Electronic Supplementary Material (ESI) for Materials Advances.

Near-infrared absorbing aza-BODIPYs with the 1,7-di-*tert*-butyl groups by low-barrier rotation for a photothermal application†

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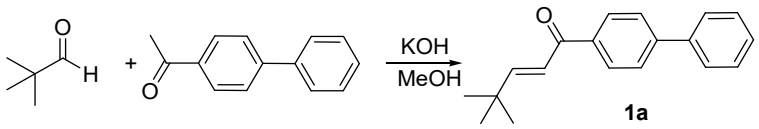
1. Synthesis

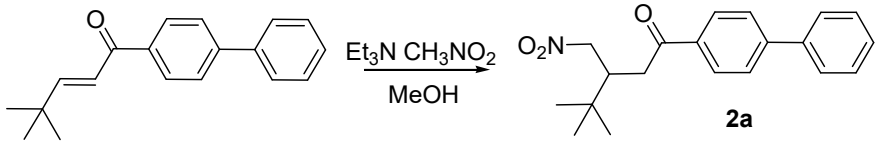
Synthesis of (E)-1-([1,1'-biphenyl]-4-yl)-4,4-dimethylpent-2-en-1-one



1a

2g of KOH was added to 1-([1,1'-biphenyl]-4-yl)ethan-1-one (1.0 g, 5.1 mmol) and pivalaldehyde(1.5 ml, 17.4 mmol) in anhydrous methanol (20 ml), and then the mixture was refluxed for 12 h. The solvent was removed under reduced pressure, and the resulting crude mixture was separated by column chromatography (*n*-hexane : CH_2Cl_2 = 1:1) to afford **1a** (1.21g, 90%) as white powder. ^{1}H NMR (400 MHz, $CDCl_3$): 8.01 (d, ^3J = 8.0 Hz, 2H), 7.69 (d, ^3J = 8.0 Hz, 2H), 7.64 (d, ^3J = 8.0 Hz, 2H), 7.47 (t, ^3J = 8.0 Hz, 2H), 7.41 (t, ^3J = 8.0 Hz, 1H), 7.10 (d, ^3J = 16.0 Hz, 1H), 6.83 (d, ^3J = 16.0 Hz, 1H), 1.18 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 190.8, 159.3, 145.1, 139.8, 136.7, 128.9, 128.7, 127.9, 127.1, 126.9, 120.7, 34.0, 28.6.

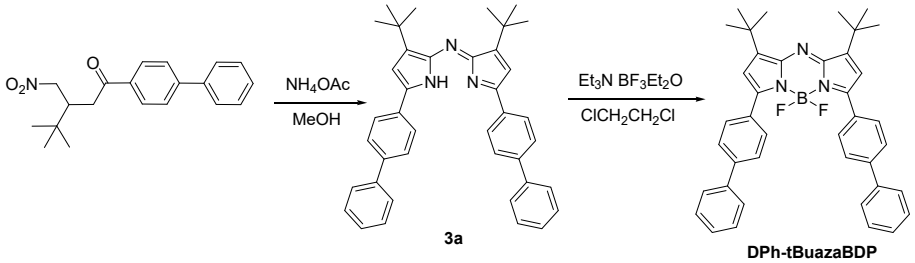
Synthesis of 1-([1,1'-biphenyl]-4-yl)-4,4-dimethyl-3-(nitromethyl)pentan-1-one



2a

Triethylamine (2 ml) and nitromethane (1.5 ml) were added to (E)-1-([1,1'-biphenyl]-4-yl)-4,4-dimethylpent-2-en-1-one (1.21g, 4.6 mmol) in anhydrous methanol (20 ml). The mixture was refluxed for 24 h. The solvent was removed under reduced pressure, and resulting crude mixture was separated by column chromatography (*n*-hexane : CH_2Cl_2 = 1:1) to afford **2a** (1.04 ml, 70%) as light yellow oil.

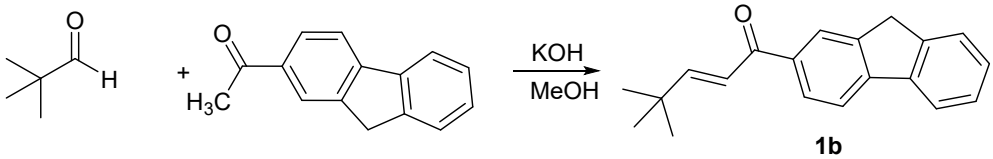
*Synthesis of **DPh-tBuazaBDP***



3a **DPh-tBuazaBDP**

Ammonium acetate was added to **2a** (1.04ml, 3.2mmol) in anhydrous methanol (20 ml) and refluxed for 24 h. The solvent was removed under reduced pressure, and the resulting crude mixture was subjected to column chromatography (*n*-hexane: CH_2Cl_2 = 3:1) to obtain **3a** (0.9 g, 55%) as a blue solid. After then, under N_2 triethylamine (0.5 ml, 3.6 mmol) was added to **3a** in 1,2-dichloroethane (10 ml), and stired for 15 minutes. $BF_3{\cdot}Et_2O$ (1 ml, 7.9 mmol) was subsequently dropped into the solution, and the mixture was stirred for 4 hour at 80 °C. the organic layer was washed with water, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (*n*-hexane: CH_2Cl_2 = 3:1), and then recrystallized from CH_2Cl_2/*n*-hexane to obtain **DPh-tBuazaBDP** (0.54 g, 50%) as green solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.09 (d, ^3J = 8.5 Hz, 4H), 7.68 (d, ^3J = 8.5 Hz, 4H), 7.64 (d, ^3J = 8.5 Hz, 4H), 7.45 (t, ^3J = 8.5 Hz, 4H), 7.37 (d, ^3J = 8.5 Hz, 4H), 6.66 (s, 2H), 1.51 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 157.7, 144.1, 143.2, 140.3, 130.7, 130.2, 128.9, 128.0, 127.3, 124.5, 123.6, 119.5, 31.1, 29.8. HRMS (ESI) m/z calcd for $C_{40}H_{38}BF_2N_3Na^+$ $(M+Na)^+$ 632.30191, found 632.30200.

Synthesis of (E)-1-(9H-fluoren-2-yl)-4,4-dimethylpent-2-en-1-one

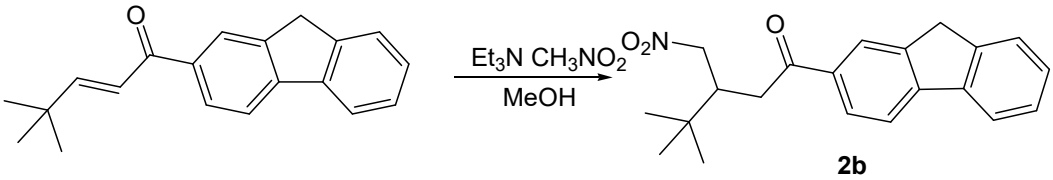


1b

2g of KOH was added to Acetyl fluorine (1g, 4.8mmol) and pivalaldehyde(1.5ml 17.4mmol)) in anhydrous methanol (20ml). The mixture was refluxed at 90℃ for 12h. The solvent was removed under reduced pressure, The resulting crude mixture was separated by column chromatography (n-hexane:CH_2Cl_2=1:1) to afford **1b** (1.13g, 85%) in white powder form. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.13 (s, 1H), 7.99 (d, ^3J = 8 Hz, 1H), 7.85 (d, ^3J = 8 Hz, 2H), 7.59 (d, ^3J = 8 Hz, 1H), 7.35-7.44 (m, 2H), 7.11 (d, ^3J = 16 Hz, 1H), 6.87 (d, ^3J = 16 Hz, 1H), 3.97 (s, 2H), 1.18 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 191.3, 159.2, 146.1, 144.6, 143.4, 140.7, 136.8,

128.1, 127.1, 125.4, 125.3, 121.1, 120.9, 119.7, 37.1, 34.3, 28.9.

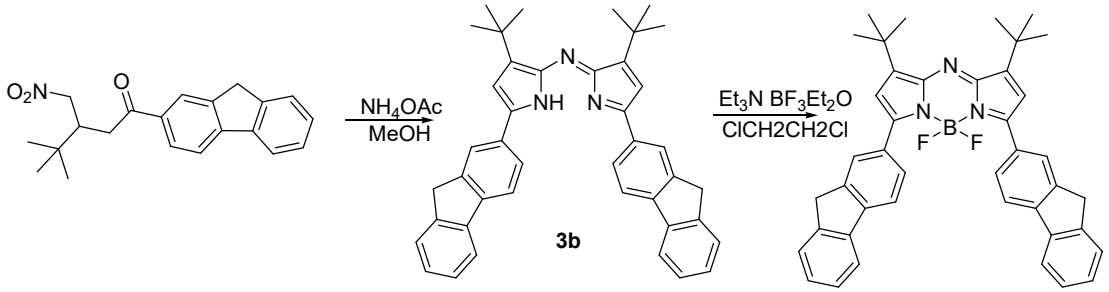
Synthesis of 1-(9H-fluoren-2-yl)-4,4-dimethyl-3-(nitromethyl)pentan-1-one



2b

1-(9H-fluoren-2-yl)-4,4-dimethyl-3-(nitromethyl)pentan-1-one(1.13g,4.1mmol),triethylamine(2.5ml) and nitromethane(2ml) were added in anhydrous methanol (20ml).The mixture was refluxed at 130℃ for 24h.The solvent was removed under reduced pressure and resulting crude mixture was separated by column chromatography (*n*-hexane : CH_2Cl_2 = 1:1) to afford **2b** (0.90g, 65%) as light yellow oil.

*Synthesis of **Flu-tBuazaBDP***

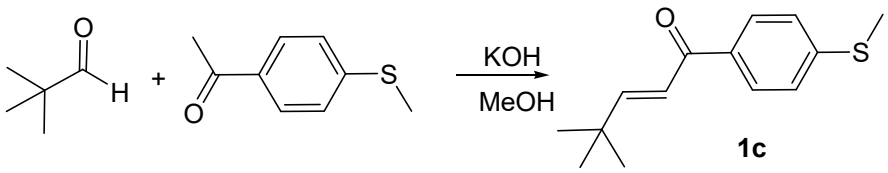


3b **Flu-tBuazaBDP**

Ammonium acetate was added to the 3b (0.90g, 2.7mmol) anhydrous methanol (20ml) mixture suspension, refluxed at 130°C for 24h, and the solvent was removed under reduced pressure. The resulting crude mixture was subjected to column chromatography (n-hexane: CH_2Cl_2 = 2:1) to obtain **3b** (0.78g, 50%) as a blue solid. Under N_2, dissolve **3b** in 10ml 1,2-dichloroethane, add triethylamine (0.5 ml, 3.6 mmol), stir for 15 minutes, slowly drop BF_3Et_2O (1 ml, 7.9 mmol) into the solution, 80℃ After reacting for 4 h, the organic layer was washed with water, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (*n*-hexane: CH_2Cl_2 = 3:1), and then recrystallized from CH_2Cl_2/*n*-hexane to obtain **Flu-tBuazaBDP** (0.38g, 45%) as a

green powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 8.05 (d, ^{3}J = 8.0 Hz, 2H), 7.84 (d, ^{3}J = 8.0 Hz, 2H), 7.81 (d, ^{3}J = 8.0 Hz, 2H), 7.55 (d, ^{3}J = 8.0 Hz, 2H), 7.38 8.05 (d, ^{3}J = 8.0 Hz, 2H), 7.35 (s, 2H), 7.33 (d, ^{3}J = 8.0 Hz, 2H), 6.67 (s, 2H), 3.95 (s, 4H), 1.52 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 158.2, 156.5, 144.3, 143.4, 141.1, 130.4, 128.9, 127.6, 127.1, 126.2, 125.2, 124.5, 123.6, 120.6, 120.1, 119.7, 37.1, 31.1, 29.8. HRMS (ESI) m/z calcd for $C_{42}H_{38}BF_2N_3Na^+$ $(M+Na)^+$ 656.30191, found 656.30182.

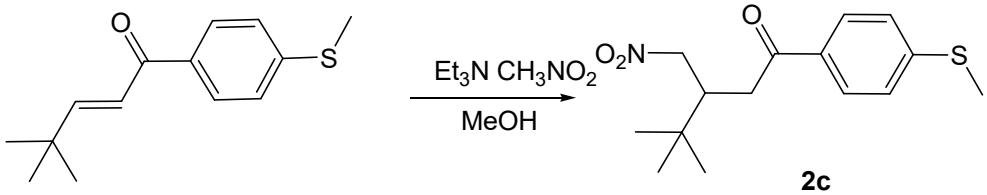
Synthesis of (E)-4,4-dimethyl-1-(4-(methylthio)phenyl)pent-2-en-1-one



1c

2g of KOH was added to 1-(4-(methylthio)phenyl)ethan-1-one(1 g, 6.0 mmol) and pivalaldehyde(1.5 ml, 17.4 mmol)) in anhydrous methanol (20 ml). The mixture was refluxed at 90℃ for 12 h.The solvent was removed under reduced pressure, The resulting crude mixture was separated by column chromatography (*n*-hexane: CH_2Cl_2 = 1:1) to afford **1c** (1.13 g, 80%) as light light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.86 (d, ^{3}J = 8 Hz, 2H), 7.28 (d, ^{3}J = 8 Hz, 2H), 7.05 (d, ^{3}J = 16 Hz, 1H), 6.75 (d, ^{3}J = 16 Hz, 1H), 2.52 (s, 2H), 1.15 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 190.4, 159.3, 145.3, 134.6, 129.1, 125.2, 120.7, 34.3, 28.9, 15.0.

