Characterization and Reactivity Studies of Dinuclear Iridium Hydride Complexes Prepared from Iridium Catalysts with N,P and C,N Ligands Under Hydrogenation Conditions

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Supplementary Information

Characterization

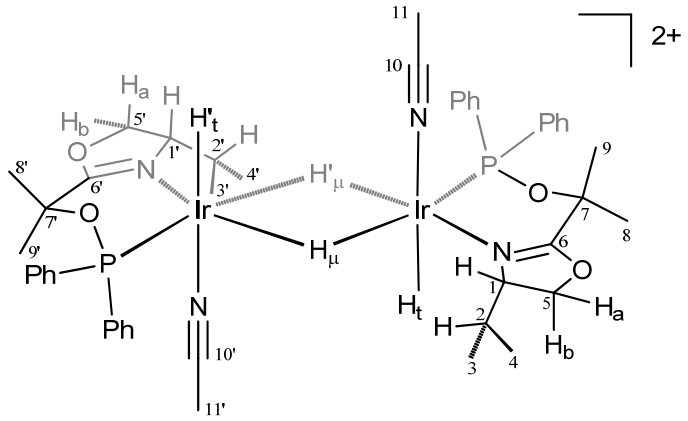
A. Characterization and labeling of complexes **7**, **9a**, **9b**, **10** and **11** S2

B. ^{1}H, ^{31}P and ^{13}C NMR spectra for complexes **5**, **6**,**7**, **8**, **9a**, **9b**, **10** and **11** S8

C. Identification of the byproducts S32

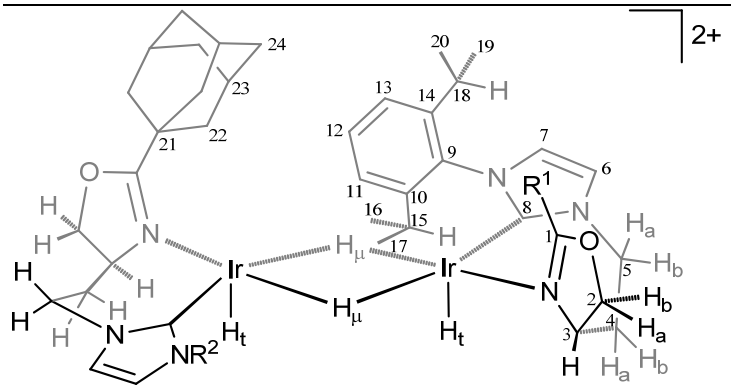
D. X-ray Crystallography S41

Table S1. ^{1}H- and ^{13}C-NMR data for the cation of salt **7** in CD_2Cl_2 at 233 K.



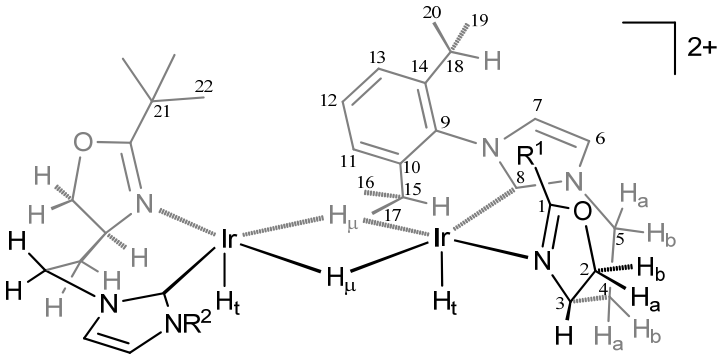
Position	δ(^{1}H) [ppm]	δ(^{13}C) [ppm]
Ir-H_t	–20.24	-
Ir-H_μ	–17.94	-
1	3.93	74.2
2	2.37	29.6
3	0.54	12.7
4	0.65	18.4
5_a	4.57	70.1
5_b	4.45	70.1
6	-	169.1
7	-	80.6
8	1.45	26.4
9	1.73	27.4
10	-	121.0
11	1.91	3.0
Ir-H'_t	–20.04	-
Ir-H'_μ	–17.84	-
1'	3.74	78.5
2'	2.34	28.5
3'	0.77	13.6
4'	0.67	18.8
$5'_a$	4.47	70.0
$5'_b$	4.40	70.0
6'	-	169.8
7'	-	80.7
8'	1.37	26.3
9'	1.76	27.6
10'	-	120.8
11'	1.78	2.3

Table S2. ^{1}H- and ^{13}C-NMR data for the cation of salt **9a** in CD_2Cl_2 at rt.



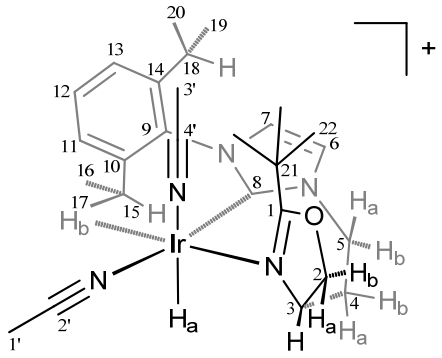
Position	δ(^{1}H) [ppm]	δ(^{13}C) [ppm]
Ir-H_t	–36.85	-
Ir-H_μ	–18.40	-
1	-	181.6
2_a	4.76	74.1
2_b	4.30	74.1
3	4.35	66.9
4_a	2.34	34.6
4_b	2.08	34.6
5_a	3.74	46.0
5_b	4.11	46.0
6	6.95	126.7
7	6.96	124.6
8	-	133.4
9	-	137.6
10	-	147.5
11	7.14	124.4
12	7.38	130.3
13	7.28	124.3
14	-	145.5
15	1.50	29.1
16	0.92	25.8
17	1.32	22.3
18	2.70	29.9
19	1.08	25.9
20	1.30	23.8
21	-	37.2
22	1.95/1.10	36.3
23	2.00	27.7
24	1.83/1.62	35.8

Table S3. ^{1}H- and ^{13}C-NMR data for the cation (major isomer) of salt **9b** in CD_2Cl_2 at 243 K .



Position	δ(^{1}H) [ppm]	δ(^{13}C) [ppm]
Ir-H_t	–34.45	-
Ir-H_μ	–18.90	-
1	-	181.4
2_a	4.82	73.9
2_b	4.40	73.9
3	4.48	66.1
4_a	2.70	32.5
4_b	2.06	32.5
5_a	3.69	45.7
5_b	4.20	45.7
6	6.97	126.2
7	6.97	123.8
8	-	132.2
9	-	136.9
10	-	147.3
11	7.17	123.8
12	7.37	130.3
13	7.23	124.3
14	-	145.0
15	1.75	28.4
16	0.88	25.5
17	1.22	22.3
18	2.34	28.9
19	1.01	26.0
20	1.19	22.0
21	-	34.2
22	0.80	23.4

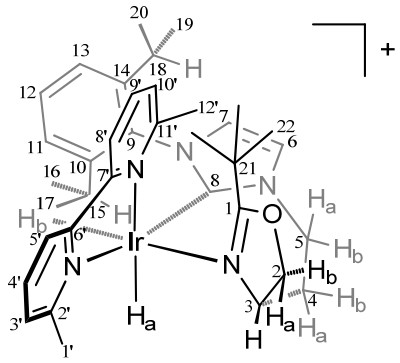
Table S4. ^{1}H- and ^{13}C-NMR data for the cation of salt **10** in CD_2Cl_2 at 263 K.



Position	δ(^{1}H) [ppm]	δ(^{13}C) [ppm]
1’	2.21	3.4
2’	-	118.1
3’	2.29	4.6
4’	-	119.8

Position	δ(^{1}H) [ppm]	δ(^{13}C) [ppm]
Ir-H_a	-21.93	-
Ir-H_b	-26.12	-
1	-	179.4
2_a	4.12	71.9
2_b	4.01	71.9
3	4.09	70.7
4_a	2.00	36.2
4_b	1.71	36.2
5_a	4.53	45.6
5_b	3.90	45.6
6	6.98	120.6
7	6.87	123.2
8	-	154.2
9	-	138.0
10	-	145.6
11	7.26	124.0
12	7.46	129.7
13	7.24	124.1
14	-	146.0
15	2.25	28.7
16	1.03	25.3
17	1.24	22.1
18	2.24	28.6
19	1.00	25.1
20	1.22	21.9
21	-	34.9
22	1.35	27.9

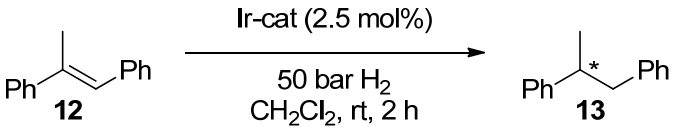
Table S5. ^{1}H- and ^{13}C-NMR data for the cation of salt **11** in CD_2Cl_2 at 295 K.



Position	δ(^{1}H) [ppm]	δ(^{13}C) [ppm]
1’	2.76	30.8
2’	-	162.2
3’	7.43	126.9
4’	7.79	138.2
5’	7.93	121.5
6’	-	159.6
7’	-	158.4
8’	7.91	120.9
9’	7.76	137.7
10’	7.41	127.3
11’	-	161.5
12’	2.65	26.6

Position	δ(^{1}H) [ppm]	δ(^{13}C) [ppm]
Ir-H_a	–21.92	-
Ir-H_b	–28.62	-
1	-	180.7
2_a	4.19	72.9
2_b	4.09	72.9
3	4.86	73.7
4_a	2.26	36.3
4_b	1.82	36.3
5_a	4.81	46.6
5_b	4.02	46.6
6	7.10	121.1
7	6.91	123.9
8	-	158.2
9	-	138.5
10	-	146.4
11	7.13	124.6
12	7.28	129.6
13	6.98	123.8
14	-	145.3
15	2.23	28.9
16	1.06	25.3
17	1.32	22.8
18	2.37	28.9
19	0.96	24.7
20	0.34	21.4
21	-	34.5
22	0.59	27.3

Table S6. Hydrogenation of (*E*)-1,2-diphenyl-1-propene (**12**) catalyzed by C,N iridium complexes **9a** and **9b** with increased catalyst loading and decreased substrate concentration

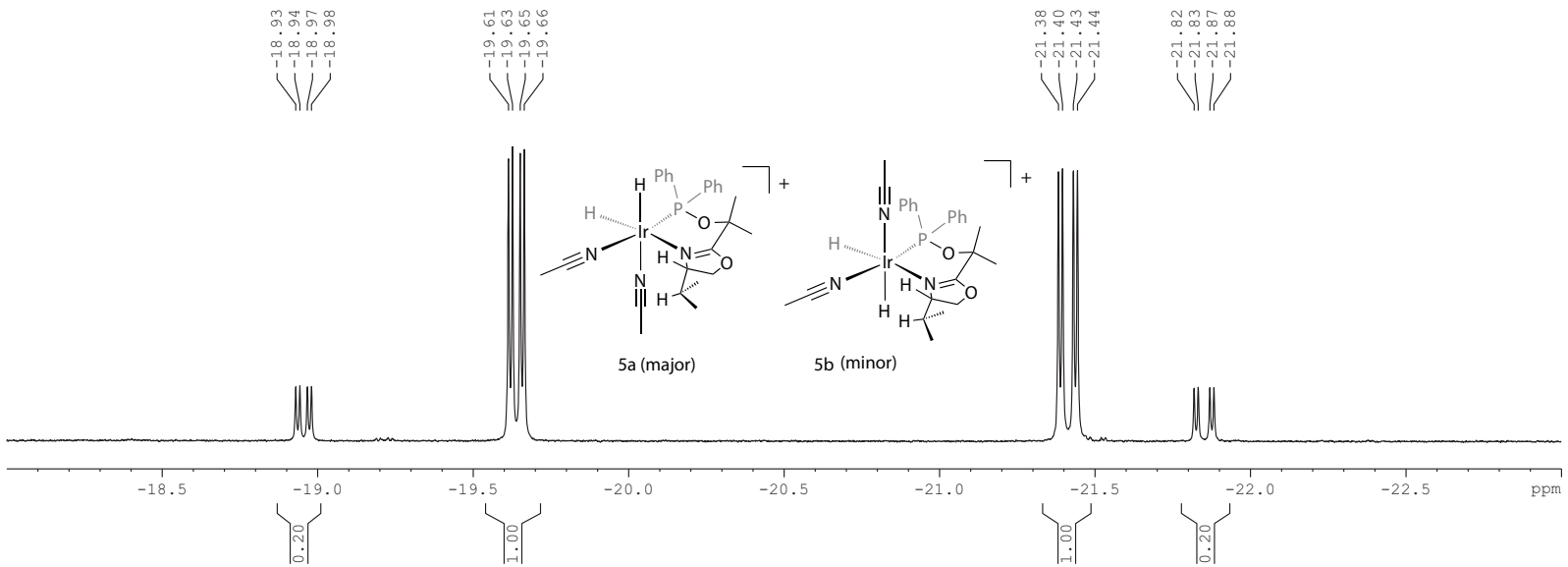


entry	cat.	cat. loading (mol%)	molarity (M)	pressure (bar)	**13** (%)[a]	*ee* **13** (%)[b]
1[c]	**9a**	2.5	0.06	50	53	nd
2[c]	**9b**	2.5	0.06	50	5	nd

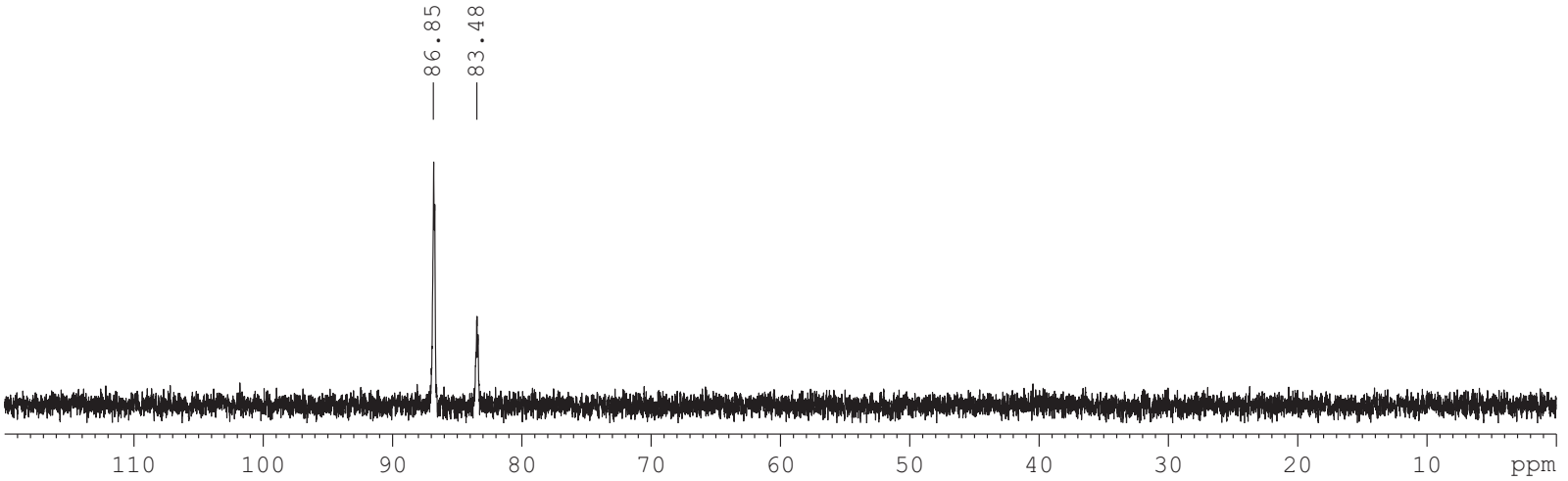
[a]Yields were determined by GC analysis. [b]Enantioselectivities were determined by HPLC on chiral stationary phase [c]Average values of at least two experiments.

