Supporting Information for

Deprotonated Salicylaldehyde as Visible Light Photocatalyst

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1. Photo of the lamp and the reaction

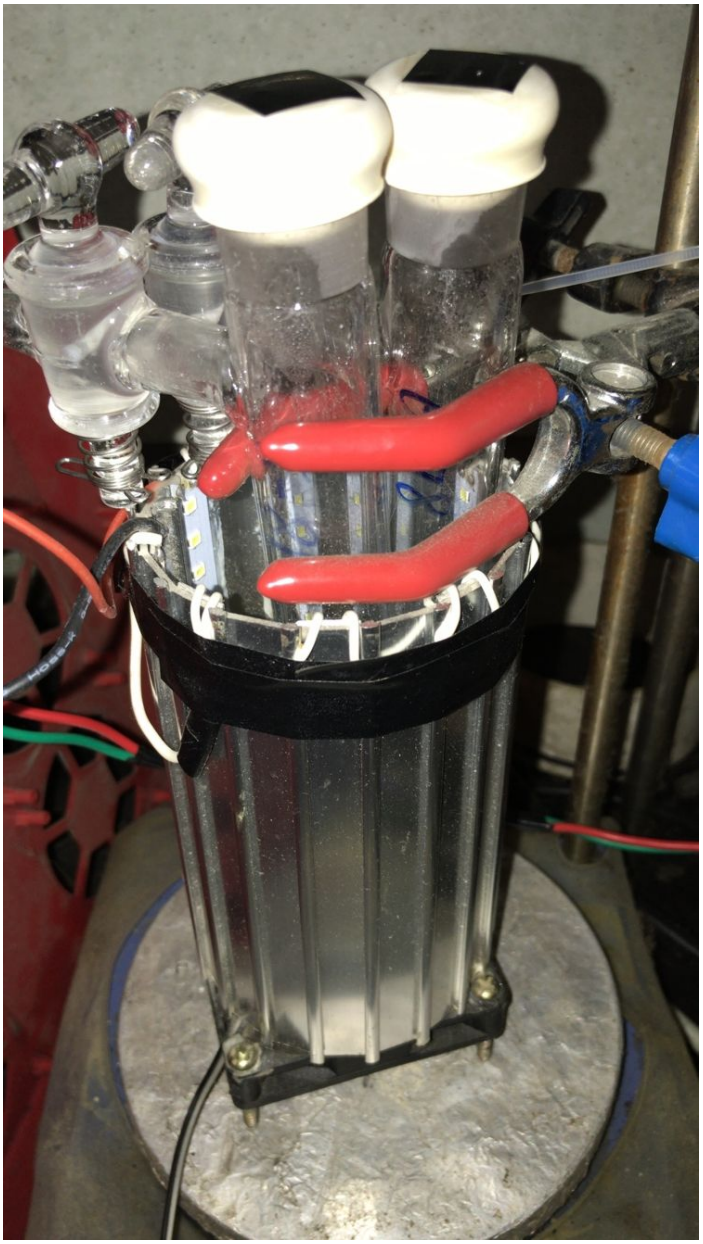


Figure S1. Photo of the lamp and the reaction.

2. Measurement of fluorescence quantum yield (Φ)

Φ was measured by the optical dilute method with a standard of quinine sulfate (Φ_r = 0.55, quinine in 0.05 M sulfuric acid) calculated by:

$$\Phi_s = \left(\frac{F_s}{F_r}\right) \times \left(\frac{1 - 10^{-A_r}}{1 - 10^{-A_s}}\right) \times \left(\frac{\eta_s}{\eta_r}\right)^2 \times \Phi_r$$ Where the subscripts s and r refer to the sample and reference standard solution respectively; F is the integrated intensity; A is the absorbance at the excitation wavelength; η is the refractive index of the solutions. Error for Φ values (± 10%) are estimated.

3. Fluorescence quenching experiment

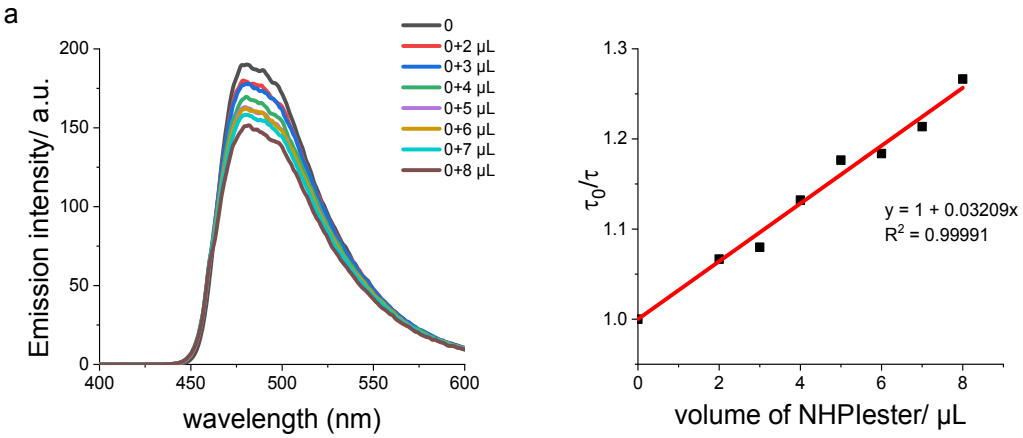


Figure S2. Fluorescence quenching effect of catalyst by NHPI ester in DMSO.
A stock solution of salicylaldehyde (0.10 M, in dry DMSO) was prepared in a volumetric flask and diluted by dry DMSO to 1.0 mM for the quenching experiment. Then K_3PO_4 was added as the base. The fluorescence measurement was monitored at least 1 h after the addition of base. A quartz cuvette (1 cm × 1 cm × 3 cm) was filled with the abovementioned 1.0 mM DMSO solution (3 mL) and its fluorescence was recorded with excitation at 458 nm in the spectrometer. Quenching experiments were performed with the injection of 1 μL solution of NHPI ester in DMSO (0.1 M) respectively by auto-pipette.

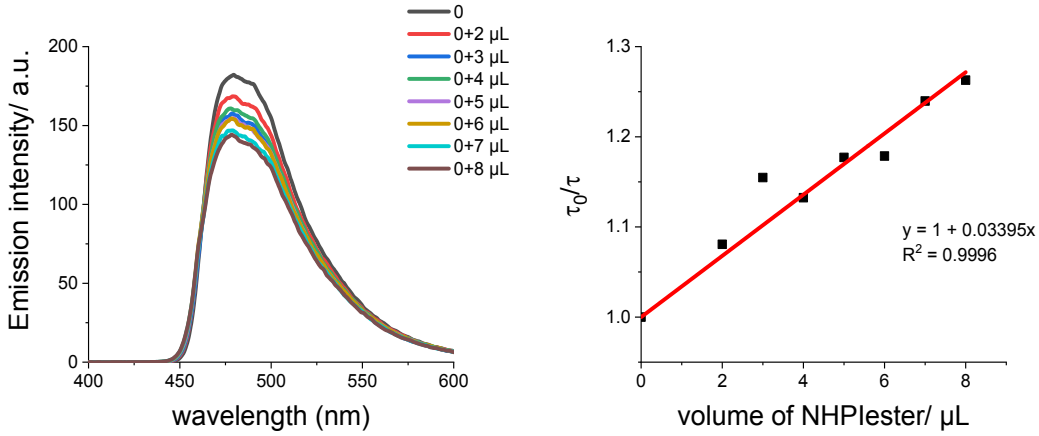


Figure S3. Fluorescence quenching effect of catalyst by NHPI ester in DMAc.
A stock solution of salicylaldehyde (0.10 M, in dry DMAc) was prepared in a volumetric flask and diluted by dry DMAc to 1.0 mM for the quenching experiment. Then K_3PO_4 was added as the base. The fluorescence measurement was monitored at least 1 h after the addition of base. A quartz cuvette (1 cm × 1 cm × 3 cm) was filled with the abovementioned 1.0 mM DMAc solution (3 mL) and its fluorescence was recorded with excitation at 458 nm in the spectrometer. Quenching experiments were performed with the injection of 1 μL solution of NHPI ester in DMAc (0.1 M) respectively by auto-pipette.

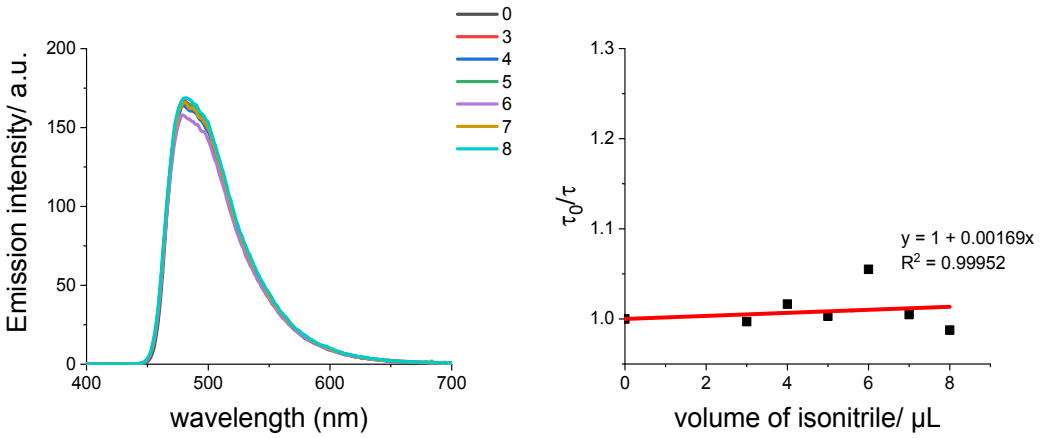


Figure S4. Fluorescence quenching effect of catalyst by isonitrile in DMSO.

A stock solution of salicylaldehyde (0.10 M, in dry DMSO) was prepared in a volumetric flask and diluted by dry DMSO to 1.0 mM for the quenching experiment. Then K_3PO_4 was added as the base. The fluorescence measurement was monitored at least 1 h after the addition of base. A quartz cuvette (1 cm × 1 cm × 3 cm) was filled with the abovementioned 1.0 mM DMSO solution (3 mL) and its fluorescence was recorded with excitation at 458 nm in the spectrometer. Quenching experiments were performed with the injection of 1 μL solution of isonitrile in DMSO (0.1 M) respectively by auto-pipette.

4. Calculation of apparent quantum efficiency (A. Q. E.)

In principle, it takes one photon to excite one deprotonated salicylaldehyde molecule to generate one alkyl radical. The energy of one photon (E_{photon}) with wavelength of λ_{inc} (nm) is calculated using the following equation:

$$E_{\text{photo}} = \frac{hc}{\lambda_{inc}}$$

λ_{inc} (nm)	405	430	450	520	595	620
E_{photo} (J)	4.9 x 10^{-19}	4.6 x 10^{-19}	4.4 x 10^{-19}	3.8 x 10^{-19}	3.3 x 10^{-19}	3.2 x 10^{-19}

Where h (J•s) is Planck's constant, c (m•s^{-1}) is the speed of light and λ_{inc} (m) is the wavelength of the incident light. And the total energy of the incident monochromatic light (E_{total}) is calculated using the following equation:

$$E_{\text{total}} = PSt$$

λ_{inc} (nm)	405	430	450	520	595	620
E_{total} (J)	112.32	112.32	95.04	86.40	64.80	60.48

Where P (W•cm^{-2}) is the power density of the incident light, S (cm^2) is the irradiation area and t (s) is the photoreaction tiom. The total number of the incident can be obtained through the following equation:

$$\text{Number of incident photons} = \frac{E_{\text{total}}}{E_{\text{photo}}}$$

λ_{inc} (nm)	405	430	450	520	595	620
Number of incident photons (mmol)	0.38	0.41	0.36	0.38	0.33	0.31

Because it is difficult determine the number of reacted electrons via experimental methods, as a result, the apparent quantum yield (A. Q. Y.) is defined as follows:

$$\text{A. Q. Y.} = \frac{\text{Number of product}}{\text{Number of incident photos}} \times 100\%$$

λ_{inc} (nm)	405	430	450	520	595	620
A.Q.Y. (%)	44.2	41.5	47.2	0	0	0

5. NMR Data

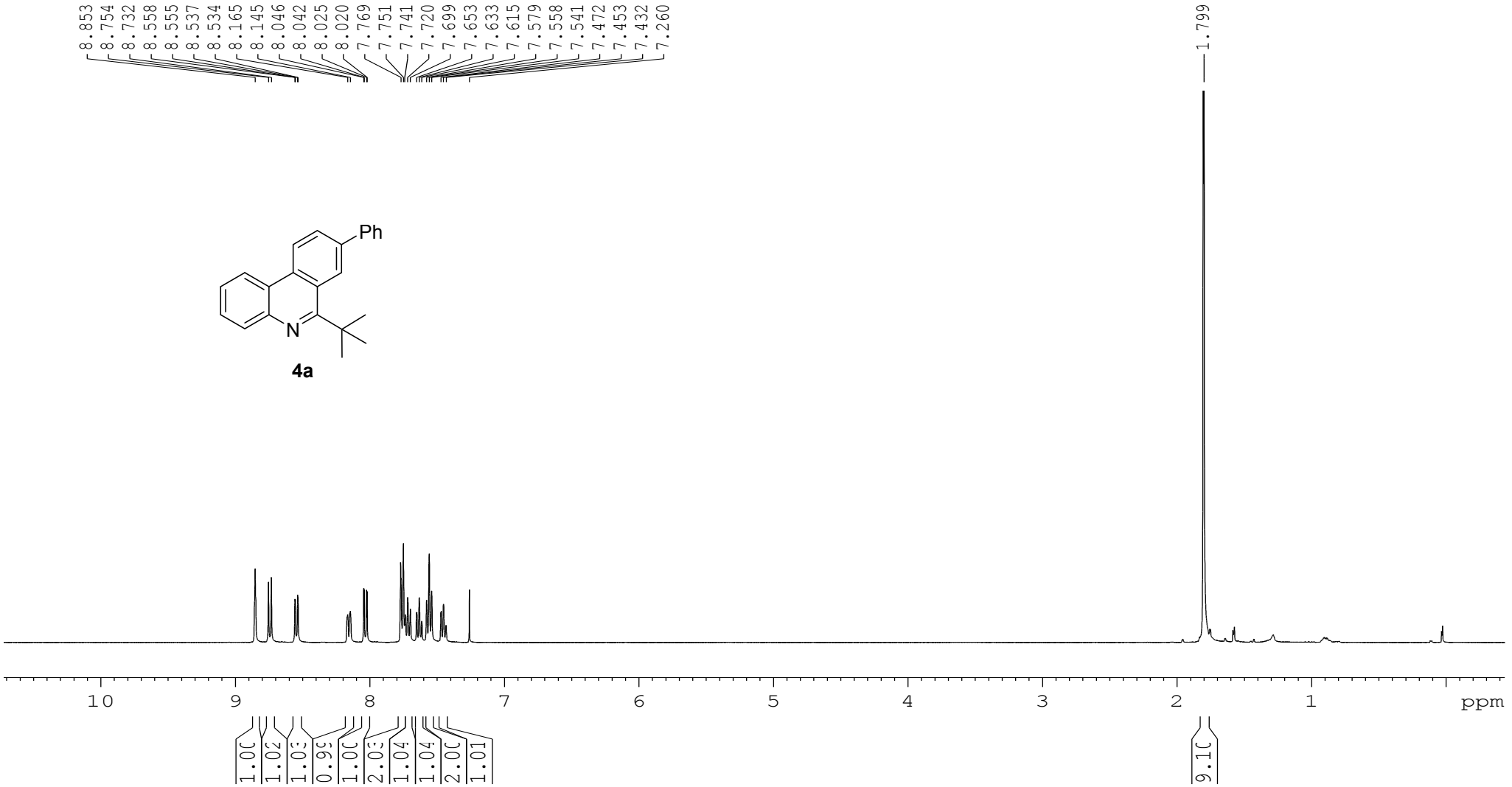


Figure S5. ^{1}H NMR spectrum of **4a** ($CDCl_3$, 400 MHz).

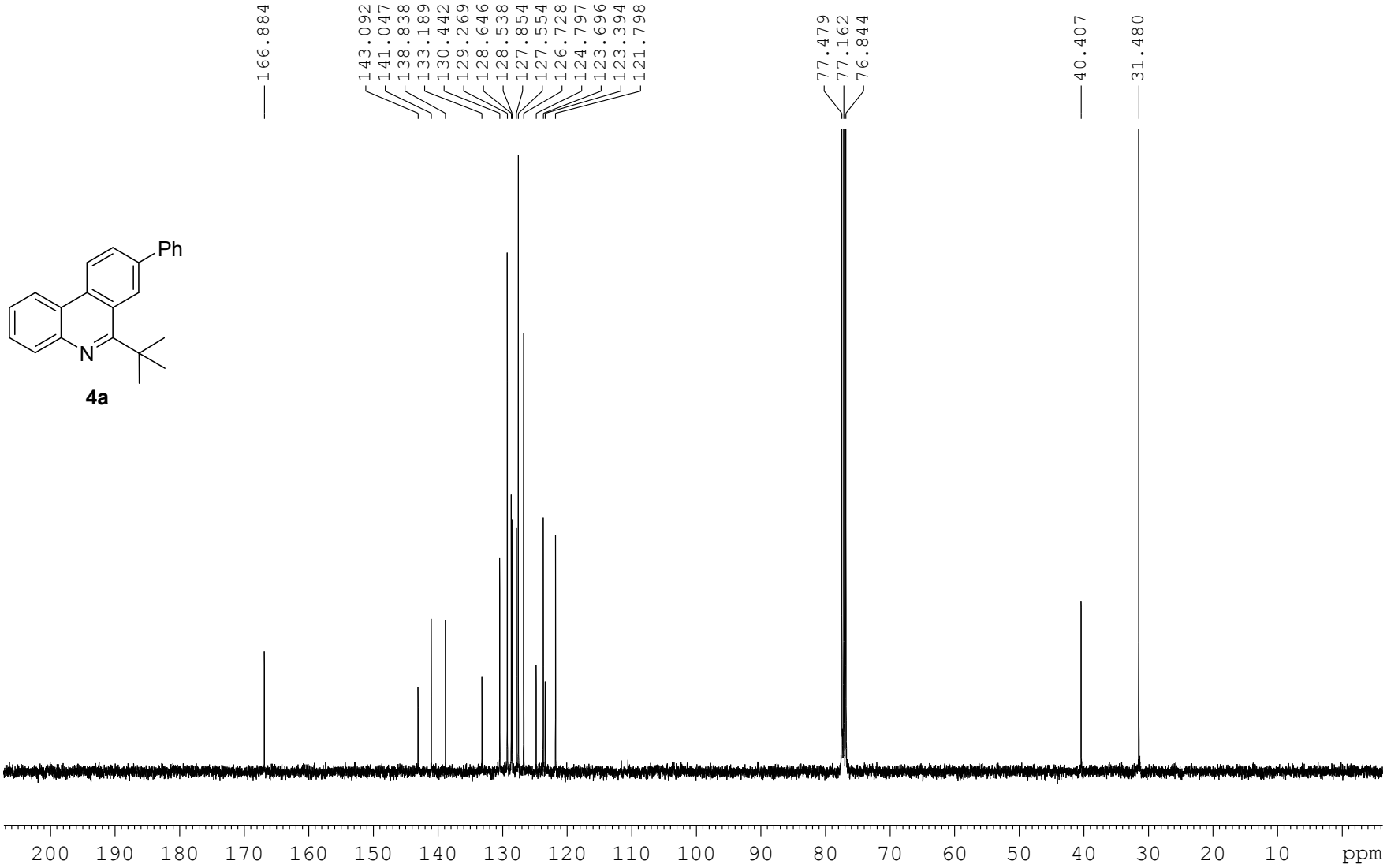


Figure S6. ^{13}C NMR spectrum of **4a** ($CDCl_3$, 100 MHz).

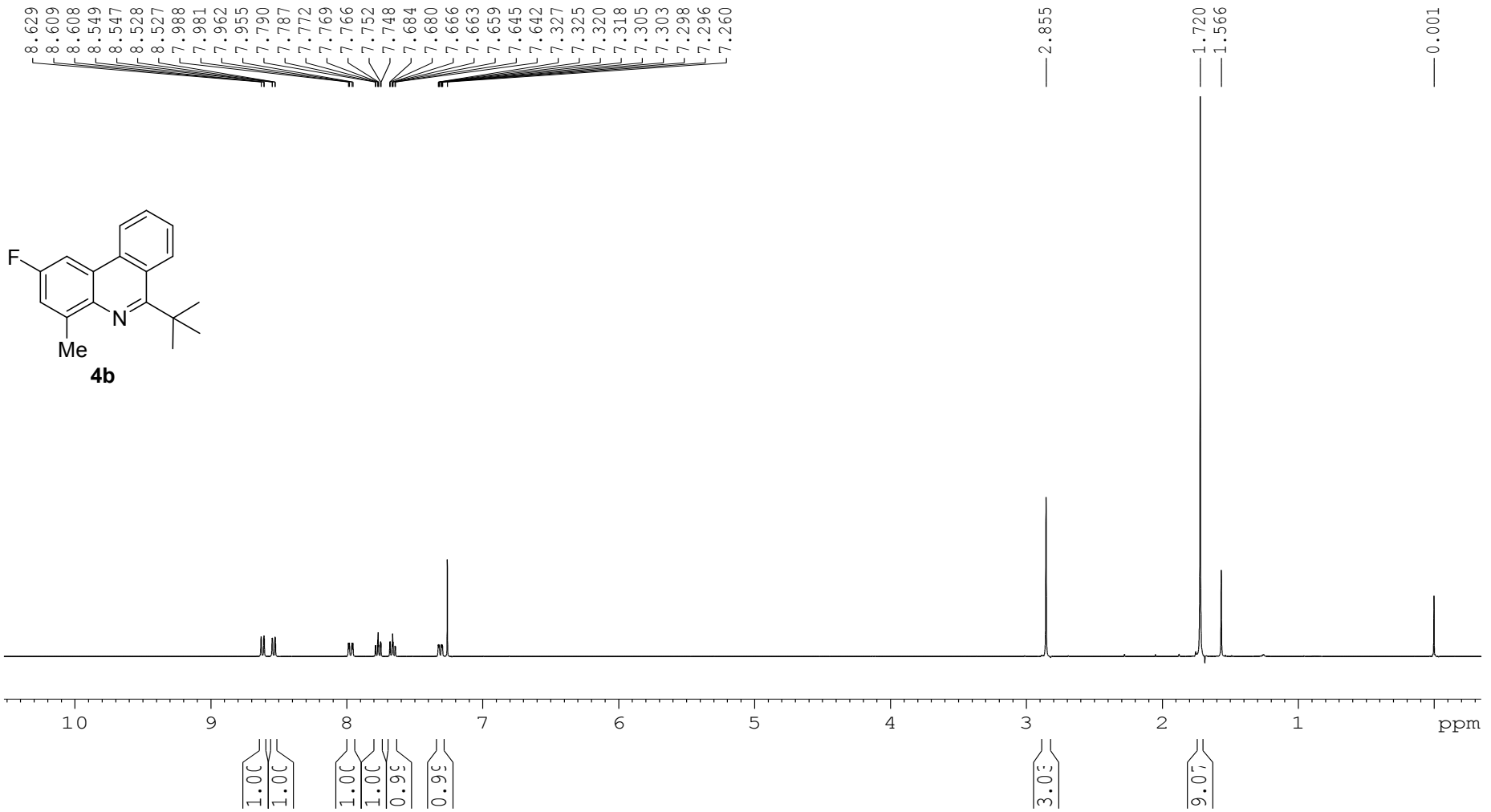


Figure S7. ^{1}H NMR spectrum of **4b** ($CDCl_3$, 400 MHz).

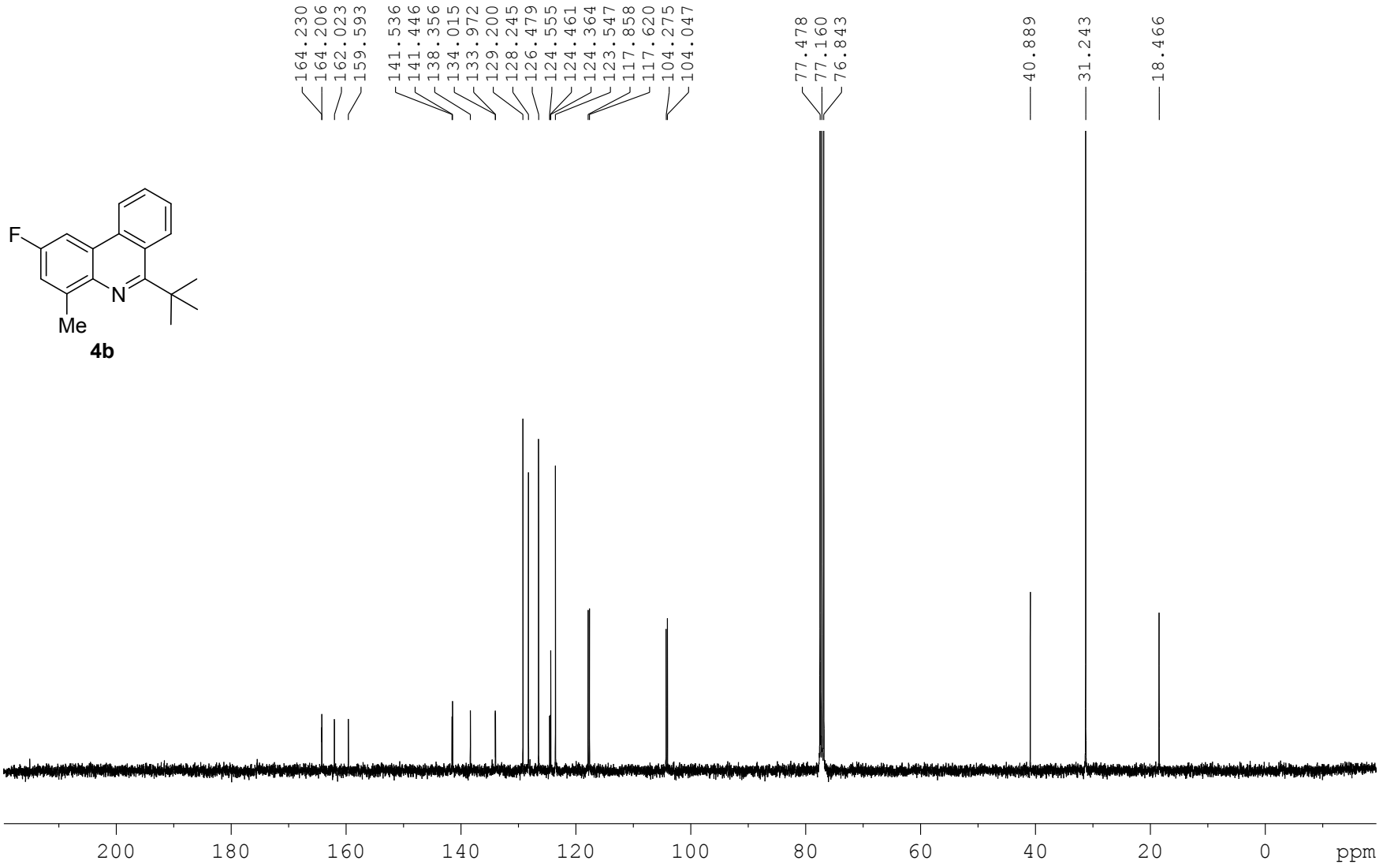


Figure S8. ^{13}C NMR spectrum of **4b** ($CDCl_3$, 100 MHz).