Synthesis of 4,4-dimethyl-1-(4-(methylthio)phenyl)-3(nitromethyl)pentan-1-one

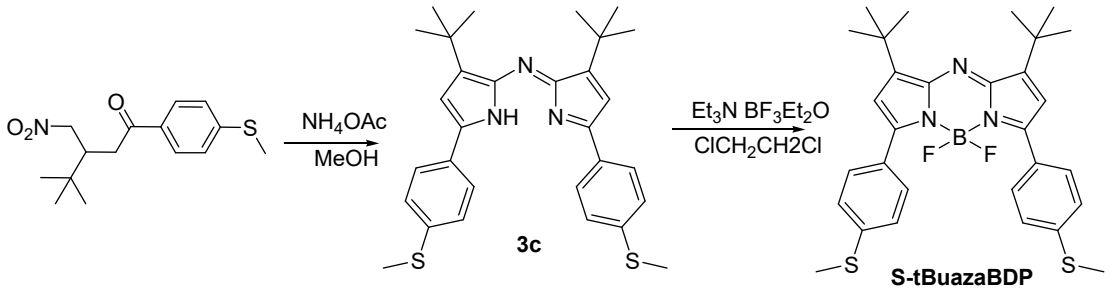


2c

(E)-4,4-dimethyl-1-(4-(methylthio)phenyl)pent-2-en-1-one (1.13g, 4.8 mmol) , triethylamine (2.5 ml) and nitromethane (2 ml) were added in anhydrous methanol (20 ml). The mixture was refluxed at 130℃ for 24 h. The solvent was removed under reduced pressure.and resulting crude mixture was separated by

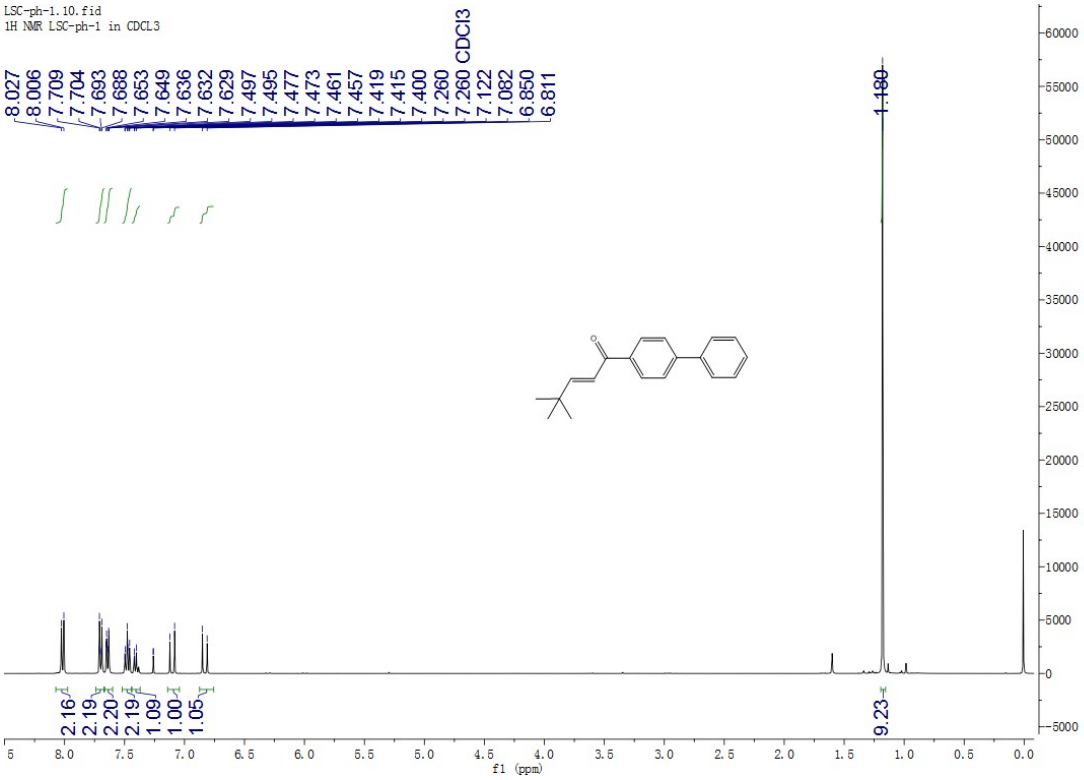
column chromatography (*n*-hexane: CH_2Cl_2 =1:1) to afford **2c** (0.79 ml, 55%) as light yellow oil.

Synthesis of ***S-tBuazaBDP***



Ammonium acetate was added to **2c** (0.79 ml, 2.6 mmol) anhydrous methanol (20 ml) mixture suspension, refluxed at 130 °C for 24 h, and the solvent was removed under reduced pressure. The resulting crude mixture was subjected to column chromatography (*n*-hexane: CH_2Cl_2 = 4:1) to obtain **3c** (0.53 g, 40%) as a blue solid. Under N_2, dissolve **3c** (0.53 g, 1.1 mmol) in 10 ml 1,2-dichloroethane, add triethylamine (0.5 ml, 3.6 mmol), stir for 15 minutes, slowly drop BF_3 Et_2O (1 ml 7.9 mmol) into the solution, 80 °C After reacting for 4 h, the organic layer was washed with water, brine and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (*n*-hexane: CH_2Cl_2 = 3:1), and then recrystallized from CH_2Cl_2/*n*-hexane to obtain **S-tBuazaBDP** (0.20 g, 35%) as a green powder. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 7.93 (d, ^3J = 8.5 Hz, 4H), 7.27 (d, ^3J = 8.5 Hz, 4H), 6.58 (s, 2H), 2.52 (s, 6H), 1.48 (s, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 157.1, 142.8, 131.0, 129.9, 128.9, 125.5, 124.5, 119.1, 53.5, 31.1, 29.8. HRMS (ESI) m/z calcd for $C_{30}H_{34}BF_2N_3S_2Na^+$ $(M+Na)^+$ 572.21475, found 572.21497.

2. NMR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1H NMR LSC-ph-1 in CDCL3
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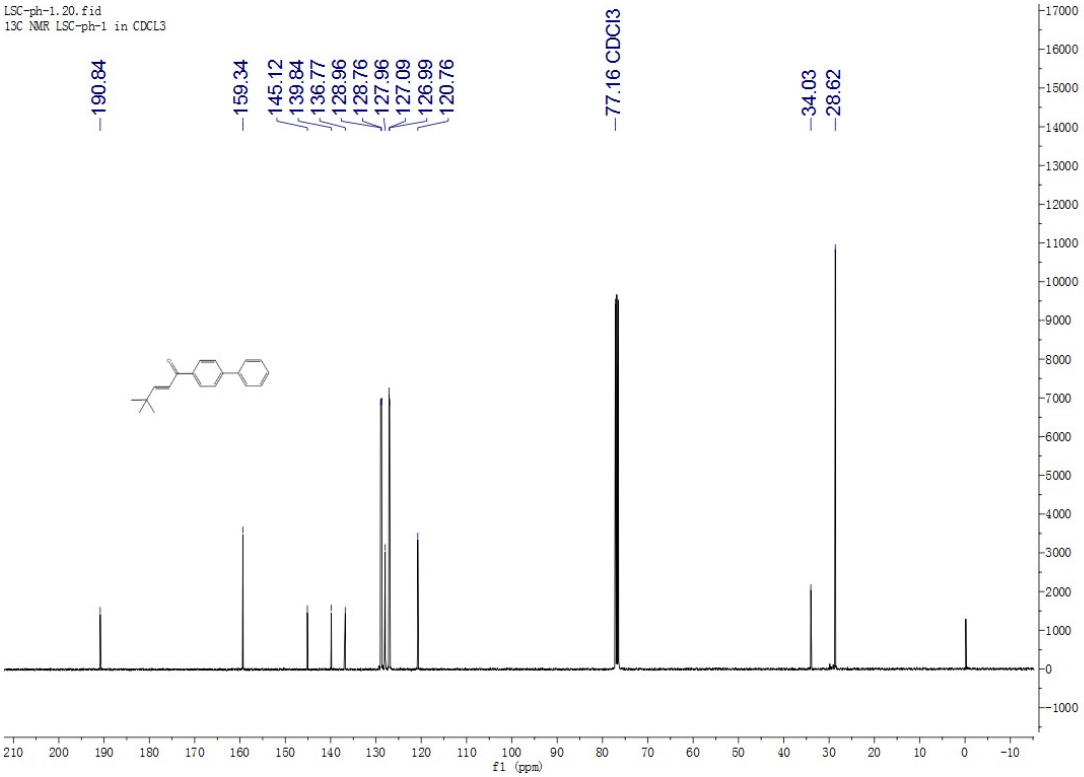
8.006
7.709
7.704
7.693
7.688
7.653
7.649
7.636
7.632
7.629
7.497
7.495
7.477
7.473
7.461
7.457
7.419
7.415
7.400
7.260 CDCl3
7.122
7.082
6.850
6.811
1.180
2.16
2.19
2.20
2.19
1.09
1.00
1.05
9.23
f1 (ppm)


LSC-ph-1.20.fid
13C NMR LSC-ph-1 in CDCL3
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159.34
145.12
139.84
136.77
128.96
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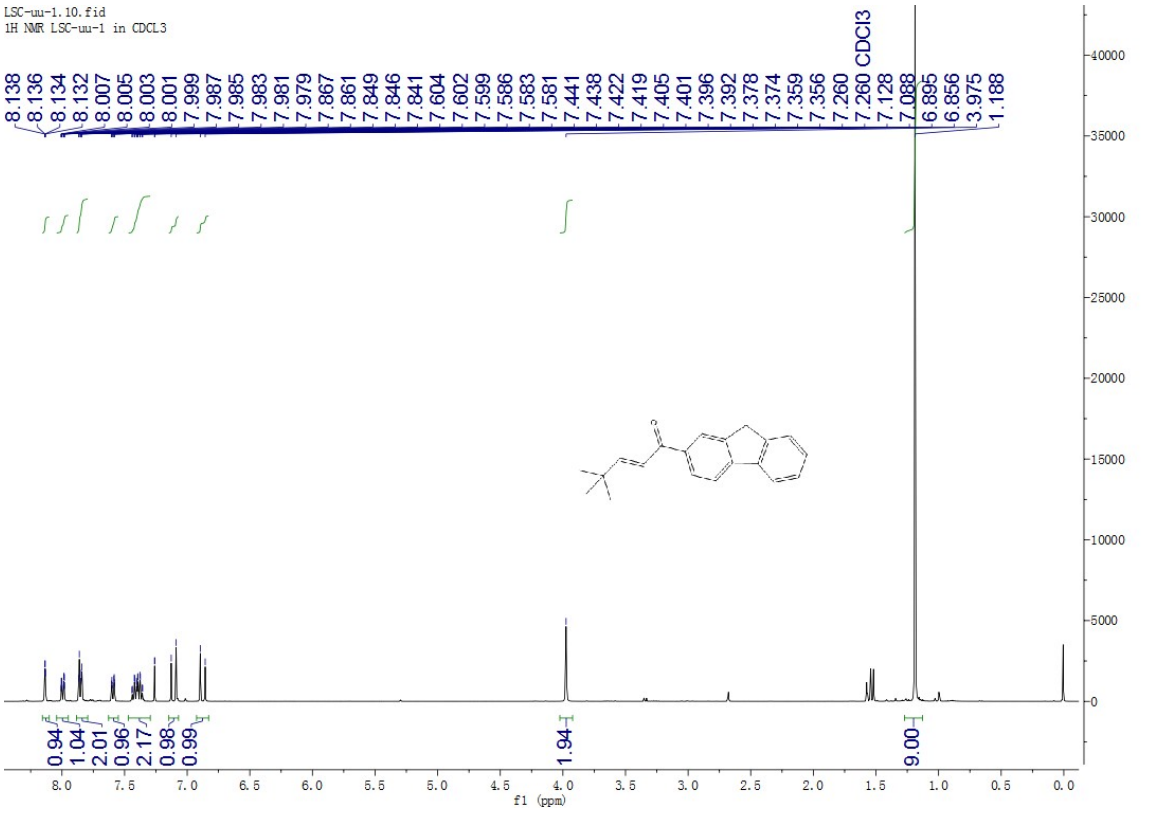
127.96
127.09
126.99
120.76
77.16 CDCl3
34.03
28.62
f1 (ppm)


