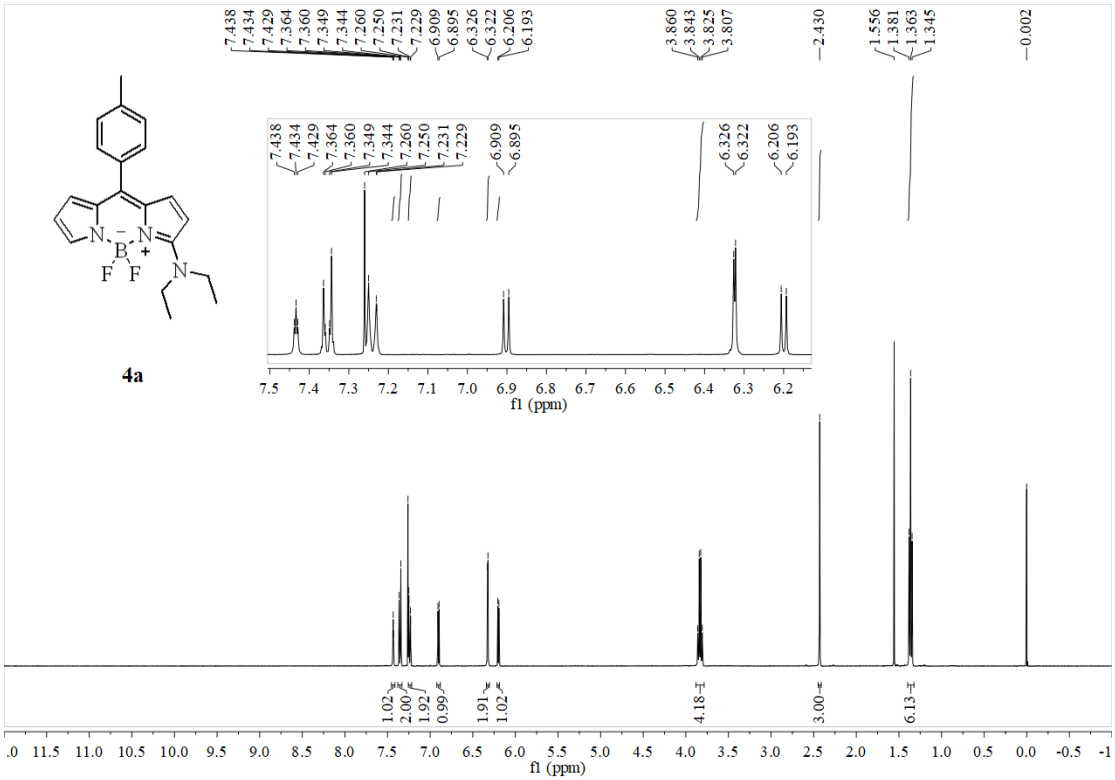
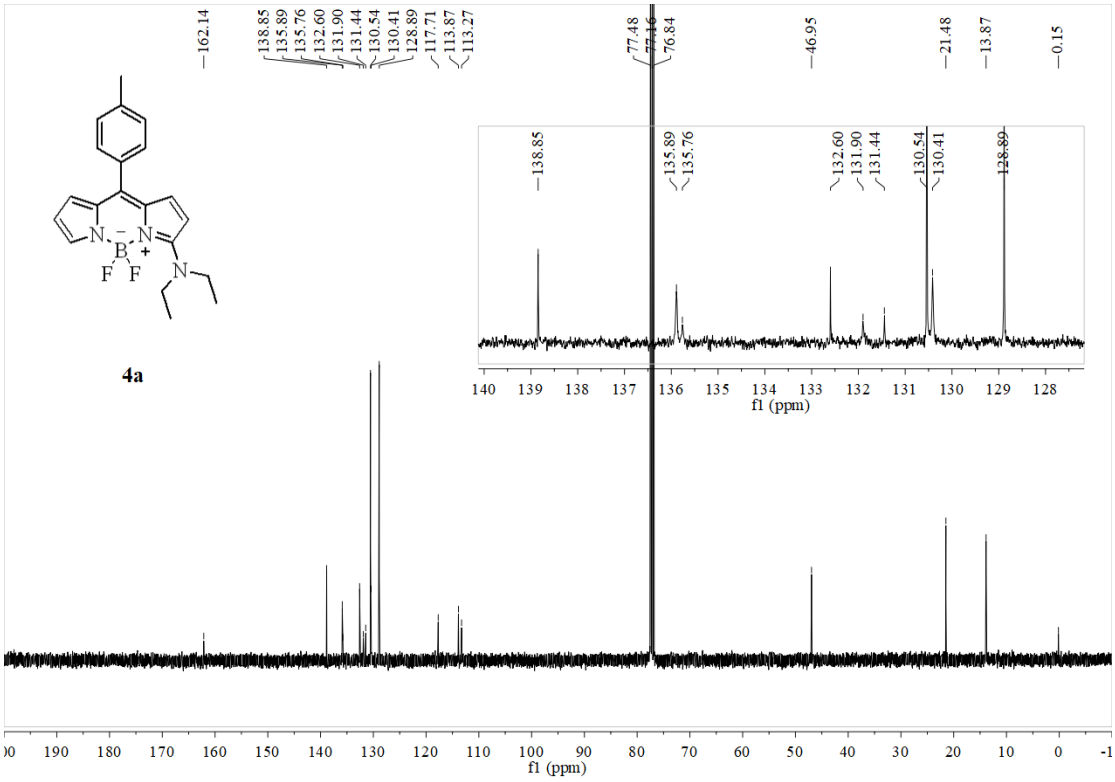
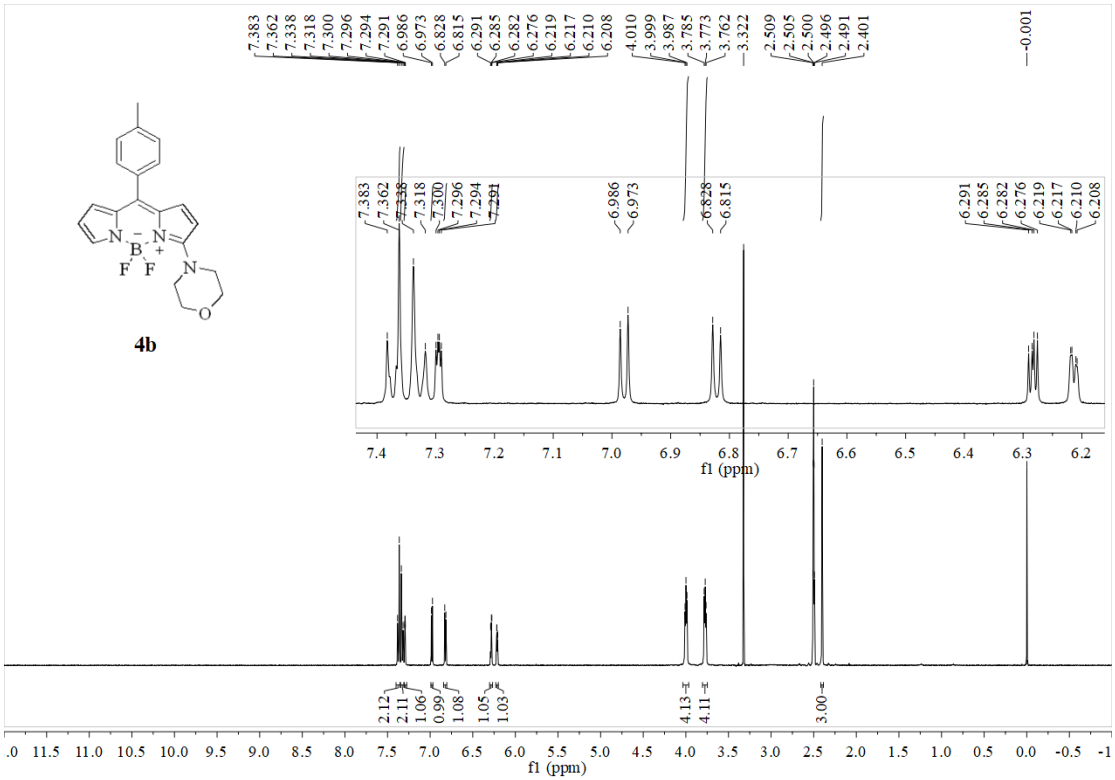
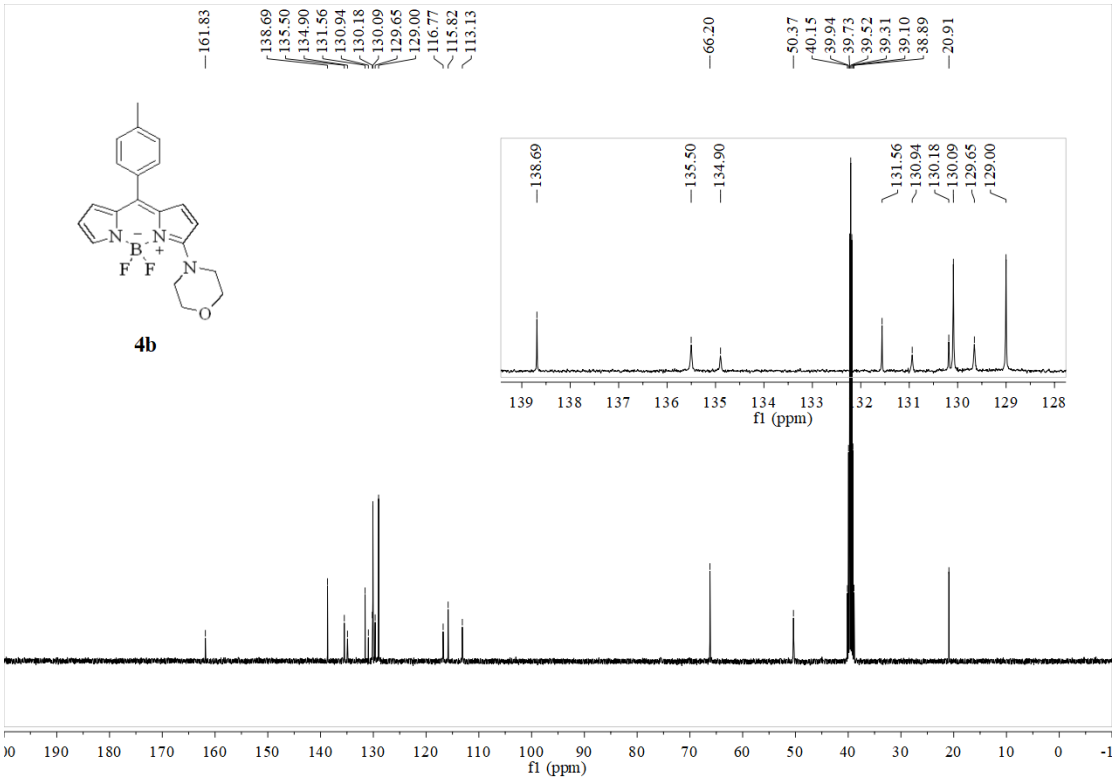
39.73
39.52
39.31
39.10
38.89
20.95
0.16
f1 (ppm)

