Electronic Supplementary Material (ESI) for Chemical Communications

Metal-free TEMPO-Catalyzed Oxidative C-C Bond Formation from Csp^3-H Bonds Using Molecular Oxygen as The Oxidant

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Supporting Information

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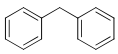
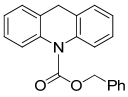
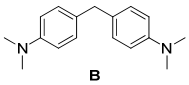
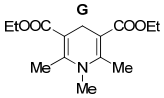
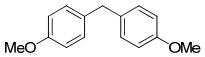
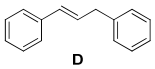
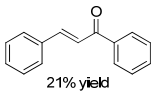
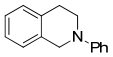
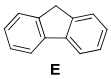
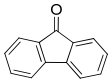
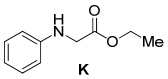
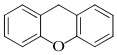
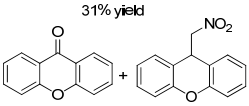
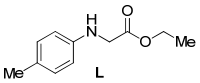
1. General Remarks

All manipulations were conducted with a standard Schlenk tube under dioxygen atmosphere, ^{1}H-NMR spectra were recorded on Bruker AVIII-400 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C-NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.00 ppm). Mass spectra were recorded by PE SCLEX QSTAR spectrometer. HR-MS were obtained using electrospray ionization (ESI) mass spectrometer. Unless otherwise noted, materials and solvents obtained from commercial suppliers were used without further purification.

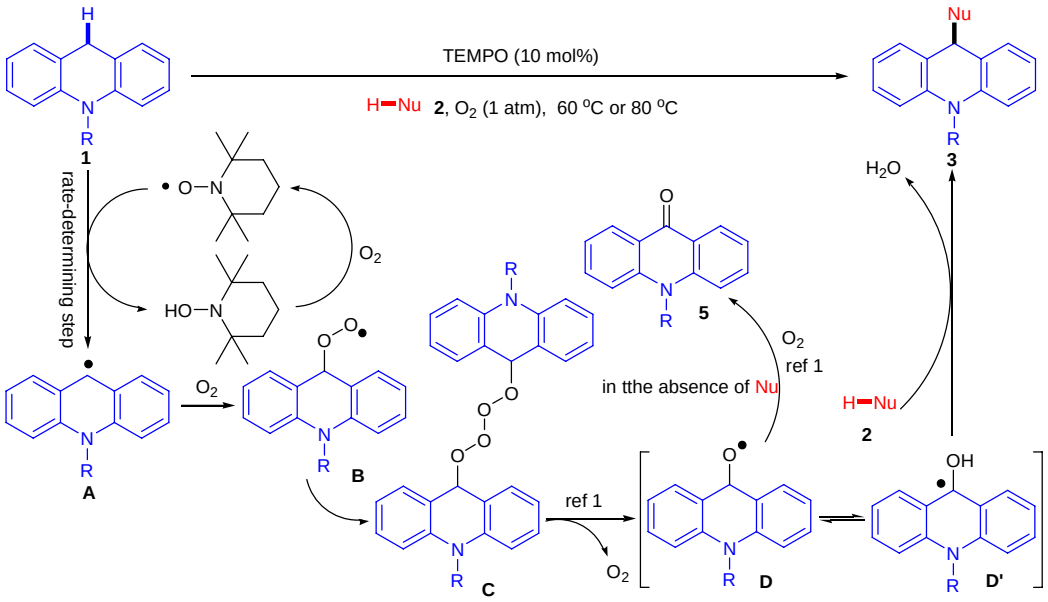
2. The substrates investigated in this reaction

Entry	Substrate	Isolated products	Entry	Substrate	Isolated products
1	 A	Starting materials	7	 G	80% starting material recovered Not characterized by-products
2	 B	Starting materials	8	 H	Not characterized by-products
3	 C	Starting materials	9	 I	Starting materials
4[b]	 D	 21% yield	10	 J	Starting materials
5[b]	 E	 31% yield	11	 K	Starting materials
6[c]	 F	 73% 12%	12	 L	Starting materials

[a] Reaction conditions: substrate (0.2 mmol), **2a** (0.5 mL), TEMPO (0.02 mmol), stirred at 60 °C under O_2 (1 atm) for 24 h. [b] The reaction was carried out at 100 °C for 3 days. [c] The reaction was carried out at 100 °C for 59h.

3. The proposed Mechanism

The plausible mechanism of this transformation is proposed in the following Scheme 2. Initially, TEMPO abstracts a hydrogen atom from the benzyl C-H bonds of 9,10-dihydroacridine **1** to produce the benzyl radical **A** and TEMPOH. Subsequently, the intermediates **D** and/or **D'** are generated in the presence of molecular oxygen via **B** and **C** as previously reported process.[1] The conversion from the intermediates **D** and/or **D'** with the nucleophile **2** to the product **3** is uknown yet. The radical coupling with nucleophiles maybe involved in this step.[2] In the absence of any nucleophile, the hydroperoxyl **D** and/or **D'** can be oxidized to ketone **5**.[1] We have tried to synthesize some intermediates such as hydroperoxyl or hydroxyl intermediate, but failed due to the unstability of these compounds. More detailed studies are needed to understand the mechanism.



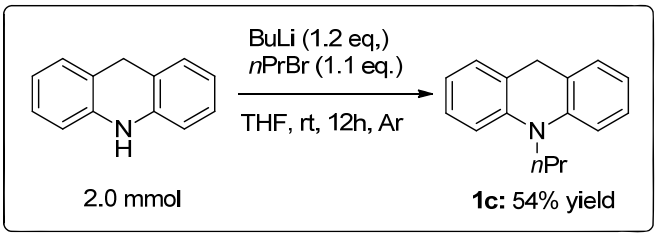
Proposed mechanism for the transformation

4. Preparation of substrates

9,10-Dihydroacridine **1a**, **1b**, **1d**, **1i** and **1m** were prepared according to reported methods.[3]

9,10-Dihydroacridine **1c** was synthesised according to the synthetic method of **1b**.

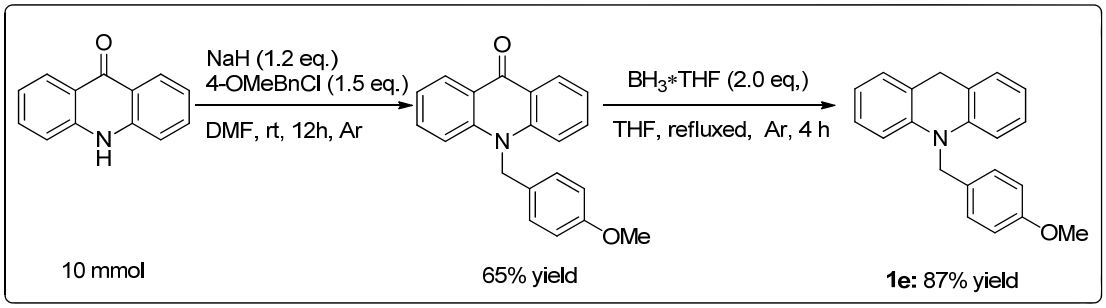
10-Propyl-9,10-dihydroacridine (1c)[4]



The reaction was carried out on 2.0 mmol and the product **1c** was obtained in 54% yield as a white solid. IR:(KBr) ν_{max} 2961, 1596, 1480, 1374, 1260, 748 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.17 (t, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.6 Hz, 2H), 6.89-6.86 (m, 4H), 3.95 (s, 2H), 3.80 (t, *J* = 7.6 Hz, 2H), 1.88-1.79 (m, 2H), 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 142.1, 128.0, 126.8, 123.5, 120.2, 112.3, 47.5, 32.9, 19.0, 11.2; MS (70 eV): m/z (%): 223.2 (7) $[M]^+$, 179.9 (100).

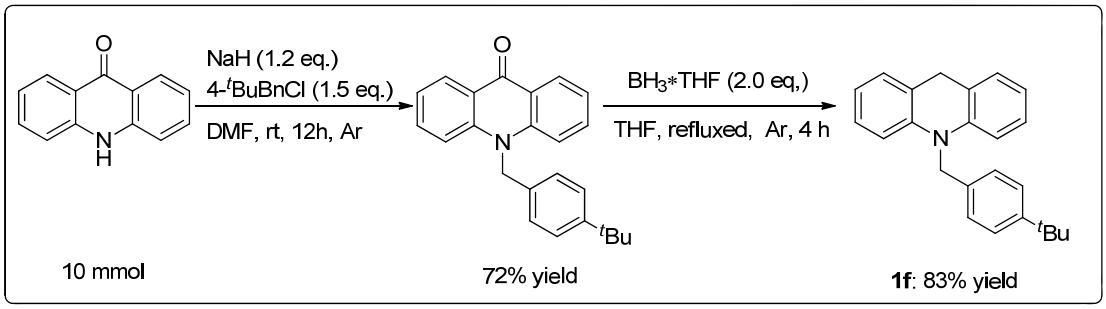
9,10-Dihydroacridine **1e-1h** were prepared according to the synthetic method of **1d**.

10-(4-Methoxybenzyl)-9,10-dihydroacridine (1e)



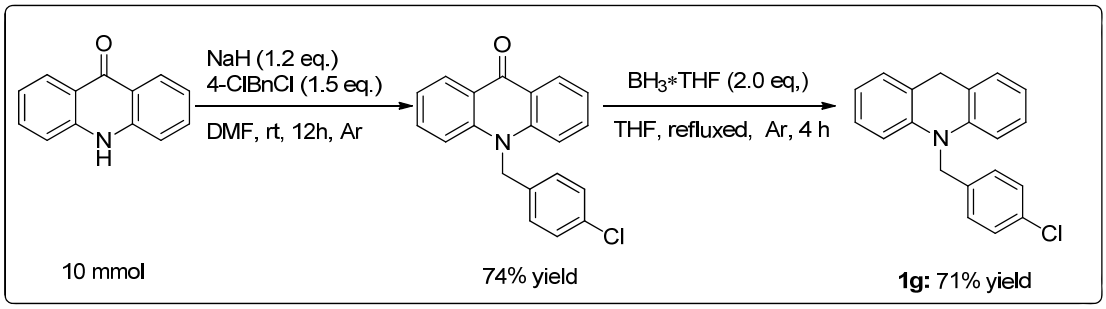
The reaction was carried out on 10.0 mmol and the product **1e** was obtained in 57% total yield in two steps as a white solid. IR:(KBr) ν_{max} 2912, 1595, 1513, 1481, 1376, 1251, 750 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.17-7.04 (m, 6H), 6.91-6.85 (m, 4H), 6.70 (d, *J* = 7.6 Hz, 2H), 5.09 (s, 2H), 4.09 (m, 2H), 3.79 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 142.2, 128.7, 127.9, 127.3, 127.0, 123.2, 120.5, 114.1, 113.1, 55.2, 50.2, 32.6; MS (70 eV): m/z (%): 301.2 (5) $[M]^+$, 121.1 (100); HRMS m/z (ESI): Calcd. for $C_{21}H_{18}NO$ $[M-H]^+$ 300.1388, Found: 300.1393.

10-(4-(Tert-butyl)benzyl)-9,10-dihydroacridine (1f)



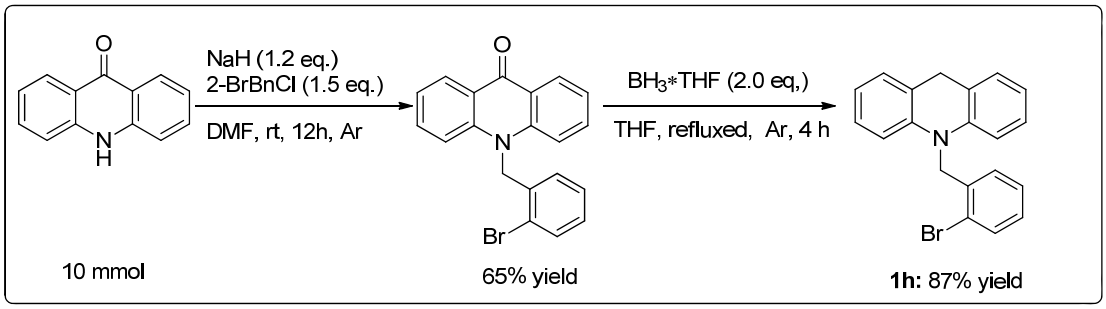
The reaction was carried out on 10.0 mmol and the product **1f** was obtained in 60% total yield in two steps as a white solid. IR:(KBr) ν_{max} 2962, 1595, 1480, 1370, 1265, 750 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.31 (d, J = 8.4 Hz, 2H), 7.13 (t, J = 8.4 Hz, 4H), 7.04 (t, J = 7.4 Hz, 2H), 6.87 (t, J = 7.2 Hz, 2H), 6.69 (d, J = 8.0 Hz, 2H), 5.09 (s, 2H), 4.08 (d, 2H), 1.30 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 149.6, 142.2, 133.8, 127.9, 127.0, 125.8, 125.6, 123.1, 120.5, 113.2, 50.6, 34.4, 32.6, 31.4; MS (70 eV): m/z (%): 327.2 (33) $[M]^+$, 147.2 (100); HRMS m/z (ESI): Calcd. for $C_{24}H_{24}N$ $[M-H]^+$ 326.1909, Found: 326.1907.

10-(4-Chlorobenzyl)-9,10-dihydroacridine (1g)



The reaction was carried out on 10.0 mmol and the product **1g** was obtained in 53% total yield in two steps as a white solid. IR:(KBr) ν_{max} 2911, 1594, 1477, 1371, 1266, 1232, 746 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.26 (d, J = 8.4 Hz, 2H), 7.14 (t, J = 8.6 Hz, 4H), 7.04 (t, J = 7.8 Hz, 2H), 6.89 (t, J = 7.4 Hz, 2H), 6.61 (d, J = 8.4 Hz, 2H), 5.08 (s, 2H), 4.07 (d, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 141.9, 135.5, 132.6, 128.9, 128.1, 127.7, 127.0, 123.3, 120.8, 112.9, 50.2, 32.5; MS (70 eV): m/z (%): 305.1 (10) $[M]^+$, 179.9 (100); HRMS m/z (ESI): Calcd. for $C_{20}H_{15}NCl$ $[M-H]^+$ 304.0893, Found: 304.0900.

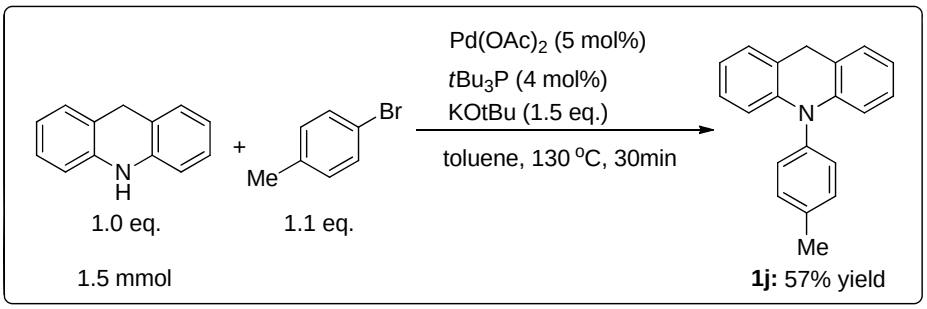
10-(2-Bromobenzyl)-9,10-dihydroacridine (1h)



The reaction was carried out on 10.0 mmol and the product **1h** was obtained in 57% total yield in two steps as a white solid. IR:(KBr) ν_{max} 2935, 1594, 1480, 1370, 1267, 1229, 747 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.65 (d, *J* = 7.2 Hz, 1H), 7.16-7.08 (m, 4H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.93-6.87 (m, 3H), 6.54 (d, *J* = 8.0 Hz, 2H), 5.06 (s, 2H), 4.10 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 141.6, 134.9, 133.0, 128.6, 128.3, 128.1, 127.5, 127.1, 132.1, 122.4, 120.8, 112.9, 52.0, 32.4; MS (70 eV): m/z (%): 349.0 (10) $[M]^+$, 179.9 (100); HRMS m/z (ESI): Calcd. for $C_{20}H_{15}NBr$ $[M-H]^+$ 348.0388, Found: 348.0384.

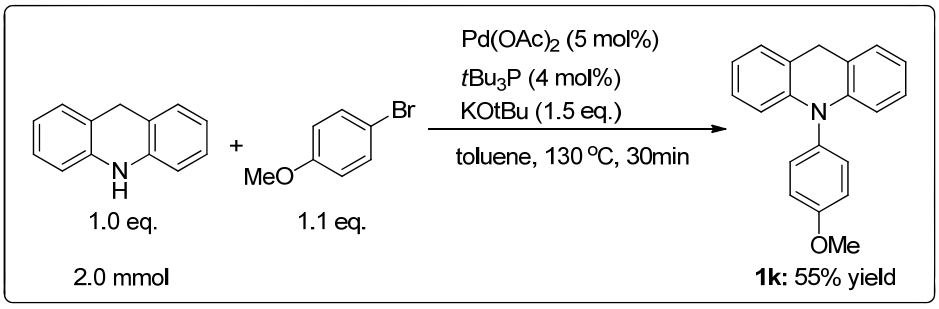
9,10-Dihydroacridine **1j-1l** were prepared according to the synthetic method of **1i**.

10-(*p*-Tolyl)-9,10-dihydroacridine (1j)



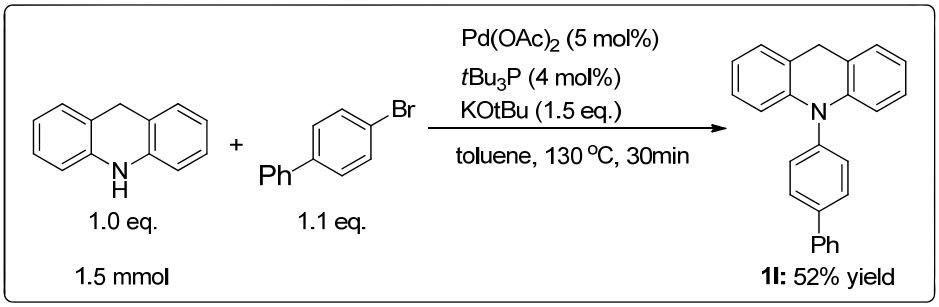
The reaction was carried out on 1.5 mmol and the product **1j** was obtained in 57% yield as a white solid. IR:(KBr) ν_{max} 2917, 1595, 1478, 1315, 1275, 749 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.39 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.12 (d, *J* = 7.2 Hz, 2H), 6.92 (t, *J* = 7.4 Hz, 2H), 6.83 (t, *J* = 7.2 Hz, 2H), 6.21 (d, *J* = 8.4 Hz, 2H), 4.21 (s, 2H), 2.46 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 142.8, 138.3, 138.0, 131.4, 130.9, 128.3, 126.6, 120.7, 120.4, 114.0, 31.9, 21.3; MS (70 eV): m/z (%): 271.3 $[M]^+$; HRMS m/z (ESI): Calcd. for $C_{20}H_{16}N$ $[M-H]^+$ 270.1283, Found: 270.1284.

10-(4-Methoxyphenyl)-9,10-dihydroacridine (1k)



The reaction was carried out on 2.0 mmol and the product **1k** was obtained in 55% yield as a white solid. IR:(KBr) ν_{max} 2931, 1593, 1510, 1479, 1315, 1246, 749 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.23 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 4H), 6.94 (t, *J* = 7.6 Hz, 2H), 6.84 (t, *J* = 7.2 Hz, 2H), 6.23 (d, *J* = 8.4 Hz, 2H), 4.21 (s, 2H), 3.90 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 159.1, 143.0, 133.6, 132.2, 128.3, 126.6, 120.8, 120.4, 115.9, 113.9, 55.5, 31.9; MS (70 eV): m/z (%): 287.3 $[M]^+$; HRMS m/z (ESI): Calcd. for $C_{20}H_{16}NO$ $[M-H]^+$ 286.1232, Found: 286.1231.

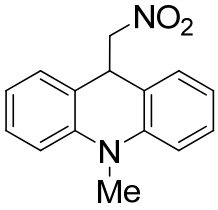
10-([1,1'-Biphenyl]-4-yl)-9,10-dihydroacridine (1l)



The reaction was carried out on 1.5 mmol and the product **1l** was obtained in 52% yield as a white solid. IR:(KBr) ν_{max} 2919, 1597, 1481, 1317, 1268, 751 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.83 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.42-7.38 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.97 (t, *J* = 7.6 Hz, 2H), 6.86 (t, *J* = 7.2 Hz, 2H), 6.29 (d, *J* = 8.0 Hz, 2H), 4.24 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 142.7, 141.0, 140.3, 140.2, 131.6, 129.5, 128.9, 128.4, 127.7, 127.2, 126.7, 120.8, 120.5, 114.0, 31.9; MS (70 eV): m/z (%): 333.3 $[M]^+$, 77.0 (100); HRMS m/z (ESI): Calcd. for $C_{25}H_{18}N$ $[M-H]^+$ 332.1439, Found: 332.1436.

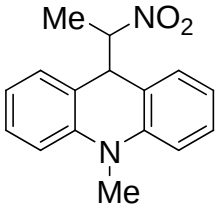
5. Experimental procedures and characterization of products

10-Methyl-9-(nitromethyl)-9,10-dihydroacridine (3aa)



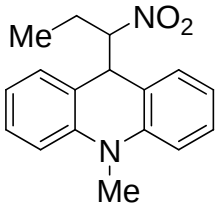
Typical procedure: 10-methyl-9,10-dihydroacridine **1a** (39.5 mg, 0.2 mmol) and TEMPO (3.2 mg, 0.02 mmol) were placed in a 25 mL Schlenk tube. Then CH_3NO_2 **2a** 0.5 mL was added. The reaction mixture was stirred at 60 ℃ under O_2 (1 atm) for 18 h as monitored by TLC. The solvent was removed and the residue was purified by silica gel column chromatography (PE/Et_2O = 10/1) to afford 46.9 mg (92 % yield) of **3aa**. **3aa**: white solid; IR:(KBr) ν_{max} 2913, 1594, 1538, 1472, 1334, 1265, 761 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.28 (t, *J* = 7.8 Hz, 2H), 7.21 (d, *J* = 6.8 Hz, 2H), 6.99-6.95 (m, 4H), 4.79 (t, *J* = 8.0 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 2H), 3.40 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 142.4, 128.5, 128.2, 121.33, 121.31, 112.6, 78.9, 43.1, 33.0; MS (70 eV): m/z (%): 254.2 (7) $[M]^+$, 194.1 (100); HRMS m/z (ESI): Calcd. for $C_{15}H_{15}N_2O_2$ $[M+H]^+$ 255.1128, Found: 255.1126.

10-Methyl-9-(1-nitroethyl)-9,10-dihydroacridine (3ab)



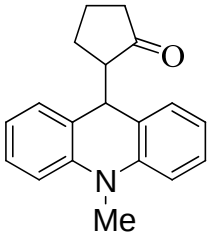
The reaction of 10-methyl-9,10-dihydroacridine **1a** (39.3 mg, 0.2 mmol), TEMPO (3.5 mg, 0.02 mmol) in nitroethane **2b** (0.5 mL) at 60 ℃ under dioxygen for 18 h afforded 51.9 mg (97 %) of **3ab**. **3ab**: white solid; IR:(KBr) ν_{max} 2909, 1595, 1547, 1474, 1337, 1270, 756 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.31-7.25 (m, 2H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.01-6.93 (m, 4H), 4.58-4.51 (m, 1H), 4.43 (d, *J* = 8.8 Hz, 1H), 3.40 (s, 3H), 1.33 (d, *J* = 6.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 142.9, 142.3, 129.4, 128.4, 128.3, 122.2, 121.3, 120.9, 120.6, 112.6, 112.4, 85.6, 48.9, 33.0, 16.6; MS (70 eV): m/z (%): 268.2 (5) $[M]^+$, 194.1 (100); HRMS m/z (ESI): Calcd. for $C_{16}H_{17}N_2O_2$ $[M+H]^+$ 269.1285, Found: 269.1286.

10-Methyl-9-(1-nitropropyl)-9,10-dihydroacridine (3ac)



The reaction of 10-methyl-9,10-dihydroacridine **1a** (39.5 mg, 0.2 mmol), TEMPO (3.2 mg, 0.02 mmol) in 1-nitropropane **2c** (0.5 mL) at 60 ℃ under dioxygen for 27 h afforded 54.9 mg (97 %) of **3ac**. **3ac**: white solid; IR:(KBr) ν_{max} 2975, 2931, 1594, 1550, 1474, 1370, 1339, 1269, 1132, 749 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.32-7.20 (m, 3H), 7.11 (d, *J* = 7.6 Hz, 1H), 7.02-6.93 (m, 4H), 4.40-4.35 (m, 2H), 3.41 (s, 3H), 2.02-1.92 (m, 1H), 1.59-1.50 (m, 1H), 0.77 (t, *J* = 7.4 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 142.9, 142.2, 129.5, 128.3, 128.2, 128.1, 122.2, 121.3, 121.1, 120.9, 112.6, 112.3, 92.0, 48.4, 33.0, 24.6, 10.2; MS (70 eV): m/z (%): 282.2 (4) $[M]^+$, 194.1 (100); HRMS m/z (ESI): Calcd. for $C_{17}H_{19}N_2O_2$ $[M+H]^+$ 283.1441, Found: 283.1441.

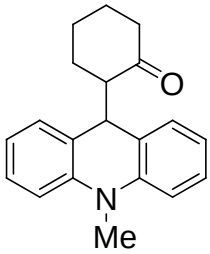
2-(10-Methyl-9,10-dihydroacridin-9-yl)cyclopentanone (3ad)



The reaction of 10-methyl-9,10-dihydroacridine **1a** (39.3 mg, 0.2 mmol), TEMPO (3.5 mg, 0.02 mmol) in cyclopentanone **2d** (0.5 mL) at 80 ℃ under dioxygen for 36 h afforded 44.7 mg (81 %) of **3ad**. **3ad**: white solid; IR:(KBr) ν_{max} 2965, 2888, 1734,

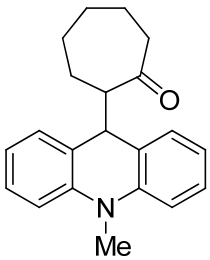
1593, 1478, 1346, 1269, 1146, 1130, 757 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.25-7.18 (m, 3H), 7.09 (d, *J* = 7.2 Hz, 1H), 7.95 (t, *J* = 7.4 Hz, 1H), 6.89-6.85 (m, 3H), 4.69 (d, *J* = 2.8 Hz, 1H), 3.37 (s, 3H), 2.31-2.16 (m, 2H), 1.83-1.63 (m, 3H), 1.55-1.35 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 219.1, 143.5, 142.7, 129.1, 128.0, 127.3, 127.0, 126.3, 123.5, 120.8, 120.6, 111.9, 111.8, 59.4, 41.8, 38.7, 32.9, 24.5, 20.3; MS (70 eV): m/z (%): 277.1 (3) $[M]^+$, 194.2 (100); HRMS m/z (ESI): Calcd. for $C_{19}H_{19}NNaO$ $[M+Na]^+$ 300.1359, Found: 300.1360.

2-(10-Methyl-9,10-dihydroacridin-9-yl)cyclohexanone (3ae)



The reaction of 10-methyl-9,10-dihydroacridine **1a** (39.5 mg, 0.2 mmol), TEMPO (3.2 mg, 0.02 mmol) in cyclohexanone **2e** (0.5 mL) at 80 ℃ under dioxygen for 36 h afforded 51.5 mg (88 %) of **3ae**. **3ae**: white solid; IR:(KBr) ν_{max} 2921, 1707, 1593, 1475, 1339, 1269, 1129, 757 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.24-7.17 (m, 3H), 6.95-6.89 (m, 4H), 4.66 (d, *J* = 6.8 Hz, 1H), 3.36 (s, 3H), 2.55-2.50 (m, 1H), 2.40-2.31 (m, 1H), 2.30-2.15 (m, 1H), 1.91-1.88 (m, 1H), 1.73-1.69 (m, 1H), 1.64-1.55 (m, 2H), 1.49-1.38 (m, 1H), 1.29-1.19 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 212.0, 143.5, 142.9, 129.7, 129.0, 127.3, 127.0, 126.8, 124.7, 120.6, 120.3, 112.0, 111.9, 56.6, 42.5, 41.5, 32.9, 30.4, 27.9, 24.6; MS (70 eV): m/z (%): 291.2 (3) $[M]^+$, 194.3 (100); HRMS m/z (ESI): Calcd. for $C_{20}H_{21}NNaO$ $[M+Na]^+$ 314.1515, Found: 314.1516.

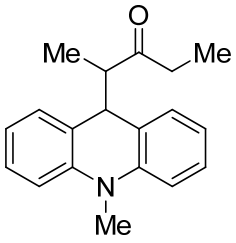
2-(10-Methyl-9,10-dihydroacridin-9-yl)cycloheptanone (3af)



The reaction of 10-methyl-9,10-dihydroacridine **1a** (39.3 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in cycloheptanone **2f** (0.5 mL) at 80 ℃ under dioxygen for 36 h afforded 22.6 mg (37 %) of **3af**. **3af**: white solid; IR:(KBr) ν_{max} 2923, 1699, 1593, 1476, 1339, 1268, 749 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.22-7.16 (m, 3H), 7.07 (d, *J* = 6.8 Hz, 1H), 6.93-6.89 (m, 4H), 4.39 (d, *J* = 6.8 Hz, 1H), 3.37 (s, 3H), 2.65-2.59 (m, 1H), 2.13-2.10 (m, 2H), 1.73-1.71 (m, 3H), 1.60-1.56 (m, 1H), 1.33-1.11 (m, 3H), 1.03-0.97 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 215.8, 143.3, 142.9, 129.1, 128.8, 127.3, 127.1, 125.6, 123.9, 120.7, 120.4, 112.2, 112.0,

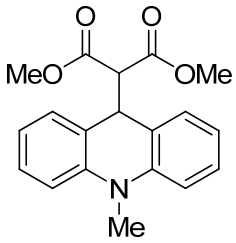
59.5, 46.2, 43.7, 32.9, 29.2, 28.0, 26.8, 24.9; MS (70 eV): m/z (%): 305.3 (3) $[M]^+$, 194.0 (100); HRMS m/z (ESI): Calcd. for $C_{21}H_{23}NNaO$ $[M+Na]^+$ 328.1672, Found: 328.1673.

2-(10-Methyl-9,10-dihydroacridin-9-yl)pentan-3-one (3ag)



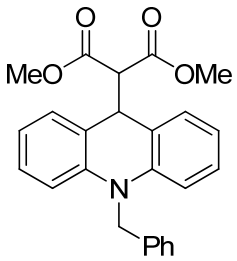
The reaction of 10-methyl-9,10-dihydroacridine **1a** (39.7 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in pentan-3-one **2g** (0.5 mL) at 80 ℃ under dioxygen for 36 h afforded 11.7 mg (21 %) of **3ag**. **3ag**: white solid; IR:(KBr) ν_{max} 2929, 1712, 1595, 1476, 1340, 1273, 1129, 759 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.26-7.16 (m, 3H), 7.03-6.87 (m, 5H), 4.02 (d, *J* = 10.0 Hz, 1H), 3.42 (s, 3H), 2.86-2.78 (m, 1H), 2.12-2.02 (m, 1H), 1.60-1.52 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 3H), 0.73 (t, *J* = 7.2 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 215.4, 142.7, 142.6, 129.4, 128.5, 127.2, 127.1, 125.7, 124.9, 120.7, 120.4, 112.1, 112.0, 48.5, 47.4, 37.7, 32.9, 15.1, 7.1; MS (70 eV): m/z (%): 279.2 (2) $[M]^+$, 194.0 (100); HRMS m/z (ESI): Calcd. for $C_{19}H_{22}NO$ $[M+H]^+$ 280.1696, Found: 280.1698.

Dimethyl 2-(10-methyl-9,10-dihydroacridin-9-yl)malonate (3ah)



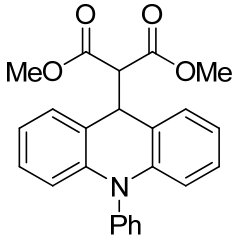
The reaction of 10-methyl-9,10-dihydroacridine **1a** (39.5 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in dimethyl malonate **2h** (0.5 mL) at 80 ℃ under dioxygen for 36 h afforded 58.8 mg (90 %) of **3ah**. **3ah**: white solid; IR:(KBr) ν_{max} 2956, 1758, 1594, 1475, 1341, 1260, 1134, 924, 763, 556 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.27-7.22 (m, 4H), 6.96-6.91 (m, 4H), 4.77 (d, *J* = 10.6 Hz, 1H), 3.63 (d, *J* = 10.6 Hz, 1H), 3.50 (s, 6H), 3.42 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 142.8, 128.5, 127.7, 123.2, 120.7, 112.2, 55.6, 52.2, 44.1, 33.0; MS (70 eV): m/z (%): 325.2 (5) $[M]^+$, 194.3 (100); HRMS m/z (ESI): Calcd. for $C_{19}H_{20}NO_4$ $[M+H]^+$ 326.1387, Found: 326.1391.

Dimethyl 2-(10-benzyl-9,10-dihydroacridin-9-yl)malonate (3dh)



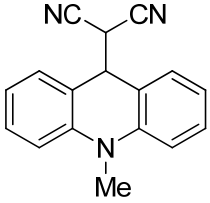
The reaction of 10-benzyl-9,10-dihydroacridine **1d** (54.5 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in dimethyl malonate **2h** (0.5 mL) at 80 ℃ under dioxygen for 24 h afforded 68.5 mg (85 %) of **3dh**. **3dh**: white solid; IR:(KBr) ν_{max} 2951, 2924, 1731, 1594, 1475, 1371, 1242, 1160, 1027, 758 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.31-7.24 (m, 5H), 7.15 (d, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.91 (t, *J* = 7.4 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 5.25 (s, 2H), 4.85 (d, *J* = 10.5 Hz, 1H), 3.63 (d, *J* = 10.5 Hz, 1H), 3.51 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 141.4, 136.4, 128.7, 128.6, 127.8, 126.9, 126.3, 122.8, 120.8, 113.6, 57.3, 52.3, 50.4, 43.9; MS (70 eV): m/z (%): 401.1 (9) $[M]^+$, 270.1 (100); HRMS m/z (ESI): Calcd. for $C_{25}H_{23}NNaO_4$ $[M+Na]^+$ 424.1519, Found: 424.1518.

Dimethyl 2-(10-phenyl-9,10-dihydroacridin-9-yl)malonate (3ih)



The reaction of 10-phenyl-9,10-dihydroacridine **1i** (51.9 mg, 0.2 mmol), TEMPO (3.2 mg, 0.02 mmol) in dimethyl malonate **2h** (0.5 mL) at 80 ℃ under dioxygen for 24 h afforded 59.6 mg (77 %) of **3ih**. **3ih**: white solid; IR:(KBr) ν_{max} 2950, 1755, 1734, 1593, 1475, 1315, 1277, 1256, 1147, 756 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.63 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.03 (t, *J* = 7.6 Hz, 2H), 6.90 (t, *J* = 7.2 Hz, 2H), 6.39 (d, *J* = 8.0 Hz, 2H), 4.92 (d, *J* = 10.0 Hz, 1H), 3.73 (d, *J* = 10.0 Hz, 1H), 3.51 (s, 6H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 167.8, 142.3, 140.3, 131.1, 130.6, 128.6, 127.4, 127.5, 121.1, 120.9, 114.2, 58.1, 52.4, 43.6; MS (70 eV): m/z (%): 387.1 (3) $[M]^+$, 256.1 (100); HRMS m/z (ESI): Calcd. for $C_{24}H_{21}NNaO_4$ $[M+Na]^+$ 410.1363, Found: 410.1363.

