Electronic Supporting Information

Functionalization of 10-azacorroles: nitration, bromination and acylation

Sha Li, Yuhuan Zhu, Xiaofang Li,* Shaowei Zhang,* Michał J. Białek, and Piotr J. Chmielewski*

Key Laboratory of Theoretical Organic Chemistry and Functional Molecules, Ministry of Education, School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, Hunan 411201, China

E-mail: lixiaofang@iccas.ac.cn, swzhang@hnust.edu.cn, piotr.chmielewski@uwr.edu.pl

Table of contents

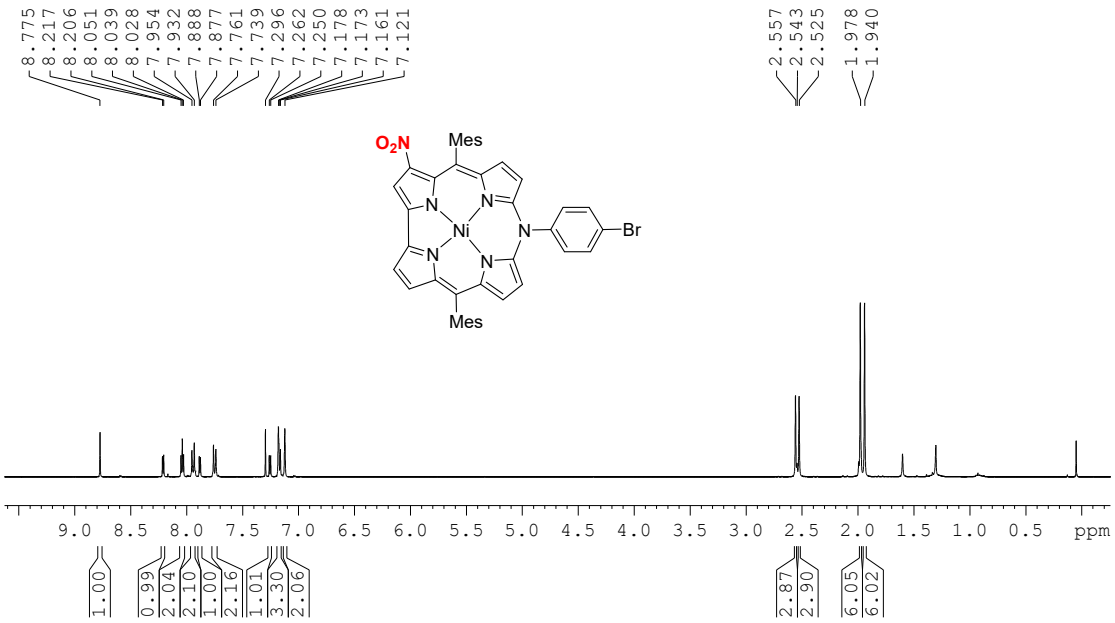


Figure S1. ^{1}H NMR spectrum of **2a** (400 MHz, 298 K, $CDCl_3$).

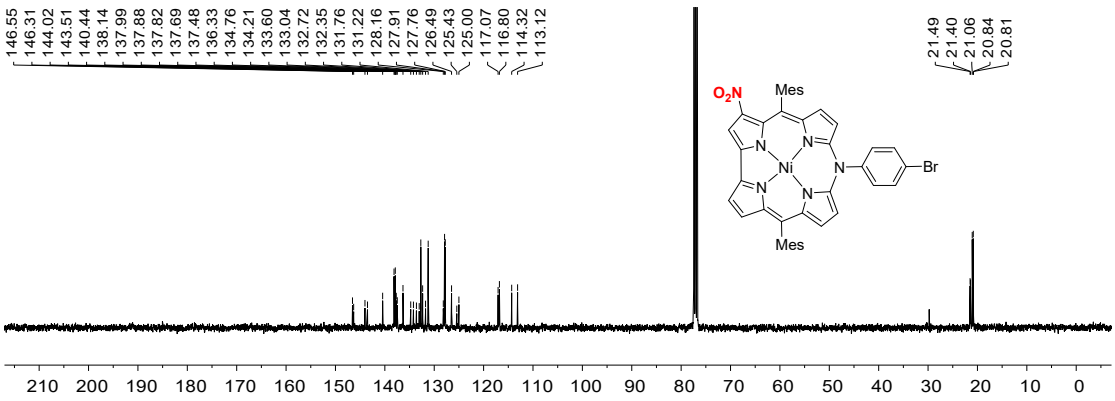


Figure S2. ^{13}C NMR spectrum of **2a** (100 MHz, 298 K, $CDCl_3$).

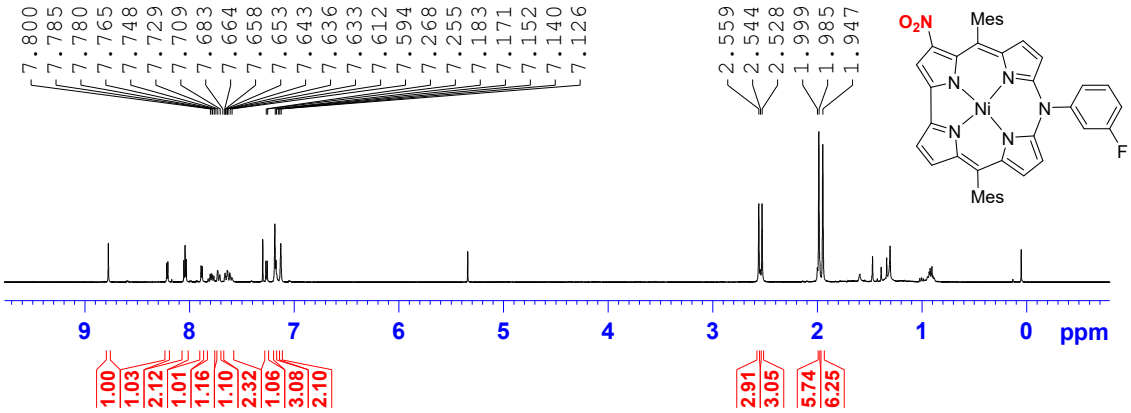


Figure S3. ^{1}H NMR spectrum of **2b** (400 MHz, 298 K, CDCl3).

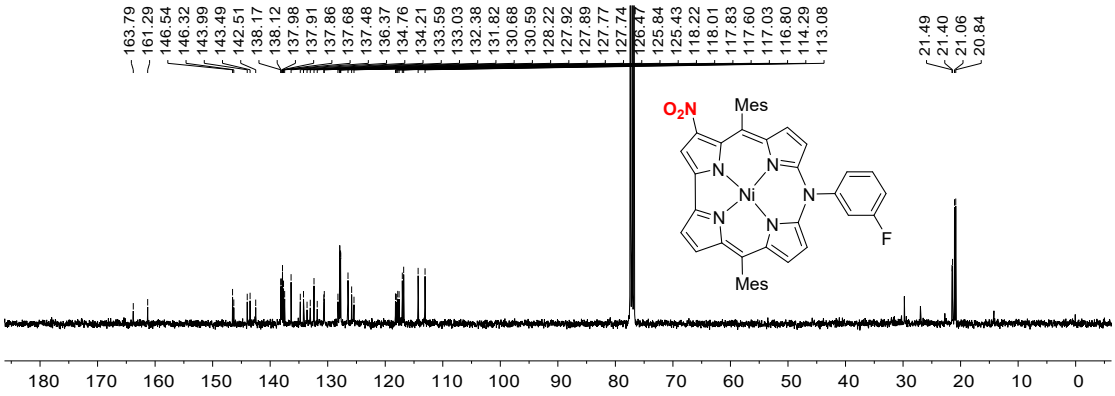


Figure S4. ^{13}C NMR spectrum of **2b** (100 MHz, 298 K, $CDCl_3$).

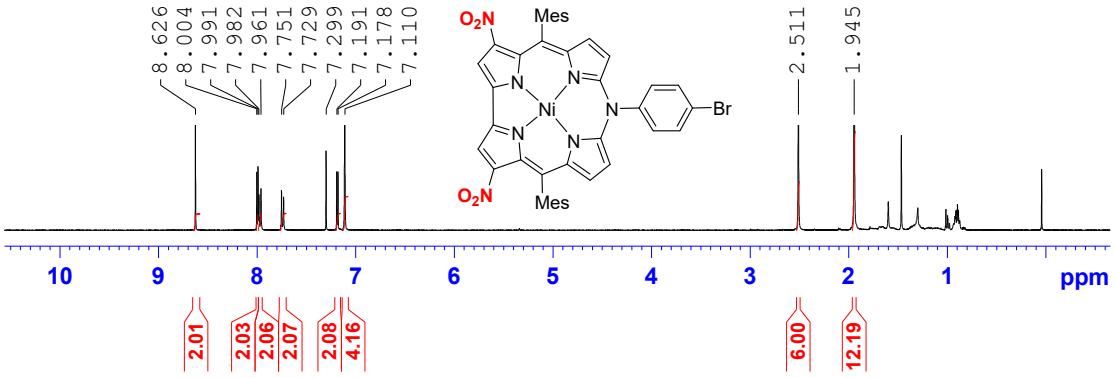


Figure S5. ^{1}H spectrum of **3a** (400 MHz, 298 K, $CDCl_3$).

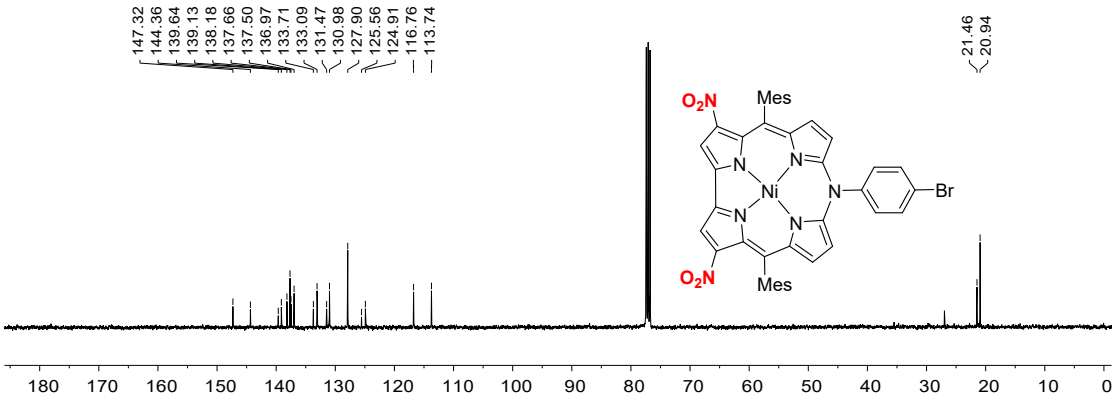


Figure S6. ^{13}C spectrum of **3a** (100 MHz, 298 K, $CDCl_3$).

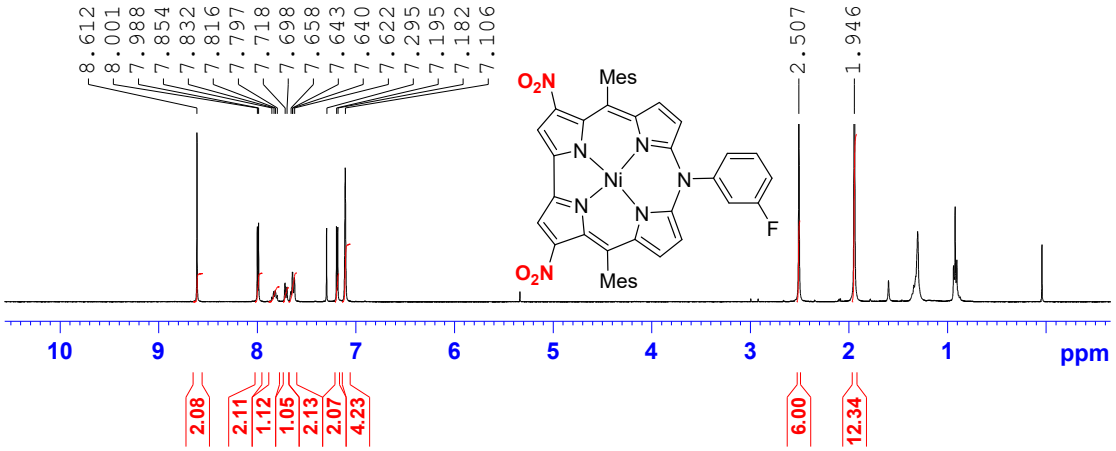


Figure S7. ^{1}H NMR spectrum of **3b** (400 MHz, 298 K, $CDCl_3$).

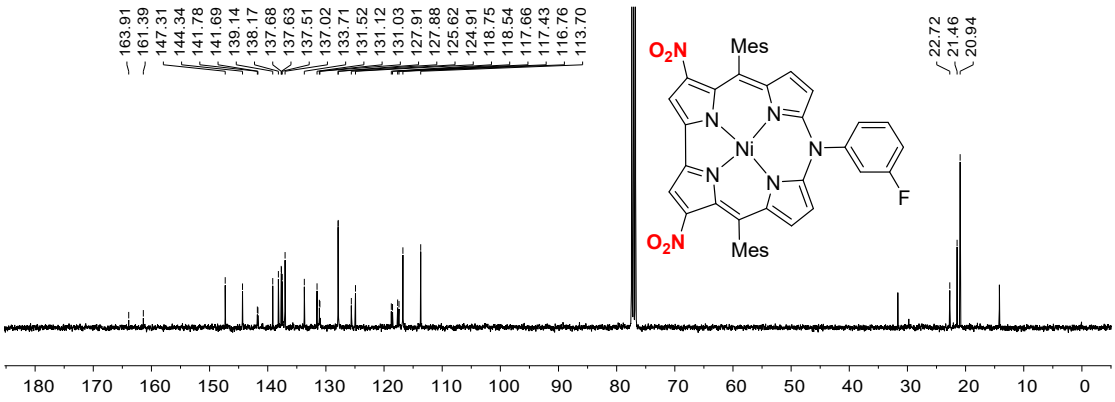


Figure S8. ^{13}C NMR spectrum of **3b** (100 MHz, 298 K, $CDCl_3$).

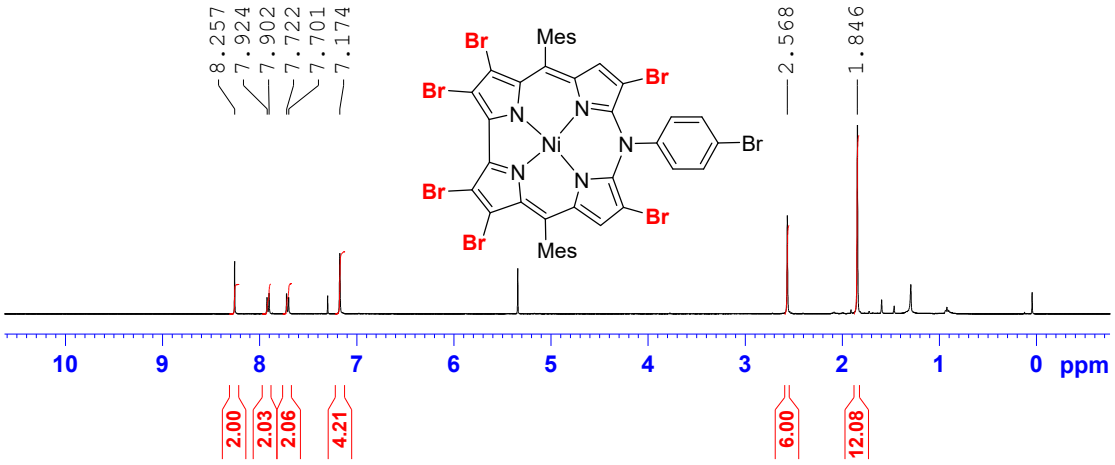


Figure S9. ^{1}H spectrum of **4a** (400 MHz, 298 K, $CDCl_3$).

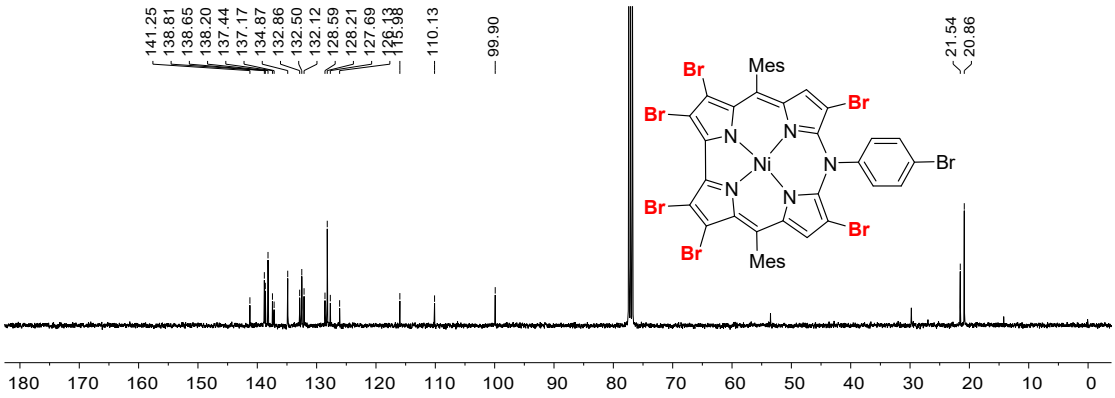


Figure S10. ^{13}C spectrum of **4a** (100 MHz, 298 K, $CDCl_3$).

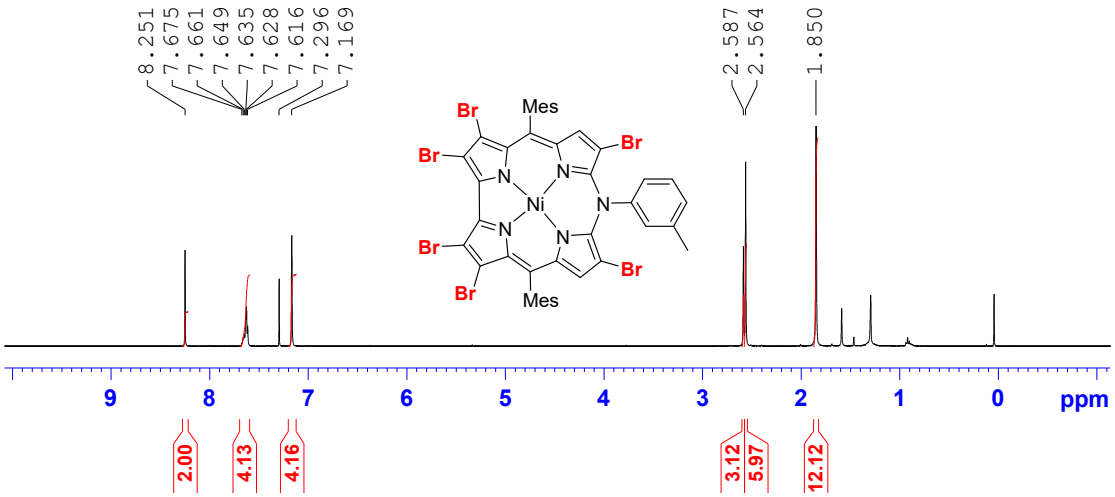


Figure S11. ^{1}H spectrum of **4b** (400 MHz, 298 K, $CDCl_3$).