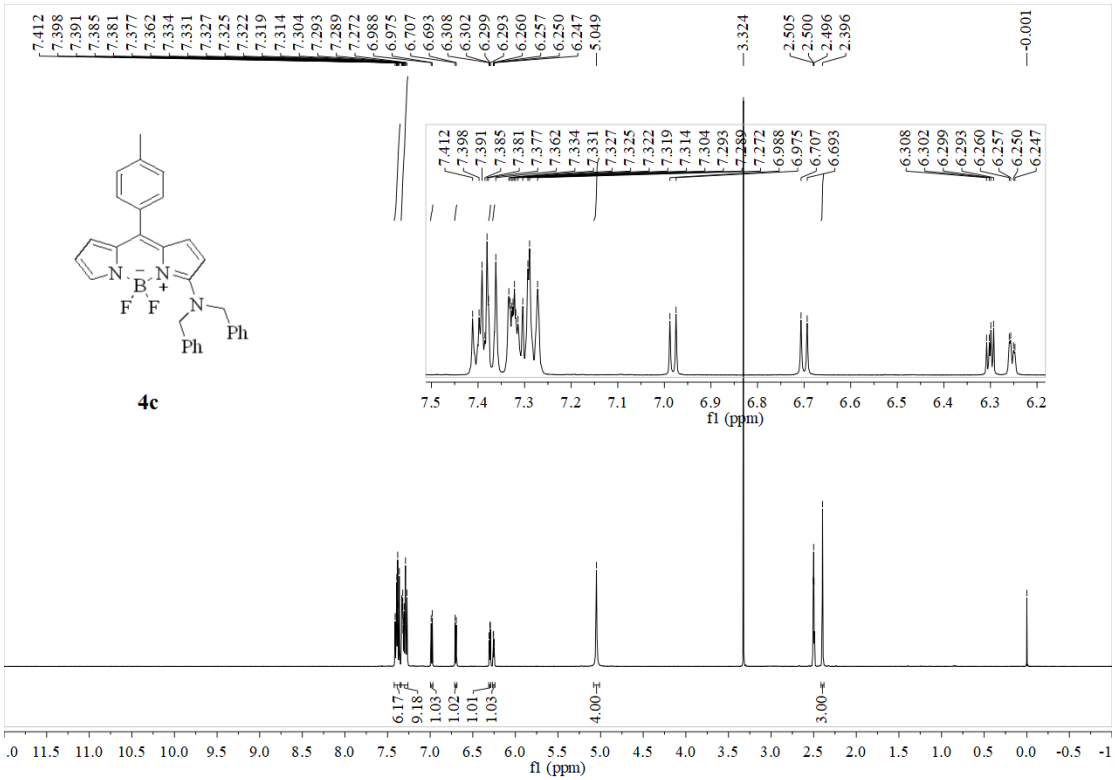
3q

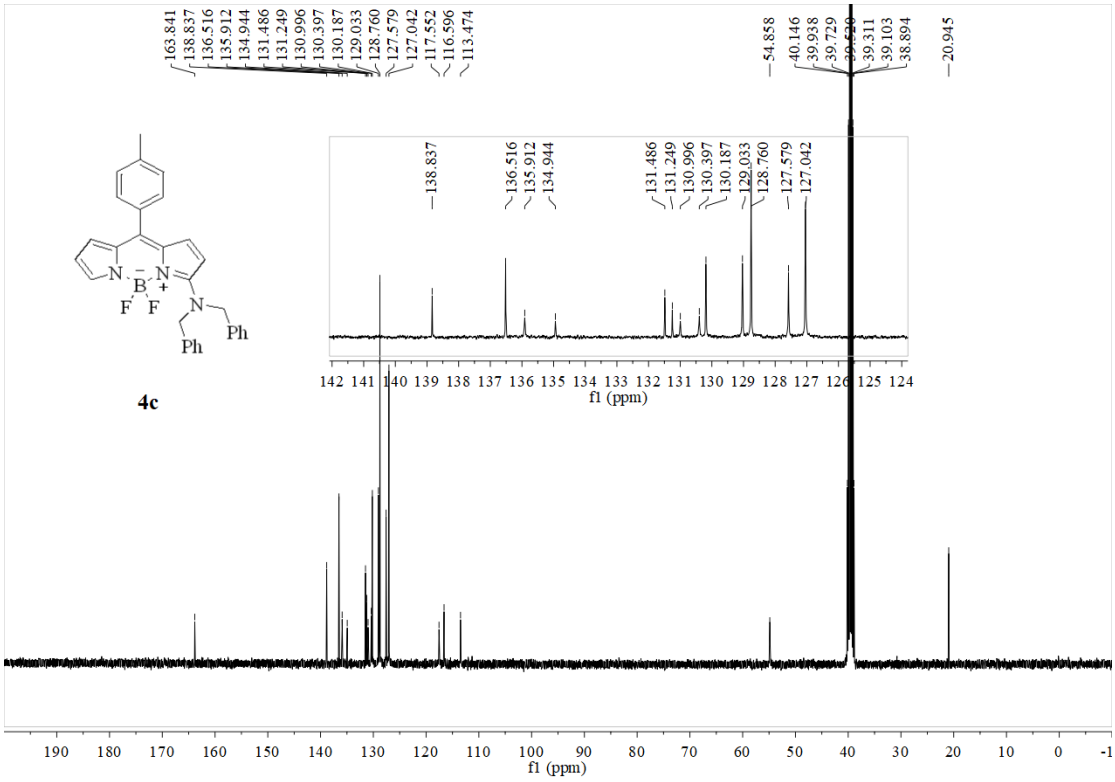

7.438
7.434
7.429
7.364
7.360
7.349
7.344
7.260
7.250
7.231
7.229
6.909
6.895
6.326
6.322
6.206
6.193
3.860
3.843
3.825
3.807
2.430
1.556
1.381
1.363
1.345
0.002
4a
f1 (ppm)
1.02
2.00
1.92
0.99
1.91
1.02
4.18
3.00
6.13

