

***tert*-Butylhydroperoxide mediated radical cyanoalkylation/
cyanoalkenylation of 2-anilino-1,4-naphthoquinones with
vinylarenes/arylalkynes and azobis(alkylcarbonitrile)s**

Supporting Information

Contents:

- | | |
|--|--------------------|
| 1. General procedure for synthesis- 4aaa in gram-scale and 12 | S-1 |
| 2. ¹ H NMR and ¹³ C NMR spectra of all synthesized compounds | S-2 to S-47 |
| 3. NOESY of the compound 6oda | S-48 |
| 4. HRMS data of the control experiments for the adduct 7 & 8 | S-49 |

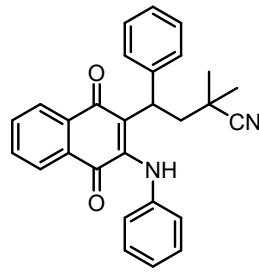
Procedure for gram-scale synthesis of 4-(1,4-dioxo-3-(phenylamino)-1,4-dihydronaphthalen-2-yl)-2,2-dimethyl-4-phenylbutanenitrile (4aaa):

To a solution of 2-(phenylamino) naphthalene-1,4-dione (**1a**, 4.01 mmol, 1.0 g), styrene (**2a**, 8.02 mmol, 0.835 g) and AIBN (**3a**, 8.02 mmol, 1.32g) in chloroform (40 mL) was added TBHP (8.02 mmol). The reaction mixture was stirred at 80 °C for 12 hours. After completion of the reaction (as monitored by TLC), water was added to the reaction mixture and extracted with ethyl acetate (3×30 mL). The organic layer was washed with brine (1×20 mL) and dried over anhydrous sodium sulfate. The organic layer was concentrated under reduced pressure and purified by column chromatography on silica gel (ethyl acetate : hexane = 10 : 1) to yield the pure product **4aaa** (1.22g, 72%).

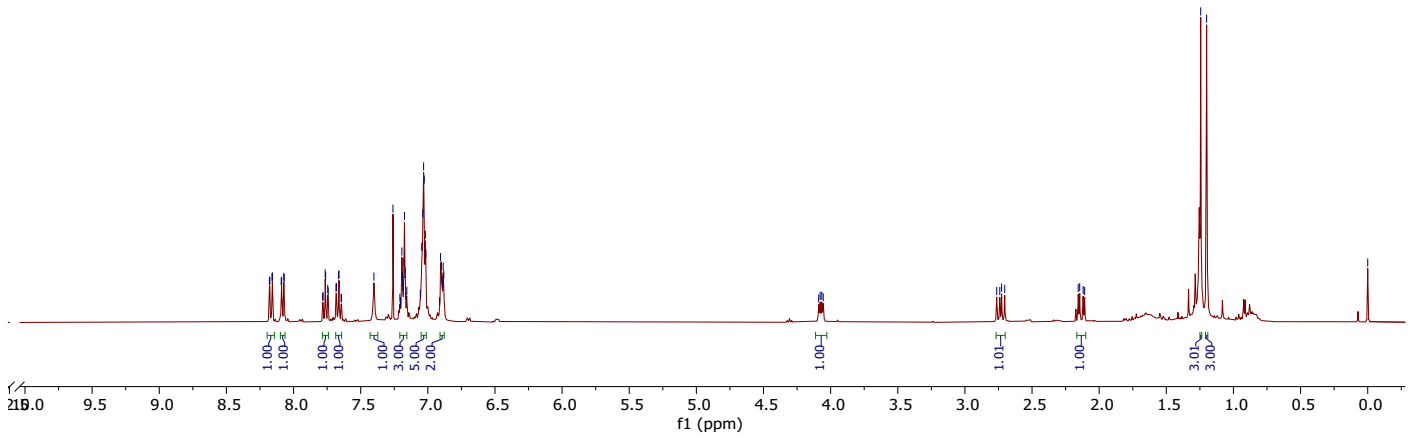
Procedure for the preparation of 4-(3-hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2,2-dimethyl-4-phenylbutanenitrile (12):

To a solution of 2-hydroxynaphthalene-1,4-dione (**11**, 0.20 mmol), styrene (**2a**, 0.40 mmol) and AIBN (**3a**, 0.40 mmol) in chloroform (1.5-2 mL) was added TBHP (0.40 mmol). The reaction mixture was stirred at 80 °C for about 12 hours. After completion of the reaction (as monitored by TLC), water was added to the reaction mixture and extracted with ethyl acetate (3×10 mL). The organic layer was washed with brine (1×10 mL) and dried over anhydrous sodium sulfate. The organic layer was concentrated under reduced pressure and purified by column chromatography on silica gel (ethyl acetate : hexane =1 : 4) to yield the pure product **12** (44 mg, 64%).

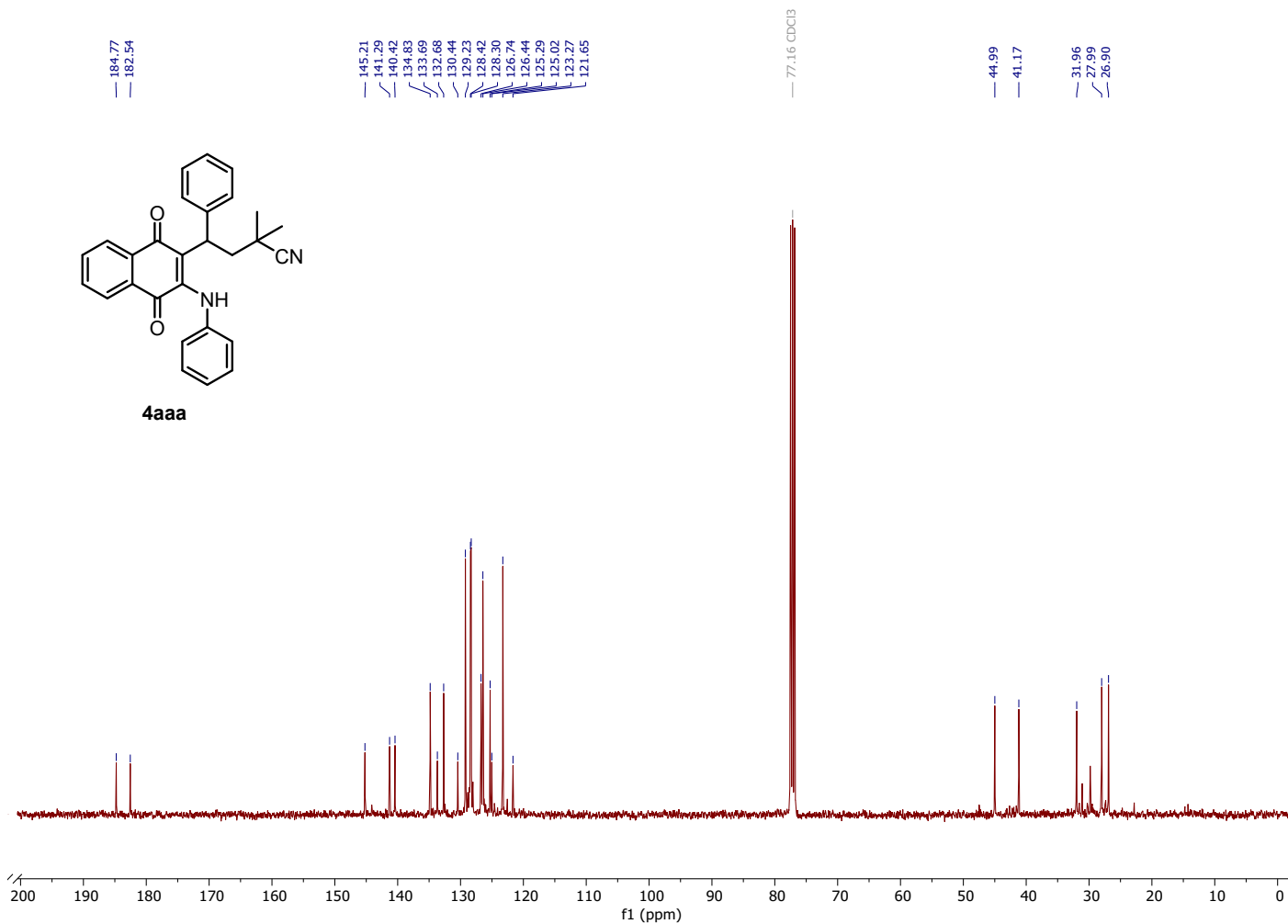
¹H-NMR (400 MHz, Chloroform-*d*)



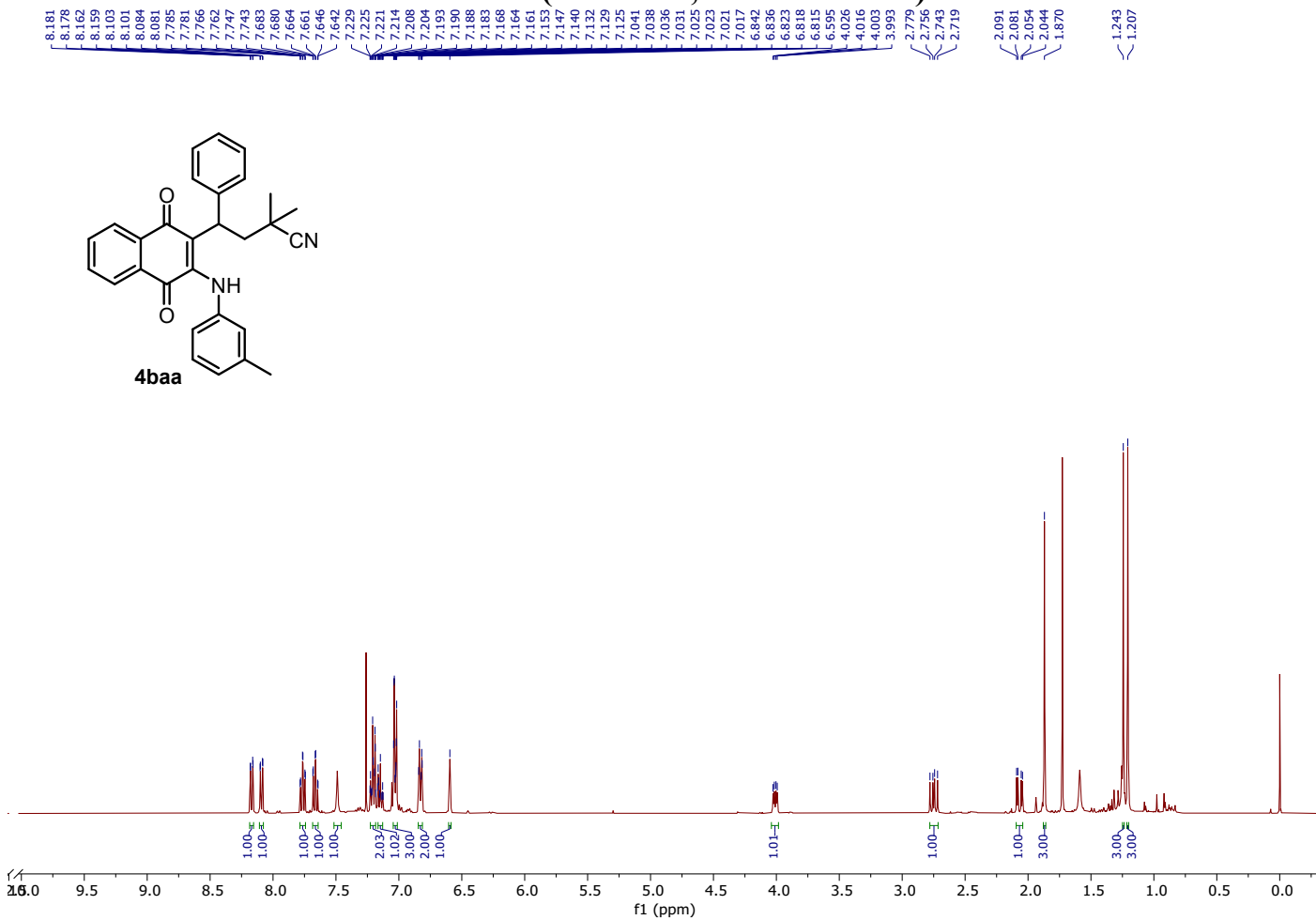
4aaa



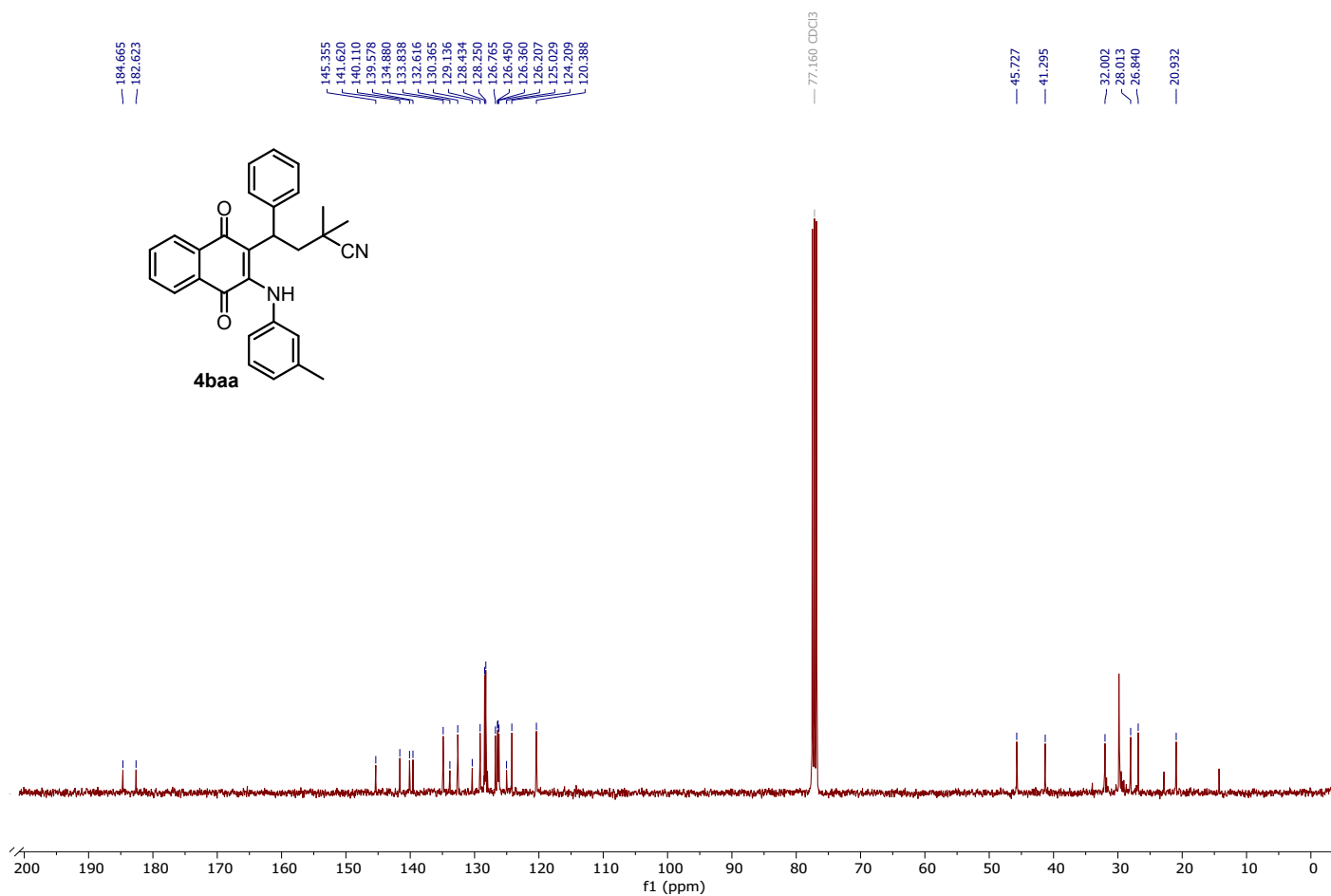
¹³C-NMR (100 MHz, Chloroform-*d*)



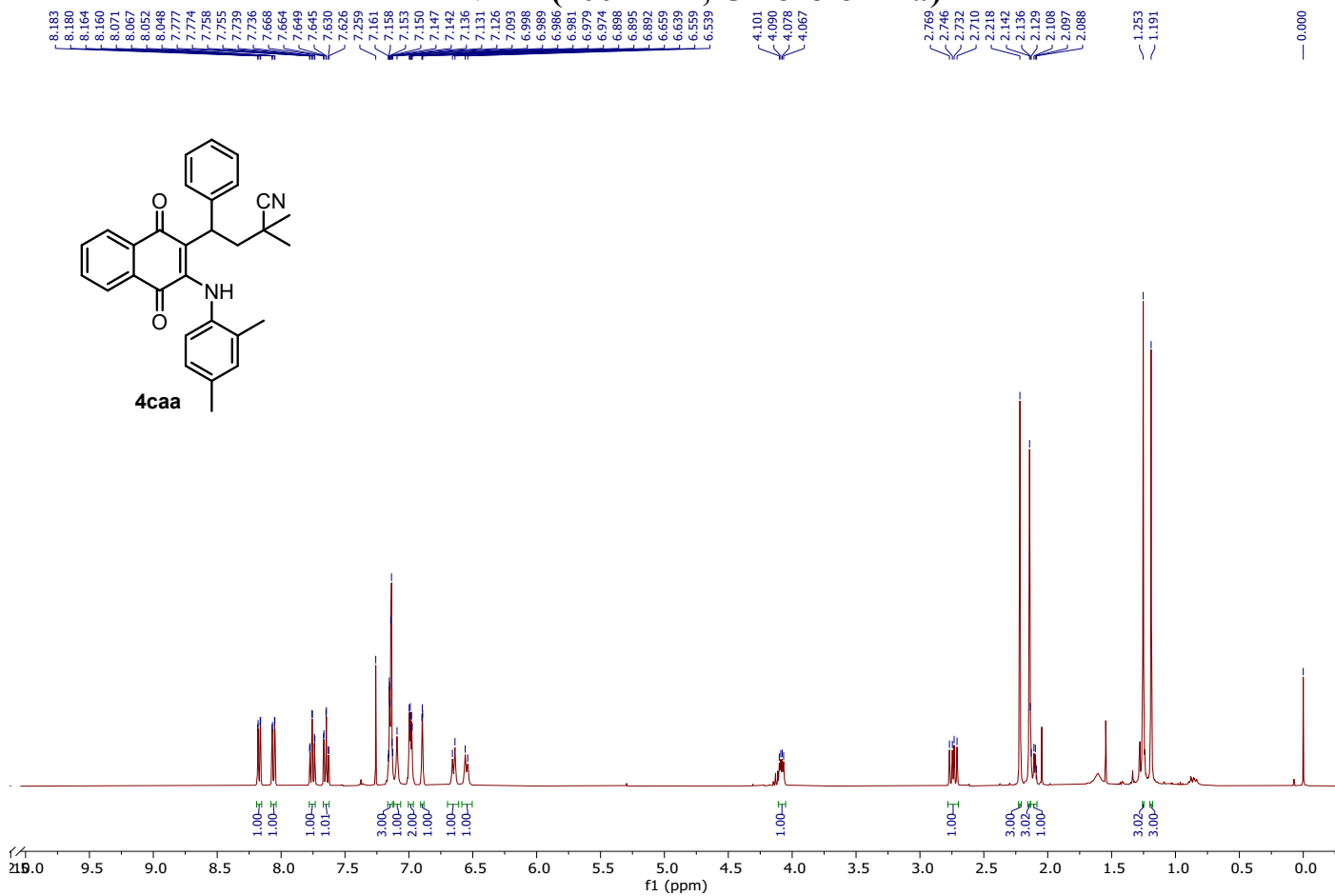
¹H-NMR (400 MHz, Chloroform-*d*)



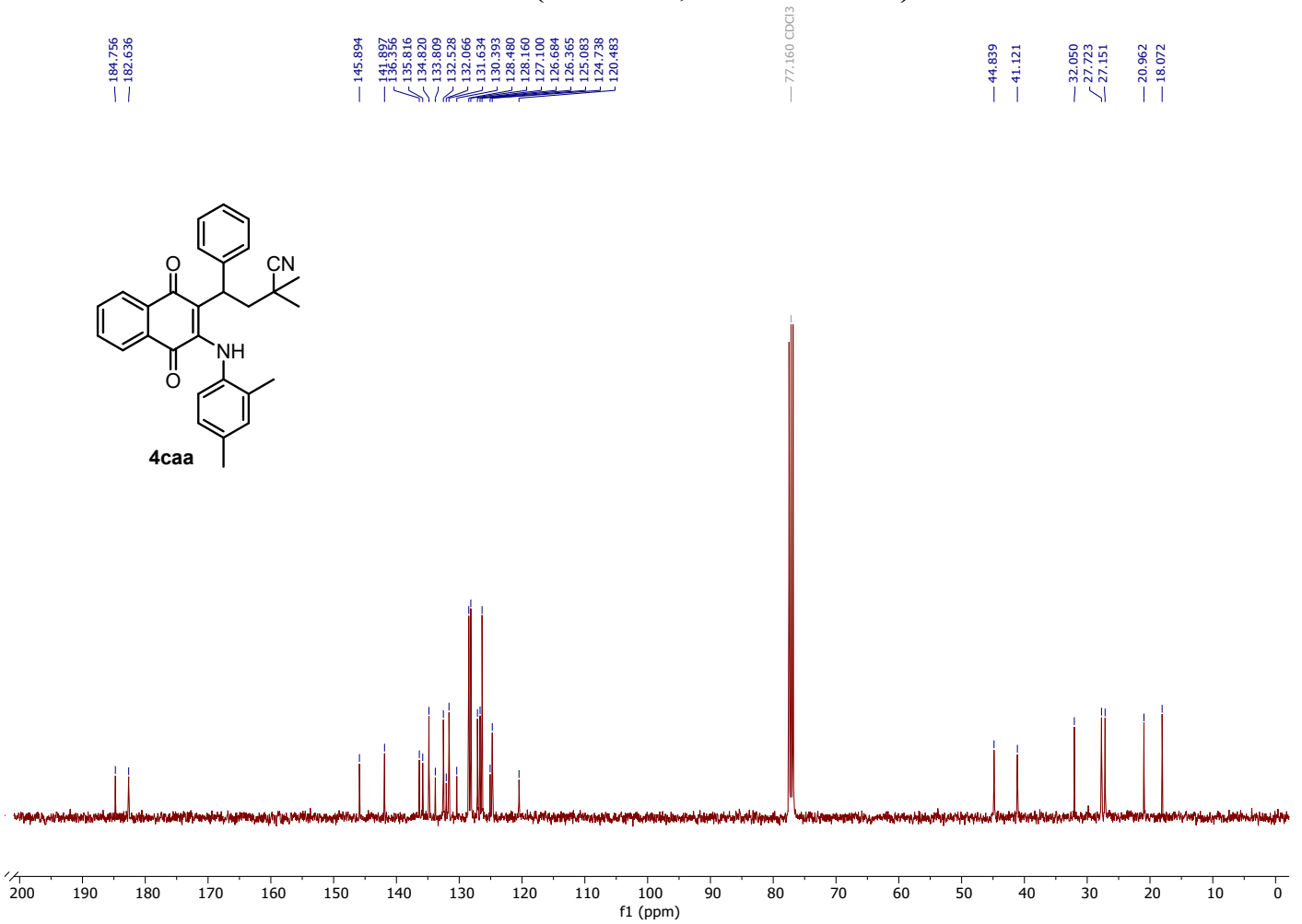
¹³C-NMR (100 MHz, Chloroform-*d*)



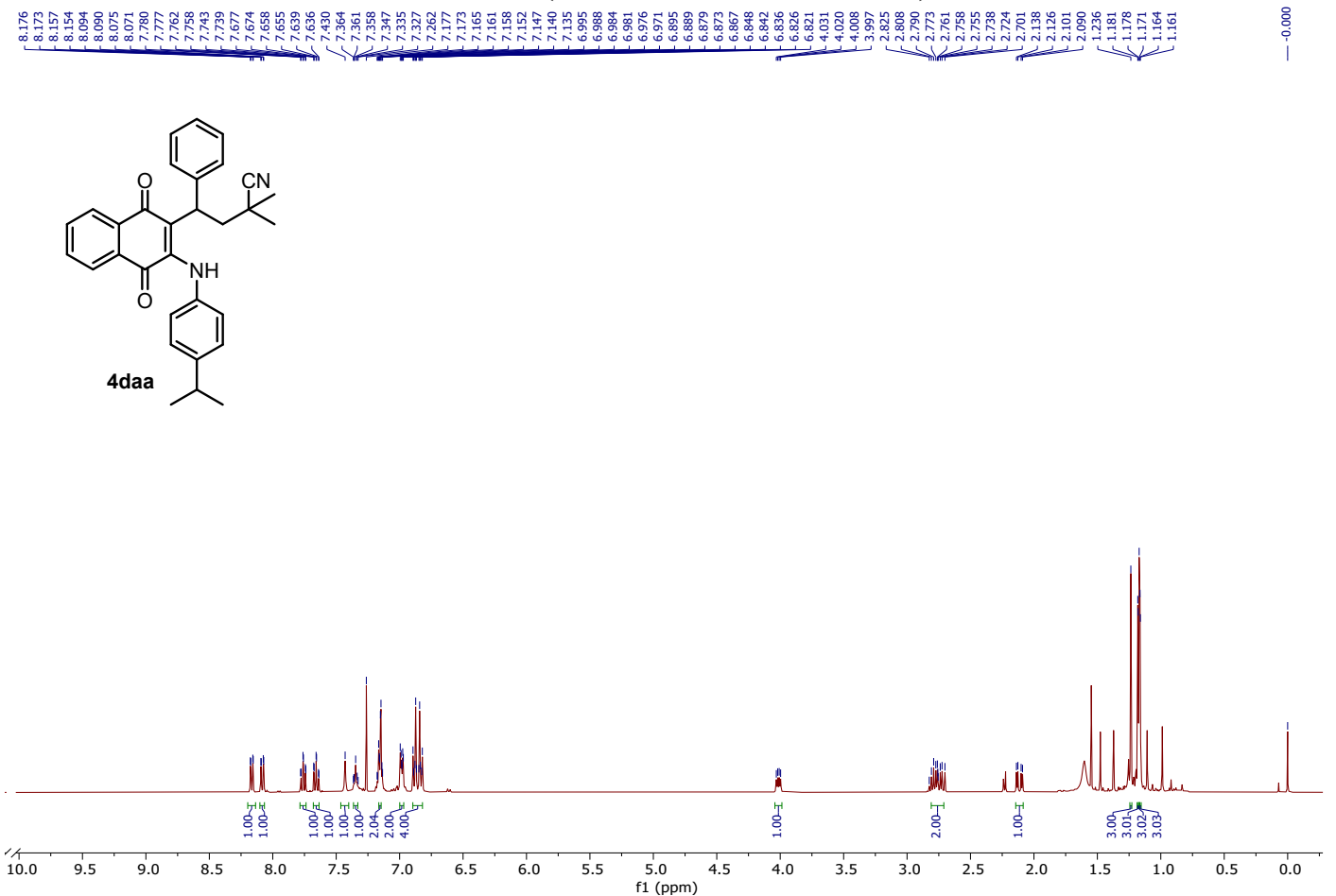
¹H-NMR (400 MHz, Chloroform-*d*)



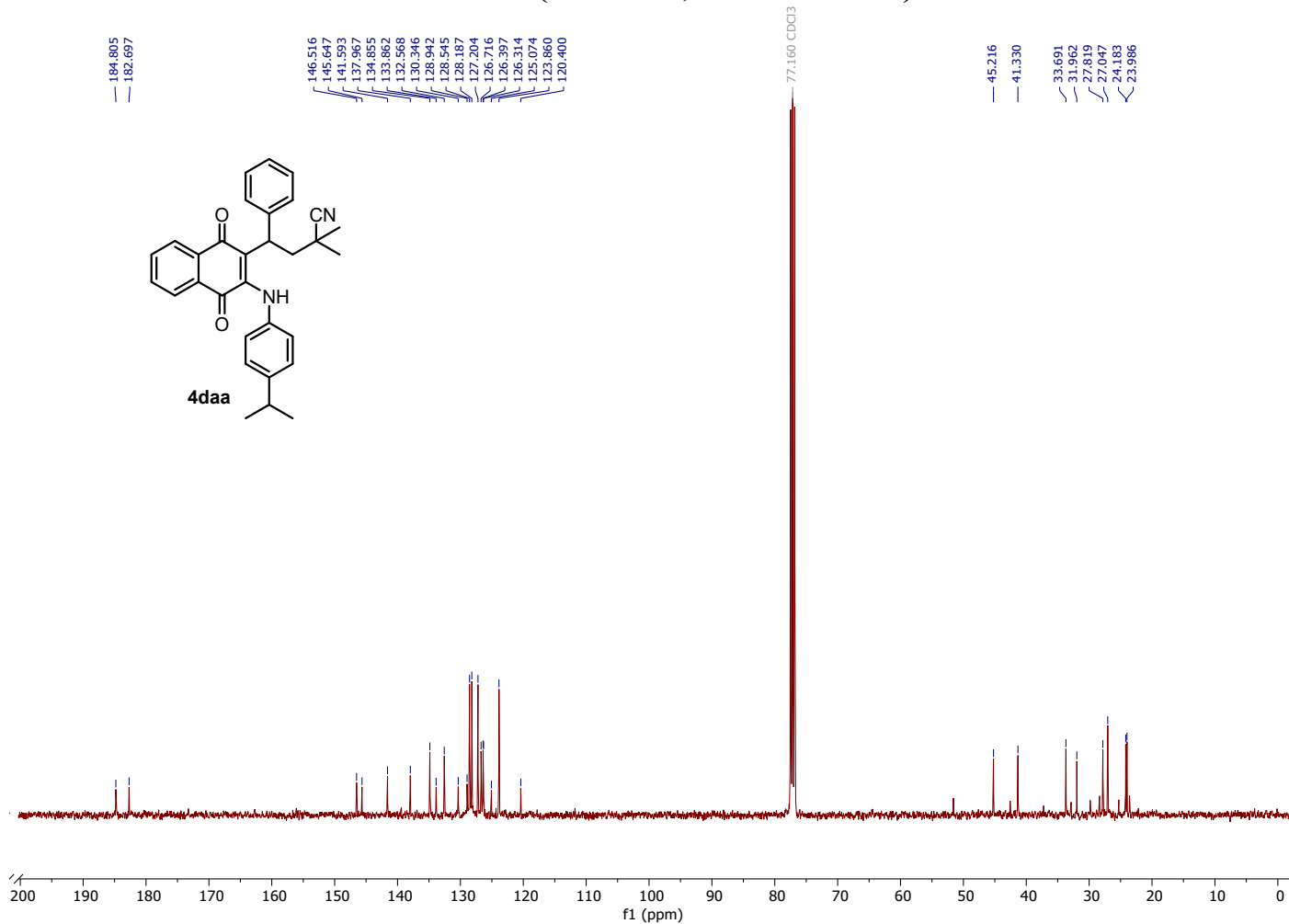
¹³C-NMR (100 MHz, Chloroform-*d*)



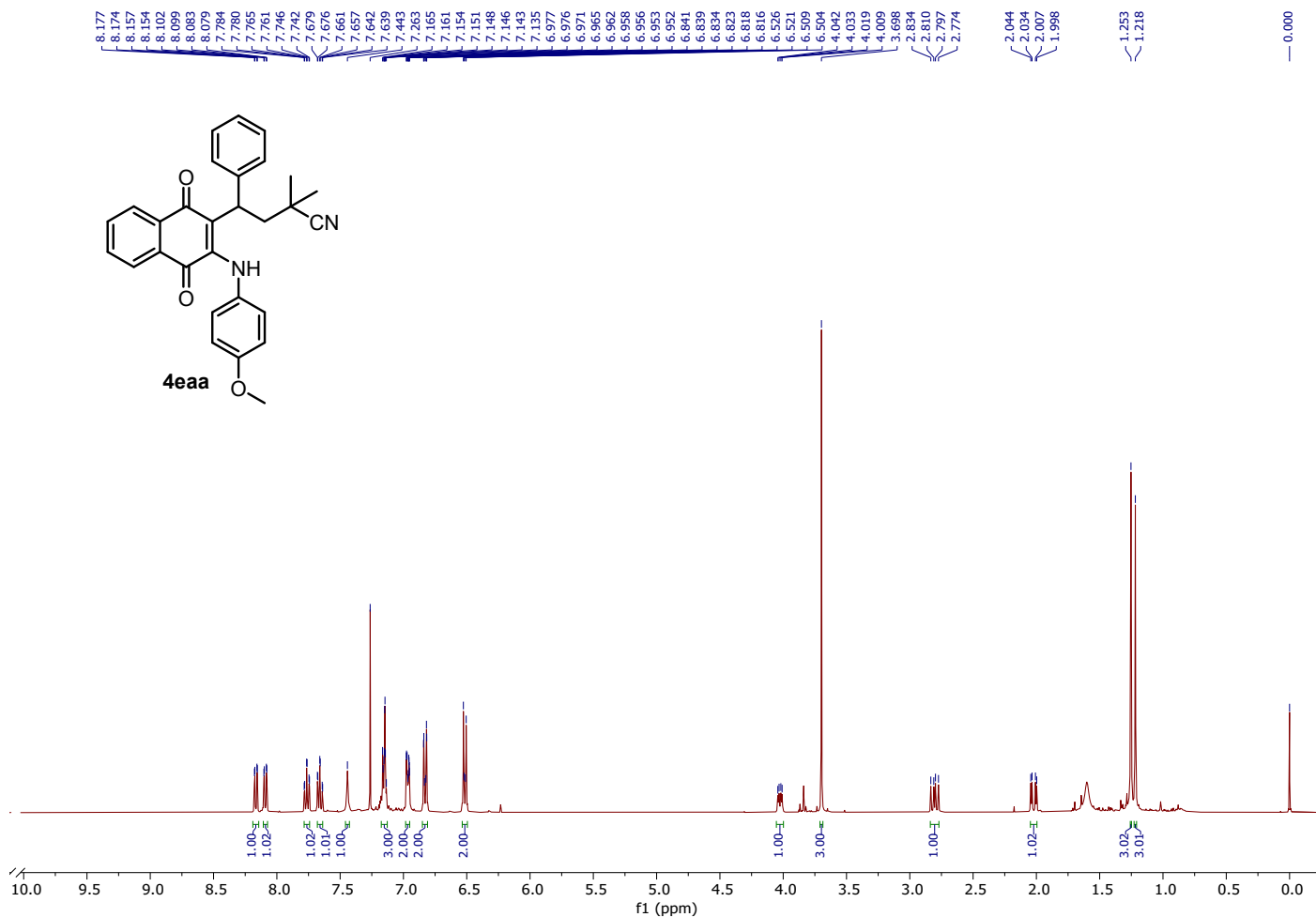
¹H-NMR (400 MHz, Chloroform-*d*)



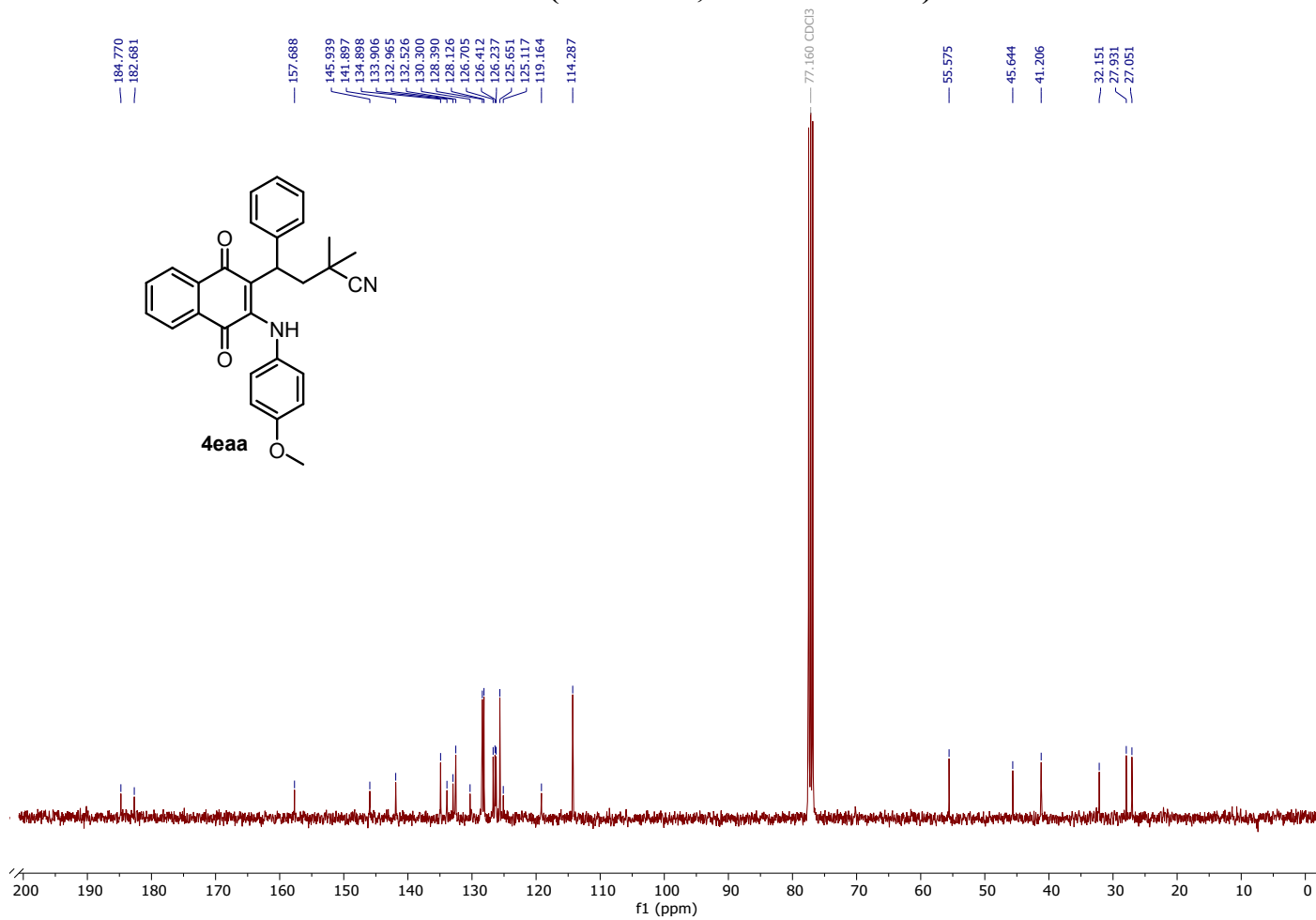
¹³C-NMR (100 MHz, Chloroform-*d*)



