Synthesis, Structure and Properties of Semi-internally BN-substituted Annulated Thiophenes

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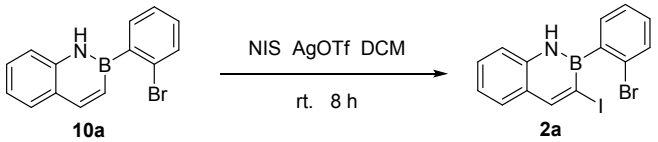
Content

1 General Experimental Methods.

All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 mesh). The ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts are referenced against external $BF_3 \cdot Et_2O$ (^{11}B), and $CFCl_3$(^{19}F). HRMS were acquired in ESI mode (positive ion) with the TOF mass analyzer used. UV-vis absorption spectra were determined on a Shimadzu UV-1601PC Spectrophotometer. Photoluminescence (PL) spectra were carried out on a Shimadzu RF-5301 Luminescence Spectrometer. IR spectra were recorded on a MAGNA-560 spectrometer made by Nicolet Company. The commercially available catalysts and reagents were purchased from J&K Scientific.

2 Optimization for the iodination of B-aryl-2,1-borazaronaphthalenes.

Table S1. Optimization for the Iodation reaction of B-aryl-2,1-borazaronaphthalenes with NIS catalyzed by Lewis acid.



10a **2a**

Entry	Lewis acid	Lewis acid equiv	NIS equiv	Yield (%)
1	---	---	1.0	trace
2	$AlCl_3$	1.0	1.0	19%
3	$Yb(OTf)_3$	1.0	1.0	trace
4	BF_3OEt_2	1.0	1.0	trace
5	AgOTf	1.0	1.0	56%
6	$Cu(OTf)_2$	1.0	1.0	28%
7	$In(OTf)_3$	1.0	1.0	53%
8	AgOTf	0.1	1.0	60%
9	AgOTf	0.1	1.5	63%
10	AgOTf	0.1	2.0	28%

11	AgOTf	0.1	1.2	73%
12	AgOTf	0.1	1.1	96%

[a] Reaction conditions: 1.0 equiv of **10**, 0.1 equiv of AgOTf, 1.1 equiv of NIS, DCM (0.1 mol/L), room temperature, 8 h, at atmosphere.

3 X-ray Crystallographic Studies of Compound 3a, 4b, 4c, 6, 7 and 3a'.

Data collections for compounds **3a**, **4b**, **4c**, **6**, **7** and **3a'** were performed on a Rigaku Saturn CCD diffractometer using graphite-monochromated MoK (λ = 0.71073 Å) or CuK (λ = 1.54184 Å) radiation. The structures of **3a**, **4b**, **4c**, **6**, **7** and **3a'** were solved by use of SHELXTL program[1]. Refinements were performed on F2 anisotropically for all the non-hydrogen atoms by the full-matrixleast-squaresmethod.

Table S2. Crystallographic data and structure refinement details for **3a** and **3a'.**

	3a'	**3a**
formula	$C_{16}H_{10}S$	$C_{14}H_{10}BNS$
fw	234.3	235.10
T (K)	293(2)	296(2) K
cryst syst	monoclinic	monoclinic
space group	$P2_1$	P 21/c
a, (Å)	6.1910(9)	5.977(7)
b, (Å)	23.723(3)	8.264(10)
c, (Å)	7.8254(10)	24.38(3)
α, (deg)	90	89.28(2)
β, (deg)	90.872(13)	101.30(3)
γ, (deg)	90	90.04(2)
V, (Å^3)	1149.2(3)	1181(2)
Z	4	4
Dcalc, (g / cm^3)	1.354	1.322
M(mm^{-1})	0.251	0.246
F(000)	488	488
cryst size (mm)	0.22 × 0.2 × 0.1	0.22 x 0.21 x 0.18
λ (Å)	MoK (0.71073)	MoK (0.71073)
2θ range, (deg)	5.206 to 50.018	1.704 to 26.498

Index ranges	-7 ≤ h ≤ 7, -26 ≤ k ≤ 28, -9 ≤ l ≤ 7	-7≤ h≤ 7, -10≤ k≤ 5, -30≤ l≤ 30
reflns collected	5671	4977
indep reflns/R_{int}	3468/0.0443	2391/0.1151
params	3468/1/259	2391/0/154
GOF on F^2	1.025	1.099
$R1$, w$R2$ [I>2σ(I)]	0.0628, 0.1222	0.1273, 0.3732
$R1$, w$R2$ (all data)	0.1031, 0.1430	0.1569, 0.3864
Largest diff. peak/hole / e Å^{-3}	0.29/-0.22	0.605, -0.600

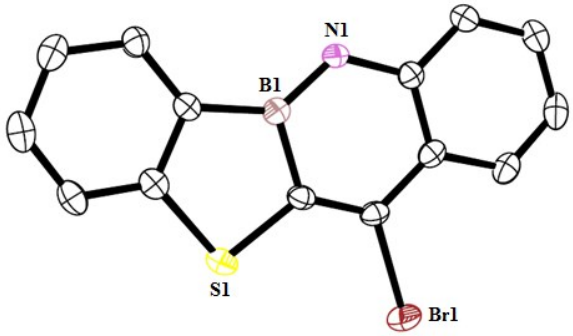


Figure S1. Molecular structure drawing of **4b** with thermal ellipsoids at 30 % probability. Hydrogen atoms have been omitted for clarity.

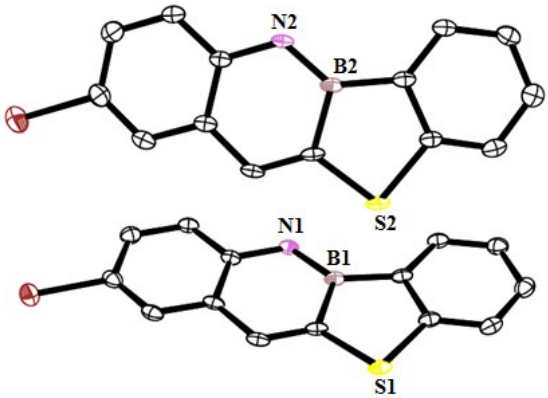


Figure S2. Molecular structure drawing of **4c** with thermal ellipsoids at 30 % probability. Hydrogen atoms have been omitted for clarity.

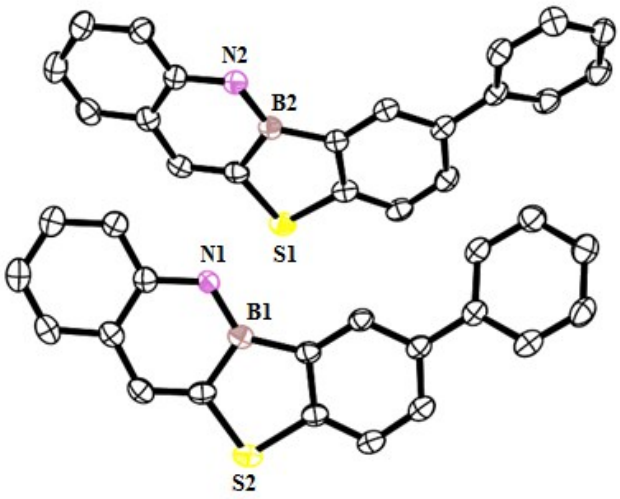


Figure S3. Molecular structure drawing of **7** with thermal ellipsoids at 30 % probability. Hydrogen atoms have been omitted for clarity.

Table S3. Crystallographic data and structure refinement details for **4b**, **4c**, and **7**.

	4b	**4c**	**7**
formula	$C_{14}H_9BBrNS$	$C_{14}H_9BBrNS$	$C_{40}H_{28}B_2N_2S_2$
fw	314	314	622.38
T (K)	293(2)	150.00(10)	296(2)
cryst syst	orthorhombic	monoclinic	monoclinic
space group	Fdd2	$P2_1/n$	Cc
a, (Å)	28.1429(16)	9.64453(12)	10.013(5)
b, (Å)	35.0042(16)	27.2283(3)	10.289(6)
c, (Å)	4.9701(2)	9.74695(13)	29.682(14)
α, (deg)	90	90	90
β, (deg)	90	100.1159(13)	97.703(10)
γ, (deg)	90	90	90
V, ($Å^3$)	4896.1(4)	2519.80(6)	3030.0(3)
Z	16	8	4
Dcalc, (g / cm^3)	1.704	1.655	1.364
M(mm^{-1})	3.505	5.794	0.210
F(000)	2496	1248	1296
cryst size (mm)	0.25 × 0.1 × 0.09	0.2 × 0.18 × 0.16	0.22 x 0.21 x 0.18
λ (Å)	MoK (0.71073)	CuK (1.54184)	MoK (0.71073)

2θ range, (deg)	4.654 to 50.014	6.492 to 134.124	2.770 to 26.494
Index ranges	-32 ≤ h ≤ 32, -41 ≤ k ≤ 41, -5 ≤ l ≤ 4	-7 ≤ h ≤ 11, -32 ≤ k ≤ 31, -11 ≤ l ≤ 11	-12≤ h≤ 11, -12≤ k≤ 11, -25≤ l≤ 37
reflns collected	8248	16156	9617
indep reflns/R_{int}	1992/0.0378	4508/0.0383	5087/0.0716
params	1992/1/164	4508/0/325	5087/2/415
GOF on F^2	1.024	1.122	1.012
$R1$, w$R2$ [I>2σ(I)]	0.0283, 0.0487	0.0443, 0.1184	0.0535, 0.1120
$R1$, w$R2$ (all data)	0.0346, 0.0508	0.0454, 0.1193	0.0848, 0.1224
Largest diff. peak/hole / e Å^{-3}	0.28/-0.37	0.85/-0.69	0.233/-0.198

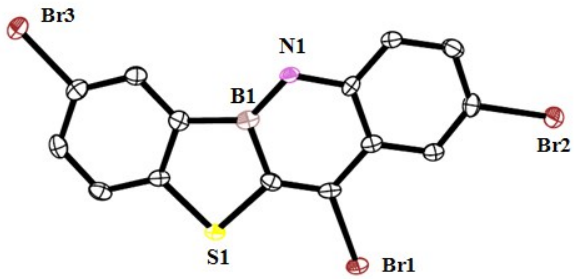


Figure S4. Molecular structure drawing of **6** with thermal ellipsoids at 50 % probability. Hydrogen atoms and solvent molecules have been omitted for clarity.

Table S4. Crystallographic data and structure refinement details for **6.**

	6
formula	$C_{16}H_{13}BBr_3NOS_2$
fw	549.93
T (K)	150.01(10)
cryst syst	monoclinic
space group	$P2_1/n$
a, (Å)	4.82588(13)
b, (Å)	33.6687(8)
c, (Å)	11.3791(3)
α, (deg)	90

β, (deg)	90.609(2)
γ, (deg)	90
V, (Å^3)	1848.78(8)
Z	4
Dcalc, (g / cm^3)	1.976
M(mm^{-1})	10.235
F(000)	1064
cryst size (mm)	0.25×0.13×0.12
λ (Å)	CuK (1.54184)
2θ range, (deg)	5.25 to 134.104
Index ranges	-5 ≤ h ≤ 5, -40 ≤ k ≤ 36, -12 ≤ l ≤ 13
reflns collected	6835
indep reflns/R_{int}	3300/0.0370
params	3300/12/221
GOF on F^2	1.032
R1, wR2 [I>2σ(I)]	0.0405, 0.1047
R1, wR2 (all data)	0.0448, 0.1097
Largest diff. peak/hole / e Å^{-3}	0.62/-0.74

4 DFT Calculations.

Calculations were performed using the Gaussian 03 suite of programs, revision C. 02.[2] The geometries were optimized as the RB3LYP/6-311+G(d, p) level, and energies were calculated at the same level of theory. Nucleus independent chemical shifts (NICS) were calculated using the gauge invariant atomic orbital (GIAO) approach at the GIAO-B3LYP/6-311+G (d, p) level.

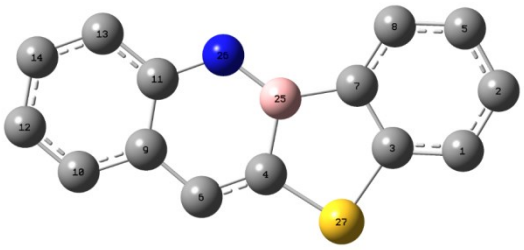


Figure S5. Optimized geometry of **3a**.

Table S5. Cartesian coordinates for **3a** (Number of imaginary frequencies of **3a** is 0; Total energy of **3a** is -1017.56834020 Hartreee)

Tag	Symbol	X	Y	Z
1	C	3.90975646	0.63257355	0.00015173
2	C	4.62554530	-0.56152850	-0.00016780
3	C	2.51577177	0.57962672	0.00031303
4	C	-0.00129334	1.11069493	-0.00023224
5	C	3.96310173	-1.79394257	-0.00029517
6	C	-1.28147164	1.56728818	-0.00033413
7	C	1.81645513	-0.65149579	0.00006062
8	C	2.57271078	-1.83274274	-0.00020223
9	C	-2.37848524	0.63138826	-0.00010294
10	C	-3.71838087	1.07691151	-0.00016431
11	C	-2.14088292	-0.77302429	0.00007795
12	C	-4.77802233	0.19031898	-0.00010864
13	C	-3.22806722	-1.66360170	0.00015824
14	C	-4.52806308	-1.19095626	0.00007297
15	H	4.43085931	1.58326760	0.00026591
16	H	5.70962307	-0.53212866	-0.00028872
17	H	-1.53050876	2.62585044	-0.00038682
18	H	4.53525077	-2.71456797	-0.00050056
19	H	-3.90422553	2.14591186	-0.00026902
20	H	2.06926748	-2.79525522	-0.00010788
21	H	-0.74985190	-2.25565613	0.00051019
22	H	-5.79715809	0.55823367	-0.00020878
23	H	-3.03553363	-2.73222484	0.00029107
24	H	-5.35426033	-1.89257658	0.00006534
25	B	0.29391610	-0.39204139	0.00020136
26	N	-0.83620929	-1.24774629	0.00023633
27	S	1.49489843	2.04840720	0.00016285

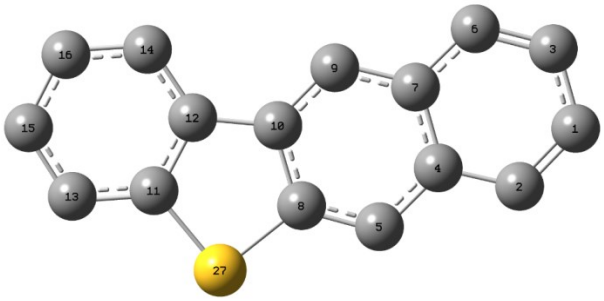


Figure S6. Optimized geometry of **3a'**.

Table S6. Cartesian coordinates for **3a'** (Number of imaginary frequencies of **3a'** is 0; Total energy of **3a'** is -1014.12007831 Hartreee)

Tag	Symbol	X	Y	Z
1	C	4.7394493	0.1667931	-0.0005450
2	C	3.7070495	1.0715414	-0.0002559
3	C	4.4725988	-1.2253422	-0.0003576
4	C	2.3533305	0.6364756	0.0001897
5	C	1.2735061	1.5521300	0.0002943
6	C	3.1781961	-1.6808836	0.0000642
7	C	2.0818442	-0.7742484	0.0002877
8	C	-0.0169925	1.0779496	0.0003622
9	C	0.7417318	-1.2226148	0.0004234
10	C	-0.3058114	-0.3224960	0.0004256
11	C	-2.4984612	0.6056139	0.0000052
12	C	-1.7391601	-0.5821933	0.0001782
13	C	-3.8922355	0.5810814	-0.0003311
14	C	-2.4096471	-1.8115923	0.0001563
15	C	-4.5360224	-0.6523696	-0.0004925
16	C	-3.7986053	-1.8432370	-0.0001972
17	H	5.7662624	0.5147487	-0.0010292
18	H	3.9117262	2.1371133	-0.0002883
19	H	5.2974067	-1.9288226	-0.0005512
20	H	1.4798588	2.6167434	0.0003275
21	H	2.9719107	-2.7462424	0.0002999
22	H	0.5474723	-2.2901205	0.0006286
23	H	-4.4642681	1.5014744	-0.0005720
24	H	-1.8458084	-2.7378247	0.0004602
25	H	-5.6193793	-0.6889016	-0.0008600
26	H	-4.3157728	-2.7956043	-0.0002742
27	S	-1.4896270	2.0598618	0.0000383

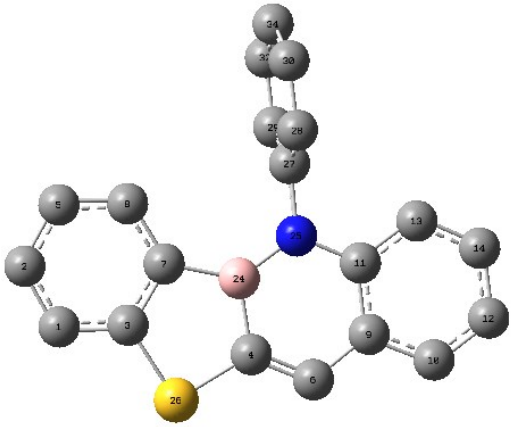


Figure S7. Optimized geometry of **3d**.

Table S7. Cartesian coordinates for **3d** (Number of imaginary frequencies of **3d** is 0; Total energy of **3d** is -1248.66328278 Hartreee)

Tag	Symbol	X	Y	Z
1	C	-4.21370754	-1.08052526	-0.00008203
2	C	-4.76558511	0.19700317	-0.00006972
3	C	-2.82521786	-1.21242426	-0.00004620
4	C	-0.41353474	-2.08836321	0.00001569
5	C	-3.94247417	1.32754156	-0.00004146
6	C	0.78049635	-2.73265738	0.00007760
7	C	-1.96120181	-0.08881168	-0.00000696
8	C	-2.55892208	1.18293851	-0.00001237
9	C	2.00148975	-1.97174505	0.00004050
10	C	3.24836121	-2.63394638	0.00002849
11	C	1.98878003	-0.54457478	0.00004545
12	C	4.44179132	-1.93973257	0.00001543
13	C	3.21546072	0.14660172	0.00003825
14	C	4.41860772	-0.53859730	0.00001750
15	H	-4.85457065	-1.95513113	-0.00013529
16	H	-5.84404034	0.31229679	-0.00009139
17	H	0.86766678	-3.81656840	0.00011497
18	H	-4.38462709	2.31735851	-0.00004581
19	H	3.24952133	-3.71902157	0.00003557
20	H	-1.93475409	2.06866022	-0.00003665
21	H	5.38558831	-2.47211868	0.00000775
22	H	3.21887055	1.22793830	0.00005980
23	H	5.34748755	0.02042895	0.00000228
24	B	-0.48275025	-0.55854152	0.00001602

25	N	0.76313473	0.14245577	0.00008848
26	S	-2.02341922	-2.80801695	-0.00005601
27	C	0.78576477	1.58588366	0.00007836
28	C	0.78406040	2.28200479	1.20844081
29	C	0.78458234	2.28199305	-1.20847446
30	C	0.77457478	3.67585768	1.20636015
31	H	0.78276319	1.72904117	2.14052254
32	C	0.77523735	3.67585686	-1.20639817
33	H	0.78382913	1.72891498	-2.14048152
34	C	0.77000112	4.37489176	0.00001219
35	H	0.76774105	4.21399186	2.14739443
36	H	0.76916818	4.21399977	-2.14743038
37	H	0.76048468	5.45882835	0.00004600

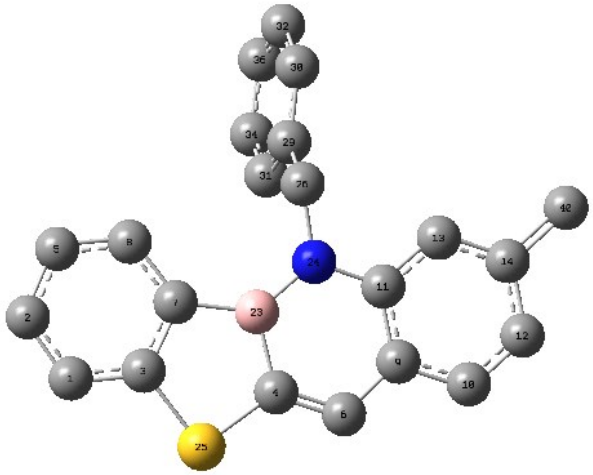


Figure S8. Optimized geometry of **3f**.

Table S8. Cartesian coordinates for **3f** (Number of imaginary frequencies of **3f** is 0; Total energy of **3f** is -1327.31173755 Hartreee)

Tag	Symbol	X	Y	Z
1	C	4.79964661	-0.18465189	0.07069569
2	C	5.06832657	1.12877699	-0.29888084
3	C	3.47870534	-0.63364041	0.05687278
4	C	1.32704362	-2.00404249	0.28790261
5	C	4.02770284	1.98668462	-0.66654787
6	C	0.31015324	-2.88341736	0.47193013
7	C	2.39799961	0.19927996	-0.33352051
8	C	2.71544397	1.52571591	-0.67808408

9	C	-1.03846251	-2.47583906	0.1942906
10	C	-2.10795792	-3.37160597	0.40980187
11	C	-1.33684908	-1.17348201	-0.30492884
12	C	-3.41670483	-3.01922106	0.16238863
13	C	-2.68658088	-0.8344407	-0.53536279
14	C	-3.72309465	-1.73045702	-0.313097
15	H	5.60497266	-0.84578951	0.37069128
16	H	6.09126586	1.48882834	-0.29050395
17	H	0.46349884	-3.89924613	0.82852171
18	H	4.24296111	3.01430566	-0.93612593
19	H	-1.87519338	-4.3633017	0.78395754
20	H	1.93010205	2.22360058	-0.9438023
21	H	-4.21464497	-3.7320894	0.34148183
22	H	-2.94136133	0.16130063	-0.87015281
23	B	1.05927695	-0.59272682	-0.23944693
24	N	-0.29803644	-0.26490312	-0.55420393
25	S	3.04604455	-2.28912547	0.55583678
26	C	-0.62803625	1.00987162	-1.20409623
27	H	0.28100875	1.35944287	-1.69345223
28	H	-1.34228663	0.82557362	-2.01074776
29	C	-1.16136509	2.10742826	-0.29438977
30	C	-1.82911601	3.19421126	-0.87056183
31	C	-0.97090967	2.09178331	1.08799732
32	C	-2.29342711	4.24475766	-0.08318801
33	H	-1.98931262	3.21816284	-1.94474482
34	C	-1.43884018	3.14112749	1.87889833
35	H	-0.46066526	1.25575303	1.55118928
36	C	-2.0996988	4.22059125	1.297708
37	H	-2.80991822	5.07825733	-0.54625828
38	H	-1.28559093	3.11208581	2.95195037
39	H	-2.4634913	5.03483252	1.91407041
40	C	-5.15644435	-1.33520801	-0.57075891
41	H	-5.59347422	-1.94217119	-1.37050418
42	H	-5.77315741	-1.48421276	0.32083131
43	H	-5.23676226	-0.2867032	-0.86354349

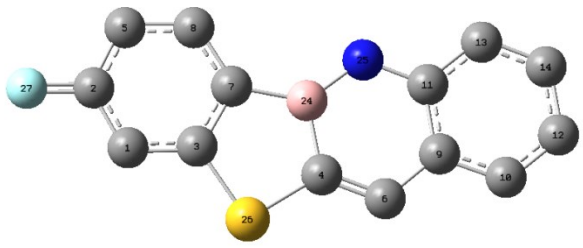


Figure S9. Optimized geometry of **3g**.

Table S9. Cartesian coordinates for **3g** (Number of imaginary frequencies of **3g** is 0; Total energy of **3g** is -1116.83736937 Hartreee)

Tag	Symbol	X	Y	Z
1	C	-3.52559506	0.74767322	0.00004164
2	C	-4.23744549	-0.43958509	0.00040759
3	C	-2.13351971	0.65738255	-0.00022136
4	C	0.39175965	1.13175069	0.00007341
5	C	-3.63397378	-1.69327022	0.00044299
6	C	1.67986741	1.56378384	0.00038666
7	C	-1.46119192	-0.59016643	-0.00005285
8	C	-2.24496346	-1.75313178	0.00028201
9	C	2.75822481	0.60617729	0.00017101
10	C	4.10646177	1.02531828	0.00036068
11	C	2.49241688	-0.79299643	-0.000182
12	C	5.14812819	0.11771022	0.00031521
13	C	3.56149498	-1.70507203	-0.00020453
14	C	4.8705593	-1.25821217	0.00001487
15	H	-4.05185599	1.6940505	-0.00008276
16	H	1.94943266	2.61723904	0.00044062
17	H	-4.24964636	-2.58359138	0.0006114
18	H	4.31361312	2.0903923	0.00061899
19	H	-1.7663278	-2.72759947	0.00034481
20	H	1.07319958	-2.24820535	-0.00042807
21	H	6.17438114	0.4652284	0.0005142
22	H	3.34796257	-2.76968094	-0.00043064
23	H	5.68261048	-1.97615094	-0.0000303
24	B	0.06547462	-0.36411424	-0.00045575
25	N	1.17834748	-1.24209444	-0.00042327
26	S	-1.08525571	2.10200388	-0.00069759
27	F	-5.59093607	-0.37585373	0.00042586

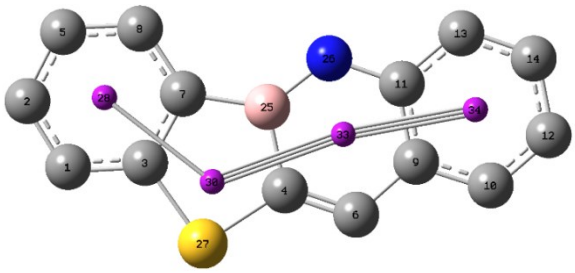


Figure S10. NICS(1)zz values (in ppm) of **3a** calculated at the GIAO-B3LYP/6-311+G (d, p) level.

Table S10. Cartesian coordinates for NICS calculations on **3a** (Number of imaginary frequencies of **3a** is 0; Total energy of **3a** is -1017.56834020 Hartreee)

1	C	3.9097568	0.6325736	0.0001517
2	C	4.6255457	-0.5615285	-0.0001678
3	C	2.5157720	0.5796268	0.0003130
4	C	-0.0012933	1.1106950	-0.0002322
5	C	3.9631020	-1.7939427	-0.0002952
6	C	-1.2814717	1.5672883	-0.0003341
7	C	1.8164553	-0.6514958	0.0000606
8	C	2.5727110	-1.8327429	-0.0002022
9	C	-2.3784854	0.6313883	-0.0001029
10	C	-3.7183812	1.0769116	-0.0001643
11	C	-2.1408831	-0.7730243	0.0000780
12	C	-4.7780227	0.1903190	-0.0001086
13	C	-3.2280675	-1.6636018	0.0001582
14	C	-4.5280634	-1.1909564	0.0000730
15	H	4.4308596	1.5832677	0.0002659
16	H	5.7096235	-0.5321287	-0.0002887
17	H	-1.5305089	2.6258506	-0.0003868
18	H	4.5352511	-2.7145682	-0.0005006
19	H	-3.9042258	2.1459120	-0.0002690
20	H	2.0692676	-2.7952554	-0.0001079
21	H	-0.7498520	-2.2556563	0.0005102
22	H	-5.7971585	0.5582337	-0.0002088
23	H	-3.0355339	-2.7322250	0.0002911
24	H	-5.3542608	-1.8925767	0.0000653
25	B	0.2939161	-0.3920414	0.0002014
26	N	-0.8362094	-1.2477464	0.0002363
27	S	1.4948985	2.0484074	0.0001629
28	Bq	3.2340002	-0.6045000	1.0000001
29	Bq	3.2340002	-0.6045000	-1.0000001
30	Bq	1.3070136	0.9368156	1.0000001
31	Bq	1.3070136	0.9368156	-1.0000001
32	Bq	-1.0733559	0.1199671	-1.0000001
33	Bq	-1.0733559	0.1199671	1.0000001
34	Bq	-3.4618336	-0.2883334	1.0000001
35	Bq	-3.4618336	-0.2883334	-1.0000001

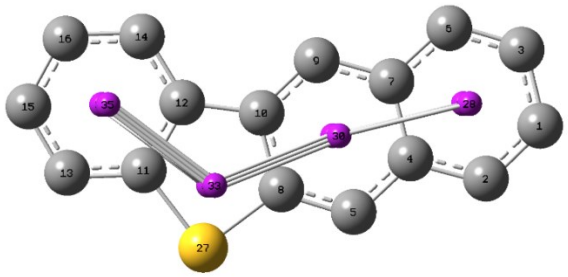


Figure S11. NICS(1)zz values (in ppm) of **3a'** calculated at the GIAO-B3LYP/6-311+G (d, p) level.

Table S11. Cartesian coordinates for NICS calculations on **3a'** (Number of imaginary frequencies of **3a'** is 0; Total energy of **3a'** is -1014.12007831 Hartreee)

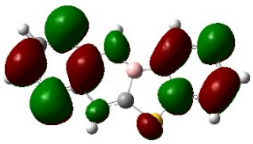
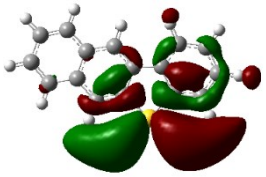
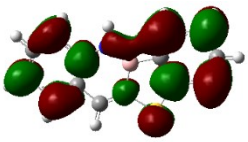
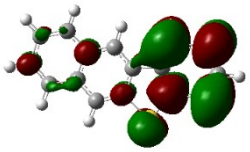
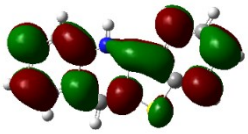
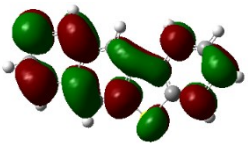
Tag	Symbol	X	Y	Z
1	C	4.7394497	0.1667931	-0.0005451
2	C	3.7070497	1.0715415	-0.0002559
3	C	4.4725991	-1.2253423	-0.0003576
4	C	2.3533307	0.6364756	0.0001897
5	C	1.2735062	1.5521301	0.0002943
6	C	3.1781963	-1.6808837	0.0000642
7	C	2.0818444	-0.7742485	0.0002877
8	C	-0.0169925	1.0779497	0.0003623
9	C	0.7417318	-1.2226149	0.0004234
10	C	-0.3058114	-0.3224960	0.0004256
11	C	-2.4984614	0.6056140	0.0000052
12	C	-1.7391603	-0.5821934	0.0001782
13	C	-3.8922357	0.5810814	-0.0003311
14	C	-2.4096473	-1.8115924	0.0001563
15	C	-4.5360228	-0.6523697	-0.0004925
16	C	-3.7986056	-1.8432371	-0.0001972
17	H	5.7662628	0.5147487	-0.0010292
18	H	3.9117264	2.1371134	-0.0002883
19	H	5.2974071	-1.9288228	-0.0005512
20	H	1.4798589	2.6167436	0.0003275
21	H	2.9719109	-2.7462426	0.0002999
22	H	0.5474724	-2.2901207	0.0006286
23	H	-4.4642684	1.5014745	-0.0005720
24	H	-1.8458085	-2.7378250	0.0004602
25	H	-5.6193797	-0.6889017	-0.0008600
26	H	-4.3157732	-2.7956045	-0.0002742
27	S	-1.4896271	2.0598620	0.0000383

28	Bq	3.4215496	-0.3009938	-1.0001666
29	Bq	3.4224509	-0.3006729	0.9998333
30	Bq	1.0213334	0.1578333	-1.0000001
31	Bq	1.0213334	0.1578333	1.0000001
32	Bq	-1.2800957	0.9415095	1.0000001
33	Bq	-1.2800957	0.9415095	-1.0000001
34	Bq	-3.1456669	-0.6170000	1.0000001
35	Bq	-3.1456669	-0.6170000	-1.0000001

Table S12. Electronic energies (E, in a.u.), entropies (S, in cal/mol K) and Gibbs free energies (G, in a.u.) for the structures **3a**, **3a'**, **3d**, **3f** and **3g**, calculated by the B3LYP/6-311+G(d,p) method at 298.15 K.

Species	*E*	*S*	*G*
3a	-1017.193225	108.818	-1017.243984
3a'	-1013.901324	107.403	-1013.951411
3d	-1248.360573	132.983	-1248.422814
3f	-1326.918303	136.578	-1326.982252
3g	-1116.626809	113.514	-1116.679799

Table S13. DFT calculated orbital levels and orbital plots for **3a** and **3a'** at the B3LYP/6-311+G(d,p) level.

	3a	**3a'**
LUMO+3	 -0.35 eV	 -0.21 eV
LUMO+2	 -0.52 eV	 -0.65 eV
LUMO+1	 -0.78 eV	 -0.94 eV

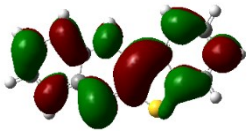
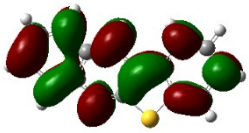
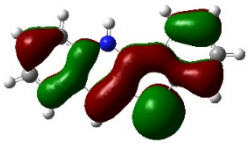
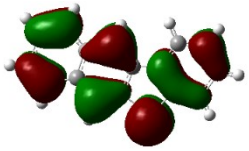
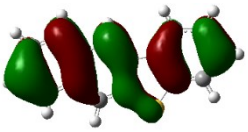
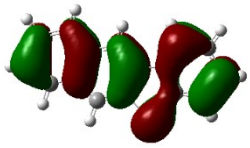
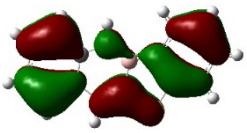
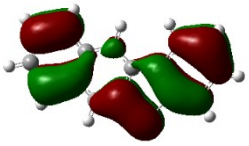
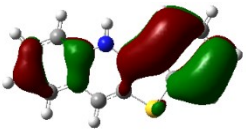
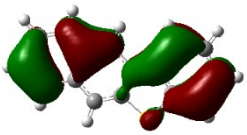
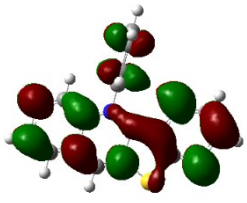
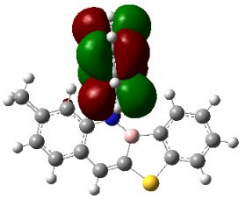
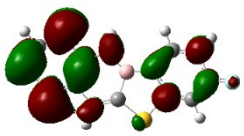
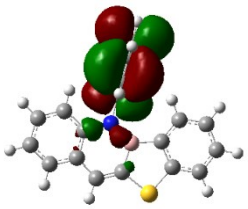
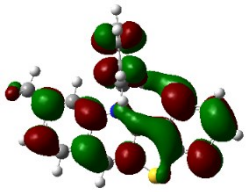
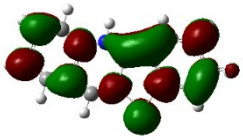
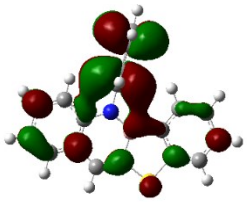
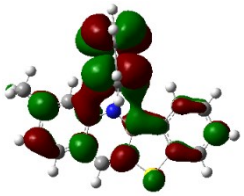
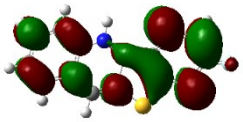
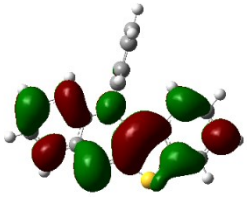
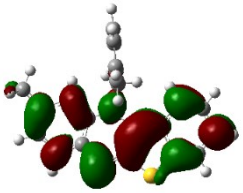
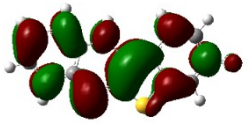
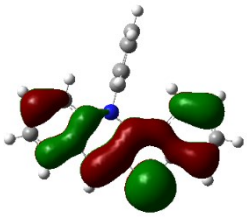
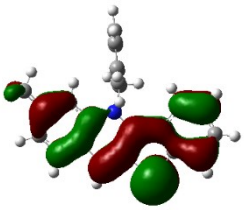
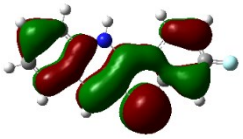
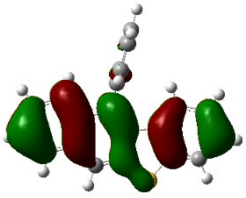
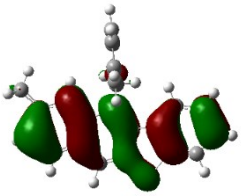
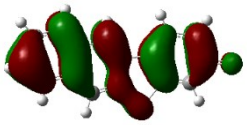
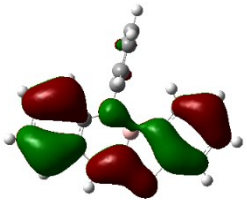
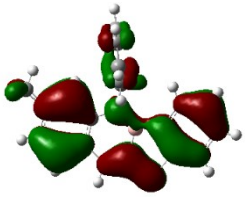
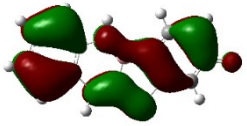
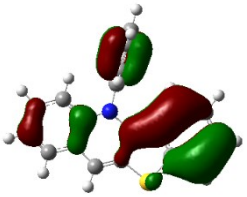
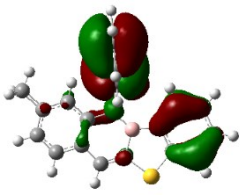
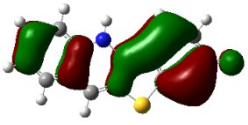
LUMO	 -1.84 eV	 -1.84 eV
HOMO	 -5.71 eV	 -5.74 eV
HOMO-1	 -6.35 eV	 -6.35 eV
HOMO-2	 -6.90 eV	 -6.93 eV
HOMO-3	 -7.38 eV	 -7.64 eV

Table S14. DFT calculated orbital levels and orbital plots for **3d**, **3f** and **3g** at the B3LYP/6-311+G(d,p) level.

