ELECTRONIC SUPPLEMENTARY INFORMATION

3,6,13,16-Tetraalkylporphycenes: Synthesis and Exploration of Effect of Alkyl Groups on Structure, Photophysical Properties, and Basicity

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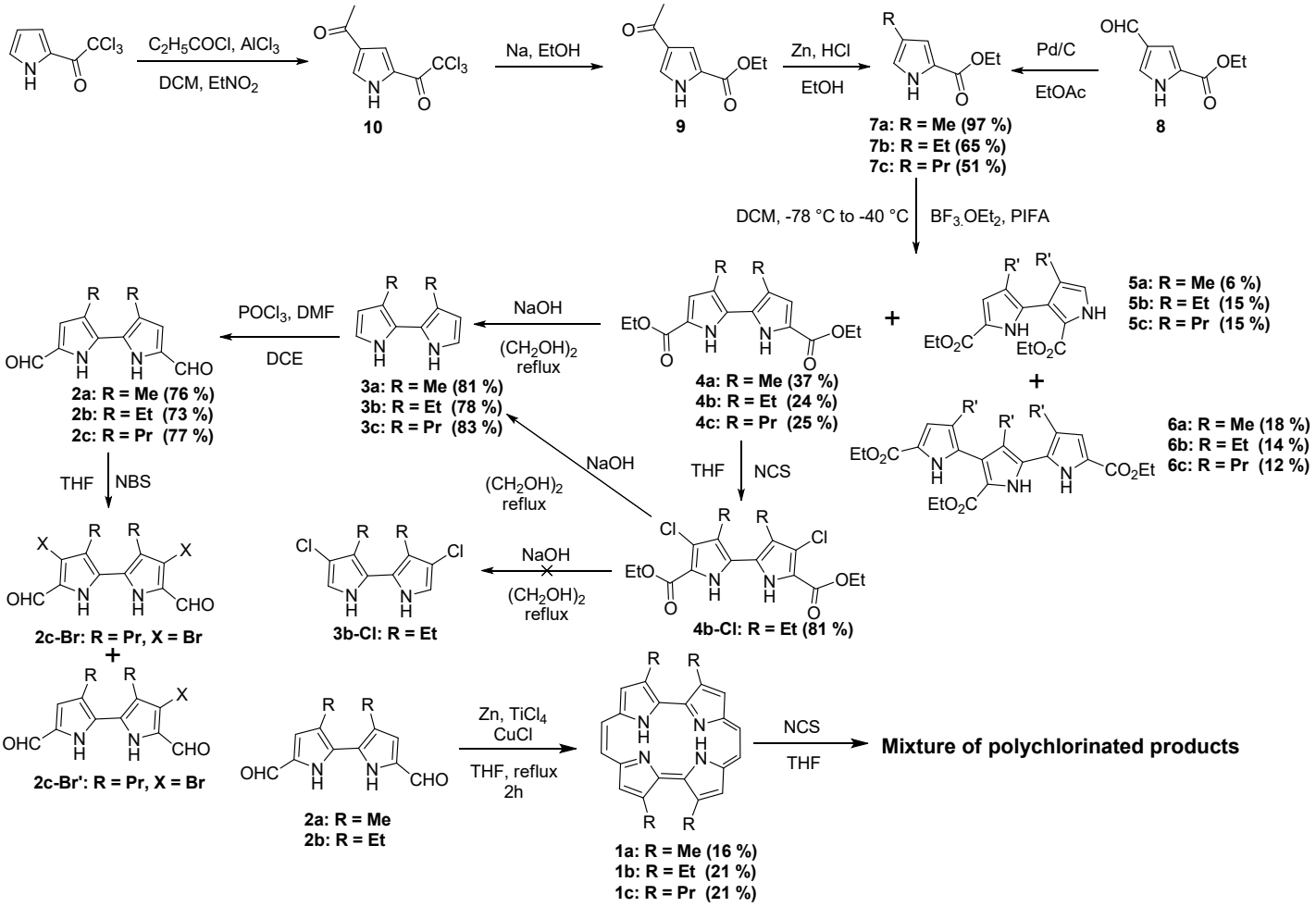

3. NMR Spectra and HRMS data for compounds:

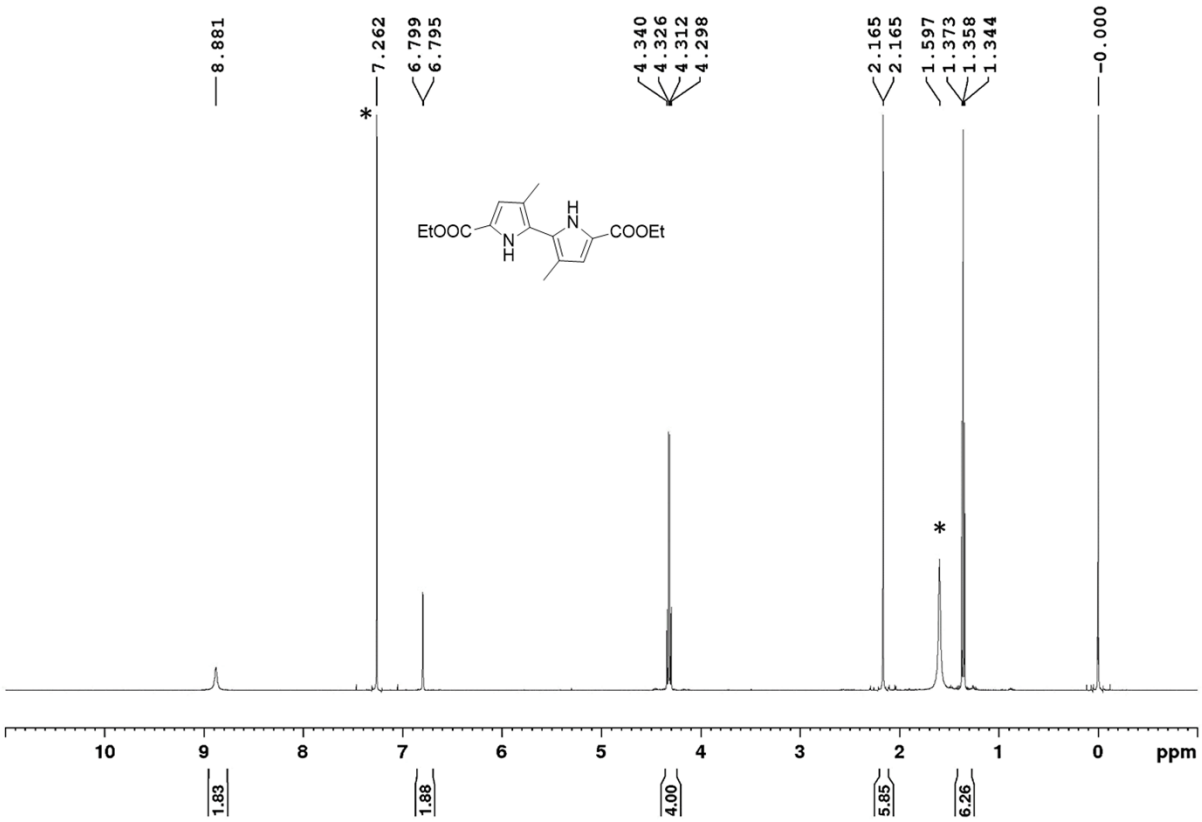

Figure S1. ^{1}H NMR spectrum of the compound **4a** (500 MHz, $CDCl_3$**,** TMS, δ = 0 ppm). * Residual solvent peak: $CDCl_3$, H_2O.

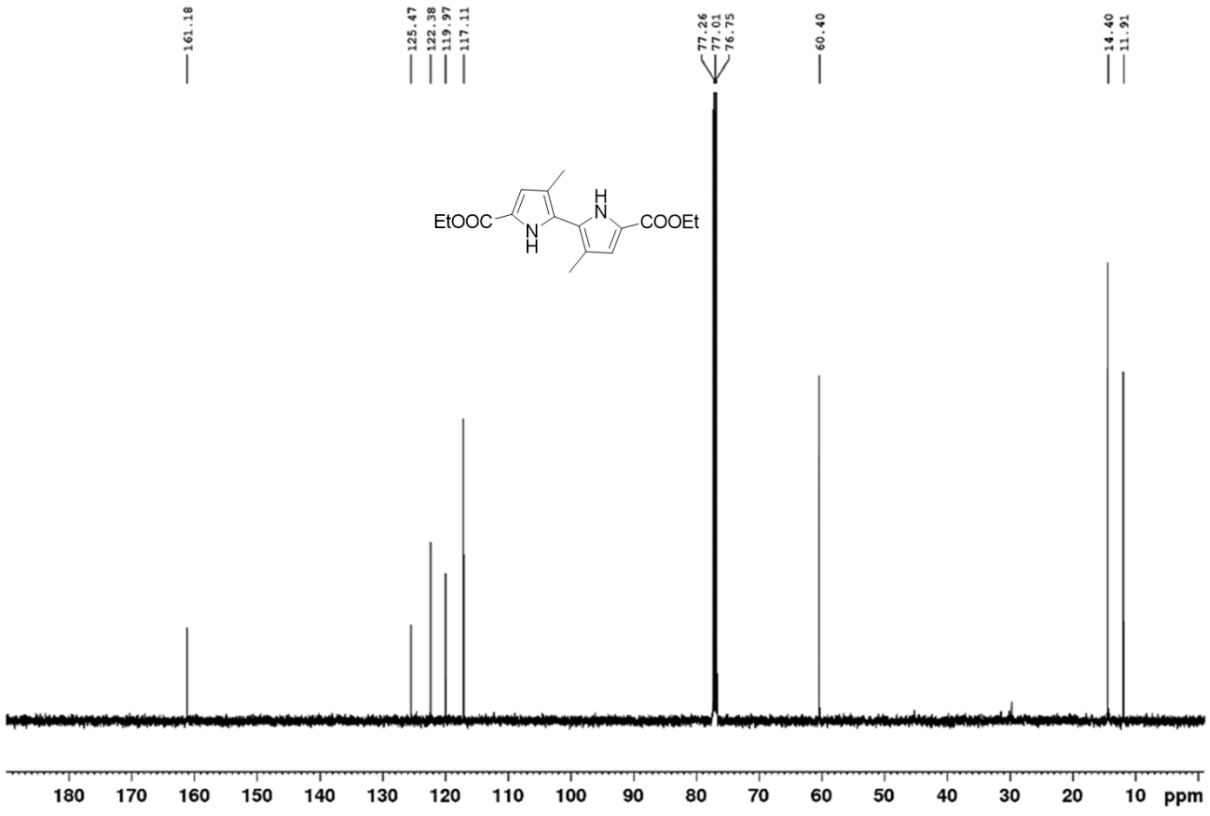

Figure S2. ^{13}C NMR spectrum of the compound **4a** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

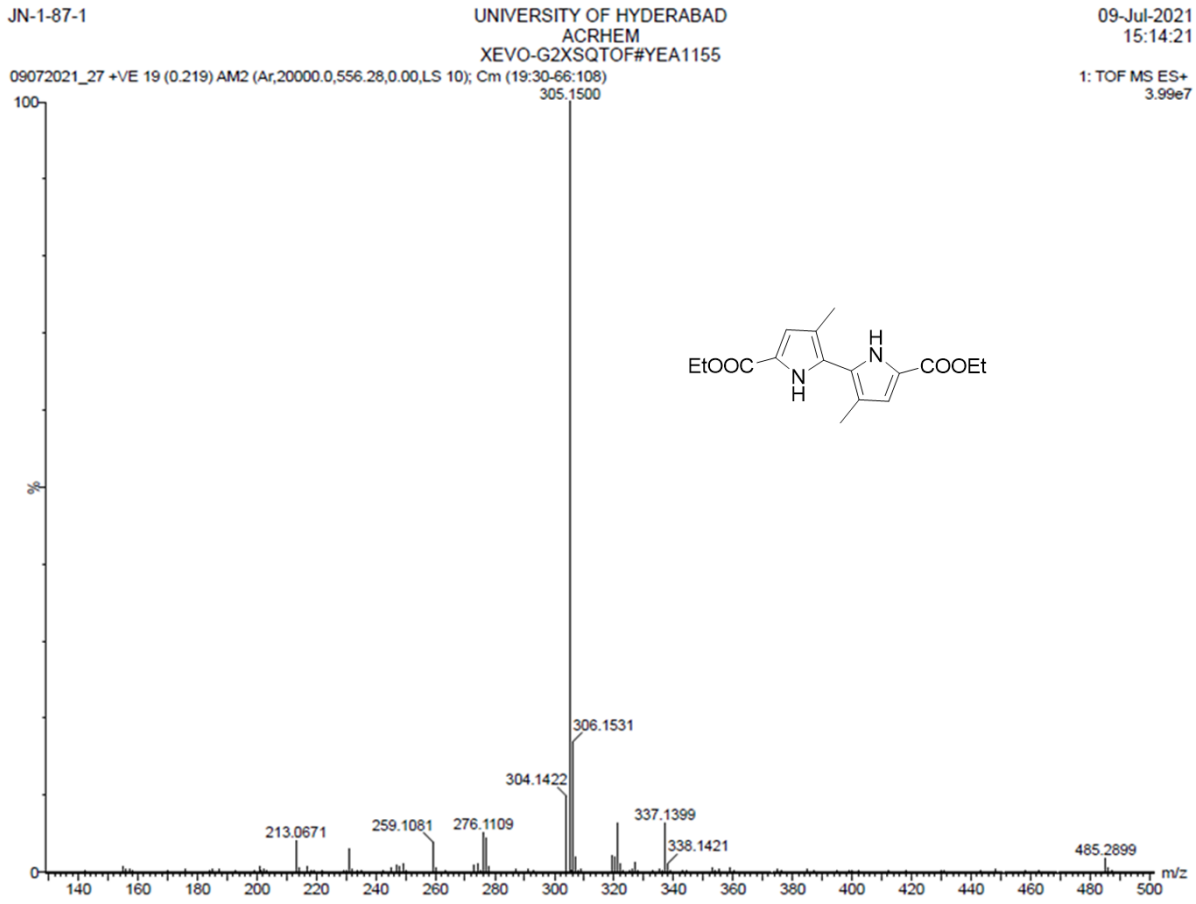

Figure S3. HRMS data of **4a:** $[M+H]^+$ Calcd for $C_{16}H_{21}N_2O_4$: 305.1501; found: 305.1500.

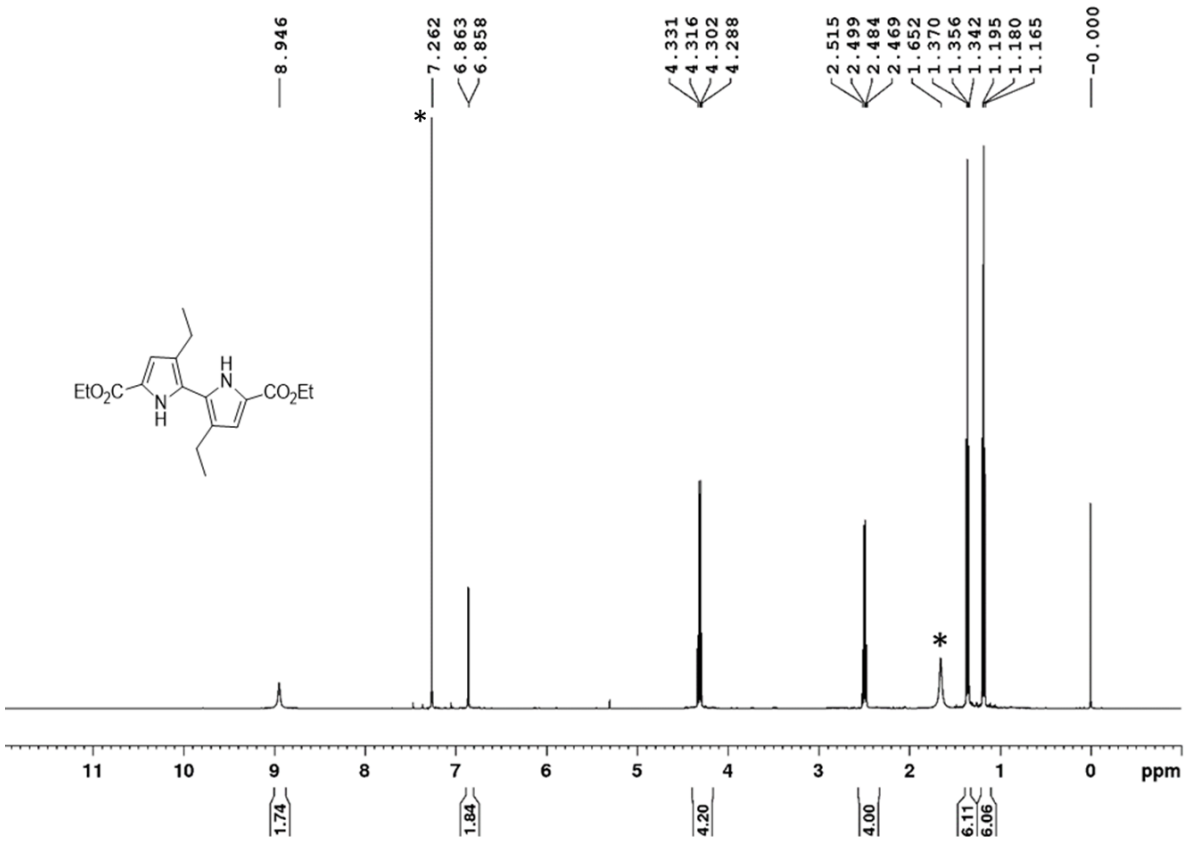

Figure S4. ^{1}H NMR spectrum of the compound **4b** (500 MHz, $CDCl_3$ (TMS, δ = 0 ppm)**)**. * Residual solvent peak: $CDCl_3$, H_2O.

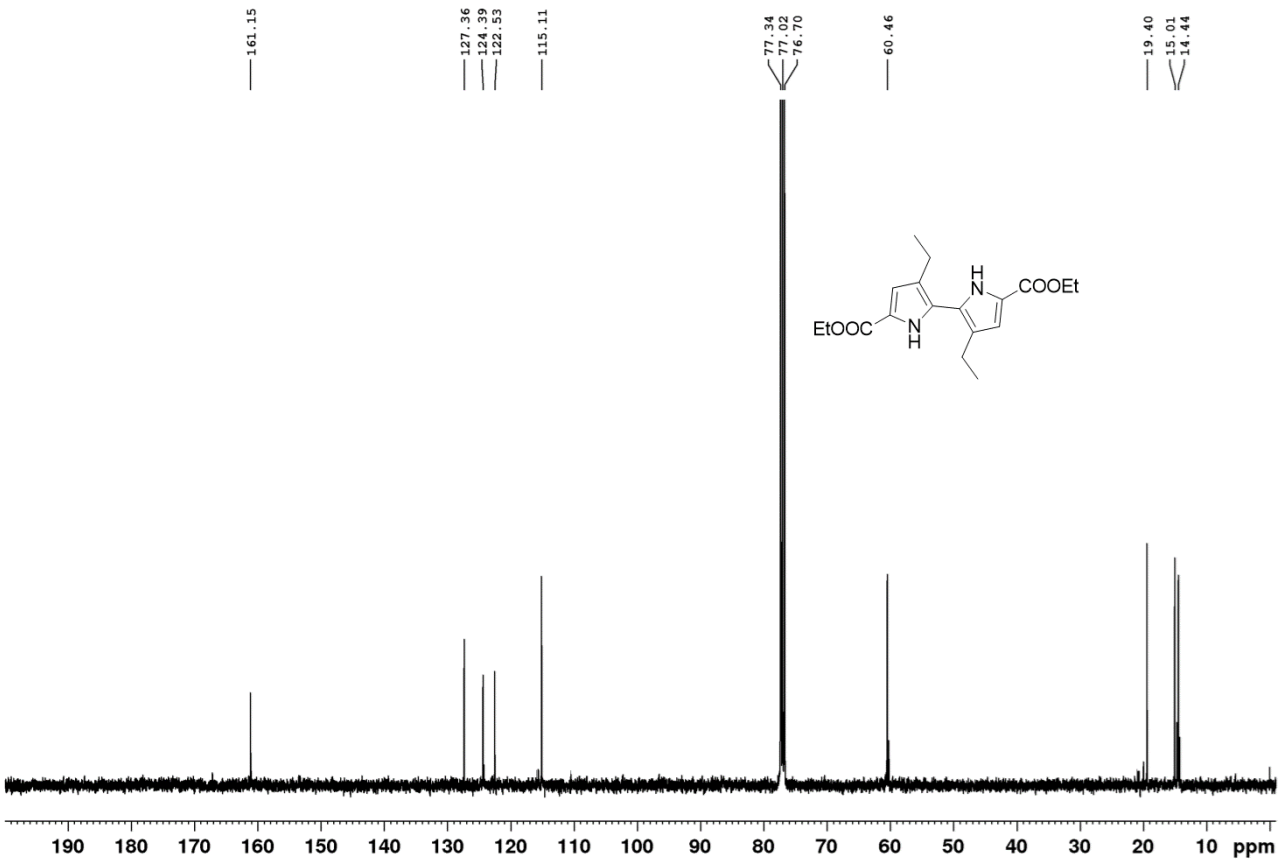

Figure S5. ^{13}C NMR spectrum of the compound **4b** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

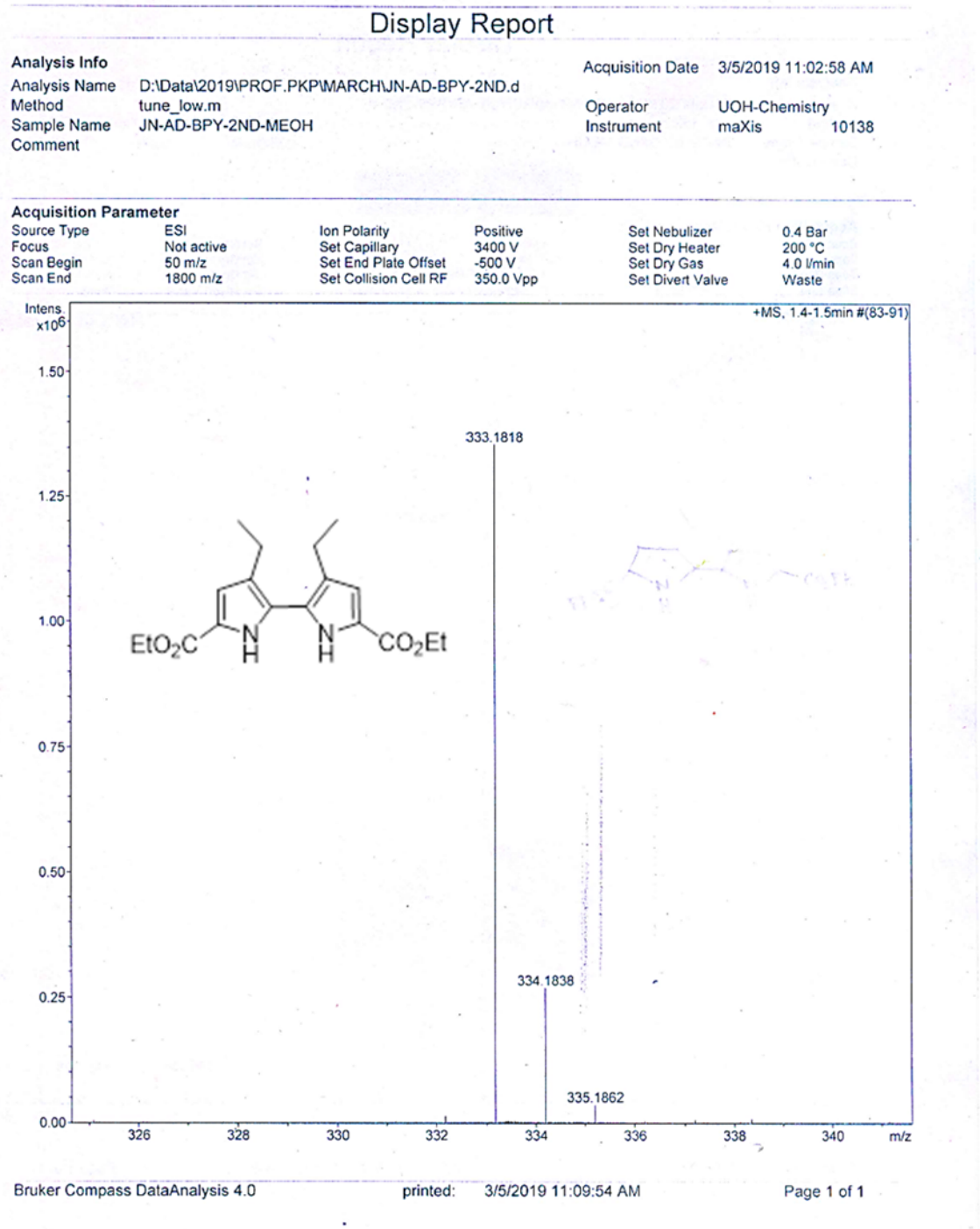

Figure S6. HRMS data of **4b:** $[M+H]^+$ Calcd for $C_{18}H_{25}N_2O_4$: 333.1814; found: 333.1818.

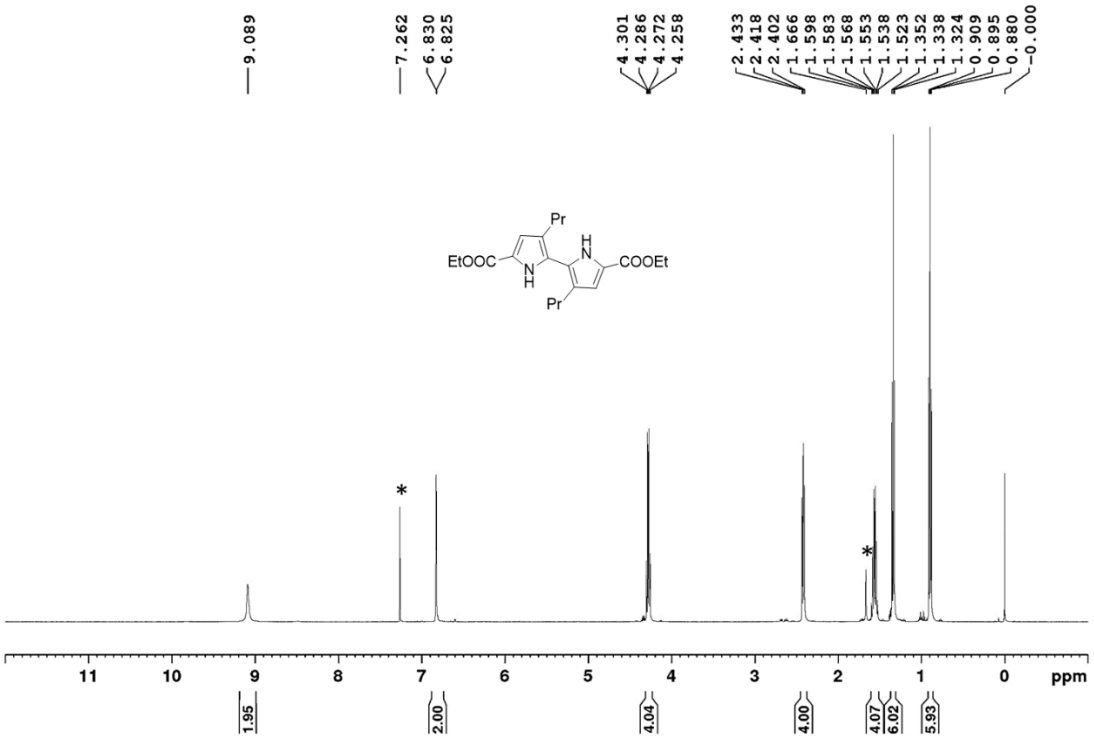

Figure S7. [1]H NMR spectrum of the compound **4c** (500 MHz, $CDCl_3$ TMS, δ = 0 ppm)**)**.* residual solvent peak: $CDCl_3$, H_2O.

