Supplemental Material

for

Periphery-Fused Chiral A_2B-Type Subporphyrin

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Contents:

i. HR-MALDI-FT-ICR-MS Spectra

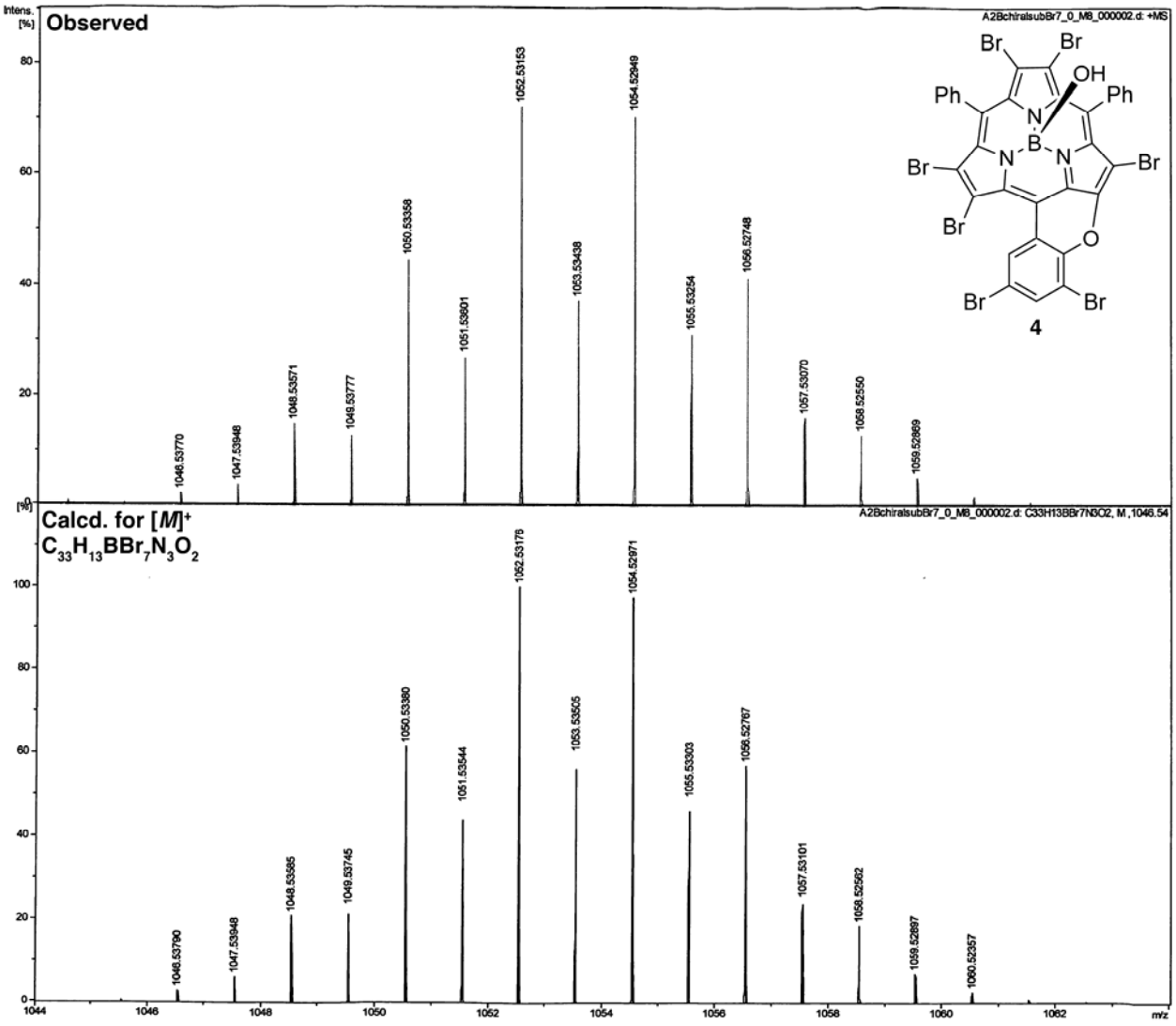


Figure S1. High-resolution mass spectrum of **4**, observed spectrum (top) and isotopic patterns calculated for $C_{33}H_{13}BBr_7N_3O_2$ as a $[M]^+$ ion (bottom).