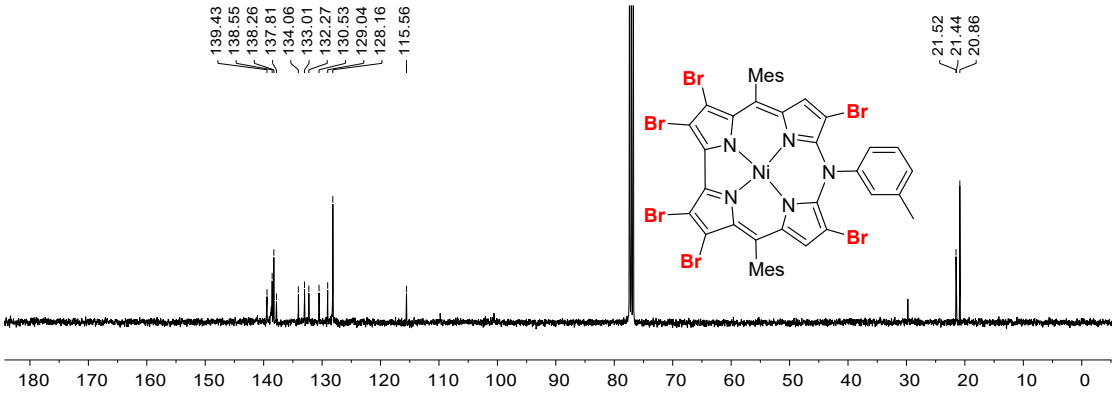


Figure S12. ^{13}C spectrum of **4b** (100 MHz, 298 K, $CDCl_3$).

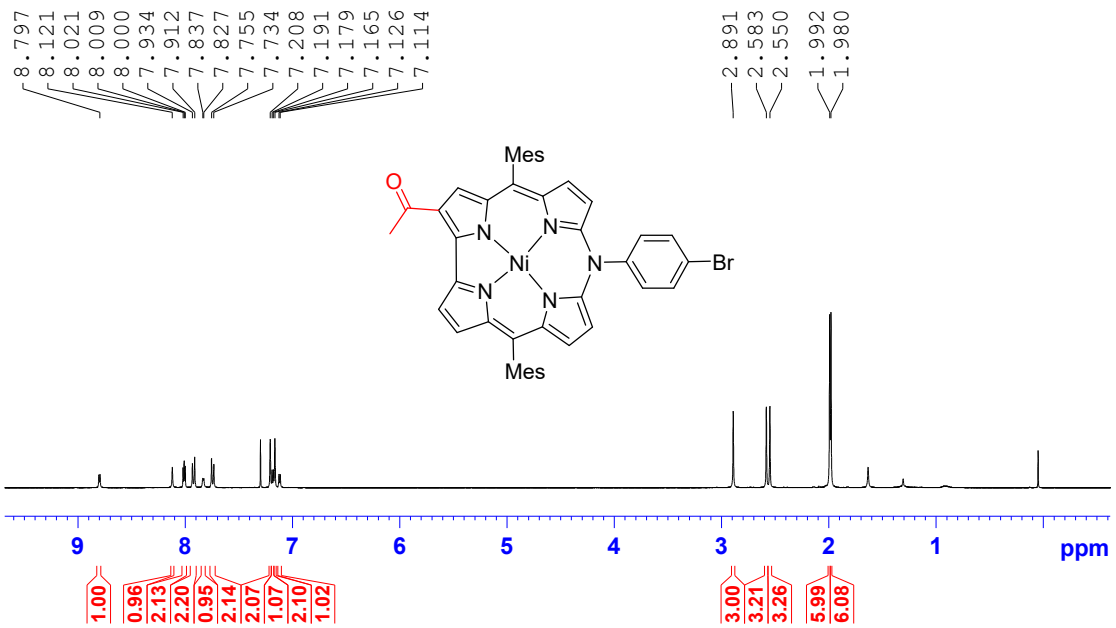


Figure S13. ^{1}H NMR spectrum of **5a** (400 MHz, 298 K, $CDCl_3$).

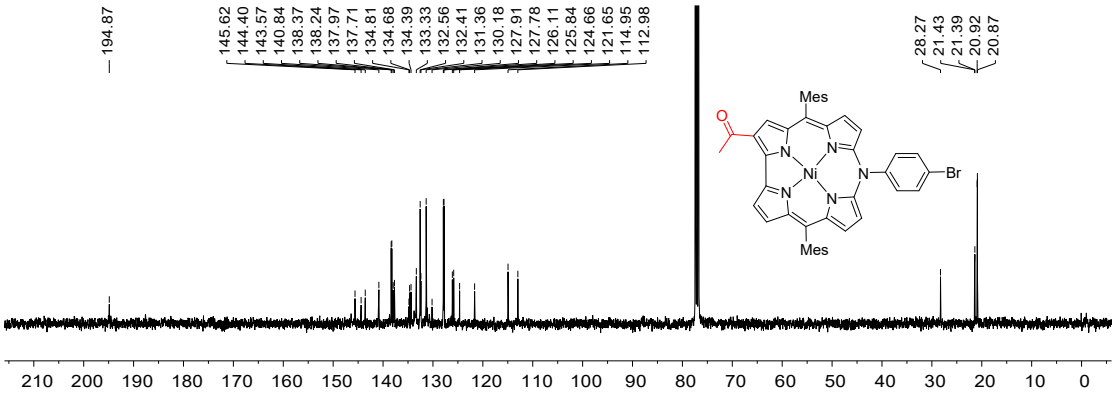


Figure S14. ^{13}C NMR spectrum of **5a** (100 MHz, 298 K, $CDCl_3$).

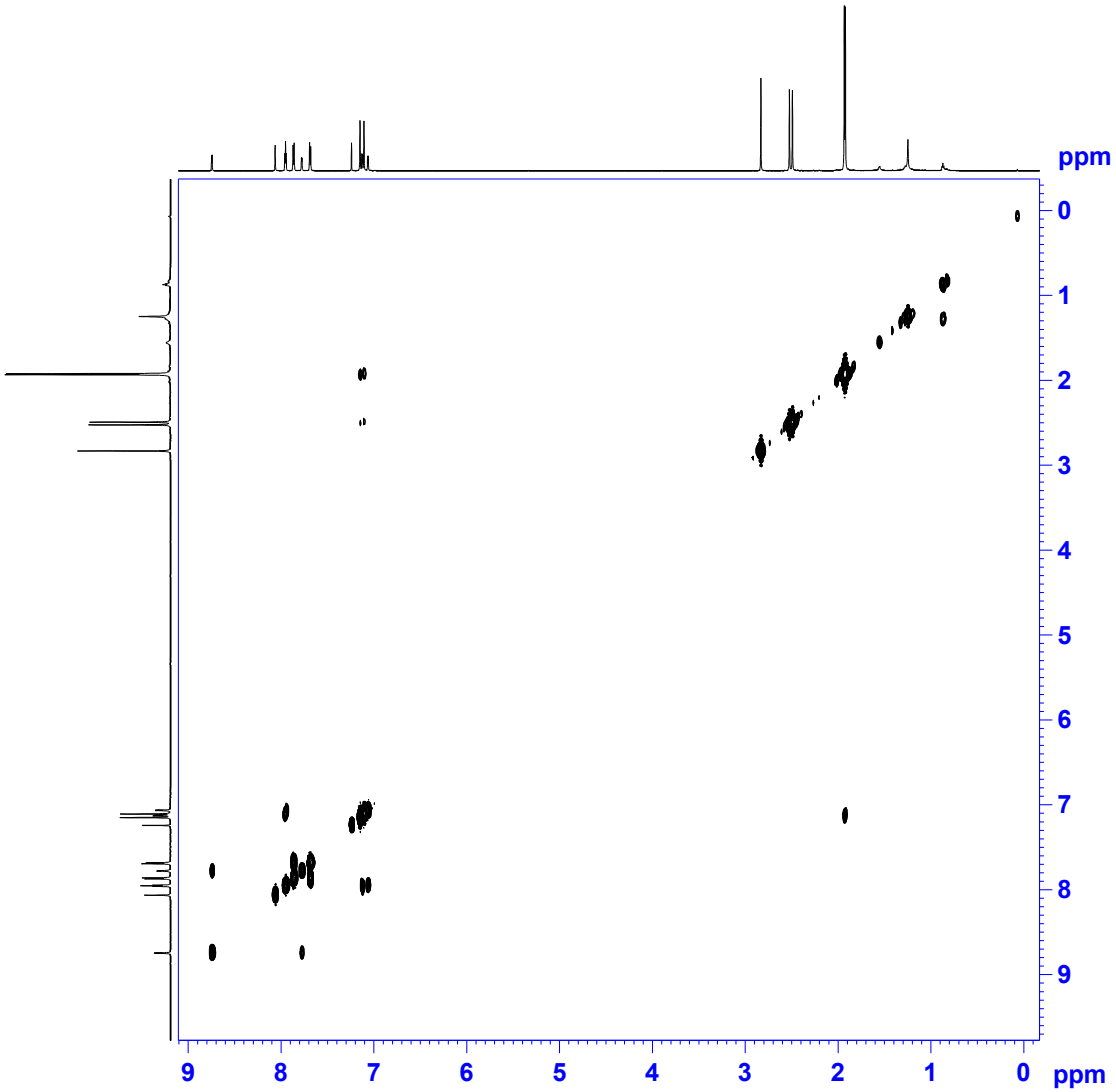


Figure S15. ^{1}H, ^{1}H COSY spectrum of **5a** (700 MHz, 298 K, $CDCl_3$).

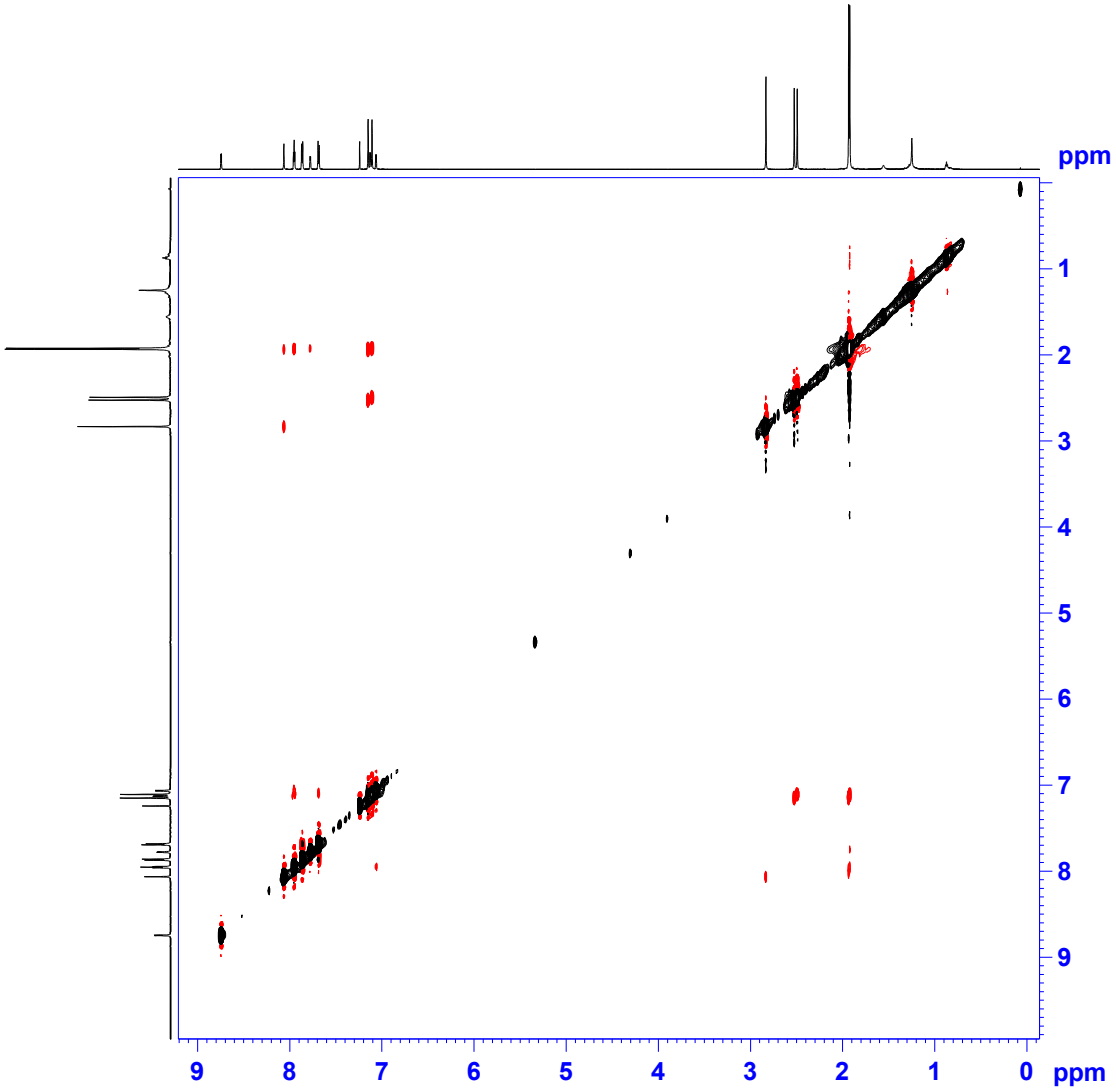


Figure S16. ^{1}H, ^{1}H NOESY spectrum of **5a** (700 MHz, 298 K, $CDCl_3$).

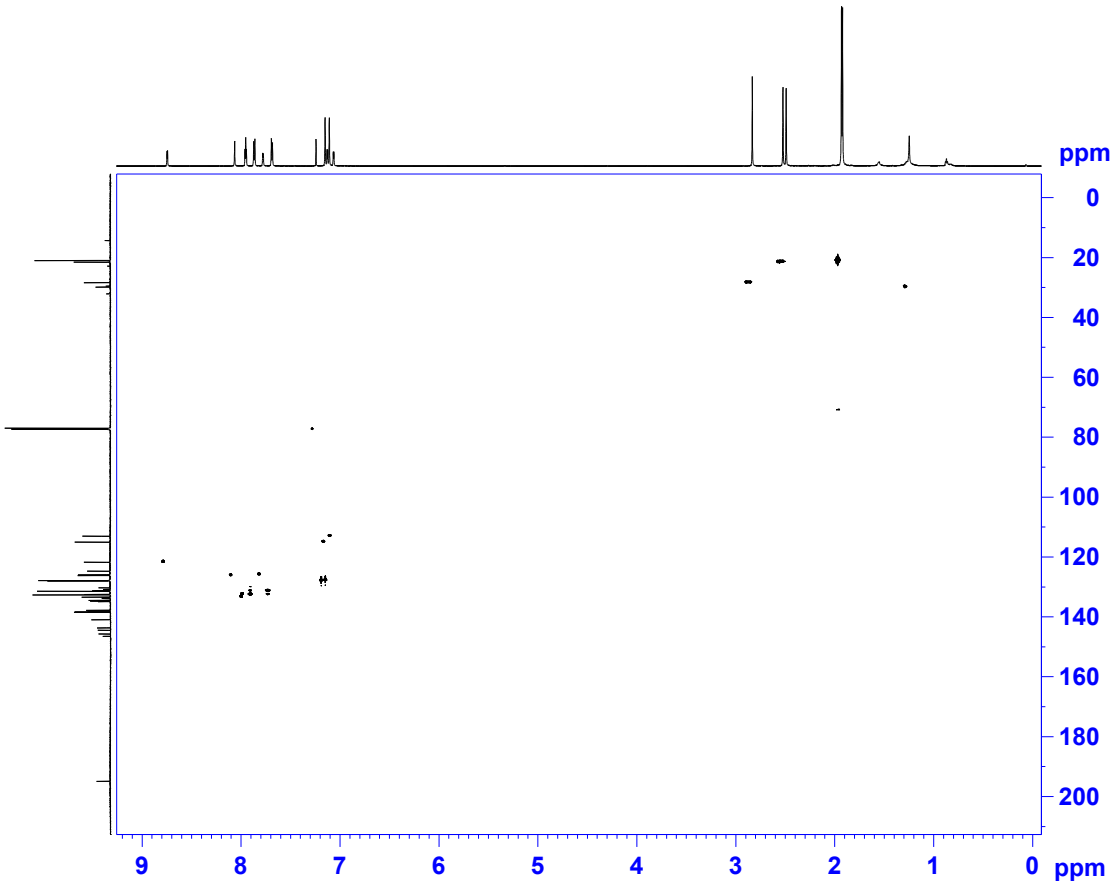


Figure S17. ^{1}H, ^{13}C HSQC spectrum of **5a** (700/175 MHz, 298 K, $CDCl_3$).

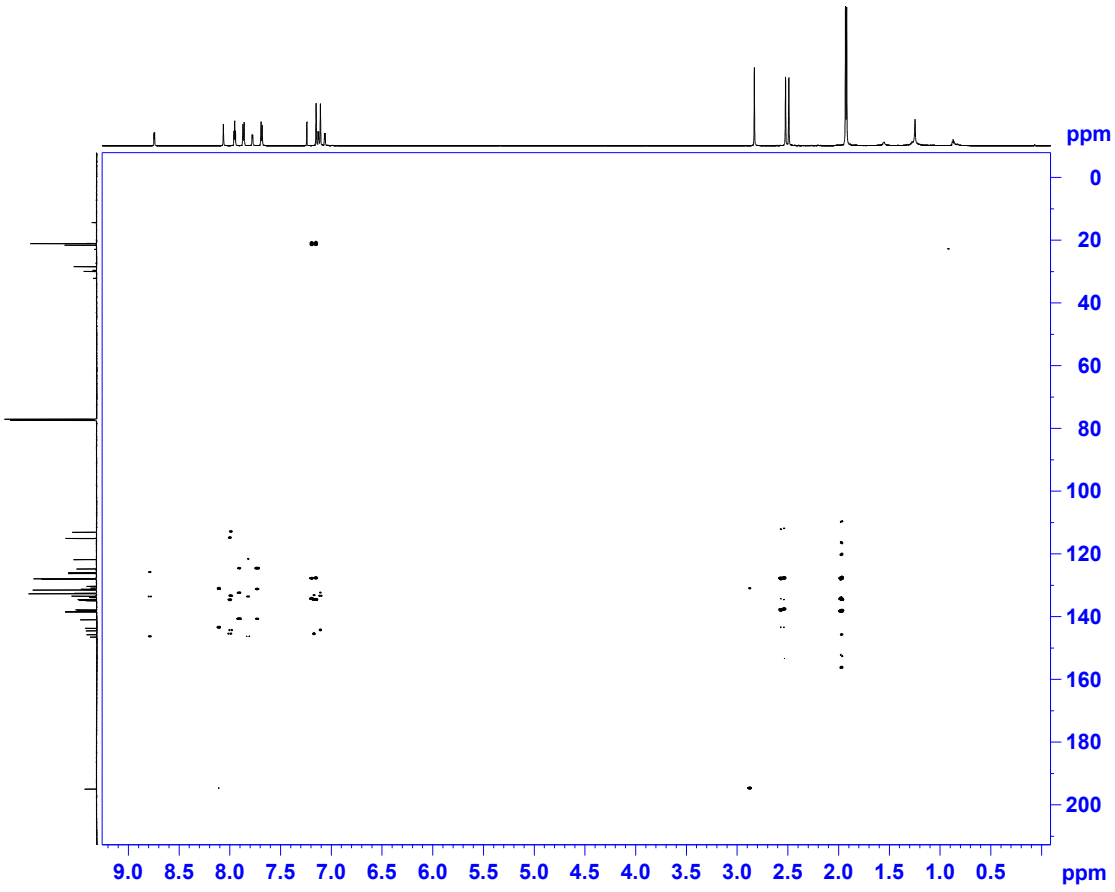


Figure S18. ^{1}H, ^{13}C HMBC spectrum of **5a** (700/175 MHz, 298 K, $CDCl_3$).