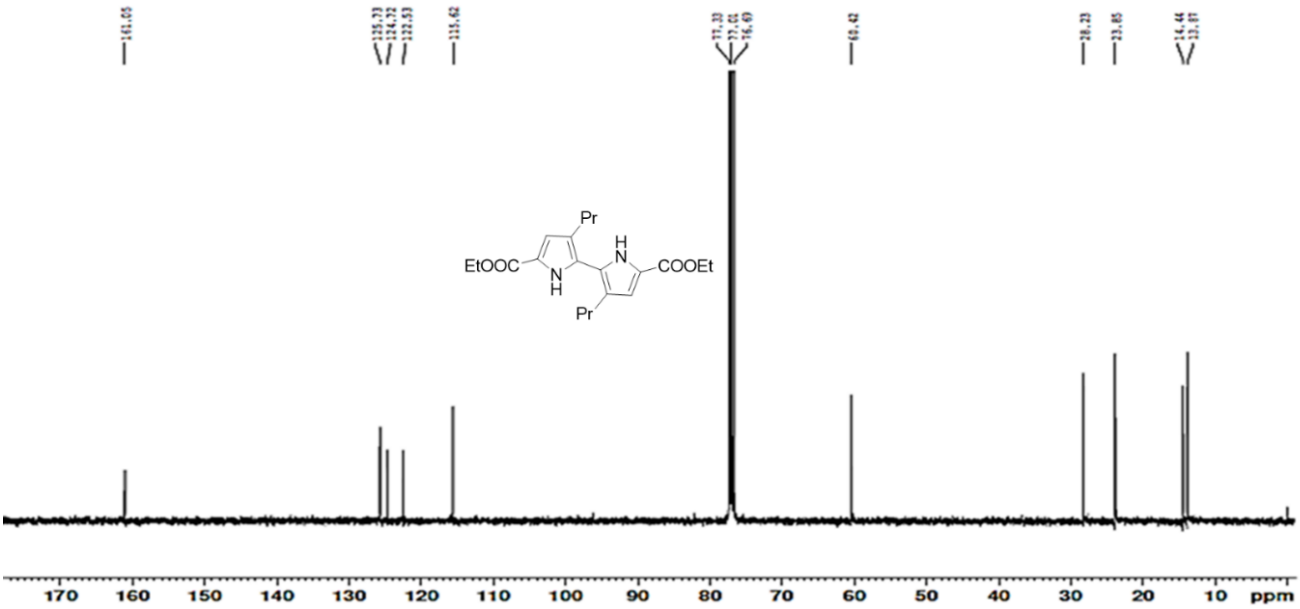

Figure S8. [13]C NMR spectrum of the compound **4c** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

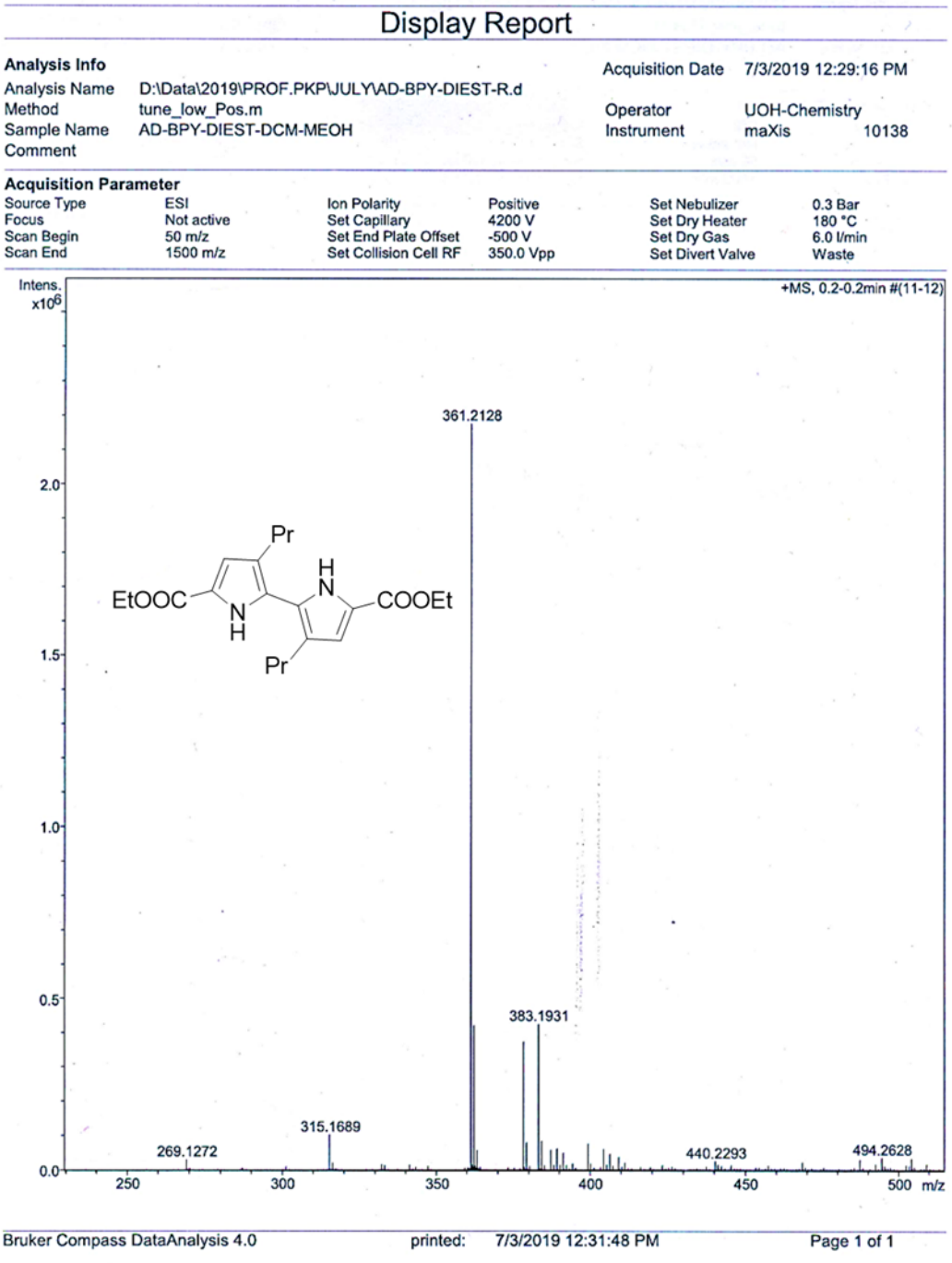

Figure S9. HRMS data of **4c:** $[M+H]^+$ Calcd for $C_{20}H_{29}N_2O_4$: 361.2127; found: 361.2128.

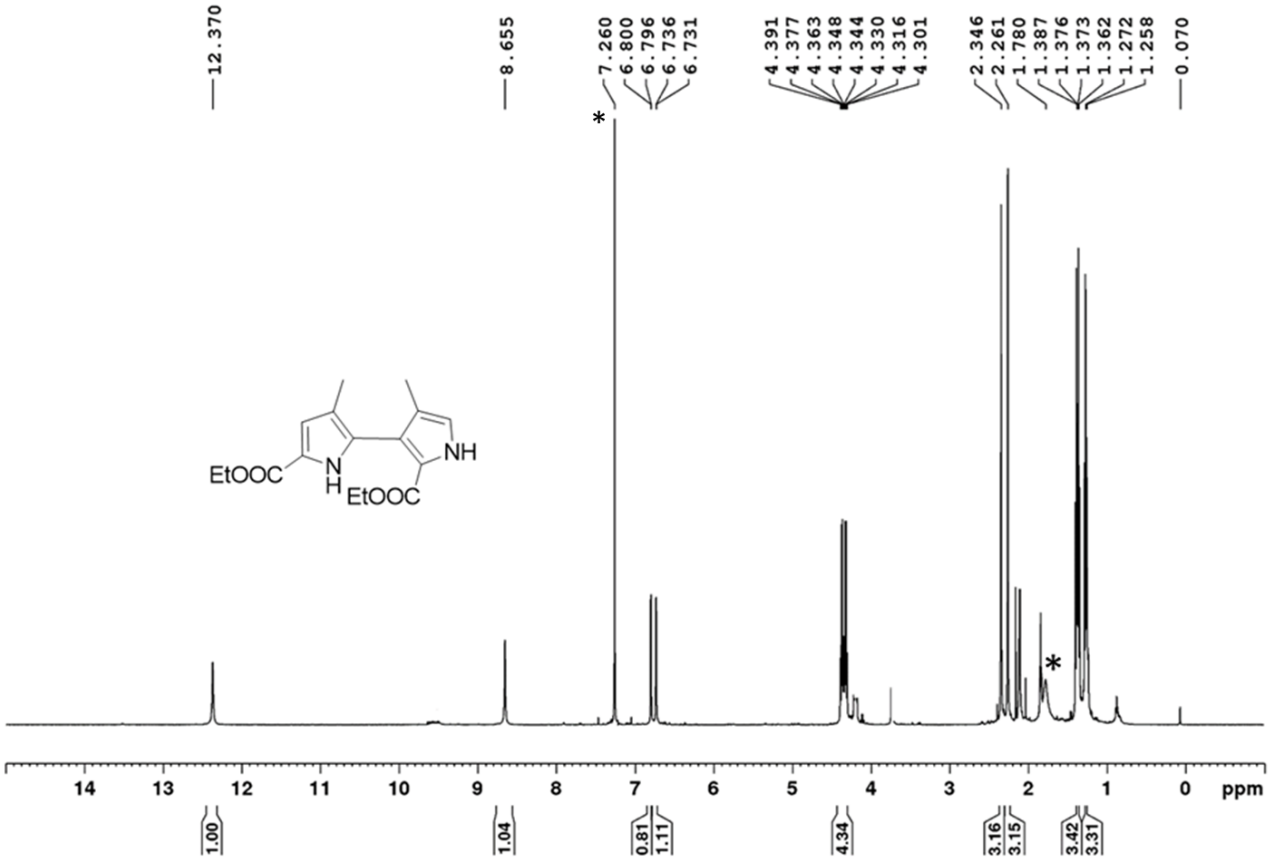

Figure S10. ^{1}H NMR spectrum of the compound **5a** (500 MHz, $CDCl_3$ (δ = 7.26)**)**. * Residual solvent peak: $CDCl_3$, H_2O.

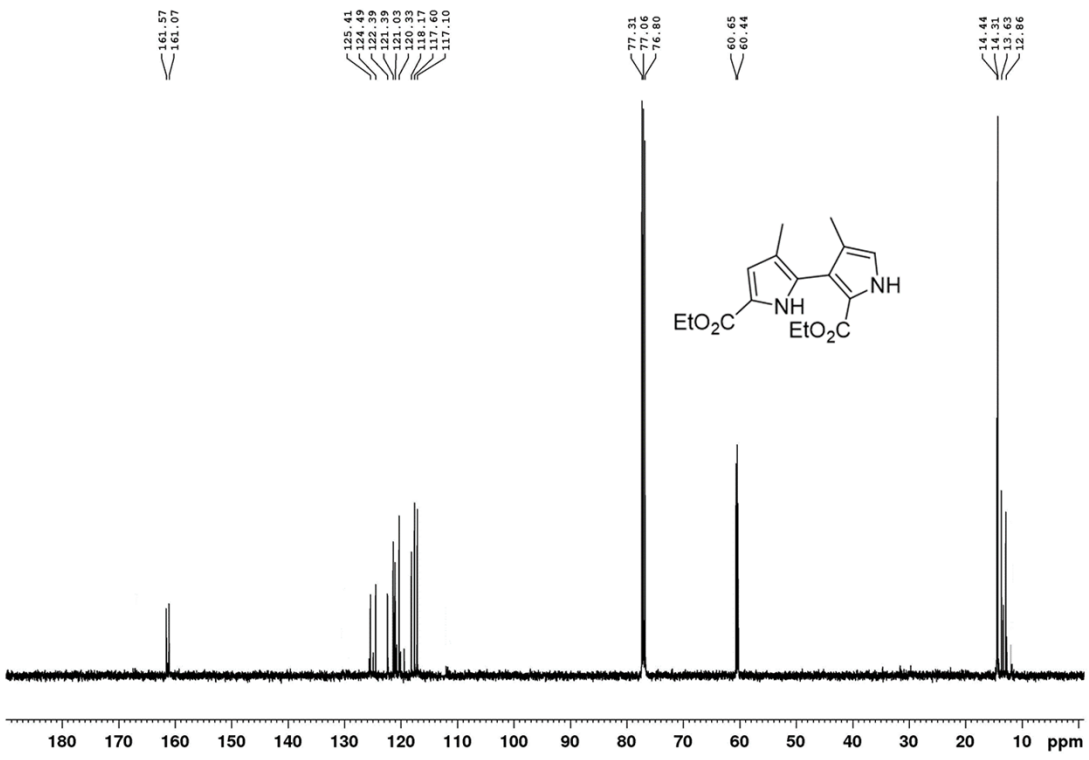

Figure S11. ^{13}C NMR spectrum of the compound **5a** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

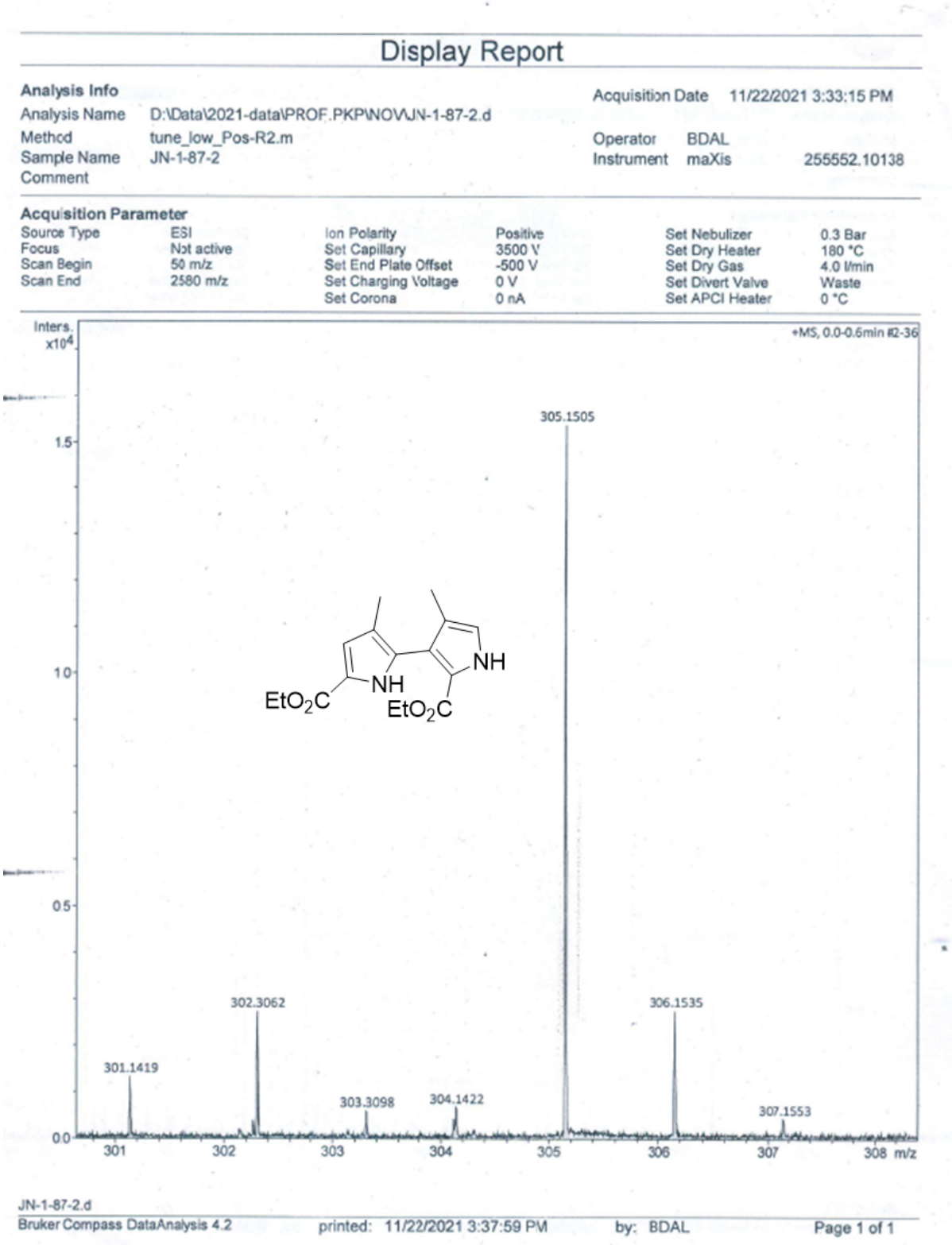

Figure S12. HRMS data of **5a:** $[M+H]^+$ Calcd for $C_{16}H_{21}N_2O_4$: 305.1501; found: 305.1505.

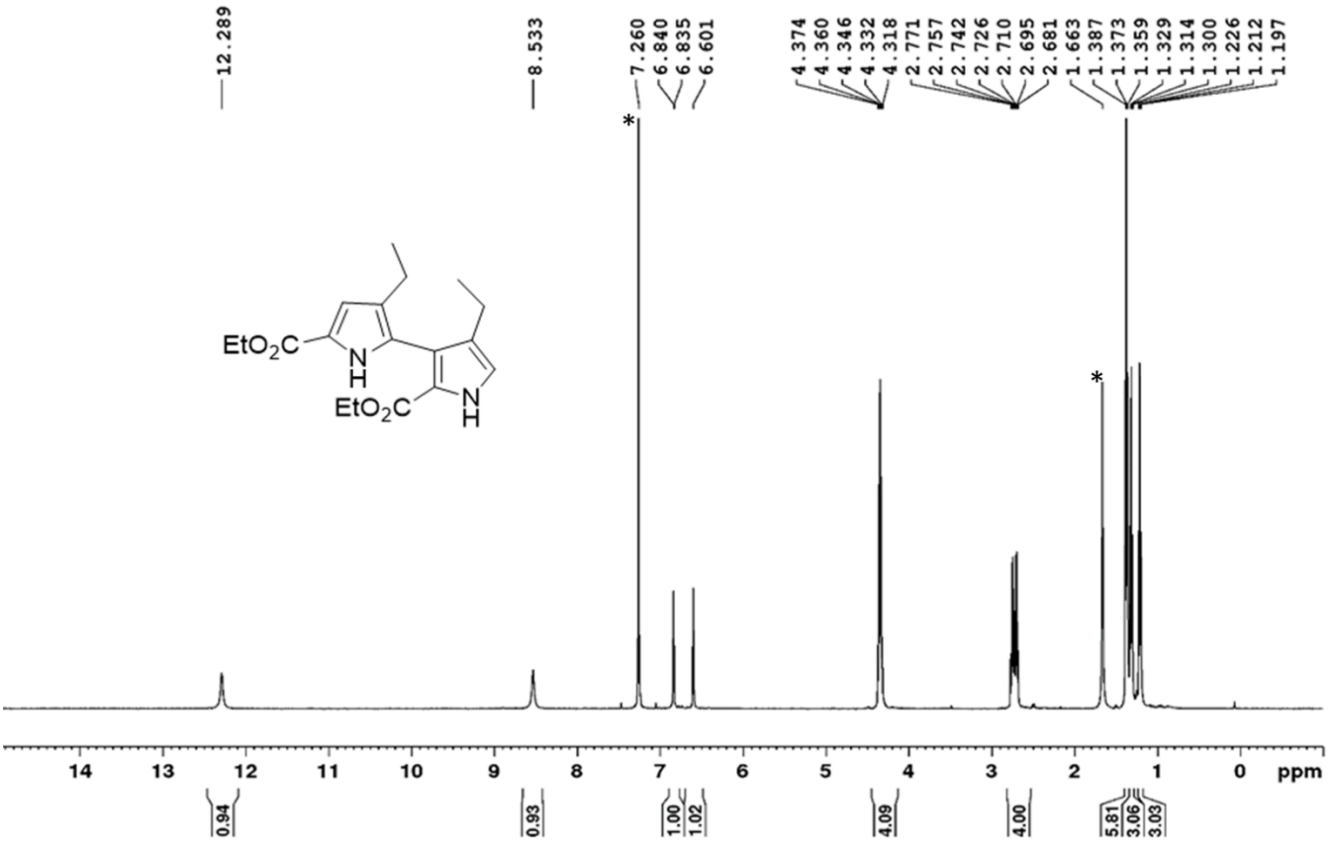

Figure S13. ^{1}H NMR spectrum of the compound **5b** (500 MHz, $CDCl_3$ (δ = 7.26)**)**. * Residual solvent peak: $CDCl_3$, H_2O.

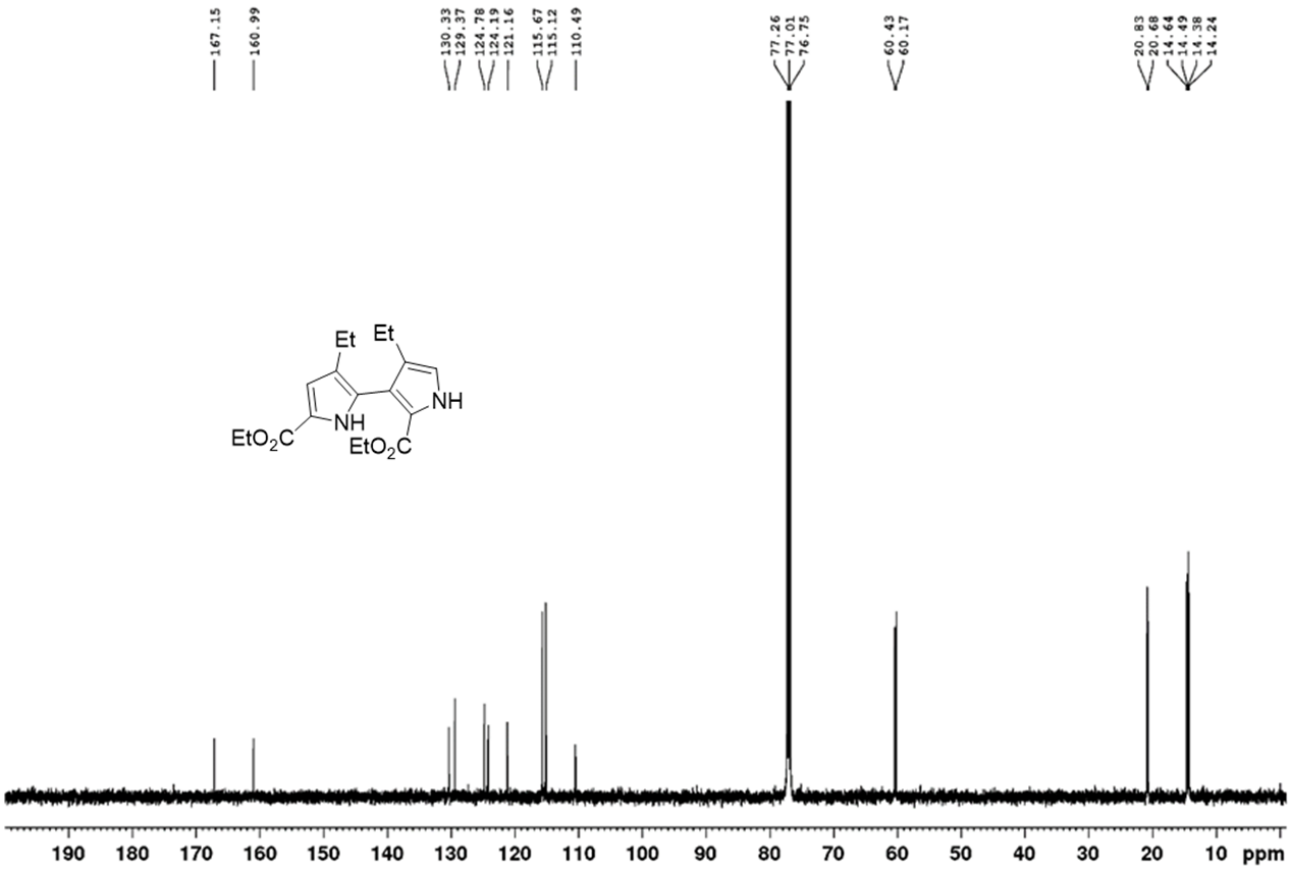

Figure S14. ^{13}C NMR spectrum of the compound **5b** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

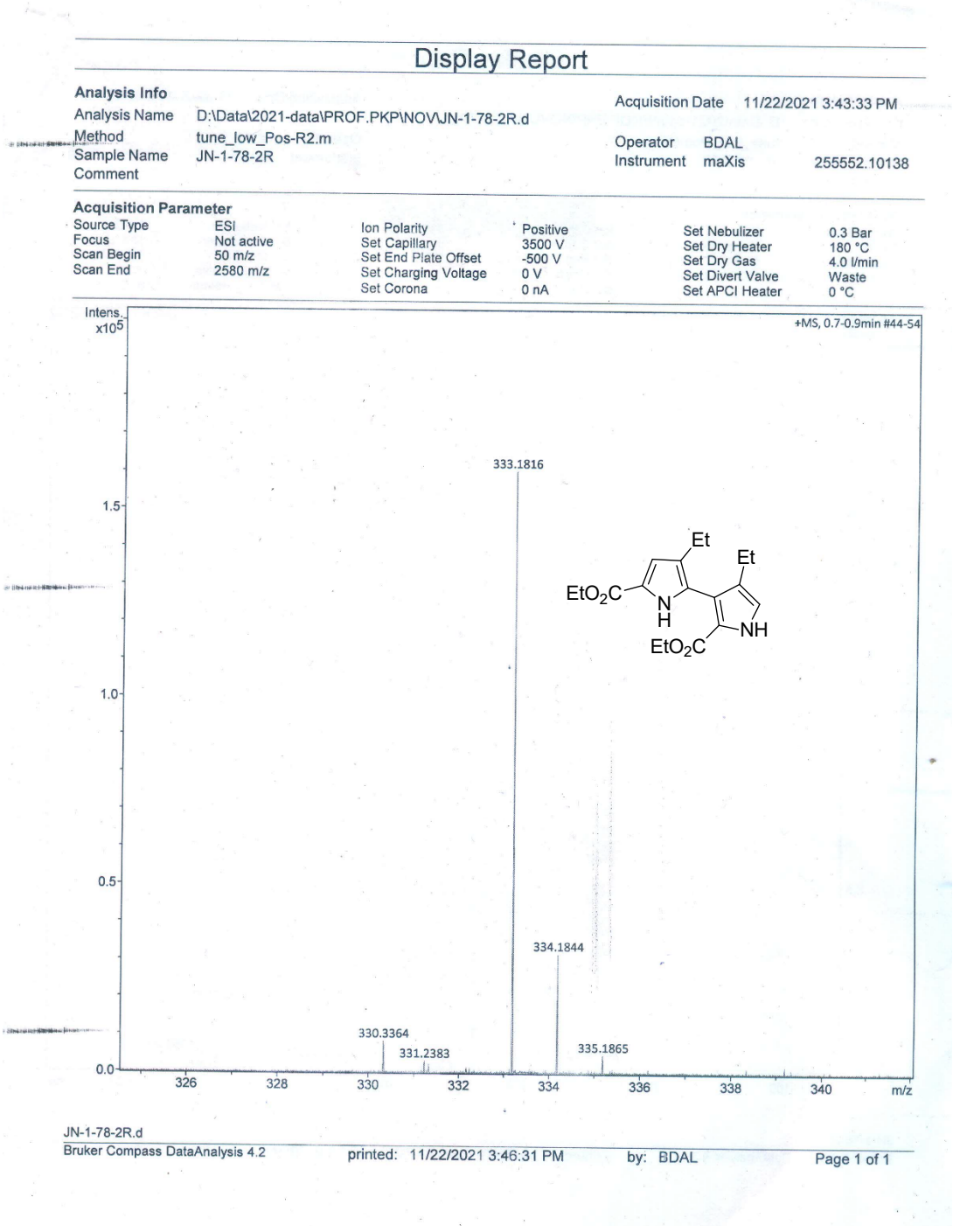

Figure S15. HRMS data of **5b:** $[M+H]^+$ Calcd for $C_{18}H_{25}N_2O_4$: 333.1814; found: 333.1816.

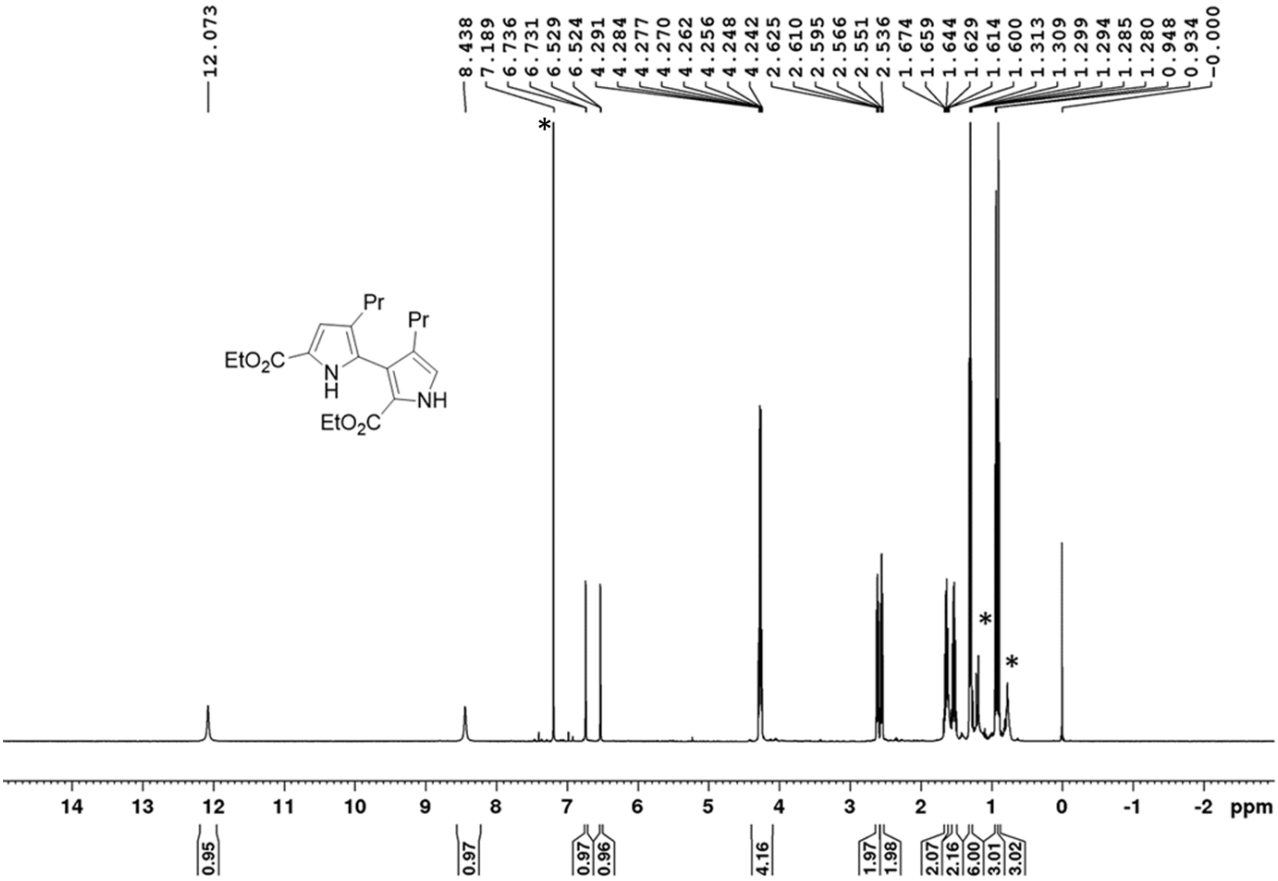

Figure S16. ^{1}H NMR spectrum of the compound **5c** (500 MHz, $CDCl_3$ TMS, δ = 0 ppm**)**. * Residual solvent peak: $CDCl_3$, H_2O and grease.