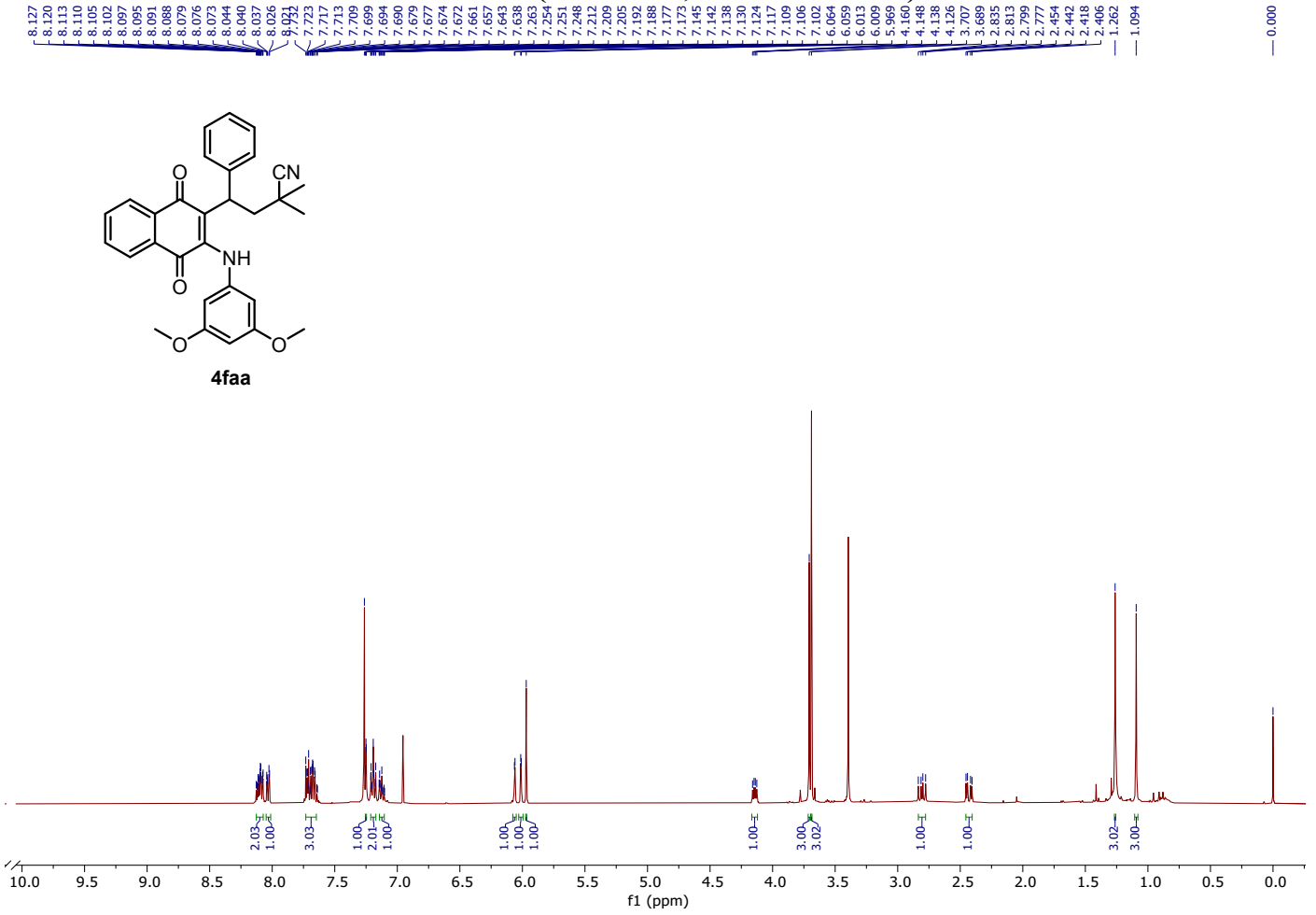
¹H-NMR (400 MHz, Chloroform-*d*)



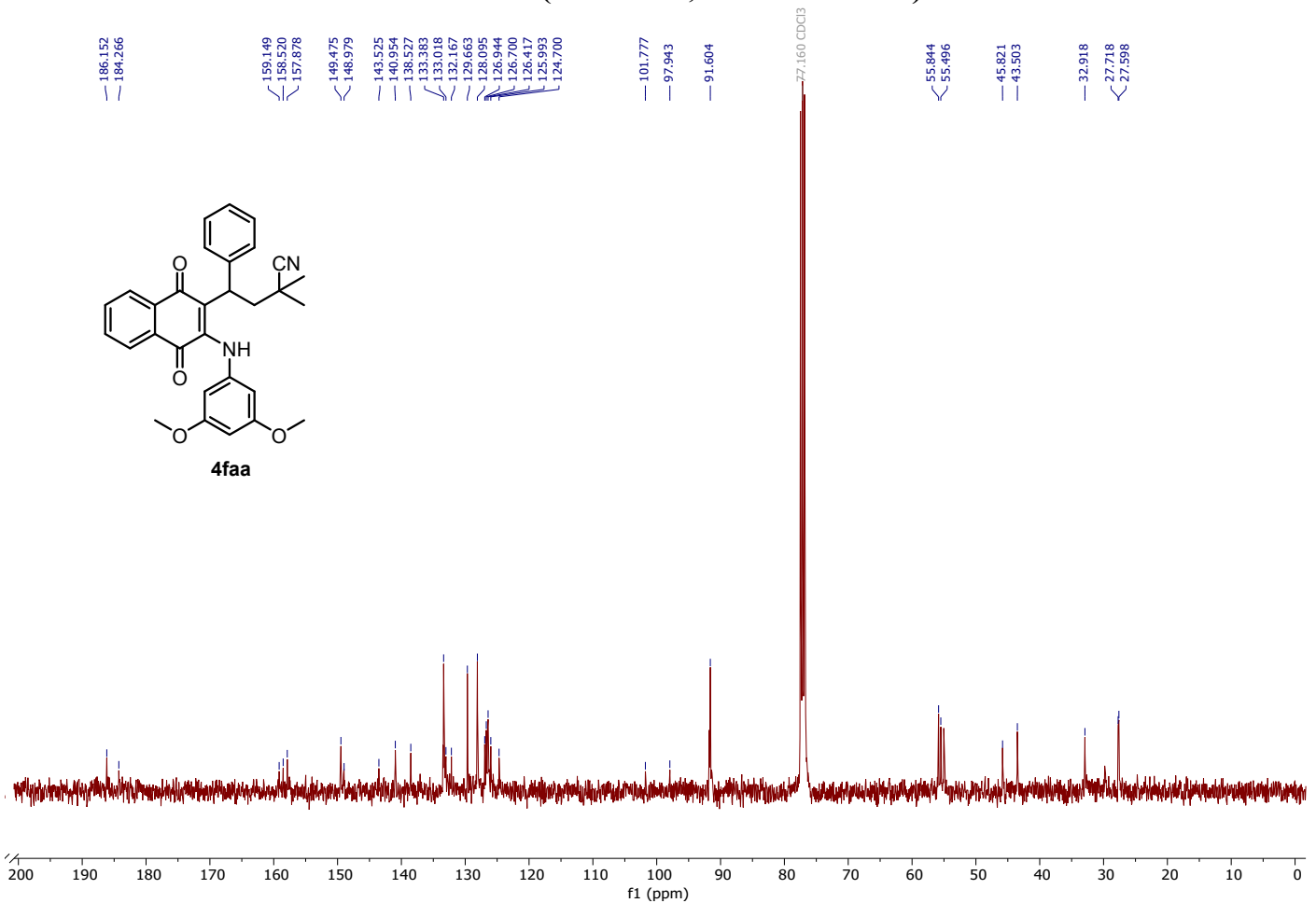
¹³C-NMR (100 MHz, Chloroform-*d*)



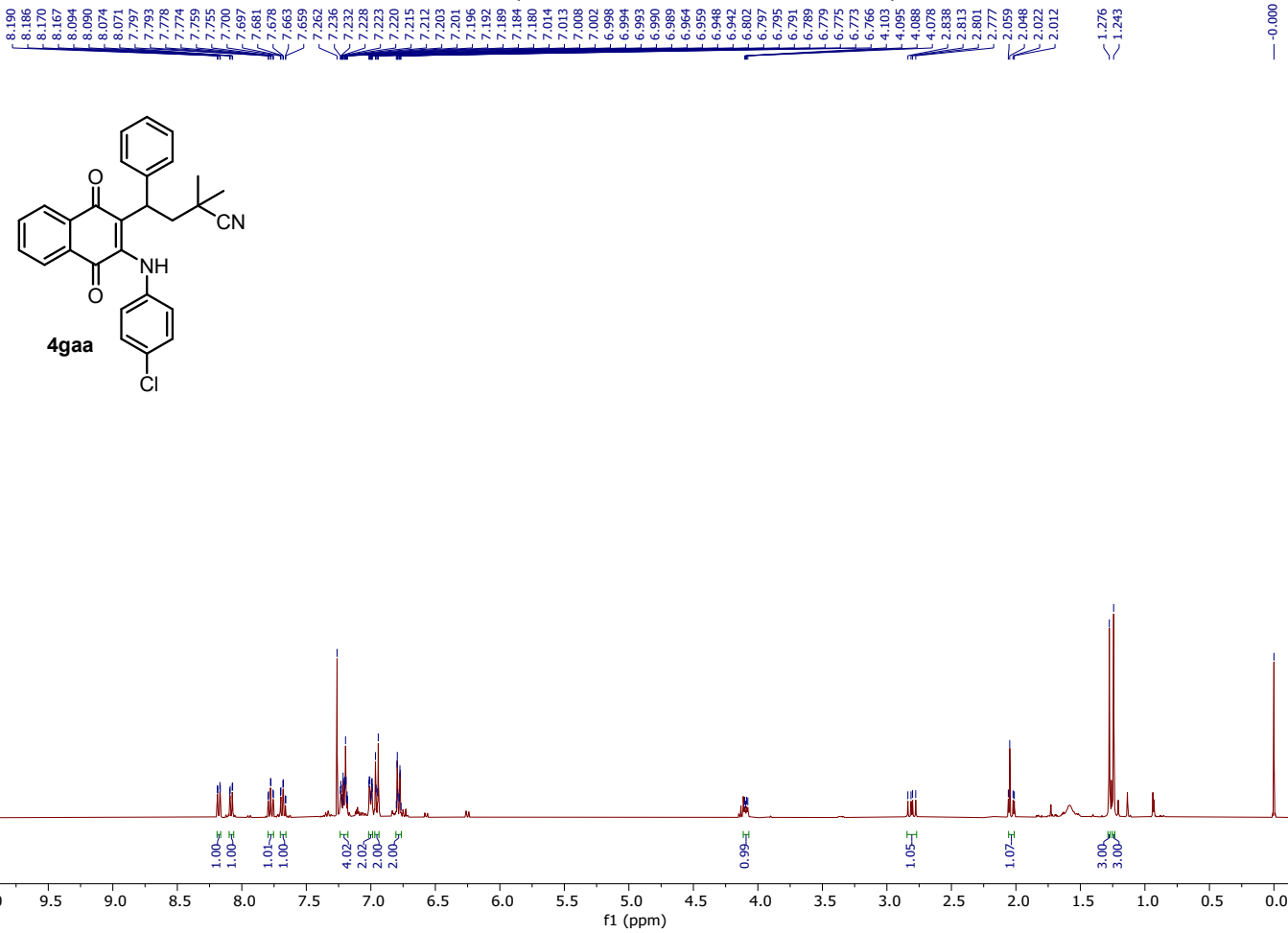
¹H-NMR (400 MHz, Chloroform-*d*)



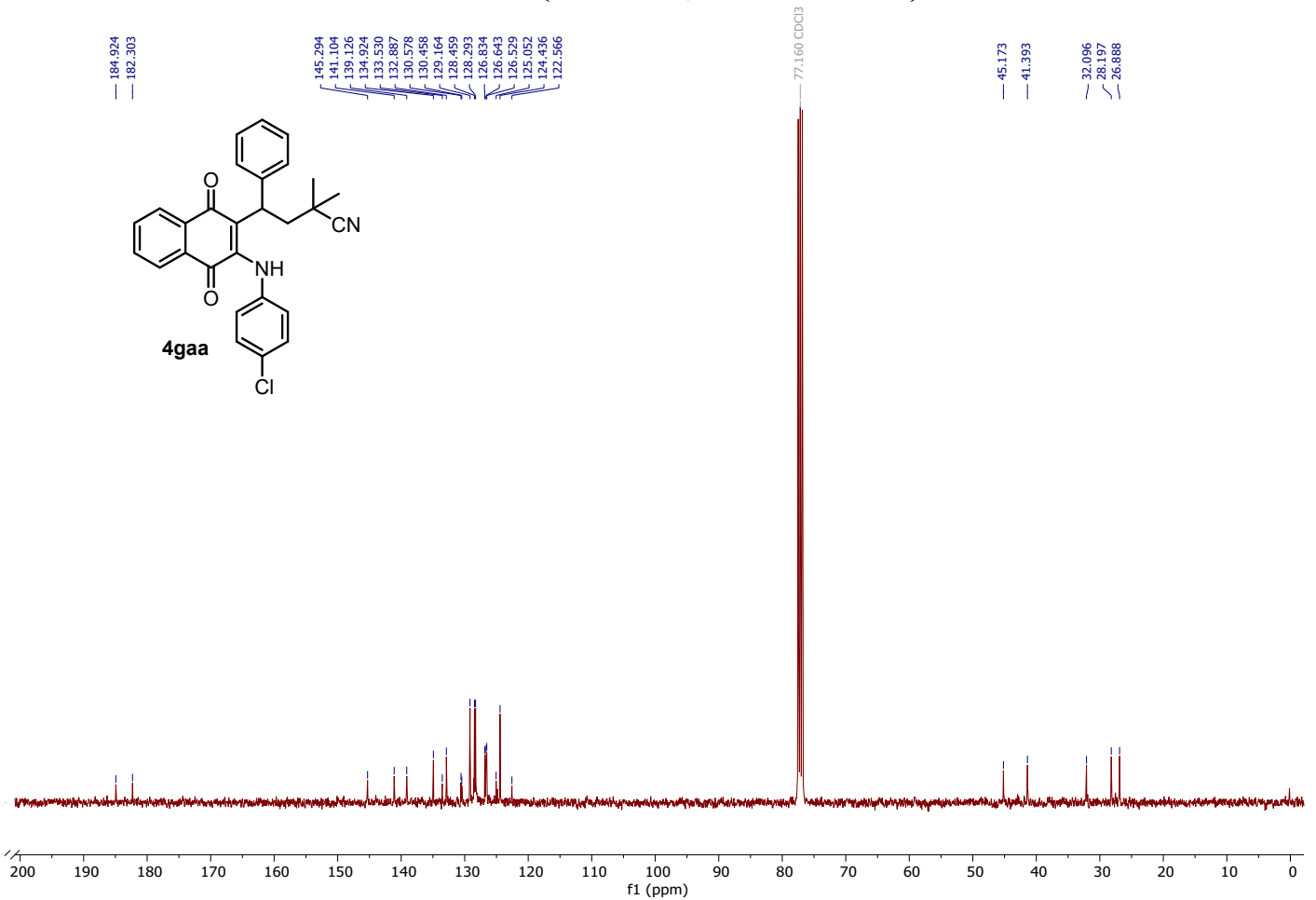
¹³C-NMR (100 MHz, Chloroform-*d*)



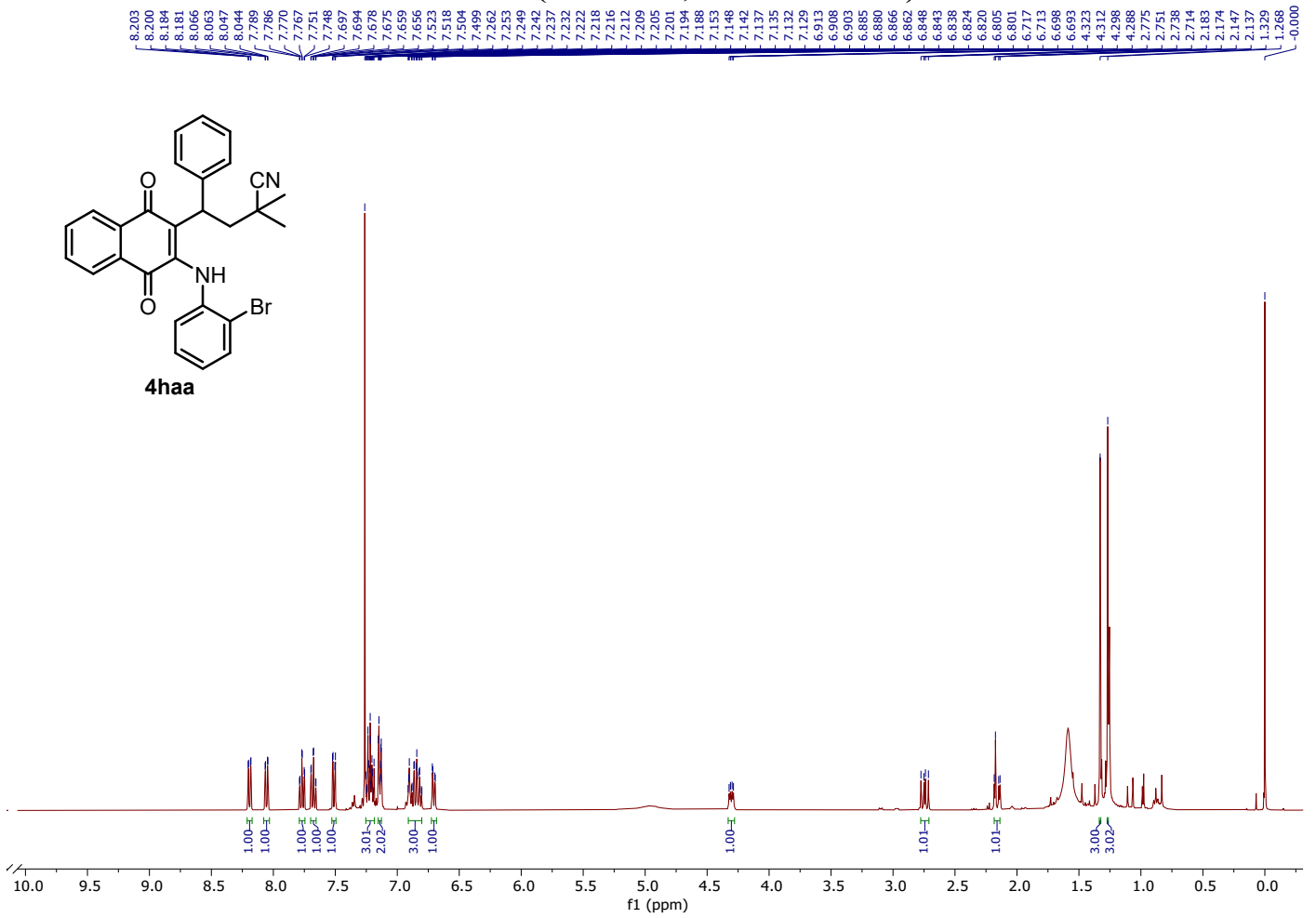
¹H-NMR (400 MHz, Chloroform-d)



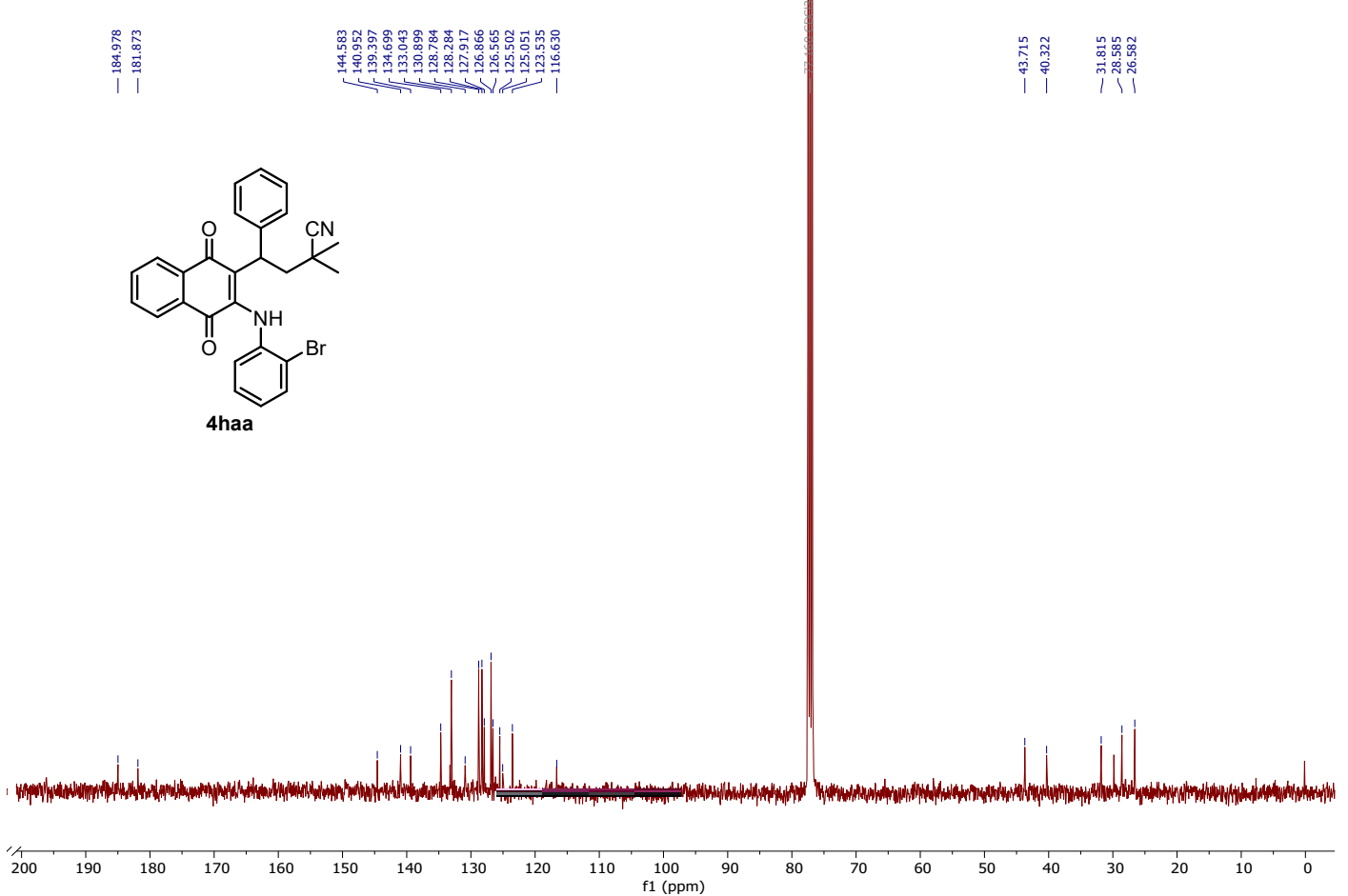
¹³C-NMR (100 MHz, Chloroform-d)



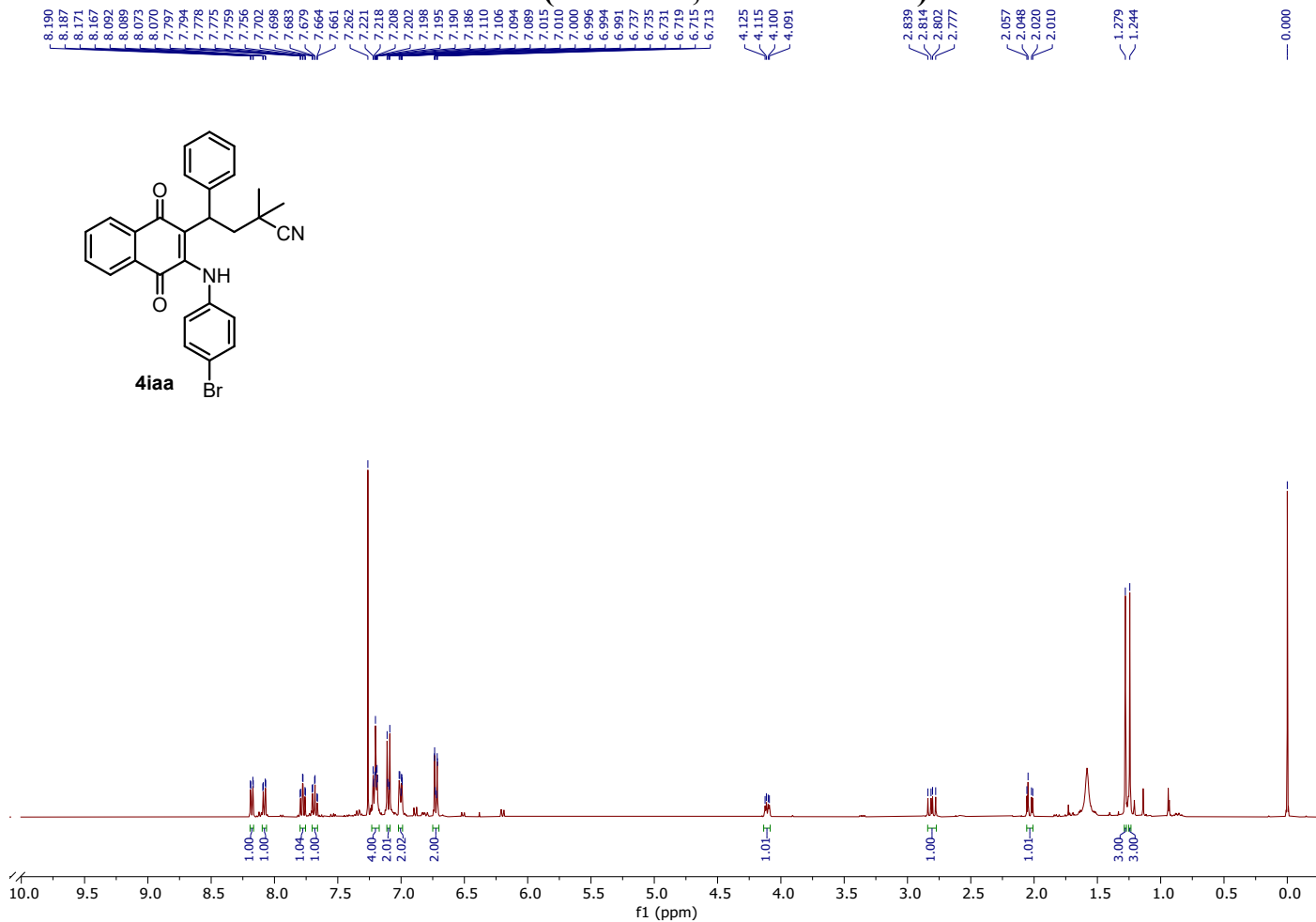
¹H-NMR (400 MHz, Chloroform-d)



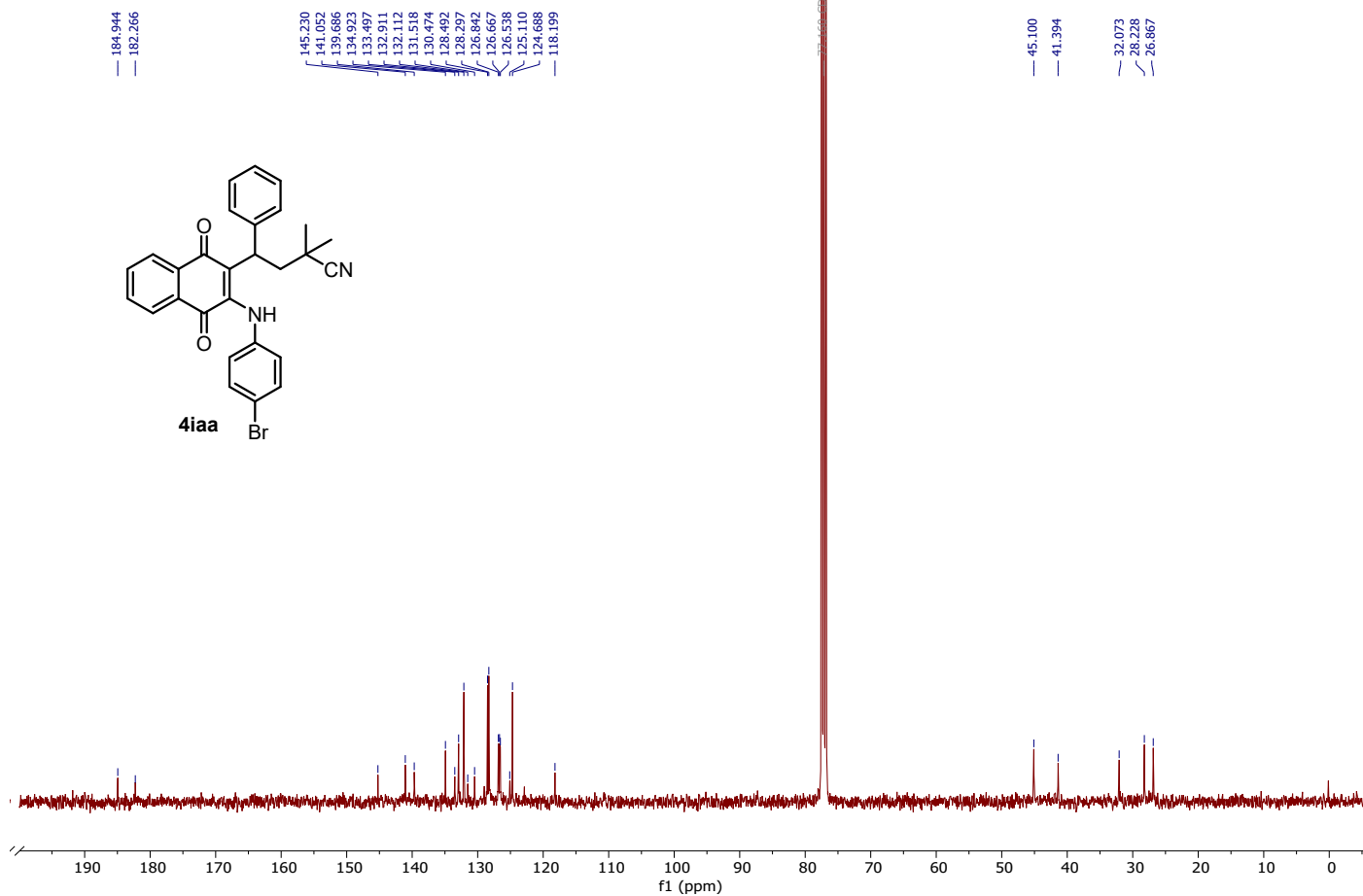
¹³C-NMR (100 MHz, Chloroform-d)



¹H-NMR (400 MHz, Chloroform-*d*)

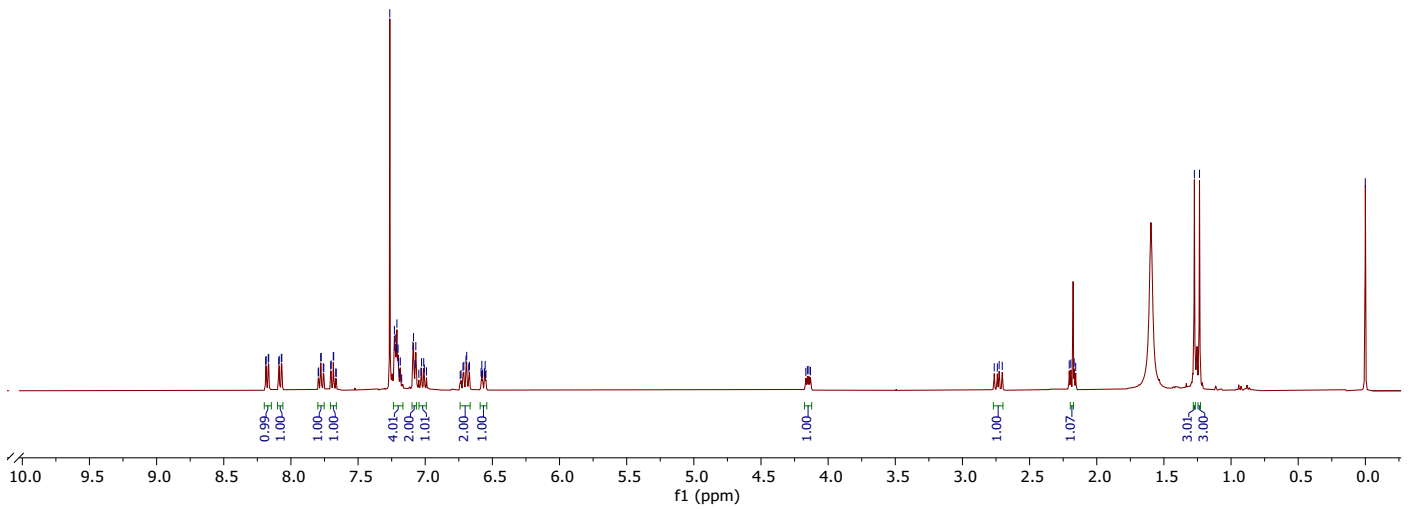
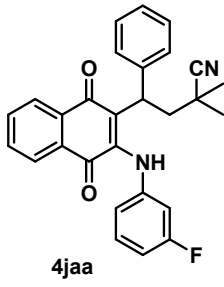


¹³C-NMR (100 MHz, Chloroform-*d*)



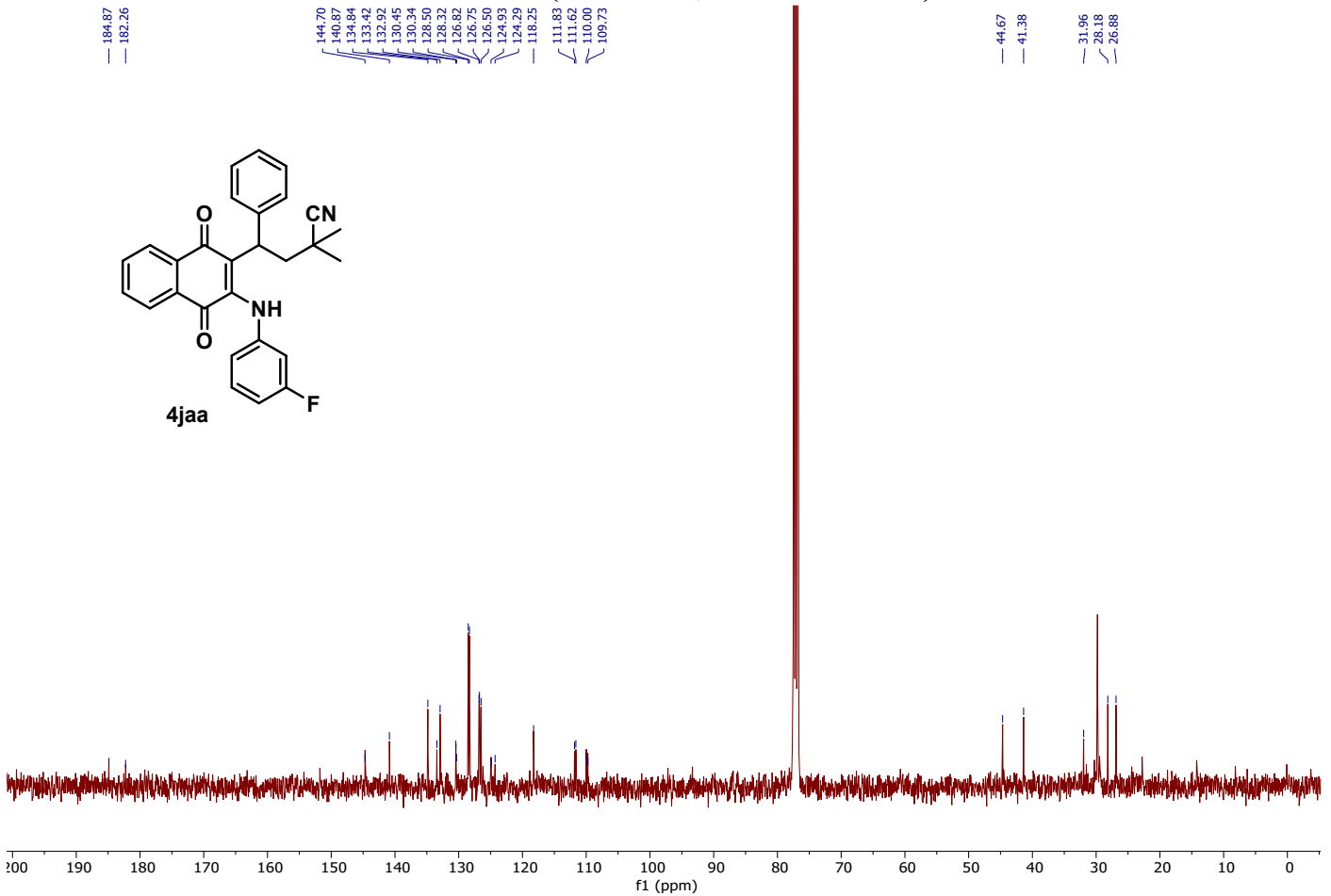
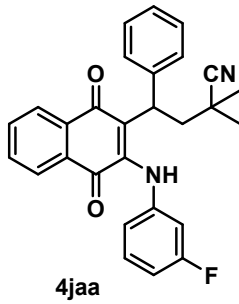
¹H-NMR (400 MHz, Chloroform-*d*)

8.188, 8.185, 8.169, 8.165, 8.091, 8.087, 8.071, 8.068, 7.797, 7.793, 7.778, 7.774, 7.759, 7.755, 7.704, 7.700, 7.685, 7.681, 7.666, 7.663, 7.264, 7.229, 7.223, 7.219, 7.215, 7.211, 7.202, 7.198, 7.193, 7.186, 7.175, 7.092, 7.087, 7.076, 7.070, 7.048, 7.032, 7.032, 7.032, 7.011, 7.007, 6.991, 6.970, 6.730, 6.728, 6.719, 6.715, 6.697, 6.691, 6.675, 6.671, 6.584, 6.579, 6.573, 6.559, 6.554, 6.548, 4.166, 4.155, 4.143, 4.132, 2.763, 2.740, 2.727, 2.704, 2.205, 2.193, 2.168, 2.157, 1.273, 1.235, 0.000

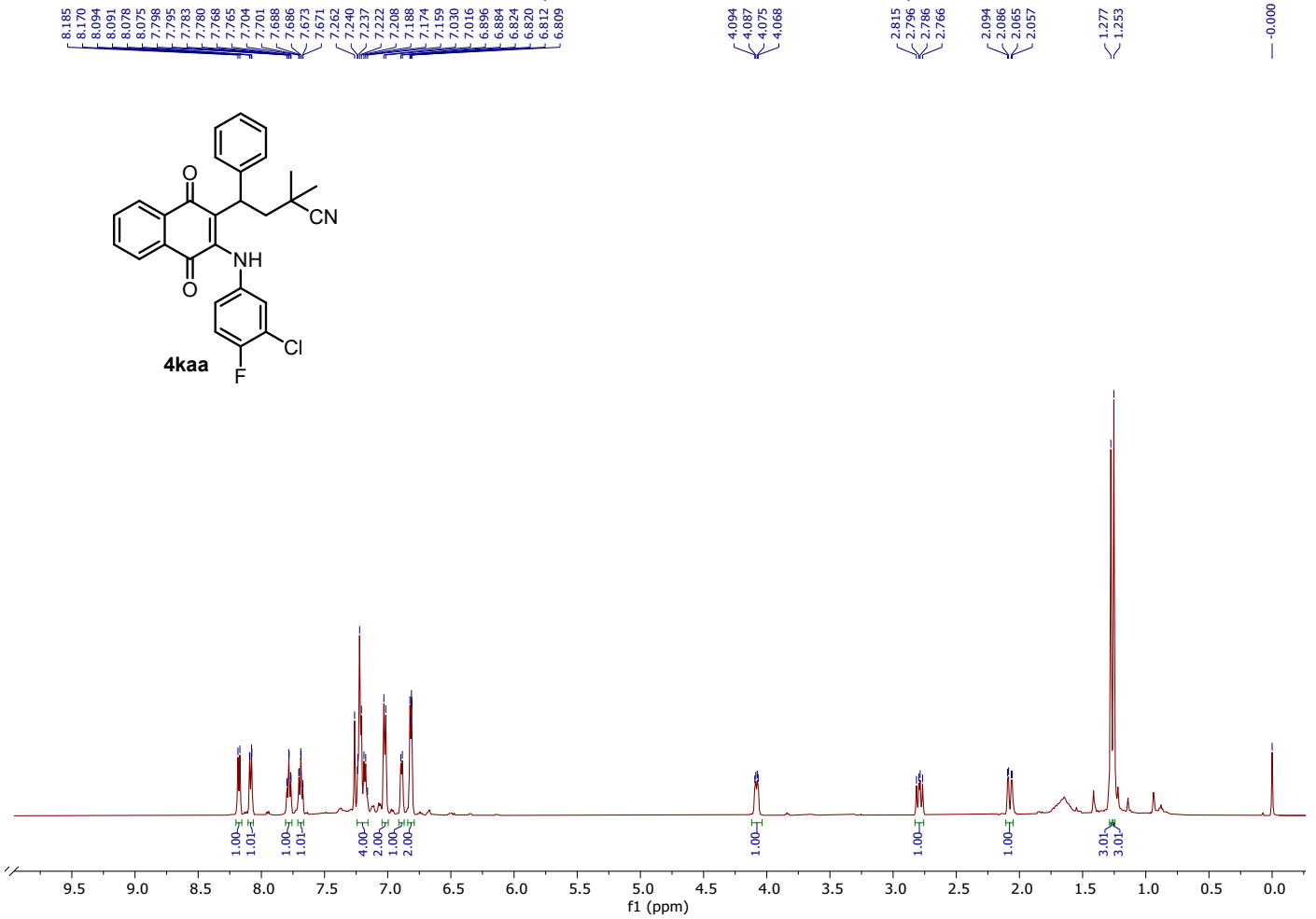


¹³C-NMR (100 MHz, Chloroform-*d*)