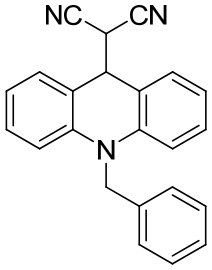
2-(10-Methyl-9,10-dihydroacridin-9-yl)malononitrile (3ai)



The reaction of 10-methyl-9,10-dihydroacridine **1a** (39.7 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) and malononitrile **2i** (70.0 mg, 1.0 mmol) in DCE (0.3 mL) at

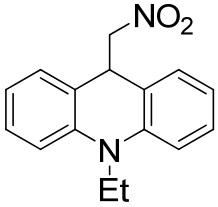
80 ℃ under dioxygen for 16 h afforded 39.5 mg (76 %) of **3ai**. **3ai**: yellowish solid; IR:(KBr) ν_{max} 2890, 2252, 1595, 1475, 1337, 1273, 1129, 891, 758 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.41-7.36 (m, 4H), 7.10-7.02 (m, 4H), 4.57 (d, *J* = 8.4 Hz, 1H), 3.70 (d, *J* = 8.4 Hz, 1H), 3.44 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 142.2, 129.5, 129.3, 121.6, 119.1, 113.0, 111.9, 46.1, 33.2, 28.6; MS (70 eV): m/z (%): 259.3 (3) $[M]^+$, 194.3 (100); HRMS m/z (ESI): Calcd. for $C_{17}H_{12}N_3$ $[M-H]^-$ 258.1037, Found: 258.1030.

2-(10-Benzyl-9,10-dihydroacridin-9-yl)malononitrile (3di)



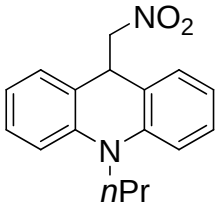
The reaction of 10-benzyl-9,10-dihydroacridine **1d** (54.5 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) and malononitrile **2i** (66.8 mg, 1.0 mmol) in DCE (0.3 mL) at 80 ℃ under dioxygen for 16 h afforded 65.9 mg (98 %) of **3ai**. **3ai**: yellowish solid; IR:(KBr) ν_{max} 2892, 2251, 1596, 1482, 1454, 1376, 1268, 1221, 753 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.35-7.23 (m, 5H), 7.14 (d, *J* = 7.2 Hz, 2H), 7.07 (t, *J* = 7.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.19 (s, 2H), 4.71 (d, *J* = 6.4 Hz, 1H), 3.73 (d, *J* = 6.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 141.3, 136.1, 129.8, 129.2, 128.9, 127.2, 125.9, 121.7, 118.3, 114.3, 111.8, 51.5, 45.7, 31.3; MS (70 eV): m/z (%): 91.1 (100); HRMS m/z (ESI): Calcd. for $C_{23}H_{16}N_3$ $[M-H]^-$ 334.1350, Found: 334.1341.

10-Ethyl-9-(nitromethyl)-9,10-dihydroacridine (3ba)



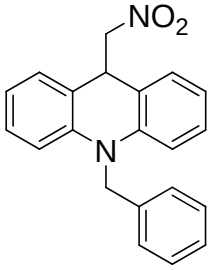
The reaction of 10-ethyl-9,10-dihydroacridine **1b** (42.1 mg, 0.2 mmol), TEMPO (3.5 mg, 0.02 mmol) in CH_3NO_2 **2a** (0.5 mL) at 60 ℃ under dioxygen for 18 h afforded 47.2 mg (88 %) of **3ba**. **3ba**: white solid; IR:(KBr) ν_{max} 2982, 2914, 1594, 1542, 1477, 1372, 1258, 753 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.27 (t, *J* = 7.9 Hz, 2H), 7.19 (d, *J* = 7.3 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.94 (t, *J* = 7.3 Hz, 2H), 4.78 (t, *J* = 7.7 Hz, 1H), 4.28 (d, *J* = 7.7 Hz, 2H), 4.03 (q, *J* = 7.0 Hz, 2H), 1.39 (t, *J* = 7.0 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 140.6, 128.6, 128.5, 121.1, 120.8, 112.8, 80.0, 42.9, 40.0, 11.3; MS (70 eV): m/z (%): 268.2 (7) $[M]^+$, 208.2 (100); HRMS m/z (ESI): Calcd. for $C_{16}H_{17}N_2O_2$ $[M+H]^+$ 269.1284, Found: 269.1284.

9-(Nitromethyl)-10-propyl-9,10-dihydroacridine (3ca)



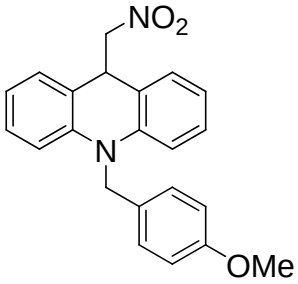
The reaction of 10-propyl-9,10-dihydroacridine **1c** (45.0 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH_3NO_2 (0.5 mL) at 60 ℃ under dioxygen for 18 h afforded 45.6 mg (81 %) of **3ca**. **3ca**: white solid; IR:(KBr) ν_{max} 2957, 2891, 1594, 1541, 1477, 1376, 1277, 745 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.27 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.2 Hz, 2H), 6.96 (m, 4H), 4.79 (t, *J* = 7.7 Hz, 1H), 4.30 (d, *J* = 7.7 Hz, 2H), 3.87 (t, *J* = 7.6 Hz, 2H), 1.90-1.80 (m, 2H), 1.06 (t, *J* = 7.6 Hz, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 140.9, 128.5, 128.4, 121.0, 120.8, 113.0, 79.9, 47.2, 42.9, 18.8, 11.2; MS (70 eV): m/z (%): 282.2 (10) $[M]^+$, 222.2 (100); HRMS m/z (ESI): Calcd. for $C_{17}H_{19}N_2O_2$ $[M+H]^+$ 283.1441, Found: 283.1442.

10-Benzyl-9-(nitromethyl)-9,10-dihydroacridine (3da)



The reaction of 10-benzyl-9,10-dihydroacridine **1d** (54.7 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH_3NO_2 **2a** (0.5 mL) at 60 ℃ under dioxygen for 18 h afforded 48.5 mg (73 %) of **3da**. **3da**: yellowish solid; IR:(KBr) ν_{max} 2918, 1594, 1553, 1478, 1374, 1266, 749 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.32-7.22 (m, 5H), 7.16-7.12 (m, 4H), 6.95 (t, *J* = 7.2 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 5.21 (s, 2H), 4.89 (t, *J* = 7.6 Hz, 1H), 4.39 (d, *J* = 7.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 141.0, 136.1, 128.8, 128.5, 128.3, 127.0, 126.1, 121.4, 120.7, 113.8, 80.4, 50.4, 42.7; MS (70 eV): m/z (%): 330.2 (6) $[M]^+$, 91.1 (100); HRMS m/z (ESI): Calcd. for $C_{21}H_{19}N_2O_2$ $[M+H]^+$ 331.1441, Found: 331.1439.

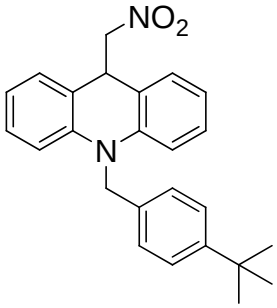
10-(4-Methoxybenzyl)-9-(nitromethyl)-9,10-dihydroacridine (3ea)



The reaction of 10-(4-methoxybenzyl)-9,10-dihydroacridine **1e** (60.5 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH_3NO_2 **2a** (0.5 mL) at 60 ℃ under dioxygen for 18 h afforded 53.1 mg (74 %) of **3ea**. **3ea**: yellowish solid; IR:(KBr) ν_{max} 2918, 2891,

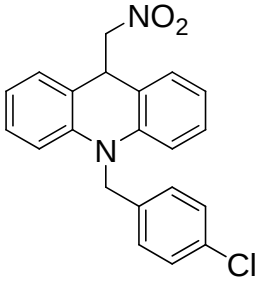
1595, 1544, 1511, 1481, 1376, 1251, 750 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.2 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 2H), 6.82 (t, *J* = 8.0 Hz, 4H), 5.15 (s, 2H), 4.88 (t, *J* = 7.7 Hz, 1H), 4.38 (d, *J* = 7.7 Hz, 2H), 3.76 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 158.6, 141.1, 128.6, 128.3, 127.7, 127.2, 121.4, 120.7, 114.2, 113.8, 80.4, 55.2, 49.8, 42.7; MS (70 eV): m/z (%): 360.2 (3) $[M]^+$, 121.1 (100); HRMS m/z (ESI): Calcd. for $C_{22}H_{20}N_2NaO_3$ $[M+Na]^+$ 383.1369, Found: 383.1366.

10-(4-*Tert*-butylbenzyl)-9-(nitromethyl)-9,10-dihydroacridine (3fa)



The reaction of 10-(4-*tert*-butylbenzyl)-9,10-dihydroacridine **1f** (65.8 mg, 0.2 mmol), TEMPO (3.2 mg, 0.02 mmol) in CH_3NO_2 **2a** (0.5 mL) at 60 ℃ under dioxygen for 18 h afforded 63.3 mg (82 %) of **3fa**. **3fa**: yellowish solid; IR:(KBr) ν_{max} 2961, 1595, 1551, 1478, 1374, 1268, 754 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.14 (t, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.17 (s, 2H), 4.89 (t, *J* = 7.7 Hz, 1H), 4.38 (d, *J* = 7.7 Hz, 2H), 1.29 (s, 9H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 149.9, 141.1, 132.9, 128.6, 128.3, 125.7, 125.6, 121.4, 120.7, 113.9, 80.5, 50.2, 42.7, 34.4, 31.3; MS (70 eV): m/z (%): 386.2 (1) $[M]^+$, 117.0 (100); HRMS m/z (ESI): Calcd. for $C_{25}H_{26}N_2NaO_2$ $[M+Na]^+$ 409.1891, Found: 409.1891.

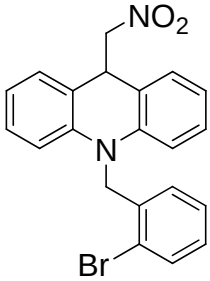
10-(4-Chlorobenzyl)-9-(nitromethyl)-9,10-dihydroacridine (3ga)



The reaction of 10-(4-chlorobenzyl)-9,10-dihydroacridine **1g** (61.5 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH_3NO_2 **2a** (0.5 mL) at 60 ℃ under dioxygen for 18 h afforded 64.5 mg (88 %) of **3ga**. **3ga**: yellowish solid; IR:(KBr) ν_{max} 2917, 1595, 1553, 1478, 1375, 1270, 755 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.25 (m, 4H), 7.16 (t, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 2H), 6.74 (d, *J* = 8.0 Hz, 2H), 5.17 (s, 2H), 4.89 (t, *J* = 7.6 Hz, 1H), 4.39 (d, *J* = 7.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 140.8, 134.5, 132.8, 129.0, 128.6, 128.4, 127.5, 121.7, 120.8, 113.6, 80.4, 49.8, 42.6; MS (70 eV): m/z (%): 364.2 (1) $[M]^+$, 125.0 (100);

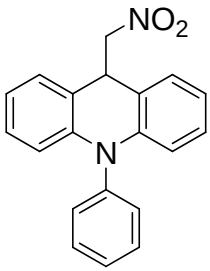
HRMS m/z (ESI): Calcd. for $C_{21}H_{18}ClN_2O_2$ $[M+H]^+$ 365.1051, Found: 365.1054.

10-(2-Bromobenzyl)-9-(nitromethyl)-9,10-dihydroacridine (3ha)



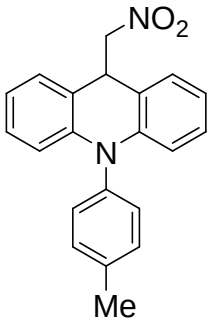
The reaction of 10-(2-bromobenzyl)-9,10-dihydroacridine **1h** (70.4 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in CH_3NO_2 **2a** (0.5 mL) at 60 ℃ under dioxygen for 18 h afforded 74.6 mg (91 %) of **3ha**. **3ha**: yellowish solid; IR:(KBr) ν_{max} 2961, 1594, 1548, 1477, 1372, 1266, 1027, 758, 742 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.68 (d, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 6.8 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 3H), 7.09 (t, *J* = 7.2 Hz, 1H), 6.98 (t, *J* = 7.4 Hz, 2H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.67 (d, *J* = 8.9 Hz, 2H), 5.16 (s, 2H), 4.92 (t, *J* = 7.7 Hz, 1H), 4.41 (d, *J* = 7.7 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 140.6, 134.1, 133.2, 128.8, 128.7, 128.4, 128.1, 127.4, 122.3, 121.7, 120.7, 113.6, 80.6, 51.7, 42.6; MS (70 eV): m/z (%): 410.1 (1) $[M]^+$, 169.1 (100); HRMS m/z (ESI): Calcd. for $C_{21}H_{18}BrN_2O_2$ $[M+H]^+$ 409.0546, Found: 409.0551.

9-(Nitromethyl)-10-phenyl-9,10-dihydroacridine (3ia)



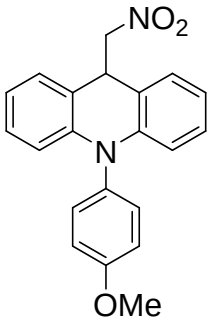
The reaction of 10-phenyl-9,10-dihydroacridine **1i** (51.8 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH_3NO_2 **2a** (0.5 mL) at 60 ℃ under dioxygen for 18 h afforded 53.7 mg (85 %) of **3ia**. **3ia**: yellowish solid; IR:(KBr) ν_{max} 2912, 1594, 1548, 1474, 1375, 1312, 1270, 746, 702 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.63 (t, *J* = 7.6 Hz, 2H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 7.2 Hz, 2H), 6.93 (t, *J* = 7.4 Hz, 2H), 6.36 (d, *J* = 8.0 Hz, 2H), 4.97 (t, *J* = 7.5 Hz, 1H), 4.48 (d, *J* = 7.5 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 141.9, 140.1, 130.9, 130.8, 128.6, 128.3, 128.2, 121.4, 118.8, 114.5, 81.2, 42.3; MS (70 eV): m/z (%): 316.2 (1) $[M]^+$, 77.0 (100); HRMS m/z (ESI): Calcd. for $C_{20}H_{17}N_2O_2$ $[M+H]^+$ 317.1285, Found: 317.1289.

9-(Nitromethyl)-10-*p*-tolyl-9,10-dihydroacridine (3ja)



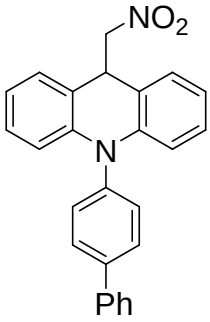
The reaction of 10-*p*-tolyl-9,10-dihydroacridine **1j** (54.7 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in CH_3NO_2 **2a** (0.5 mL) at 60 ℃ under dioxygen for 18 h afforded 57.1 mg (86 %) of **3ja**. **3ja**: yellowish solid; IR:(KBr) ν_{max} 3026, 2923, 1594, 1548, 1511, 1475, 1374, 1314, 1270, 747 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.24-7.18 (m, 4H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 2H), 6.38 (d, *J* = 8.0 Hz, 2H), 4.96 (t, *J* = 7.3 Hz, 1H), 4.47 (d, *J* = 7.3 Hz, 2H), 2.48 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 142.1, 138.5, 137.3, 131.5, 130.5, 128.3, 128.2, 121.4, 118.8, 114.6, 81.2, 42.3, 21.3; MS (70 eV): m/z (%): 330.2 (7) $[M]^+$, 270.2 (100); HRMS m/z (ESI): Calcd. for $C_{21}H_{19}N_2O_2$ $[M+H]^+$ 331.1441, Found: 331.1442.

10-(4-Methoxyphenyl)-9-(nitromethyl)-9,10-dihydroacridine (3ka)



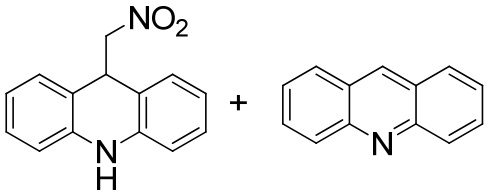
The reaction of 10-(4-methoxyphenyl)-9,10-dihydroacridine **1k** (57.6 mg, 0.2 mmol), TEMPO (3.3 mg, 0.02 mmol) in CH_3NO_2 **2a** (1.0 mL) at 60 ℃ under dioxygen for 18h afforded 62.2 mg (90 %) of **3ka**. **3ka**: yellowish solid; IR:(KBr) ν_{max} 3035, 2913, 1592, 1544, 1513, 1473, 1315, 1249, 1035, 758 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.23 (d, *J* = 8.0 Hz, 4H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.07 (t, *J* = 7.6 Hz, 2H), 6.93 (t, *J* = 7.2 Hz, 2H), 6.40 (d, *J* = 8.0 Hz, 2H), 4.96 (t, *J* = 7.5 Hz, 1H), 4.47 (d, *J* = 7.5 Hz, 2H), 3.91 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 159.4, 142.3, 132.5, 131.8, 128.3, 128.2, 121.4, 118.8, 116.0, 114.5, 81.2, 55.5, 42.3; MS (70 eV): m/z (%): 346.2 (3) $[M]^+$, 62.9 (100); HRMS m/z (ESI): Calcd. for $C_{21}H_{19}N_2O_2$ $[M+H]^+$ 347.1390, Found: 347.1395.

10-(Biphenyl-4-yl)-9-(nitromethyl)-9,10-dihydroacridine (3la)



The reaction of 10-(biphenyl-4-yl)-9,10-dihydroacridine **1l** (67.0 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in CH_3NO_2 **2a** (0.5 mL) at 60 ℃ under dioxygen for 18h afforded 53.3 mg (68 %) of **3la**. **3la**: yellowish solid; IR:(KBr) ν_{max} 3031, 2952, 1593, 1543, 1478, 1375, 1315, 1268, 753, 745 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 7.85 (d, *J* = 7.6 Hz, 2H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 2H), 7.43-7.38 (m, 3H), 7.26 (d, *J* = 7.2 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 2H), 6.46 (d, *J* = 8.4 Hz, 2H), 4.99 (t, *J* = 7.4 Hz, 1H), 4.50 (d, *J* = 7.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 141.9, 141.5, 140.0, 139.2, 131.2, 129.5, 129.0, 128.4, 128.3, 127.8, 127.2, 121.5, 118.9, 114.6, 81.2, 42.3; MS (70 eV): m/z (%): 392.2 (7) $[M]^+$, 77.0 (100); HRMS m/z (ESI): Calcd. for $C_{26}H_{21}N_2O_2$ $[M+H]^+$ 393.1598, Found: 393.1605.

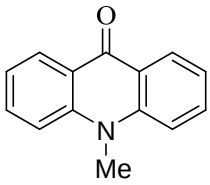
9-(Nitromethyl)-9,10-dihydroacridine (3ma) and acridine (4)



3ma **4**

The reaction of 9,10-dihydroacridine **1m** (36.5 mg, 0.2 mmol), TEMPO (3.4 mg, 0.02 mmol) in CH_3NO_2 **2a** (0.5 mL) at 60 ℃ under dioxygen for 18h afforded 41.0 mg (43 % **3ma** and 57 % **4**) of **3ma** and **4** (**3ma**:**4** = 1:1); ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) **3ma** δ 7.19-7.15 (m, 4H), 6.92 (t, *J* = 7.4 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.55 (s, 1H), 4.87 (t, *J* = 7.6 Hz, 1H), 4.36 (d, *J* = 7.6 Hz, 2H), **4** δ 8.75 (s, 1H), 8.24 (d, *J* = 8.6 Hz, 2H), 7.98 (d, *J* = 8.6 Hz, 2H), 7.77 (t, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.2 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) **3ma** δ 139.6, 128.4, 121.4, 117.8, 113.9, 80.2, 41.9, **4** δ: 149.0, 136.0, 130.2, 129.2, 128.1, 126.5, 125.6; MS (70 eV): m/z (%):**3ma**: 240.2 $[M]^+$; **4:** 179.2 $[M]^+$.

10-methylacridin-9(10H)-one (5)



The reaction of 10-methyl-9,10-dihydroacridine **1a** (39.5 mg, 0.2 mmol), TEMPO

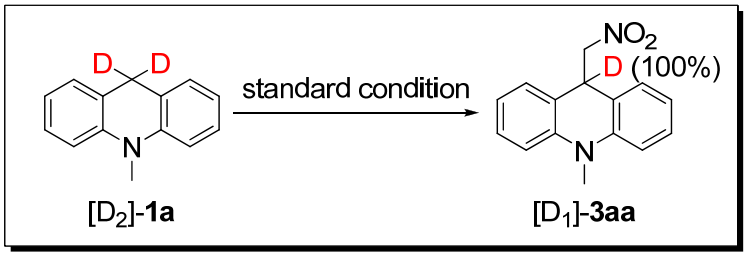
(3.5 mg, 0.02 mmol) in CH_3CN (0.5 mL) at 80 ℃ under dioxygen for 40 h afforded 42.2 mg (100 %) of **5**. **5**: white solid; IR:(KBr) ν_{max} 2925, 1757, 1631, 1595, 1490, 1490, 1368, 1290, 1268, 1180, 755 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$, ppm) δ 8.55 (d, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.27 (t, *J* = 7.4 Hz, 2H), 3.86 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$, ppm) δ 178.1, 142.5, 133.7, 127.7, 122.5, 121.2, 114.7, 33.5; MS (70 eV): m/z (%): 209.2 $[M]^+$. HRMS m/z (ESI): Calcd. for $C_{14}H_{12}NO$ $[M+H]^+$ 210.0913, Found: 210.0910.

Reference:

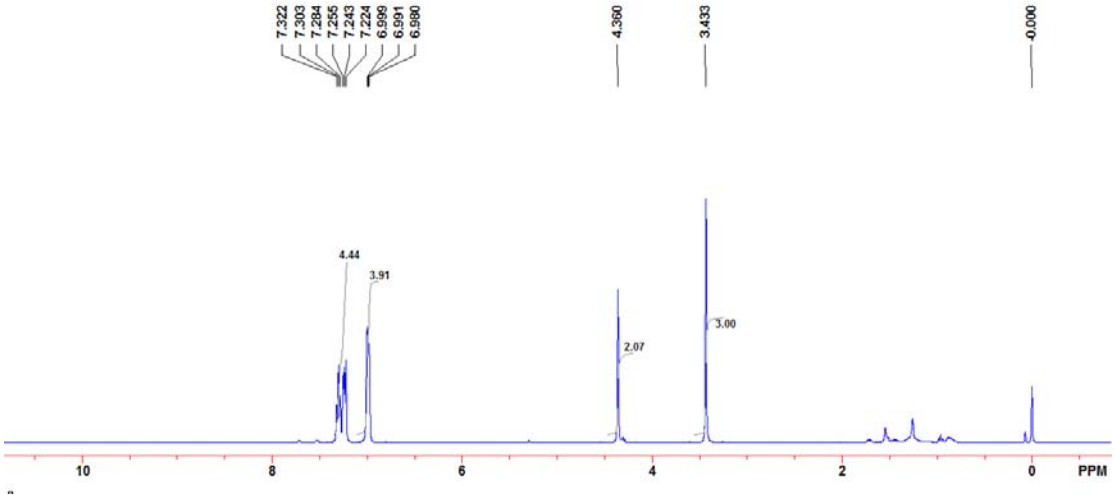
(1) (a) K. G. Konya, T. Paul, S. Lin, J. Lusztyk, K. U. Ingold, *J. Am. Chem. Soc.* 2000, **122**, 7518.; (b) F. Recupero, C. Punta, *Chem. Rev*. **2007**, *107*, 3800.
(2) We thanks the referee's kind suggestion: R. A. Rossi, A. B. Pierini, A. B. Peñéñory *Chem. Rev*. 2003, **103**, 71.
(3) Pintér, Á.; Sud, A.; Sureshkumar, D.; Klussmann, M. *Angew. Chem. Int. Ed.* 2010, **49**, 5004.
(4) Charblt, J. J.; Galy, A. M.; Galy, J. P,; Barbe, J. *J. Chem. Eng. Data* 1989, **34**, 136.

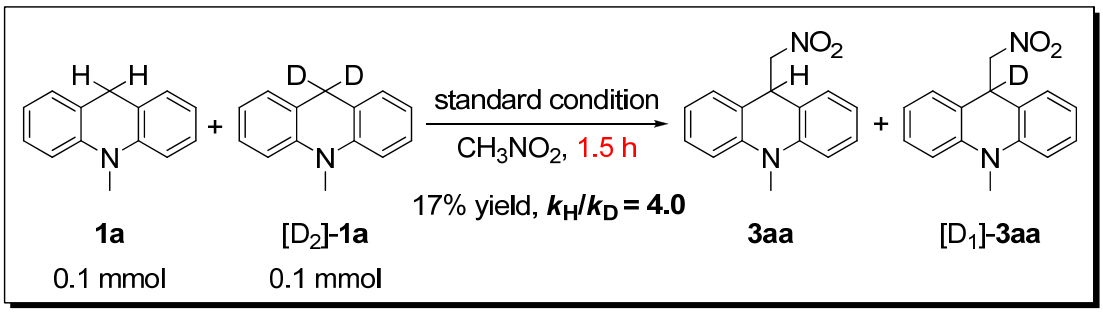
6. Mechanistic Studies

6.1 intermolecular Kinetic Isotopic Effect (KIE) Studies

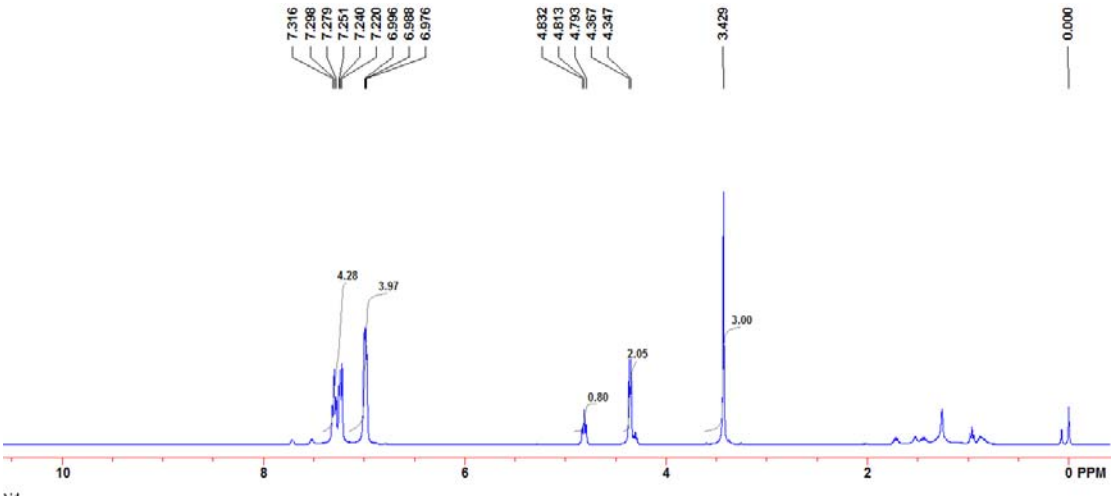


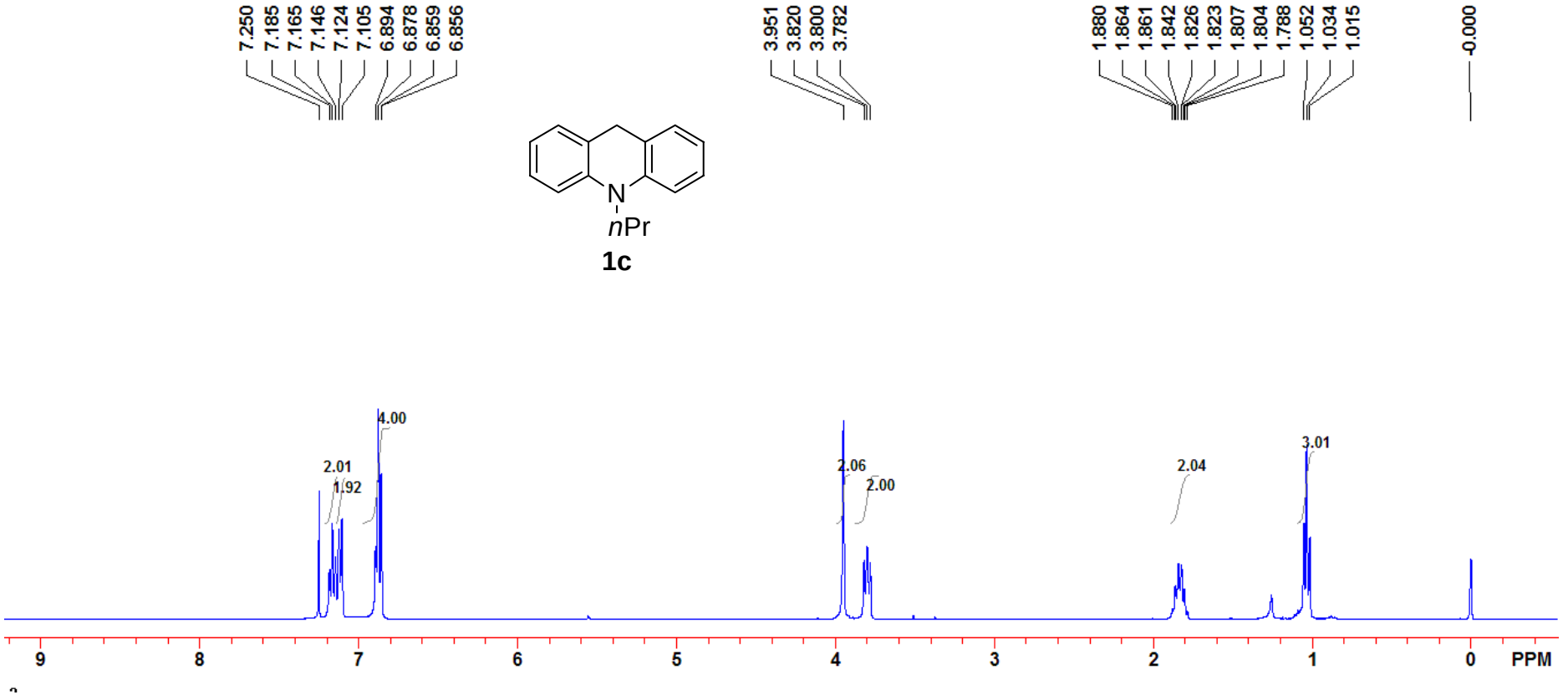
[D2]-**1a** [D1]-**3aa**





1a 0.1 mmol [D2]-**1a** 0.1 mmol **3aa** [D1]-**3aa**





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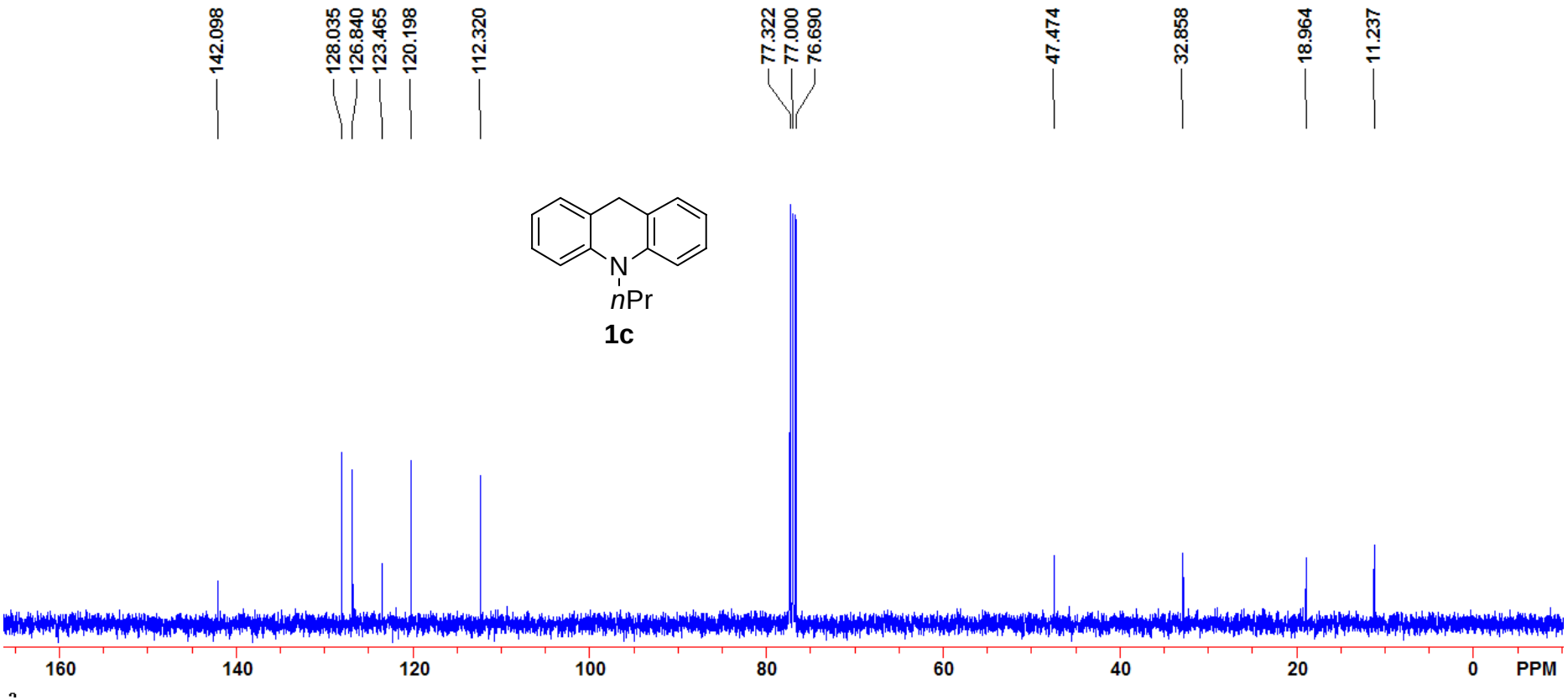

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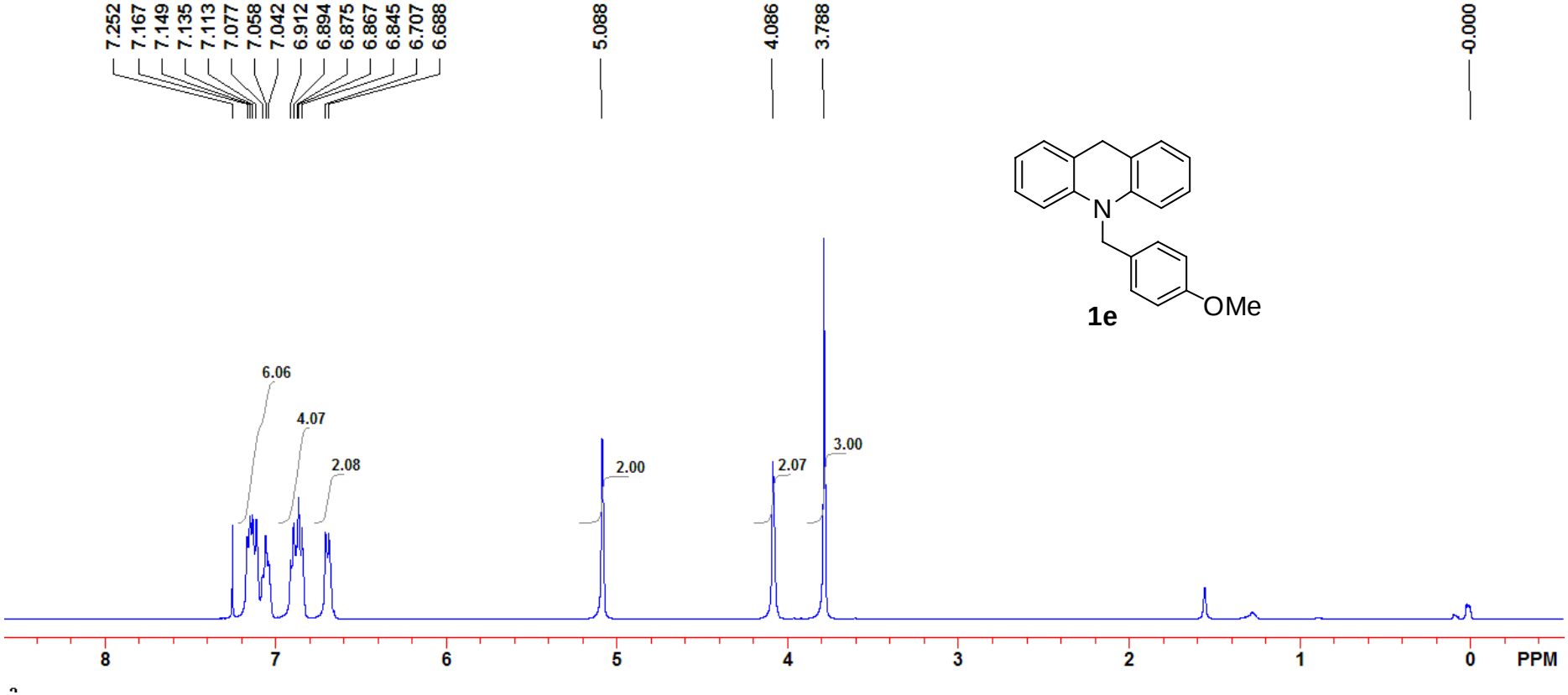