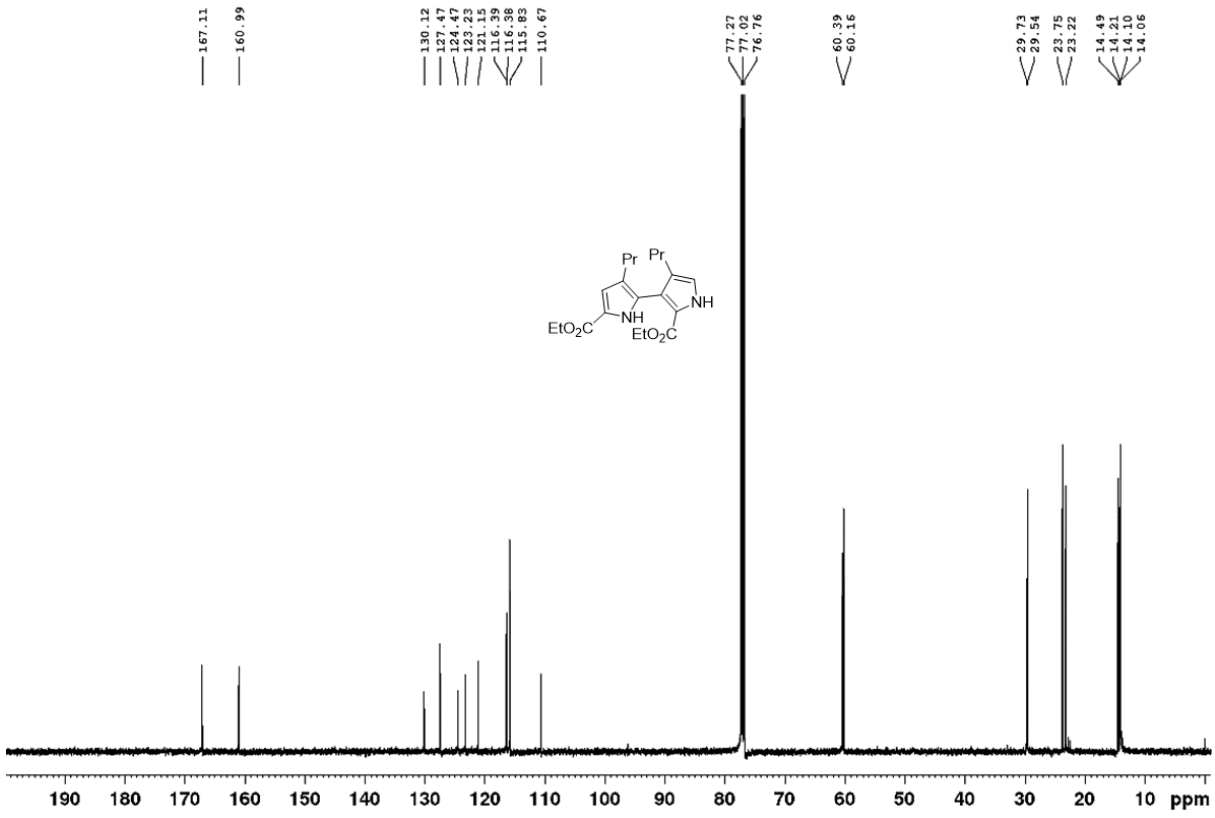

Figure S17. ^{13}C NMR spectrum of the compound **5c** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

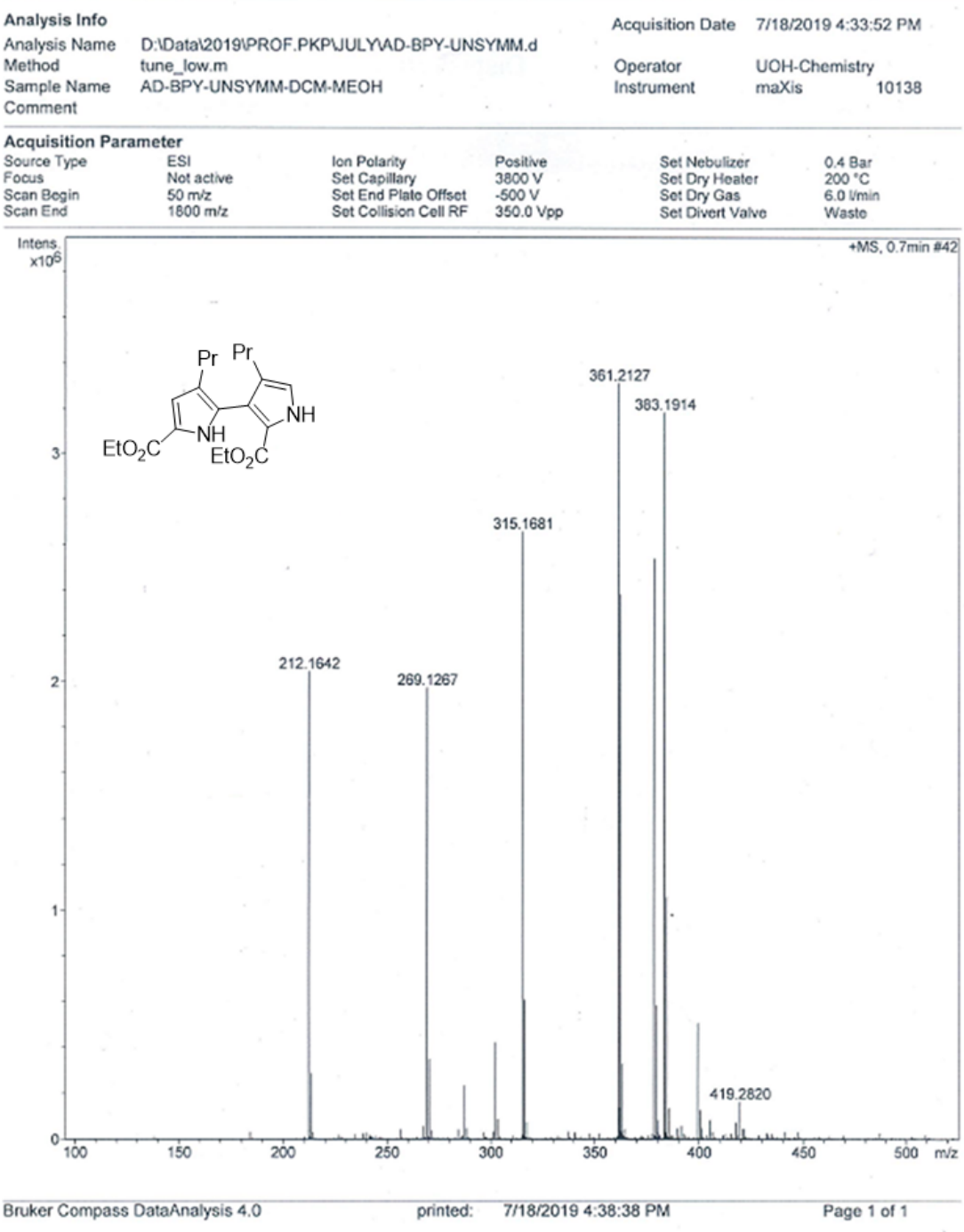

Figure S18. HRMS data of **5c:** $[M+H]^+$ Calcd for $C_{20}H_{29}N_2O_4$: 361.2127; found: 361.2128.

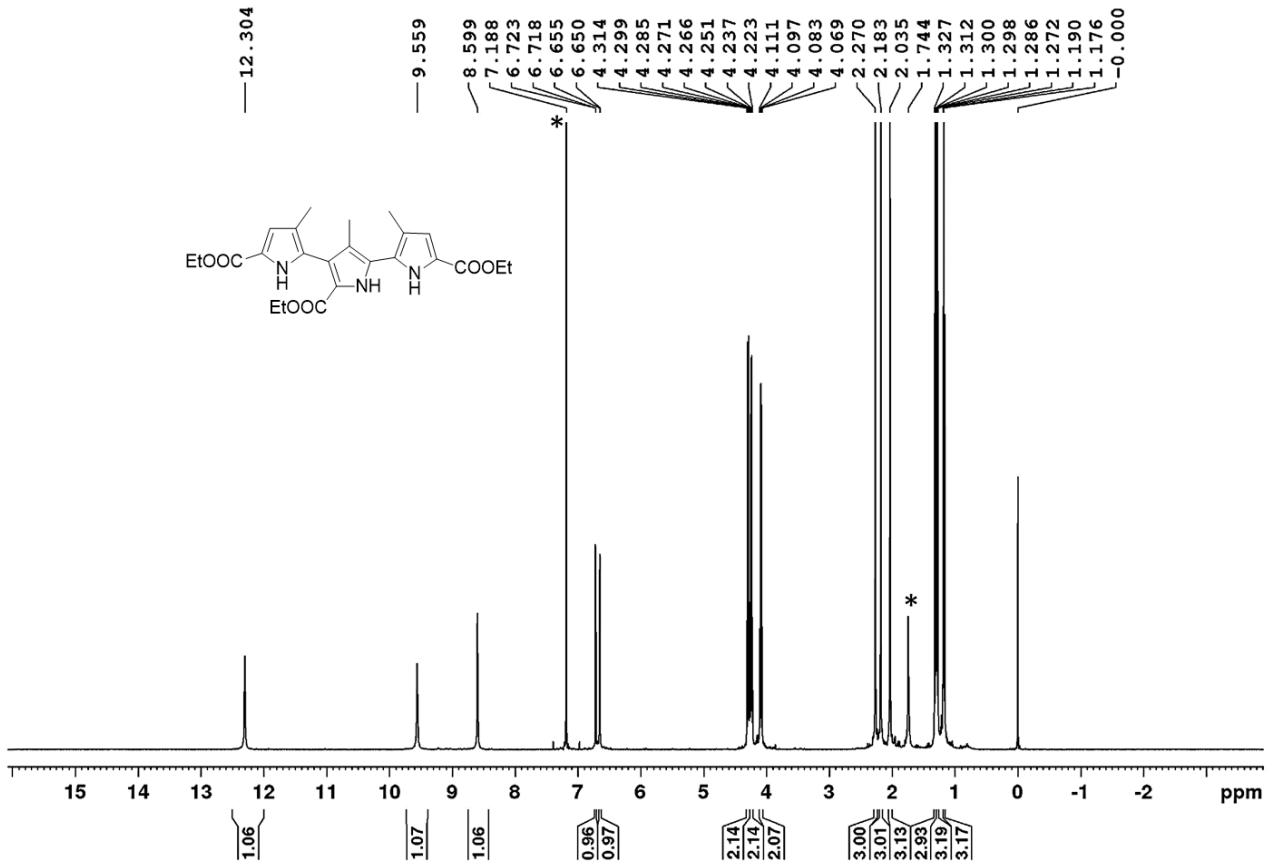

Figure S19. ^{1}H NMR spectrum of the compound **6a** (500 MHz, $CDCl_3$ TMS, δ = 0 ppm)**)** * Residual solvent peak: $CDCl_3$, H_2O.

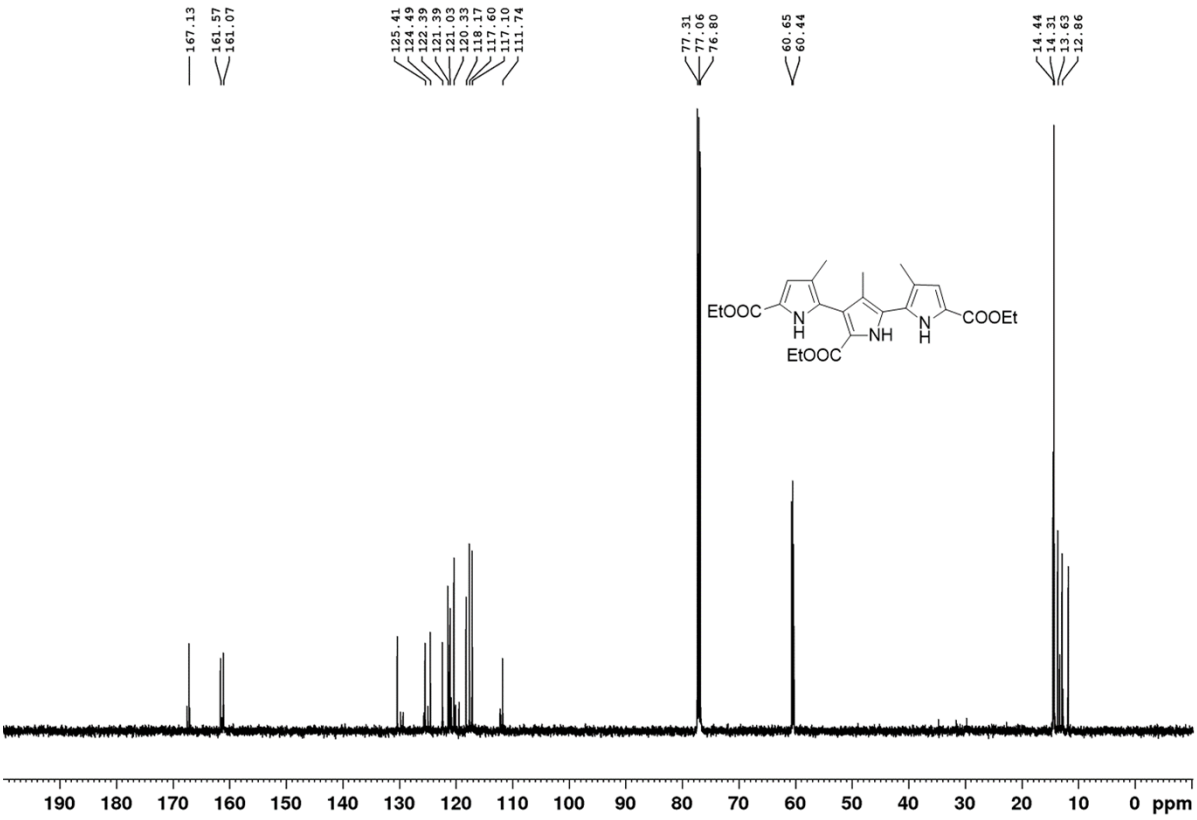

Figure S20. ^{13}C NMR spectrum of the compound **6a** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

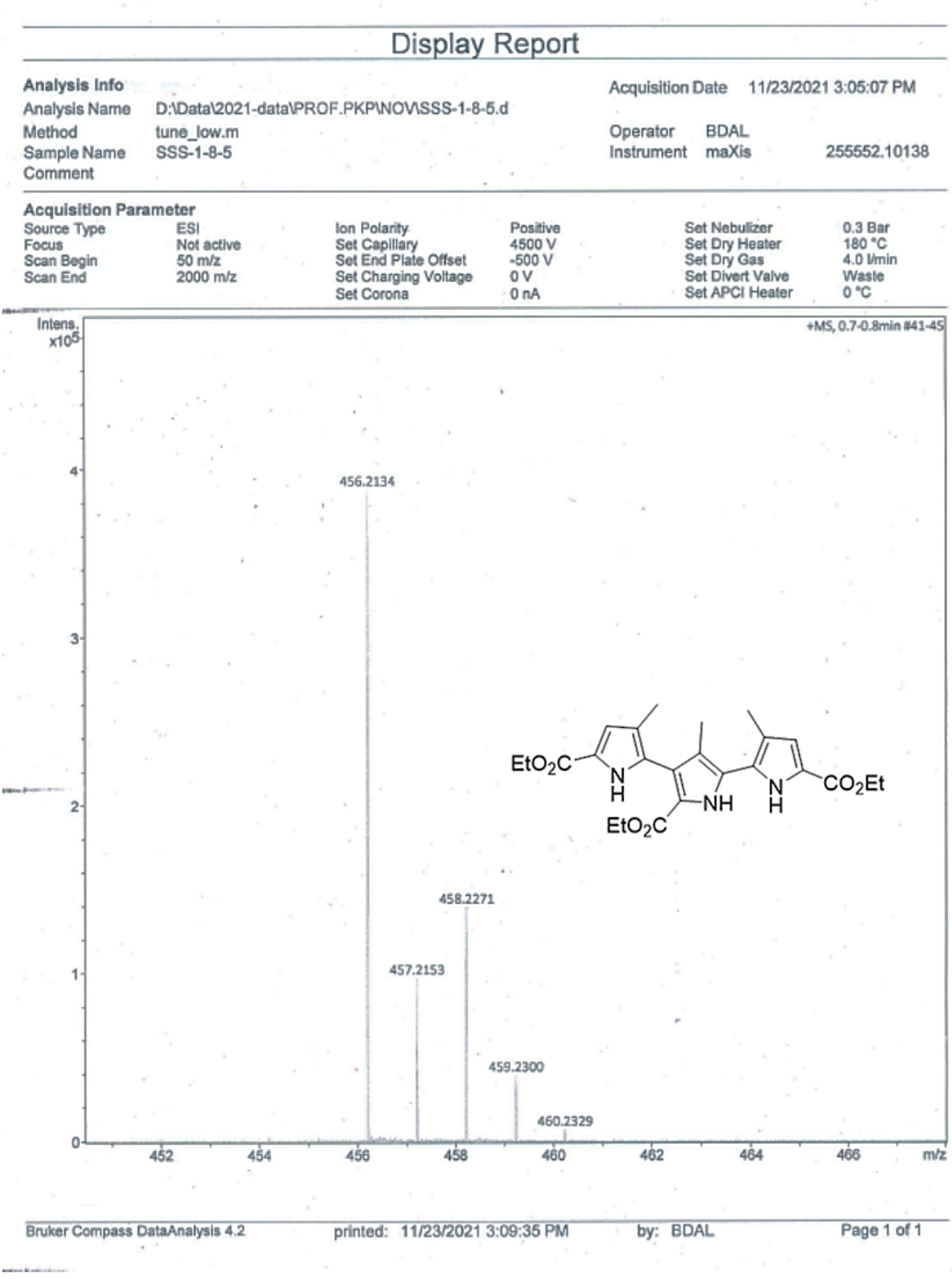

Figure S21. HRMS data of **6a:** $[M+H]^+$ Calcd for $C_{24}H_{30}N_3O_6$: 456.2134; found: 456.2134.

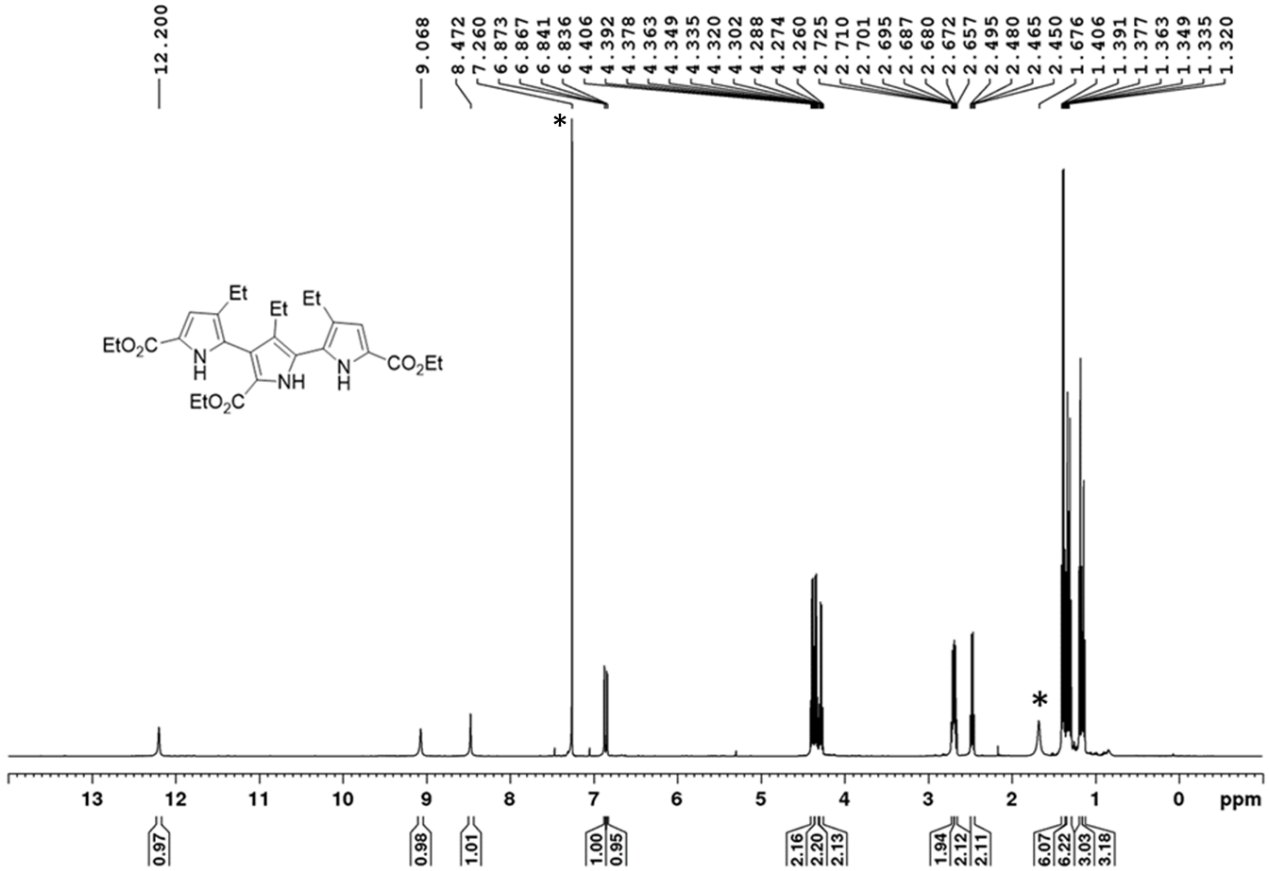

Figure S22. ^{1}H NMR spectrum of the compound **6b** (500 MHz, $CDCl_3$ (δ = 7.26)**)**. * Residual solvent peak: $CDCl_3$, H_2O.

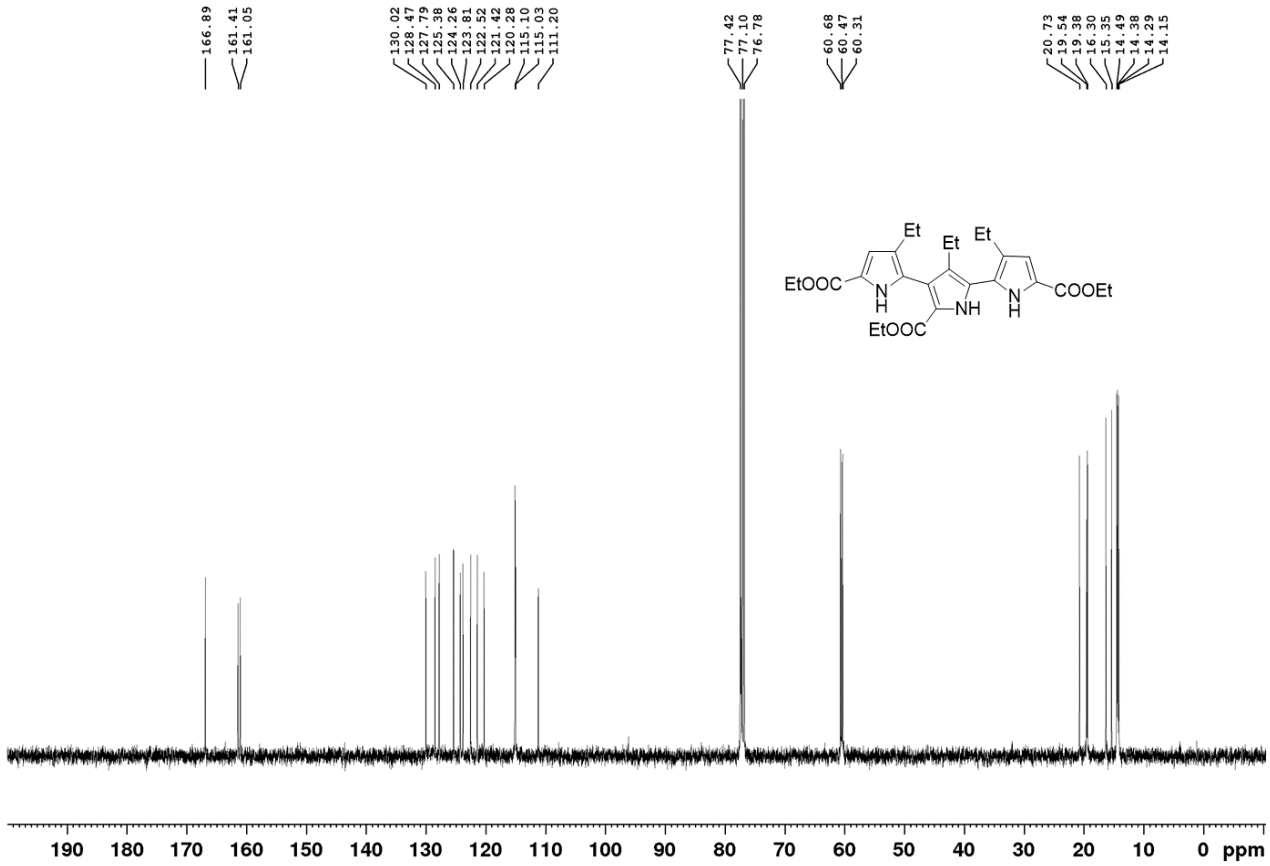

Figure S23. ^{13}C NMR spectrum of the compound **6b** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

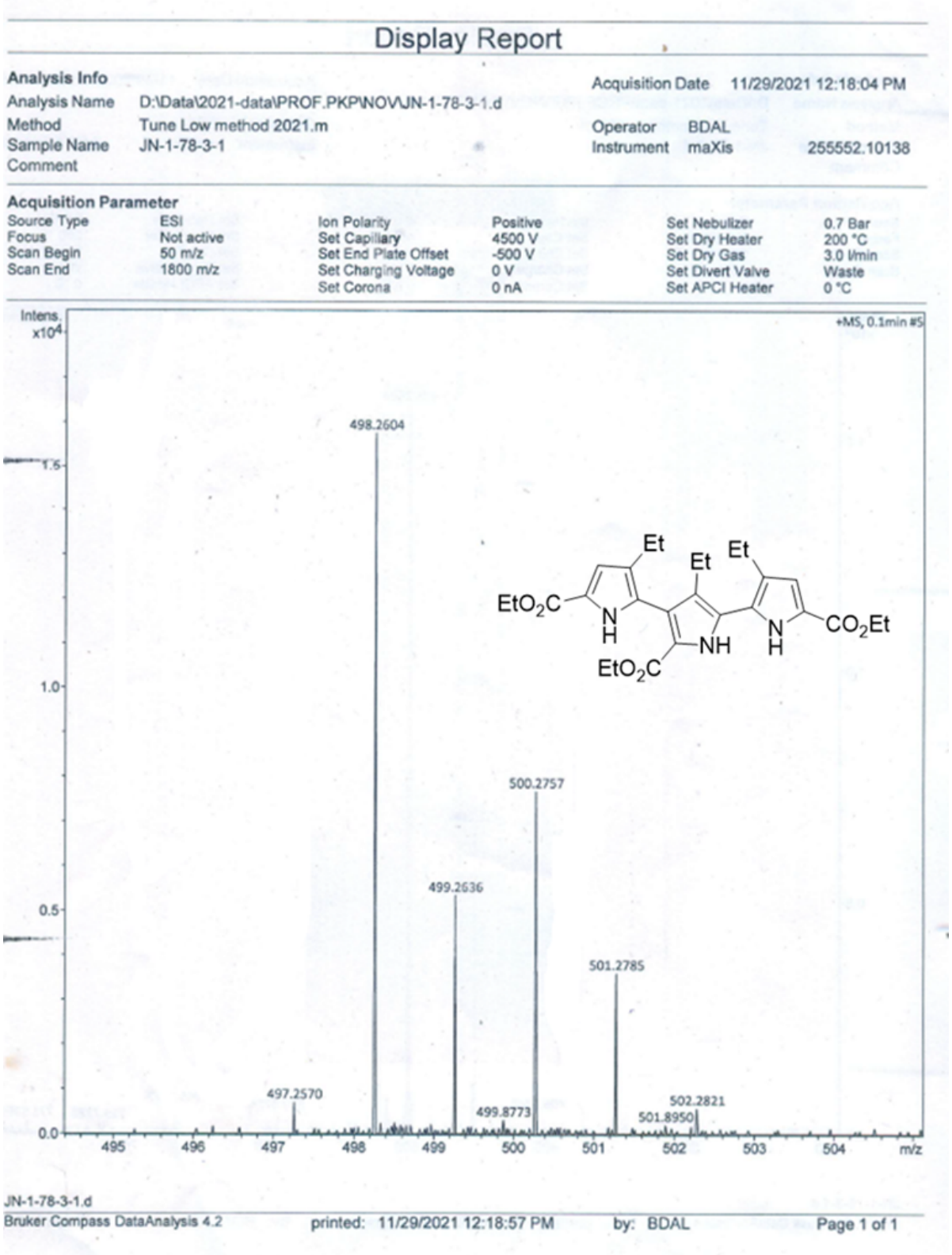

Figure S24. HRMS data of **6b:** $[M+H]^+$ Calcd for $C_{27}H_{36}N_3O_6$: 498.2604; found: 498.2604.

