Electronic Supplementary Information for *PCCP*

Noble-metal-free BODIPY-cobaloxime photocatalysts for visible-light-driven hydrogen production

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Electronic Supplementary Information (ESI):

Table S1-S4 & Fig. S1-S11

Table S1 Crystallographic data for **B1**, **B2** and **B3**.

BODIPY	**B1**	**B2**	**B3**
formula	$C_{36}H_{36}B_2F_4N_6$	$C_{18}H_{16}BF_2I_2N_3$	$C_{36}H_{36}B_2F_4N_6$
formula weight	650.33	576.92	650.33
crystal system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$	$Cmcm$	$P2_1$
a (Å)	24.7836(17)	16.771(3)	7.1055(3)
b (Å)	6.7289(3)	15.274(3)	12.1329(6)
c (Å)	20.9423(13)	7.6839(15)	19.1171(7)
α (deg)	90	90	90
β (deg)	114.264(8)	90	96.1670(10)
γ (deg)	90	90	90
Z, D_{calcd}(g m^{-3})	4, 1.357	4, 1.933	2, 1.318
V (Å^3)	3184.0(3)	1968.3(7)	1638.55(12)
μ (mm^{-1})	0.10	3.22	0.09
F (000)	1360	1080	434
T (K)	173(2)	173(2)	173(2)
no. of reflns collected	18476	7664	10658
no. of unique reflns.	5589 (R_{int} = 0.024)	975 (R_{int} = 0.055)	5660 (R_{int} = 0.046)
no. of observed reflns	4716	794	3869
parameters	433	505	434
R indices	R_1 = 0.0517,	R_1 = 0.0522,	R_1 = 0.0608,
[I > 2σ(I)][a,b]	wR_2 = 0.1432	wR_2 = 0.1526	wR_2 = 0.1536
R indices	R_1 = 0.0612,	R_1 = 0.0612,	R_1 = 0.1067,
all data	wR_2 = 0.1523	wR_2 = 0.1896	wR_2 = 0.2339
GOF	1.012	1.086	1.165
Max., min electron Density (e Å^{-3})	0.50, -0.45	1.40, -1.05	0.38, -0.38

[a] $R_1 = \Sigma| |F_o|-|F_c| |/ \Sigma|F_o|$, [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/ \Sigma w(F_o^2)^2]^{1/2}$

Table S2 Crystallographic data for **Co-B1, Co-B2 and Co-B3**.

BODIPY	**Co-B1**	**Co-B2**	**Co-B3**
formula	$C_{26}H_{32}BClCoF_2N_7O_4$	$C_{26}H_{30}BClCoF_2I_2N_7O_4$	$C_{26}H_{32}BClCoF_2N_7O_4$
formula weight	650.33	901.56	649.78
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$C2/m$
a (Å)	14.3736(11)	8.6580(3)	32.1886(10)
b (Å)	14.8242(11)	13.6093(5)	13.8873(5)
c (Å)	14.1707(12)	30.6990(13)	8.4320(3)
α (deg)	90	90	90
β (deg)	97.653(2)	92.9690	104.759(3)
γ (deg)	90	90	90
Z, D_{calcd}(g m^{-3})	4, 1.442	4, 1.658	4, 1.184
V (Å^3)	2992.6(4)	3612.4(2)	3644.8(2)
μ (mm^{-1})	0.72	2.308	0.59
F (000)	1344	1760	1344
T (K)	293(2)	293(2)	173(2)
no. of reflns collected	22496	27213	20089
no. of unique reflns.	5261 (R_{int} = 0.024)	6349 (R_{int} = 0.065)	3327 (R_{int} = 0.032)
no. of observed reflns	3027	4683	2918
parameters	380	451	214
R indices	R_1 = 0.0713,	R_1 = 0.0612,	R_1 = 0.0519,
[I > 2σ(I)][a,b]	wR_2 = 0.1824	wR_2 = 0.1669	wR_2 = 0.1618
R indices	R_1 = 0.2570,	R_1 = 0.0864,	R_1 = 0.0588,
all data	wR_2 = 0.1523	wR_2 = 0.1995	wR_2 = 0.1685
GOF	1.116	1.049	1.065
Max., min electron Density (e Å^{-3})	0.65, -0.81	2.09, -1.11	1.12, -0.36

[a] $R_1 = \Sigma| |F_o|-|F_c| |/ \Sigma|F_o|$, [b] $wR_2 = [\Sigma w(F_o^2-F_c^2)^2]/ \Sigma w(F_o^2)^2]^{1/2}$

Table S3 Selected bond lengths and bond angles of **Co-B1**, **Co-B2•CH_2Cl_2**, and **Co-B3**.

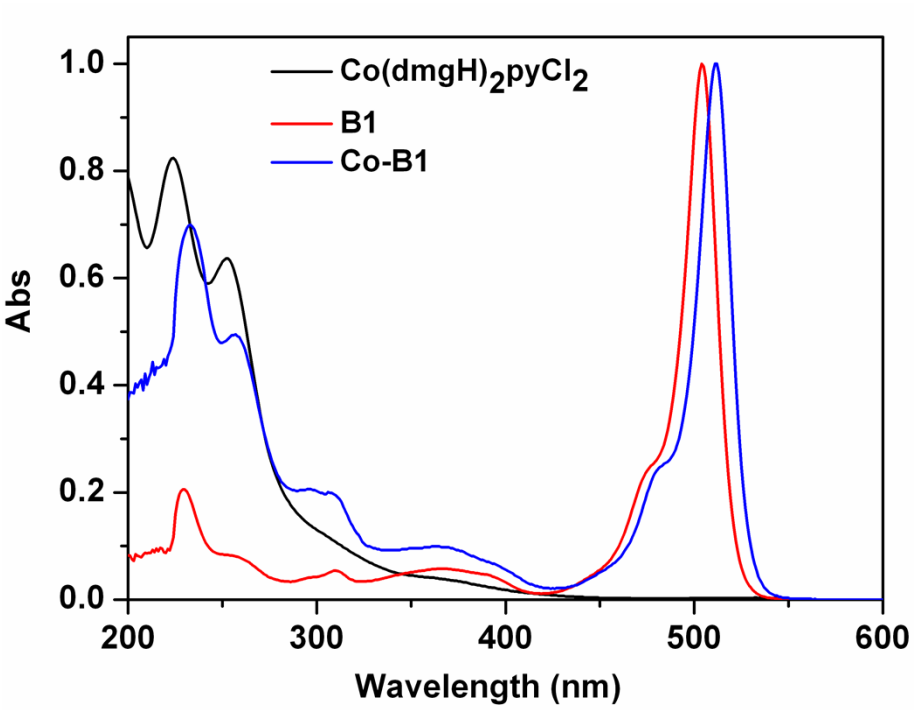
Co-B1		**Co-B2•CH_3CN**		**Co-B3**	
Bond lengths		Bond lengths		Bond lengths	
Co1-Cl1	2.224(2)	Co1-Cl1	2.229(2)	Co1-Cl1	2.240(1)
Co1-N3	1.952(5)	Co1-N3	1.955(5)	Co1-N1	1.898(2)
Co1-N4	1.892(5)	Co1-N4	1.904(6)	Co1-N1^{i}	1.898(2)
Co1-N5	1.897(5)	Co1-N5	1.895(6)	Co1-N2	1.896(2)
Co1-N6	1.872(5)	Co1-N6	1.887(5)	Co1-N2^{i}	1.896(2)
Co1-N7	1.871(5)	Co1-N7	1.896(5)	Co1-N3	1.958(3)
Bond angles		Bond angles		Bond angles	
N7-Co1-N6	81.6(2)	N6-Co1-N5	179.4(3)	N2^{i}-Co1-N2	98.8(1)
N7-Co1-N4	178.0(2)	N6-Co1-N7	81.1(2)	N2^{i}-Co1-N1^{i}	81.3(1)
N6-Co1-N4	98.6(2)	N5-Co1-N7	98.6(2)	N2-Co1-N1^{i}	178.9(1)
N7-Co1-N5	98.6(3)	N6-Co1-N4	98.8(2)	N2^{i}-Co1-N1	178.9(1)
N6-Co1-N5	179.5(2)	N5-Co1-N4	81.5(2)	N1^{i}-Co1-N1	98.6(2)
N4-Co1-N5	81.0(2)	N7-Co1-N4	179.4(2)	N2^{i}-Co1-N3	89.88(9)
N7-Co1-N3	88.5(2)	N6-Co1-N3	91.4(2)	N2-Co1-N3	89.88(9)
N6-Co1-N3	89.4(2)	N5-Co1-N3	89.0(2)	N1^{i}-Co1-N3	91.26(9)
N4-Co1-N3	89.5(2)	N7-Co1-N3	90.9(2)	N1-Co1-N3	91.26(9)
N5-Co1-N3	90.2(2)	N4-Co1-N3	89.7(2)	N2-Co1-N1	81.3(1)
N7-Co1-Cl1	90.7(2)	N6-Co1-Cl1	90.7(2)	N2^{i}-Co1-Cl1	89.96(7)
N6-Co1-Cl1	89.5(2)	N5-Co1-Cl1	88.8(2)	N2-Co1-Cl1	89.96(7)
N4-Co1-Cl1	91.3(2)	N7-Co1-Cl1	88.7(2)	N1^{i}-Co1-Cl1	88.90(7)
N5-Co1-Cl1	90.9(2)	N4-Co1-Cl1	90.7(2)	N1-Co1-Cl1	88.90(7)
N3-Co1-Cl1	178.7(2)	N3-Co1-Cl1	177.8(2)	N3-Co1-Cl1	179.8(1)

Table S4 The free energies for the IET reactions of **Co-B2 and Co-B4**.

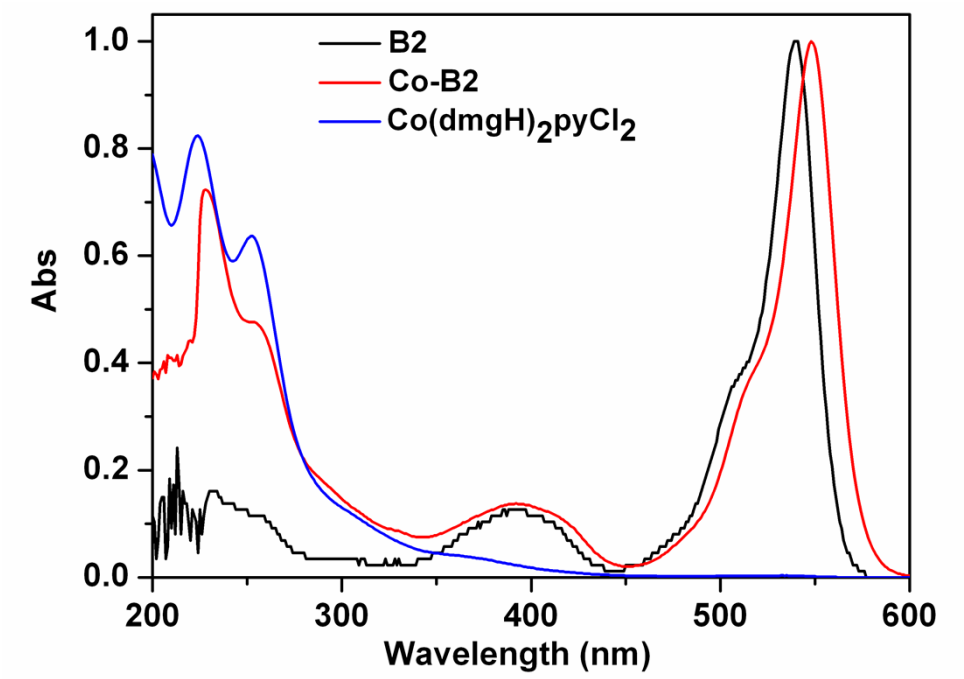
Complex	ΔG_1(eV)[a]	ΔG_2(eV)[b]
Co-B2	0.67	-0.25
Co-B4	0.55	-0.31

[a]The free energy of the formation of Co(I) species from ^{3}**BDP*** to the Co complex was calculated from the equation, $\Delta G_1 = E$(**BDP**$^{+\cdot}$/**BDP**) – E(Co^{II}/Co^{I}) – E(^{3}**BDP***). [b]The free energy of the formation of Co(I) species from **BDP**$^{-\cdot}$ to the Co complex was calculated from the equation, $\Delta G_2 = E$(**BDP**$^{-\cdot}$/**BDP**) – E(Co^{II}/Co^{I}).

