Supporting Information

Organophotoredox-catalyzed cyanoalkylation of 1,4-quinones

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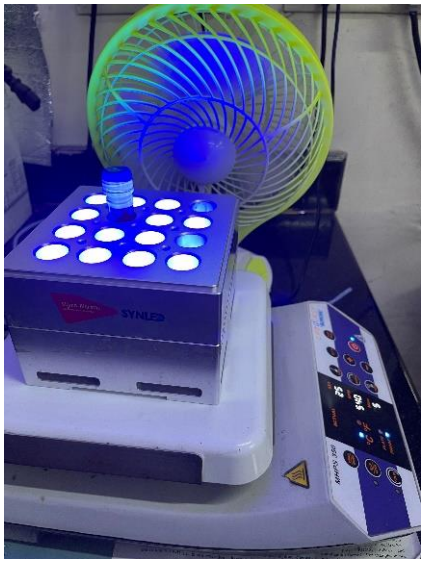
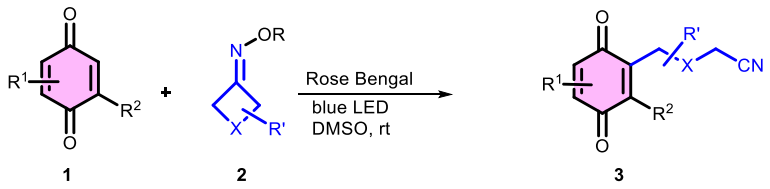
1. General information:

Unless otherwise noted, reagents obtained from commercial suppliers were used without further purification. Reactions were monitored by silica gel thin-layer chromatography (TLC). Silica gel (100-200 mesh) packed in glass column was used for the column chromatography. NMR spectra were recorded at 400, 500 MHz (H) and at 101, 125 MHz (C), respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.0 ppm) as internal standard, and coupling constants (J) are measured in hertz (Hz). High-resolution mass spectra (HRMS) were recorded using ESI-TOF techniques. Melting points of solids were recorded using Electrothermal (IA9100) melting point apparatus. Irradiation was performed with *syn*LED parallel photoreactor (blue LED, 465nm) purchased from Sigma-Aldrich.



2. Experimental procedures:

General procedure for the visible-light promoted cyanoalkylation of quinones:



Quinone **1** (0.3 mmol), oxime ester **2** (0.36 mmol) and 2 mol% of Rose Bengal were weighed in a vial and DMSO (3 mL) was added to this mixture. The vial was back filled with N_2 and it was introduced into the *syn*LED parallel photoreactor (12 W blue LED 465 nm). After completion of reaction (6 hours), the resulting mixture was then diluted with ethyl acetate (15 mL), and washed successively with water (10 mL × 2), aq. $NaHCO_3$ solution (10 mL × 2) and brine solution (10 mL × 2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to get the desired compound **3**.

Quinones **1a-1d** and **1j-1n** are commercially available. Quinones **1e-1i** were synthesized from the known procedures available in the literature[1]. Oxime esters were prepared by the known procedures in the literature[2].

Analytical data of the cyanoalkylated compounds 3:

4-(3-Hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)butanenitrile (3aa): Yellow solid (52.8 mg, 73%); mp = 130 – 132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 7.7, 1.2 Hz, 1H), 8.09 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.78 (td, *J* = 7.6, 1.4 Hz, 1H), 7.70 (td, *J* = 7.6, 1.3 Hz, 1H), 7.48 (s, 1H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.41 (t, *J* = 7.3 Hz, 2H), 1.95 (p, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 181.1, 153.7, 135.2, 133.2, 132.8, 129.4, 126.9, 126.3, 121.8, 119.6, 24.1, 22.4, 17.1; HRMS(ESI) calcd for $C_{14}H_{12}O_3N$ $[M+H]^+$ = 242.0812, found = 242.0804.

4-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)butanenitrile (3ba): Yellow solid (34.5 mg, 51%); mp = 85 – 86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.05 (m, 2H), 7.78 – 7.72 (m, 2H), 6.84 (s, 1H), 2.77 – 2.70 (m, 2H), 2.46 (t, *J* = 7.1 Hz, 2H), 1.99 (p, *J* =7.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.0, 184.9, 149.3, 135.9, 134.1, 134.0, 132.2, 126.8, 126.4, 119.0, 29.1, 24.2, 17.2; HRMS(ESI) calcd for $C_{14}H_{11}O_2N$ $[M]^+$ = 225.0789, found = 225.0795.

4-(3-Methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)butanenitrile (3ca): Yellow solid (47.4 mg, 66%); mp = 139 – 140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.03 (m, 2H), 7.73 – 7.67 (m, 2H), 2.79 (t, *J* = 7.8 Hz, 2H), 2.45 (t, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.87 (p, *J* = 7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.1, 184.7, 144.9, 144.6, 133.8, 133.8, 132.1, 132.1, 126.6, 126.5, 119.4, 26.3, 24.6, 17.6, 13.0; HRMS(ESI) calcd for $C_{15}H_{14}O_2N$ $[M+H]^+$ = 240.1019, found = 240.1017.

4-(3-Chloro-1,4-dioxo-1,4-dihydronaphthalen-2-yl)butanenitrile (3da): Red sticky mass (47.5 mg, 61%)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 – 8.06 (m, 2H), 7.82 – 7.70 (m, 2H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.48 (t, *J* = 7.2 Hz, 2H), 1.96 (p, *J* = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 182.3, 177.5, 146.1, 144.4, 134.6, 134.4, 131.6, 131.4, 127.5, 127.3, 119.1, 27.6, 23.7, 17.5; HRMS(ESI) calcd for $C_{14}H_{10}O_2NCl$ $[M]^+$ = 259.0400, found = 259.0393.

3-(3-Cyanopropyl)-1,4-dioxo-1,4-dihydronaphthalen-2-yl acetate (3ea): Yellow semi-solid (63.7 mg, 75%)**;** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.08 (m, 2H), 7.80 – 7.71 (m, 2H), 2.75 (t, *J* = 7.4 Hz, 2H), 2.46 (s, 3H), 2.41 (t, *J* = 6.9 Hz, 2H), 1.91 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.5, 177.9, 168.5, 152.3, 137.1, 134.5, 134.3, 132.0, 130.9, 126.9, 119.3, 24.3, 23.2, 20.6, 17.2; HRMS(ESI) calcd for $C_{16}H_{13}O_4NNa$ $[M+Na]^+$ = 305.0664, found = 305.0662.

3-(3-Cyanopropyl)-1,4-dioxo-1,4-dihydronaphthalen-2-yl pivalate (3fa): Yellow solid (75.1 mg, 77%); mp = 115 – 117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.06 (m, 2H), 7.78 – 7.72

(m, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 1.90 (p, *J* = 7.5 Hz, 2H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 177.9, 176.2, 152.5, 137.1, 134.4, 134.2, 132.1, 131.1, 126.9, 126.9, 119.2, 39.7, 27.3, 24.3, 23.4, 17.3; HRMS(ESI) calcd for $C_{19}H_{19}O_4NNa$ $[M+Na]^+$ = 347.1133, found = 347.1135.

4-(1,4-Dioxo-3-phenoxy-1,4-dihydronaphthalen-2-yl)butanenitrile (3ga): Yellow solid (59.0 mg, 62%); mp = 120 – 122 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.01 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.77 (td, *J* = 7.5, 1.5 Hz, 1H), 7.73 (td, *J* = 7.5, 1.4 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.14 – 7.08 (m, 1H), 6.99 – 6.94 (m, 2H), 2.81 (t, *J* = 7.4 Hz, 2H), 2.42 (t, *J* = 7.3 Hz, 2H), 1.94 (p, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.0, 179.5, 157.3, 154.4, 136.9, 134.4, 134.1, 132.1, 131.4, 130.0, 126.9, 126.8, 123.7, 119.3, 116.2, 24.6, 23.4, 17.4; HRMS(ESI) calcd for $C_{20}H_{15}O_3N$ $[M]^+$ = 317.1051, found = 317.1053.

4-(3-(2-Methoxyphenyl)-1,4-dioxo-1,4-dihydronaphthalen-2-yl)butanenitrile (3ha): Yellow semi-solid (49.7 mg, 50%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.13 (m, 1H), 8.13 – 8.09 (m, 1H), 7.80 – 7.70 (m, 2H), 7.47 – 7.40 (m, 1H), 7.10 – 7.04 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 3.77 (s, 3H), 2.60 – 2.53 (m, 2H), 2.28 – 2.20 (m, 2H), 1.80 (p, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.3, 183.7, 156.6, 146.3, 145.9, 133.9, 133.7, 132.4, 132.3, 130.7, 129.8, 126.9, 126.6, 122.6, 120.9, 119.3, 111.4, 55.7, 27.5, 24.7, 17.2; HRMS(ESI) calcd for $C_{21}H_{17}O_3N$ $[M]^+$ = 331.1208, found = 331.1209.

4-(3-(4-Methoxyphenyl)-1,4-dioxo-1,4-dihydronaphthalen-2-yl)butanenitrile (3ia): Yellow semi-solid (51.7 mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.08 (m, 2H), 7.77 – 7.74 (m, 2H), 7.17 – 7.11 (m, 2H), 7.03 – 6.99 (m, 2H), 3.87 (s, 3H), 2.66 (t, *J* = 7.3 Hz, 2H), 2.29 (t, *J* = 7.3 Hz, 2H), 1.82 (p, *J* = 7.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.4, 184.6, 160.2, 147.3,

145.5, 134.0, 133.9, 132.2, 132.2, 130.5, 126.9, 126.5, 125.2, 119.1, 114.1, 55.5, 27.5, 25.2, 17.5; HRMS(ESI) calcd for $C_{21}H_{17}O_3N$ $[M]^+$ = 331.1208, found = 331.1209.

4-(1,4-Dioxo-1,4-dihydroanthracen-2-yl)butanenitrile (3ja): Yellow syrup (29.7 mg, 36%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 15.8 Hz, 2H), 8.09 – 8.05 (m, 2H), 7.72 – 7.68 (m, 2H), 6.95 (s, 1H), 2.79 (t, *J* = 7.1 Hz, 2H), 2.49 (t, *J* = 7.1 Hz, 2H), 2.03 (p, *J* = 7.1 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.6, 184.5, 150.8, 137.4, 135.0, 130.4, 130.4, 129.8, 129.7, 129.4, 128.8, 128.7, 128.6, 119.0, 29.3, 24.2, 17.2; HRMS(ESI) calcd for $C_{18}H_{13}O_2N$ $[M]^+$ = 275.0946, found = 275.0946.

4-(2,5-Dimethyl-3,6-dioxocyclohexa-1,4-dien-1-yl)butanenitrile (3ka): Yellow syrup (40.2 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 – 6.57 (br, 1H), 2.64 (t, *J* = 7.0 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.06 (s, 3H), 2.04 (s, 3H), 1.79 (p, *J* = 7.3 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 187.6, 187.5, 145.6, 142.5, 141.9, 133.5, 119.3, 25.8, 24.5, 17.5, 16.0, 12.1; HRMS(ESI) calcd for $C_{12}H_{17}O_2N_2$ $[M+NH_4]^+$ = 221.1284, found = 221.1272.

4-(2,4-Dimethyl-3,6-dioxocyclohexa-1,4-dien-1-yl)butanenitrile (3la): Yellow syrup (40.8 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (q, *J* = 1.5 Hz, 1H), 2.62 (t, *J* = 7.1 Hz, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 2.08 (s, 3H), 2.04 (d, *J* = 1.58 Hz, 3H), 1.79 (p, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.9, 187.2, 145.9, 142.3, 142.1, 133.3, 119.3, 25.6, 24.5, 17.4, 16.1, 12.5; HRMS(ESI) calcd for $C_{12}H_{14}O_2N$ $[M+H]^+$ = 204.1019, found = 204.1008.

4-(4,5-Dimethoxy-2-methyl-3,6-dioxocyclohexa-1,4-dien-1-yl)butanenitrile (3ma): Red syrup (40.3 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.00 (s, 3H), 4.00 (s, 3H), 2.63 (t, *J* = 7.0 Hz, 2H), 2.41 (t, *J* = 7.0 Hz, 2H), 2.07 (s, 3H), 1.79 (p, *J* = 9.6, 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.2, 184.1, 144.7, 144.5, 140.5, 140.2, 119.3, 61.4, 25.6, 24.5, 17.4, 12.2; HRMS(ESI) calcd for $C_{13}H_{15}O_4N$ $[M]^+$ = 249.1001, found = 249.1000.

4-(3-Hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-4-phenylbutanenitrile (3ab): Yellow semi-solid (50.4 mg, 53%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.7, 0.9 Hz, 1H), 8.06 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.76 (td, *J* = 7.6, 1.3 Hz, 1H), 7.71 (s, 1H), 7.68 (td, *J* = 7.5, 1.2 Hz, 1H), 7.48 (d, *J* = 7.3 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 4.56 (t, *J* = 8.1 Hz, 1H), 2.75 – 2.59 (m, 2H), 2.45 – 2.25 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.2, 181.6, 153.3, 140.8, 135.5, 133.3, 132.9, 129.2, 128.9, 128.6, 127.3, 126.4, 125.8, 123.4, 119.5, 40.7, 27.7, 16.3; HRMS(ESI) calcd for $C_{20}H_{16}O_3N$ $[M+H]^+$ = 318.1124, found = 318.1124.

4-(2-Bromophenyl)-4-(3-hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)butanenitrile (3ac): Yellow semi-solid (52.3 mg, 44%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.05 (m, 2H), 7.77 (td, *J* = 7.6, 1.3 Hz, 1H), 7.70 (td, *J* = 7.5, 1.1 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.31 – 7.27 (m, 1H), 7.15 – 7.06 (m, 1H), 4.90 – 4.78 (m, 1H), 2.72 – 2.60 (m, 1H), 2.57 – 2.47 (m, 1H), 2.46 – 2.41 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.1, 181.5, 153.9, 140.2, 135.6, 133.4, 133.3, 132.9, 129.9, 129.2, 128.7, 127.6, 127.4, 126.5, 125.0, 122.2, 119.5, 40.5, 28.6, 16.1; HRMS(ESI) calcd for $C_{20}H_{15}O_3NBr$ $[M+H]^+$ = 396.0229, found = 396.0214.

