Electronic Supplementary Information

Tetra-Porphyrin Molecular Tweezers: Two Binding Sites Linked via a Polycyclic Scaffold and Rotating Phenyl Diimide Core

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Contents

NMR annotations

S = solvent I = impurity

G = grease W = H_2O

A = acetone SM = starting material

C = $CDCl_3$ D = DMSO-d_6

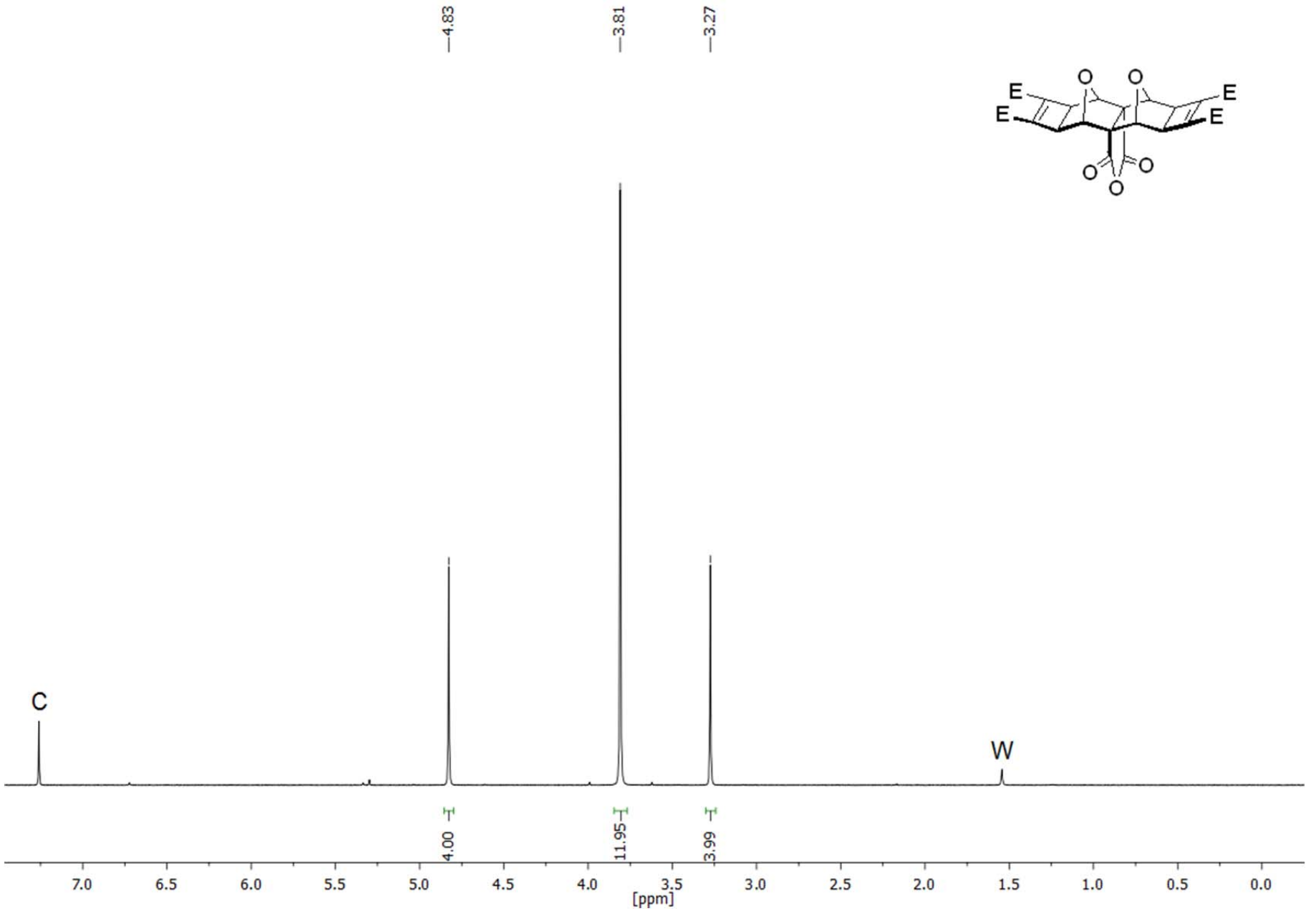
M = CD_2Cl_2

Structure Abbreviations

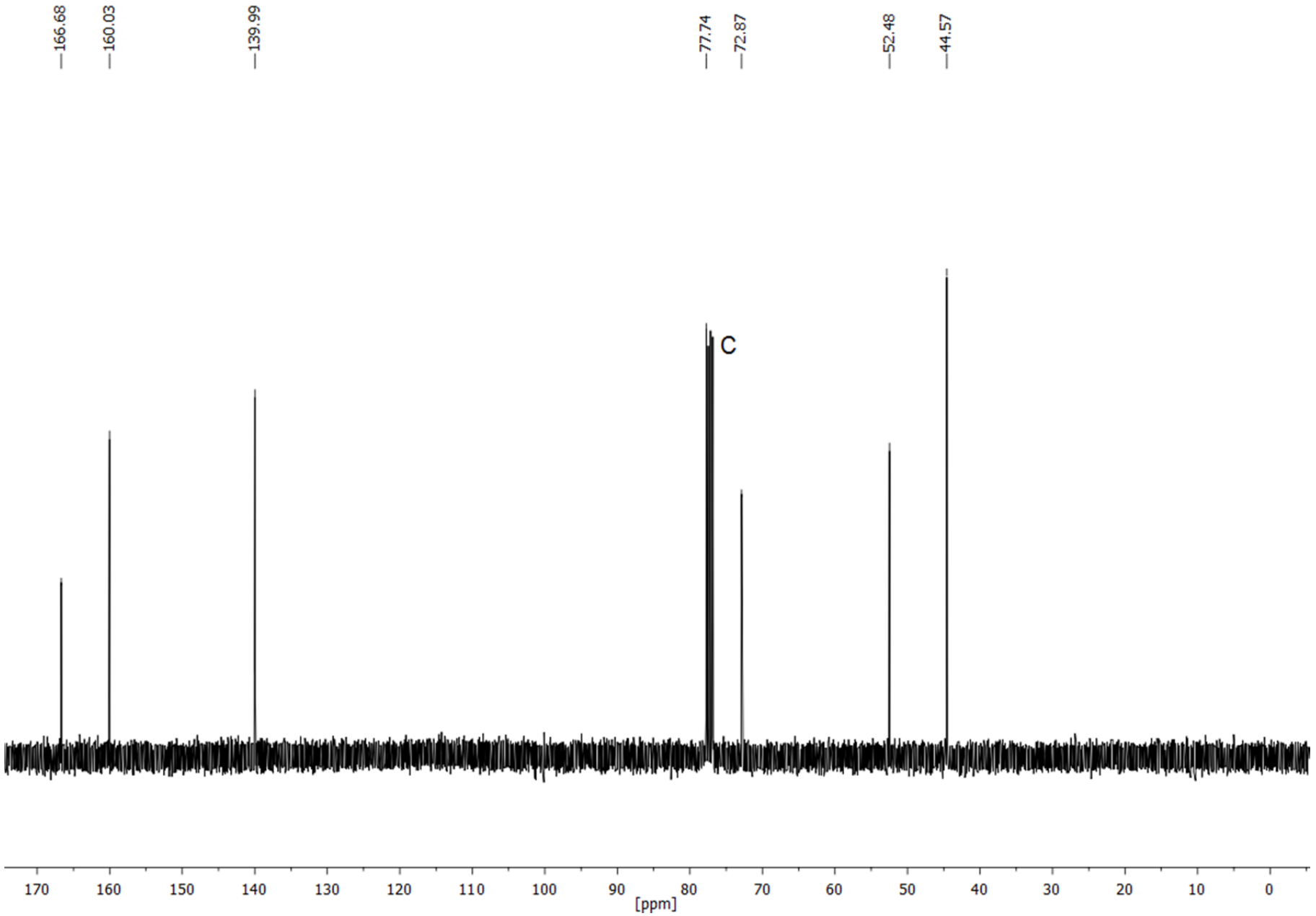
E = CO_2CH_3

Ph = phenyl

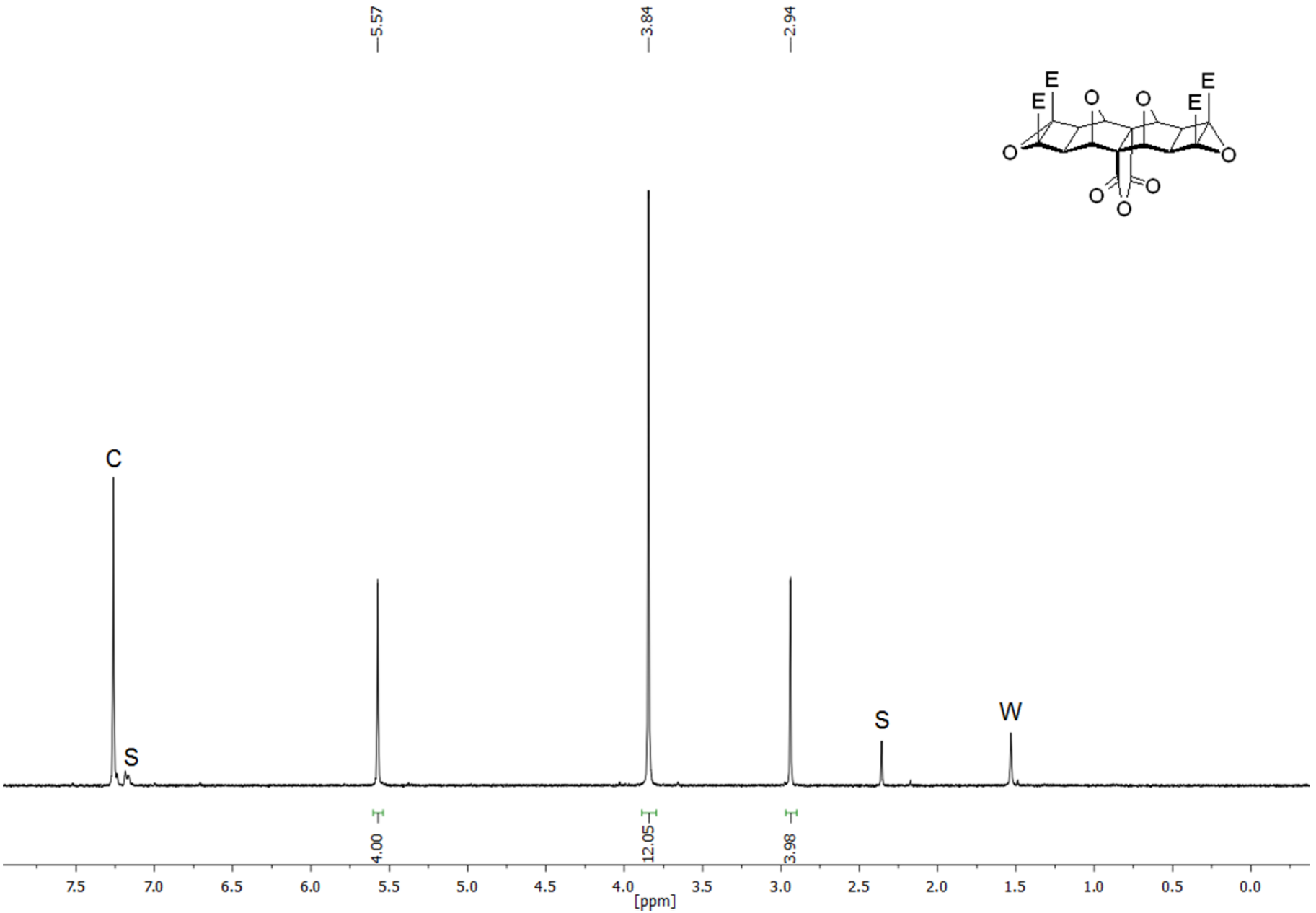
S1: 400 MHz ^{1}H NMR Mitsudo anhydride **4**



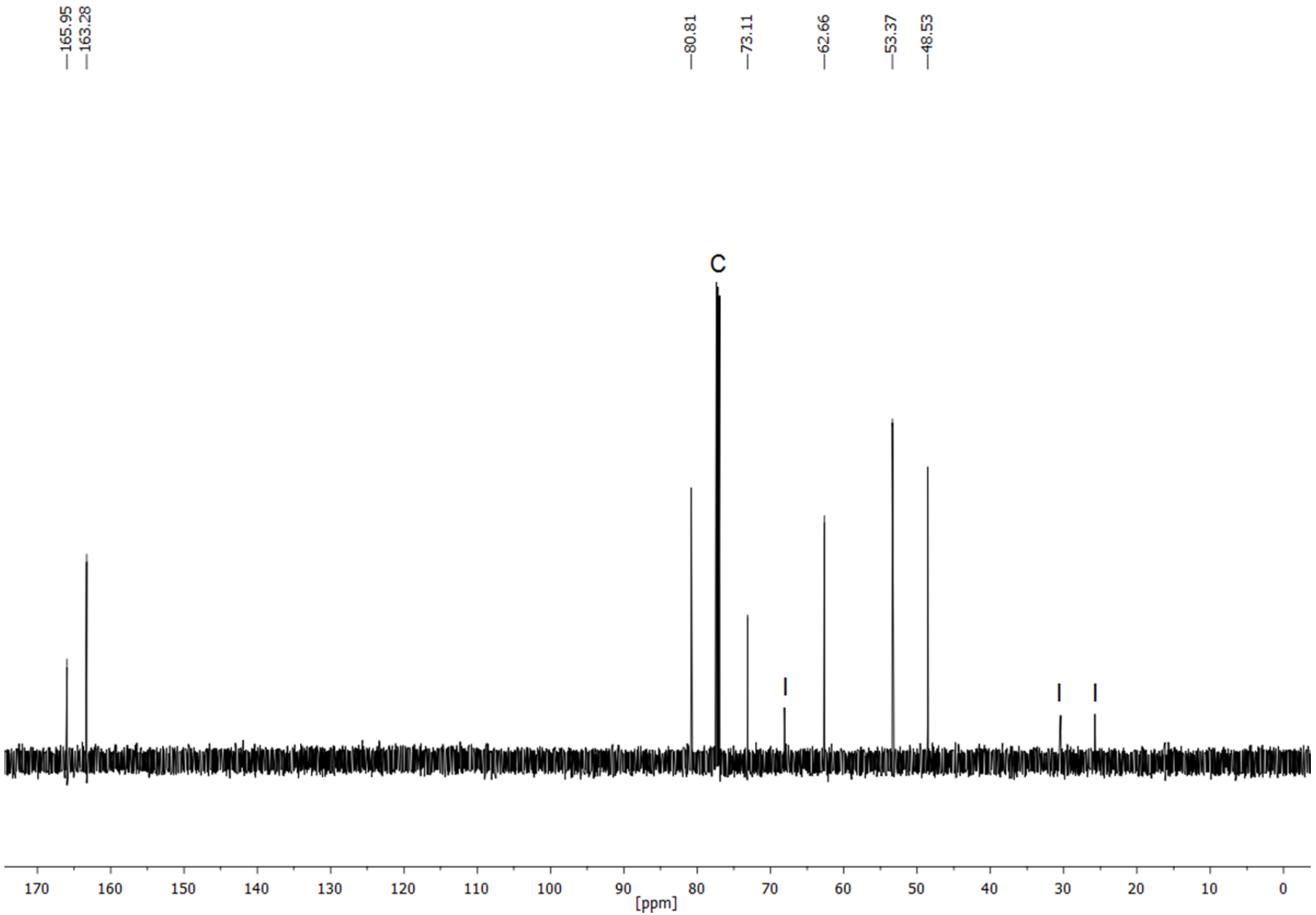
S2: 100 MHz ^{13}C NMR Mitsudo anhydride **4**



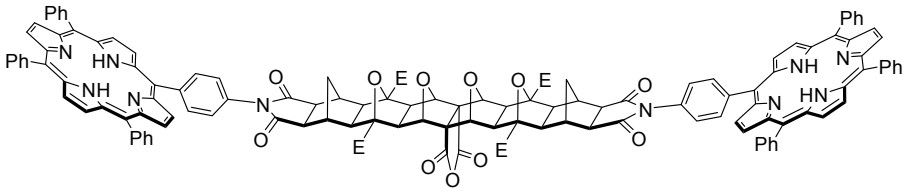
S3: 400 MHz ^{1}H NMR bis-epoxide anhydride **5**



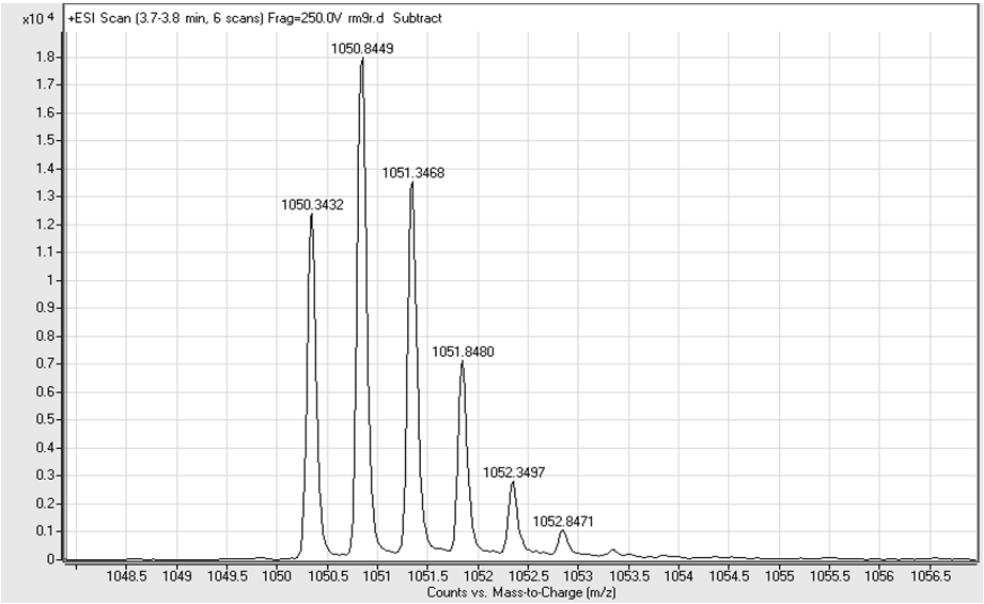
S4: 150 MHz ^{13}C NMR bis-epoxide anhydride **5**