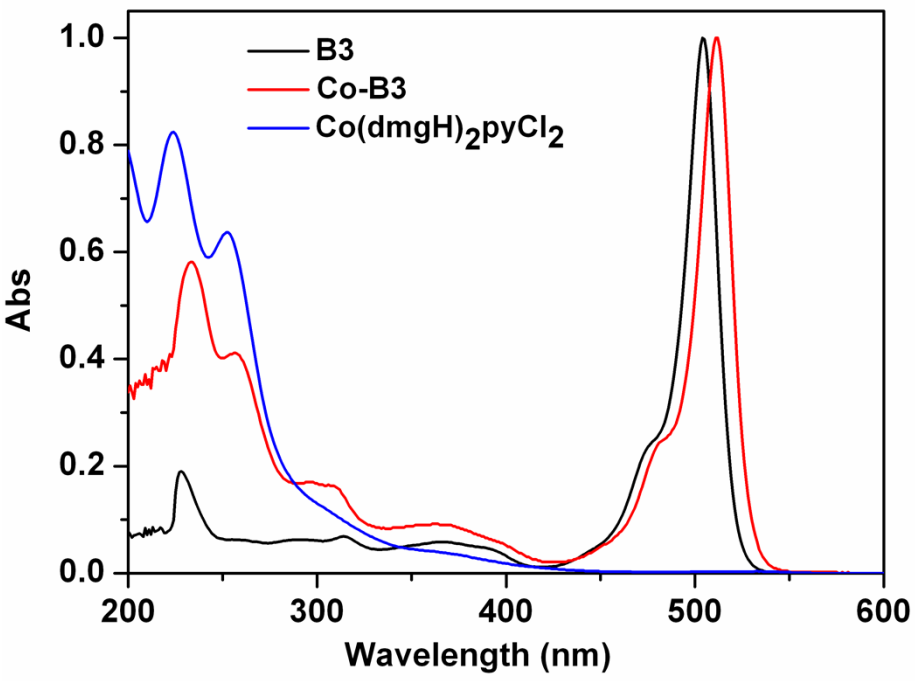
(a)


Co(dmgH)2pyCl2
B1
Co-B1
Abs
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
200
300
400
500
600

(b)


B2
Co-B2
Co(dmgH)2pyCl2
Abs
Wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
200
300
400
500
600

(c)



(d)

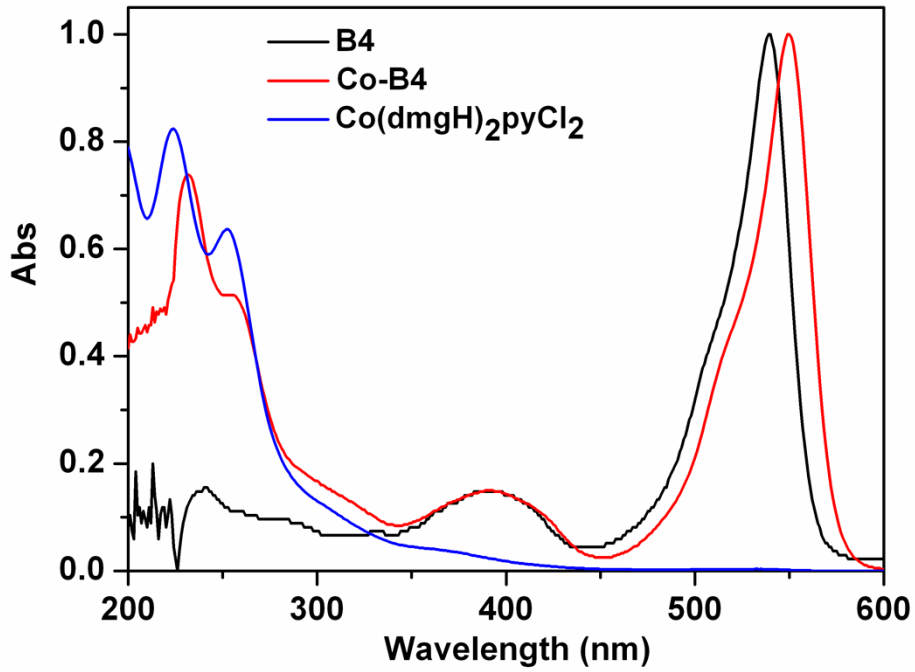


Figure S1. Absorption spectra of BODIPY derivatives **Bn** (n =1-4) and BODIPY-cobaloxime complexes **Co-Bn** (n = 1-4). c = 1.0 × 10^{-5} M in CH_3CN, at room temperature.

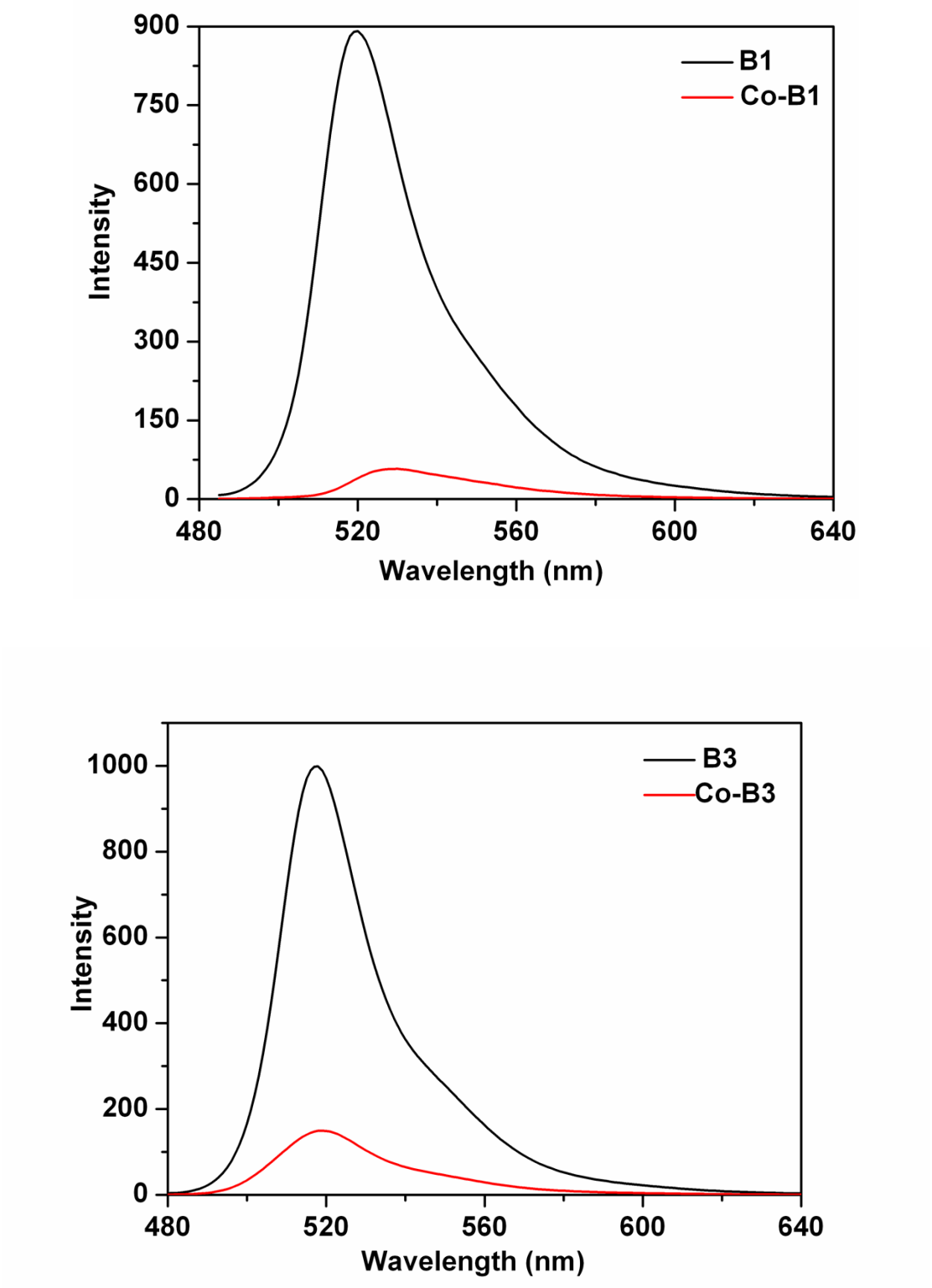


Figure S2. Fluorescence emission spectra of **B1** and **Co-B1** (top), and **B3** and **Co-B3** (bottom) in CH_3CN.

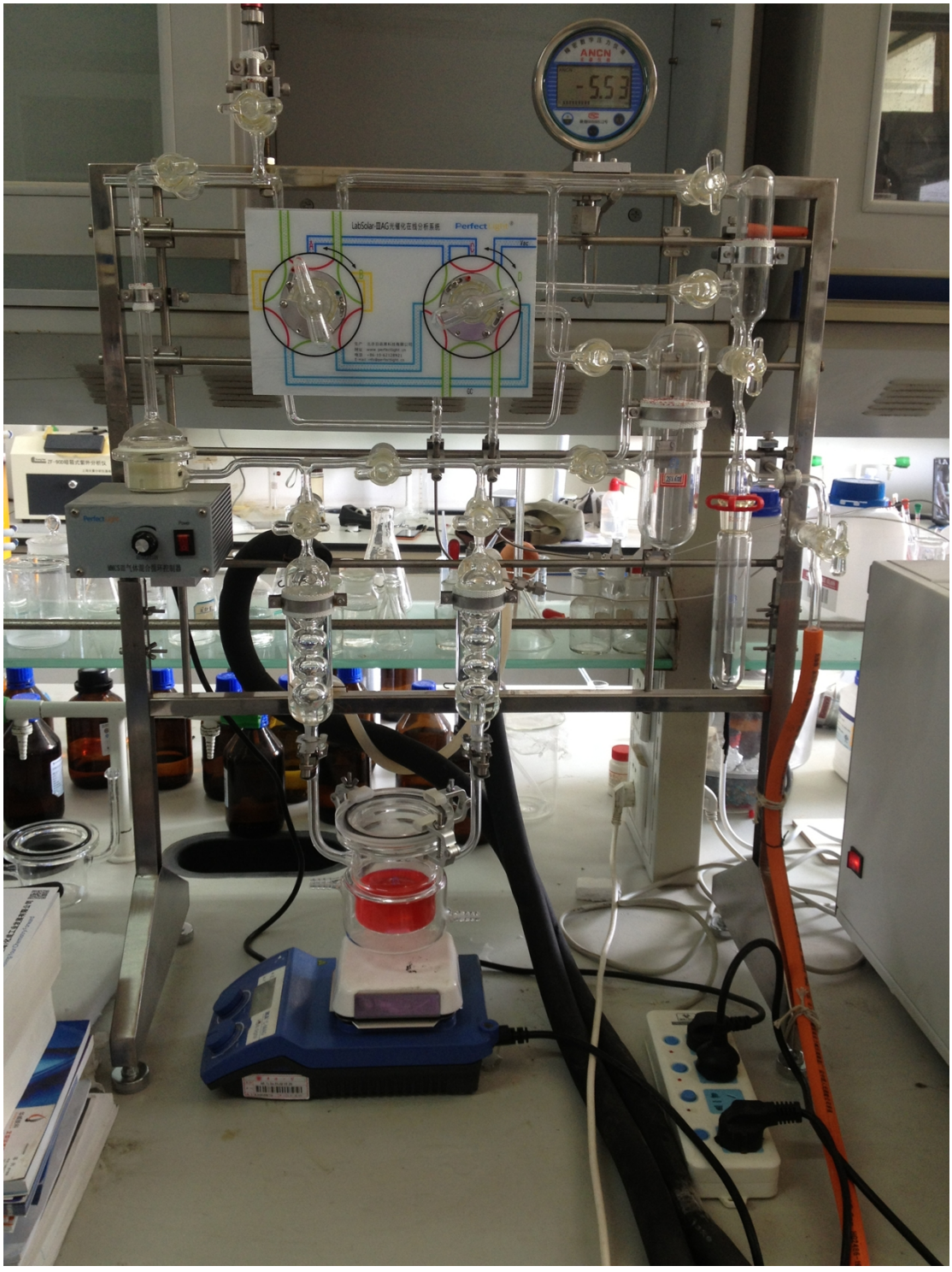
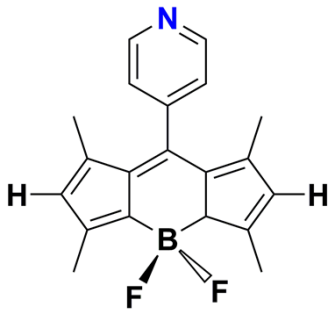