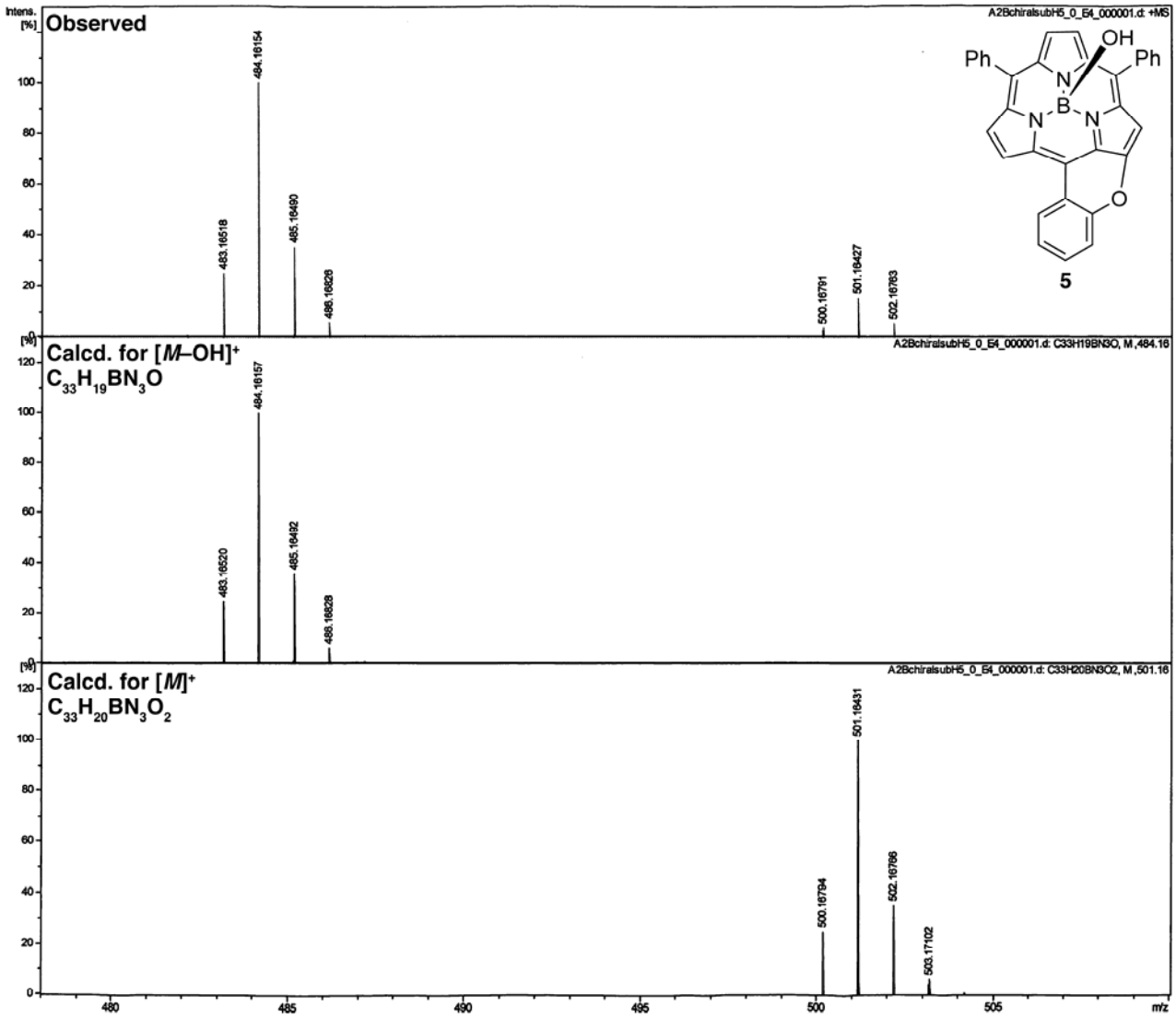


Figure S2. High-resolution mass spectrum of **5**, observed spectrum (top) and isotopic patterns calculated for $C_{33}H_{19}BN_3O$ as a $[M–OH]^+$ ion (middle) and $C_{33}H_{20}BN_3O_2$ as a $[M]^+$ ion (bottom).

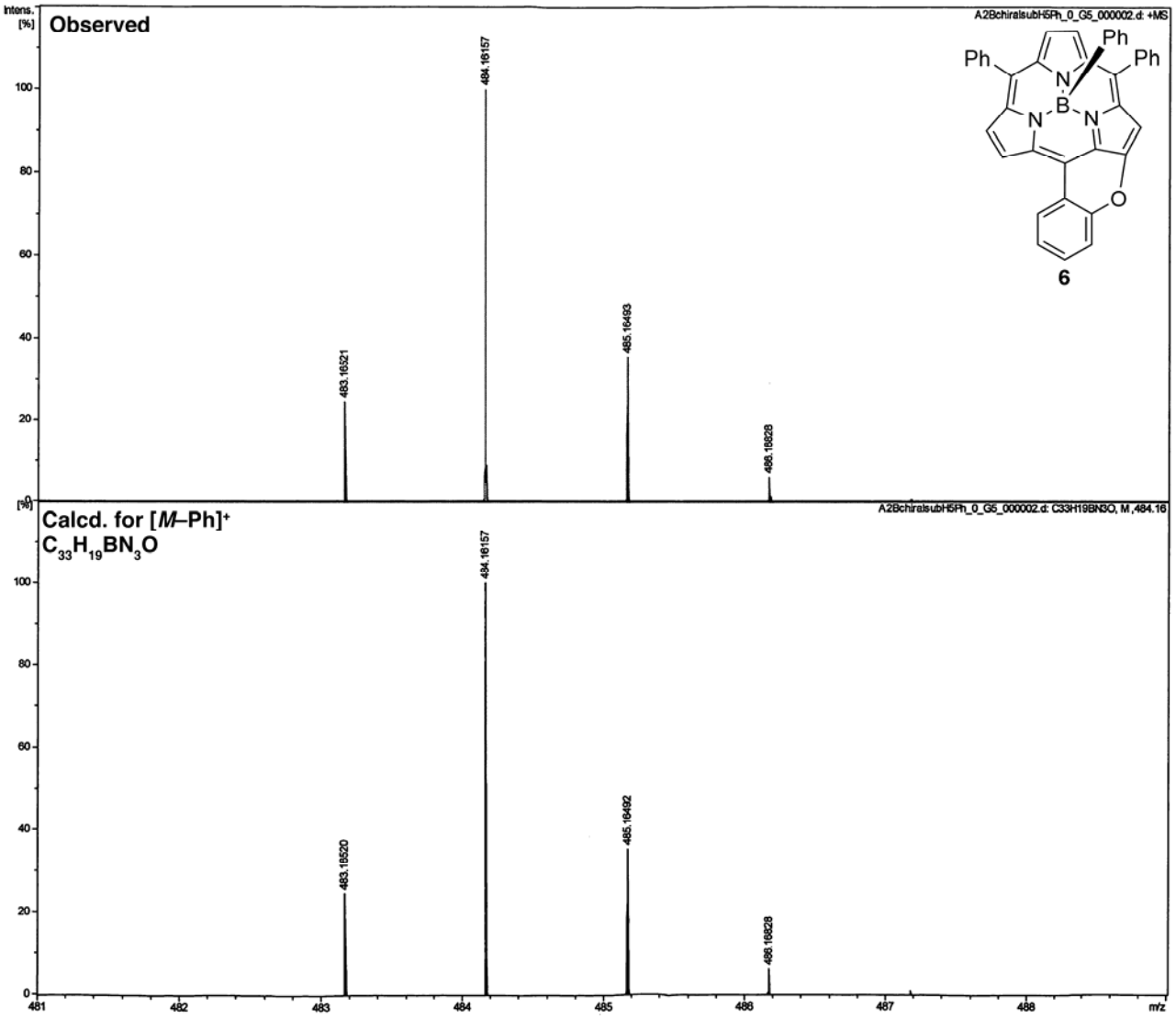


Figure S3. High-resolution mass spectrum of **6**, observed spectrum (top) and isotopic patterns calculated for $C_{33}H_{19}BN_3O$ as a $[M–Ph]^+$ ion (bottom).

ii. ^{1}H NMR Spectra

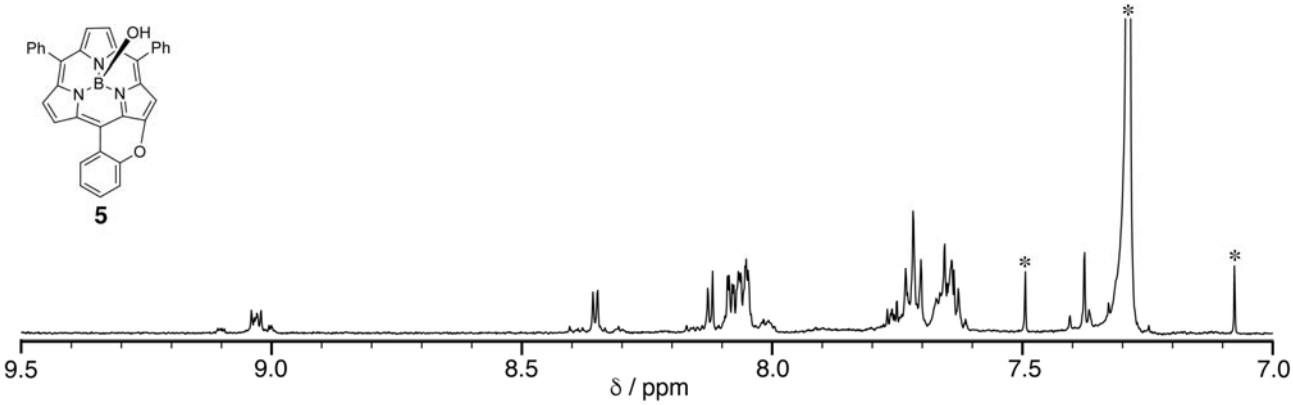


Figure S4. ^{1}H NMR spectrum of **5** in $CDCl_3$. ∗ indicates residual solvent signals.

