Supporting Information for:

Synthesis and coordination chemistry of *N^1,N^2,N^3*-trisubstituted benzamidrazones

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Experimental

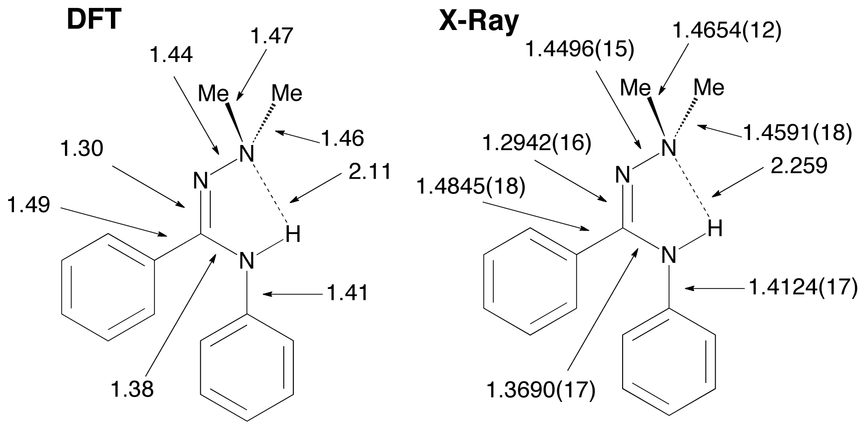
General experimental: Unless otherwise indicated, operations were performed under anhydrous conditions and inert atmosphere employing standard Schlenk-line and glovebox techniques. Glassware was dried in an oven at 160 °C overnight or flame-dried prior to use. NMR spectra were acquired using Bruker AV-300, AVQ-400 and AVB-400 spectrometers. Chemical shifts are reported as part per million (ppm, δ) and ^{1}H and ^{13}C chemical shifts are referenced to the corresponding residual protic solvent resonance. Mass spectral data were obtained at the QB3 Mass Spectrometry Facility operated by the College of Chemistry, University of California, Berkeley. Fast atom bombardment mass spectra were recorded on a Micromass ZAB2-EQ magnetic sector instrument. Infrared spectral data were recorded on a Thermo Scientific Nicolet iS10 spectrometer fitted with a Smart OMNI-transmission or Smart iTR device as either KBR discs, neat solids or thin films. Elemental analyses were recorded by the UC Berkeley micro-mass facility. Solvents were dried through a push-still system *via* passage through alumina. $[(\text{cymene})\text{RuCl}_2]_2$ was purchased from Sigma-Aldrich and used without further purification. $[\text{Cp}^*\text{MCl}_2]_2$ (M = Rh, Ir) were synthesised by literature methods.[1] NaOAc was purchased from Sigma-Aldrich and used as received and lithium hexamethyldisilazide (LiHMDS) was freshly prepared from *n*-BuLi and hexamethyldisilazane and recrystallised before use. Whilst compounds **1e** and **1f** are literature known, for completion, detailed characterisation data are provided in the supporting information.[2]

Representative procedure for synthesis of *N^1,N^2,N^3*-benzamidrazones: On a Schlenk-line, a Schlenk-tube was flame-dried under vacuum and *N*-methylbenzamide (6.25 g, 46.6 mmol) added under a purge of argon. Dry toluene (30 mL) was added *via* cannula and solid PCl_5 (9.72 g, 46.6 mmol) was added to the resultant slurry. The reaction mixture was warmed until homogeneous and stirred for 2 h at room temperature, after which the solvent was removed *in vacuo*. Additional dry toluene (2 x 20 mL) was added and removed under reduced pressure to azetropically distil any remaining $POCl_3$. *N*-Methylbenzimidoyl chloride was obtained as a slightly yellow oil and used directly. A toluene solution of the imidoyl chloride in dry toluene (20 mL) was added to a mixture of triethylamine (7.1 g, 69.9 mmol) and 1,1-dimethylhydrazine (2.80 g, 46.6 mmol) in toluene solution (20 mL) in a separate Schlenk-tube. Upon addition, an exothermic reaction was observed (the Schlenk tube became hot) along with the precipitation of a colourless solid from solution. The tube was sealed and after 16-48 h at room temperature the reaction was quenched by dilution with toluene (100 mL) and H_2O (100 mL). The phases were separated and the aqueous layer back-extracted with DCM (100 mL), the combined organics were dried over magnesium sulphate and the solvent removed under vacuum to give the crude product as viscous yellow oil.

1e: Isolation by chromatography on silica gel using a 95:4:1 mixture of dichloromethane:methanol:$NH_4OH_{(aq)}$ as an elutent gave **1e** (1.28 g, 5.06 mmol, 21 %) as a light yellow oil . ^{1}H NMR (400 MHz, 298 K, C_6D_6) δ 2.56 (s, 2H, -N*Me₂*), 4.04 (d, 2H, *J* = 6.8 Hz, C*H*₂Ph), 6.63 (broad t, 1H, *J* = 6.8 Hz, -N*H*), 7.05-7.07 (m, 2H, Ar*H*), 7.12-7.24 (m, 6H, Ar*H*), 7.66-7.68 (m, 2H, Ar*H*); ^{13}C NMR (100 MHz, 298 K, C_6D_6) δ 47.5, 48.5, 127.5, 127.6, 129.1, 129.2, 129.8, 134.9, 141.0, 162.5; Infrared (solid, cm^{-1}) 3305, 2976, 2855, 1599, 1570, 1496; m/z (ESI, +ve) 254 (100 %, $[M+H]^+$), 209 (10 %, $[M-N(CH_3)_2]^+$); HR-MS (ESI, +ve) calcd. for $C_{16}H_{20}N_3$ 254.1652 found 254.1646.[2]

1f: Isolation by chromatography on silica gel gave **1f** as a colourless solid (2.31 g, 9.67 mmol, 48 %) using a 95:4:1 mixture of dichloromethane:methanol:NH_4OH as an elutent. X-ray quality crystals could be isolated by recrystallisation from hexane at -35 °C. ^1H NMR (400 MHz, 298 K, C_6D_6) δ 2.49 (s, 6H, -N*Me*$_2$), 6.53 (d, 2H, *J* = 7.2, Ar*H*), 6.69 (dd, 1H, *J* = 7.6 and 7.6 Hz, Ar*H*), 6.85 (dd, 2H, *J* = 7.6 and 8.0 Hz), 6.96-7.01 (m, 3H, Ar*H*), 7.67 (d, 2H, *J* = 8.0 Hz, Ar*H*), 8.01 (broad s, 1H, N*H*); ^{13}C NMR (100 MHZ, 298 K, C_6D_6) δ 47.4, 121.2, 122.6, 128.2, 129.3, 129.5, 130.1, 134.6, 142.0, 157.2; Infrared (solid, cm^{-1}) 3311, 3037, 2855, 2820, 1594, 1561, 1496, 1367; m/z (ESI, +ve) 240 (40 %, [M+H]$^+$), 195 (100 %, [M-N(CH_3)$_2$]); HR-MS (ESI, +ve) calcd. for $C_{15}H_{18}N_3$ 240.1495 found 240.1493.[2]

Figure S1. Comparison of solid-state and DFT (B3LYP, 6,31G+(d,p)) data for compound **1f**, bond lengths listed in Angstroms



References

1 J. W. Kang, K. Moseley, and P. M. Maitlis, *J. Am. Chem. Soc.* 1969, **91**, 5970.

2 (a) R. F. Smith, D. S. Johnson, C. L. Hyde, T. C. Rosenthal, A. C. Bates, *J. Org. Chem.*, 1971, **36**, 1155; (b) R. F. Smith, D. S. Johnson, R. A. Abgott, M. J. Madden,