LSC-uu-1.10.fid
1H NMR LSC-uu-1 in CDCL3
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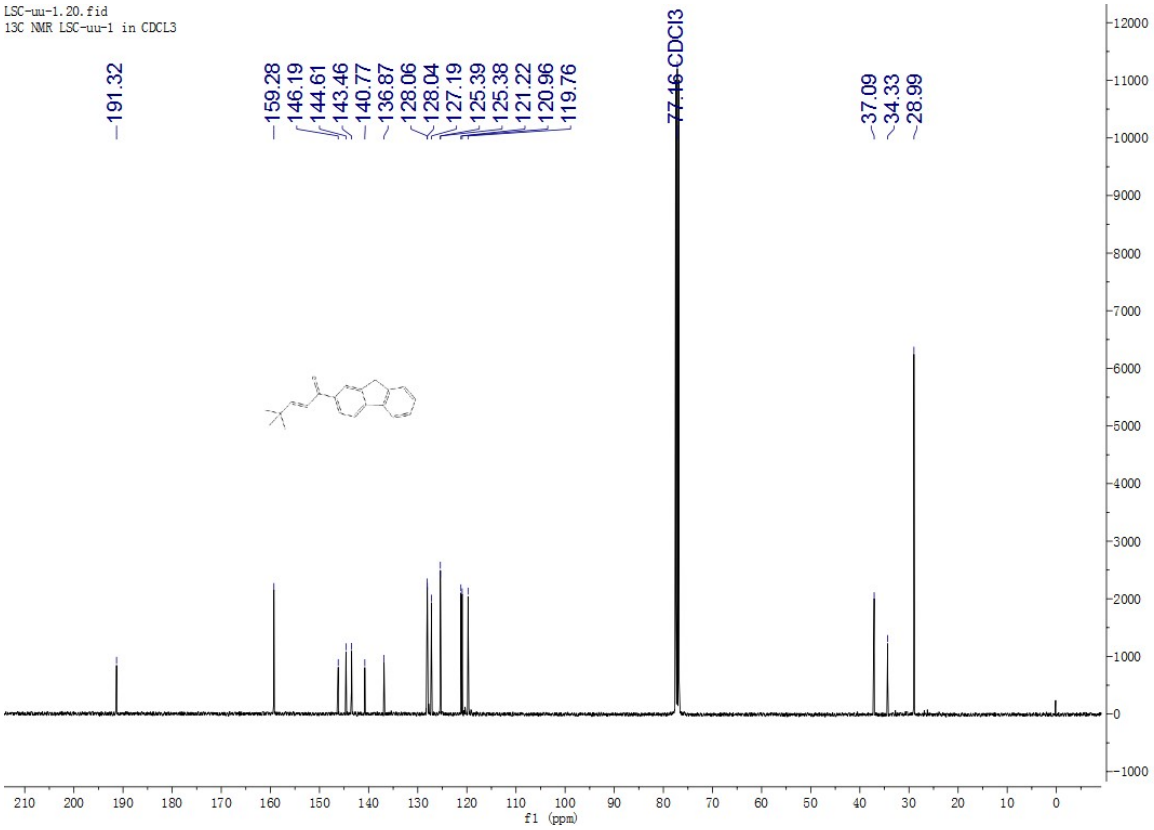
8.136
8.134
8.132
8.007
8.005
8.003
8.001
7.999
7.987
7.985
7.983
7.981
7.979
7.867
7.861
7.849
7.846
7.841
7.604
7.602
7.599
7.586
7.583
7.581
7.441
7.438
7.422
7.419
7.405
7.401
7.396
7.392
7.378
7.374
7.359
7.356
7.260 CDCl3
7.128
7.088
6.895
6.856
3.975
1.188
0.94
1.04
2.01
0.96
2.17
0.98
0.99
1.94
9.00
f1 (ppm)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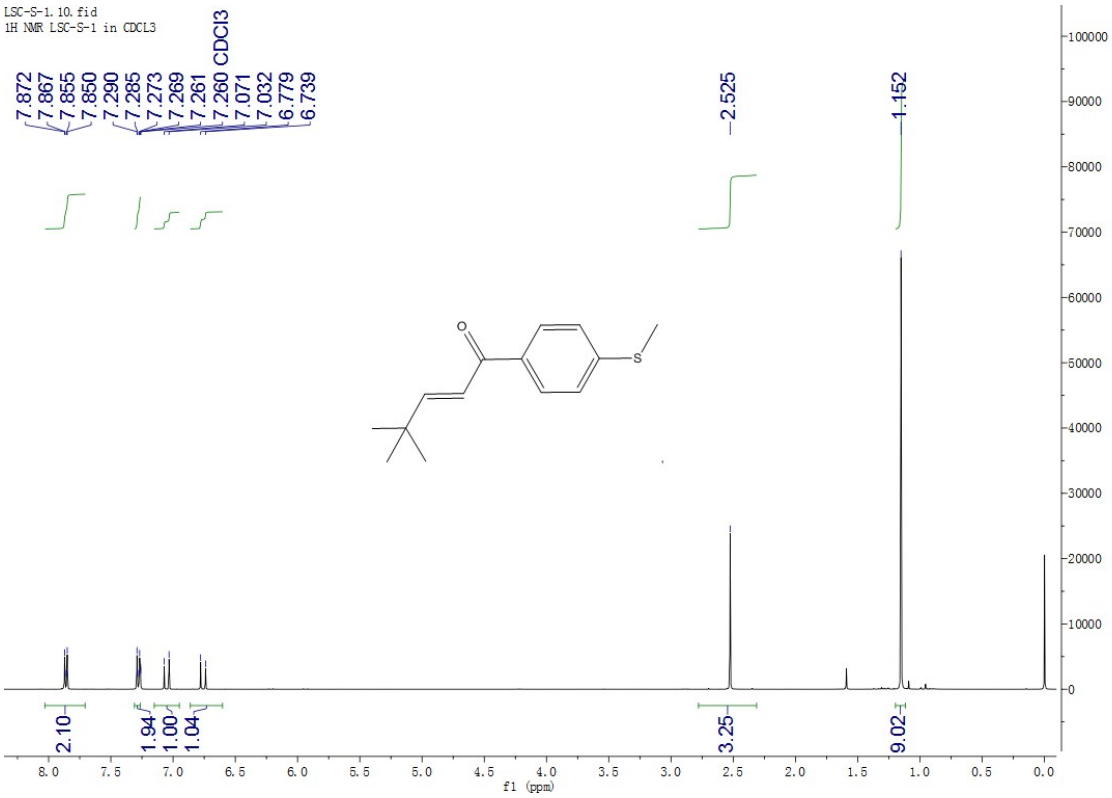
13C NMR LSC-uu-1 in CDCL3
191.32
159.28
146.19
144.61
143.46
140.77
136.87
128.06
128.04
127.19
125.39
125.38
121.22
120.96
119.76
77.16 CDCl3
37.09
34.33
28.99
f1 (ppm)


LSC-S-1.10.fid
1H NMR LSC-S-1 in CDCL3
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7.867
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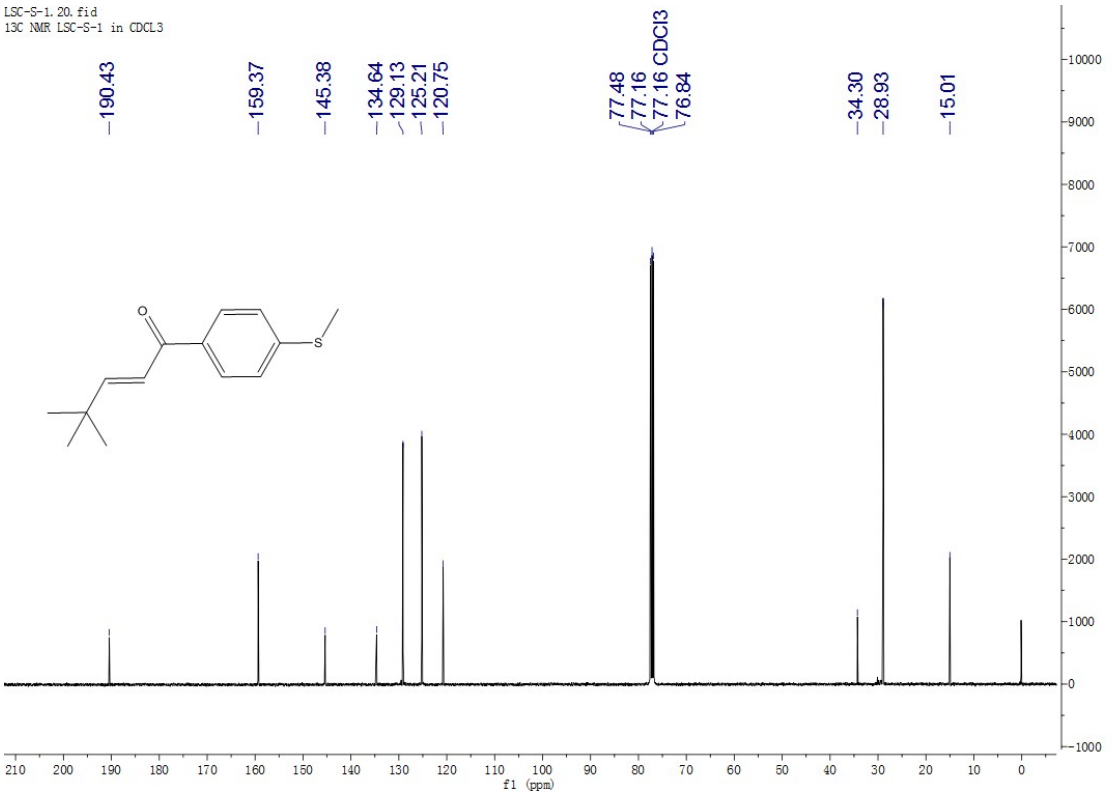
7.850
7.290
7.285
7.273
7.269
7.261
7.260 CDCl3
7.071
7.032
6.779
6.739
2.525
1.152
O
S
2.10
1.94
1.00
1.04
3.25
9.02
f1 (ppm)


LSC-S-1.20.fid
13C NMR LSC-S-1 in CDCL3
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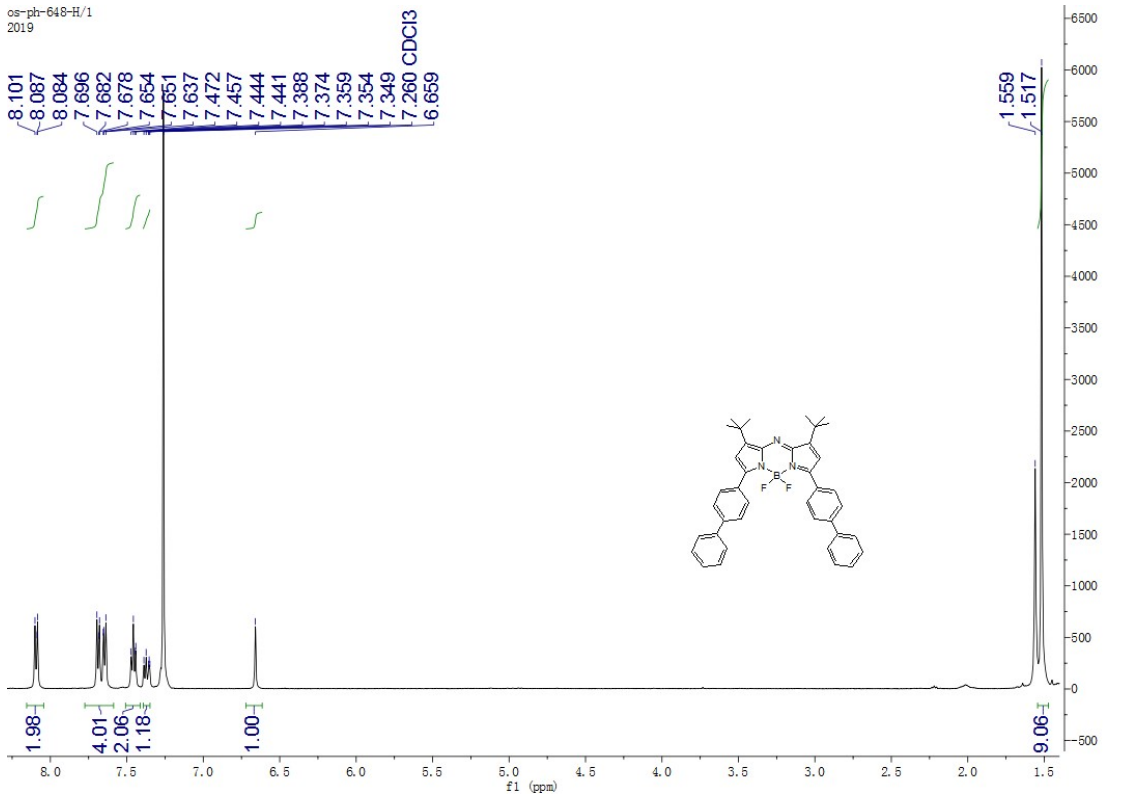
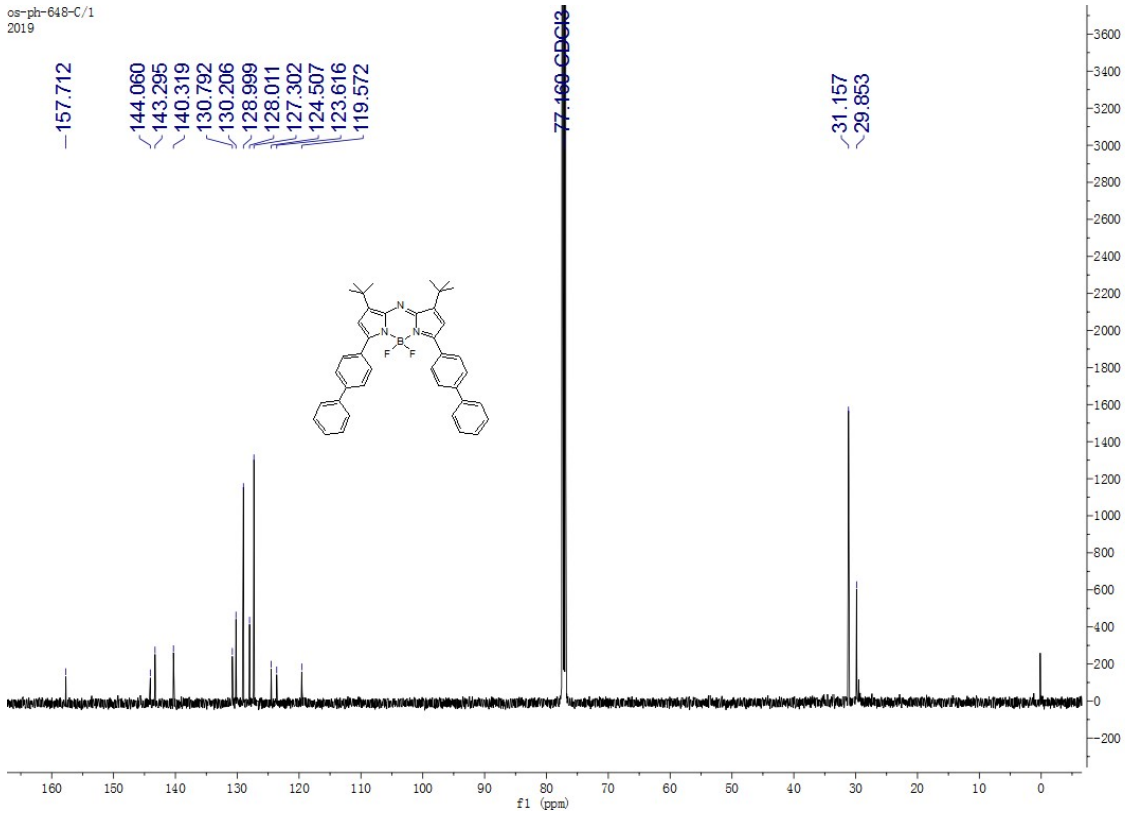
145.38
134.64
129.13
125.21
120.75
77.48
77.16
77.16 CDCl3
76.84
34.30
28.93
15.01
O
S
f1 (ppm)


os-ph-648-H/1
2019
8.101
8.087
8.084
7.696
7.682
7.678
7.654
7.651
7.637
7.472
7.457
7.444
7.441
7.388
7.374
7.359
7.354
7.349
7.260 CDCl3
6.659
1.559
1.517
1.98
4.01
2.06
1.18
1.00
9.06
f1 (ppm)