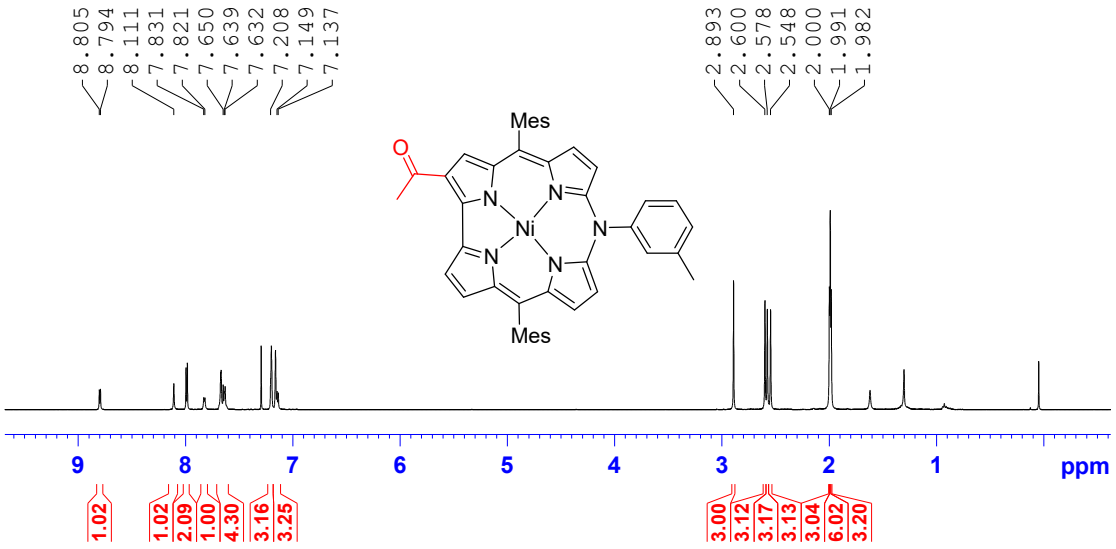


Figure S19. ^{1}H NMR spectrum of **5b** (400 MHz, 298 K, $CDCl_3$).

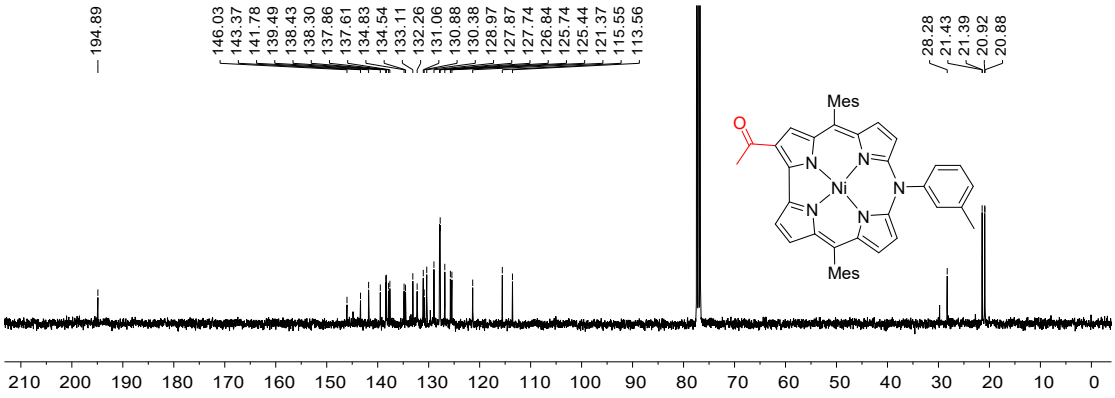


Figure S20. ^{13}C NMR spectrum of **5b** (100 MHz, 298 K, $CDCl_3$).

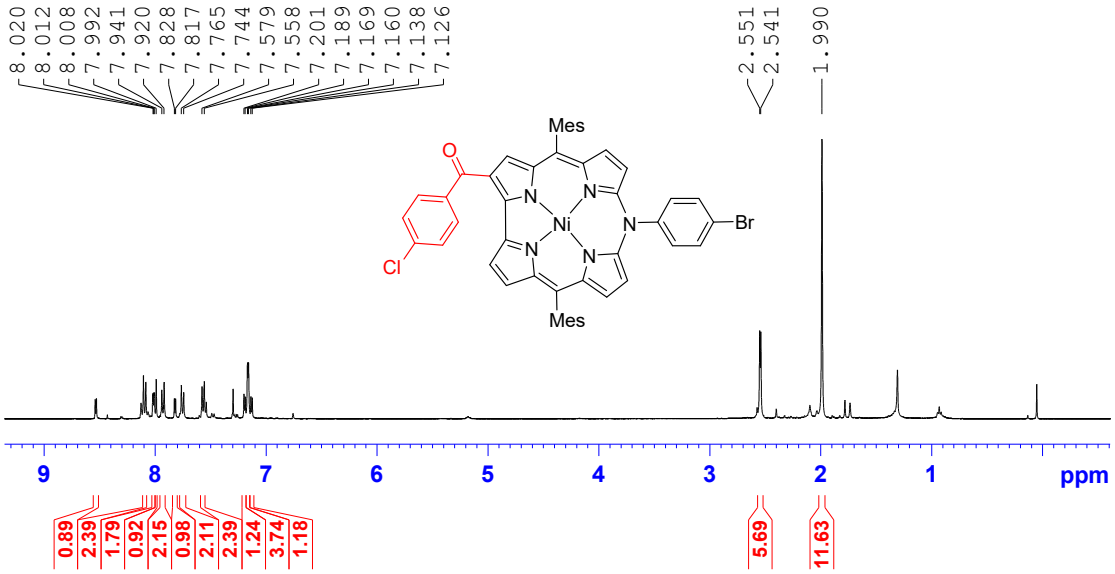


Figure S21. ^{1}H NMR spectrum of **5c** (400 Mhz, 298 K, $CDCl_3$).

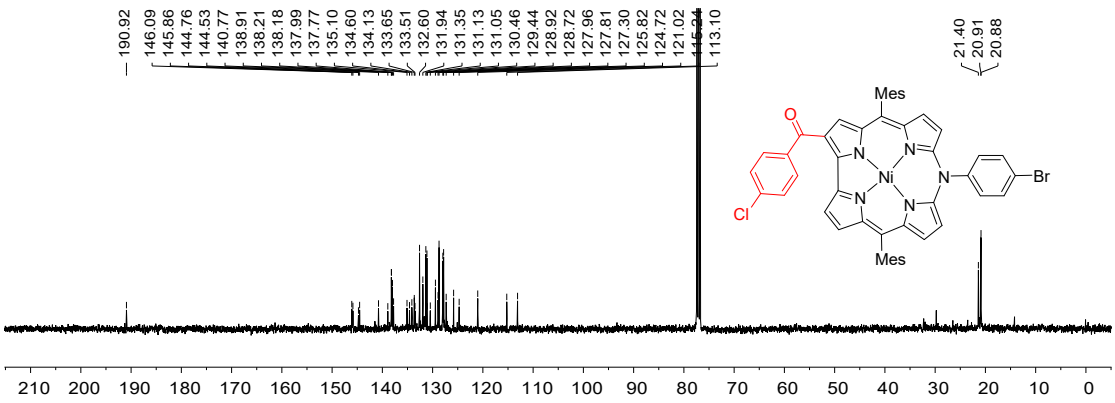


Figure S22. ^{13}C NMR spectrum of **5c** (100 Mhz, 298 K, $CDCl_3$).

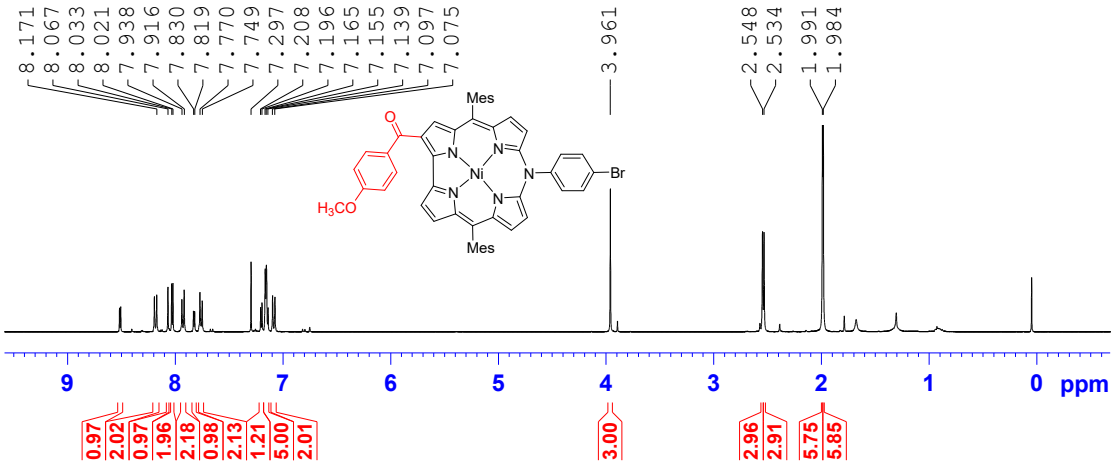


Figure S23. ^{1}H NMR spectrum of **5d** (400Mhz, 298 K, $CDCl_3$).

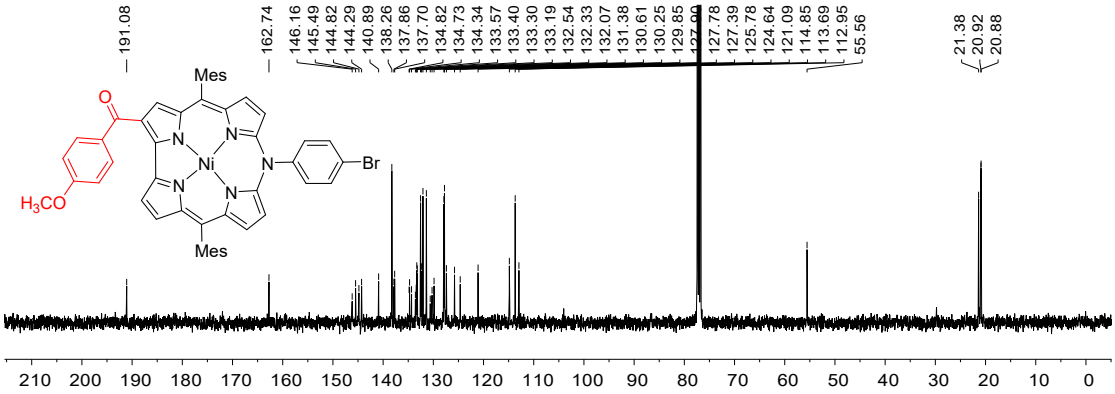


Figure S24. ^{13}C NMR spectrum of **5d** (100 Mhz, 298 K, $CDCl_3$).

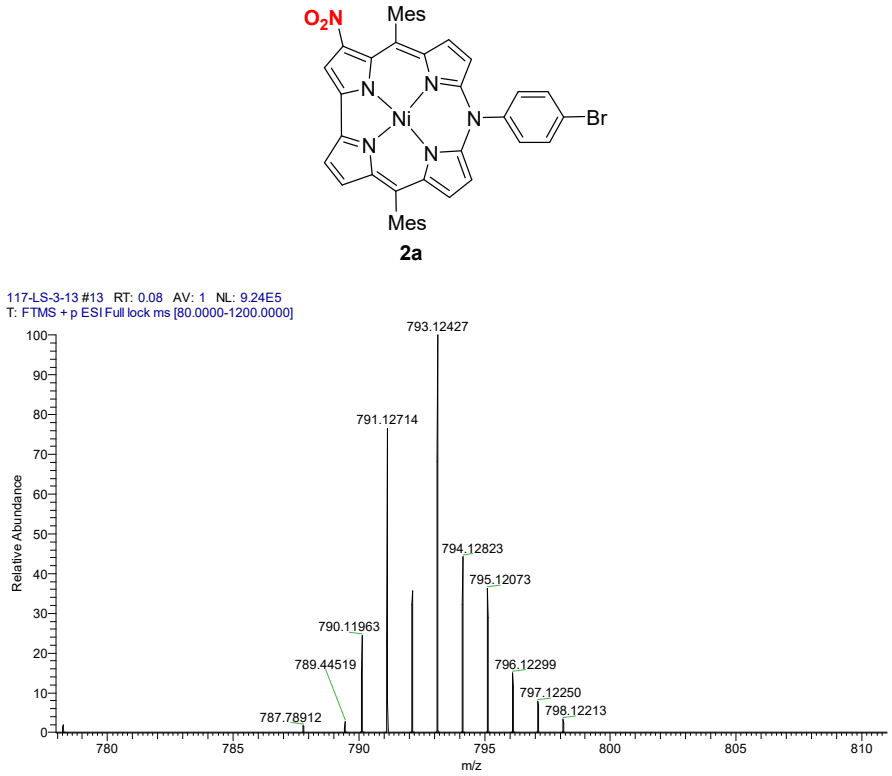


Figure S25. ESI(+) HRMS spectrum of **2a**.

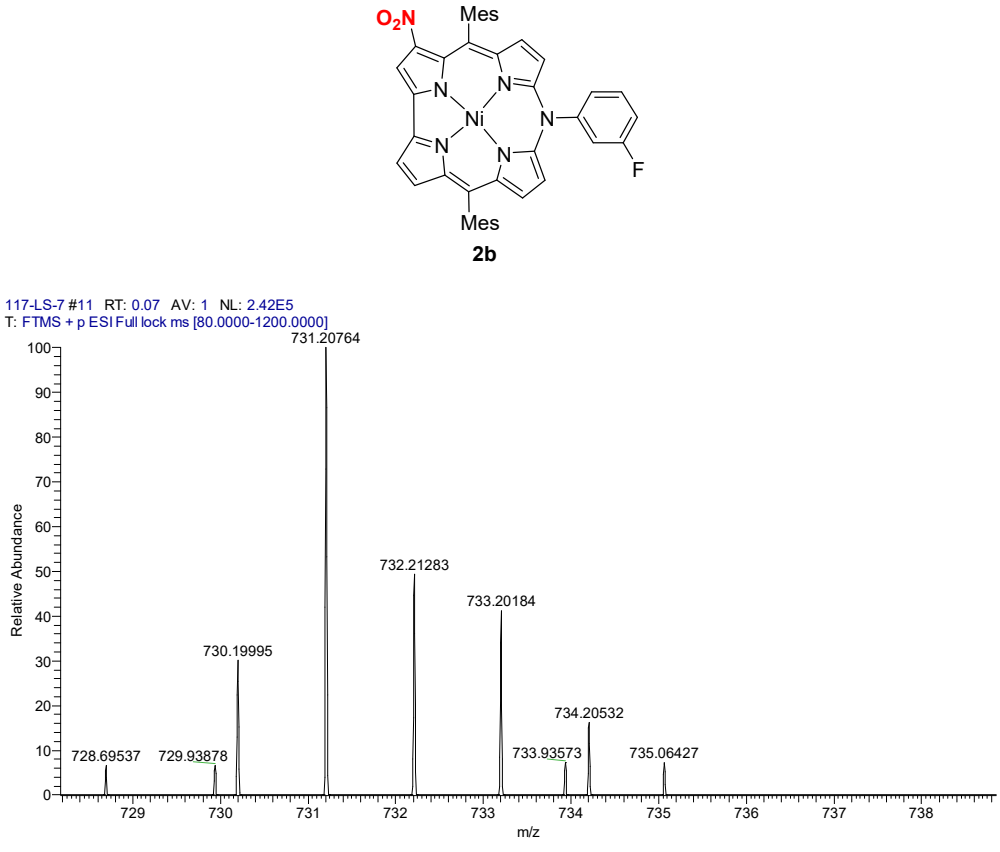
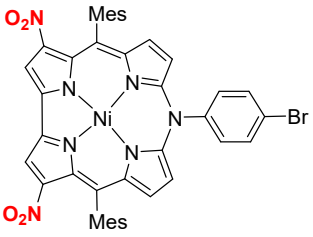


Figure S26. ESI(-) HRMS spectrum of **2b**.



3a

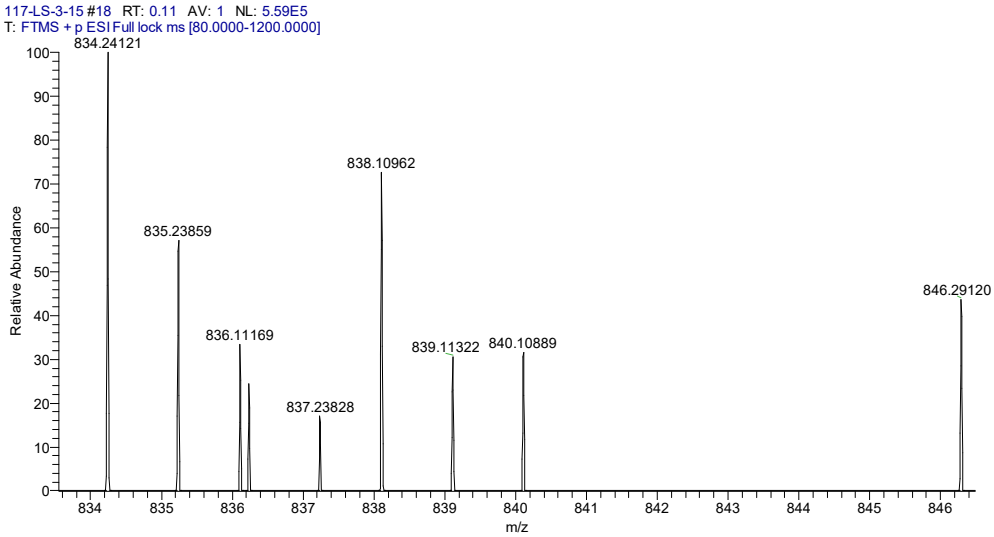
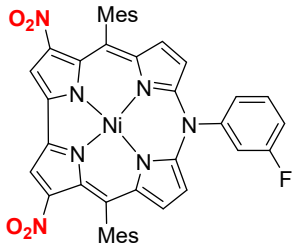


Figure S27. ESI(+) HRMS spectrum of **3a**.



3b

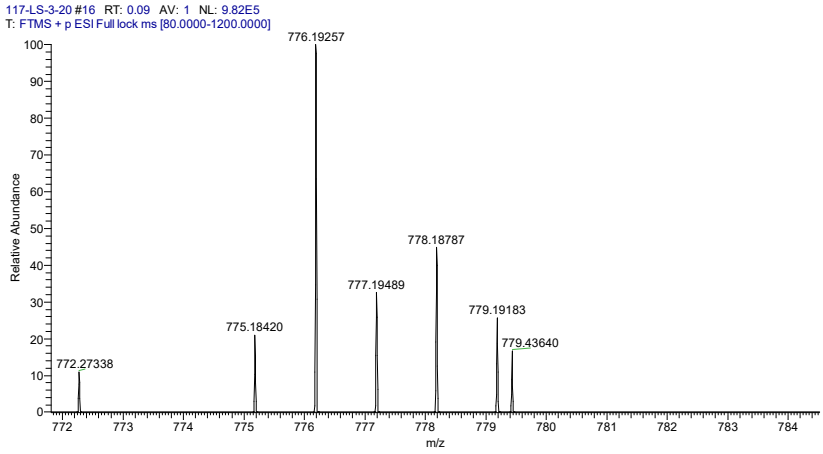
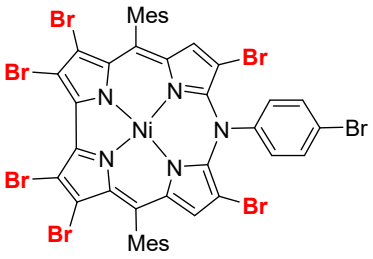


Figure S28. ESI(+) HRMS spectrum of **3b**.



