

Supporting information

Exploiting Novel Process Windows for the Synthesis of meso-Substituted Porphyrins under Continuous-Flow Conditions

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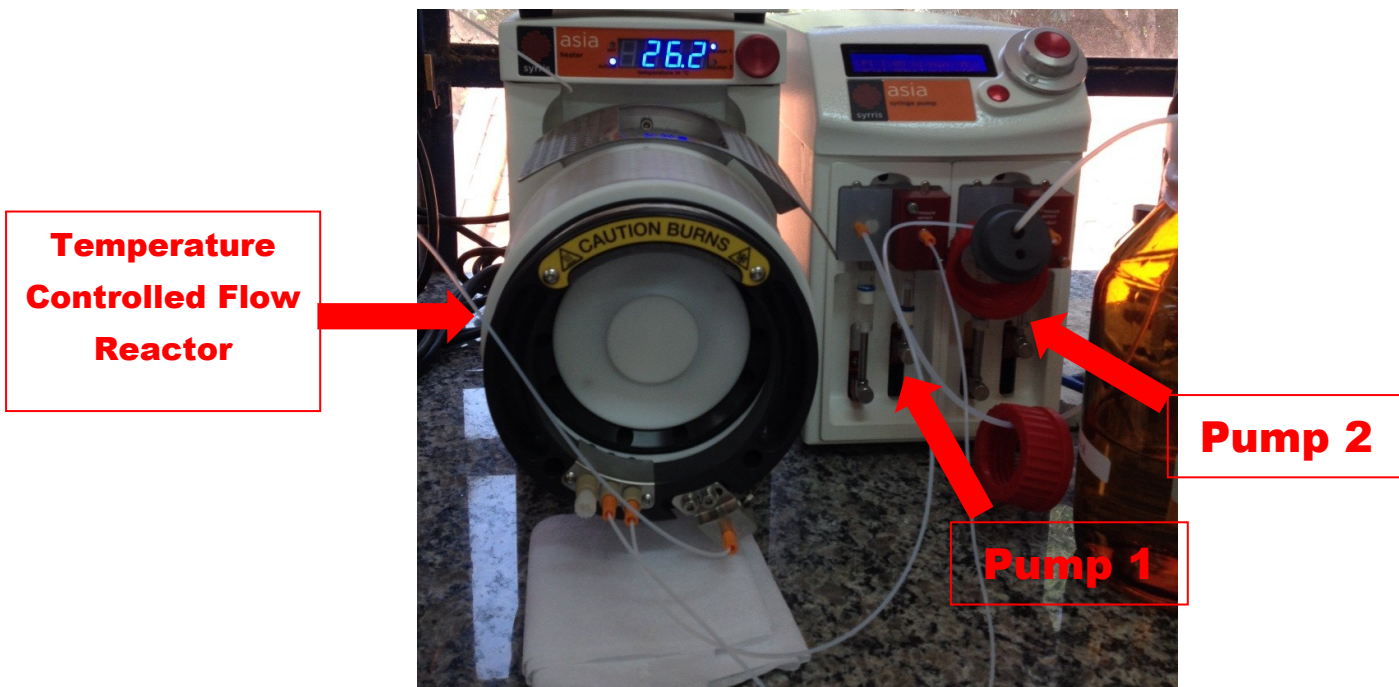


Figure S0- Flow Chemistry Equipment (Syrris) and synthesized samples.

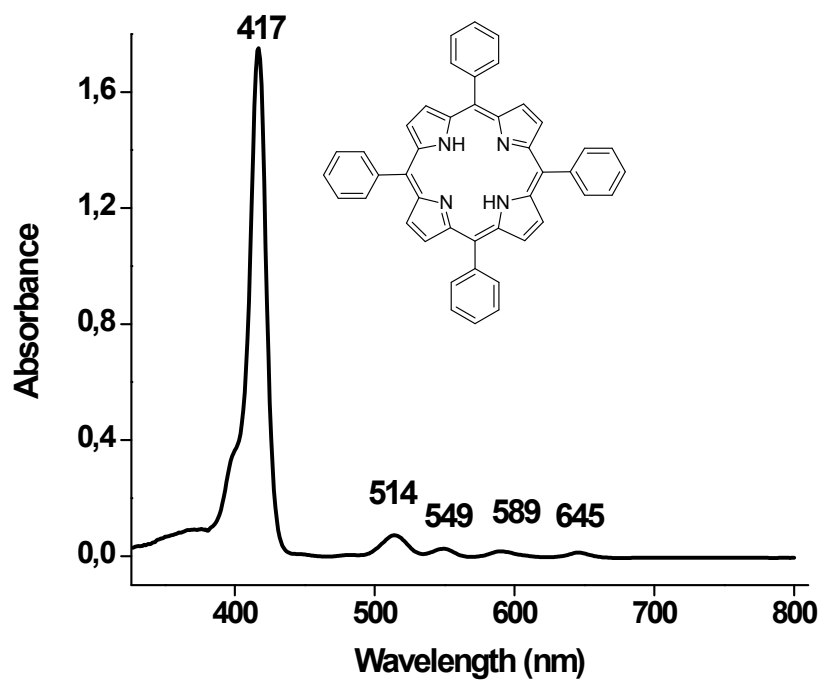


Figure S1. UV-Vis spectrum of *meso*-tetraphenylporphyrin (3) in CH_2Cl_2 .

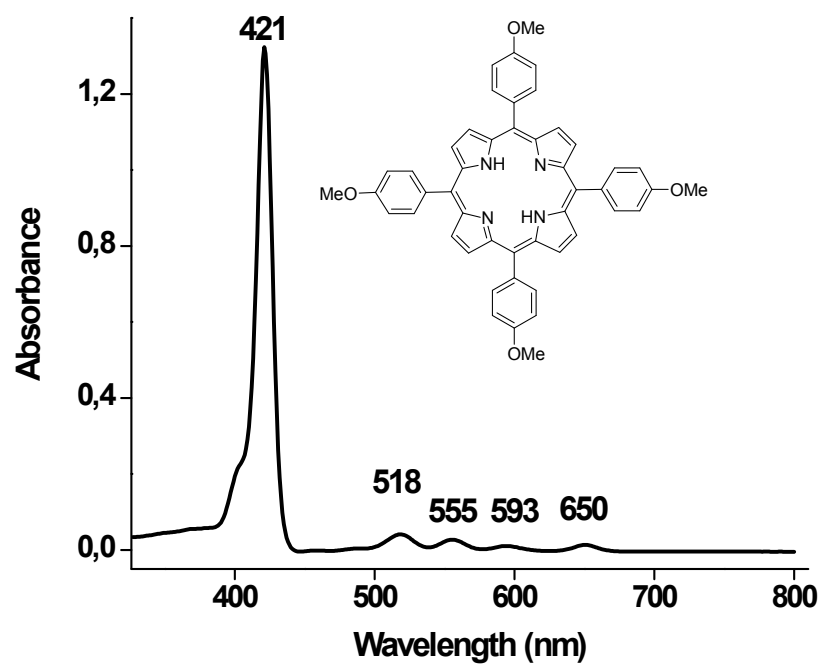


Figure S2. UV-Vis spectrum of *meso*-tetra(4-methoxyphenyl)porphyrin (5a) in CH_2Cl_2 .

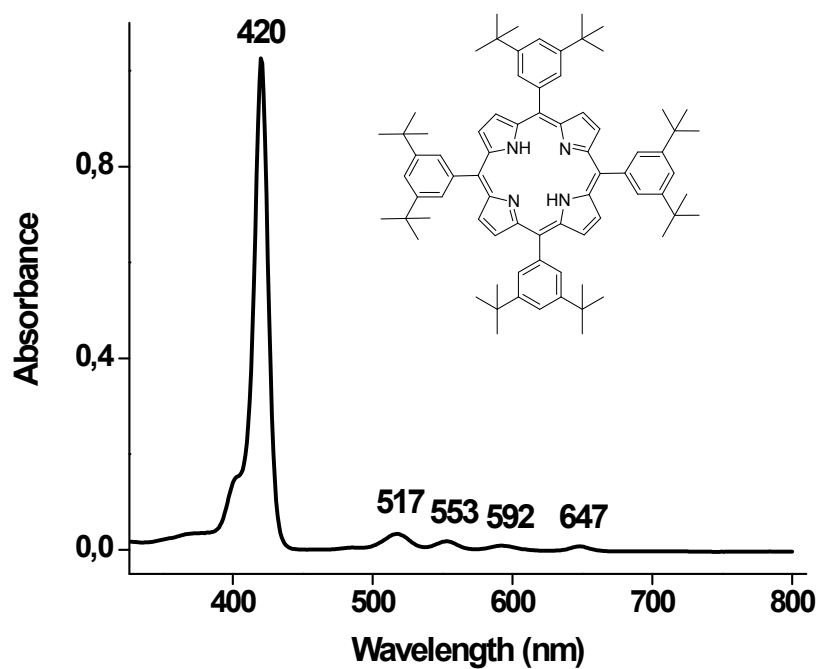


Figure S3. UV-Vis spectrum of *meso*-tetra(3,5-di-tert-butylphenyl)porphyrin (**5b**) in CH_2Cl_2 .

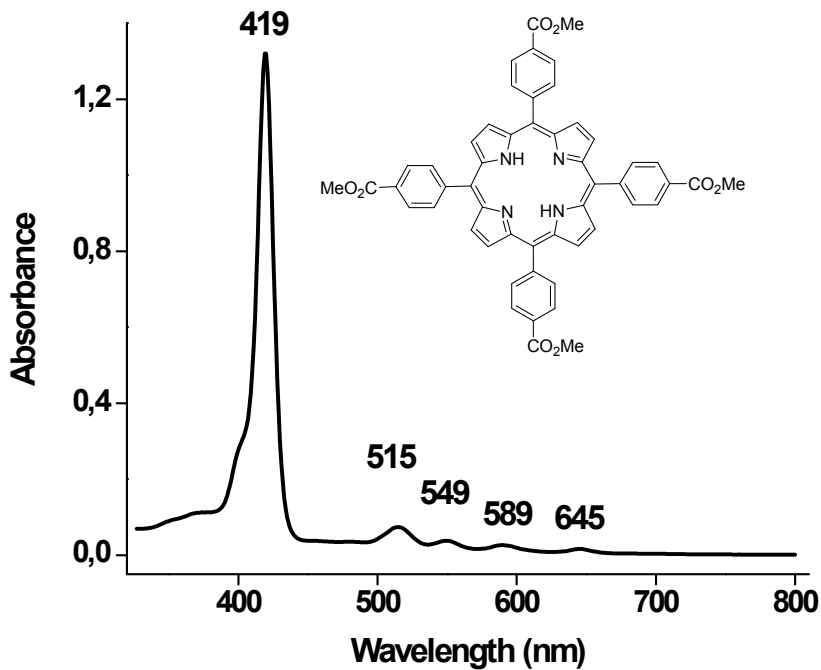


Figure S4. UV-Vis spectrum of *meso*-tetra(4-methoxycarbonylphenyl)porphyrin (**5c**) in CH_2Cl_2 .

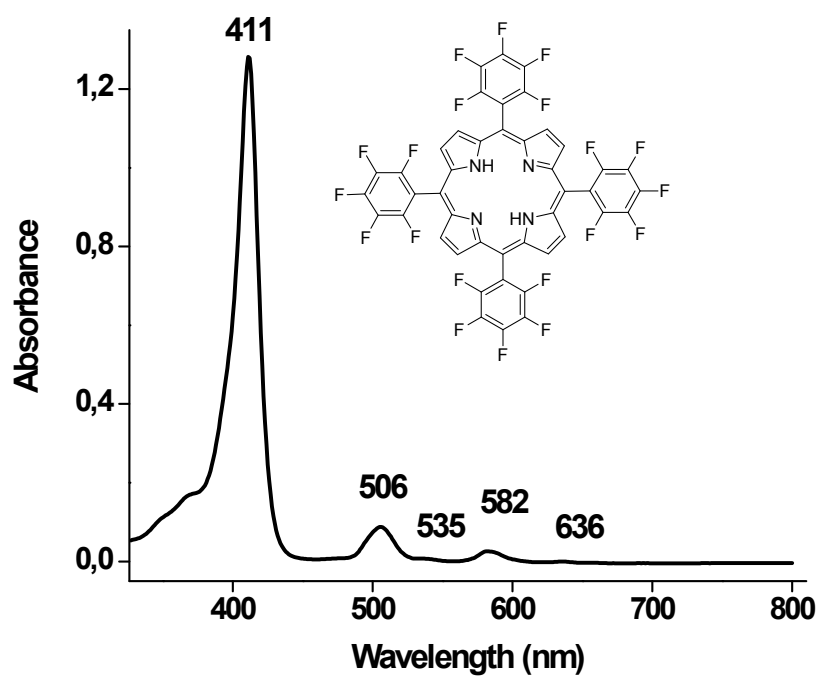


Figure S5. UV-Vis spectrum of *meso*-tetra(pentafluorophenyl)porphyrinin (**5d**) CH_2Cl_2 .

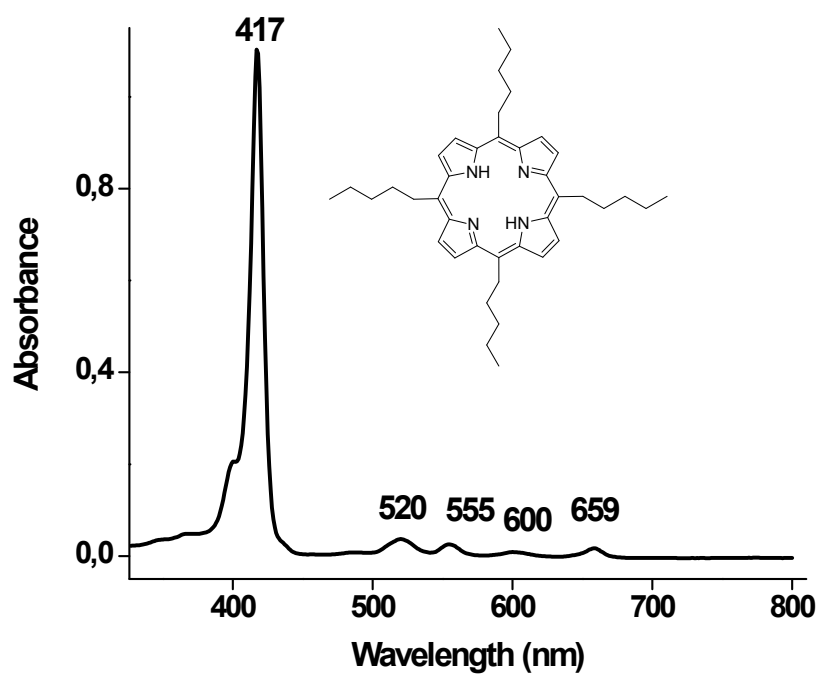


Figure S6. UV-Vis spectrum of *meso*-tetra(pentyl)porphyrinin (**5e**) in CH_2Cl_2 .