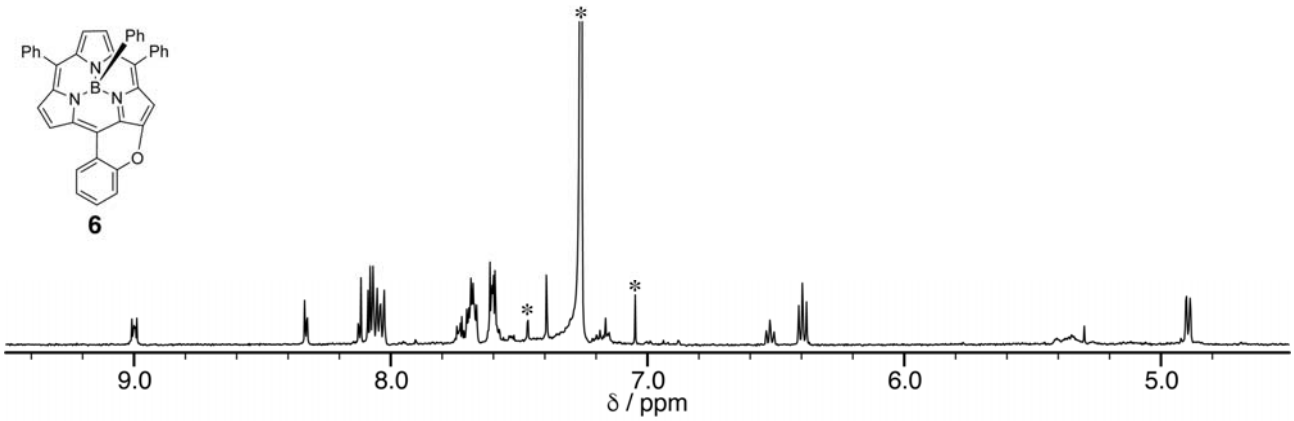


Figure S5. ^{1}H NMR spectrum of **6** in $CDCl_3$. ∗ indicates residual solvent signals.

iii. Racemization of 5 at 40 °C

After chiral resolution of **5**, the CD spectrum was measured. Because of the incomplete separation and racemization during removing solvent from the eluted fraction, the CD intensities were relatively low compared with those of **4** and **6**. By heating the sample solution at 40 °C, the CD intensities gradually decreased due to racemization in solution.

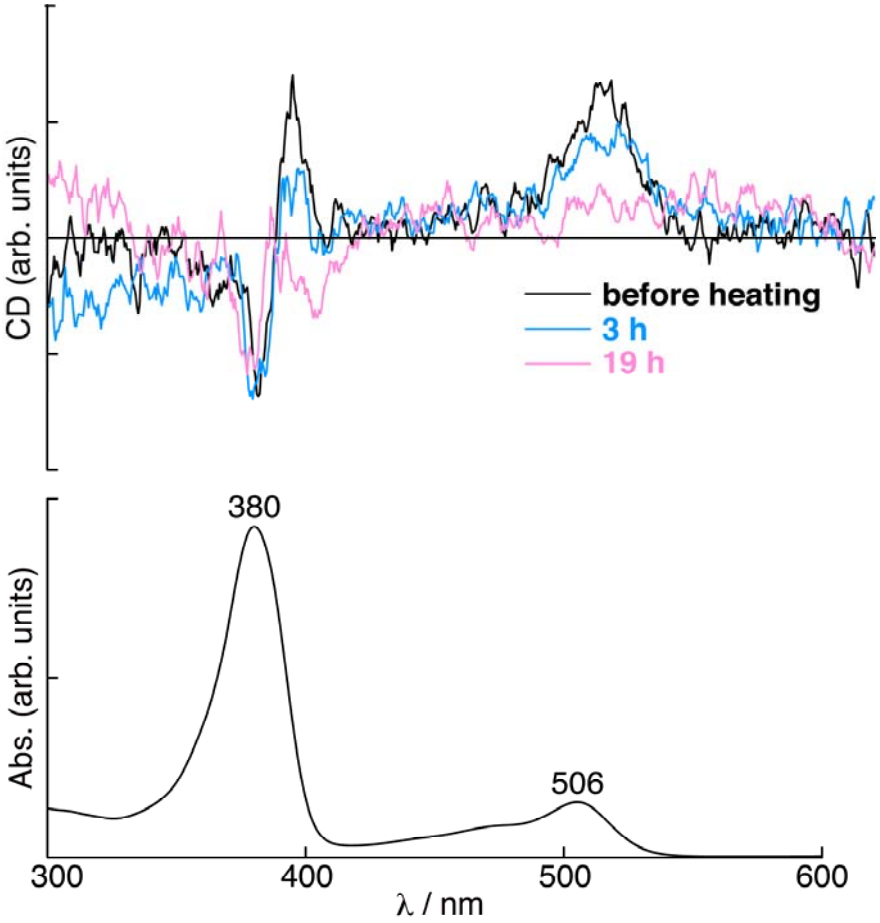


Figure S6. CD (top) and UV/vis absorption (bottom) spectra of **5** in CH_2Cl_2 after chiral resolution (black line) and after heating at 40 °C for 3 h (aqua blue line) and 19 h (pink line).

iv. Theoretical Calculations

Table S1. Selected transition wavelengths, oscillator strengths, rotatory strengths, and major contributions of **4'** calculated by the TDDFT method at the B3LYP/6-311G(d,p) level.

No.	wavelength [nm]	f[a]	R (velocity)[b]	Major contributions[d]
1	478	0.14	2.0 (**4'*P***)[c]	H–1→L+1 (19%), HOMO→LUMO (77%)
			–2.0 (**4'*M***)[c]	
2	463	0.02	–0.3 (**4'*P***)	H–1→LUMO (38%), HOMO→L+1 (59%)
			0.3 (**4'*M***)	
3	401	0.05	–9.6 (**4'*P***)	H–2→LUMO (67%), H–2→L+1 (12%), H–1→L+1 (12%)
			9.6 (**4'*M***)	
4	389	0.13	6.3 (**4'*P***)	H–3→LUMO (34%), H–2→LUMO (11%), H–2→L+1 (19%), H–1→LUMO (20%)
			–6.3 (**4'*M***)	
5	384	0.07	36.7 (**4'*P***)	H–3→LUMO (56%), H–2→L+1 (19%)
			–36.7 (**4'*M***)	
6	373	0.01	–1.1 (**4'*P***)	H–6→LUMO (12%), H–4→LUMO (64%)
			1.1 (**4'*M***)	
7	365	0.11	–26.1 (**4'*P***)	H–5→LUMO (50%), H–3→L+1 (25%)
			26.1 (**4'*M***)	
8	361	0.53	57.2 (**4'*P***)	H–3→L+1 (25%), H–1→L+1 (36%), HOMO→LUMO (12%)
			–57.2 (**4'*M***)	
9	357	0.16	–21.7 (**4'*P***)	H–5→LUMO (12%), H–4→L+1 (13%), H–3→L+1 (33%), H–2→L+1 (12%)
			21.7 (**4'*M***)	
10	354	0.52	–22.3 (**4'*P***)	H–5→LUMO (22%), H–3→L+1 (10%), H–2→L+1 (20%), H–1→LUMO (13%)
			22.3 (**4'*M***)	
11	351	0.08	–30.5 (**4'*P***)	H–6→LUMO (66%)
			30.5 (**4'*M***)	
12	347	0.12	–23.0 (**4'*P***)	H–6→L+1 (14%), H–4→LUMO (13%), H–4→L+1 (46%)
			23.0 (**4'*M***)	

