Supporting Information

Bright Green PhOLEDs Using Cyclometalated Diiridium(III) Complexes with Bridging Oxamidato Ligands as Phosphorescent Dopants

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X-ray crystallography

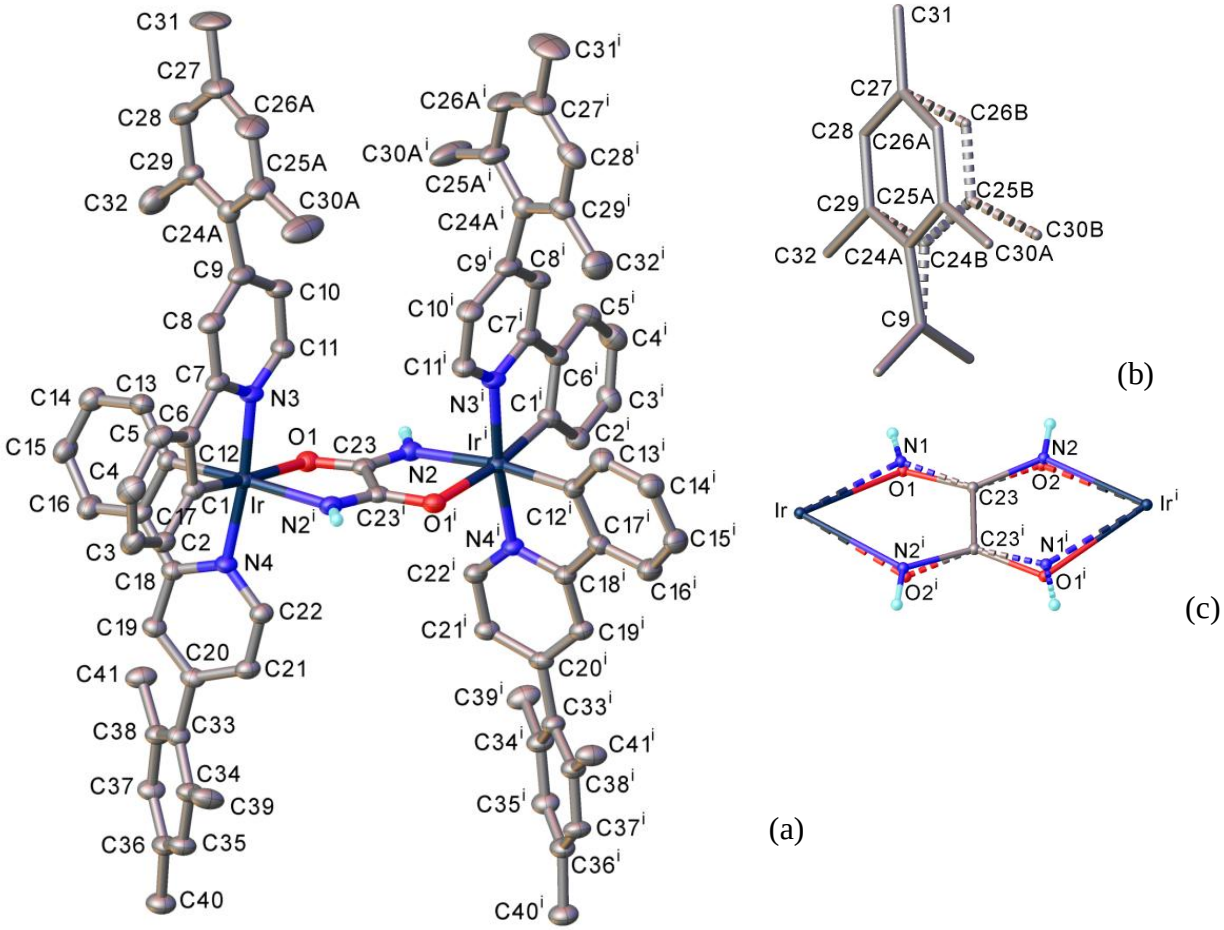


Figure S1. (a) Molecular structure of **5** (major component), (b) disorder of the mesityl group. (c) disorder of the bridging system. Here and below atomic displacement ellipsoids are shown at the 50% probability level. H atoms, except oxamidato, are omitted for clarity. Primed atoms were generated by a crystallographic twofold axis (transformation ½ -*x*, *y*, 1-*z*).

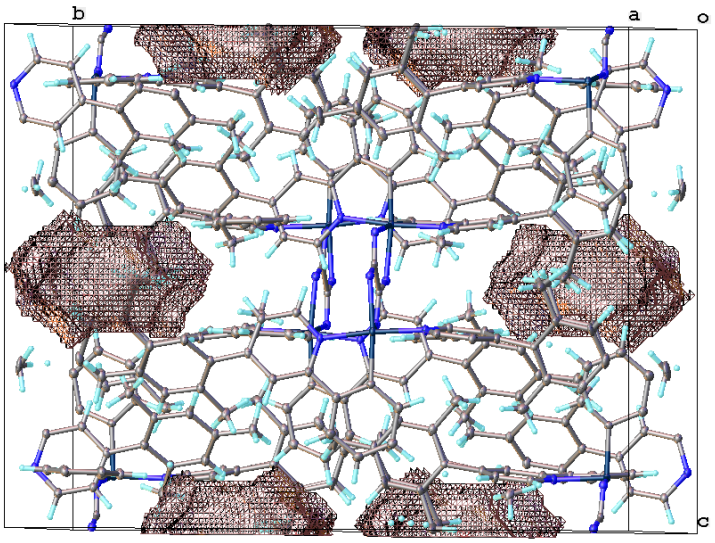


Figure S2. Solvent-accessible voids in the structure of **5**, presumably occupied by disordered hexane molecules.

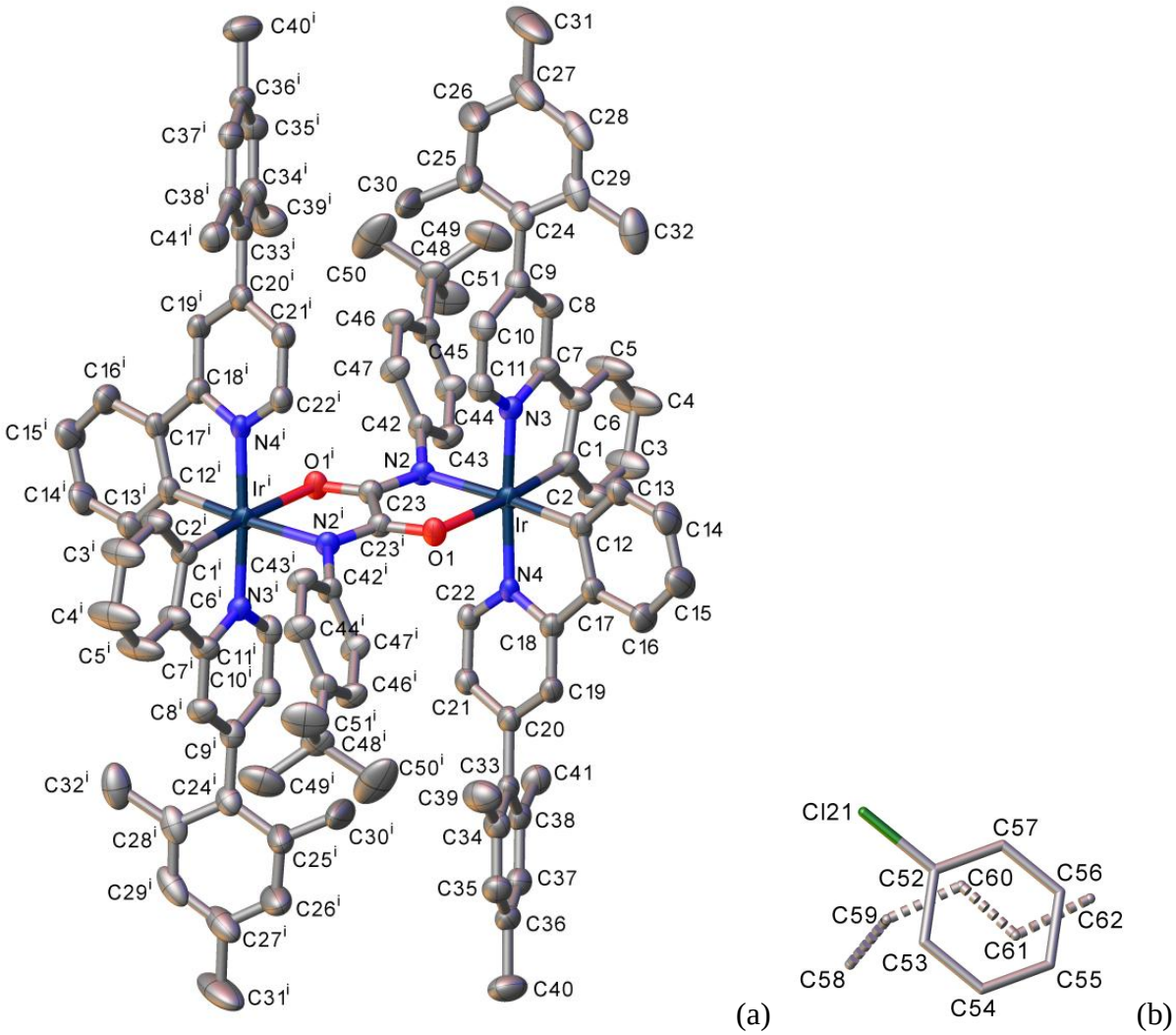


Figure S3. (a) Molecular structure of **6**; (b) disorder of chlorobenzene and pentane of crystallisation.

Table S1. Crystal data for **5** and **6**

Compound	**5**·hexane	**6**·PhCl·pentane
CCDC	1521969	1521970
Formula	$C_{88}H_{88}Ir_2N_6O_2$	$C_{113}H_{115}ClIr_2N_6O_2$
$D_{calc.}$/ g cm^{-3}	1.546	1.420
μ/mm^{-1}	3.48	2.91
Formula Weight	1646.04	2008.95
Size/mm^3	0.05×0.03×0.02	0.08×0.06×0.05
T/K	100	120
Crystal System	monoclinic	triclinic
Space Group	*I*2/*a* (#15)	*P*-1 (#2)
a/Å	15.122(3)	12.0305(6)
b/Å	24.292(4)	12.8786(6)
c/Å	19.265(5)	16.9004(8)
α/°	90	73.088(2)
β/°	92.237(2)	70.775(2)
γ/°	90	78.292(2)
V/Å^3	7071(3)	2348.8(2)
Z	4	1
Θ_{max}/°	29.6	26.4
Refls. total/unique	42109, 10354	37364, 9580
Reflections with $I>2\sigma(I)$	7944	7606
R_{int}	0.044	0.051
Parameters/restraints	440, 10	619, 577
Δρ max/min, eÅ^{-3}	1.70, -1.87	1.36, -0.80
wR_2 (all data)	0.083	0.086
R_1 [$I>2\sigma(I)$ data]	0.034	0.038

Computations

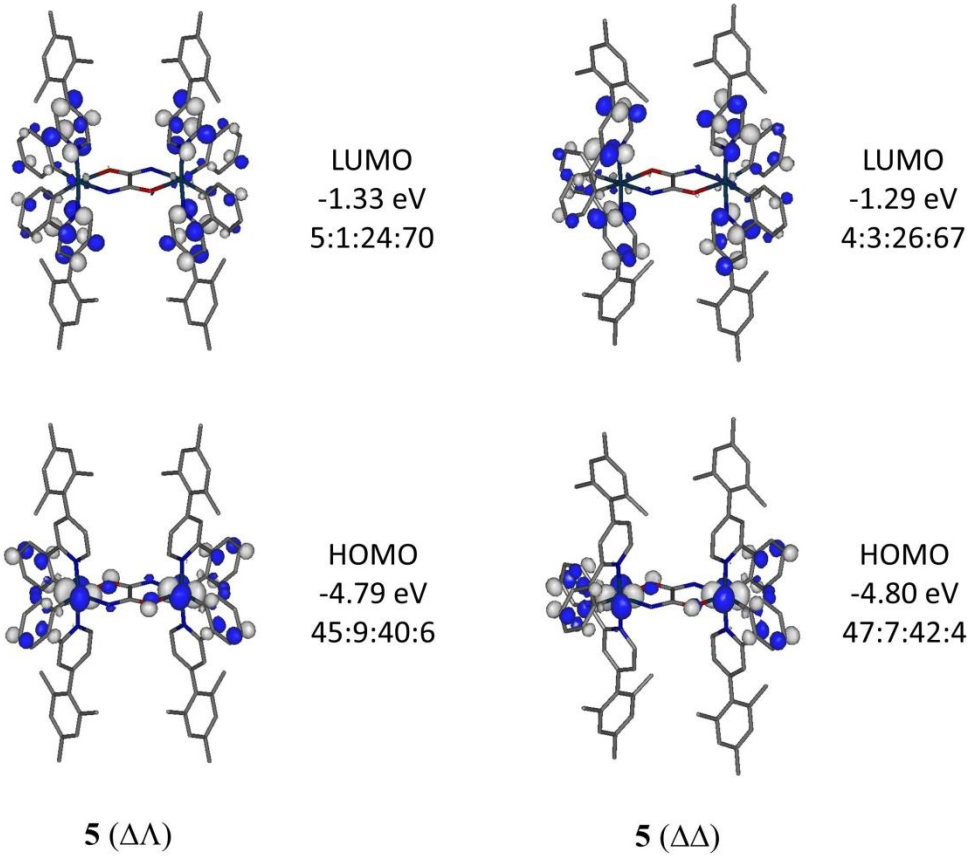


Figure S4. Frontier orbitals for **5**(ΔΔ) and **5**(ΔΛ). Contour values are plotted at ±0.035 e bohr^{-3}. The Ir:bridge:phenyl:pyridyl ratios represent the atom/group MO contributions in percentages.