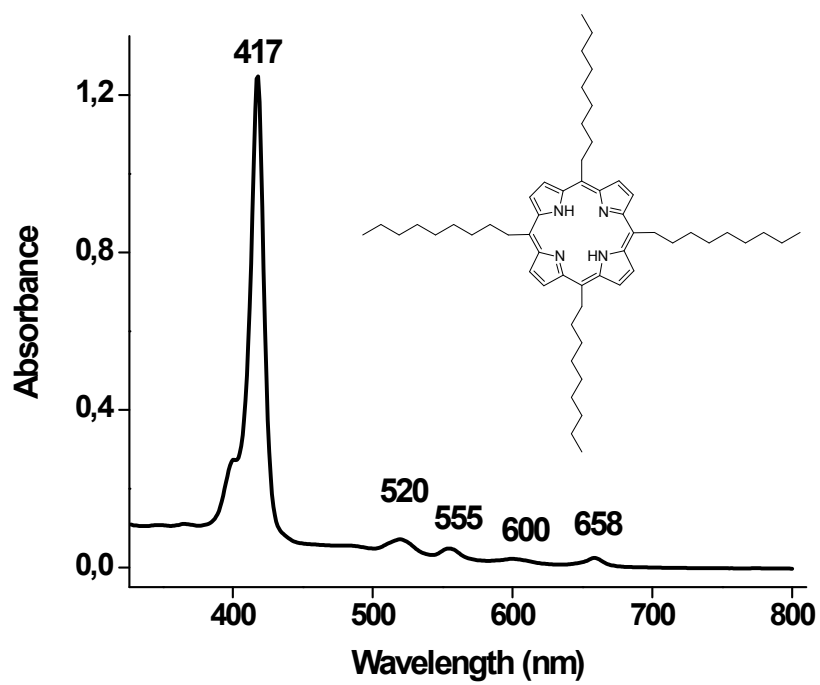


Figure S7. UV-Vis spectrum of *meso*-tetra(nonyl)porphyrinin (**5f**) CH_2Cl_2 .

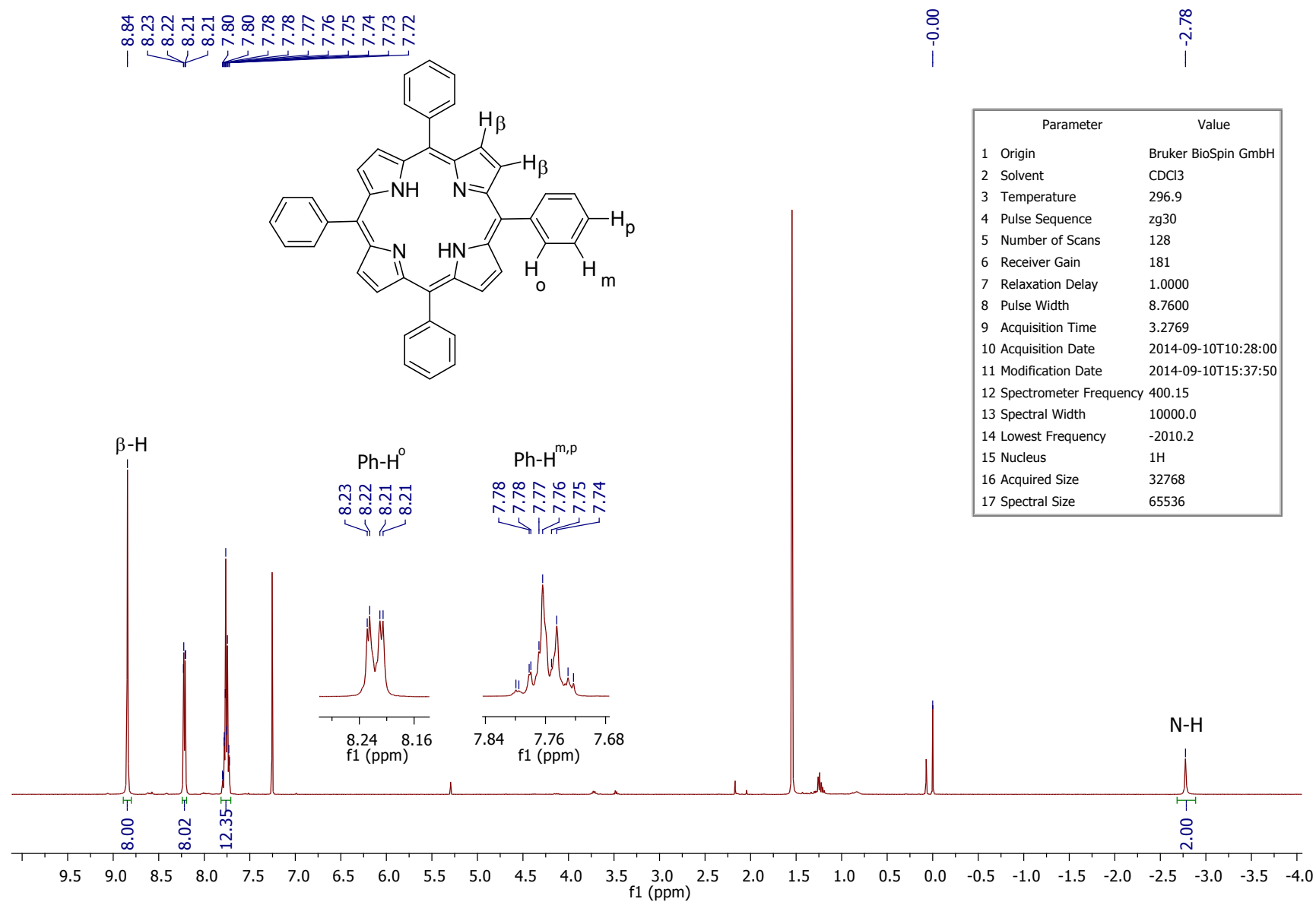


Figure S8. 1H NMR (400 MHz) of **3** in $CDCl_3$.

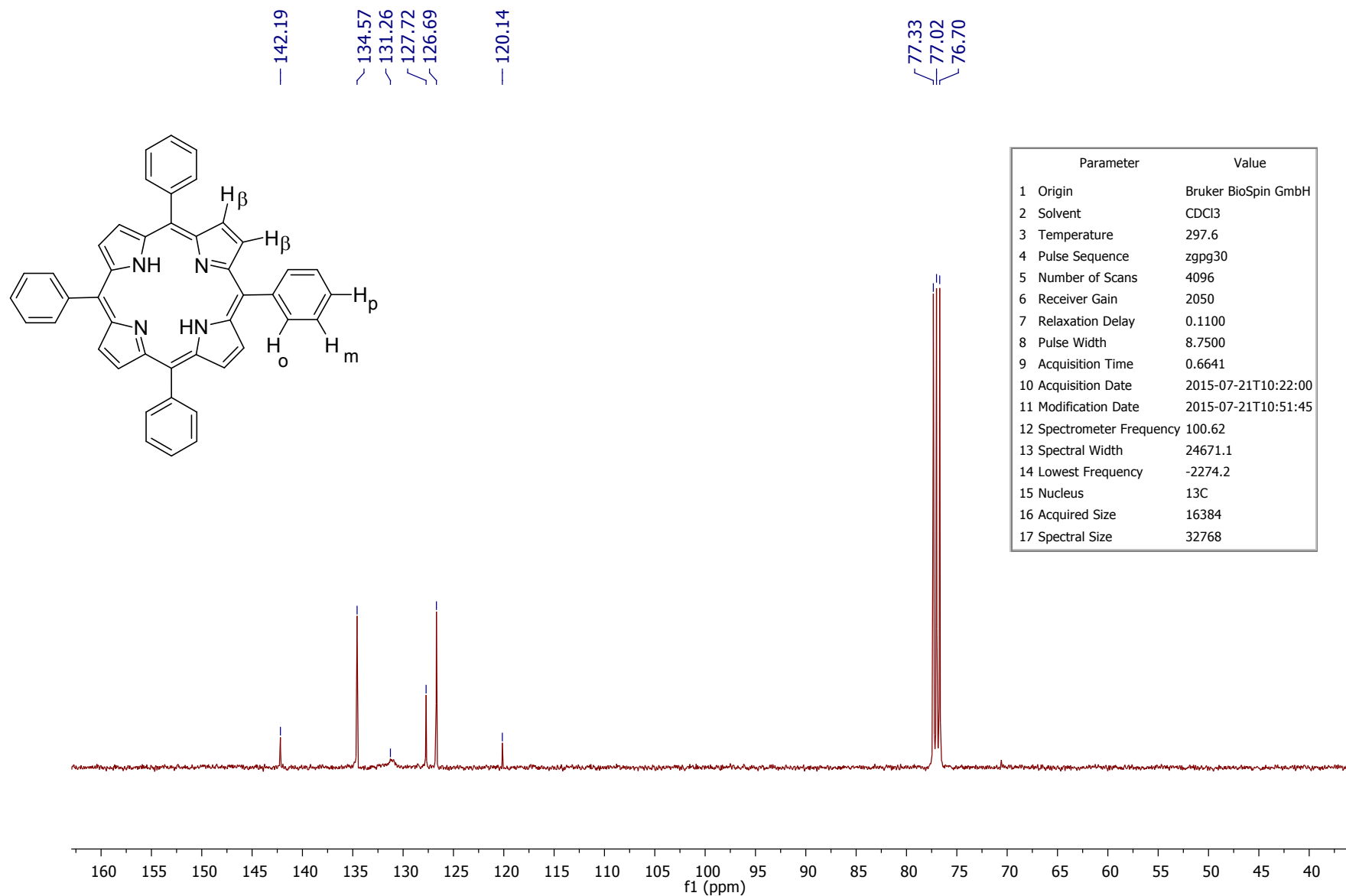


Figure S9. ¹³C NMR (100 MHz) of **3** in CDCl₃.

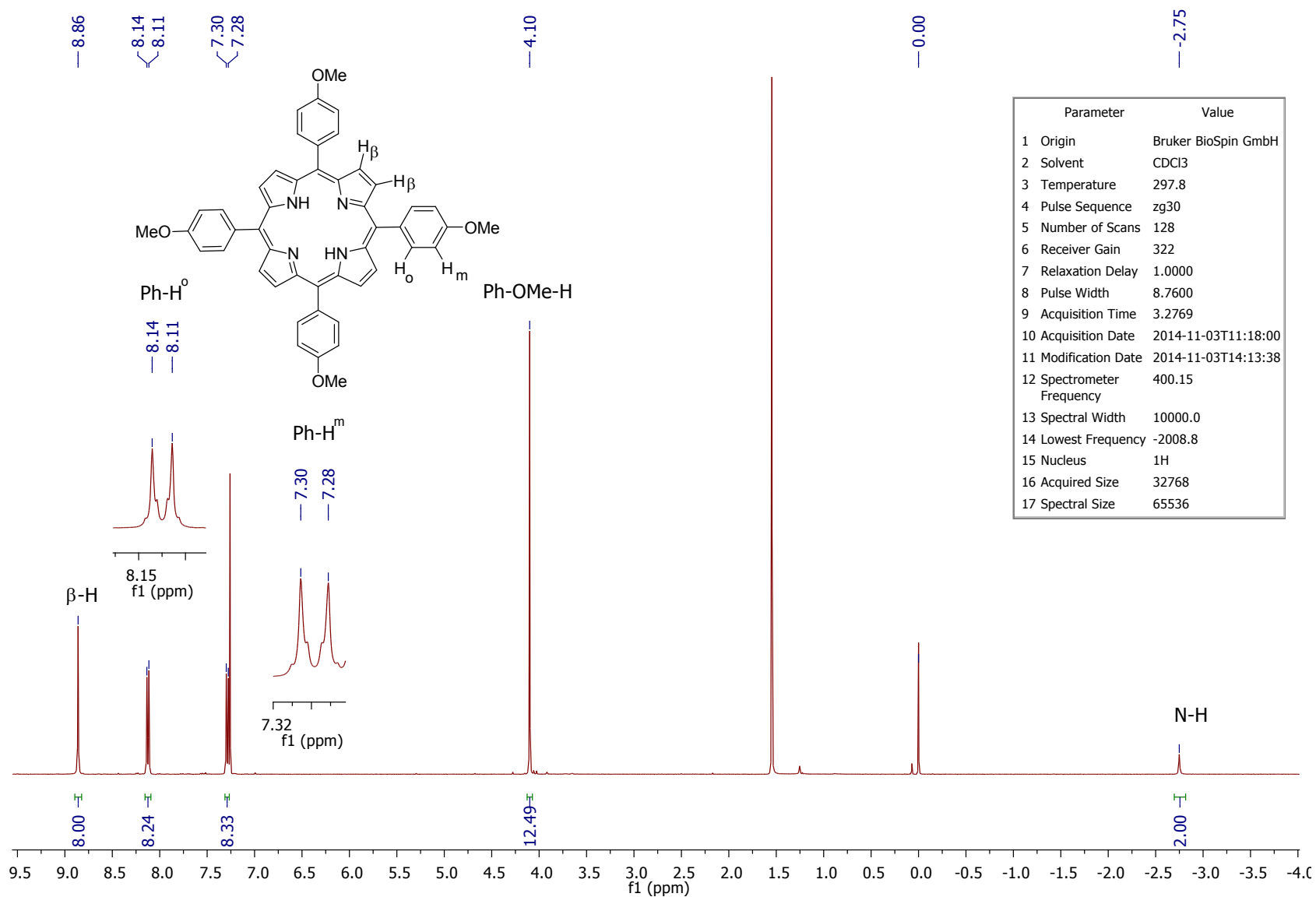


Figure S10. ¹H NMR (400 MHz) of **5a** in CDCl₃.