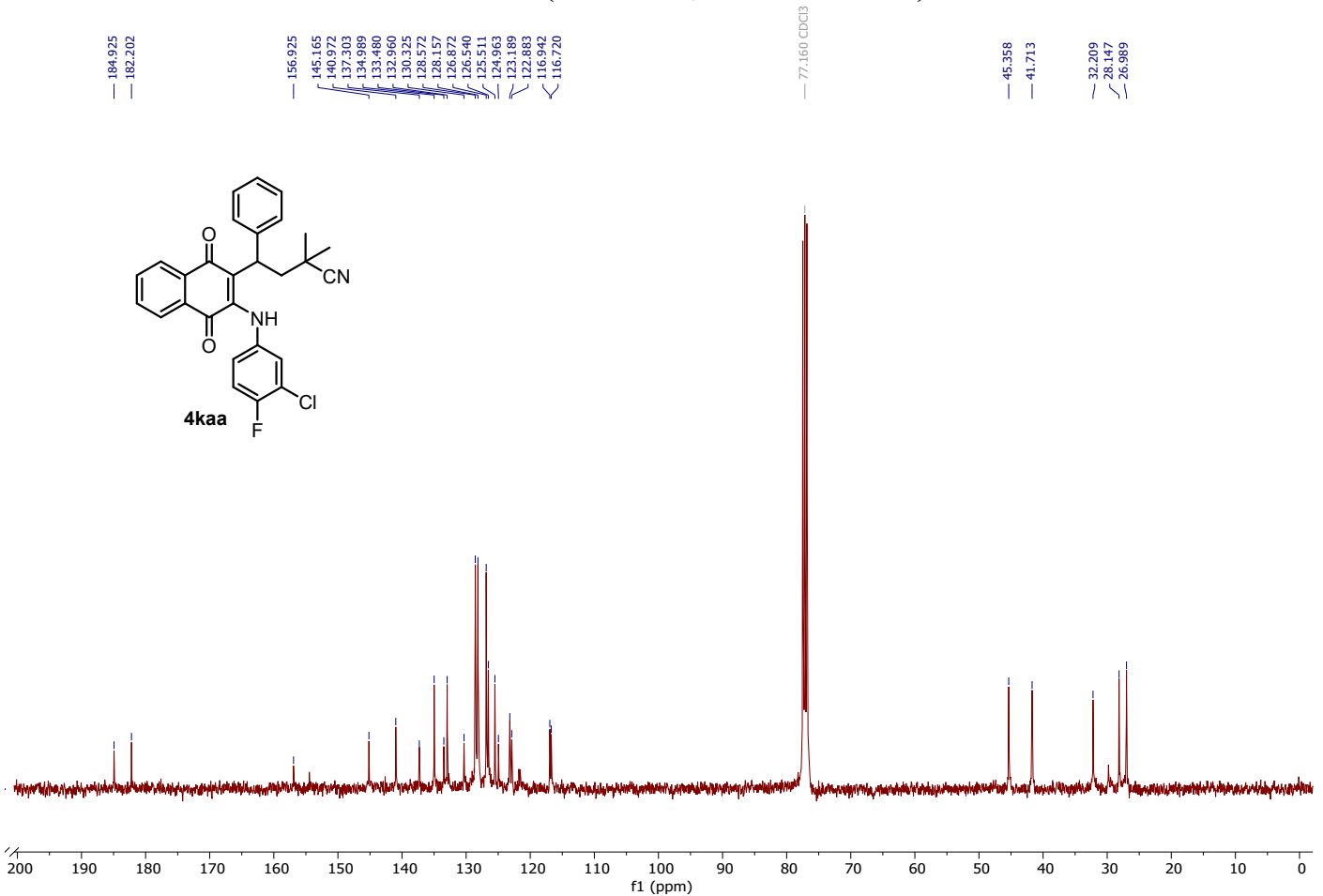
184.87, 182.26, 144.70, 140.87, 139.84, 135.42, 132.92, 130.45, 130.34, 128.50, 128.32, 126.82, 126.75, 126.50, 124.93, 124.29, 118.25, 111.83, 111.62, 110.00, 109.73, 44.67, 41.38, 31.96, 28.18, 26.88



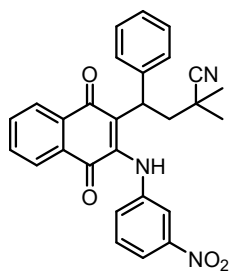
¹H-NMR (500 MHz, Chloroform-*d*)



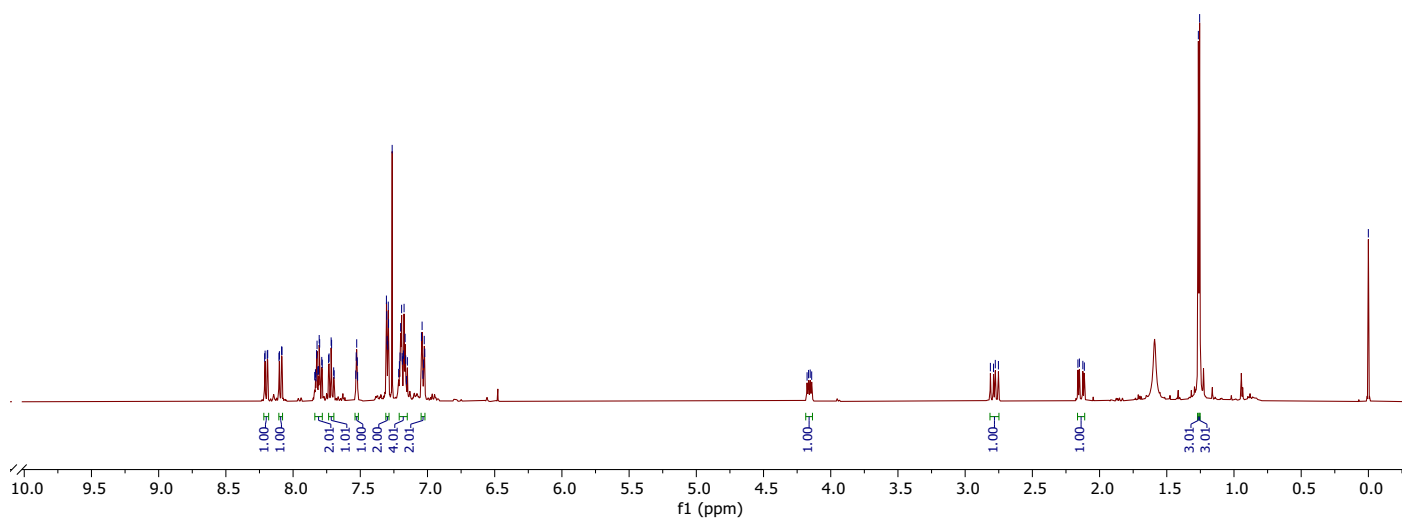
¹³C-NMR (100 MHz, Chloroform-*d*)



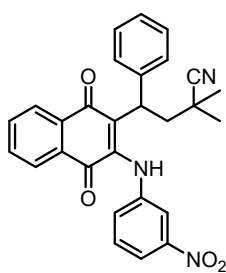
¹H-NMR (400 MHz, Chloroform-*d*)



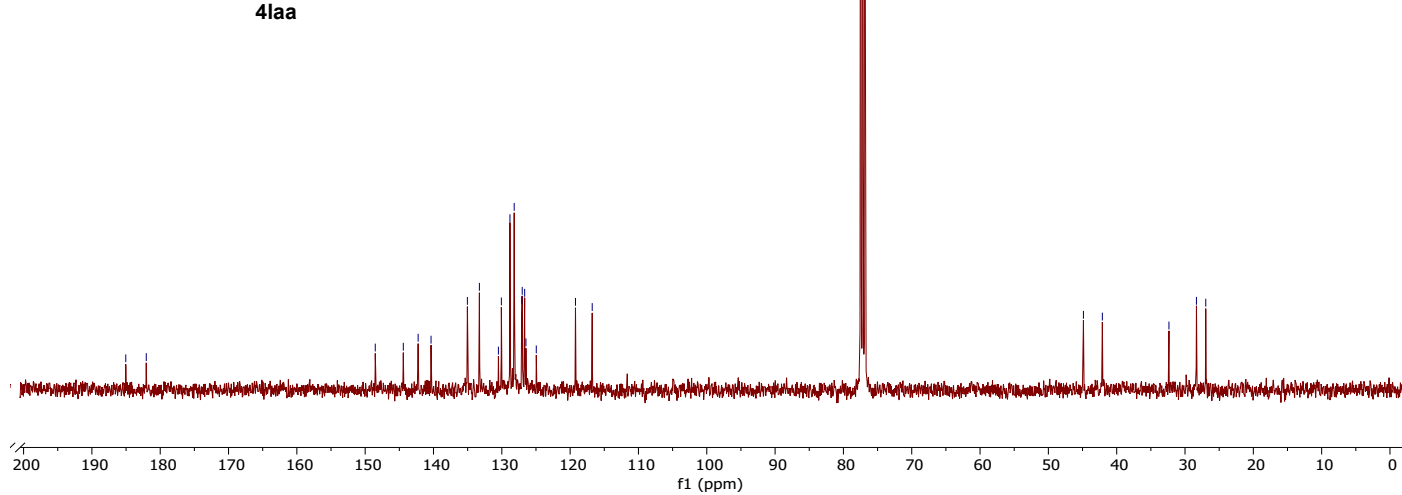
41aa



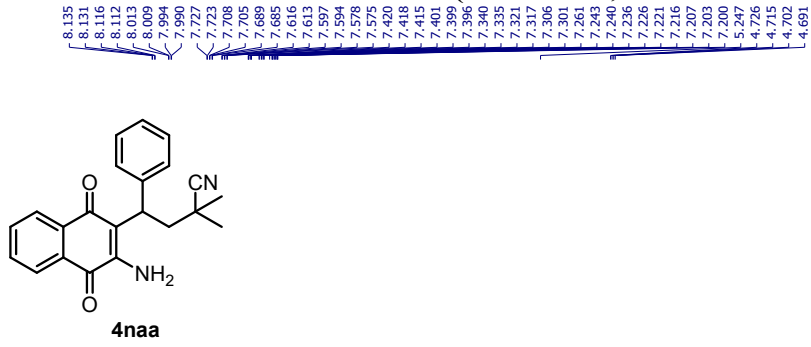
¹³C-NMR (100 MHz, Chloroform-*d*)



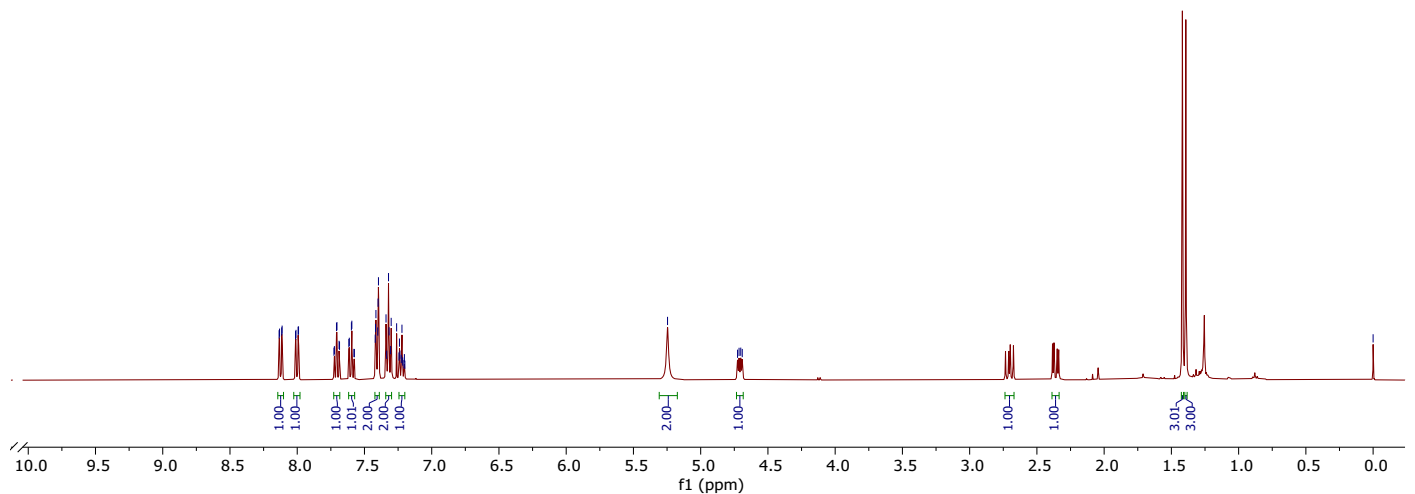
41aa



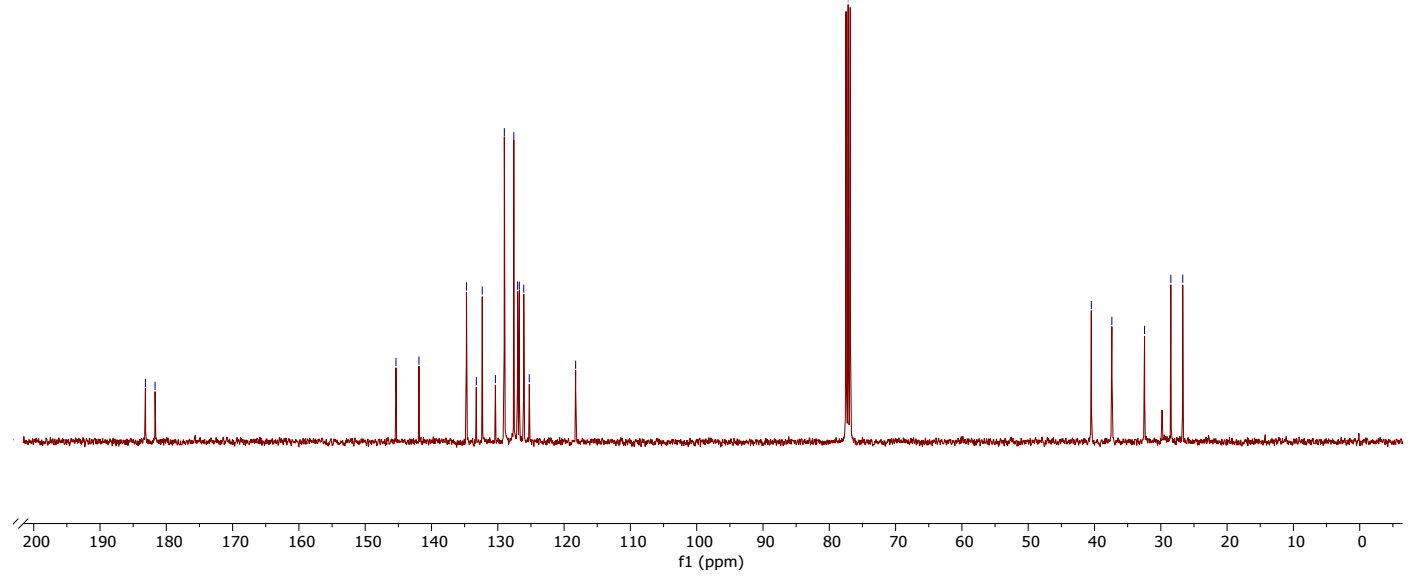
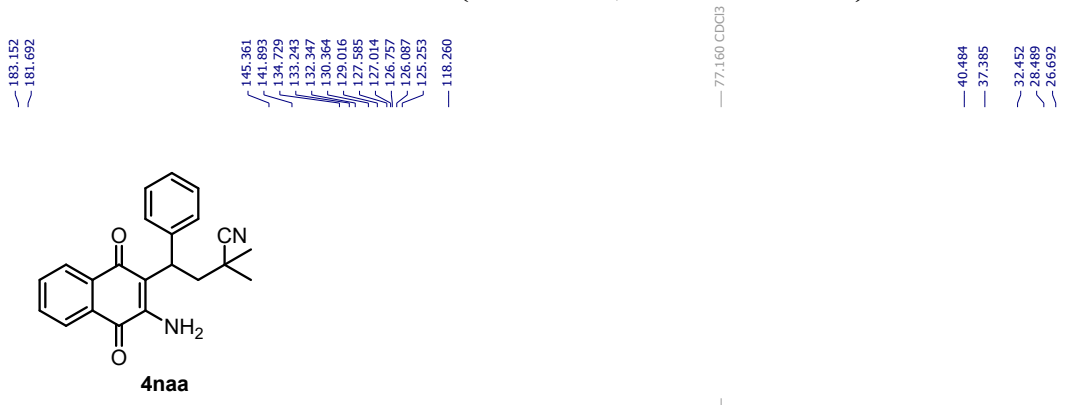
¹H-NMR (400 MHz, Chloroform-d)



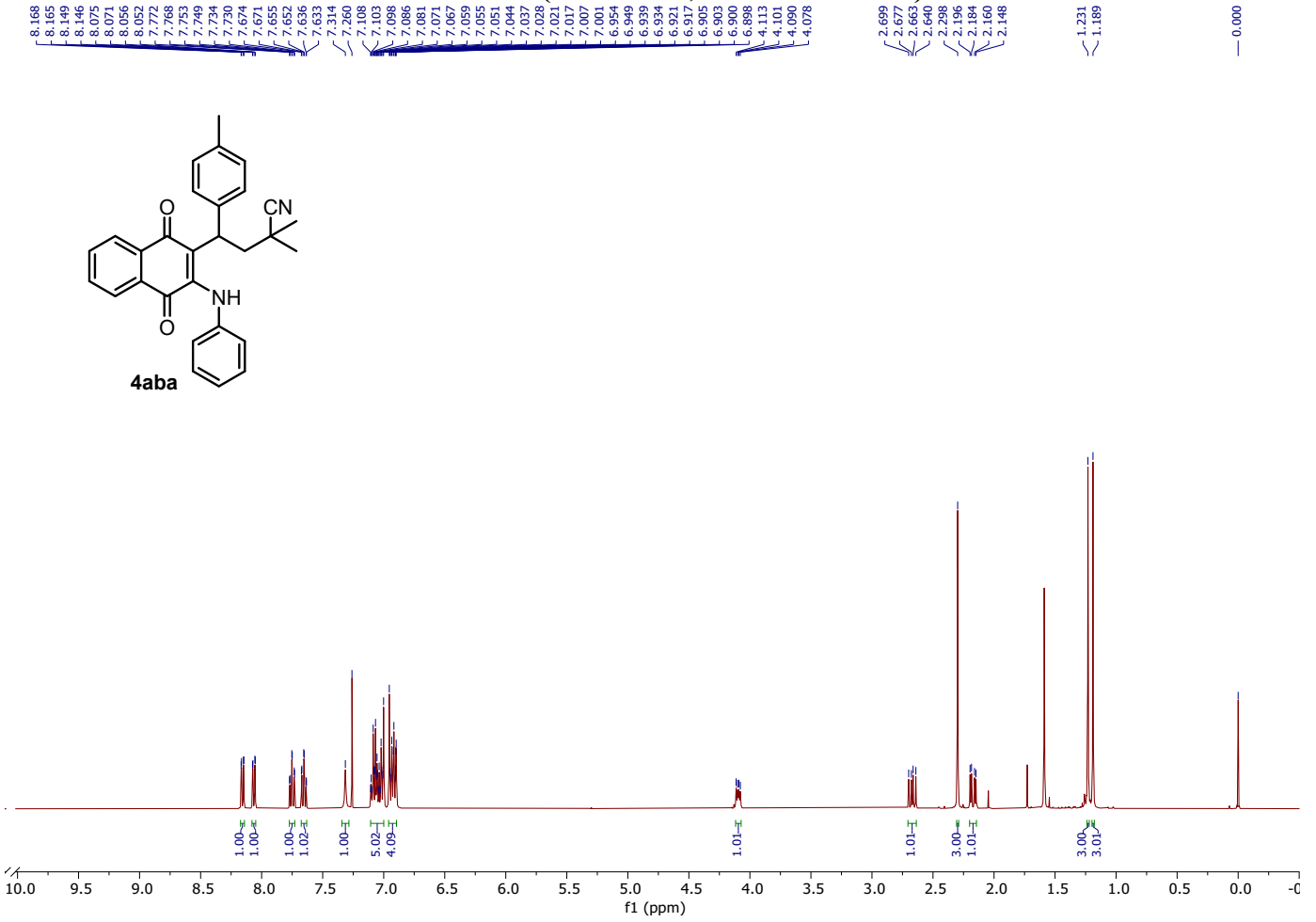
0.000



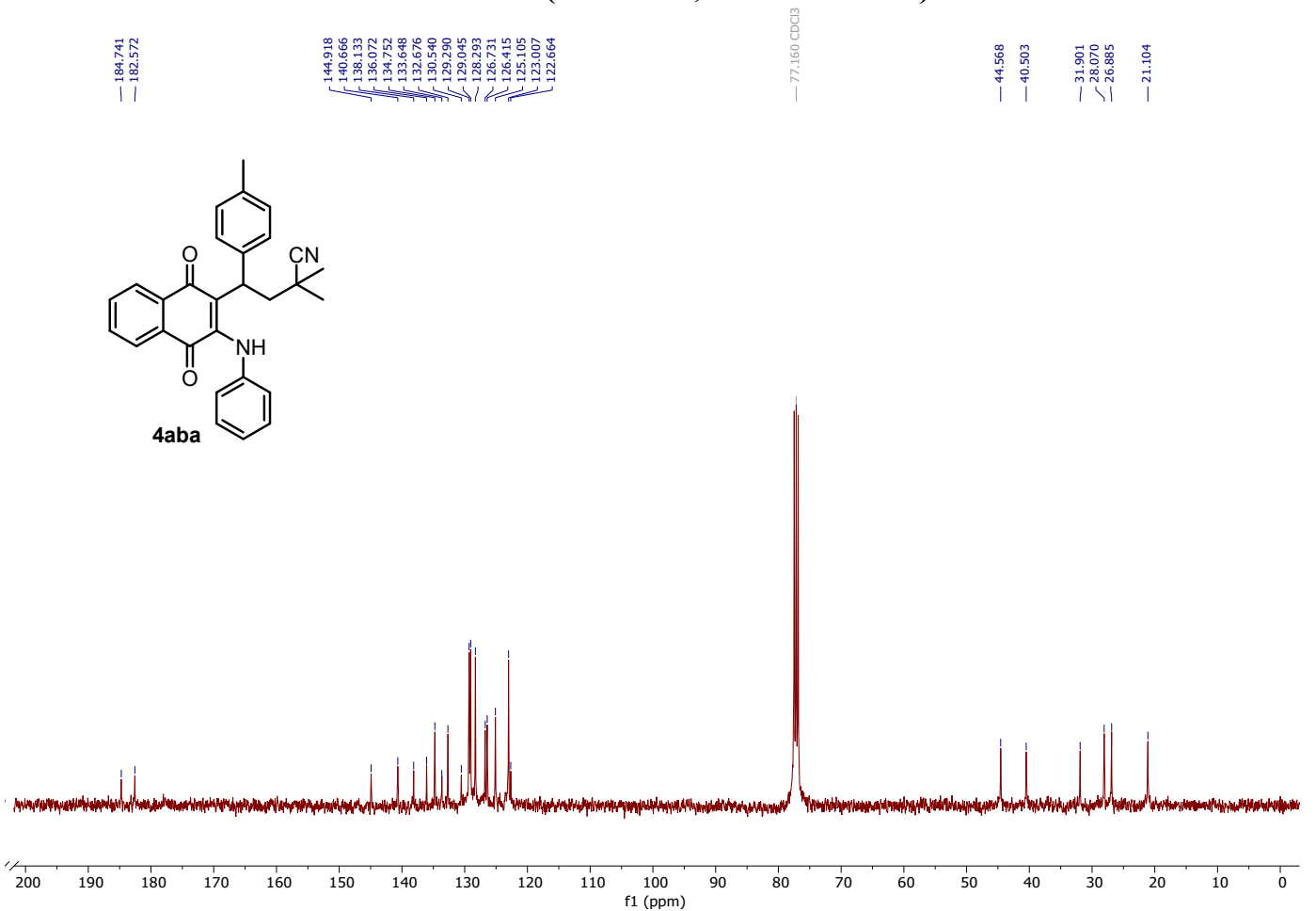
¹³C-NMR (100 MHz, Chloroform-d)



¹H-NMR (400 MHz, Chloroform-*d*)

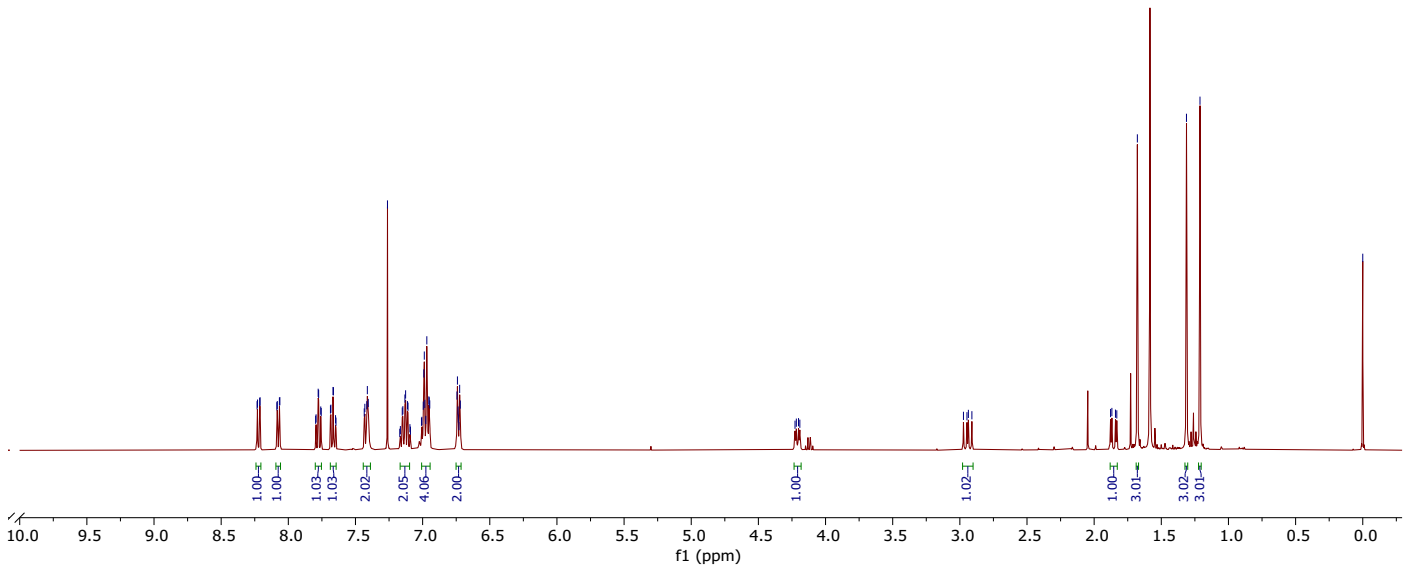
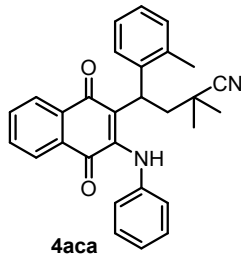


¹³C-NMR (100 MHz, Chloroform-*d*)



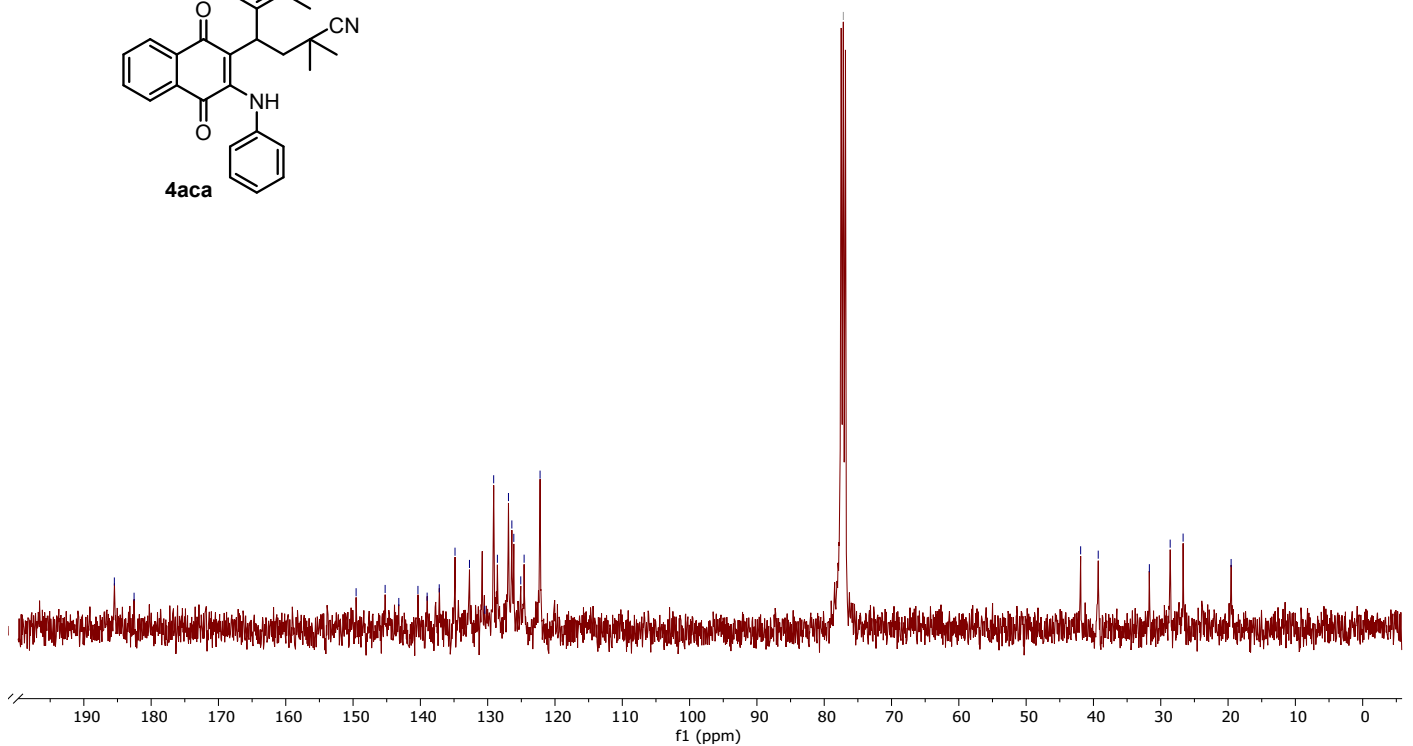
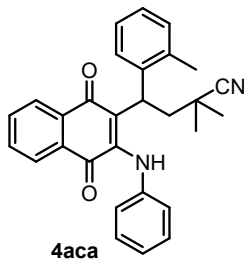
¹H-NMR (400 MHz, Chloroform-*d*)

8.233, 8.229, 8.213, 8.210, 8.085, 8.082, 8.066, 8.063, 7.797, 7.778, 7.774, 7.759, 7.755, 7.686, 7.683, 7.667, 7.664, 7.648, 7.645, 7.435, 7.430, 7.416, 7.412, 7.405, 7.262, 7.170, 7.166, 7.152, 7.147, 7.137, 7.127, 7.113, 7.109, 7.095, 7.091, 7.009, 7.006, 6.995, 6.991, 6.988, 6.984, 6.977, 6.969, 6.953, 6.951, 6.947, 6.744, 6.741, 6.736, 6.734, 6.728, 6.726, 6.720, 6.718, 6.710, 6.237, 4.317, 4.301, 4.191, 4.073, 2.823, 2.827, 2.826, 2.820, 1.828, 1.828, 1.641, 1.631, 1.628, 1.315, 1.212, 0.000

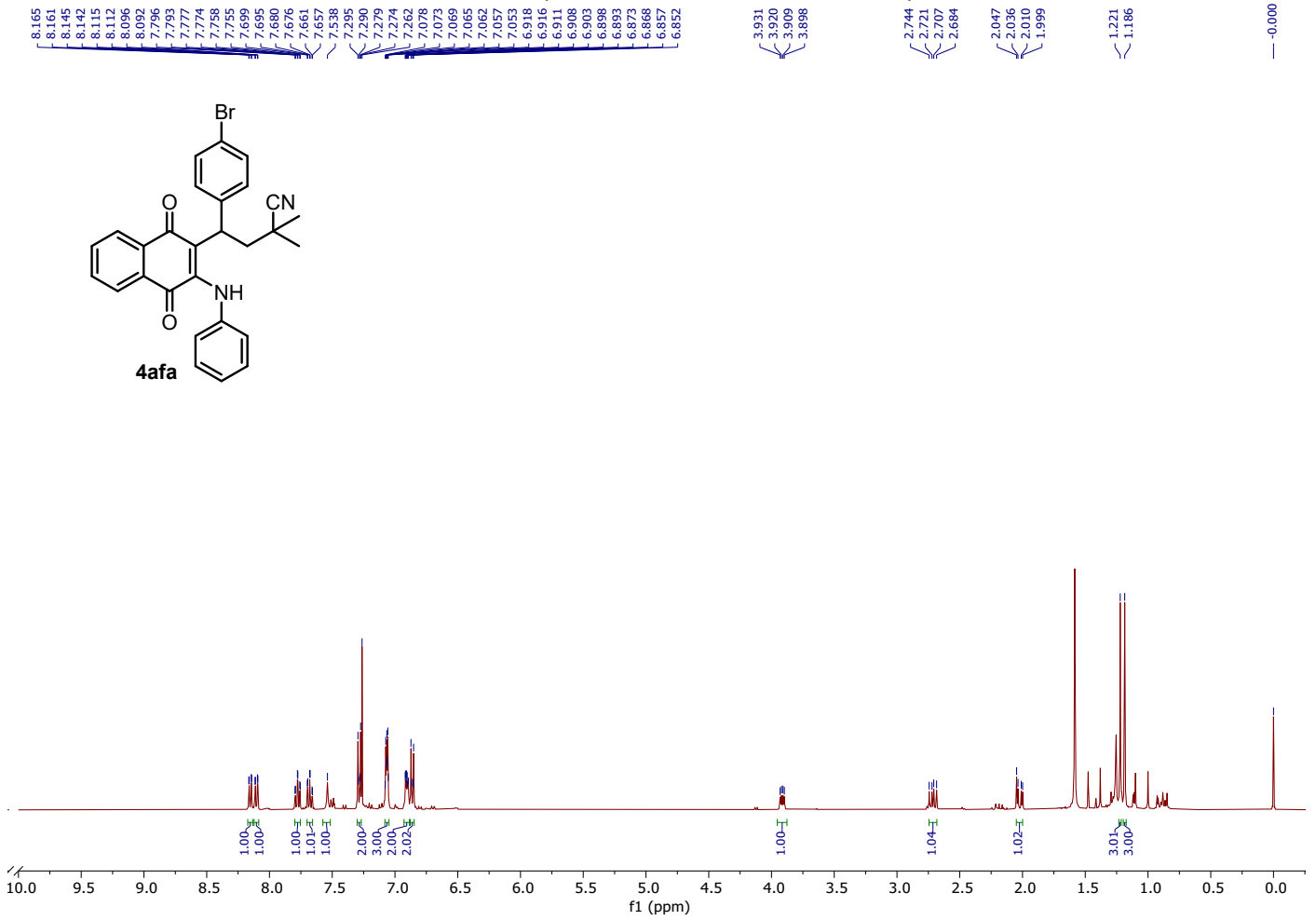


¹³C-NMR (100 MHz, Chloroform-*d*)

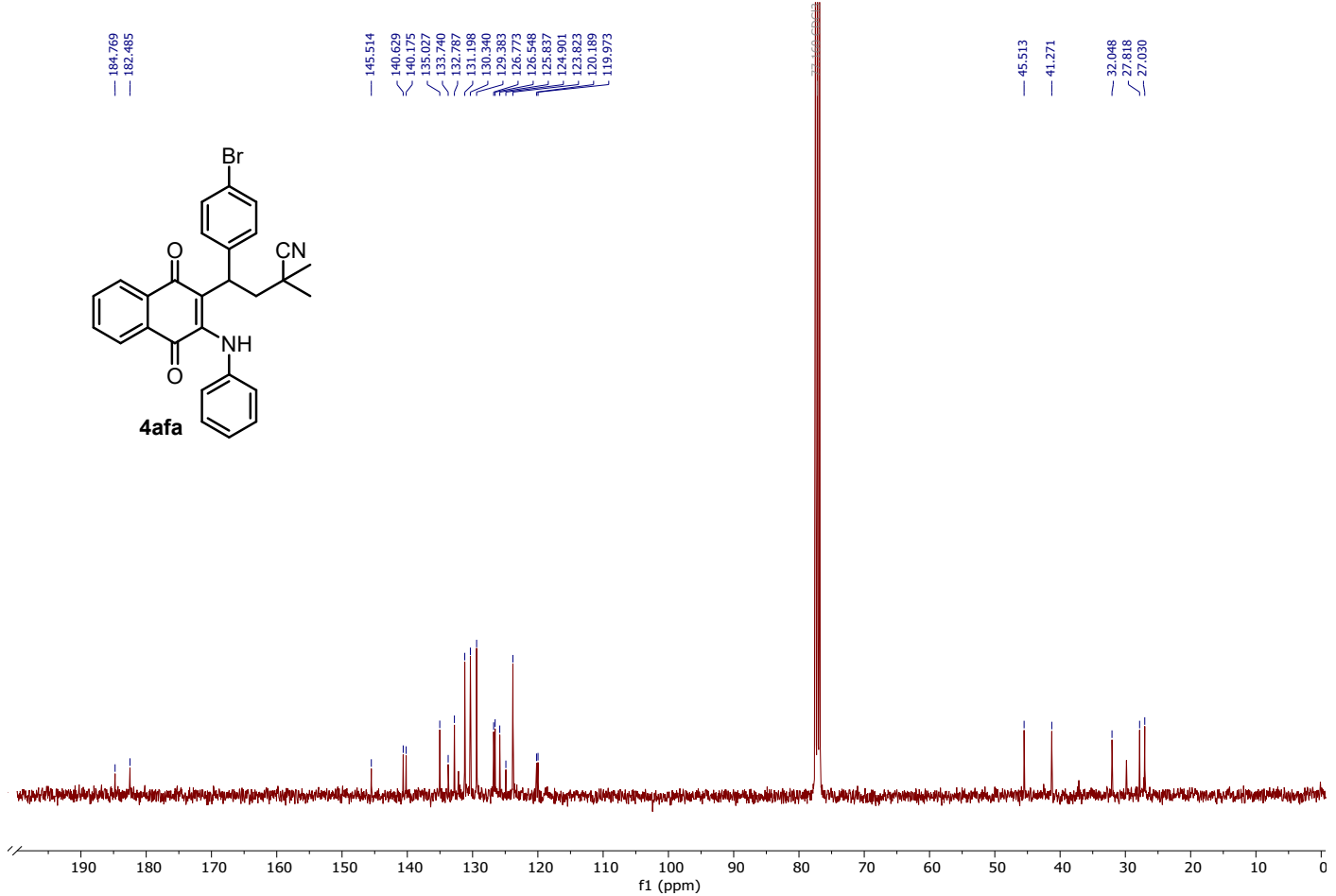
185.465, 182.535, 149.548, 145.236, 143.205, 140.361, 138.995, 137.196, 134.854, 132.704, 130.422, 129.111, 128.555, 126.911, 126.410, 125.087, 124.587, 122.217, 77.160 CDCl₃, 41.904, 39.290, 31.682, 28.600, 26.680, 19.546