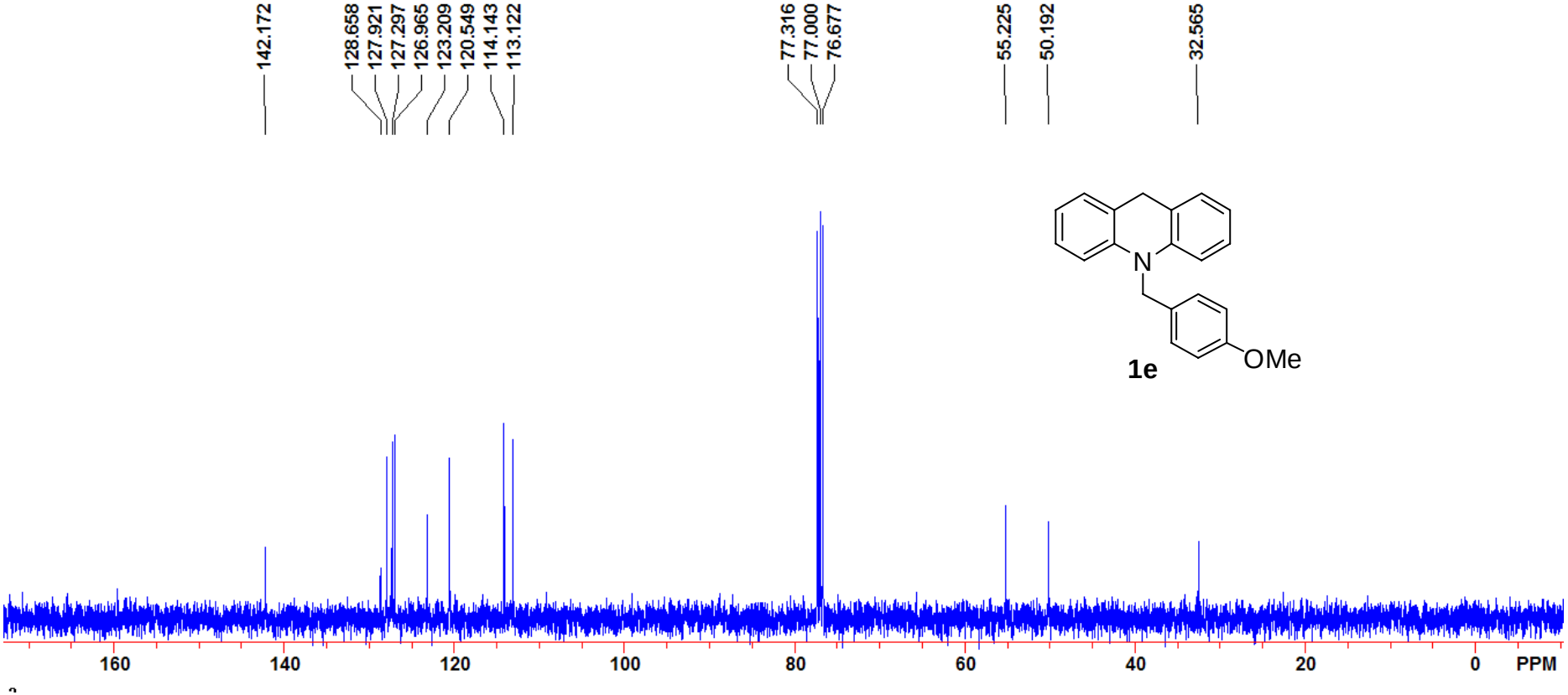

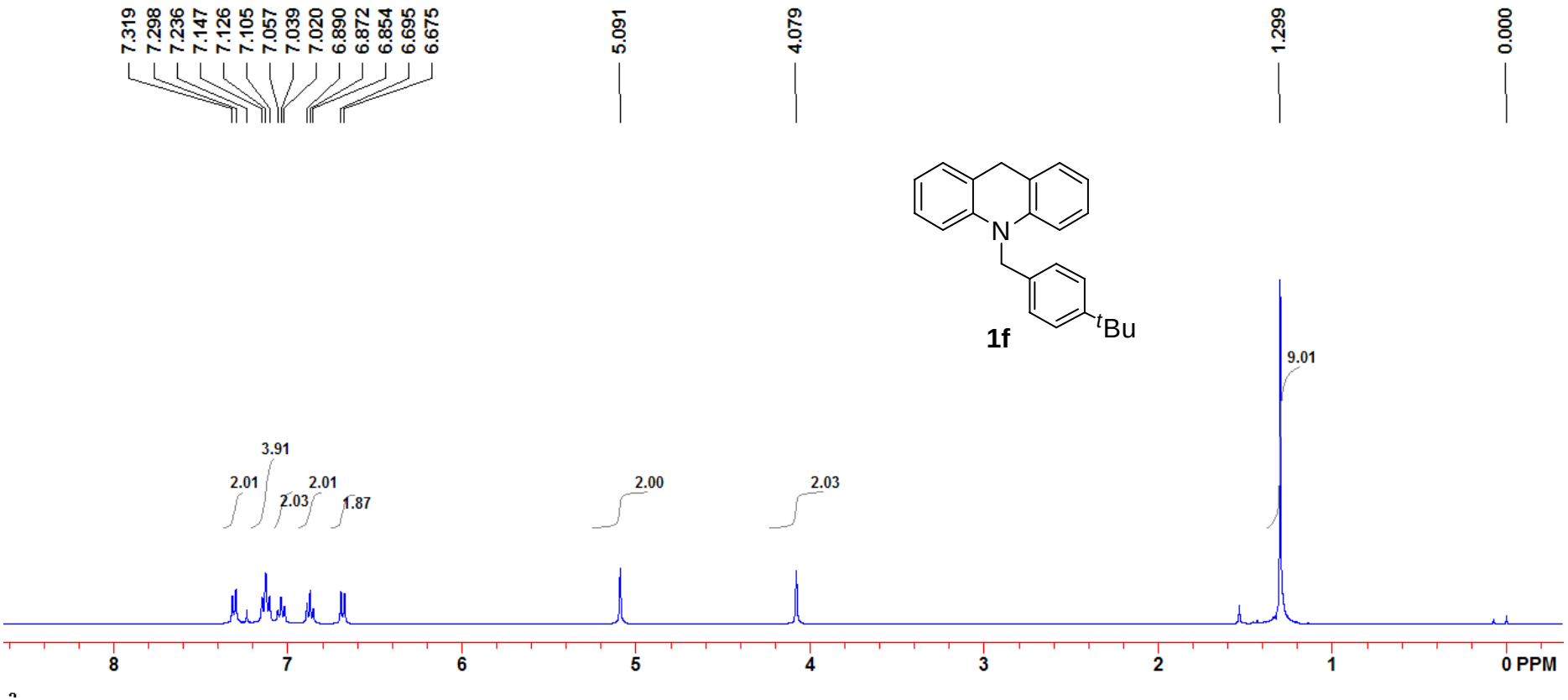

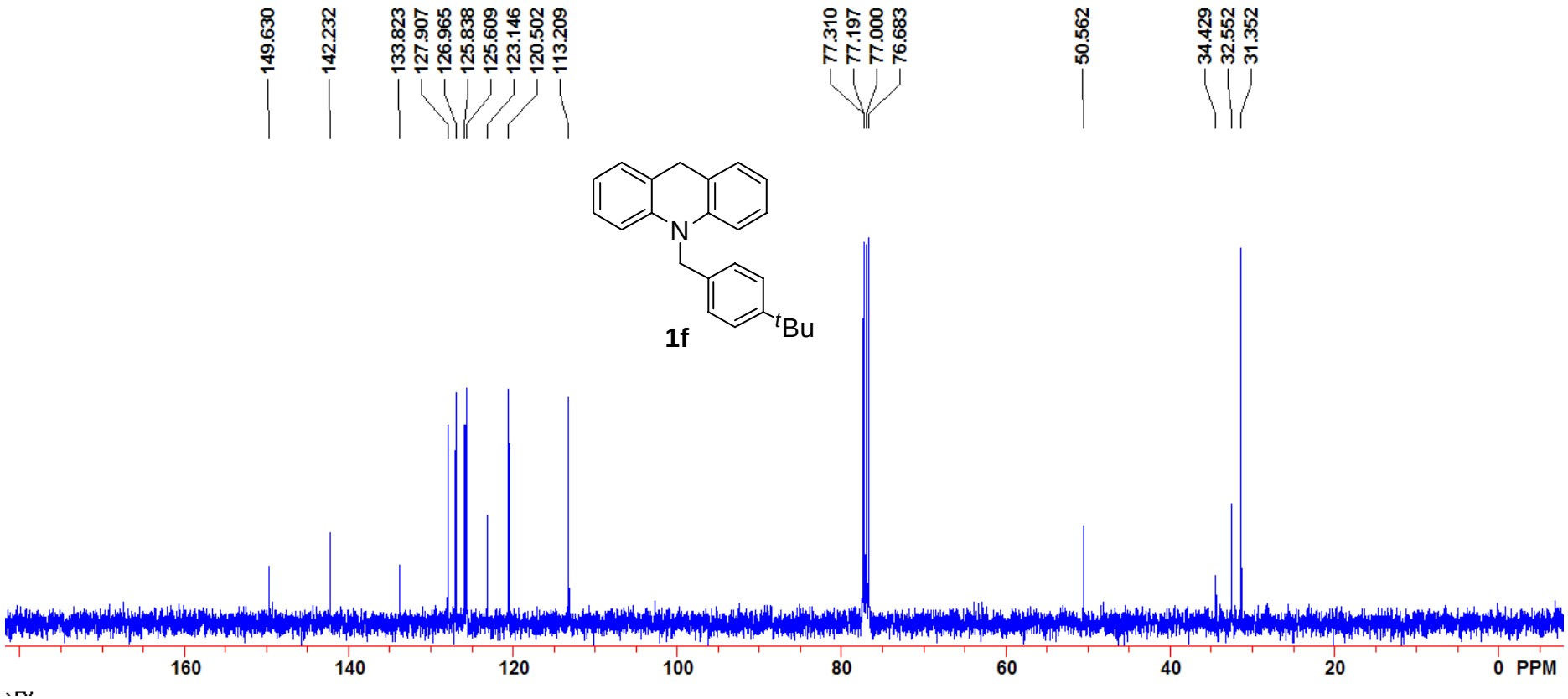

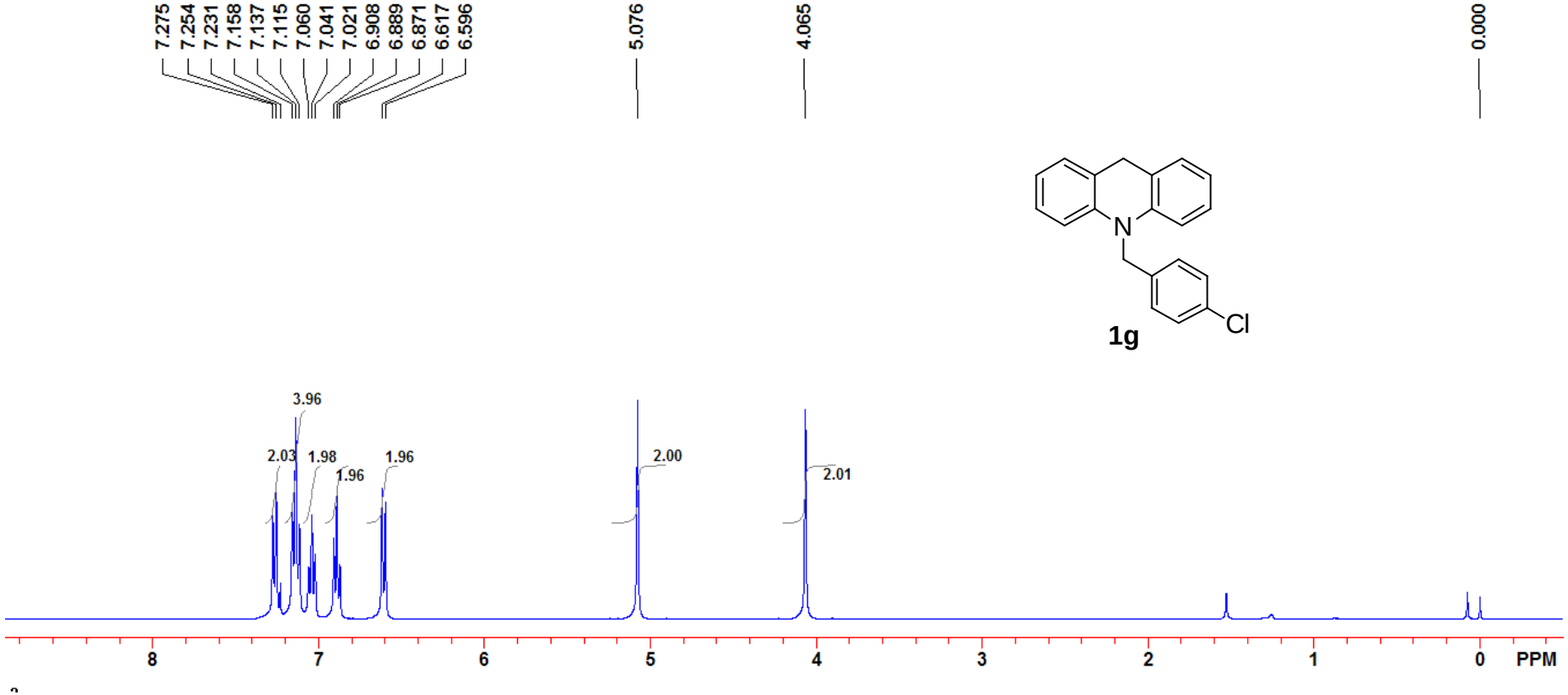

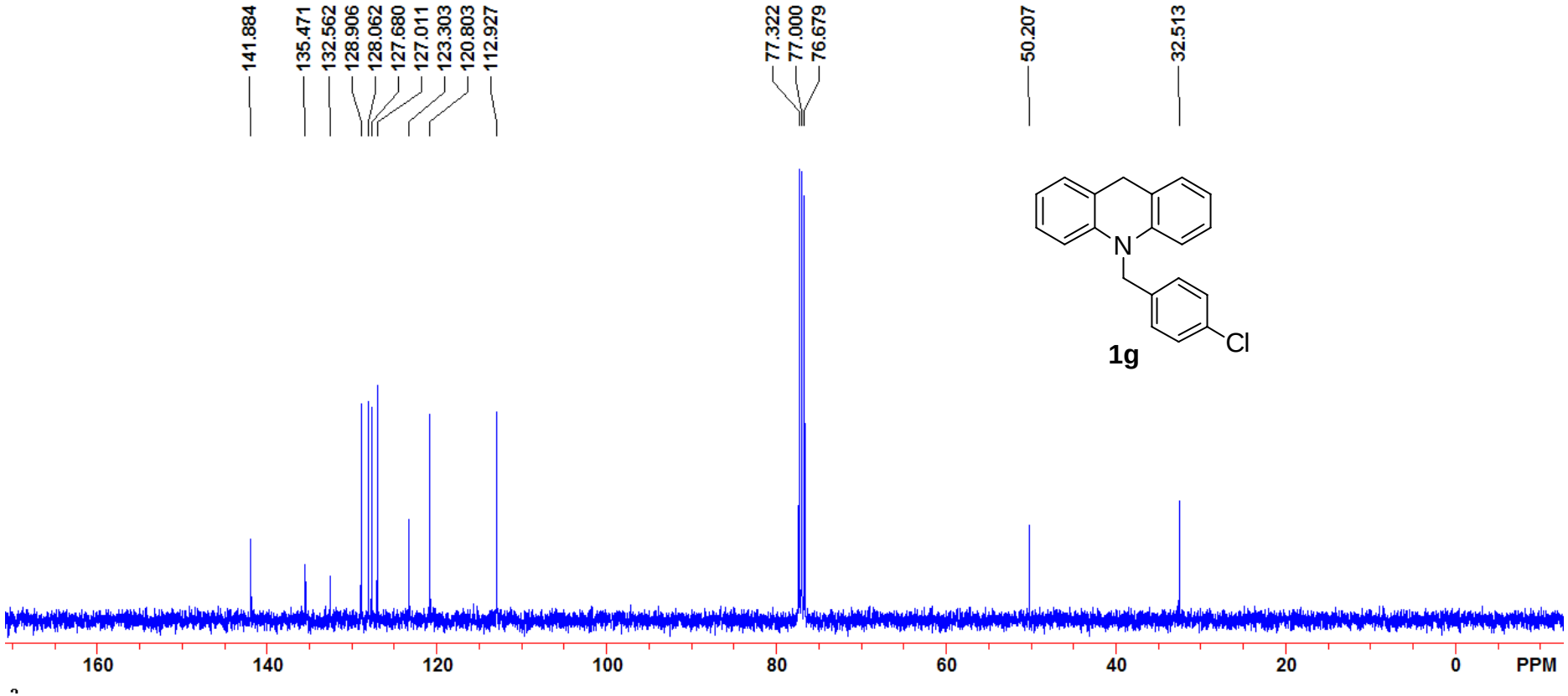

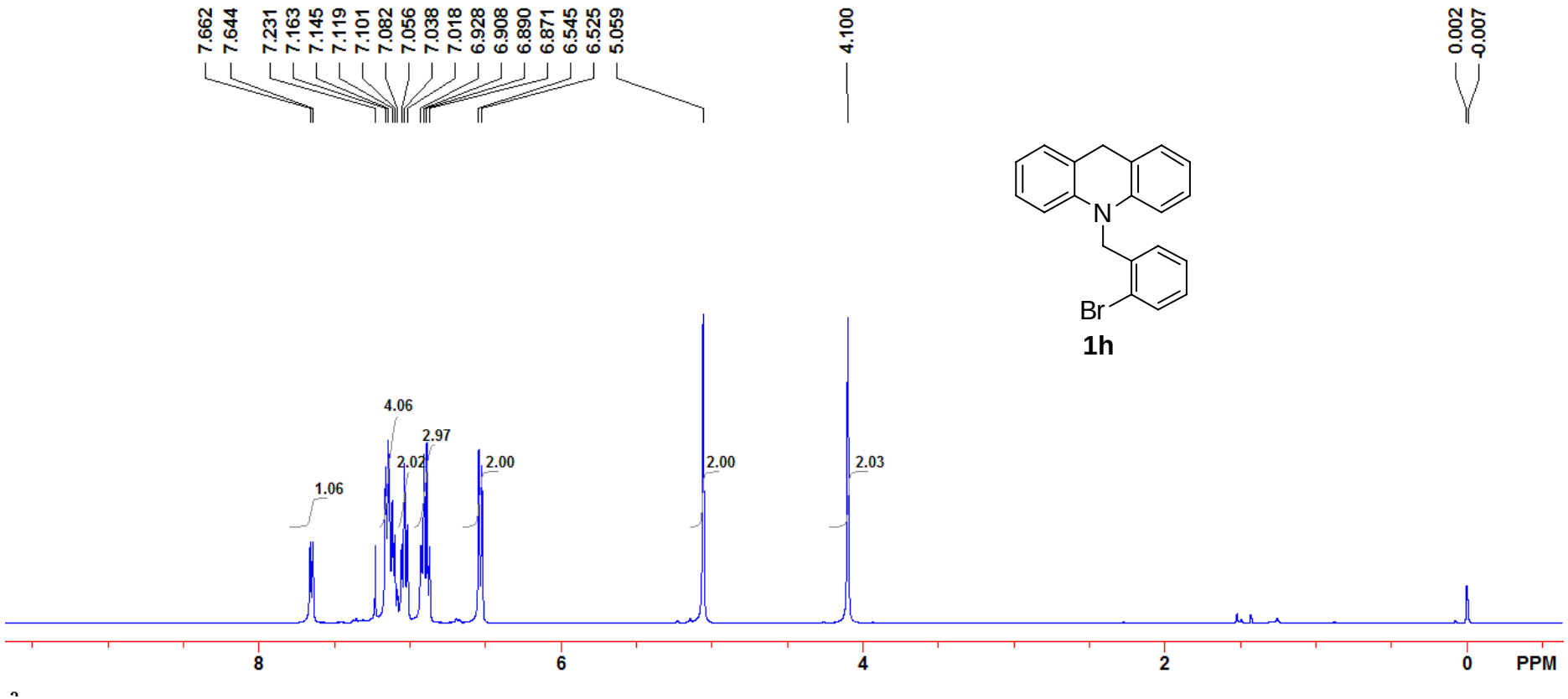

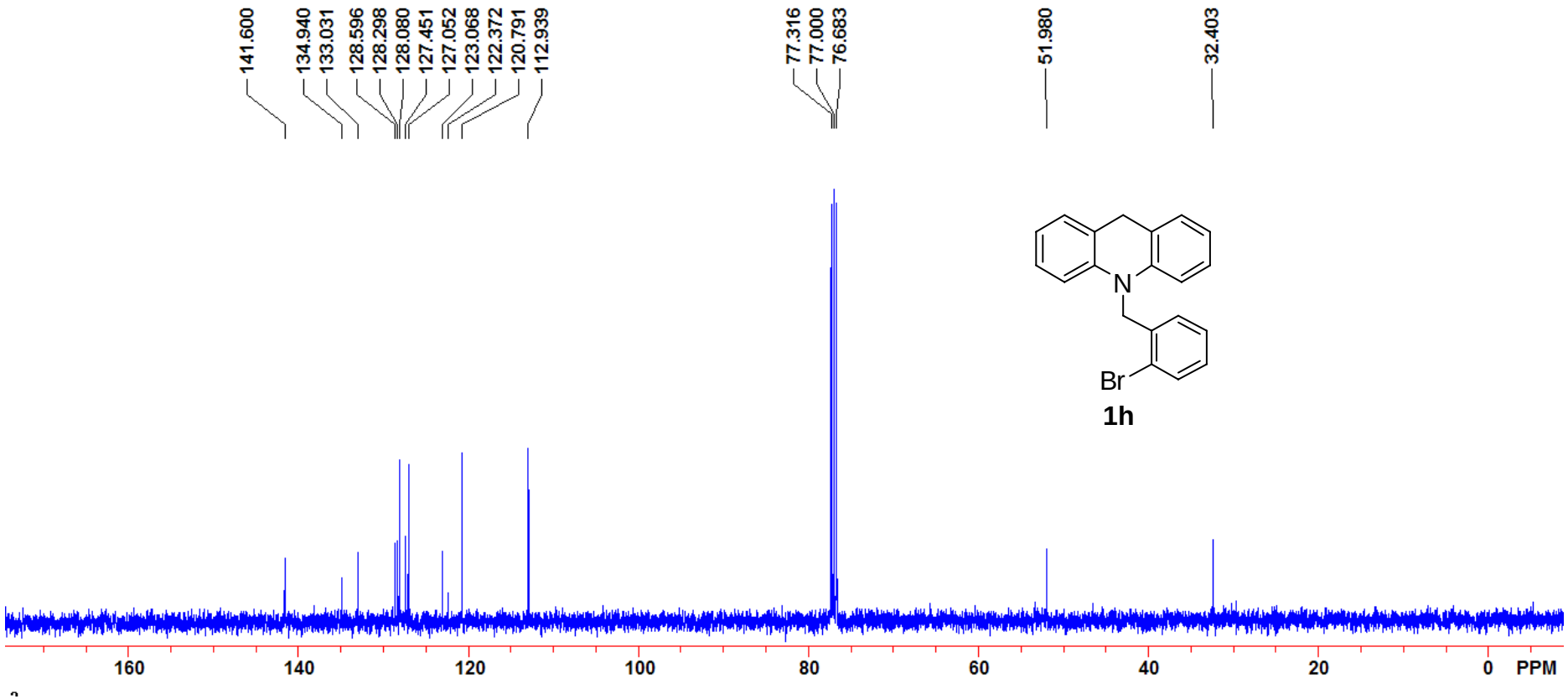

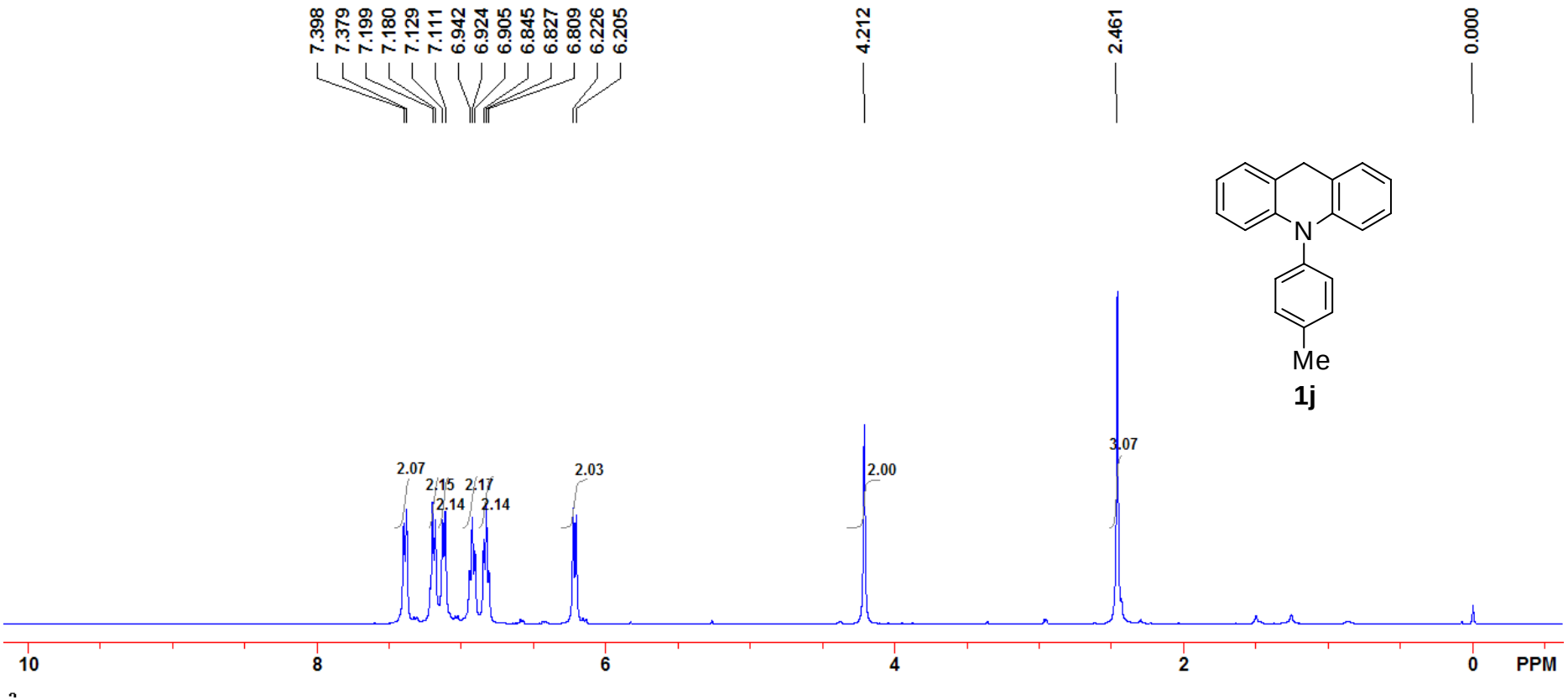

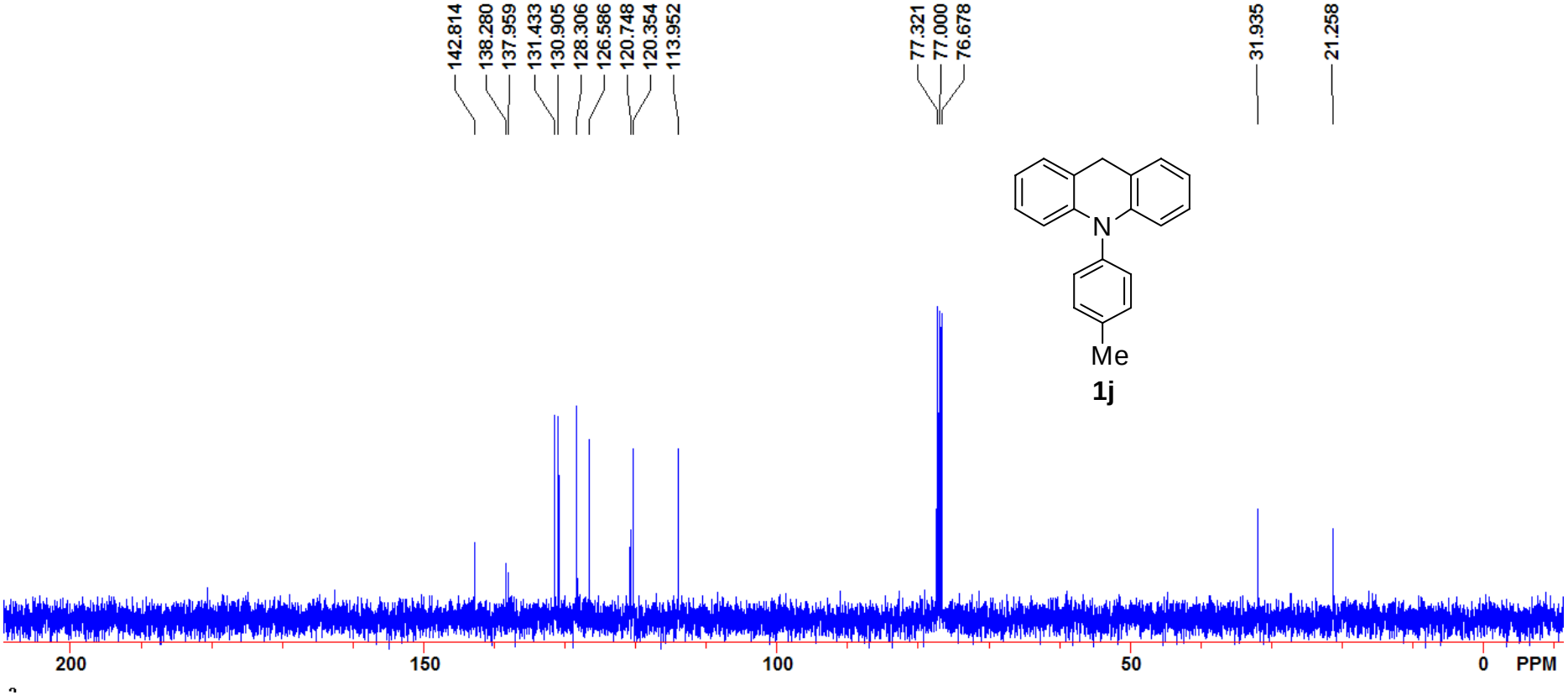

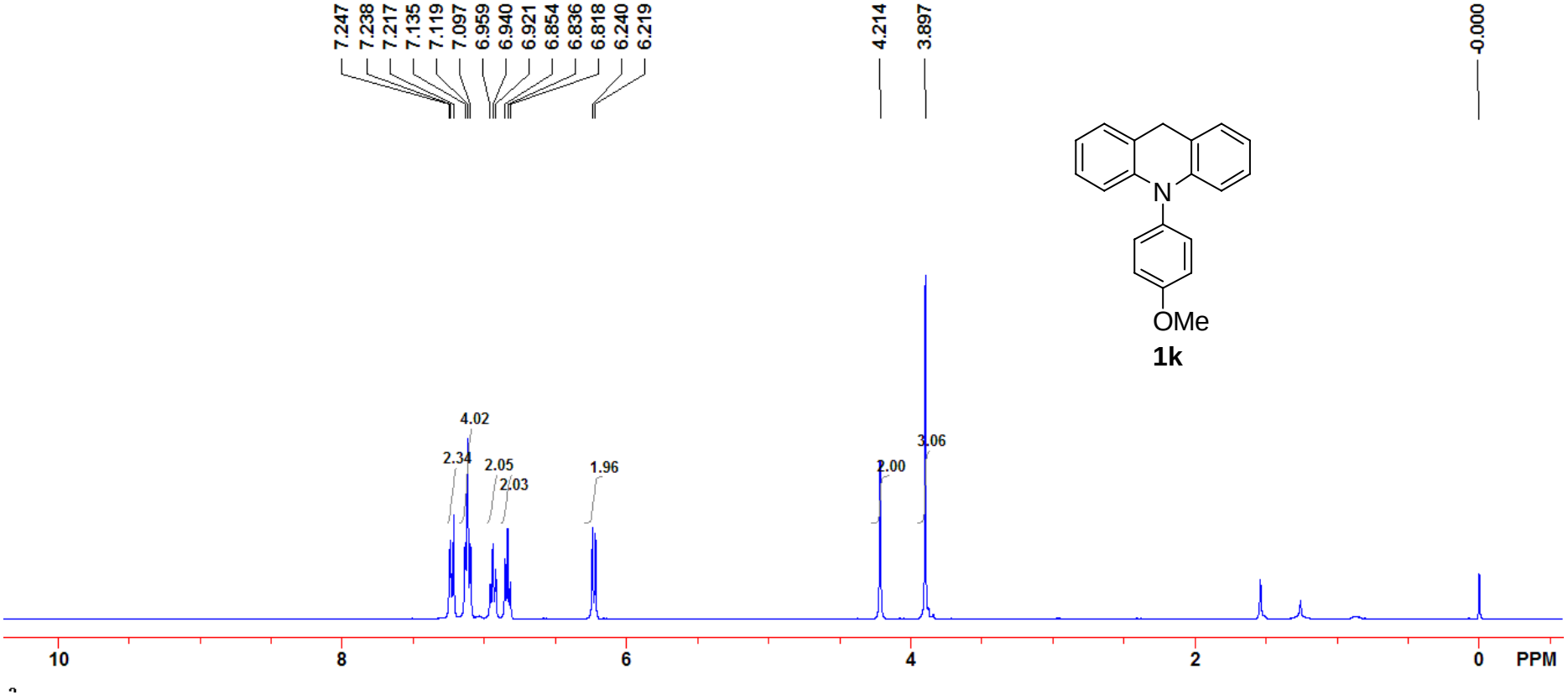

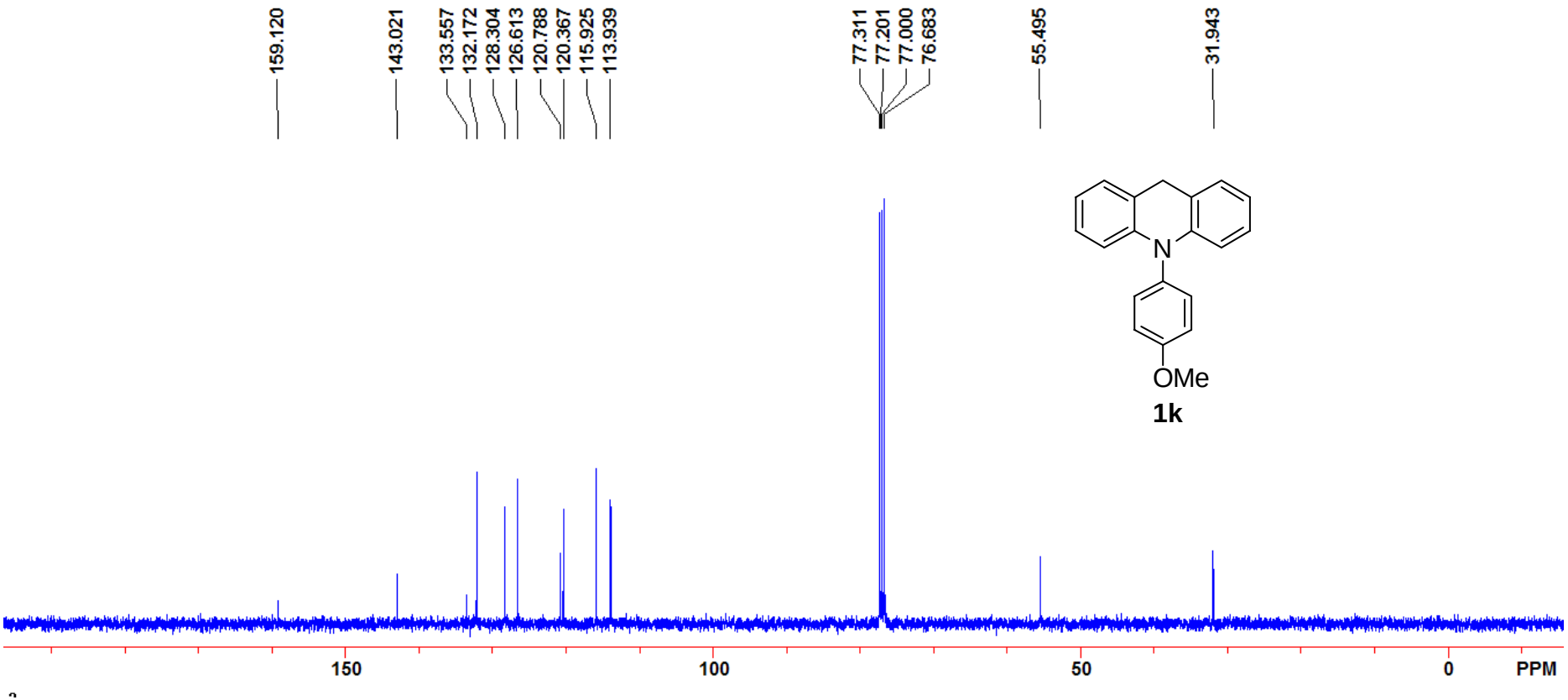

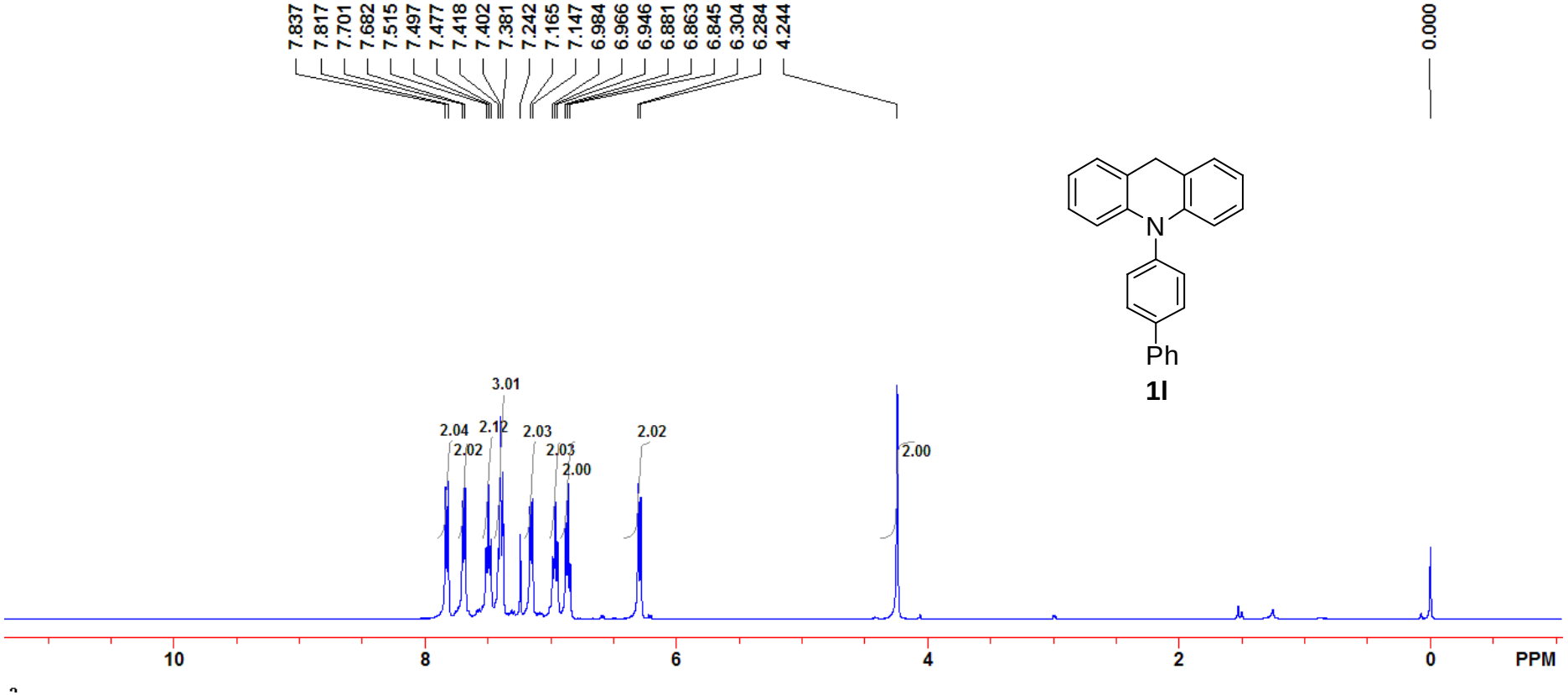