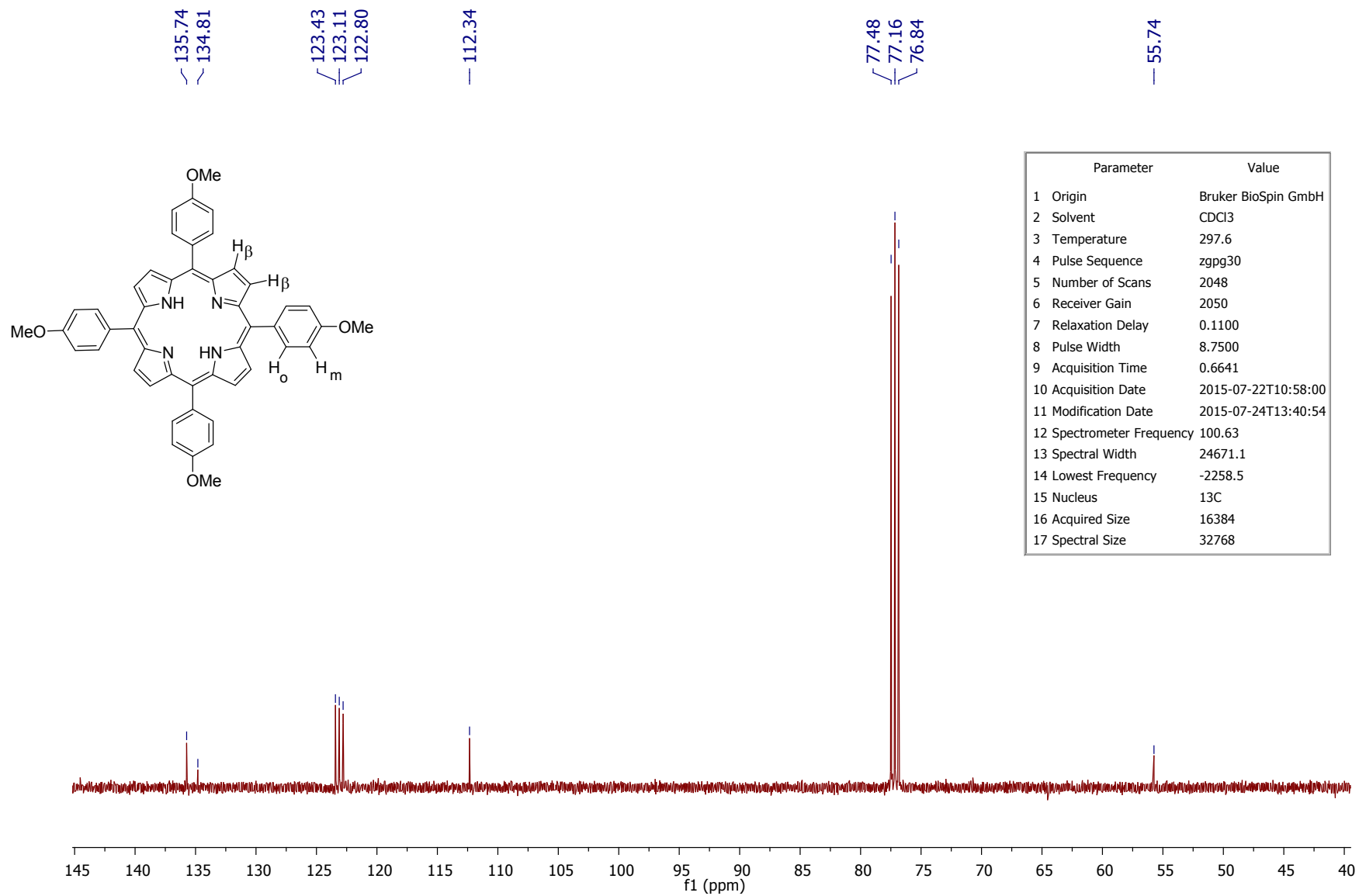


Figure S11. ^{13}C NMR (100 MHz) of **5a** in CDCl_3

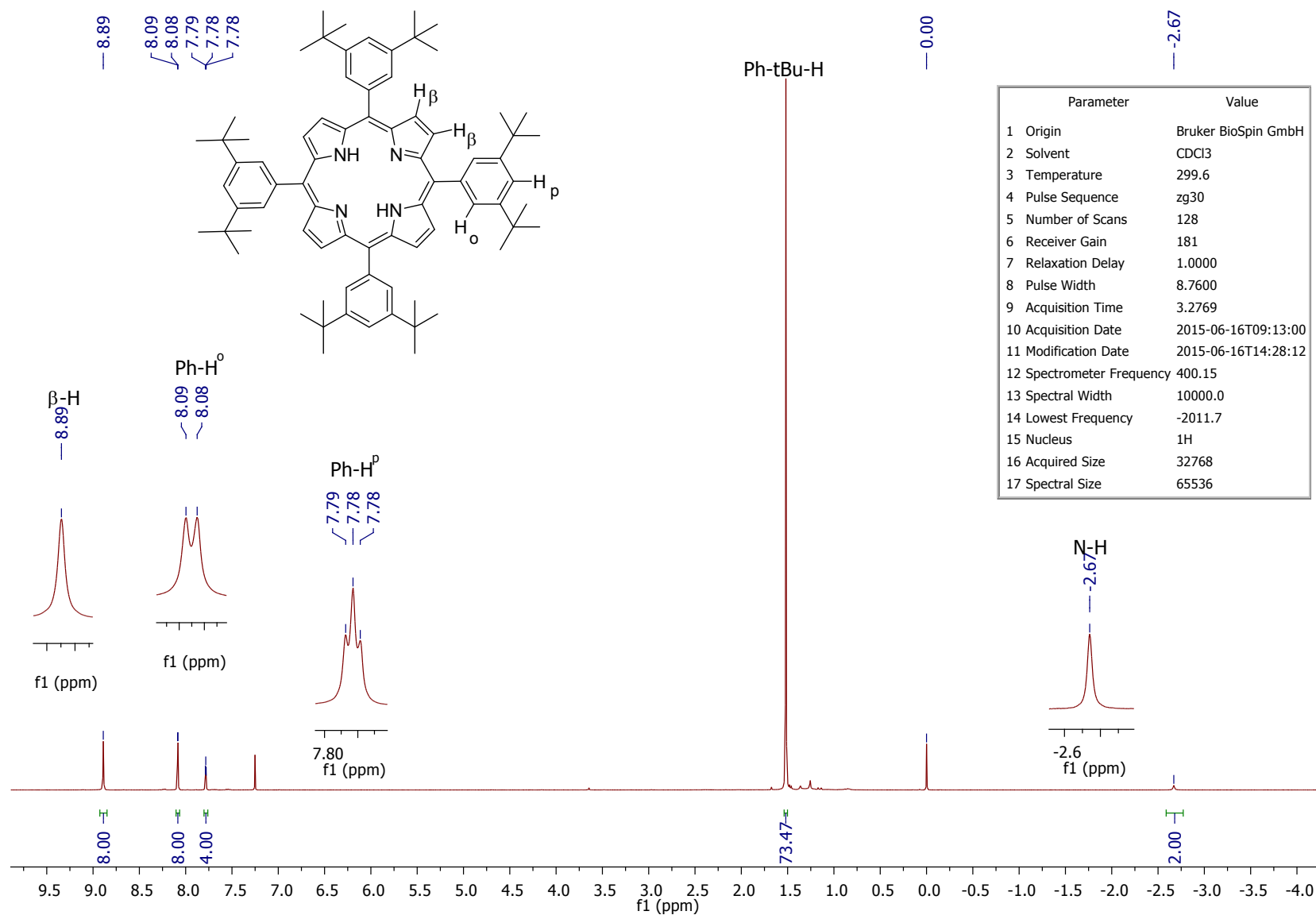


Figure S12. ¹H NMR (400 MHz) of **5b** CDCl₃.

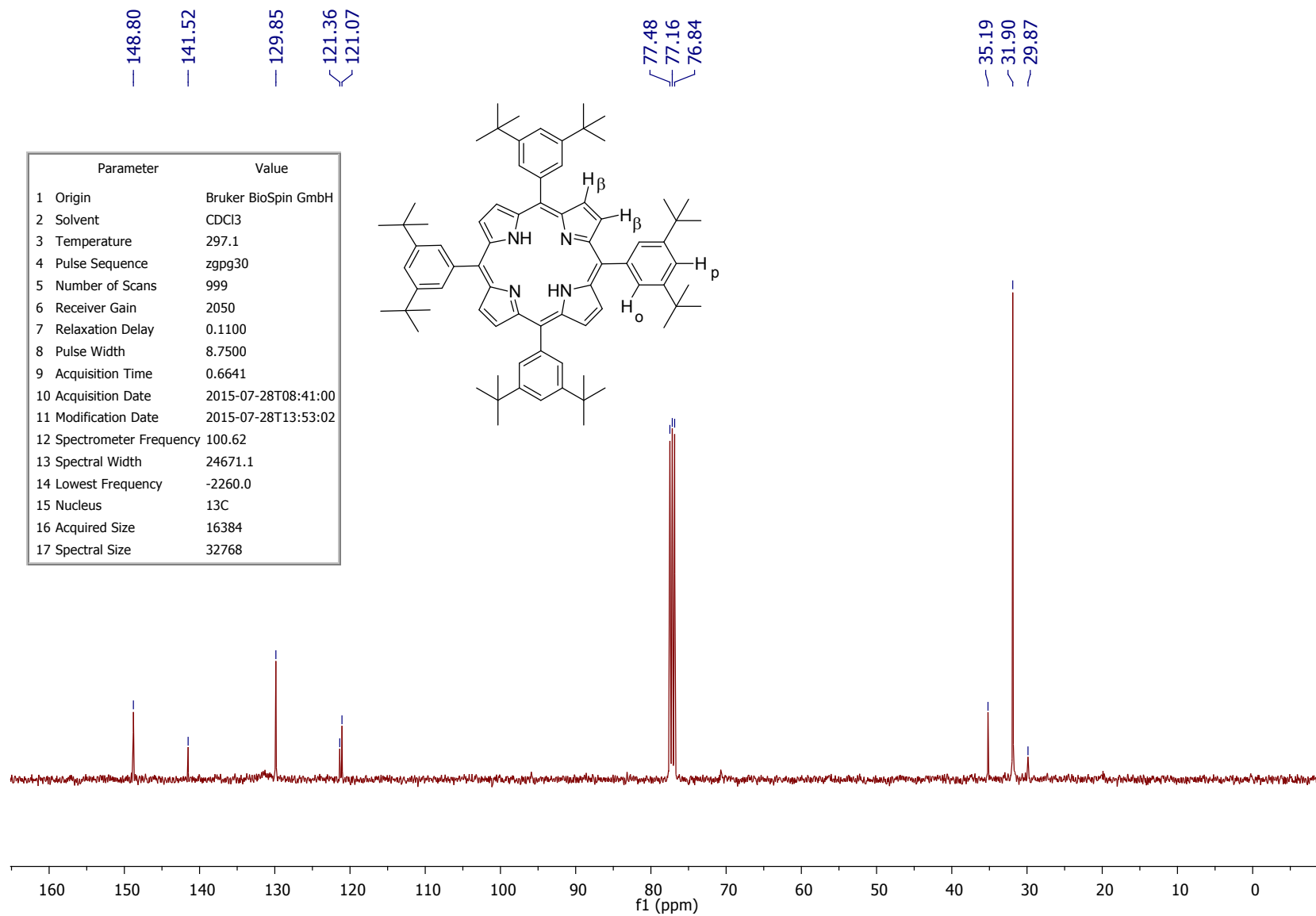


Figure S13. ¹³C NMR (100 MHz) of **5b** in CDCl₃.

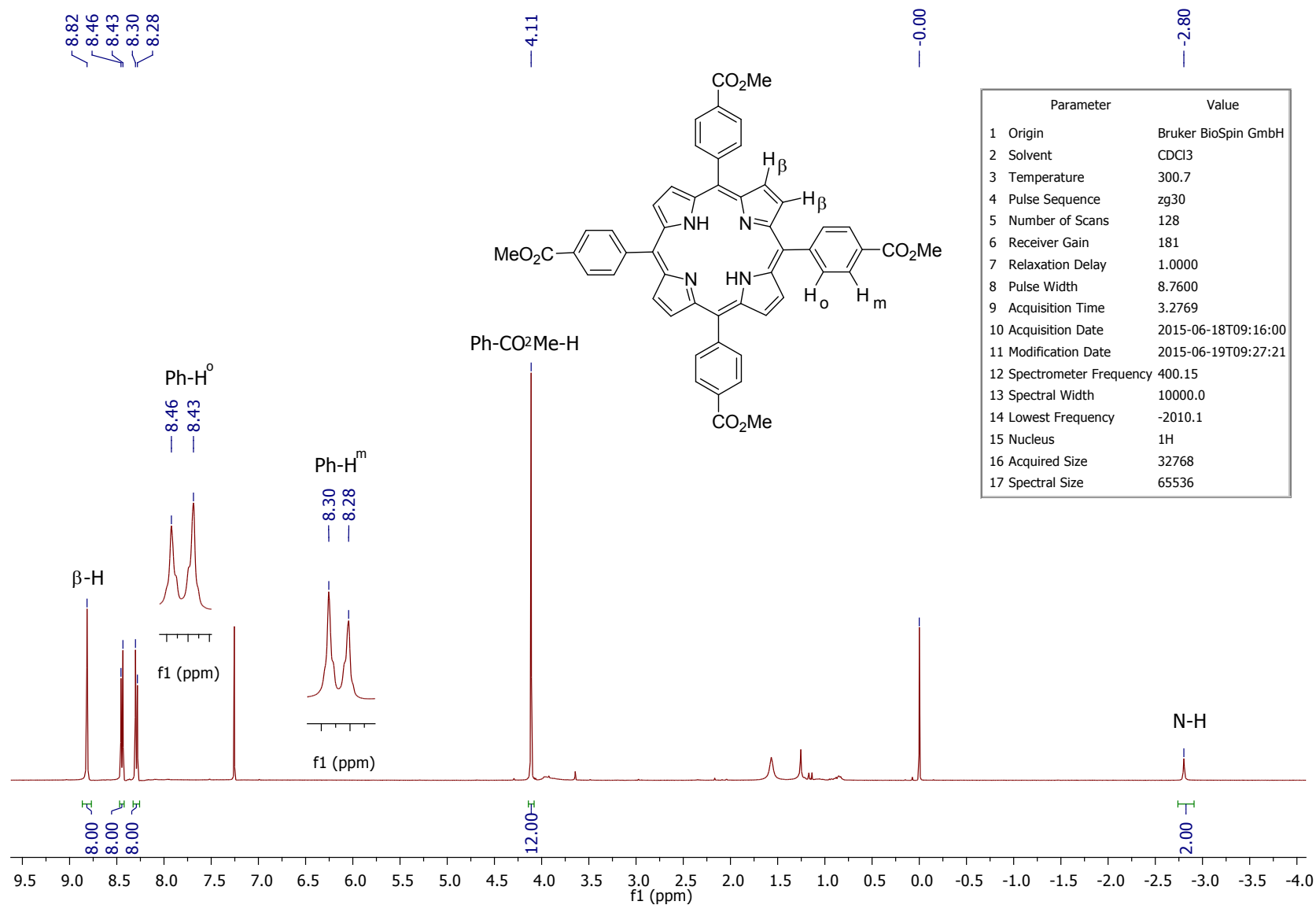


Figure S14. ^1H NMR (400 MHz) of **5c** in CDCl_3 .