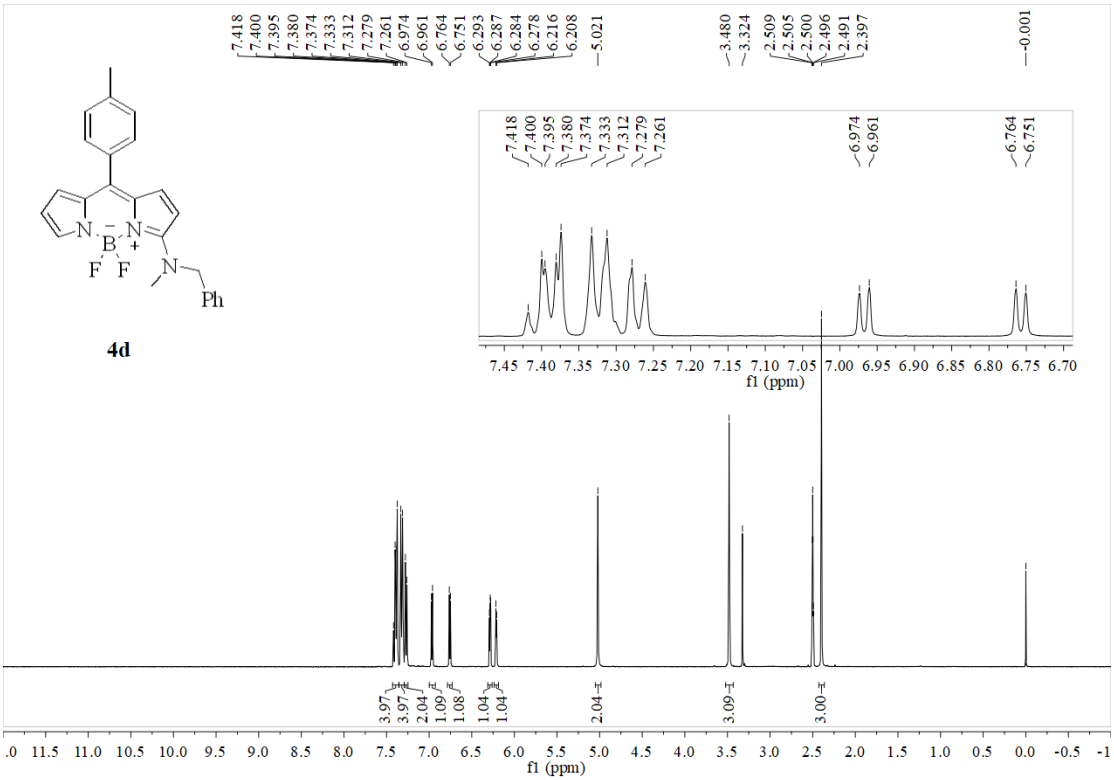

162.14
138.85
135.89
135.76
132.60
131.90
131.44
130.54
130.41
128.89
117.71
113.87
113.27
77.48
77.16
76.84
46.95
21.48
13.87
0.15
4a
f1 (ppm)

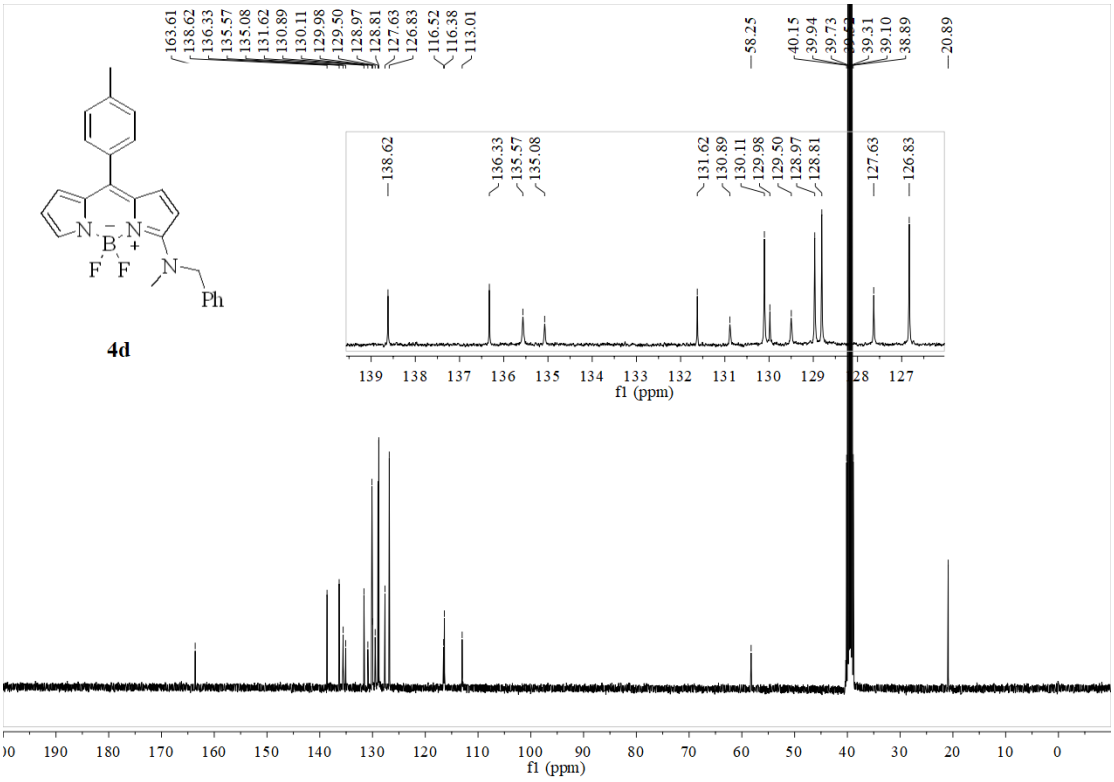

4b
f1 (ppm)

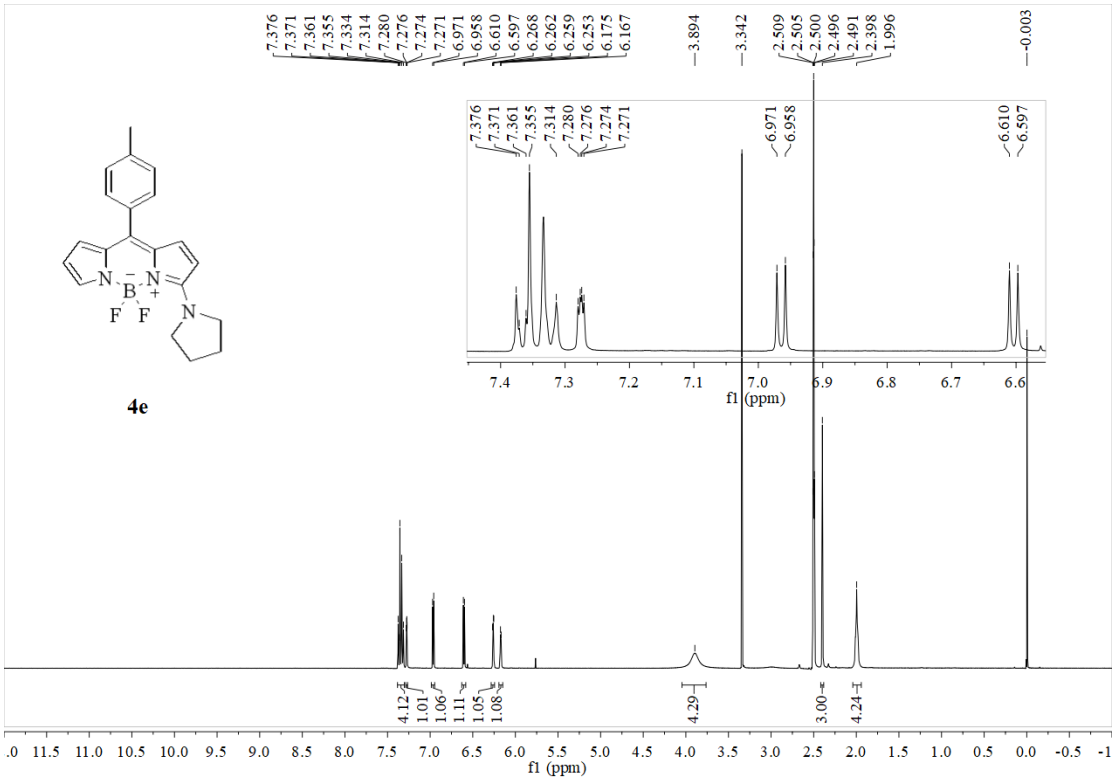

4b
f1 (ppm)


7.412
7.398
7.391
7.385
7.381
7.377
7.362
7.334
7.331
7.327
7.325
7.322
7.319
7.314
7.304
7.293
7.289
7.272
6.988
6.975
6.707
6.693
6.308
6.302
6.299
6.293
6.260
6.257
6.250
6.247
5.049
3.324
2.505
2.500
2.496
2.396
0.001
F
F
N
Ph
Ph
4c
f1 (ppm)
6.17
9.18
1.03
1.02
1.01
1.03
4.00
3.00