4-(3-Bromophenyl)-4-(3-hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)butanenitrile (3ad): Yellow semi-solid (55.9 mg, 47%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.7, 1.0 Hz, 1H), 8.08 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.78 (td, *J* = 7.6, 1.4 Hz, 1H), 7.73 (s, 1H), 7.70 (td, *J* = 7.5, 1.3 Hz, 1H), 7.61 (t, *J* = 1.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 4.53 (t, *J* = 8.1 Hz, 1H), 2.72 – 2.57 (m, 2H), 2.44 – 2.26 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.0, 181.5, 153.5, 143.1, 135.6, 133.5, 132.8, 131.5, 130.5, 130.4, 129.2, 127.4, 127.3, 126.5, 122.9, 122.6, 119.3, 40.3, 27.5, 16.2; HRMS(ESI) calcd for $C_{20}H_{14}O_3NBr$ $[M]^+$ = 395.0157, found = 395.0240.

4-(4-Bromophenyl)-4-(3-hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)butanenitrile (3ae): Yellow solid (59.43 mg, 50%); mp = 135 – 137 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.06 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.77 (td, *J* = 7.6, 1.1 Hz, 1H), 7.69 (td, *J* = 7.4, 1.1 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 4.52 (t, *J* = 8.1 Hz, 1H), 2.64 (q, *J* = 7.5 Hz, 2H), 2.41 – 2.30 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.1, 181.5, 153.5, 139.8, 135.6, 133.4, 132.8, 131.9, 130.3, 129.2, 127.3, 126.5, 122.8, 121.2, 119.3, 40.1, 27.5, 16.2; HRMS(ESI) calcd for $C_{20}H_{14}O_3NBr$ $[M]^+$ = 395.0157, found = 395.0151.

4-(3-Hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-5-phenylpentanenitrile (3af): Red solid (46.7 mg, 47%); mp = 105 – 107 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 12.7, 7.7 Hz, 1H), 8.06 (dd, *J* = 12.7, 7.7 Hz, 1H), 7.77 (td, *J* = 7.6, 1.4 Hz, 1H), 7.68 (td, *J* = 7.5, 1.3 Hz, 1H), 7.25 – 7.11 (m, 5H), 3.68 – 3.57 (m, 1H), 3.15 – 3.02 (m, 2H), 2.46 – 2.31 (m, 1H), 2.30 – 2.20 (t, *J* = 7.7 Hz, 2H), 2.13 – 1.97 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.6, 181.1, 154.1, 139.6, 135.4, 133.3, 132.9, 129.2, 129.0, 128.6, 127.2, 126.5, 126.4, 123.1, 119.7, 38.9, 37.3, 27.8, 16.1; HRMS(ESI) calcd for $C_{21}H_{17}O_3N$ $[M]^+$ = 331.1208, found = 331.1202.

3-(4-(*tert*-Butyl)phenyl)-4-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)butanenitrile (3cg): Yellow oil (45.7 mg, 41%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.00 (m, 2H), 7.78 – 7.64 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 3.32 – 3.15 (m, 2H), 2.93 (dd, *J* = 12.4, 7.6 Hz, 1H), 2.81 – 2.69 (m, 2H), 1.93 (s, 3H), 1.28(s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.9, 184.9, 151.0, 145.6, 143.8, 137.7, 133.8, 132.2, 132.1, 126.9, 126.5, 125.9, 118.7, 41.4, 34.7, 33.8, 31.4, 24.3, 13.2; HRMS(ESI) calcd for $C_{25}H_{26}O_2N$ $[M+H]^+$ = 372.1958, found = 372.1940.

3-((3-Hydroxy-1,4-dioxo-1,4-dihydronaphthalen-2-yl)methyl)heptanenitrile (3ah): Yellow solid (57.9 mg, 65%); mp = 141 – 143 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.7, 1.0 Hz, 1H), 8.09 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.77 (td, *J* = 7.6, 1.4 Hz, 1H), 7.70 (td, *J* = 7.5, 1.3 Hz,

1H), 7.50 (s, 1H), 2.76 (dd, *J* = 13.1, 5.6 Hz, 1H), 2.61 (dd, *J* = 13.1, 8.6 Hz, 1H), 2.42 – 2.27 (m, 2H), 2.17 – 2.05 (m, 1H), 1.62 – 1.44 (m, 2H), 1.43 – 1.28 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 184.8, 181.2, 154.2, 135.3, 133.3, 132.9, 129.5, 127.1, 126.5, 121.6, 118.9, 35.1, 33.9, 28.9, 28.0, 22.8, 22.1, 14.1; HRMS(ESI) calcd for $C_{18}H_{20}O_3N$ $[M+H]^+$ = 298.1438, found = 298.1423.

2-(2-(3-Methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)-2,3-dihydro-1H-inden-1-yl)acetonitrile (3ci): Yellow solid (54.0 mg, 55%); mp = 210 – 211°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 1H), 8.08 – 8.01 (m, 1H), 7.75 – 7.68 (m, 2H), 7.33 – 7.26 (m, 4H), 4.18 – 4.06 (m, 1H), 3.80 – 3.67 (m, 1H), 3.38 (dd, *J* = 15.6, 9.5 Hz, 1H), 3.23 (dd, *J* = 15.6, 9.3 Hz, 1H), 2.80 – 2.67 (m, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.9, 146.2, 146.1, 142.2, 133.8, 133.8, 132.7, 132.1, 128.1, 127.3, 126.6, 125.0, 123.3, 118.3, 46.4, 45.9, 37.8, 22.3, 13.5; HRMS(ESI) calcd for $C_{22}H_{18}O_2N$ $[M+H]^+$ = 328.1332, found = 328.1279.

2-((3-Methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)methoxy)acetonitrile (3cj): Yellow solid (44.1 mg, 61%); mp = 110 – 113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 – 8.04 (m, 2H), 7.82 – 7.71 (m, 2H), 4.72 (s, 2H), 4.36 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.2, 183.9, 148.5, 139.3, 134.1, 134.0, 132.3, 131.8, 126.7, 115.9, 64.2 56.6, 13.1; HRMS(ESI) calcd for $C_{14}H_{12}O_3N$ $[M+H]^+$ = 242.0812, found = 242.0804.

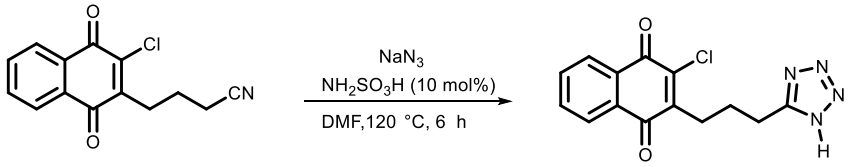
3. Gram-scale experiment:

Quinone **1a** (1.0 g, 5.95 mmol), oxime ester **2a** (1.8 g, 7.14 mmol) and 2 mol% of Rose Bengal were weighed in a round-bottom flask and DMSO (59.5 ml) was added to this mixture. The flask was back filled with N_2 and it was introduced into the Penn *PhD* photoreactor m2 (blue LED 450 nm). After completion of reaction (8 hours), the resulting mixture was then diluted with ethyl acetate (10 mL), and washed successively with water (20 mL × 2), aq. $NaHCO_3$ solution (30 mL

× 2) and brine solution (30 mL × 2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to get the desired compound **3aa** (1.02 g, 71%).

4. Transformation of cyanoalkylated product:

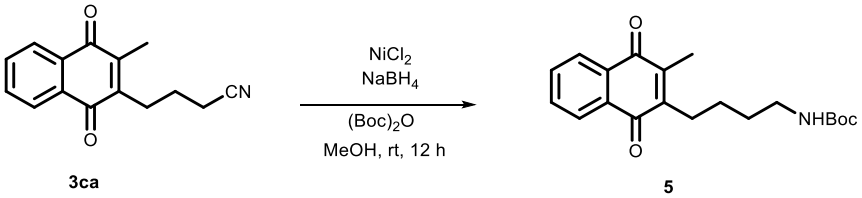
2-(3-(1H-tetrazol-5-yl)propyl)-3-chloronaphthalene-1,4-dione (4):



3da **4**

A mixture of **3da** (51.9 mg, 0.2 mmol), sodium azide (19.5 mg, 0.3 mmol) and sulfamic acid (1mg, 0.01 mmol) was stirred at 120 °C in DMF (0.5 mL) for 6 hours. After completion of the reaction, the reaction mixture was cooled to room temperature, then 5 mL diethyl ether was added to the mixture and stirred for 10 minutes. The catalyst, separated by simple gravity filteration, washed with diethyl ether (2 × 3 mL) and dried at 40 °C for 30 minutes, gave the tetrazole in 64% yield. Orange syrup (38.7 mg, 64%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 5.22 (s, 1H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.44 (t, *J* = 6.9 Hz, 2H), 1.92 (p, *J* = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.9, 181.4, 145.7, 134.7, 133.1, 132.5, 130.6, 126.5, 126.2, 120.2, 114.6, 23.7, 23.3, 17.3; HRMS(ESI) calcd for $C_{14}H_{12}O_2N_2$ $[M\text{-}N_2\text{-}Cl+H]^+$ = 240.0898, found = 240.0898.

***tert*-Butyl (4-(3-methyl-1,4-dioxo-1,4-dihydronaphthalen-2-yl)butyl)carbamate (5):**

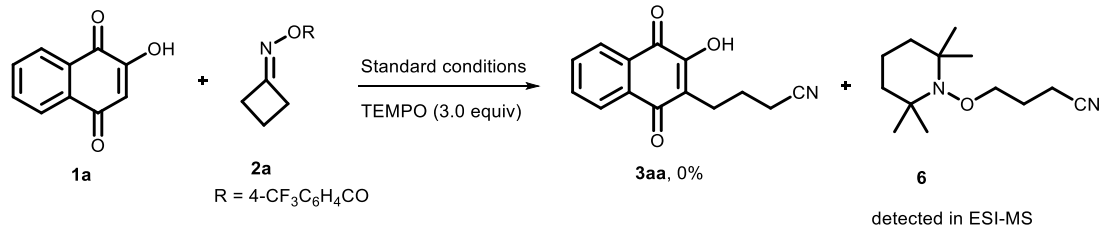


3ca **5**

A mixture of **3ca** (23.9 mg, 0.1 mmol), $NiCl_2$ (32.4 mg, 0.25 mmol), $(Boc)_2O$ (130.9 mg, 0.6 mmol) in dry methanol (4 mL) was cooled to 40 °C. Then, $NaBH_4$ (26.48 mg, 0.7 mmol) was added in small portions. The mixture was allowed to stir overnight at room temperature. The reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic phase was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to get the desired compound **5** in 61% yield. Yellow syrup (20.9 mg, 61%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.71 – 7.65 (m, 2H), 4.59 (s, 1H), 3.23 – 3.11 (m, 2H), 2.64 (t, *J* = 6.2 Hz, 2H), 2.18 (s, 3H), 1.68 – 1.53 (m, 2H), 1.53 – 1.46 (m, 2H), 1.42 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.4, 184.9, 156.2, 147.1, 143.6, 133.5, 132.3, 126.4, 79.3, 40.3, 30.4, 28.6, 26.8, 25.9, 12.9; HRMS(ESI) calcd for $C_{20}H_{24}O_4N$ $[M-H]^-$ = 342.1699, found = 342.1703.

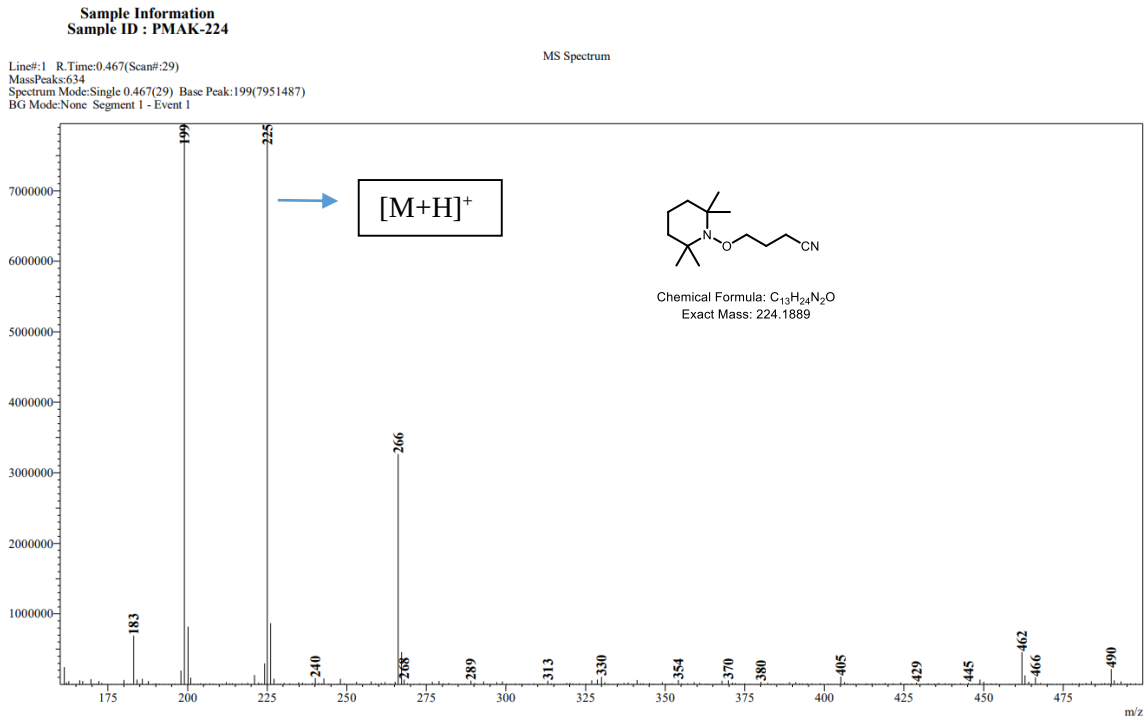
5. Control experiments for mechanistic studies:

Radical inhibition/trapping experiments:

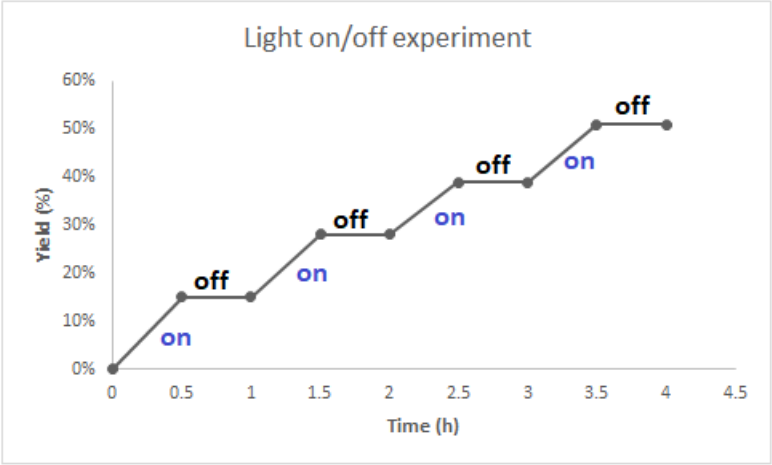


Quinone **1a** (52.2 mg, 0.3 mmol), oxime ester **2a** (92.6 mg, 0.36 mmol), 2 mol% of Rose Bengal and TEMPO (140.6 mg, 0.9 mmol) were weighed in a vial and DMSO (3 mL) was added to this mixture. The vial was back filled with N_2 and it was introduced into the *syn*LED parallel photoreactor (blue LED 439 nm). After 6 hours, the resulting mixture was diluted with ethyl acetate (5 mL), and washed successively with water (3 mL) and brine (5 mL × 2). The organic layer was dried over anhydrous sodium sulfate and concentrated. In this reaction, the formation of product **3aa** was completely suppressed.