os-ph-648-C/1
2019
157.712
144.060
143.295
140.319
130.792
130.206
128.999
128.011
127.302
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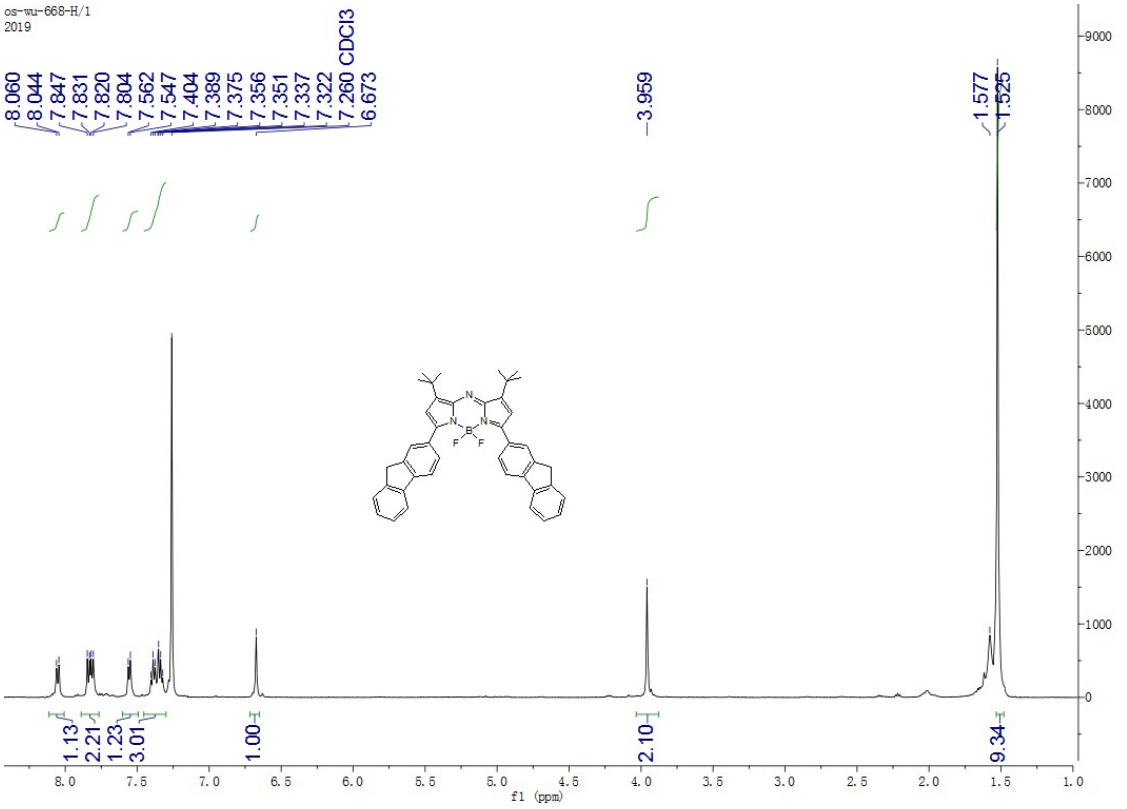
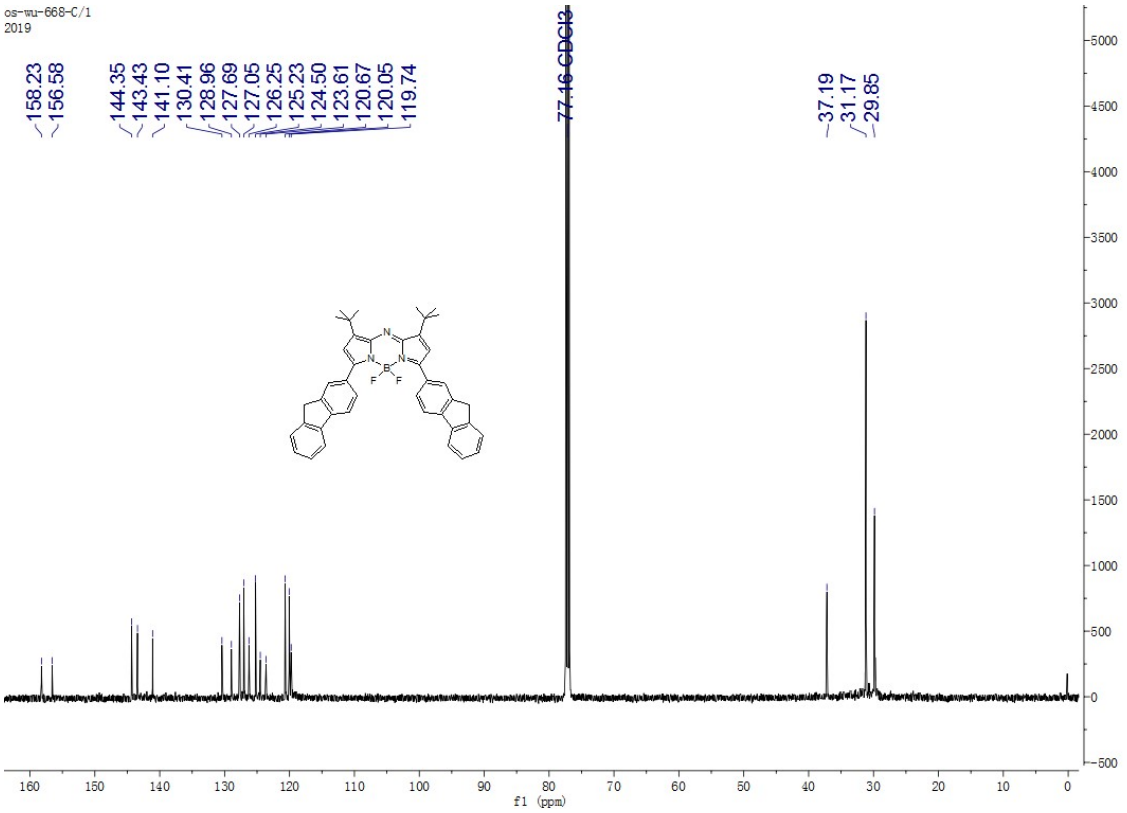
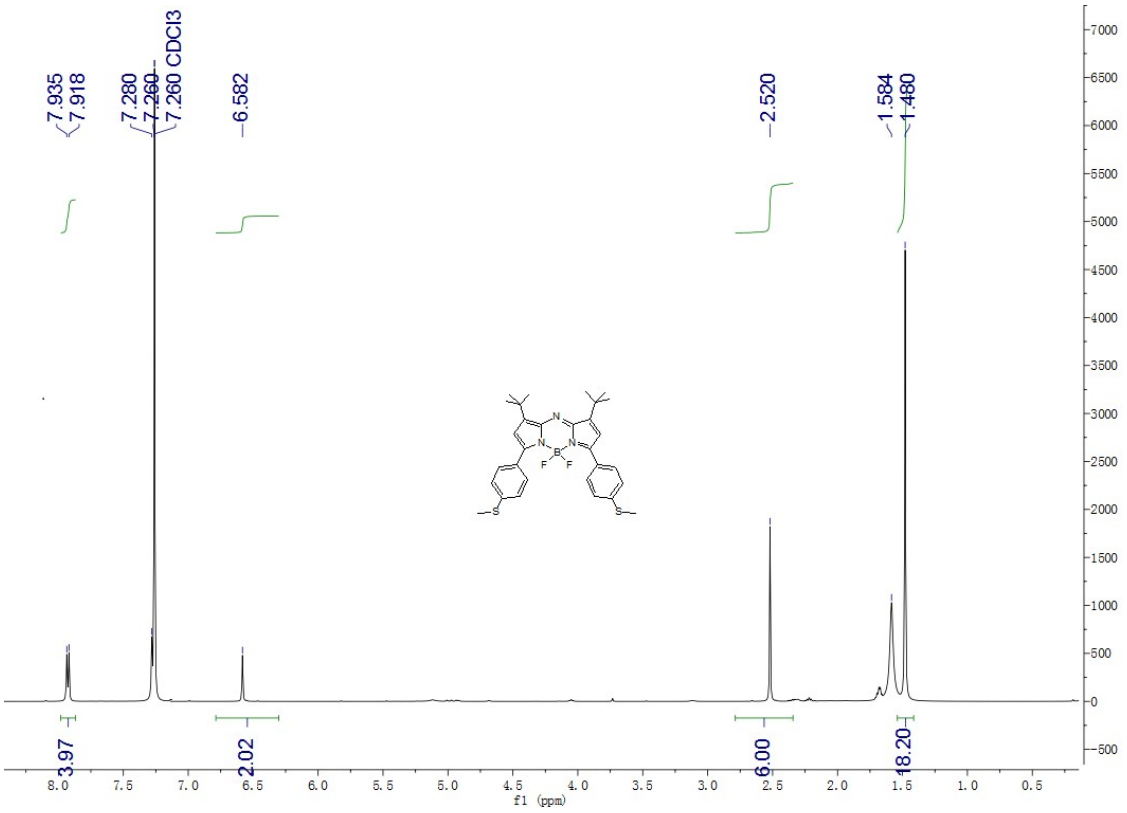
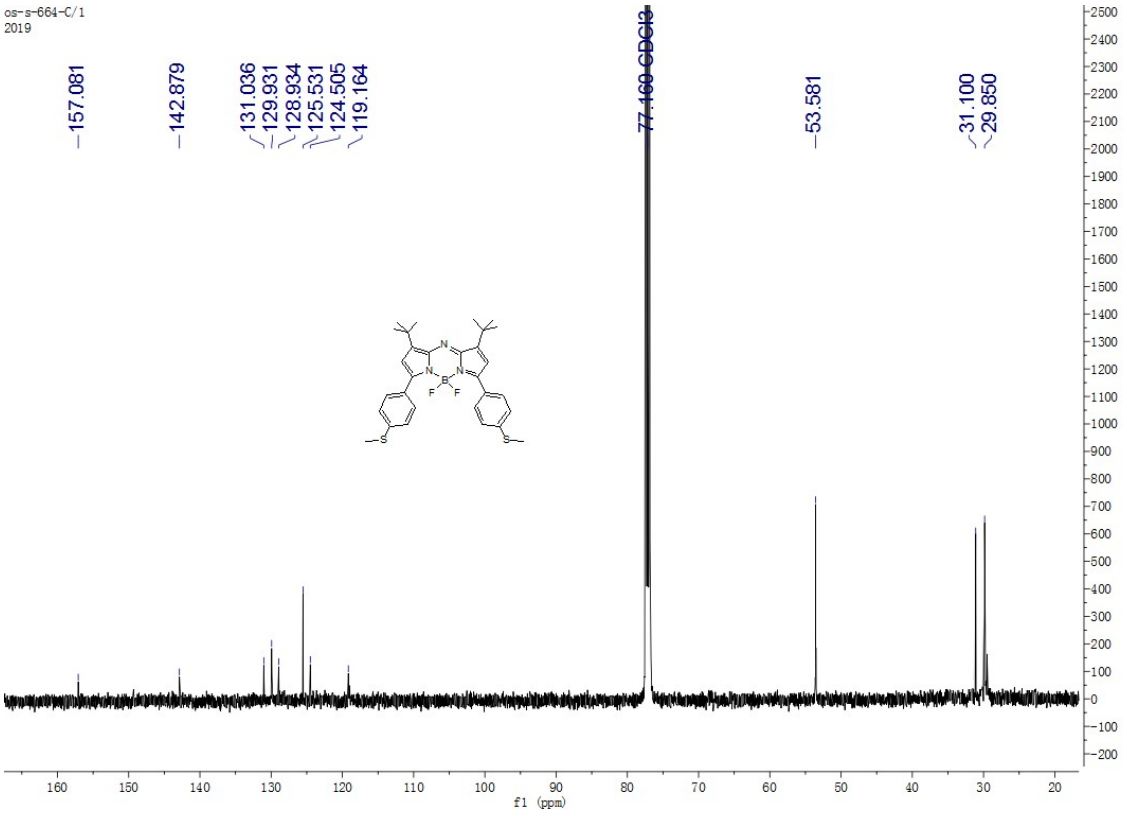
119.572
77.160 CDCl3
31.157
29.853
f1 (ppm)

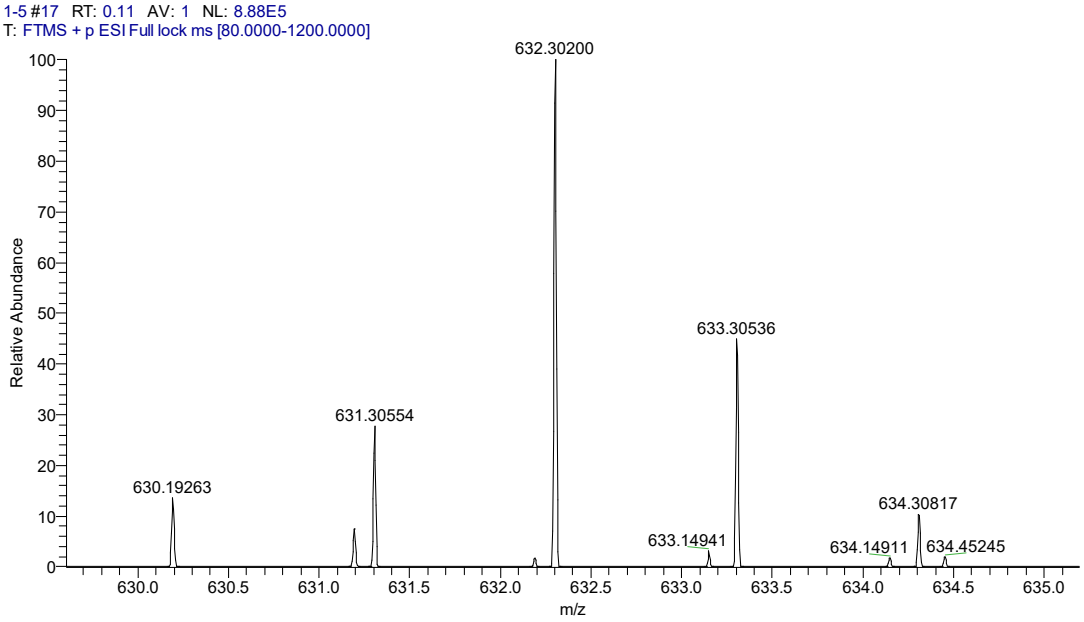

os-wu-668-H/1
2019
8.060
8.044
7.847
7.831
7.820
7.804
7.562
7.547
7.404
7.389
7.375
7.356
7.351
7.337
7.322
7.260 CDCl3
6.673
3.959
1.577
1.525
1.13
2.21
1.23
3.01
1.00
2.10
9.34
f1 (ppm)


os-wu-668-C/1
2019
158.23
156.58
144.35
143.43
141.10
130.41
128.96
127.69
127.05
126.25
125.23
124.50
123.61
120.67
120.05
119.74
77.46 CDCl3
37.19
31.17
29.85
f1 (ppm)