Spectra of the stereoisomeric complexes 5a and **5b at 295 K**

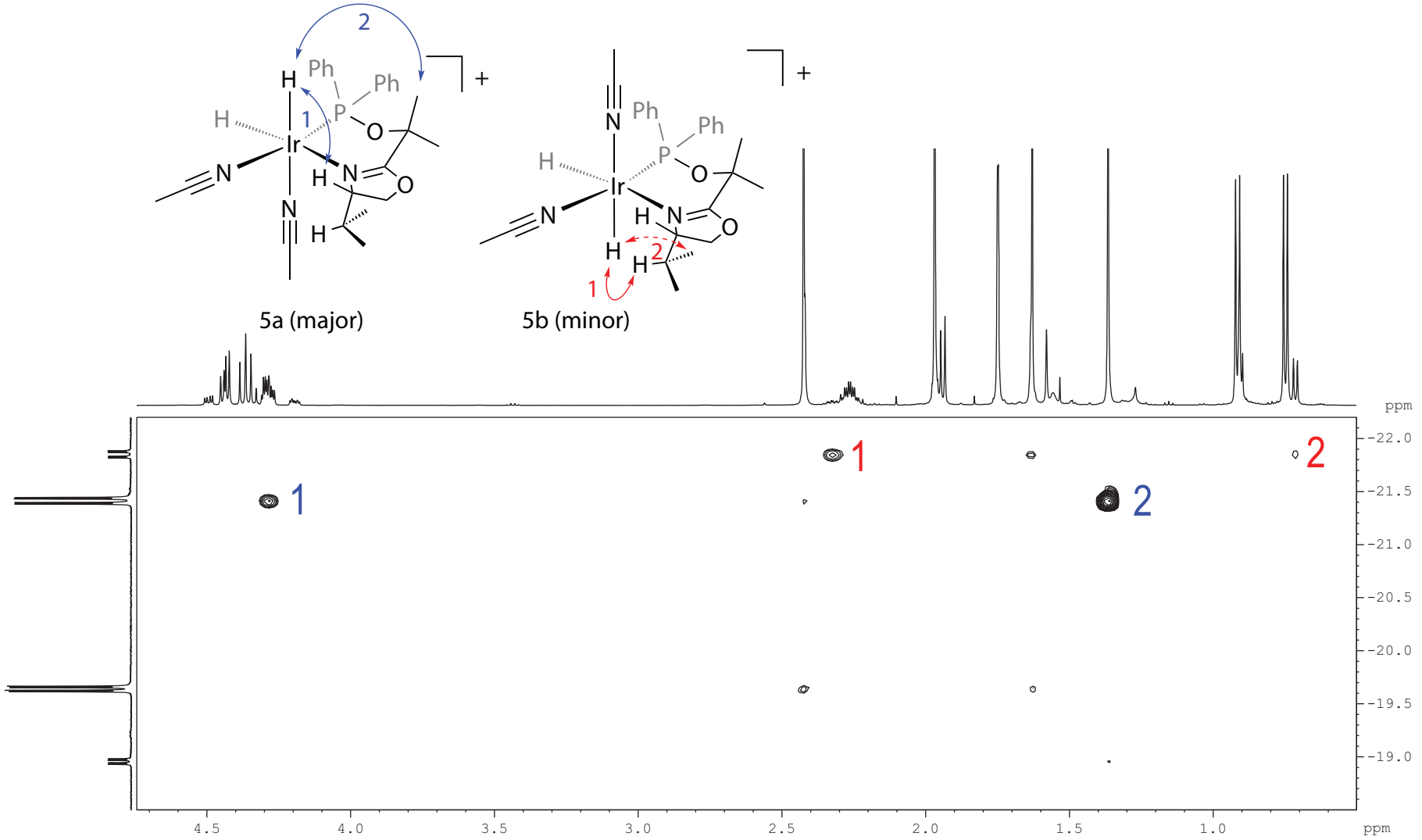
500 MHz 1H NMR of stereoisomeric complexes 5a and 5b (hydride region)



202 MHz 31P{1H} NMR of stereoisomeric complexes 5a and 5b

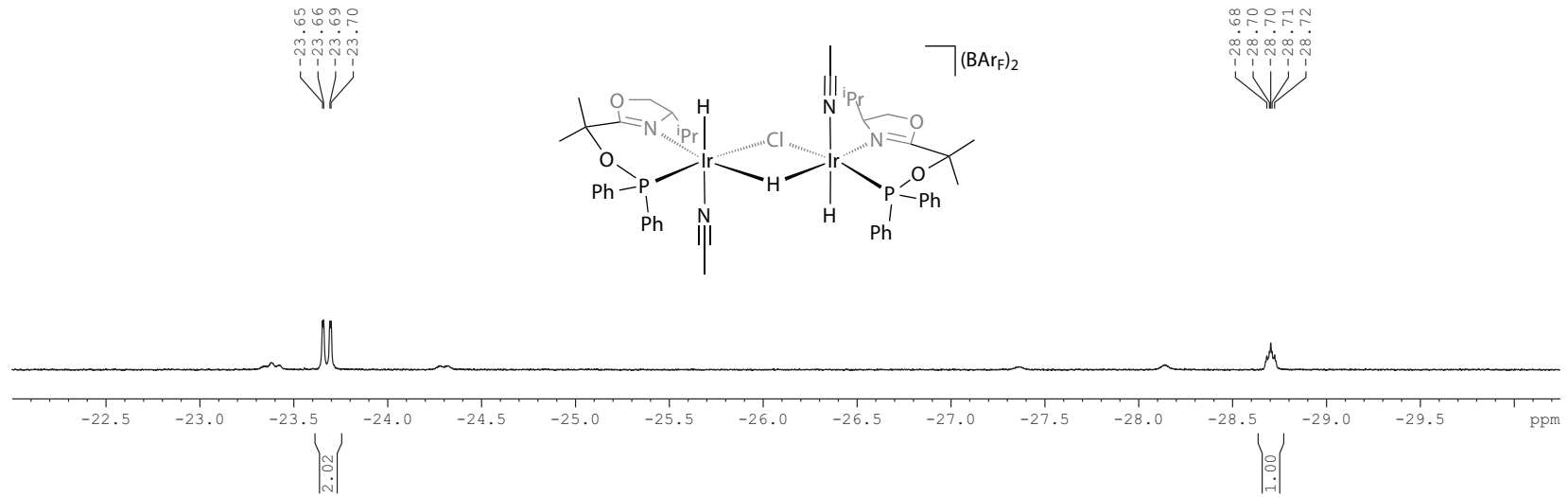


Section of the NOESY of stereoisomeric complexes 5a and 5b

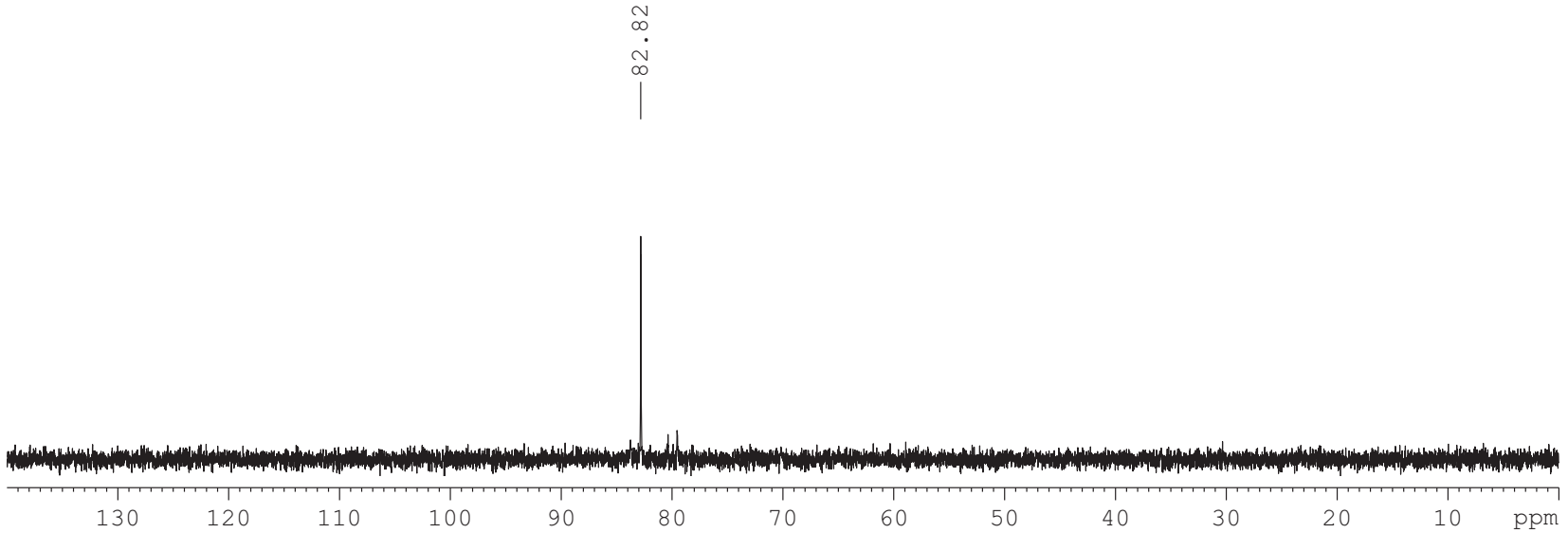


Spectra for complex 6 at 295 K

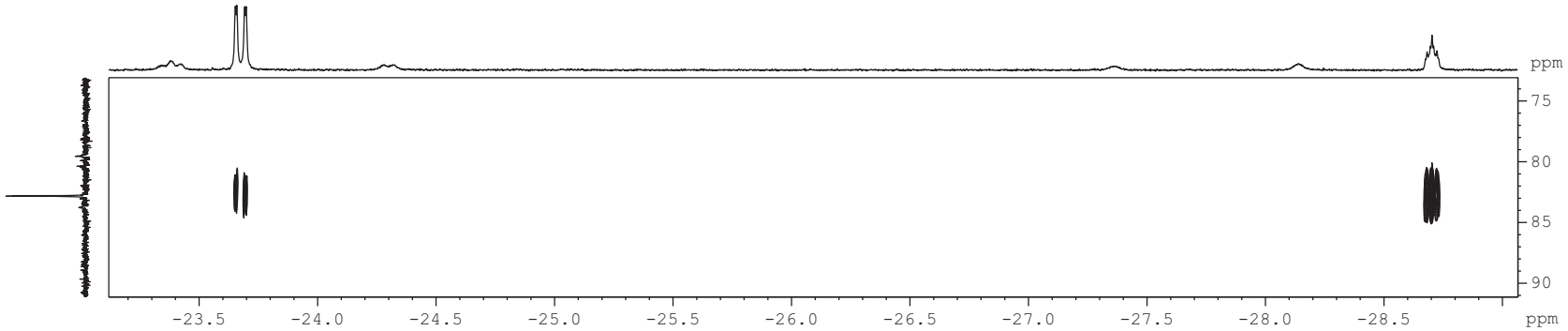
500 MHz 1H NMR of a single crystal of complex 6 (hydride region)



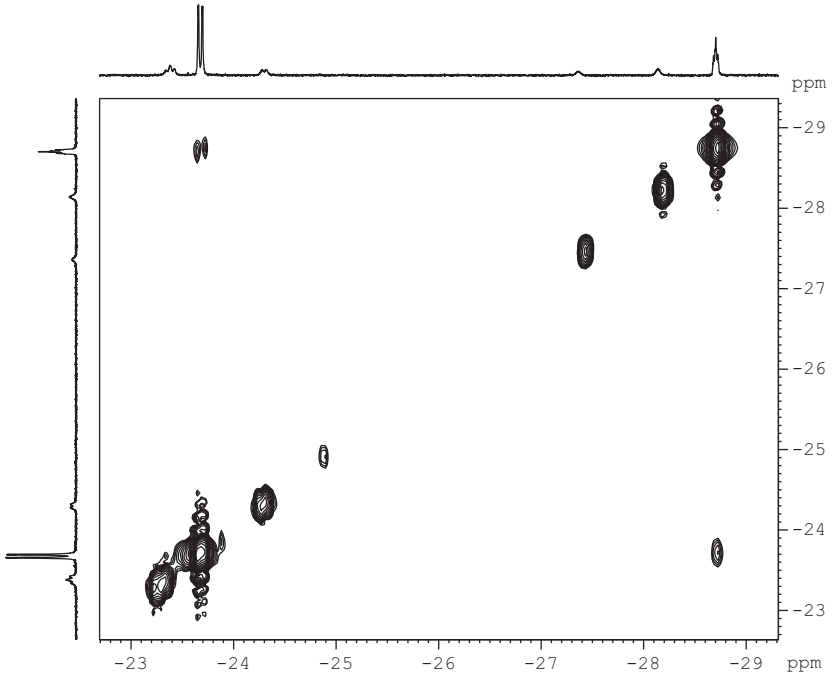
202 MHz 31P{1H} NMR of a single crystal of complex 6.



1H-31P HMBC of complex 6.

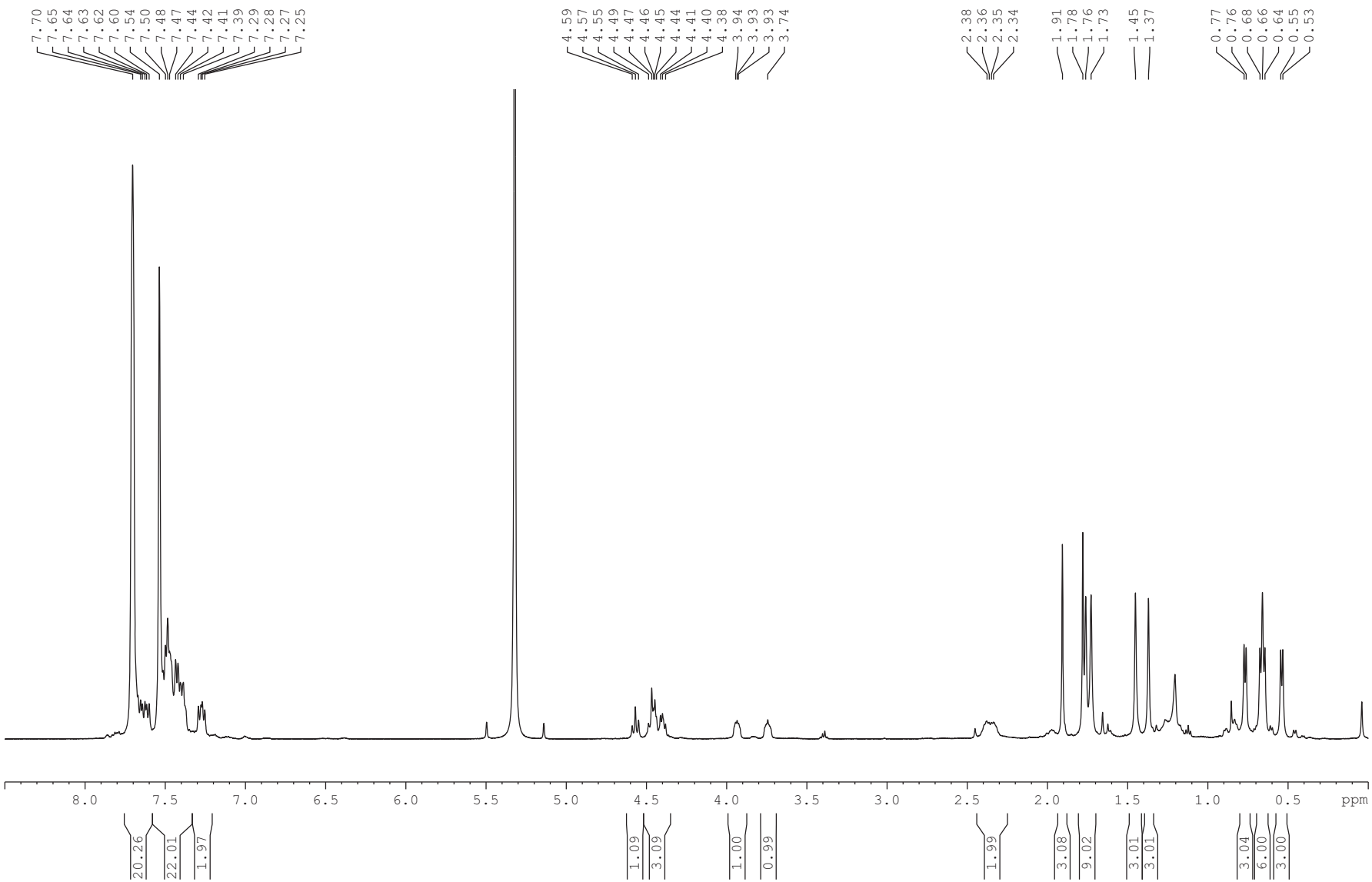


H-H COSY of complex 6 (hydride region).

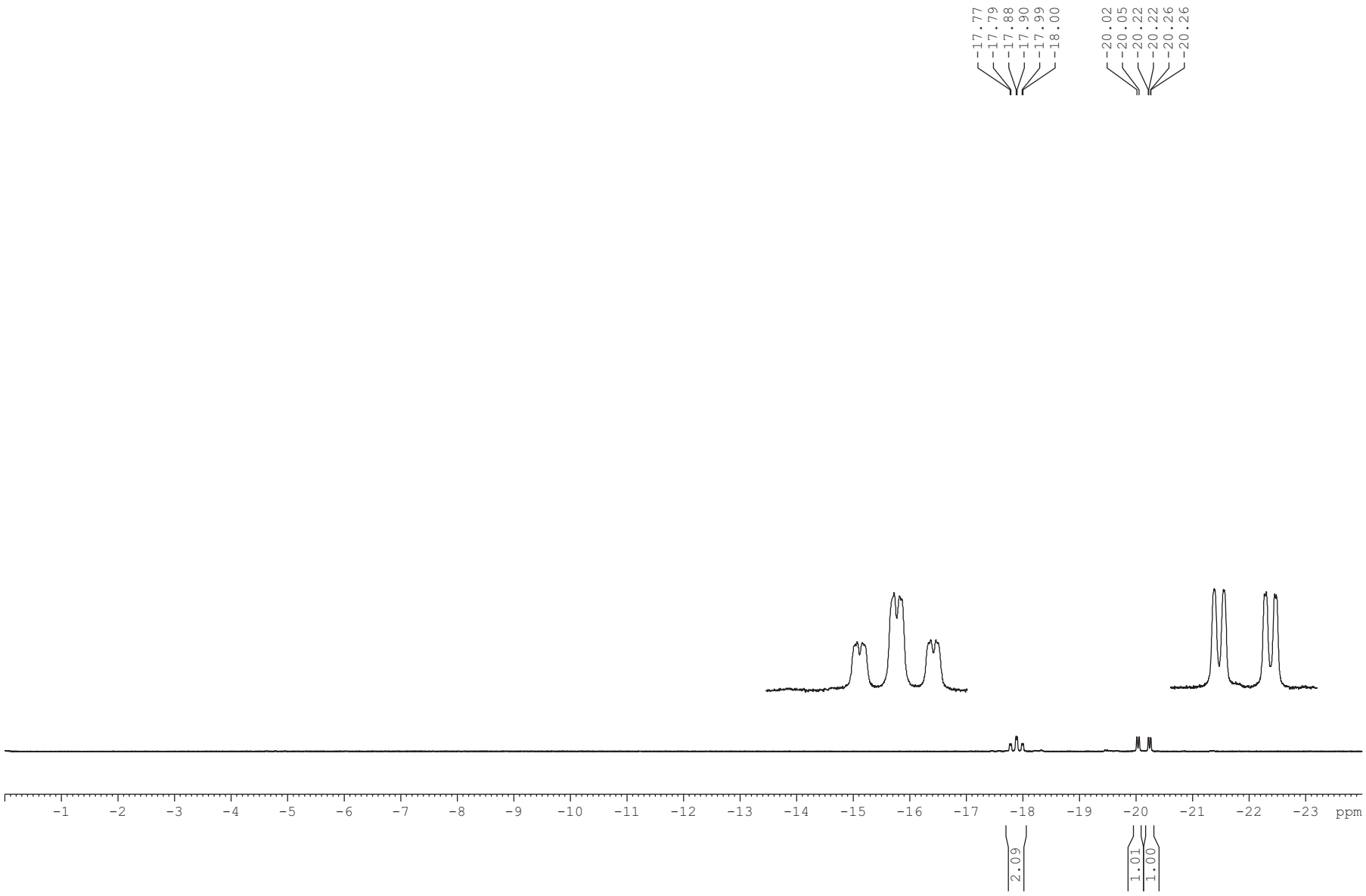


Spectra for complex 7 at 233 K.