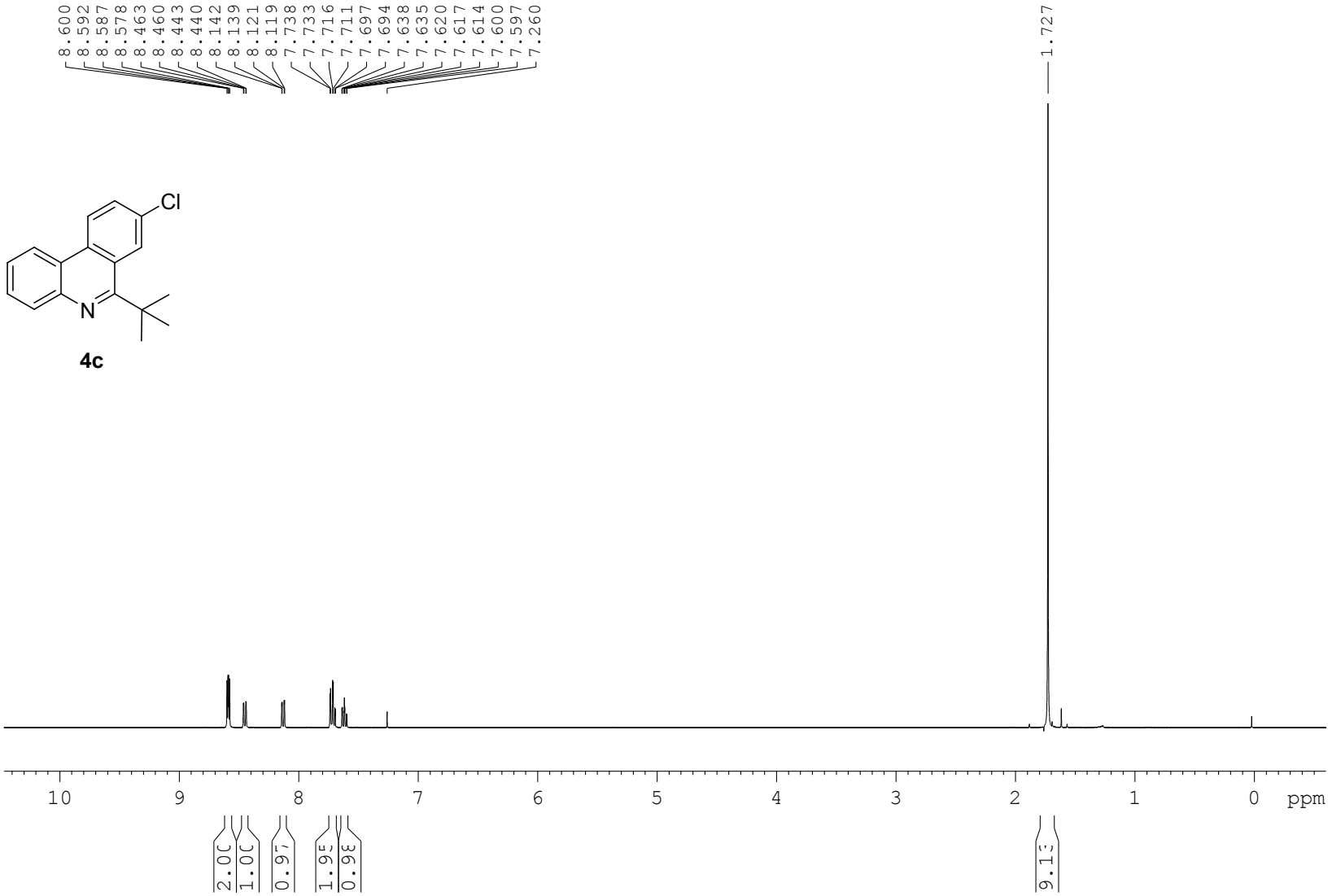


Figure S9. ^{1}H NMR spectrum of **4c** ($CDCl_3$, 400 MHz).

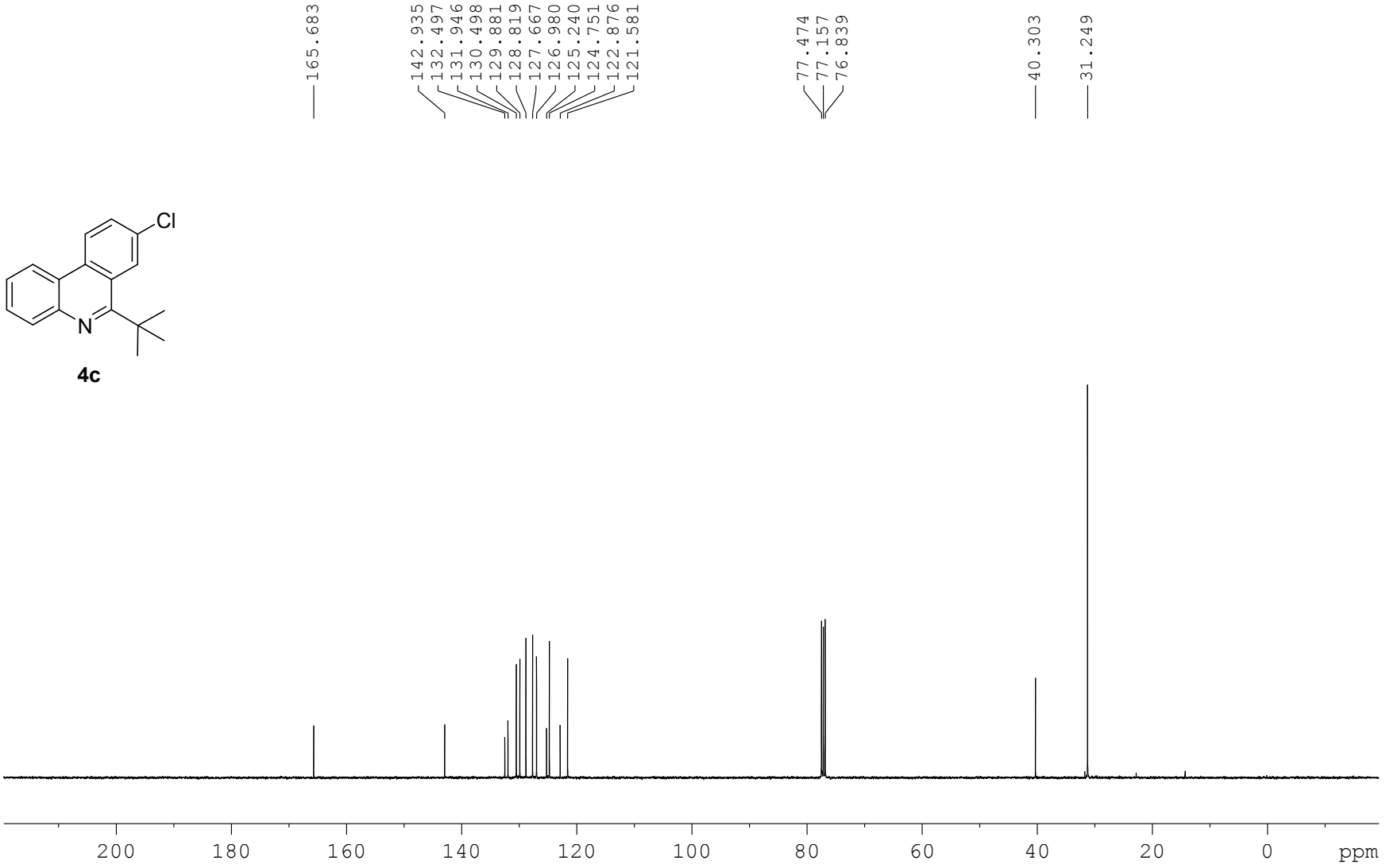


Figure S10. ^{13}C NMR spectrum of **4c** ($CDCl_3$, 100 MHz).

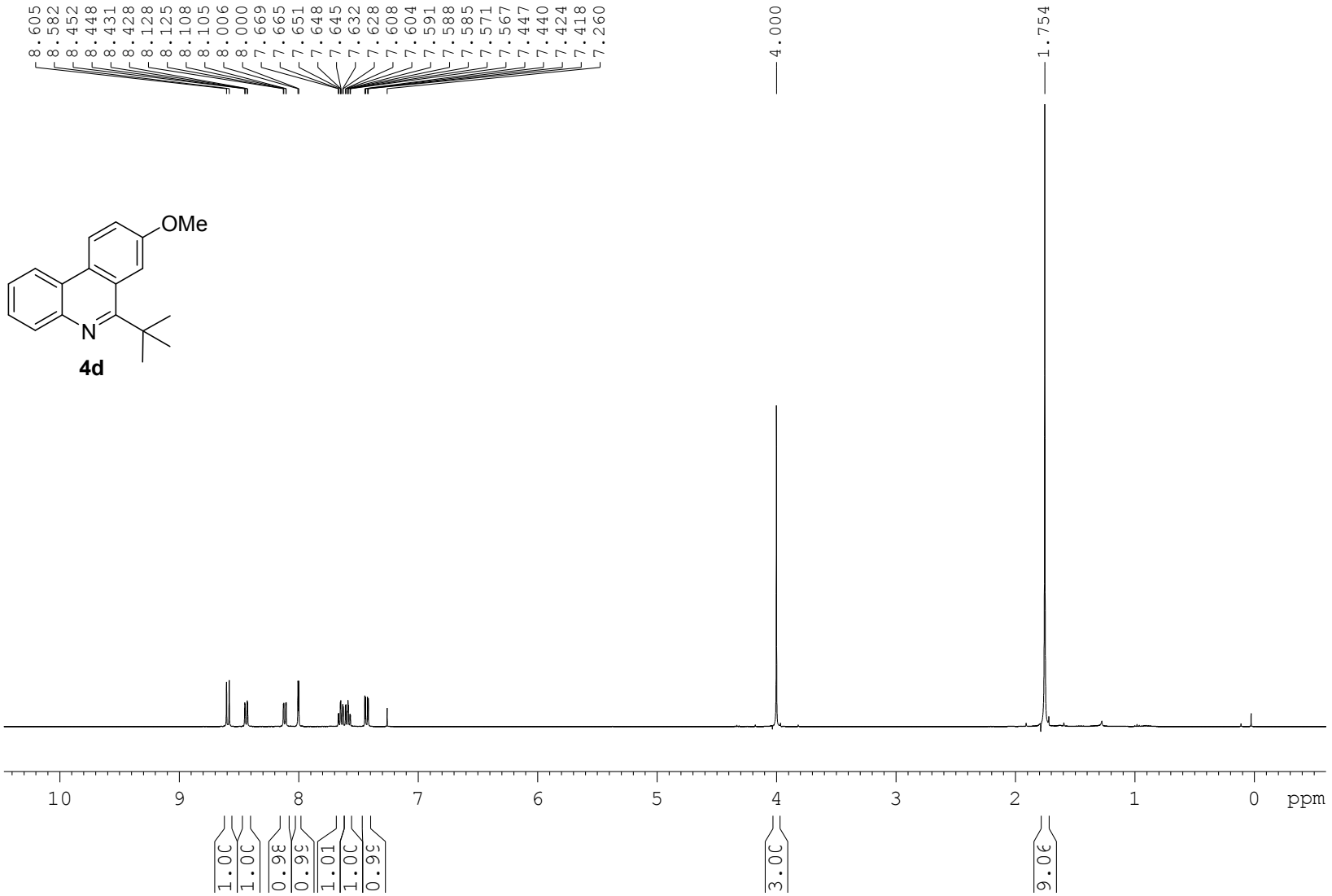


Figure S11. ^{1}H NMR spectrum of **4d** ($CDCl_3$, 400 MHz).

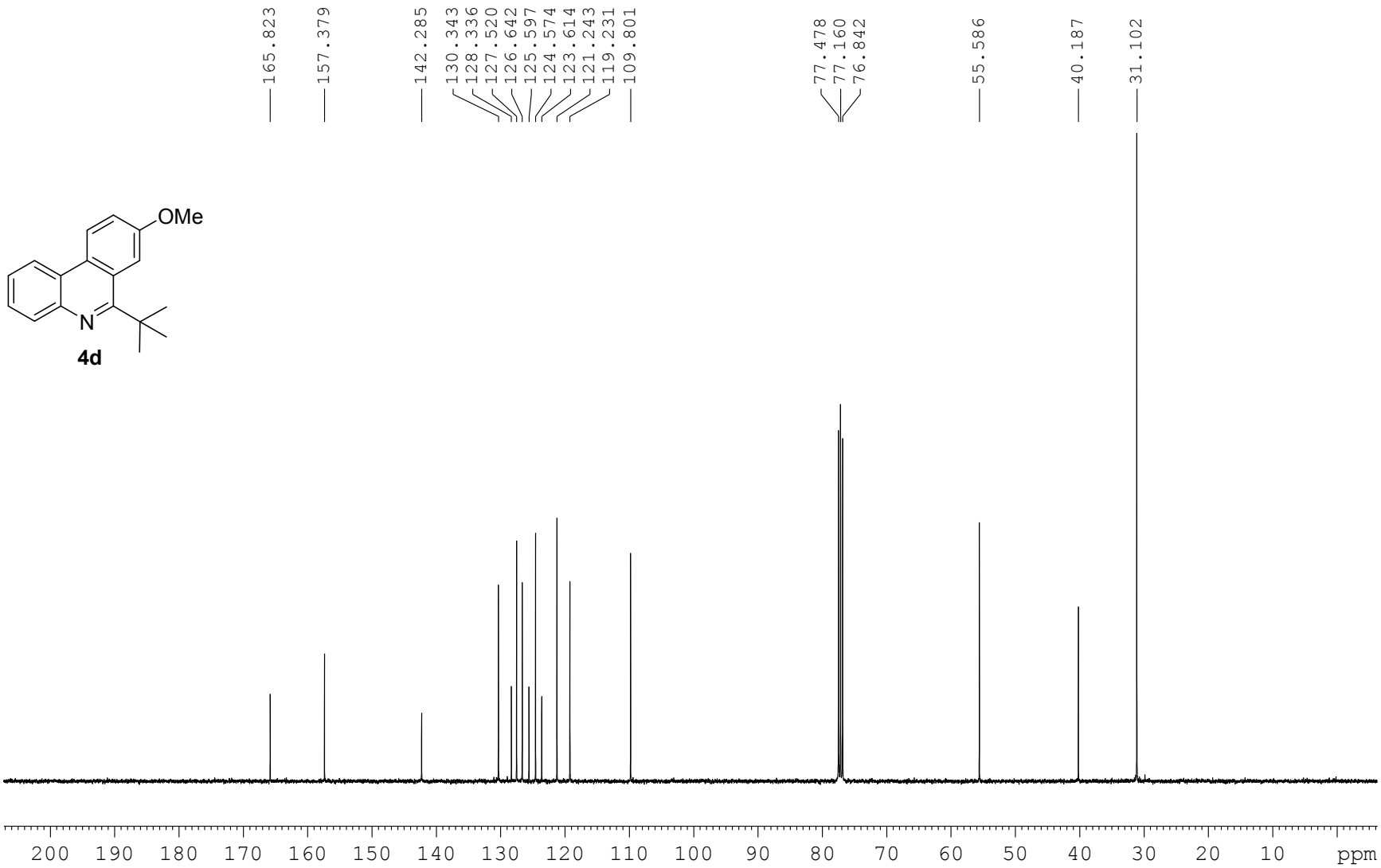


Figure S12. ^{13}C NMR spectrum of **4d** ($CDCl_3$, 100 MHz).

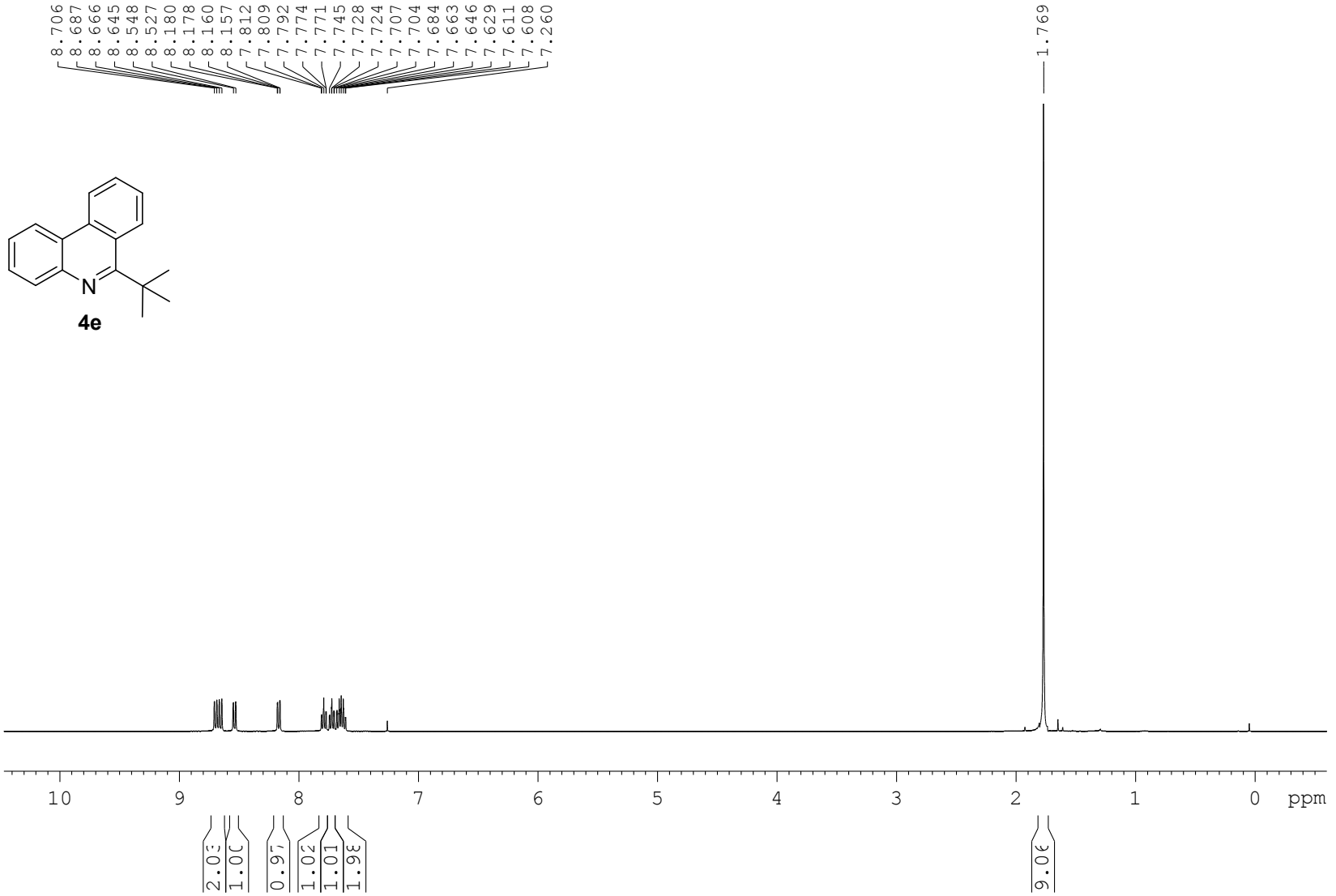

8.706
8.687
8.666
8.645
8.548
8.527
8.180
8.178
8.160
8.157
7.812
7.809
7.792
7.774
7.771
7.745
7.728
7.724
7.707
7.704
7.684
7.663
7.646
7.629
7.611
7.608
7.260
1.769
N
4e
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
1.00
0.97
1.02
1.01
1.93
9.06

Figure S13. ^{1}H NMR spectrum of **4e** ($CDCl_3$, 400 MHz).

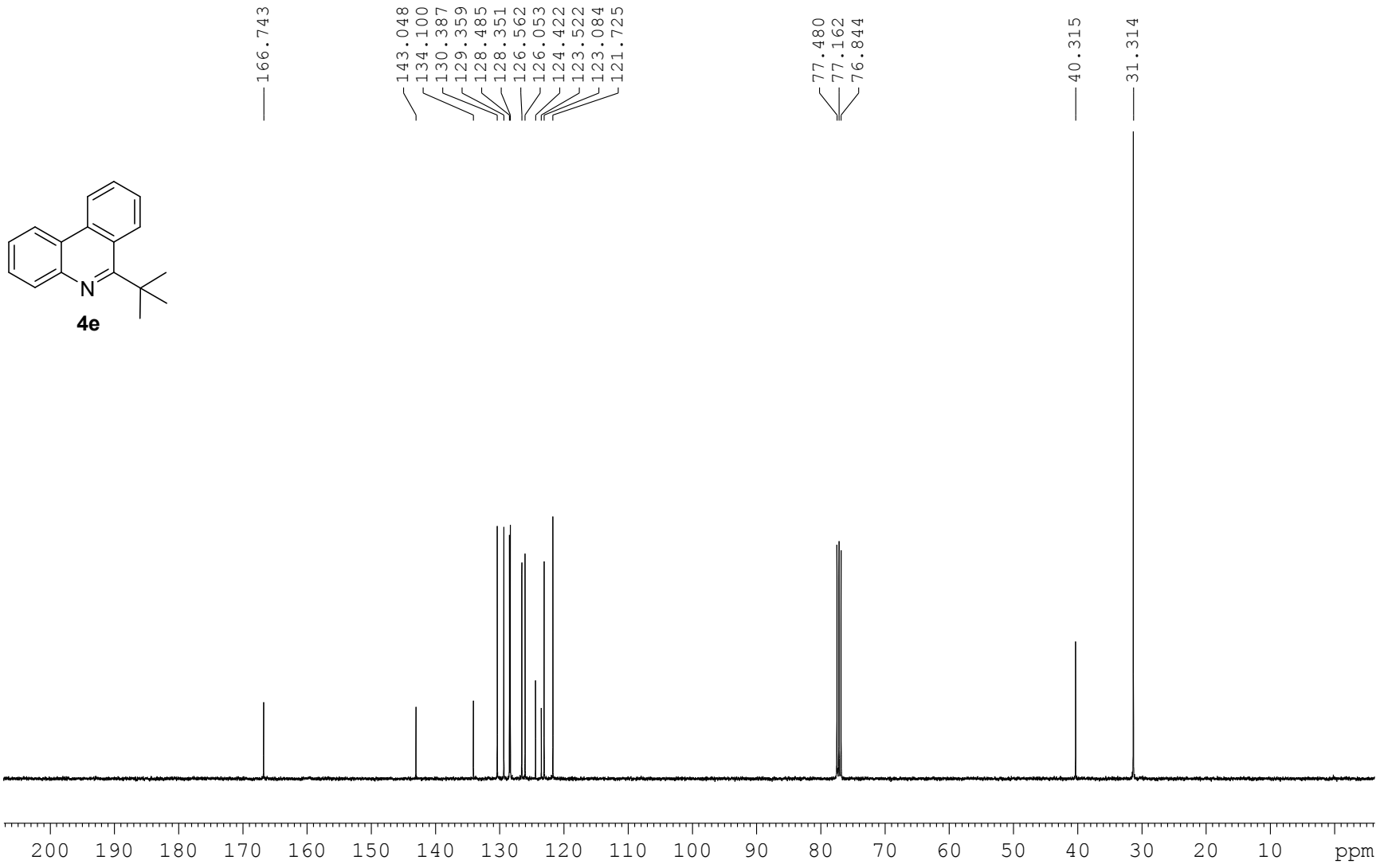


Figure S14. ^{13}C NMR spectrum of **4e** ($CDCl_3$, 100 MHz).

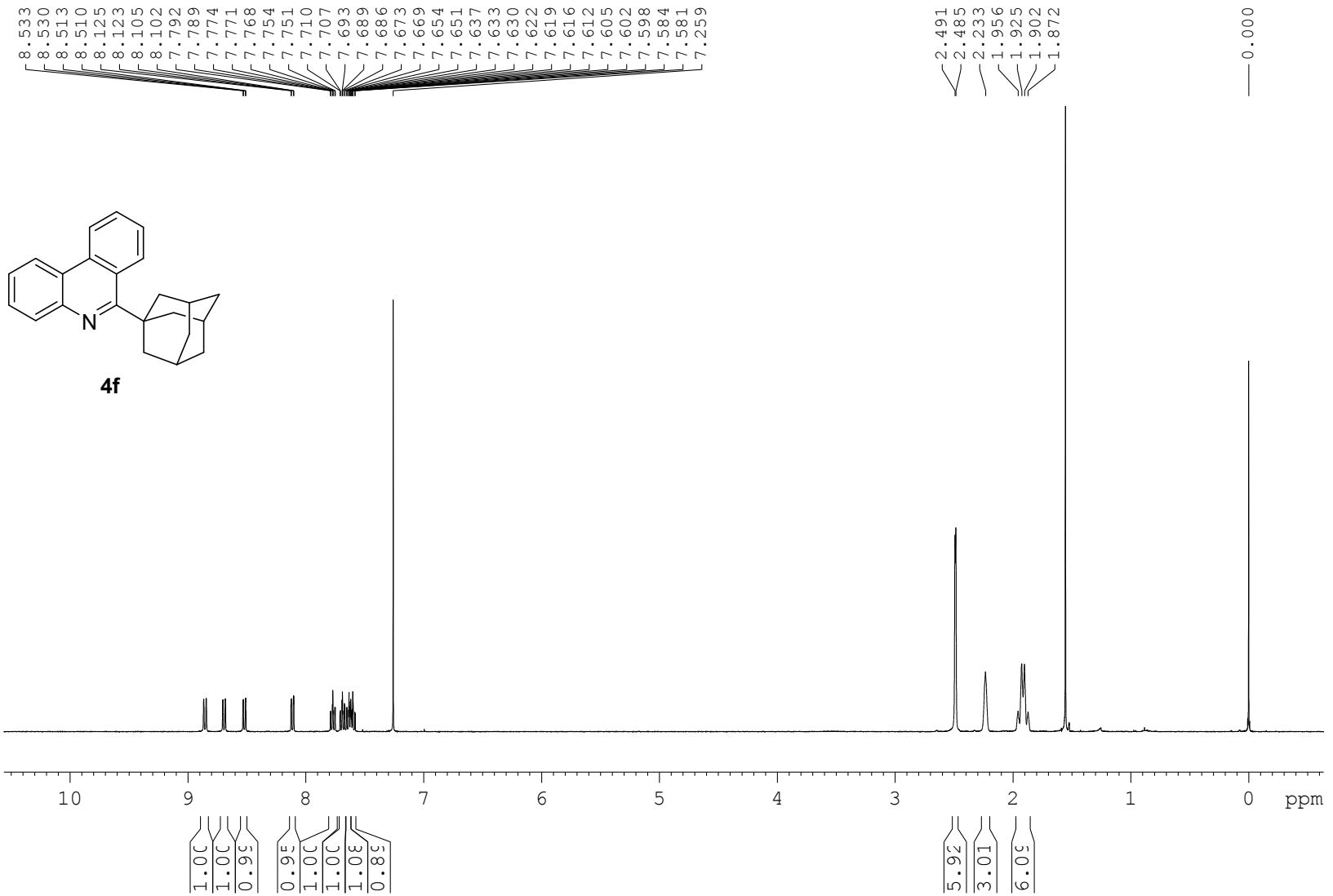


Figure S15. ^{1}H NMR spectrum of **4f** ($CDCl_3$, 400 MHz).