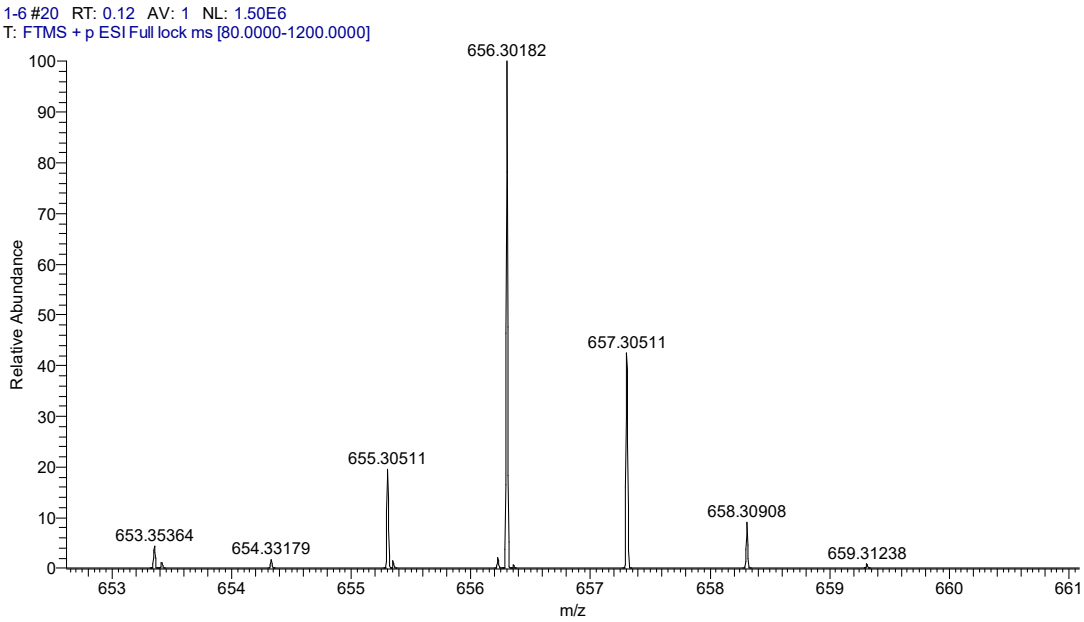

7.935
7.918
7.280
7.260
7.260 CDCl3
6.582
2.520
1.584
1.480
3.97
2.02
6.00
18.20
f1 (ppm)


os-s-664-C/1
2019
157.081
142.879
131.036
129.931
128.934
125.531
124.505
119.164
77.160 CDCl3
53.581
31.100
29.850
f1 (ppm)

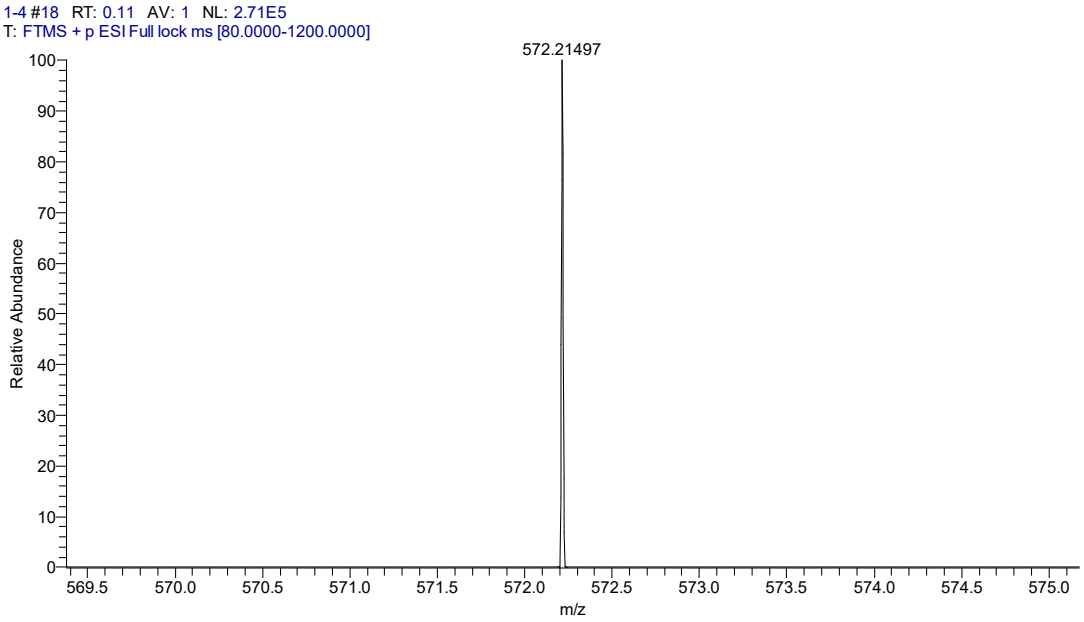
3. HRMS



DPh-tBuazaBDP: HRMS (ESI) m/z calcd for $C_{40}H_{38}BF_2N_3Na^+$ $(M+Na)^+$ 632.30191, found 632.30200.



Flu-tBuazaBDP: HRMS (ESI) m/z calcd for $C_{42}H_{38}BF_2N_3Na^+$ $(M+Na)^+$ 656.30191, found 656.30182.



S-tBuazaBDP: HRMS (ESI) m/z calcd for $C_{30}H_{34}BF_2N_3S_2Na^+$ $(M+Na)^+$ 572.21475, found 572.21497.

4. Fig. S1-13

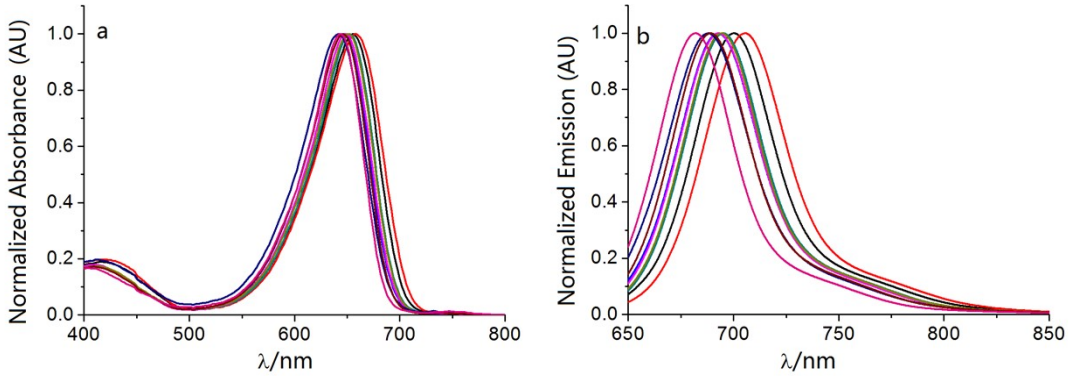


Fig. S1. a) Absorption and b) emission spectra of 5 μM **DPh-tBuazaBDP** in DMF, DMSO, CH_2Cl_2, toluene, $CHCl_3$, THF, CH_3CN, CH_3COOEt and *n*-hexane. λ_{ex} = 630 nm.

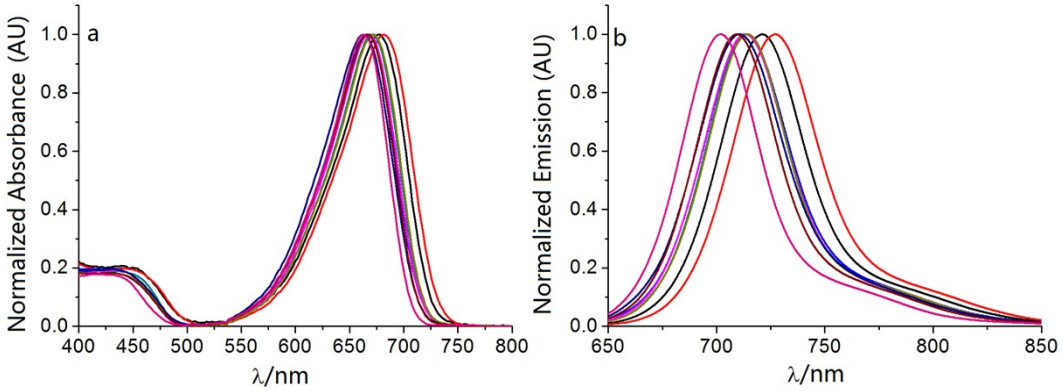


Fig. S2. a) Absorption and b) emission spectra of 5 μM **Flu-tBuazaBDP** in DMF, DMSO, CH_2Cl_2, toluene, $CHCl_3$, THF, CH_3CN, CH_3COOEt and *n*-hexane. λ_{ex} = 630 nm

Table S1 Optical properties of **aza-BODIPYs** in various solvents at 298 K.

Dye	solvent	$\lambda_{abs}/\lambda_{em}$ (nm)	Stokes shift (nm)	Fwhm (nm)	ε [M^{-1} cm^{-1}]	ϕ
DPh-tBuazaBDP	DMF	656/700	44	69	81500	0.11
	DMSO	658/705	47	72	82000	0.11
	CH_2Cl_2	650/693	43	69	83000	0.13
	toluene	652/695	43	65	85000	0.12
	$CHCl_3$	648/693	45	65	82500	0.14
	THF	652/694	42	66	84000	0.12
	CH_3CN	642/686	44	69	81000	0.10
	CH_3COOEt	646/689	43	66	83500	0.12

	n-hexane	644/682	38	61	81000	0.16
	DMF	678/721	43	74	82000	0.10
	DMSO	682/726	45	77	83500	0.10
	CH_2Cl_2	668/713	45	74	84000	0.11
	toluene	670/714	44	71	86000	0.11
Flu-tBuazaBDP	$CHCl_3$	668/713	45	72	83000	0.14
	THF	672/714	42	72	85500	0.10
	CH_3CN	662/710	48	74	82500	0.09
	CH_3COOEt	666/709	43	71	85000	0.12
	n-hexane	662/701	39	66	83000	0.14

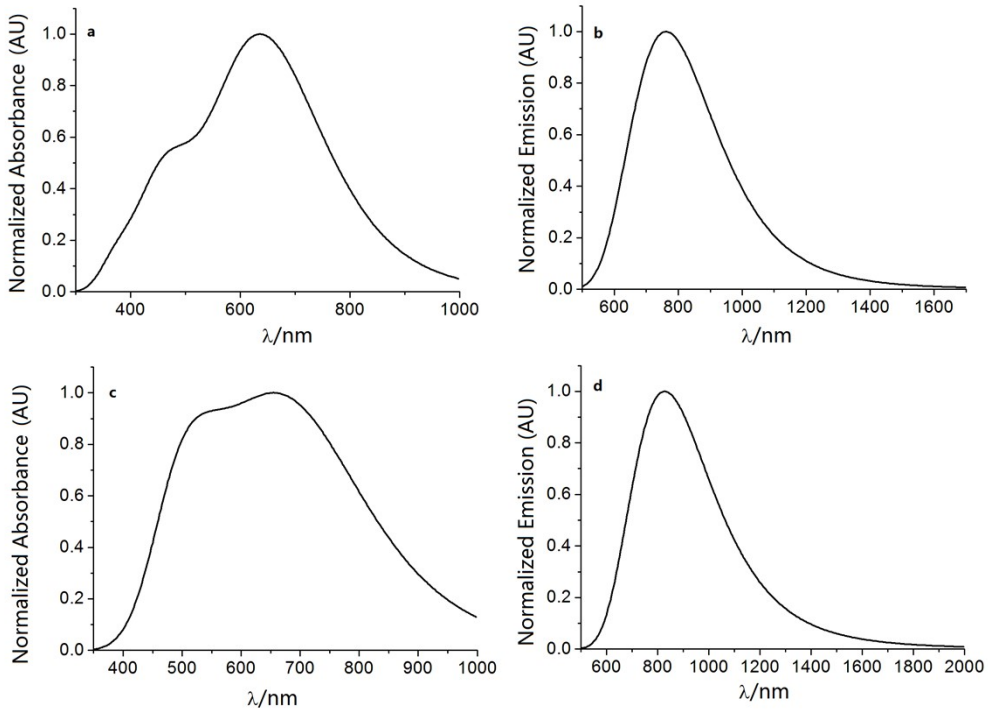


Fig. S3 Calculated electronic spectra of **S-tBuazaBDP** (a, b) and **S-PhazaBDP** (c, d).

Table. S2 Best computed estimate for λ_{abs}, λ_{em} and Oscillator strength of **S-tBuazaBDP** and **S-PhazaBDP**.

Dye	λ_{abs} [nm]	Oscillator strength	λ_{em} [nm]	Oscillator strength
S-tBuazaBDP	642.78	0.8026	761.68	0.9665
S-PhazaBDP	689.88	0.822	828.36	0.9684

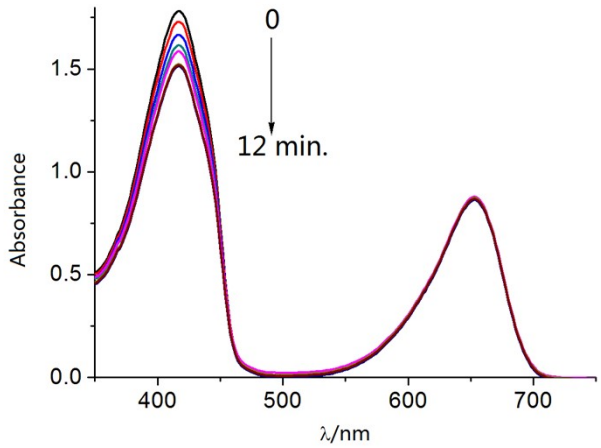


Fig. S4 Time-dependent photodegradation of DPBF with 8 μM **Ph-tBuazaBDP**.