The cyanoalkyl-TEMPO adduct **6** was characterized by ESI-MS.



Light on/off experiment:



Quinone **1a** (52.2 mg, 0.3 mmol), oxime ester **2a** (92.6 mg, 0.36 mmol), 2 mol% of Rose Bengal and internal standard 1,3,5-trimethoxy benzene (50.5 mg, 0.3 mmol) were weighed in a vial and DMSO (3 mL) was added to this mixture. After backfilling with N_2, this vial was irradiated with

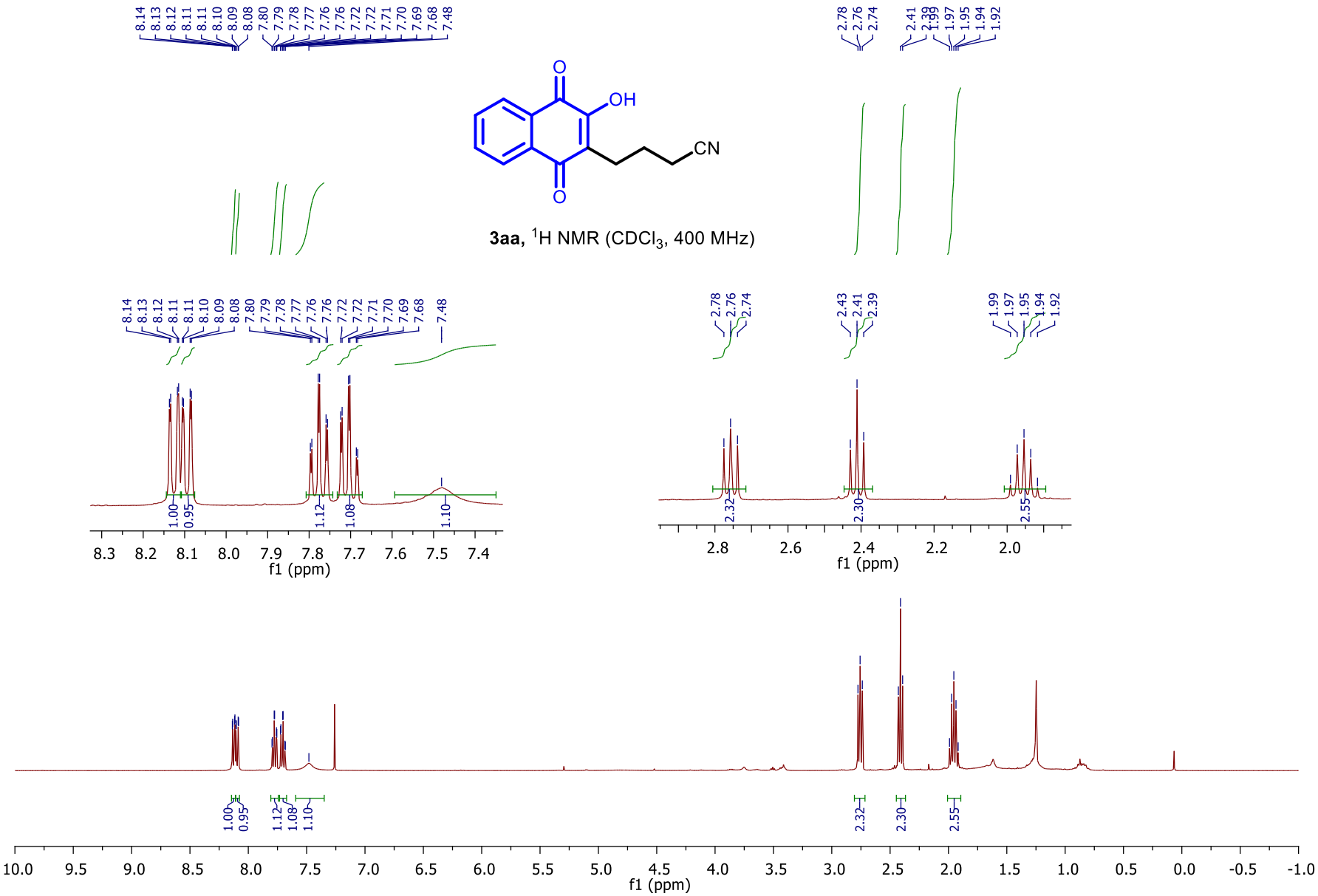
blue LED alternately over 30 minutes (i.e. the reaction mixture was under light for 30 minutes followed by in the absence of light for the next 30 minutes). After each 30 minutes of interval, some aliquot was removed from the reaction mixture and analyzed by ^{1}H nmr to determine the yield. As shown in the above graph, there was no progress in this transformation when the light was switched off. The results of this experiment indicate that continuous irradiation is necessary for this transformation, indicating that the possibility of a radical chain mechanism is highly unlikely in this scenario.

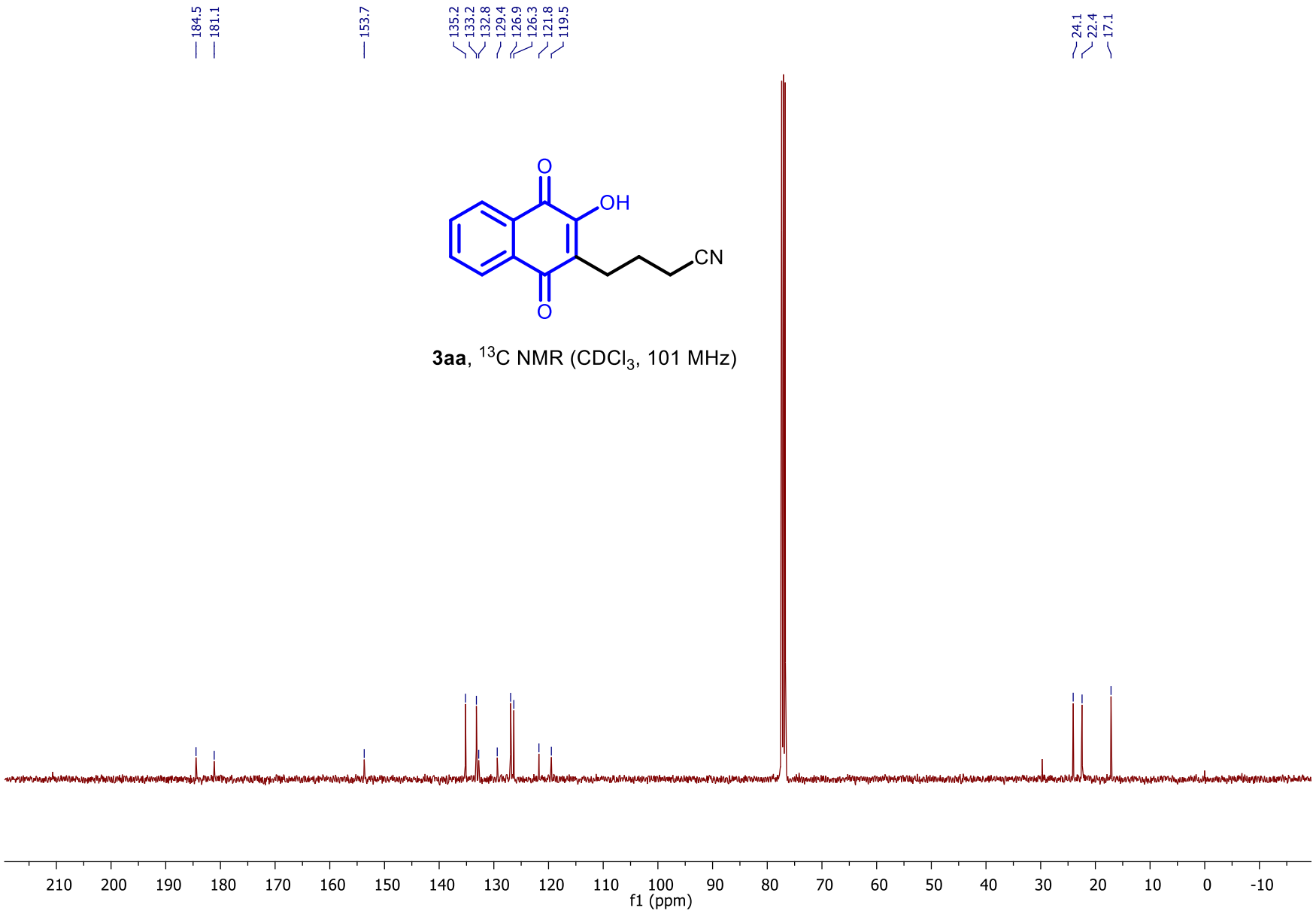
6. References:

1. a) R. B. Smith, C. Canton, N. S. Lawrence, C. Livingstone and J. Davis, *New J. Chem.*, 2006, **30**, 1718–1724; b) D. Wang, B. Ge, S. Yang, H. Miao and Y. Ding, *Russ. J. Gen. Chem.*, 2014, **84**, 1615–1621; c) K. Chinea and A. K. Banerjee, *Nat. Prod. Commun.*, 2015, **10**, 1237–1238; d) N. Suematsu, M. Ninomiya, H. Sugiyama, T. Udagawa, K. Tanaka and M. Koketsu, *Bioorganic Med. Chem. Lett.*, 2019, **29**, 2243–2247.

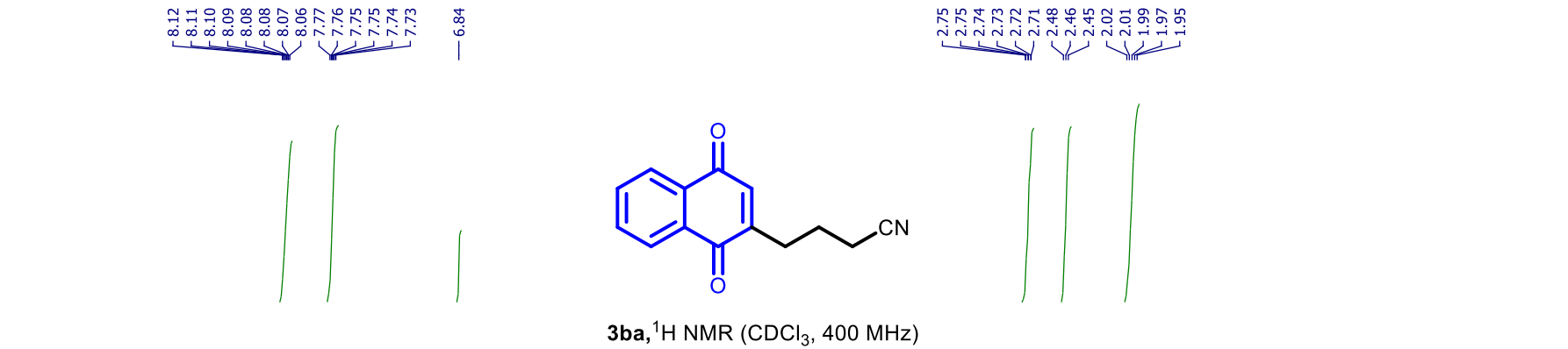
2. a) L. Li, H. Chen, M. Mei and L. Zhou, *Chem. Commun*, 2017, **53**, 11544-11547; b) X. Shen, J. J. Zhao and S. Yu, *Org. Lett.*, 2018, **20**, 5523–5527; c) X. Y. Yu, J. R. Chen, P. Z. Wang, M. N. Yang, D. Liang and W. J. Xiao, *Angew. Chem., Int. Ed.*, 2018, **57**, 738–743; d) Y. Liu, Q.-L. Wang, Z. Chen, H. Li, B.-Q. Xiong, P.-L. Zhang and K.-W. Tang, *Chem. Commun*, 2020, **56**, 3011; e) X. Zhao, L. Ji, Y. Gao, T. Sun, J. Qiao, A. Li and K. Lu, *J. Org. Chem.*, 2021, **86**, 11399–11406; f) N. Zhou, Z. Xia, S. Wu, K. Kuang, Q. Xu and M. Zhang, *J. Org. Chem.*, 2021, **86**, 15253–15262.