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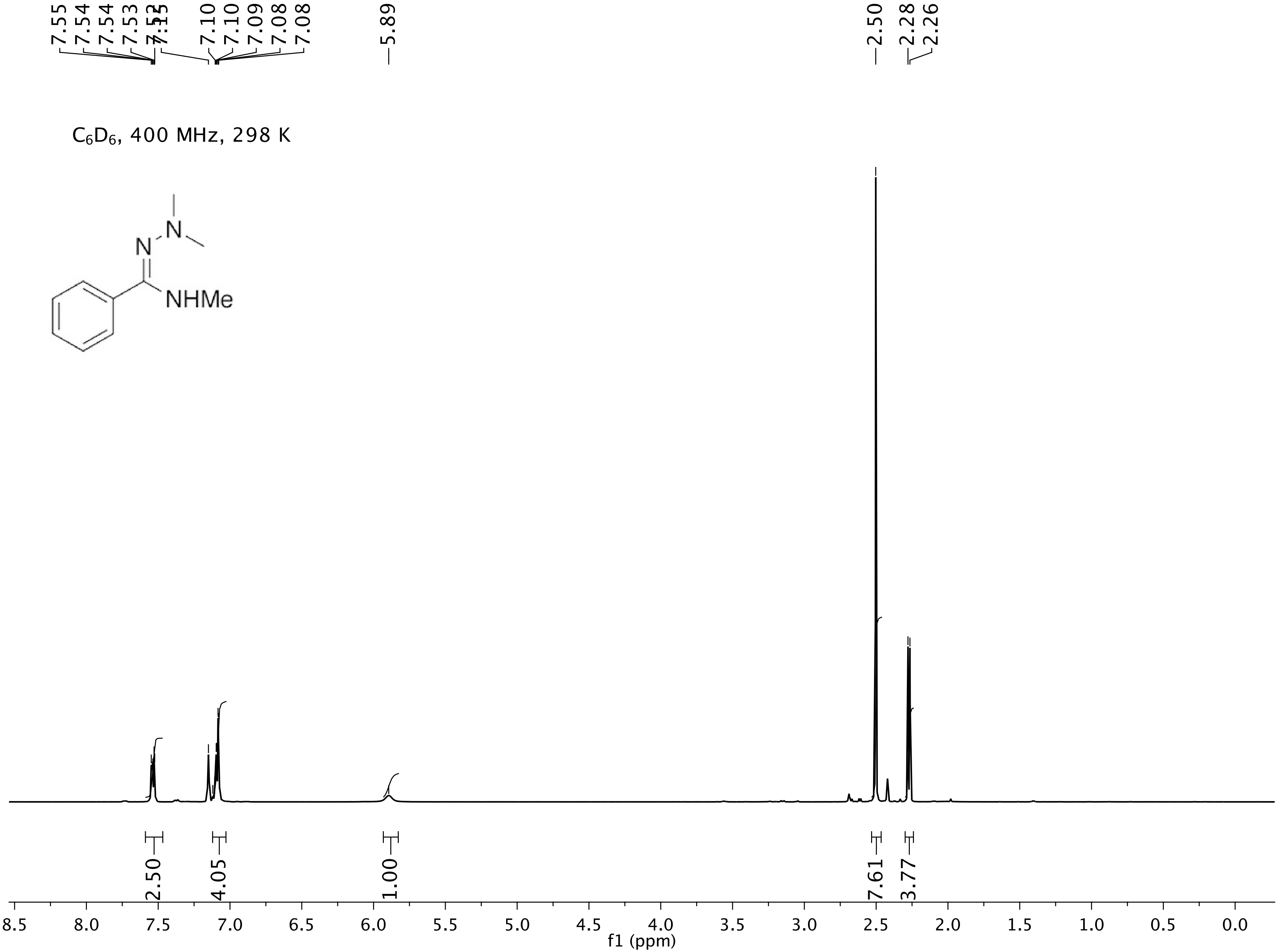
J. Org. Chem. 1973, **38**, 1344; (c) R. F. Smith, R. R. Soelch, T. P. Feltz, M. J. Martinelli and S. M. Geer, *J. Heterocyclic Chem.*, 1981, **18**, 319.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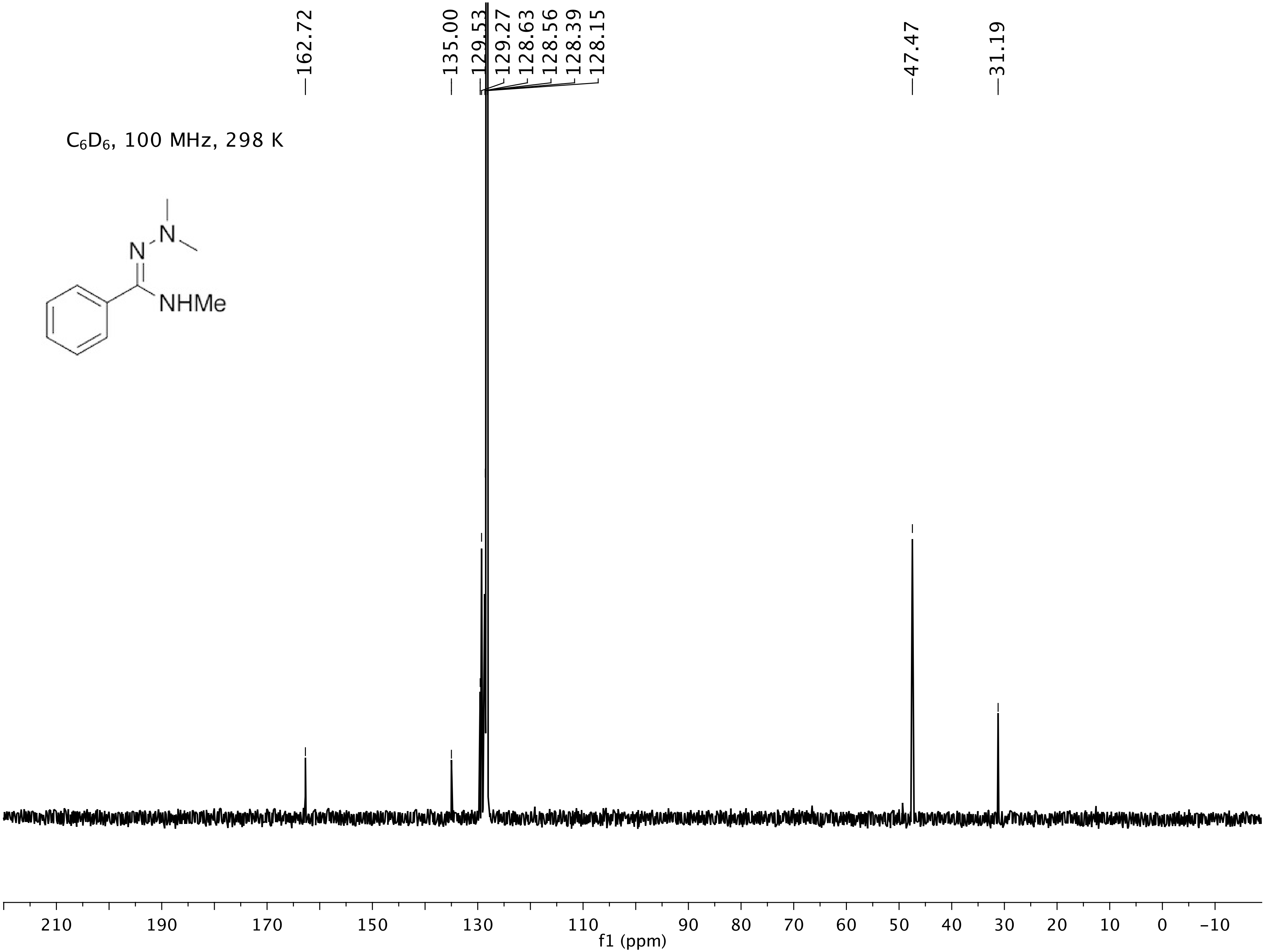
7.54
7.54
7.53
7.52
7.15
7.10
7.10
7.09
7.08
7.08
5.89
2.50
2.28
2.26
C$_6$D$_6$, 400 MHz, 298 K
N
N
NHMe
2.50
4.05
1.00
7.61
3.77
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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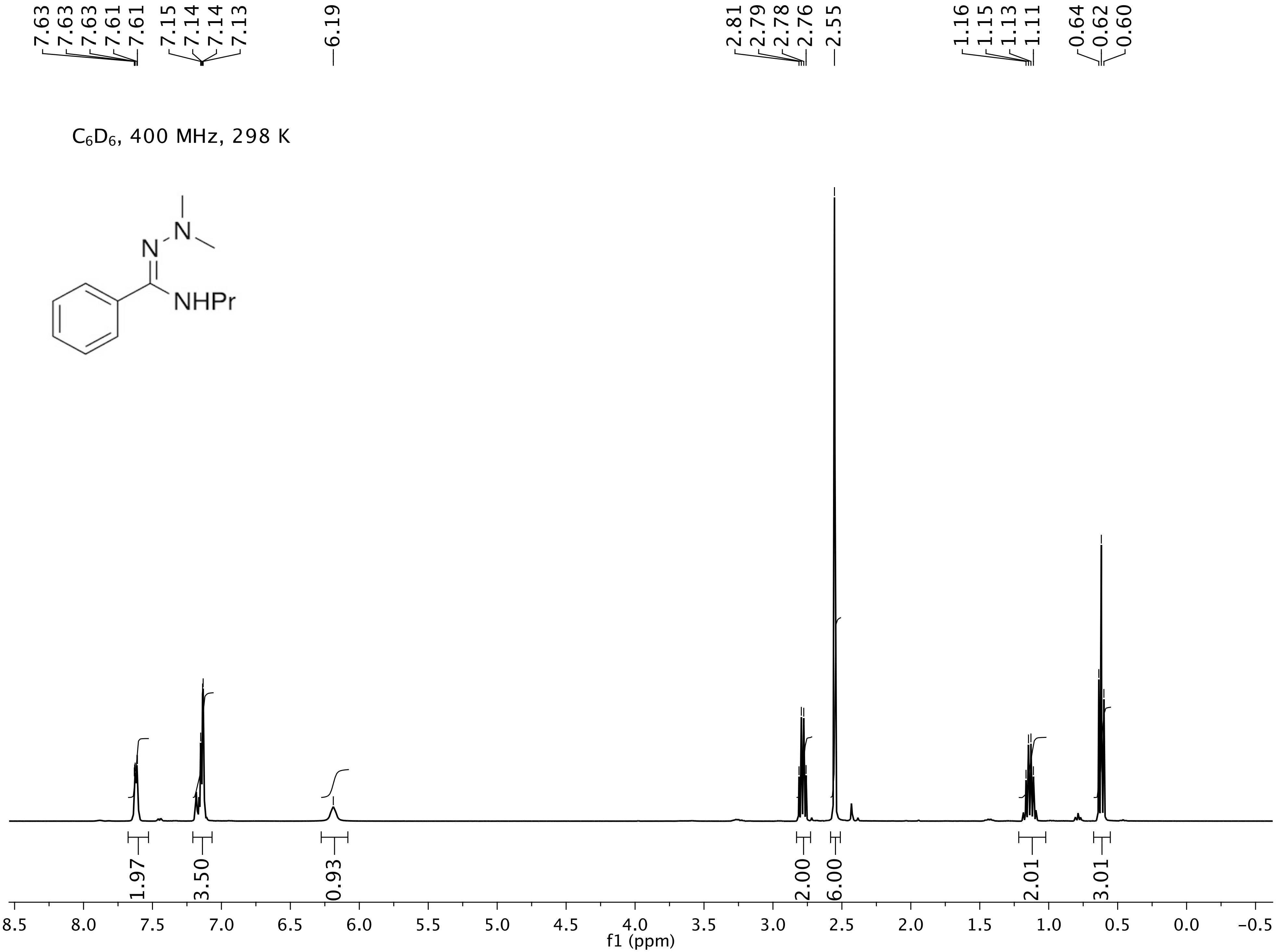
31.19
C_6D_6, 100 MHz, 298 K
N
N
NHMe
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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7.63
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7.14
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2.78
2.76
2.55
1.16
1.15
1.13
1.11
0.64
0.62
0.60
C6D6, 400 MHz, 298 K
N
N
NHPr
1.97
3.50
0.93
2.00
6.00
2.01
3.01
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
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1.5
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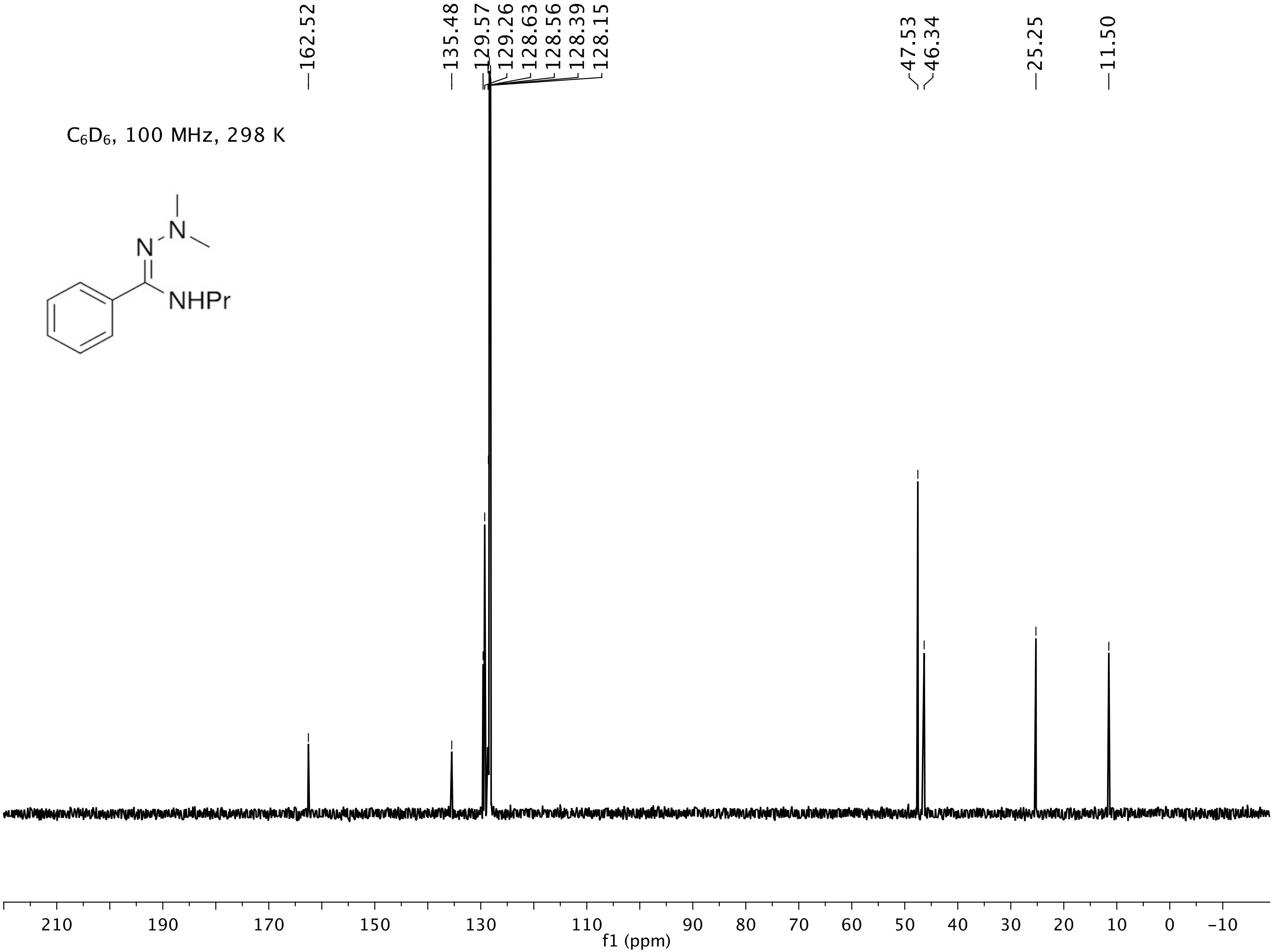
–0.5