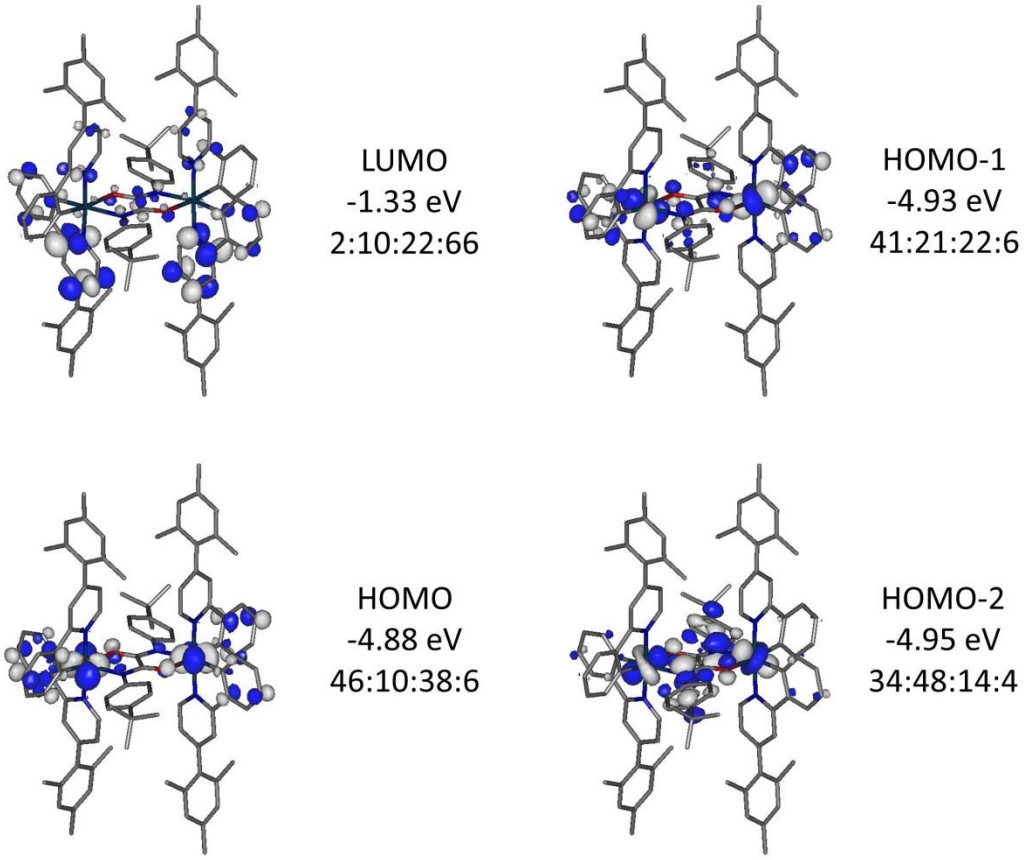


Figure S5. Important orbitals for **6**(ΔΔ). Contour values are plotted at ±0.035 e bohr^{-3}. The Ir:bridge:phenyl:pyridyl ratios represent the atom/group MO contributions in percentages.

Table S2. Selected bond distances in Å for computed and experimental geometries of complexes **2**, **4**, **5** and **6**.

	2 (ΔΛ)	**2** (ΔΛ)	**4** (ΔΔ)	**4** (ΔΔ)	**5** (ΔΔ)	**5** (ΔΔ)	**6** (ΔΛ)	**6** (ΔΛ)
	calc	expt[a]	calc	expt[b]	calc	expt	calc	expt
Ir-N(3)(OPy)	2.043	2.030(5)	2.063	2.048(13) 2.025(13)	2.042	2.042(3)	2.047	2.023(4)
Ir-N(4)(NPy)	2.058	2.029(5)		2.052(13) 2.027(13)	2.058	2.032(3)	2.058	2.040(4)
Ir-C(1)(OPh)	2.010	1.993(5)	2.011	1.992(17)	2.009	1.993(4)	2.017	1.982(4)
Ir-C(12)(NPh)	2.029	2.008(6)		2.03(2)	2.029	2.013(3)	2.020	2.013(4)
Ir-O(1)	2.212	2.20(2)			2.209	2.194(13)	2.163	2.184(3)
Ir-O(2)		2.180(15)				2.19(2)		
Ir-N(1)(br)	2.154	2.18(2)			2.152	2.13(2)	2.247	2.147(3)
Ir-N(2)(br)		2.132(15)				2.135(18)		
N(1)-C(br)	1.315	1.30(2)			1.314	1.30(3)	1.332	1.309(5)
N(2)-C(br)		1.278(16)				1.307(19)		
O(1)-C(br)	1.305	1.30(2)			1.305	1.286(14)	1.305	1.269(5)
O(2)-C(br)		1.299(16)				1.28(3)		
C-C(br)	1.518	1.523(12)			1.517	1.526(7)	1.505	1.514(8)
Ir-Cl			2.597	2.529(5)				
Ir-Cl				2.529(4)				
Ir…Ir’	5.781	5.718	3.944	3.812	5.775	5.688	5.829	5.726

[a] M. Graf, R. Czerwieniec and K. Sünkel, *Zeit. Anorg. Allg. Chem.*, 2013, **639**, 1090–1094.

[b] D. Rota Martir, C. Momblona, A. Pertegás, D. B. Cordes, A. M. Z. Slawin, H. J. Bolink and E. Zysman-Colman, *ACS Appl. Mater. Interfaces*, 2016, **8**, 33907–33915.

Table S3. Orbital energies and % MO contributions for **4** (ΔΔ).

	eV	Symmetry	Ir	Cl	Ph	Py	Mes
LUMO +5	-0.84	A	0	0	12	86	2
LUMO +4	-0.94	B_3	2	0	10	86	2
LUMO +3	-1.21	B_2	6	1	22	69	2
LUMO +2	-1.31	A	6	1	18	73	2
LUMO +1	-1.36	B_3	4	1	24	69	2
LUMO	-1.37	B_1	8	1	26	63	2
HOMO	-4.91	A	44	6	44	6	0
HOMO -1	-4.98	B_2	49	1	44	6	0
HOMO -2	-5.41	B_3	62	18	8	12	0
HOMO -3	-5.47	B_2	62	18	10	10	0
HOMO -4	-5.70	B_1	52	2	26	20	0
HOMO -5	-5.83	A	69	1	15	15	0

Table S4. Orbital energies and % MO contributions for **5** (ΔΛ). NH = NHs at bridge, C_2 = carbons at bridge, NPh = phenyl *trans* to nitrogen at bridge, OPh = phenyl *trans* to oxygen at bridge, NPy = pyridyl group of ppy with NPh, OPy = pyridyl group of ppy with OPh.

	eV	Symmetry	Ir	NH	O	C_2	NPh	OPh	NPy	OPy	Mes
LUMO +4	-0.82	A_u	2	2	1	2	6	6	36	43	2
LUMO +3	-1.18	A_u	6	0	0	0	10	10	37	35	2
LUMO +2	-1.21	A_g	6	0	0	0	10	8	42	32	2
LUMO +1	-1.27	A_g	4	0	0	0	10	14	31	39	2
LUMO	-1.33	A_u	5	0	0	1	12	12	34	34	2
HOMO	-4.79	A_g	45	2	6	1	20	20	4	2	0
HOMO -1	-4.84	A_u	45	1	2	0	22	22	4	4	0
HOMO -2	-5.06	A_g	57	16	11	0	4	2	4	6	0
HOMO -3	-5.23	A_u	57	10	14	1	4	4	4	6	0
HOMO -4	-5.61	A_g	69	0	2	2	8	4	11	4	0
HOMO -5	-5.67	A_u	47	0	0	2	19	12	12	8	0

Table S5. Orbital energies and % MO contributions for **5** (ΔΔ).

	eV	Symmetry	Ir	NH	O	C_2	NPh	OPh	NPy	OPy	Mes
LUMO +4	-0.83	A	4	3	2	3	4	4	38	40	2
LUMO +3	-1.19	B	4	0	0	0	10	12	37	35	2
LUMO +2	-1.24	A	6	0	0	0	10	10	40	32	2
LUMO +1	-1.27	B	6	0	0	0	12	12	34	34	2
LUMO	-1.29	A	4	1	1	1	12	14	30	35	2
HOMO	-4.80	A	47	1	5	1	22	20	2	2	0
HOMO -1	-4.83	B	45	1	2	0	22	22	4	4	0
HOMO -2	-5.10	B	57	15	11	1	4	2	4	6	0
HOMO -3	-5.27	A	59	10	15	1	3	4	4	4	0
HOMO -4	-5.61	B	67	1	2	2	8	6	10	4	0
HOMO -5	-5.67	A	59	1	3	3	12	6	10	6	0

Table S6. Orbital energies and % MO contributions for **6** (ΔΛ). Bu = $tBuC_6H_4$ group.

	eV	Symmetry	Ir	N	O	C_2	Bu	NPh	OPh	NPy	OPy	Mes
LUMO +6	-0.81	A_u	0	1	2	3	2	10	4	60	16	2
LUMO +5	-0.82	A_g	2	0	0	0	0	12	2	76	6	2
LUMO +4	-1.08	A_u	4	17	15	28	24	0	0	6	6	0
LUMO +3	-1.21	A_u	6	0	0	0	0	6	16	20	50	2
LUMO +2	-1.23	A_g	6	1	0	0	1	2	20	8	60	2
LUMO +1	-1.32	A_g	4	0	1	0	0	20	4	61	8	2
LUMO	-1.38	A_u	4	1	1	3	2	16	6	49	16	2
HOMO	-4.82	A_g	39	9	7	1	18	10	12	2	2	0
HOMO -1	-4.91	A_u	47	2	2	0	3	18	22	2	4	0
HOMO -2	-4.96	A_g	39	11	6	1	15	8	14	2	4	0
HOMO -3	-5.14	A_u	35	11	18	2	22	2	6	2	2	0
HOMO -4	-5.65	A_g	70	0	2	2	2	6	6	6	6	0
HOMO -5	-5.73	A_u	31	1	0	0	10	18	22	4	14	0
HOMO -6	-5.75	A_g	2	1	1	0	3	41	36	8	8	0
HOMO -7	-5.77	A_g	28	5	4	1	38	8	8	2	6	0

Table S7. Orbital energies and % MO contributions for **6** (ΔΔ).

	eV	Symmetry	Ir	N	O	C_2	Bu	NPh	OPh	NPy	OPy	Mes
LUMO +6	-0.79	B	2	0	0	0	0	8	6	43	39	2
LUMO +5	-0.80	A	2	1	1	3	2	8	4	55	22	2
LUMO +4	-1.11	A	4	15	15	27	23	0	0	8	8	0
LUMO +3	-1.23	B	4	0	0	0	0	8	16	22	48	2
LUMO +2	-1.27	A	6	1	0	0	0	4	18	14	55	2
LUMO +1	-1.30	B	6	0	0	0	0	16	8	46	22	2
LUMO	-1.33	A	2	2	2	3	3	18	4	52	12	2
HOMO	-4.88	A	46	2	4	1	3	17	21	2	4	0
HOMO -1	-4.93	B	41	6	4	1	10	12	20	2	4	0
HOMO -2	-4.95	B	34	14	6	2	26	8	6	2	2	0
HOMO -3	-5.18	A	37	11	18	2	22	2	4	2	2	0
HOMO -4	-5.64	B	67	1	2	2	2	6	6	8	6	0
HOMO -5	-5.72	A	38	4	5	1	4	20	18	4	6	0
HOMO -6	-5.78	A	18	0	0	0	4	30	28	8	12	0
HOMO -7	-5.78	B	6	0	0	0	6	36	34	8	10	0

Table S8. TD-DFT data from optimised geometries of the complexes, **1**, **2**, **4**, **5** and **6** and comparison with observed lowest energy absorption bands and emission maxima.

	TD-DFT $S_0 \rightarrow S_1$ (nm)	Oscillator strength (*f*)	TD-DFT $S_0 \rightarrow T_1$ (nm)	Observed λ_{abs} (nm)	Observed λ_{em} (nm)	Observed Stokes shift (cm^{-1})
1 (ΔΛ)	476	0.0112	506	497 [a]	521 [a]	930
1 (ΔΔ)	470	0.0200	498	497 [a]	523 [a]	1000
2 (ΔΛ)	449	0.0405	488	498 [b]	523 [b]	960
2 (ΔΔ)	448	0.0409	490	498 [b]	523 [b]	960
4 (ΔΔ)	445	0.0685	485	492	518	1020
5 (ΔΛ)	452	0.0673	490	500	529	1100
5 (ΔΔ)	448	0.0669	487	500	529	1100
6 (ΔΛ)	449	0.0462	512	500	522	840
6 (ΔΔ)	441	0.0385	503	500	522	840

[a] Y. Zheng, A. S. Batsanov, M. A. Fox, H. A. Al-Attar, K. Abdullah, V. Jankus, M. R. Bryce and A. P. Monkman, *Angew. Chem. Int. Ed.*, 2014, **53**, 11616–11619.

[b] M. Graf, R. Czerwieniec and K. Sünkel, *Zeit. Anorg. Allg. Chem.*, 2013, **639**, 1090–1094.