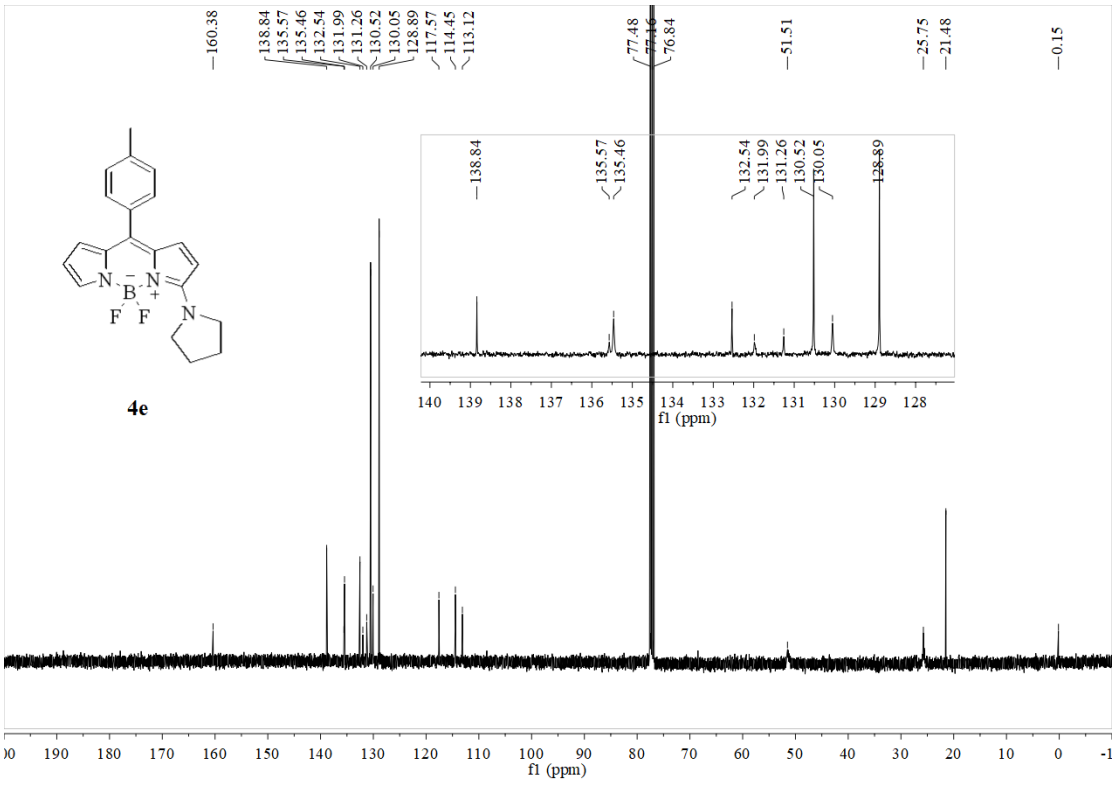

163.841
138.837
136.516
135.912
134.944
131.486
131.249
130.996
130.397
130.187
129.033
128.760
127.579
127.042
117.552
116.596
113.474
54.858
40.146
39.938
39.729
39.520
39.311
39.103
38.894
20.945
F
F
N
Ph
Ph
4c
f1 (ppm)


7.418
7.400
7.395
7.380
7.374
7.333
7.312
7.279
7.261
6.974
6.961
6.764
6.751
6.293
6.287
6.284
6.278
6.216
6.208
5.021
3.480
3.324
2.509
2.505
2.500
2.496
2.491
2.397
-0.001
F F
Ph
4d
f1 (ppm)

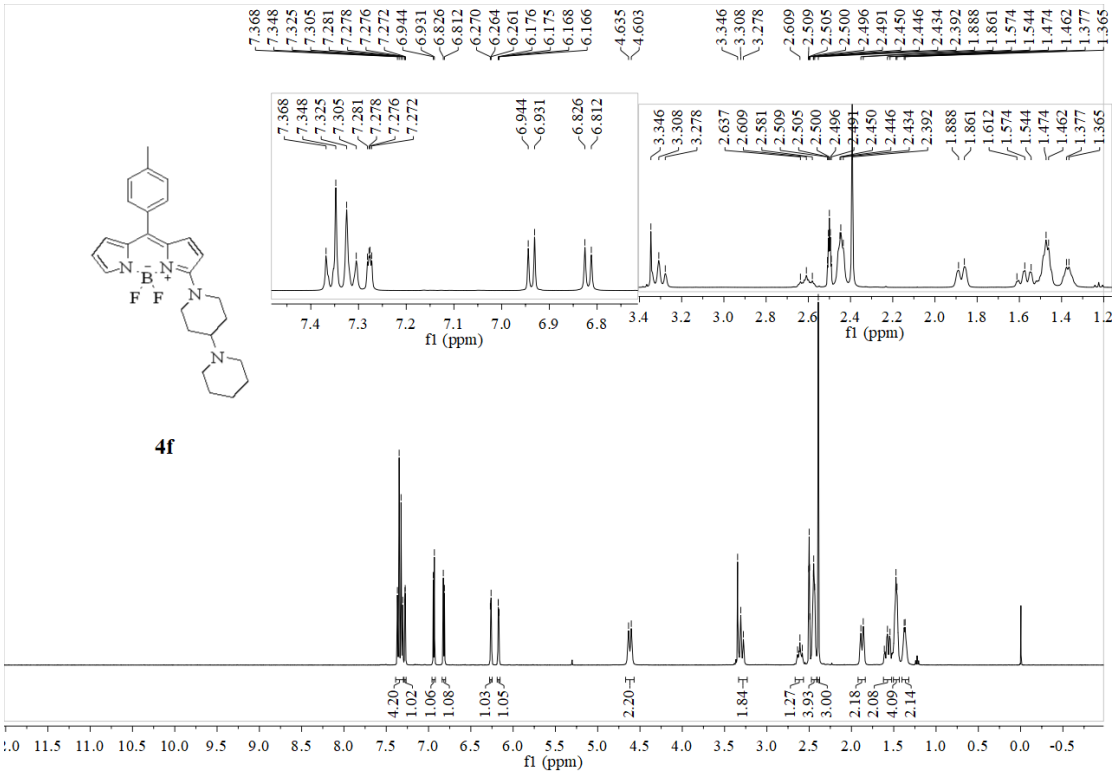

163.61
138.62
136.33
135.57
135.08
131.62
130.89
130.11
129.98
129.50
128.97
128.81
127.63
126.83
116.52
116.38
113.01
58.25
40.15
39.94
39.73
39.52
39.31
39.10
38.89
20.89
F F
Ph
4d
f1 (ppm)

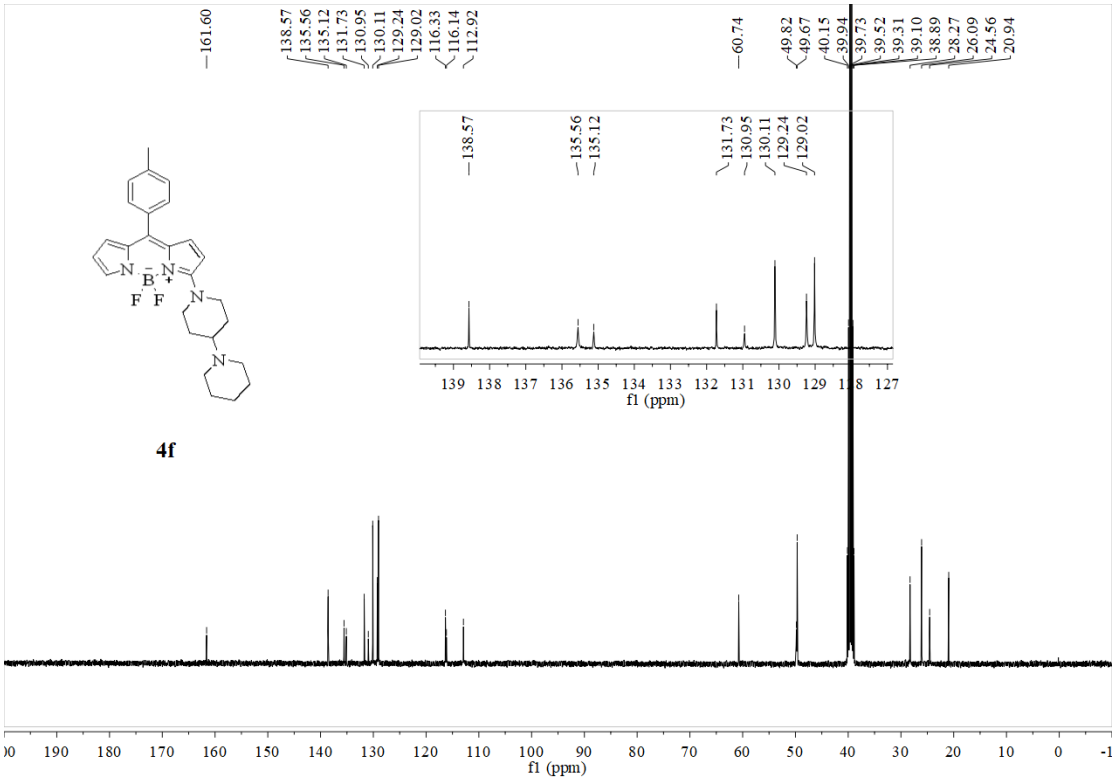

7.376
7.371
7.361
7.355
7.334
7.314
7.280
7.276
7.274
7.271
6.971
6.958
6.610
6.597
6.268
6.262
6.259
6.253
6.175
6.167
3.894
3.342
2.509
2.505
2.500
2.496
2.491
2.398
1.996
0.003
4.12
1.01
1.06
1.11
1.05
1.08
4.29
3.00
4.24
f1 (ppm)