f1 (ppm)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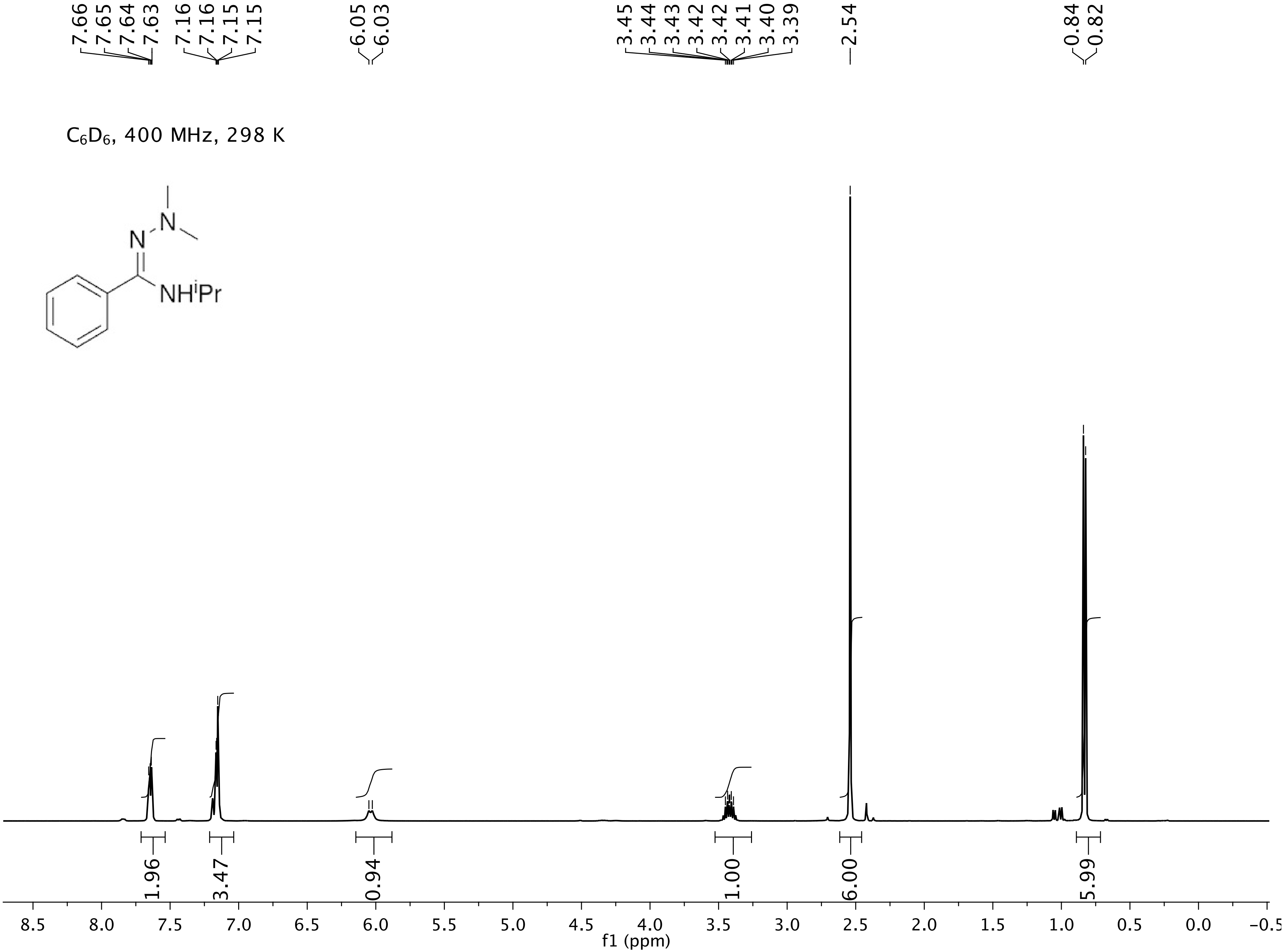
128.15
47.53
46.34
25.25
11.50
C_6D_6, 100 MHz, 298 K
N
N
NHPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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7.16
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7.15
6.05
6.03
3.45
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3.43
3.42
3.42
3.41
3.40
3.39
2.54
0.84
0.82
C6D6, 400 MHz, 298 K
N
N
NHiPr
1.96
3.47
0.94
1.00
6.00
5.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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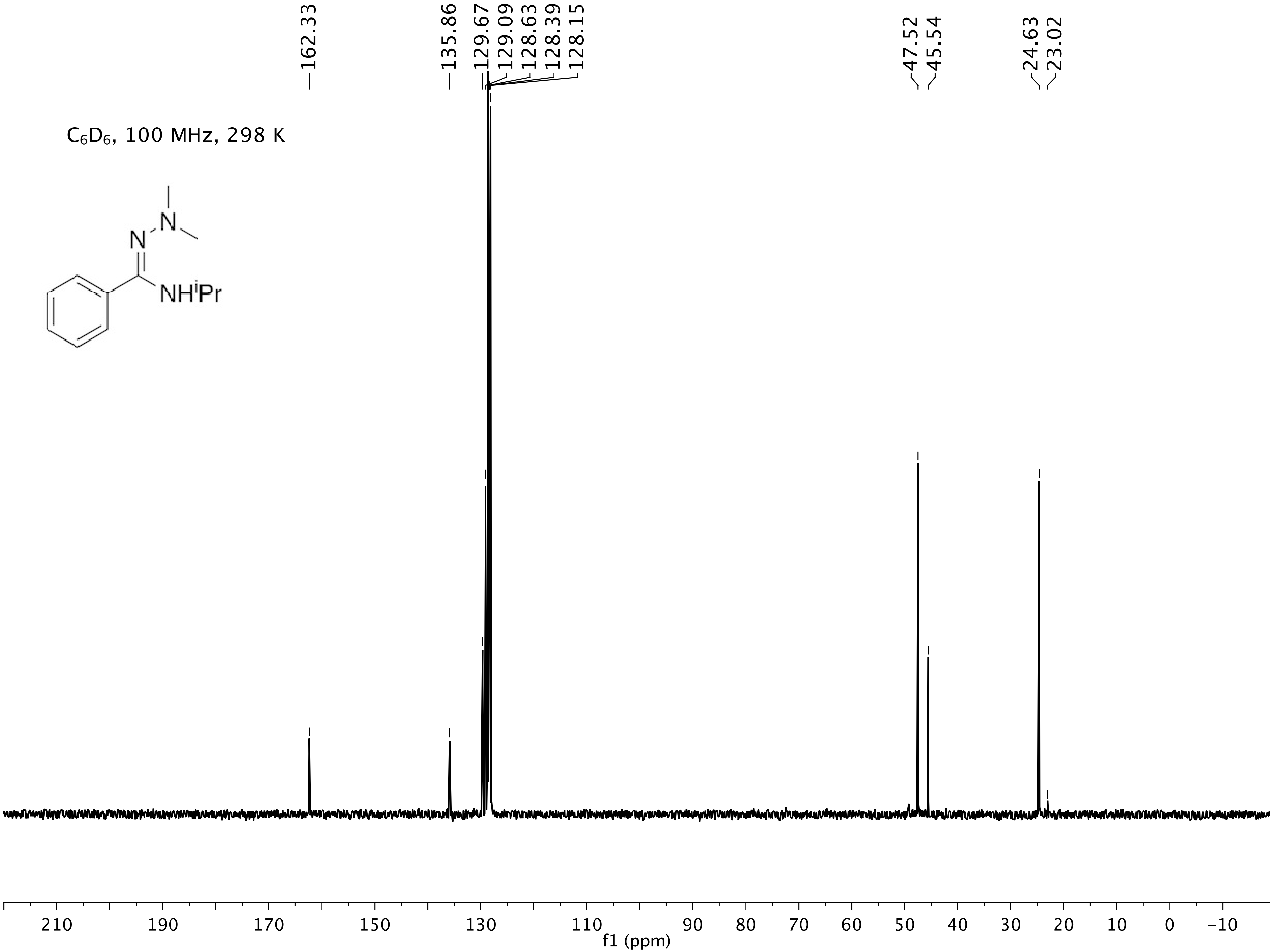
f1 (ppm)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129.09
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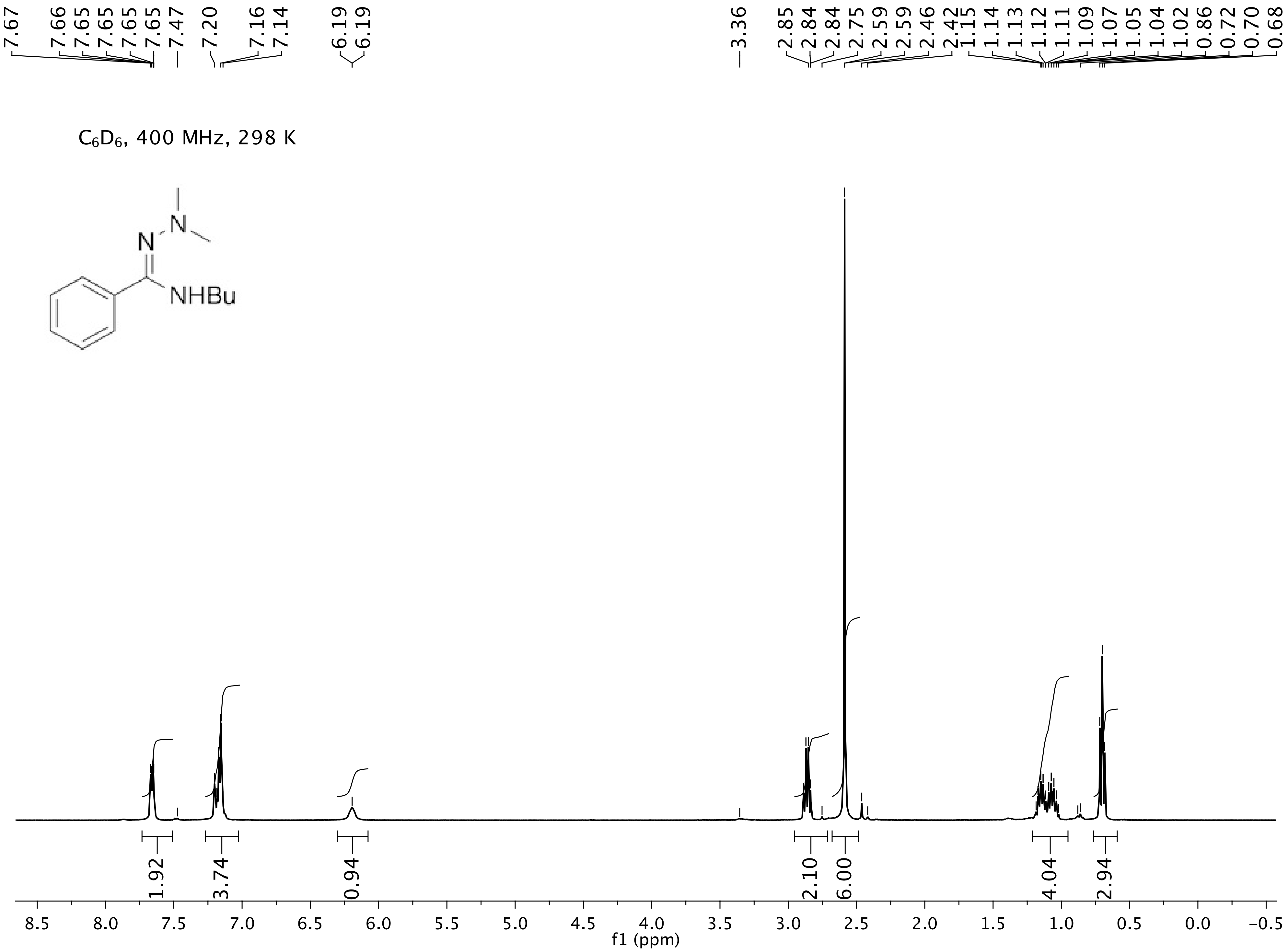
128.39
128.15
47.52
45.54
24.63
23.02
C6D6, 100 MHz, 298 K
N
N
NHiPr
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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7.65
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7.14
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2.85
2.84
2.84
2.75
2.59
2.59
2.46
2.42
1.15
1.14
1.13
1.12
1.11
1.09
1.07
1.05
1.04
1.02
0.86
0.72
0.70
0.68
C6D6, 400 MHz, 298 K
