Supplementary Information for

A Synthetic Toolbox for Sustainable Methods in Porphyrin Chemistry

Karolina Urbańska,[a] Liam Cribbin,[a] Brendan Twamley,[b] Fiach O Ceallaigh[a] and Mathias O. Senge[a]*

[a] School of Chemistry, Trinity Biomedical Sciences Institute, 152-160 Pearse Street, Trinity College Dublin, The University of Dublin, Dublin, D02 R590, Ireland.

[b] School of Chemistry, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland.

Analytical methods, ^{1}H, $^{13}C\{^{1}H\}$, ^{19}F, NMR, UV/Vis, IR, HRMS-ESI (*m/z*) and HRMS-APCI (*m/z*) and X-ray crystallographic data

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Analytical methods

NMR spectra were recorded on a Bruker Advance III 400 MHz, a Bruker Advance HD400 and an Agilent 400 spectrometer for ^{1}H (400.13 MHz), ^{19}F (376 MHz) and $^{13}C\{^{1}H\}$ (100.61 MHz) NMR spectra. A Bruker Avance II 600 NMR was employed for ^{1}H (600.13 MHz) and $^{13}C\{^{1}H\}$ (150.9 MHz) NMR spectra. NMR experiments were performed in general at 298 K. Resonances δ are given in ppm units and referenced to the deuterium peak in the NMR solvents, $CDCl_3$ (δ_H = 7.26 ppm, δ_C = 77.20 ppm), CD_2Cl_2 (δ_H = 5.32 ppm, δ_C = 53.84 ppm), CD_3COOD (δ_H = 11.65, 2.04 ppm, δ_C = 178.99, 20.00 ppm), $(CD_3)_2SO$ (δ_H = 3.33, 2.50 ppm, δ_C = 39.52 ppm). Signal multiplicities are abbreviated as follows: singlet = s, doublet = d, triplet = t, multiplet = m, doublet of quartets = dq, quintet = qui, apparent broad singlet = appbrs, apparent doublet = appd, apparent doublet of doublets = appdd, apparent triplet = appt.

High resolution mass spectra (HRMS) were obtained through atmospheric pressure chemical ionization (APCI) experiments or electrospray ionization (ESI) experiments performed on a Bruker microTOF-Q III spectrometer interfaced to a Dionex UltiMate 3000 LC. UV/Vis absorption measurements were recorded in solutions using a Shimadzu UV-2600i spectrophotometer with quartz glass 10 mm cuvettes (1 cm path length quartz cell) at 25 °C. IR measurements were conducted on a PerkinElmer Spectrum 100 FT-IR. Melting points (Mp) were measured using a Stuart SP-10-point apparatus and were left uncorrected. Analytical thin layer chromatography was performed using silica gel 60 (fluorescence indicator F254, precoated sheets, 0.2 mm thickness, 20 cm × 20 cm; Merck) and visualized by UV irradiation (λ = 254 nm).

References cited in the Supplementary Information are listed in the article reference list.

Substrate scope

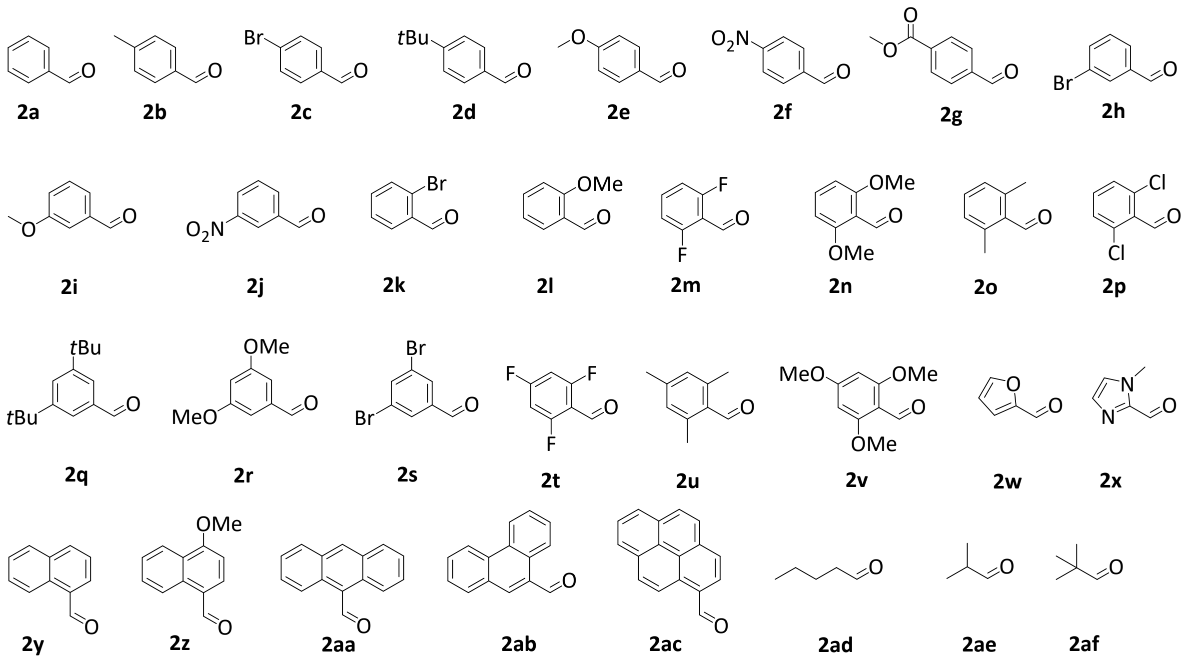


Figure S1: Scope of aldehydes **2a**-**af** used in this study.

Waste contributions for calculation of E-factors

Table S1. Calculation of total waste mass for determination of E-factors.

Waste contributions						
	4a		**7a**		**11a**	
	flow	batch[77]	flow	batch	flow	batch
Scale, mmol	2.25	2.25	0.75	0.75	1.10	1.10
Solvents, g						
Reaction	20	233	20	178	13	146
Elution	66	93	40	40	0	66
Crystallization	33	96	20	20	78	39
Reagents, g						
Benzaldehyde	0.17	0.08	0.05	0.03	0.08	0.05
Pyrrole	0.10	0.05	0.07	0.04	0.09	0.06
Acid	0.26	0.26	0.09	0.09	0.21	0.02
TEA	0.23	0.23	0.08	0.08	0.11	0.00
DDQ	0.45	0.53	0.14	0.14	0.75	1.00
Silica	10	72	5	5	0	10
Waste total, g	**130**	**495**	**85**	**251**	**92**	**262**

Experimental setup

A five-stage cascaded continuous stirred tank reactor (fReactor) was mounted on a magnetic stirrer. Feeds 1 and 2 were simultaneously supplied by syringe pumps 1 and 2 (Figure S3). The setup was shielded from light. The crude reaction mixture containing porphyrinogens **3a-af**, **6a-af** and **10a-af** was collected into an RBF equipped with a magnetic stir bar and shielded from light; these were oxidised in batch conditions according to General Procedures A-C.

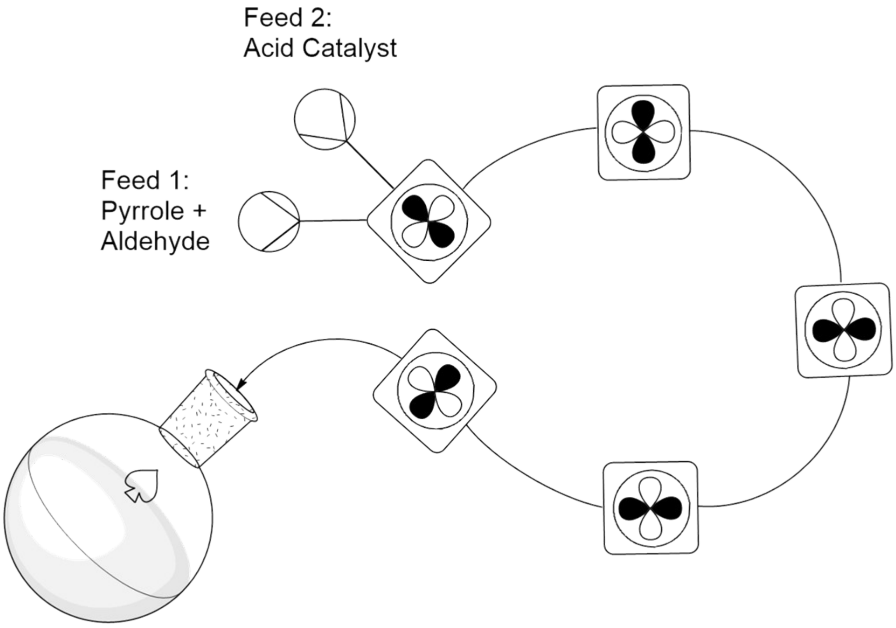


Figure S2. Schematic representation of the continuous stirred tank reactor.

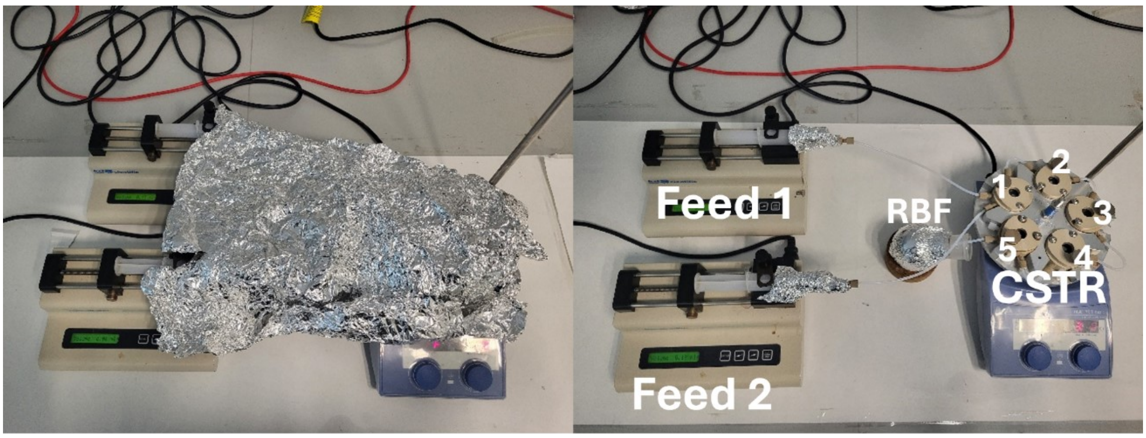
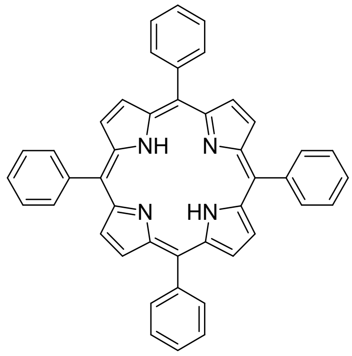
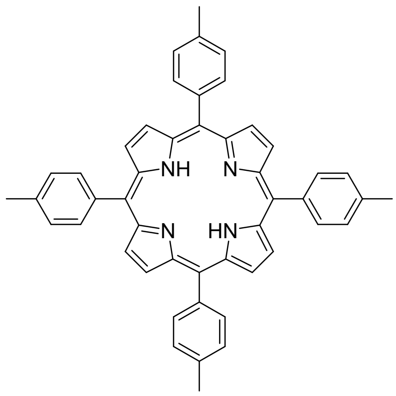


Figure S3. Photographs of the CSTR reaction setup. Left: reaction mixture protected from light. Right: uncovered setup showing two syringe pumps (Feed 1 and Feed 2) supplying the reagents into module 1 of the continuous stirred tank reactor (CSTR). Reaction mixture containing the porphyrinogen (**3a-af**, **6a-af**, **10a-af**) is collected into a round bottomed flask (RBF) shielded from light and equipped with a magnetic stir bar.

Compound characterization for compounds **4a**-**4ae**

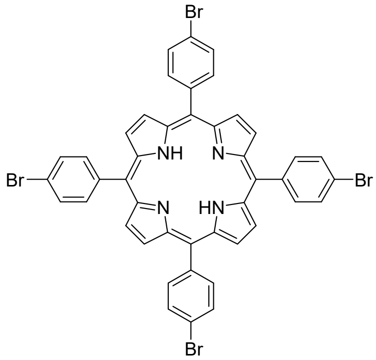


5,10,15,20-Tetraphenylporphyrin (4a): Synthesis via **General Procedure A** or **General Procedure B** yielded a purple solid (general procedure A: 104 mg, 30% yield (2.25 mmol scale); general procedure B: 32 mg, 28% yield (0.75 mmol scale). Mp >300 °C (from methanol); lit. mp > 300 °C.[22] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.89 (s, 8 H, pyrrole *CH*), 8.26 (dd, ^{3}J = 7.8 Hz, ^{4}J = 1.9 Hz, 8 H, *o*-Ph), 7.84-7.76 (m, 12 H, *m*,*p*-Ph), -2.72 ppm (s, 2 H, *NH*). ^{13}C{^{1}H) NMR (100 MHz; $CDCl_3$; 298 K) δ_c = 142.2, 134.6, 131.3, 127.7, 126.7 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 417 (5.48), 514 (4.80), 548 (4.12), 589 (4.08), 644 (3.78) nm. HRMS-APCI (*m/z*): [M+H]$^+$ calculated for $[C_{44}H_{31}N_4]^+$: 615.2543; found 615.2541. IR (ATR): ṽ = 3317, 3057, 2924, 2856, 2703, 2616, 2536, 1953, 1890, 1817, 1595, 1557, 1469, 1442, 1346, 1252, 1222, 1178, 1155, 1072, 1032, 1000, 979, 962, 794, 696 cm^{-1}. Characterization data in agreement with literature.[22,49,85]



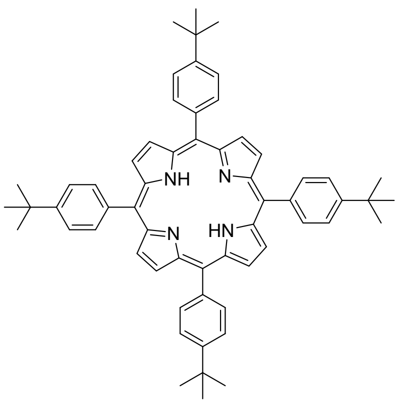
5,10,15,20-Tetrakis(4-methylphenyl)porphyrin (4b): Synthesis via **General Procedure A** yielded a purple solid (124 mg, 33% yield). Mp >300 °C (from methanol) ; lit. mp > 300 °C.[86] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.88 (s, 8 H, pyrrole *CH*), 8.12 (d, ^{3}J = 7.8 Hz, 8 H, *o*-Ph), 7.58 (d, ^{3}J = 7.8 Hz, 8 H, *m*-Ph), 2.73 (s, 12 H, CH_3), -2.74 ppm (s, 2 H, NH). ^{13}C{^{1}H} NMR (150 MHz; $CDCl_3$; 298 K) δ_C = 139.3, 137.3, 134.5, 130.9, 127.4, 120.1, 21.5 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 419 (5.59), 516 (4.81), 551 (4.48), 591 (4.29), 647 (4.13) nm. HRMS-APCI (*m/z*): [M+H]$^+$ calculated for $[C_{48}H_{39}N_4]^+$: 671.3169; found 671.3177. IR (ATR): ṽ = 3317, 3147, 3056, 3022, 2923, 2854, 2090, 1953, 1888, 1816, 1770, 1594, 1574, 1557, 1492, 1473, 1440, 1399, 1349, 1252, 1221, 1189, 1178, 1154, 1072, 1032, 1000, 979, 964, 876, 851, 812, 795, 721, 695, 656 cm^{-1}.

Characterization data in agreement with literature.[56,86]



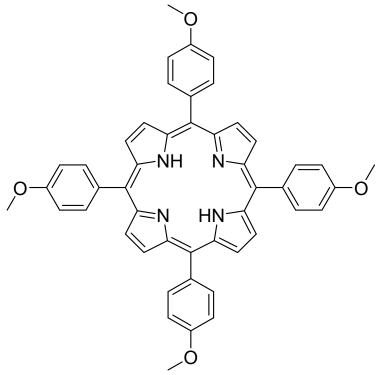
5,10,15,20-Tetrakis(4-bromophenyl)porphyrin (4c): Synthesis via **General Procedure A** yielded a purple solid (105 mg, 20% yield). Mp > 300 °C (from methanol); lit. mp > 300 °C.[87] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.83 (s, 8 H, pyrrole *CH*), 8.06 (d, ^3J = 8.0 Hz, 8 H, *o*-Ph), 7.89 (d, ^3J = 8.0 Hz, 8 H, *m*-Ph), -2.86 ppm (s, 2 H, *NH*). ^{13}C{^{1}H} NMR (100 MHz; $CDCl_3$; 298 K) δ_c = 140.8, 135.8, 130.0, 122.7, 119.0 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 419 (5.54), 515 (4.11), 549 (3.69), 590 (3.49), 648 (3.34) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{44}H_{27}Br_4N_4]^+$: 926.8964; found 926.8956. IR (ATR): ṽ = 3319, 1557, 1475, 1392, 1349, 1212, 1177, 1070, 1012, 982, 962, 842, 797, 793, 784, 732 cm^{-1}.

Characterization data in agreement with literature.[43a,44a,87]

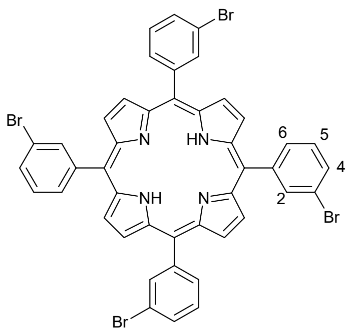


5,10,15,20-Tetrakis((4-*tert*-butyl)phenyl)porphyrin (4d): Synthesis via **General Procedure A** yielded a purple solid (204 mg, 43% yield). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[88] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.91 (s, 8 H, pyrrole *CH*), 8.19 (d, ^3J = 8.1 Hz, 8 H, *o*-Ph), 7.79 (d, ^3J = 8.1 Hz, 8 H, *m*-Ph), 1.64 (s, 36 H, *t*Bu), -2.70 ppm (s, 2 H, *NH*). ^{13}C{^{1}H) NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 150.5, 139.3, 134.5, 123.6, 120.1, 31.7 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 420 (5.57), 517 (4.19), 553 (3.97), 592 (3.69), 648 (3.70) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{60}H_{63}N_4]^+$: 839.5047;

found 839.5055. IR (ATR): ṽ = 3317, 2960, 2906, 2869, 2718, 2617, 2542, 1919, 1815, 1696, 1612, 1564, 1506, 1475, 1399, 1363, 1268, 1223, 1197, 1110, 1025, 985, 966, 882, 849, 797, 735, 711 cm^{-1}.
Characterization data in agreement with literature.[88]

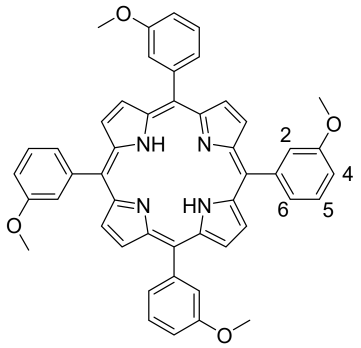


5,10,15,20-Tetrakis(4-methoxyphenyl)porphyrin (4e): Synthesis via **General Procedure A** yielded a purple solid (109 mg, 26% yield). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[33] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.89 (s, 8 H, pyrrole *CH*), 8.15 (d, ^3J = 8.5 Hz, 8 H, *o*-Ph), 7.32 (d, ^3J = 8.5 H, 8 H, *m*-Ph), 4.13 (s, 12 H, OCH_3), -2.72 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 159.4, 135.6, 134.7, 130.8, 55.6 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 421 (5.61), 518 (4.83), 555 (4.63), 593 (4.33), 650 (4.21). HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{48}H_{39}N_4O_4]^+$: 735.2966; found 735.2962. IR (ATR): ṽ = 3316, 3138, 3034, 2925, 2832, 2712, 2622, 2540, 2075, 1888, 1604, 1574, 1501, 1459, 1352, 1287, 1245, 1175, 1106, 984, 963, 840, 804, 784, 748, 736, 712 cm^{-1}.
Characterization data in agreement with literature.[33]



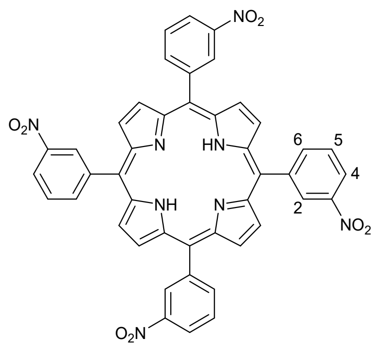
5,10,15,20-Tetrakis(3-bromophenyl)porphyrin (4h): Synthesis via **General Procedure A** yielded a purple solid (38 mg, 7% yield). Mp >300 °C (from methanol); lit. mp > 300 °C.[86] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.85 (s, 8 H, pyrrole *CH*), 8.37 (m, 4 H, C(2)*H*), 8.14 (m, 4 H, C(6)*H*), 7.94 (m, 4 H, C(4)*H*), 7.64 (m, 4 H, C(5)*H*), -2.90 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (150 MHz; $CDCl_3$; 298 K) δ_C = 142.6, 135.5, 135.4, 132.2, 130.2, 127.7, 127.6, 125.9, 118.8 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 418 (5.61), 514 (4.32), 548 (4.04), 589 (3.98), 645 (3.82) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{44}H_{27}Br_4N_4]^+$: 926.8964; found 926.8956. IR (ATR): ṽ = 3649, 3325, 3139, 3058, 2925, 2724, 2611, 2535, 2160, 2032, 1978, 1825, 1588, 1557, 1465, 1402, 1346, 1249, 1159, 1072, 971, 886, 802, 771, 730, 689 cm^{-1}.

Characterization data in agreement with literature.[86]



5,10,15,20-Tetrakis(3-methoxyphenyl)porphyrin (4i): Synthesis via **General Procedure A** yielded a purple solid (100 mg, 24% yield). Mp > 300 °C (from methanol); lit. mp > 300 °C.[86] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.90 (s, 8 H, pyrrole *CH*), 7.83-7.79 (m, 4 H, C(6)*H*), 7.78 (m, 4 H, C(2)*H*), 7.64 (m, 4 H, C(5)*H*), 7.33 (m, 4 H, C(4)*H*), -2.78 ppm (s, 2 H, *NH*). ^{13}C{^{1}H} NMR (150 MHz; $CDCl_3$; 298 K) δ_C = 158.1, 143.6, 127.8, 127.6, 120.6, 120.0, 113.7, 55.6 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 418 (5.60), 514 (4.27), 549 (4.09), 589 (3.94), 644 (3.83) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{48}H_{39}N_4O_4]^+$: 735.2966; found 735.2960. IR (ATR): ṽ = 3321, 2961, 2919, 2870, 2719, 2618, 2542, 1817, 1596, 1576, 1463, 1401, 1350, 1266, 1164, 1110, 1044, 969, 913, 851, 797, 728, 697 cm^{-1}.

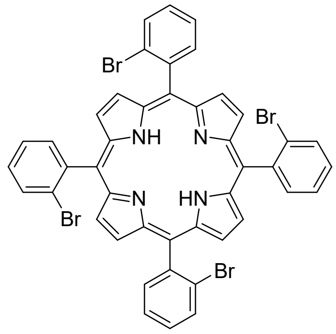
Characterization data in agreement with literature.[86]



5,10,15,20-Tetrakis(3-nitrophenyl) porphyrin (4j): Synthesis via **General Procedure A** yielded a purple solid (20 mg, 4%). Mp > 300 °C (from methanol); lit. mp > 300 °C.[86] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 9.12 (m, 4 H, C(2)*H*), 8.84 (s, 8 H, pyrrole *CH*), 8.75 (m, 4 H, C(6)*H*), 8.59 (m, 4 H, C(5)*H*), 8.03 (m, 4 H, C(4)*H*), -2.79 ppm (s, 2 H, *NH*). ^{13}C{^{1}H} NMR (150 MHz; $CDCl_3$; 298 K) δ_C = 147.1, 143.2, 139.8, 131.3, 128.4, 128.0, 12.4, 118.1 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 420 (5.60), 514 (4.40), 548 (4.09), 589 (4.01), 643 (3.93) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{44}H_{27}N_8O_8]^+$:

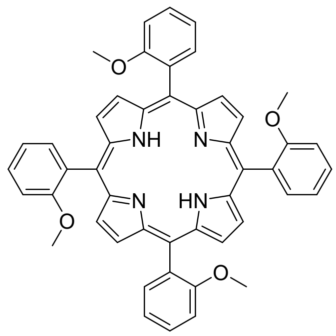
795.1946; found 795.1955. IR (ATR): ṽ = 4000, 3068, 2963, 2922, 2855, 1704, 1616, 1533, 1472, 1398, 1345, 1202, 1166, 1087, 1023, 935, 906, 799, 729, 677 cm^{-1}.

Characterization data in agreement with literature.[86]



5,10,15,20-Tetrakis(2-bromophenyl)porphyrin (4k): Synthesis via **General Procedure A** yielded a purple solid (38 mg, 7% yield). No further purification was performed to separate atropisomers. Mp > 300 °C (from methanol); lit. mp > 300 °C.[86] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.68 (s, 8 H, pyrrole *CH*), 8.27-7.98 (m, 8 H, Ar), 7.73-7.60 (m, 8 H, Ar), -2.60 ppm (s, 2 H, *NH*). ^{13}C{^{1}H) NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 142.5, 135.3, 135.2, 132.0, 130.9, 130.0, 127.6, 127.4, 125.8, 118.6 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 418 (5.53), 513 (4.31), 542 (4.05), 588 (3.96), 642 (3.76) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{44}H_{27}Br_4N_4]^+$: 926.8964; found 926.8956. IR (ATR): ṽ = 3314, 2160, 2016, 1560, 1464, 1422, 1348, 1212, 1189, 1157, 1052, 1026, 982, 966, 879, 799, 749, 721 cm^{-1}.

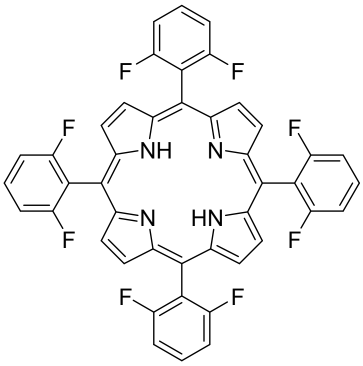
Characterization data in agreement with literature.[43b,86]



5,10,15,20-Tetrakis(2-methoxyphenyl) porphyrin (4l): Synthesis via **General Procedure A** yielded a purple solid as a mixture of atropisomers (33 mg, 8% yield). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[86] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.74 (s, 8 H, pyrrole *CH*), 8.12-7.92 (m, 4 H), 7.82-7.68 (m, 4 H, Ar), 7.42-7.21 (m, 8 H, Ar), 3.62-3.54 (s, 4x3 H, OCH_3), -2.59 ppm (s, 2 H, *NH*). ^{13}C{^{1}H) NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 159.6, 159.5, 159.5, 159.5, 159.4, 135.7, 135.7, 135.6, 135.6, 135.5, 131.3, 131.2, 130.5, 129.7, 119.4, 115.5, 115.5, 110.9, 110.9, 55.9 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 417 (5.58), 512 (4.37), 545 (4.19), 588 (4.12), 643 (4.05) nm. HRMS-APCI (*m/z*): $[M+H]^+$

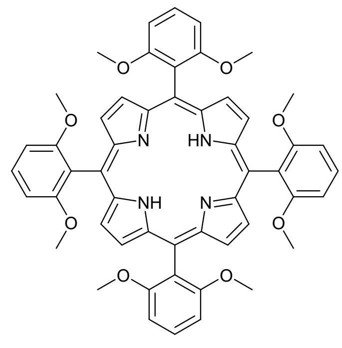
calculated for $[C_{48}H_{39}N_4O_4]^+$: 735.2966; found 735.2967. IR (ATR): ṽ = 2833, 1598, 1581, 1493, 1463, 1434, 1351, 1251, 1179, 1117, 1051, 1025, 966, 802, 758 cm^{-1}.

Characterization data in agreement with literature.[43b,86]



5,10,15,20-Tetrakis(2,6-difluorophenyl)porphyrin (4m): Synthesis via **General Procedure A** yielded a purple solid (48 mg, 11% yield). Mp >300 °C (from *n*-hexane). ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.87 (s, 8 H, pyrrole *CH*), 7.85-7.75 (m, 4 H, *p*-Ph), 7.42-7.37 (m, 8 H, *m*-Ph), -2.76 ppm (s, 2 H, *NH*). ^{13}C{^{1}H) NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 163.7, 161.2, 131.1, 131.0, 119.0, 118.8, 118.5, 111.4, 111.2, 106.1 ppm. ^{19}F NMR (376 MHz; $CDCl_3$; 298 K) δ_F = -108.2 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 412 (5.62), 507 (4.41), 537 (3.61), 584 (3.91), 643 (3.06) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{44}H_{23}F_8N_4]^+$: 759.1789; found 759.1785. IR (ATR): ṽ = 3338, 3113, 2925, 2855, 2740, 2632, 2549, 1936, 1624, 1589, 1558, 1461, 1343, 1274, 1235, 1157, 1072, 999, 961, 879, 818, 797, 778, 710 cm^{-1}.

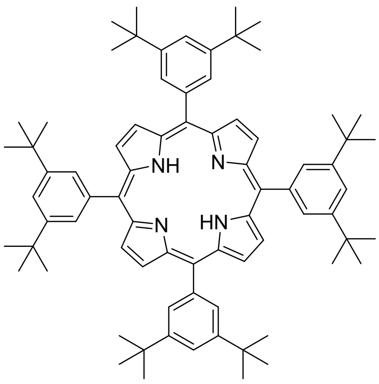
Characterization data in agreement with literature.[43b]



5,10,15,20-Tetrakis(2,6-dimethoxyphenyl)porphyrin (4n): Synthesis via **General Procedure A** yielded a purple solid (18 mg, 4%). Mp >300 °C (from *n*-hexane); lit. mp > 300 °C.[89] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.93 (s, 8 H, pyrrole CH), 7.40 (m, 8 H, *m*-Ph), 6.90 (m, 4 H, *p*-Ph), 3.96 (s, 24 H, OCH_3), -2.82 ppm (s, 2 H, *NH*). ^{13}C{^{1}H) NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 158.9, 144.0, 119.8, 113.9, 100.2, 55.7 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 417 (5.46), 512 (4.12), 543 (3.37), 588 (3.55), 641 (2.85) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{52}H_{47}N_4O_8]^+$: 855.3388; found

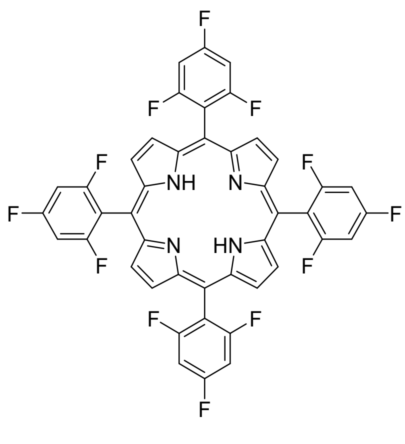
855.3370. IR (ATR): ṽ = 3673, 3306, 3088, 2931, 2834, 2537, 2162, 2033, 1977, 1733, 1588, 1469, 1429, 1344, 1299, 1247, 1103, 1035, 964, 796, 718 cm^{-1}.

Characterization data in agreement with literature.[89]



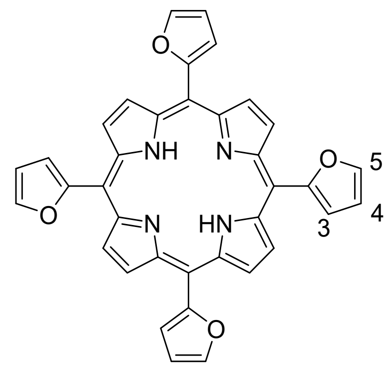
5,10,15,20-Tetrakis(3,5-di-*tert*-butyl-phenyl)porphyrin (4q): Synthesis via **General Procedure A** yielded a purple solid (196 mg, 33% yield). Mp >300 °C (from methanol); lit. mp > 300 °C.[90] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.97 (s, 8 H, pyrrole CH), 8.16 (d, ^{4}J = 1.7 Hz, 8 H, *o*-Ph), 7.85 (t, ^{4}J = 1.7 Hz, 4 H, *m*-Ph), 1.59 (s, 72 H, *t*Bu), -2.60 ppm (s, 2 H, *NH*). $^{13}C\{^{1}H\}$ NMR (150 MHz; $CDCl_3$, 298 K) δ_C = 148.7, 148.7, 148.7, 141.4, 131.2, 129.7, 121.3, 121.3, 121.2, 121.0, 35.1, 31.2 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 420 (5.47), 517 (4.07), 552 (3.84), 592 (3.62), 648 (3.61) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{76}H_{95}N_4]^+$: 1063.7551; found 1063.7567. IR (ATR): ṽ = 3320, 2961, 2870, 1815, 1590, 1473, 1425, 1363, 1298, 1246, 1204, 1154, 1078, 1000, 978, 914, 879, 801, 738, 713 cm^{-1}.

Characterization data in agreement with literature[56,90]

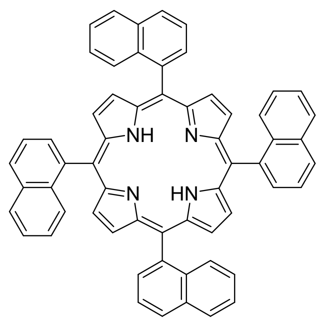


5,10,15,20-Tetrakis(2,4,6-trifluorophenyl)porphyrin (4t): Synthesis via **General Procedure A** yielded a purple solid (52 mg, 11% yield). Mp > 300 °C (from *n*-hexane). ^{1}H NMR (400 MHz; $CDCl_3$, 298 K) δ_H = 8.93 (s, 8 H, pyrrole *CH*), 8.26 (dd, ^{3}J = 8.6 Hz, ^{3}J = 6.8 Hz, 8 H, *m*-Ph), -2.79 ppm (s, 2 H, *NH*). $^{13}C\{^{1}H\}$ NMR (100 MHz; $CDCl_3$, 298 K) δ_C = 164.8, 163.8, 163.7, 163.7, 163.6, 162.3, 162.1, 161.4, 161.3, 161.2, 161.1, 115.2, 115.2, 115.0, 115.0, 114.8, 114.8, 105.4, 100.6, 100.6, 100.5, 100.3, 100.2,

100.1, 100.1 ppm. ^{19}F NMR (376 MHz; $CDCl_3$, 298 K) δ_F = -105.2, -105.9 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 412 (5.49), 506 (4.27), 536 (3.30), 583 (3.74), 635 (1.99) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{44}H_{19}F_{12}N_4]^+$: 831.1413; found 831.1420. IR (ATR): ṽ = 2368, 1633, 1593, 1383, 1440, 1352, 1175, 1118, 1037, 997, 966, 842, 794, 729, 713 cm^{-1}.
Characterization data in agreement with literature.[44e,91]



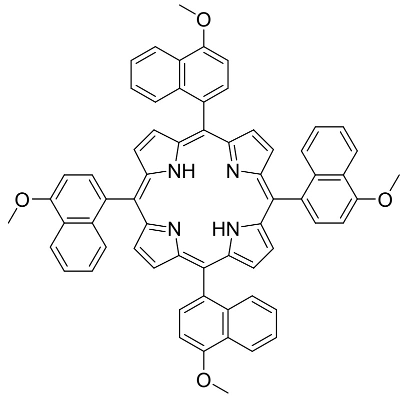
5,10,15,20-Tetra(furan-2-yl)porphyrin (4w): Synthesis via **General Procedure A** yielded a purple solid (45 mg, 14% yield). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[54] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 9.15 (s, 8 H, pyrrole *CH*), 8.12 (m, 4 H, C(3)*H*), 7.32 (m, 4 H, C(4)*H*), 7.03 (m, 4 H, C(5)*H*), -2.60 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (150 MHz; $CDCl_3$, 298 K) δ 154.3, 144.4, 131.4, 116.9, 111.9, 109.3 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 433 (5.23), 528 (3.88), 574 (3.84), 669 (3.21) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{36}H_{23}N_4O_4]^+$: 575.1714; found 575.1723. IR (ATR): ṽ = 3324, 3122, 2925, 2855, 1560, 1471, 1376, 1257, 1190, 1153, 1078, 1020, 975, 920, 885, 794, 718 cm^{-1}.
Characterization data in agreement with literature.[54,92]



5,10,15,20-Tetrakis(naphthalen-1-yl)porphyrin (4y): Synthesis via **General Procedure A** yielded a purple solid (122 mg, 27%). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[93] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.50 (m, 8 H, Ar*H*), 8.26 (m, 8 H, Ar*H*), 8.12-8.09 (m, 4 H, Ar*H*), 7.85-7.82 (m, 4 H, Ar*H*), 7.47 (m, 4 H, Ar*H*), 7.20 (m, 4 H, Ar*H*), 7.12 (m, 4 H, Ar*H*), -2.22 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 139.2, 136.8, 136.7, 132.9, 132.8, 131.3, 128.7, 127.8, 126.2, 125.7, 124.2, 117.7 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 423 (5.51), 515 (4.16), 548 (3.19), 589 (3.38), 645 (1.85) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{60}H_{39}N_4]^+$: 815.3169; found 815.3183. IR

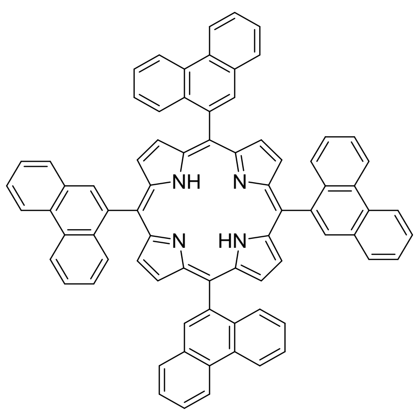
(ATR): ṽ = 3315, 3138, 3047, 2963, 2936, 2704, 2527, 2161, 2032, 1976, 1817, 1578, 1558, 1505, 1473, 1433, 1399, 1372, 1343, 1255, 1248, 1227, 1168, 1155, 1149, 1096, 1063, 1047, 1016, 979, 965, 949, 914, 887, 867, 829, 803, 789, 740, 729, 710, 652 cm^{-1}.

Characterization data in agreement with literature.[43b,93]



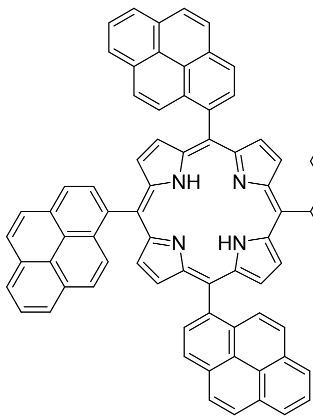
5,10,15,20-Tetrakis(4-methoxynaphthalen-1-yl)porphyrin (4z): Synthesis via **General Procedure A** yielded purple solid (105 mg, 20%). Mp > 300 °C (from *n*-hexane). ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.53 (s, 8 H, pyrrole *CH*; m, 4 H, Ar*H*; overlapping), 8.18-8.13 (m, 4 H, Ar*H*), 7.50-7.46 (m, 4 H, Ar*H*), 7.20-7.13 (m, 12 H, Ar*H*), 4.28 (s, 12 H, OCH_3), -2.21 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 155.8, 137.6, 132.7, 132.6, 131.5, 128.6, 126.6, 124.9, 124.7, 121.7, 117.7, 102.5, 55.8 ppm. UV/Vis (CH_2Cl_2; 298 K): λ_{max} (log ε) = 429 (5.12), 518 (4.35), 552 (3.80), 591 (3.83), 647 (3.73) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{64}H_{47}N_4O_4]^+$: 935.3592; found 935.3604. IR (ATR): ṽ = 3653, 3323, 3059, 2937, 2832, 2200, 1689, 1581, 1510, 1461, 1373, 1346, 1320, 1259, 1235, 1157, 1097, 1068, 1024, 979, 935, 799, 755, 735, 711 cm^{-1}.

Characterization data in agreement with literature.[44h]

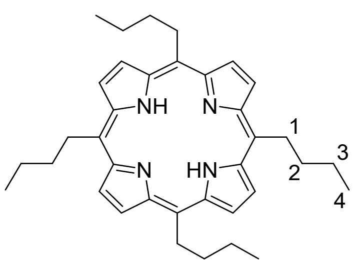


5,10,15,20-Tetra(phenanthren-9-yl)porphyrin (4ab): Synthesis via **General Procedure A** yielded a purple solid (90 mg, 16% yield). Mp > 300 °C (from methanol). ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.96 (m, 8 H, Ar*H*), 8.63-8.54 (s, 8 H, pyrrole *CH*; m, 4 H, Ar*H*; overlapping), 8.04 (app s, 4H, Ar*H*),

7.85-7.76 (m, 8 H, Ar*H*), 7.63 (m, 4 H, Ar*H*), 7.26-7.21 (m, 8 H, Ar*H*), -2.06 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 137.6, 136.2, 133.7, 133.6, 130.9, 130.7, 130.1, 129.6, 129.1, 127.4, 127.3, 126.7, 126.3, 122.8, 122.5, 117.7 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 426 (5.39), 516 (4.17), 549 (3.62), 590 (3.70), 647 (3.43) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{76}H_{47}N_4]^+$: 1015.3795; found 1015.3790. IR (ATR): ṽ = 3317, 3067, 2929, 2711, 2608, 2535, 1959, 1814, 1712, 1613, 1559, 1476, 1450, 1347, 1264, 1162, 1041, 980, 940, 902, 798, 719 cm^{-1}.
Characterization data in agreement with literature.[94]

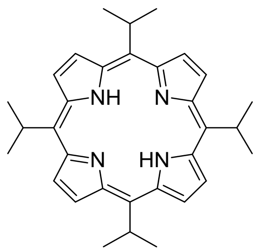


5,10,15,20-Tetra(pyren-1-yl)porphyrin (4ac): Synthesis via **General Procedure A** yielded a purple solid (53 mg, 8% yield). Mp > 300 °C (from methanol); lit. mp > 300 °C.[95] ^1H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.90-8.74 (m, 4 H, Ar*H*), 8.50-8.23 (s, 8 H, pyrrole *CH*; m, 16 H, Ar*H*; overlapping), 8.13-7.97 (m, 8 H, Ar*H*). 7.78-7.47 (m, 8 H, Ar*H*), -1.95 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 136.7, 132.7, 131.7, 131.5, 130.8, 128.1, 127.8, 127.6, 127.2, 126.3, 125.6, 125.3, 124.6, 124.1, 122.8, 118.5 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 324 (5.08), 337 (5.14), 432 (5.57), 520 (4.51), 556 (3.92), 593 (3.73), 649 (3.35) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{84}H_{47}N_4]^+$: 1111.3795; found 1111.3838. IR (ATR): ṽ = 3320, 3042, 2928, 1928, 1809, 1585, 1473, 1348, 1229, 1183, 1152, 1062, 960, 898, 840, 802, 716, 681 cm^{-1}.
Characterization data in agreement with literature.[95,96]



5,10,15,20-Tetra(*n*-butyl)porphyrin (4ad): Synthesis via **General Procedure A** yielded a purple solid (20 mg, 8% yield). Mp 239 °C (from *n*-hexane); lit. mp > 300 °C.[97] ^1H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 9.49 (s, 8 H, pyrrole *CH*), 4.97 (t, ^3J = 7.4 Hz, 8 H, C(1)H_2), 2.54 (m, 8 H, C(2)H_2), 1.92-1.80 (m, 8 H, C(3)*H*$_2$), 1.18 (t, ^3J = 7.6 Hz, 12 H, CH_3), -2.60 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$; 298 K) δ_C = 118.4, 40.8, 35.3, 23.7, 14.2 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 417 (5.66), 519 (4.24), 554 (4.04), 601 (3.64), 658 (3.88) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{36}H_{47}N_4]^+$: 535.3795; found 535.3796. IR (ATR): ṽ = 3328, 3127, 2953, 2921, 2856, 2638, 1819, 1779, 1556, 1487, 1462, 1355, 1232, 1166, 1066, 975, 936, 914, 791, 736 cm^{-1}.

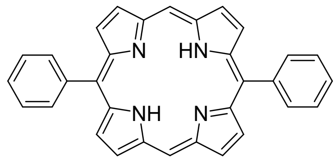
Characterization data in agreement with literature.[44g,55,97]



5,10,15,20-Tetra(isopropyl)porphyrin (4ae): Synthesis via **General Procedure A** yielded a purple solid (21 mg, 8% yield). Mp >300 °C (from *n*-hexane). ^1H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 9.51 (s, 8 H, pyrrole C*H*), 5.37 (sep, ^3J = 7.3 Hz, 4 H, C*H*(CH_3)$_2$), 2.38 (d, ^3J = 7.3 Hz, 24 H, CH_3), -1.73 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ (100 MHz; $CDCl_3$; 298 K) δ_C = 143.7, 129.1, 123.7, 35.2, 28.7 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 420 (5.32), 523 (4.04), 559 (3.85), 602 (3.60), 658 (3.60) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{32}H_{39}N_4]^+$: 479.3169; found 479.3165. IR (ATR): ṽ = 3322, 3156, 2960, 2928, 2872, 1685, 1556, 1457, 1363, 1305, 1262, 1177, 1121, 1038, 1023, 969, 913, 789, 728 cm^{-1}.

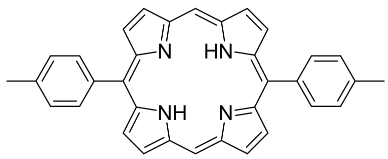
Characterization data in agreement with literature.[33,55]

Compound characterization for compounds **7a**-**7ae** and **8c**-**8g**



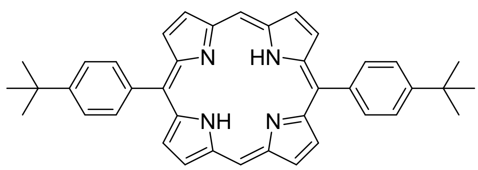
5,15-Diphenylporphyrin (7a): Synthesis via **General Procedure B** yielded a purple solid (77 mg, 44% yield). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[98] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 10.30 (s, 2 H, *meso CH*), 9.39 (d, ^{3}J = 4.5 Hz, 4 H, pyrrole *CH*), 9.10 (d, ^{3}J = 4.5 Hz, 4 H, pyrrole *CH*), 8.29 (m, 4 H, *o*-Ph), 7.82 (m, 6 H, *m,p*-Ph), -3.09 ppm (s, 2 H, *NH*). ^{13}C{^{1}H} NMR (150 MHz; $CDCl_3$; 298 K) δ_C = 147.2, 145.2, 141.4, 134.9, 131.6, 131.1, 127.8, 127.1, 120.6, 119.9, 105.3 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 406 (5.59), 502 (4.24), 535 (3.72), 575 (3.73), 629 (3.20) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{32}H_{23}N_4]^+$: 463.1917; found 463.1914. IR (ATR): ṽ = 2971, 2929, 2866, 2366, 2364, 2085, 1578, 1532, 1482, 1437, 1407, 1323, 1277, 1267, 1237, 1195, 1174, 1145, 1066, 1053, 1032, 1000, 985, 972, 954, 925, 904, 857, 795, 784, 747, 717, 688 cm^{-1}.

Characterization data in agreement with literature.[98,99]

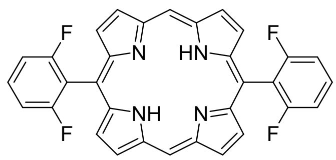


5,15-Bis(4-methylphenyl)porphyrin (7b): Synthesis via **General Procedure B** yielded a purple solid (37 mg, 20% yield). Mp > 300 °C (from *n*-hexane). ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 10.30 (s, 2 H, *meso CH*), 9.39 (d, ^{3}J = 4.5 Hz, 4 H, pyrrole *CH*), 9.10 (d, ^{3}J = 4.5 Hz, 4 H, pyrrole *CH*), 8.16 (d, ^{3}J = 7.6 Hz, 4 H, *o*-Ph), 7.61 (d, ^{3}J = 7.6 Hz, 4 H, *m*-Ph), 2.73 (s, 6 H), -3.09 ppm (s, 2 H, *NH*). ^{13}C{^{1}H} NMR (150 MHz; $CDCl_3$; 298 k) δ_c = 147.3, 145.2, 145.1, 138.5, 13.4, 134.8, 131.5, 131,1, 127.8, 119.2, 105.2, 21.5 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 406 (5.40), 503 (4.02), 537 (3.41), 576 (3.31), 630 (2.36) nm. HRMS-APCI (m/z): $[M+H]^+$ calculated for $[C_{34}H_{27}N_4]^+$: 491.2230; found 491.2230. IR (ATR): ṽ = 3268, 3112, 3024, 2923, 2874, 2545, 2163, 2041, 1977, 1816, 1707, 1580, 1491, 1407, 1327, 1235, 1181, 1143, 1050, 987, 956, 852, 783, 738, 693 cm^{-1}.

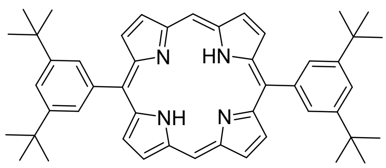
Characterization data in agreement with literature.[99]



5,15-Bis(4-*tert*-butylphenyl)porphyrin (7d): Synthesis via **General Procedure B** yielded a purple solid (38 mg, 18%). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[65e] ^{1}H NMR (400 MHz; $CDCl_3$, 298 K) δ_H = 10.74 (s, 2 H, *meso CH*), 9.32 (d, ^3J = 4.8 Hz, 4 H, pyrrole *CH*), 8.91 (d, ^3J = 4.8 Hz, 4 H, pyrrole *CH*), 8.43 (d, ^3J = 8.2 Hz, 4 H, *o*-Ph), 8.01 (d, ^3J = 8.2 Hz, 4 H, *m*-Ph), 1.66 (s, 18 H, *t*Bu), -0.59 (s, 2 H, *NH*) ppm. $^{13}C\{^1H\}$ NMR (150 MHz; $CDCl_3$; 298 K) δ_C = 153.2, 146.9, 143.2, 138.6, 136.7, 129.1, 128.4, 125.6, 121.9, 106.4, 31.7 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 407 (5.48), 503 (4.11), 537 (3.71), 576 (3.63), 631 (3.27) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{40}H_{39}N_4]^+$: 575.3169; found 575.3158. IR (ATR): ṽ = 2955, 2928, 2866, 1792, 1708, 1461, 1397, 1362, 1267, 1239, 1194, 1146, 1107, 1046, 973, 959, 850, 788, 747, 691 cm^{-1}.
Characterization data in agreement with literature.[65e]



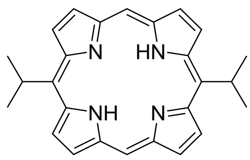
5,15-Bis(2,6-difluorophenyl)porphyrin (7m): Synthesis via **General Procedure B** yielded a purple solid (52 mg, 26% yield). Mp > 300 °C (from methanol); lit. mp > 300 °C.[100] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 10.32 (s, 2 H, *meso CH*), 9.42 (d, ^3J = 4.5 Hz, 4 H, pyrrole *CH*), 9.04 (d, ^3J = 4.5 Hz, 4 H, pyrrole *CH*), 7.87-7.77 (m, 2 H, *p*-Ph), 7.46-7.39 (m, 4 H, *m*-Ph), -3.16 ppm (s, 2H, *NH*). ^{19}F NMR (376 MHz; $CDCl_3$) δ_F = -108.4 ppm. $^{13}C\{^1H\}$ NMR (150 MHz; $CDCl_3$; 298 K) δ_c = 163.7, 161.2, 146.8, 145.7, 132.4, 131.0, 130.9, 130.1, 118.4, 111.6, 111.3, 105.7, 104.7 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 402 (5.41), 498 (4.22), 531 (3.82), 574 (3.76),627 (3.45) nm. HRMS-APCI (m/z): $[M+H]^+$ calculated for $[C_{32}H_{19}F_4N_4]^+$: 535.1540; found 535.1543. IR (ATR): ṽ = 3311, 3065, 2927, 2743, 2169, 2036, 1712, 1623, 1575, 1460, 1409, 1339, 1270, 1231, 1193, 1138, 1049, 991, 954, 911, 853, 781, 739, 691 cm^{-1}.
Characterization data in agreement with literature.[100]



5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrin (7q): Synthesis via **General Procedure B** yielded a purple solid (108 mg, 42% yield). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[101] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 10.30 (s, 2 H, *meso CH*), 9.44 (d, ^3J = 4.5 H, 4 H, pyrrole *CH*), 9.20 (d, ^3J = 4.5 Hz, 4 H, pyrrole *CH*), 8.22 (d, ^4J = 1.8 Hz, 4 H, *o*-Ph), 7.91 (t, ^4J = 1.8 Hz, 2 H, *p*-Ph), 1.64 (s, 36 H, *t*Bu), -2.93 (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (150 MHz; $CDCl_3$; 298 K) δ_c = 149.2, 147.5, 145.1, 140.5, 31.6, 131.3, 130.3, 121.2, 120.5, 105.1, 35.2, 31.9 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 408 (5.28), 504 (3.91), 537

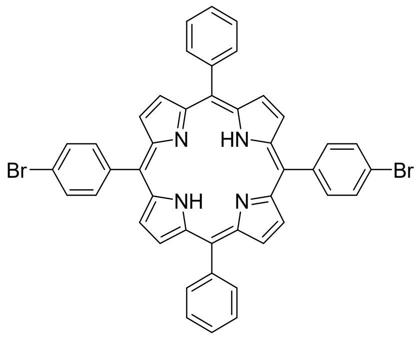
(3.50), 575 (3.48), 630 (3.14) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{48}H_{55}N_4]^+$: 687.4421;found 687.4414. IR (ATR): ṽ = 3305, 2961, 2869, 2516, 2163, 2038, 1980, 1736, 1592, 1476, 1363, 1250, 1049, 963, 917, 856, 790, 738 cm^{-1}.

Characterization data in agreement with literature.[101,102]



5,15-Diisopropylporphyrin (7ae): Synthesis via **General Procedure B** yielded a purple solid (23 mg, 16% yield). Mp > 300 °C (from methanol); lit. mp 320-323 °C.[103] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 10.22 (s, 2 H, *meso CH*), 9.76 (d, ^3J = 4.5 Hz, 4 H, pyrrole *CH*), 9.44 (d, ^3J = 4.5 Hz, 4 H, pyrrole *CH*), 5.73 (sept, ^3J = 7.2 Hz, 2 H, C*H*$(CH_3)_2$), 2.50 (d, ^3J = 7.2 H, 12 H, CH_3), -2.44 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (150 MHz; $CDCl_3$; 298 K) δ_c = 147.2, 143.4, 132.0, 128.2, 125.1, 104.3, 34.5, 28.9 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 402 (5.38), 503 (4.04), 533 (2.88), 575 (3.31), 629 (3.28) nm. HRMS-APCI (m/z): $[M+H]^+$ calculated for $[C_{26}H_{27}N_4]^+$: 395.2230; found 395.2233. IR (ATR): ṽ = 3213, 3109, 2957, 2924, 2855, 2165, 2037, 1709, 1465, 1379, 1358, 1310, 1262, 1243, 1191, 1162, 1106, 1055, 1039, 955, 915, 853, 787, 750, 725, 688 cm^{-1}.

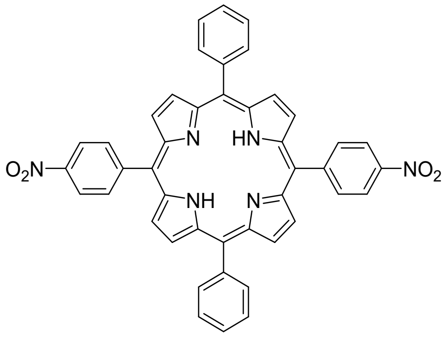
Characterization data in agreement with literature.[103]



5,15-Bis(4-bromophenyl)-10,20-diphenylporphyrin (8c): Synthesis via **General Procedure B** yielded a purple solid (57 mg, 20%). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[104] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.92 (d, ^3J = 4.7 Hz, 4 H, pyrrole *CH*), 8.87 (d, ^3J = 4.7 Hz, 4 H, pyrrole *CH*), 8.28-8.24 (m, 4 H, *o*-Ph), 8.13-8.08 (d, ^3J = 7.7 Hz, 4 H, *o*-Ph), 7.94-7.89 (d, ^3J = 7.7 Hz, 4 H, *m*-Ph), 7.85-7.76 (m, 6 H, *m*,*p*-Ph), -2.74 ppm (s, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (150 MHz; $CDCl_3$; 298 K) δ_c = 142.0,141.9, 141.1,135.9,134.6, 131.3, 130.0, 129.9, 127.9, 127.8, 126.8, 122.6, 122.5, 120.7, 120.5, 118.9, 118.7, 118.6 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 418 (5.60), 514 (4.18), 549 (3.69), 588 (3.39), 644 (2.60) nm. HRMS-APCI (*m/z*): $[M+H]^+$ calculated for $[C_{44}H_{29}Br_2N_4]^+$: 771.0753; found 771.0748. IR

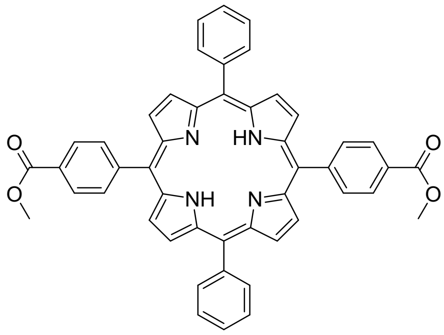
(ATR): ṽ = 3317, 2929, 2561, 2494, 2167, 2034, 1977, 1690, 1554, 1474, 1394, 1352, 1179, 1070, 1011, 965, 846, 796, 727, 700 cm^{-1}.

Characterization data in agreement with literature.[104]



5,15-Bis(4-nitrophenyl)-10,20-diphenylporphyrin (8f): Synthesis via **General Procedure B** yielded a purple solid (29 mg, 11%). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[105] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.89 (d, ^3J = 4.5 Hz, 4 H, pyrrole *CH*), 8.75 (d, ^3J = 4.5 Hz, 4 H, pyrrole *CH*), 8.64 (d, ^3J = 7.1 Hz, 4 H, *o*-Ph), 8.38 (d, ^3J = 7.1 Hz, 4 H, *m*-Ph), 8.20 (m, 4 H, *o*-Ph), 7.85-7.70 (m, 6 H, *m*,*p*-Ph), -2.79 ppm (s, 2 H, *NH*). ^{13}C{^{1}H) NMR (150 MHz; $CDCl_3$; 298 K) δ_C = 148.9, 147.8, 141.6, 135.1, 134.6, 128.1, 126.9, 122.0, 117.2 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 420 (5.04), 515 (3.74), 551 (3.37), 590 (3.03), 647 (2.77) nm. HRMS-APCI (*m/z*): [M+H]$^+$ calculated for $[C_{44}H_{29}N_6O_4]^+$: 705.2245; found 705.2245. IR (ATR): ṽ = 3649, 3311, 3106, 3069, 2931, 2611, 2540, 2457, 2162, 2032, 1980, 1701, 1594, 1512, 1402, 1341, 1223, 1108, 965, 846, 796, 696 cm^{-1}.

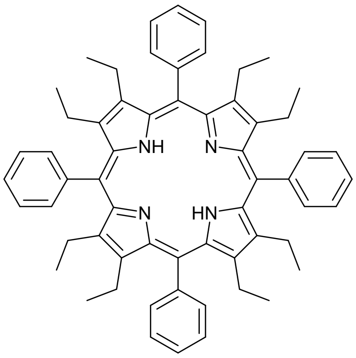
Characterization data in agreement with literature.[105]



Dimethyl 4,4'-(10,20-diphenylporphyrin-5,15-diyl)dibenzoate (8g): Synthesis via **General Procedure B** yielded a purple solid (14 mg, 5% yield). Mp > 300 °C (from *n*-hexane); lit. mp > 300 °C.[106] ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.90 (d, ^3J = 5.0 Hz, 4 H, pyrrole *CH*), 8.82 (d, ^3J = 5.0 H, 4 H, pyrrole *CH*), 8.48 (d, ^3J =7.8 Hz, 4 H, *o*-Ph), 8.34 (d, ^3J = 7.8 Hz, 4 H, *m*-Ph), 8.26-8.22 (m, 4 H, *o*-Ph), 7.85-7.75 (m, 6 H, *m*,*p*-Ph), 4.14 (s, 6 H, OCH_3), -2.75 ppm (s, 2 H, *NH*). ^{13}C{^{1}H) NMR (150 MHz; $CDCl_3$; 298 K) δ_C = 167.3, 147.0, 141.9, 134.6, 129.7, 128.0, 126.8, 120.6, 119.0, 52.5 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 419 (5.43), 515 (4.04), 549 (3.62), 589 (3.45), 645 (3.45) nm. HRMS-ESI (m/z): [M+H]$^+$

calculated for $[C_{48}H_{35}N_4O_4]^+$: 731.2653; found 731.2659. IR (ATR): $\tilde{\nu}$ = 3320, 2954, 2716, 2613, 2545, 2163, 1984, 1717, 1603, 1565, 1473, 1435, 1403, 1273, 1181, 1103, 965, 869, 795, 723, 705 cm^{-1}. Characterization data in agreement with literature.[106]

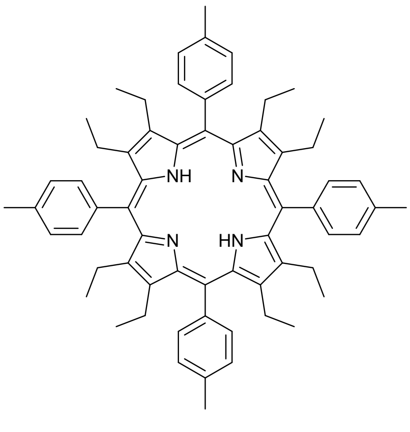
Compound characterization for compounds **11a**-**11s**



2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetraphenylporphyrin (11a): Synthesis via **General Procedure C** yielded purple crystals (70 mg, 30% yield). Mp > 300 °C (from KOH/EtOH 0.4%, w/v). ^{1}H NMR (400 MHz; C_6D_6; 298 K) δ_H = 8.30 (d, ^{3}J = 7.7 Hz, 8 H, *Ph*), 7.40-7.42 (m, 12 H, overlapping, *Ph*), 2.67 (m, 8 H, *CH$_2$*CH$_3$), 2.21 (appbrs, 8 H, *CH$_2$*CH$_3$), 0.56 ppm (t, ^{3}J = 7.4 Hz, 24 H, CH$_2$*CH$_3$*). ^{13}C{^{1}H) NMR (100 MHz; C_6D_6; 298 K) δ_c = 141.4, 136.0, 127.3, 118.4, 19.8, 17.3 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 455 (5.09), 555 (3.78), 600 (3.62), 634 (3.36), 707 (3.25) nm. HRMS-APCI (m/z): $[M+H]^+$ calculated for $[C_{60}H_{63}N_4]^+$: 839.5046; found 839.5047. IR (ATR): ṽ = 2961, 2924, 2869, 1596, 1493, 1442, 1371, 1347, 1314, 1277, 1262, 1172, 1133, 1089, 1071, 1052, 1016, 950, 876, 838, 791, 753, 735, 699 cm^{-1}.

Characterization data in agreement with literature.[76f]

Note: N-H protons may be 'missing' or broaden extensively in ^{1}H NMR spectra of free-base and dicationic dodecasubstituted porphyrins due to their fast exchange on the NMR timescale, because of slower N-H tautomerism or chemical exchange with other solvents in solution.[76f,107]

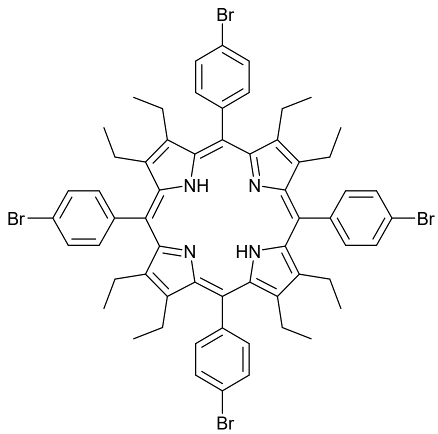


2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetrakis(4-methyl)phenylporphyrin (11b): Synthesis via **General Procedure C** yielded purple crystals (72 mg, 29%). Mp > 300 °C (from KOH/EtOH 0.4%, w/v). ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.20 (d, ^{3}J = 7.6 Hz, 8 H, *Ph*), 7.48 (d, ^{3}J = 7.6 Hz, 8 H, *Ph*), 2.68 (s, 12 H, Ph-*CH$_3$*), 1.43-2.52 (appbrs, 16 H, overlapping, *CH$_2$*CH$_3$), 0.46 (appbrs, 24H, CH$_2$*CH$_3$*), -2.05

ppm (brs, 2 H, *NH*). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$; 298 K) δ_c = 138.2, 137.9, 127.8, 117.8, 21.8, 19.4, 17.0 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 457 (5.22), 556 (4.06), 604 (3.95), 636 (3.80), 707 (3.71) nm. HRMS-APCI (m/z): $[(M+H)]^+$ calculated for $[C_{64}H_{71}N_4]^+$: 895. 5673; found: 895.5686. IR (ATR): ṽ = 2962, 2923, 2870, 1695, 1508, 1450, 1372, 1312, 1179, 1105, 1055, 1013, 956, 792, 777 cm^{-1}.

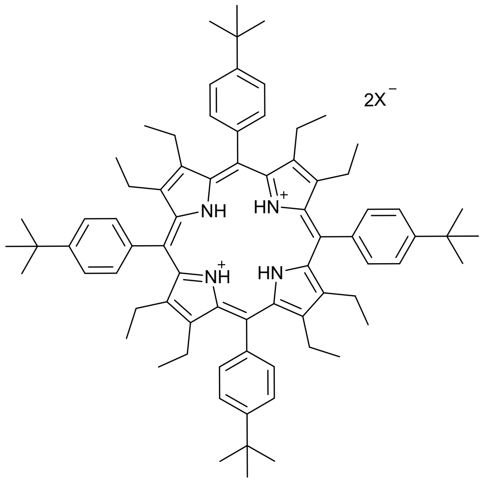
Characterization data in agreement with literature.[68]

Note: 'Free base' of compound **11b** reported in the literature but full characterization not previously described.[67,108]



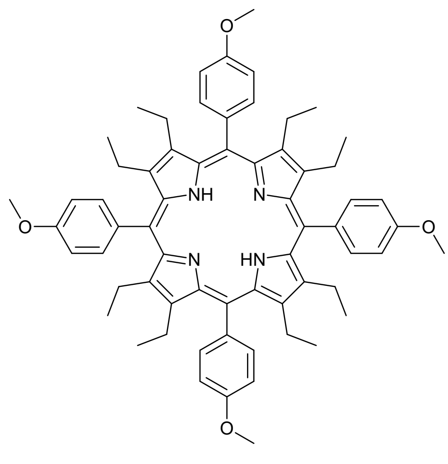
5,10,15,20-Tetrakis(4-bromo)-2,3,7,8,12,13,17,18-octaethylporphyrin (11c): Synthesis via **General Procedure C** yielded a purple solid (63mg, 20% yield). > 300 °C (from KOH/EtOH 0.4%, w/v); lit. mp > 300 °C.[76d] ^1H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.19 (d, ^3J = 8.3 Hz, 8H, *Ph*), 7.85 (d, ^3J = 8.3 Hz, 8H, *Ph*), 2.05-2.54 (appbrd, 16H, CH_2CH_3), 0.47 (apps, 24H, CH_2CH_3), -2.09 (brs, 2H, *NH*). $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$; 298 K) δ_c = 140.3, 139.6, 130.4, 123.2, 122.1, 121.7, 116.9, 19.5, 16.9 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 460 (5.35), 557 (4.17), 604 (4.07), 638 (3.90), 707 (3.83) nm. HRMS-APCI (m/z): $[(M+H)]^+$ calculated for $[C_{60}H_{59}N_4Br_4]^+$: 1151.1468; found: 1151.1435. IR (ATR): ṽ = 3650, 2972, 2929, 2871, 2871, 1699, 1620, 1587, 1488, 1453, 1392, 1374, 1315, 1263, 1176, 1133, 1102, 1069, 1011, 953, 825, 798, 782, 693 cm^{-1}.

Characterization data in agreement with literature.[76d]



2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetrakis(4-*tert*-butyl)phenylporphyrindiium (11d): Compound previously not reported in the literature. Counteranion was not identified. Synthesis via **General Procedure C** yielded a green solid (12 mg, 4% yield). Mp 295-300 °C (decomposition) (from methanol). ^{1}H NMR (400 MHz; CD_2Cl_2; 298 K) δ_H = 8.47 (d, ^{3}J = 7.9 Hz, 8H, *Ph*), 7.90 (d, ^{3}J = 7.9 Hz, 8H, *Ph*), 2.38 (dq, ^{2}J = 14.8 HZ, ^{3}J = 7.4 Hz, 8H, CH_2CH$_3$), 2.15 (dq, ^{2}J = 14.8 HZ, ^{3}J = 7.4 Hz, 8H, CH_2CH_3), 2.09 (s, 45H, C$(CH_3)_3$) 0.27 ppm (t, ^{3}J = 7.4 Hz, 24H, CH_2CH_3). ^{13}C{^{1}H) NMR (100 MHz; CD_2Cl_2; 298 K) δ_c = 153.7, 145.0, 137.8, 137.2, 135.8, 125.6, 118.1, 35.4, 31.7, 18.8, 15.8 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 477 (5.23), 642 (3.69), 696 (4.33) nm. HRMS-APCI (m/z): [(M-3H)]$^{-}$ calculated for [$C_{76}H_{93}N_4$]$^{+}$: 1061.7406 found 1061.7393 IR (ATR): ṽ = 3673, 2968, 2928, 2903, 2871, 1706, 1606, 1549, 1515, 1465, 1403, 1364, 1316, 1267, 1194, 1107, 1058, 1019, 961, 859, 791, 814, 751, 662 cm^{-1}.

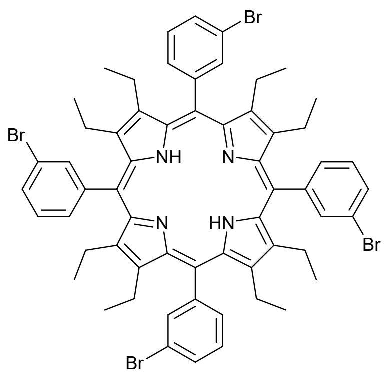
Note: N-H protons may be ‘missing’ or broaden extensively in ^{1}H NMR spectra of free-base and dicationic dodecasubstituted porphyrins due to their fast exchange on the NMR timescale, because of slow N-H tautomerism or chemical exchange with other solvents in solutions.[76f,107]



2,3,7,8,12,13,17,18-Octaethyl-5,10,15,20-tetrakis(4-methoxy)phenylporphyrin (11e): Synthesis via **General Procedure C** yielded a purple/red solid (119 mg, 45% yield). Mp > 300 °C (from KOH/EtOH 0.4%, w/v). ^{1}H NMR (600 MHz; $(CD_3)_2SO$; 298 K) δ_H = 8.40 (d, ^3J = 8.2 Hz, 8H, *Ph*), 7.54 (d, *J* = 8.2 Hz, 8H, *Ph*), 4.07 (s, 12H, O*CH₃*), 2.45-2.11 (appbrs, 16H, CH_2CH$_3$), 0.00 ppm (appbrs, 24H, CH$_2$$CH_3$). ^{13}C{^{1}H) NMR (100 MHz; $(CD_3)_2SO$; 298 K) δ_c = 161.3, 130.2, 114.2, 55.7, 17.7, 15.0 ppm. UV/Vis ($(CH_3)_2SO$; 25 °C): λ_{max} (log ε) = 476 (4.72), 656 (2.97), 706 (3.52) nm. HRMS-APCI (m/z): $[(M+H)]^+$ calculated for $[C_{64}H_{71}N_4O_4]^+$: 959.5470; found: 959.5464. IR (ATR): ṽ = 3416, 2214, 1637, 1595, 1536, 1511, 1418, 1254, 1173, 1020, 867, 786 cm^{-1}.

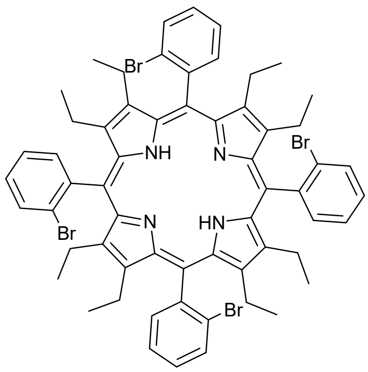
Characterization data in agreement with literature.[76a]

Note: N-H protons may be 'missing' or broaden extensively in ^{1}H NMR spectra of free-base and dicationic dodecasubstituted porphyrins due to their fast exchange on the NMR timescale, because of slow N-H tautomerism or chemical exchange with other solvents in solution.[76f,107]

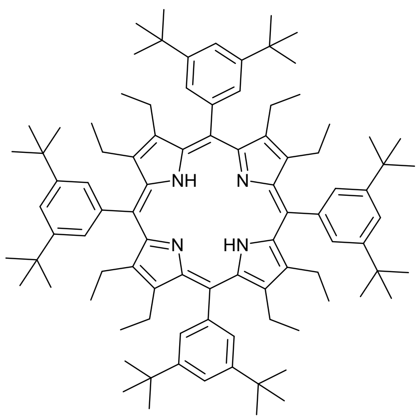


5,10,15,20-Tetrakis(3-bromo)phenyl-2,3,7,8,12,13,17,18-octaethylporphyrin (11h): Synthesis via **General Procedure C** yielded a purple solid (62 mg, 19% yield). Mp > 300 °C (from KOH/EtOH 0.4%, w/v). ^{1}H NMR (400 MHz; CD_2Cl_2; 298 K) δ_H = 8.55 (m, 4H, *Ph*), 8.29-8.27 (m, 4H, *Ph*), 7.91 (m, 4H, *Ph*), 7.63-7.61 (m, 4H, *Ph*), 2.55 (appbrs, 8H, CH_2CH$_3$), 2.02 (appbrs, 8H, CH_2CH$_3$) 0.44 (appbrs, 24H, CH$_2$$CH_3$), -2.10 ppm (brs, 2H, *NH*). ^{13}C{^{1}H) NMR (100 MHz; CD_2Cl_2; 298 K) δ_c = 142.2, 138.5, 134.9, 131.8, 129.2, 121.7, 117.2, 19.5, 16.8 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 458 (5.17), 556 (3.99), 602 (3.84), 631 (3.70), 706 (3.52) nm. HRMS-APCI (m/z): $[(M+H)]^+$ calculated for $[C_{60}H_{59}N_4Br_4]^+$: 1151.1468; found: 1151.1452. IR (ATR): ṽ = 2960, 2915, 2865, 1586, 1557, 1449, 1402, 1373, 1345, 1262, 1228, 1134, 1056, 1018, 994, 937, 833, 775, 691 cm^{-1}.

Note: 'Free base' of compound **11h** reported in the literature without full characterization.[76e]



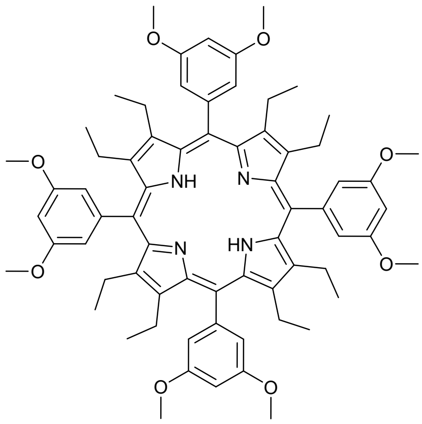
5,10,15,20-Tetrakis(2-bromophenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (11k): Synthesis via **General Procedure C** yielded a purple solid as an atropisomeric mixture (6 mg, 2% yield). Mp > 300 °C (from KOH/EtOH 0.4%, w/v). ^{1}H NMR (400 MHz; CD_2Cl_2; 298 K) δ_H = 8.44-8.27 (m, 4H, *Ph*), 7.97 (d, ^{3}J = 7.7 Hz, 4H, *Ph*), 7.69 (m, 4H, *Ph*), 7.61 (m, 4H, *Ph*), 2.59 (appbrs, 8H, *CH₂*CH₃), 2.01 (appbrs, 8H, *CH₂*CH₃), 0.69-0.45 (m, 24H, CH₂*CH₃*), -1.69 (brs, 2H, *NH*). ^{13}C{^{1}H) NMR (100 MHz; CD_2Cl_2; 298 K) δ_c = 147.3, 140.9, 137.6, 132.9, 130.6, 128.4-127.9, 126.9, 20.1-19.3, 16.8-16.3 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 461 (5.49), 559 (4.36), 600 (4.13), 634 (4.07), 704 (3.82) nm. HRMS-APCI (m/z): $[(M+H)]^+$ calculated for $[C_{60}H_{59}N_4Br_4]^+$: 1151.1468; found: 1151.1469. IR (ATR): ṽ = 3674, 2973, 2929, 2871, 1698, 1630, 1426, 1375, 1261, 1134, 1052, 1016, 955, 833, 751, 698 cm^{-1}.
Note: 'Free base' of compound **11h** reported in the literature without full characterization.[76e]



5,10,15,20-Tetrakis(3,5-di-*tert*-butyl)phenyl-2,3,7,8,12,13,17,18-octaethylporphyrin (11q): Compound not previously reported in the literature. Synthesis via **General Procedure C** yielded a purple solid (20 mg, 6% yield). Mp 295 °C (decomposition) (from KOH/EtOH 0.4%, w/v). ^{1}H NMR (400 MHz; $CDCl_3$; 298 K) δ_H = 8.29 (d, ^{4}J = 1.8 Hz, 4H, *Ph*), 8.16 (d, ^{4}J = 1.8 Hz, 4H, *Ph*), 2.36 (dq, ^{2}J = 14.7 Hz, ^{3}J = 7.6 Hz, 8 H, *CH₂*CH₃), 1.98 (dq, ^{2}J = 14.7 Hz, ^{3}J = 7.6 Hz, 8H, *CH₂*CH₃) 1.57 (s, 72H, C*(CH₃)₃*), 0.39 ppm (t, ^{3}J = 7.6 Hz, 24H, CH₂*CH₃*). ^{13}C{^{1}H) NMR (100 MHz; CD_2Cl_2; 298 K) δ_c = 150.3, 144.5, 138.2, 132.1, 122.8, 118.6, 35.3, 18.6, 16.2 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 455 (5.05), 553 (3.89), 596 (3.80), 635 (3.70), 702 (3.69) nm. HRMS-APCI (m/z): $[(M+H)]^+$ calculated for $[C_{92}H_{127}N_4]^+$:

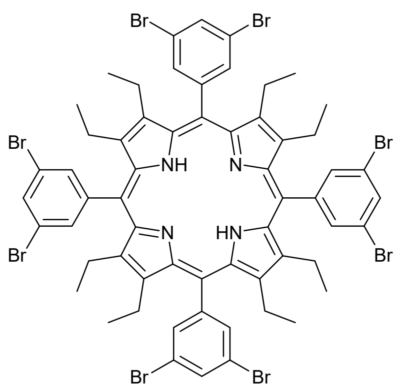
1288.0055; found: 1288.0030. IR (ATR): ṽ = 3689, 2965, 2926, 2903, 2870, 1701, 1593, 1455, 1430, 1394, 1364, 1249, 1057, 945, 901, 871, 827, 753, 716 cm^{-1}.

Note: Very poor solubility of the 'free base' compound **11q**. N-H protons may be 'missing' or broaden extensively in ^1H NMR spectra of free-base and dicationic dodecasubstituted porphyrins due to their fast exchange on the NMR timescale, because of slow N-H tautomerism or chemical exchange with other solvents in solution.[76f,107]



5,10,15,20-Tetrakis(3,5-dimethoxy)phenyl-2,3,7,8,12,13,17,18-octaethylporphyrin (11r): Synthesis via **General Procedure C** yielded a purple solid (85 mg, 29% yield). Mp 258-262 °C (decomposition) (from KOH/EtOH 0.4%, w/v); lit. mp 260 °C (decomposition).[76c] ^1H NMR (400 MHz; C_6D_6; 298 K) δ_H = 7.65 (d, ^4J = 2.3 Hz, 8 H, *Ph*), 7.01 (d, ^4J = 2.3 Hz, 4H, *Ph*), 3.42 (s, 24 H, O*CH₃*), 2.88 (dq, ^2J = 14.3 Hz, ^3J = 7.3 Hz, 8H, CH_2CH_3), 2.55 (appbrs, 8H, CH_2CH_3), 0.73 (t, ^3J = 7.3 Hz, 24H, CH_2CH_3), -0.72 ppm (brs, 2H, *NH*). $^{13}C\{^1H\}$ NMR (100 MHz; C_6D_6; 298 K) δ_c = 160.1, 143.4, 118.4, 114.6, 101.8, 55.3, 19.9, 17.8 ppm. UV/Vis (CH_2Cl_2; 25 °C): λ_{max} (log ε) = 455 (5.21), 552 (4.00), 597 (3.81), 630 (3.67), 700 (3.52) nm. HRMS-APCI (m/z): $[M-H]^-$ calculated for $[C_{68}H_{77}N_4O_8]^+$: 1077.5747; found 1077.5773. IR (ATR): ṽ = 2964, 2920, 2856, 1697, 1587, 1455, 1418, ,1353, 1315, 1194, 1147, 1059, 1017, 944, 927, 837, 799, 694 cm^{-1}.

Characterization data in agreement with literature.[76c]



5,10,15,20-Tetrakis(3,5-dibromophenyl)-2,3,7,8,12,13,17,18-octaethylporphyrin (11s): Compound not previously reported in the literature. Synthesis via **General Procedure C** yielded a purple solid (141 mg, 35% yield). Mp > 300 °C (from KOH/EtOH 0.4%, w/v). ^{1}H NMR (400 MHz; CD_3COOD; 298 K) δ_H = 8.80 (d, ^{4}J = 1.7 Hz, 8H, *Ph*), 8.27 (t, ^{4}J = 1.7 Hz, 4H, *Ph*), 2.61 (dq, ^{2}J = 14.9 Hz, ^{3}J = 7.4 Hz, 8H, CH_2CH_3), 2.25 (dq, ^{2}J = 14.9 Hz, ^{3}J = 7.4 Hz, 8H, CH_2CH_3), 0.22 ppm (t, ^{3}J = 7.4 Hz, 24H, CH_2CH_3). $^{13}C\{^{1}H\}$ NMR (100 MHz; CD_3COOD; 298 K) δ_c = 143.9, 141.1, 139.6, 138.9, 136.1, 126.0, 123.7, 117.5, 15.6 ppm. UV/Vis ($CHCl_3$:TEA, 99:1, v/v; 25 °C): λ_{max} (log ε) = 458 (4.68), 554 (3.96), 594 (3.87), 626 (3.83), 699 (3.77) nm. HRMS)-APCI (m/z: $[(M+H)]^{3+}$ calculated for $[C_{60}H_{57}Br_8N_4]^{3+}$: 1464.8045; found: 1464.7929. IR (ATR): ṽ = 3670, 3649, 2976, 2927, 1573, 1546, 1403, 1382, 1261, 1105, 1057, 1023, 943, 859, 822, 789, 758, 739, 698 cm^{-1}.