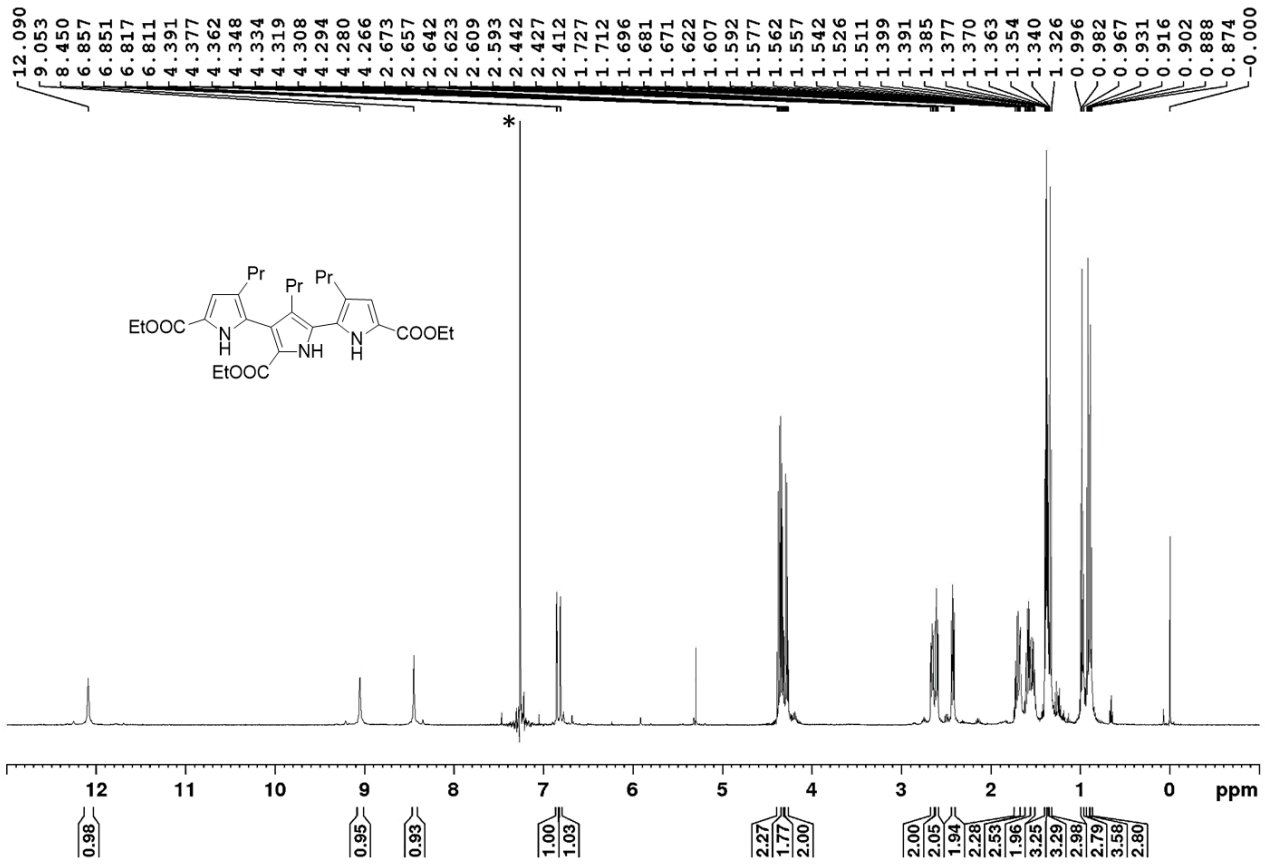

Figure S25. ^{1}H NMR spectrum of the compound **6c** (500 MHz, $CDCl_3$ TMS, δ = 0 ppm**)** * Residual solvent peak: $CDCl_3$.

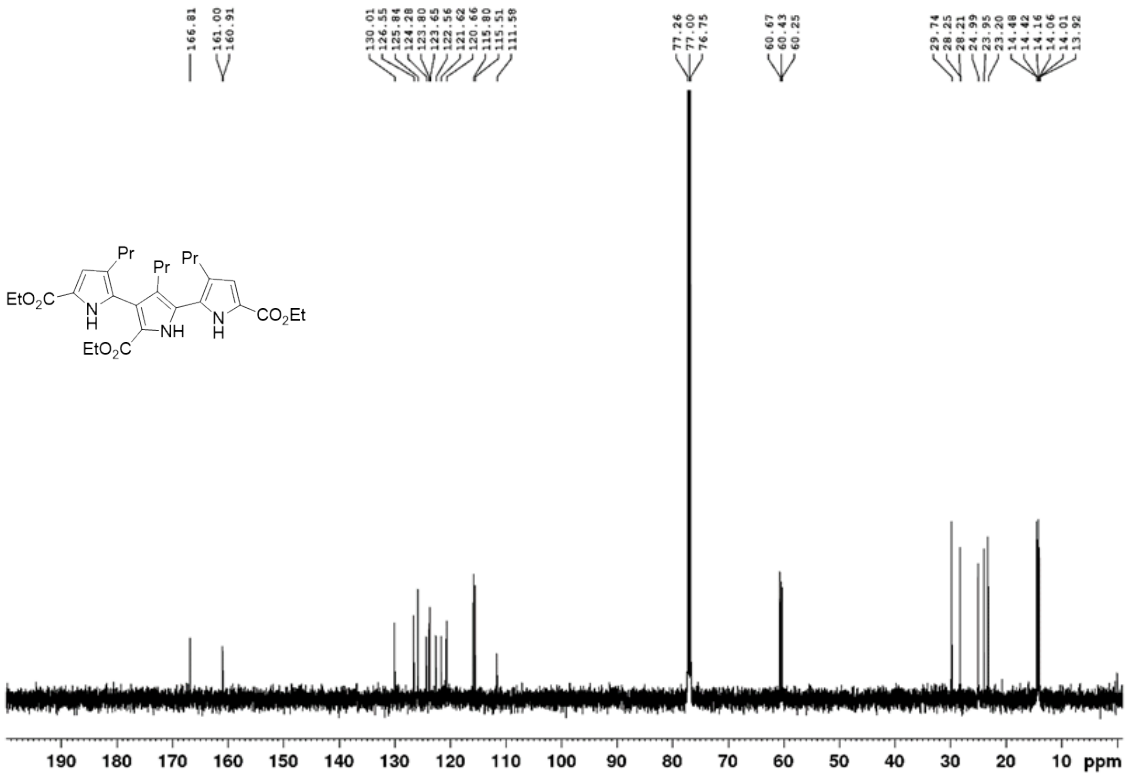

Figure S26. ^{13}C NMR spectrum of the compound **6c** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

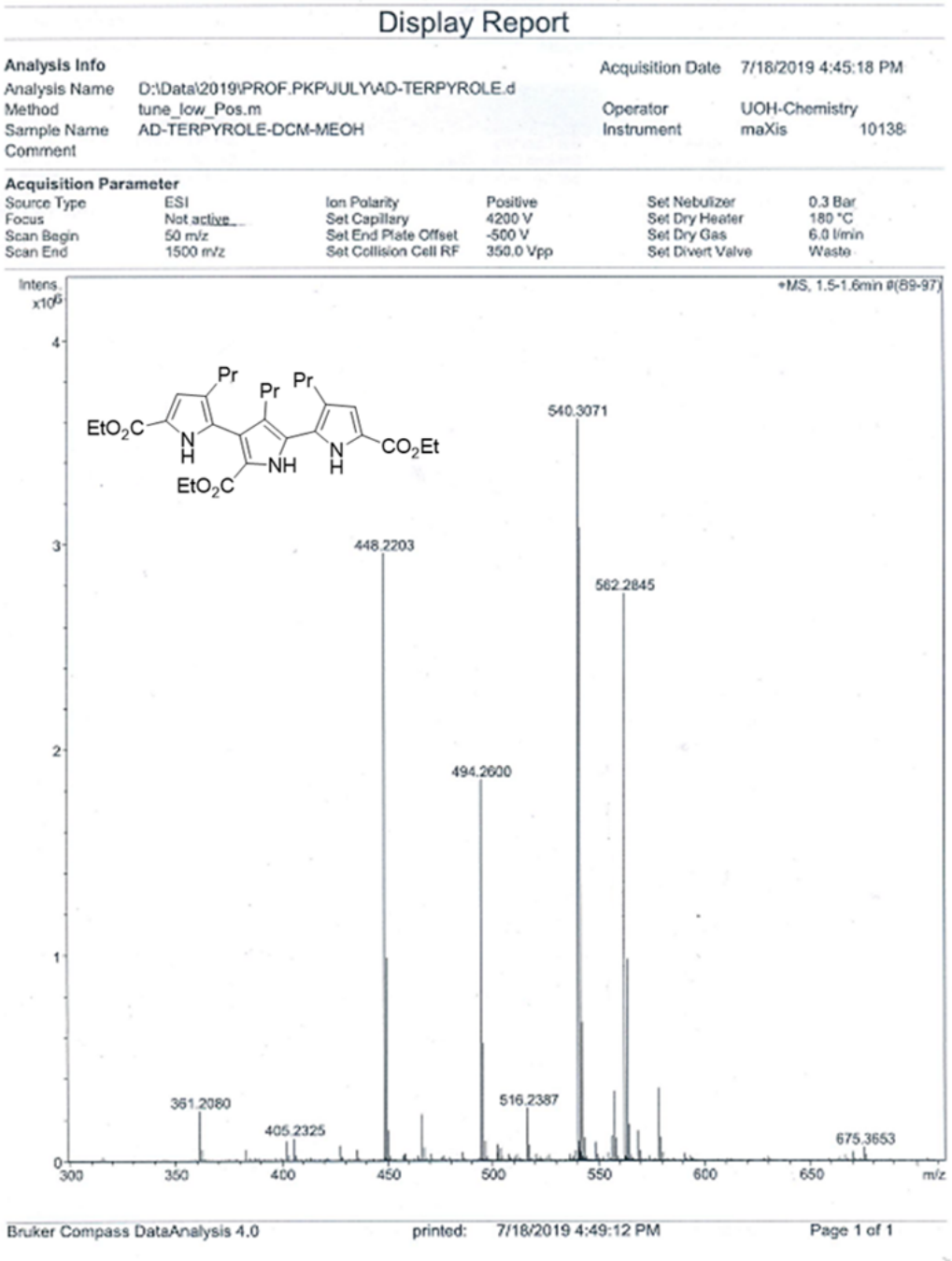

Figure S27. HRMS data of **6c:** $[M+H]^+$ Calcd for $C_{30}H_{41}N_3O_6$: 540.3073; found: 540.3071.

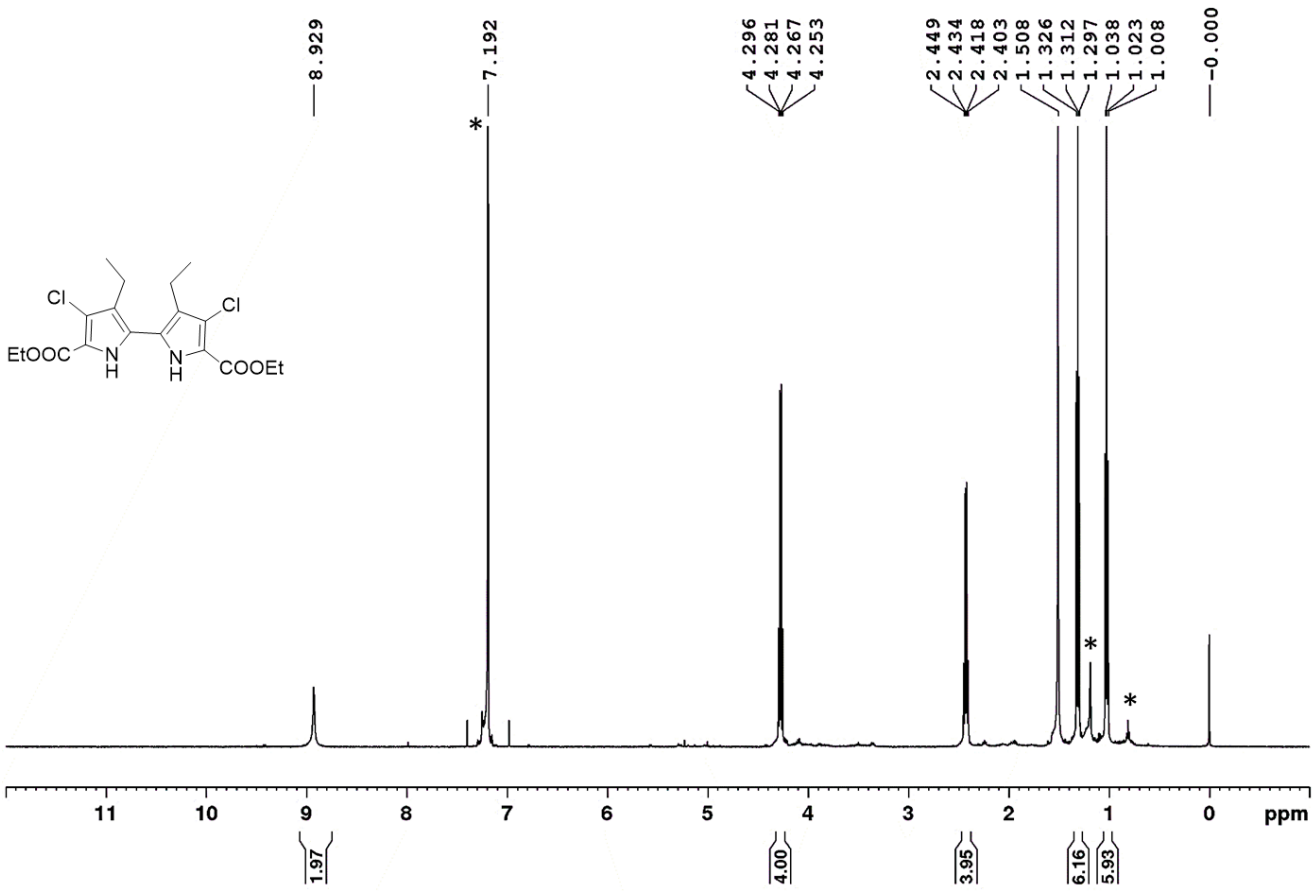

Figure S28. ^{1}H NMR spectrum of the compound **4b-Cl** (500 MHz, $CDCl_3$, TMS, δ = 0 ppm)**)**. *Residual belongs to $CDCl_3$, H_2O and grease.

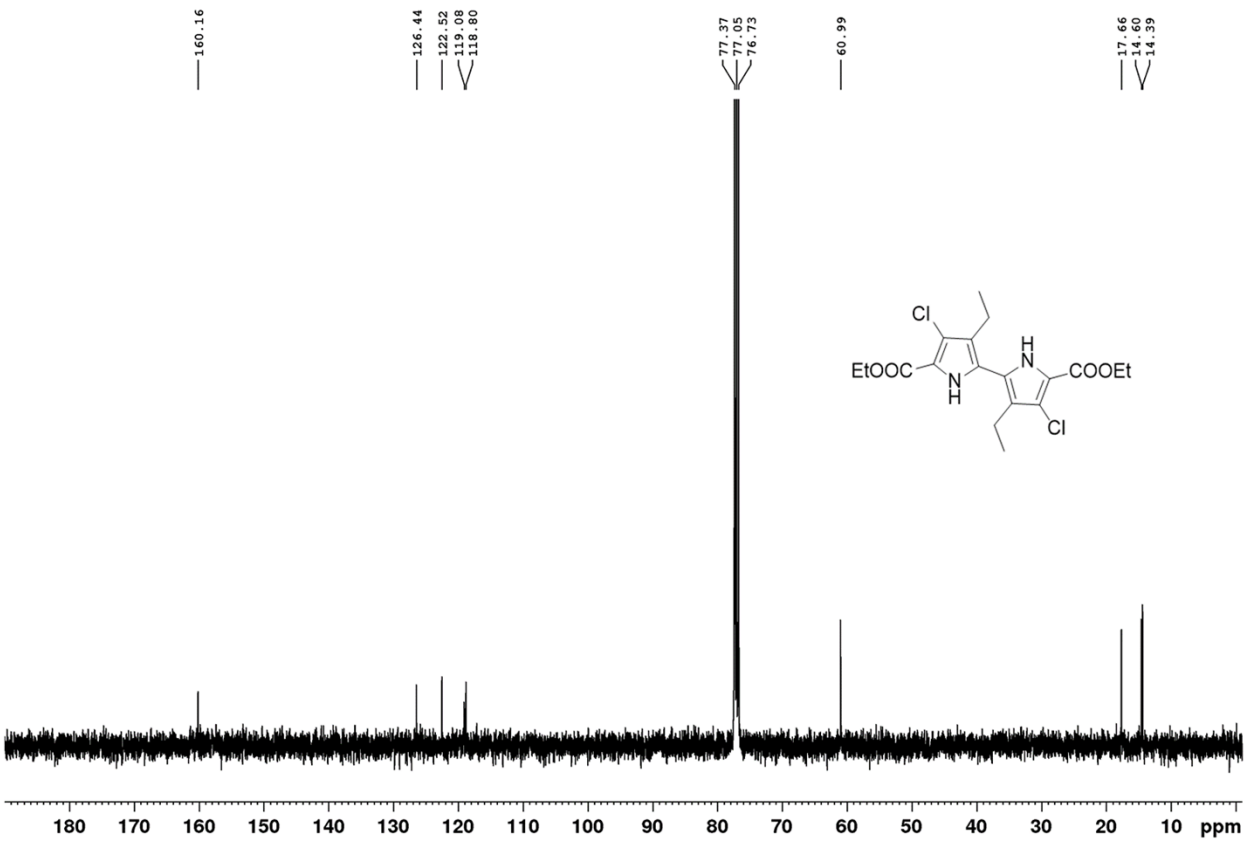

Figure S29. ^{13}C NMR spectrum of **4b-Cl** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

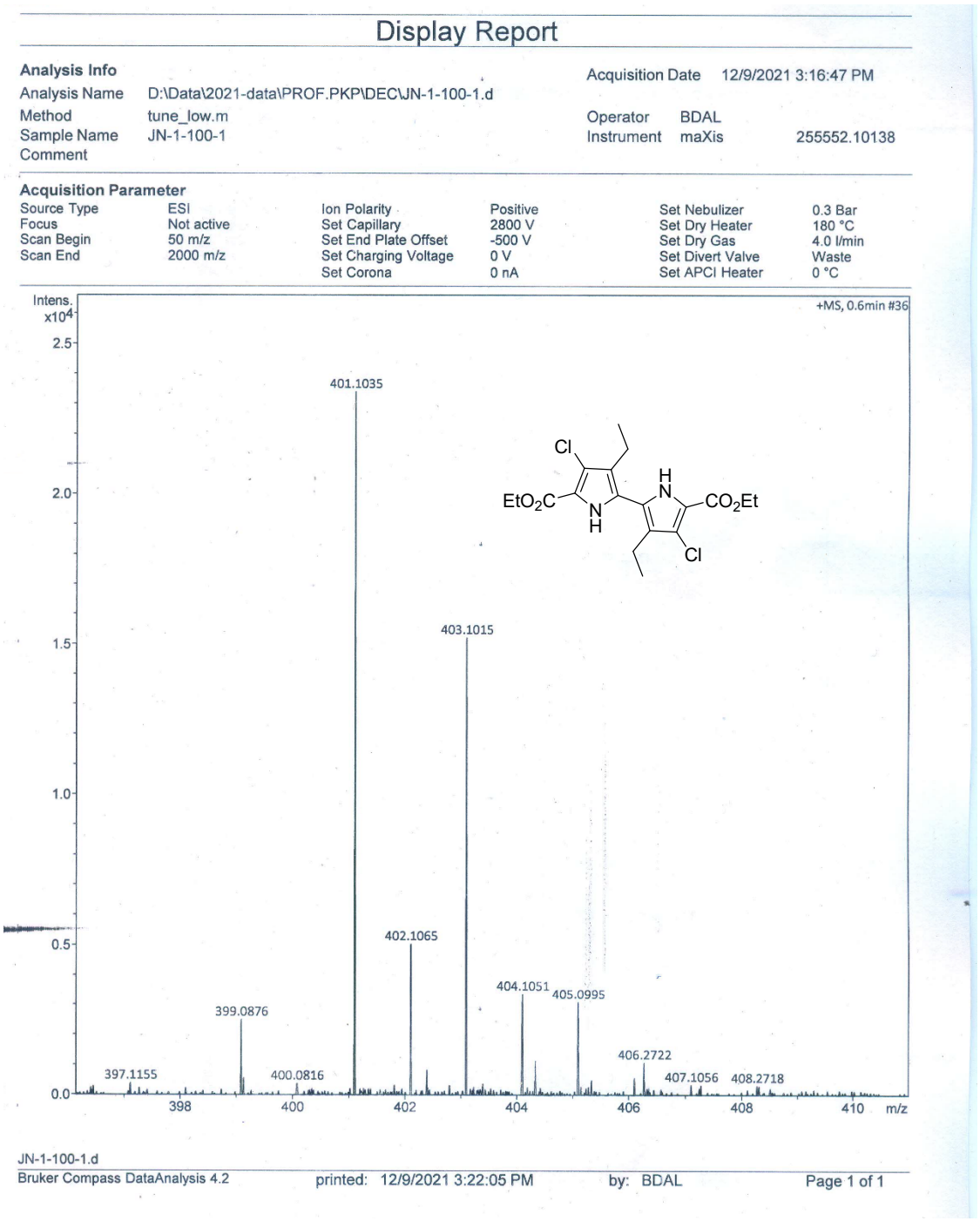

Figure S30. HRMS data of **4b-Cl:** $[M+H]^+$ Calcd for $C_{18}H_{23}N_2O_4Cl_2$: 401.1035; found: 401.1035.

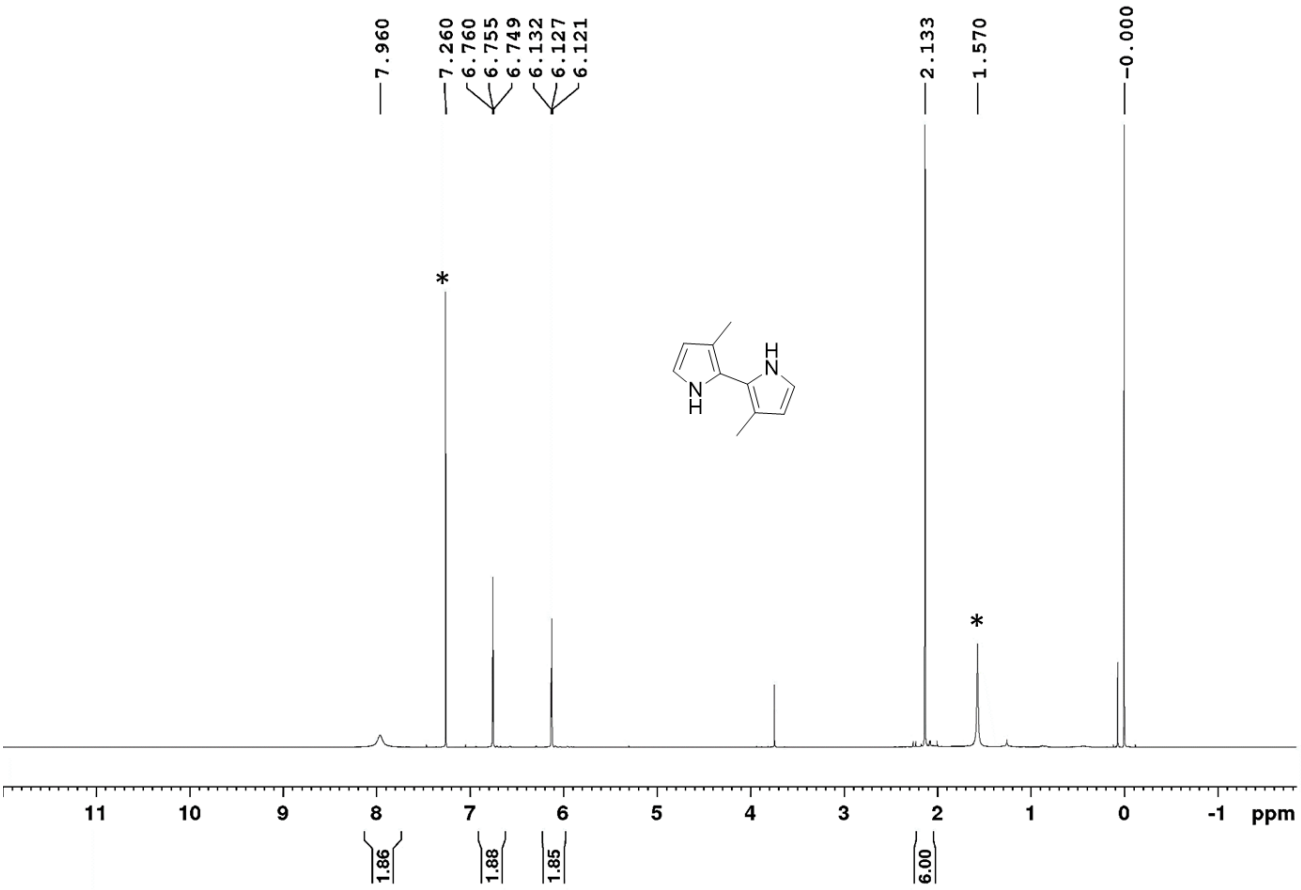

Figure S31. ^{1}H NMR spectrum of the compound **3a** (500 MHz, $CDCl_3$ TMS, δ = 0 ppm**)**. * Residual solvent peak: $CDCl_3$, H_2O.

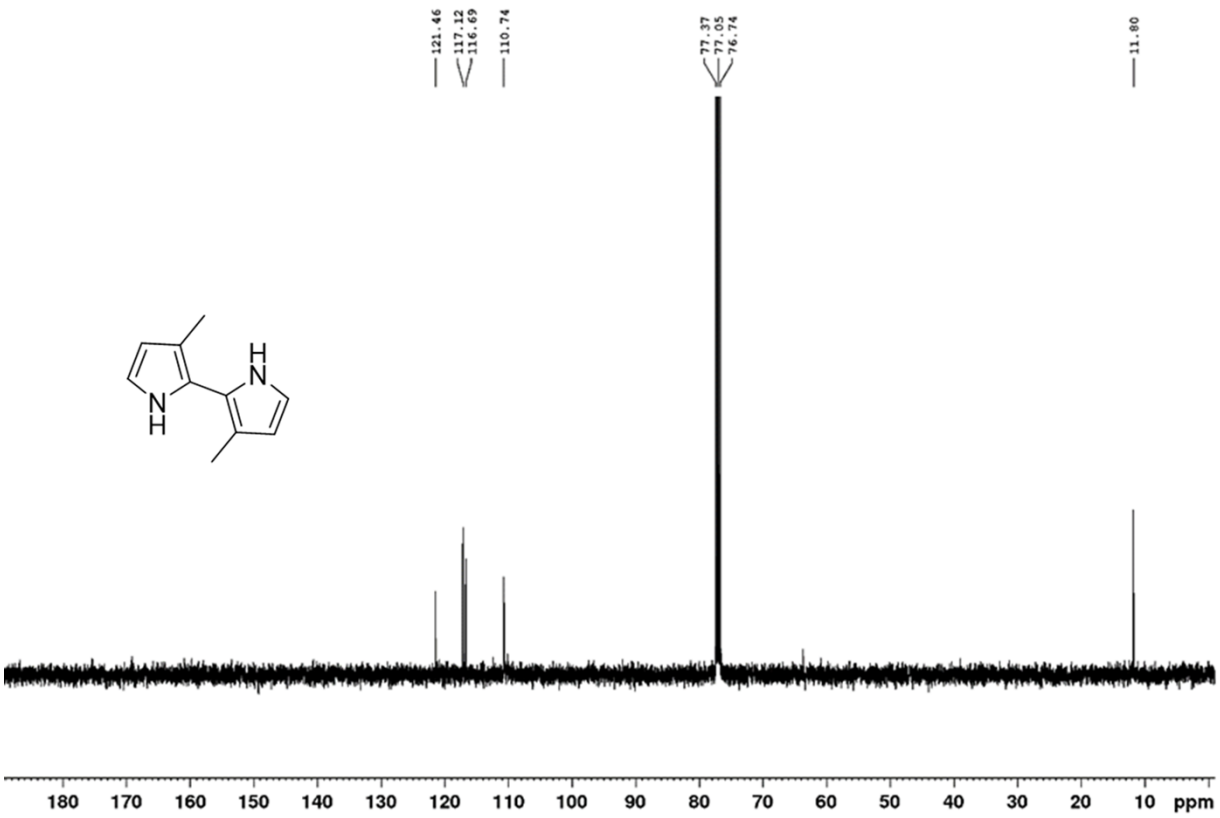

Figure S32. ^{13}C NMR spectrum of the compound **3a** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

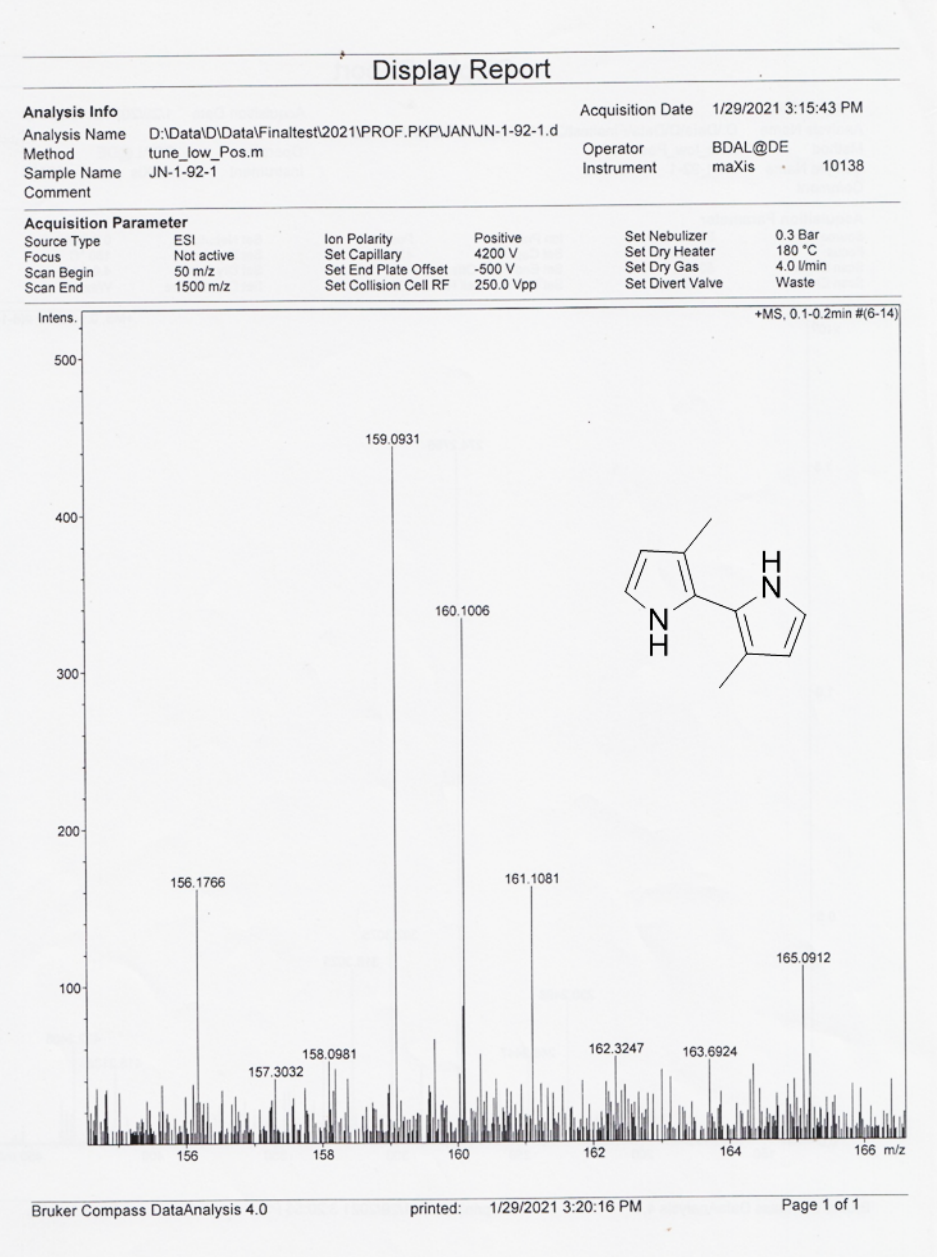

Figure S33. HRMS data of **3a:** $[M+H]^+$ Calcd for $C_{10}H_{12}N_2$: 160.1000; found: 160.1006.