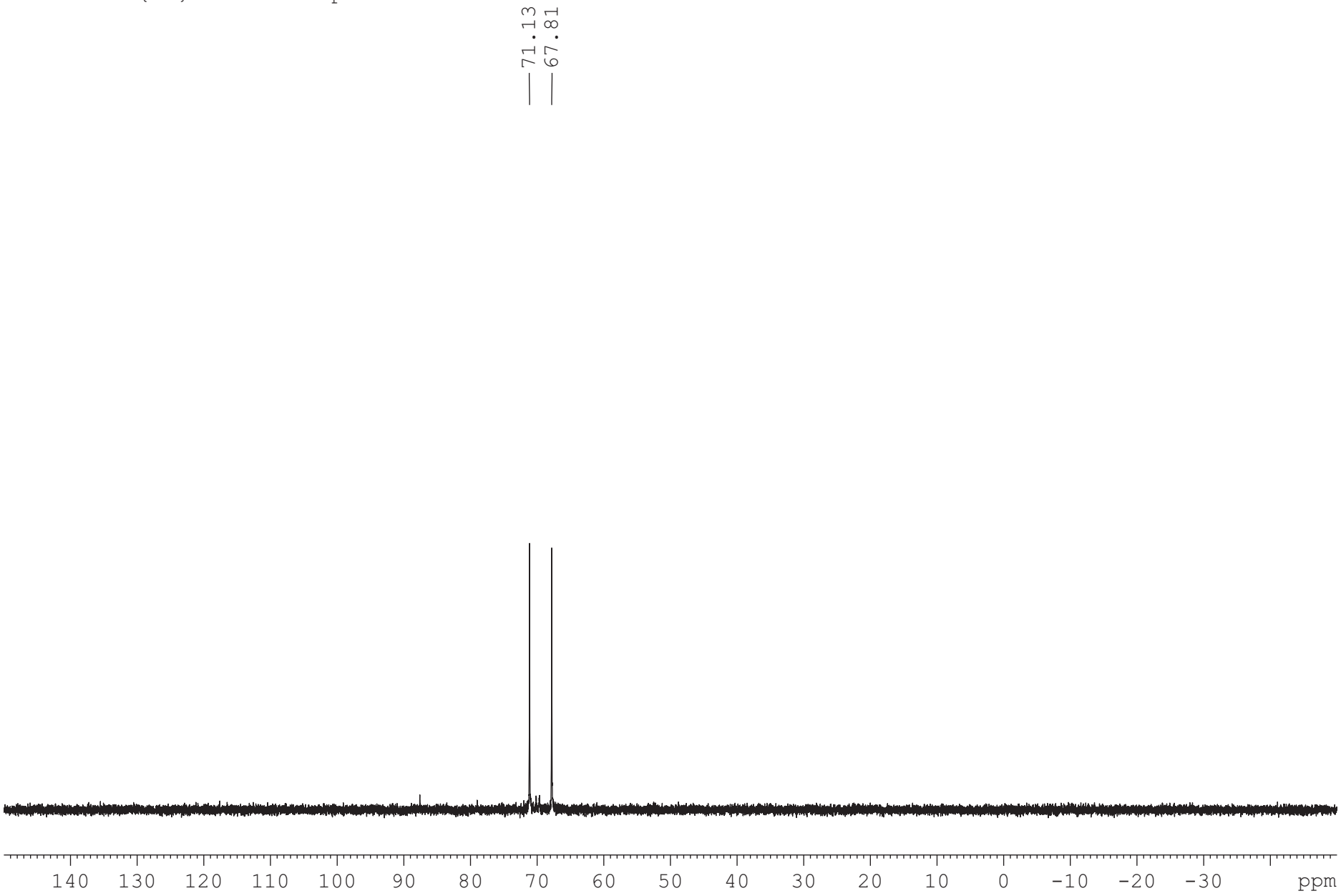
500 MHz 1H NMR of complex 7

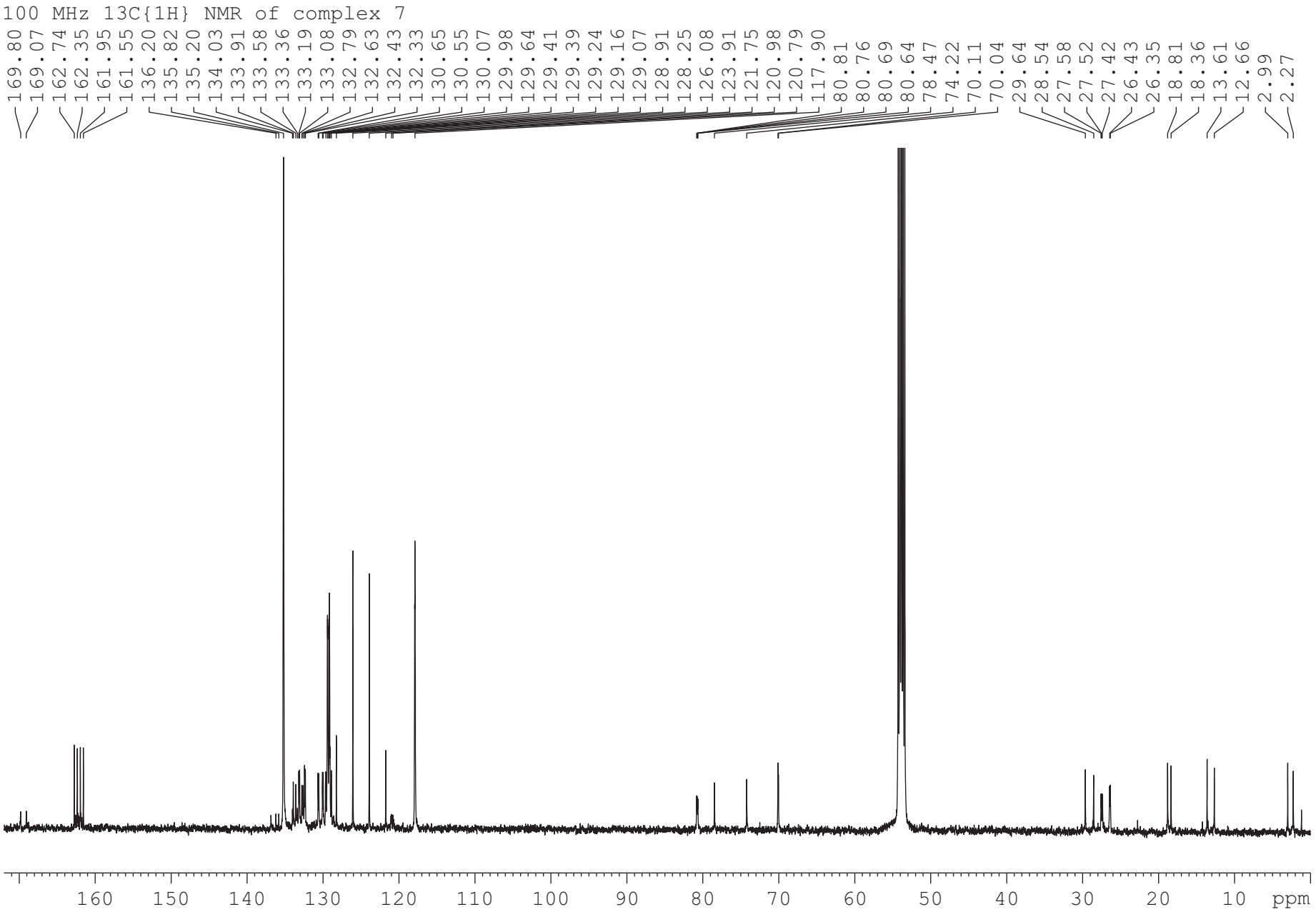


500 MHz 1H NMR of complex 7 (hydride region)



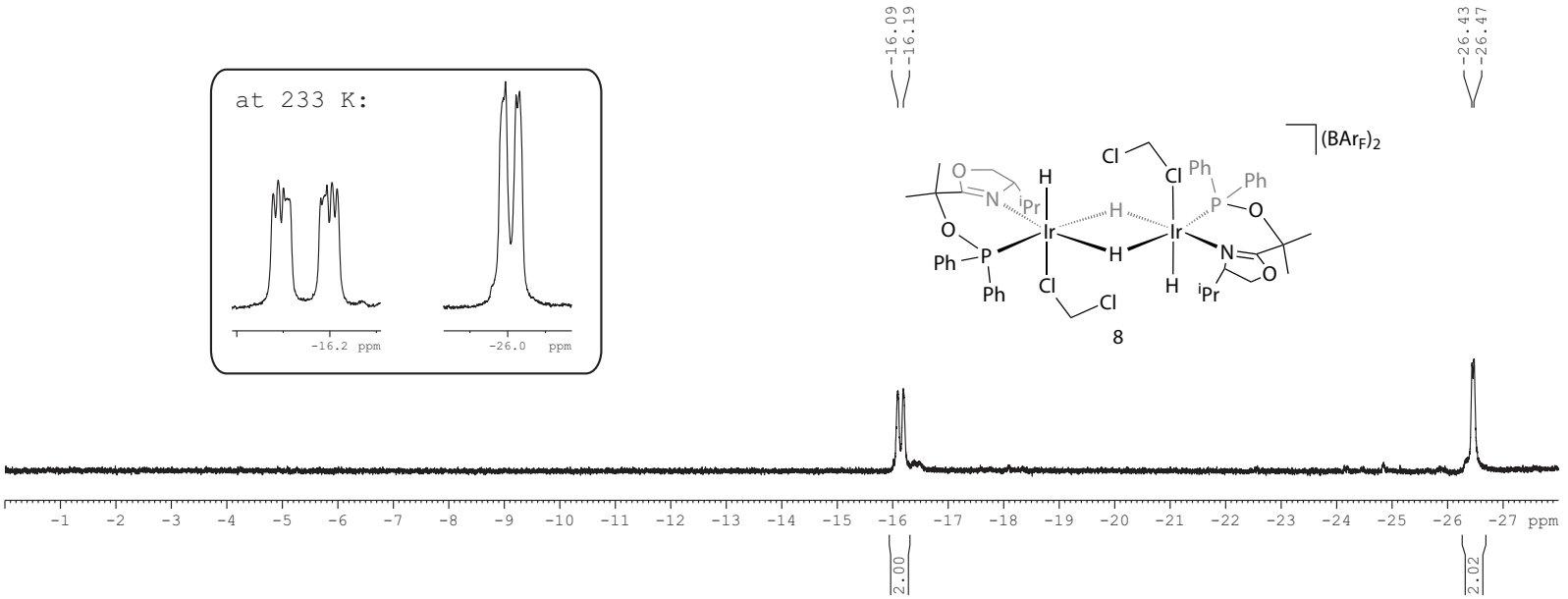
202 MHz 31P{1H} NMR of complex 7



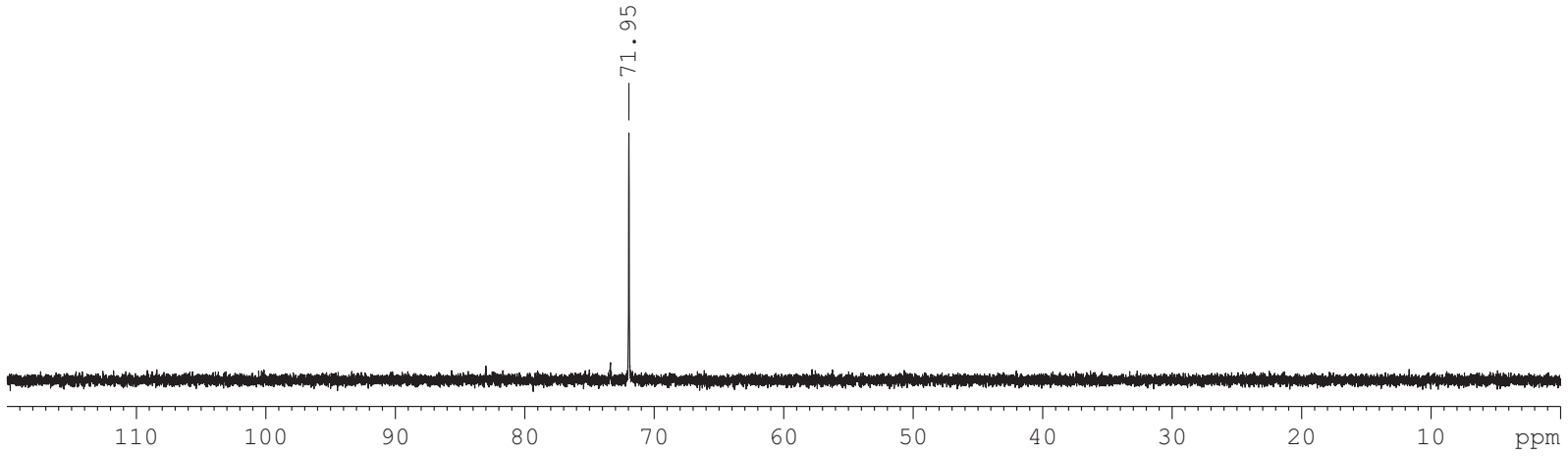

100 MHz 13C{1H} NMR of complex 7
169.80
169.07
162.74
162.35
161.95
161.55
136.20
135.82
135.20
134.03
133.91
133.58
133.36
133.19
133.08
132.79
132.63
132.43
132.33
130.65
130.55
130.07
129.98
129.64
129.41
129.39
129.24
129.16
129.07
128.91
128.25
126.08
123.91
121.75
120.98
120.79
117.90
80.81
80.76
80.69
80.64
78.47
74.22
70.11
70.04
29.64
28.54
27.58
27.52
27.42
26.43
26.35
18.81
18.36
13.61
12.66
2.99
2.27
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Spectra for complex 8 at 295 K

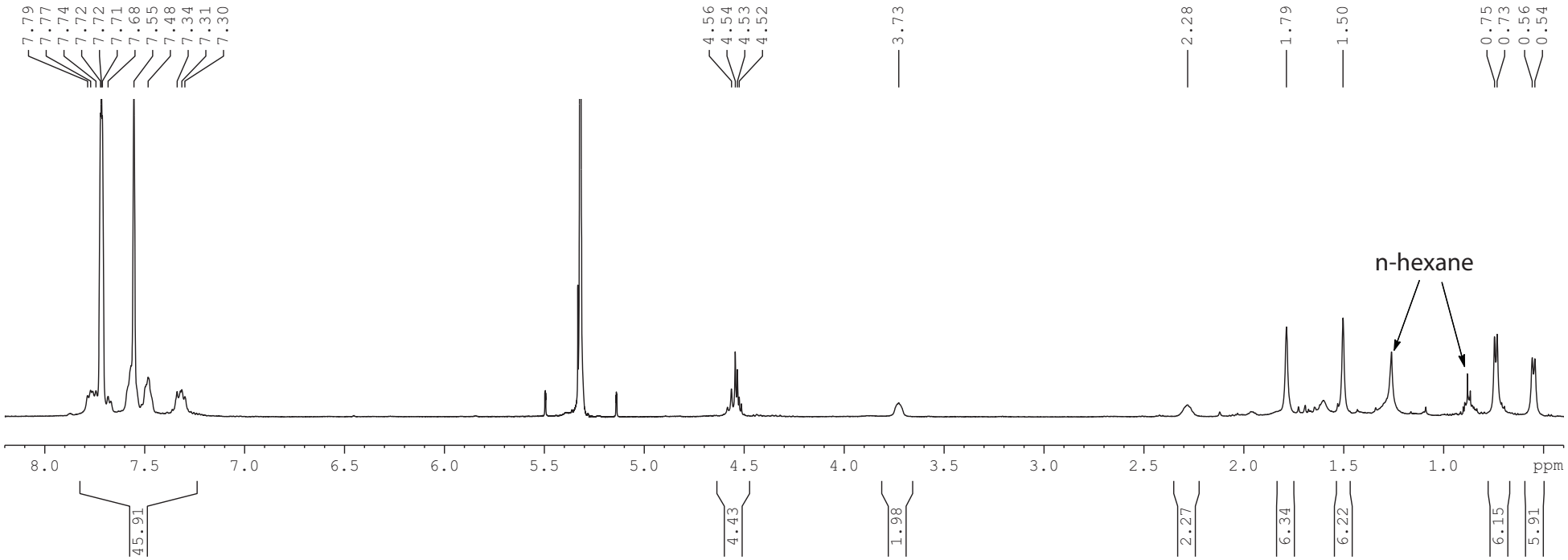
500 MHz 1H NMR of a single crystal of complex 8 in CD2CL2 (hydride region)