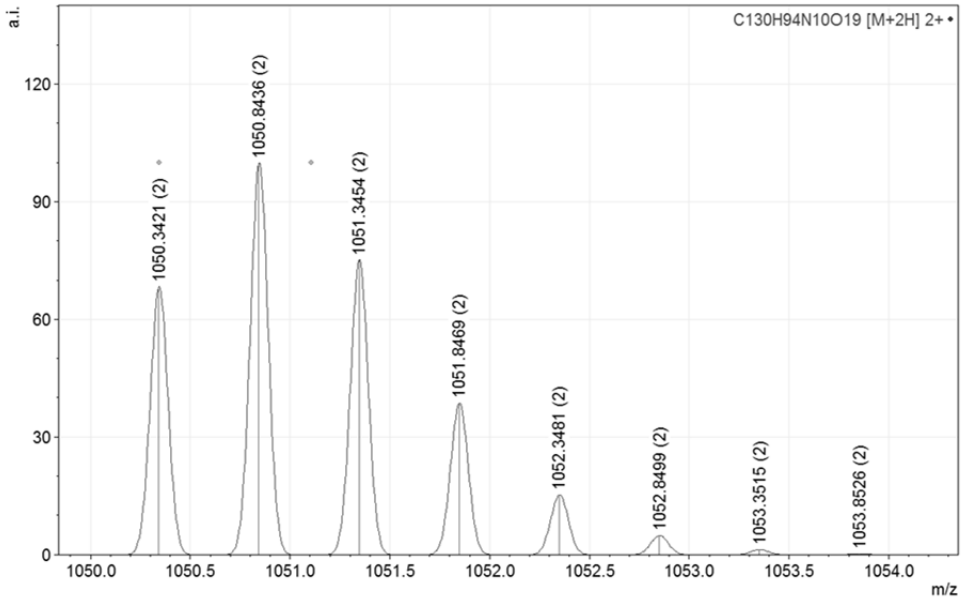


S5: HRMS (ESI-TOF-MS) experimental and predicted bis-porphyrin anhydride **7**



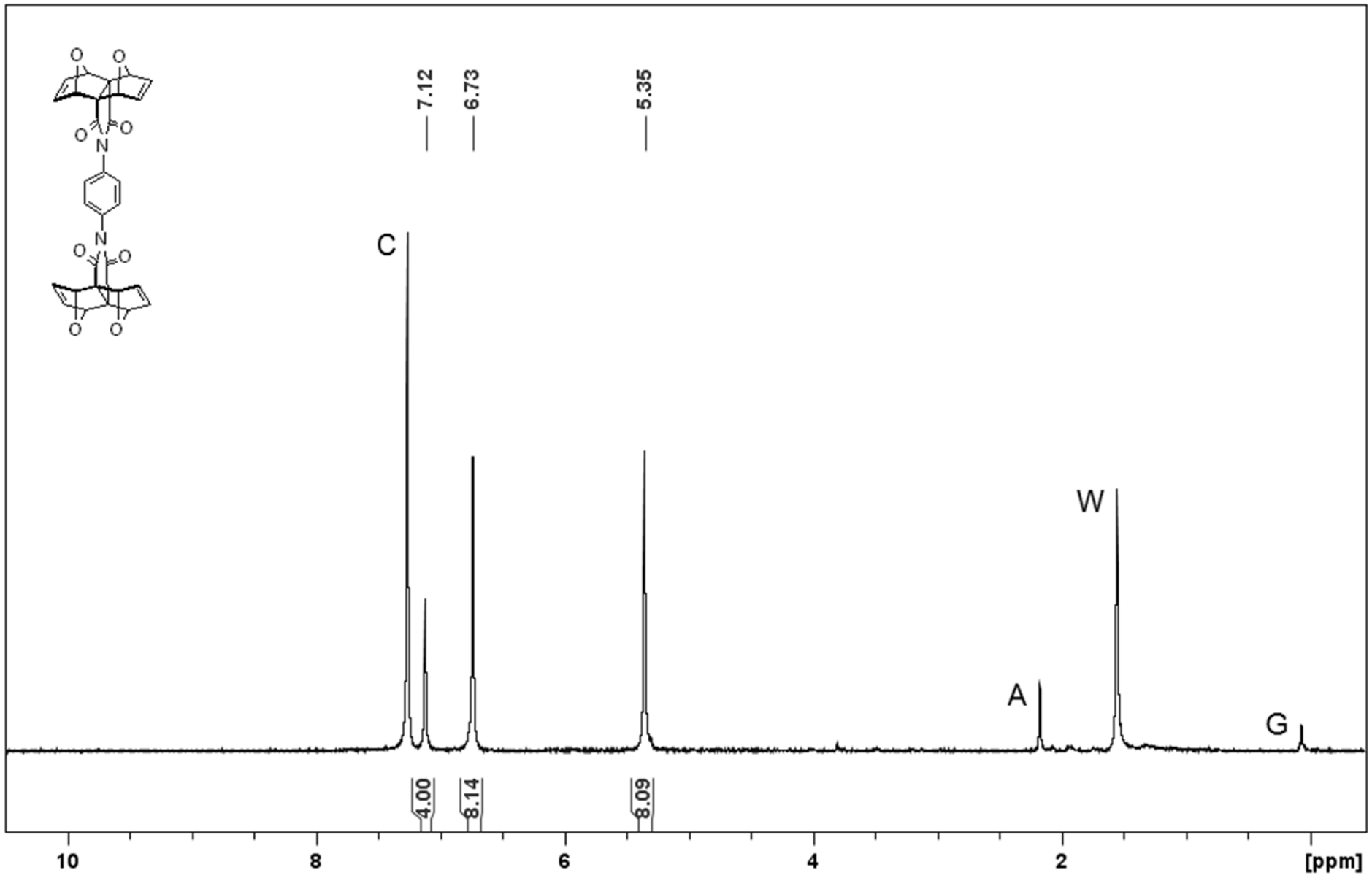
7



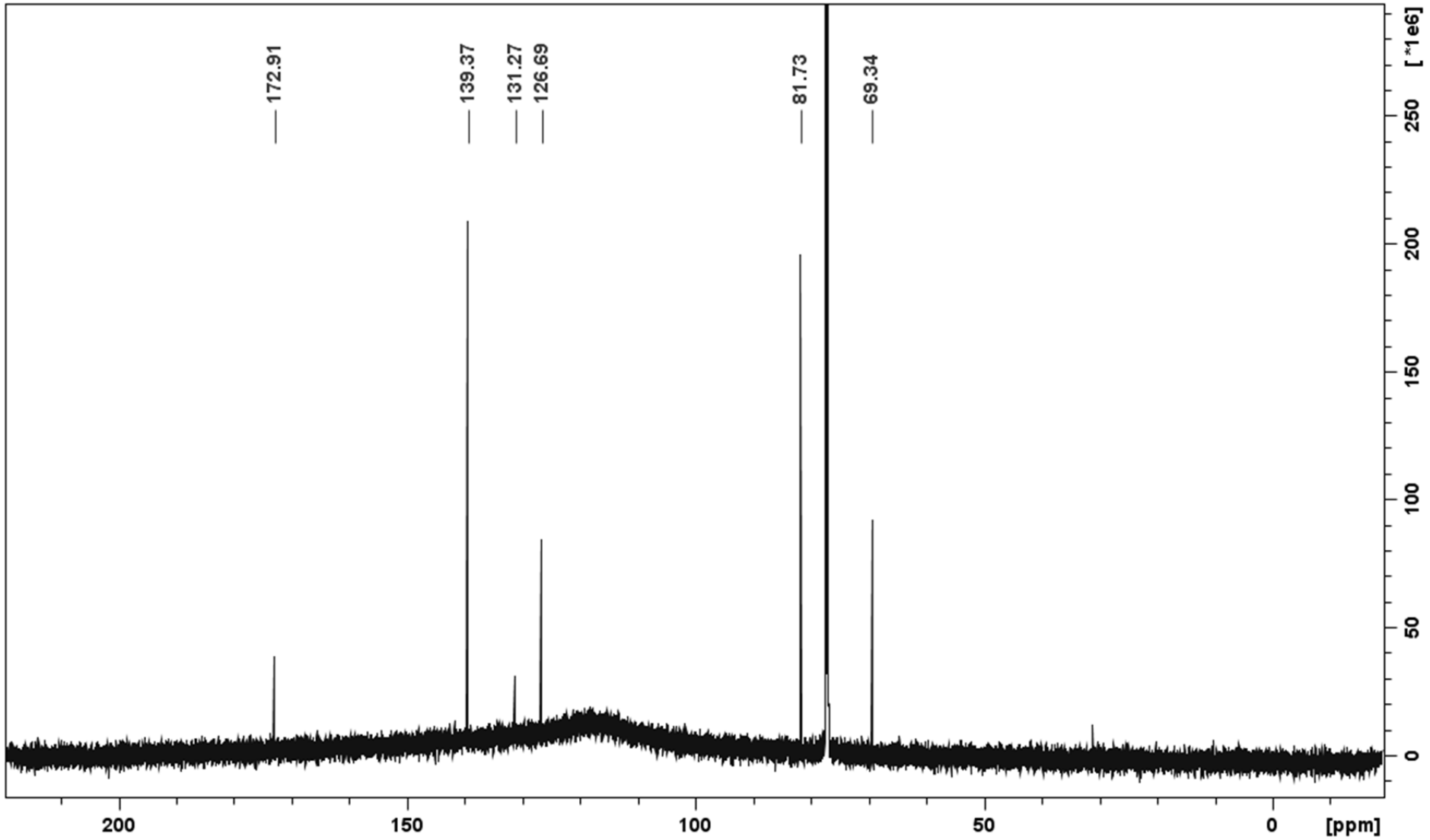


$C_{130}H_{96}N_{10}O_{19}^{2+}$ $[M+2H]^{2+}$: Calcd. 1050.3421. Found 1050.3432.

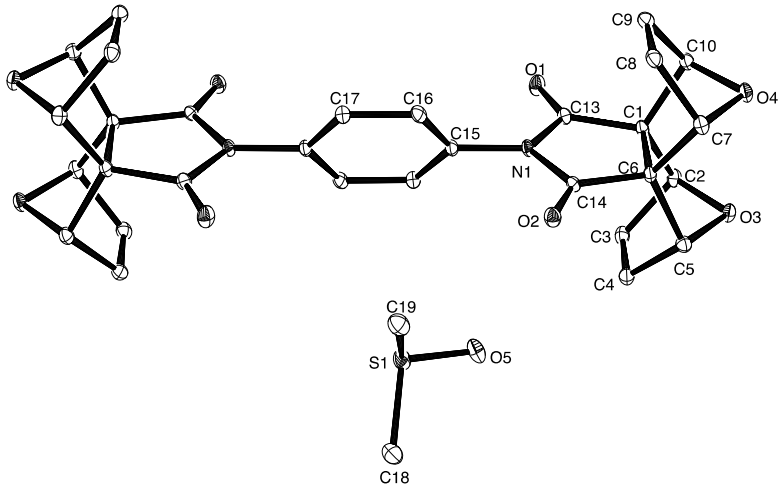
S6: 600 MHz ^{1}H NMR non-Mitsudo phenyl diimide **9**



S7: 150 MHz ^{13}C NMR non-Mitsudo phenyl diimide **9**



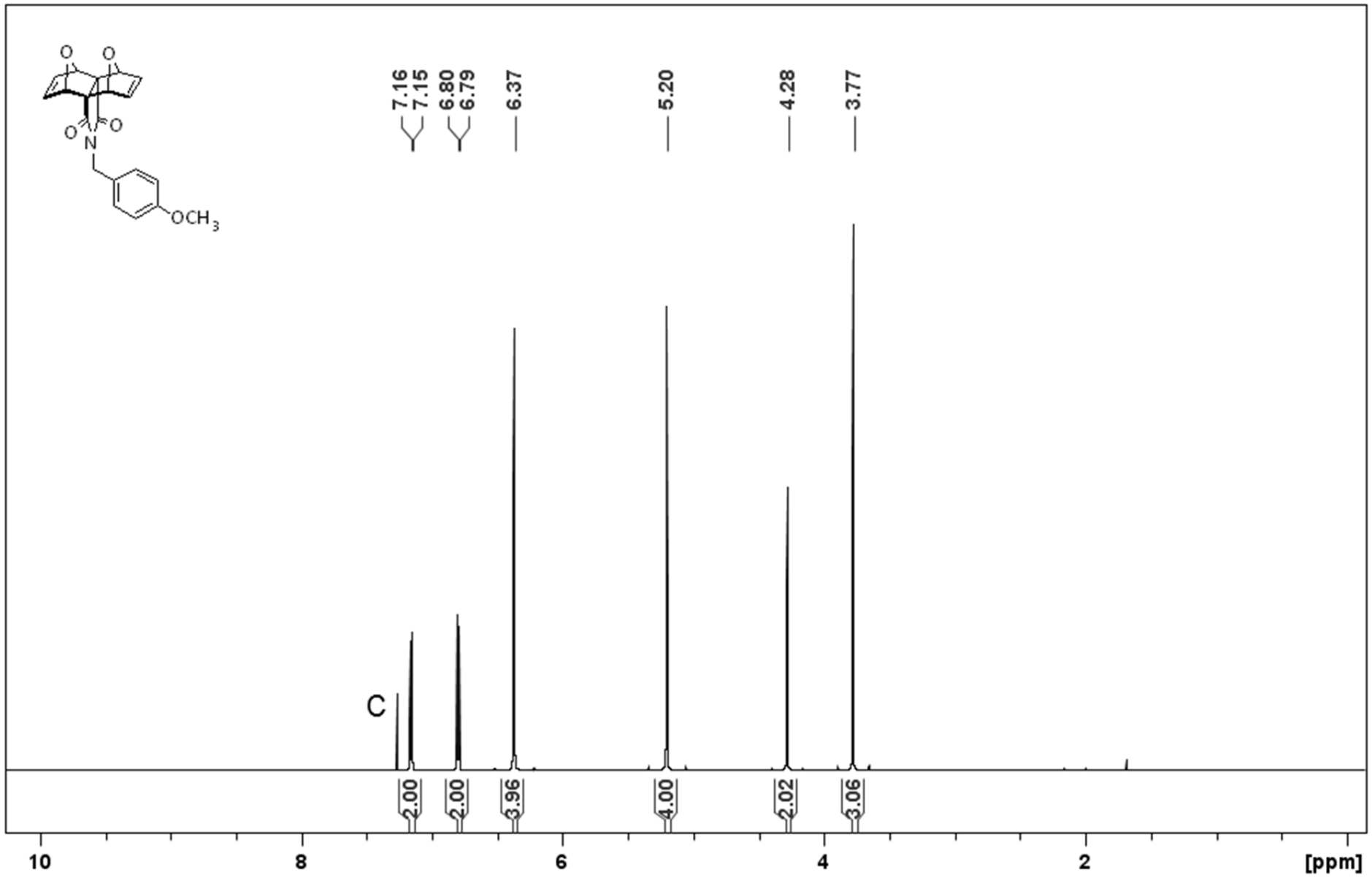
S8: X-Ray Crystal Data and Structure Refinement non-Mitsudo phenyl diimide **9** (CCDC 1486430)

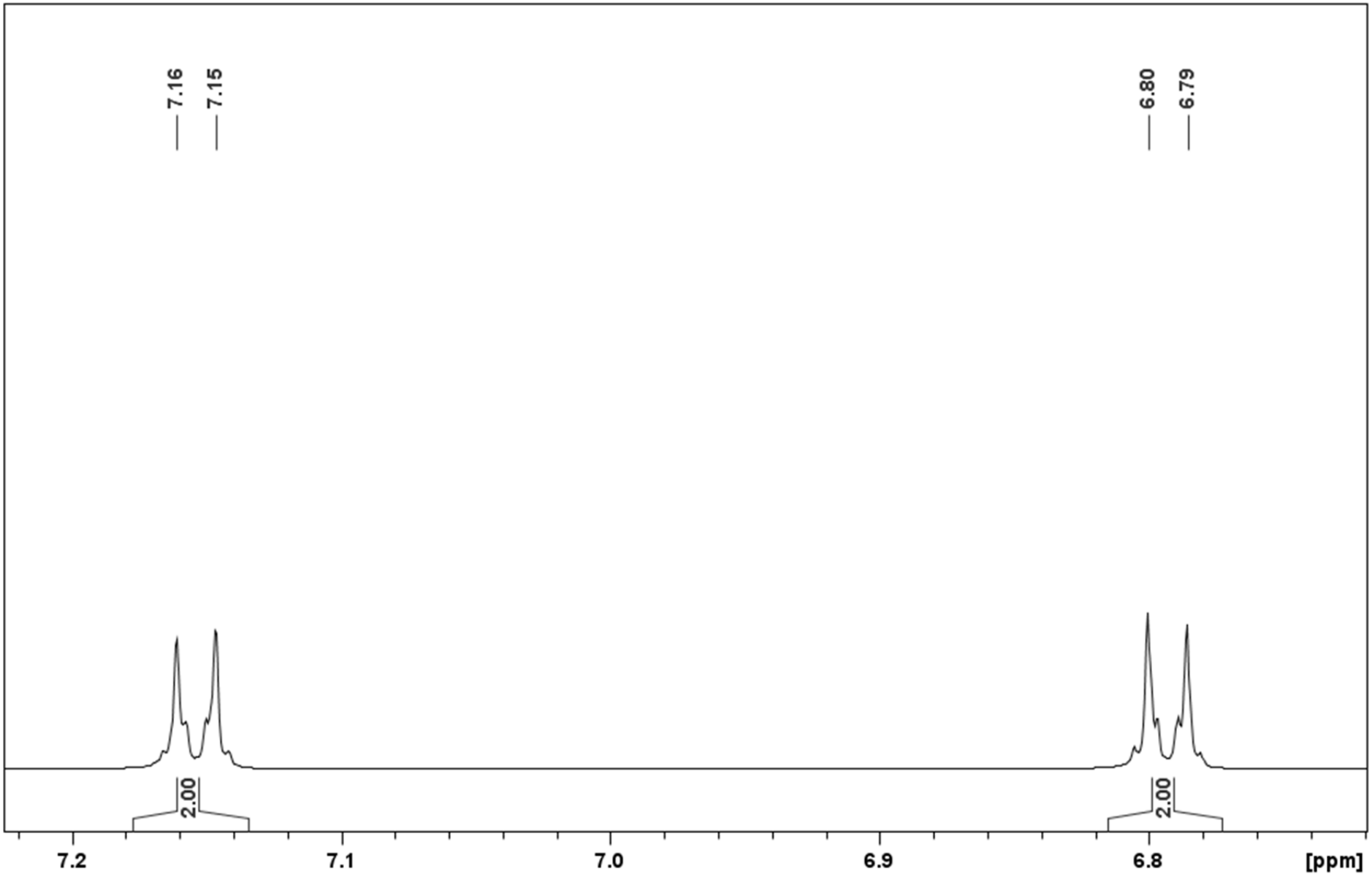


Thermal ellipsoid plot, ellipsoids are at the 30% probability level.

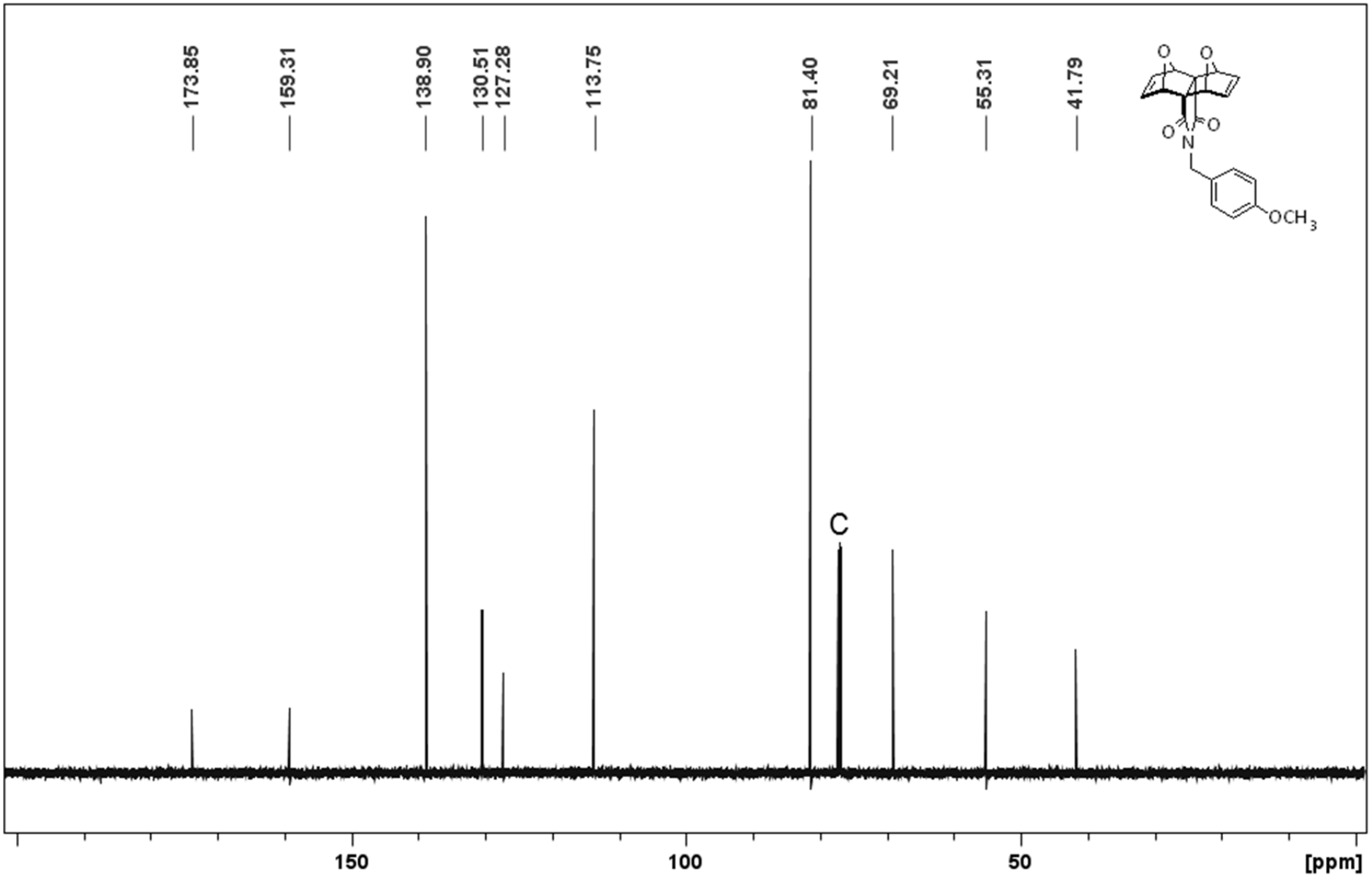
Crystal data: $C_{30}H_{20}N_2O_8$ .2(DMSO) M = 692.73, T = 100.0 K, λ = 1.54184 Å, space group P-1 , a = 7.6974(5) b = 9.8515(7), c = 10.6292(9)) *Å*, α = 91.428(7) β = 93.661(7) γ = 96.076(6) V = 799.45(10) $Å^3$, Z = 1, D_c = 1.439 Mg M^{-3} μ(Cu-Kα) 2.052 mm^{-1}, F(000) = 362, crystal size 0.50 x 0.2 x 0.03 mm^3, 5636 reflections measured θ_{max} = 77°, 3169 independent reflections [R(int) = 0.0669], the final R was 0.0552 [I > 2σ(I) 2585 data] and *w*R(F^2) was 0.1515 (all data).