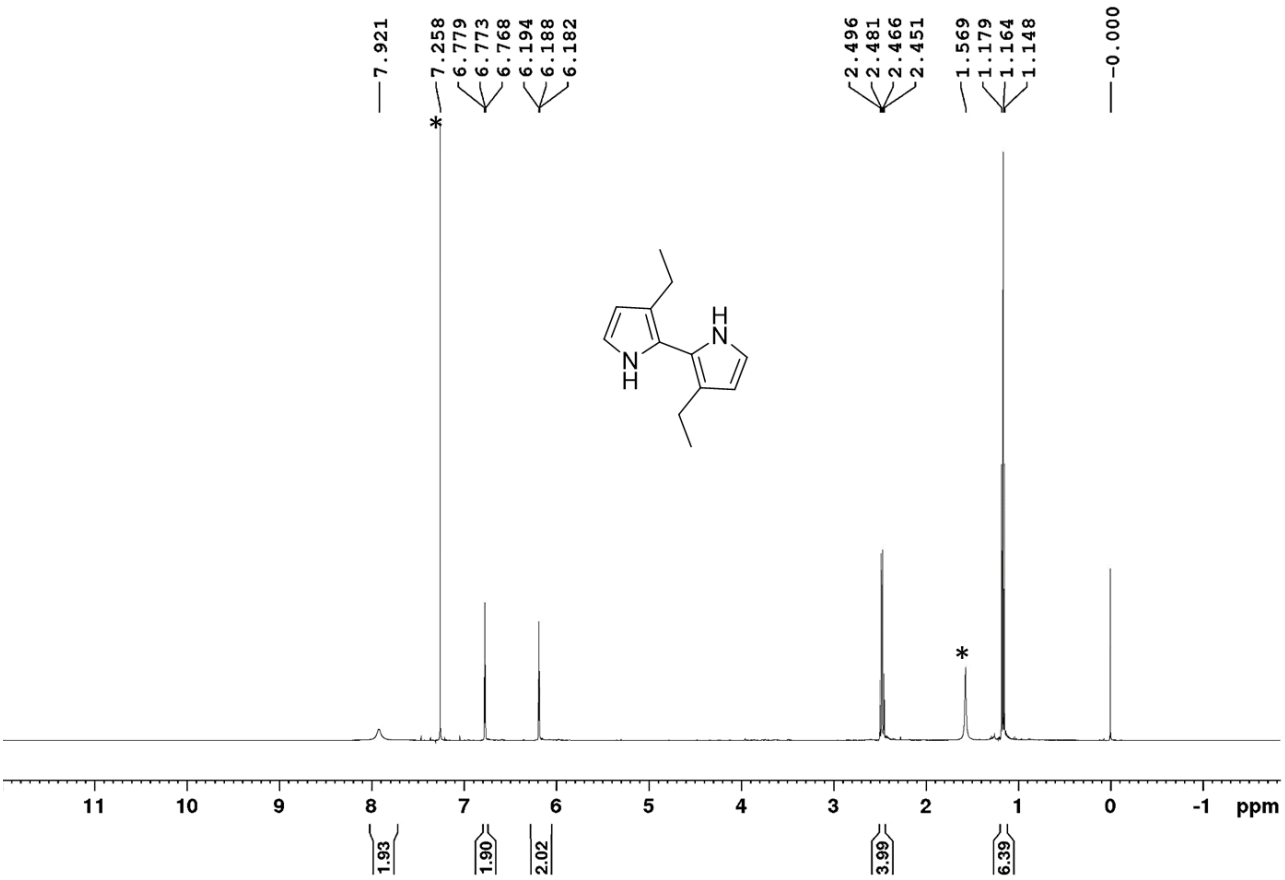

Figure S34. ^{1}H NMR spectrum of the compound **3b** (500 MHz, $CDCl_3$, TMS, δ = 0 ppm)**)**. * Residual solvent peak: $CDCl_3$, H_2O.

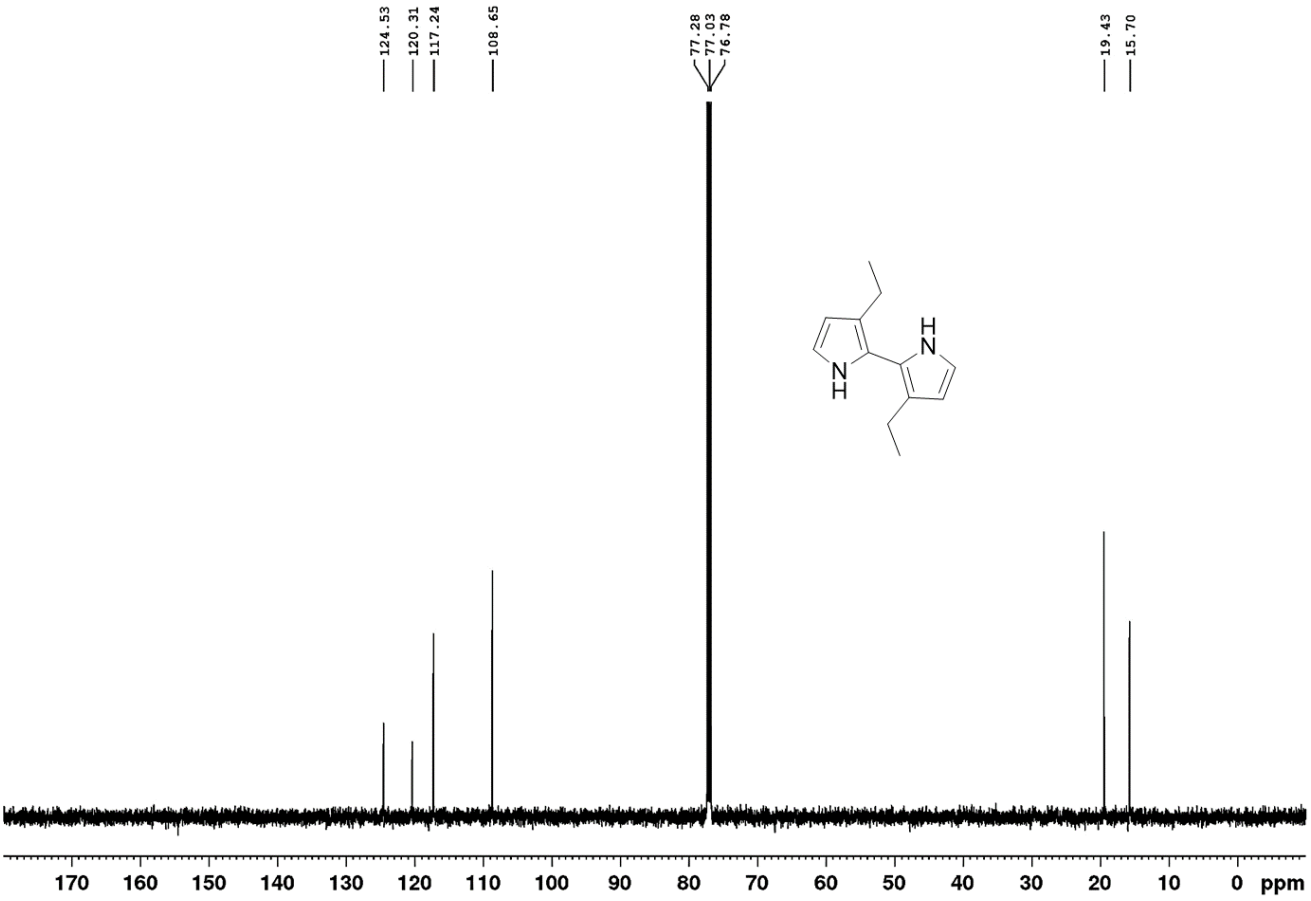

Figure S35. ^{13}C NMR spectrum of the compound **3b** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

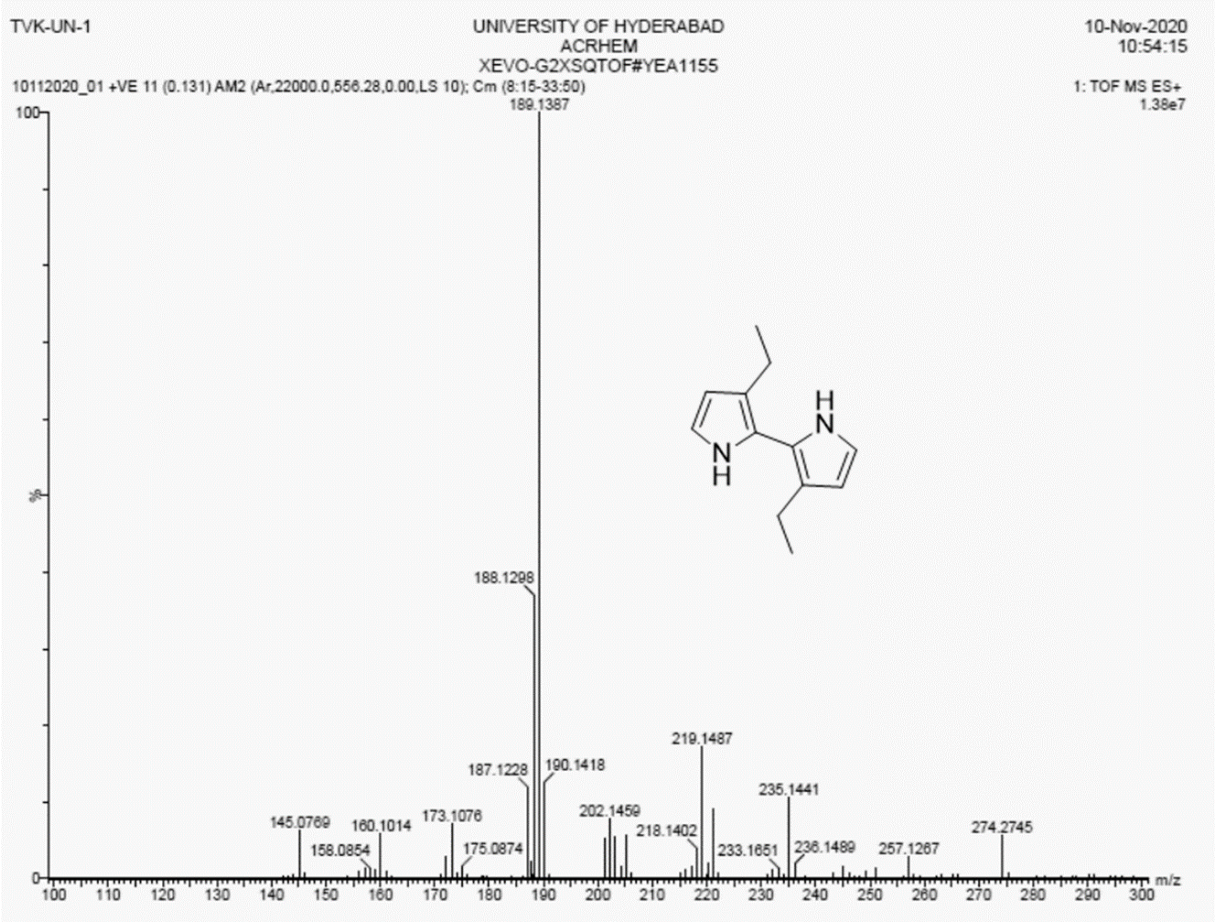

Figure S36. HRMS data of **3b:** $[M+H]^+$ Calcd for $C_{12}H_{17}N_2$: 189.1391; found: 189.1387

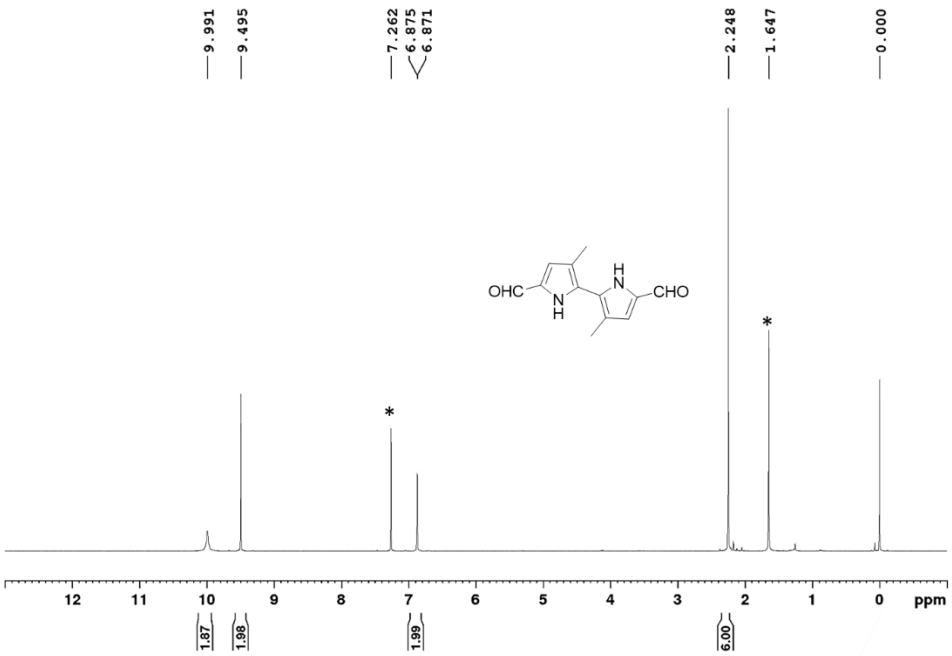

Figure S37. ^{1}H NMR spectrum of the compound **2a** (500 MHz, $CDCl_3$, TMS, δ = 0 ppm)**)** * Residual solvent peak: $CDCl_3$, H_2O.

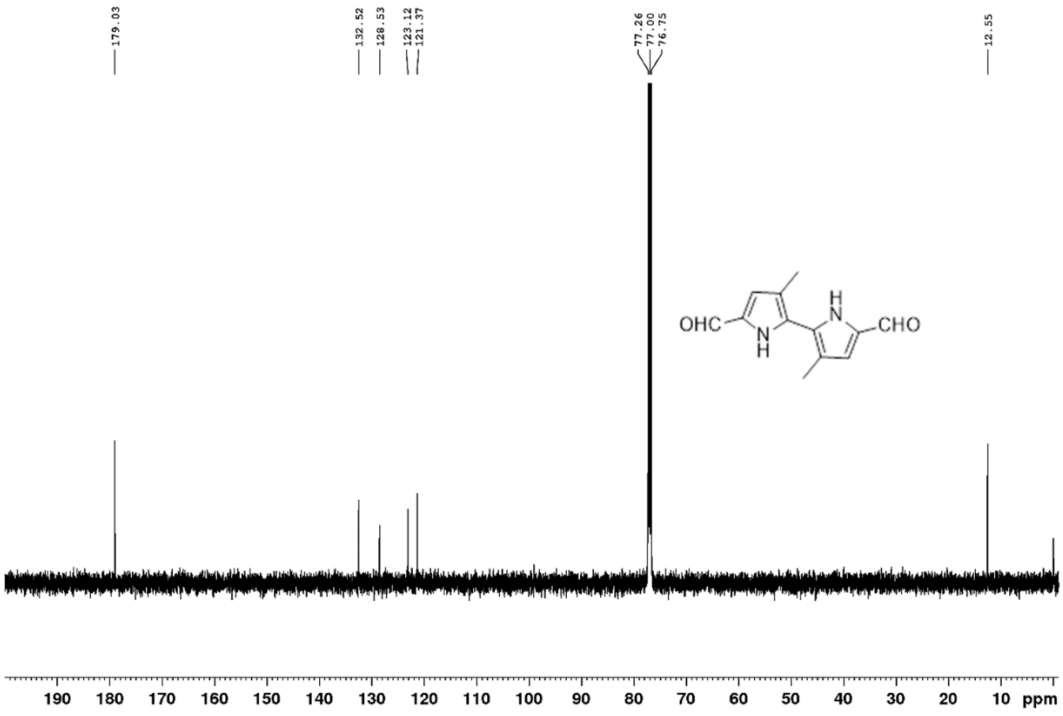

Figure S38. ^{13}C NMR spectrum of the compound **2a** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

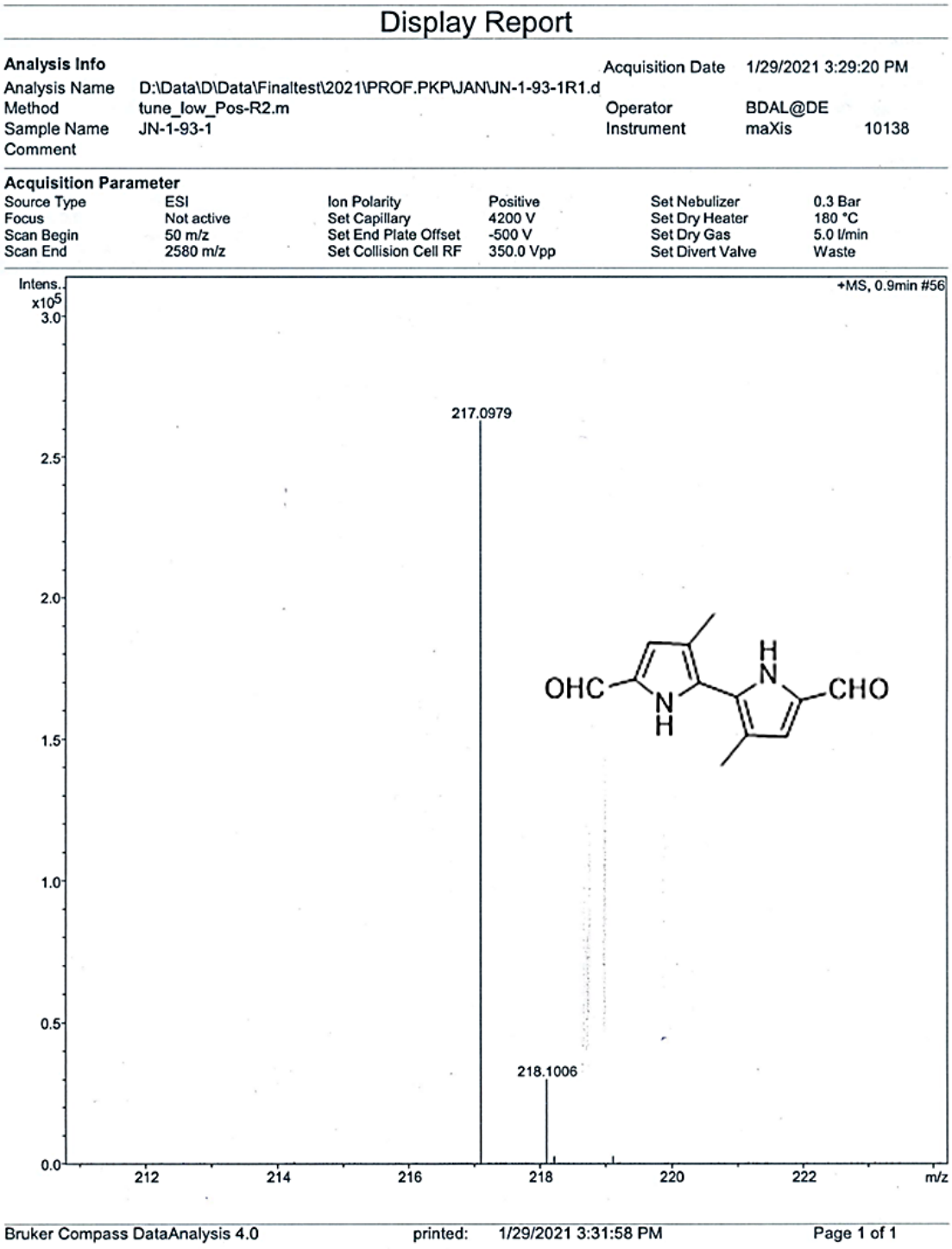

Figure S39. HRMS data of **2a:** $[M+H]^+$ Calcd for $C_{12}H_{13}N_2O_2$: 217.0977; found: 217.0979.

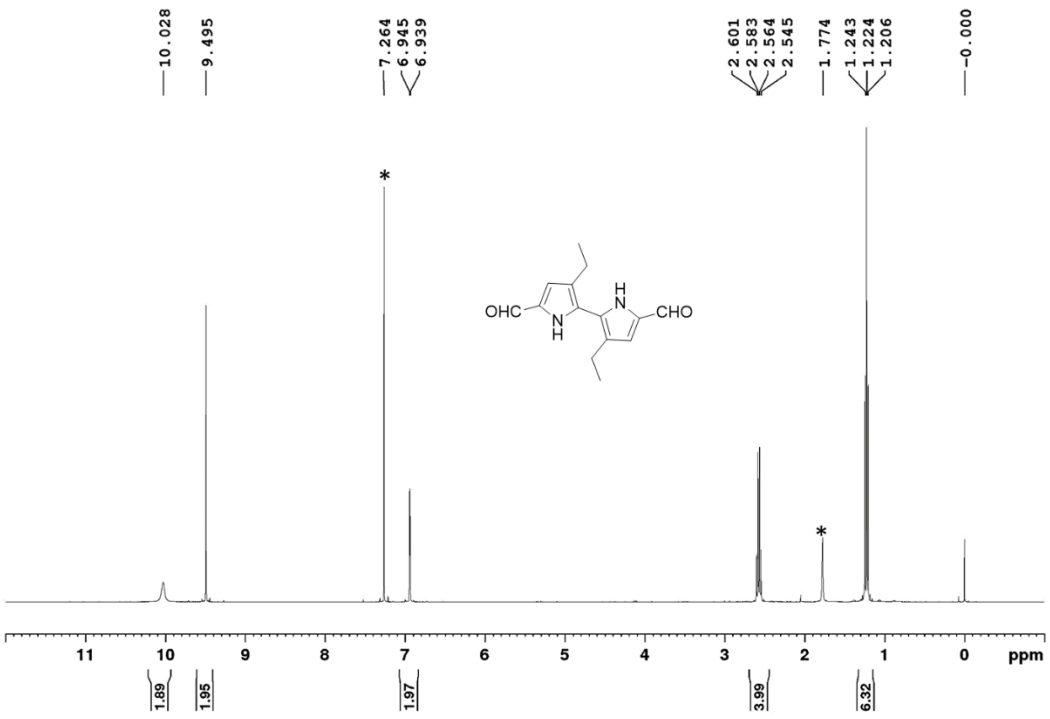

Figure S40. ^{1}H NMR spectrum of the compound **2b** (500 MHz, $CDCl_3$ TMS, δ = 0 ppm)**).** * Residual solvent peak: $CDCl_3$, H_2O.

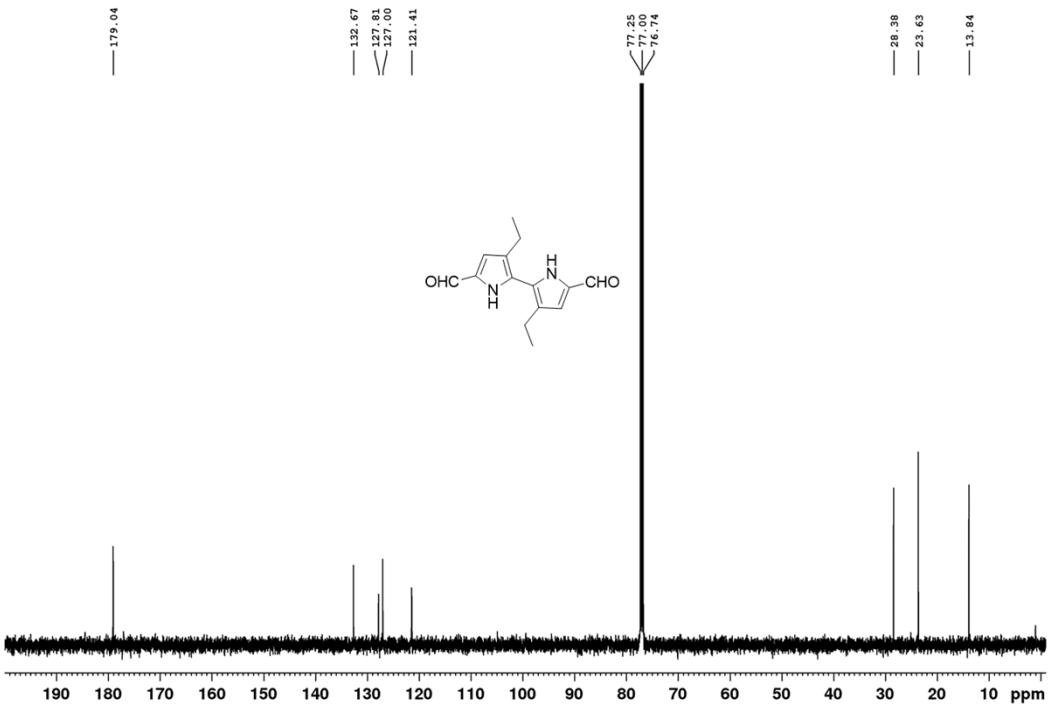

Figure S41. ^{13}C NMR spectrum of the compound **2b** (126 MHz, (δ = 77 ppm)).

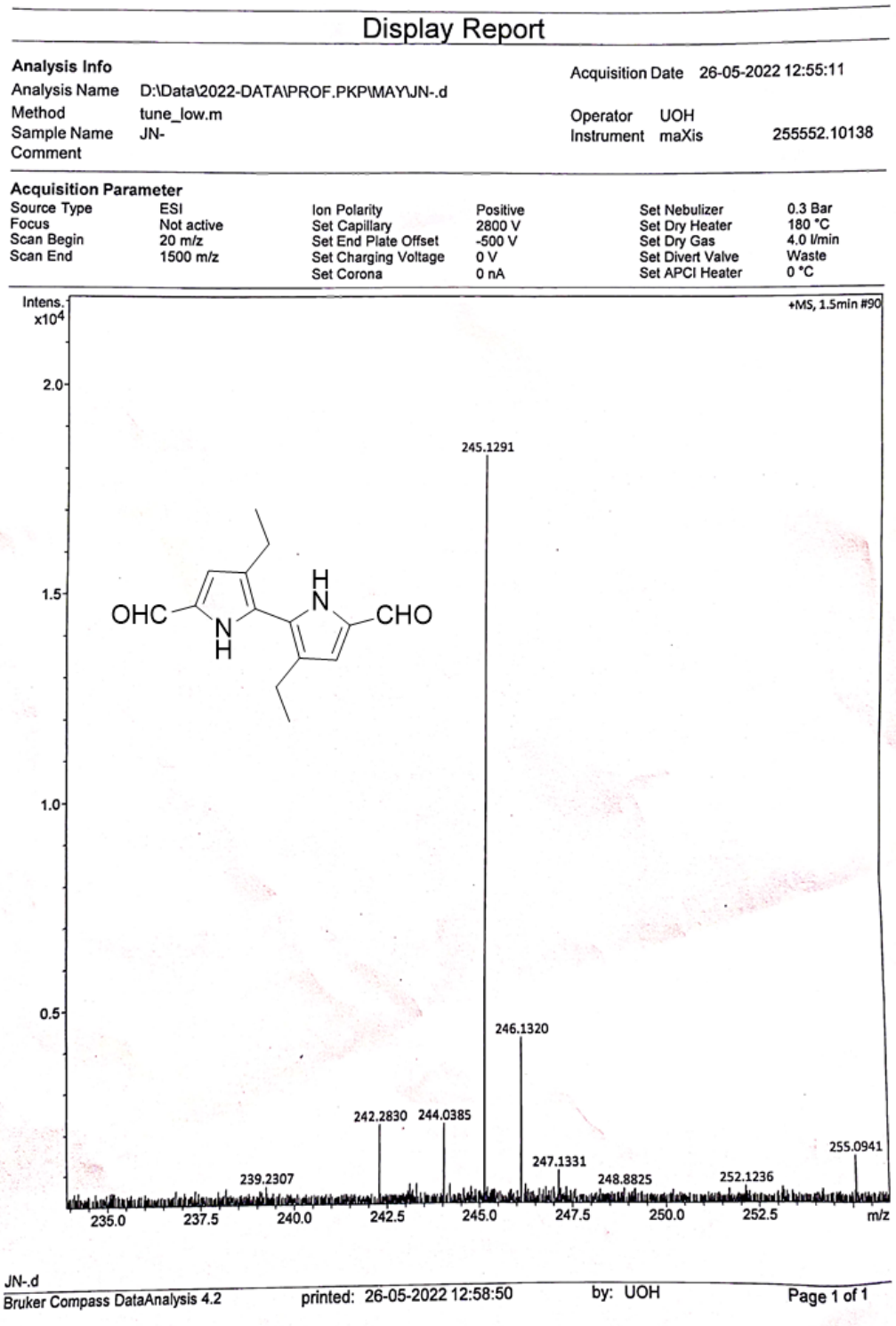

Figure S42. HRMS data of compound **2b:** $[M+H]^+$ Calcd for $C_{14}H_{17}N_2O_2$: 245.1290; found: 245.1291.