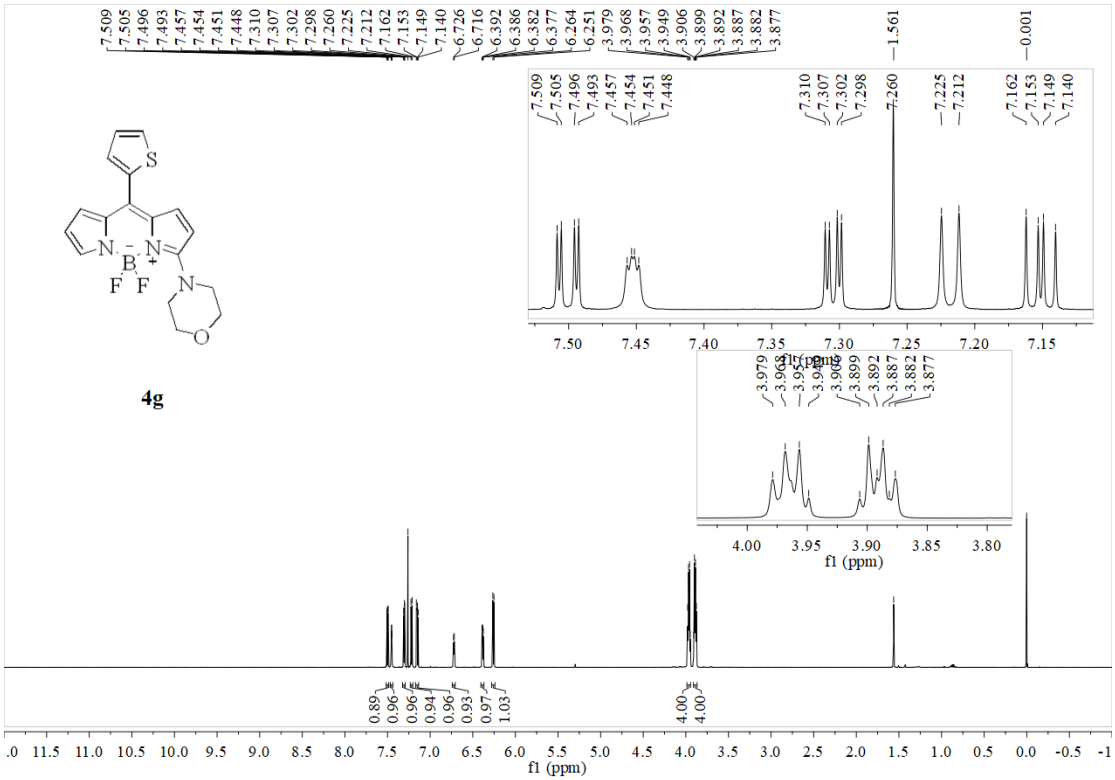
4e

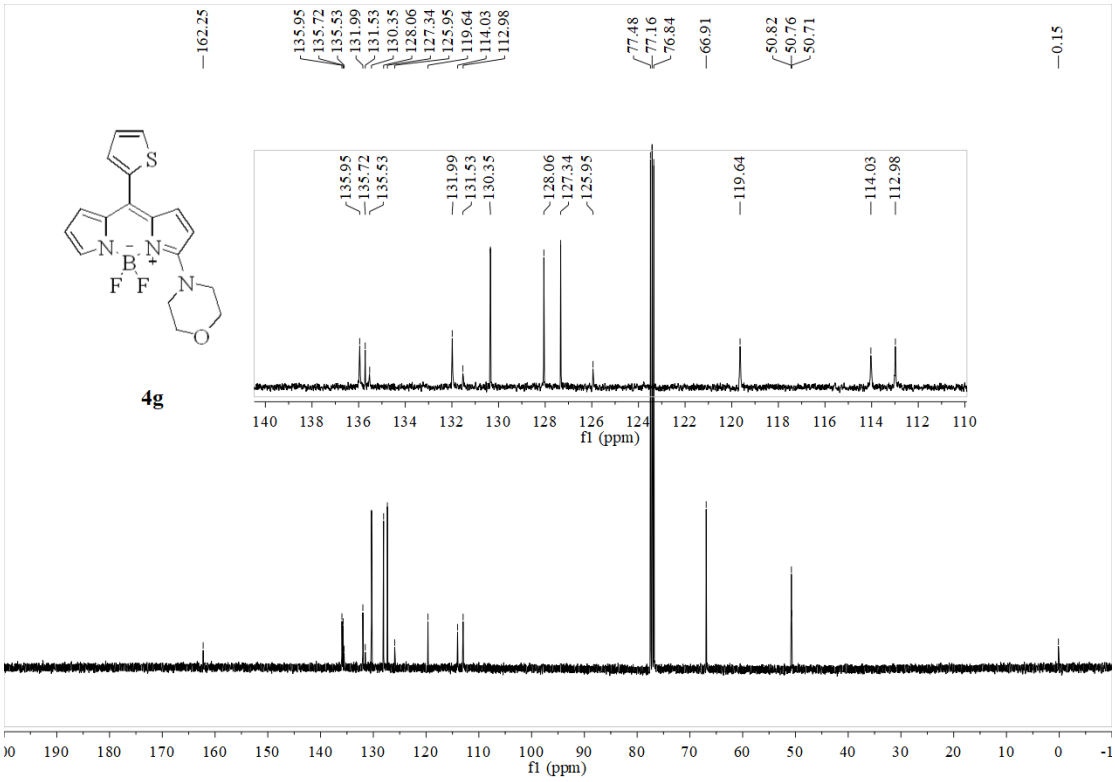

160.38
138.84
135.57
135.46
132.54
131.99
131.26
130.52
130.05
128.89
117.57
114.45
113.12
77.48
77.16
76.84
51.51
25.75
21.48
0.15
f1 (ppm)