N
N
NHBu
1.92
3.74
0.94
2.10
6.00
4.04
2.94
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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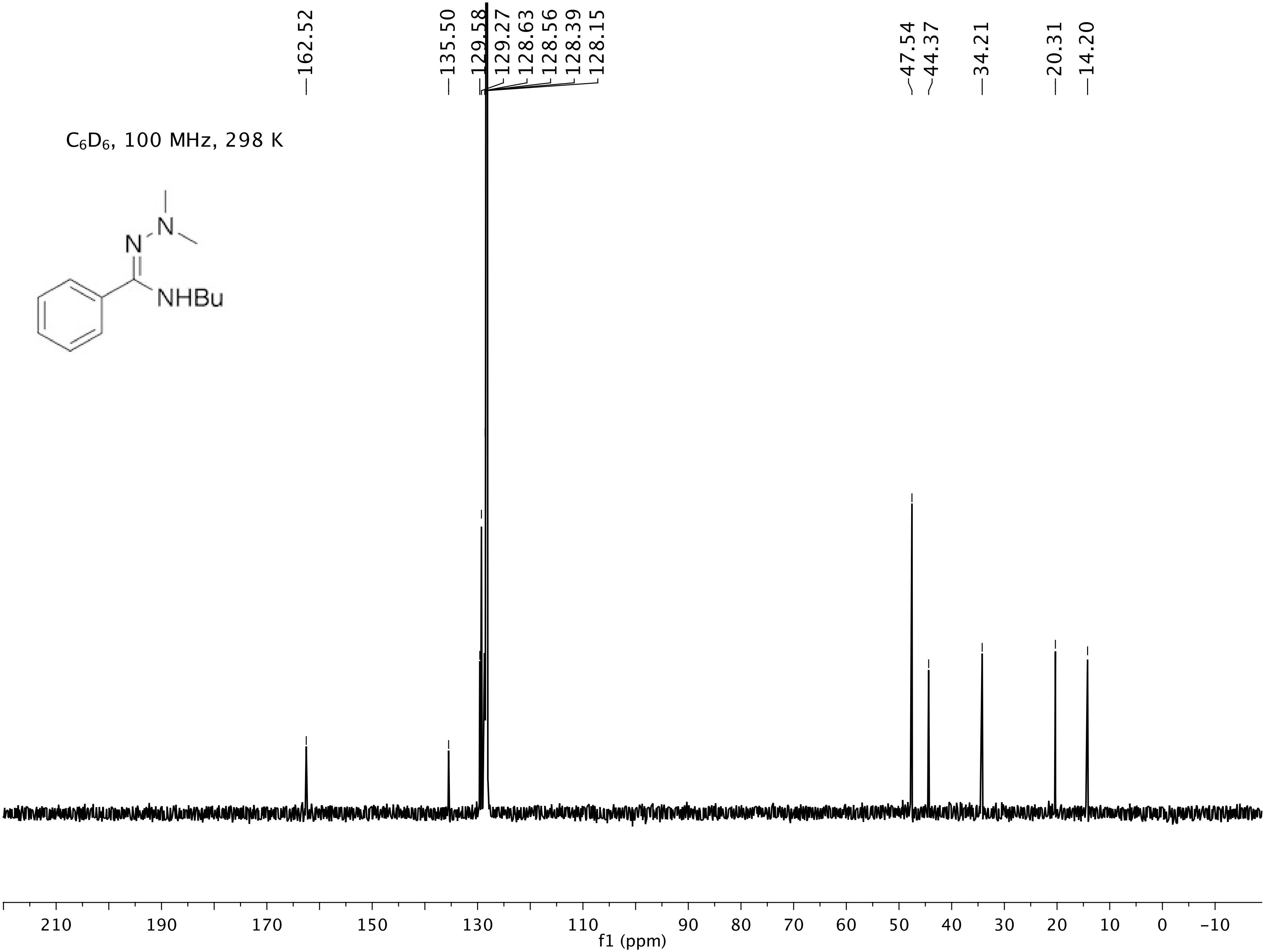
-0.5
f1 (ppm)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129.58
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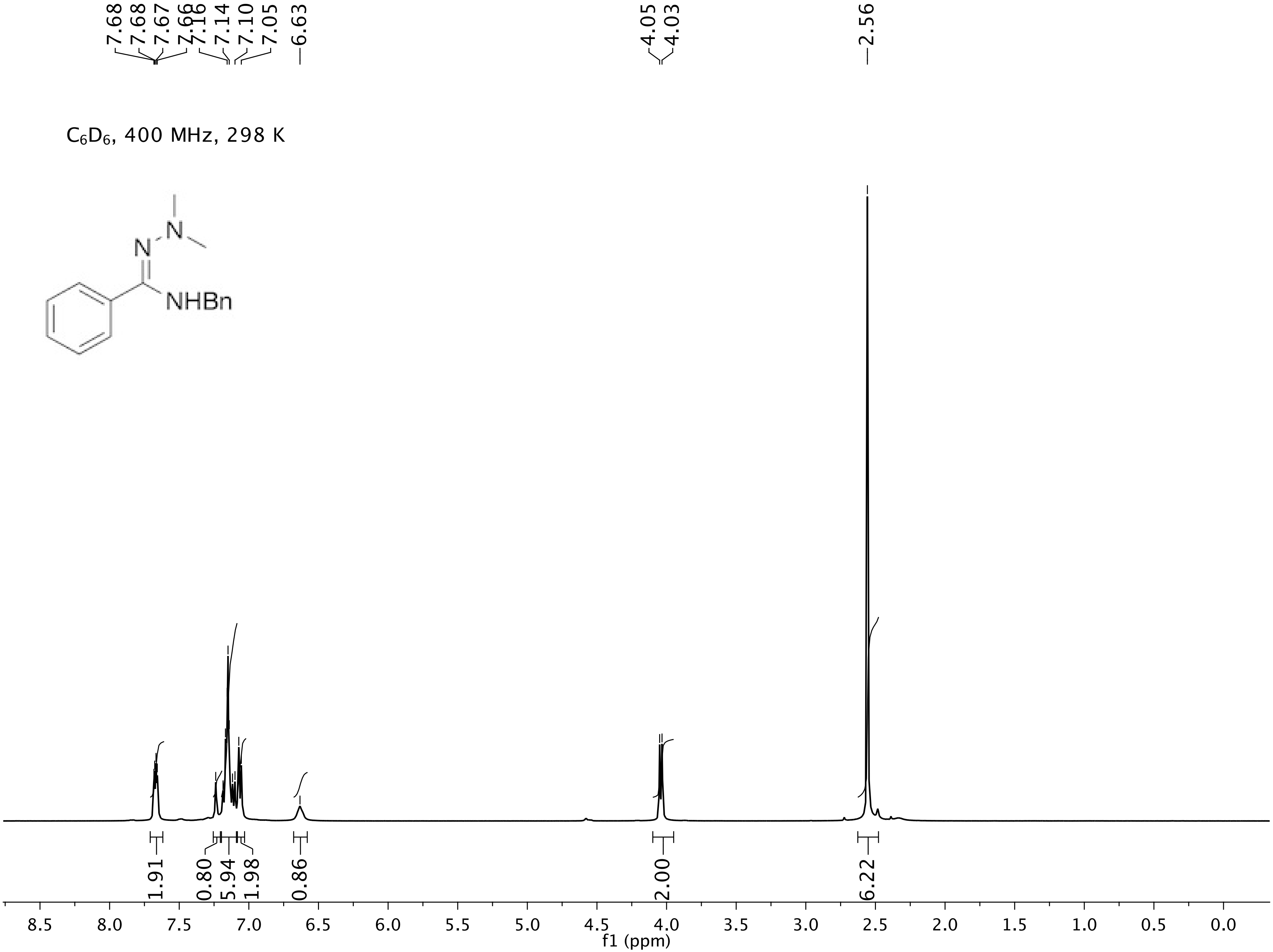
128.63
128.56
128.39
128.15
47.54
44.37
34.21
20.31
14.20
C6D6, 100 MHz, 298 K
N
N
NHBu
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
–10
f1 (ppm)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7.67
7.66
7.16
7.14
7.10
7.05
6.63
4.05
4.03
2.56
C6D6, 400 MHz, 298 K
N
N
NHBn
1.91
0.80
5.94
1.98
0.86
2.00
6.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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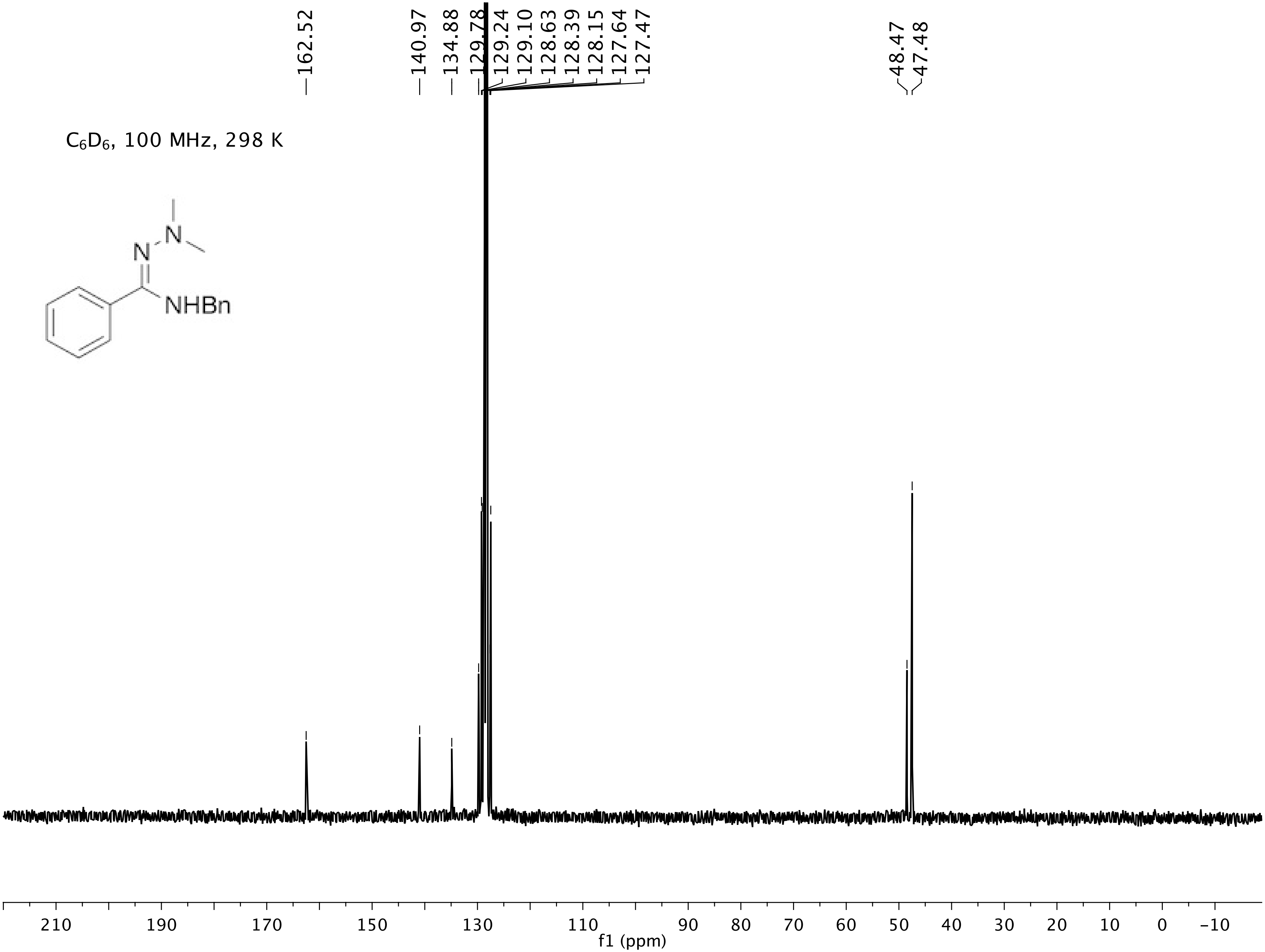
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.78
129.24
129.10
128.63
128.39
128.15
127.64
127.47
48.47
47.48
C6D6, 100 MHz, 298 K
N
N
NHBn
210
190
170
150
130
110
90
80
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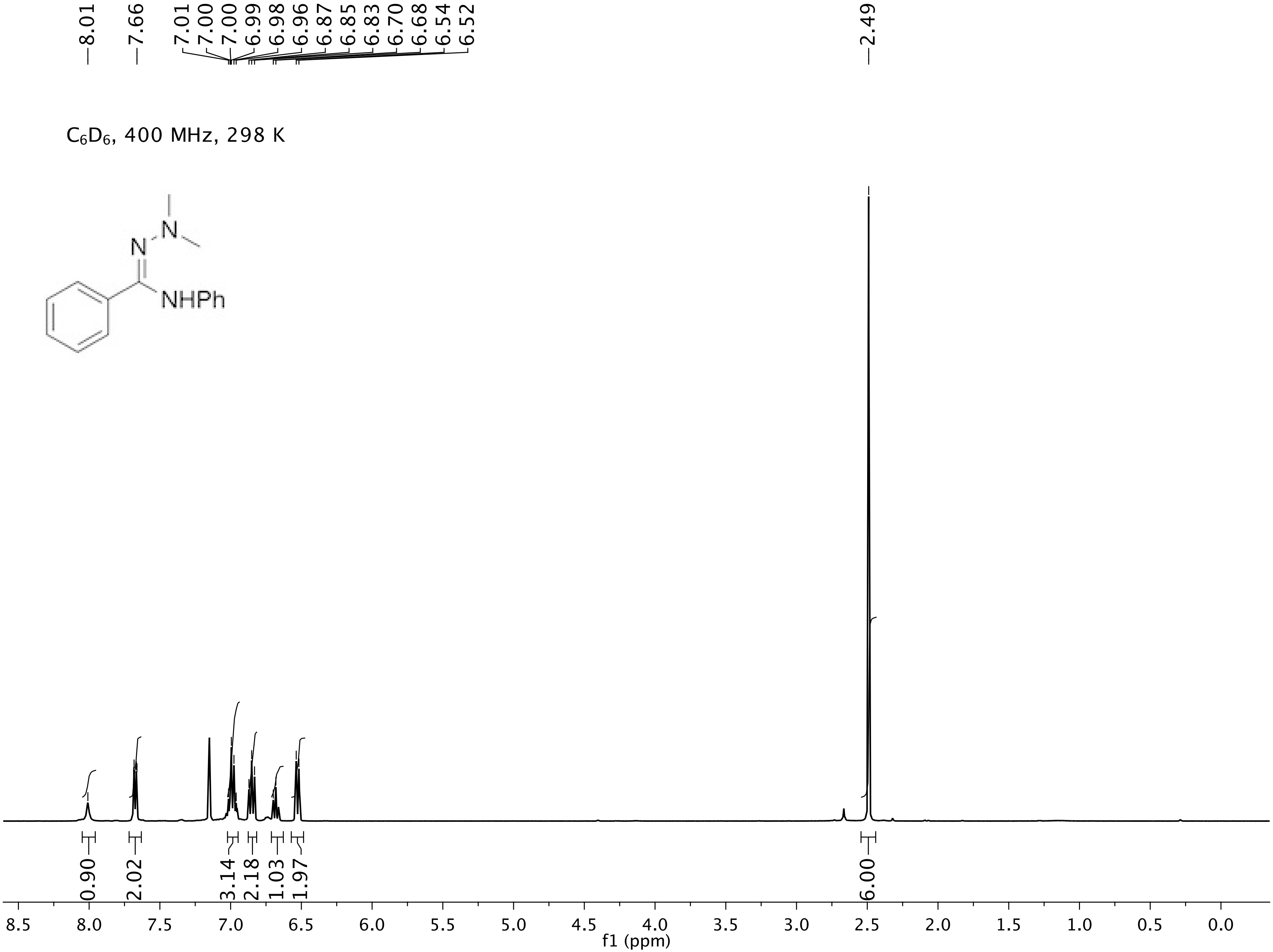
60
50
40
30
20
10
0
–10
f1 (ppm)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6.68
6.54
6.52
2.49
C6D6, 400 MHz, 298 K