4a

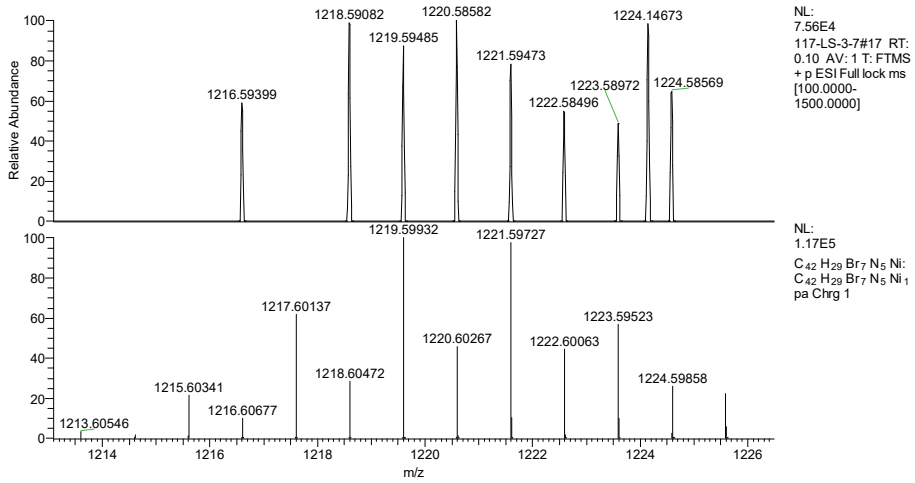
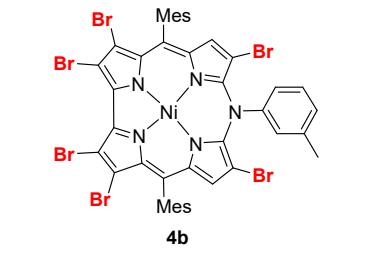


Figure S29. ESI(+) HRMS spectrum of **4a**.



4b

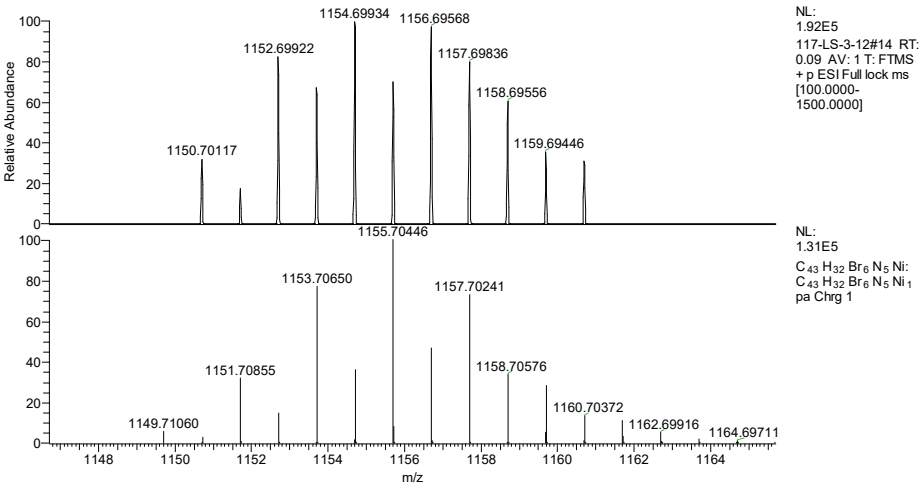
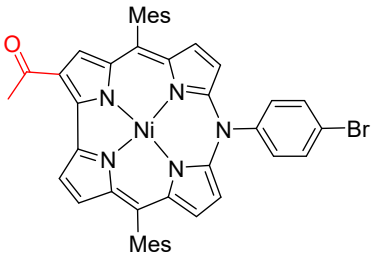


Figure S30. ESI(+) HRMS spectrum of **4b**.



5a

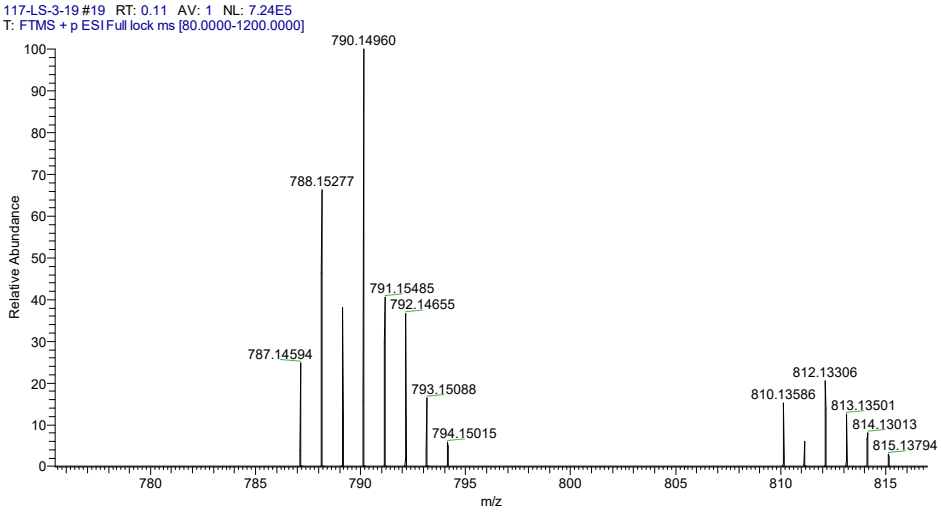
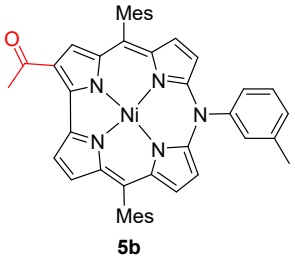


Figure S31. ESI(+) HRMS spectrum of **5a**.



5b

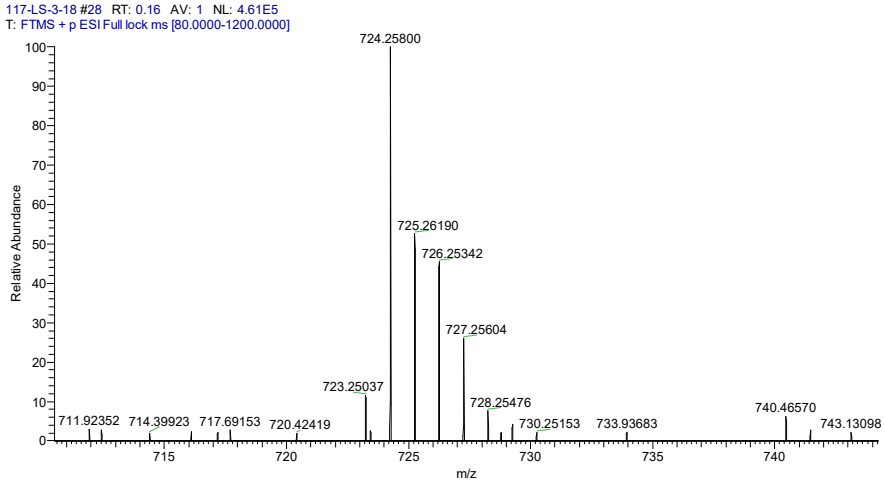
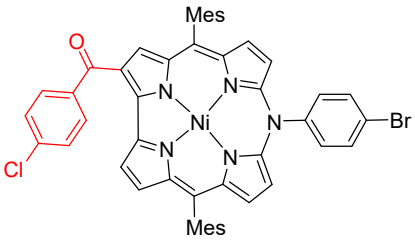


Figure S32. ESI(+) HRMS spectrum of **5b**.



5c

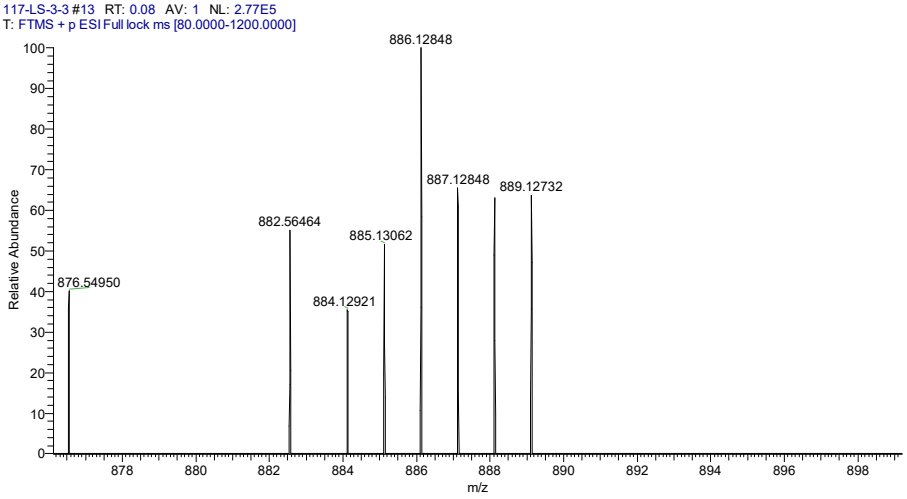
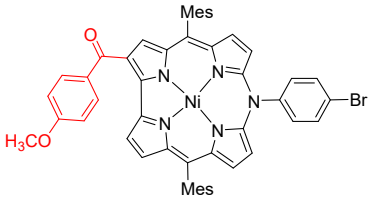


Figure S33. ESI(+) HRMS spectrum of **5c**



5d

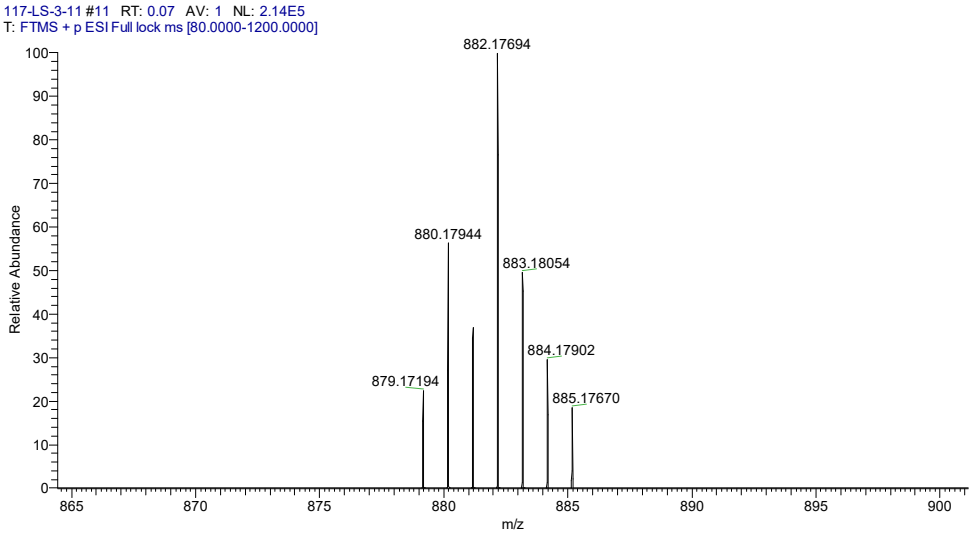


Figure S34. ESI(+) HRMS spectrum of **5d.**

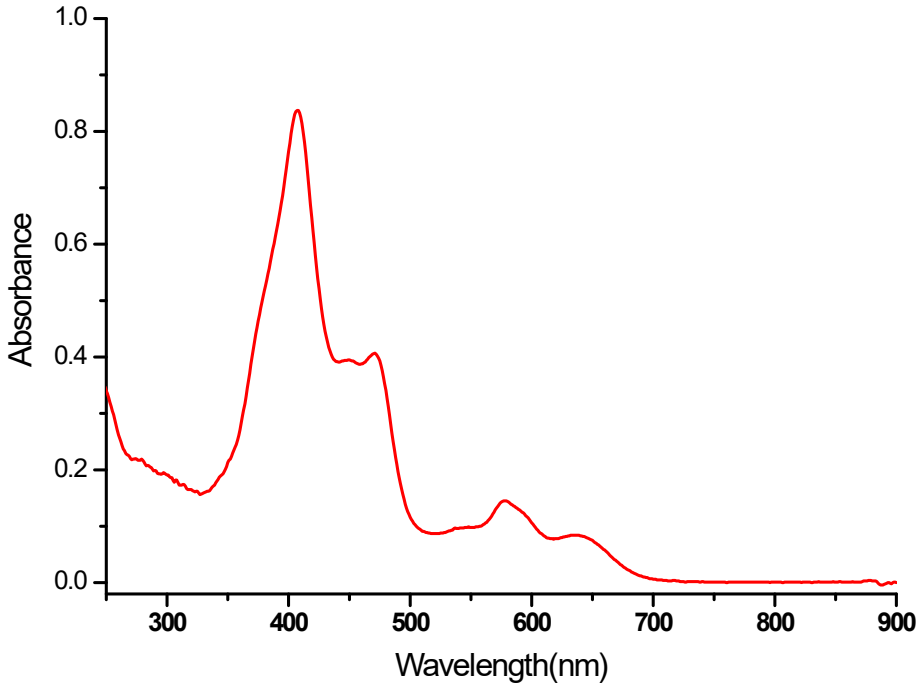


Figure S35. UV-vis spectrum of 2**a** (CH_2Cl_2).

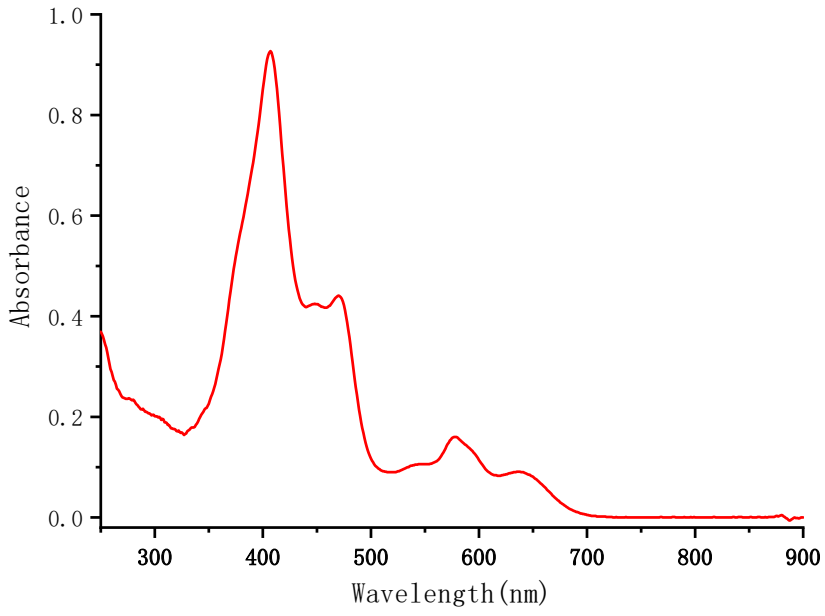


Figure S36. UV-vis spectrum of **2b** (CH_2Cl_2).

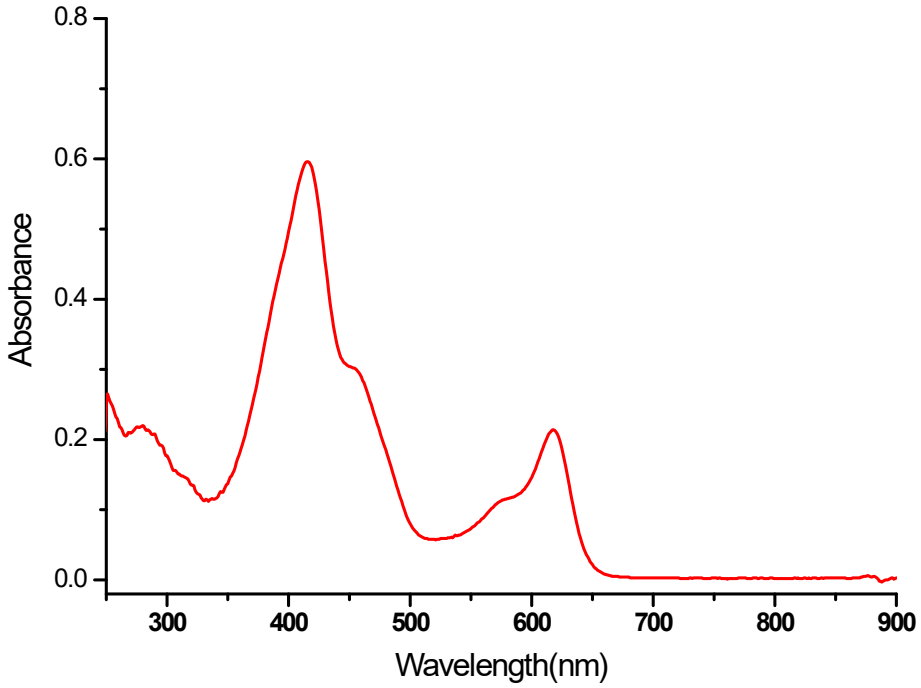


Figure S37. UV-vis spectrum of **3a** (CH_2Cl_2).

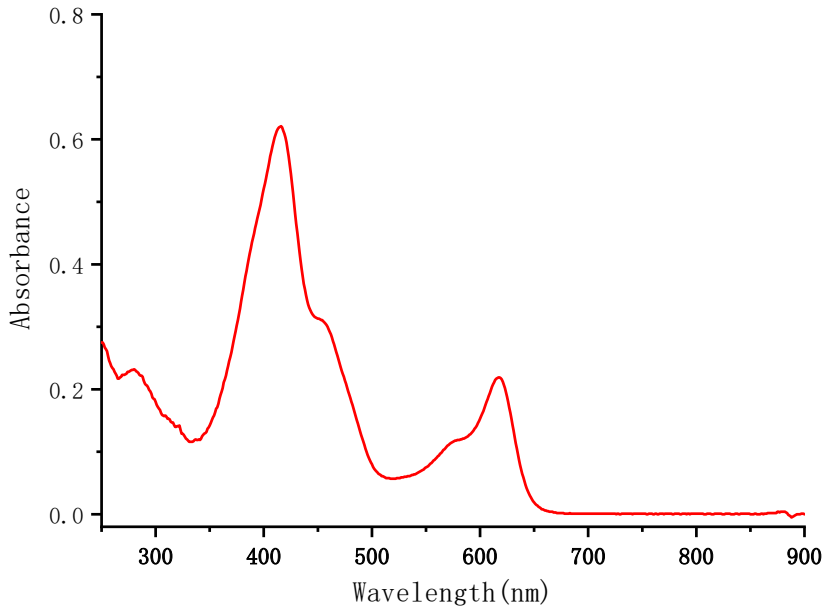


Figure S38. UV-vis spectrum of **3b** (CH_2Cl_2).

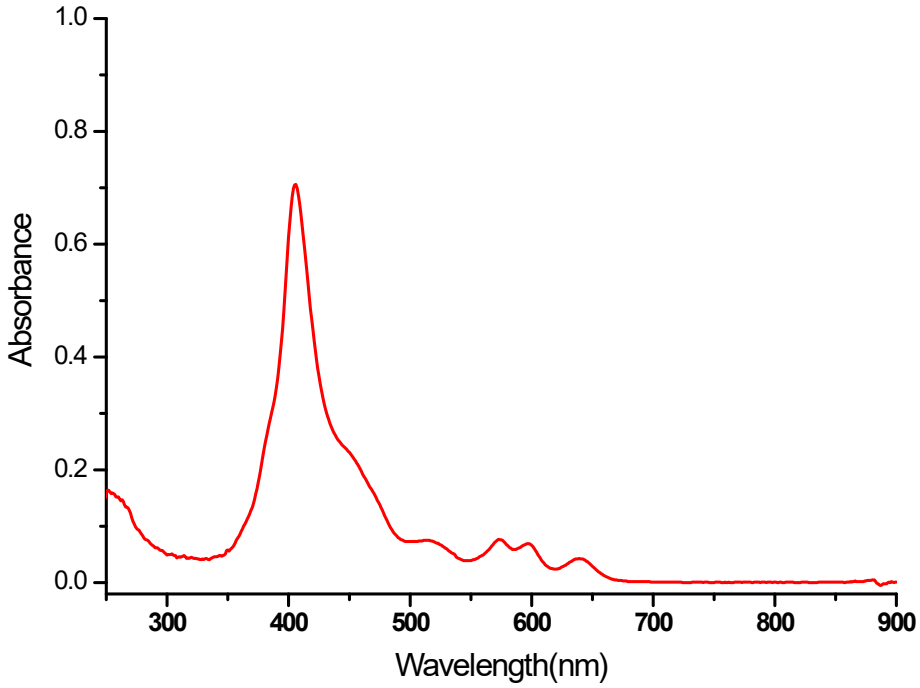


Figure S39. UV-vis spectrum of **4a** (CH_2Cl_2).