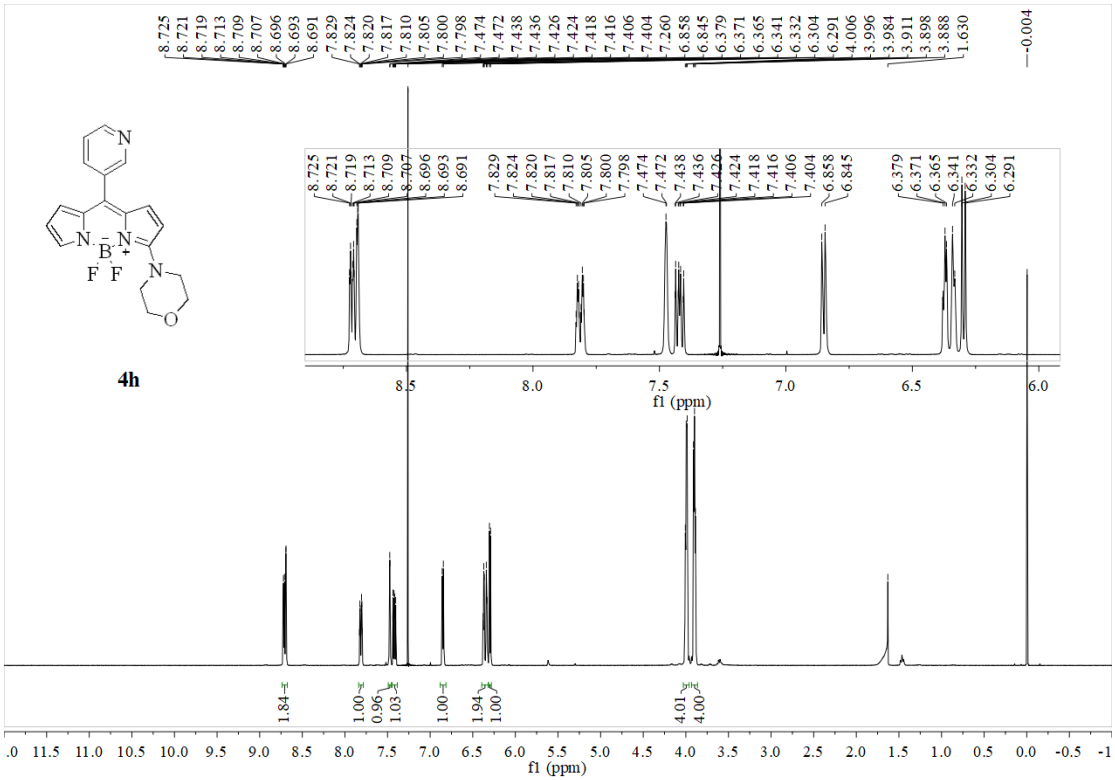
4e

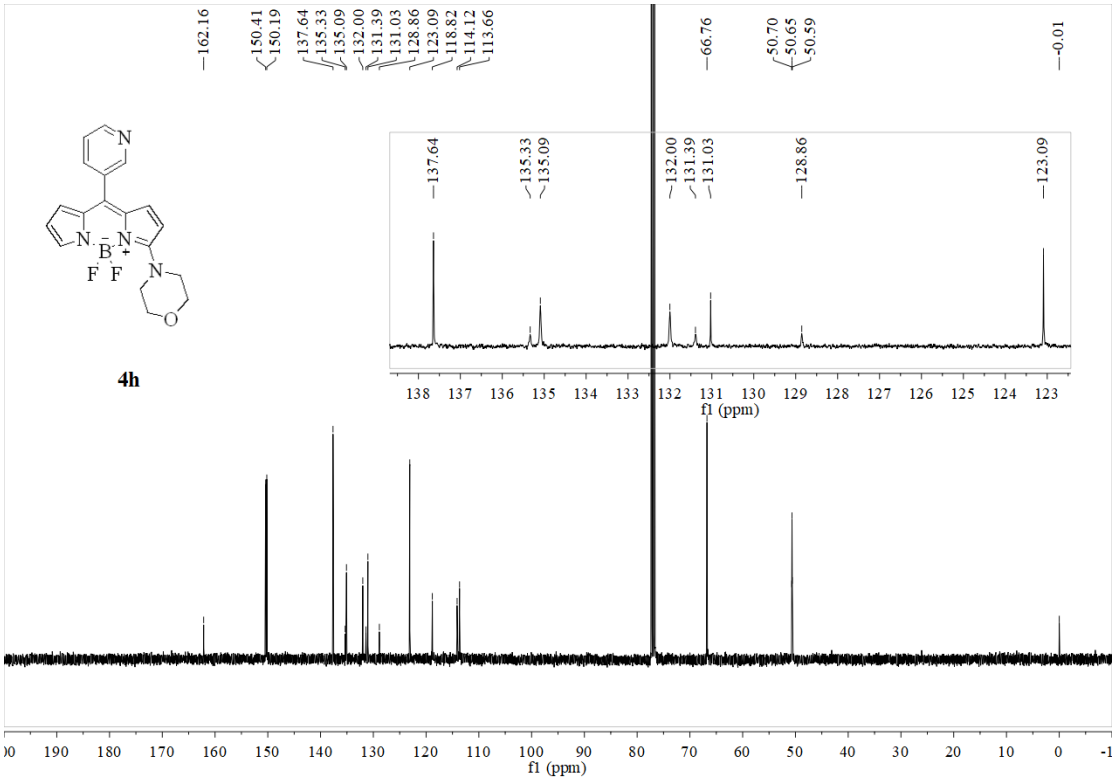

4f
fl (ppm)

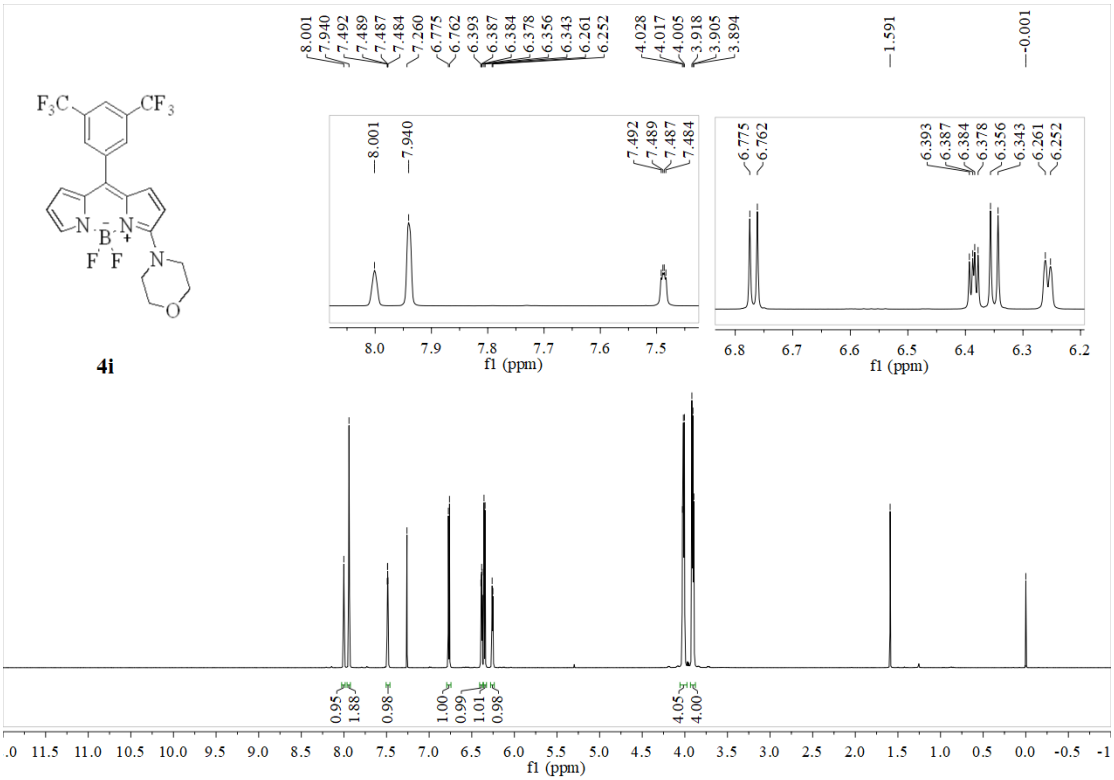

4f
fl (ppm)

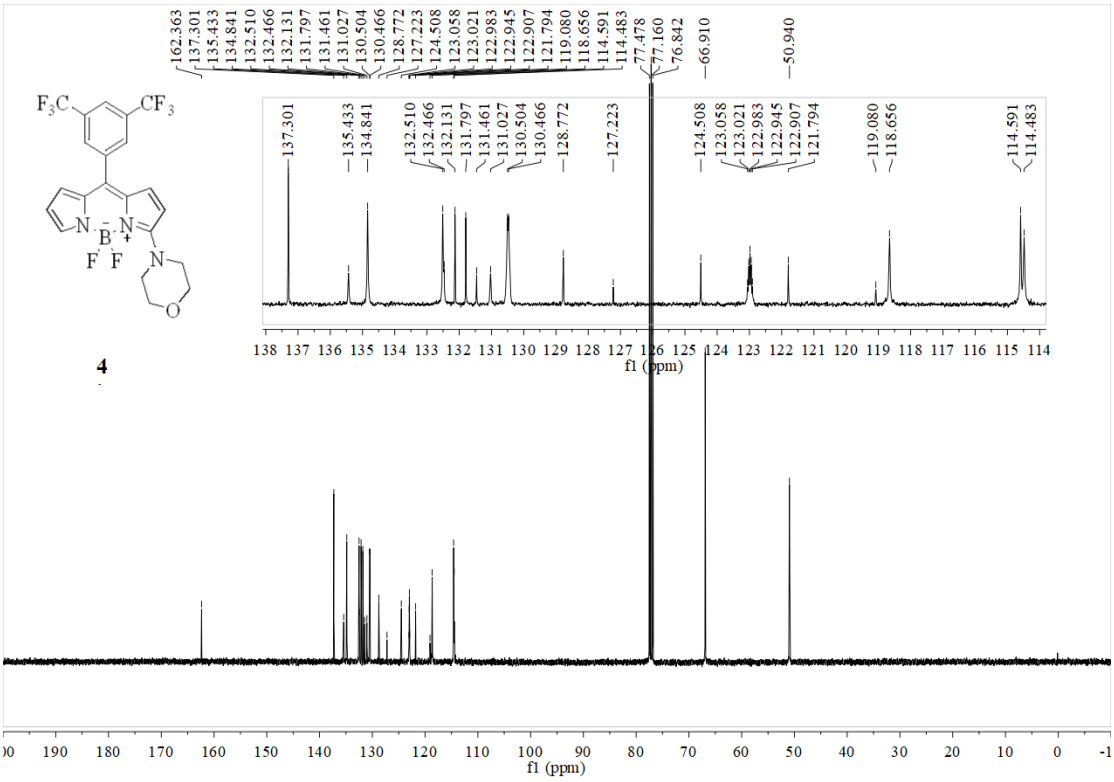

4g
f1 (ppm)

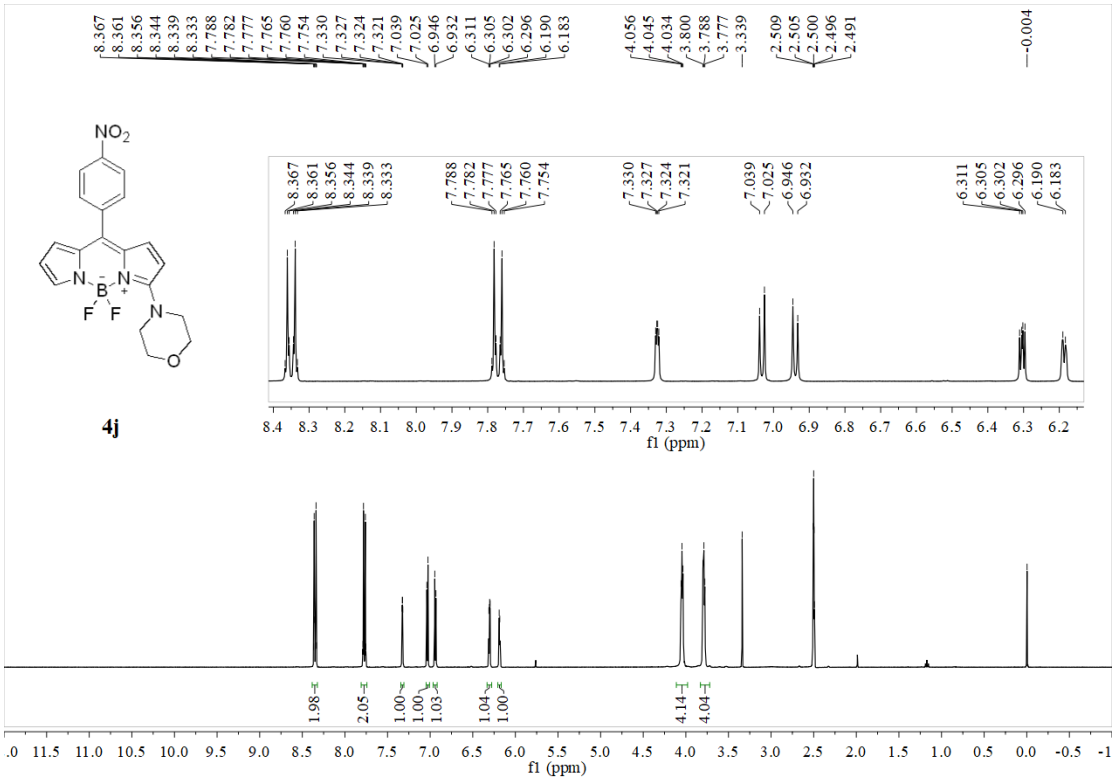

4g
f1 (ppm)