N
N
NHPh
0.90
2.02
3.14
2.18
1.03
1.97
6.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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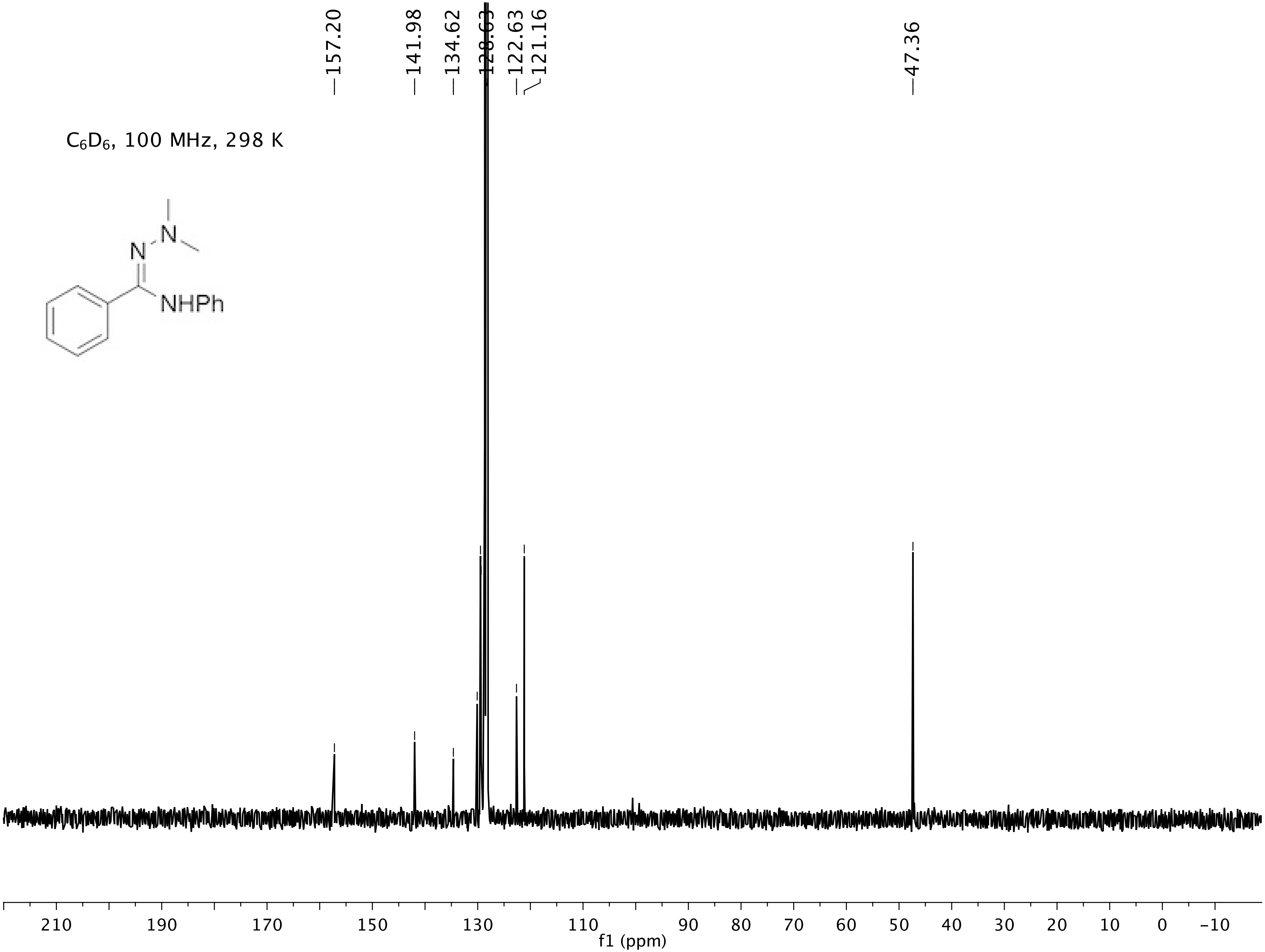
f1 (ppm)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121.16
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C_6D_6, 100 MHz, 298 K
N
N
NHPh
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190
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150
130
110
90
80
70
60
50
40
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20
10
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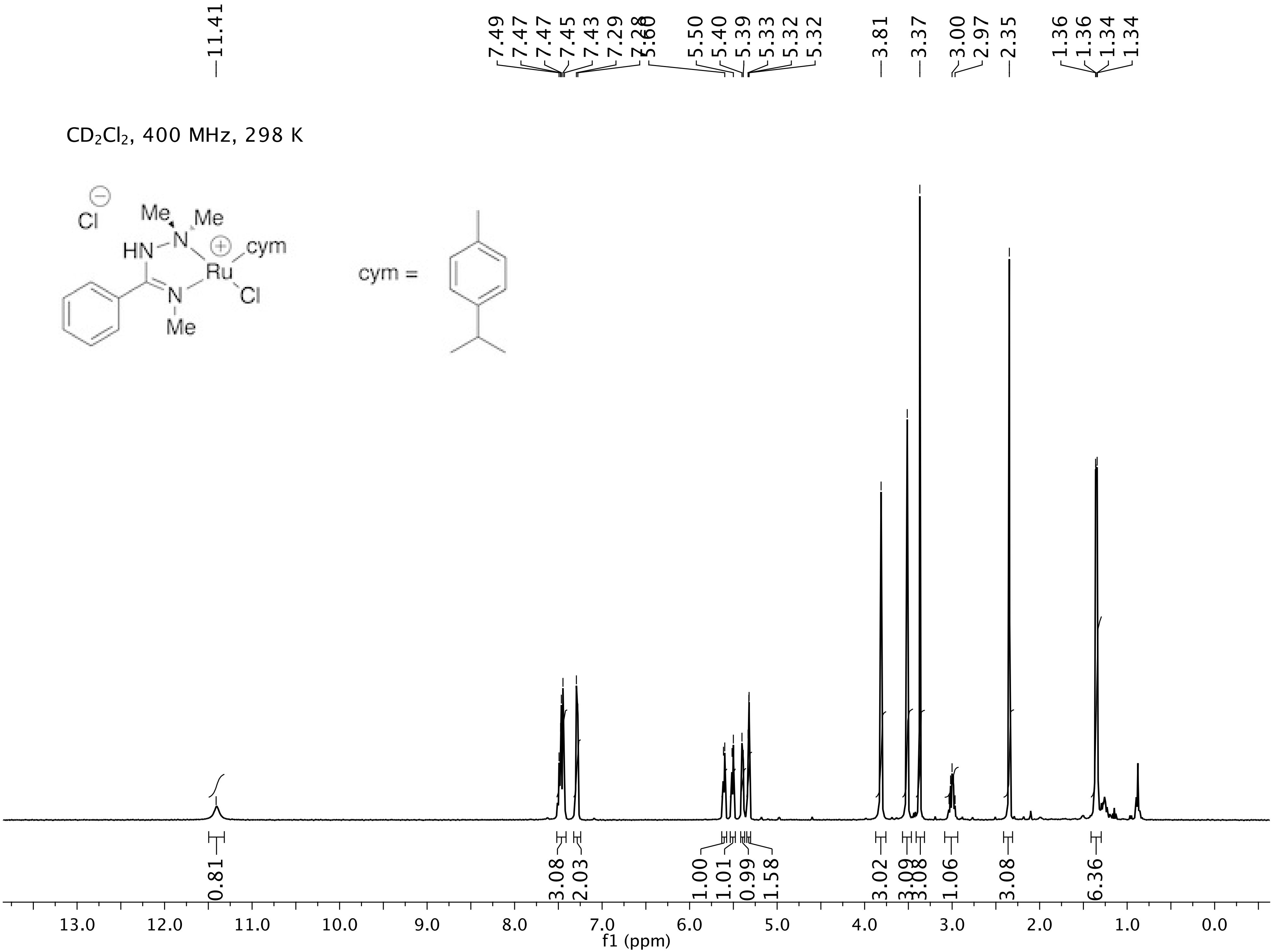
–10
f1 (ppm)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7.29
7.28
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5.33
5.32
5.32
3.81
3.37
3.00
2.97
2.35
1.36
1.36
1.34
1.34
CD₂Cl₂, 400 MHz, 298 K
Cl
Me
Me
HN
N
cym
Ru
N
Cl
Me
cym =
0.81
3.08
2.03
1.00
1.01
0.99
1.58
3.02
3.09
3.08
1.06
3.08
6.36
13.0
12.0
11.0
10.0
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8.0
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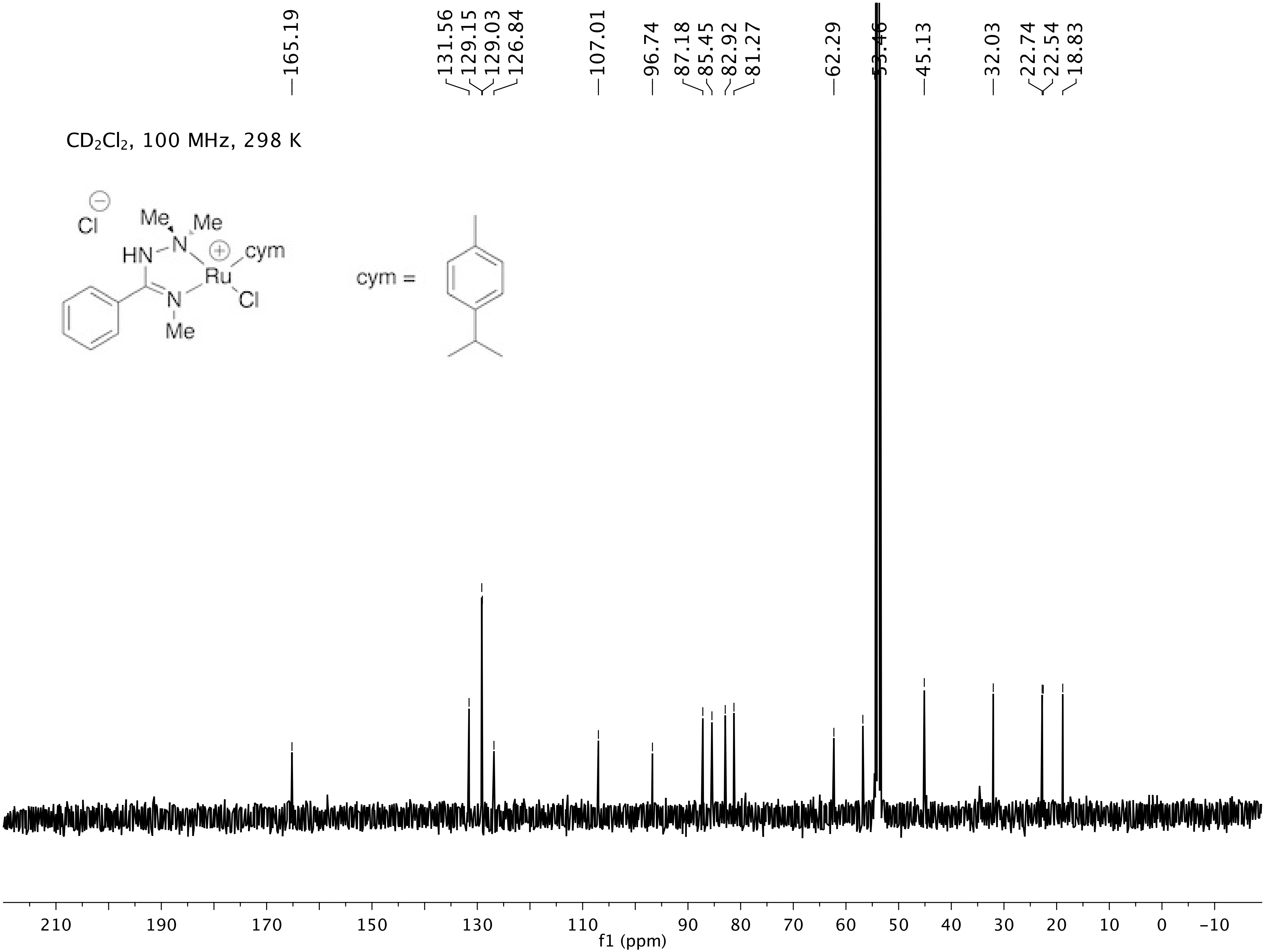
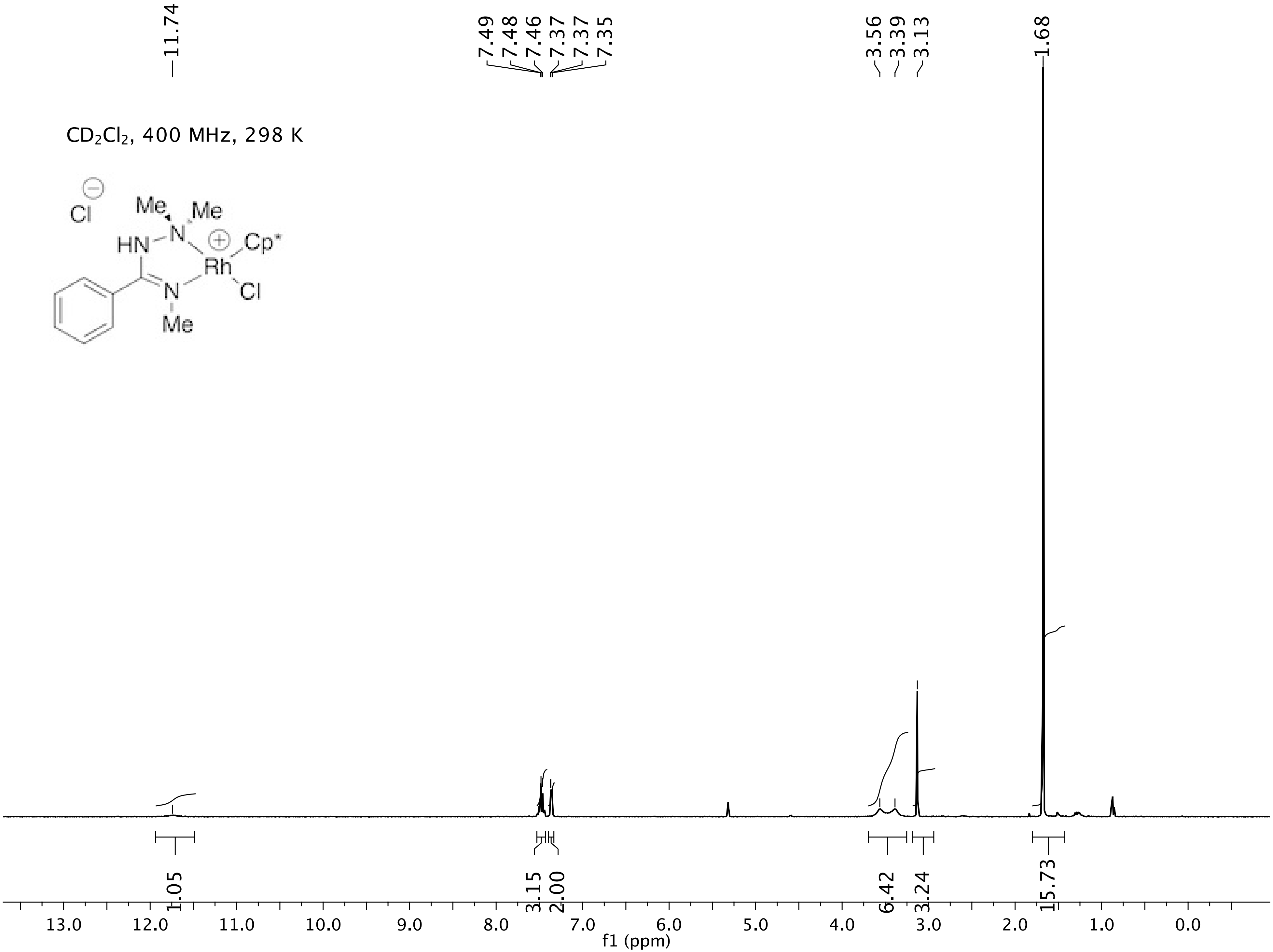
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