S9: 600 MHz ^{1}H NMR PMB protected imide **11**

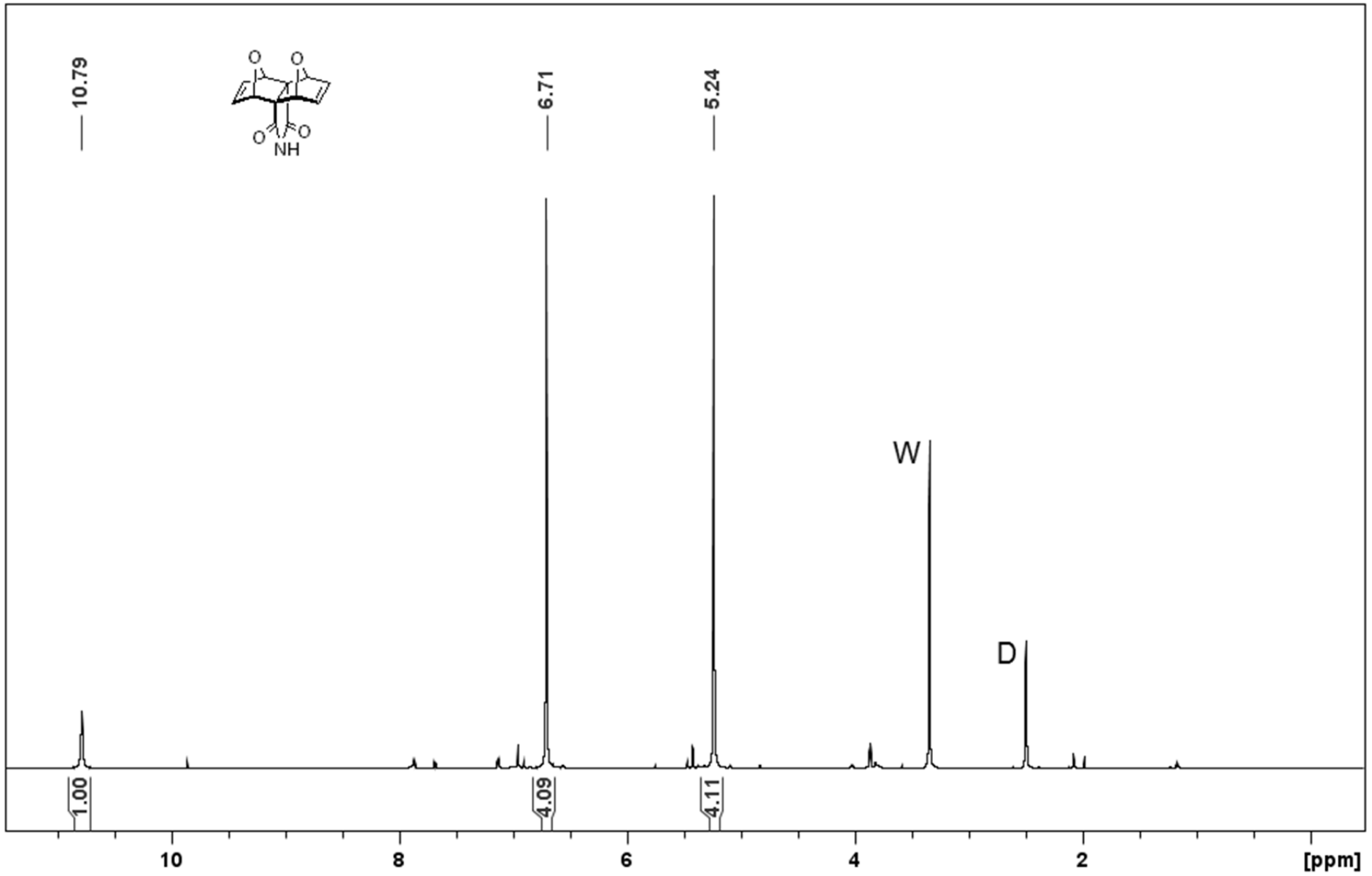



7.16
7.15
6.80
6.79
2.00
2.00
7.2
7.1
7.0
6.9
6.8
[ppm]

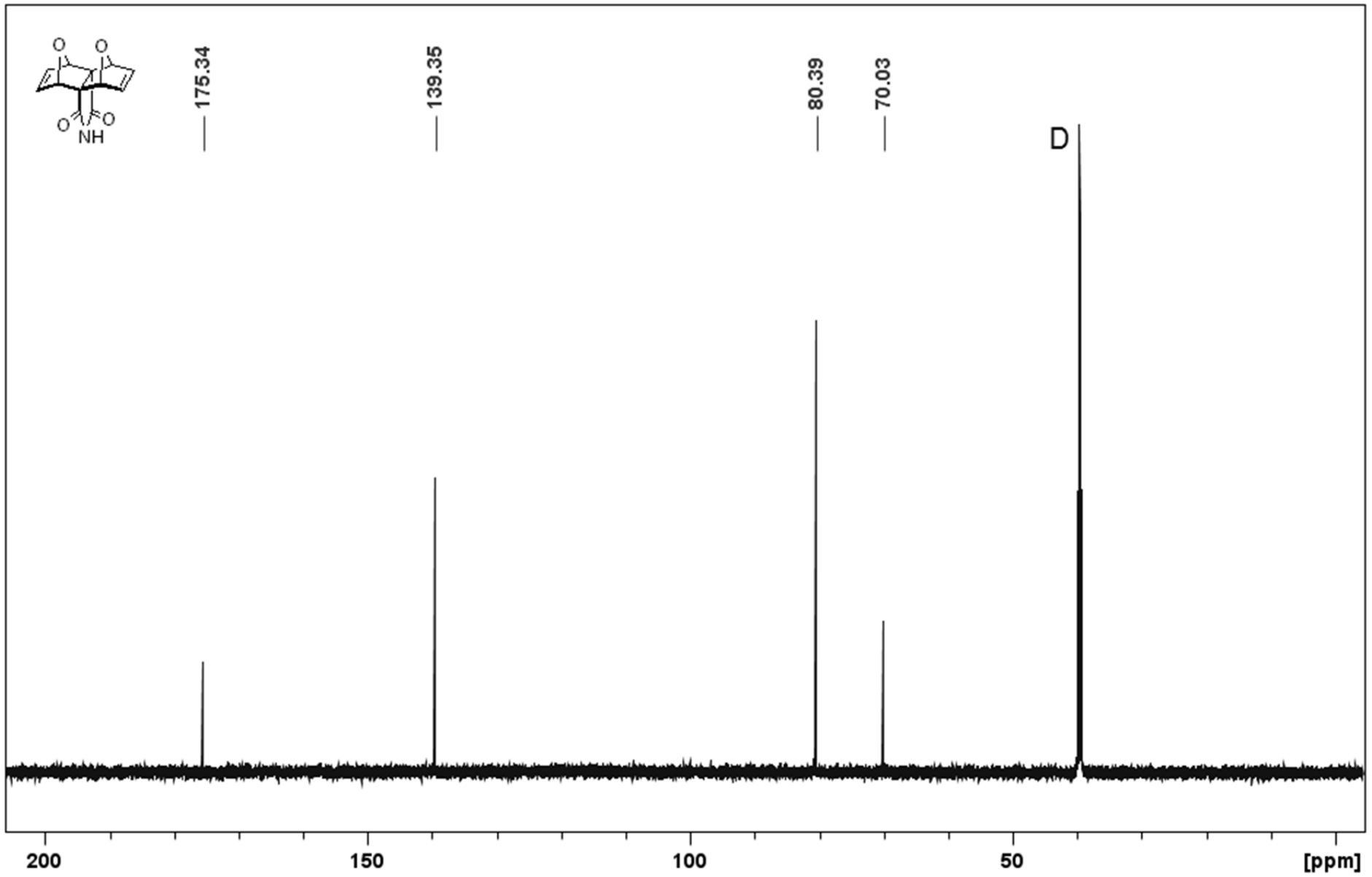
S10: 150 MHz ^{13}C NMR PMB protected imide **11**



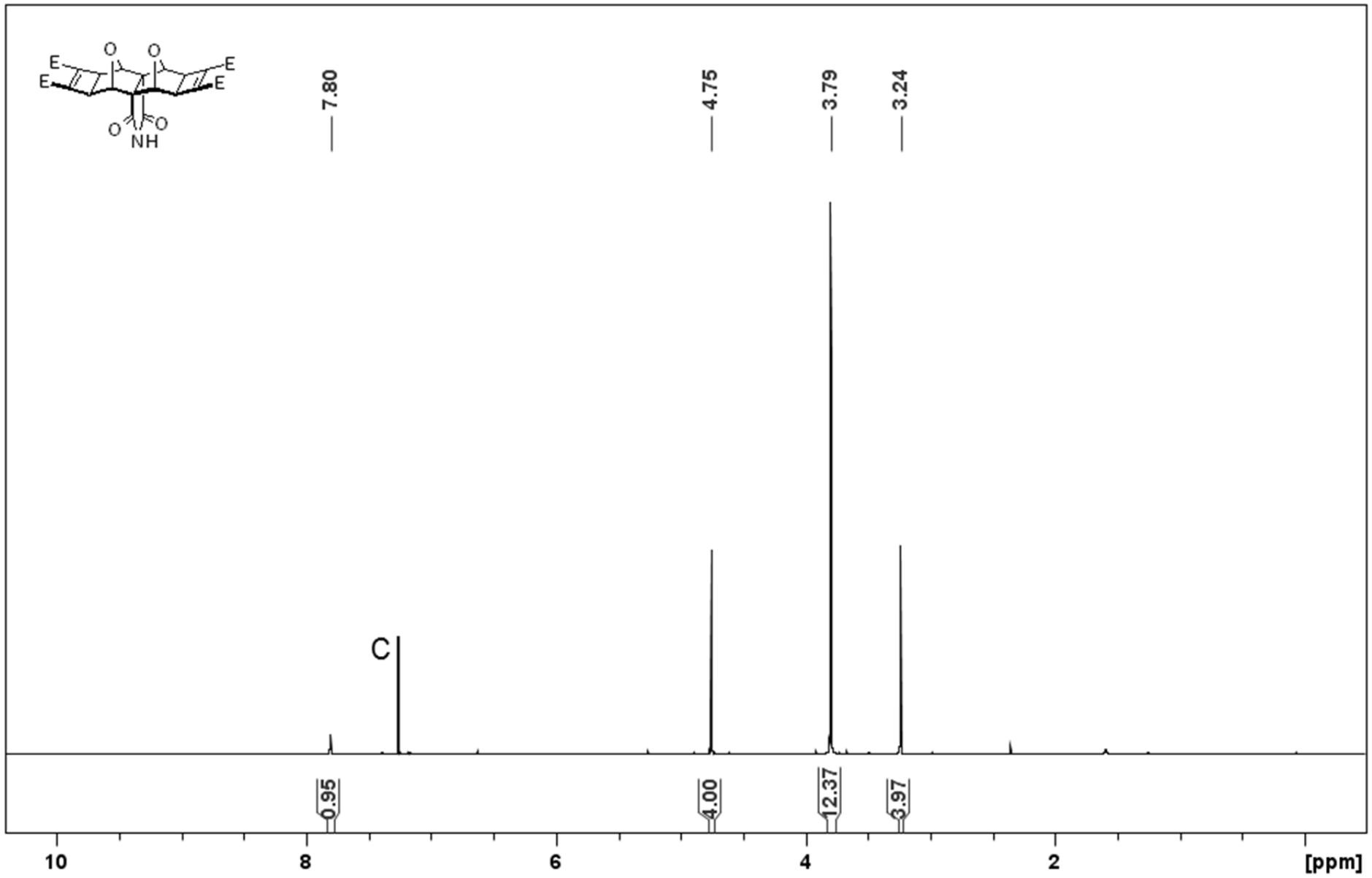
S11: 600 MHz ^{1}H NMR Imide **12**



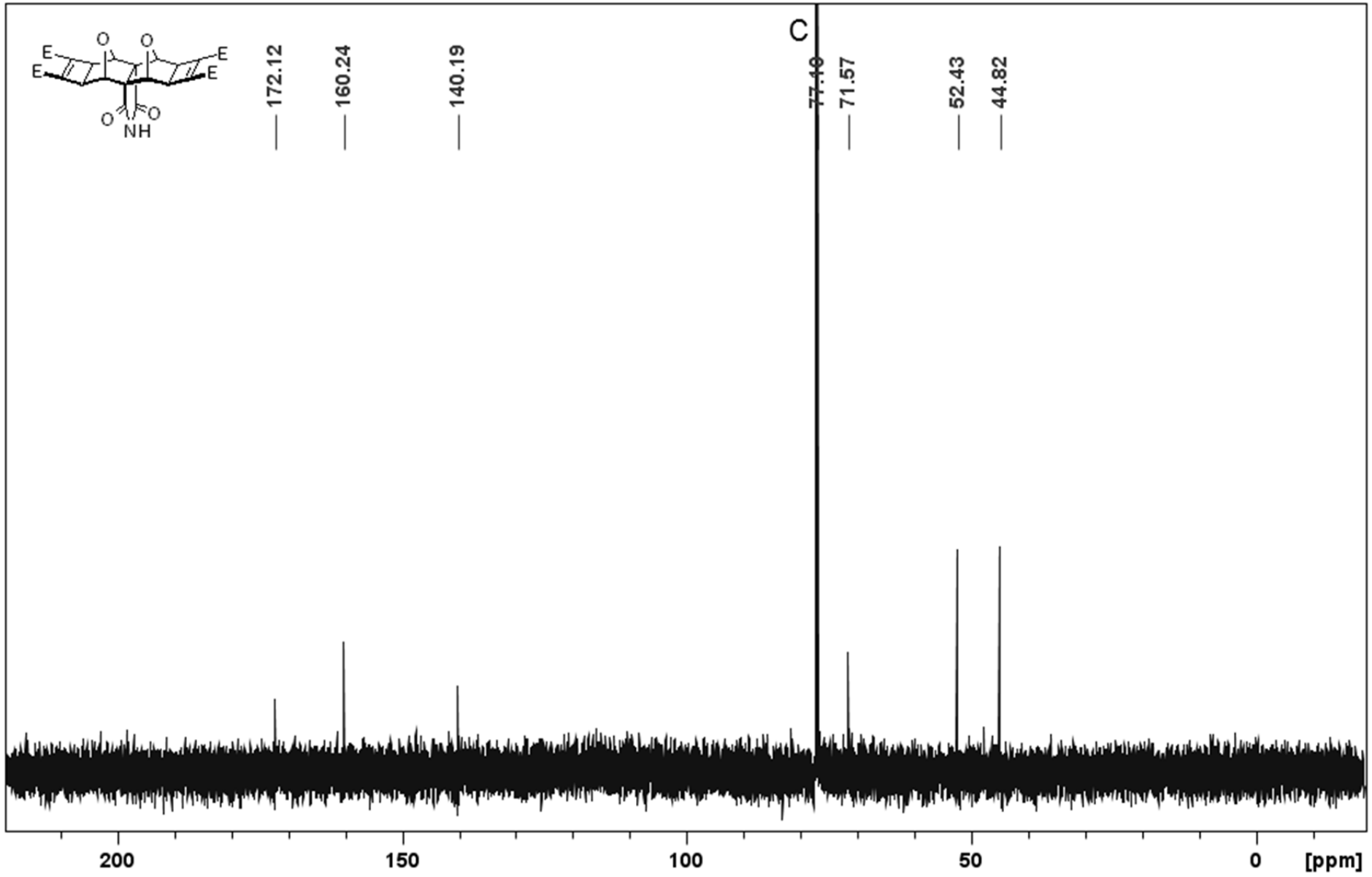
S12: 150 MHz ^{13}C NMR Imide **12**

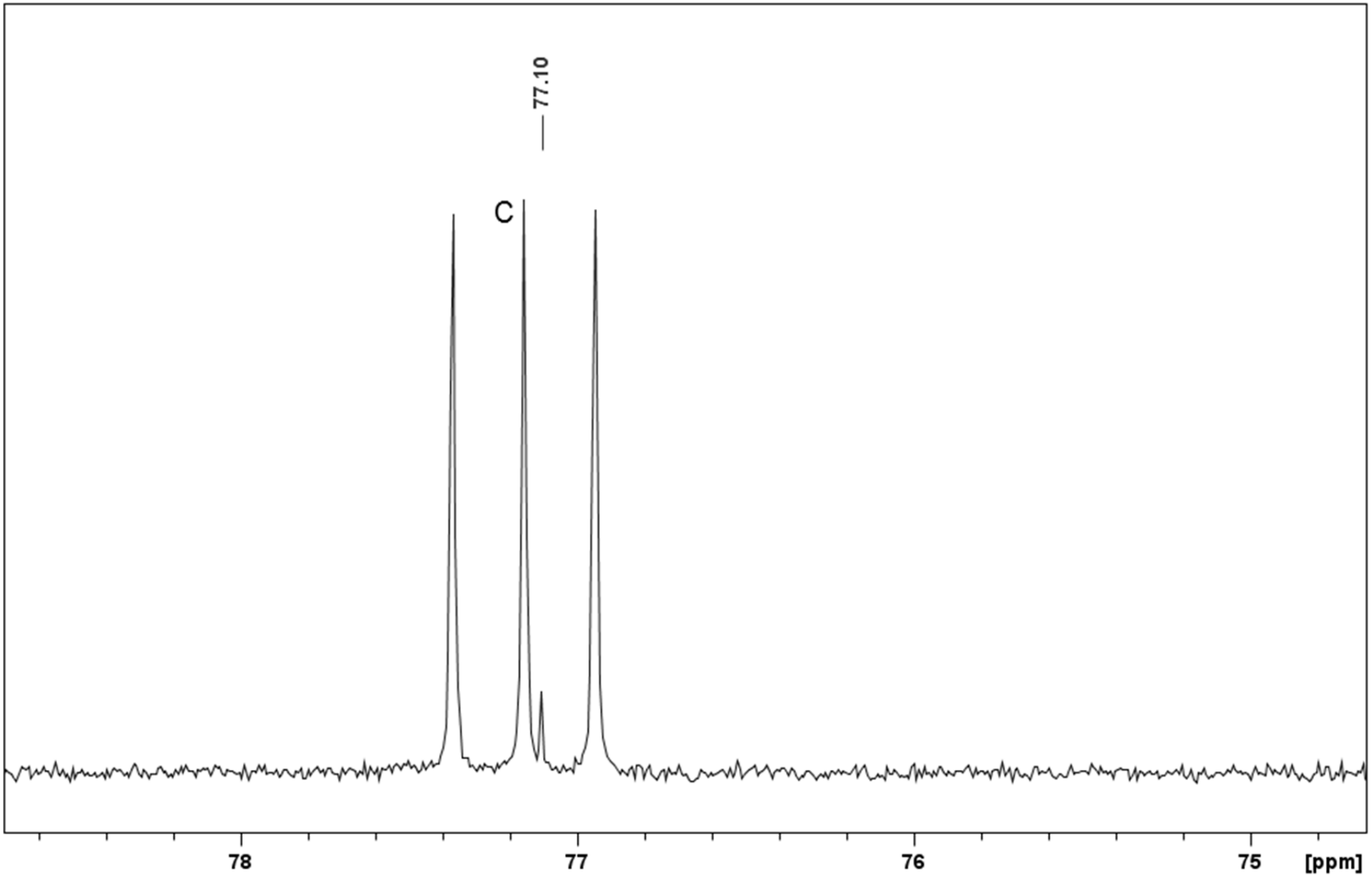


S13: 600 MHz ^{1}H NMR Mitsudo imide **13**



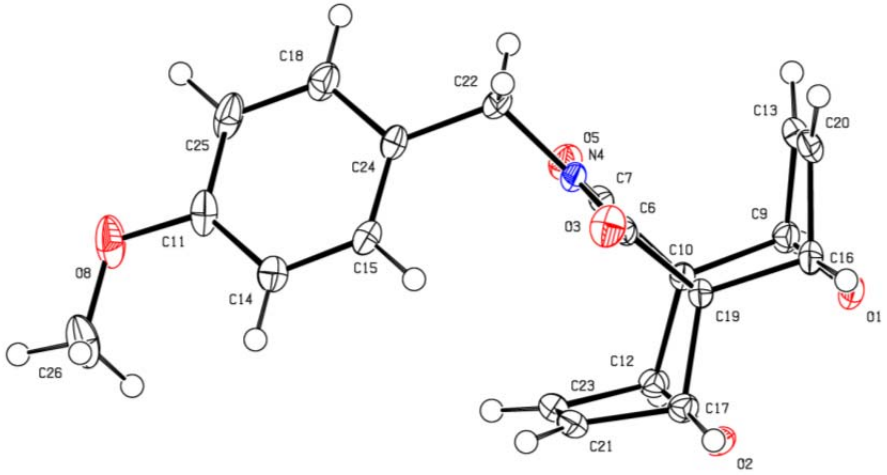
S14: 150 MHz ^{13}C NMR Mitsudo imide **13**



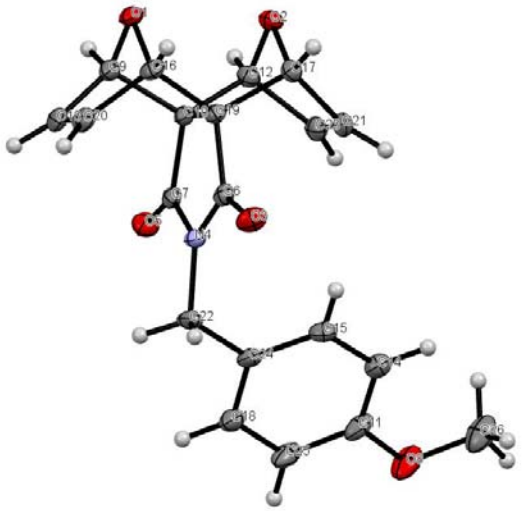

77.10
C
78
77
76
75
[ppm]

S15: X-Ray Crystal Structure Data and Refinement for Compounds **11-13** (CCDC 1486427-1486429)

PMB protected imide **11** (CCDC 1486427)



Parameter	**PMB protected imide 11**
Empirical formula	C20 H17 N O5
Formula weight	351.35
Temperature (K)	150
Wavelength (Å)	0.071073
Crystal system	triclinic
Space group	'P 21/n'
Unit cell dimensions	a=7.4138(4) b=22.8374(10) c=9.5317(5)
Theta max	29.27
Reflections used	3830
Final R indices [I > 2σ(I)]	
R1	0.0439
wR2	0.1067
Data completeness	0.879

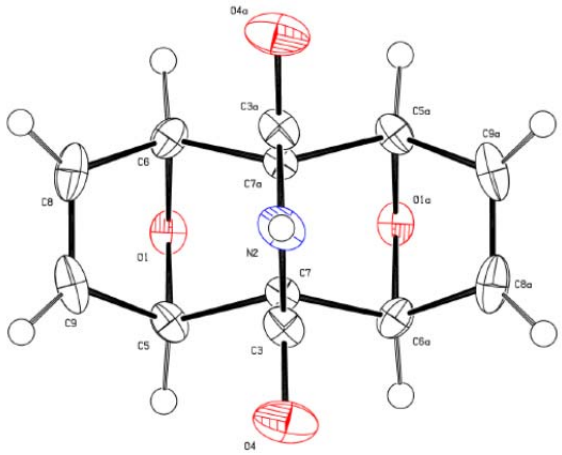


Bond Angles

Number	Atom1	Atom2	Atom3	Angle
1	C9	O1	C16	96.4(1)
2	C12	O2	C17	96.7(1)
3	C6	N4	C7	113.8(1)
4	C6	N4	C22	124.0(1)
5	C7	N4	C22	122.2(1)
6	O3	C6	N4	124.6(1)
7	O3	C6	C19	127.4(1)
8	N4	C6	C19	108.0(1)
9	N4	C7	O5	124.3(1)
10	N4	C7	C10	108.0(1)
11	O5	C7	C10	127.6(1)
12	C11	O8	C26	117.6(1)
13	O1	C9	H9	115.3
14	O1	C9	C10	101.5(1)
15	O1	C9	C13	101.5(1)
16	H9	C9	C10	115.3
17	H9	C9	C13	115.3
18	C10	C9	C13	106.2(1)
19	C7	C10	C9	113.8(1)
20	C7	C10	C12	116.1(1)
21	C7	C10	C19	105.2(1)
22	C9	C10	C12	116.6(1)
23	C9	C10	C19	101.2(1)
24	C12	C10	C19	100.9(1)
25	O8	C11	C14	124.5(1)
26	O8	C11	C25	115.4(1)
27	C14	C11	C25	120.0(1)
28	O2	C12	C10	100.6(1)
29	O2	C12	H12	115.3
30	O2	C12	C23	101.2(1)
31	C10	C12	H12	115.3
32	C10	C12	C23	107.2(1)
33	H12	C12	C23	115.3
34	C9	C13	H13	127.2
35	C9	C13	C20	105.5(1)
36	H13	C13	C20	127.3
37	C11	C14	H14	120.5
38	C11	C14	C15	118.8(1)
39	H14	C14	C15	120.6
40	C14	C15	H15	119.1
41	C14	C15	C24	121.9(1)
42	H15	C15	C24	119.1
43	O1	C16	H16	115.5
44	O1	C16	C19	100.4(1)
45	O1	C16	C20	101.1(1)
46	H16	C16	C19	115.6
47	H16	C16	C20	115.6
48	C19	C16	C20	106.7(1)
49	O2	C17	H17	115.5
50	O2	C17	C19	100.9(1)
51	O2	C17	C21	101.3(1)
52	H17	C17	C19	115.4
53	H17	C17	C21	115.4