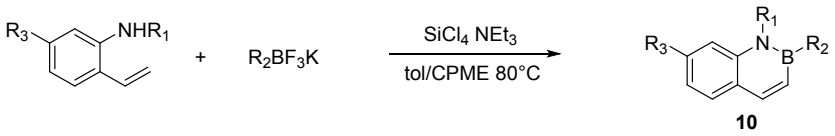
	3d	**3g**	**3f**
LUMO+3	 -0.63 eV	 -0.60 eV	 -0.47 eV

LUMO+2	 -0.90 eV	 -0.65 eV	 -0.70 eV
LUMO+1	 -1.00 eV	 -0.81 eV	 -0.92 eV
LUMO	 -1.79 eV	 -1.77 eV	 -1.92 eV
HOMO	 -5.63 eV	 -5.57 eV	 -5.90 eV
HOMO-1	 -6.28 eV	 -6.23 eV	 -6.43 eV
HOMO-2	 -6.80 eV	 -6.72 eV	 -7.03 eV
HOMO-3			

	-7.21 eV	-7.01 eV	-7.50 eV

5 Syntheses of compounds 2–10.

5.1 Syntheses of Functionalized 2,1-Borazaronaphthalenes (10).



10a: R_1= H, R_2= 2-bromophenyl, R_3= H
10b: R_1= n-Bu, R_2= 2-bromophenyl, R_3= H
10c: R_1= Bn, R_2= 2-bromophenyl, R_3= H
10d: R_1= Ph, R_2= 2-bromophenyl, R_3= H
10e: R_1= thien-3-yl, R_2= 2-bromophenyl, R_3= H
10f: R_1= Bn, R_2= 2-bromophenyl, R_3= Me
10g: R_1= H, R_2= 2-bromo-4-fluorophenyl, R_3= H
10h: R_1= H, R_2= 2-bromo-4-methylphenyl, R_3= H
10a: R_1= H, R_2= 3-bromothien-2-yl, R_3= H

Scheme S1. The reaction route and the structure of the compound **10a-10i**

10a-10c and **10f**-**10i** were synthesized as described in literature.[3, 4]

N-phenyl-2-(2-bromophenyl)-2,1-borazaronaphthalene (10d) were prepared according to the process described below. To an oven-dried Schlenk flask with a stir bar was added the potassium 2-bromophenyltrifluoroborate (6.13 g, 23.3 mmol, 1.0 equiv). After the flask was evacuated under vacuum and purged with argon, cyclopentyl methyl ether (CPME) in toluene (50 mL, 0.5 M, CPME/toluene = 1:1) were added followed by the addition of N-phenyl-2-vinylaniline (5.0 g, 25.6 mmol, 1.2 equiv), $SiCl_4$ (2.67 mL, 23.3 mmol, 1.0 equiv), and NEt_3 (6.47 mL, 46.6 mmol, 1.5 equiv). The mixture was stirred at 80 °C for 16 h. It was filtered with silica gel and the remaining residues were washed with n-hexane. The combined solution was evaporated to dryness under vacuum to give the crude product, which was purified by flash column chromatography.

1-Phenyl-2-(2-bromophenyl)-2,1-borazaronaphthalene (**10d**). **10d** was obtained as white solid (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 11.4 Hz, 1H), 7.75 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.41–7.27 (m, 4H), 7.28–7.18 (m, 4H), 7.06–6.90 (m, 5H).

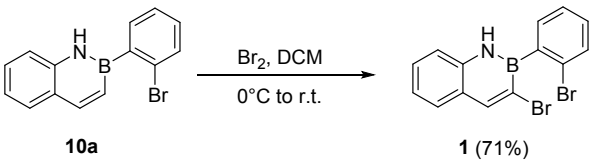
N-(thien-3-yl)-2-(2-bromophenyl)-2,1-borazaronaphthalene (10e) were prepared according to the process described below. To a toluene solution (28 mL) of allylpalladium(II) chloride dimer (26 mg, 0.07 mmol, , 5 mol %), JohnPhos (41 mg, 0.14 mmol, 10 mol %) and t-BuONa (2.7 g, 28.0 mmol, 2.0 equiv) was added 3-Bromothiophene (2.3 g, 14.0 mmol, 1.0 equiv) and 2-vinylaniline (2.0 g, 16.8 mmol, 1.2 equiv). The resulting mixture was heated to 80 ºC for 12 hours. The reaction mixture was cooled, diluted with Et_2O (30 mL), then filtered over silica gel and washed with dichloromethane/hexanes (1:50). The solvent was removed in vacuo and the product N-（thien-3-yl）-2-vinylaniline was obtained as a yellow oil (65%) that was used without further purification.

N-(thien-3-yl)-2-vinylaniline (7.3 g, 36.3 mmol, 1.5 equiv) was added to an oven-dried Schlenk bottle with a stir bar and purged with Ar three times. CPME (45 mL) and toluene (45 mL) were added, followed by potassium 2-bromophenyltrifluoroborate (6.4 g, 24.2 mmol, 1.0 equiv) and $SiCl_4$ (2.8 mL, 24.2 mmol, 1.0 equiv) under Ar. The resulting mixture was heated to 80 °C for 16 h and then cooled to room temperature and diluted with hexanes (70 mL). The reaction mixture was filtered over celite and removed in vacuo. The product was purified by column chromatography on silica gel with dichloromethane/hexanes (1:30).

N-(thien-3-yl)-2-(2-bromophenyl)-2,1-borazaronaphthalene (**10e**). **10e** was obtained as a white solid (29%).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 12.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.38 (q, *J* = 8.0 Hz, 2H), 7.21–7.27 (m, 2H), 6.96–7.12 (m, 7H). ^{13}C NMR (101MHz, $CDCl_3$): δ 145.2,

142.3, 141.9, 132.9, 131.2, 129.9, 128.8, 128.5, 127.5, 126.3, 126.1, 125.8, 125.2, 121.7, 120.8, 117.6.

5.2 General procedure for the synthesis of compound 1.



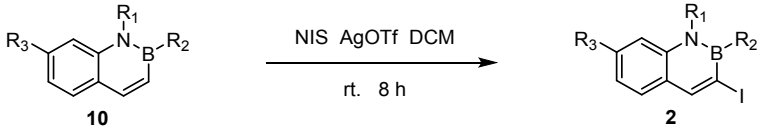
10a **1** (71%)

Scheme S2. General procedure for the synthesis of compound **1.**

Compound **1** were prepared according to the process described below. Under an argon atmosphere, to a dichloromethane solution (10 mL) of **10a** (0.45 g, 1.6 mmol, 1 equiv) was added a solution of Br_2 (92 μL, 1.8 mmol, 1.1 equiv) in dichloromethane (10 mL) over 30 min at 0 °C. After the completion of the dropwise addition, the reaction mixture was slowly returned to room temperature. The mixture was then suction-filtered over Celite, and the solvent was removed in vacuo. The product was purified by column chromatography on silica gel with dichloromethane/hexanes (1:50).

2-(2-Bromophenyl)-3-bromo-2,1-borazaronaphthalene (**1**). **1** was obtained as white solid (71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 8.10 (s, 1H), 7.63 (dd, *J* = 11.4, 8.0 Hz, 2H), 7.53 – 7.44 (m, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.32 – 7.24 (m, 3H).

5.3 General procedure for the synthesis of compounds (2).



10 **2**

2a: R_1= H, R_2= 2-bromophenyl, R_3= H
2b: R_1= n-Bu, R_2= 2-bromophenyl, R_3= H
2c: R_1= Bn, R_2= 2-bromophenyl, R_3= H
2d: R_1= Ph, R_2= 2-bromophenyl, R_3= H
2e: R_1= thien-3-yl, R_2= 2-bromophenyl, R_3= H
2f: R_1= Bn, R_2= 2-bromophenyl, R_3= Me
2g: R_1= H, R_2= 2-bromo-4-fluorophenyl, R_3= H
2h: R_1= H, R_2= 2-bromo-4-methylphenyl, R_3= H
2a: R_1= H, R_2= 3-bromothien-2-yl, R_3= H

Scheme S3. General procedure for the synthesis of compounds **2.**

Procedures for the compounds **2** were prepared according to the process described below. To a solution of compounds **10** (1.0 equiv) and N-succinimide iodide (1.1 equiv) in DCM (0.1 M) at atmosphere, AgOTf (0.1 equiv) was added and allowed to stir for 8 h under room temperature. After the consumption of compounds **1** (monitored by TLC), the reaction mass was poured into An aqueous solution of sodium bisulfite, extracted with DCM and dried (Na_2SO_4). The solvent was then evaporated in vacuo and the crude product was purified using silica gel chromatography (hexane/DCM 20: 1).

2-(2-Bromophenyl)-3-iodo-2,1-borazaronaphthalene (**2a**). **2a** was obtained as white solid (96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.97 (s, 1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.9 Hz, 1H), 7.54–7.48 (m, 1H), 7.42–7.36 (m, 2H), 7.32–7.24 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.37, 138.94, 133.90, 131.90, 130.28, 129.17, 128.66, 126.44, 126.38, 126.37, 122.16, 118.45.

1-Butyl-2-(2-bromophenyl)-3-iodo-2,1-borazaronaphthalene (**2b**). **2b** was obtained as white solid (80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 7.69–7.51 (m, 4H), 7.43–7.38 (m, 1H), 7.32–7.24 (m, 3H), 4.09–3.81 (m, 2H), 1.91–1.57 (m, 2H), 1.32–1.19 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.71, 140.23, 132.69, 131.75, 129.86, 129.63, 129.17, 128.10, 126.64, 125.90, 121.61, 115.85, 49.73, 31.72, 20.22, 13.59.

1-Benzyl-2-(2-bromophenyl)-3-iodo-2,1-borazaronaphthalene (**2c**). **2c** was obtained as white solid (81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.64 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.42–7.36 (m, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.25–7.15 (m, 6H), 7.04 (d, *J* = 7.3 Hz, 2H),

5.26 (dd, *J* = 50.4, 16.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.40, 140.23, 137.81, 132.49, 131.74, 129.83, 129.62, 129.24, 128.70, 128.18, 127.05, 126.72, 125.91, 125.79, 121.97, 117.45, 53.97.

1-Phenyl-2-(2-bromophenyl)-3-iodo-2,1-borazaronaphthalene (**2d**). **2d** was obtained as white solid (95%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 7.68 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.41–7.28 (m, 5H), 7.27–7.21 (m, 2H), 7.14–7.08 (m, 2H), 7.06–6.97 (m, 2H), 6.84 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.96, 143.33, 141.96, 132.84, 131.11, 129.51, 129.13, 129.04, 128.97, 128.90, 128.39, 127.55, 127.53, 127.01, 125.99, 125.89, 122.17, 118.20.

1-(Thien-3-yl)-2-(2-bromophenyl)-3-iodo-2,1-borazaronaphthalene (**2e**). **2e** was obtained as white solid (80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.82 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.65 (dd, *J* = 5.0, 3.2 Hz, 1H), 7.47–7.42 (m, 2H), 7.37–7.31 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.09, 141.88, 141.80, 141.51, 141.44, 132.79, 132.13, 131.08, 129.16, 129.09, 128.98, 127.01, 126.93, 126.74, 126.03, 125.88, 125.60, 125.55, 125.48, 122.33, 121.05, 120.42, 117.88. It‘s possible that the introduction of iodine atoms restricts the rotation of the two freely rotating aromatic rings, which causes splitting of the carbon spectrum. We have not observed similar phenomena in the NMR spectra of **1e** and **3e**.

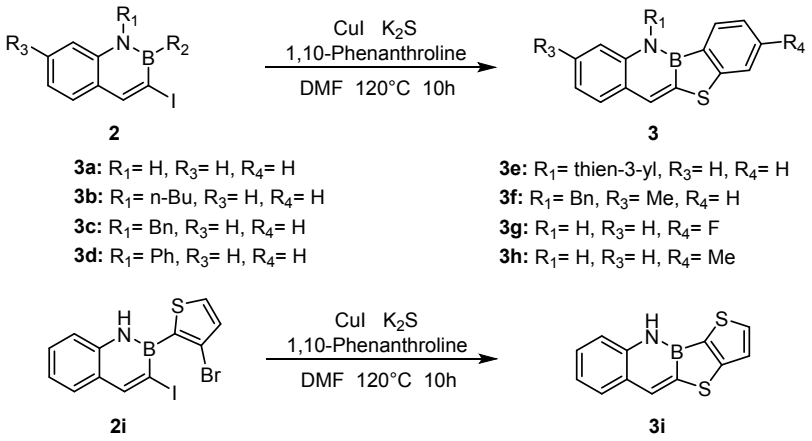
1-Benzyl-2-(2-bromophenyl)-3-iodo-7-methyl-2,1-borazaronaphthalene (**2f**). **2f** was obtained as white solid (91%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.57 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.26–7.13 (m, 7H), 7.05 (d, *J* = 7.6 Hz, 3H), 5.24 (dd, *J* = 57.6, 16.8 Hz, 2H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.15, 140.34, 139.63, 137.94, 132.52, 131.66, 129.72, 129.41, 128.64, 126.95, 126.63, 126.09, 125.87, 125.79, 123.40, 117.42, 53.77, 22.32.

2-(2-Bromo-4-fluorophenyl)-3-iodo-2,1-borazaronaphthalene (**2g**). **2g** was obtained as white solid (80%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.97 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.55–7.48 (m, 1H), 7.43–7.35 (m, 2H), 7.33–7.24 (m, 2H), 7.12 (td, *J* = 8.4, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.89 (d, *J* = 252.6 Hz), 153.54, 138.90, 135.11 (d, *J* = 8.1 Hz), 129.30, 128.71, 126.39, 126.40 (d, *J* = 8.7 Hz), 122.31, 119.49 (d, *J* = 23.3 Hz), 118.49, 114.03 (d, *J* = 20.0 Hz).

2-(2-Bromo-4-methylphenyl)-3-iodo-2,1-borazaronaphthalene (**2h**). **2h** was obtained as white solid (70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 7.95 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.52–7.43 (m, 2H), 7.31–7.18 (m, 4H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.29, 140.57, 139.00, 133.82, 132.50, 129.11, 128.62, 127.37, 126.33, 126.23, 122.07, 118.42, 21.20.

2-(3-bromothien-2-yl)-3-iodo-2,1-borazaronaphthalene (**2i**). **2i** was obtained as white solid (48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (s, 1H), 8.61 (s, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 4.8 Hz, 1H), 7.54–7.48 (m, 1H), 7.33 (d, *J* = 8.0 Hz, 1H), 7.27–7.23 (m, 1H), 7.21 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.67, 138.89, 131.76, 130.79, 129.41, 128.59, 126.20, 122.26, 118.42, 115.28.

5.4 Procedures for Synthesis of Semi-Internally BN-substituted Annulated Thiophene (3).



Scheme S4. The cyclization route of the compound **3a-3i**

A flame-dried test tube containing a magnetic stirring bar was charged with compounds **2** (1.0 equiv), K_2S (2.0 equiv), cuprous iodide (0.2 equiv) and anhydrous 1 ,10-phenanthroline (0.4 equiv) and DMF (0.2 M) under argon. The mixture was heated at 120 °C for 12 h, allowed to cool to room temperature, and extracted with DCM. The combined organic layers were dried with $MgSO_4$ and then concentrated under vacuum. The residue was purified by column chromatography on silica gel (hexane-DCM 10: 1).

Benzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**3a**). **3a** was obtained as pale yellow solid (78%). Mp: 210−212 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.23 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.54–7.46 (m, 3H), 7.34–7.28 (m, 2H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.15. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.58, 137.66, 133.36, 131.21, 130.86, 128.74, 127.31, 125.76, 123.72, 123.55, 121.57, 118.89. HRMS (ESI) m/z calculated for $C_{14}H_{11}BNS$ $[M + H]^+$: 236.0705, found:236.0708. IR (neat): *v* = 472, 640, 695, 749, 1432, 1588, 1635, 3052, 3365, 3451 cm^{-1}.

1-Butylbenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**3b**). **3b** was obtained as white solid (45%). Mp: 93−94 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.18 (d, *J* = 7.6 Hz, 1H), 7.81–7.74 (m, 3H), 7.62–7.56 (m, 1H), 7.56–7.50 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 4.63 (s, 2H), 2.12–1.95 (m, 2H), 1.71–1.60 (m, 2H), 1.09 (t, *J* = 7.6 Hz, 3H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.00. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.47, 139.32, 133.48, 132.54, 130.28, 129.61, 127.47, 126.86, 124.00, 123.68, 121.05, 114.77, 47.90, 32.29, 20.63, 14.10. HRMS (ESI) m/z calculated for $C_{18}H_{19}BNS$ $[M + H]^+$: 292.1331, found:292.1330. IR (neat): *v* = 484, 606, 647, 747, 1062, 1215, 1283, 1385, 1425, 1482, 1596, 1635, 2918, 2957, 3055, 3452 cm^{-1}.

1-Benzylbenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**3c**). **3c** was obtained as pale yellow solid (47%). Mp: 158−160 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 7.97 (d, *J* = 7.6 Hz, 1H), 7.80 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.53–7.47 (m, 1H), 7.46–7.41 (m, 1H), 7.33–7.22 (m, 7H), 5.87 (s, 2H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.23. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.64, 139.66, 137.48, 133.94, 132.64, 130.56, 129.37, 129.00, 127.63, 127.42, 126.97, 126.19, 123.96, 123.78, 121.44, 115.91, 52.22. HRMS (ESI) m/z calculated for $C_{21}H_{17}BNS$ $[M + H]^+$: 326.1175, found:326.1179. IR (neat): *v* = 484, 606, 647, 747, 1062, 1215, 1283, 1385, 1425, 1482, 1596, 1635, 2918, 2957, 3055, 3452 cm^{-1}.

1-Phenylbenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**3d**). **3d** was obtained as pale yellow solid (46%). Mp: 146−147 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.83 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.70–7.59 (m, 4H), 7.44–7.34 (m, 4H), 7.34–7.28 (m, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.98 (t, *J* = 7.0 Hz, 1H), 6.50 (d, *J* = 7.2 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.53. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.39, 142.90, 140.78, 133.67, 132.61, 130.57, 130.25, 128.92, 128.51, 128.21, 127.28, 126.02, 123.45, 123.39, 121.54, 117.29. HRMS (ESI) m/z calculated for $C_{20}H_{15}BNS$ $[M + H]^+$: 312.1018,

found:312.1019. IR (neat): *v* = 488, 620, 698, 749, 899, 1022, 1063, 1156, 1208, 1343, 1428, 1491, 1591, 3053, 3441 cm^{-1}.

1-(Thien-3-yl)benzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**3e**). **3e** was obtained as yellow solid (53%). Mp: 183-184 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.82 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.65 (dd, *J* = 4.8, 3.2 Hz, 1H), 7.47–7.42 (m, 2H), 7.37–7.31 (m, 2H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 7.6 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.97. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.40, 141.37, 140.72, 133.80, 132.48, 130.74, 128.90, 127.42, 127.25, 126.97, 126.13, 123.53, 123.47, 121.74, 121.33, 117.06. HRMS (ESI) m/z calculated for $C_{18}H_{13}BNS_2$ $[M + H]^+$: 318.0582, found:318.0586. IR (neat): *v* = 486, 602, 655, 696, 729, 757, 1062, 1209, 1281, 1342, 1393, 1428, 1533, 1591, 1632, 3049, 3097, 3448 cm^{-1}.

1-Benzyl-9-methylbenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**3f**). **3f** was obtained as pale yellow solid (45%). Mp: 239-240 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.39 (s, 1H), 7.36–7.26 (m, 5H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.12 (d, *J* = 8.0 Hz, 1H), 5.84 (s, 2H), 2.43 (s, 3H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.99. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.67, 139.83, 137.88, 137.62, 133.90, 132.58, 130.37, 129.18, 128.97, 127.34, 126.22, 124.87, 123.92, 123.66, 122.95, 115.92, 52.09, 22.22. HRMS (ESI) m/z calculated for $C_{22}H_{19}BNS$ $[M + H]^+$: 340.1331, found: 340.1331. IR (neat): *v* = 479, 659, 693, 732, 809, 963, 1062, 1356, 1425, 1464, 1534, 1589, 3024, 3450 cm^{-1}.

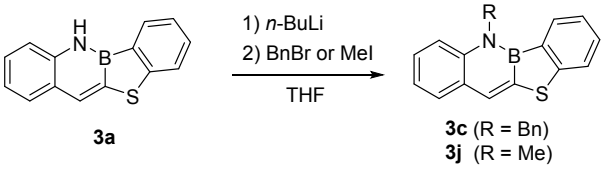
4-Fluorobenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**3g**). **3g** was obtained as white solid (53%). Mp: 219−220 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 8.19 (s, 1H), 7.97 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.51–7.47 (m, 2H), 7.40 (dd, *J* = 9.6, 2.2 Hz, 1H), 7.32–7.27 (m,

1H), 7.03 (ddd, *J* = 8.9, 8.3, 2.3 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.86; ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.82. ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.80(d, *J* = 251.6 Hz), 156.70 (d, *J* = 9.4 Hz), 137.69, 133.41 (d, *J* = 1.7 Hz), 132.45 (d, *J* = 9.5 Hz), 128.82, 127.52, 125.48, 121.65, 118.86, 111.59 (d, *J* = 22.1 Hz), 110.59 (d, *J* = 24.0 Hz). HRMS (ESI) m/z calculated for $C_{14}H_{10}BFNS$ $[M + H]^+$: 254.1094, found: 254.1090. IR (neat): *v* = 474, 636, 688, 753, 819, 851, 1217, 1259, 1384, 1462, 1556, 1597, 3366, 3450 cm^{-1}.

4-Methylbenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**3h**). **3h** was obtained as yellow solid (59%). Mp: 199−200 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 8.19 (s, 1H), 7.93 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.50–7.45 (m, 2H), 7.31–7.26 (m, 1H), 7.14 (dd, *J* = 7.6, 0.4 Hz, 1H), 2.47 (s, 3H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.63. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.94, 141.46, 137.72, 133.12, 130.97, 128.69, 127.21, 125.70, 124.96, 124.11, 121.43, 118.82, 21.97. HRMS (ESI) m/z calculated for $C_{15}H_{13}BNS$ $[M + H]^+$: 250.0862, found: 250.0855. IR (neat): *v* = 480, 603, 644, 691, 752, 1060, 1341, 1416, 1558, 1600, 3051, 3366, 3449 cm^{-1}.

Thieno[2,3-b]-2,1-borazaronaphtho[2,3-d]thiophene (**3i**). **3i** was obtained as pale yellow solid (69%). Mp: 217−219 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.26 (s, 1H), 7.90 (d, *J* = 4.8 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.52–7.44 (m, 2H), 7.37 (d, *J* = 4.8 Hz, 1H), 7.32–7.26 (m, 1H). ^{11}B NMR (128 MHz, DMSO) δ 28.83. ^{13}C NMR (101 MHz, DMSO) δ 156.11, 138.94, 138.54, 135.65, 129.15, 128.16, 124.67, 123.40, 121.32, 119.50. HRMS (ESI) m/z calculated for $C_{12}H_9BNS_2$ $[M + H]^+$: 242.0269, found: 242.0262. IR (neat): *v* = 486, 602, 655, 729, 757, 1062, 1281, 1342, 1393, 1428, 1533, 1591, 3049, 3097, 3448 cm^{-1}.

6 Derivatization of compound 3a at the N-H site.



3a

3c (R = Bn)
3j (R = Me)

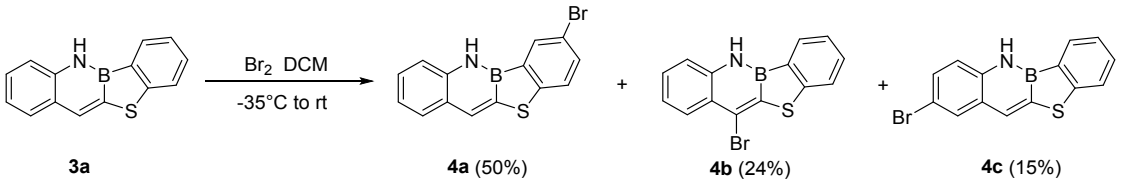
Scheme S5. Reation of compound **3a** at the N-H site

To a dried Schlenk flask charged with **3a** (100 mg, 0.426 mmol, 1.0 equiv) and anhydrous THF 4mL under Argon, stired at -78 ºC for 10 min. Then added n-BuLi (255 µL, 2.5 mol/L in haxane, 1.5 equiv) under the protect of Argon. Keep stirring in -78 ºC for 1h and roomtemperature for 1h. Then ICH_3 (53 µL, 0.85 mmol, 2.0 equiv) was added to the mixture under Argon, and stirred in roomtemperature for 2h. The resulting mixture was successively washed with water and extracted twice with EtOAc . The combined organic layers were dried over $MgSO_4$. The compound **3j** was obtained as white powder (90%) by silica gel chromatography. Compound **3c** could be synthesised by the same procedure, and the only difference is the ICH_3 should be replaced by the BnBr. The compound **3c** was obtained as pale yellow solid (95%) by silica gel chromatography.

1-Methylbenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**3j**). **3j** was obtained as white powder (90%). Mp: 170−171 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.2 Hz, 1H), 8.21 (s, 1H), 7.82–7.71 (m, 3H), 7.61 (ddd, *J* = 8.6, 7.1, 1.6 Hz, 1H), 7.50–7.54 (m, 1H), 7.40–7.31 (m, 2H), 4.20 (s, 3H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.64. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.36, 140.42, 133.29, 132.79, 130.30, 129.21, 127.51, 126.58, 123.95, 123.52, 121.26, 114.75, 35.87. HRMS (ESI) m/z calculated for $C_{15}H_{13}BNS$ $[M + H]^+$: 250.0862, found: 250.0861. IR (neat): *v* = 483, 604, 644 , 703, 752, 1061, 1208, 1349, 1377, 1425, 1594, 2929, 2960, 3045, 3451 cm^{-1}.

7 The bromination of compound 3a.

7.1 Procedure for the single bromination of 3a.



3a **4a** (50%) **4b** (24%) **4c** (15%)

Scheme S6. the single bromination of **3a**

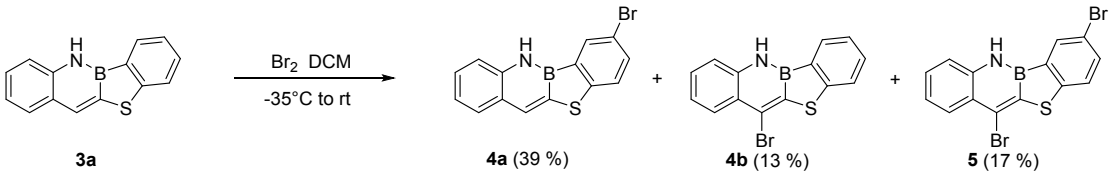
To a dried Schlenk flask charged with **3a** (50 mg, 0.21 mmol, 1.0 equiv) and dichloromethane (2 mL), then drop added the solution of Br_2 (11 μL, 0.21 mmol, 1.0 equiv) in DCM (2 mL) with constant pressure drop funnel under Argon at -35℃ over 1h. Then remove the mixture to room temperature and bring to room temperature slowly when the dropwise was comleted, and stirred at room temperature overnight. The resulting mixture was then suction-filtered with Buchner funnel, and the solvent was removed in vacuo. The products was purified by column chromatography on silica gel with ethyl acetate /hexanes (1:100).

3-Bromobenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**4a**). **4a** was obtained as white powder (50%). Mp: 189−192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.24 (s, 1H), 8.15 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.64–7.56 (m, 2H), 7.54–7.47 (m, 2H), 7.35–7.28 (m, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.13. ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.12, 137.59, 133.99, 133.84, 133.38, 128.83, 127.64, 125.75, 125.10, 121.87, 118.99, 117.73. HRMS (ESI) m/z calculated for $C_{14}H_{10}BBrNS$ $[M + H]^+$: 313.9810, found: 313.9797. IR (neat): *v* = 469, 751, 807, 1027, 1072, 1261, 1428, 1588, 2854, 2923, 2957, 3335, 3452 cm^{-1}.

6-Bromobenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**4b**). **4b** was obtained as white powder (24 %). Mp: 203−206 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.96 (dd, *J* = 7.4, 0.5 Hz, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.55–7.50 (m, 2H), 7.47 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.36 (ddd, *J* = 8.2, 6.9, 1.4 Hz, 1H), 7.32 (td, *J* = 7.4, 0.9 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 32.64. ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.93, 138.55, 131.61, 131.24, 128.23, 127.76, 127.61, 124.17, 124.01, 123.68, 122.38, 119.13. HRMS (ESI) m/z calculated for $C_{14}H_{10}BBrNS$ $[M + H]^+$: 313.9810, found: 313.9803. IR (neat): *v* = 435, 512, 614, 686, 743, 932, 1062, 1325, 1420, 1555, 1589, 3047, 3373, 3462 cm^{-1}.

8-Bromobenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**4c**). **4c** was obtained as white powder (15%). Mp: 207 - 208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.07 (s, 1H), 8.00 (d, *J* = 7.3 Hz, 1H), 7.84 (d, *J* = 1.3 Hz, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.56–7.49 (m, 2H), 7.38–7.29 (m, 2H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.96. ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.49, 136.36, 131.93, 131.91, 131.25, 131.15, 130.69, 129.97, 127.13, 123.74, 120.32, 114.07. HRMS (ESI) m/z calculated for $C_{14}H_{10}BBrNS$ $[M + H]^+$: 313.9810, found: 313.9769. IR (neat): *v* = 468, 630, 693, 737, 808, 1193, 1428, 1552, 1589, 2924, 3323, 3370, 3413, 3469 cm^{-1}.

7.2 Procedure for the Double Bromination of 3a.



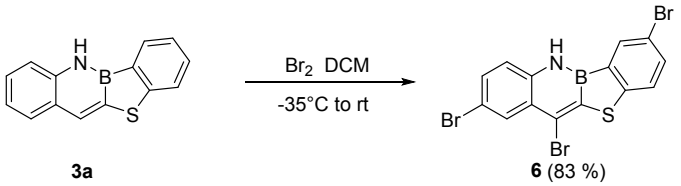
3a **4a** (39 %) **4b** (13 %) **5** (17 %)

Scheme S7. the Double Bromination of **3a**

To a dried Schlenk flask charged with **3a** (200 mg, 0.85 mmol) and dichloromethane (5 mL), then drop added the solution of Br_2 (66 μL，1.5 equiv) in DCM (5 mL) with constant pressure drop funnel under Argon at -35℃ over 1 h. Then remove the mixture to room temperature and bring to room temperature slowly when the dropwise was comleted, and stirred at room temperature overnight. The resulting mixture was then suction-filtered with Buchner funnel, and the solvent was removed in vacuo. The product was purified by column chromatography on silica gel with ethyl acetate /hexanes (1:100).

3,6-Dibromobenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**5**). **5** was obtained as white powder (17 %). Mp: 270−272 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.64 (s, 1H), 8.38 (d, *J* = 2.0 Hz, 1H), 8.11 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.76–7.71 (m, 2H), 7.69–7.64 (m, 1H), 7.42–7.46 (m, 1H). ^{11}B NMR (128 MHz, DMSO) δ 34.31. ^{13}C NMR (101 MHz, DMSO) δ 150.27, 139.46, 134.81, 133.41, 128.80, 126.88, 126.74, 125.58, 123.12, 122.42, 119.74, 117.78. HRMS (ESI) m/z calculated for $C_{14}H_9BBr_2NS$ $[M + H]^+$: 391.8916, found: 391.8905. IR (neat): *v* = 431, 498, 519, 701, 745, 806, 939, 1068, 1325, 1383, 1422, 1549, 1580, 1738, 2853, 2922, 3357, 3453 cm^{-1}.

7.3 Procedure for the trible Bromination of 3a.



3a **6** (83 %)

Scheme S8. the trible Bromination of **3a.**

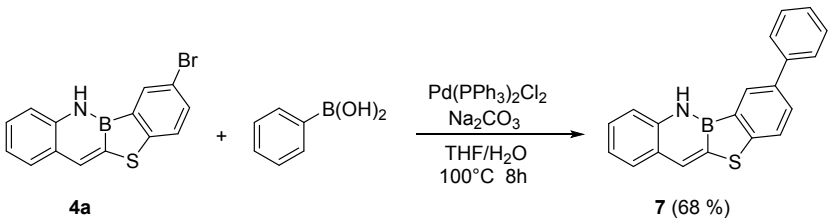
To a dried Schlenk flask charged with **3a** (200 mg, 0.85 mmol, 1.0 equiv) and dichloromethane(10 mL), then drop added the solution of Br_2 (219 μL, 4.25 mmol, 5.0 equiv) in

DCM (10 mL) with constant pressure drop funnel under Argon at -35℃ over 1 h. Then remove the mixture to room temperature and bring to room temperature slowly when the dropwise was comleted, and stirred at room temperature overnight. The resulting mixrure was then suction-filtered with Buchner funnel, and the white solid was washed with DCM and dried in vacuo, then the white solid is **6** (83 %).

3,6,8-Tribromobenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene(**6**). **6** was obtained as white powder (83 %). Mp: 326–327 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.72 (s, 1H), 8.33 (d, *J* = 2.0 Hz, 1H), 8.17 (d, *J* = 2.1 Hz, 1H), 7.82–7.73 (m, 3H), 7.68 (d, *J* = 8.8 Hz, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 37.68. ^{13}C NMR (101 MHz, DMSO) δ 150.18, 138.38, 134.84, 133.67, 131.28, 128.47, 125.64, 124.93, 124.63, 121.91, 117.94, 114.36. HRMS (ESI) m/z calculated for $C_{14}H_8BBr_3NS$ $[M + H]^+$: 469.8021, found: 469.8011. IR (neat): *v* = 514, 636, 706, 732, 808, 945, 1070, 1191, 1323, 1376, 1429, 1547, 1581, 3351, 3420 cm^{-1}.

8 Procedures for the Suzuki Cross-Coupling Reaction of bromides.

8.1 Procedure for the Suzuki Cross-Coupling Reaction of bromide 4a.

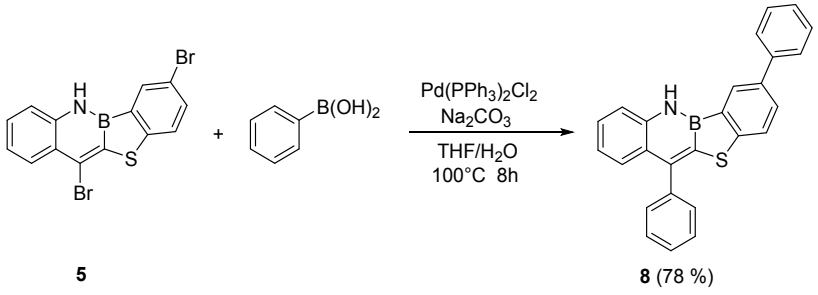


Scheme S9. the Suzuki Cross-Coupling Reaction of **4a**

To a dried Schlenk flask charged with **4a** (50 mg, 0.16 mmol，1.0 equiv), phenylboronic acid (58.2 mg, 0.48 mmol, 3.0 equiv), $Pd(PPh_3)_2Cl_2$ (5.6 mg, 0.008 mmol, 5 mol%), and Na_2CO_3 (101.3 mg, 0.96 mmol, 6.0 equiv) was added THF (2 mL) and H_2O (2 mL) under Argon. The mixture was heated and stirred at 100°C for 8 h. The resulting mixture was successively washed with water (50 mL) and extracted twice with EtOAc (30 mL). The combined organic layers were dried over Na_2SO_4. And the compound **7** was obtained as white powder (68%) by silica gel chromatography.

3-phenylbenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**7**). **7** was obtained as white powder (68 %).Mp: 183−185 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 8.27 (d, *J* = 1.5 Hz, 1H), 8.25 (s, 1H), 7.81–7.74 (m, 3H), 7.70 (s, 1H), 7.68 (s, 1H), 7.54–7.47 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.34–7.28 (m, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 34.50. ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.64, 141.23, 137.68, 136.73, 133.59, 129.98, 129.75, 128.88, 128.78, 127.40, 127.17, 127.11, 125.79, 123.88, 121.64, 118.94. HRMS (ESI) m/z calculated for $C_{20}H_{14}BNS$ $[M + H]^+$: 312.1018, found: 312.1015. IR (neat): *v* = 475, 538, 608, 691, 754, 819, 850, 1029, 1071, 1202, 1257, 1339, 1372, 1442, 1559, 1592, 1636, 2959, 3053, 3361, 3456 cm^{-1}.

8.2 Procedure for the Suzuki Cross-Coupling Reaction of bromide 5.



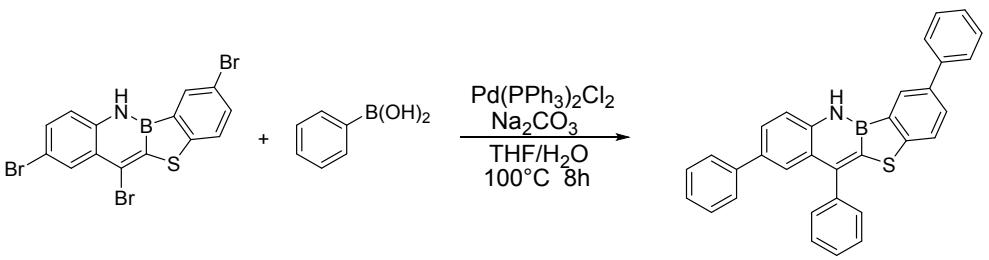
5 **8** (78 %)

Scheme S10. the Suzuki Cross-Coupling Reaction of bromide **5**

To a dried Schlenk flask charged with **5** (18 mg, 0.0460 mmol，1.0 equiv), phenylboronic acid (38 mg, 0.3099 mmol, 7.0 equiv), $Pd(PPh_3)_2Cl_2$ (1.6 mg, 0.0022 mmol, 5 mol%), and Na_2CO_3 (65 mg, 0.62 mmol, 14.0 equiv) was added THF (1 mL) and H_2O (1 mL) under Argon. The mixture was heated and stirred at 100°C for 8 h. The resulting mixture was successively washed with water (50 mL) and extracted twice with EtOAc (30 mL). The combined organic layers were dried over Na_2SO_4. And the compound **8** was obtained as pale yellow powder (78 %) by silica gel chromatography.

3,6,-Diphenylbenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**8**). **8** was obtained as yellow powder (78 %). Mp: 168–171 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.51 (s, 1H), 8.59 (d, *J* = 1.7 Hz, 1H), 7.86–7.75 (m, 5H), 7.66–7.48 (m, 9H), 7.43–7.38 (m, 1H), 7.27–7.20 (m, 1H). ^{11}B NMR (128 MHz, $CDCl_3$) δ 37.34. ^{13}C NMR (101 MHz, DMSO) δ 152.61, 144.43, 140.27, 139.35, 139.05, 135.75, 130.17, 129.20, 129.01, 128.84, 128.81, 128.14, 127.44, 127.20, 126.55, 126.02, 124.18, 123.67, 121.09, 119.56. HRMS (ESI) m/z calculated for $C_{26}H_{19}BNS$ $[M + H]^+$: 388.1331, found: 388.1341. IR (neat): *v* = 475, 622, 697, 758, 816, 1078, 1189, 1260, 1377, 1456 ,1490, 1556, 1599, 2852, 2922, 2956, 3412 cm^{-1}.