CD$_2$Cl$_2$, 100 MHz, 298 K



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7.46
7.37
7.37
7.35
3.56
3.39
3.13
1.68
CD₂Cl₂, 400 MHz, 298 K
Cl
Me
Me
HN
N
Cp*
Rh
N
Cl
Me
1.05
3.15
2.00
6.42
3.24
15.73
13.0
12.0
11.0
10.0
9.0
8.0
7.0
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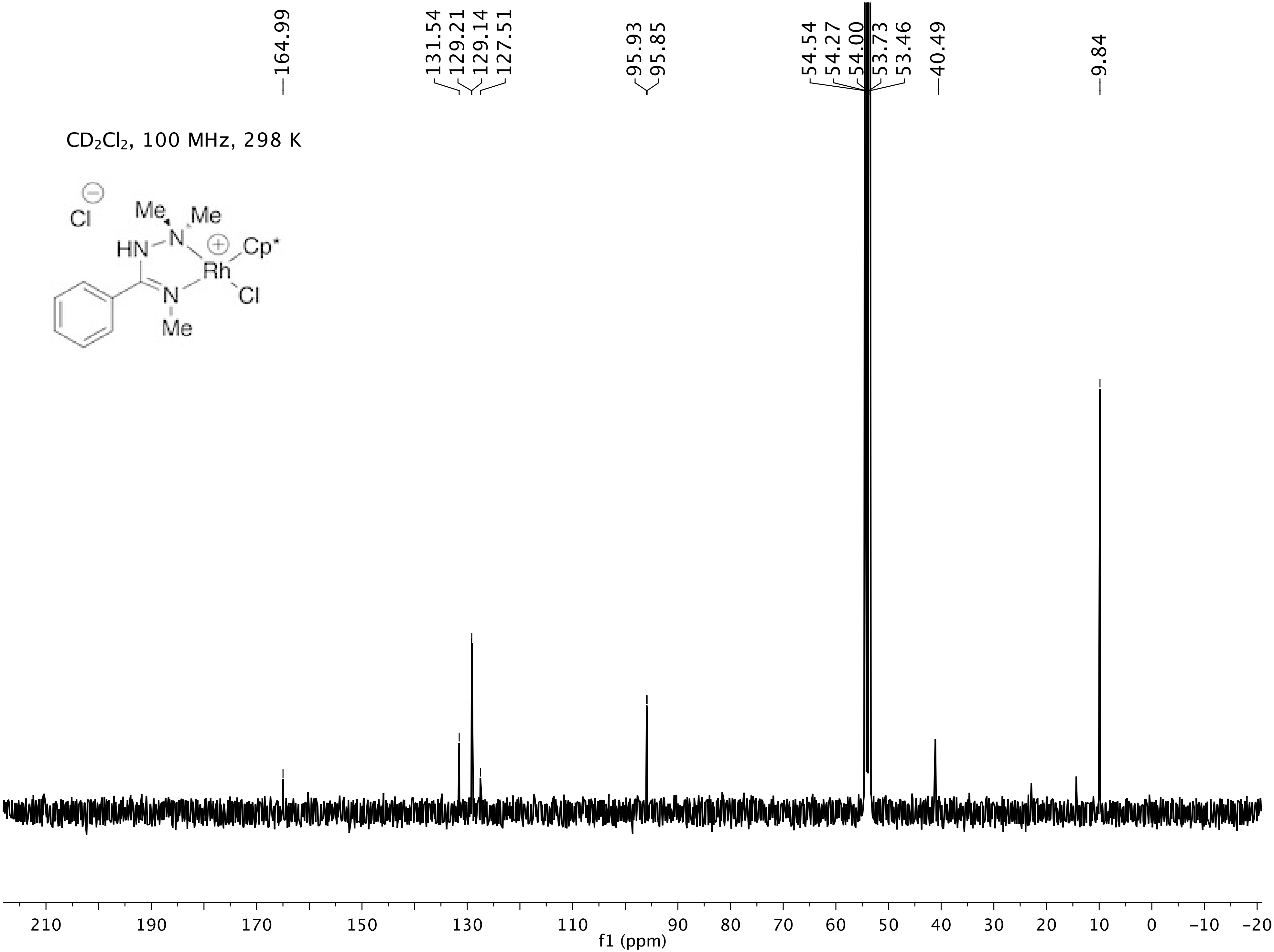
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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95.93
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54.00
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40.49
9.84
CD2Cl2, 100 MHz, 298 K
Cl
Me
Me
HN
N
Cp*
Rh
N
Cl
Me
210
190
170
150
130
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90
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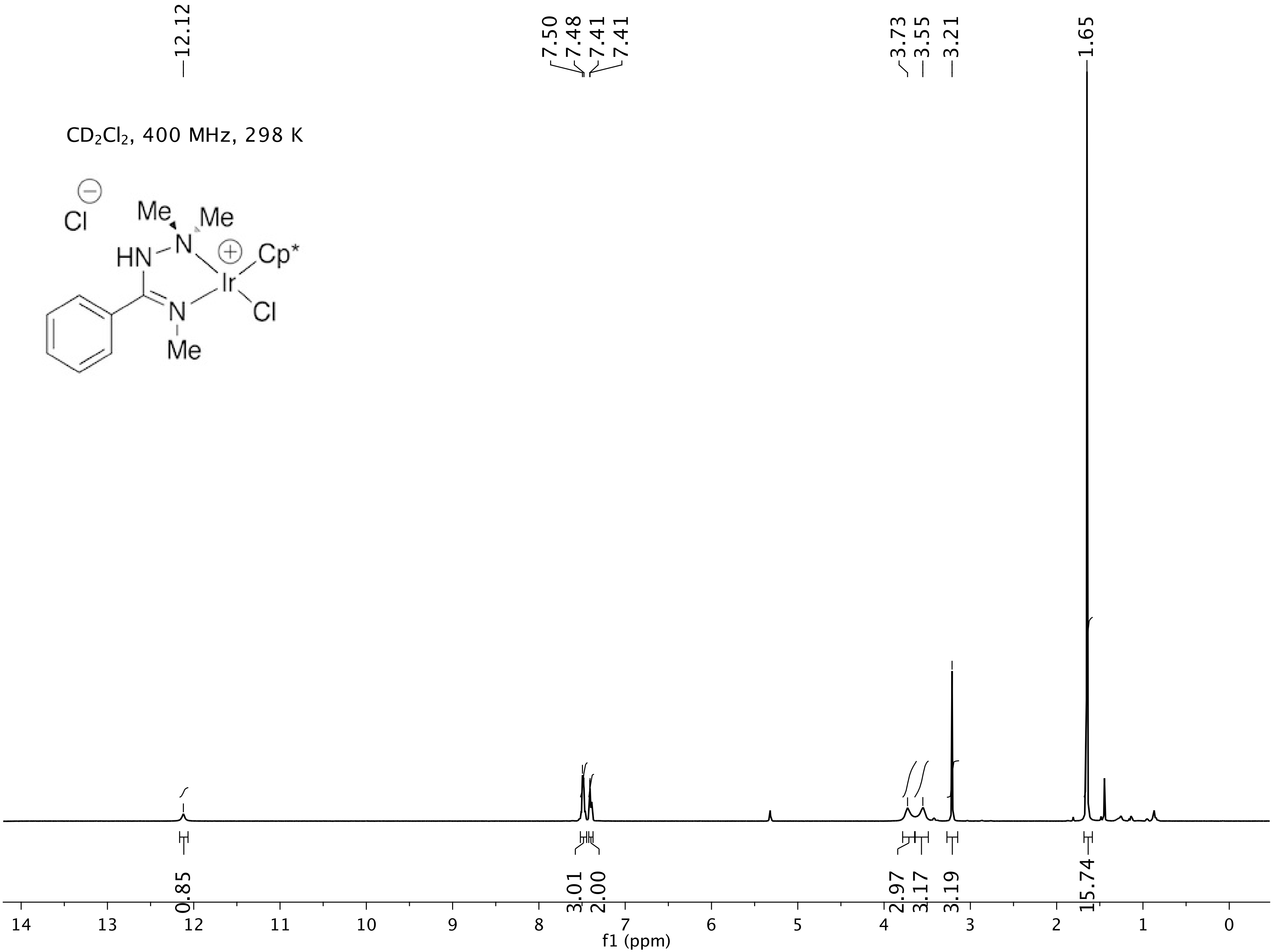
70
60
50
40
30
20
10
0
–10
–20
f1 (ppm)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3.73