7. NMR spectra:

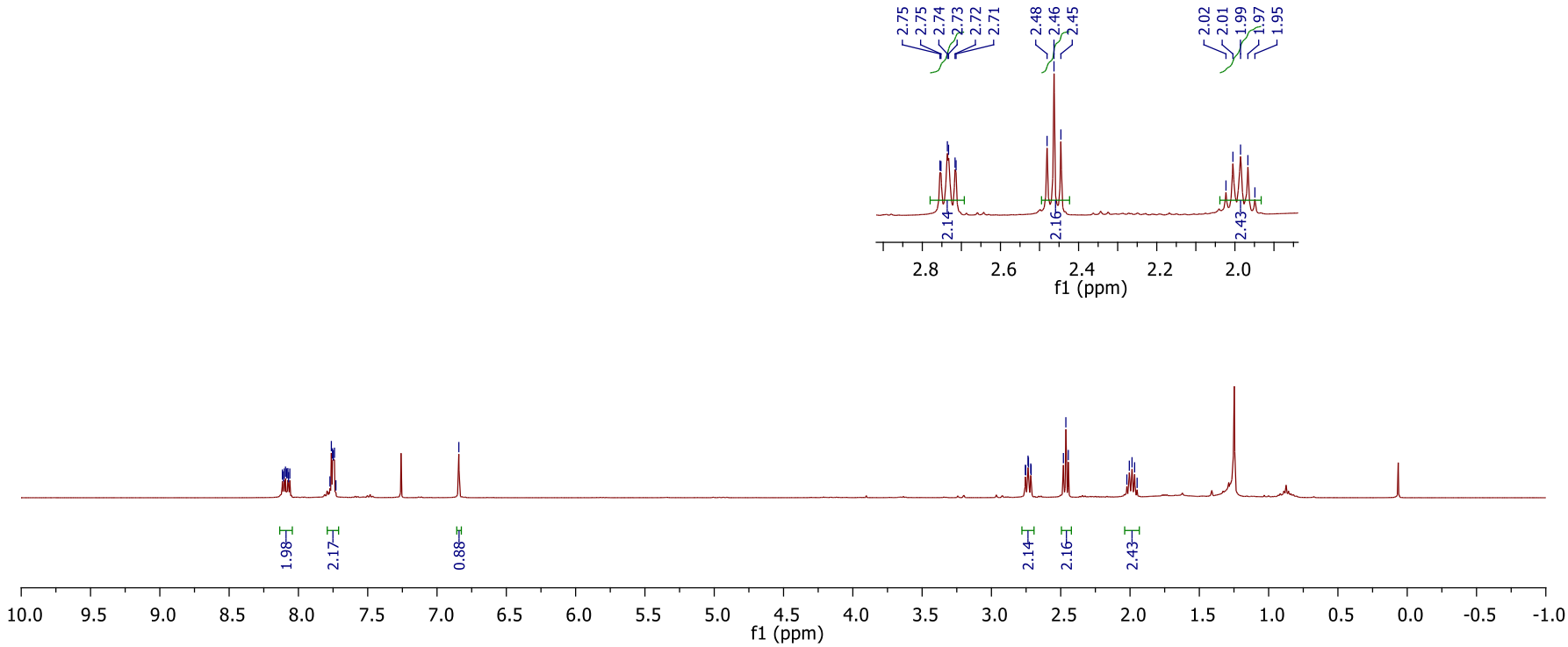


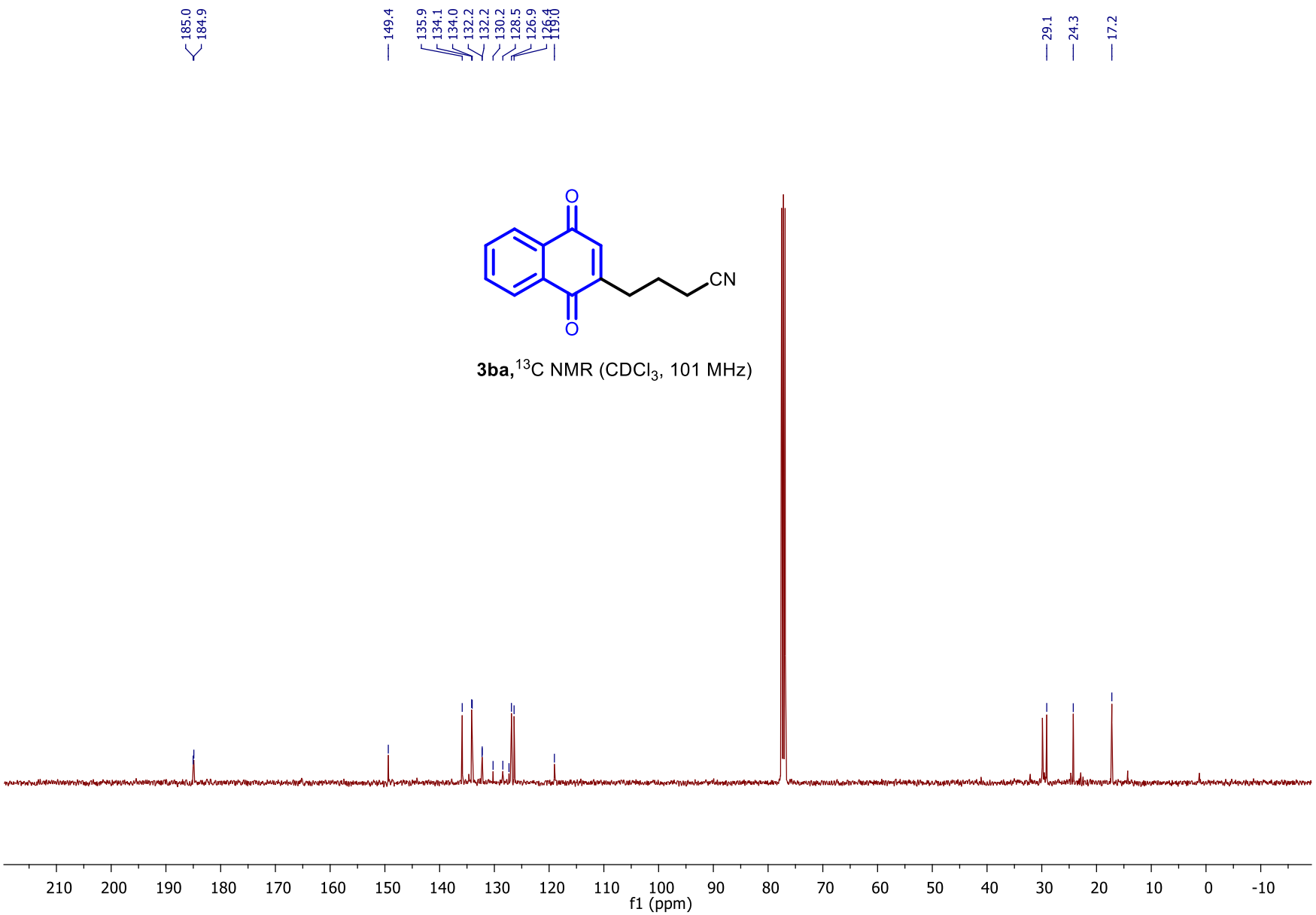


3aa, ^{13}C NMR ($CDCl_3$, 101 MHz)

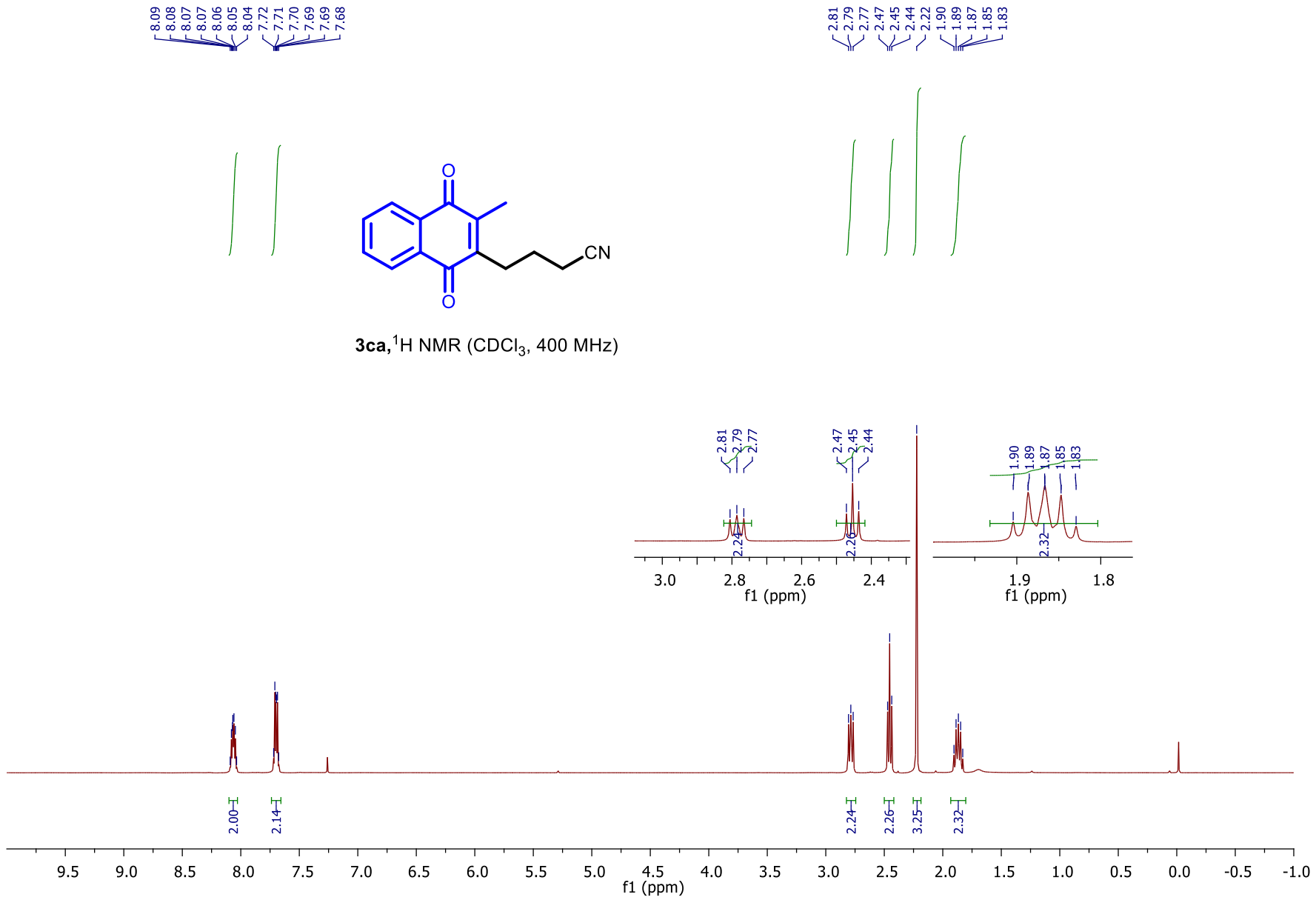


3ba, ^{1}H NMR ($CDCl_3$, 400 MHz)