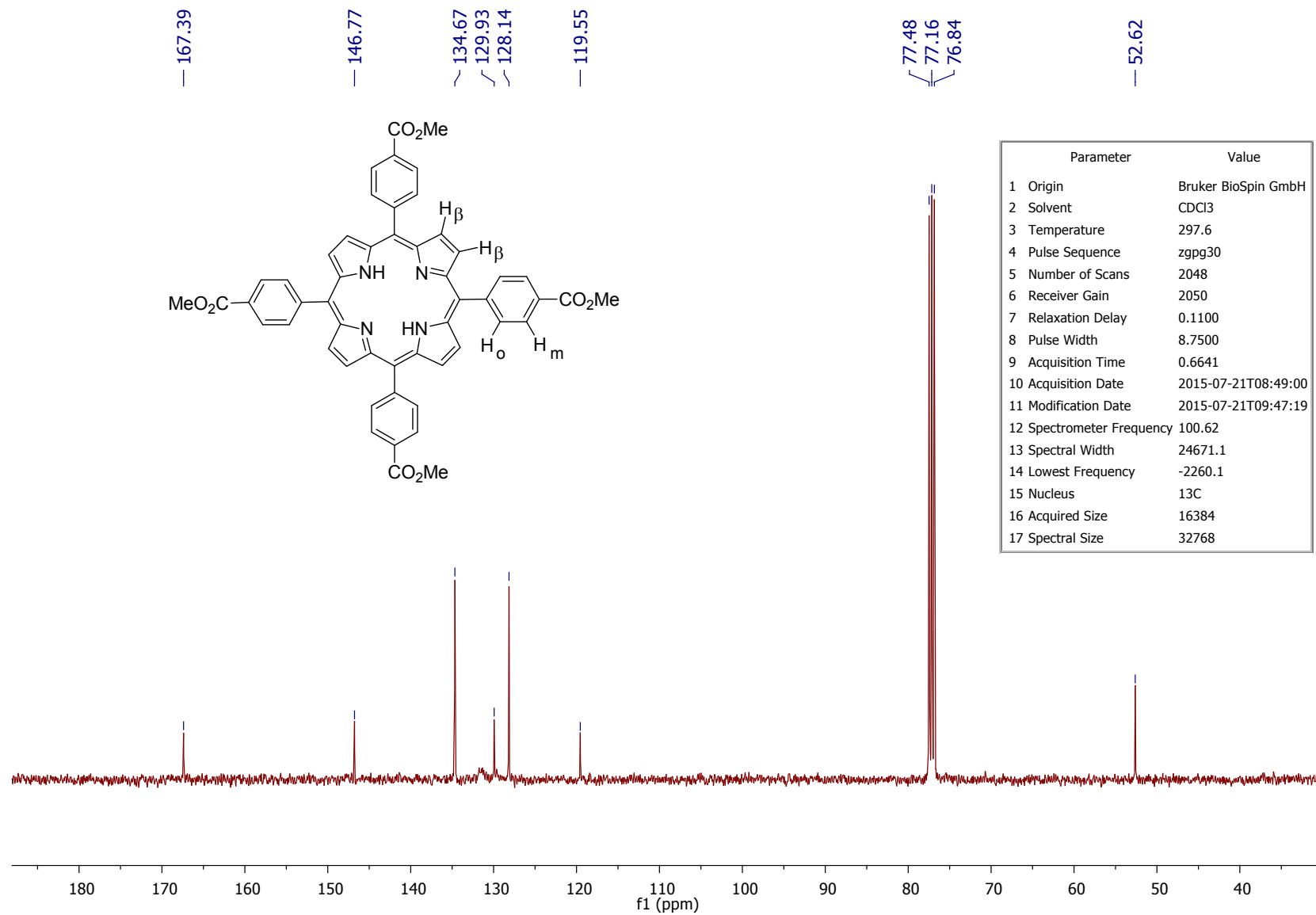


Figure S15. ¹³C NMR (100 MHz) of **5c** in CDCl₃.

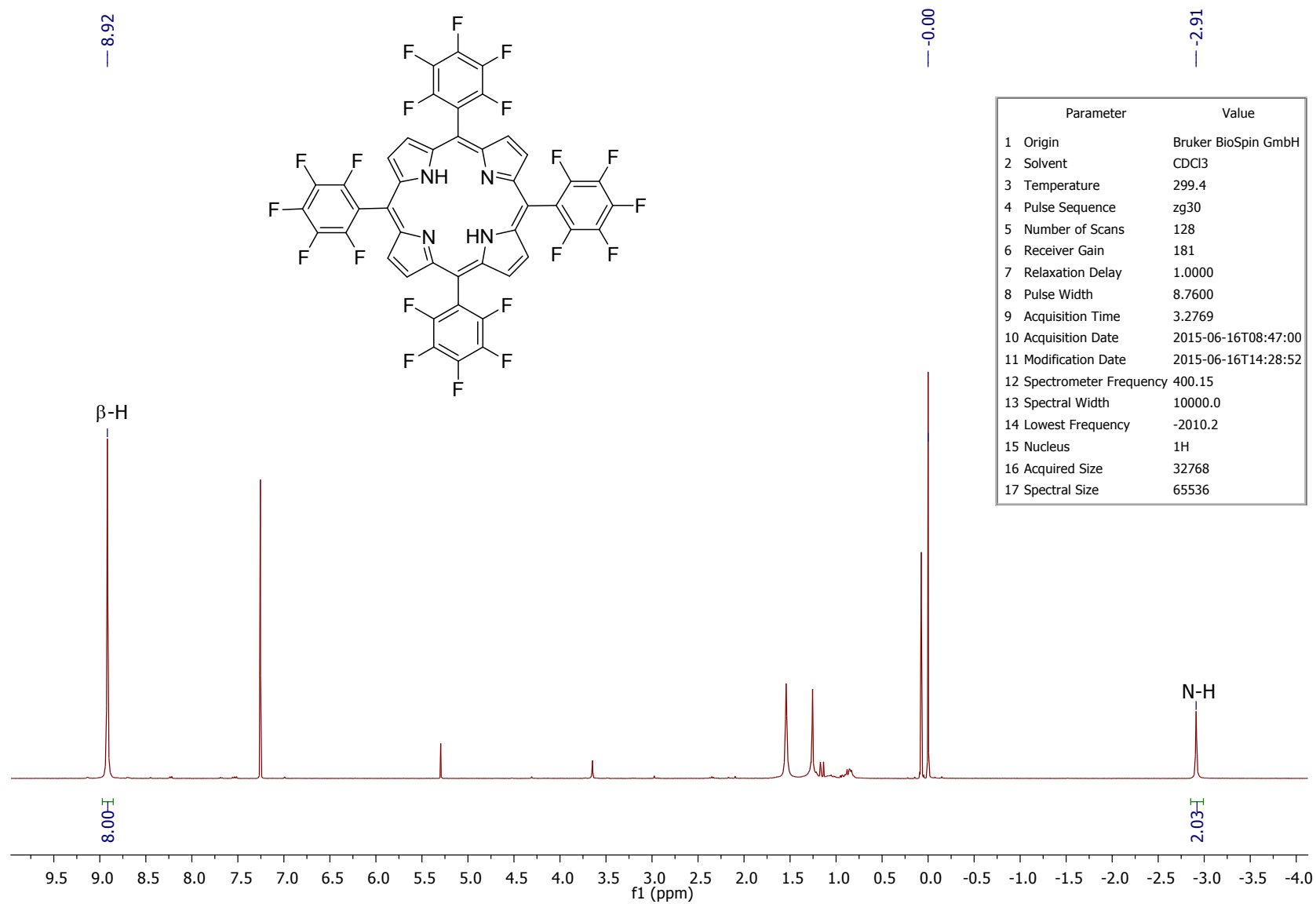


Figure S16. ¹H NMR (400 MHz) of **5d** in CDCl₃.

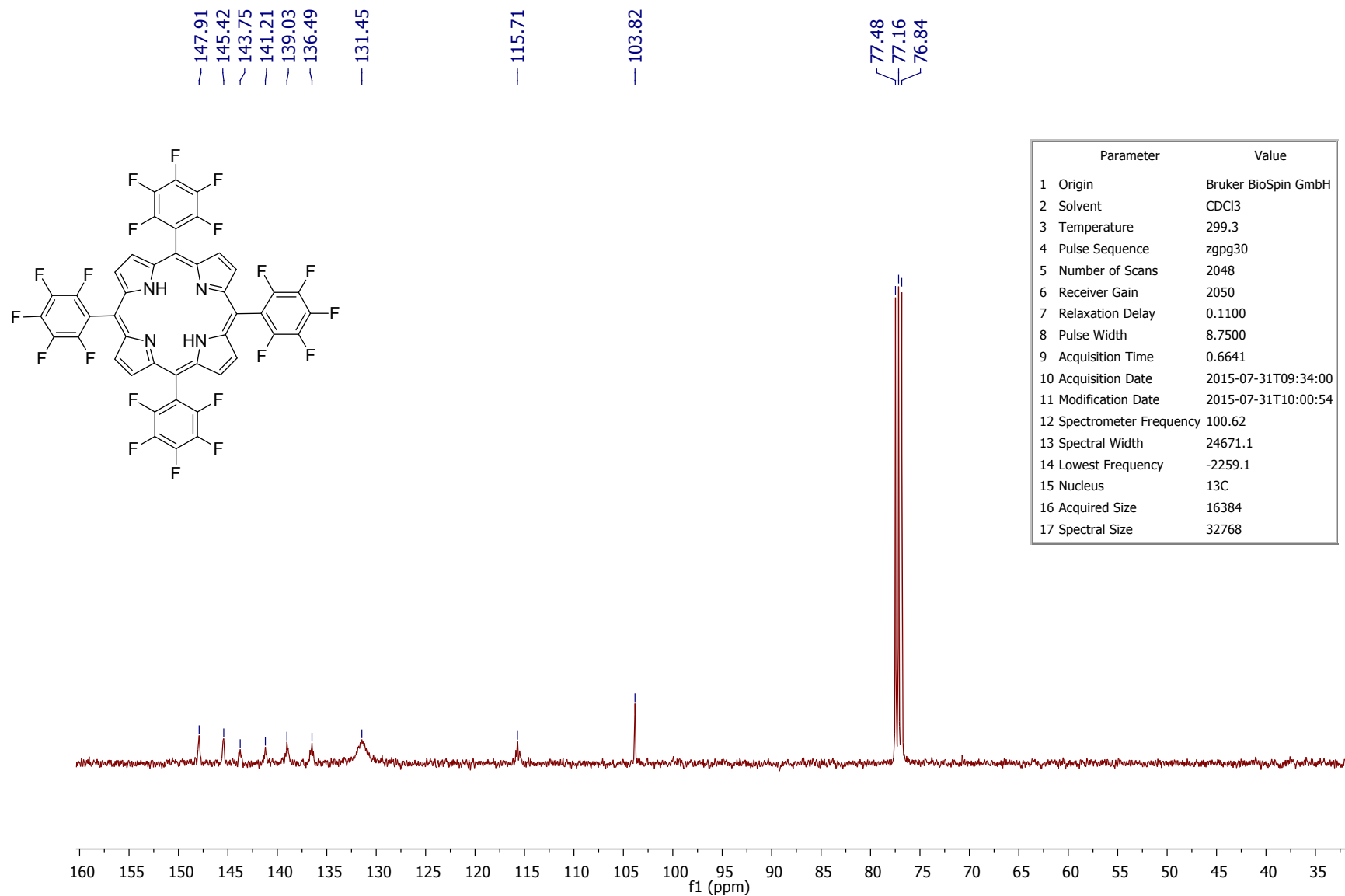


Figure S17. ¹³C NMR (100 MHz) of **5d** in CDCl₃.