Note: Due to the very poor solubility of the 'free' base compound **11s,** the ^{1}H NMR and $\{^{1}H\}$ ^{13}C NMR was measured in deuterated acetic acid, hence the dication salt of **11s** was instead analyzed. N-H protons may be 'missing' or broaden extensively in ^{1}H NMR spectra of free-base and dicationic dodecasubstituted porphyrins due to their fast exchange on the NMR timescale, because of slow N-H tautomerism or chemical exchange with other solvents in solution.[76f,107]

^{1}H, $^{13}C\{^{1}H\}$ and

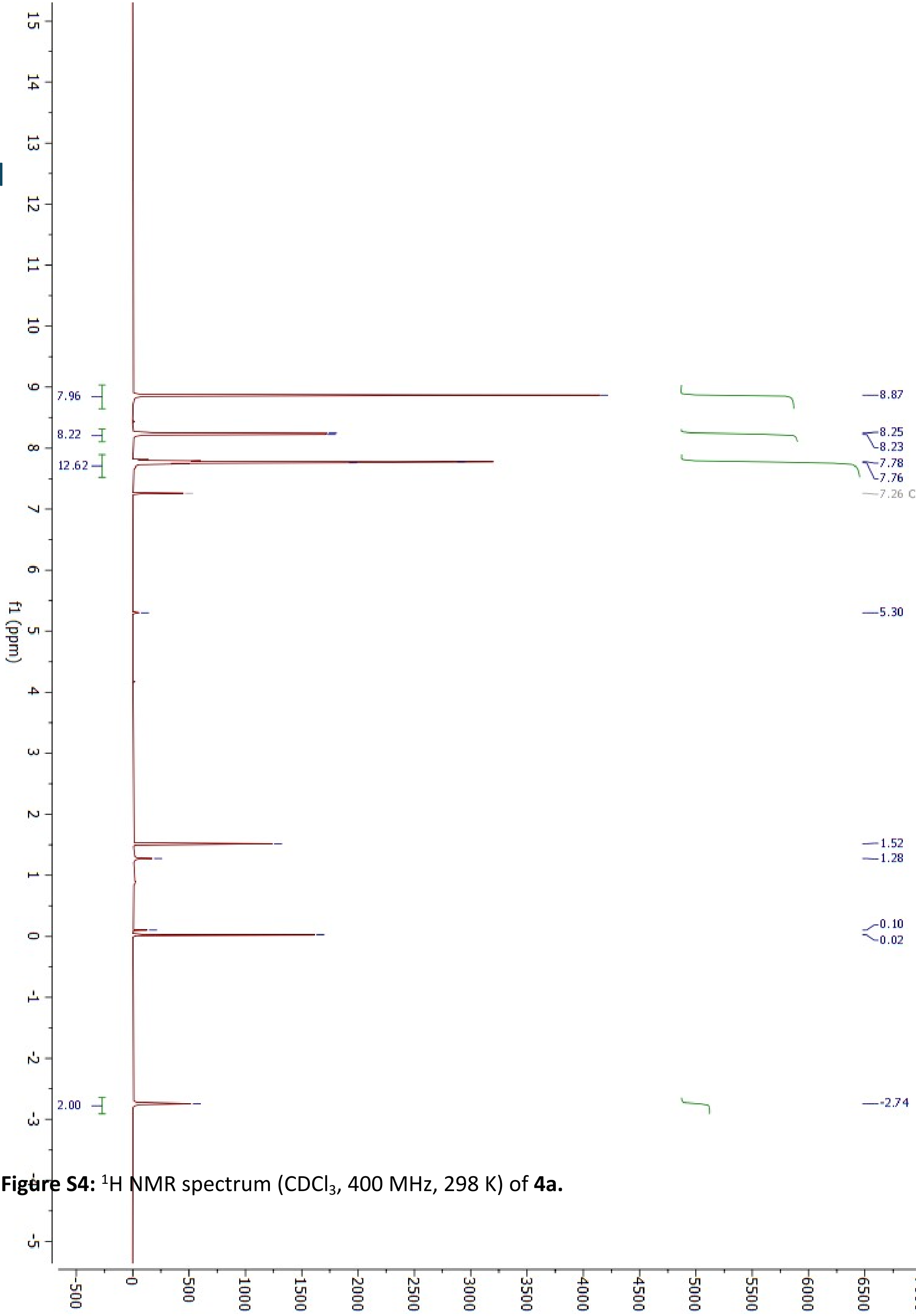


Figure S4: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4a.**

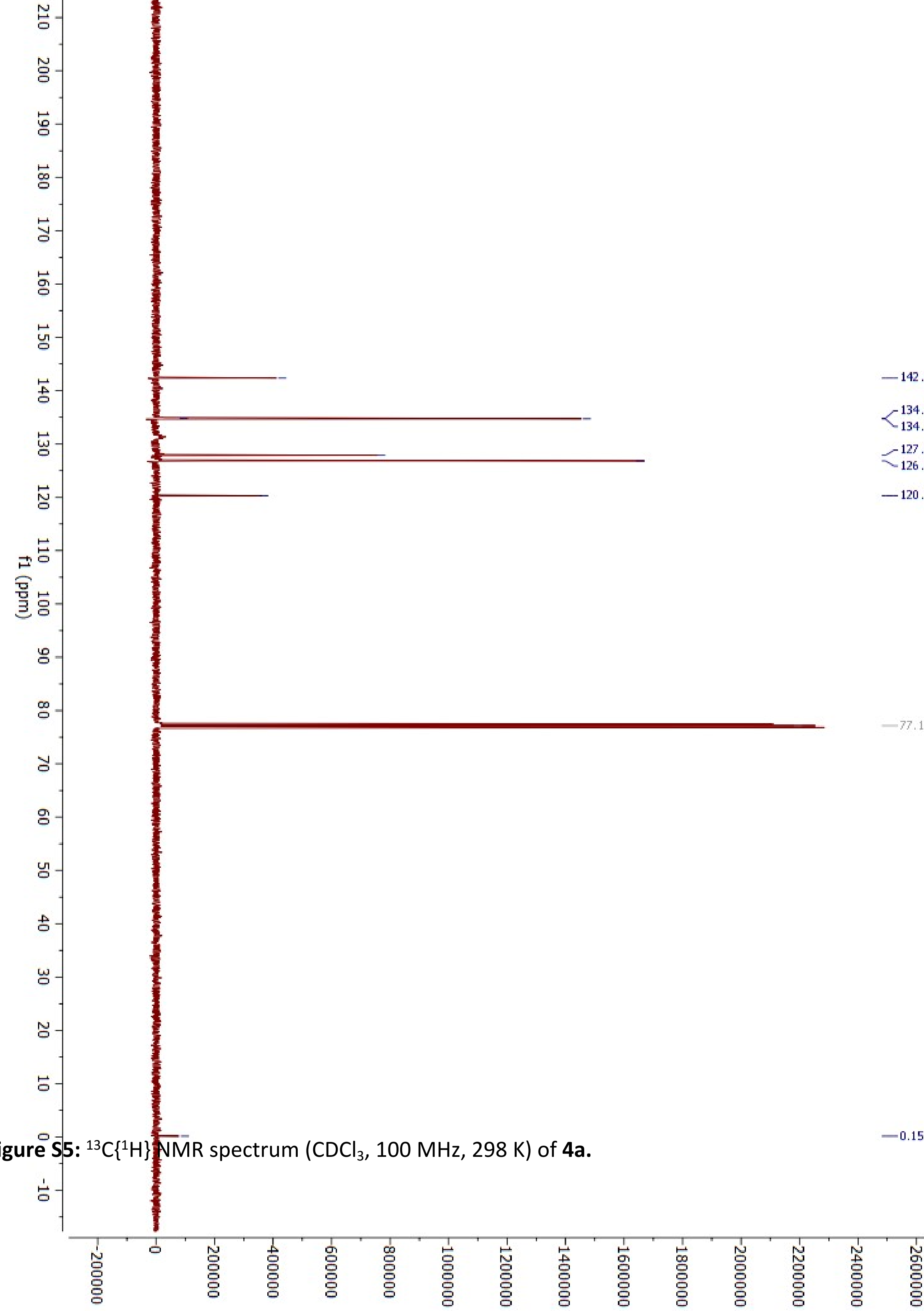


Figure S5: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4a.**

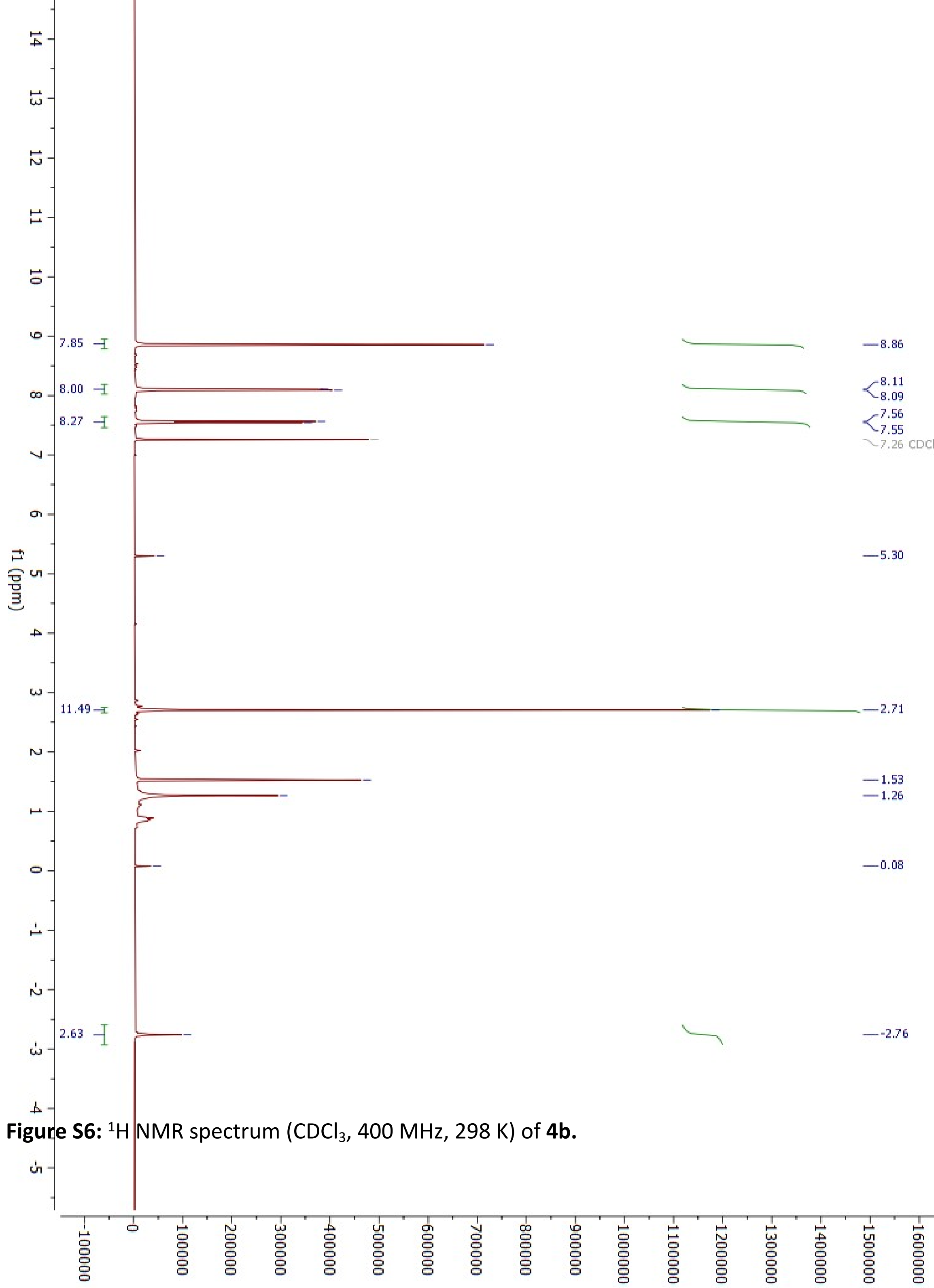


Figure S6: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4b.**

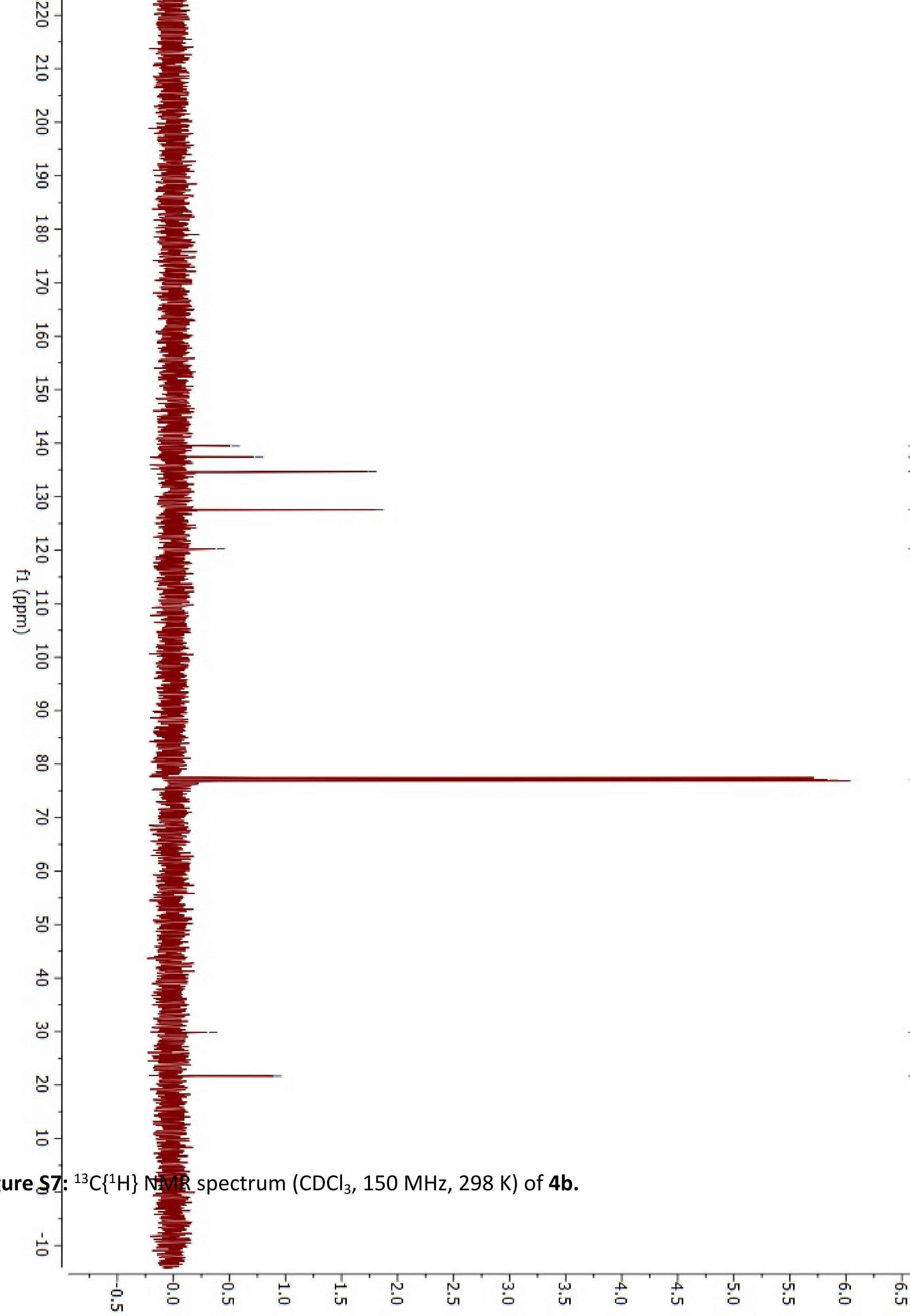


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **4b.**

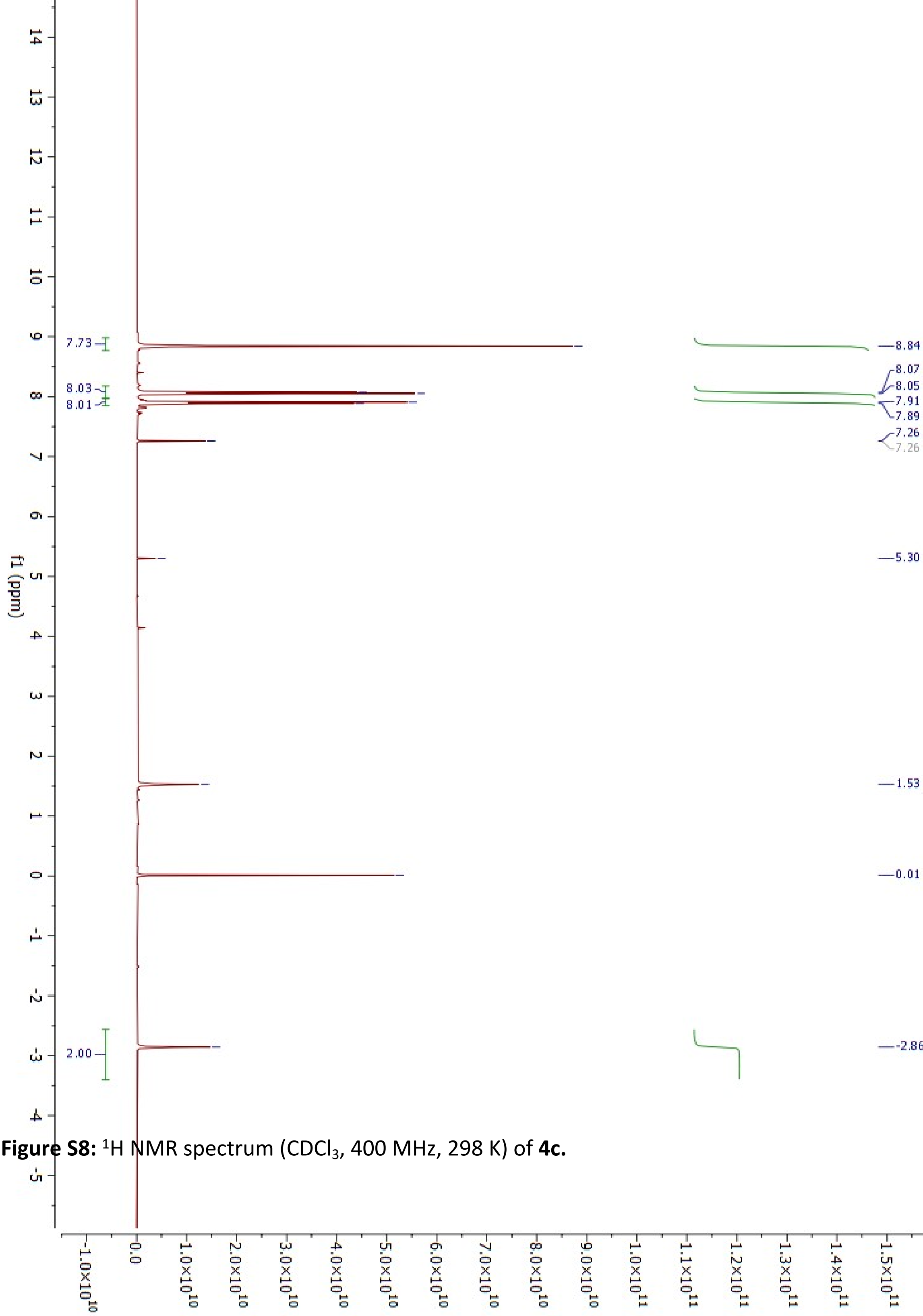


Figure S8: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4c.**

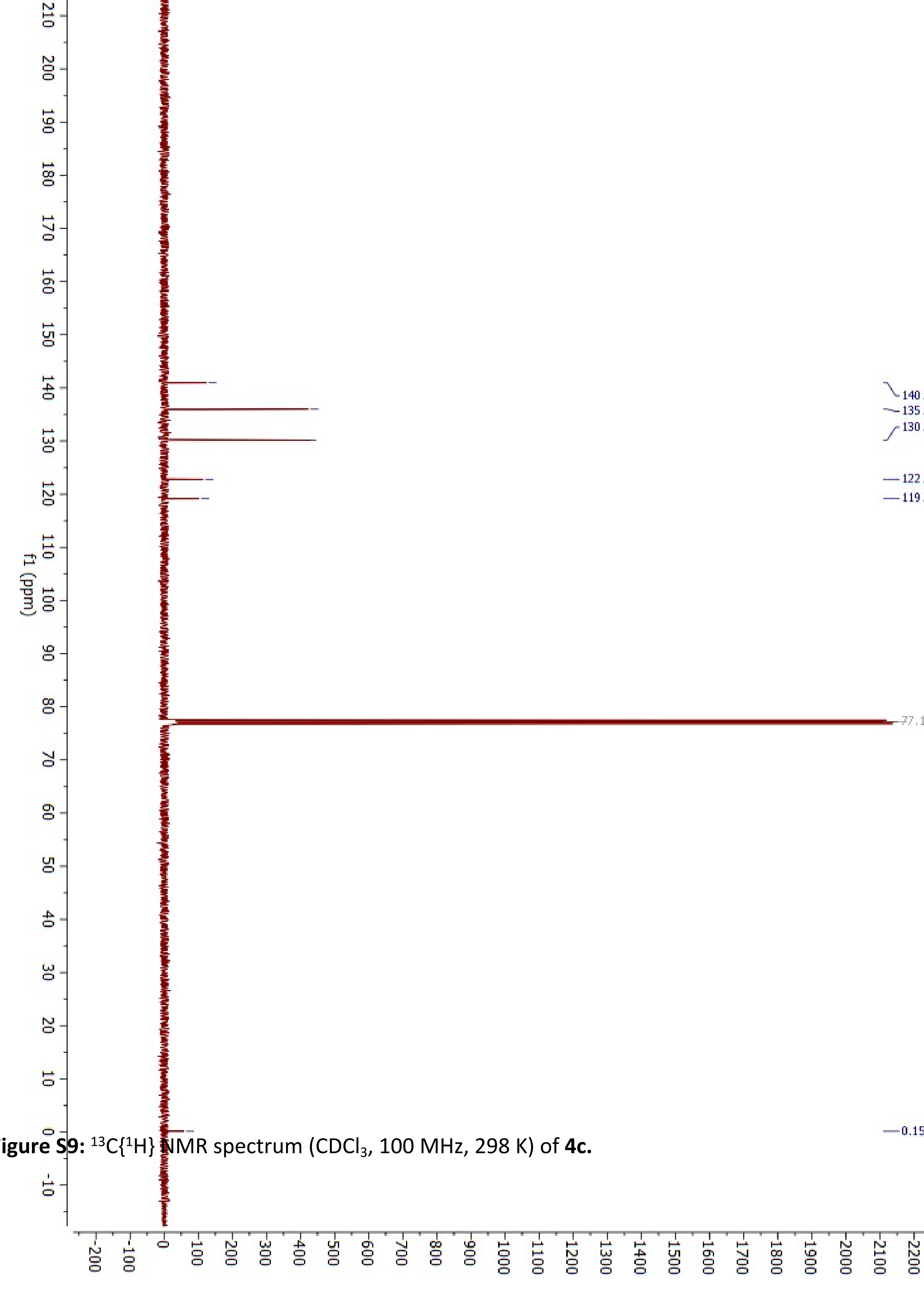


Figure S9: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4c.**

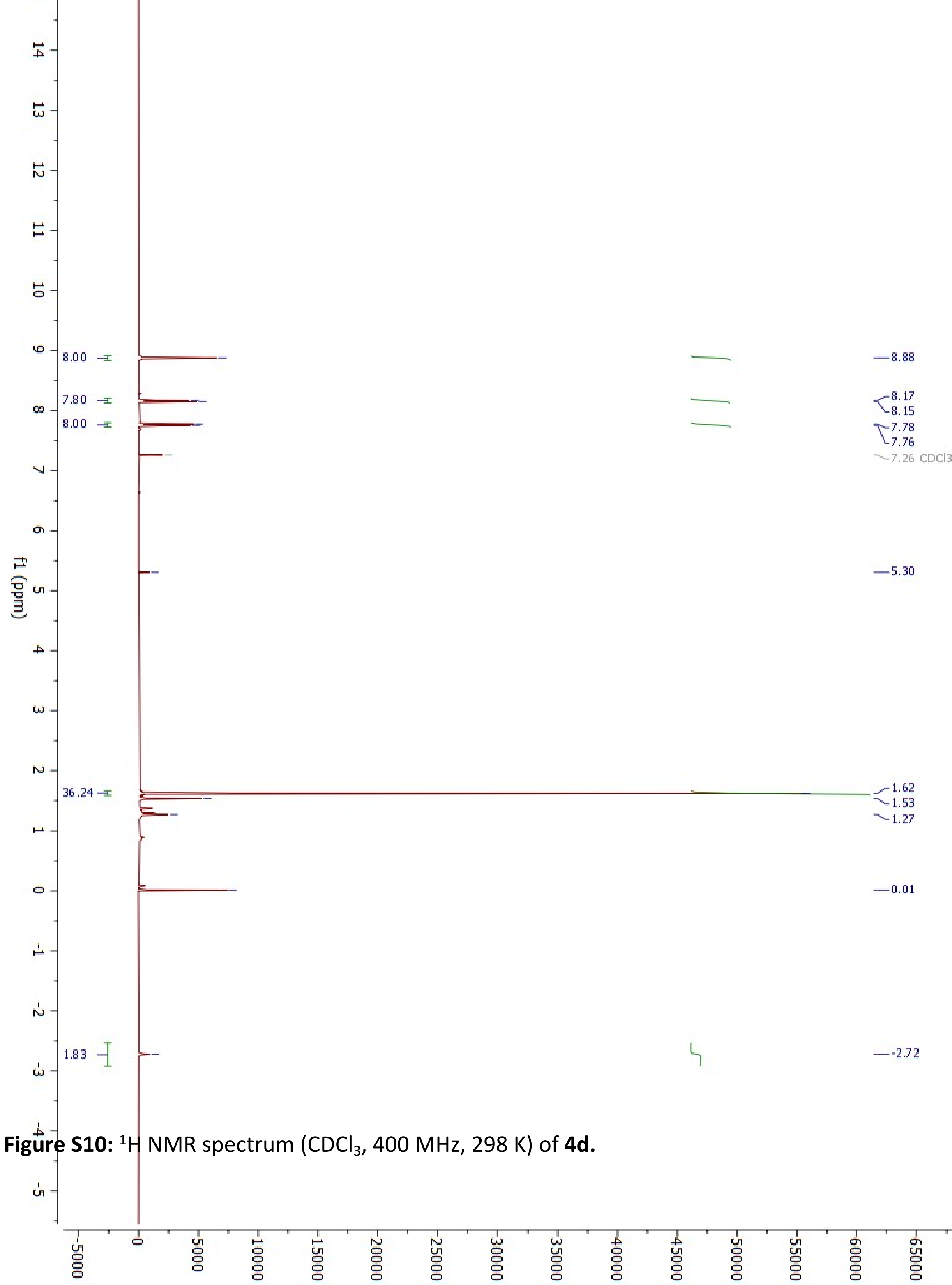


Figure S10: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4d.**

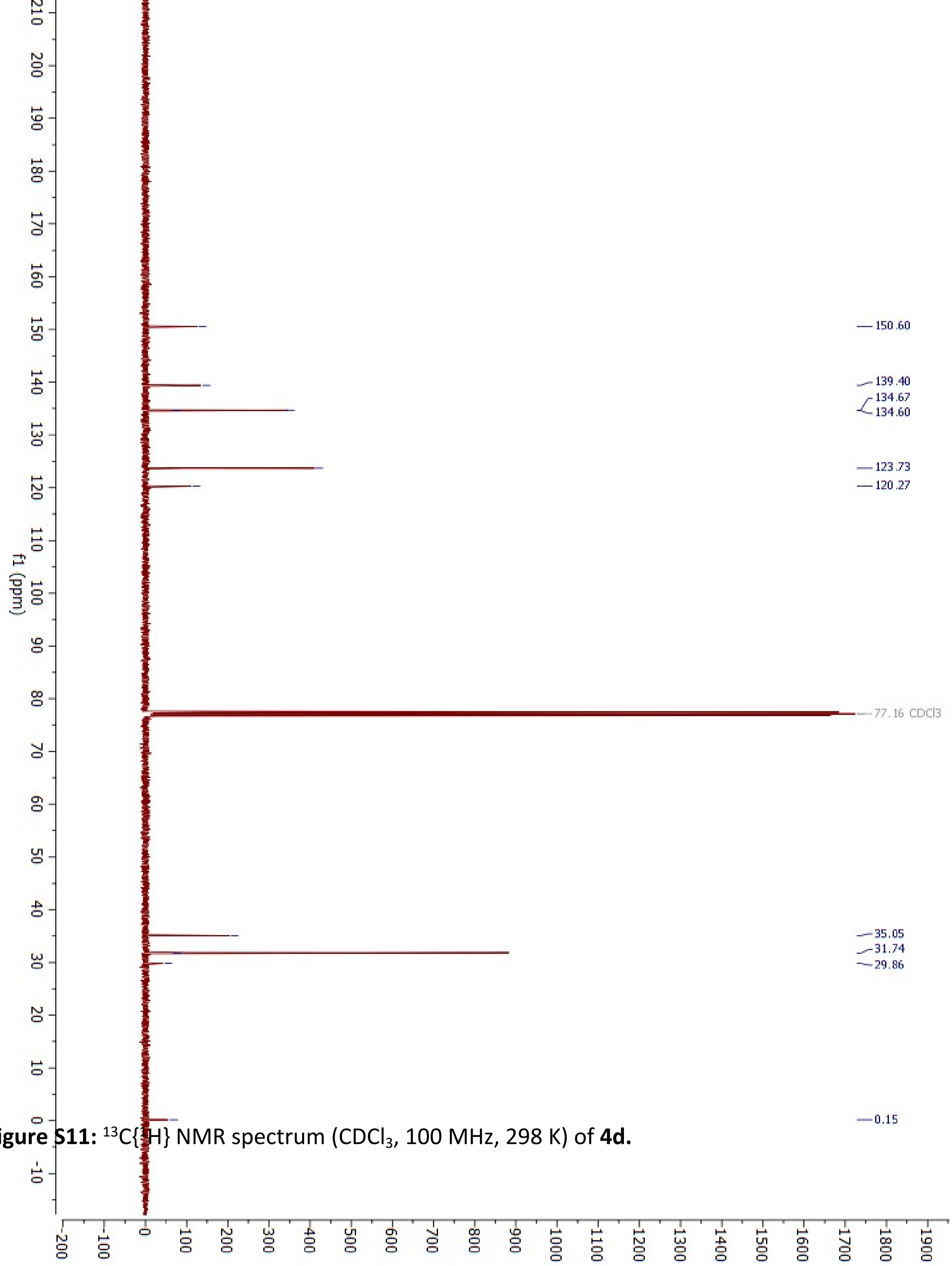


Figure S11: $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4d.**

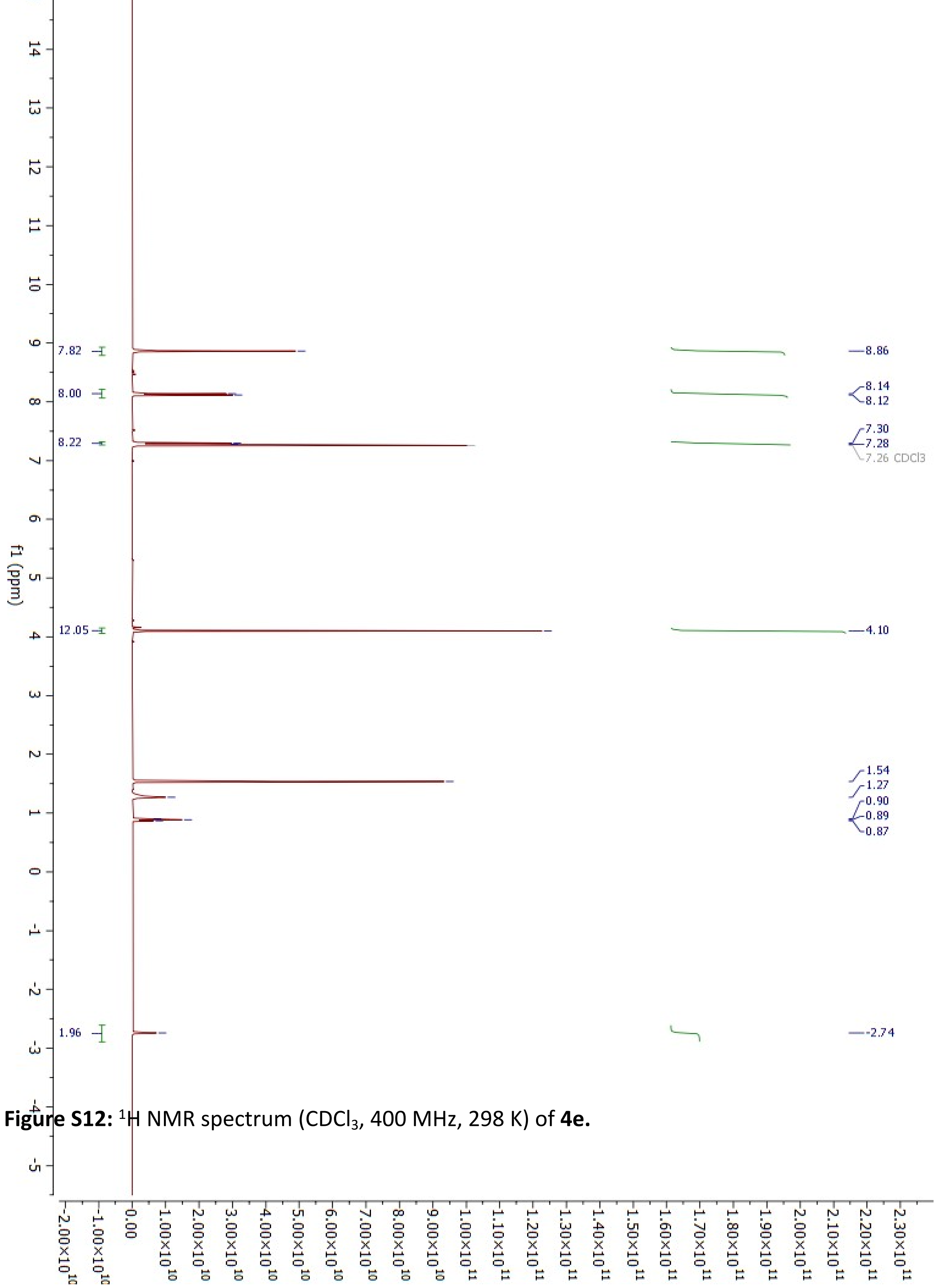


Figure S12: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4e.**

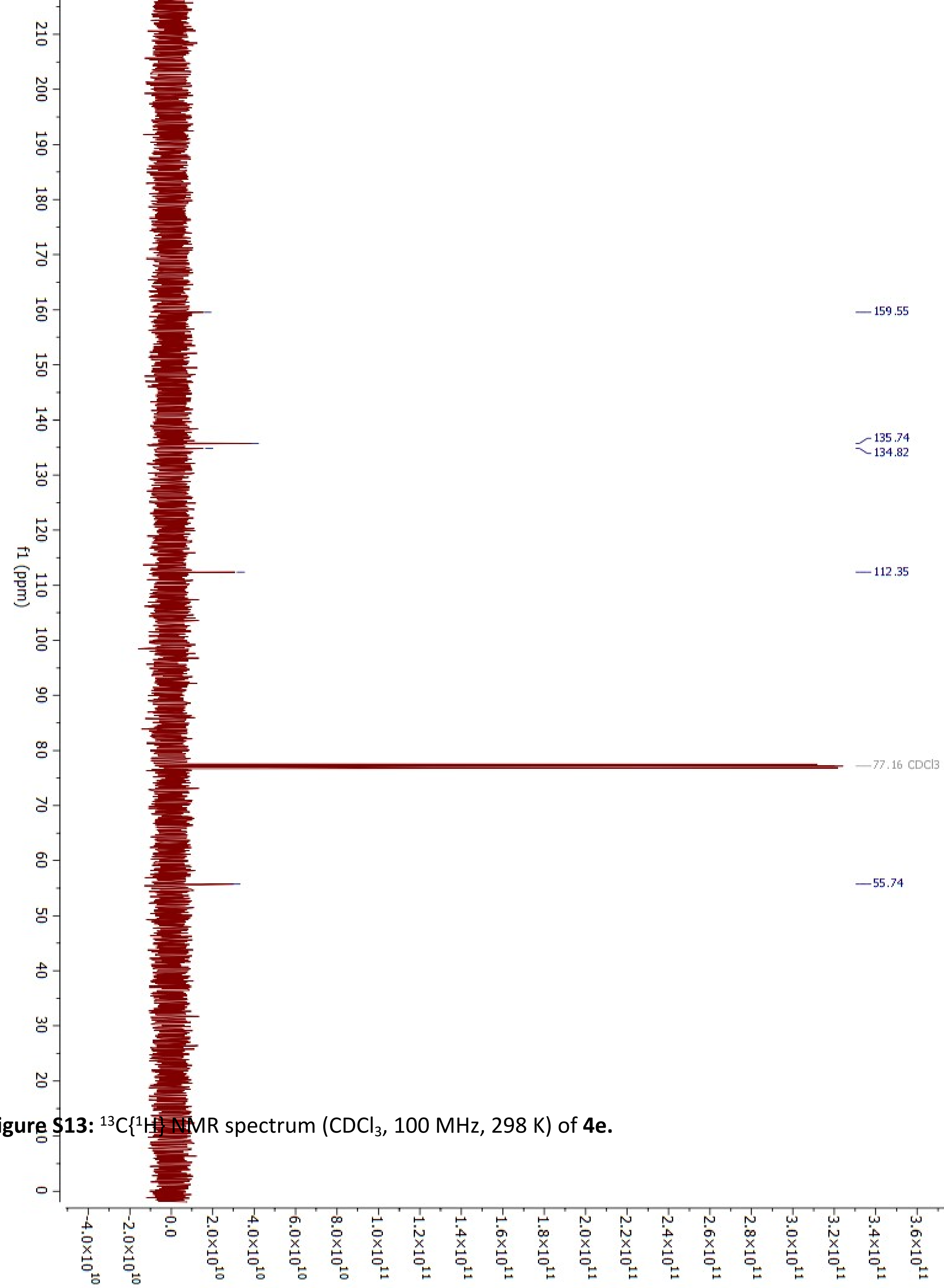


Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4e.**

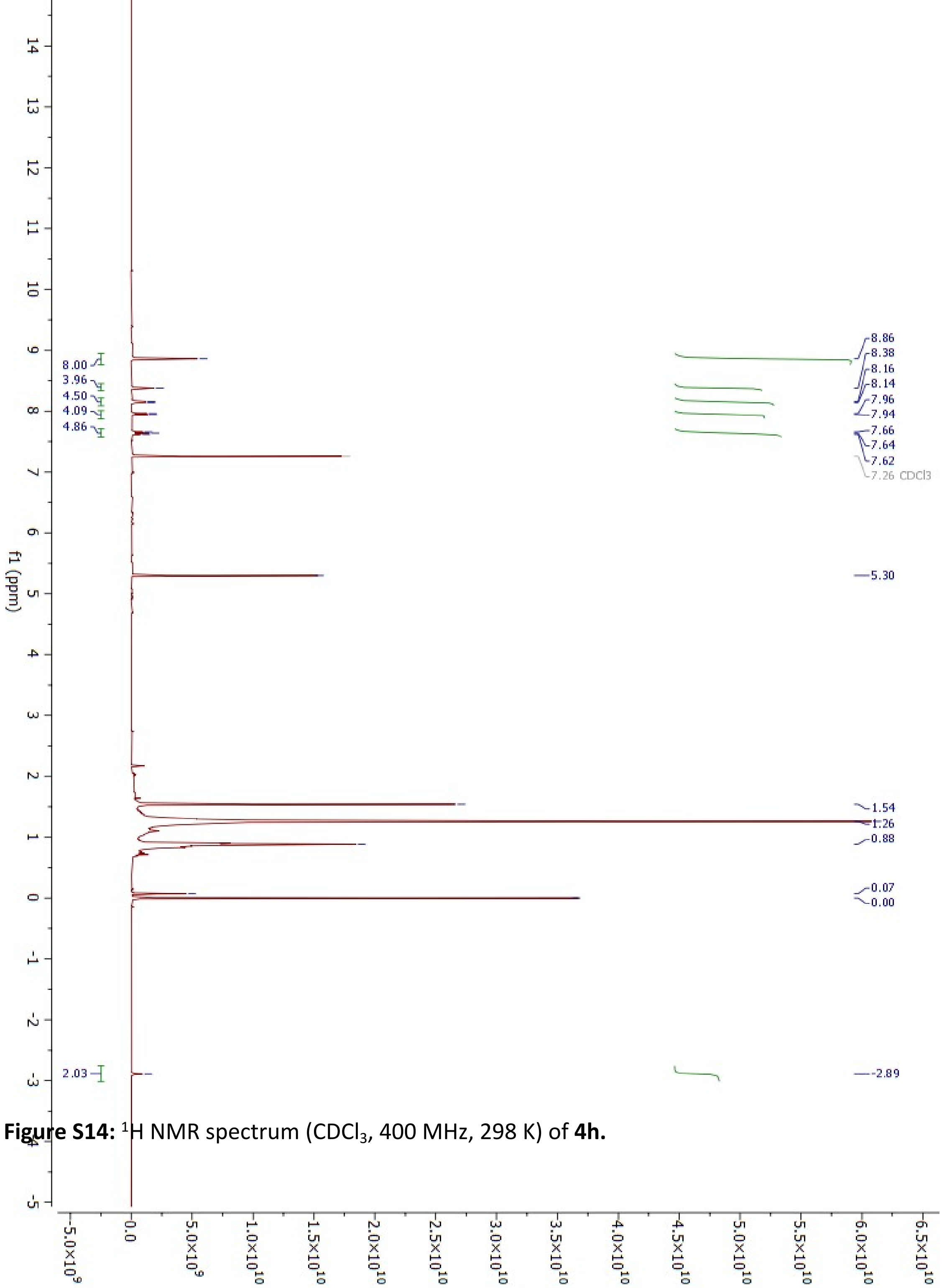


Figure S14: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4h.**

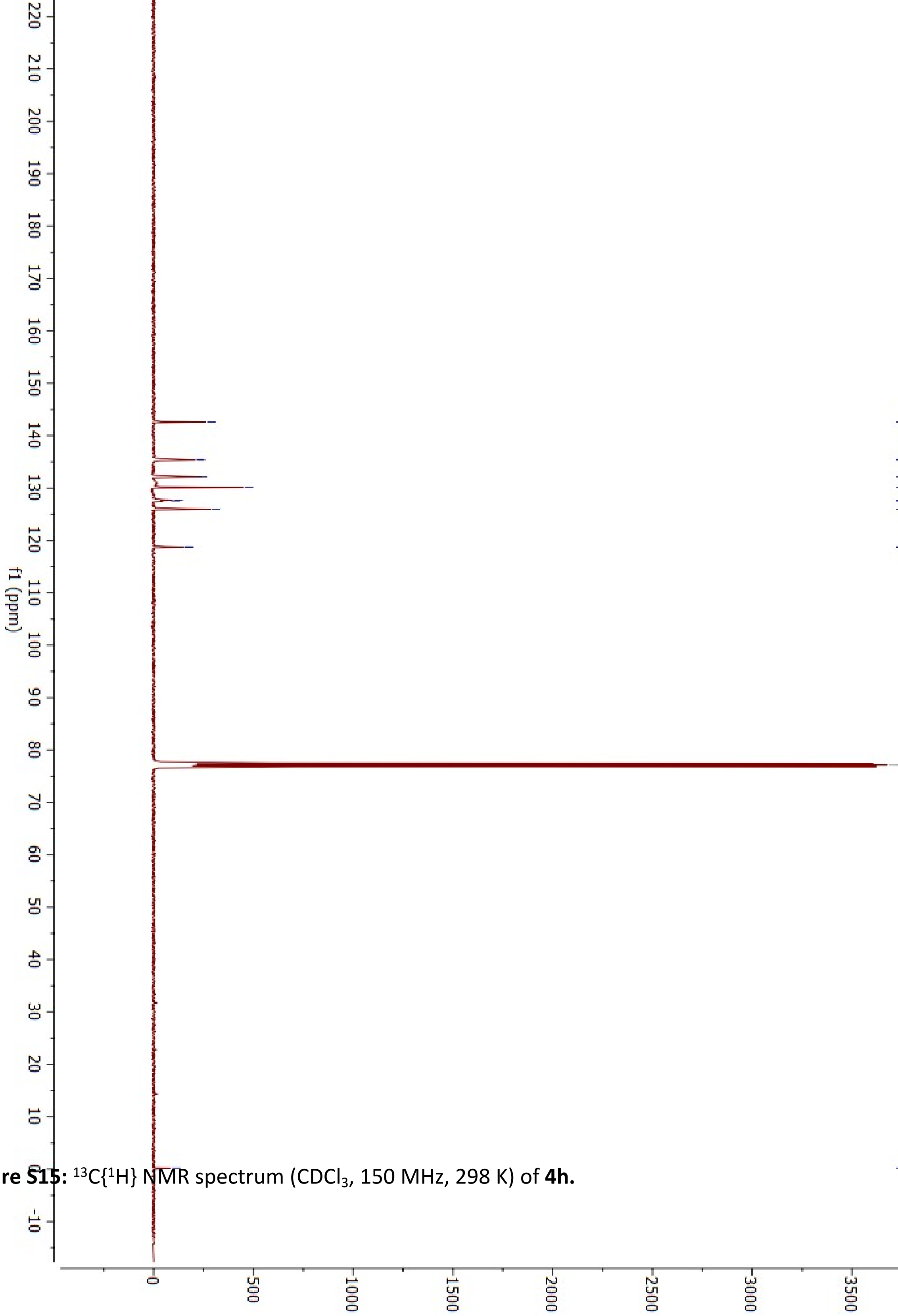


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **4h.**

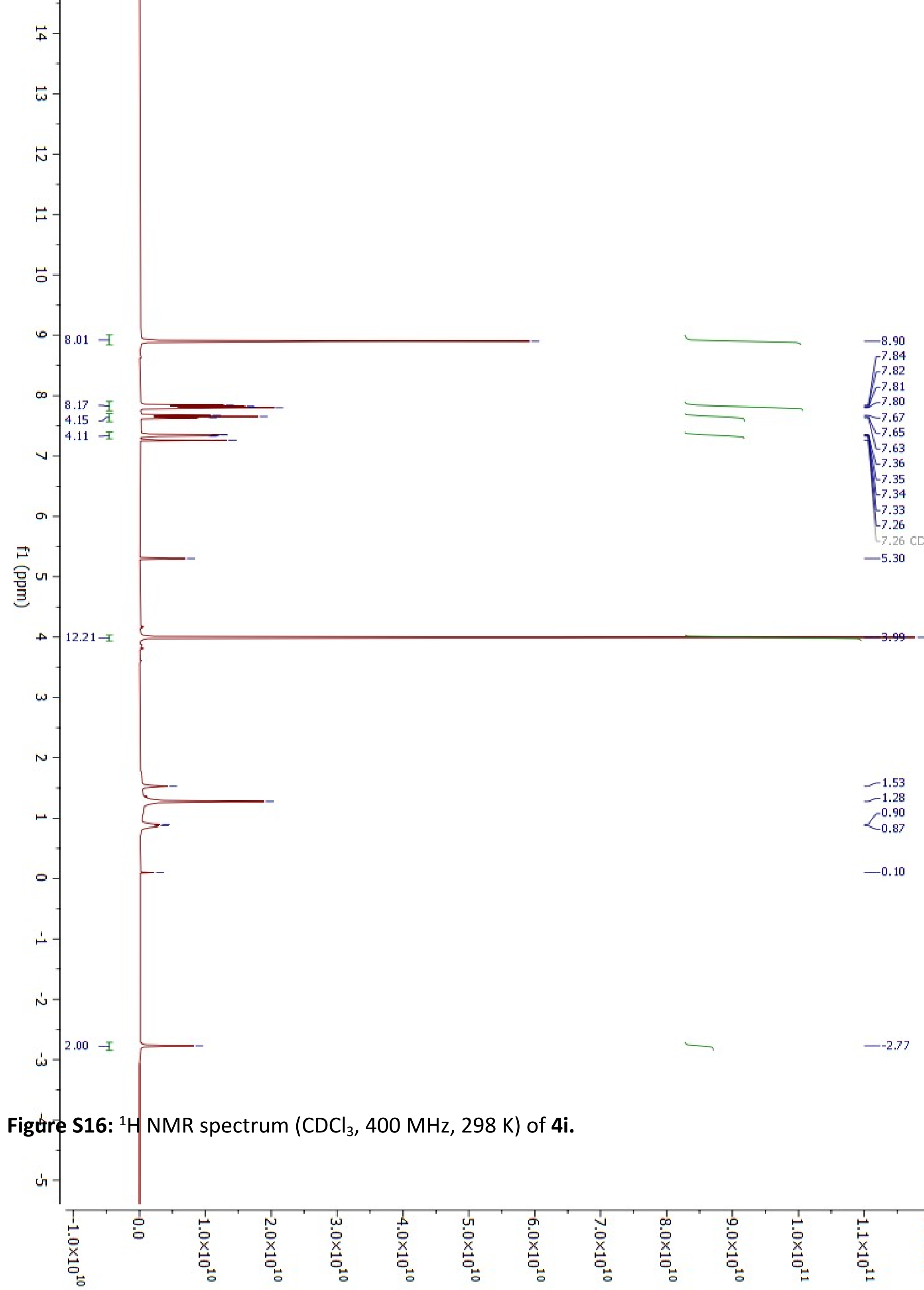


Figure S16: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4i.**

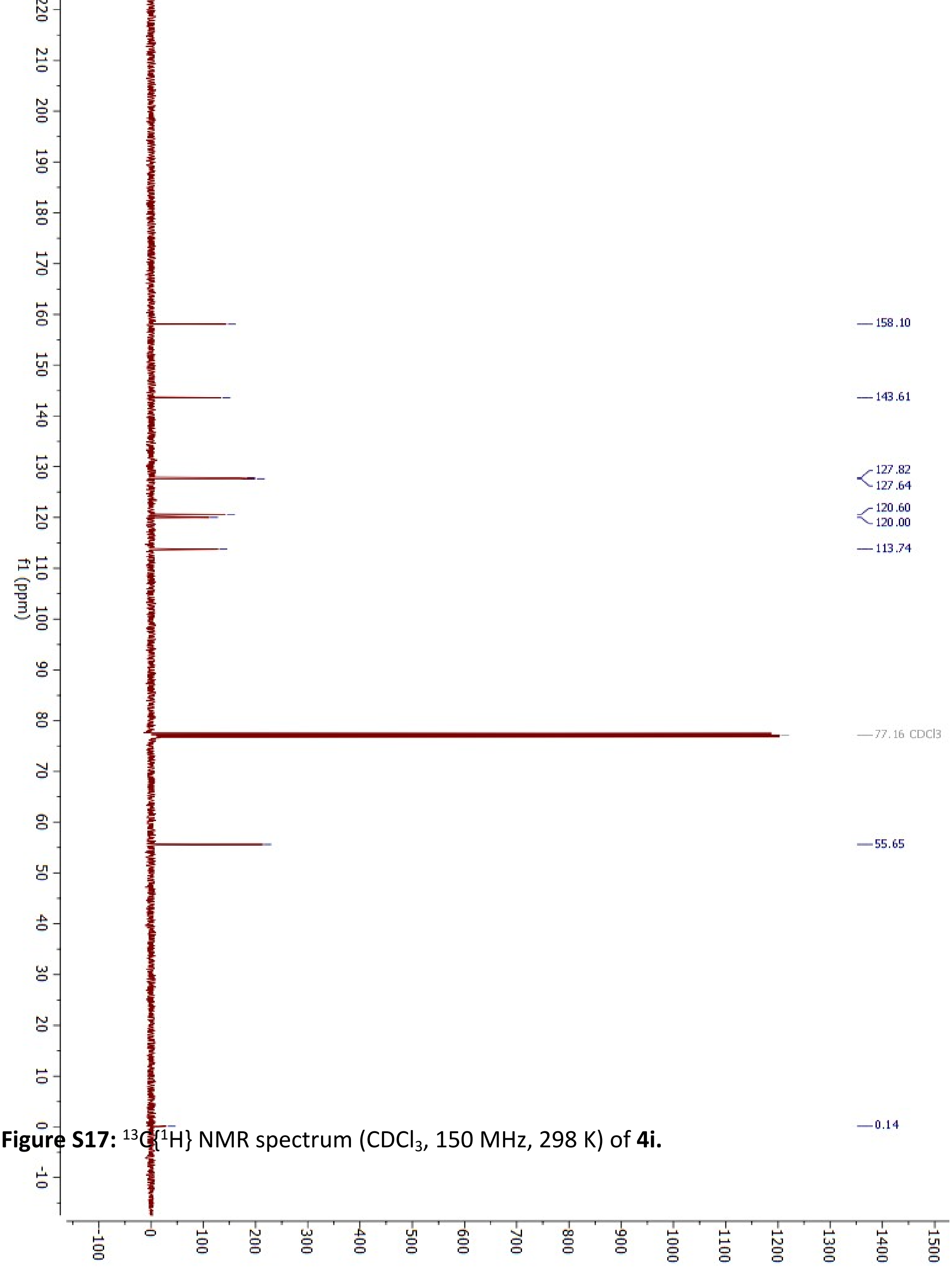


Figure S17: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **4i.**

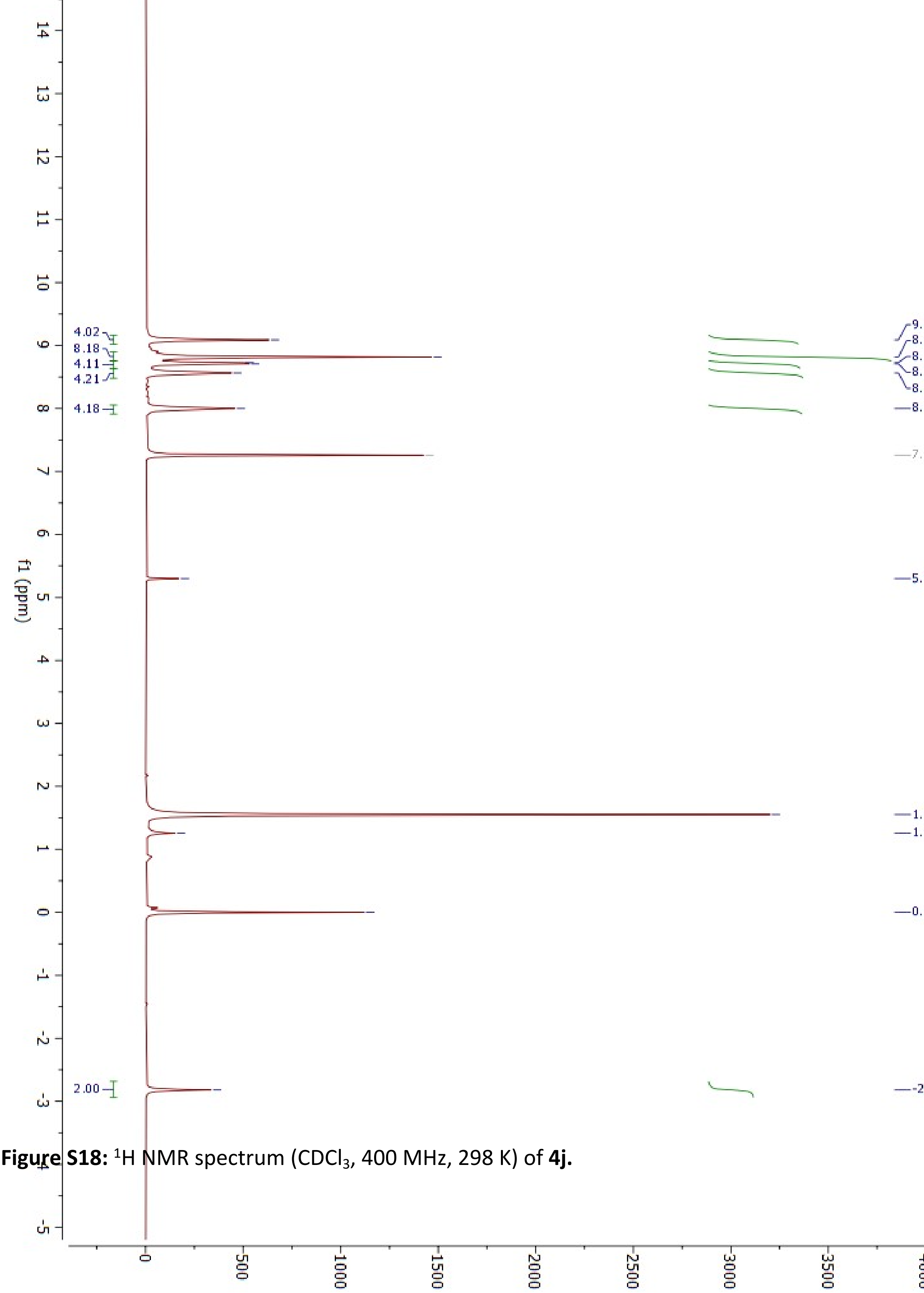


Figure S18: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4j.**

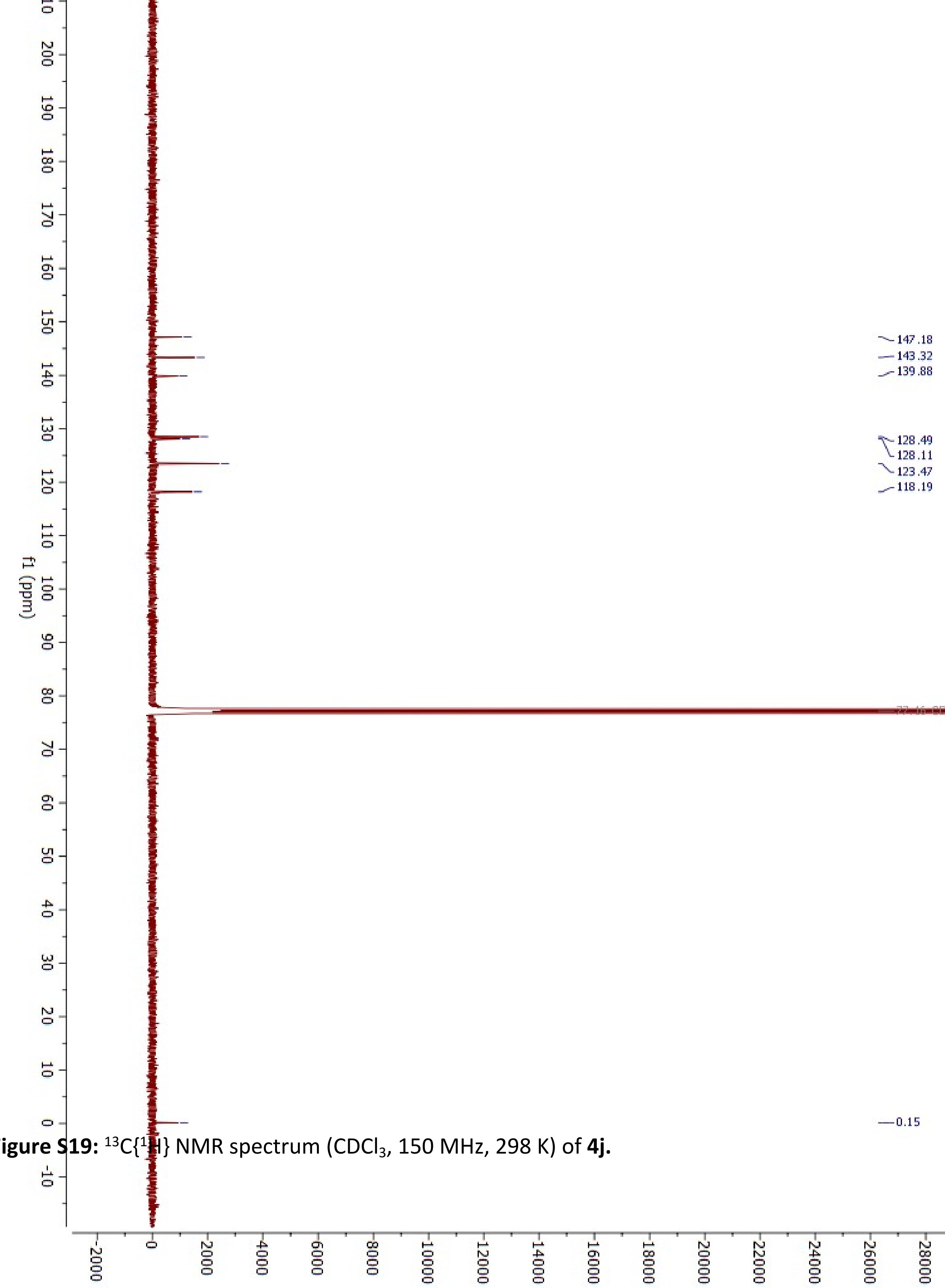


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **4j.**

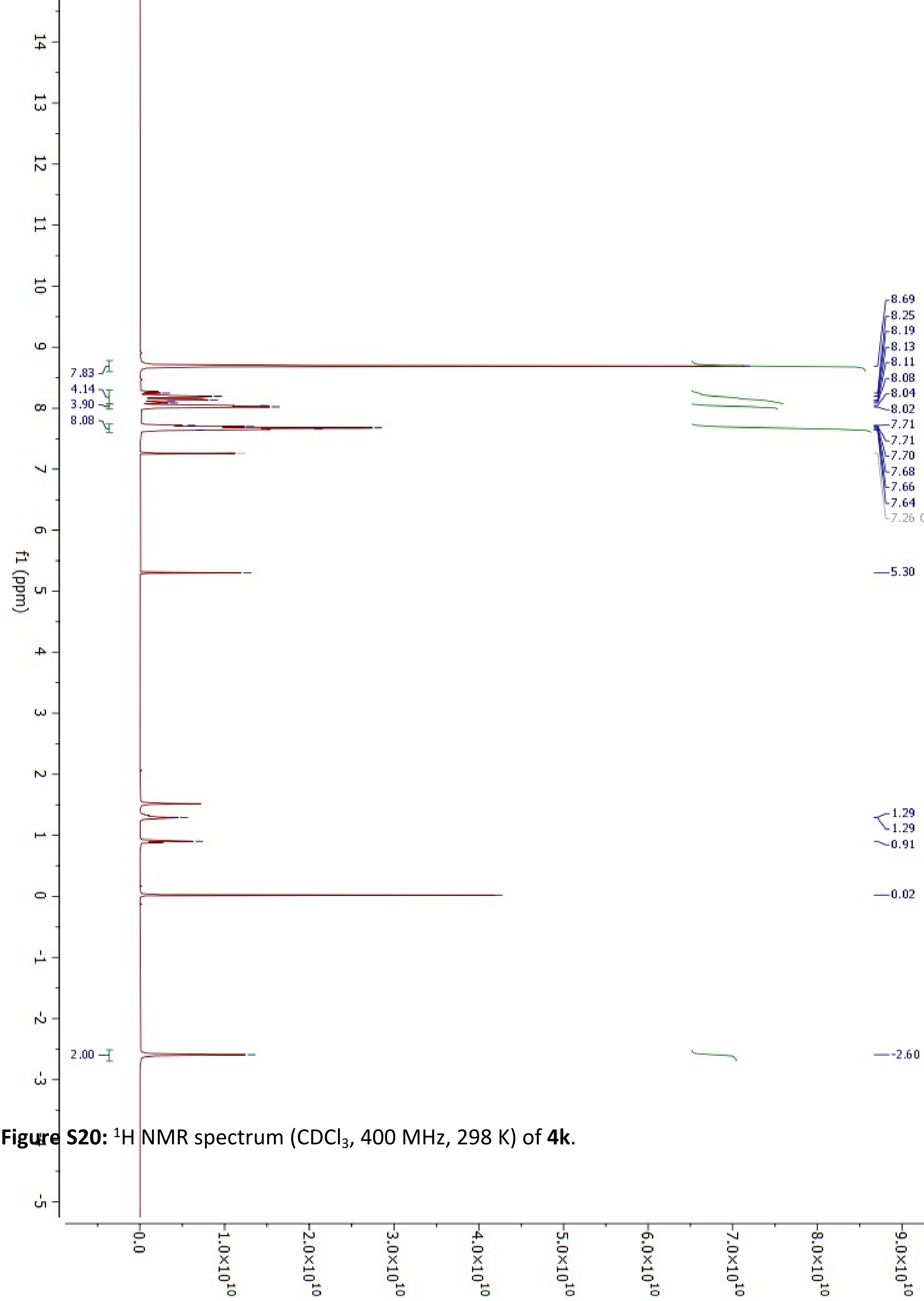


Figure S20: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4k**.