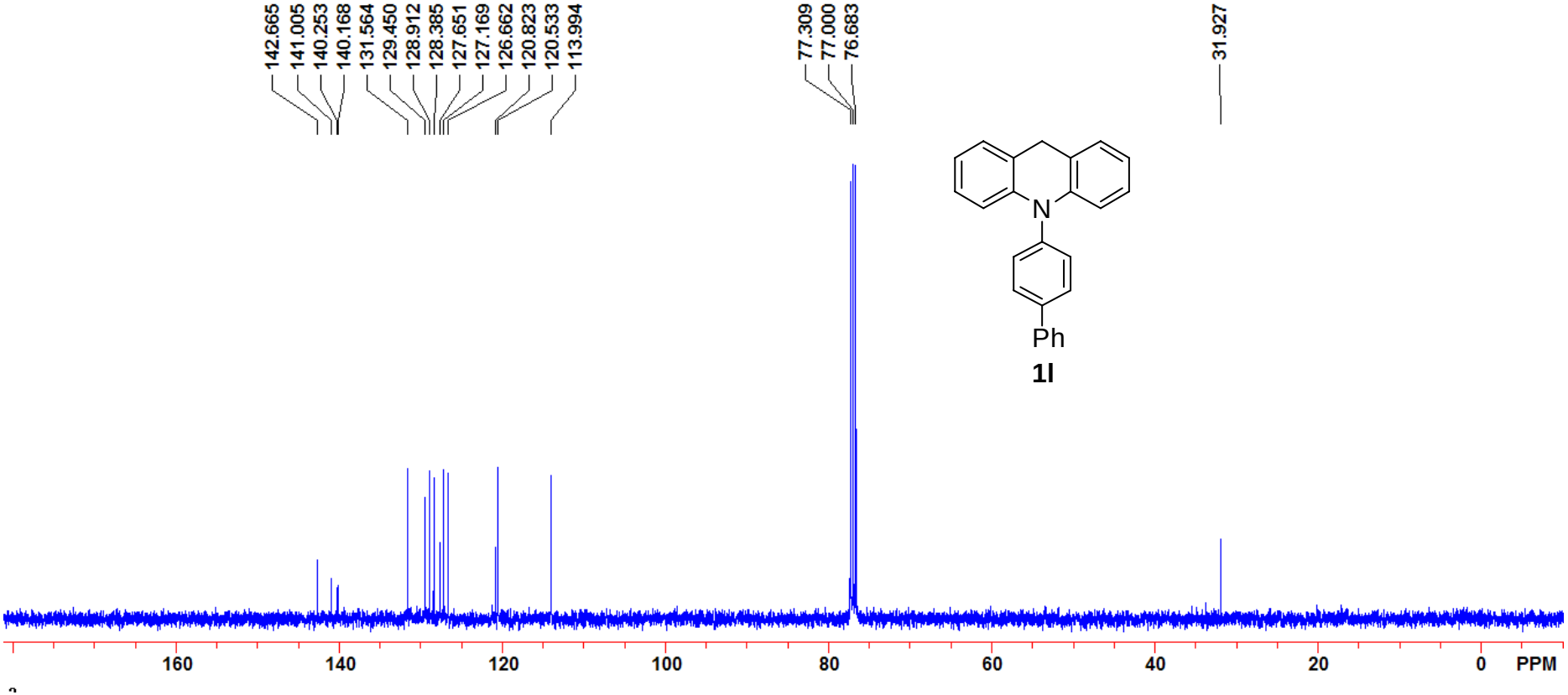

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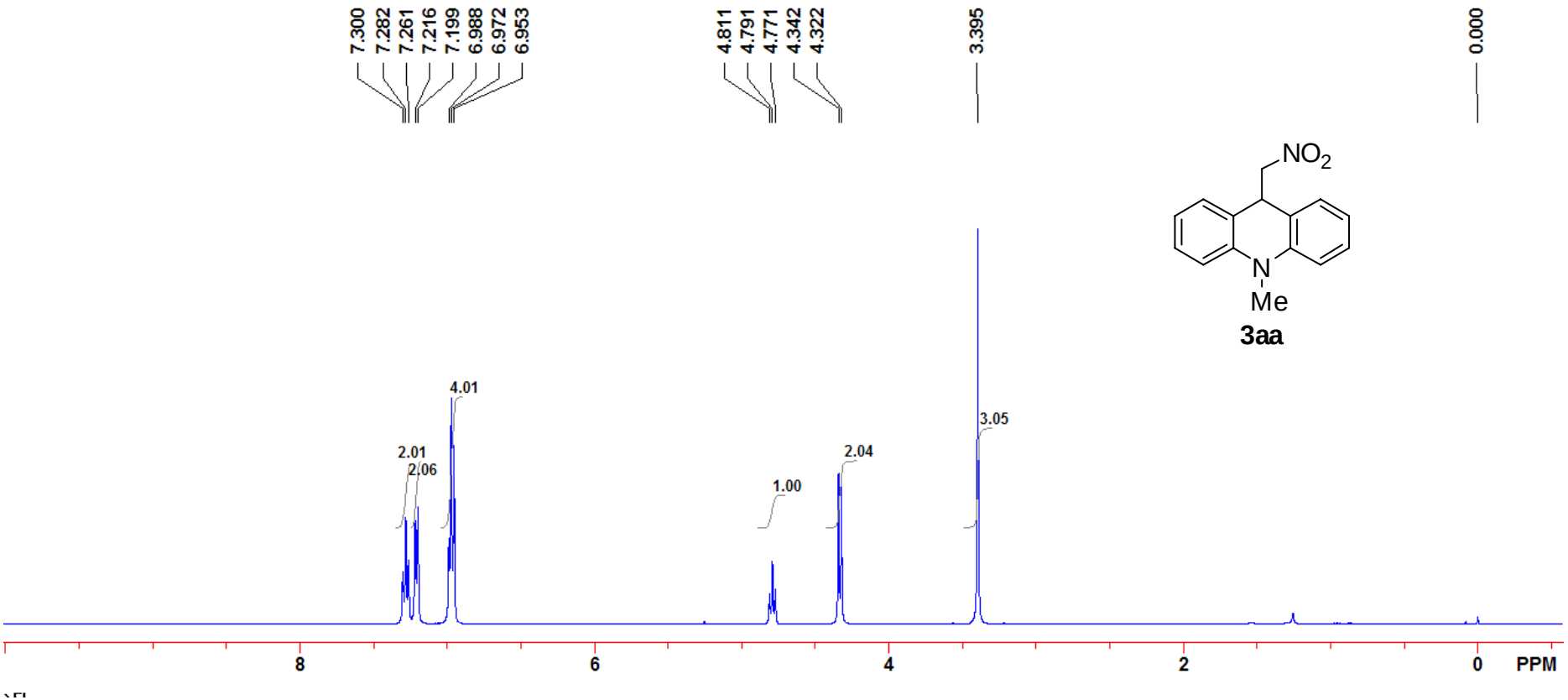

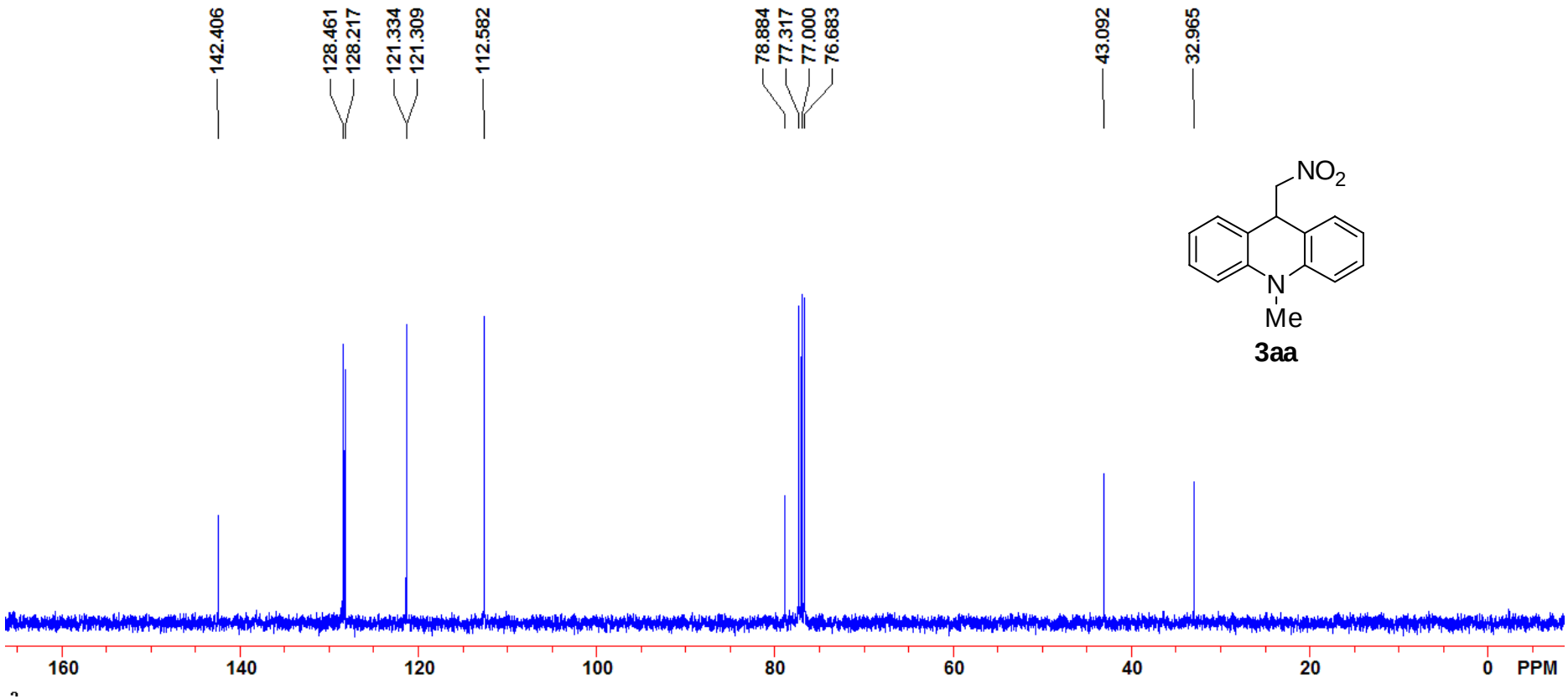

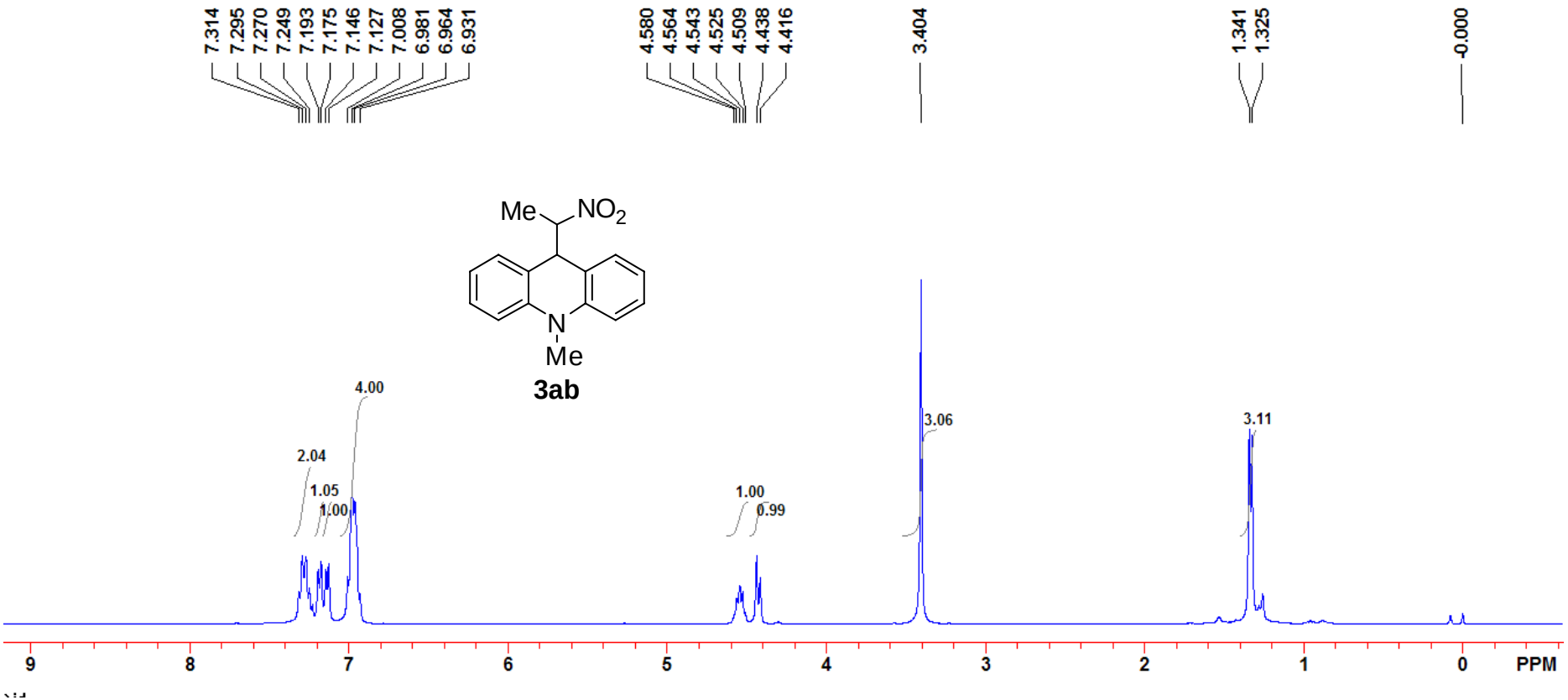

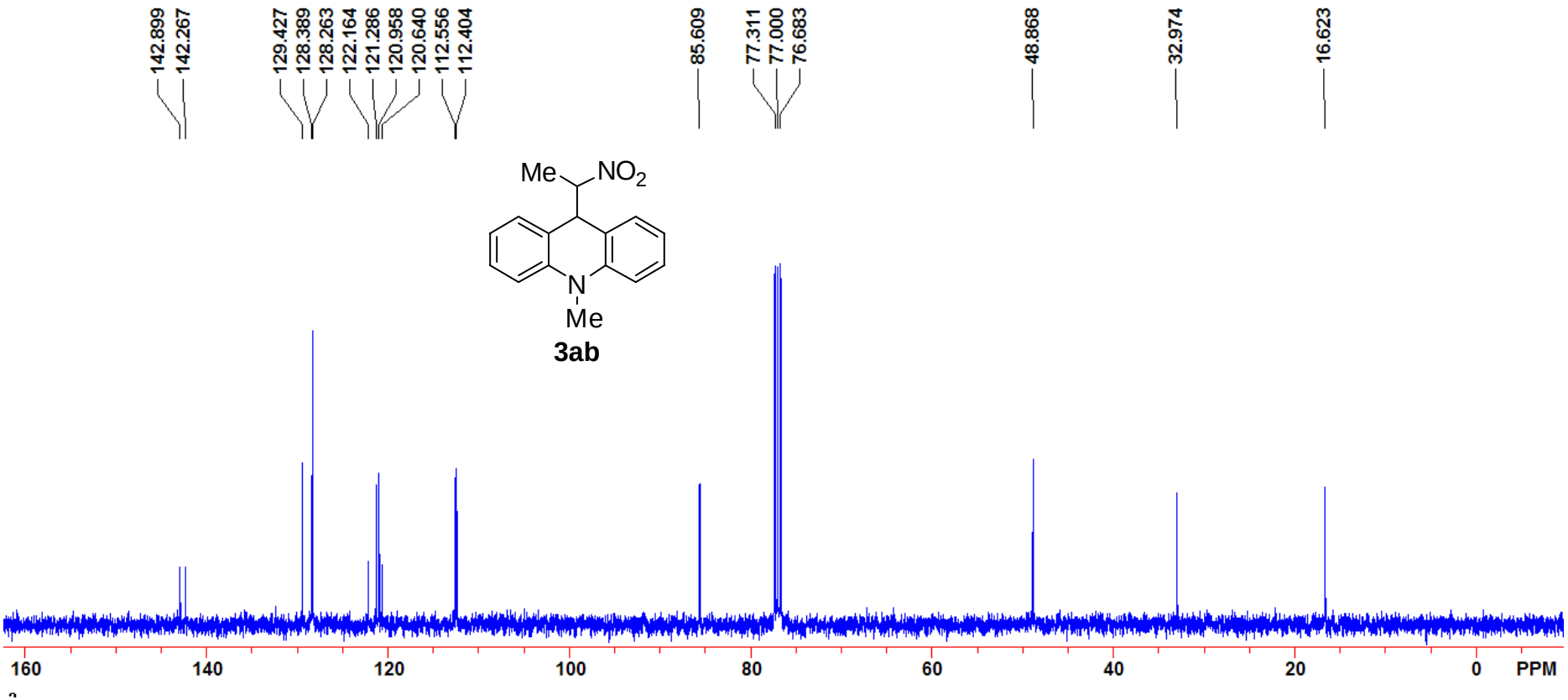

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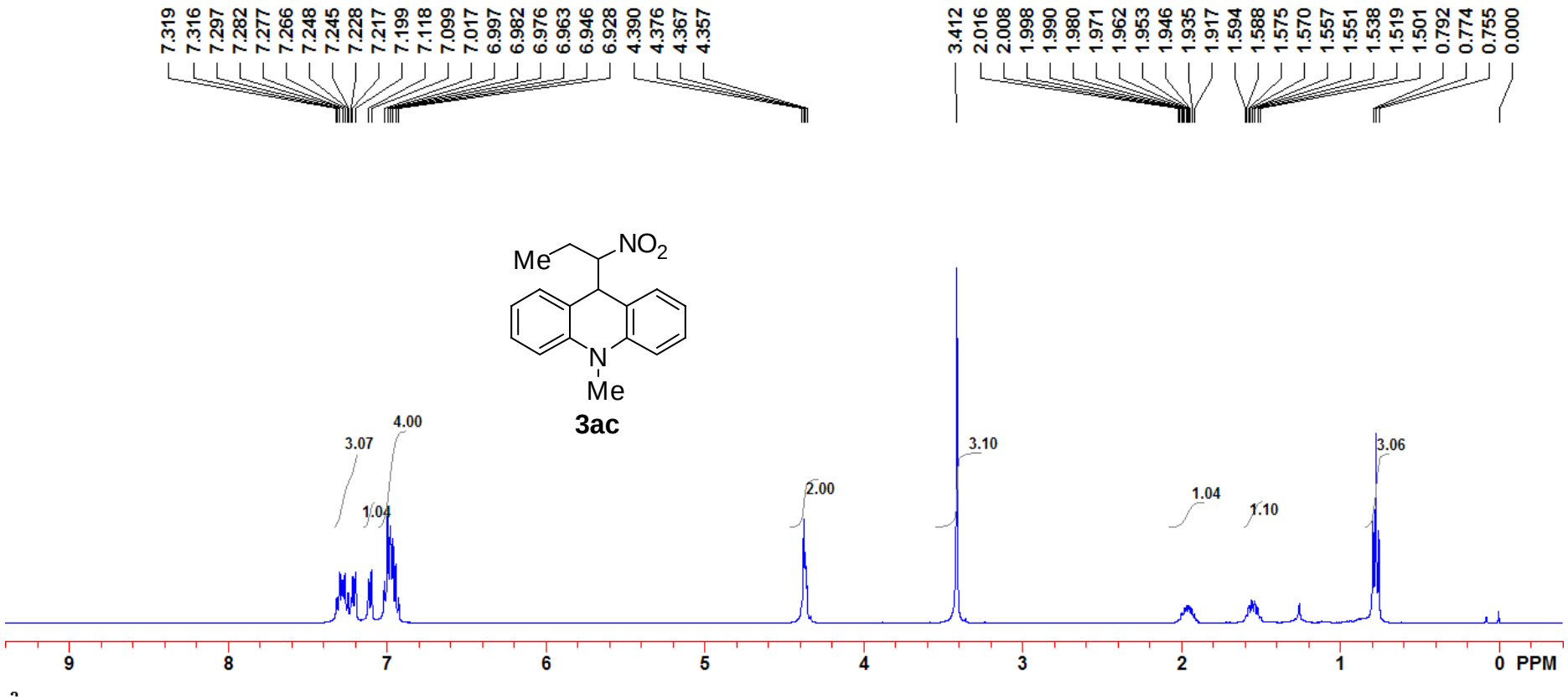

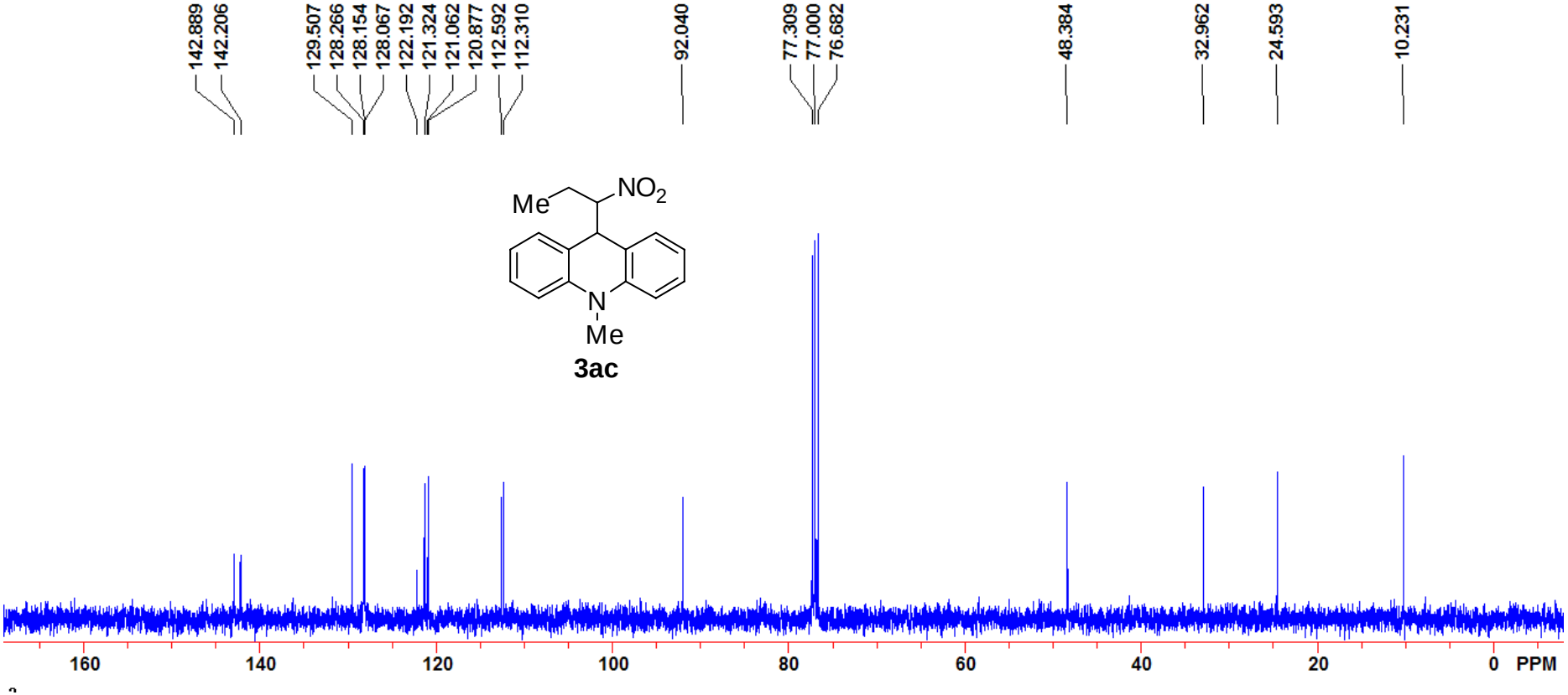

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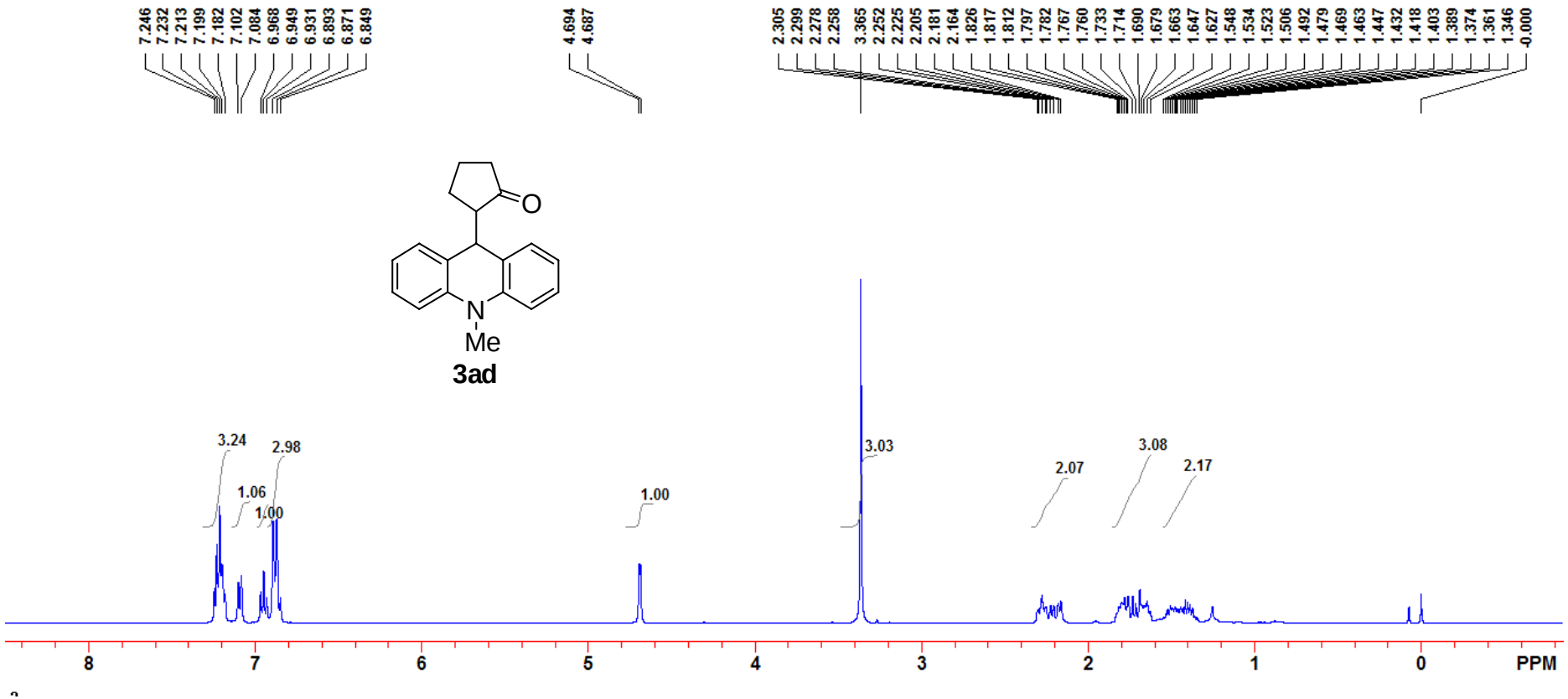