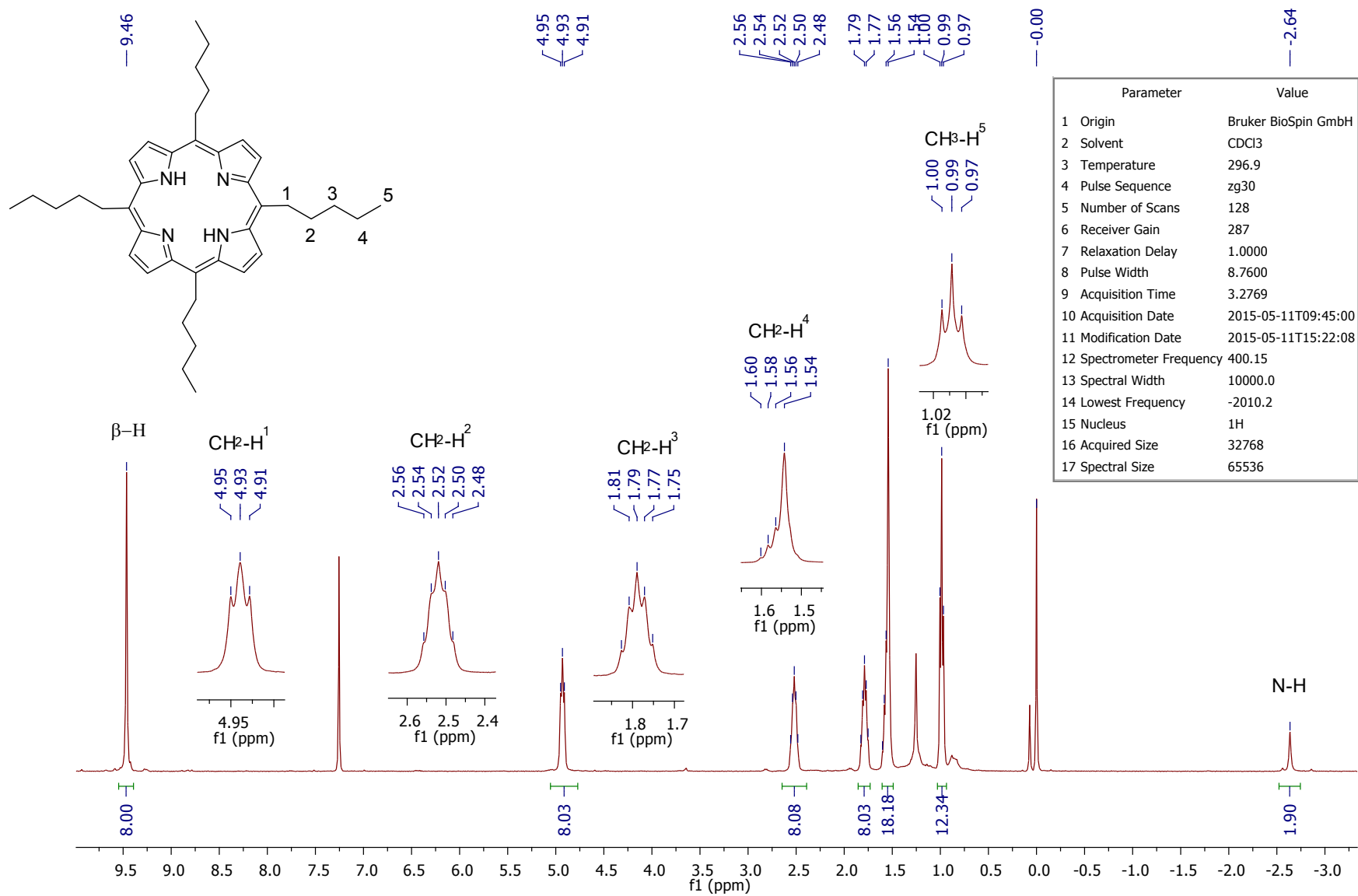


Figure S18. ¹H NMR (400 MHz) of **5e** in CDCl₃.

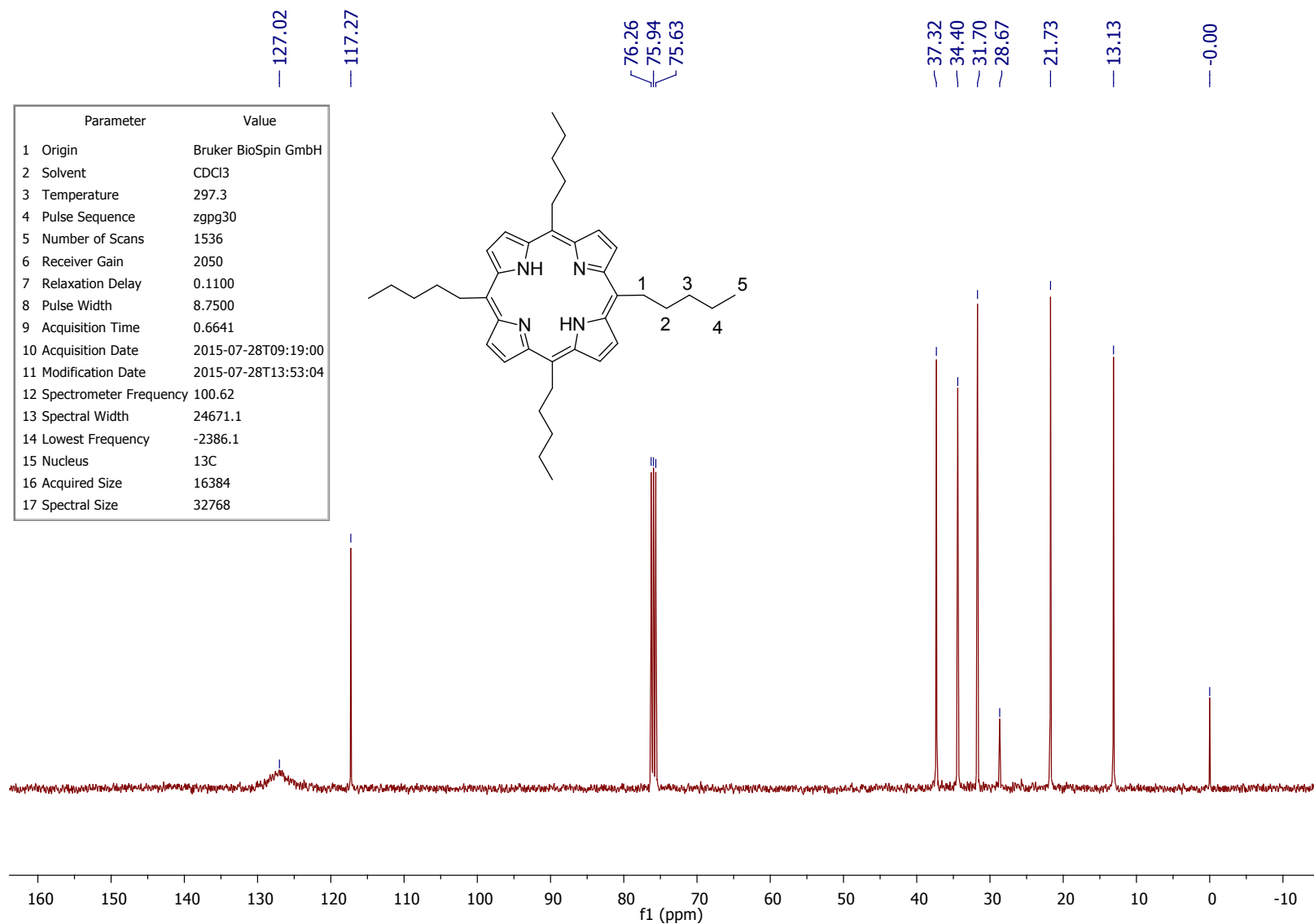


Figure S19. ¹³C NMR (100 MHz) of **5e** in CDCl₃.

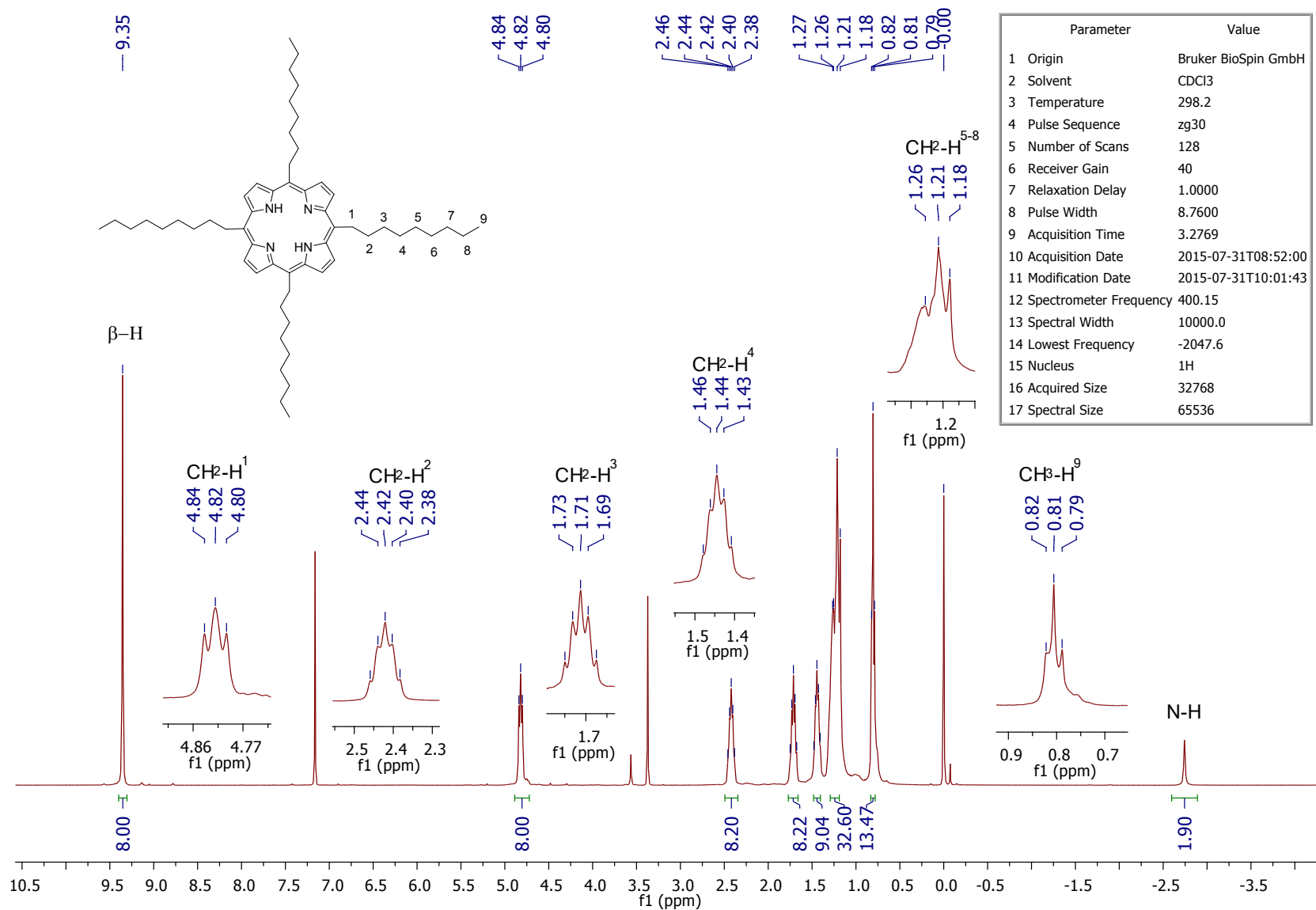


Figure S20. ¹H NMR (400 MHz) of **5f** in CDCl₃.

Parameter	Value
1 Origin	Bruker BioSpin GmbH
2 Solvent	CDCl ₃
3 Temperature	297.3
4 Pulse Sequence	zgpg30
5 Number of Scans	1536
6 Receiver Gain	2050
7 Relaxation Delay	0.1100
8 Pulse Width	8.7500
9 Acquisition Time	0.6641
10 Acquisition Date	2015-07-28T09:53:00
11 Modification Date	2015-07-28T13:53:06
12 Spectrometer Frequency	100.62
13 Spectral Width	24671.1
14 Lowest Frequency	-2260.8
15 Nucleus	¹³ C
16 Acquired Size	16384
17 Spectral Size	32768

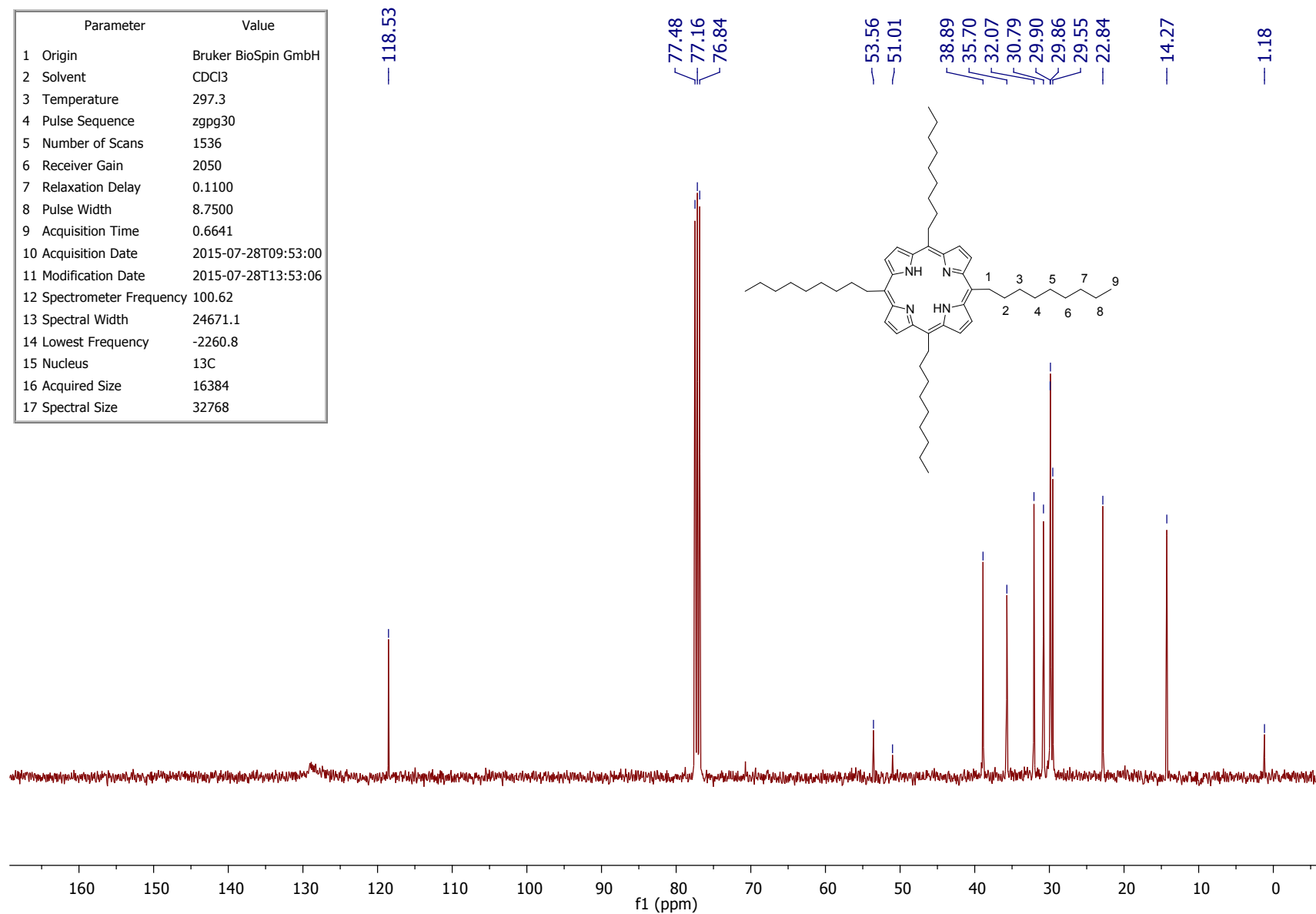


Figure S21. ¹³C NMR (100 MHz) of **5f** in CDCl₃.