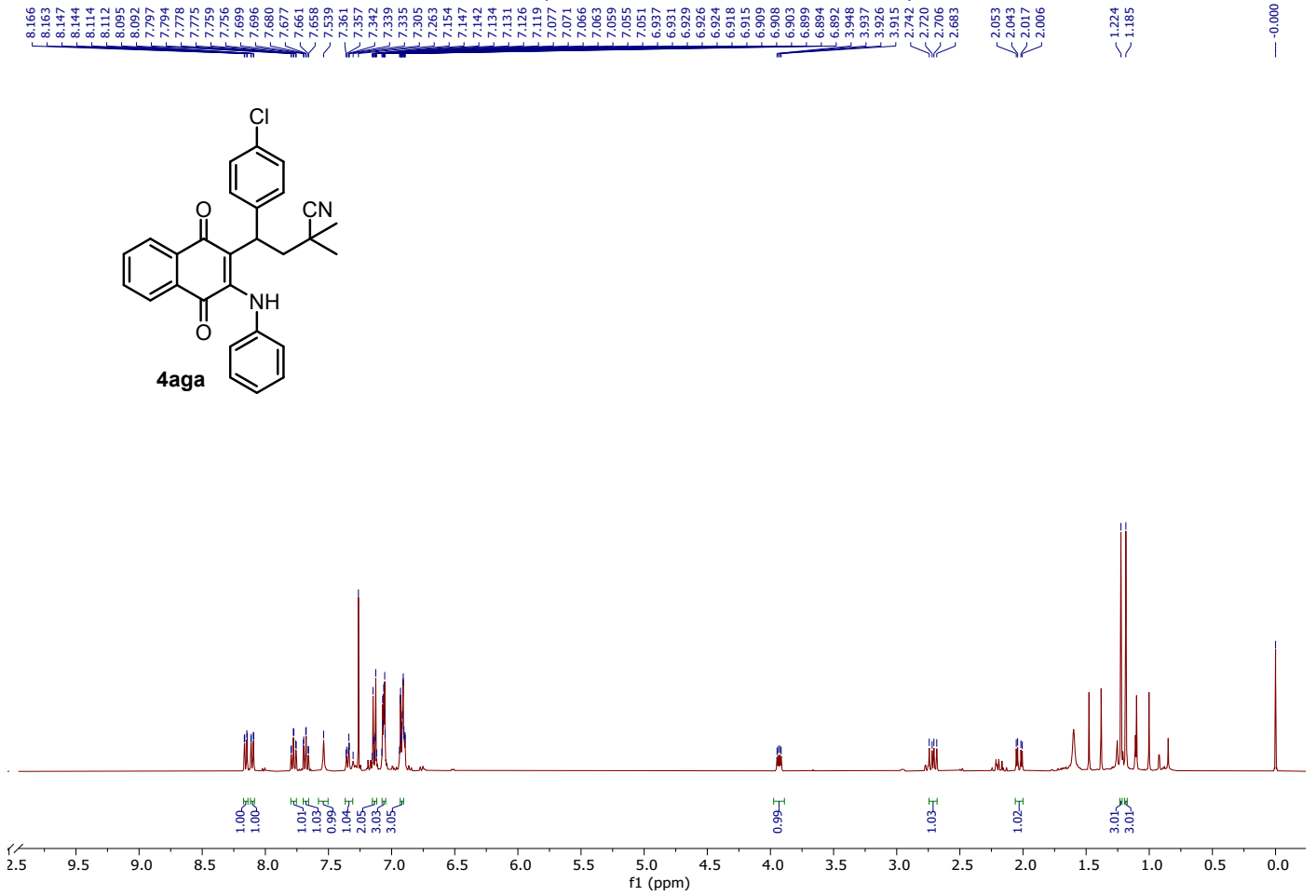
¹H-NMR (400 MHz, Chloroform-*d*)



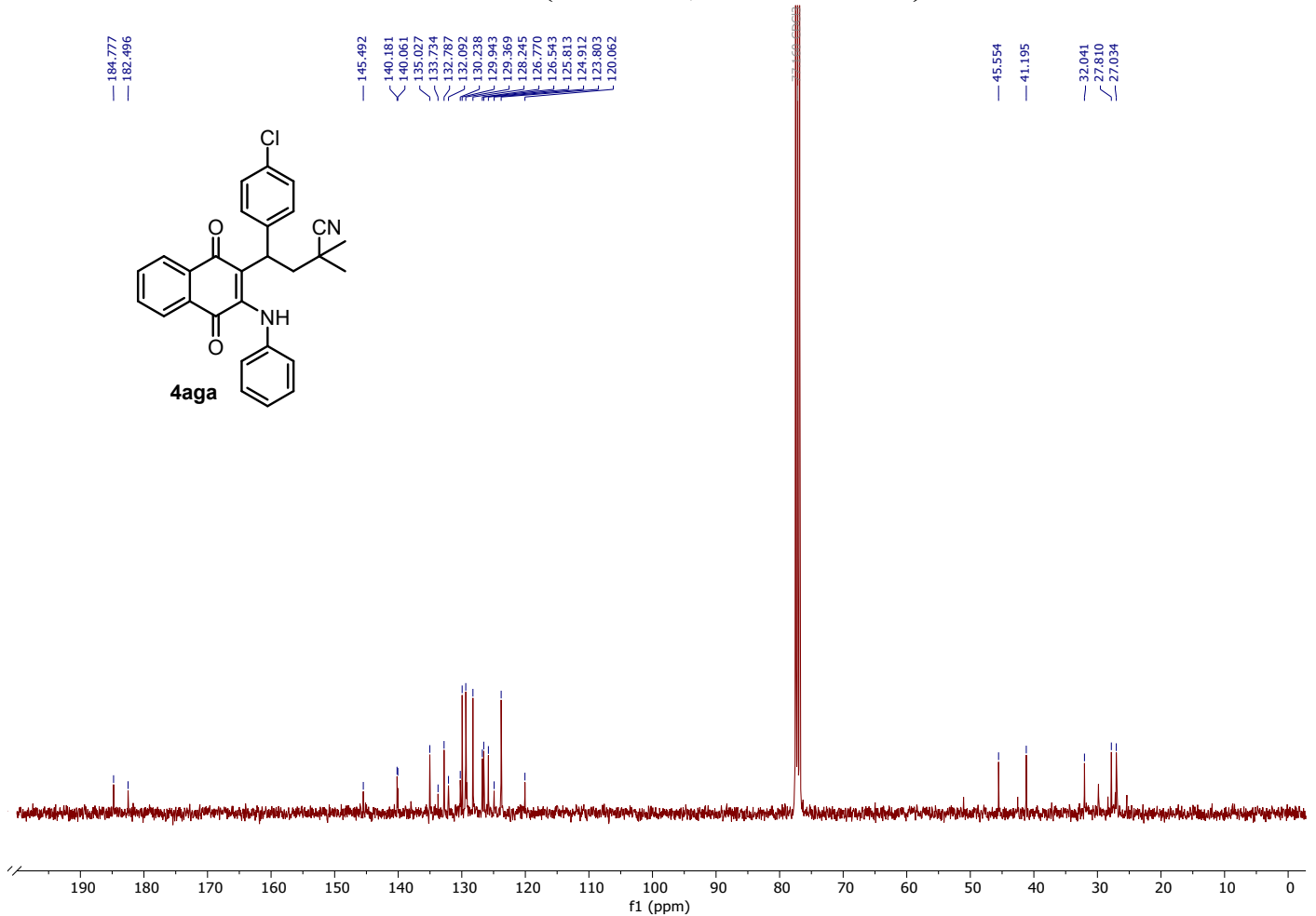
¹³C-NMR (100 MHz, Chloroform-*d*)



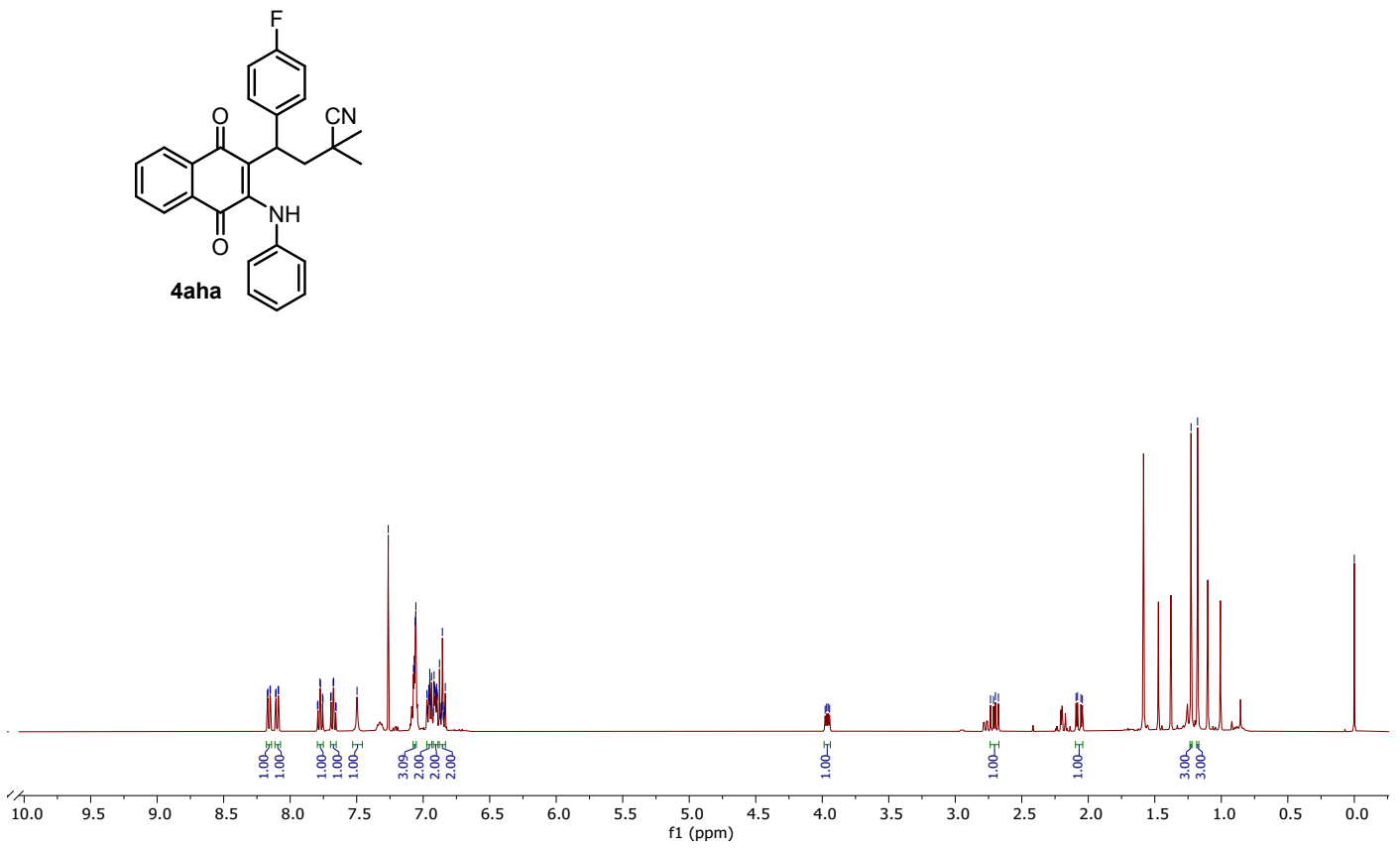
¹H-NMR (400 MHz, Chloroform-*d*)



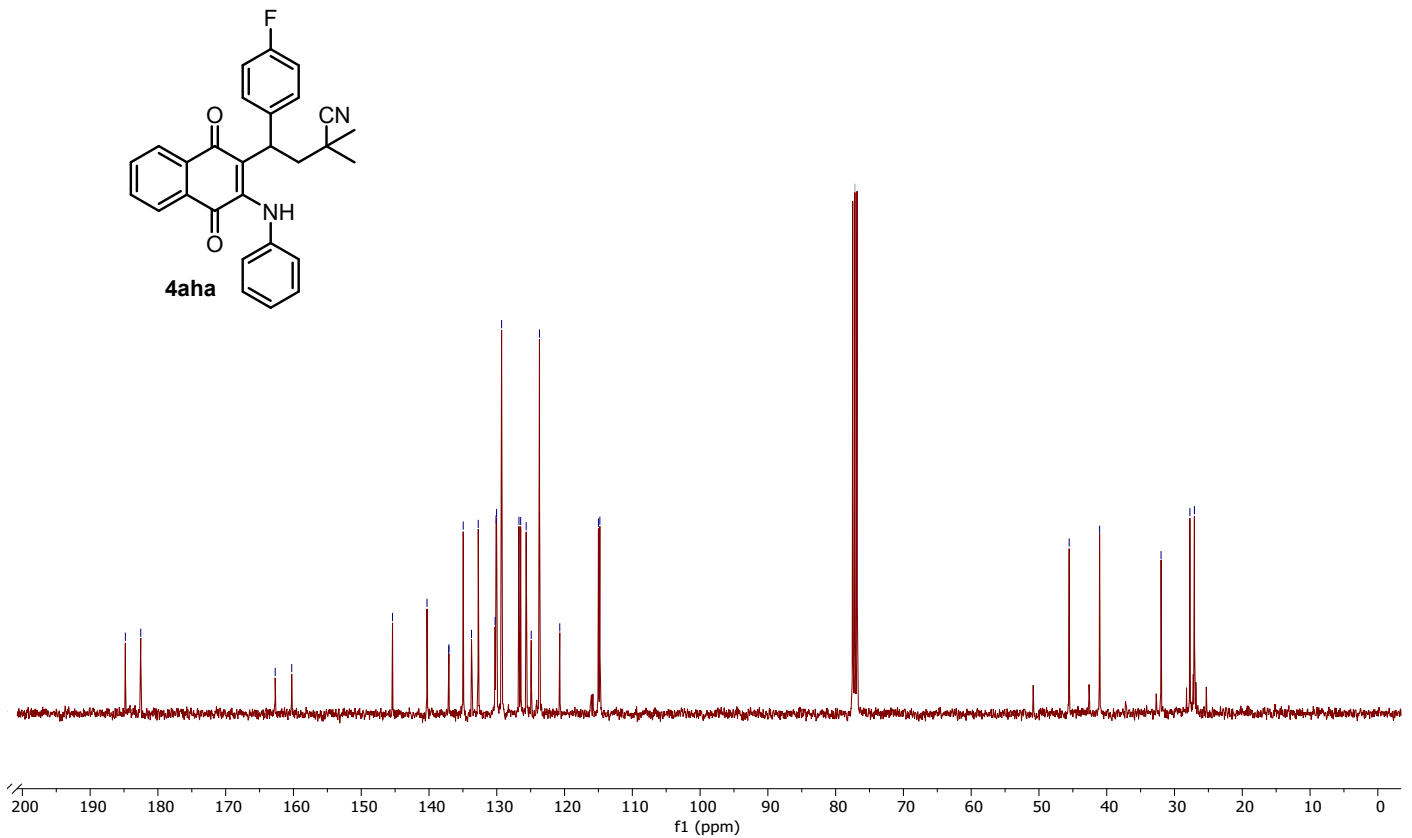
¹³C-NMR (100 MHz, Chloroform-*d*)



¹H-NMR (400 MHz, Chloroform-*d*)

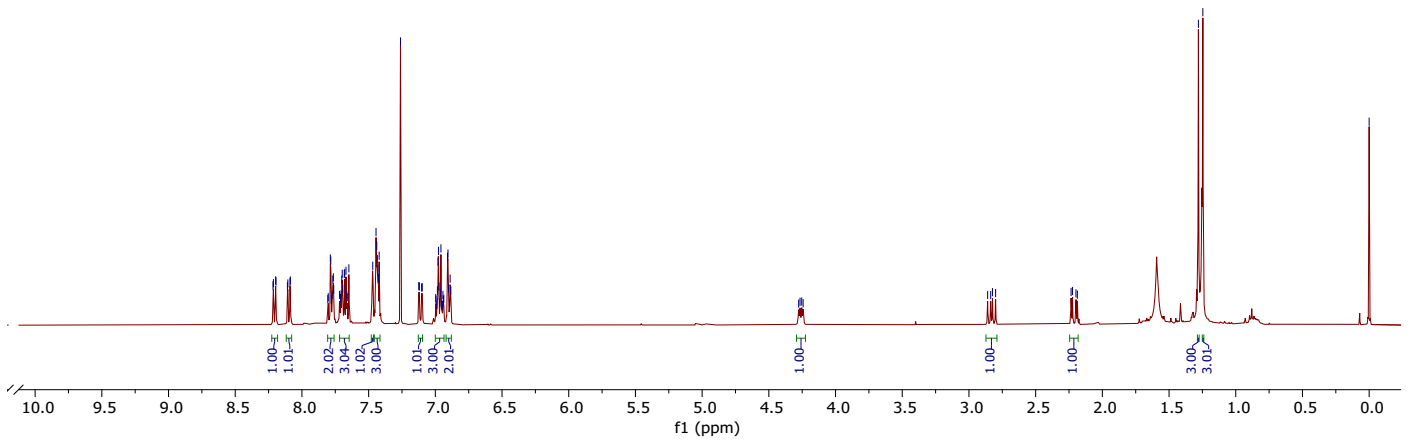
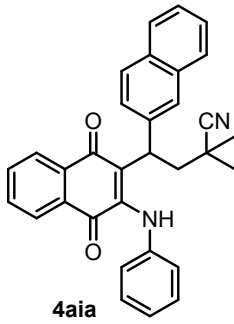


¹³C-NMR (100 MHz, Chloroform-*d*)



¹H-NMR (400 MHz, Chloroform-*d*)

8.217, 8.214, 8.197, 8.194, 8.109, 8.105, 8.090, 8.086, 7.806, 7.803, 7.787, 7.784, 7.780, 7.774, 7.768, 7.764, 7.762, 7.718, 7.710, 7.706, 7.701, 7.698, 7.694, 7.682, 7.679, 7.670, 7.664, 7.660, 7.648, 7.469, 7.445, 7.439, 7.434, 7.431, 7.427, 7.421, 7.261, 7.124, 7.120, 7.103, 7.098, 6.997, 6.995, 6.988, 6.984, 6.980, 6.976, 6.973, 6.966, 6.963, 6.958, 6.948, 6.943, 6.941, 6.936, 6.909, 6.905, 6.900, 6.894, 6.889, 6.884, 4.277, 4.266, 4.254, 4.243, 2.860, 2.837, 2.824, 2.800, 2.234, 2.224, 2.198, 2.187, 1.280, 1.247, 0 ppm



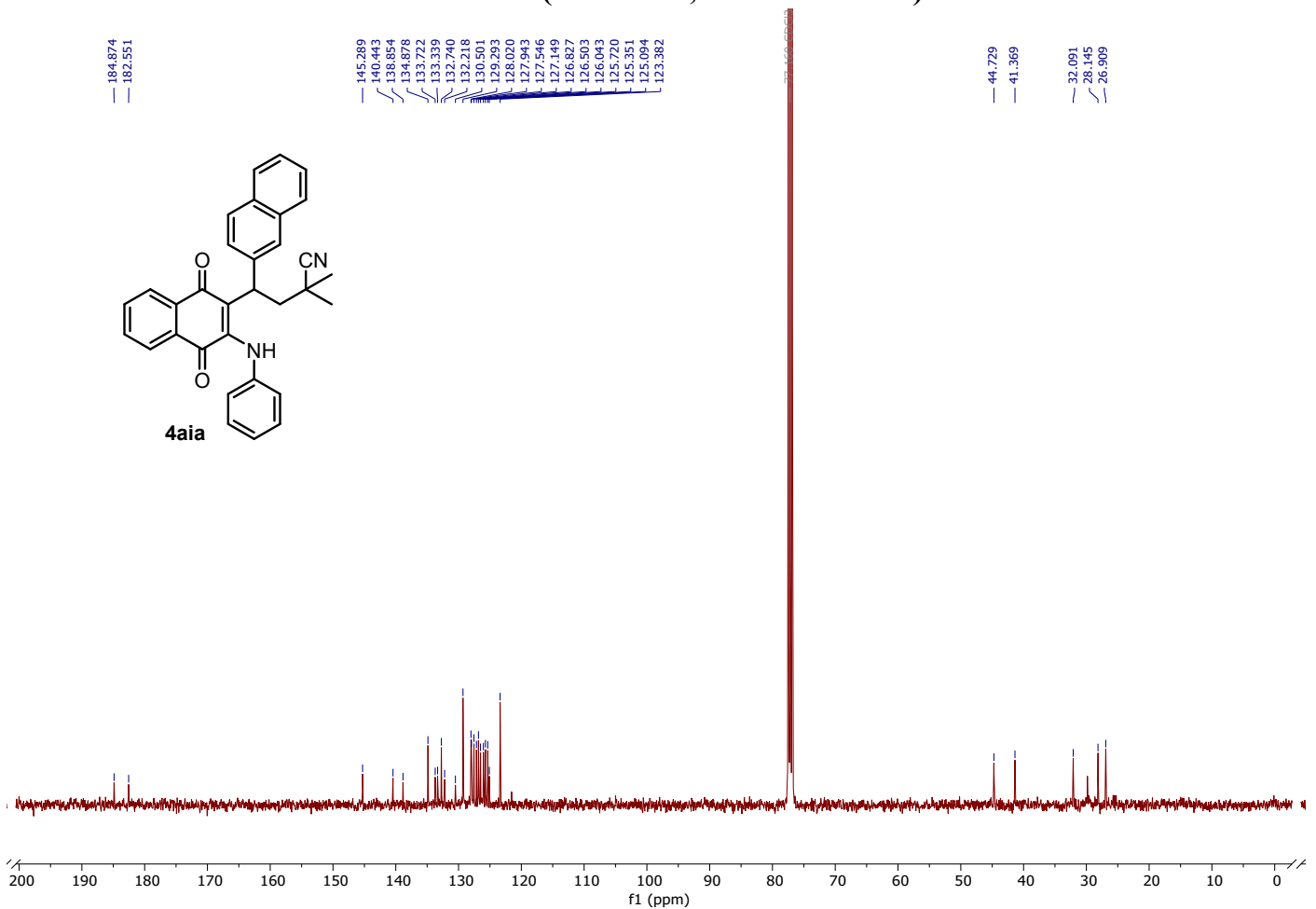
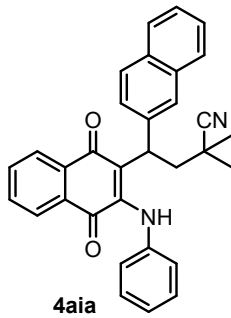
¹³C-NMR (100 MHz, Chloroform-*d*)

184.874
182.551

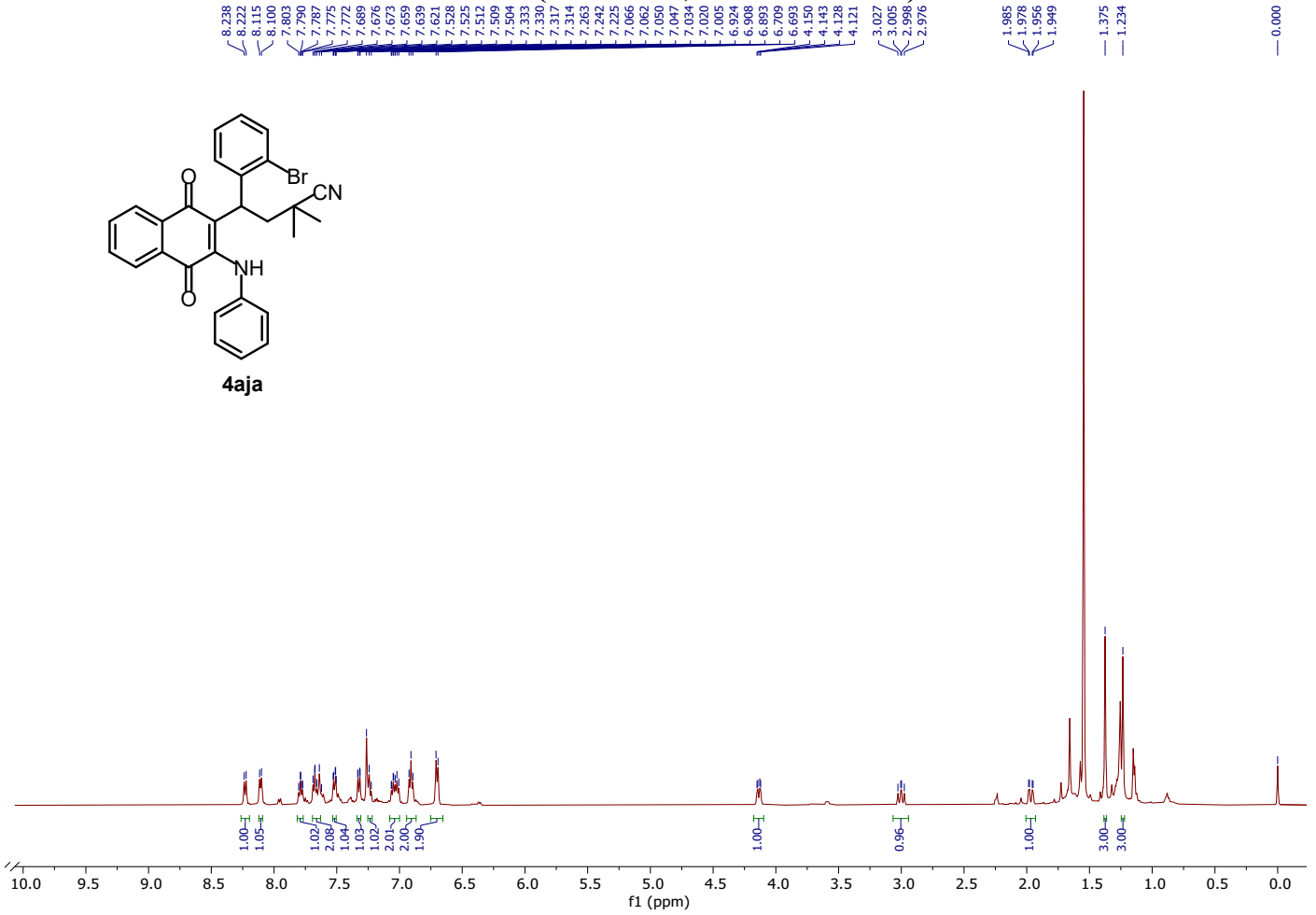
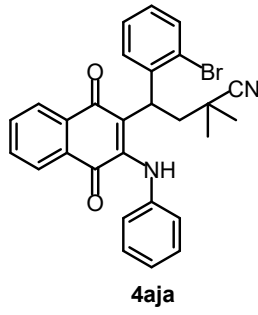
145.389, 140.443, 138.856, 134.878, 133.776, 133.772, 133.339, 132.710, 132.216, 130.501, 129.293, 128.020, 127.943, 127.546, 127.149, 126.827, 126.503, 126.043, 125.720, 125.351, 125.094, 123.382

44.729
41.369

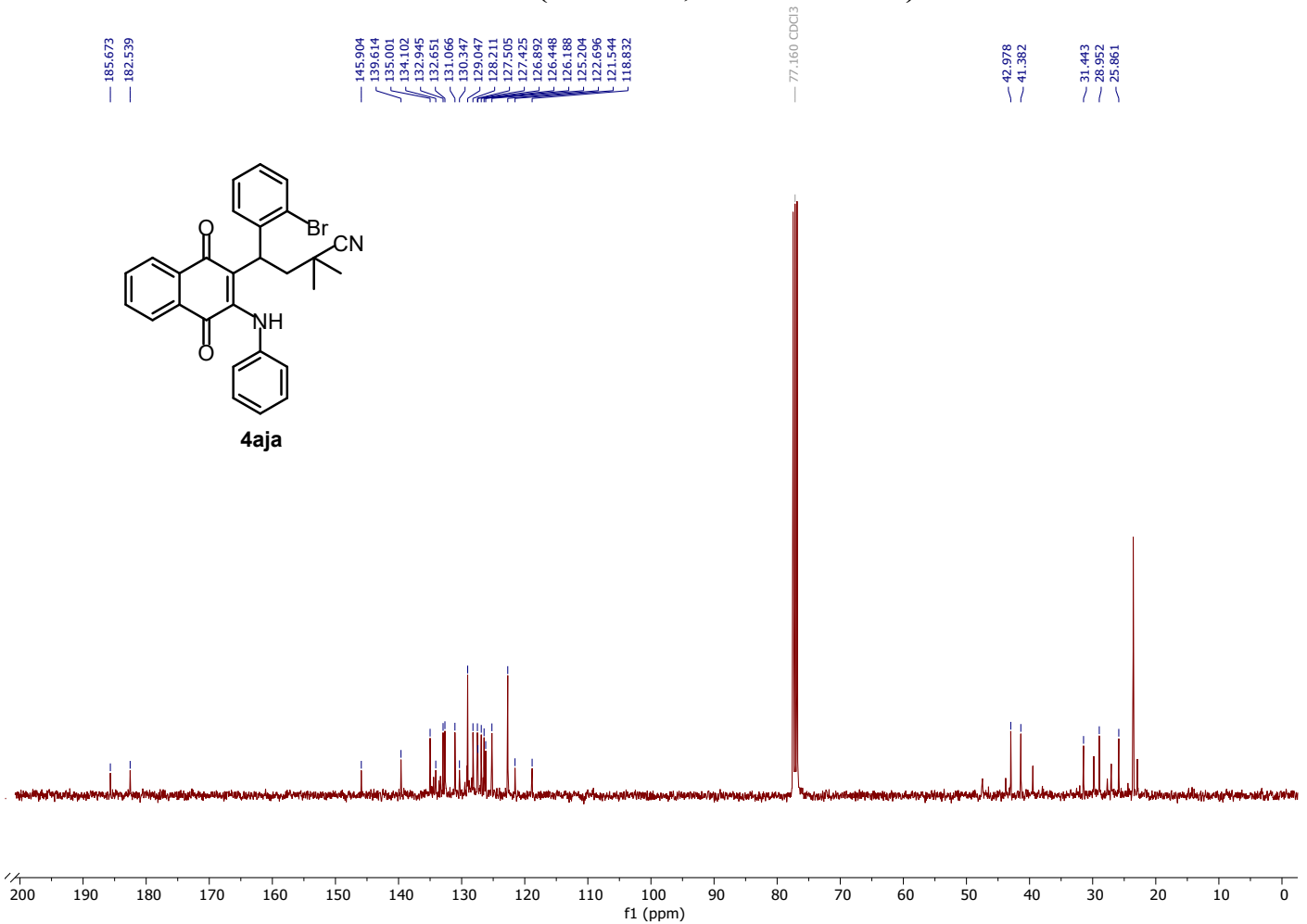
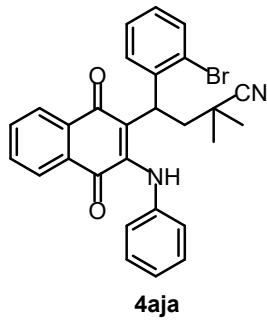
32.091
28.145
26.909



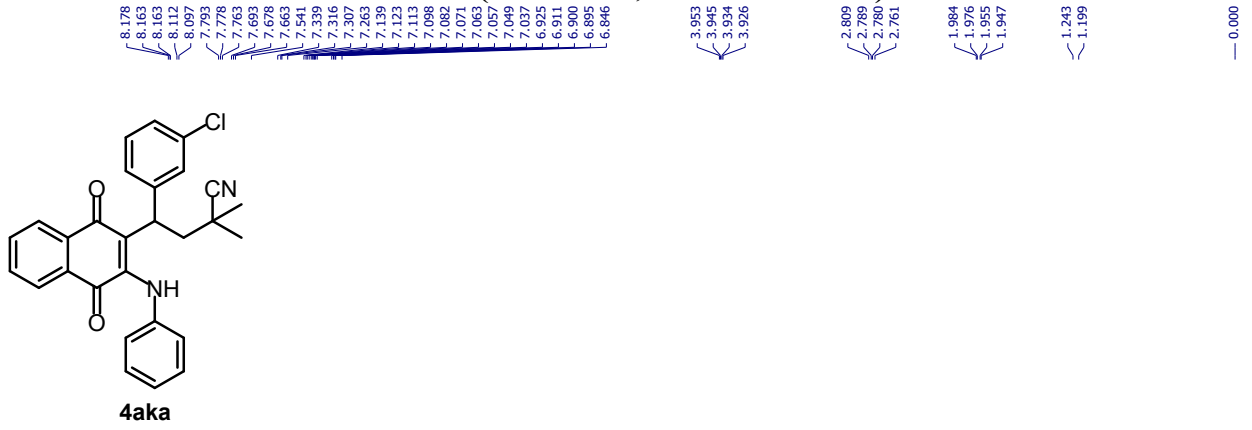
¹H-NMR (500 MHz, Chloroform-d)



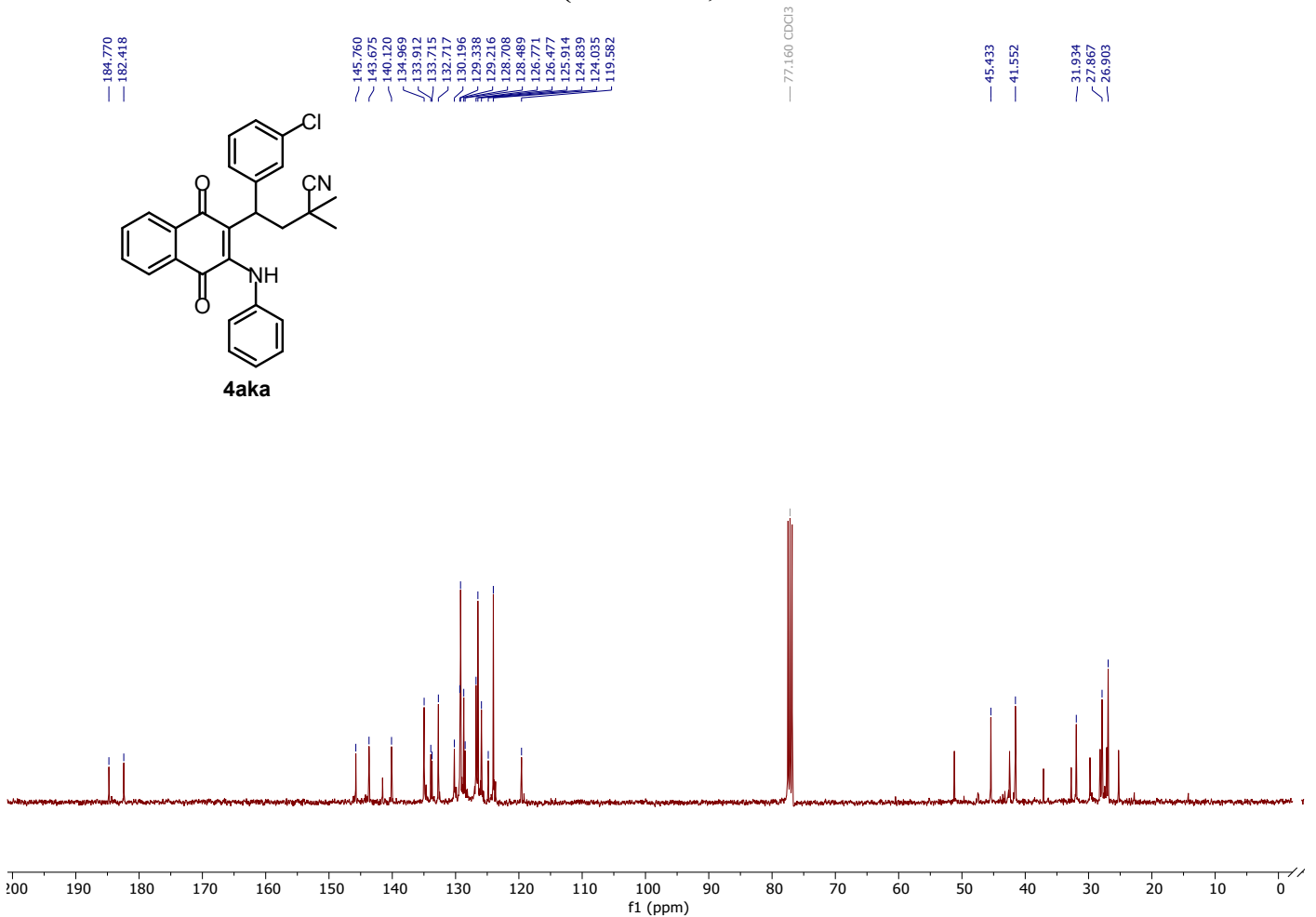
¹³C-NMR (100 MHz, Chloroform-d)



¹H-NMR (500 MHz, Chloroform-*d*)



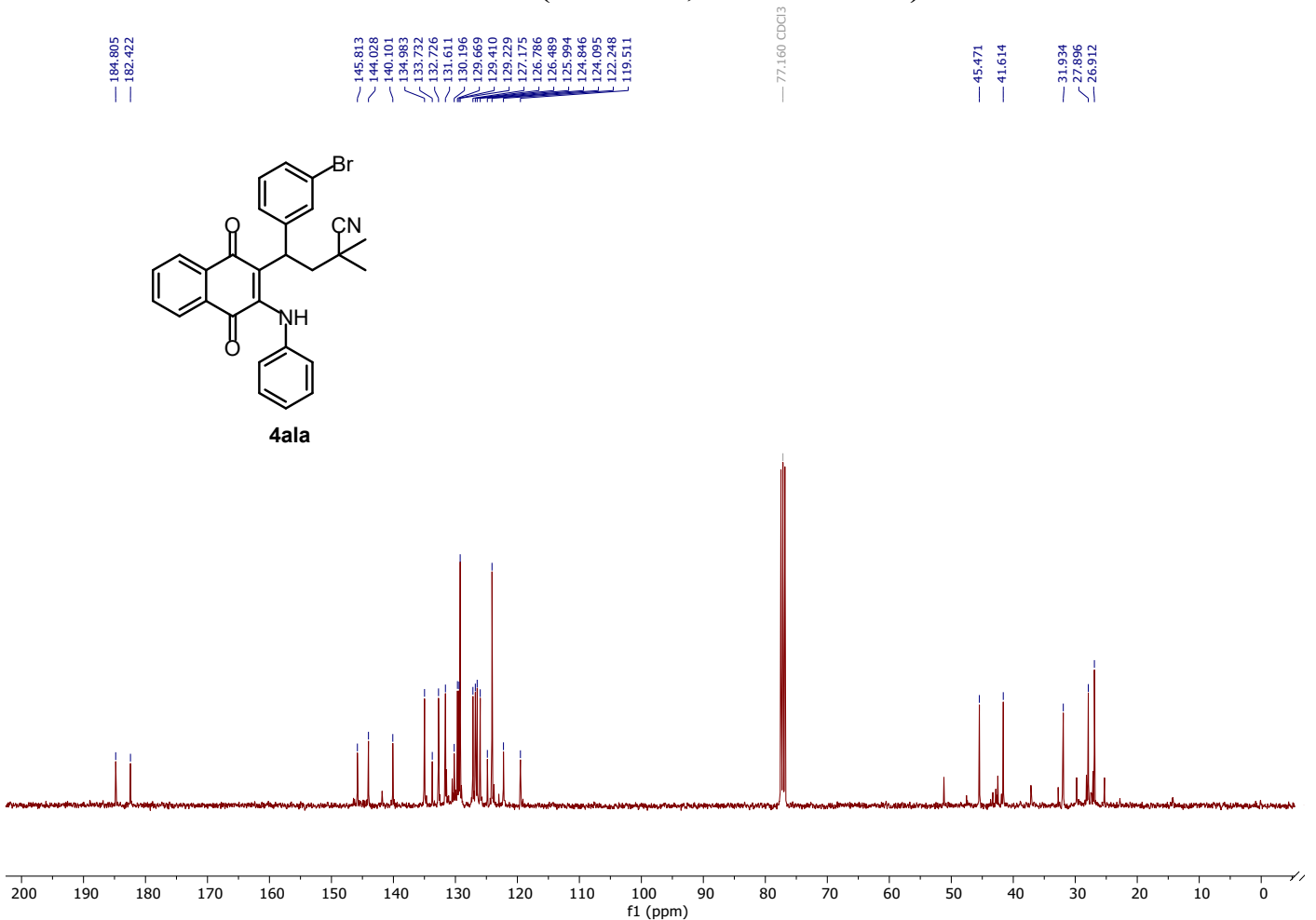
¹³C-NMR (100 MHz, Chloroform)