[a] Oscillator strength. [b] Rotatory strength [10^{-40} erg•esu•cm•G^{-1}]. [c] **4'*P*** and **4'*M*** denote ***P*** and ***M*** isomers, respectively.
[d] H and L denote the HOMO and LUMO, respectively.

Table S2. Selected transition wavelengths, oscillator strengths, rotatory strengths, and major contributions of **6'** calculated by the TDDFT method at the B3LYP/6-311G(d,p) level.

No.	wavelength [nm]	f[a]	R (velocity)[b]	Major contributions[d]
1	477	0.16	7.57 (**6'*P***)[c]	H–1→L+1 (18%), HOMO→LUMO (80%)
			–7.57 (**6'*M***)[c]	
2	461	0.09	5.36 (**6'*P***)	H–1→LUMO (28%), HOMO→L+1 (70%)
			–5.36 (**6'*M***)	
3	365	0.61	25.9 (**6'*P***)	H–2→L+1 (12%), H–1→LUMO (52%), HOMO→L+1 (22%)
			–25.9 (**6'*M***)	
4	361	0.43	–14.3 (**6'*P***)	H–2→LUMO (14%), H–1→L+1 (56%), HOMO→LUMO (12%)
			14.3 (**6'*M***)	
5	342	0.21	–13.2 (**6'*P***)	H–2→LUMO (55%), H–2→L+1 (23%), H–1→L+1 (13%)
			13.2 (**6'*M***)	
6	335	0.16	–36.0 (**6'*P***)	H–3→LUMO (13%), H–2→LUMO (21%), H–2→L+1 (51%)
			36.0 (**6'*M***)	

[a] Oscillator strength. [b] Rotatory strength [10^{-40} erg•esu•cm•G^{-1}]. [c] **6'*P*** and **6'*M*** denote ***P*** and ***M*** isomers, respectively.
[d] H and L denote the HOMO and LUMO, respectively.

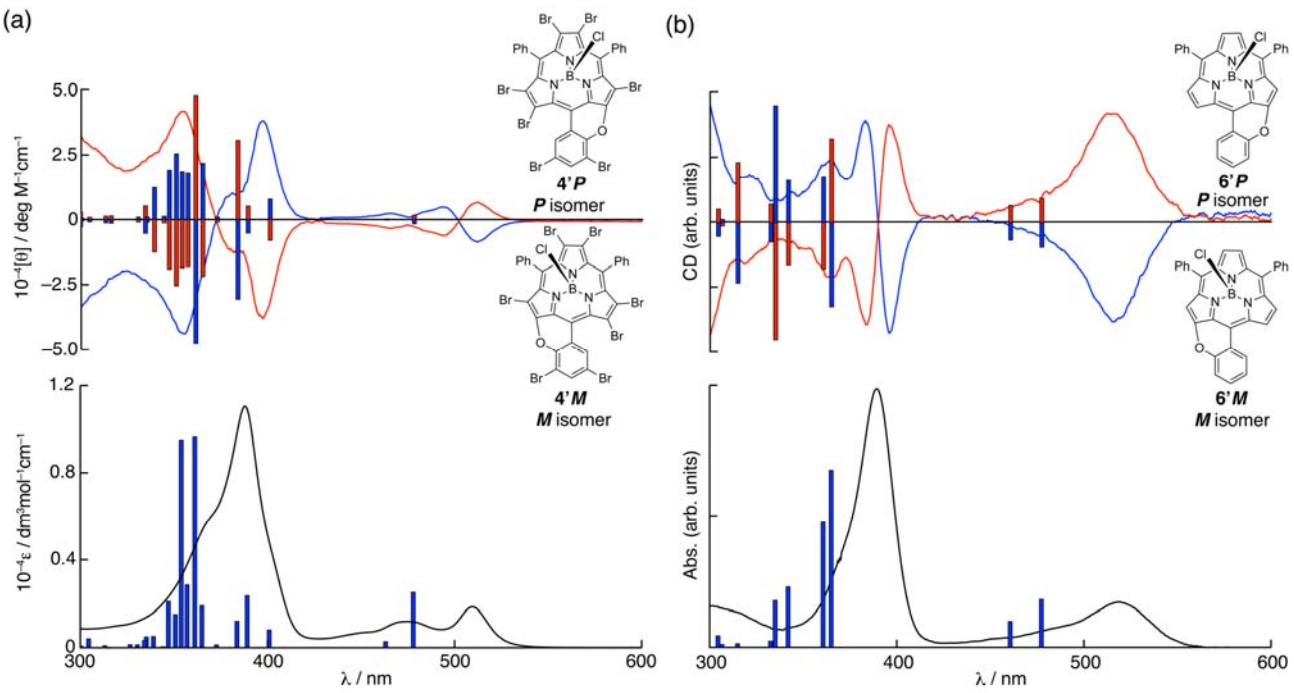
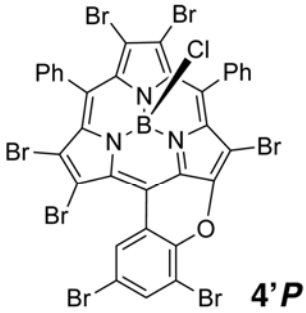


Figure S7. Theoretical absorption and CD spectra of the ***P*** (red bars) and ***M*** (blue bars) isomers of (a) **4'** and (b) **6'** calculated by the TDDFT method at the B3LYP/6-311G(d,p) level. The observed absorption and CD spectra of **4** and **6** are overlapping (**4Fr1** and **6Fr1**: blue line and **4Fr2** and **6Fr2**: red line).