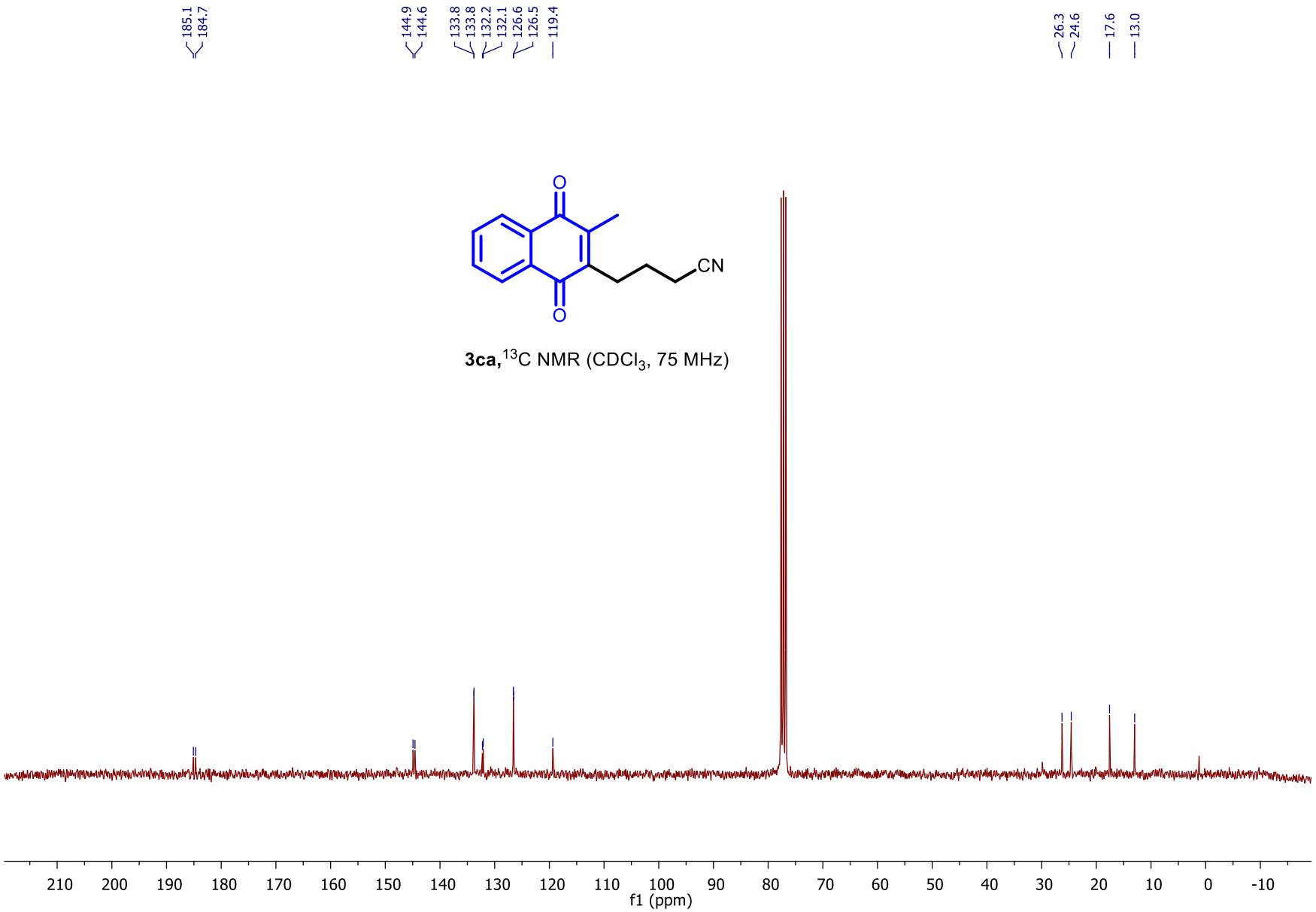




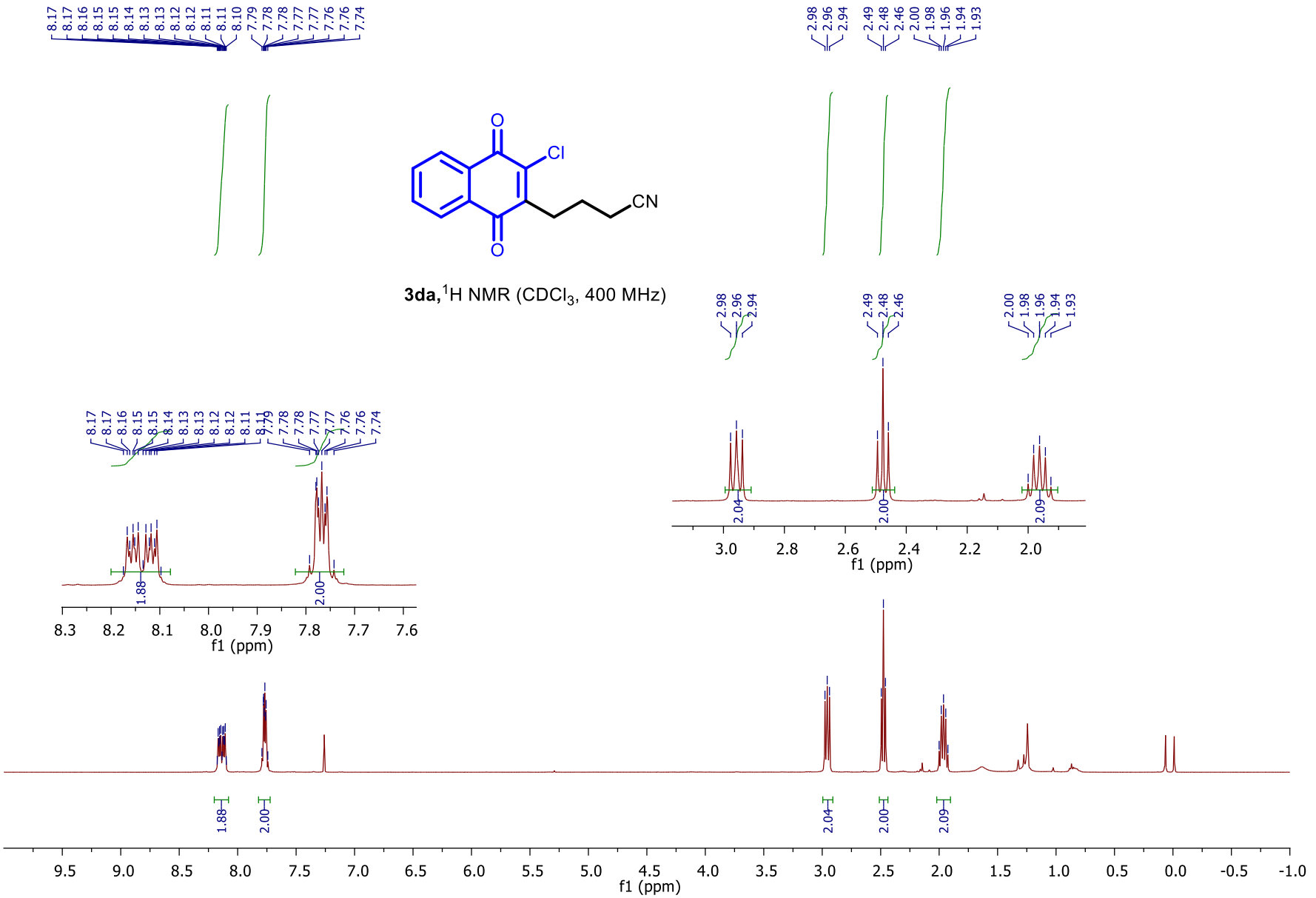
3ba, ^{13}C NMR ($CDCl_3$, 101 MHz)



3ca, ^{1}H NMR ($CDCl_3$, 400 MHz)



3ca, ^{13}C NMR ($CDCl_3$, 75 MHz)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8.13
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8.12
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7.78
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7.76
7.74
2.98
2.96
2.94
2.49
2.48
2.46
2.00
1.98
1.96
1.94
1.93
O
Cl
CN
O
3da,1H NMR (CDCl3, 400 MHz)
1.88
2.00
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
f1 (ppm)
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2.00
2.09
3.0
2.8
2.6
2.4
2.2
2.0
f1 (ppm)
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2.00
2.04
2.00
2.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
1.5
1.0
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0.0
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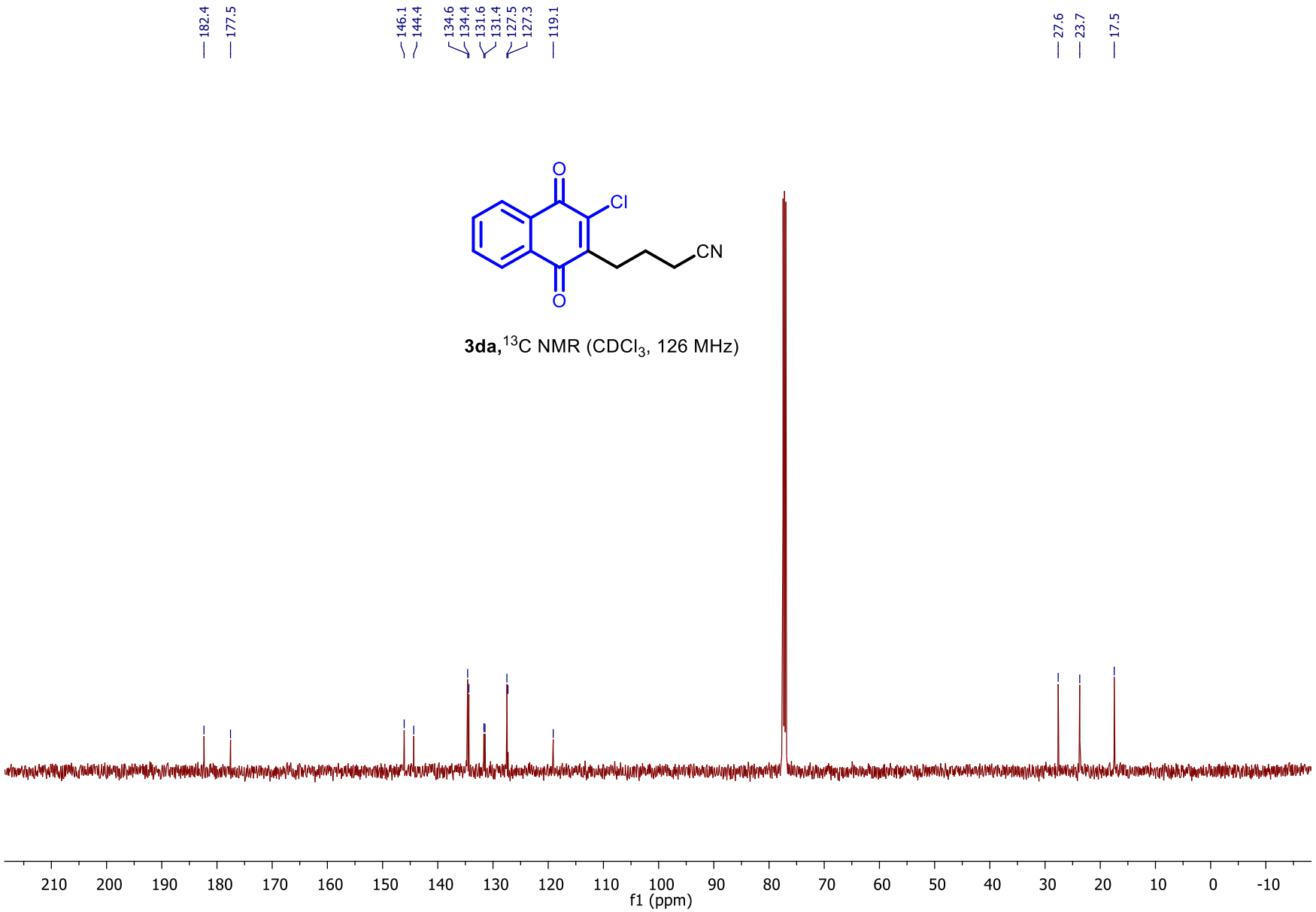
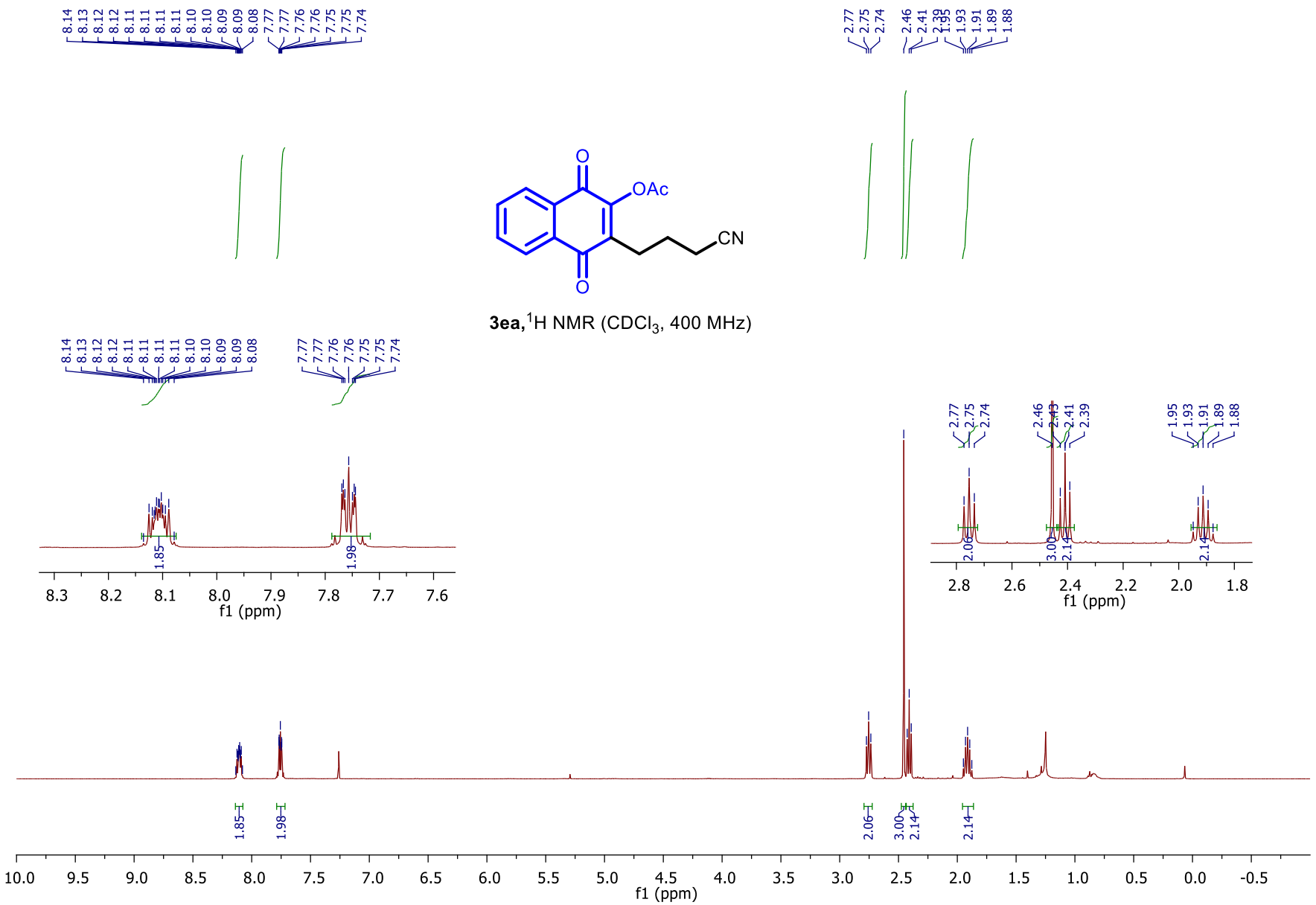
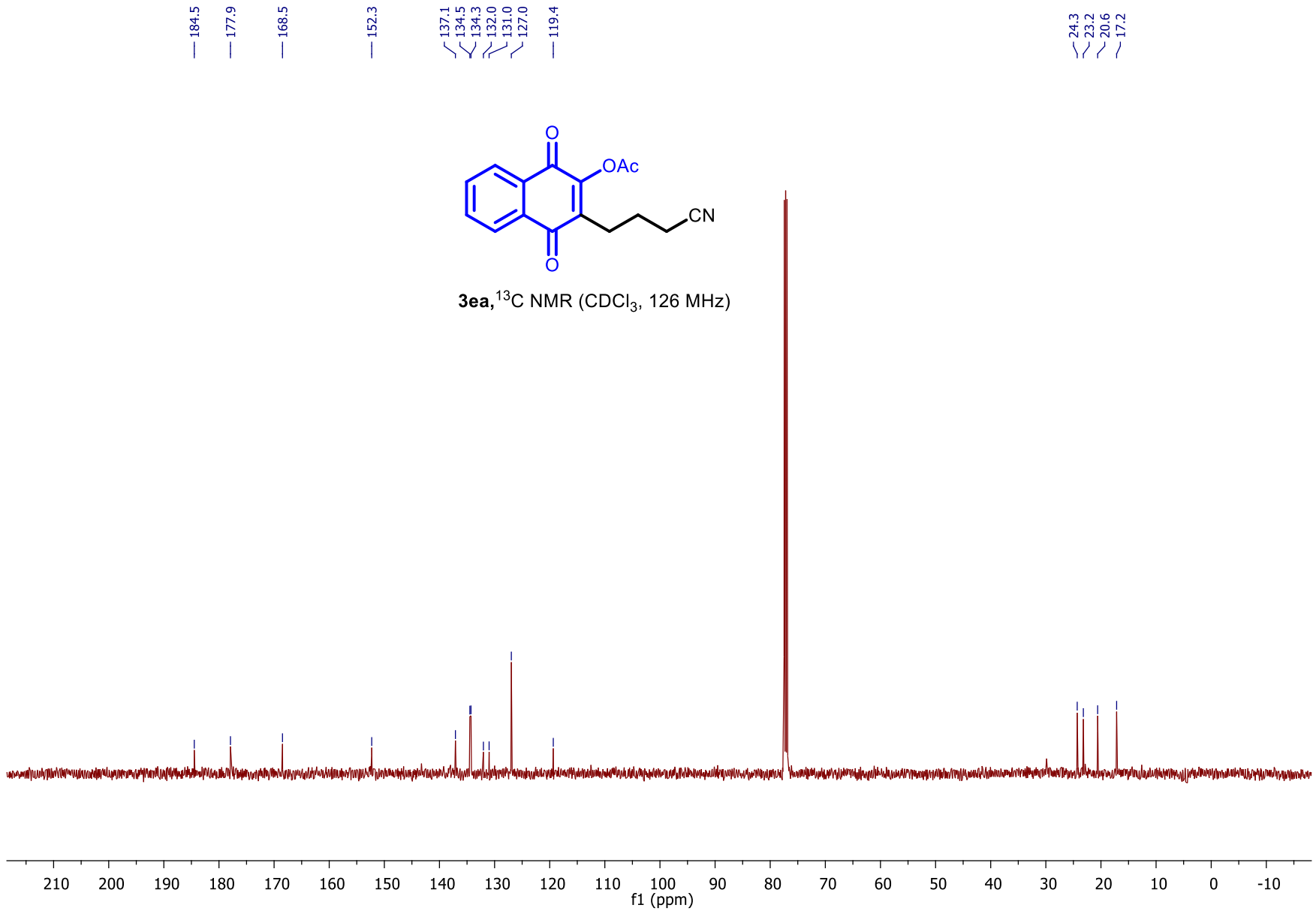
-1.0
f1 (ppm)