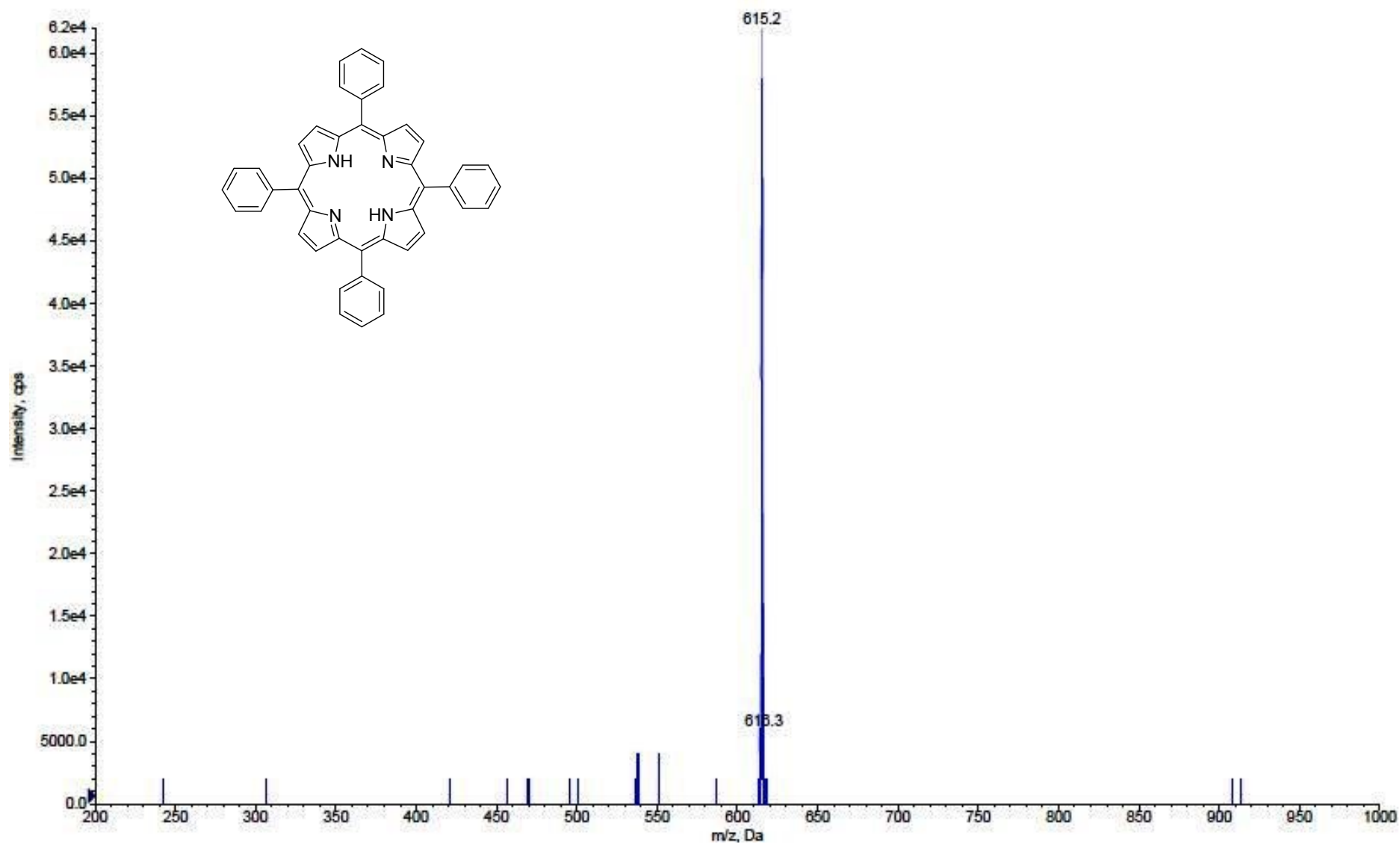


Figure S22: Mass Spectrum of Molecular ion($[M+H]^+$) of 3.

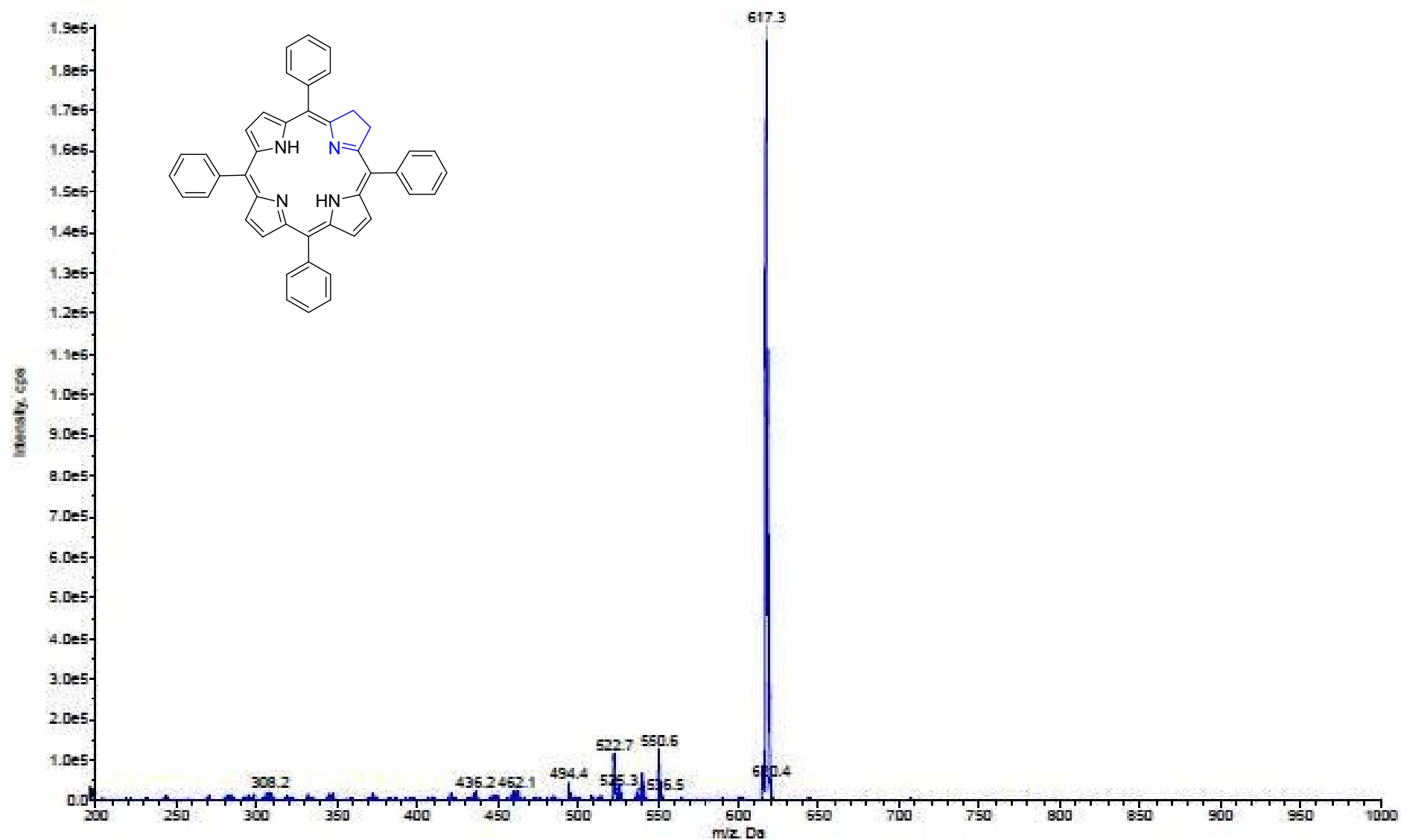


Figure S23: Mass Spectrum of Molecular ion($[M+H]^+$) of *meso*-tetraphenylchlorin.

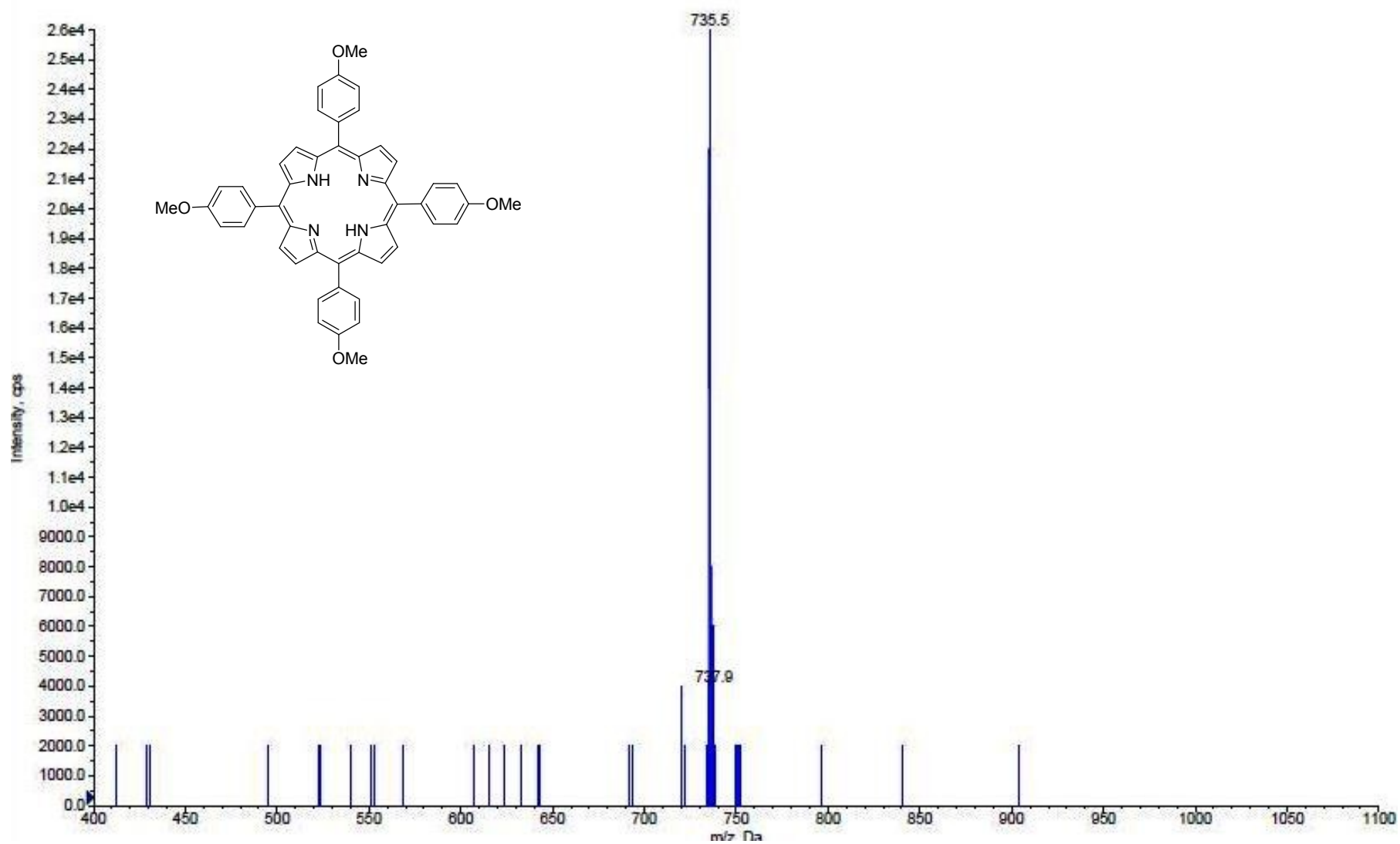


Figure S24: Mass Spectrum of Molecular ion ($[M+H]^+$) of 5a.