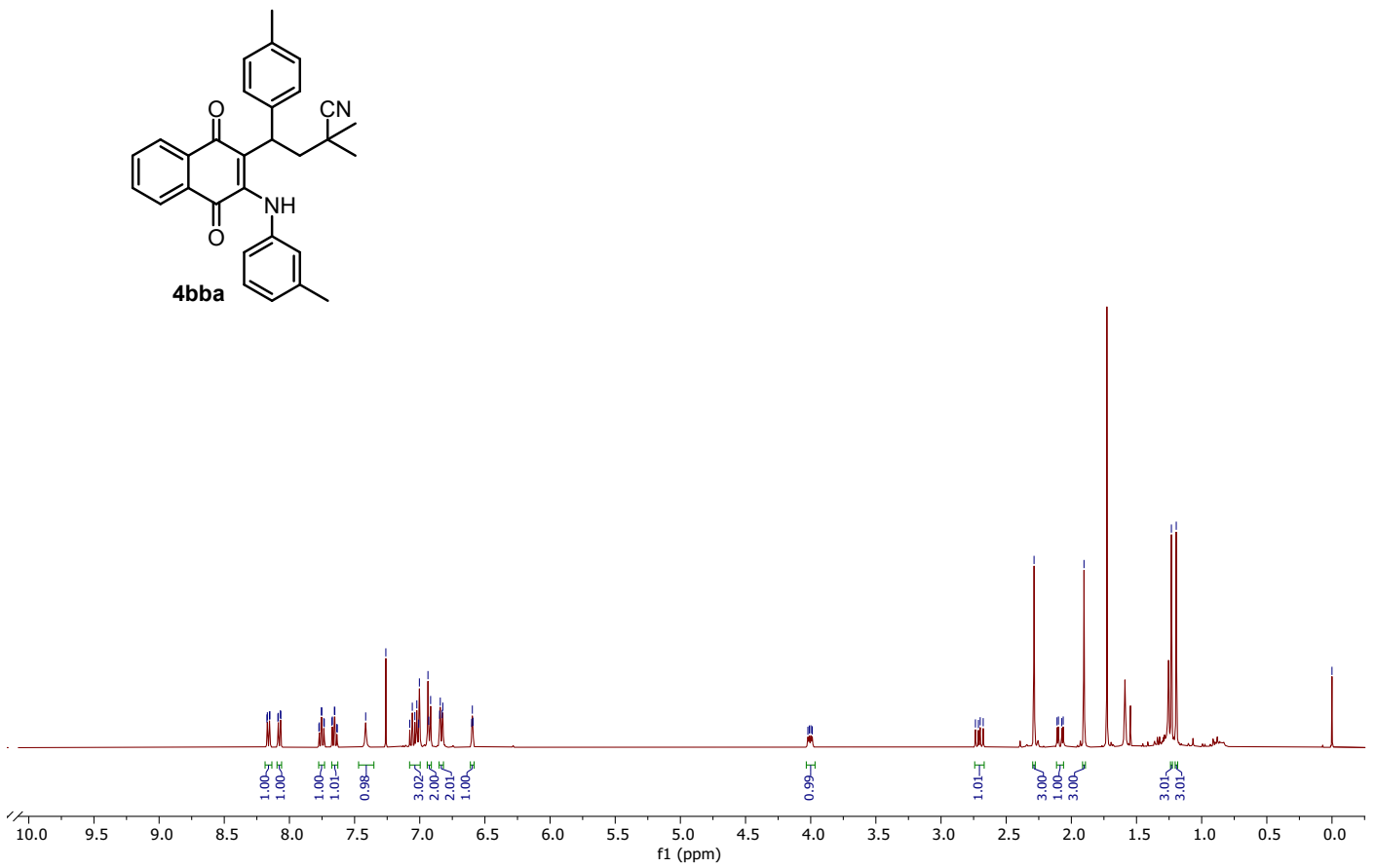
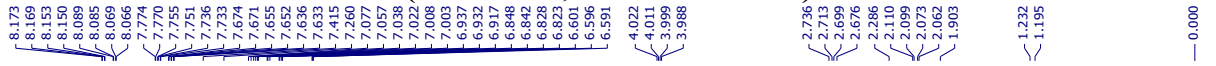
¹H-NMR (500 MHz, Chloroform-*d*)



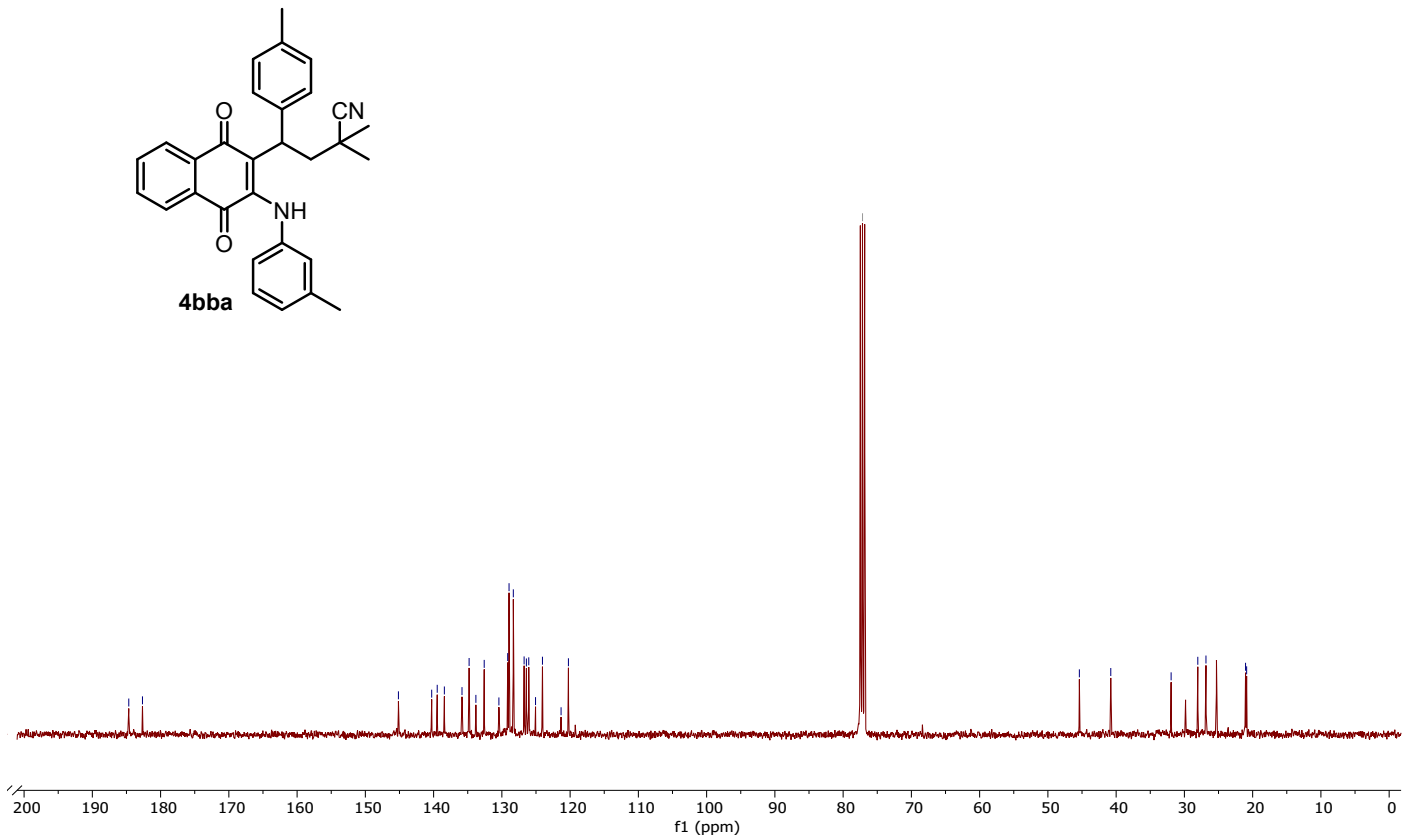
¹³C-NMR (100 MHz, Chloroform-*d*)



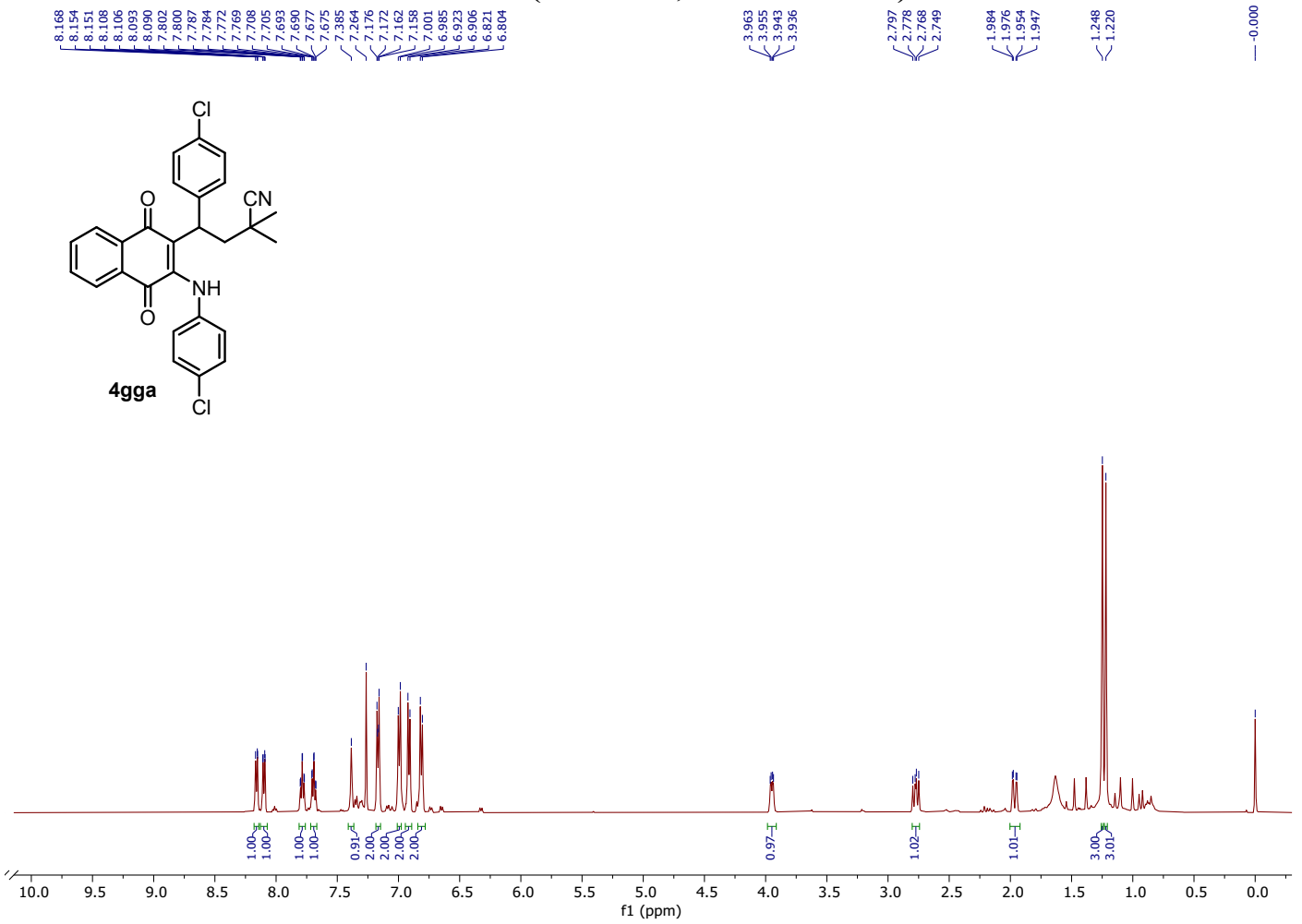
¹H-NMR (400 MHz, Chloroform-*d*)



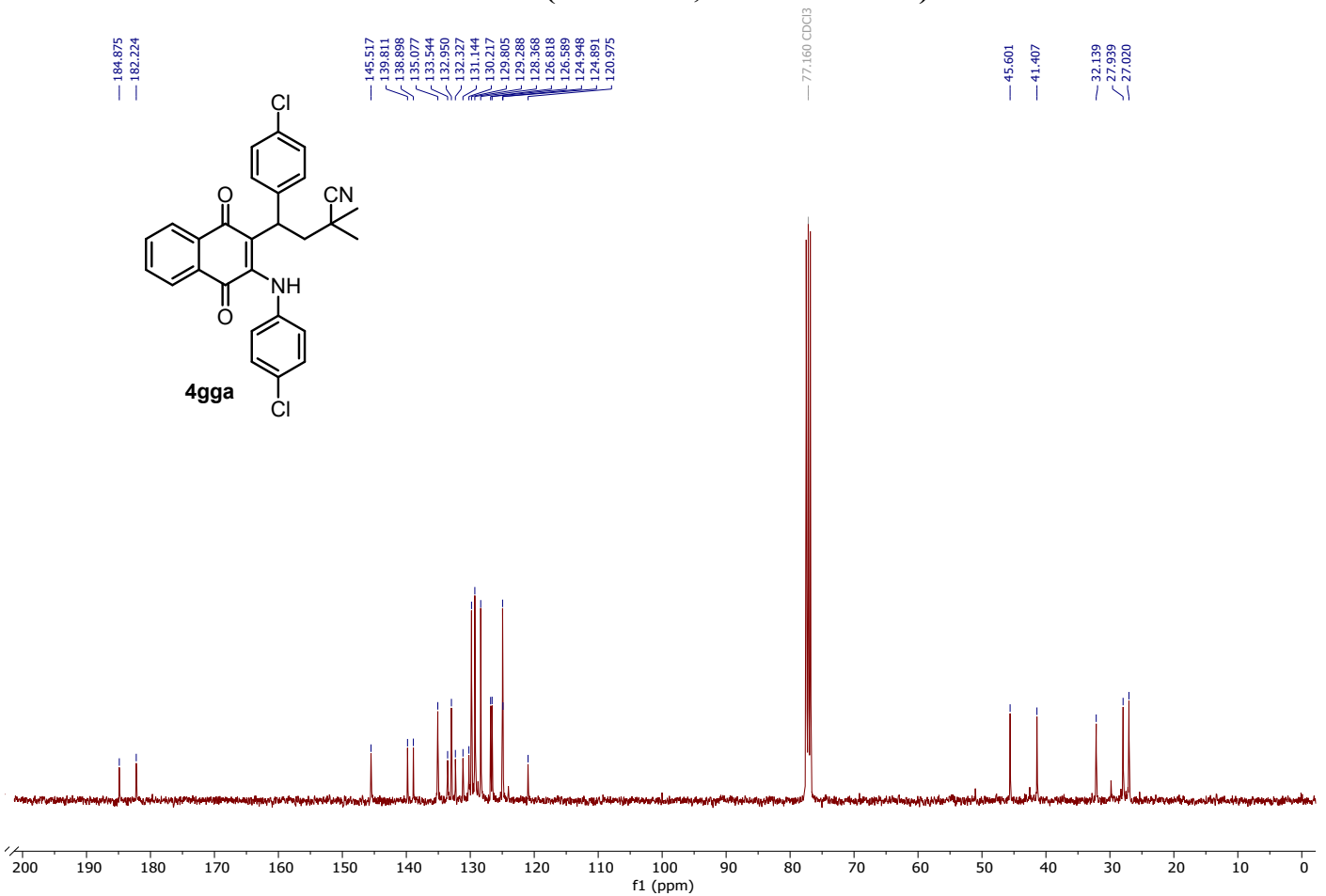
¹³C-NMR (100 MHz, Chloroform-*d*)



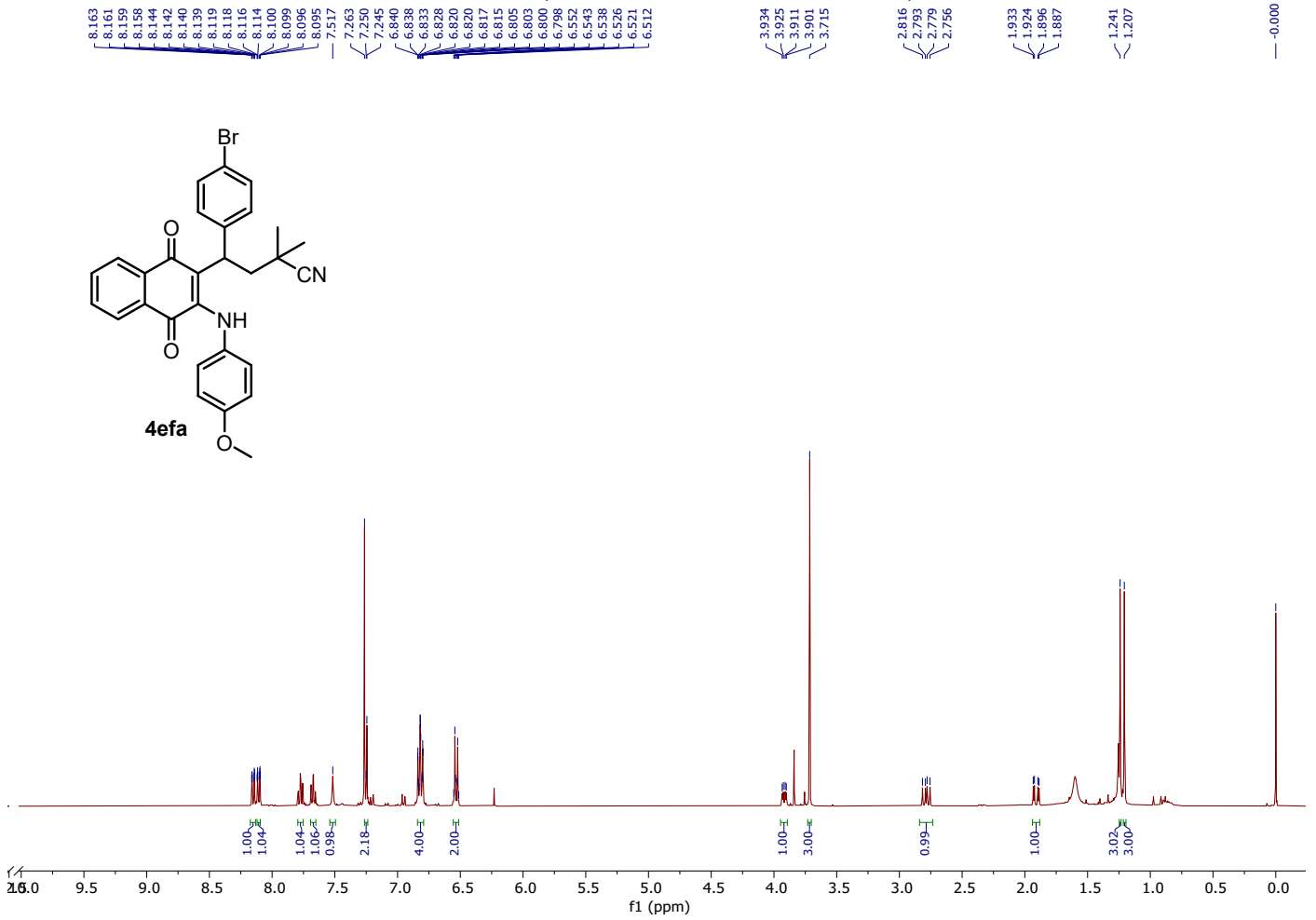
¹H-NMR (500 MHz, Chloroform-d)



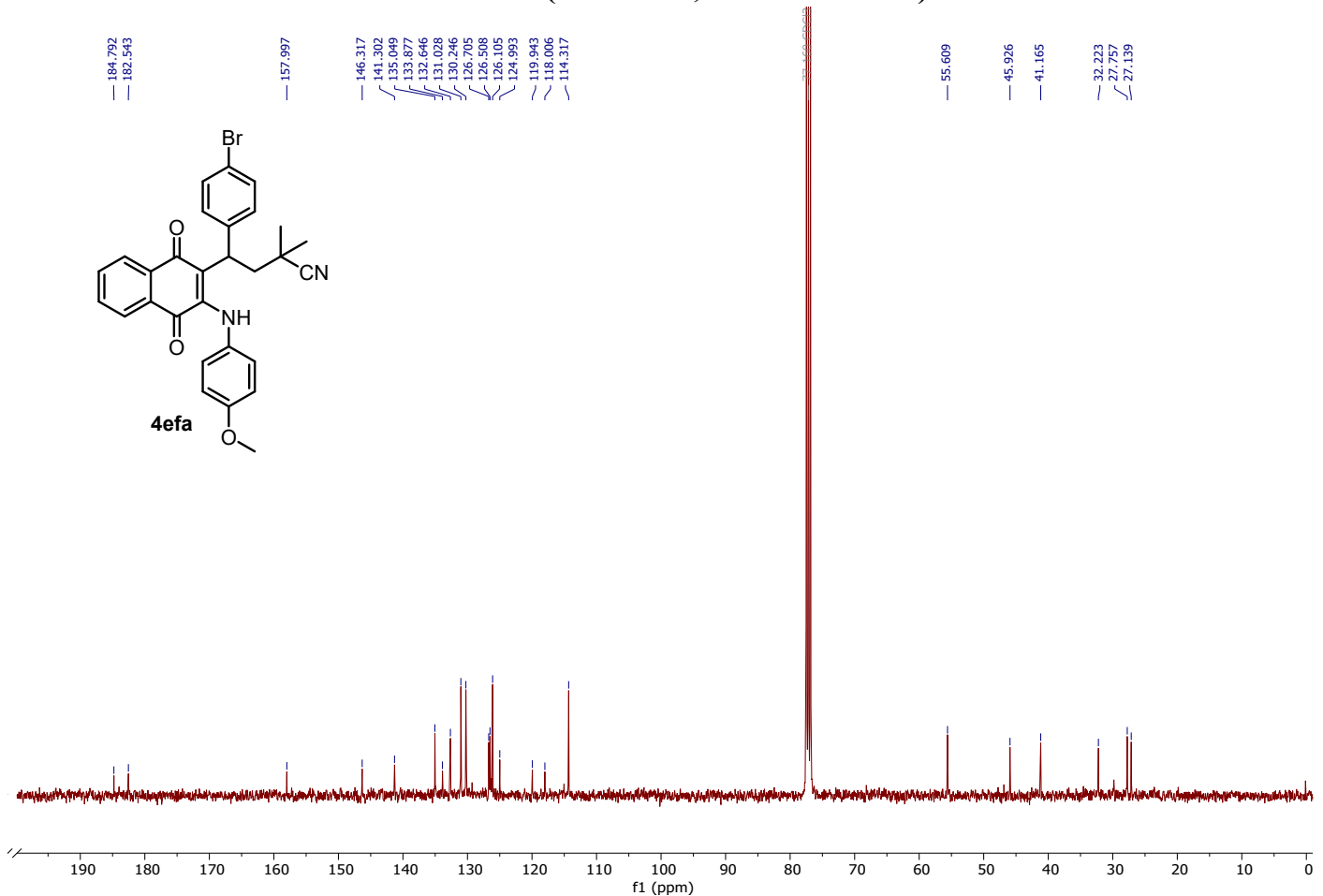
¹³C-NMR (100 MHz, Chloroform-d)



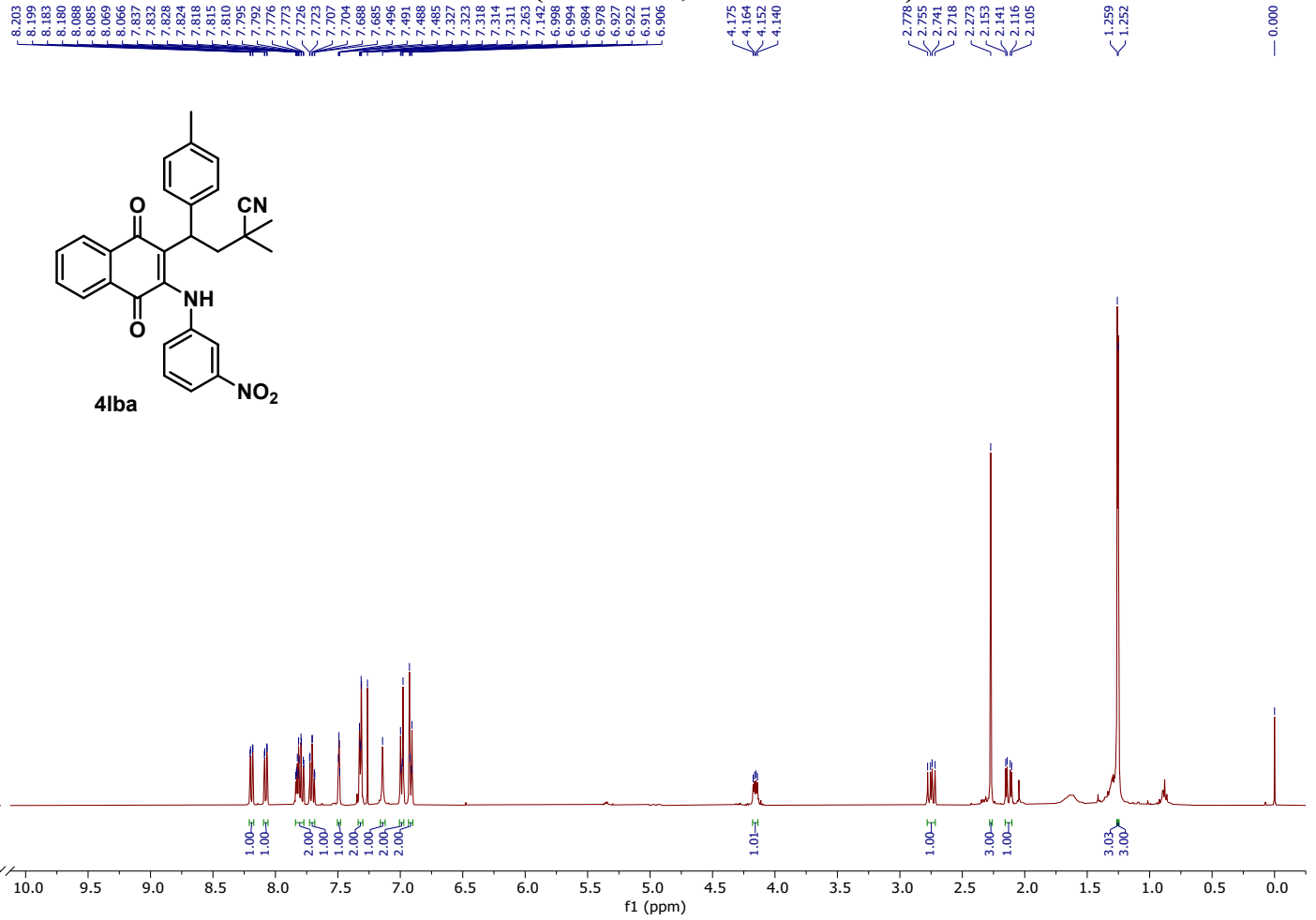
¹H-NMR (400 MHz, Chloroform-*d*)



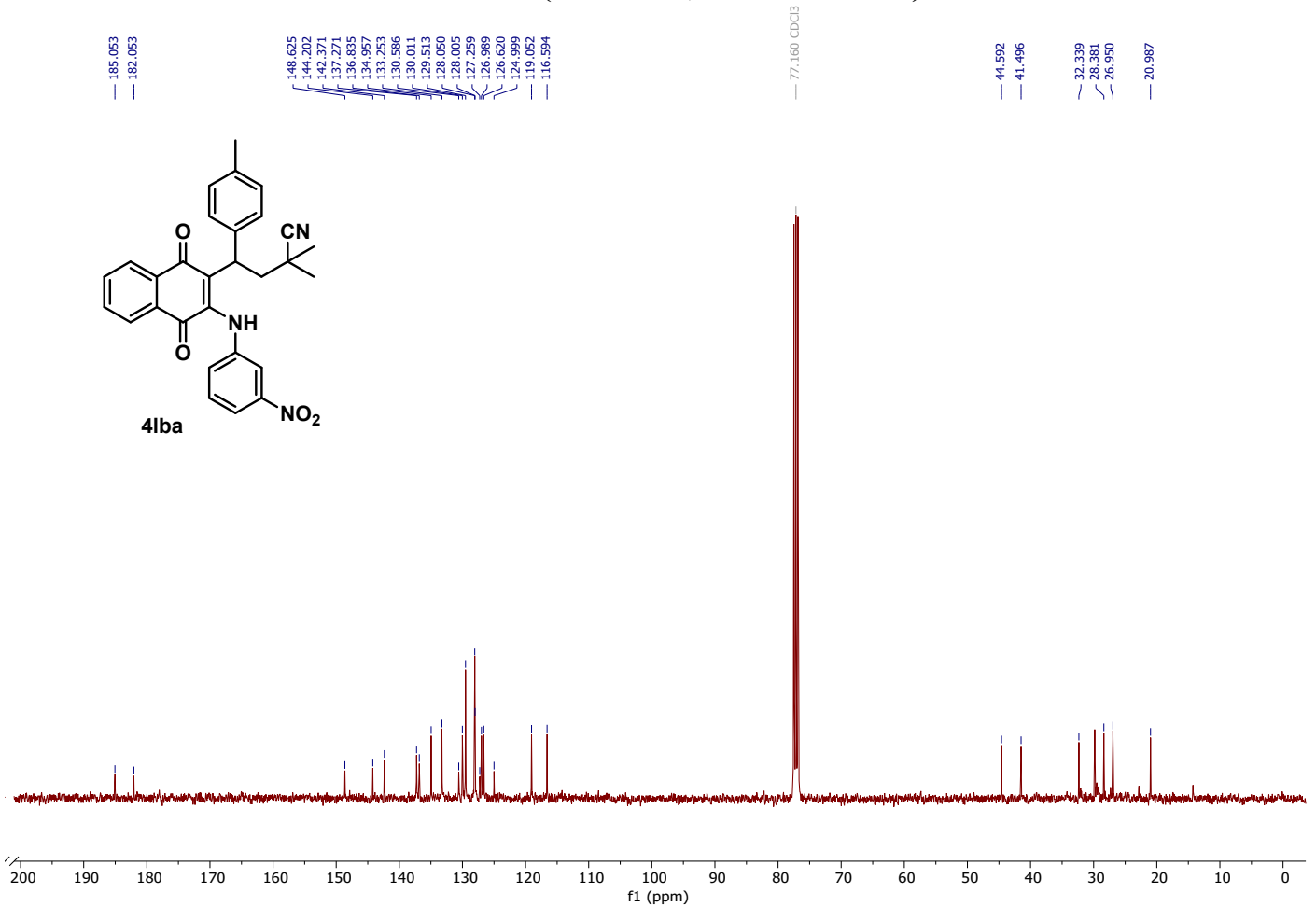
¹³C-NMR (100 MHz, Chloroform-*d*)



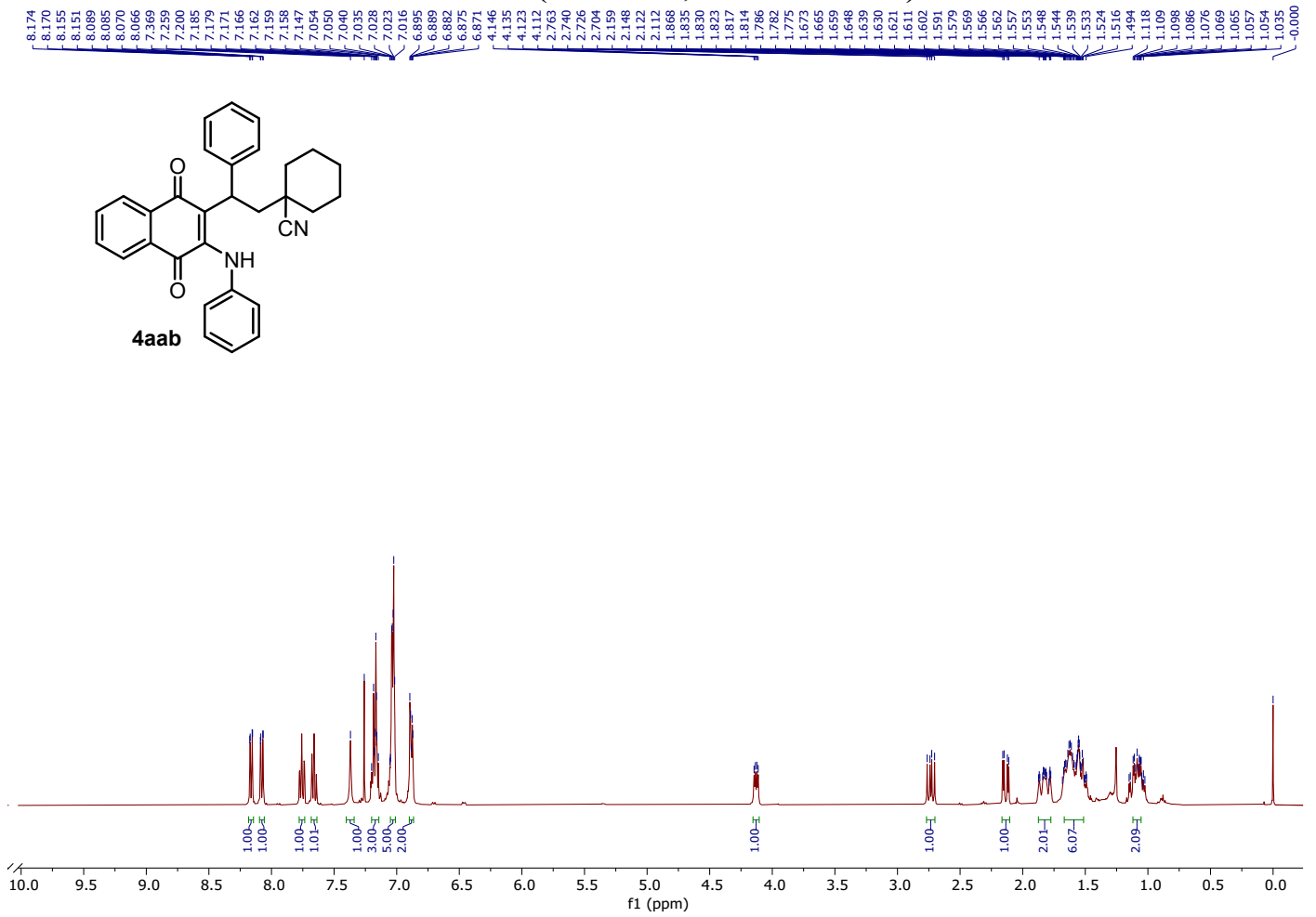
¹H-NMR (400 MHz, Chloroform-*d*)



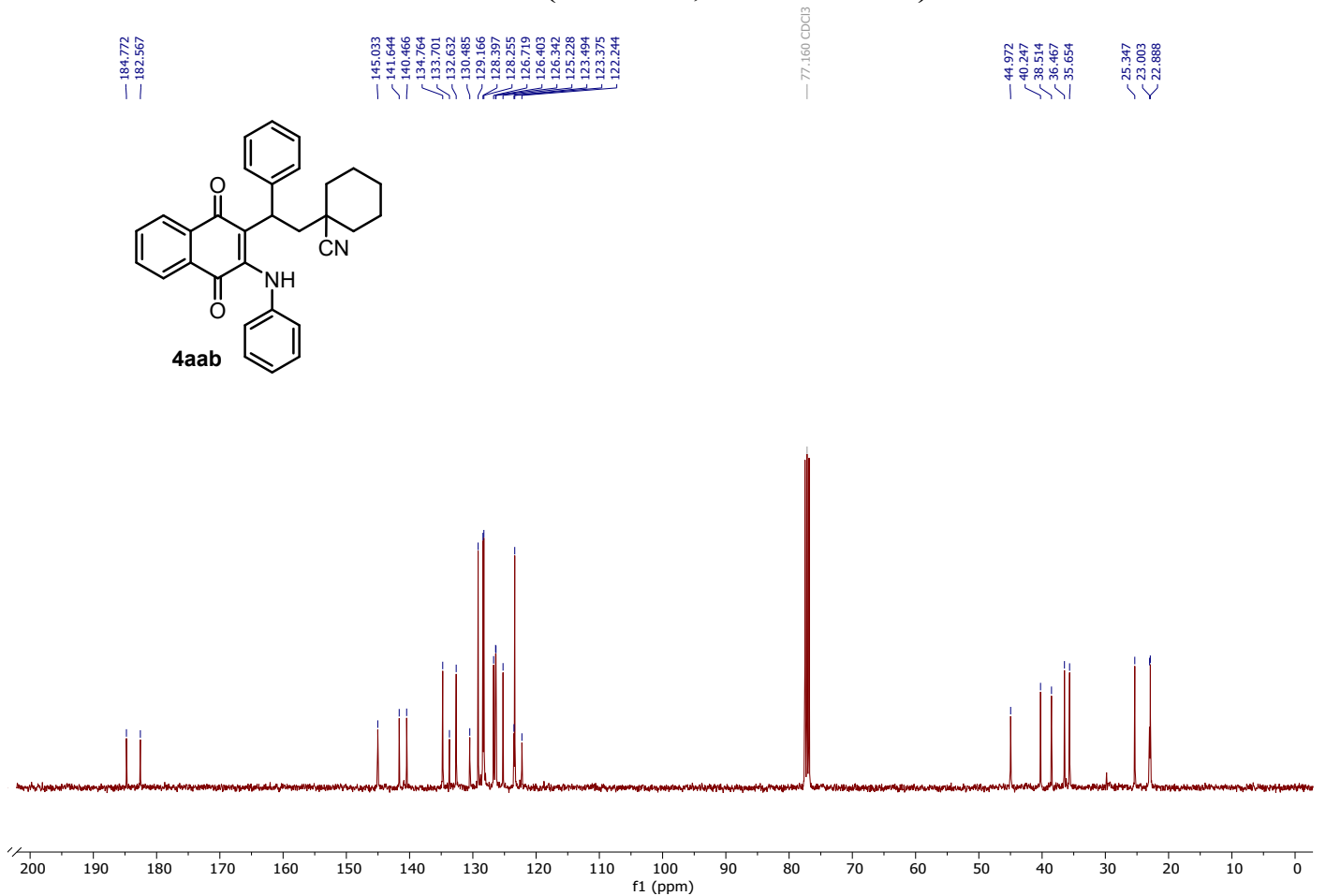
¹³C-NMR (100 MHz, Chloroform-*d*)