Figure S3. Pyrex top-irradiation reaction vessel connected to a glass closed gas circulation system.

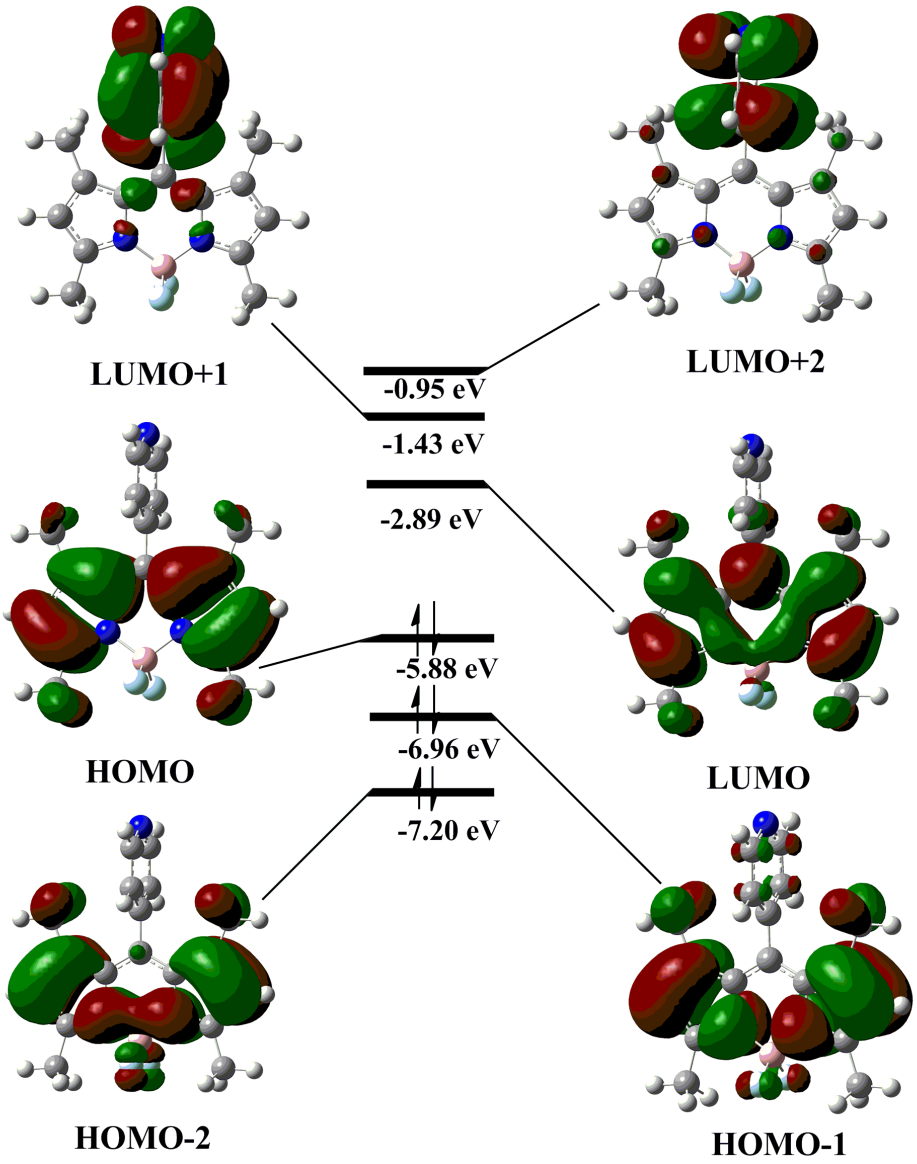
B1:



Optimized Geometry of B1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.215380	0.000270	1.144886
2	6	0	-2.820364	0.000269	1.198755
3	6	0	-2.098151	0.000092	0.000047
4	6	0	-2.820348	-0.000121	-1.198672
5	6	0	-4.215364	-0.000121	-1.144823
6	6	0	-0.602907	0.000055	0.000059
7	6	0	0.085121	-1.224796	0.000044
8	6	0	-0.376094	-2.583904	-0.000044
9	6	0	-1.776685	-3.123775	-0.000125
10	6	0	0.768882	-3.376801	0.000052
11	6	0	1.900045	-2.537512	0.000032
12	6	0	3.335510	-2.953188	0.000043
13	6	0	1.900308	2.537373	-0.000077
14	6	0	3.335820	2.952888	-0.000116
15	6	0	0.769240	3.376786	-0.000025
16	6	0	-0.375825	2.584016	-0.000091
17	6	0	-1.776344	3.124073	-0.000108
18	6	0	0.085237	1.224849	-0.000007
19	7	0	-4.916067	0.000078	0.000027
20	7	0	1.489888	-1.247504	-0.000027
21	7	0	1.490010	1.247410	-0.000060
22	5	0	2.402023	-0.000092	0.000032
23	9	0	3.230844	-0.000146	-1.147398
24	9	0	3.230625	-0.000121	1.147632
25	1	0	-4.795544	0.000408	2.065146
26	1	0	-2.311480	0.000411	2.158112
27	1	0	-2.311450	-0.000291	-2.158021
28	1	0	-4.795516	-0.000279	-2.065091
29	1	0	-1.746720	-4.217643	-0.000091
30	1	0	-2.342954	-2.801606	-0.880540

31	1	0	-2.343073	-2.801553	0.880190
32	1	0	0.798468	-4.459360	0.000083
33	1	0	3.860657	-2.569010	0.881707
34	1	0	3.860516	-2.569479	-0.881913
35	1	0	3.405653	-4.043919	0.000322
36	1	0	3.860953	2.568659	0.881533
37	1	0	3.406086	4.043611	0.000149
38	1	0	3.860753	2.569111	-0.882086
39	1	0	0.798947	4.459342	-0.000002
40	1	0	-1.746231	4.217937	-0.000169
41	1	0	-2.342699	2.802007	0.880288
42	1	0	-2.342732	2.801906	-0.880442



Excitation Energies and Oscillator Strengths：

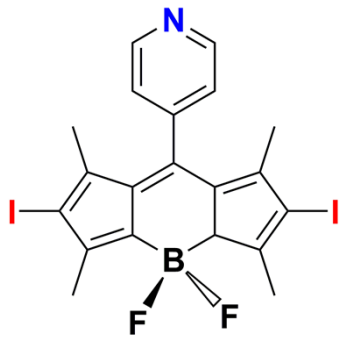
HOMO = 85

LUMO = 86

Triplets calculated separately

Excited State 1:	Triplet-A	1.5121 eV	819.96 nm	f=0.0000	<S**2>=2.000
85 -> 86	0.71036				
85 <- 86	0.11789				
Excited State 2:	Triplet-A	2.7212 eV	455.62 nm	f=0.0000	<S**2>=2.000
84 -> 86	0.69184				
Excited State 1:	Singlet-A	2.8665 eV	432.53 nm	f=0.5844	<S**2>=0.000
84 -> 86	0.12872				
85 -> 86	0.69836				
85 <- 86	-0.10516				
Excited State 2:	Singlet-A	3.3962 eV	365.07 nm	f=0.0727	<S**2>=0.000
84 -> 86	0.69320				
85 -> 86	-0.13163				
Excited State 3:	Singlet-A	3.6573 eV	339.01 nm	f=0.0490	<S**2>=0.000
83 -> 86	0.70389				
Excited State 4:	Singlet-A	3.7786 eV	328.12 nm	f=0.0000	<S**2>=0.000
85 -> 87	0.70594				
Excited State 5:	Singlet-A	4.0542 eV	305.82 nm	f=0.0021	<S**2>=0.000
81 -> 86	0.70640				
Excited State 6:	Singlet-A	4.1492 eV	298.82 nm	f=0.0000	<S**2>=0.000
82 -> 86	0.70618				
Excited State 7:	Singlet-A	4.3180 eV	287.14 nm	f=0.0090	<S**2>=0.000
85 -> 88	0.70182				
Excited State 8:	Singlet-A	4.4340 eV	279.62 nm	f=0.0000	<S**2>=0.000
79 -> 86	0.70502				
Excited State 9:	Singlet-A	4.8869 eV	253.71 nm	f=0.0056	<S**2>=0.000
82 -> 87	0.70474				
Excited State 10:	Singlet-A	4.8888 eV	253.61 nm	f=0.0020	<S**2>=0.000
84 -> 87	0.70424				