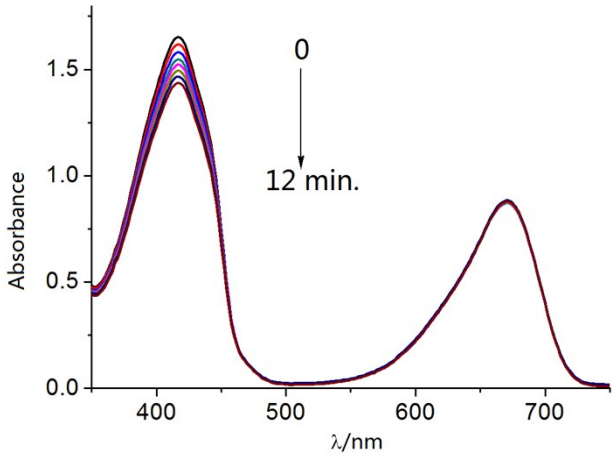


Fig. S5 Time-dependent photodegradation of DPBF with 8 μM **Flu-tBuazaBDP**.

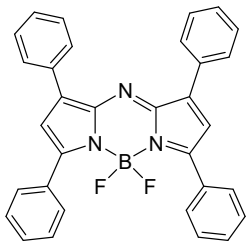


Fig. S6 Structure of **tetraphenyl aza-BODIPY**.

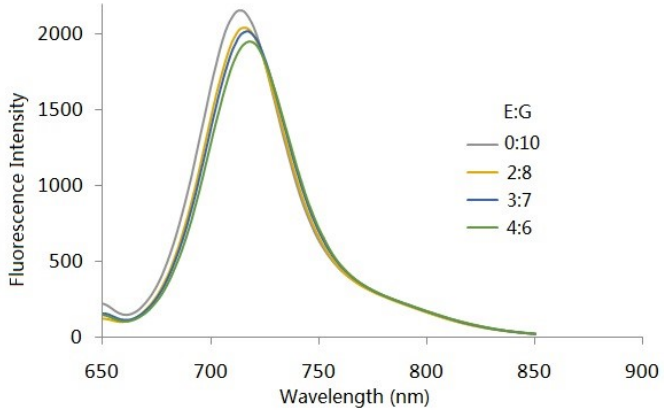


Fig. S7 Fluorescence intensity changes of 12 μM **S-tBuazaBDP**, as a function of viscosity in the mixture of ethylene glycol (E) and glycerol (G). Excitation wavelength: 620 nm.

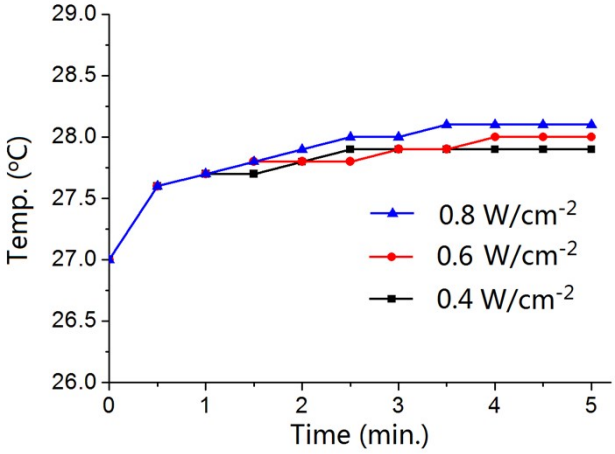


Fig. S8 Temperature change of 10 ml water including 5 mg DSPE-PEG2000 under 690 nm laser irradiation with different exposure intensity (0.4, 0.6 and 0.8 $W \cdot cm^{-2}$).

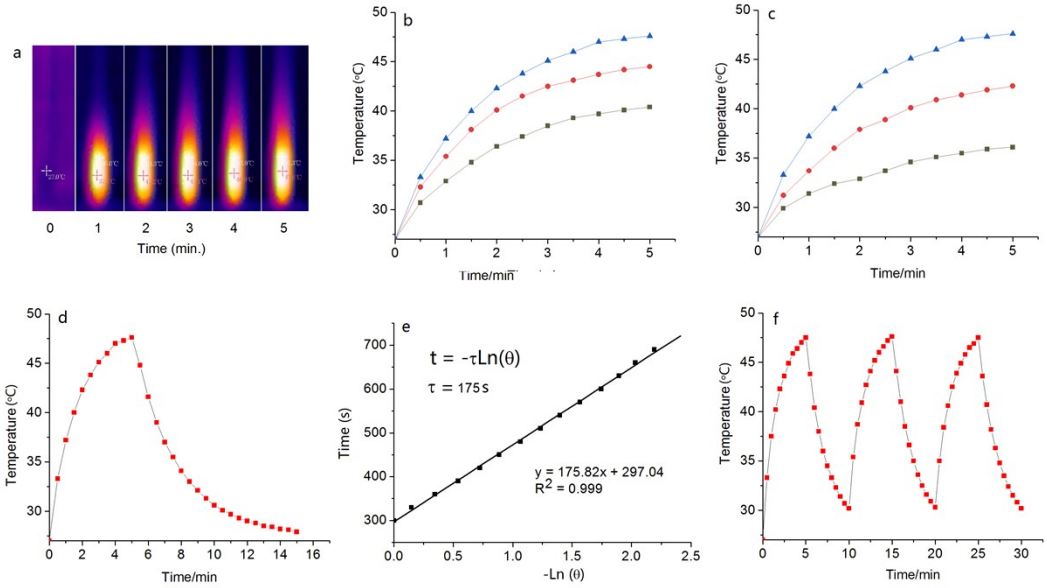


Fig. S9 a) Photothermal images (27-47.6 °C) of **Flu-tBuazaBDP** NPs in water under 690 nm laser irradiation (0.8 W cm^{-2}, 5 min). b) Photothermal conversion of **Flu-tBuazaBDP** NPs at different concentrations (20, 40 and 80 μM) under 690 nm laser irradiation (0.8 W cm^{-2}). c) Photothermal conversion of **Flu-tBuazaBDP** NPs (80 μM) under 690 nm laser irradiation with different exposure intensity (0.4, 0.6 and 0.8 W cm^{-2}). d) Photothermal response curves of **Flu-tBuazaBDP** NPs aqueous solutions (80 μM) under irradiation and after naturally cooling to room temperature. e) Linear fitting of -Lnθ and time. f) Photothermal stability study of **Flu-tBuazaBDP** NPs during three circles of heating-cooling processes.

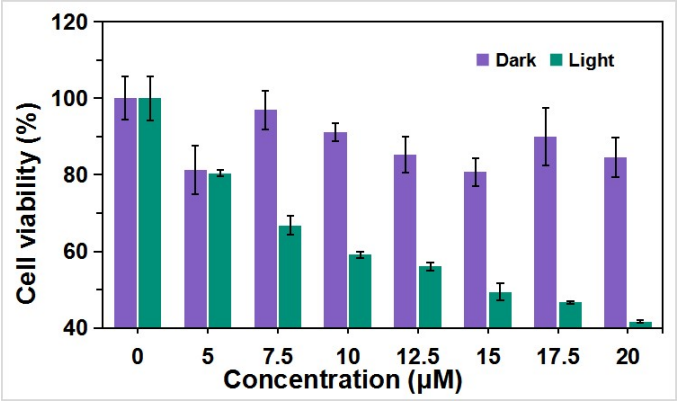


Fig. S10 The cell viability under different **S-tBuazaBDP-**NPs concentration under no light or 635 nm NIR light radiation (10 mW·cm^{-2}, 10 min), respectively.

5. Data of X-ray analysis of **S-tBuazaBDP**

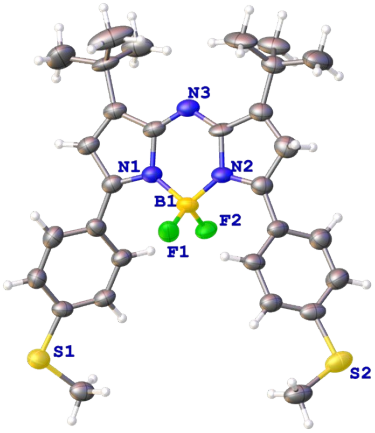


Table 1 Crystal data and structure refinement for exp_3226.

Identification code	exp_3226
Empirical formula	$C_{30}H_{35}BF_2N_3S_2$
Formula weight	550.54
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.3095(9)
b/Å	16.4925(16)
c/Å	18.8024(15)
α/°	99.542(7)
β/°	103.146(7)
γ/°	92.561(7)
Volume/Å^3	3355.5(5)
Z	4
ρ_{calc}g/cm^3	1.090
μ/mm^{-1}	1.695
F(000)	1164.0
Crystal size/mm^3	0.13 × 0.1 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.908 to 149.414
Index ranges	-7 ≤ h ≤ 13, -19 ≤ k ≤ 20, -23 ≤ l ≤ 21
Reflections collected	21675
Independent reflections	12906 [R_{int} = 0.1479, R_{sigma} = 0.1627]
Data/restraints/parameters	12906/31/701
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.1153, wR_2 = 0.3329
Final R indexes [all data]	R_1 = 0.1816, wR_2 = 0.4002
Largest diff. peak/hole / e Å^{-3}	0.87/-0.80

Crystal structure determination of [exp_3226]

Crystal Data for $C_{30}H_{35}BF_2N_3S_2$ (M =550.54 g/mol): triclinic, space group P-1 (no. 2), a = 11.3095(9) Å, b = 16.4925(16) Å, c = 18.8024(15) Å, α = 99.542(7)°, β = 103.146(7)°, γ = 92.561(7)°, V = 3355.5(5) Å^3, Z = 4, T = 149.99(10) K, μ(Cu Kα) = 1.695 mm^{-1}, *Dcalc* = 1.090 g/cm^3, 21675 reflections measured (4.908° ≤ 2Θ ≤ 149.414°), 12906 unique (R_{int} = 0.1479, R_{sigma} = 0.1627) which were used in all calculations. The final R_1 was 0.1153 (I > 2σ(I)) and wR_2 was 0.4002 (all data).