Mass spectra

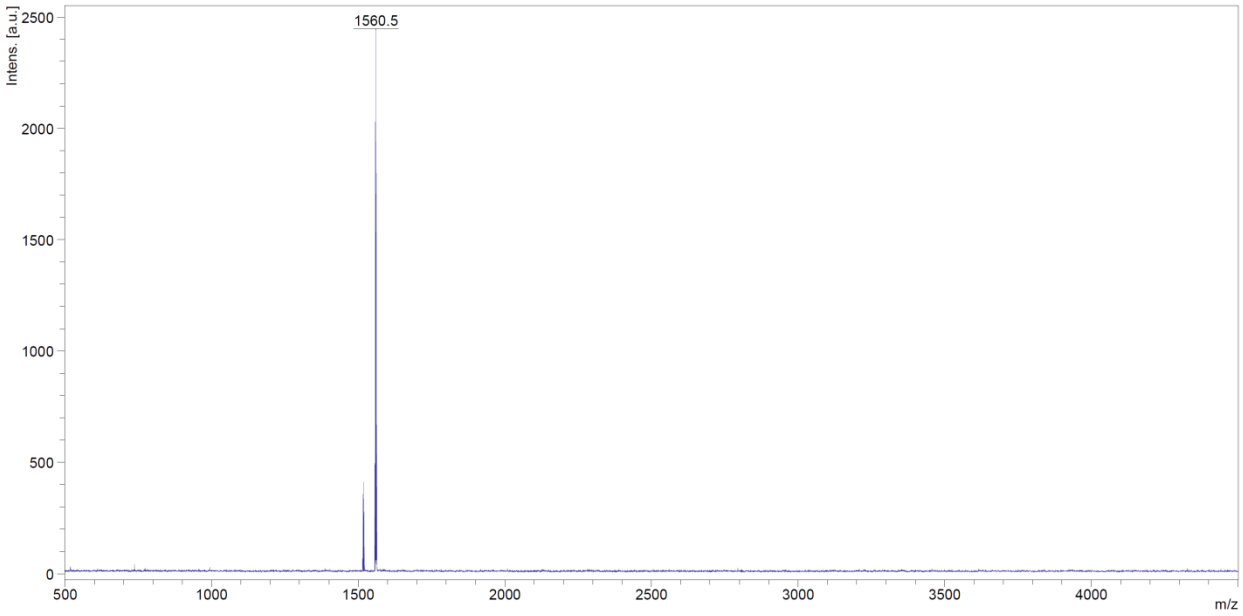


Figure S6. MALDI-TOF mass spectrum of complex **5.**

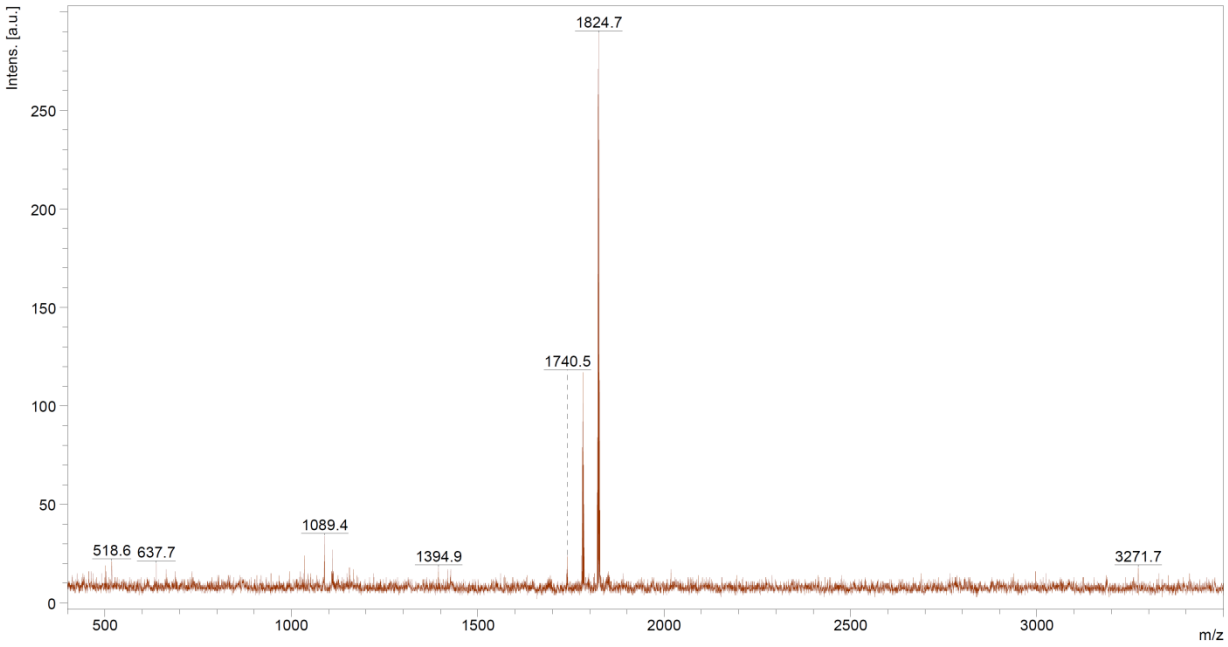


Figure S7. MALDI-TOF mass spectrum of complex **6.**

Thermal analysis

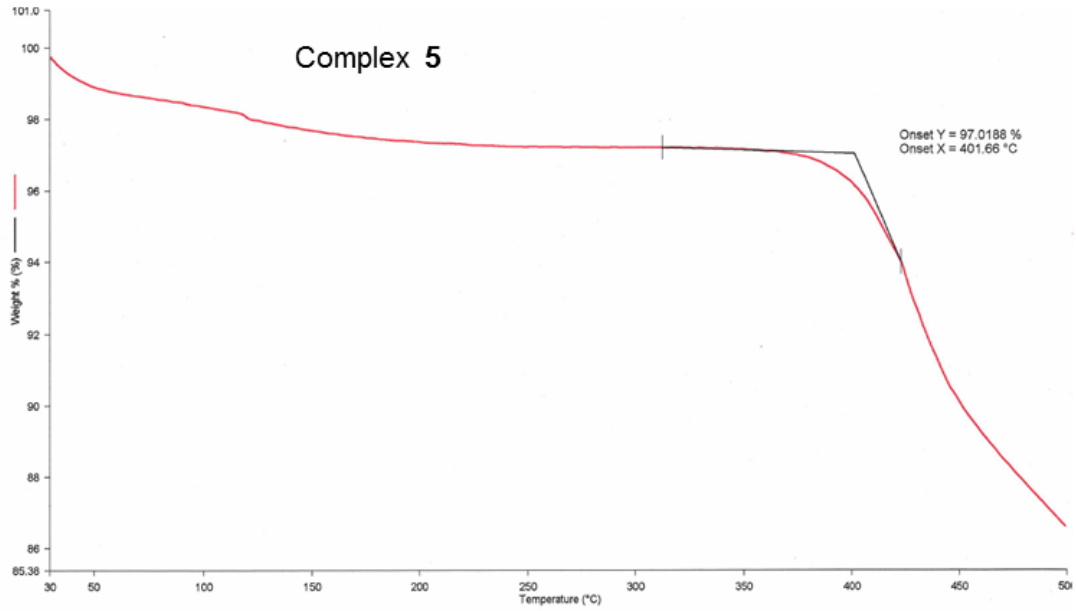


Figure S8. TGA trace of complex **5.**

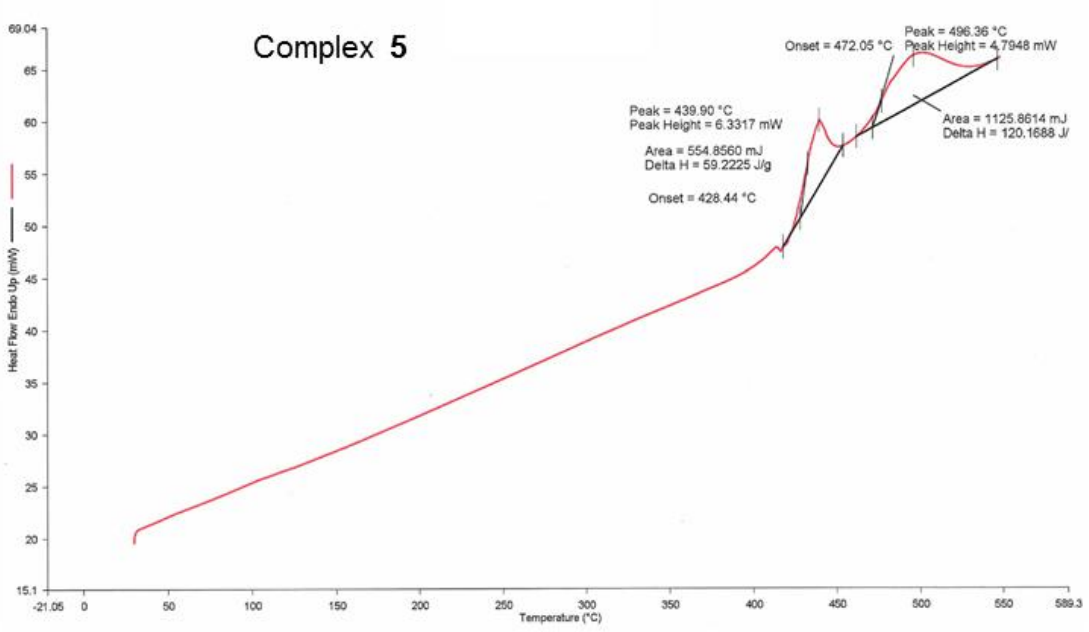


Figure S9. DSC trace of complex **5**

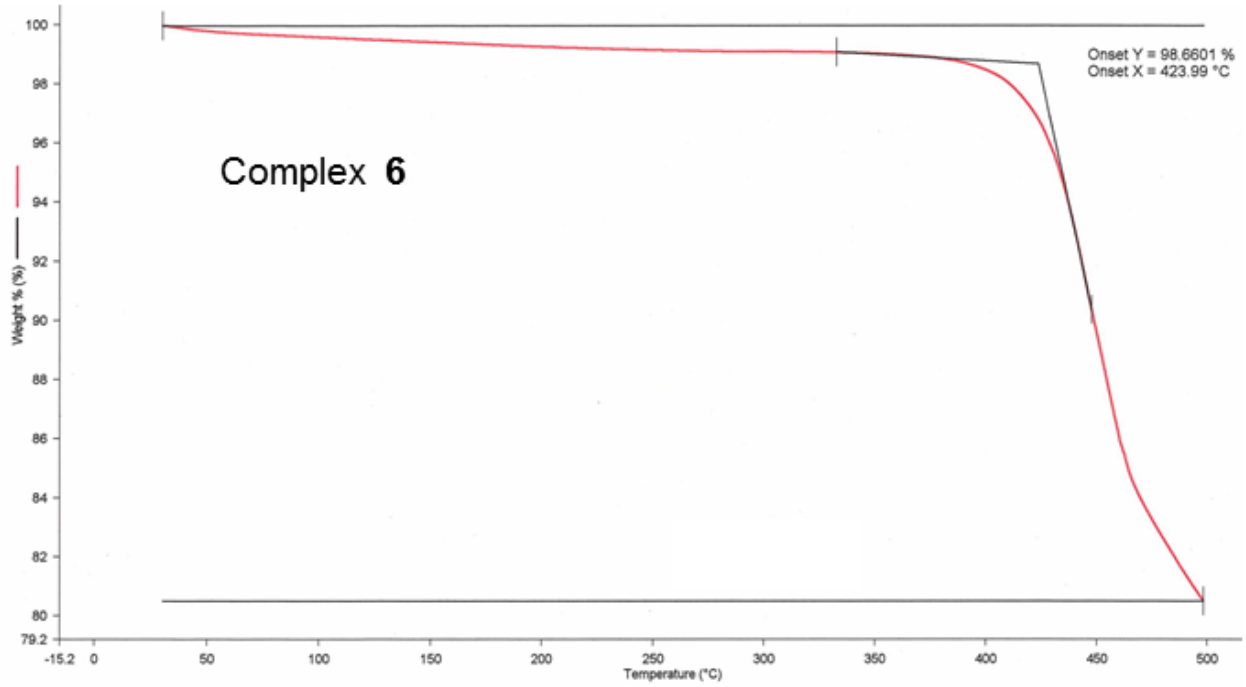


Figure S10. TGA trace of complex **6.**

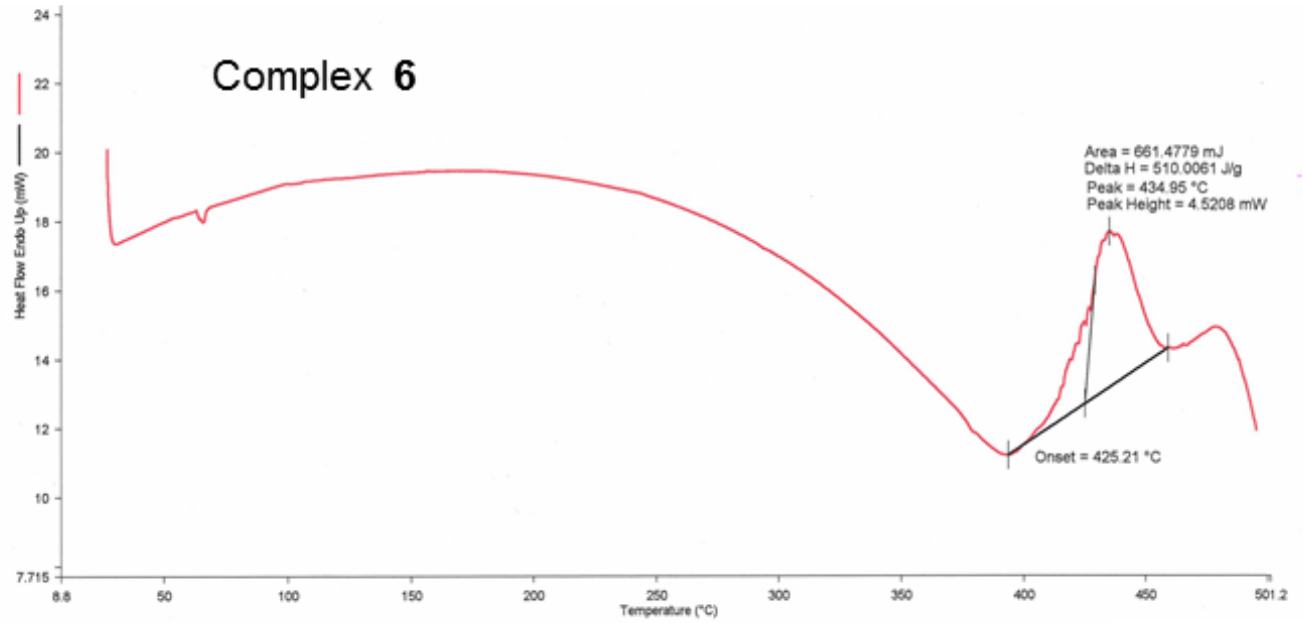


Figure S11. DSC trace of complex **6.**

PhOLED data

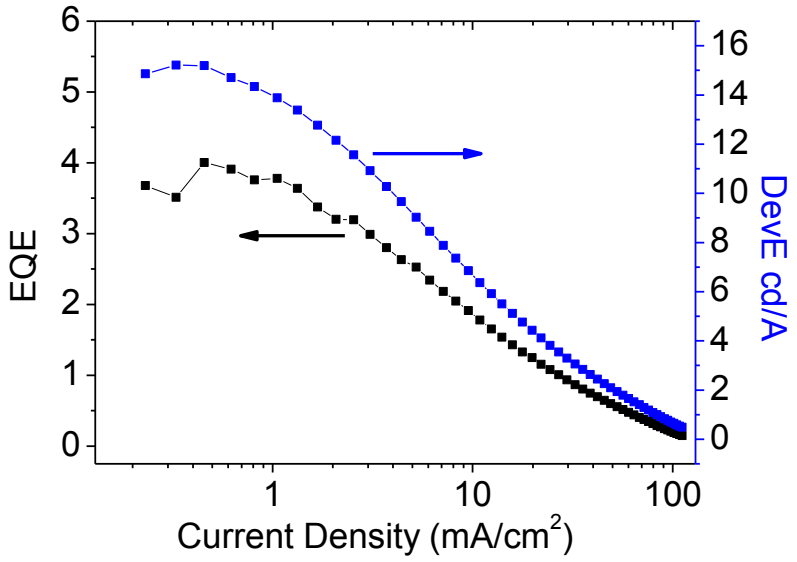
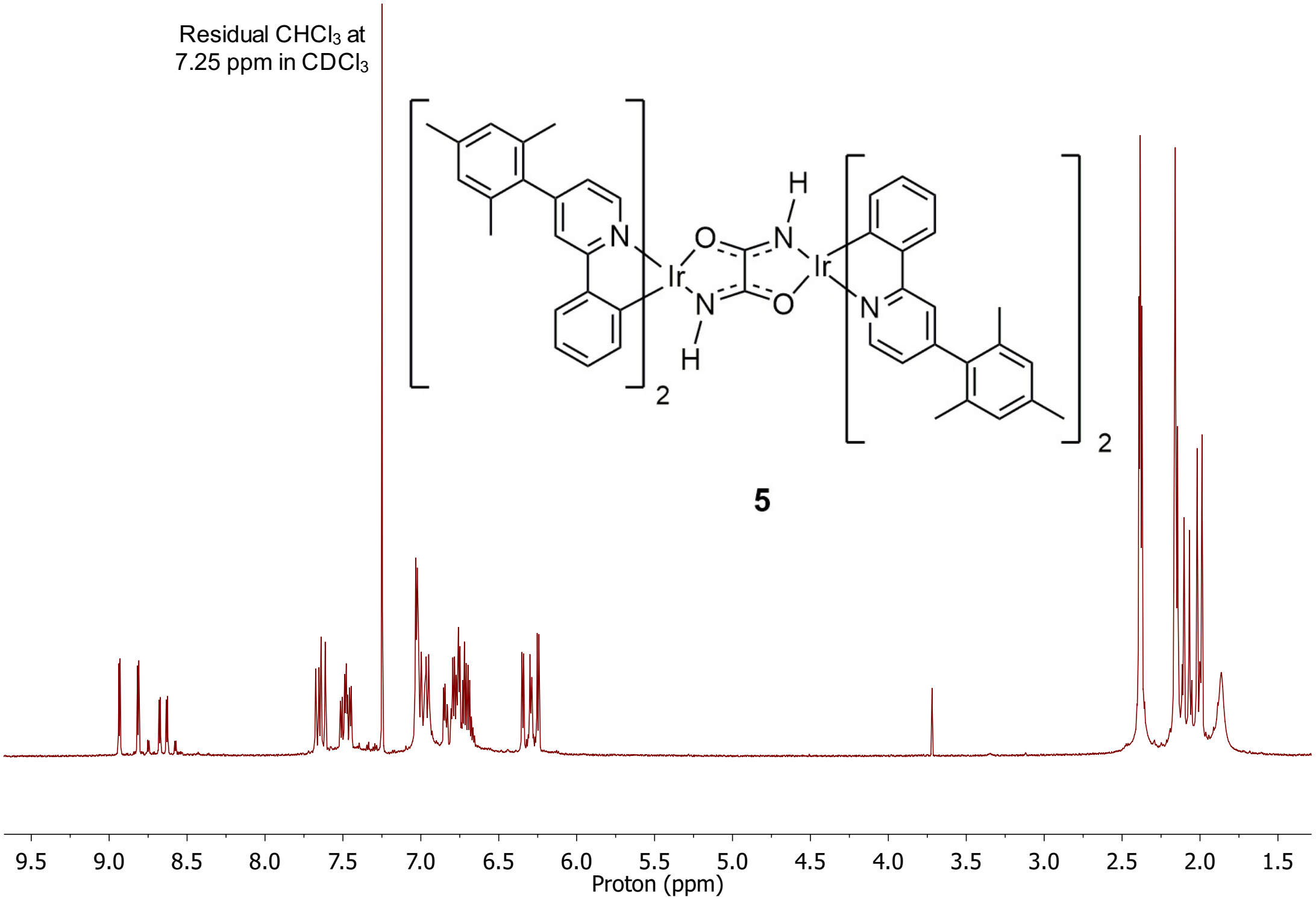