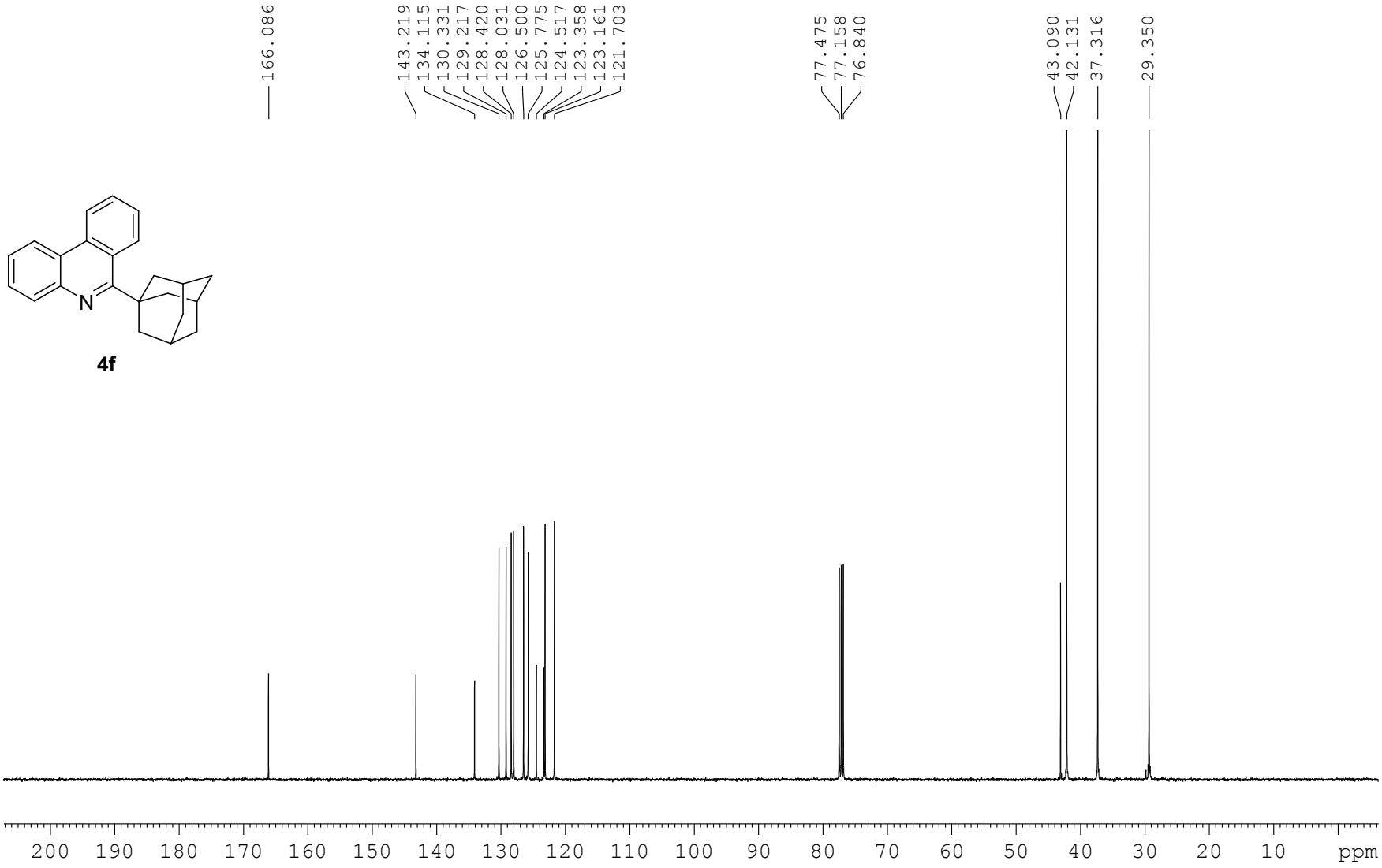


Figure S16. ^{13}C NMR spectrum of **4f** ($CDCl_3$, 100 MHz).

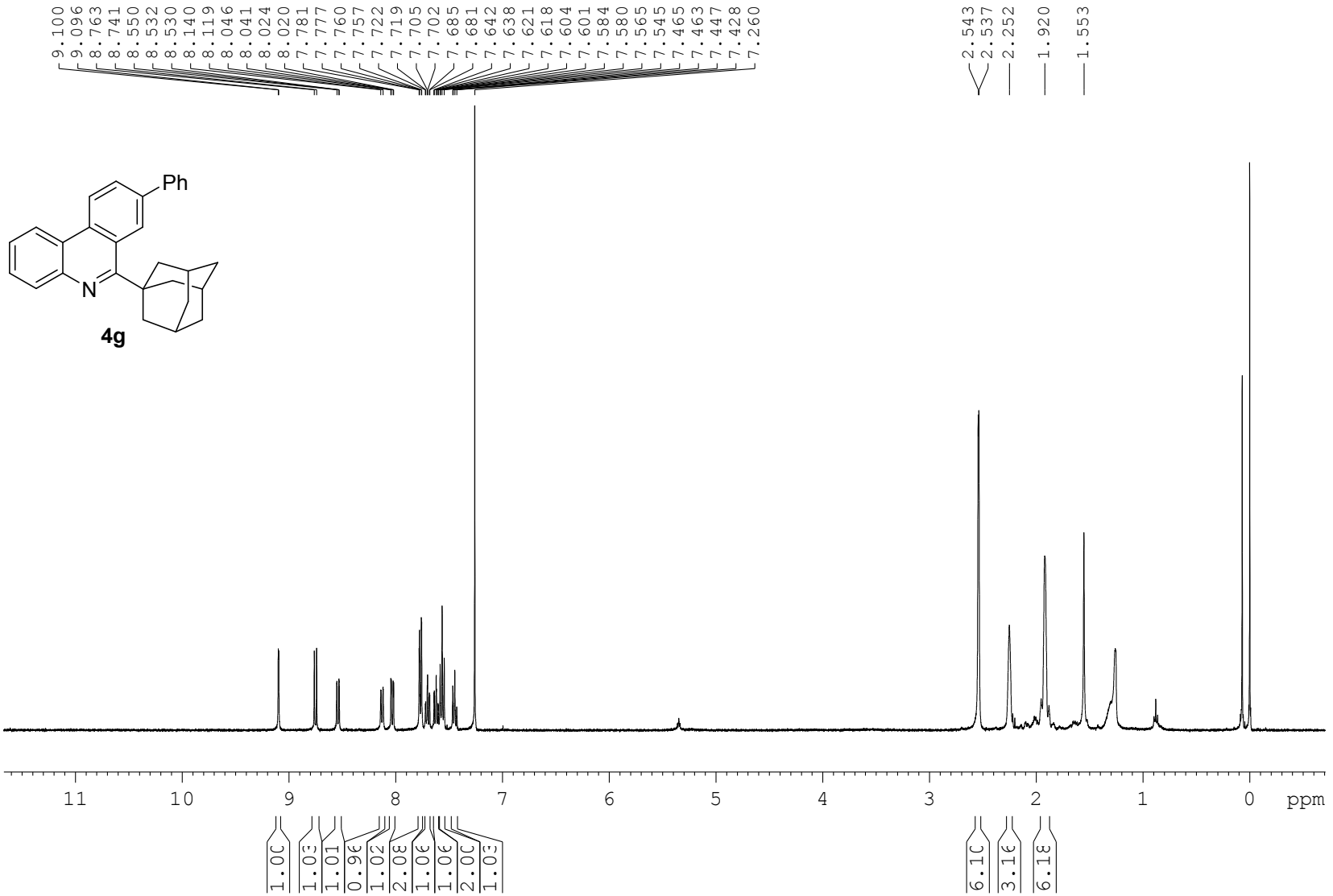


Figure S17. ^{1}H NMR spectrum of **4g** ($CDCl_3$, 400 MHz).

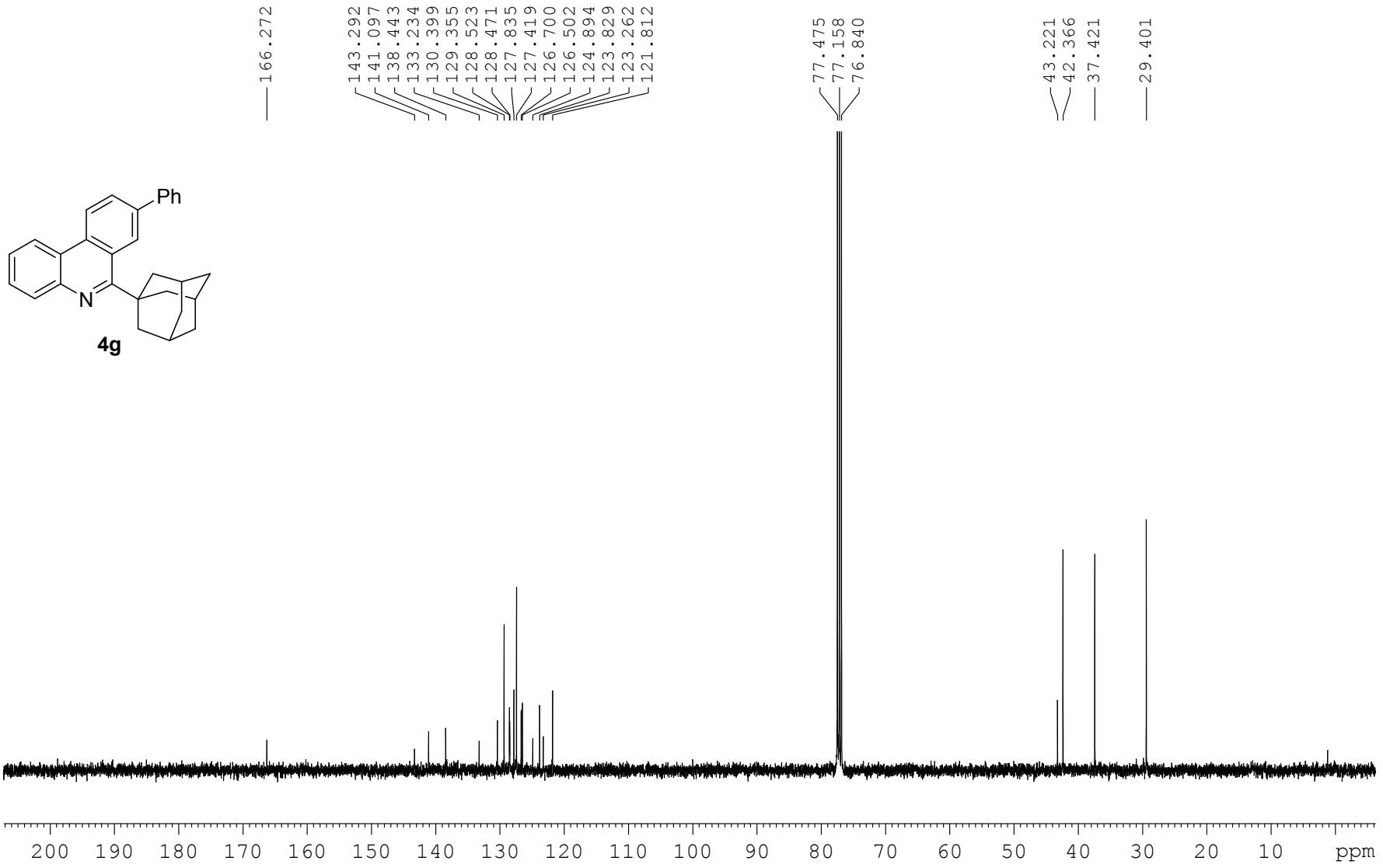


Figure S18. ^{13}C NMR spectrum of **4g** ($CDCl_3$, 100 MHz).

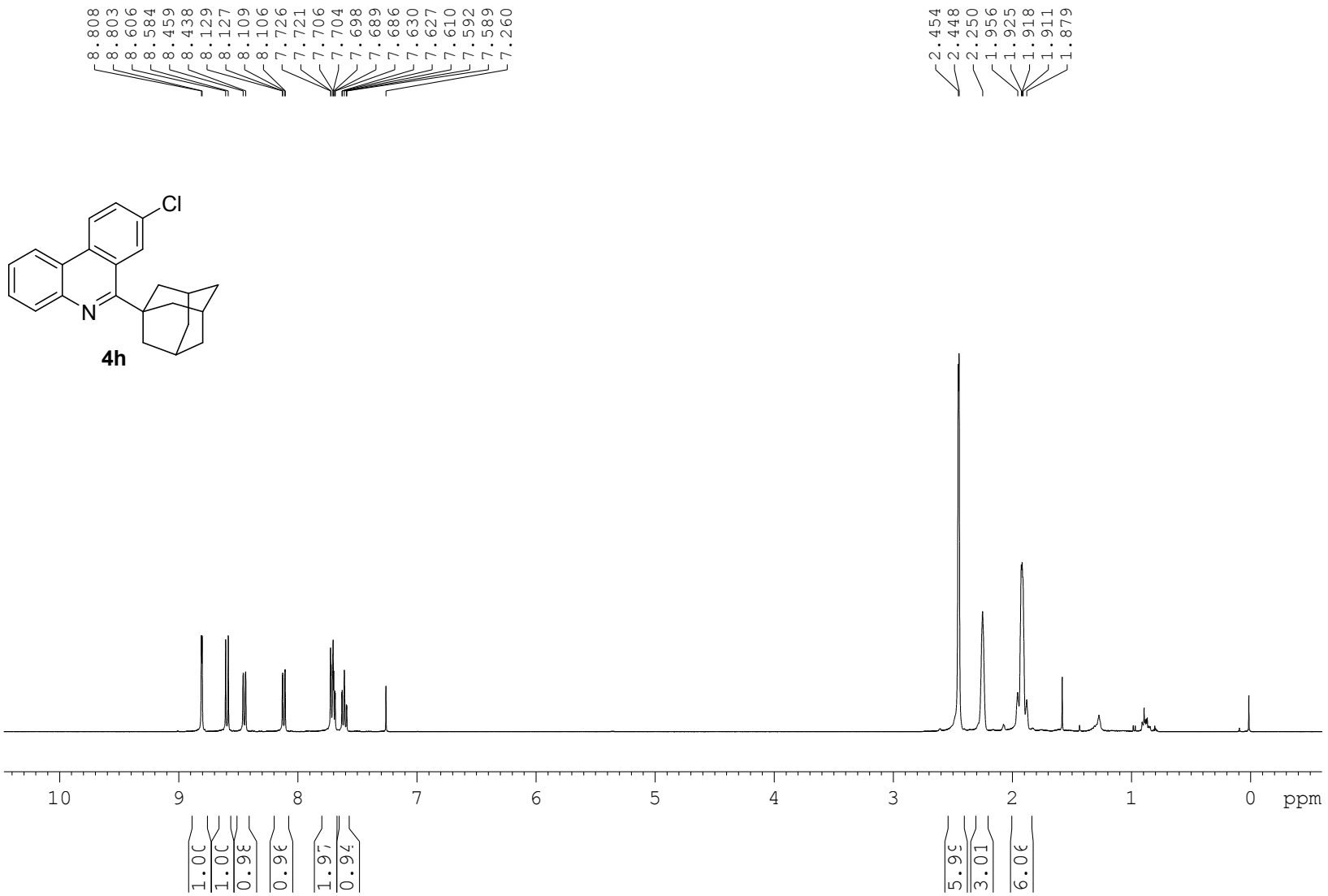

8.808
8.803
8.606
8.584
8.459
8.438
8.129
8.127
8.109
8.106
7.726
7.721
7.706
7.704
7.698
7.689
7.686
7.630
7.627
7.610
7.592
7.589
7.260
2.454
2.448
2.250
1.956
1.925
1.918
1.911
1.879
Cl
N
4h
10
9
8
7
6
5
4
3
2
1
0
ppm

Figure S19. ^{1}H NMR spectrum of **4h** ($CDCl_3$, 400 MHz).

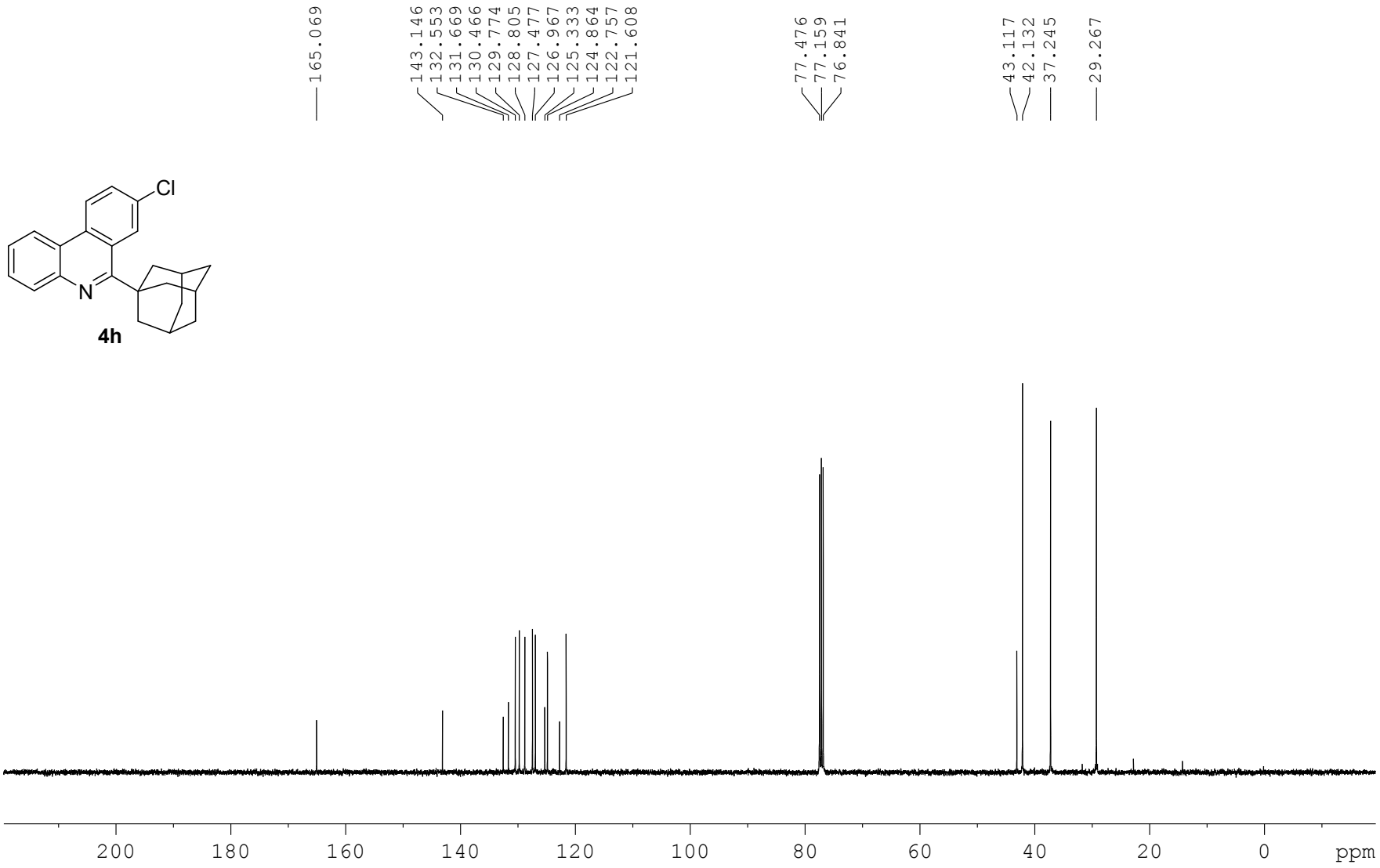
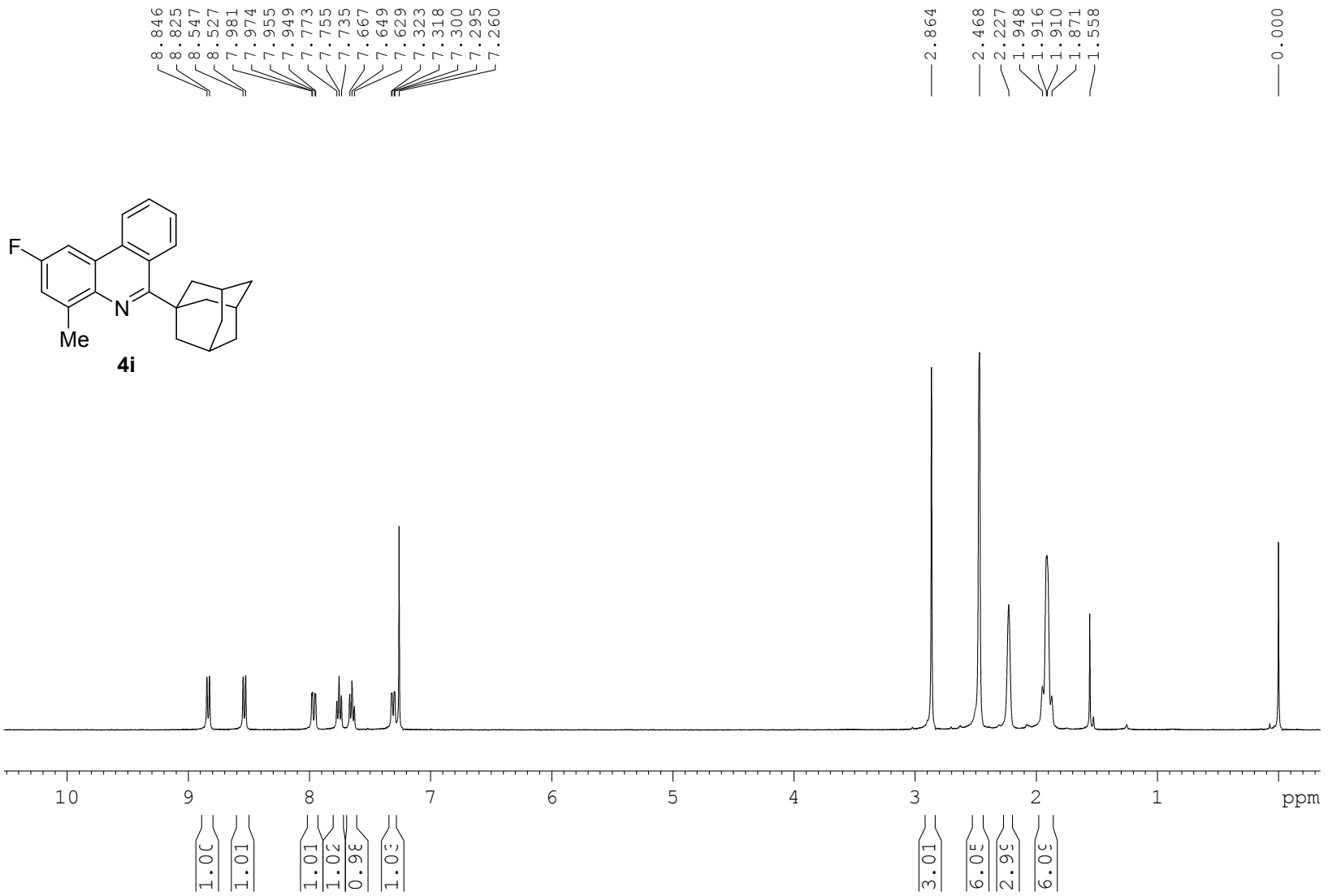


Figure S20. ^{13}C NMR spectrum of **4h** ($CDCl_3$, 100 MHz).


8.846
8.825
8.547
8.527
7.981
7.974
7.955
7.949
7.773
7.755
7.735
7.667
7.649
7.629
7.323
7.318
7.300
7.295
7.260
2.864
2.468
2.227
1.948
1.916
1.910
1.871
1.558
0.000
F
N
Me
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.01
1.02
0.96
1.03
3.01
6.05
2.95
6.05

4i

Figure S21. ^{1}H NMR spectrum of **4i** ($CDCl_3$, 400 MHz).

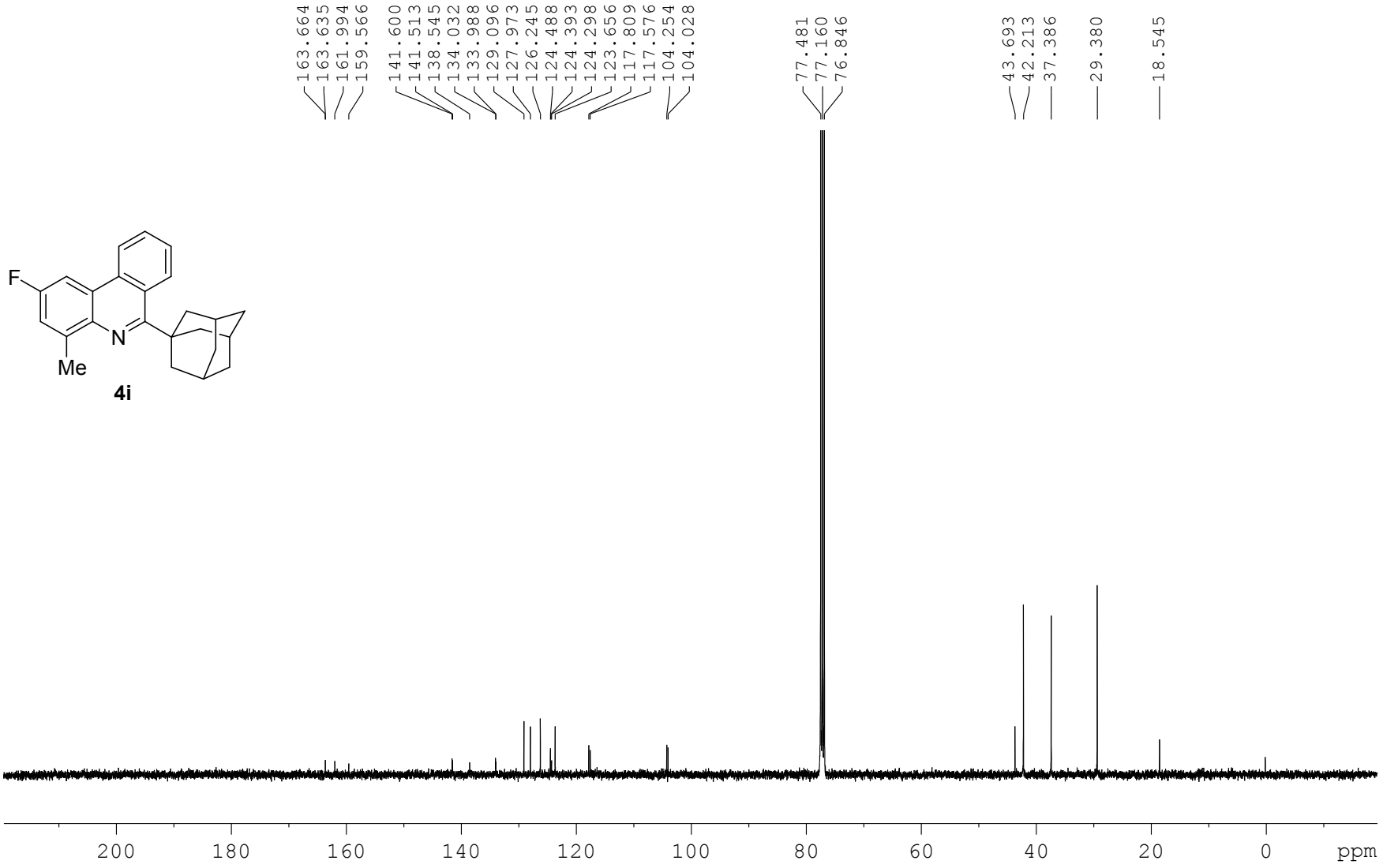
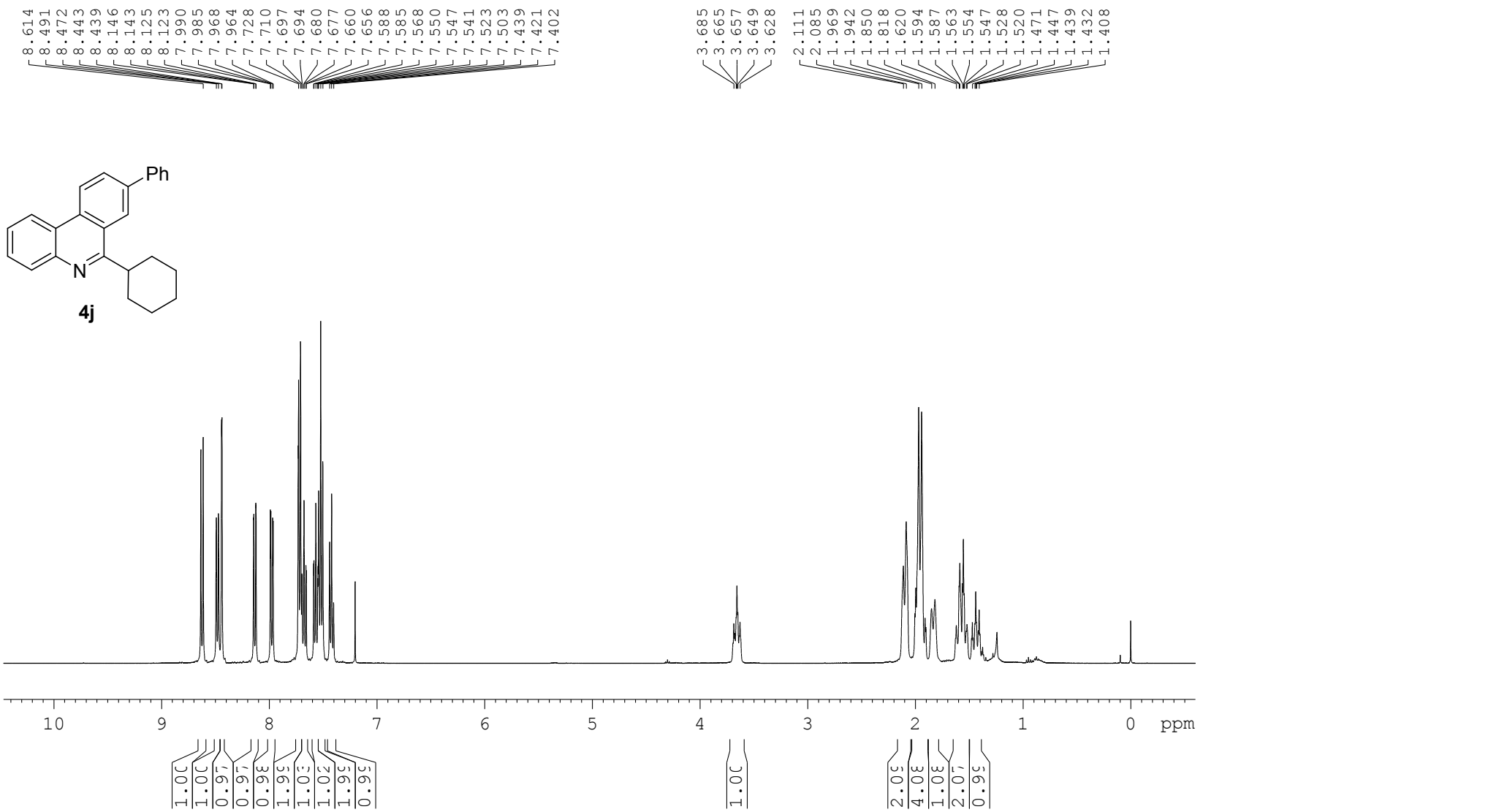


Figure S22. ^{13}C NMR spectrum of **4i** ($CDCl_3$, 100 MHz).