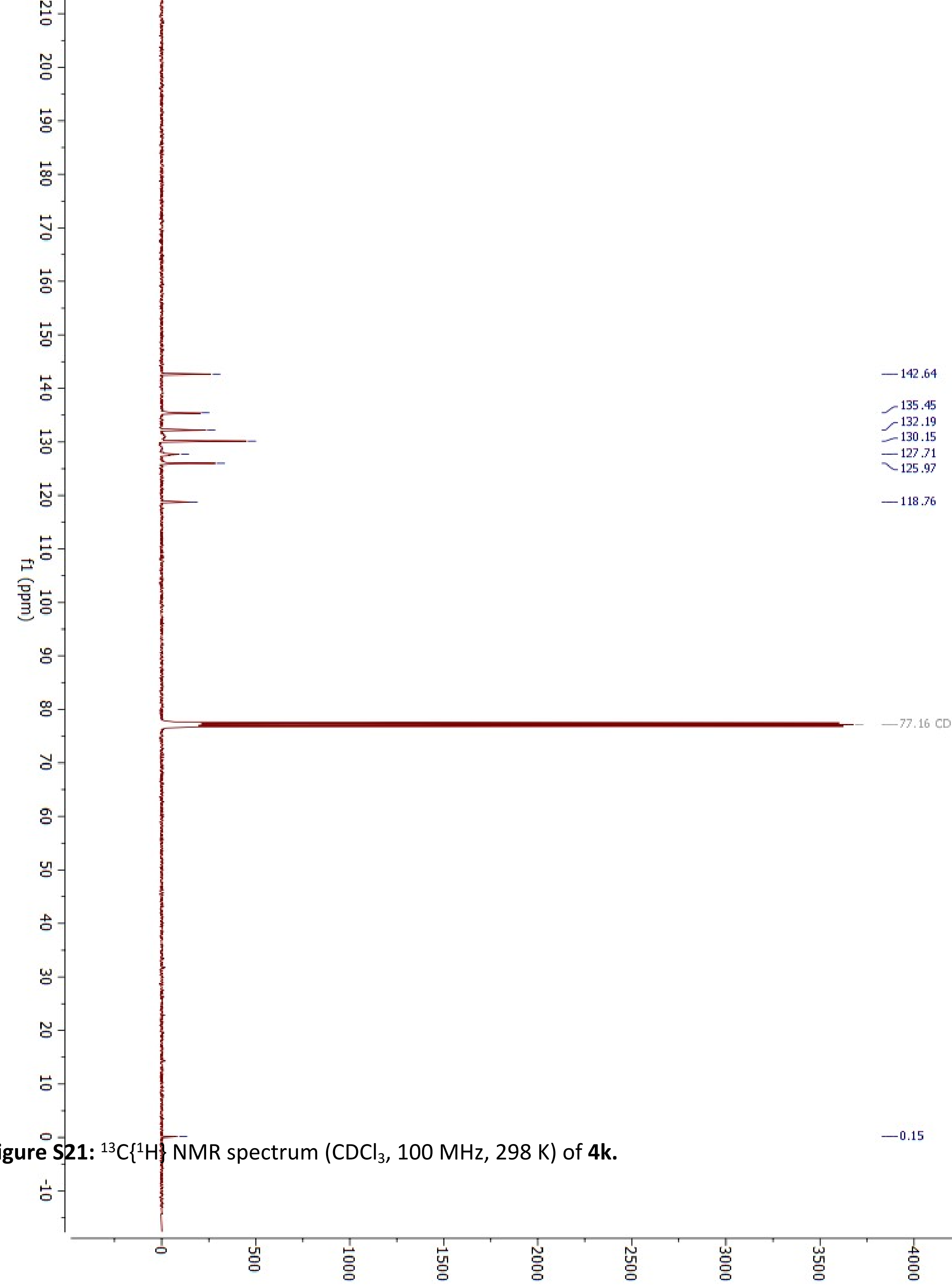


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4k.**

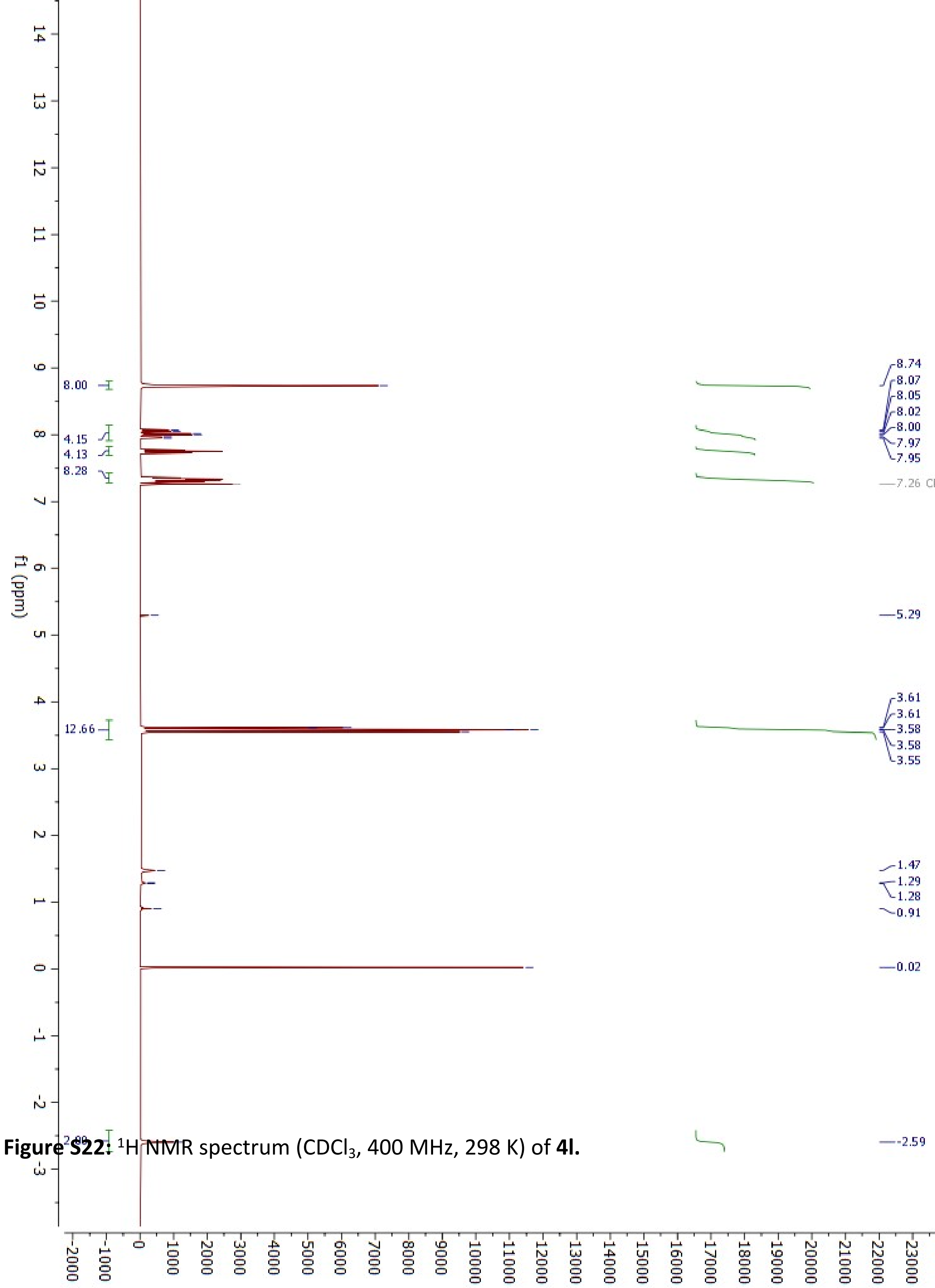


Figure S22: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4l.**

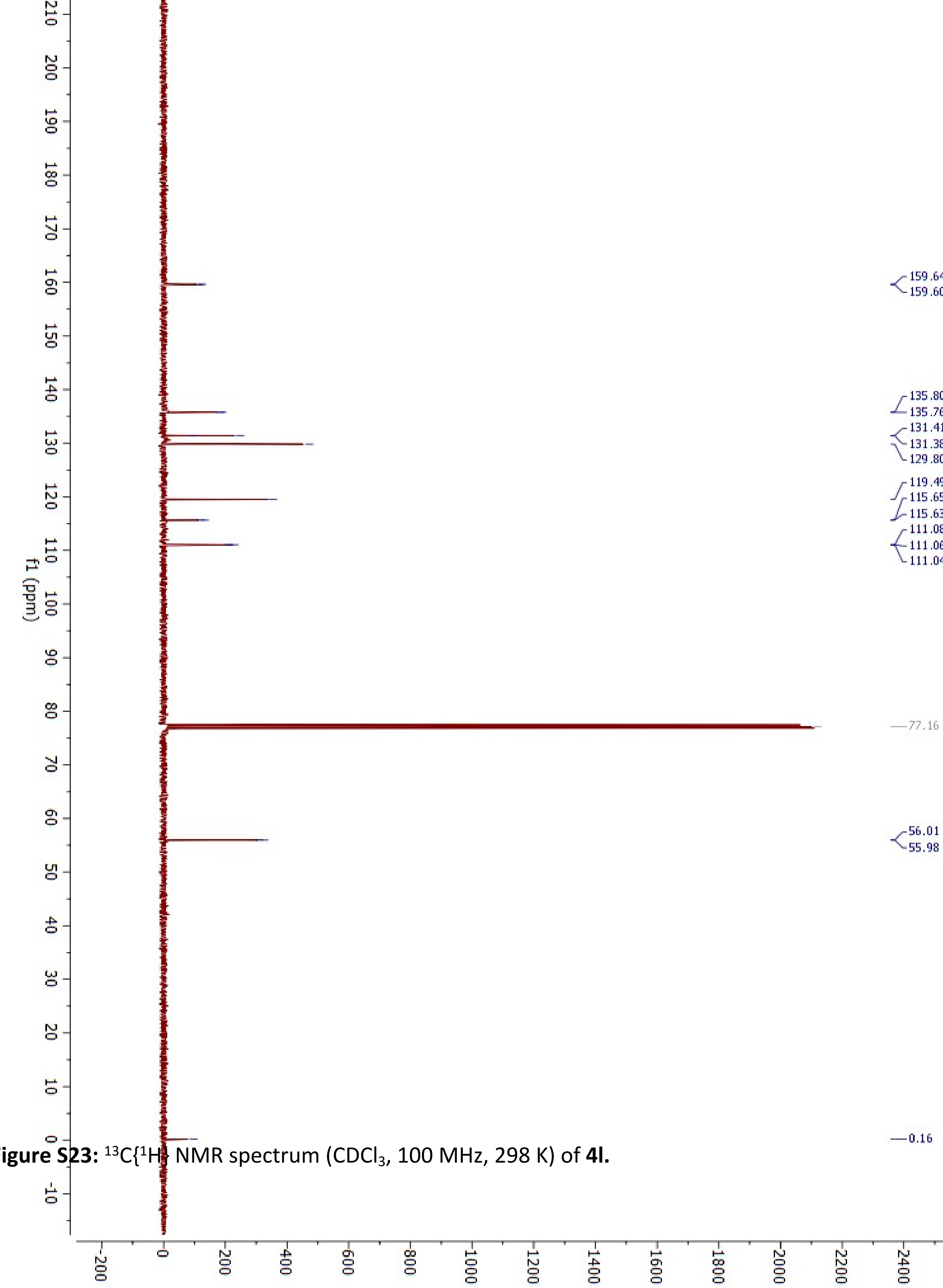


Figure S23: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4l.**

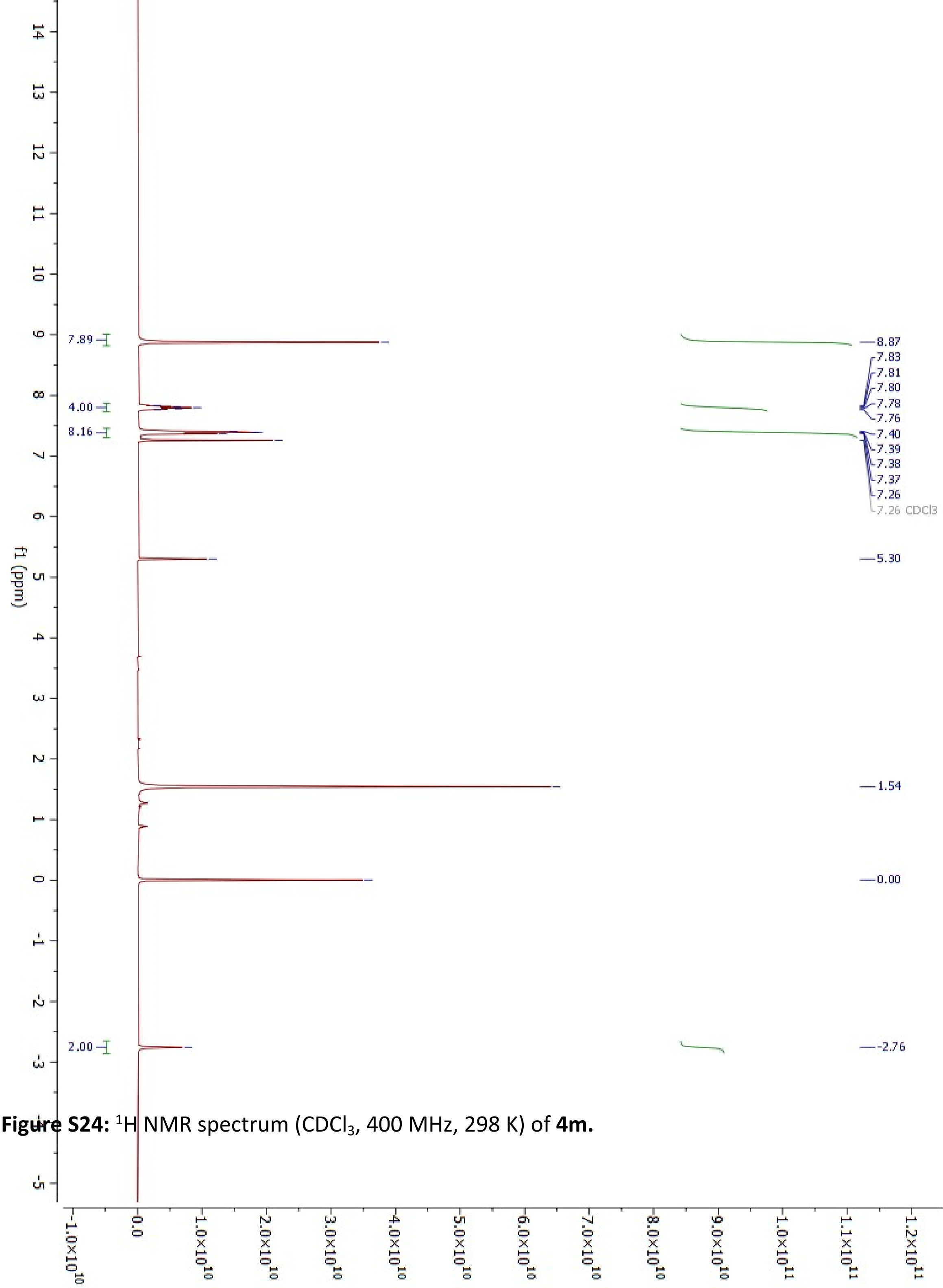


Figure S24: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4m.**

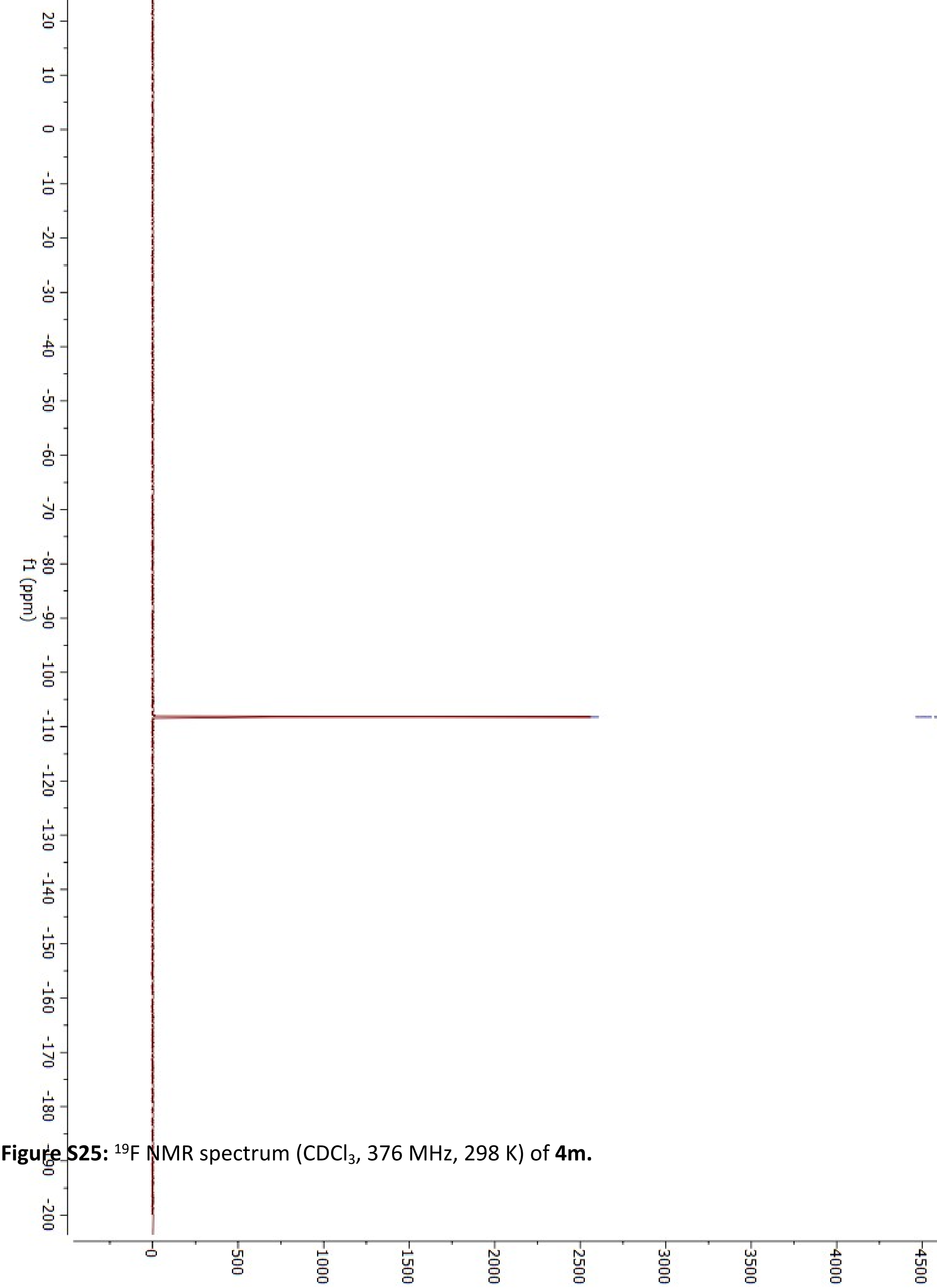


Figure S25: ^{19}F NMR spectrum ($CDCl_3$, 376 MHz, 298 K) of **4m.**

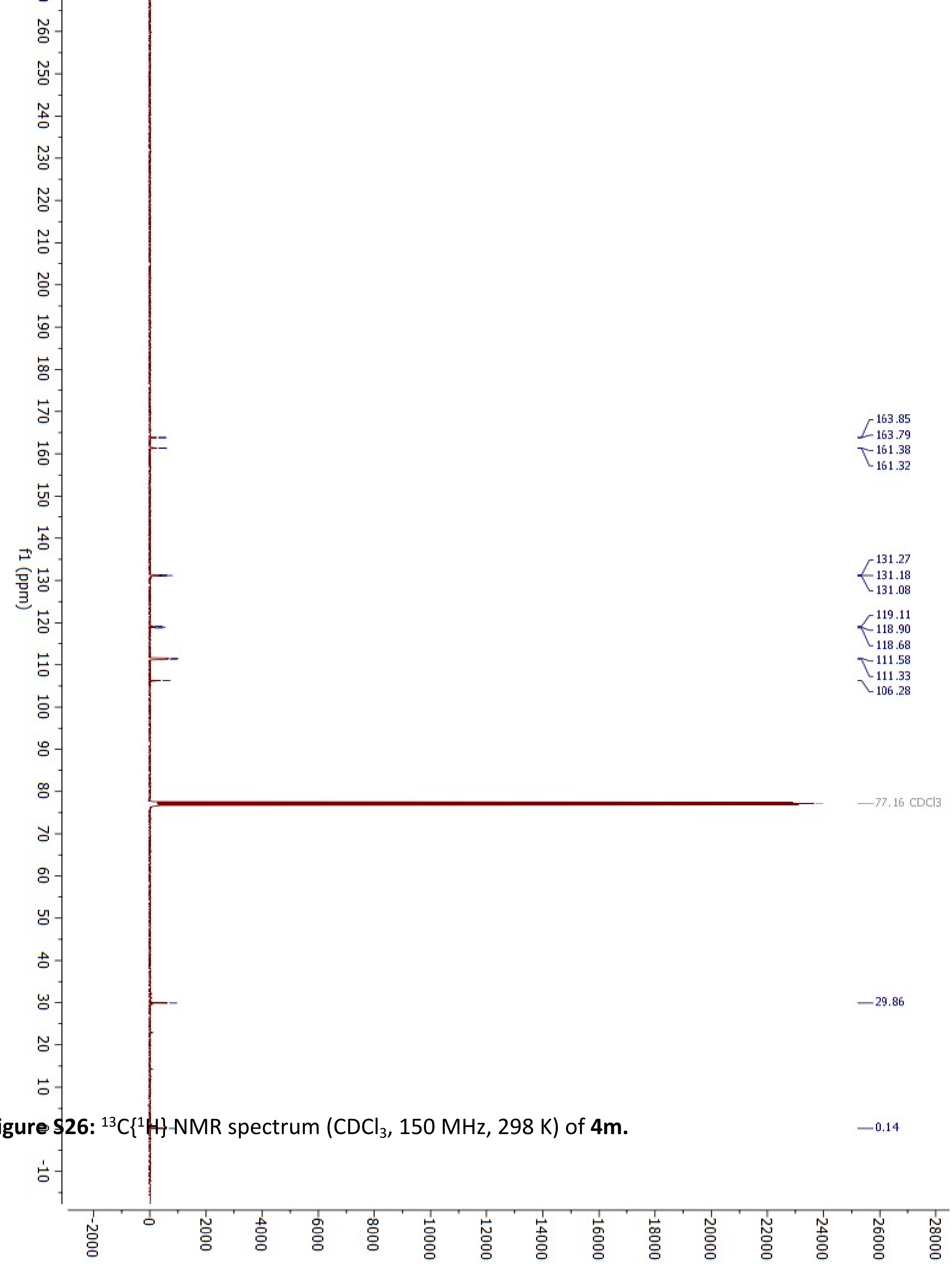


Figure S26: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **4m.**

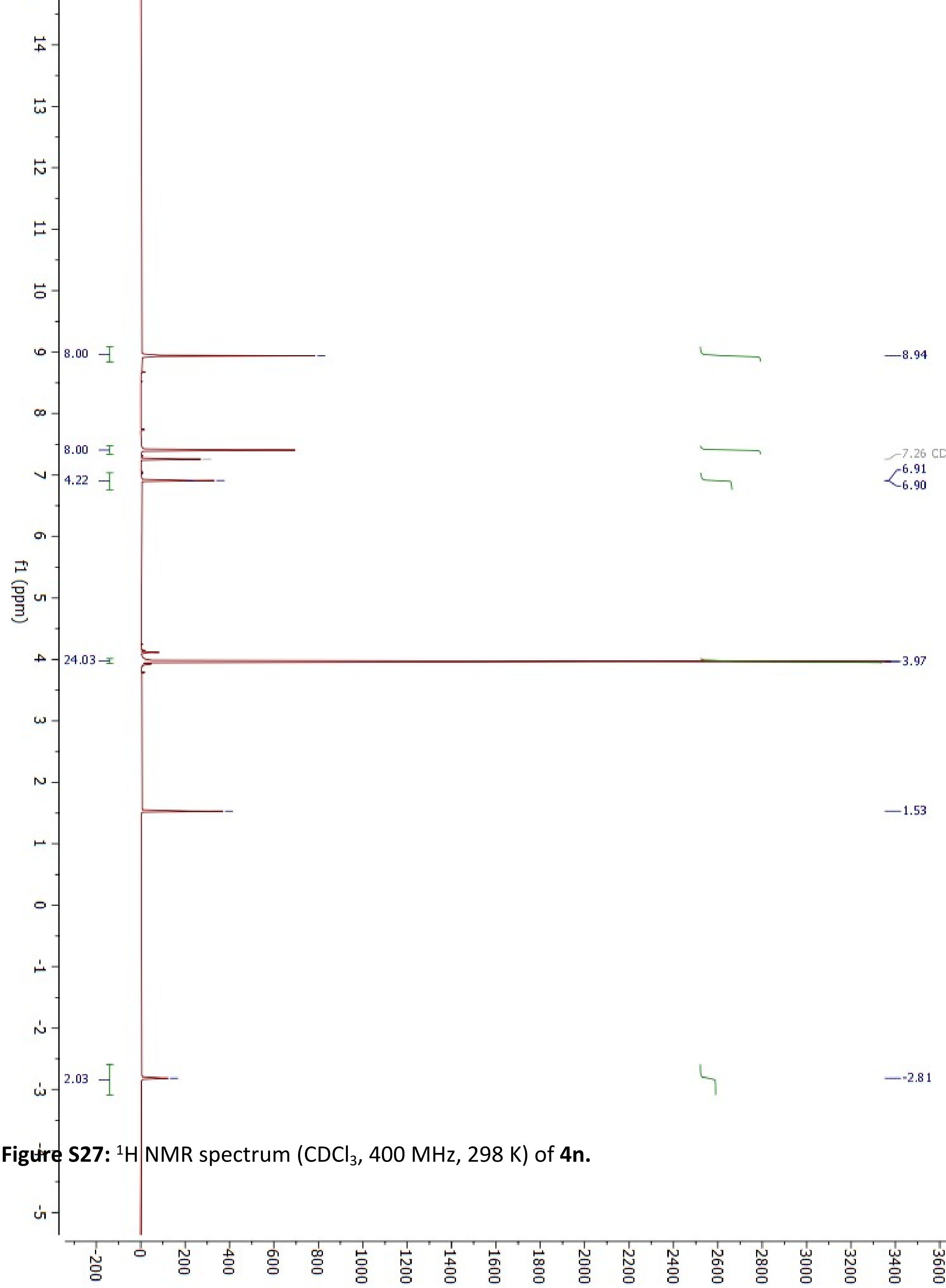


Figure S27: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4n.**

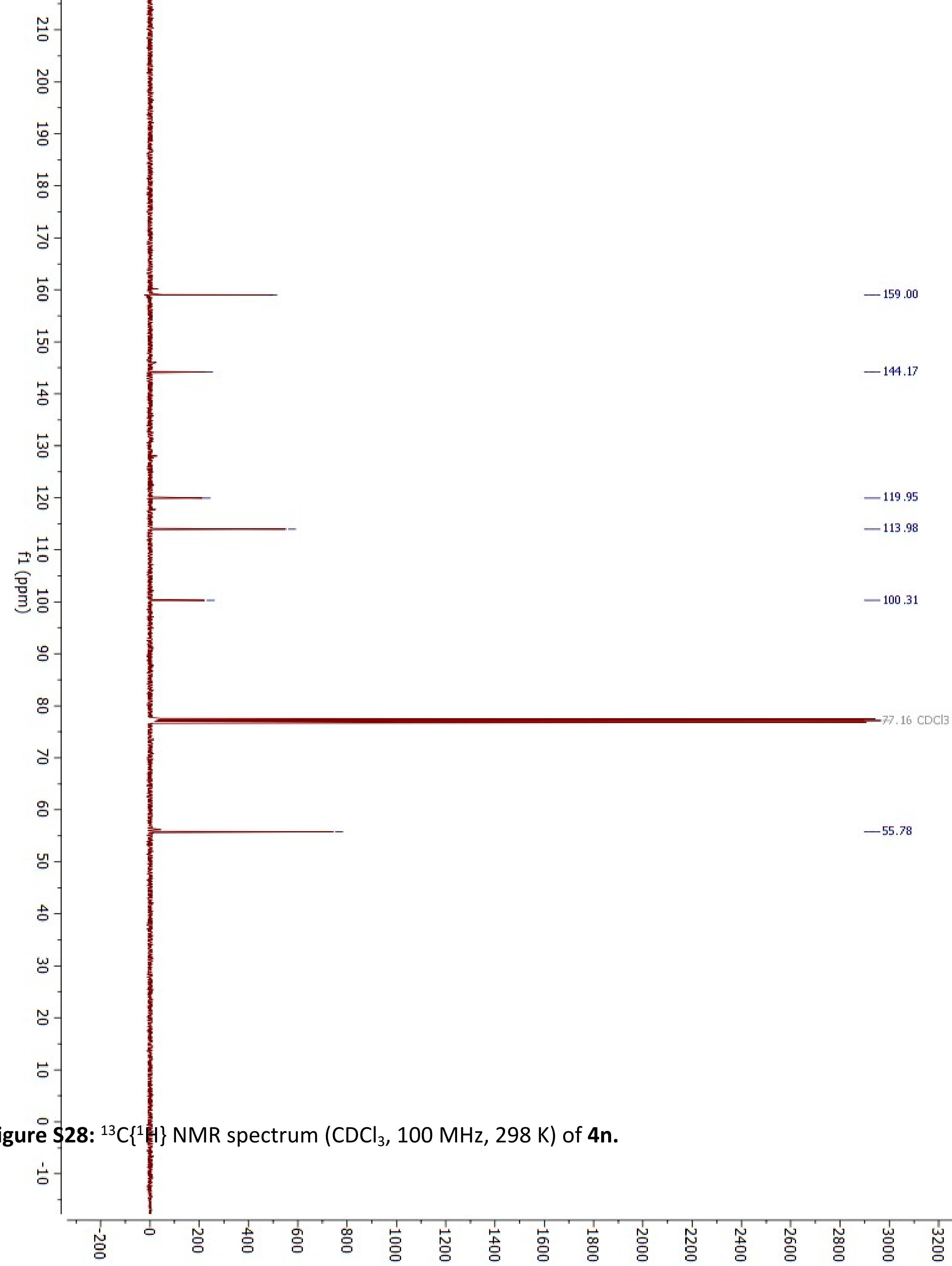


Figure S28: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4n.**

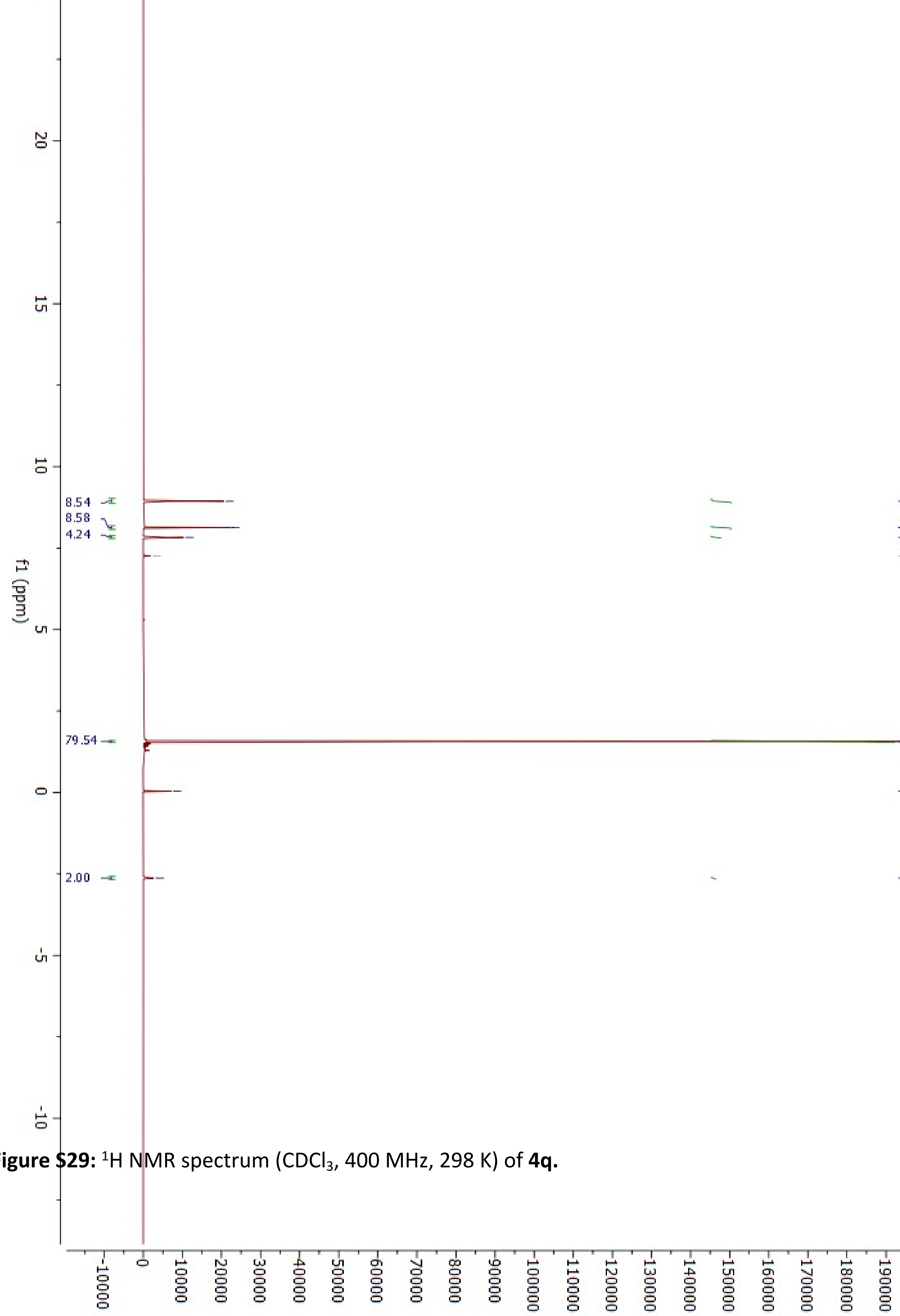


Figure S29: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4q.**

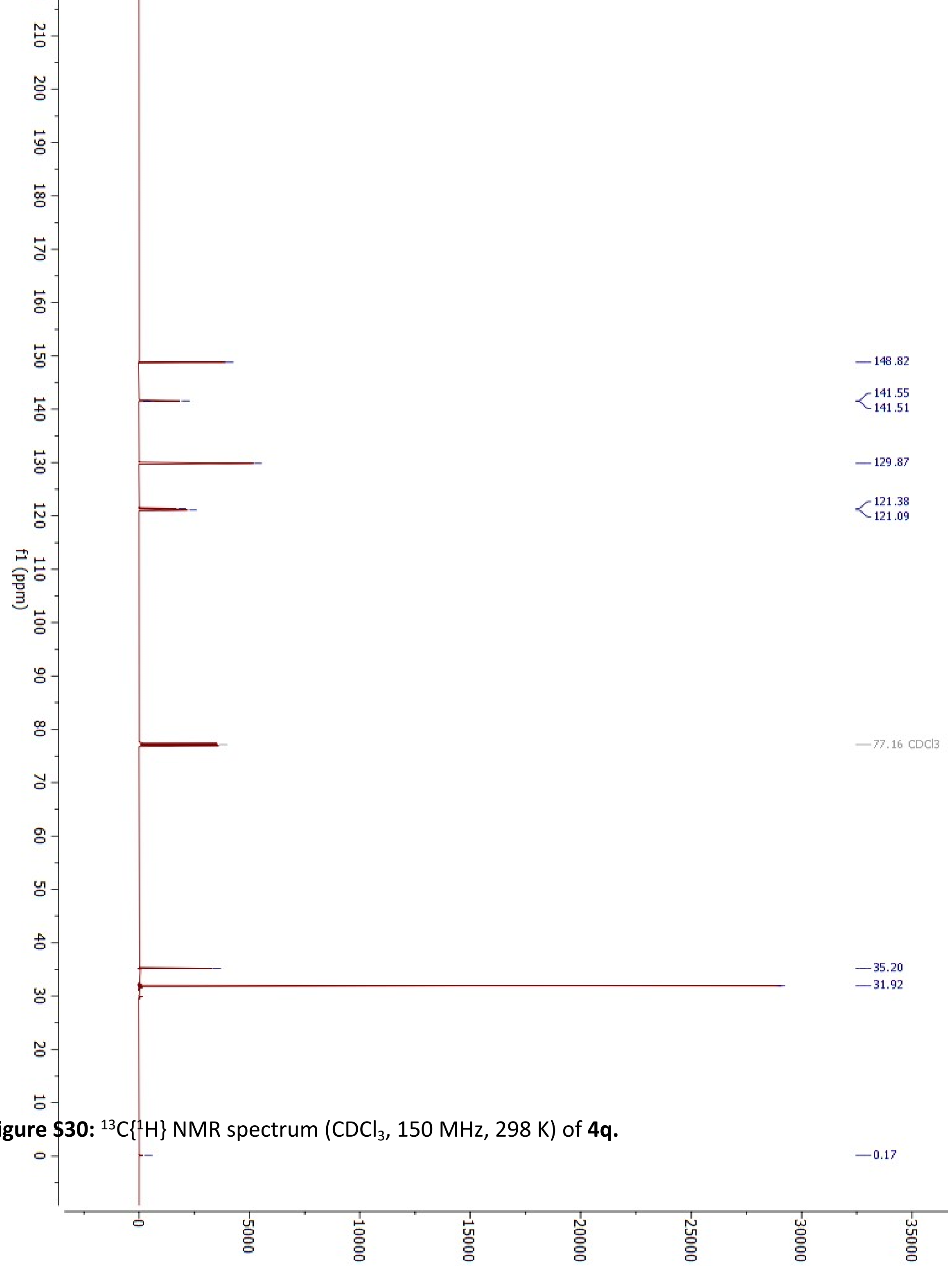


Figure S30: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **4q.**

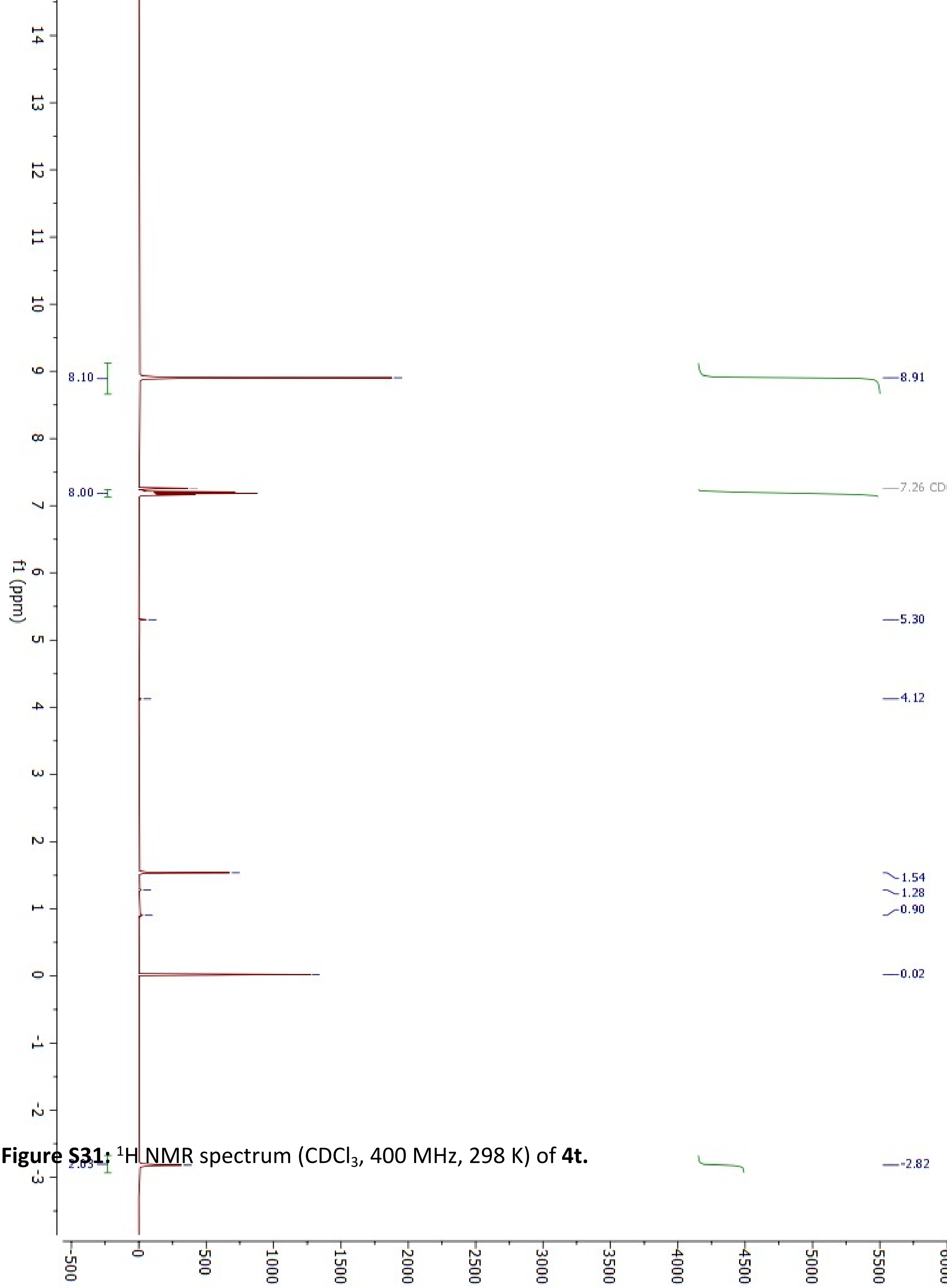


Figure S31: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4t.**

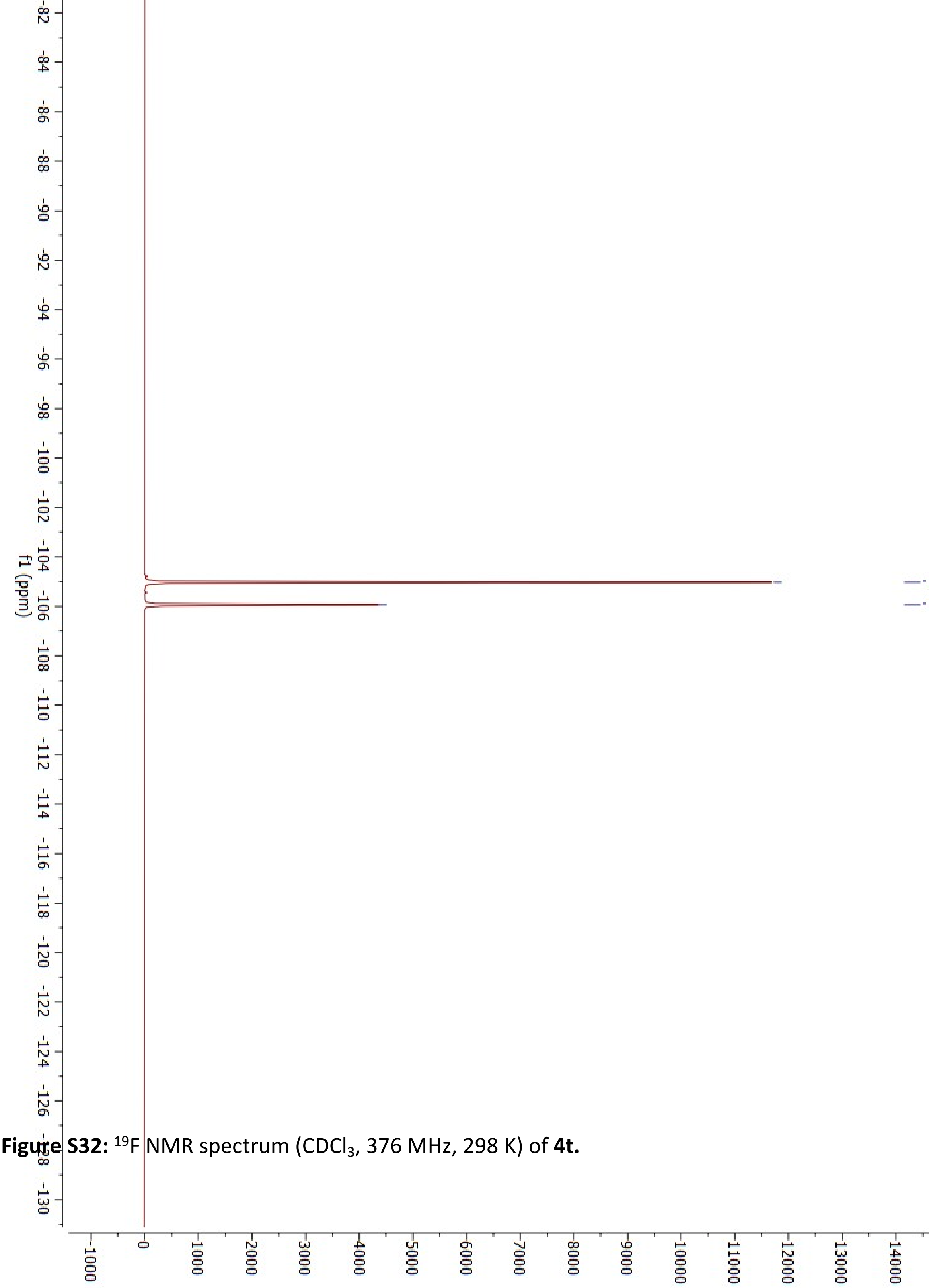


Figure S32: ^{19}F NMR spectrum ($CDCl_3$, 376 MHz, 298 K) of **4t.**

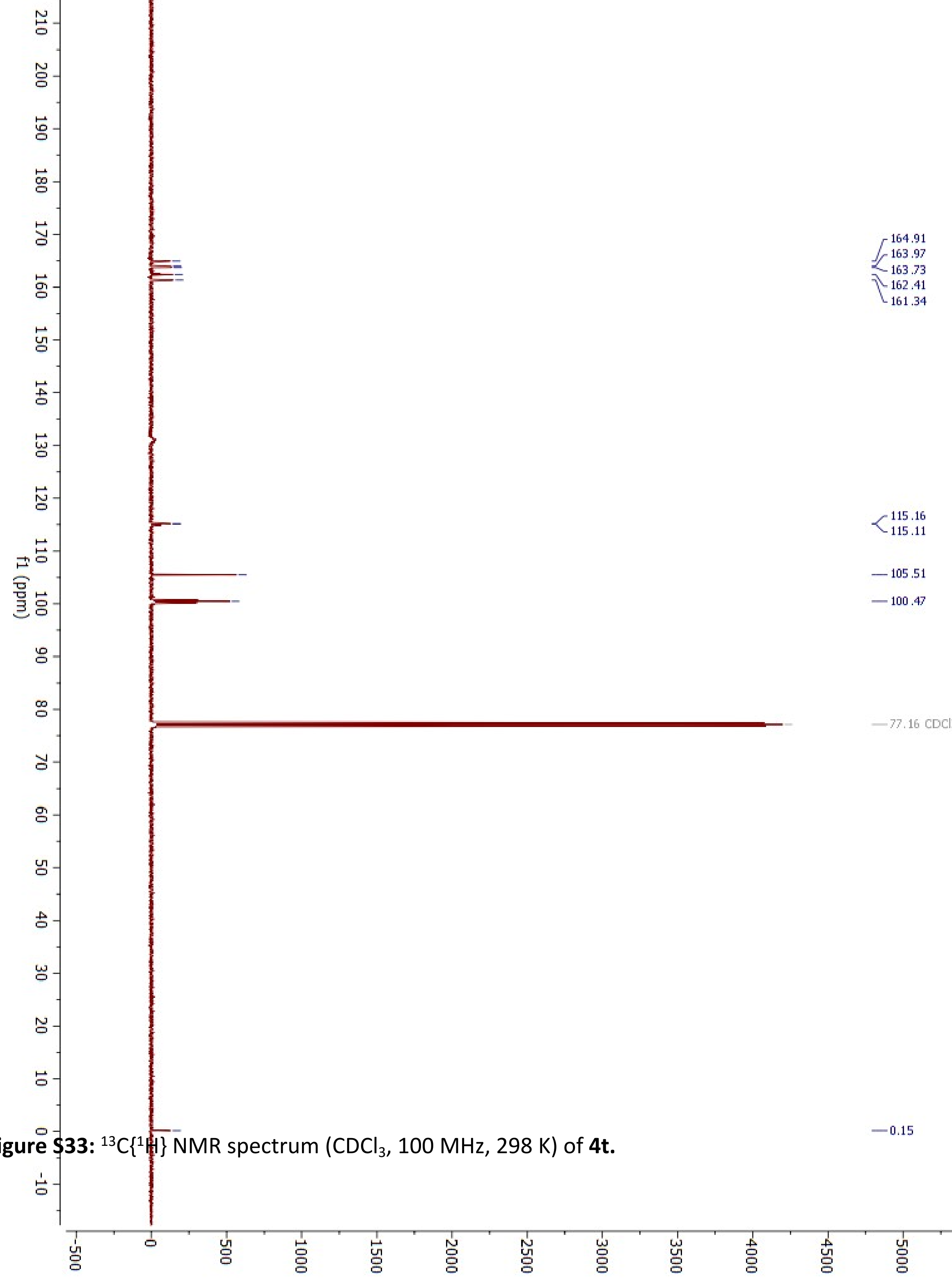


Figure S33: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4t.**

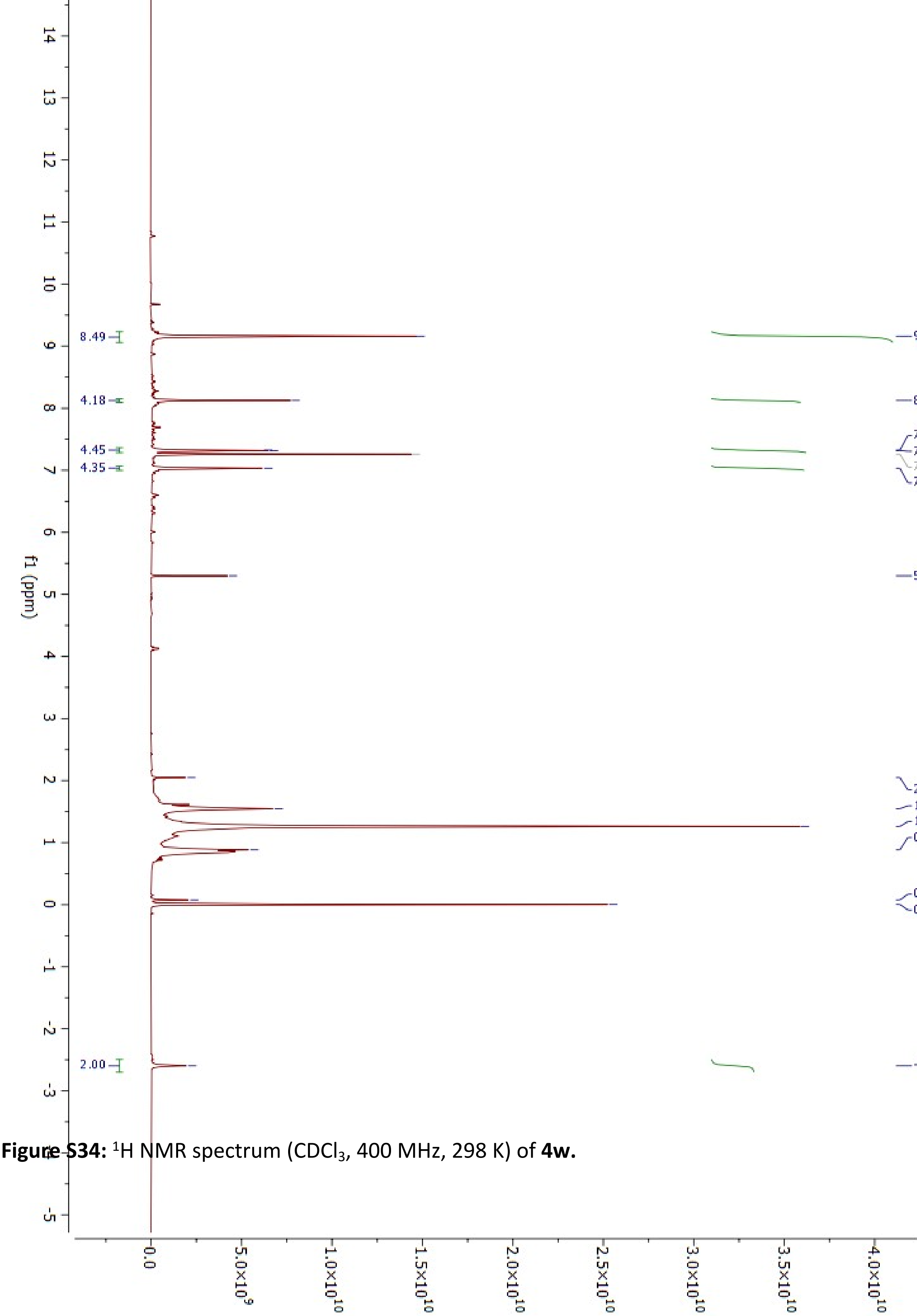


Figure S34: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4w.**

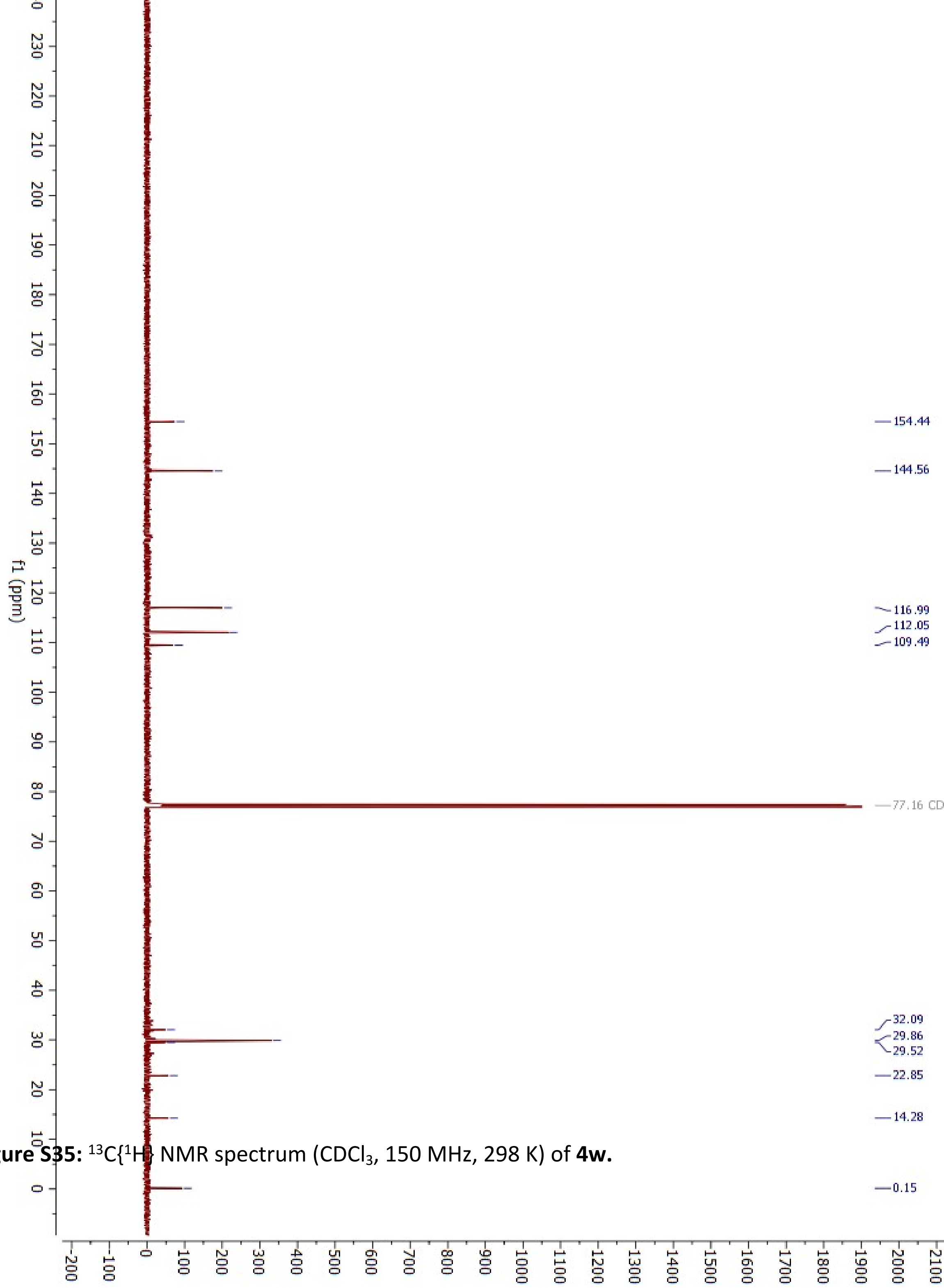


Figure S35: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **4w.**

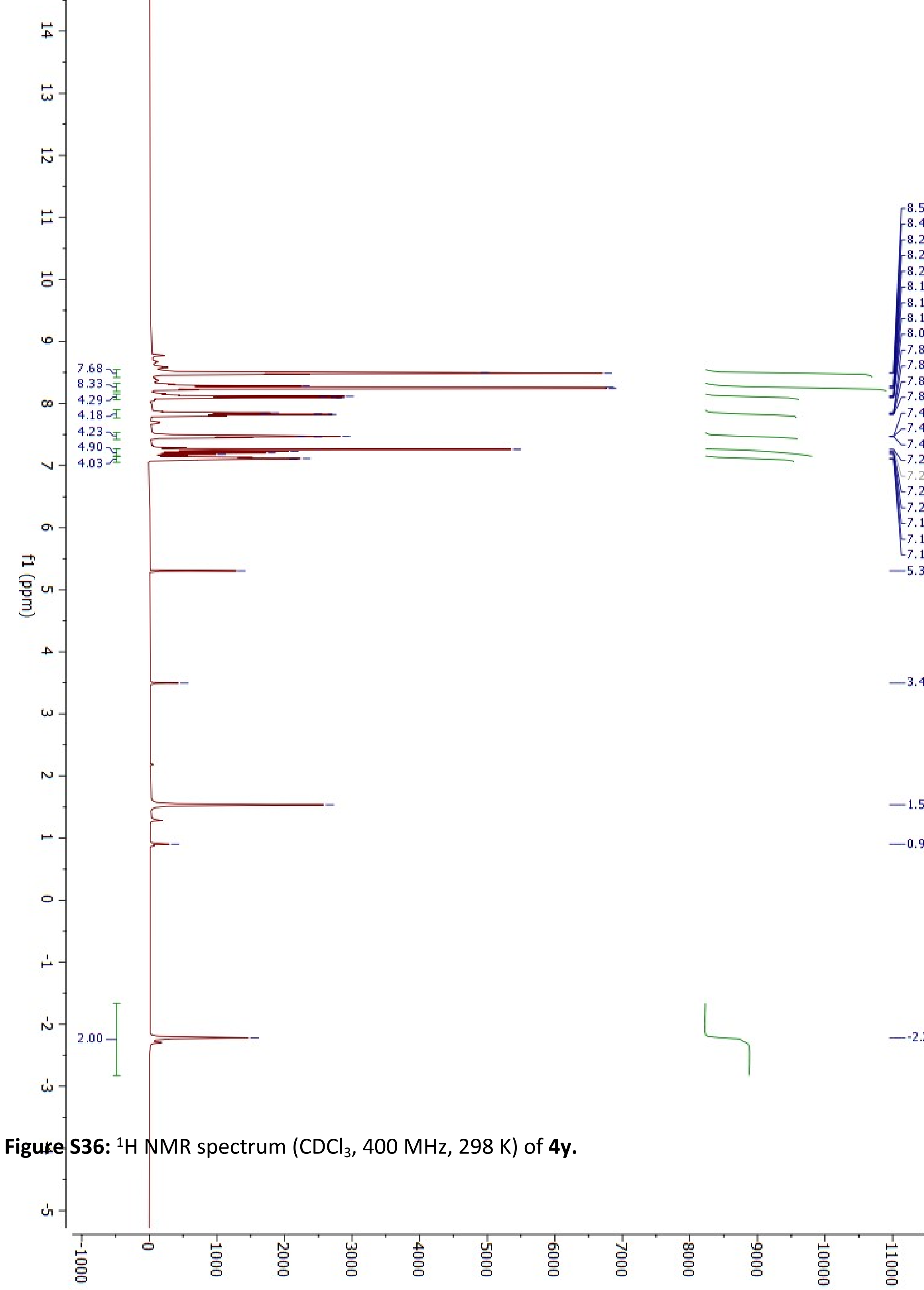


Figure S36: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4y.**

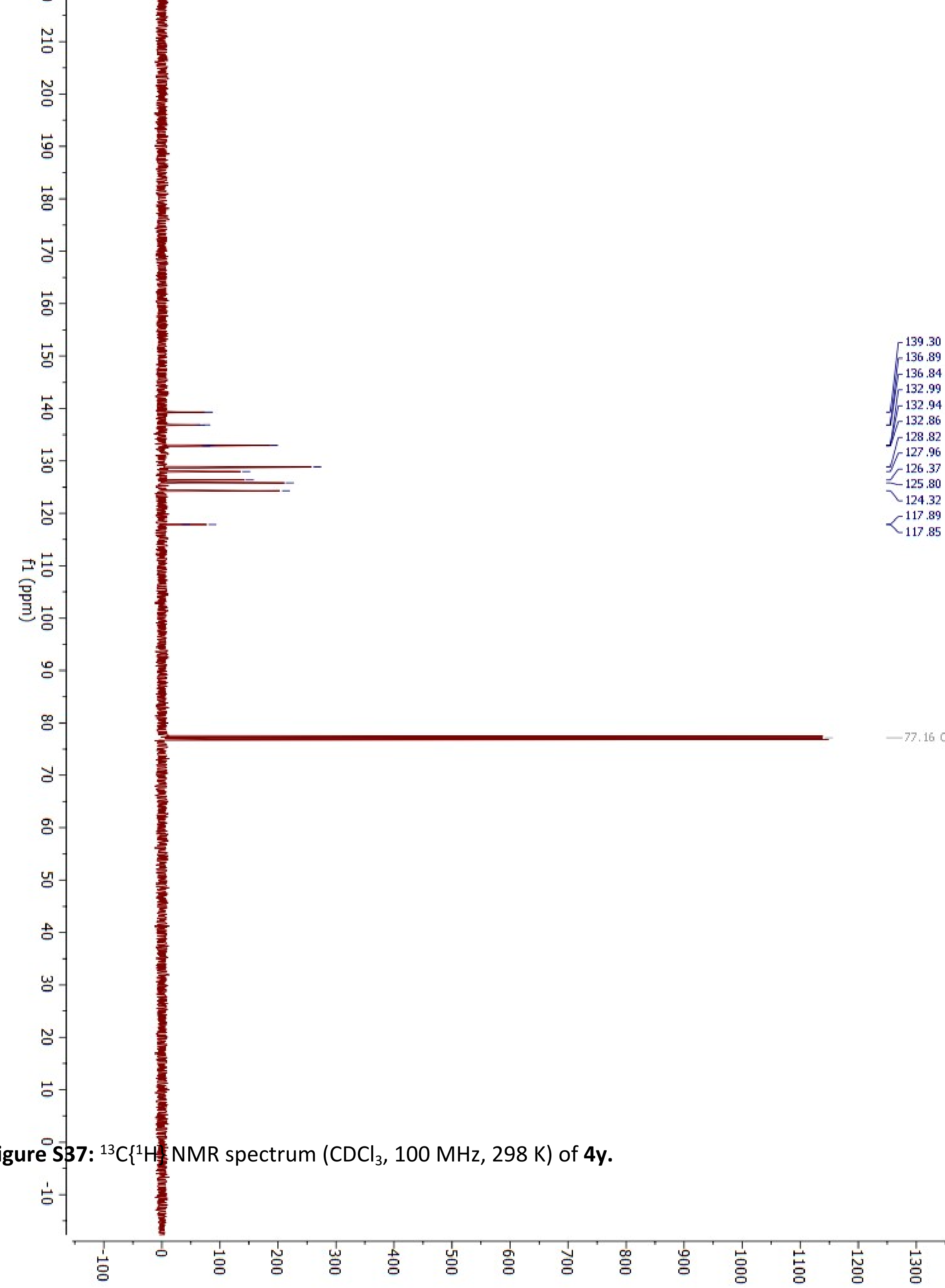


Figure S37: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4y.**

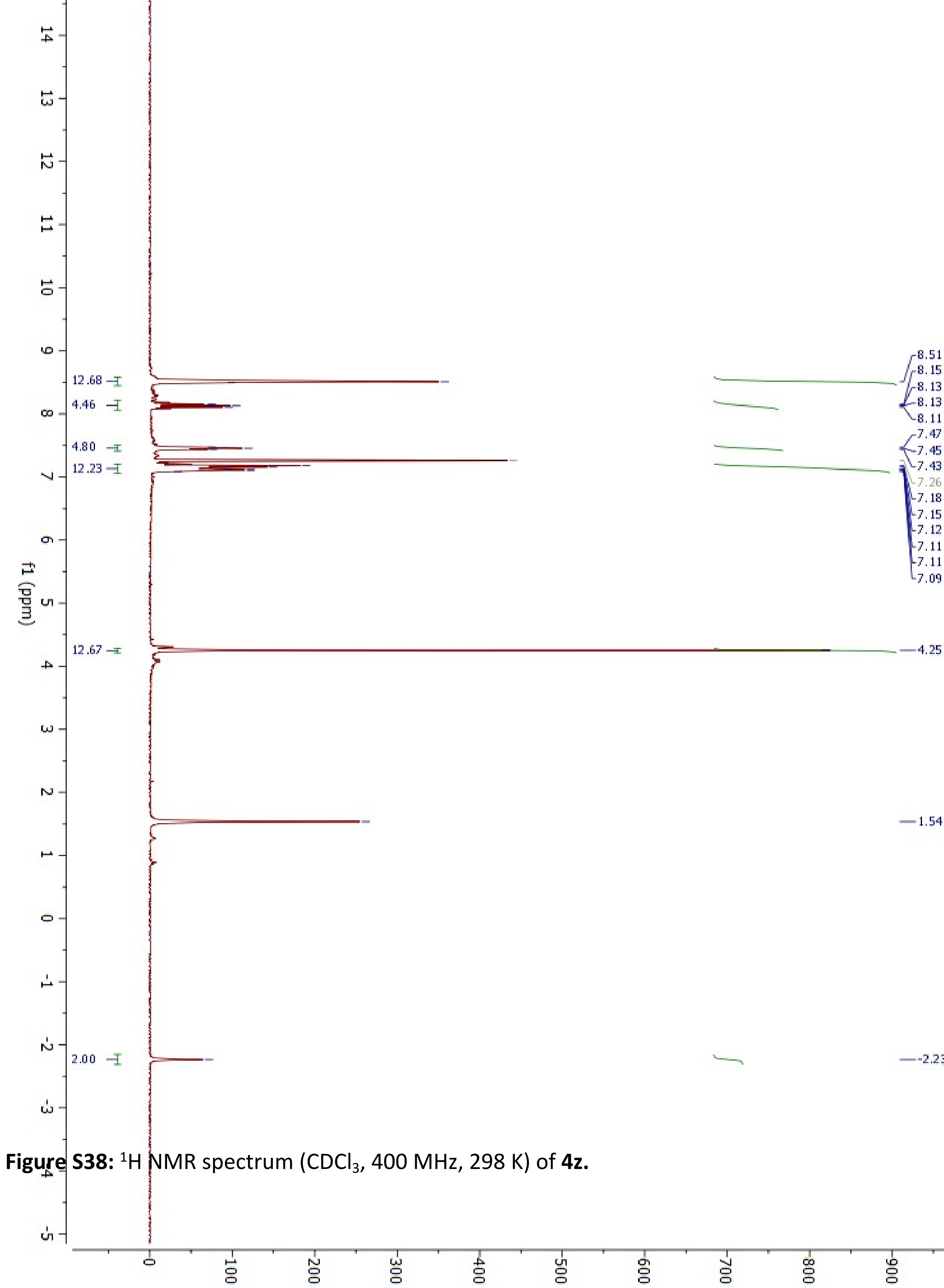


Figure S38: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4z.**

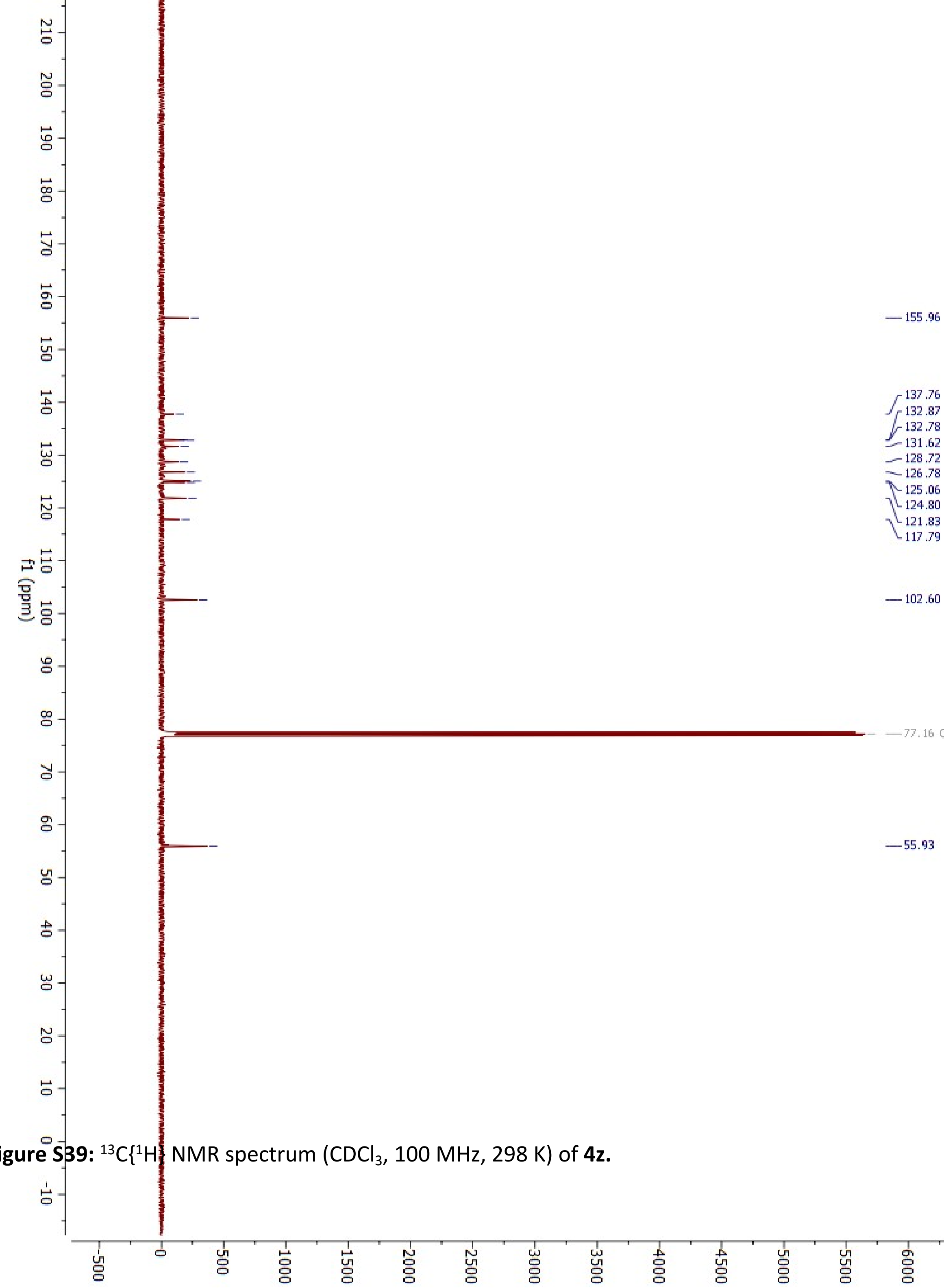


Figure S39: $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4z.**

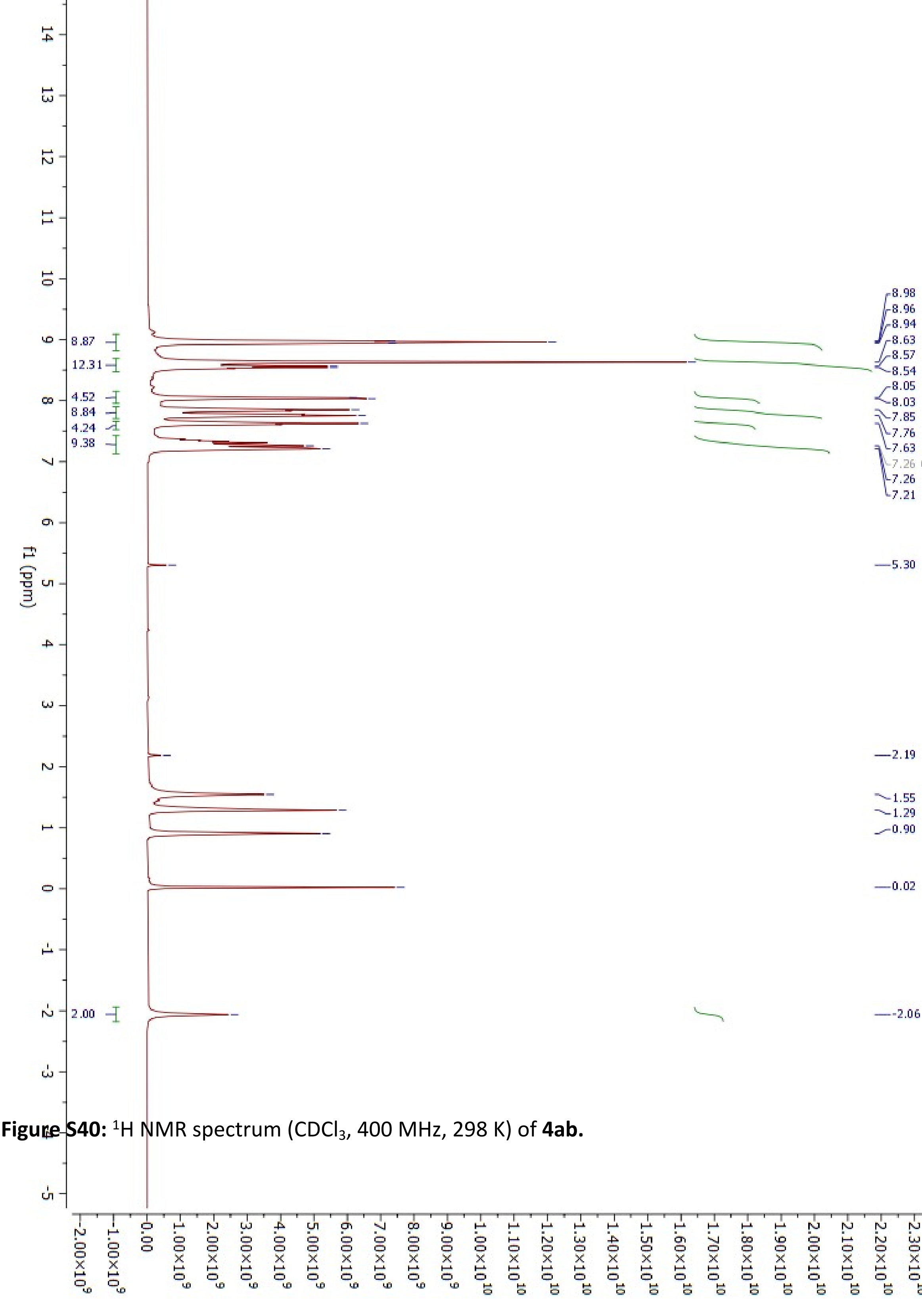


Figure S40: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4ab.**

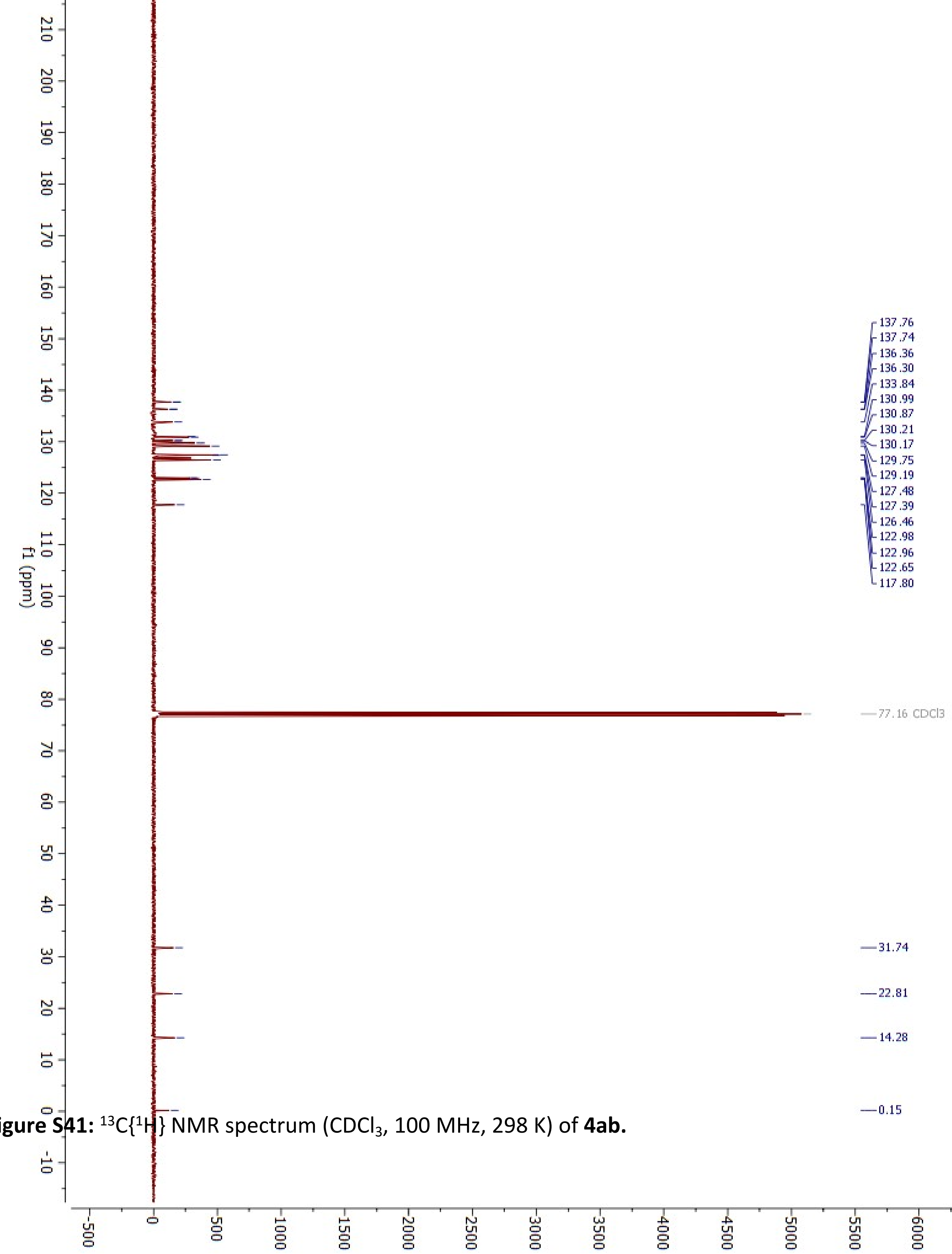


Figure S41: $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4ab.**

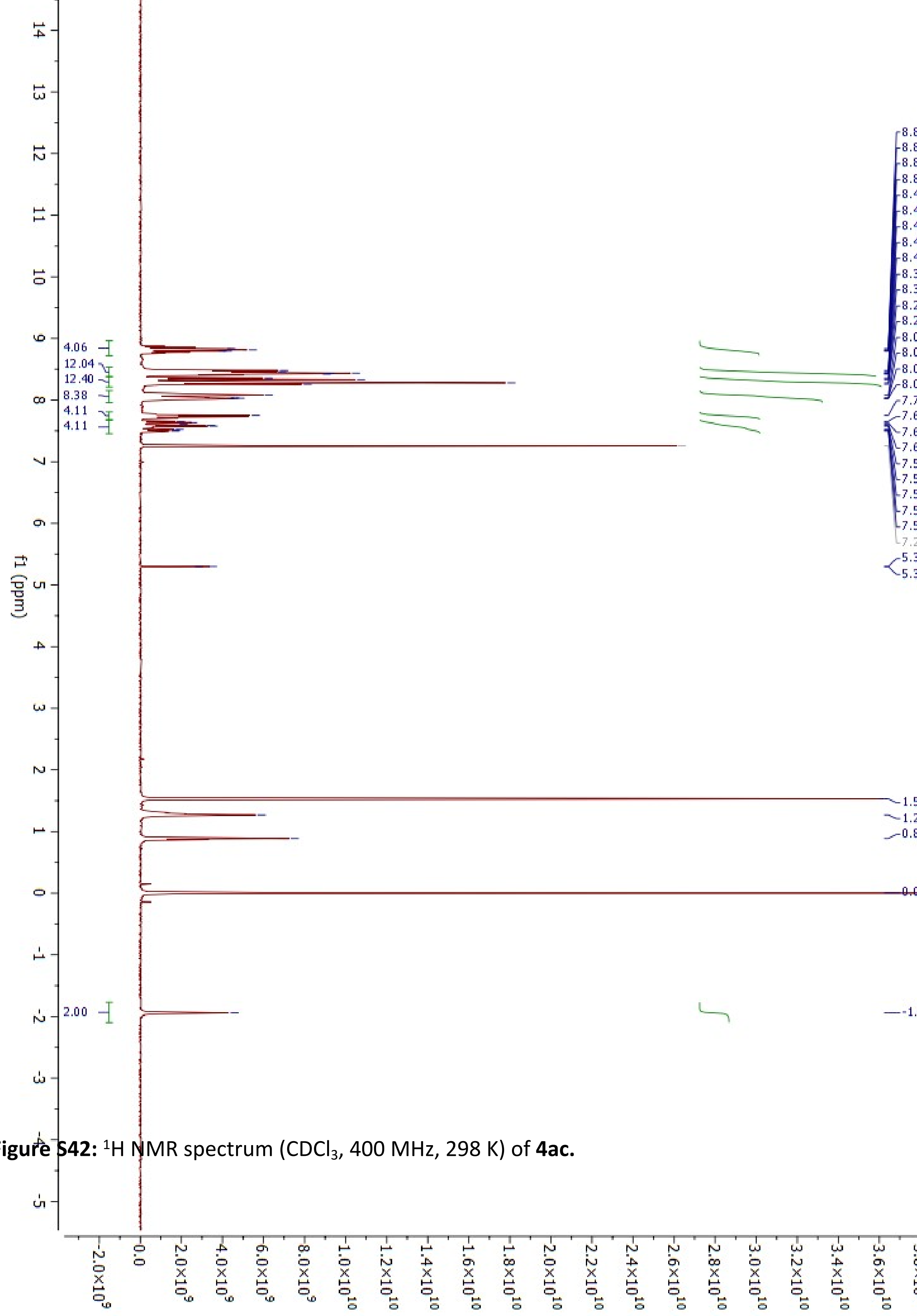


Figure S42: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4ac.**

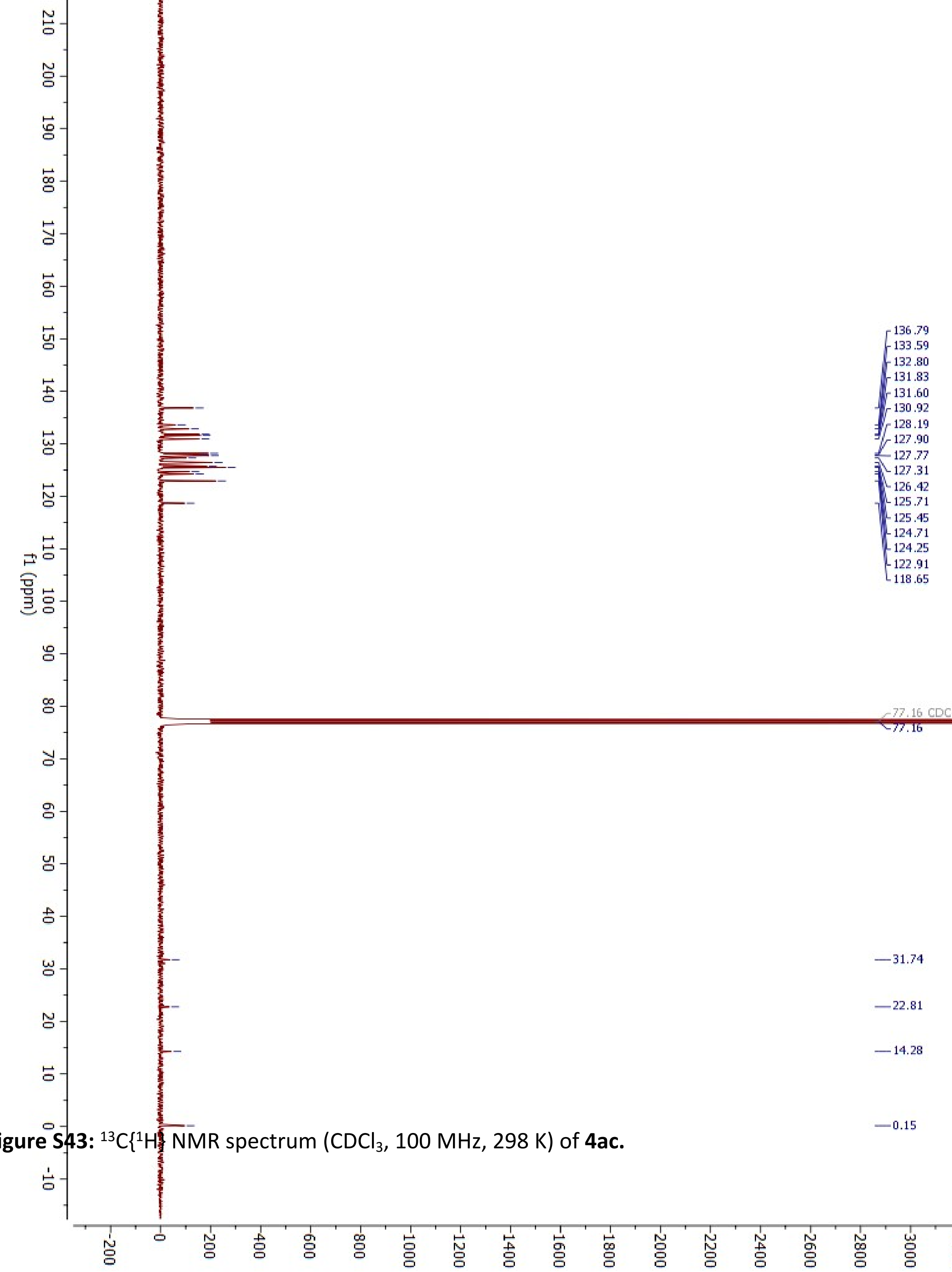


Figure S43: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4ac.**

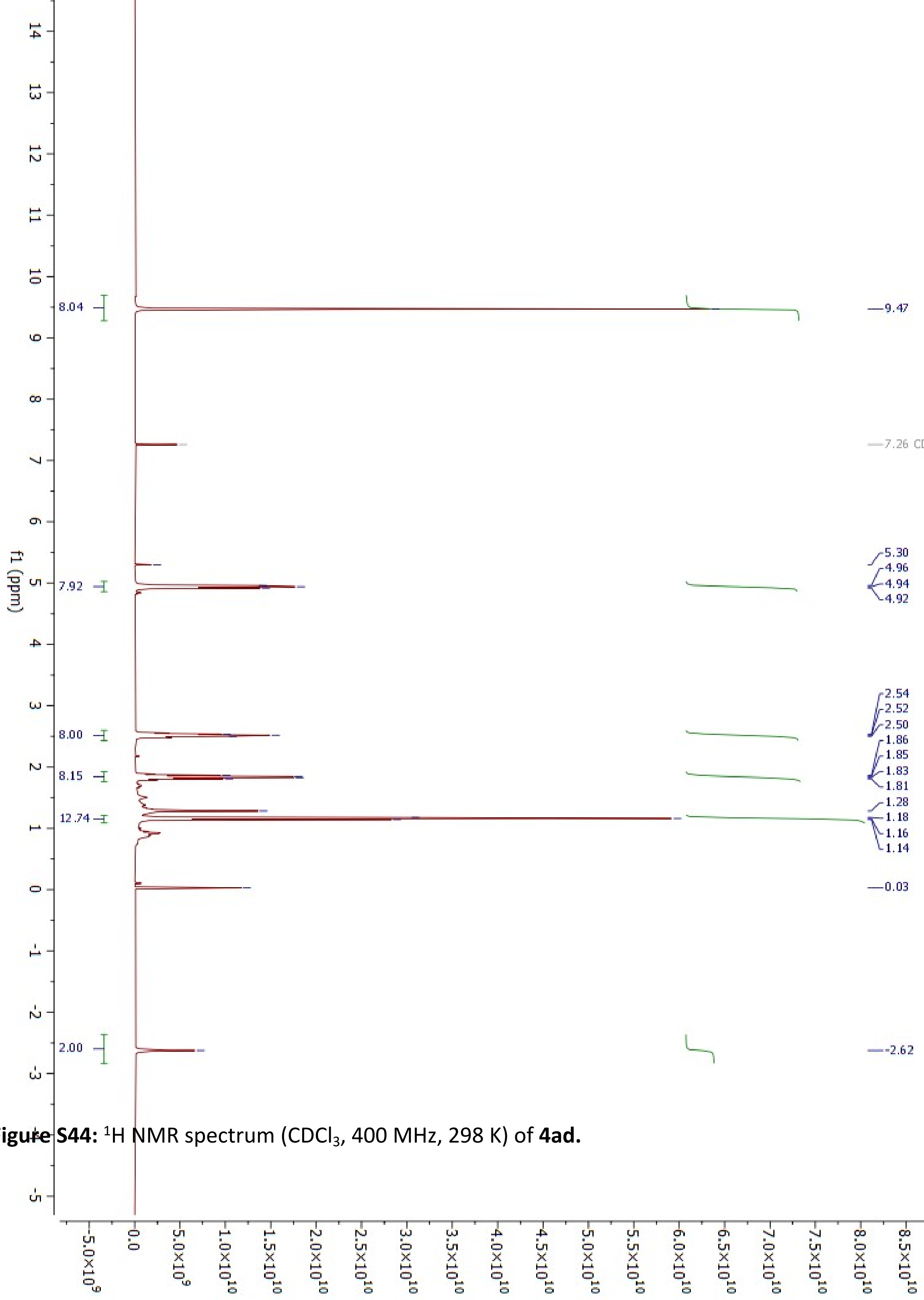


Figure S44: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4ad.**

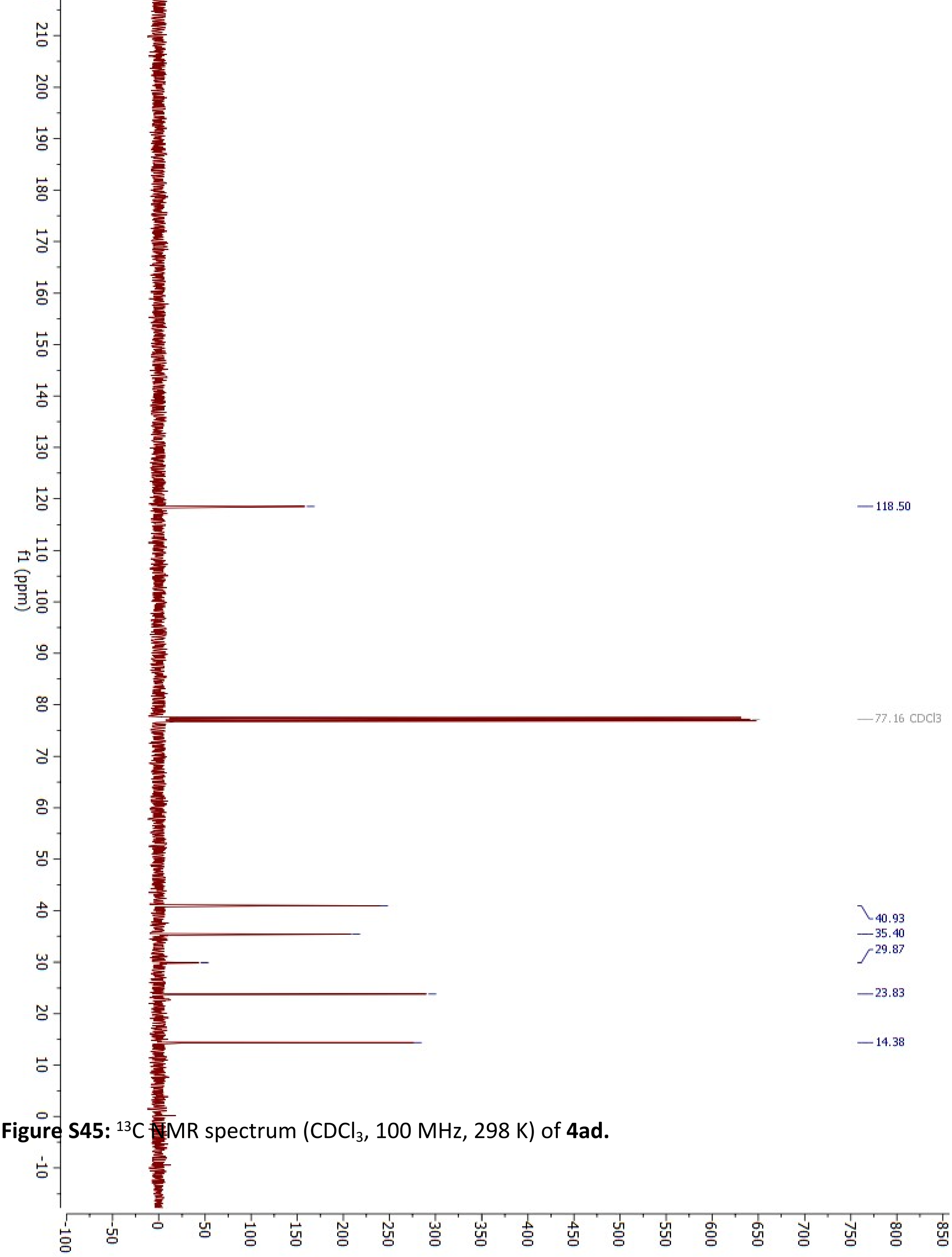


Figure S45: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **4ad.**

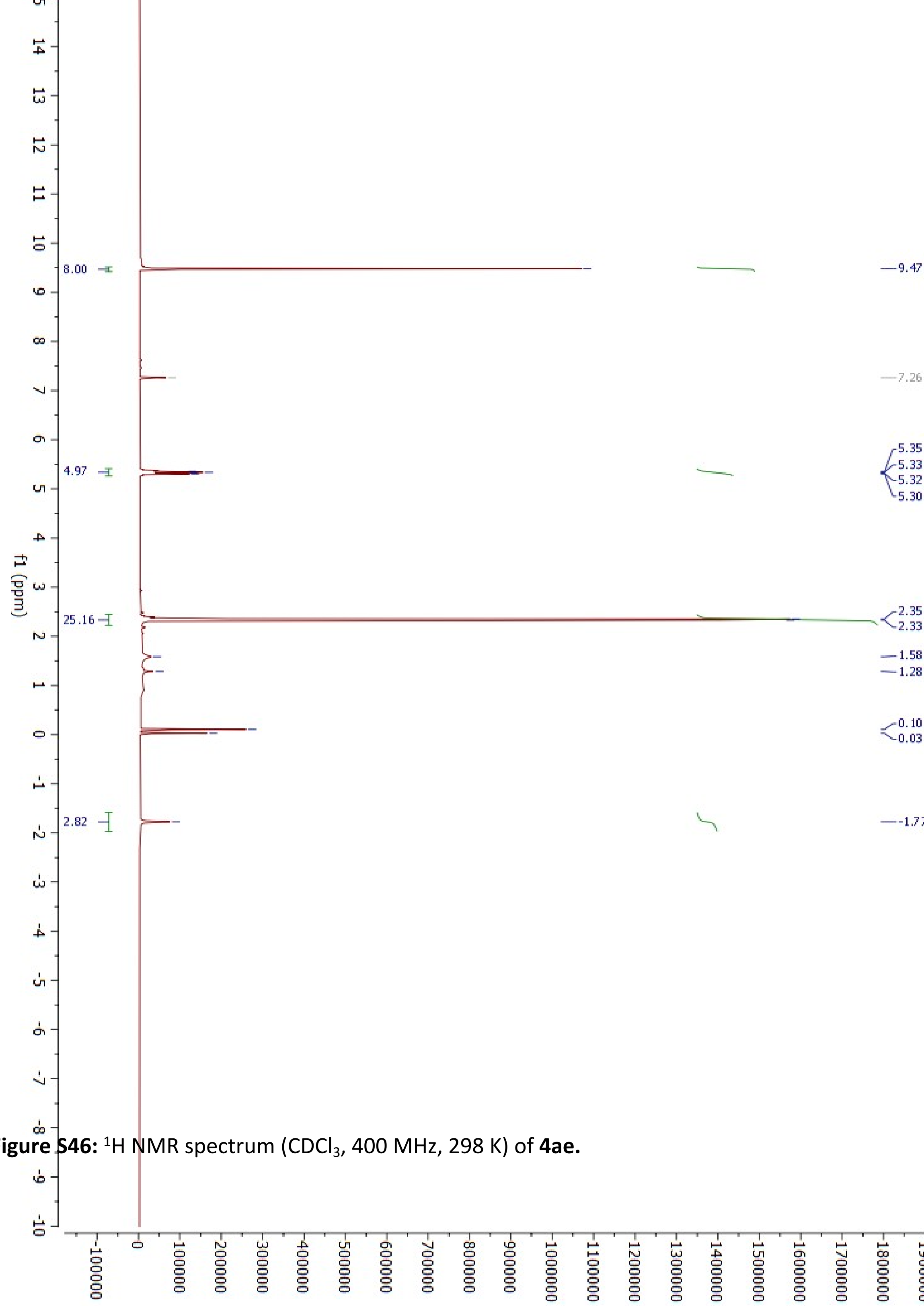


Figure S46: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **4ae.**

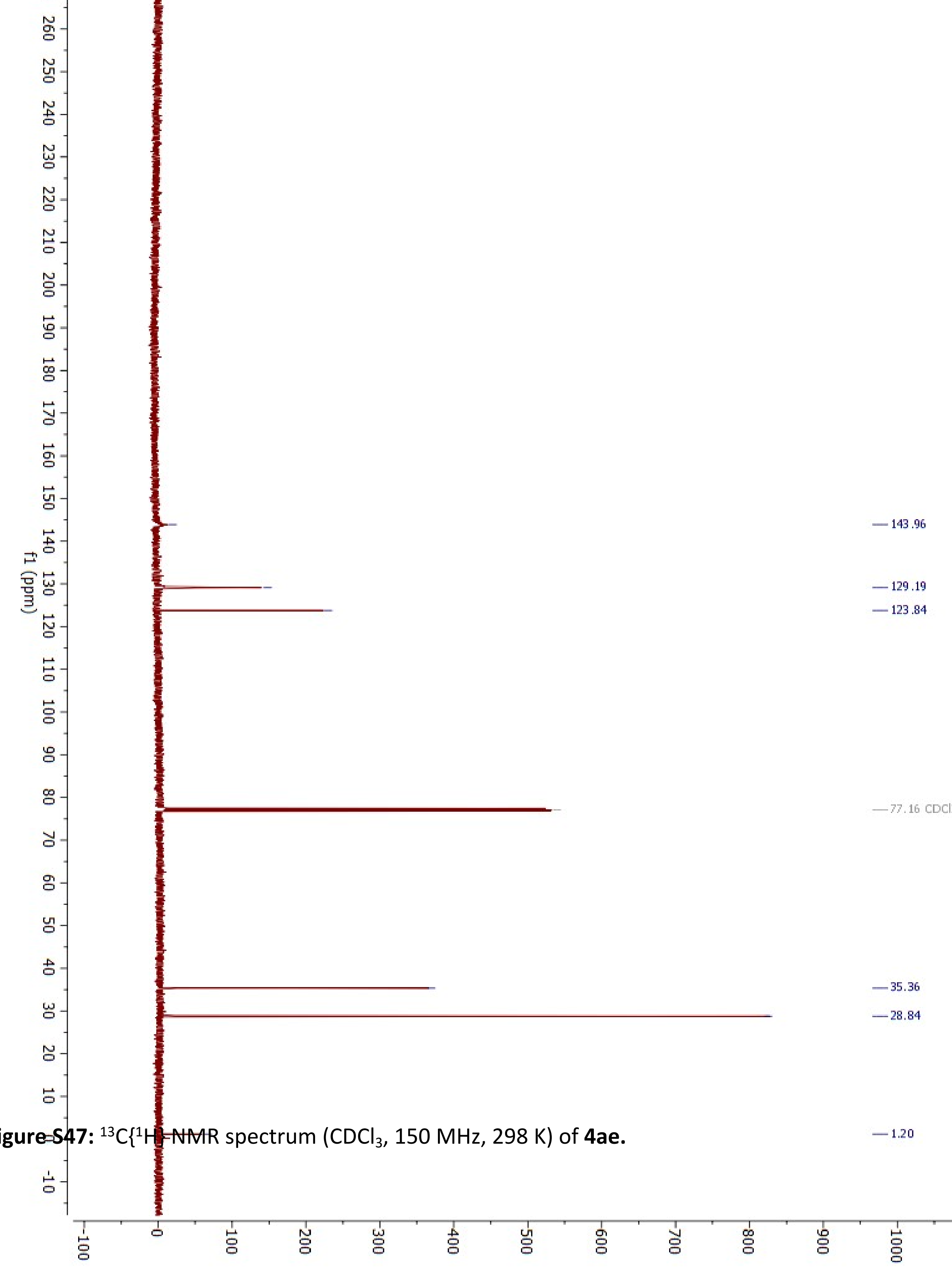


Figure S47: $^{13}C\{^{1}H\}$-NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **4ae.**