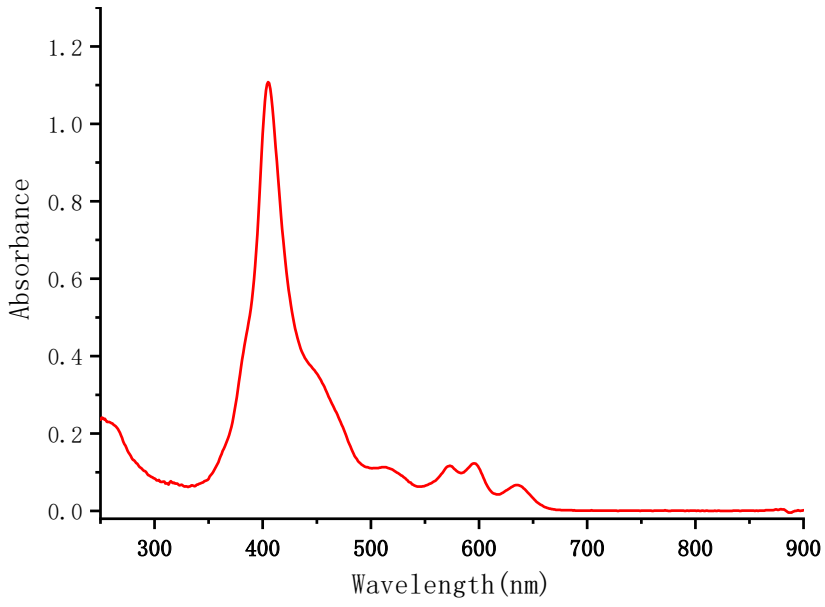


Figure S40. UV-vis spectrum of **4b** (CH_2Cl_2).

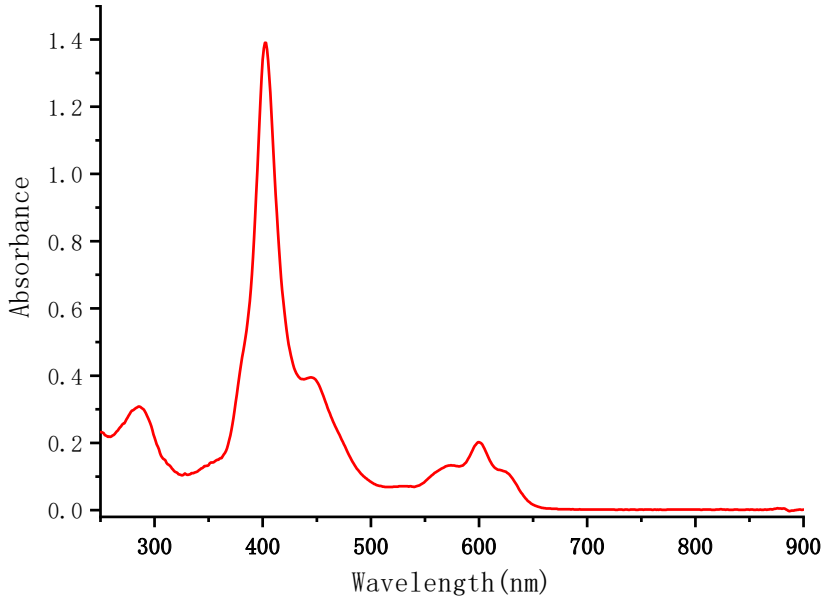


Figure S41. UV-vis spectrum of **5a** (CH_2Cl_2).

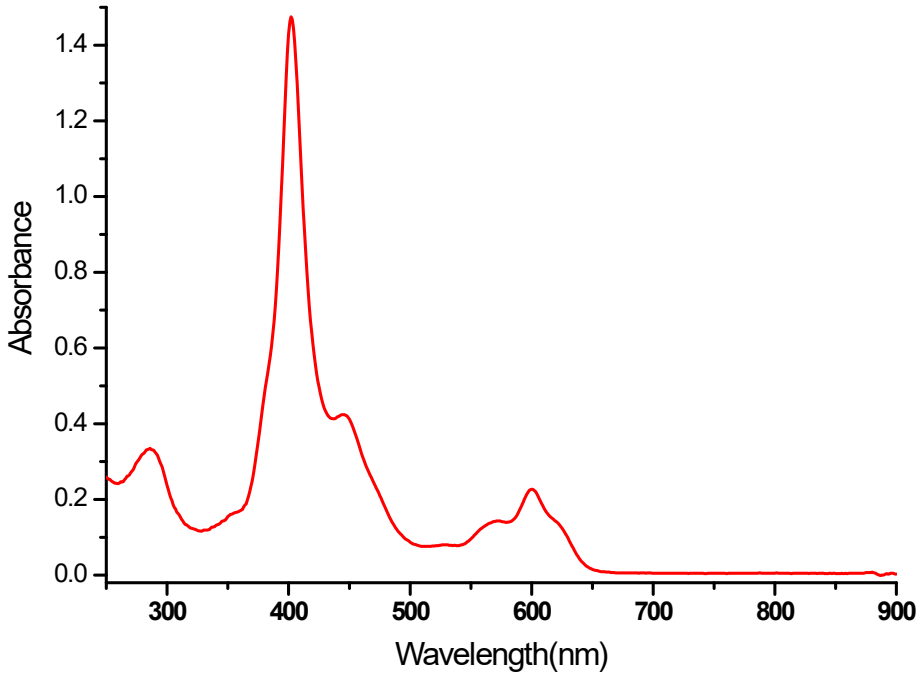


Figure S42. UV-vis spectrum of **5b** (CH_2Cl_2).

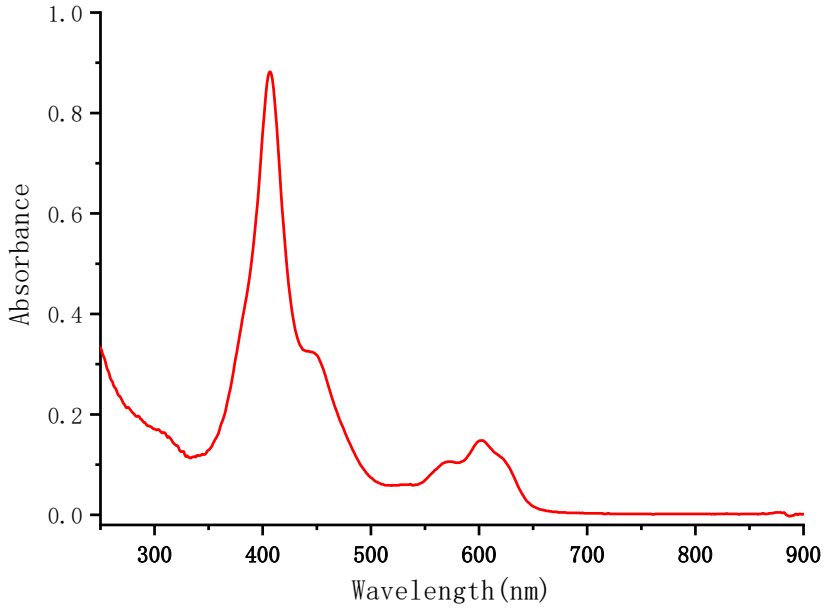


Figure S43. UV-vis spectrum of **5c** (CH_2Cl_2).

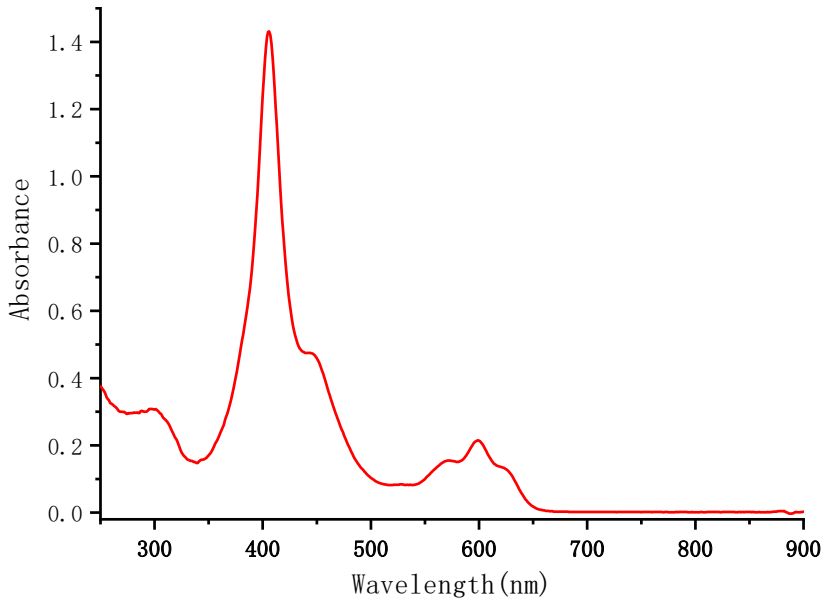
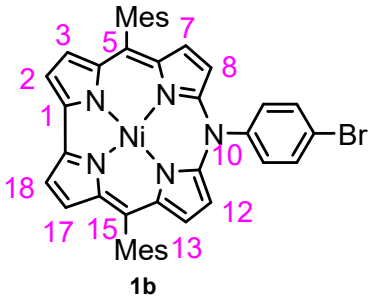
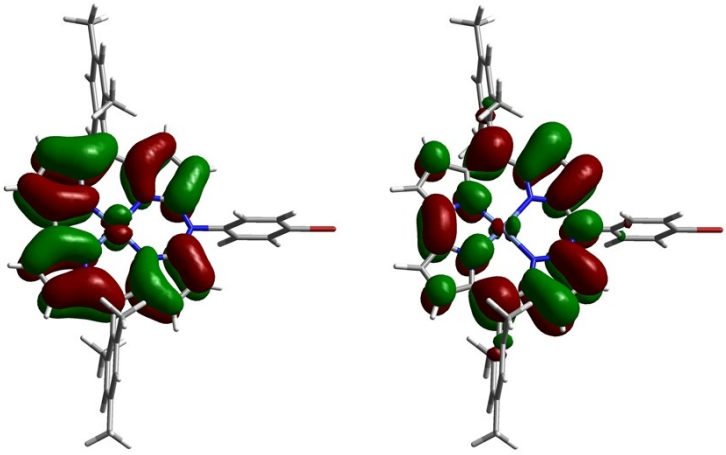


Figure S44. UV-vis spectrum of **5d** (CH_2Cl_2).



1b



HOMO LUMO

Figure S45. Kohn-Sham frontier orbital distributions in **1a** (isosurface 0.02).

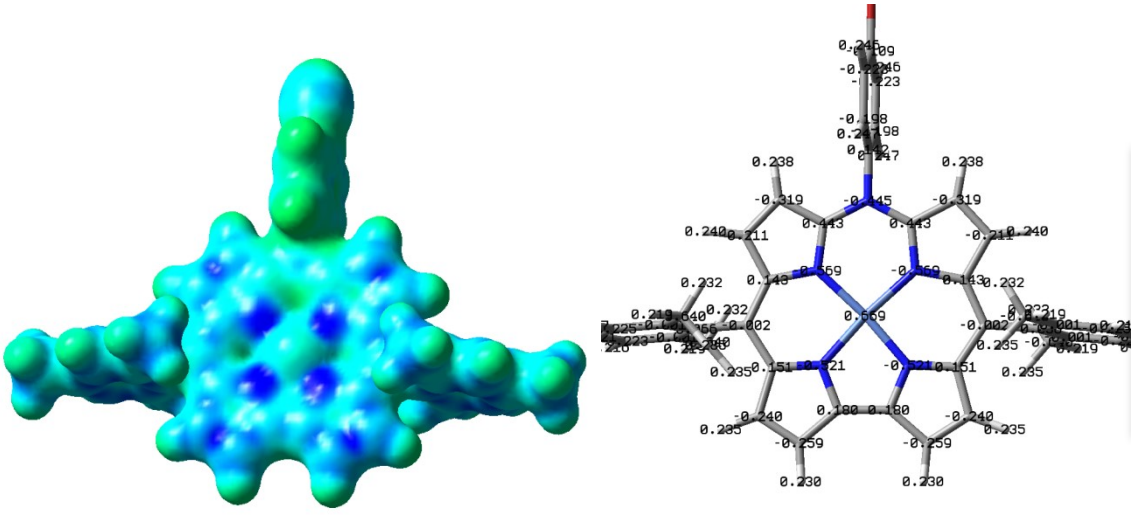


Figure S46. Electrostatic potential and charge distribution in **1a** calculated by NBO approach.

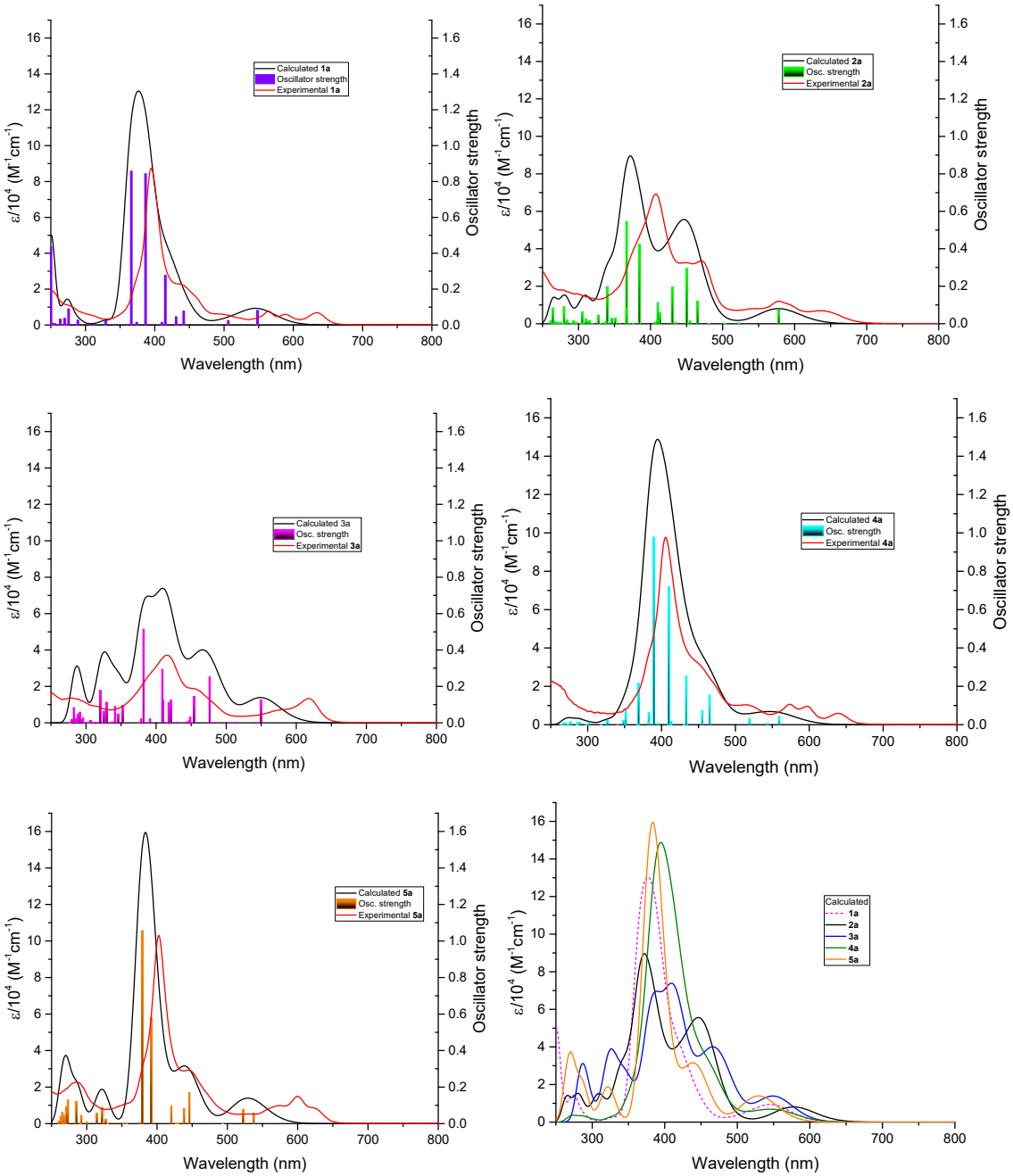


Figure S47 Calculated (black traces) and experimental (red traces) UV-Vis spectra along with histograms representing oscillator strengths of the transitions obtained by TD DFT for DFT-optimized models of the substituted azacorroles **1a**-**5**a.