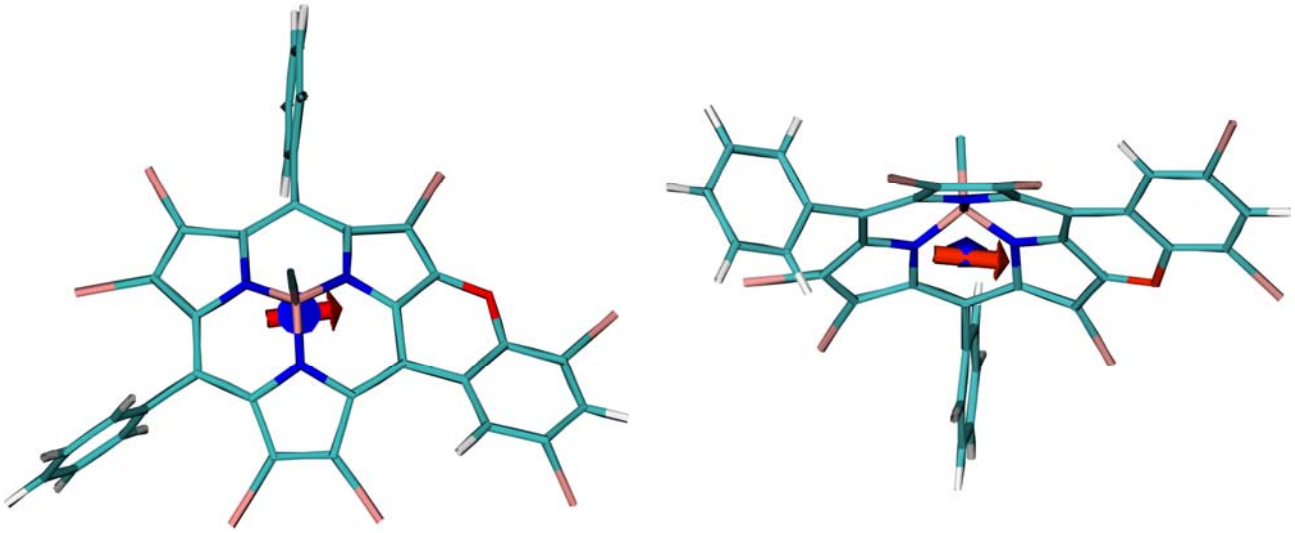
v. Analyses of Transition Dipole Moments

Transition electric (TEDM) and transition magnetic (TMDM) dipole moments were generated from the TDDFT data by Multiwfn (Lu T.; Chen F., Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580–592.) and visualized by VMD (Humphrey, W.; Dalke, A.; Schulten, K., VMD - Visual Molecular Dynamic. *J. Molec. Graphics* **1996**, *14*, 33–38.).



4'*P*

1st transition (λ = 478 nm)



2nd transition (λ = 463 nm)

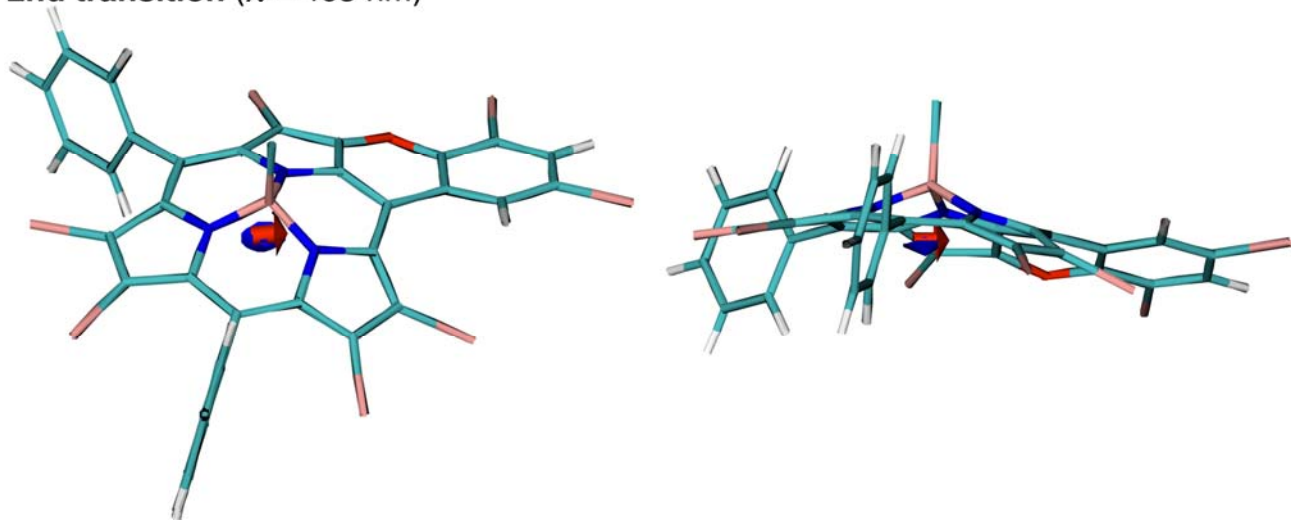


Figure S8. TEDM (red arrow) and TMDM (blue arrow) of **4'*P***, top view: left and side view: right.