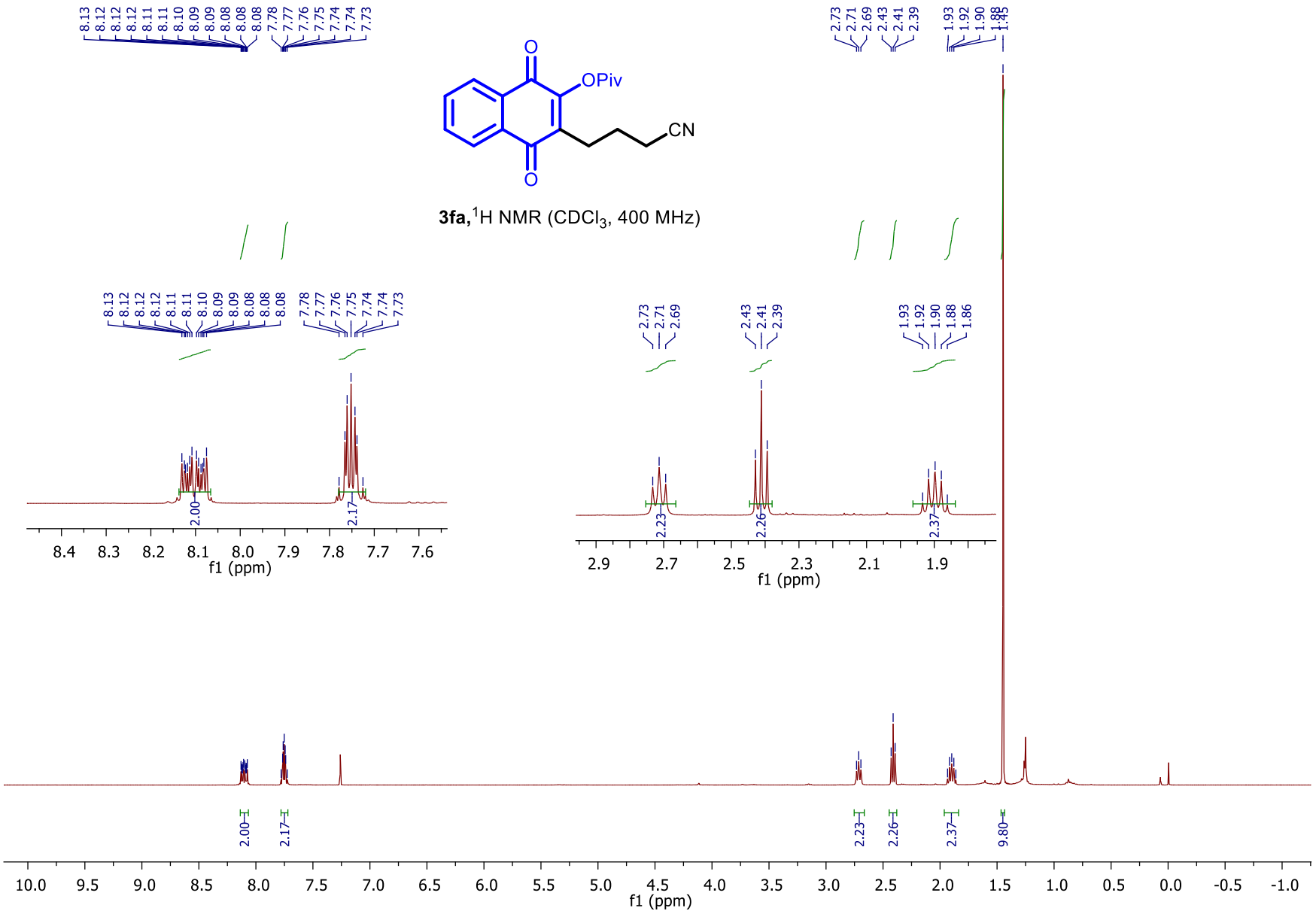
3da, ^{13}C NMR ($CDCl_3$, 126 MHz)



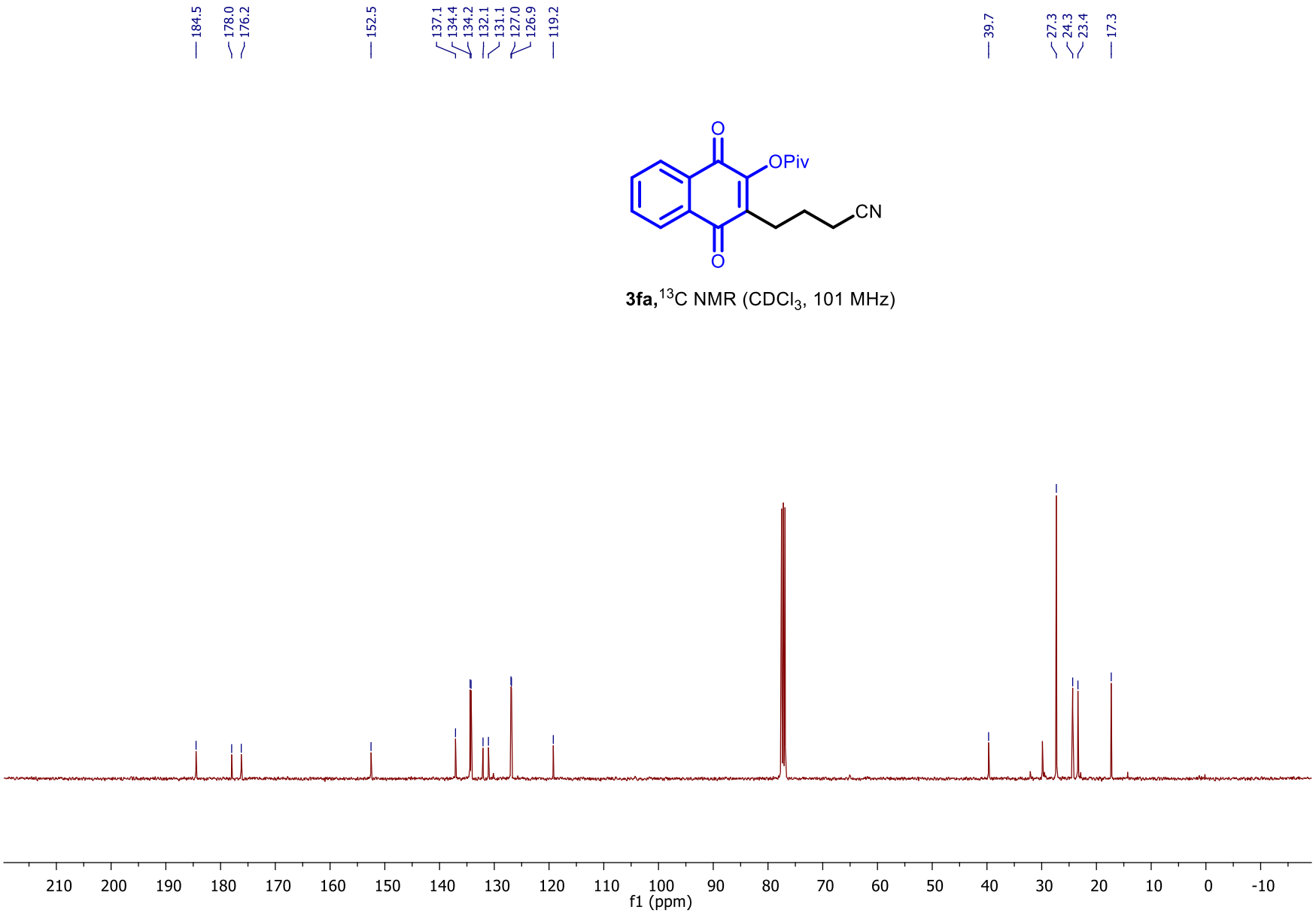
3ea, ^{1}H NMR ($CDCl_3$, 400 MHz)



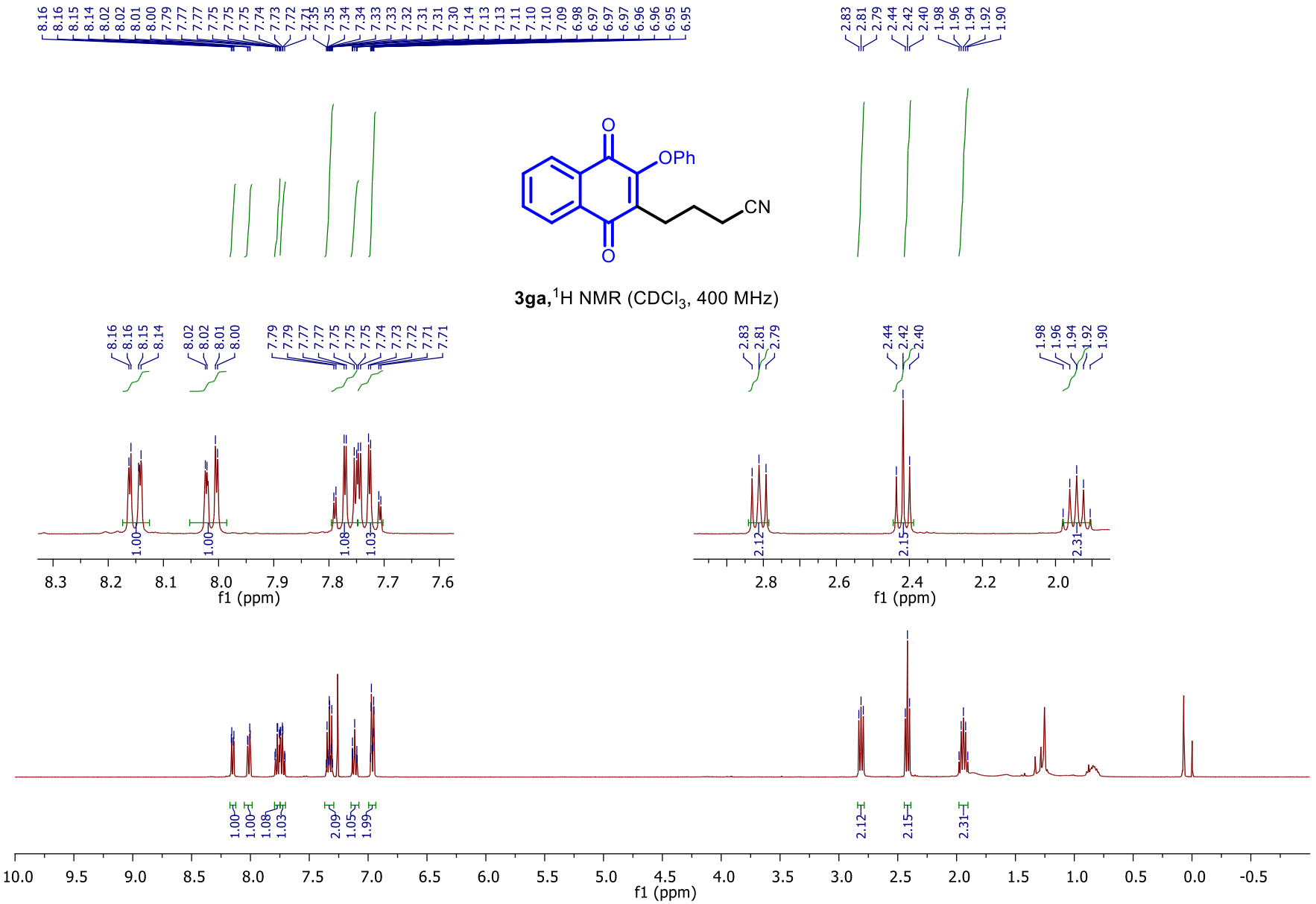
3ea, ^{13}C NMR ($CDCl_3$, 126 MHz)



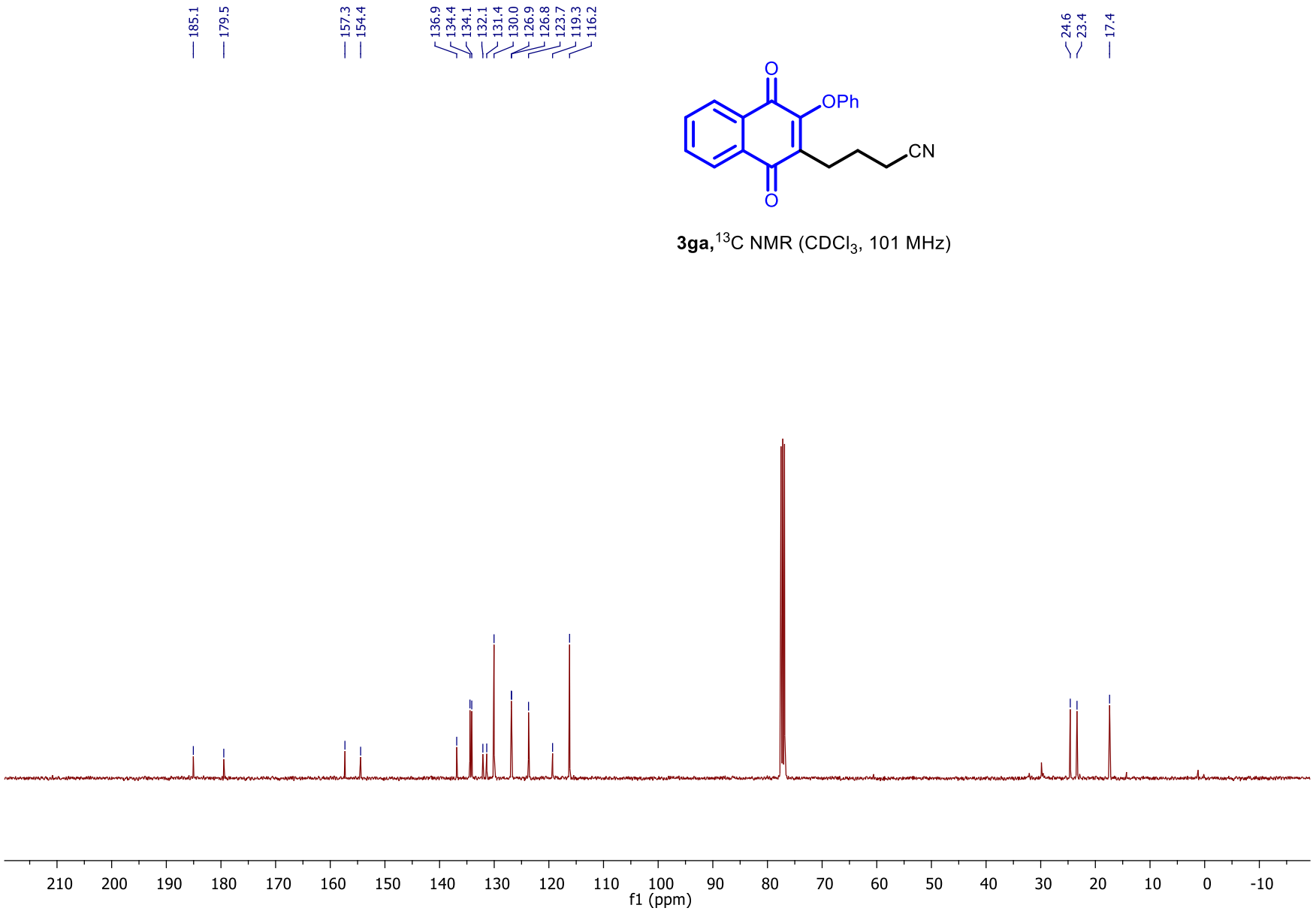
3fa,^{1}H NMR ($CDCl_3$, 400 MHz)