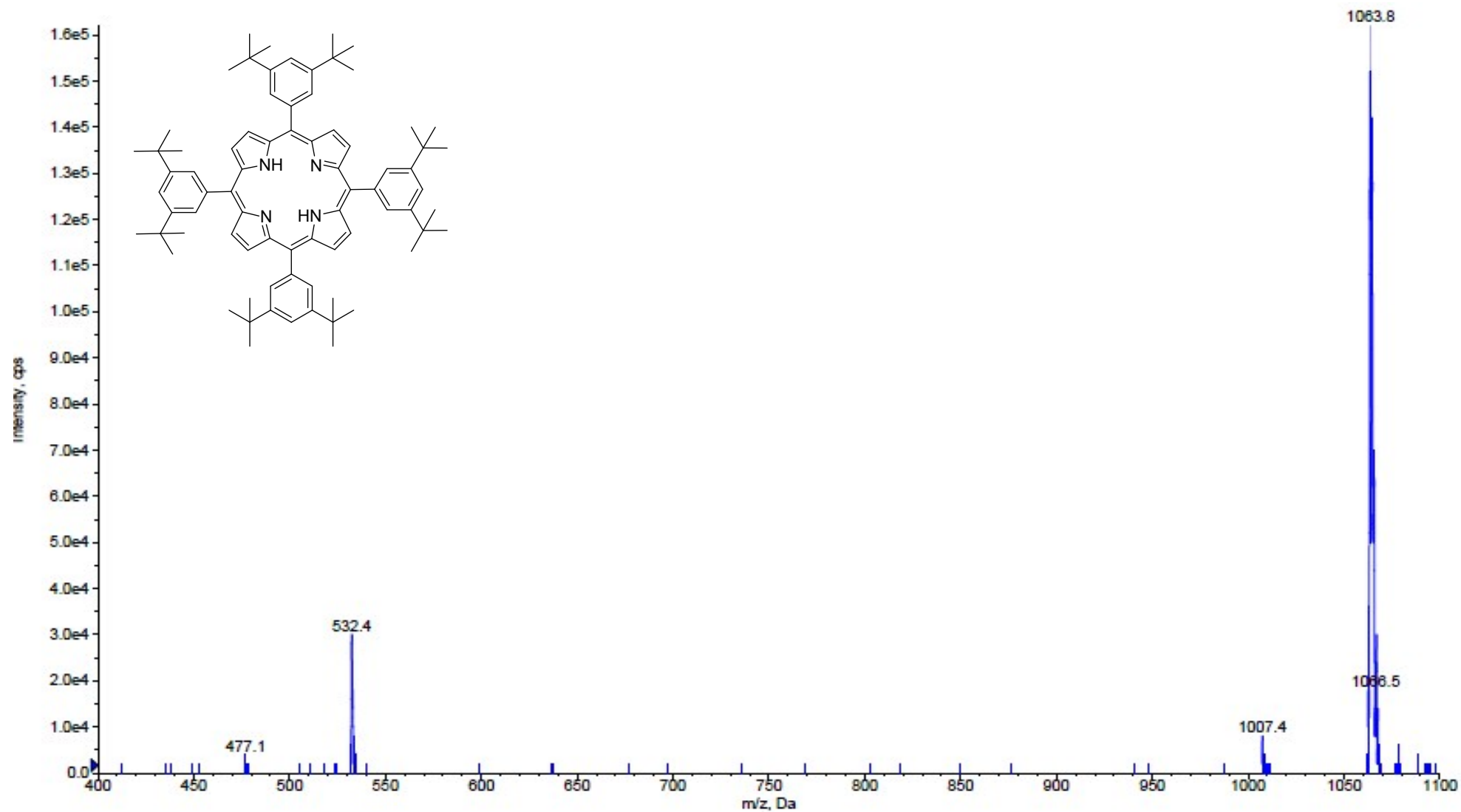


Figure S25: Mass Spectrum of Molecular ion ($[M+H]^+$) of **5b**.

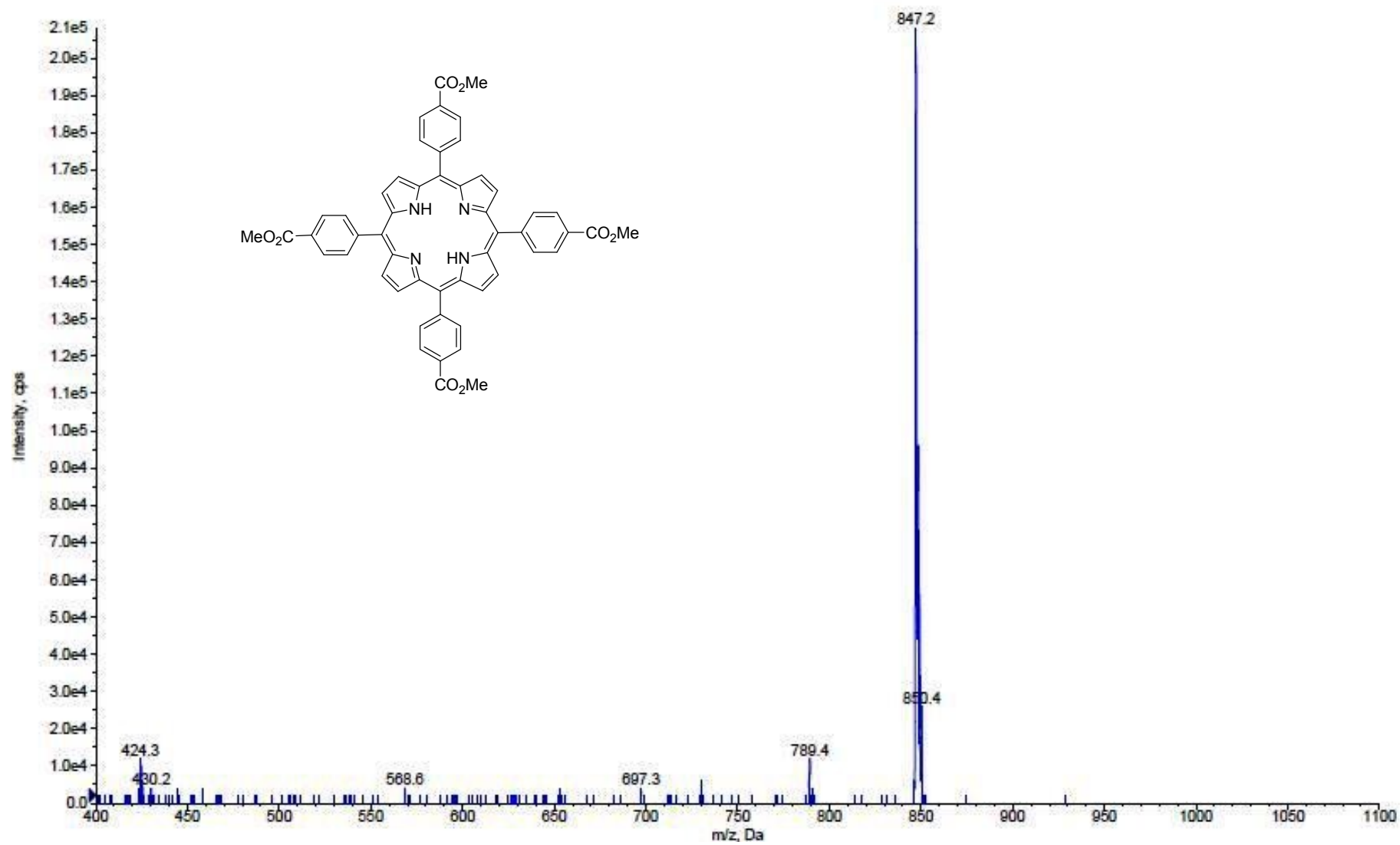


Figure S26: Mass Spectrum of Molecular ion ($[M+H]^+$) of **5c**.

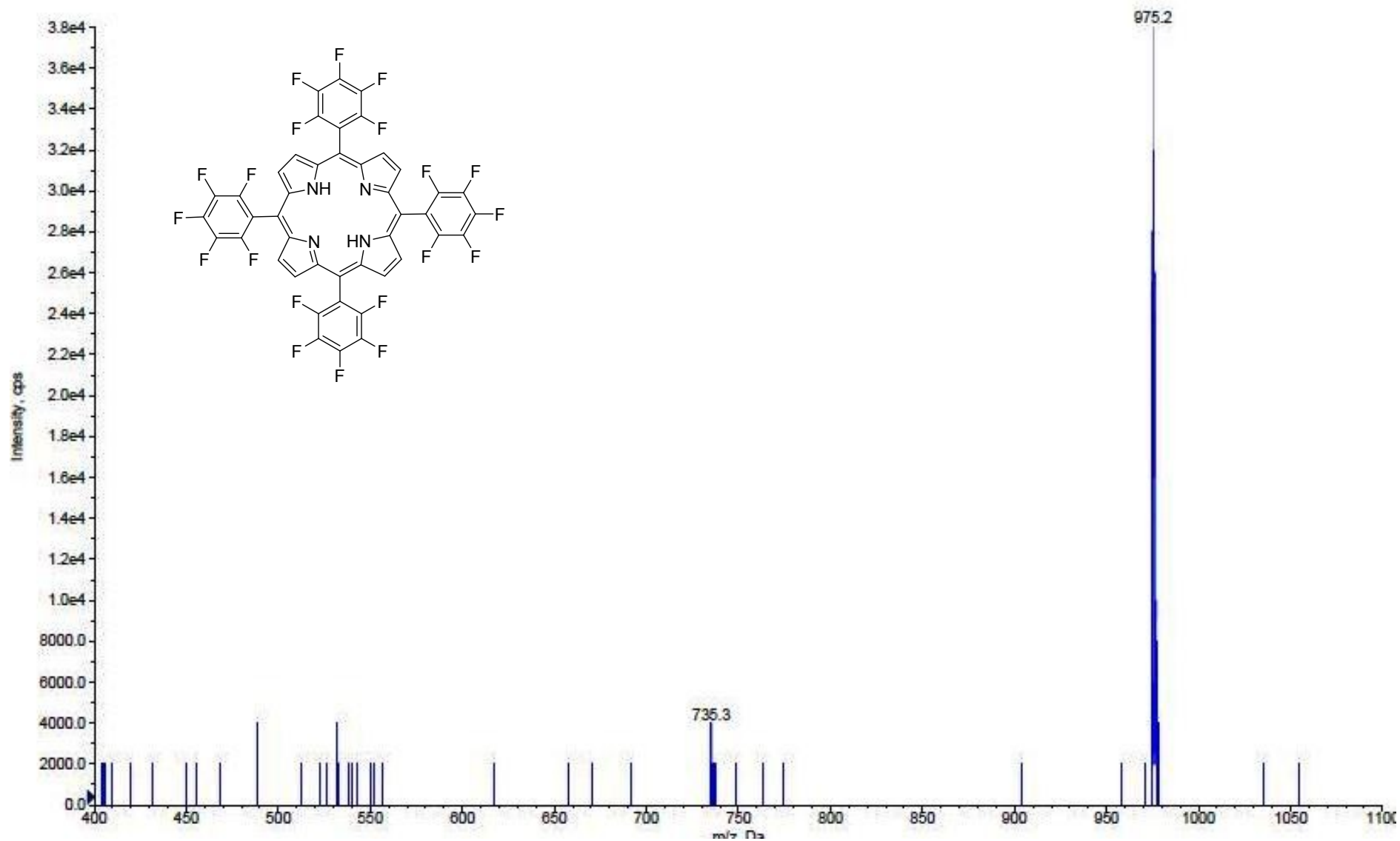


Figure S27: Mass Spectrum of Molecular ion ($[M+H]^+$) of 5d.

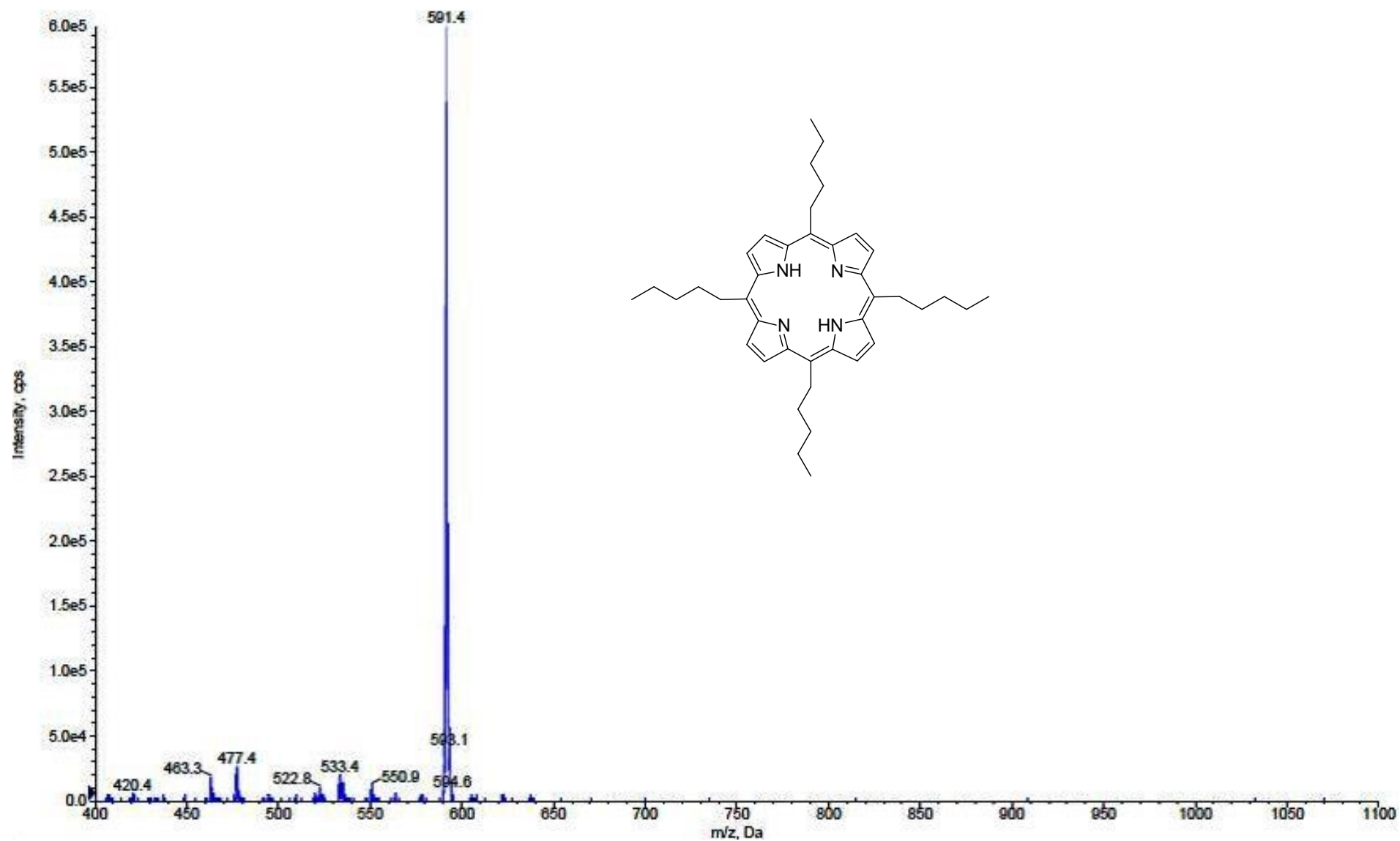


Figure S28: Mass Spectrum of Molecular ion ($[M+H]^+$) of 5e.