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for exp_3226. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
S1	1935.3(13)	6237.4(10)	1477.1(9)	54.2(4)
S2	5938.4(13)	4255.3(11)	6298.5(8)	59.8(4)
F1	6265(3)	3964.1(19)	2738.2(17)	55.9(9)
F2	4690(2)	3046(2)	2705.0(16)	49.1(8)
N1	5573(3)	2952(3)	1627(2)	38.3(10)
N2	6646(3)	2527(3)	2793(2)	38.8(10)
N3	6798(3)	1795(3)	1601(2)	41.7(11)
C1	5877(4)	2357(3)	488(3)	43.7(13)
C2	5231(4)	3041(3)	408(3)	43.2(13)
C3	5022(4)	3379(3)	1109(3)	39.1(12)
C4	6138(4)	2322(3)	1264(3)	41.0(13)
C5	4266(4)	4071(3)	1229(3)	39.6(12)
C6	3404(4)	4050(3)	1656(3)	41.4(12)
C7	2678(4)	4701(3)	1733(3)	42.5(13)
C8	2777(4)	5379(3)	1394(3)	38.9(12)
C9	3606(5)	5385(4)	951(3)	46.7(14)
C10	4348(5)	4726(4)	853(3)	49.7(15)
C11	1115(5)	6069(4)	2157(3)	51.4(15)
C12	7024(4)	1880(3)	2333(3)	39.6(12)
C13	7633(5)	1330(4)	2771(3)	47.3(9)
C14	7578(5)	1636(4)	3493(3)	52.0(15)
C15	6960(4)	2377(3)	3498(3)	43.2(13)
C16	8214(5)	557(4)	2506(3)	48.3(9)
C17	8840(7)	192(5)	3171(4)	88(2)
C18	9151(5)	783(4)	2093(4)	76(2)
C19	7235(5)	-70(4)	1989(4)	66(2)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_3226. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C20	7505(6)	1651(6)	15(4)	111(3)
C21	5518(6)	908(4)	-138(4)	71.0(17)
C22	5663(8)	1954(5)	-893(4)	92(2)
C23	6165(5)	1741(4)	-123(3)	51.5(10)
C24	6722(4)	2875(3)	4155(3)	43.3(13)
C25	6356(5)	2477(4)	4683(3)	53.3(16)
C26	6141(5)	2910(4)	5315(3)	57.7(16)
C27	6255(4)	3772(4)	5460(3)	47.3(14)
C28	6617(4)	4187(4)	4955(3)	45.9(14)
C29	6828(4)	3734(3)	4308(3)	44.1(13)
C30	6210(5)	5337(4)	6291(3)	64.2(19)
B1	5773(5)	3155(4)	2492(3)	41.6(14)
S3	-3136.0(13)	6437.3(10)	1433.9(8)	53.1(4)
S4	1226.9(14)	4448.6(11)	6208.0(8)	58.6(4)
F3	-711(2)	2891.2(18)	2461.1(15)	40.9(7)
F4	757(2)	3957.3(18)	2672.6(15)	40.7(7)
N4	301(3)	3037(3)	1485(2)	38.2(10)
N5	1556(3)	1900(3)	1434(2)	37.7(10)
N6	1380(3)	2570(3)	2637(2)	38.8(10)
C31	595(4)	2471(3)	336(3)	39.9(12)
C32	-71(4)	3142(3)	268(3)	41.8(13)
C33	852(4)	2410(3)	1104(3)	36.5(11)
C34	-273(4)	3480(3)	979(3)	34.9(11)
C35	-1008(4)	4167(3)	1104(3)	37.7(12)
C36	-1632(4)	4272(3)	1665(3)	39.3(12)
C37	-2306(4)	4953(3)	1772(3)	40.8(13)
C38	-2366(4)	5550(3)	1332(3)	35.6(12)
C39	-1777(4)	5445(3)	747(3)	43.2(13)
C40	-1114(4)	4761(3)	641(3)	43.1(13)
C41	-3683(6)	6392(4)	2247(3)	67.7(19)
C42	974(4)	1889(4)	-271(3)	44.9(14)
C43	2382(5)	2053(4)	-147(3)	55.4(16)
C44	661(5)	984(4)	-230(3)	55.4(16)
C45	370(5)	2075(4)	-1033(3)	56.8(17)
C46	1829(4)	1968(3)	2163(3)	38.2(12)
C47	2651(4)	1516(3)	2603(3)	40.7(13)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_3226. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C48	2700(4)	1854(3)	3330(3)	43.6(13)
C49	1905(4)	2501(3)	3344(3)	38.2(12)
C50	3278(4)	774(3)	2313(3)	44.9(14)
C51	4209(5)	538(4)	2953(4)	61.6(16)
C52	2304(5)	47(4)	1963(4)	57.8(17)
C53	3937(5)	997(4)	1728(3)	59.1(17)
C54	1679(4)	2979(4)	4016(3)	43.8(13)
C55	2656(4)	3207(4)	4633(3)	44.4(14)
C56	2489(4)	3640(4)	5287(3)	51.5(16)
C57	1326(5)	3888(4)	5359(3)	48.6(14)
C58	358(5)	3633(4)	4747(3)	47.4(14)
C59	510(4)	3195(4)	4079(3)	45.9(14)
C60	-380(5)	4504(4)	6110(3)	57.7(17)
B5	411(5)	3140(4)	2335(3)	38.4(14)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for exp_3226. 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}
S1	58.0(7)	54.7(8)	50.3(8)	8.3(6)	12.2(6)	18.4(6)
S2	50.9(7)	79.3(11)	41.3(7)	-8.7(7)	8.4(6)	7.4(7)
F1	89(2)	36.7(17)	37.0(16)	-1.1(13)	10.6(15)	2.6(16)
F2	47.2(14)	62.4(19)	44.8(16)	10.8(14)	21.2(12)	22.4(13)
N1	38.4(19)	38(2)	37(2)	1.1(18)	10.5(16)	7.3(17)
N2	33.4(18)	42(2)	41(2)	0.6(18)	12.2(16)	10.9(17)
N3	34.6(18)	46(2)	42(2)	-1.8(19)	10.1(17)	7.5(18)
C1	42(2)	44(3)	42(3)	-6(2)	15(2)	2(2)
C2	44(2)	46(3)	38(3)	-2(2)	15(2)	0(2)
C3	37(2)	42(3)	36(2)	-1(2)	9.0(19)	-1(2)
C4	40(2)	42(3)	39(2)	-6(2)	15(2)	1(2)
C5	44(2)	36(3)	34(2)	0(2)	4(2)	5(2)
C6	42(2)	48(3)	36(2)	4(2)	13.7(19)	10(2)
C7	40(2)	50(3)	37(2)	0(2)	14(2)	5(2)
C8	36(2)	40(3)	37(2)	-1(2)	7.4(19)	11(2)
C9	54(3)	46(3)	42(3)	10(2)	14(2)	7(2)
C10	53(3)	59(4)	39(3)	9(2)	13(2)	2(3)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for exp_3226. 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}
C11	44(3)	56(3)	47(3)	-1(3)	2(2)	15(2)
C12	25.7(18)	49(3)	43(3)	-7(2)	15.6(18)	11.0(19)
C13	40.2(15)	47.3(16)	53.2(16)	1.9(15)	12.8(14)	10.3(14)
C14	40(2)	55(3)	59(3)	8(3)	7(2)	6(2)
C15	40(2)	45(3)	41(3)	1(2)	6(2)	7(2)
C16	41.2(15)	46.0(16)	55.8(17)	1.0(15)	11.9(15)	13.4(14)
C17	105(5)	82(5)	76(5)	5(4)	19(4)	55(4)
C18	61(3)	61(4)	114(5)	-7(4)	50(3)	20(3)
C19	44(3)	52(4)	96(5)	-14(3)	24(3)	10(3)
C20	46.2(17)	176(8)	82(5)	-59(5)	19(2)	2(3)
C21	70(3)	55(2)	79(4)	-22(2)	27(3)	-3.8(19)
C22	136(6)	84(5)	49(2)	-10(2)	22(3)	16(4)
C23	50.4(16)	56(2)	45.8(18)	-17.0(17)	25.8(17)	3.1(16)
C24	45(2)	49(3)	34(2)	1(2)	6(2)	16(2)
C25	58(3)	54(4)	46(3)	7(3)	10(3)	12(3)
C26	63(3)	64(4)	49(3)	8(3)	20(3)	12(3)
C27	34(2)	59(3)	41(3)	-9(2)	0(2)	15(2)
C28	45(2)	51(3)	38(3)	0(2)	6(2)	12(2)
C29	45(2)	43(3)	42(3)	0(2)	8(2)	16(2)
C30	60(3)	78(4)	49(3)	-8(3)	10(3)	23(3)
B1	47(3)	34(3)	41(3)	-5(2)	12(2)	8(2)
S3	57.8(7)	53.3(8)	50.4(8)	8.4(6)	14.4(6)	22.8(6)
S4	59.8(8)	70.7(10)	36.1(7)	-9.7(7)	5.1(6)	13.0(7)
F3	32.9(12)	51.5(17)	37.7(14)	6.4(13)	7.6(11)	8.1(12)
F4	41.5(13)	41.5(16)	36.9(14)	-2.2(12)	10.4(11)	9.3(12)
N4	40.7(19)	39(2)	33(2)	-3.5(17)	12.0(16)	5.4(17)
N5	32.4(17)	44(2)	33(2)	-4.1(17)	6.9(16)	7.2(17)
N6	33.6(18)	44(2)	34(2)	-2.6(18)	6.0(16)	1.8(17)
C31	34(2)	45(3)	34(2)	-4(2)	3.0(19)	4(2)
C32	38(2)	54(3)	33(2)	2(2)	9.9(19)	8(2)
C33	36(2)	40(3)	32(2)	-8(2)	14.9(18)	9.5(19)
C34	33(2)	39(3)	33(2)	3.6(19)	10.7(18)	6.2(19)
C35	27.9(19)	48(3)	35(2)	-3(2)	8.7(18)	9.6(19)
C36	35(2)	53(3)	29(2)	4(2)	6.7(18)	8(2)
C37	34(2)	50(3)	38(2)	1(2)	11.3(19)	6(2)
C38	21.9(17)	47(3)	36(2)	3(2)	5.0(17)	18.2(18)
C39	47(3)	41(3)	41(3)	7(2)	10(2)	14(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for exp_3226. 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}
C40	43(2)	51(3)	33(2)	-1(2)	12(2)	-2(2)
C41	76(4)	74(4)	52(4)	7(3)	11(3)	39(3)
C42	37(2)	60(3)	33(2)	-2(2)	6(2)	8(2)
C43	43(3)	80(4)	42(3)	5(3)	12(2)	10(3)
C44	56(3)	53(3)	51(3)	-9(3)	10(3)	14(3)
C45	61(3)	68(4)	35(3)	-10(3)	10(2)	10(3)
C46	34(2)	40(3)	39(2)	-1(2)	9.3(19)	9.3(19)
C47	31(2)	52(3)	40(3)	5(2)	10.0(19)	9(2)
C48	37(2)	48(3)	44(3)	5(2)	9(2)	4(2)
C49	25.8(19)	51(3)	38(2)	0(2)	12.7(18)	10.7(19)
C50	36(2)	51(3)	46(3)	0(2)	10(2)	20(2)
C51	57(2)	62(3)	64(3)	2(2)	13(2)	27(2)
C52	50(3)	50(3)	73(4)	-4(3)	23(3)	14(2)
C53	43(3)	73(4)	60(4)	-2(3)	19(2)	15(3)
C54	42(2)	51(3)	36(3)	4(2)	7(2)	8(2)
C55	33(2)	60(3)	35(3)	1(2)	5(2)	12(2)
C56	34(2)	73(4)	41(3)	5(3)	-3(2)	13(2)
C57	51(3)	50(3)	38(3)	0(2)	4(2)	8(2)
C58	40(2)	65(4)	35(3)	4(2)	6(2)	10(2)
C59	37(2)	60(3)	36(3)	-2(2)	6(2)	11(2)
C60	61(3)	66(4)	46(3)	-1(3)	18(3)	17(3)
B5	38(2)	36(3)	40(3)	4(2)	7(2)	11(2)

Table 4 Bond Lengths for exp_3226.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C8	1.747(5)	S3	C38	1.741(5)
S1	C11	1.792(6)	S3	C41	1.785(7)
S2	C27	1.765(6)	S4	C57	1.737(6)
S2	C30	1.799(7)	S4	C60	1.792(6)
F1	B1	1.385(7)	F3	B5	1.399(6)
F2	B1	1.386(7)	F4	B5	1.389(6)
N1	C3	1.350(7)	N4	C33	1.408(6)
N1	C4	1.407(6)	N4	C34	1.362(6)
N1	B1	1.566(7)	N4	B5	1.553(7)
N2	C12	1.404(6)	N5	C33	1.317(6)
N2	C15	1.358(7)	N5	C46	1.319(6)

Table 4 Bond Lengths for exp_3226.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N2	B1	1.549(7)	N6	C46	1.412(6)
N3	C4	1.319(7)	N6	C49	1.353(6)
N3	C12	1.324(6)	N6	B5	1.548(7)
C1	C2	1.381(8)	C31	C32	1.372(7)
C1	C4	1.433(7)	C31	C33	1.430(7)
C1	C23	1.507(7)	C31	C42	1.518(7)
C2	C3	1.419(7)	C32	C34	1.432(7)
C3	C5	1.475(7)	C34	C35	1.455(7)
C5	C6	1.399(7)	C35	C36	1.388(7)
C5	C10	1.396(8)	C35	C40	1.407(8)
C6	C7	1.390(7)	C36	C37	1.398(7)
C7	C8	1.387(8)	C37	C38	1.381(8)
C8	C9	1.390(7)	C38	C39	1.403(7)
C9	C10	1.416(8)	C39	C40	1.394(7)
C12	C13	1.423(8)	C42	C43	1.560(7)
C13	C14	1.383(8)	C42	C44	1.537(8)
C13	C16	1.523(8)	C42	C45	1.528(8)
C14	C15	1.435(8)	C46	C47	1.422(7)
C15	C24	1.452(7)	C47	C48	1.376(7)
C16	C17	1.520(9)	C47	C50	1.525(7)
C16	C18	1.516(9)	C48	C49	1.427(7)
C16	C19	1.521(8)	C49	C54	1.455(7)
C20	C23	1.496(8)	C50	C51	1.525(8)
C21	C23	1.521(9)	C50	C52	1.541(8)
C22	C23	1.534(10)	C50	C53	1.544(8)
C24	C25	1.403(8)	C54	C55	1.394(7)
C24	C29	1.392(8)	C54	C59	1.410(7)
C25	C26	1.360(8)	C55	C56	1.374(7)
C26	C27	1.397(9)	C56	C57	1.424(7)
C27	C28	1.380(8)	C57	C58	1.387(7)
C28	C29	1.392(7)	C58	C59	1.391(7)

Table 5 Bond Angles for exp_3226.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	S1	C11	103.9(3)	C38	S3	C41	103.4(3)
C27	S2	C30	103.3(3)	C57	S4	C60	103.5(3)
C3	N1	C4	107.0(4)	C33	N4	B5	121.8(4)

Table 5 Bond Angles for exp_3226.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C3	N1	B1	129.5(4)	C34	N4	C33	107.4(4)
C4	N1	B1	122.9(4)	C34	N4	B5	130.7(4)
C12	N2	B1	123.3(4)	C33	N5	C46	121.0(4)
C15	N2	C12	107.4(4)	C46	N6	B5	122.1(4)
C15	N2	B1	127.8(4)	C49	N6	C46	107.5(4)
C4	N3	C12	119.4(4)	C49	N6	B5	130.3(4)
C2	C1	C4	105.8(5)	C32	C31	C33	106.1(4)
C2	C1	C23	127.0(5)	C32	C31	C42	128.2(5)
C4	C1	C23	127.0(5)	C33	C31	C42	125.7(5)
C1	C2	C3	108.2(5)	C31	C32	C34	108.9(5)
N1	C3	C2	109.9(5)	N4	C33	C31	109.0(4)
N1	C3	C5	126.1(5)	N5	C33	N4	123.8(4)
C2	C3	C5	123.9(5)	N5	C33	C31	127.1(4)
N1	C4	C1	108.9(5)	N4	C34	C32	108.5(4)
N3	C4	N1	124.1(5)	N4	C34	C35	127.6(4)
N3	C4	C1	127.0(5)	C32	C34	C35	123.9(5)
C6	C5	C3	121.5(5)	C36	C35	C34	123.2(5)
C10	C5	C3	118.5(5)	C36	C35	C40	117.1(5)
C10	C5	C6	119.8(5)	C40	C35	C34	119.7(5)
C7	C6	C5	119.8(5)	C35	C36	C37	121.0(5)
C6	C7	C8	121.8(5)	C38	C37	C36	121.5(5)
C7	C8	S1	125.2(4)	C37	C38	S3	125.4(4)
C7	C8	C9	118.2(5)	C37	C38	C39	118.6(4)
C9	C8	S1	116.6(4)	C39	C38	S3	116.0(4)
C8	C9	C10	121.3(5)	C40	C39	C38	119.4(5)
C5	C10	C9	119.0(5)	C39	C40	C35	122.3(5)
N2	C12	C13	109.6(5)	C31	C42	C43	107.2(4)
N3	C12	N2	124.2(5)	C31	C42	C44	111.0(5)
N3	C12	C13	126.2(5)	C31	C42	C45	110.3(5)
C12	C13	C16	127.5(5)	C44	C42	C43	109.4(5)
C14	C13	C12	105.7(5)	C45	C42	C43	108.2(5)
C14	C13	C16	126.8(5)	C45	C42	C44	110.6(5)
C13	C14	C15	108.6(5)	N5	C46	N6	123.2(4)
N2	C15	C14	108.6(5)	N5	C46	C47	127.7(5)
N2	C15	C24	126.5(5)	N6	C46	C47	108.9(4)
C14	C15	C24	124.8(5)	C46	C47	C50	126.1(5)
C13	C16	C17	109.5(5)	C48	C47	C46	106.0(5)
C18	C16	C13	109.2(5)	C48	C47	C50	127.8(5)