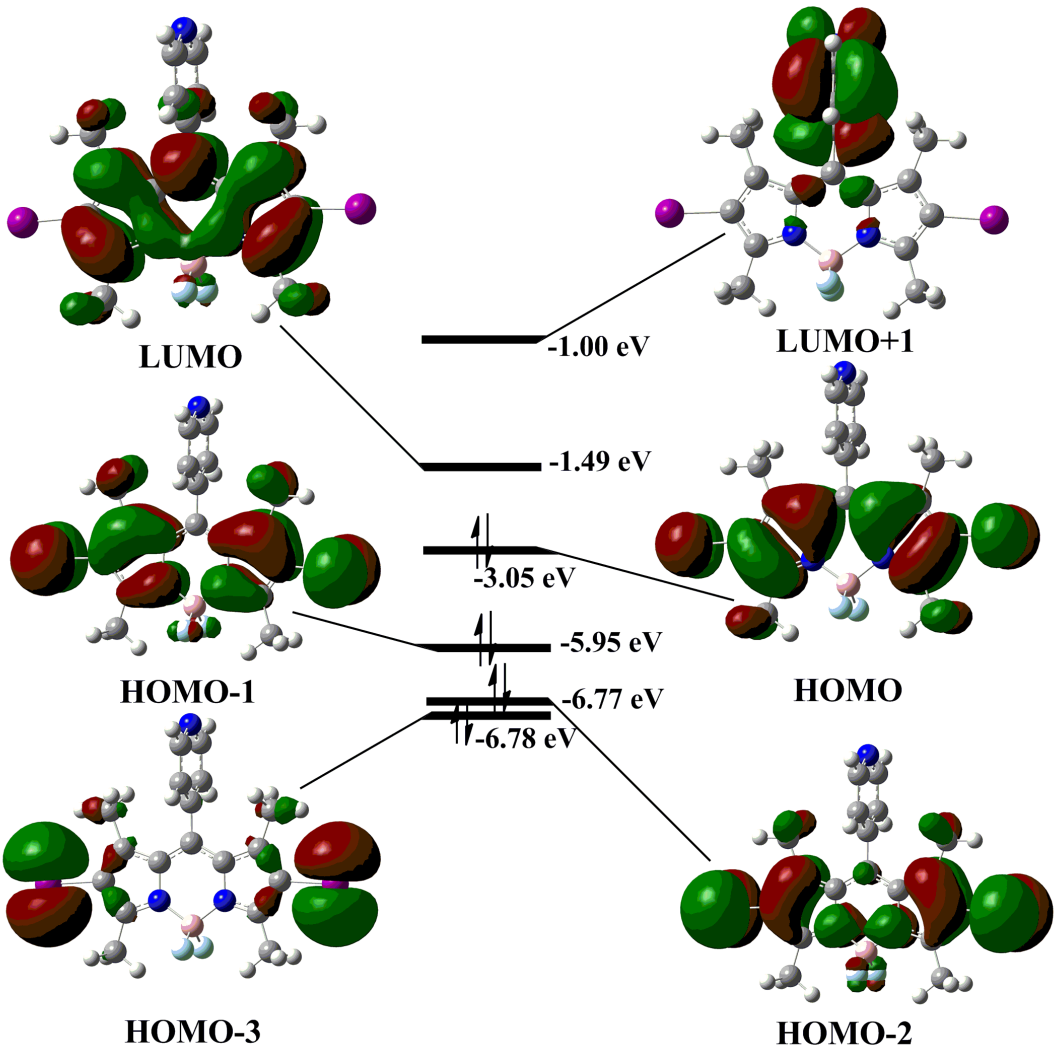
B2:



Optimized Geometry of B2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000061	4.545024	1.145624
2	6	0	0.000056	3.149703	1.199756
3	6	0	0.000012	2.428755	0.000225
4	6	0	-0.000007	3.149750	-1.199270
5	6	0	0.000024	4.545071	-1.145077
6	6	0	0.000000	0.933711	0.000227
7	6	0	-1.226373	0.246091	0.000148
8	6	0	-2.582529	0.716044	-0.000010
9	6	0	-3.087034	2.126733	-0.000086
10	6	0	-3.365869	-0.434861	-0.000075
11	53	0	-5.476433	-0.545485	-0.000320
12	6	0	-2.532377	-1.574108	0.000005
13	6	0	-2.952389	-3.006183	0.000016
14	6	0	2.532363	-1.574120	0.000413
15	6	0	2.952367	-3.006199	0.000384
16	6	0	3.365859	-0.434876	0.000135
17	53	0	5.476423	-0.545505	-0.000374
18	6	0	2.582523	0.716032	0.000026
19	6	0	3.087025	2.126721	-0.000248
20	6	0	1.226367	0.246082	0.000276
21	7	0	0.000051	5.244981	0.000286
22	7	0	-1.249117	-1.156623	0.000111
23	7	0	1.249104	-1.156631	0.000394
24	5	0	-0.000009	-2.070318	0.000502
25	9	0	0.000172	-2.890260	-1.148720
26	9	0	-0.000195	-2.889622	1.150209
27	1	0	0.000084	5.125387	2.065681
28	1	0	0.000074	2.640676	2.159005
29	1	0	-0.000033	2.640769	-2.158543
30	1	0	0.000019	5.125472	-2.065111
31	1	0	-4.179737	2.134182	0.000456
32	1	0	-2.747900	2.680257	-0.881482
33	1	0	-2.747002	2.680719	0.880657
34	1	0	-2.100815	-3.684962	0.000309
35	1	0	-3.569623	-3.219558	-0.881337
36	1	0	-3.570120	-3.219396	0.881056
37	1	0	2.100795	-3.684970	0.004105
38	1	0	3.573023	-3.218574	0.879542
39	1	0	3.566666	-3.220421	-0.882839
40	1	0	4.179728	2.134174	-0.000158
41	1	0	2.747361	2.680682	0.880655

42	1	0	2.747519	2.680269	-0.881483



Excitation Energies and Oscillator Strengths:

HOMO = 137

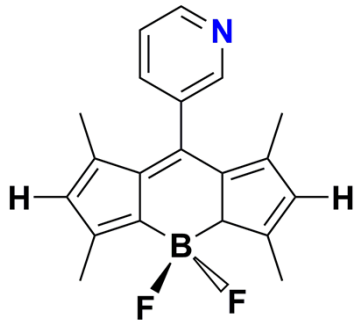
LUMO = 138

Triplets calculated separately

Excited State 1:	Triplet-A	1.5135 eV	819.19 nm	f=0.0000	<S**2>=2.000
136 ->138	-0.16847				
137 ->138	0.69352				
137 <-138	0.10477				
Excited State 2:	Triplet-A	2.4937 eV	497.19 nm	f=0.0000	<S**2>=2.000
128 ->138	0.12645				
136 ->138	0.66932				
137 ->138	0.15992				
Excited State 3:	Triplet-A	2.6454 eV	468.68 nm	f=0.0000	<S**2>=2.000
130 ->138	-0.11442				
135 ->138	0.68230				

Excited State 1:	Singlet-A	2.6570 eV	466.63 nm	f=0.5505	<S**2>=0.000
136 ->138	0.21358				
137 ->138	0.67552				
Excited State 2:	Singlet-A	3.1910 eV	388.54 nm	f=0.0527	<S**2>=0.000
135 ->138	0.70260				
Excited State 3:	Singlet-A	3.2292 eV	383.94 nm	f=0.3204	<S**2>=0.000
136 ->138	0.67141				
137 ->138	-0.21717				
Excited State 4:	Singlet-A	3.7906 eV	327.09 nm	f=0.0000	<S**2>=0.000
134 ->138	0.70607				
Excited State 5:	Singlet-A	3.8192 eV	324.64 nm	f=0.0000	<S**2>=0.000
133 ->138	0.69736				
137 ->139	0.11148				
Excited State 6:	Singlet-A	3.8248 eV	324.16 nm	f=0.0000	<S**2>=0.000
133 ->138	-0.11197				
137 ->139	0.69421				
Excited State 7:	Singlet-A	3.9236 eV	316.00 nm	f=0.0043	<S**2>=0.000
131 ->138	0.70575				
Excited State 8:	Singlet-A	4.0022 eV	309.79 nm	f=0.0001	<S**2>=0.000
132 ->138	0.70624				
Excited State 9:	Singlet-A	4.0194 eV	308.46 nm	f=0.0000	<S**2>=0.000
135 ->142	0.12800				
137 ->141	0.69047				
Excited State 10:	Singlet-A	4.2698 eV	290.37 nm	f=0.0000	<S**2>=0.000
129 ->138	0.70362				

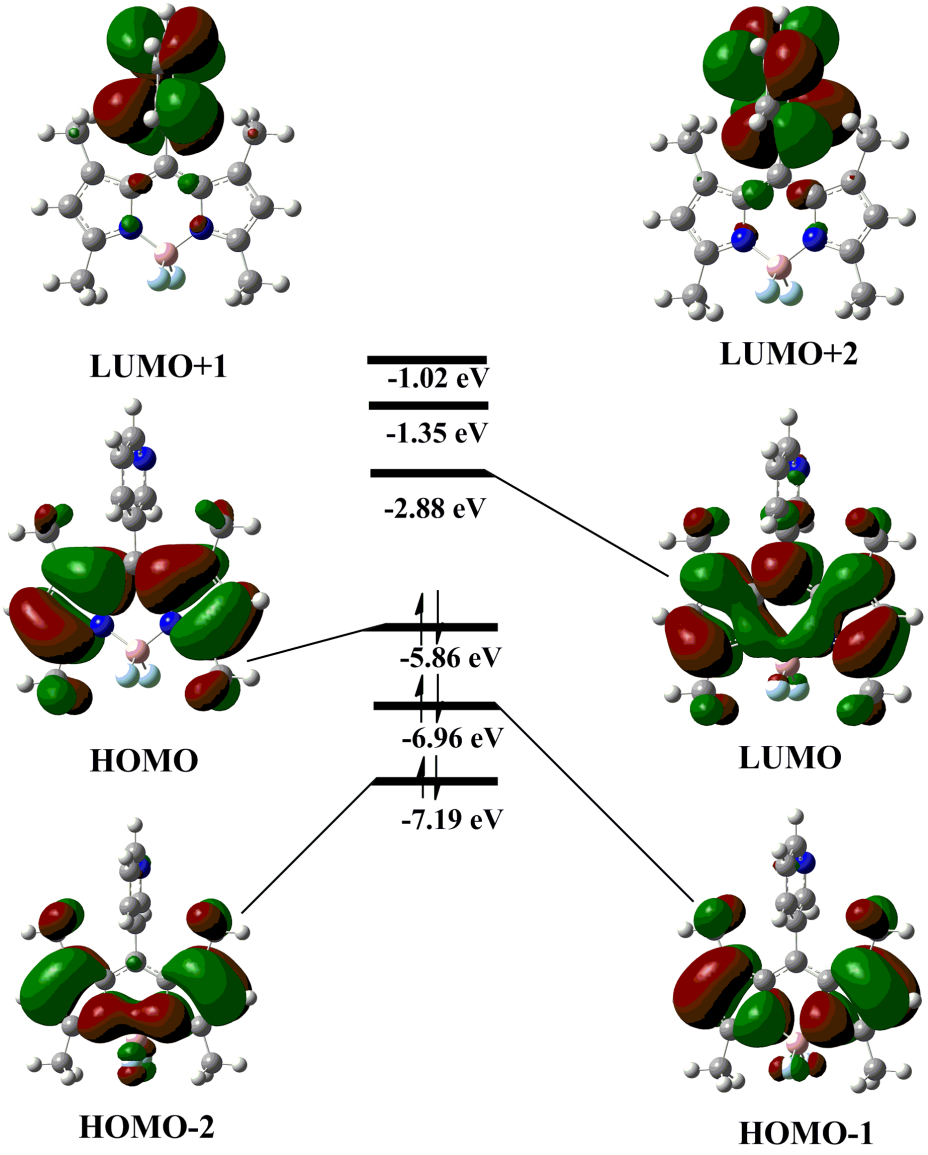
B3:



Optimized Geometry of B3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	2.399729	0.000001	0.004737
2	7	0	1.487762	1.247573	0.001422
3	7	0	1.487764	-1.247573	0.001446
4	7	0	-4.159598	0.000173	-1.250767

5	9	0	3.232879	-0.000009	-1.139488
6	9	0	3.224427	0.000013	1.155531
7	6	0	1.897558	2.537845	-0.002062
8	6	0	0.766040	3.376654	-0.002519
9	6	0	-0.378580	2.583036	0.001454
10	6	0	0.083104	1.224274	0.004400
11	6	0	3.332942	2.953914	-0.005183
12	6	0	-1.779695	3.121991	0.001264
13	6	0	-0.606653	-0.000002	0.008506
14	6	0	0.083107	-1.224275	0.004395
15	6	0	-0.378576	-2.583036	0.001381
16	6	0	0.766044	-3.376653	-0.002603
17	6	0	1.897561	-2.537844	-0.002057
18	6	0	3.332946	-2.953912	-0.005157
19	6	0	-1.779692	-3.121990	0.001116
20	6	0	-2.100049	-0.000004	0.017485
21	6	0	-2.821259	0.000166	-1.185104
22	6	0	-4.839633	0.000013	-0.093329
23	6	0	-4.219773	-0.000164	1.158142
24	6	0	-2.826539	-0.000178	1.213858
25	1	0	0.795238	4.459240	-0.005771
26	1	0	3.861201	2.566967	0.873398
27	1	0	3.402857	4.044665	-0.001625
28	1	0	3.855131	2.573335	-0.890200
29	1	0	-1.750489	4.215947	-0.003662
30	1	0	-2.345076	2.803821	0.883656
31	1	0	-2.347574	2.796522	-0.877146
32	1	0	0.795243	-4.459240	-0.005913
33	1	0	3.861204	-2.566931	0.873410
34	1	0	3.855136	-2.573367	-0.890188
35	1	0	3.402862	-4.044663	-0.001560
36	1	0	-1.750488	-4.215944	-0.004202
37	1	0	-2.347656	-2.796200	-0.877117
38	1	0	-2.344987	-2.804140	0.883681
39	1	0	-2.291848	0.000297	-2.135916
40	1	0	-5.924476	0.000028	-0.172771
41	1	0	-4.815799	-0.000289	2.065592
42	1	0	-2.309486	-0.000315	2.169616