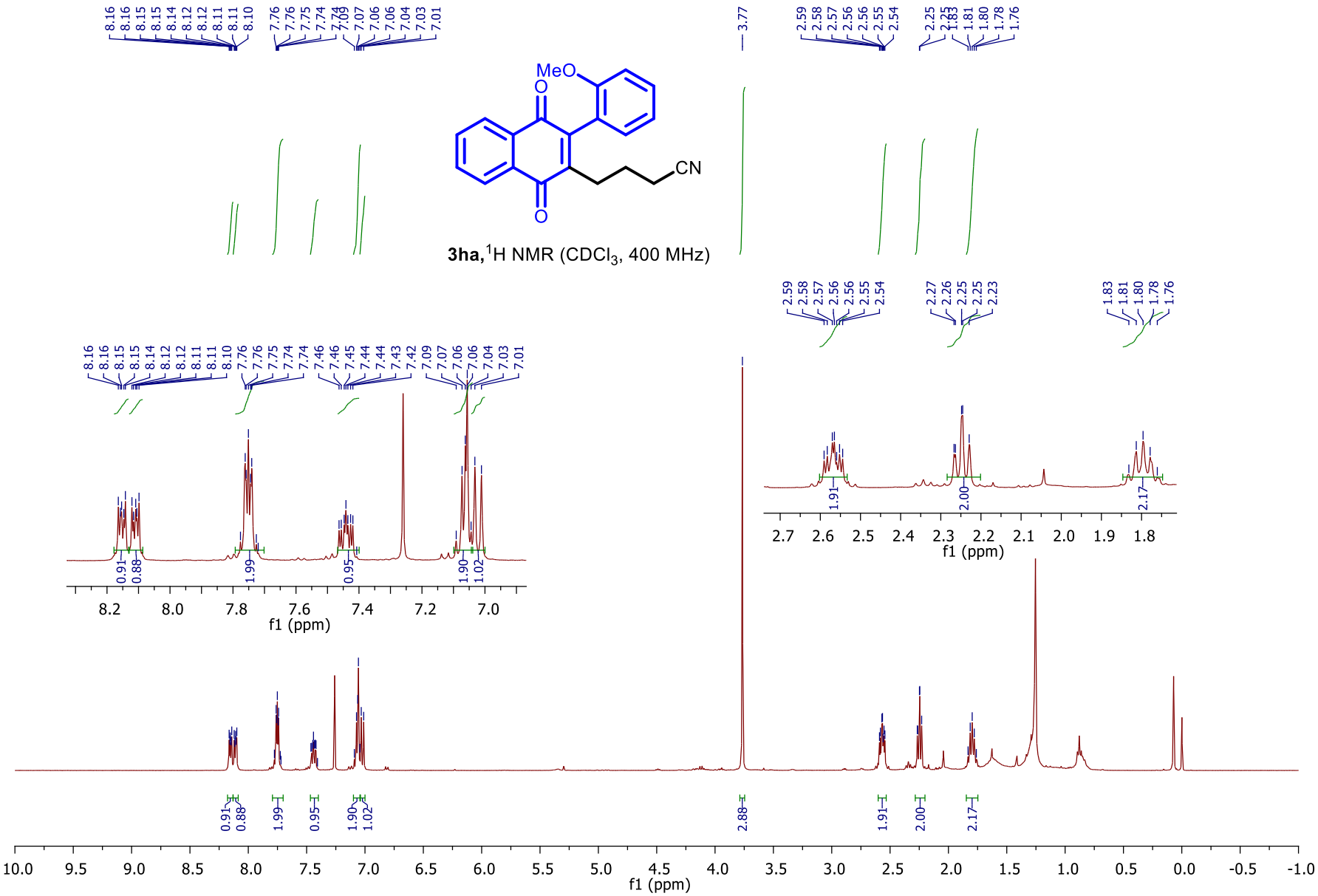
3fa, ^{13}C NMR ($CDCl_3$, 101 MHz)



3ga,^{1}H NMR ($CDCl_3$, 400 MHz)



3ga, ^{13}C NMR ($CDCl_3$, 101 MHz)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CN
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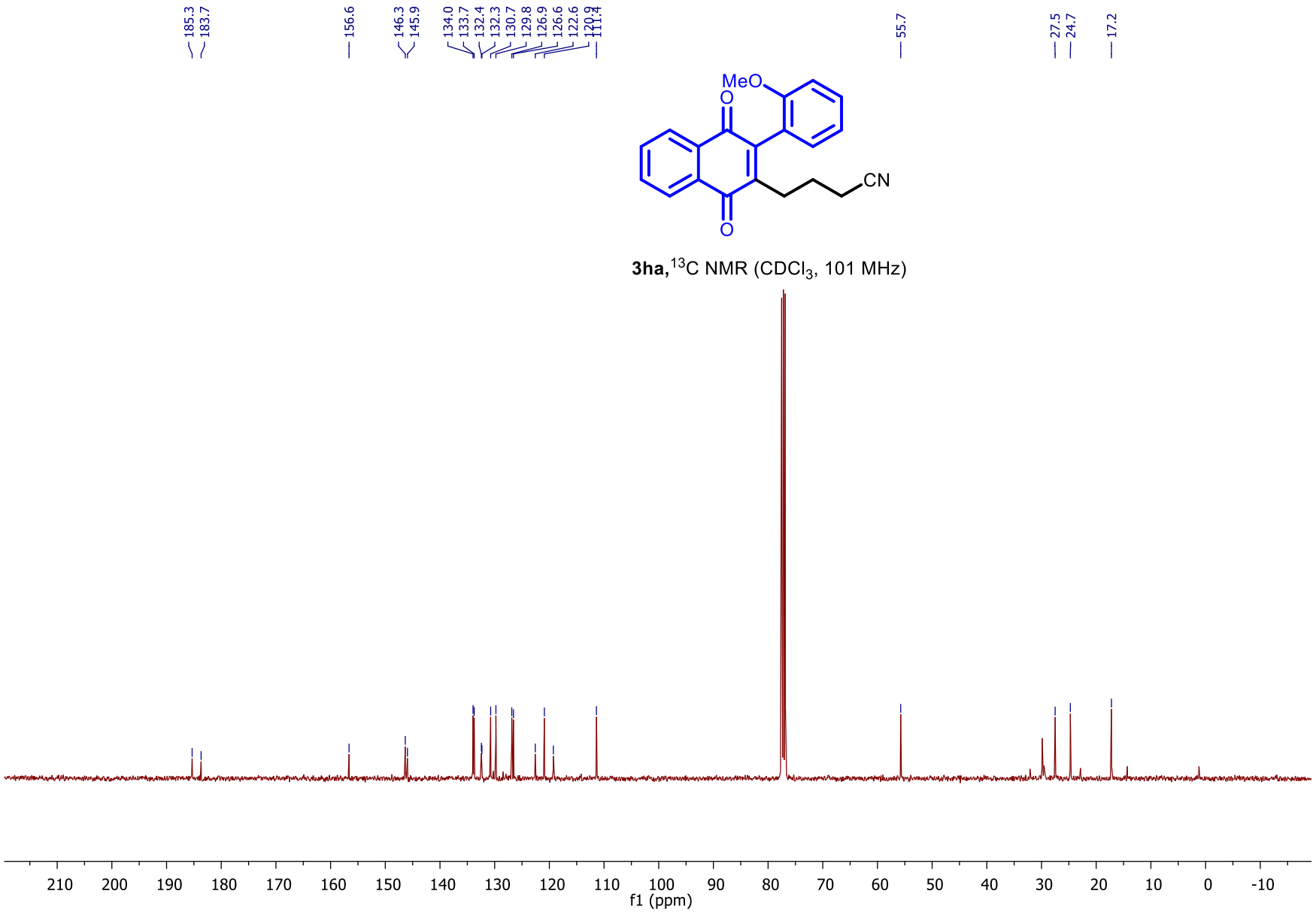
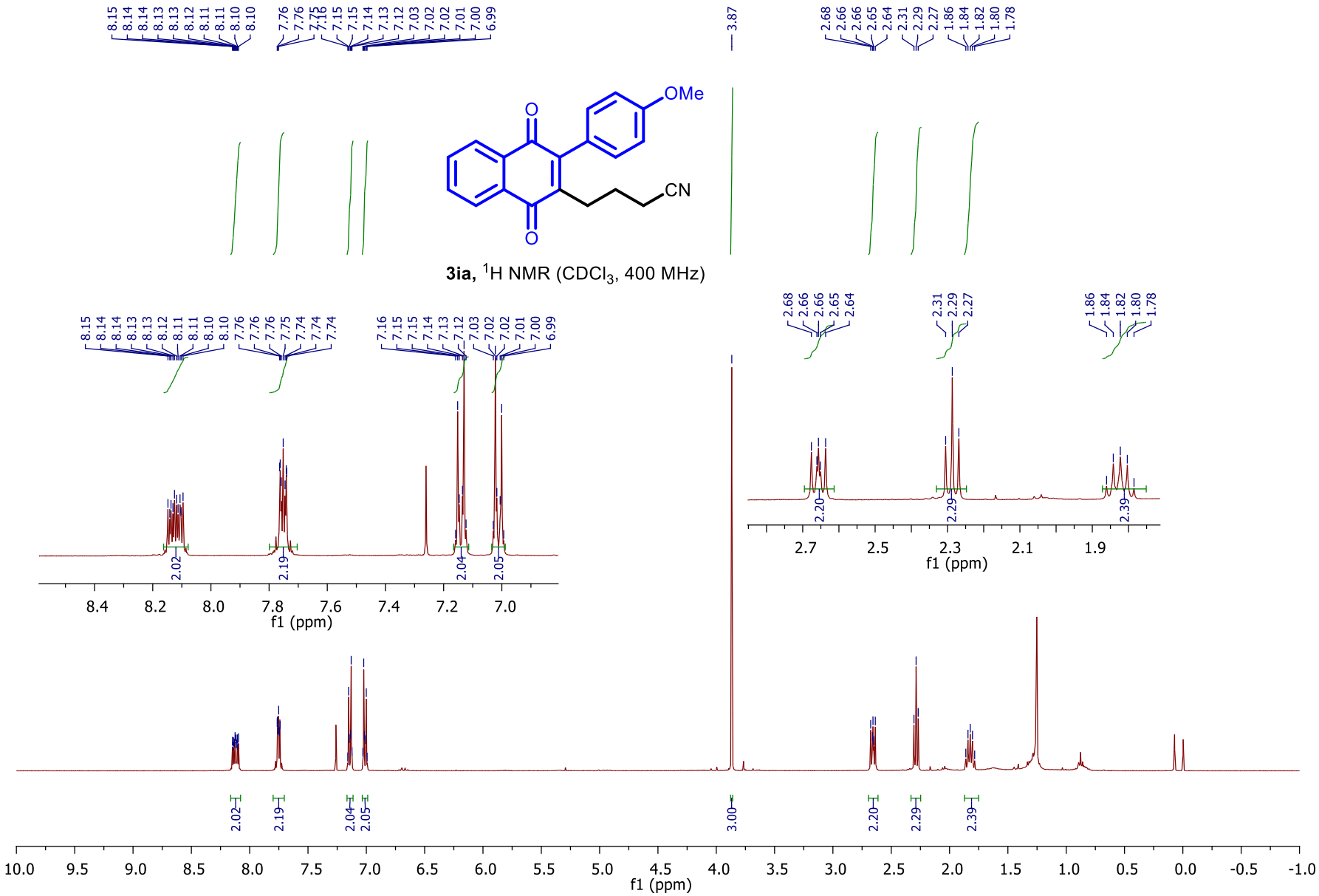
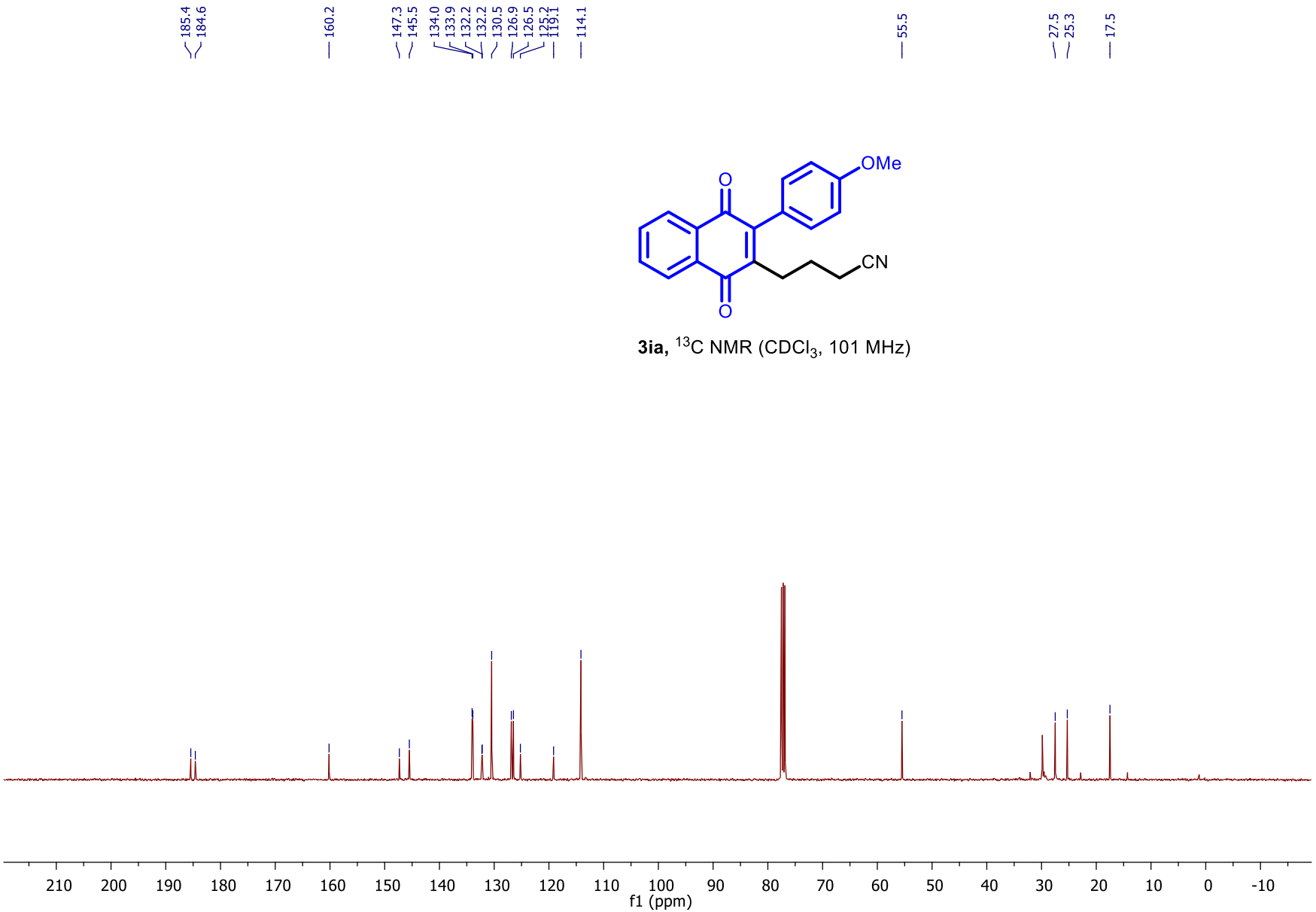
f1 (ppm)