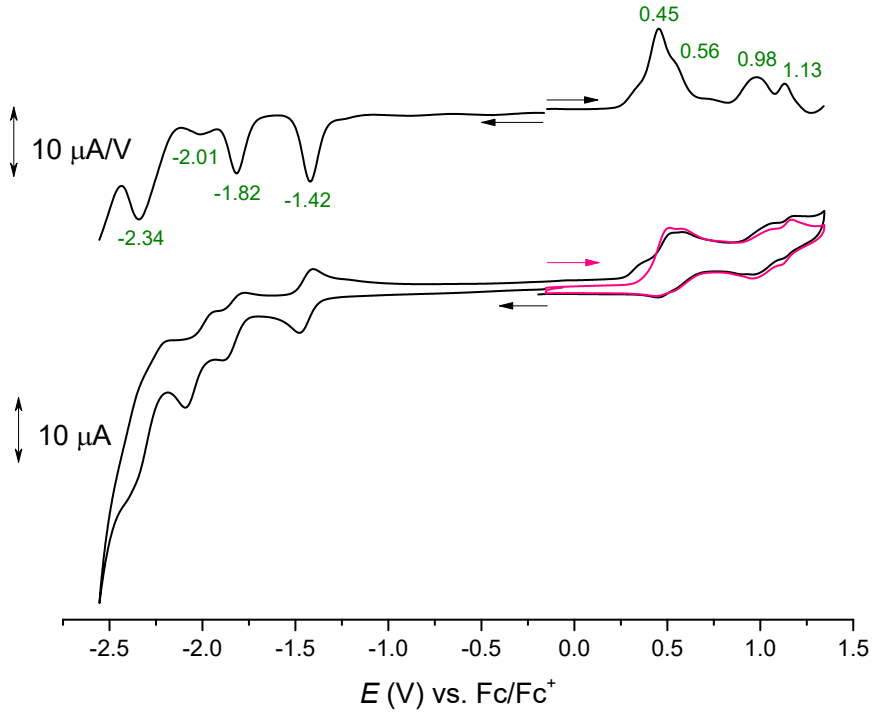


Figure S48 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **2a** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

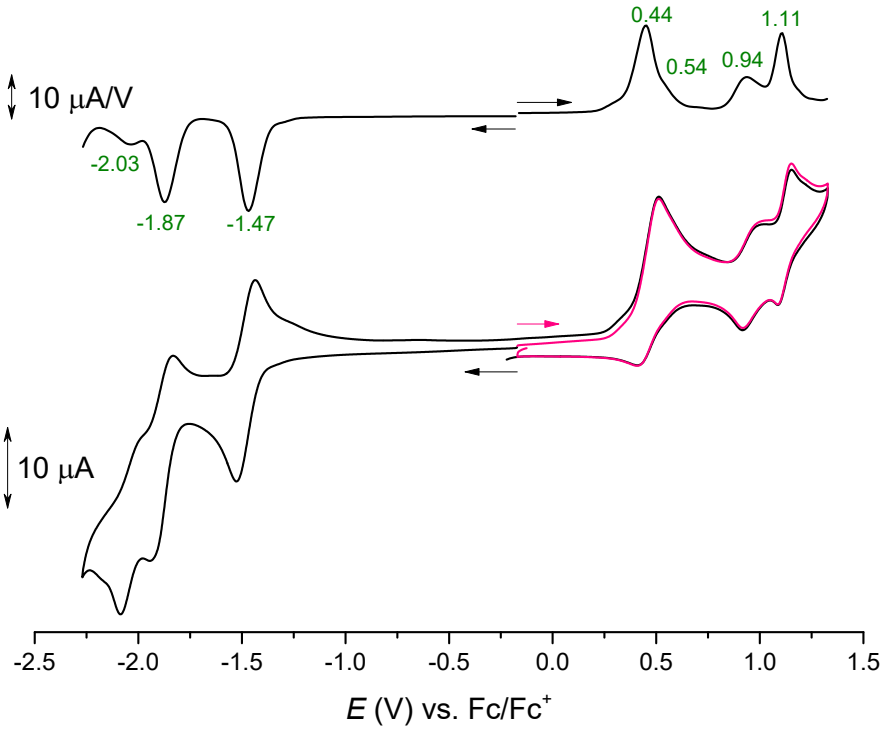


Figure S49 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **2b** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

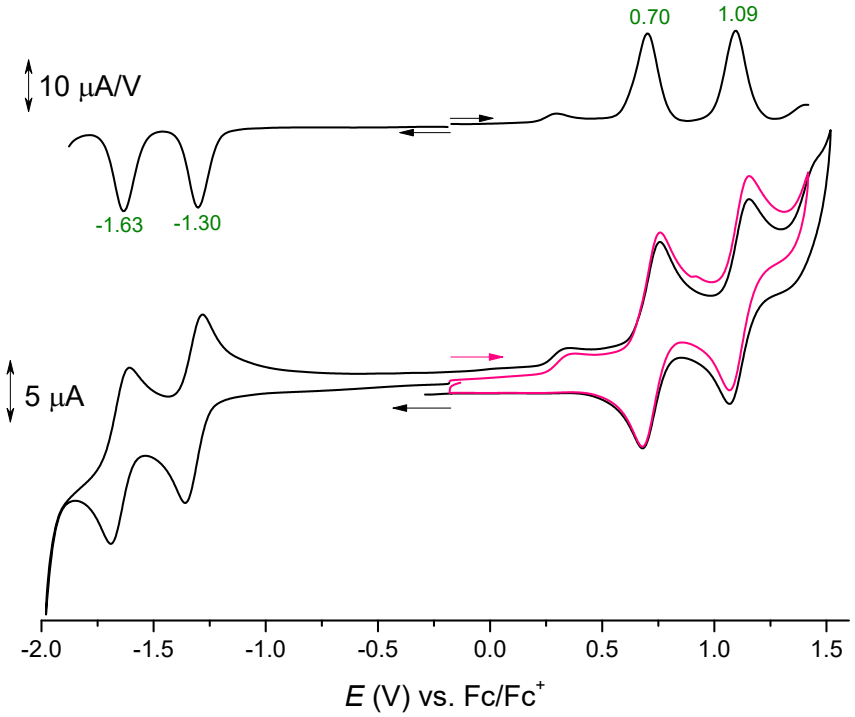


Figure S50 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **3a** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

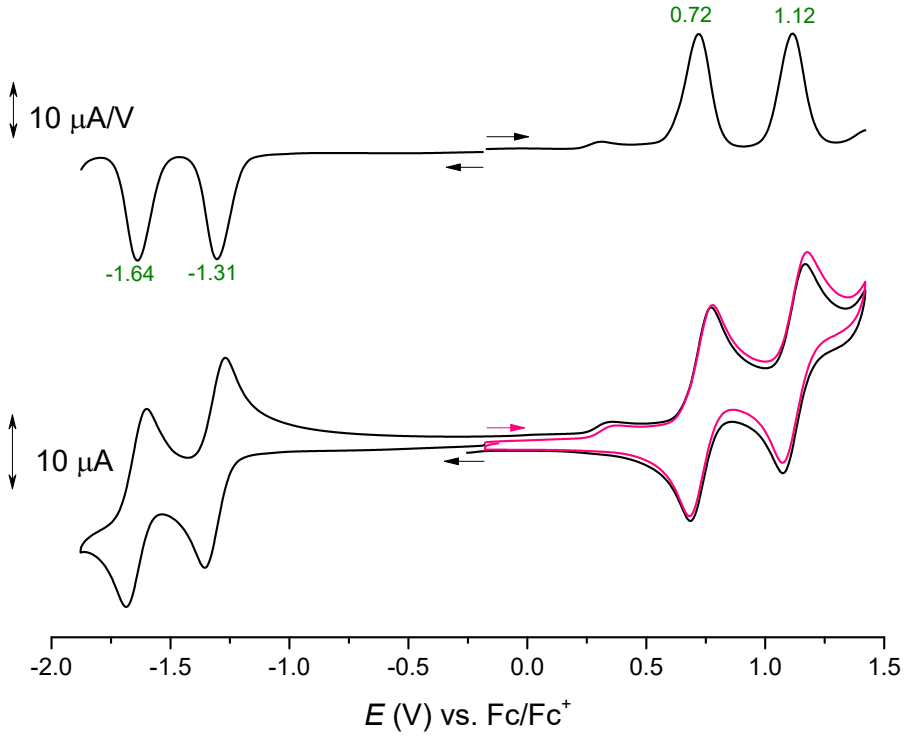


Figure S51 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **3b** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

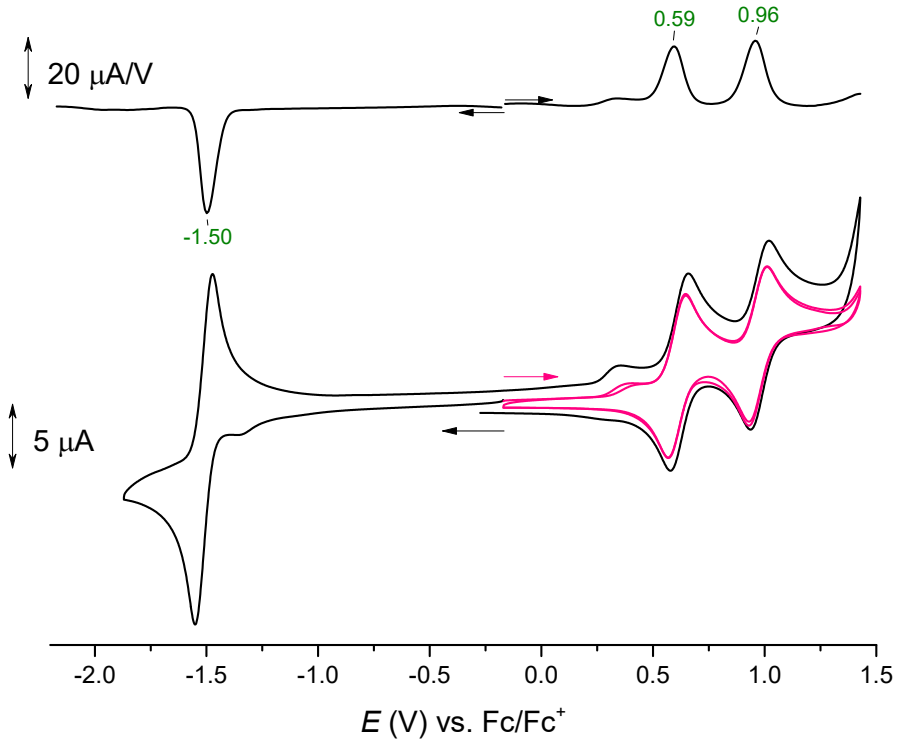


Figure S52 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **4a** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

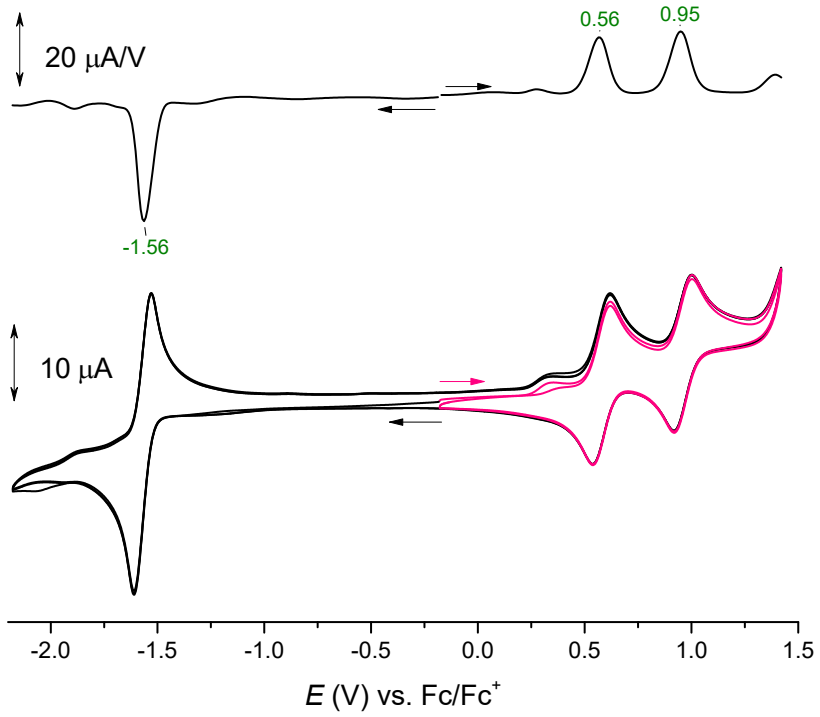


Figure S53 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **4b** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

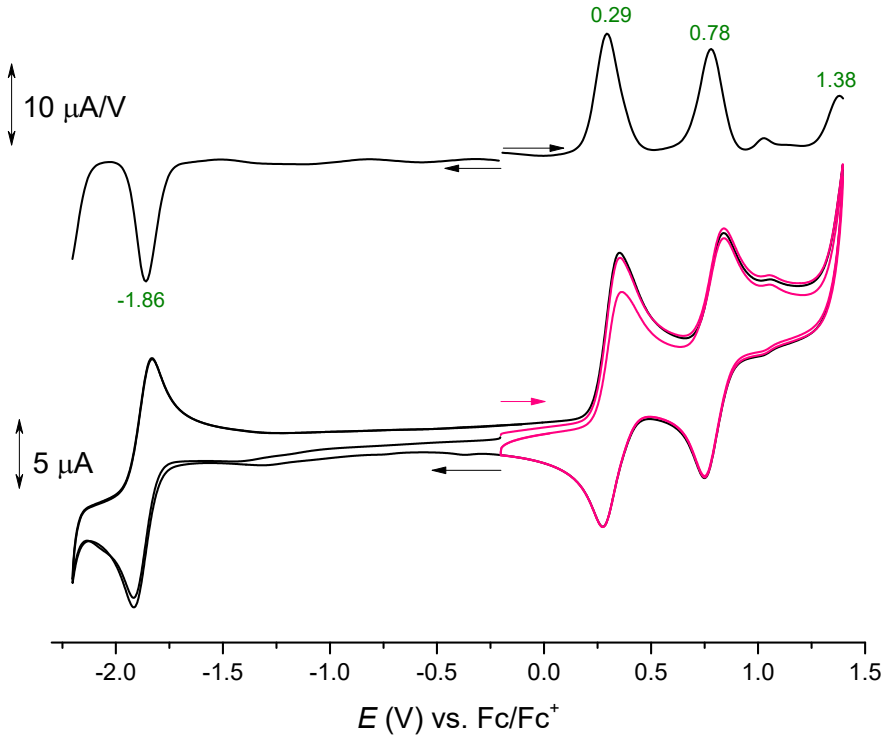


Figure S54 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **5a** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

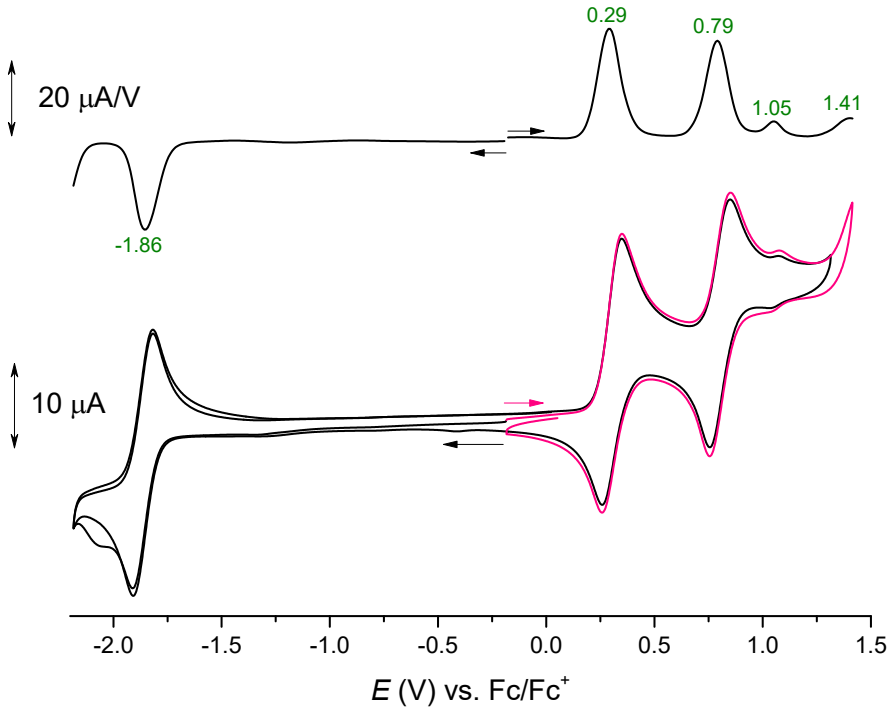


Figure S55 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **5b** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

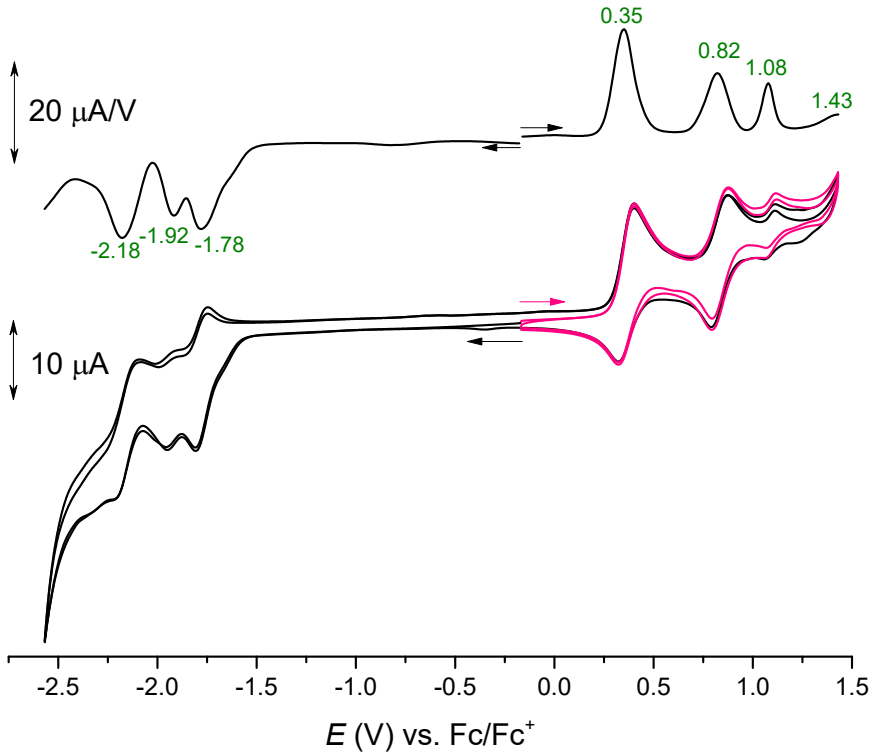


Figure S56 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **5c** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

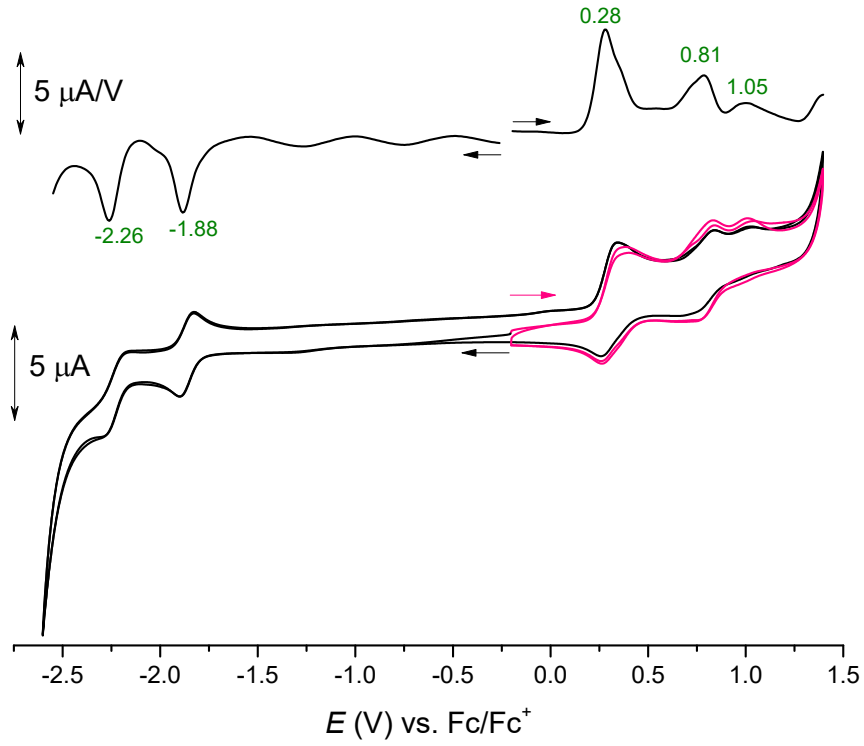


Figure S57 Cyclic (lower traces) and differential pulse (upper traces) voltammograms for **5d** in dichloromethane solution. The green numbers are the electrode potentials in volts. The horizontal arrows indicate directions of the potential advances.

Table S1. Electrochemical data for the 10-azacorrole derivatives (DCM, electrode potentials in V *vs*. Fc/Fc^+)

Entry	Compd.	E_{Red3}	E_{Red2}	E_{Red1}	E_{Ox1}	E_{Ox2}	E_{Ox3}	ΔE
1	**2a**	–2.01[a]	–1.82	–1.42	0.45	0.98	1.13	1.87
2	**2b**	–2.03[a]	–1.87	–1.47	0.44	0.94	1.11	1.91
3	**3a**	-	–1.63	–1.30	0.70	1.09	-	2.00
4	**3b**	-	–1.64	–1.31	0.72	1.12	-	2.03
5	**4a**	-	-	–1.50	0.59	0.96		2.09
6	**4b**	-	-	–1.56	0.56	0.95		2.12
7	**5a**	-	-	–1.86	0.29	0.78	1.38[a]	2.15
8	**5b**	-	-	–1.86	0.29	0.79	1.41[a]	2.15
9	**5c**	–2.18	–1.92[a]	–1.78	0.35	0.82	1.08[a]	2.13
10	**5d**		–2.26	–1.88	0.28	0.91	1.05[a]	2.16
11	**1(3-Me)**[b]			-2.09	0.16	0.68		2.25
12	**1(3-F)**[c]			-2.07	0.10	0.69		2.17
13	**1(4-Br)**[d]			-2.08	0.18	0.68		2.26

[a] Irreversible couple. [b] Data from *Chem. Commun.*, 2023, **59**, 3739 (ref. [45]) for *N*-(3-methylphenyl)-10-azacorrole. [c] Data from *Chem. Commun.*, 2023, **59**, 3739 (ref. [45]) for *N*-(3-fluorophenyl)-10-azacorrole. [d] Data from *Chem. Commun.*, 2023, **59**, 3739 (ref. [45]) for *N*-(4-bromophenyl)-10-azacorrole.