Excitation Energies and Oscillator Strengths:

HOMO = 85

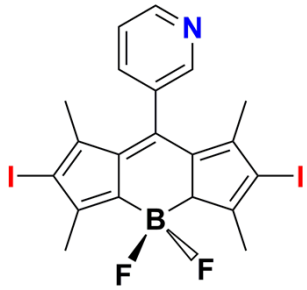
LUMO = 86

Triplets calculated separately

Excited State	1:	Triplet-A	1.5098 eV	821.17 nm	f=0.0000	<S**2>=2.000
85 -> 86		0.71043				
85 <- 86		0.11801				
Excited State	2:	Triplet-A	2.7254 eV	454.93 nm	f=0.0000	<S**2>=2.000
84 -> 86		0.69331				
Excited State	1:	Singlet-A	2.8635 eV	432.98 nm	f=0.5841	<S**2>=0.000
84 -> 86		0.12893				
85 -> 86		0.69850				
85 <- 86		-0.10524				
Excited State	2:	Singlet-A	3.4033 eV	364.30 nm	f=0.0732	<S**2>=0.000

84 -> 86	0.69311				
85 -> 86	-0.13192				
Excited State 3:	Singlet-A	3.6558 eV	339.14 nm	f=0.0417	<S**2>=0.000
83 -> 86	0.70400				
81 -> 87	-0.10368				
81 -> 88	0.51379				
85 -> 87	-0.27035				
Excited State 4:	Singlet-A	3.8866 eV	319.01 nm	f=0.0046	<S**2>=0.000
85 -> 87	0.70154				
Excited State 5:	Singlet-A	3.8945 eV	318.36 nm	f=0.0003	<S**2>=0.000
81 -> 86	0.70208				
Excited State 6:	Singlet-A	4.0765 eV	304.14 nm	f=0.0772	<S**2>=0.000
82 -> 86	0.69263				
Excited State 7:	Singlet-A	4.1948 eV	295.57 nm	f=0.0092	<S**2>=0.000
85 -> 88	0.70031				
Excited State 8:	Singlet-A	4.6509 eV	266.58 nm	f=0.0008	<S**2>=0.000
79 -> 86	0.70218				
Excited State 9:	Singlet-A	4.9146 eV	252.28 nm	f=0.0036	<S**2>=0.000
80 -> 87	0.11811				
82 -> 87	0.68128				
83 -> 87	0.13547				
Excited State 10:	Singlet-A	4.9323 eV	251.37 nm	f=0.2064	<S**2>=0.000
80 -> 86	0.66149				
85 -> 93	-0.20776				

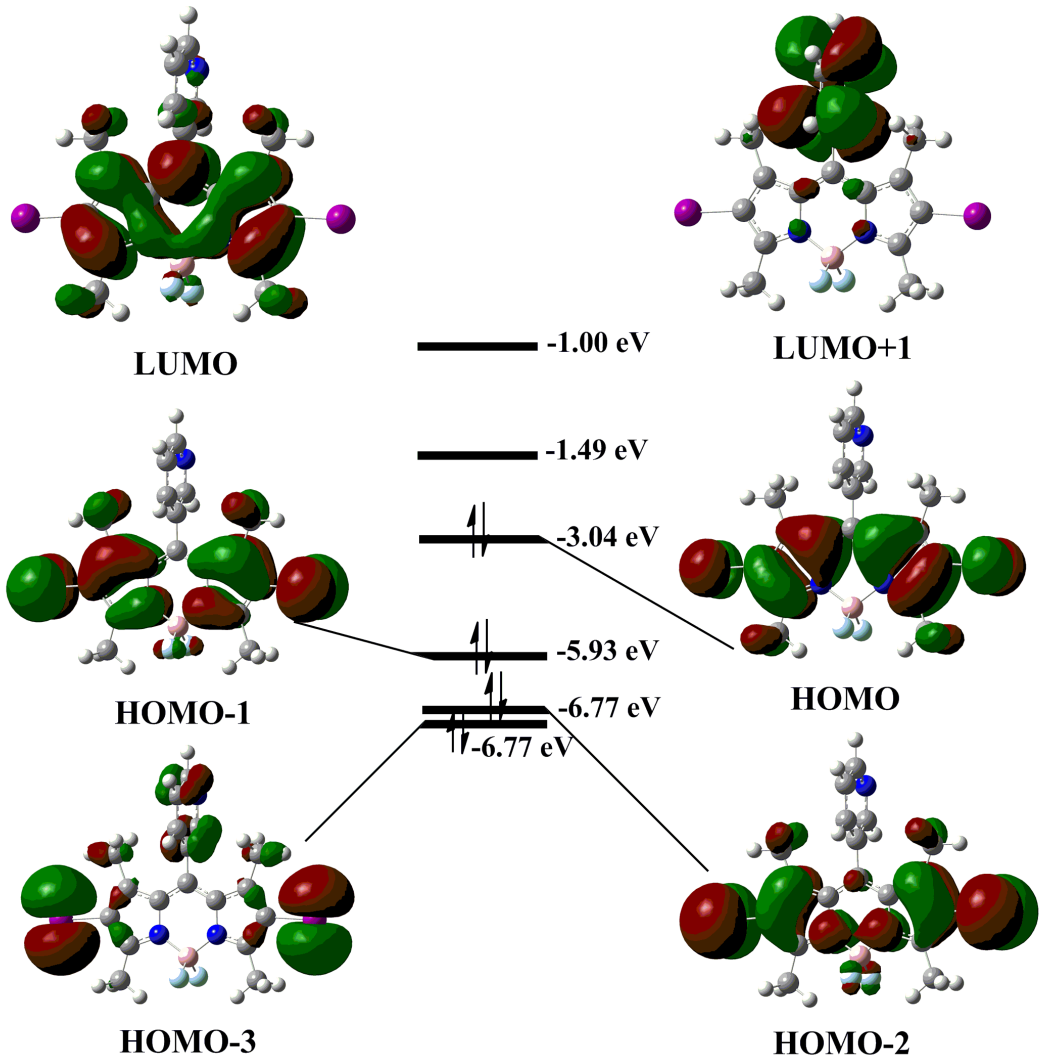
4.



Optimized Geometry of B3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	5	0	-0.000023	-2.069769	0.002486
2	7	0	1.249248	-1.156152	0.002027
3	7	0	-1.249282	-1.156134	0.002061
4	7	0	0.000247	4.487005	-1.251294
5	9	0	-0.000044	-2.890133	-1.146447
6	9	0	-0.000014	-2.888972	1.152493
7	6	0	2.532809	-1.573144	0.001150

8	6	0	3.365619	-0.433394	0.001610
9	53	0	5.476399	-0.542801	-0.001309
10	6	0	2.581502	0.717087	0.003553
11	6	0	1.225819	0.246394	0.004437
12	6	0	2.953454	-3.005078	-0.000965
13	6	0	3.084972	2.128373	0.004045
14	6	0	-0.000001	0.935700	0.008164
15	6	0	-1.225838	0.246414	0.004440
16	6	0	-2.581521	0.717116	0.003519
17	6	0	-3.365645	-0.433359	0.001604
18	53	0	-5.476426	-0.542746	-0.001321
19	6	0	-2.532846	-1.573115	0.001178
20	6	0	-2.953503	-3.005045	-0.000921
21	6	0	-3.084998	2.128400	0.003939
22	6	0	0.000031	2.428622	0.016890
23	6	0	0.000200	3.148731	-1.186499
24	6	0	0.000141	5.167363	-0.094014
25	6	0	-0.000015	4.547536	1.157997
26	6	0	-0.000075	3.154264	1.214048
27	1	0	2.102051	-3.684092	0.001999
28	1	0	3.574407	-3.218584	0.877726
29	1	0	3.567578	-3.217903	-0.884650
30	1	0	4.177744	2.136671	-0.000328
31	1	0	2.749074	2.680942	0.887229
32	1	0	2.742421	2.684027	-0.874921
33	1	0	-2.102104	-3.684065	0.001936
34	1	0	-3.567725	-3.217845	-0.884542
35	1	0	-3.574361	-3.218566	0.877834
36	1	0	-4.177768	2.136690	-0.000968
37	1	0	-2.742012	2.684184	-0.874768
38	1	0	-2.749548	2.680842	0.887378
39	1	0	0.000290	2.619366	-2.137319
40	1	0	0.000191	6.252123	-0.173708
41	1	0	-0.000090	5.143619	2.065310
42	1	0	-0.000193	2.637116	2.169707



Excitation Energies and Oscillator Strengths:

HOMO = 137

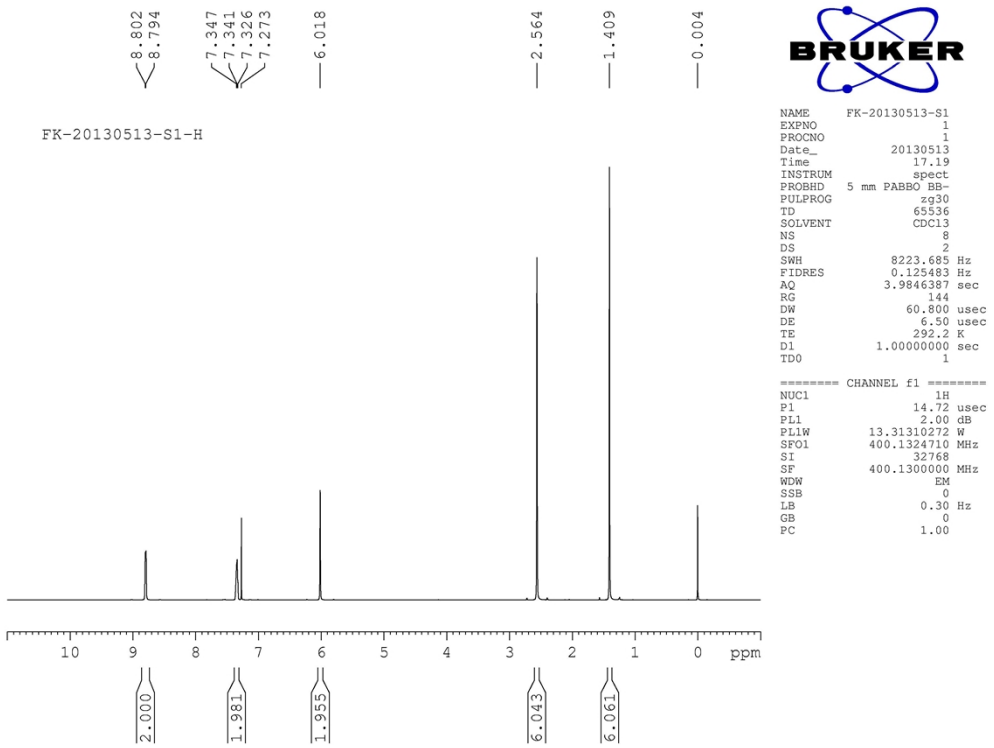
LUMO = 138

Triplets calculated separately

Excited State	1:	Triplet-A	1.5118 eV	820.09 nm	f=0.0000	<S**2>=2.000
136 ->138		0.16725				
137 ->138		0.69387				
137 <-138		0.10487				
Excited State	2:	Triplet-A	2.4982 eV	496.29 nm	f=0.0000	<S**2>=2.000
136 ->138		0.66966				
137 ->138		-0.15866				
Excited State	3:	Triplet-A	2.6490 eV	468.05 nm	f=0.0000	<S**2>=2.000
130 ->138		-0.11086				
135 ->138		0.68190				
Excited State	1:	Singlet-A	2.6569 eV	466.65 nm	f=0.5538	<S**2>=0.000
136 ->138		-0.21219				
137 ->138		0.67602				