8.3 Procedure for the Suzuki Cross-Coupling Reaction of bromide 6.



6 **9** (80 %)

Scheme S11. the Suzuki Cross-Coupling Reaction of bromide **6.**

To a dried Schlenk flask charged with **6** (50 mg, 0.1066 mmol，1.0 equiv), phenylboronic acid (130 mg, 1.066 mmol, 10.0 equiv), $Pd(PPh_3)_2Cl_2$ (3.8 mg, 0.0080 mmol, 5 mol %), and Na_2CO_3 (226 mg, 2.1320 mmol, 6.0 equiv) was added THF (2 mL) and H_2O (2 mL) under Argon. The mixture was heated and stirred at 100°C for 8 h. The resulting mixture was successively washed with water (50 mL) and extracted twice with EtOAc (30 mL). The combined organic layers were dried over Na_2SO_4. And the compound 9 was obtained as yellow powder (80 %) by silica gel chromatography.

3,6,8-Triphenylbenzo[b]-2,1-borazaronaphtho[2,3-d]thiophene (**9**). **9** was obtained as yellow powder (80 %). Mp: 205–208 °C. ^{1}H NMR (400 MHz, DMSO) δ 11.60 (s, 1H), 8.60 (d, *J* = 1.7 Hz, 1H), 7.92–7.87 (m, 2H), 7.86–7.83 (m, 1H), 7.81–7.74 (m, 4H), 7.67–7.62 (m, 2H), 7.60–7.51 (m, 7H), 7.46–7.39 (m, 3H), 7.34–7.29 (m, 1H). ^{11}B NMR (128 MHz, $CDCl_3$/DMSO=1:1) δ 39.73. ^{13}C NMR (101 MHz, DMSO) δ 152.62, 144.45, 140.27, 140.26, 138.92, 138.91, 135.81, 133.13, 130.17, 129.27, 129.01, 128.99 128.92, 128.88, 128.29, 127.21, 126.95, 126.56, 126.49, 126.30, 124.44, 123.87, 123.69, 120.23. HRMS (ESI) m/z calculated for $C_{32}H_{23}BNS$ $[M + H]^+$: 464.1644, found: 464.1643. IR (neat): *v* = 505, 635, 695, 759, 803, 1023, 1078, 1186, 1260, 1344, 1439, 1488, 1556, 1595, 2962, 3026, 3372, 3403 cm^{-1}.

9 UV-Vis and Emission spectra of compounds 3a–3j, 3a’ and 7-9.

For this part, all experiments were performed in DCM solution at 10^{-6} mol/L. Emission maximum was measured in DCM excited at 285 nm.

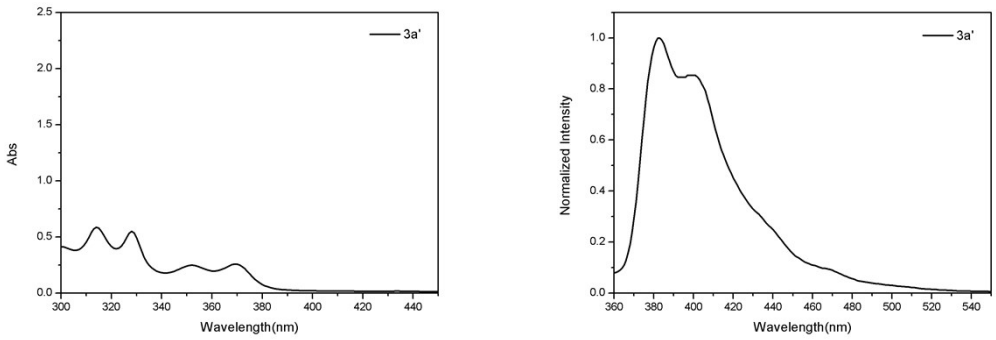


Figure S12. UV−vis spectra (left) and emission spectra (right) of compound **3a’.**

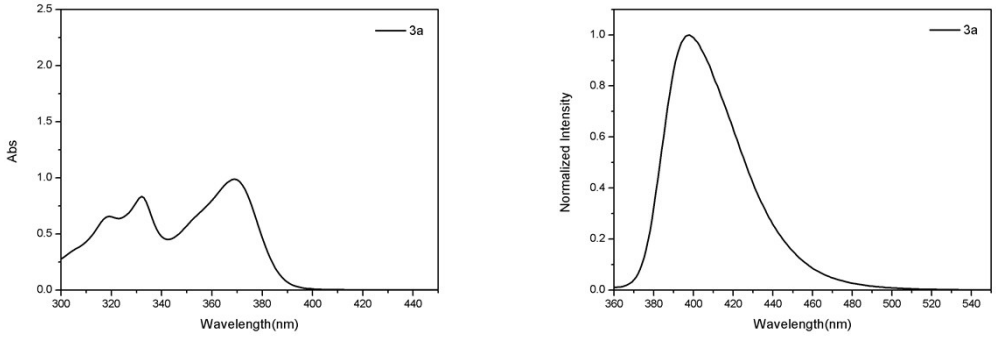


Figure S13. UV−vis spectra (left) and emission spectra (right) of compound **3a.**

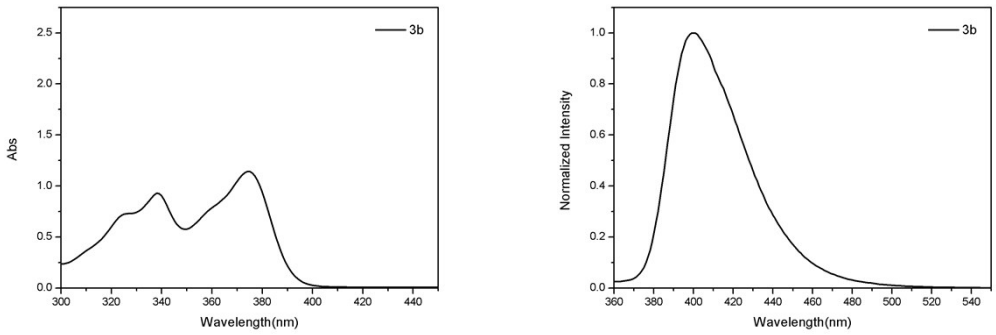


Figure S14. UV−vis spectra (left) and emission spectra (right) of compound **3b.**

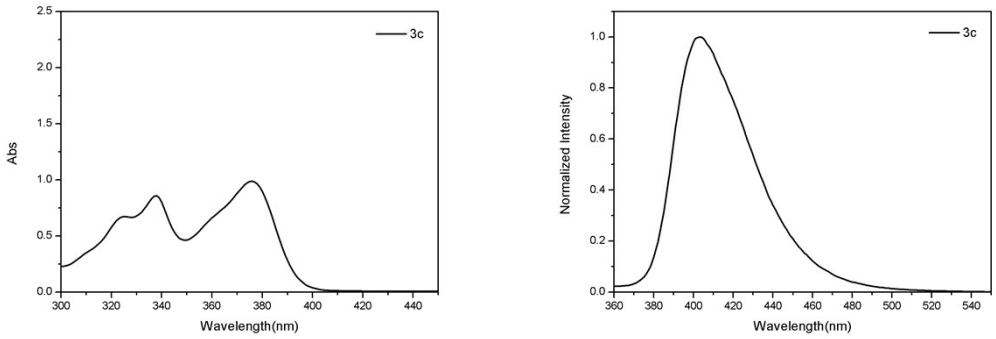


Figure S15. UV−vis spectra (left) and emission spectra (right) of compound **3c.**

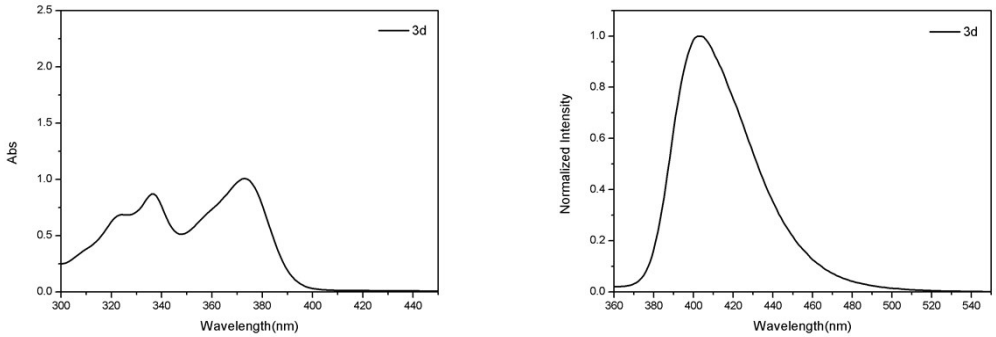


Figure S16. UV−vis spectra (left) and emission spectra (right) of compound **3d.**

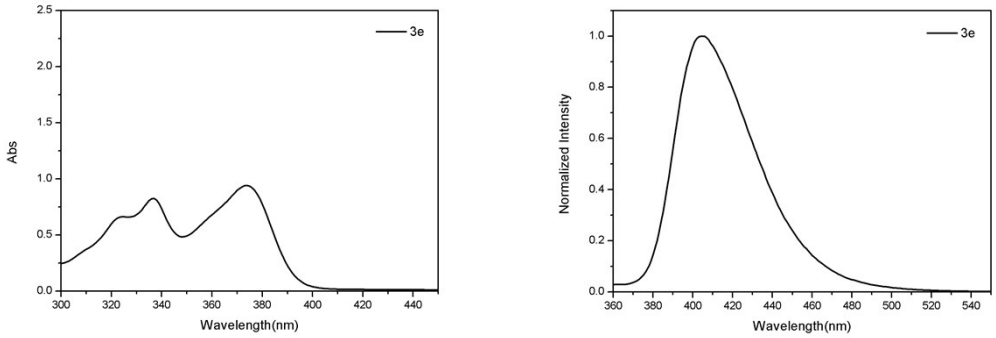


Figure S17. UV−vis spectra (left) and emission spectra (right) of compound **3e.**

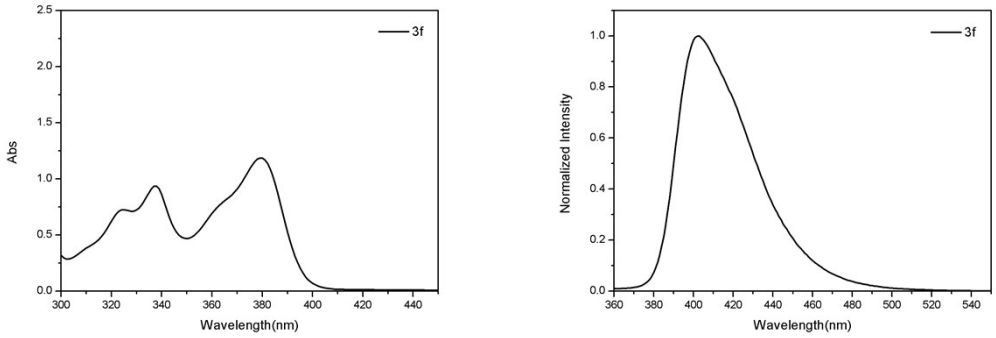


Figure S18. UV−vis spectra (left) and emission spectra (right) of compound **3f.**

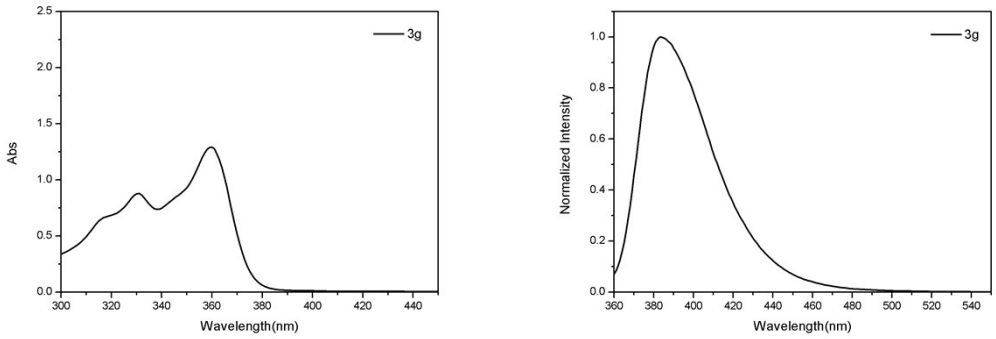


Figure S19. UV−vis spectra (left) and emission spectra (right) of compound **3g.**

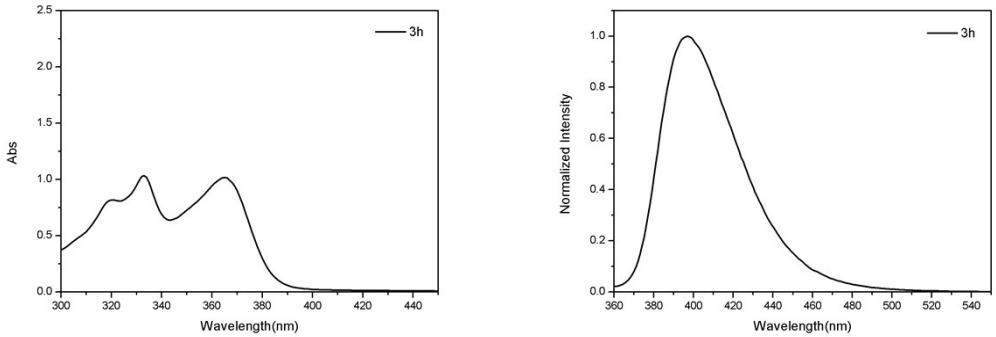


Figure S20. UV−vis spectra (left) and emission spectra (right) of compound **3h.**

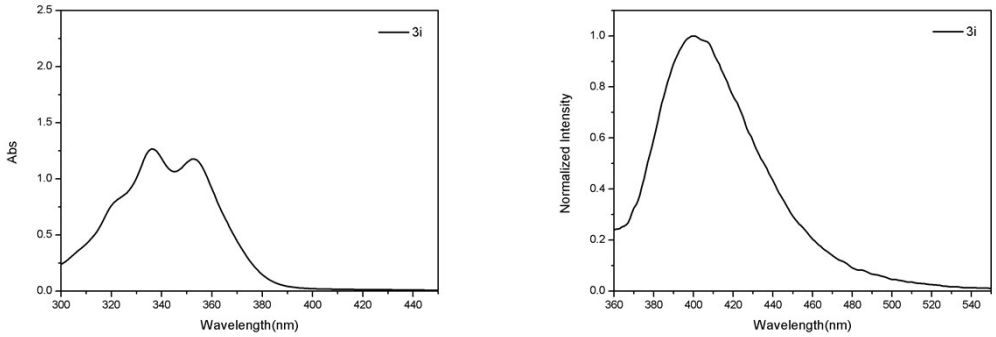


Figure S21. UV−vis spectra (left) and emission spectra (right) of compound **3i.**

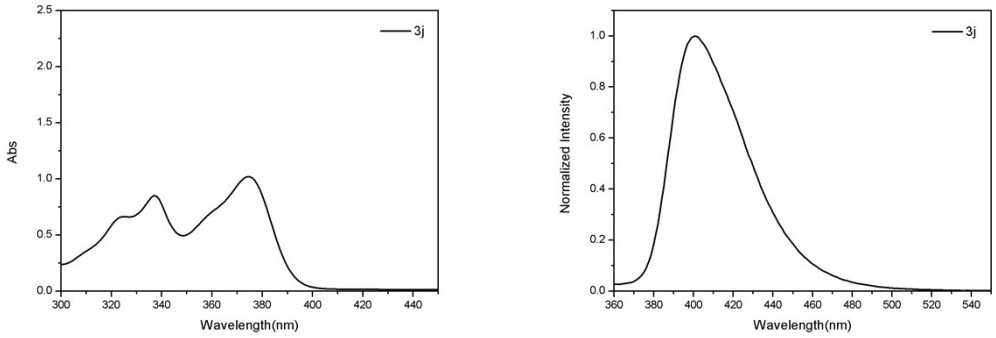


Figure S22. UV−vis spectra (left) and emission spectra (right) of compound **3j.**

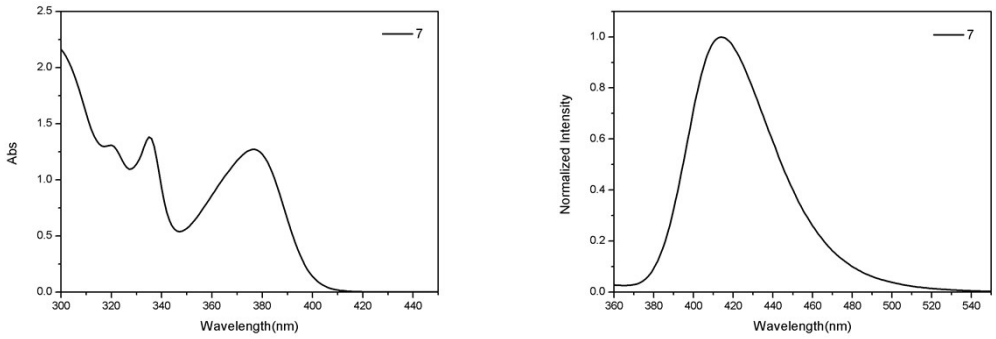


Figure S23. UV−vis spectra (left) and emission spectra (right) of compound **7.**

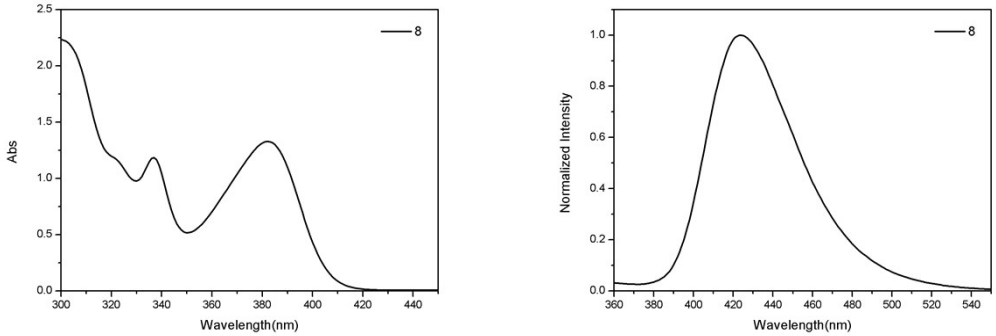


Figure S24. UV−vis spectra (left) and emission spectra (right) of compound **8.**

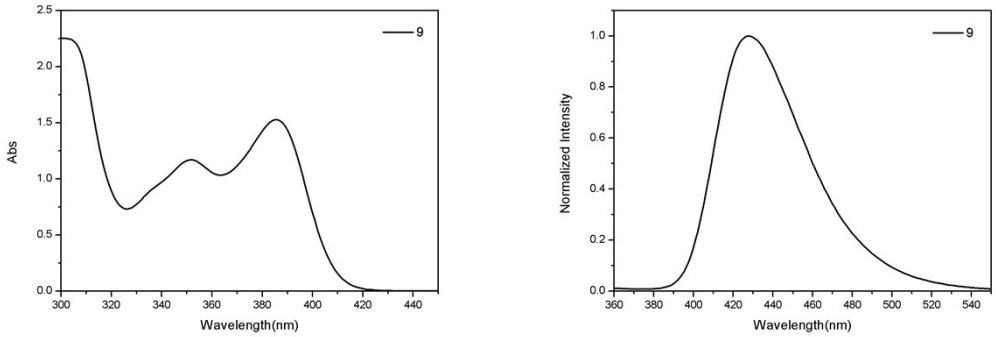


Figure S25. UV−vis spectra (left) and emission spectra (right) of compound **9.**

10 References.

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Montgomery, T. Vreven, Jr., K. N. Kudin, J. C. Burant, J. M. Millam,S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W.Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian* 03, *Revision* C.02, Gaussian, Inc., Wallingford CT, **2004**.

3 H. Huang, Z. Pan, C. Cui, Synthesis of BN-embedded tetraphenes and their photophysical properties, *Chem. Commun.,* 2016, **52**, 4227.

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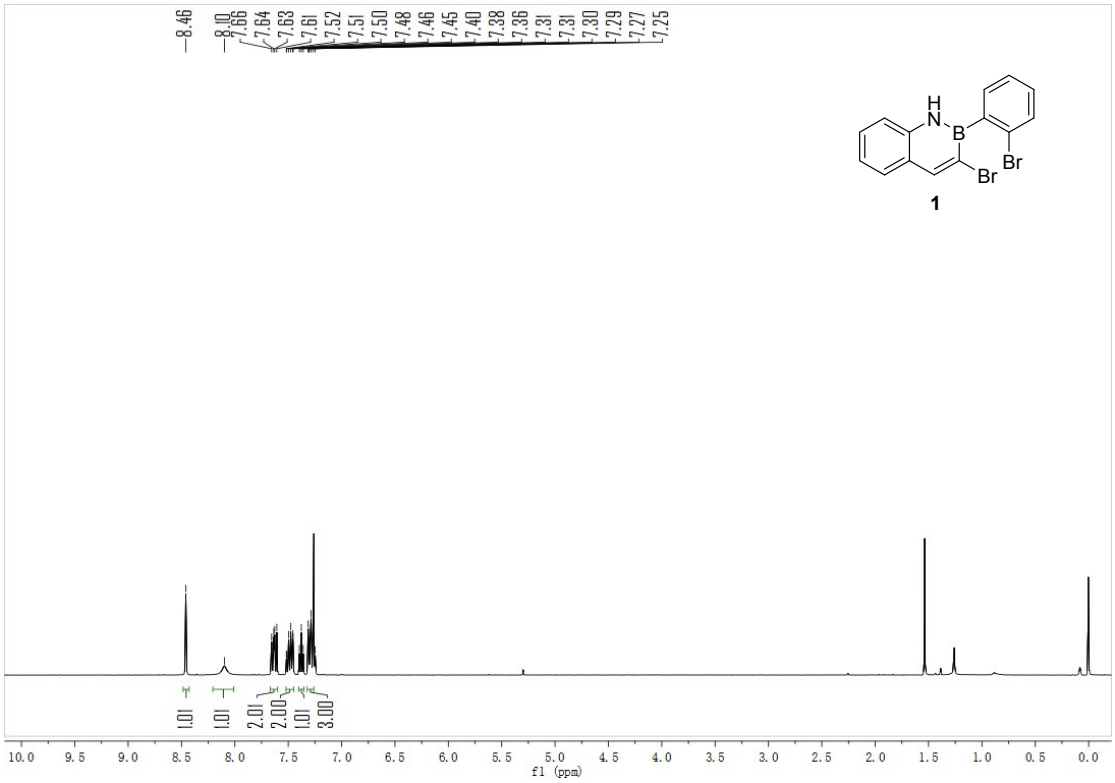
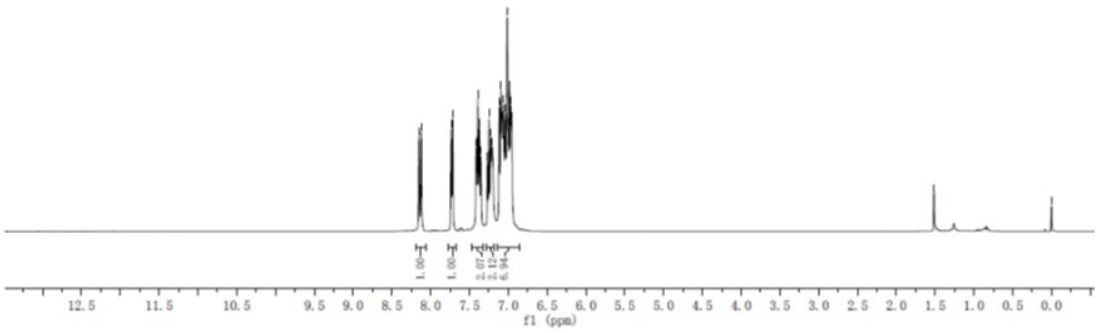
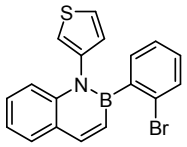
11 Scanned NMR Spectra of All New Compounds.



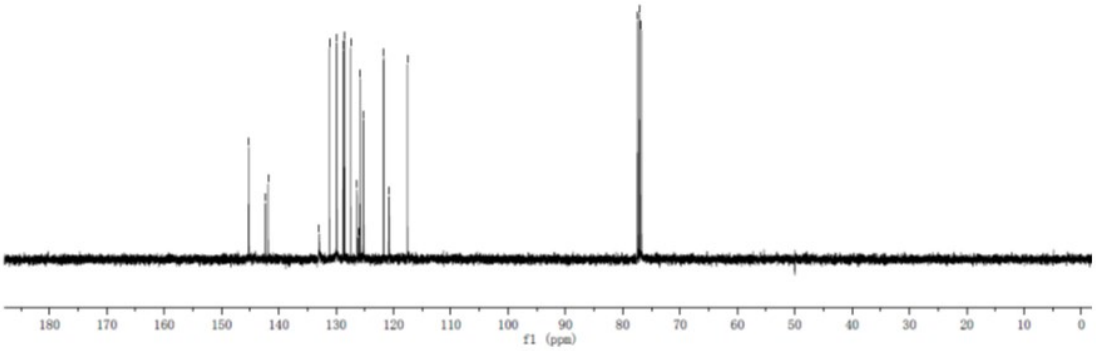
1

10e




S
N
B
Br

10e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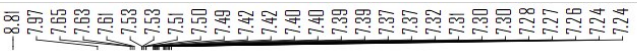
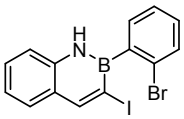
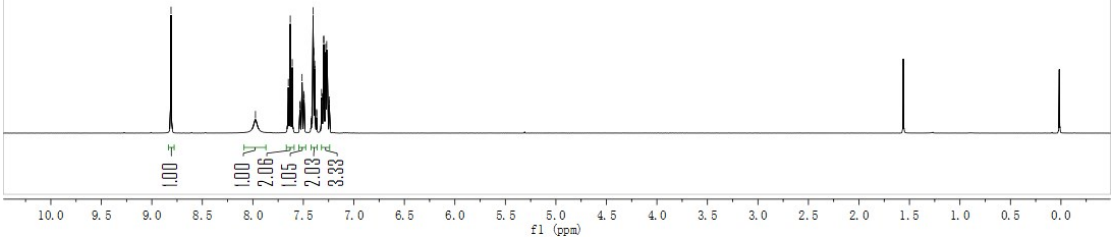