Figure S13. PhOLED data for complex **6** in low MWt PVK host with an additional spin-coated layer of TFB. Device structure: ITO/PEDOT:PSS (45 nm)/ TFB (60 nm)/ PVK:OXD-7(40%):Ir complex **6**(5%) (70 nm)/TPBi (30 nm)/LiF/Al.

NMR Spectra


Residual $CHCl_3$ at
7.25 ppm in $CDCl_3$
H
N
O
N
Ir
Ir
N
N
H
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2
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9.0
8.5
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7.5
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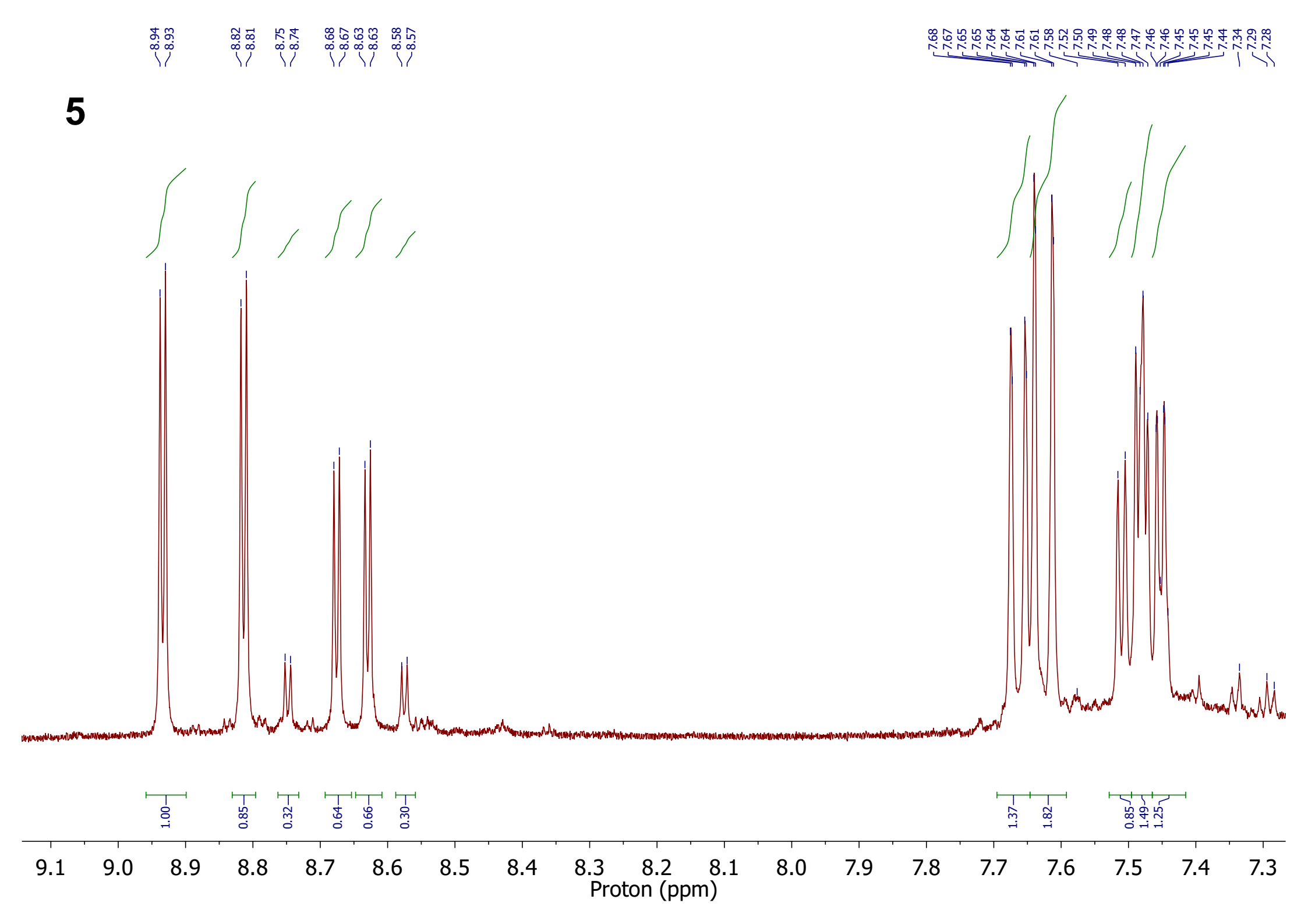
2.5
2.0
1.5
Proton (ppm)


5
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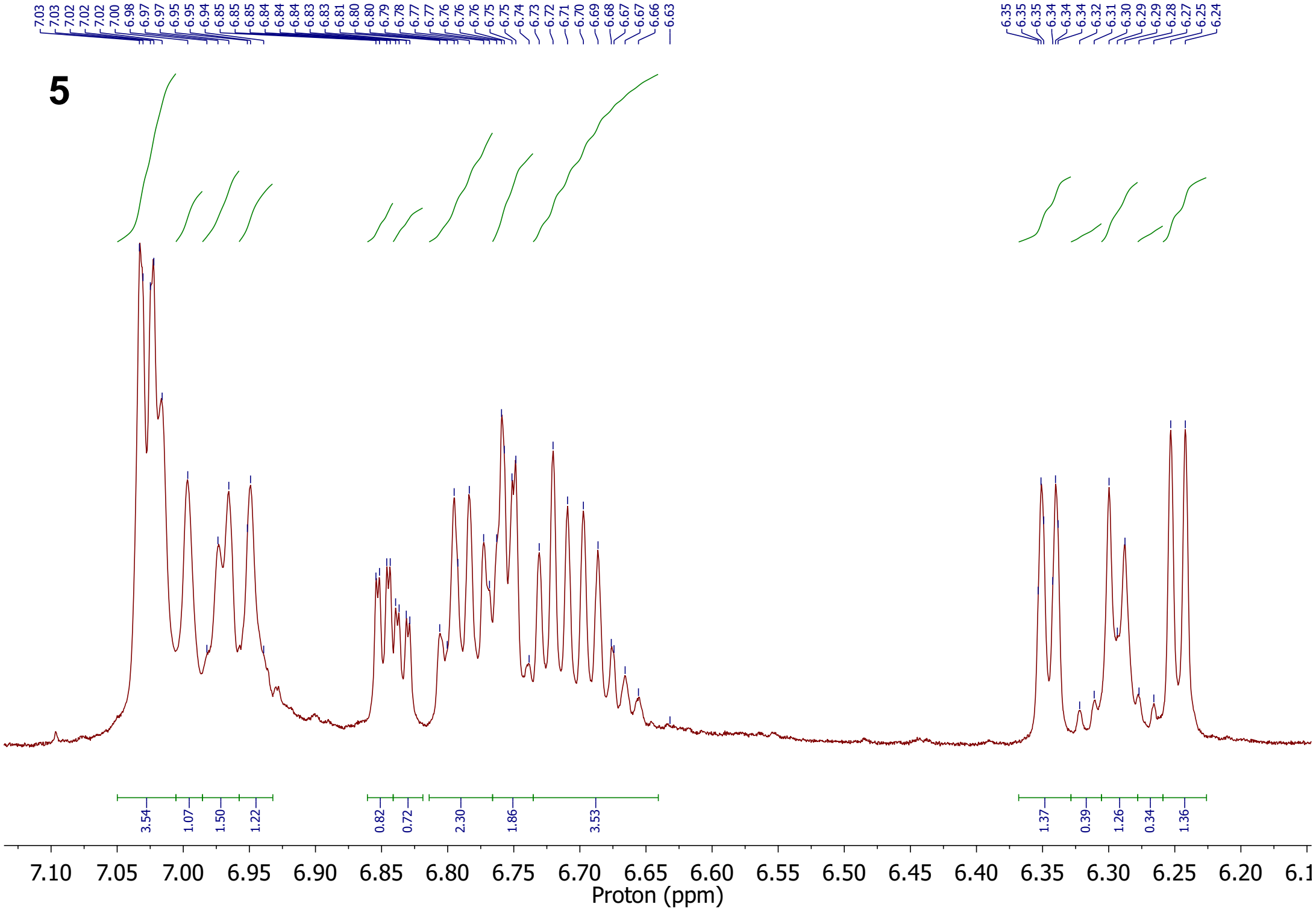
7.3
Proton (ppm)