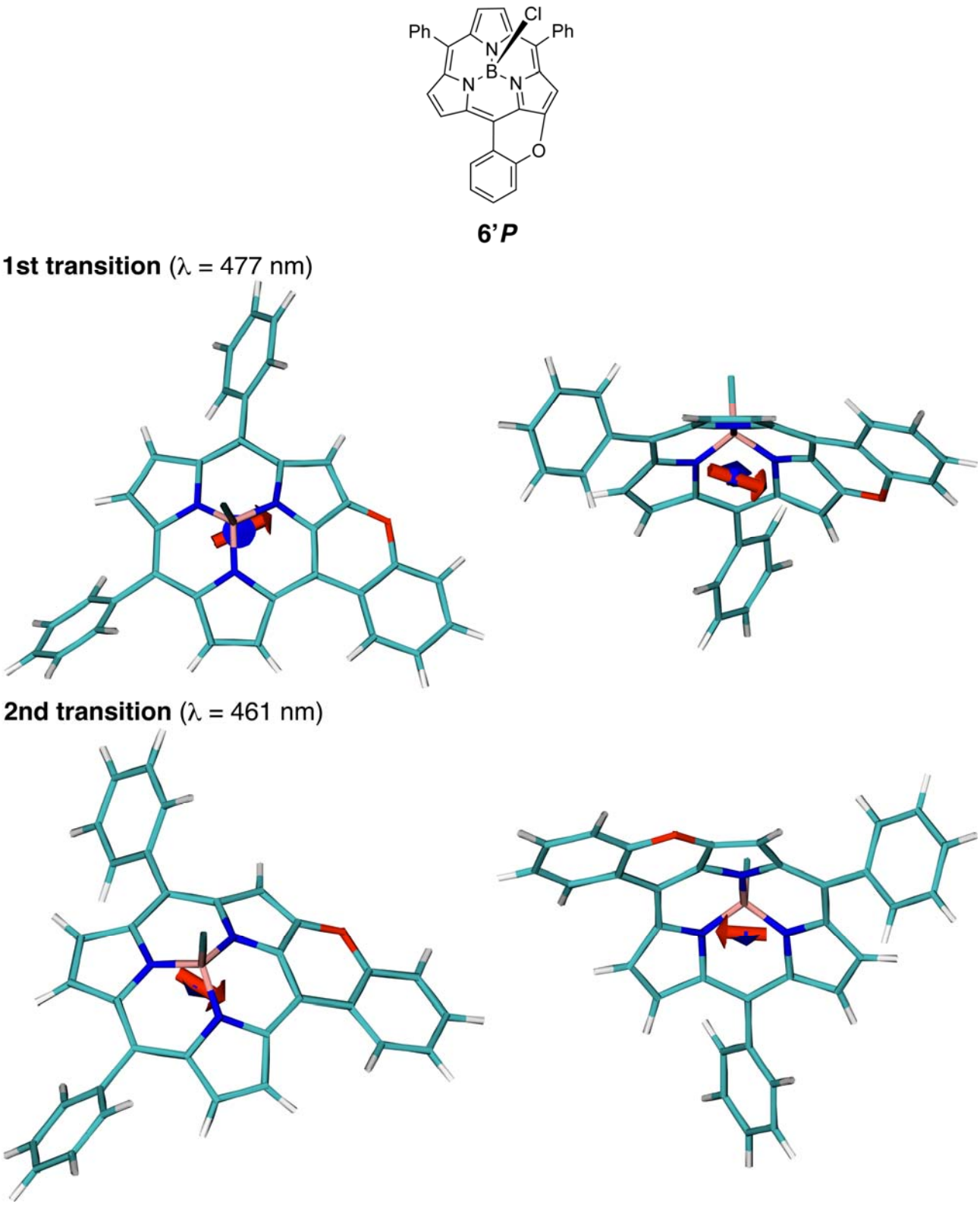
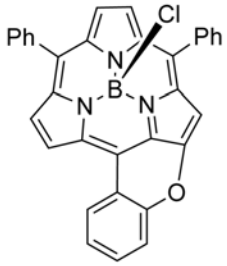
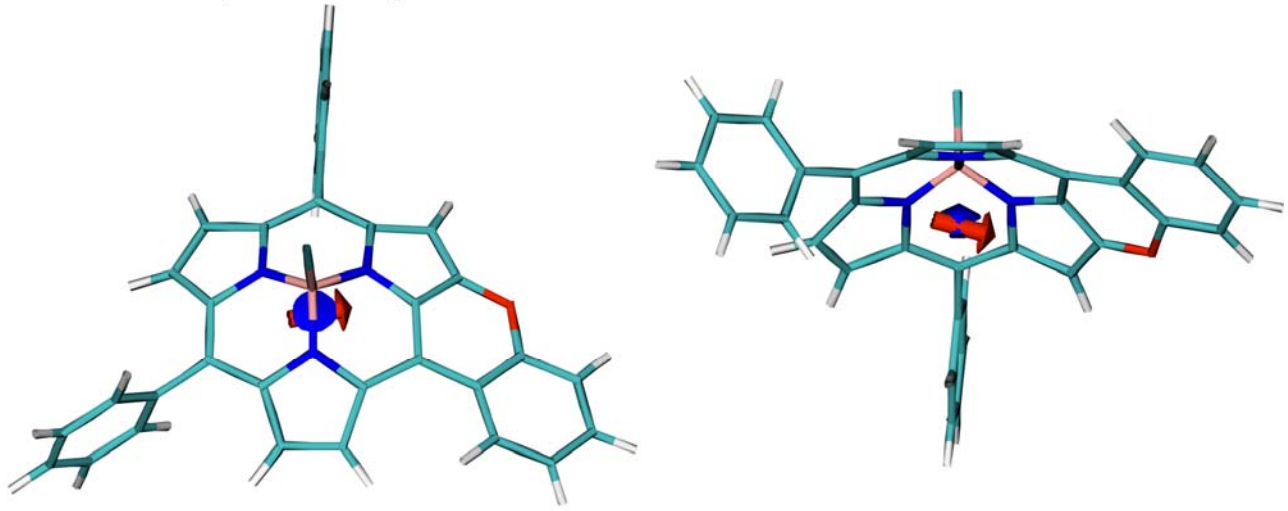


Figure S9. TEDM (red arrow) and TMDM (blue arrow) of **6'*P***, top view: left and side view: right.



6'*P*-90

1st transition (λ = 453 nm)



2nd transition (λ = 442 nm)

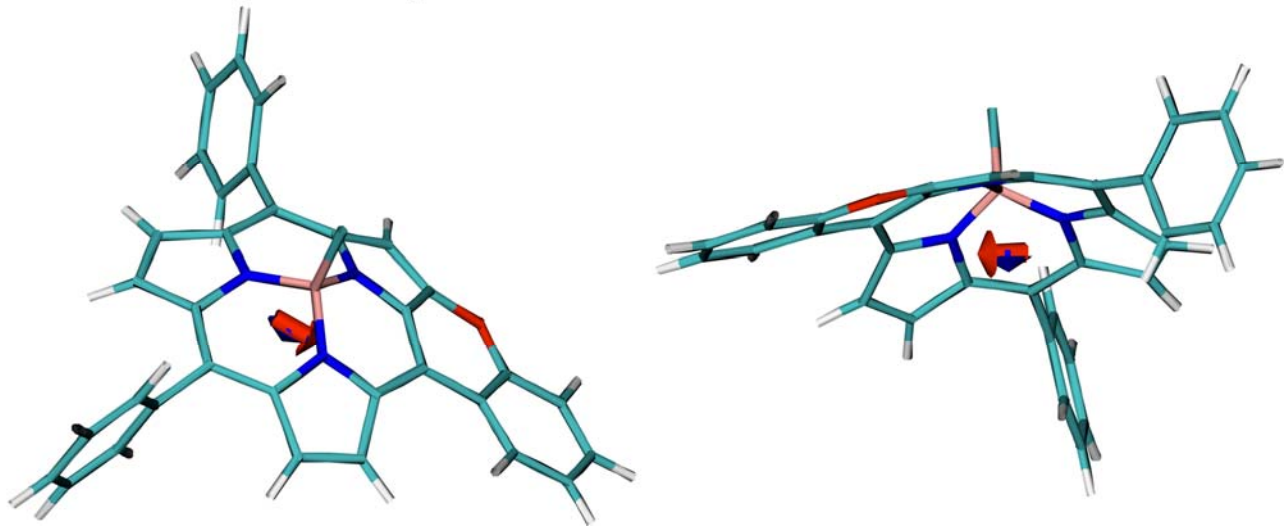


Figure S10. TEDM (red arrow) and TMDM (blue arrow) of **6'*P*-90**, top view: left and side view: right.

vi. Theoretical ^{1}H NMR Chemical Shifts of 6'

Theoretical ^{1}H NMR chemical shifts of **6'** were calculated at the B3LYP/6-311G(d,p) level with gauge-including atomic orbitals (GIAOs) using the DFT-optimized geometries.