8.614
8.491
8.472
8.443
8.439
8.146
8.143
8.125
8.123
7.990
7.985
7.968
7.964
7.728
7.710
7.697
7.694
7.680
7.677
7.660
7.656
7.588
7.585
7.568
7.550
7.547
7.541
7.523
7.503
7.439
7.421
7.402
3.685
3.665
3.657
3.649
3.628
2.111
2.085
1.969
1.942
1.850
1.818
1.620
1.594
1.587
1.563
1.554
1.547
1.528
1.520
1.471
1.447
1.439
1.432
1.408
Ph
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4j
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9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
0.97
0.97
0.96
1.99
1.03
1.02
1.95
0.95
1.00
2.00
4.00
1.00
2.07
0.95

Figure S23. ^{1}H NMR spectrum of **4j** ($CDCl_3$, 400 MHz).

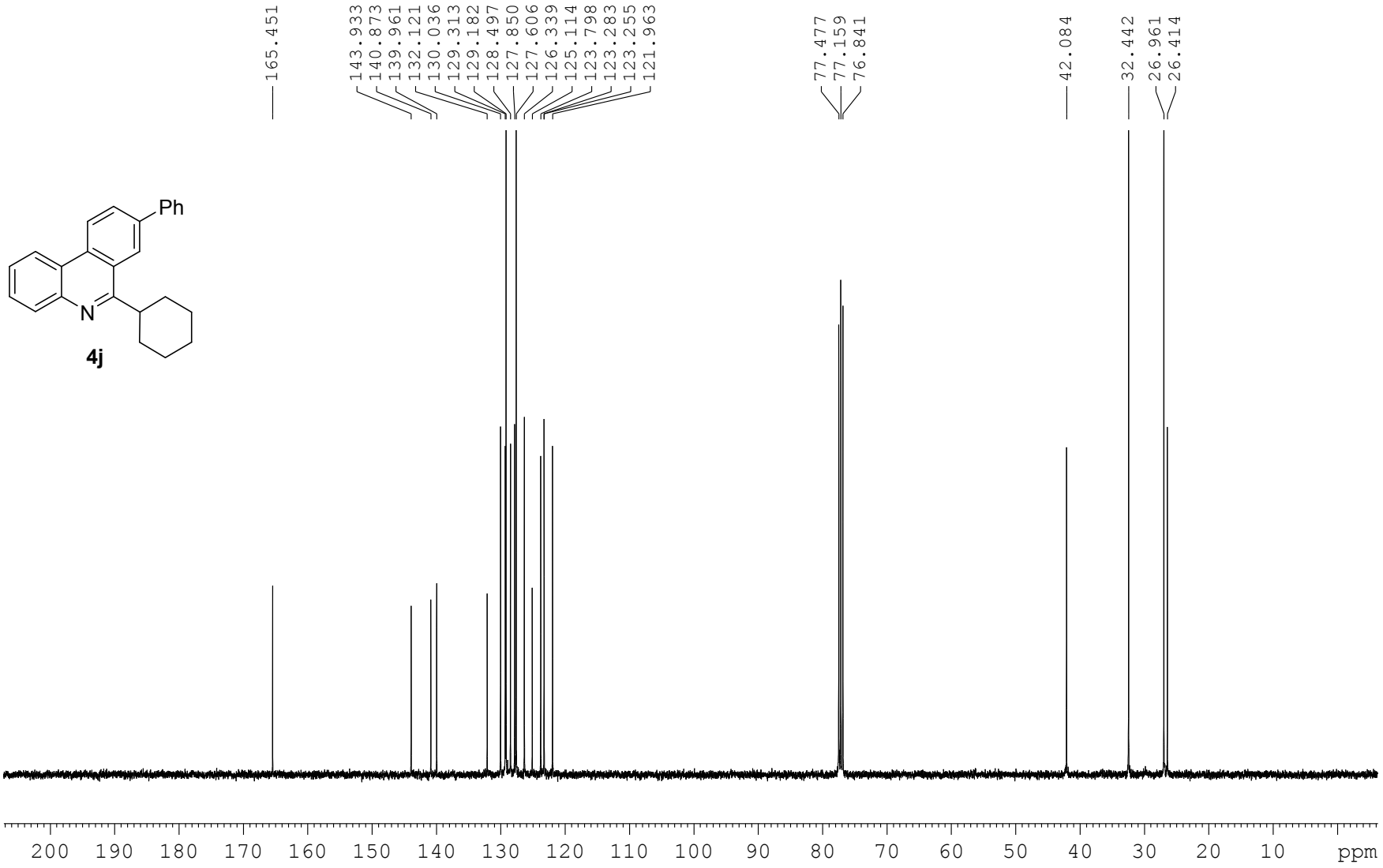


Figure S24. ^{13}C NMR spectrum of **4j** ($CDCl_3$, 100 MHz).

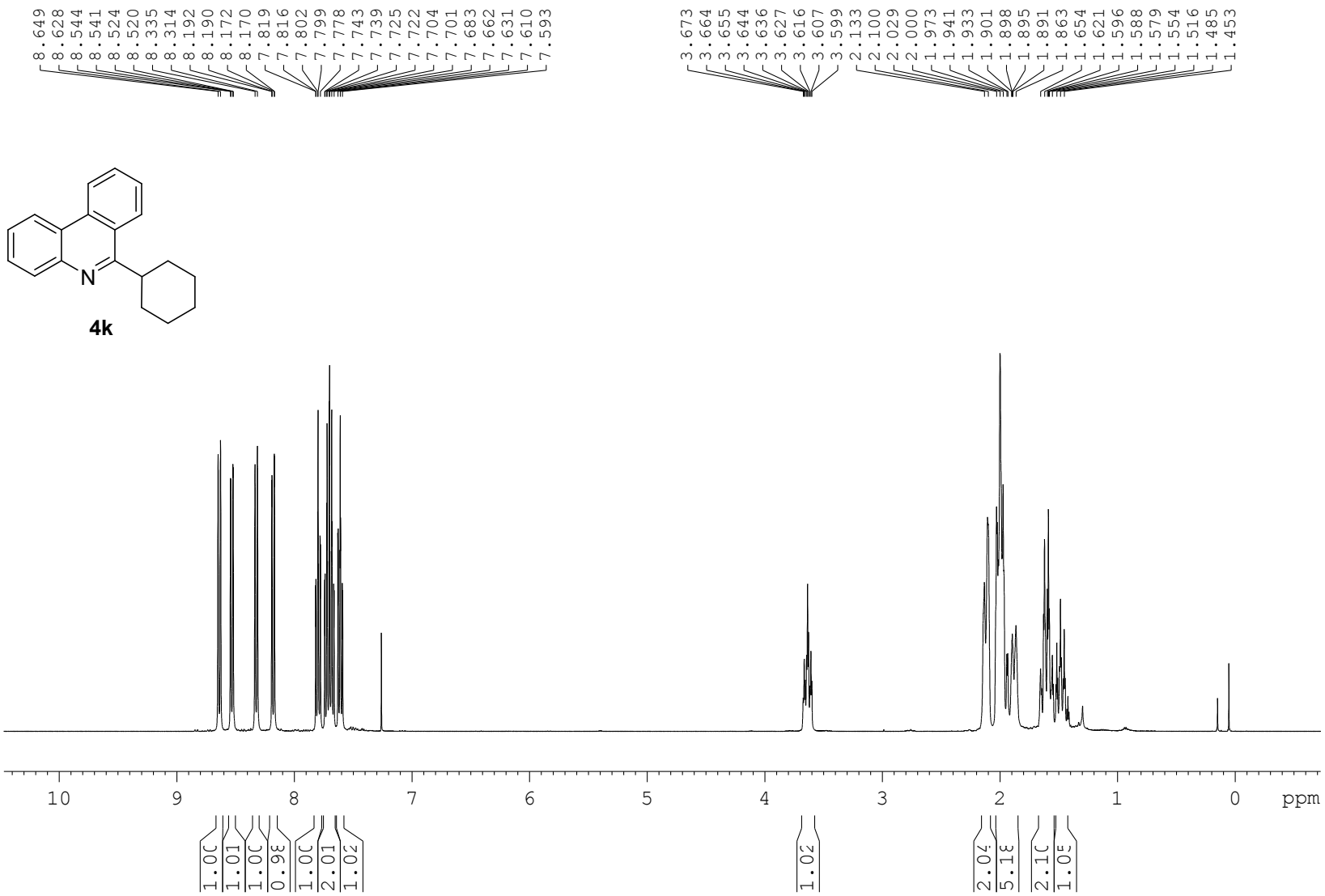


Figure S25. ^{1}H NMR spectrum of **4k** ($CDCl_3$, 400 MHz).

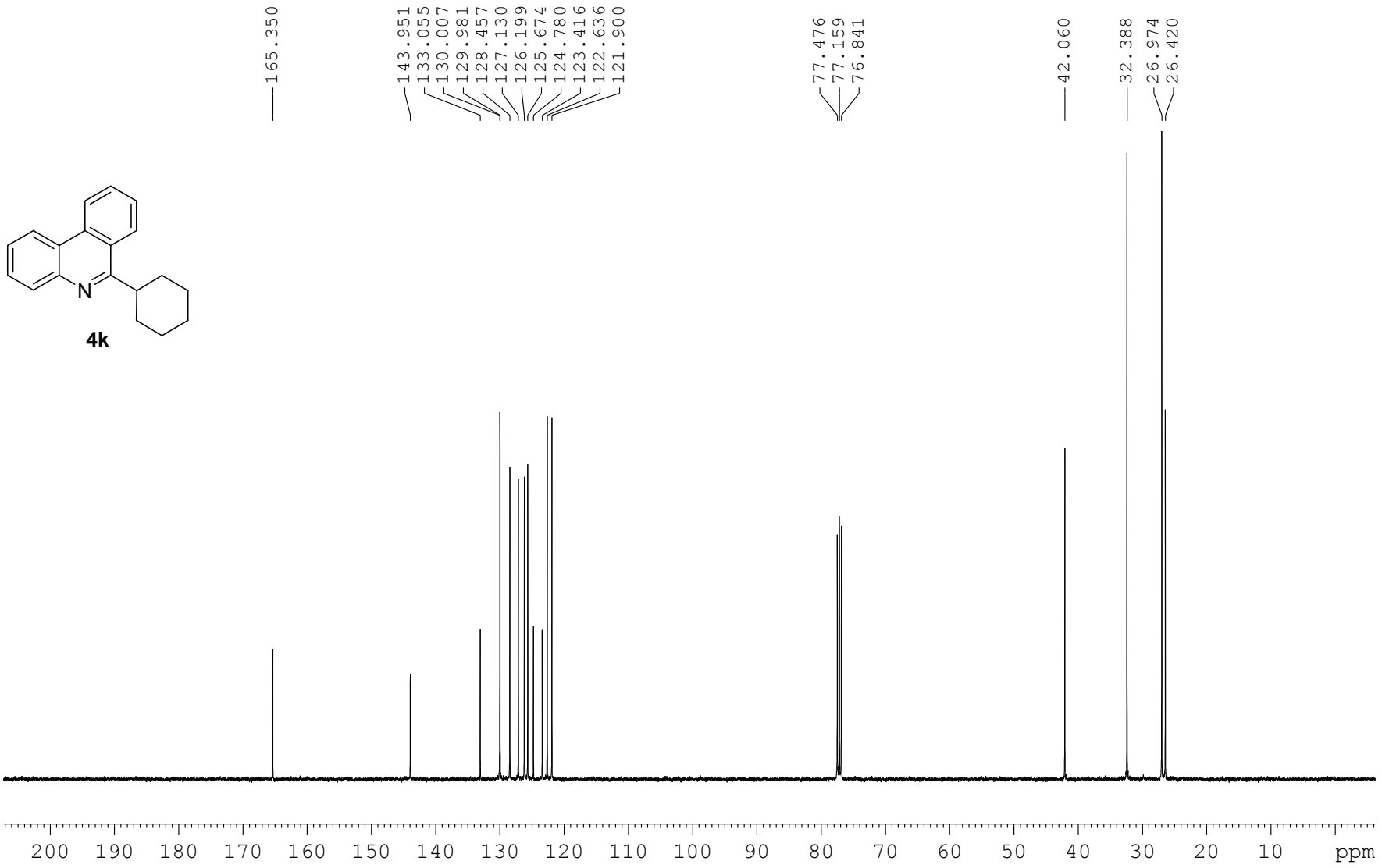


Figure S26. ^{13}C NMR spectrum of **4k** ($CDCl_3$, 100 MHz).

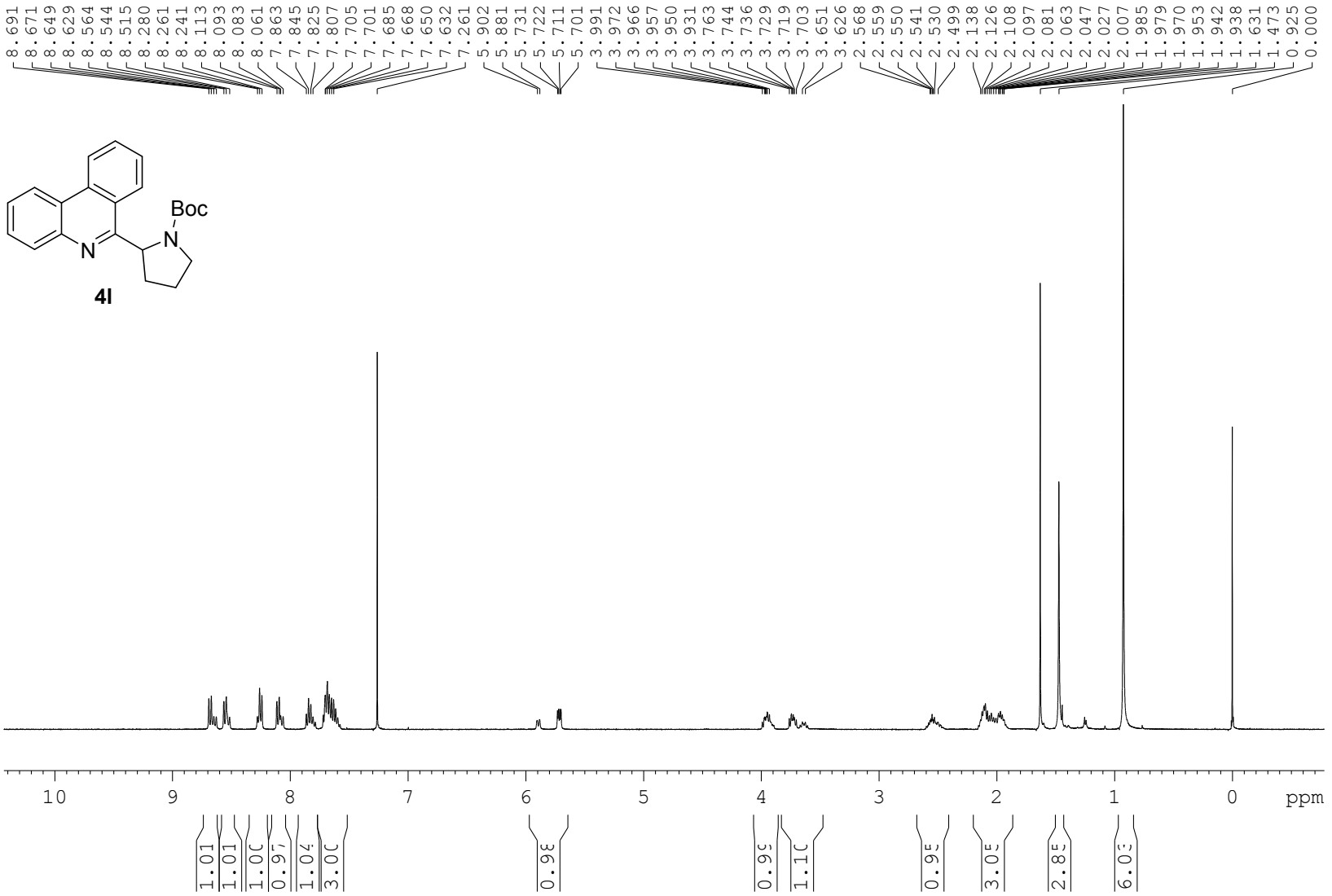

8.691
8.671
8.649
8.629
8.564
8.544
8.515
8.280
8.261
8.241
8.113
8.093
8.083
8.061
7.863
7.845
7.825
7.807
7.705
7.701
7.685
7.668
7.650
7.632
7.261
5.902
5.881
5.731
5.722
5.711
5.701
3.991
3.972
3.966
3.957
3.950
3.931
3.763
3.744
3.736
3.729
3.719
3.703
3.651
3.626
2.568
2.559
2.550
2.541
2.530
2.499
2.138
2.126
2.108
2.097
2.081
2.063
2.047
2.027
2.007
1.985
1.979
1.970
1.953
1.942
1.938
1.631
1.473
0.925
0.000
Boc
N
N
4l
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.01
1.00
0.97
1.04
3.00
0.93
0.95
1.10
0.95
3.05
2.85
6.03

Figure S27. ^{1}H NMR spectrum of **4l** ($CDCl_3$, 400 MHz).

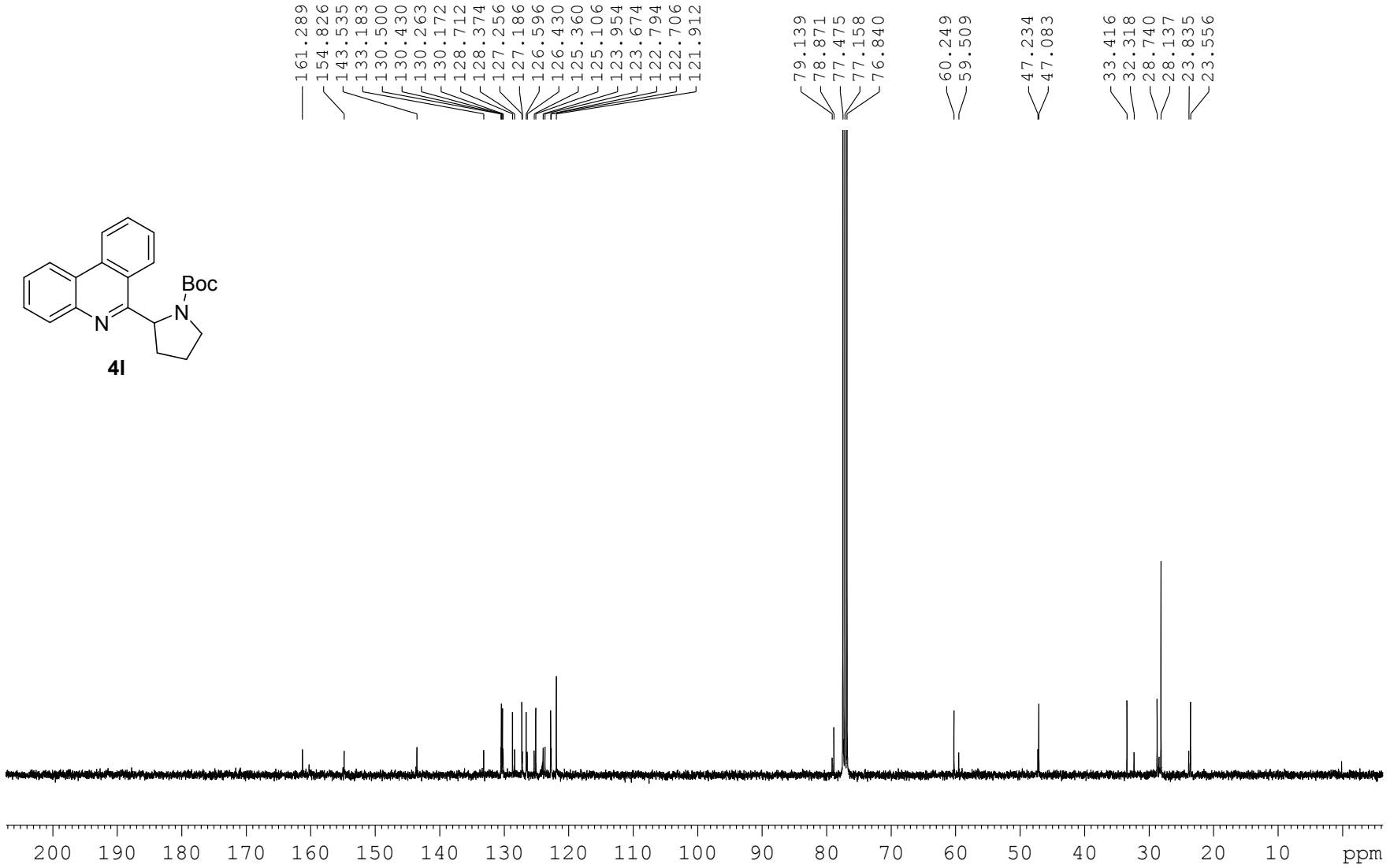


Figure S28. ^{13}C NMR spectrum of **4l** ($CDCl_3$, 100 MHz).

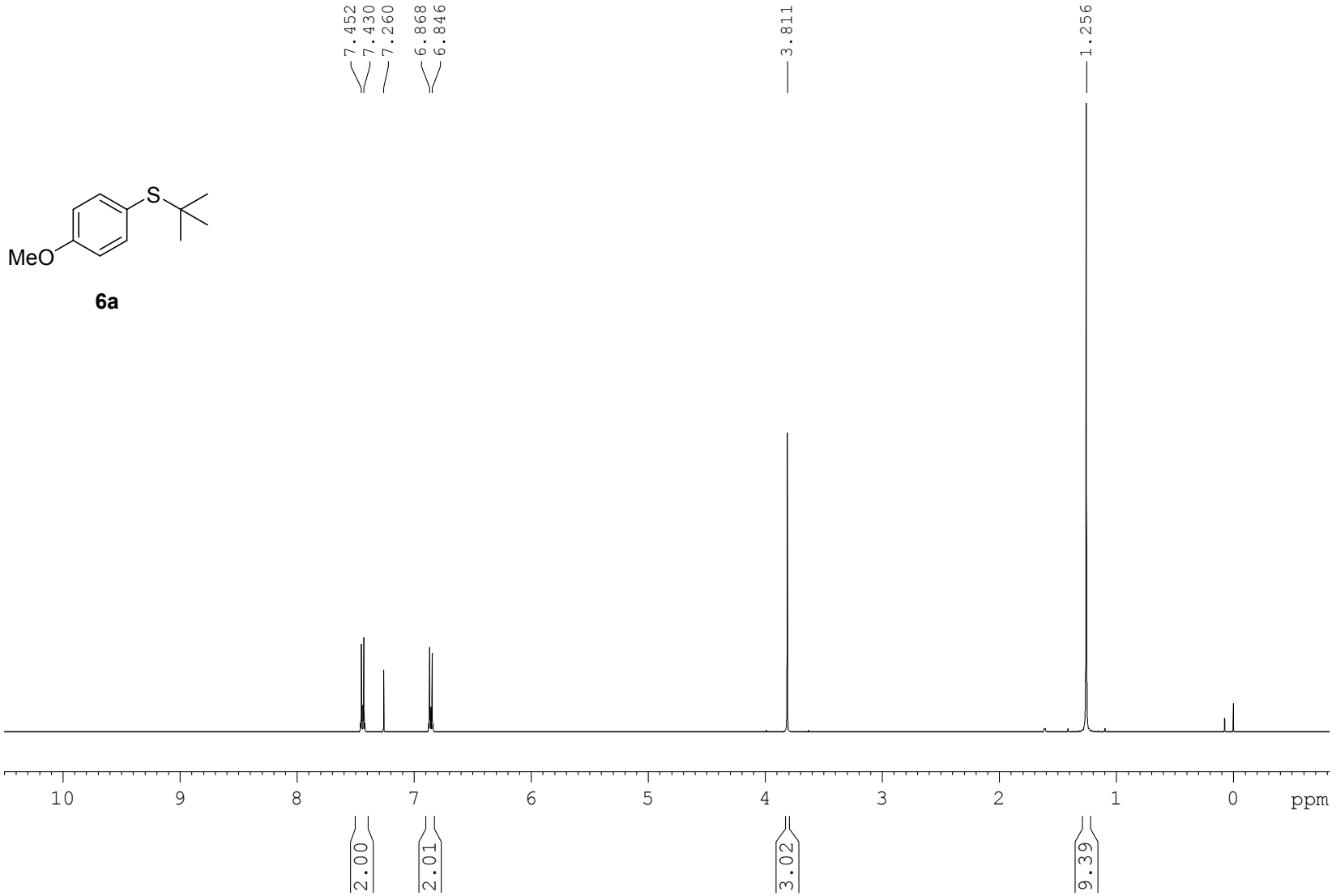


Figure S29. ^{1}H NMR spectrum of **6a** ($CDCl_3$, 400 MHz).