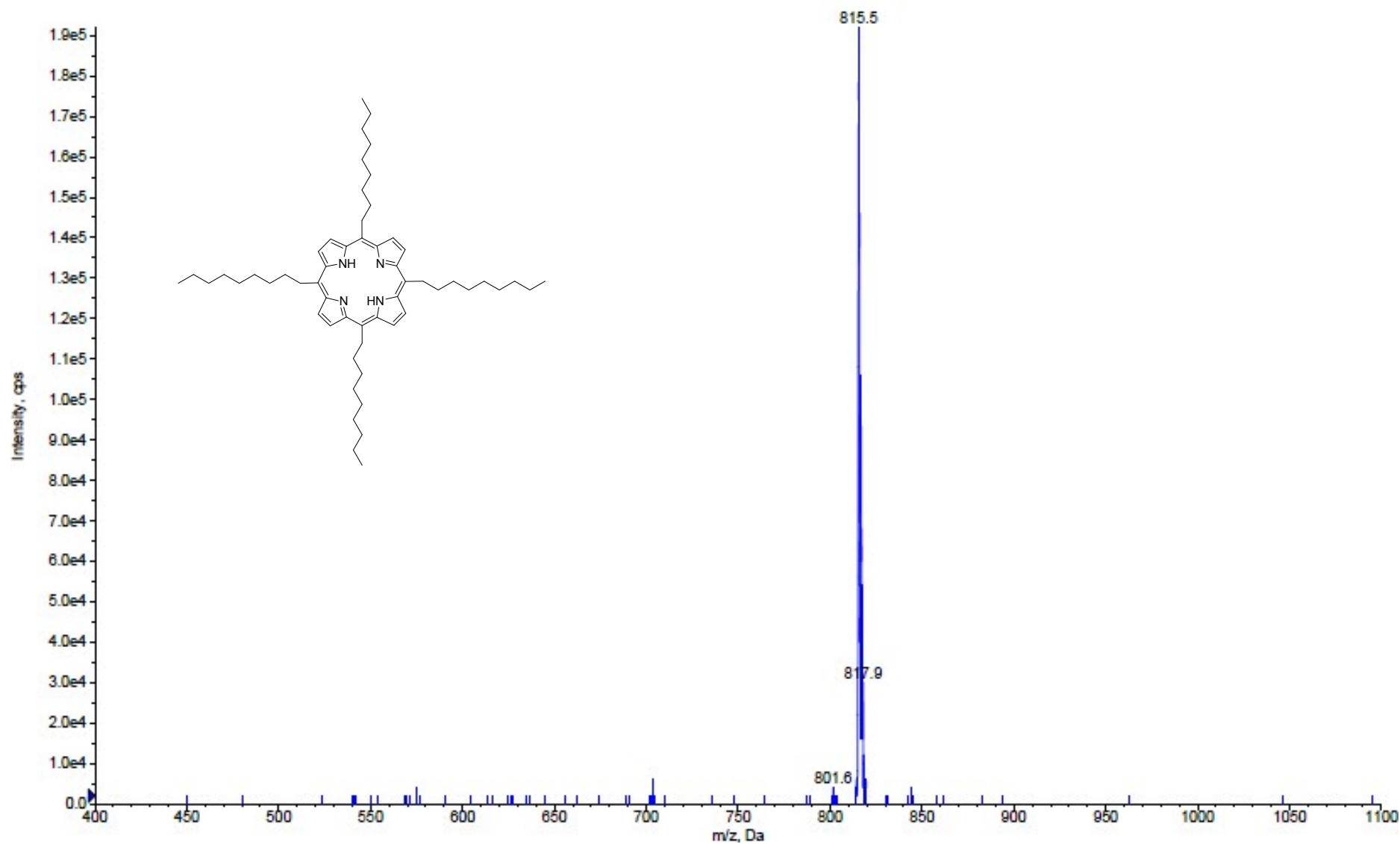


Figure S29: Mass Spectrum of Molecular ion ($[M+H]^+$) of **5f**.

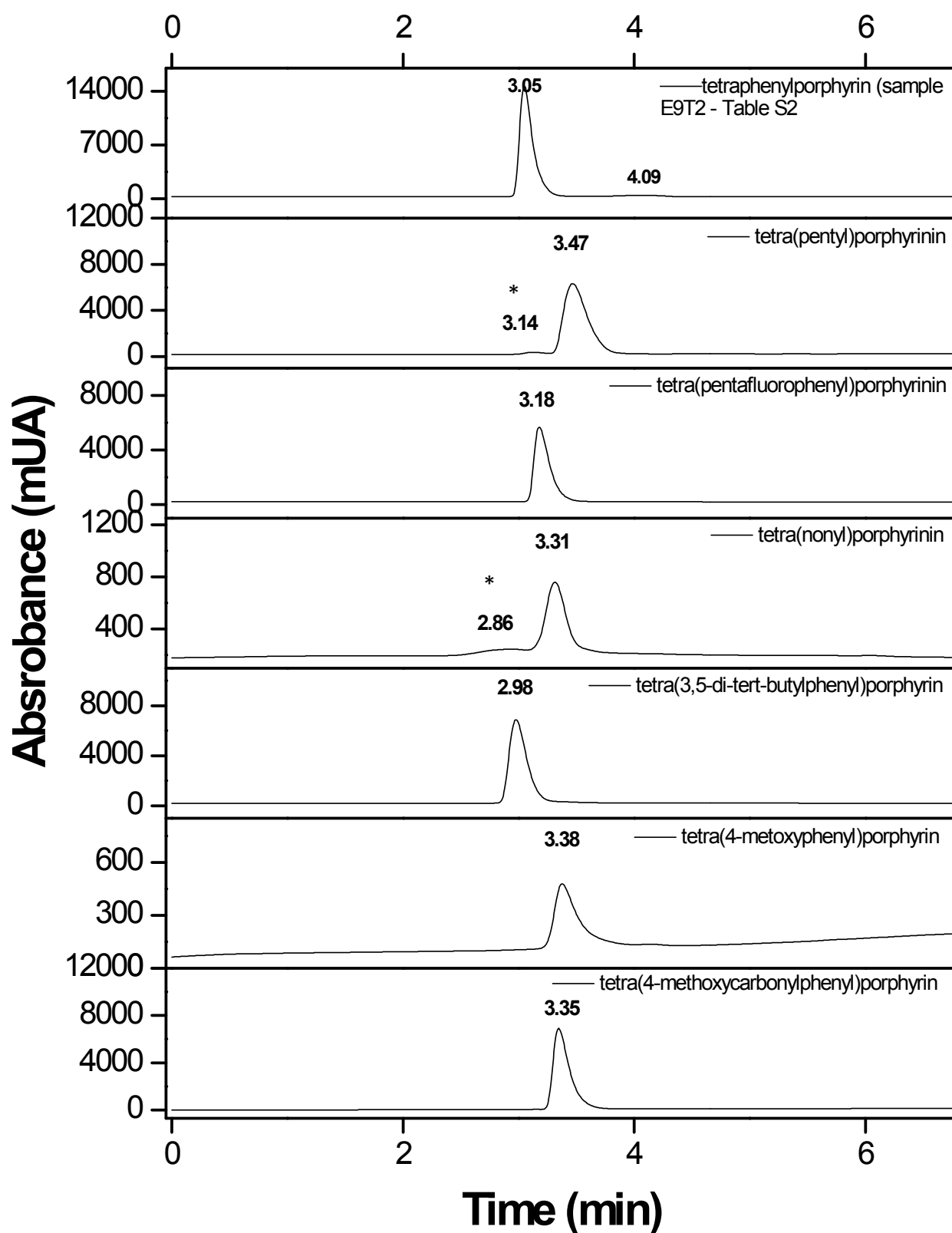


Figure S35. HPLC chromatograms of porphyrins - run at $1\text{ mL}\cdot\text{min}^{-1}$ and 90% of dichloromethane: 10% hexane as eluent, except for TPP in which was used only dichloromethane. (*) these low amounts of impurities do not correspond to chlorin derivatives as checked by hyphenated technique (MS).

Table S1. HPLC quantifying for *meso*-tetraphenylporphyrins (samples of Table 1).

Sample ^(a)		RT (min)	Area	(%)
E1T1	porphyrin	3.05	148000.00	97.8
	chlorin	4.12	3260.00	2.2
E2T1	porphyrin	3.05	156000.00	98.4
	chlorin	4.11	2580.00	1.6
E3T1	porphyrin	3.05	144000.00	98.7
	chlorin	4.13	1960.00	1.3
E4T1	porphyrin	3.05	136000.00	98.8
	chlorin	4.12	1600.00	1.2
E5T1	porphyrin	3.05	147000.00	97.8
	chlorin	4.12	3260.00	2.2
E6T1	porphyrin	3.05	128000.00	98.3
	chlorin	4.12	2160.00	1.7
E7T1	porphyrin	3.05	138000.00	100.0
	chlorin			0.0
E8T1	porphyrin	3.05	165000.00	98.7
	chlorin	4.1	2150.00	1.3
E9T1	porphyrin	3.05	166000.00	97.7
	chlorin	4.1	3840.00	2.3
E10T1	porphyrin	3.05	150000.00	97.3
	chlorin	4.09	4170.00	2.7
E11T1	porphyrin	3.05	144000.00	98.3
	chlorin	4.08	2520.00	1.7
E12T1	porphyrin	3.05	144000.00	98.1
	chlorin	4.07	2750.00	1.9

^(a)ExTy = Entry number and Table number referring Tables of the article.

Table S2. HPLC quantifying for *meso*-tetraphenylporphyrins (samples of Table 2).

Sample ^(a)		RT (min)	Area	(%)
E1T2	porphyrin	-	-	-
	chlorin	-	-	-
E2T2	porphyrin	3.04	137000.00	97.7
	chlorin	4.18	3170.00	2.3
E3T2	porphyrin	3.04	143000.00	97.5
	chlorin	4.02	3610.00	2.5
E4T2	porphyrin	3.04	147000.00	99.4
	chlorin	4.03 ¹⁾	865.00	0.6
E5T2	porphyrin	-	-	-
	chlorin	-	-	-
E6T2	porphyrin	3.05	120000.00	97.2
	chlorin	4.12	3410.00	2.8
E7T2	porphyrin	3.04	146000.00	97.4
	chlorin	4.12	3870.00	2.6
E8T2	porphyrin	3.05	108000.00	99.4
	chlorin	4.10	664.00	0.6
E9T2	porphyrin	3.05	117000.00	97.2
	chlorin	4.09	3320.00	2.8
E10T2	porphyrin	3.05	131000.00	96.7
	chlorin	4.12	4540.00	3.3
E11T2	porphyrin	3.05	155000.00	97.6
	chlorin	4.13	3760.00	2.4
E12T2	porphyrin	3.05	142000.00	99.5
	chlorin	4.11	775.00	0.5

^(a)ExTy = Entry number and Table number referring Tables of the article.

Table S3. HPLC quantifying for *meso*-tetraphenylporphyrins (samples of Table 3).

Sample ^(a)		RT (min)	Area	(%)
E1T3 ^(b)	porphyrin	-	-	-
	chlorin	-	-	-
E2T3	porphyrin	3.07	155000.00	97.1
	chlorin	4.11	4610.00	2.9
E3T3	porphyrin	3.06	148000.00	97.6
	chlorin	4.11	3600.00	2.4
E4T3	porphyrin	3.06	146000.00	99.4
	chlorin	4.11	889.00	0.6
E5T3	porphyrin	-	-	-
	chlorin	-	-	-
E6T3	porphyrin	3.07	146000.00	97.1
	chlorin	4.11	4430.00	2.9
E7T3	porphyrin	3.07	134000.00	97.5
	chlorin	4.12	3460.00	2.5
E8T3	porphyrin	3.06	114000.00	99.4
	chlorin	4.04	709.00	0.6
E9T3	porphyrin	3.07	144000.00	96.8
	chlorin	4.09	4760.00	3.2
E10T3	porphyrin	3.06	149000.00	96.2
	chlorin	4.07	5840.00	3.8
E11T3	porphyrin	3.06	151000.00	97.7
	chlorin	4.08	3610.00	2.3
E12T3	porphyrin	3.06	138000.00	99.4
	chlorin	3.88	838.00	0.6

^(a)ExTy = Entry number and Table number referring Tables of the article.

Table S5. HPLC quantifying for *meso*-substituted porphyrins (samples of Table 4).

Entry	sample	RT (min)	Area	(%)	DAD (mAU)	[M+H] ⁺	Molecular Formula
1	<i>meso</i> -tetra(4-methoxyphenyl)porphyrin (5a)	3.38	5230	100	518; 555; 593; 650	734.8	C ₄₈ H ₃₈ N ₄ O ₄
2	<i>meso</i> -tetra(3,5-di- <i>tert</i> -butylphenyl)porphyrin (5b)	2.98	6680	100	517; 553; 592; 647	1063.8	C ₇₆ H ₉₄ N ₄
3	<i>meso</i> -tetra(4-methoxycarbonylphenyl)porphyrin (5c)	3.35	69400	100	515; 549; 589; 645	847.2	C ₅₂ H ₃₈ N ₄ O ₈
4	<i>meso</i> -tetra(pentafluorophenyl)porphyrin (5d)	3.18	51700	100	506; 535; 582; 636	975.2	C ₄₄ H ₁₀ F ₂₀ N ₄
5	<i>meso</i> -tetra(pentyl)porphyrin (5e) ^(b)	3.47	86600	>98	520; 555; 600; 658	591.4	C ₄₀ H ₅₄ N ₄
6	<i>meso</i> -tetra(nonyl)porphyrin (5f) ^(b)	3.31	6420	>98	519; 554; 600; 658	815.5	C ₅₆ H ₈₆ N ₄
7	<i>meso</i> -tetraphenylporphyrin (3) ^(a)	3.05	108000	99.4	514; 549; 589; 645	615.2	C ₄₄ H ₃₀ N ₄
	Corresponding chlorin	4.1	66	0.6	518; 546; 598; 652	617.4	C ₄₄ H ₃₂ N ₄

^(a) It corresponds to sample of entry 8, Table 2. ^(b) It was detected small amounts of non-chlorin derivative impurities as confirmed by hyphenated technique (MS).