Table 5 Bond Angles for exp_3226.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C18	C16	C17	109.3(5)	C47	C48	C49	109.0(5)
C18	C16	C19	109.6(5)	N6	C49	C48	108.7(4)
C19	C16	C13	109.4(4)	N6	C49	C54	126.6(4)
C19	C16	C17	109.8(6)	C48	C49	C54	124.7(5)
C1	C23	C21	108.4(5)	C47	C50	C52	108.6(4)
C1	C23	C22	112.1(5)	C47	C50	C53	109.5(5)
C20	C23	C1	111.0(5)	C51	C50	C47	109.7(4)
C20	C23	C21	108.2(6)	C51	C50	C52	109.6(5)
C20	C23	C22	111.3(6)	C51	C50	C53	109.1(4)
C21	C23	C22	105.5(5)	C52	C50	C53	110.2(5)
C25	C24	C15	118.9(5)	C55	C54	C49	118.4(4)
C29	C24	C15	124.9(5)	C55	C54	C59	118.6(5)
C29	C24	C25	116.3(5)	C59	C54	C49	122.9(4)
C26	C25	C24	121.6(6)	C56	C55	C54	120.8(5)
C25	C26	C27	121.2(6)	C55	C56	C57	121.7(5)
C26	C27	S2	116.5(5)	C56	C57	S4	117.7(4)
C28	C27	S2	124.6(5)	C58	C57	S4	125.7(4)
C28	C27	C26	118.9(5)	C58	C57	C56	116.6(5)
C27	C28	C29	119.1(6)	C57	C58	C59	122.5(5)
C28	C29	C24	122.9(6)	C58	C59	C54	119.7(5)
F1	B1	N1	108.5(5)	F3	B5	N4	109.4(4)
F1	B1	N2	112.6(4)	F3	B5	N6	109.5(5)
F2	B1	F1	110.0(4)	F4	B5	F3	110.0(4)
F2	B1	N1	111.4(4)	F4	B5	N4	110.2(5)
F2	B1	N2	108.8(5)	F4	B5	N6	110.8(4)
N2	B1	N1	105.5(4)	N6	B5	N4	106.9(4)

Table 6 Torsion Angles for exp_3226.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C8	C9	C10	179.1(4)	S3	C38	C39	C40	178.3(4)
S2	C27	C28	C29	-179.3(4)	S4	C57	C58	C59	179.0(5)
N1	C3	C5	C6	-42.9(7)	N4	C34	C35	C36	-26.7(8)
N1	C3	C5	C10	142.8(5)	N4	C34	C35	C40	153.7(5)
N2	C12	C13	C14	2.1(6)	N5	C46	C47	C48	175.2(5)
N2	C12	C13	C16	-178.6(5)	N5	C46	C47	C50	-8.2(9)
N2	C15	C24	C25	139.5(6)	N6	C46	C47	C48	-0.8(6)
N2	C15	C24	C29	-40.5(8)	N6	C46	C47	C50	175.8(5)

Table 6 Torsion Angles for exp_3226.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N3	C12	C13	C14	-175.7(5)	N6	C49	C54	C55	-143.1(5)
N3	C12	C13	C16	3.7(9)	N6	C49	C54	C59	39.5(9)
C1	C2	C3	N1	3.3(6)	C31	C32	C34	N4	2.1(6)
C1	C2	C3	C5	-174.3(5)	C31	C32	C34	C35	-176.3(4)
C2	C1	C4	N1	4.0(6)	C32	C31	C33	N4	1.7(5)
C2	C1	C4	N3	-175.9(5)	C32	C31	C33	N5	-173.7(5)
C2	C1	C23	C20	126.0(7)	C32	C31	C42	C43	110.3(6)
C2	C1	C23	C21	-115.3(6)	C32	C31	C42	C44	-130.3(6)
C2	C1	C23	C22	0.7(8)	C32	C31	C42	C45	-7.3(8)
C2	C3	C5	C6	134.4(5)	C32	C34	C35	C36	151.3(5)
C2	C3	C5	C10	-40.0(7)	C32	C34	C35	C40	-28.2(7)
C3	N1	C4	N3	177.9(5)	C33	N4	C34	C32	-1.0(5)
C3	N1	C4	C1	-2.0(5)	C33	N4	C34	C35	177.3(5)
C3	N1	B1	F1	-49.6(7)	C33	N4	B5	F3	-108.0(5)
C3	N1	B1	F2	71.6(7)	C33	N4	B5	F4	131.0(4)
C3	N1	B1	N2	-170.4(4)	C33	N4	B5	N6	10.5(6)
C3	C5	C6	C7	-177.5(4)	C33	N5	C46	N6	1.2(7)
C3	C5	C10	C9	178.5(4)	C33	N5	C46	C47	-174.2(5)
C4	N1	C3	C2	-0.7(5)	C33	C31	C32	C34	-2.3(6)
C4	N1	C3	C5	176.8(5)	C33	C31	C42	C43	-71.1(7)
C4	N1	B1	F1	120.0(5)	C33	C31	C42	C44	48.3(6)
C4	N1	B1	F2	-118.8(5)	C33	C31	C42	C45	171.3(5)
C4	N1	B1	N2	-0.9(6)	C34	N4	C33	N5	175.2(5)
C4	N3	C12	N2	-2.8(7)	C34	N4	C33	C31	-0.4(5)
C4	N3	C12	C13	174.7(5)	C34	N4	B5	F3	72.6(6)
C4	C1	C2	C3	-4.3(6)	C34	N4	B5	F4	-48.4(7)
C4	C1	C23	C20	-59.0(8)	C34	N4	B5	N6	-168.9(5)
C4	C1	C23	C21	59.8(7)	C34	C35	C36	C37	178.7(4)
C4	C1	C23	C22	175.8(6)	C34	C35	C40	C39	-178.2(4)
C5	C6	C7	C8	0.2(7)	C35	C36	C37	C38	-0.8(7)
C6	C5	C10	C9	4.1(7)	C36	C35	C40	C39	2.2(7)
C6	C7	C8	S1	-178.2(4)	C36	C37	C38	S3	-177.9(4)
C6	C7	C8	C9	1.9(7)	C36	C37	C38	C39	2.8(7)
C7	C8	C9	C10	-1.0(7)	C37	C38	C39	C40	-2.3(7)
C8	C9	C10	C5	-2.0(8)	C38	C39	C40	C35	-0.2(7)
C10	C5	C6	C7	-3.3(7)	C40	C35	C36	C37	-1.7(7)
C11	S1	C8	C7	6.4(5)	C41	S3	C38	C37	3.9(5)
C11	S1	C8	C9	-173.7(4)	C41	S3	C38	C39	-176.8(4)

Table 6 Torsion Angles for exp_3226.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C12	N2	C15	C14	1.6(5)	C42	C31	C32	C34	176.5(5)
C12	N2	C15	C24	-178.5(5)	C42	C31	C33	N4	-177.2(4)
C12	N2	B1	F1	-123.9(5)	C42	C31	C33	N5	7.4(8)
C12	N2	B1	F2	113.9(5)	C46	N5	C33	N4	-2.5(7)
C12	N2	B1	N1	-5.8(6)	C46	N5	C33	C31	172.3(5)
C12	N3	C4	N1	-4.6(7)	C46	N6	C49	C48	0.1(5)
C12	N3	C4	C1	175.3(5)	C46	N6	C49	C54	-177.9(5)
C12	C13	C14	C15	-1.1(6)	C46	N6	B5	F3	106.6(5)
C12	C13	C16	C17	176.0(6)	C46	N6	B5	F4	-131.9(5)
C12	C13	C16	C18	56.4(7)	C46	N6	B5	N4	-11.7(6)
C12	C13	C16	C19	-63.6(8)	C46	C47	C48	C49	0.8(6)
C13	C14	C15	N2	-0.3(6)	C46	C47	C50	C51	172.7(5)
C13	C14	C15	C24	179.8(5)	C46	C47	C50	C52	-67.5(7)
C14	C13	C16	C17	-4.8(8)	C46	C47	C50	C53	53.0(7)
C14	C13	C16	C18	-124.4(6)	C47	C48	C49	N6	-0.6(6)
C14	C13	C16	C19	115.6(6)	C47	C48	C49	C54	177.5(5)
C14	C15	C24	C25	-40.6(7)	C48	C47	C50	C51	-11.5(8)
C14	C15	C24	C29	139.4(6)	C48	C47	C50	C52	108.3(6)
C15	N2	C12	N3	175.5(5)	C48	C47	C50	C53	-131.2(6)
C15	N2	C12	C13	-2.3(5)	C48	C49	C54	C55	39.2(8)
C15	N2	B1	F1	71.7(7)	C48	C49	C54	C59	-138.2(6)
C15	N2	B1	F2	-50.6(7)	C49	N6	C46	N5	-175.8(5)
C15	N2	B1	N1	-170.2(4)	C49	N6	C46	C47	0.4(5)
C15	C24	C25	C26	178.8(5)	C49	N6	B5	F3	-69.9(6)
C15	C24	C29	C28	-178.5(5)	C49	N6	B5	F4	51.6(7)
C16	C13	C14	C15	179.6(5)	C49	N6	B5	N4	171.8(5)
C23	C1	C2	C3	171.6(5)	C49	C54	C55	C56	-178.3(6)
C23	C1	C4	N1	-171.9(5)	C49	C54	C59	C58	178.1(6)
C23	C1	C4	N3	8.2(9)	C50	C47	C48	C49	-175.7(5)
C24	C25	C26	C27	1.1(9)	C54	C55	C56	C57	-1.2(10)
C25	C24	C29	C28	1.6(7)	C55	C54	C59	C58	0.7(9)
C25	C26	C27	S2	179.6(4)	C55	C56	C57	S4	-179.0(5)
C25	C26	C27	C28	-1.3(8)	C55	C56	C57	C58	3.2(9)
C26	C27	C28	C29	1.6(7)	C56	C57	C58	C59	-3.4(9)
C27	C28	C29	C24	-1.8(7)	C57	C58	C59	C54	1.5(9)
C29	C24	C25	C26	-1.2(8)	C59	C54	C55	C56	-0.8(9)
C30	S2	C27	C26	178.9(4)	C60	S4	C57	C56	-172.1(5)
C30	S2	C27	C28	-0.2(5)	C60	S4	C57	C58	5.6(7)

Table 6 Torsion Angles for exp_3226.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
B1	N1	C3	C2	170.1(5)	B5	N4	C33	N5	-4.4(7)
B1	N1	C3	C5	-12.3(8)	B5	N4	C33	C31	-180.0(4)
B1	N1	C4	N3	6.3(7)	B5	N4	C34	C32	178.5(5)
B1	N1	C4	C1	-173.6(4)	B5	N4	C34	C35	-3.2(8)
B1	N2	C12	N3	8.4(7)	B5	N6	C46	N5	7.0(7)
B1	N2	C12	C13	-169.4(5)	B5	N6	C46	C47	-176.8(4)
B1	N2	C15	C14	168.0(5)	B5	N6	C49	C48	177.0(5)
B1	N2	C15	C24	-12.1(8)	B5	N6	C49	C54	-1.0(9)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_3226.

Atom	*x*	*y*	*z*	U(eq)
H2	4972.26	3249.69	-38.85	52
H6	3315.59	3591.56	1891.97	50
H7	2096.97	4681.34	2024.91	51
H9	3676.56	5839.99	708.77	56
H10	4893.7	4729.33	536.82	60
H11A	555.05	5568.8	1967.54	77
H11B	649.21	6542.79	2261.78	77
H11C	1691.12	6001.58	2615.1	77
H14A	8411.66	1756.02	3816.11	62
H14B	7132.74	1222.83	3683.93	62
H17A	9479.95	594.86	3496.49	132
H17B	9203.26	-309.65	2998.87	132
H17C	8240.52	56.63	3445.21	132
H18A	8748.02	1010.31	1659.32	114
H18B	9538.76	289.4	1930.03	114
H18C	9770.72	1196.53	2423.13	114
H19A	6622.17	-207.82	2254.11	99
H19B	7607.02	-570.89	1824.24	99
H19C	6845.87	164.1	1557.13	99
H20A	7941.52	2188.48	51.6	166
H20B	7670.79	1260.12	-396.57	166
H20C	7778.71	1444.72	479.7	166
H21A	5799.25	736.57	342.7	107
H21B	5701.03	497.56	-530.36	107
H21C	4636.43	951.77	-236.89	107

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_3226.

Atom	*x*	*y*	*z*	U(eq)
H22A	4830.43	2114.71	-930.84	138
H22B	5658.11	1470.86	-1275.78	138
H22C	6180.21	2412.1	-963.89	138
H25	6257.08	1891.65	4596.77	64
H26	5907.54	2620.85	5665.48	69
H28	6721.6	4772.49	5046.72	55
H29	7054.22	4024.51	3956.51	53
H30A	5727.47	5467.85	5827.71	96
H30B	7077.66	5469.3	6327.53	96
H30C	5973.22	5662.25	6713.97	96
H32	-351.42	3348.61	-177.31	50
H36	-1600.59	3875.31	1980.2	47
H37	-2733.09	5006.23	2155.33	49
H39	-1828.37	5836.52	425.3	52
H40	-719.78	4693.28	241.88	52
H41A	-4194.57	5876.13	2174.11	102
H41B	-4163.71	6861.45	2338.81	102
H41C	-2989.79	6415.11	2673.29	102
H43A	2790.91	1892.37	320.06	83
H43B	2590.63	2641.7	-125.14	83
H43C	2648.55	1729.39	-559.55	83
H44A	-222.59	881.53	-302.44	83
H44B	1072.99	873.04	257.68	83
H44C	931.74	621.14	-618.75	83
H45A	608.35	1687.09	-1420.05	85
H45B	631.48	2640.17	-1062.71	85
H45C	-517.88	2015.62	-1106.42	85
H48A	3544.01	2074.85	3587.6	52
H48B	2445.99	1424.36	3588.67	52
H51A	4813.96	1006.42	3183.67	92
H51B	4618.32	66.11	2763.85	92
H51C	3794.03	387.8	3323.03	92
H52A	1885.68	-84.31	2337.69	87
H52B	2696.62	-436.03	1779.87	87
H52C	1711.74	199.03	1549.06	87
H53A	3333.93	1085.09	1289.43	89
H53B	4417.87	544.08	1585.68	89

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for exp_3226.

Atom	*x*	*y*	*z*	U(eq)
H53C	4478.88	1501.74	1938.22	89
H55	3447.56	3059.69	4600.32	53
H56	3167.23	3778.82	5702.26	62
H58	-437.67	3761.42	4785.36	57
H59	-171.17	3041.57	3668.06	55
H60A	-705.96	4786.67	5697.58	87
H60B	-527.78	4809.93	6570.02	87
H60C	-783.62	3944.31	6008.45	87

Table 8 Solvent masks information for exp_3226.

Number	X	Y	Z	Volume	Electron count	Content
1	-0.583	0.000	0.500	726.2	170.8	?

Experimental

Single crystals of $C_{30}H_{35}BF_2N_3S_2$ **[exp_3226]** were **[]**. A suitable crystal was selected and **[]** on a **SuperNova, Dual, Cu at zero, AtlasS2** diffractometer. The crystal was kept at 149.99(10) K during data collection.