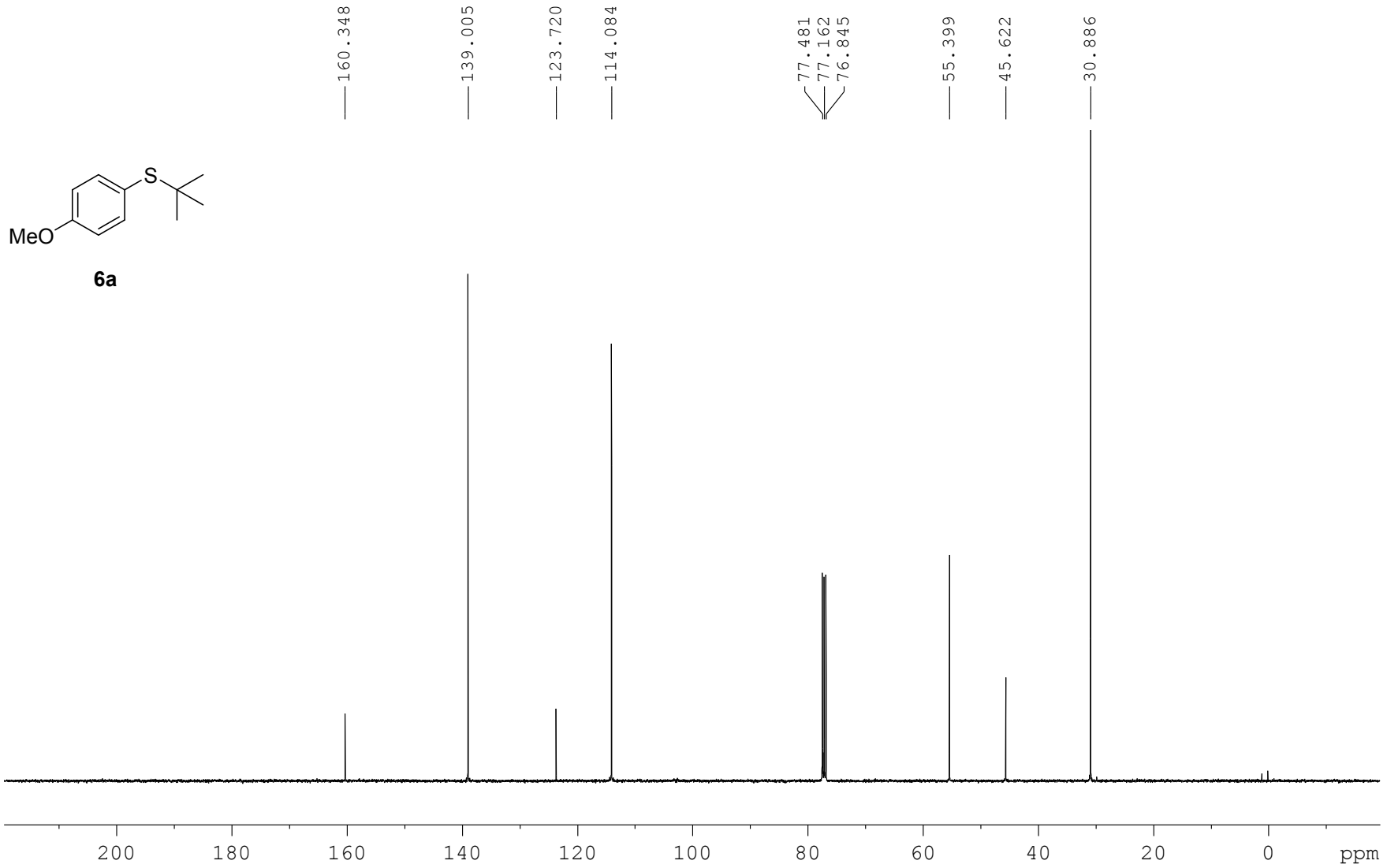
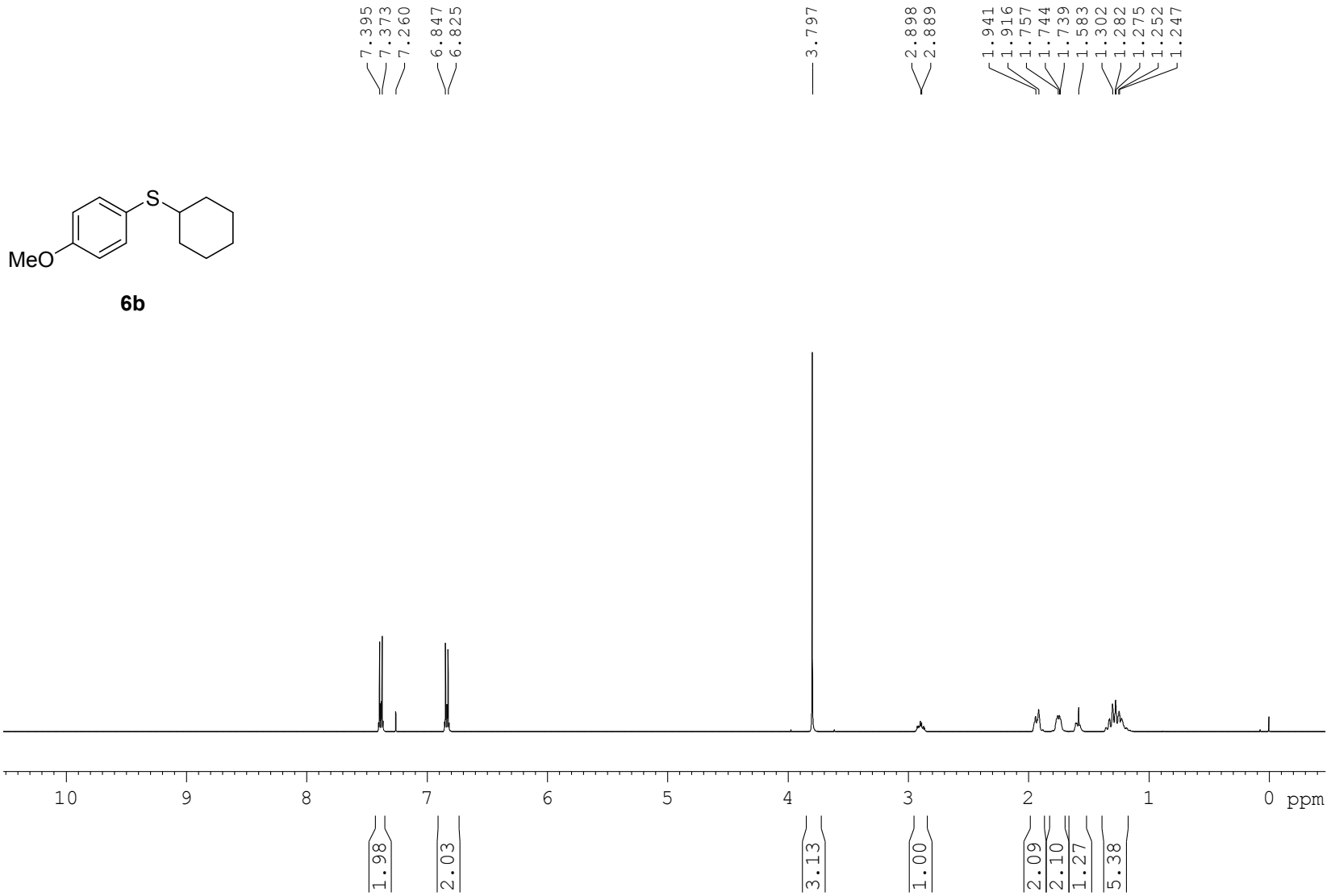


Figure S30. ^{13}C NMR spectrum of **6a** ($CDCl_3$, 100 MHz).


7.395
7.373
7.260
6.847
6.825
3.797
2.898
2.889
1.941
1.916
1.757
1.744
1.739
1.583
1.302
1.282
1.275
1.252
1.247
S
MeO
10
9
8
7
6
5
4
3
2
1
0 ppm
1.98
2.03
3.13
1.00
2.09
2.10
1.27
5.38

6b

Figure S31. ^{1}H NMR spectrum of **6b** ($CDCl_3$, 400 MHz).

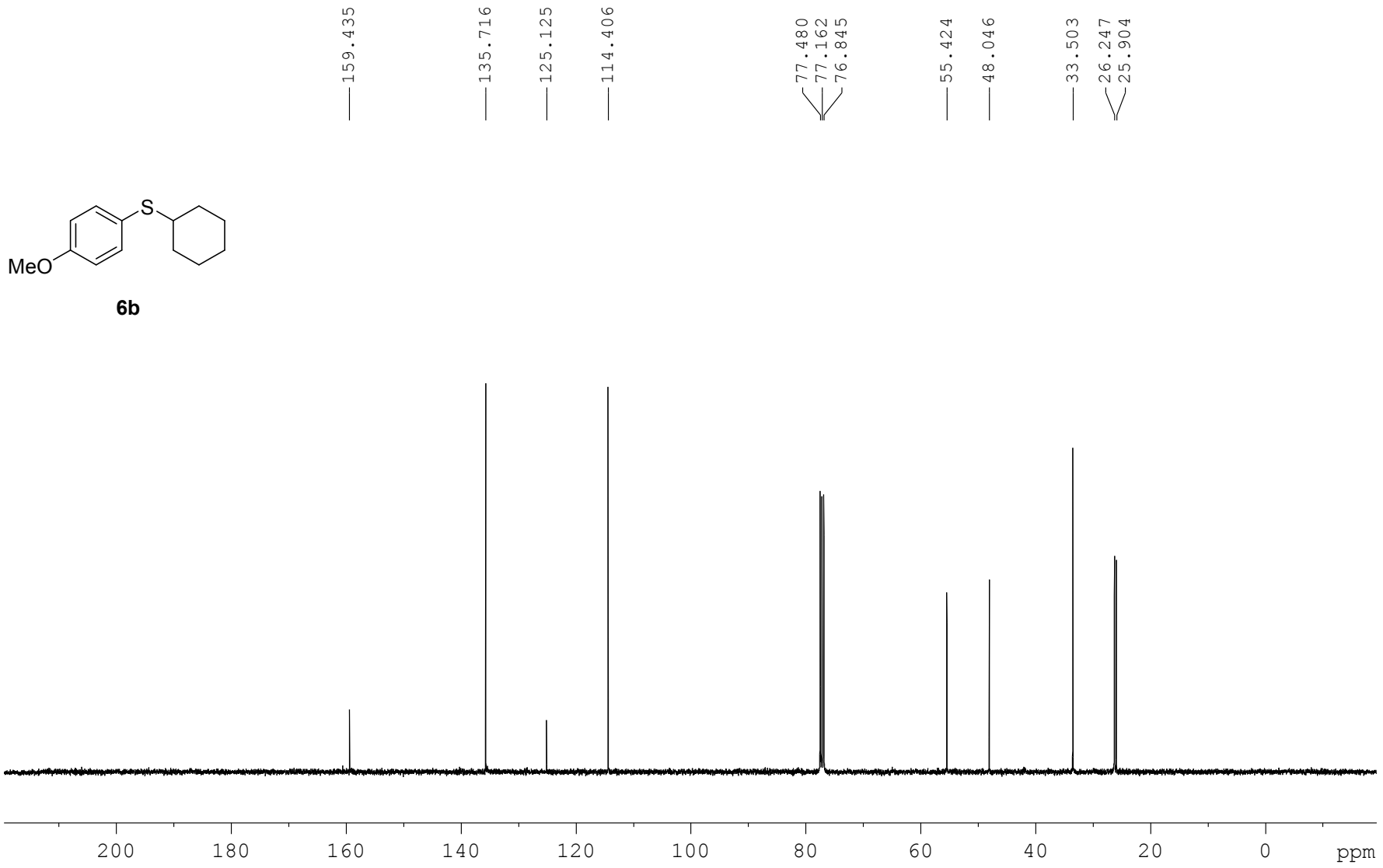
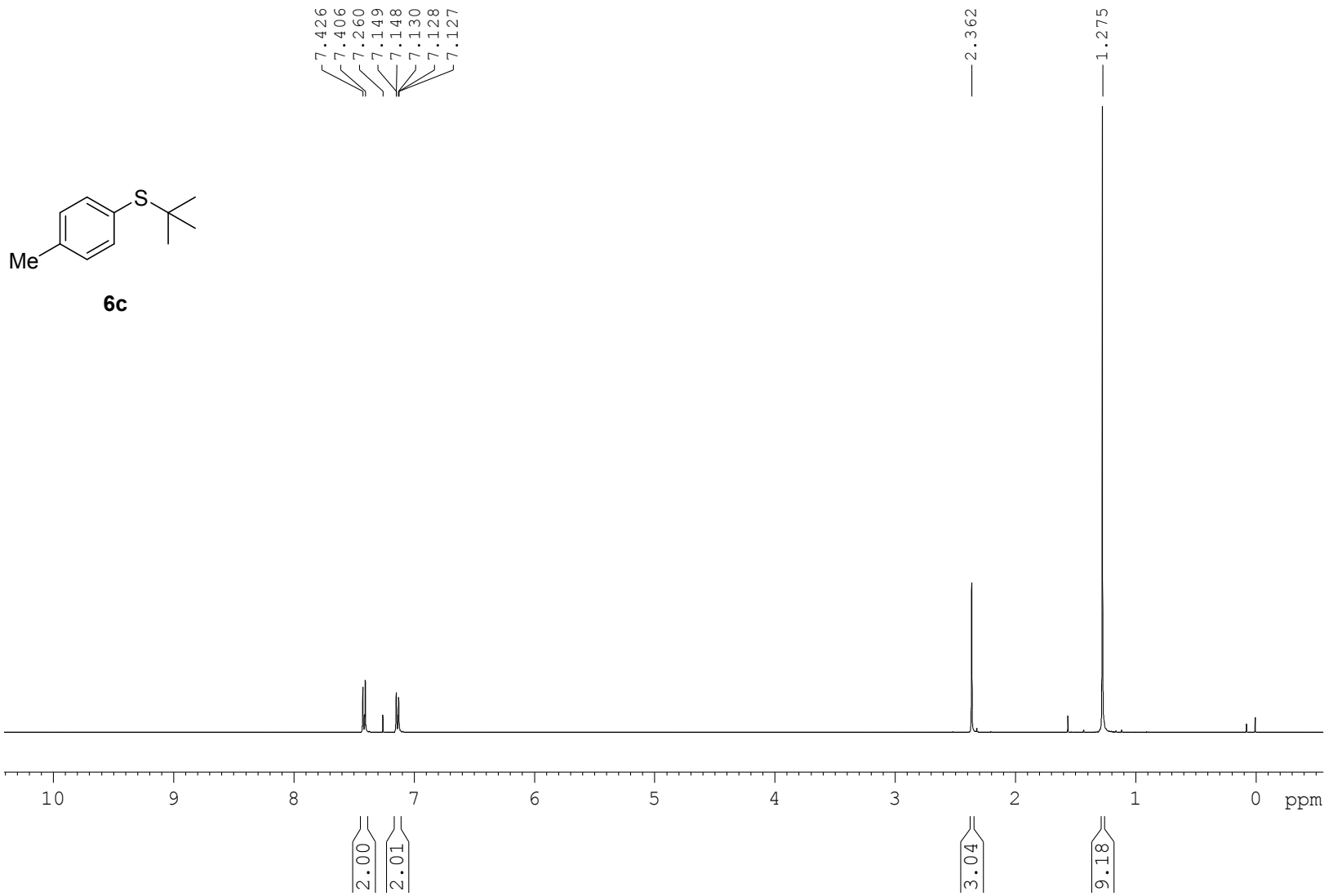


Figure S32. ^{13}C NMR spectrum of **6b** ($CDCl_3$, 100 MHz).


7.426
7.406
7.260
7.149
7.148
7.130
7.128
7.127
2.362
1.275
S
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.01
3.04
9.18

6c

Figure S33. ^{1}H NMR spectrum of **6c** ($CDCl_3$, 400 MHz).

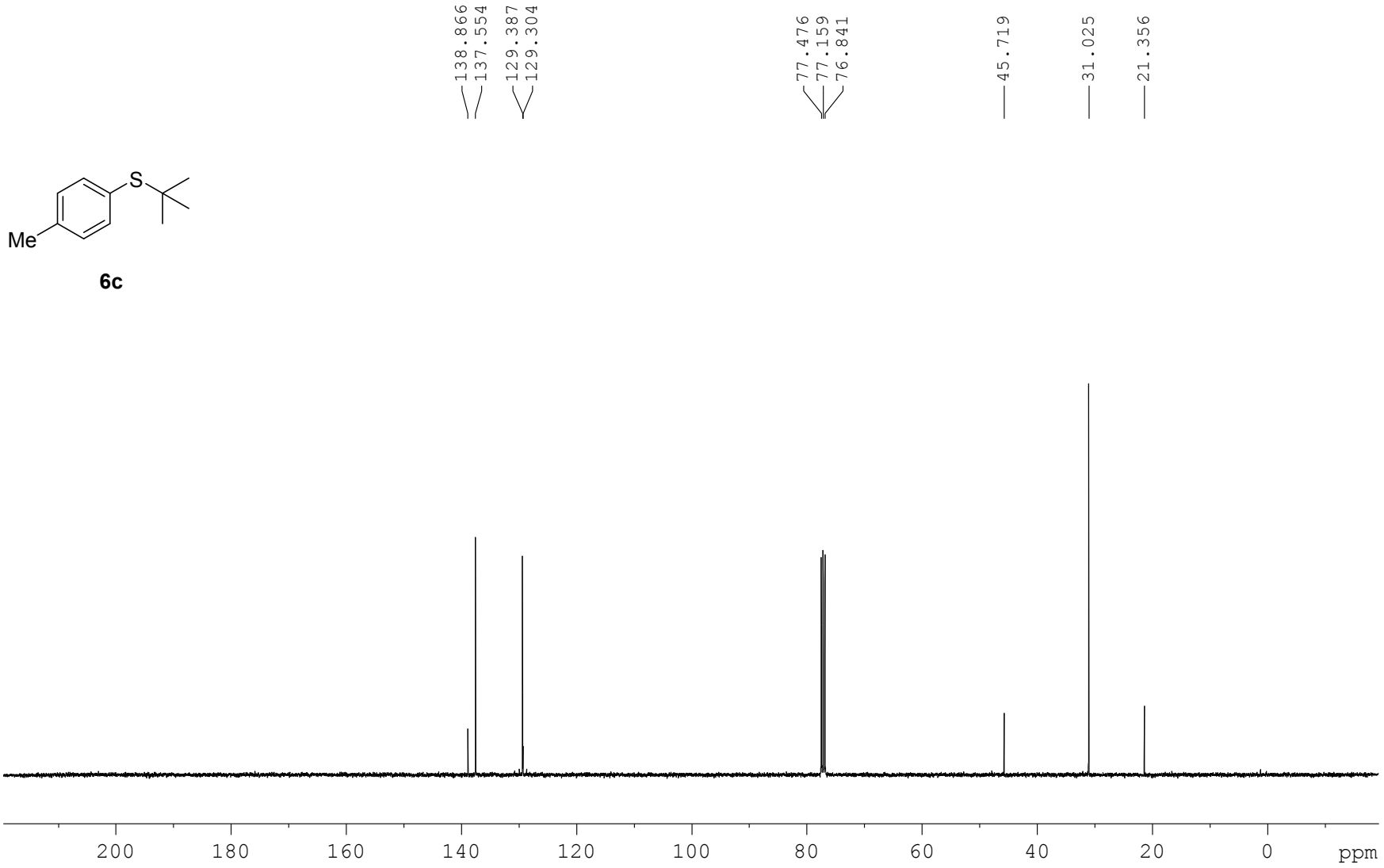
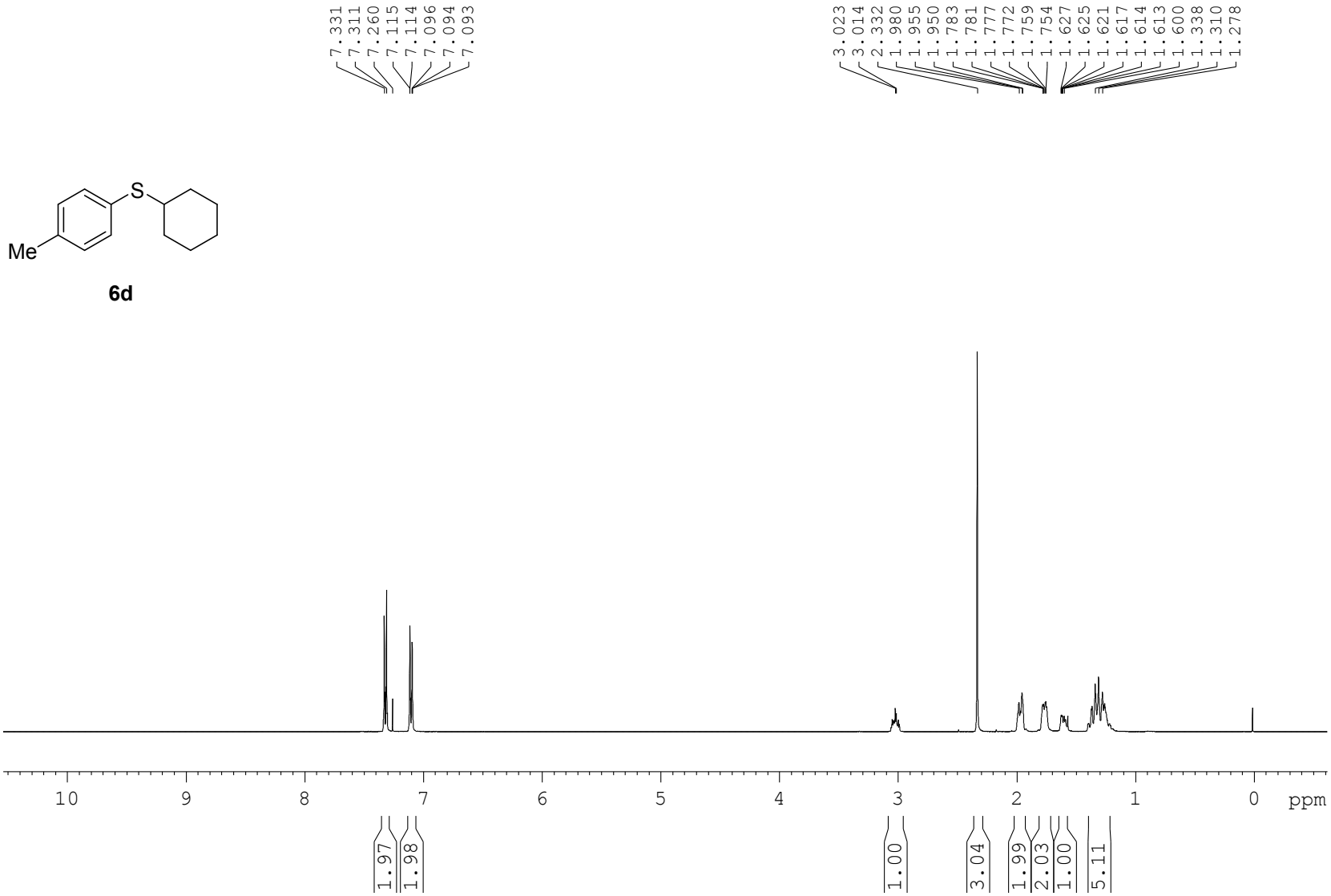


Figure S34. ^{13}C NMR spectrum of **6c** ($CDCl_3$, 100 MHz).


7.331
7.311
7.260
7.115
7.114
7.096
7.094
7.093
3.023
3.014
2.332
1.980
1.955
1.950
1.783
1.781
1.777
1.772
1.759
1.754
1.627
1.625
1.621
1.617
1.614
1.613
1.600
1.338
1.310
1.278
S
Me
10
9
8
7
6
5
4
3
2
1
0
ppm
1.97
1.98
1.00
3.04
1.99
2.03
1.00
5.11

6d

Figure S35. ^{1}H NMR spectrum of **6d** ($CDCl_3$, 400 MHz).

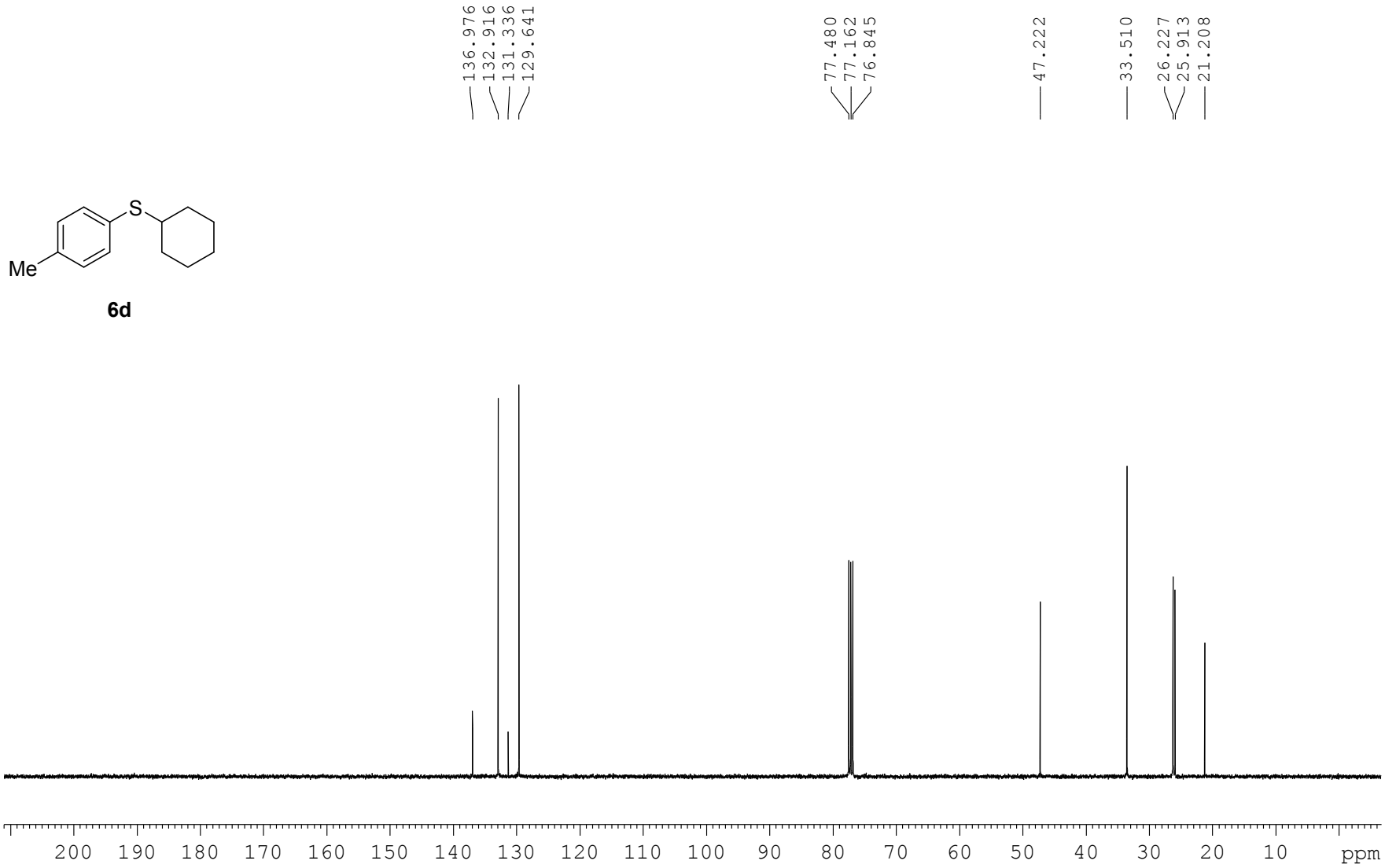
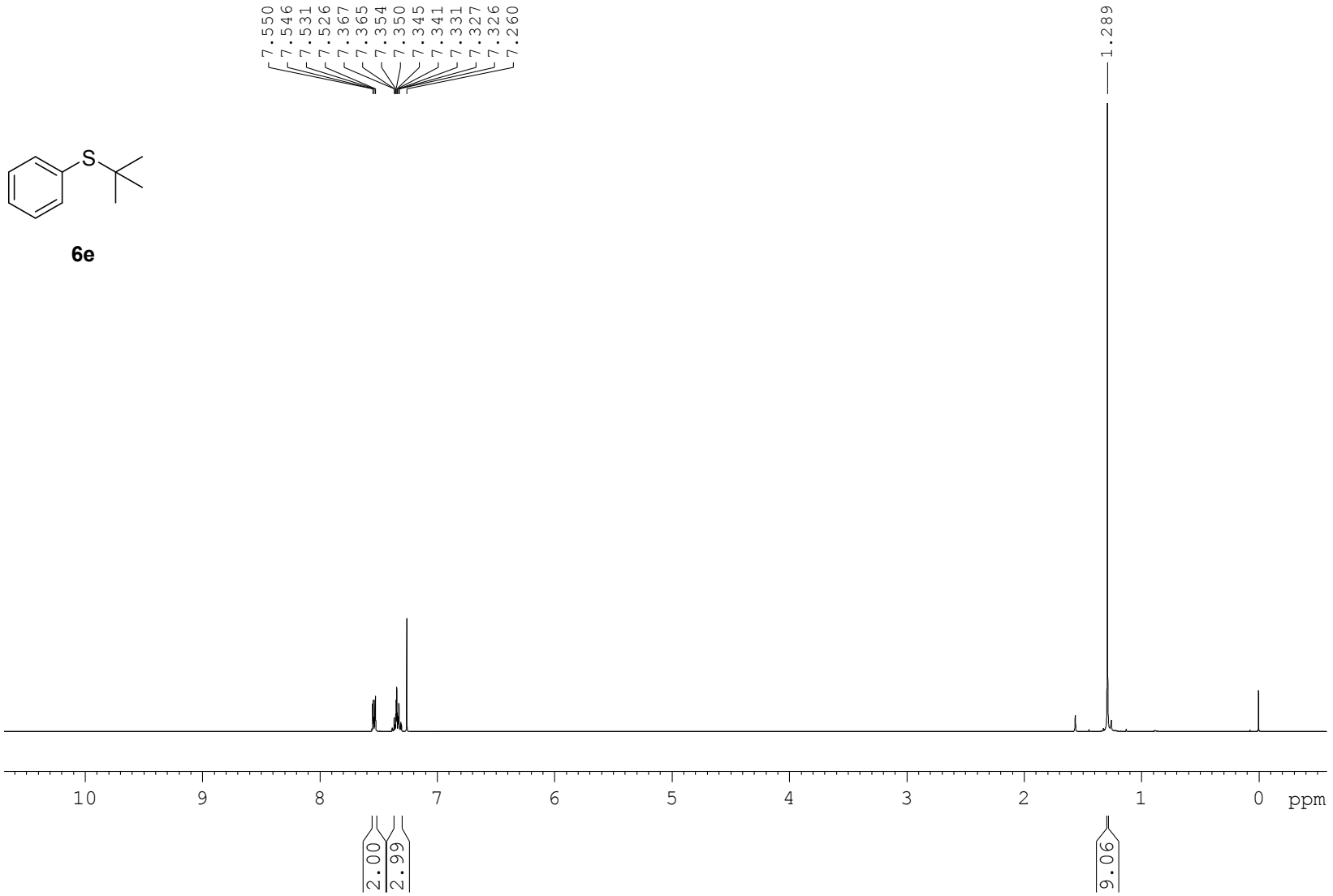


Figure S36. ^{13}C NMR spectrum of **6d** ($CDCl_3$, 100 MHz).