202 MHz 31P{1H} NMR of a single crystal of complex 8 in CD2CL2

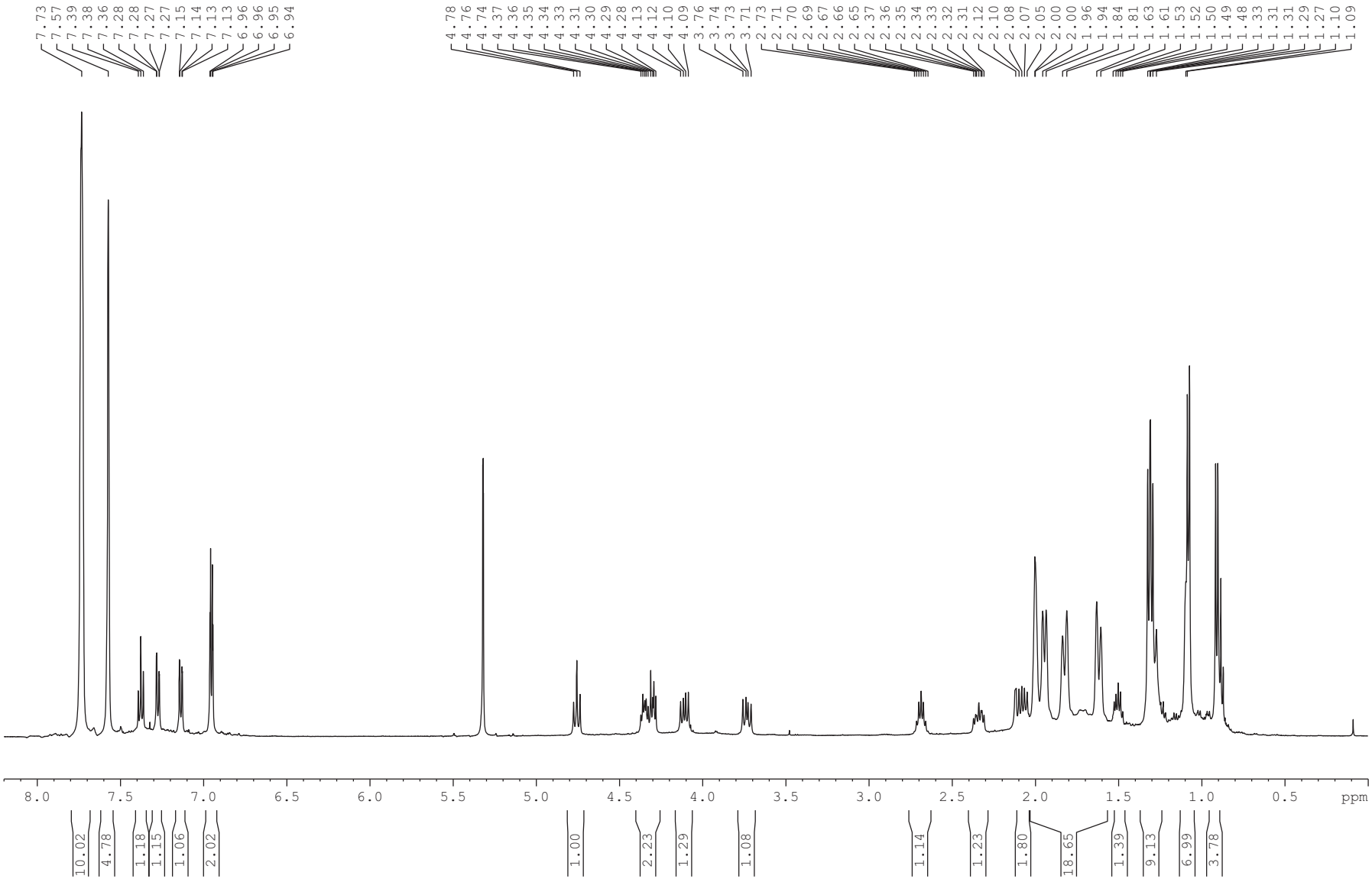


500 MHz 1H NMR of a single crystal of complex 8 in CD2CL2 (region 8.2-0 ppm)

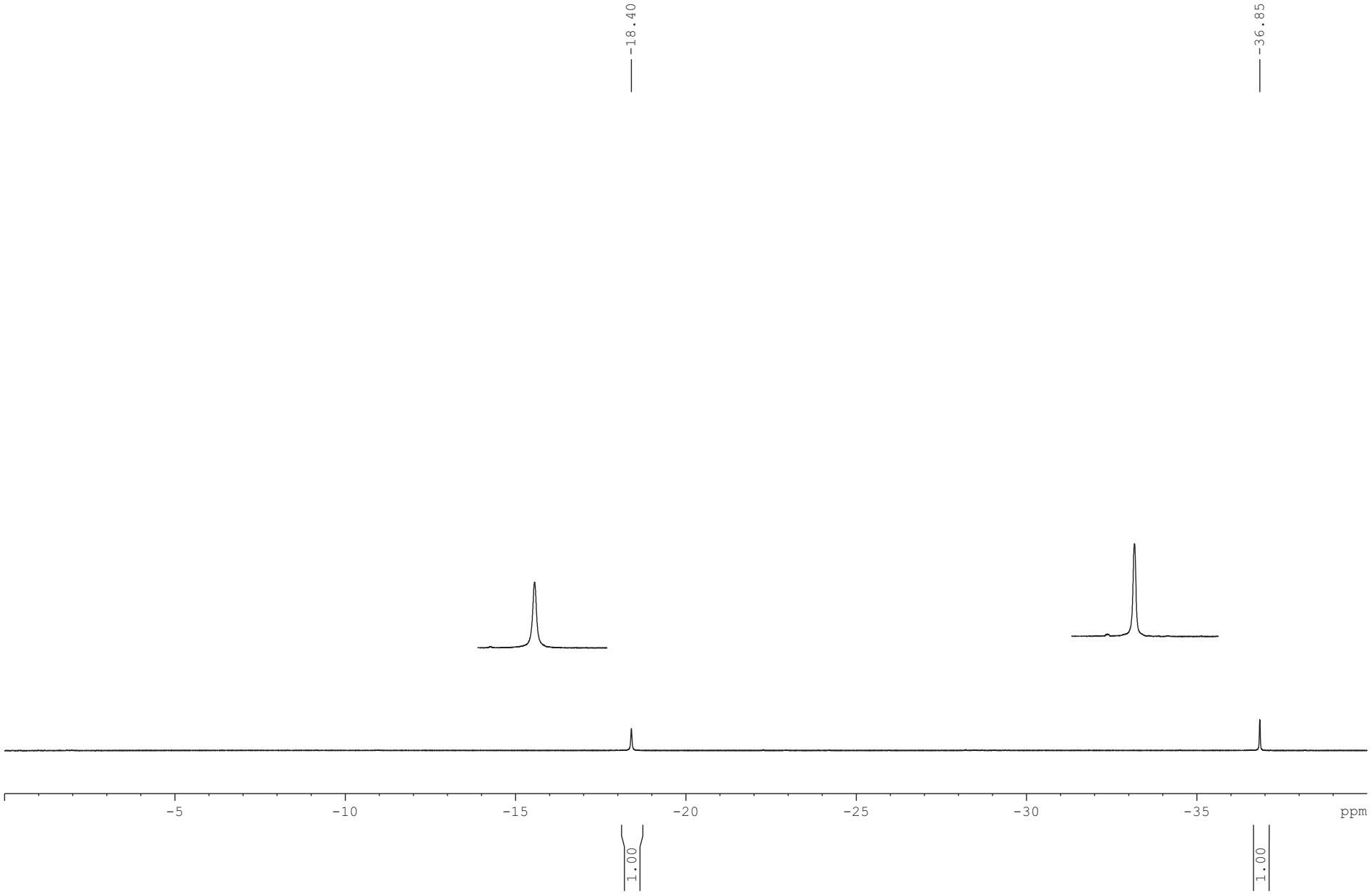


Spectra complex 9a at 295 K.