Excited State 2:	Singlet-A	3.1937 eV	388.22 nm	f=0.0536	<S**2>=0.000
135 ->138	0.70231				
Excited State 3:	Singlet-A	3.2339 eV	383.39 nm	f=0.3185	<S**2>=0.000
136 ->138	0.67217				
137 ->138	0.21621				
Excited State 4:	Singlet-A	3.7419 eV	331.34 nm	f=0.0004	<S**2>=0.000
131 ->138	-0.38481				
134 ->138	0.58937				
Excited State 5:	Singlet-A	3.8254 eV	324.11 nm	f=0.0000	<S**2>=0.000
133 ->138	0.70628				
Excited State 6:	Singlet-A	3.8418 eV	322.72 nm	f=0.0003	<S**2>=0.000
131 ->138	0.58674				
134 ->138	0.38865				
Excited State 7:	Singlet-A	3.9271 eV	315.71 nm	f=0.0059	<S**2>=0.000
132 ->138	0.47605				
137 ->139	0.51909				
Excited State 8:	Singlet-A	3.9596 eV	313.13 nm	f=0.0495	<S**2>=0.000
132 ->138	0.51581				
137 ->139	-0.47331				
Excited State 9:	Singlet-A	3.9940 eV	310.43 nm	f=0.0052	<S**2>=0.000
137 ->140	0.70011				
Excited State 0:	Singlet-A	4.0252 eV	308.02 nm	f=0.0000	<S**2>=0.000
135 ->142	0.12724				
137 ->141	0.69209				

(a)



(b)

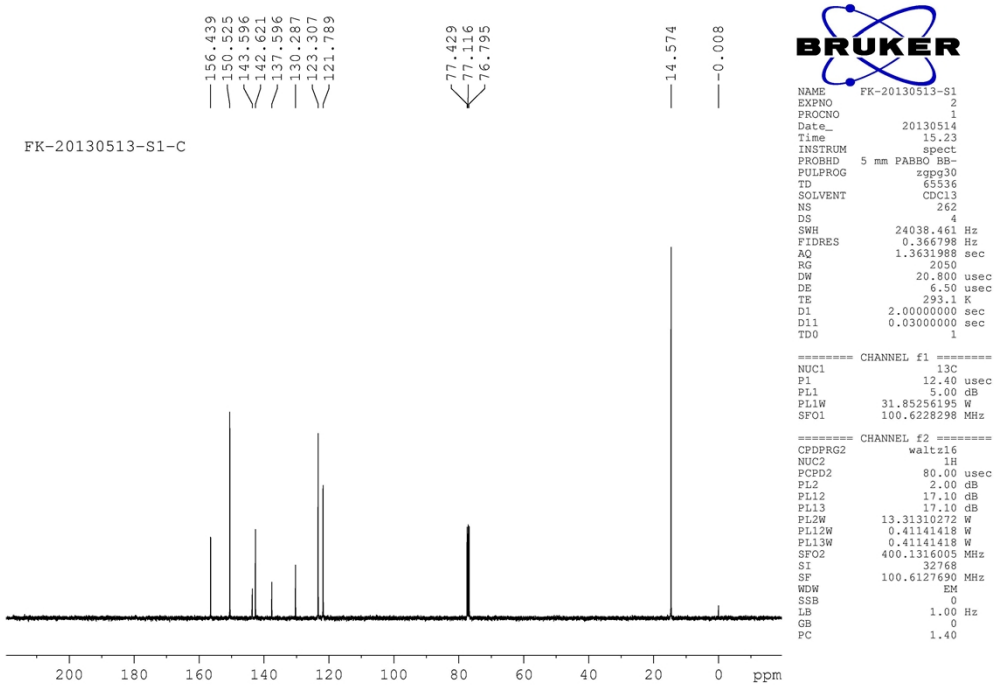
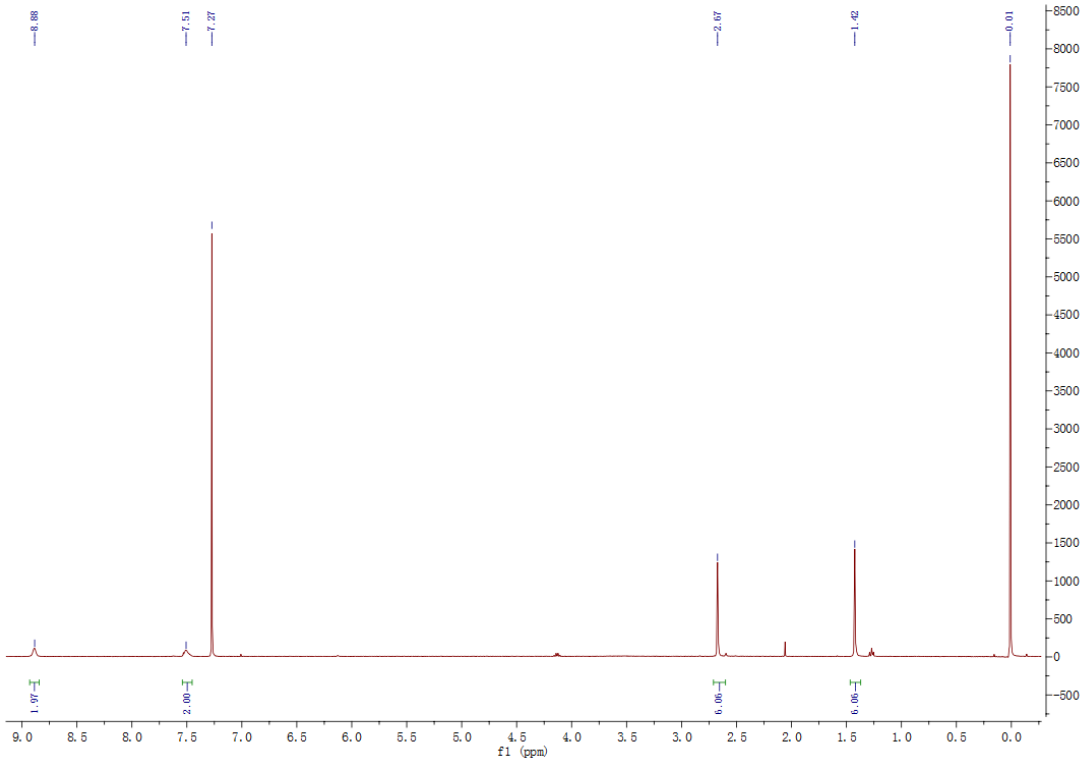
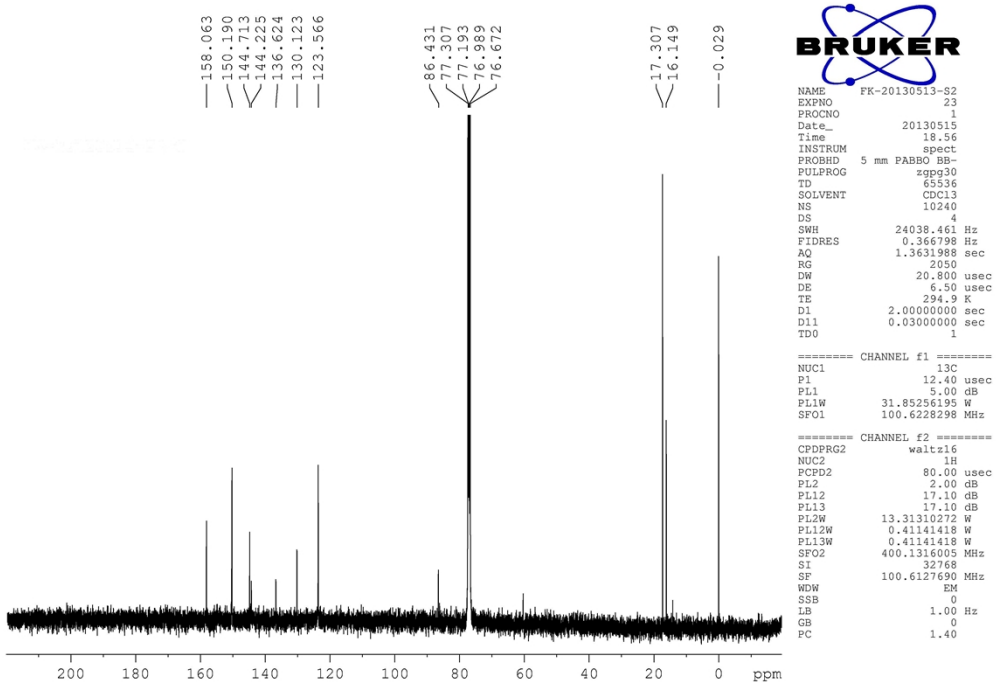


Figure S4. (a) ^{1}H NMR and (b)^{13}C NMR spectrum of **B1**.

(a)



(b)

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NAME          FK-20130513-S2
EXPNO                     23
PROCNO                     1
Date_               20130515
Time                   18.56
INSTRUM                spect
PROBHD    5 mm PABBO BB-
PULPROG              zgpg30
TD                    65536
SOLVENT                CDCl3
NS                     10240
DS                         4
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631988 sec
RG                      2050
DW                   20.800 usec
DE                    6.50 usec
TE                   294.9 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

========  CHANNEL f1 ========
NUC1                     13C
P1                     12.40 usec
PL1                     5.00 dB
PL1W             31.85256195 W
SFO1            100.6228298 MHz

========  CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                     1H
PCPD2                  80.00 usec
PL2                     2.00 dB
PL12                   17.10 dB
PL13                   17.10 dB
PL2W             13.31310272 W
PL12W             0.41141418 W
PL13W             0.41141418 W
SFO2            400.1316005 MHz
SI                       32768
SF              100.6127690 MHz
WDW                        EM
SSB                         0
LB                       1.00 Hz
GB                          0
PC                       1.40
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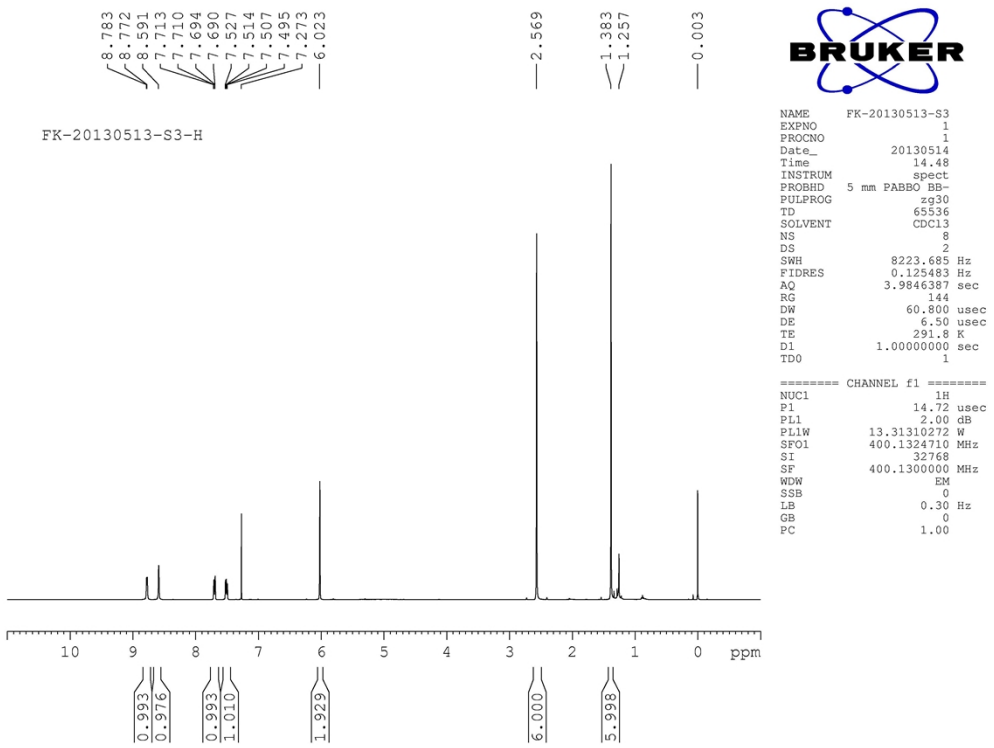
Figure S5. (a) ^{1}H NMR and (b)^{13}C NMR spectrum of **B2**.