7.550
7.546
7.531
7.526
7.367
7.365
7.354
7.350
7.345
7.341
7.331
7.327
7.326
7.260
1.289
S
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.99
9.06

6e

Figure S37. ^{1}H NMR spectrum of **6e** ($CDCl_3$, 400 MHz).

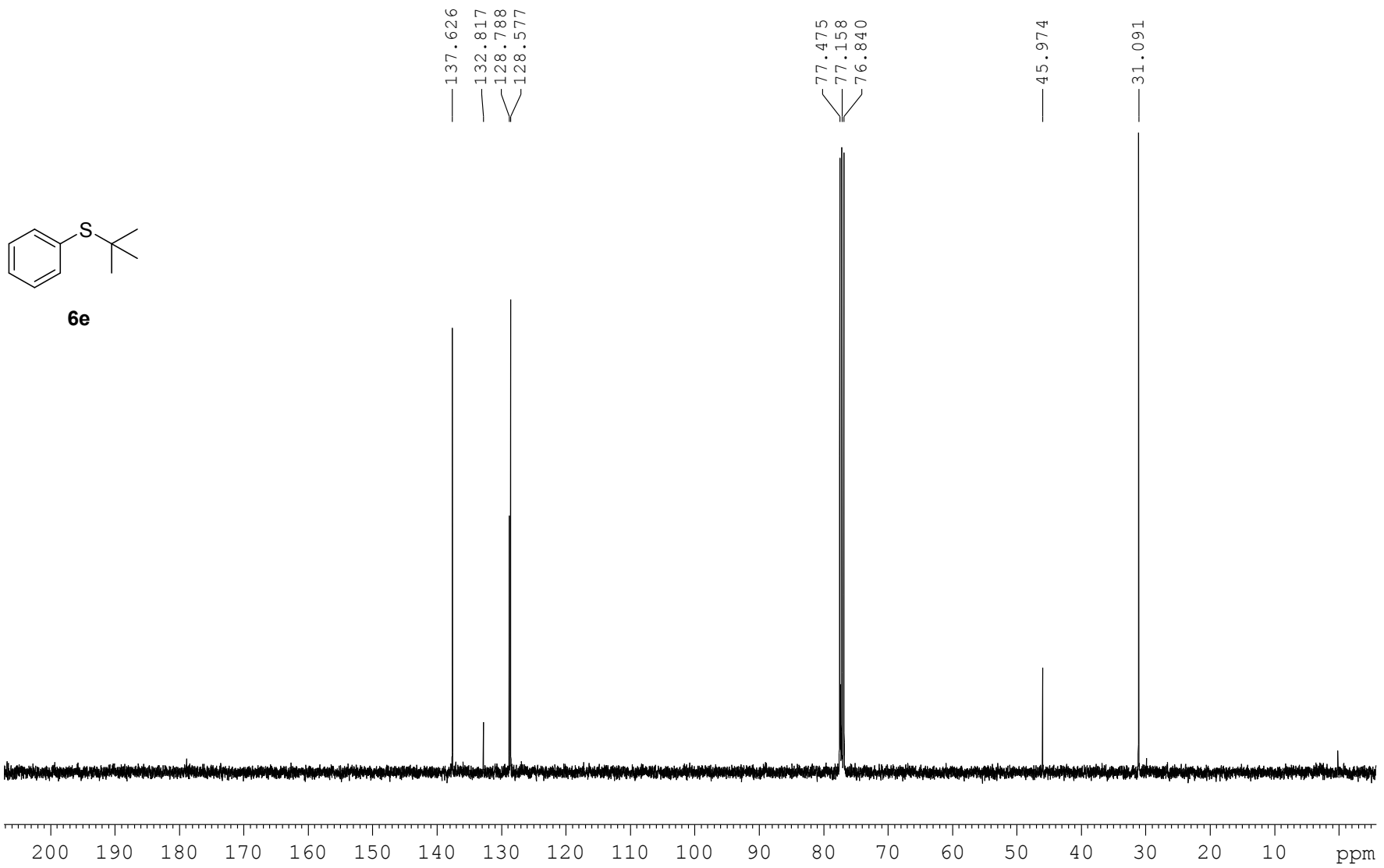


Figure S38. ^{13}C NMR spectrum of **6e** ($CDCl_3$, 100 MHz).

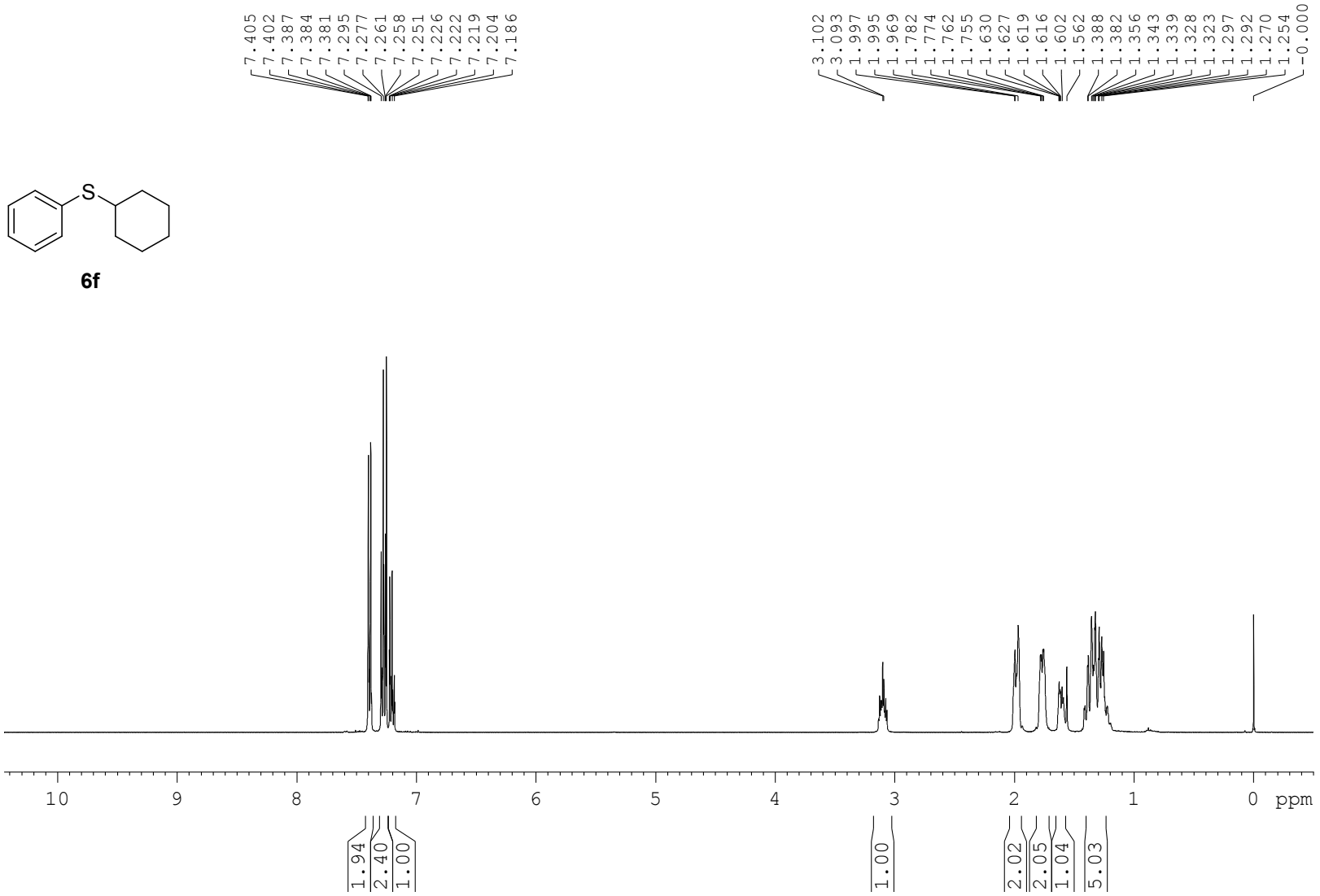


Figure S39. ^{1}H NMR spectrum of **6f** ($CDCl_3$, 400 MHz).

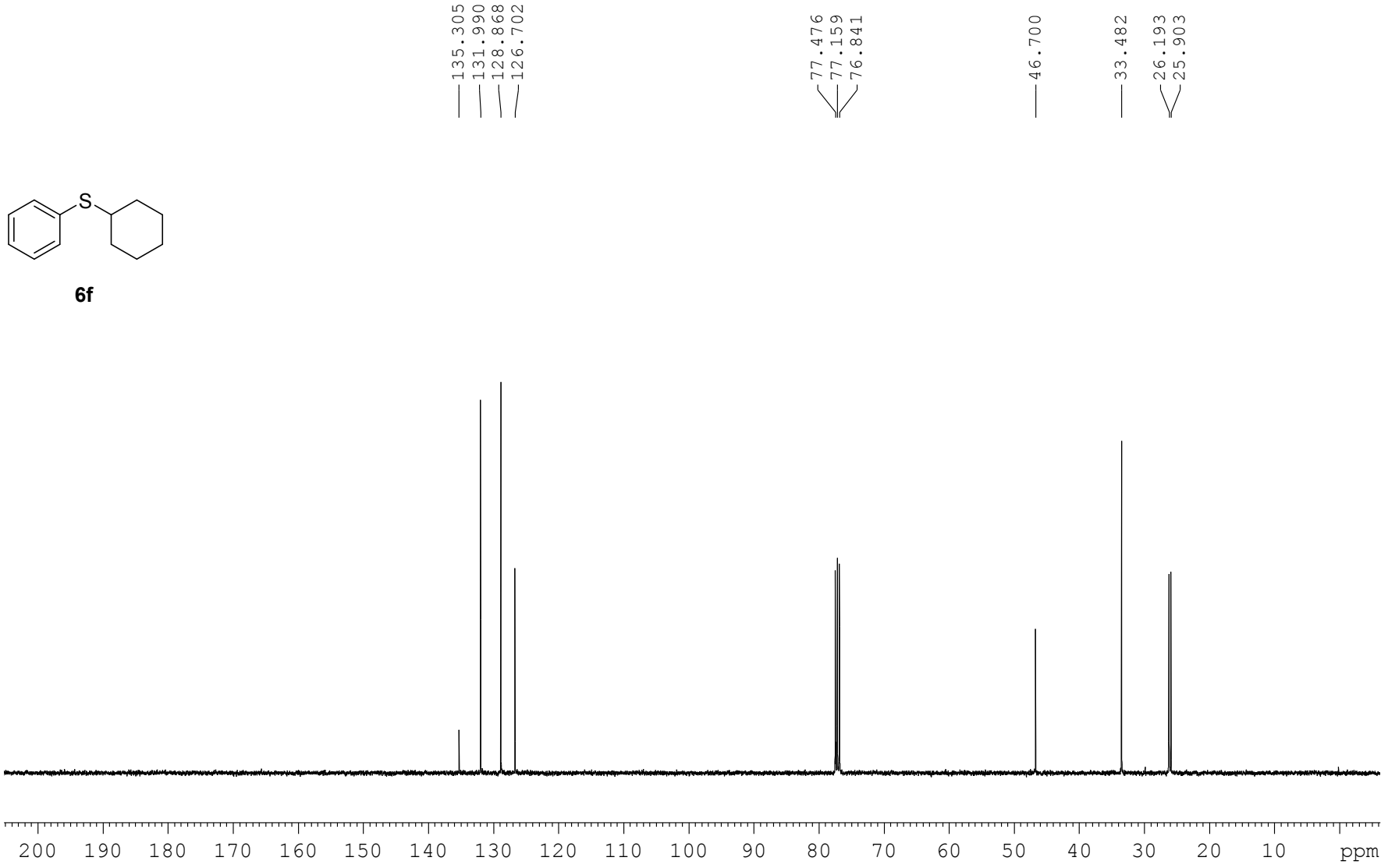


Figure S40. ^{13}C NMR spectrum of **6f** ($CDCl_3$, 100 MHz).

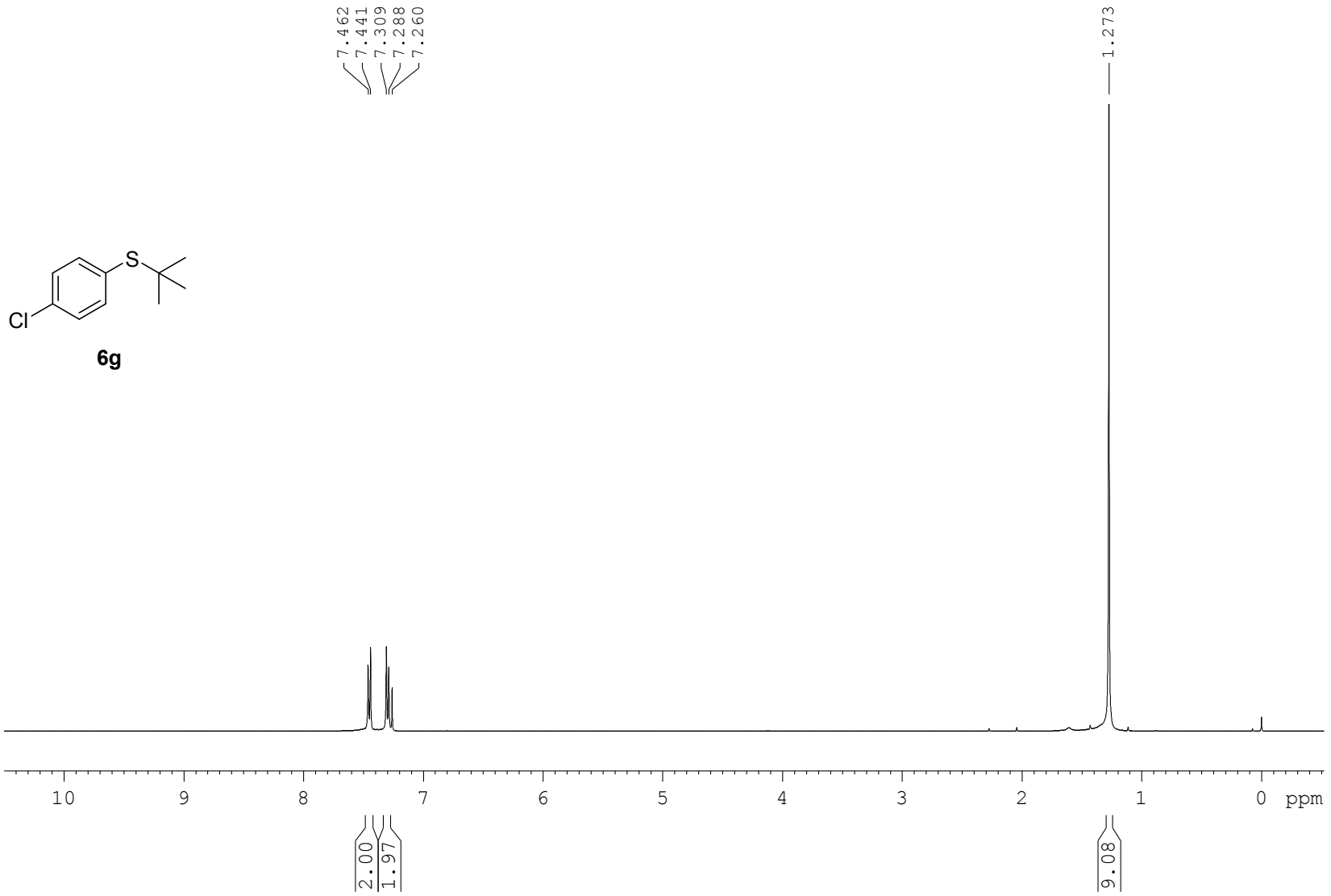


Figure S41. ^{1}H NMR spectrum of **6g** ($CDCl_3$, 400 MHz).

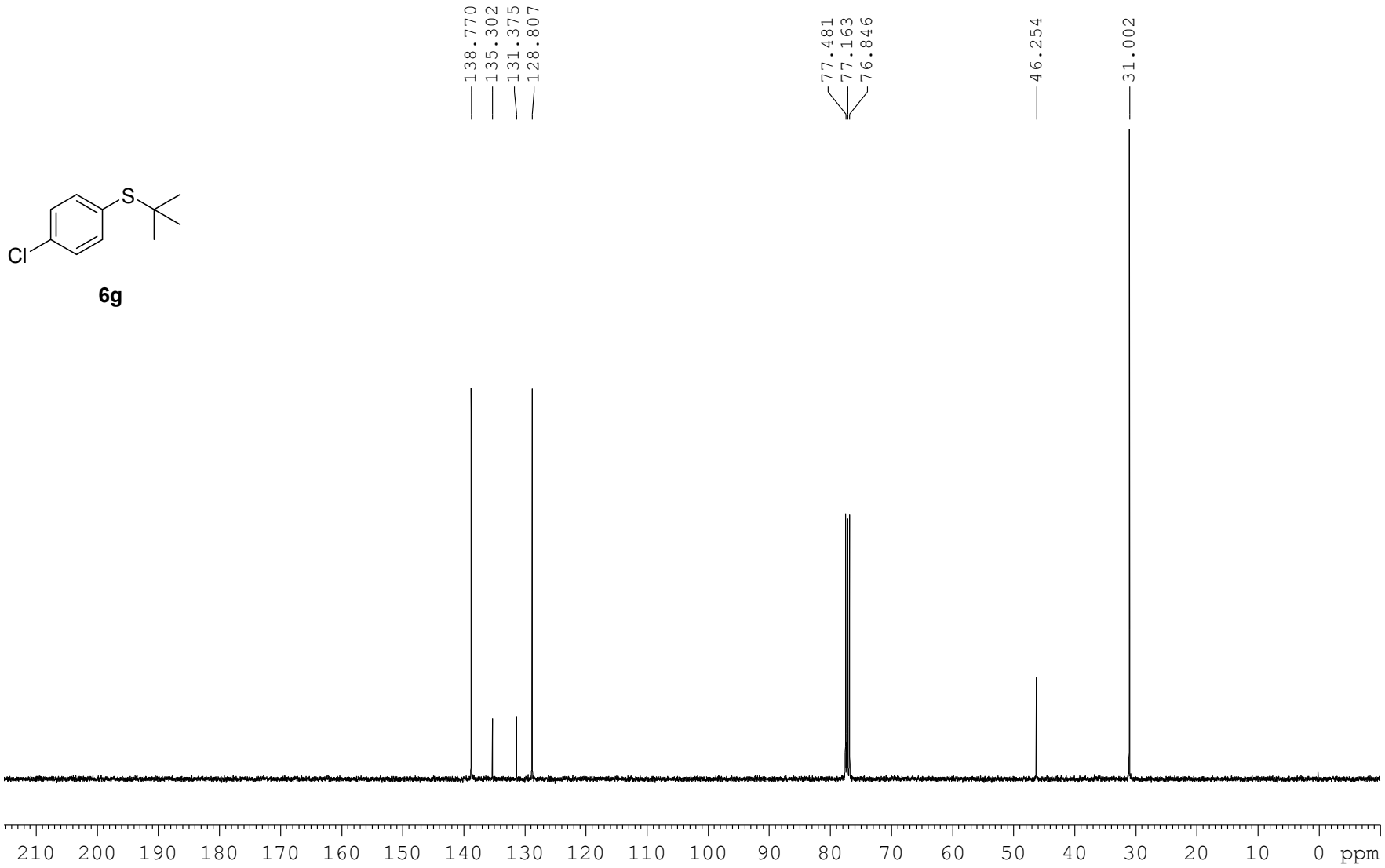


Figure S42. ^{13}C NMR spectrum of **6g** ($CDCl_3$, 100 MHz).

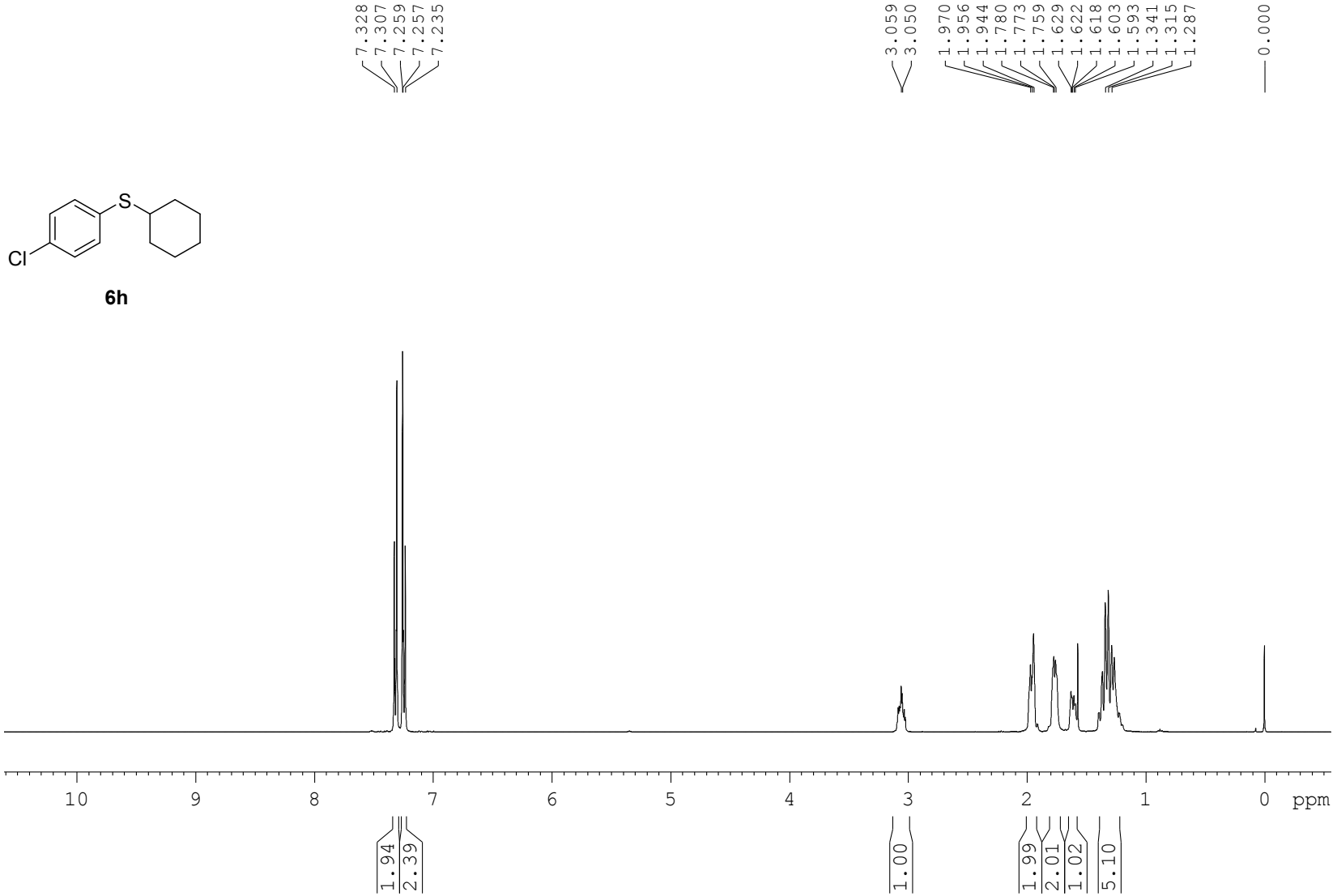


Figure S43. ^{1}H NMR spectrum of **6i** ($CDCl_3$, 400 MHz).