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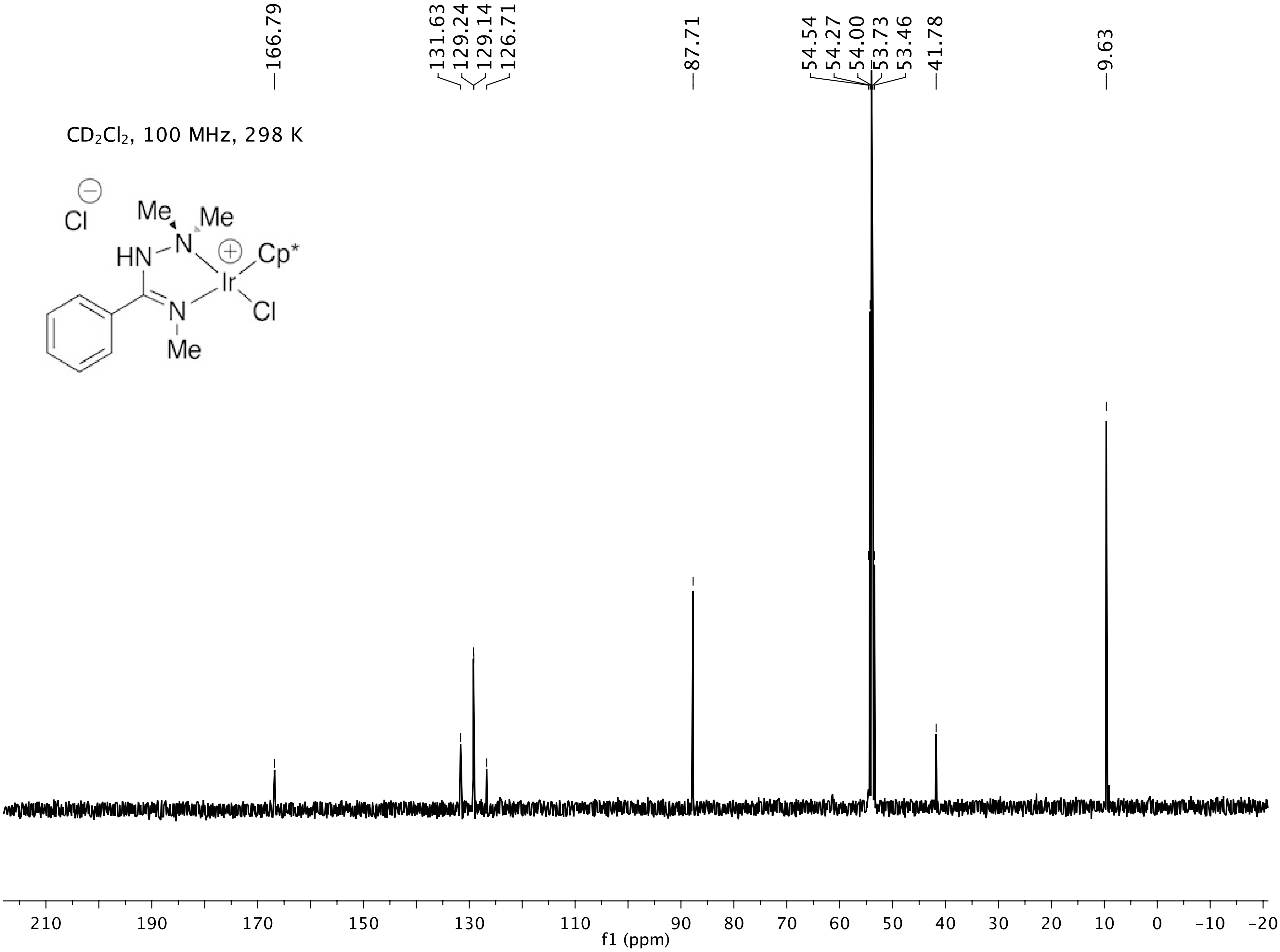
3.21
1.65
CD$_2$Cl$_2$, 400 MHz, 298 K
Cl
Me
Me
HN
N
Cp*
Ir
N
Cl
Me
0.85
3.01
2.00
2.97
3.17
3.19
15.74
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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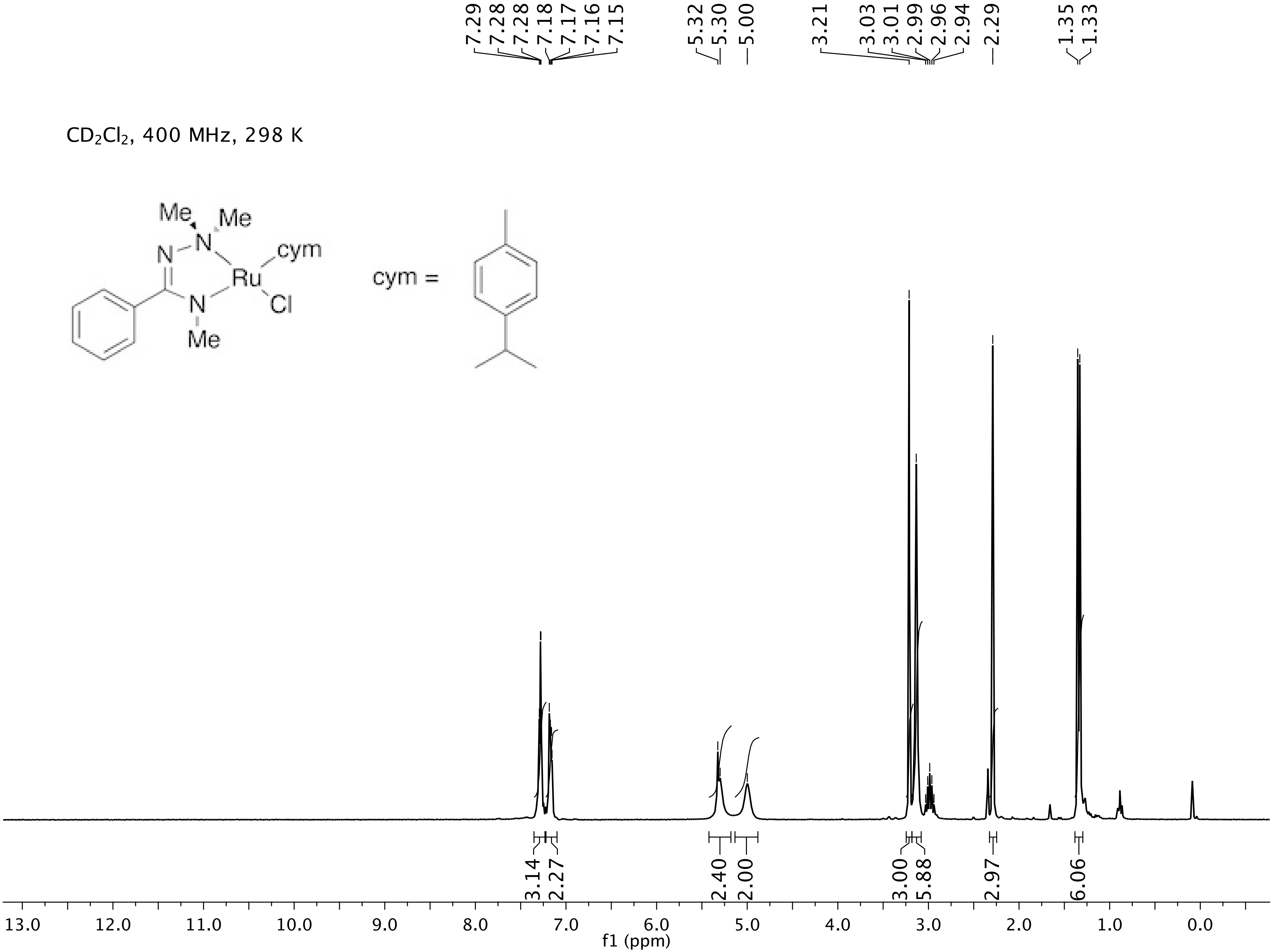
129.14
126.71
87.71
54.54
54.27
54.00
53.73
53.46
41.78
9.63
CD₂Cl₂, 100 MHz, 298 K
Cl
Me
Me
HN
N
Ir
Cp*
N
Cl
Me
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
–10
–20
f1 (ppm)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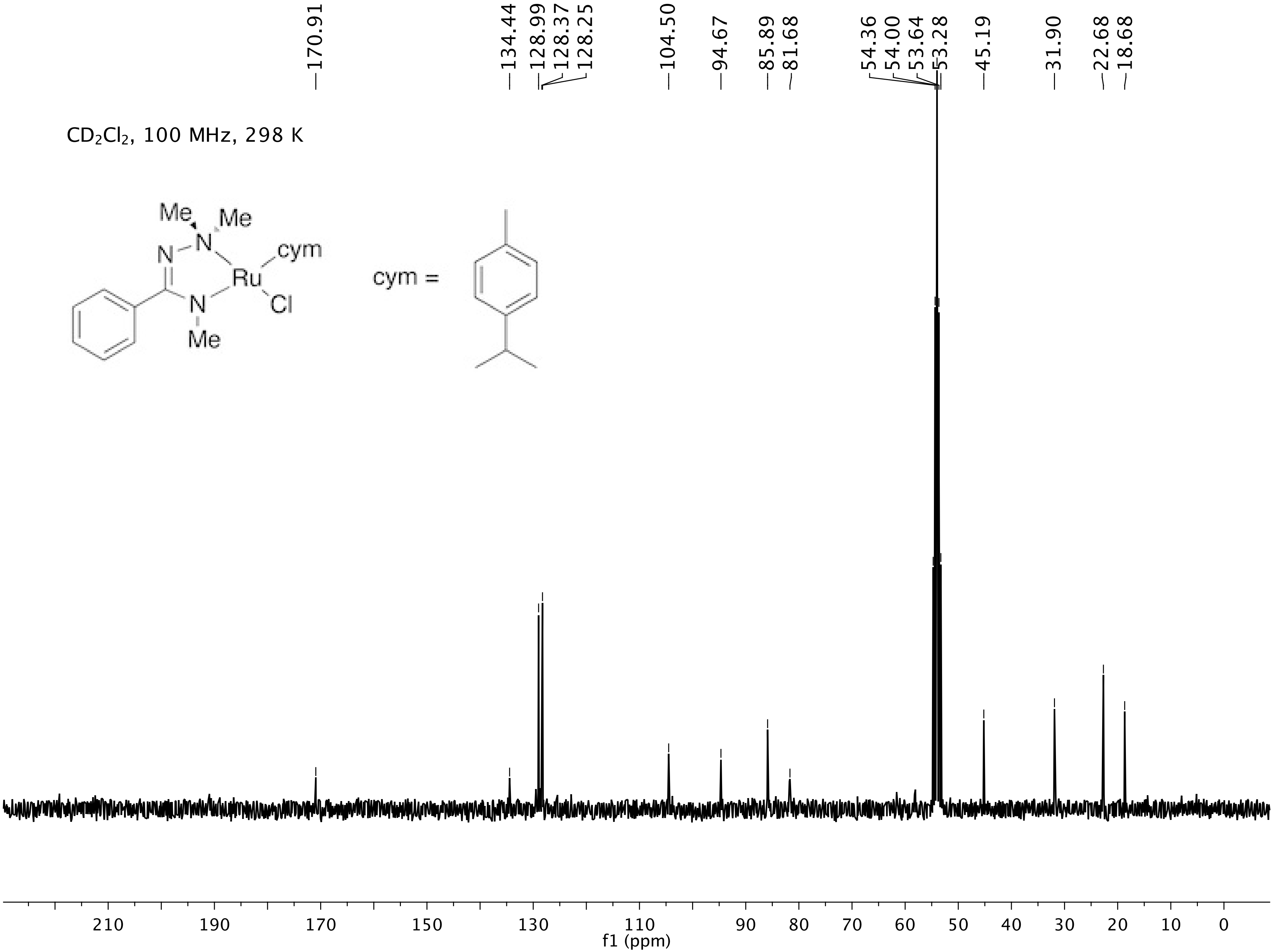
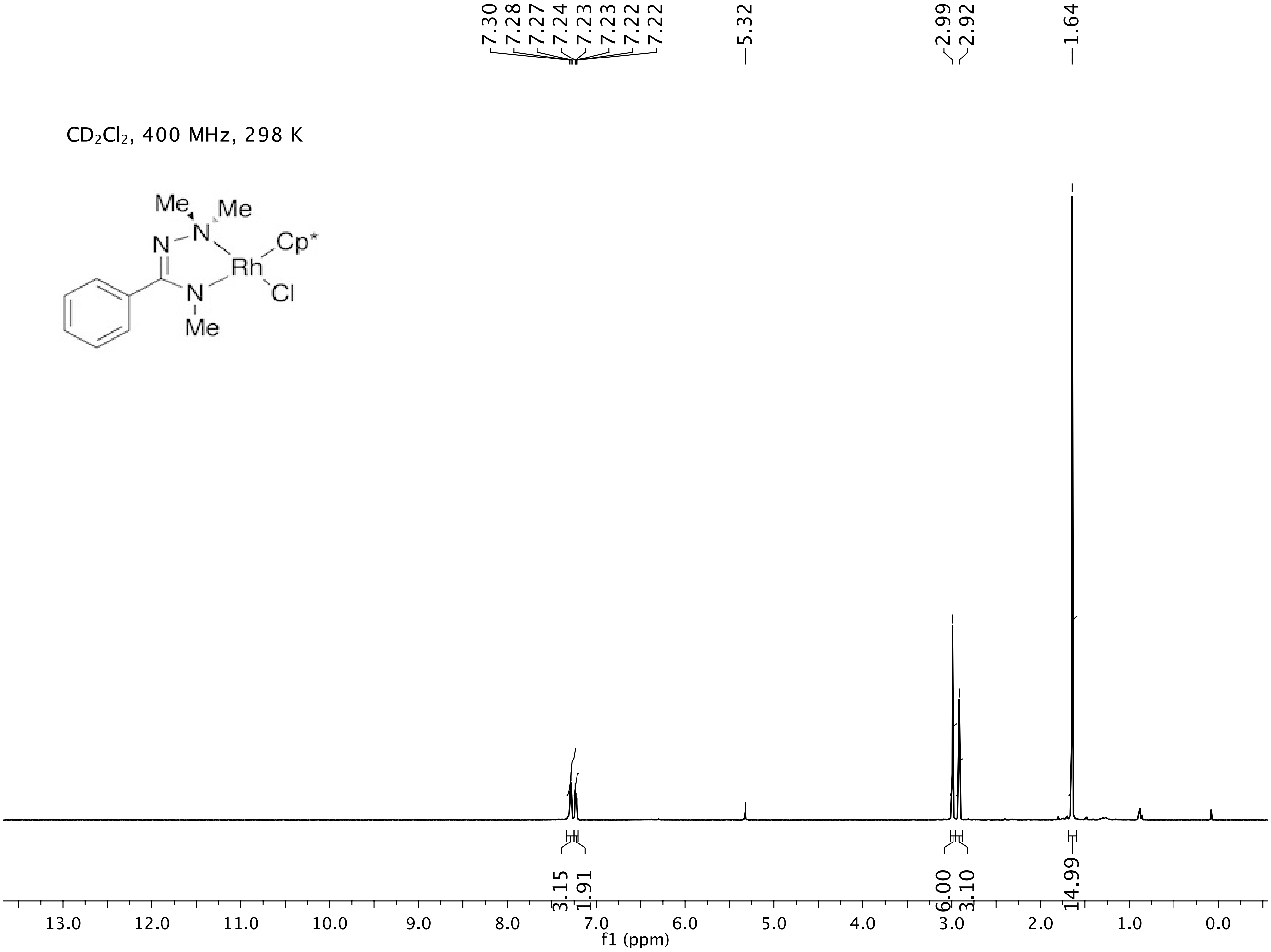
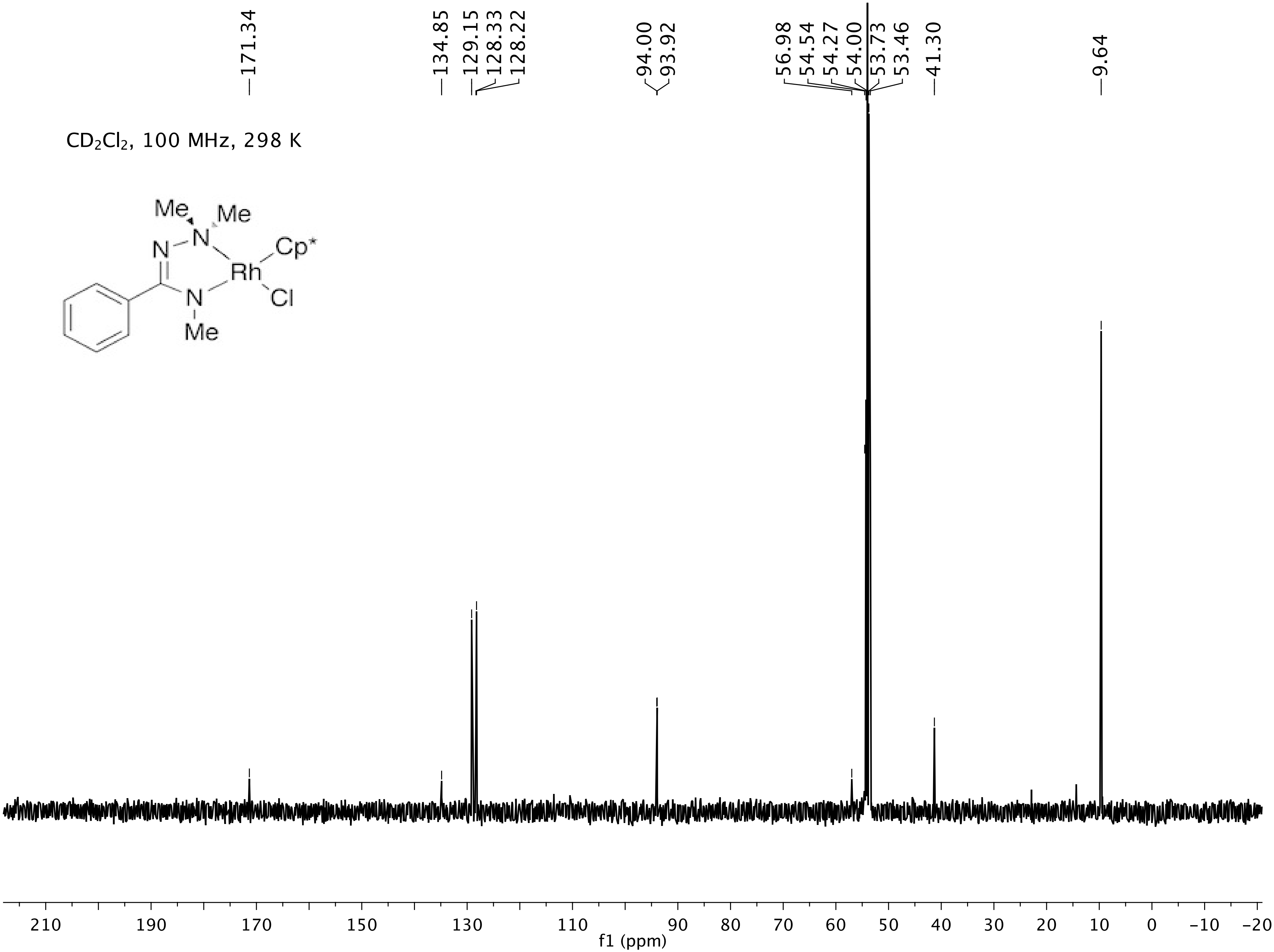
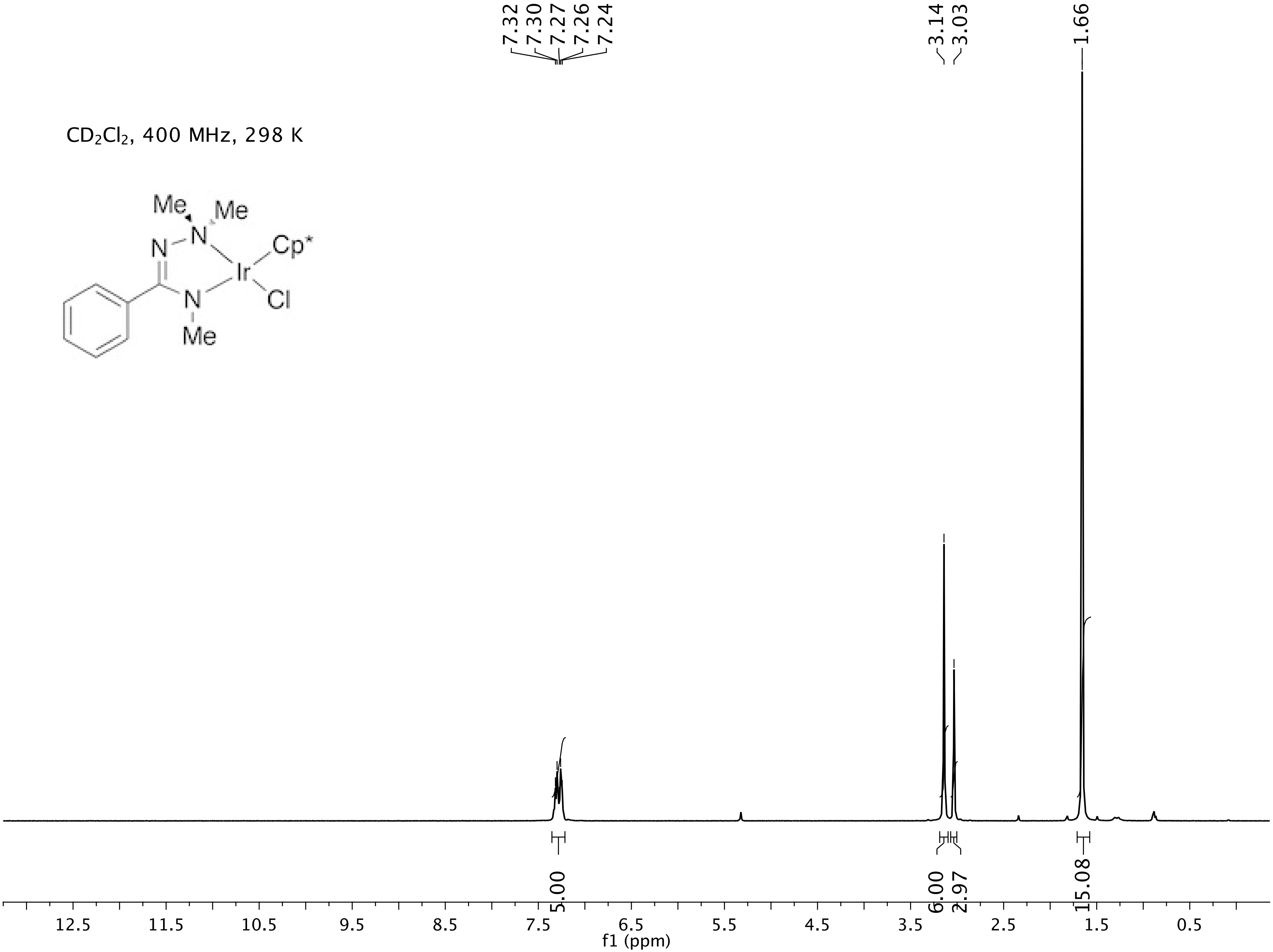
7.16
7.15
5.32
5.30
5.00
3.21
3.03
3.01
2.99
2.96
2.94
2.29
1.35
1.33
CD$_2$Cl$_2$, 400 MHz, 298 K
Me
Me
N
N
Ru
cym
N
Cl
Me
cym =
3.14
2.27
2.40
2.00
3.00
5.88
2.97
6.06
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