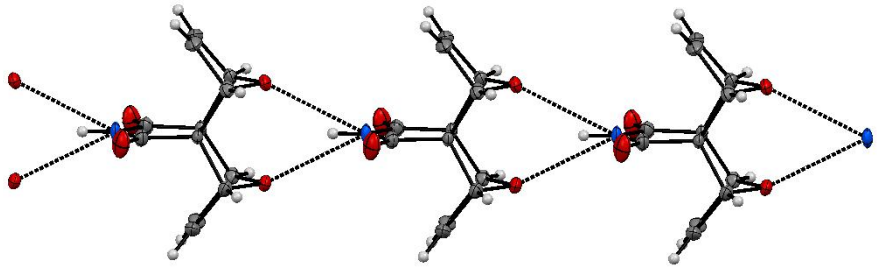
54	C19	C17	C21	106.4(1)	67	C17	C21	H21	127.3	80	C15	C24	C22	121.6(1)
55	H18	C18	C24	119.8	68	C17	C21	C23	105.5(1)	81	C18	C24	C22	119.9(1)
56	H18	C18	C25	119.8	69	H21	C21	C23	127.2	82	C11	C25	C18	120.3(2)
57	C24	C18	C25	120.4(1)	70	N4	C22	H22A	109.1	83	C11	C25	H25	119.9
58	C6	C19	C10	104.8(1)	71	N4	C22	H22B	109.1	84	C18	C25	H25	119.8
59	C6	C19	C16	115.5(1)	72	N4	C22	C24	112.5(1)	85	O8	C26	H26A	109.4
60	C6	C19	C17	114.7(1)	73	H22A	C22	H22B	107.8	86	O8	C26	H26B	109.4
61	C10	C19	C16	101.2(1)	74	H22A	C22	C24	109.2	87	O8	C26	H26C	109.5
62	C10	C19	C17	101.4(1)	75	H22B	C22	C24	109.1	88	H26A	C26	H26B	109.5
63	C16	C19	C17	116.3(1)	76	C12	C23	C21	105.7(1)	89	H26A	C26	H26C	109.5
64	C13	C20	C16	106.2(1)	77	C12	C23	H23	127.1	90	H26B	C26	H26C	109.5
65	C13	C20	H20	126.9	78	C21	C23	H23	127.2					
66	C16	C20	H20	126.9	79	C15	C24	C18	118.5(1)					

Imide **12** (CCDC 1486428)

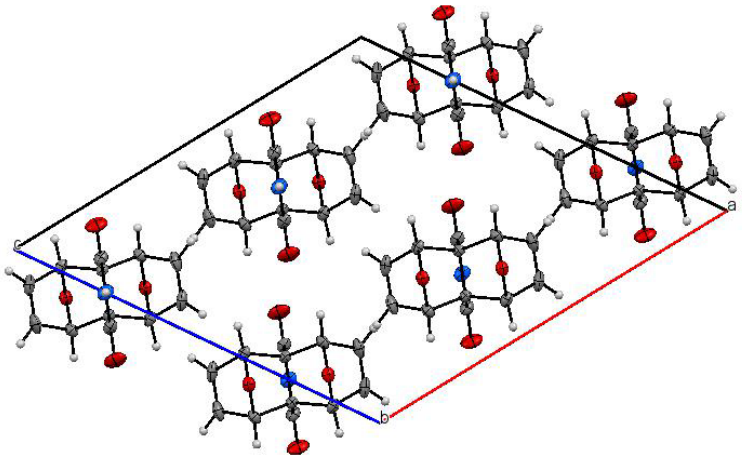


Parameter	**Imide 12**
Empirical formula	C12 H9 N O4
Formula weight	231.2
Temperature (K)	150
Wavelength (Å)	0.071073
Crystal system	monoclinic
Space group	'C 1 2/c 1'
Unit cell dimensions	a=13.5746(16) b=6.6256(4) c=13.5089(16)
Theta max	29.2
Reflections used	944
Final R indices [I > 2σ(I)]	
R1	0.0445
wR2	0.1272
Data completeness	0.883

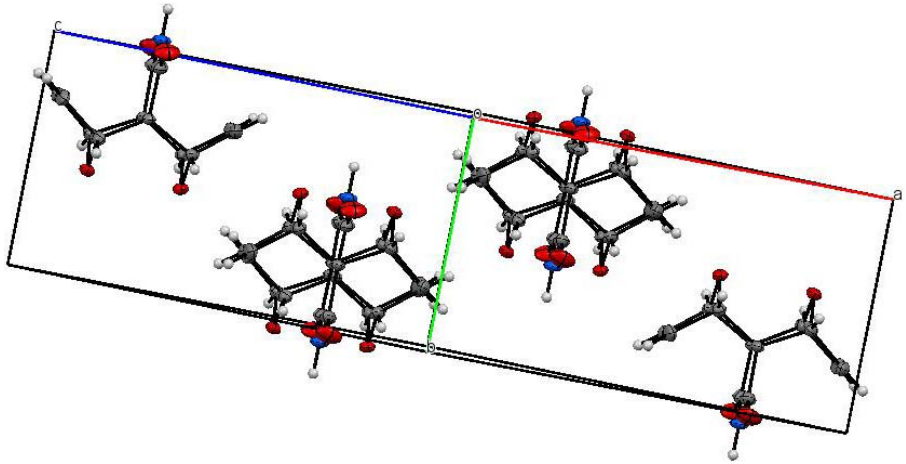
The crystal packing of compound **12** was stabilised by intermolecular N—H···O hydrogen bonding (ORTEP diagrams generated in Mercury, Version 3.0).



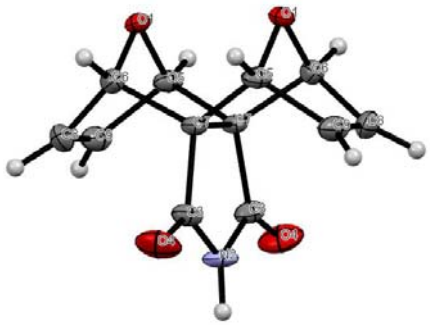
hydrogen bonding



packing (viewing down b axis)



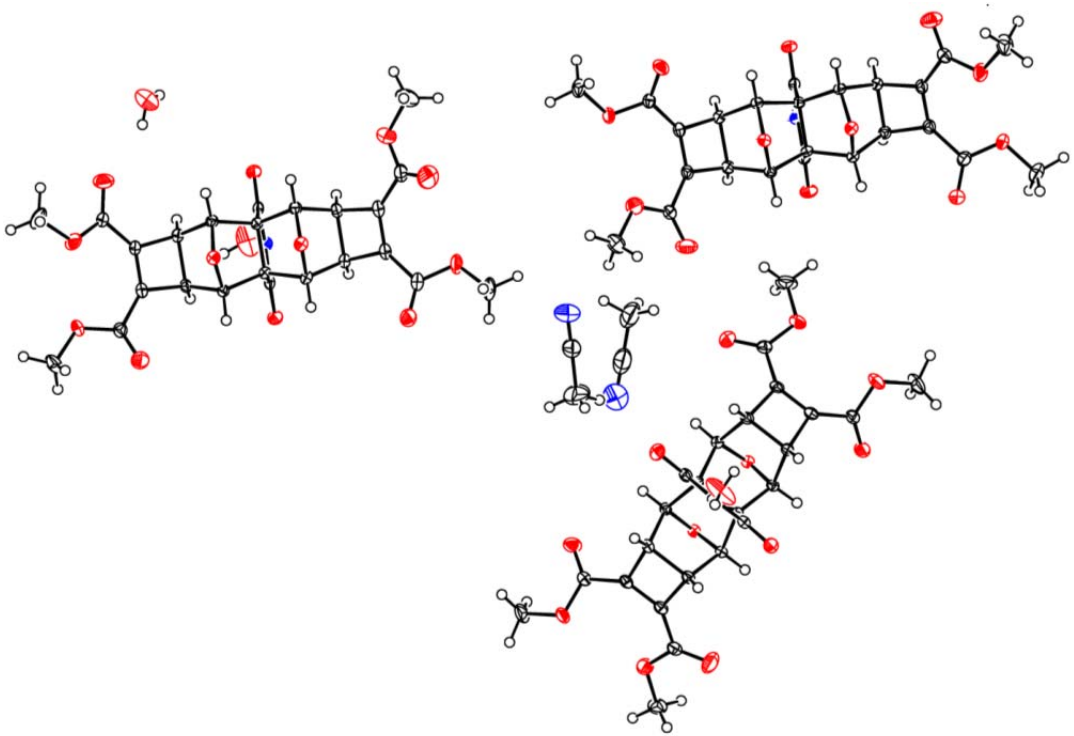
packing (a&c axes)



Bond Angles

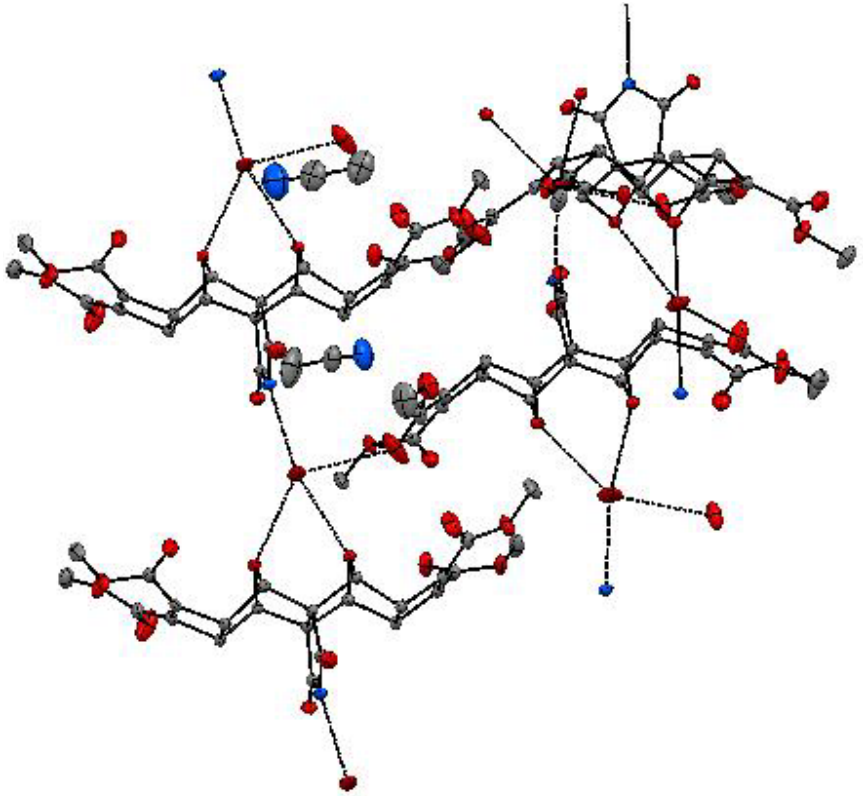
Number	Atom1	Atom2	Atom3	Angle
1	C5	O1	C6	96.6(1)
2	H2	N2	C3	122.6
3	H2	N2	C3	122.6
4	C3	N2	C3	114.7
5	N2	C3	C7	107.7
6	N2	C3	O4	124.9
7	C7	C3	O4	127.4(1)
8	O1	C5	H5	115.5
9	O1	C5	C7	100.3(1)
10	O1	C5	C9	100.5(1)
11	H5	C5	C7	115.5
12	H5	C5	C9	115.6
13	C7	C5	C9	107.3(1)
14	O1	C6	H6	115.6
15	O1	C6	C8	100.6(1)
16	O1	C6	C7	101.3(1)
17	H6	C6	C8	115.5
18	H6	C6	C7	115.5
19	C8	C6	C7	106.4(1)
20	C3	C7	C5	114.7(1)
21	C3	C7	C6	115.9(1)
22	C3	C7	C7	104.9(1)
23	C5	C7	C6	115.5(1)
24	C5	C7	C7	101.6(1)
25	C6	C7	C7	101.3(1)
26	C6	C8	H8	127
27	C6	C8	C9	106.0(2)
28	H8	C8	C9	127
29	C5	C9	C8	106.0(2)
30	C5	C9	H9	127
31	C8	C9	H9	127
32	C5	O1	C6	96.6(1)
33	N2	C3	C7	107.7
34	N2	C3	O4	124.9
35	C7	C3	O4	127.4(1)
36	O1	C5	H5	115.5
37	O1	C5	C7	100.3(1)
38	O1	C5	C9	100.5(1)
39	H5	C5	C7	115.5
40	H5	C5	C9	115.6
41	C7	C5	C9	107.3(1)
42	C7	C6	O1	101.3(1)
43	C7	C6	H6	115.5
44	C7	C6	C8	106.4(1)
45	O1	C6	H6	115.6
46	O1	C6	C8	100.6(1)
47	H6	C6	C8	115.5
48	C6	C7	C7	101.3(1)
49	C6	C7	C3	115.9(1)
50	C6	C7	C5	115.5(1)
51	C7	C7	C3	104.9(1)
52	C7	C7	C5	101.6(1)
53	C3	C7	C5	114.7(1)
54	C6	C8	H8	127
55	C6	C8	C9	106.0(2)
56	H8	C8	C9	127
57	C5	C9	C8	106.0(2)
58	C5	C9	H9	127
59	C8	C9	H9	127

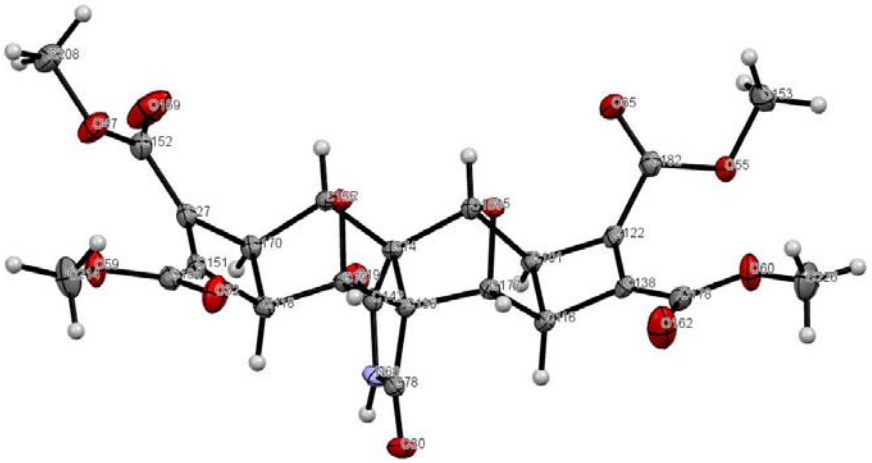
Mitsudo imide **13** (CCDC 1486429)

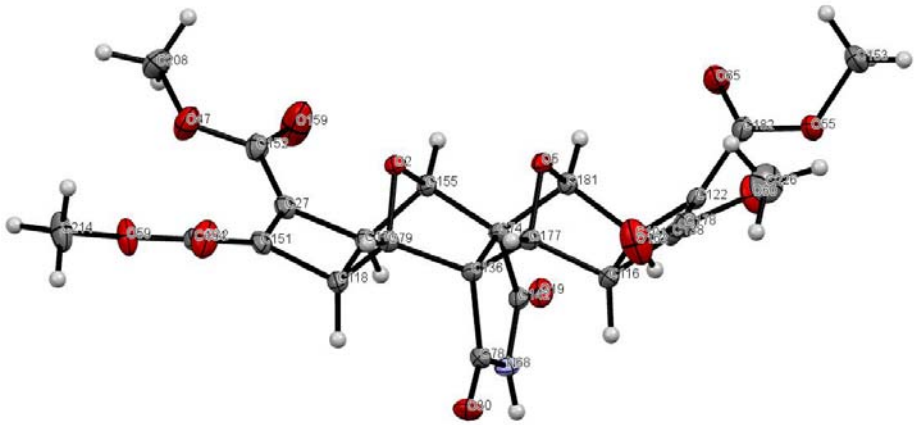


Parameter	**Mitsudo imide 13**
Empirical formula	3(C24 H21 N O12), 2(C2 H3 N), 3(H2 O)
Formula weight	1682.41
Temperature (K)	150
Wavelength (Å)	0.071073
Crystal system	monoclinic
Space group	'P 21/c'
Unit cell dimensions	a=9.0952(2) b=6.6256(6) c=24.0116(5)
Theta max	29.4
Reflections used	14596
Final R indices [I > 2σ(I)]	
R1	0.0569
wR2	0.1424
Data completeness	0.866

The crystal packing of compound **13** was stabilised by intermolecular N—H···O hydrogen bonding (ORTEP diagram generated in Mercury, Version 3.0, H atoms removed for clarity).