H
N
B
Br
I

2a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1.05
2.03
3.33
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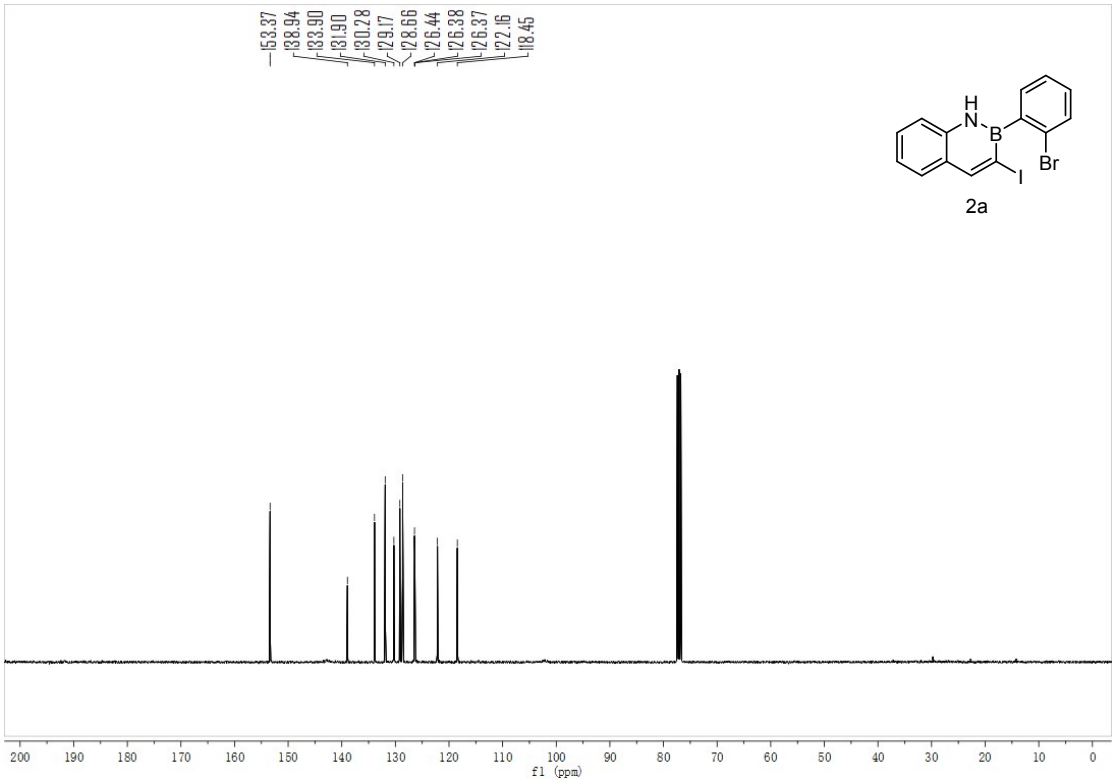
f1 (ppm)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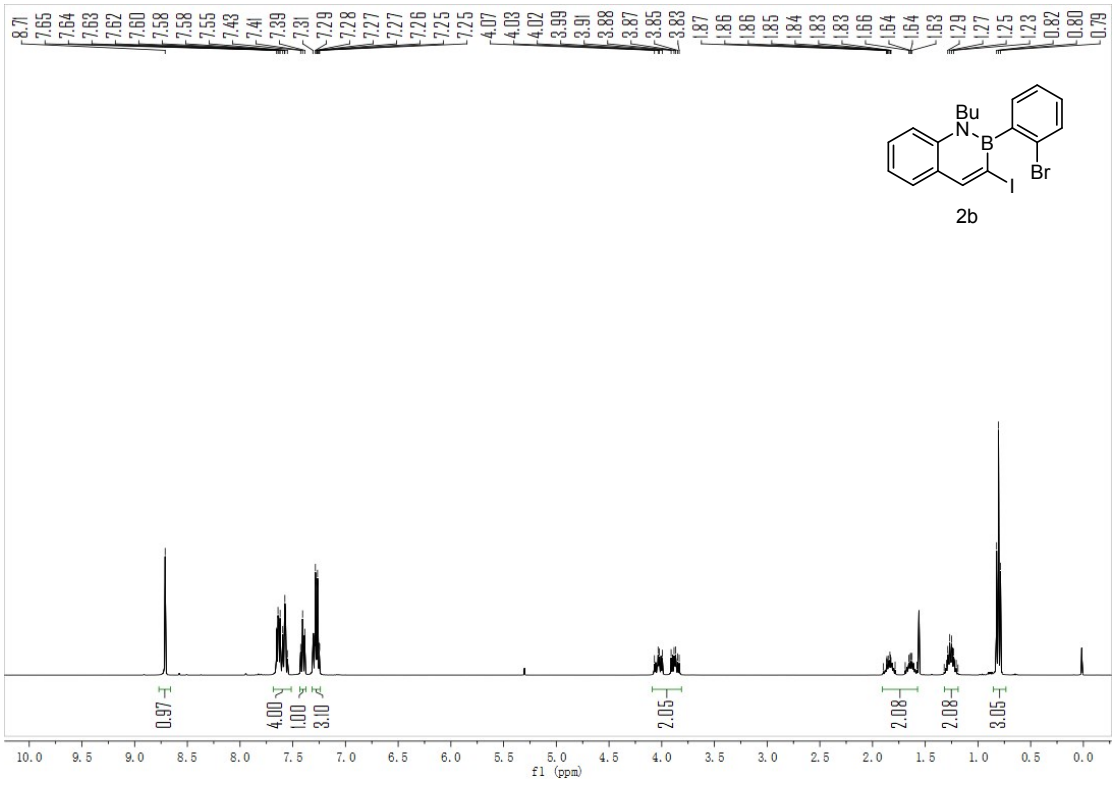
H
N
B
Br
I
2a
f1 (ppm)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7.29
7.28
7.27
7.27
7.26
7.25
7.25
4.07
4.03
4.02
3.99
3.91
3.88
3.87
3.85
3.83
1.87
1.86
1.86
1.85
1.84
1.83
1.83
1.66
1.64
1.64
1.63
1.29
1.27
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0.80
0.79
Bu
N
B
Br
I
2b
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1.00
3.10
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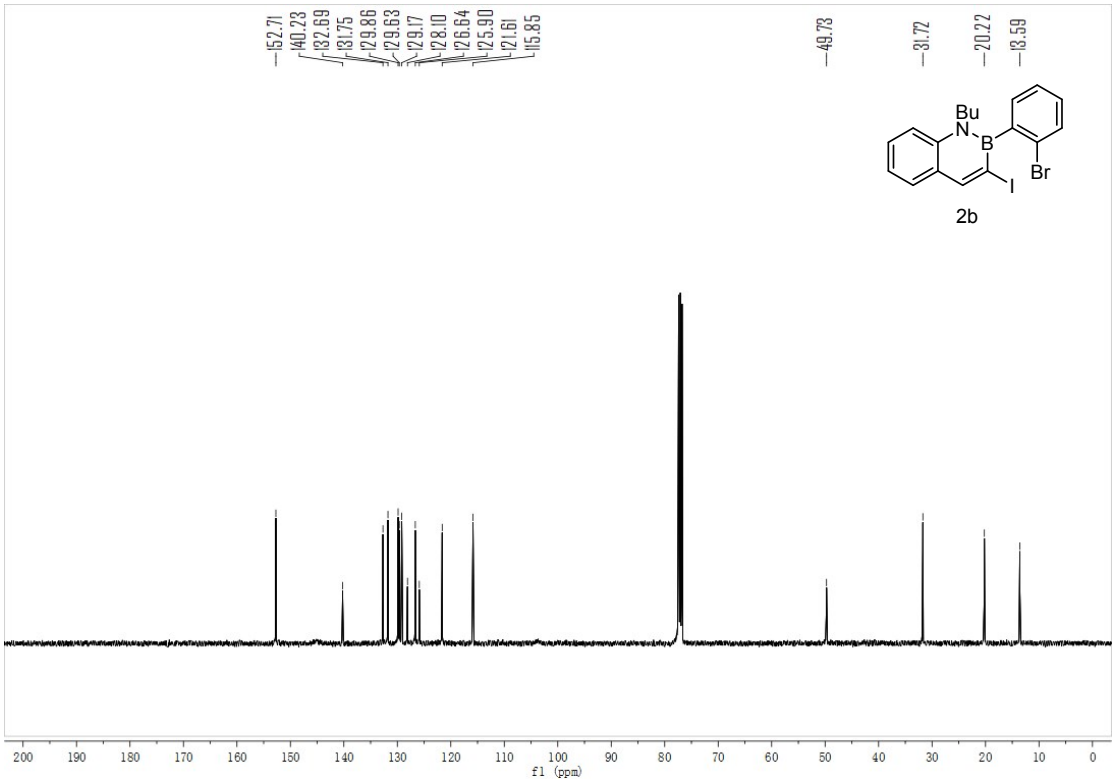
2.08
2.08
3.05
f1 (ppm)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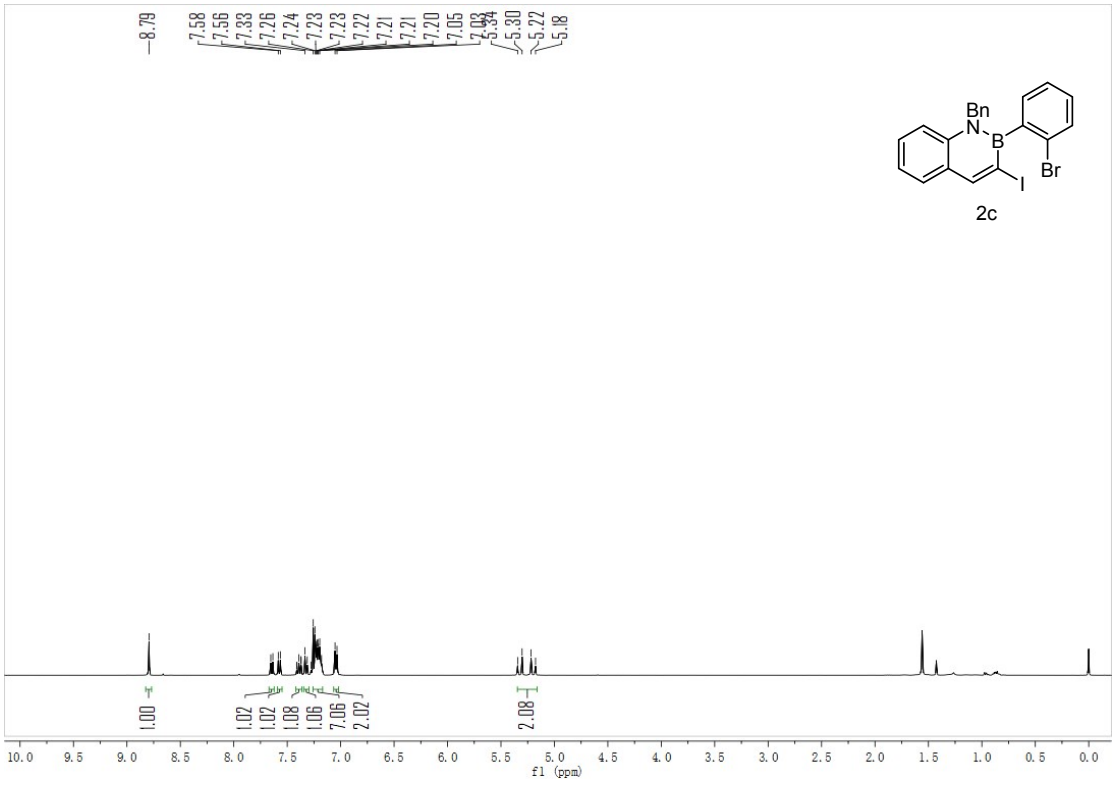
Bu
N
B
Br
I
2b
f1 (ppm)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7.20
7.05
5.30
5.22
5.18
Bn
N
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Br
I
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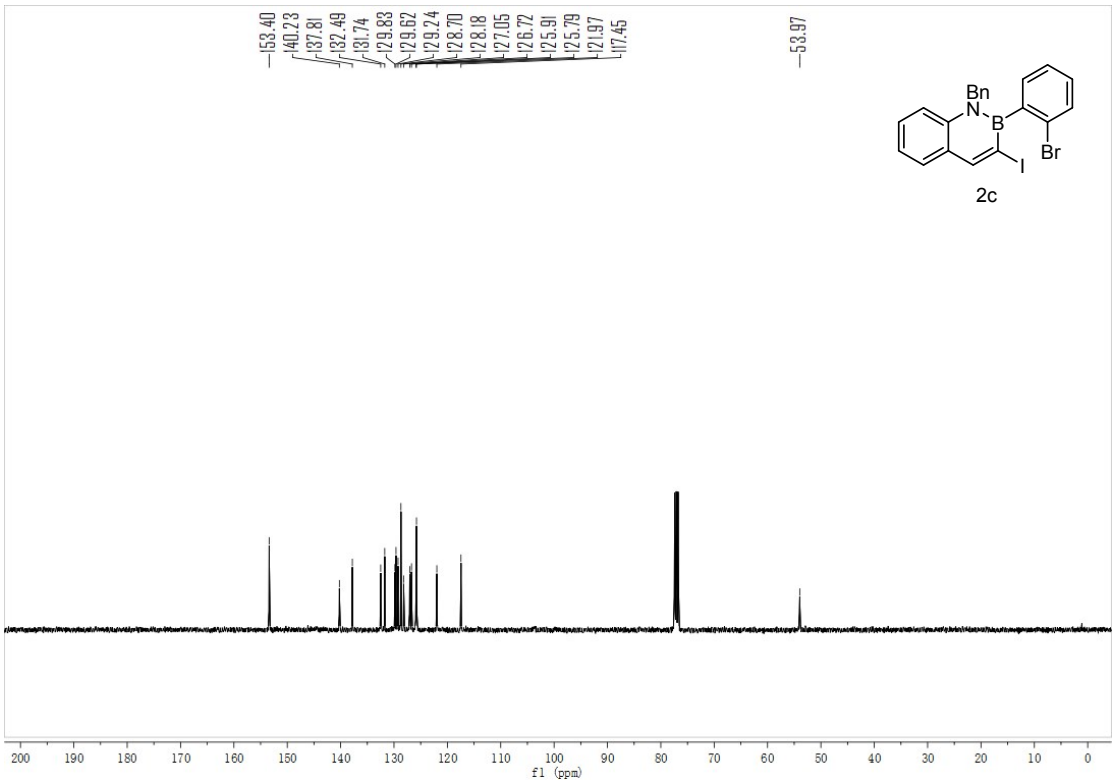
2.02
2.08
f1 (ppm)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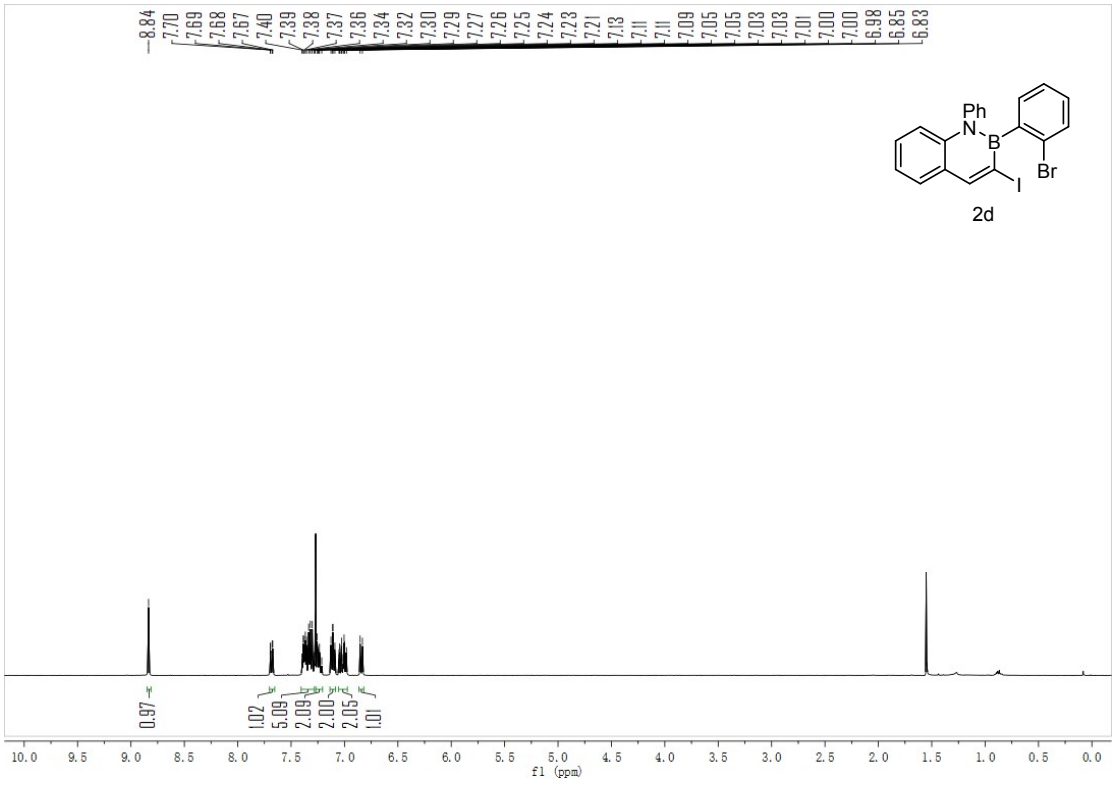
2c
f1 (ppm)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7.11
7.09
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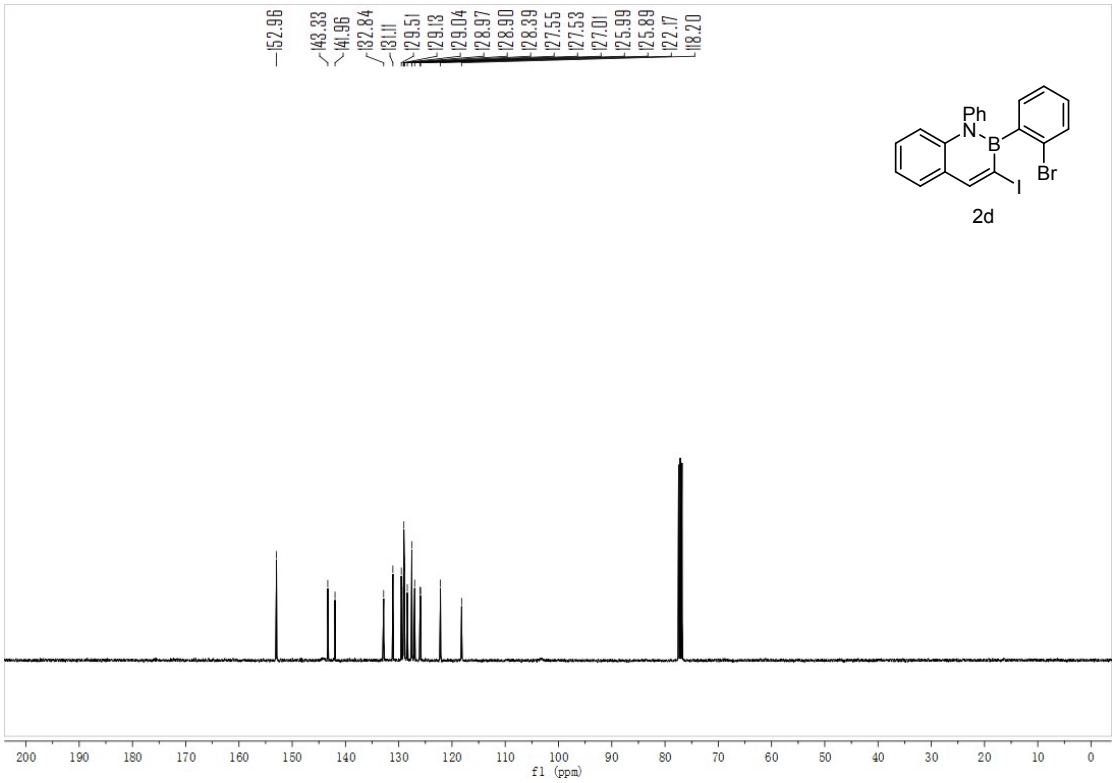
f1 (ppm)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Ph
N
B
Br
I
2d
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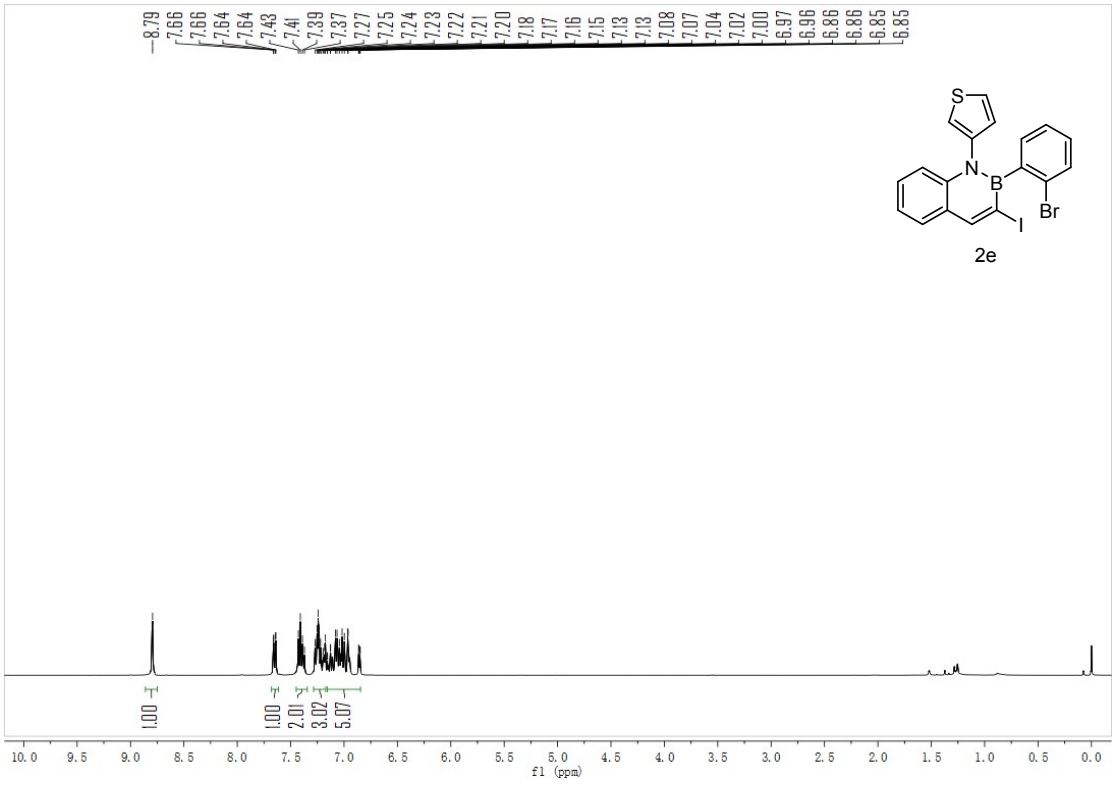
f1 (ppm)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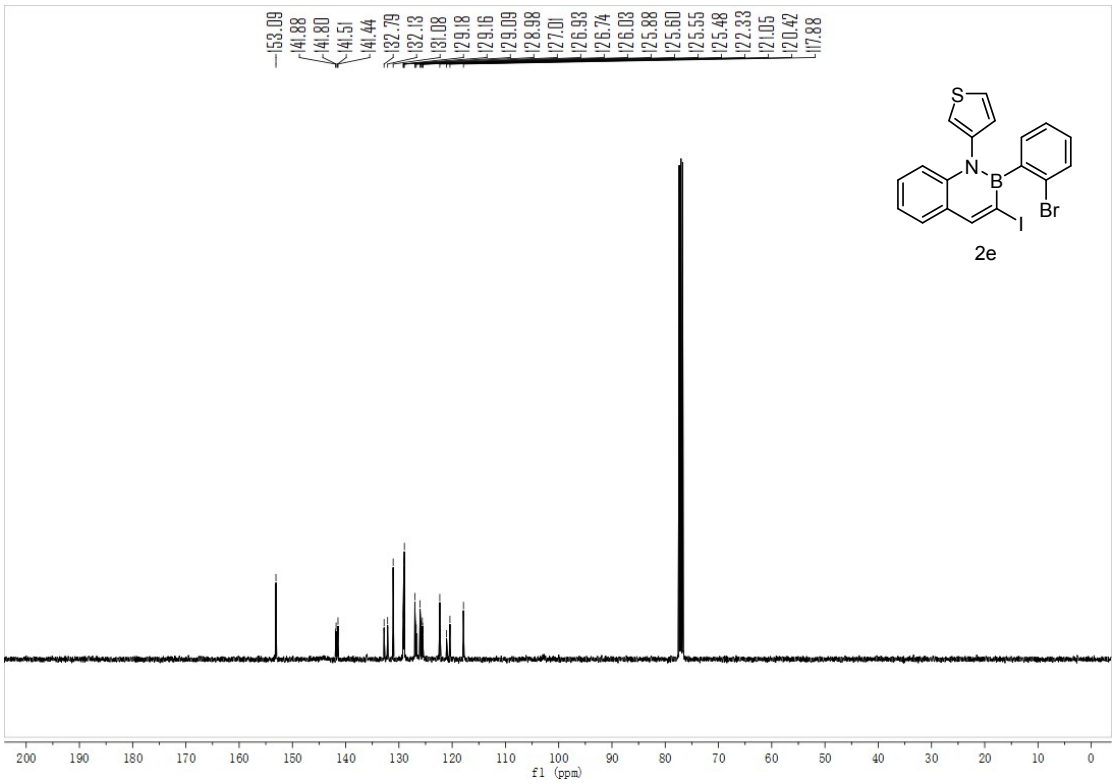
7.17
7.16
7.15
7.13
7.13
7.08
7.07
7.04
7.02
7.00
6.97
6.96
6.86
6.86
6.85
6.85
S
N
B
Br
I
2e
1.00
1.00
2.01
3.02
5.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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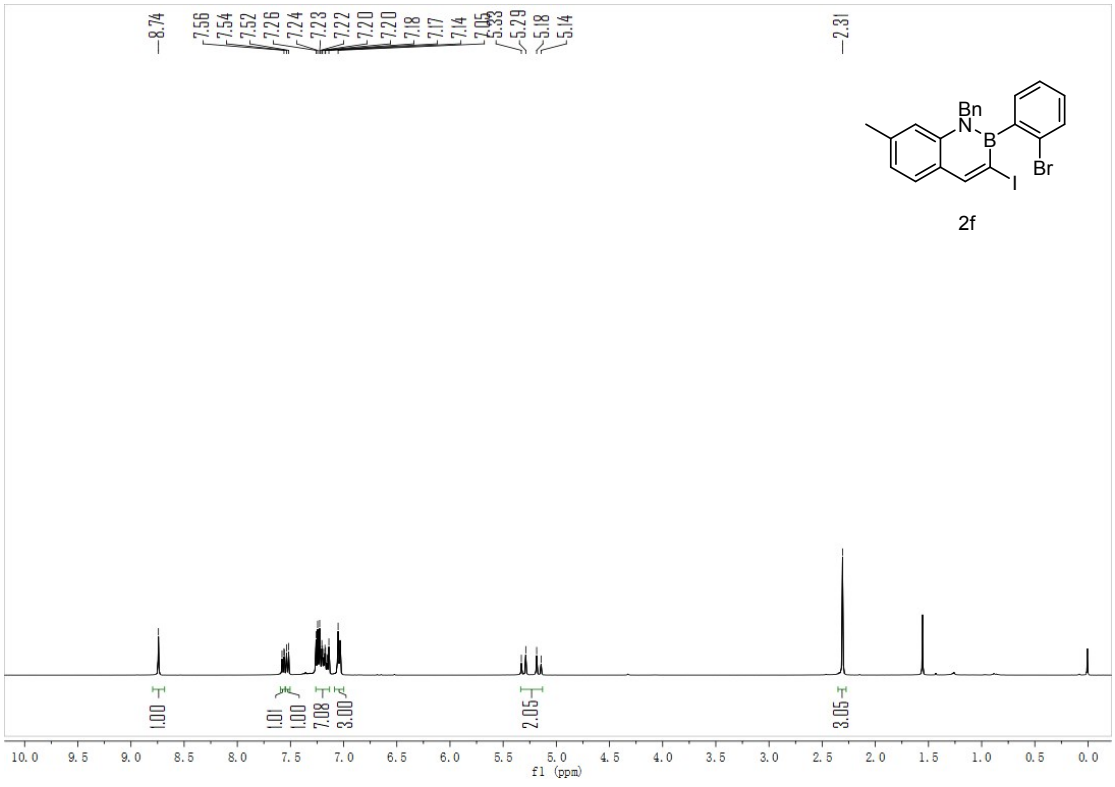
126.03
125.88
125.60
125.55
125.48
122.33
121.05
120.42
117.88
S
N
B
Br
I
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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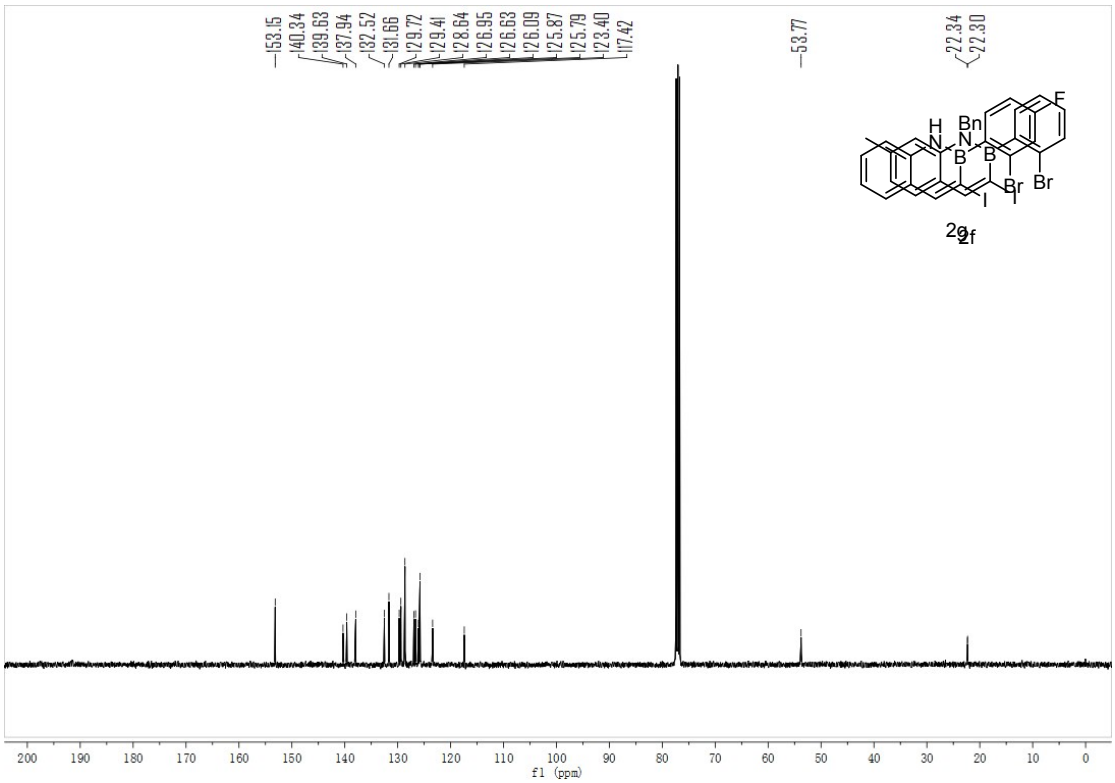
7.54
7.52
7.26
7.24
7.23
7.22
7.20
7.20
7.18
7.17
7.14
7.05
5.33
5.29
5.18
5.14
2.31
Bn
N
B
Br
I
2f
1.00
1.01
1.00
7.08
3.00
2.05
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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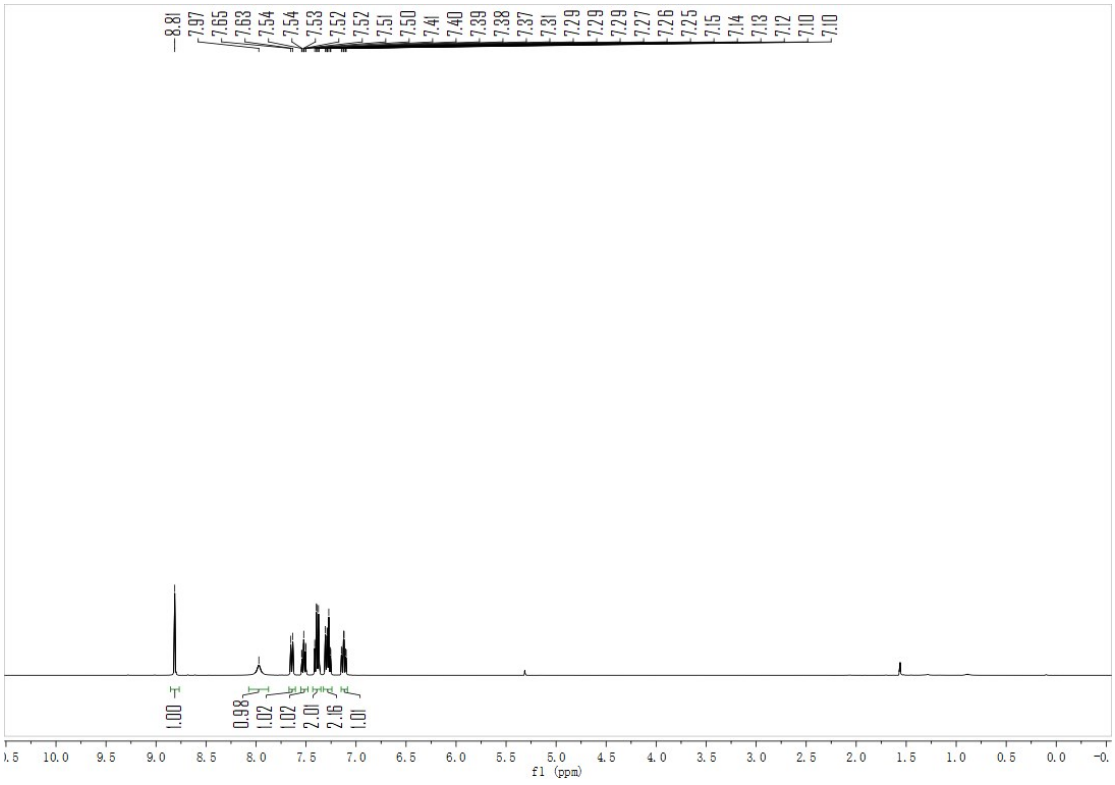
140.34
139.63
137.94
132.52
131.66
129.72
129.41
128.64
126.95
126.63
126.09
125.87
125.79
123.40
117.42
53.77
22.34
22.30
H
N
Bn
N
B
B
Br
Br
I
F
2f
f1 (ppm)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7.63
7.54
7.54
7.53
7.52
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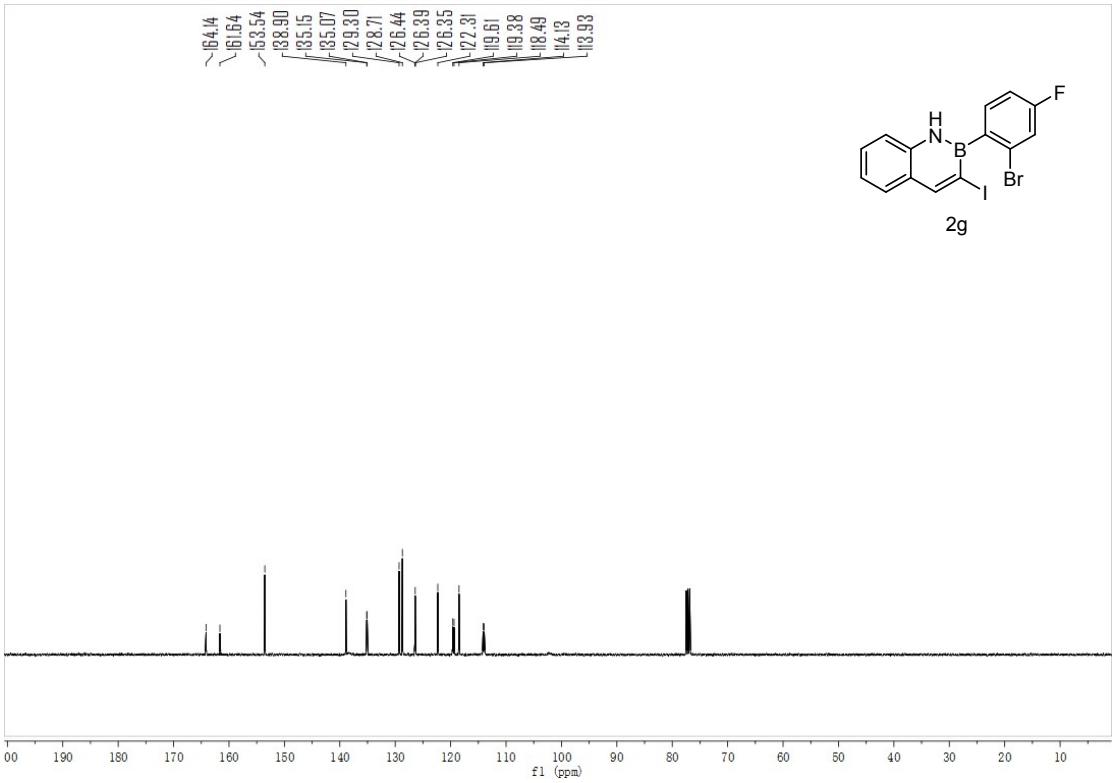
7.51
7.50
7.41
7.40
7.39
7.38
7.37
7.31
7.29
7.29
7.29
7.27
7.26
7.25
7.15
7.14
7.13
7.12
7.10
7.10
1.00
0.98
1.02
1.02
2.01
2.16
1.01
f1 (ppm)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135.07
129.30
128.71
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126.39
126.35
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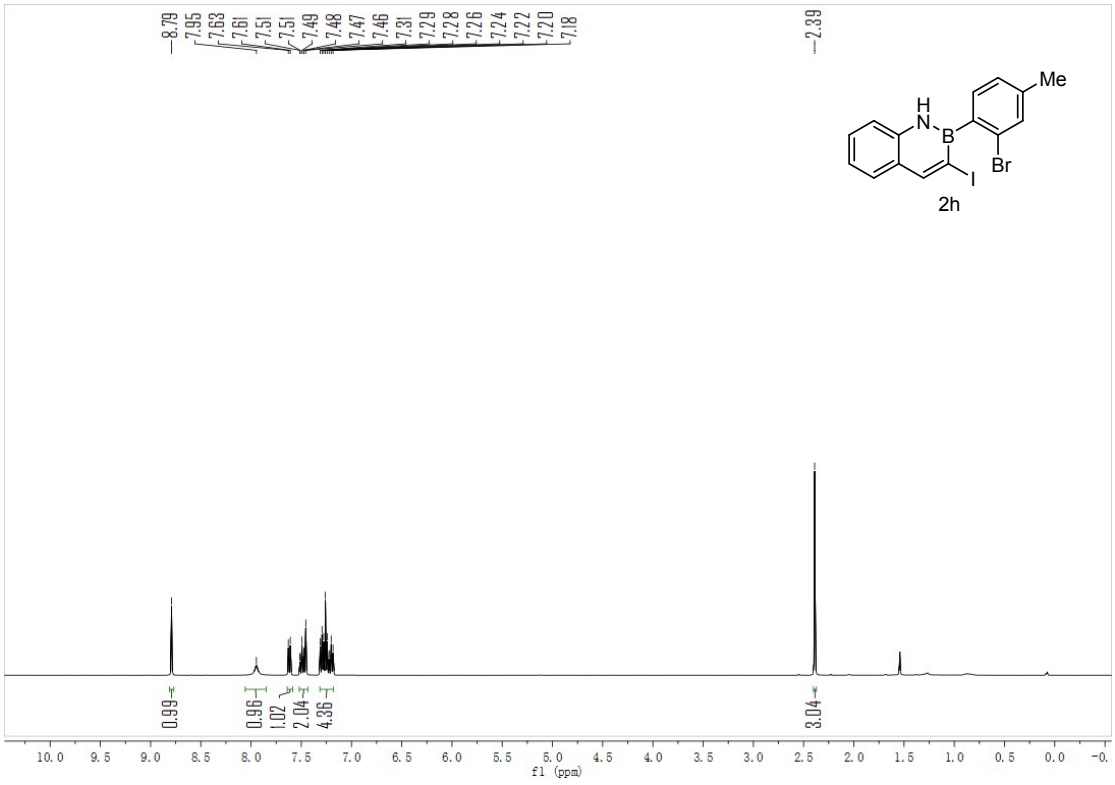
119.38
118.49
114.13
113.93
H
N
B
F
Br
I
2g
f1 (ppm)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7.95
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7.51
7.49
7.48
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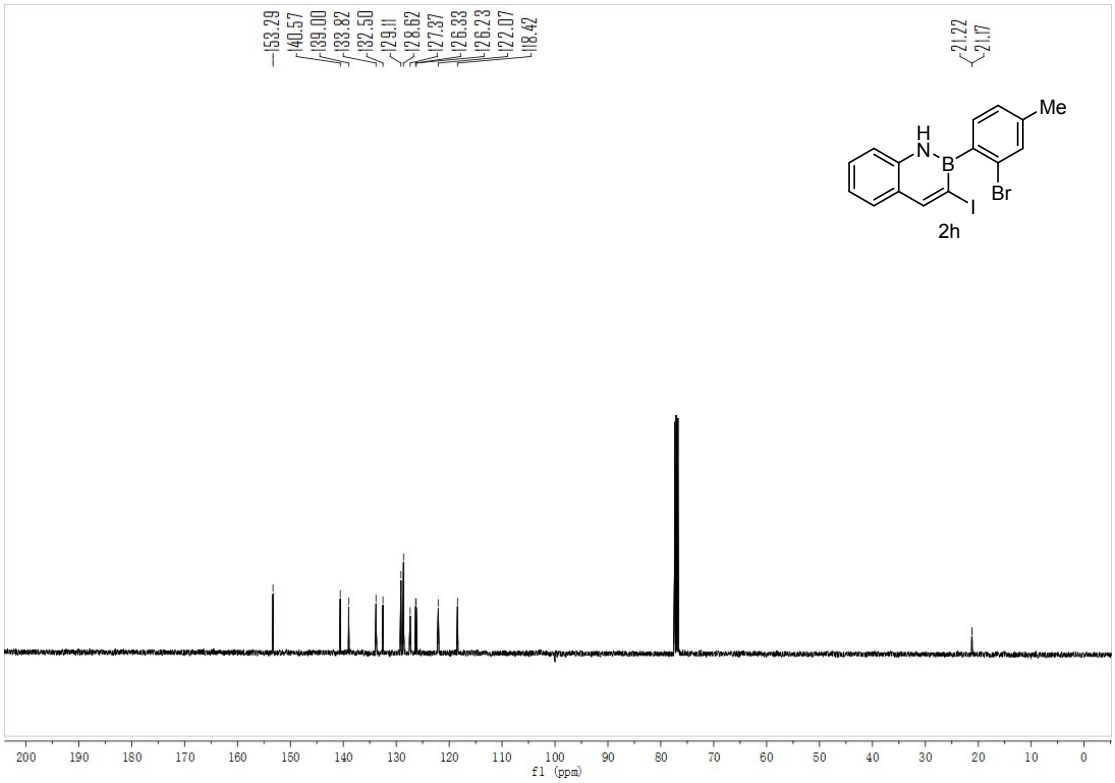
7.46
7.31
7.29
7.28
7.26
7.24
7.22
7.20
7.18
2.39
H
N
B
Me
Br
I
2h
0.99
0.96
1.02
2.04
4.36
3.04
f1 (ppm)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140.57
139.00
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127.37
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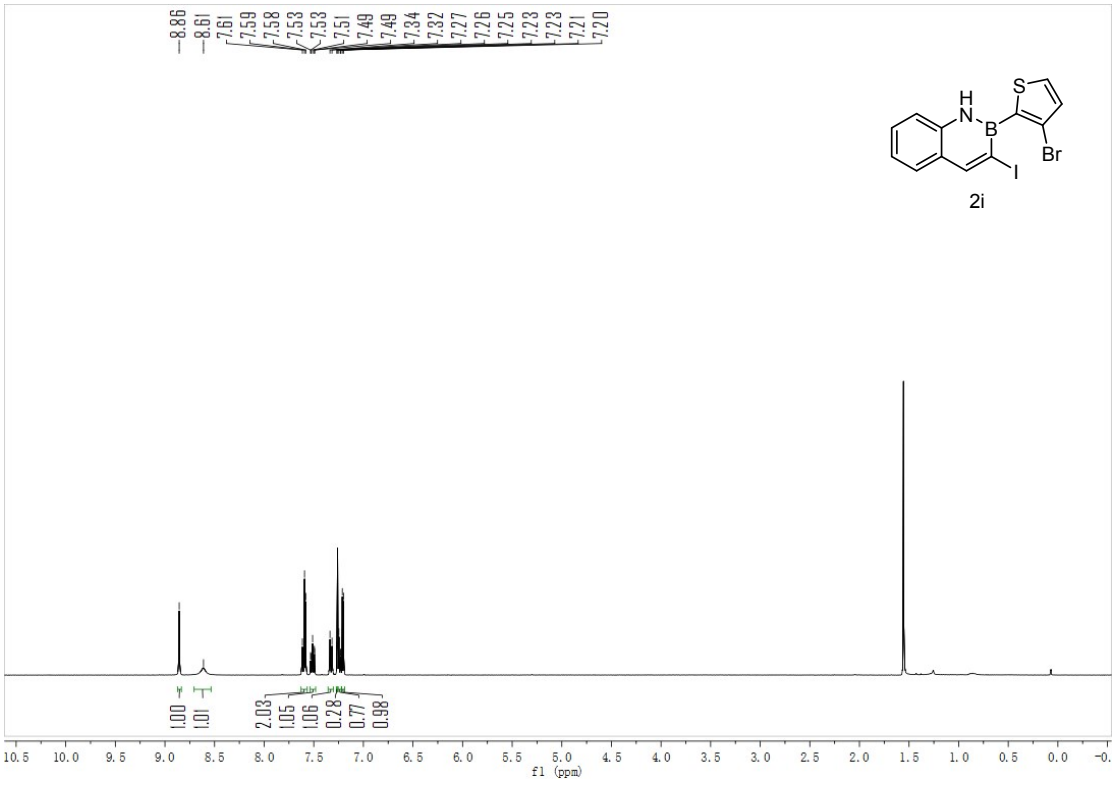
122.07
118.42
21.22
21.17
Me
H
N
B
Br
I
2h
f1 (ppm)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8.61
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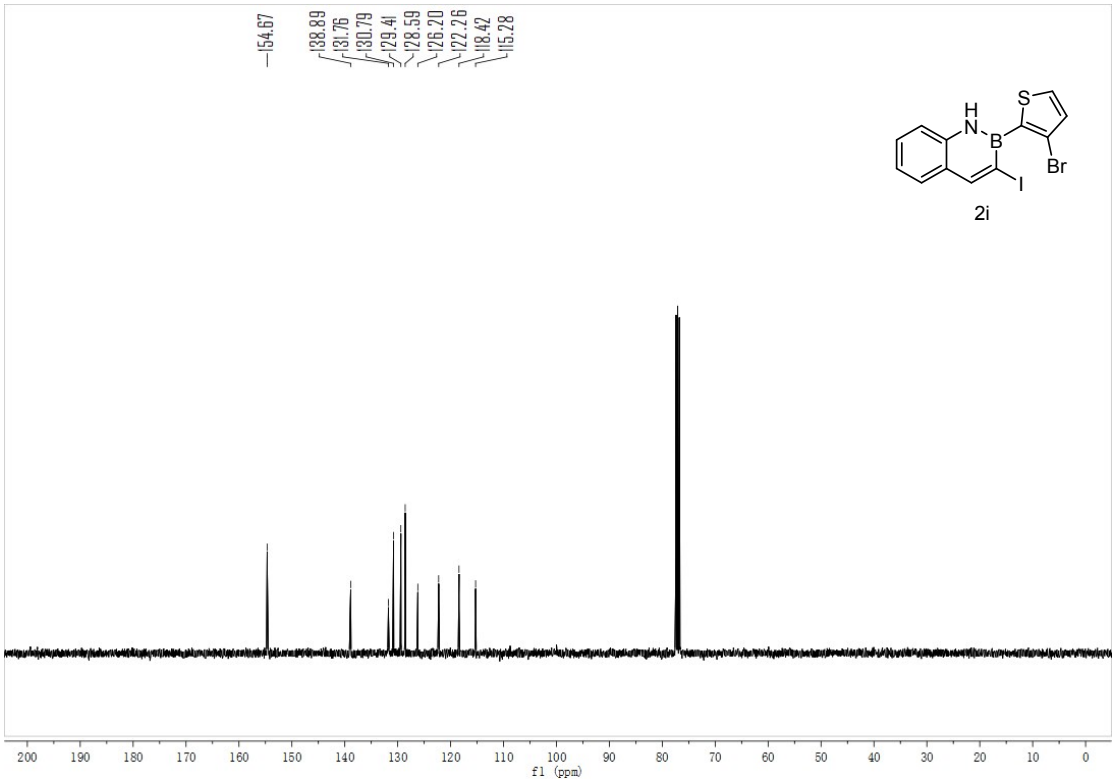
7.53
7.51
7.49
7.49
7.34
7.32
7.27
7.26
7.25
7.23
7.23
7.21
7.20
S
H
N
B
Br
I
2i
1.00
1.01
2.03
1.05
1.06
0.28
0.77
0.98
f1 (ppm)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130.79
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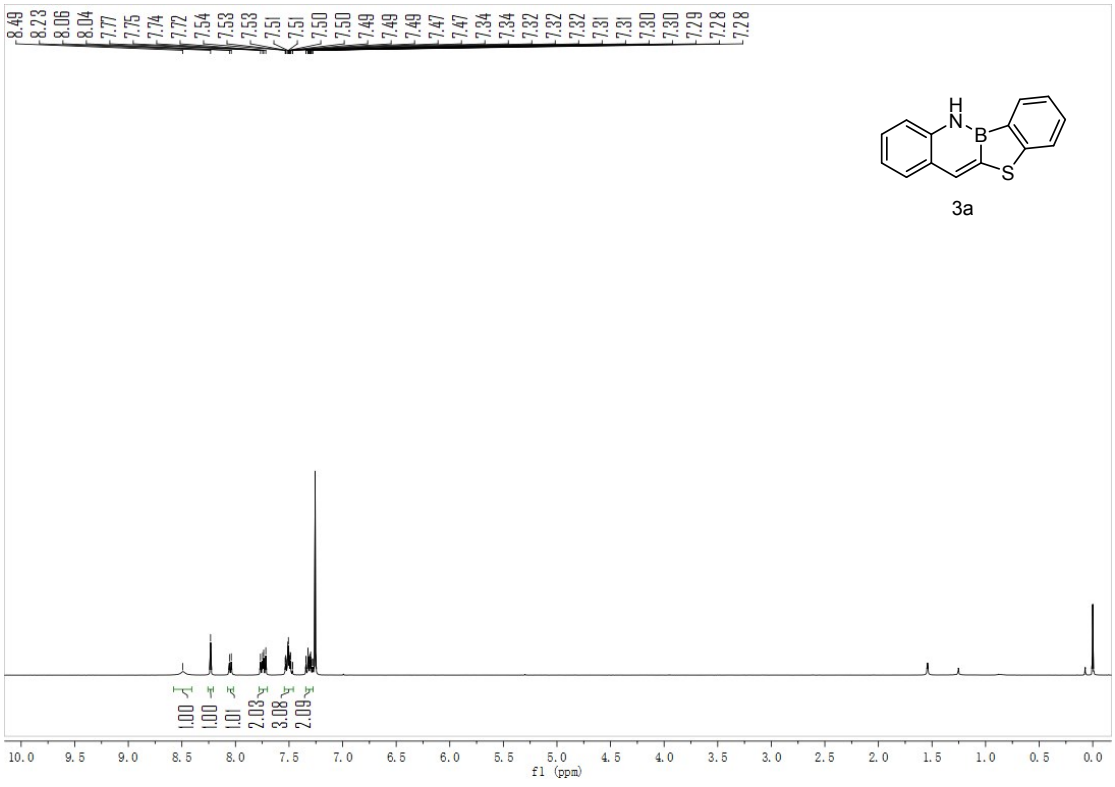
126.20
122.26
118.42
115.28
H
N
B
S
Br
I
2i
f1 (ppm)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8.23
8.06
8.04
7.77
7.75
7.74
7.72
7.54
7.53
7.53
7.51
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7.50
7.50
7.49
7.49
7.49
7.47
7.47
7.34
7.34
7.32
7.32
7.31
7.31
7.30
7.30
7.29
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N
B
S
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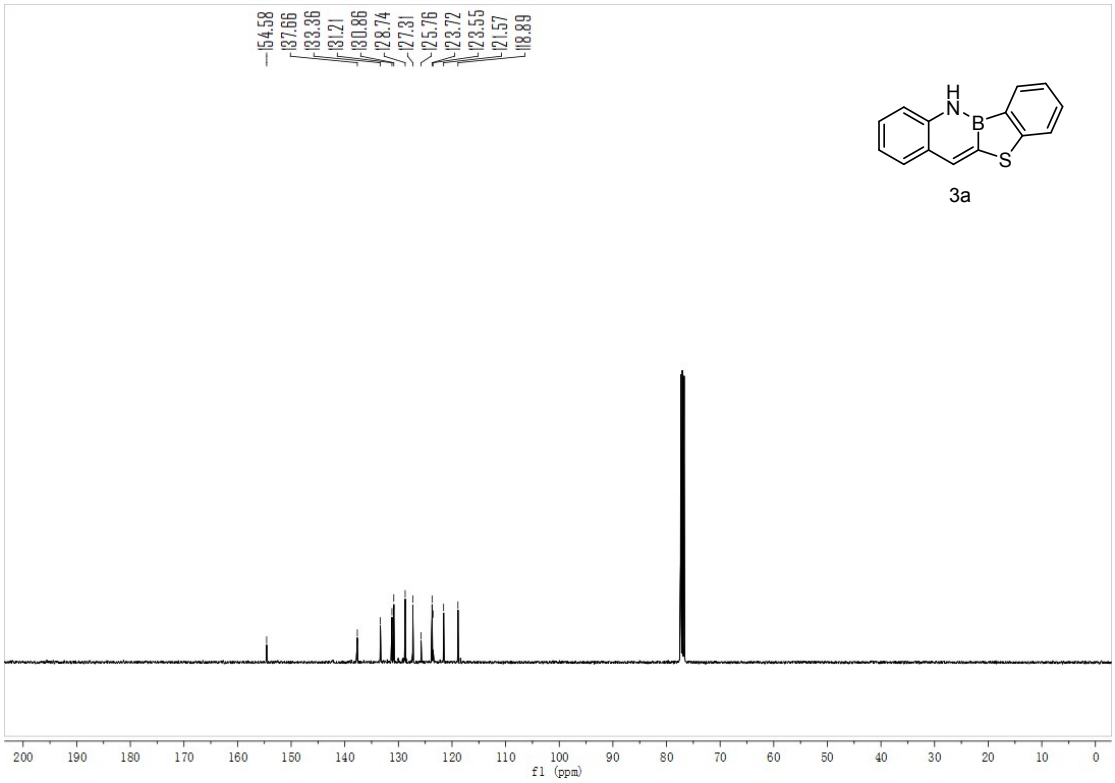
1.01
2.03
3.08
2.09
f1 (ppm)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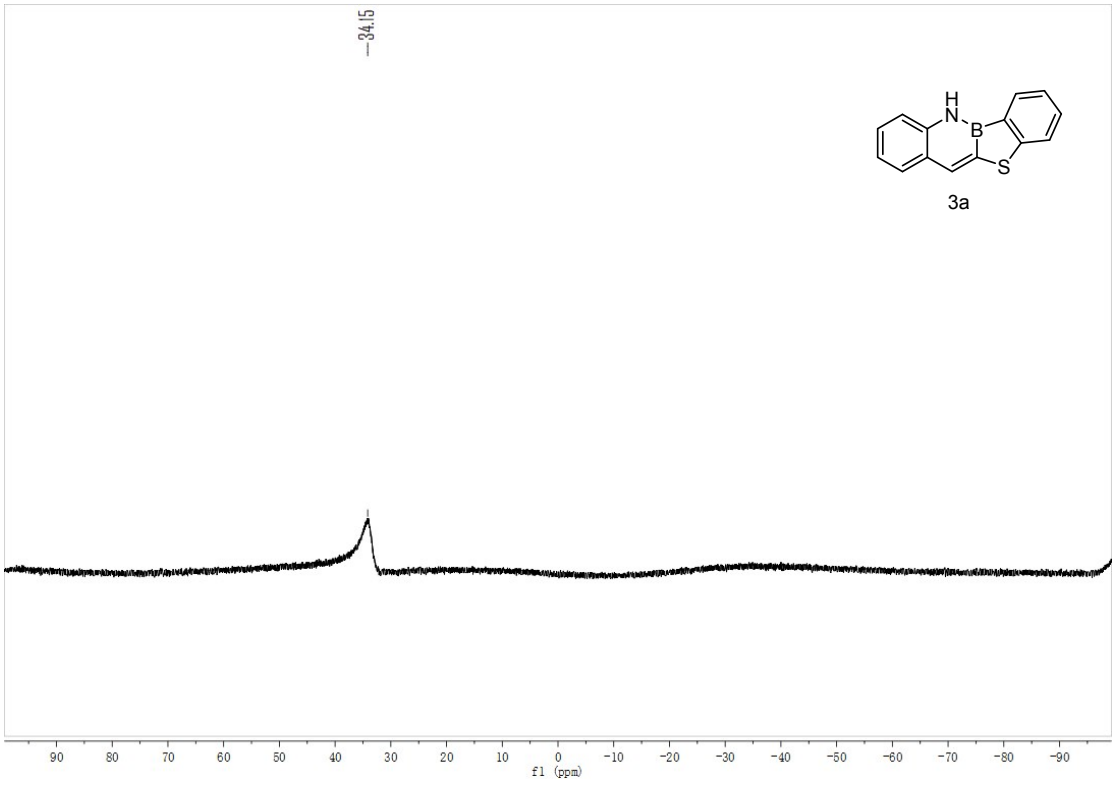
137.66
133.36
131.21
130.86
128.74
127.31
125.76
123.72
123.55
121.57
118.89
H
N
B
S
3a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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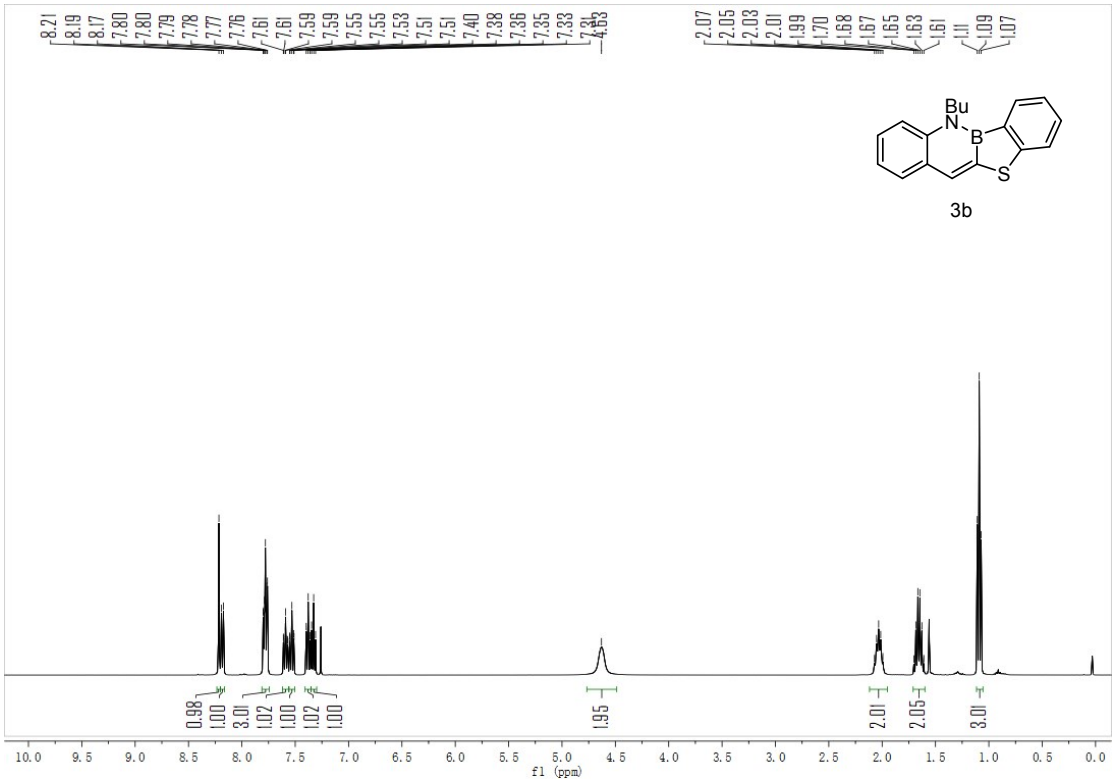
H
N
B
S
3a
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