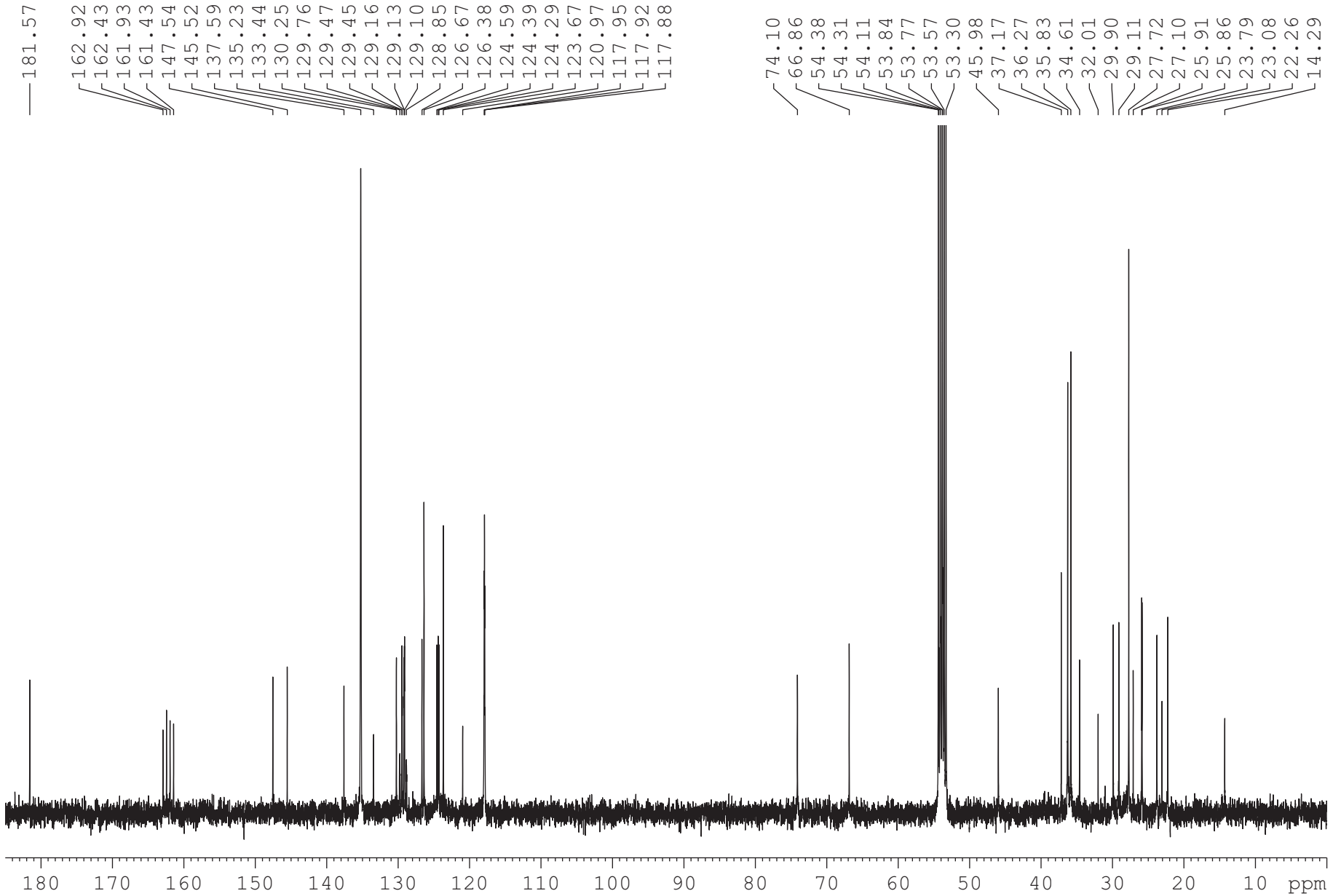
500 MHz 1H NMR of complex 9a



500 MHz 1H NMR of complex 9a (hydride region)

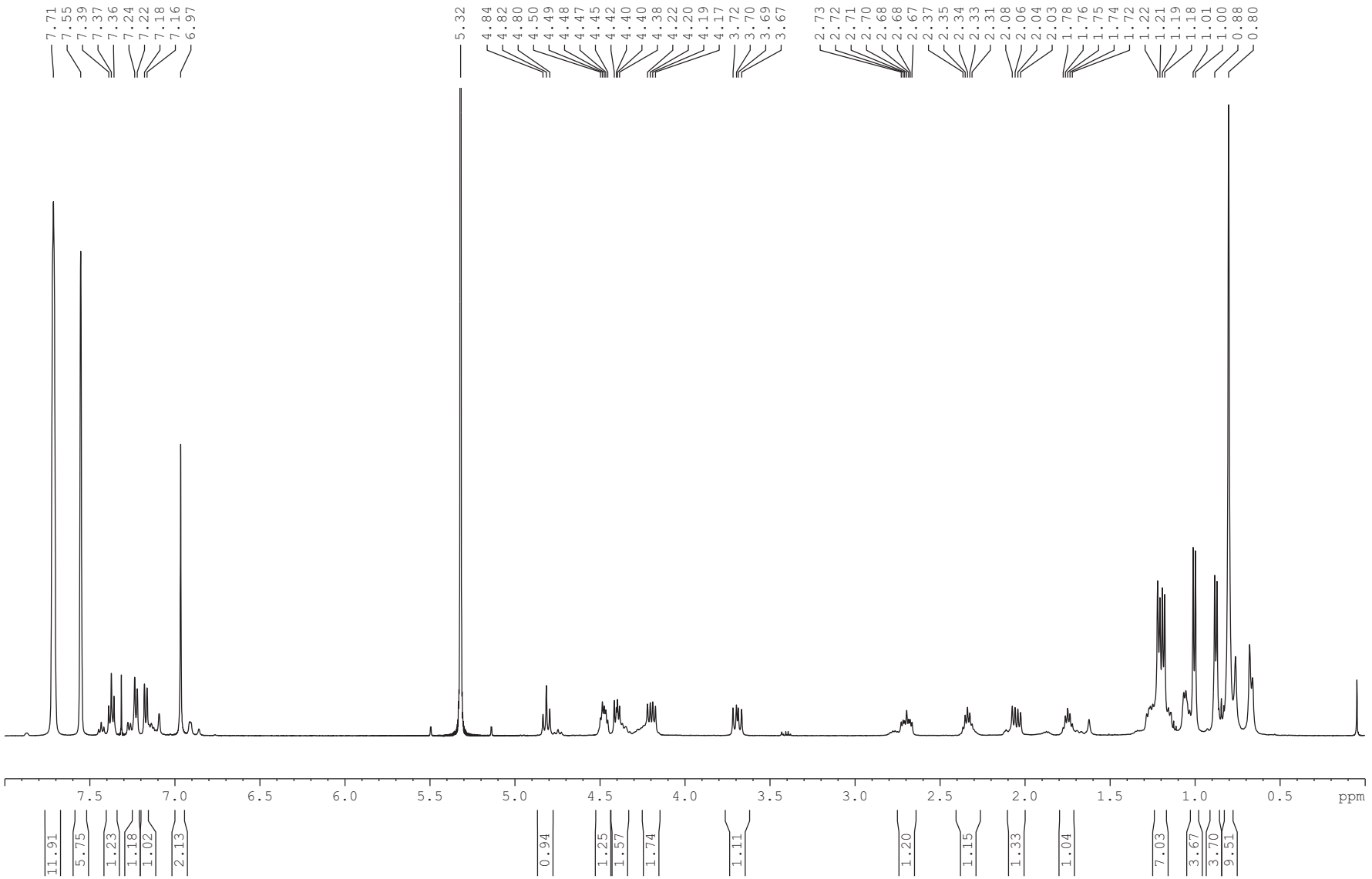


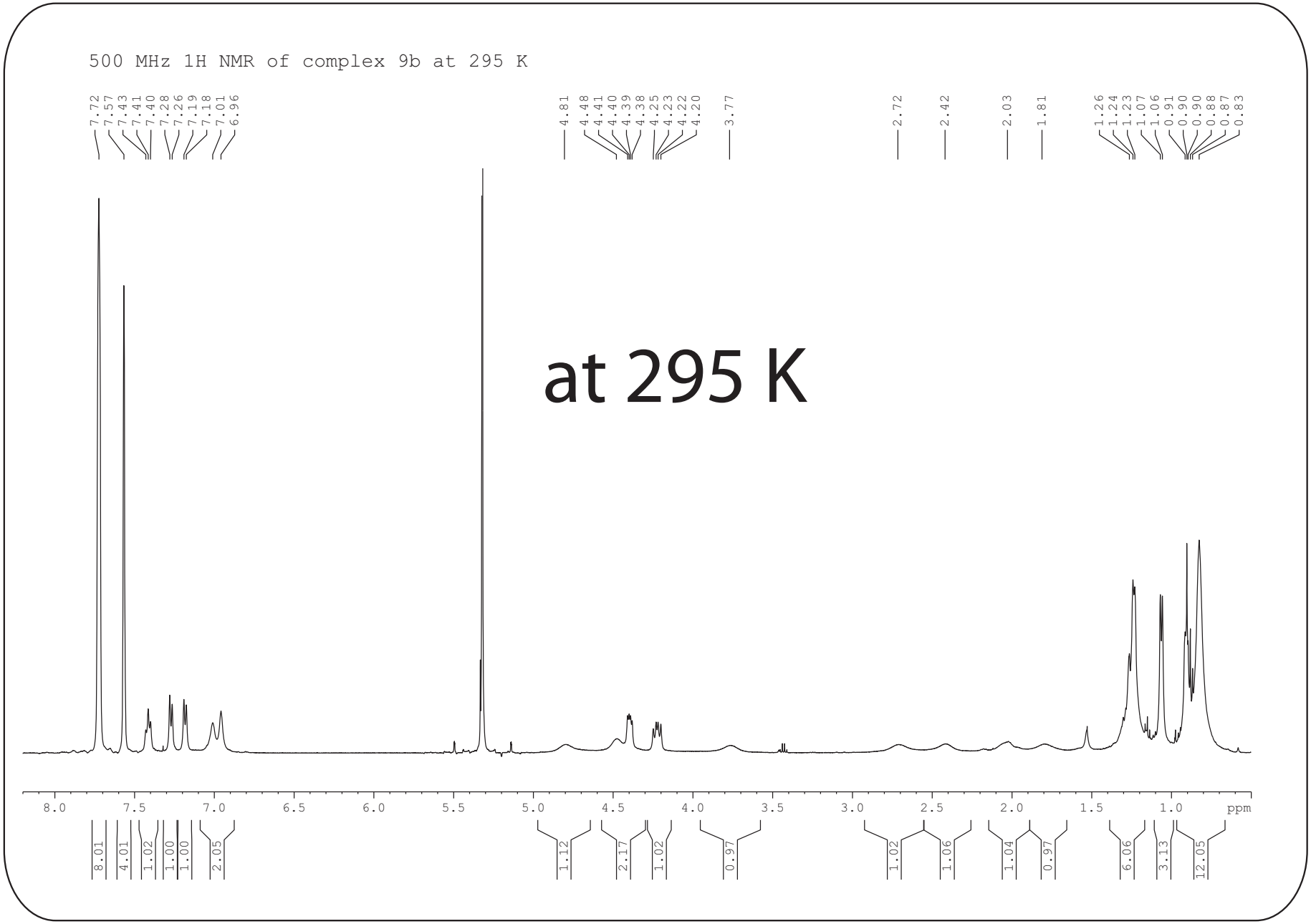
100 MHz 13C{1H} spectrum of complex 9a



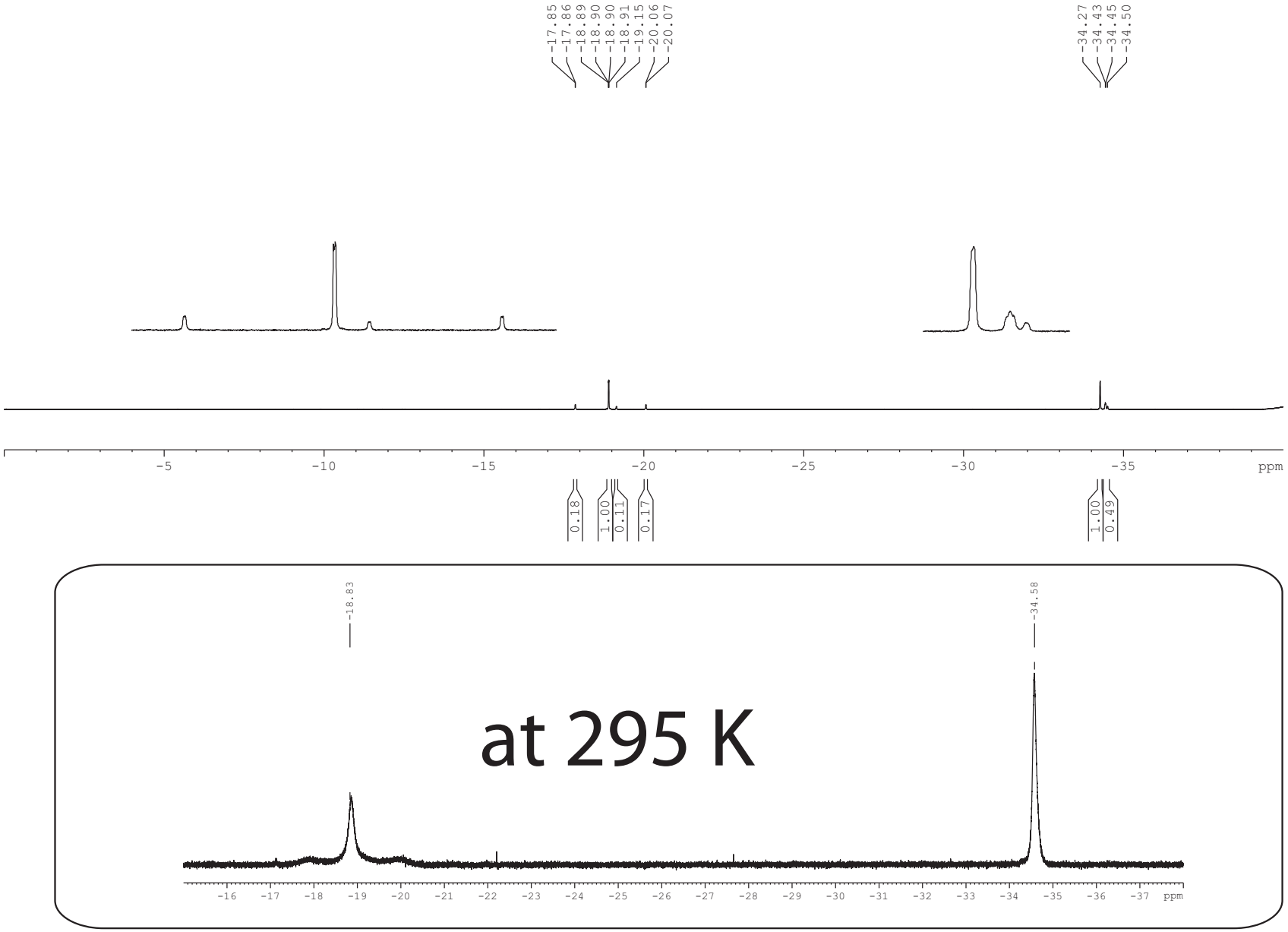
Spectra of complex 9b at 243 K.

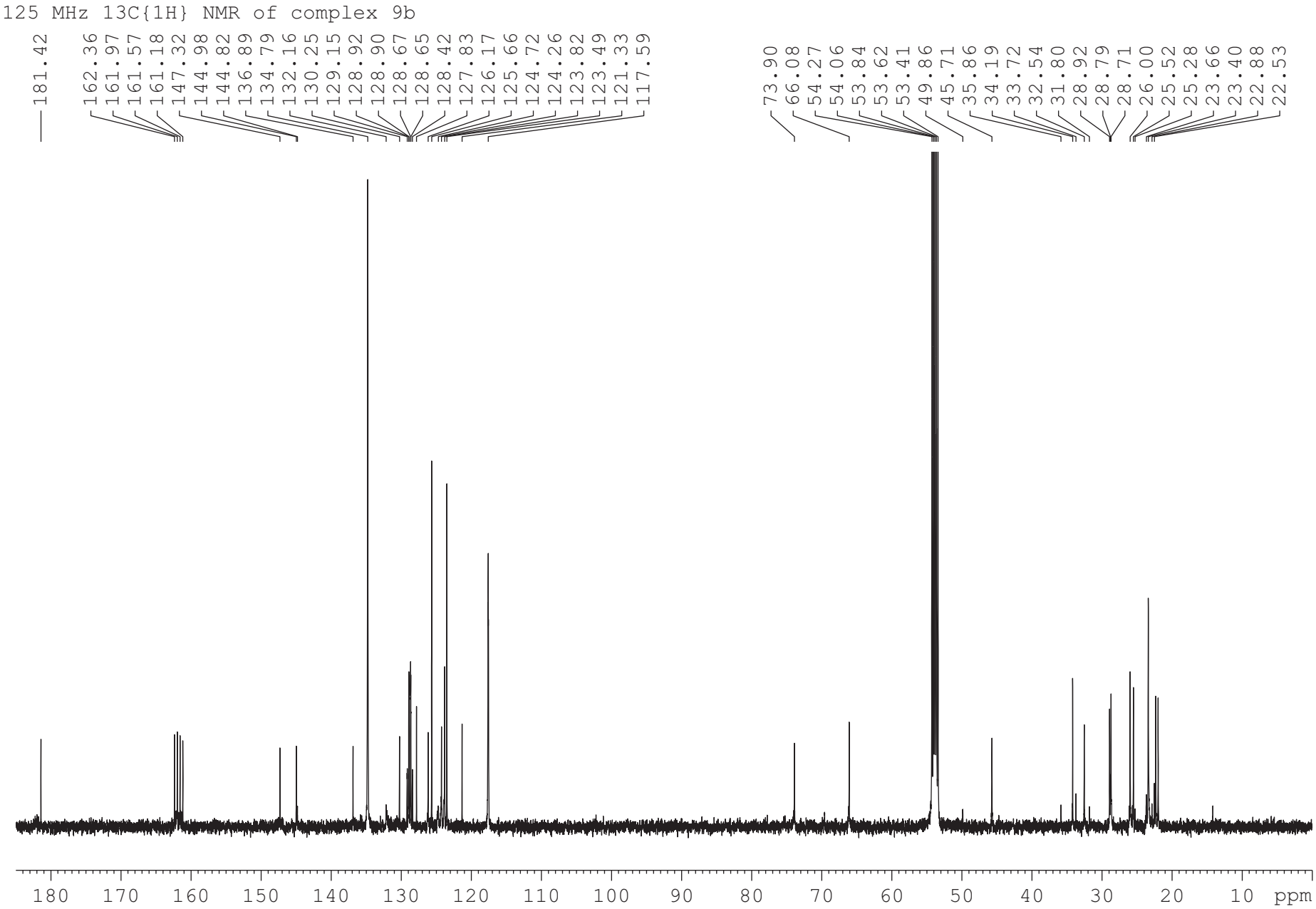
500 MHz 1H NMR of complex 9b



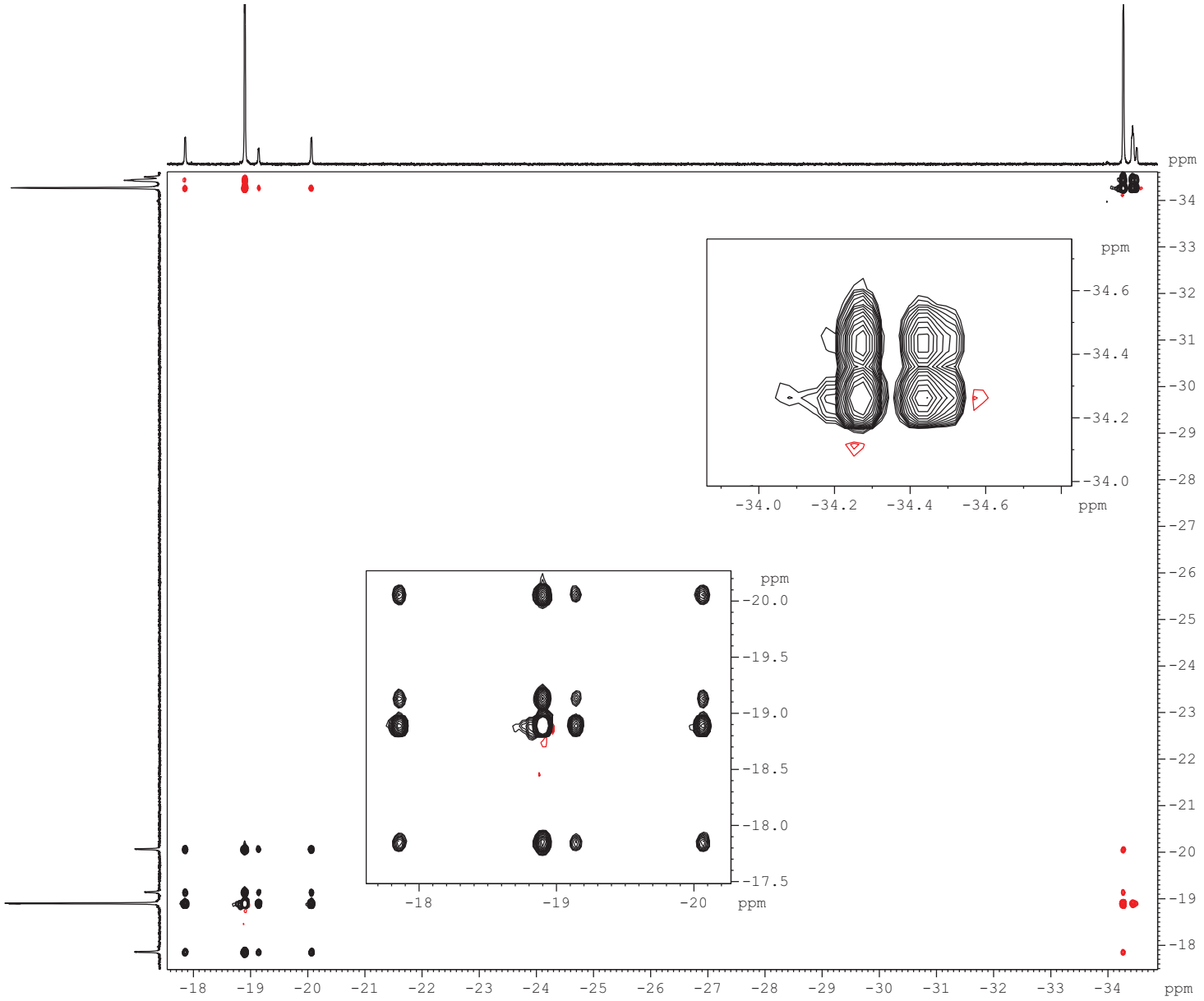

500 MHz 1H NMR of complex 9b at 295 K
7.72
7.57
7.43
7.41
7.40
7.28
7.26
7.19
7.18
7.01
6.96
4.81
4.48
4.41
4.40
4.39
4.38
4.25
4.23
4.22
4.20
3.77
2.72
2.42
2.03
1.81
1.26
1.24
1.23
1.07
1.06
0.91
0.90
0.88
0.87
0.83
at 295 K
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
8.01
4.01
1.02
1.00
1.00
2.05
1.12
2.17
1.02
0.97
1.02
1.06
1.04
0.97
6.06
3.13
12.05

500 MHz 1H NMR of complex 9b (hydrides)



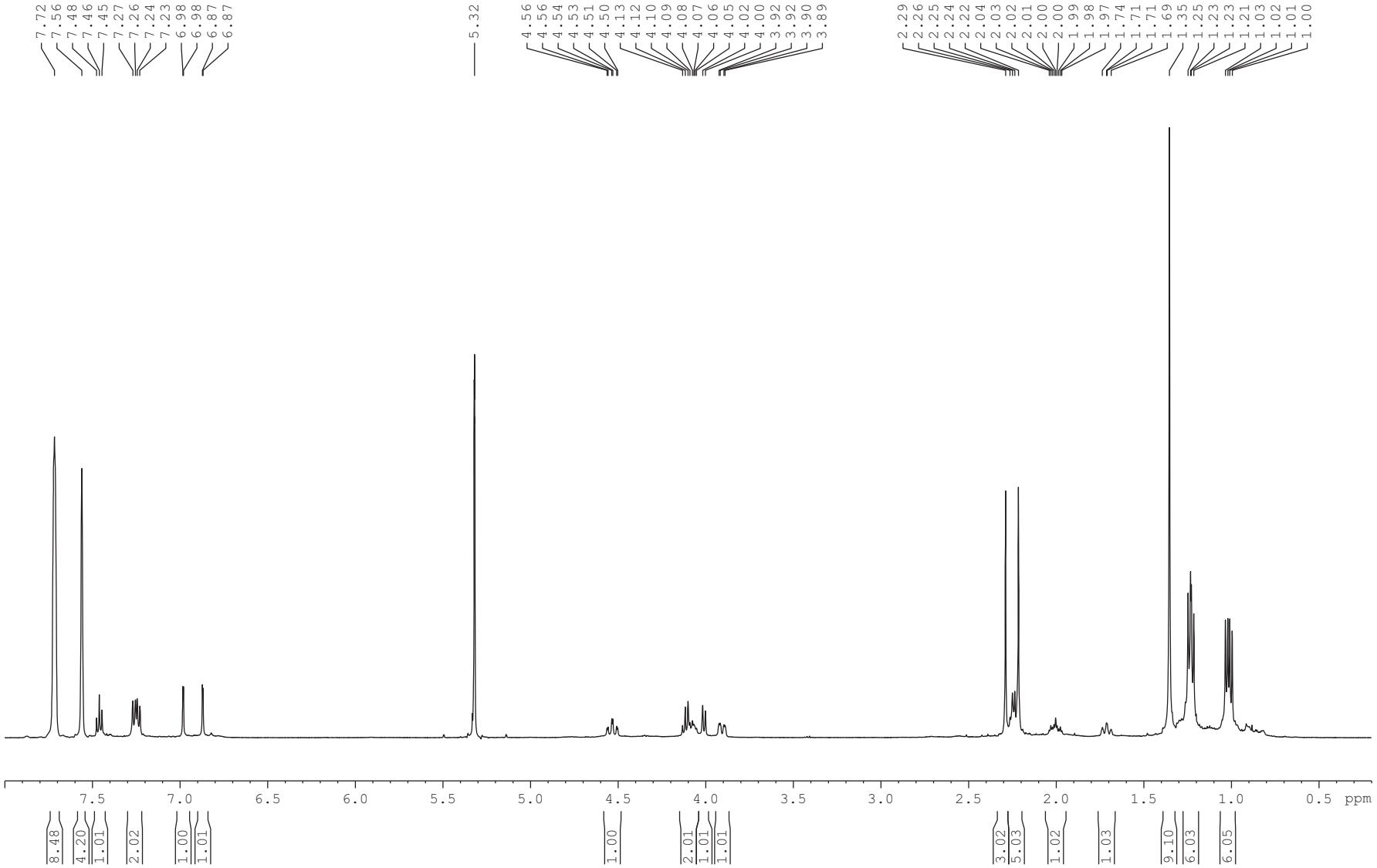

125 MHz 13C{1H} NMR of complex 9b
181.42
162.36
161.97
161.57
161.18
147.32
144.98
144.82
136.89
134.79
132.16
130.25
129.15
128.92
128.90
128.67
128.65
128.42
127.83
126.17
125.66
124.72
124.26
123.82
123.49
121.33
117.59
73.90
66.08
54.27
54.06
53.84
53.62
53.41
49.86
45.71
35.86
34.19
33.72
32.54
31.80
28.92
28.79
28.71
26.00
25.52
25.28
23.66
23.40
22.88
22.53
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Phase sensitive 2D NOESY of complex 9b showing the selective exchange cross-peaks between the major compound and the minor species