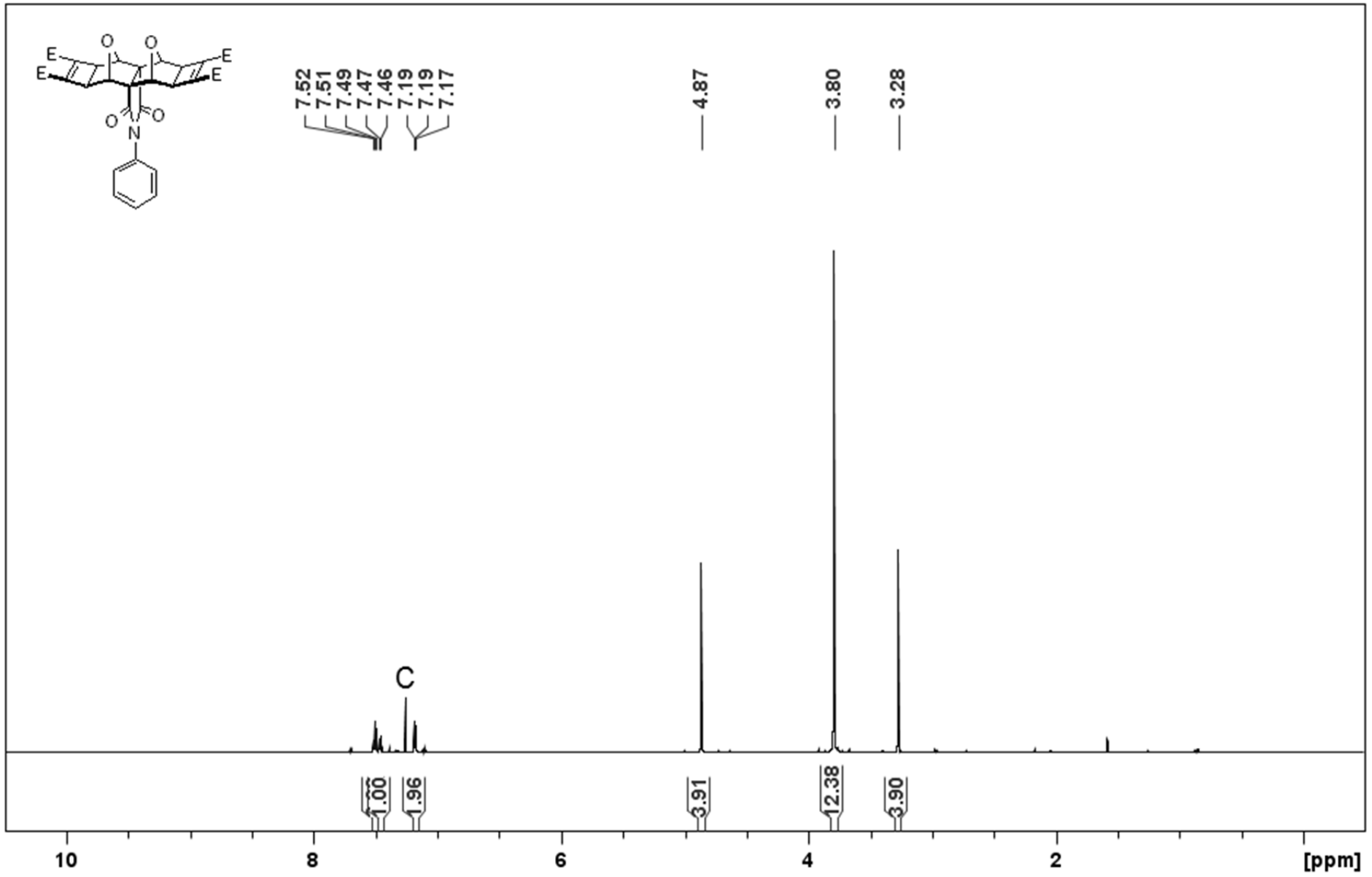


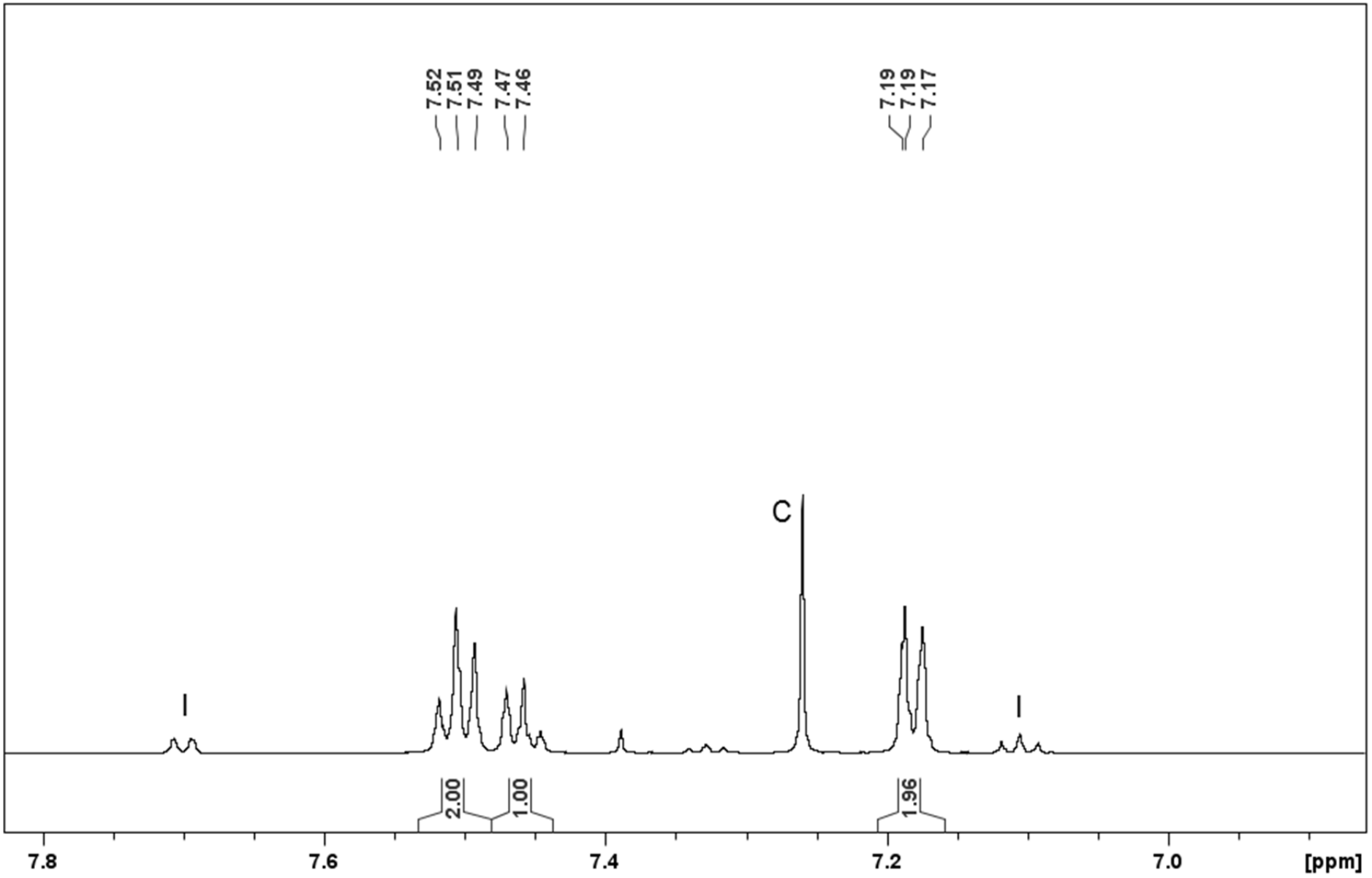
Bond Angles

Number	Atom1	Atom2	Atom3	Angle
1	C79	O2	C155	97.9(1)
2	C177	O5	C181	98.1(1)
3	C151	C27	C152	137.9(2)
4	C151	C27	C170	94.7(2)
5	C152	C27	C170	127.0(2)
6	C152	O47	C208	116.0(2)
7	C153	O55	C182	114.8(2)
8	C194	O59	C214	115.0(2)
9	C178	O60	C226	114.9(2)
10	H68	N68	C78	122.7
11	H68	N68	C142	122.6
12	C78	N68	C142	114.7(2)
13	C136	C74	C142	104.8(1)
14	C136	C74	C155	102.0(1)
15	C136	C74	C181	101.8(1)
16	C142	C74	C155	115.3(2)
17	C142	C74	C181	115.8(2)
18	C155	C74	C181	114.5(2)
19	O30	C78	N68	125.6(2)
20	O30	C78	C136	126.6(2)
21	N68	C78	C136	107.8(2)
22	O2	C79	H79	114.1
23	O2	C79	C118	102.4(1)
24	O2	C79	C136	101.8(1)
25	H79	C79	C118	114.2
26	H79	C79	C136	114
27	C118	C79	C136	108.9(1)
28	H101	C101	C116	117.3
29	H101	C101	C122	117.1
30	H101	C101	C181	117.2
31	C116	C101	C122	85.3(1)
32	C116	C101	C181	101.4(1)
33	C122	C101	C181	113.3(2)
34	C101	C116	H116	117.4
35	C101	C116	C138	85.5(1)
36	C101	C116	C177	100.8(1)
37	H116	C116	C138	117.5
38	H116	C116	C177	117.4
39	C138	C116	C177	112.9(2)
40	C79	C118	H118	116.9
41	C79	C118	C151	114.4(2)
42	C79	C118	C170	101.0(1)
43	H118	C118	C151	116.9
44	H118	C118	C170	117
45	C151	C118	C170	85.4(1)
46	C101	C122	C138	94.4(2)
47	C101	C122	C182	126.8(2)
48	C138	C122	C182	136.0(2)
49	C74	C136	C78	104.7(1)
50	C74	C136	C79	101.6(1)
51	C74	C136	C177	101.6(1)
52	C78	C136	C79	116.2(2)
53	C78	C136	C177	114.7(2)

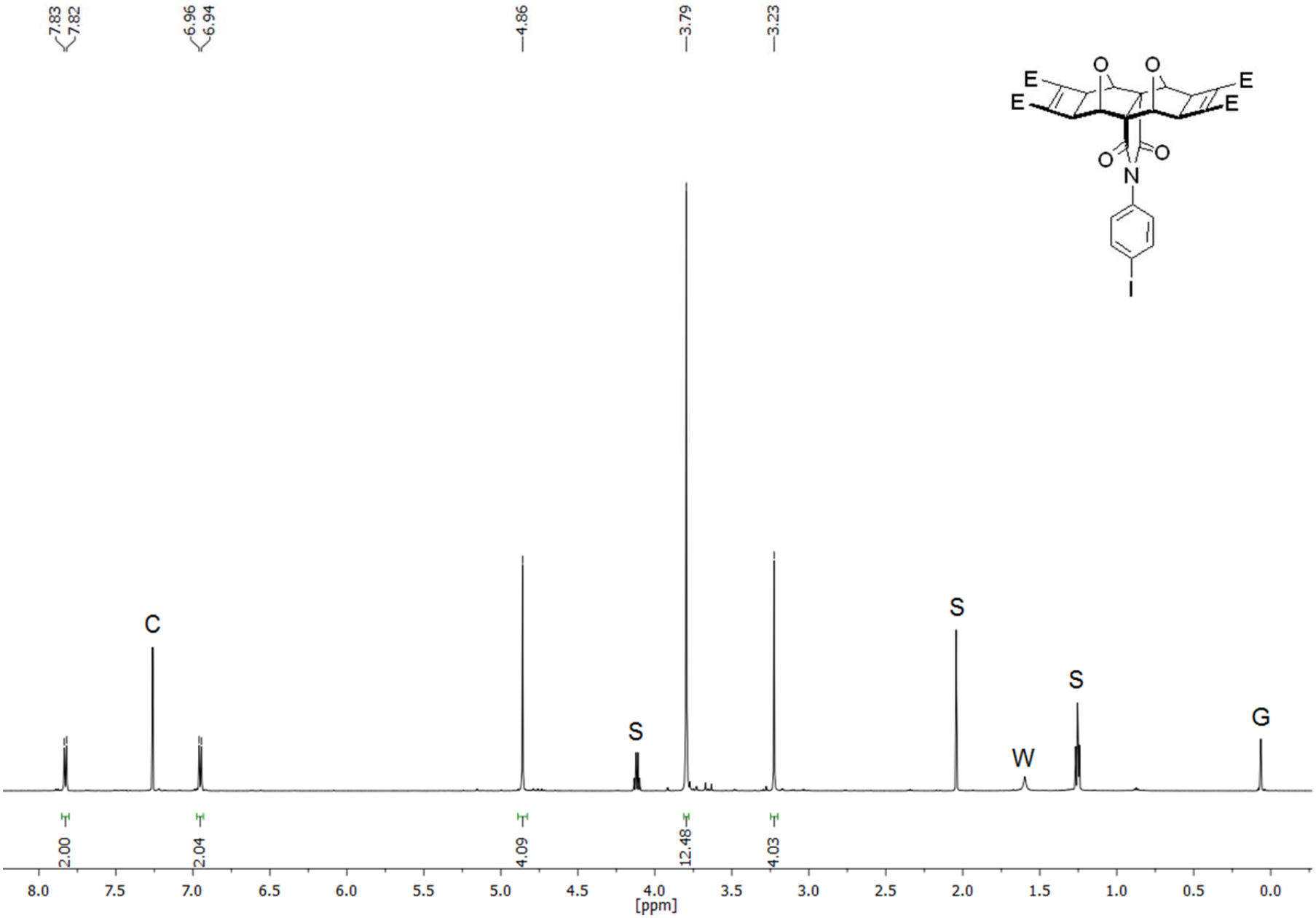
54	C79	C136	C177	115.1(2)	78	H155	C155	C170	114.3	102	O65	C182	C122	120.2(2)
55	C116	C138	C122	94.9(2)	79	C27	C170	C118	85.6(1)	103	O32	C194	O59	125.4(2)
56	C116	C138	C178	126.5(2)	80	C27	C170	C155	114.2(2)	104	O32	C194	C151	120.4(2)
57	C122	C138	C178	136.9(2)	81	C27	C170	H170	116.8	105	O59	C194	C151	114.2(2)
58	O19	C142	N68	125.2(2)	82	C118	C170	C155	101.5(1)	106	O47	C208	H20A	109.5
59	O19	C142	C74	126.8(2)	83	C118	C170	H170	116.8	107	O47	C208	H20B	109.5
60	N68	C142	C74	108.0(2)	84	C155	C170	H170	116.9	108	O47	C208	H20C	109.4
61	C27	C151	C118	94.4(2)	85	O5	C177	C116	102.3(1)	109	H20A	C208	H20B	109.4
62	C27	C151	C194	138.3(2)	86	O5	C177	C136	101.8(1)	110	H20A	C208	H20C	109.4
63	C118	C151	C194	126.3(2)	87	O5	C177	H177	114	111	H20B	C208	H20C	109.5
64	C27	C152	O47	113.9(2)	88	C116	C177	C136	109.3(1)	112	O59	C214	H21A	109.5
65	C27	C152	O159	121.2(2)	89	C116	C177	H177	114.1	113	O59	C214	H21B	109.4
66	O47	C152	O159	124.9(2)	90	C136	C177	H177	114	114	O59	C214	H21C	109.5
67	O55	C153	H15A	109.5	91	O60	C178	C138	113.4(2)	115	H21A	C214	H21B	109.5
68	O55	C153	H15B	109.5	92	O60	C178	O162	125.2(2)	116	H21A	C214	H21C	109.5
69	O55	C153	H15C	109.5	93	C138	C178	O162	121.4(2)	117	H21B	C214	H21C	109.4
70	H15A	C153	H15B	109.5	94	O5	C181	C74	101.6(1)	118	O60	C226	H22A	109.5
71	H15A	C153	H15C	109.5	95	O5	C181	C101	101.8(1)	119	O60	C226	H22B	109.4
72	H15B	C153	H15C	109.3	96	O5	C181	H181	114.1	120	O60	C226	H22C	109.4
73	O2	C155	C74	101.8(1)	97	C74	C181	C101	109.8(2)	121	H22A	C226	H22B	109.6
74	O2	C155	H155	114.3	98	C74	C181	H181	114.1	122	H22A	C226	H22C	109.4
75	O2	C155	C170	102.0(1)	99	C101	C181	H181	114.1	123	H22B	C226	H22C	109.6
76	C74	C155	H155	114.3	100	O55	C182	O65	125.2(2)					
77	C74	C155	C170	108.8(1)	101	O55	C182	C122	114.6(2)					

S16: 600 MHz ^{1}H NMR Mitsudo phenyl imide **14a**

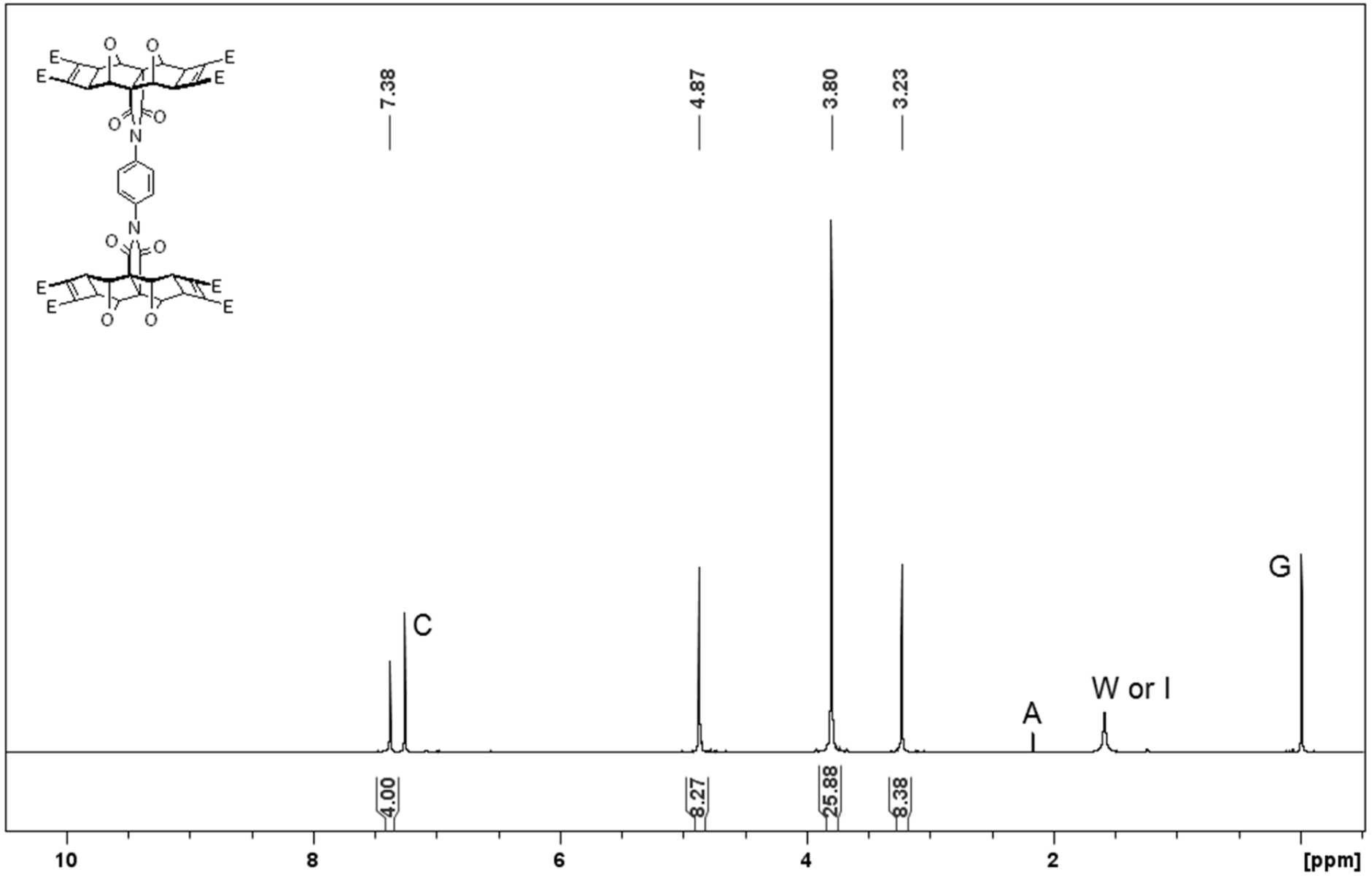



7.52
7.51
7.49
7.47
7.46
7.19
7.19
7.17
C
I
I
2.00
1.00
1.96
7.8
7.6
7.4
7.2
7.0
[ppm]

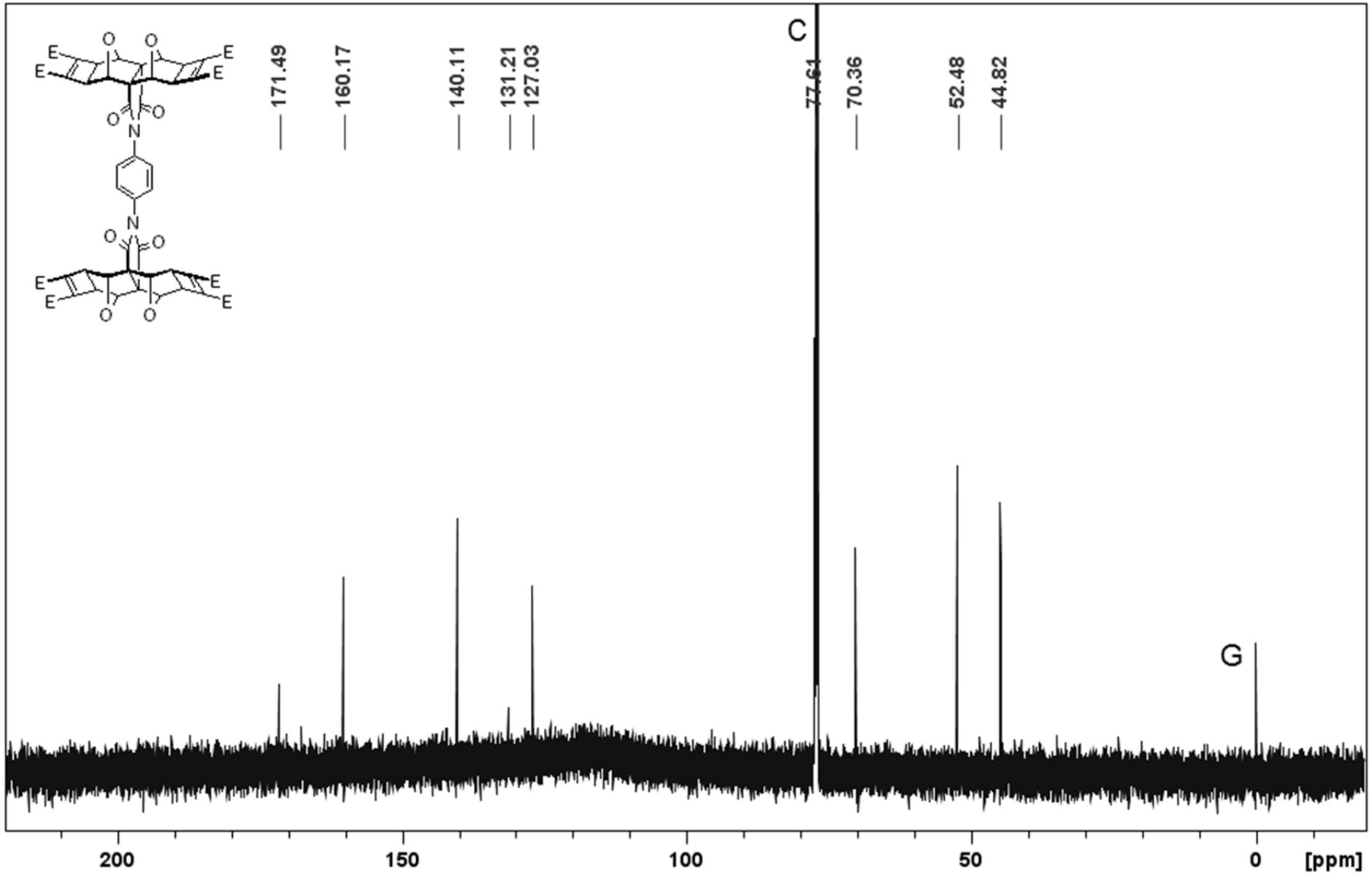
S17: 600 MHz ^{1}H NMR Mitsudo 4-iodophenyl imide **14b**