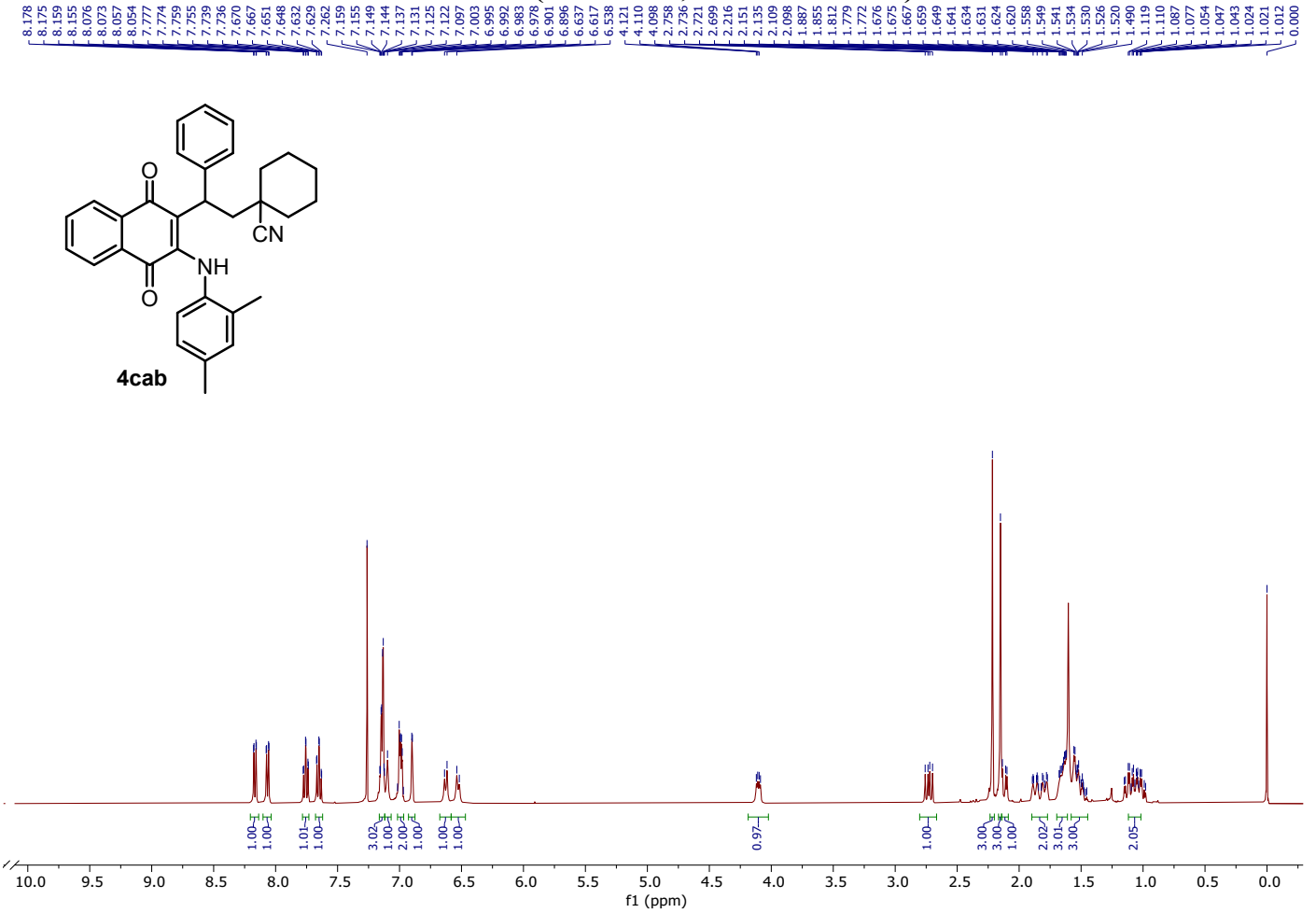
¹H-NMR (400 MHz, Chloroform-*d*)



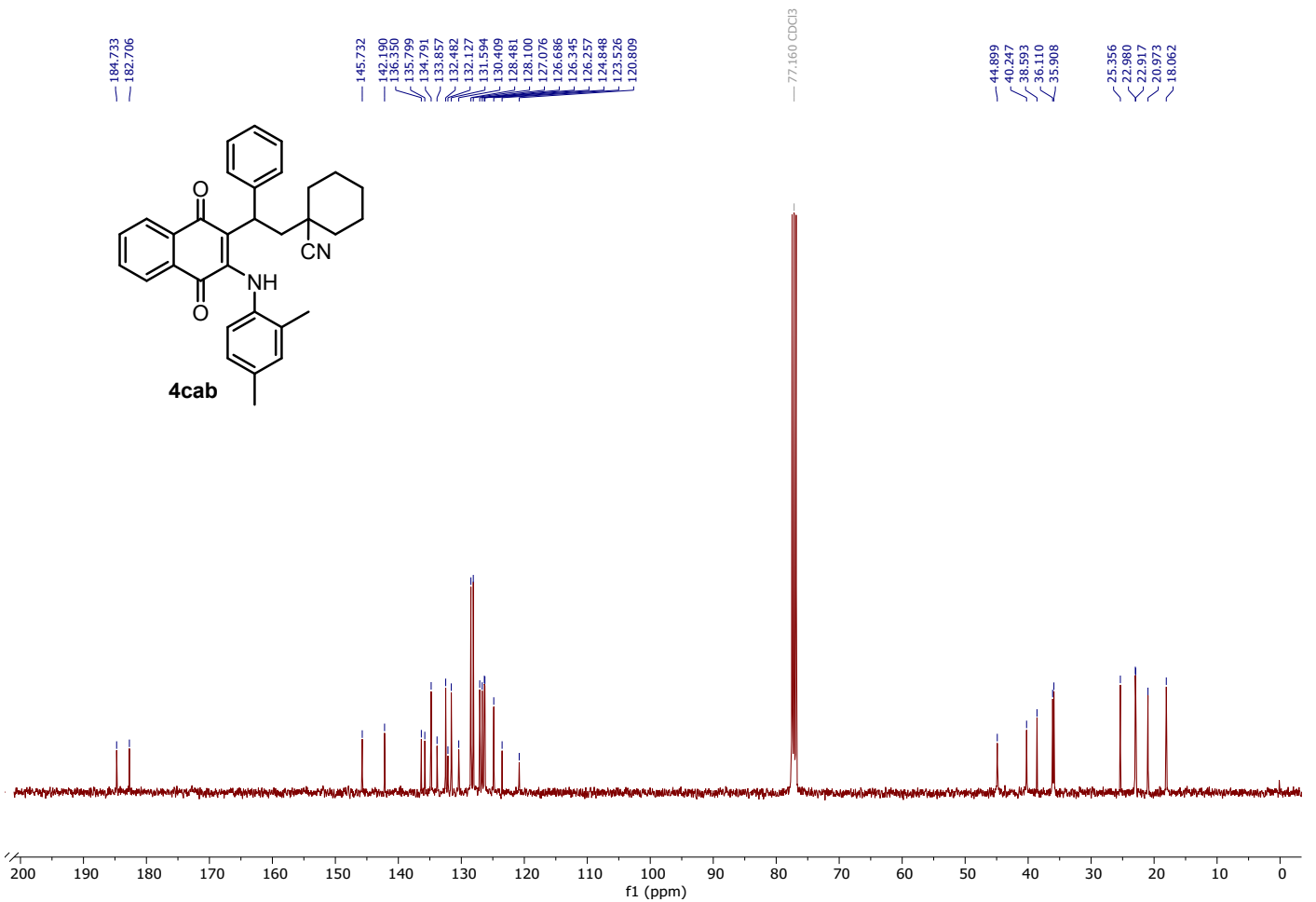
¹³C-NMR (100 MHz, Chloroform-*d*)



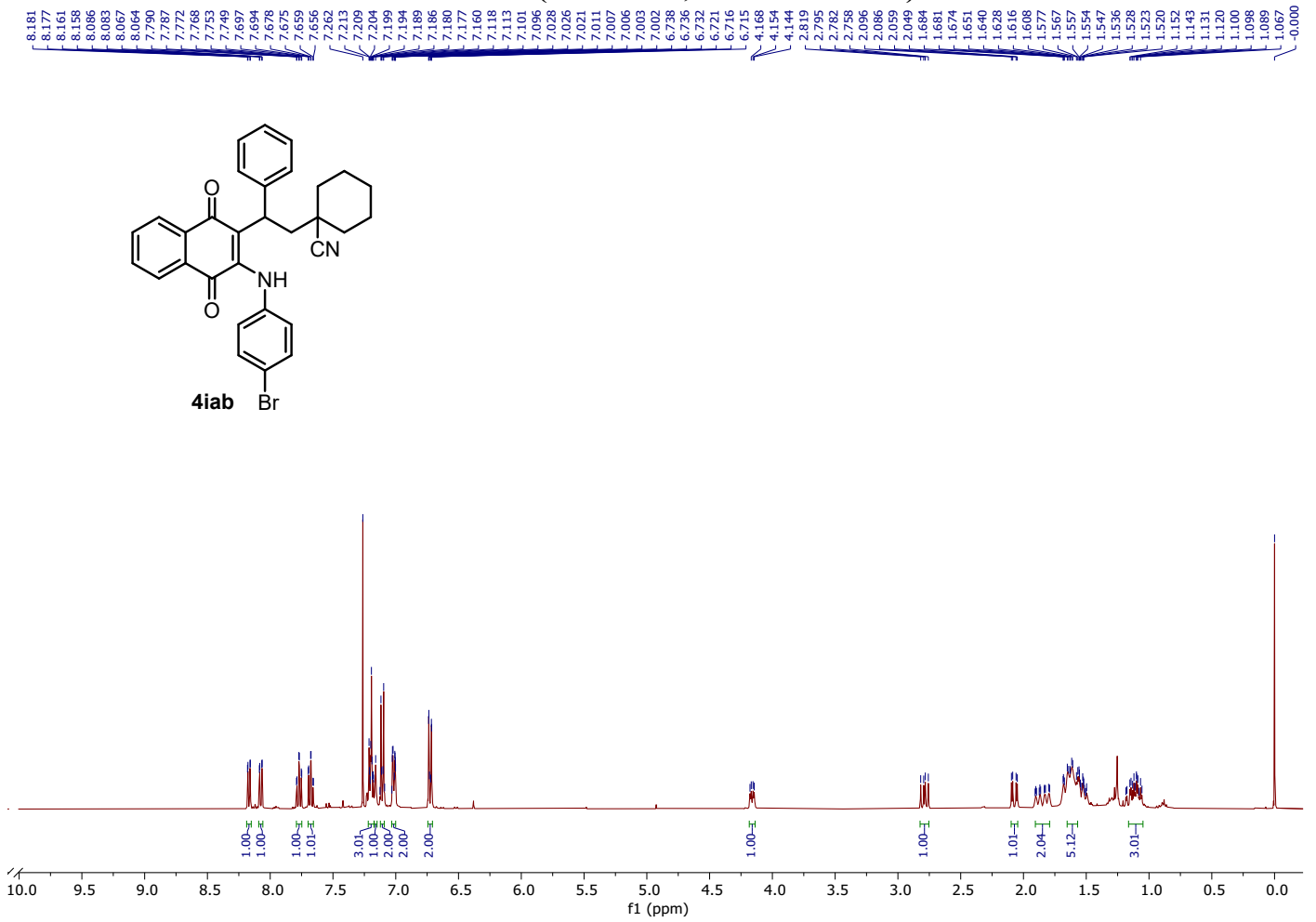
¹H-NMR (400 MHz, Chloroform-*d*)



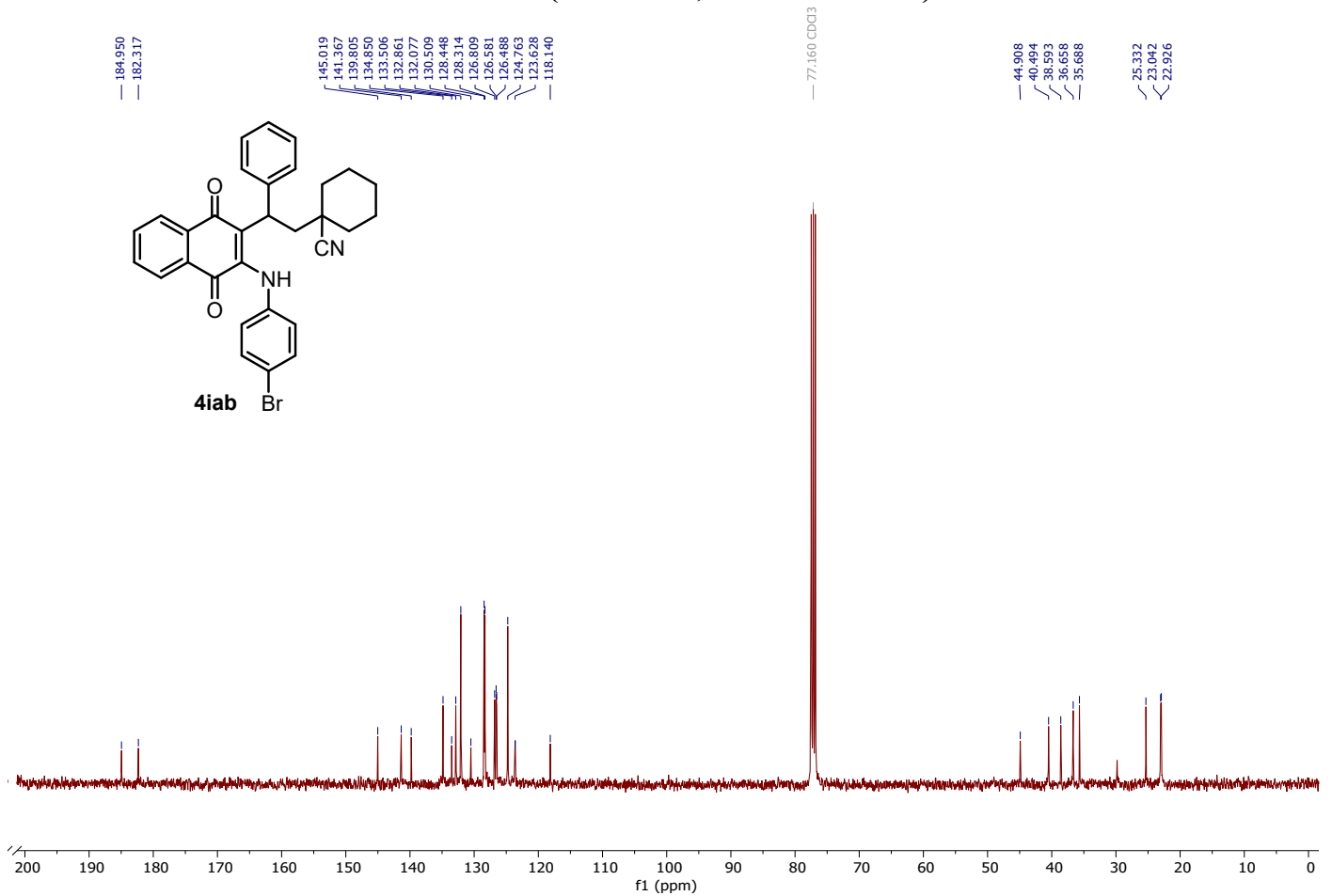
¹³C-NMR (100 MHz, Chloroform-*d*)



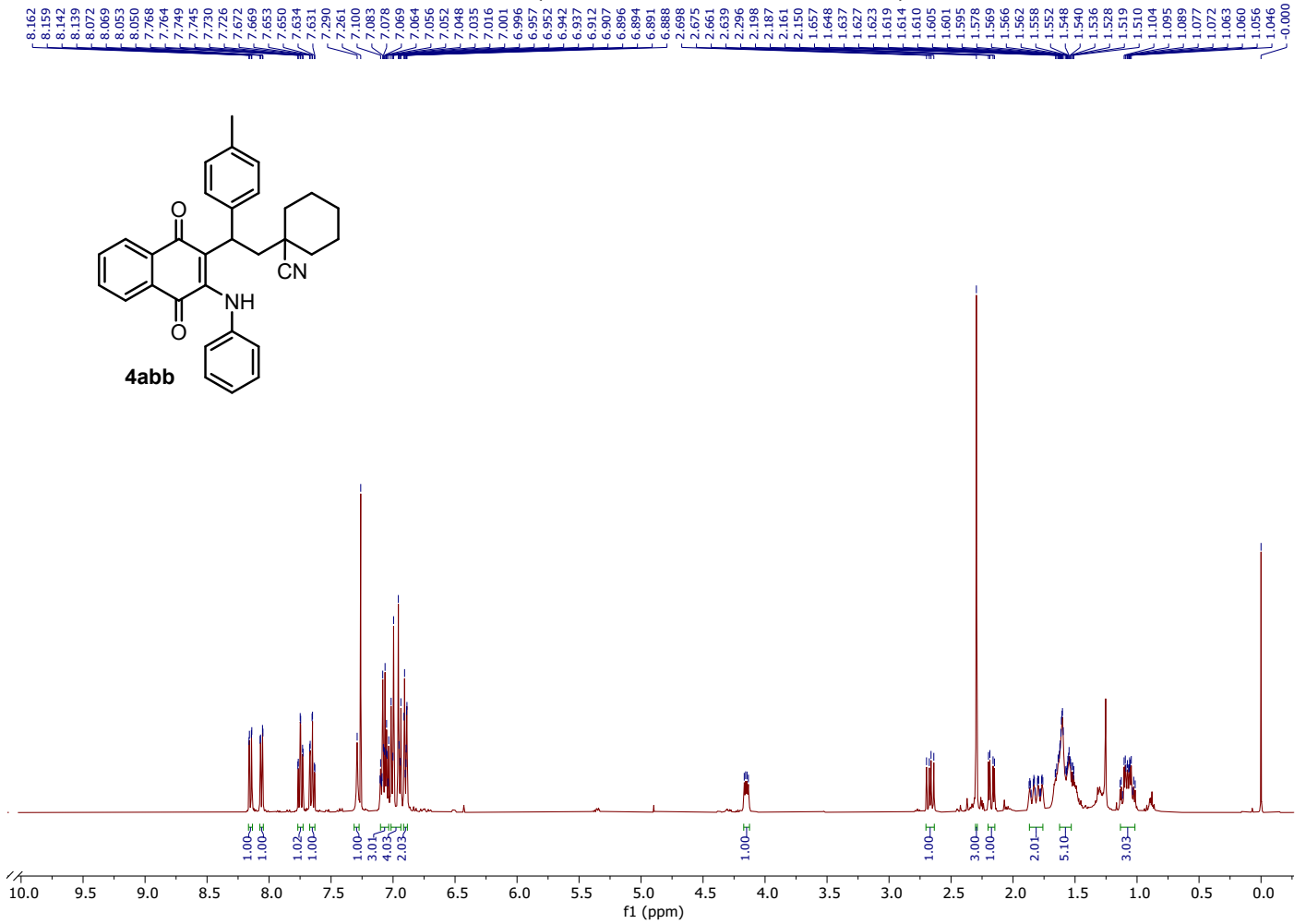
¹H-NMR (400 MHz, Chloroform-*d*)



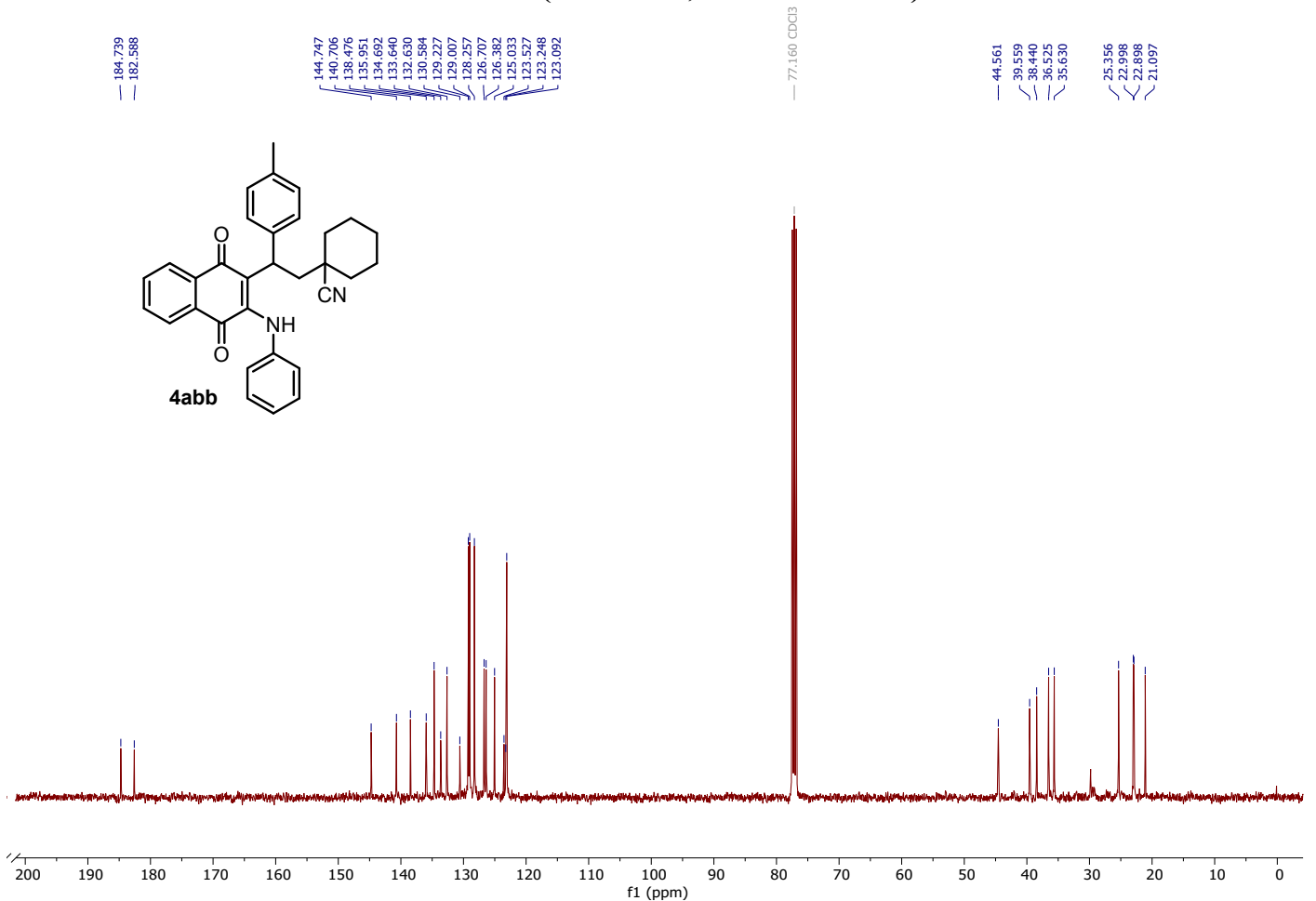
¹³C-NMR (100 MHz, Chloroform-*d*)



¹H-NMR (400 MHz, Chloroform-*d*)

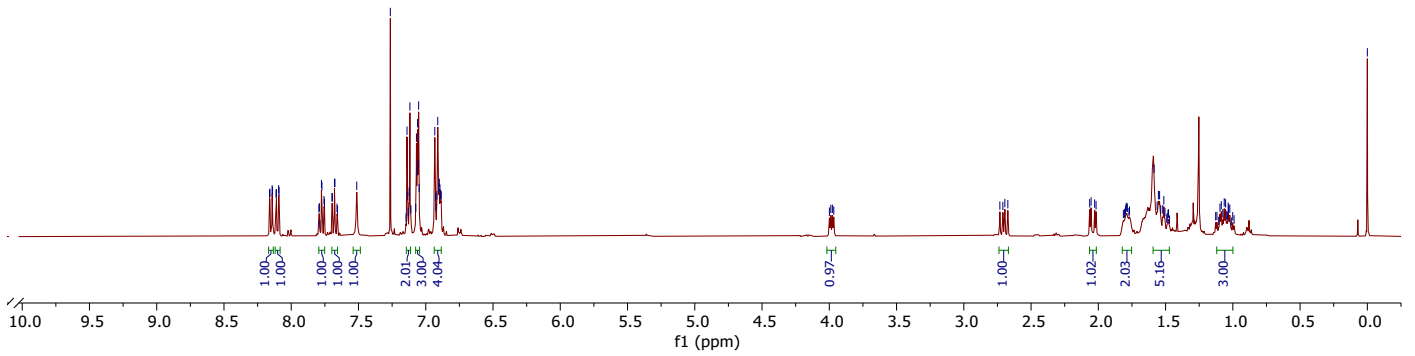
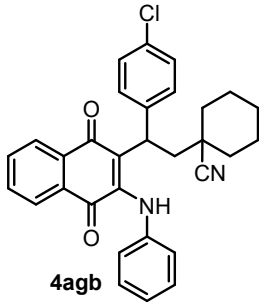


¹³C-NMR (100 MHz, Chloroform-*d*)



¹H-NMR (400 MHz, Chloroform-*d*)

8.162, 8.158, 8.142, 8.139, 8.113, 8.110, 8.094, 8.090, 7.794, 7.791, 7.775, 7.772, 7.756, 7.753, 7.697, 7.694, 7.679, 7.675, 7.660, 7.656, 7.513, 7.263, 7.139, 7.134, 7.131, 7.123, 7.118, 7.110, 7.074, 7.069, 7.064, 7.061, 7.058, 7.055, 7.049, 6.933, 6.927, 6.924, 6.924, 6.917, 6.911, 6.902, 6.896, 6.894, 6.890, 6.886, 6.885, 3.989, 3.989, 3.977, 3.967, 3.967, 2.732, 2.710, 2.695, 2.673, 2.064, 2.054, 2.027, 2.017, 1.814, 1.804, 1.802, 1.798, 1.793, 1.788, 1.784, 1.772, 1.768, 1.585, 1.563, 1.553, 1.544, 1.536, 1.521, 1.513, 1.505, 1.482, 1.478, 1.096, 1.086, 1.075, 1.064, 1.054, 1.045, 1.035, 1.031, 1.023, 0.000

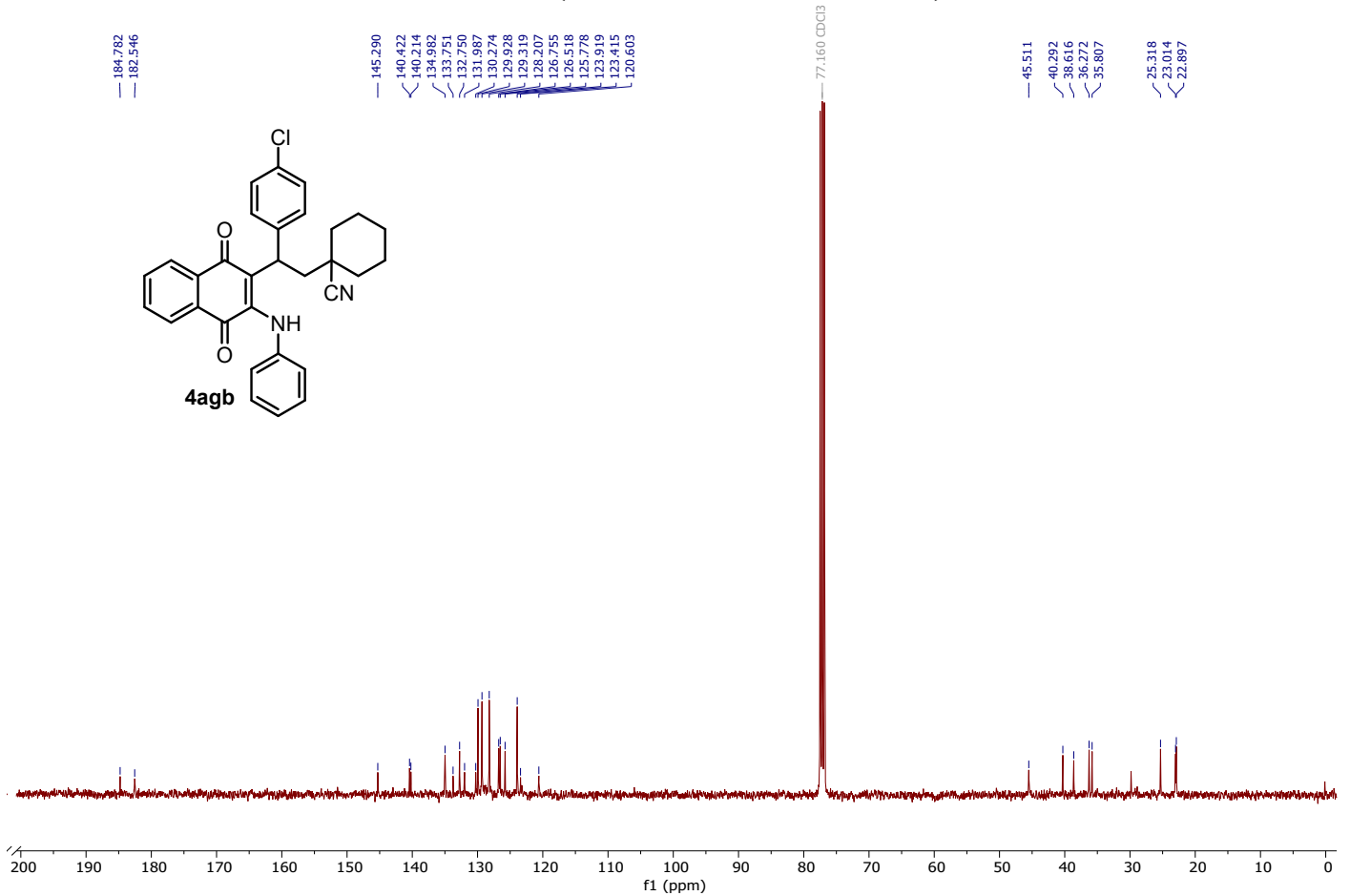
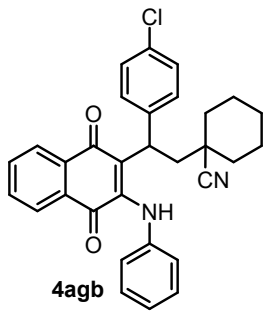


¹³C-NMR (100 MHz, Chloroform-*d*)

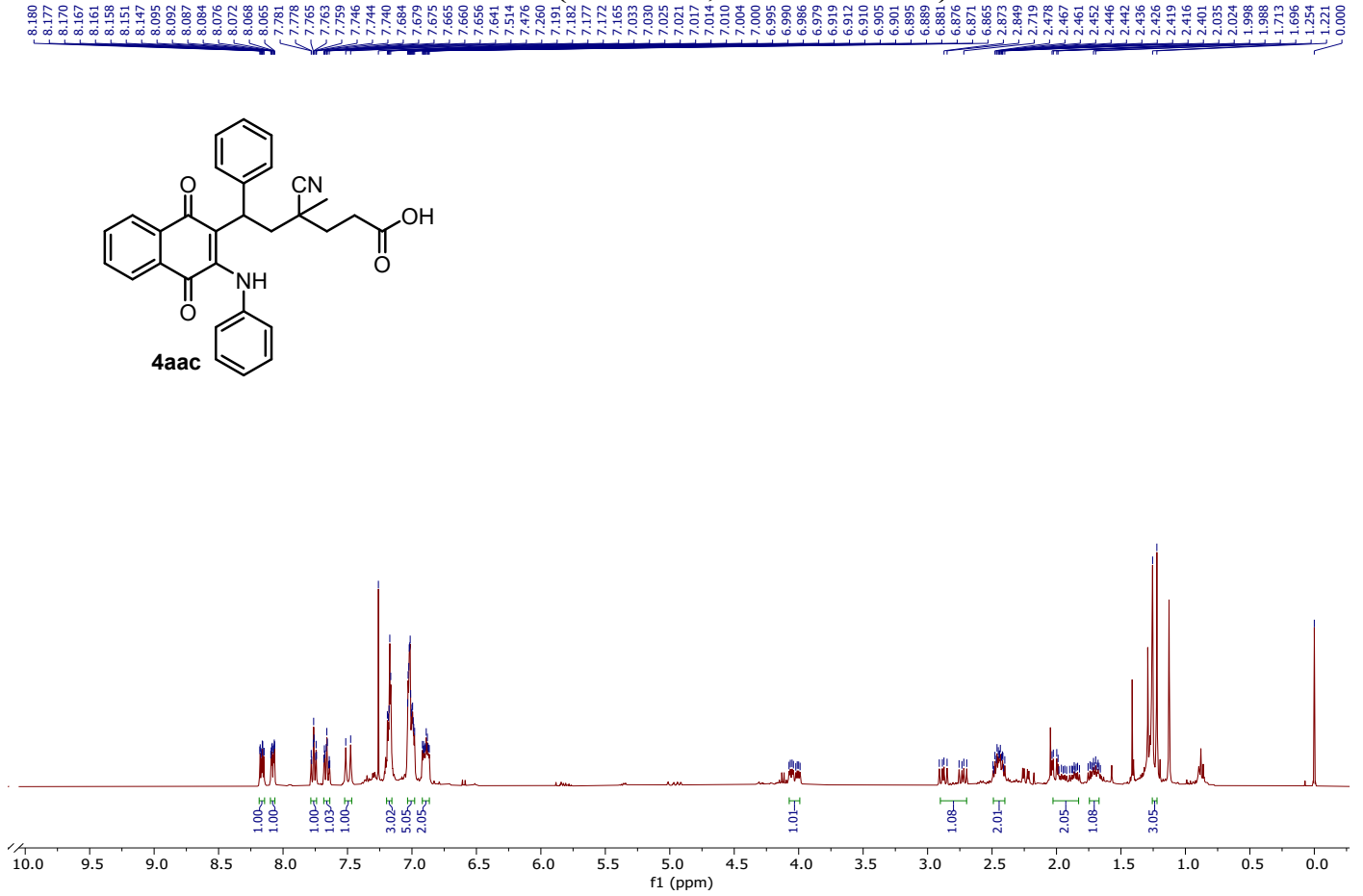
184.782, 182.546

145.290, 140.422, 140.214, 134.982, 133.751, 132.750, 131.987, 130.274, 129.928, 129.319, 128.207, 126.755, 126.518, 125.778, 125.919, 125.415, 120.603

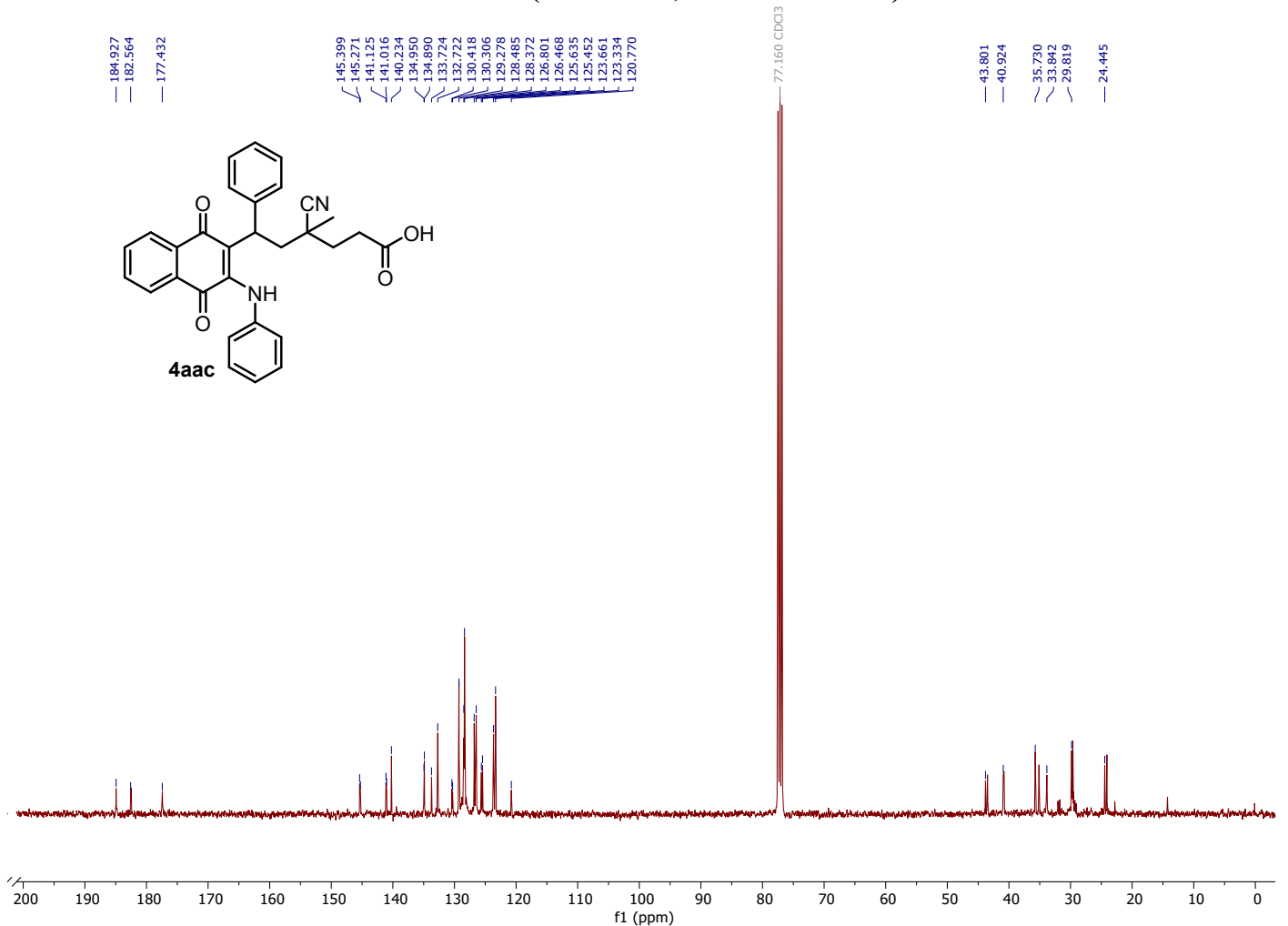
77.160 CDCl₃, 45.511, 40.292, 38.616, 36.272, 35.807, 25.318, 23.014, 22.897



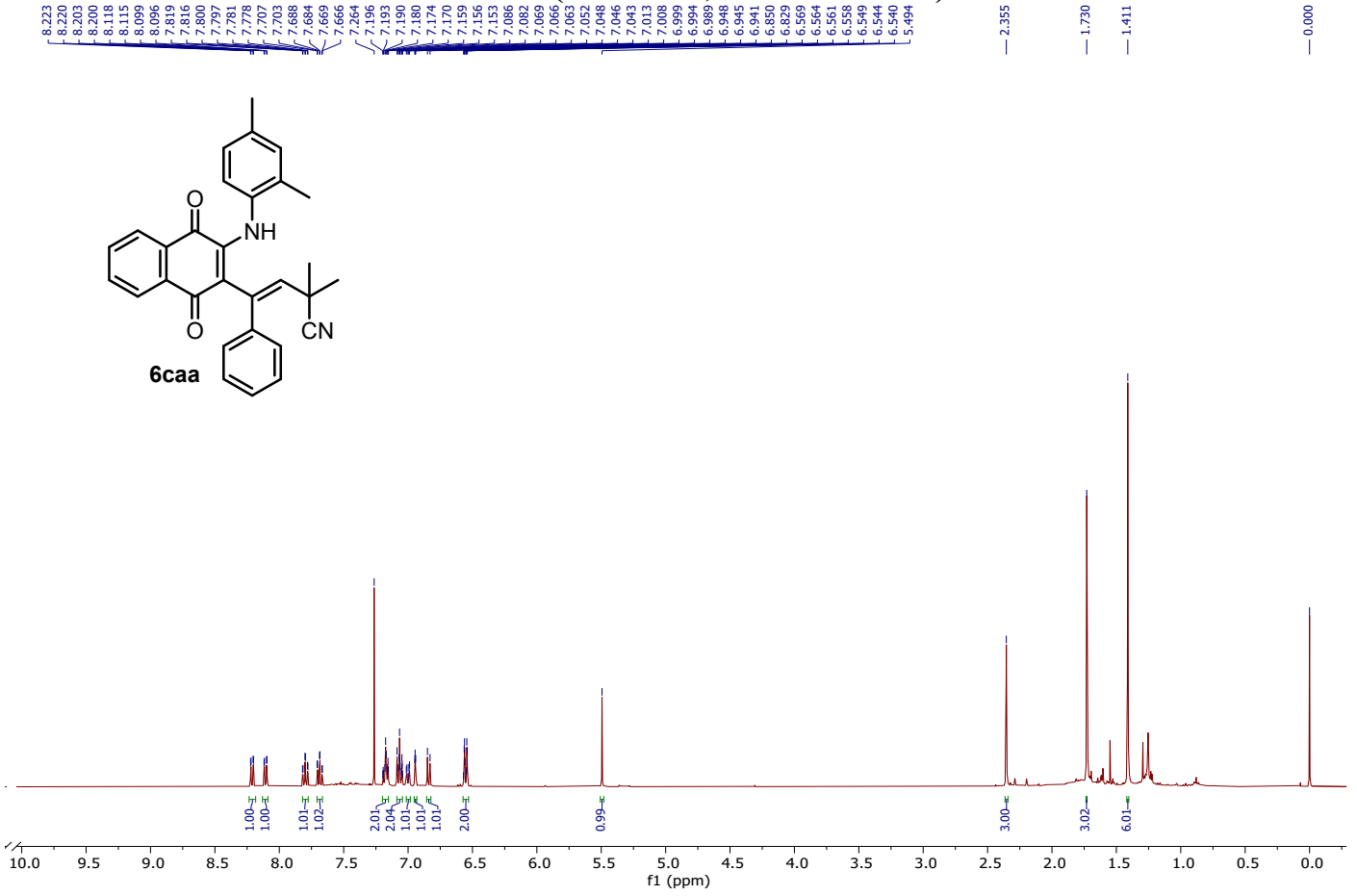
¹H-NMR (400 MHz, Chloroform-*d*)