8.21
8.19
8.17
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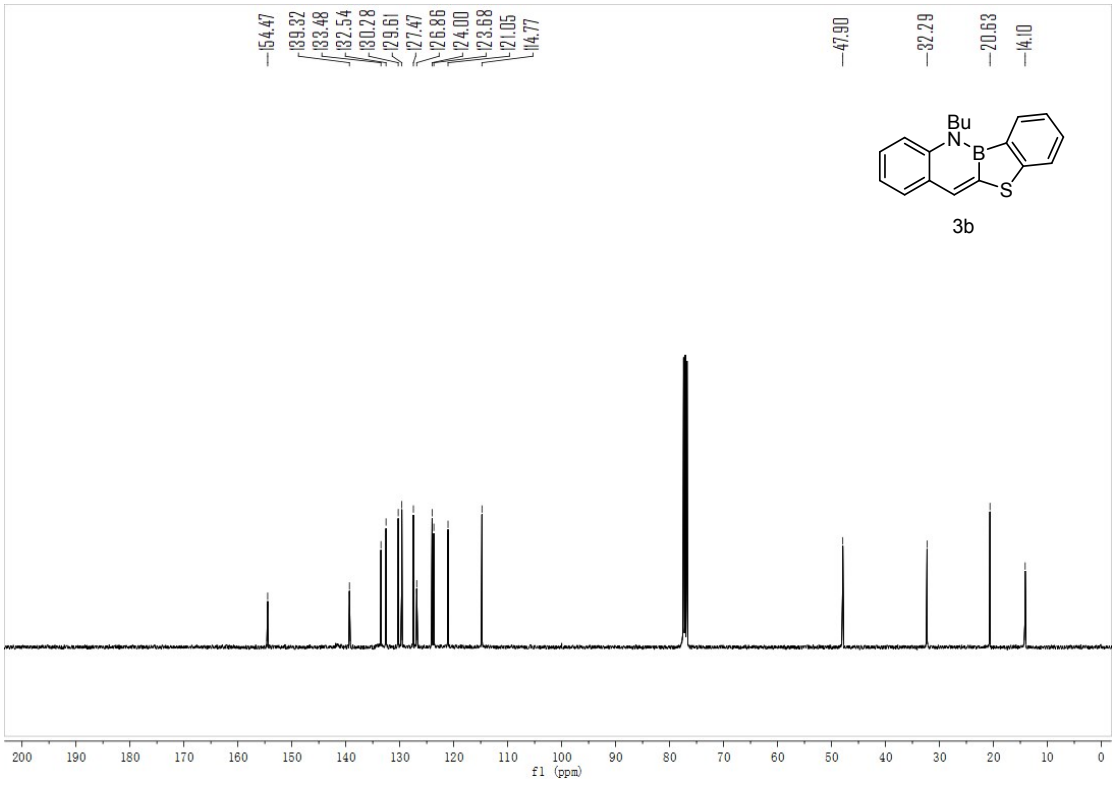
7.80
7.79
7.78
7.77
7.76
7.61
7.61
7.59
7.59
7.55
7.55
7.53
7.51
7.51
7.40
7.38
7.38
7.35
7.33
7.31
4.63
2.07
2.05
2.03
2.01
1.99
1.70
1.68
1.67
1.65
1.63
1.61
1.11
1.09
1.07
Bu
N
B
S
3b
0.98
1.00
3.01
1.02
1.00
1.02
1.00
1.95
2.01
2.05
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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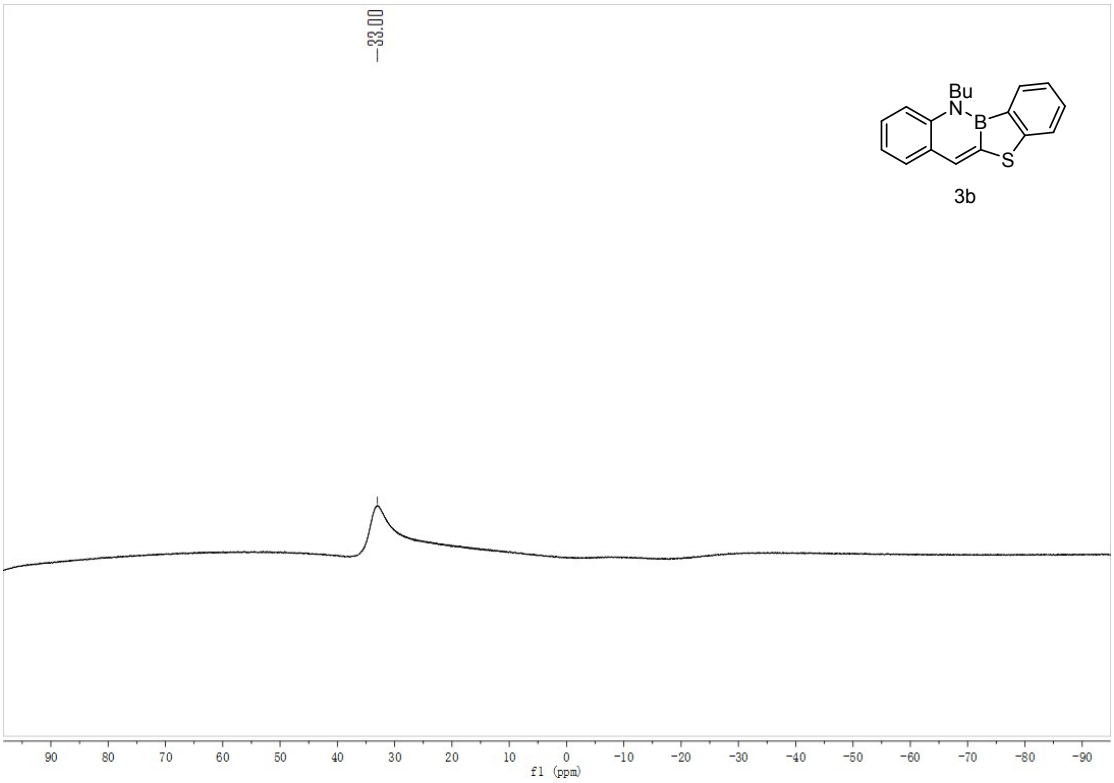
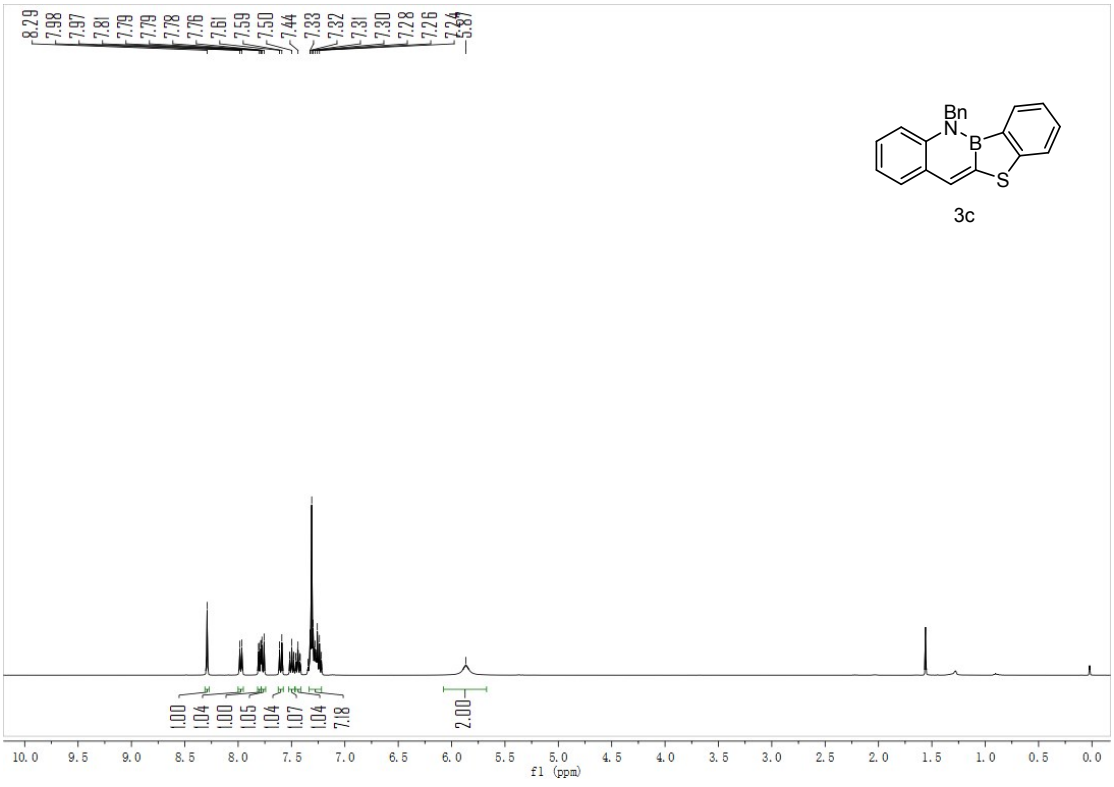
133.48
132.54
130.28
129.61
127.47
126.86
124.00
123.68
121.05
114.77
47.90
32.29
20.63
14.10
Bu
N
B
S
3b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


33.00
Bu
N
B
S
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

3b


8.29
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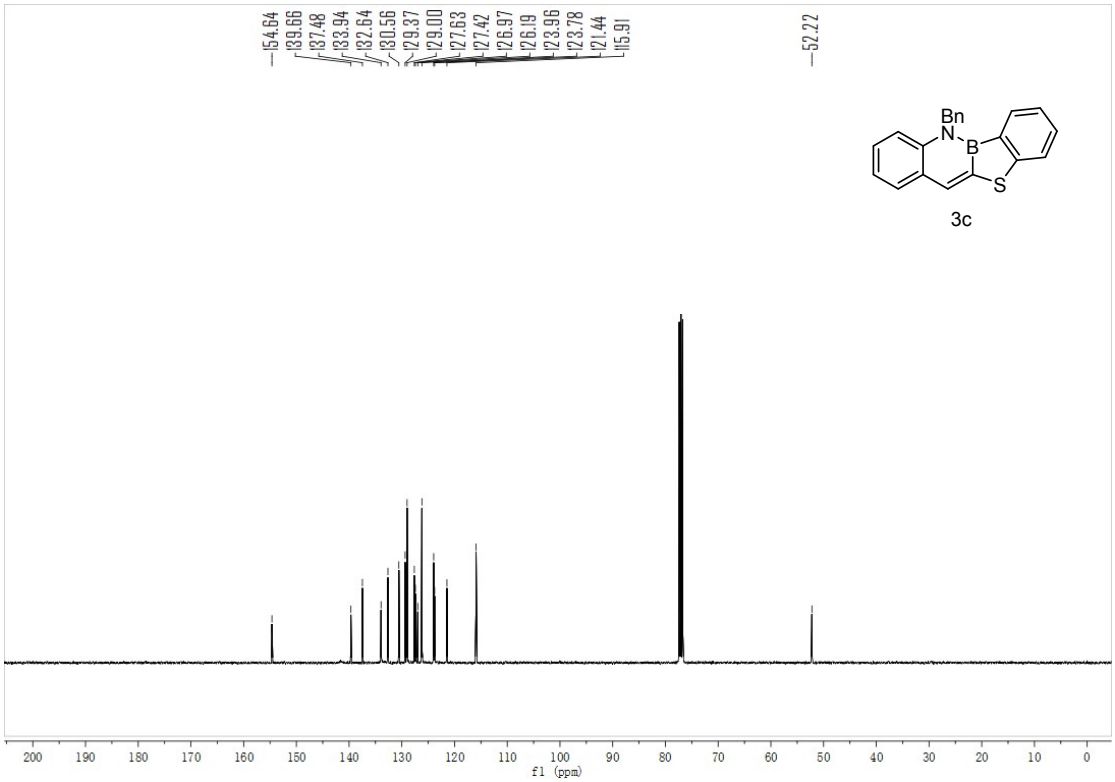
7.81
7.79
7.79
7.78
7.76
7.61
7.59
7.50
7.44
7.33
7.32
7.31
7.30
7.28
7.26
7.24
5.87
Bn
N
B
S
1.00
1.04
1.00
1.05
1.04
1.07
1.04
7.18
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3c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132.64
130.56
129.37
129.00
127.63
127.42
126.97
126.19
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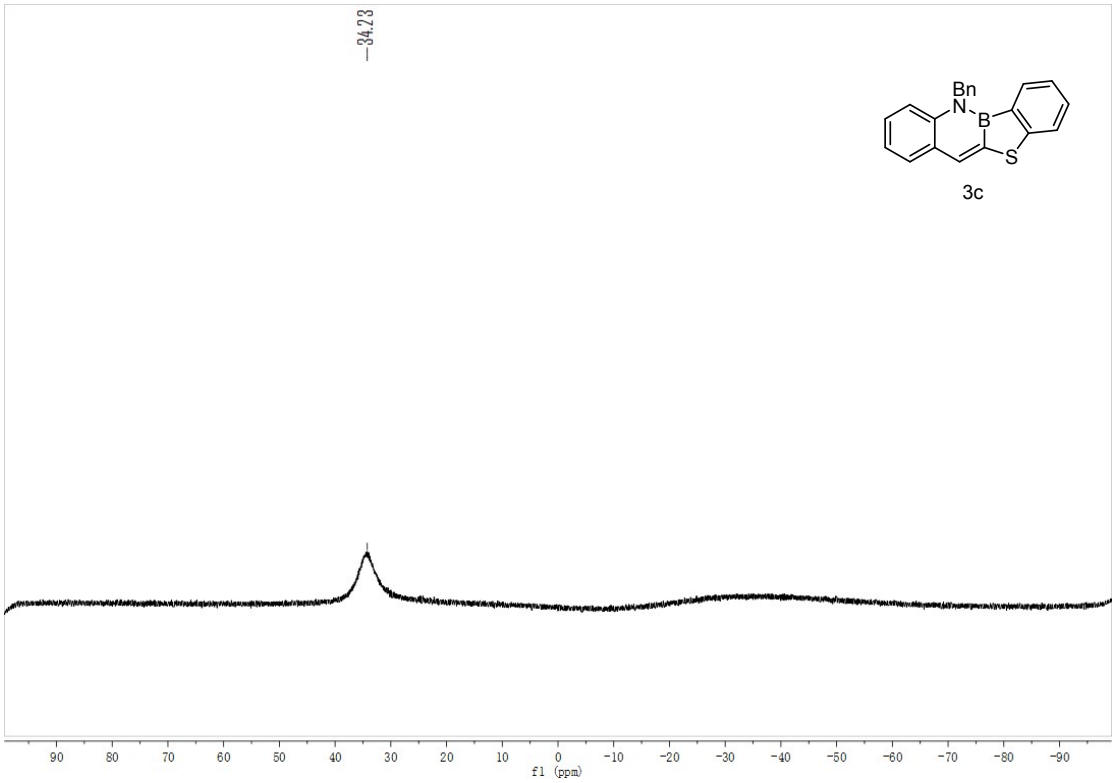
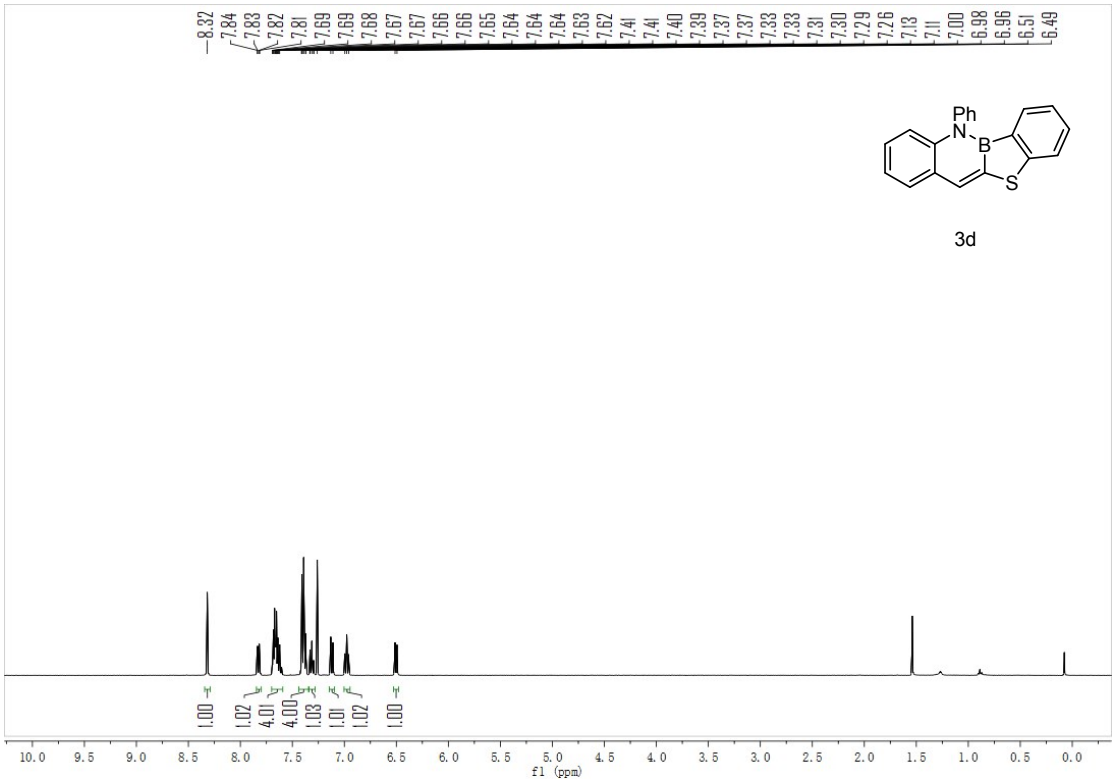
52.22
Bn
N
B
S
3c
f1 (ppm)


34.23
Bn
N
B
S
3c
f1 (ppm)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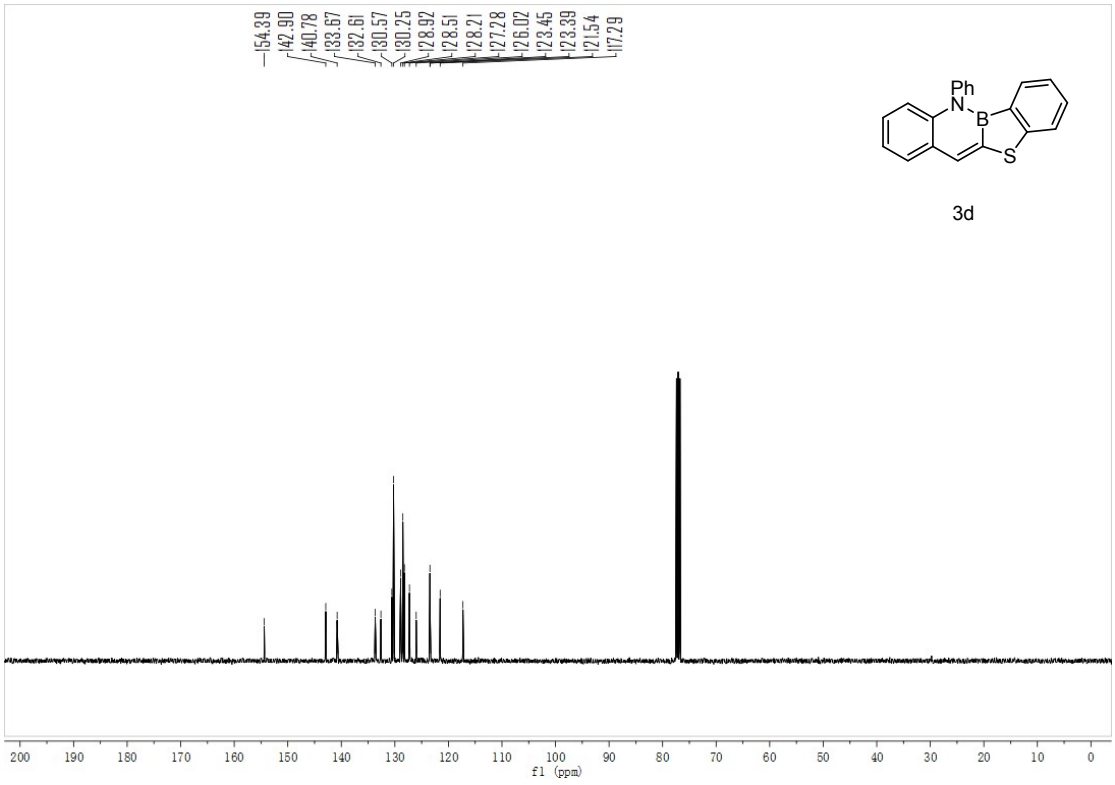
7.84
7.83
7.82
7.81
7.69
7.69
7.68
7.67
7.67
7.66
7.66
7.65
7.64
7.64
7.64
7.63
7.62
7.41
7.41
7.40
7.39
7.37
7.37
7.33
7.33
7.31
7.30
7.29
7.26
7.13
7.11
7.00
6.98
6.96
6.51
6.49
Ph
N
B
S
3d
1.00
1.02
4.01
4.00
1.03
1.01
1.02
1.00
f1 (ppm)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132.61
130.57
130.25
128.92
128.51
128.21
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126.02
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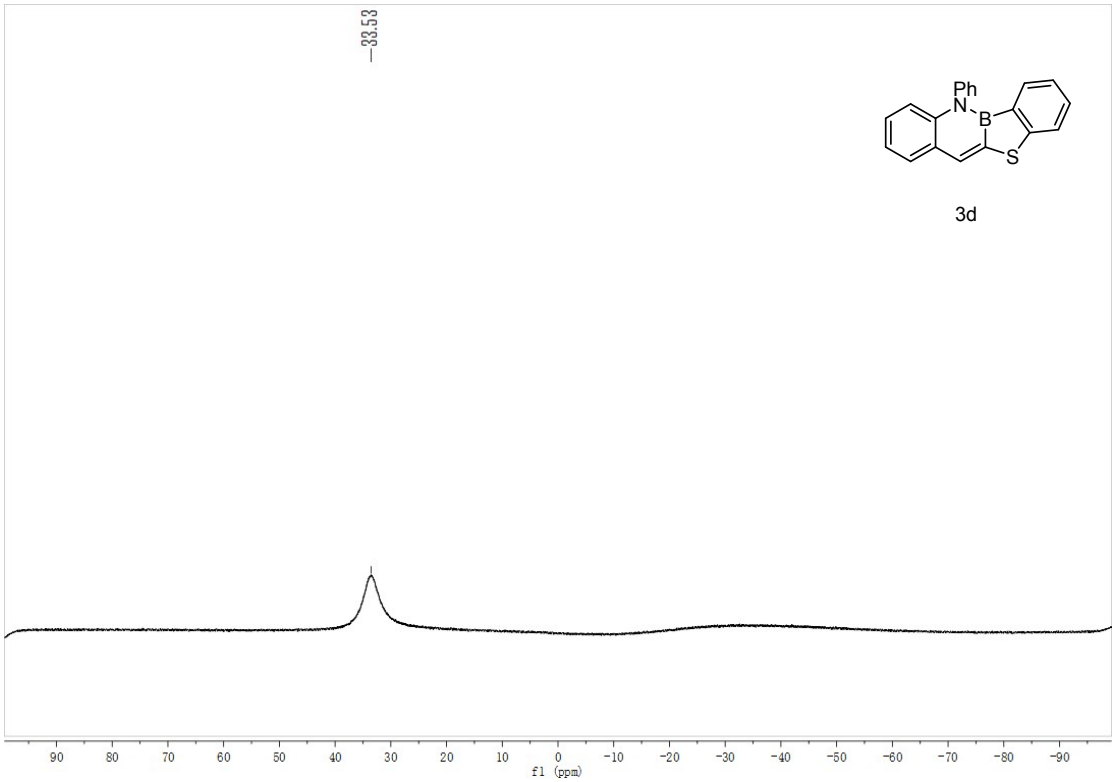
117.29
Ph
N
B
S
3d
f1 (ppm)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Ph
N
B
S
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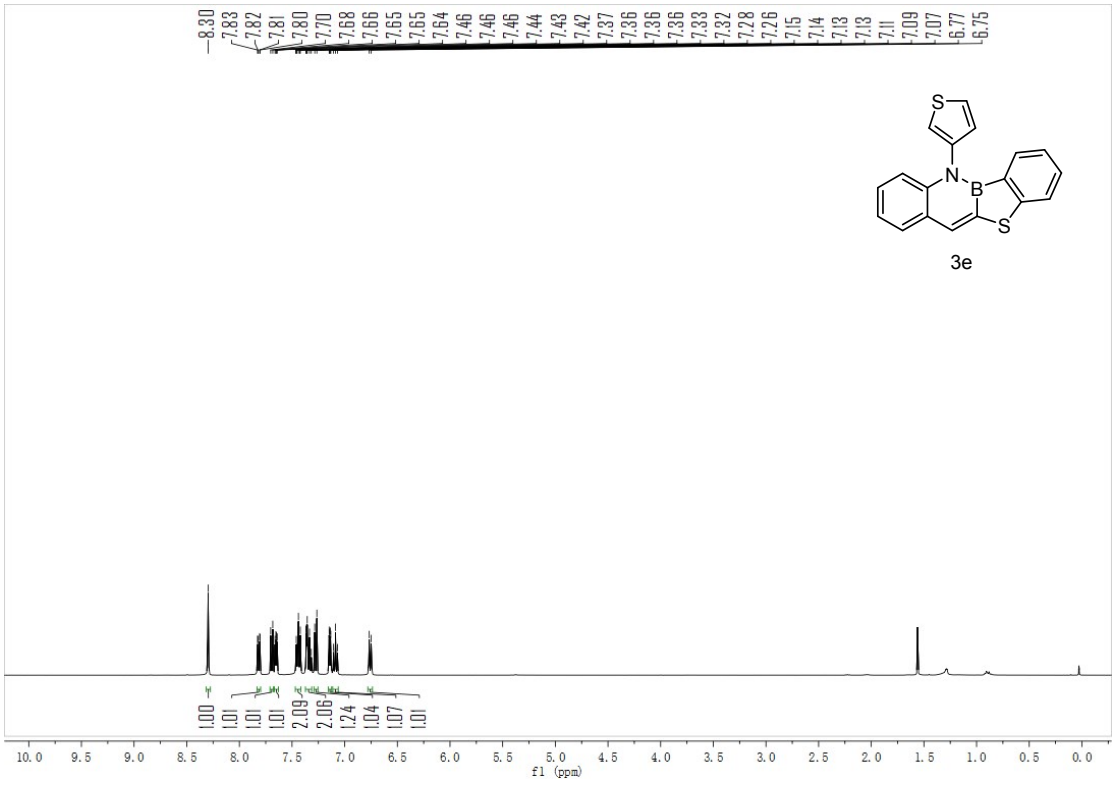
f1 (ppm)