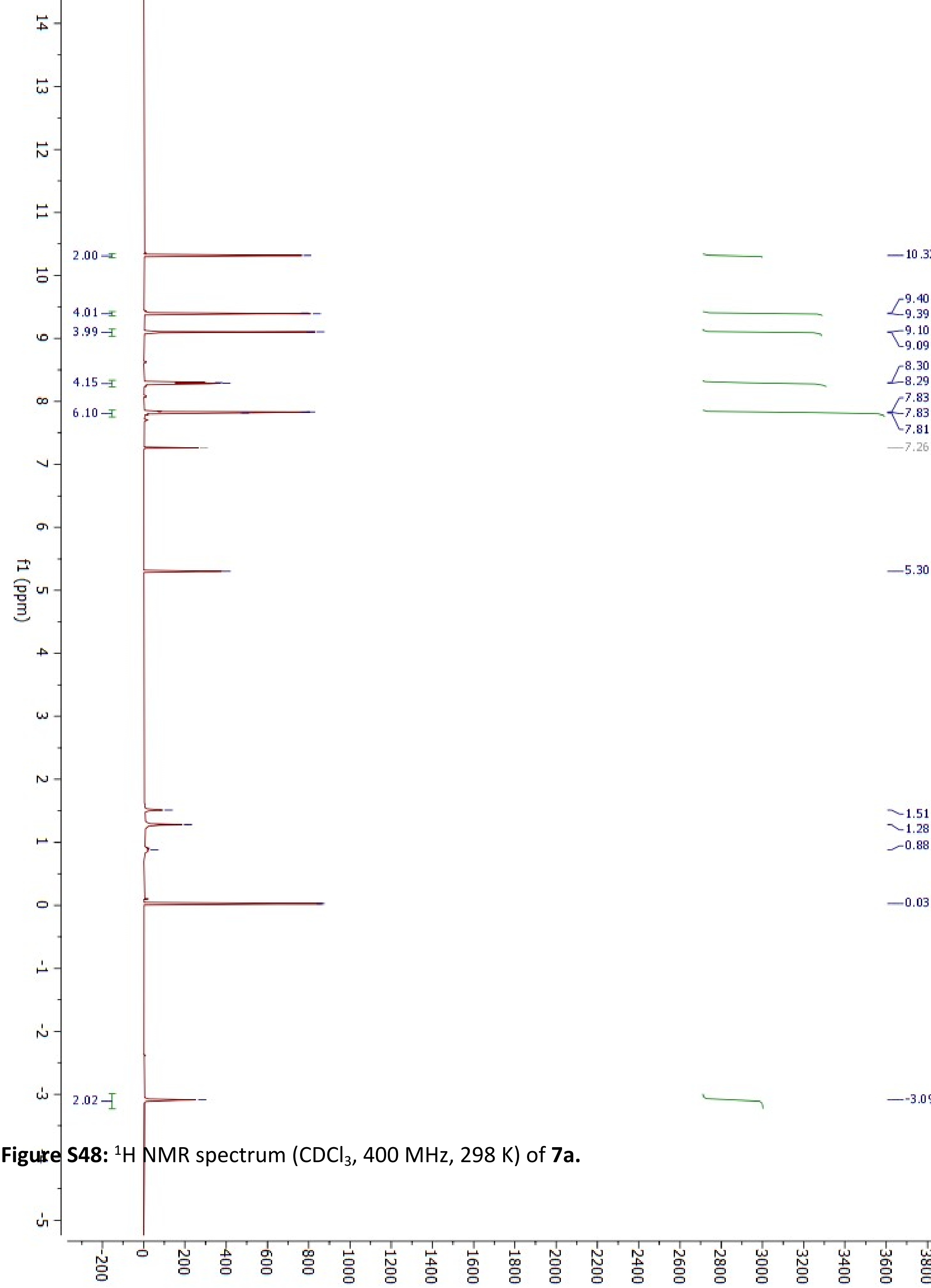


Figure S48: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **7a.**

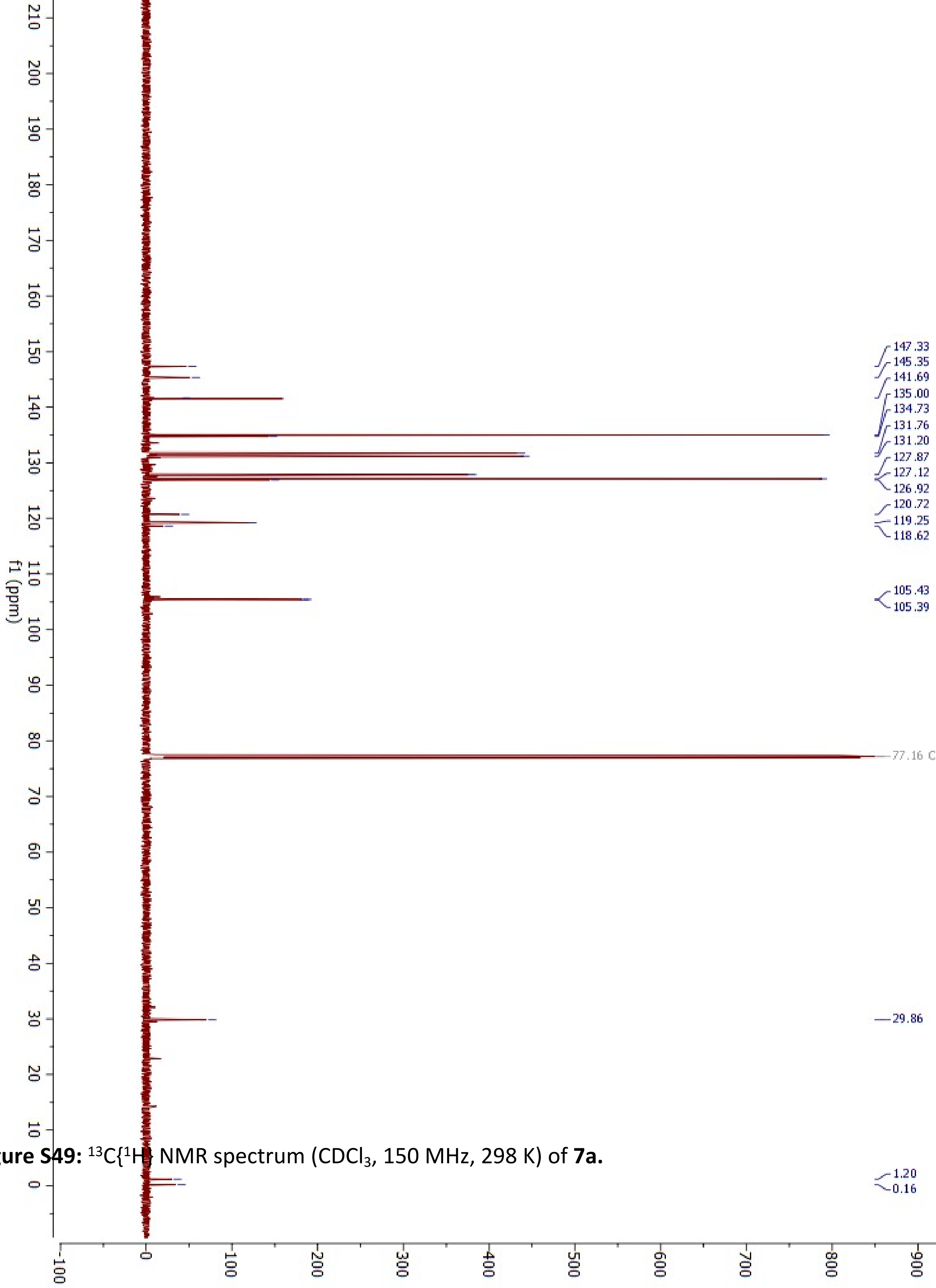


Figure S49: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **7a.**

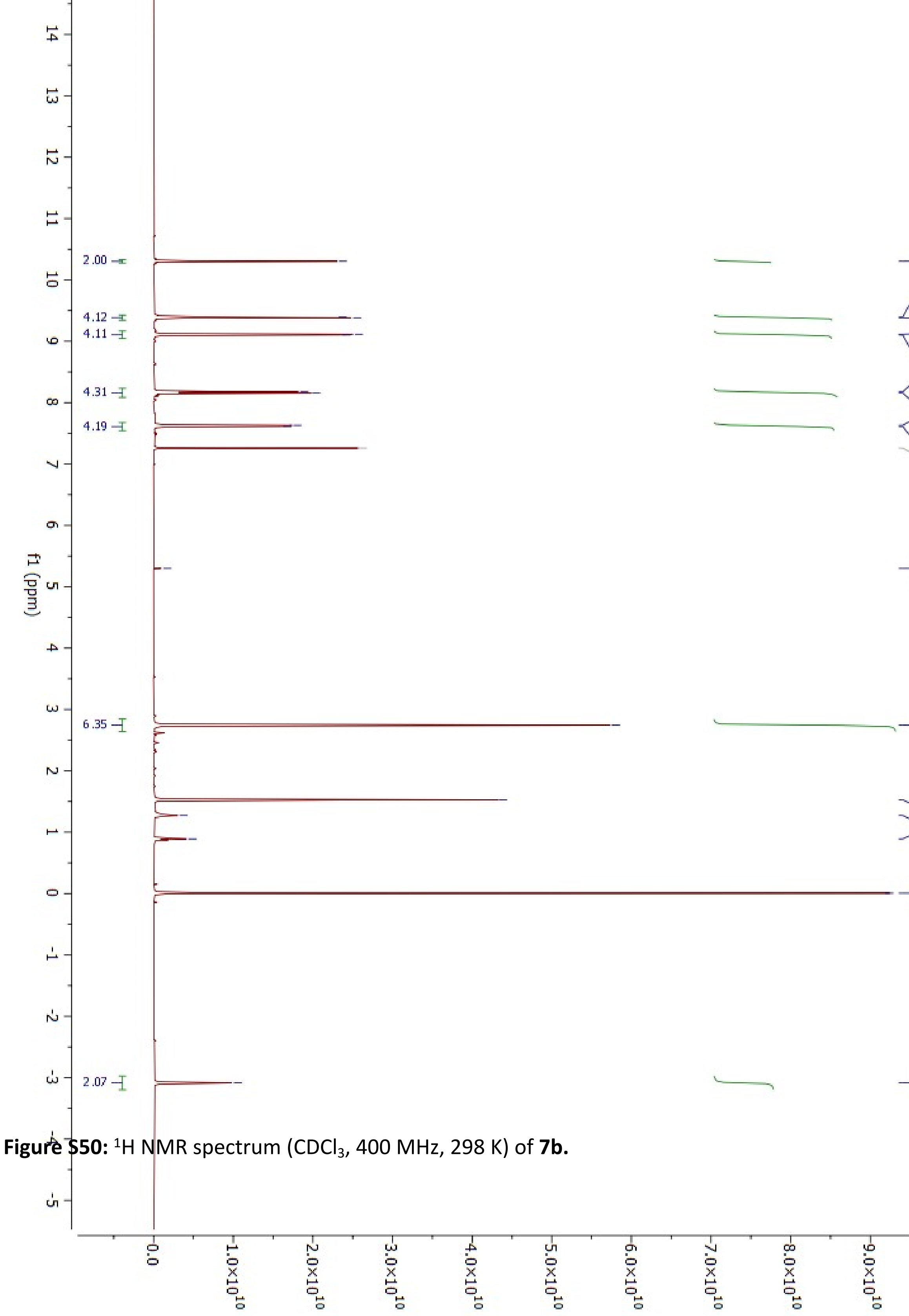


Figure S50: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **7b.**

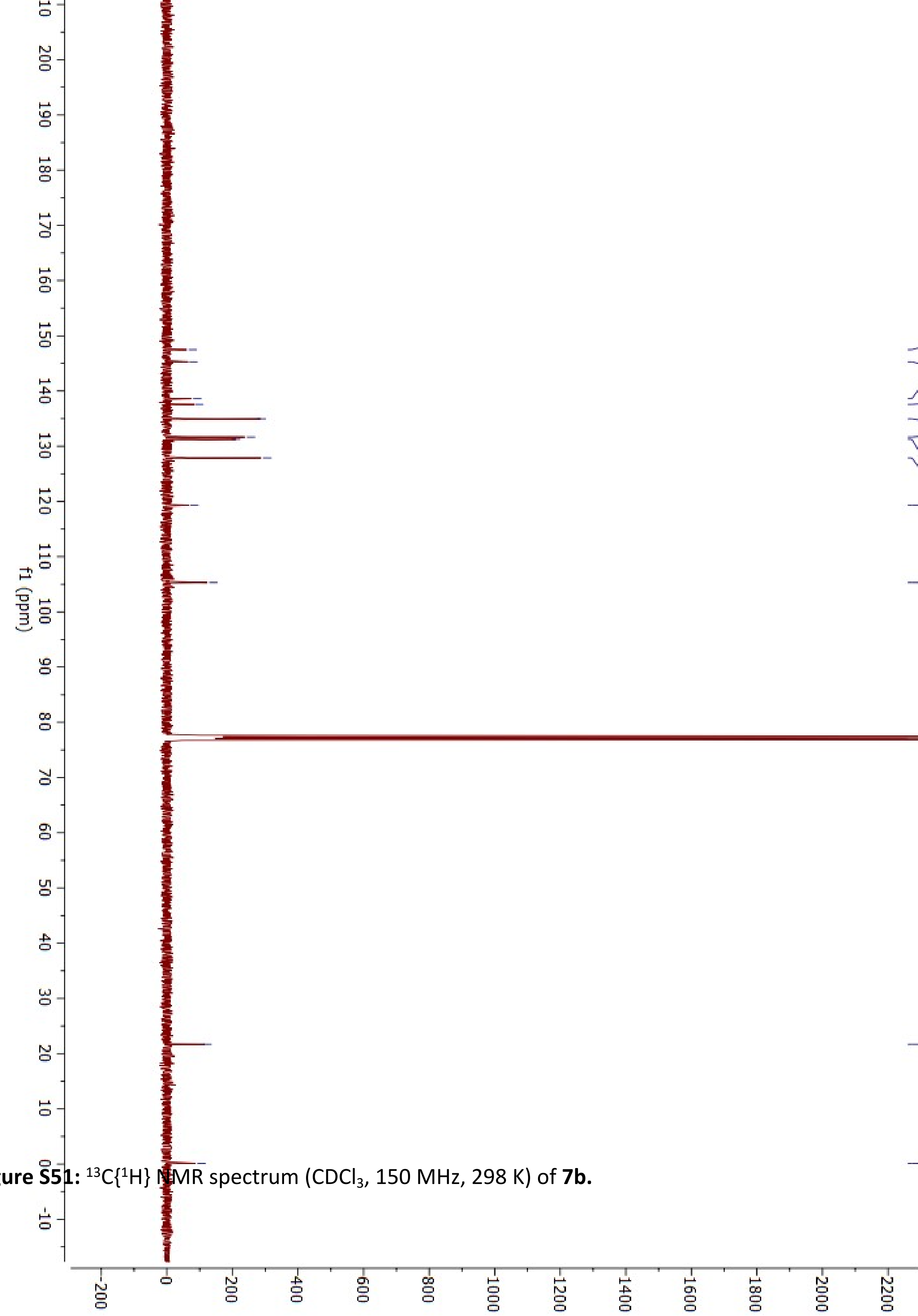


Figure S51: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **7b.**

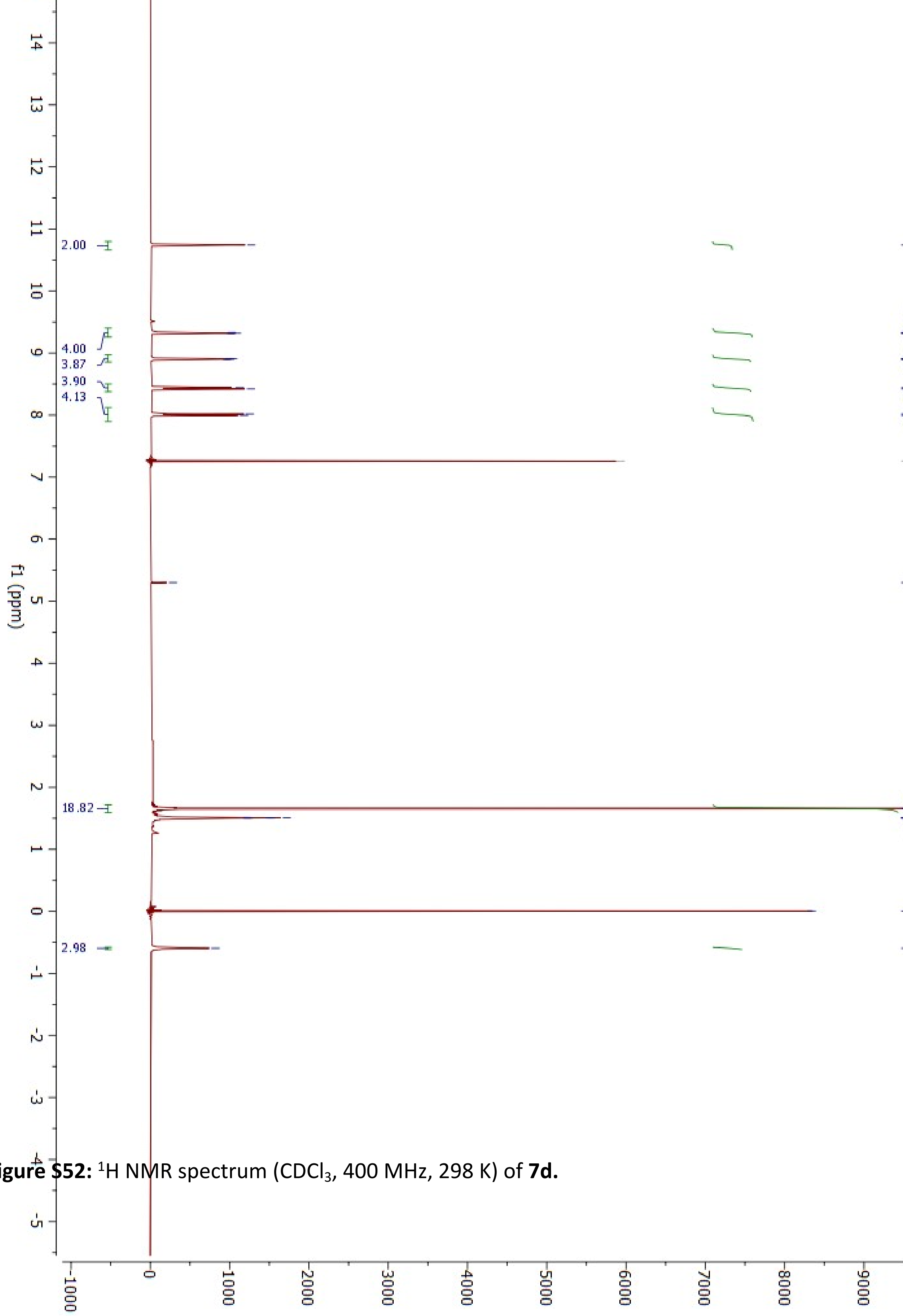


Figure S52: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **7d.**

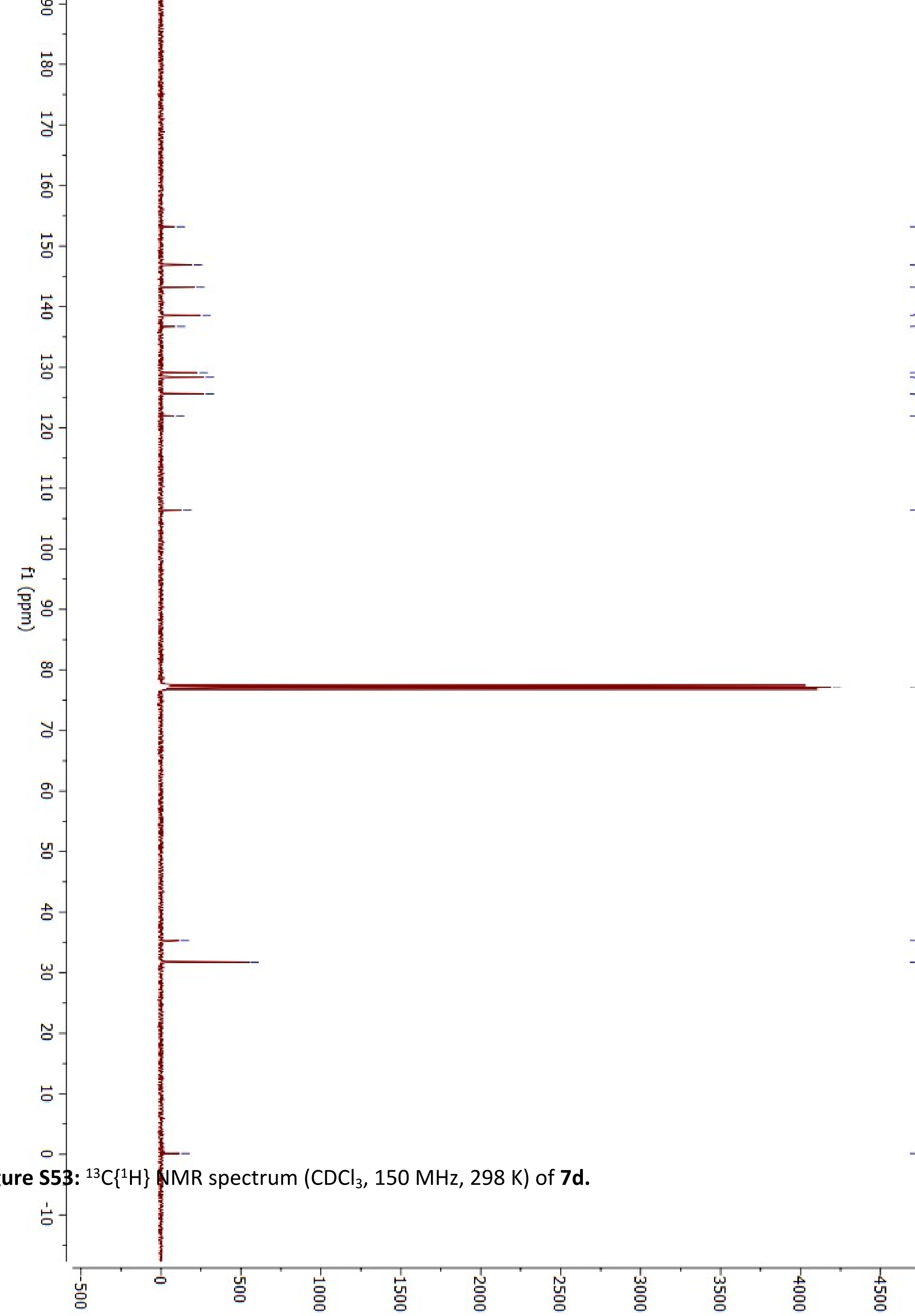


Figure S53: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **7d.**

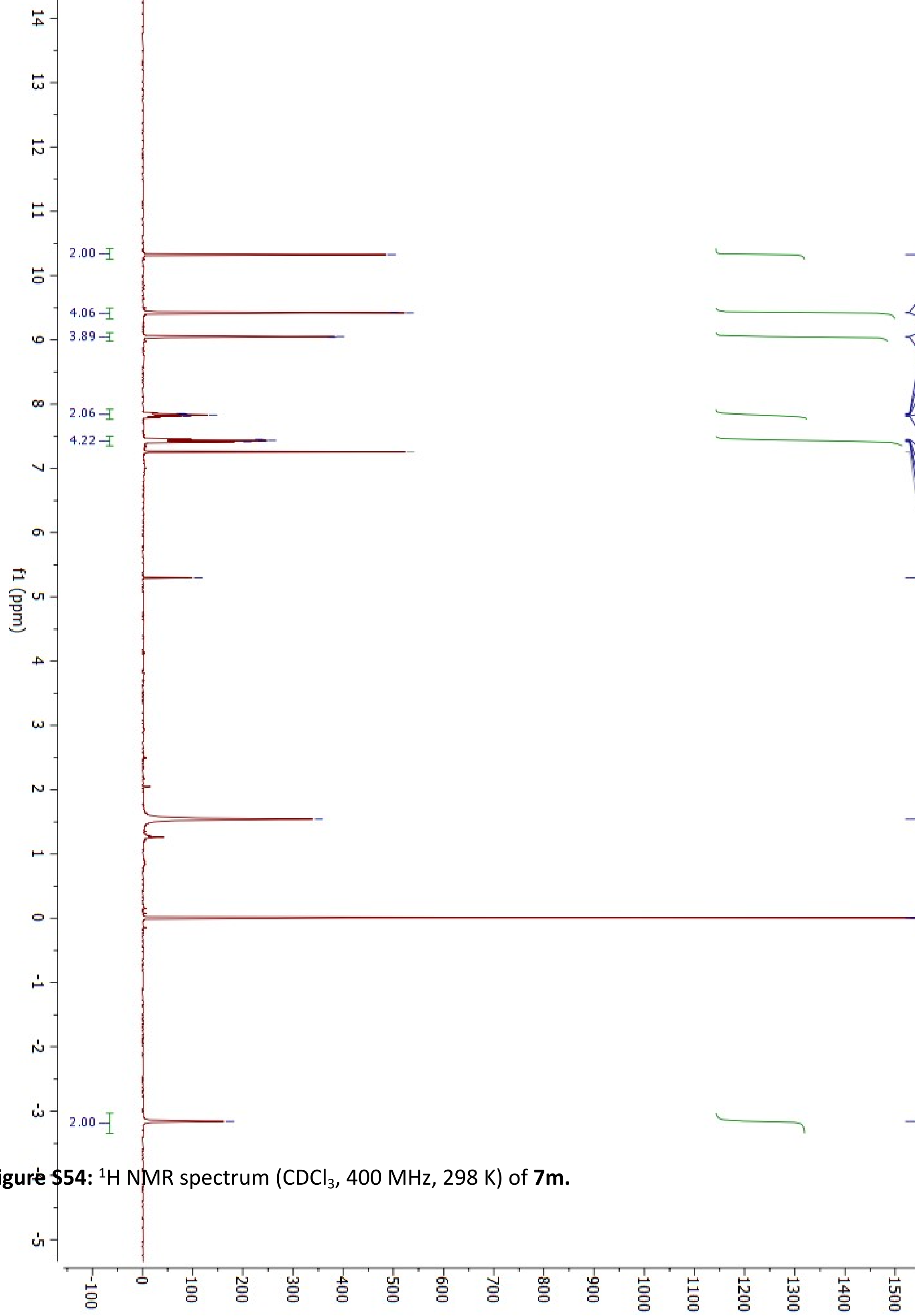


Figure S54: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **7m.**

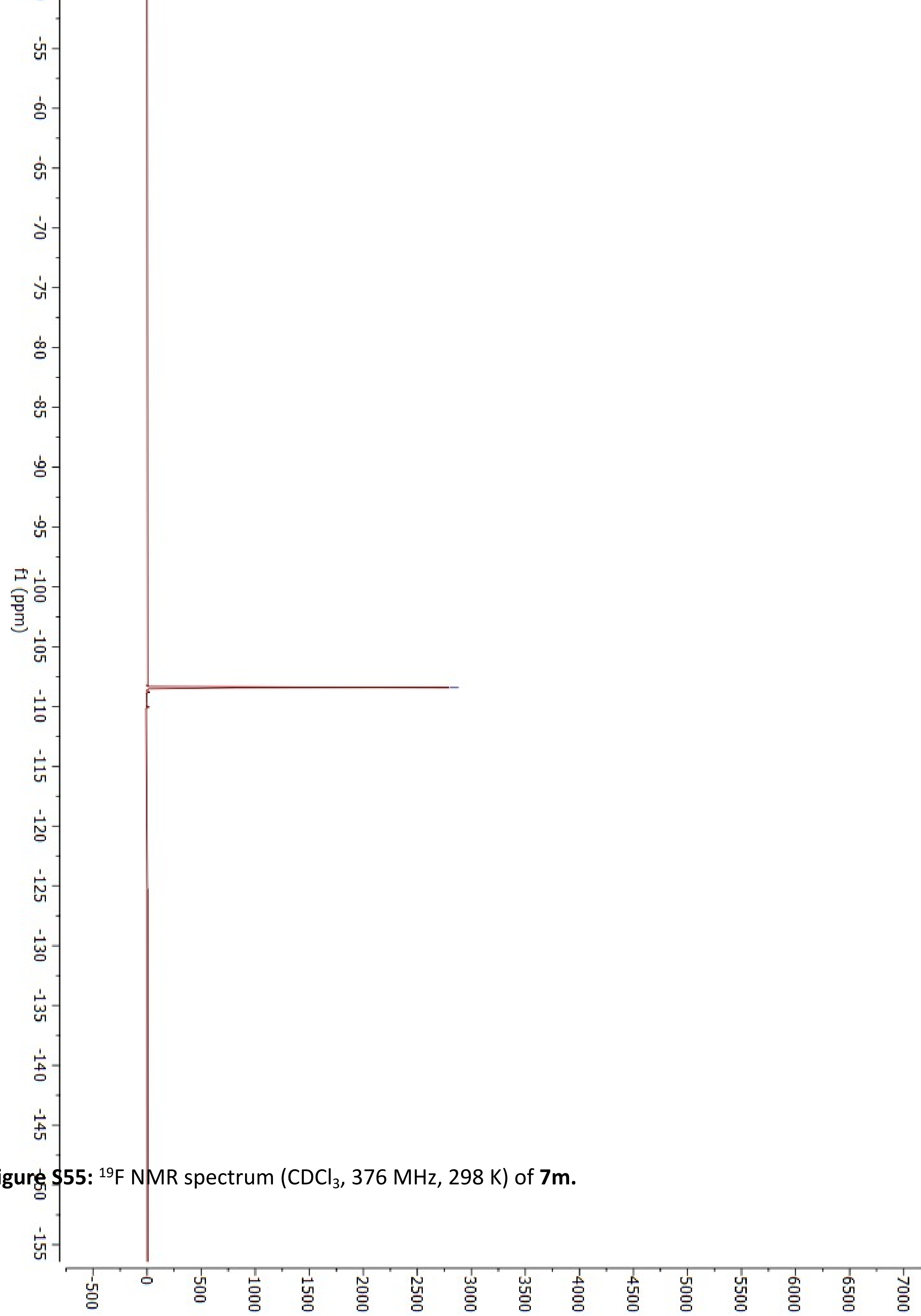


Figure S55: ^{19}F NMR spectrum ($CDCl_3$, 376 MHz, 298 K) of **7m.**

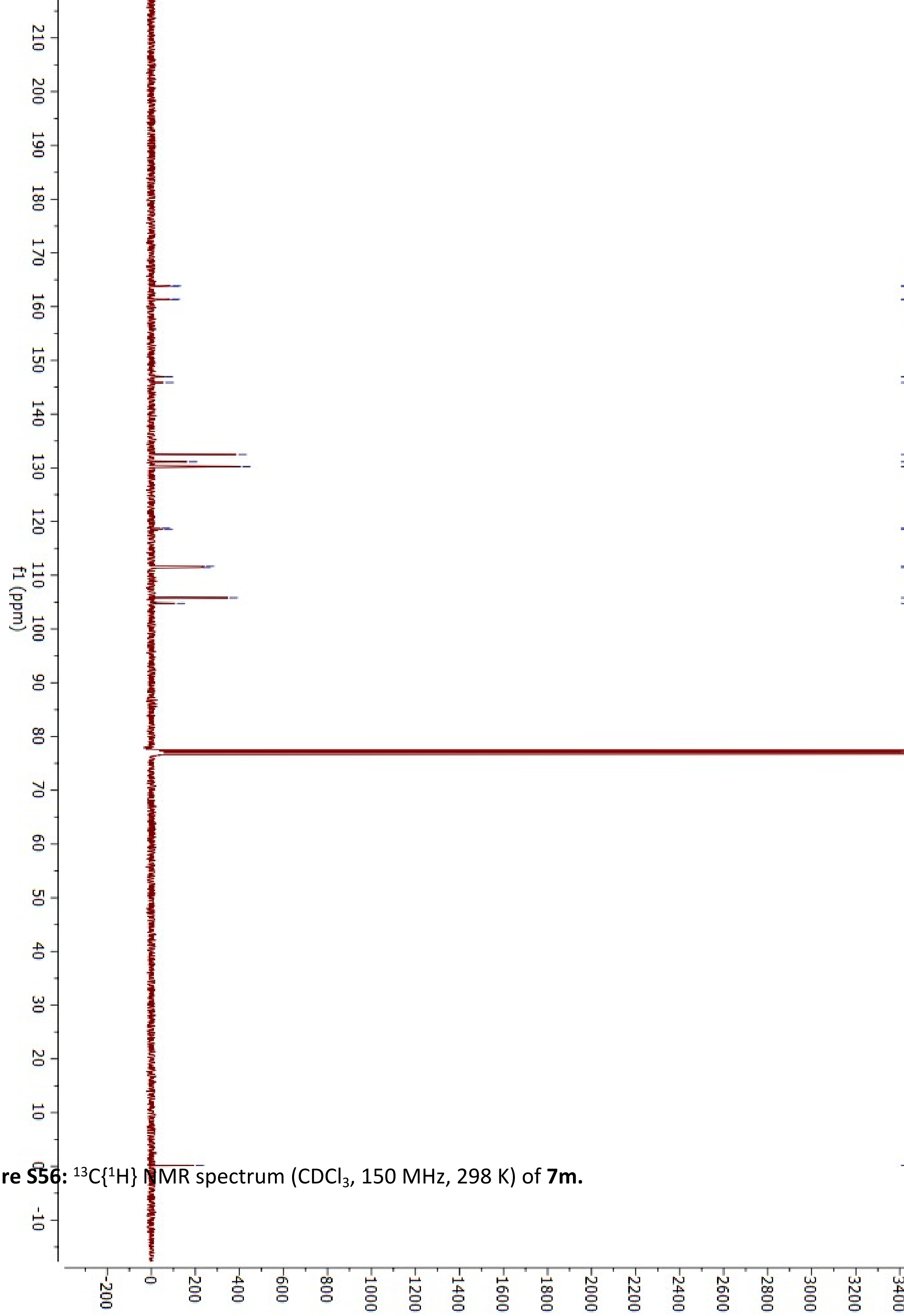


Figure S56: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **7m.**

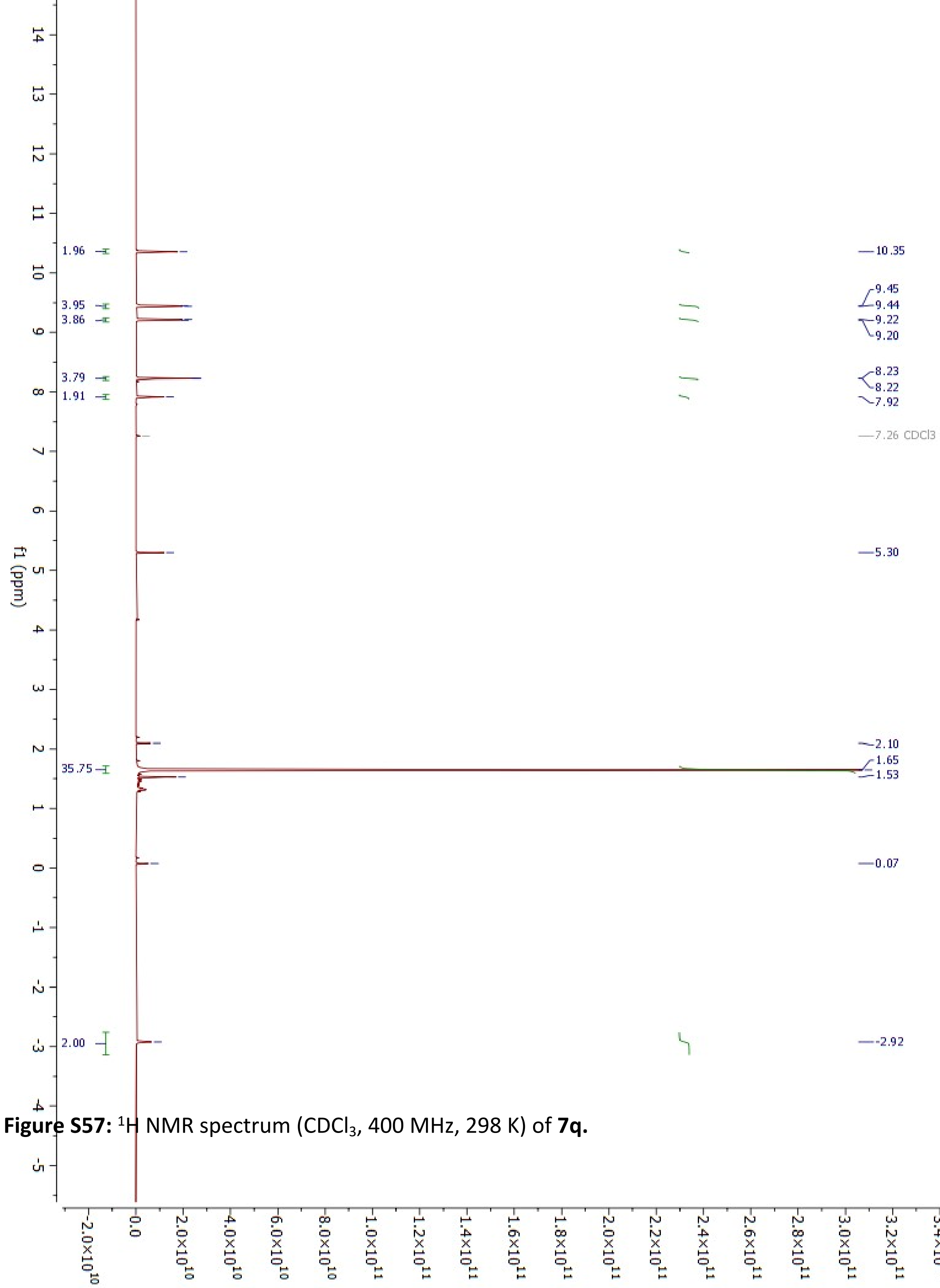


Figure S57: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **7q.**

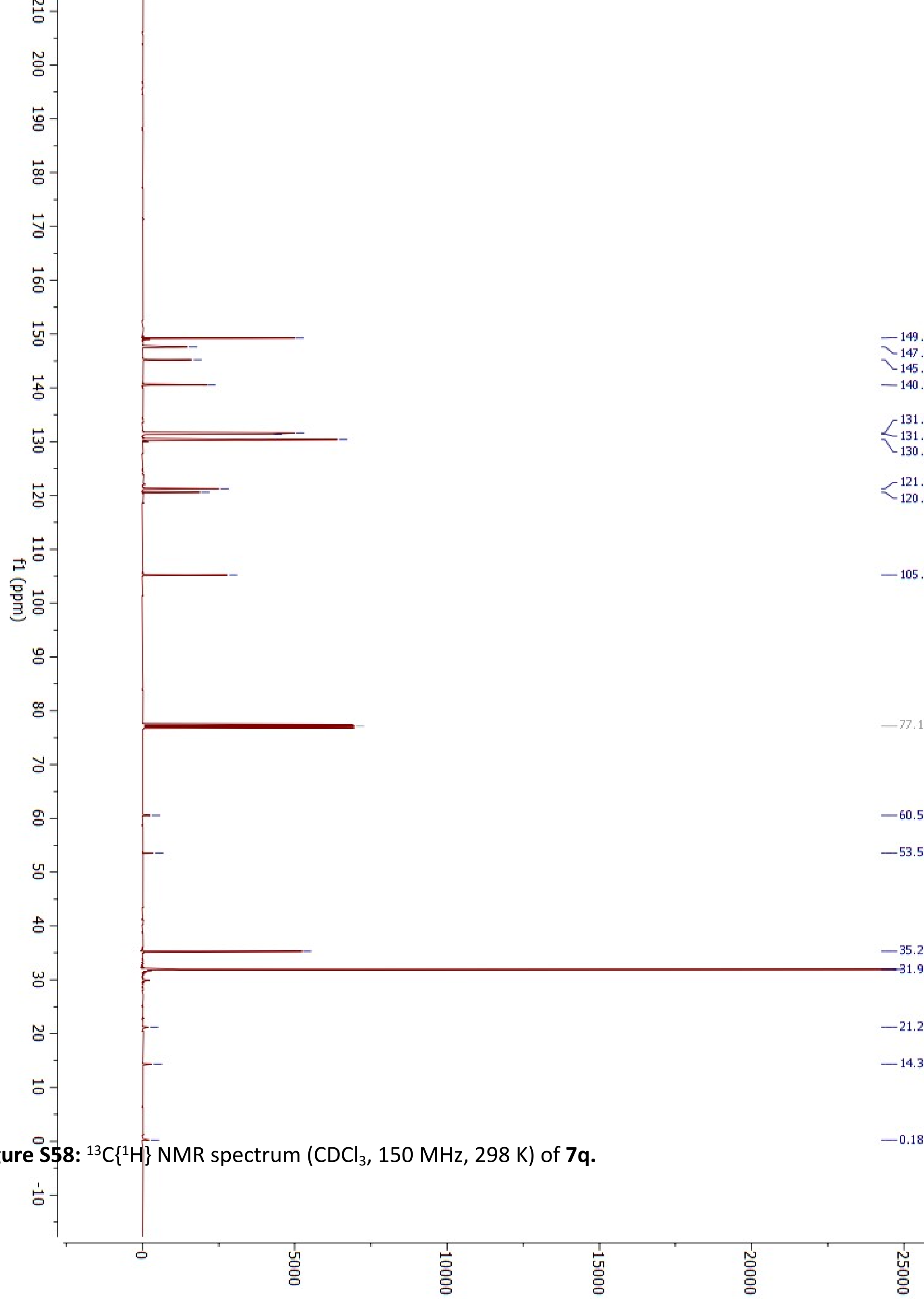


Figure S58: $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **7q.**

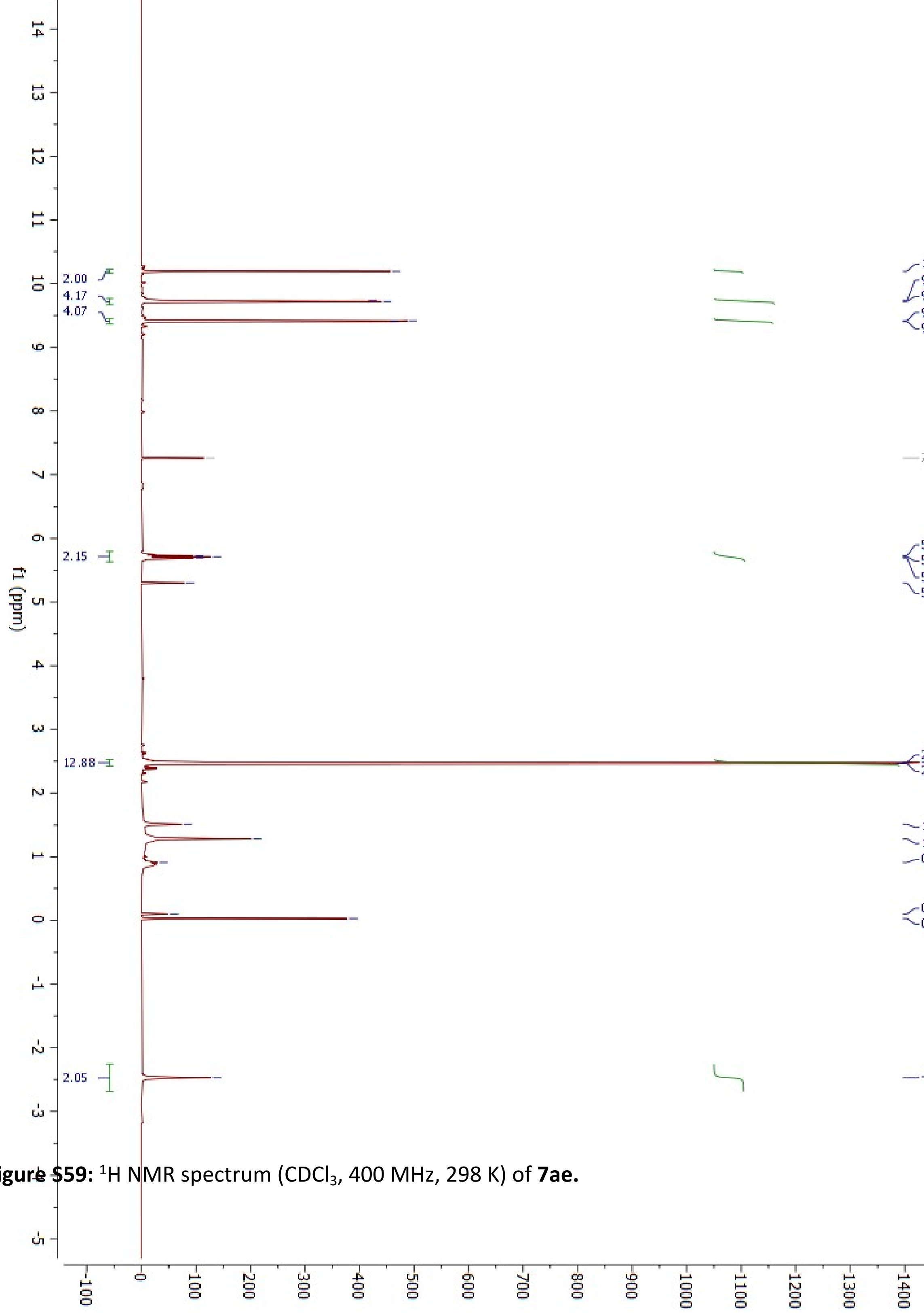


Figure S59: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **7ae.**

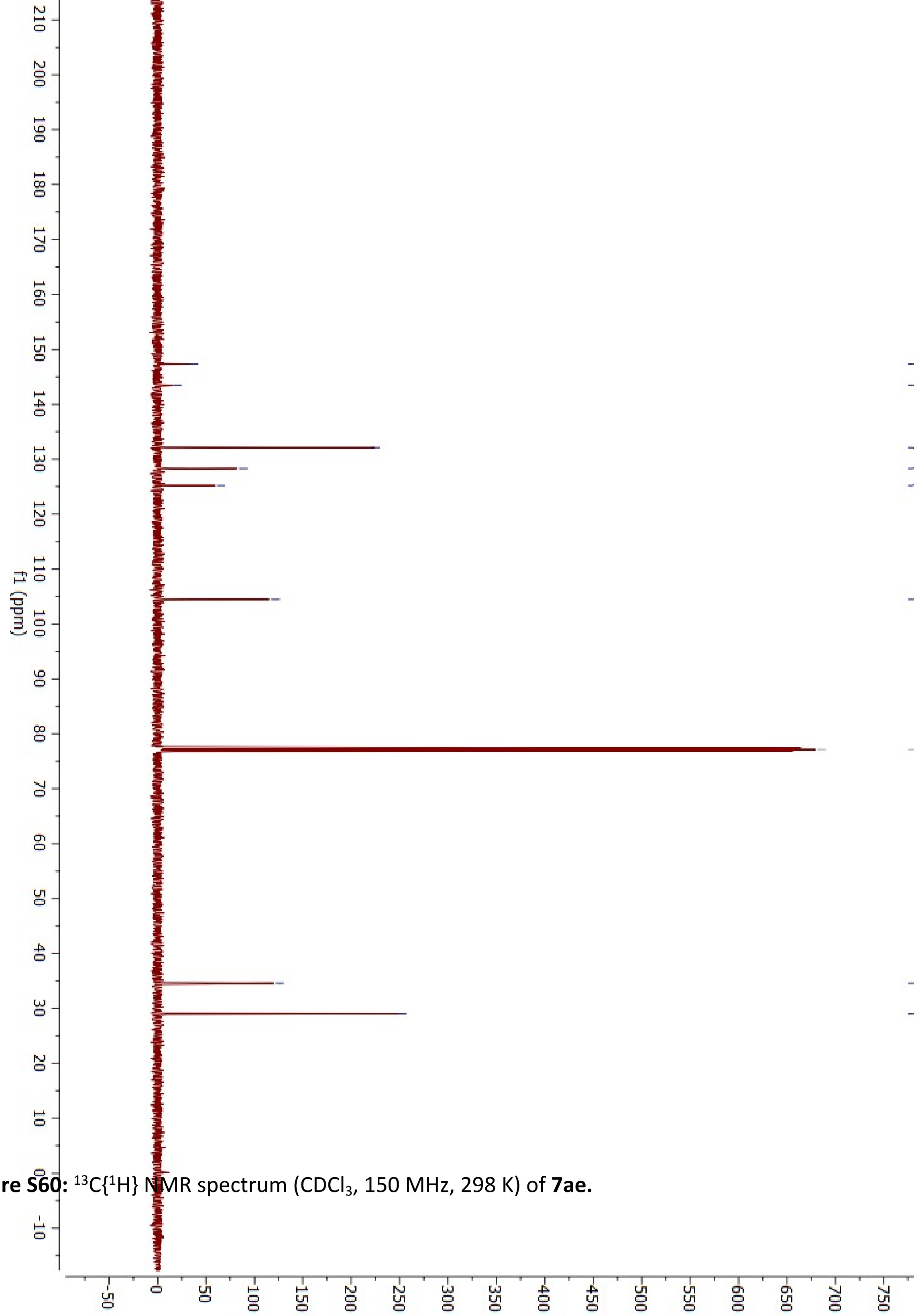


Figure S60: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **7ae.**

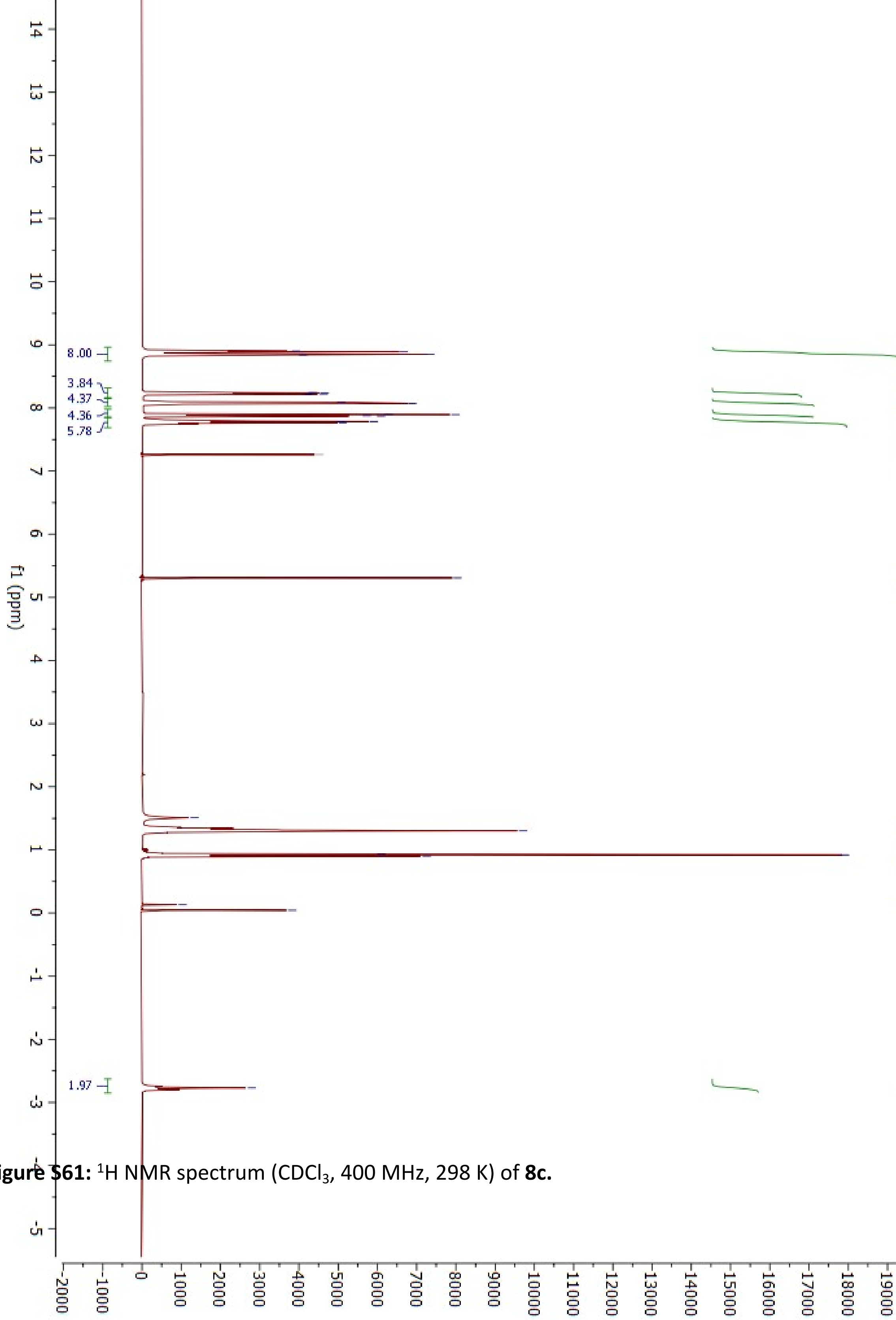


Figure S61: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **8c.**

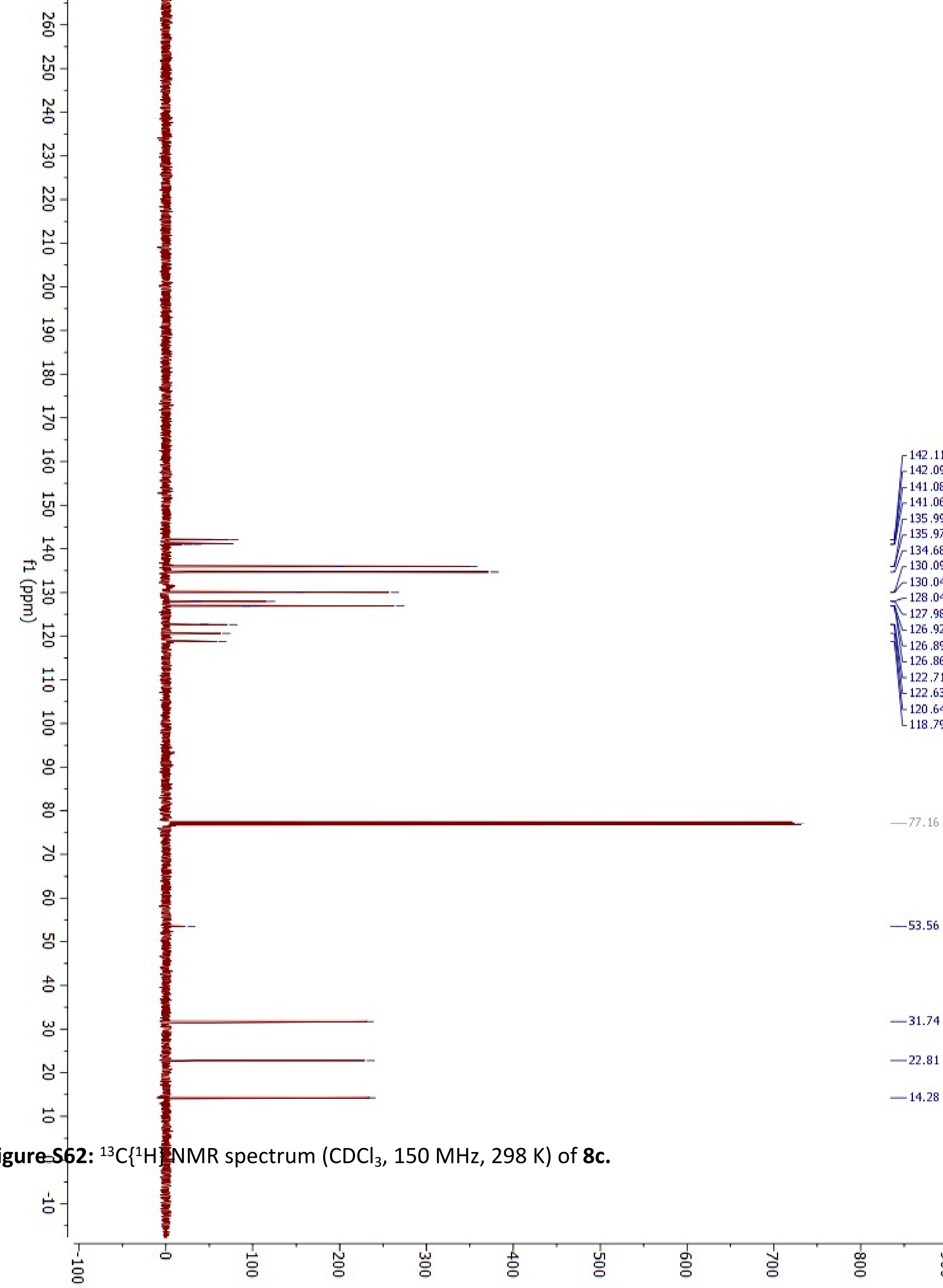


Figure S62: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **8c.**

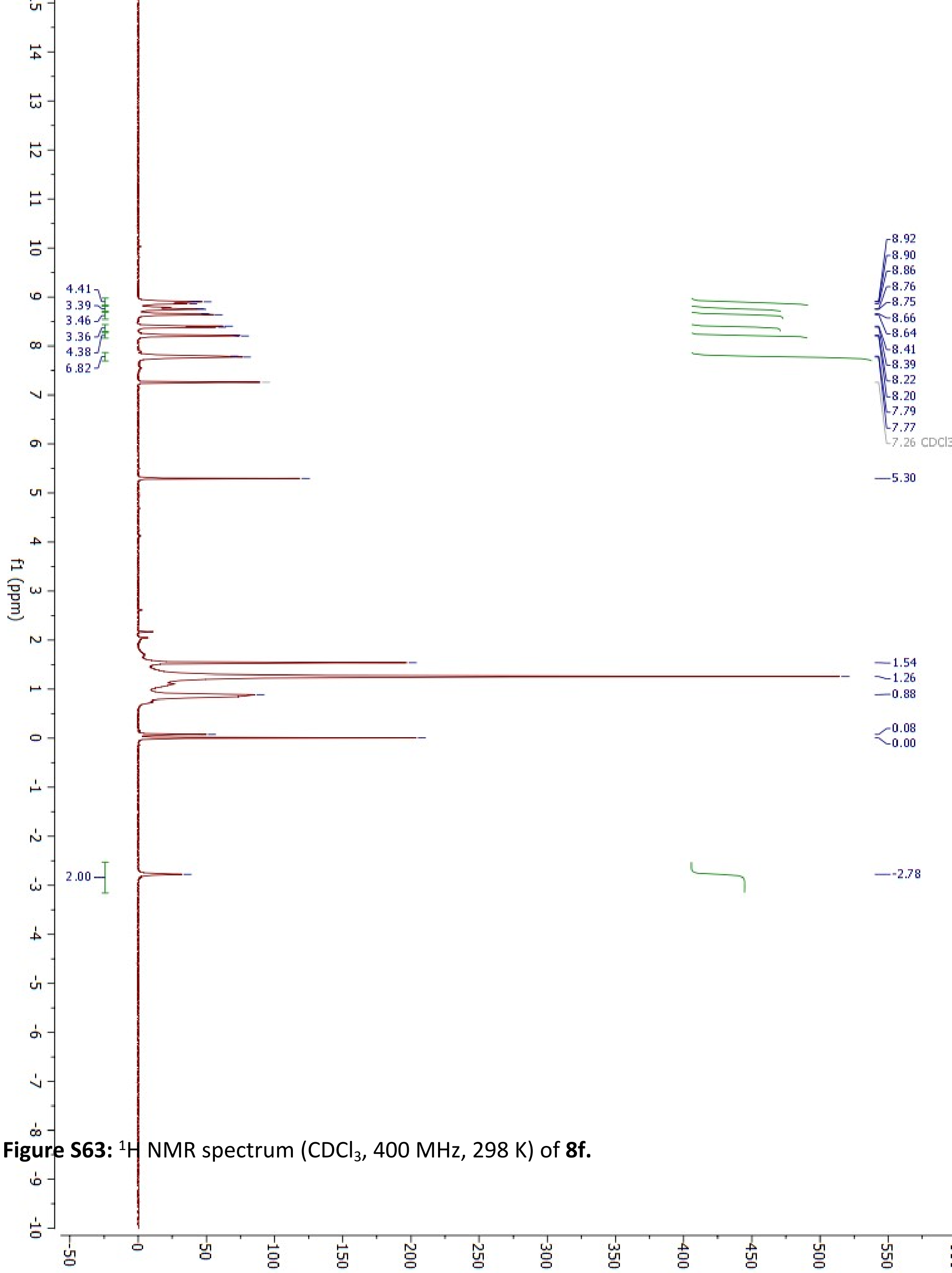


Figure S63: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **8f.**

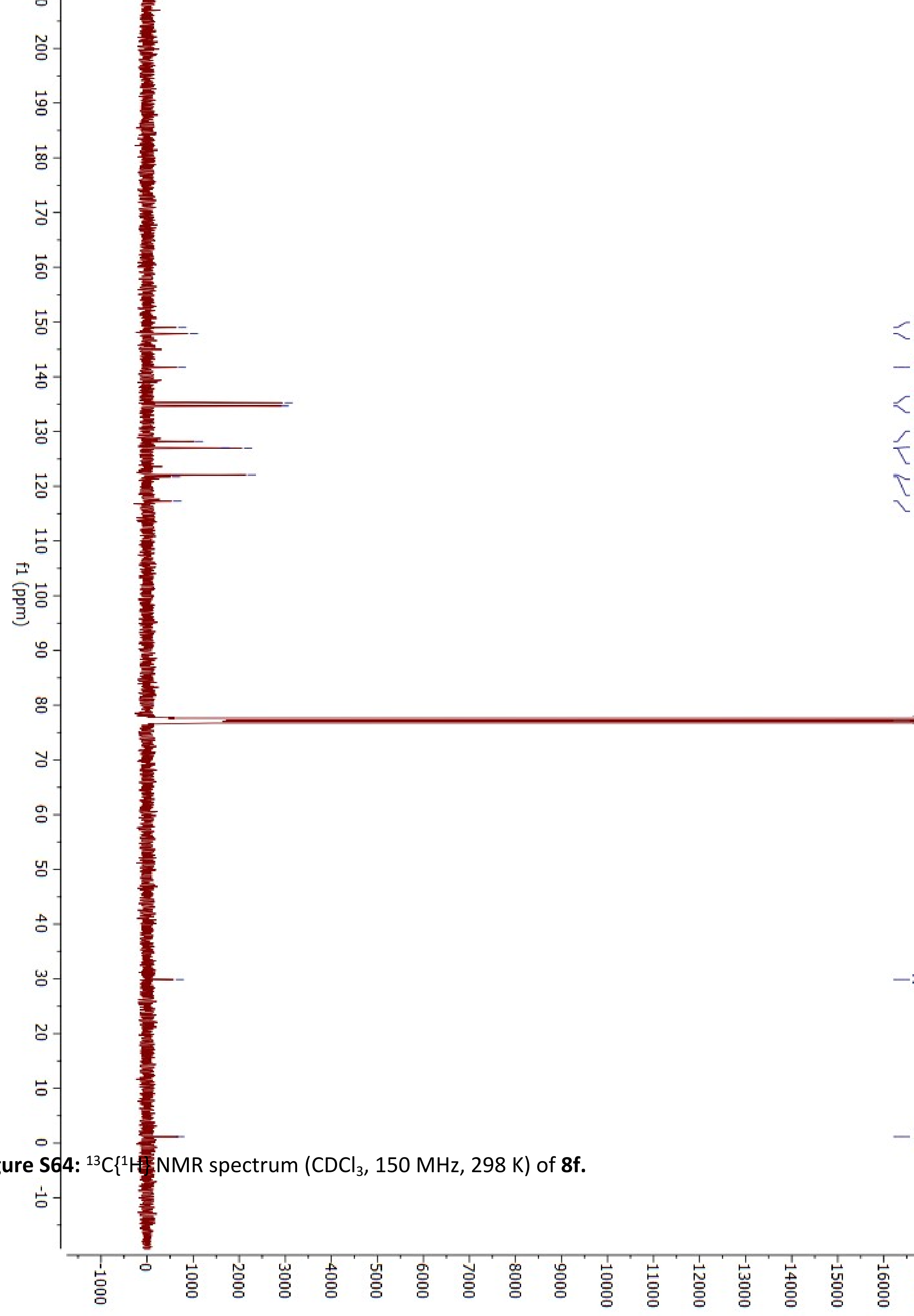


Figure S64: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **8f.**

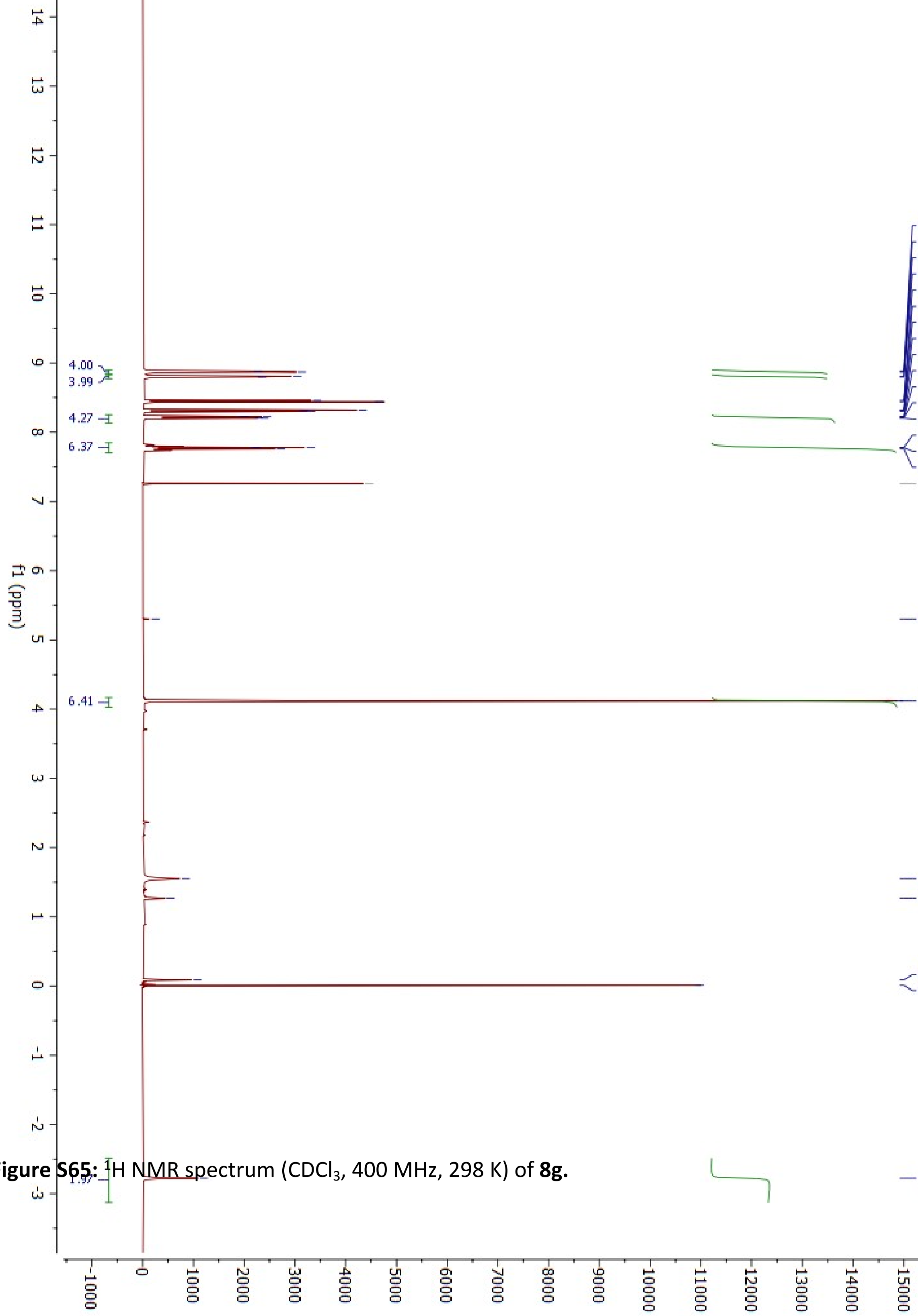


Figure S65: ^1H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **8g.**

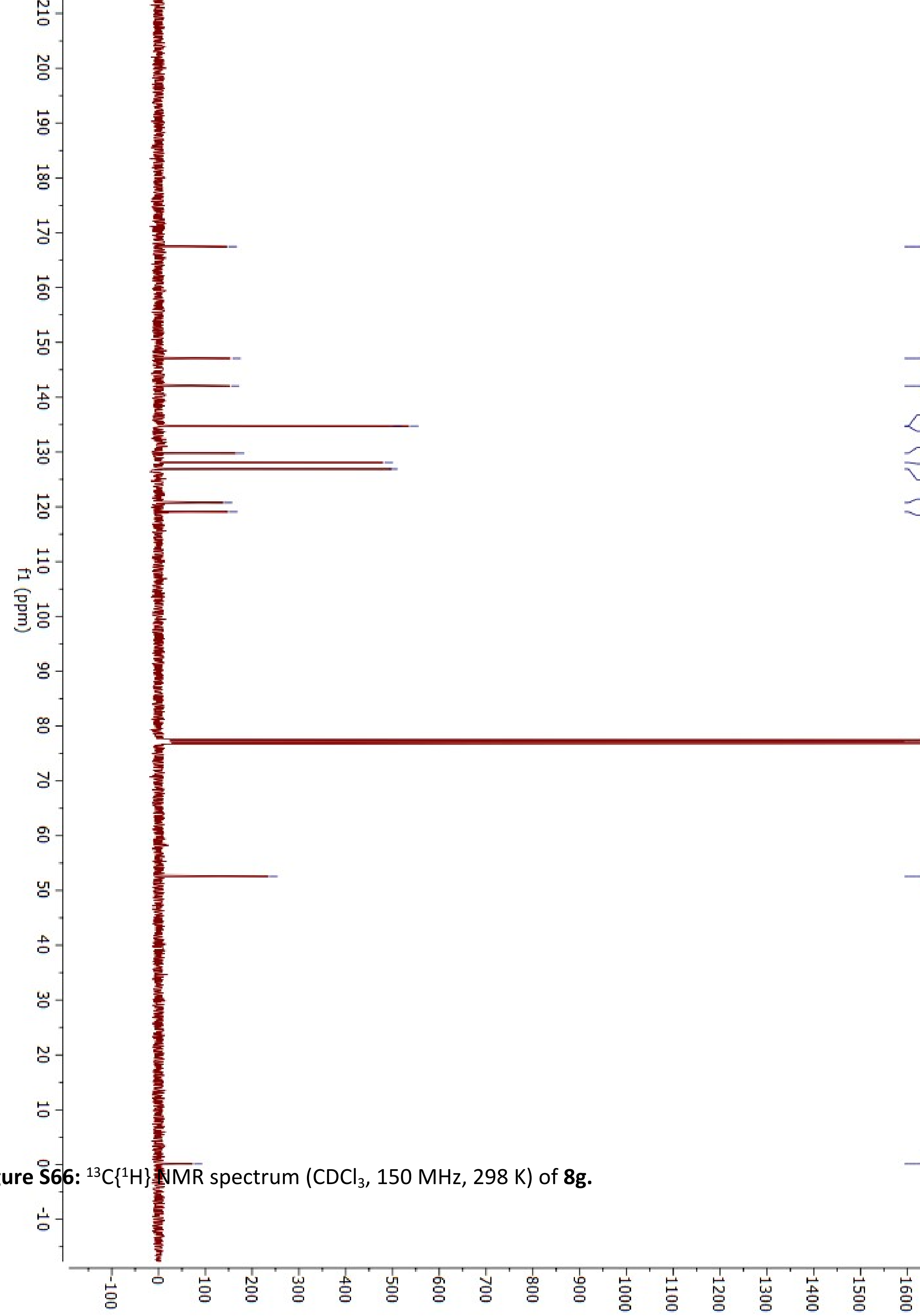


Figure S66: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 150 MHz, 298 K) of **8g.**

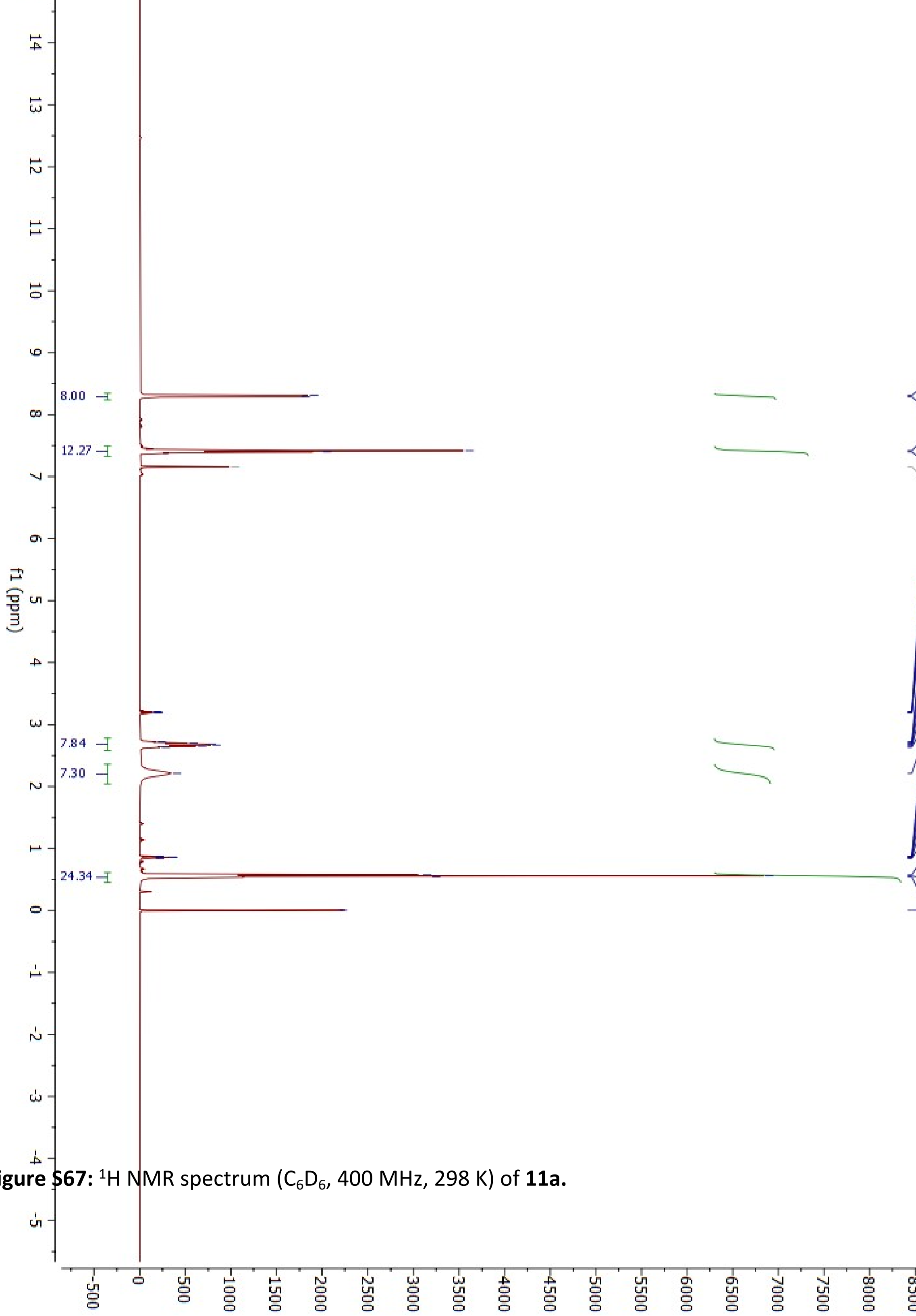


Figure S67: ^{1}H NMR spectrum (C_6D_6, 400 MHz, 298 K) of **11a.**

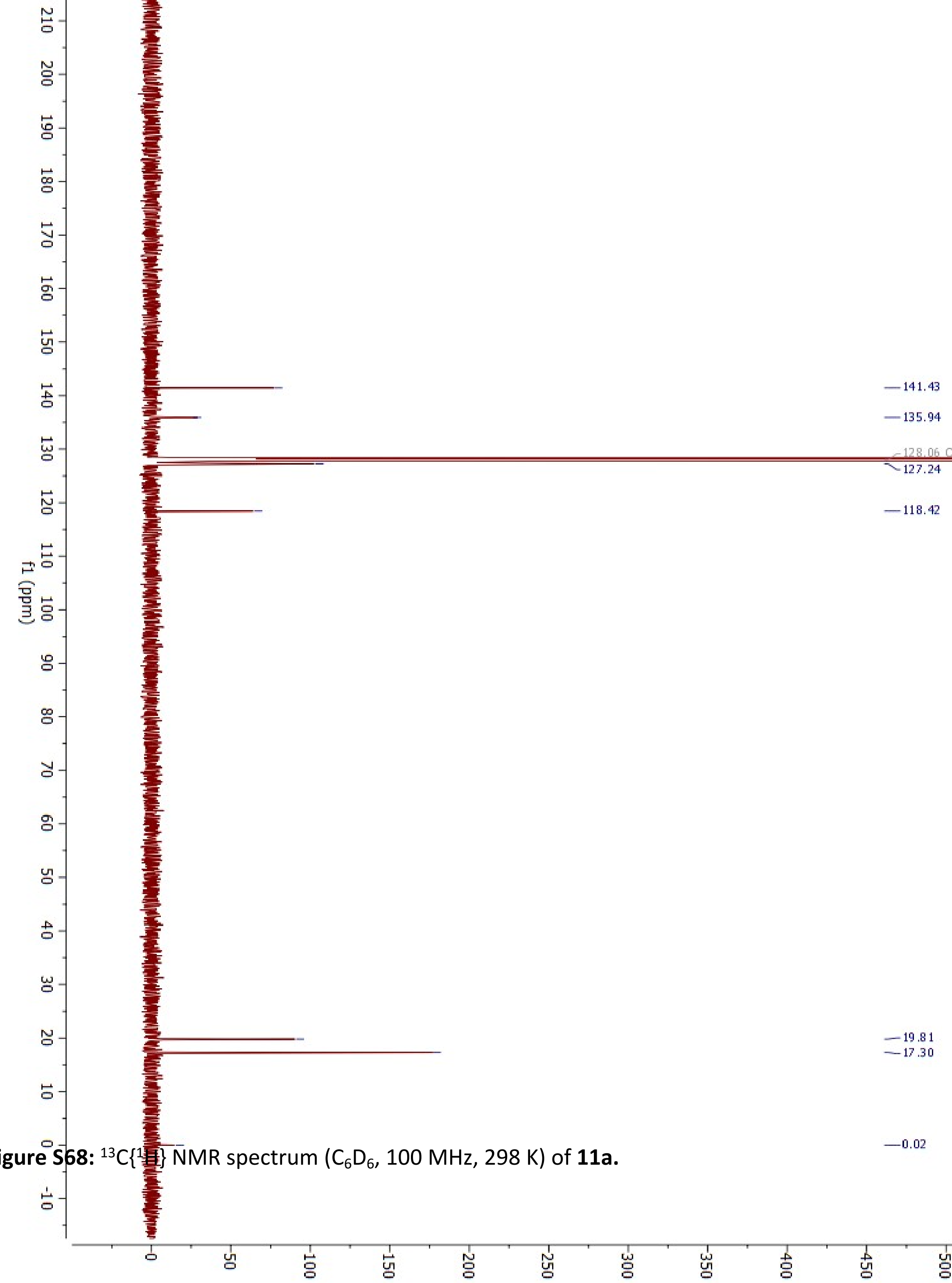


Figure S68: $^{13}C\{^{1}H\}$ NMR spectrum (C_6D_6, 100 MHz, 298 K) of **11a.**

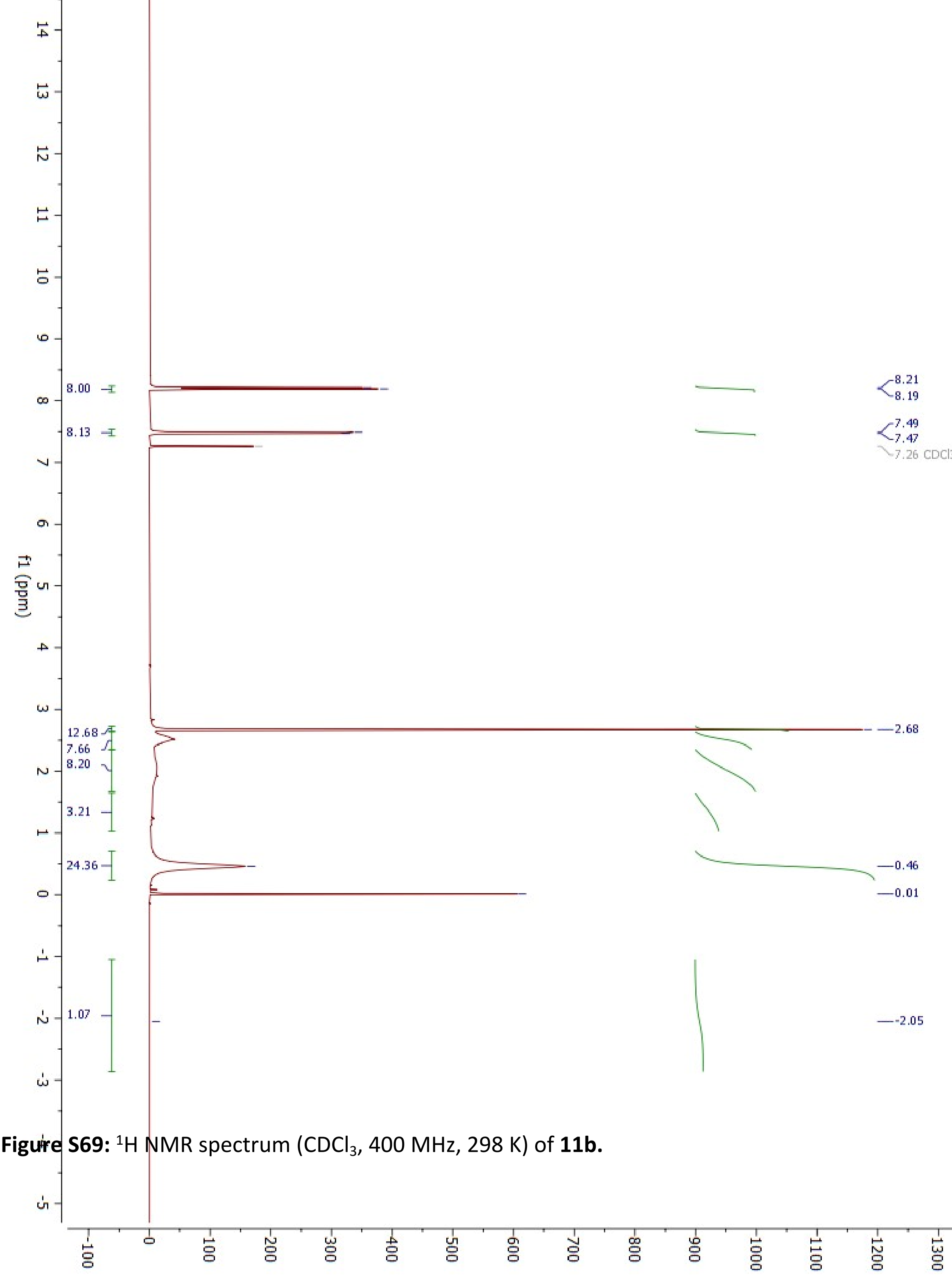


Figure S69: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **11b.**

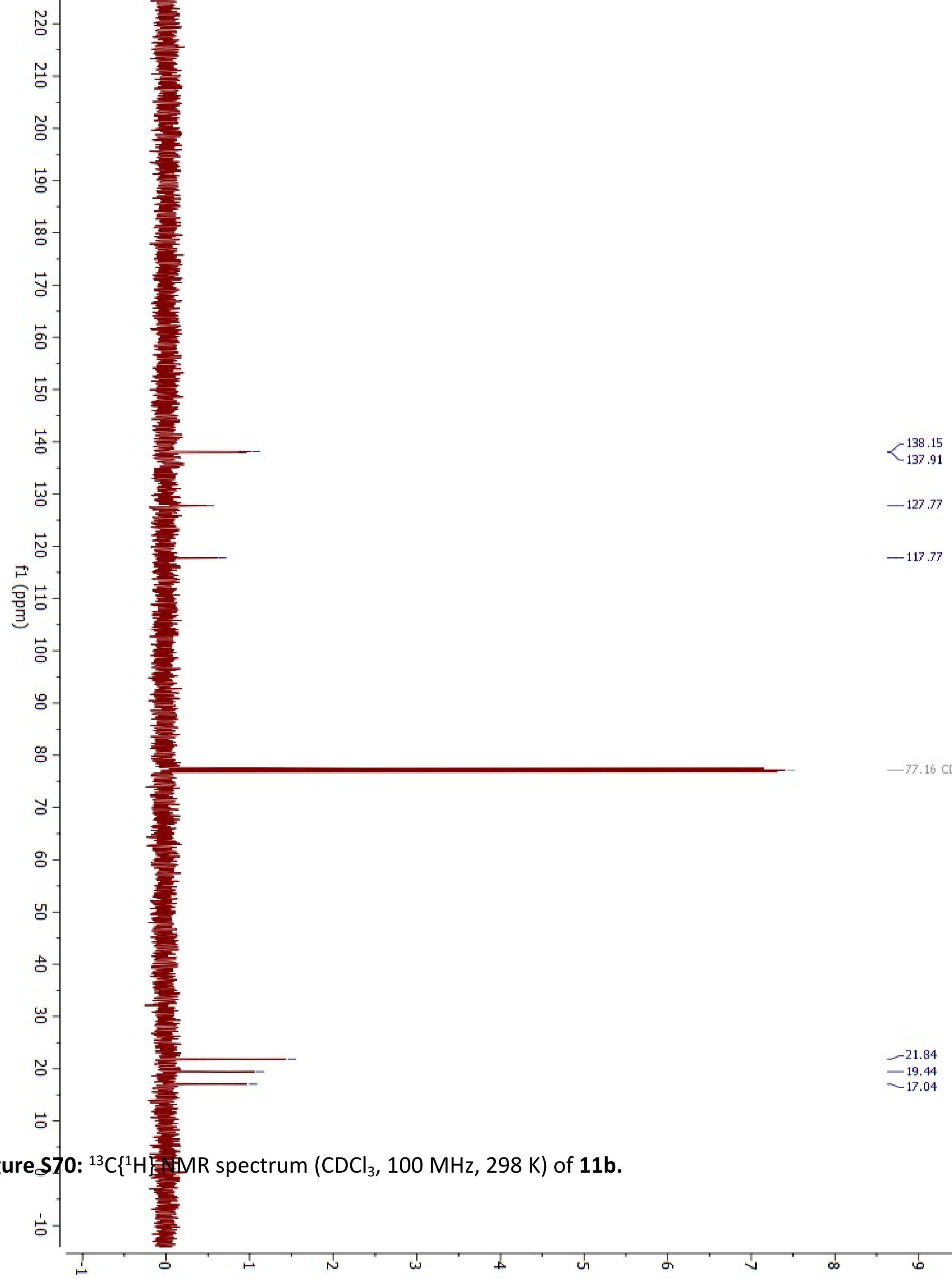


Figure S70: $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of **11b.**

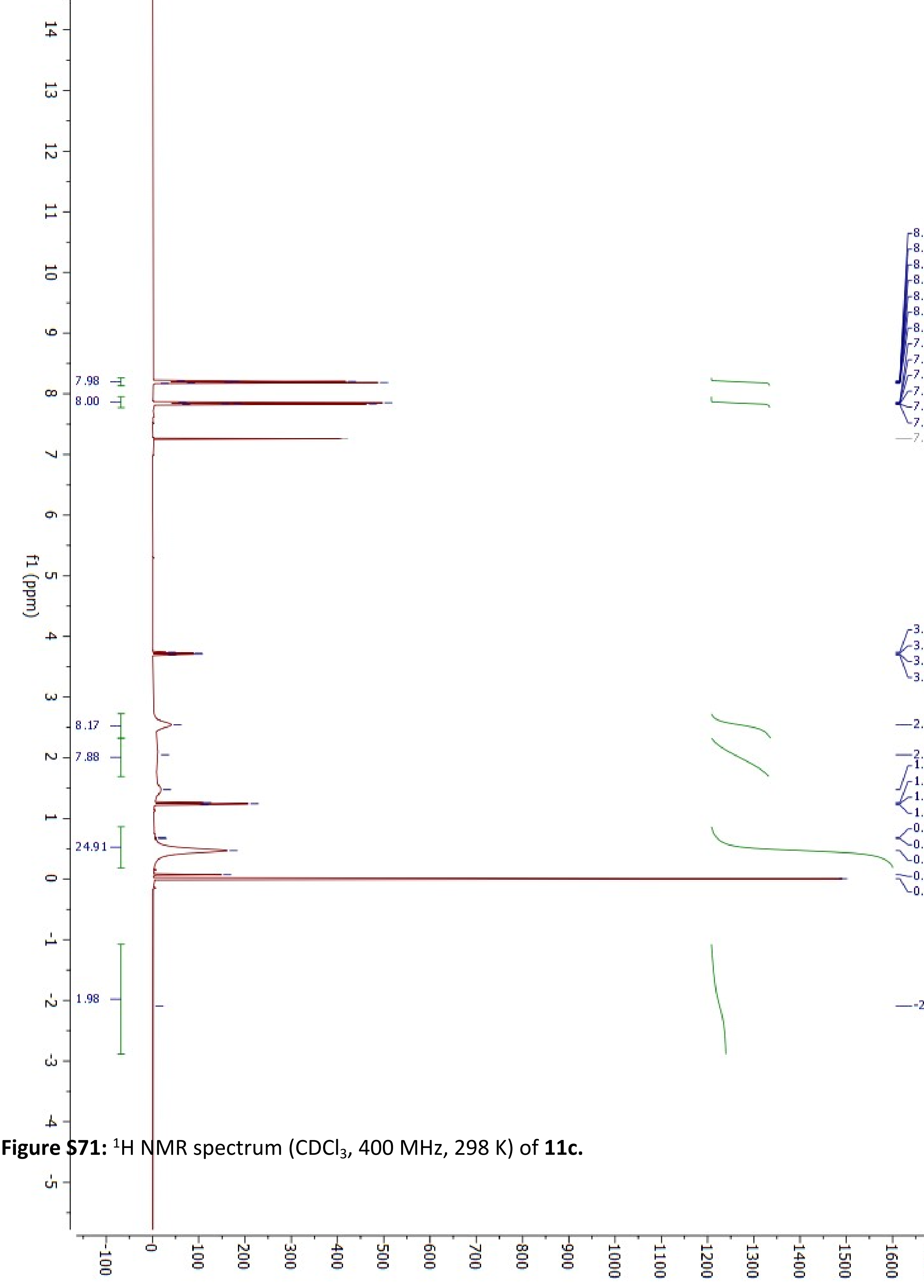


Figure S71: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **11c.**

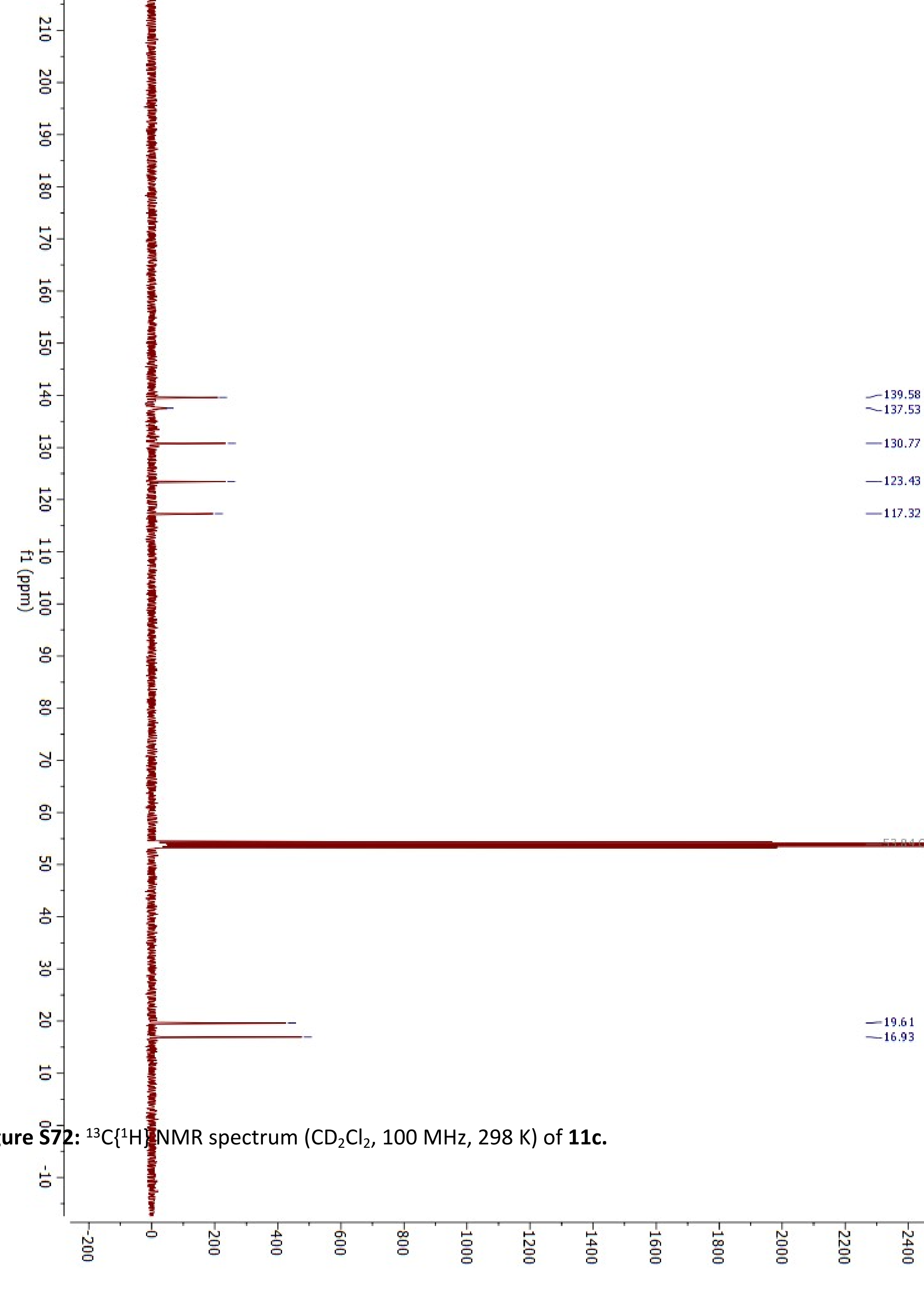


Figure S72: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 298 K) of **11c.**

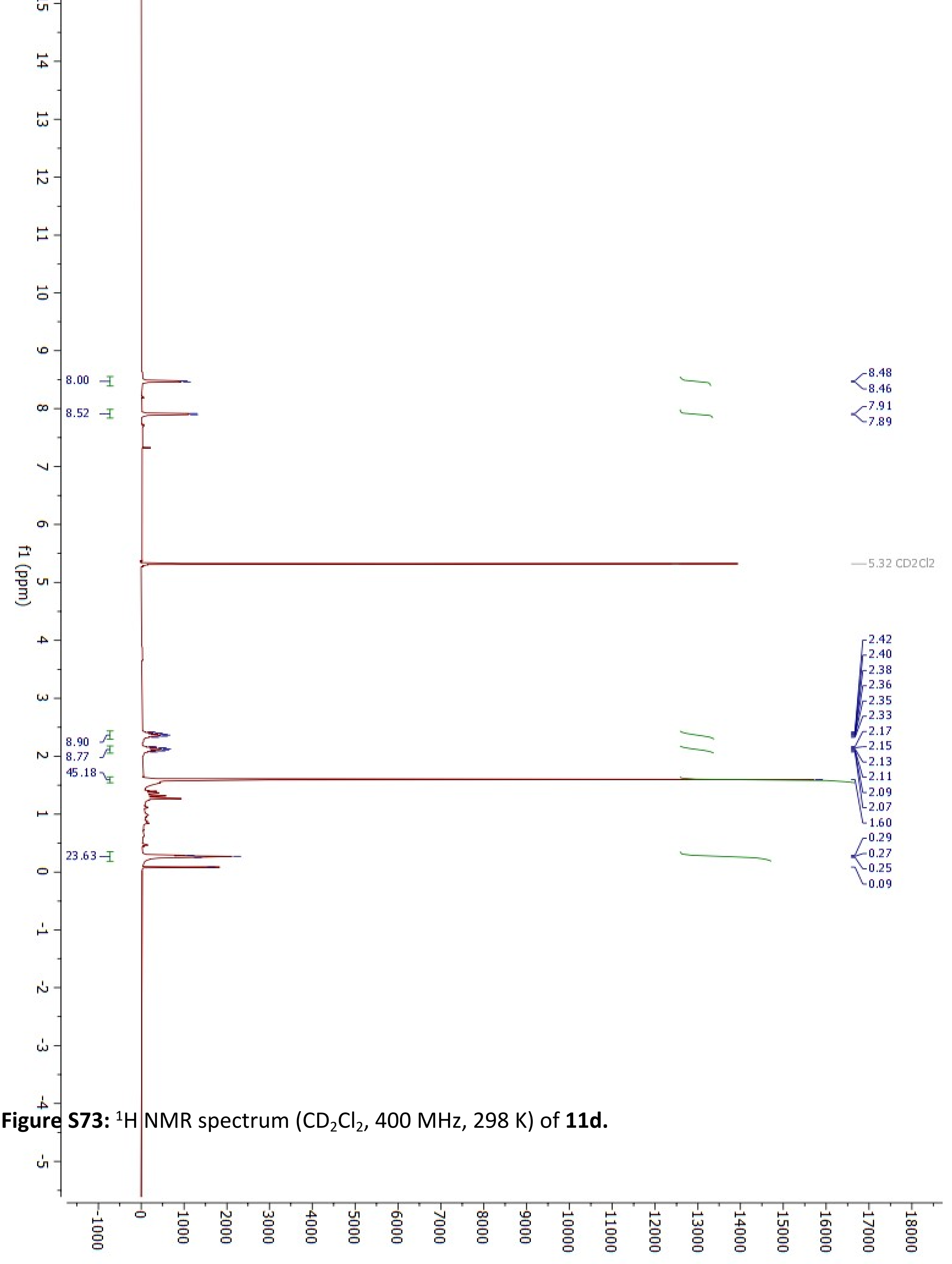


Figure S73: ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of **11d.**

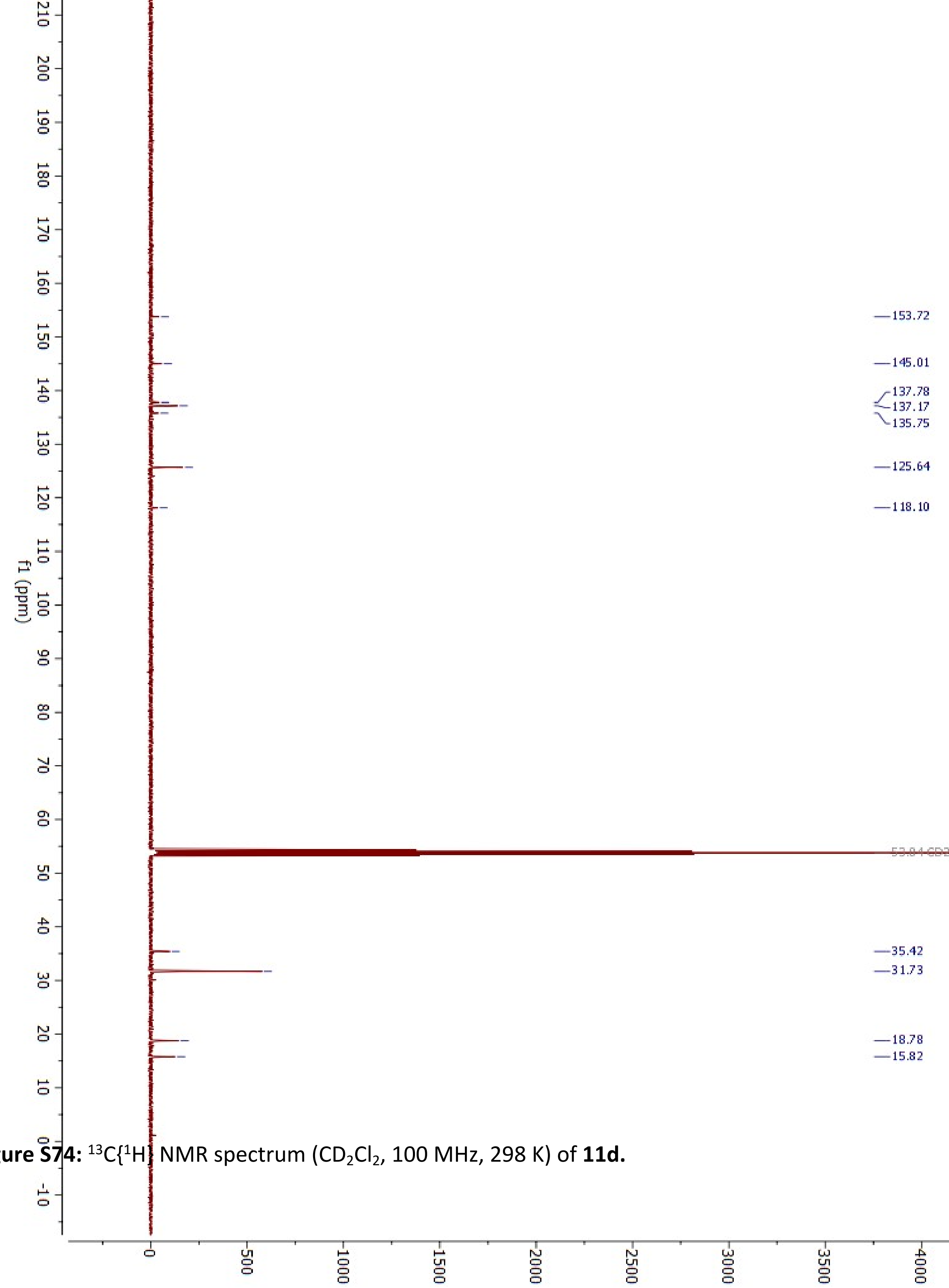


Figure S74: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 298 K) of **11d.**