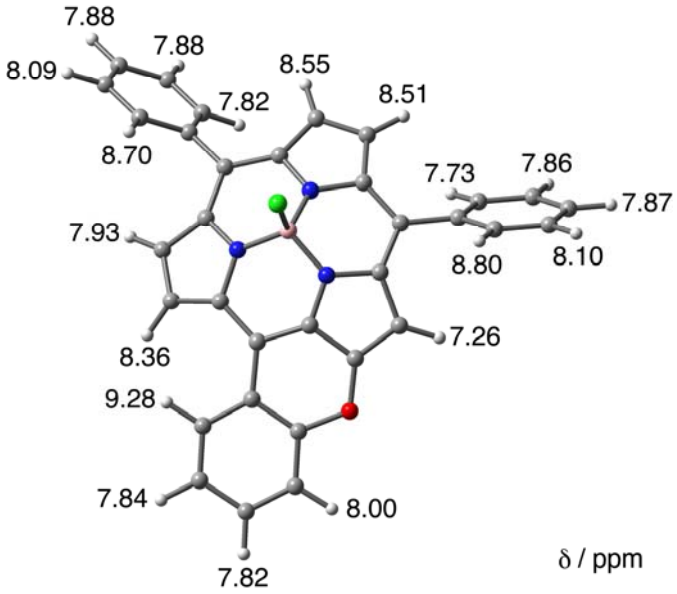


Figure S11. Theoretical ^{1}H NMR chemical shifts of **6'**.

vii. Appendix

Table Appx-1. Cartesian coordinates of the DFT optimized geometry of **4'*P*** at the B3LYP/6-311G(d,p).

	Symbol	X	Y	Z
1	O	3.130168	2.330189	−0.249013
2	N	0.049665	1.125317	0.845061
3	N	−0.162673	−1.248635	0.71757
4	N	−2.090338	0.178962	0.693505
5	C	−0.401633	2.374013	0.491827
6	C	0.788207	3.102872	0.081293
7	C	1.847078	2.209075	0.141335
8	C	1.351001	0.961429	0.580153
9	C	2.012651	−0.265577	0.468369
10	C	1.174004	−1.429757	0.4225
11	C	1.247131	−2.768726	−0.095074
12	C	−0.033782	−3.309412	−0.11288
13	C	−0.953276	−2.30806	0.355175
14	C	−2.37546	−2.165289	0.305634
15	C	−2.926959	−0.867723	0.419139
16	C	−4.202813	−0.243354	0.140322
17	C	−4.027622	1.131206	0.164884
18	C	−2.638625	1.413076	0.464313
19	C	−1.805383	2.565955	0.401765
20	C	3.457924	−0.067029	0.284927
21	C	3.938035	1.226568	−0.073969
22	C	5.307427	1.437803	−0.263878
23	C	6.224023	0.416674	−0.059511
24	H	7.279365	0.597759	−0.203571
25	C	5.757367	−0.825484	0.361474
26	C	4.407414	−1.068669	0.53833
27	H	4.077091	−2.030845	0.894189
28	C	−3.243075	−3.346589	0.020888
29	C	−3.629061	−4.189856	1.066978
30	H	−3.298073	−3.974605	2.076433
31	C	−4.434837	−5.297096	0.815539
32	H	−4.730603	−5.94324	1.634156
33	C	−4.857646	−5.573837	−0.482649
34	H	−5.482969	−6.437669	−0.678014
35	C	−4.475085	−4.737198	−1.52936
36	H	−4.8006	−4.948052	−2.541699
37	C	−3.674033	−3.627947	−1.278914
38	H	−3.374976	−2.979452	−2.094302
39	C	−2.35649	3.923235	0.113197
40	C	−2.559997	4.827546	1.159849
41	H	−2.33148	4.528127	2.176237
42	C	−3.057246	6.102003	0.900892
43	H	−3.214787	6.794033	1.72028
44	C	−3.348318	6.486662	−0.40596
45	H	−3.732895	7.480133	−0.607209
46	C	−3.141546	5.592001	−1.45406
47	H	−3.362779	5.88719	−2.473445
48	C	−2.649475	4.316561	−1.196131
49	H	−2.487257	3.622303	−2.01259
50	B	−0.763533	−0.013832	1.317595
51	Cl	−0.848349	−0.115798	3.218485
52	Br	0.933371	4.870159	−0.543065
53	Br	−5.392196	2.384448	−0.146188
54	Br	−5.834776	−1.103719	−0.210699
55	Br	−0.445451	−5.031459	−0.743597
56	Br	2.742039	−3.642743	−0.838681
57	Br	5.942952	3.155685	−0.788816
58	Br	7.018696	−2.219784	0.714705

Table Appx-2. Cartesian coordinates of the DFT optimized geometry of **4'*M*** at the B3LYP/6-311G(d,p).

	Symbol	X	Y	Z
1	O	–3.130168	2.330189	–0.249013
2	N	–0.049665	1.125317	0.845061
3	N	0.162673	–1.248635	0.71757
4	N	2.090338	0.178962	0.693505
5	C	0.401633	2.374013	0.491827
6	C	–0.788207	3.102872	0.081293
7	C	–1.847078	2.209075	0.141335
8	C	–1.351001	0.961429	0.580153
9	C	–2.012651	–0.265577	0.468369
10	C	–1.174004	–1.429757	0.4225
11	C	–1.247131	–2.768726	–0.095074
12	C	0.033782	–3.309412	–0.11288
13	C	0.953276	–2.30806	0.355175
14	C	2.37546	–2.165289	0.305634
15	C	2.926959	–0.867723	0.419139
16	C	4.202813	–0.243354	0.140322
17	C	4.027622	1.131206	0.164884
18	C	2.638625	1.413076	0.464313
19	C	1.805383	2.565955	0.401765
20	C	–3.457924	–0.067029	0.284927
21	C	–3.938035	1.226568	–0.073969
22	C	–5.307427	1.437803	–0.263878
23	C	–6.224023	0.416674	–0.059511
24	H	–7.279365	0.597759	–0.203571
25	C	–5.757367	–0.825484	0.361474
26	C	–4.407414	–1.068669	0.53833
27	H	–4.077091	–2.030845	0.894189
28	C	3.243075	–3.346589	0.020888
29	C	3.629061	–4.189856	1.066978
30	H	3.298073	–3.974605	2.076433
31	C	4.434837	–5.297096	0.815539
32	H	4.730603	–5.94324	1.634156
33	C	4.857646	–5.573837	–0.482649
34	H	5.482969	–6.437669	–0.678014
35	C	4.475085	–4.737198	–1.52936
36	H	4.8006	–4.948052	–2.541699
37	C	3.674033	–3.627947	–1.278914
38	H	3.374976	–2.979452	–2.094302
39	C	2.35649	3.923235	0.113197
40	C	2.559997	4.827546	1.159849
41	H	2.33148	4.528127	2.176237
42	C	3.057246	6.102003	0.900892
43	H	3.214787	6.794033	1.72028
44	C	3.348318	6.486662	–0.40596
45	H	3.732895	7.480133	–0.607209
46	C	3.141546	5.592001	–1.45406
47	H	3.362779	5.88719	–2.473445
48	C	2.649475	4.316561	–1.196131
49	H	2.487257	3.622303	–2.01259
50	B	0.763533	–0.013832	1.317595
51	Cl	0.848349	–0.115798	3.218485
52	Br	–0.933371	4.870159	–0.543065
53	Br	5.392196	2.384448	–0.146188
54	Br	5.834776	–1.103719	–0.210699
55	Br	0.445451	–5.031459	–0.743597
56	Br	–2.742039	–3.642743	–0.838681
57	Br	–5.942952	3.155685	–0.788816
58	Br	–7.018696	–2.219784	0.714705

Table Appx-3. Cartesian coordinates of the DFT optimized geometry of **6'*P*** at the B3LYP/6-311G(d,p).