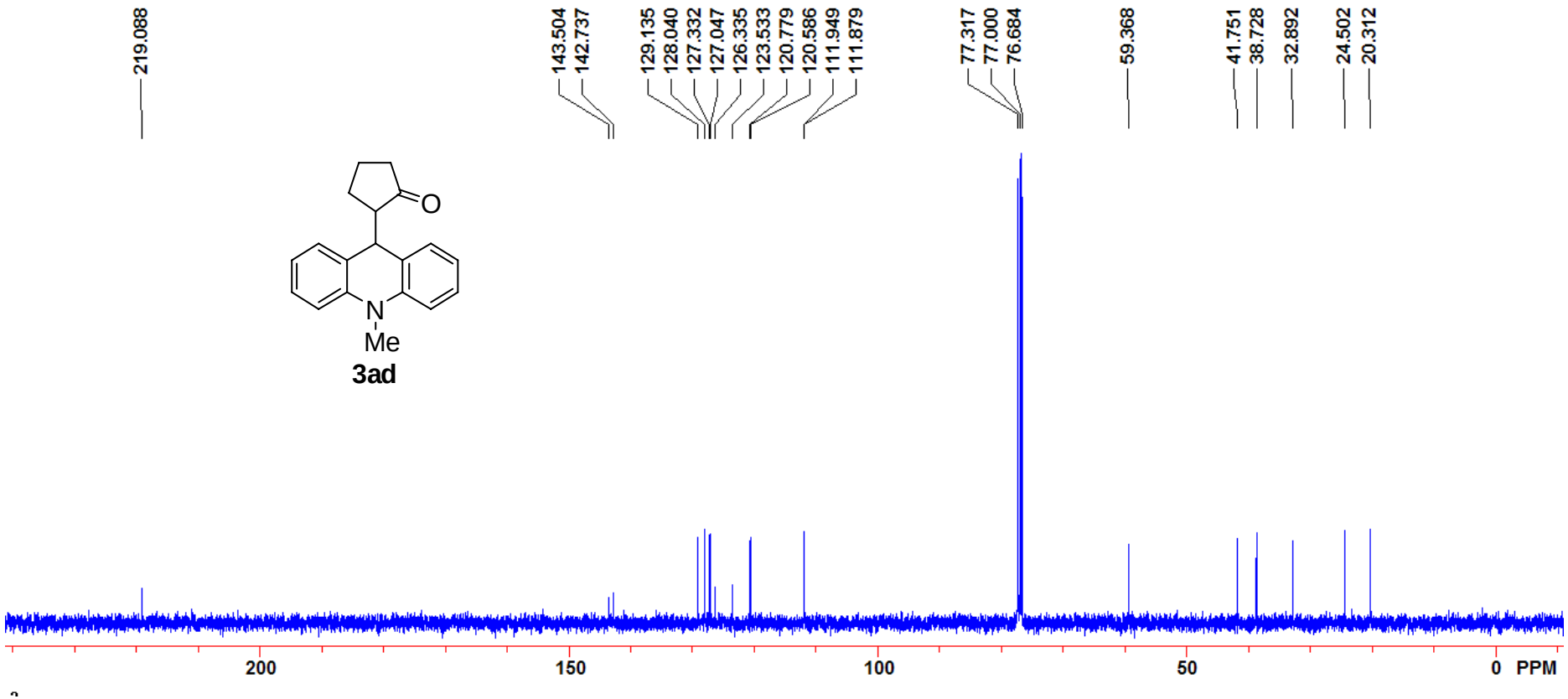

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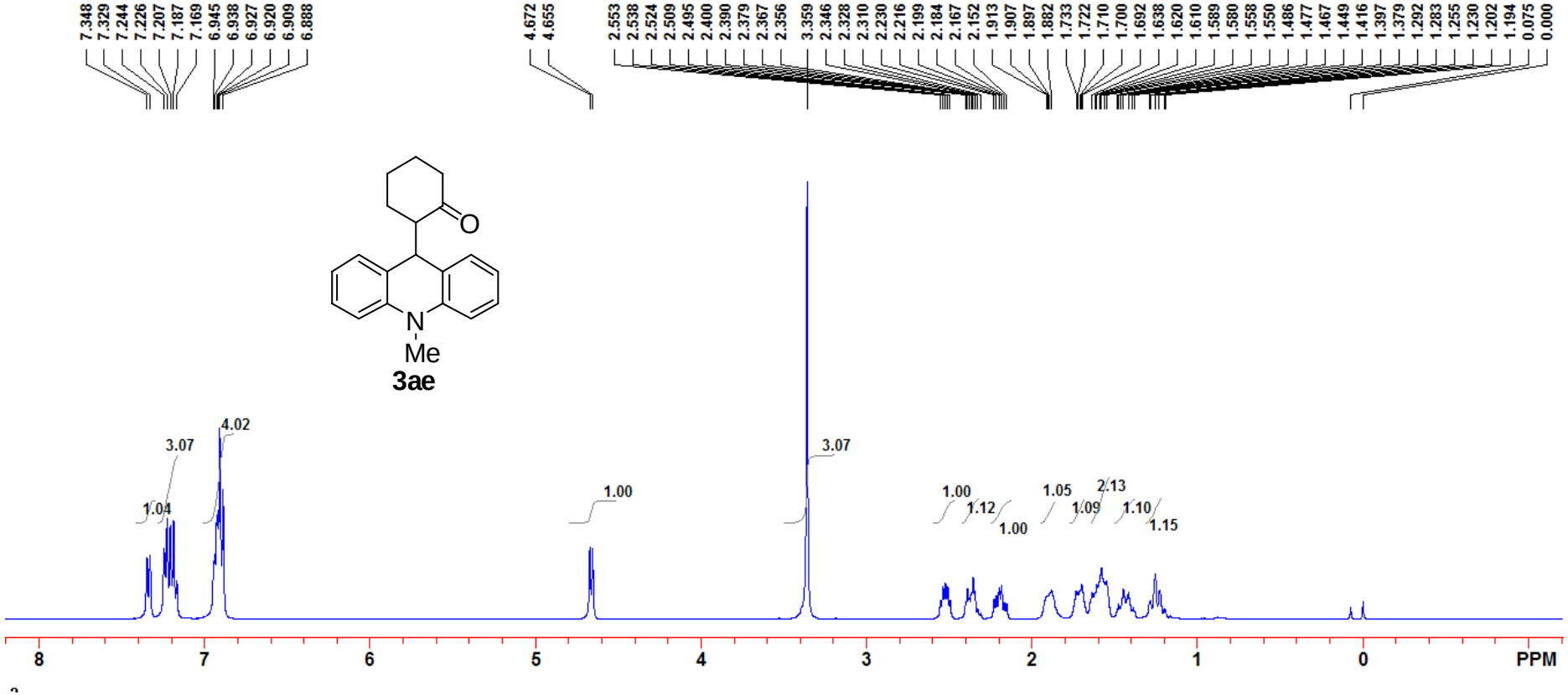

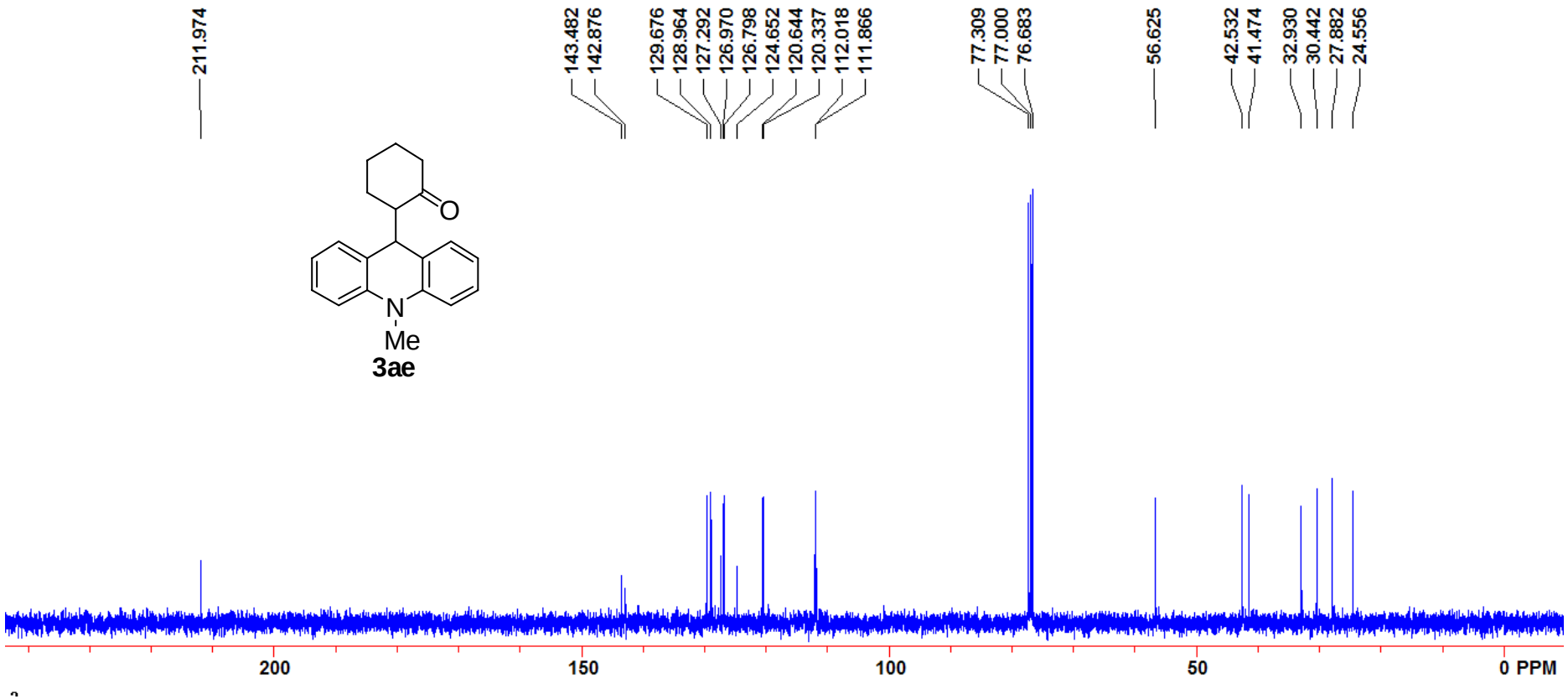

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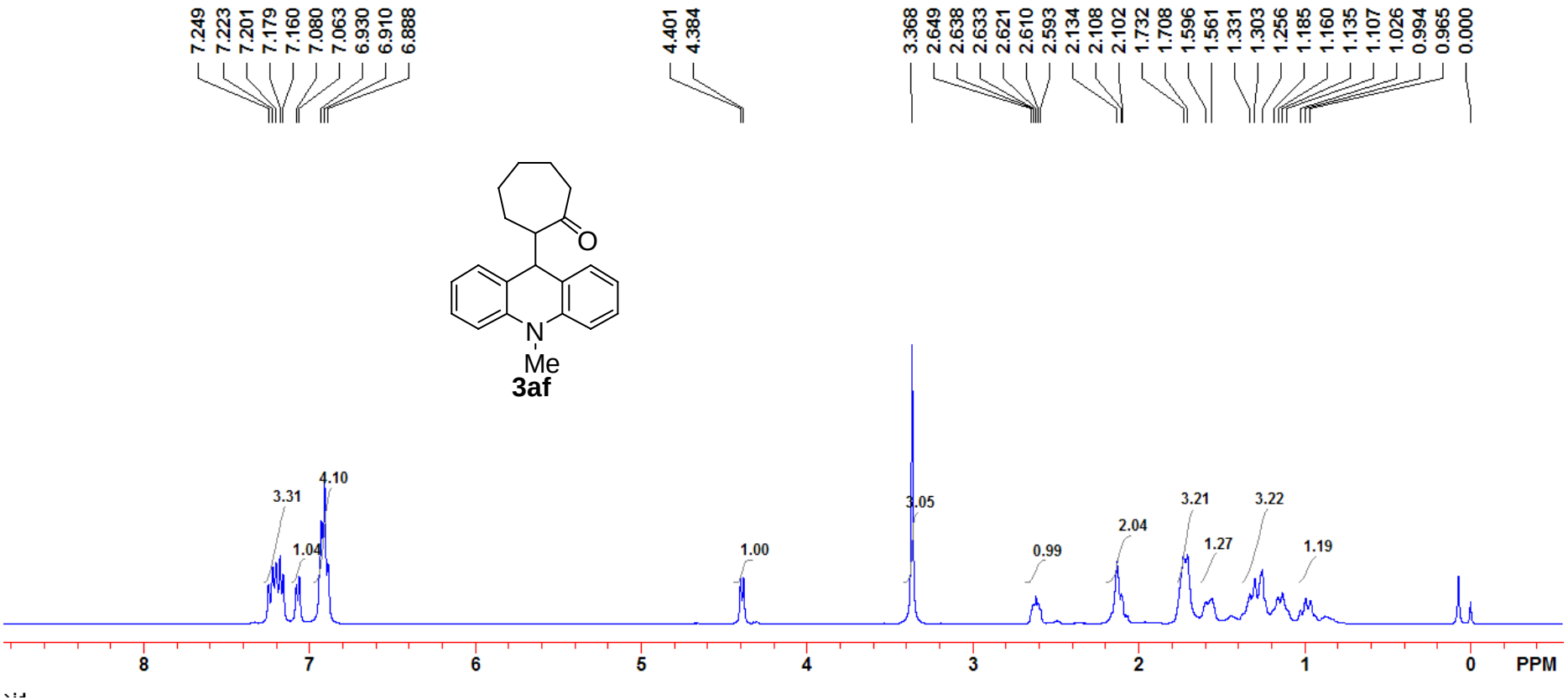

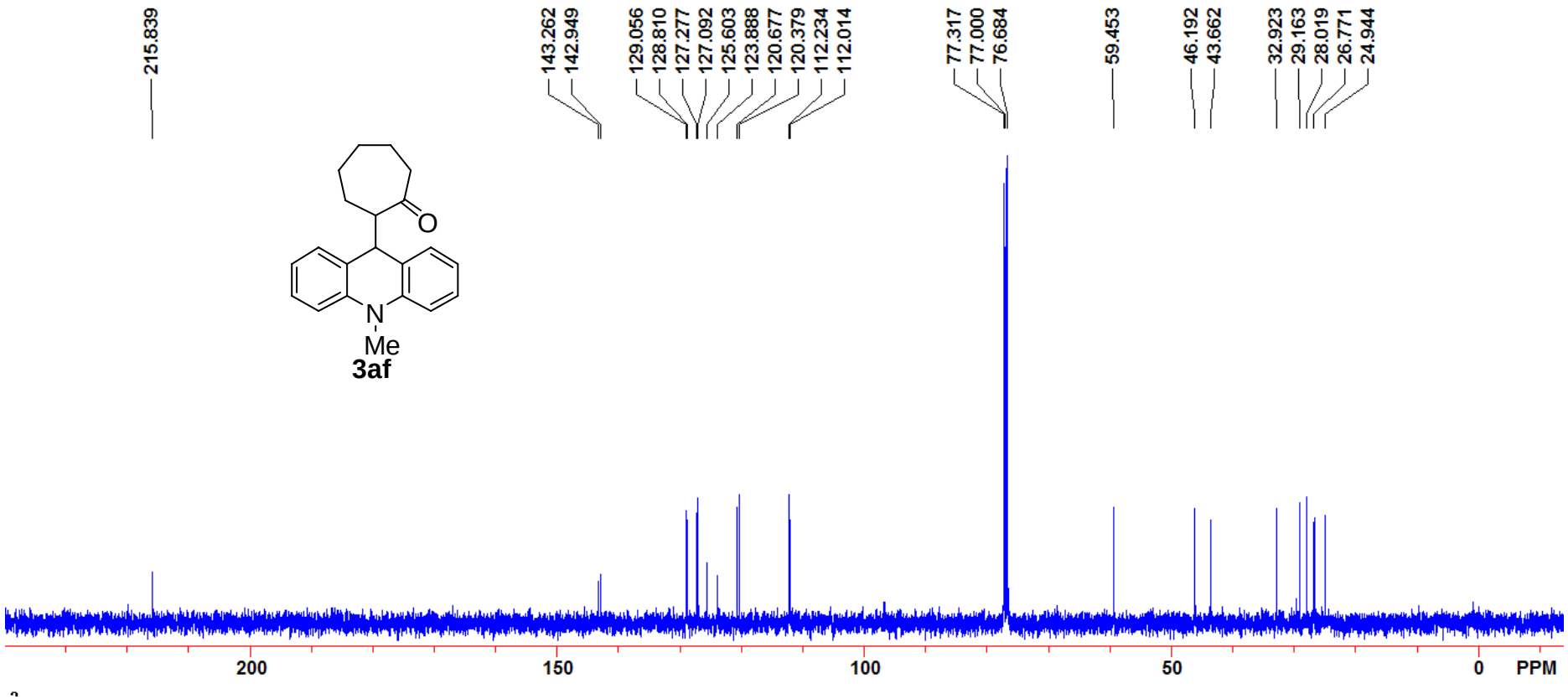

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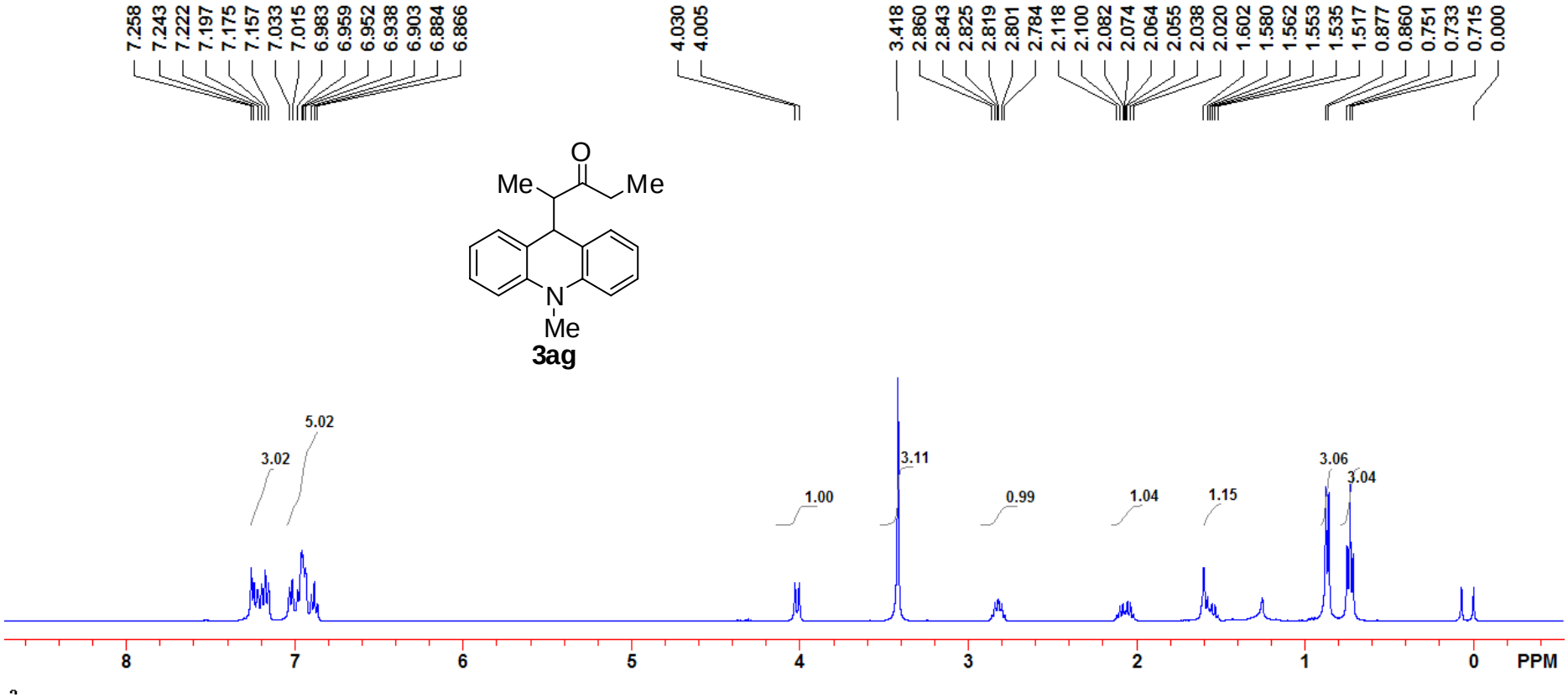

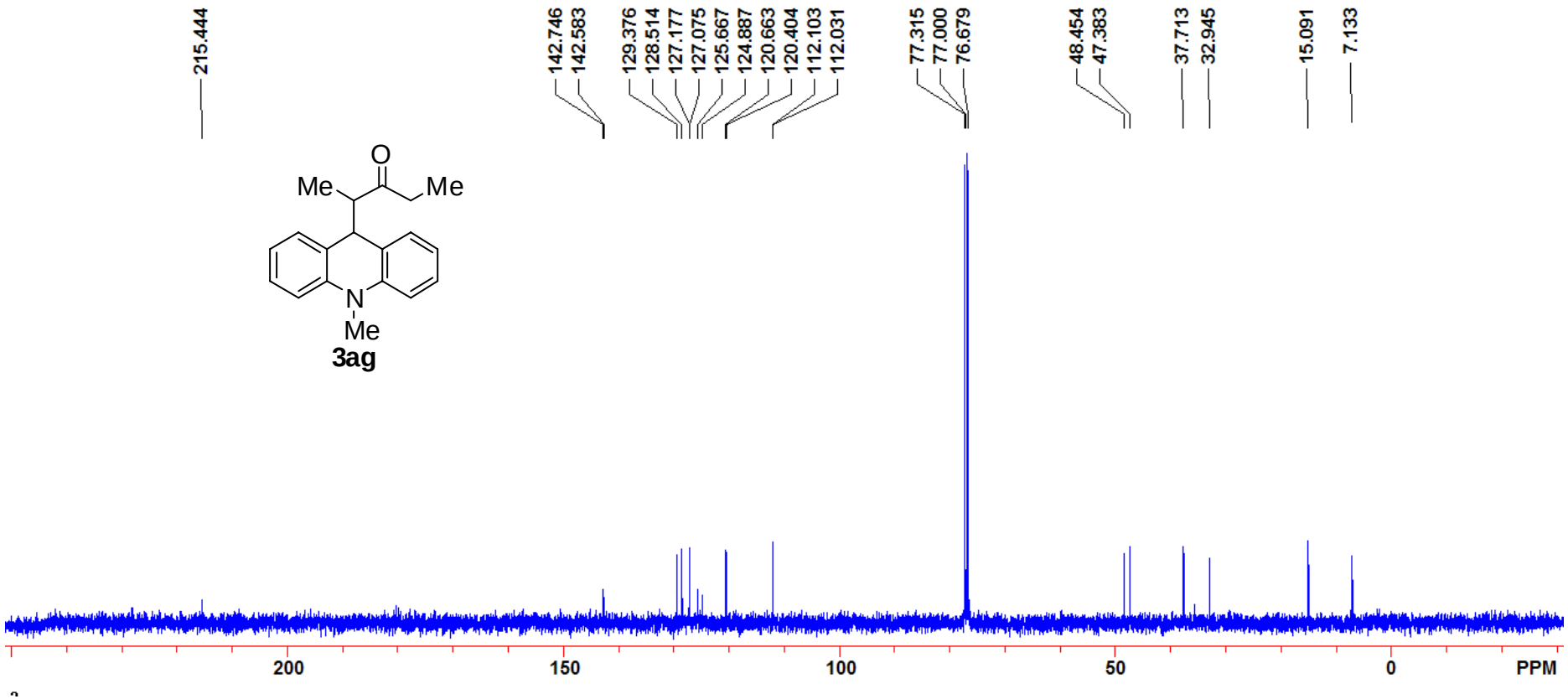

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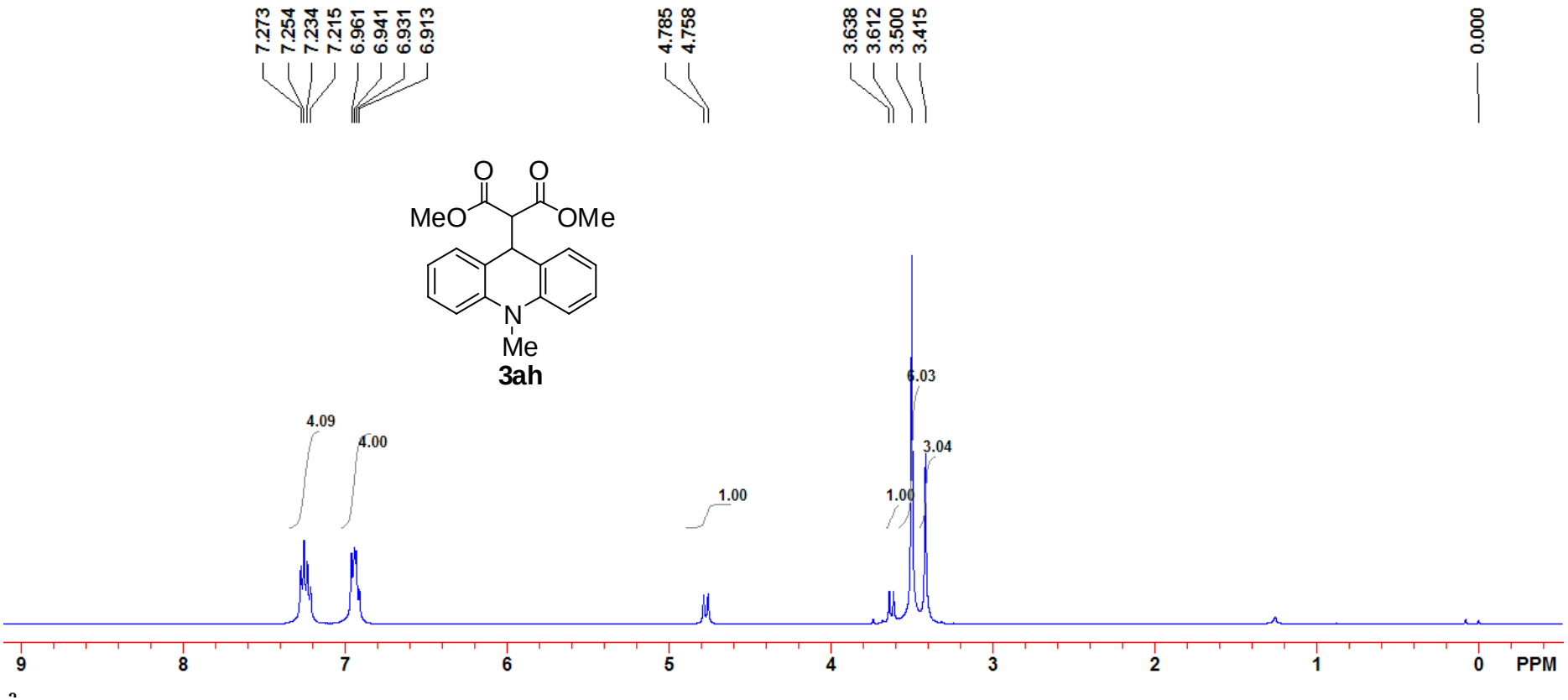