5
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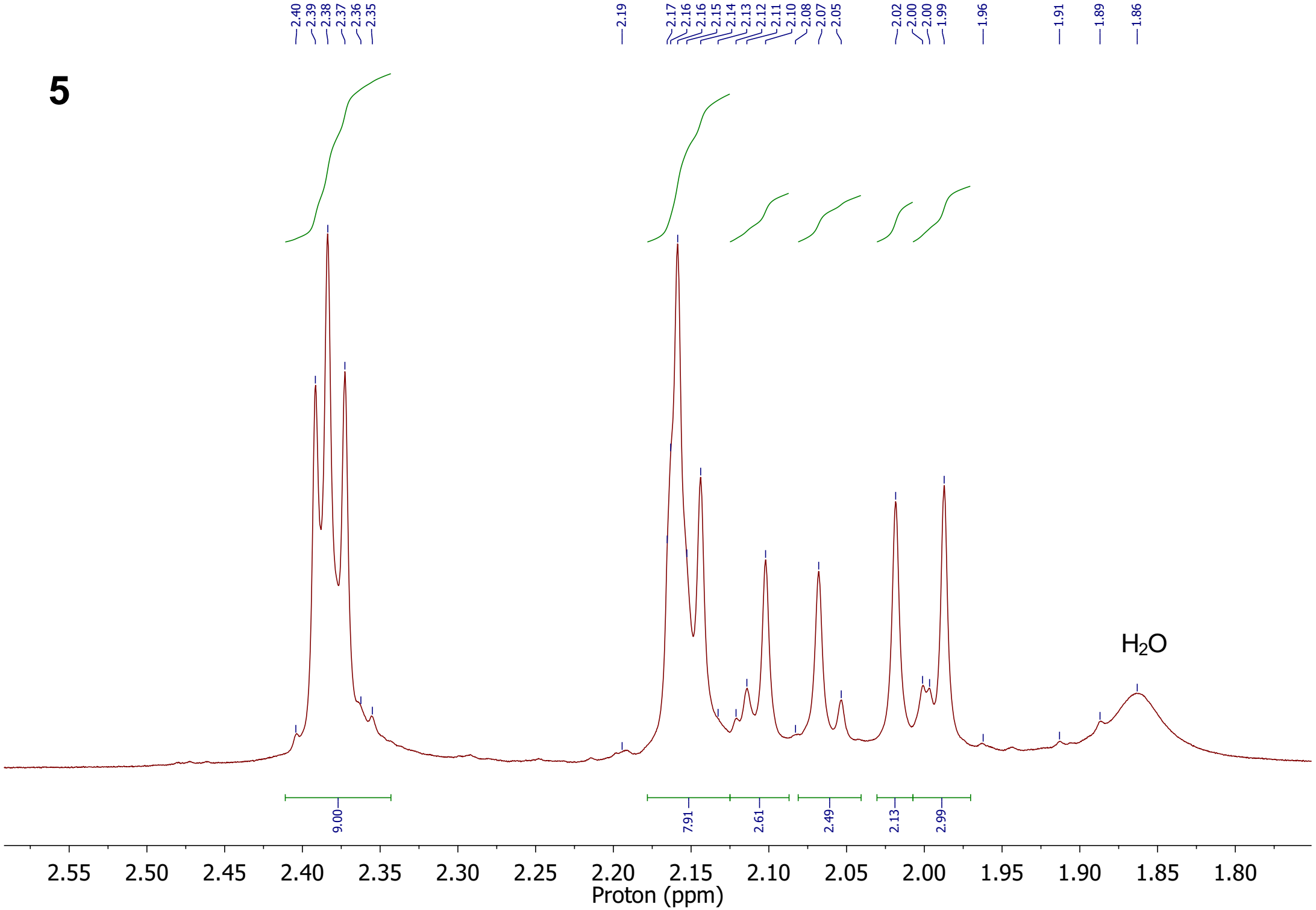
3.54 1.07 1.50 1.22 0.82 0.72 2.30 1.86 3.53 1.37 0.39 1.26 0.34 1.36
7.10 7.05 7.00 6.95 6.90 6.85 6.80 6.75 6.70 6.65 6.60 6.55 6.50 6.45 6.40 6.35 6.30 6.25 6.20 6.1
Proton (ppm)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2.38
2.37
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2.00
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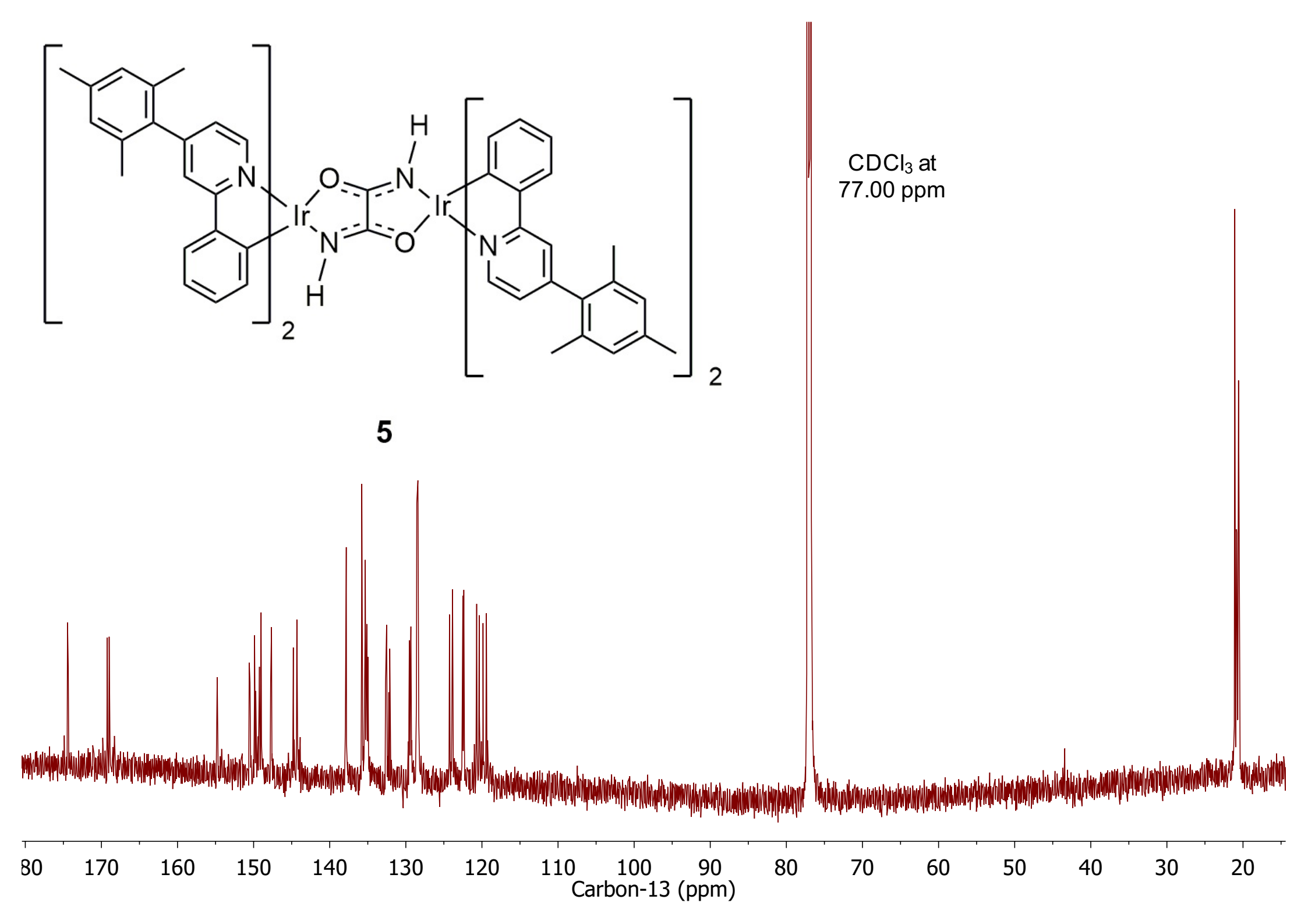
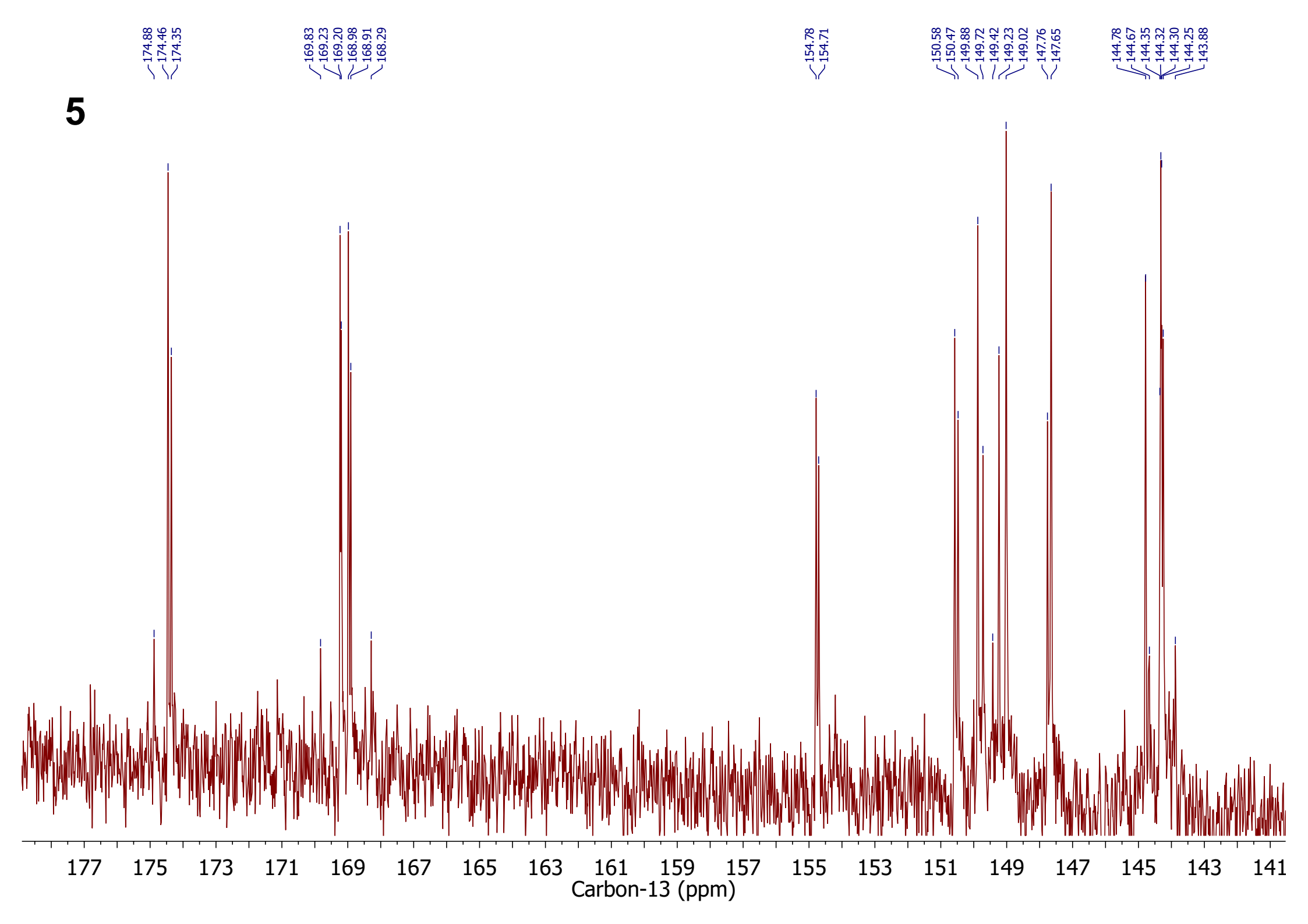
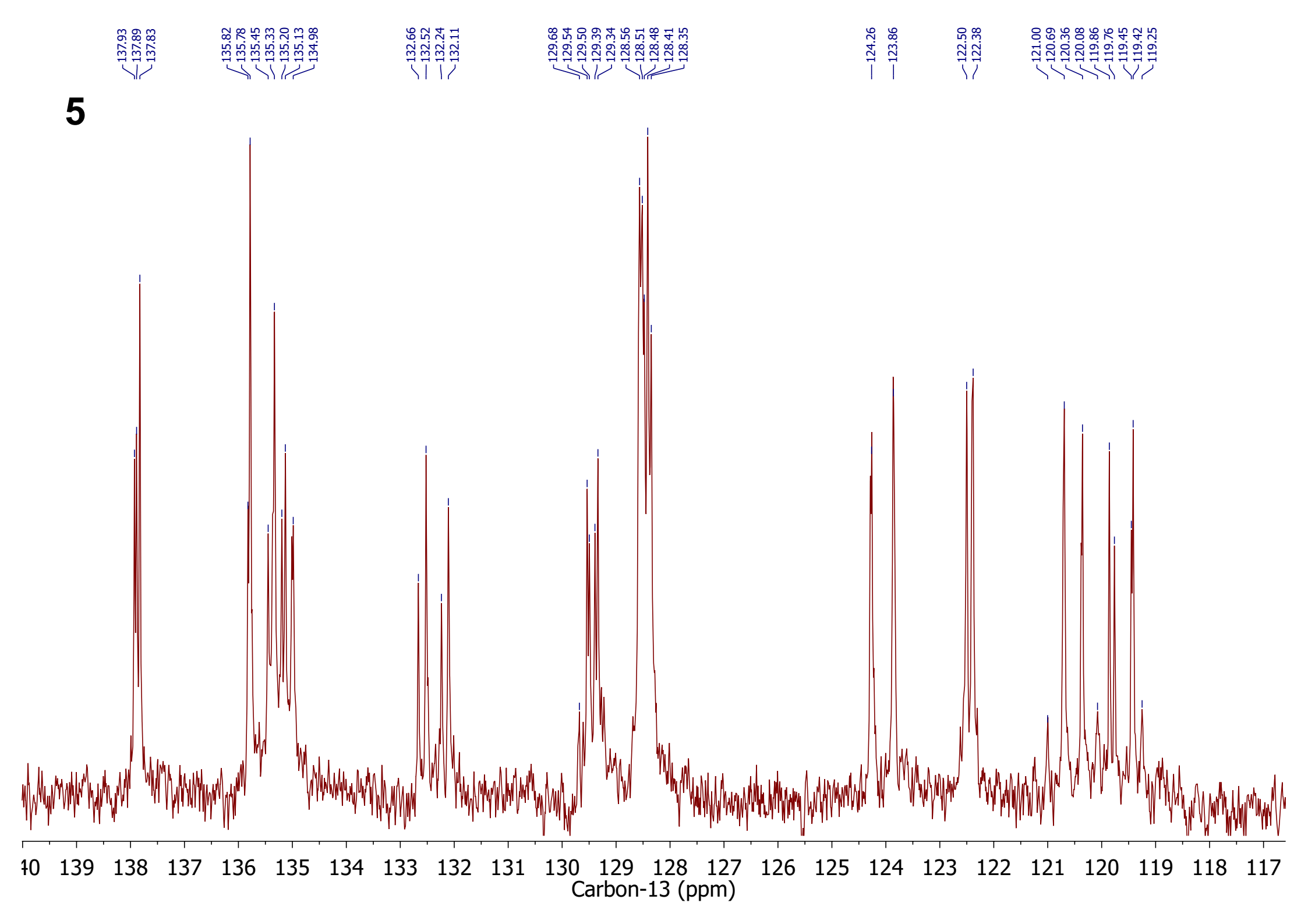
1.85
1.80
Proton (ppm)