3d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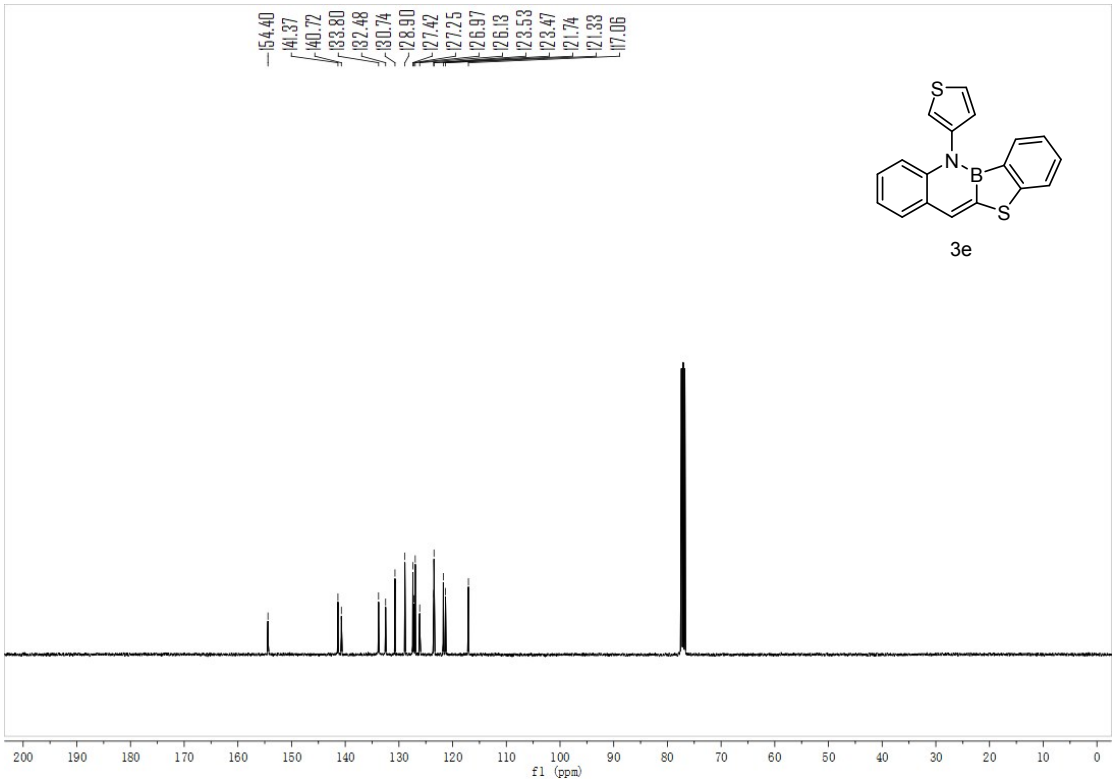
7.70
7.68
7.66
7.65
7.65
7.64
7.46
7.46
7.46
7.44
7.43
7.42
7.37
7.36
7.36
7.36
7.33
7.32
7.28
7.26
7.15
7.14
7.13
7.13
7.11
7.09
7.07
6.77
6.75
S
N
B
S
1.00
1.01
1.01
1.01
2.09
2.06
1.24
1.04
1.07
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3e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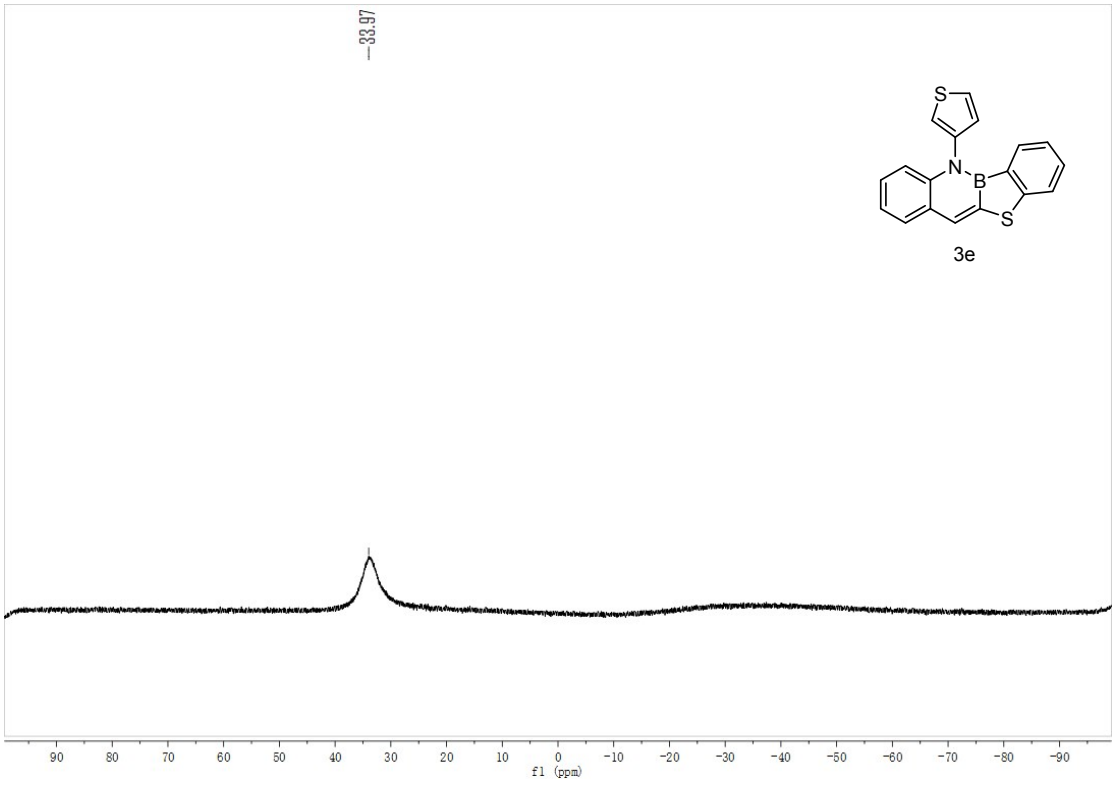
130.74
128.90
127.42
127.25
126.97
126.13
123.53
123.47
121.74
121.33
117.06
S
N
B
S
3e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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S
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B
S
3e
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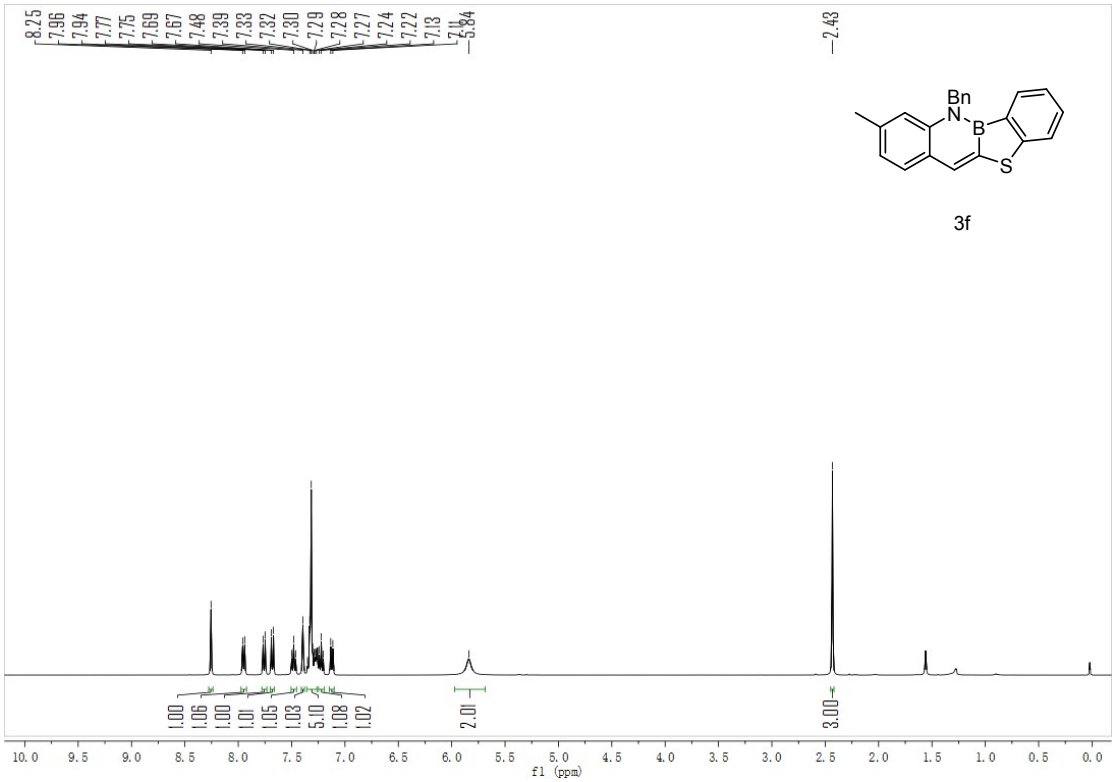
f1 (ppm)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7.69
7.67
7.48
7.39
7.33
7.32
7.30
7.29
7.28
7.27
7.24
7.22
7.13
7.10
5.84
2.43
Bn
N
B
S
1.00
1.06
1.00
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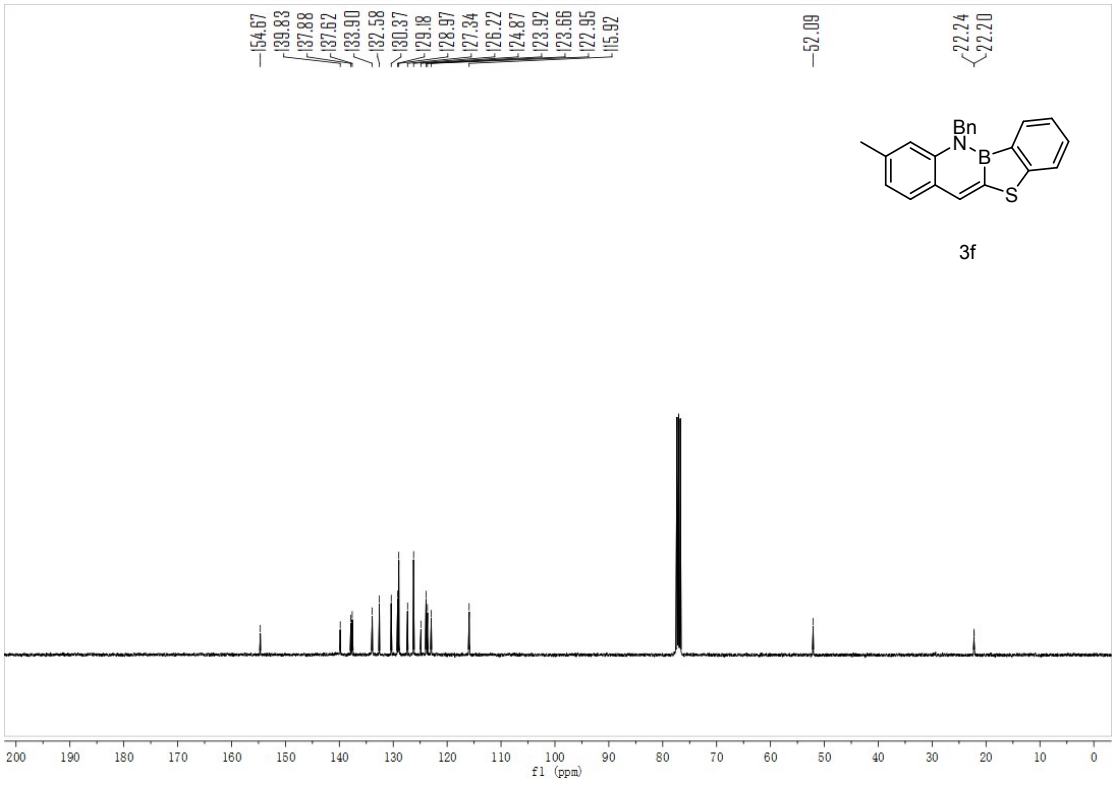
1.05
1.03
5.10
1.08
1.02
2.01
3.00
f1 (ppm)

3f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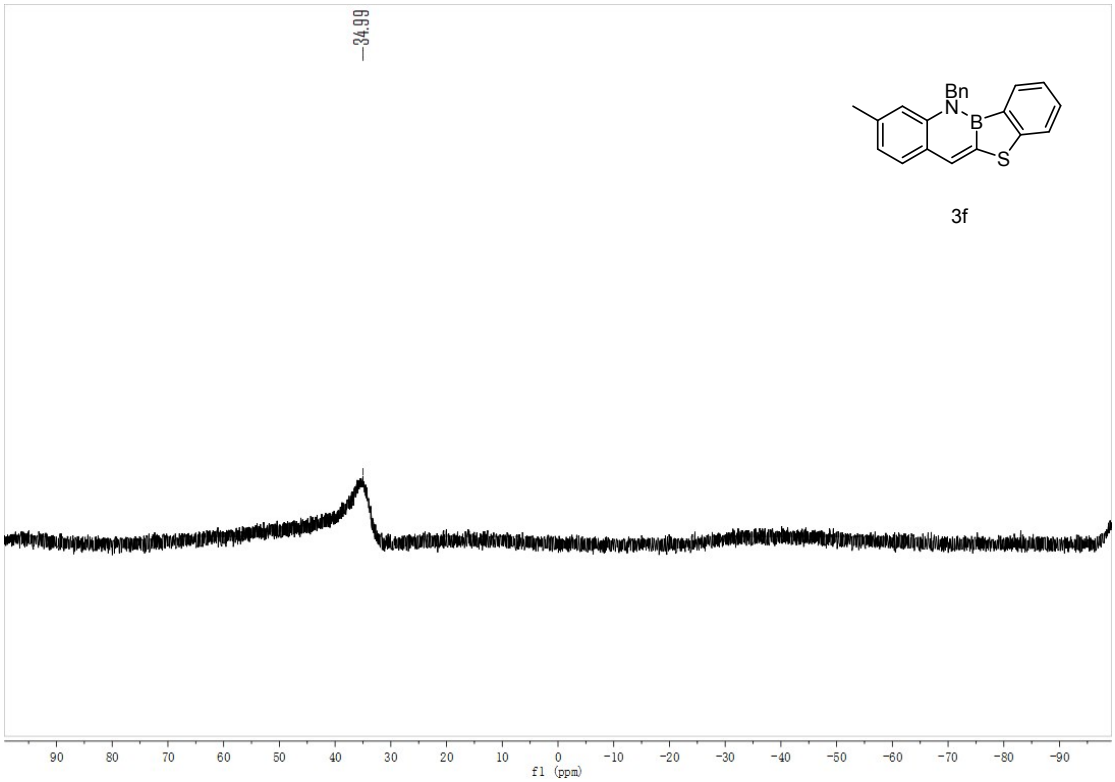
133.90
132.58
130.37
129.18
128.97
127.34
126.22
124.87
123.92
123.66
122.95
115.92
52.09
22.24
22.20
Bn
N
B
S
f1 (ppm)

3f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Bn
N
B
S
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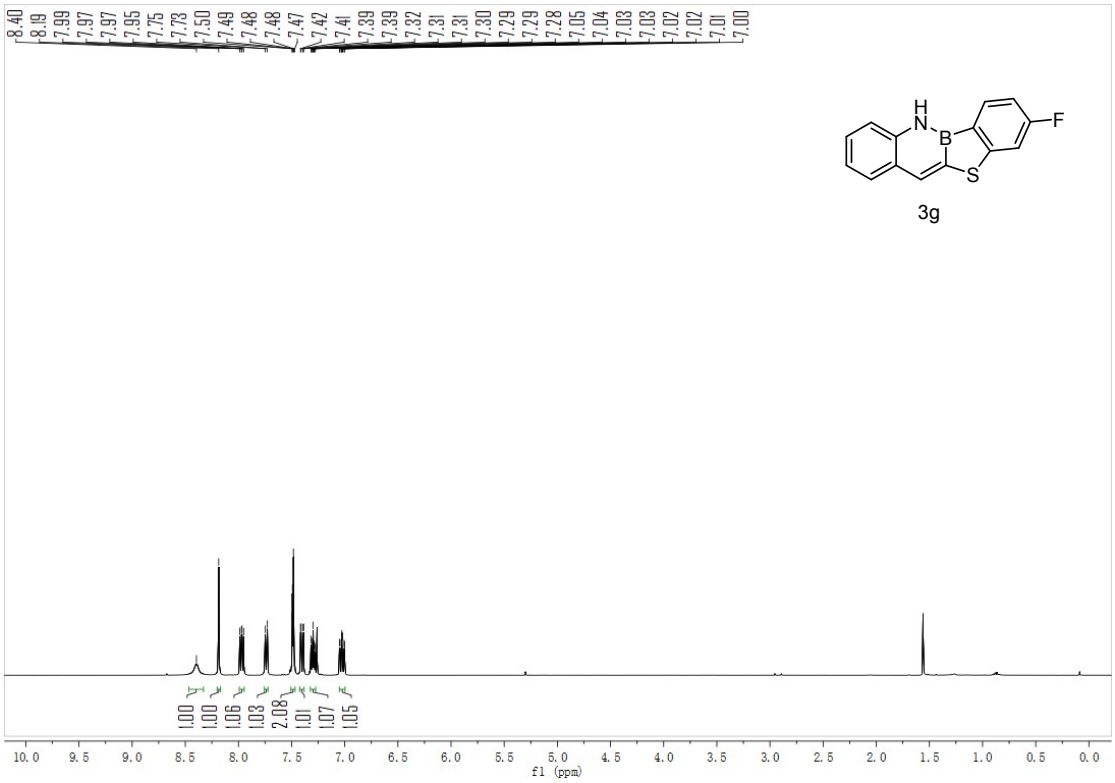
f1 (ppm)

3f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8.19
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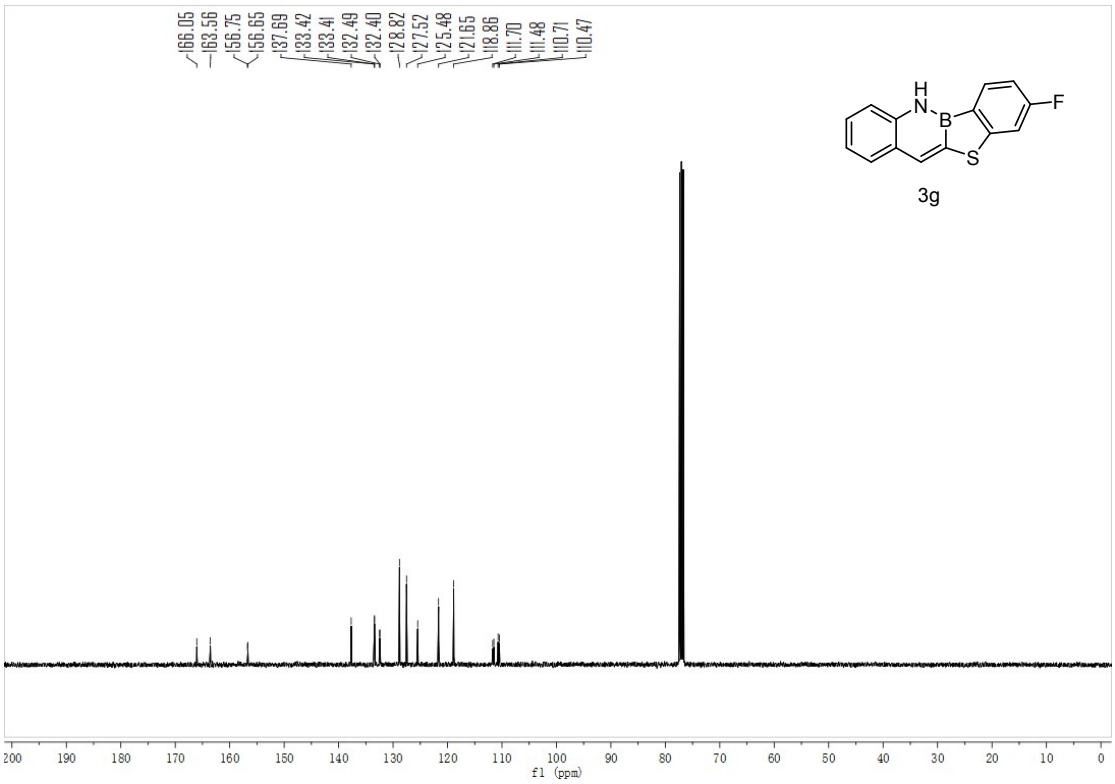
7.97
7.97
7.95
7.75
7.73
7.50
7.49
7.48
7.48
7.47
7.42
7.41
7.39
7.39
7.32
7.31
7.31
7.30
7.29
7.29
7.28
7.05
7.04
7.03
7.03
7.02
7.02
7.01
7.00
H
N
B
S
F
1.00
1.00
1.06
1.03
2.08
1.01
1.07
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

3g


166.05
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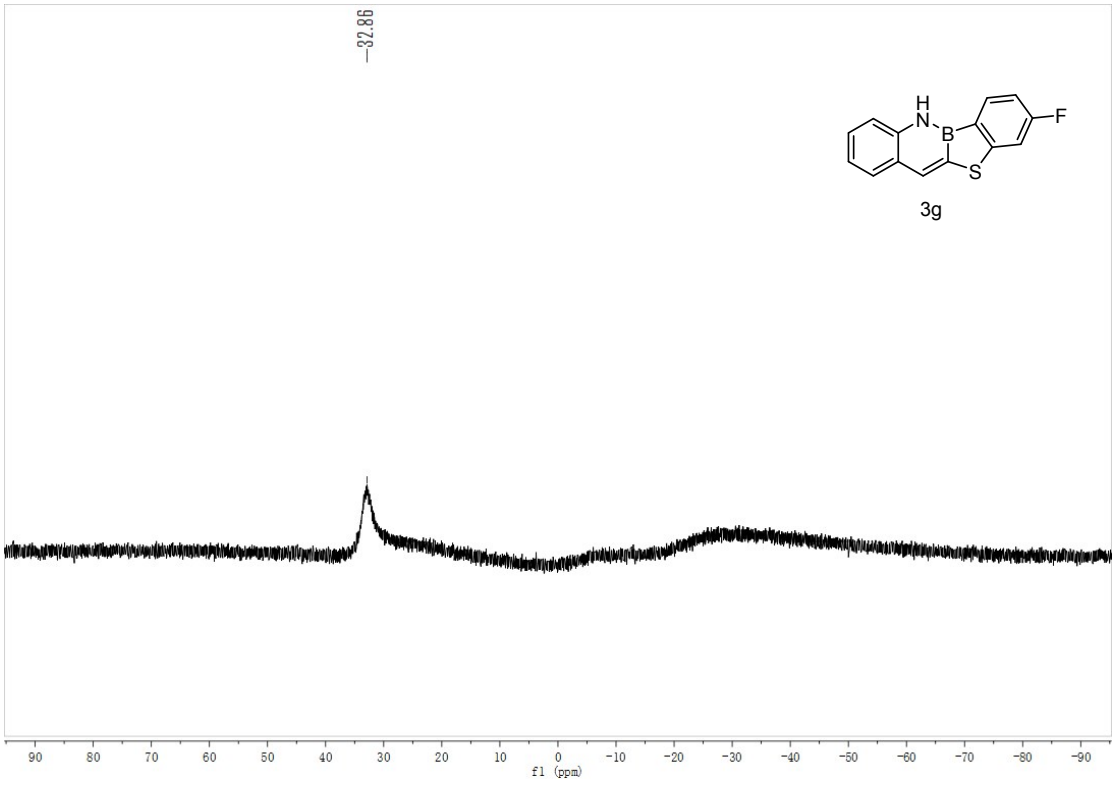
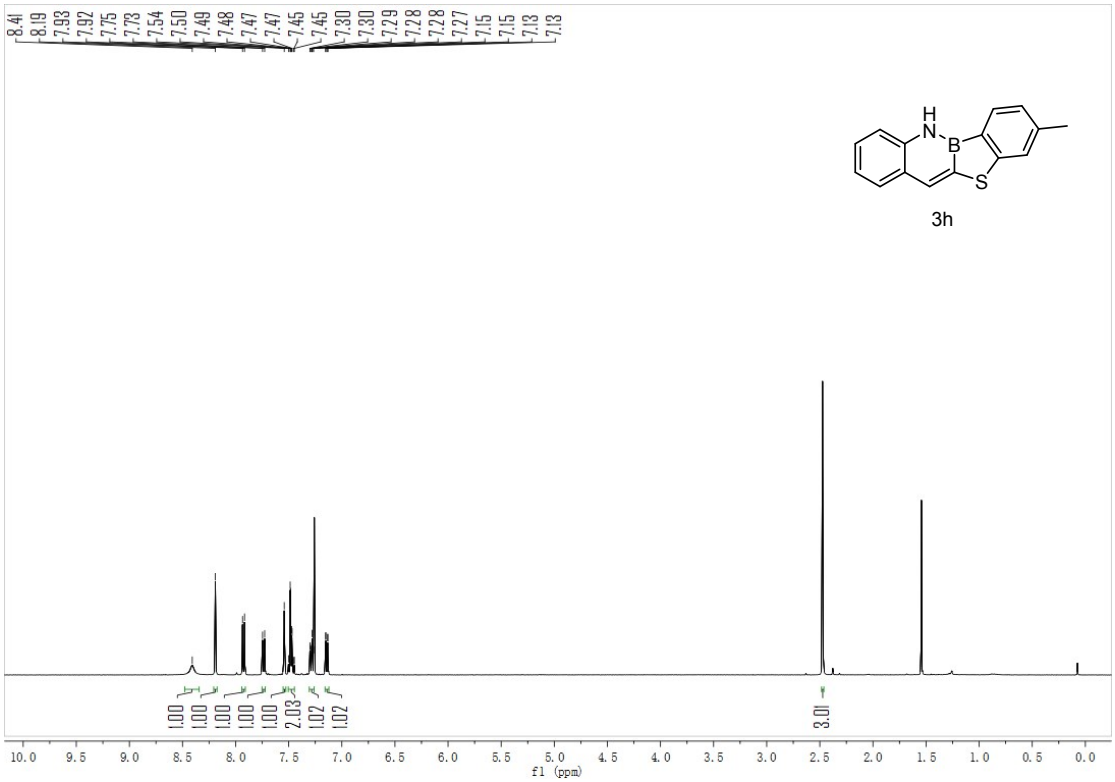
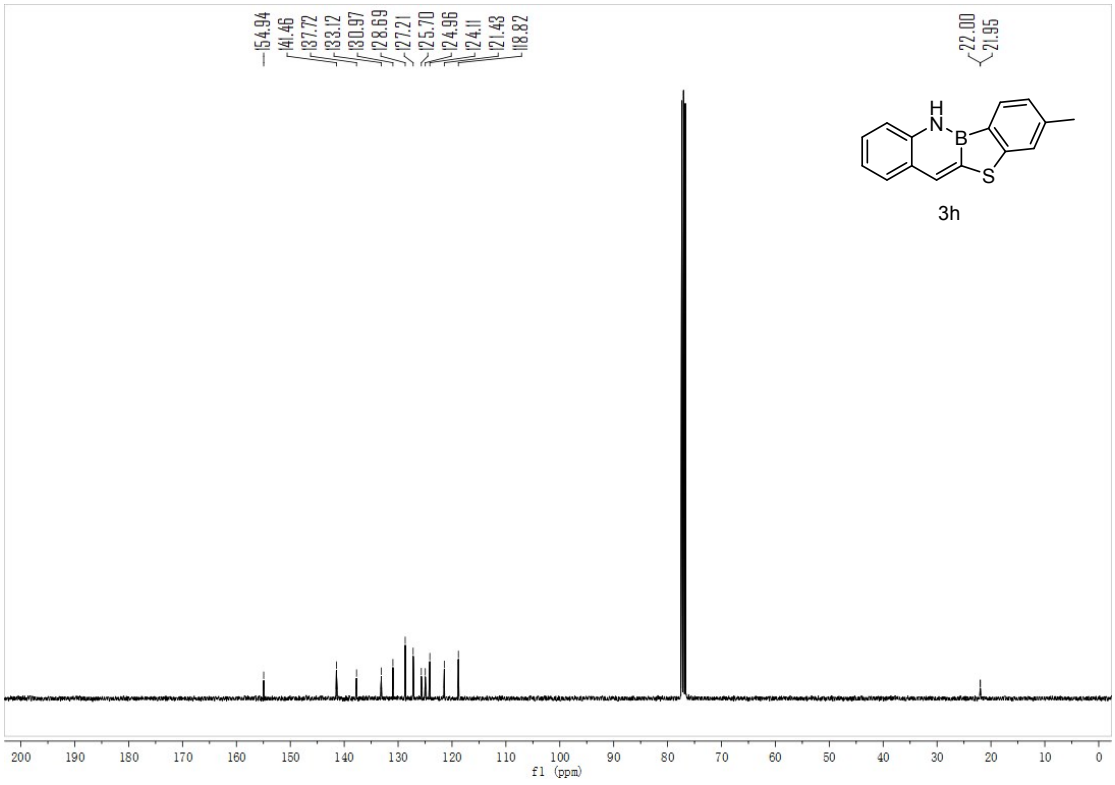
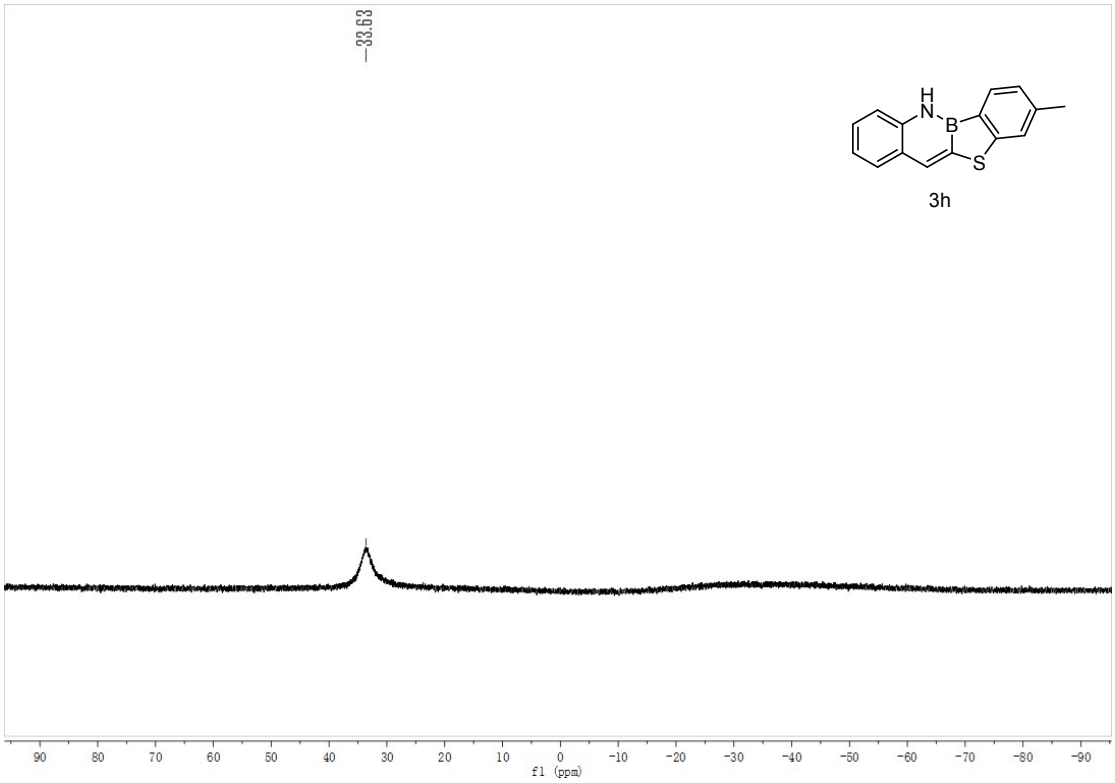
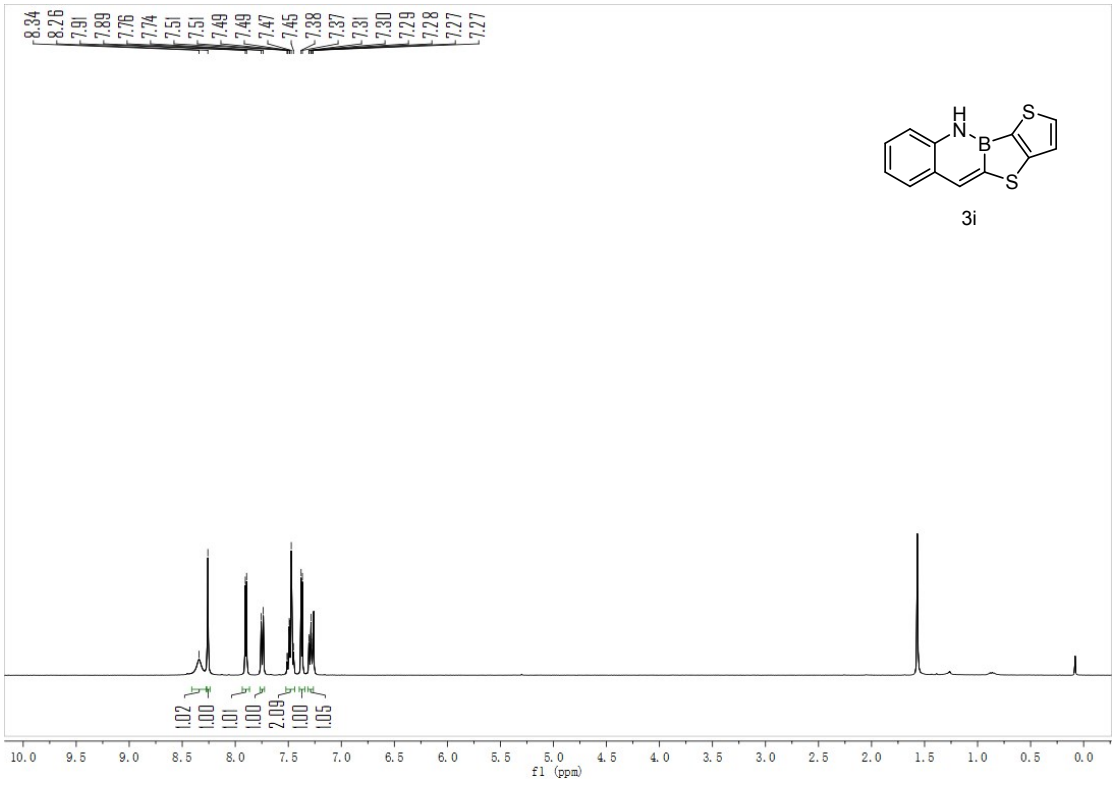
156.65
137.69
133.42
133.41
132.49
132.40
128.82
127.52
125.48
121.65
118.86
111.70
111.48
110.71
110.47
H
N
B
S
F
3g
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

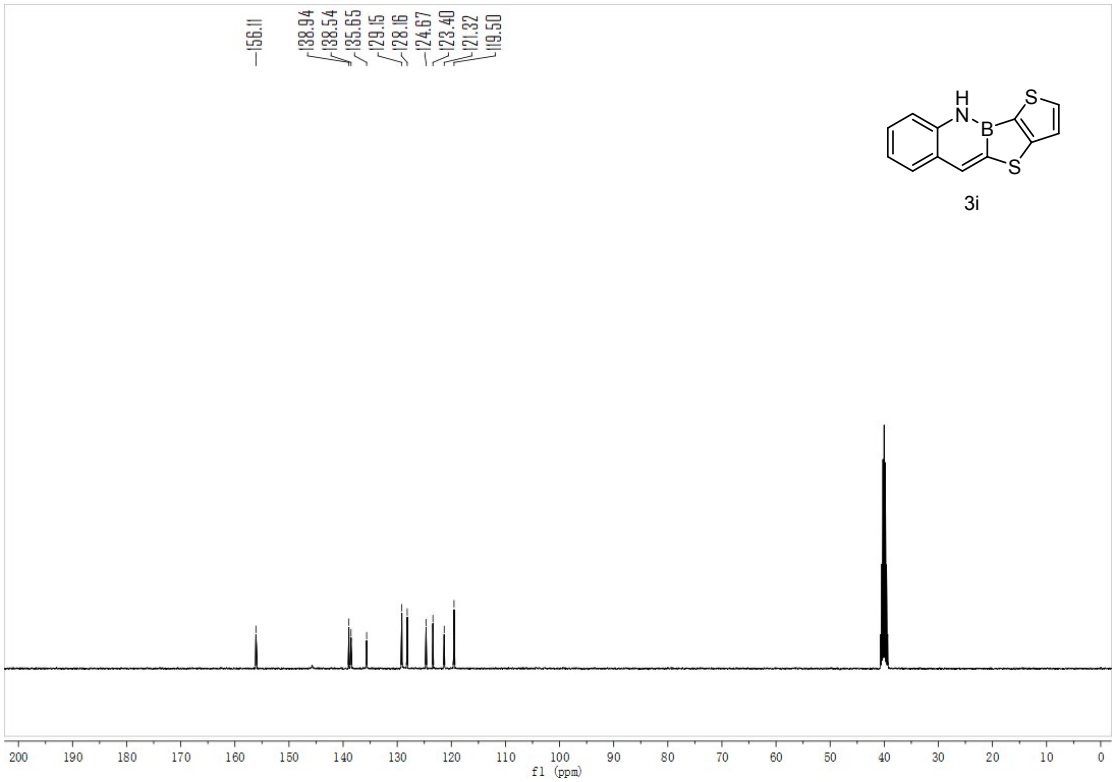

32.86
H
N
B
S
F
3g
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

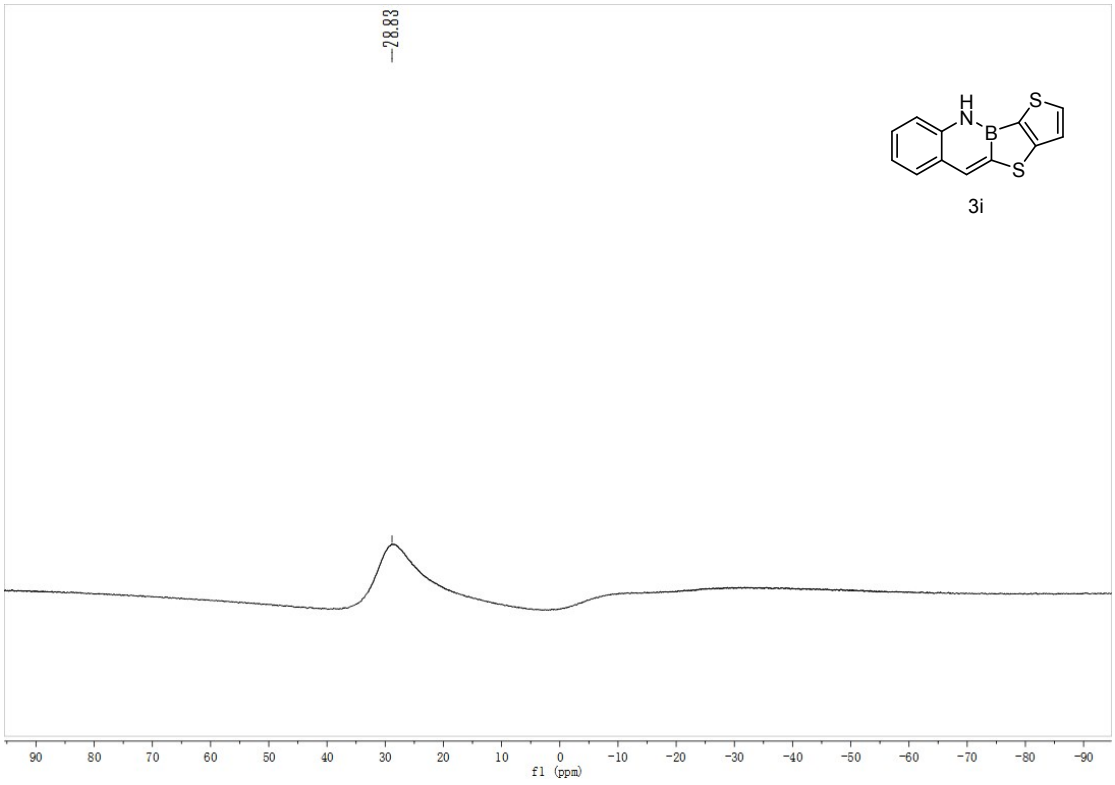

8.41
8.19
7.93
7.92
7.75
7.73
7.54
7.50
7.49
7.48
7.47
7.47
7.45
7.45
7.30
7.30
7.29
7.28
7.28
7.27
7.15
7.15
7.13
7.13
H
N
B
S
3h
1.00
1.00
1.00
1.00
1.00
2.03
1.02
1.02
8.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