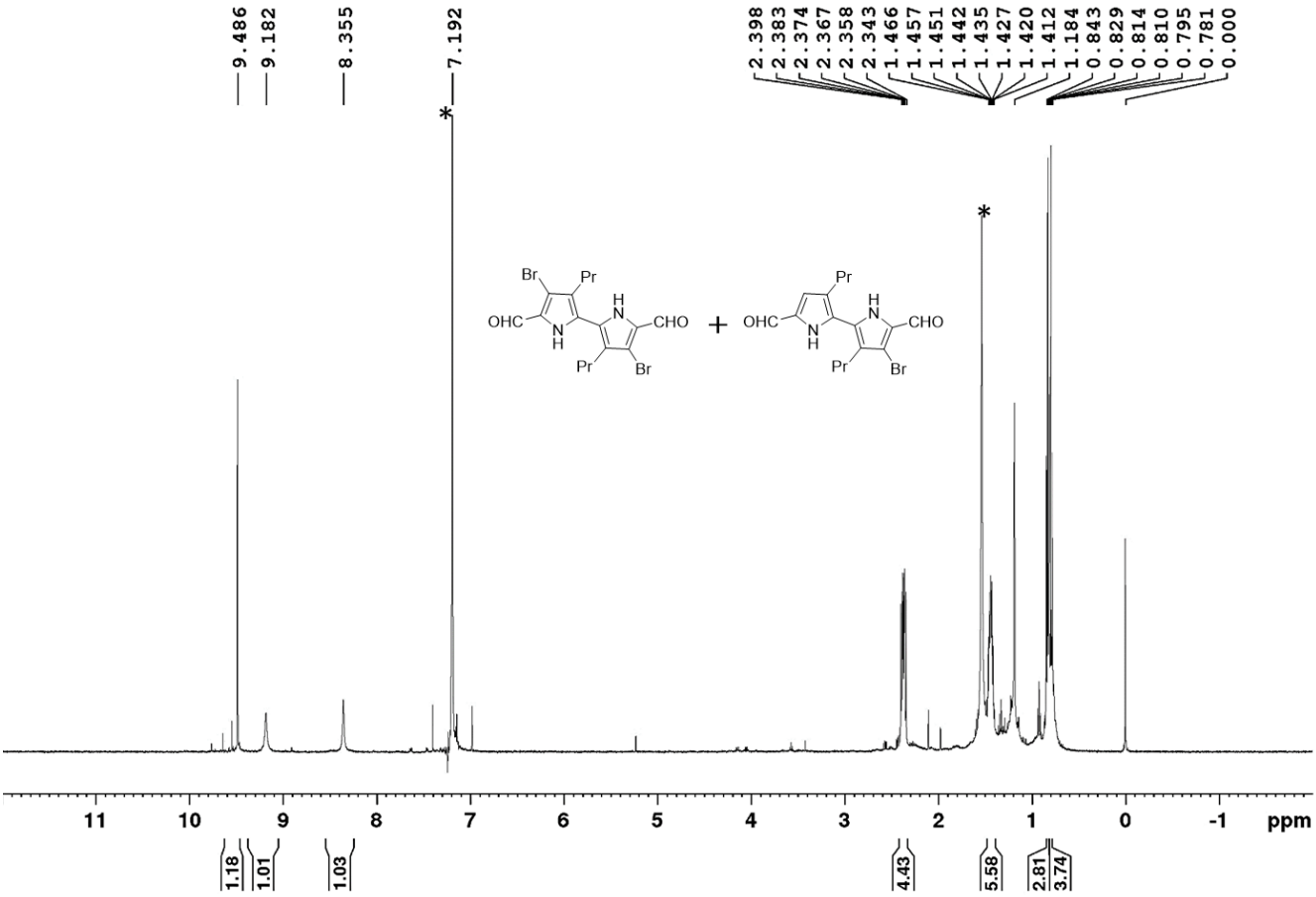

Figure S43. ^{1}H NMR spectrum of the inseparable mixture of compounds **2c-Br** and **2c-Br′** (500 MHz, $CDCl_3$, TMS, δ = 0 ppm).

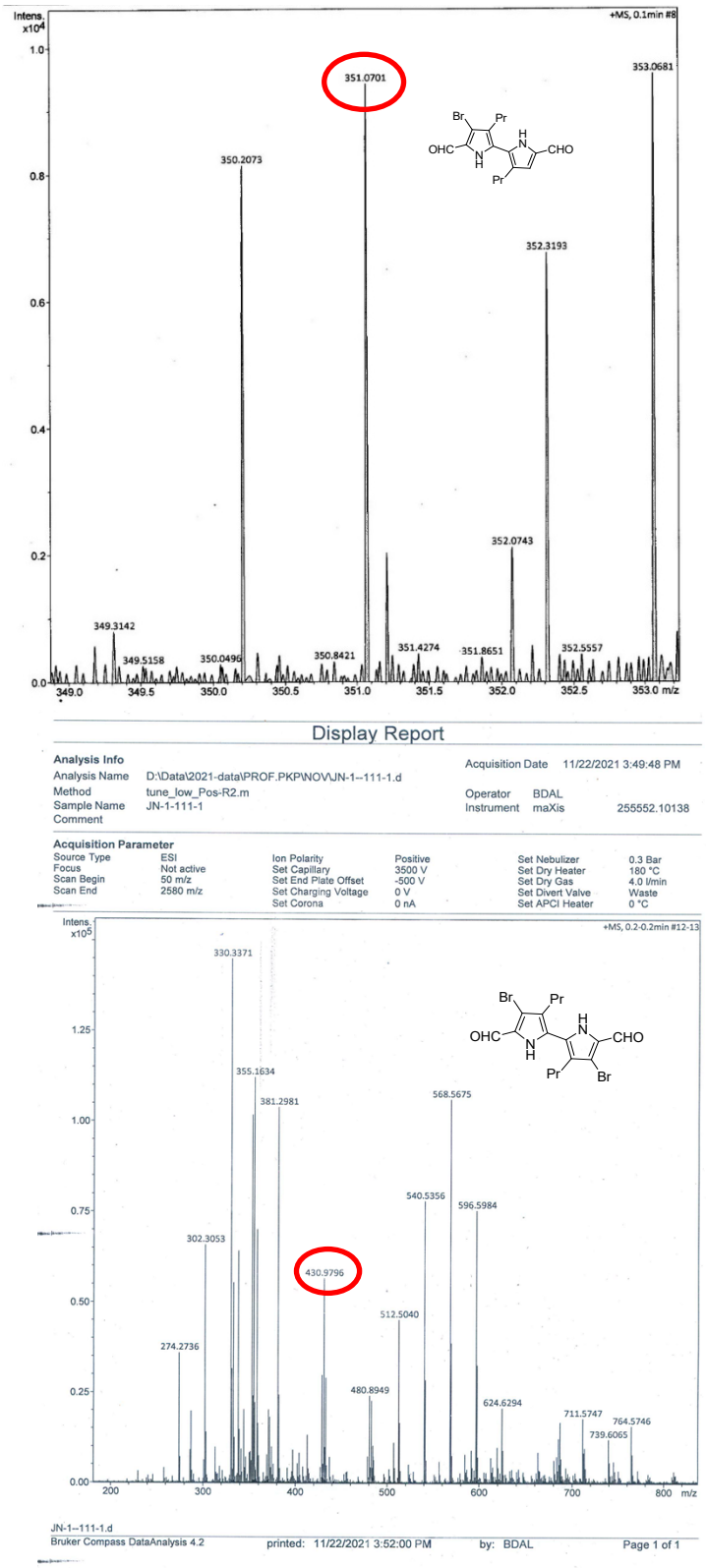

Figure S44. HRMS data of compound **2c-Br:** $[M+H]^+$ Calcd for $C_{16}H_{19}Br_2N_2O_2$: 430.9793 found : 430.9796. **2c-Br′**: $C_{16}H_{20}BrN_2O_2$: 351.0708; found: 351.0701(top expanded and bottom full spectra).

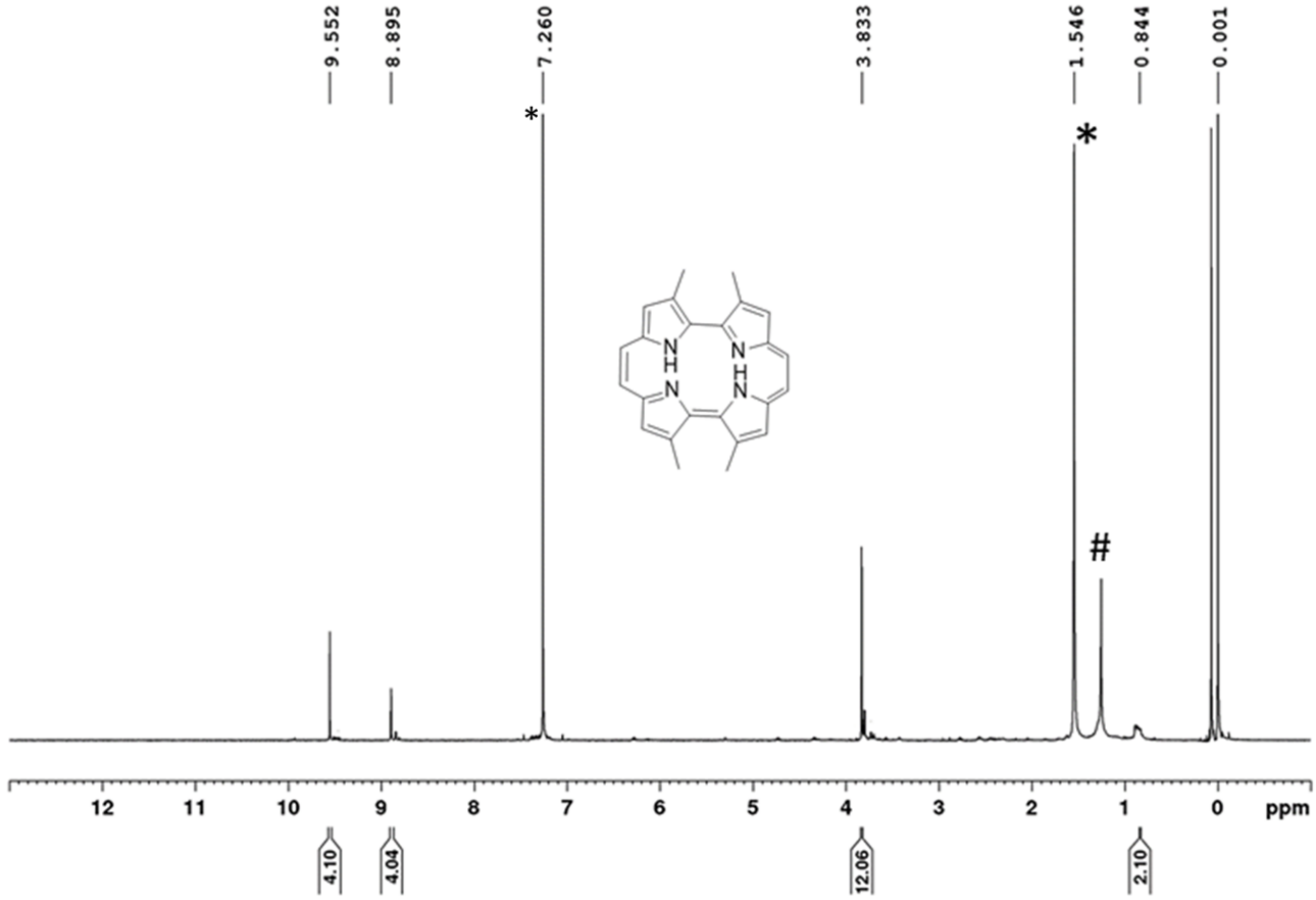

Figure S45. ^{1}H NMR spectrum of the compound **1a** (500 MHz, $CDCl_3$, TMS, δ = 0 ppm**)**. * Residual solvent peak: $CDCl_3$, H_2O, # belongs to grease.

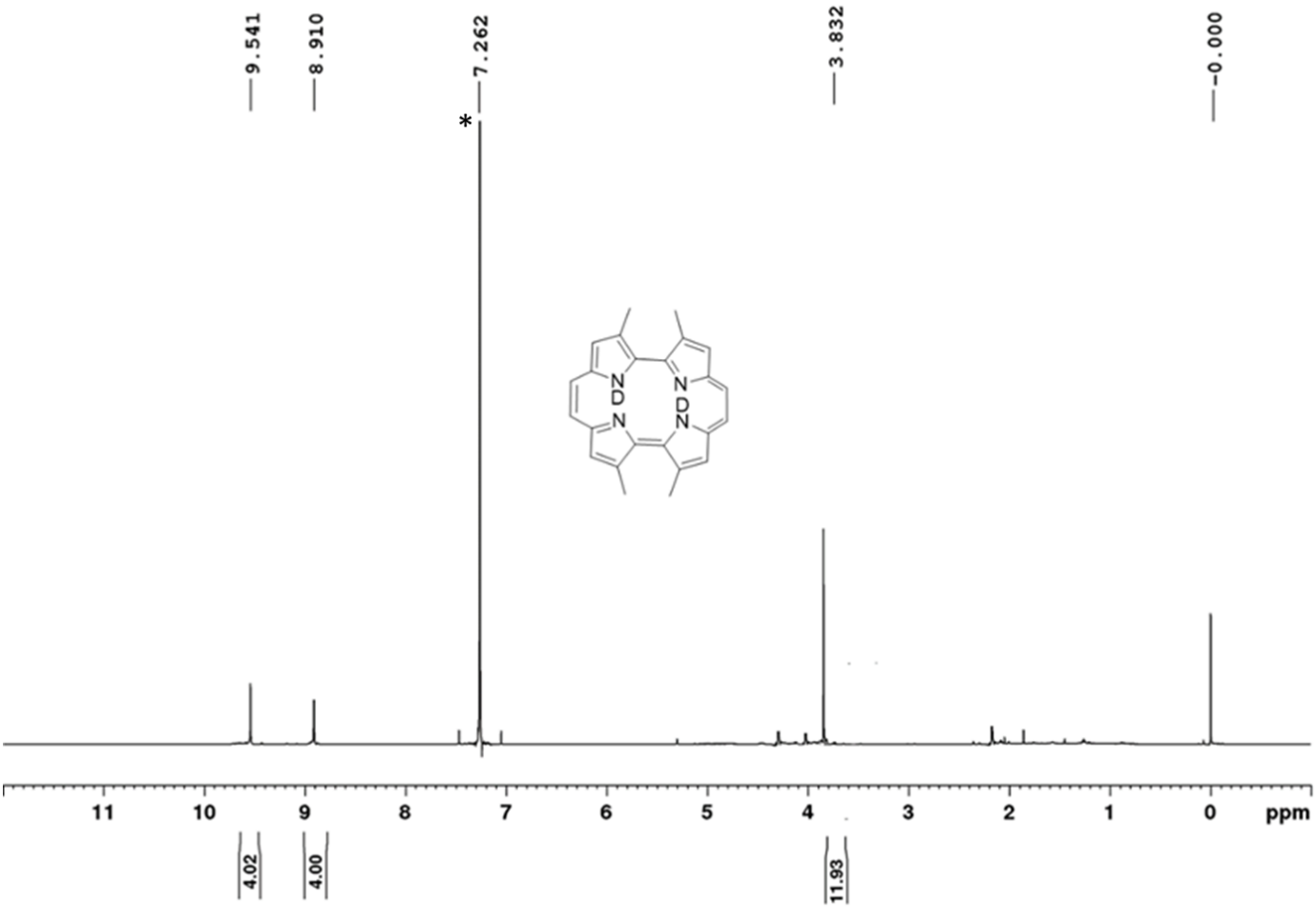

Figure S46. ^{1}H NMR spectrum of the compound **1a** after D_2O exchange (500 MHz, $CDCl_3$, TMS, $\delta = 0$ ppm**)**. * Residual solvent peak: $CDCl_3$.

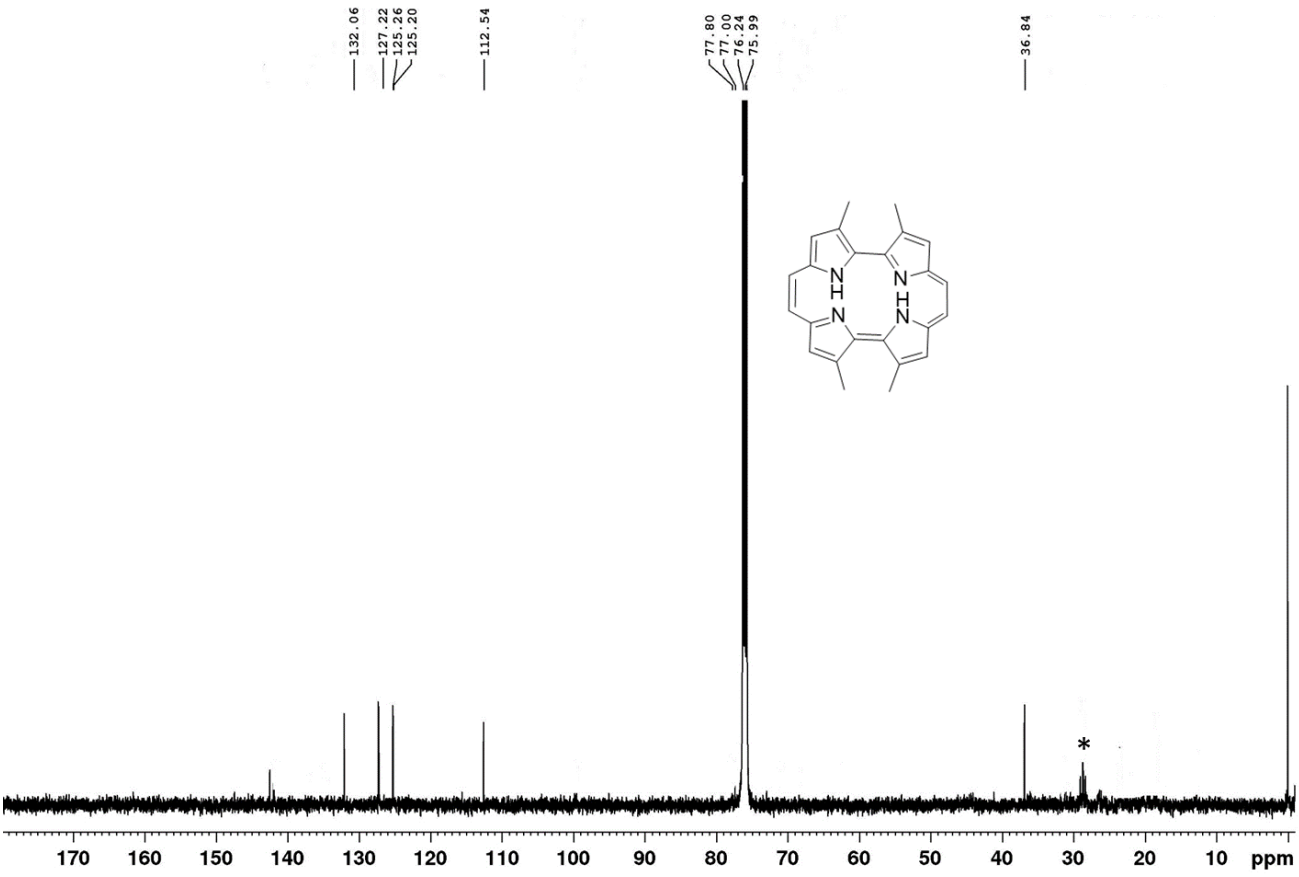

Figure S47. ^{13}C NMR spectrum of the compound **1a** (126 MHz, $CDCl_3$ (δ = 77 ppm)). * grease.

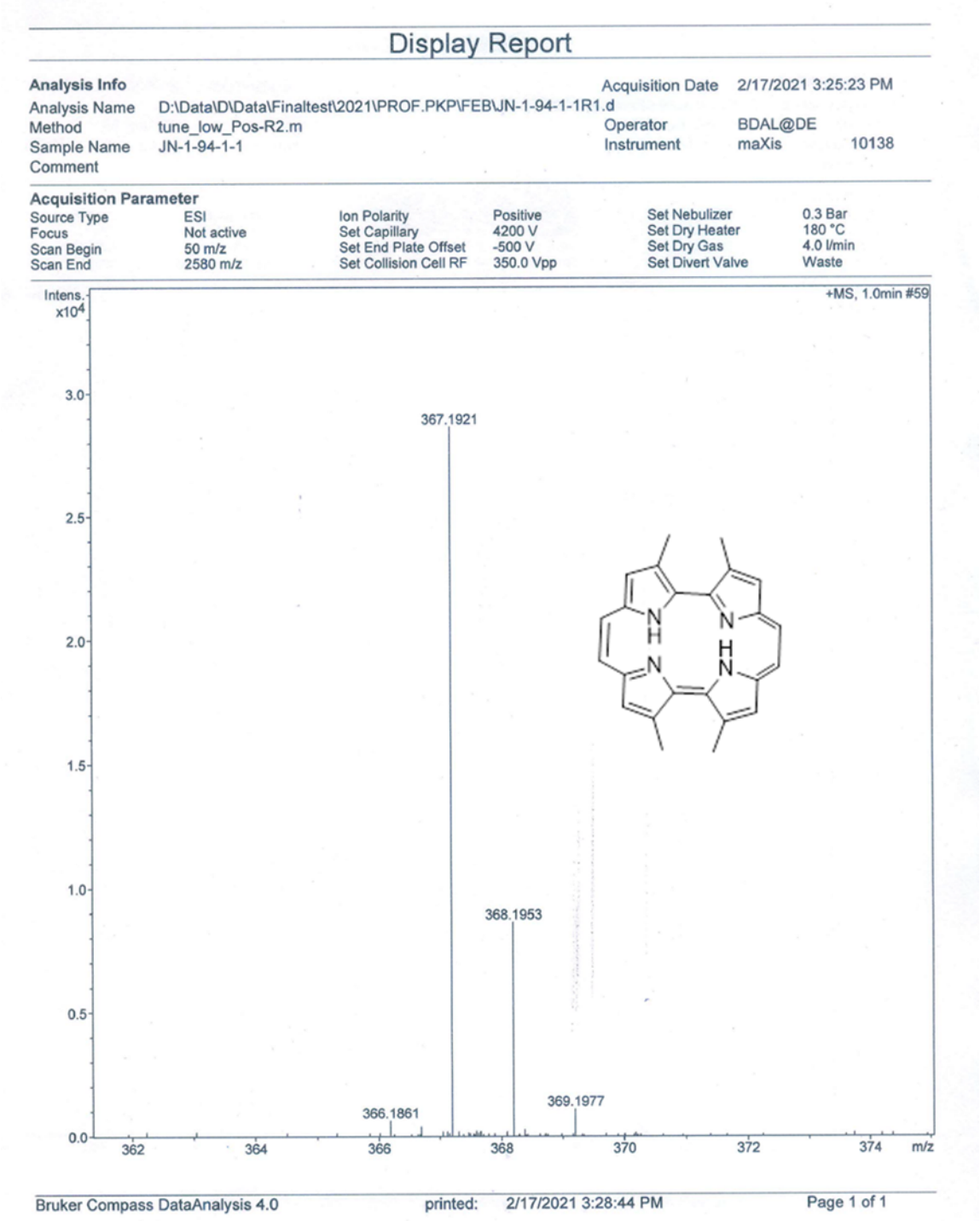

Figure S48. HRMS data of **1a:** $[M+H]^+$ Calcd for $C_{24}H_{23}N_4$: 367.1922; found: 367.1921.

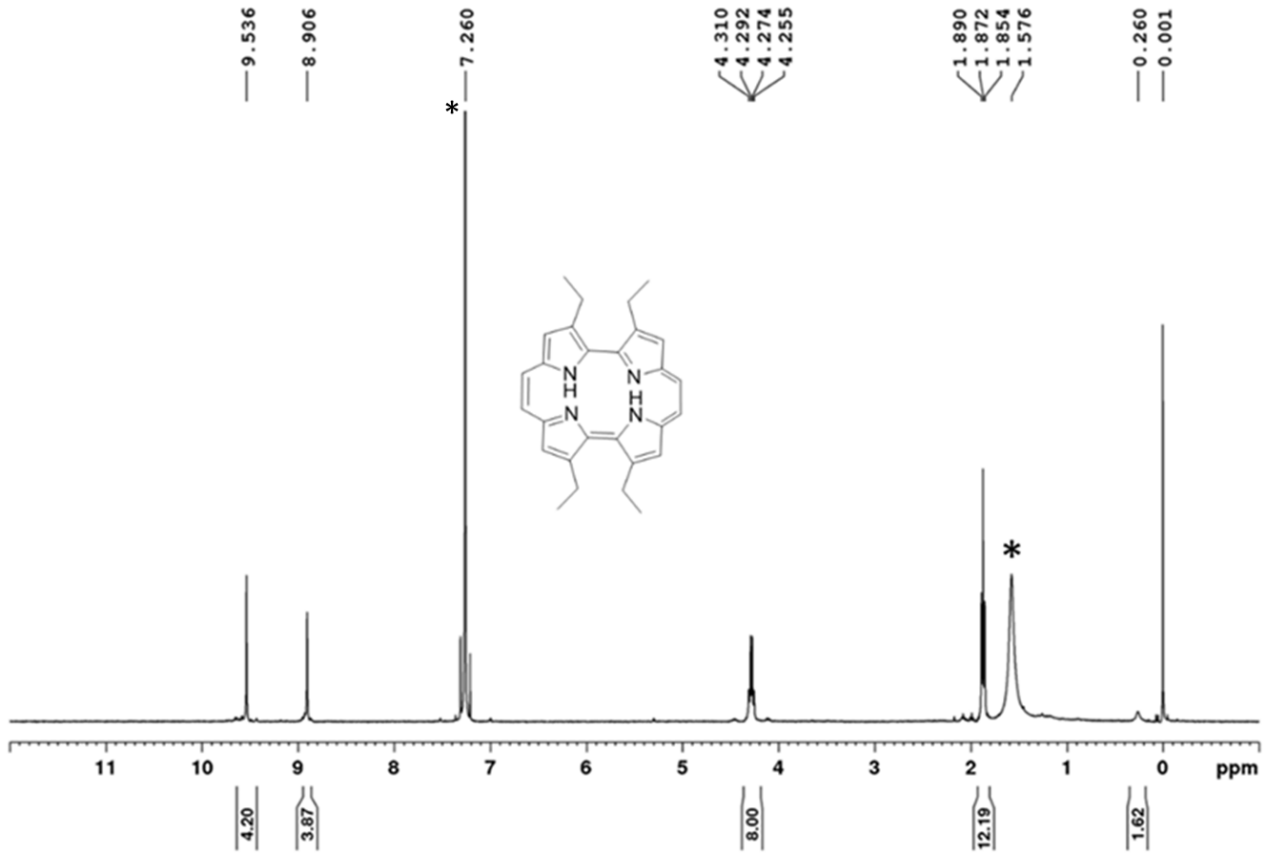

Figure S49. ^{1}H NMR spectrum of the compound **1b** (500 MHz, $CDCl_3$, TMS, δ = 0 ppm**)**. * Residual solvent peak: $CDCl_3$, H_2O

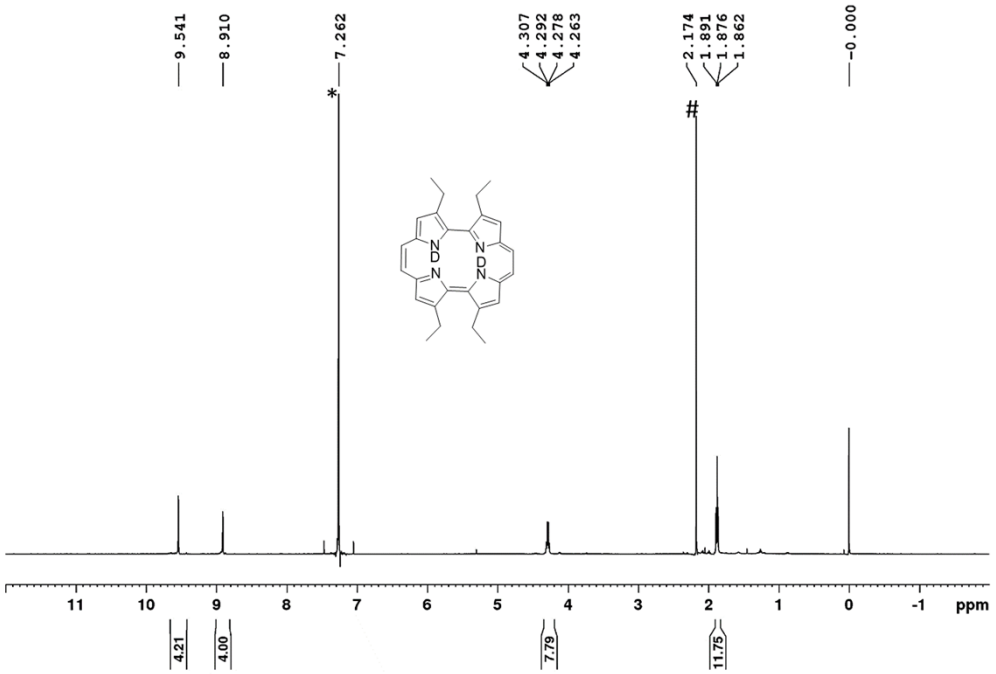

Figure S50. ^{1}H NMR spectrum of the compound **1b** after D_2O exchange (500 MHz, $CDCl_3$, TMS, δ = 0 ppm**)**. *Residual solvent peak: $CDCl_3$, # acetone.