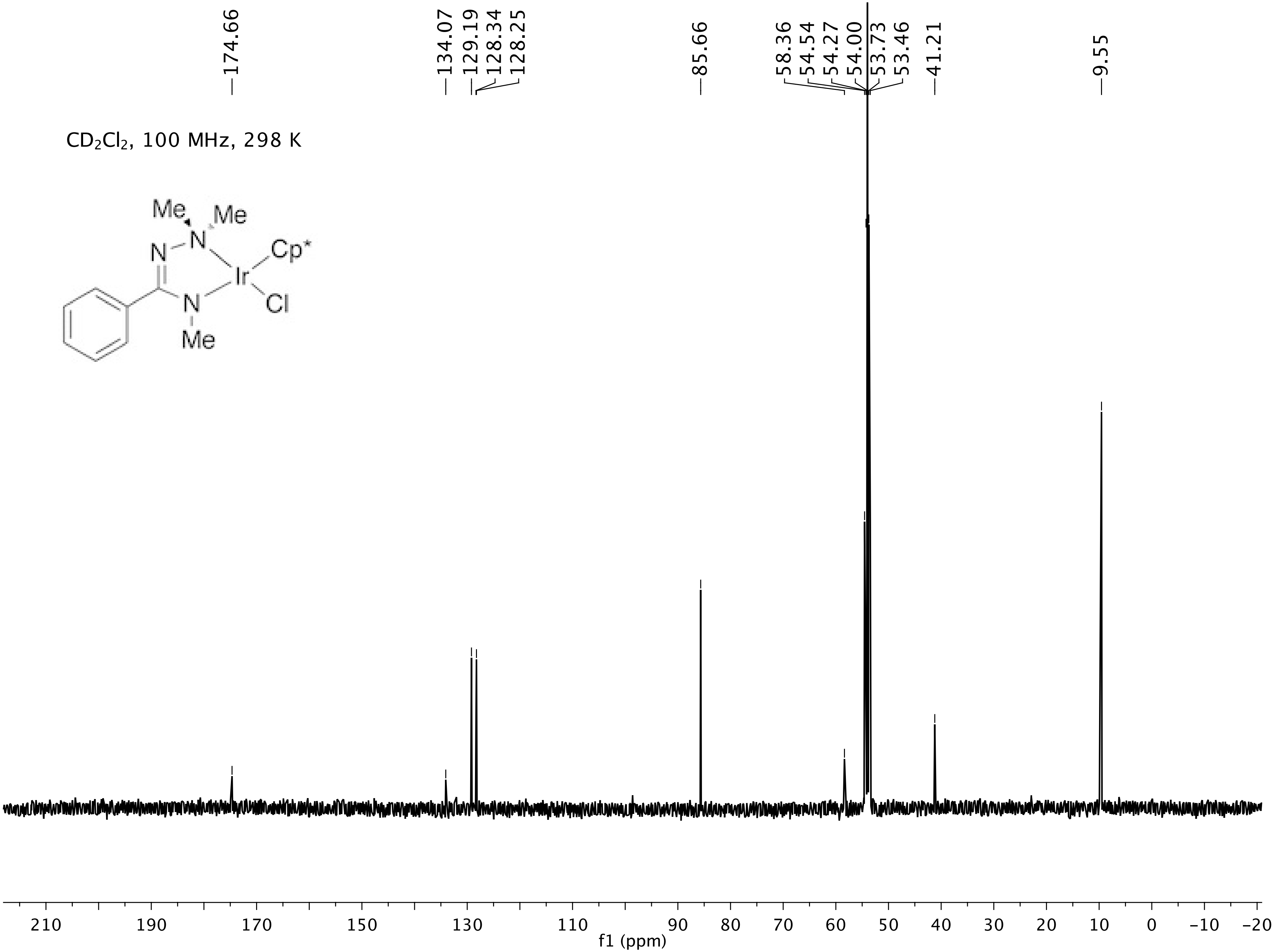


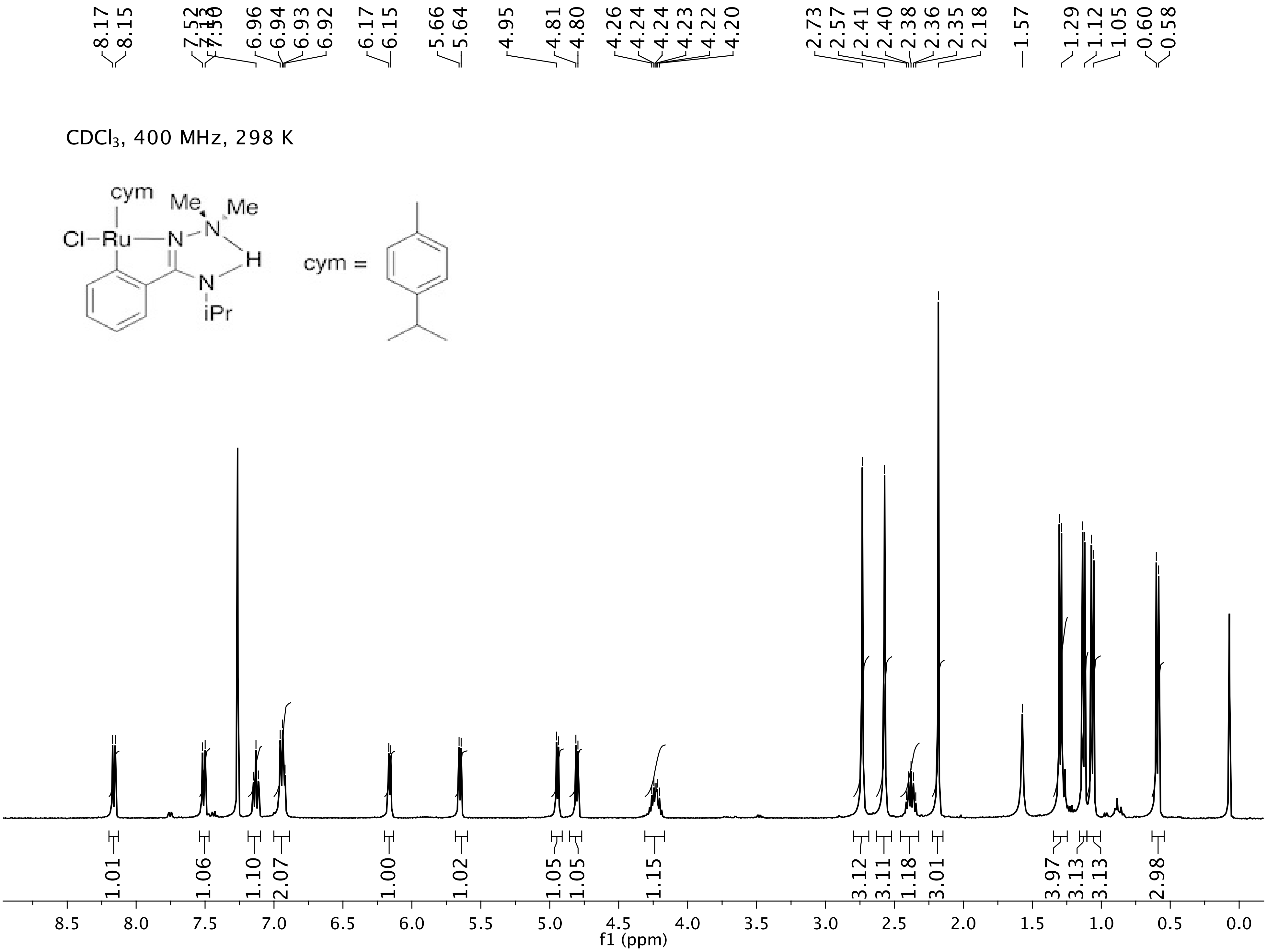
CD$_2$Cl$_2$, 100 MHz, 298 K

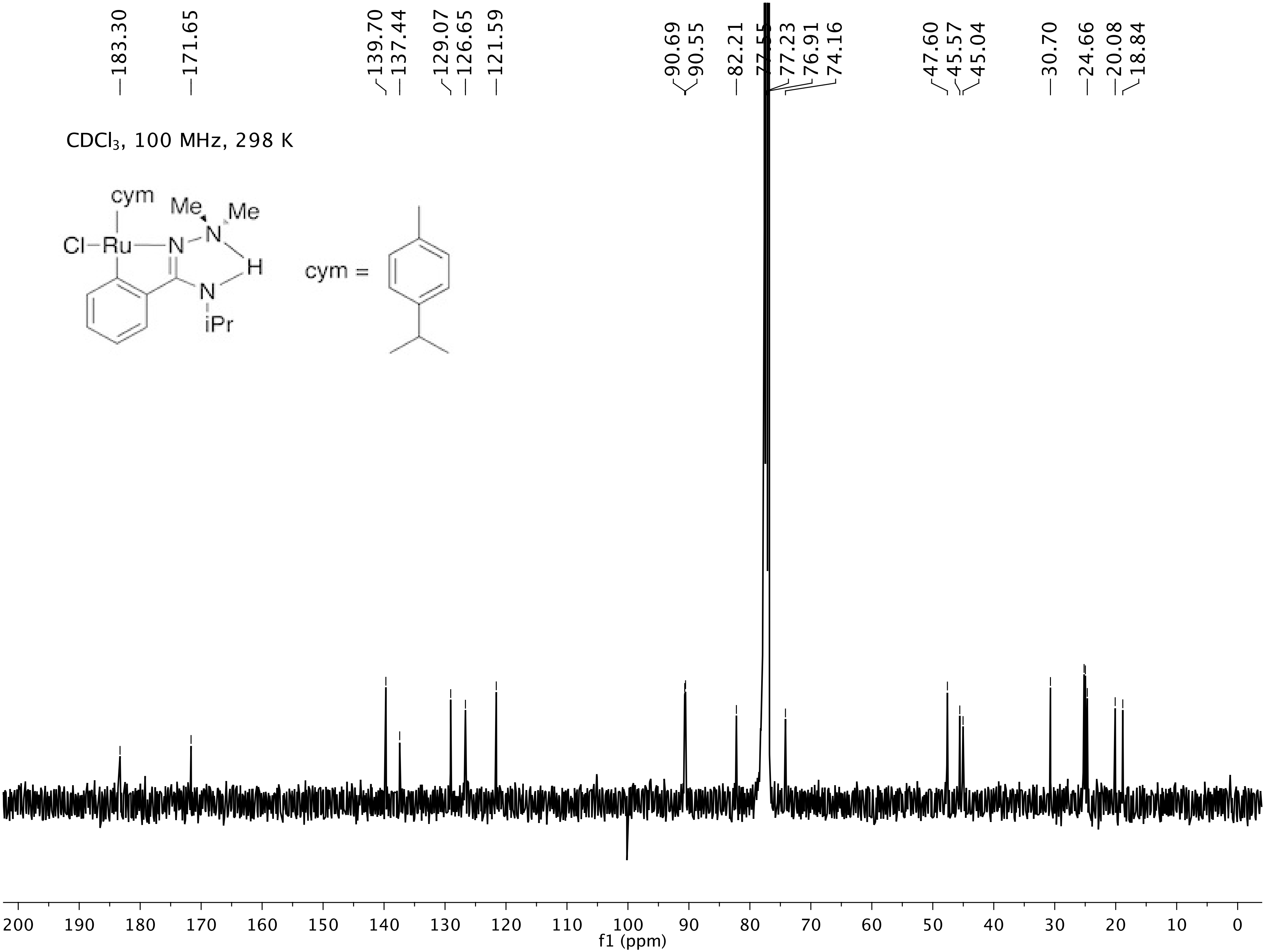

CD$_2$Cl$_2$, 400 MHz, 298 K


171.34
134.85
129.15
128.33
128.22
94.00
93.92
56.98
54.54
54.27
54.00
53.73
53.46
41.30
9.64
CD₂Cl₂, 100 MHz, 298 K
Me
Me
N
N
Cp*
Rh
N
Cl
Me
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
–10
–20
f1 (ppm)


CD$_2$Cl$_2$, 400 MHz, 298 K
Me
Me
N
N
Cp*
Ir
N
Cl
Me
7.32
7.30
7.27
7.26
7.24
3.14
3.03
1.66
5.00
6.00
2.97
15.08
12.5
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


174.66
134.07
129.19
128.34
128.25
85.66
58.36
54.54
54.27
54.00
53.73
53.46
41.21
9.55
CD$_2$Cl$_2$, 100 MHz, 298 K
Me
Me
N
N
Cp*
Ir
N
Cl
Me
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
–10
–20
f1 (ppm)


CDCl$_3$, 400 MHz, 298 K


183.30
171.65
139.70
137.44
129.07
126.65
121.59
90.69
90.55
82.21
77.55
77.23
76.91
74.16
47.60
45.57
45.04
30.70
24.66
20.08
18.84
CDCl$_3$, 100 MHz, 298 K
cym
Me
Me
Cl
Ru
N
N
H
N
iPr
cym =
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)