(a)



(b)

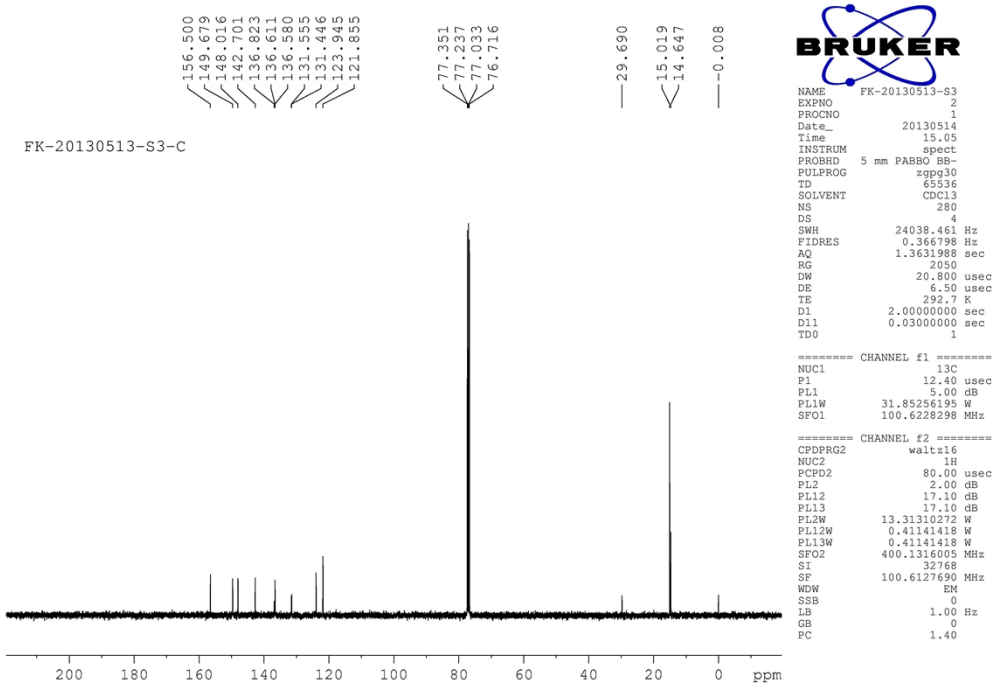
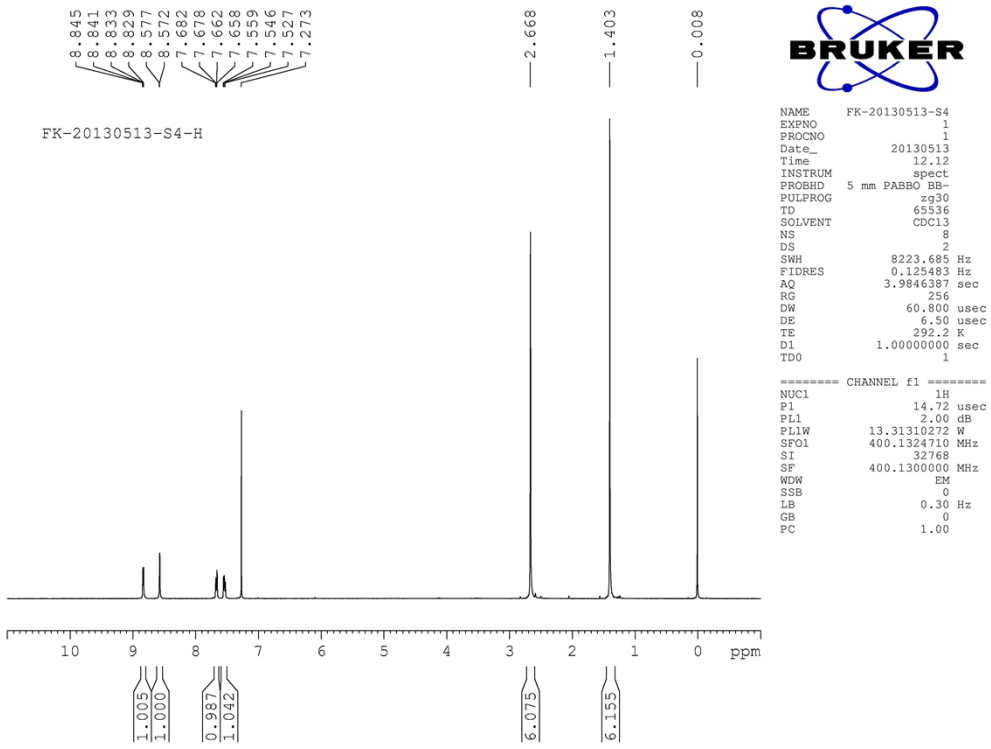


Figure S6. (a) ^{1}H NMR and (b)^{13}C NMR spectrum of **B3**.

(a)



(b)

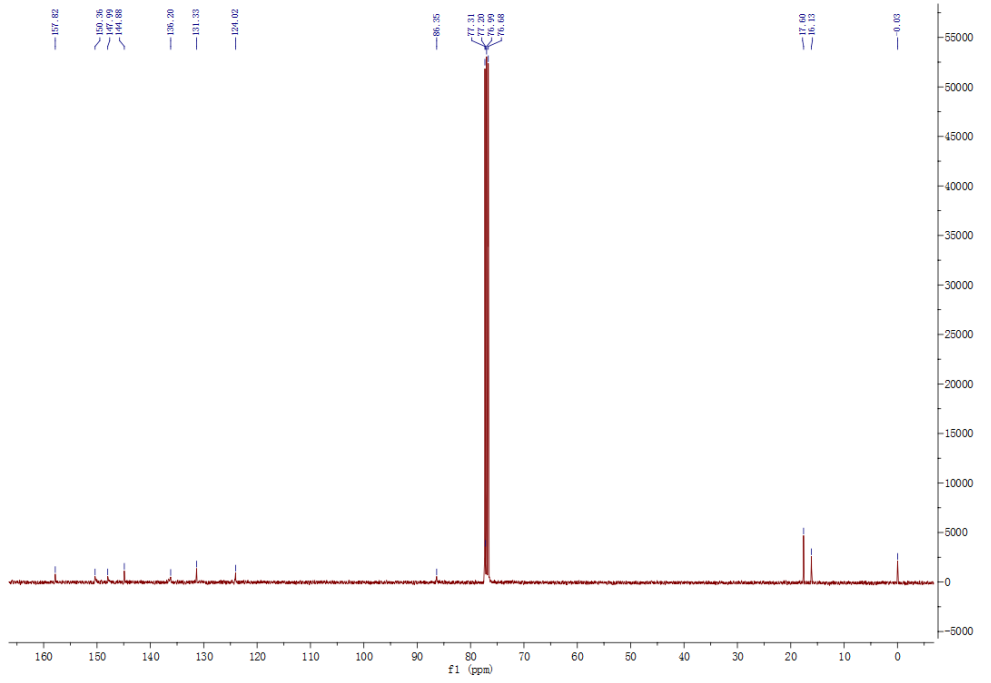
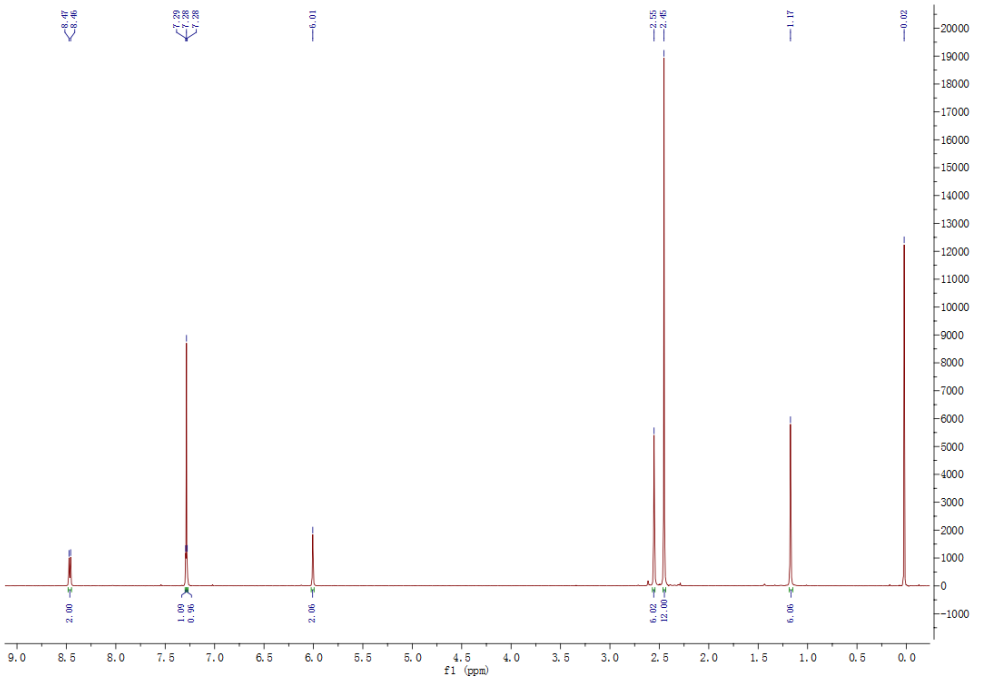


Figure S7. (a) ^{1}H NMR and (b)^{13}C NMR spectrum of **B4**.