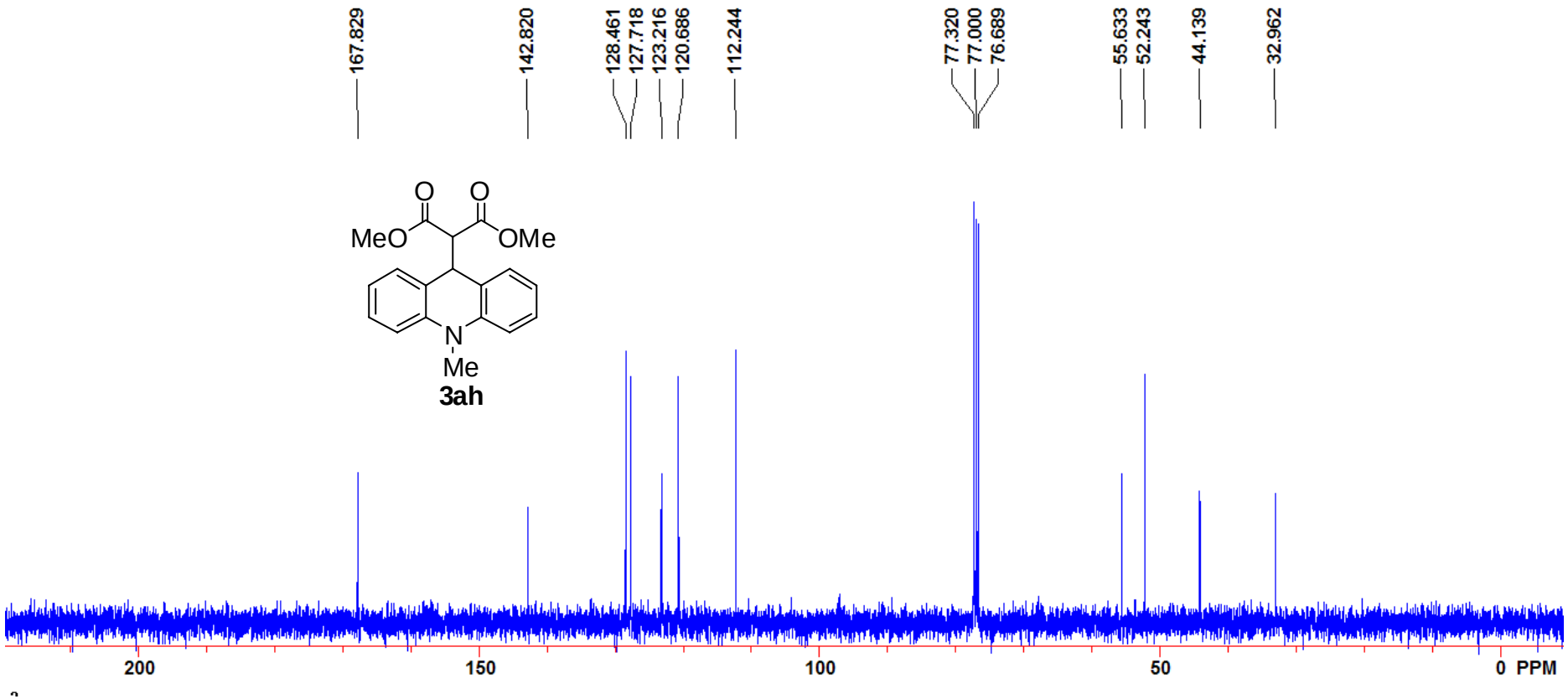

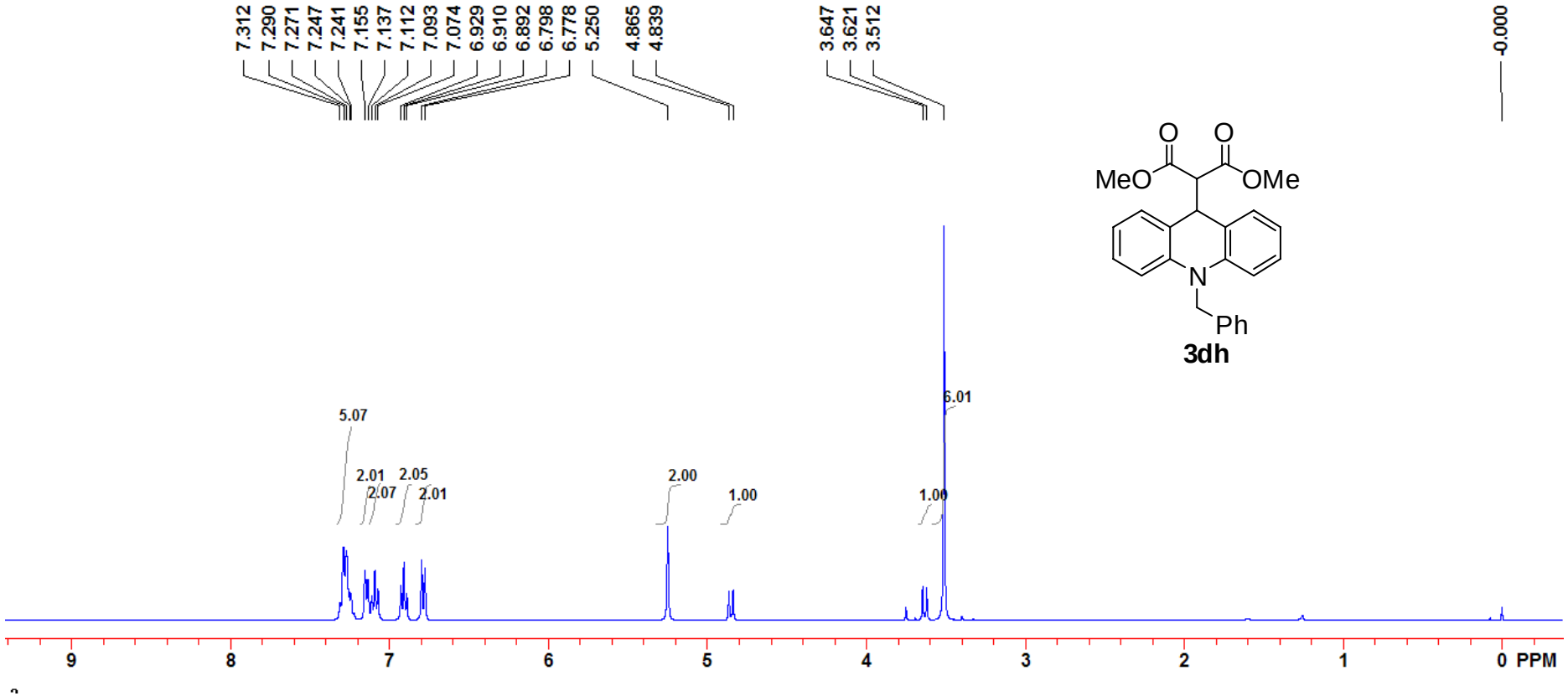

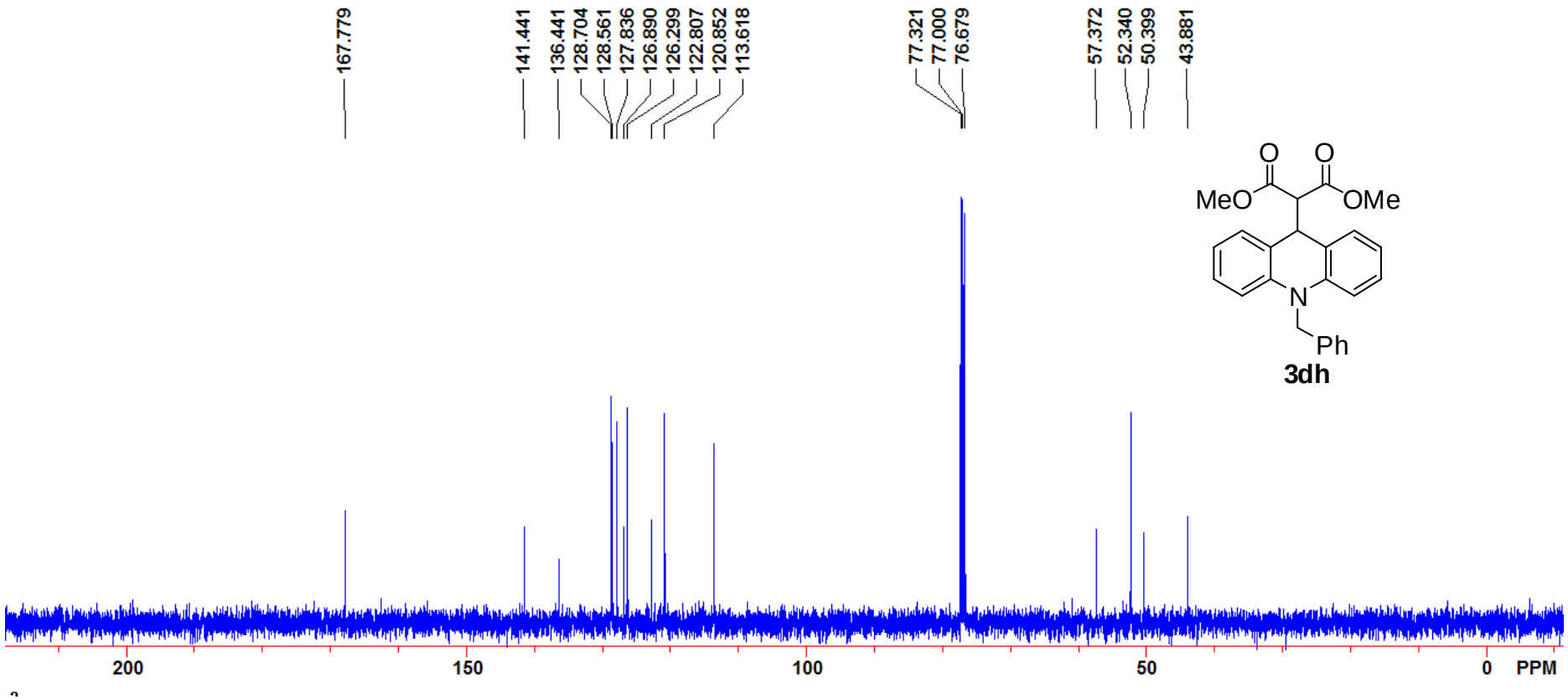

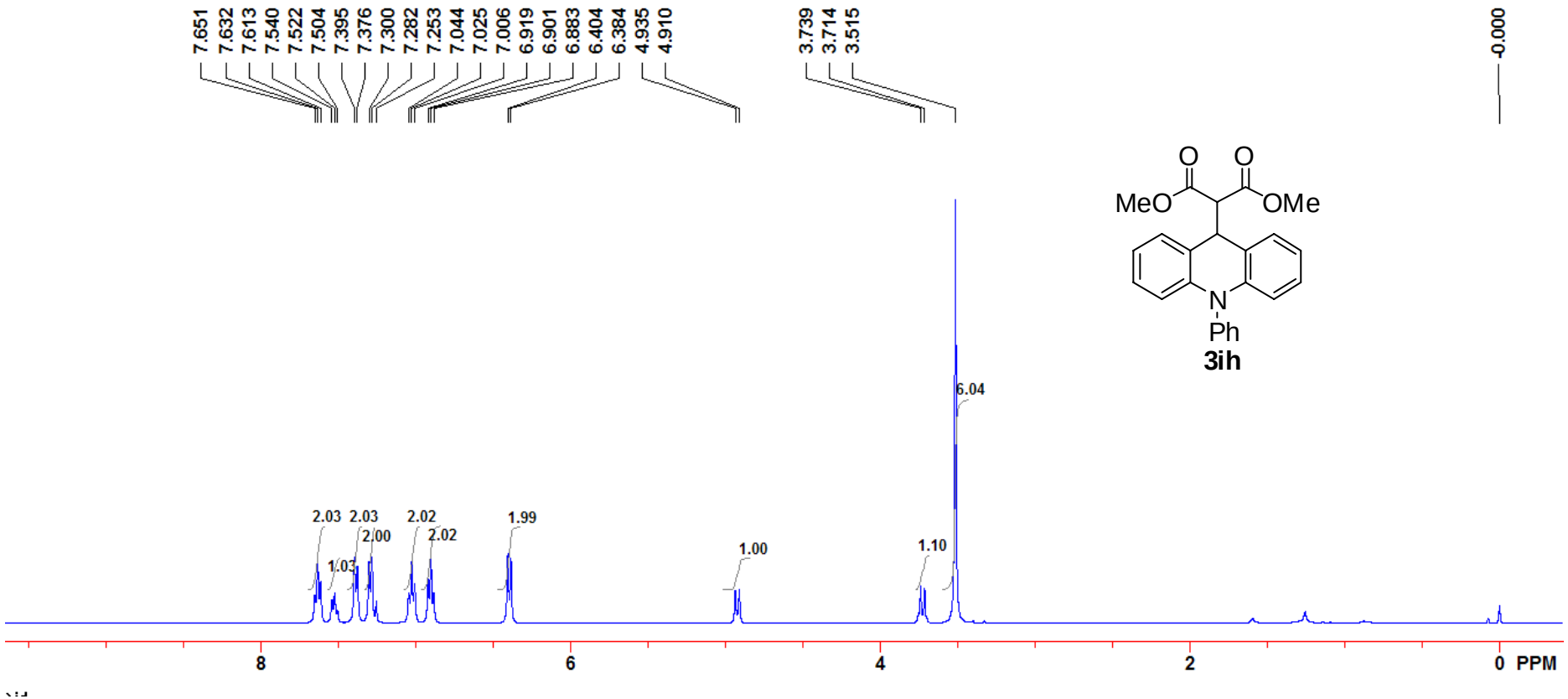

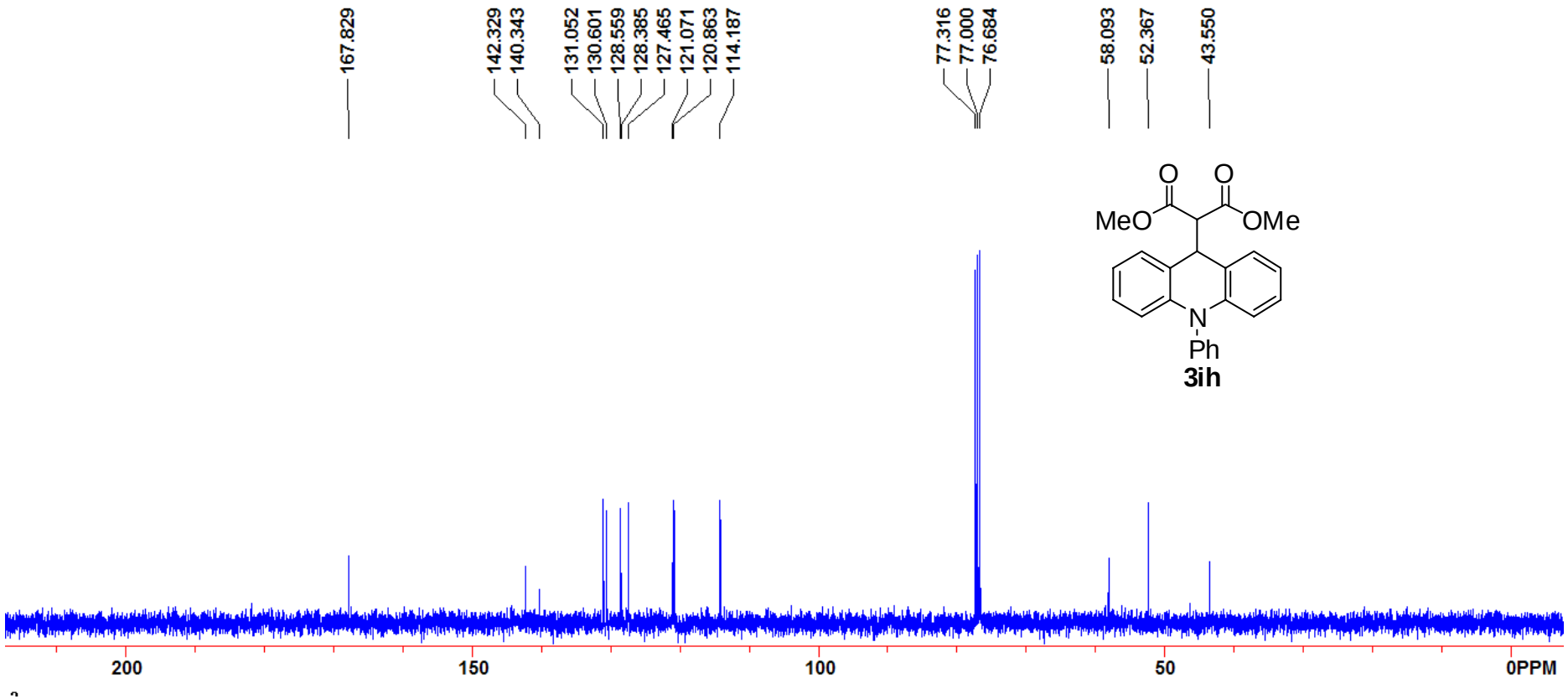

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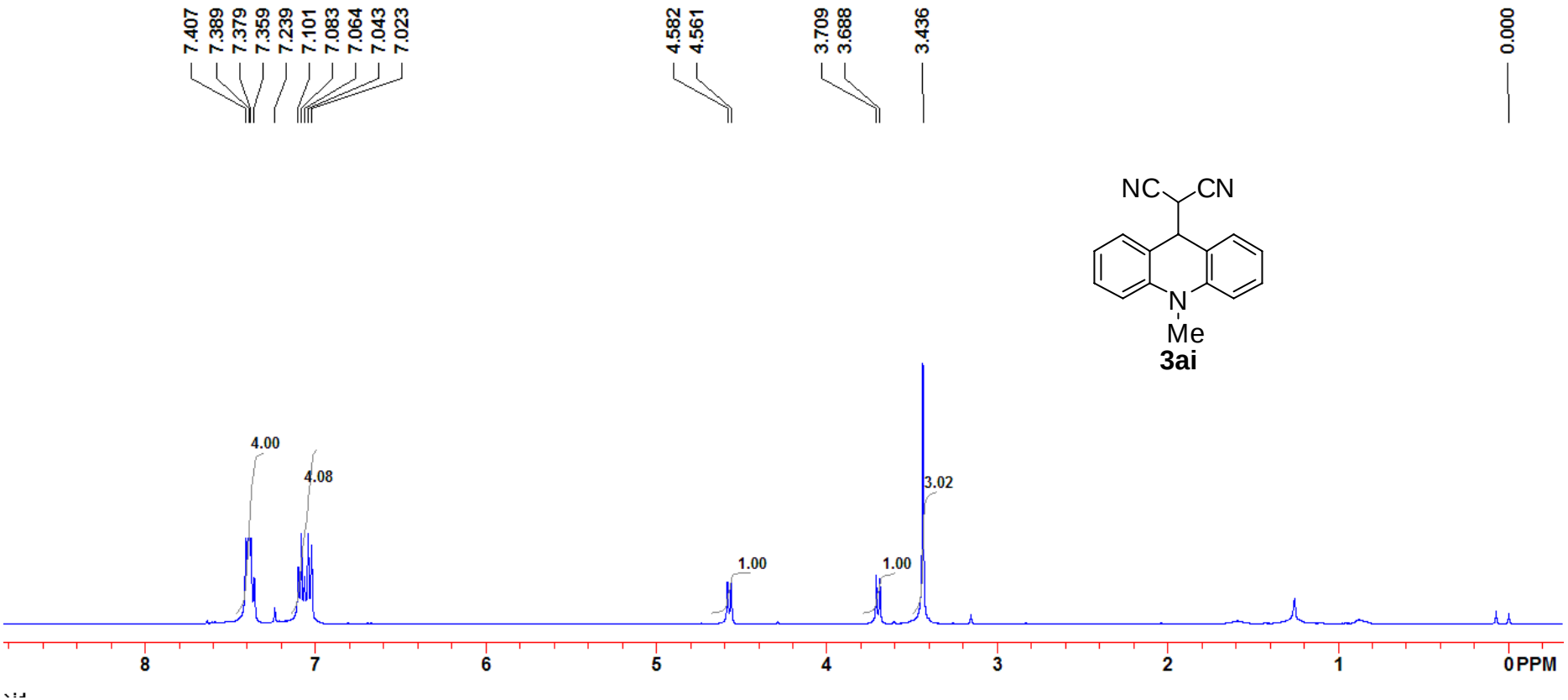

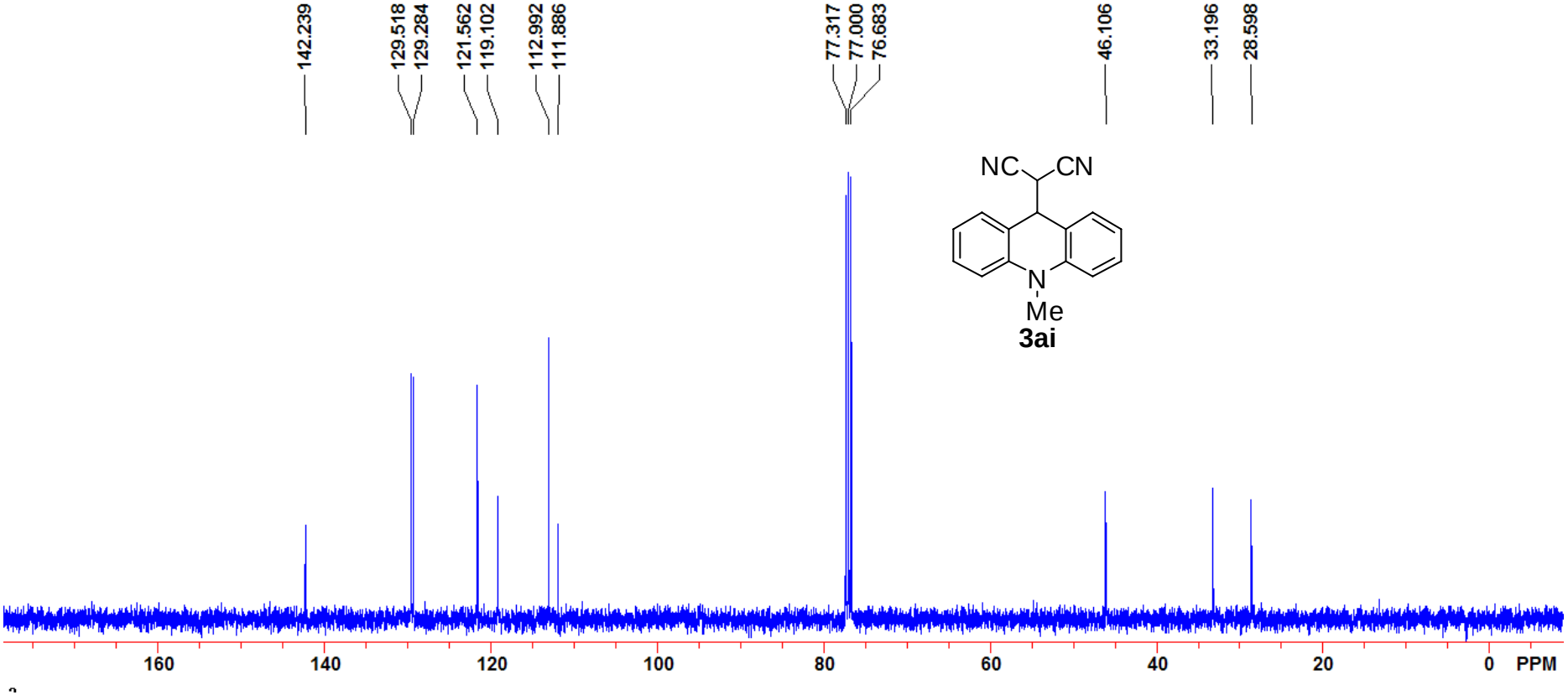

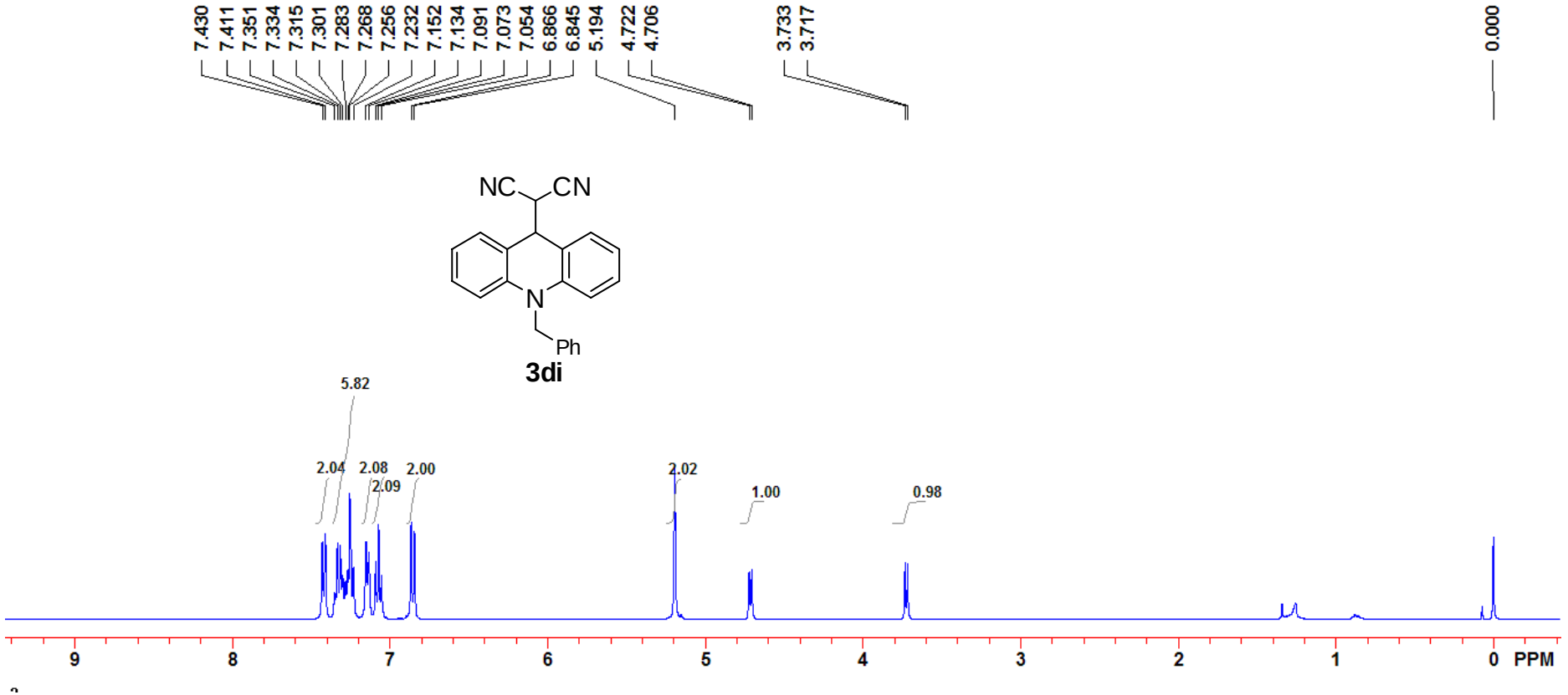

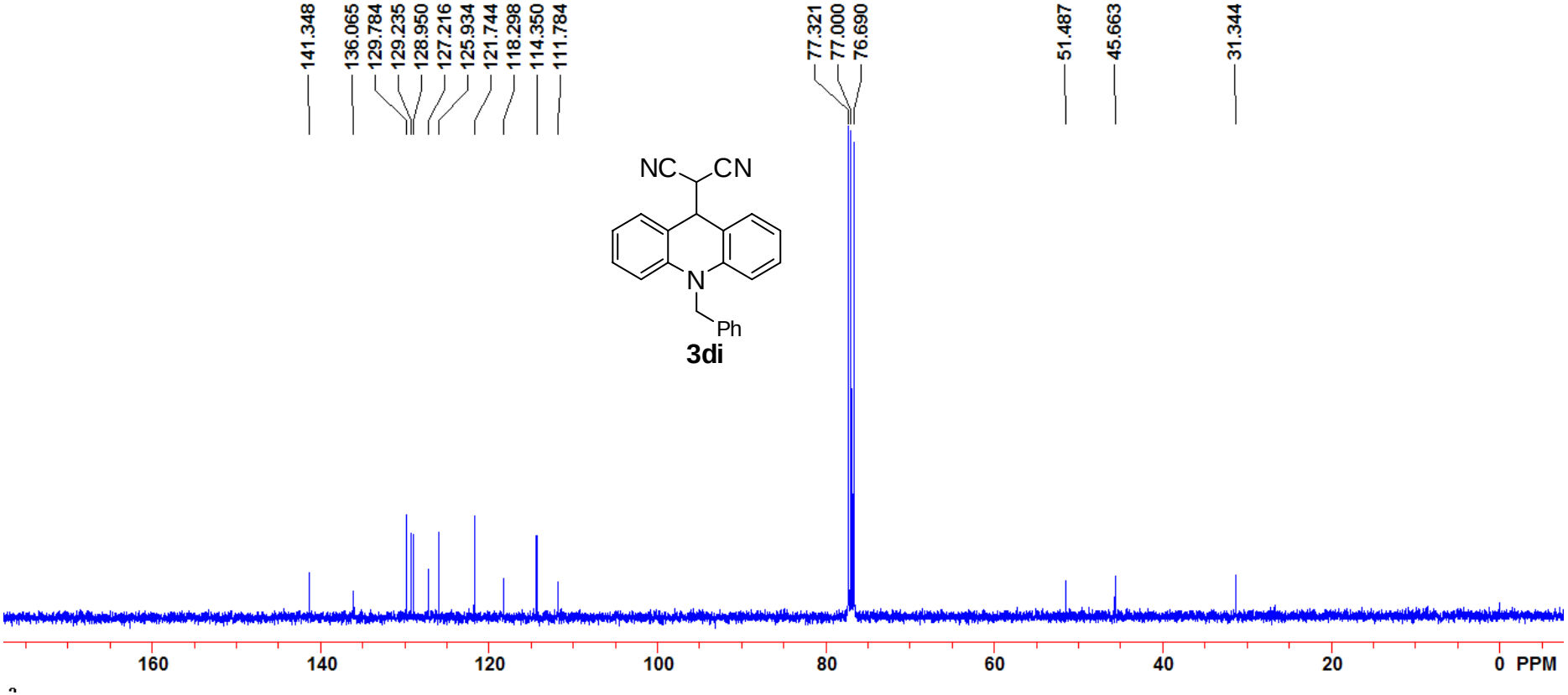

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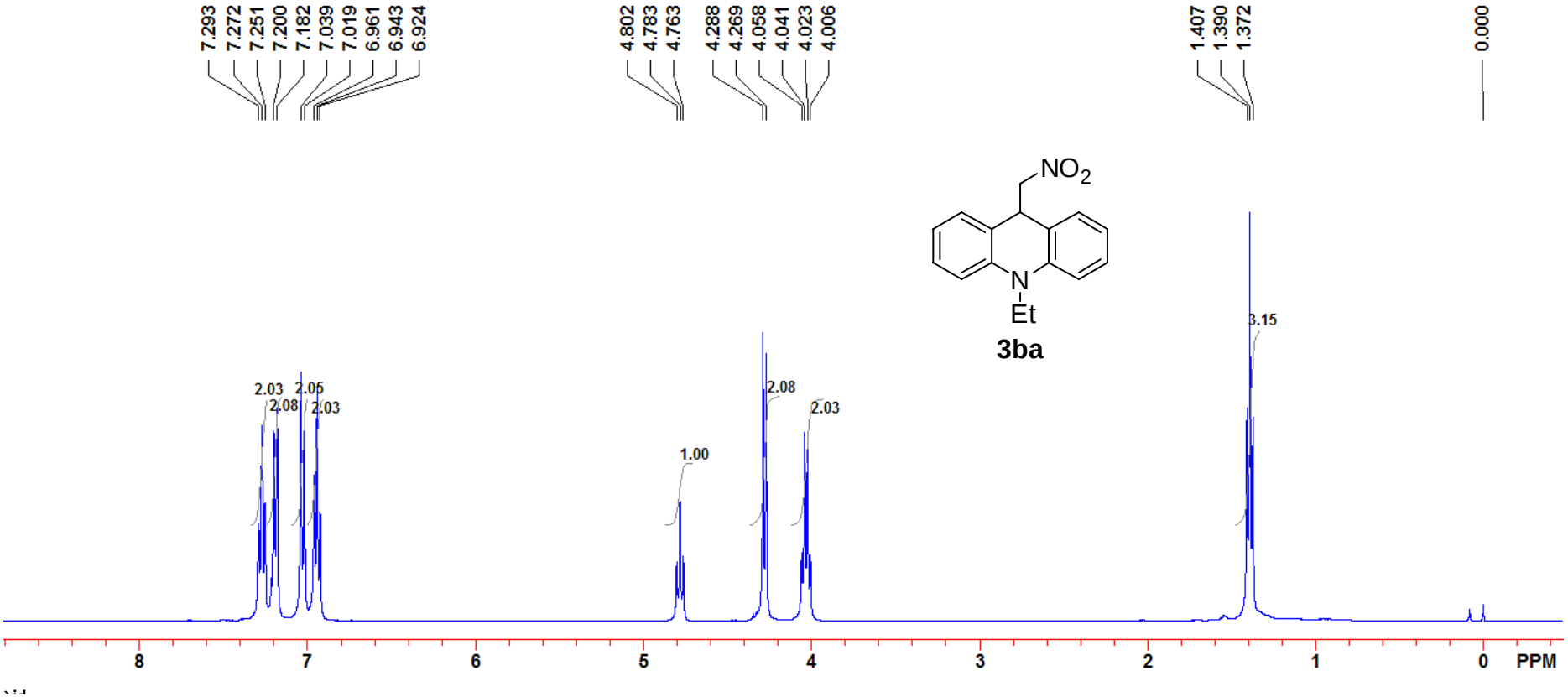

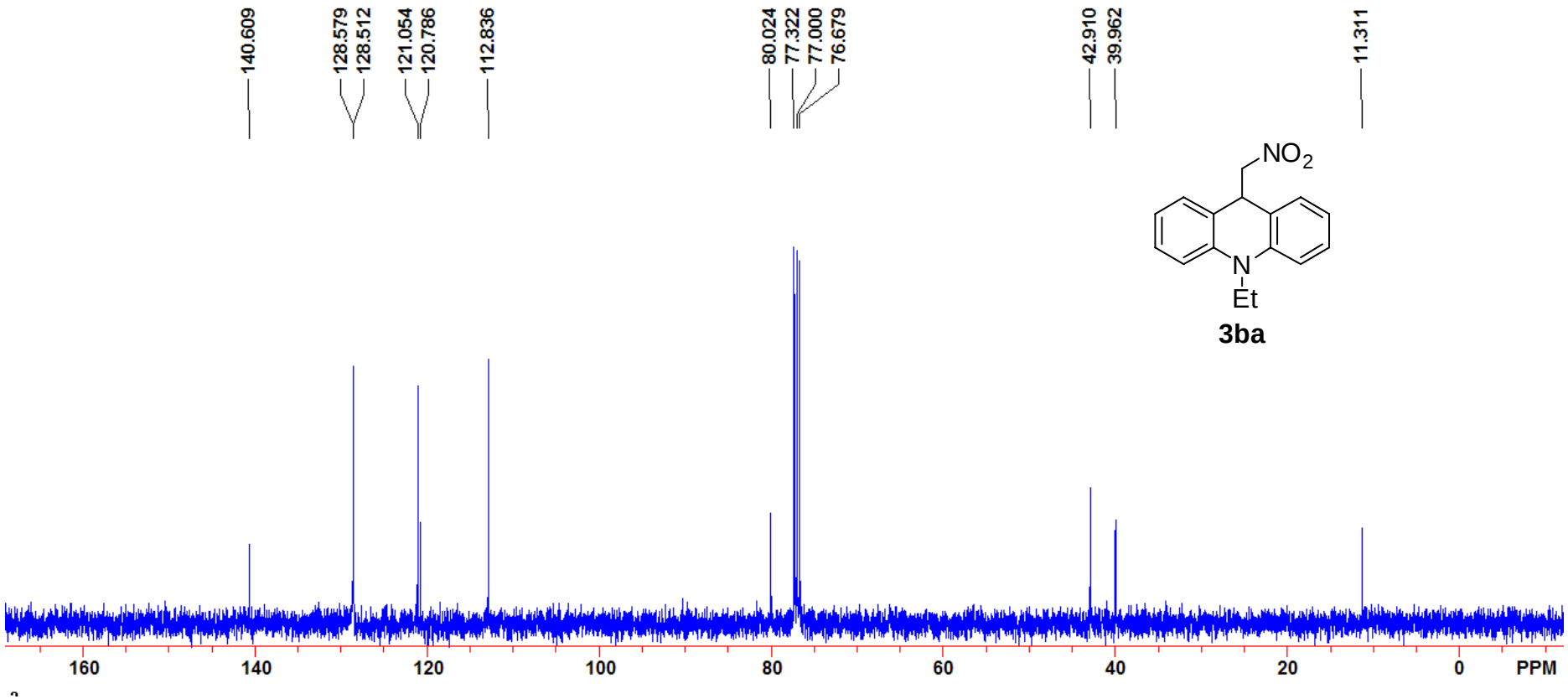

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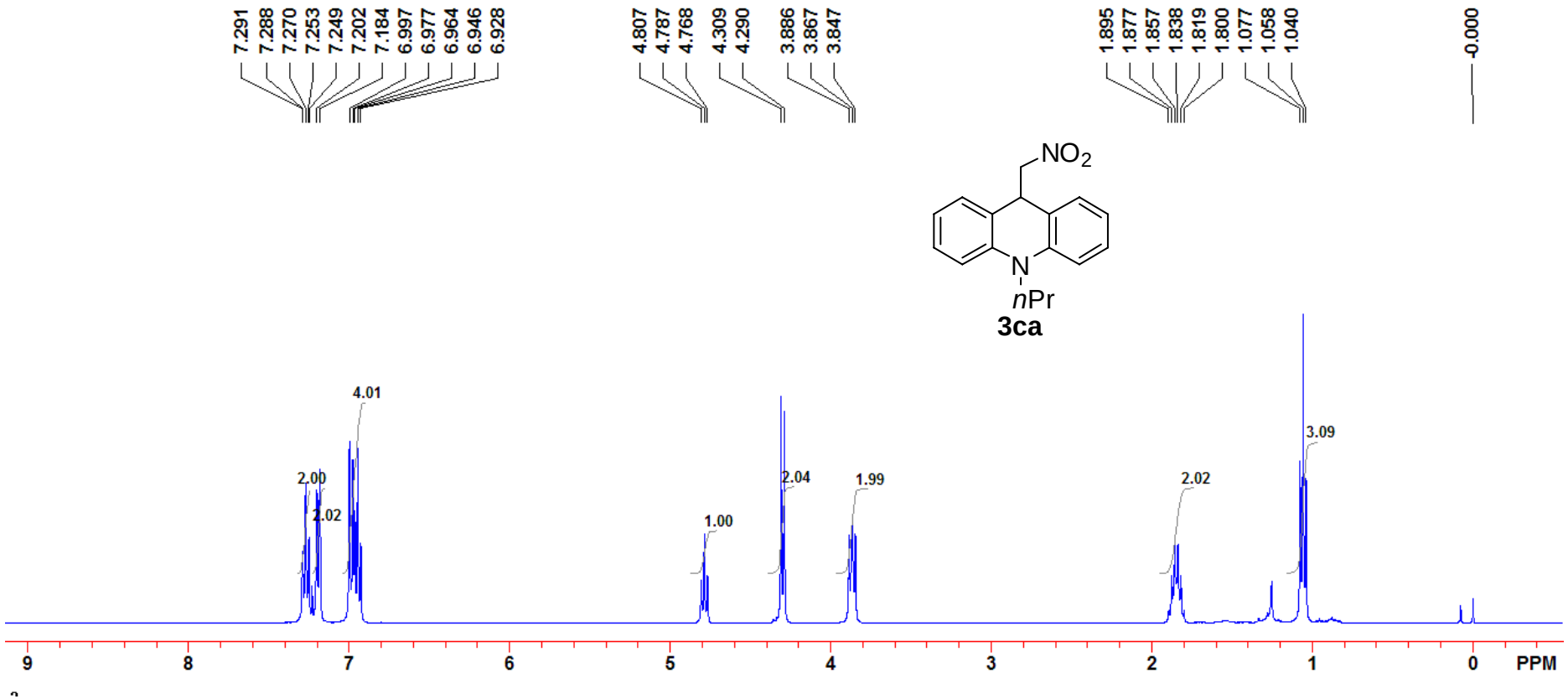