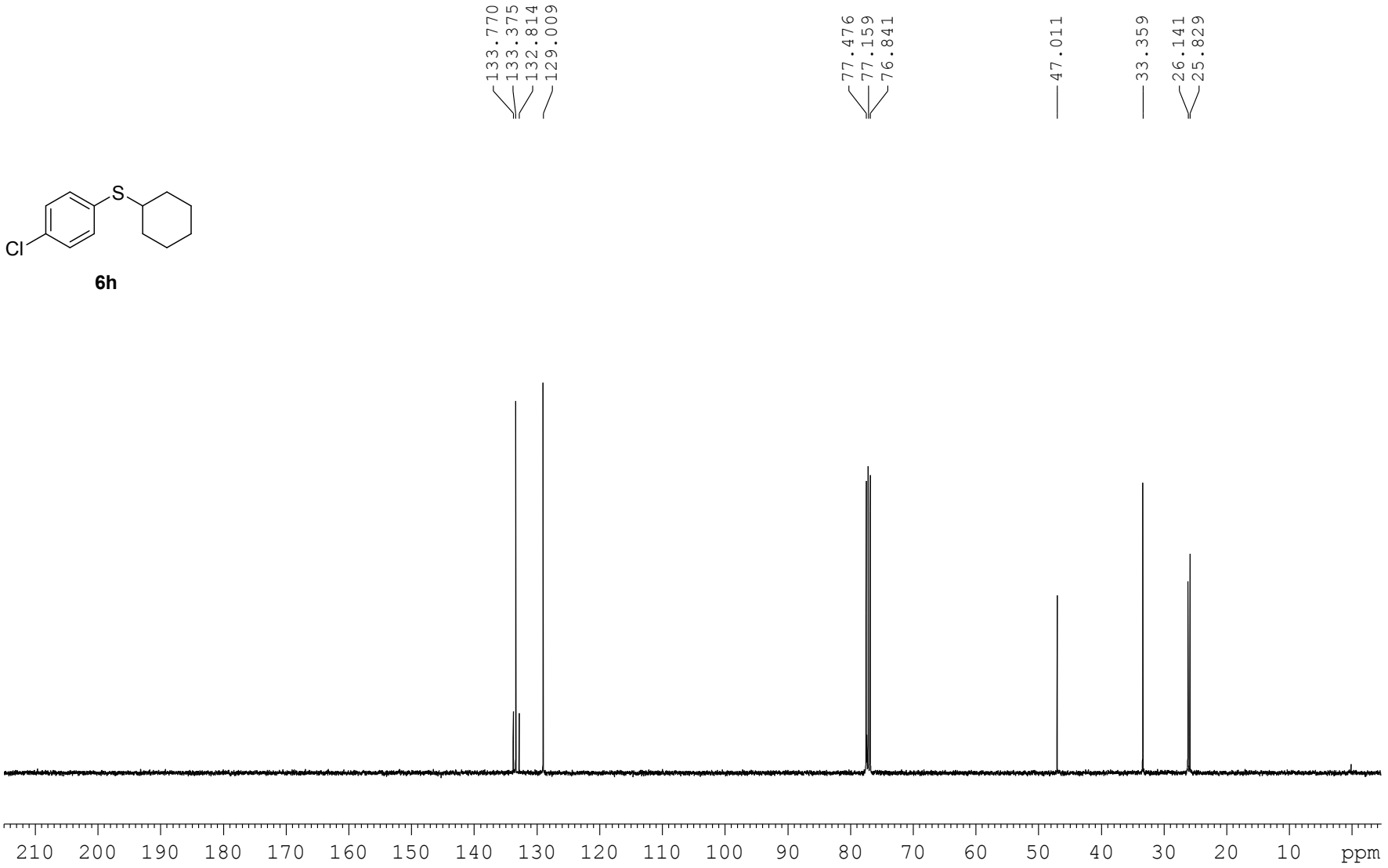


Figure S44. ^{13}C NMR spectrum of **6i** ($CDCl_3$, 100 MHz).

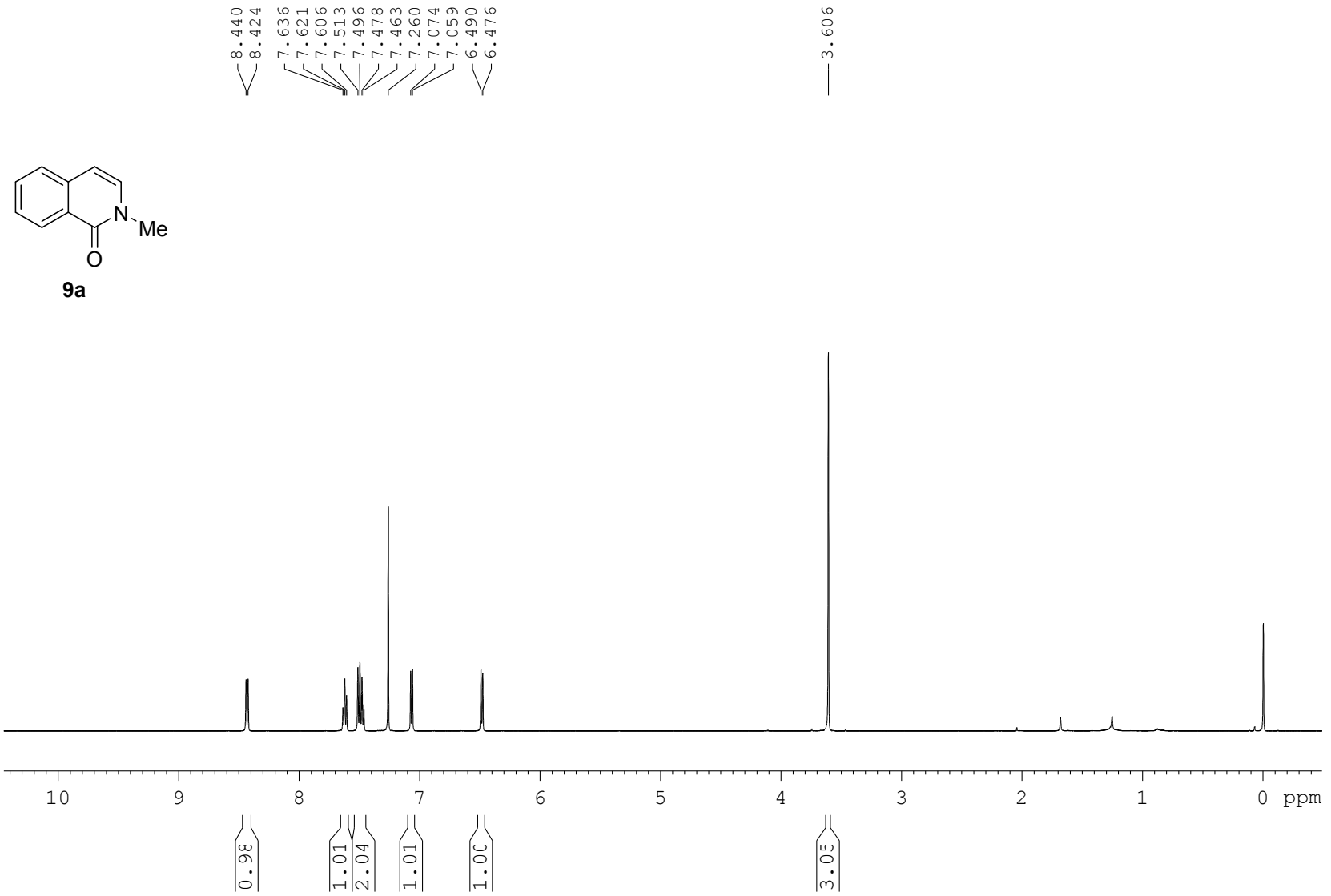


Figure S45. ^{1}H NMR spectrum of **9a** ($CDCl_3$, 500 MHz).

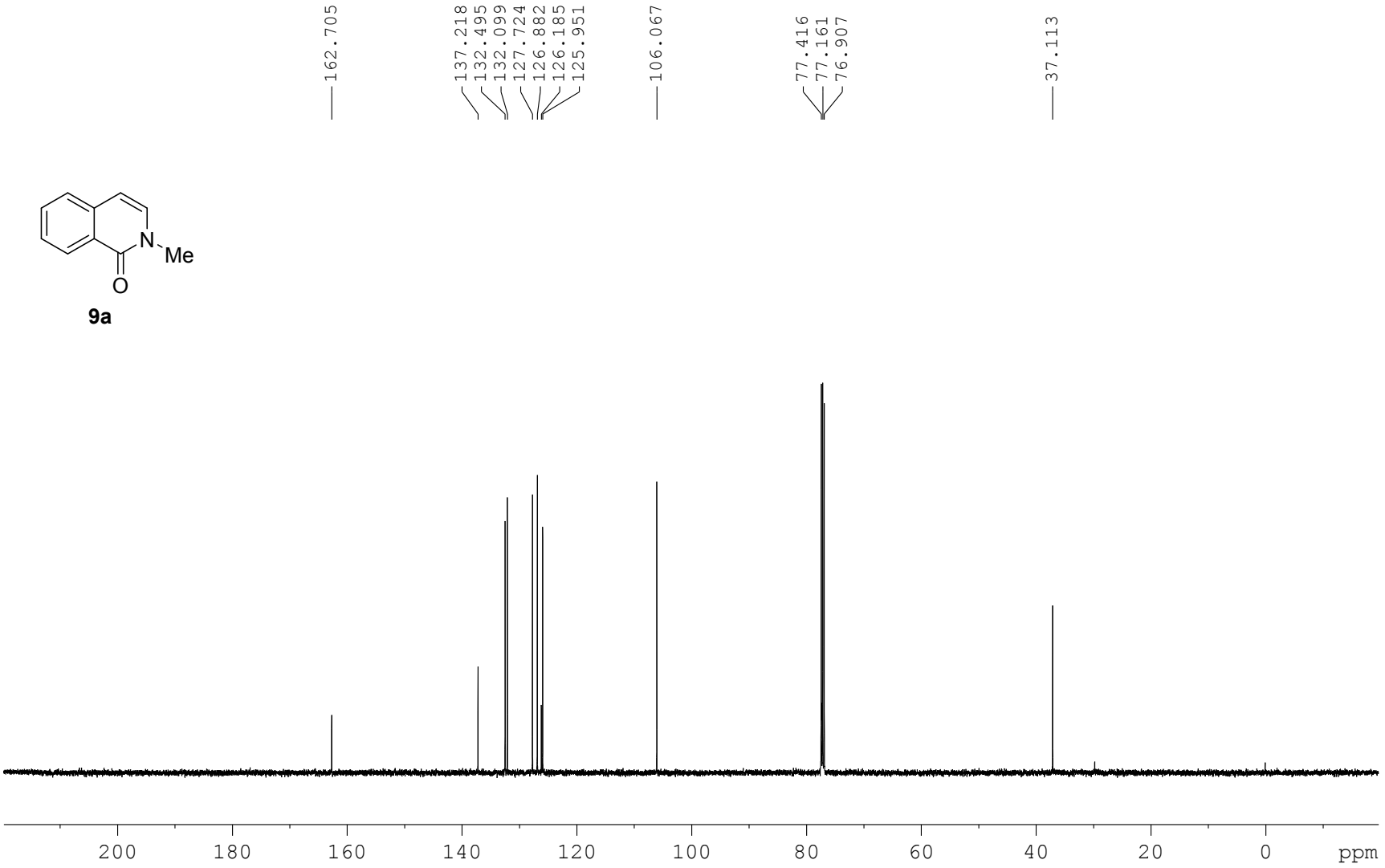


Figure S46. ^{13}C NMR spectrum of **9a** ($CDCl_3$, 125 MHz).

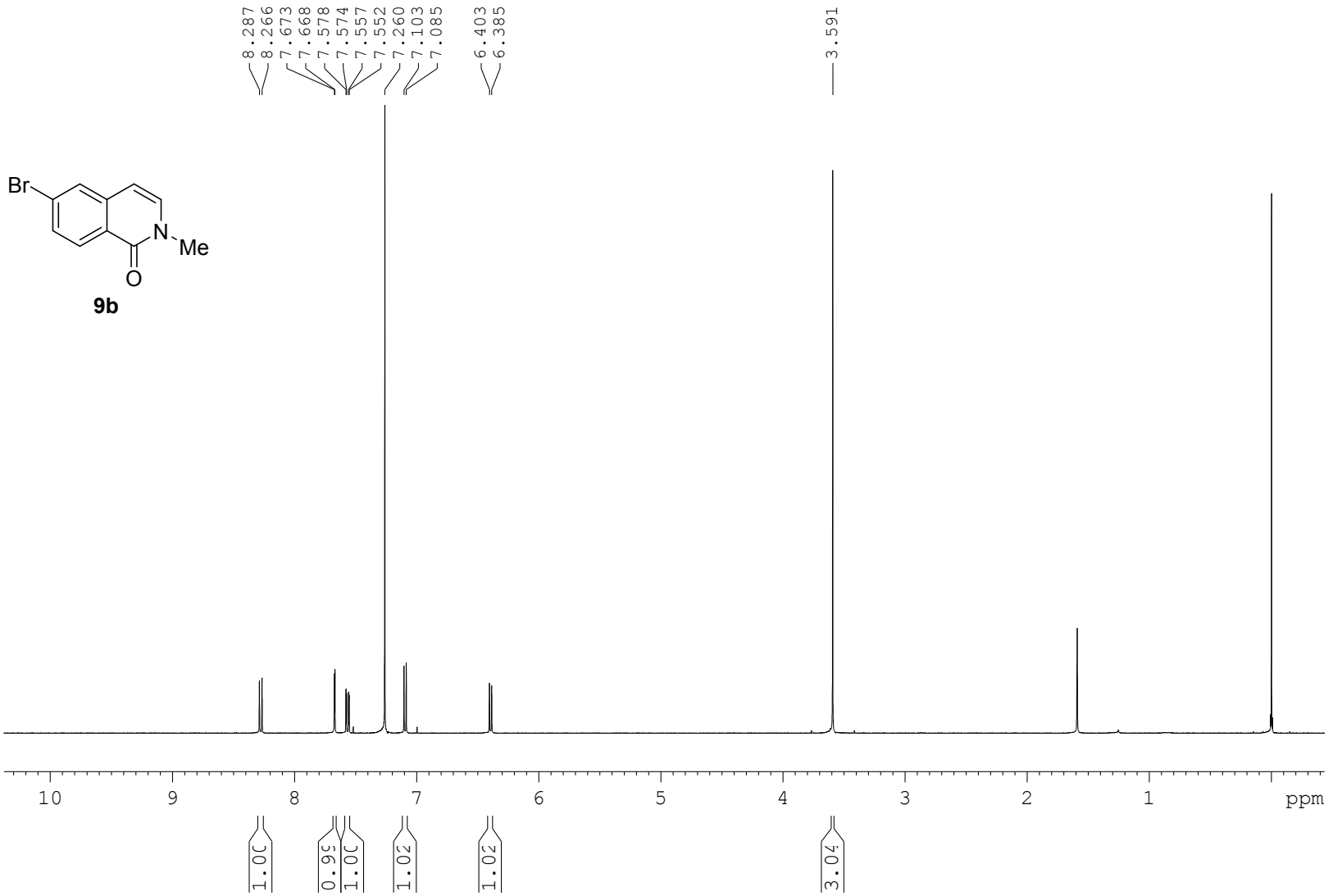


Figure S47. ^{1}H NMR spectrum of **9b** ($CDCl_3$, 400 MHz).

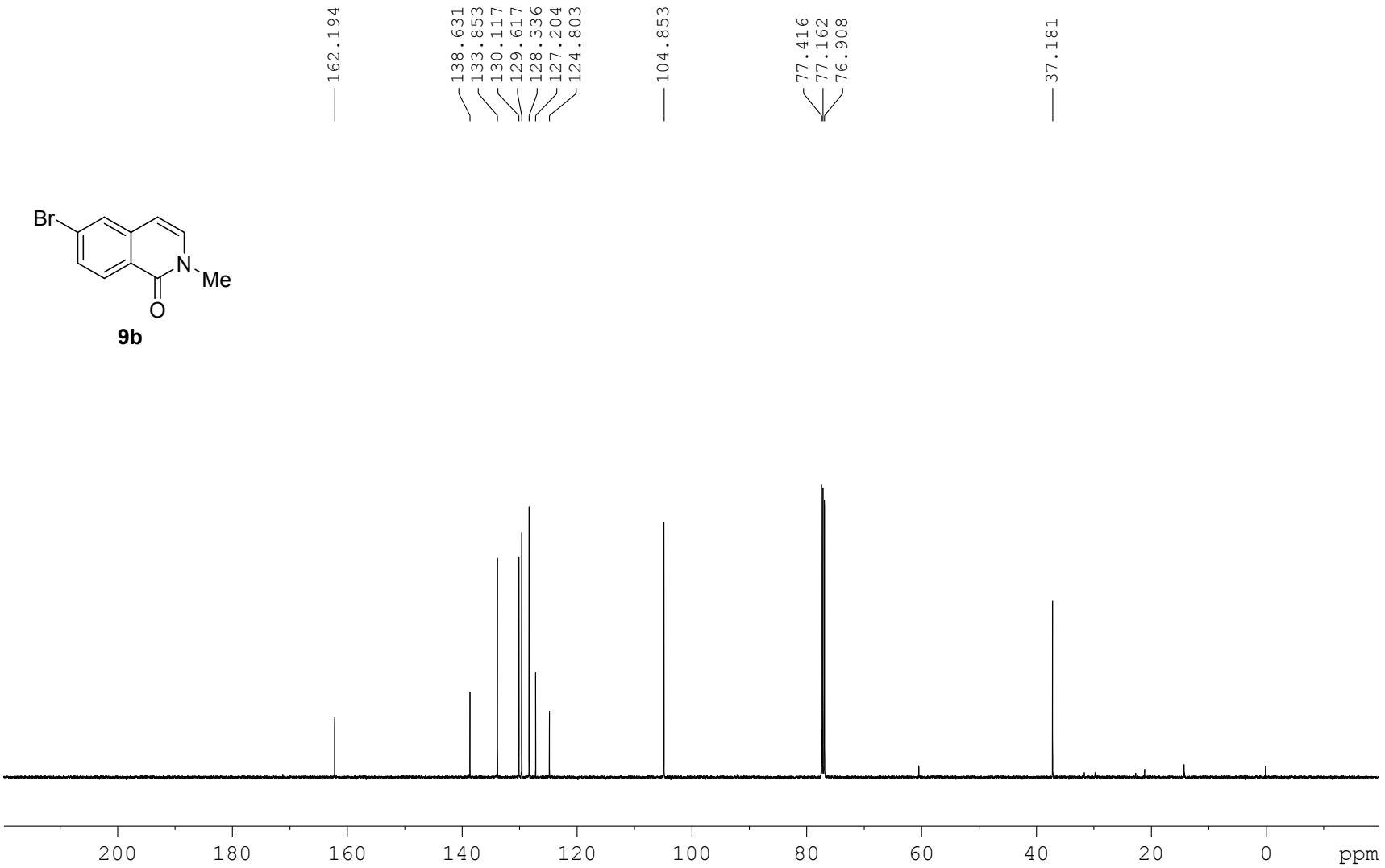


Figure S48. ^{13}C NMR spectrum of **9b** ($CDCl_3$, 100 MHz).

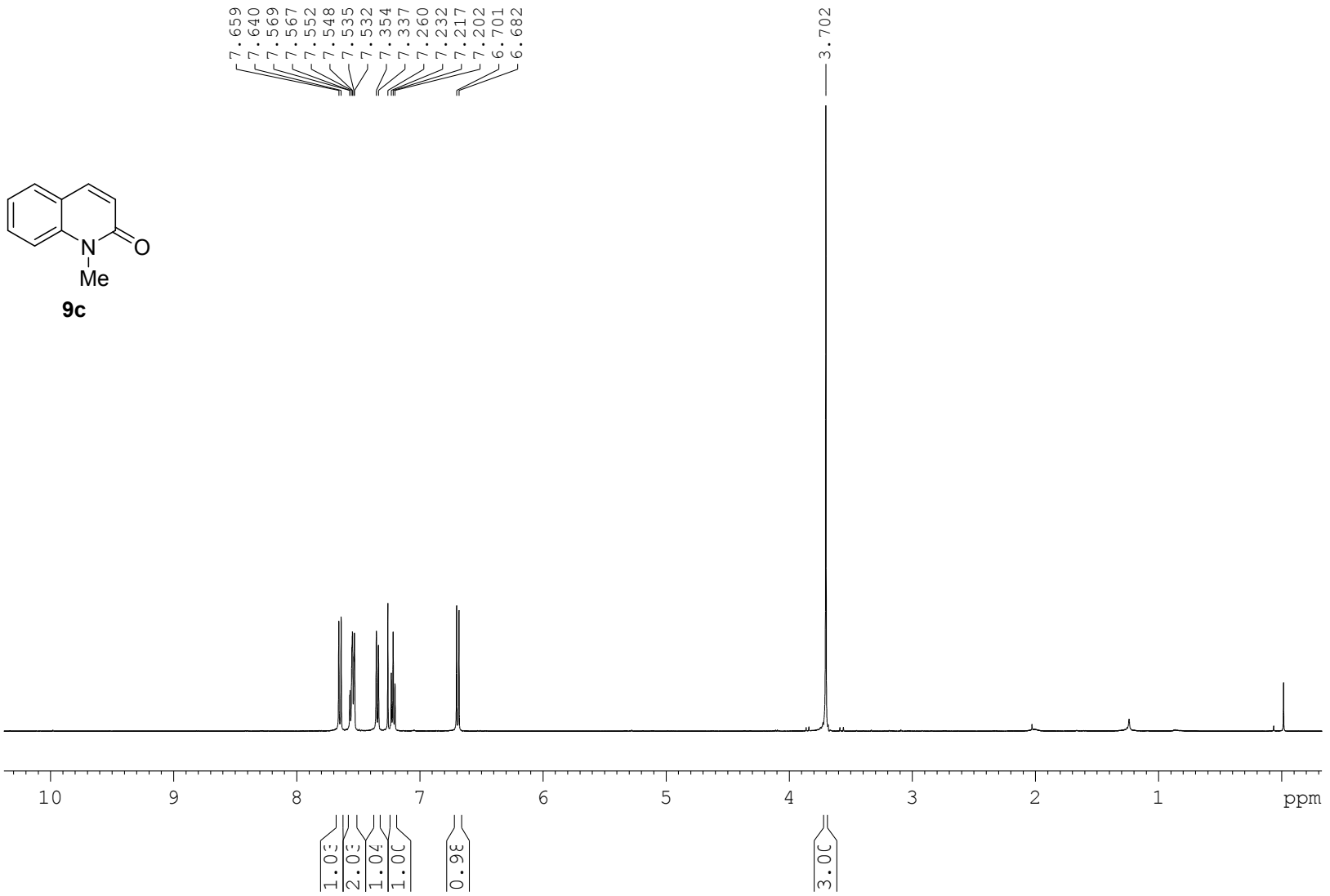


Figure S49. ^{1}H NMR spectrum of **9c** ($CDCl_3$, 500 MHz).

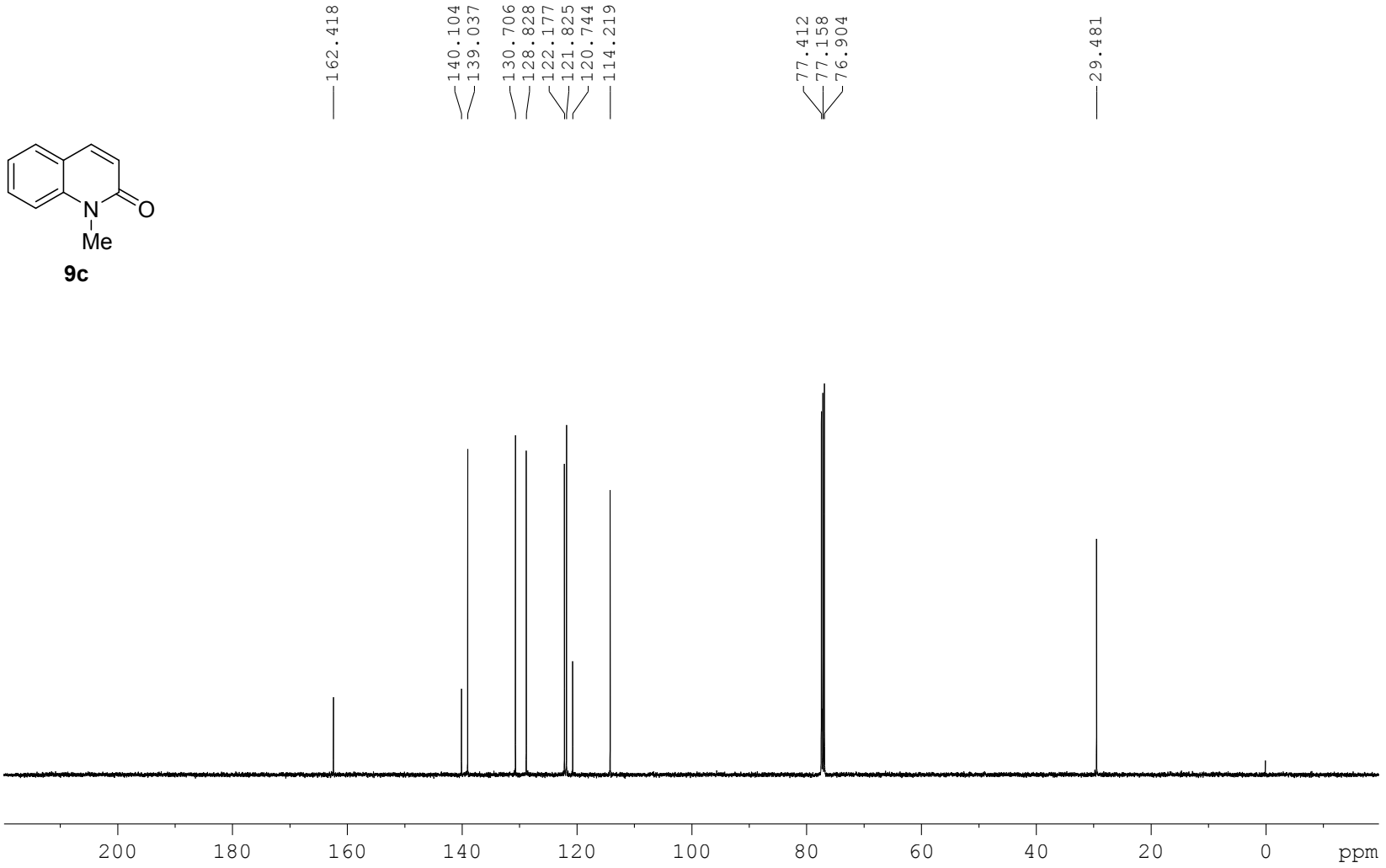


Figure S50. ^{13}C NMR spectrum of **9c** ($CDCl_3$, 125 MHz).

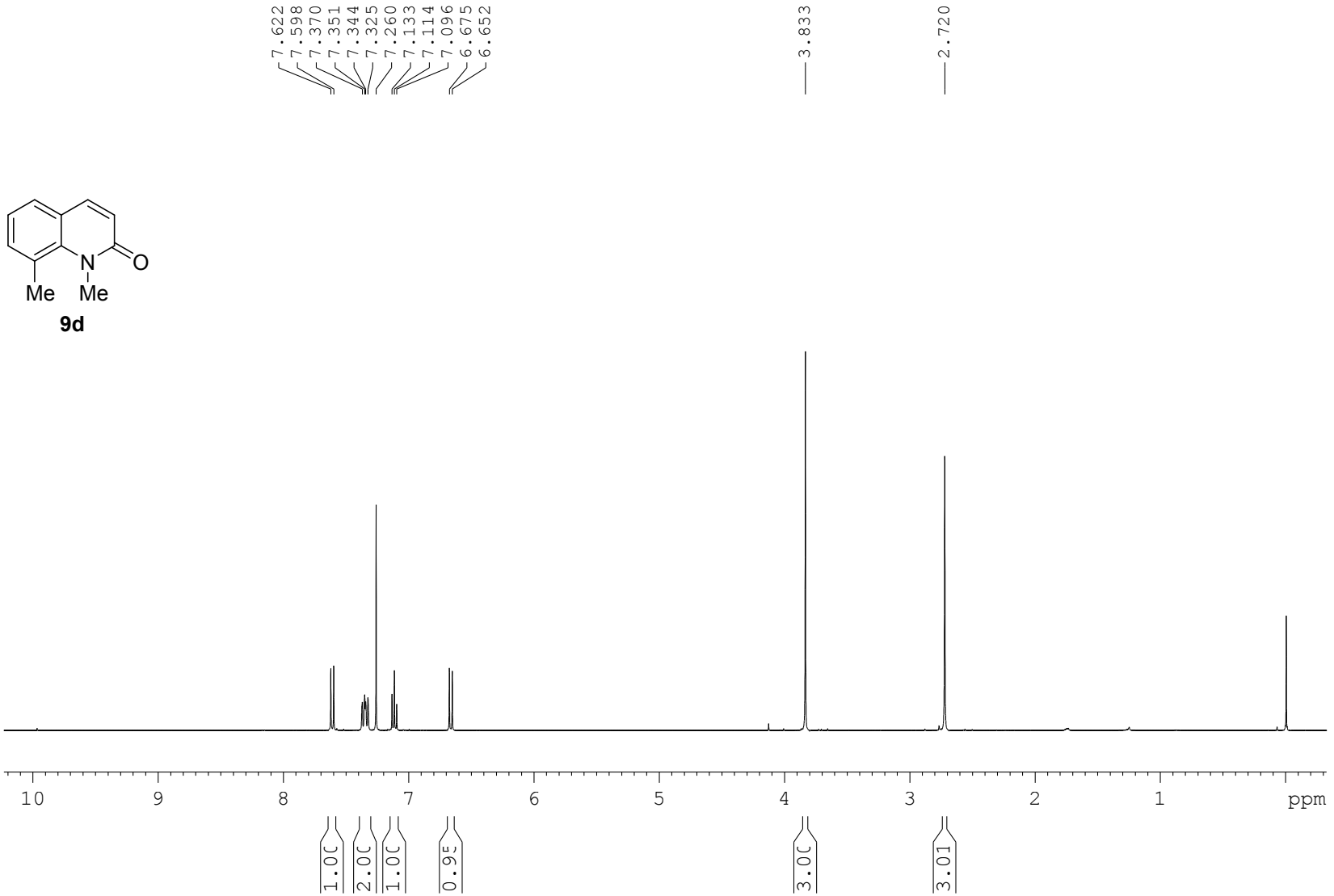


Figure S51. ^{1}H NMR spectrum of **9d** ($CDCl_3$, 400 MHz).