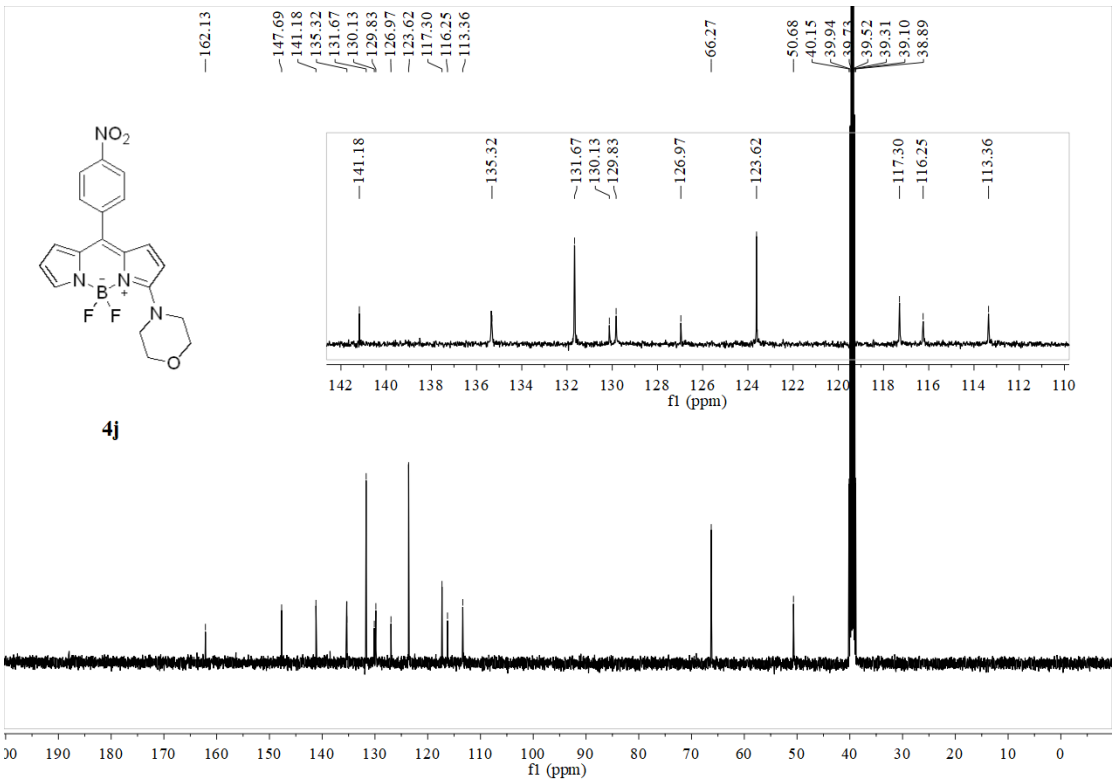

8.725
8.721
8.719
8.713
8.709
8.707
8.696
8.693
8.691
7.829
7.824
7.820
7.817
7.810
7.805
7.800
7.798
7.474
7.472
7.438
7.436
7.426
7.424
7.418
7.416
7.406
7.404
7.260
6.858
6.845
6.379
6.371
6.365
6.341
6.332
6.304
6.291
4.006
3.996
3.984
3.911
3.898
3.888
1.630
-0.004
4h
f1 (ppm)
1.84
1.00
0.96
1.03
1.00
1.94
1.00
4.01
4.00

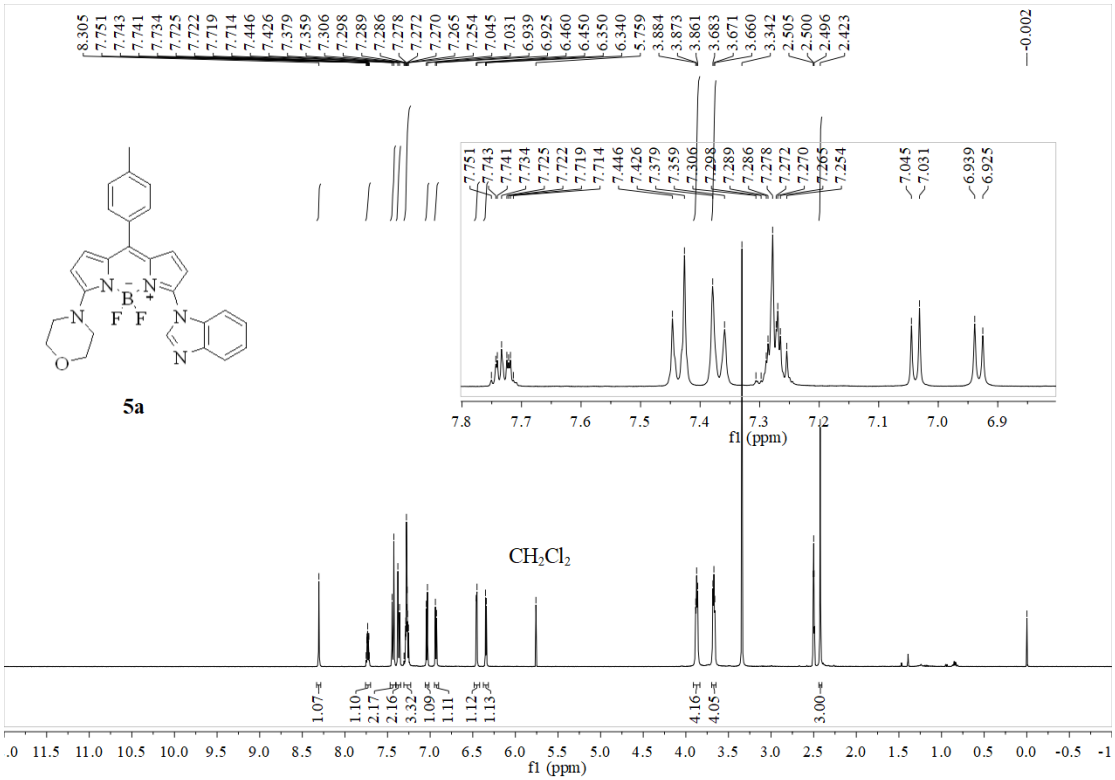

162.16
150.41
150.19
137.64
135.33
135.09
132.00
131.39
131.03
128.86
123.09
118.82
114.12
113.66
66.76
50.70
50.65
50.59
-0.01
4h
f1 (ppm)