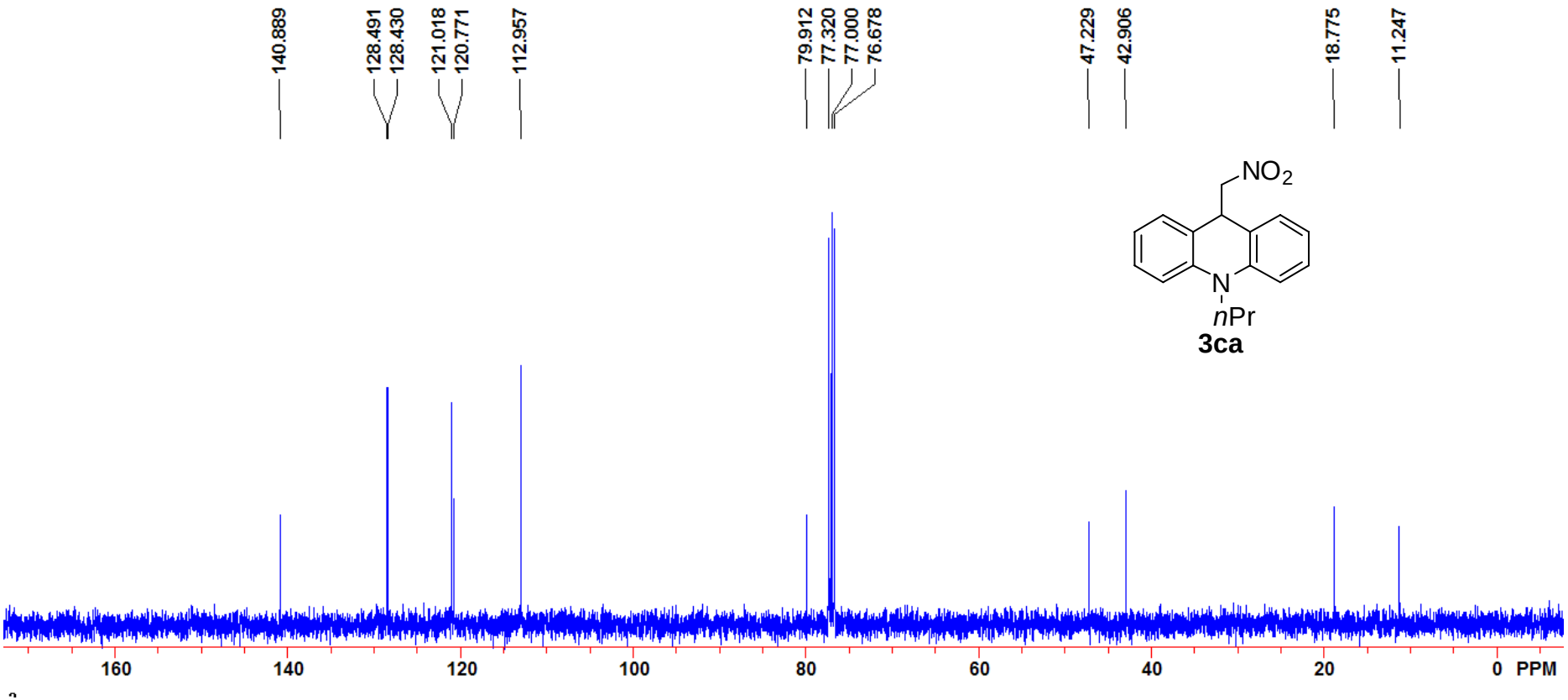

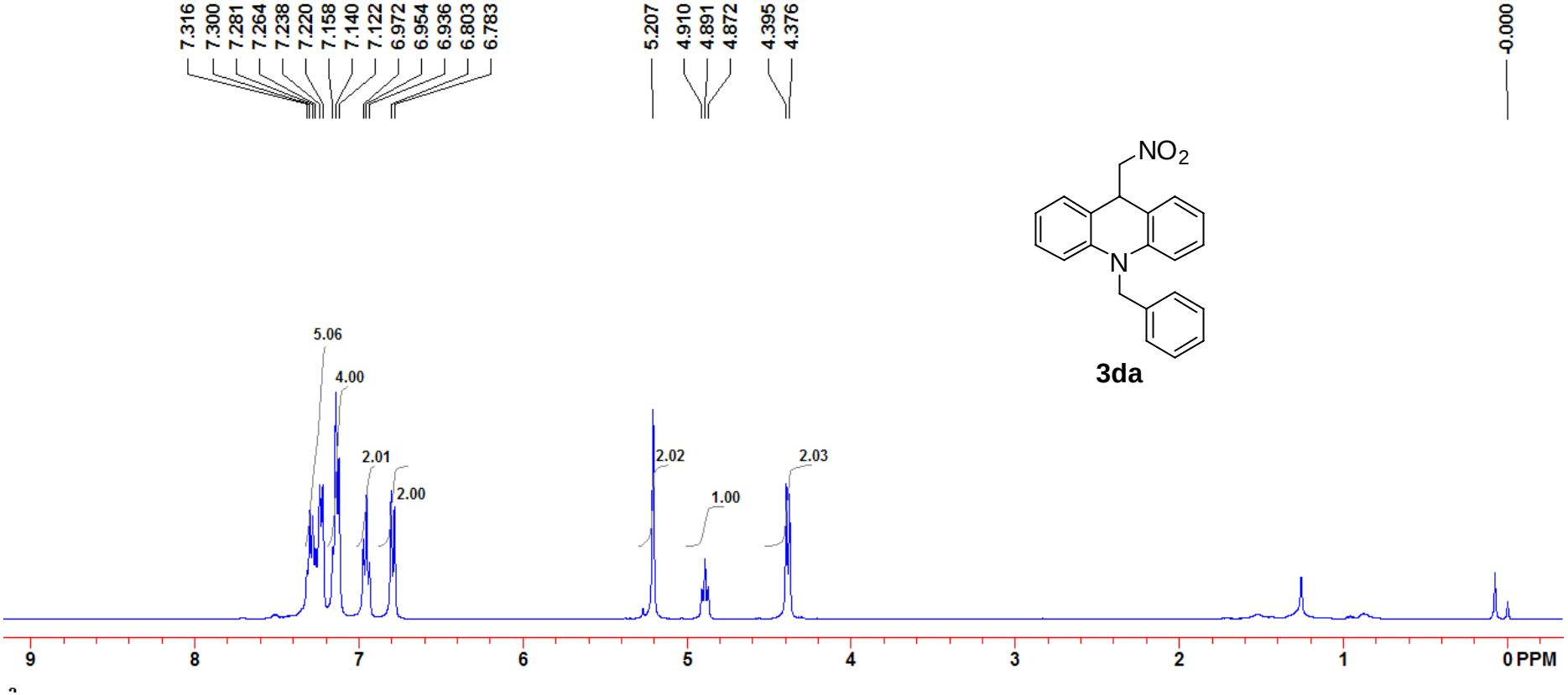

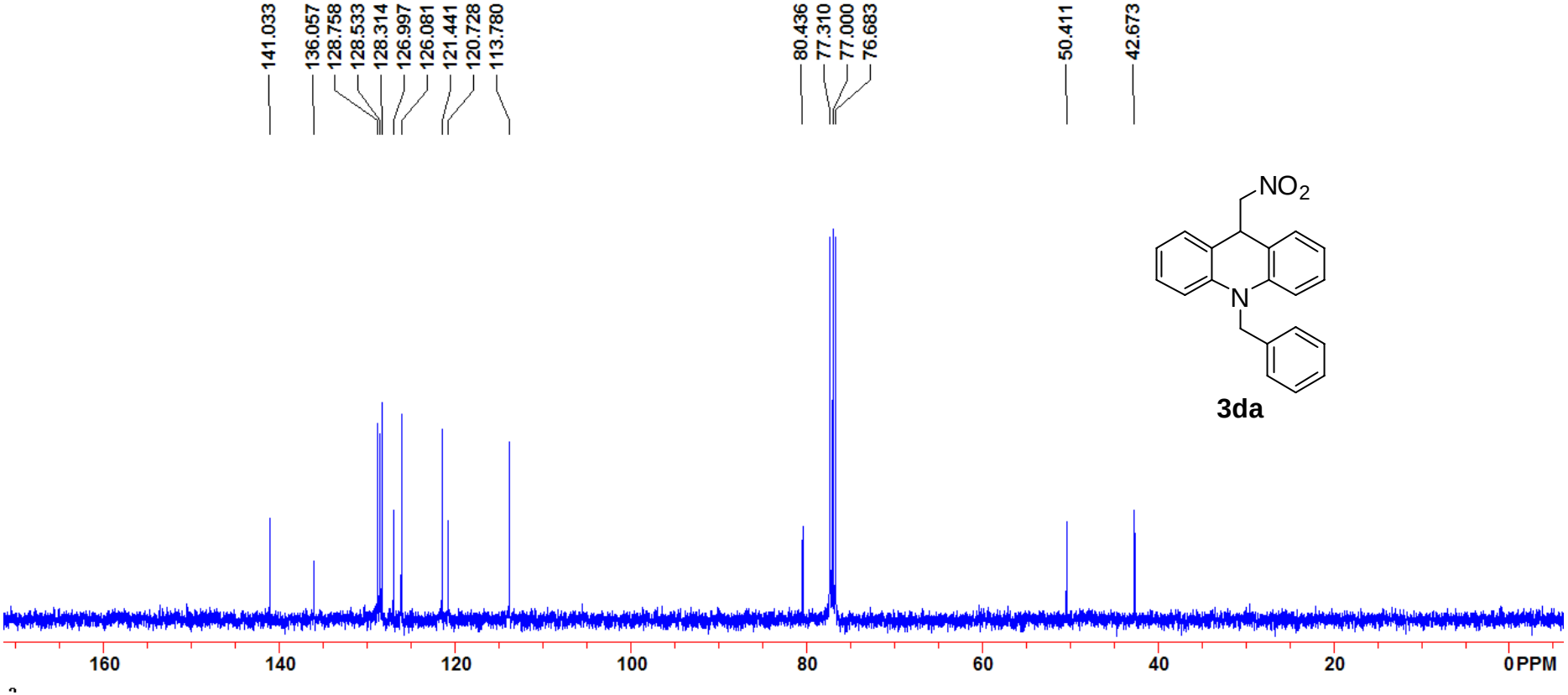

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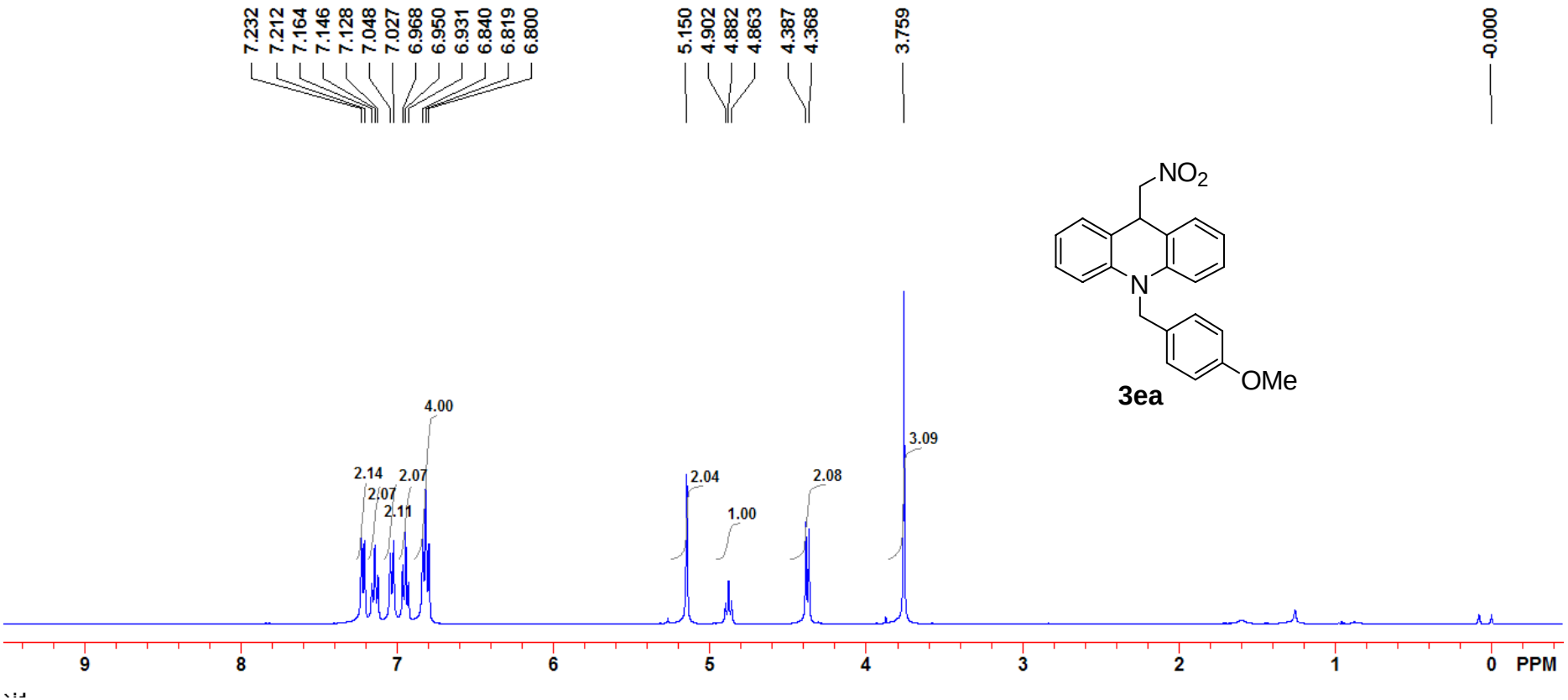

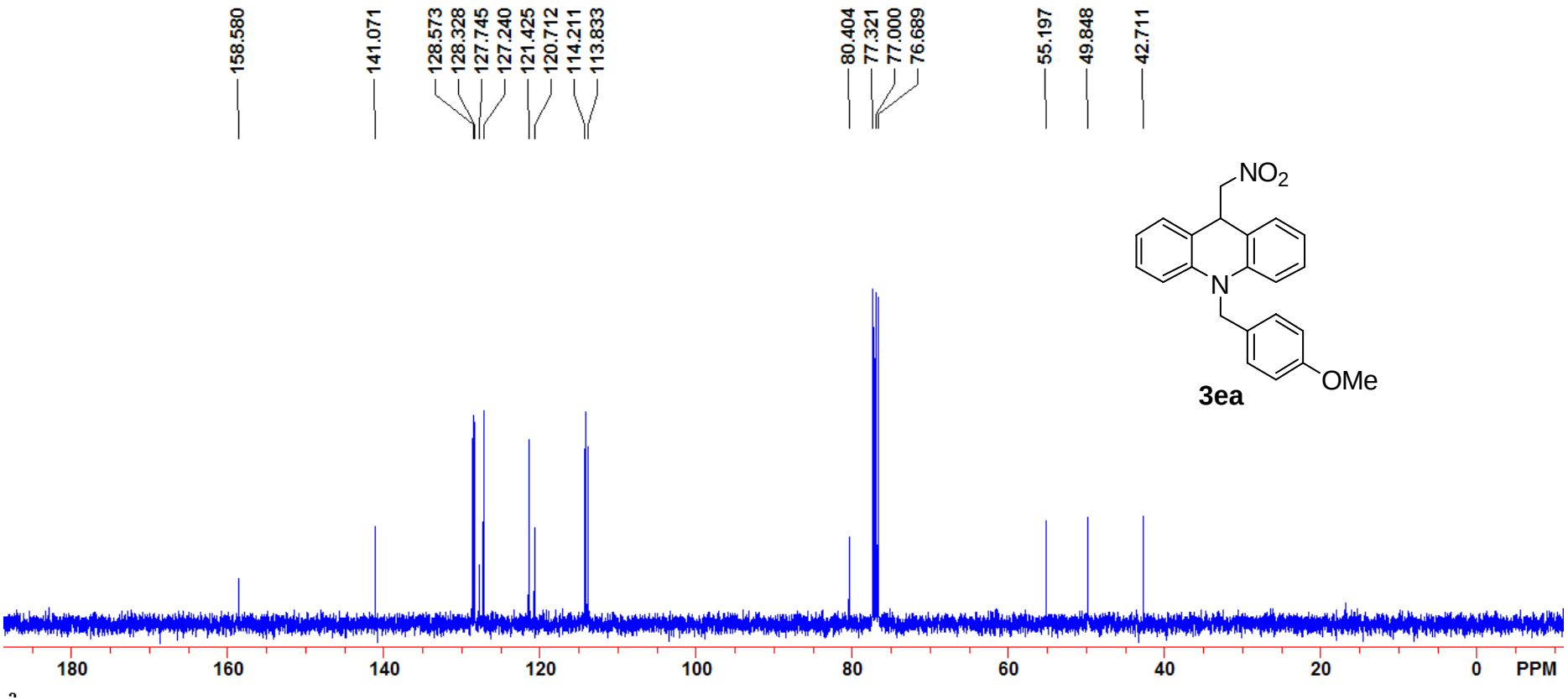

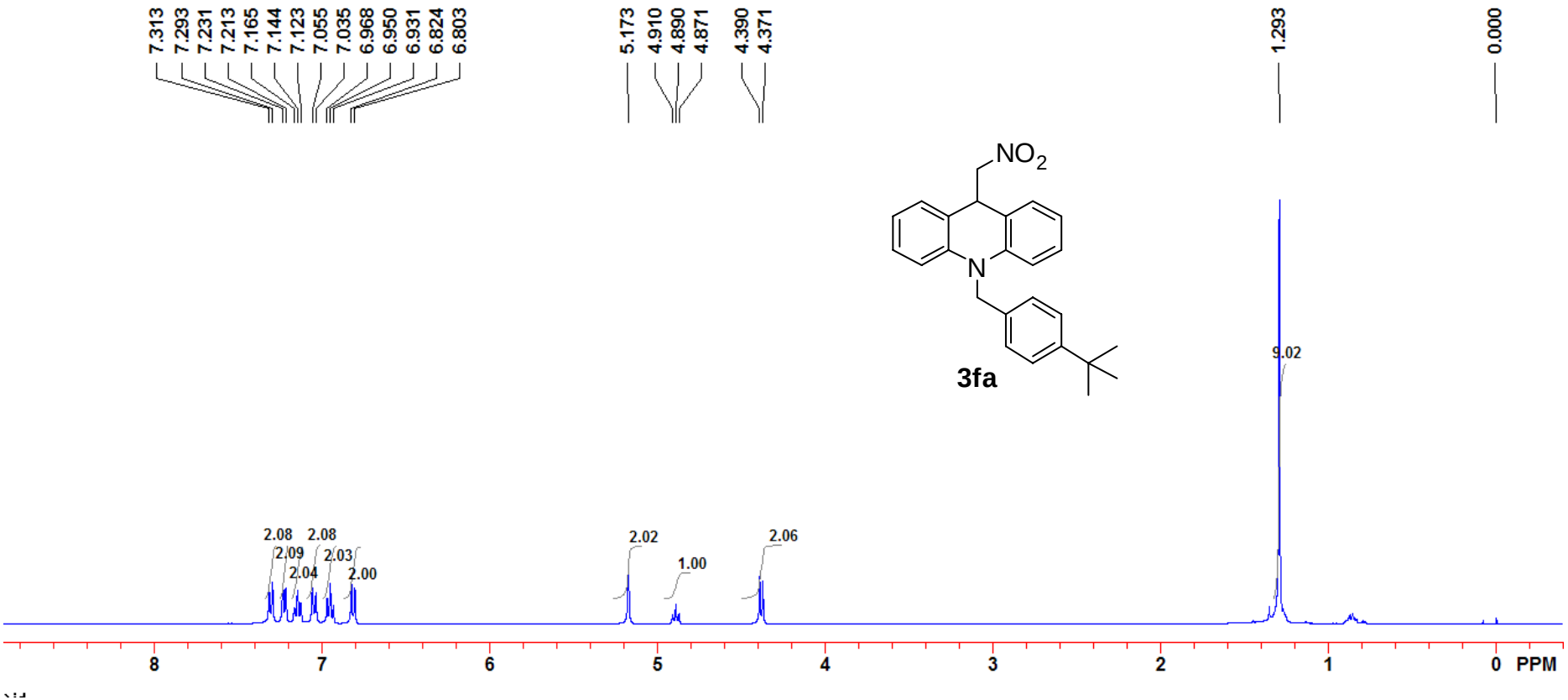

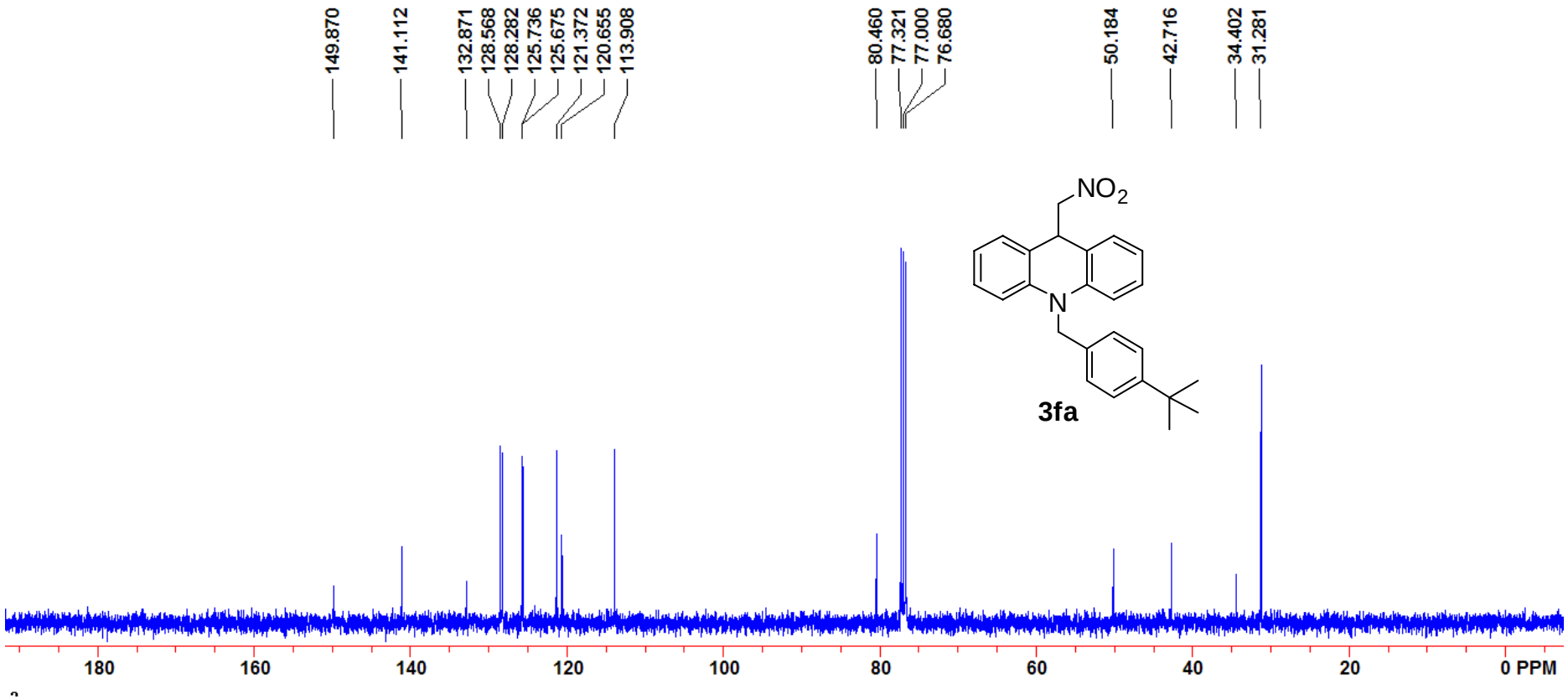

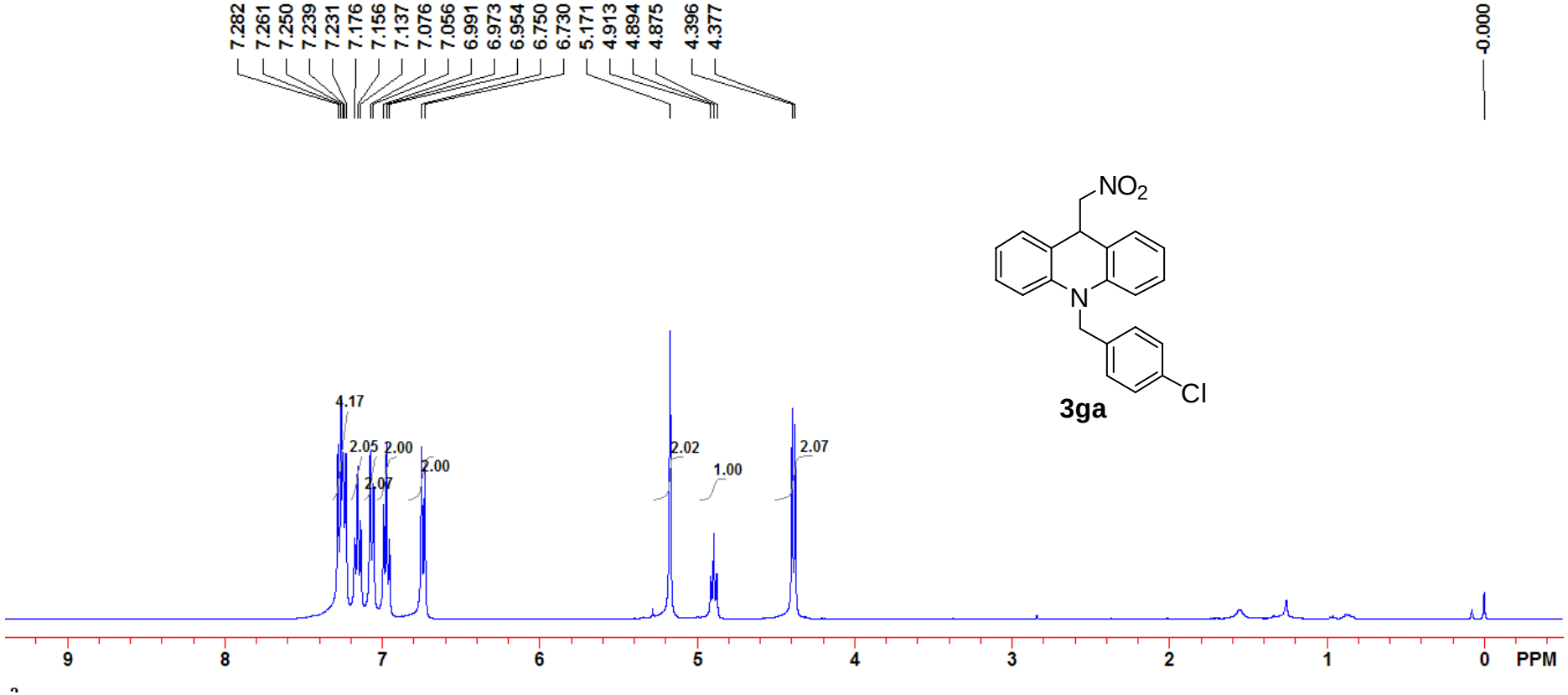

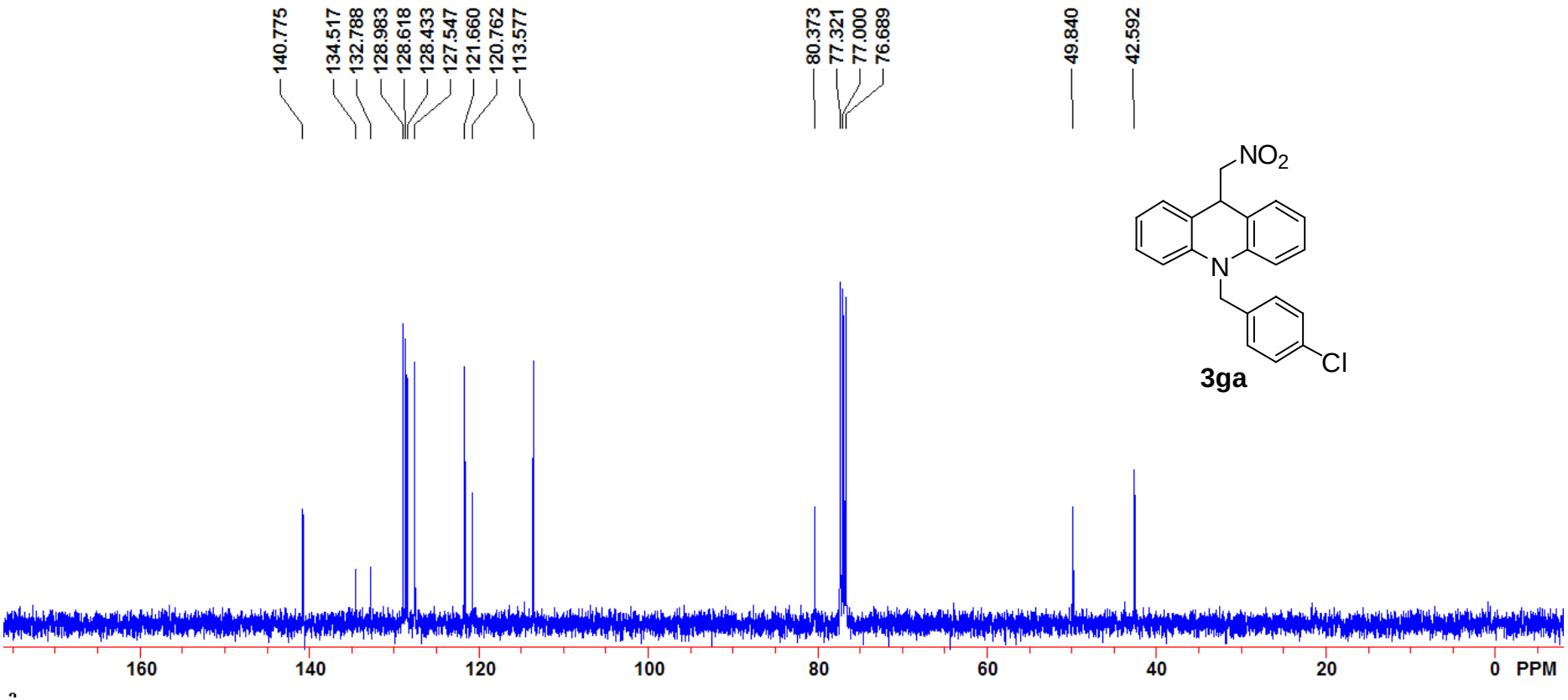

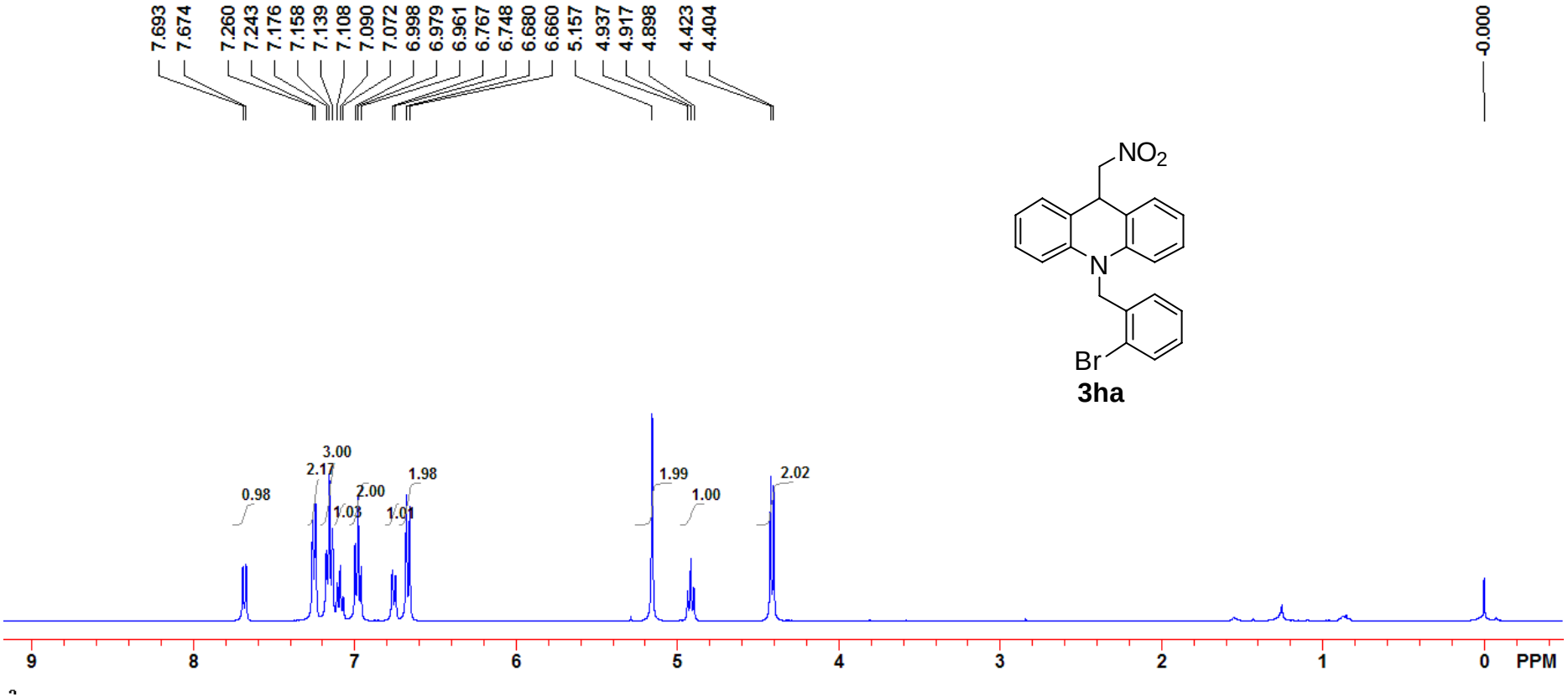

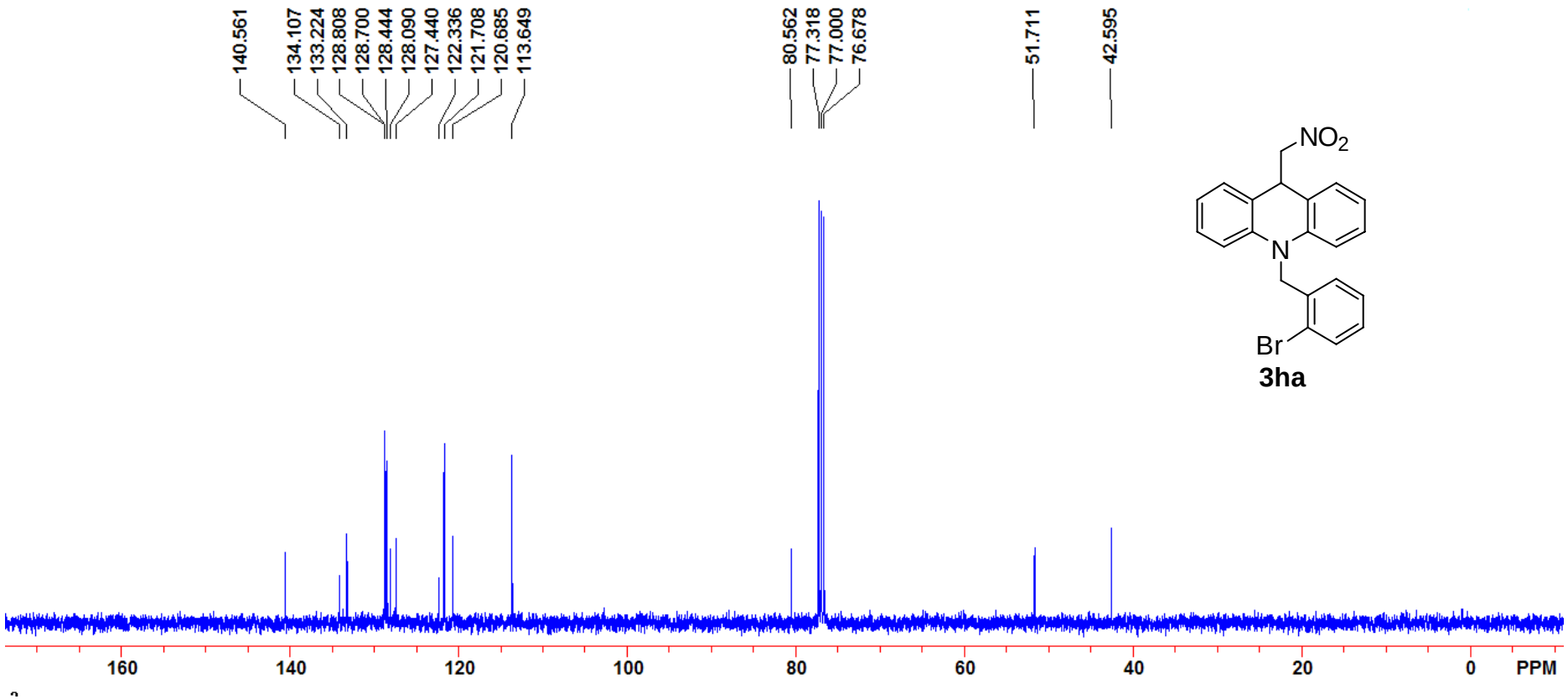

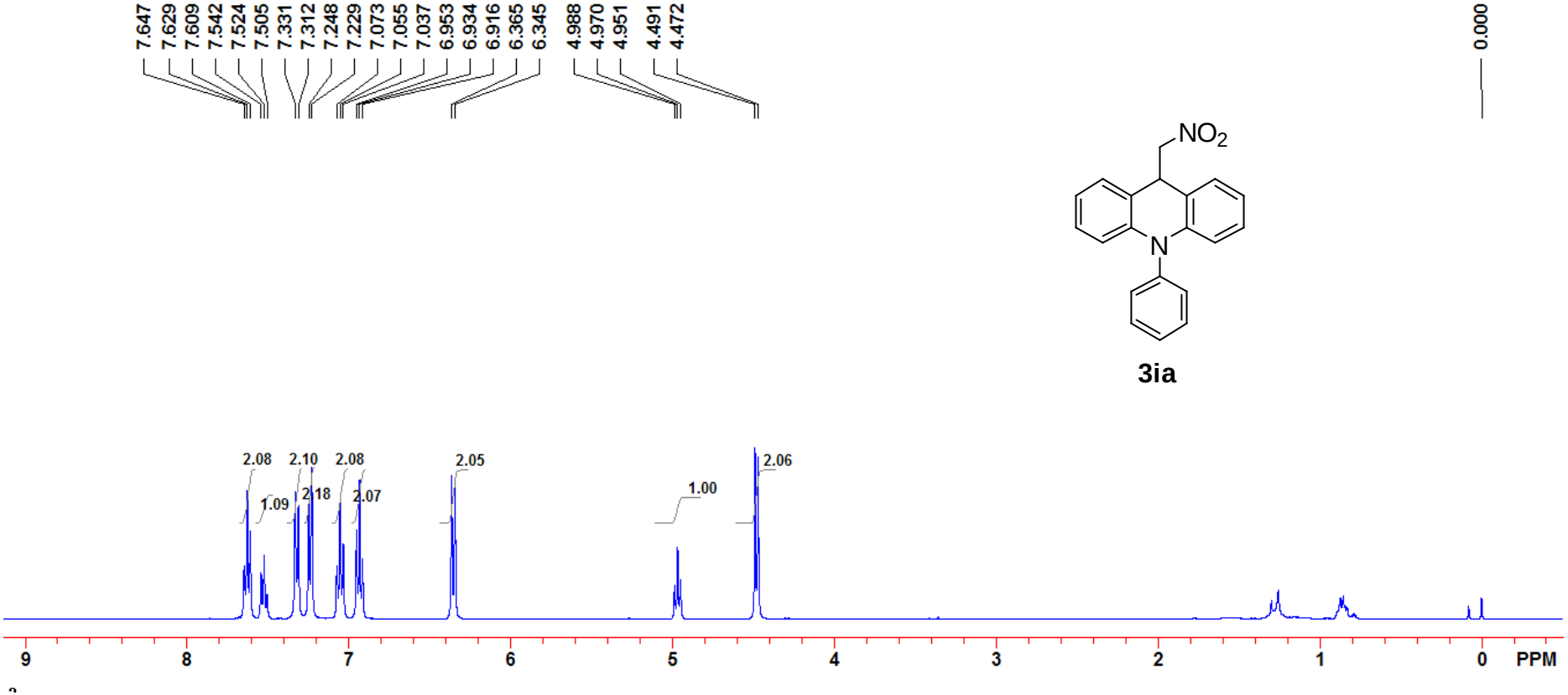

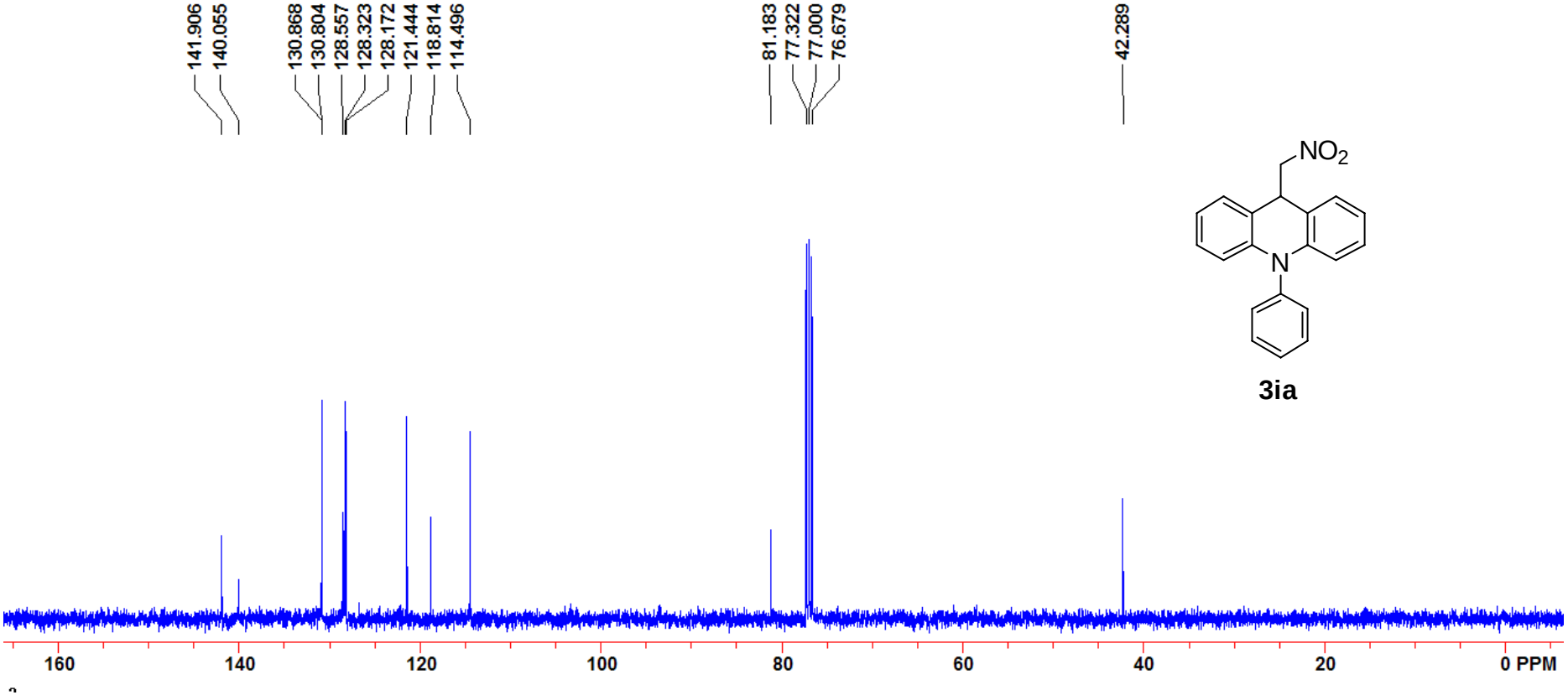

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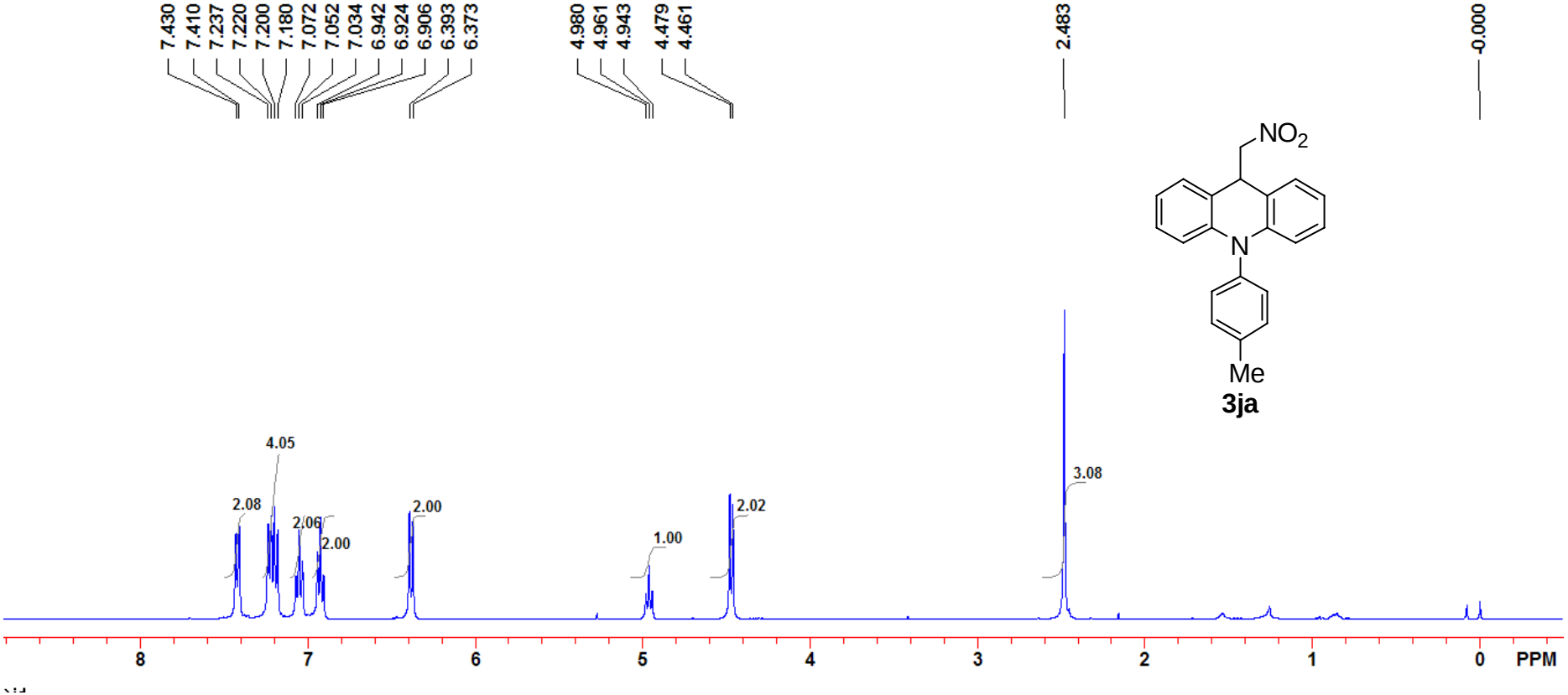