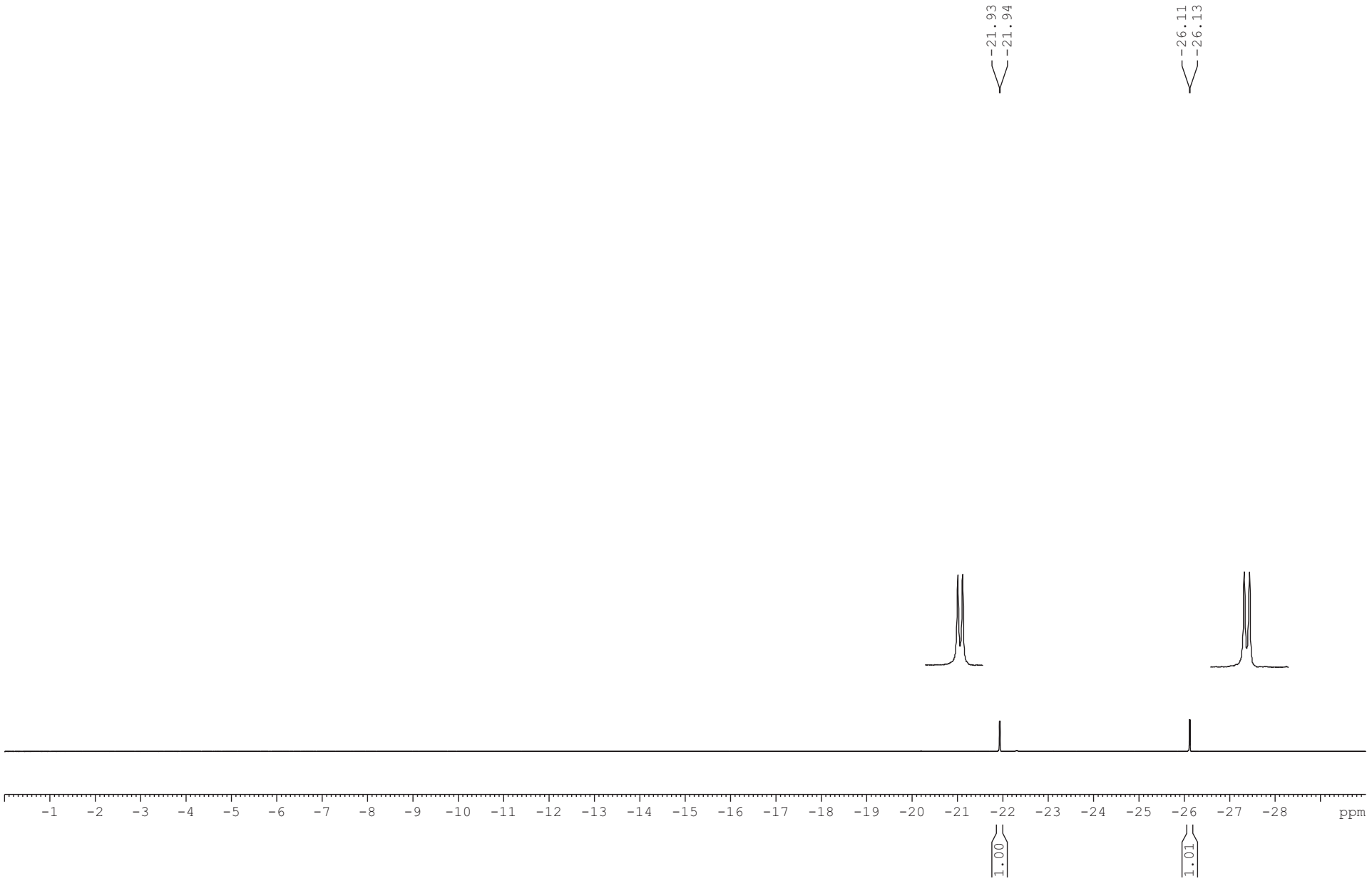


Spectra of complex 10 at 263 K

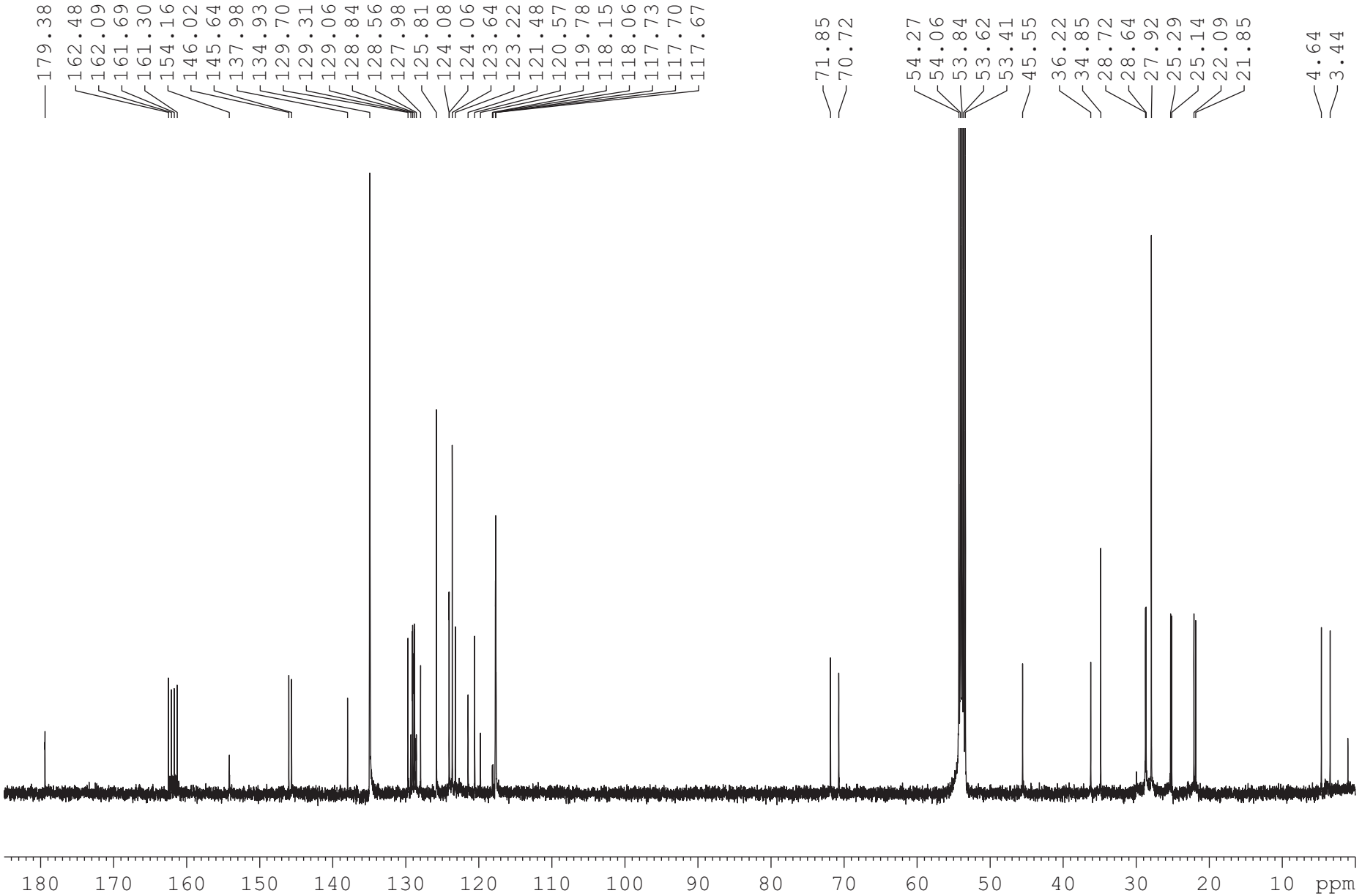
500 MHz 1H NMR of complex 10



500 MHz 1H NMR of complex 10 (hydrides)

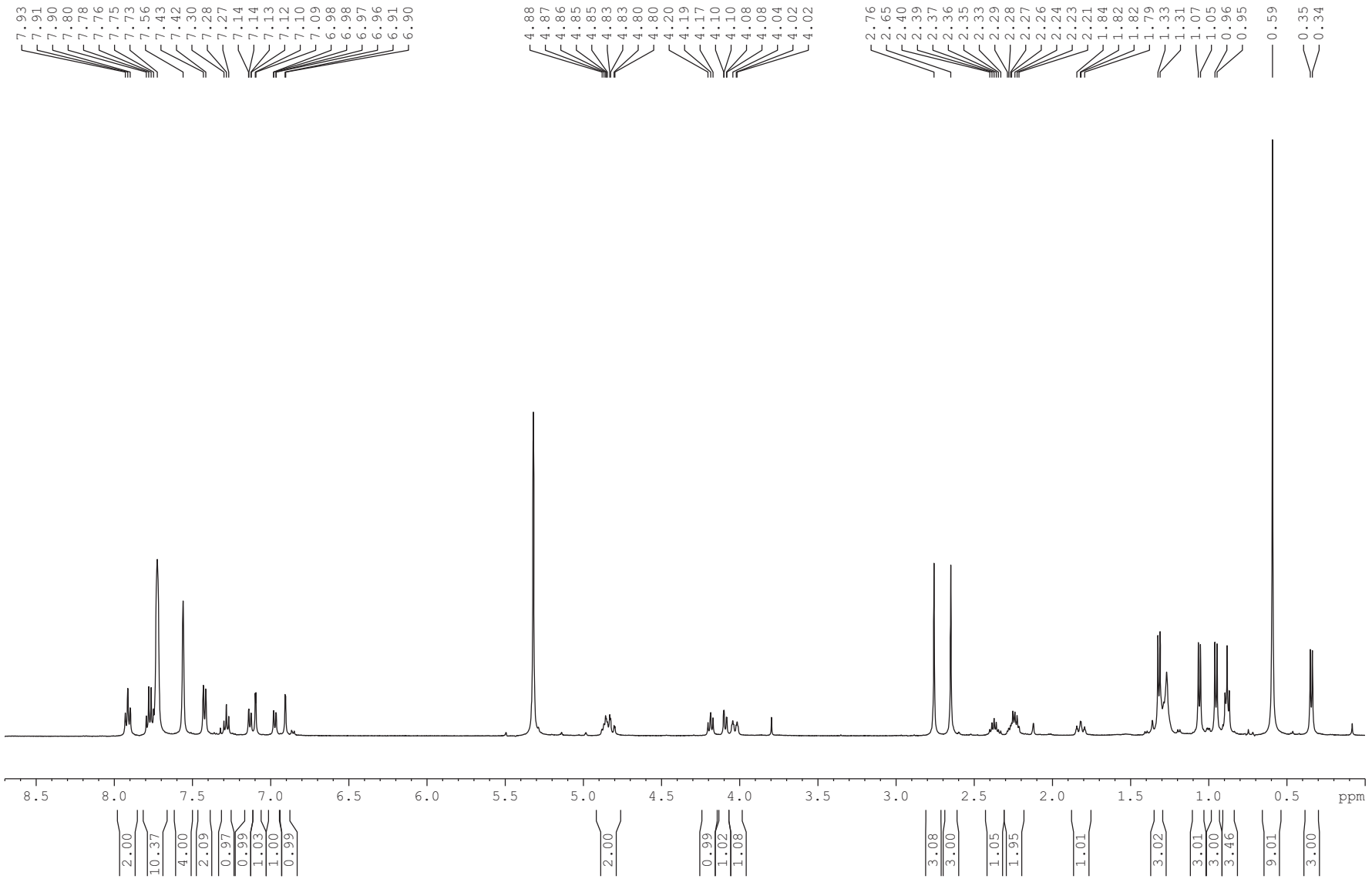


125 MHz 13C{1H} NMR of complex 10

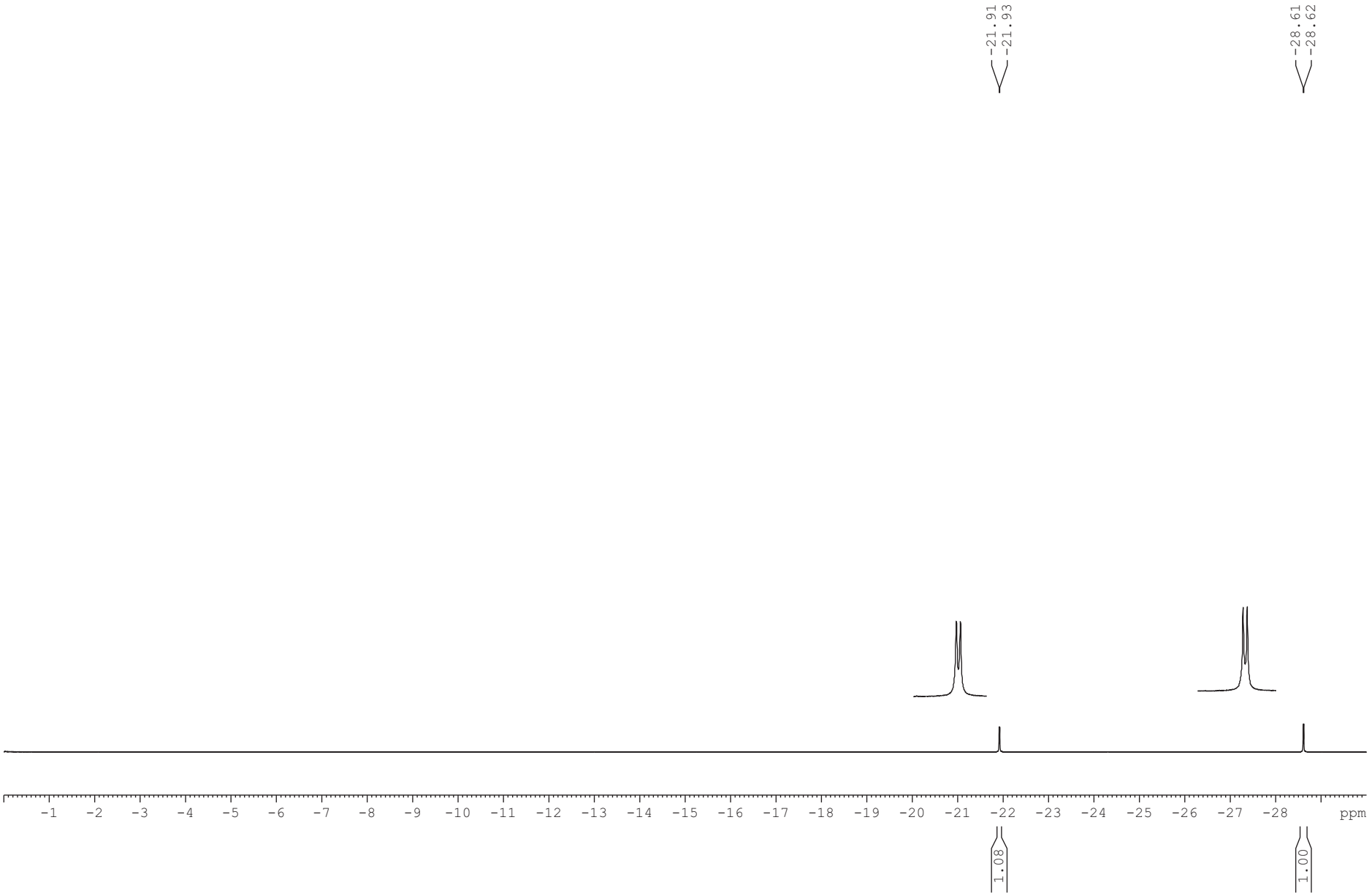


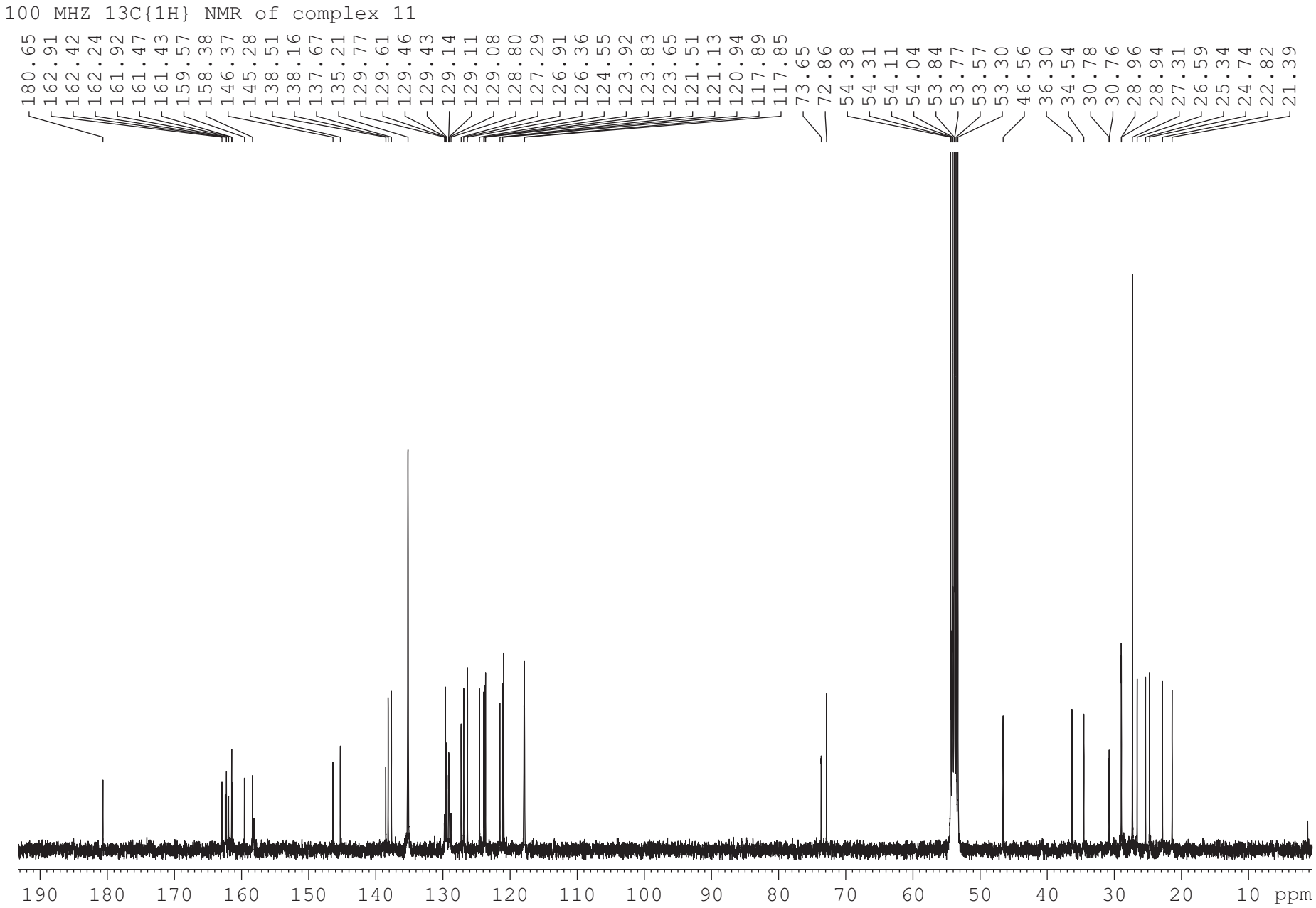
Spectra of complex 11 at 295 K

500 MHz 1H NMR of complex 11

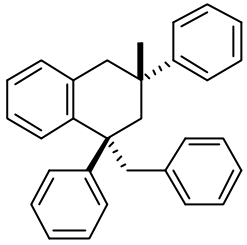


500 MHz 1H NMR of complex 11 (hydrides)

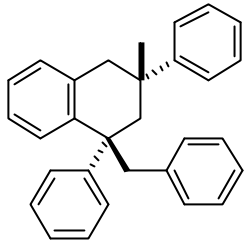



100 MHZ 13C{1H} NMR of complex 11
180.65
162.91
162.42
162.24
161.92
161.47
161.43
159.57
158.38
146.37
145.28
138.51
138.16
137.67
135.21
129.77
129.61
129.46
129.43
129.14
129.11
129.08
128.80
127.29
126.91
126.36
124.55
123.92
123.83
123.65
121.51
121.13
120.94
117.89
117.85
73.65
72.86
54.38
54.31
54.11
54.04
53.84
53.77
53.57
53.30
46.56
36.30
34.54
30.78
30.76
28.96
28.94
27.31
26.59
25.34
24.74
22.82
21.39
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