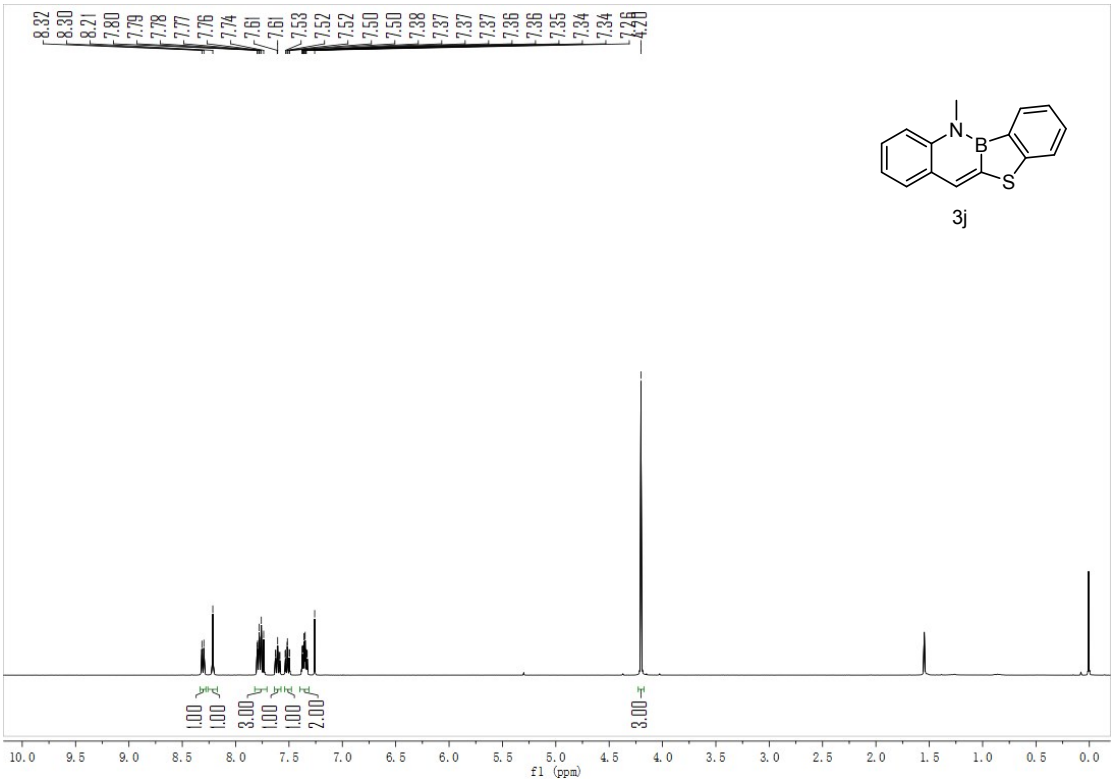

154.94
141.46
137.72
133.12
130.97
128.69
127.21
125.70
124.96
124.11
121.43
118.82
22.00
21.95
H
N
B
S
3h
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

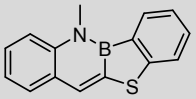

33.63
H
N
B
S
3h
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


8.34
8.26
7.91
7.89
7.76
7.74
7.51
7.51
7.49
7.49
7.47
7.45
7.38
7.37
7.31
7.30
7.29
7.28
7.27
7.27
H
N
B
S
S
3i
1.02
1.00
1.01
1.00
2.09
1.00
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

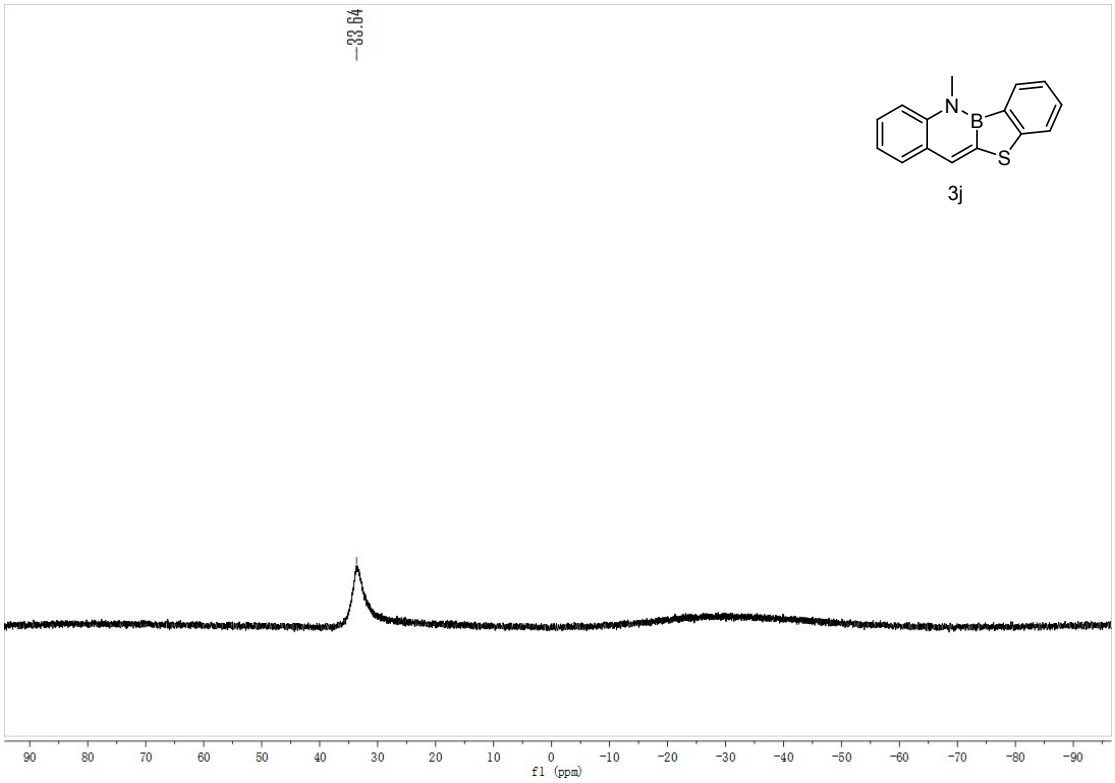

156.11
138.94
138.54
135.65
129.15
128.16
124.67
123.40
121.32
119.50
H
N
B
S
S
3i
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

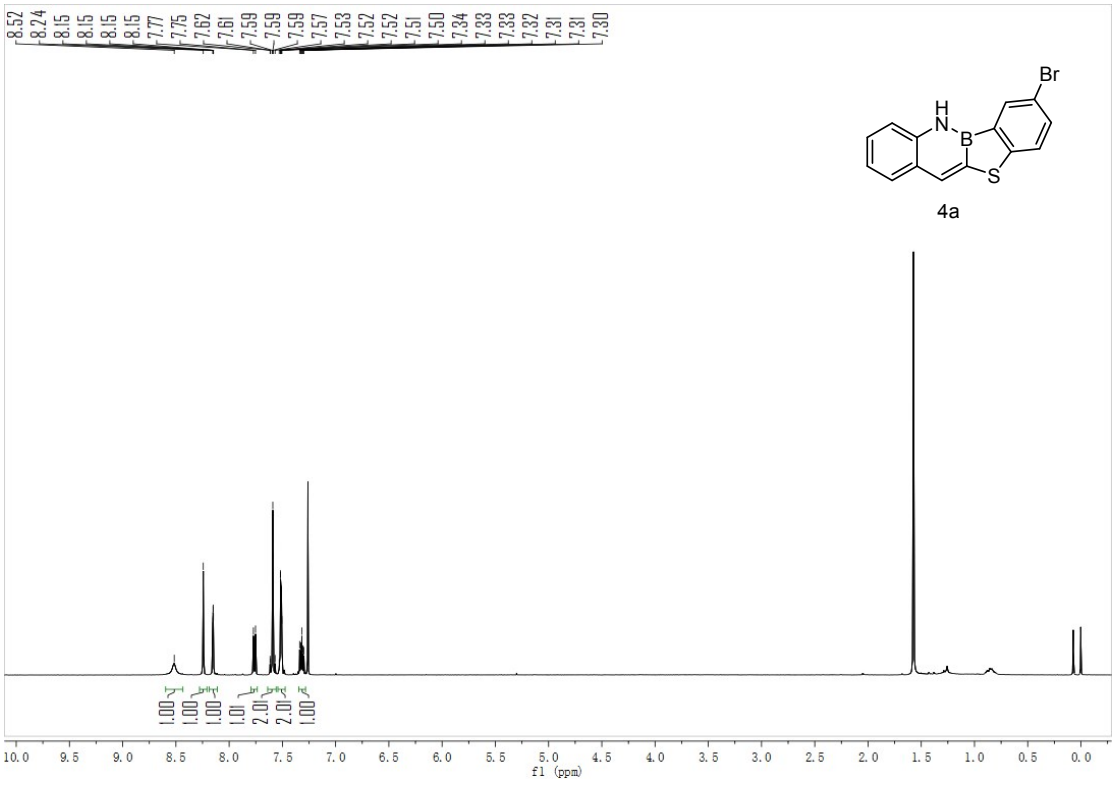

28.83
H
N
B
S
S
3i
90
80
70
60
50
40
30
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
f1 (ppm)

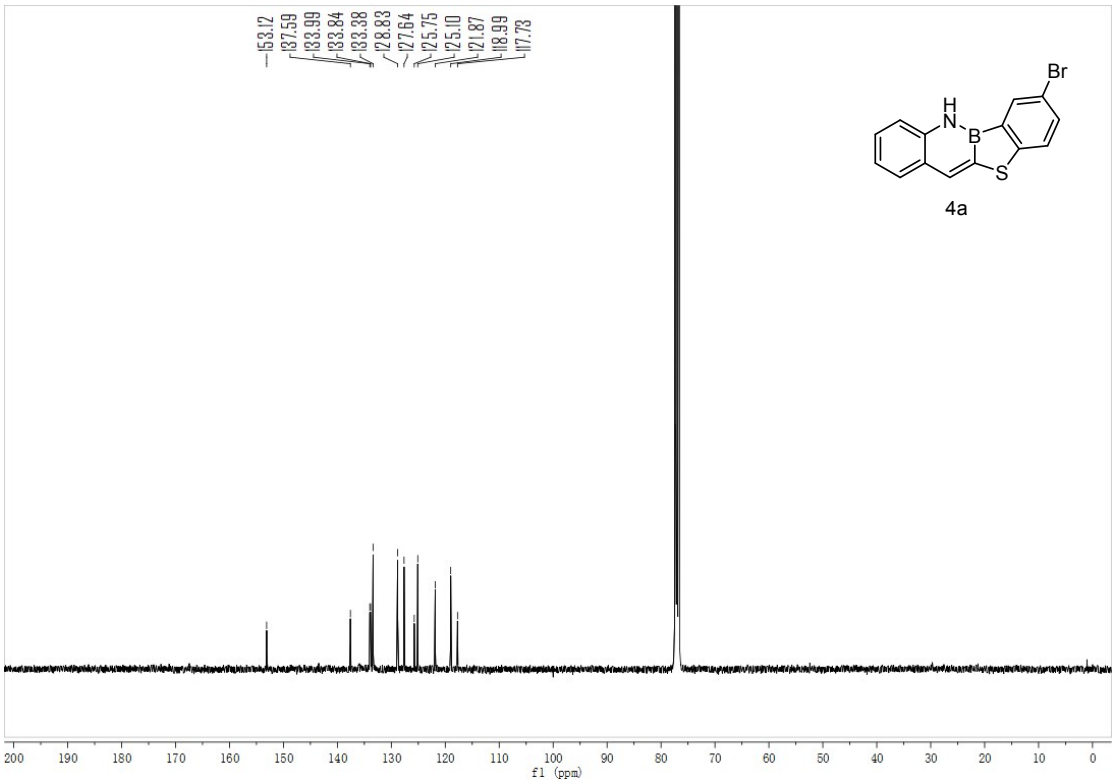

8.32
8.30
8.21
7.80
7.79
7.78
7.77
7.76
7.74
7.61
7.53
7.52
7.52
7.50
7.50
7.38
7.37
7.37
7.37
7.36
7.36
7.35
7.34
7.34
7.26
4.20
N
B
S
3j
1.00
1.00
8.00
1.00
1.00
2.00
8.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

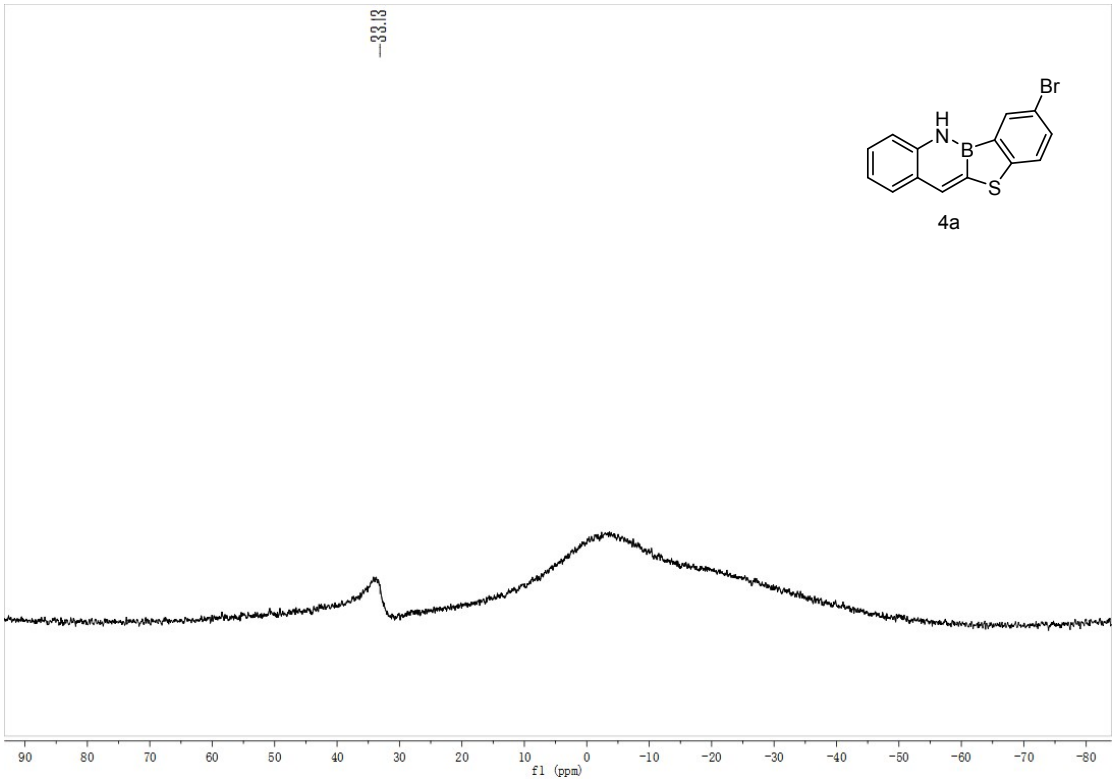

N
B
S

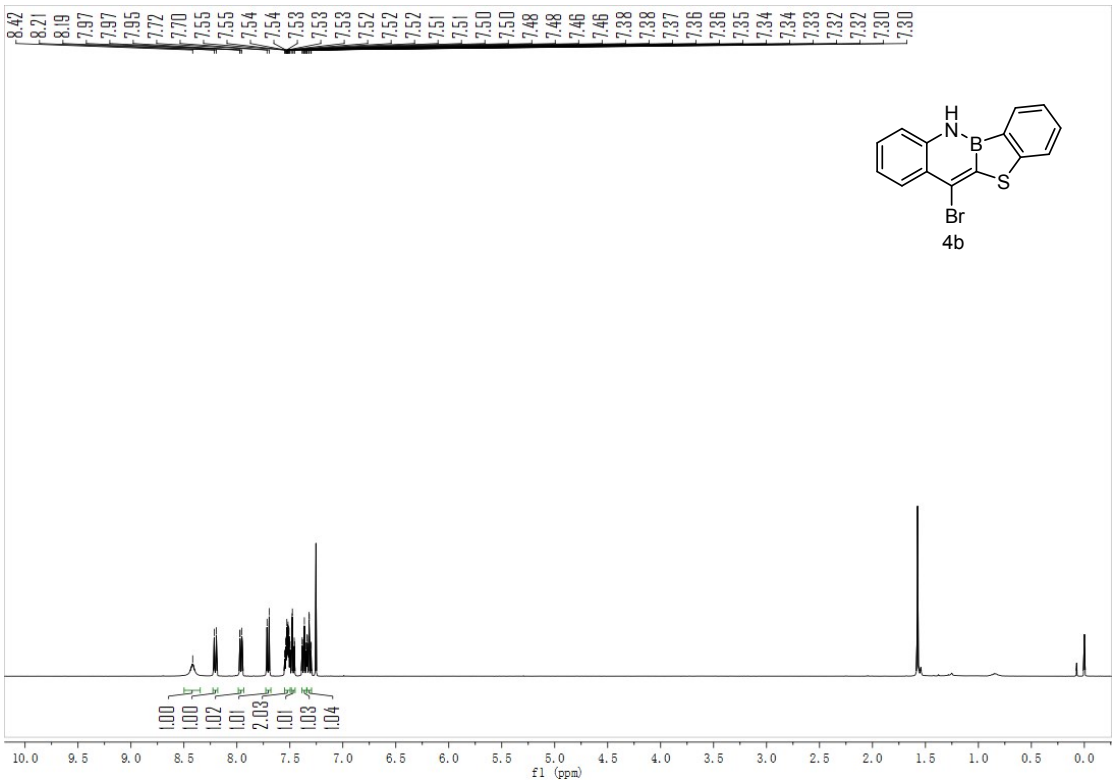
3j

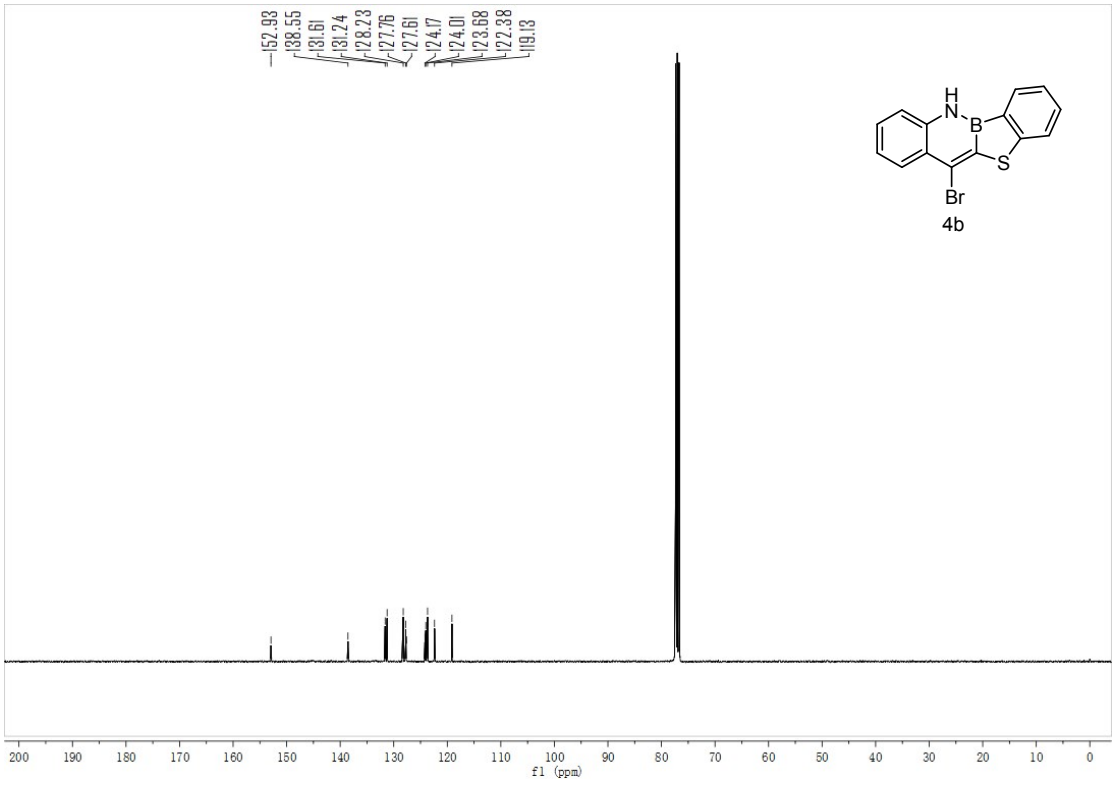

33.64
N
B
S
3j
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

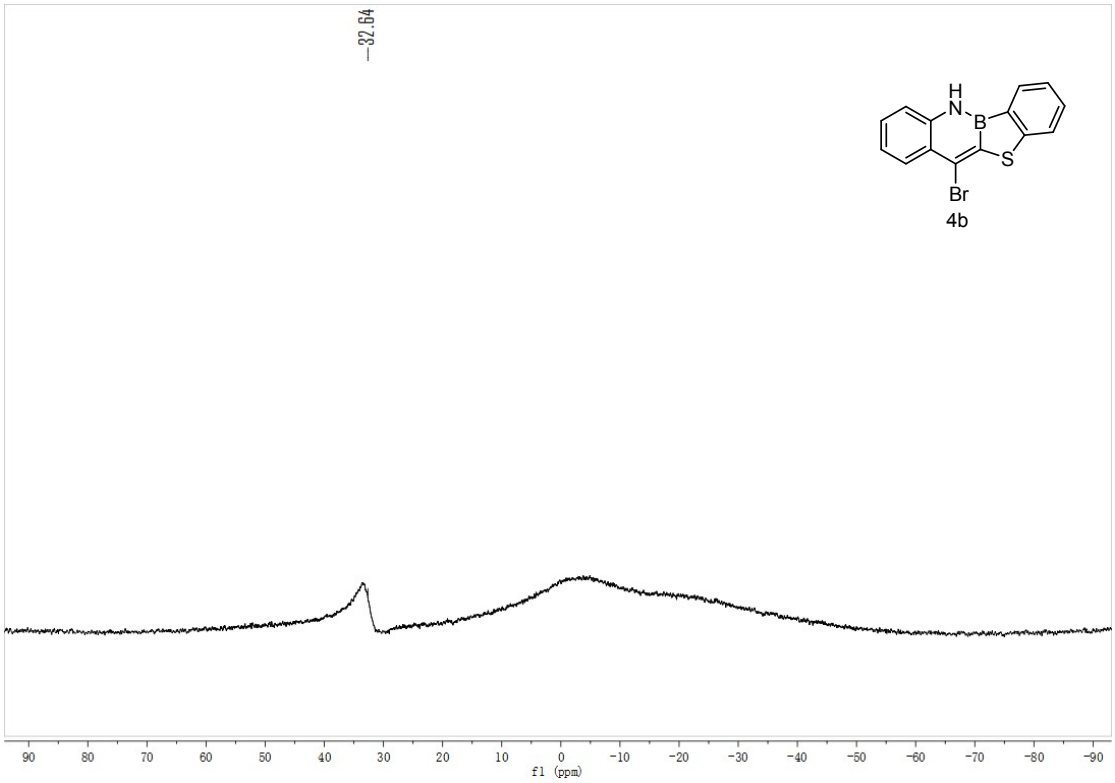

8.52
8.24
8.15
8.15
8.15
8.15
7.77
7.75
7.62
7.61
7.59
7.59
7.59
7.57
7.53
7.52
7.52
7.51
7.50
7.34
7.33
7.33
7.32
7.31
7.31
7.30
Br
H
N
B
S
4a
1.00
1.00
1.00
1.01
2.01
2.01
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

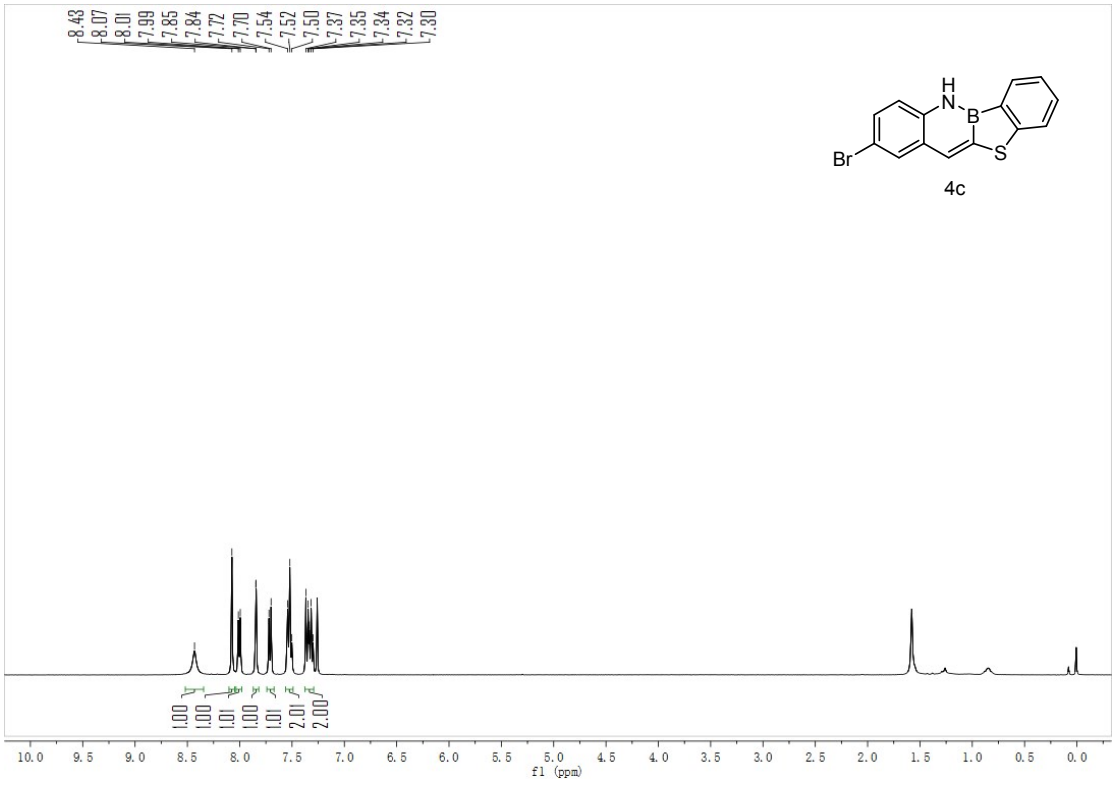

153.12
137.59
133.99
133.84
133.38
128.83
127.64
125.75
125.10
121.87
118.99
117.73
Br
H
N
B
S
4a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

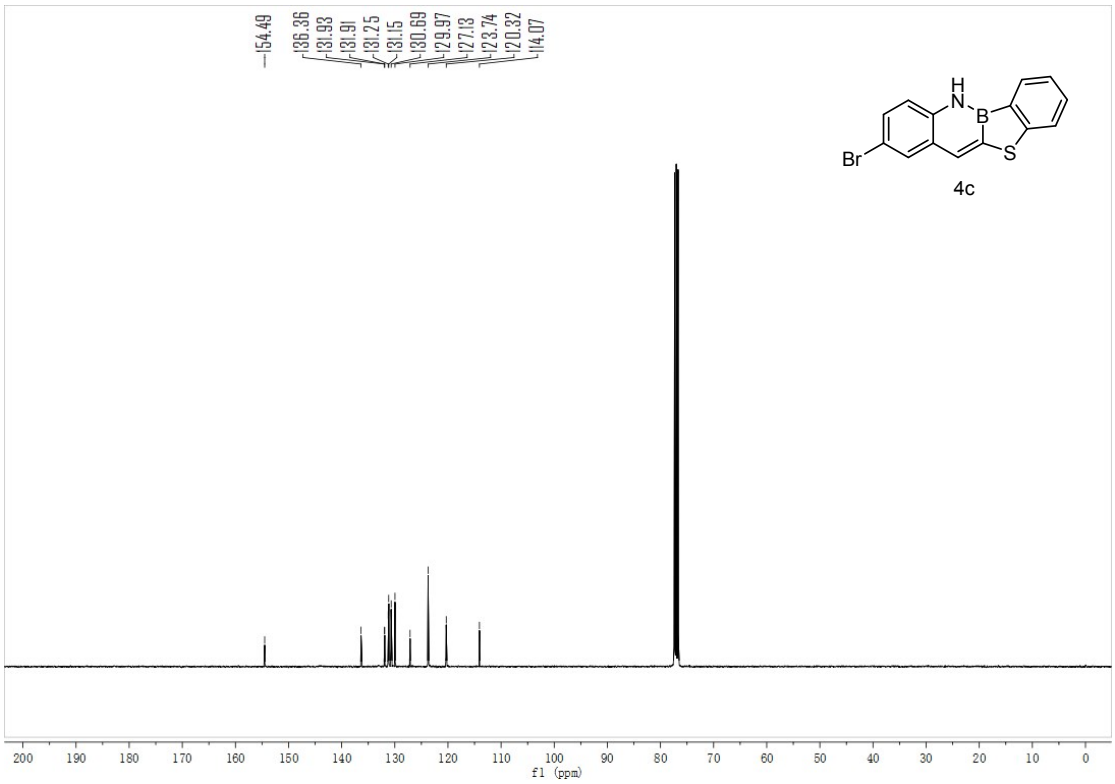

33.13
Br
H
N
B
S
4a
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

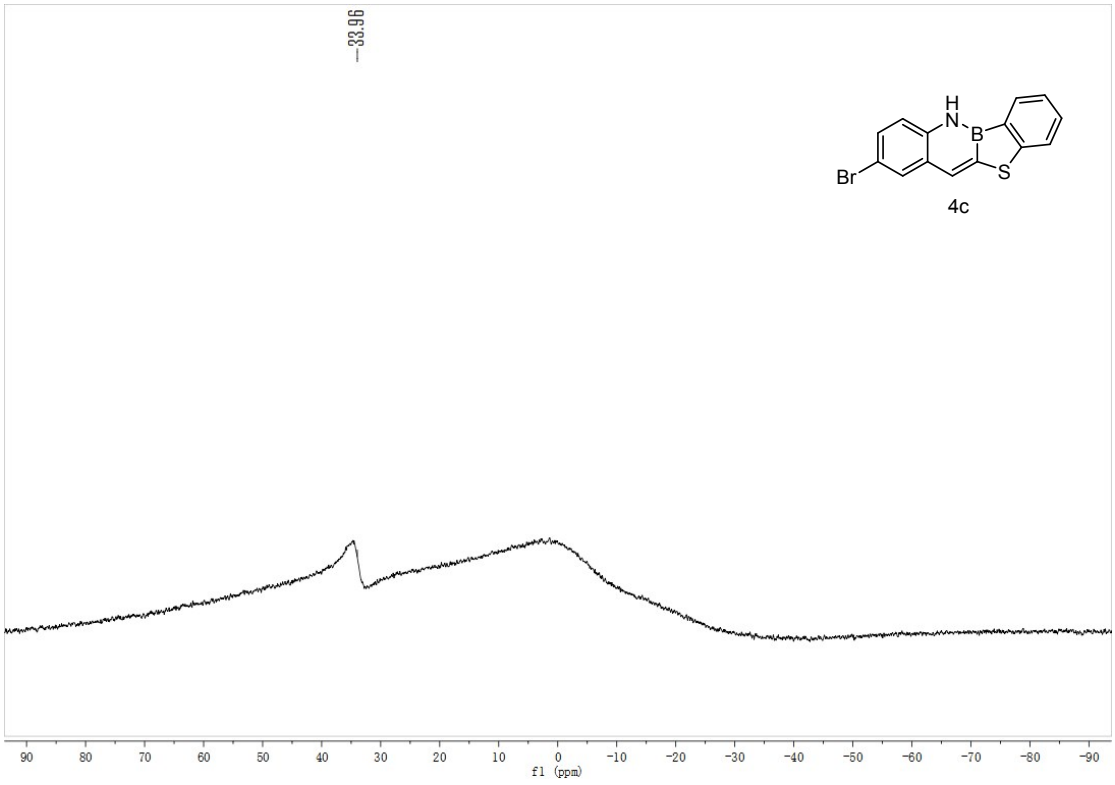

8.42
8.21
8.19
7.97
7.97
7.95
7.72
7.70
7.55
7.55
7.54
7.54
7.53
7.53
7.53
7.52
7.52
7.52
7.51
7.51
7.50
7.50
7.48
7.48
7.46
7.46
7.38
7.38
7.37
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.30
7.30
H
N
B
S
Br
4b
1.00
1.00
1.02
1.01
2.03
1.01
1.03
1.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

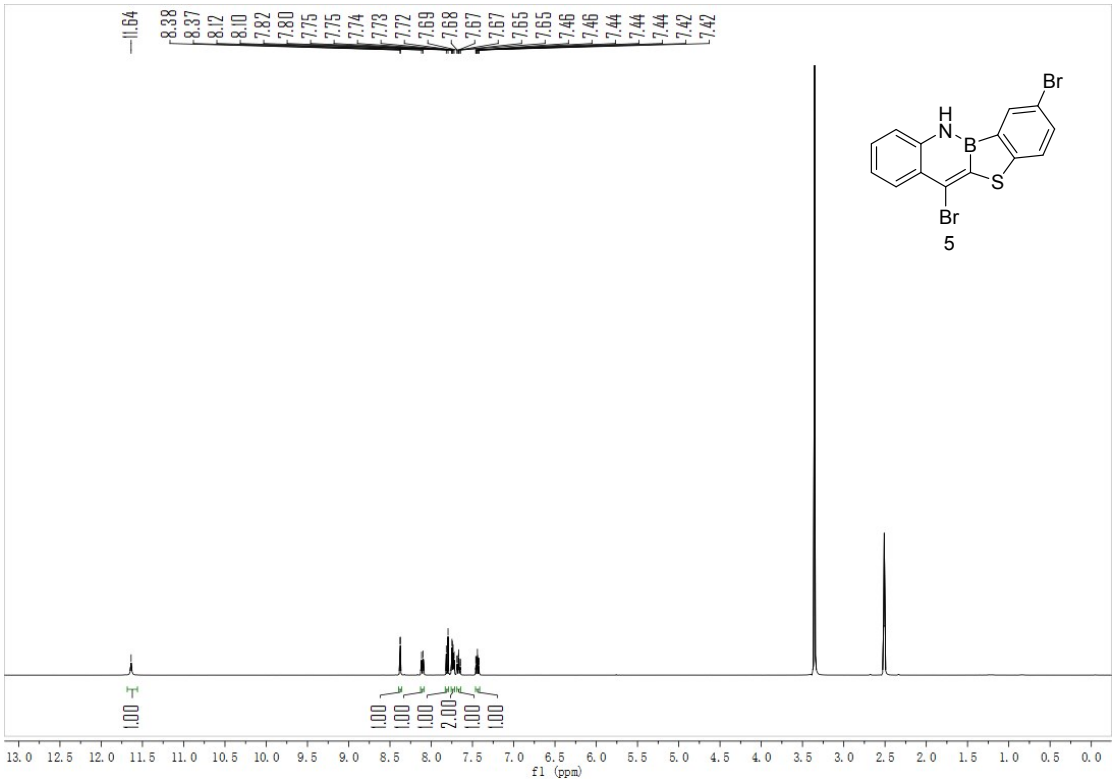

152.93
138.55
131.61
131.24
128.23
127.76
127.61
124.17
124.01
123.68
122.38
119.13
H
N
B
S
Br
4b
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

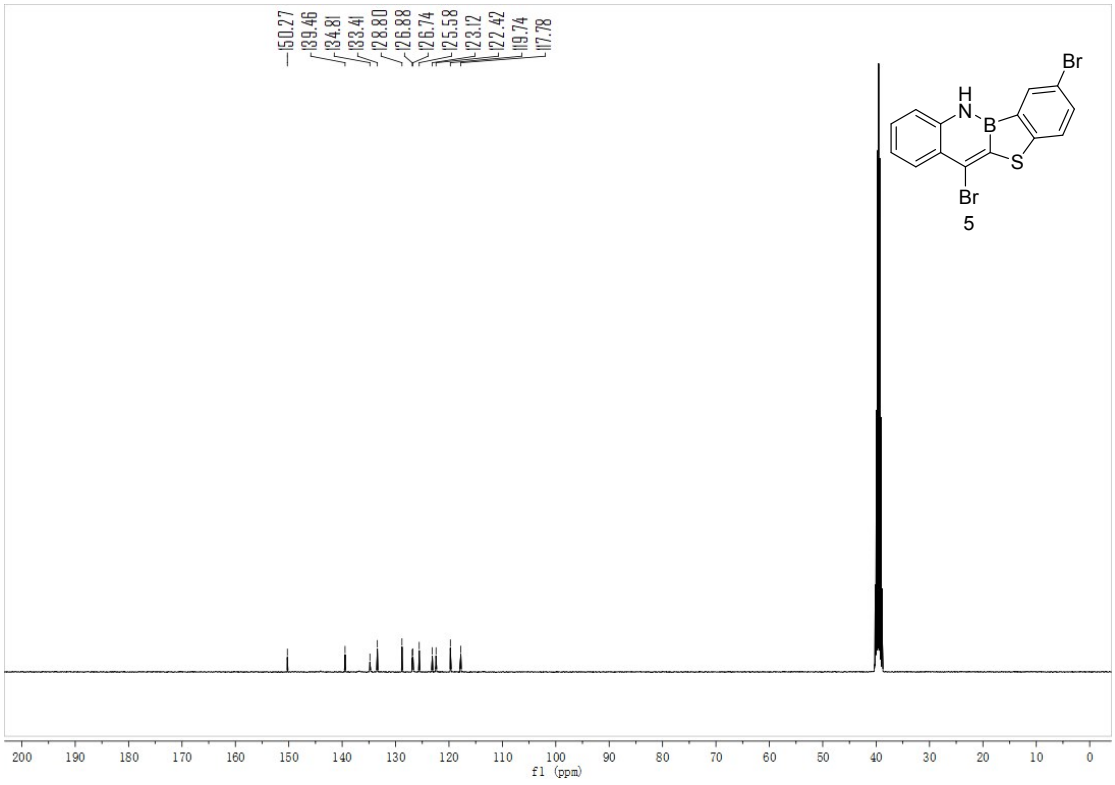

32.64
H
N
B
S
Br
4b
f1 (ppm)

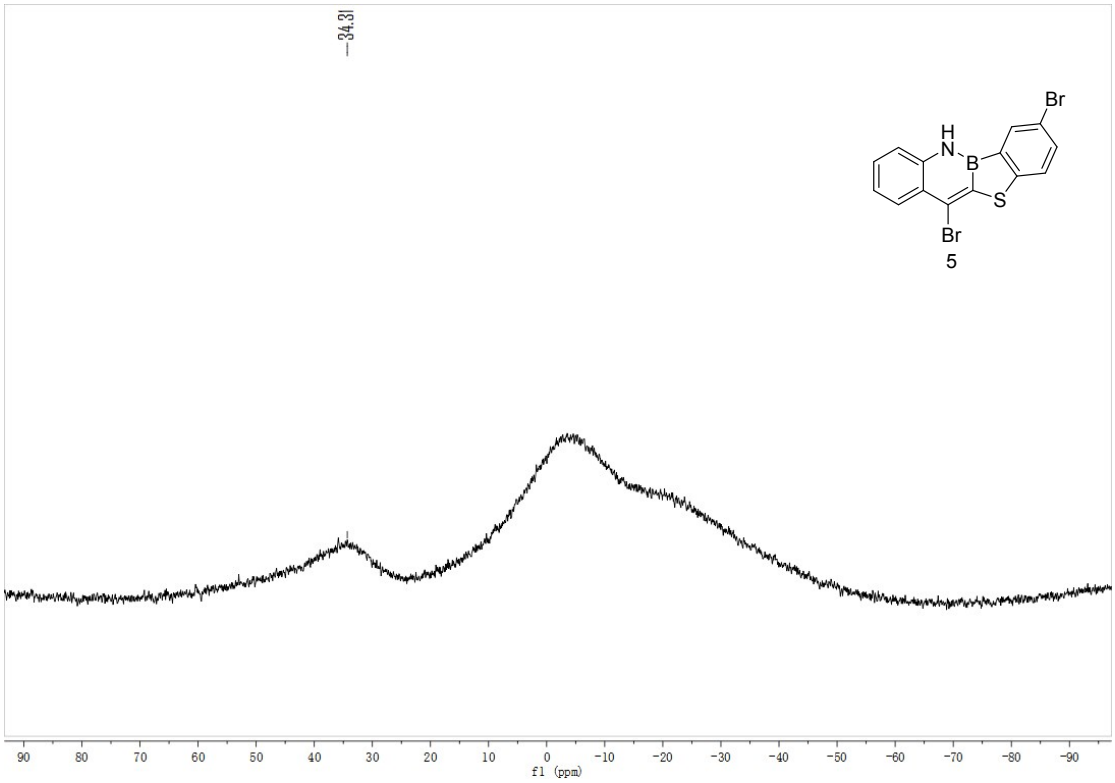

8.43
8.07
8.01
7.99
7.85
7.84
7.72
7.70
7.54
7.52
7.50
7.37
7.35
7.34
7.32
7.30
H
N
B
S
Br
4c
1.00
1.00
1.01
1.00
1.01
2.01
2.00
f1 (ppm)