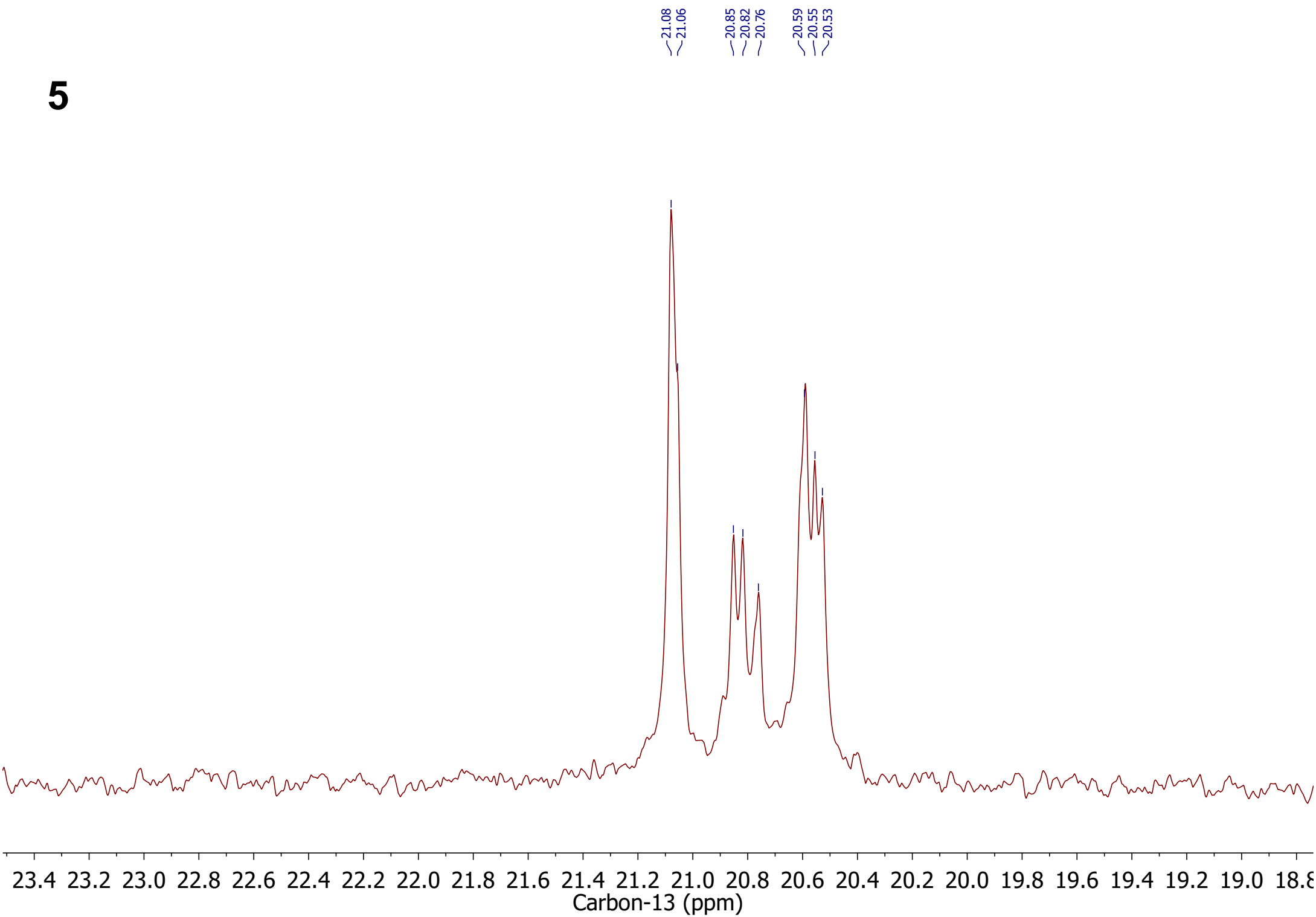

H
N
O
N
Ir
Ir
N
O
N
H
2
2
CDCl3 at
77.00 ppm
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
Carbon-13 (ppm)

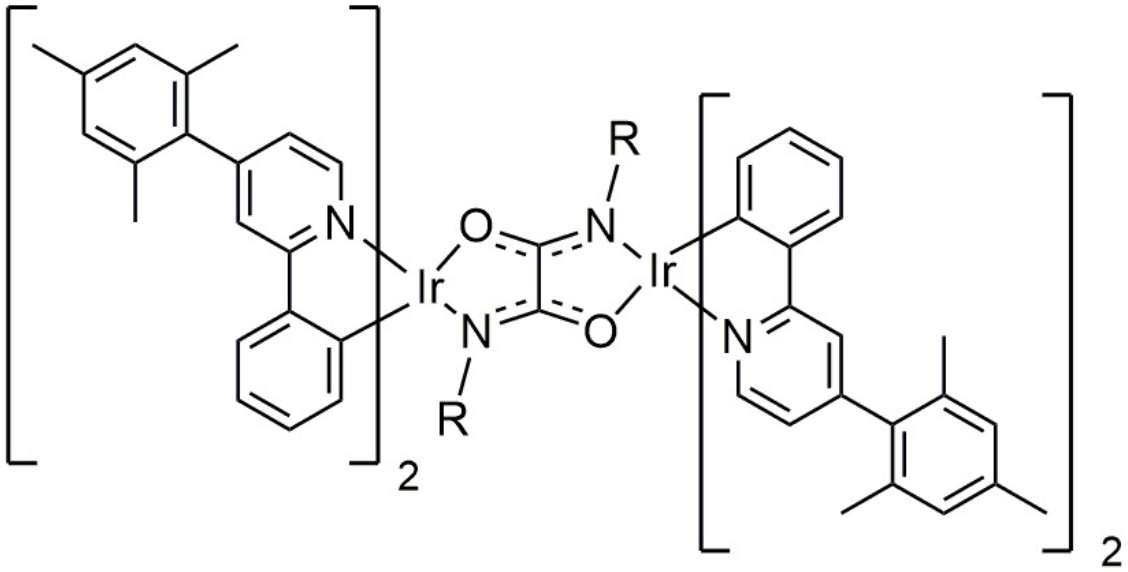
5


5
174.88
174.46
174.35
169.83
169.23
169.20
168.98
168.91
168.29
154.78
154.71
150.58
150.47
149.88
149.72
149.42
149.23
149.02
147.76
147.65
144.78
144.67
144.35
144.32
144.30
144.25
143.88
177
175
173
171
169
167
165
163
161
159
157
155
153
151
149
147
145
143
141
Carbon-13 (ppm)


5
137.93
137.89
137.83
135.82
135.78
135.45
135.33
135.20
135.13
134.98
132.66
132.52
132.24
132.11
129.68
129.54
129.50
129.39
129.34
128.56
128.51
128.48
128.41
128.35
124.26
123.86
122.50
122.38
121.00
120.69
120.36
120.08
119.86
119.76
119.45
119.42
119.25
140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117
Carbon-13 (ppm)

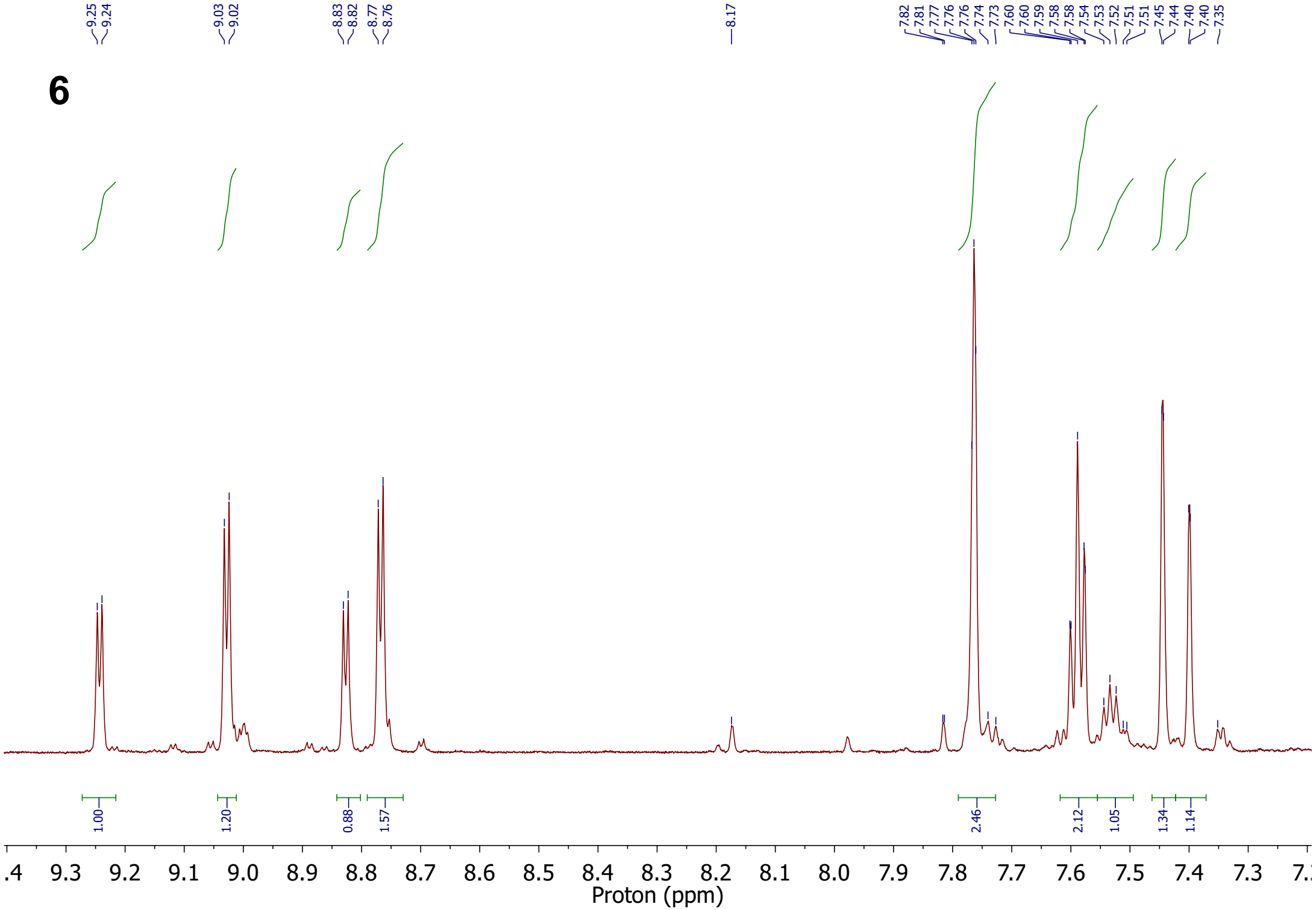
5

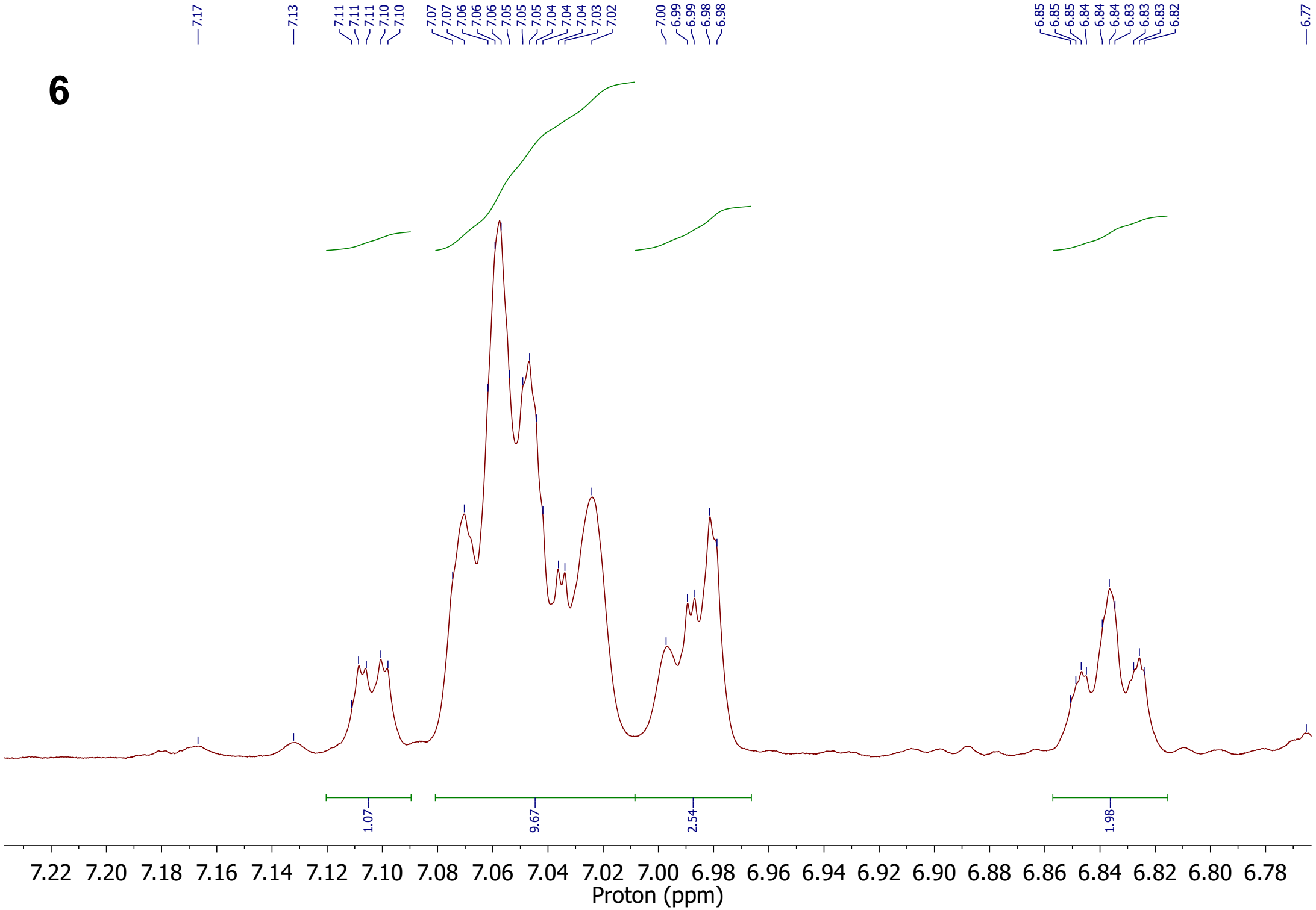

21.08
21.06
20.85
20.82
20.76
20.59
20.55
20.53
23.4 23.2 23.0 22.8 22.6 22.4 22.2 22.0 21.8 21.6 21.4 21.2 21.0 20.8 20.6 20.4 20.2 20.0 19.8 19.6 19.4 19.2 19.0 18.8
Carbon-13 (ppm)

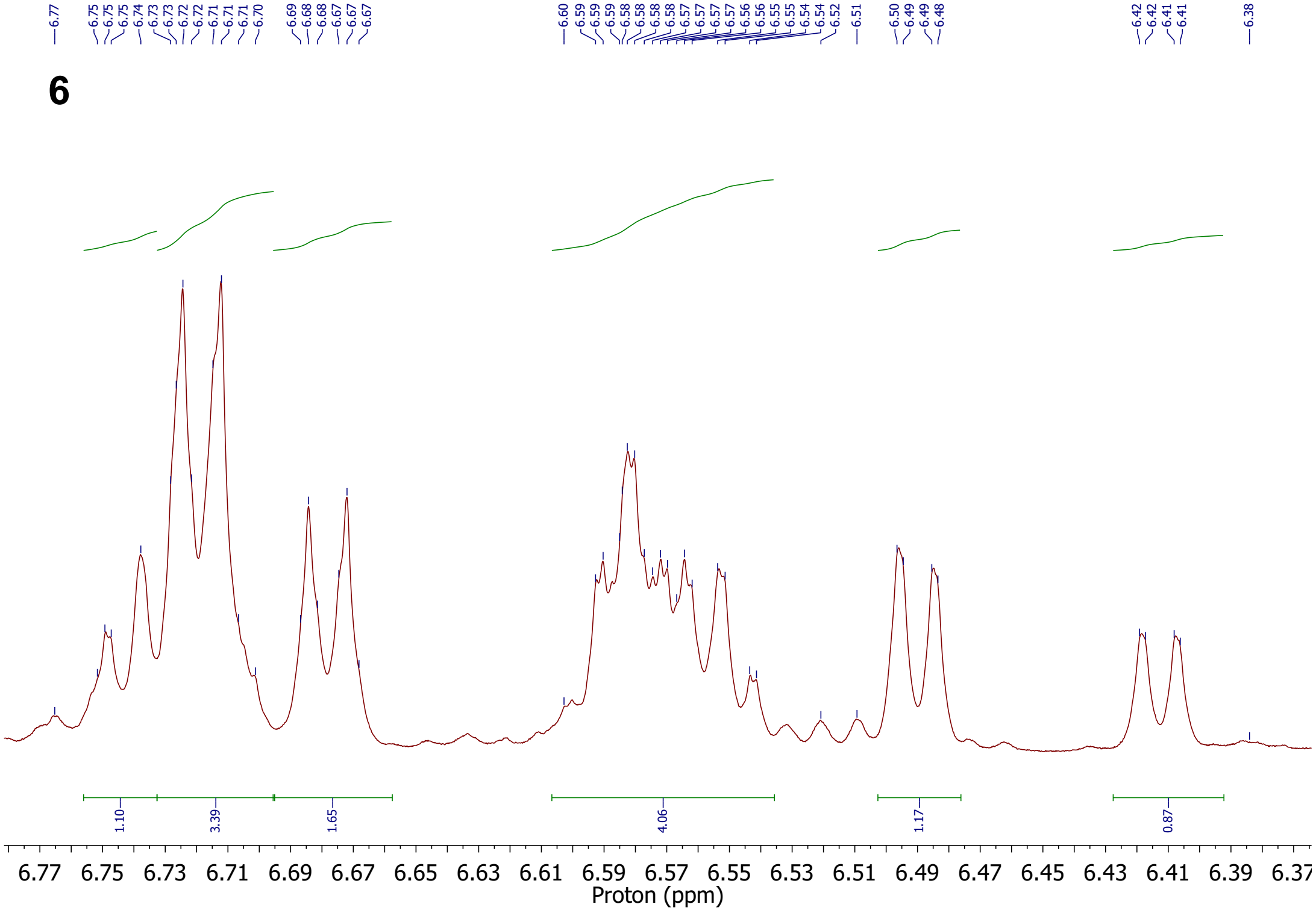

R
N
O
N
Ir
Ir
N
O
N
R
2
2

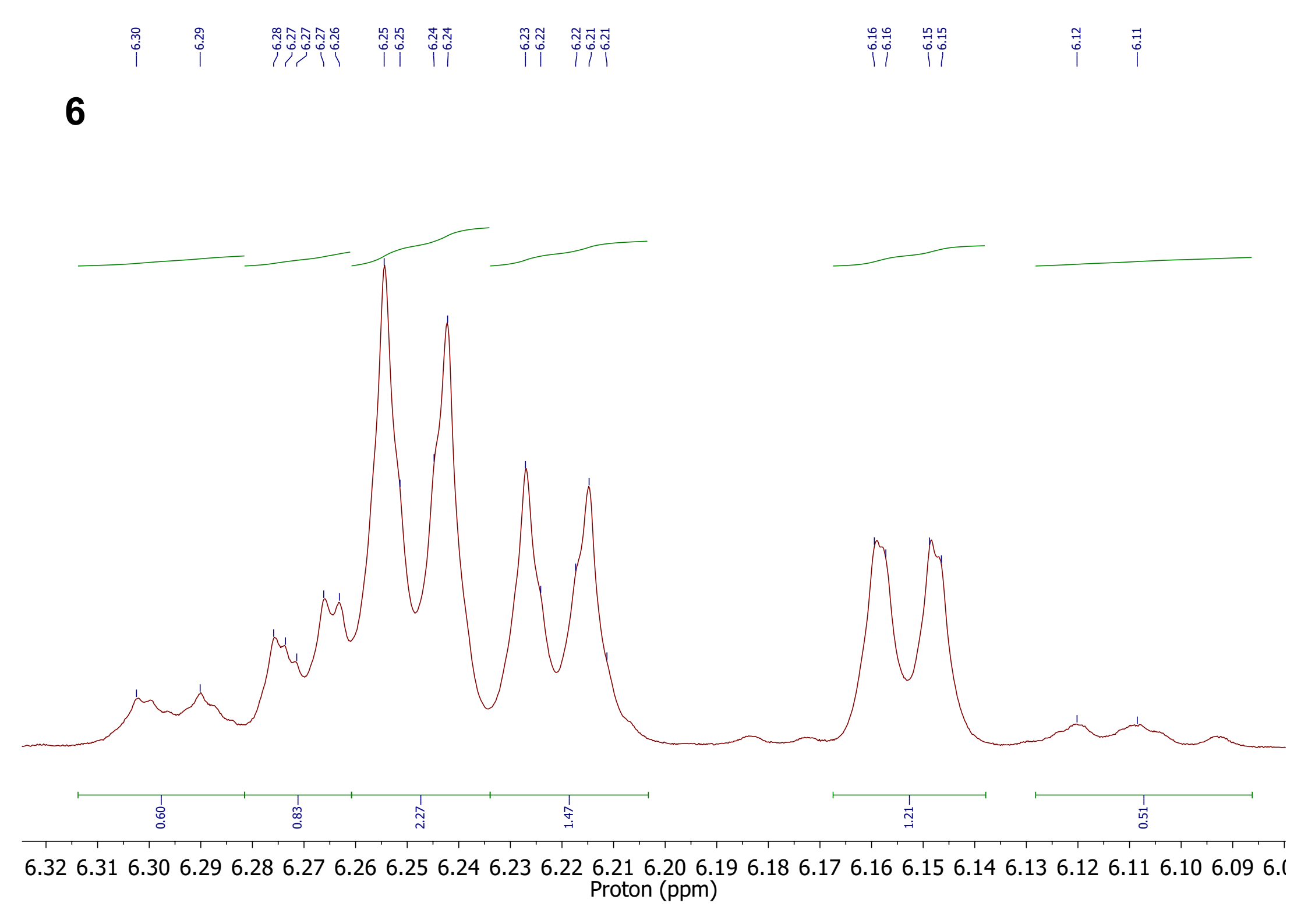
6 R = 4-*t*Bu-C_6H_4

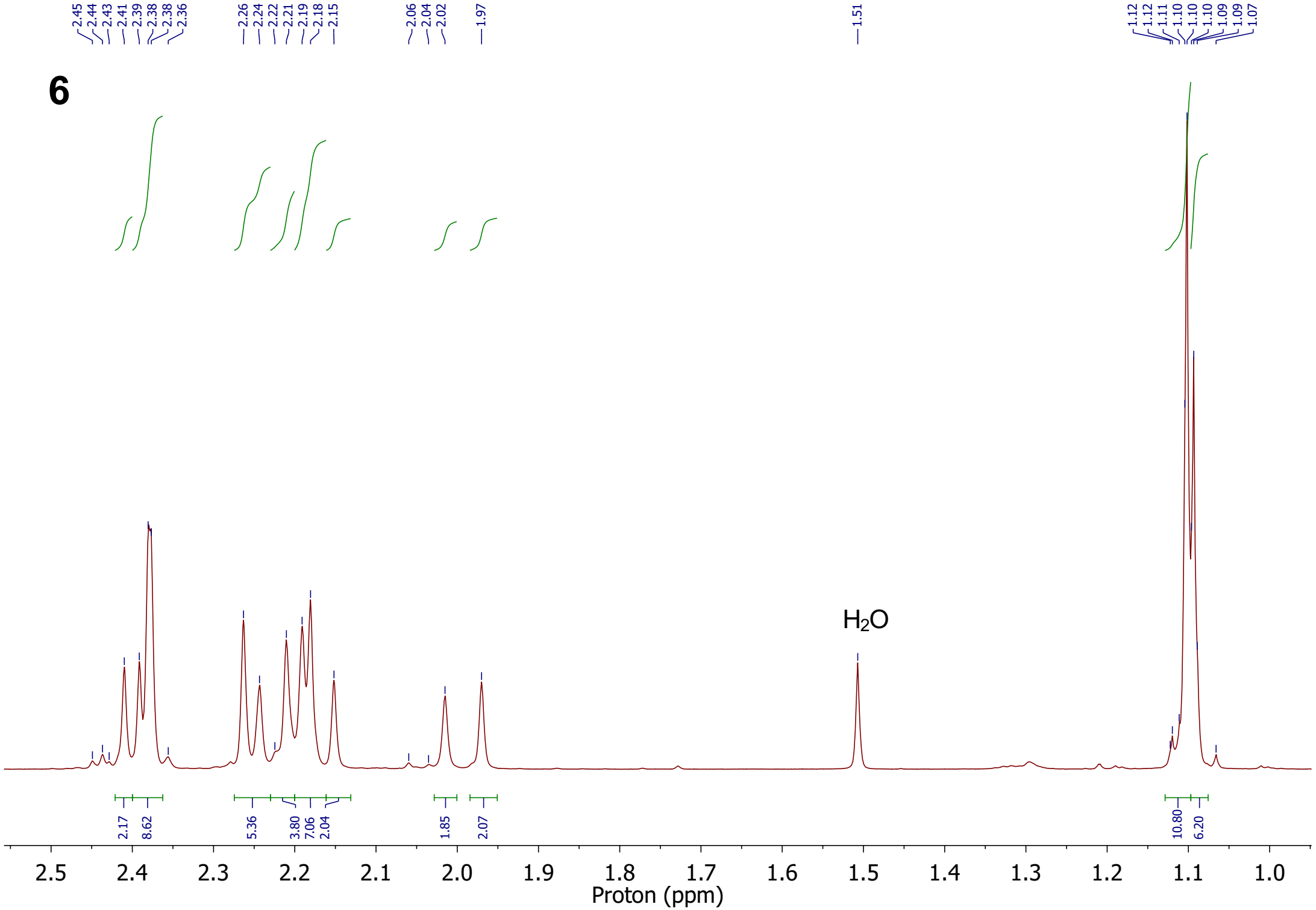
Residual CHDCl2 at
5.32 ppm in CD2Cl2
.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Proton (ppm)

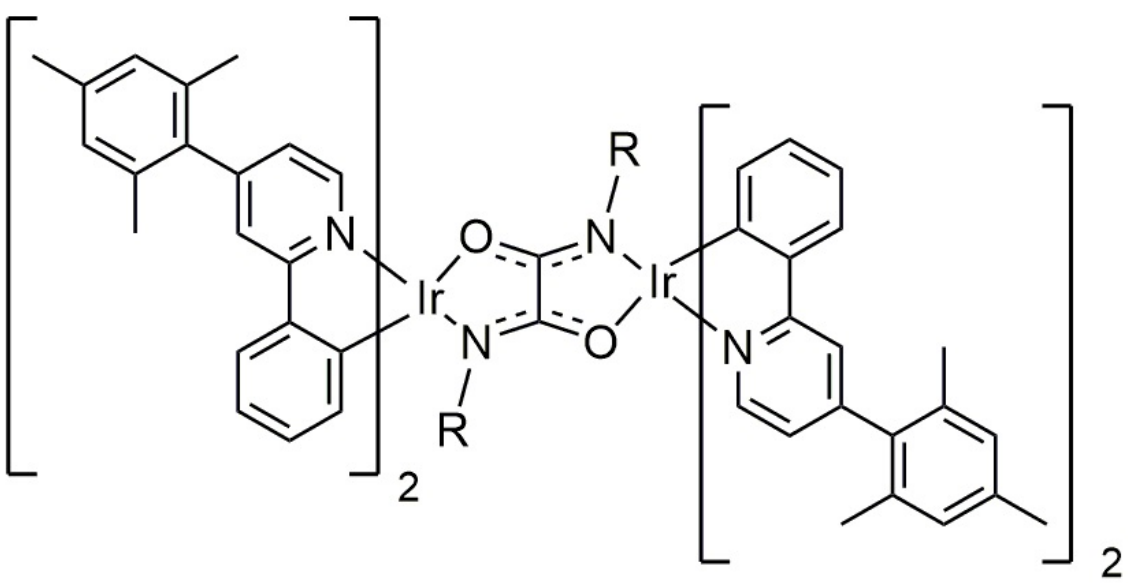

6
9.25
9.24
9.03
9.02
8.83
8.82
8.77
8.76
8.17
7.82
7.81
7.77
7.76
7.76
7.74
7.73
7.60
7.60
7.59
7.58
7.58
7.54
7.53
7.52
7.51
7.51
7.45
7.44
7.40
7.40
7.35
1.00
1.20
0.88
1.57
2.46
2.12
1.05
1.34
1.14
9.3
9.2
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
Proton (ppm)


6
7.17
7.13
7.11
7.11
7.11
7.10
7.10
7.07
7.07
7.06
7.06
7.06
7.05
7.05
7.05
7.04
7.04
7.04
7.03
7.02
7.00
6.99
6.99
6.98
6.98
6.85
6.85
6.85
6.84
6.84
6.84
6.83
6.83
6.83
6.82
6.77
1.07
9.67
2.54
1.98
7.22 7.20 7.18 7.16 7.14 7.12 7.10 7.08 7.06 7.04 7.02 7.00 6.98 6.96 6.94 6.92 6.90 6.88 6.86 6.84 6.82 6.80 6.78
Proton (ppm)