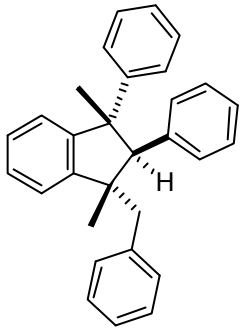
Identification of the byproducts *rel-(1S,3S)-1-benzyl-3-methyl-1,3-diphenyl-1,2,3,4-tetrahydronaphthalene, rel-(1R,3S)-1-benzyl-3-methyl-1,3-diphenyl-1,2,3,4-tetrahydronaphthalene and rel-(1S,2S,3S)-1-benzyl-1,3-dimethyl-2,3-diphenyl-2,3-dihydro-1H-indene*



rel-**P1**



rel-**P2**

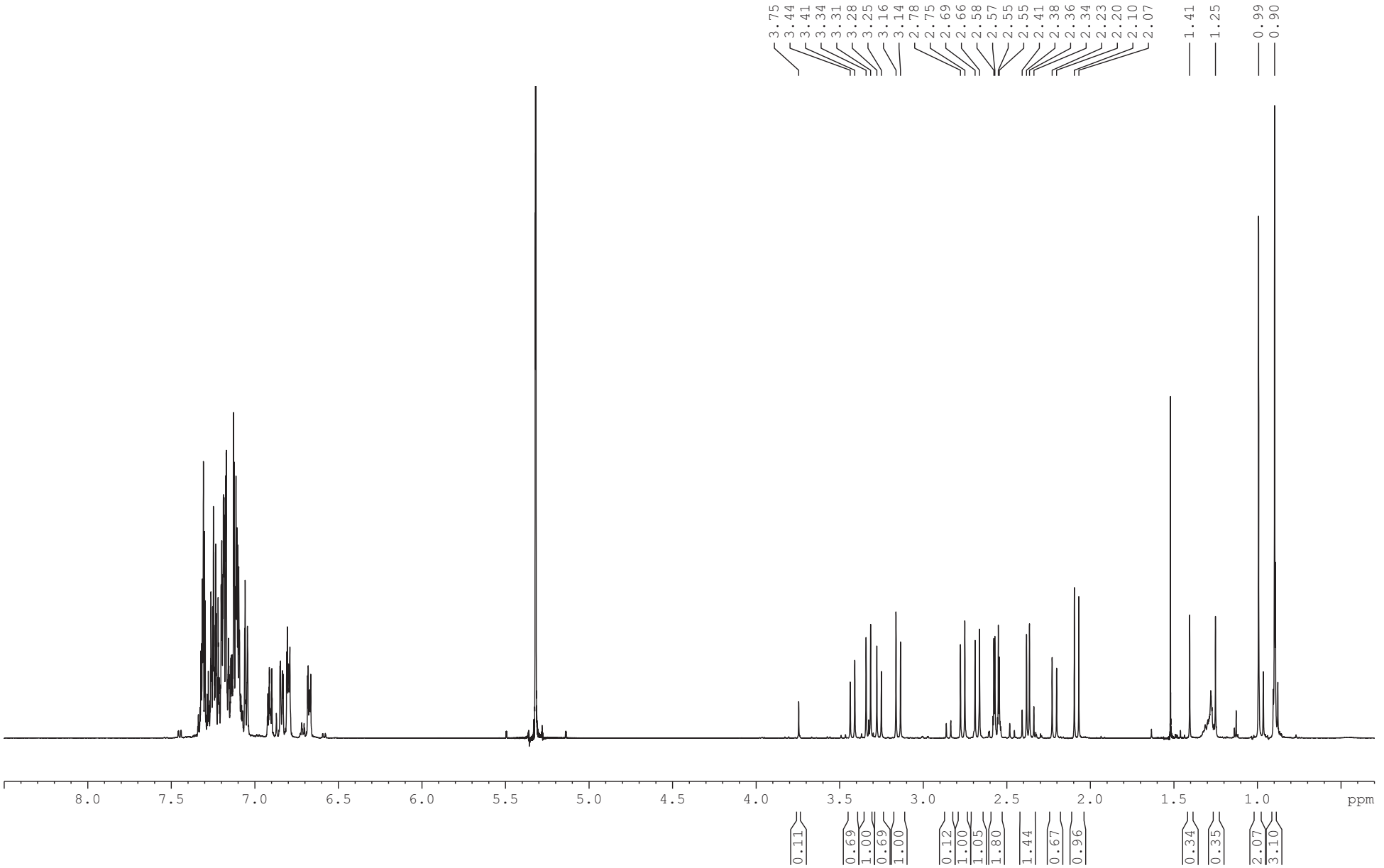


rel-**P3**

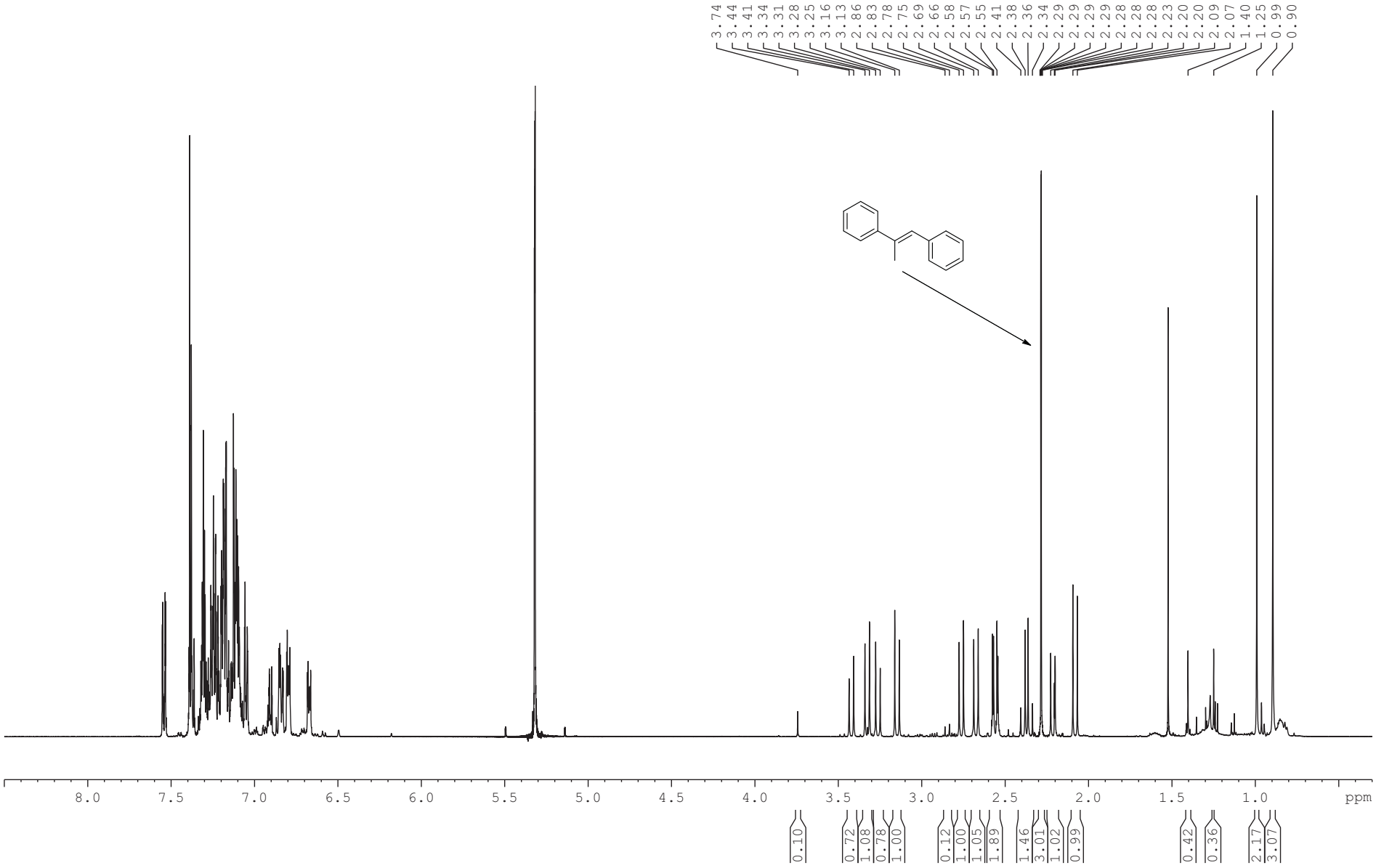
Sulfuric acid (95%, 89 μL, 1.29 mmol) was added to a CH_2Cl_2 solution (5 mL) of (*E*)-1,2-diphenyl-1-propene (500 mg, 2,57 mmol) and stirred at room temperature for 1 h. After that time the solvent was completely evaporated, the residue dissolved in hexane (15 mL) and filtered over a short column of silica gel (washed with 10 mL hexane). Evaporation of the solvent afforded the crude product as a mixture of **P1**, **P2** and **P3** in a ratio of ~ 1:0.7:0.1. The regioisomers could be partially separated by semipreparative HPLC on an OD-column (hexane, 25°C, 8.0 mL/min, 194 nm). The products were identified by ^{1}H, ^{13}C NMR (see following spectra) and HR EI-MS and the relative configuration was assigned on the basis of NOE spectroscopy.

HR EI-MS: M = $C_{30}H_{28}$
rel-(1S,3S)-1-benzyl-3-methyl-1,3-diphenyl-1,2,3,4-tetrahydronaphthalene: Calcd m/z for ($[M–C_7H_7]^{\bullet+}$: 297.1638; Found: 297.1644.
rel-(1R,3S)-1-benzyl-3-methyl-1,3-diphenyl-1,2,3,4-tetrahydronaphthalene: Calcd m/z for ($[M–C_7H_7]^{\bullet+}$: 297.1638; Found: 297.1643.
rel-(1S,2S,3S)-1-benzyl-1,3-dimethyl-2,3-diphenyl-2,3-dihydro-1H-indene: Calcd m/z for ($[M–C_7H_7]^{\bullet+}$: 297.1638; Found: 297.1635.

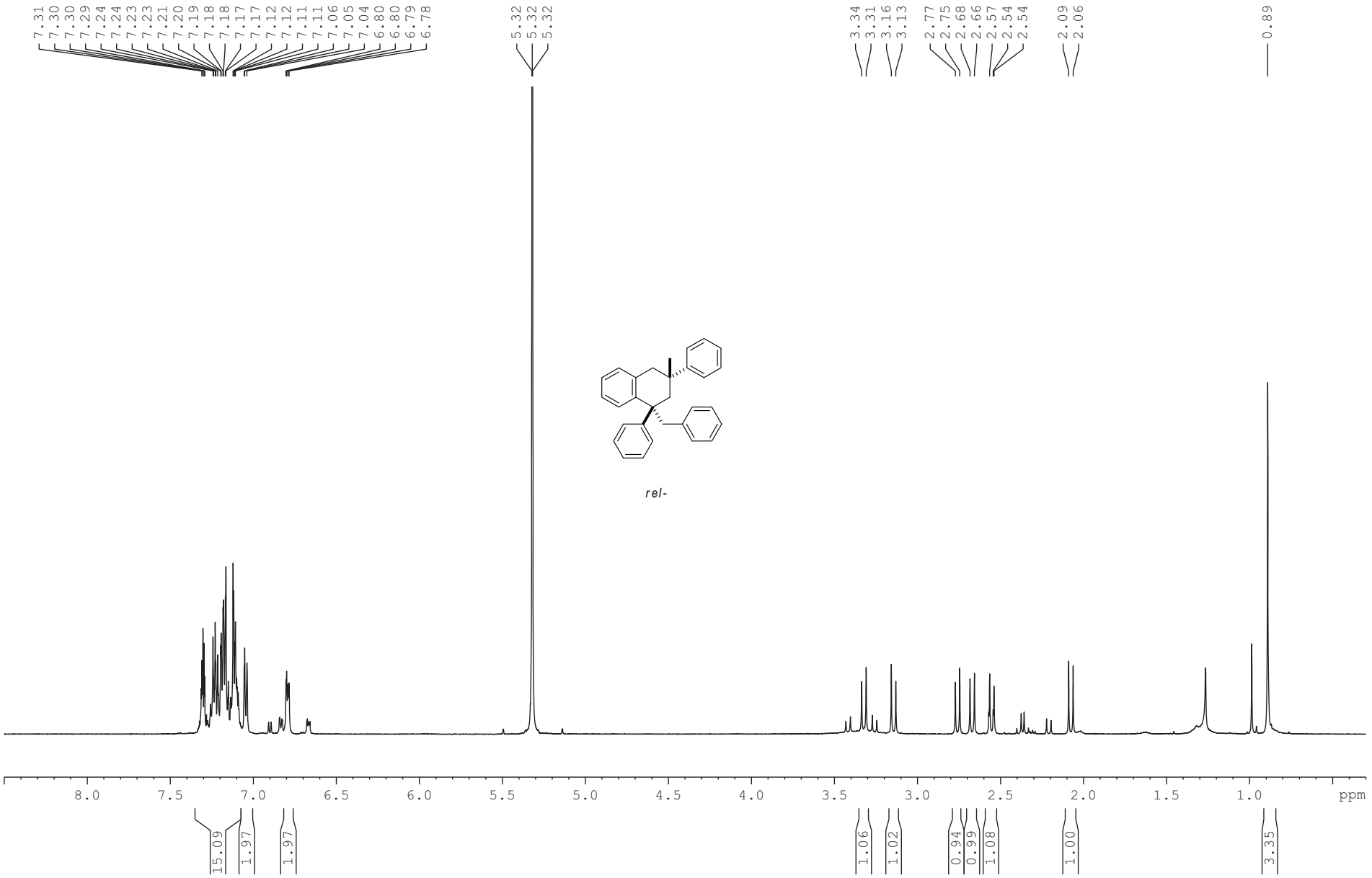
500 MHz 1H NMR of the crude containing P1,P2 and P3(reaction with sulfuric acid).



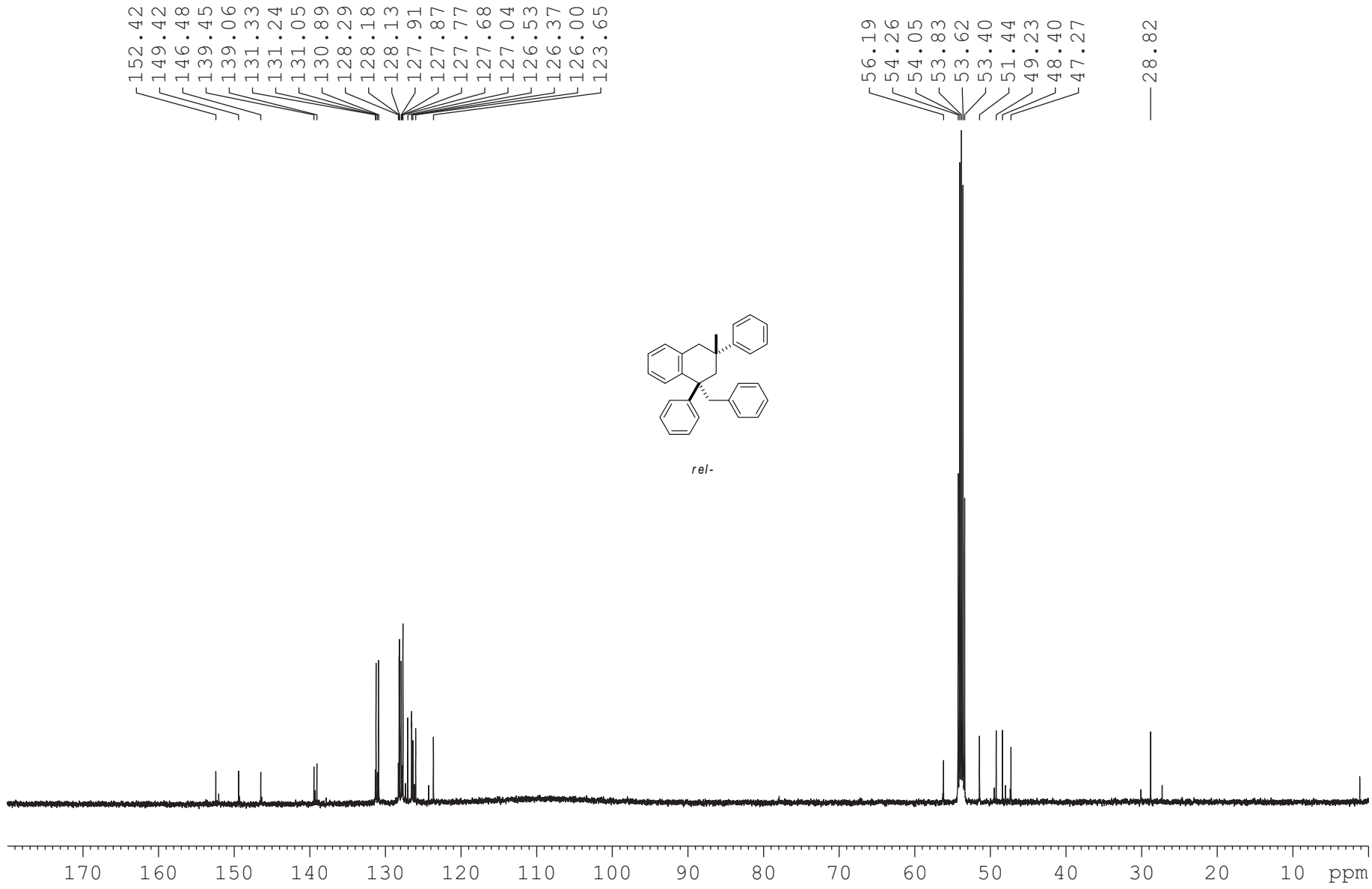
500 MHz 1H NMR of the crude of entry 7 in Table 1 showing the byproduct formation (crude contains(E)-1,2-diphenyl-1-propene, P1,P2 and P3).