	Symbol	X	Y	Z
1	O	4.006231	−1.506737	−0.57379
2	N	1.175372	0.072354	0.736121
3	N	−0.811272	−1.268946	0.599435
4	N	−0.928854	1.118988	0.530282
5	C	1.83706	1.209223	0.34161
6	C	3.12829	0.786483	−0.146387
7	H	3.889674	1.425894	−0.56072
8	C	3.119284	−0.59858	−0.104433
9	C	1.868403	−1.031013	0.403963
10	C	1.319336	−2.303976	0.227308
11	C	−0.105252	−2.399061	0.249192
12	C	−1.067514	−3.300762	−0.306163
13	H	−0.855206	−4.274832	−0.716626
14	C	−2.292964	−2.660489	−0.333443
15	H	−3.207351	−3.042815	−0.758866
16	C	−2.116448	−1.341308	0.195769
17	C	−2.907619	−0.15548	0.089515
18	C	−2.254815	1.095697	0.19031
19	C	−2.572789	2.449761	−0.18687
20	H	−3.54459	2.805086	−0.489687
21	C	−1.409501	3.188263	−0.152788
22	H	−1.306346	4.226966	−0.422343
23	C	−0.331686	2.317273	0.248842
24	C	1.087335	2.412013	0.210326
25	C	2.319902	−3.284496	−0.191412
26	C	3.617515	−2.838359	−0.5613
27	C	4.600674	−3.73571	−0.967897
28	H	5.570756	−3.342137	−1.244787
29	C	4.326188	−5.095102	−1.009314
30	H	5.097162	−5.788295	−1.323914
31	C	3.06517	−5.564287	−0.634123
32	H	2.853284	−6.62668	−0.645966
33	C	2.085688	−4.670515	−0.230941
34	H	1.122273	−5.041103	0.094813
35	C	−4.338638	−0.268074	−0.27847
36	C	−5.193027	−1.078828	0.484636
37	H	−4.796713	−1.595543	1.350922
38	C	−6.540182	−1.200008	0.156815
39	H	−7.18592	−1.823482	0.764982
40	C	−7.059648	−0.517431	−0.941058
41	H	−8.109127	−0.611673	−1.195713
42	C	−6.220249	0.283752	−1.712646
43	H	−6.612639	0.806481	−2.577835
44	C	−4.872739	0.40632	−1.387124
45	H	−4.220653	1.004195	−2.012385
46	C	1.783152	3.673687	−0.136073
47	C	2.850172	4.120481	0.658651
48	H	3.132785	3.547319	1.534056
49	C	3.525047	5.29768	0.349466
50	H	4.340698	5.630076	0.981771
51	C	3.149864	6.050775	−0.761033
52	H	3.674956	6.968267	−1.001095
53	C	2.098389	5.613906	−1.564326
54	H	1.809893	6.185222	−2.439641
55	C	1.423192	4.43616	−1.257918
56	H	0.630145	4.086793	−1.907993
57	B	−0.23659	−0.016288	1.182006
58	Cl	−0.395661	0.020638	3.090256

Table Appx-4. Cartesian coordinates of the DFT optimized geometry of **6'*M*** at the B3LYP/6-311G(d,p).

	Symbol	X	Y	Z
1	O	–4.006231	–1.506737	–0.57379
2	N	–1.175372	0.072354	0.736121
3	N	0.811272	–1.268946	0.599435
4	N	0.928854	1.118988	0.530282
5	C	–1.83706	1.209223	0.34161
6	C	–3.12829	0.786483	–0.146387
7	H	–3.889674	1.425894	–0.56072
8	C	–3.119284	–0.59858	–0.104433
9	C	–1.868403	–1.031013	0.403963
10	C	–1.319336	–2.303976	0.227308
11	C	0.105252	–2.399061	0.249192
12	C	1.067514	–3.300762	–0.306163
13	H	0.855206	–4.274832	–0.716626
14	C	2.292964	–2.660489	–0.333443
15	H	3.207351	–3.042815	–0.758866
16	C	2.116448	–1.341308	0.195769
17	C	2.907619	–0.15548	0.089515
18	C	2.254815	1.095697	0.19031
19	C	2.572789	2.449761	–0.18687
20	H	3.54459	2.805086	–0.489687
21	C	1.409501	3.188263	–0.152788
22	H	1.306346	4.226966	–0.422343
23	C	0.331686	2.317273	0.248842
24	C	–1.087335	2.412013	0.210326
25	C	–2.319902	–3.284496	–0.191412
26	C	–3.617515	–2.838359	–0.5613
27	C	–4.600674	–3.73571	–0.967897
28	H	–5.570756	–3.342137	–1.244787
29	C	–4.326188	–5.095102	–1.009314
30	H	–5.097162	–5.788295	–1.323914
31	C	–3.06517	–5.564287	–0.634123
32	H	–2.853284	–6.62668	–0.645966
33	C	–2.085688	–4.670515	–0.230941
34	H	–1.122273	–5.041103	0.094813
35	C	4.338638	–0.268074	–0.27847
36	C	5.193027	–1.078828	0.484636
37	H	4.796713	–1.595543	1.350922
38	C	6.540182	–1.200008	0.156815
39	H	7.18592	–1.823482	0.764982
40	C	7.059648	–0.517431	–0.941058
41	H	8.109127	–0.611673	–1.195713
42	C	6.220249	0.283752	–1.712646
43	H	6.612639	0.806481	–2.577835
44	C	4.872739	0.40632	–1.387124
45	H	4.220653	1.004195	–2.012385
46	C	–1.783152	3.673687	–0.136073
47	C	–2.850172	4.120481	0.658651
48	H	–3.132785	3.547319	1.534056
49	C	–3.525047	5.29768	0.349466
50	H	–4.340698	5.630076	0.981771
51	C	–3.149864	6.050775	–0.761033
52	H	–3.674956	6.968267	–1.001095
53	C	–2.098389	5.613906	–1.564326
54	H	–1.809893	6.185222	–2.439641
55	C	–1.423192	4.43616	–1.257918
56	H	–0.630145	4.086793	–1.907993
57	B	0.23659	–0.016288	1.182006
58	Cl	0.395661	0.020638	3.090256