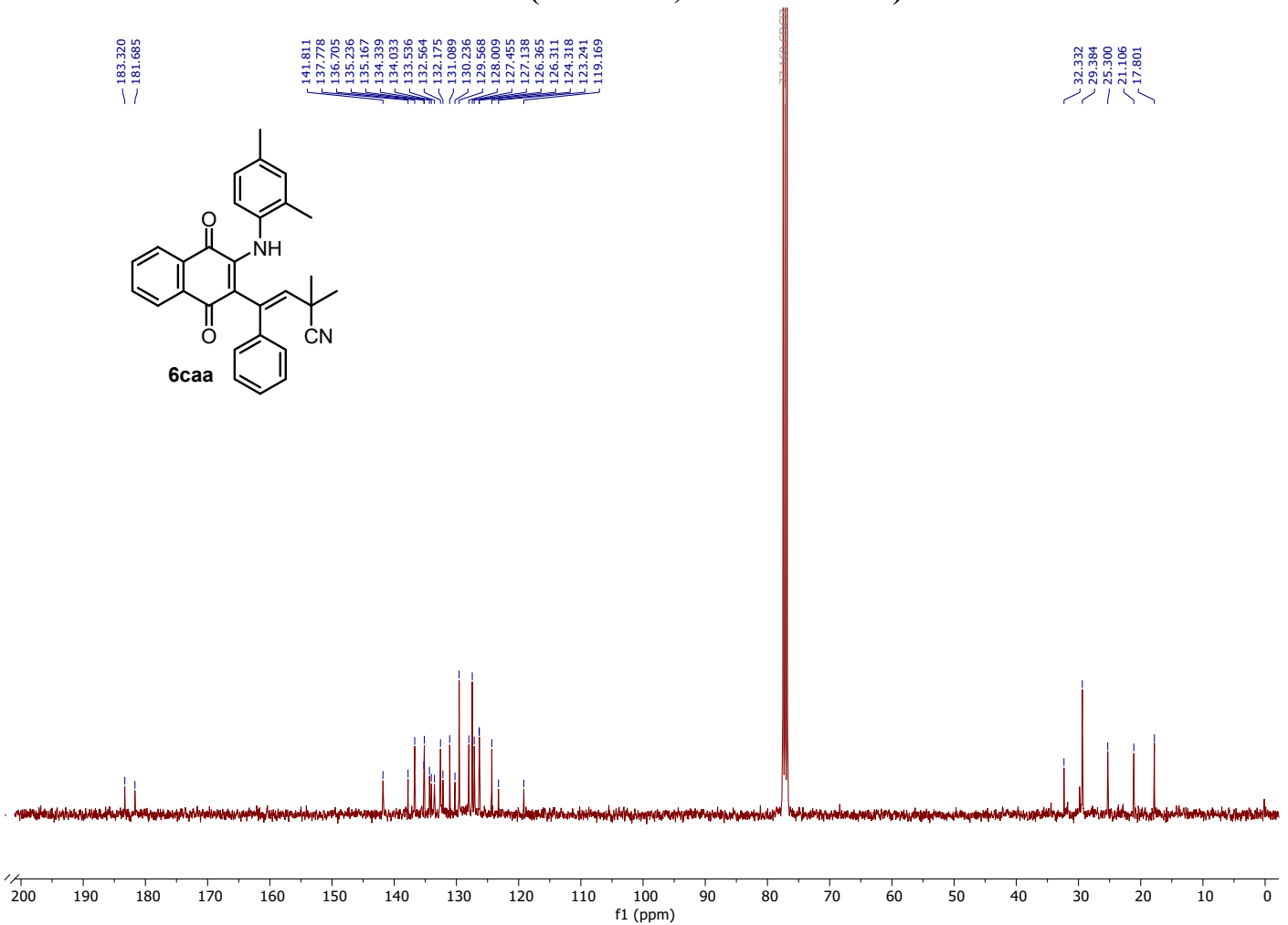
¹³C-NMR (100 MHz, Chloroform-*d*)



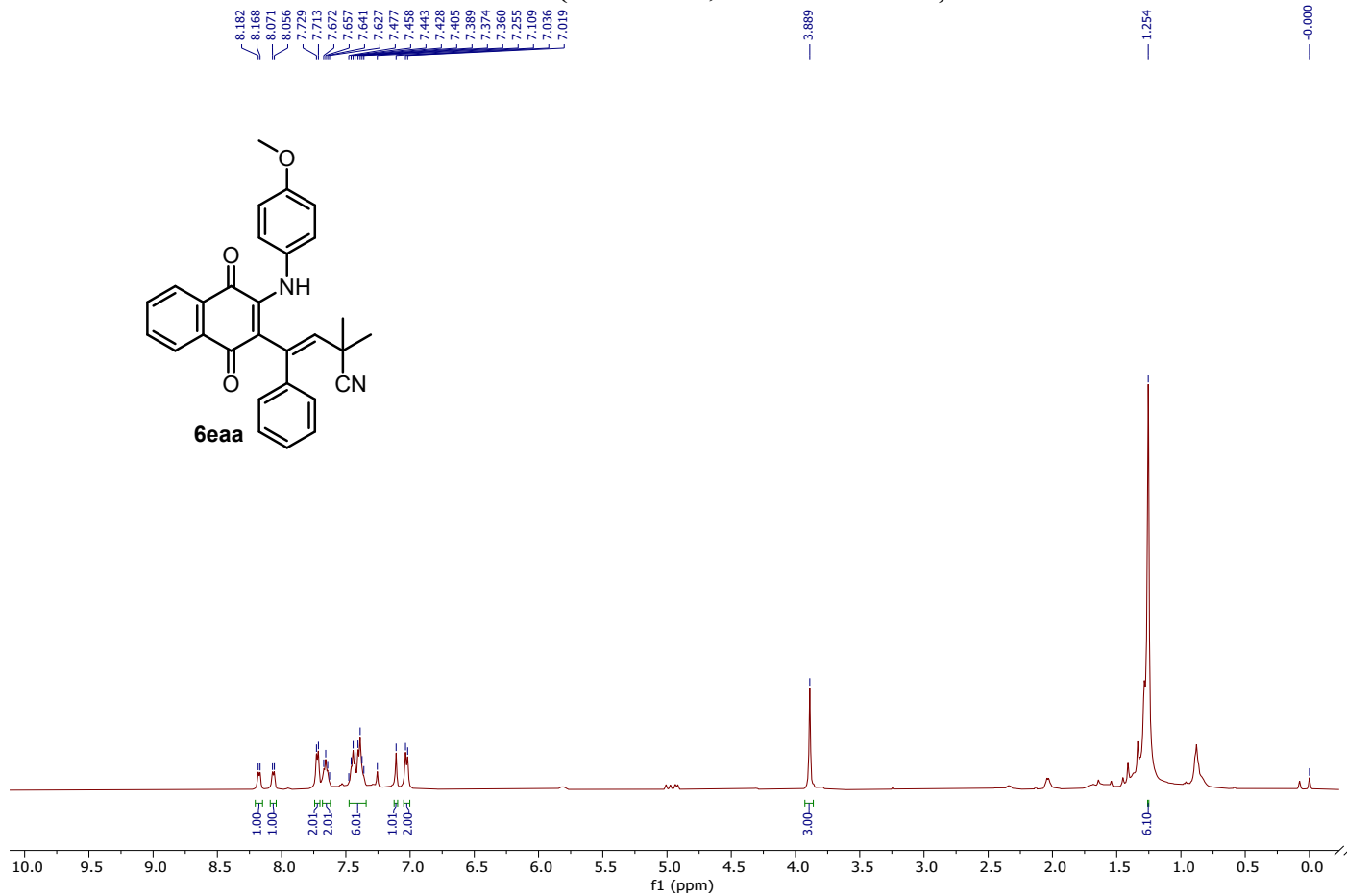
¹H-NMR (400 MHz, Chloroform-*d*)



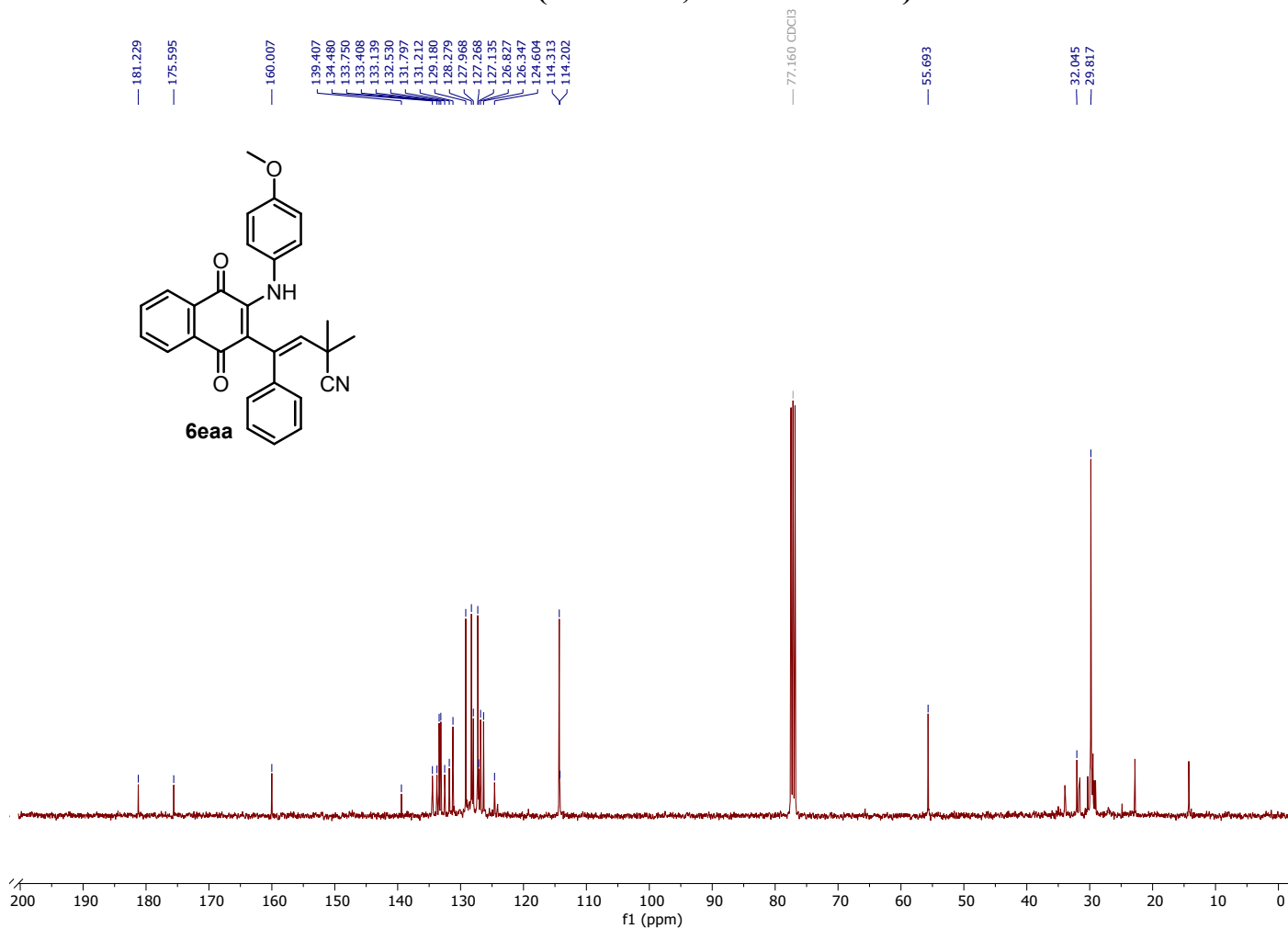
¹³C-NMR (100 MHz, Chloroform-*d*)



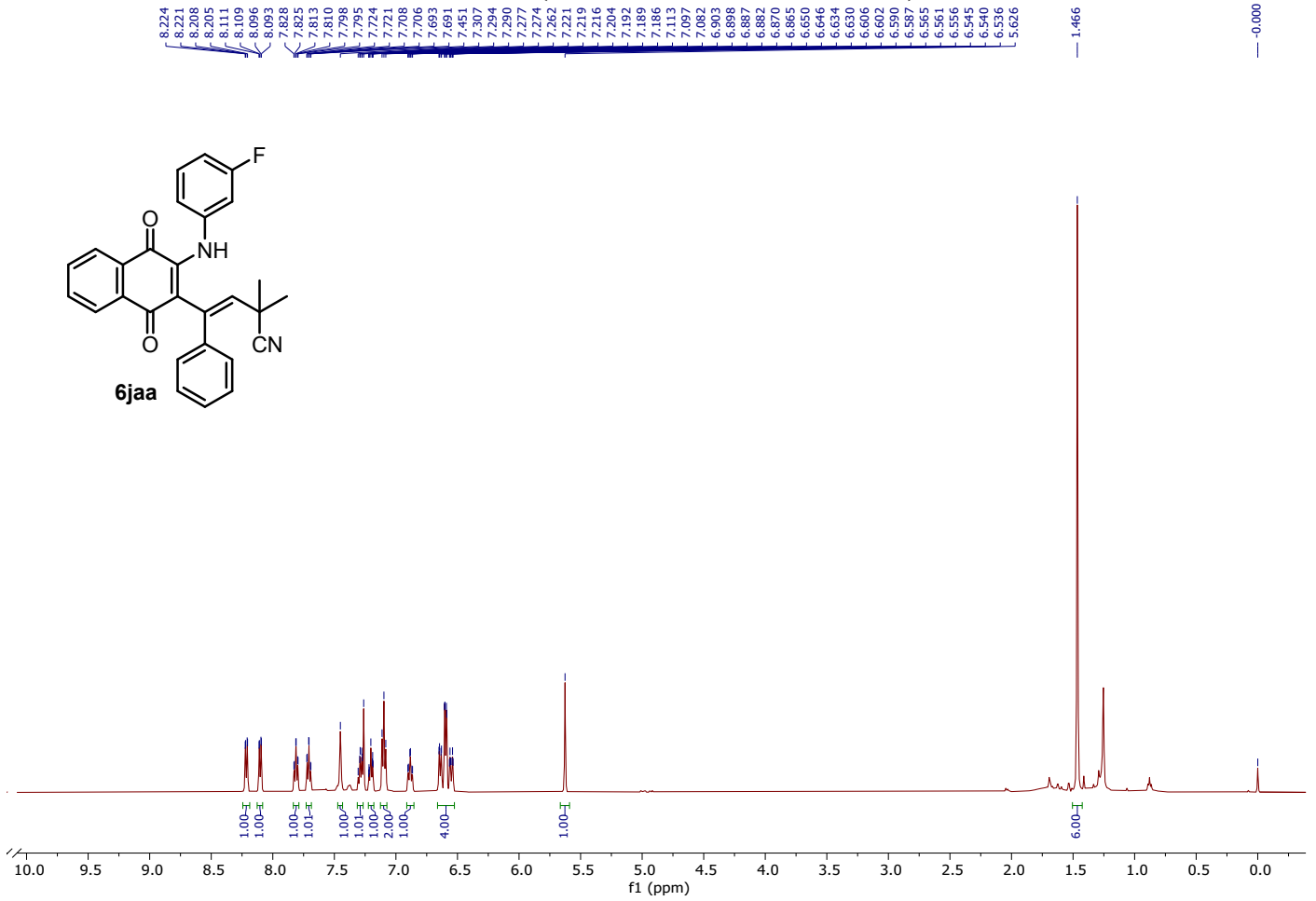
¹H-NMR (500 MHz, Chloroform-*d*)



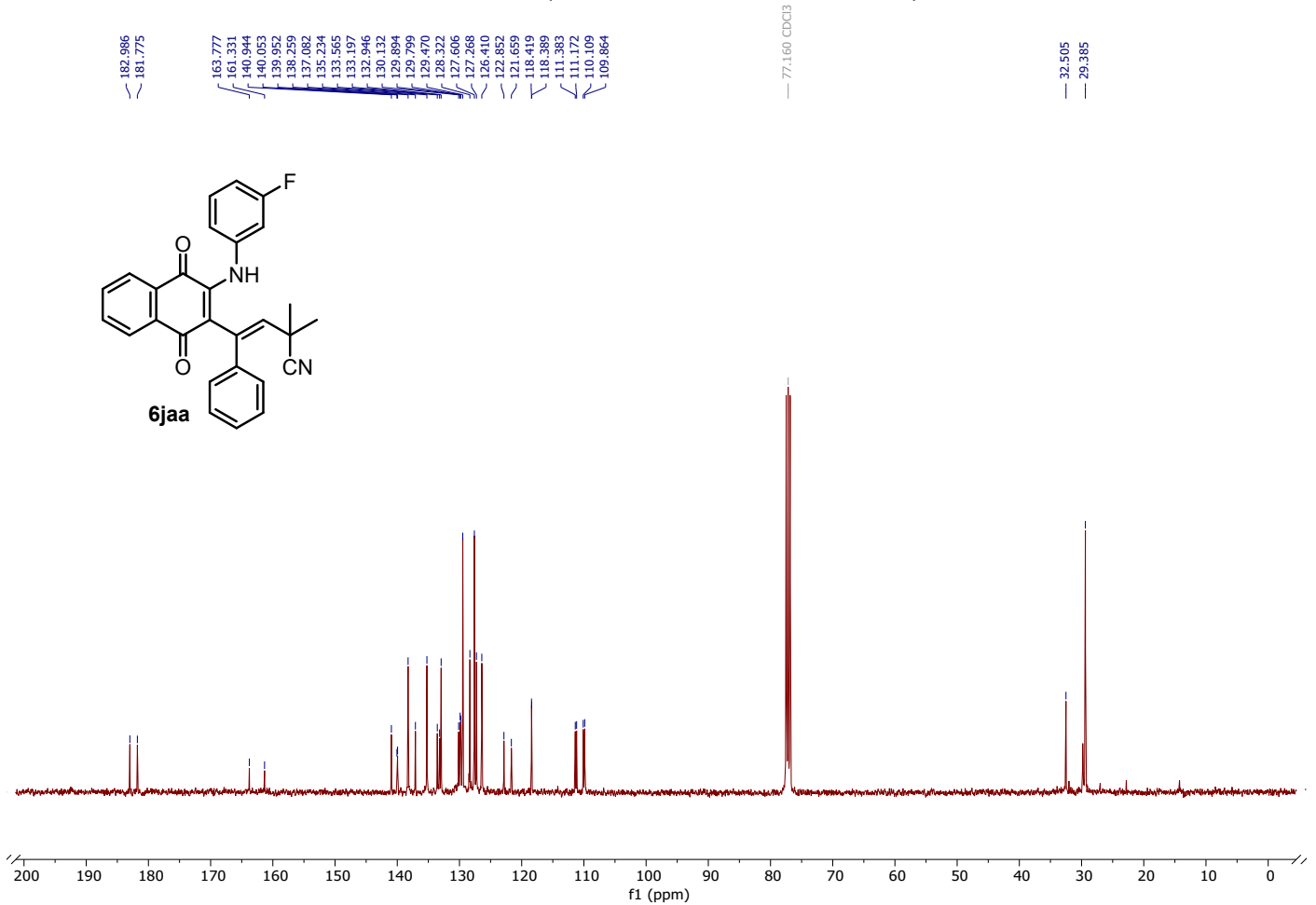
¹³C-NMR (100 MHz, Chloroform-*d*)



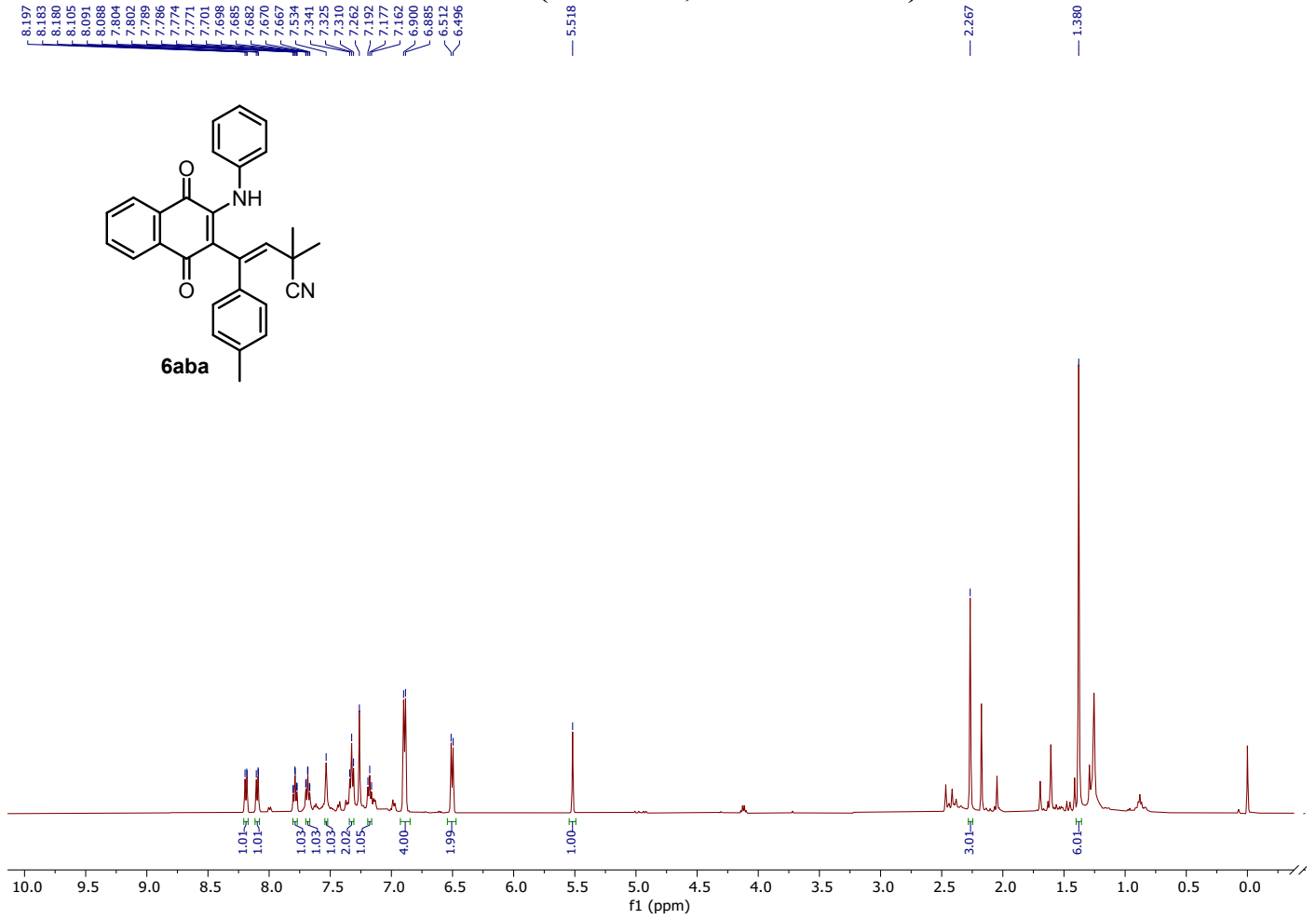
¹H-NMR (500 MHz, Chloroform-*d*)



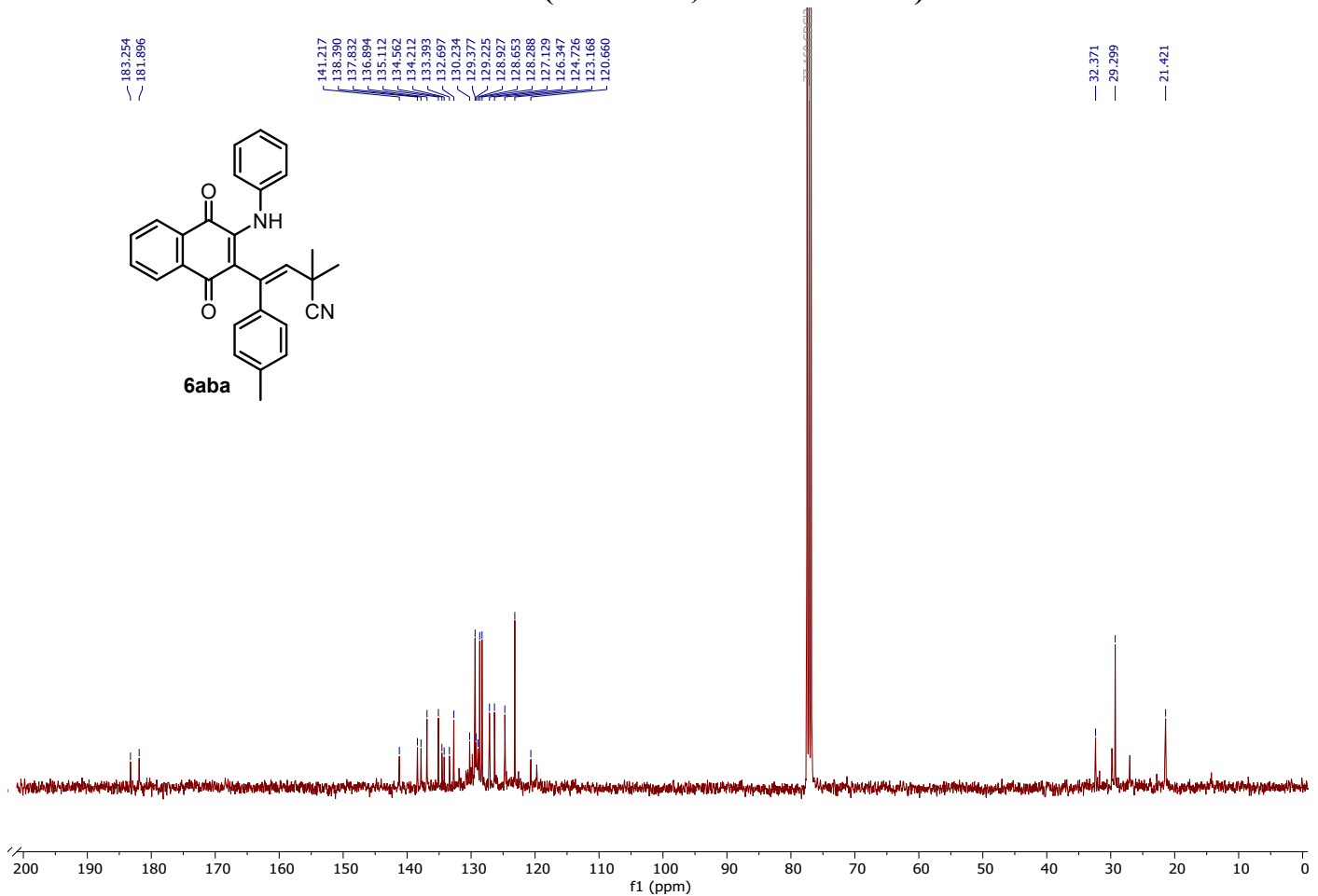
¹³C-NMR (100 MHz, Chloroform-*d*)



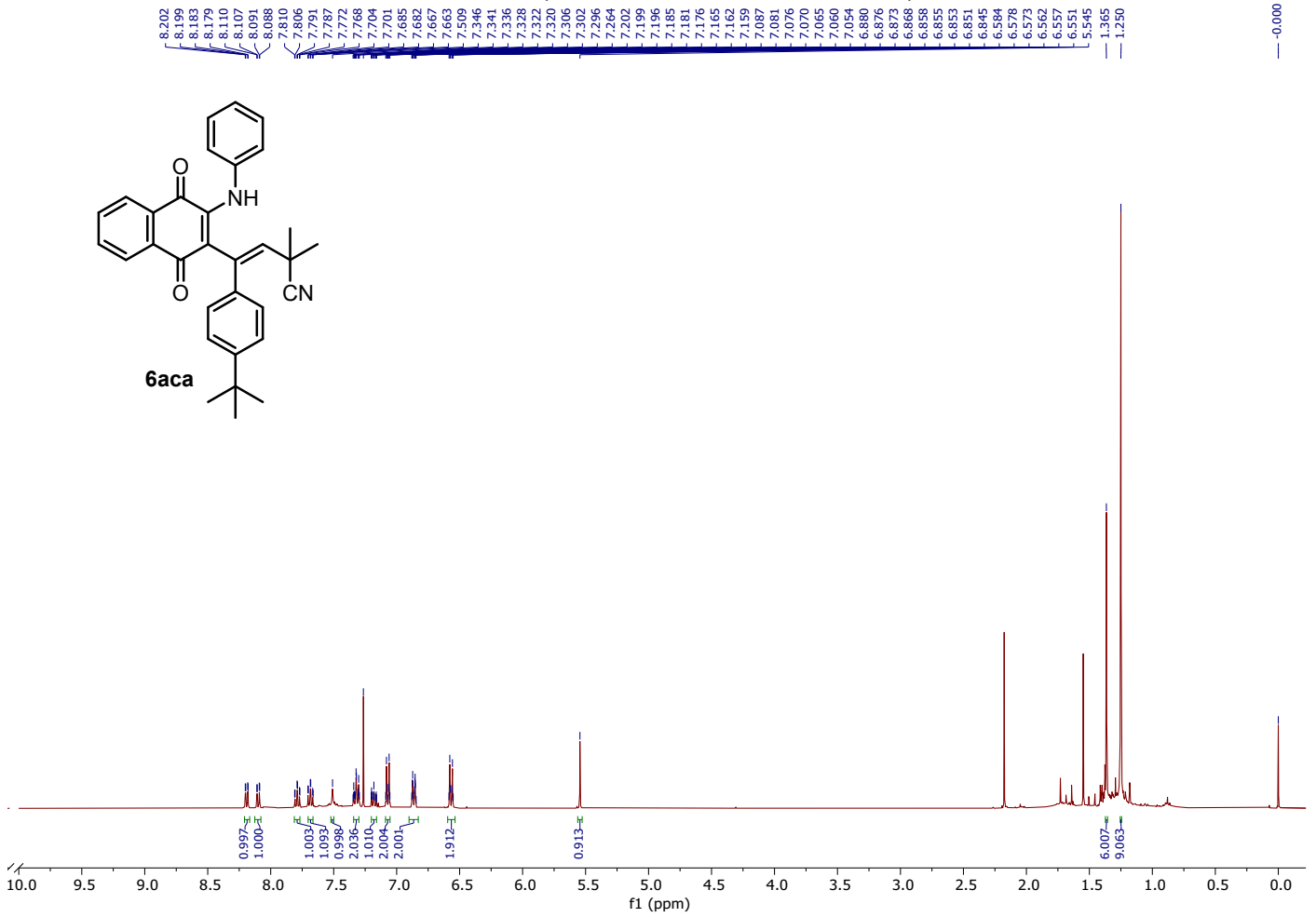
¹H-NMR (500 MHz, Chloroform-*d*)



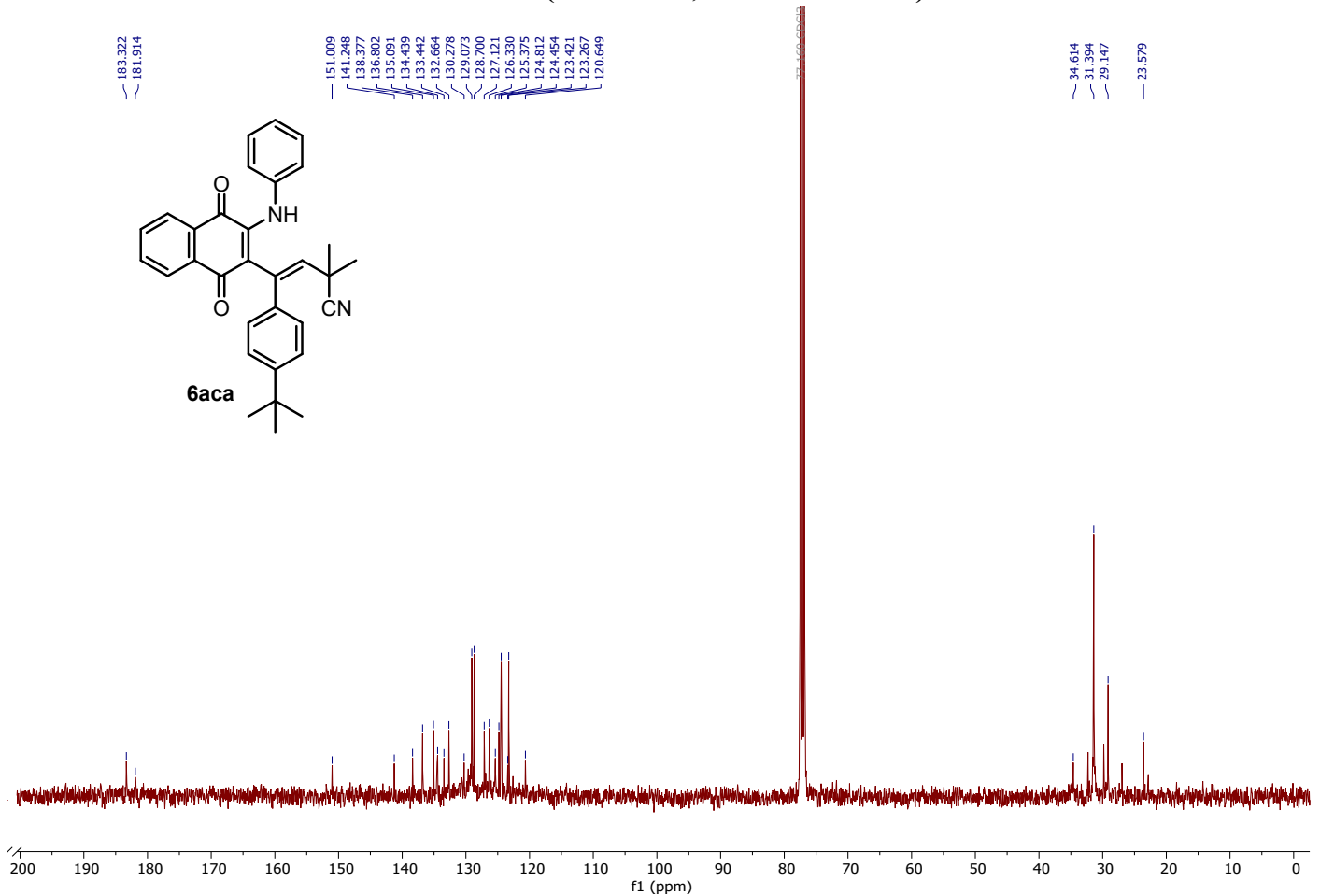
¹³C-NMR (100 MHz, Chloroform-*d*)



¹H-NMR (400 MHz, Chloroform-*d*)



¹³C-NMR (100 MHz, Chloroform-*d*)

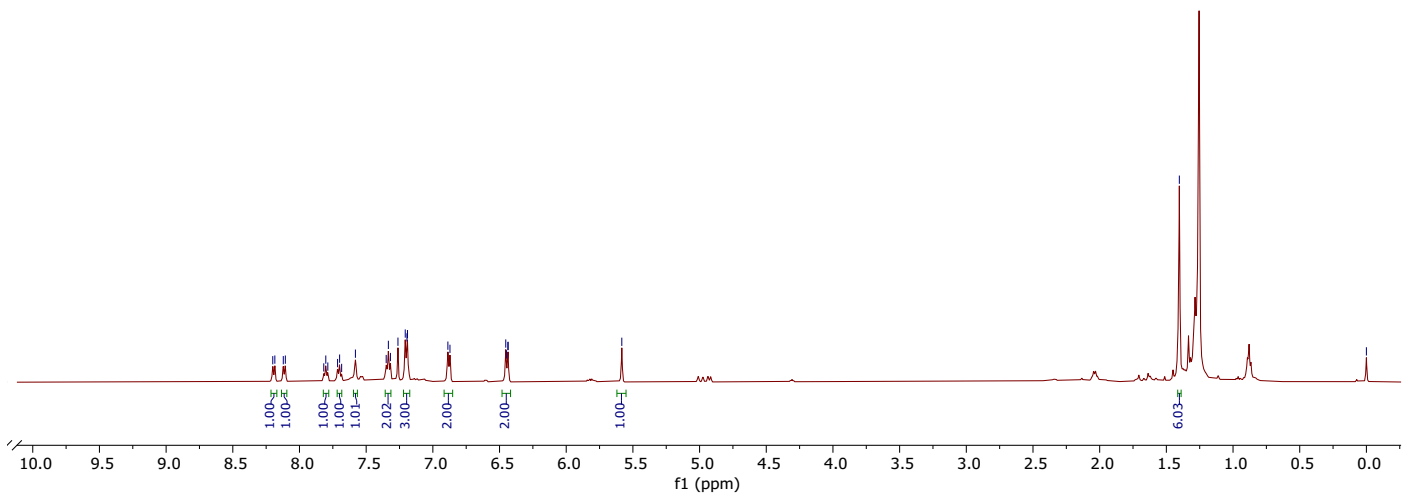
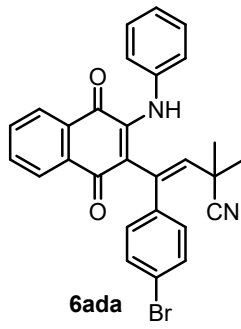


¹H-NMR (500 MHz, Chloroform-*d*)

8.200
8.185
8.121
8.106
7.818
7.803
7.788
7.714
7.699
7.684
7.581
7.350
7.333
7.318
7.262
7.207
7.194
7.190
6.887
6.872
6.453
6.449
6.437
6.436
5.583