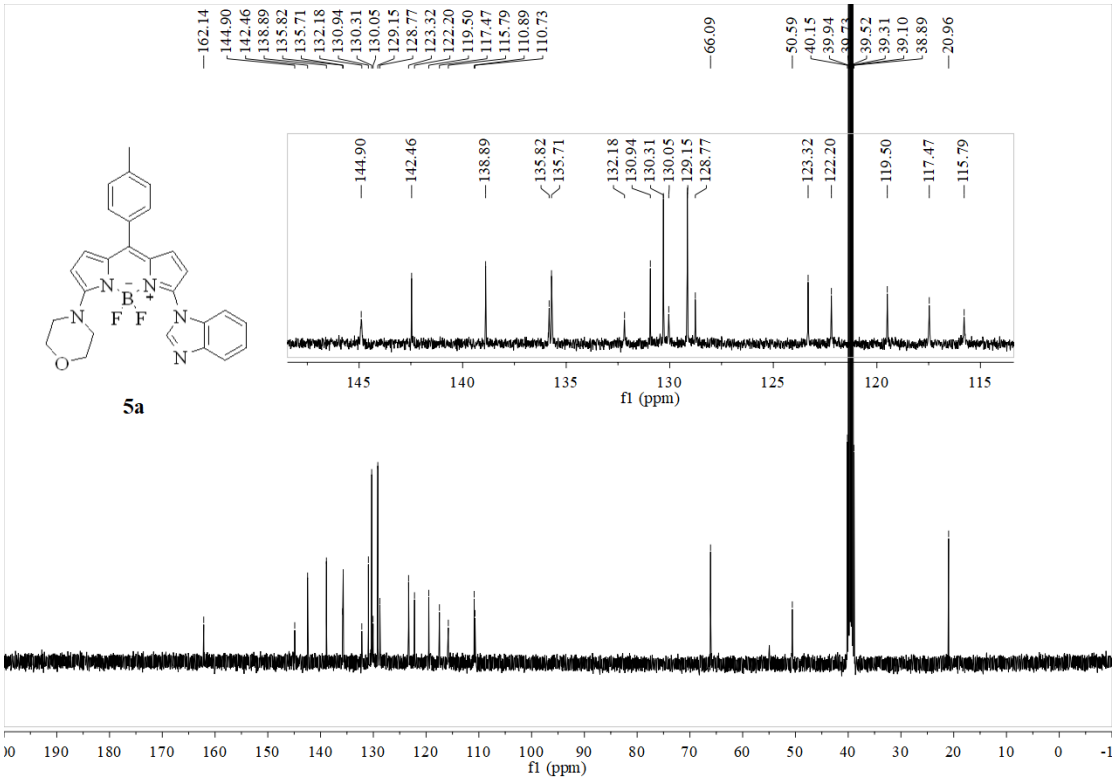

8.001
7.940
7.492
7.489
7.487
7.484
7.260
6.775
6.762
6.393
6.387
6.384
6.378
6.356
6.343
6.261
6.252
4.028
4.017
4.005
3.918
3.905
3.894
1.591
0.001
F3C
CF3
F F
N
O
4i
f1 (ppm)
0.95
1.88
0.98
1.00
0.99
1.01
0.98
4.05
4.00

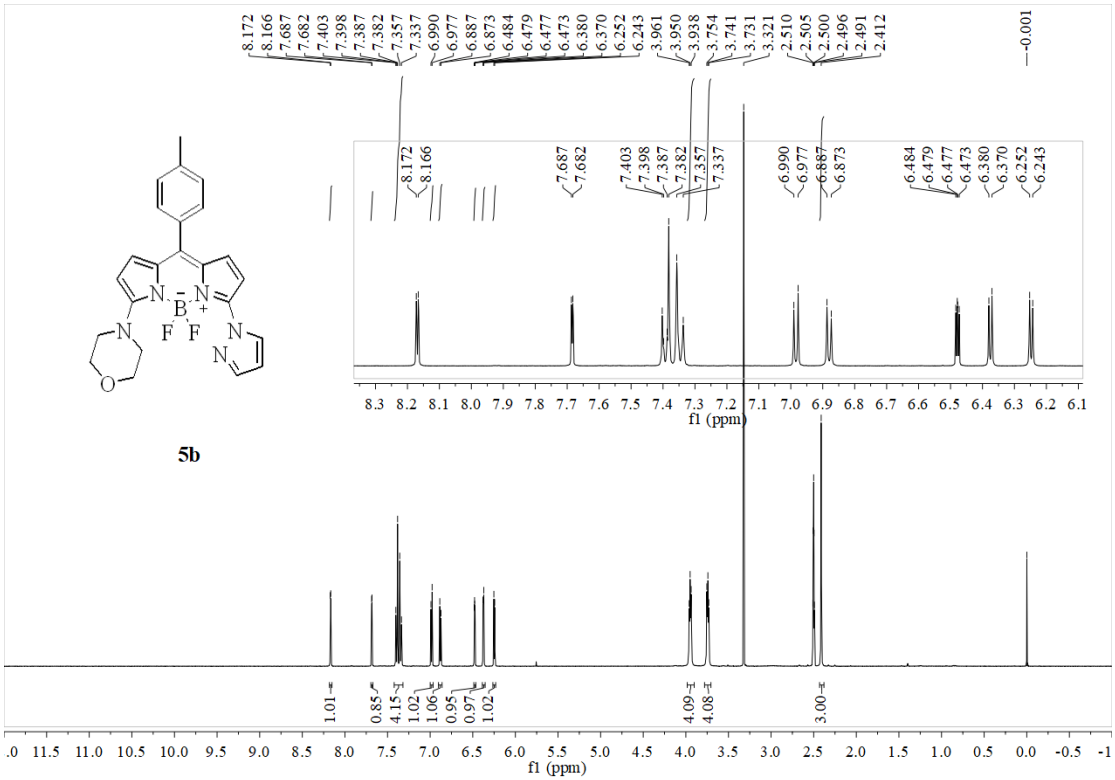

162.363
137.301
135.433
134.841
132.510
132.466
132.131
131.797
131.461
131.027
130.504
130.466
128.772
127.223
124.508
123.058
123.021
122.983
122.945
122.907
121.794
119.080
118.656
114.591
114.483
77.478
77.160
76.842
66.910
50.940
F3C
CF3
F F
N
O
4
f1 (ppm)

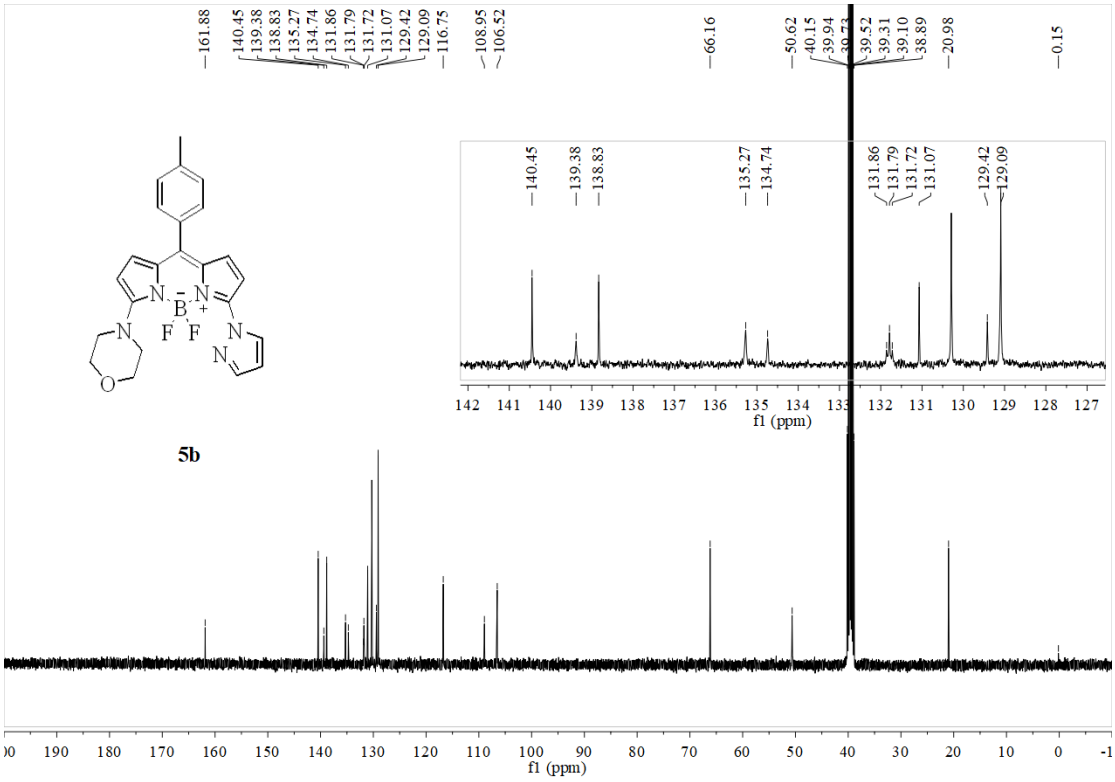

8.367
8.361
8.356
8.344
8.339
8.333
7.788
7.782
7.777
7.765
7.760
7.754
7.330
7.327
7.324
7.321
7.039
7.025
6.946
6.932
6.311
6.305
6.302
6.296
6.190
6.183
4.056
4.045
4.034
3.800
3.788
3.777
3.339
2.509
2.505
2.500
2.496
2.491
-0.004
NO2
4j
f1 (ppm)
1.98
2.05
1.00
1.00
1.03
1.04
1.00
4.14
4.04


162.13
147.69
141.18
135.32
131.67
130.13
129.83
126.97
123.62
117.30
116.25
113.36
66.27
50.68
40.15
39.94
39.73
39.52
39.31
39.10
38.89
NO2
4j
f1 (ppm)


5a
CH2Cl2
f1 (ppm)


5a
f1 (ppm)


8.172
8.166
7.687
7.682
7.403
7.398
7.387
7.382
7.357
7.337
6.990
6.977
6.887
6.873
6.484
6.479
6.477
6.473
6.380
6.370
6.252
6.243
3.961
3.950
3.938
3.754
3.741
3.731
3.321
2.510
2.505
2.500
2.496
2.491
2.412
-0.001
5b
f1 (ppm)
1.01
0.85
4.15
1.02
1.06
0.95
0.97
1.02
4.09
4.08
3.00


161.88
140.45
139.38
138.83
135.27
134.74
131.86
131.79
131.72
131.07
129.42
129.09
116.75
108.95
106.52
66.16
50.62
40.15
39.94
39.73
39.52
39.31
39.10
38.89
20.98
0.15
5b
f1 (ppm)