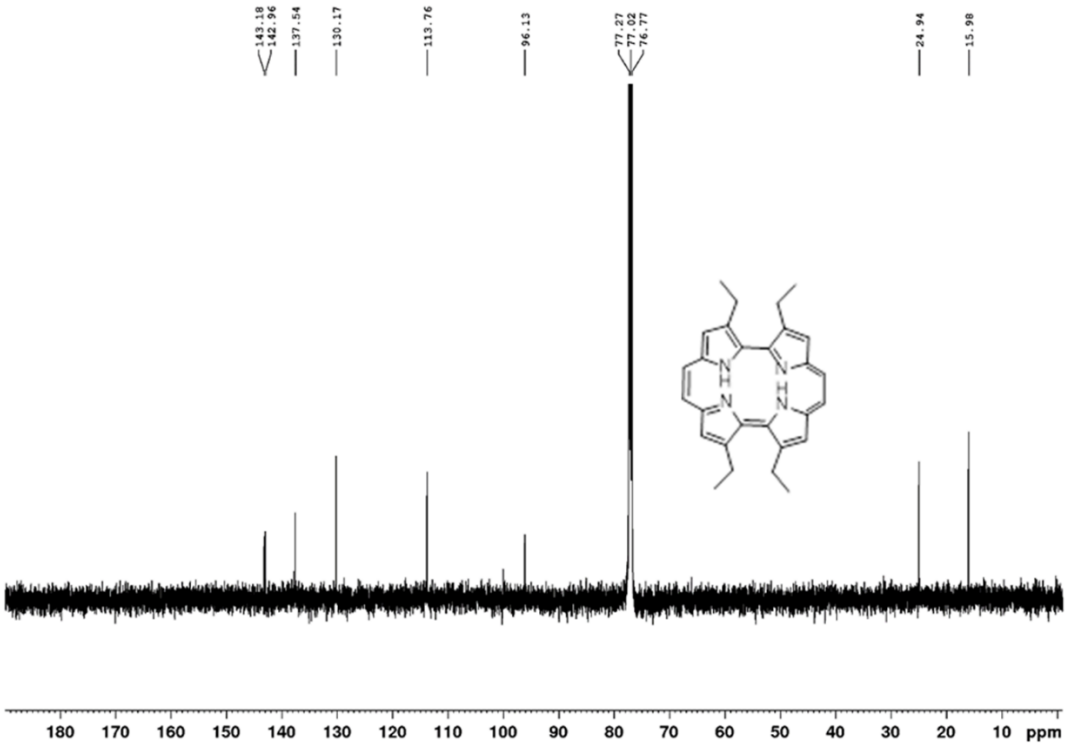

Figure S51. ^{13}C NMR spectrum of the compound **1b** (126 MHz, $CDCl_3$ (δ = 77 ppm)).

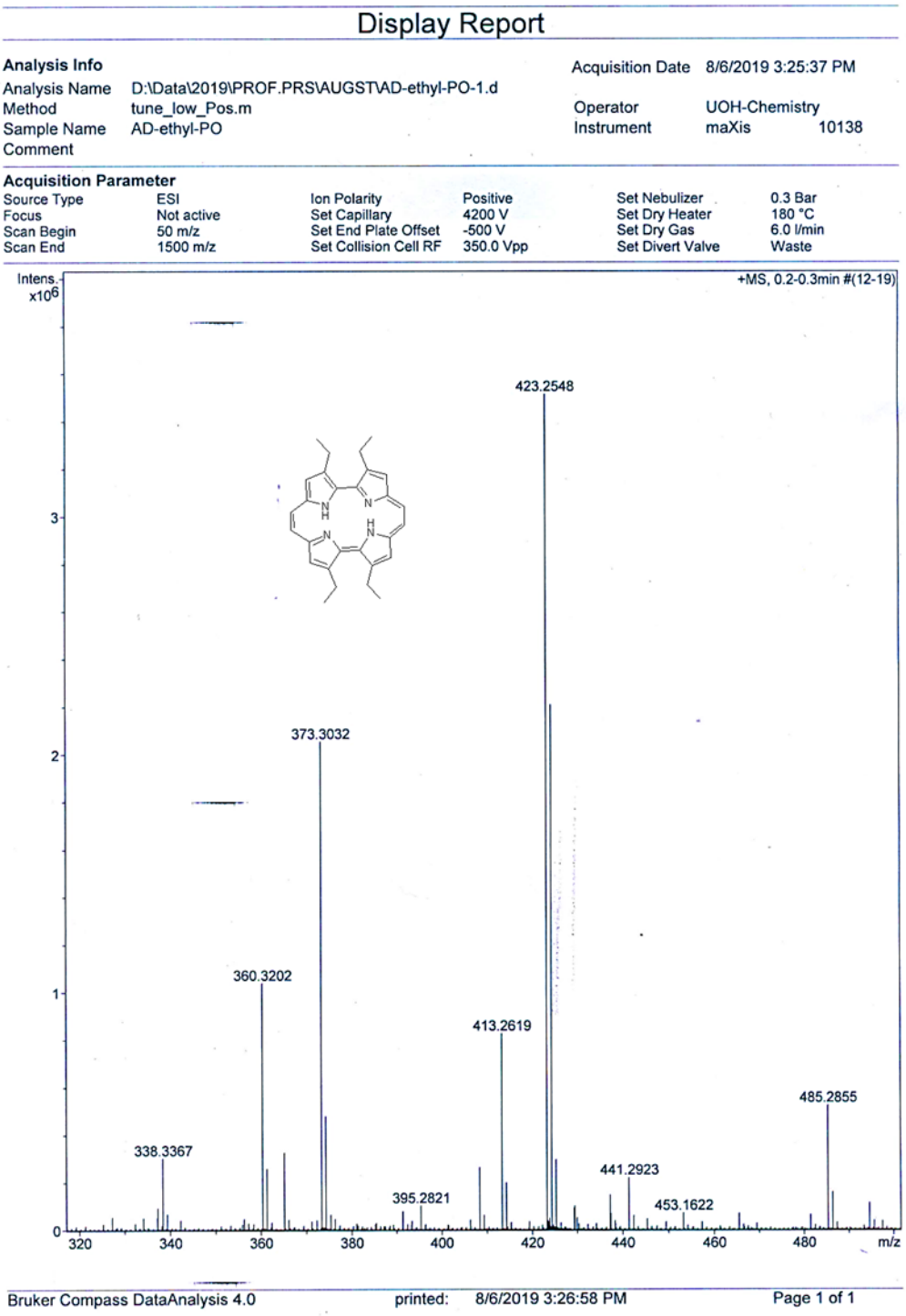

Figure S52. HRMS data of **1b:** $[M+H]^+$ Calcd for $C_{28}H_{31}N_4$: 423.2549; found: 423.2548.

4. CRYSTALLOGRAPHIC DATA

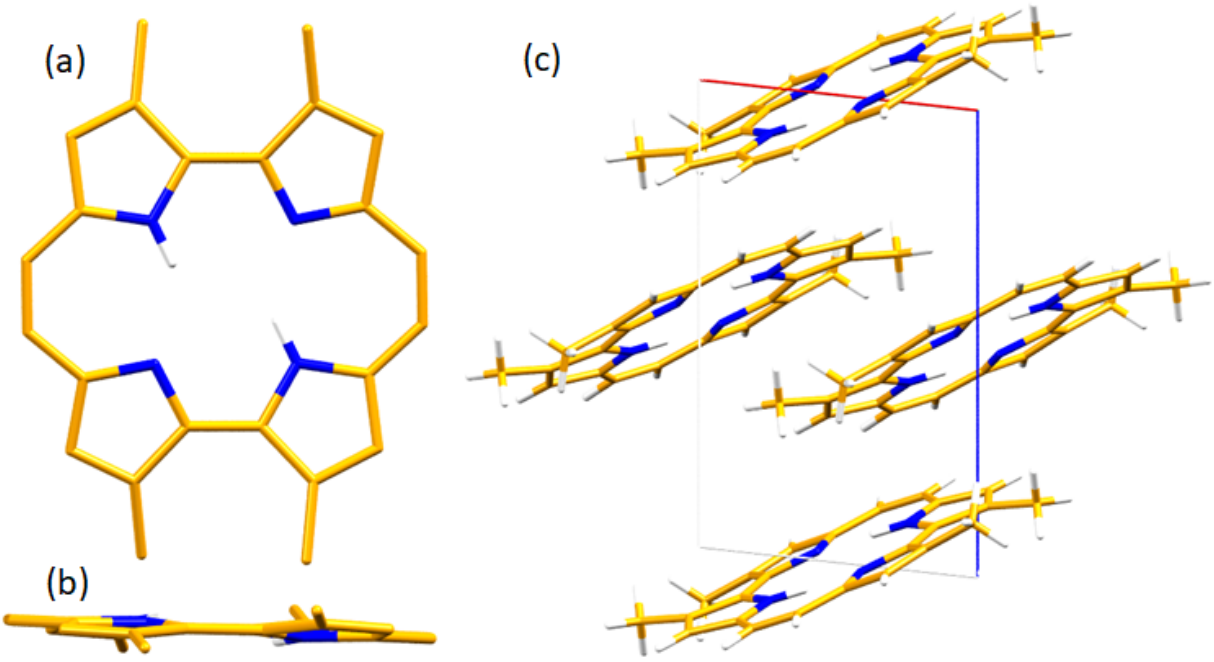

Figure S53. (a) Crystal structures of **1a** (a) top on, (b) side on view and **(c)** packing diagram viewed through b axis, Hydrogens are removed for clarity, except NH protons. Colour code: C, yellow; N, blue; H, white.

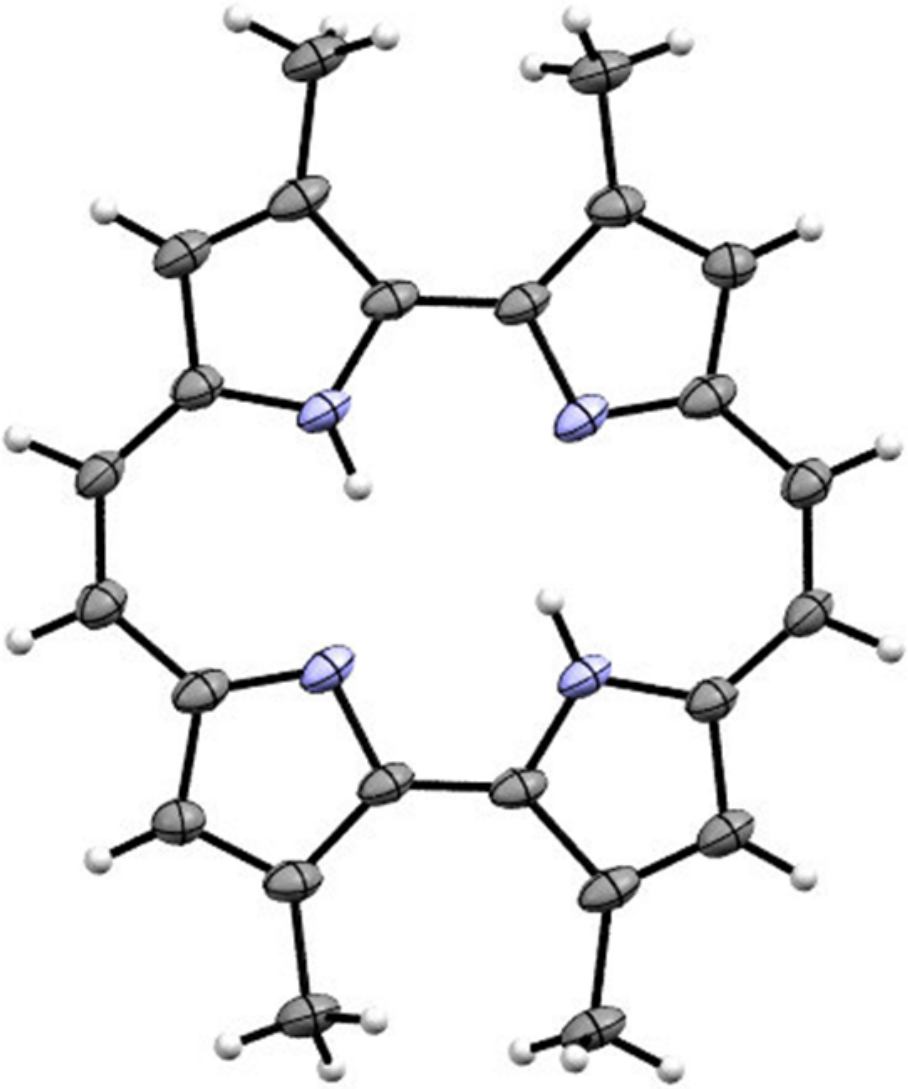

Figure S54. Thermal ellipsoid plot of crystal structure **1a** viewed at 50% probability level.

Table S1 (Crystallographic parameters of **1a):**

Empirical formula	$C_{24}H_{22}N_4$
Formula weight	366.45
Temperature	111(2)K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic $P2_1/n$
Unit cell dimensions	a = 6.9895(3) alpha = 90 deg. b = 10.9365(10) beta = 96.278(4) deg. c = 11.6318(6) gamma = 90 deg.

Volume	883.81(10) A^3
Z, Calculated density	2, 1.377 Mg/m^3
Absorption coefficient	0.083 mm^{-1}
F(000)	388
2Theta range for data collection	5.128 to 51.36 deg.
Limiting indices	$-8 \le h \le 8, -13 \le k \le 13, -14 \le l \le 14$
Reflections collected / unique	5331 / 1587 [R_{int} = 0.1059]
Data / restraints / parameters	1587/0/129
Goodness-of-fit on F^2	1.022
Final R indices [I>2sigma(I)]	R_1 = 0.0825, wR_2 = 0.2061
R indices (all data)	R_1 = 0.1170, wR_2 = 0.2514
Extinction coefficient	n/a
Largest diff. peak and hole	0.37 and -0.47 $e.A^{-3}$

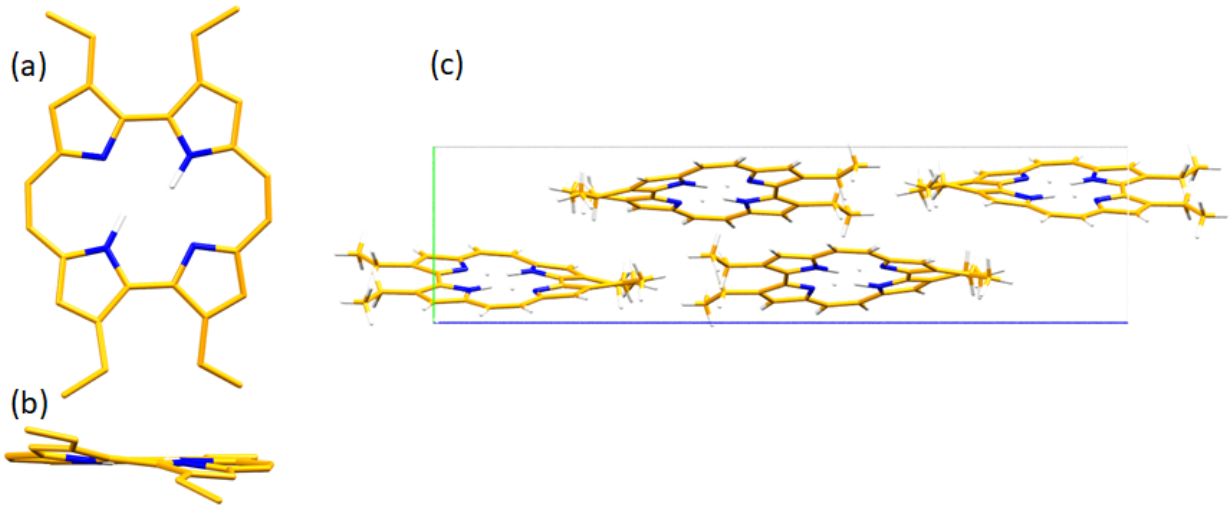

Figure S55. (a) Crystal structures of **1b** (a) top on, (b) side on view, Hydrogens are removed for clarity, except NH protons and **(c)** packing diagram viewed through a axis. Colour code: C, yellow; N, blue; H, white.

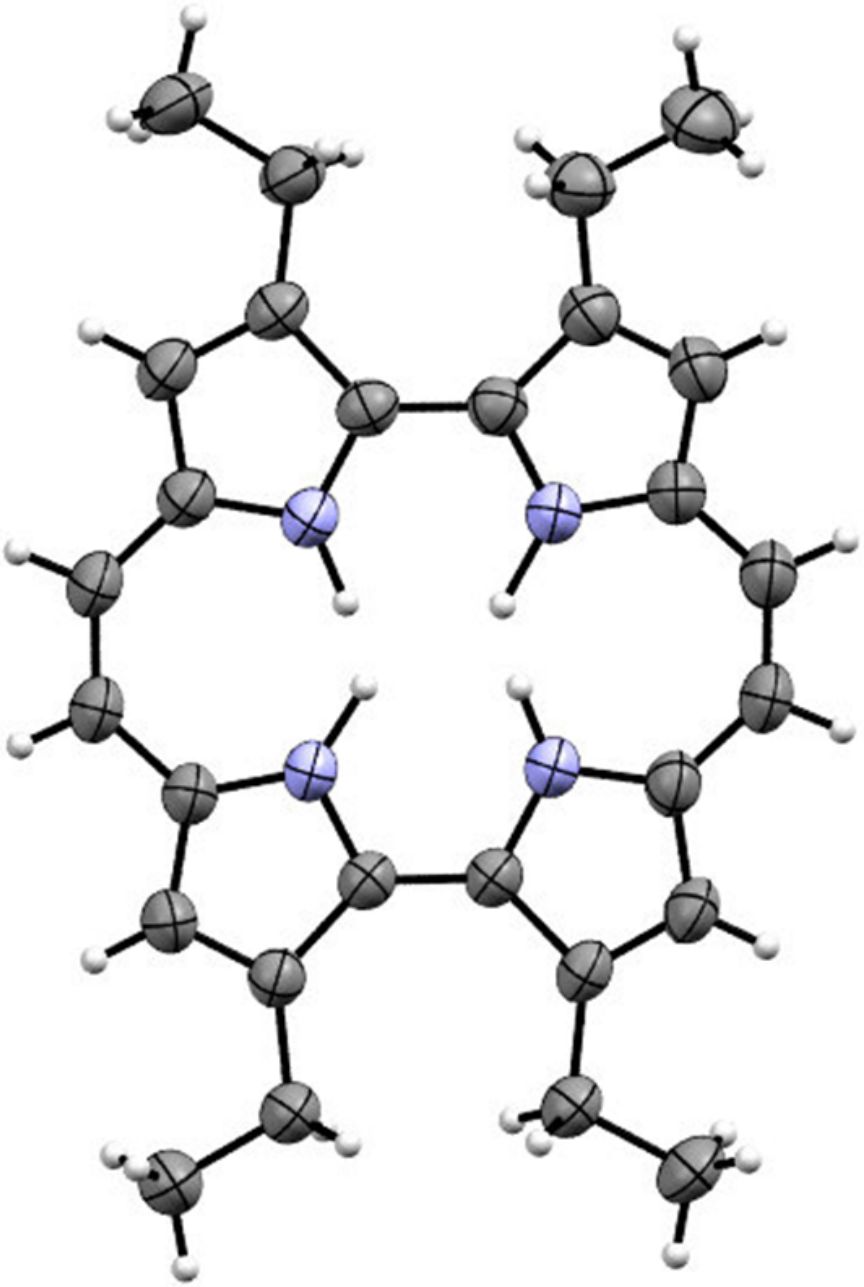

Figure S56. Thermal ellipsoid plot of crystal structure **1b** viewed at 50% probability level.

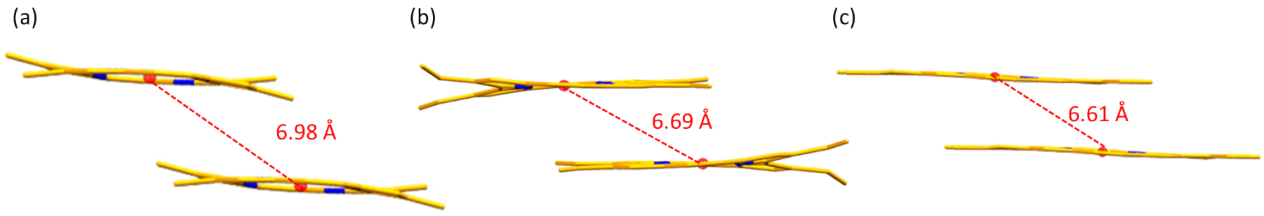

Figure S57. Centroid-centroid distance of (a) **1a**, (b) **1b** and (c) **1c**.

Table S2 (Crystallographic parameters of **1b):**

Empirical formula	$C_{28}H_{30}N_4$
Formula weight	422.56
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic $P2_1/c$
Unit cell dimensions	a = 9.8726(4) alpha = 90 deg. b = 7.4607(3) beta = 96.255(4) deg. c = 29.6443(12) gamma = 90 deg.
Volume	2170.50(15) A^3
Z, Calculated density	4, 1.293 Mg/m^3
Absorption coefficient	0.077 mm^{-1}
F(000)	904
2Theta range for data collection	4.15 to 53.834 deg.
Limiting indices	-12<=h<=12, -9<=k<=9, -37<=l<=36
Reflections collected / unique	16271/ 4467 [R(int) = 0.0730]
Data / restraints / parameters	4467 / 0 / 310
Goodness-of-fit on F^2	0.923
Final R indices [I>2sigma(I)]	R1 = 0.0599, wR2 = 0.1308
R indices (all data)	R1 = 0.1244, wR2 = 0.1630
Extinction coefficient	n/a
Largest diff. peak and hole	0.494 and -0.195 $e.A^{-3}$

5. PHOTOPHYSICAL DATA:

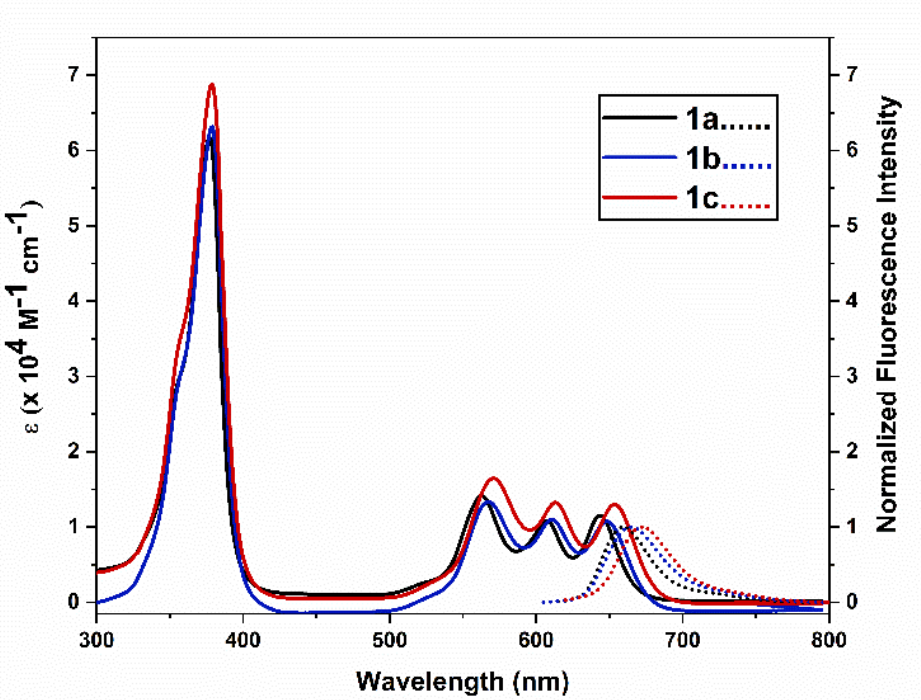

Figure S58. The overlay diagram of UV-vis (bold line) and Fluorescence spectra (dash dot line) of **1a** and **1b** in chloroform at rt.

Table S3: Fluorescence quantum yield and emission maxima (λ_{max}) at λ_{exc} (557 nm) in chloroform (25 °C).

Samples	Fluorescence λ_{max} (nm)	Φ_f
1a	660	0.11
1b	665	0.12
1c	672	0.062

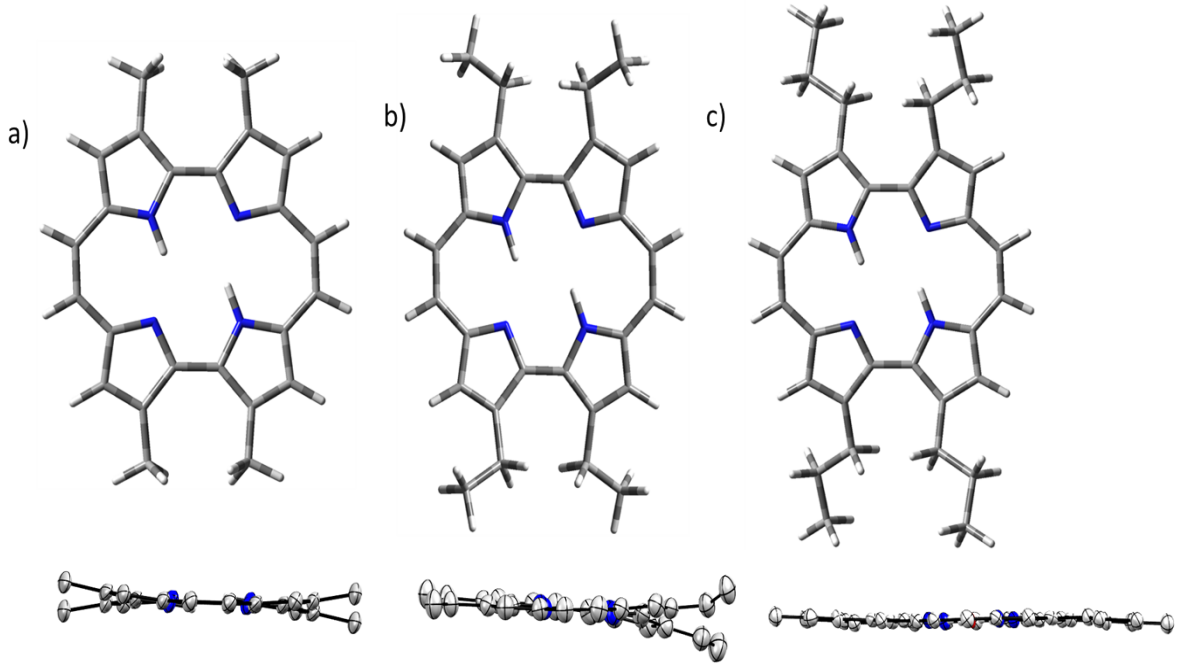

Figure 59: DFT-Optimized structures of **(a) 1a (b) 1b** and **(c) 1c** calculated at B3LYP/6-31G+(D, P).

Table S4 : Structure and energy parameters of tetraalkylporphycenes and its interaction with TFA.