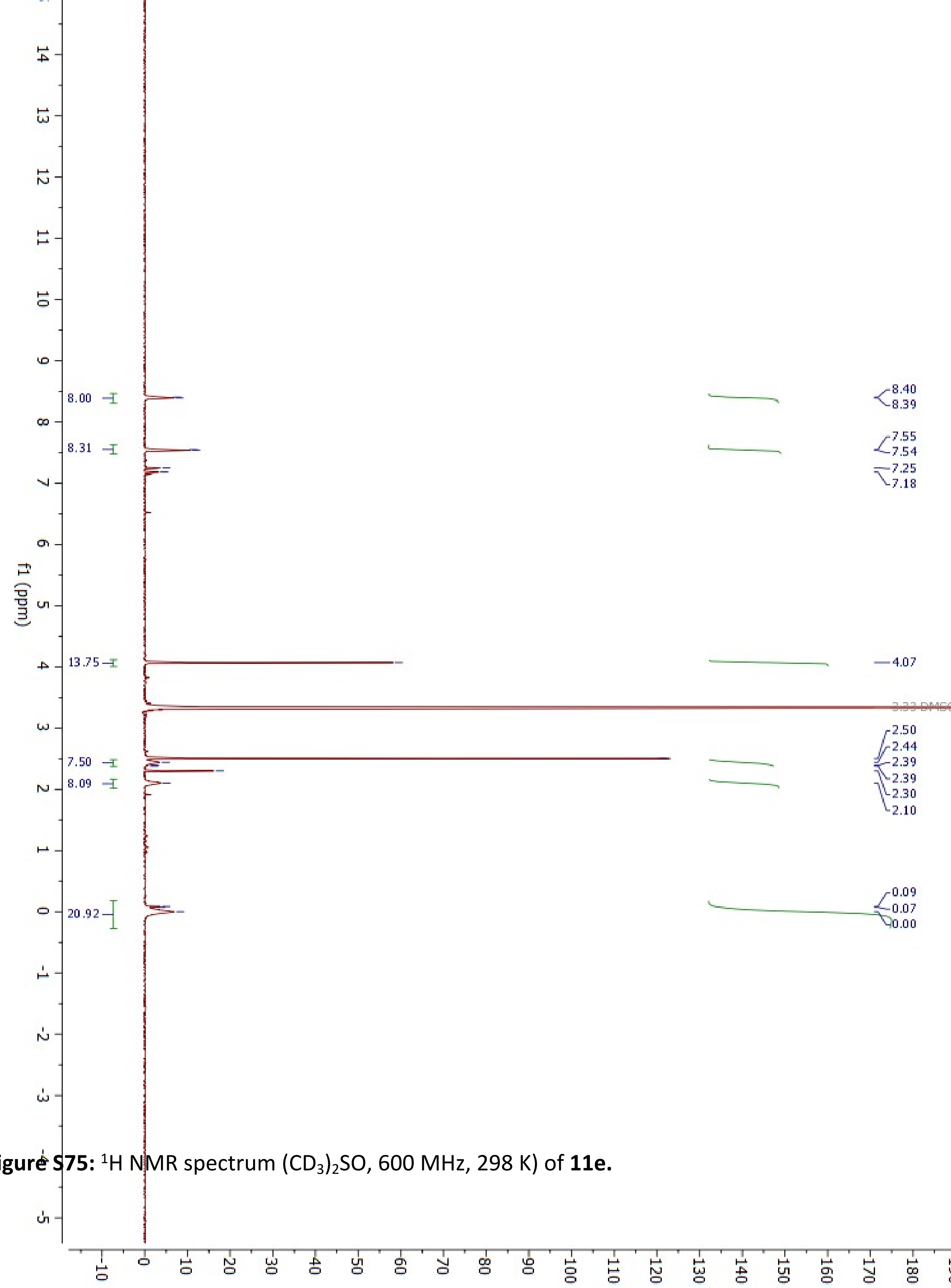


Figure S75: ^{1}H NMR spectrum $(CD_3)_2SO$, 600 MHz, 298 K) of **11e.**

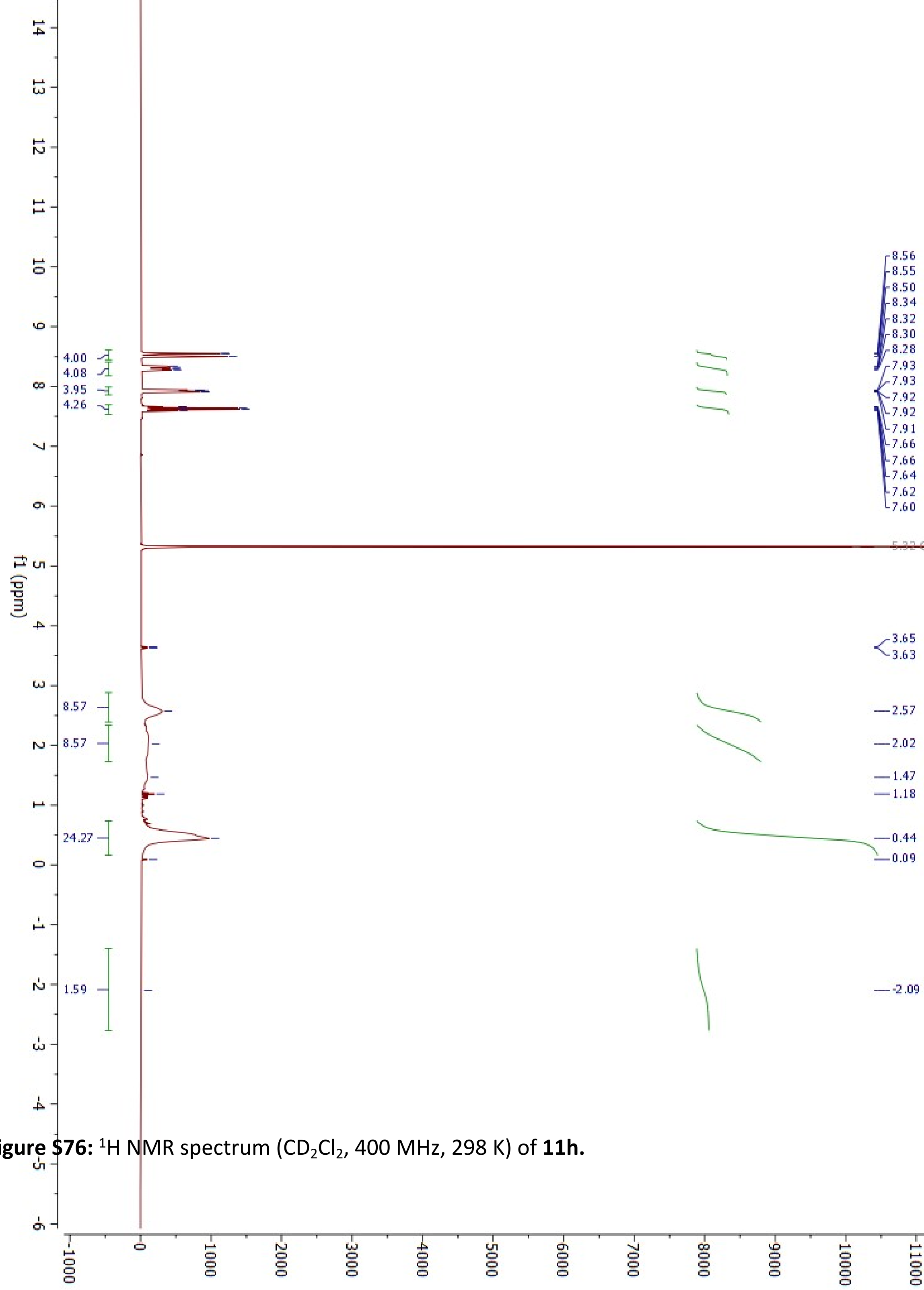


Figure S76: ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of **11h.**

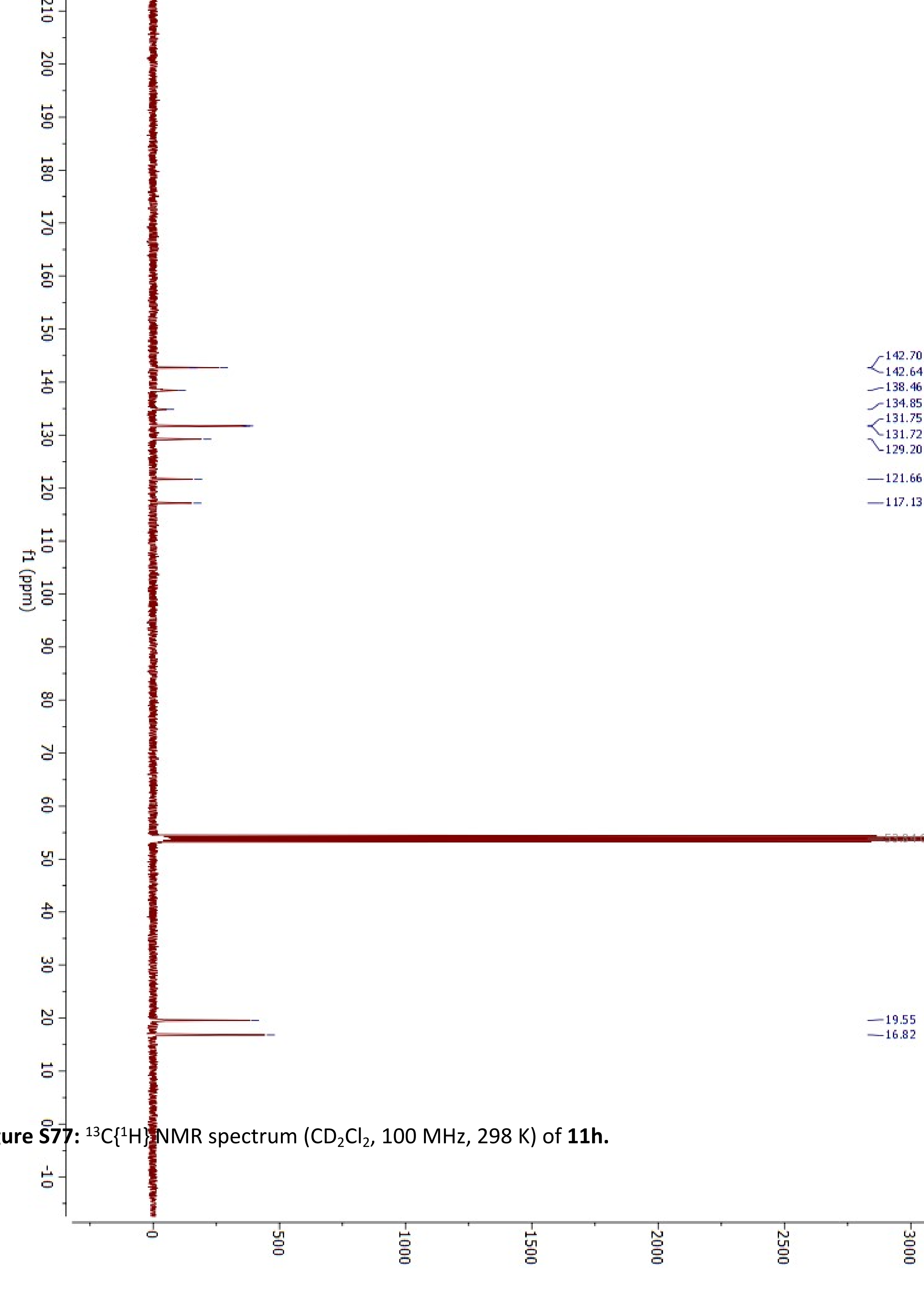


Figure S77: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 100 MHz, 298 K) of **11h.**

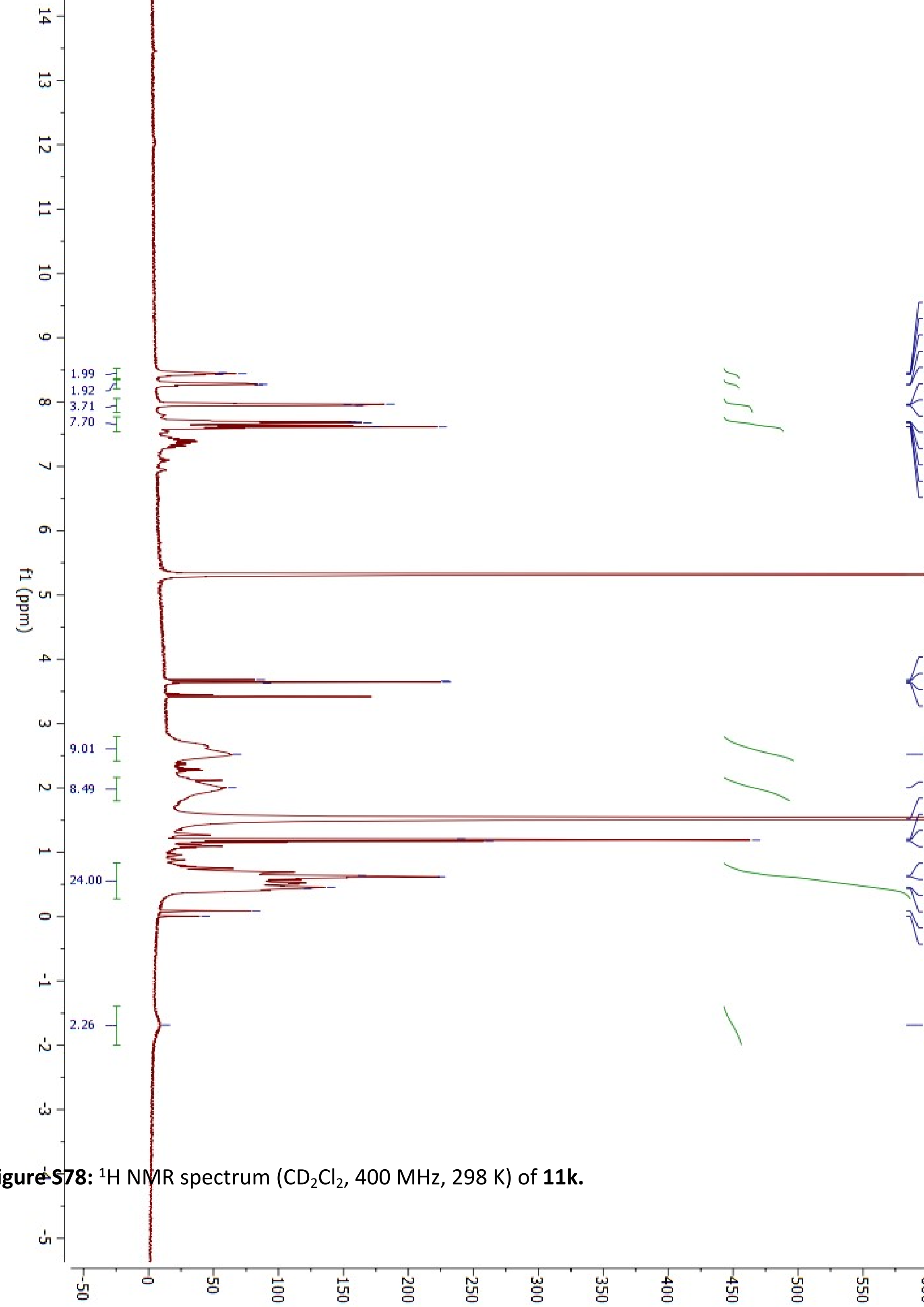


Figure S78: ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of **11k.**

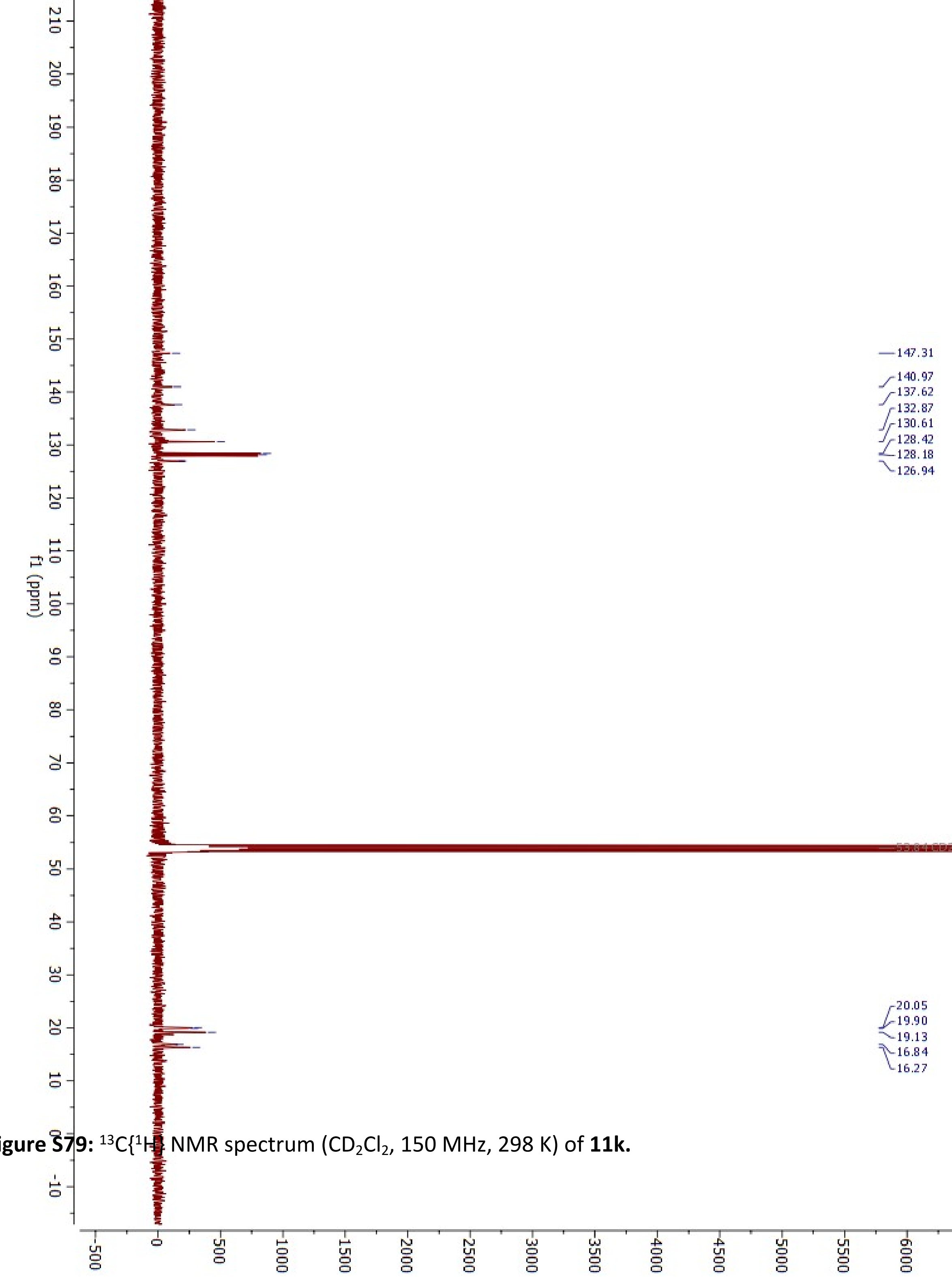


Figure S79: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 150 MHz, 298 K) of **11k.**

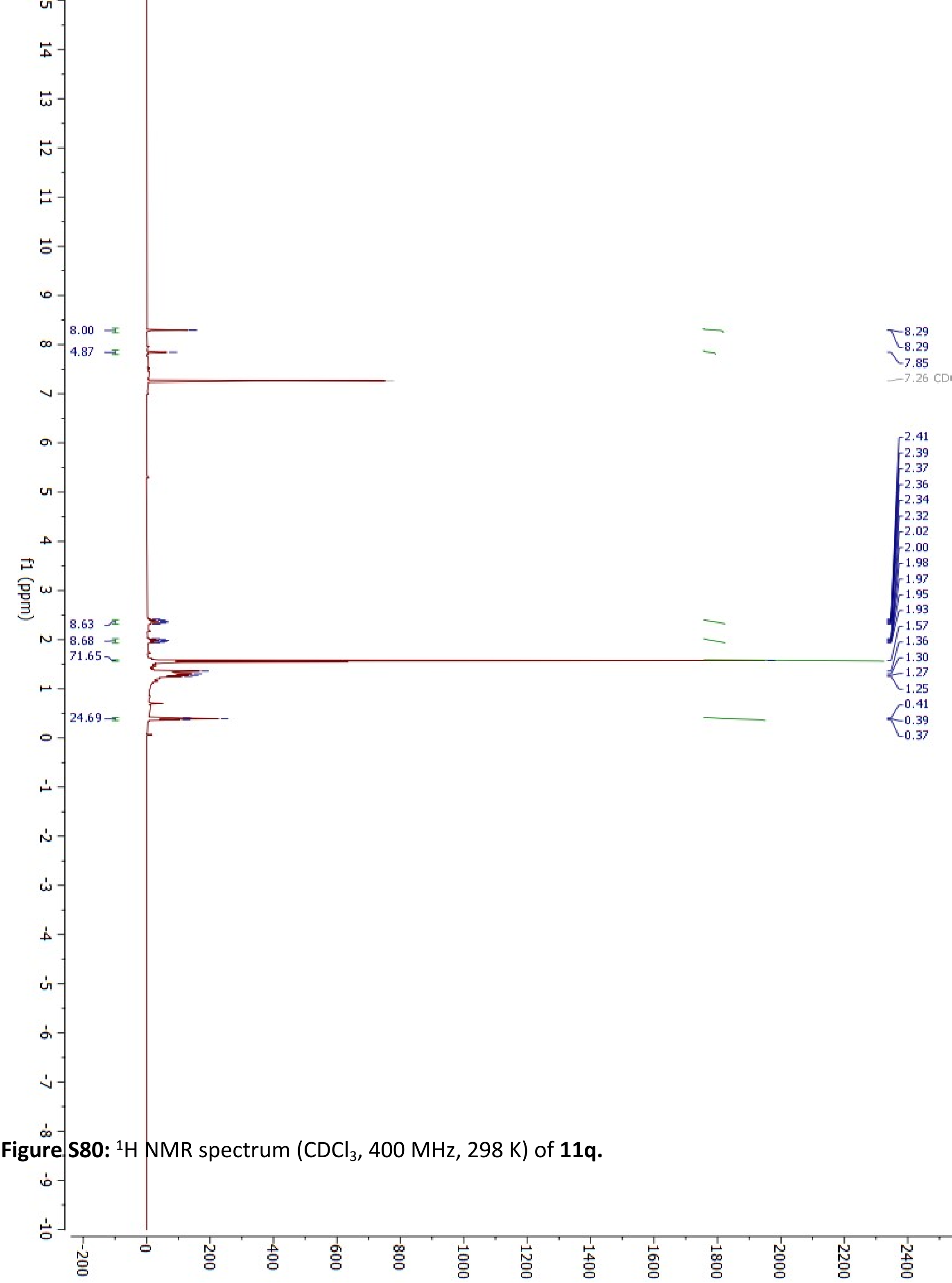


Figure S80: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of **11q.**

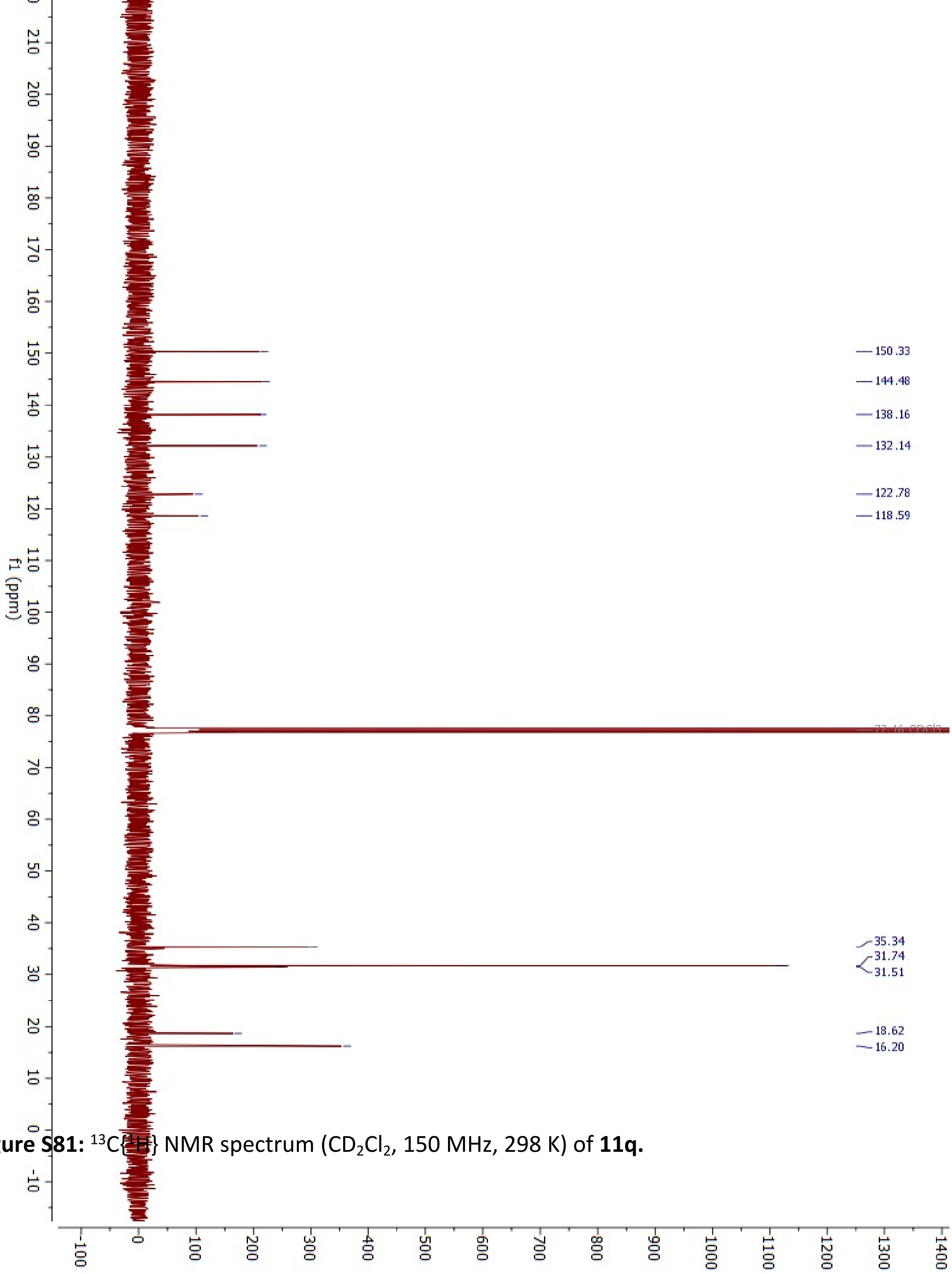


Figure S81: $^{13}C\{^{1}H\}$ NMR spectrum (CD_2Cl_2, 150 MHz, 298 K) of **11q.**

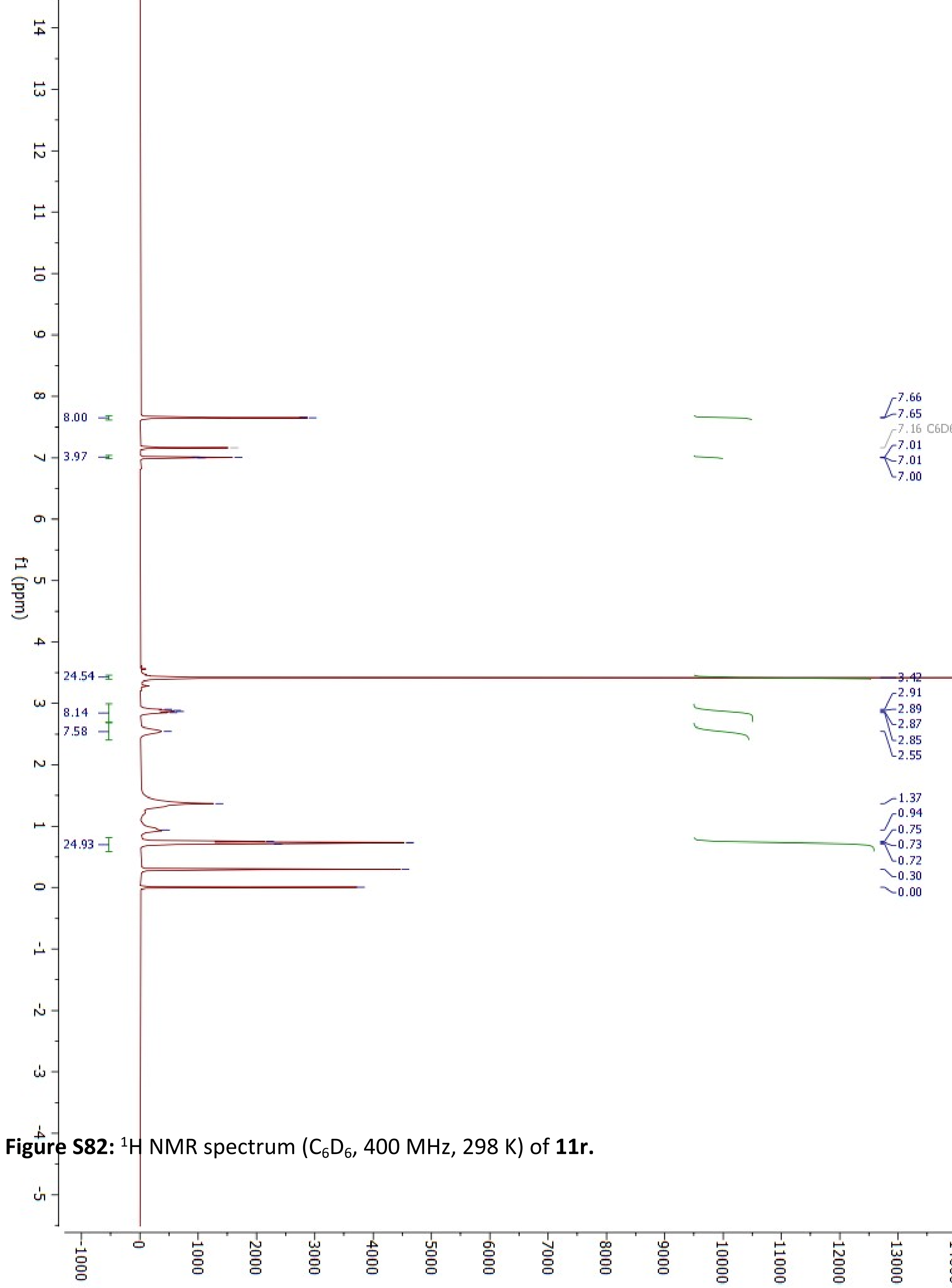


Figure S82: ^{1}H NMR spectrum (C_6D_6, 400 MHz, 298 K) of **11r.**

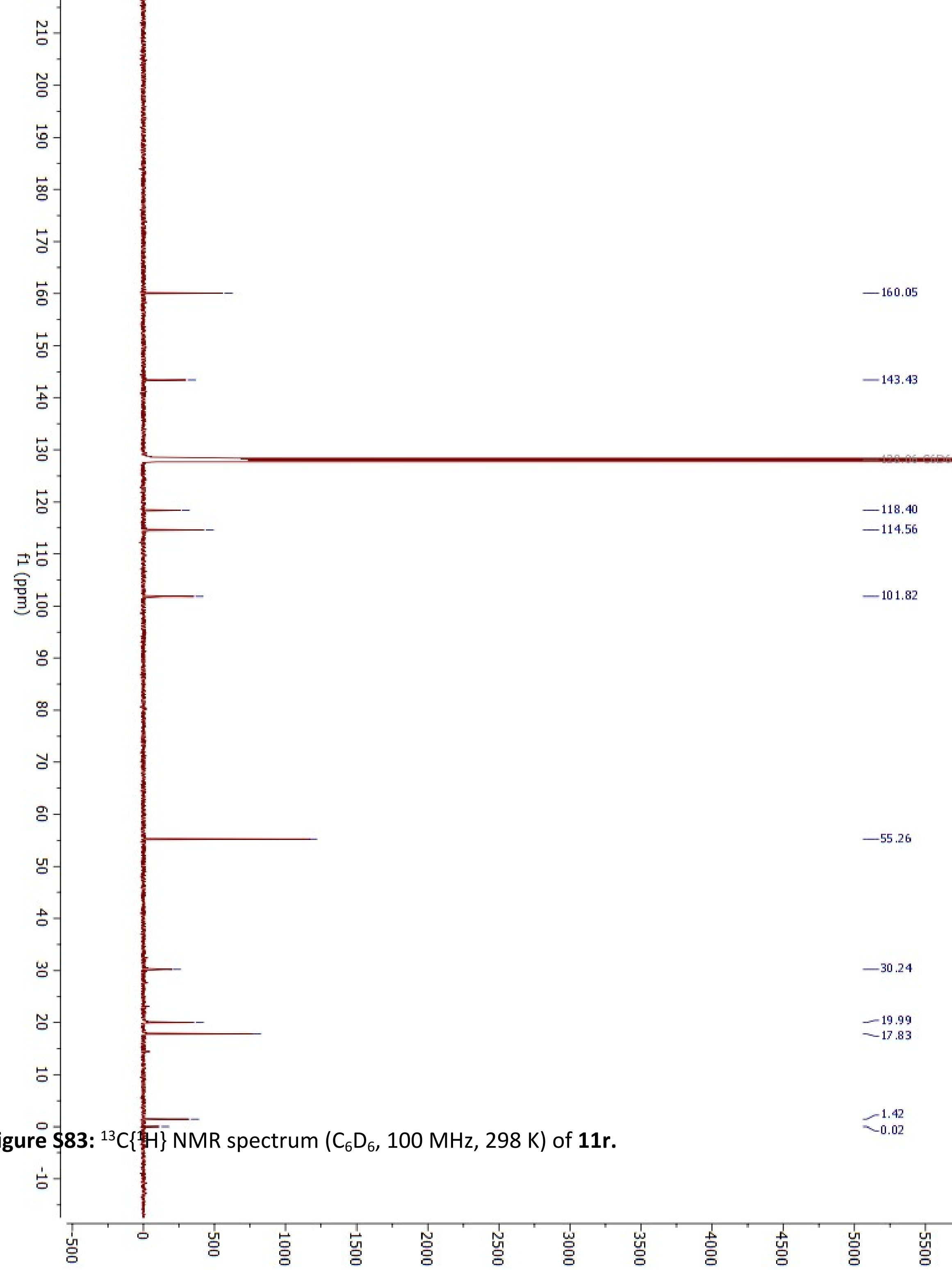


Figure S83: $^{13}C\{^1H\}$ NMR spectrum (C_6D_6, 100 MHz, 298 K) of **11r.**

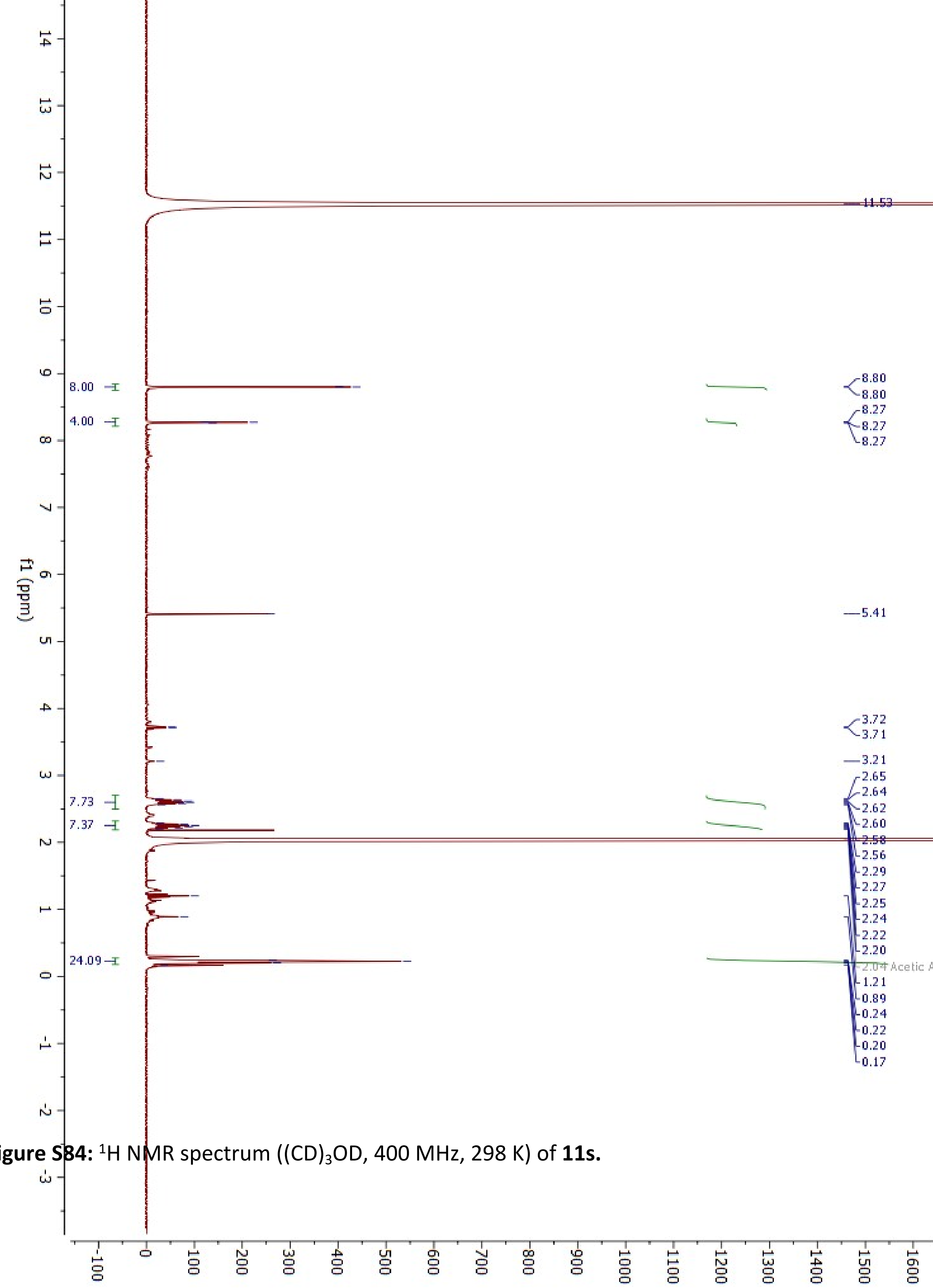


Figure S84: ^{1}H NMR spectrum ($(CD)_3OD$, 400 MHz, 298 K) of **11s.**

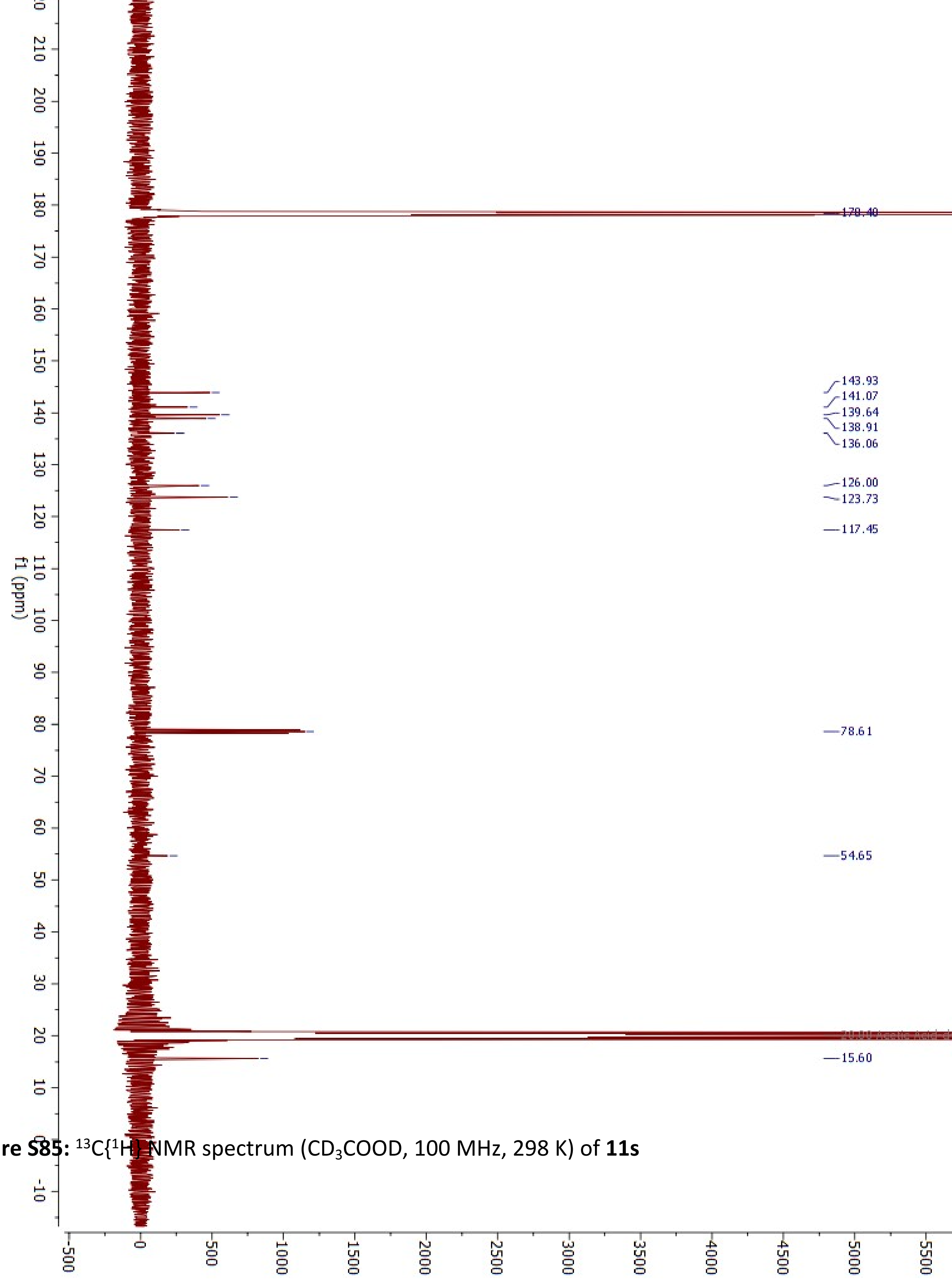


Figure S85: $^{13}C\{^{1}H\}$ NMR spectrum (CD_3COOD, 100 MHz, 298 K) of **11s**

UV/Vis spectra

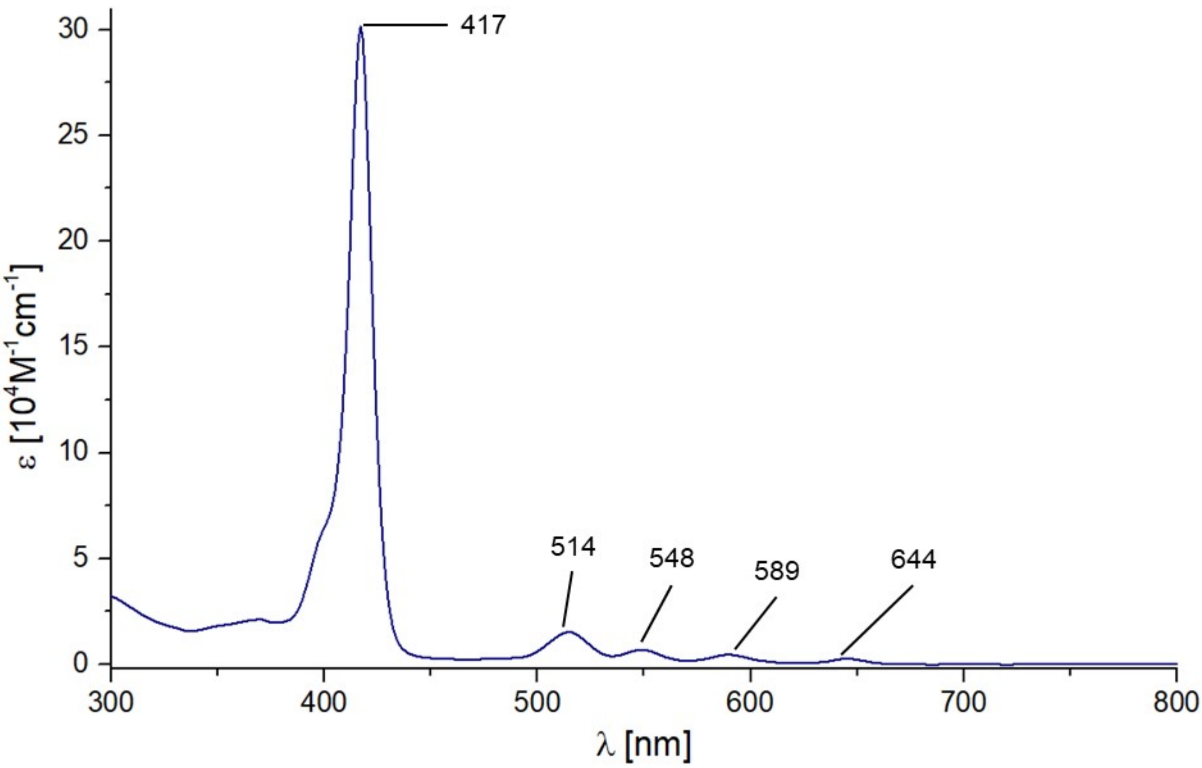


Figure S86: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4a**.

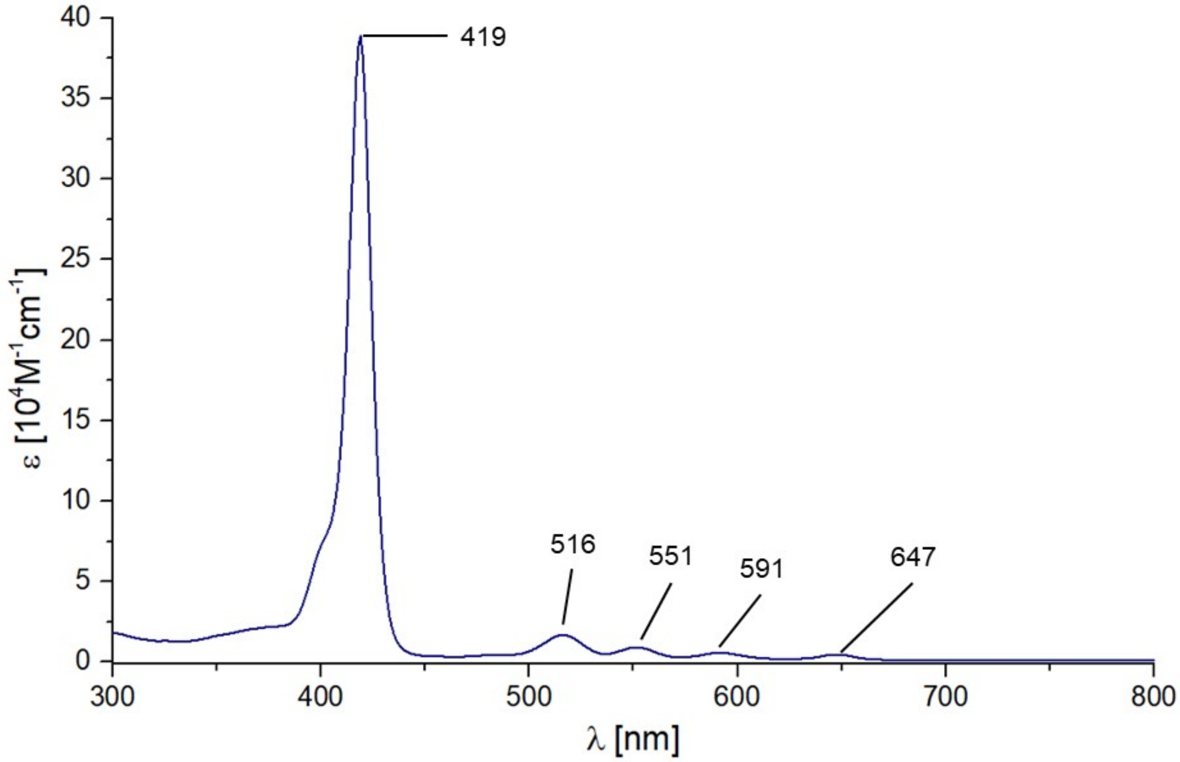


Figure S87: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4b**.

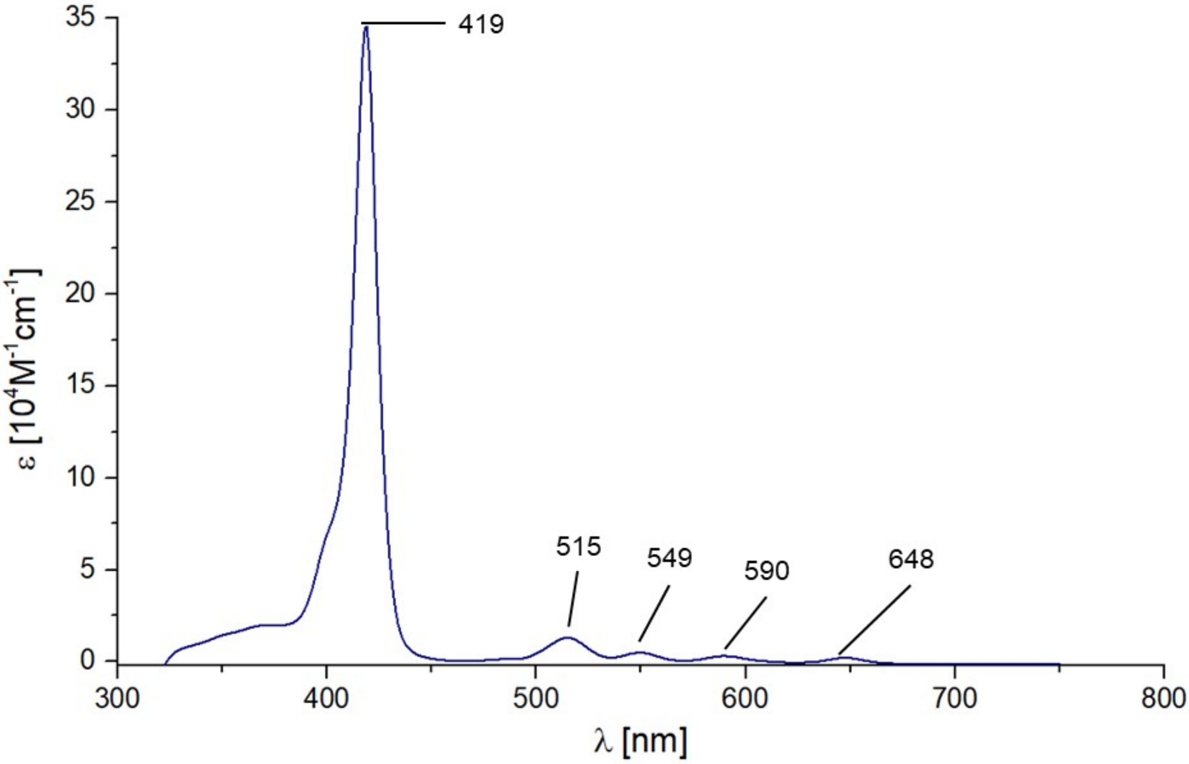


Figure S88: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4c**.

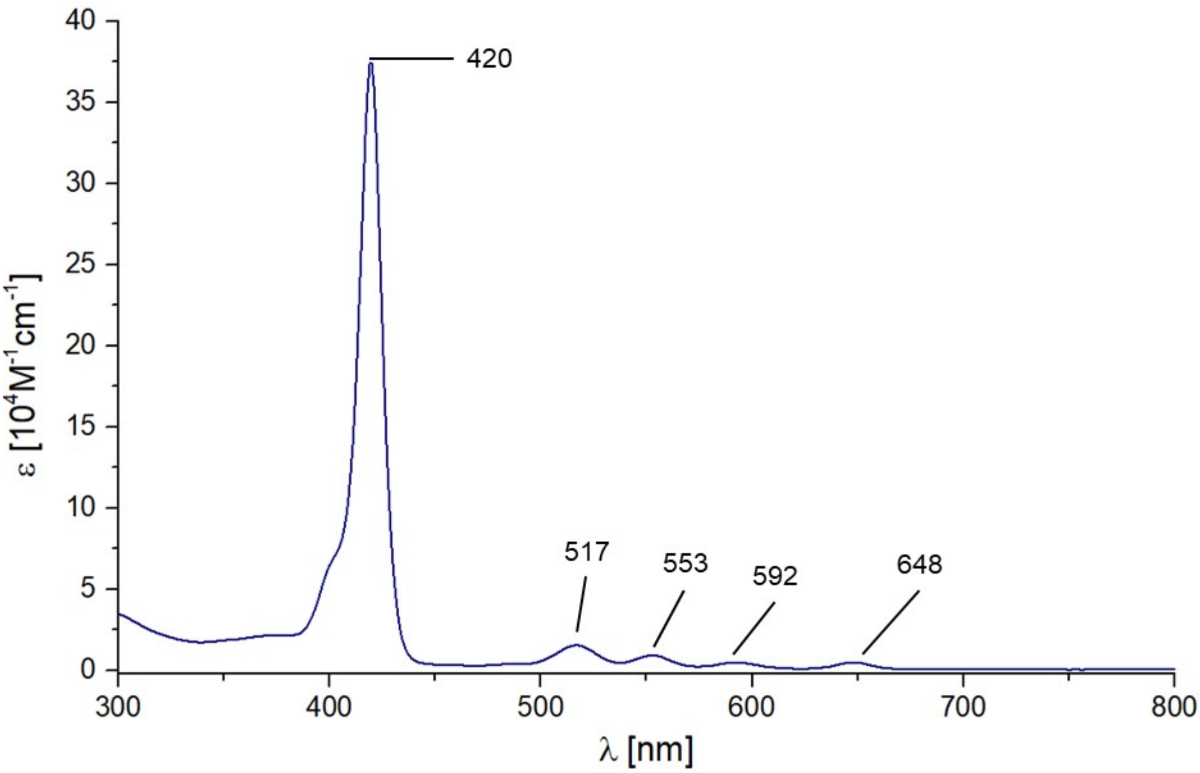


Figure S89: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4d**.

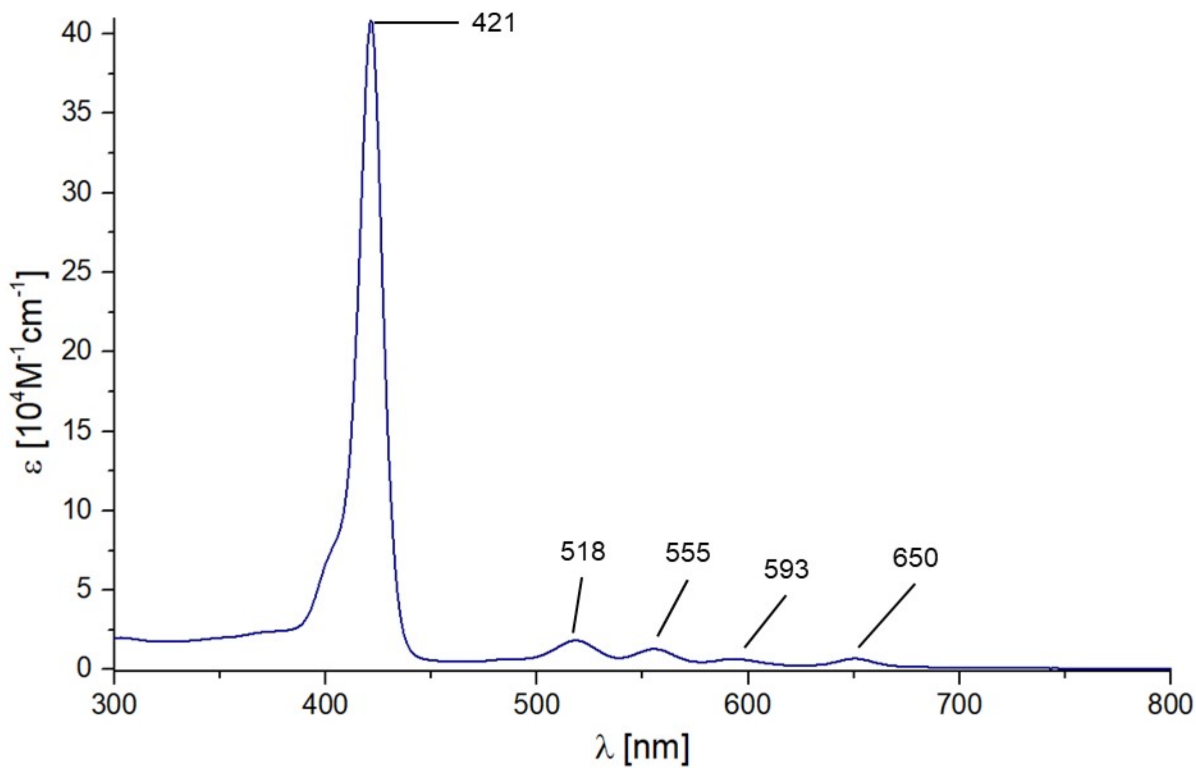


Figure S90: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4e**.

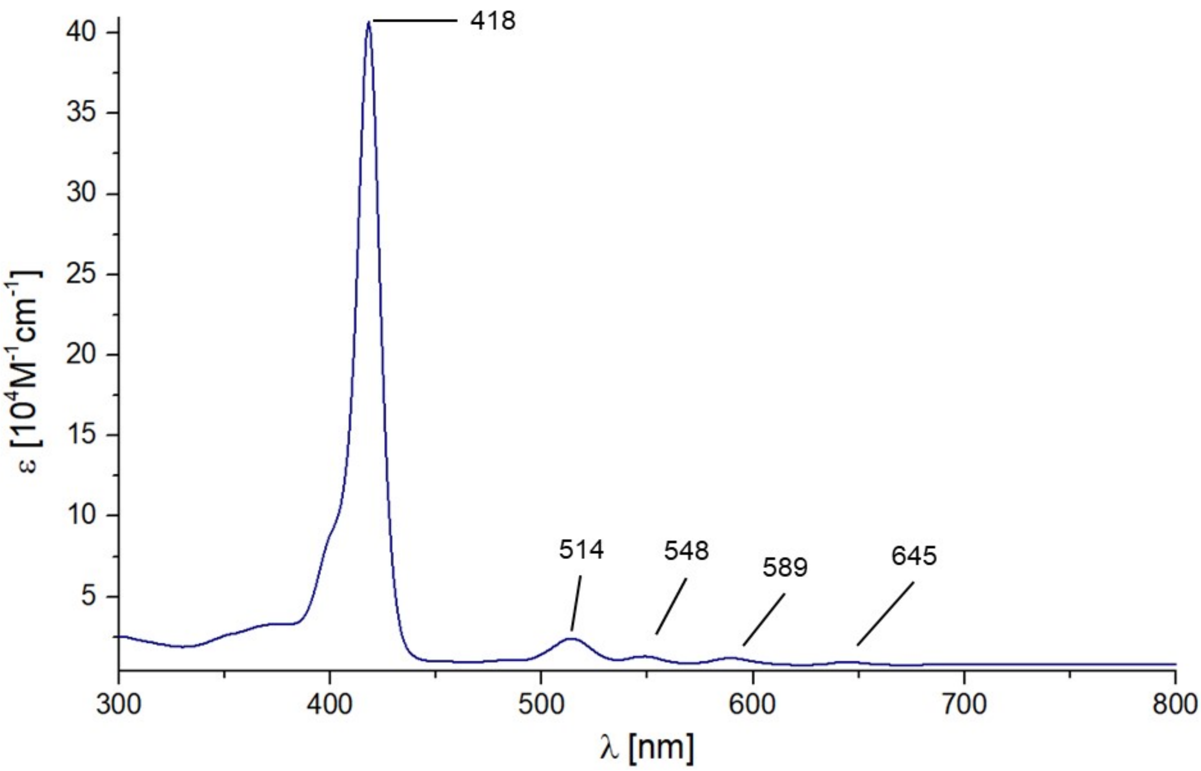


Figure S91: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4h**.

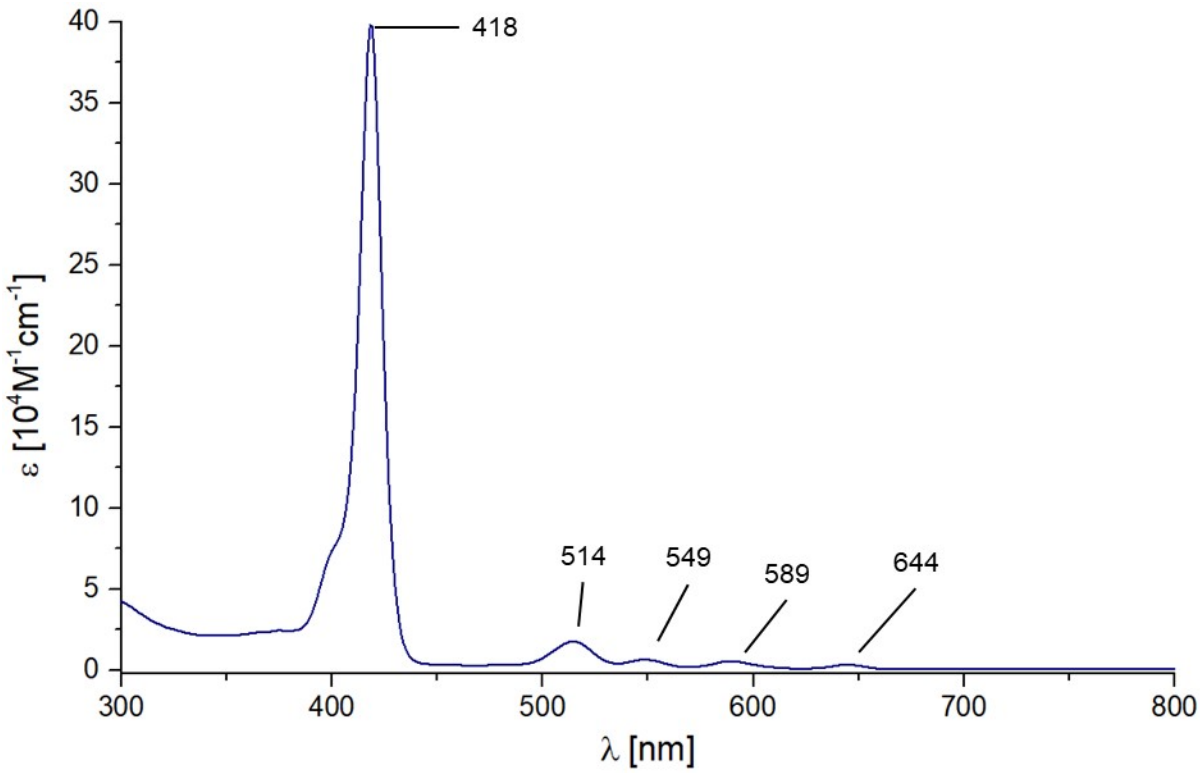


Figure S92: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4i**.

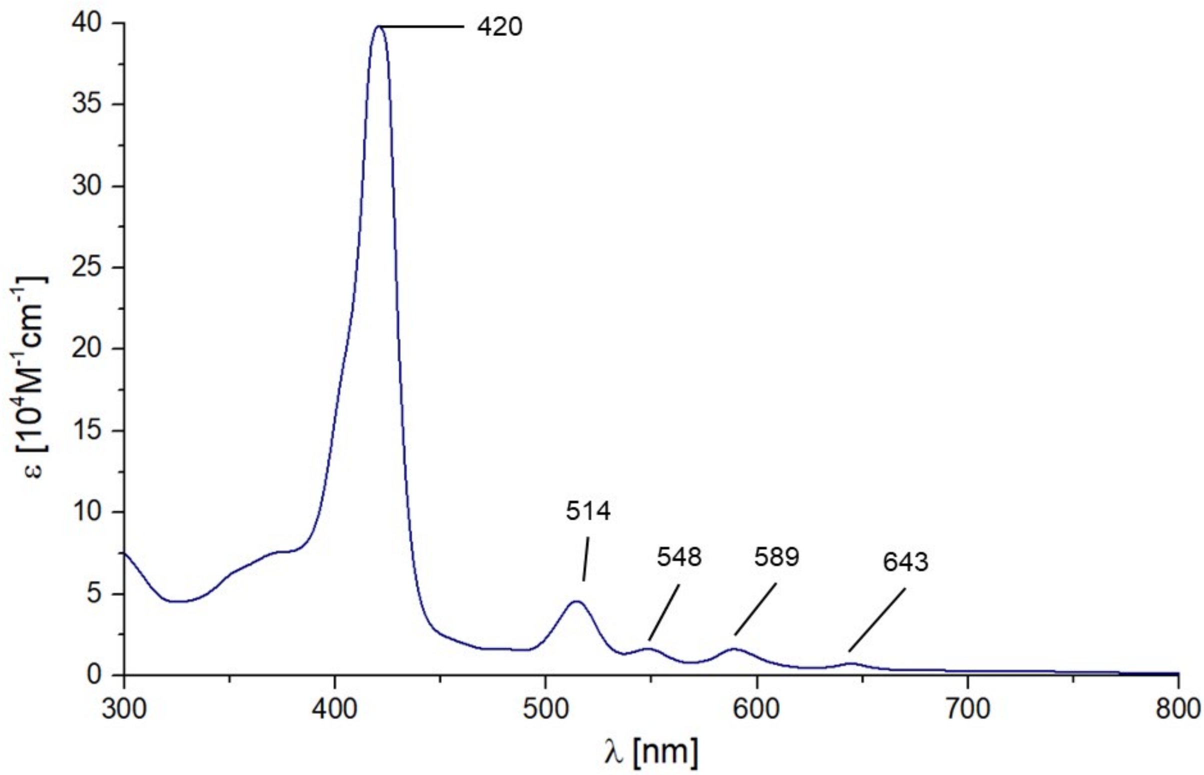


Figure S93: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4j**.

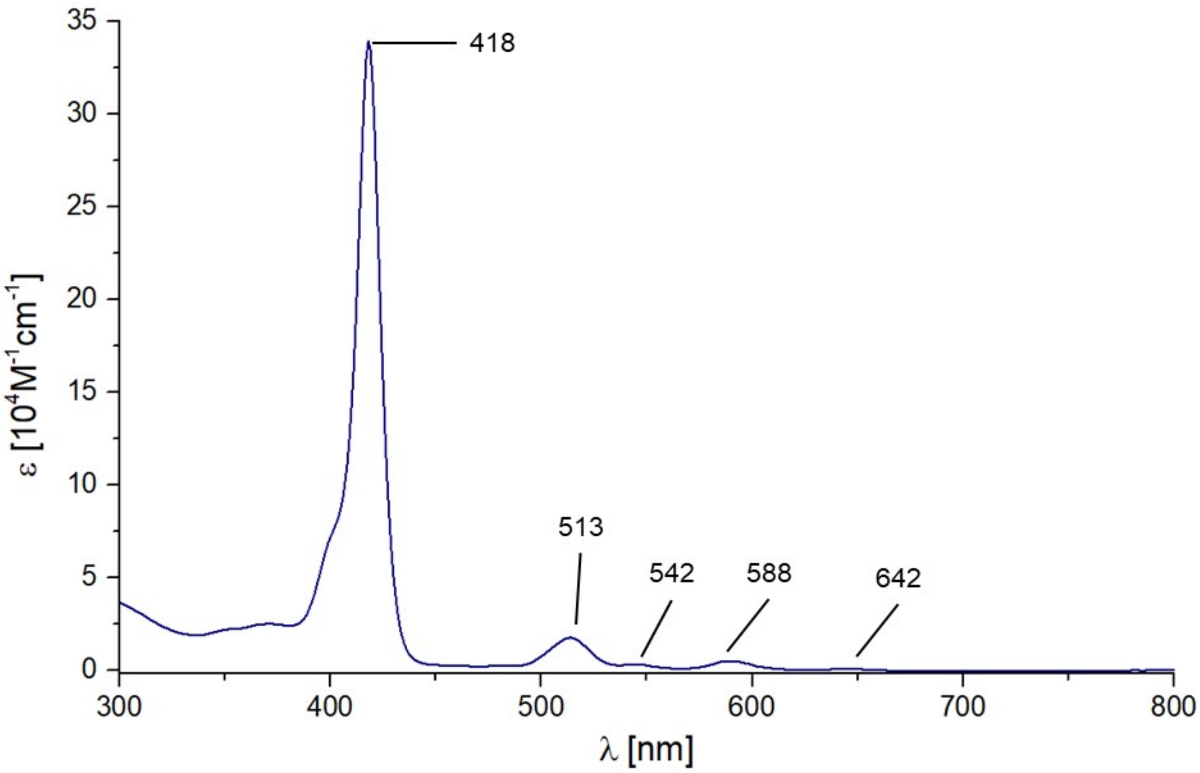


Figure S94: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4k**.

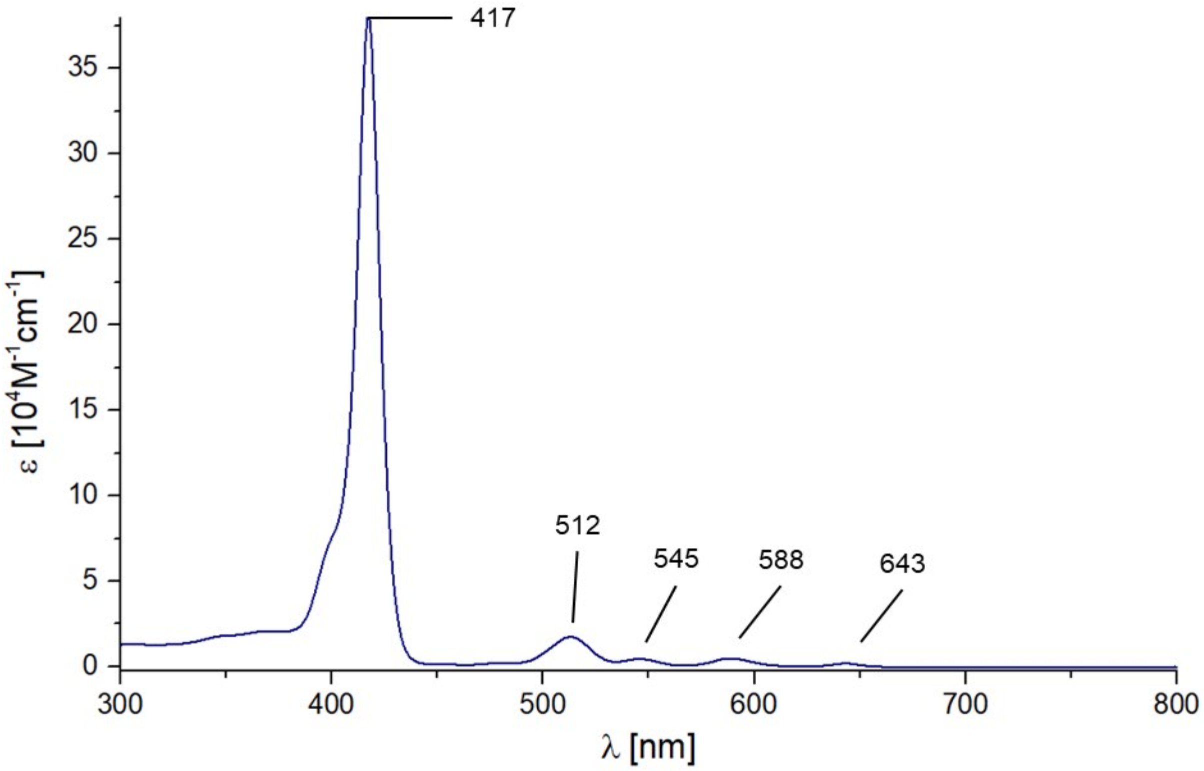


Figure S95: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4l**.

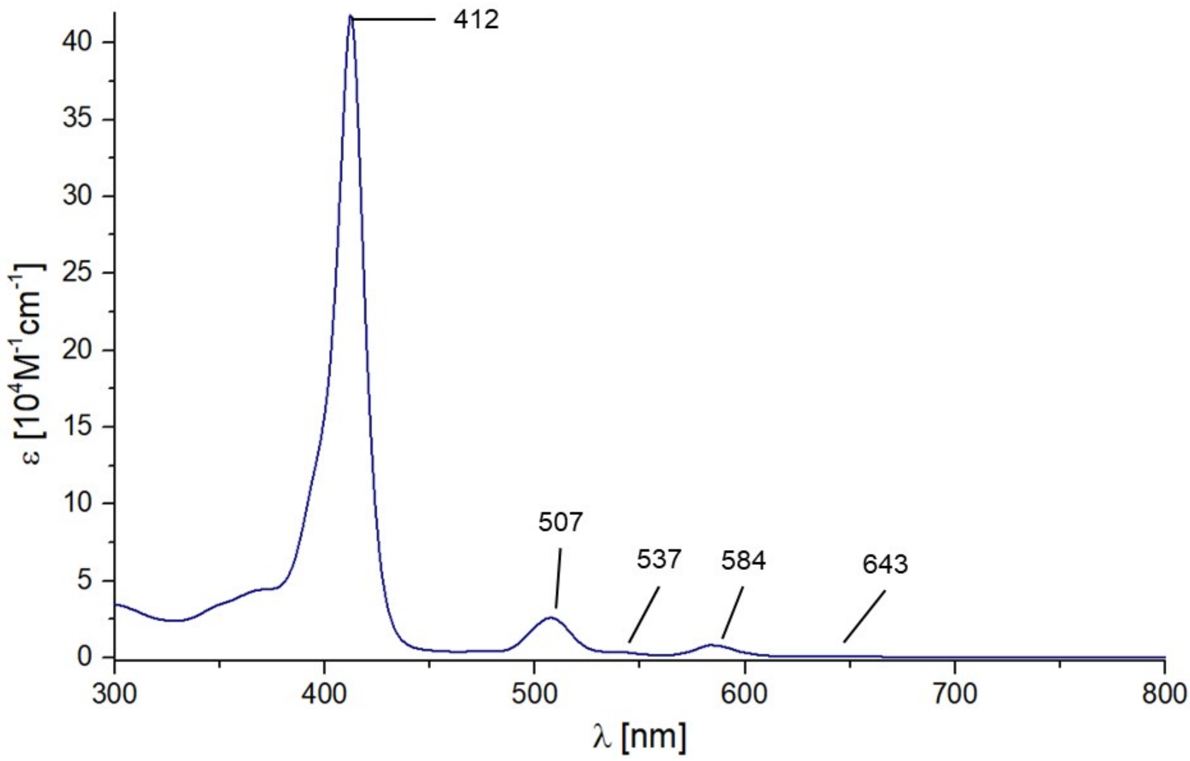


Figure S96: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4m**.

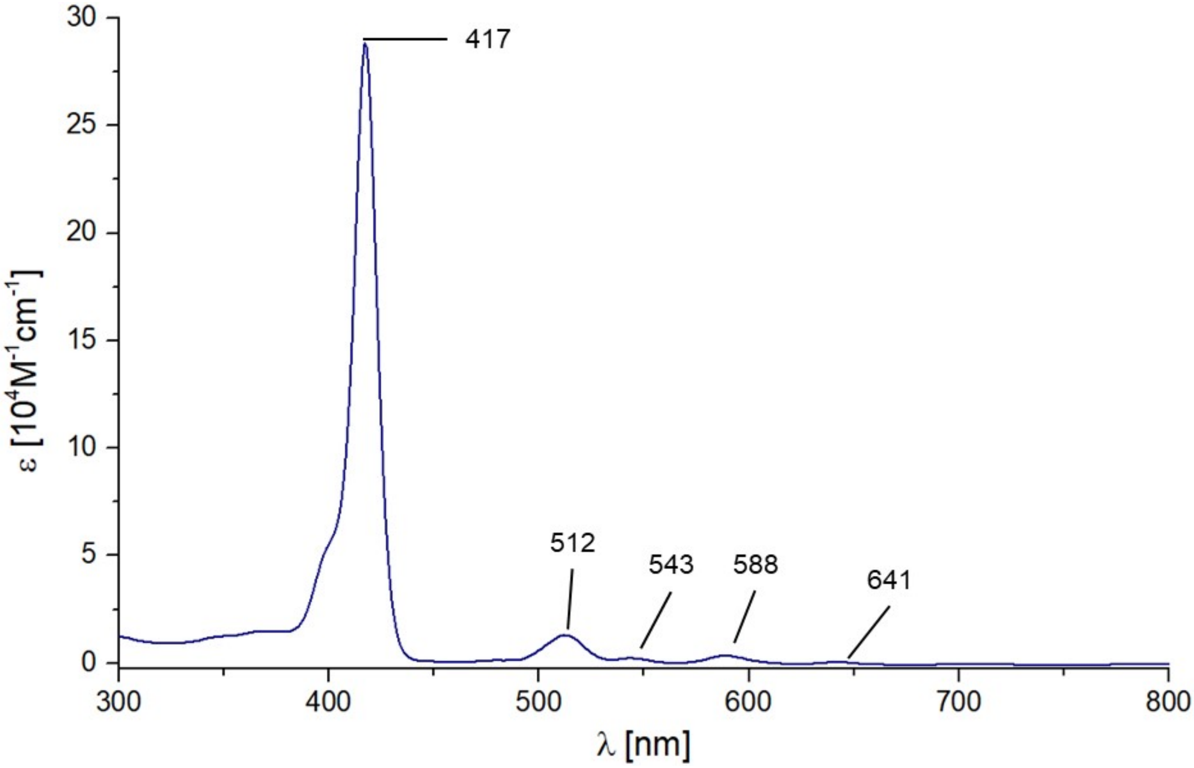


Figure S97: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4n**.

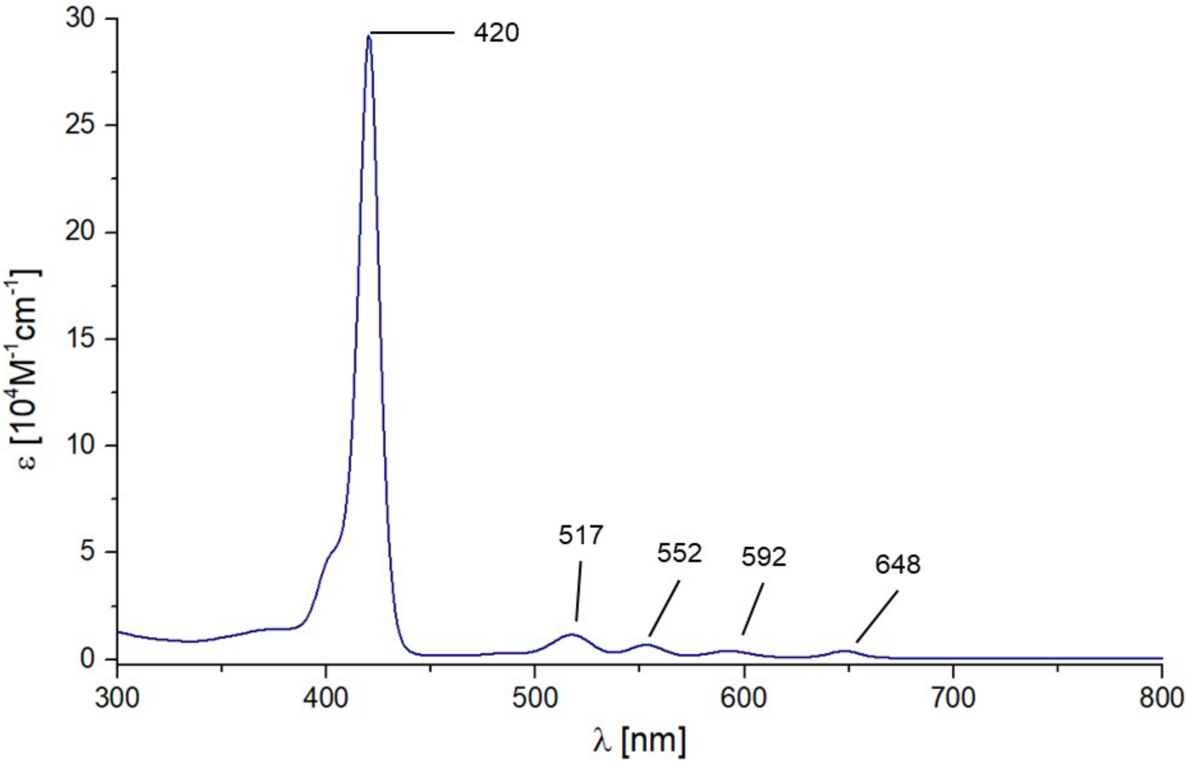


Figure S98: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4q**.

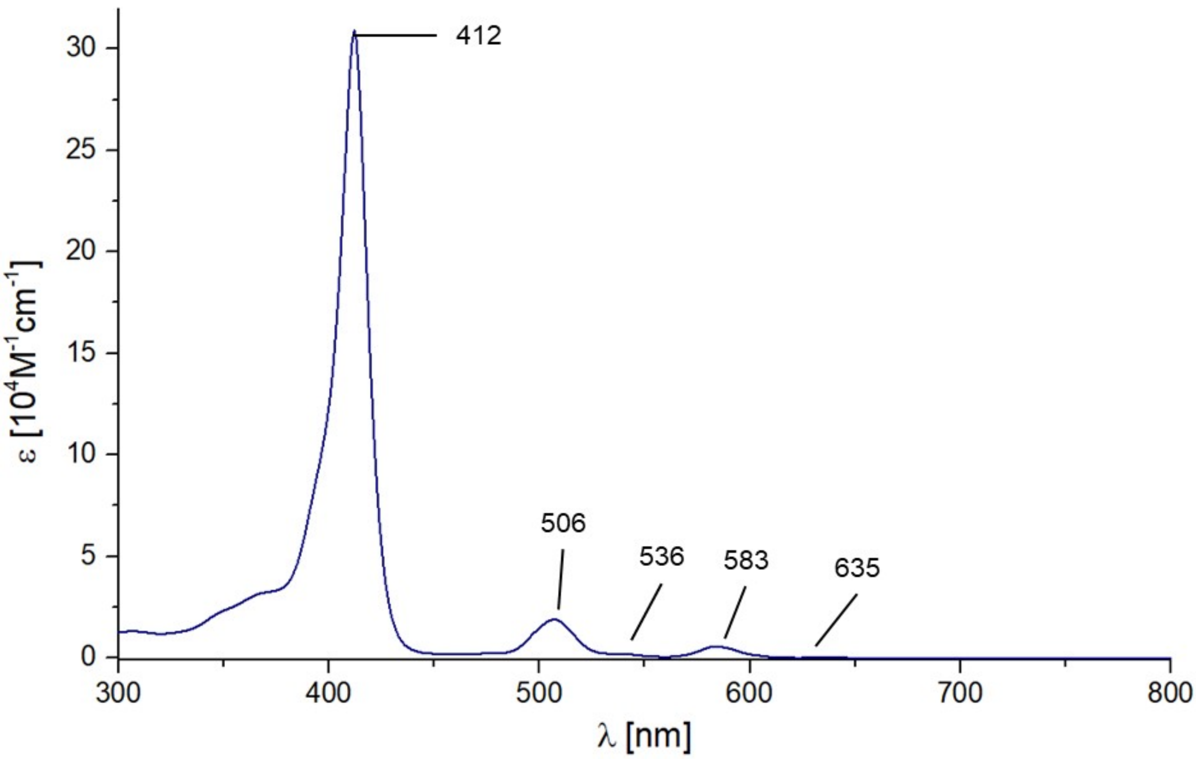


Figure S99: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4t**.

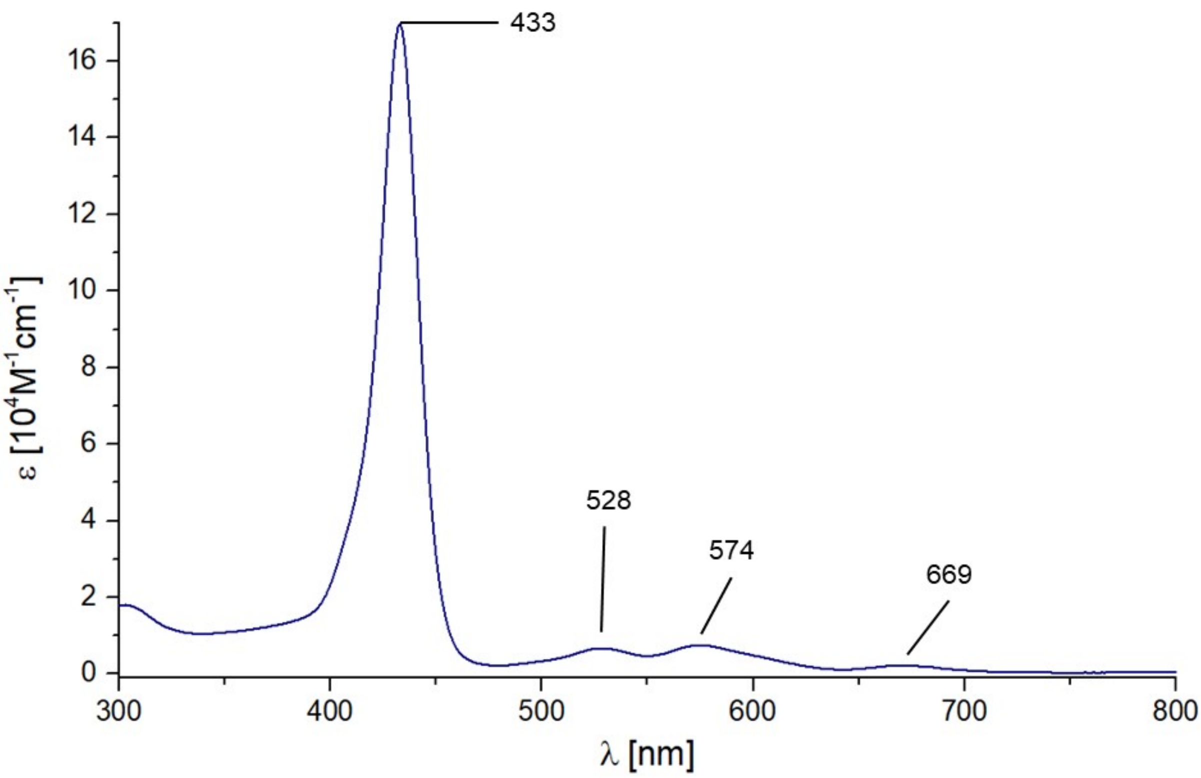


Figure S100: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4w**.

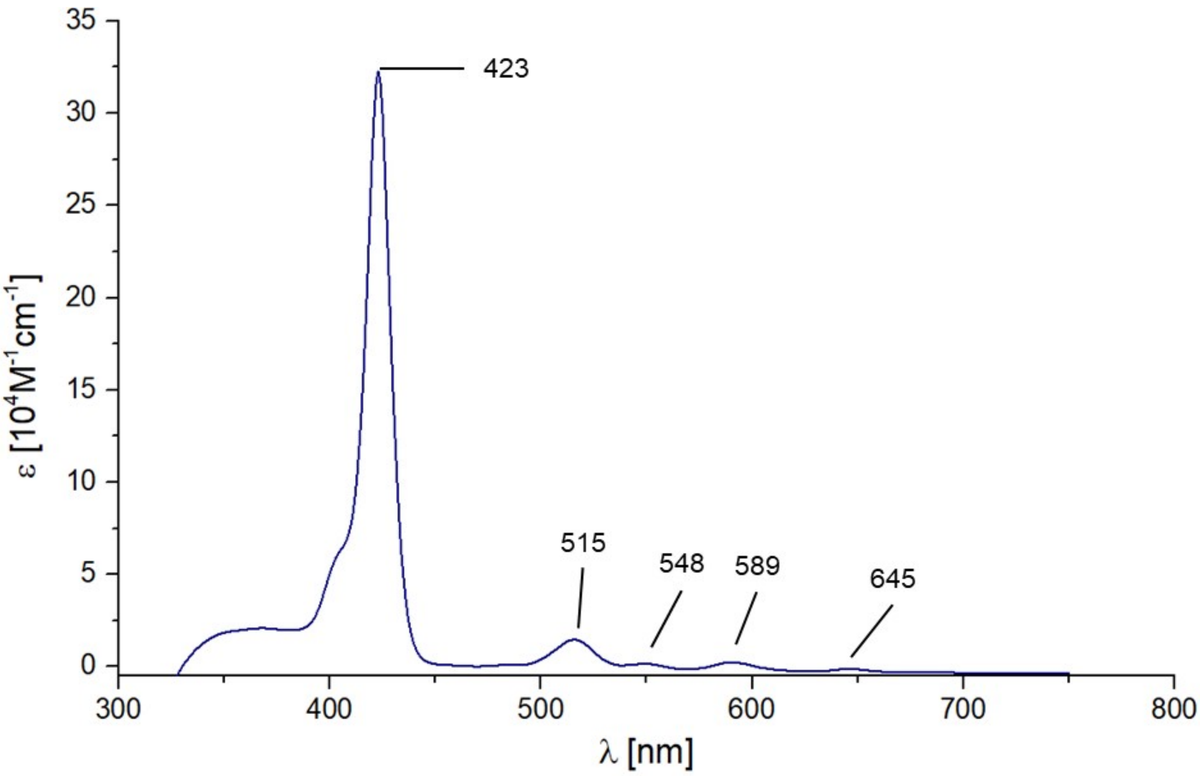


Figure S101: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4y**.

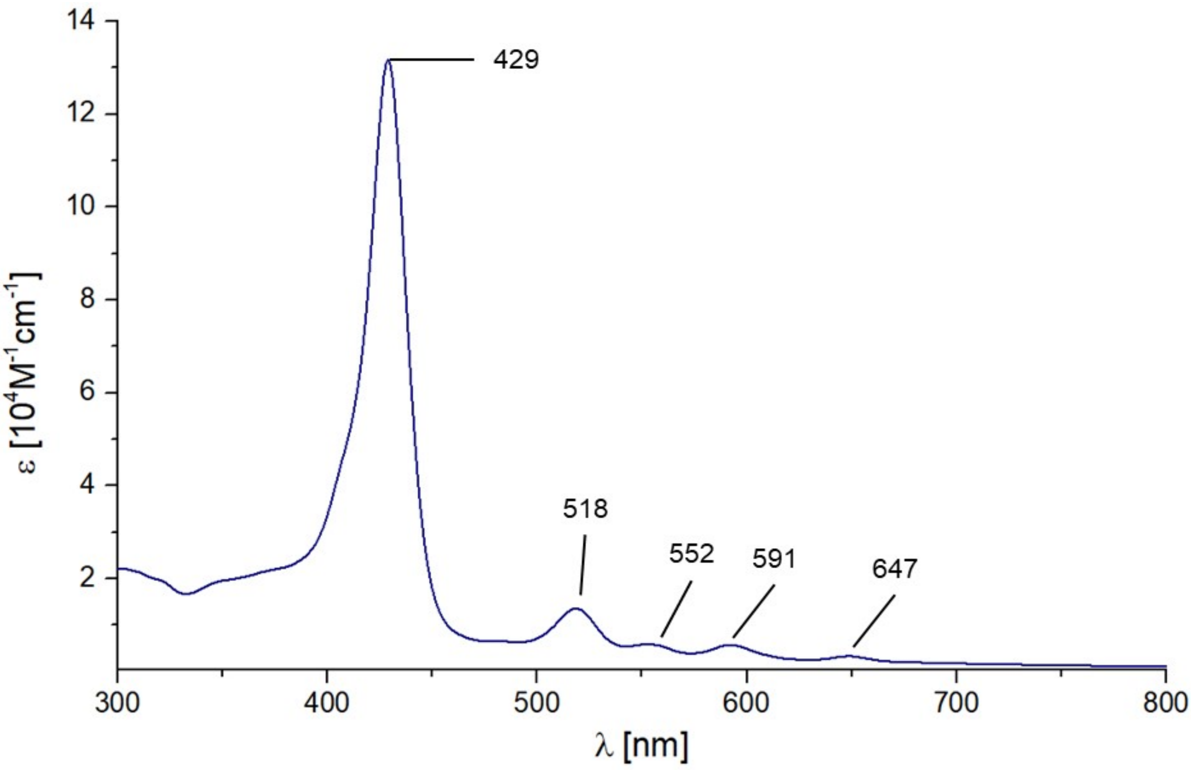


Figure S102: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4z**.

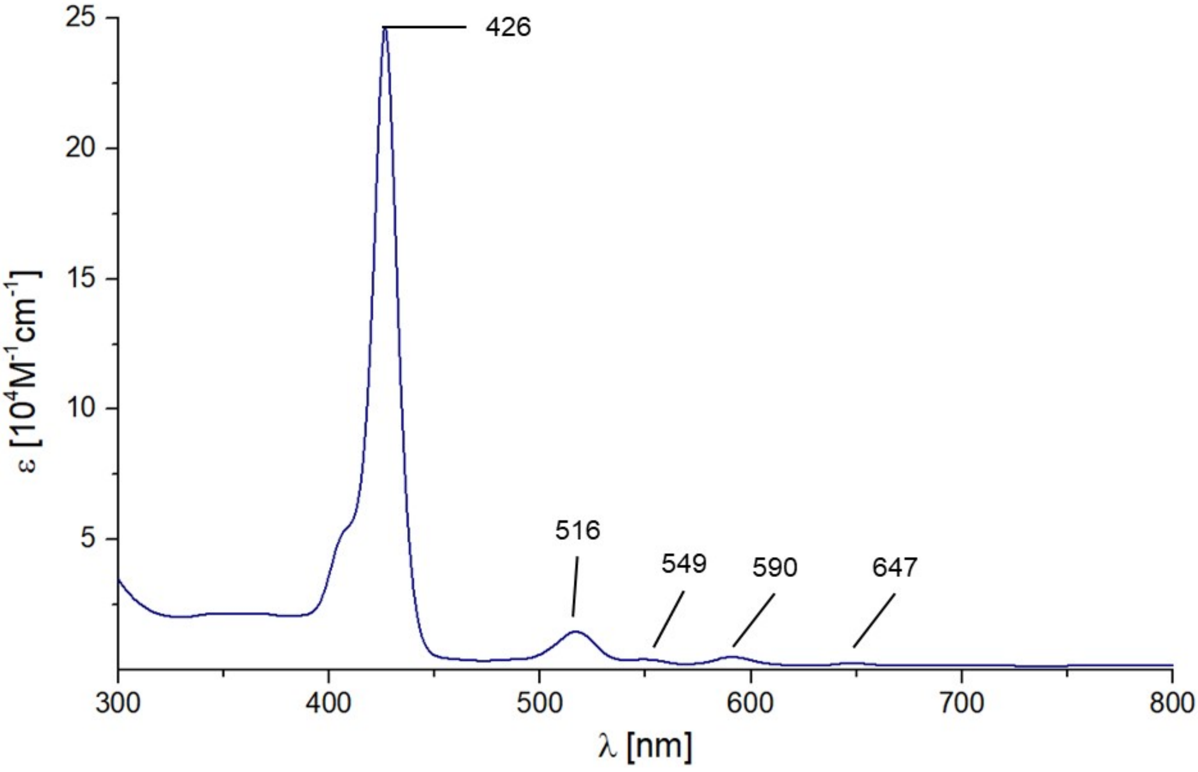


Figure S103: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4ab**.