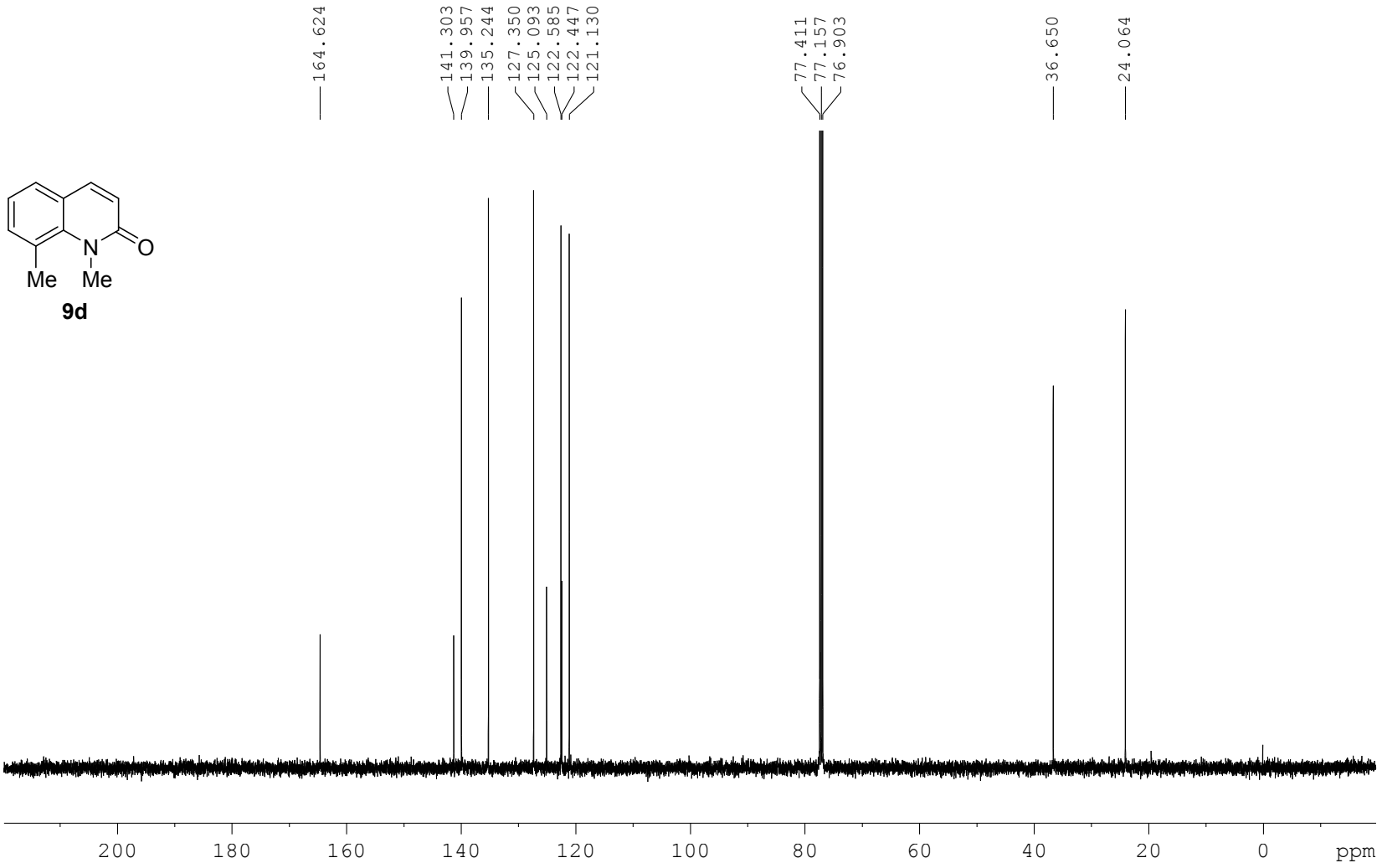


Figure S52. ^{13}C NMR spectrum of **9d** ($CDCl_3$, 100 MHz).

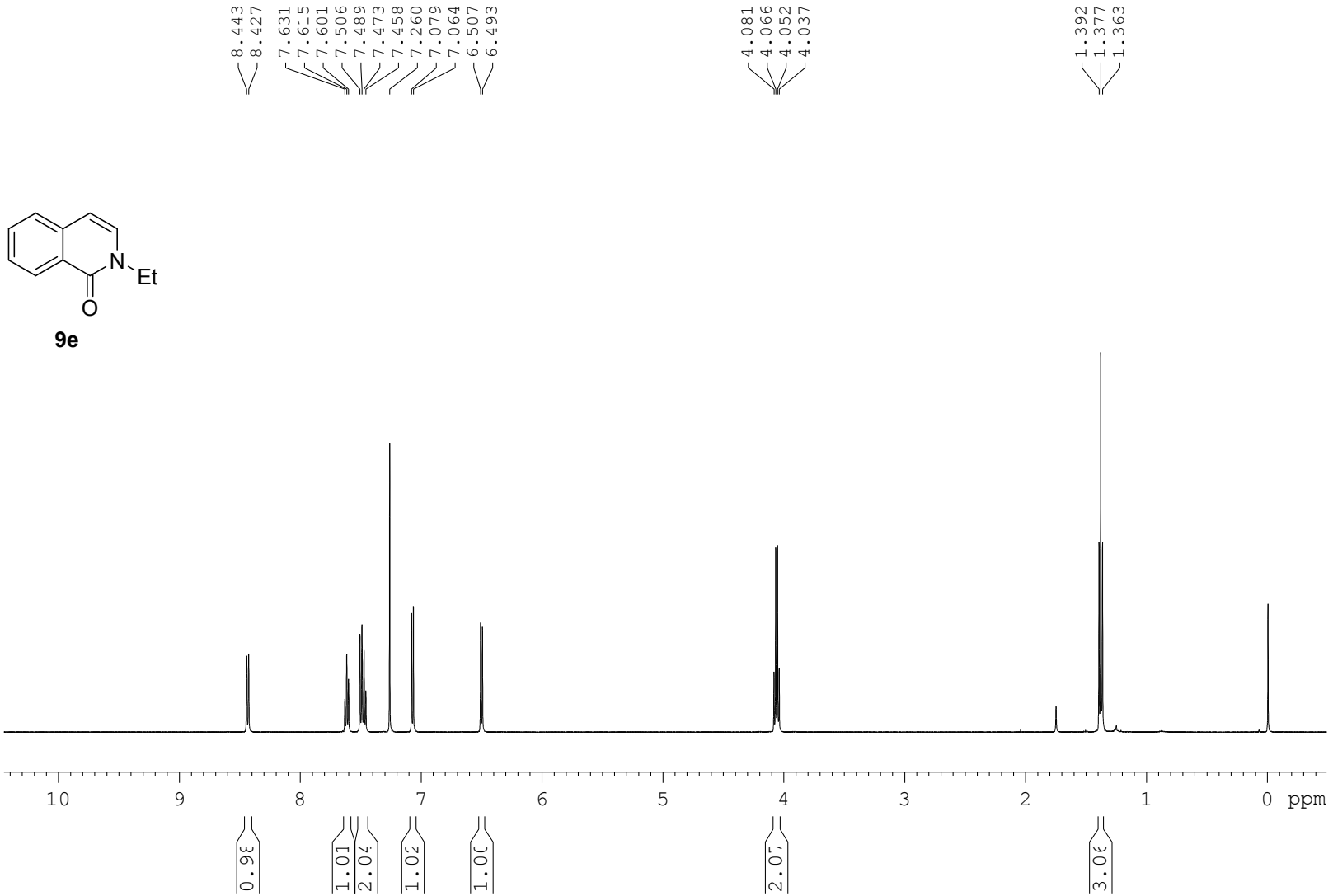


Figure S53. ^{1}H NMR spectrum of **9e** ($CDCl_3$, 500 MHz).

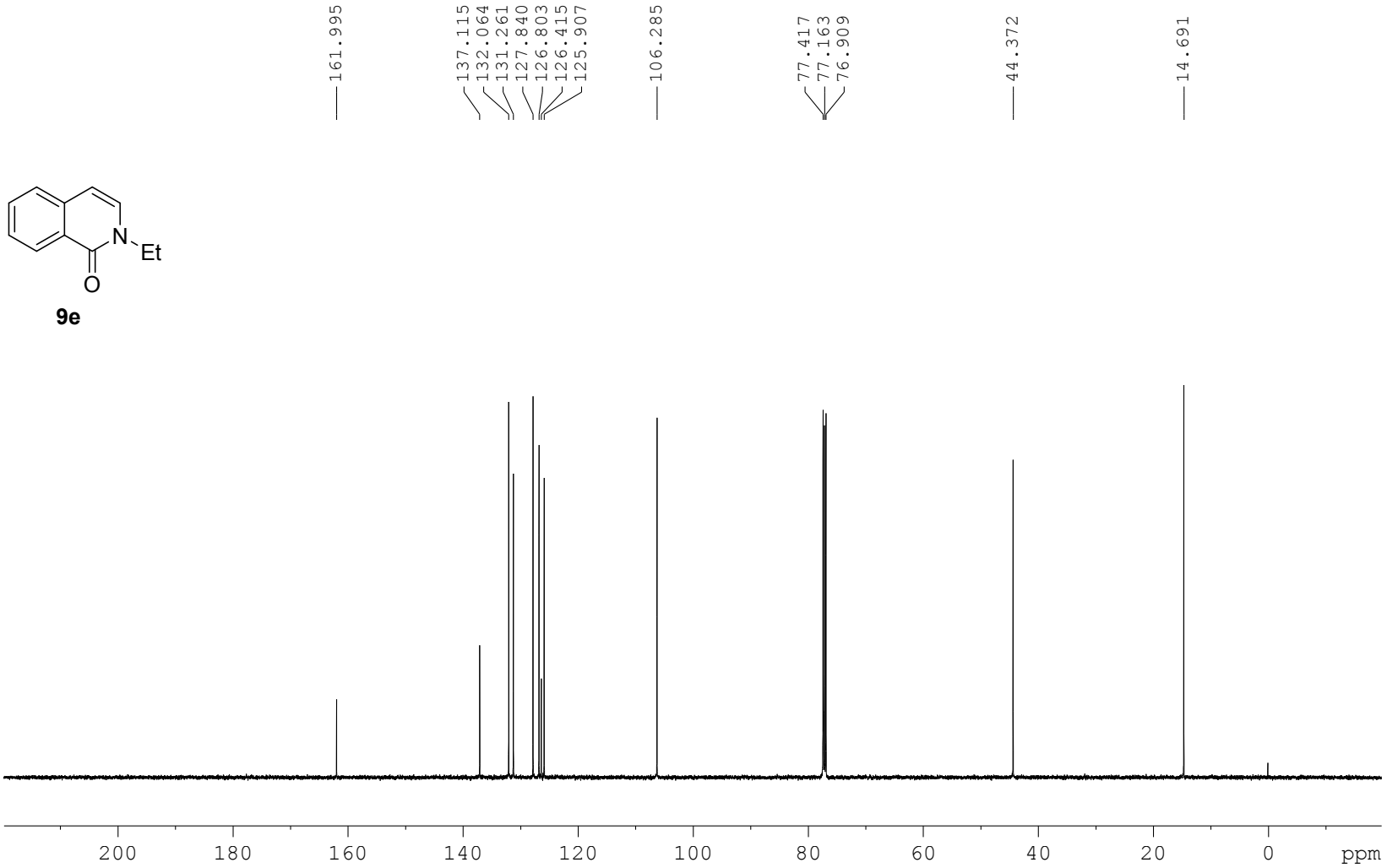


Figure S54. ^{13}C NMR spectrum of **9e** ($CDCl_3$, 125 MHz).

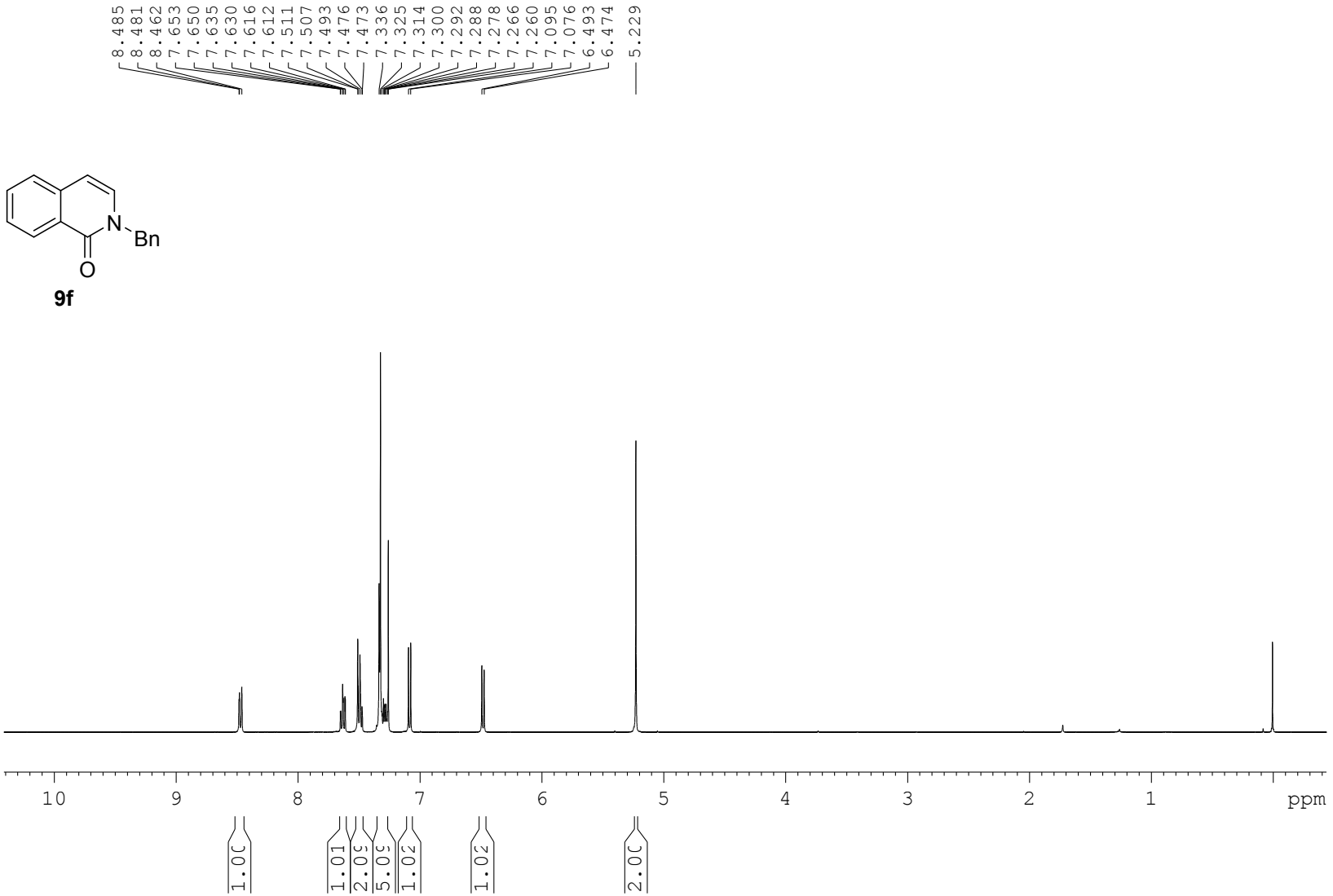


Figure S55. ^{1}H NMR spectrum of **9f** ($CDCl_3$, 400 MHz).

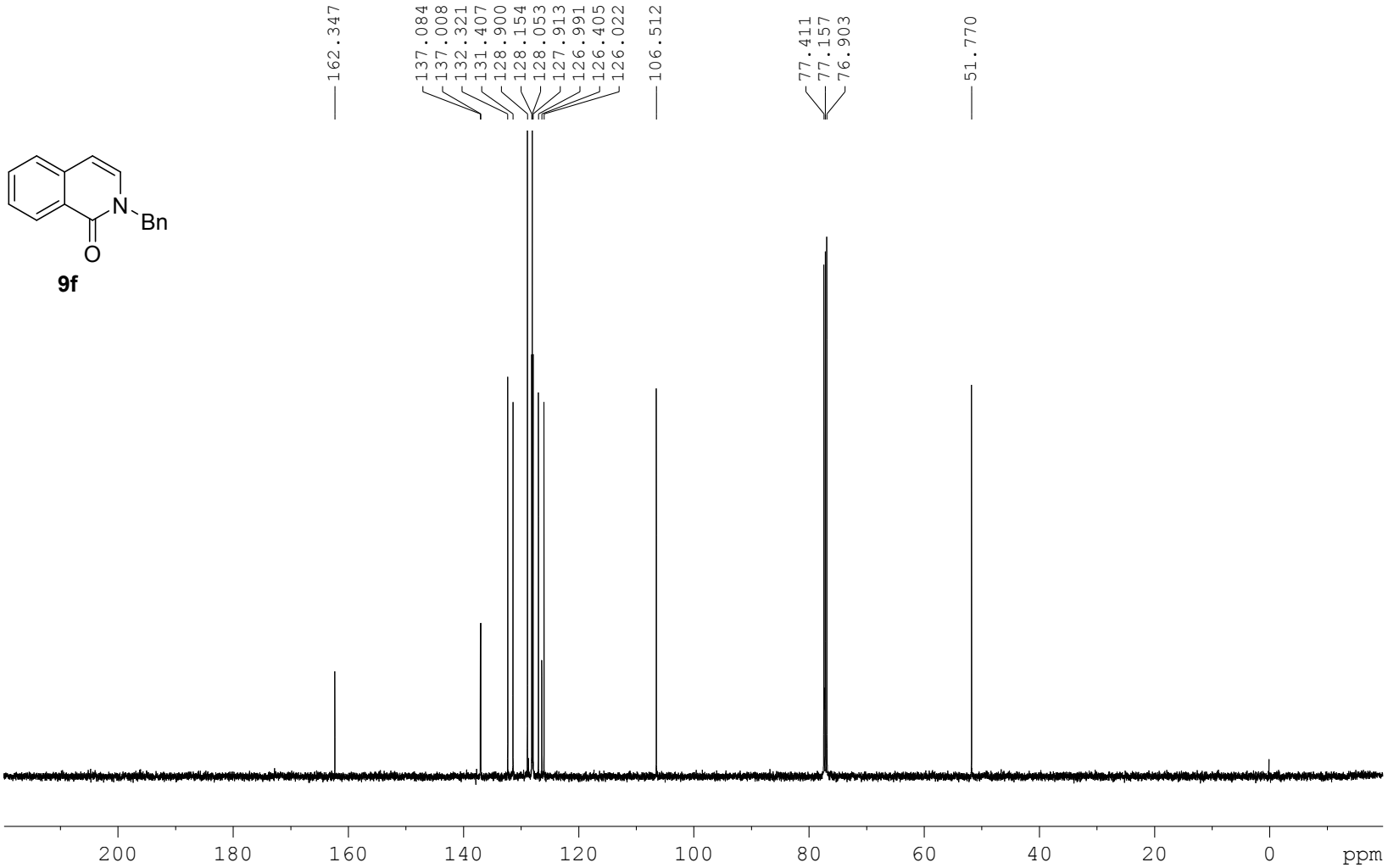


Figure S56. ^{13}C NMR spectrum of **9f** ($CDCl_3$, 100 MHz).

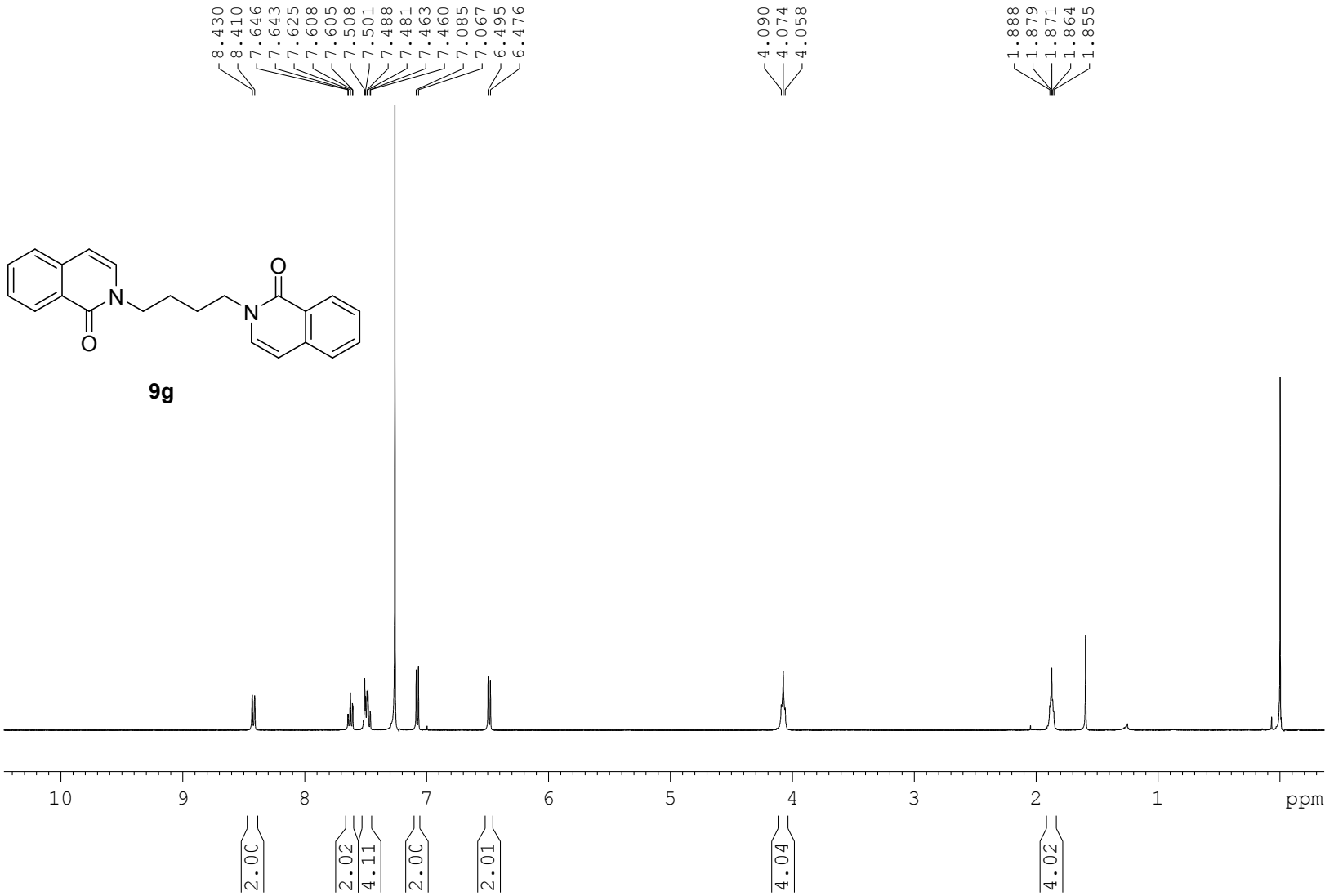


Figure S57. ^{1}H NMR spectrum of **9g** ($CDCl_3$, 400 MHz).

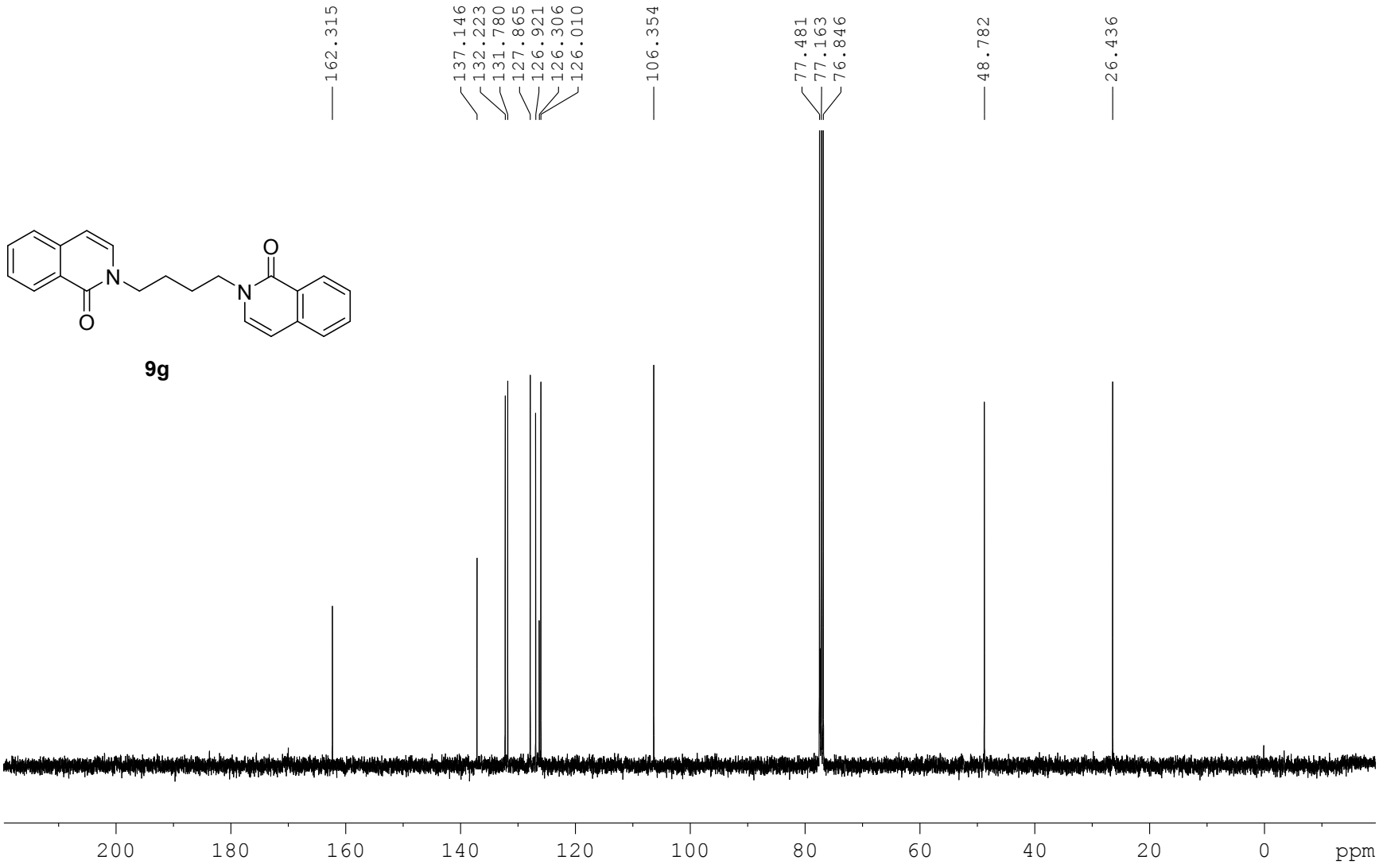


Figure S58. ^{13}C NMR spectrum of **9g** ($CDCl_3$, 100 MHz).