6
6.77
6.75
6.75
6.75
6.74
6.73
6.73
6.72
6.72
6.71
6.71
6.71
6.70
6.69
6.68
6.68
6.67
6.67
6.67
6.60
6.59
6.59
6.59
6.58
6.58
6.58
6.58
6.57
6.57
6.57
6.57
6.56
6.56
6.55
6.55
6.54
6.54
6.52
6.51
6.50
6.49
6.49
6.48
6.42
6.42
6.41
6.41
6.38
1.10
3.39
1.65
4.06
1.17
0.87
6.77 6.75 6.73 6.71 6.69 6.67 6.65 6.63 6.61 6.59 6.57 6.55 6.53 6.51 6.49 6.47 6.45 6.43 6.41 6.39 6.37
Proton (ppm)

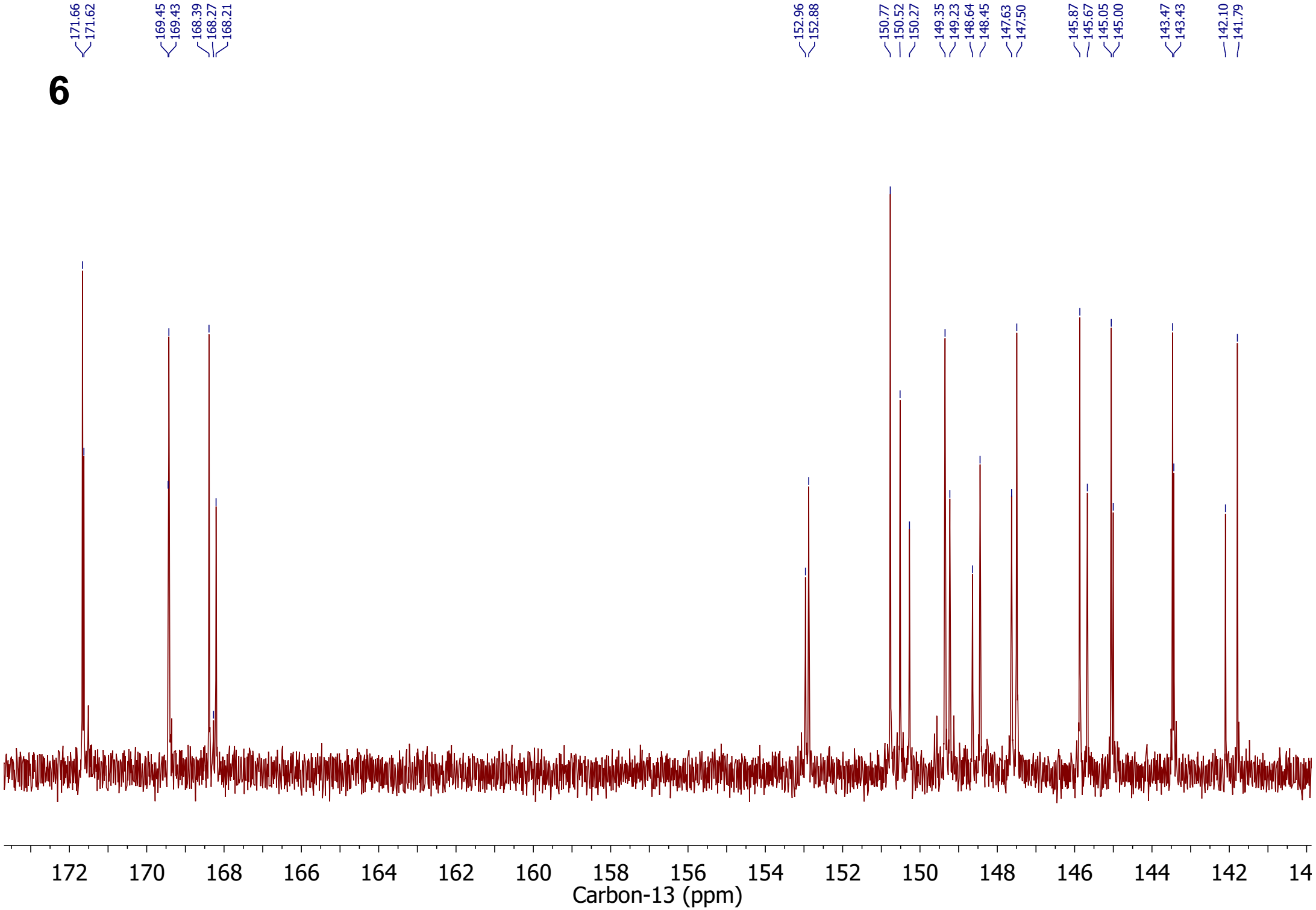

6
6.30
6.29
6.28
6.27
6.27
6.27
6.26
6.25
6.25
6.24
6.24
6.23
6.22
6.22
6.21
6.21
6.16
6.16
6.15
6.15
6.12
6.11
0.60
0.83
2.27
1.47
1.21
0.51
6.32 6.31 6.30 6.29 6.28 6.27 6.26 6.25 6.24 6.23 6.22 6.21 6.20 6.19 6.18 6.17 6.16 6.15 6.14 6.13 6.12 6.11 6.10 6.09 6.0
Proton (ppm)

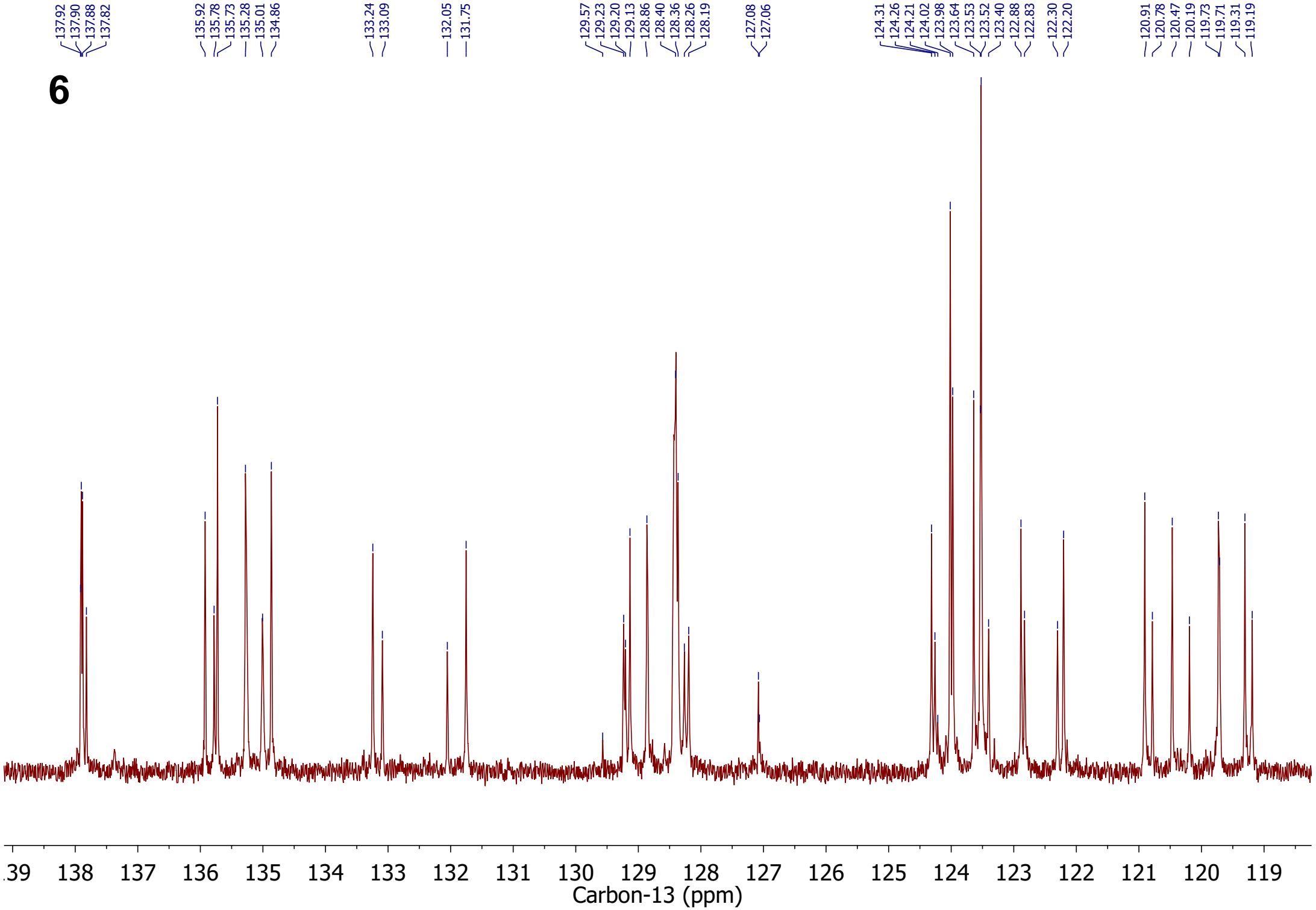

6
2.45
2.44
2.43
2.41
2.39
2.38
2.38
2.36
2.26
2.24
2.22
2.21
2.19
2.18
2.15
2.06
2.04
2.02
1.97
1.51
1.12
1.12
1.11
1.10
1.10
1.10
1.09
1.09
1.07
H2O
2.17
8.62
5.36
3.80
7.06
2.04
1.85
2.07
10.80
6.20
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1.0
Proton (ppm)

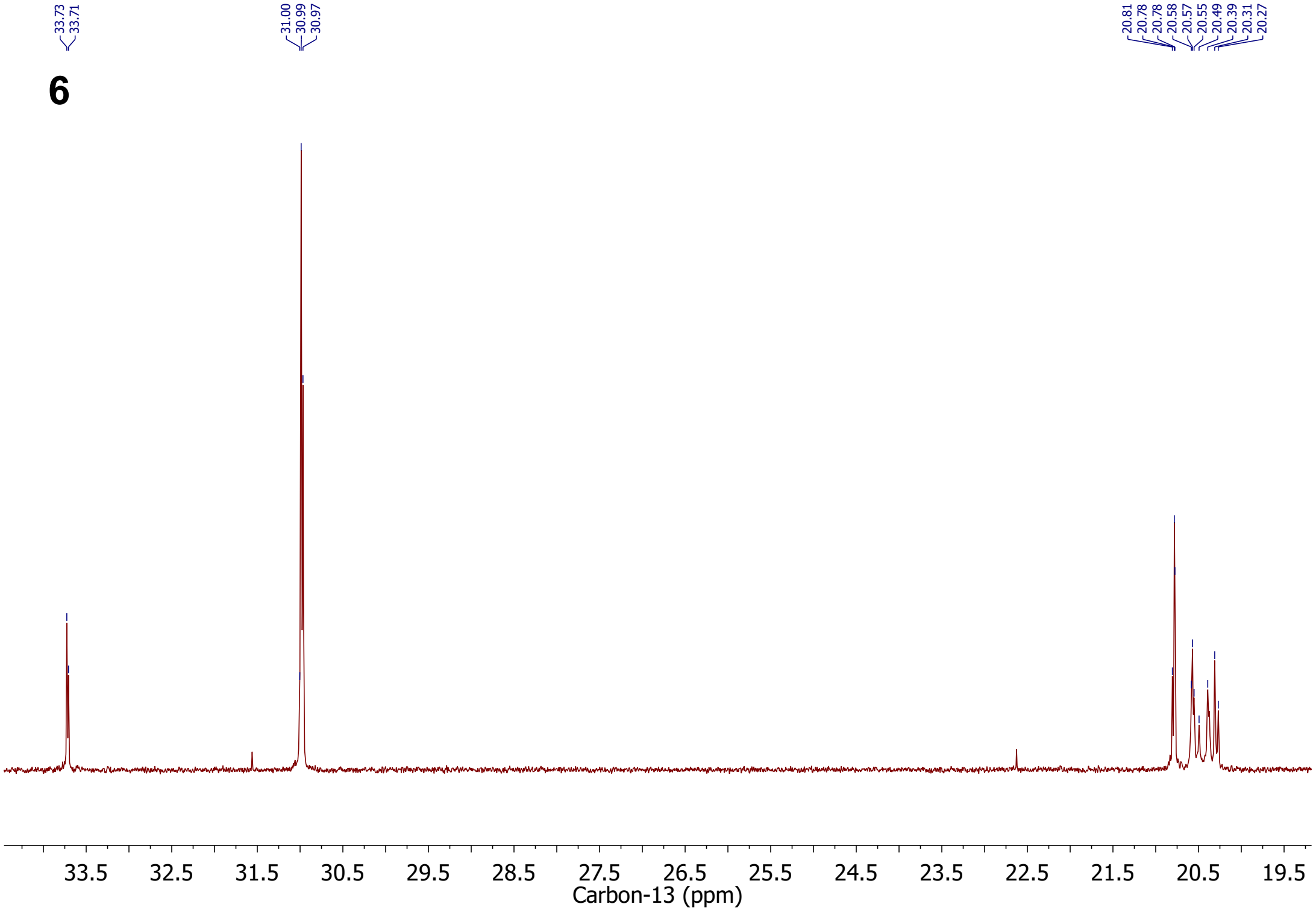

R
N
O
N
Ir
Ir
N
O
N
R
2
2

6 R = 4-*t*Bu-C_6H_4

CD_2Cl_2 at
53.38 ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
Carbon-13 (ppm)


171.66
171.62
169.45
169.43
168.39
168.27
168.21
152.96
152.88
150.77
150.52
150.27
149.35
149.23
148.64
148.45
147.63
147.50
145.87
145.67
145.05
145.00
143.47
143.43
142.10
141.79
6
172
170
168
166
164
162
160
158
156
154
152
150
148
146
144
142
14
Carbon-13 (ppm)


6
137.92
137.90
137.88
137.82
135.92
135.78
135.73
135.28
135.01
134.86
133.24
133.09
132.05
131.75
129.57
129.23
129.20
129.13
128.86
128.40
128.36
128.26
128.19
127.08
127.06
124.31
124.26
124.21
124.02
123.98
123.64
123.53
123.52
123.40
122.88
122.83
122.30
122.20
120.91
120.78
120.47
120.19
119.73
119.71
119.31
119.19
139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119
Carbon-13 (ppm)


33.73
33.71
31.00
30.99
30.97
20.81
20.78
20.78
20.58
20.57
20.55
20.49
20.39
20.31
20.27
6
33.5
32.5
31.5
30.5
29.5
28.5
27.5
26.5
25.5
24.5
23.5
22.5
21.5
20.5
19.5
Carbon-13 (ppm)