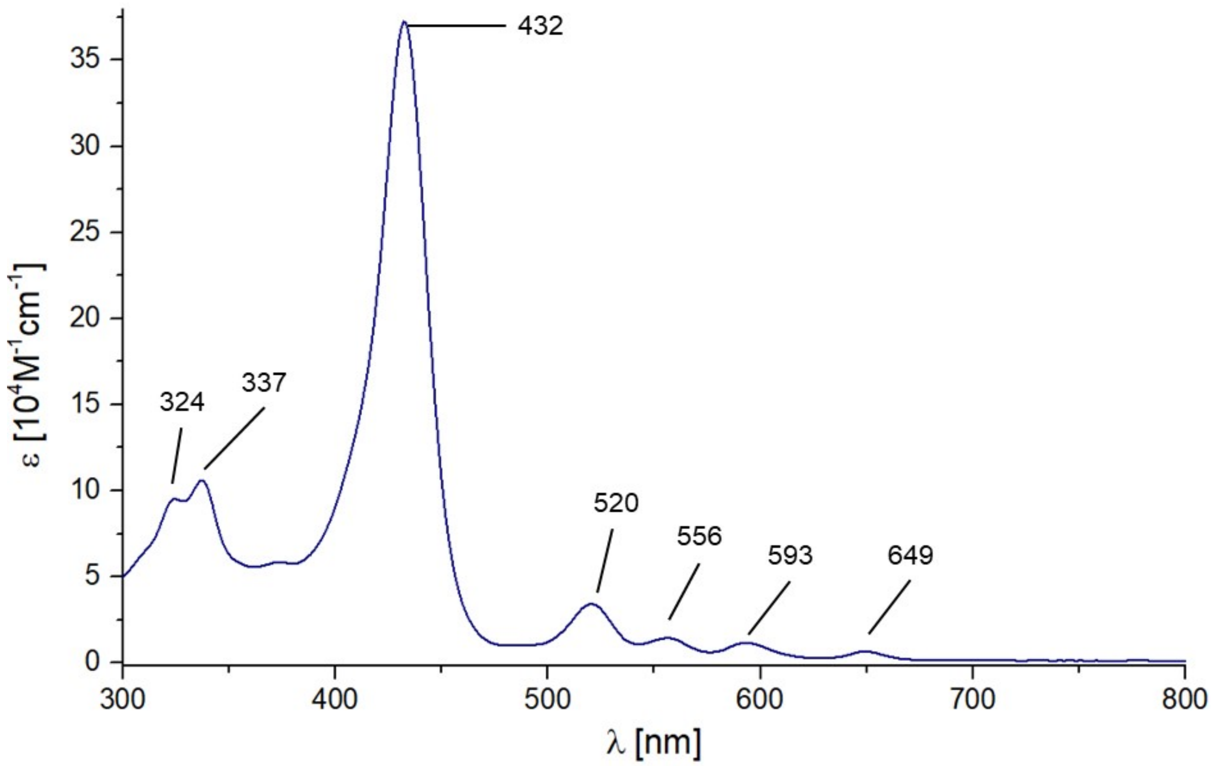


Figure S104: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4ac**.

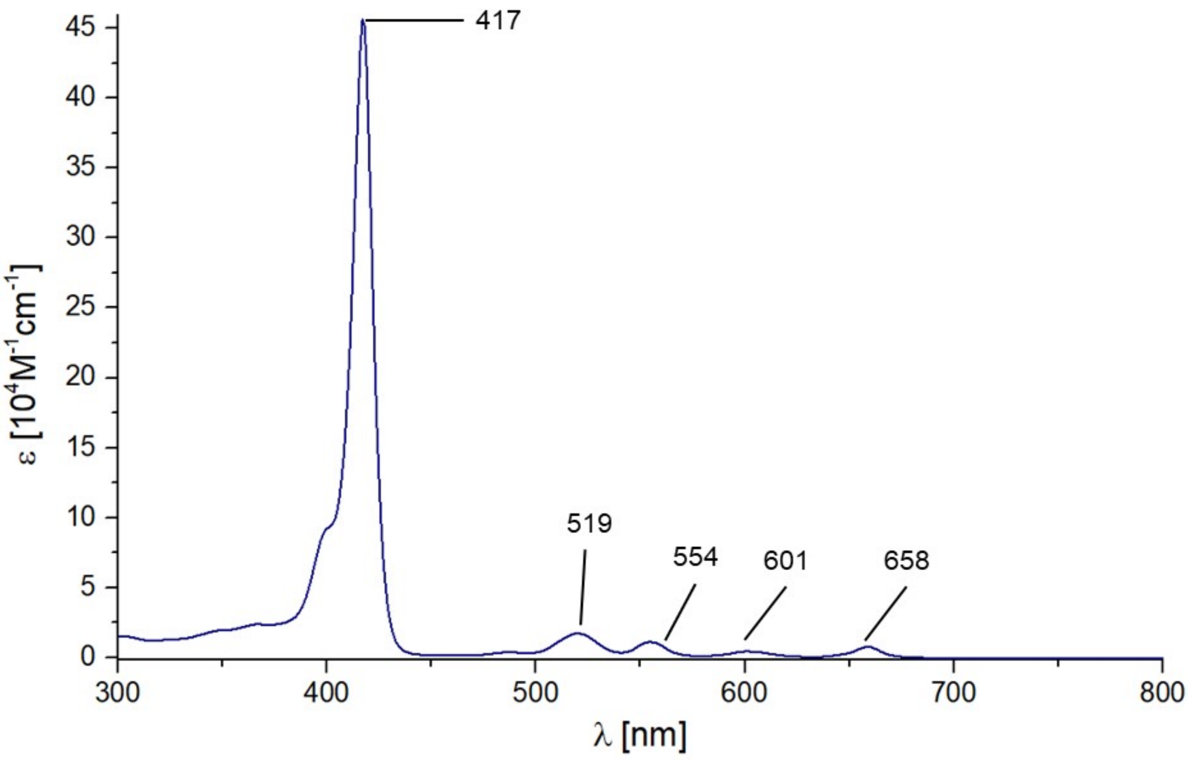


Figure S105: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4ad**.

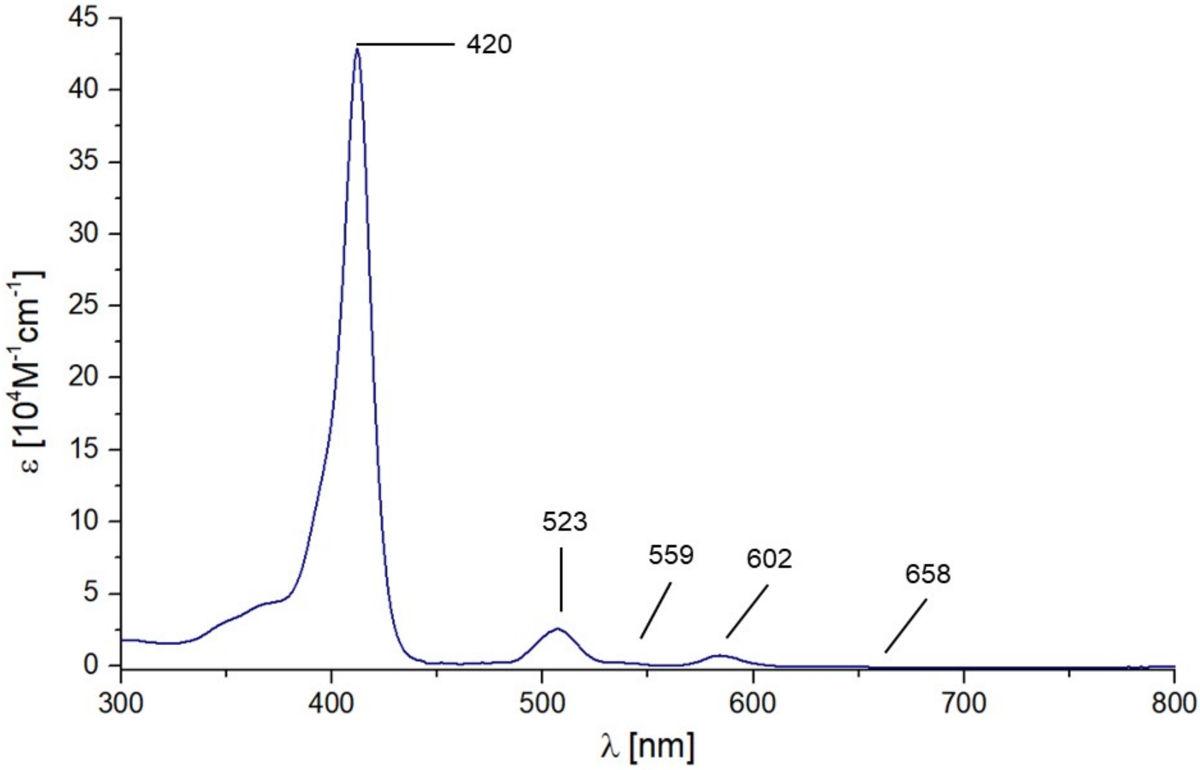


Figure S106: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **4ae**.

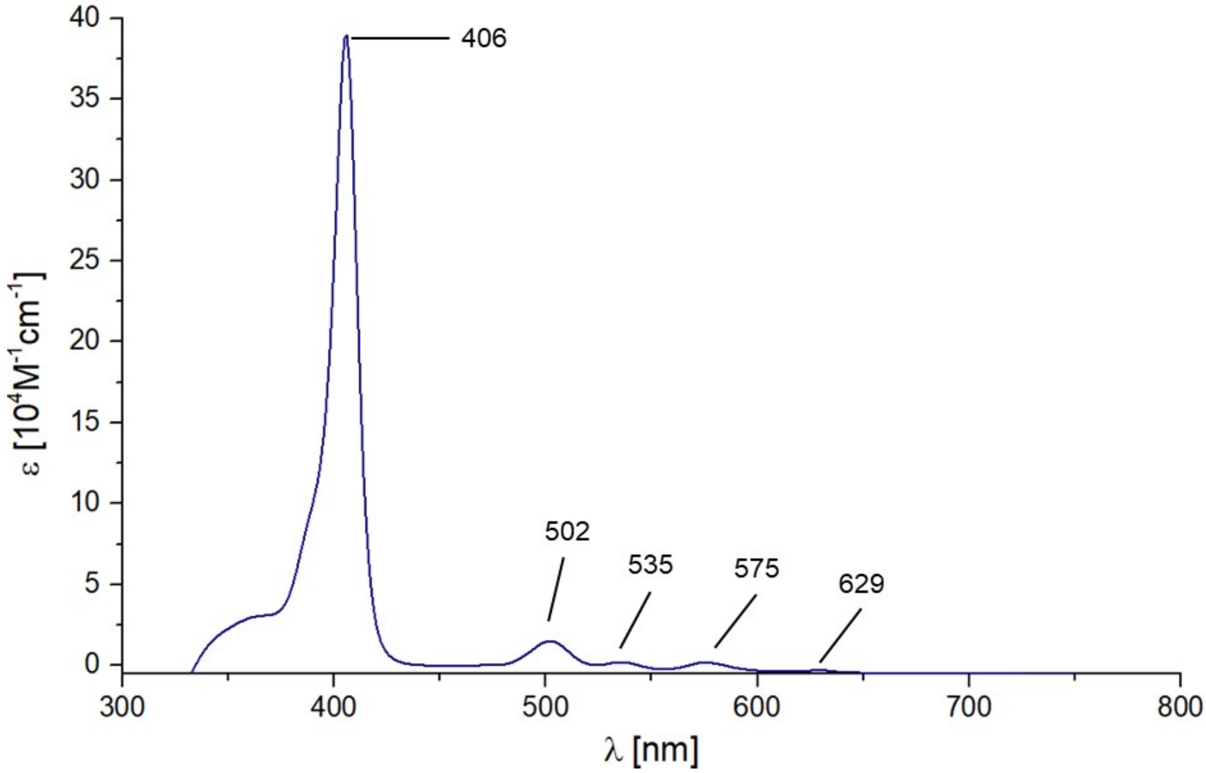


Figure S107: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **7a**.

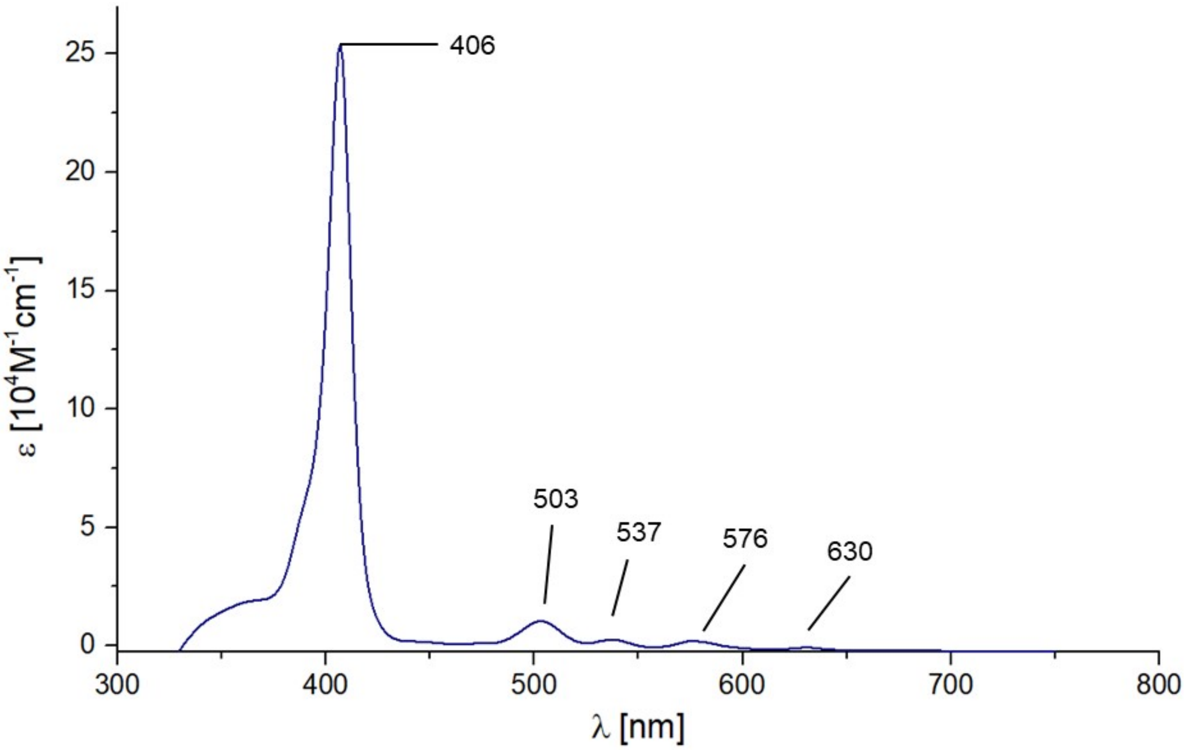


Figure S108: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **7b**.

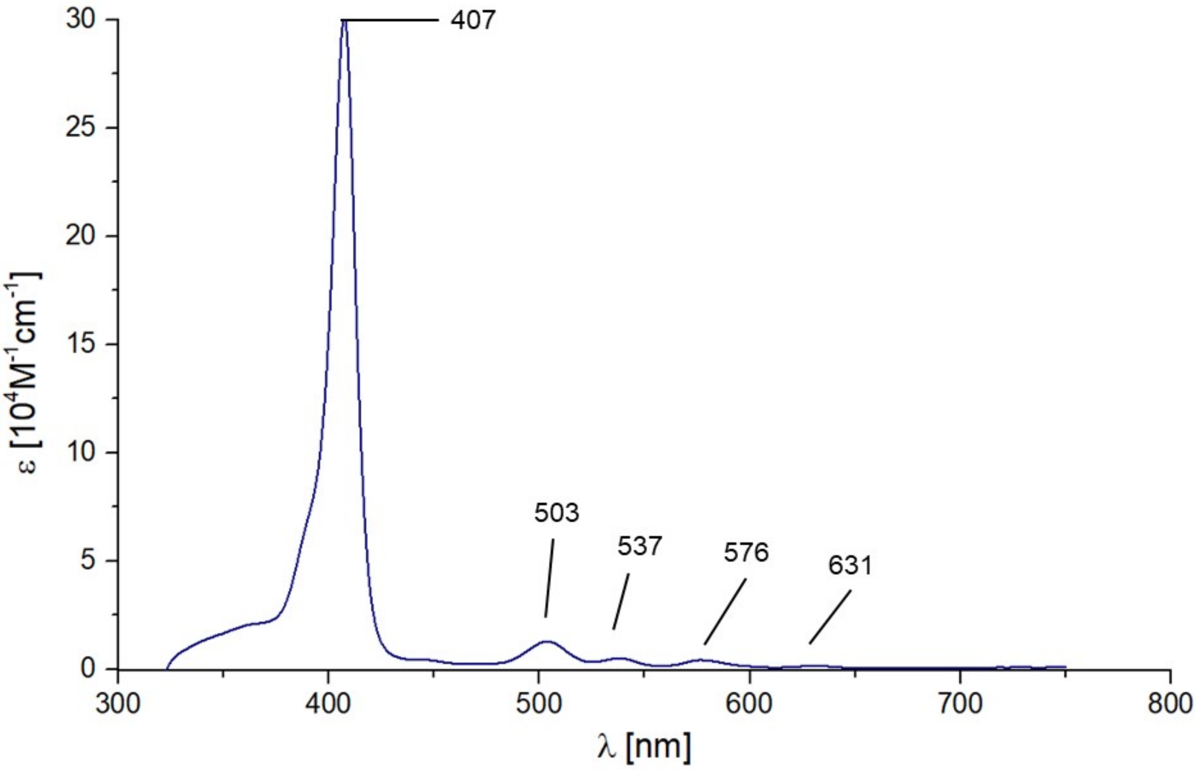


Figure S109: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **7d**.

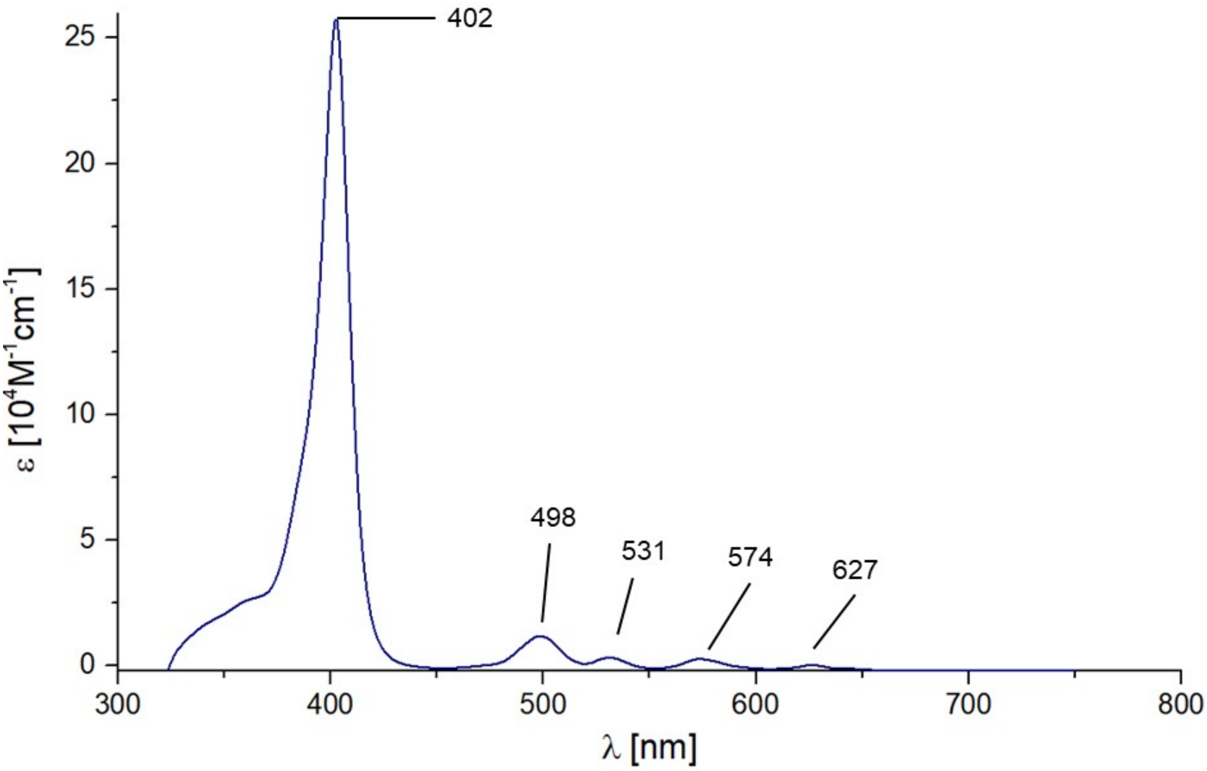


Figure S110: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **7m**.

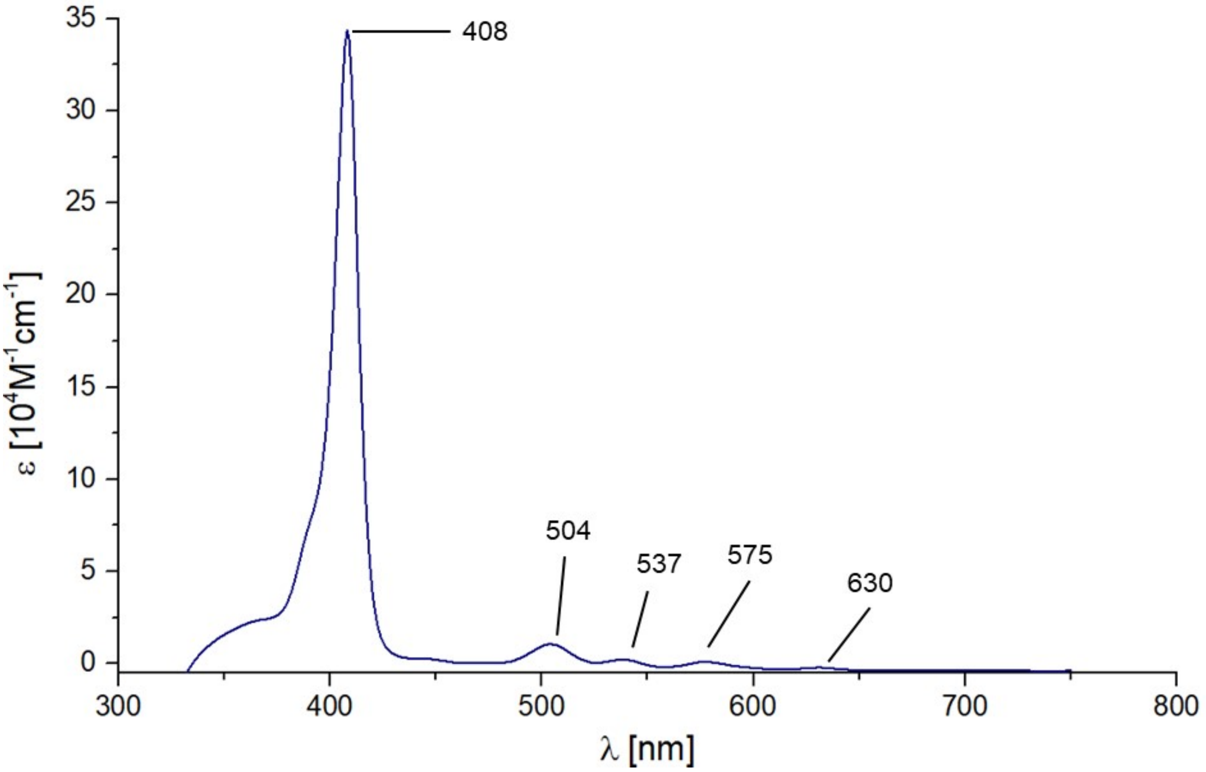


Figure S111: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **7q**.

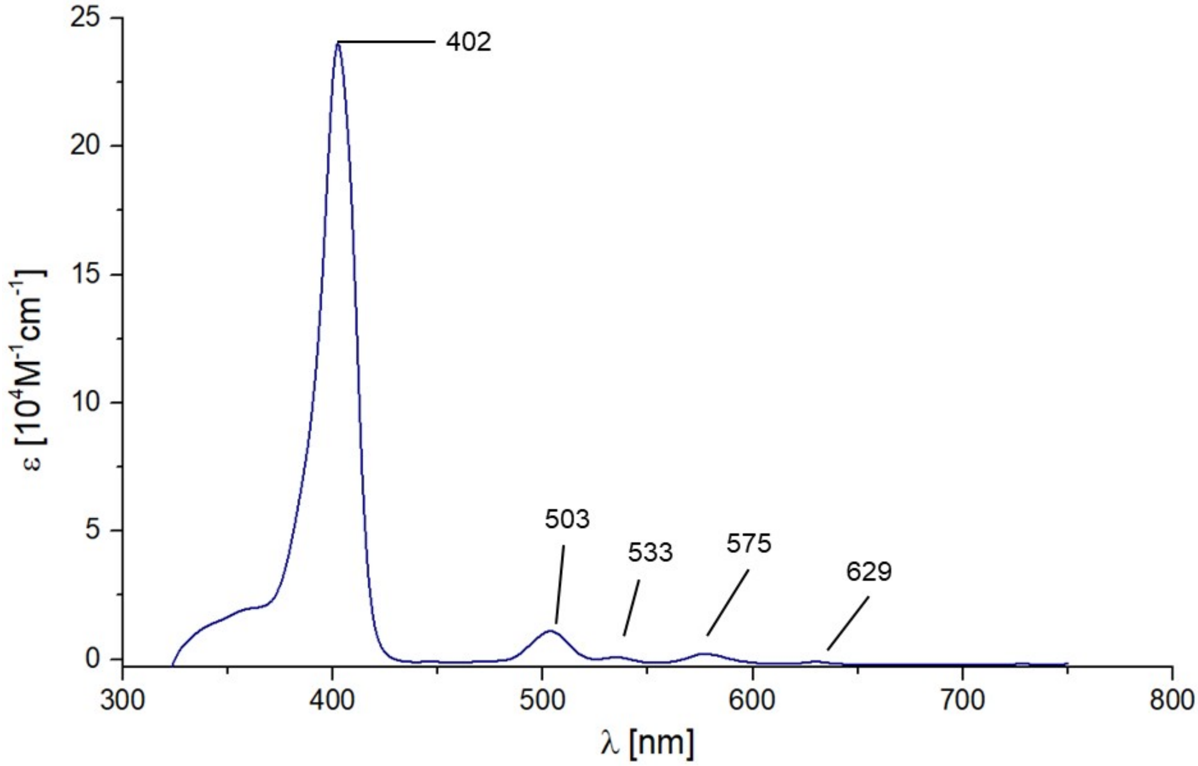


Figure S112: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **7ae**.

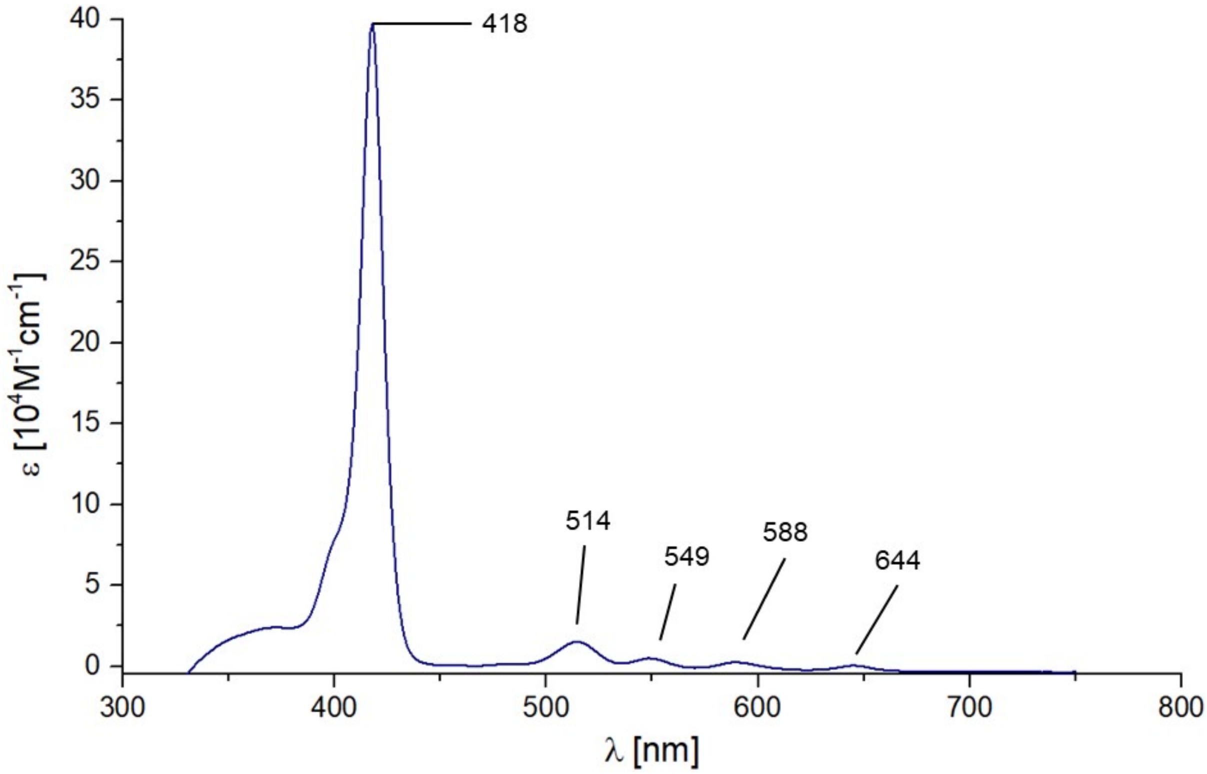


Figure S113: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **8c**.

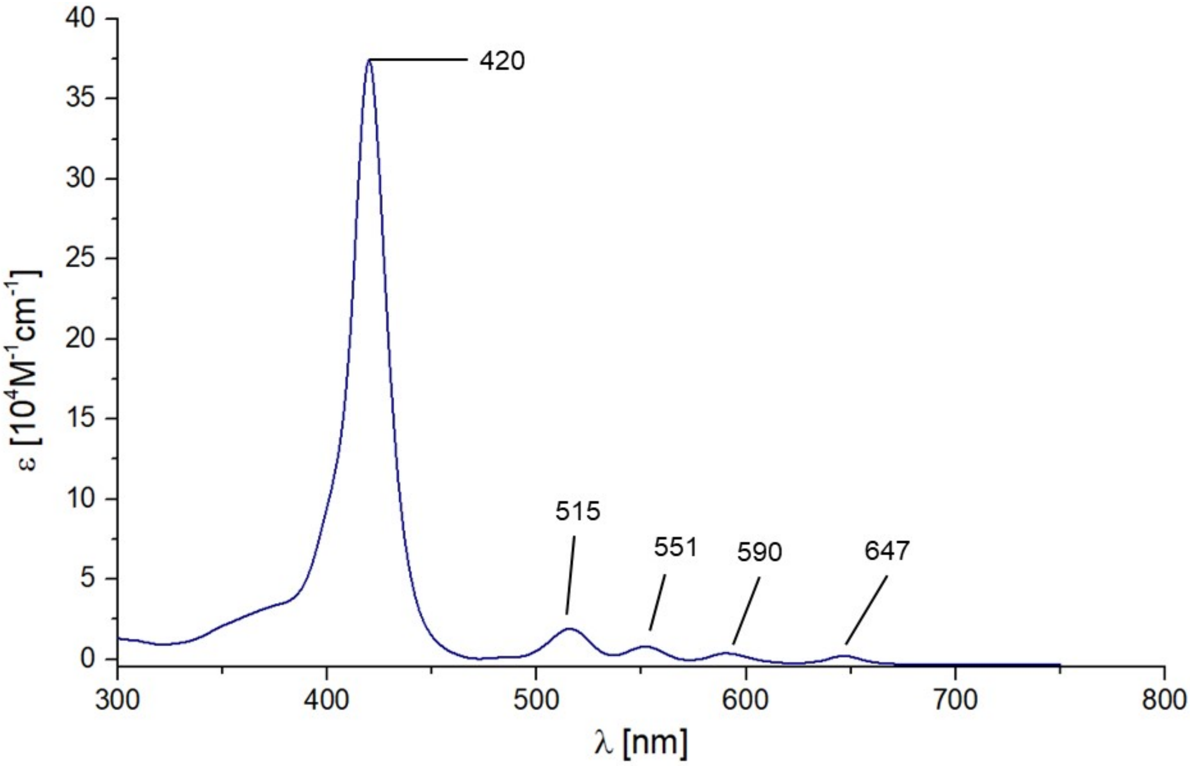


Figure S114: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **8f**.

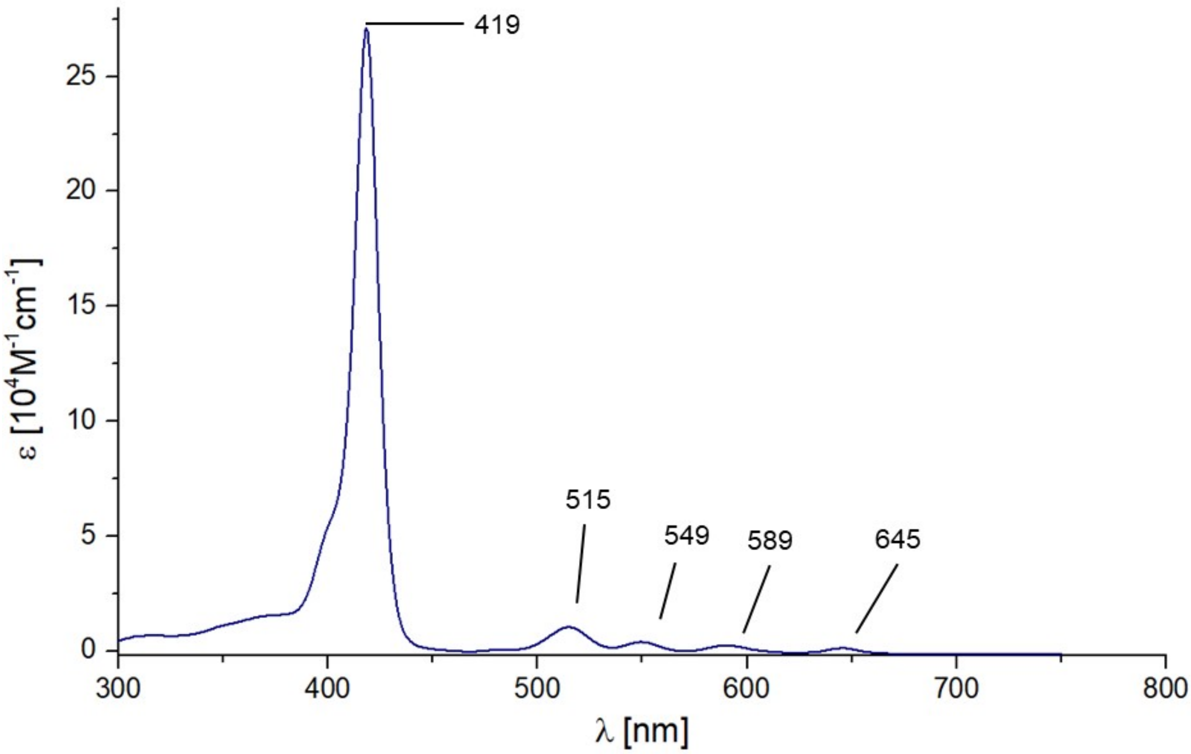


Figure S115: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **8g**.

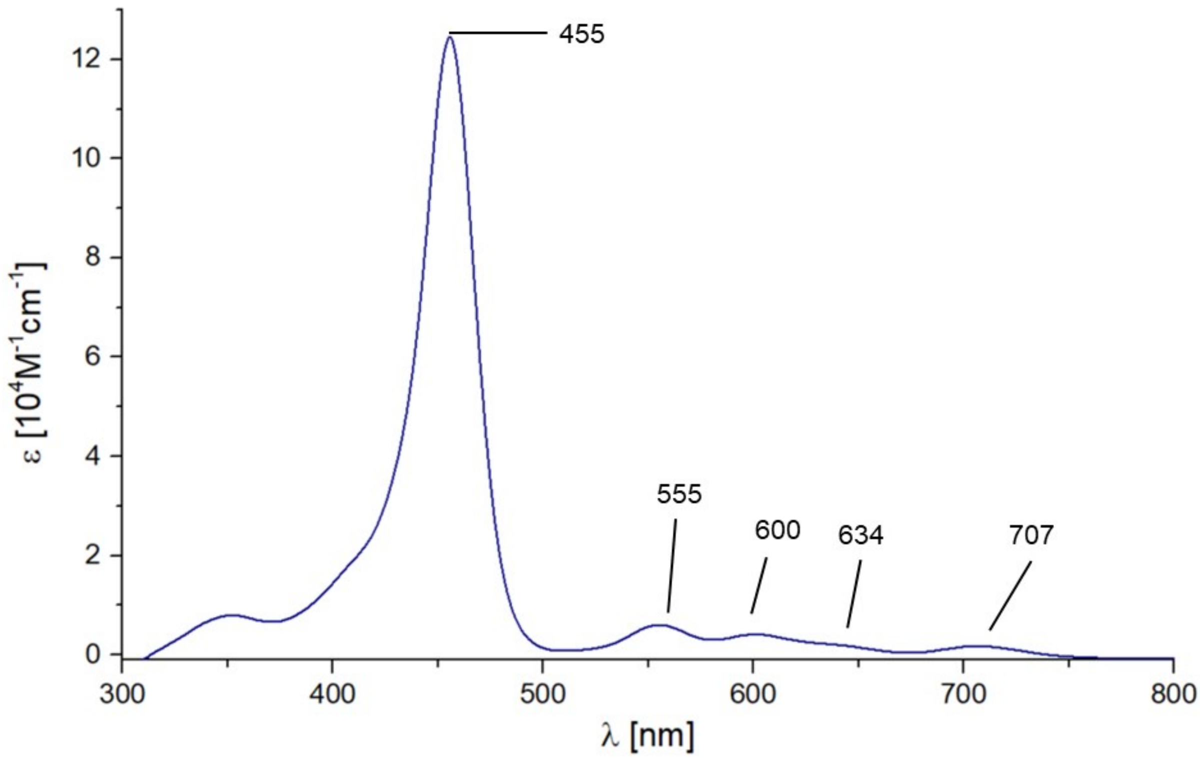


Figure S116: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **11a**.

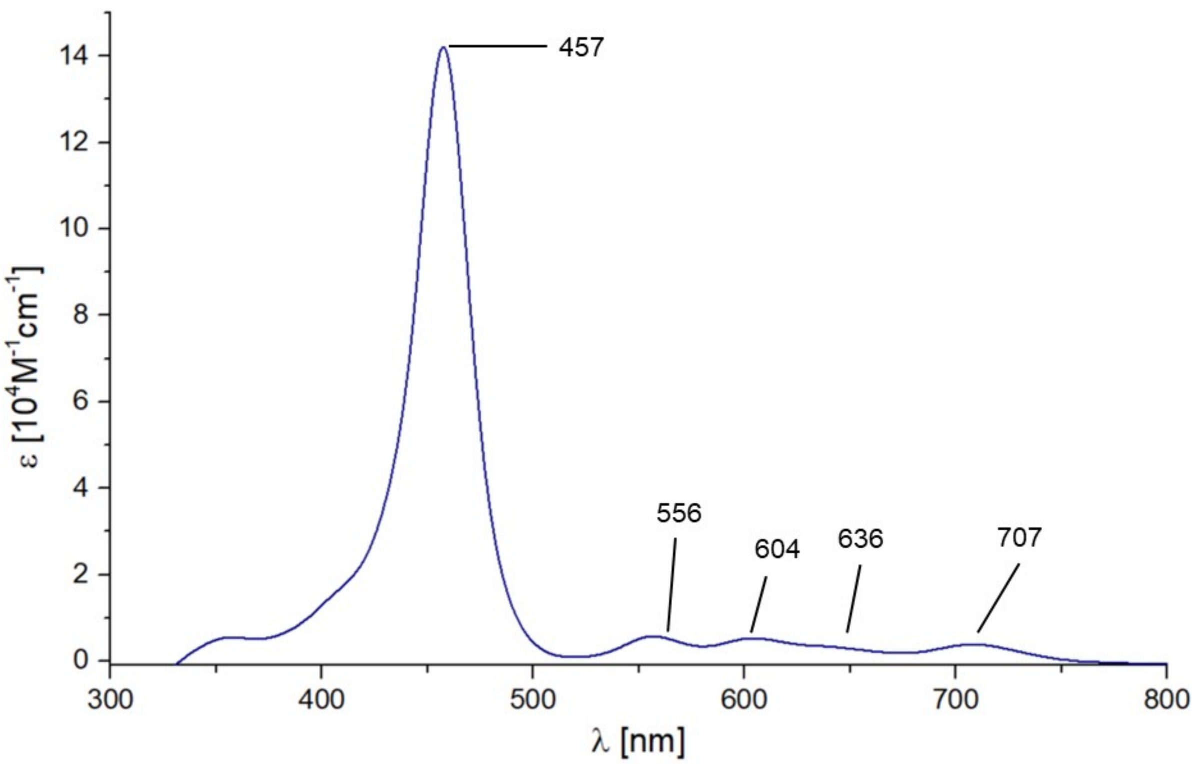


Figure S117: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **11b**.

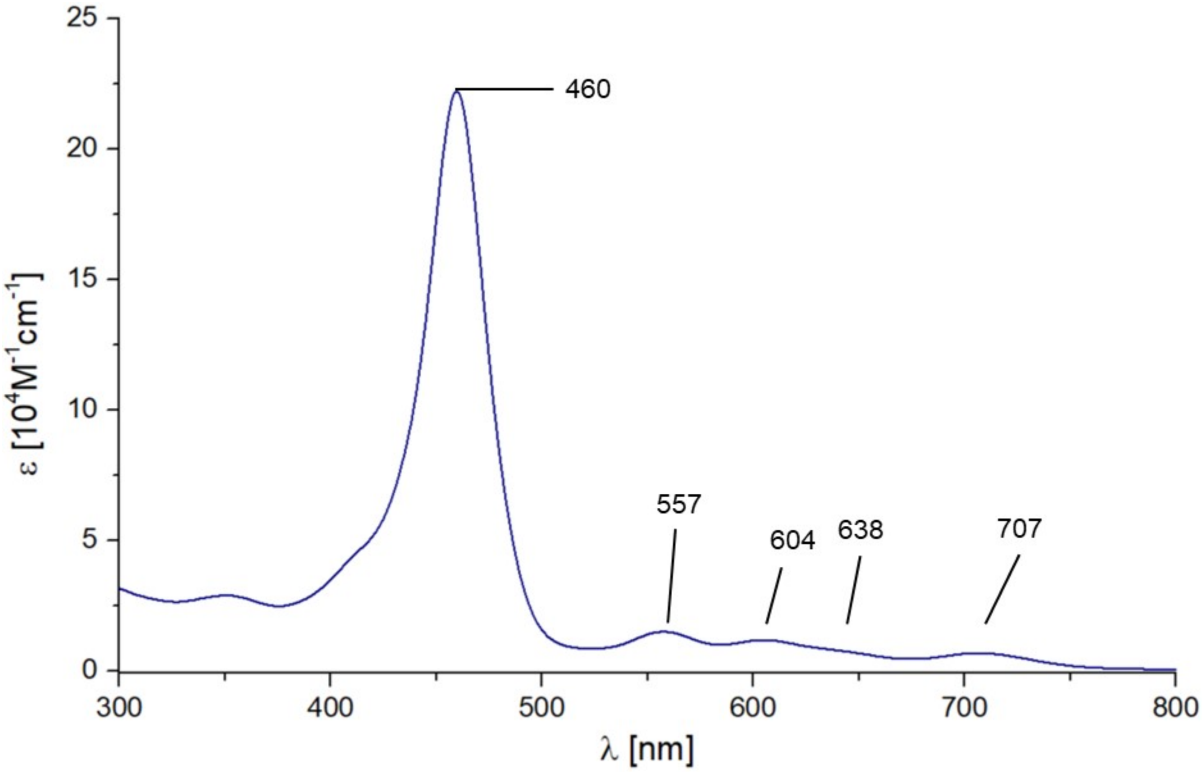


Figure S118: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **11c**.

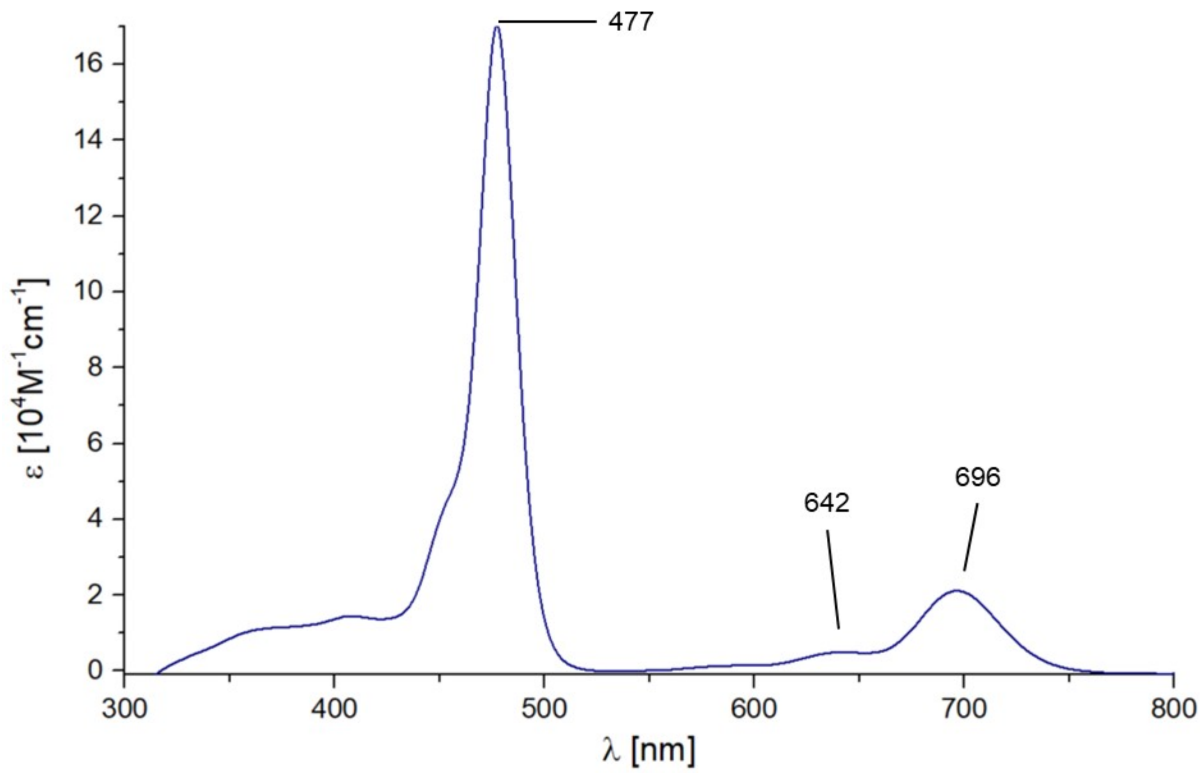


Figure S119: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **11d**.

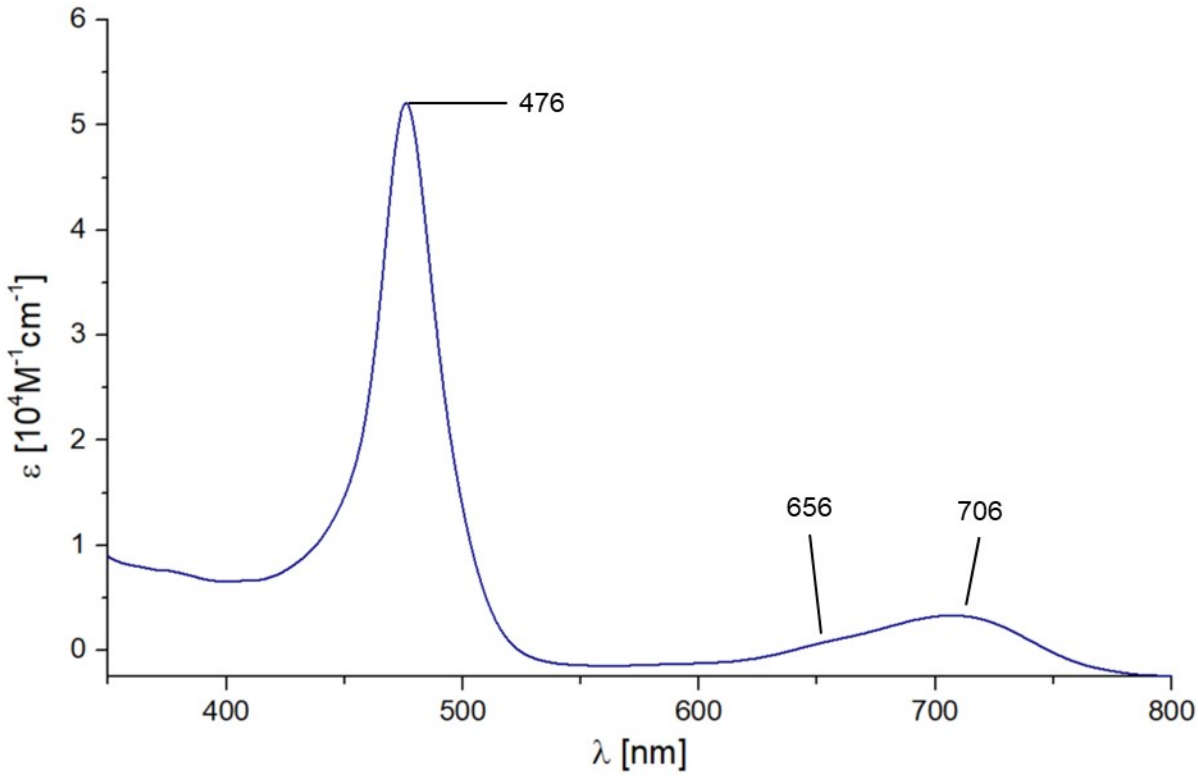


Figure S120: UV/Vis absorption spectrum (DMSO; 25 °C) of **11e**.

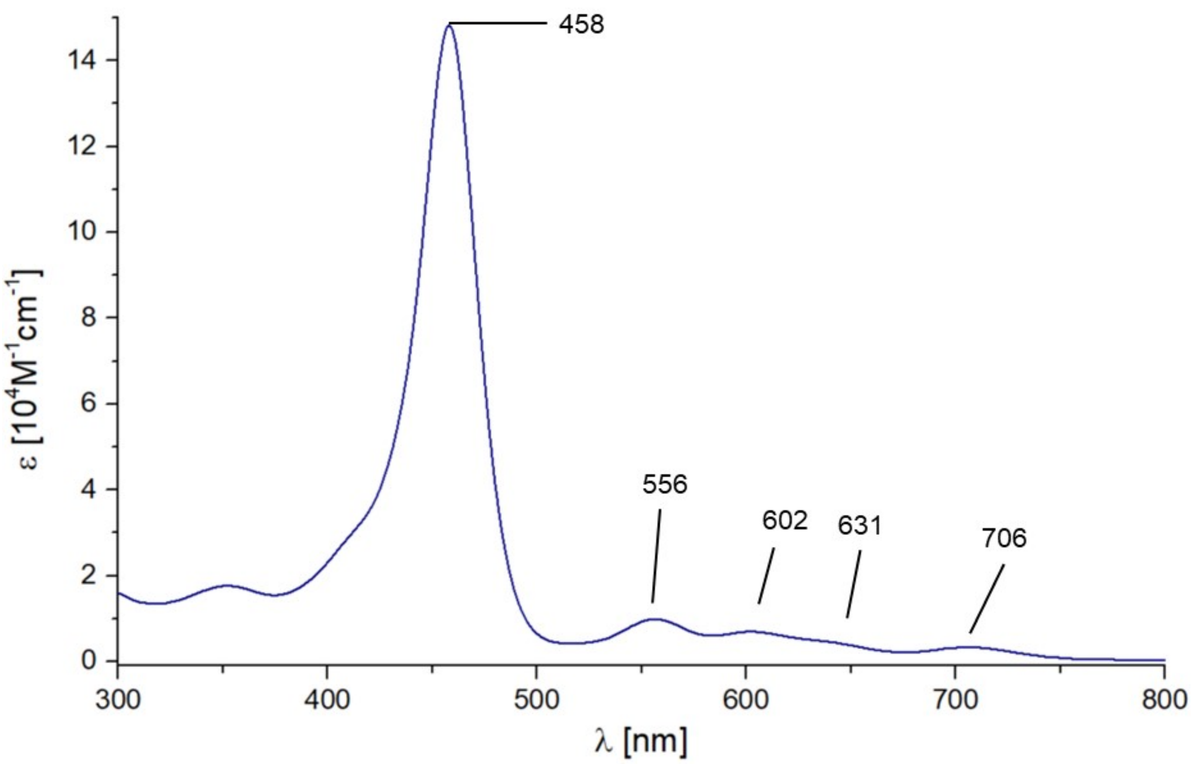


Figure S121: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **11h**.

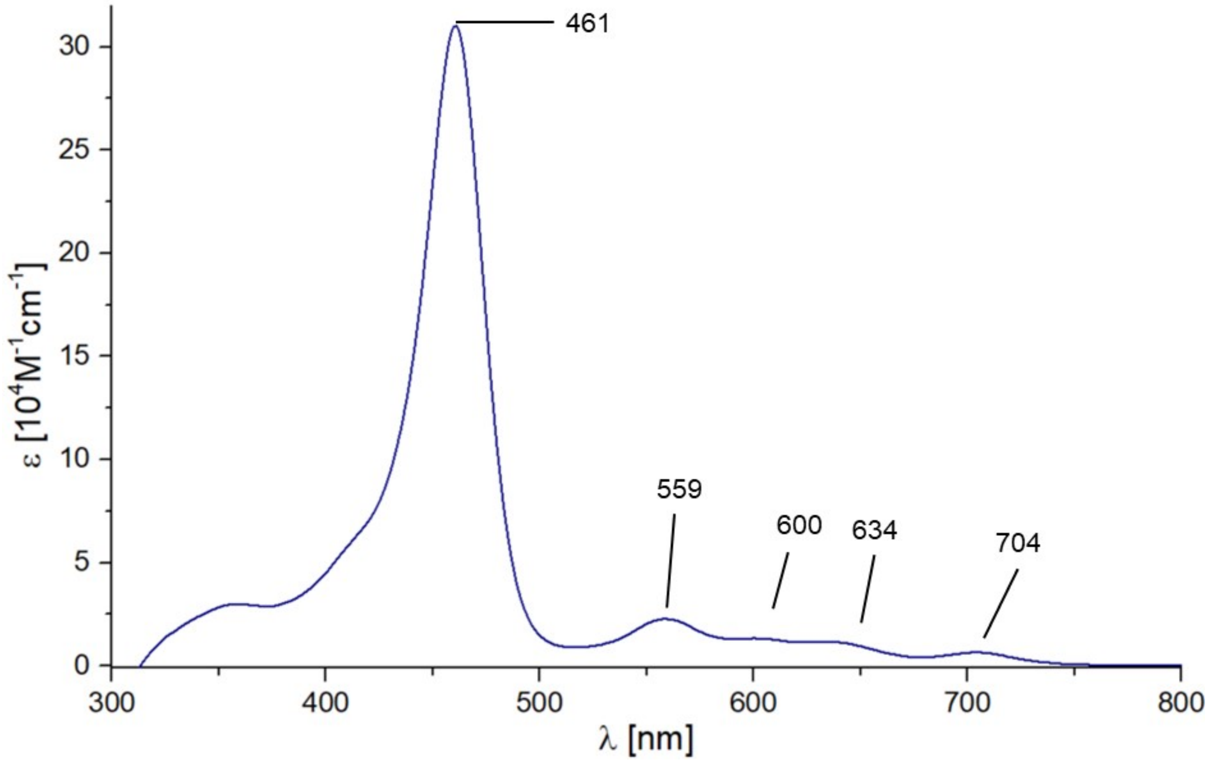


Figure S122: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **11k**.

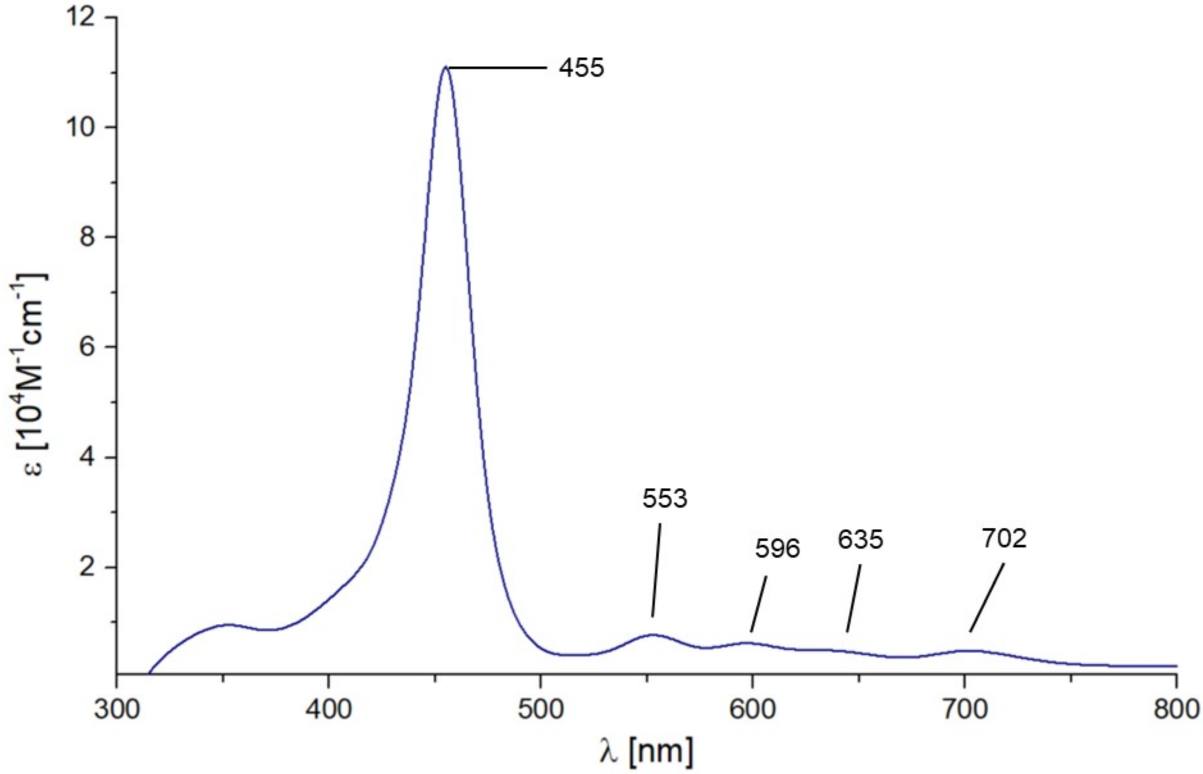


Figure S123: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **11q**.

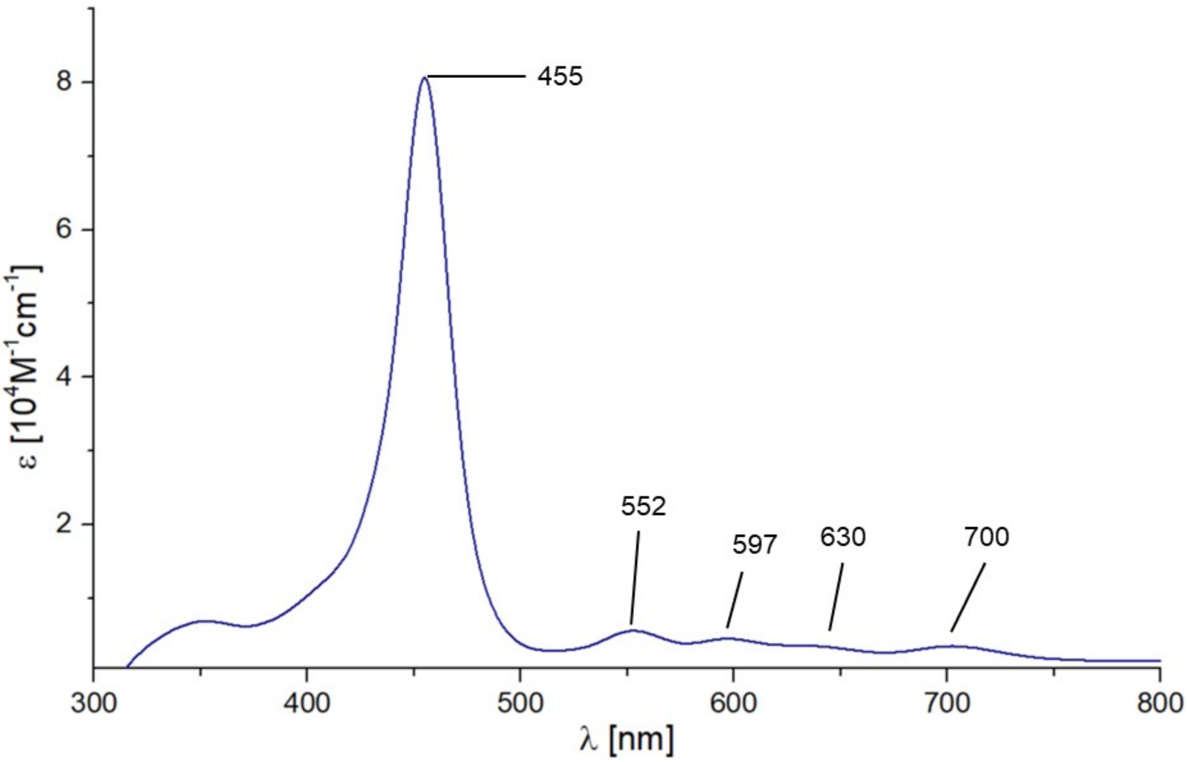


Figure S124: UV/Vis absorption spectrum (CH_2Cl_2; 25 °C) of **11r**.

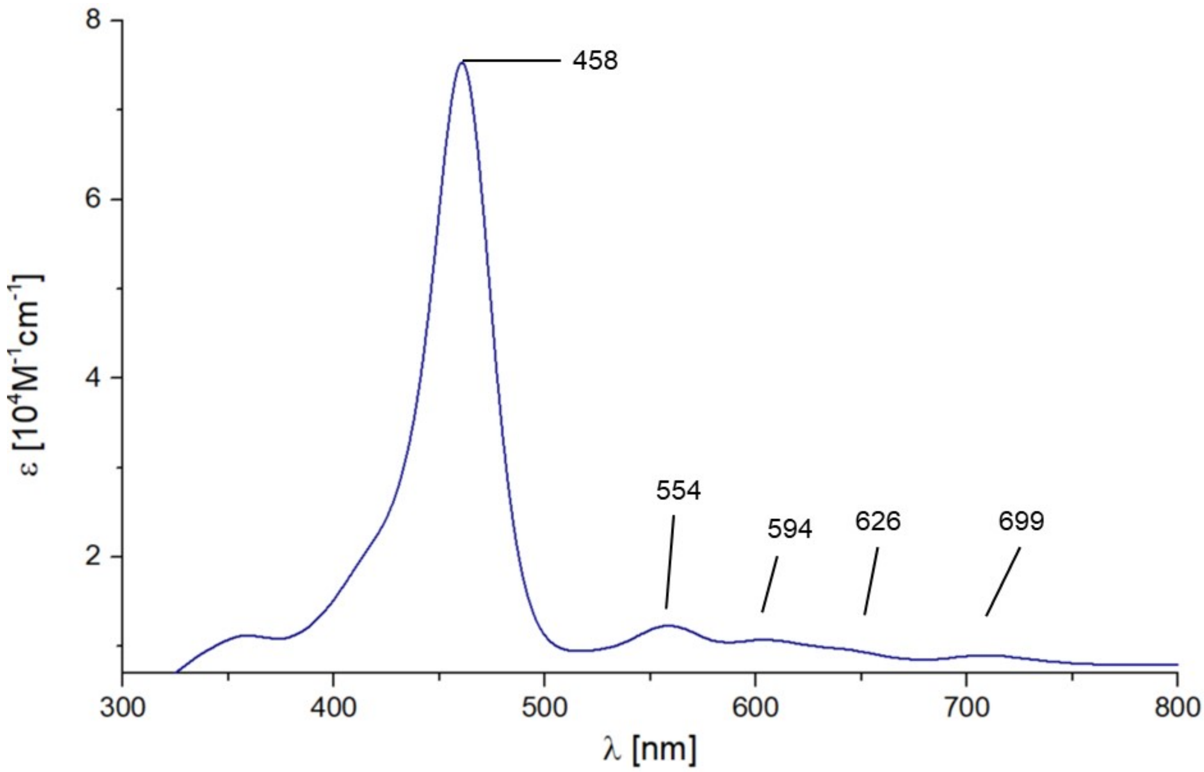
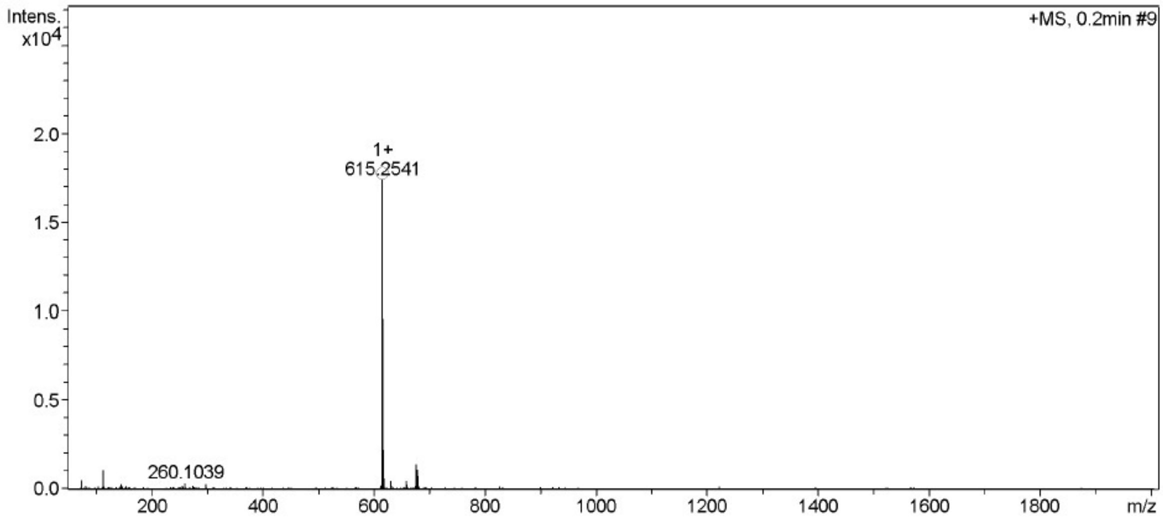


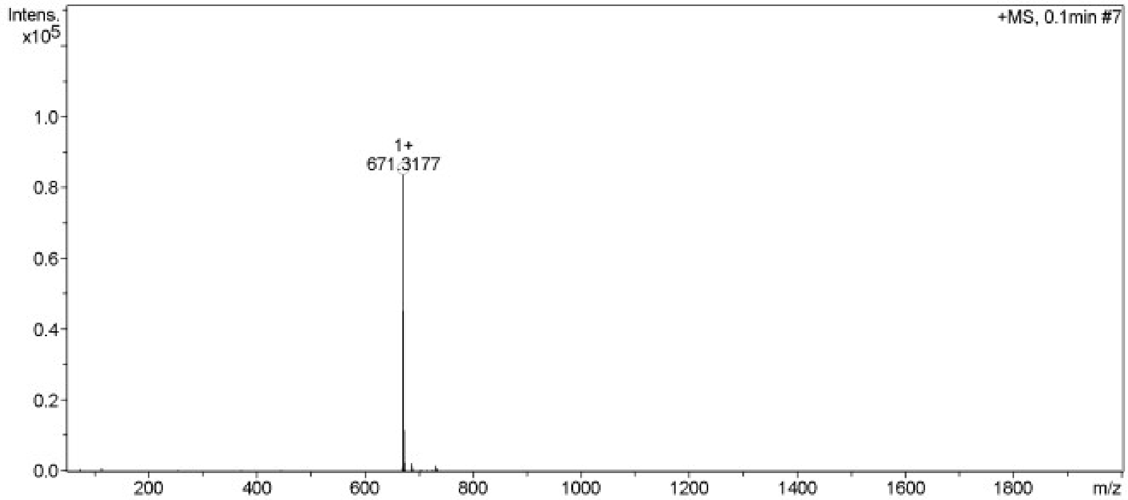
Figure S125: UV/Vis absorption spectrum (($CDCl_3$:TEA, 99:1, v/v); 25 °C) of **11s**.

HRMS spectra



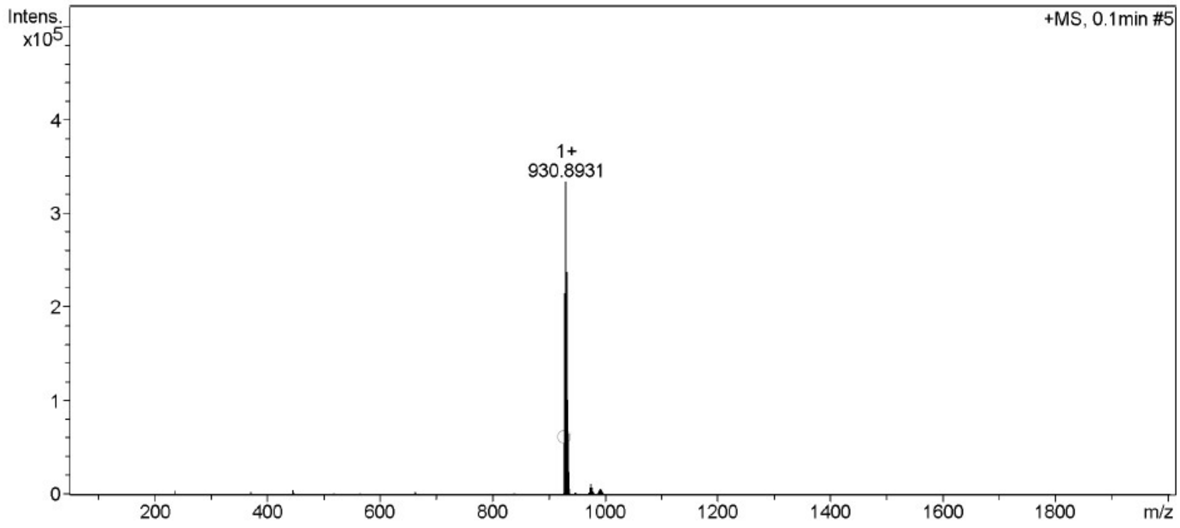
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
615.254129	1	C44H31N4	615.254323	0.2	0.3	31.5	ok	even	30.8

Figure S126: HRMS-APCI (m/z) spectrum of **4a.**



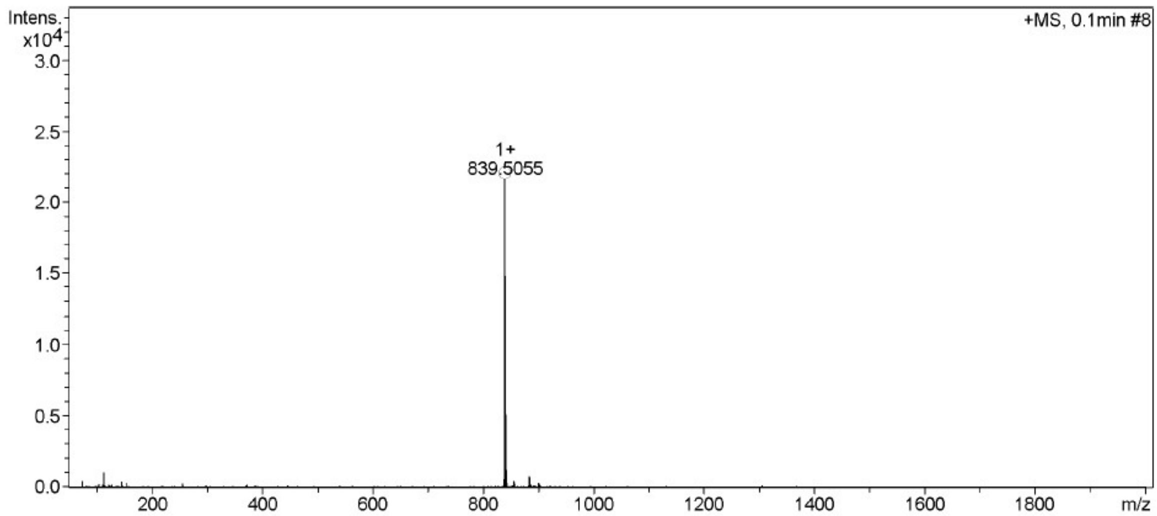
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
671.317721	1	C48H39N4	671.316924	-0.8	-1.2	31.5	ok	even	3.5

Figure S127: HRMS-APCI (m/z) spectrum of **4b**.



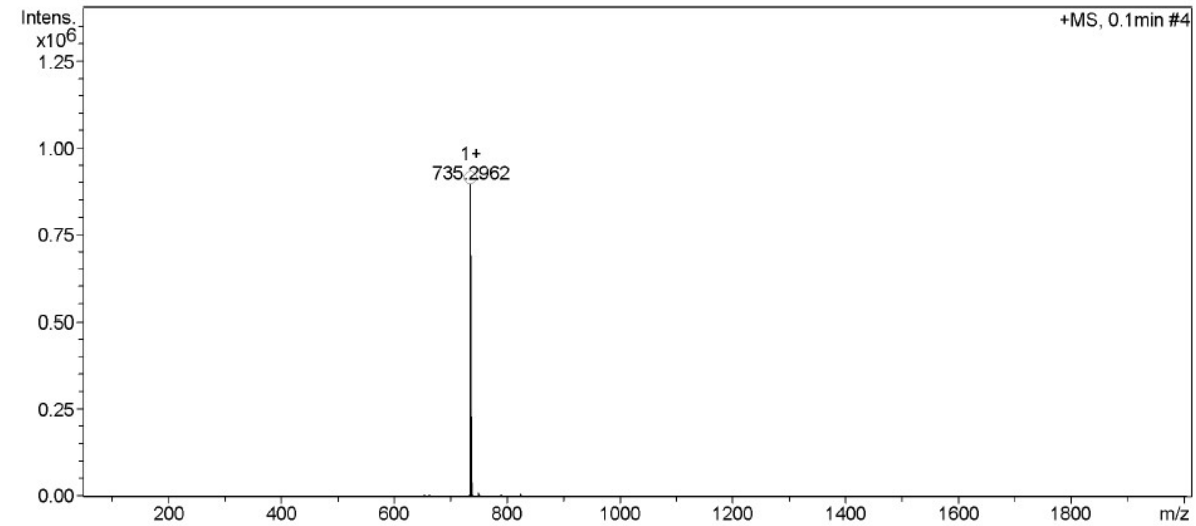
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
926.895590	1	C44H27Br4N4	926.896372	-0.8	-0.8	31.5	ok	even	8.8

Figure S128: HRMS-APCI (m/z) spectrum of **4c**.



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
839.505453	1	C60H63N4	839.504724	0.7	0.9	31.5	ok	even	11.0

Figure S129: HRMS-APCI (m/z) spectrum of **4d**.



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e¯ Conf	mSigma
735.296245	1	C48H39N4O4	735.296582	-0.3	-0.5	31.5	ok	even	114.1

Figure S130: HRMS-APCI (m/z) spectrum of **4e**.

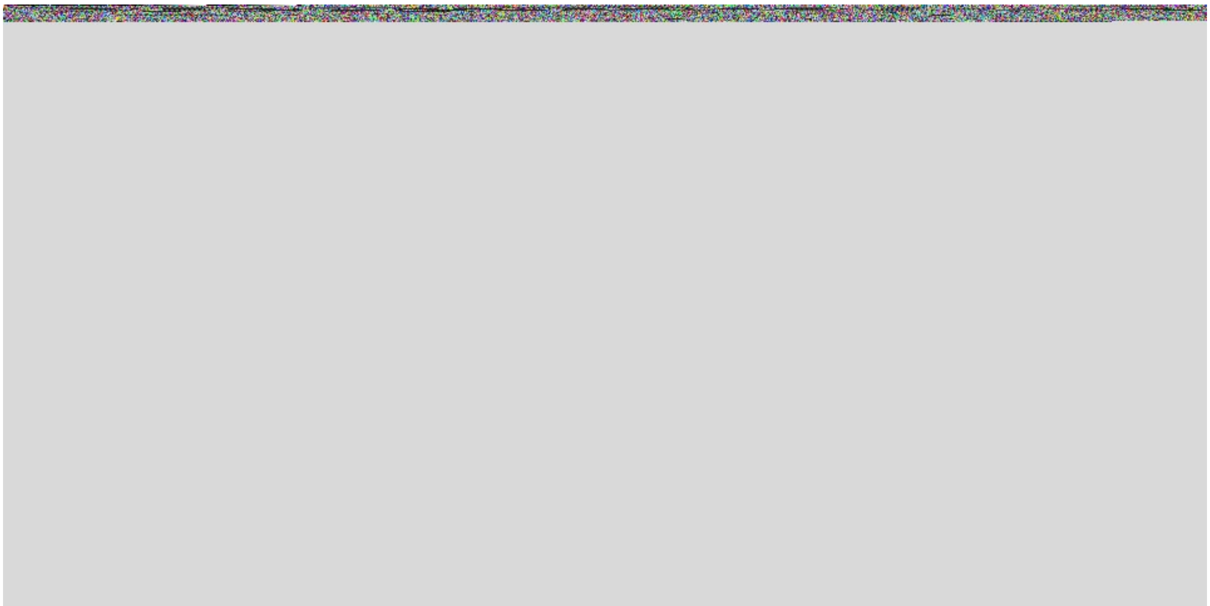
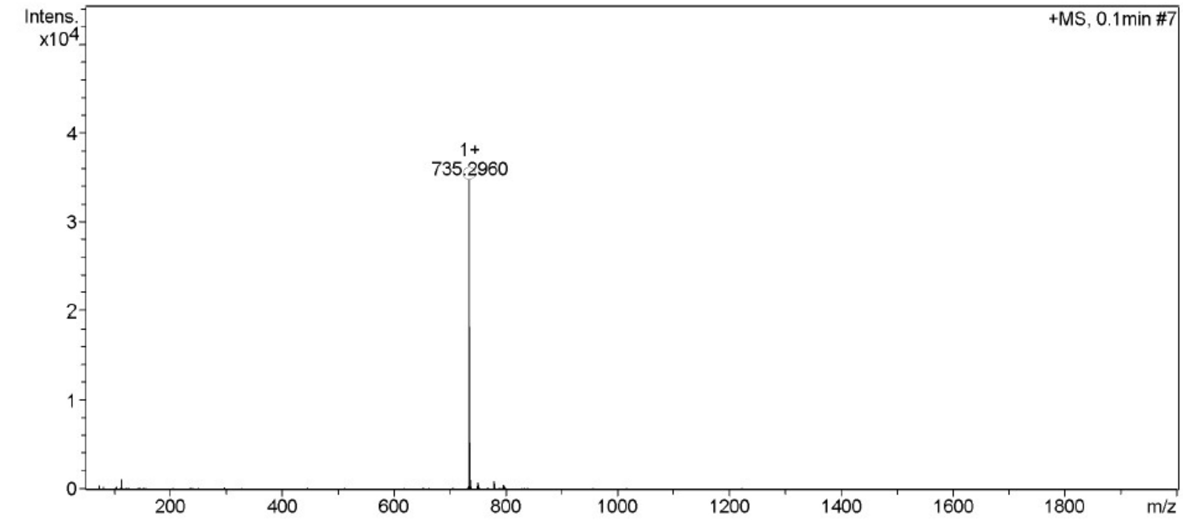
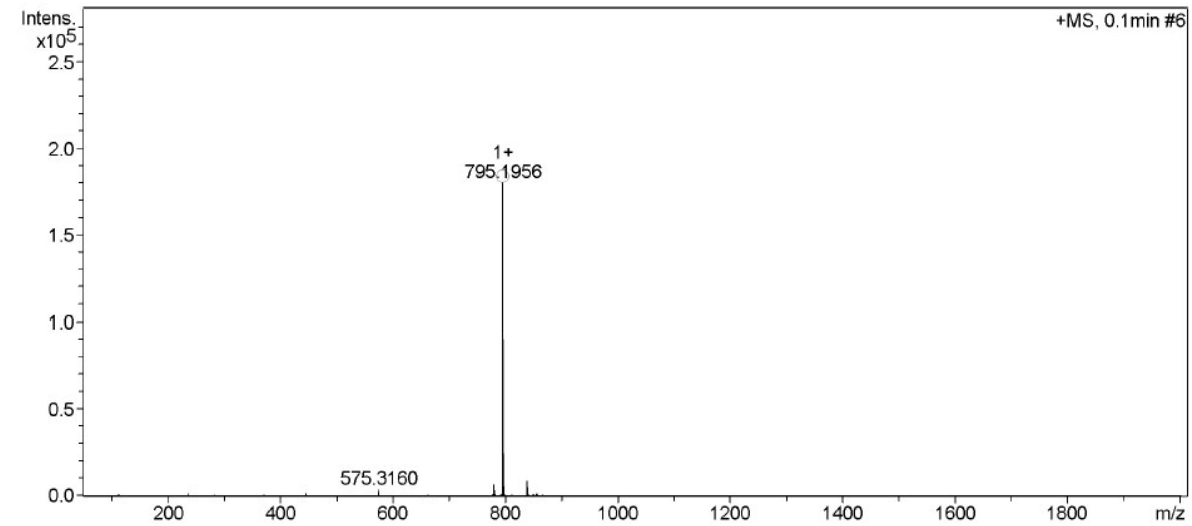


Figure S131: HRMS-APCI (m/z) spectrum of **4h**.



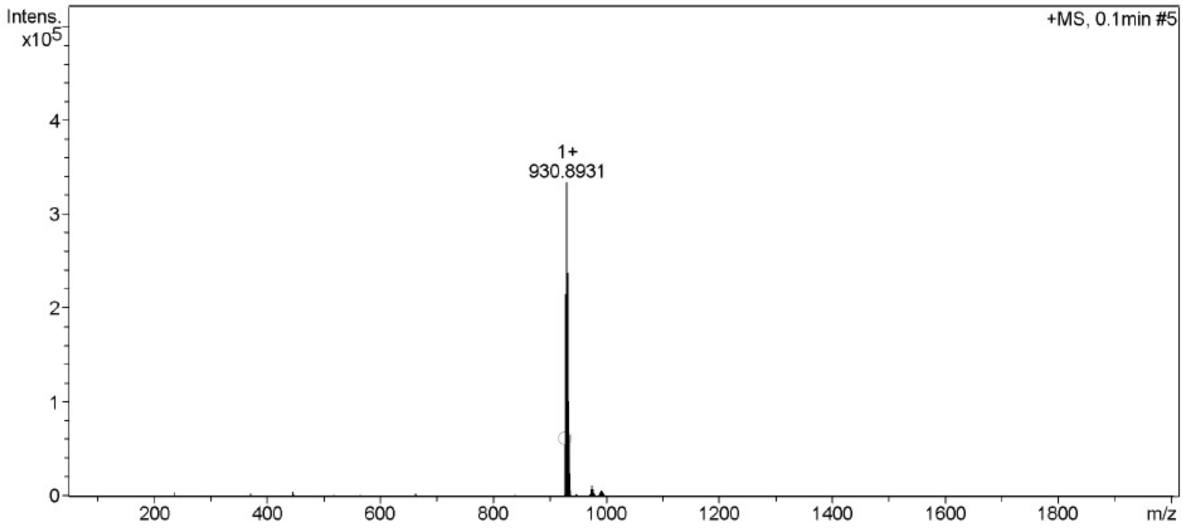
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
735.295967	1	C48H39N4O4	735.296582	0.6	0.8	31.5	ok	even	5.7

Figure S132: HRMS-APCI (m/z) spectrum of **4i**.



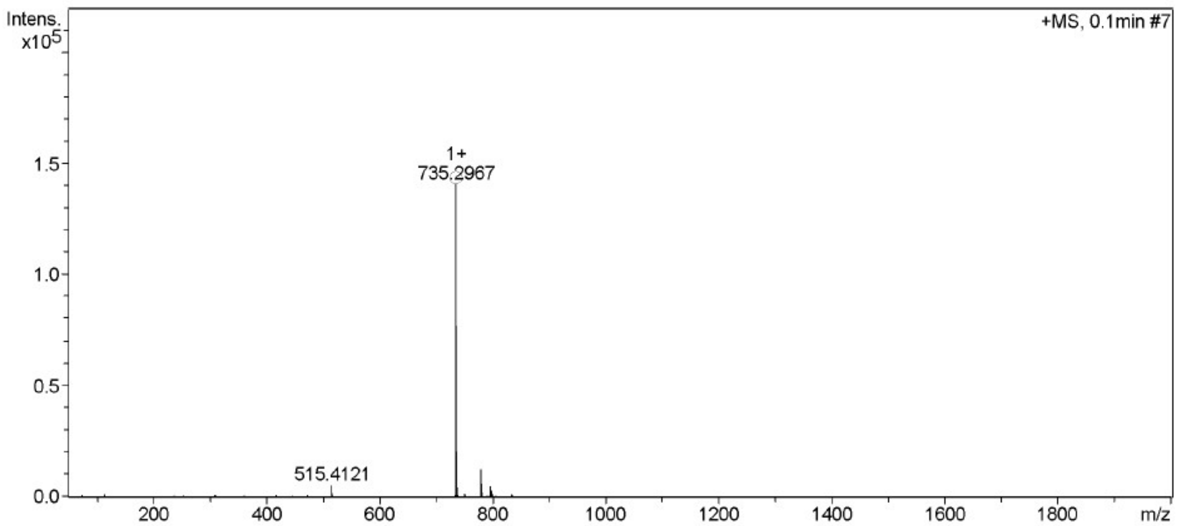
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
795.195578	1	C44H27N8O8	795.194636	0.9	1.2	35.5	ok	even	5.2

Figure S133: HRMS-APCI (m/z) spectrum of **4j**.



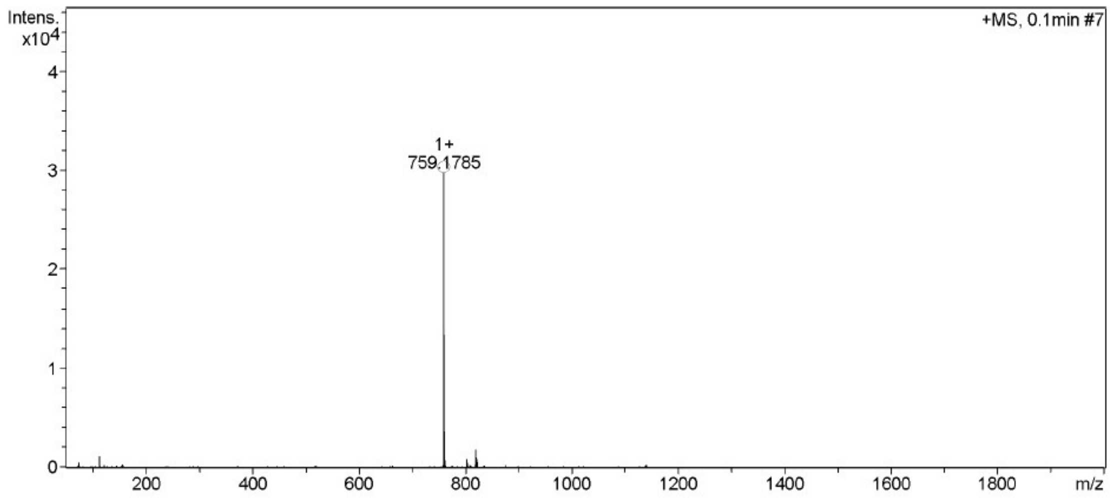
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
926.895590	1	C44H27Br4N4	926.896372	-0.8	-0.8	31.5	ok	even	8.8

Figure S134: HRMS-APCI (m/z) spectrum of **4k**.



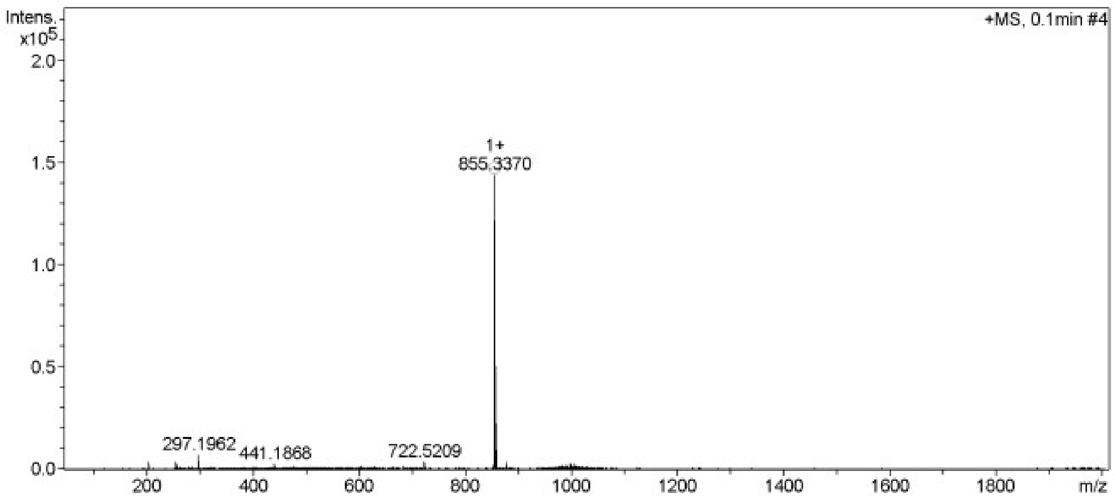
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
735.296672	1	C48H39N4O4	735.296582	-0.1	-0.1	31.5	ok	even	5.4

Figure S135: HRMS-APCI (m/z) spectrum of **4l**.