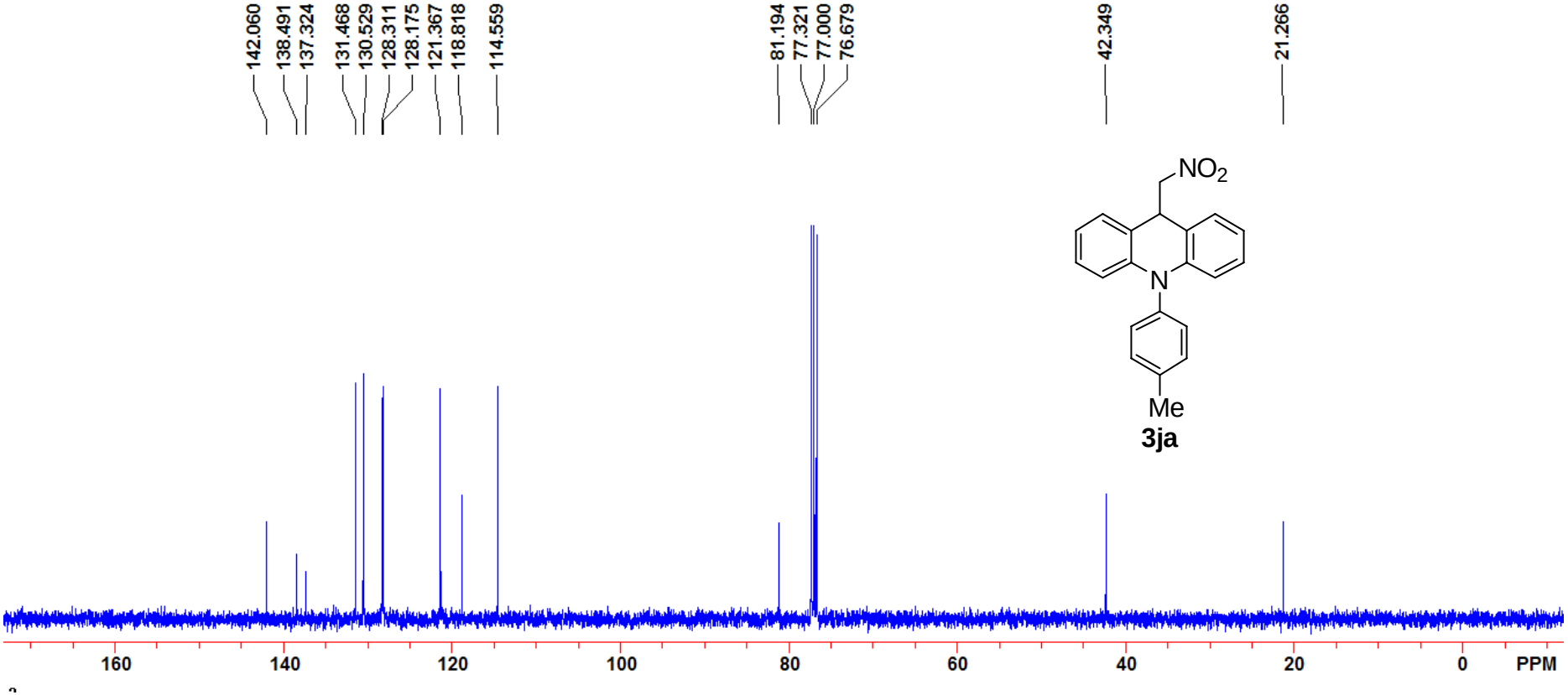

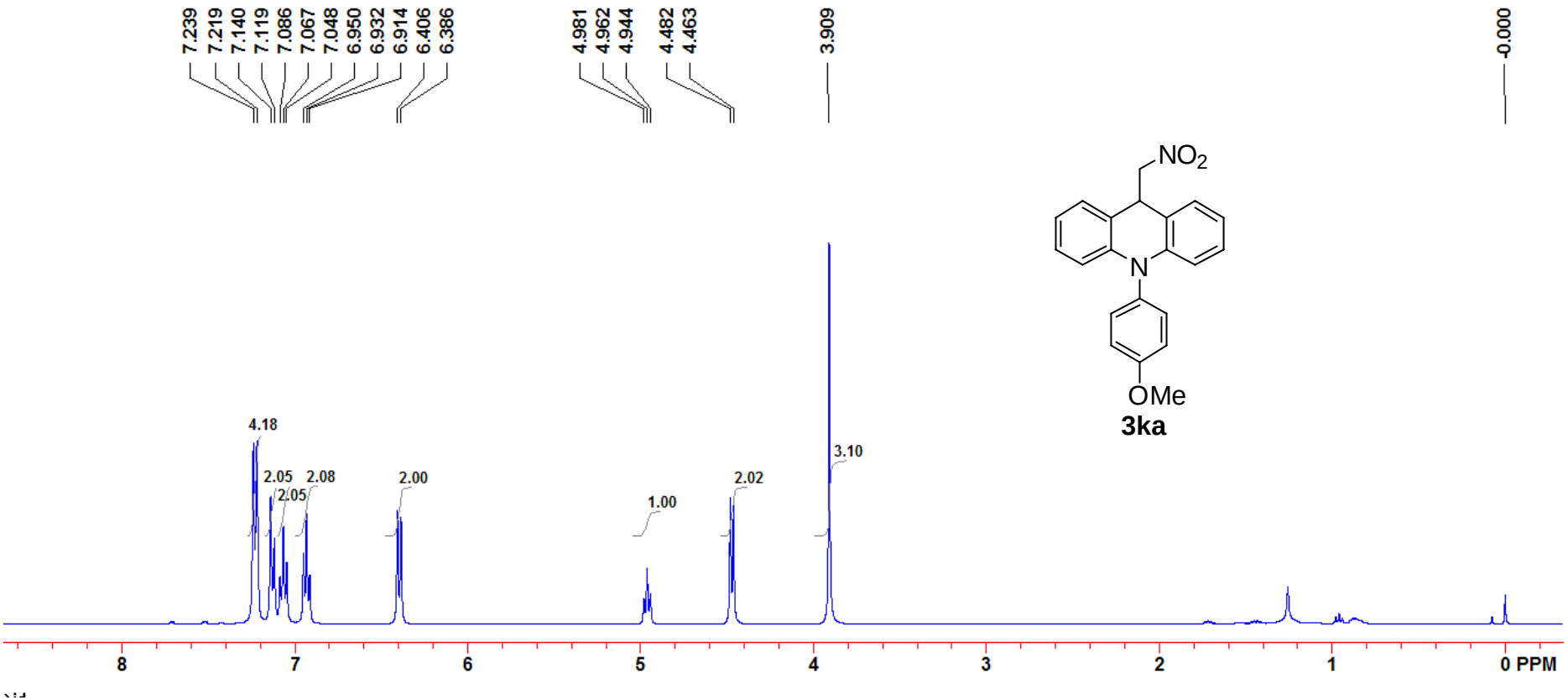

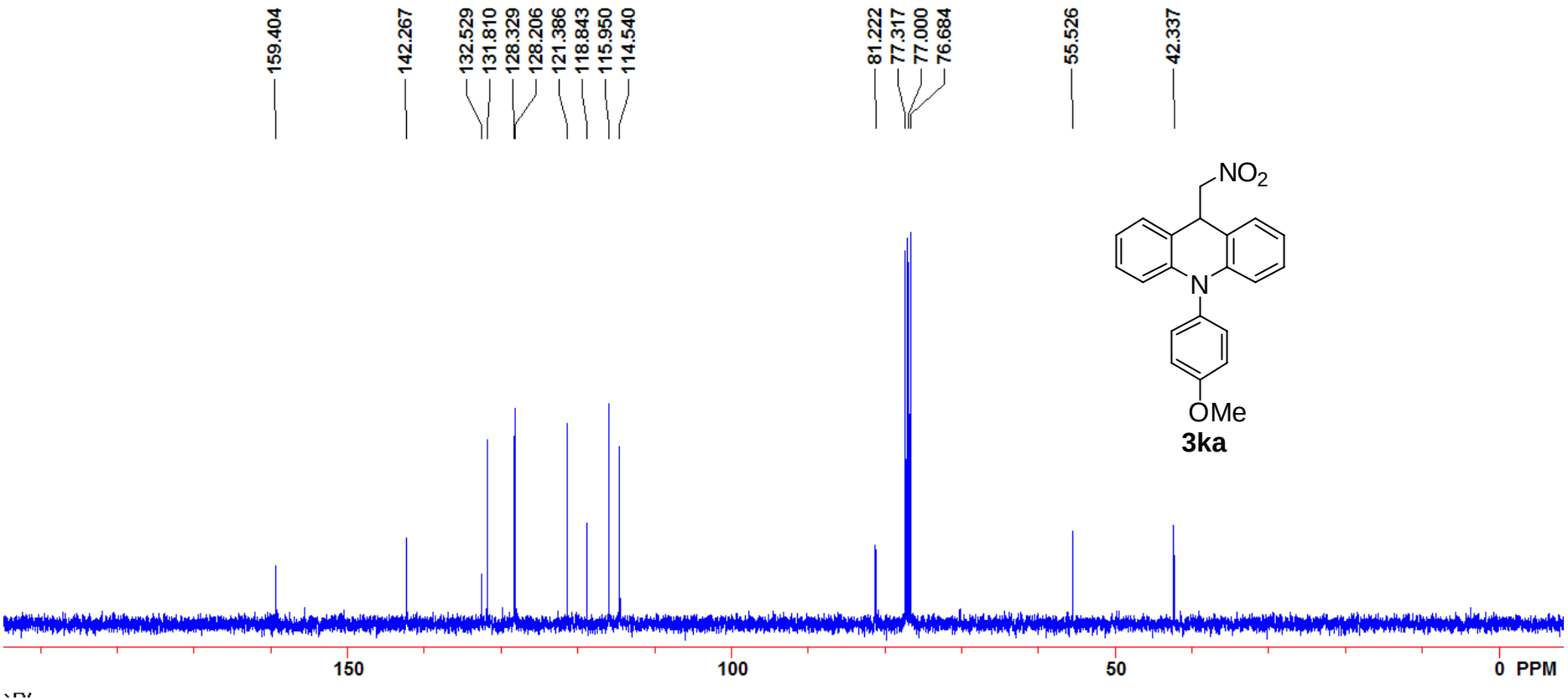

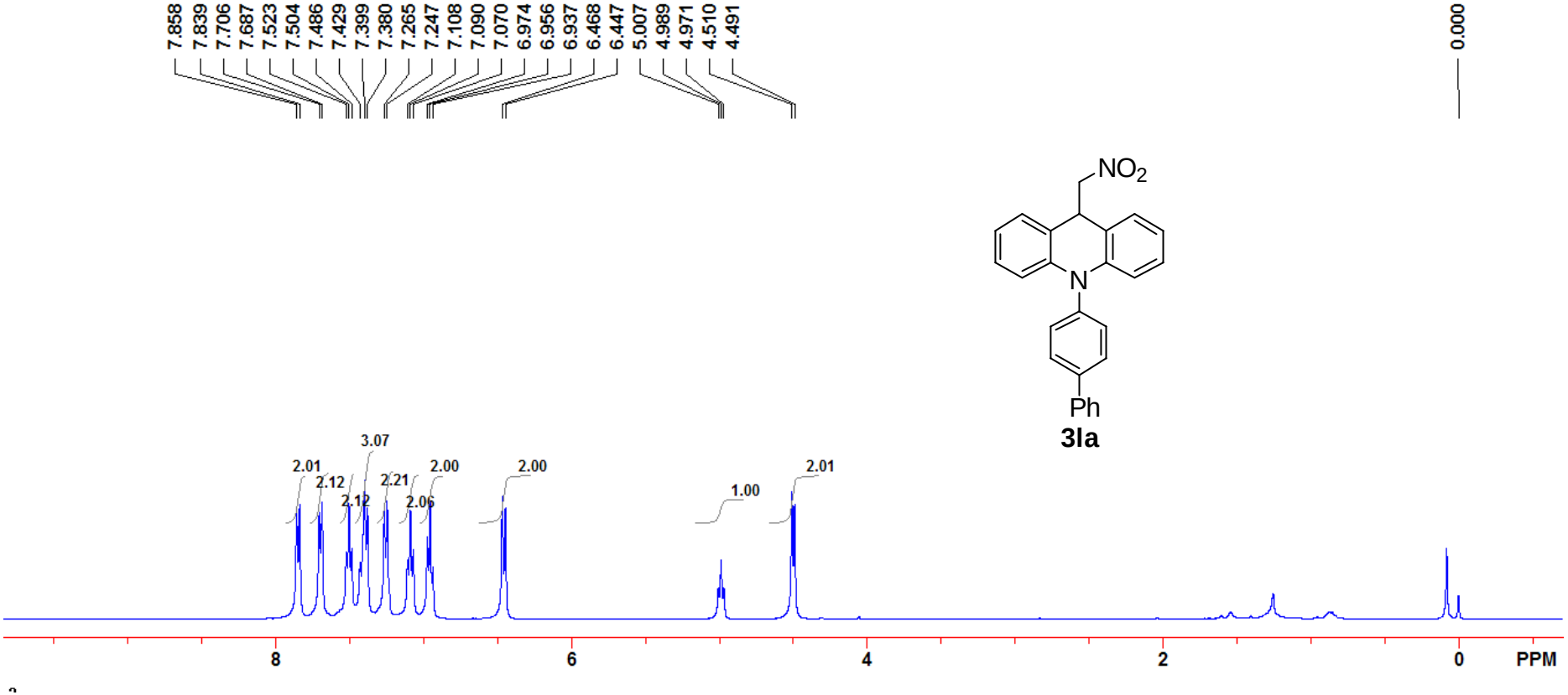

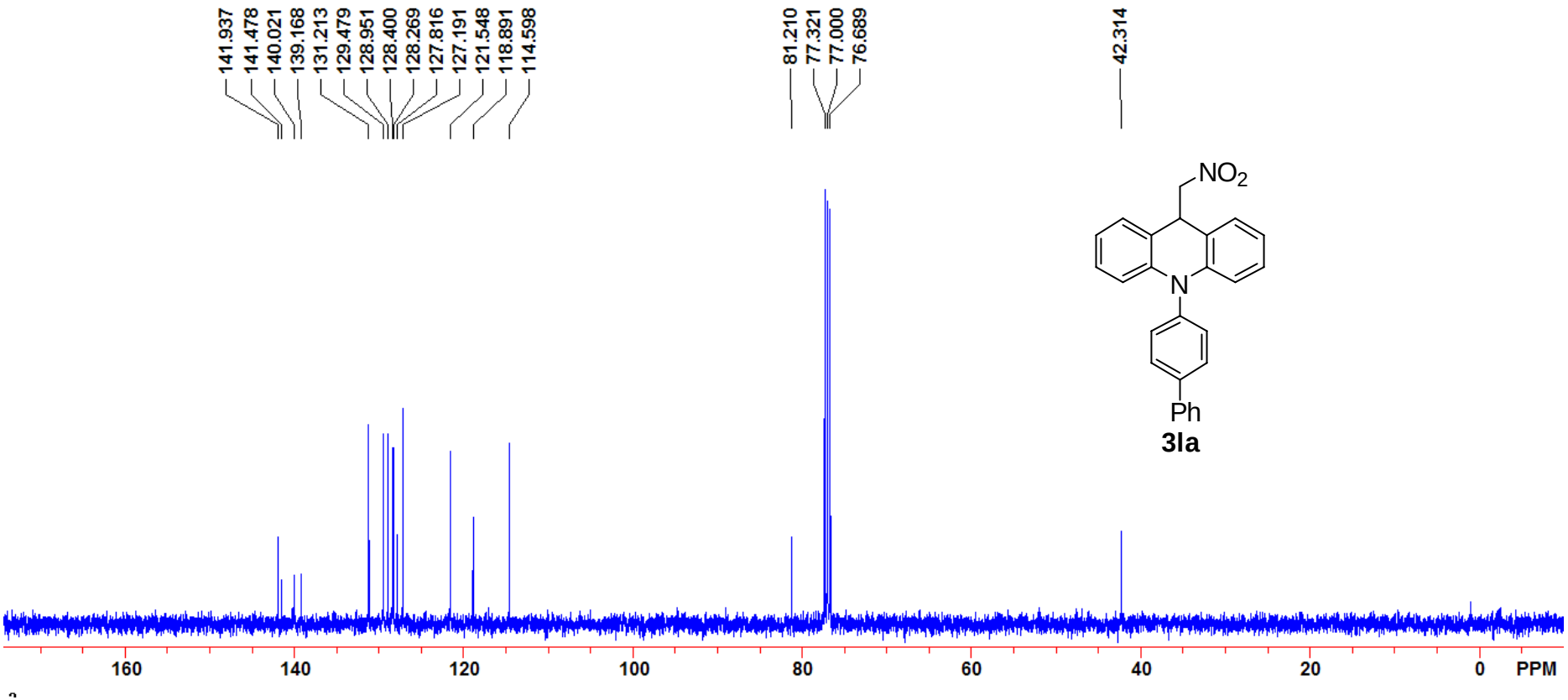

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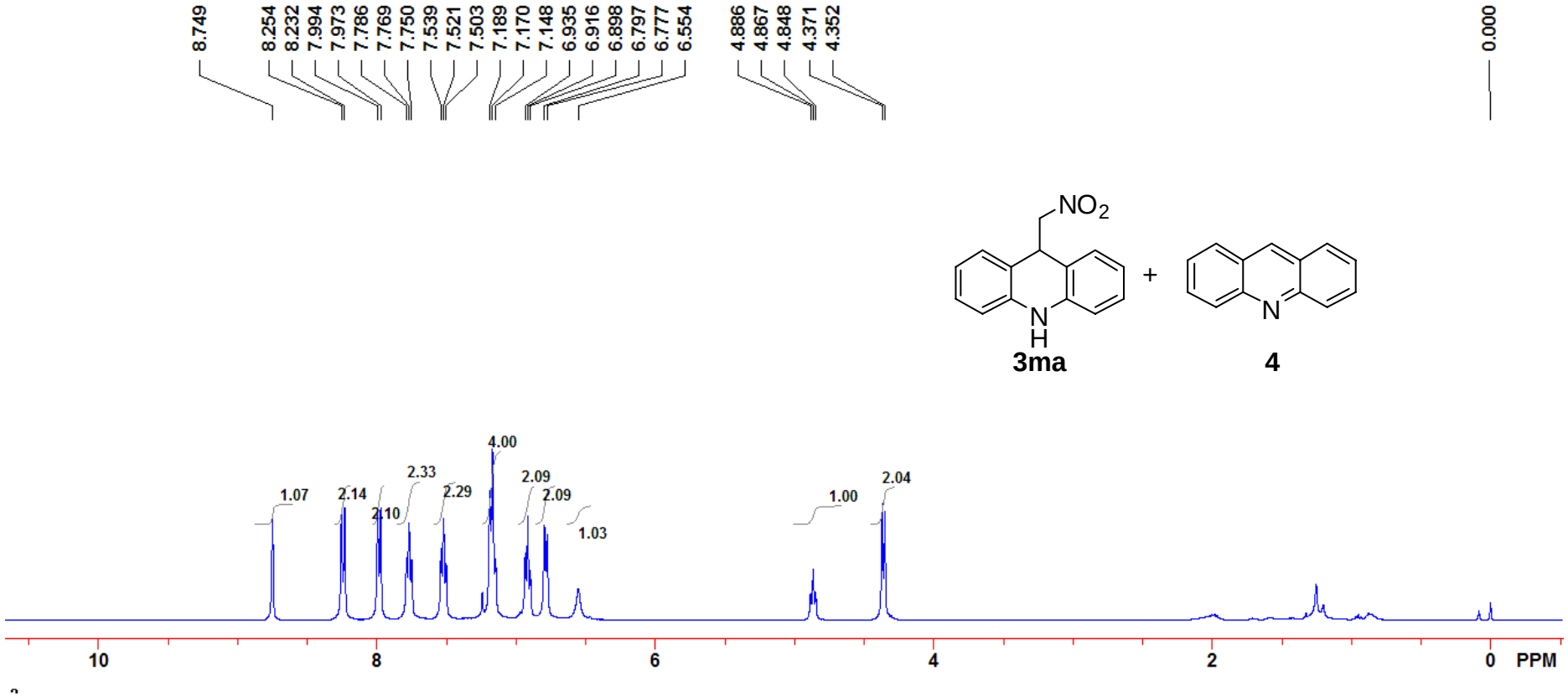

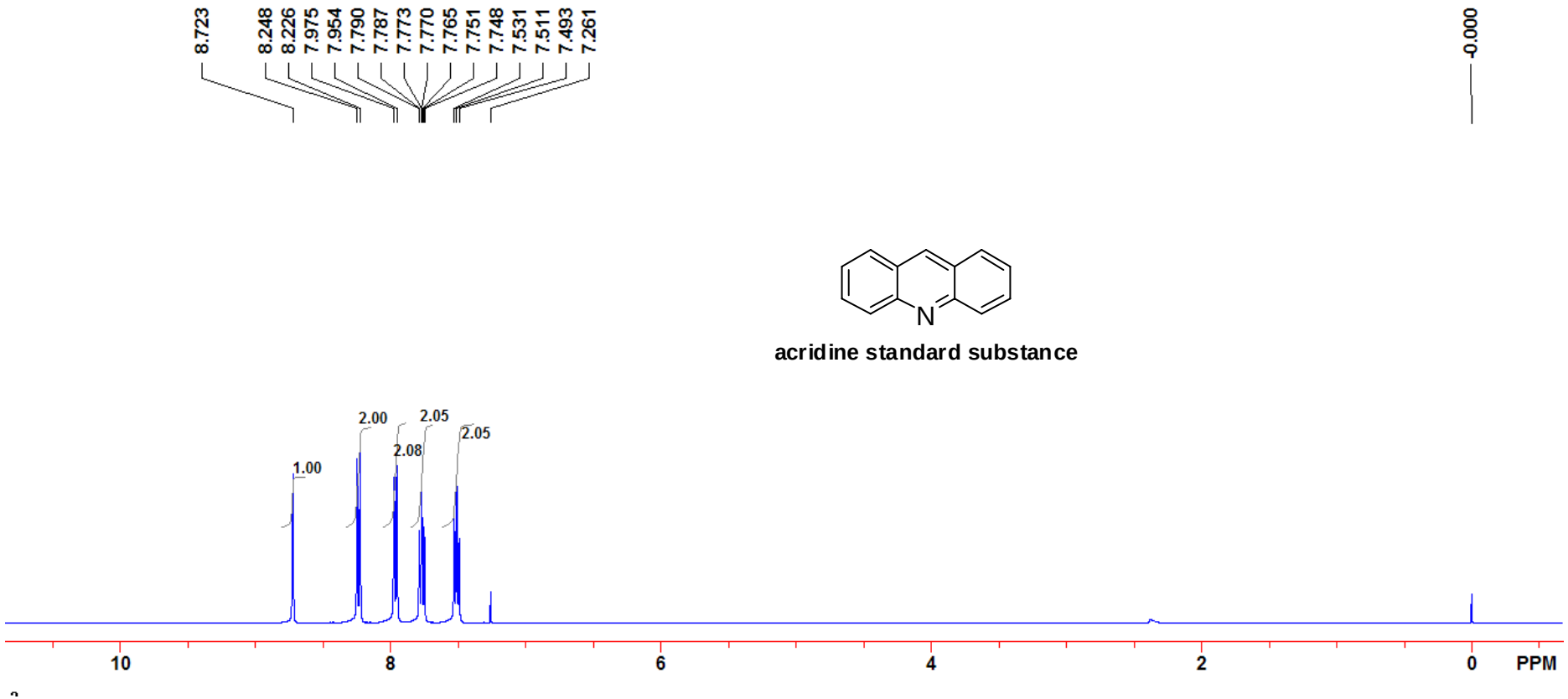

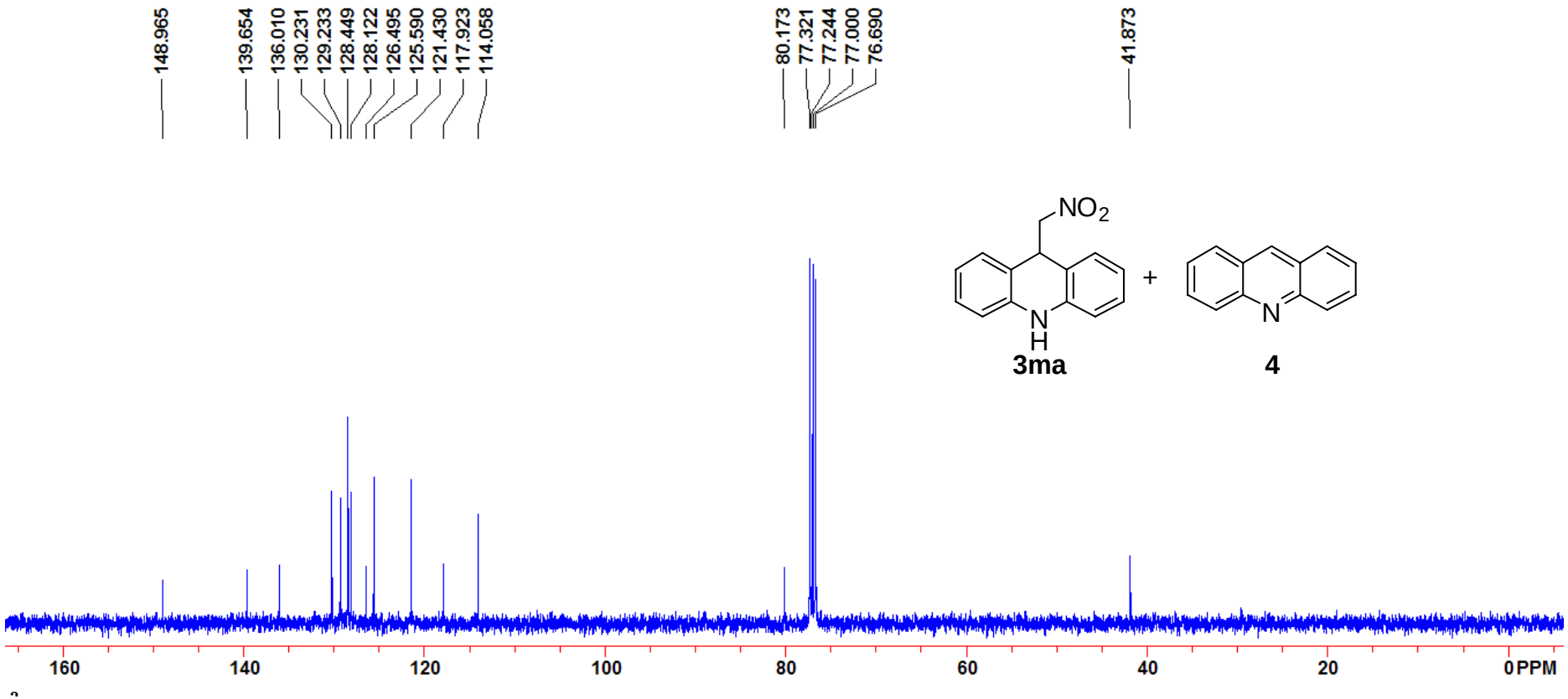

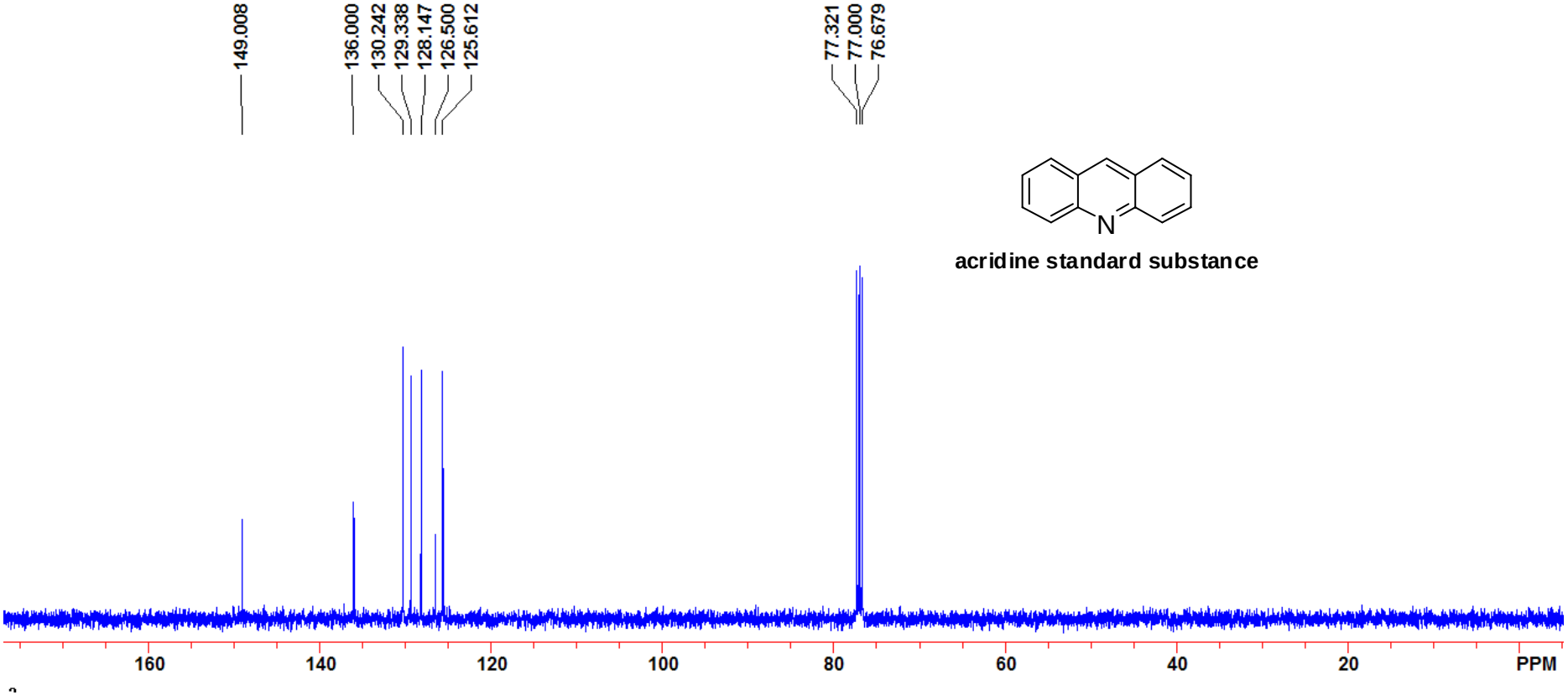

acridine standard substance