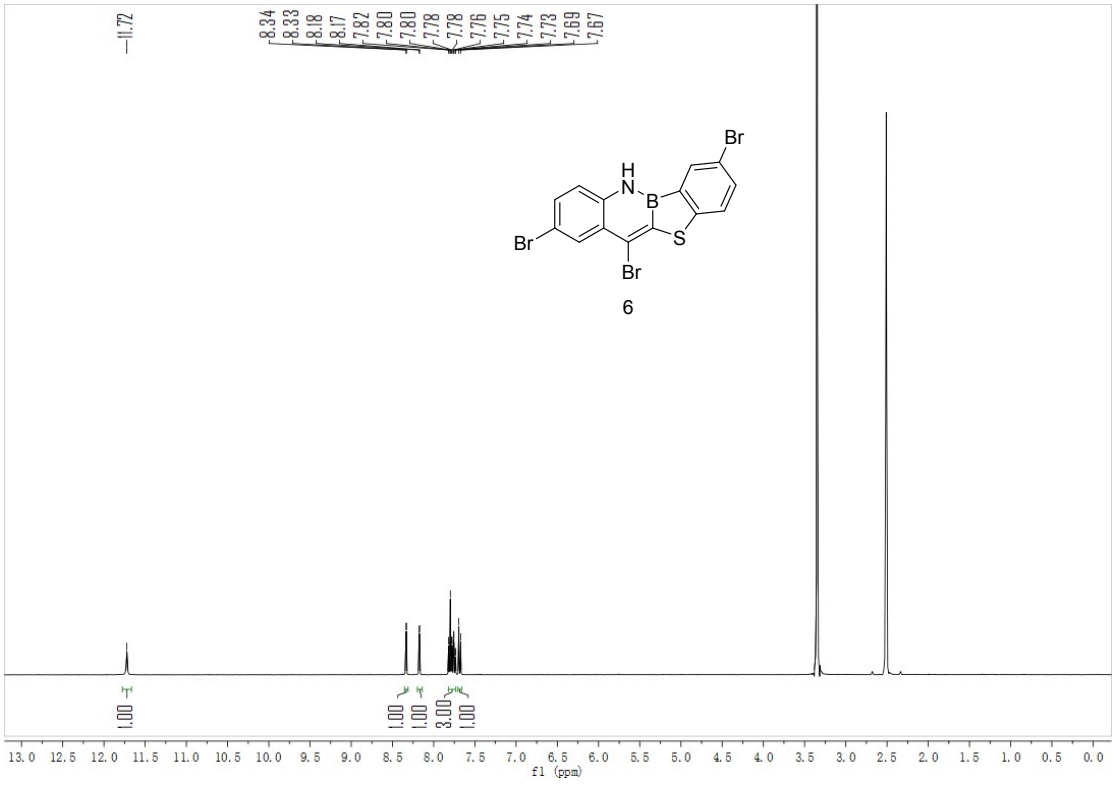

154.49
136.36
131.93
131.91
131.25
131.15
130.69
129.97
127.13
123.74
120.32
114.07
H
N
B
S
Br
4c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

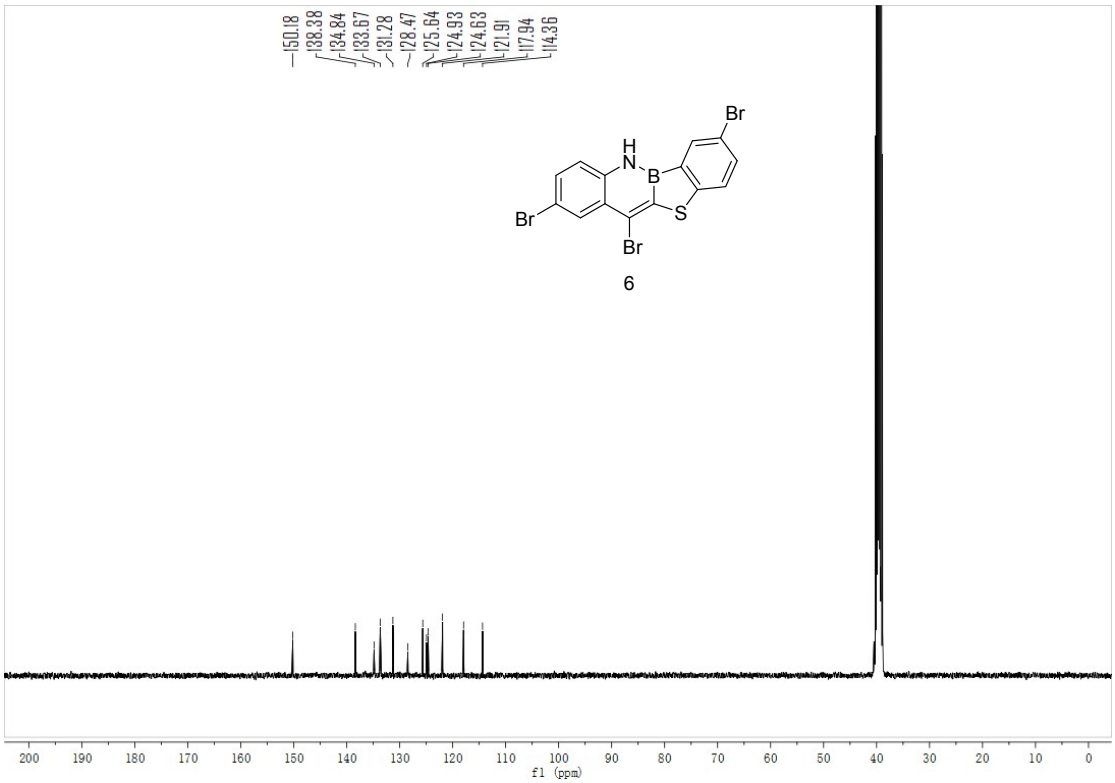

33.96
H
N
B
S
Br
4c
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

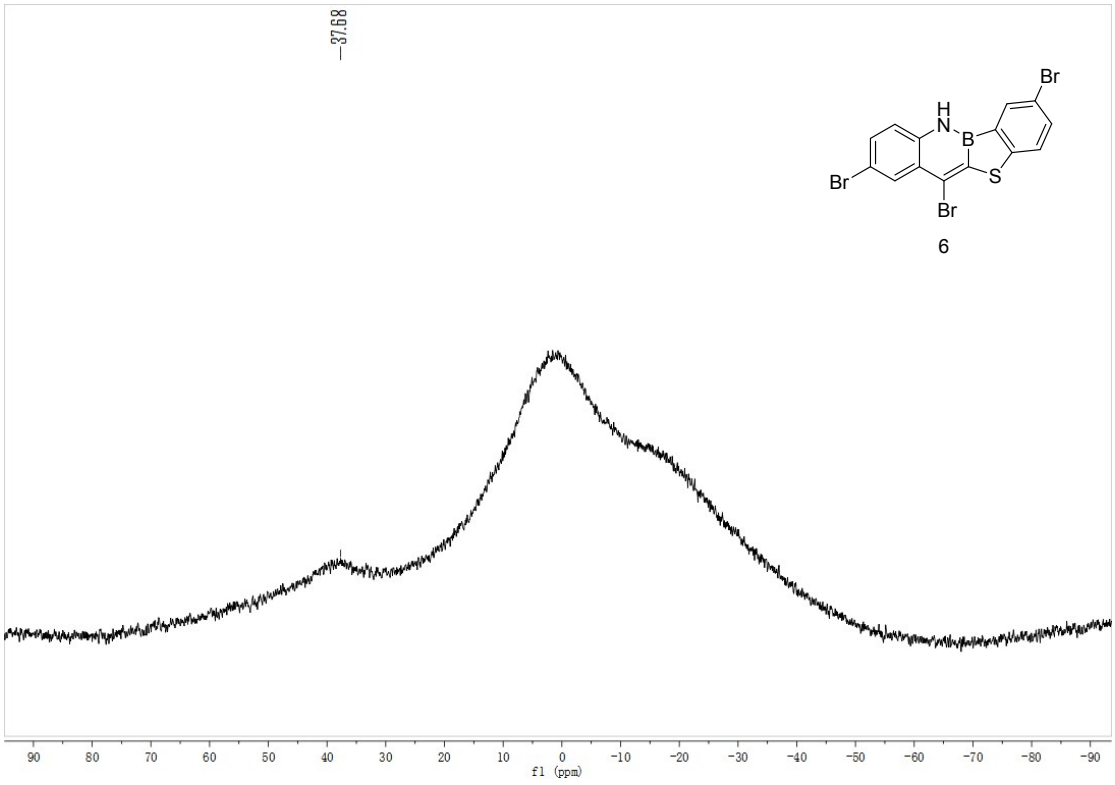

11.64
8.38
8.37
8.12
8.10
7.82
7.80
7.75
7.75
7.74
7.73
7.72
7.69
7.68
7.67
7.67
7.65
7.65
7.46
7.46
7.44
7.44
7.44
7.42
7.42
Br
H
N
B
S
Br
5
1.00
1.00
1.00
1.00
2.00
1.00
1.00
f1 (ppm)

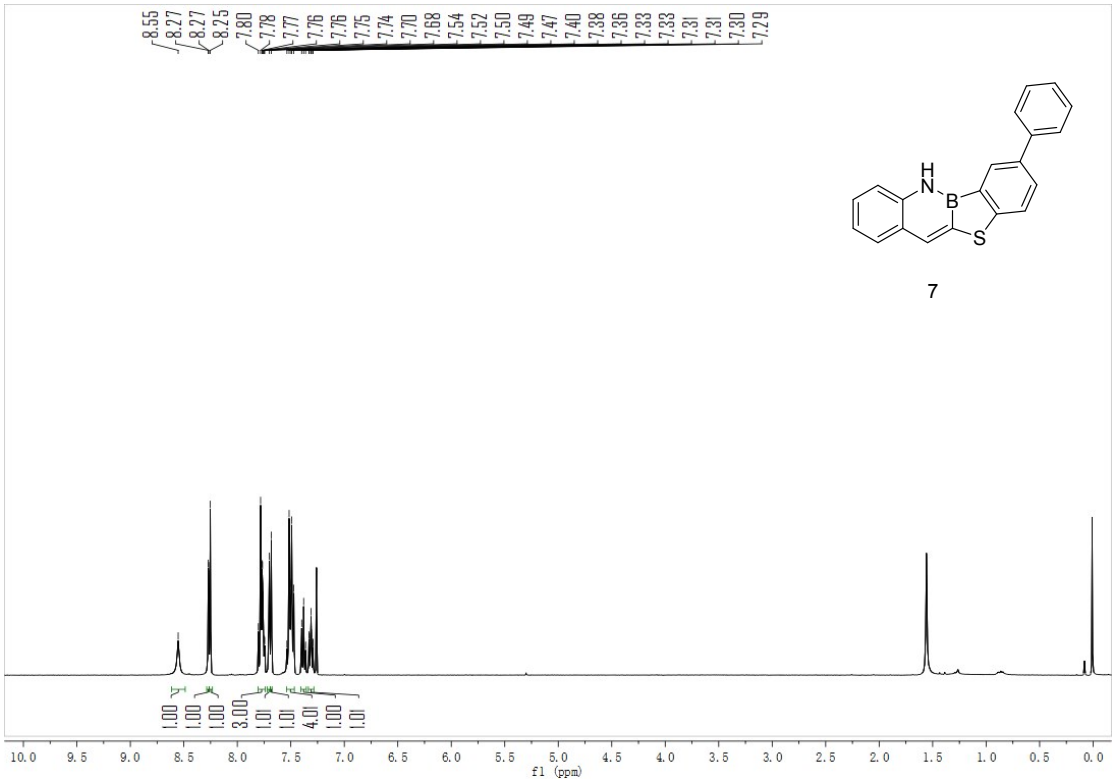

150.27
139.46
134.81
133.41
128.80
126.88
126.74
125.58
123.12
122.42
119.74
117.78
Br
H
N
B
S
Br
5
f1 (ppm)


34.31
Br
H
N
B
S
Br
5
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


11.72
8.34
8.33
8.18
8.17
7.82
7.80
7.80
7.78
7.78
7.76
7.75
7.74
7.73
7.69
7.67
Br
H
N
B
S
Br
Br
6
1.00
1.00
1.00
3.00
1.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


150.18
138.38
134.84
133.67
131.28
128.47
125.64
124.93
124.63
121.91
117.94
114.36
Br
H
N
B
S
Br
Br
6
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


37.68
Br
H
N
B
S
Br
Br
6
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


8.55
8.27
8.27
8.25
7.80
7.78
7.77
7.76
7.76
7.75
7.74
7.70
7.68
7.54
7.52
7.50
7.49
7.47
7.40
7.38
7.36
7.33
7.33
7.31
7.31
7.30
7.29
H
N
B
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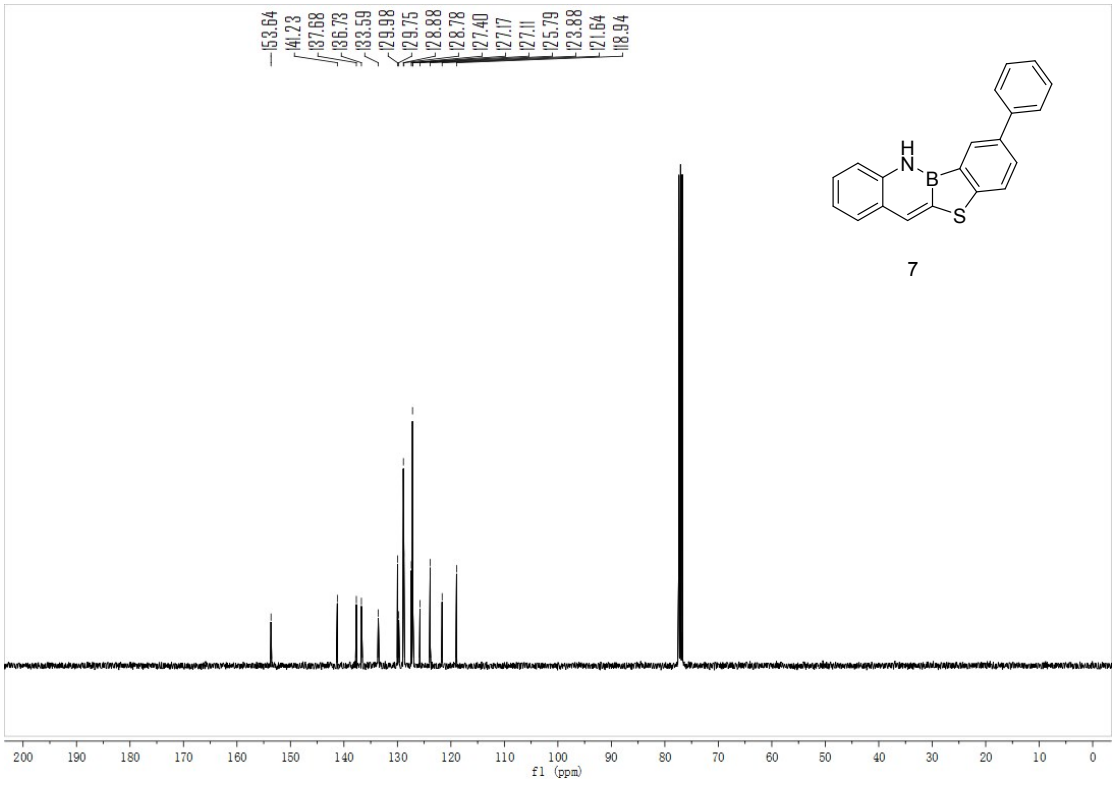
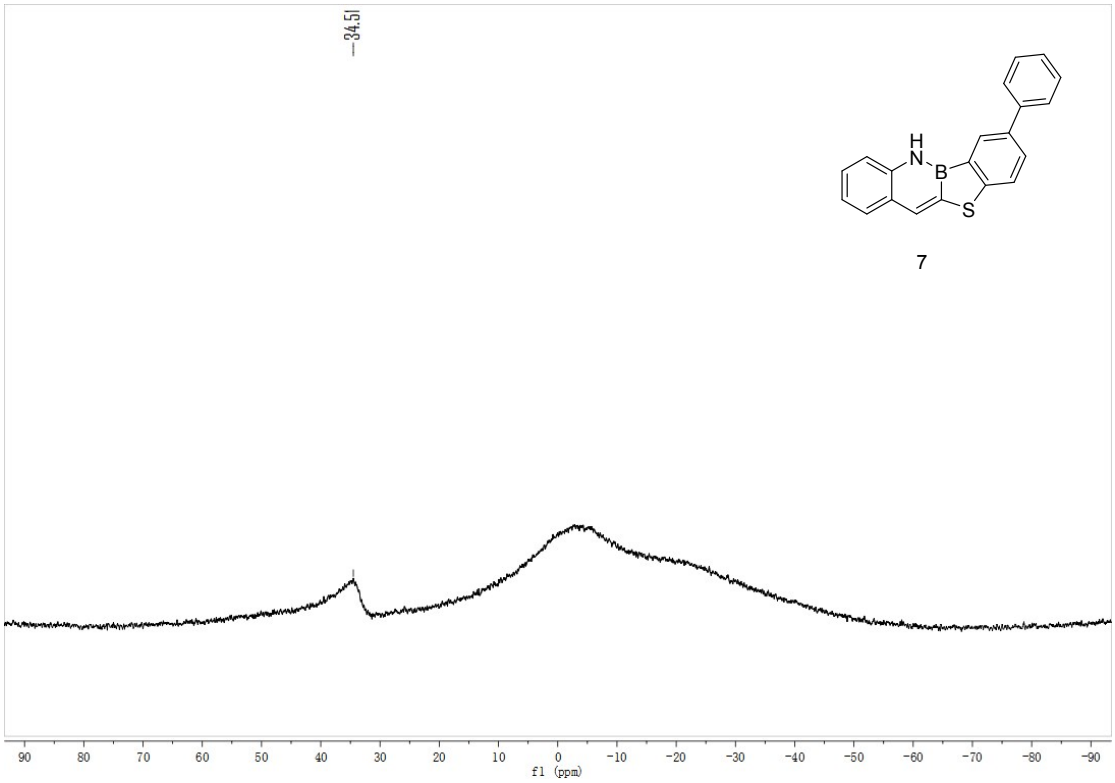
1.01
4.01
1.00
1.01
f1 (ppm)

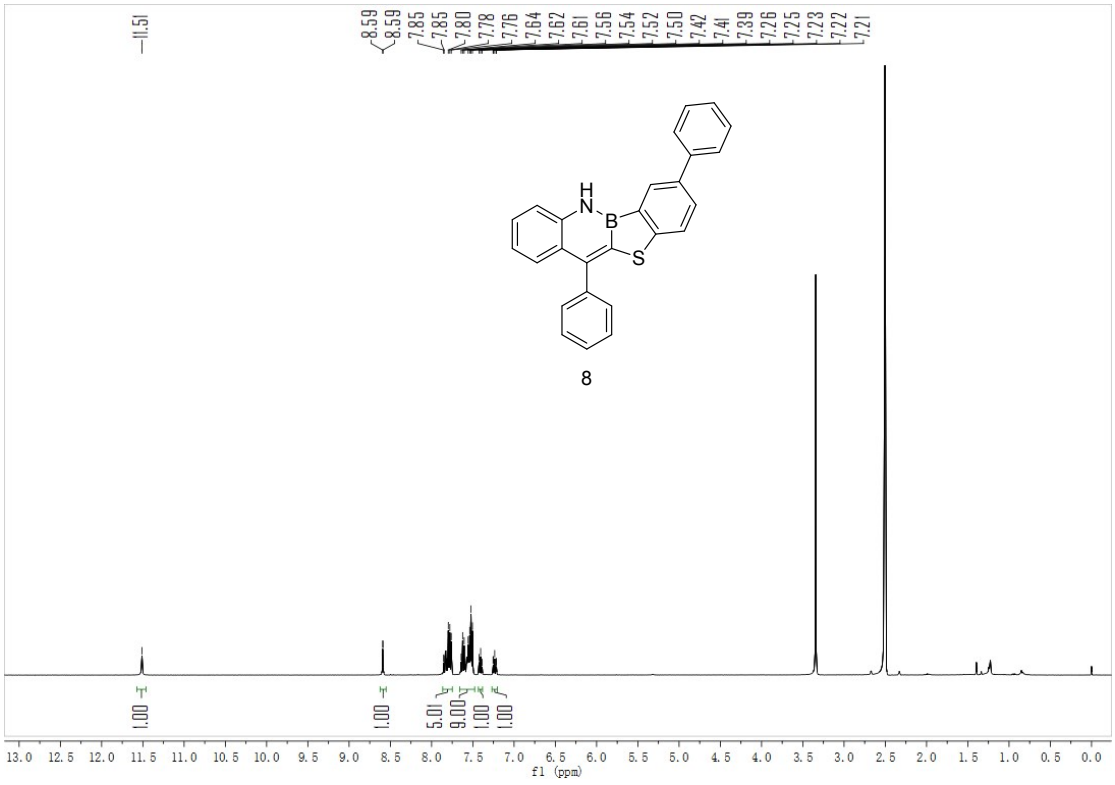
7


153.64
141.23
137.68
136.73
133.59
129.98
129.75
128.88
128.78
127.40
127.17
127.11
125.79
123.88
121.64
118.94
H
N
B
S
f1 (ppm)

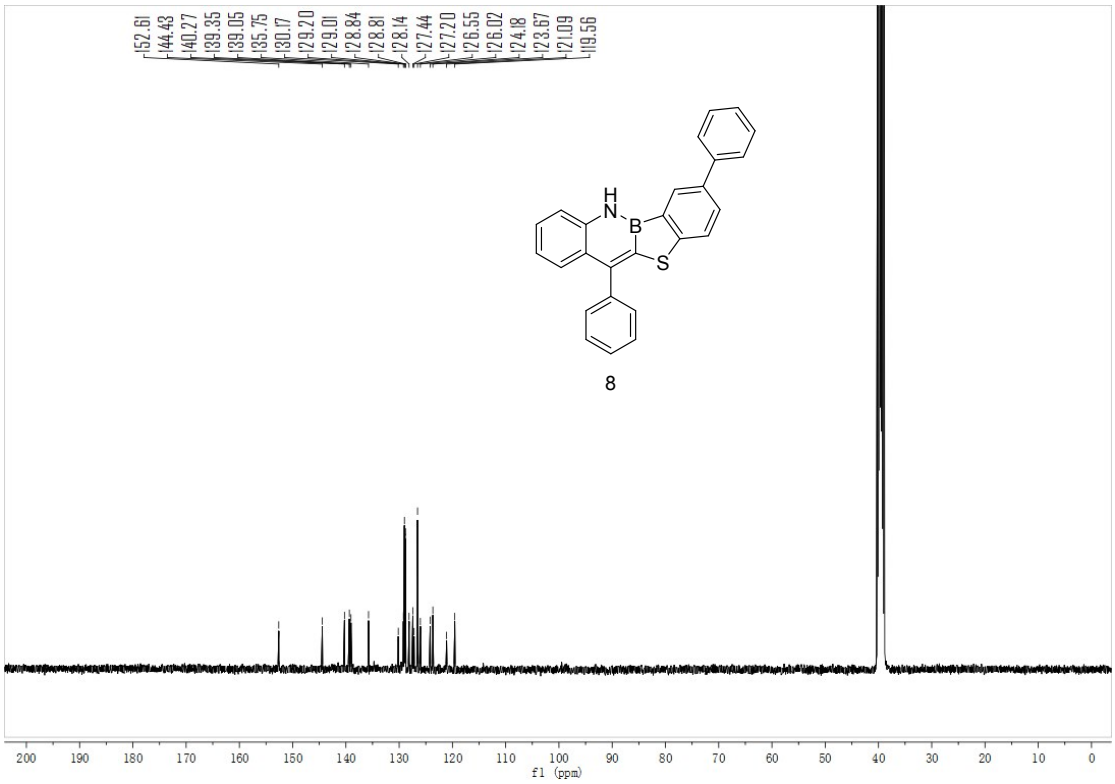
7

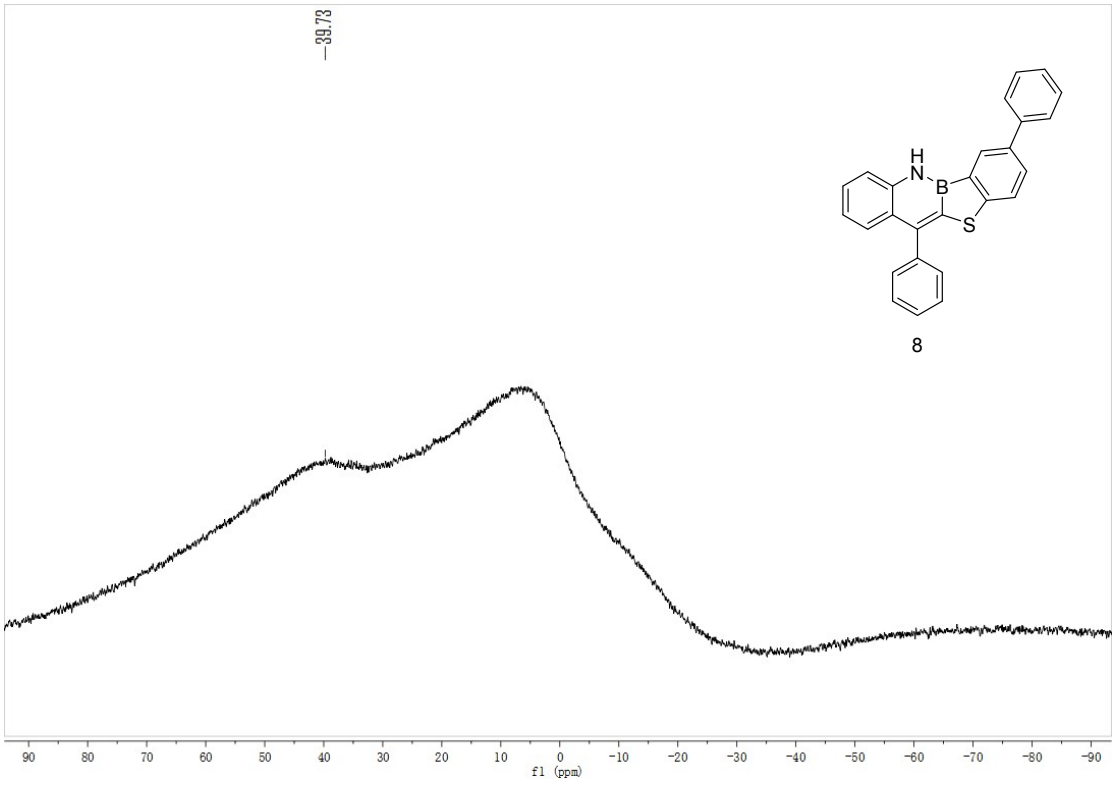

34.51
H
N
B
S
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)

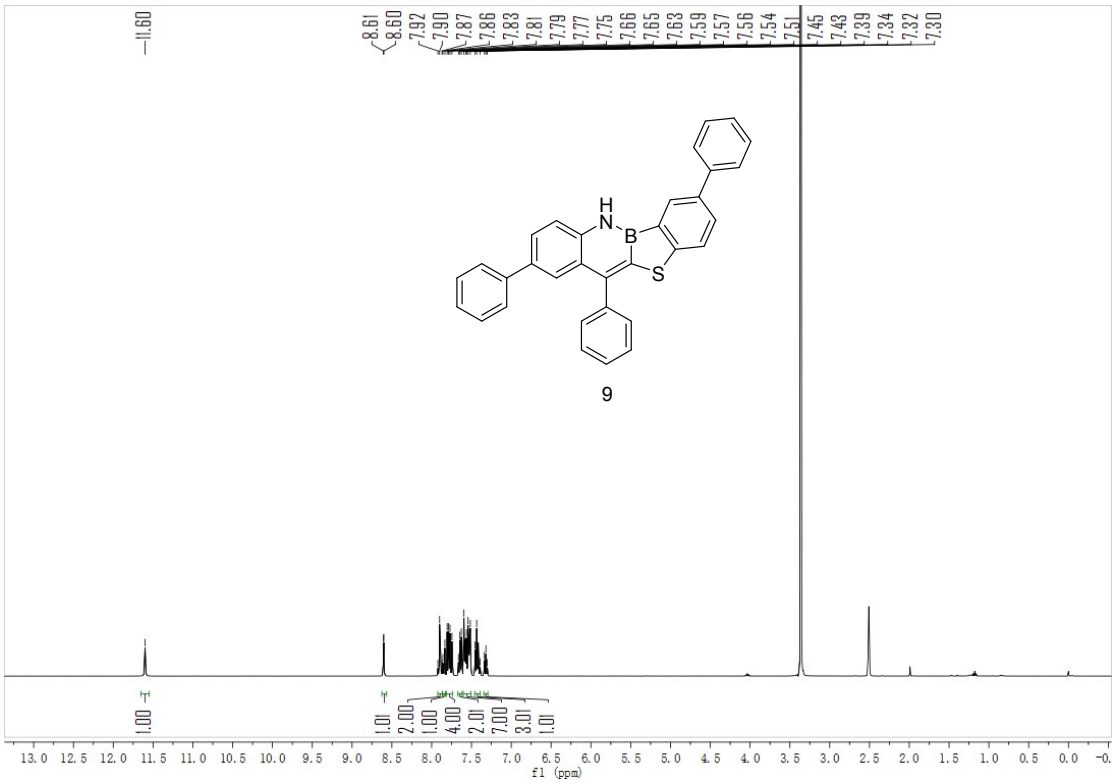
7


11.51
8.59
8.59
7.85
7.85
7.80
7.78
7.76
7.64
7.62
7.61
7.56
7.54
7.52
7.50
7.42
7.41
7.39
7.26
7.25
7.23
7.22
7.21
H
N
B
S
1.00
1.00
5.01
9.00
1.00
1.00
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

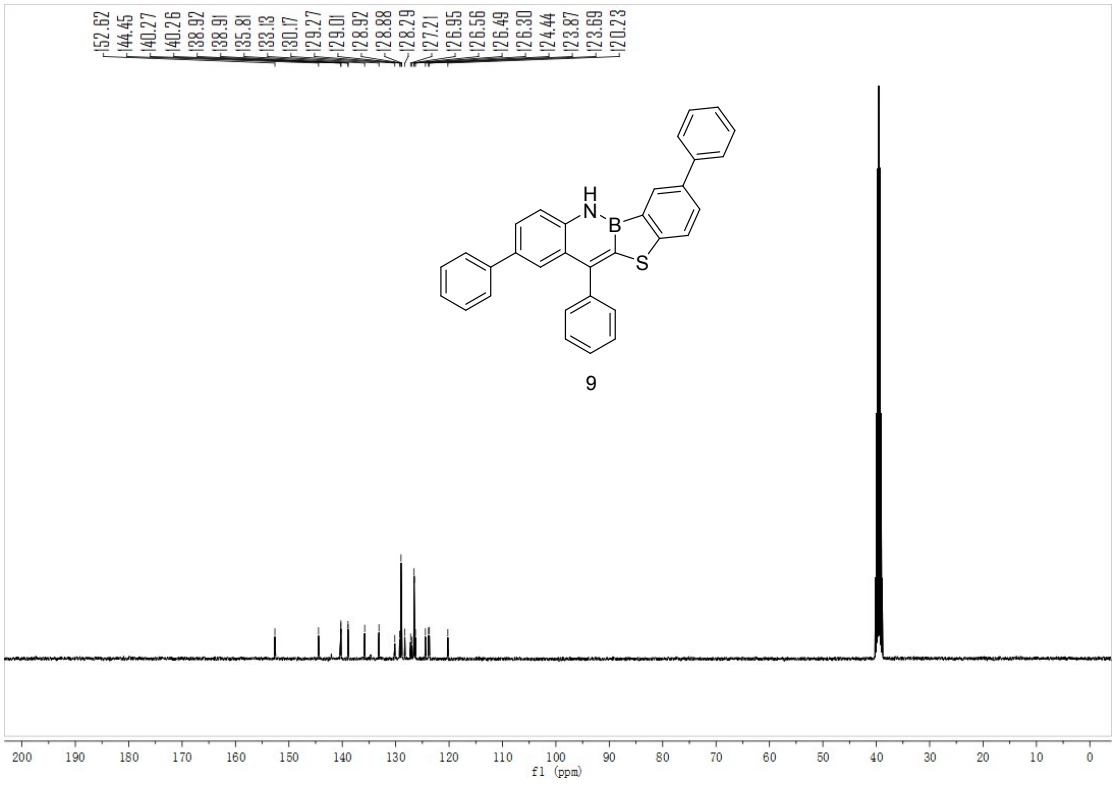
8


152.61
144.43
140.27
139.35
139.05
135.75
130.17
129.20
129.01
128.84
128.81
128.14
127.44
127.20
126.55
126.02
124.18
123.67
121.09
119.56
H
N
B
S
8
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

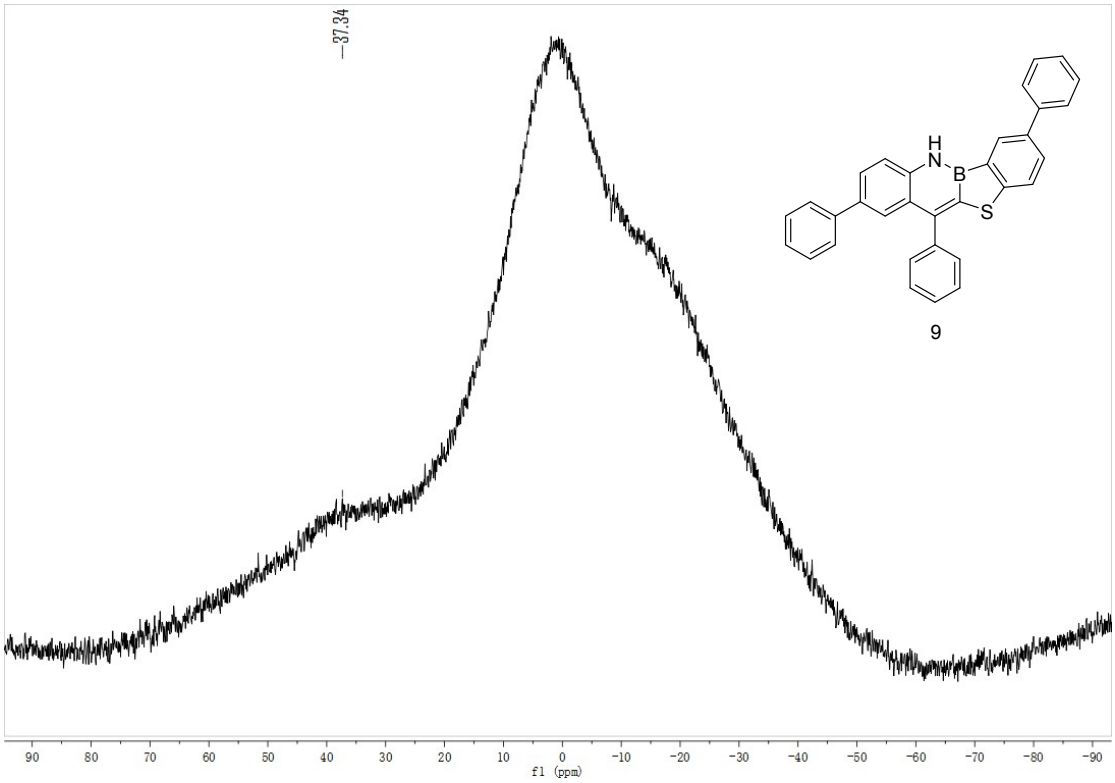

39.73
H
N
B
S
8
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


11.60
8.61
8.60
7.92
7.90
7.87
7.86
7.83
7.81
7.79
7.77
7.75
7.66
7.65
7.63
7.59
7.57
7.56
7.54
7.51
7.45
7.43
7.39
7.34
7.32
7.30
H
N
B
S
1.00
1.01
2.00
1.00
4.00
2.01
7.00
3.01
1.01
f1 (ppm)

9


152.62
144.45
140.27
140.26
138.92
138.91
135.81
133.13
130.17
129.27
129.01
128.92
128.88
128.29
127.21
126.95
126.56
126.49
126.30
124.44
123.87
123.69
120.23
H
N
B
S
f1 (ppm)

9


37.34
H
N
B
S
9
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1 (ppm)