Table S2 Electronic transitions calculated for **1a**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs
1	18235.4	548.4	0.0801	HOMO->LUMO (87%)
2	19754.9	506.2	0.0246	H-1->LUMO (23%), HOMO->L+1 (72%)
3	19925.9	501.9	0	H-3->L+4 (51%), HOMO->L+4 (33%)
4	20520.4	487.3	0.0019	H-4->L+4 (91%)
5	21090.6	474.1	0	H-15->L+4 (10%), H-2->L+4 (83%)
6	22632.7	441.8	0.0768	H-2->LUMO (66%), H-1->LUMO (25%)
7	23049.7	433.8	0.0003	H-4->LUMO (99%)
8	23217.5	430.7	0.0454	H-3->LUMO (40%), H-1->L+1 (53%)
9	24084.5	415.2	0.2764	H-3->L+1 (29%), H-2->LUMO (29%), H-1->LUMO (29%), HOMO->L+1 (13%)
10	24365.2	410.4	0.0136	H-2->L+1 (90%)
11	24757.2	403.9	0	H-4->L+1 (99%)
12	25863.8	386.6	0.8422	H-3->LUMO (45%), H-1->L+1 (38%)
13	26746.2	373.9	0.0146	H-17->L+4 (94%)
14	27311.5	366.1	0.8567	H-3->L+1 (62%), H-1->LUMO (22%), HOMO->L+1 (14%)
15	27818.1	359.5	0.0001	H-6->L+1 (26%), H-5->LUMO (73%)
16	27836.6	359.2	0	H-6->LUMO (72%), H-5->L+1 (27%)
17	28875.5	346.3	0	HOMO->L+2 (99%)
18	29245.7	341.9	0.0003	H-8->LUMO (44%), H-7->LUMO (33%), H-7->L+1 (21%)
19	29247.3	341.9	0.0007	H-8->LUMO (33%), H-8->L+1 (20%), H-7->LUMO (44%)
20	30232.9	330.8	0	H-3->L+4 (29%), HOMO->L+4 (66%)
21	30381.3	329.1	0.0225	H-9->LUMO (98%)
22	30475.7	328.1	0.0002	HOMO->L+3 (99%)
23	30962.8	323.0	0	H-1->L+2 (92%)
24	31005.6	322.5	0	H-6->LUMO (27%), H-5->L+1 (73%)
25	31031.4	322.3	0	H-6->L+1 (74%), H-5->LUMO (26%)
26	31266.1	319.8	0	H-1->L+4 (92%)
27	31960.5	312.9	0	H-8->L+1 (49%), H-7->LUMO (19%), H-7->L+1 (26%)
28	31964.6	312.8	0.0002	H-8->LUMO (20%), H-8->L+1 (27%), H-7->L+1 (51%)
29	32067.8	311.8	0.0026	H-9->L+1 (94%)
30	32613.0	306.6	0.0022	H-1->L+3 (99%)
31	33888.2	295.1	0	H-10->LUMO (99%)
32	34610.1	288.9	0.0264	H-11->LUMO (97%)
33	34829.4	287.1	0.0003	HOMO->L+5 (97%)
34	34859.3	286.9	0.0001	HOMO->L+6 (97%)
35	35433.5	282.2	0	H-2->L+2 (99%)
36	35744.9	279.8	0	H-3->L+2 (98%)
37	36269.9	275.7	0.0897	H-11->L+1 (85%)
38	36293.3	275.5	0.0008	H-10->L+1 (96%)
39	36507.1	273.9	0	H-17->LUMO (97%)

40	36747.4	272.1	0	H-4->L+2 (100%)
41	36814.4	271.6	0.0044	HOMO->L+8 (91%)
42	36844.2	271.4	0.0017	H-2->L+3 (94%)
43	36846.6	271.4	0.0001	HOMO->L+9 (93%)
44	37053.1	269.9	0.0366	H-13->LUMO (25%), H-12->LUMO (51%)
45	37199.9	268.8	0	H-3->L+3 (98%)
46	37636.2	265.7	0.0003	H-15->LUMO (58%), H-14->LUMO (36%)
47	37779.0	264.7	0	HOMO->L+7 (99%)
48	37790.3	264.6	0.0001	H-1->L+5 (96%)
49	37816.9	264.4	0	H-1->L+6 (96%)
50	37950.0	263.5	0.032	H-16->LUMO (25%), H-13->LUMO (25%), H-12->LUMO (34%), HOMO->L+10 (10%)
51	38146.8	262.1	0	H-4->L+3 (100%)
52	38313.8	261.0	0	H-17->L+1 (99%)
53	38569.4	259.3	0.0001	H-15->LUMO (14%), H-14->LUMO (32%), H-12->L+1 (49%)
54	39091.3	255.8	0.0066	H-16->LUMO (55%), H-13->LUMO (19%), HOMO->L+10 (23%)
55	39358.2	254.1	0.0023	H-16->L+1 (15%), H-15->LUMO (11%), H-13->L+1 (59%)
56	39519.6	253.0	0.0083	H-15->L+1 (41%), H-14->L+1 (50%)
57	39813.9	251.2	0.0017	H-1->L+8 (95%)
58	39824.4	251.1	0.0075	H-1->L+9 (93%)
59	39980.1	250.1	0.4369	H-15->L+1 (13%), H-13->LUMO (15%), HOMO->L+10 (50%)
60	40381.8	247.6	0.0001	H-1->L+7 (99%)

Table S3 Electronic transitions calculated for **2a**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs
1	17311.1	577.7	0.0738	HOMO->LUMO (92%)
2	19140.3	522.5	0.0038	H-1->LUMO (36%), HOMO->L+1 (60%)
3	19841.2	504.0	0.0008	H-3->L+4 (19%), H-2->L+4 (18%), HOMO->L+4 (19%)
4	19952.5	501.2	0.0027	H-5->L+4 (56%), H-5->L+5 (24%)
5	20772.8	481.4	0.0005	H-3->L+4 (23%), H-3->L+5 (10%), H-2->L+4 (29%), H-2->L+5 (13%)
6	21510.8	464.9	0.1214	H-2->LUMO (58%), H-1->LUMO (13%), HOMO->L+1 (10%)
7	21990.7	454.7	0.0148	H-5->LUMO (79%)
8	22203.6	450.4	0.2951	H-2->LUMO (20%), H-1->LUMO (28%), H-1->L+1 (14%), HOMO->L+1 (10%)
9	22965.8	435.4	0.0049	H-4->LUMO (81%)
10	23219.9	430.7	0.1959	H-3->LUMO (45%), H-1->L+1 (15%)
11	24224.9	412.8	0.0568	H-3->LUMO (21%), H-3->L+1 (11%), H-2->L+1 (43%), H-1->L+1 (13%)
12	24388.6	410.0	0.1124	H-2->L+1 (31%), H-1->L+1 (19%), HOMO->L+2 (24%)
13	24445.1	409.1	0.0198	H-5->L+1 (86%)
14	24648.3	405.7	0.0067	H-6->LUMO (97%)
15	25980.7	384.9	0.4233	H-3->L+1 (57%), H-2->L+1 (16%)
16	26568.7	376.4	0.0028	H-17->L+4 (60%), H-17->L+5 (26%)
17	26942.1	371.2	0.0002	H-7->LUMO (25%), H-7->L+1 (73%)
18	27266.4	366.8	0.5457	H-7->LUMO (10%), H-1->L+1 (15%), HOMO->L+2 (48%)
19	27274.4	366.6	0.0838	H-7->LUMO (64%), H-7->L+1 (22%)

20	27962.4	357.6	0.0002	H-8->LUMO (95%)
21	28427.8	351.8	0.0011	H-8->L+1 (88%)
22	28456.9	351.4	0.0296	H-4->L+1 (84%)
23	28901.3	346.0	0.0305	H-9->LUMO (83%)
24	29402.1	340.1	0.1978	H-1->L+2 (73%)
25	29578.0	338.1	0.0124	H-3->L+4 (10%), HOMO->L+4 (45%), HOMO->L+5 (19%)
26	29711.0	336.6	0.0002	H-6->L+1 (99%)
27	30326.4	329.7	0.0006	HOMO->L+3 (96%)
28	30538.6	327.5	0.0423	H-13->LUMO (10%), H-11->LUMO (24%), H-4->L+2 (11%)
29	31299.2	319.5	0.0016	H-1->L+4 (64%), H-1->L+5 (27%)
30	31390.3	318.6	0.0002	H-10->LUMO (96%)
31	31754.9	314.9	0.0162	H-9->L+1 (93%)
32	31971.0	312.8	0.0135	H-2->L+2 (10%), HOMO->L+4 (27%), HOMO->L+5 (59%)
33	32222.7	310.3	0.0264	H-4->L+2 (19%), H-3->L+2 (27%), H-2->L+2 (42%)
34	32276.7	309.8	0.0188	H-4->L+2 (36%), H-3->L+2 (12%), H-2->L+2 (32%)
35	32730.0	305.5	0.0639	H-11->LUMO (24%), H-4->L+2 (20%), H-3->L+2 (39%)
36	32796.9	304.9	0.0016	H-1->L+3 (95%)
37	33060.7	302.5	0.0025	H-5->L+2 (97%)
38	33737.4	296.4	0.0048	H-6->L+2 (95%)
39	34149.5	292.8	0.0051	H-10->L+1 (72%)
40	34151.9	292.8	0.0141	H-13->LUMO (13%), H-12->LUMO (13%), H-11->LUMO (28%), H-10->L+1 (25%)
41	34489.1	289.9	0.0011	H-1->L+4 (29%), H-1->L+5 (68%)
42	35187.6	284.2	0.0194	H-21->LUMO (15%), H-20->LUMO (14%), H-17->LUMO (12%), H-12->LUMO (16%)
43	35330.3	283.0	0.0133	H-16->LUMO (15%), H-12->LUMO (23%), H-11->L+1 (30%)
44	35727.1	279.9	0.0913	H-13->LUMO (12%), H-12->LUMO (15%), H-11->L+1 (48%)
45	35893.3	278.6	0.0029	H-17->LUMO (66%)
46	36198.2	276.3	0.0001	HOMO->L+6 (98%)
47	36259.5	275.8	0.006	H-15->LUMO (61%), H-12->LUMO (12%)
48	36724.8	272.3	0.0003	H-7->L+2 (94%)
49	36733.7	272.2	0	H-2->L+3 (98%)
50	36743.4	272.2	0.0057	H-16->LUMO (10%), H-14->LUMO (62%)
51	37306.4	268.1	0.0001	H-3->L+3 (98%)
52	37323.3	267.9	0.0093	H-19->LUMO (14%), H-14->LUMO (10%), H-13->LUMO (35%), H-13->L+1 (11%)
53	37486.2	266.8	0.0001	H-8->L+2 (99%)
54	37493.5	266.7	0.0049	HOMO->L+7 (94%)
55	37781.4	264.7	0.0844	H-16->LUMO (33%), H-15->LUMO (13%), H-12->L+1 (19%)
56	38075.8	262.6	0.0041	H-17->L+1 (43%), H-12->L+1 (15%)
57	38212.9	261.7	0	H-5->L+3 (97%)
58	38223.4	261.6	0.0051	H-17->L+1 (19%), H-12->L+1 (26%), HOMO->L+9 (31%)
59	38264.6	261.3	0.0032	H-2->L+4 (12%), H-2->L+5 (29%), HOMO->L+9 (41%)
60	38277.5	261.3	0.0138	H-17->L+1 (19%), H-2->L+4 (15%), H-2->L+5 (32%), HOMO->L+9 (12%)

Table S4 Electronic transitions calculated for **3a**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs
1	18187.8	549.8	0.1248	H-1->L+1 (10%), HOMO->LUMO (86%)
2	18578.2	538.3	0.0015	H-1->LUMO (13%), HOMO->L+1 (80%)
3	19512.2	512.5	0.0013	H-8->L+4 (77%)
4	19834.8	504.2	0.0004	H-5->L+4 (49%), HOMO->L+4 (23%)
5	20522.8	487.3	0.0013	H-4->L+4 (67%)
6	20991.4	476.4	0.2517	H-1->LUMO (71%), HOMO->L+1 (10%)
7	22008.5	454.4	0.1437	H-5->LUMO (19%), H-4->L+1 (11%), H-2->LUMO (19%), H-1->L+1 (37%)
8	22251.2	449.4	0.0009	H-8->LUMO (57%), H-4->LUMO (17%), H-3->LUMO (14%)
9	22294.0	448.6	0.0318	H-5->LUMO (10%), H-3->L+1 (22%), H-2->LUMO (50%), H-1->L+1 (13%)
10	22361.7	447.2	0.0114	H-8->LUMO (24%), H-3->LUMO (46%), H-2->L+1 (19%)
11	22506.9	444.3	0.0053	H-8->LUMO (12%), H-4->LUMO (63%)
12	23242.5	430.2	0.0015	H-8->L+1 (96%)
13	23747.4	421.1	0.1254	H-7->LUMO (33%), H-6->L+1 (10%), H-4->L+1 (34%)
14	23836.9	419.5	0.001	H-7->L+1 (25%), H-6->LUMO (68%)
15	23926.4	417.9	0.1088	H-7->LUMO (27%), H-6->L+1 (17%), H-4->L+1 (33%)
16	24416.8	409.6	0.1253	H-5->L+1 (56%), HOMO->L+2 (17%)
17	24456.3	408.9	0.2932	H-5->LUMO (53%), H-1->L+1 (17%)
18	25483.9	392.4	0.0003	H-3->LUMO (30%), H-2->L+1 (60%)
19	25559.7	391.2	0.0207	H-3->L+1 (64%), H-2->LUMO (27%)
20	26171.9	382.1	0.5148	H-5->L+1 (14%), HOMO->L+2 (72%)
21	26418.7	378.5	0.0216	H-18->L+4 (71%)
22	26609.8	375.8	0.0008	H-7->L+1 (24%), H-6->LUMO (19%), H-6->L+1 (45%)
23	26613.1	375.8	0.0008	H-7->LUMO (18%), H-7->L+1 (44%), H-6->L+1 (25%)
24	28380.2	352.4	0.096	H-1->L+2 (21%), HOMO->L+3 (68%)
25	28904.5	346.0	0.0491	H-10->LUMO (33%), H-1->L+2 (56%)
26	29290.0	341.4	0.0911	H-10->LUMO (43%), H-1->L+2 (14%)
27	29645.7	337.3	0.0052	H-5->L+4 (17%), HOMO->L+4 (70%)
28	29679.6	336.9	0.001	H-11->LUMO (13%), H-10->L+1 (47%)
29	30374.0	329.2	0.113	H-10->L+1 (14%), H-1->L+3 (34%), H-1->L+4 (31%)
30	30621.6	326.6	0	H-10->L+1 (26%), H-2->L+2 (10%), H-1->L+4 (41%)
31	30636.2	326.4	0.0006	H-9->LUMO (99%)
32	30688.6	325.9	0.0635	H-11->L+1 (10%), H-10->LUMO (15%), H-3->L+2 (26%)
33	30909.6	323.5	0.0001	H-9->L+1 (99%)
34	31178.2	320.7	0.1776	H-1->L+3 (41%), H-1->L+4 (21%)
35	31699.2	315.5	0.0009	H-11->LUMO (15%), H-3->L+3 (11%), H-2->L+2 (46%), H-1->L+3 (12%)
36	31844.4	314.0	0.0034	H-4->L+2 (27%), H-3->L+2 (31%), H-2->L+3 (18%)
37	32266.2	309.9	0.0001	HOMO->L+5 (97%)
38	32542.9	307.3	0.0097	H-11->LUMO (17%), H-5->L+2 (70%)
39	32597.7	306.8	0.0121	H-6->L+2 (22%), H-4->L+2 (42%)
40	32716.3	305.7	0.0067	H-7->L+2 (73%), H-6->L+3 (20%)
41	32801.0	304.9	0.0002	H-7->L+3 (12%), H-6->L+2 (50%), H-4->L+2 (11%)

42	33235.7	300.9	0.0002	H-8->L+2 (98%)
43	33820.4	295.7	0.0268	H-11->LUMO (10%), H-5->L+2 (11%), H-4->L+3 (60%)
44	33894.6	295.0	0.0001	H-1->L+5 (96%)
45	33962.4	294.4	0.0168	HOMO->L+6 (90%)
46	34328.6	291.3	0.0584	H-11->L+1 (17%), H-5->L+3 (54%)
47	34701.2	288.2	0.0246	H-12->LUMO (28%), H-11->L+1 (32%), H-5->L+3 (12%)
48	34706.8	288.1	0.0471	H-14->LUMO (28%), H-12->L+1 (14%), H-11->LUMO (17%), H-4->L+3 (14%)
49	34784.3	287.5	0.0027	H-8->L+3 (77%)
50	34994.8	285.8	0.0097	H-21->LUMO (10%), H-12->LUMO (20%), H-3->L+2 (14%), H-2->L+3 (15%)
51	35064.1	285.2	0.0208	H-12->L+1 (18%), H-8->L+3 (18%)
52	35256.1	283.6	0.0235	H-3->L+2 (11%), H-2->L+3 (47%)
53	35276.3	283.5	0.0022	H-3->L+3 (58%), H-2->L+2 (15%)
54	35358.5	282.8	0.0121	H-13->LUMO (11%), H-12->LUMO (37%)
55	35377.1	282.7	0.0832	H-14->LUMO (14%), H-12->L+1 (52%)
56	35713.4	280.0	0.0165	H-1->L+6 (93%)
57	36094.9	277.0	0.0014	H-15->LUMO (45%), H-14->L+1 (24%), H-13->LUMO (11%)
58	36119.9	276.9	0.0006	H-15->L+1 (14%), H-14->LUMO (22%), H-13->L+1 (29%)
59	36283.7	275.6	0.0002	H-7->L+3 (58%), H-6->L+2 (23%), H-6->L+3 (14%)
60	36290.1	275.6	0	H-7->L+2 (22%), H-7->L+3 (14%), H-6->L+3 (58%)

Table S5 Electronic transitions calculated for **4a**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs
1	17879.7	559.3	0.044	H-6->L+2 (11%), HOMO->LUMO (77%)
2	18096.7	552.6	0	H-12->L+2 (17%), H-3->L+2 (27%), HOMO->L+2 (34%)
3	18404.0	543.4	0.007	H-6->L+2 (82%), HOMO->LUMO (10%)
4	19074.2	524.3	0	H-14->L+2 (17%), H-2->L+2 (64%)
5	19258.1	519.3	0.0325	H-1->LUMO (24%), HOMO->L+1 (71%)
6	21501.9	465.1	0.1542	H-2->LUMO (52%), H-1->LUMO (36%)
7	21972.2	455.1	0.0748	H-3->LUMO (32%), H-1->L+1 (55%)
8	23051.3	433.8	0.0003	H-6->LUMO (99%)
9	23067.5	433.5	0.254	H-3->L+1 (35%), H-2->LUMO (36%), H-1->LUMO (18%), HOMO->L+1 (10%)
10	23232.8	430.4	0.0008	H-3->LUMO (12%), H-2->L+1 (82%)
11	24203.1	413.2	0.0179	H-5->L+1 (29%), H-4->LUMO (67%)
12	24227.3	412.8	0.0003	H-5->LUMO (68%), H-4->L+1 (31%)
13	24374.1	410.3	0.719	H-3->LUMO (48%), H-1->L+1 (30%)