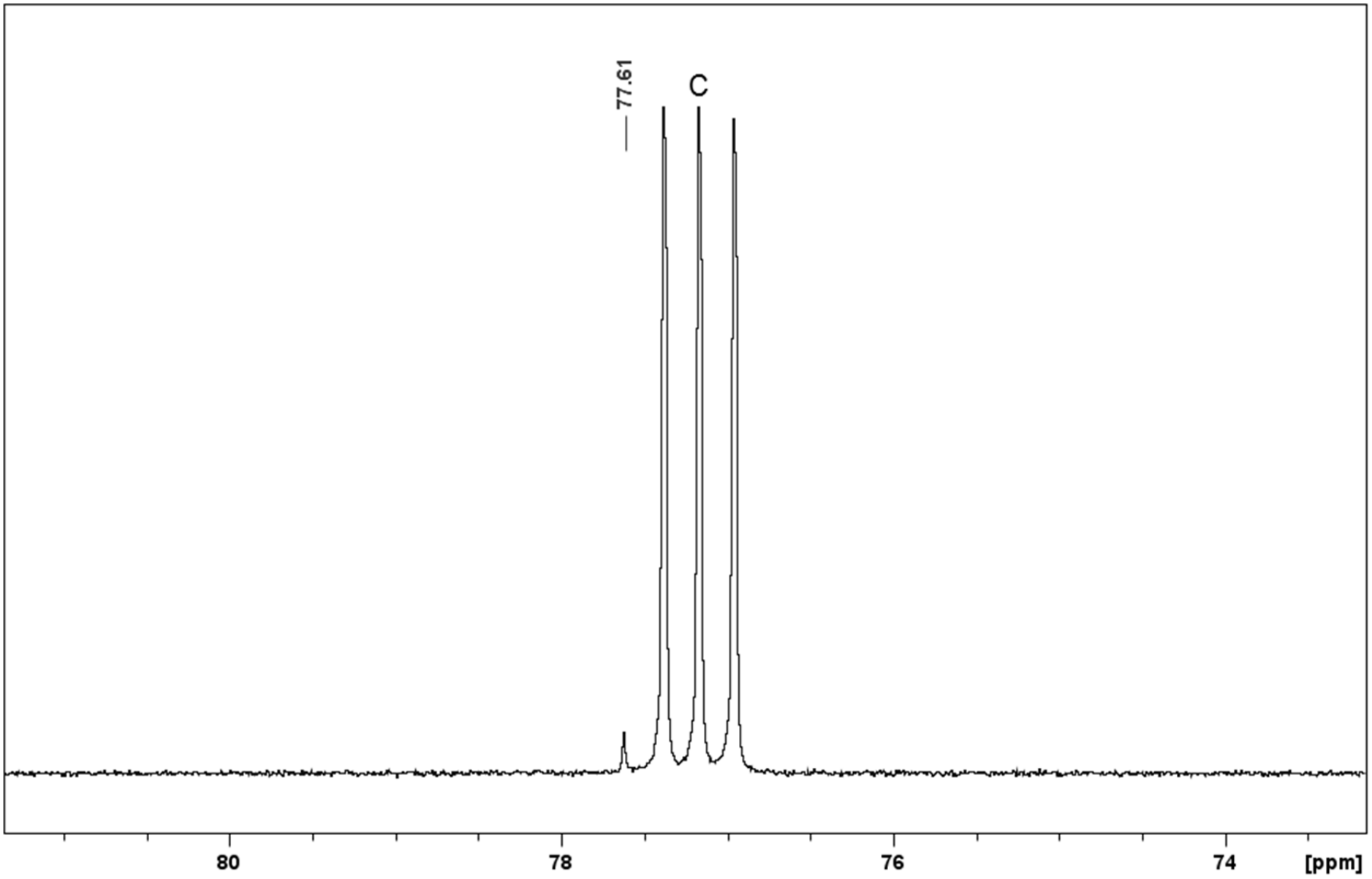


S18: 600 MHz ^{1}H NMR Mitsudo phenyl diimide **10**

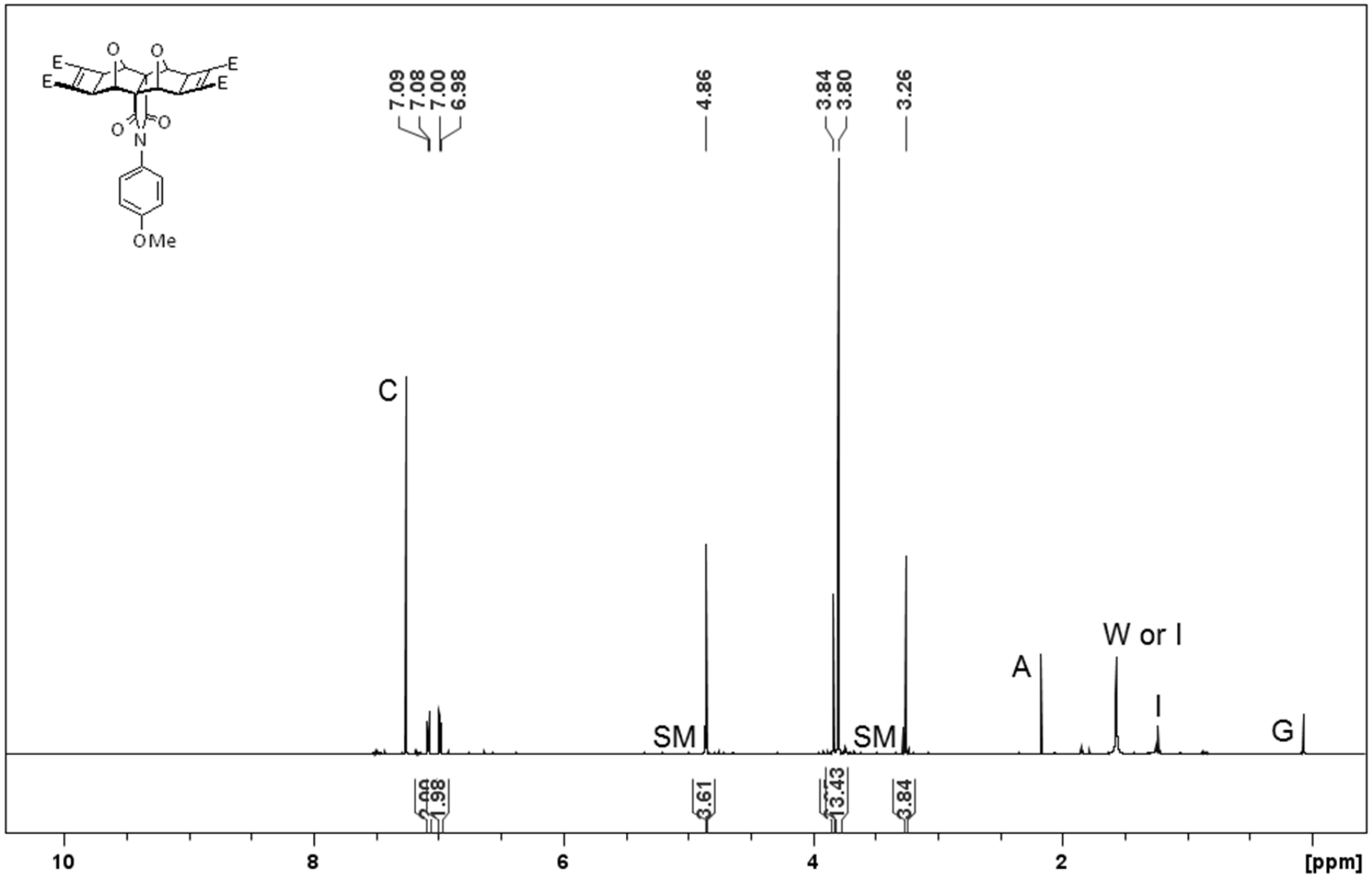


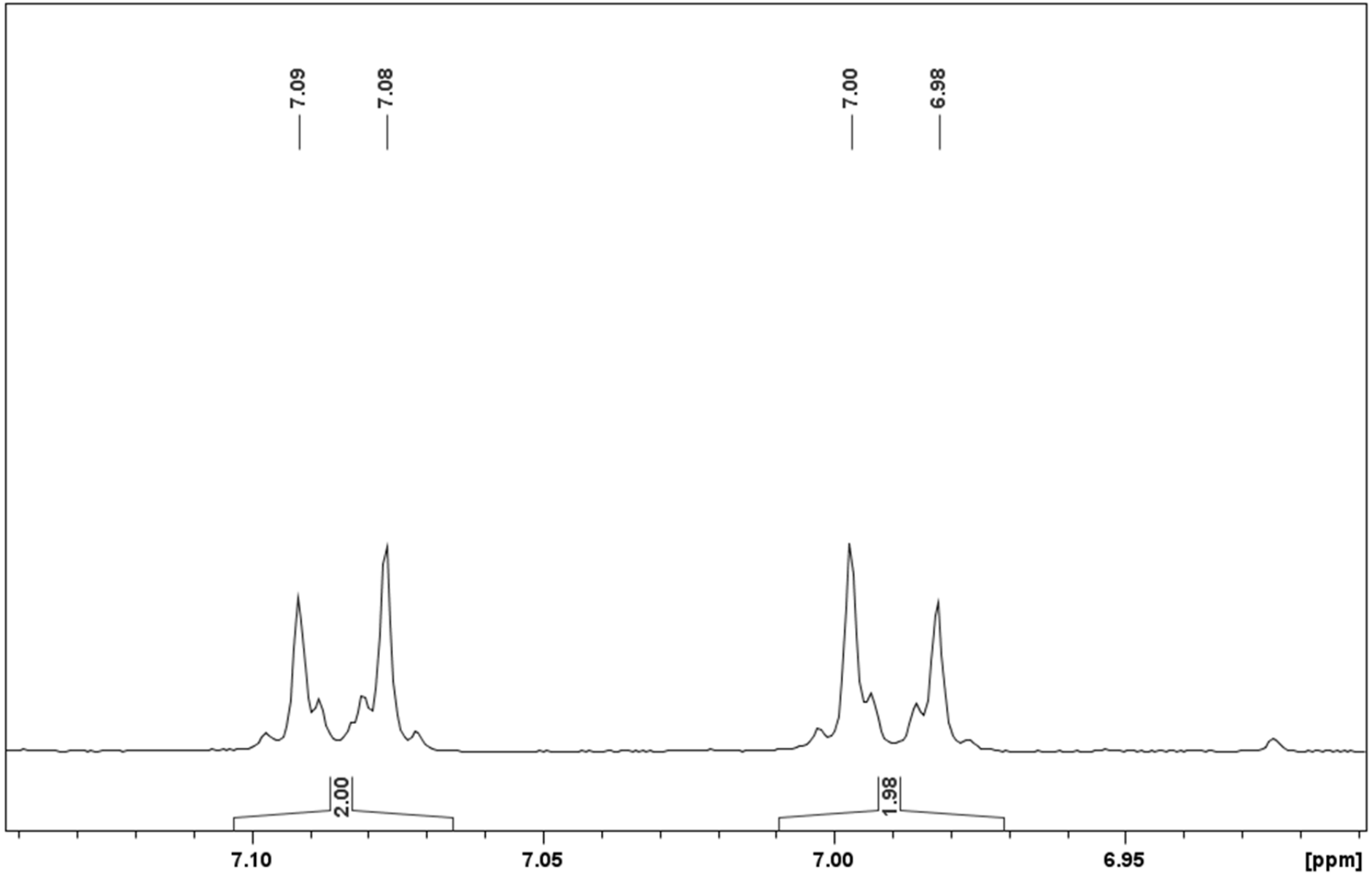
S19: 150 MHz ^{13}C NMR Mitsudo phenyl diimide **10**

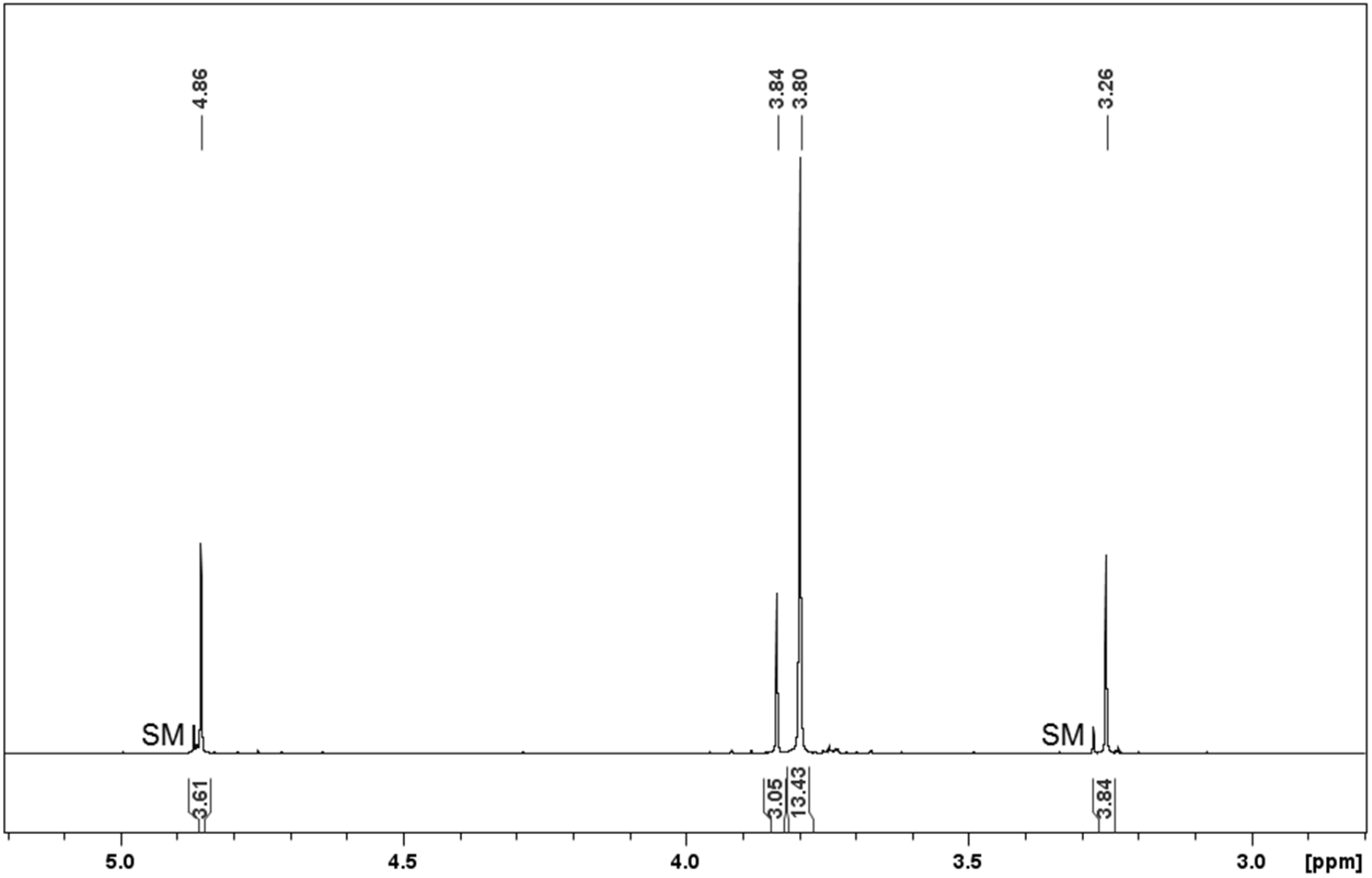



77.61
C
80
78
76
74
[ppm]

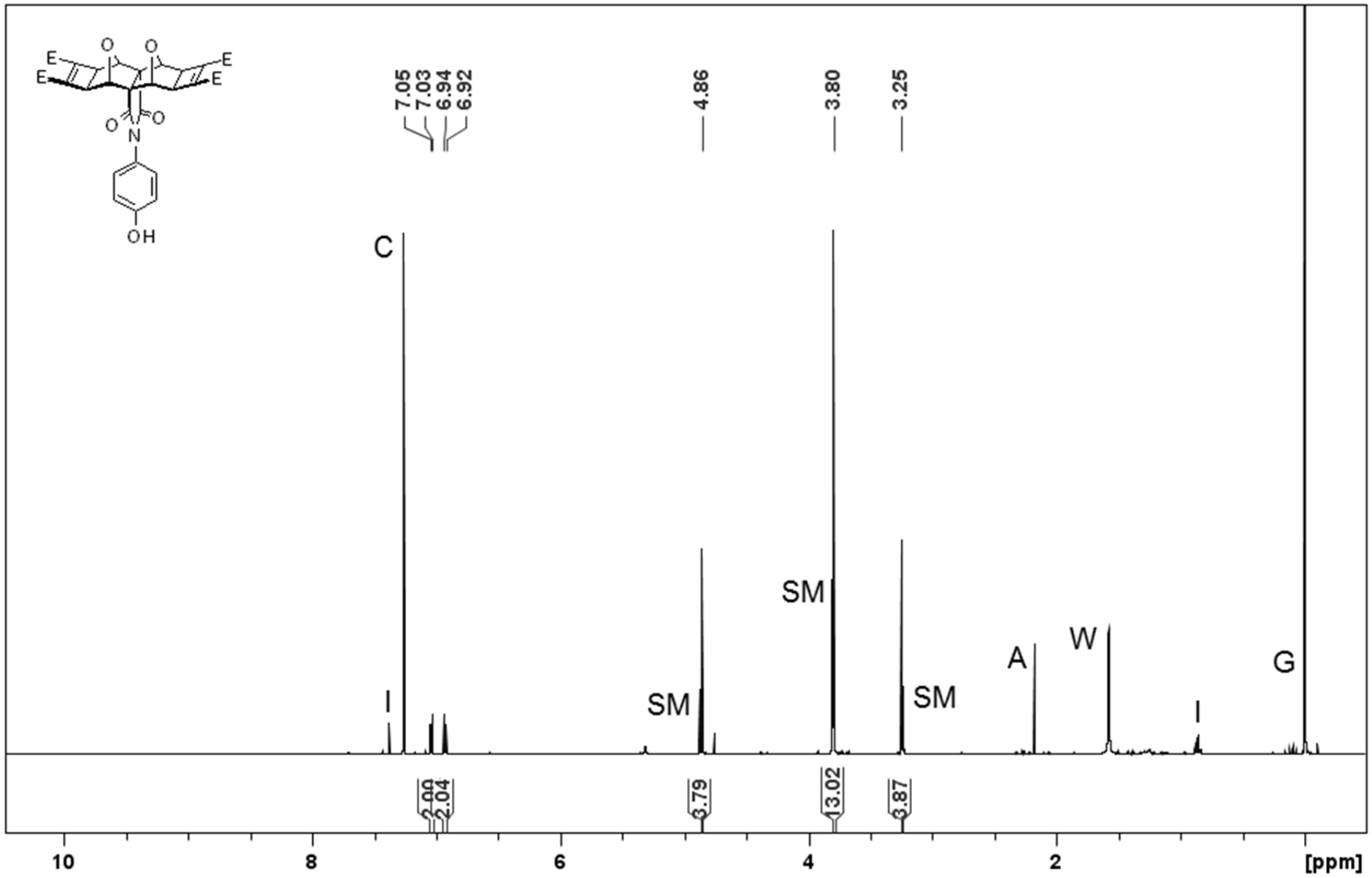
S20: 600 MHz ^{1}H NMR side product with solvent MeOH **15a**

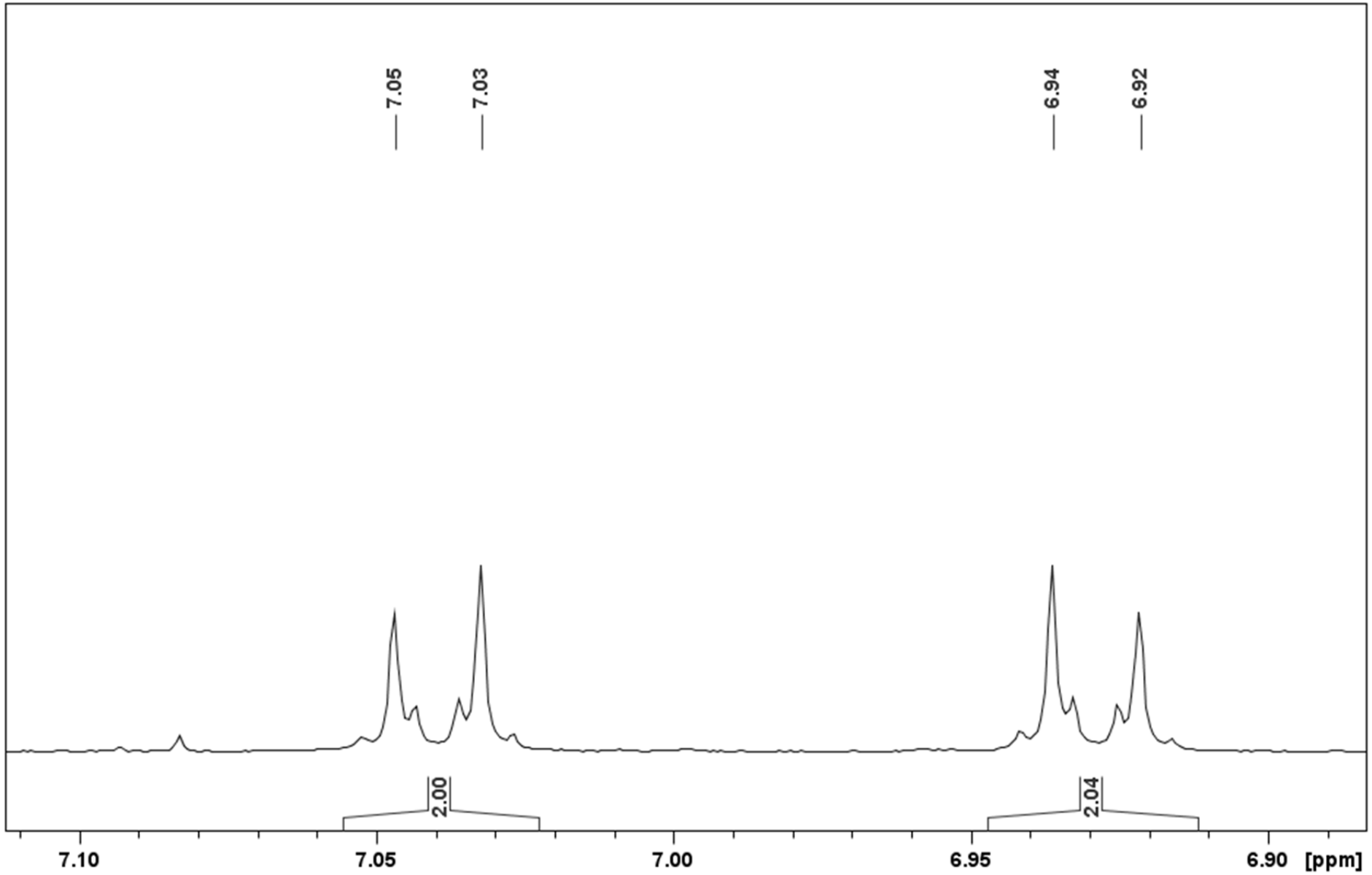


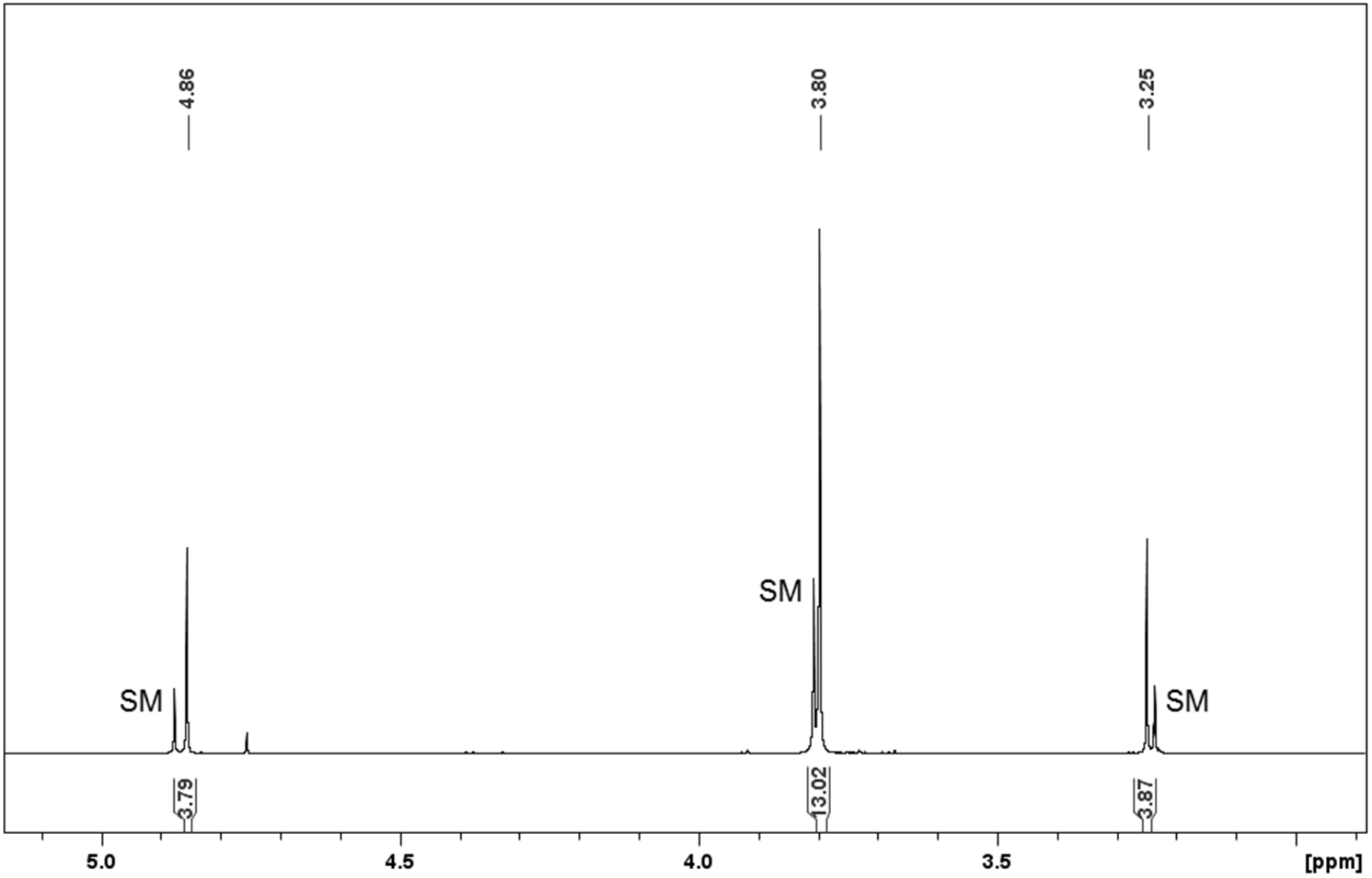

7.09
7.08
7.00
6.98
2.00
1.98
7.10
7.05
7.00
6.95
[ppm]


4.86
3.84
3.80
3.26
SM
SM
3.61
3.05
13.43
3.84
5.0
4.5
4.0
3.5
3.0
[ppm]

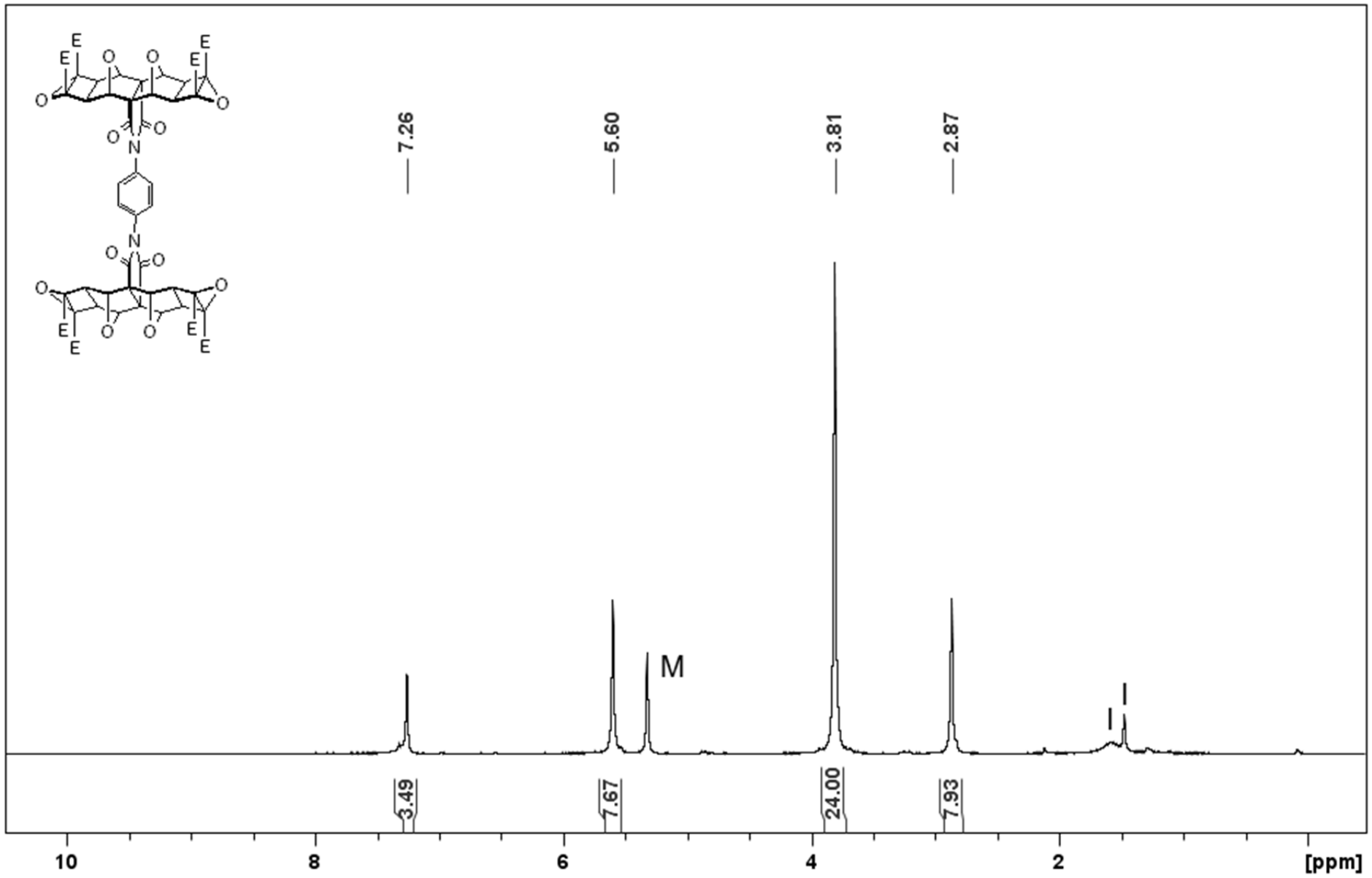
S21: 600 MHz ^{1}H NMR side product with solvent 9:1 THF/H_2O **15b**



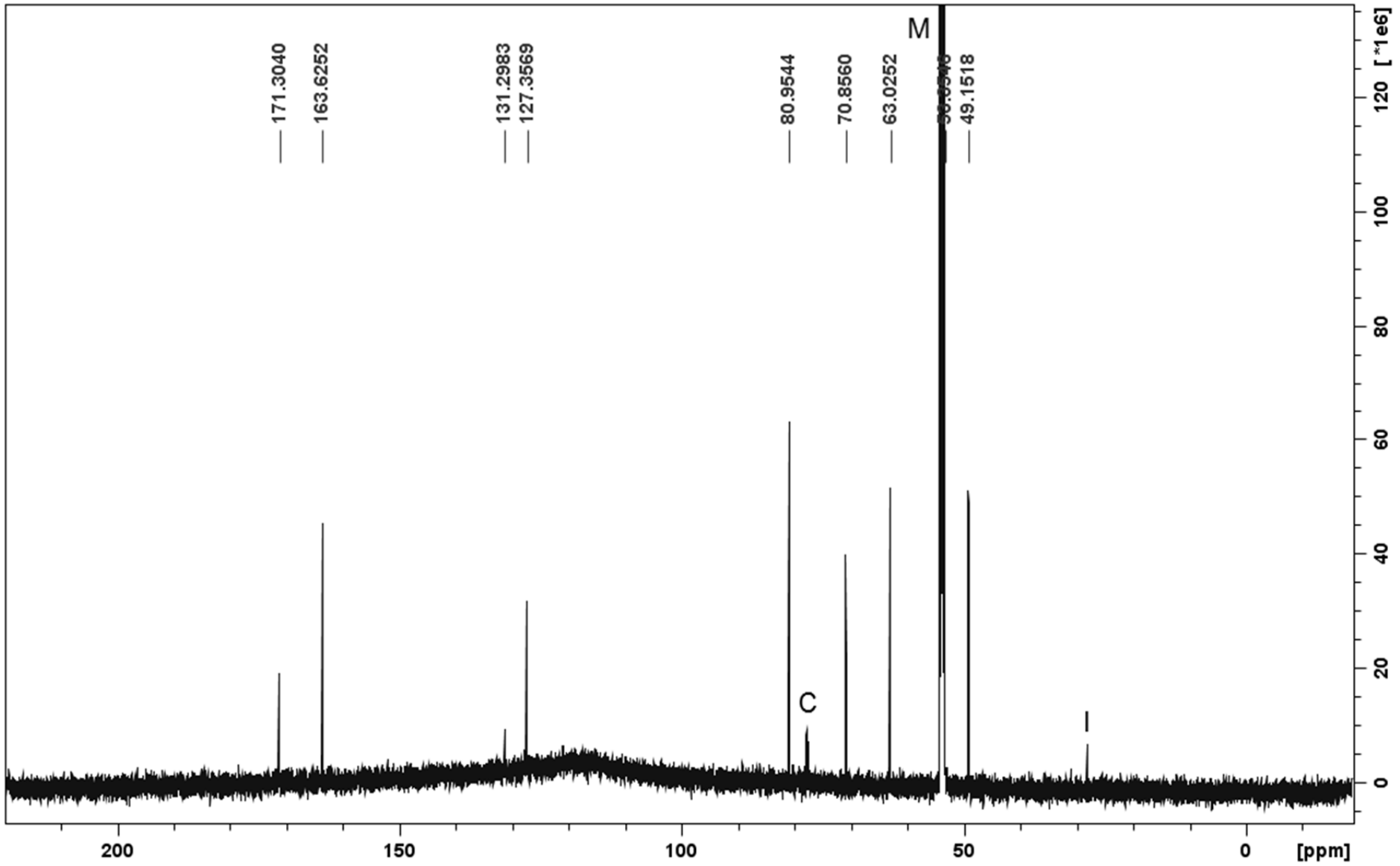

7.05
7.03
6.94
6.92
2.00
2.04
7.10
7.05
7.00
6.95
6.90
[ppm]

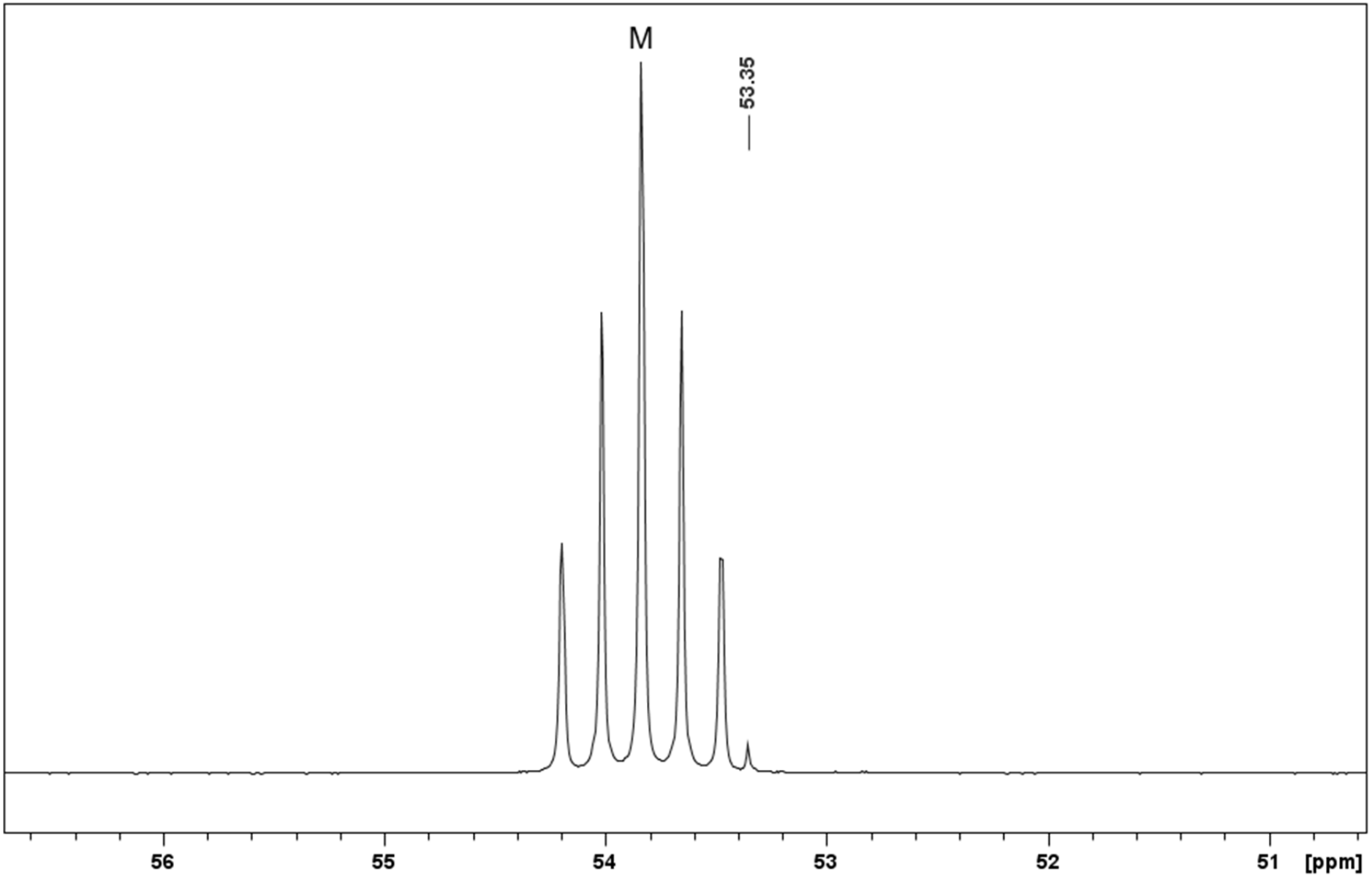

4.86
3.80
3.25
SM
SM
SM
3.79
13.02
3.87
5.0
4.5
4.0
3.5
[ppm]

S22: 600 MHz ^{1}H NMR tetra-epoxide phenyl diimide linker **16**

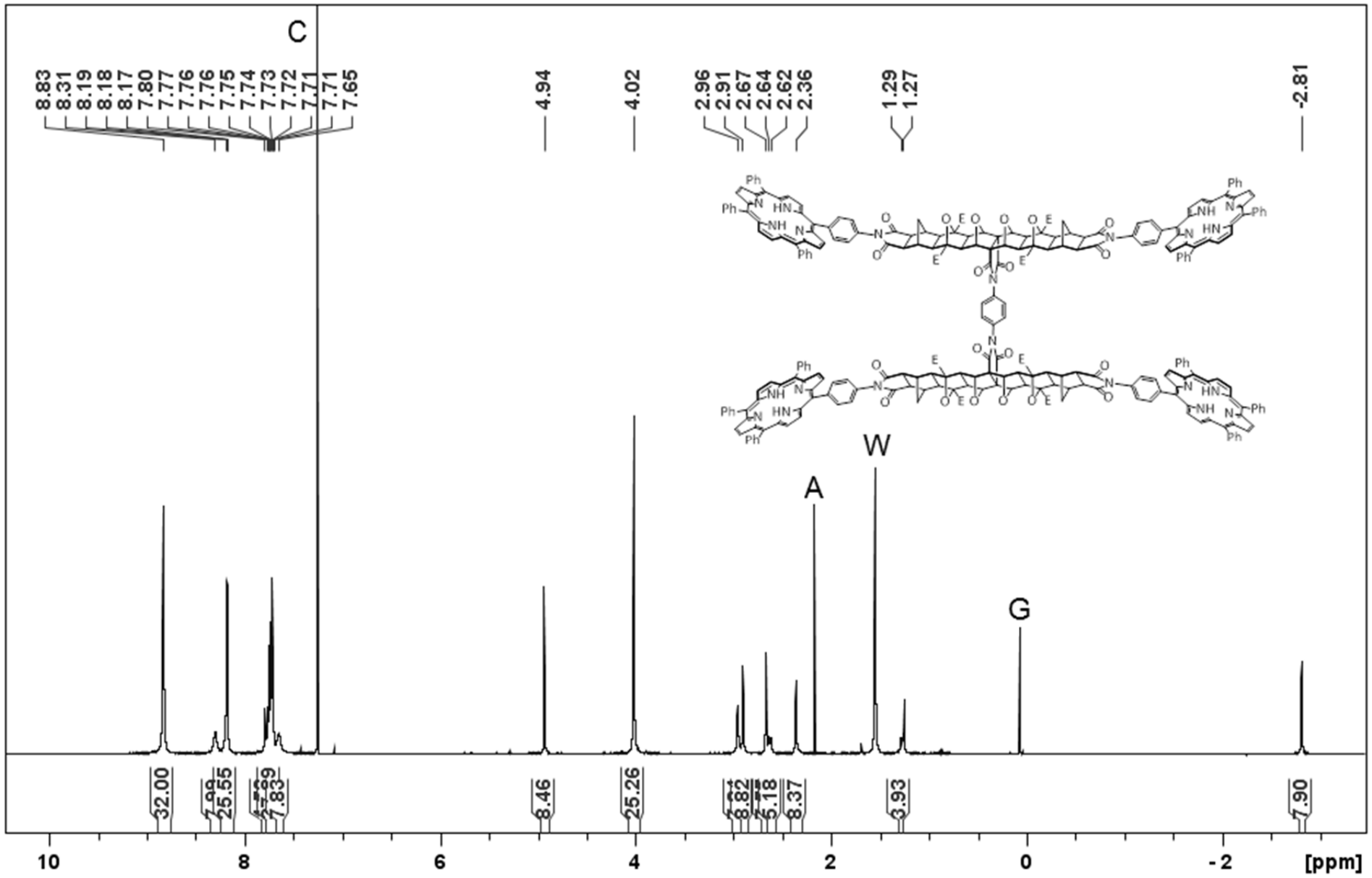


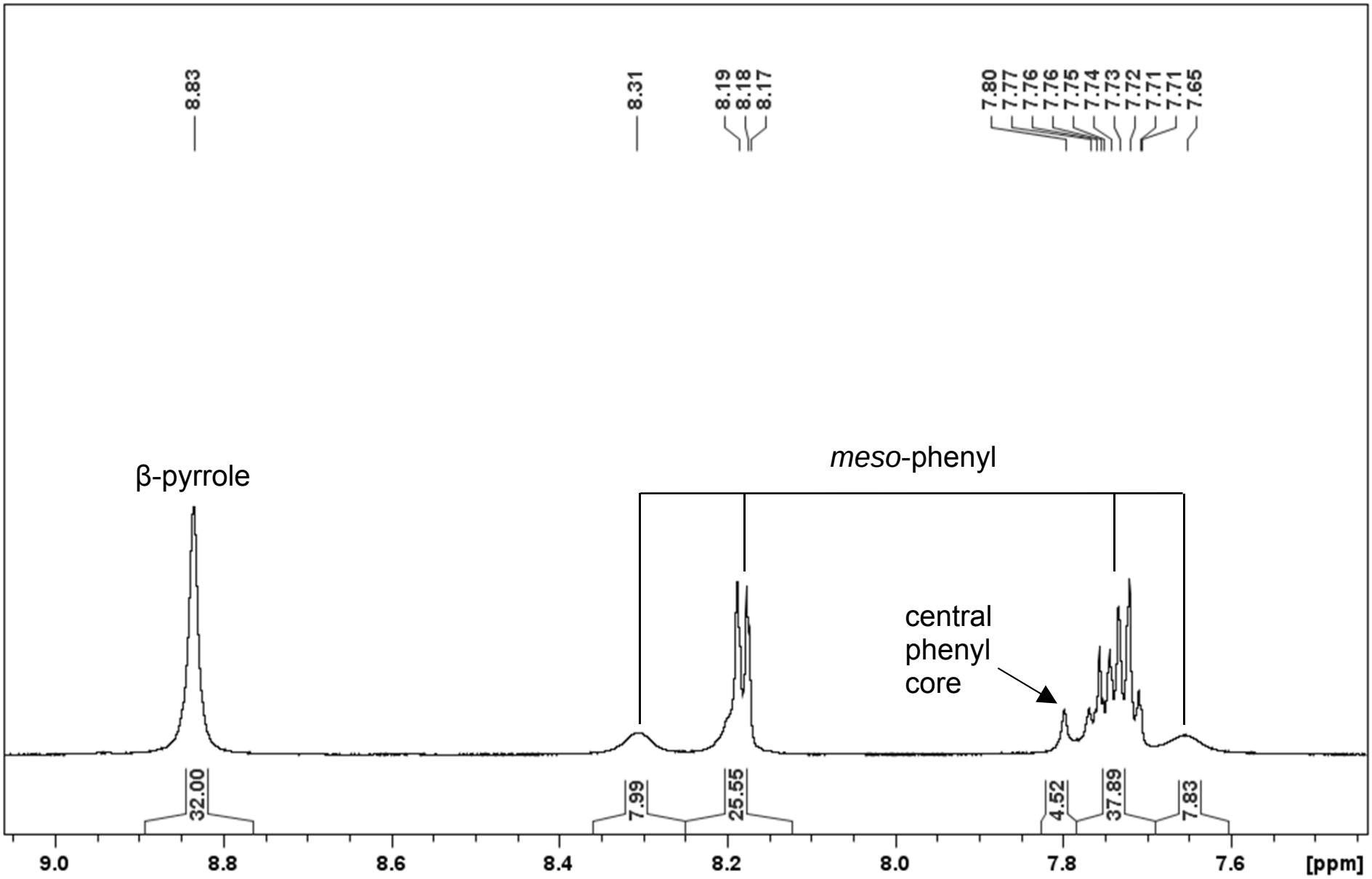
S23: 150 MHz ^{13}C NMR tetra-epoxide phenyl diimide linker **16**

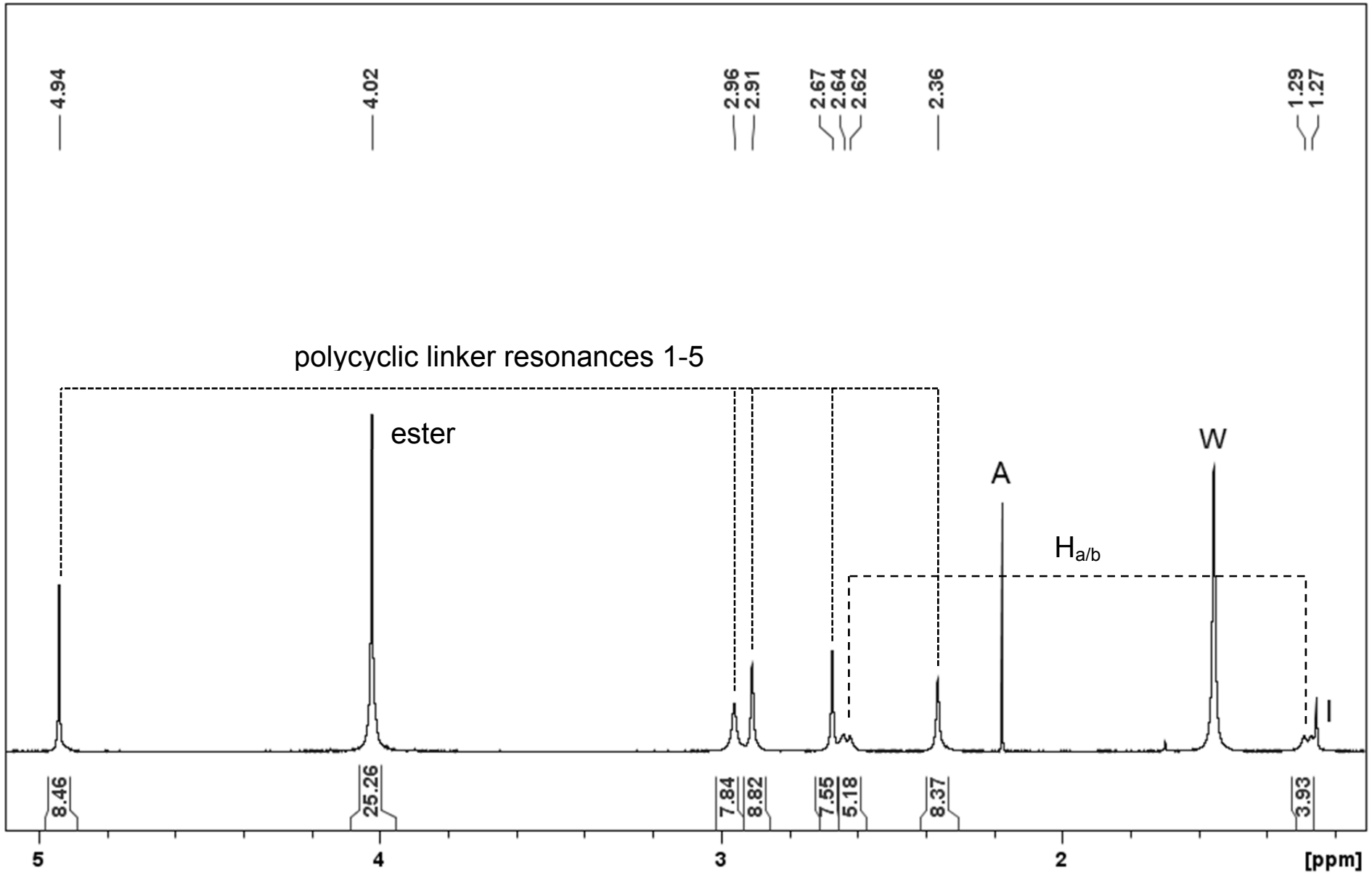


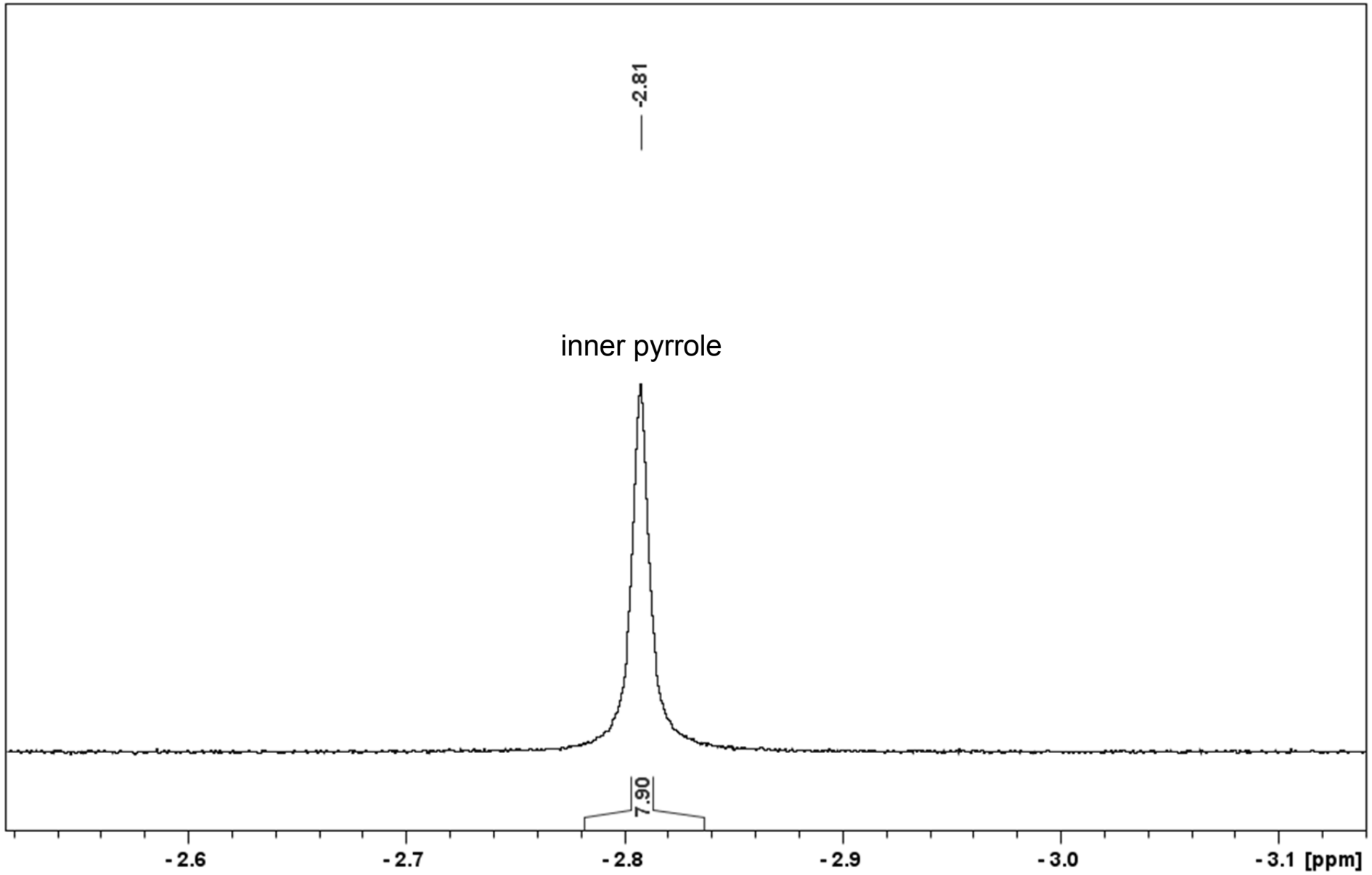

M
53.35
56
55
54
53
52
51
[ppm]

S24: 600 MHz ^{1}H NMR free base tetra-porphyrin tweezer **2**

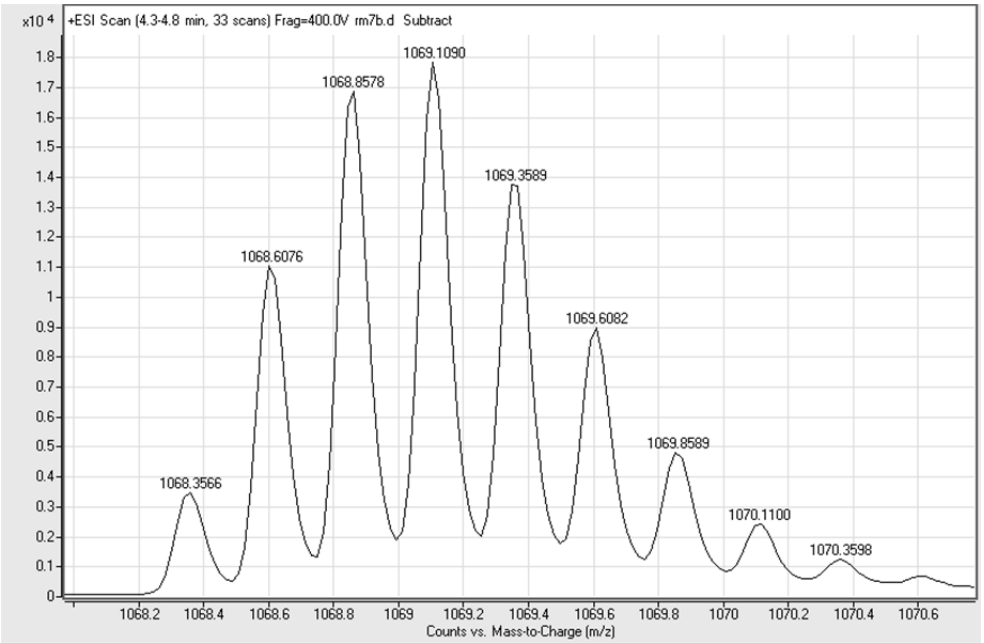


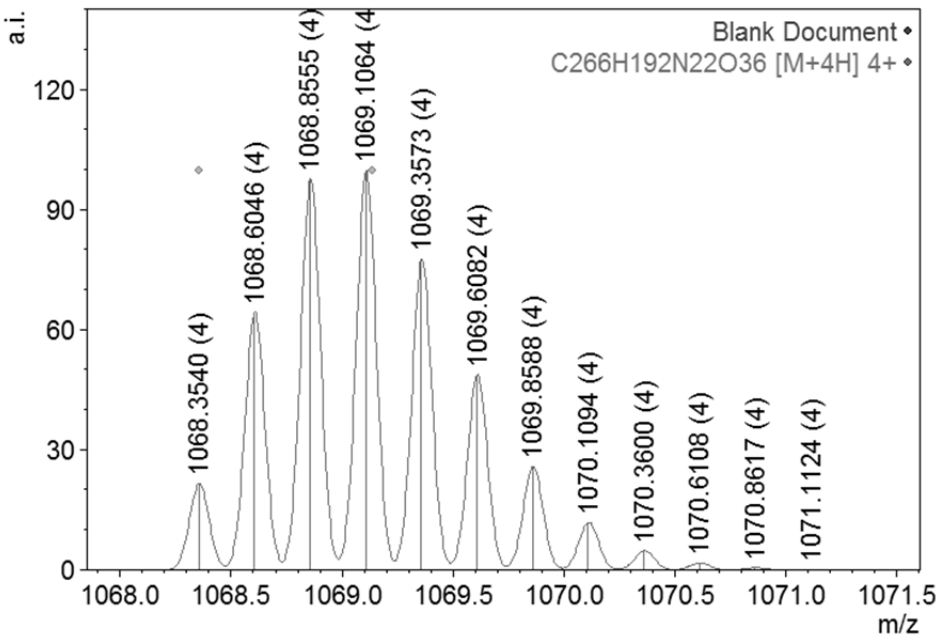

8.83
8.31
8.19
8.18
8.17
7.80
7.77
7.76
7.76
7.75
7.74
7.73
7.72
7.71
7.71
7.65
β-pyrrole
meso-phenyl
central
phenyl
core
32.00
7.99
25.55
4.52
37.89
7.83
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
[ppm]


4.94
4.02
2.96
2.91
2.67
2.64
2.62
2.36
1.29
1.27
polycyclic linker resonances 1-5
ester
A
W
$H_{a/b}$
8.46
25.26
7.84
8.82
7.55
5.18
8.37
3.93
5
4
3
2
[ppm]

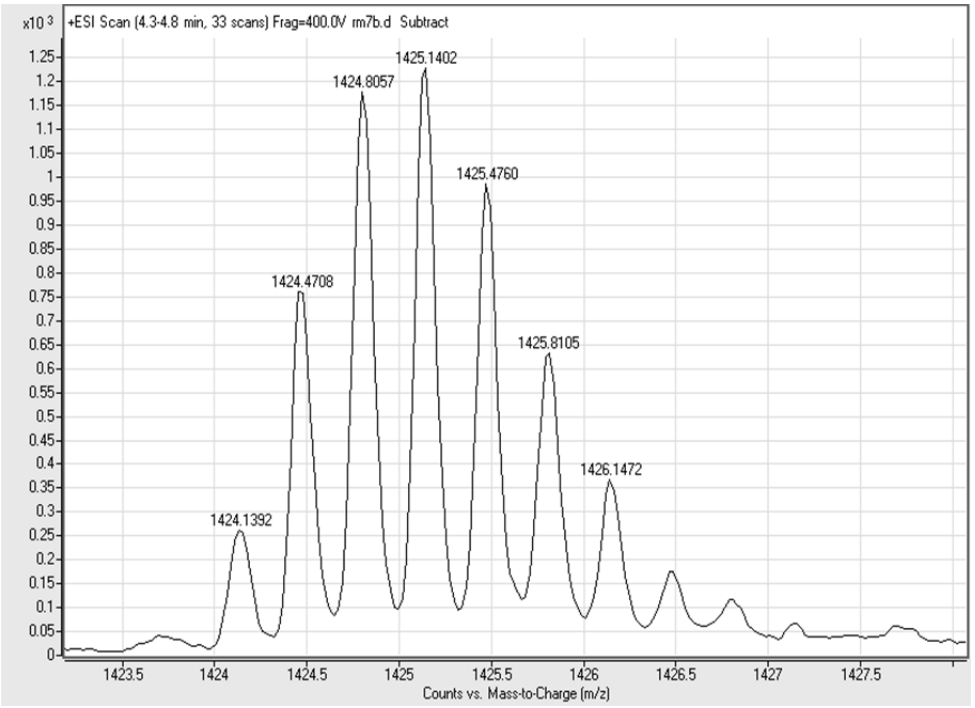

-2.81
inner pyrrole
7.90
- 2.6
- 2.7
- 2.8
- 2.9
- 3.0
- 3.1 [ppm]

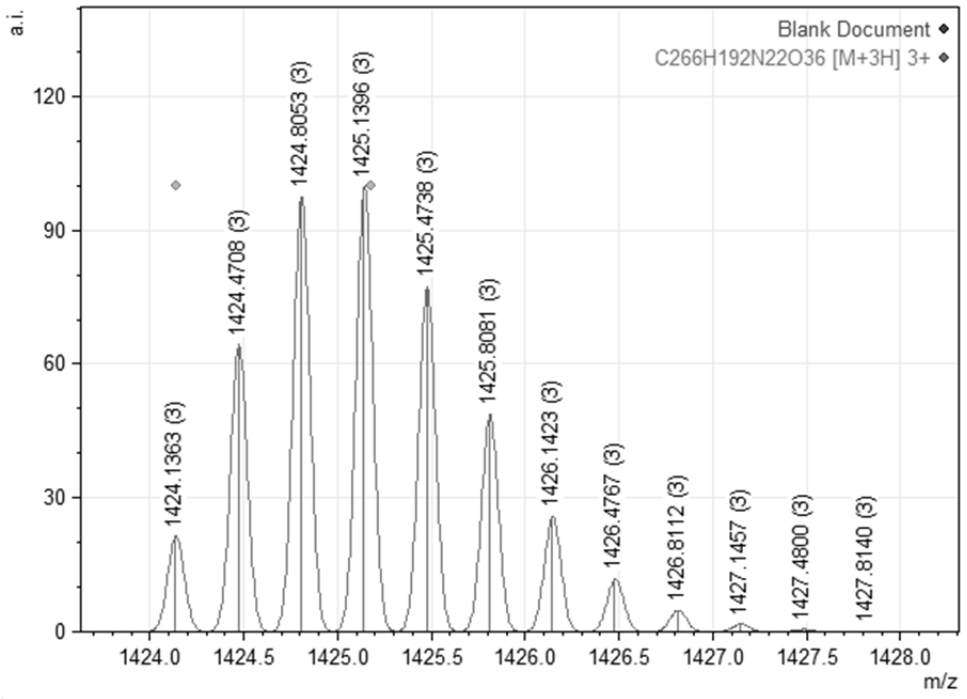
S25: HRMS (ESI-TOF-MS) experimental and predicted free base tetra-porphyrin tweezer **2**



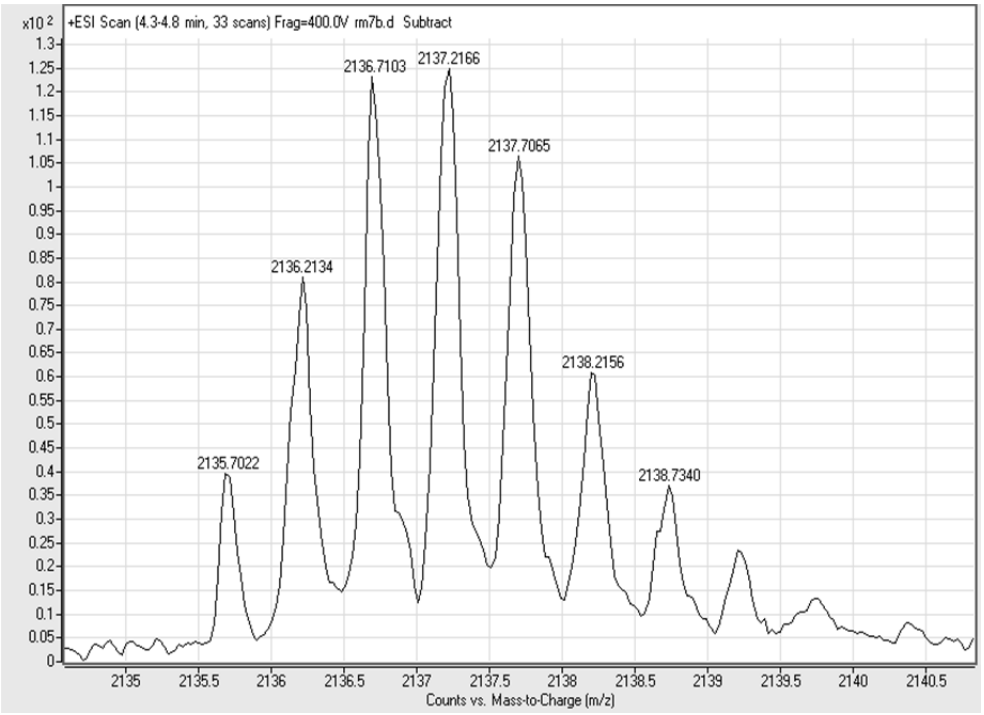


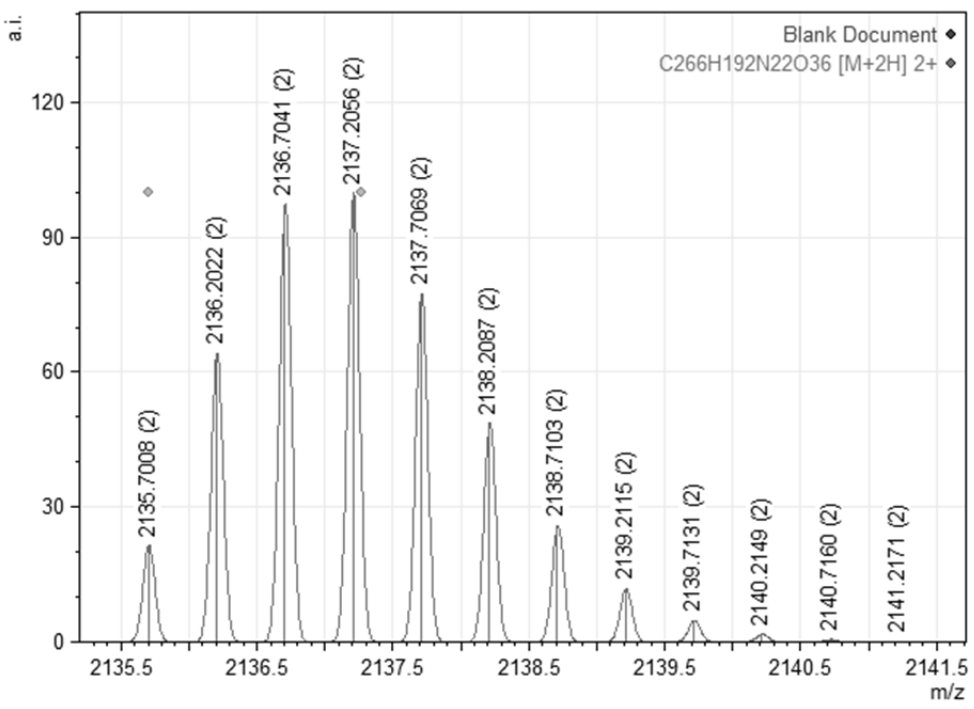
$C_{266}H_{196}N_{22}O_{36}^{4+}$ $[M+4H]^{4+}$: Calcd. 1068.3540. Found 1068.3566.





$C_{266}H_{195}N_{22}O_{36}^{3+}$ $[M+3H]^{3+}$: Calcd. 1424.1363. Found 1424.1392.





$C_{266}H_{194}N_{22}O_{36}^{2+}$ $[M+2H]^{2+}$: Calcd. 2135.7008. Found 2135.7022.

S26: UV-Vis free base tetra-porphyrin tweezer **2**