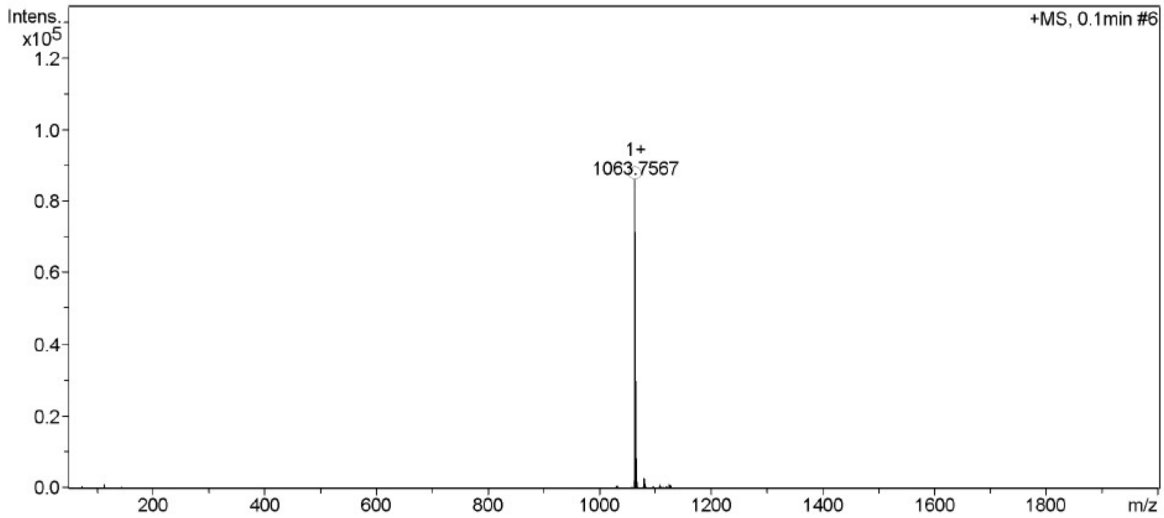
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
759.178531	1	C44H23F8N4	759.178949	0.4	0.6	31.5	ok	even	19.7

Figure S136: HRMS-APCI (m/z) spectrum of **4m**.



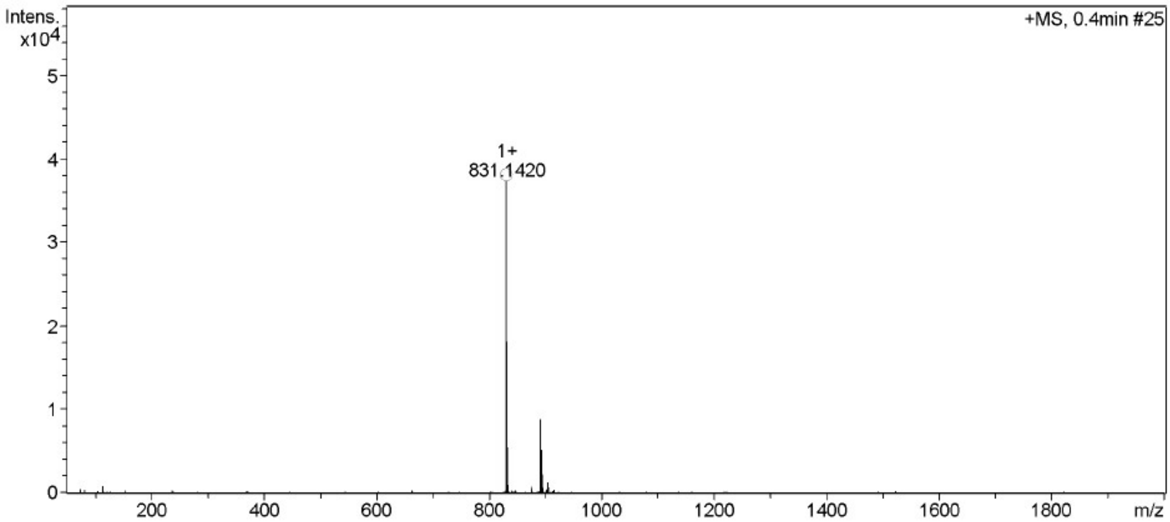
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
855.336952	1	C52H47N4O8	855.338841	-1.9	-2.2	31.5	ok	even	1.8

Figure S137: HRMS-APCI (m/z) spectrum of **4n**.



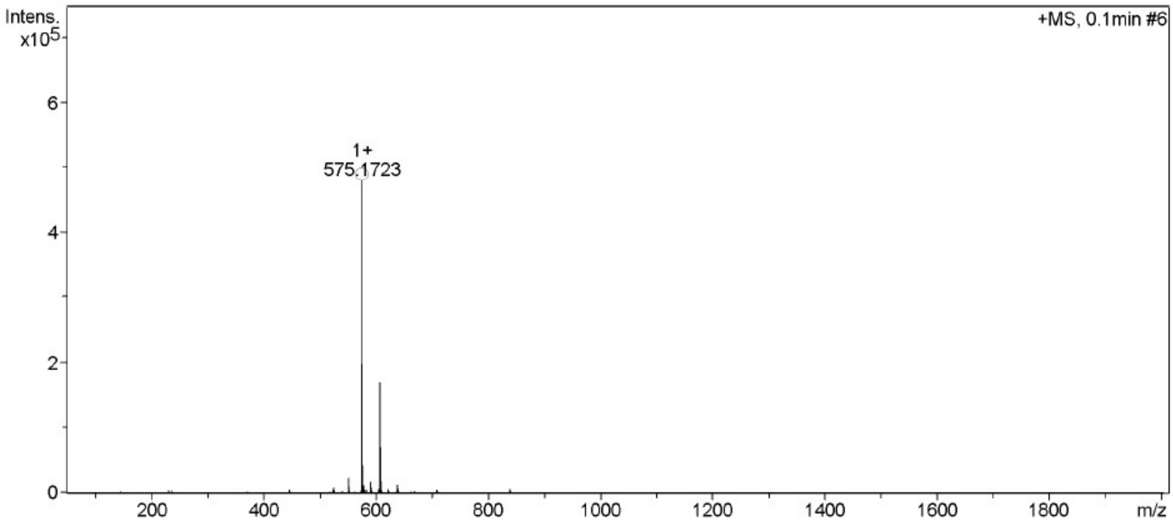
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
1063.756699	1	C76H95N4	1063.755125	1.6	1.5	31.5	ok	even	8.9

Figure S138: HRMS-APCI (m/z) spectrum of **4q**.



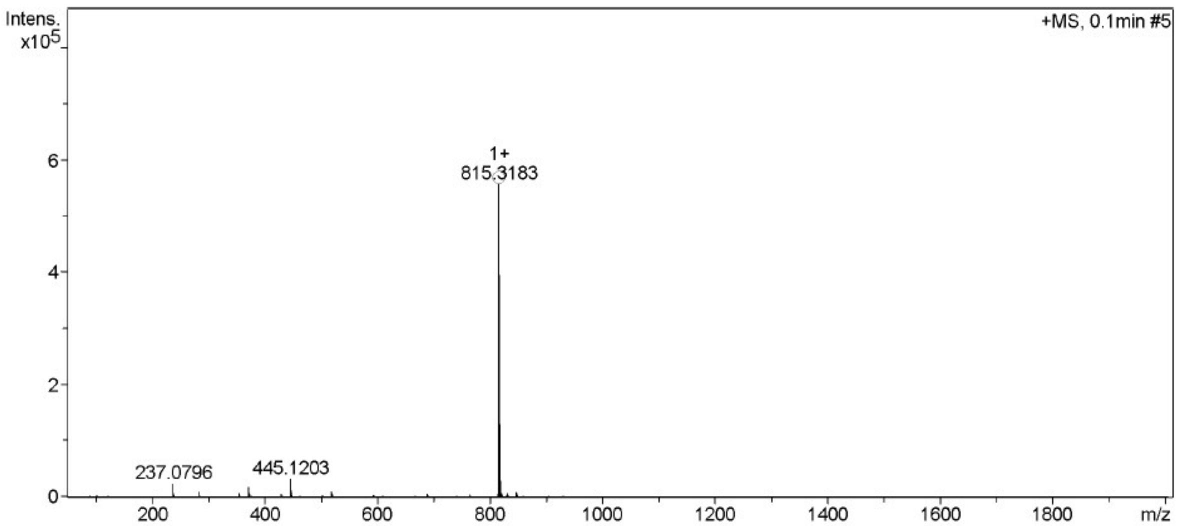
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
831.142045	1	C44H19F12N4	831.141262	-0.8	-0.9	31.5	ok	even	14.3

Figure S139: HRMS-APCI (m/z) spectrum of **4t**.



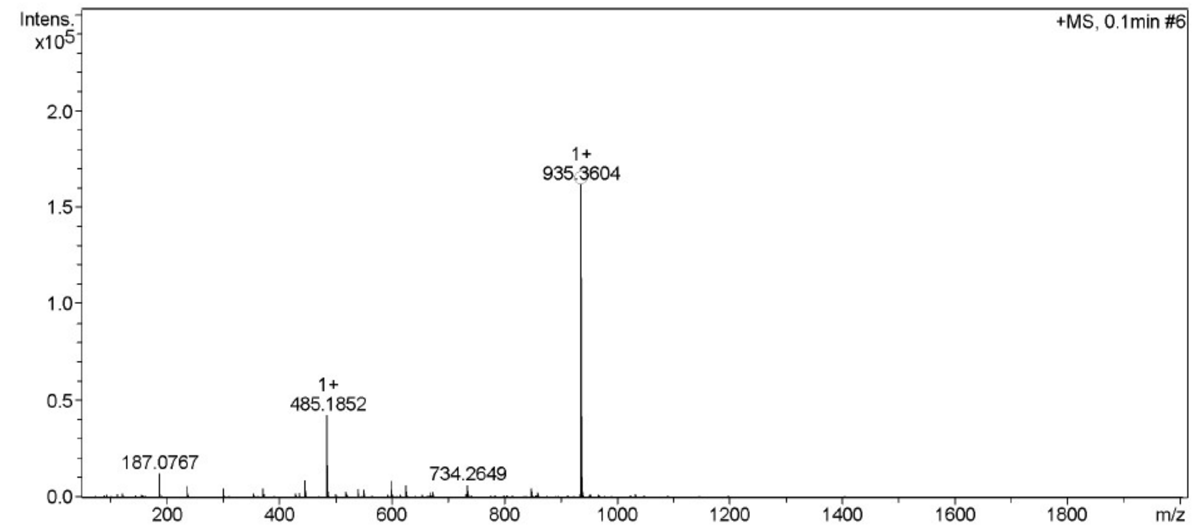
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
575.172310	1	C36H23N4O4	575.171382	-0.9	-1.6	27.5	ok	even	3.6

Figure S140: HRMS-APCI (m/z) spectrum of **4w**.



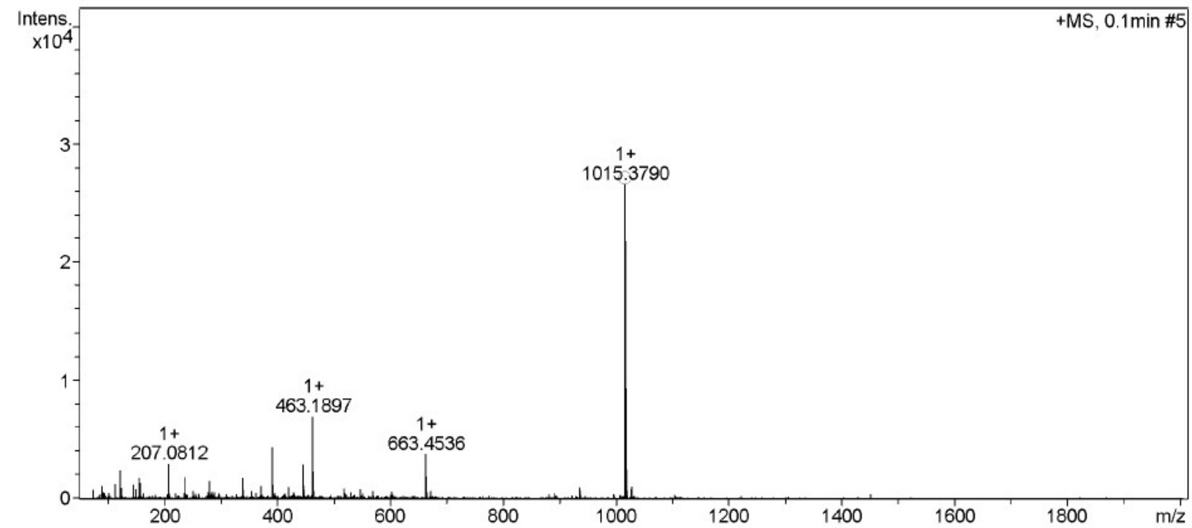
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
815.318349	1	C60H39N4	815.316924	1.4	1.7	43.5	ok	even	19.7

Figure S141: HRMS-APCI (m/z) spectrum of **4y**.



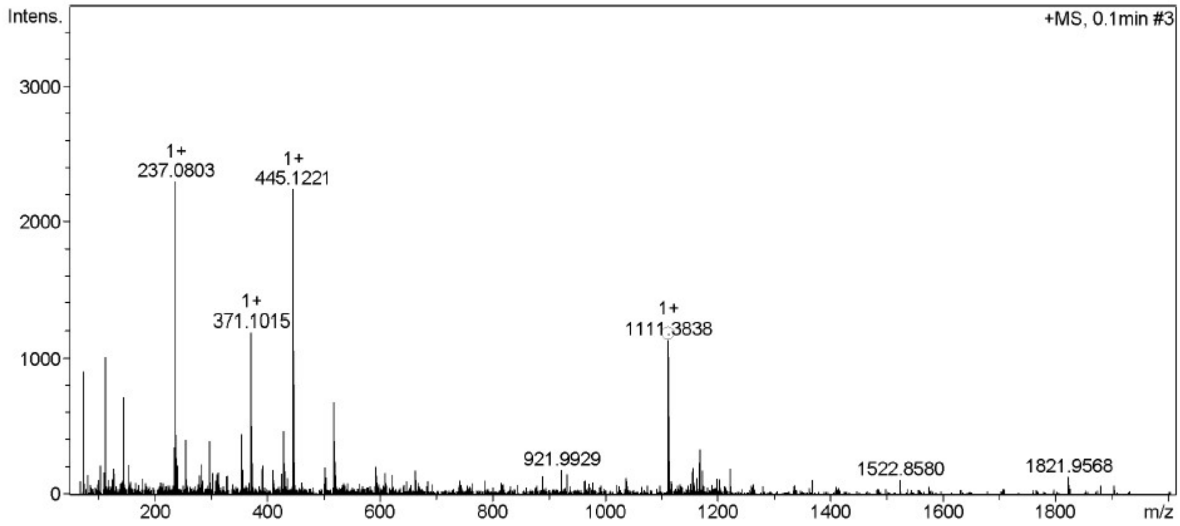
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
935.360371	1	C64H47N4O4	935.359182	-1.2	-1.3	43.5	ok	even	6.4

Figure S142: HRMS-APCI (m/z) spectrum of **4z**.



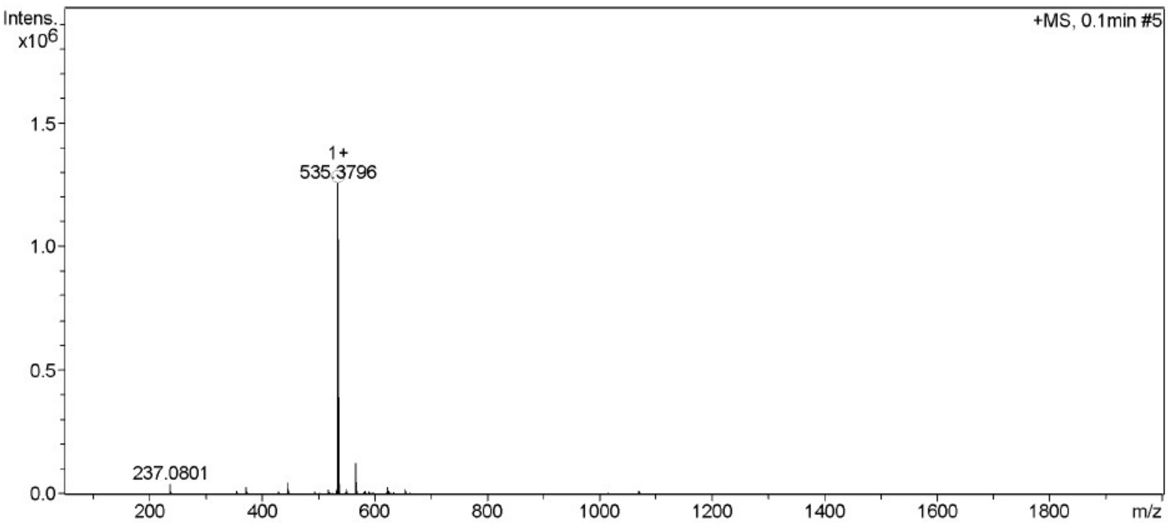
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
1015.378967	1	C76H47N4	1015.379524	0.6	0.5	55.5	ok	even	10.7

Figure S143: HRMS-APCI (m/z) spectrum of **4ab**.



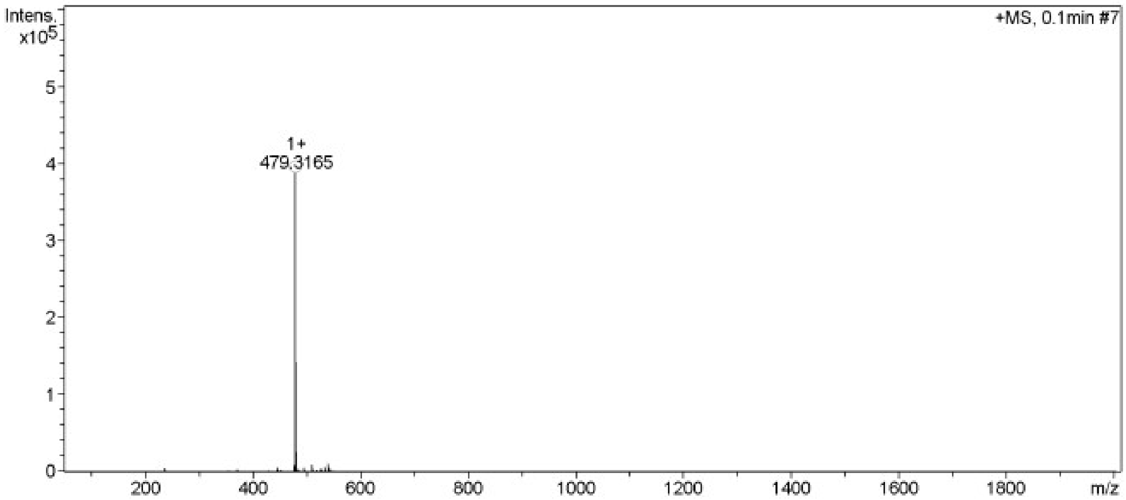
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
1111.383807	1	C84H47N4	1111.379524	4.3	3.9	63.5	ok	even	49.7

Figure S144: HRMS-APCI (m/z) spectrum of **4ac**.



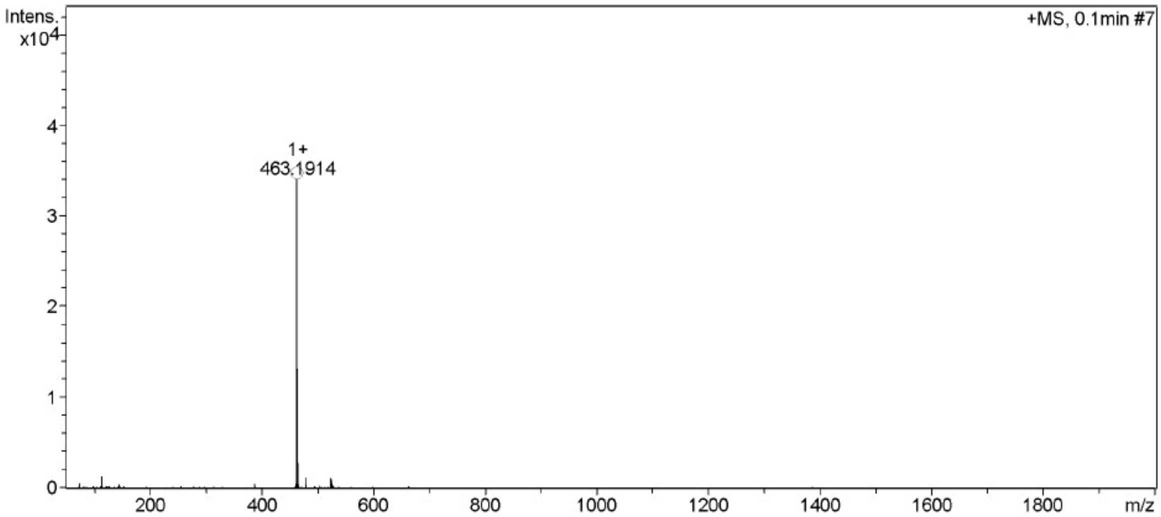
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
535.379565	1	C36H47N4	535.379524	0.0	0.1	15.5	ok	even	235.7

Figure S145: HRMS-APCI (m/z) spectrum of **4ad**.



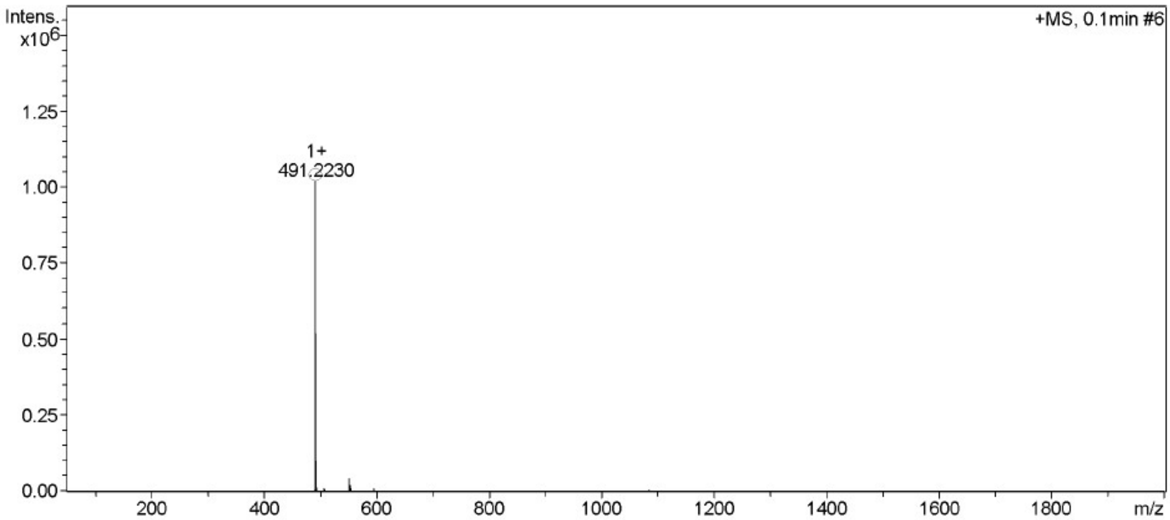
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
479.316534	1	C32H39N4	479.316924	-0.4	-0.8	15.5	ok	even	1.5

Figure S146: HRMS-APCI (m/z) spectrum of **4ae**.



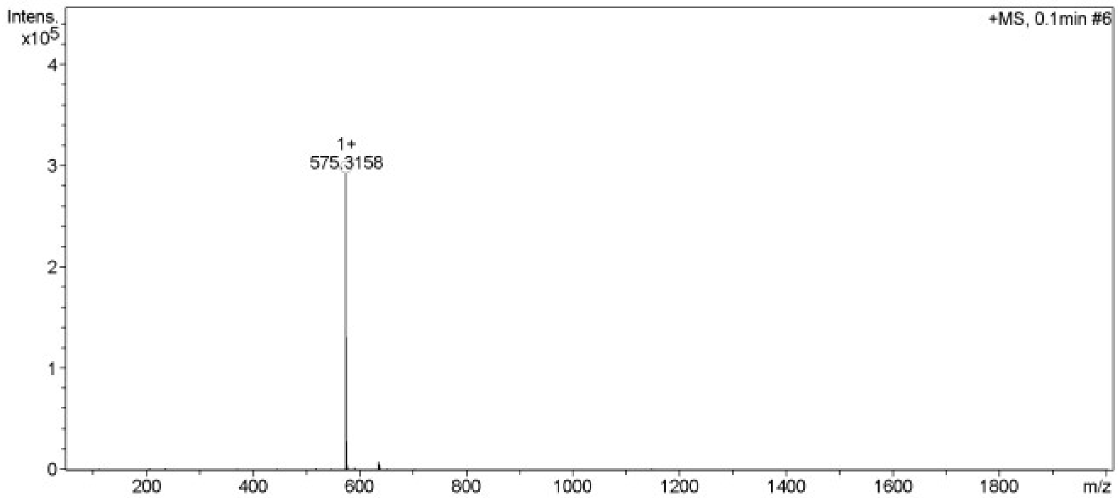
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
463.191443	1	C32H23N4	463.191723	-0.3	-0.6	23.5	ok	even	15.4

Figure S147: HRMS-APCI (m/z) spectrum of **7a**.



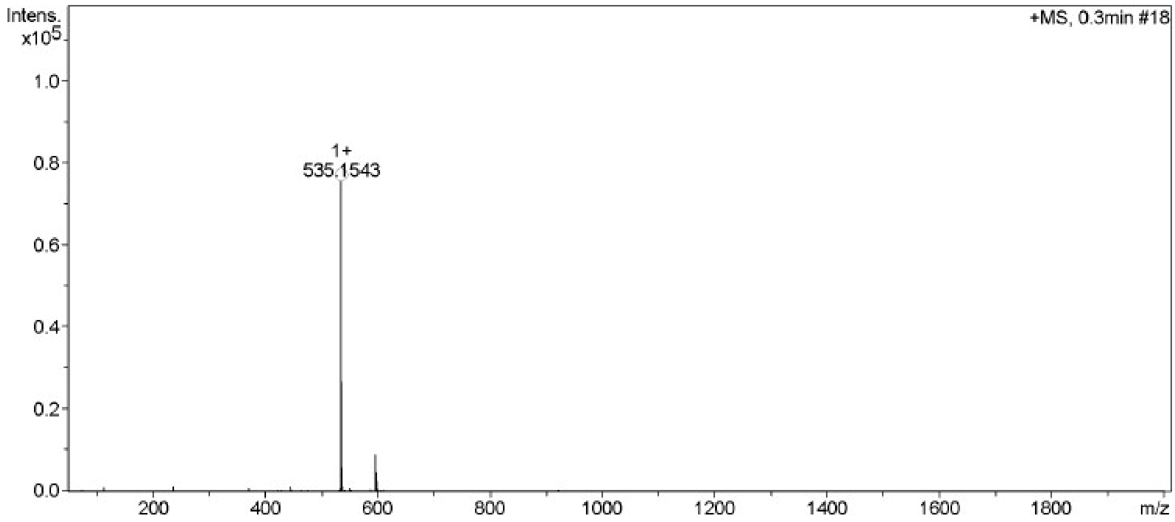
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
491.222992	1	C34H27N4	491.223023	-0.0	-0.1	23.5	ok	even	64.3

Figure S148: HRMS-APCI (m/z) spectrum of **7b**.



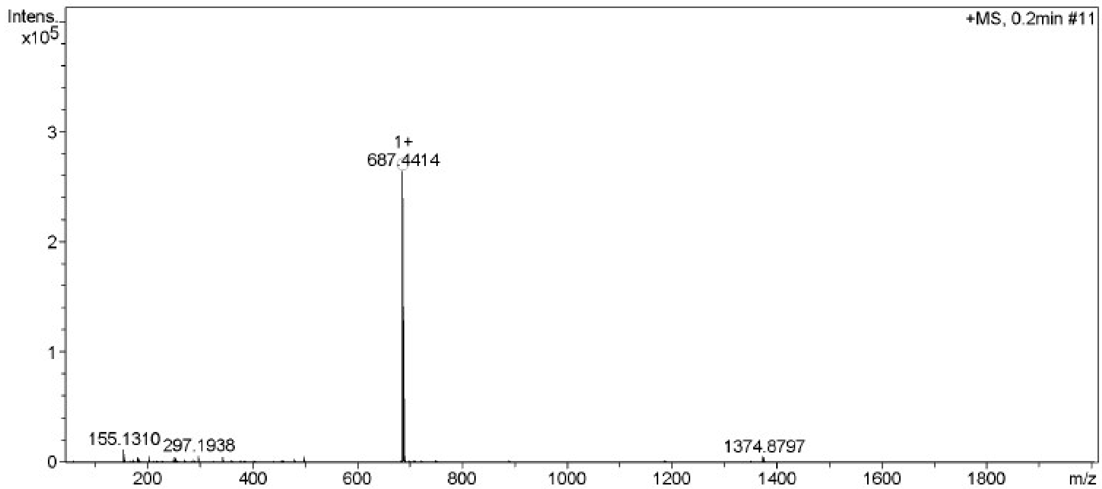
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
575.315764	1	C40H39N4	575.316924	-1.2	-2.0	23.5	ok	even	3.2

Figure S149: HRMS-APCI (m/z) spectrum of **7d**.



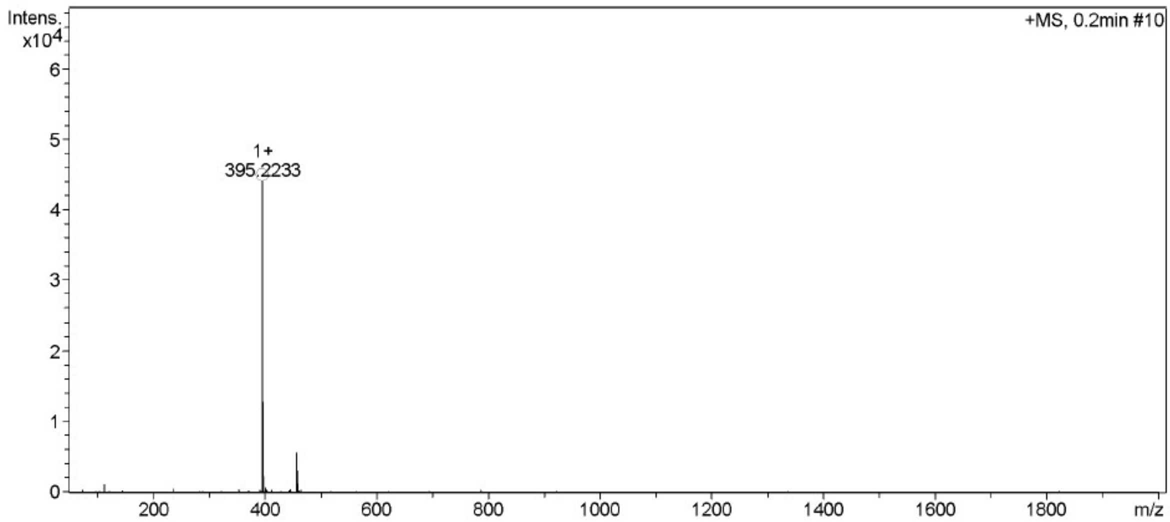
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
535.154339	1	C32H19F4N4	535.154036	0.3	0.6	23.5	ok	even	7.6

Figure S150: HRMS-APCI (m/z) spectrum of **7m**.



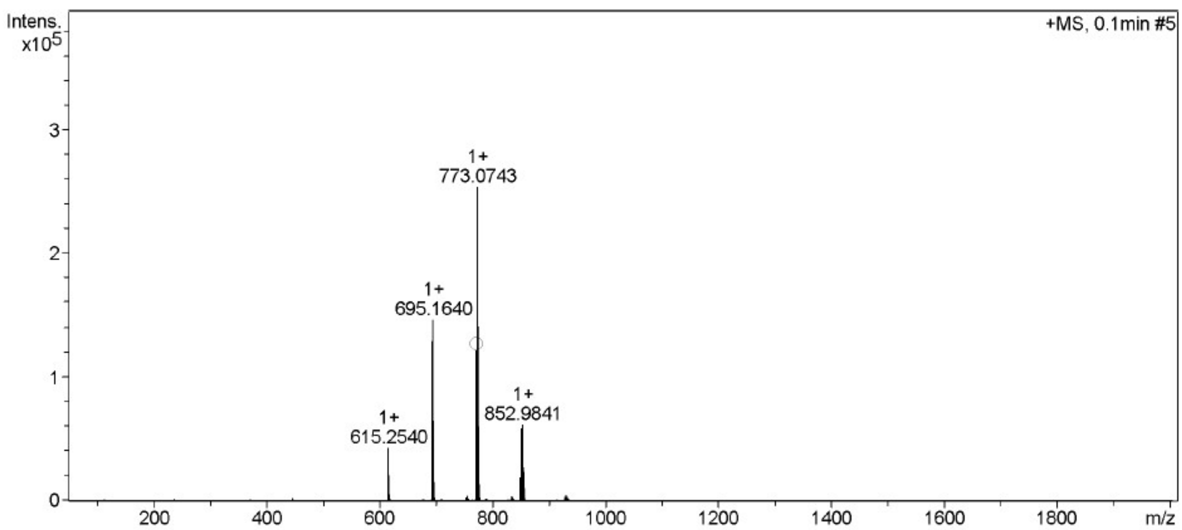
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
687.441365	1	C48H55N4	687.442124	0.8	1.1	23.5	ok	even	3.2

Figure S151: HRMS-APCI (m/z) spectrum of **7q**.



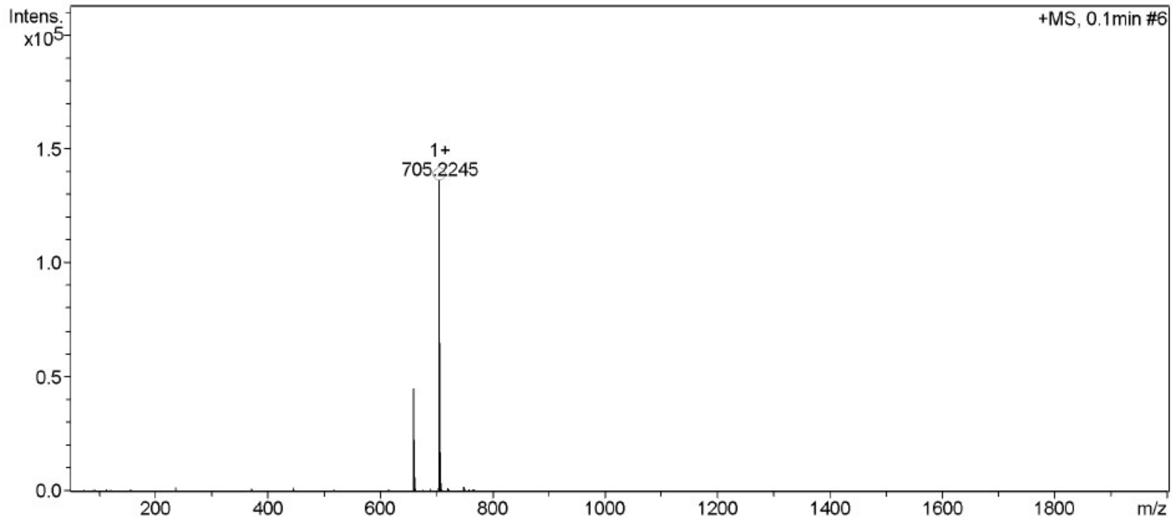
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
395.223305	1	C26H27N4	395.223023	-0.3	-0.7	15.5	ok	even	4.7

Figure S152: HRMS-APCI (m/z) spectrum of **7ae**.



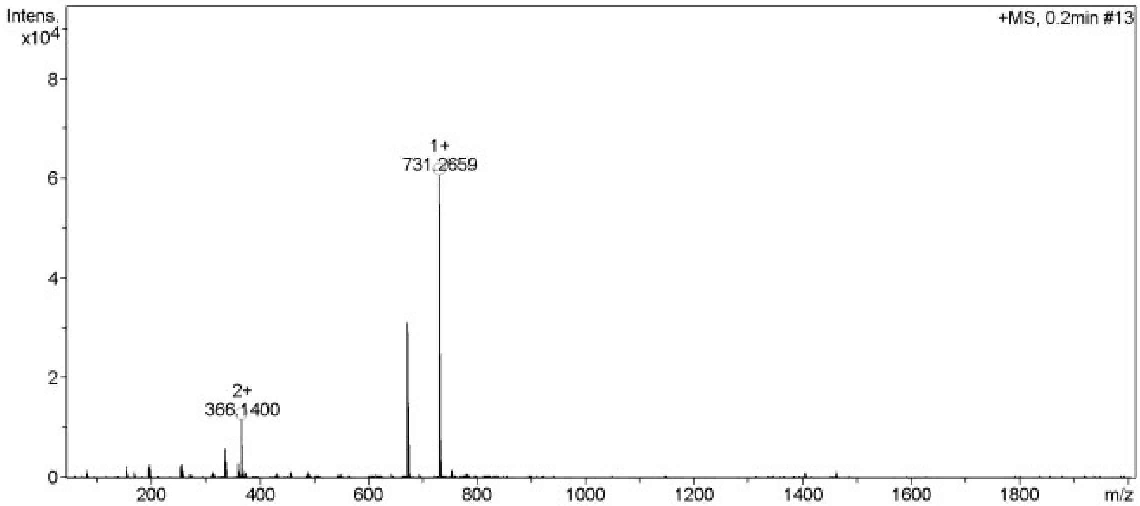
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
771.074771	1	C44H29Br2N4	771.075348	-0.6	-0.7	31.5	ok	even	6.2

Figure S153: HRMS-APCI (m/z) spectrum of **8c**.



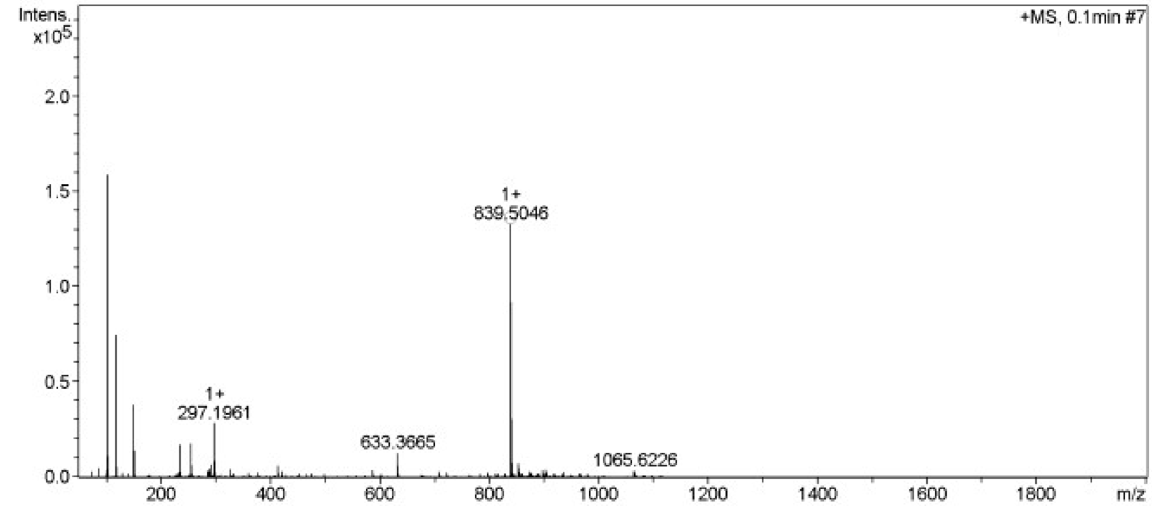
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
705.224470	1	C44H29N6O4	705.224480	-0.0	-0.0	33.5	ok	even	11.8

Figure S154: HRMS-APCI (m/z) spectrum of **8f**.



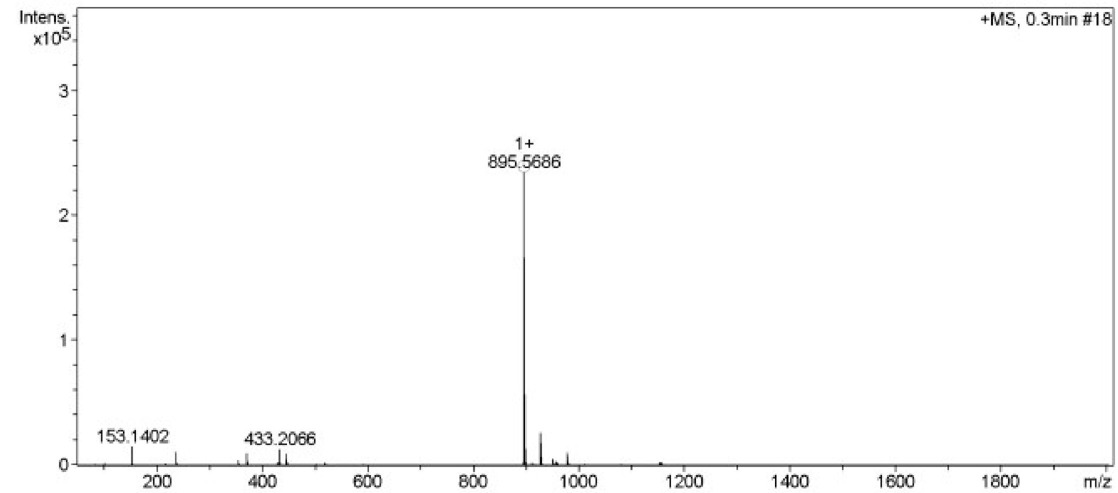
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
366.140040	1	C48H36N4O4	366.136279	-3.8	-10.3	33.0	ok	even	26.3
731.265904	1	C48H35N4O4	731.265282	-0.6	-0.9	33.5	ok	even	21.8

Figure S155: HRMS-ESI (m/z) spectrum of **8g**.



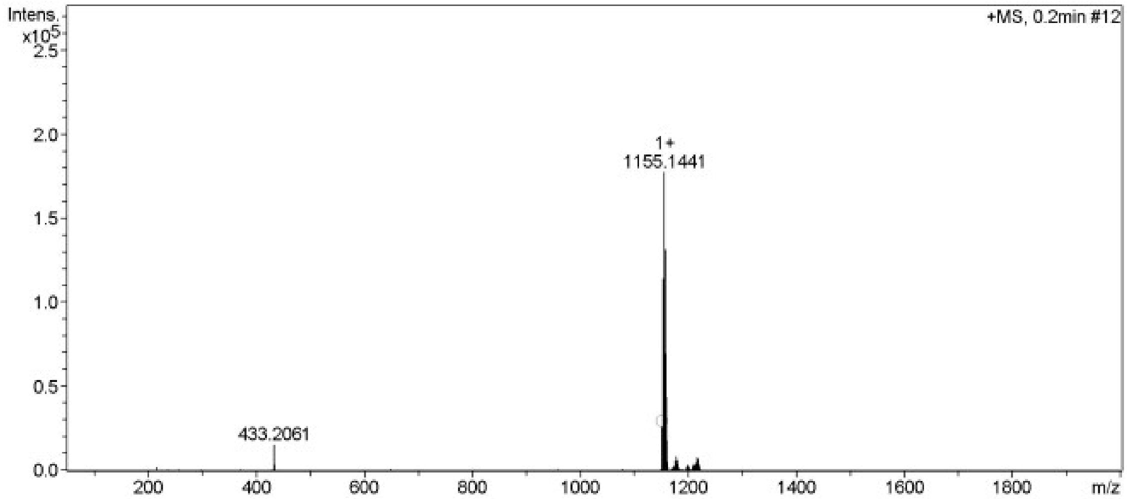
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
839.504608	1	C60H63N4	839.504724	0.1	0.1	31.5	ok	even	11.2

Figure S156: HRMS-APCI (m/z) spectrum of **11a**.



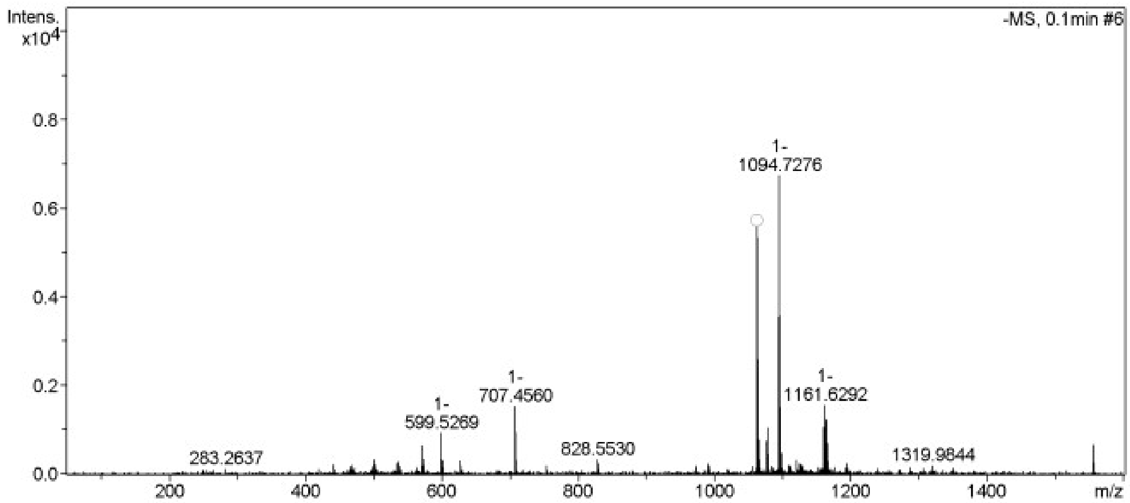
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
895.568635	1	C64H71N4	895.567325	-1.3	-1.5	31.5	ok	even	4.8

Figure S157: HRMS-APCI (m/z) spectrum of **11b**.



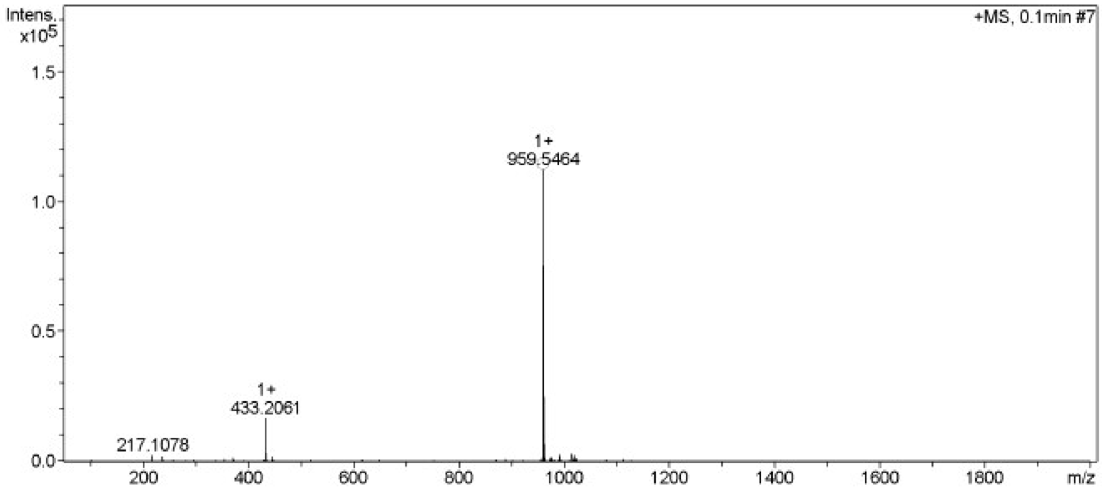
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
1151.143519	1	C60H59Br4N4	1151.146773	3.3	2.8	31.5	ok	even	13.5

Figure S158: HRMS-APCI (m/z) spectrum of **11c**.



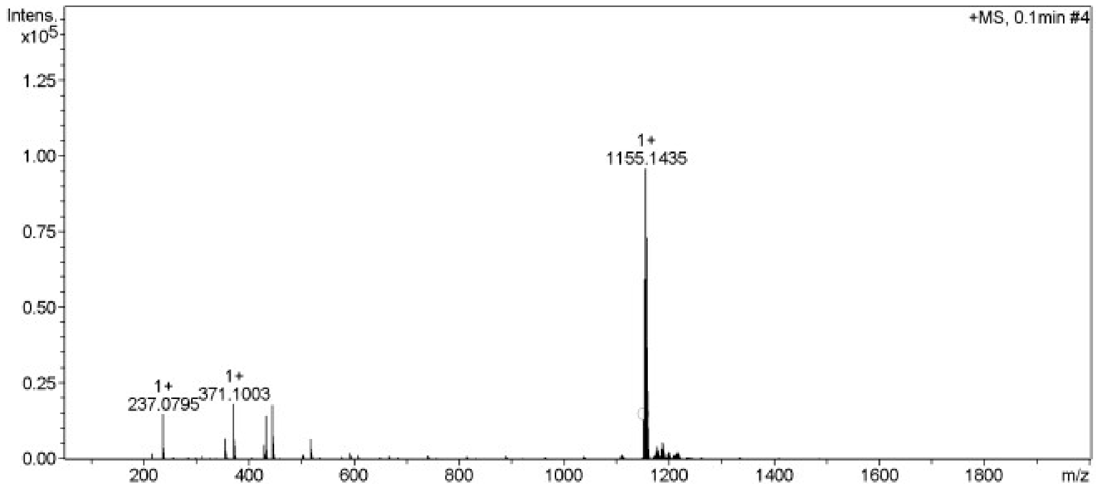
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
1061.739332	1	C76H93N4	1061.740573	1.2	1.2	32.5	ok	even	74.3

Figure S159: HRMS-APCI (m/z) spectrum of **11d**.



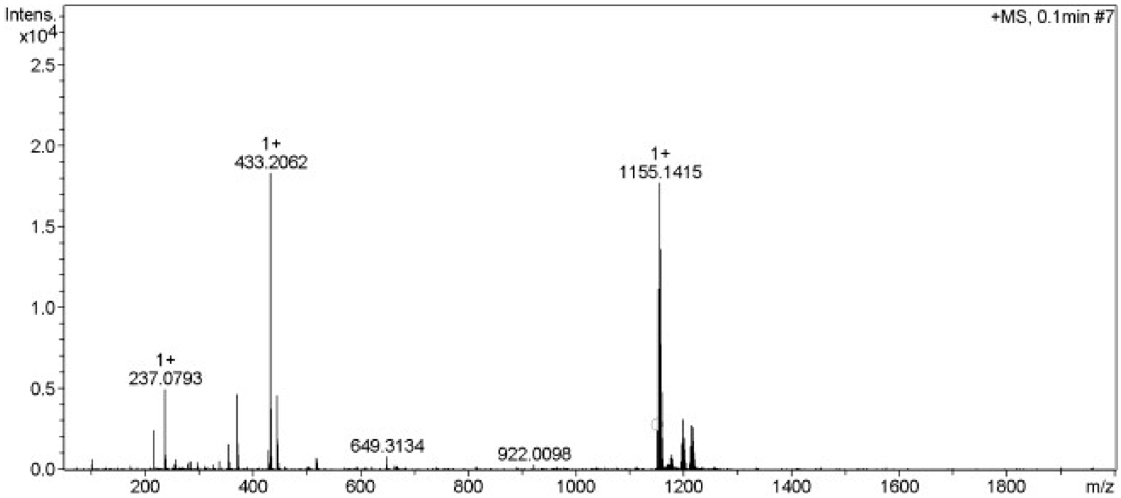
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
959.546365	1	C64H71N4O4	959.546983	0.6	0.6	31.5	ok	even	26.7

Figure S160: HRMS-APCI (m/z) spectrum of **11e**.



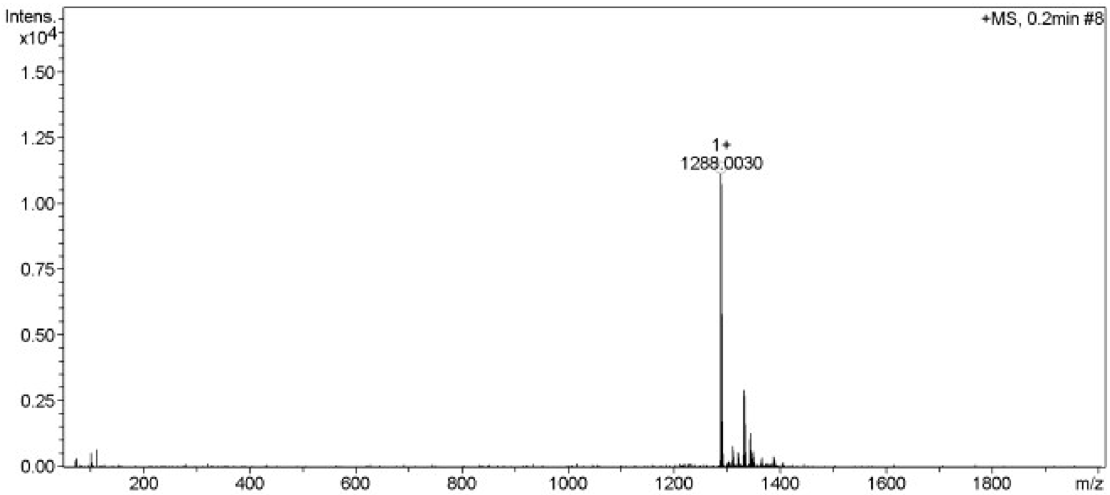
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
1151.145247	1	C60H59Br4N4	1151.146773	1.5	1.3	31.5	ok	even	15.8

Figure S161: HRMS-APCI (m/z) spectrum of **11h**.



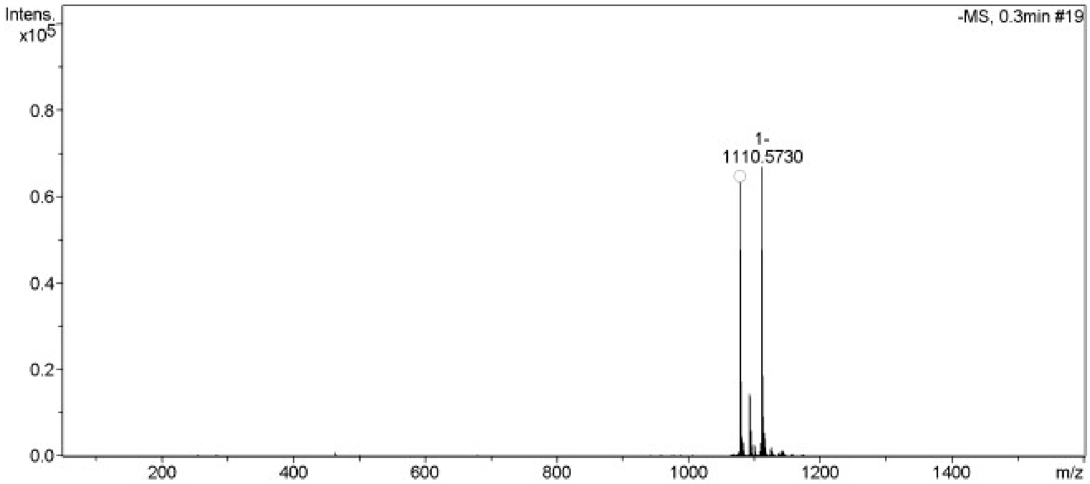
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
1151.146867	1	C60H59Br4N4	1151.146773	0.1	0.1	31.5	ok	even	11.7

Figure S162: HRMS-APCI (m/z) spectrum of **11k**.



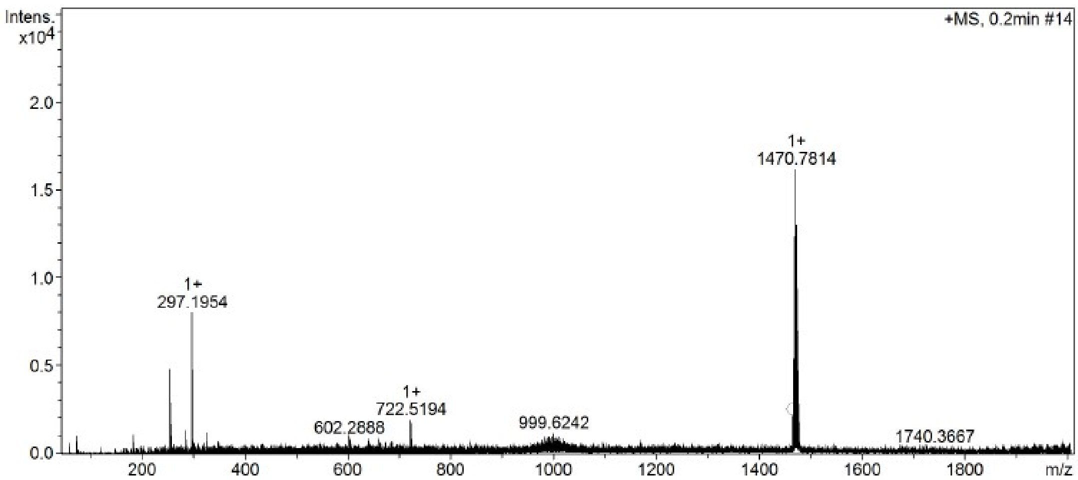
Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
1288.003040	1	C92H127N4	1288.005527	2.5	1.9	31.5	ok	even	19.2

Figure S163: HRMS-APCI (m/z) spectrum of **11q**.



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
1077.577252	1	C68H77N4O8	1077.574689	2.6	2.4	32.5	ok	even	25.4

Figure S164: HRMS-APCI (m/z) spectrum of **11r**.



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
1464.792877	1	C60H57Br8N4	1464.804471	11.6	7.9	30.5	ok	even	204.7

Figure S165: HRMS-APCI (m/z) spectrum of **11s**.

IR (ATR) spectra

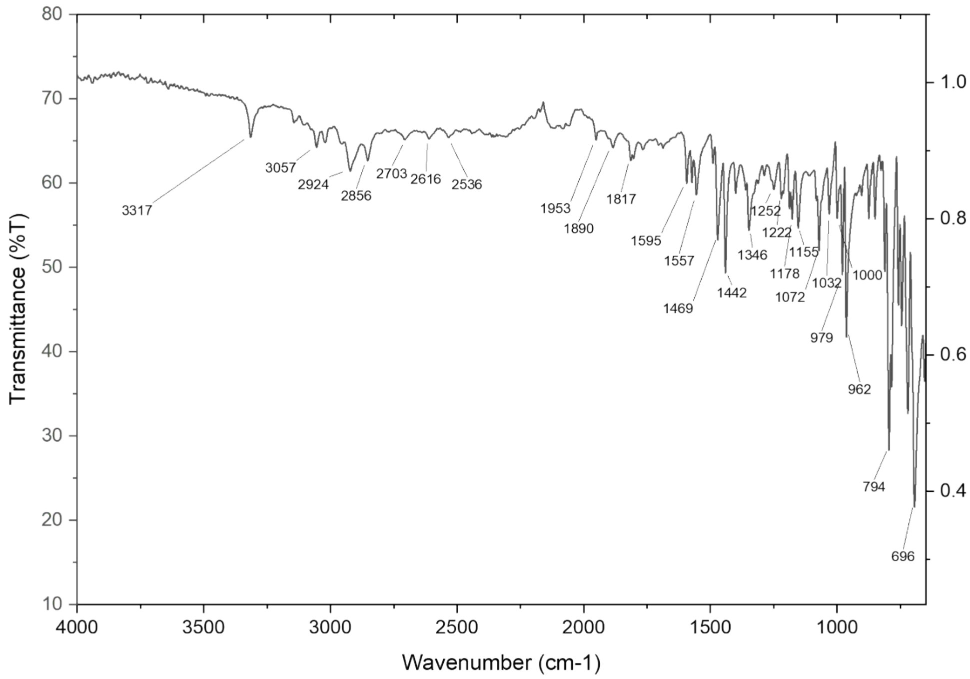


Figure S166: FTIR (ATR) spectrum of **4a**.

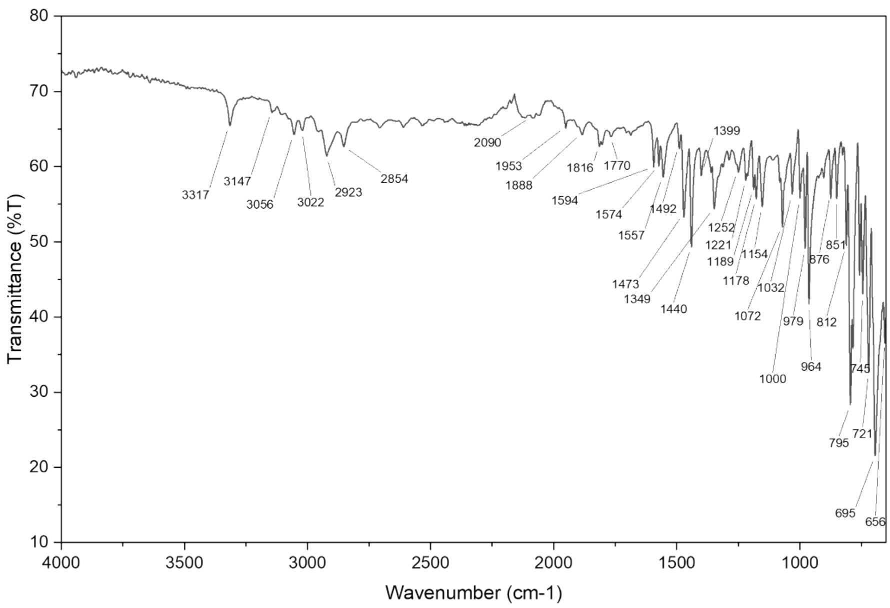


Figure S167: FTIR (ATR) spectrum of **4b**.

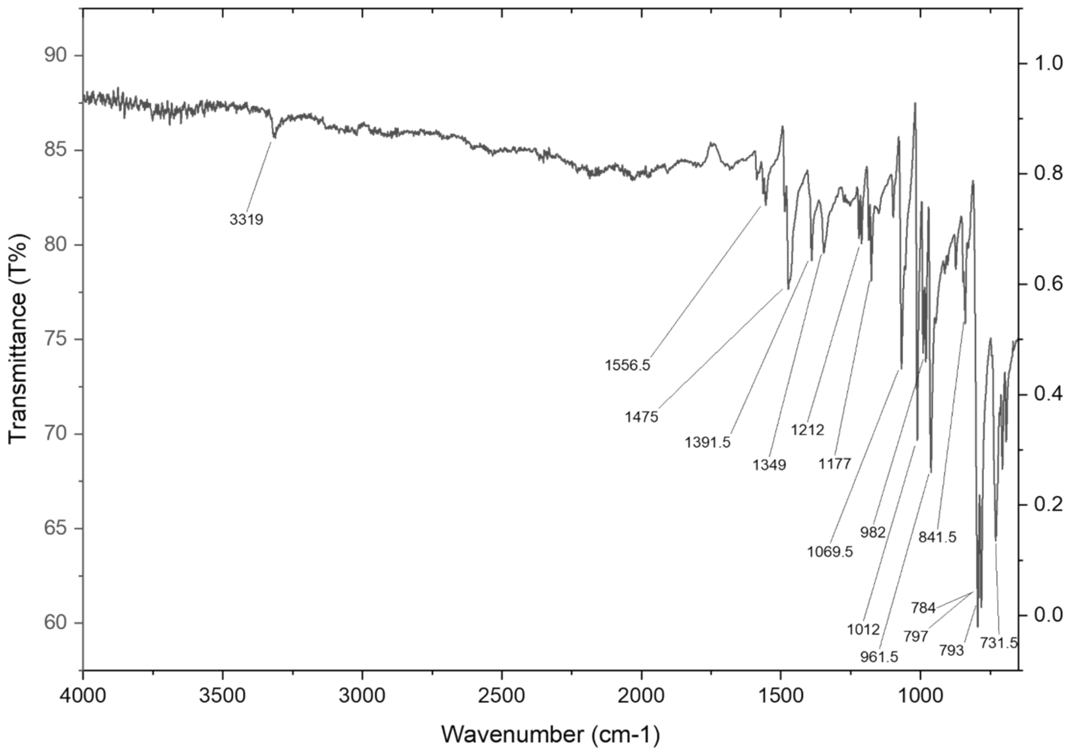


Figure S168: FTIR (ATR) spectrum of **4c**.

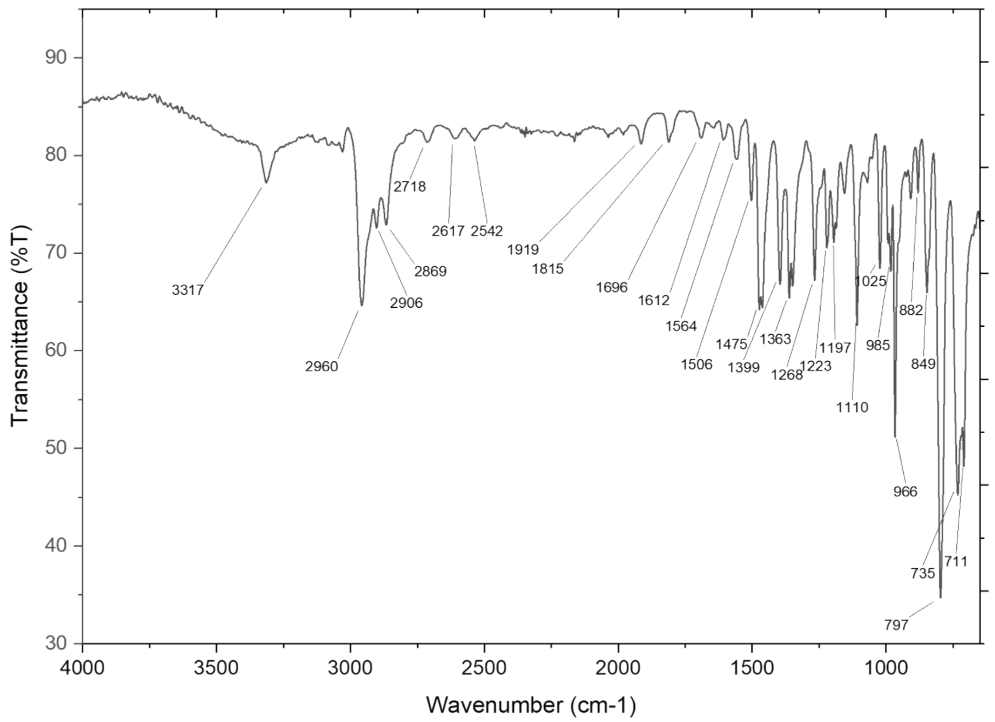


Figure S169: FTIR (ATR) spectrum of **4d**.

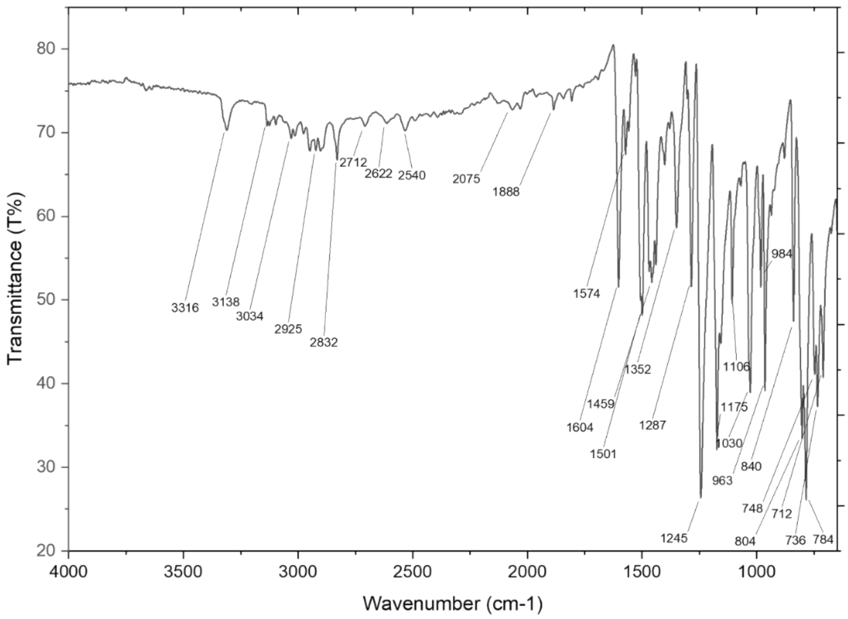


Figure S170: FTIR (ATR) spectrum of **4e**.

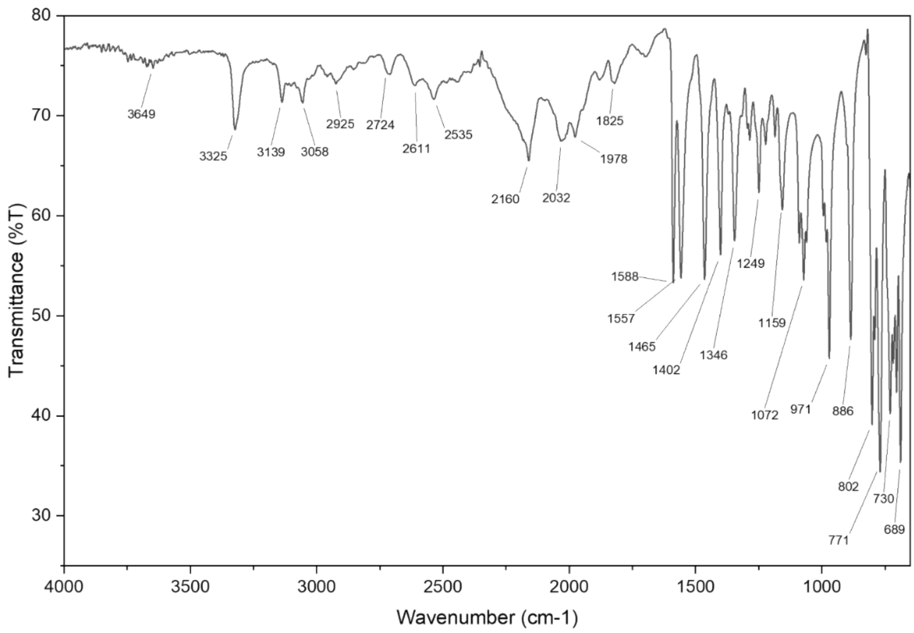


Figure S171: FTIR (ATR) spectrum of **4h**.

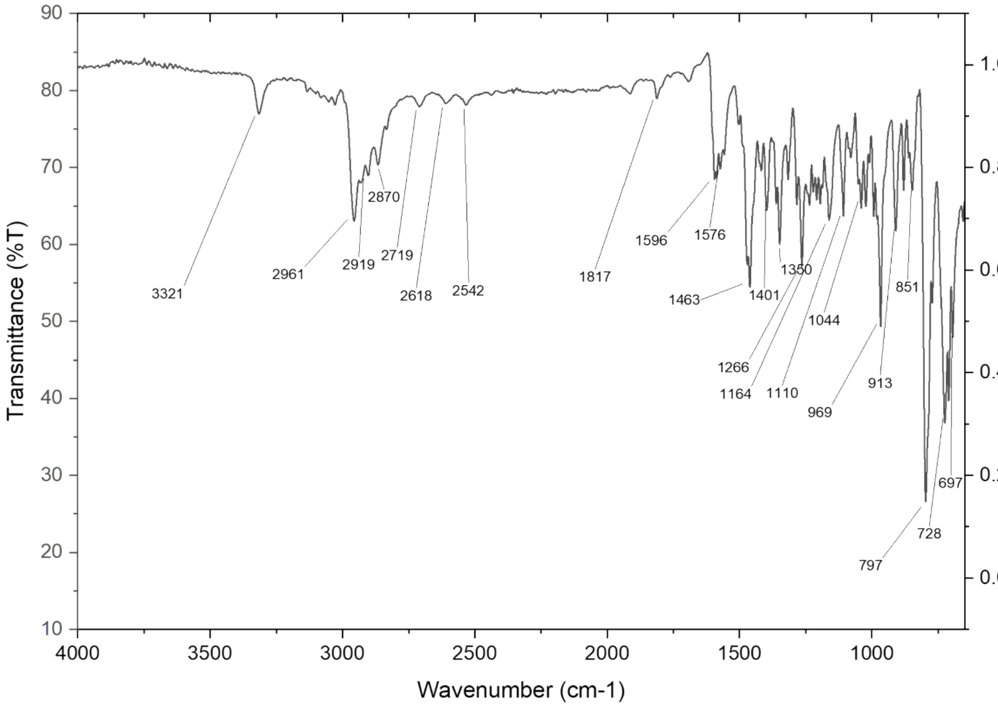


Figure S172: FTIR (ATR) spectrum of **4i.**

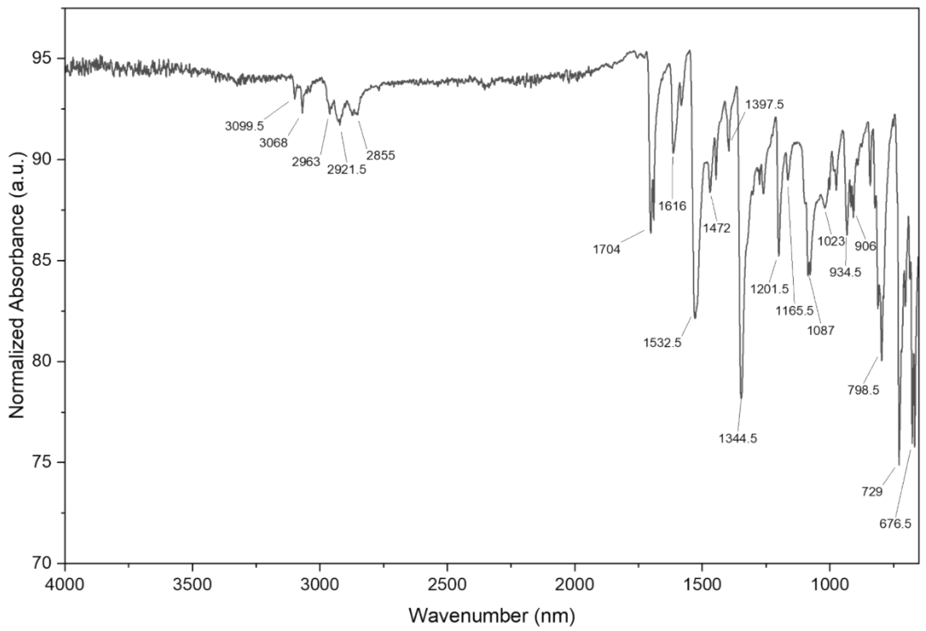


Figure S173: FTIR (ATR) spectrum of **4j**.

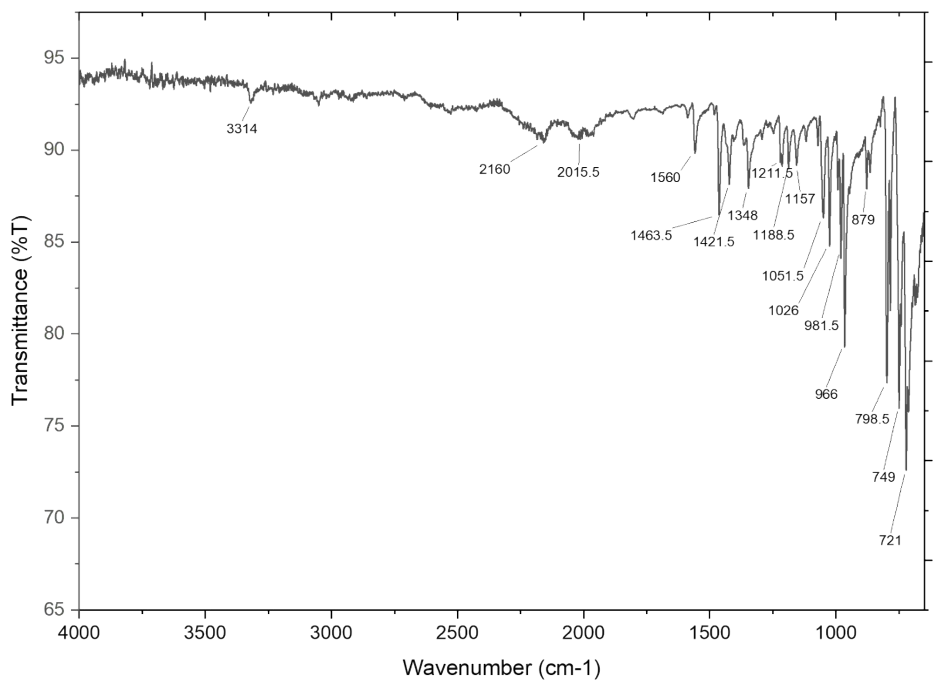


Figure S174: FTIR (ATR) spectrum of **4k**.

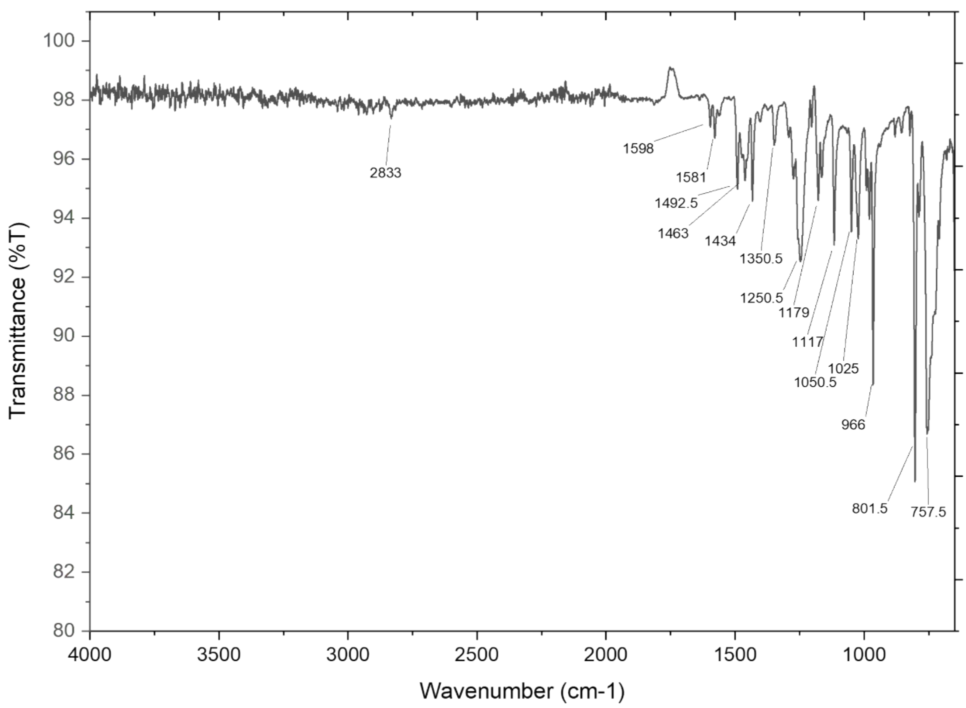


Figure S175: FTIR (ATR) spectrum of **4l**.

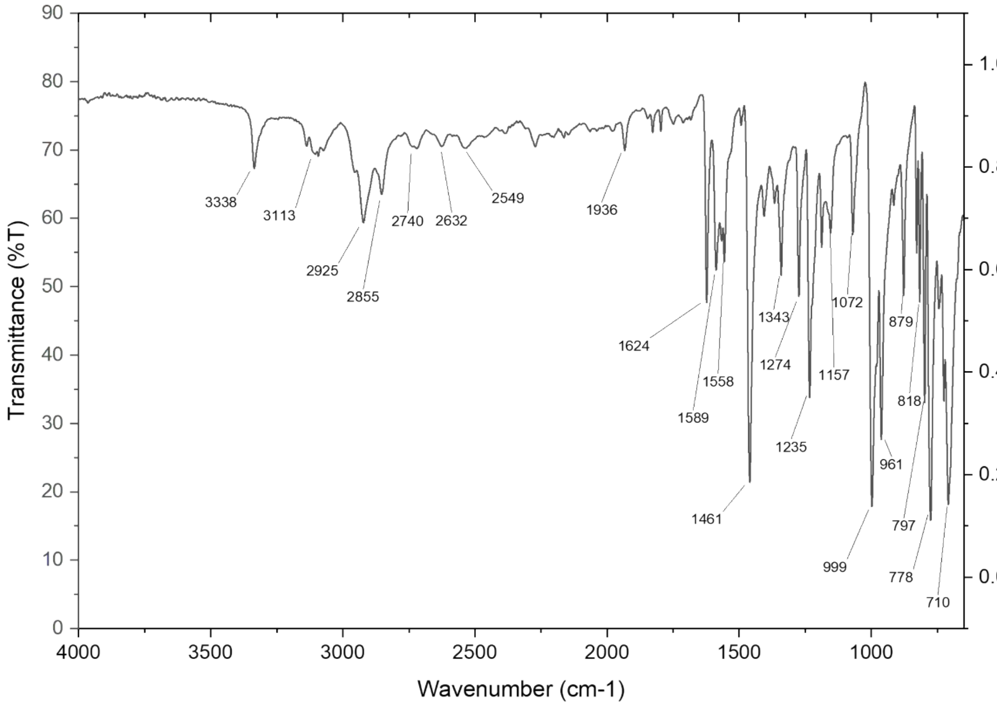


Figure S176: FTIR (ATR) spectrum of **4m**.

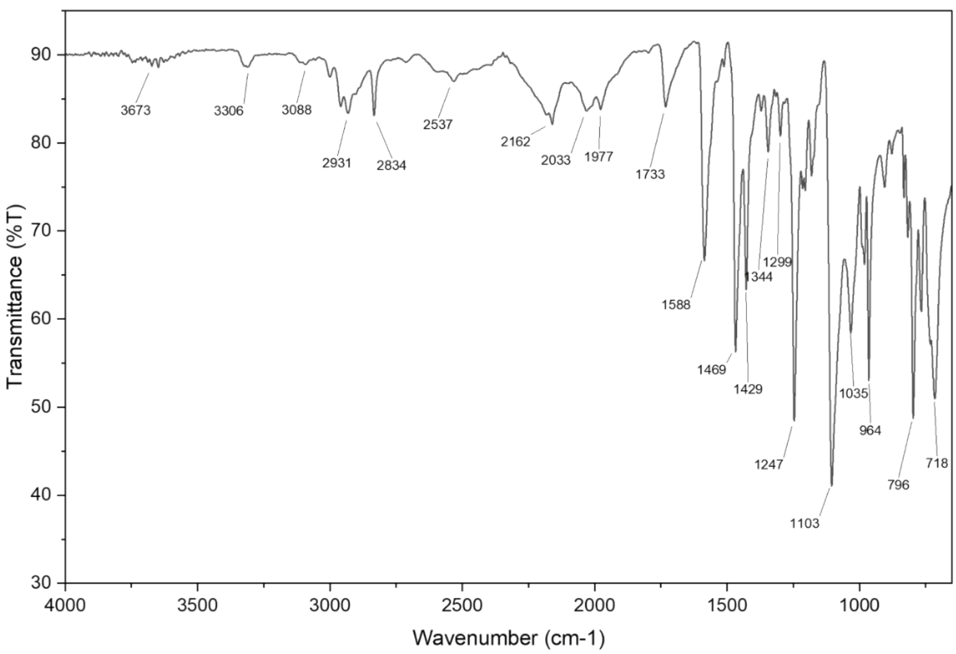


Figure S177: FTIR (ATR) spectrum of **4n**.

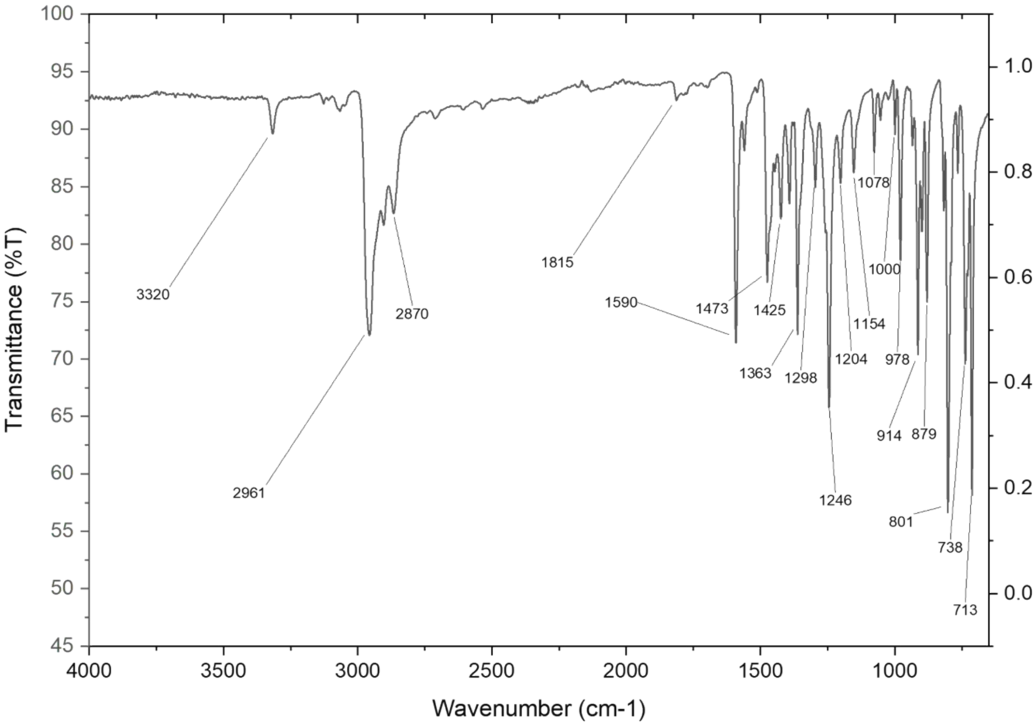


Figure S178: FTIR (ATR) spectrum of **4q**.

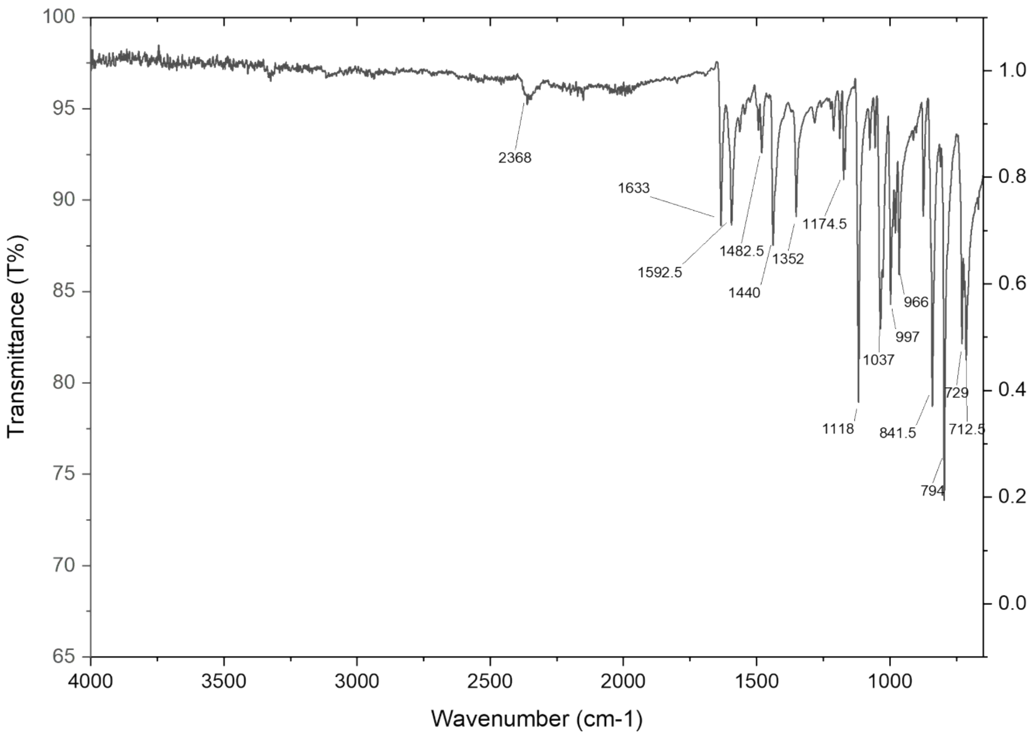


Figure S179: FTIR (ATR) spectrum of **4t**.

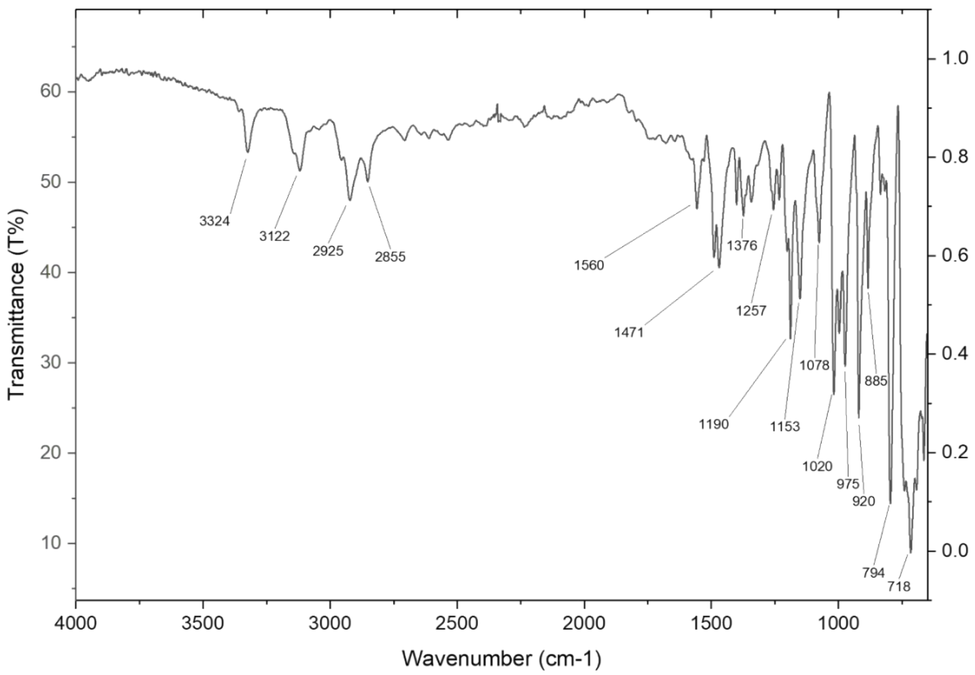


Figure S180: FTIR (ATR) spectrum of **4w**.

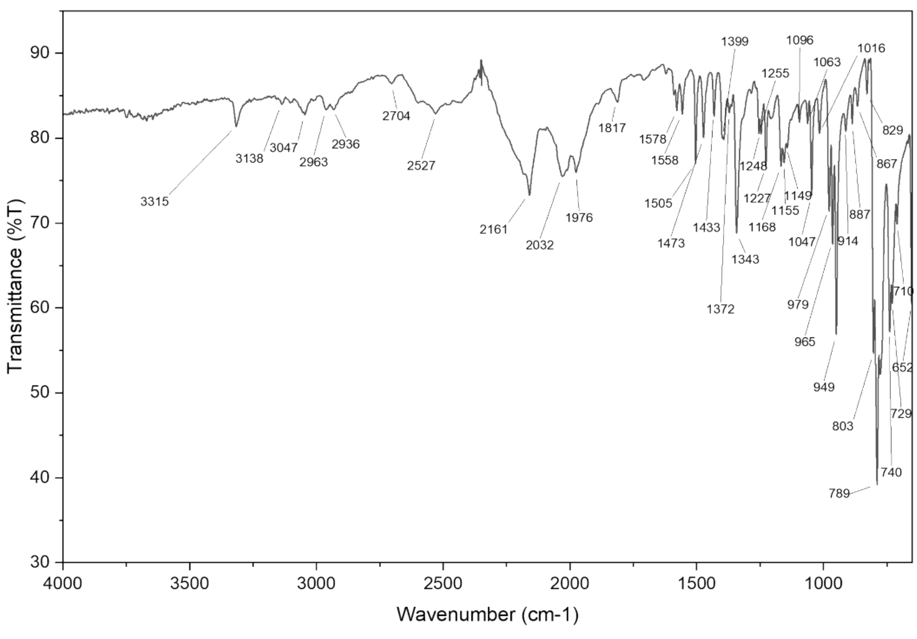


Figure S181: FTIR (ATR) spectrum of **4y**.

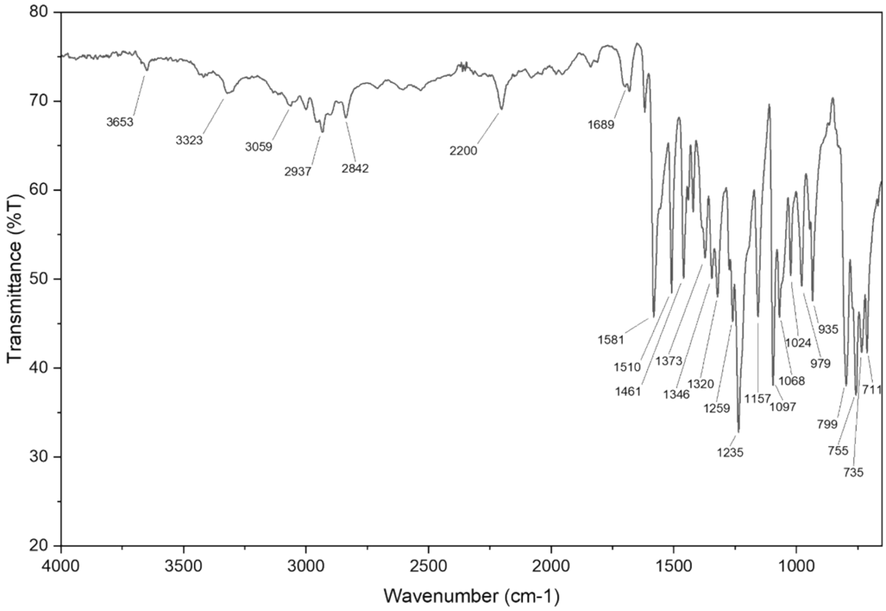


Figure S182: FTIR (ATR) spectrum of **4z**.

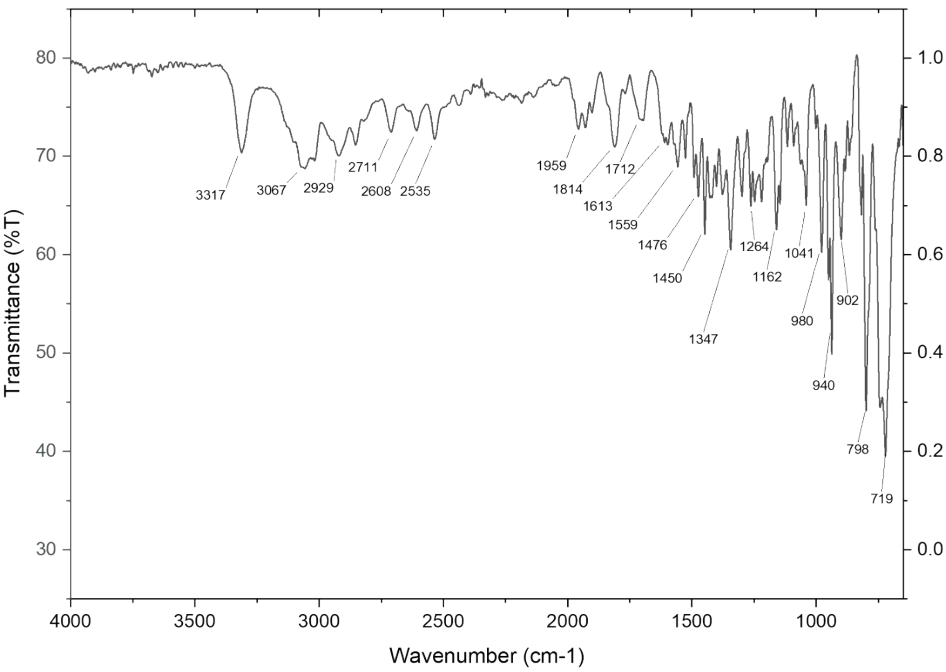


Figure S183: FTIR (ATR) spectrum of **4ab**.

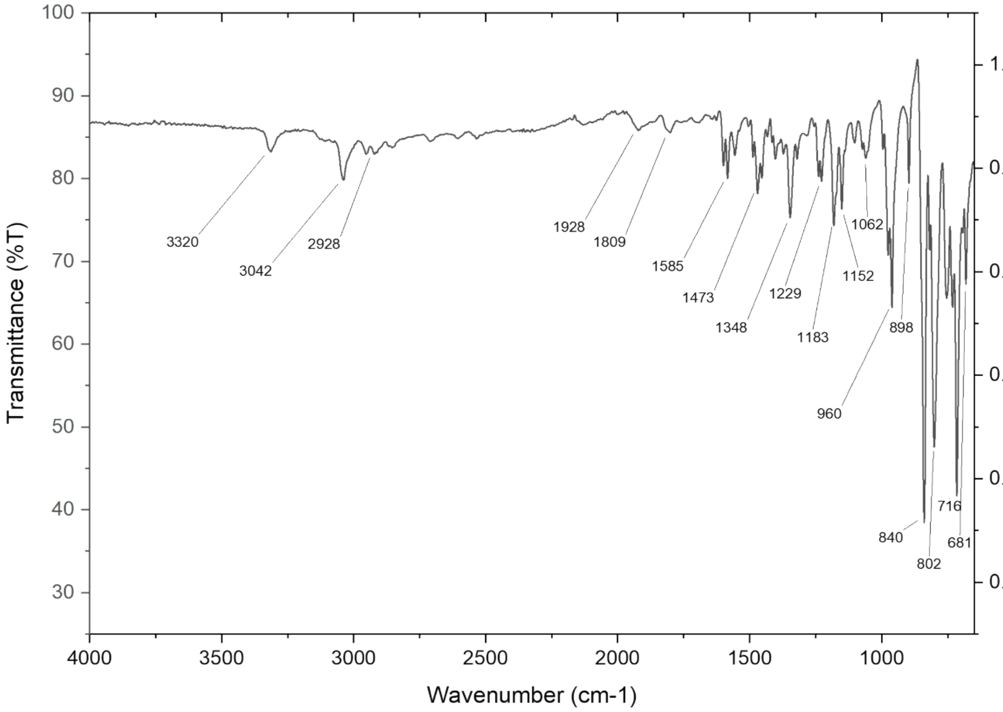


Figure S184: FTIR (ATR) spectrum of **4ac**.

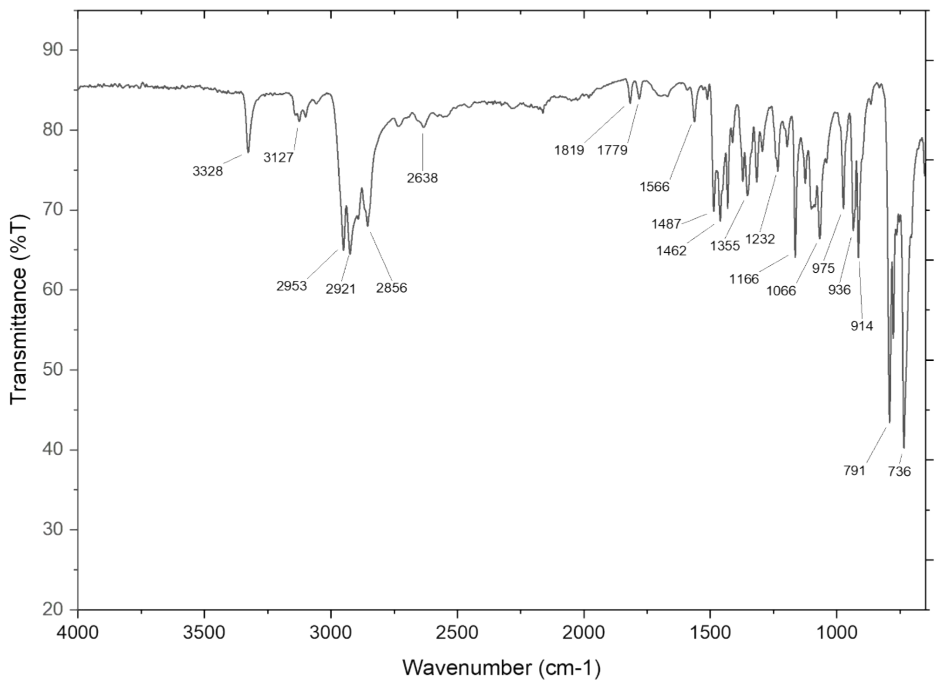


Figure S185: FTIR (ATR) spectrum of **4ad**.

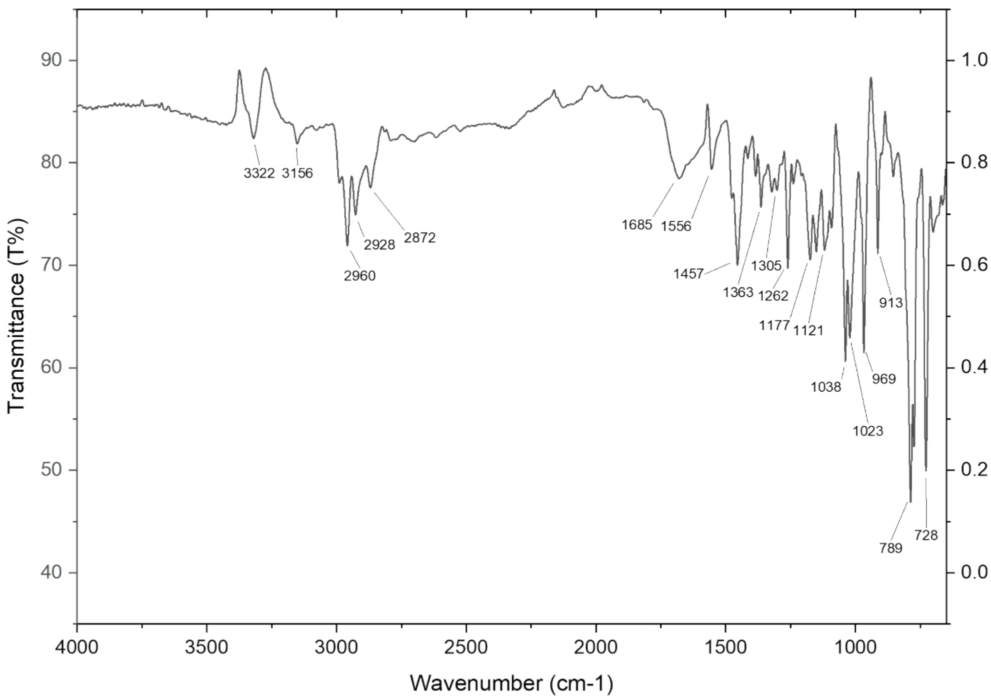


Figure S186: FTIR (ATR) spectrum of **4ae**.

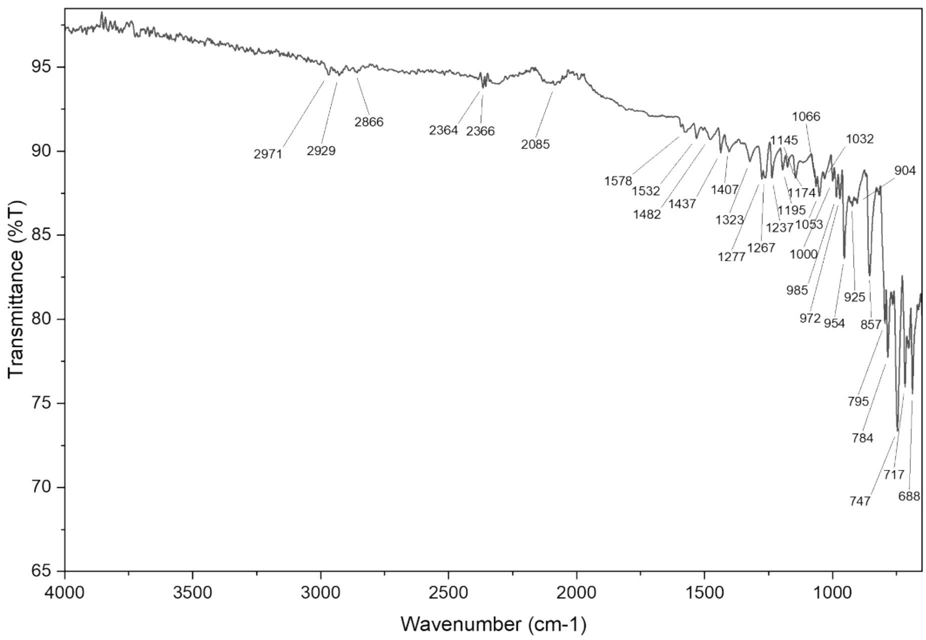


Figure S187: FTIR (ATR) spectrum of **7a.**

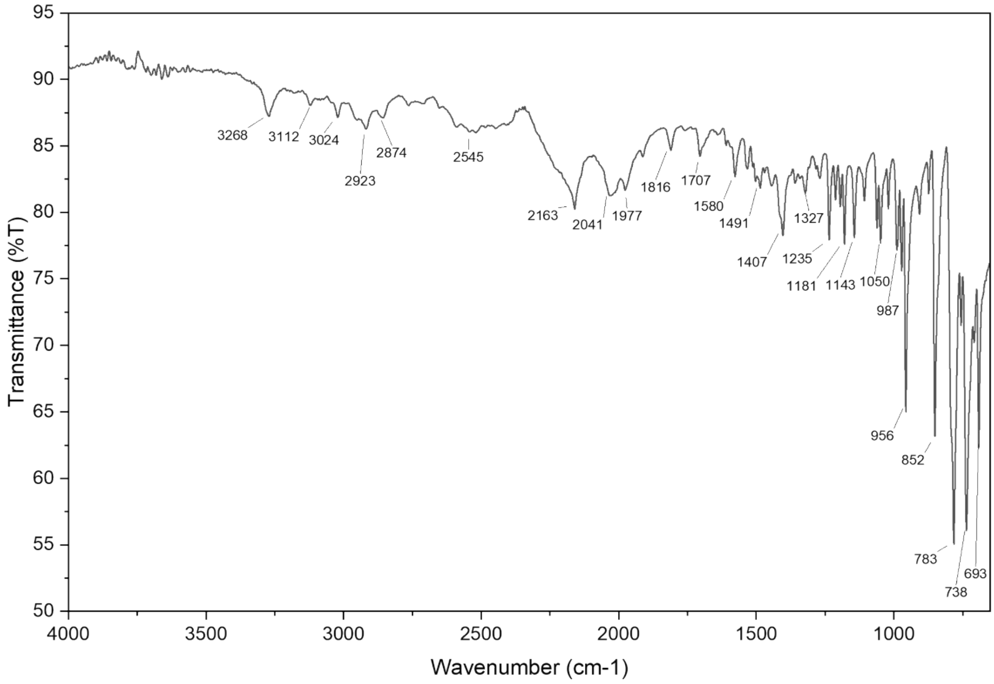


Figure S188: FTIR (ATR) spectrum of **7b**.

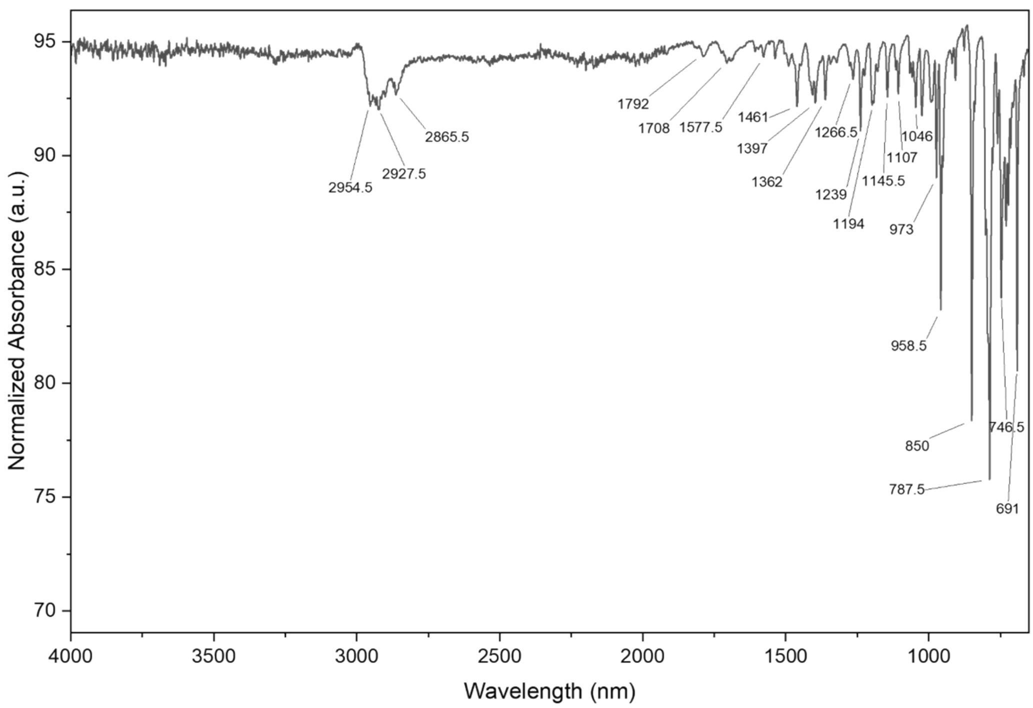


Figure S189: FTIR (ATR) spectrum of **7d**.

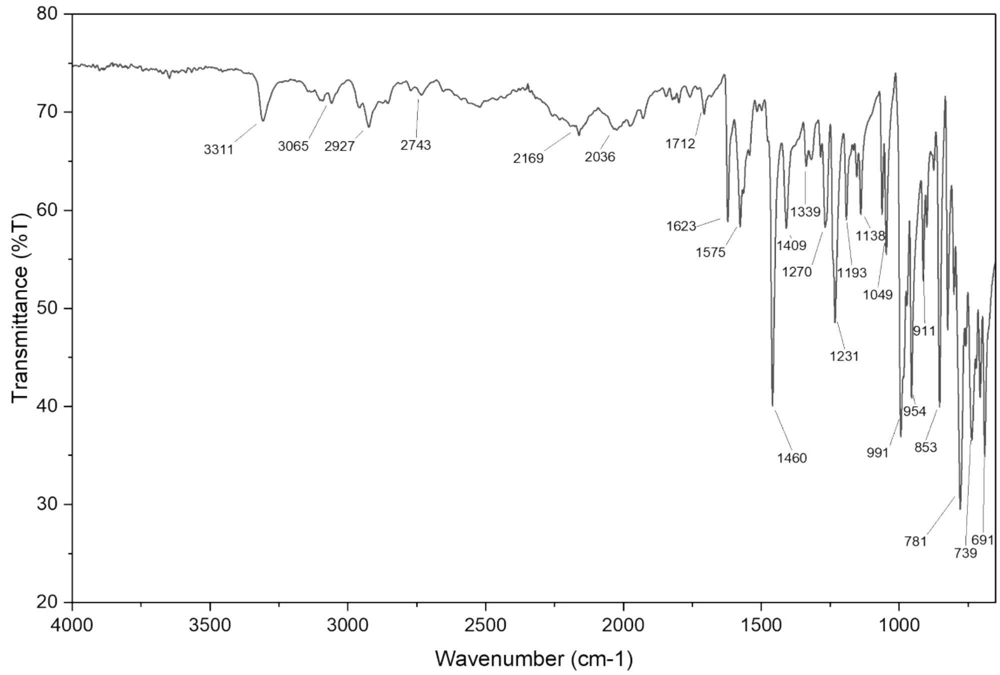


Figure S190: FTIR (ATR) spectrum of **7m**.

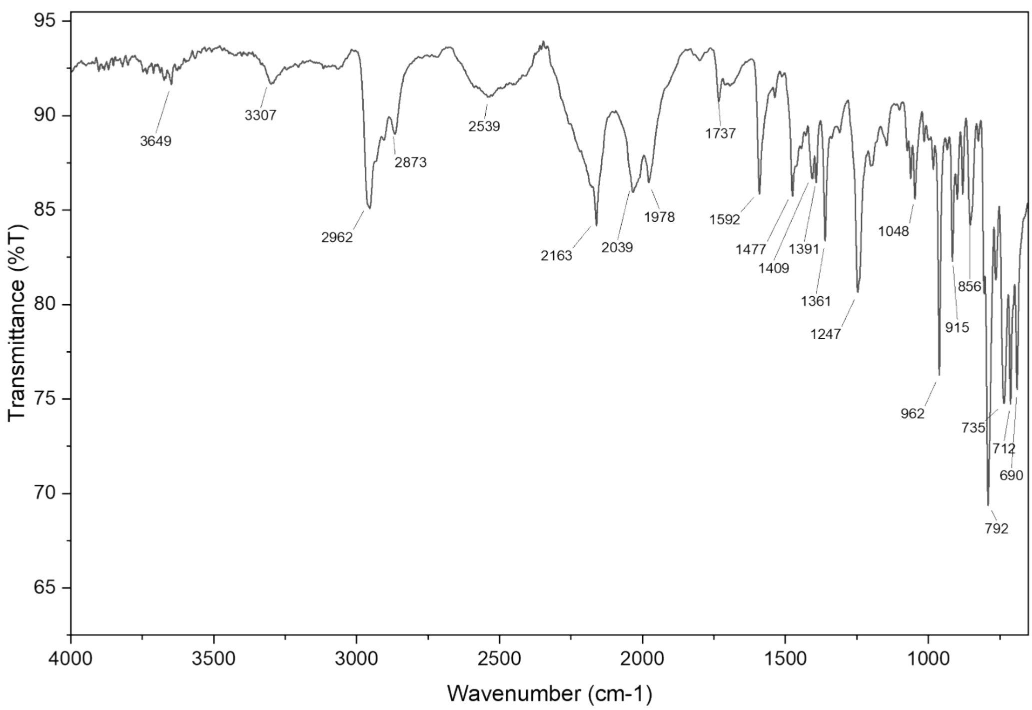


Figure S191: FTIR (ATR) spectrum of **7q**.

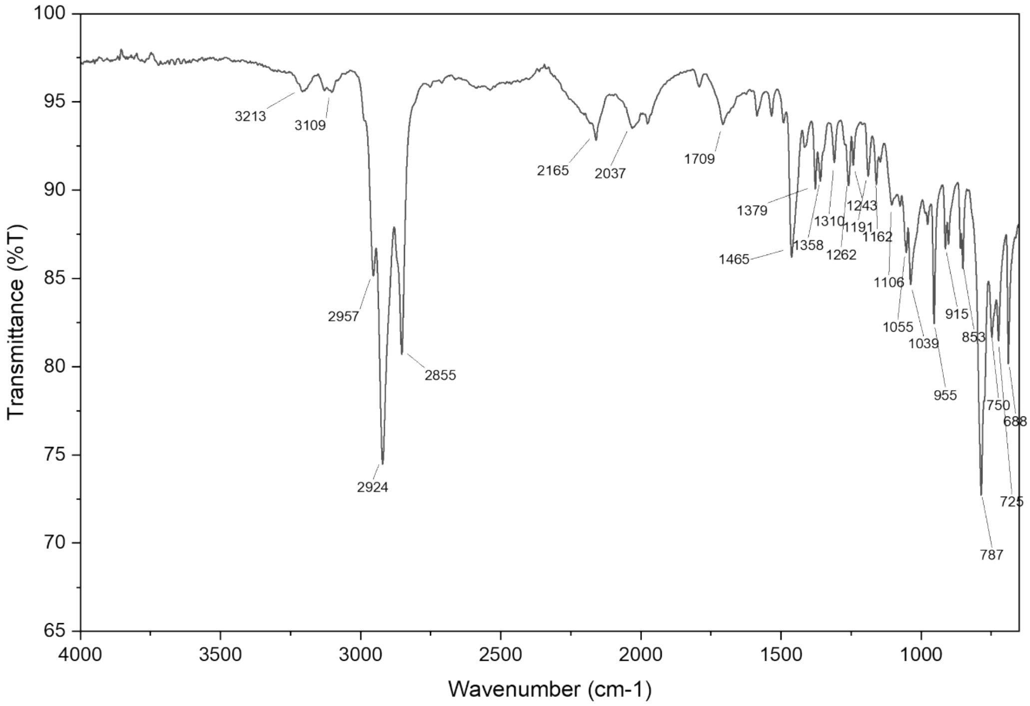


Figure S192: FTIR (ATR) spectrum of **7ae**.

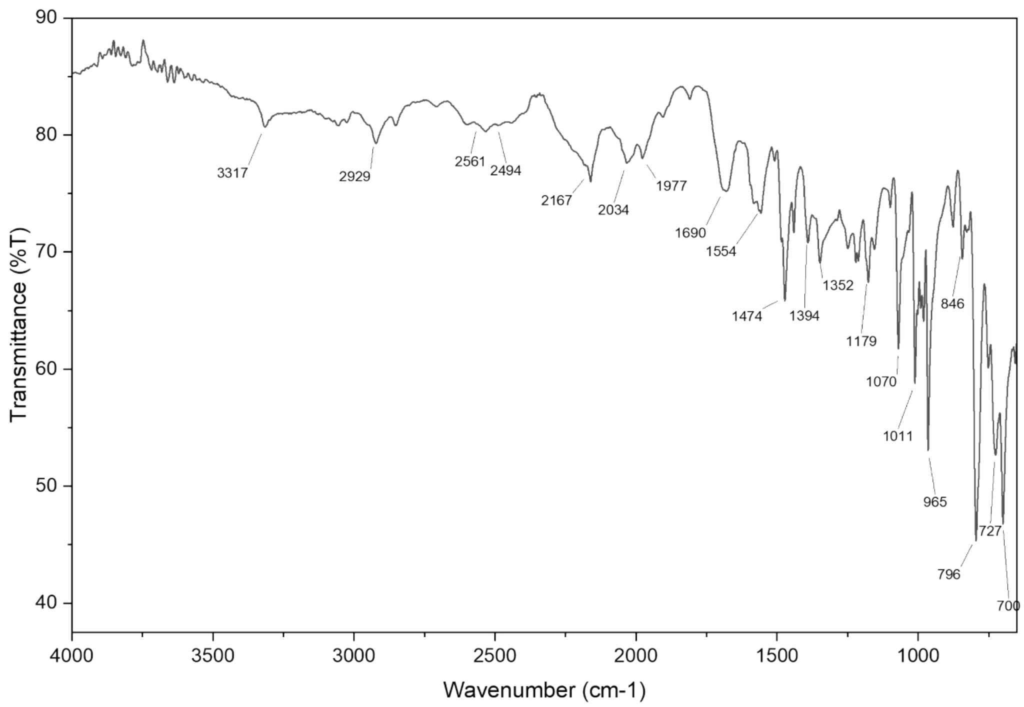


Figure S193: FTIR (ATR) spectrum of **8c**.

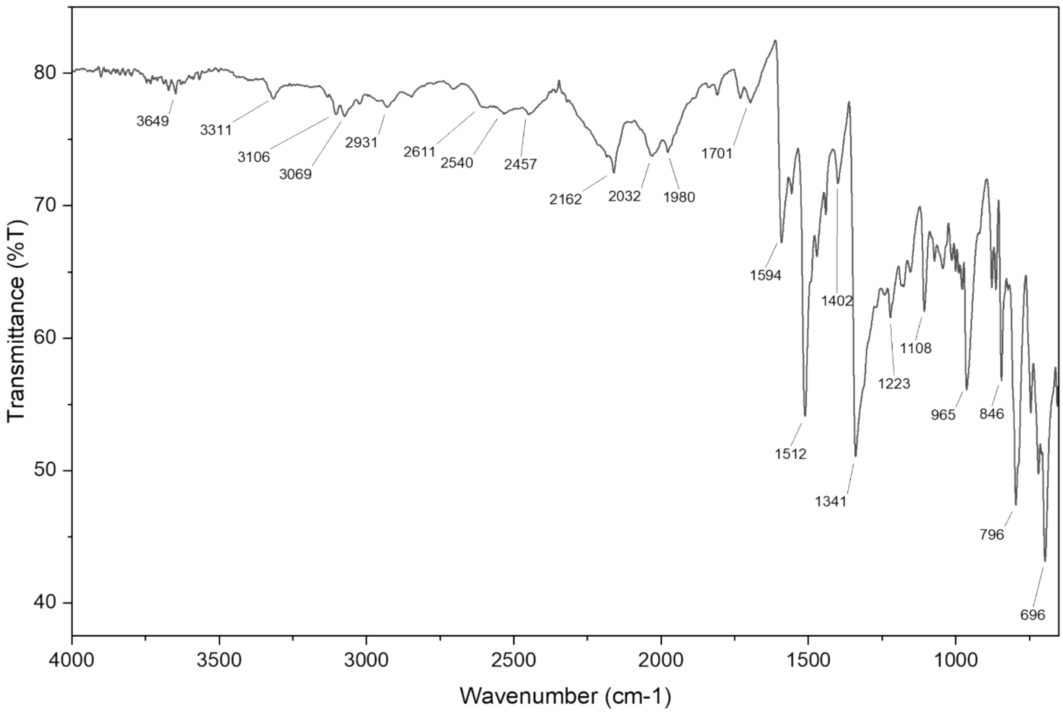


Figure S194: FTIR (ATR) spectrum of **8f**.

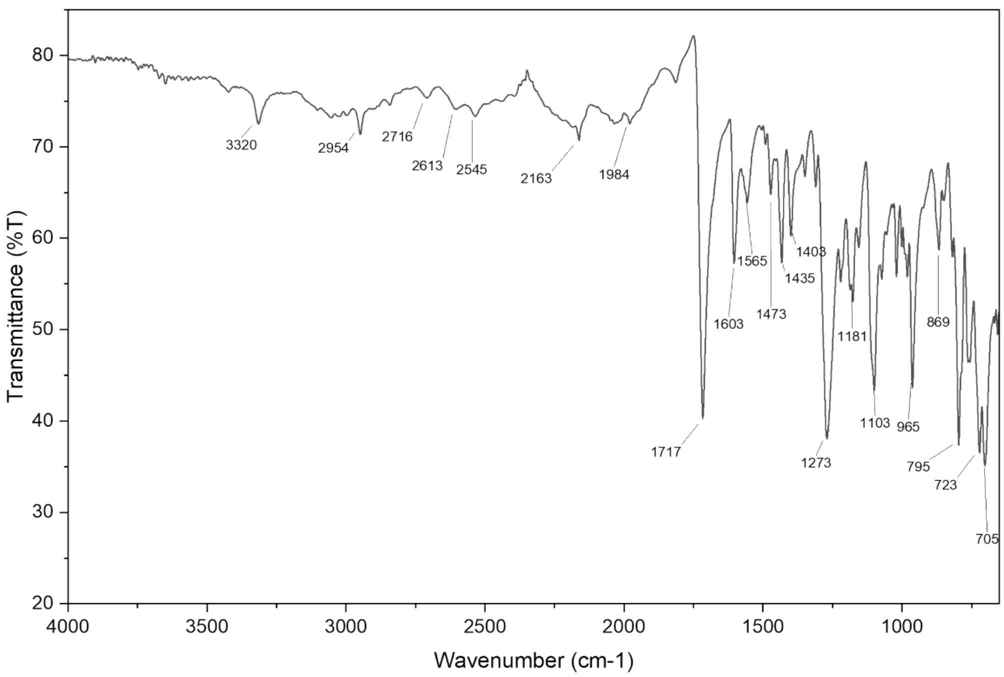


Figure S195: FTIR (ATR) spectrum of **8g**.

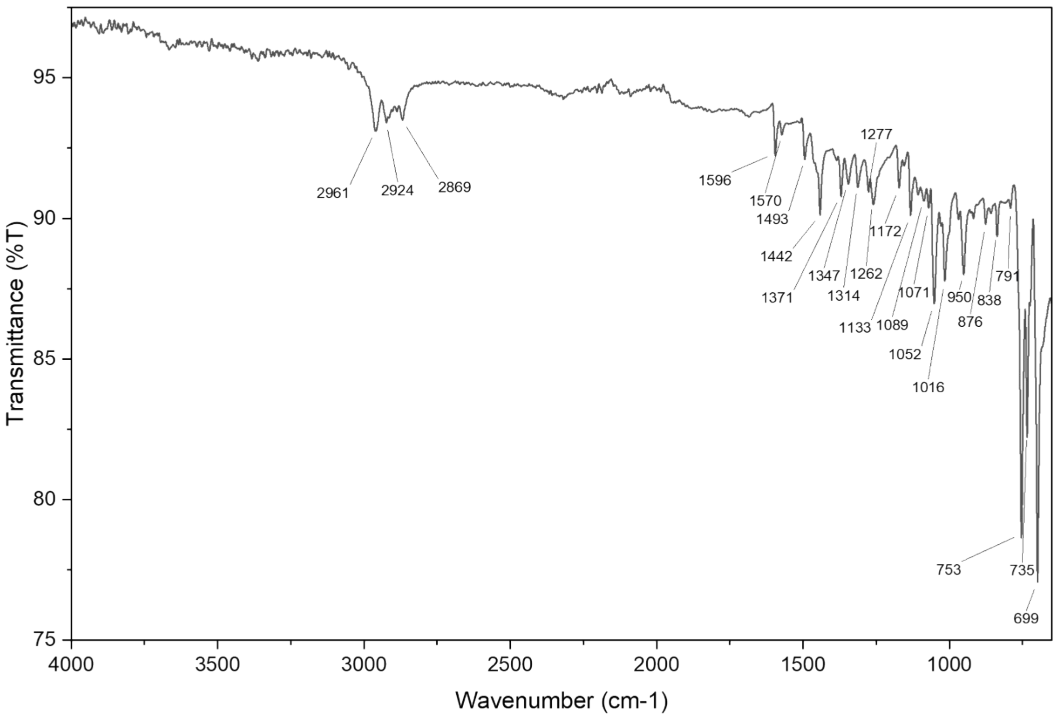


Figure S196: FTIR (ATR) spectrum of **11a**.

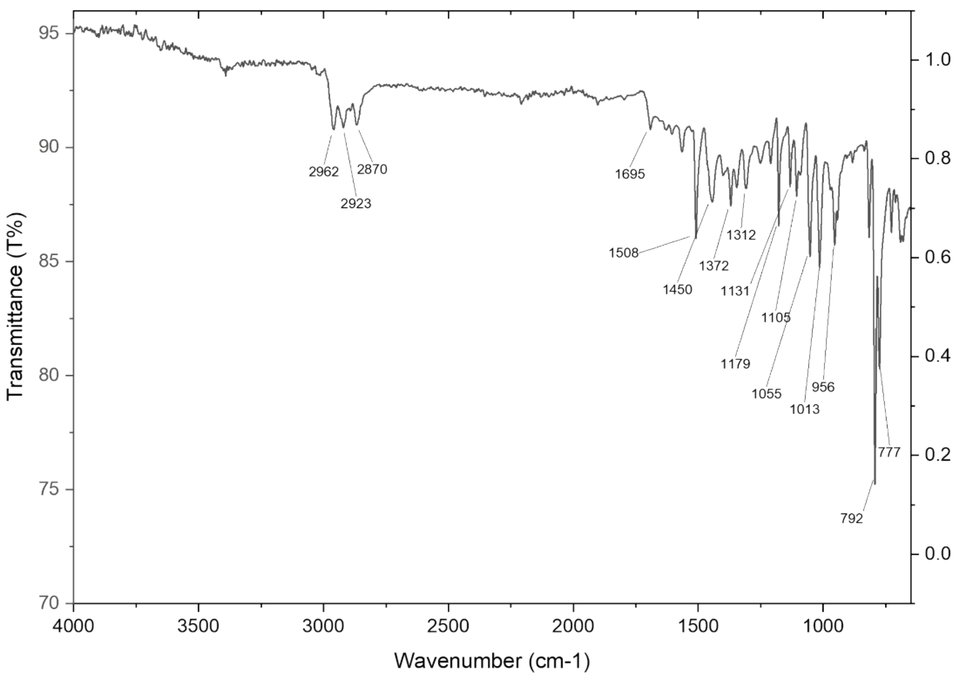


Figure S197: FTIR (ATR) spectrum of **11b**.

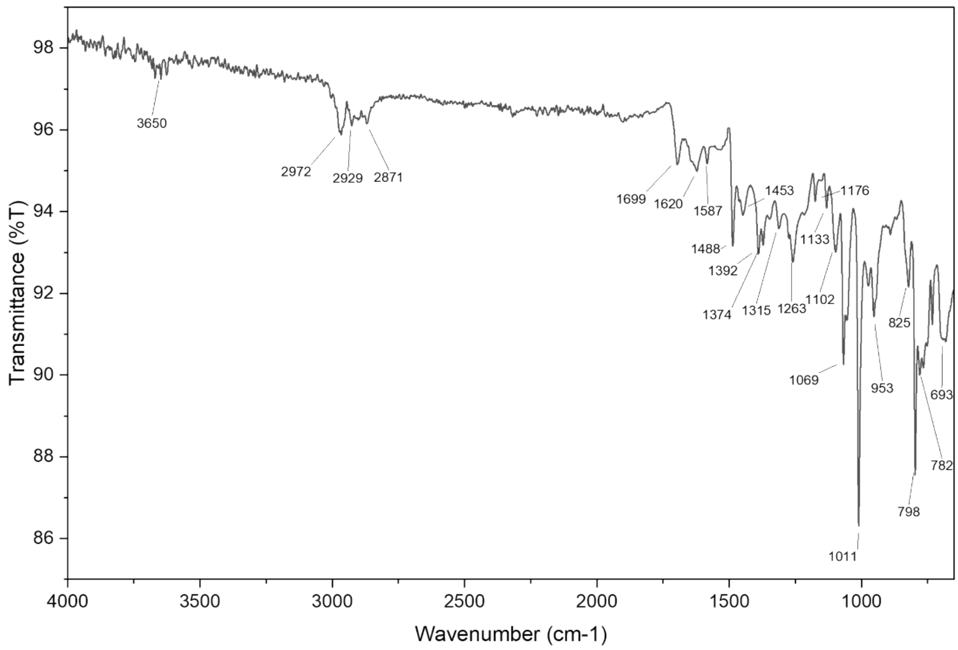


Figure S198: FTIR (ATR) spectrum of **11c**.

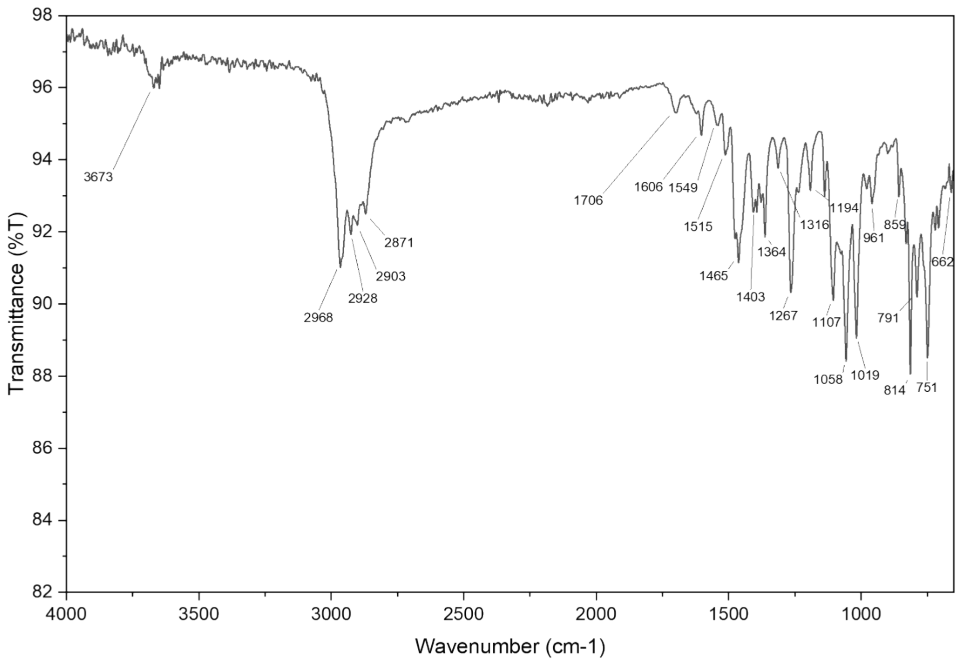


Figure S199: FTIR (ATR) spectrum of **11d**.

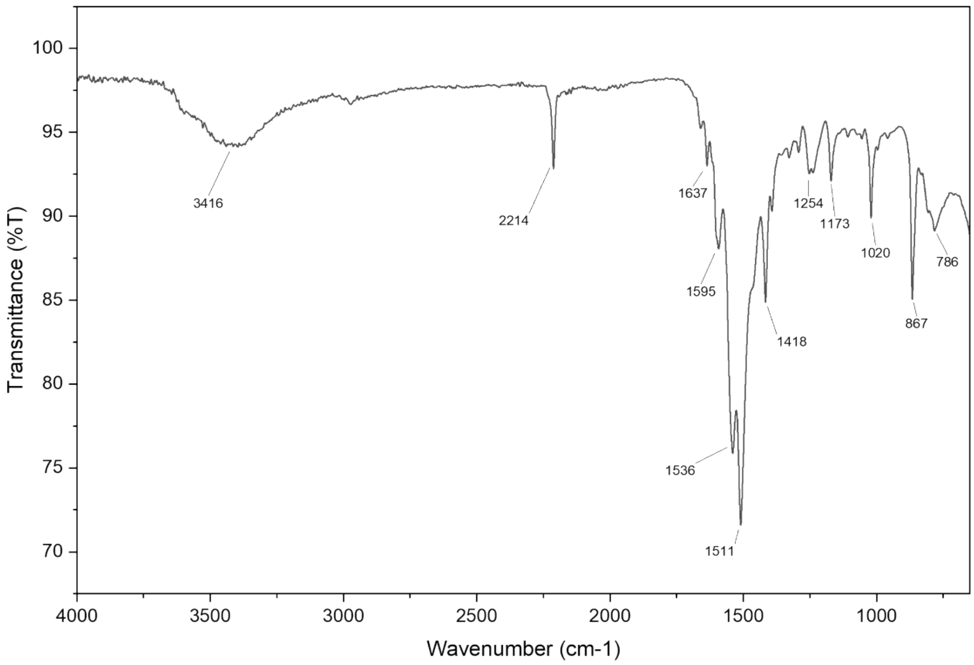


Figure S200: FTIR (ATR) spectrum of **11e**.

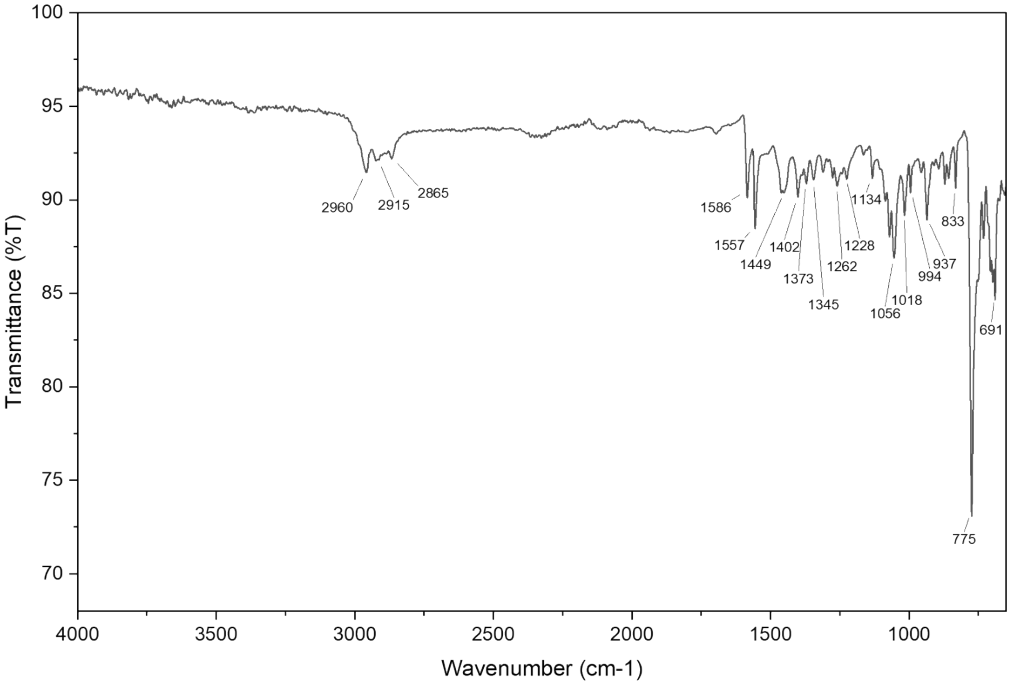


Figure S201: FTIR (ATR) spectrum of **11h**.

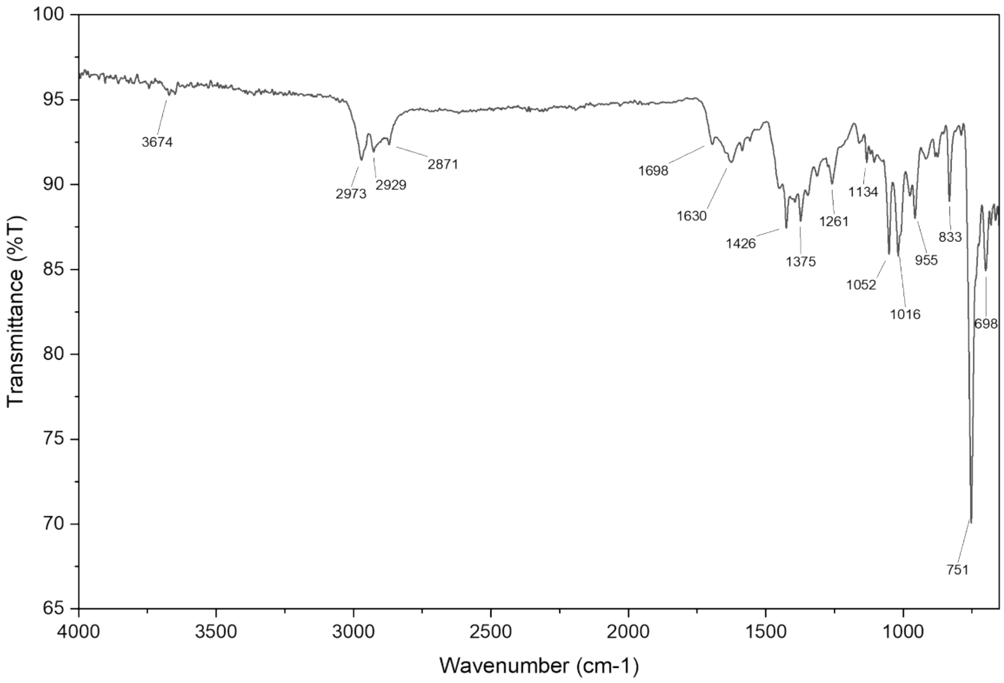


Figure S202: FTIR (ATR) spectrum of **11k.**

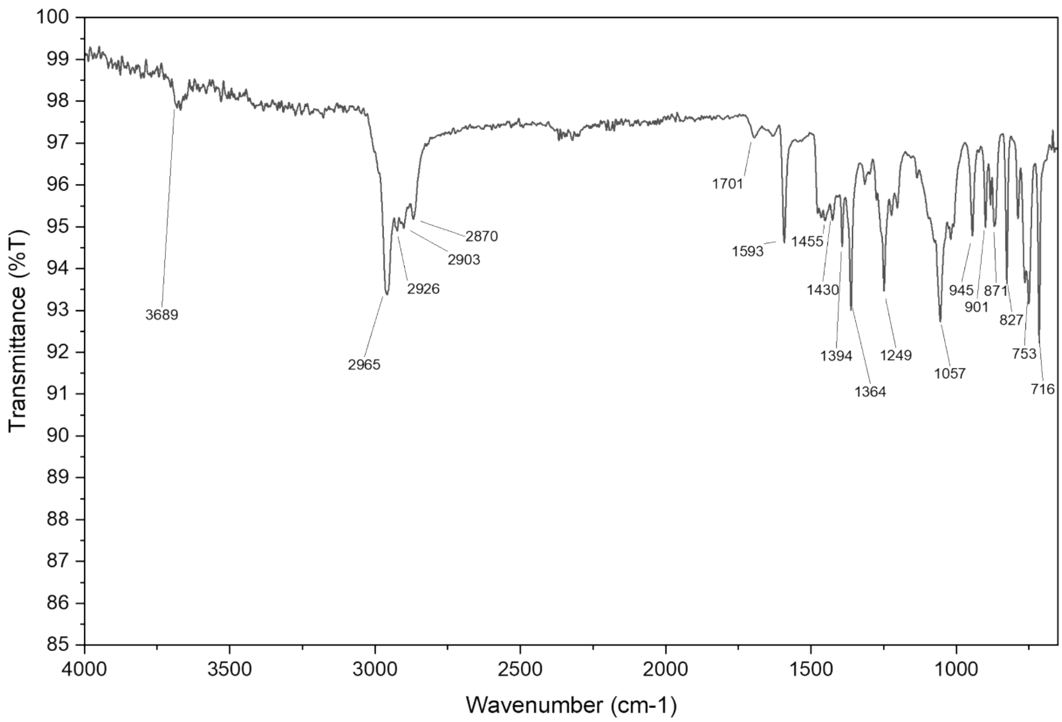


Figure S203: FTIR (ATR) spectrum of **11q**.

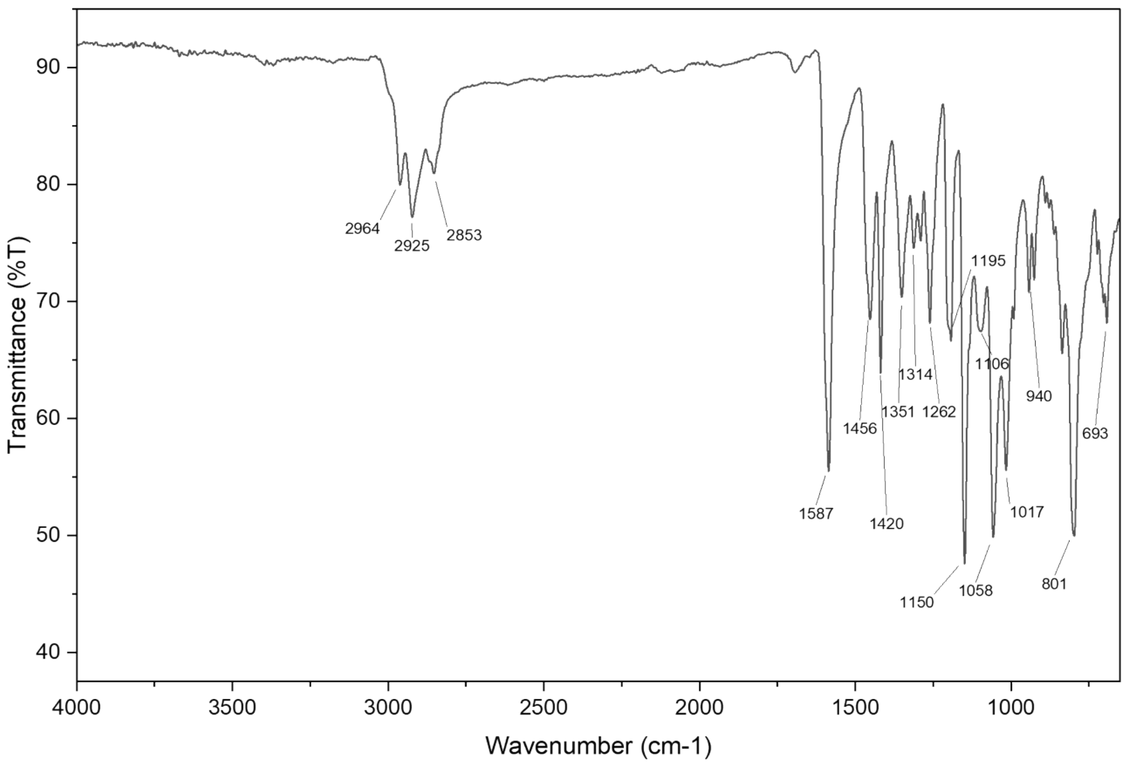


Figure S204: FTIR (ATR) spectrum of **11r**.

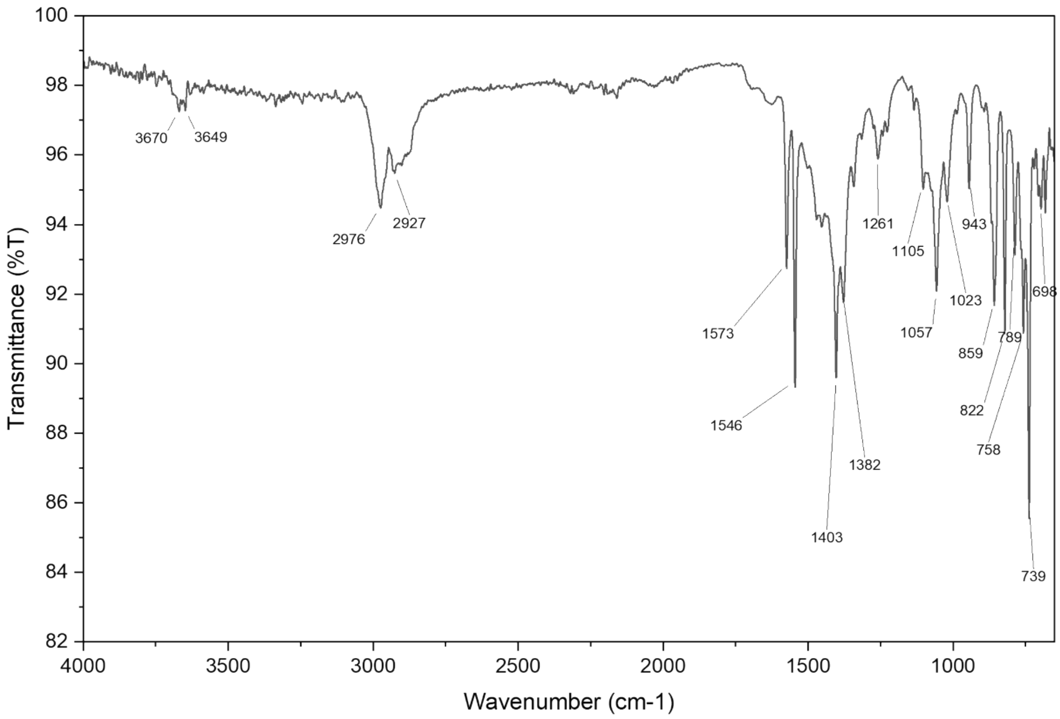


Figure S205: FTIR (ATR) spectrum of **11s**.

Single X-ray crystallographic data

Crystals of porphyrins **11a** and **11k** suitable of single crystal X-ray diffraction were grown according to a protocol developed by Hope by dissolving compounds **11a** and **11k** in deuterated Benzene and deuterated chloroform respectively and allowing for slow evaporation of the solvent over time.[109] Single crystals of **11a** and **11k** were mounted on a MiTeGen micromount with NVH immersion oil. Data for porphyrins **11a** and **11k** were collected from a shock-cooled single crystal at 100(2) K on an APEX Duo (Bruker AXS, Karlsruhe, Germany) Kappa diffractometer with a microfocus sealed X-ray tube using mirror optics as a monochromator and an APEX2 detector. The diffractometer was equipped with a Cobra low temperature device and used Cu K_α radiation (λ = 1.54178 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied.[110,111] The structure was solved by dual methods with SHELXT and refined by full-matrix least-squares method against F^2 using SHELXL.[112,113] All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atoms were refined with isotropic displacement parameters. Some of their coordinates were refined freely and some on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. All images were generated using Olex2.[114]

NSD symmetry analysis depicting insightful in- and out- of plane skeletal plots of the porphyrin core in addition to the generation of neoplastic representation of porphyrins **11a** and **11k** were achieved by utilizing an online NSD symmetry analysis tool.[115,116]

Refinement details

Crystal Data for Compound **11a**

For the refinement of the crystal data for porphyrin **11a,** donor N-H hydrogens were located and refined with restraints over two locations with 55:45% occupancy. Three of the meso-phenyl groups are disordered over three positions C39, C49 and C59 with occupancies of 84:16%, 85:15%, 84:16%, respectively. These disordered meso-phenyl carbon atoms were treated using restraints (DFIX, SADI, SIMU and RIGU) and constraints (EADP). Deuterated benzene is present over two locations with the fully occupied site modelled over two locations (75:25%) and symmetry generated site only being 15% occupied.

Crystal Data for Compound **11k**

For the refinement of the crystal data for porphyrin **11k**, each *ortho*-bromine functionalized phenyl group had bromine atoms disordered over two locations and modelled with Br1, 95:5%; Br2, 78:22%; Br3, 63:37%; Br4, 83:17% with Br1-3 mainly adopting the 'up' facing α-atropisomeric form and Br4 assuming the 'down' facing β-atropisomeric form. The phenyl ring associated with Br1, carbons (C29-C34), was also modelled over two locations with 95:5% occupancy. The phenyl ring associated with Br3 was modelled over two locations 63:37% occupancy. Pyrrolic ring carbons (C12, C13) and two ethyl group carbons (C45, C46 and C47, C48), were disordered and modelled over two locations with 75:25% occupancy. Pyrrolic hydrogens were located on the difference map with one freely refined. One of the hydrogen atoms on the previously mentioned disordered pyrrole ring was located and fixed in position. Three chloroform molecules were identified in the asymmetric unit, with chloroform carbon atom C65 being disordered over three locations with 50:40:10% occupancy. A second chloroform carbon C66 was modelled over four positions with 34:15:35:11% occupancy. The remaining chloroform carbon atom C67 was found to be disordered over two locations with 20:15% occupancy, with just a total occupancy in the 35% in the asymmetric unit. The following restraints and constraints were used in the model (DFIX, DANG, FLAT, SADI, SIMU, RIGU, EXYZ and EADP). The occupancies of the two more disordered solvent sites were constrained to unity using SUMP.

Crystallographic data for the structures presented are deposited with the Cambridge Crystallographic Data Centre.[117] CCDC 2521006(**11a**) and 2521007 (**11k**) contain the supporting crystallographic data for this manuscript. This data can be obtained from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.[118]

X-ray crystallographic data refinement table and NSD analysis

Table S2. Crystal data and structure refinement for porphyrins **11a** and **11k**.

CCDC number	**2521006**	**2521007**
Compound	**11a**	**11k**
Local TCD number	TCD2681	TCD2545
Empirical formula	$C_{66.45}H_{62}D_{6.45}N_4$	$C_{62.35}H_{60.35}Br_4Cl_{7.05}N_4$
Formula weight	929.59	1435.26
Temperature [K]	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group (number)	$P\bar{1}$ (2)	$P\bar{1}$ (2)
a **[Å]**	13.2337(3)	13.834(8)
b **[Å]**	13.8527(3)	14.203(8)
c **[Å]**	16.2506(3)	18.286(12)
α [°]	104.8644(11)	71.834(10)
β [°]	96.6037(12)	68.084(18)
γ [°]	108.1059(11)	72.224(11)
Volume [Å³]	2674.64(10)	3093(3)
Z	2	2
ρ_{calc} [gcm⁻³]	1.154	1.541
μ [mm⁻¹]	0.502	6.305
***F*(000)**	990	1445
Crystal size [mm³]	0.066×0.104×0.299	0.049×0.061×0.132
Crystal colour	clear green	brown
Crystal shape	fragment	block
Radiation	Cu K_α (λ=1.54178 Å)	Cu K_α (λ=1.54178 Å)
2θ range [°]	5.76 to 140.01 (0.82 Å)	5.34 to 139.91 (0.82 Å)
Index ranges	−16 ≤ h ≤ 15 −16 ≤ k ≤ 16 −19 ≤ l ≤ 18	−16 ≤ h ≤ 16 −15 ≤ k ≤ 17 −22 ≤ l ≤ 22
Reflections collected	47660	70587
Independent reflections	10040 R_{int} = 0.0440 R_{sigma} = 0.0325	11589 R_{int} = 0.0831 R_{sigma} = 0.0673
Completeness to θ = 67.679°	99.6 %	99.8 %
Data / Restraints / Parameters	10040 / 1172 / 859	11589 / 1631 / 926
Absorption correction T_{min}/T_{max} (method)	0.6919 / 0.7533 (multi-scan)	0.5493 / 0.7533 (multi-scan)
Goodness-of-fit on F^2	1.050	1.018
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0519 wR_2 = 0.1405	R_1 = 0.0941 wR_2 = 0.2512
Final *R* indexes [all data]	R_1 = 0.0614 wR_2 = 0.1496	R_1 = 0.1201 wR_2 = 0.2737
Largest peak/hole [eÅ⁻³]	0.38/−0.23	0.97/−0.86

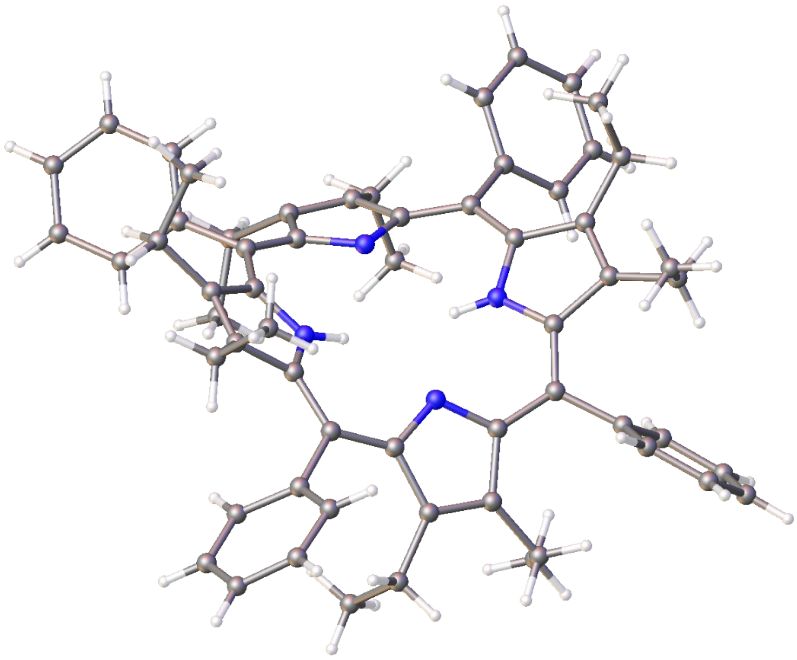


Figure S206: View of the molecular structure of porphyrin **11a** in the crystal, shows the major occupied moiety, with inner N-H hydrogens at 55% occupancy. Displacement parameters shown at 50% probability. Solvent omitted for clarity.

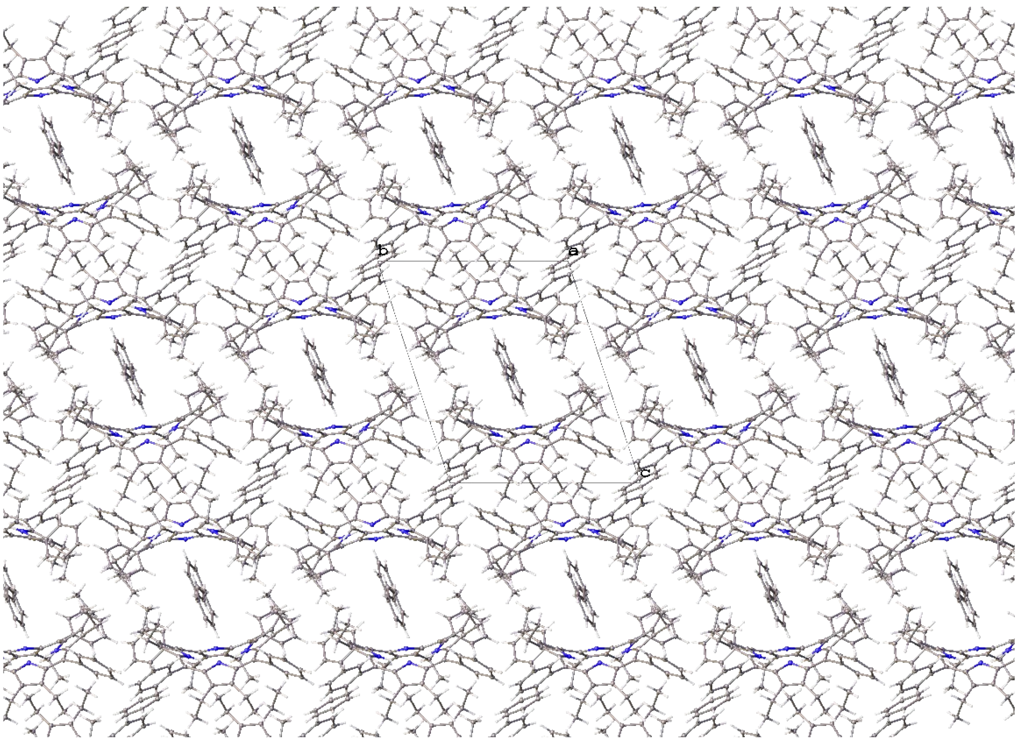


Figure S207: Schematic packing diagram of porphyrin **11a** viewed normal to the a-axis, depicting deuterated benzene in the crystal lattice.

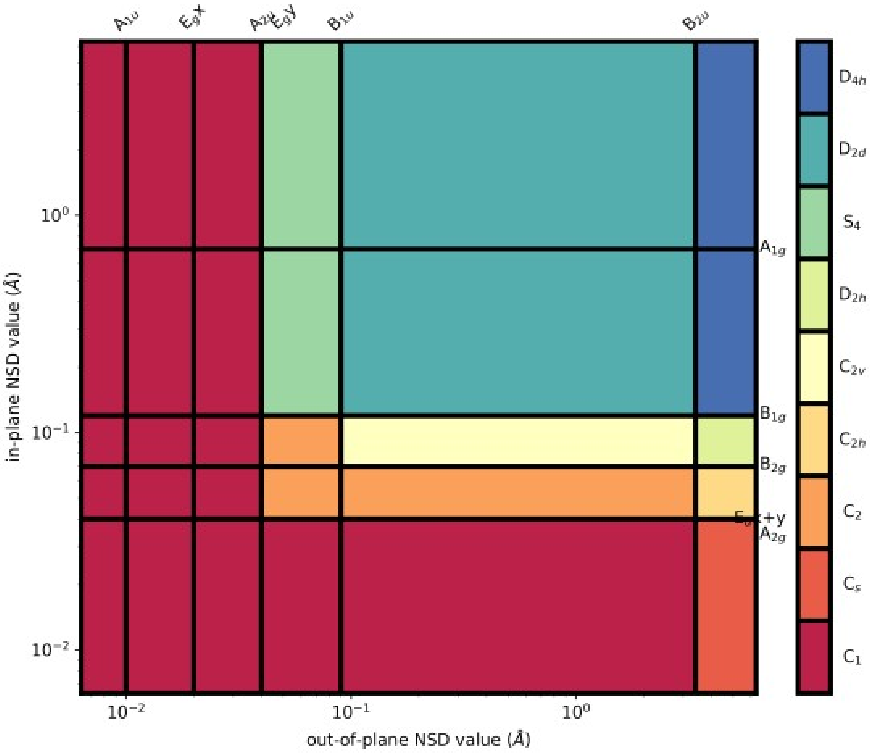


Figure S208: Neoplastic representation of the NSD symmetry elements for porphyrin **11a**.

Table S3: Mean bond distances, angles and deviations from planarity of porphyrin **11a**.

Bond Distances, Bond Angles, Atom Displacements	Mean Value (standard error)	Units
$N–C_a$	1.365(4)	(Å)
$C_a–C_b$	1.456(7)	(Å)
$C_a–C_m$	1.409(4)	(Å)
$C_b–C_b$	1.368(3)	(Å)
$\angle C_aC_bC_b$	107.0(3)	(°)
$\angle NC_aC_b$	108.4(4)	(°)
$\angle NC_aC_m$	122.6(6)	(°)
$\angle C_aNC_a$	108.7(3)	(°)
$\angle C_mC_aC_b$	128.7(5)	(°)
$\angle C_aC_mC_a$	124.1(2)	(°)
Δ24	0.5342	(Å)
ΔN	0.083(17)	(Å)
ΔC_a	0.42(2)	(Å)
ΔC_b	1.13(2)	(Å)
ΔC_m	0.027(15)	(Å)
∠ pyrrole tilt	29.4(8)	(°)
N···N dist (adj)	2.9(2)	(Å)
N···N dist (opp)	4.09(3)	(Å)

Table S4: NSD analysis for the in-plane distortion of porphyrin **11a** (in Å).

basis	Δ_{ip}	δ_{ip}	B_{2g}	B_{1g}	$E_u(x)$	$E_u(y)$	A_{1g}	A_{2g}
min.	0.52	0.06	0.07	0.12	0.00	-0.02	-0.50	0.02
ext.	0.59	0.05	0.07	0.12	0.00	-0.02	-0.50	0.02
			0.01	0.00	0.02	-0.01	-0.27	-0.03
total	0.71	0.00	0.07	0.12	0.00	-0.01	-0.48	0.02
			0.01	0.00	0.02	-0.01	-0.27	-0.03
			-0.01	-0.02	0.01	-0.01	0.42	-0.01
			0.00	0.01	0.00	0.00	0.01	0.00
			0.00	0.01	0.01	0.01	-0.03	0.00
			0.00	0.00	0.00	0.00	-0.04	
					-0.01	0.00		
comp.	0.71	0.00	0.07	0.12	0.02	0.02	0.70	0.04

Table S5: NSD analysis for the out-of-plane distortions of porphyrin **11a** (in Å).

basis	Δ_{oop}	δ_{oop}	B_{2u}	B_{1u}	A_{2u}	$E_g(x)$	$E_g(y)$	A_{1u}
min.	3.39	0.04	-3.39	0.09	0.03	0.01	0.00	-0.01
ext.	3.41	0.00	-3.38	0.09	0.03	0.01	0.00	-0.01
			0.39	-0.02	-0.02	-0.02	0.04	0.00
total	3.41	0.00	-3.38	0.09	0.03	0.01	0.00	-0.01
			0.39	-0.02	-0.02	-0.02	0.04	0.00
			0.04	0.00	0.00	-0.01	0.01	
						0.01	0.00	
						0.01	0.00	
comp	3.41	0.00	3.41	0.09	0.04	0.02	0.04	0.01

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Table S6: Coordinates for external plotting for out-of-plane and in-plane skeletal plots of the porphyrin core for porphyrin **11a**.

Atom	*x (Å)*	*y (Å)*	*z (Å)*	*r (Å)*	*theta (°)*
C1	-1.095	2.722	-0.434	2.934	66.912
C2	-0.681	3.899	-1.158	3.958	54.914
C3	0.686	3.941	-1.128	4.0	35.124
C4	1.129	2.765	-0.402	2.987	22.792
C5	2.424	2.416	0.033	3.422	-0.096
C6	2.789	1.123	0.45	3.006	-23.07
C7	3.996	0.684	1.132	4.054	-35.29
C8	3.998	-0.688	1.103	4.057	-54.761
C9	2.782	-1.091	0.406	2.988	-66.417
C10	2.408	-2.378	-0.036	3.384	-89.644
C11	1.106	-2.735	-0.432	2.95	-112.986
C12	0.675	-3.92	-1.167	3.978	-125.226
C13	-0.691	-3.949	-1.118	4.009	-144.923
C14	-1.119	-2.768	-0.383	2.986	-157.02
C15	-2.422	-2.411	0.038	3.418	179.867
C16	-2.792	-1.111	0.424	3.005	156.691
C17	-3.997	-0.677	1.138	4.054	144.61
C18	-3.996	0.686	1.109	4.054	125.261
C19	-2.791	1.102	0.398	3.001	113.458
C20	-2.398	2.387	-0.001	3.384	90.132
N21	0.023	2.027	-0.082	2.027	44.347

N22	2.052	0.018	0.11	2.052	-44.496
N23	-0.012	-2.032	-0.07	2.032	-135.326
N24	-2.073	-0.01	0.07	2.073	135.284

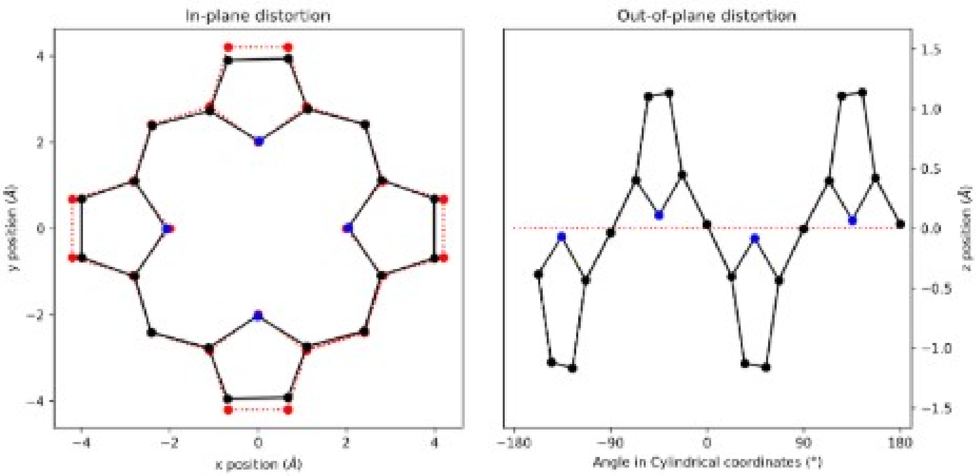

Figure S209: Out-of- and in-plane skeletal plots of the porphyrin core from NSD analysis. The porphyrin ring **11a** is represented in black (carbon) and (blue) nitrogen with reference to CuTPP (red dotted lines).

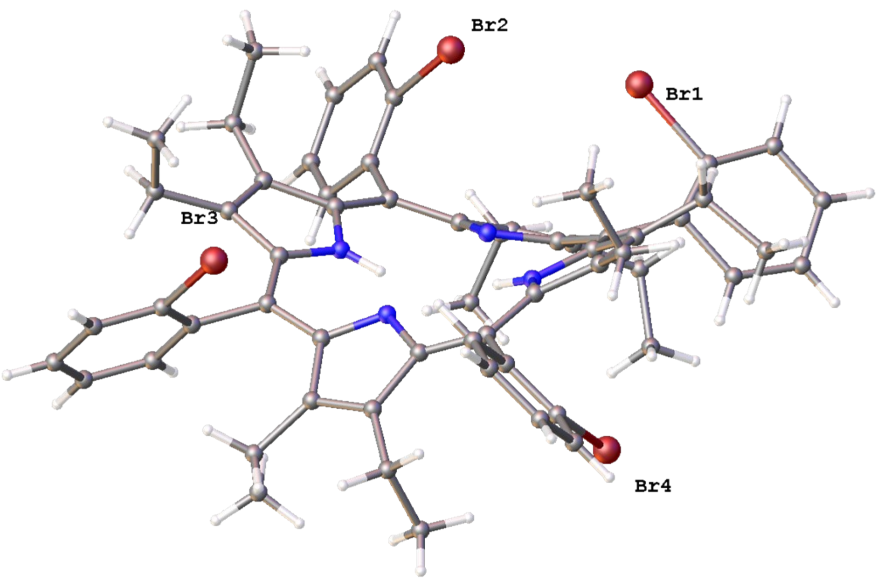

Figure S210: View of the molecular structure of porphyrin **11k** in the crystal shows, the majority occupied moiety with Br1-3 facing 'up' and Br4 facing 'down' with occupancies Br1, 95%; Br2, 78%; Br3, 63%; Br4, 83%. Disordered solvent $CHCl_3$ is omitted for clarity.

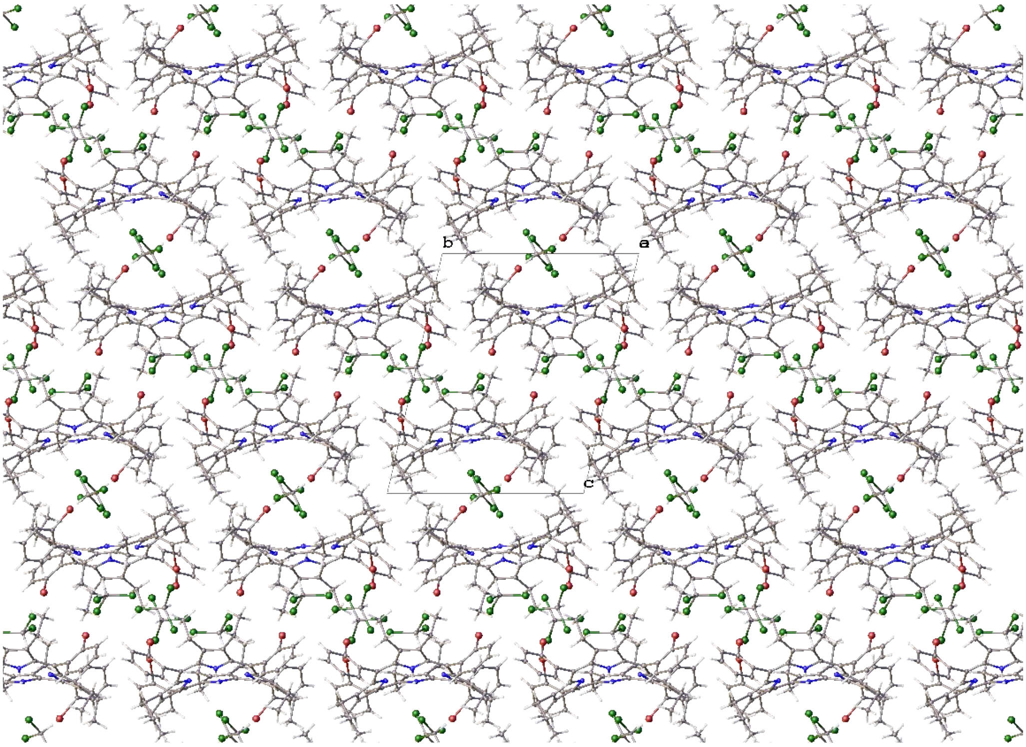

Figure S211: Schematic packing diagram of porphyrin **11k** viewed normal to the a-axis, depicting chloroform in the crystal lattice.

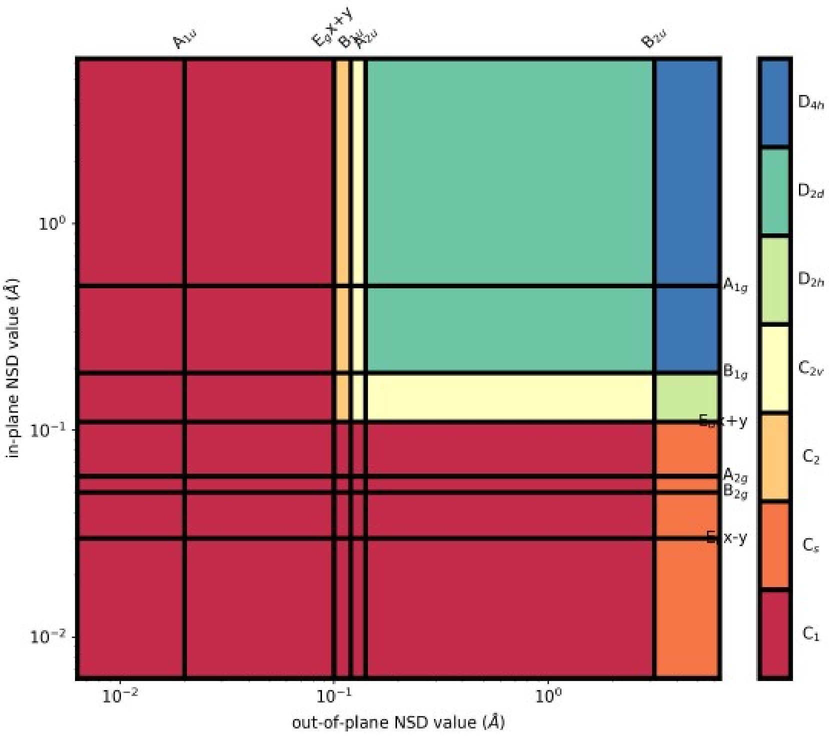

Figure S212: Neoplastic representation of the NSD symmetry elements for porphyrin **11k**.

Table S7: Mean bond distances, angles and deviations from planarity of porphyrin **11k**.

Bond Distances, Bond Angles, Atom Displacements	Mean Value (standard error)	Units
$N–C_a$	1.364(14)	(Å)
$C_a–C_b$	1.462(13)	(Å)
$C_a–C_m$	1.414(16)	(Å)
$C_b–C_b$	1.361(11)	(Å)
$\angle C_aC_bC_b$	107.1(12)	(°)
$\angle NC_aC_b$	108(2)	(°)
$\angle NC_aC_m$	123.1(8)	(°)
$\angle C_aNC_a$	108(3)	(°)
$\angle C_mC_aC_b$	128(2)	(°)
$\angle C_aC_mC_a$	124.7(6)	(°)
Δ24	0.4973	(Å)
ΔN	0.09(3)	(Å)
ΔC_a	0.39(3)	(Å)
ΔC_b	1.03(5)	(Å)
ΔC_m	0.04(3)	(Å)
∠ pyrrole tilt	26(2)	(°)
N···N dist (adj)	2.916(19)	(Å)
N···N dist (opp)	4.11(11)	(Å)

Table S8: NSD analysis for the in-plane distortion of porphyrin **11k** (in Å).

basis	Δ_{ip}	δ_{ip}	B_{2g}	B_{1g}	$E_u(x)$	$E_u(y)$	A_{1g}	A_{2g}
min.	0.36	0.05	-0.04	0.16	-0.02	0.00	-0.32	-0.03
ext.	0.43	0.03	-0.04	0.16	-0.02	0.00	-0.32	-0.03
			-0.01	0.10	-0.03	0.00	-0.21	0.05
total	0.55	0.00	-0.04	0.16	-0.02	0.00	-0.30	-0.03
			-0.01	0.10	-0.03	0.00	-0.21	0.05
			0.01	0.00	-0.01	0.02	0.34	0.02
			0.00	0.00	0.01	0.01	0.01	0.00
			-0.01	0.01	0.02	0.03	-0.01	0.00
			0.01	0.02	0.02	0.00	-0.02	
					0.02	0.01		
					-0.02	0.00		
					-0.03	0.01		
					0.01	-0.01		
					0.00	-0.01		
comp.	0.55	0.00	0.05	0.19	0.07	0.04	0.50	0.06

Table S9: NSD analysis for the out-of-plane distortions of porphyrin **11k** (in Å).

basis	Δ_{oop}	δ_{oop}	B_{2u}	B_{1u}	A_{2u}	$E_g(x)$	$E_g(y)$	A_{1u}
min.	3.12	0.03	-3.12	-0.12	0.13	0.04	0.05	0.01
ext.	3.13	0.00	-3.11	-0.12	0.12	0.04	0.04	0.01
			0.32	0.02	-0.06	0.04	-0.01	-0.01
total	3.13	0.00	-3.11	-0.12	0.13	0.04	0.04	0.01
			0.32	0.02	-0.06	0.04	-0.01	-0.01

			0.04	0.00	0.01	-0.01	-0.01	
						0.00	-0.01	
						-0.01	-0.01	
comp.	3.13	0.00	3.13	0.12	0.14	0.05	0.05	0.02

Table S10: Coordinates for external plotting for out-of-plane and in-plane skeletal plots of the porphyrin core for porphyrin **11k**.

Atom	***x (Å)***	***y (Å)***	***z (Å)***	***r (Å)***	***theta (°)***
C1	-1.111	2.788	-0.351	3.002	66.724
C2	-0.691	4.006	-1.066	4.065	54.793
C3	0.678	3.952	-1.112	4.009	35.272
C4	1.067	2.737	-0.385	2.938	23.696
C5	2.392	2.422	0.008	3.404	0.363
C6	2.816	1.114	0.383	3.028	-23.421
C7	4.107	0.682	0.957	4.163	-35.57
C8	4.083	-0.666	1.002	4.137	-54.259
C9	2.822	-1.128	0.434	3.039	-66.778
C10	2.393	-2.443	0.079	3.42	-90.598
C11	1.08	-2.777	-0.364	2.98	-113.742
C12	0.685	-4.014	-1.024	4.073	-125.312
C13	-0.664	-3.986	-1.092	4.041	-144.453
C14	-1.09	-2.74	-0.427	2.949	-156.686
C15	-2.409	-2.408	-0.025	3.406	179.995
C16	-2.835	-1.134	0.363	3.053	156.802
C17	-4.061	-0.687	0.999	4.118	144.603
C18	-4.039	0.685	1.024	4.097	125.379

C19	-2.814	1.148	0.425	3.039	112.813
C20	-2.422	2.419	0.053	3.423	90.029
N21	-0.011	2.023	-0.04	2.023	45.325
N22	2.115	-0.011	0.121	2.115	-45.304
N23	0.008	-1.991	-0.084	1.991	-134.763
N24	-2.1	0.01	0.123	2.1	134.714

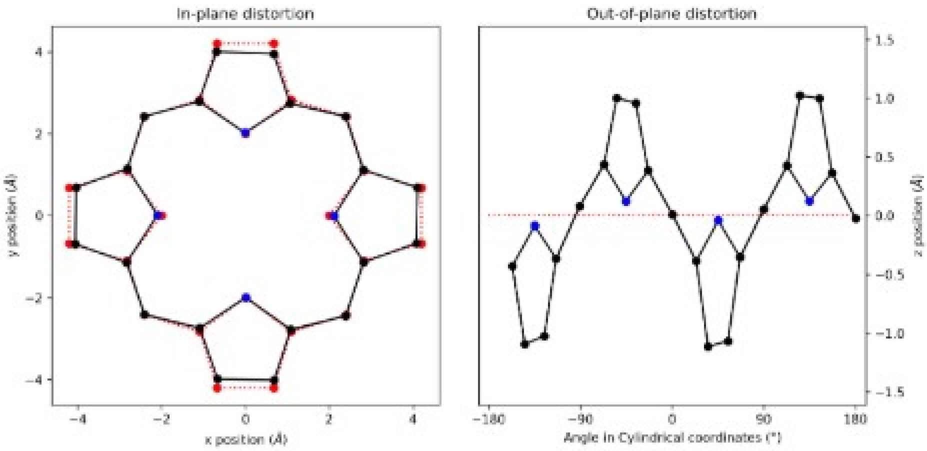

Figure S213: Out-of- and in-plane skeletal plots of the porphyrin core from NSD analysis. The porphyrin ring **11k** is represented in black (carbon) and (blue) nitrogen with reference to CuTPP (red dotted lines).