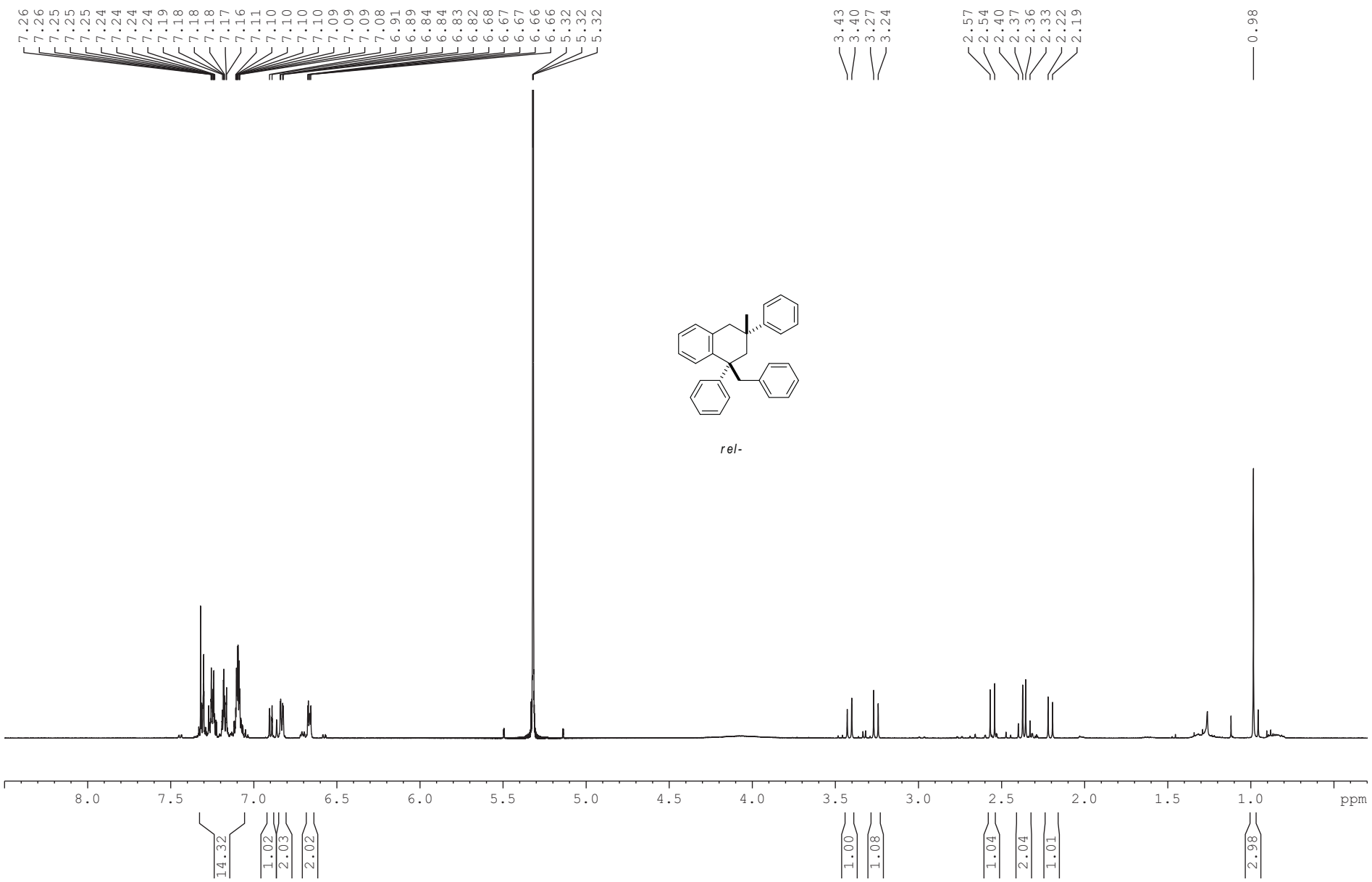
500 MHz 1H NMR of rel-(1S,3S)-1-benzyl-3-methyl-1,3-diphenyl-1,2,3,4-tetrahydronaphthalene



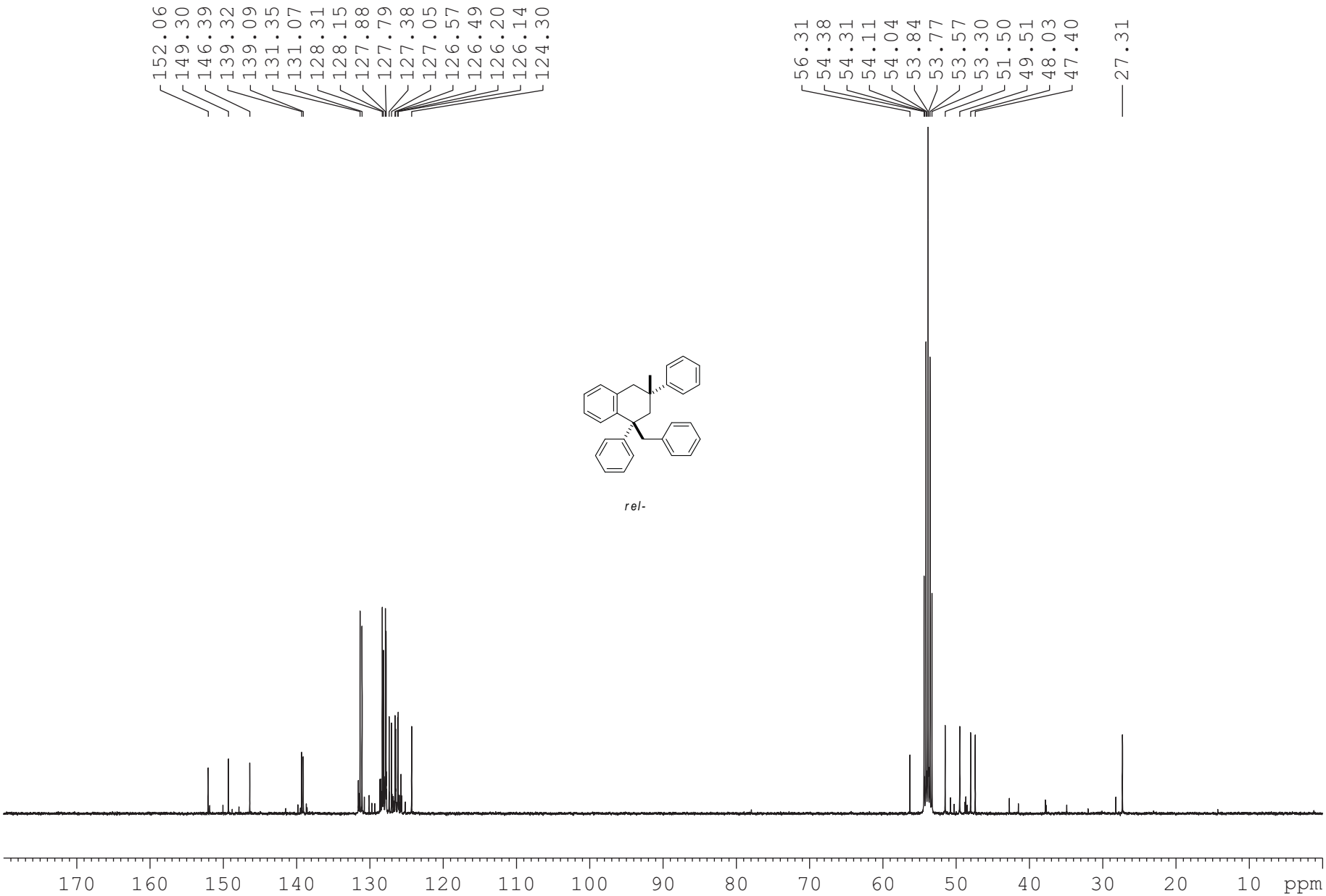
125 MHz 13C{1H} NMR of rel-(1S,3S)-1-benzyl-3-methyl-1,3-diphenyl-1,2,3,4-tetrahydronaphthalene



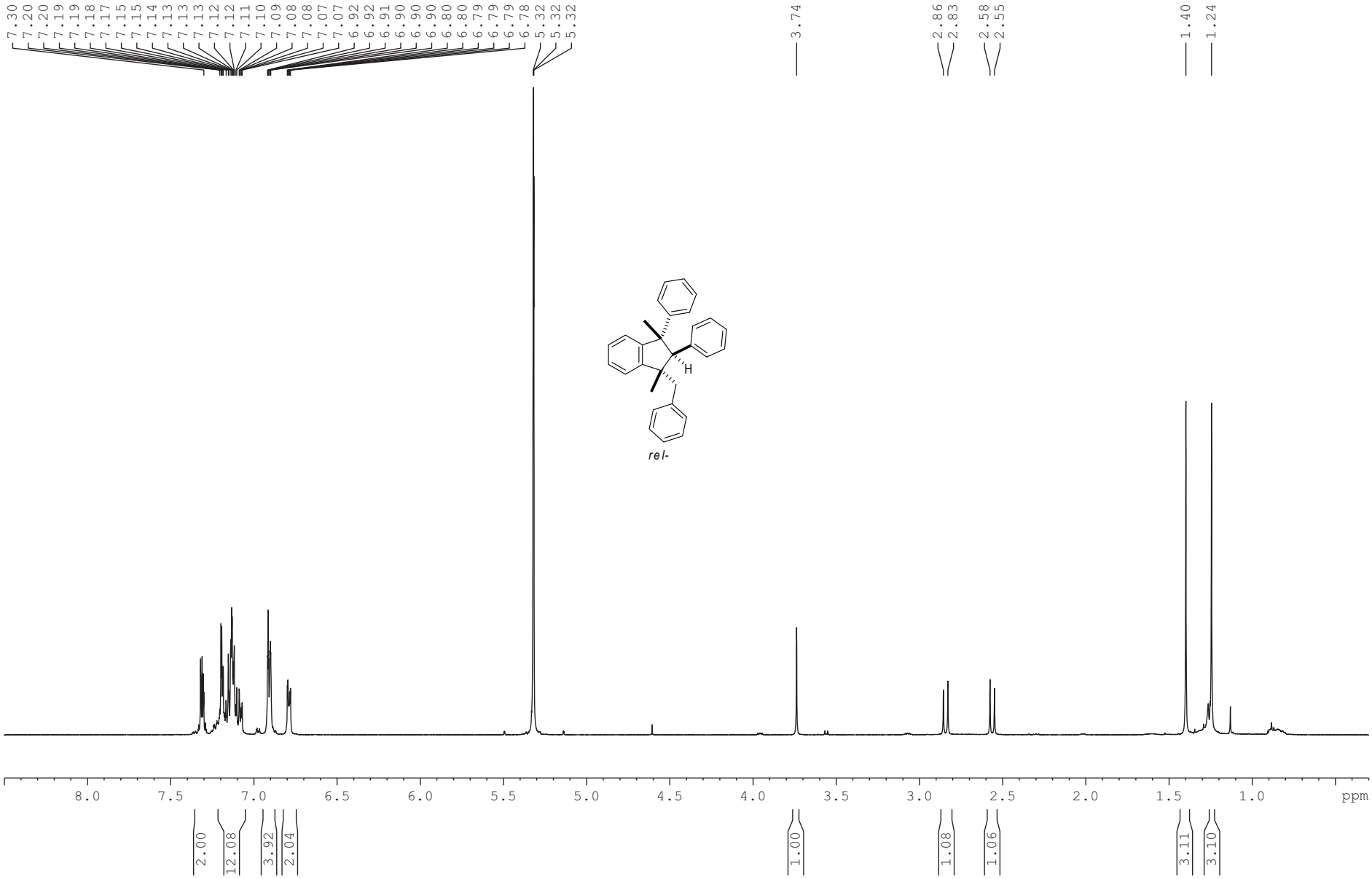
500 MHz 1H NMR of rel-(1R,3S)-1-benzyl-3-methyl-1,3-diphenyl-1,2,3,4-tetrahydronaphthalene



100 MHz 13C{1H} NMR of rel-(1R,3S)-1-benzyl-3-methyl-1,3-diphenyl-1,2,3,4-tetrahydronaphthalene



500 MHz 1H NMR of rel-(1S,2S,3S)-1-benzyl-1,3-dimethyl-2,3-diphenyl-2,3-dihydro-1H-indene

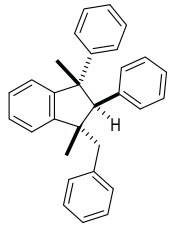


100 MHz 13C{1H} NMR of rel-(1S,2S,3S)-1-benzyl-1,3-dimethyl-2,3-diphenyl-2,3-dihydro-1H-indene

151.80
149.98
139.88
139.20
131.72
131.35
128.23
127.83
127.80
127.40
127.30
127.25
126.80
126.38
125.96
125.63
124.73

67.32
55.17
54.38
54.31
54.11
54.04
53.84
53.77
53.57
53.30
51.82
48.09

27.50
26.65



rel-

Table S7. Crystal data for complex **6**.

formula	$C_{112}H_{89}B_2Cl_5F_{48}Ir_2N_4O_4P_2$
formula weight	3109.12
Z, calculated density	1, 1.718 Mg · m^{-3}
F(000)	1529
description and size of crystal	yellow block, 0.180 · 0.311 · 0.368 mm^3
absorption coefficient	2.477 mm^{-1}
min/max transmission	0.46 / 0.64
temperature	123K
radiation(wavelength)	Mo K_α (λ = 0.71073 Å)
Crystal system, space group	triclinic, P 1
a	14.2328(7) Å
b	14.5307(7) Å
c	15.9379(8) Å
α	92.544(3)°
β	113.818(2)°
γ	92.667(3)°
V	3005.0(3) $Å^3$
min/max Θ	1.915° / 34.970°
number of collected reflections	172350
number of independent reflections	51163 (merging r = 0.034)
number of observed reflections	41743 (I>2.0σ(I))
number of refined parameters	1687
r	0.0267
rW	0.0497
goodness of fit	0.9621

Table S8. Crystal data for complex **7**.

formula	$C_{112.55}H_{87.10}B_2Cl_{5.10}F_{48}Ir_2N_4O_4P_2$
formula weight	3120.38
Z, calculated density	1, 1.669 Mg · m^{-3}
F(000)	1535.100
description and size of crystal	yellow block, 0.180 · 0.250 · 0.320 mm^3
absorption coefficient	2.401 mm^{-1}
min/max transmission	0.55 / 0.65
temperature	123K
radiation(wavelength)	Mo K_α (λ = 0.71073 Å)
Crystal system, space group	triclinic, P 1
a	12.8192(3) Å
b	16.1838(4) Å
c	17.2644(4) Å
α	67.9070(10)°
β	69.4010(10)°
γ	84.5930(10)°
V	3103.56(13) $Å^3$
min/max Θ	1.773° / 30.073°
number of collected reflections	116614
number of independent reflections	35611 (merging r = 0.026)
number of observed reflections	31146 (I>2.0σ(I))
number of refined parameters	1770
r	0.0265
rW	0.0342
goodness of fit	1.0761

Table S9. Crystal data for complex **8**.

formula	$C_{109}H_{86}B_2Cl_6F_{48}Ir_2N_2O_4P_2$
formula weight	3080.53
Z, calculated density	1, 1.689 Mg · m^{-3}
F(000)	1514.000
description and size of crystal	yellow block, 0.050 · 0.130 · 0.170 mm^3
absorption coefficient	2.479 mm^{-1}
min/max transmission	0.72 / 0.88
temperature	123K
radiation(wavelength)	Mo K_α (λ = 0.71073 Å)
Crystal system, space group	triclinic, P 1
a	13.3861(9) Å
b	14.7080(10) Å
c	16.6176(11) Å
α	103.794(4)°
β	90.144(4)°
γ	107.081(4)°
V	3027.9(4) $Å^3$
min/max Θ	1.596° / 32.577°
number of collected reflections	72716
number of independent reflections	42682 (merging r = 0.033)
number of observed reflections	34145 (I>2.0σ(I))
number of refined parameters	1744
r	0.0352
rW	0.0548
goodness of fit	1.1125

Table S10. Crystal data for complex **9b**.

formula	$C_{115}H_{104}B_2Cl_6F_{48}Ir_2N_6O_2$
formula weight	3132.81
Z, calculated density	1, 1.582 Mg · m^{-3}
F(000)	1546.000
description and size of crystal	yellow block, 0.050 · 0.110 · 0.230 mm^3
absorption coefficient	2.263 mm^{-1}
min/max transmission	0.89 / 0.89
temperature	123K
radiation(wavelength)	Mo K_α (λ = 0.71073 Å)
Crystal system, space group	triclinic, P 1
a	13.0057(9) Å
b	16.3543(12) Å
c	17.8121(12) Å
α	70.889(3)°
β	85.622(4)°
γ	66.774(4)°
V	3283.6(4) $Å^3$
min/max Θ	1.547° / 32.576°
number of collected reflections	98169
number of independent reflections	46715 (merging r = 0.040)
number of observed reflections	35395 (I>2.0σ(I))
number of refined parameters	1860
r	0.0453
rW	0.0730
goodness of fit	1.1250