14	24456.3	408.9	0.0001	H-6->L+1 (99%)
15	25317.7	395.0	0.0059	H-23->L+2 (83%)
16	25695.2	389.2	0.9775	H-3->L+1 (56%), H-1->LUMO (19%), HOMO->L+1 (14%)
17	26112.2	383.0	0.0638	H-8->L+1 (23%), H-7->LUMO (72%)
18	26146.1	382.5	0.0135	H-8->LUMO (72%), H-7->L+1 (25%)
19	27108.3	368.9	0.2152	H-9->LUMO (85%)
20	27209.9	367.5	0.0003	H-5->LUMO (32%), H-4->L+1 (68%)
21	27236.5	367.2	0.0029	H-5->L+1 (69%), H-4->LUMO (30%)
22	27529.3	363.2	0	H-3->L+2 (22%), HOMO->L+2 (64%)
23	27889.0	358.6	0	H-1->L+2 (98%)
24	28454.4	351.4	0.071	H-9->L+1 (39%), H-8->L+1 (45%), H-7->LUMO (11%)
25	28596.4	349.7	0.0022	H-8->LUMO (23%), H-7->L+1 (72%)
26	28707.7	348.3	0.023	H-9->L+1 (57%), H-8->L+1 (27%), H-7->LUMO (12%)
27	29254.5	341.8	0	H-10->LUMO (98%)
28	29372.3	340.5	0.0001	H-11->LUMO (92%)
29	30657.1	326.2	0.0227	H-11->L+1 (89%)
30	31381.4	318.7	0.0001	H-12->LUMO (86%)
31	31512.1	317.3	0.0002	H-10->L+1 (98%)
32	31762.1	314.8	0	HOMO->L+3 (99%)
33	32795.3	304.9	0	H-13->LUMO (99%)
34	33056.6	302.5	0	H-1->L+3 (99%)
35	33078.4	302.3	0.0096	H-12->L+1 (91%)
36	33097.8	302.1	0	H-13->L+1 (98%)
37	33418.0	299.2	0.0009	H-14->LUMO (75%), HOMO->L+4 (19%)
38	33641.4	297.3	0.0001	H-14->LUMO (17%), HOMO->L+4 (79%)
39	34202.7	292.4	0	H-9->L+2 (47%), H-3->L+2 (39%)
40	34635.1	288.7	0.0118	H-15->LUMO (71%), H-14->L+1 (24%)
41	34837.5	287.0	0.0113	H-15->LUMO (27%), H-14->L+1 (65%)
42	35019.8	285.6	0.0005	H-1->L+4 (95%)
43	35137.5	284.6	0	H-16->LUMO (95%)
44	36102.2	277.0	0.0001	H-4->L+2 (99%)
45	36154.6	276.6	0.0162	H-5->L+2 (97%)
46	36241.7	275.9	0	H-23->LUMO (14%), H-20->LUMO (14%), H-17->LUMO (58%)
47	36495.0	274.0	0.0005	H-11->L+2 (35%), H-7->L+2 (22%), H-2->L+2 (24%)

48	36562.7	273.5	0.0021	H-18->LUMO (28%), H-15->L+1 (68%)
49	36816.8	271.6	0	H-20->LUMO (33%), H-17->LUMO (11%), H-16->L+1 (45%)
50	36940.2	270.7	0	H-21->LUMO (27%), H-17->L+1 (67%)
51	37156.3	269.1	0.0094	H-19->LUMO (57%), HOMO->L+7 (33%)
52	37202.3	268.8	0	HOMO->L+5 (78%), HOMO->L+8 (10%)
53	37231.4	268.6	0.0001	HOMO->L+6 (85%)
54	37320.1	268.0	0.0096	H-18->LUMO (57%), H-15->L+1 (30%)
55	37331.4	267.9	0	H-2->L+3 (96%)
56	37566.9	266.2	0.0002	H-9->L+2 (17%), H-8->L+2 (73%)
57	37714.5	265.2	0	H-23->LUMO (60%), H-21->L+1 (13%), H-17->LUMO (10%)
58	37857.2	264.2	0	H-11->L+2 (15%), H-7->L+2 (75%)
59	37941.1	263.6	0.0001	H-3->L+3 (91%)
60	37987.9	263.2	0.0001	HOMO->L+5 (10%), HOMO->L+8 (77%)

Table S6 Electronic transitions calculated for **5a**

No.	Energy (cm^{-1})	Wavelength (nm)	Osc. Strength	Major contribs
1	18607.2	537.4	0.0583	HOMO->LUMO (36%), HOMO->L+1 (47%)
2	19129.1	522.8	0.0759	HOMO->LUMO (49%), HOMO->L+1 (34%)
3	19896.1	502.6	0	H-3->L+5 (47%), HOMO->L+5 (31%)
4	20263.9	493.5	0.0003	H-4->L+5 (88%)
5	20966.4	477.0	0	H-2->L+5 (77%)
6	22426.2	445.9	0.1697	H-3->LUMO (12%), H-1->LUMO (18%), H-1->L+1 (52%)
7	22811.8	438.4	0.0838	H-3->L+1 (14%), H-2->LUMO (41%), H-1->LUMO (24%), H-1->L+1 (11%)
8	23240.9	430.3	0.0004	H-4->LUMO (35%), H-4->L+1 (64%)
9	23410.2	427.2	0.0008	H-3->L+1 (10%), H-2->LUMO (31%), H-2->L+1 (51%)
10	23665.1	422.6	0	H-4->LUMO (64%), H-4->L+1 (35%)
11	23790.1	420.3	0.0946	H-3->LUMO (16%), H-3->L+1 (12%), H-2->LUMO (20%), H-2->L+1 (30%), H-1->LUMO (12%)
12	25510.5	392.0	0.5795	H-3->LUMO (48%), H-3->L+1 (21%), H-1->L+1 (11%)
13	26370.3	379.2	1.0566	H-3->LUMO (16%), H-3->L+1 (33%), H-1->LUMO (24%), HOMO->L+1 (10%)
14	26636.5	375.4	0.0063	H-18->L+5 (95%)
15	26645.3	375.3	0	H-6->LUMO (12%), H-5->LUMO (85%)
16	27001.8	370.3	0	H-6->L+1 (83%), H-5->L+1 (12%)
17	27999.5	357.1	0.0005	H-7->LUMO (97%)

18	28398.8	352.1	0.0004	H-8->L+1 (96%)
19	28556.1	350.2	0	H-9->LUMO (42%), H-9->L+1 (46%)
20	29598.1	337.9	0	H-6->L+1 (13%), H-5->L+1 (84%)
21	29719.9	336.5	0	H-6->LUMO (85%), H-5->LUMO (12%)
22	29853.0	335.0	0	HOMO->L+2 (97%)
23	30306.3	330.0	0	H-3->L+5 (22%), HOMO->L+5 (64%)
24	30357.9	329.4	0.0005	H-7->L+1 (96%)
25	30541.8	327.4	0.0125	H-10->LUMO (24%), H-8->LUMO (67%)
26	30568.4	327.1	0.0241	H-10->LUMO (50%), H-10->L+1 (12%), H-8->LUMO (30%)
27	30971.7	322.9	0.0145	H-10->LUMO (19%), H-10->L+1 (78%)
28	31022.5	322.3	0.0889	HOMO->L+3 (79%), HOMO->L+4 (11%)
29	31391.9	318.6	0	H-1->L+5 (88%)
30	31516.1	317.3	0	H-9->LUMO (55%), H-9->L+1 (43%)
31	31820.2	314.3	0.0568	HOMO->L+3 (15%), HOMO->L+4 (79%)
32	31835.5	314.1	0	H-1->L+2 (95%)
33	33334.9	300.0	0.0073	H-1->L+3 (97%)
34	33444.6	299.0	0	H-11->LUMO (72%), H-11->L+1 (27%)
35	34216.5	292.3	0.0442	H-12->LUMO (18%), H-12->L+1 (18%), H-1->L+4 (61%)
36	34336.6	291.2	0.0006	H-11->LUMO (27%), H-11->L+1 (72%)
37	35027.9	285.5	0.0301	H-12->LUMO (66%), H-1->L+4 (26%)
38	35090.0	285.0	0.1196	H-12->LUMO (11%), H-12->L+1 (75%)
39	35727.9	279.9	0	HOMO->L+6 (97%)
40	36040.1	277.5	0	H-2->L+2 (99%)
41	36094.9	277.0	0	HOMO->L+7 (96%)
42	36494.2	274.0	0	H-3->L+2 (98%)
43	36597.4	273.2	0.1284	H-13->LUMO (14%), H-2->L+3 (34%), H-2->L+4 (34%)
44	36795.8	271.8	0	H-18->LUMO (39%), H-18->L+1 (57%)
45	36899.1	271.0	0.0906	H-15->L+1 (16%), H-13->LUMO (16%), H-13->L+1 (32%)
46	37046.7	269.9	0.0004	H-4->L+3 (26%), H-4->L+4 (54%)
47	37304.8	268.1	0	H-18->LUMO (57%), H-18->L+1 (41%)
48	37338.6	267.8	0	H-4->L+2 (100%)
49	37350.7	267.7	0.0436	H-13->LUMO (42%), H-3->L+3 (25%), H-3->L+4 (11%)
50	37523.3	266.5	0.0008	H-3->L+3 (11%), H-2->L+3 (47%), H-2->L+4 (17%)
51	37657.2	265.6	0	H-9->L+3 (17%), H-9->L+4 (54%)

52	37704.8	265.2	0.0627	H-13->L+1 (16%), H-3->L+3 (24%), H-2->L+4 (30%)
53	37771.8	264.7	0.0026	HOMO->L+10 (80%)
54	37832.2	264.3	0.0214	H-16->LUMO (26%), H-16->L+1 (13%), H-15->LUMO (11%), H-15->L+1 (16%), H-13->L+1 (13%), HOMO->L+10 (13%)
55	37956.5	263.5	0.0012	HOMO->L+9 (93%)
56	38017.7	263.0	0.0375	H-16->LUMO (16%), H-15->LUMO (12%), H-3->L+3 (27%), H-3->L+4 (12%)
57	38289.6	261.2	0.0104	H-16->LUMO (16%), H-16->L+1 (11%), H-15->LUMO (14%), H-15->L+1 (24%), H-3->L+4 (21%)
58	38387.2	260.5	0.0118	H-15->LUMO (39%), H-3->L+4 (38%)
59	38506.5	259.7	0.0061	H-17->L+1 (26%), H-16->L+1 (33%), H-14->LUMO (10%), H-14->L+1 (15%)
60	38688.0	258.5	0	H-1->L+7 (88%)

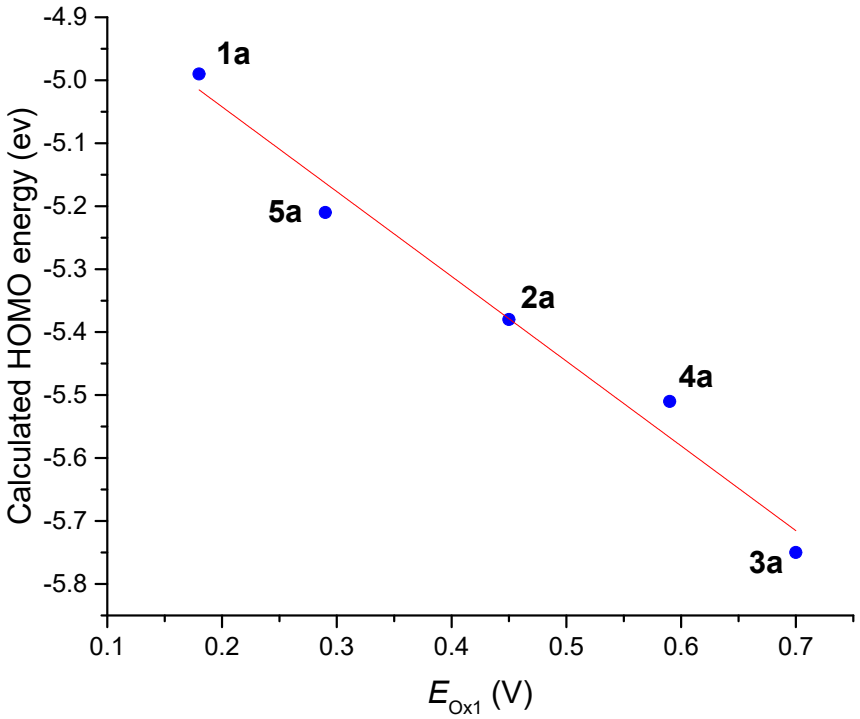


Figure S56 Correlations of calculated HOMO energy with the first oxidation potentials for the compounds **1a**-**5a.**

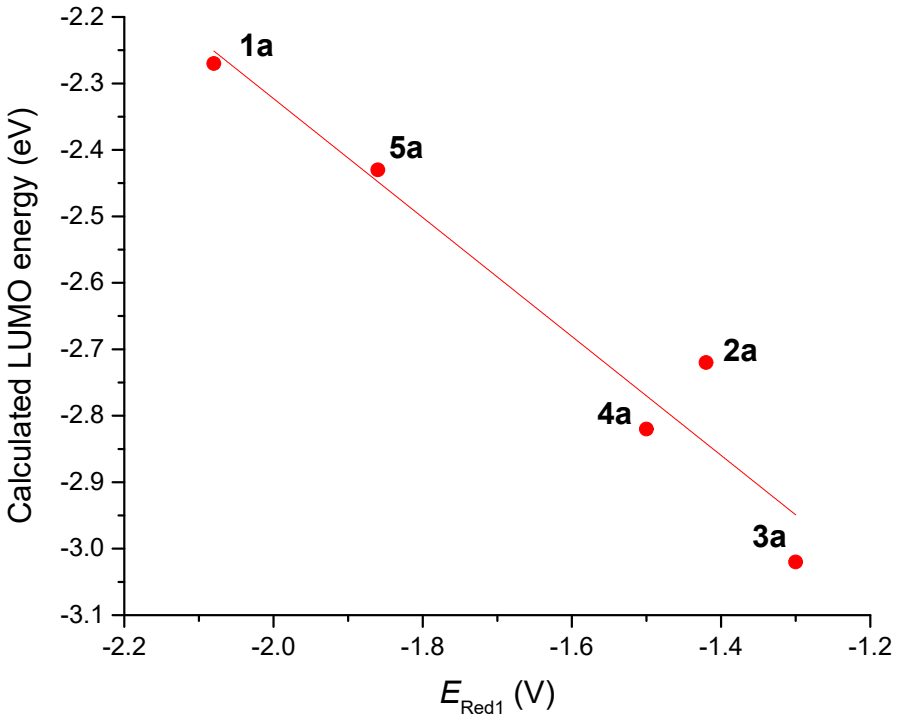


Figure S57 Correlations of calculated LUMO energy with the first reduction potentials for the compounds **1a**-**5a.**

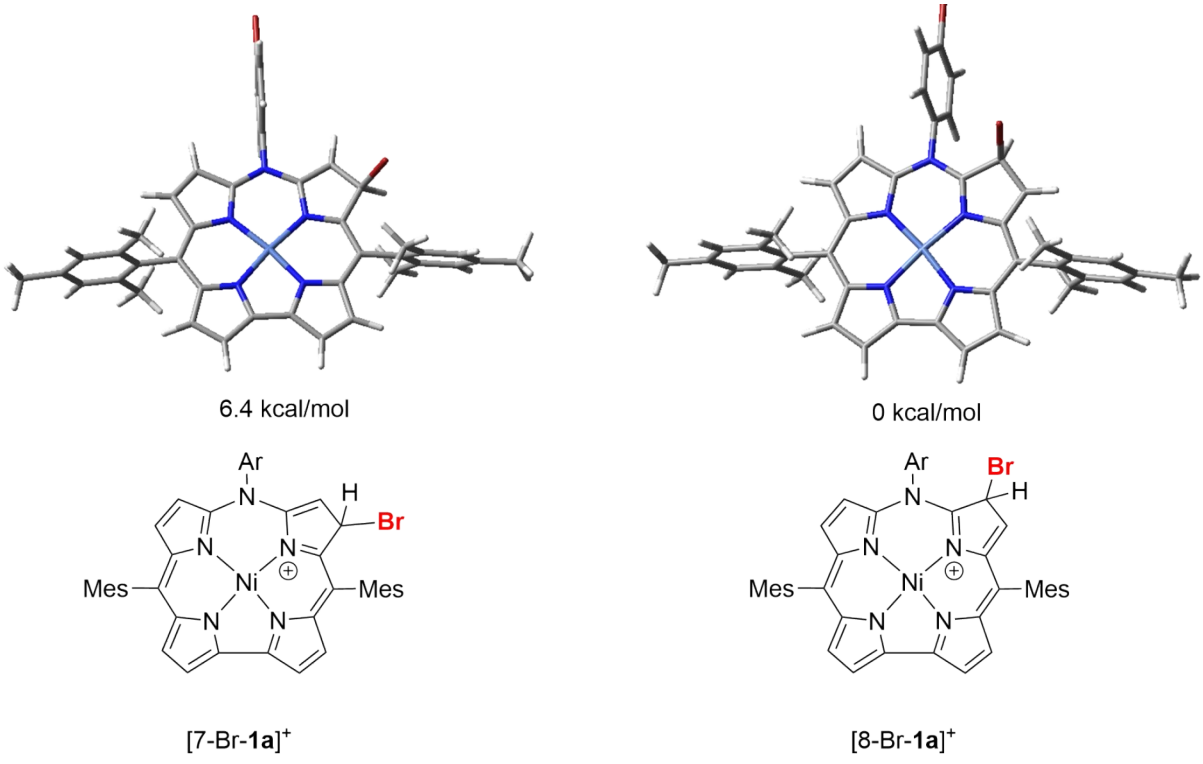


Figure S58 DFT optimized models and relative energies of possible cationic intermediates that can be formed upon addition of one bromine atom in the C7 or C8 site.

Table S7. Computational details for the optimized structures of compounds using Gaussian[1] and NBO[2] software packages

Structure / Name[a]	SCF E	ZPV[b]	lowest freq.	E	ΔH	ΔG[c]	HOMO	LUMO	HLG
	a.u.	a.u.	cm^{-1}	a.u.	a.u.	a.u.	eV	eV	eV
1a /Azacor-OF_a	-5975.541546	-5974.888266	7.24	-5974.845169	-5974.844224	-5974.971043	4.99	2.27	2.72
2a/ AzacorNO2-OF_a	-6179.879760	-6179.223692	7.73	-6179.177988	-6179.177043	-6179.308791	5.36	2.72	2.64
3a/ Azacor2NO2-OF_a	-6384.216142	-6383.557340	12.67	-6383.509010	-6383.508066	-6383.644684	5.74	3.02	2.72
4a / AzacorBr6-OF_a	-21415.096807	-21414.505078	7.05	-21414.452161	-21414.451217	-21414.604130	5.52	2.82	2.70
5a/ AzacorAc-OF_a	-6128.075675	-6127.384978	12.98	-6127.338282	-6127.337338	-6127.471184	5.21	2.43	2.78
[8-Br-**1a**]$^+$ / AzacorBr+-OF_a	-8549.179829	-8548.524711	13.73	-8548.479780	-8548.478836	-8548.609811	-	-	-
[7-Br-**1a**]$^+$ / AzacorBr+-OF_a2	-8549.168509	-8548.514201	6.97	-8548.469181	-8548.468236	-8548.599608	-	-	-

[a] Data set name (Cartesian coordinated available as *.pdb files). [b] Zero-point vibrational energy. [c] Gibbs free energy.

[1] Gaussian 16, Revision C.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

[2] NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold