Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supplementary Information for:

Molecular Designs with PEG Groups for Water-Solubilization of Sparsely Substituted Porphyrins

Phuong-Lien Doan Cao,[a] Zhiyuan Wu,[a] Phattananawee Nalaoh,[b] and Jonathan S. Lindsey[a,*]

[a] Department of Chemistry, North Carolina State University, Raleigh, NC 27695, USA
[b] Department of Chemistry, University of Tennessee, Knoxville, TN 37996, USA

Table of Contents

(1) Aggregation study in PBS + 3% BSA

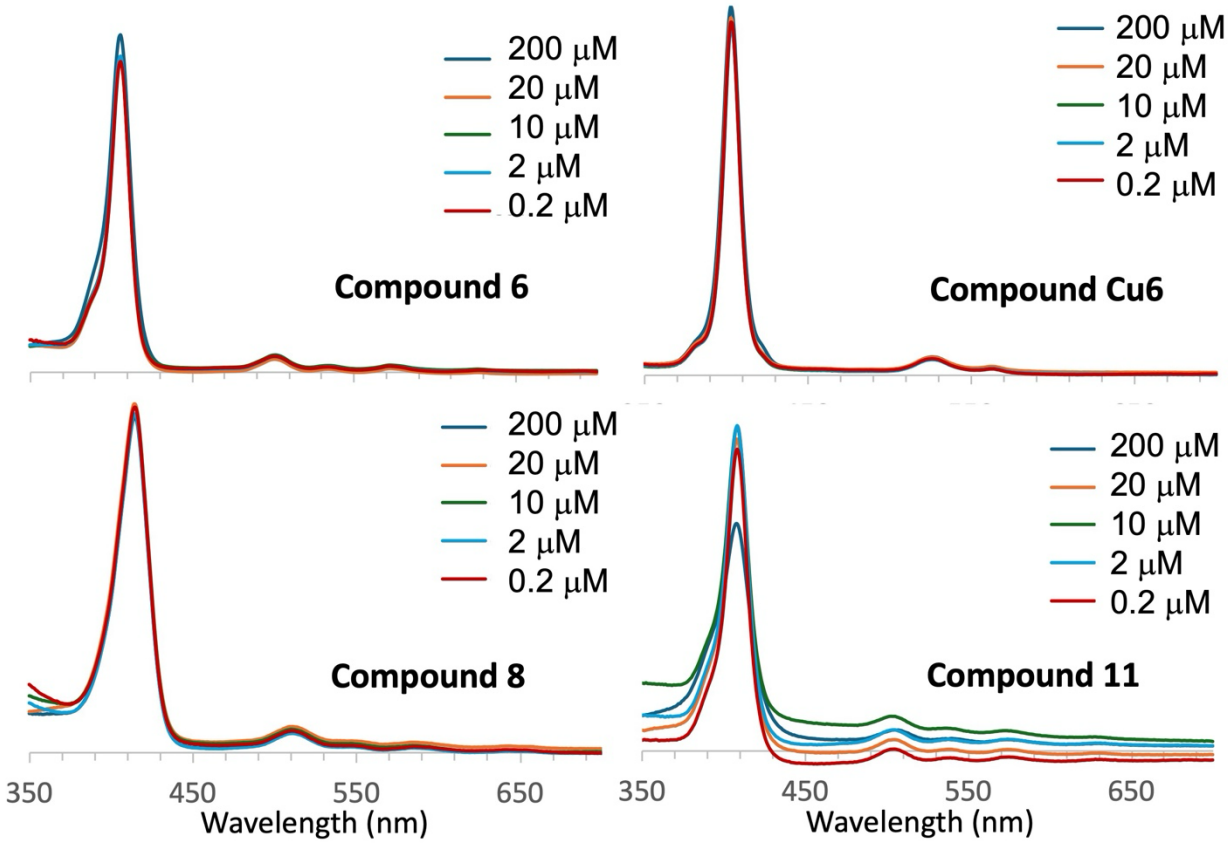


Figure S1. Absorption spectra of porphyrins as a function of concentration in PBS + 3% BSA at room temperature.

(2) Solubility

Two absorption spectra collected during the concentration-dependent self-aggregation study are displayed here without any overlays as in Figure 4 (the spectra are taken from Figure 4). The absorption spectrum of free base *trans*-A_2 porphyrin **6** shows the characteristic Soret band (406 nm) as well as the single major band (501 nm) and progression of weaker bands (534, 573 and 628 nm) in the visible region. The absorption spectrum of free base *trans*-AB porphyrin **11** shows a broadened Soret band (409 nm). The visible bands appear at the expected positions but on an underlying descending slope with increasing wavelength. The broadened Soret band is attributed to self-aggregation, as discussed in the text.

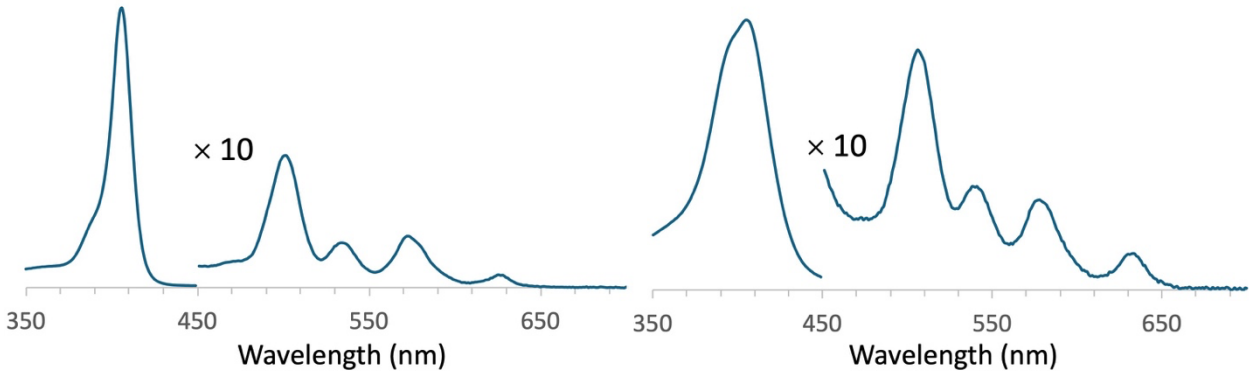


Figure S2. Absorption spectra of free base porphyrins at 200 μM in PBS at room temperature (0.1 mm pathlength cuvettes). Left panel: *trans*-A_2 porphyrin **6**. Right panel: *trans*-AB porphyrin **11**.

Photographs of the two porphyrins in solution at room temperature were collected at several concentrations. The photographs are shown in Figure S3.

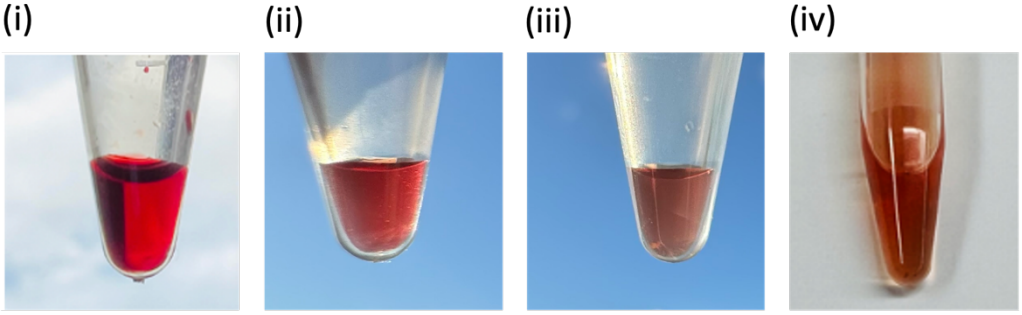


Figure S3. Photographs of porphyrins in aqueous media. See text below for sample identity.

(i) Free base *trans*-A_2 porphyrin **6** at 12 mM in water (photo with a sunlit sky background). The sample was prepared by dissolving 0.46 mg of **6** in 20 μL of water, which corresponds to 23 mg/mL (MW = 1964 Da). A transparent red solution resulted without any precipitate as observed by visual inspection. The optical clarity is indicative of a homogeneous solution.

(ii) Free base *trans*-A_2 porphyrin **6** at 1 mM in PBS (photo with a sunlit sky background). The solution appears rather clear upon visual inspection.

(iii) Free base *trans*-AB **11** at 1 mM in PBS (photo with a sunlit sky background). The sample is somewhat muddy upon visual inspection.

(iv) Free base *trans*-AB **11** at ~0.48 mM in PBS (photo). The sample, now at larger volume and hence a longer visual pathlength, appears quite muddy upon visual inspection.

The absorption spectrum of *trans*-A_2 zinc porphyrin **Zn2**, which contains PEG groups located at the 3,5-positions of the aryl groups, is shown in Figure S4. The extensive broadening of the Soret band is indicative of self-aggregation.

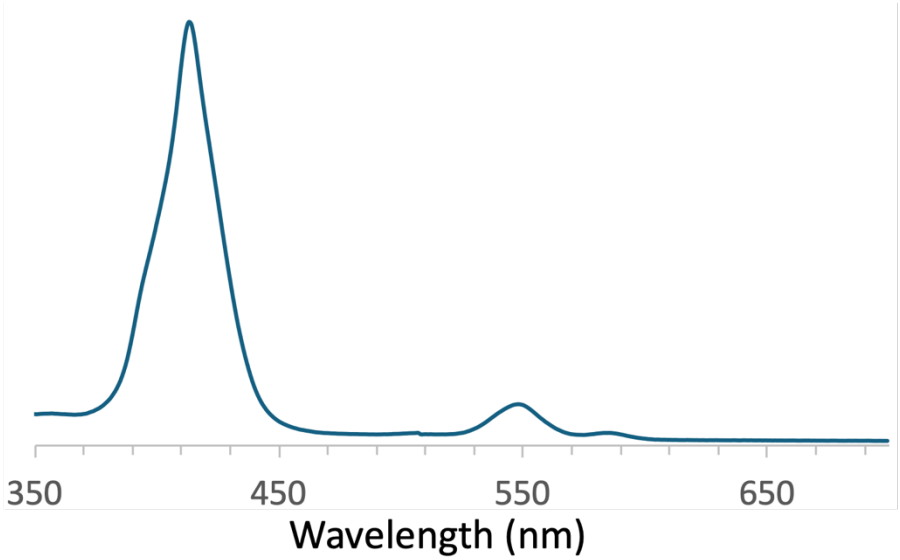


Figure S4. Absorption spectrum of porphyrin **Zn2** at 10 μM in deionized water at room temperature (1-cm pathlength cuvette).

(3) Single-crystal X-ray diffraction data

Table S1. Single-crystal X-ray structure date for **Zn5**

CCDC registry	2321457
Chemical formula	$C_{52}H_{44}N_4O_6Zn$
Formula weight (g/mol)	886.28
Temperature (K)	100
Wavelength (Å)	0.71073
Crystal size (mm)	0.266 × 0.161 × 0.065
Crystal habit	Red block
Crystal system	monoclinic
Space group	P 1 21/n 1
Unit cell dimension, *a* (Å)	10.0085(5)
Unit cell dimension, *b* (Å)	17.5831(9)
Unit cell dimension, *c* (Å)	12.4044(7)
α, deg	90
β, deg	95.778(2)
γ, deg	90
Volume ($Å^3$)	2171.8(2)
Z	2
Density (calculated) (g/cm^3)	1.355
Absorption coefficient (mm^{-1})	0.622
F(000)	924.0
Theta range for data collection, deg	4.702 to 54.2
Index ranges	$-12 \le h \le 12$, $-22 \le k \le 22$, $-15 \le l \le 15$
Reflections collected	37231
Independent reflections	4782 [R int = 0.0399, R sigma = 0.0237]
R_1	0.0334
wR_2	0.0868
R_1 (all data)	0.0353
wR_2 (all data)	0.0883
Largest diff. peak and hole ($eÅ^{-3}$)	1.24 and –0.31

Table S2. Bond lengths for **Zn5**

Atom	Atom	Length/Å
Zn2	O2[1]	2.4122(12)
Zn2	O2	2.4121(12)
Zn2	N2[1]	2.0562(12)
Zn2	N2	2.0562(12)
Zn2	N3[1]	2.0466(12)
Zn2	N3	2.0466(12)
O1	C11	1.375(2)
O1	C26	1.4261(19)
O2	C22	1.445(2)
O2	C25	1.444(2)
O4	C3	1.3751(19)
O4	C8	1.4329(18)
N2	C15	1.3684(18)
N2	C27	1.3694(18)
N3	C1	1.3694(19)
N3	C2	1.3693(18)
C1	C18	1.444(2)
C1	C20	1.396(2)
C2	C14	1.403(2)
C2	C19	1.448(2)
C3	C4	1.395(2)
C3	C17	1.397(2)
C4	C5	1.390(3)
C5	C12	1.383(3)
C6	C7	1.184(3)
C6	C8	1.470(2)
C9	C10	1.178(5)
C9	C26	1.487(4)
C11	C12	1.396(2)
C11	C17	1.398(2)
C13	C16	1.359(2)
C13	C27	1.450(2)
C14	C17	1.4973(19)
C14	C27	1.405(2)
C15	C16	1.4472(19)
C15	C20[1]	1.397(2)
C18	C19	1.357(2)
C22	C23	1.518(3)
C23	C24	1.528(4)
C24	C25	1.519(3)
C26	C21	1.490(6)
C21	C28	1.180(9)

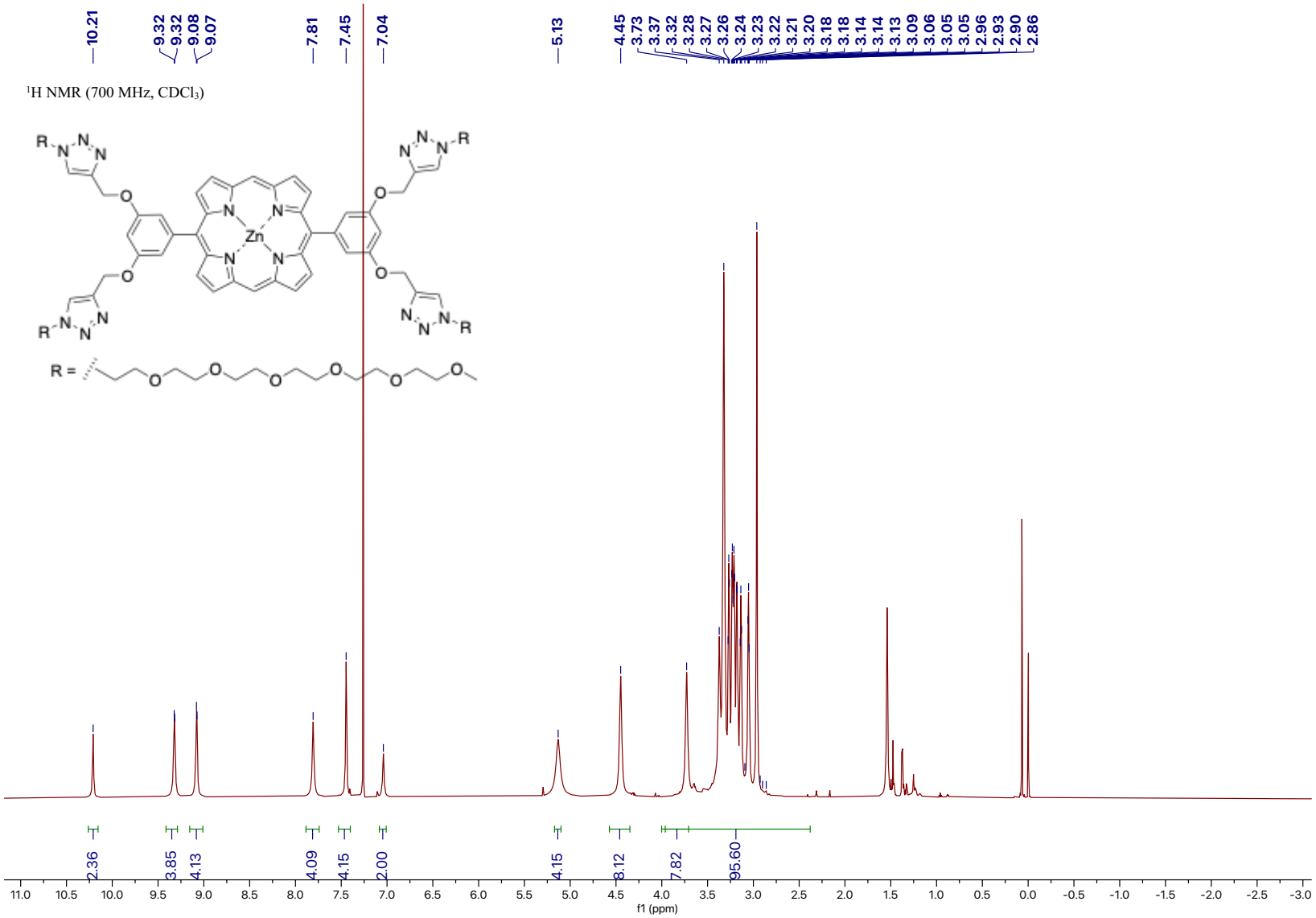
[1]1-X,1-Y,1-Z

Table S3. Bond angles for **Zn5**

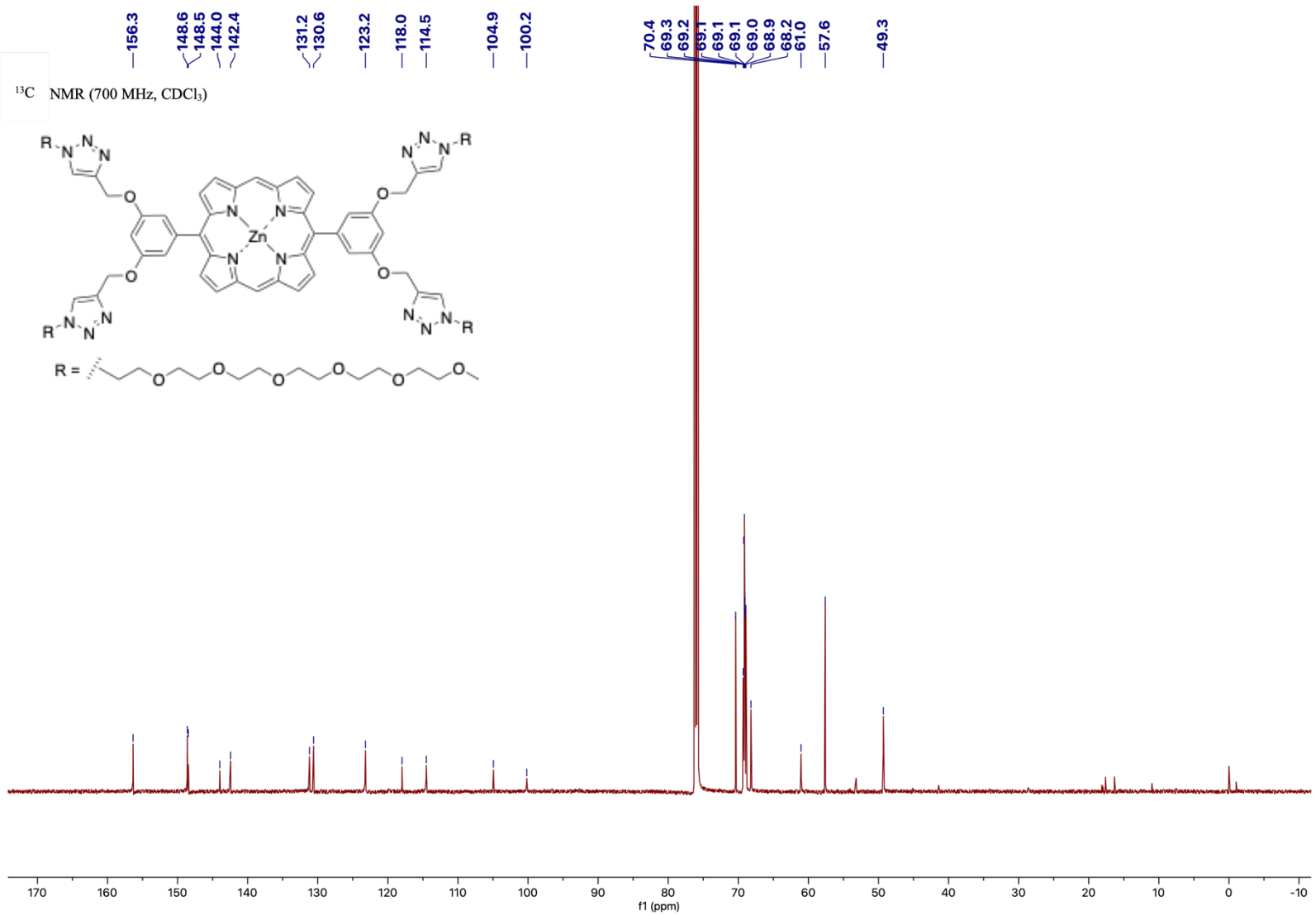
Atom	Atom	Atom	Angle/°
O2	Zn2	O2[1]	180.0
N2	Zn2	O2[1]	88.30(4)
N2[1]	Zn2	O2	88.30(4)
N2[1]	Zn2	O2[1]	91.70(4)
N2	Zn2	O2	91.70(4)
N2[1]	Zn2	N2	180.00(5)
N3	Zn2	O2	90.34(5)
N3	Zn2	O2[1]	89.66(5)
N3[1]	Zn2	O2	89.66(5)
N3[1]	Zn2	O2[1]	90.34(5)
N3	Zn2	N2[1]	90.86(5)
N3[1]	Zn2	N2[1]	89.14(5)
N3[1]	Zn2	N2	90.86(5)
N3	Zn2	N2	89.14(5)
N3	Zn2	N3[1]	180.0
C11	O1	C26	117.68(13)
C22	O2	Zn2	118.74(10)
C25	O2	Zn2	121.87(11)
C25	O2	C22	108.03(15)
C3	O4	C8	118.17(13)
C15	N2	Zn2	125.66(9)
C15	N2	C27	106.74(12)
C27	N2	Zn2	127.32(10)
C1	N3	Zn2	125.64(10)
C1	N3	C2	106.85(12)
C2	N3	Zn2	127.40(10)
N3	C1	C18	109.80(13)
N3	C1	C20	125.35(13)
C20	C1	C18	124.84(14)
N3	C2	C14	125.48(13)
N3	C2	C19	109.47(13)
C14	C2	C19	125.03(13)
O4	C3	C4	124.41(15)
O4	C3	C17	114.43(13)
C4	C3	C17	121.12(15)
C5	C4	C3	118.49(16)
C12	C5	C4	122.08(15)
C7	C6	C8	177.59(18)
O4	C8	C6	113.18(14)
C10	C9	C26	178.1(3)
O1	C11	C12	124.20(15)
O1	C11	C17	114.49(13)
C12	C11	C17	121.31(15)
C5	C12	C11	118.44(16)
C16	C13	C27	106.89(13)
C2	C14	C17	116.89(13)
C2	C14	C27	125.40(13)
C27	C14	C17	117.71(13)
N2	C15	C16	109.94(12)
N2	C15	C20[1]	125.01(13)
C20[1]	C15	C16	125.03(13)
C13	C16	C15	106.74(13)
C3	C17	C11	118.53(14)
C3	C17	C14	120.97(14)
C11	C17	C14	120.48(14)
C19	C18	C1	106.85(13)
C18	C19	C2	107.01(13)
C1	C20	C15[1]	127.27(13)
O2	C22	C23	104.27(17)
C22	C23	C24	102.50(18)
C25	C24	C23	104.23(18)
O2	C25	C24	107.41(19)
O1	C26	C9	107.60(16)
O1	C26	C21	107.2(2)
N2	C27	C13	109.68(12)
N2	C27	C14	125.18(13)
C14	C27	C13	125.12(13)
C28	C21	C26	178.7(6)

[1]1-X,1-Y,1-Z

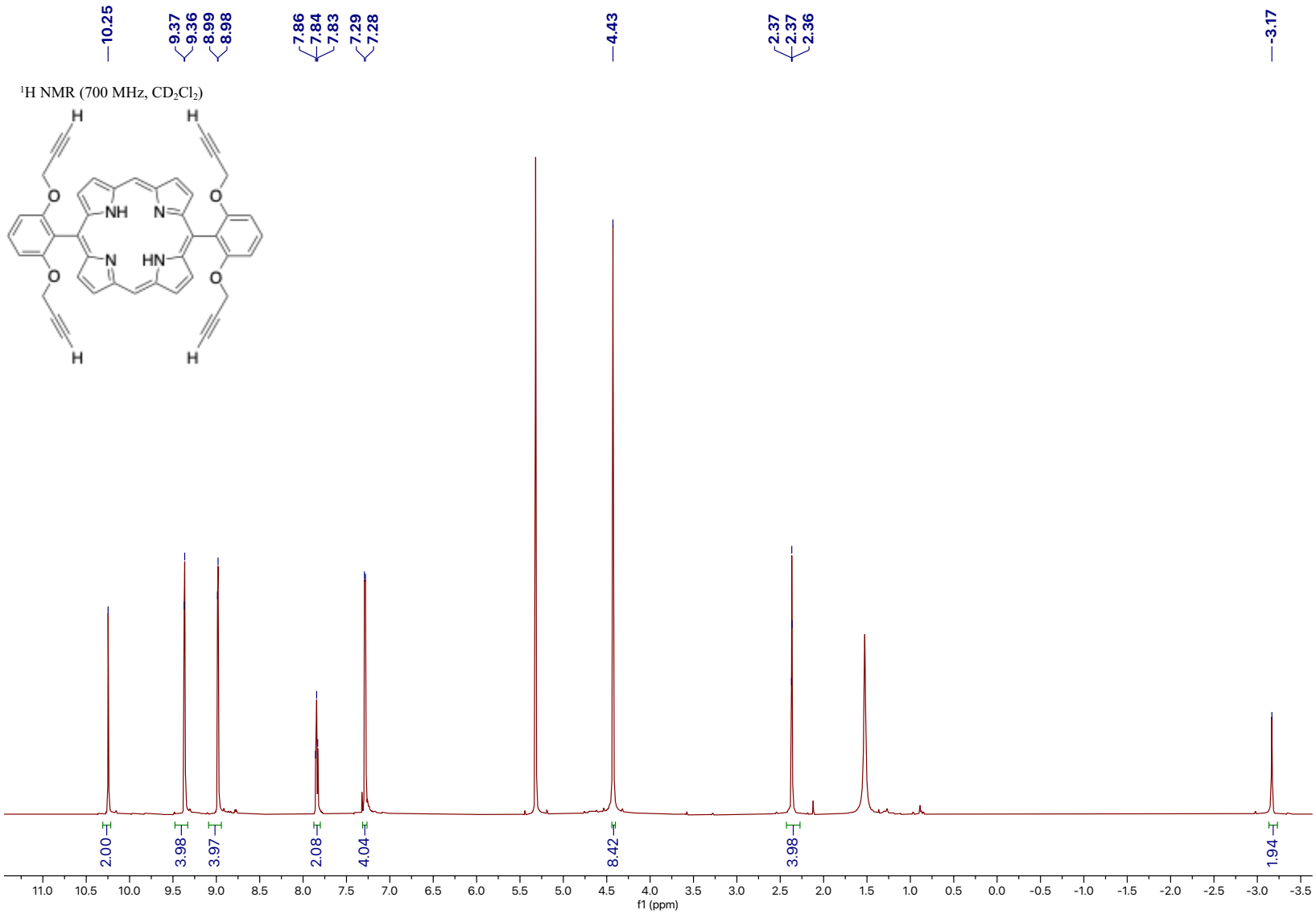
(4) Spectral data



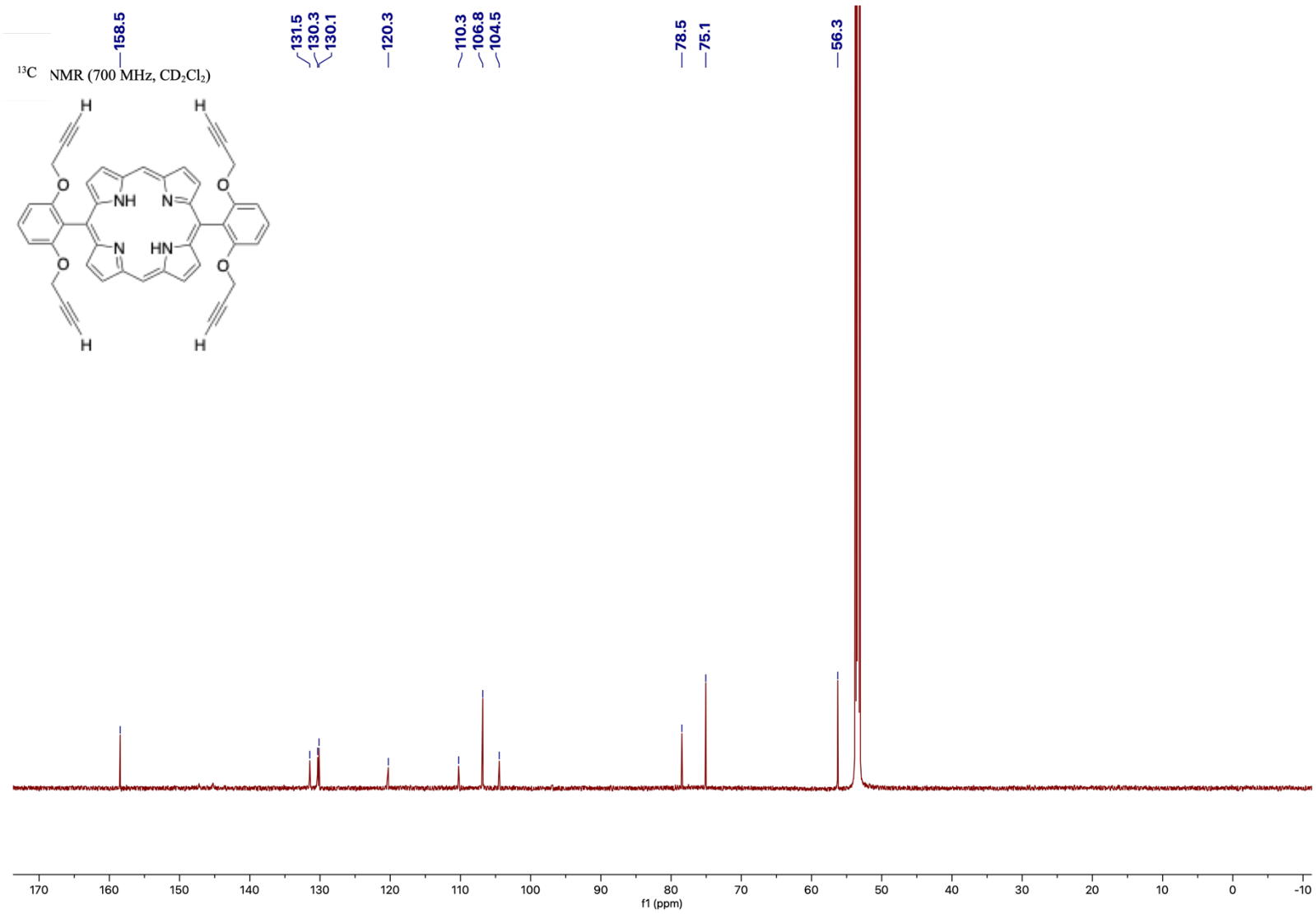
^{1}H NMR spectrum of **Zn2** (in $CDCl_3$)



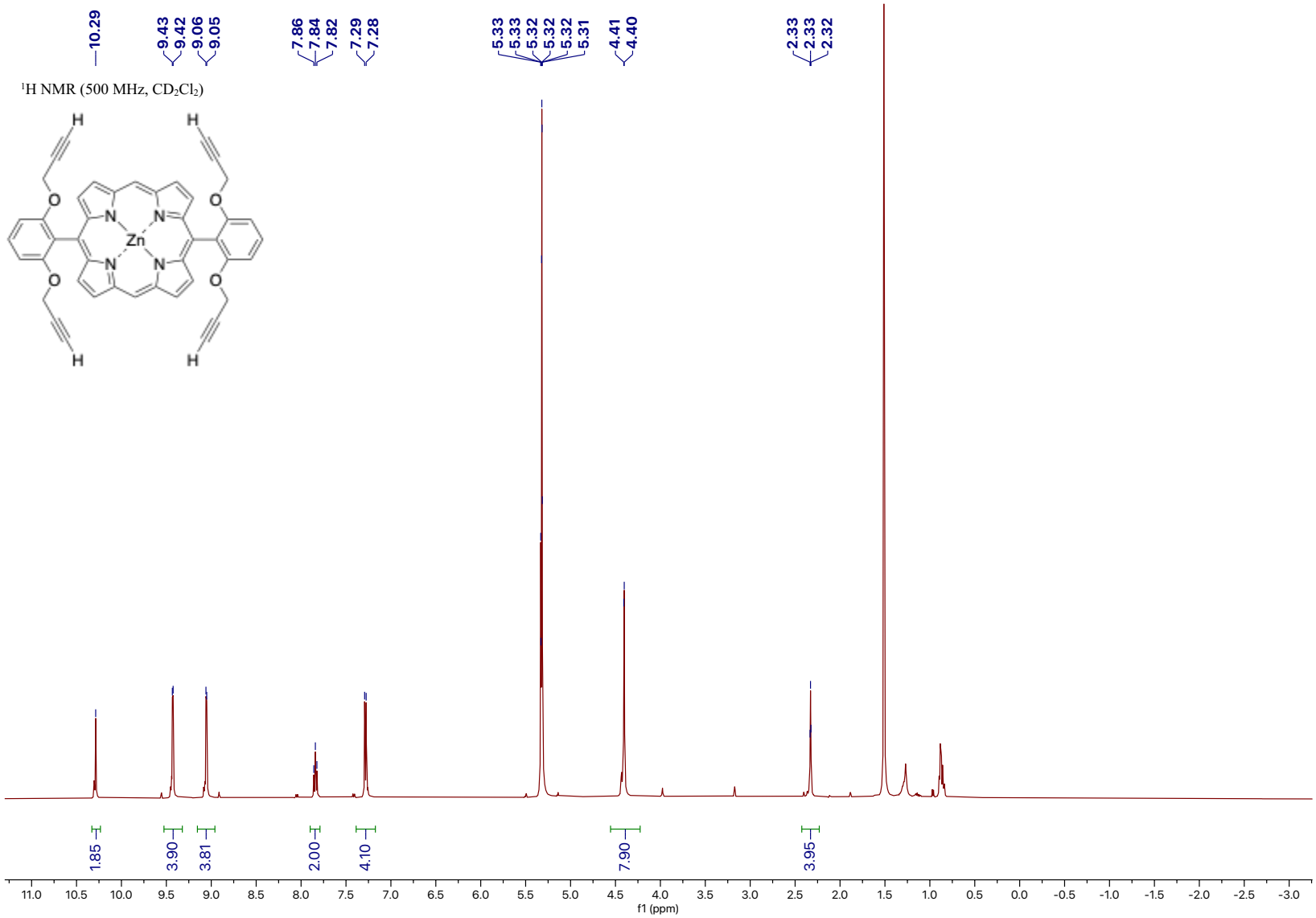
$^{13}C\{^{1}H\}$ NMR spectrum of **Zn2** (in $CDCl_3$)



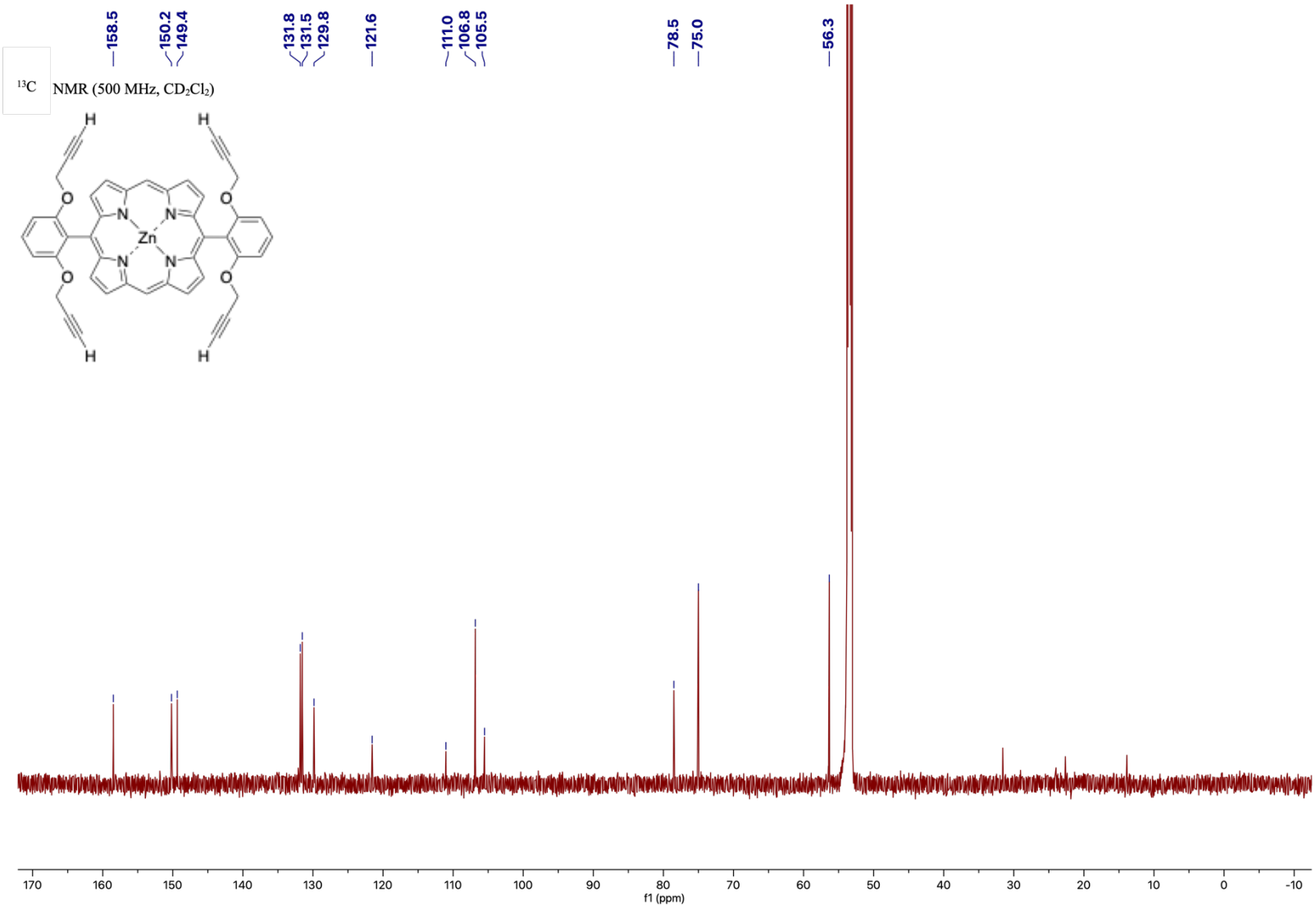
^{1}H NMR spectrum of **5** (in CD_2Cl_2)



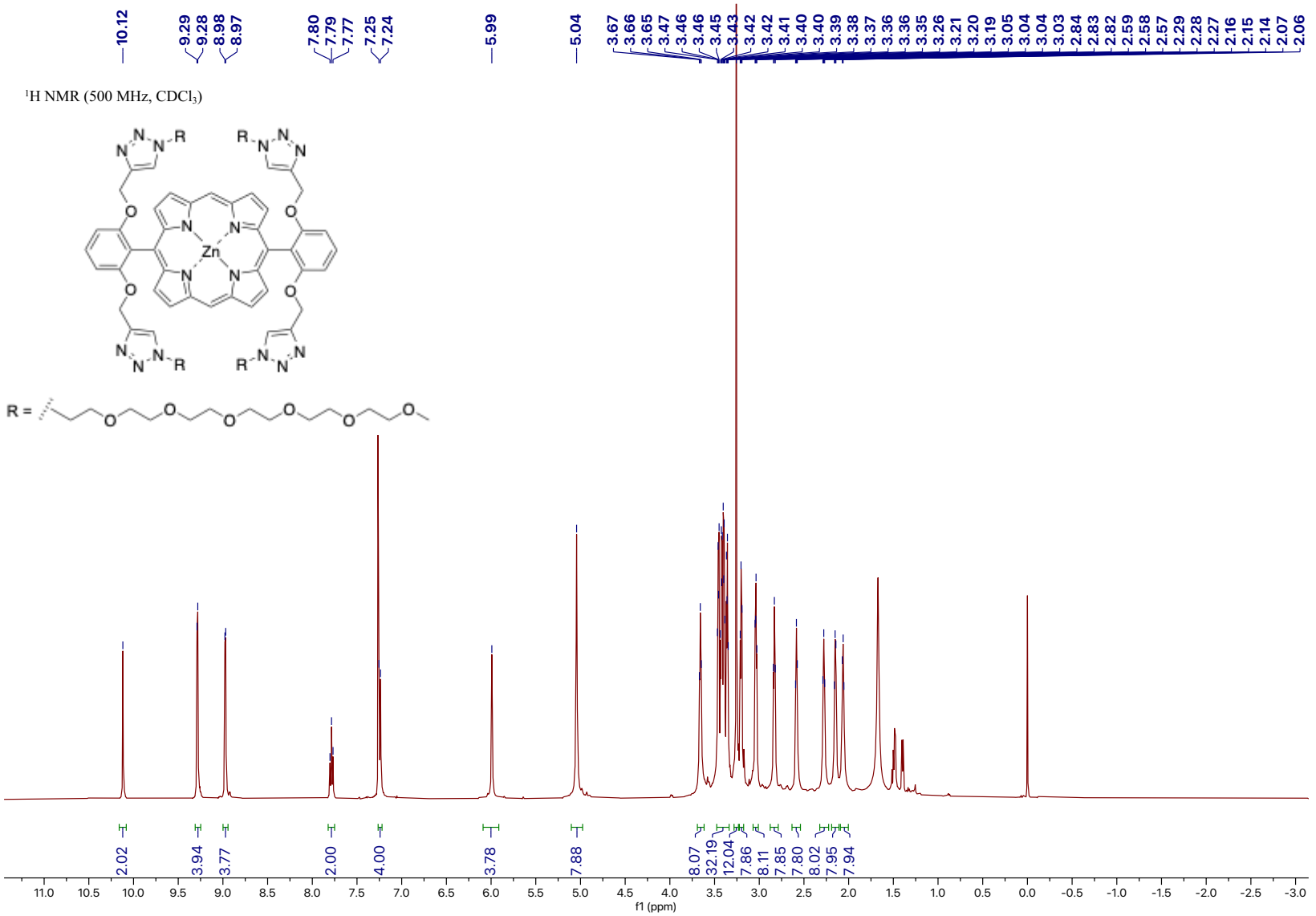
$^{13}C\{^{1}H\}$ NMR spectrum of **5** (in CD_2Cl_2)



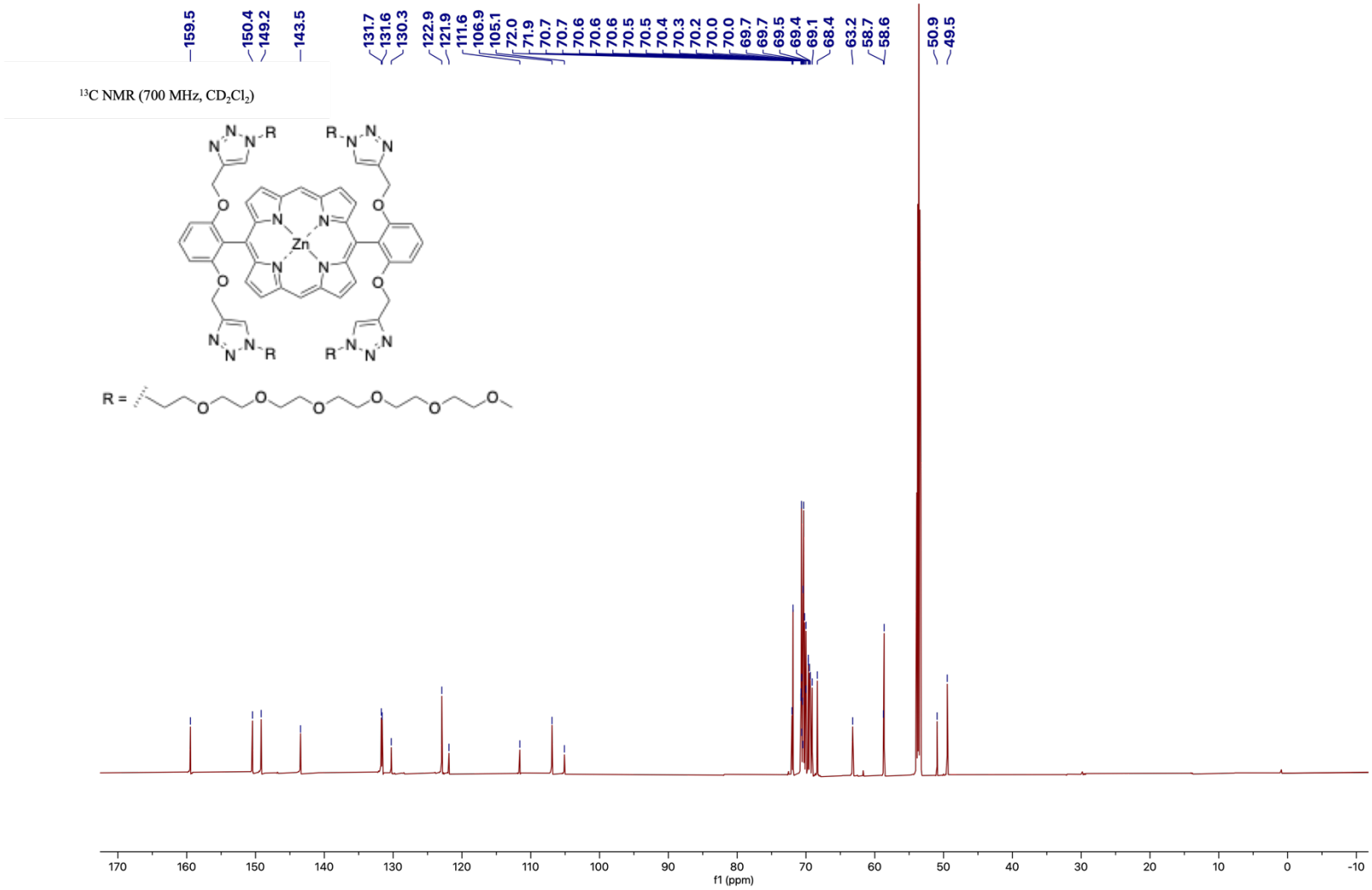
^{1}H NMR spectrum of **Zn5** (in CD_2Cl_2)



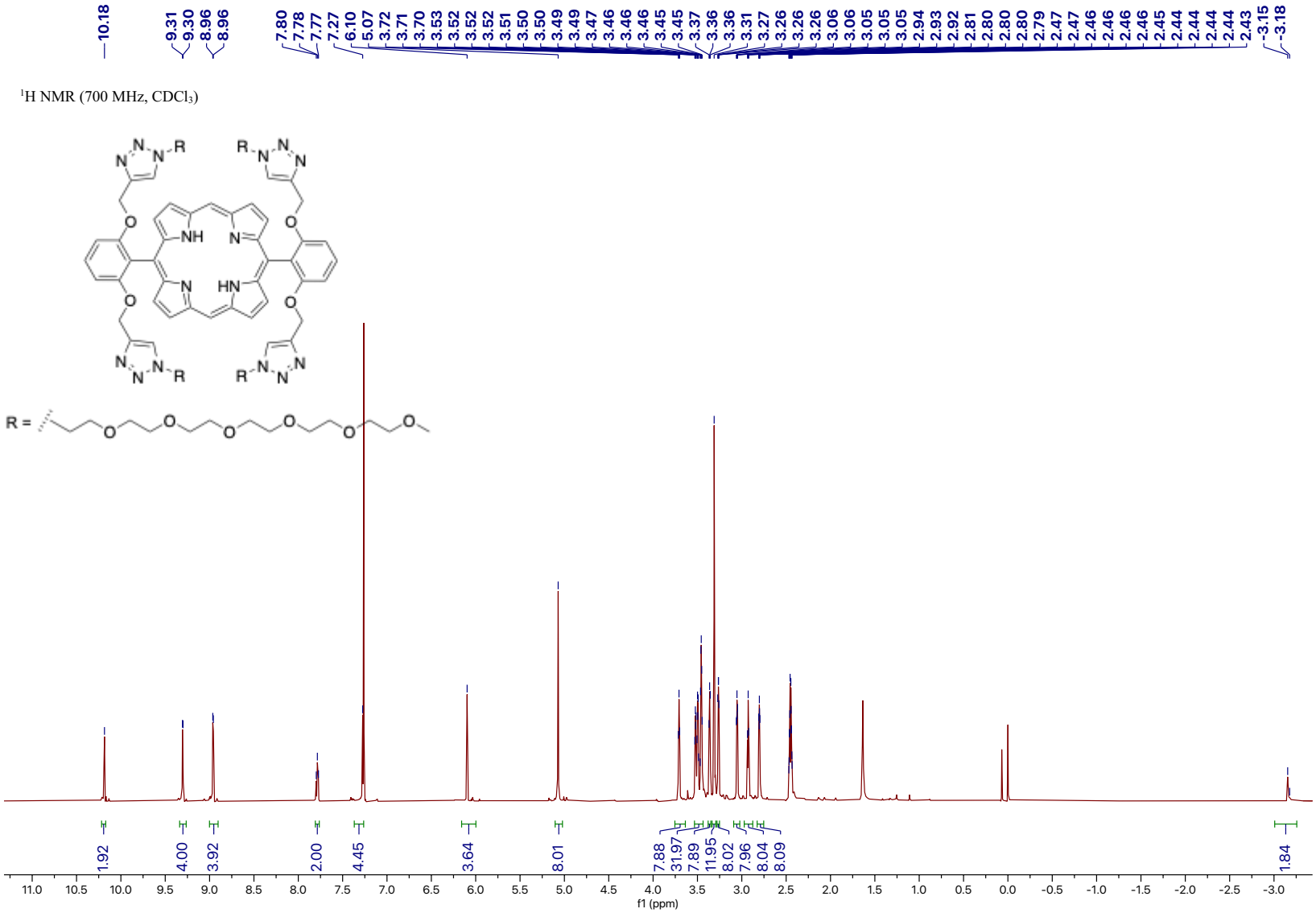
$^{13}C\{^{1}H\}$ NMR spectrum of **Zn5** (in CD_2Cl_2)



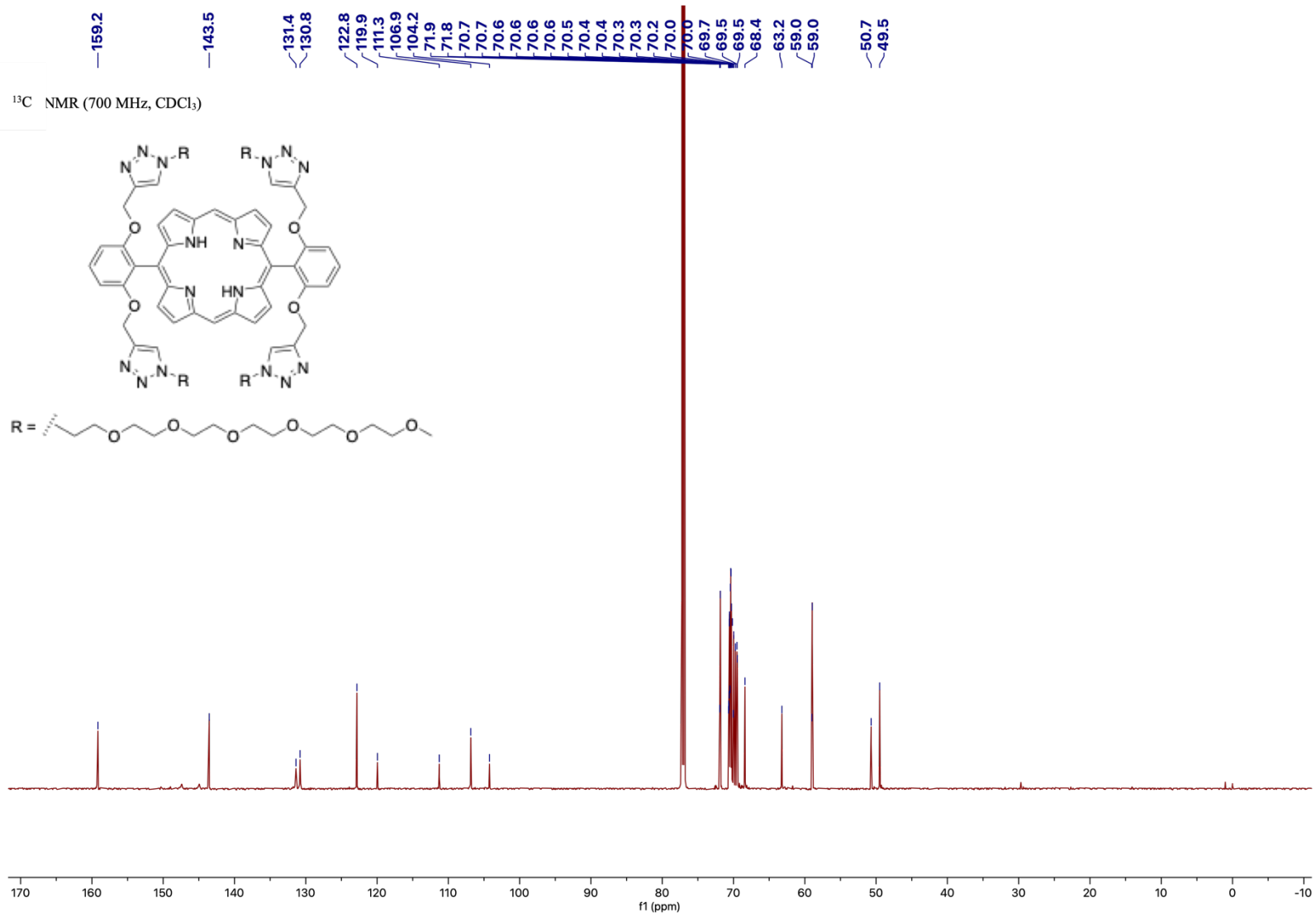
[1]H NMR spectrum of **Zn6** (in $CDCl_3$)



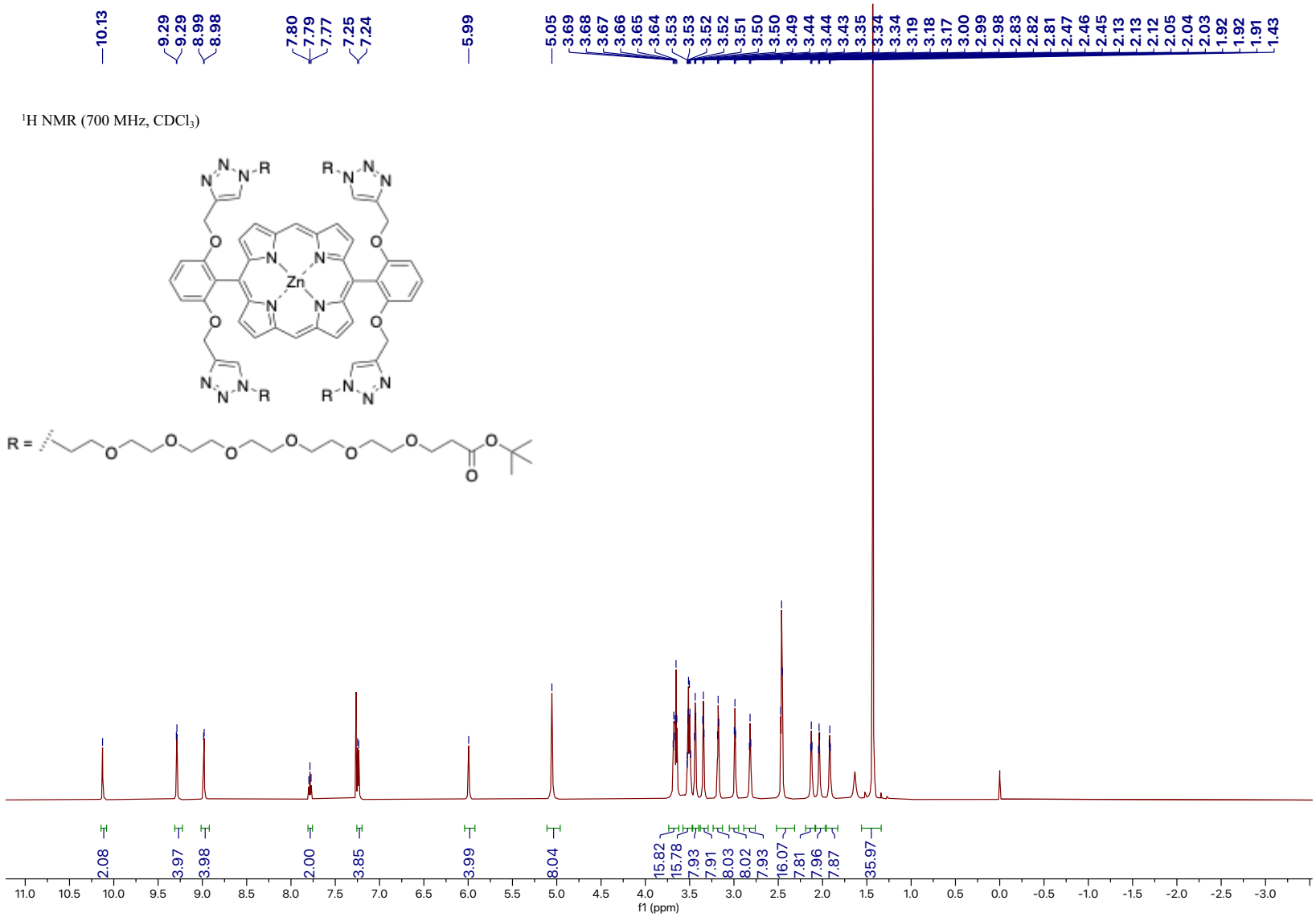
$^{13}C\{^{1}H\}$ NMR spectrum of **Zn6** (in CD_2Cl_2)



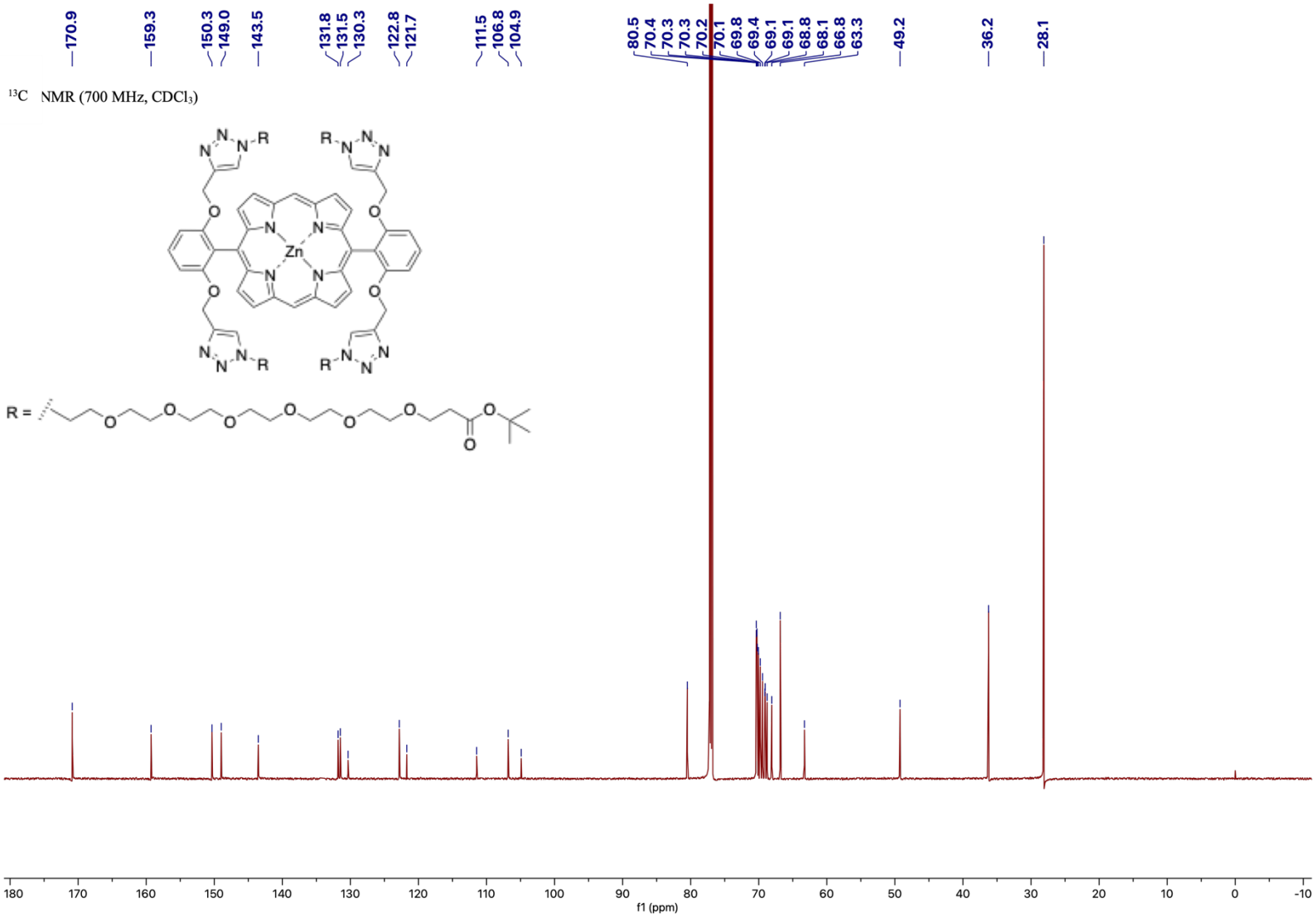
[1]H NMR spectrum of **6** (in $CDCl_3$)



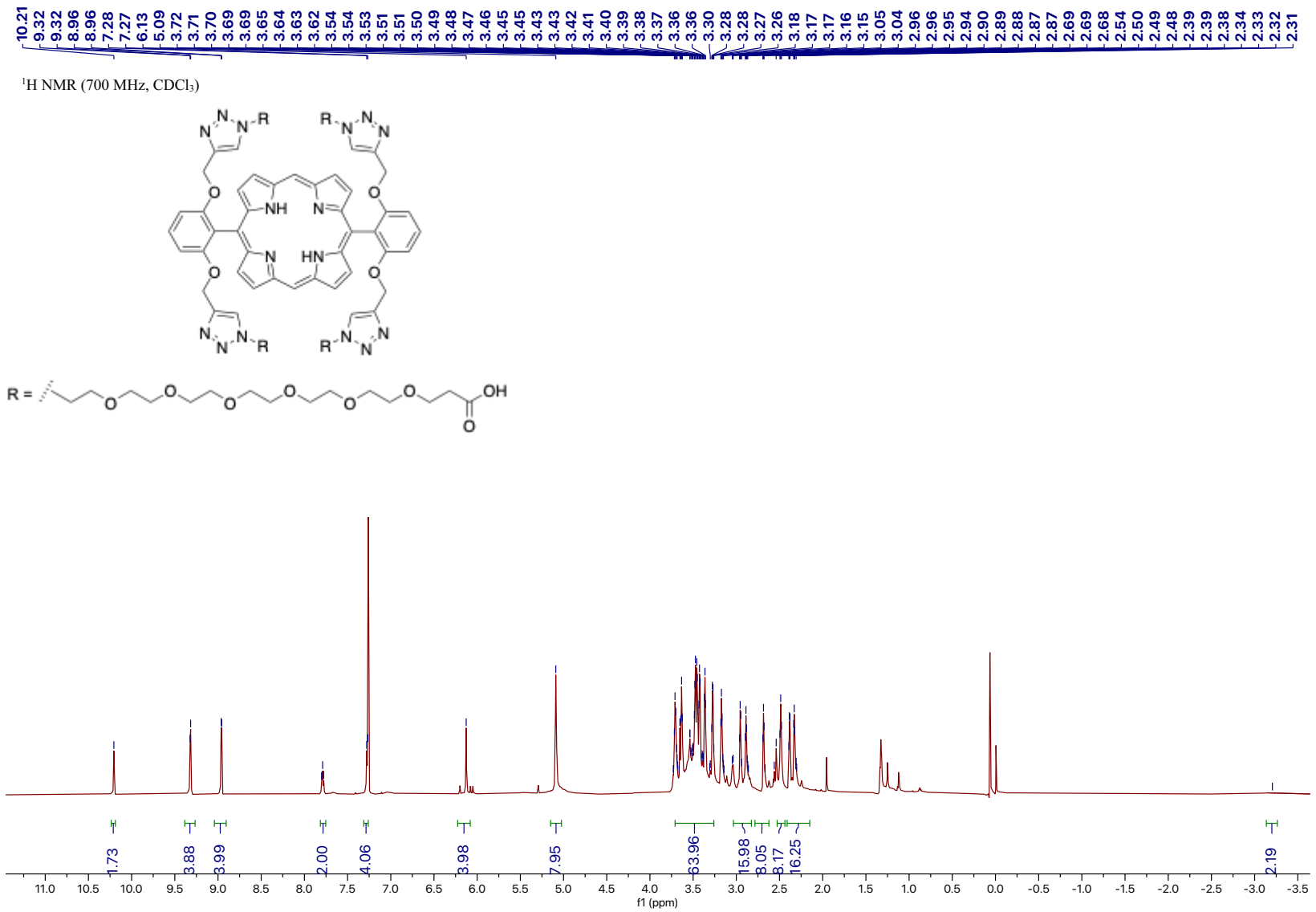
$^{13}C\{^{1}H\}$ NMR spectrum of **6** (in $CDCl_3$)



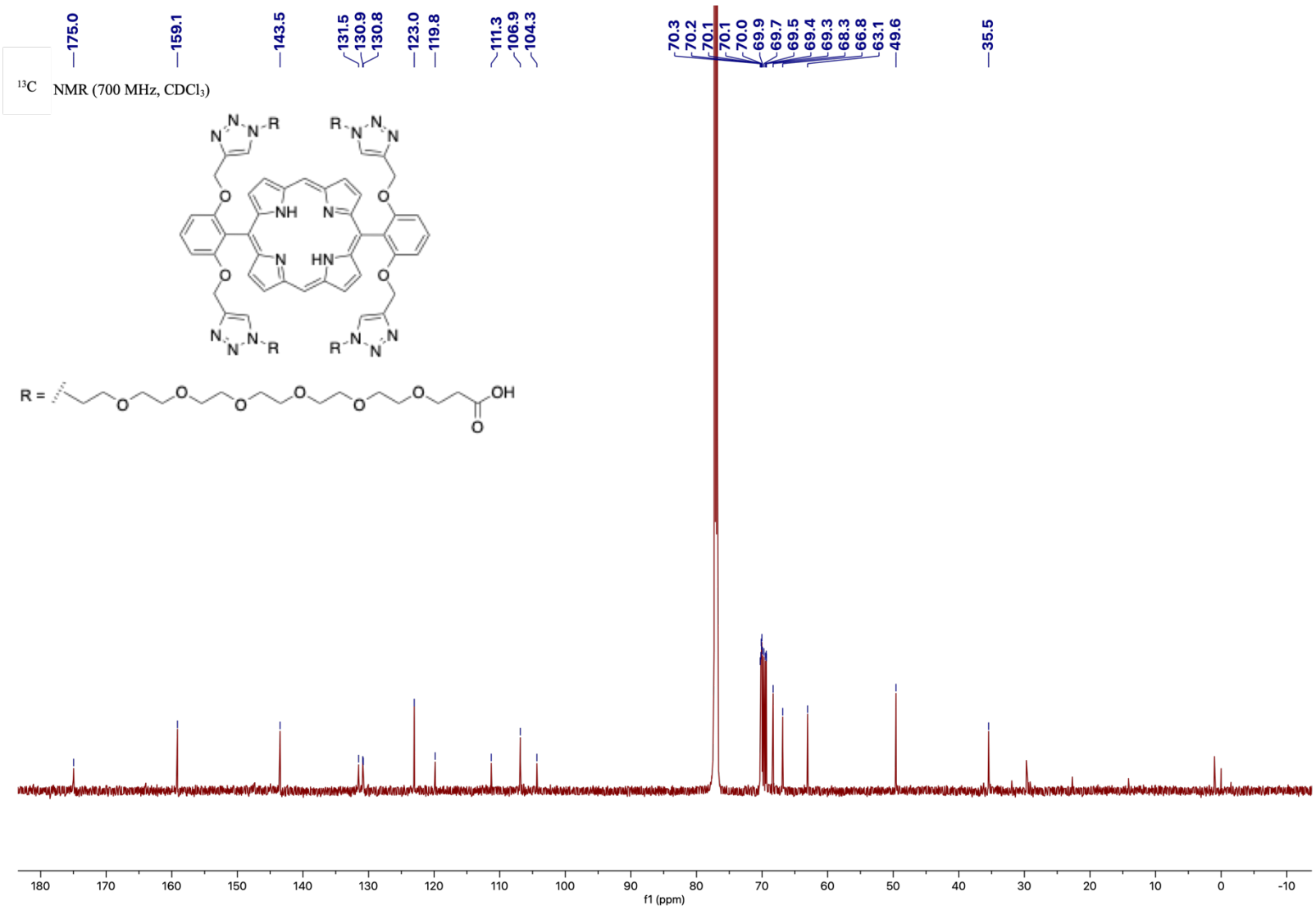
^{1}H NMR spectrum of **Zn7** (in $CDCl_3$)



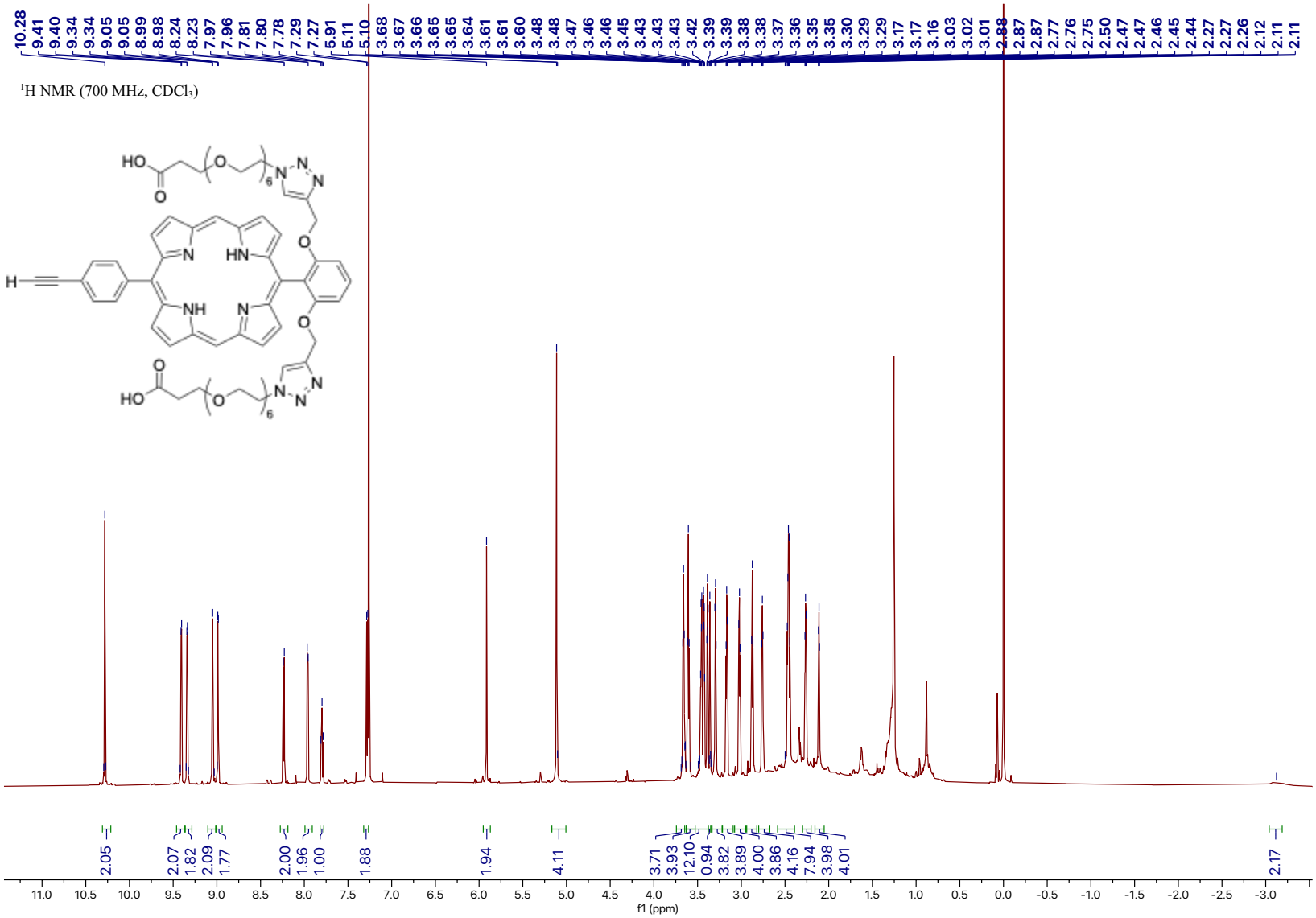
$^{13}C\{^{1}H\}$ NMR spectrum of **Zn7** (in $CDCl_3$)



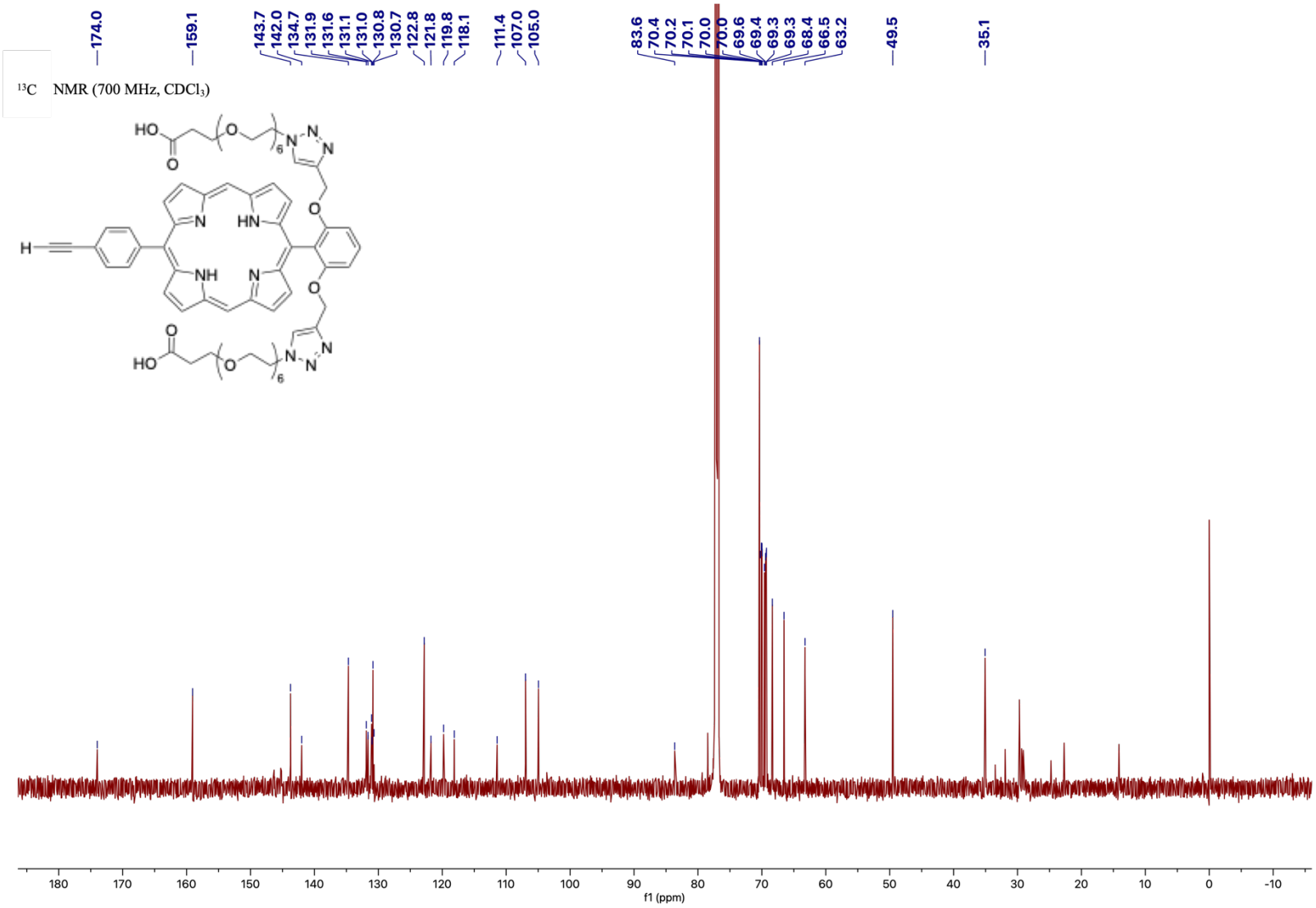
^{1}H NMR spectrum of **8** (in $CDCl_3$)



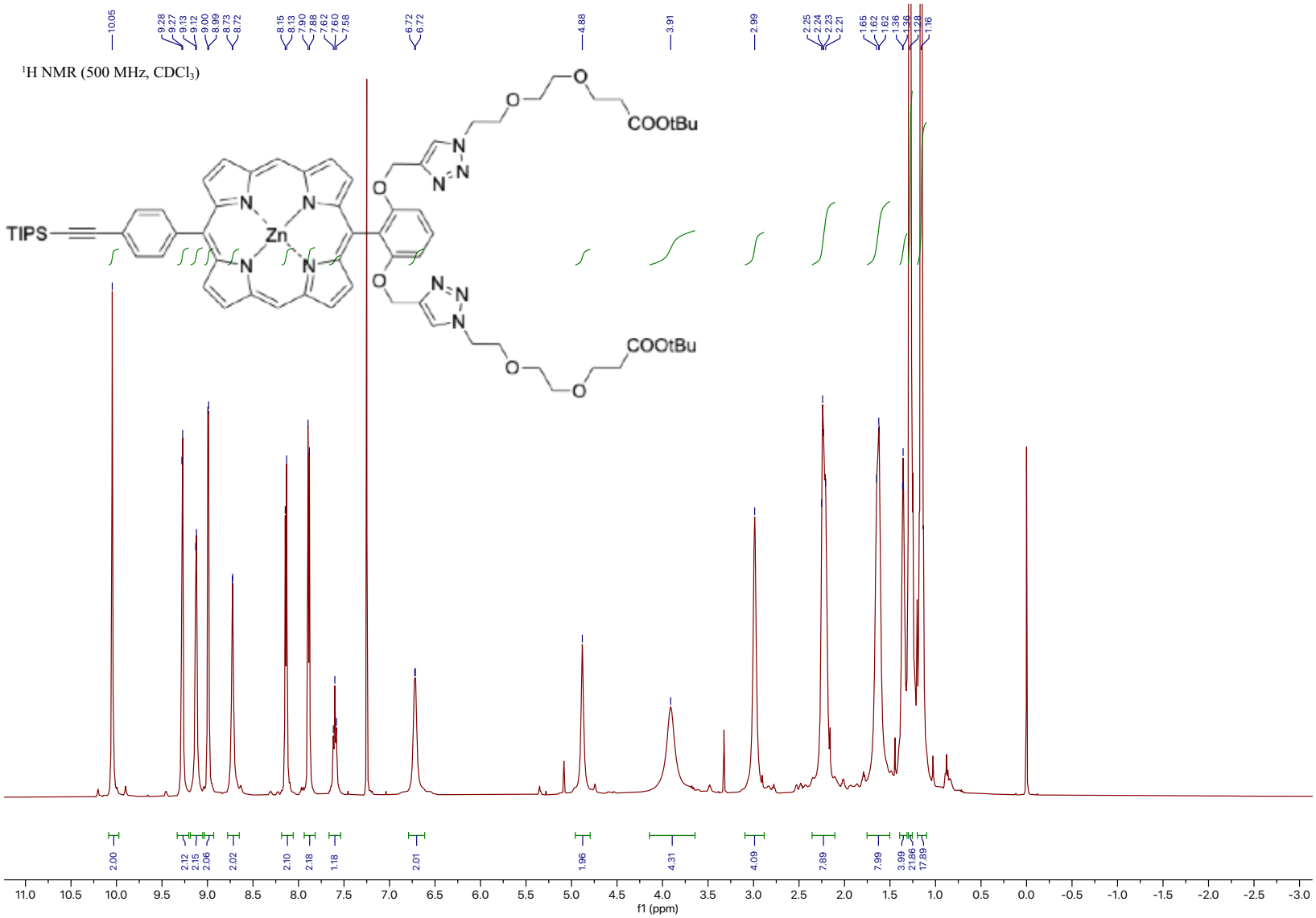
$^{13}C\{^1H\}$ NMR spectrum of **8** (in $CDCl_3$)



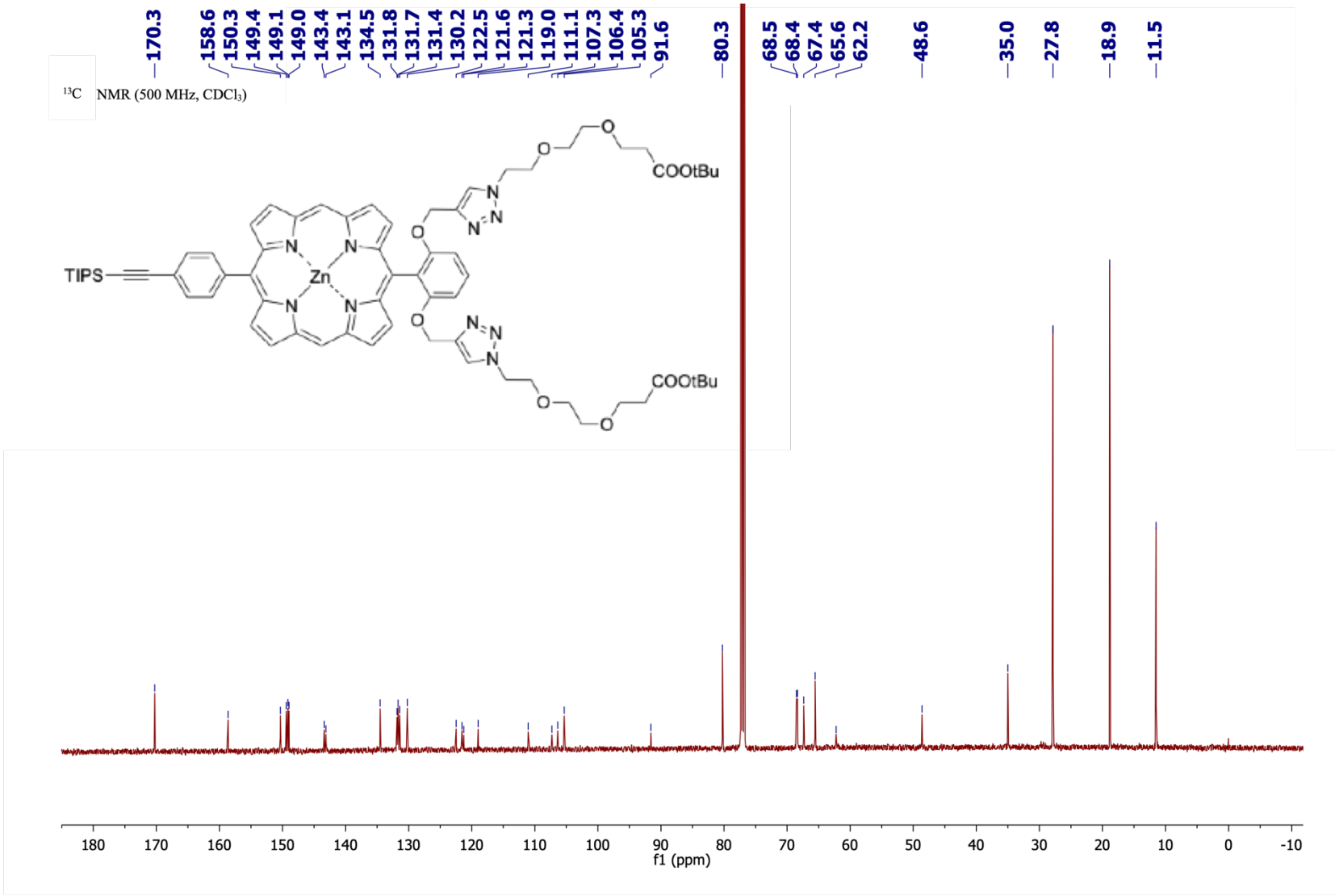
^{1}H NMR spectrum of **11** (in $CDCl_3$)



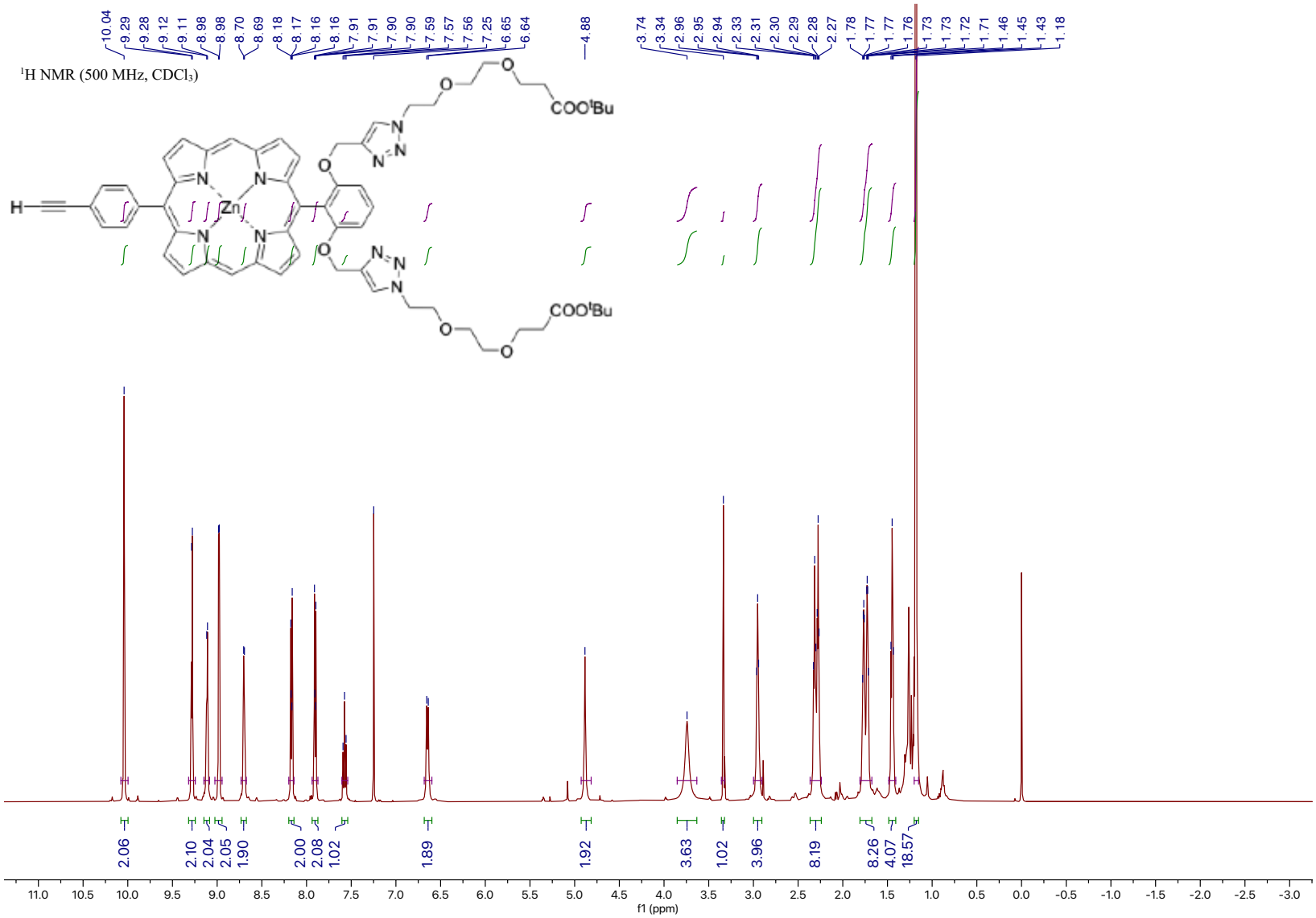
$^{13}C\{^{1}H\}$ NMR spectrum of **11** (in $CDCl_3$)



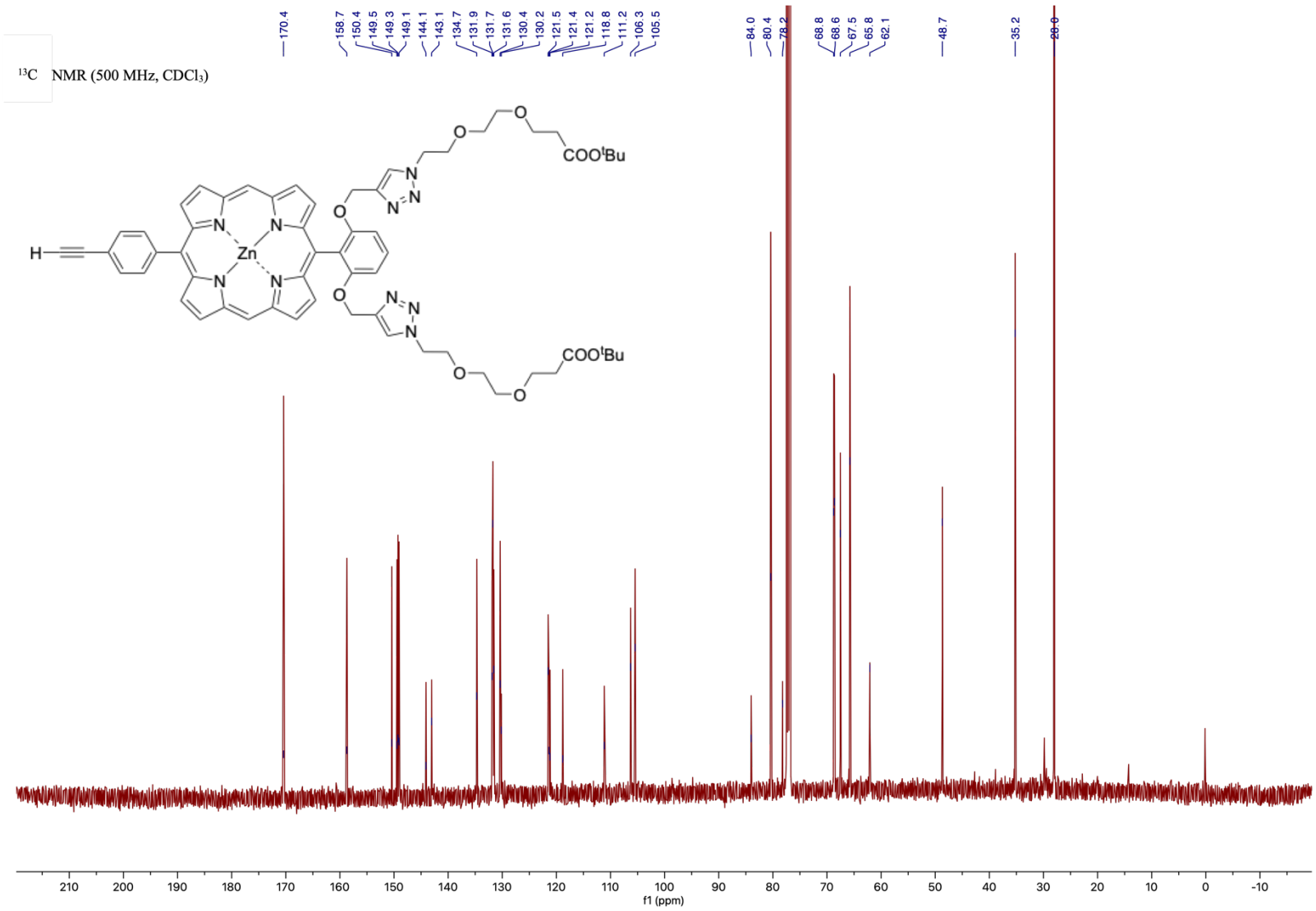
[1]H NMR spectrum of **Zn12** (in $CDCl_3$)



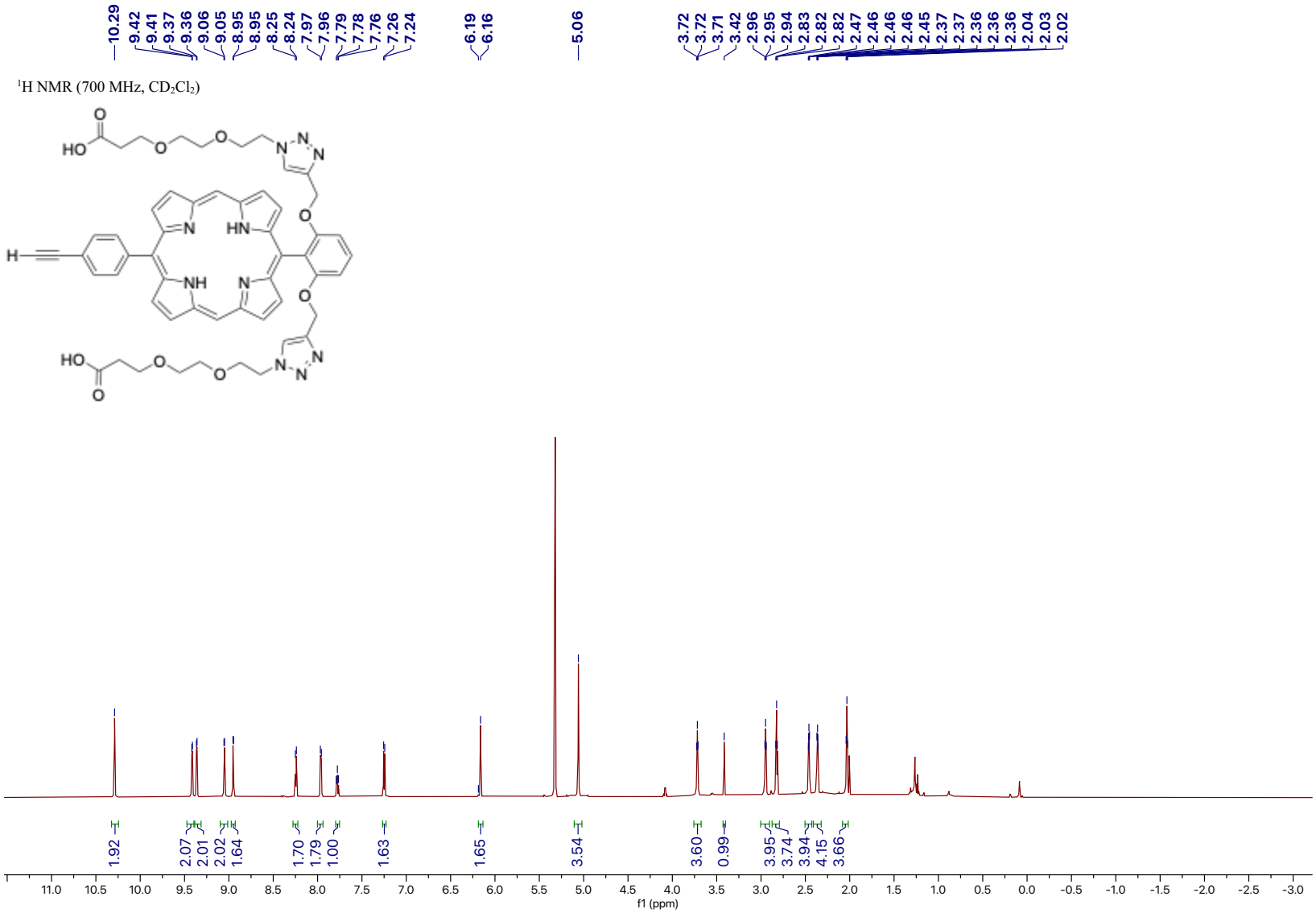
$^{13}C\{^{1}H\}$ NMR spectrum of **Zn12** (in $CDCl_3$)



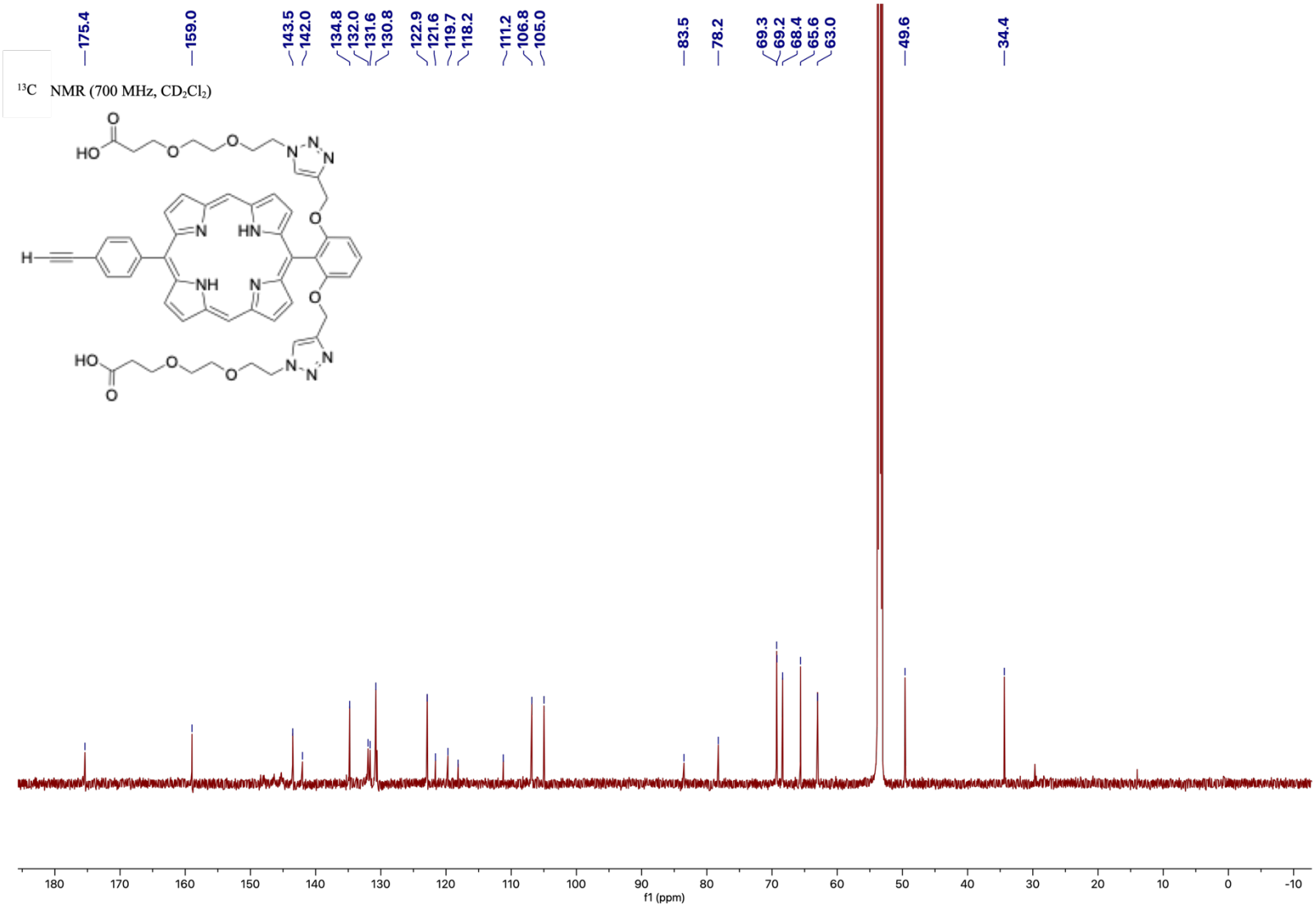
[1]H NMR spectrum of **Zn13** (in $CDCl_3$)



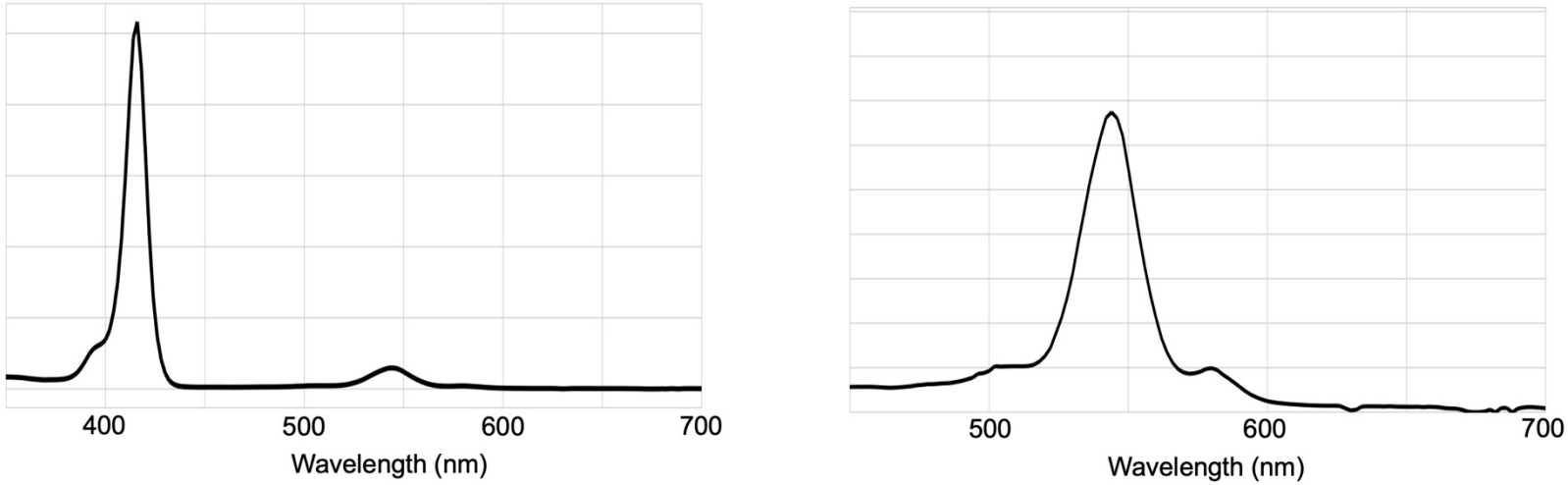
$^{13}C\{^{1}H\}$ NMR spectrum of **Zn13** (in $CDCl_3$)



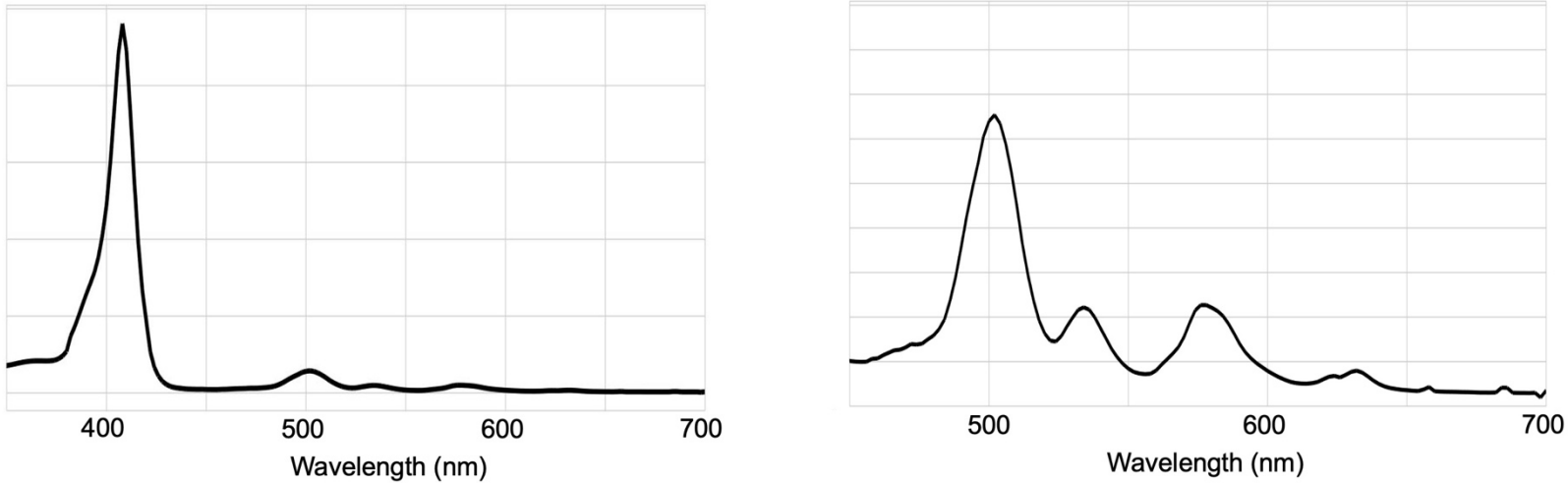
^{1}H NMR spectrum of **14** (in CD_2Cl_2)



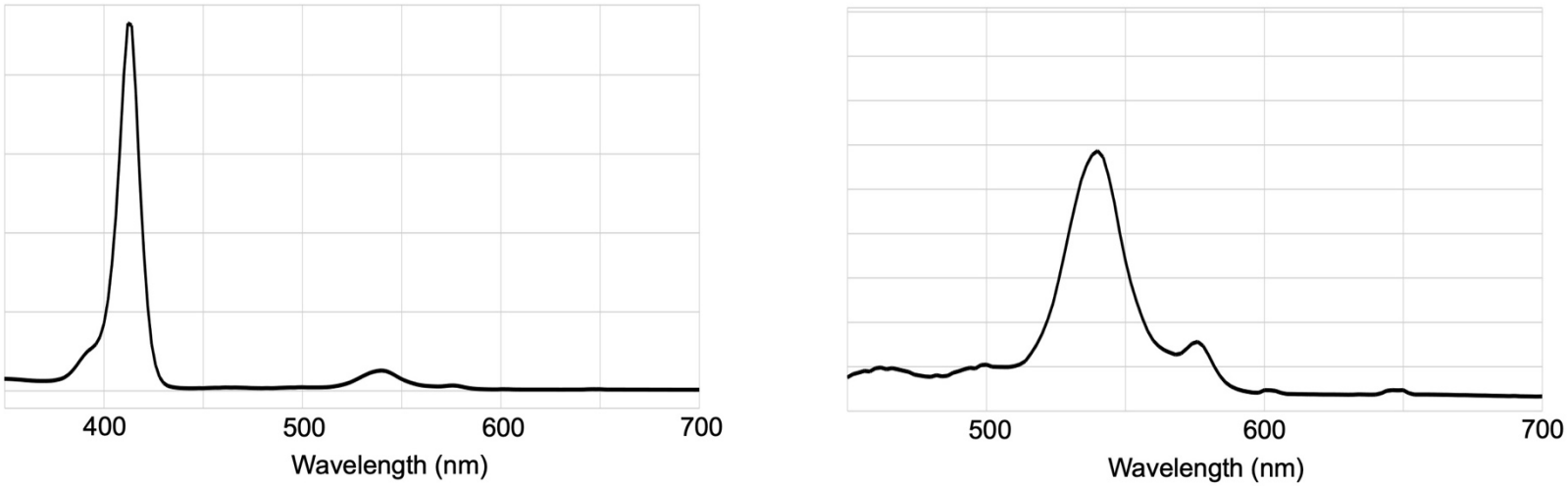
$^{13}C\{^{1}H\}$ NMR spectrum of **14** (in CD_2Cl_2)



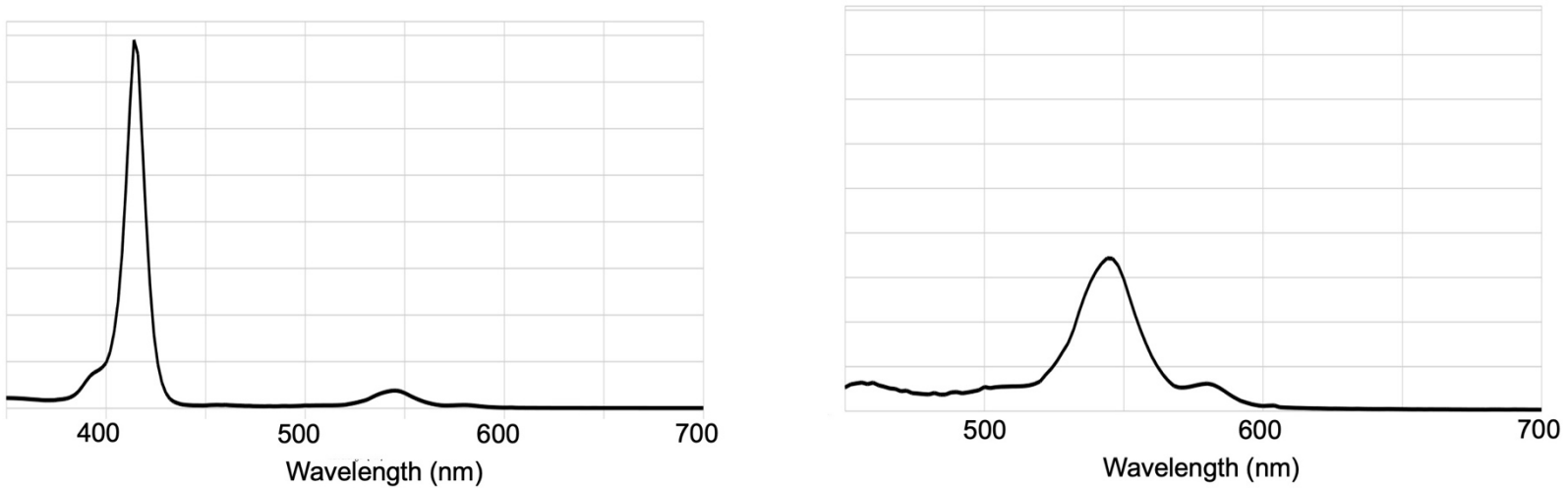
Absorption spectrum of **Zn2** (in toluene)



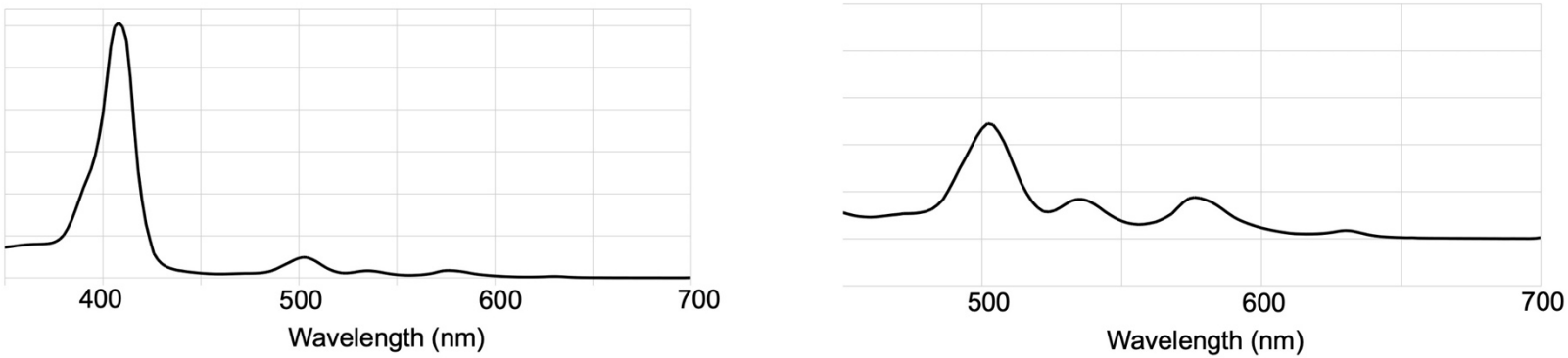
Absorption spectrum of **5** (in toluene)



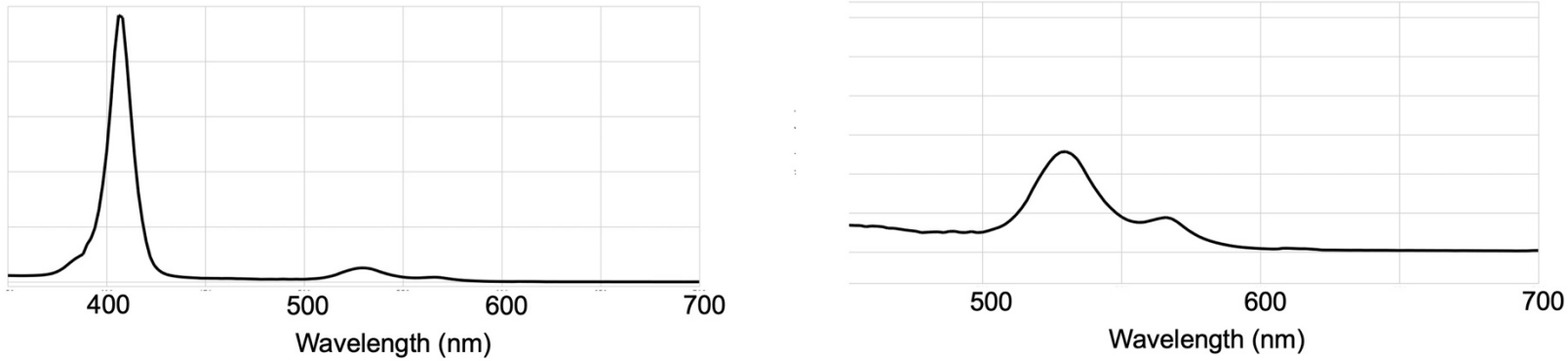
Absorption spectrum of **Zn5** (in toluene)



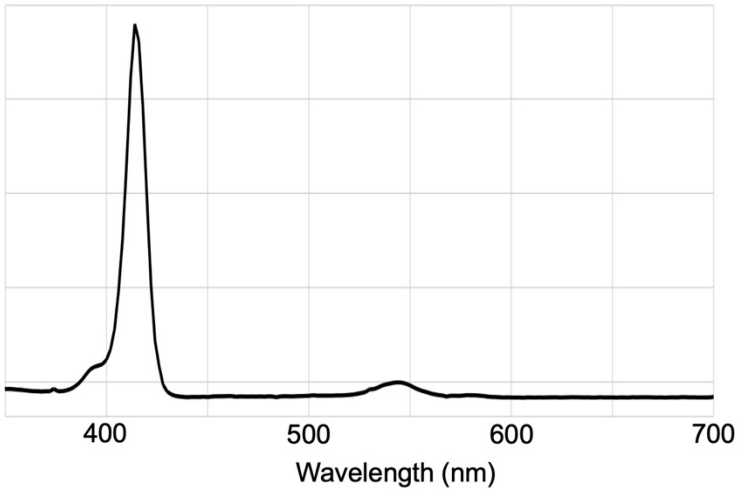
Absorption spectrum of **Zn6** (in toluene)

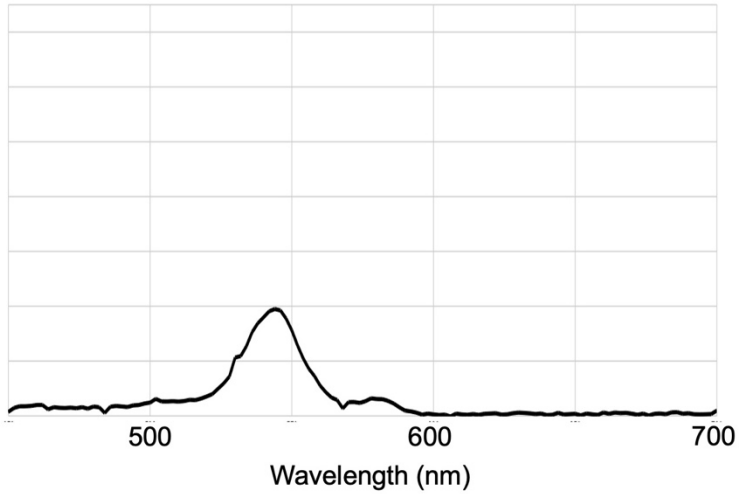


Absorption spectrum of **6** (in toluene)

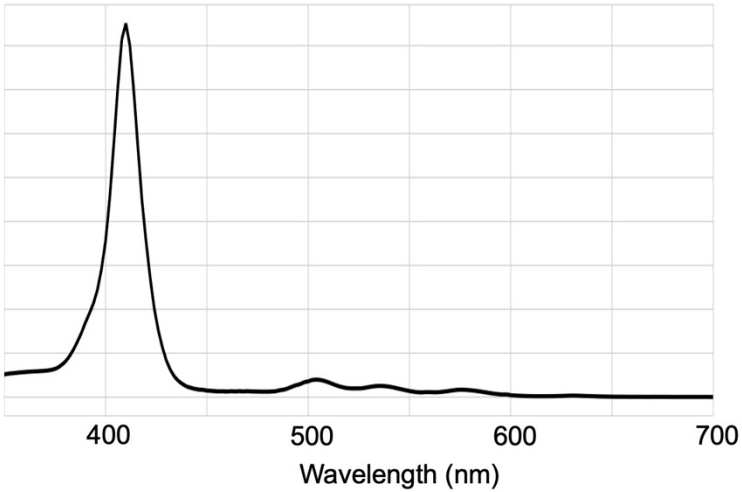


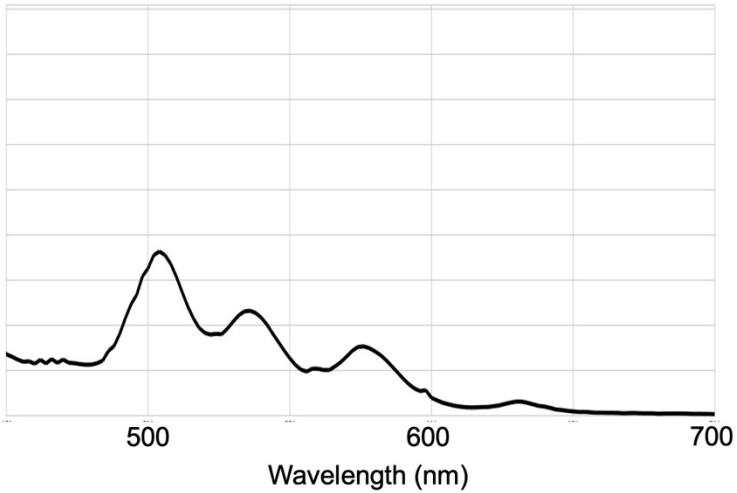
Absorption spectrum of **Cu6** (in toluene)



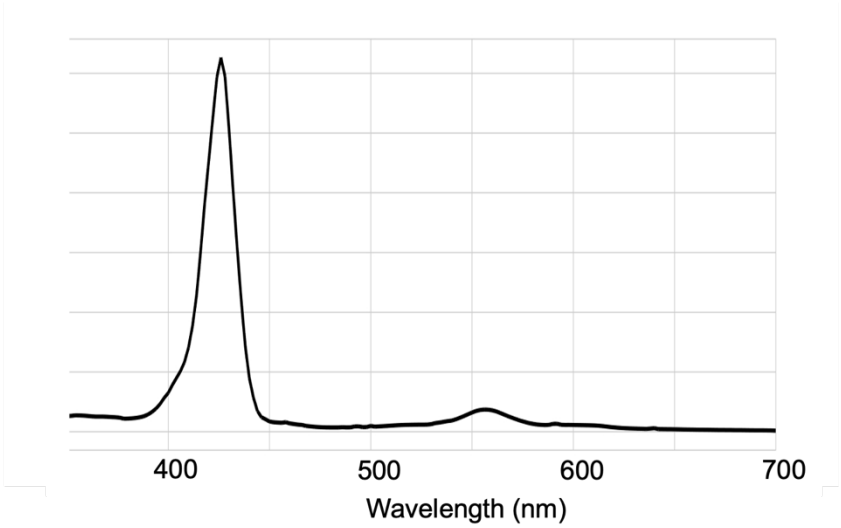


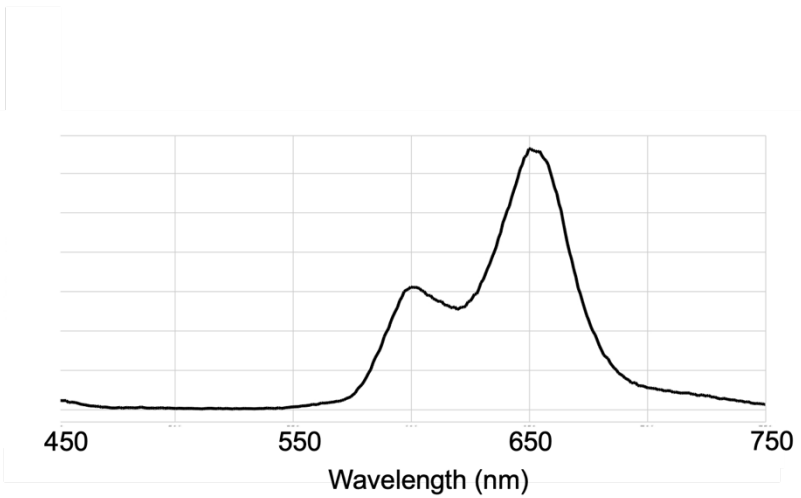
Absorption spectrum of **Zn7** (in toluene)



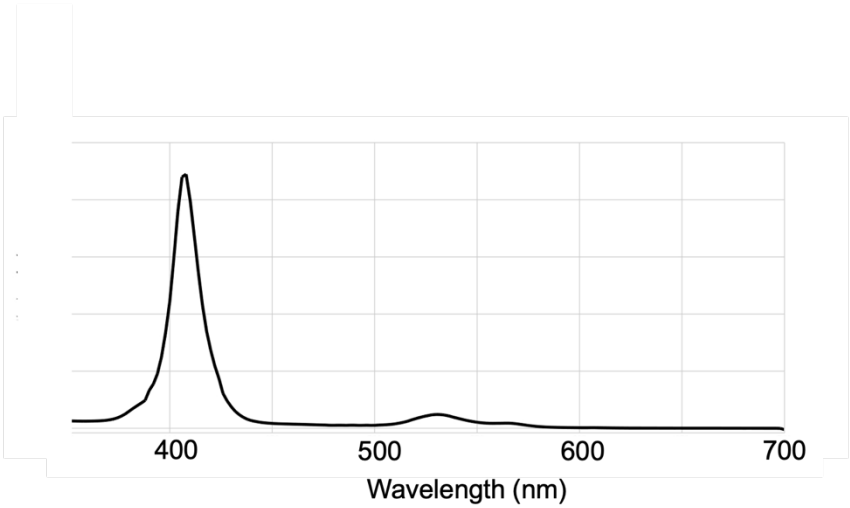


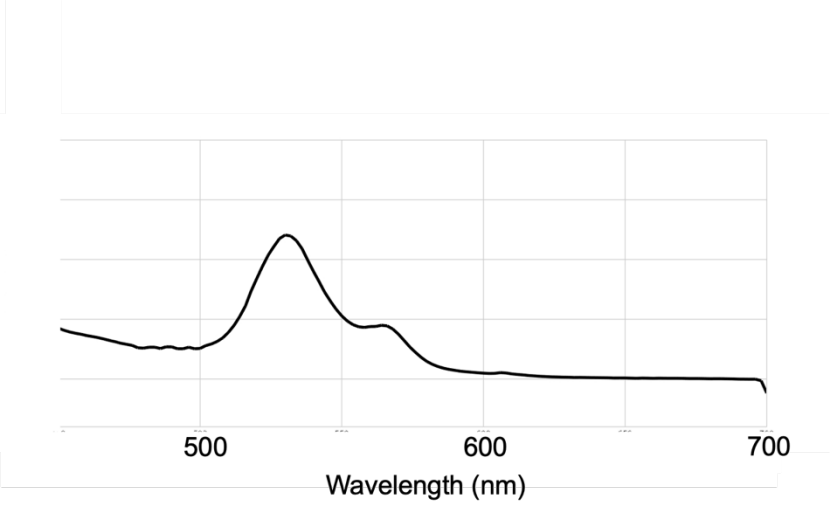
Absorption spectrum of **8** (in DMSO)



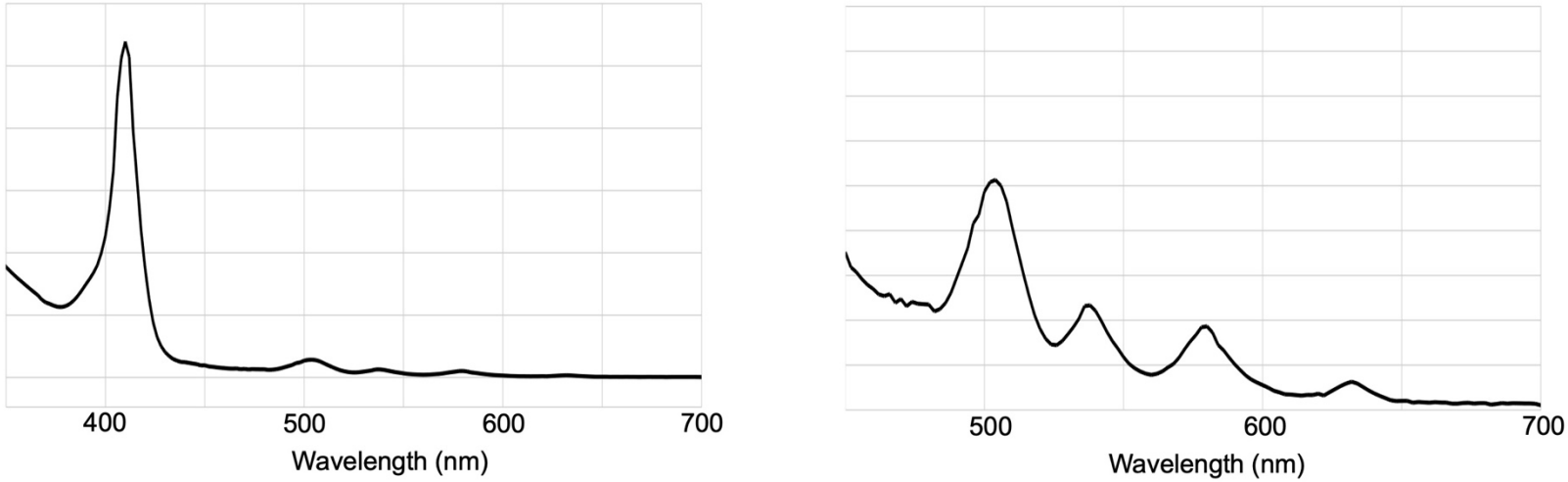


Absorption and emission spectra of **Zn8** (in DMSO)

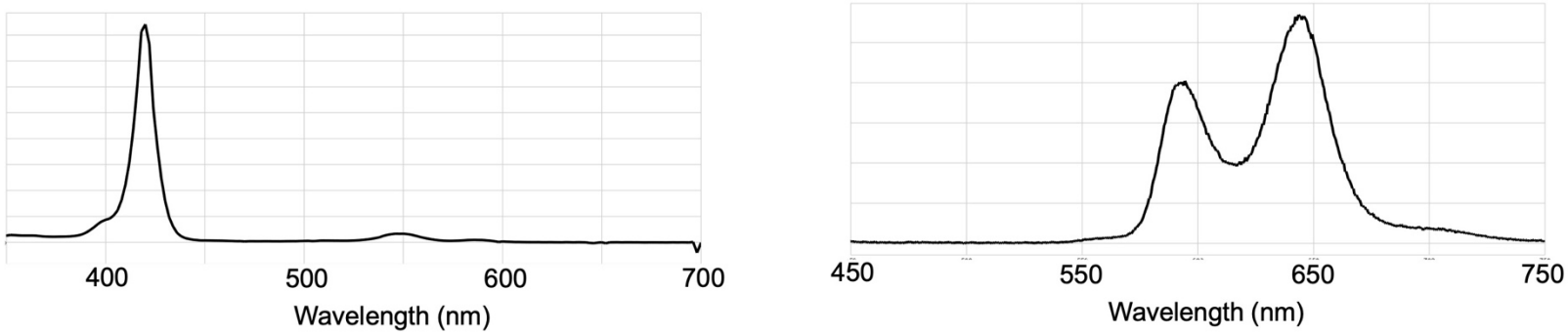




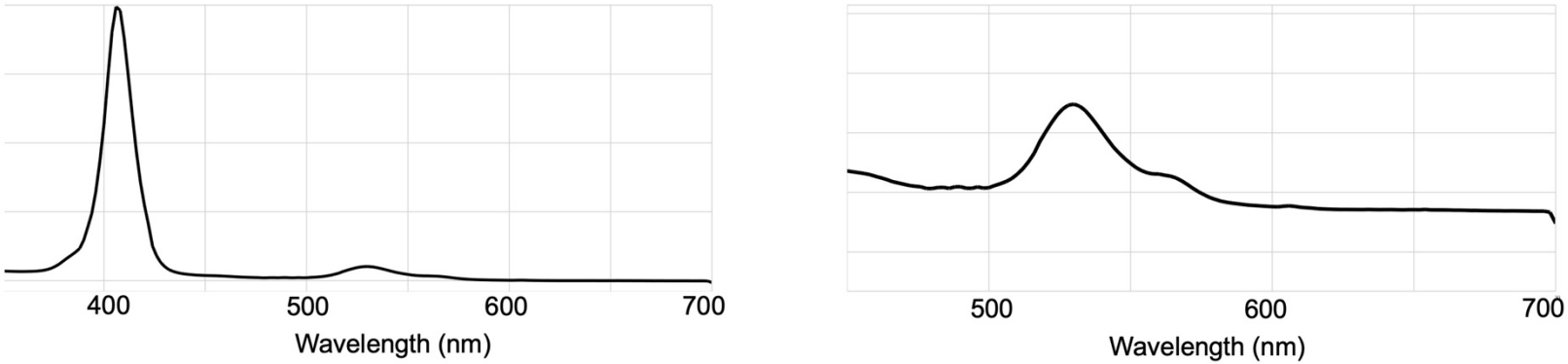
Absorption spectrum of **Cu8** (in DMSO)



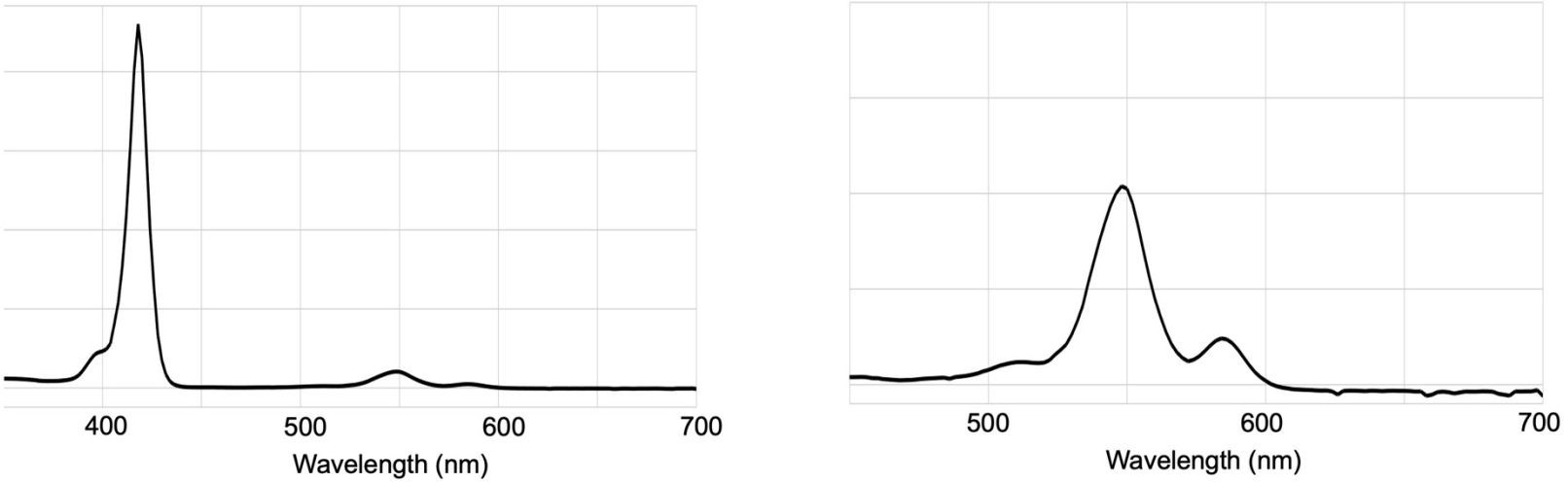
Absorption spectrum of **11** (in DMSO)



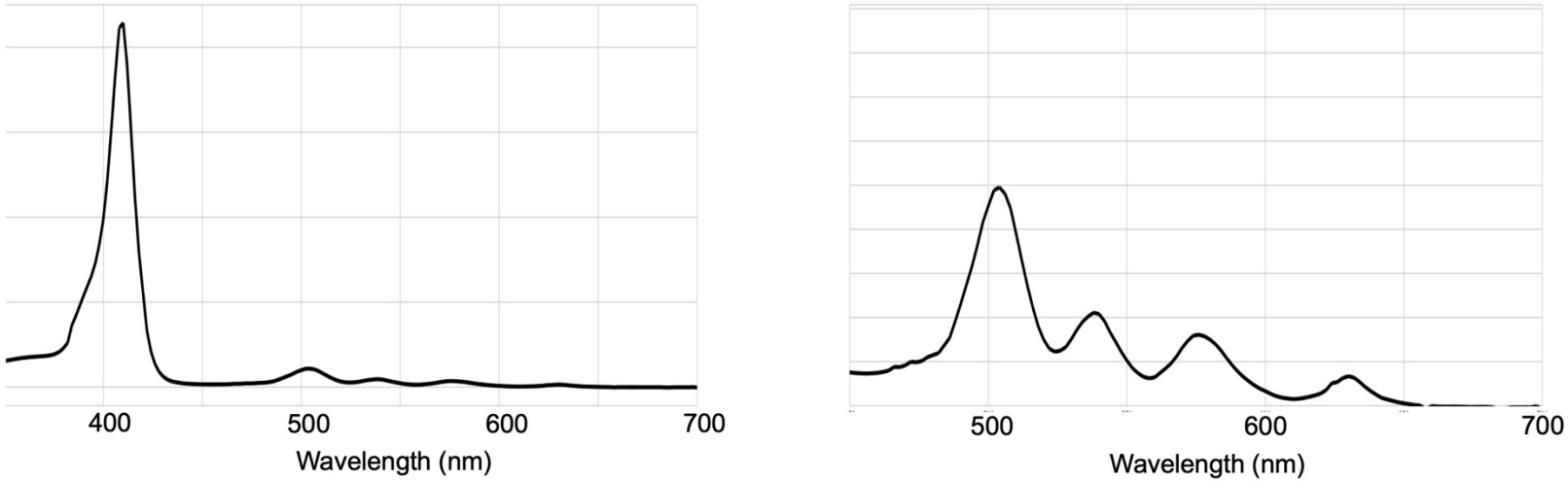
Absorption and emission spectra of **Zn11** (in DMSO)



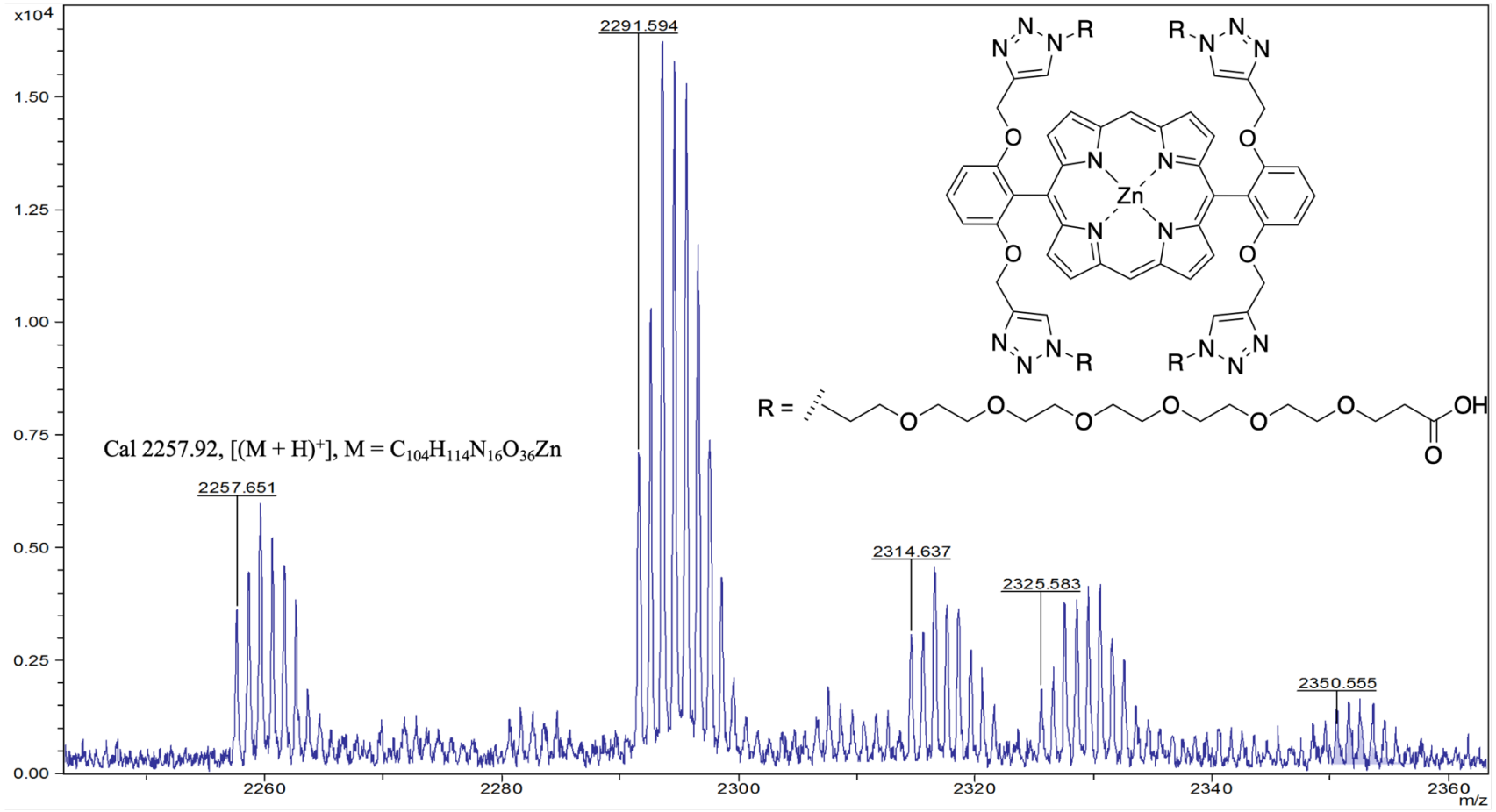
Absorption spectrum of **Cu11** (in DMSO)



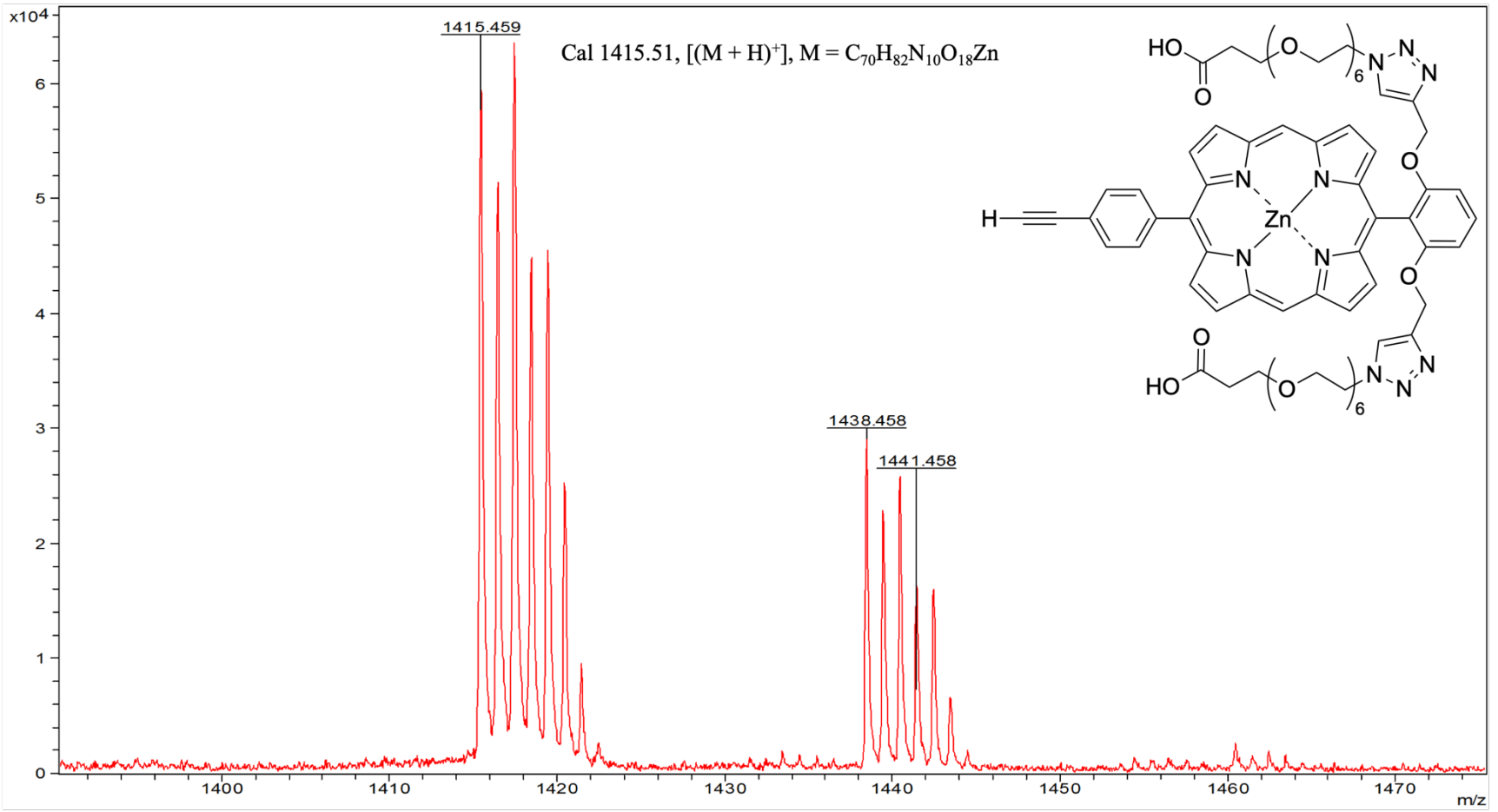
Absorption spectrum of **Zn13** (in DMSO)



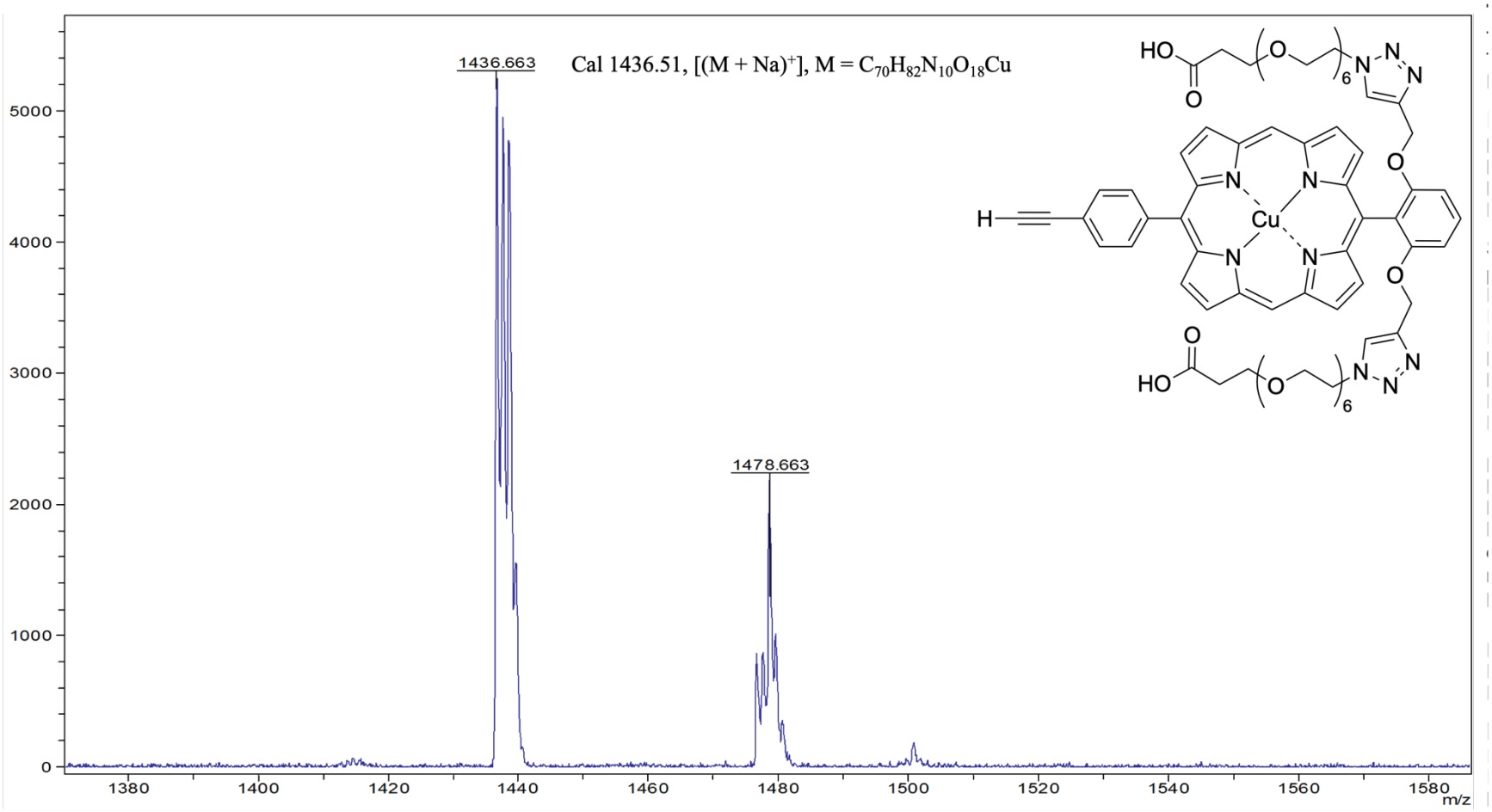
Absorption spectrum of **14** (in DMSO)



MALDI-MS of **Zn8** (using α-cyano-4-hydroxycinnamic acid as the matrix)



MALDI-MS of Zn11 (using α-cyano-4-hydroxycinnamic acid as the matrix)



MALDI-MS of Cu11 (using α-cyano-4-hydroxycinnamic acid as the matrix)