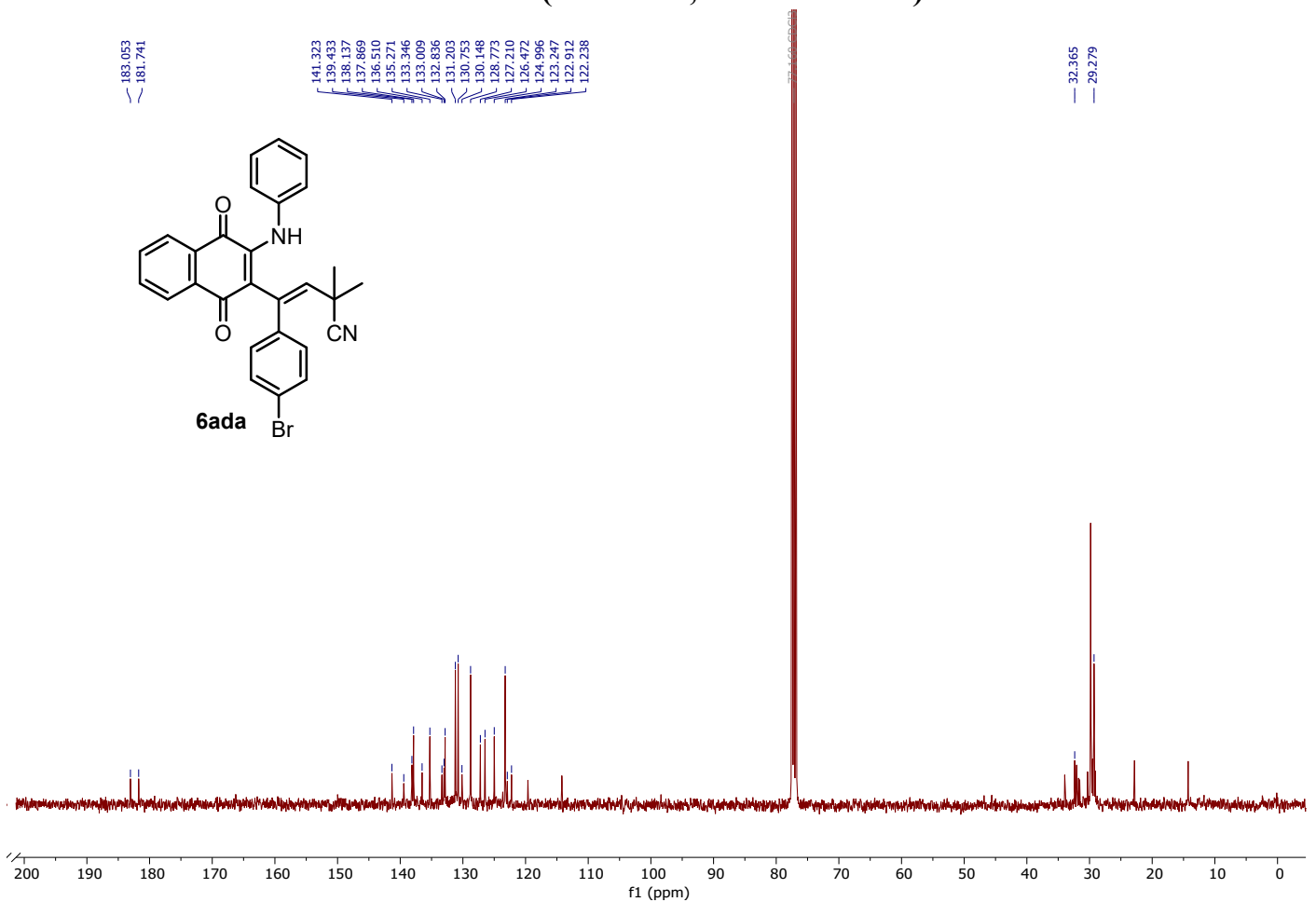
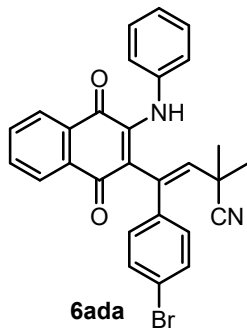
1.403

0.000

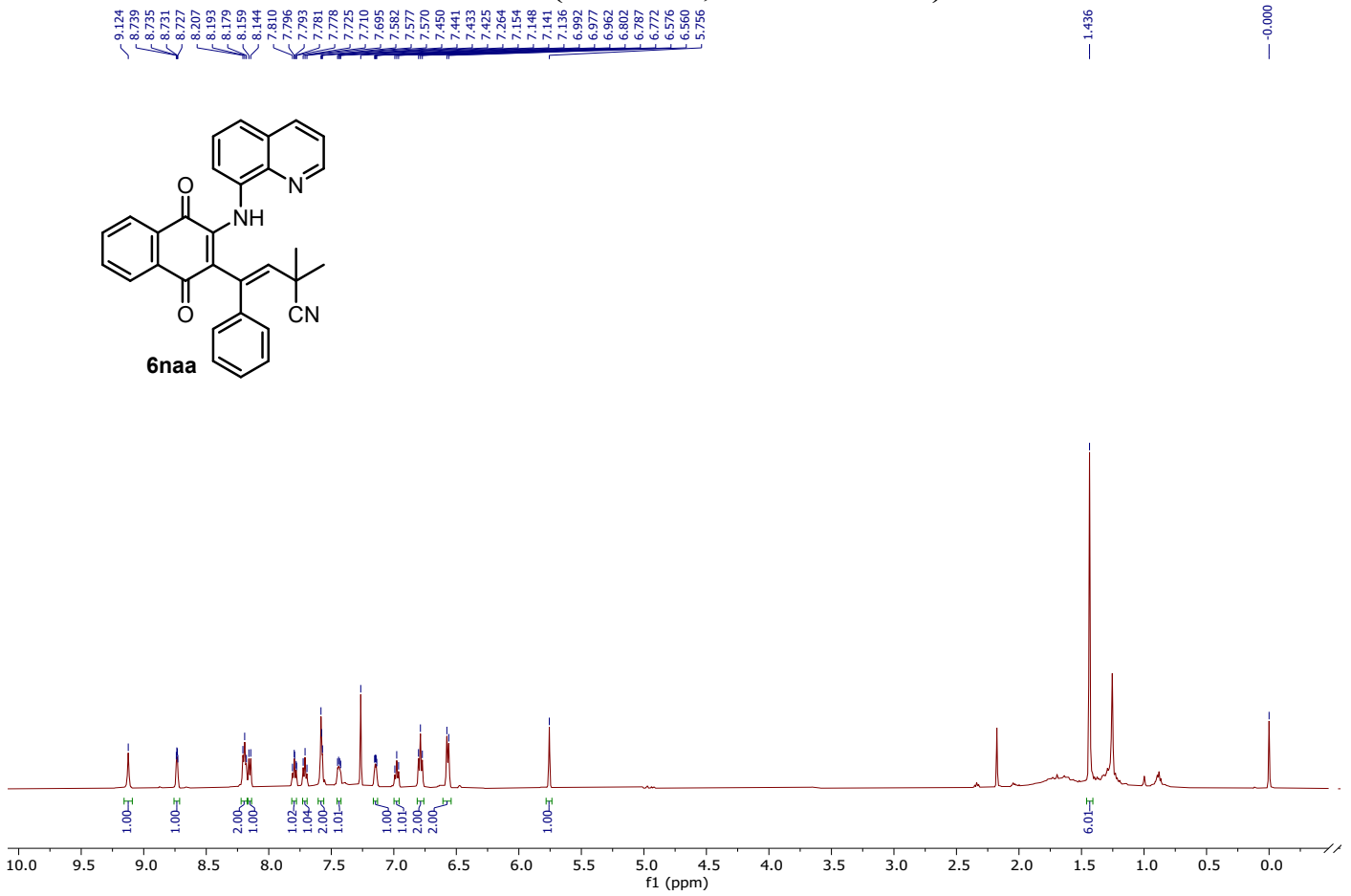


¹³C-NMR (100 MHz, Chloroform-*d*)

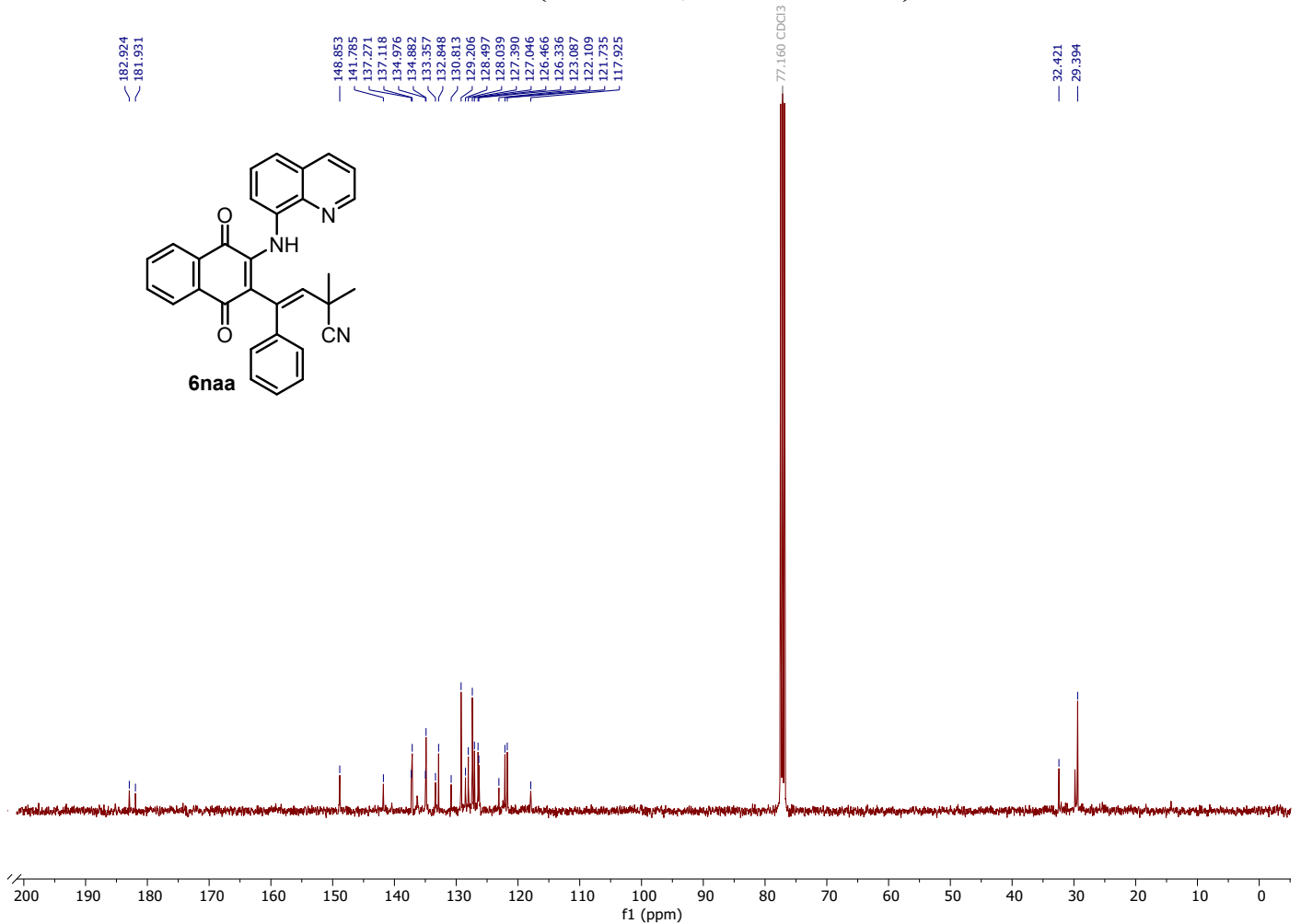
183.053
181.741
141.323
139.433
138.137
137.869
136.510
136.271
133.346
133.009
132.898
132.836
130.703
130.738
130.198
128.773
127.210
126.472
124.996
123.247
122.912
122.238
32.365
29.279



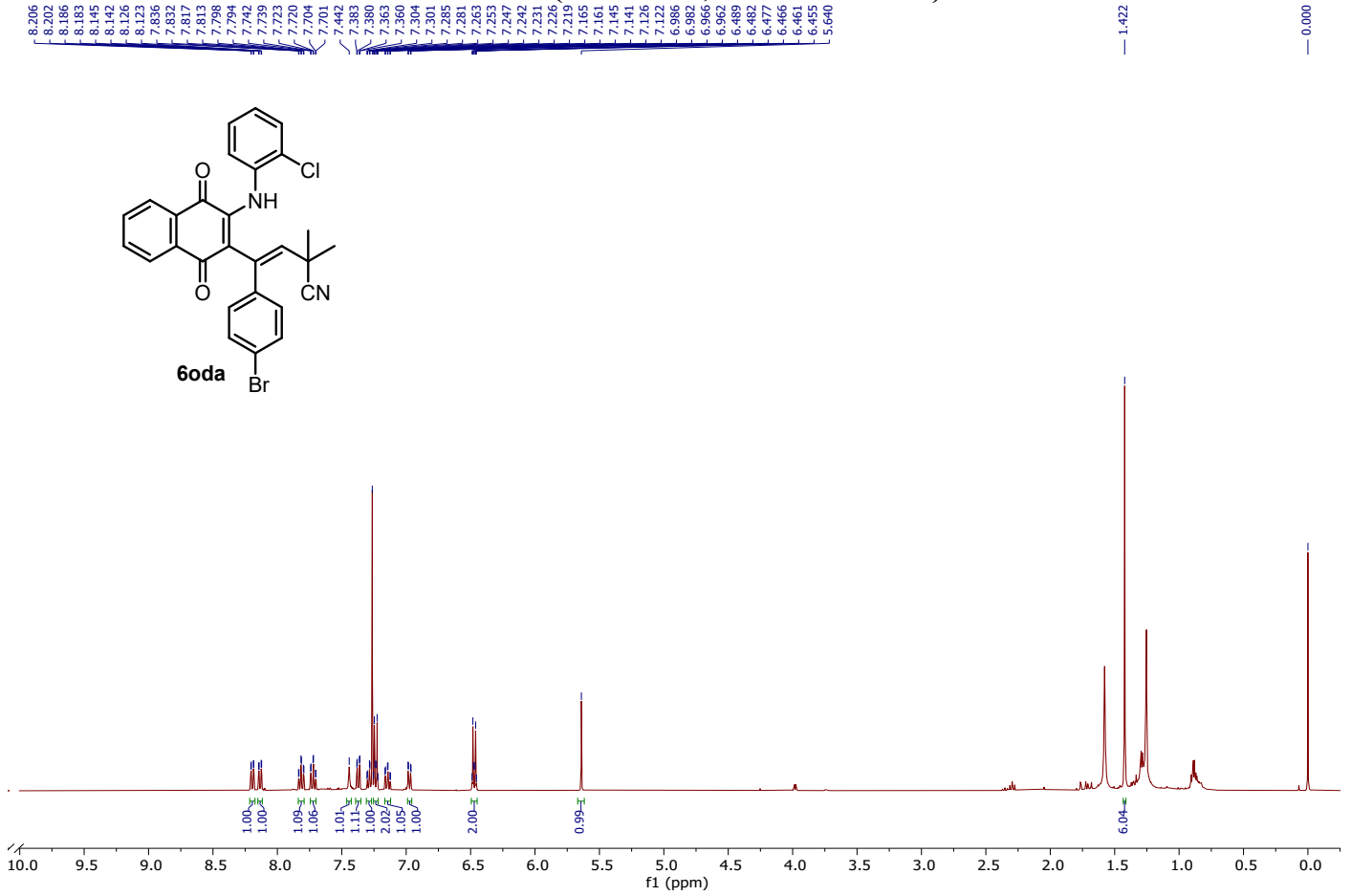
¹H-NMR (500 MHz, Chloroform-*d*)



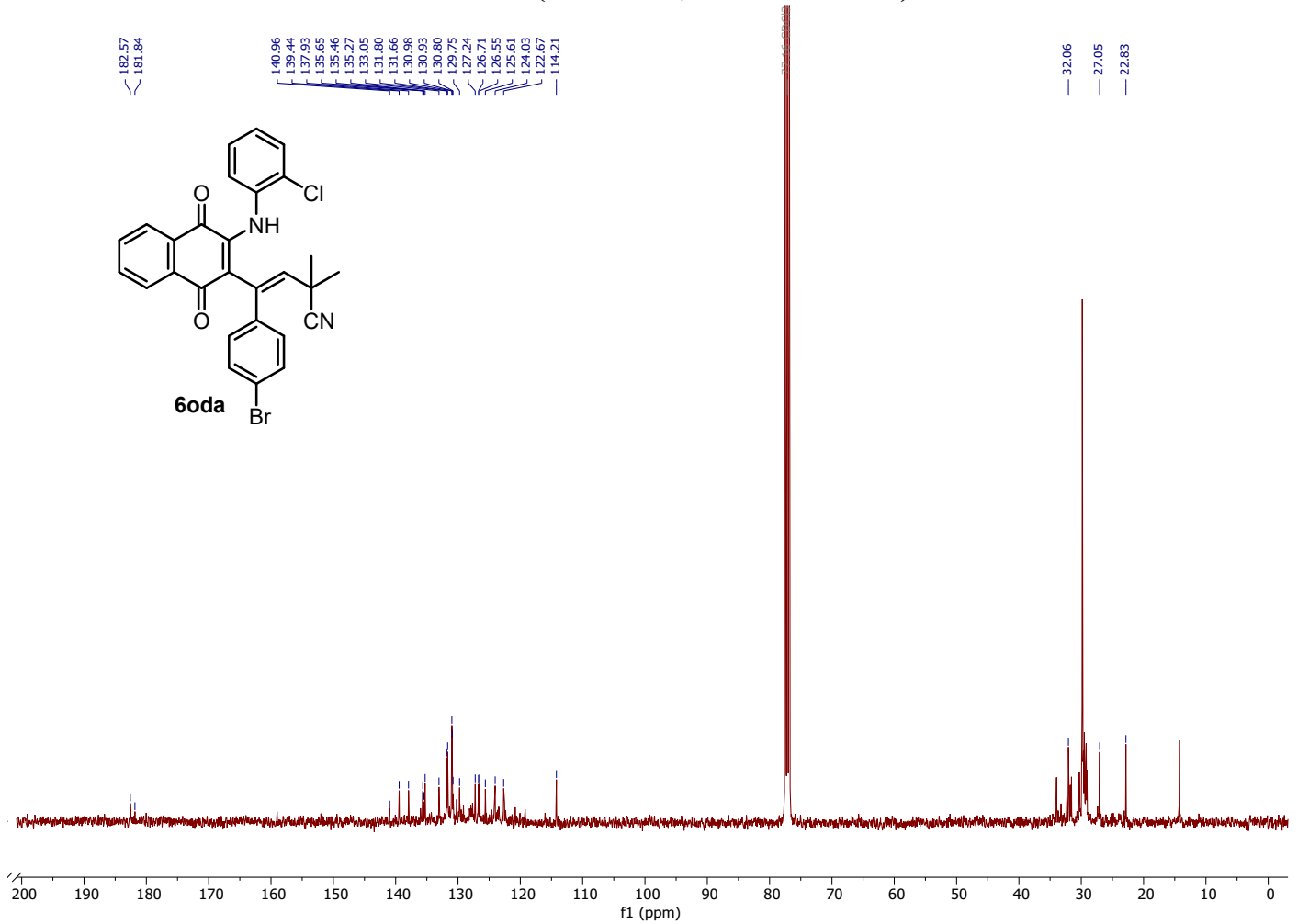
¹³C-NMR (100 MHz, Chloroform-*d*)



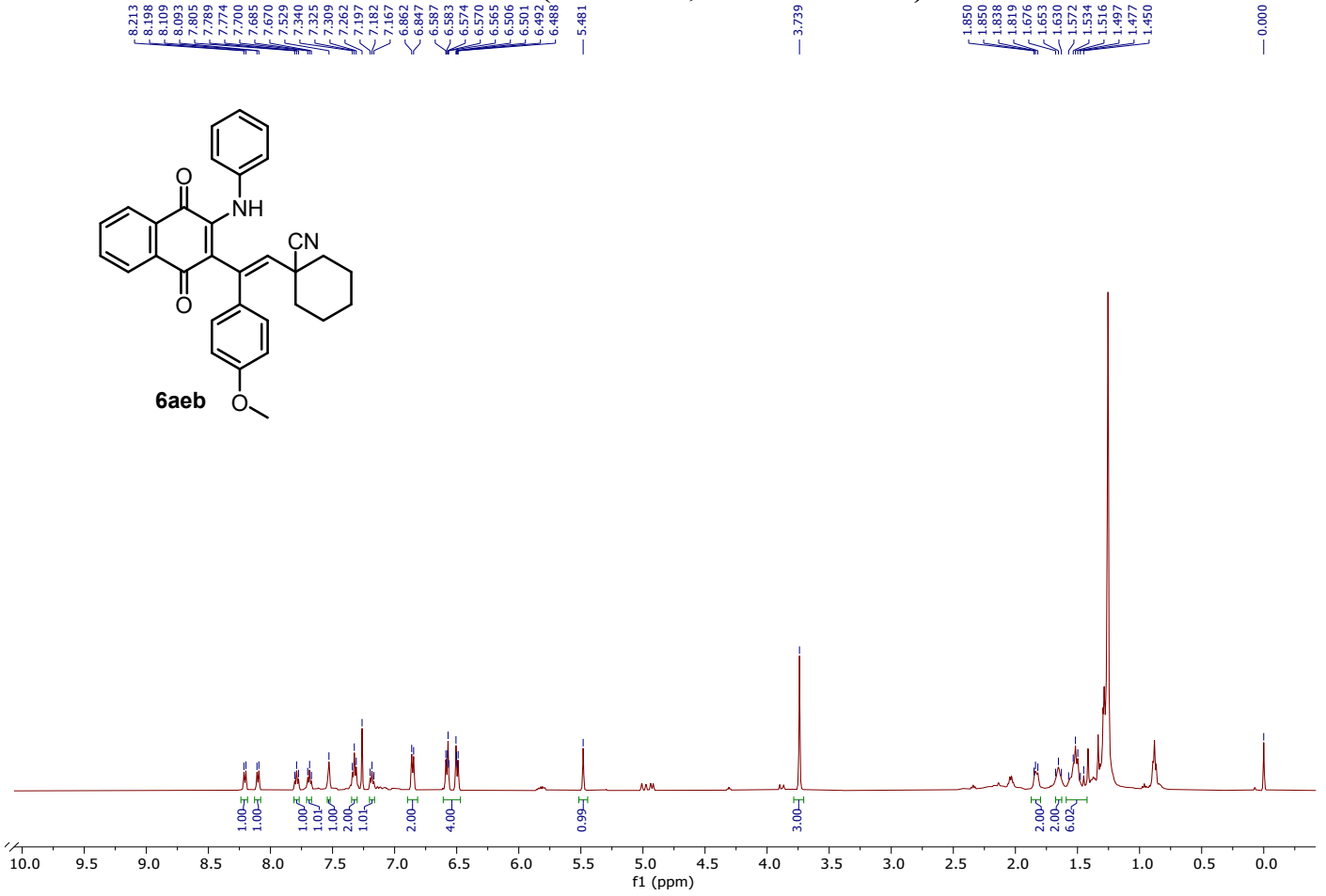
¹H-NMR (400 MHz, Chloroform-*d*)



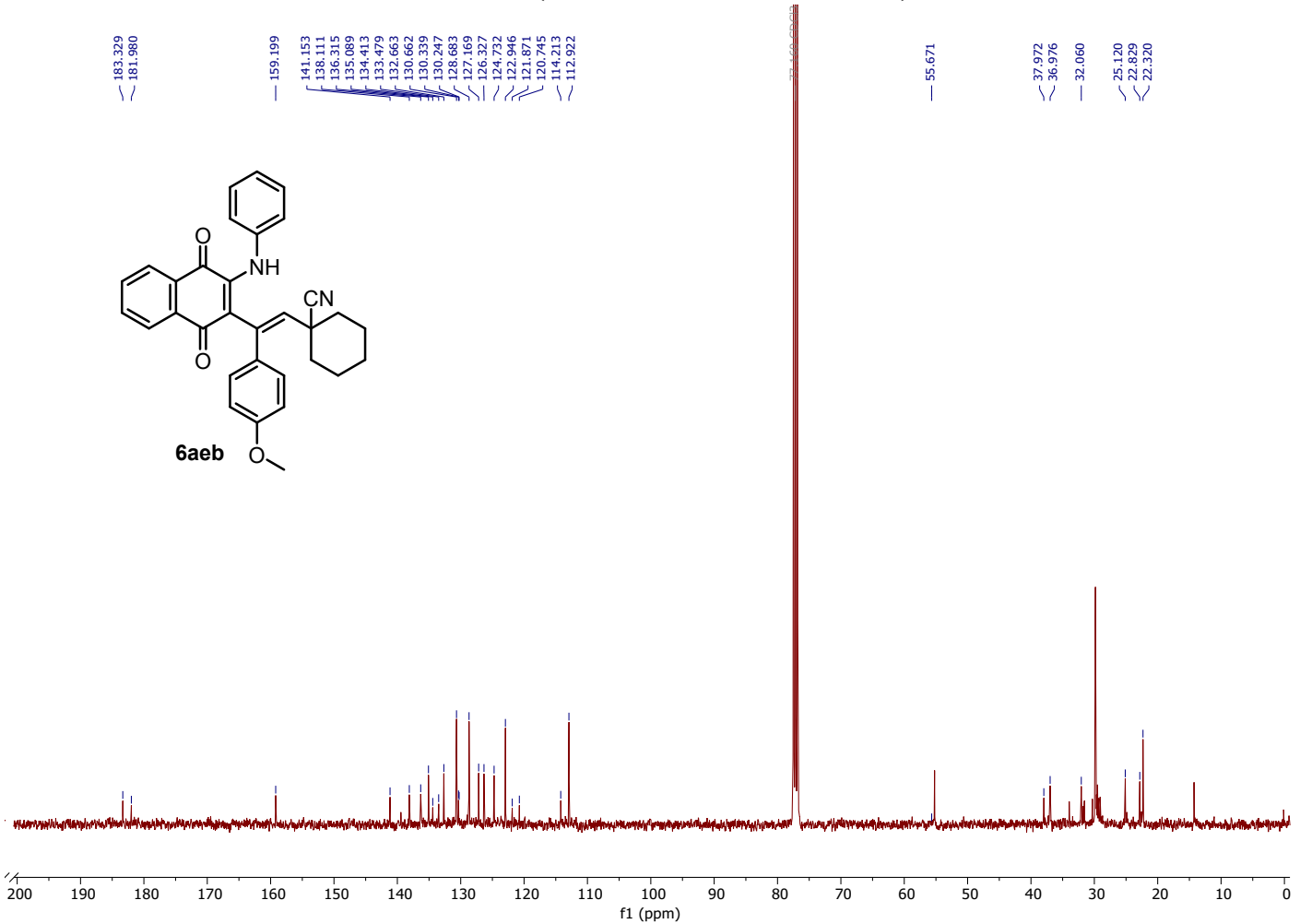
¹³C-NMR (100 MHz, Chloroform-*d*)



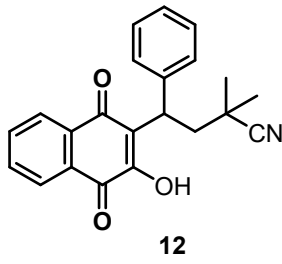
¹H-NMR (500 MHz, Chloroform-*d*)



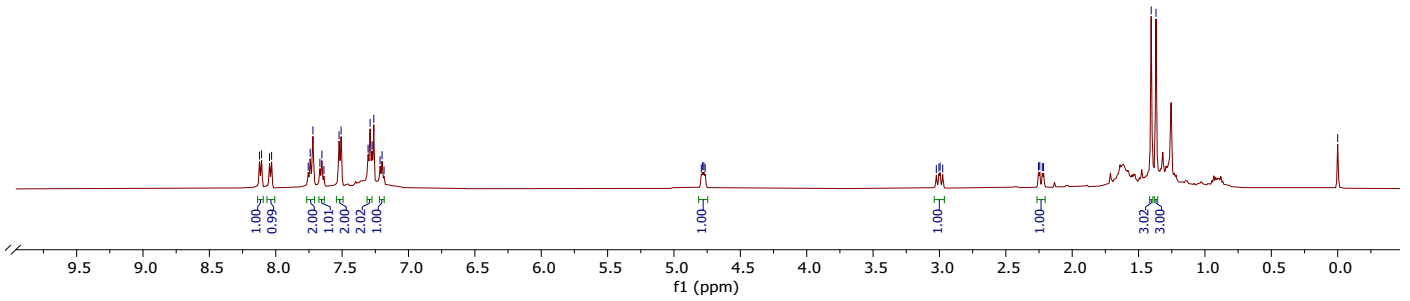
¹³C-NMR (100 MHz, Chloroform-*d*)



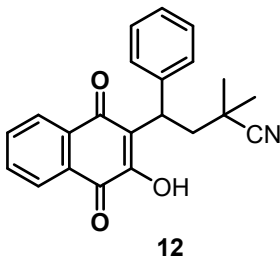
¹H-NMR (500 MHz, Chloroform-*d*)



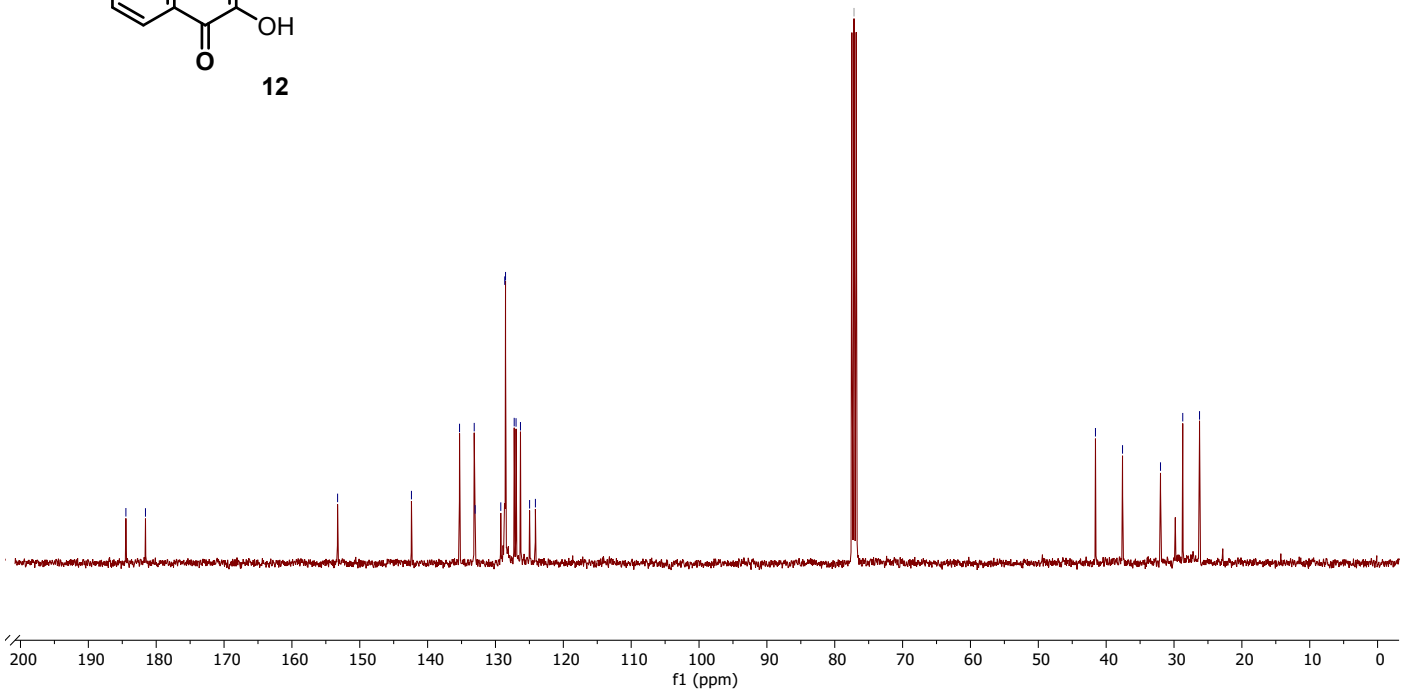
8.122, 8.107, 8.047, 8.031, 7.755, 7.740, 7.720, 7.667, 7.652, 7.637, 7.523, 7.508, 7.304, 7.289, 7.274, 7.261, 7.214, 7.199, 7.184, 4.794, 4.784, 4.775, 4.765, 3.024, 3.004, 2.995, 2.976, 2.254, 2.244, 2.225, 2.216, 1.405, 1.369, -0.000



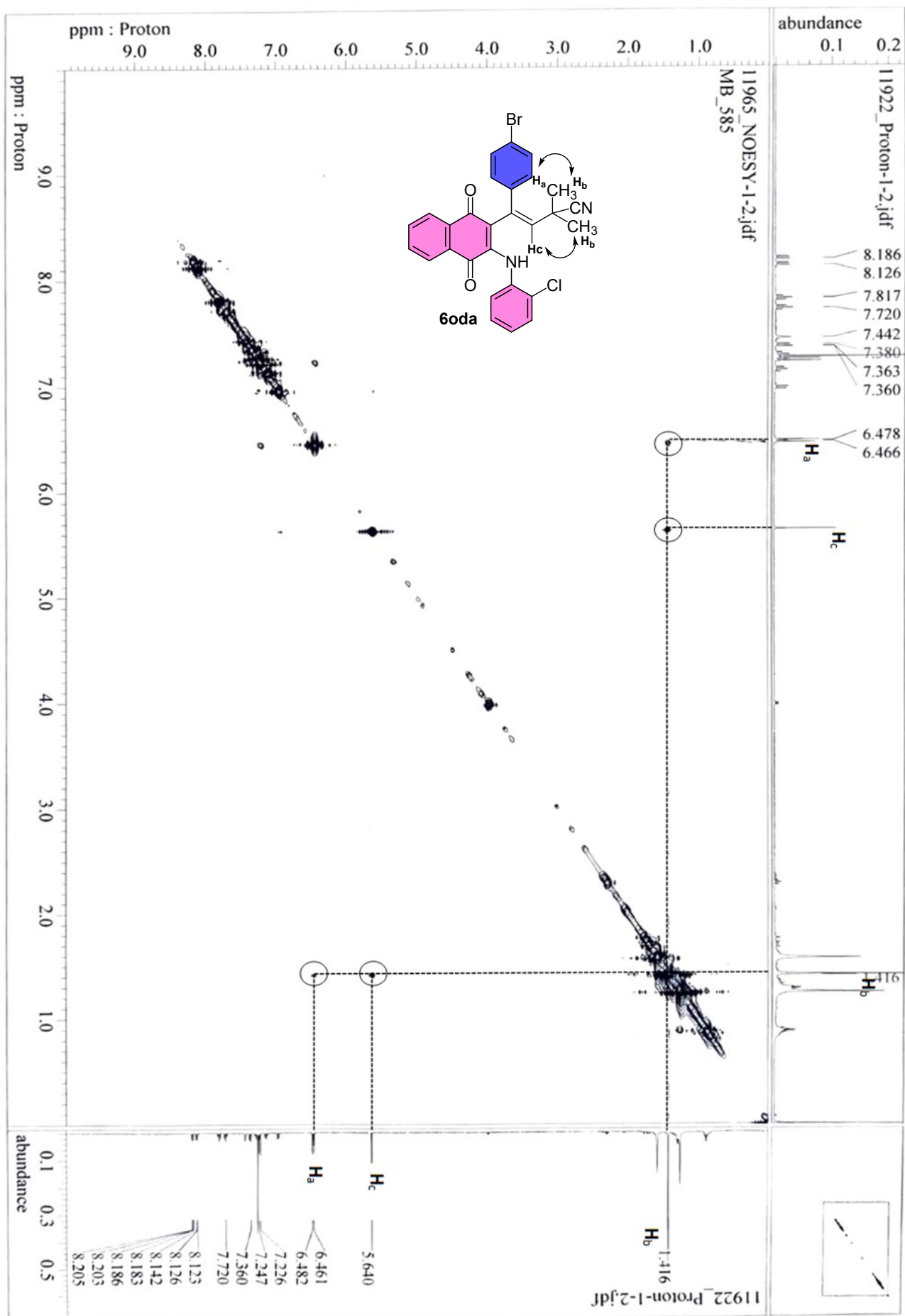
¹³C-NMR (100 MHz, Chloroform-*d*)



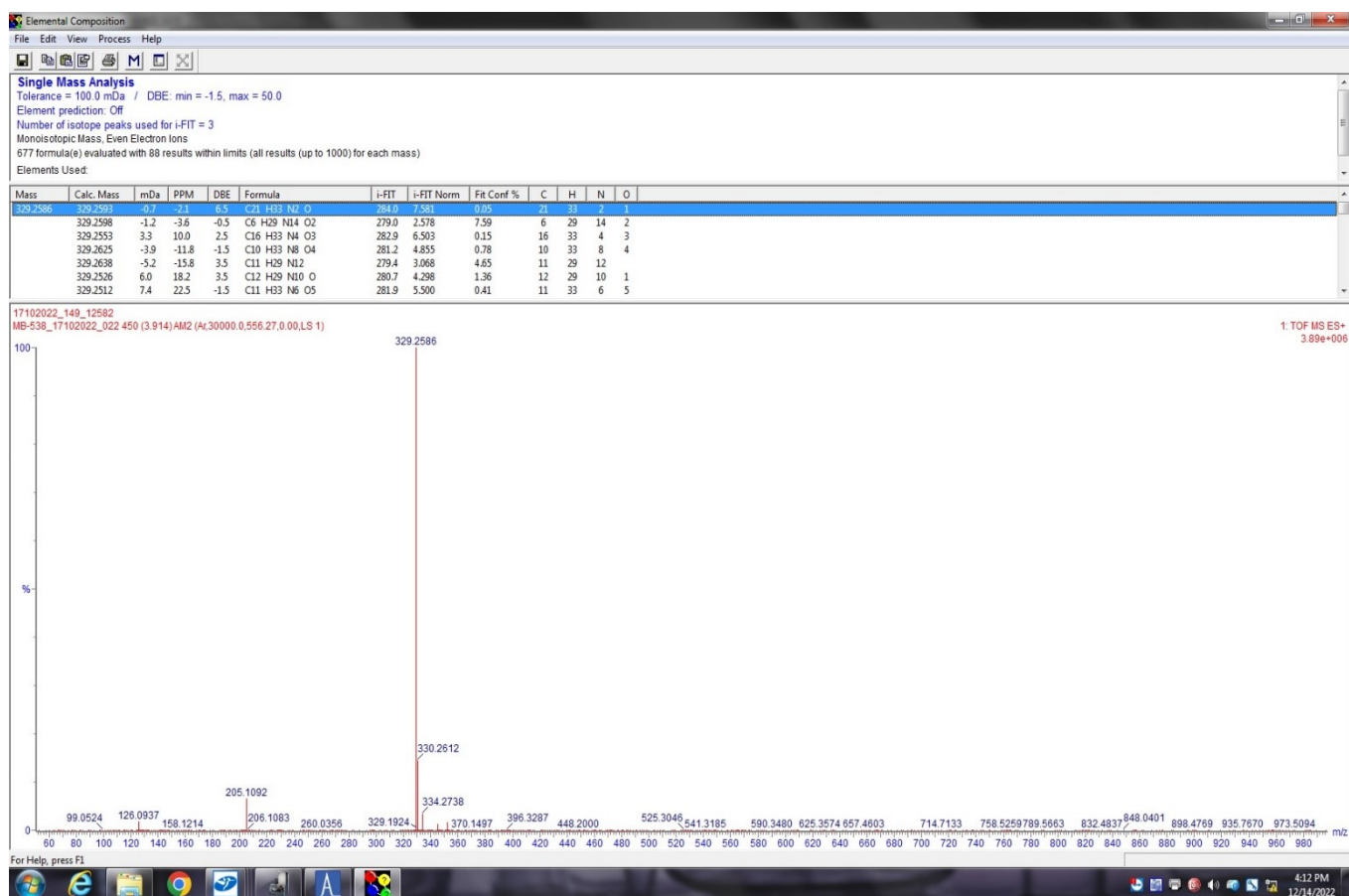
184.467, 181.580, 153.269, 142.382, 135.295, 133.132, 132.999, 129.218, 128.635, 128.519, 127.239, 126.966, 126.315, 124.971, 124.113, 77.160 CDCl3, 41.576, 37.588, 31.992, 28.714, 26.241



- **NOESY- 6oda:** No NOE observed between **H_a** and **H_c**, rather there was visible interaction only between **H_a** and **H_b**, **H_b** and **H_c**.



➤ HRMS data of the control experiment for the TEMPO-adduct (7)



➤ HRMS data of the control experiment for the diphenylethylene-adduct (8)