(a)



(b)

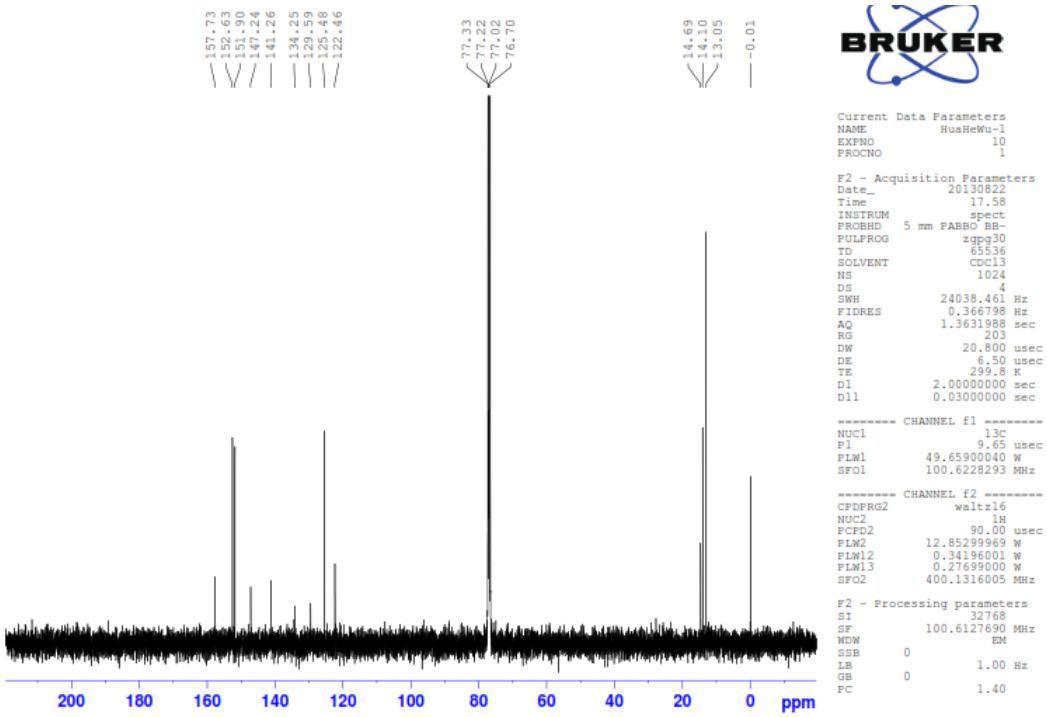
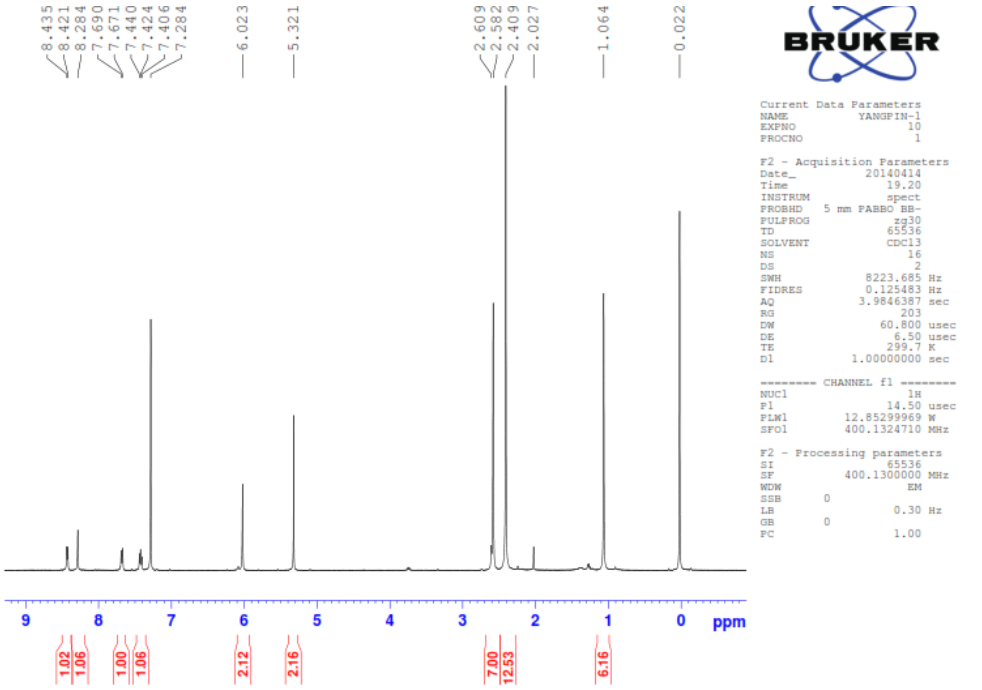


Figure S8. (a) ^{1}H NMR and (b)^{13}C NMR spectrum of **Co-B1**.

(a)



(b)

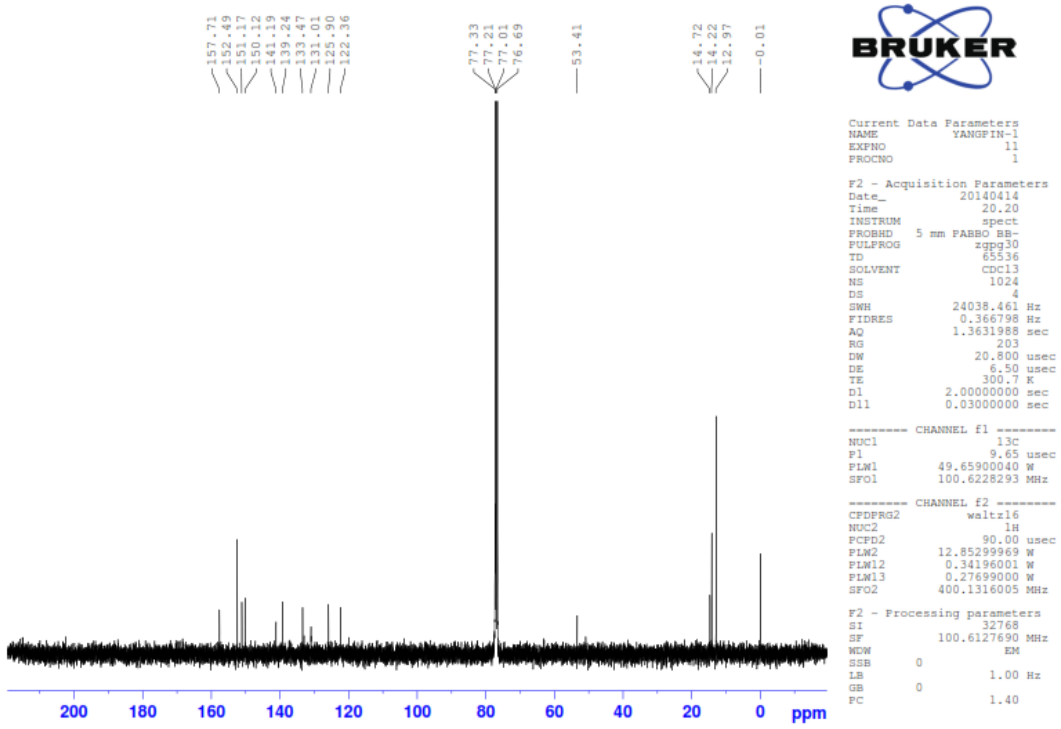


Figure S9. (a) ^{1}H NMR and (b)^{13}C NMR spectrum of **Co-B3**.

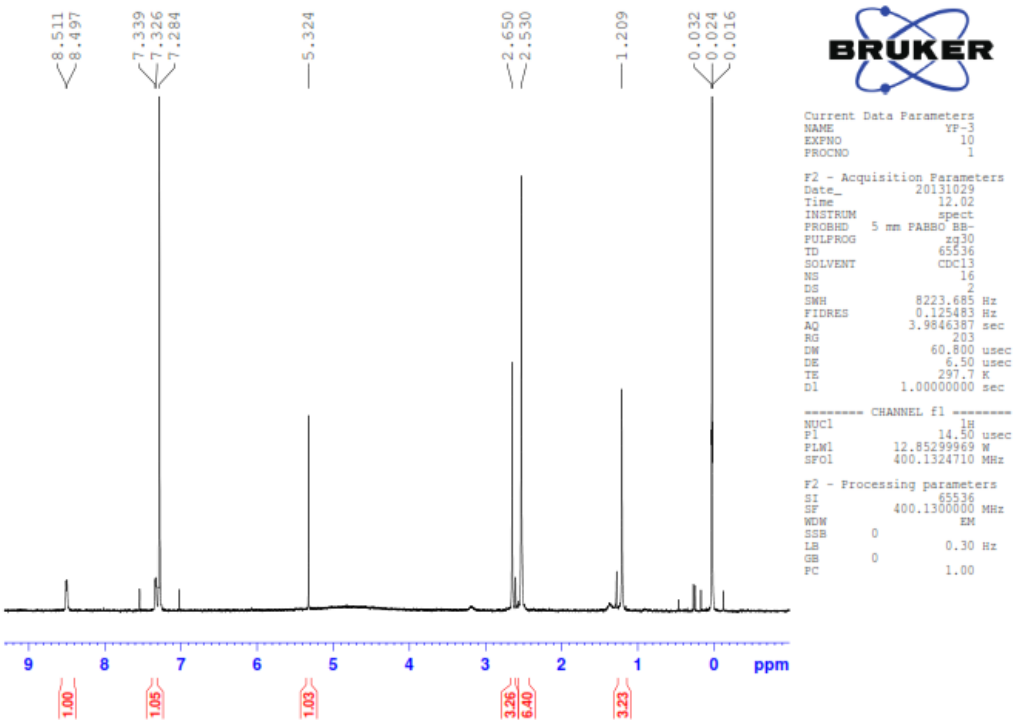


Figure S10. ^{1}H NMR spectrum of **Co-B2**.

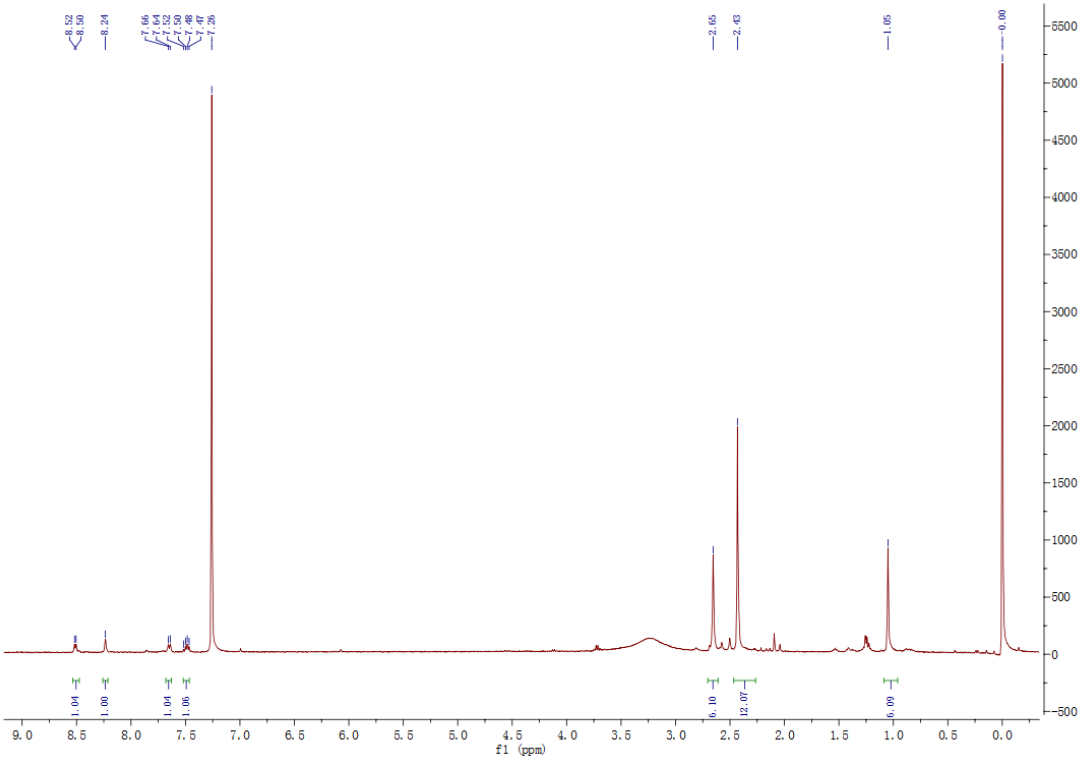


Figure S11. ^{1}H NMR spectrum of **Co-B4**.