Compound	Ground state energy, E (eV)	Θ (N-C-C-NH) (deg)	r, N···H-N (Å)	r, O-H (TFA) (Å)	r, N···H-O (Å)
1a	-1146.87	5.778, 5.779	1.890	-	-
1b	-1304.13	12.542, 12.544	1.876	-	-
1c	-1461.40	12.634, 12.640	1.893	-	-
1a.2TFA	-2200.54	15.747, 16.151	1.921	1.007	1.792
1b.2TFA	-2357.81	19.211, 19.214	1.936	1.011	1.764
1c.2TFA	-2515.08	19.376, 20.095	1.932, 1.926	1.009/1.016	1.773/1.720

Table S5: Coordinates of optimized geometry of **1a**:

Label	Symbol	X	Y	Z
1	N	-1.37263	1.349913	0.07403
2	N	-1.44312	-1.39425	-0.06388
3	H	-0.48703	-1.00801	-0.09892
4	C	-2.58935	0.73168	0.009068
5	C	-1.61183	2.689301	0.065057
6	C	-2.62744	-0.69203	0.000434
7	C	-3.07646	-2.91762	0.017382
8	H	-3.5763	-3.87678	0.058681

Label	Symbol	X	Y	Z
26	N	1.372626	-1.34991	-0.07403
27	N	1.443123	1.39425	0.063868
28	H	0.487029	1.008011	0.098893
29	C	2.589345	-0.73168	-0.00907
30	C	1.611833	-2.6893	-0.06506
31	C	2.627442	0.69203	-0.00043
32	C	3.076457	2.917619	-0.01738
33	H	3.576298	3.876782	-0.05868
34	C	1.666271	2.74221	0.06043

9	C	-1.66627	-2.74222	-0.06044
10	C	0.711951	3.772446	0.102445
11	H	1.157338	4.764215	0.116222
12	C	-3.67062	1.73087	-0.06472
13	C	-0.67639	3.744956	0.103986
14	H	-1.14307	4.72757	0.11739
15	C	-3.03267	2.937404	-0.0168
16	H	-3.49892	3.914555	-0.06178
17	C	-3.68691	-1.68118	0.065878
18	C	-5.17172	-1.52732	0.226169
19	H	-5.43144	-0.92687	1.102274
20	H	-5.61813	-2.51633	0.362411
21	H	-5.64886	-1.07064	-0.6445
22	C	-5.15698	1.597601	-0.23078
23	H	-5.42396	1.004225	-1.11049
24	H	-5.59051	2.59283	-0.36528
25	H	-5.64602	1.144683	0.635966
			6	1
35	C	-0.71195	-3.77245	-0.10245
36	H	-1.15734	-4.76422	-0.11623
37	C	3.670616	-1.73087	0.064722
38	C	0.676385	-3.74496	-0.10399
39	H	1.14307	-4.72757	-0.1174
40	C	3.032673	-2.9374	0.016796
41	H	3.498916	-3.91456	0.061781
42	C	3.686913	1.681175	-0.06587
43	C	5.171724	1.527321	-0.22616
44	H	5.431443	0.926868	-1.10226
45	H	5.618132	2.516325	-0.3624
46	H	5.648863	1.07064	0.644505
47	C	5.156975	-1.5976	0.230791
48	H	5.423955	-1.00423	1.1105
49	H	5.59051	-2.59283	0.365285
50	H	5.64602	-1.14468	-0.63595

Table S6: Coordinates of optimized geometry of **1b**

Label	Symbol	X	Y	Z
1	N	1.368131	1.349538	-0.02808
2	N	1.433827	-1.39654	-0.06342
3	N	-1.36813	-1.34955	-0.02814
4	N	-1.43384	1.396533	-0.06335
5	C	-3.64397	-1.70302	0.35496
6	C	1.603551	2.681432	0.113609
7	C	2.577553	0.723914	0.069798
8	C	3.643969	1.702986	0.355024
9	C	2.617019	-0.69261	-0.08494
10	C	-5.09408	-1.48856	0.70866
11	H	-5.66638	-1.199	-0.17969
12	H	-5.17267	-0.6456	1.405155
32	C	5.139157	-1.43251	-0.57592
33	H	5.646973	-1.15562	0.354173
34	H	5.252594	-0.57583	-1.24887
35	C	-0.69996	3.767561	-0.17504
36	H	-1.1387	4.75791	-0.2698
37	C	3.057045	-2.89968	-0.38972
38	H	3.536624	-3.85174	-0.56748
39	C	-2.61702	0.692597	-0.08498
40	C	-5.87119	2.636014	-1.18421
41	H	-5.86431	3.498775	-0.50984
42	H	-6.9177	2.378988	-1.37664
43	H	-5.41934	2.943494	-2.13311
44	C	-3.67069	1.66358	-0.32122

13	C	1.652637	-2.73504	-0.22028
14	C	-3.00869	-2.91412	0.360685
15	H	-3.44942	-3.88361	0.551768
16	C	-1.60356	-2.68147	0.113408
17	C	-2.57755	-0.72395	0.069667
18	C	0.69999	-3.76759	-0.17495
19	H	1.138751	-4.75794	-0.26956
20	C	-1.65263	2.735017	-0.22036
21	C	3.670695	-1.66361	-0.32114
22	C	-0.67686	-3.74105	0.009571
23	H	-1.13989	-4.72335	0.075676
24	C	3.008669	2.914085	0.360886
25	H	3.449449	3.88355	0.551946
26	C	5.871114	-2.636	-1.1843
27	H	5.864692	-3.49855	-0.50965
28	H	6.917487	-2.37885	-1.37729
29	H	5.418865	-2.94384	-2.13289
30	C	0.67686	3.741025	0.009664
31	H	1.13988	4.723329	0.075729
45	C	-3.05701	2.899651	-0.38995
46	H	-3.53656	3.851701	-0.56784
47	C	5.775971	2.710215	1.339363
48	H	5.800511	3.559816	0.648953
49	H	6.811317	2.469986	1.602604
50	H	5.260216	3.029966	2.250814
51	C	-5.13919	1.432563	-0.57582
52	H	-5.64691	1.155758	0.354353
53	H	-5.25279	0.575841	-1.24868
54	C	5.094083	1.488572	0.708754
55	H	5.666398	1.198746	-0.17949
56	H	5.172611	0.645756	1.405456
57	C	-5.7759	-2.71007	1.339661
58	H	-5.80019	-3.55998	0.649634
59	H	-6.81134	-2.4699	1.602607
60	H	-5.26021	-3.0293	2.251324
61	H	-0.47798	1.013528	0.003106
62	H	0.477972	-1.01354	0.003107

Table S7: Coordinates of optimized geometry of **1c**.

Label	Symbol	X	Y	Z
1	N	1.433711	1.363948	0.334173
2	N	1.379371	-1.30366	-0.35258
3	C	5.120125	-1.57525	0.266616
4	H	5.682487	-1.09061	-0.54067
5	H	5.204187	-0.90769	1.132977
6	C	3.05009	2.909557	0.383803
7	H	3.52188	3.87995	0.4417
38	N	-1.37932	1.303651	0.352544
39	C	-5.12014	1.575272	-0.26633
40	H	-5.68239	1.090483	0.540949
41	H	-5.20429	0.907843	-1.13278
42	C	-3.05004	-2.90954	-0.38397
43	H	-3.52183	-3.87994	-0.44194
44	C	-3.66468	-1.70494	-0.10137
45	C	-5.12198	-1.56194	0.260036

			8	
8	C	3.664716	1.704942	0.101218
9	C	5.121986	1.561918	-0.26028
10	H	5.67424	1.085301	0.558095
11	H	5.210828	0.885244	-1.1178
12	C	1.648768	2.699563	0.521407
13	C	5.829454	2.881269	-0.6077
14	H	5.284385	3.387842	-1.41414
15	H	5.80404	3.555527	0.257675
16	C	7.287196	2.663033	-1.02894
17	H	7.353478	2.023717	-1.91717
18	H	7.86554	2.183189	-0.23049
19	H	7.776183	3.613407	-1.26736
20	C	7.28132	-2.68936	1.034332
21	H	7.864923	-2.20593	0.241736
22	H	7.766171	-3.6432	1.267834
23	H	7.346898	-2.05679	1.927627
24	C	-0.69111	-3.70033	-0.76011
25	H	-1.13262	-4.679	-0.93196
26	C	2.616958	0.699395	0.097097
27	C	3.039584	-2.89681	-0.38791
28	H	3.488264	-3.87988	-0.43924
29	C	2.586804	-0.70823	-0.1238
30	C	3.666647	-1.71413	-0.10913
31	C	0.697214	-3.66646	-0.76045
32	H	1.168671	-4.63216	-0.93013
33	C	5.824245	-2.8985	0.605947
34	H	5.273986	-3.40988	1.405666
35	H	5.79778	-3.56482	-0.26544
46	H	-5.67415	-1.08516	-0.55831
47	H	-5.21088	-0.88542	1.117658
48	C	-1.64871	-2.69954	-0.5215
49	C	-5.82953	-2.88133	0.60716
50	H	-5.28456	-3.38806	1.413561
51	H	-5.80406	-3.55544	-0.25833
52	C	-7.2873	-2.6631	1.028304
53	H	-7.35364	-2.02393	1.916623
54	H	-7.86556	-2.18312	0.229877
55	H	-7.77634	-3.6135	1.266529
56	C	-7.28147	2.689429	-1.03358
57	H	-7.86496	2.205881	-0.24097
58	H	-7.76637	3.643289	-1.2669
59	H	-7.34715	2.056973	-1.92695
60	C	0.69117	3.700342	0.760037
61	H	1.132674	4.679022	0.931853
62	C	-2.61692	-0.69939	-0.09714
63	C	-3.03954	2.896789	0.38804
64	H	-3.48822	3.879855	0.439457
65	C	-2.58677	0.708229	0.123805
66	C	-3.66662	1.714125	0.109257
67	C	-0.69715	3.666451	0.760452
68	H	-1.16862	4.632138	0.930163
69	C	-5.82434	2.898552	-0.60536
70	H	-5.27421	3.410071	-1.40508
71	H	-5.79778	3.564739	0.266122
72	C	-1.62575	2.629839	0.526083
73	H	-0.48306	-0.96357	-0.35323
74	H	0.483111	0.963581	0.353242

		3		
36	C	1.625803	-2.62986	-0.52605
37	N	-1.43366	-1.36394	-0.33418

Table S8: Coordinates of optimized geometry of **1a-2TFA**:

Label	Symbol	X	Y	Z
1	N	0.623032	-1.30977	-1.3166
2	N	-0.0955	-1.45975	1.358694
3	H	-0.23796	-0.52491	0.963907
4	C	0.394743	-2.5395	-0.74152
5	C	0.678459	-1.51838	-2.67056
6	C	0.192323	-2.60997	0.662687
7	C	-0.12163	-3.12688	2.846595
8	H	-0.17686	-3.64516	3.795042
9	C	-0.33463	-1.72731	2.675716
10	C	0.706452	0.831743	-3.7007
11	H	0.857535	1.302048	-4.66897
12	C	0.311953	-3.57522	-1.76683
13	C	0.81927	-0.55359	-3.69213
14	H	0.991219	-0.99356	-4.67192
15	C	0.512977	-2.9184	-2.95373
16	H	0.481114	-3.35628	-3.94406
17	C	0.212089	-3.68702	1.630454
18	C	0.621372	-5.12118	1.460206
19	H	-0.16182	-5.73111	1.001721
20	H	0.839188	-5.55268	2.440941
21	H	1.522976	-5.21661	0.848707
22	C	-0.0476	-5.02835	-1.66004
23	H	0.75918	-5.63391	-1.23747
34	C	0.356533	1.748399	-2.69318
35	C	-0.70181	-0.81448	3.678771
36	H	-0.85638	-1.28517	4.646274
37	C	-0.3141	3.591854	1.750215
38	C	-0.83283	0.569846	3.666663
39	H	-1.01491	1.009096	4.644999
40	C	-0.5308	2.934741	2.933134
41	H	-0.50535	3.369889	3.924838
42	C	-0.19359	3.706834	-1.6462
43	C	-0.60999	5.138982	-1.47605
44	H	0.168931	5.752238	-1.01465
45	H	-0.82776	5.570467	-2.45681
46	H	-1.51346	5.229088	-0.86651
47	C	0.056287	5.042356	1.647114
48	H	-0.74324	5.654336	1.21998
49	H	0.269808	5.434004	2.645392
50	H	0.952843	5.187544	1.036915
51	C	3.612308	0.299024	0.043285
52	O	2.933555	1.267293	0.292407
53	O	3.239724	-0.83377	-0.52313
54	H	2.259626	-0.84179	-0.75596
55	C	-3.68	-0.35582	0.166756
56	O	-3.17242	-1.41207	0.46163

24	H	-0.26408	-5.42238	-2.65675
25	H	-0.93897	-5.18039	-1.04401
26	N	-0.62792	1.327956	1.292158
27	N	0.128551	1.48242	-1.37337
28	H	0.26812	0.548059	-0.97681
29	C	-0.38832	2.556617	0.722891
30	C	-0.69503	1.534378	2.645679
31	C	-0.17027	2.630826	-0.67865
32	C	0.140911	3.147408	-2.86339
33	H	0.189205	3.665089	-3.81257

				6
57	O	-3.16565	0.855176	0.27388
58	H	-2.23162	0.846764	0.65191
59	C	5.127839	0.251459	0.381787
60	C	-5.11598	-0.27318	-0.42092
61	F	-5.92434	0.450541	0.385544
62	F	-5.10556	0.317269	-1.63667
63	F	-5.64986	-1.4948	-0.5567
64	F	5.394514	-0.75228	1.247539
65	F	5.864599	0.04588	-0.73237
66	F	5.530897	1.400636	0.940754

Table S9: Coordinates of optimized geometry of **1b-2TFA**:

Label	Symbol	X	Y	Z
1	N	1.394777	-0.331593	-1.354619
2	N	1.441073	0.088627	1.392788
3	N	-1.394747	0.331568	1.354774
4	N	-1.441084	-0.088606	-1.392616
5	C	-3.595394	-0.356833	1.71027
6	C	1.609258	-0.156561	-2.69641
7	C	2.579809	-0.023906	-0.729456
8	C	3.595417	0.356837	-1.710057
9	C	2.619565	-0.013774	0.691423
10	C	-4.973575	-0.921954	1.481897
11	H	-6.882614	-1.272742	-2.399901
12	H	-5.868668	0.351765	-3.51094
13	C	-3.68315	0.092969	-1.671363
14	C	-3.08204	-0.028681	-2.909842
15	H	-3.569015	0.019088	-3.873564
16	C	5.562823	1.656596	-2.692761
17	H	5.698273	0.984802	-3.546948
18	H	6.544952	2.069276	-2.44105
19	H	4.919341	2.48398	-3.00892

		4.934532	1.612456	9
12	H	-5.665349	-0.12234	1.192444
13	C	1.672274	0.155071	2.736484
14	C	-2.97333	-0.238248	2.927195
15	H	-3.386692	-0.480992	3.896828
16	C	-1.609278	0.156762	2.696593
17	C	-2.5798	0.023789	0.729647
18	C	0.719902	0.286089	3.763004
19	H	1.168054	0.350904	4.751274
20	C	-1.672293	-0.154996	-2.736307
21	C	3.683126	-0.093036	1.671579
22	C	-0.66999	0.261278	3.745272
23	H	-1.128222	0.247961	4.731742
24	C	2.97331	0.238493	-2.926974
25	H	3.386633	0.481385	-3.896586
26	C	5.845386	-1.031793	2.65356
27	H	5.868585	-0.351579	3.511217
28	H	6.882592	-1.272704	2.400371
29	H	5.349071	-1.956269	2.966036
30	C	0.669976	-0.260998	-3.745107
31	H	1.128216	-0.247537	-4.731568
32	C	5.142157	-	1.44392
				8
51	C	-5.142174	0.400116	-1.443656
52	H	-5.231163	1.076986	-0.587765
53	H	-5.681152	-0.513271	-1.167009
54	C	4.973656	0.921789	-1.481662
55	H	5.665204	0.122163	-1.191749
56	H	4.93456	1.612637	-0.63178
57	C	-5.562372	-1.657379	2.692835
58	H	-4.918583	-2.484664	3.008617
59	H	-6.544403	-2.070243	2.441045
60	H	-5.697941	-0.985938	3.547273
61	H	-0.504227	-0.205201	-0.996412
62	H	0.504189	0.205235	0.996621
63	C	-0.070586	3.564781	0.377534
64	O	0.943977	3.001134	0.039041
65	O	-1.15831	3.038663	0.906192
66	H	-1.088135	2.036238	1.017683
67	C	0.070468	-3.564739	-0.377907
68	O	-0.944198	-3.001186	-0.039566
69	O	1.15825	-3.038504	-0.906335
70	H	1.088049	-2.036021	-1.017696

			0.400216	6
33	H	5.681121	0.513142	1.167159
34	H	5.23113	-1.077225	0.588146
35	C	-0.719915	-0.285869	-3.762844
36	H	-1.168065	-0.350608	-4.75112
37	C	3.082016	0.028727	2.910039
38	H	3.568994	-0.018955	3.873764
39	C	-2.619579	0.013657	-0.691226

71	C	-0.243398	5.100828	0.220024
72	C	0.243361	-5.100784	-0.220474
73	F	0.862617	5.659042	-0.291619
74	F	-1.275895	5.383975	-0.606312
75	F	-0.493946	5.684934	1.41265
76	F	-0.862742	-5.659134	0.290829
77	F	0.49428	-5.684769	-1.413071
78	F	1.275666	-5.383914	0.606129

Table S10: Coordinates of optimized geometry of **1c-2TFA**:

Label	Symbol	X	Y	Z
1	N	1.319269	0.032065	-1.39277
2	N	1.290457	-0.04477	1.387626
3	C	4.781217	1.431231	1.320205
4	H	5.539676	0.647665	1.197953
5	H	4.714853	1.942138	0.352489
6	C	2.970185	-0.16143	-2.88939
7	H	3.462887	-0.32217	-3.83791
8	C	3.569614	-0.08994	-1.64612
9	C	5.032201	-0.32368	-1.36584
10	H	5.559733	0.634075	-1.27218
11	H	5.127603	-0.8244	-0.39678
12	C	1.55437	-0.07741	-2.73275
13	C	5.751864	-1.17224	-2.42783
14	H	5.214908	-2.11988	-2.55686
15	H	5.722183	-0.6591	-3.39736
16	C	7.21131	-1.45191	-2.05253
17	H	7.277816	-2.00001	-1.10566

Label	Symbol	X	Y	Z
46	H	-5.76775	-0.73279	1.315709
47	H	-5.40155	0.751525	0.460025
48	C	-1.77907	0.078294	2.75981
49	C	-6.01228	1.043411	2.504775
50	H	-5.51022	2.008241	2.648068
51	H	-5.95186	0.51422	3.463899
52	C	-7.48588	1.273305	2.151322
53	H	-7.5865	1.835303	1.215489
54	H	-8.01985	0.323572	2.028589
55	H	-7.99571	1.841765	2.935957
56	C	-6.84049	-3.06933	-1.98686
57	H	-7.62751	-2.32032	-1.83867
58	H	-7.18438	-3.76274	-2.76131
59	H	-6.741	-3.63677	-1.05407
60	C	0.598628	-0.13744	-3.76288

18	H	7.780828	-0.52151	-1.94074
19	H	7.707386	-2.05454	-2.82041
20	C	6.615363	3.080628	1.963377
21	H	7.401903	2.328627	1.828198
22	H	6.959982	3.787802	2.725055
23	H	6.515211	3.631133	1.020606
24	C	-0.82165	0.149907	3.787446
25	H	-1.26579	0.180905	4.779122
26	C	2.497953	0.078865	-0.68685
27	C	2.832024	0.808941	2.864857
28	H	3.229147	1.193973	3.794396
29	C	2.454274	0.252148	0.721268
30	C	3.444394	0.814116	1.63736
31	C	0.563535	0.268884	3.756906
32	H	1.018455	0.436383	4.730633
33	C	5.287321	2.432724	2.370826
34	H	4.52858	3.209734	2.525647
35	H	5.416114	1.923965	3.334475
36	C	1.494751	0.303816	2.696931
37	N	-1.549	-0.01376	1.416122
38	N	-1.52221	0.066636	-1.36305
39	C	-5.00759	-1.43002	-1.31401
40	H	-5.77029	-0.6531	-1.17655
41	H	-4.94088	-1.95879	-0.35576
42	C	-3.19397	0.126997	2.923038
43	H	-3.68592	0.257454	3.876579
44	C	-3.79908	0.055256	1.681114
45	C	-5.27299	0.241023	1.420488
61	H	1.043416	-0.1753	-4.75398
62	C	-2.73075	-0.07433	0.713419
63	C	-3.0554	-0.78944	-2.84742
64	H	-3.4497	-1.17187	-3.77926
65	C	-2.6877	-0.23907	-0.69954
66	C	-3.67164	-0.80299	-1.62008
67	C	-0.78732	-0.24528	-3.73295
68	H	-1.24223	-0.40793	-4.70759
69	C	-5.51266	-2.41348	-2.38216
70	H	-4.75372	-3.18741	-2.55133
71	H	-5.64118	-1.88803	-3.33675
72	C	-1.72137	-0.28174	-2.67419
73	H	-0.602	-0.06965	1.030233
74	H	0.376104	0.154703	-1.01434
75	C	-0.4685	3.501926	-0.8413
76	O	0.575701	3.064688	-0.41751
77	O	-1.50964	2.828622	-1.29287
78	H	-1.36181	1.830425	-1.26122
79	C	-0.7426	5.028859	-0.92441
80	F	-0.91681	5.412922	-2.20908
81	F	-1.85831	5.359679	-0.23701
82	F	0.281086	5.728774	-0.41653
83	C	1.604417	-3.50587	0.895246
84	O	2.776638	-3.24379	0.753617
85	O	0.605486	-2.67887	1.132815
86	H	0.915902	-1.71391	1.202643
87	C	1.078828	-4.96585	0.808599
88	F	0.161704	-5.08981	-0.17769
89	F	0.491463	-5.3356	1.969072
90	F	2.076883	-5.82411	0.556737

6. FLUORESCENCE LIFETIME AND DECAY PROFILES

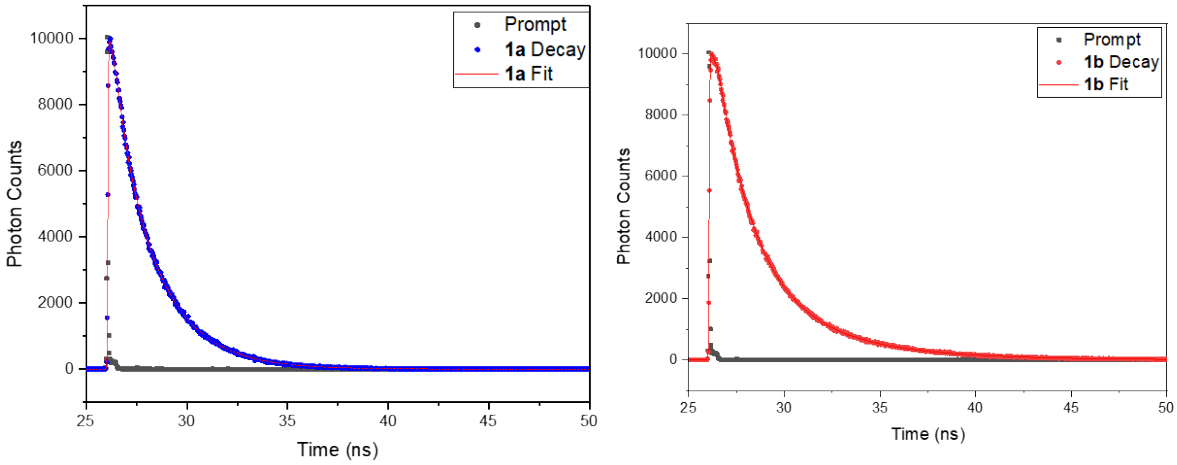

Figure S60. Fluorescence decay profiles of **1a** and **1b**.

Table S11: Average fluorescence lifetime (τ_{avg}) of porphycenes in toluene at 25 °C.

Compounds	Average Lifetime calculation (τ in "ns")			
	τ_1	τ_2	τ_{avg}	χ^2
1a	1.83	4.57	2.58	1.073627
1b	0.66	2.15	1.87	0.966259

7. SINGLET OXYGEN LUMINESCENCE SPECTRAL DATA

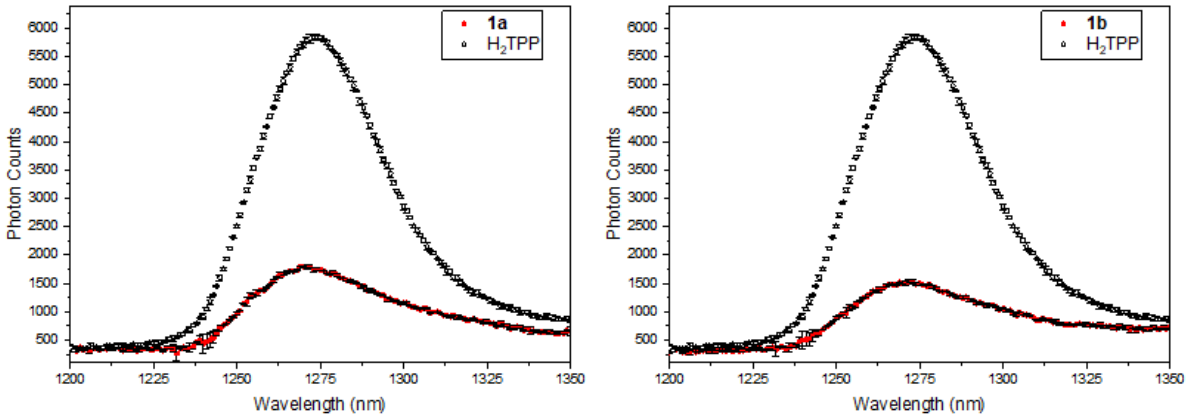

Figure S61. Singlet oxygen luminescence of optically matched H_2TPP with **1a** and **1b** in aerated toluene.

Table S12: **Singlet oxygen Quantum yield of 1a & 1b**.

Comp	Singlet oxygen Quantum yield (Φ_Δ)
1a	**0.22**
1b	**0.18**

8. CYCLIC VOLTAMMOGRAMS

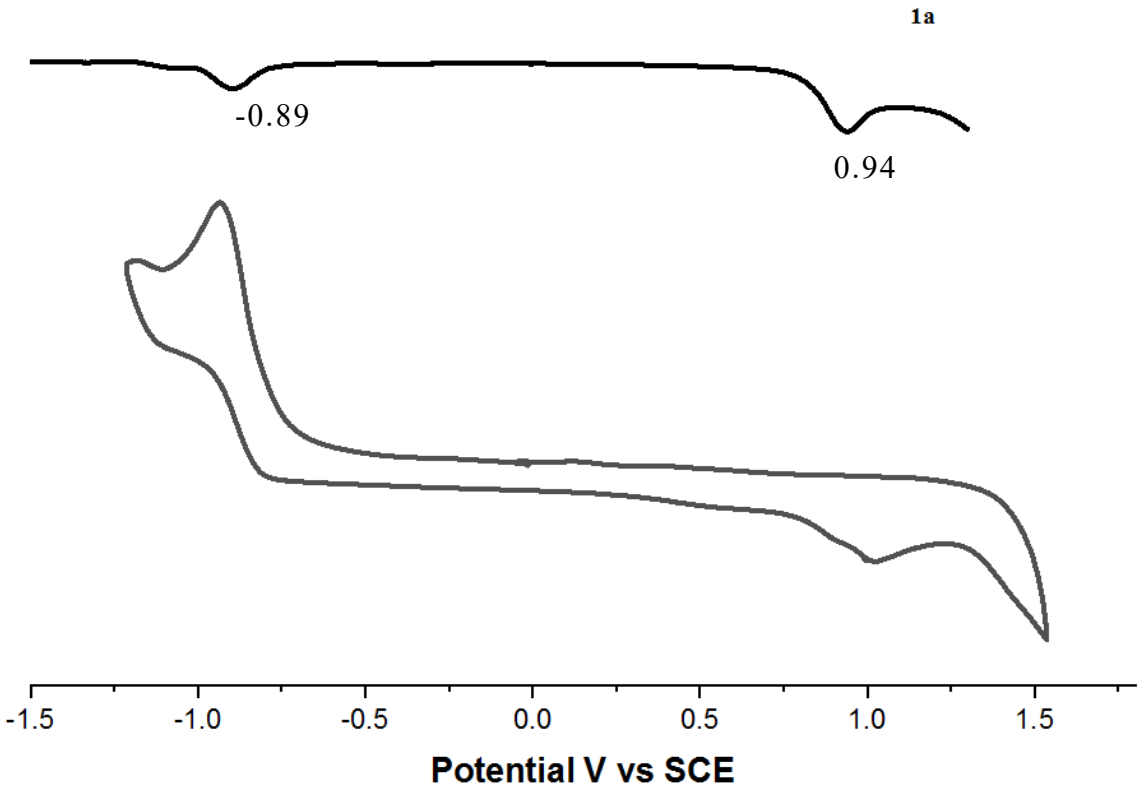

Figure S62. Cyclic voltammograms of **1a** in dichloromethane at 25 °C (scan rate 50 V/s).

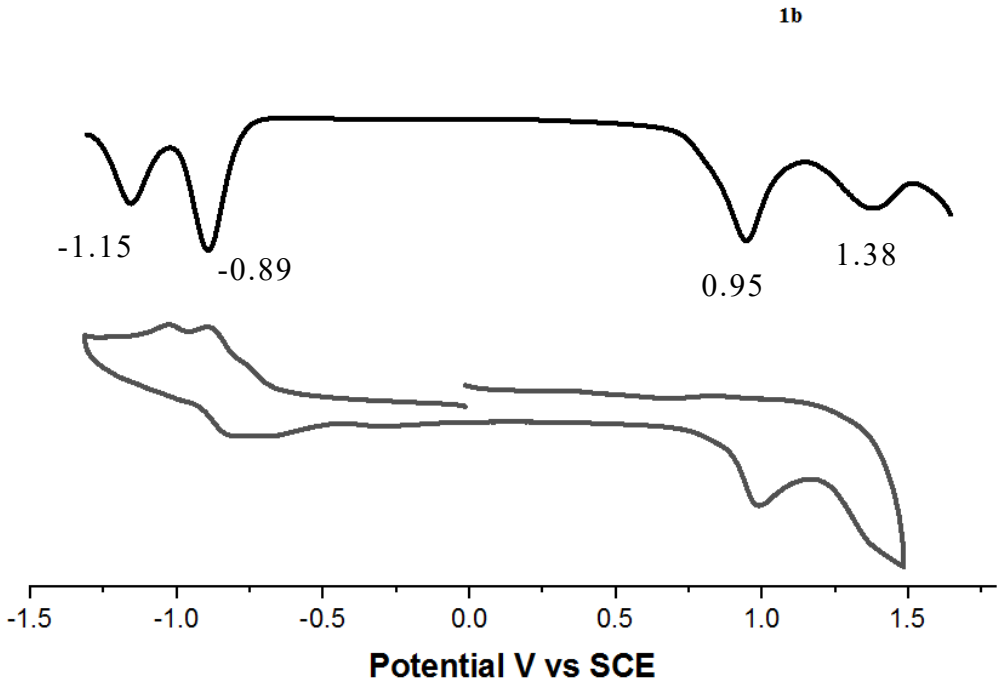

Figure S63. Combined CV (below) and DPV (above) of **1b** in dichloromethane measured at 25 °C.