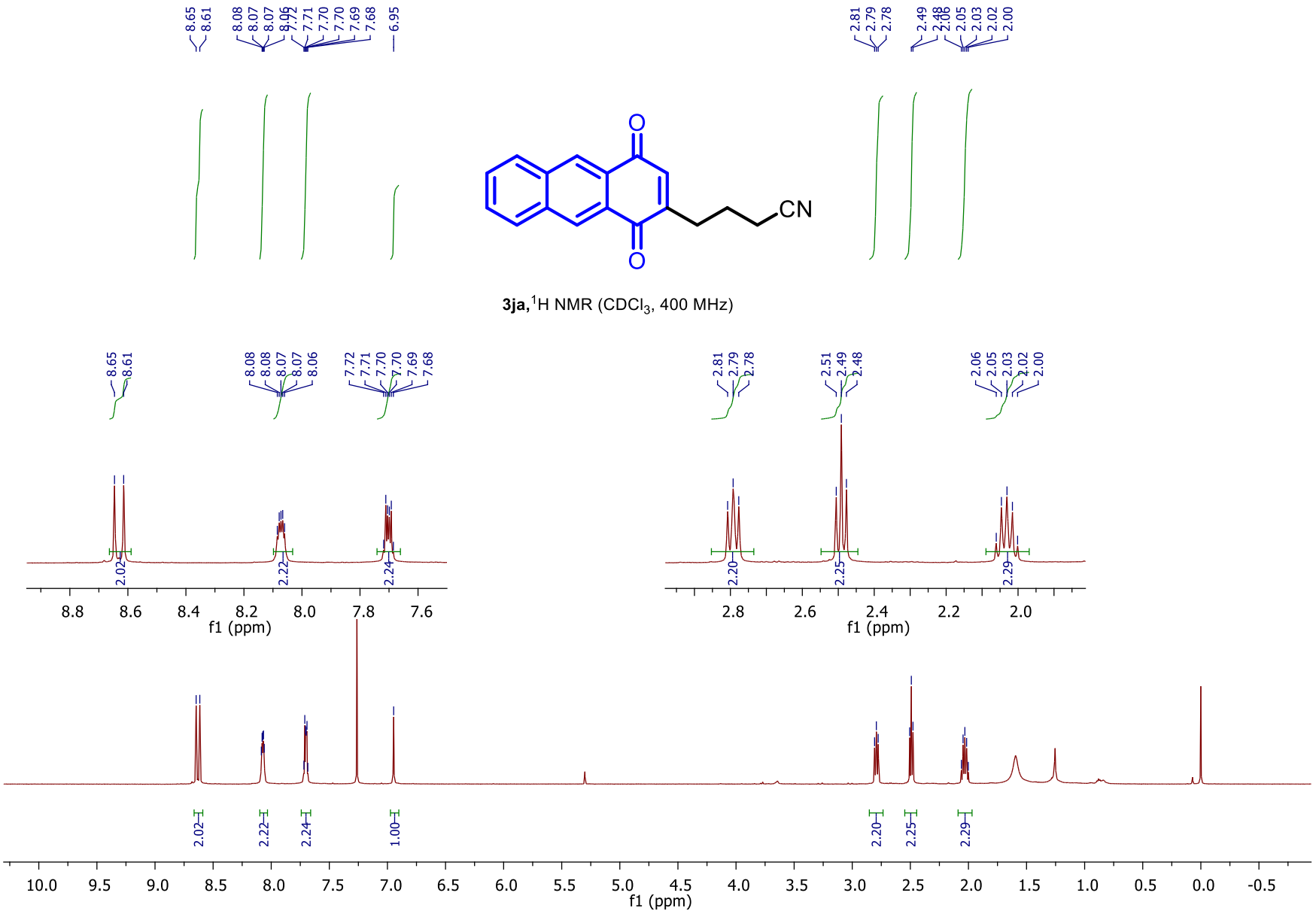
3ha, ^{13}C NMR ($CDCl_3$, 101 MHz)



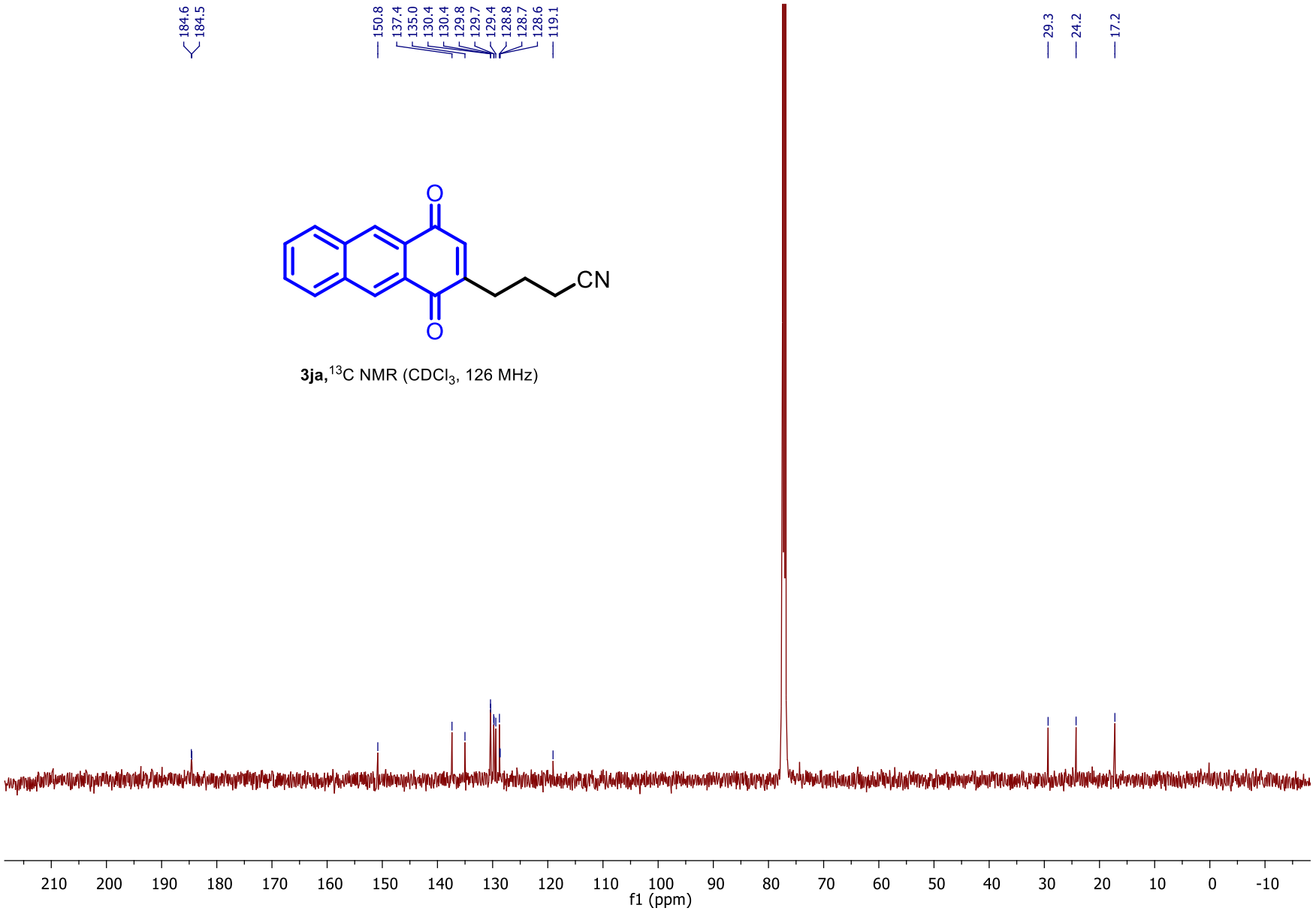
3ia, ^{1}H NMR ($CDCl_3$, 400 MHz)



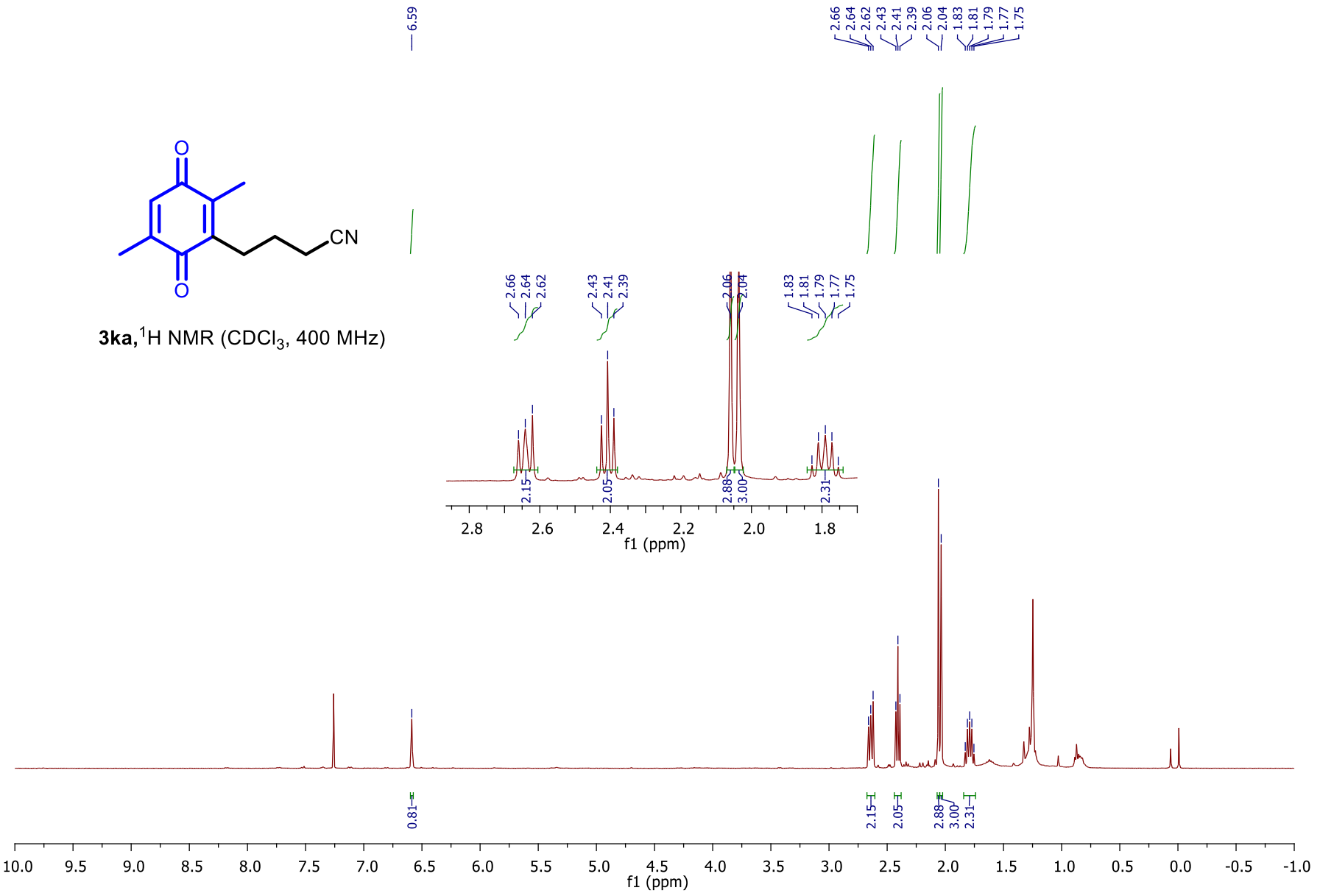
3ia, ^{13}C NMR ($CDCl_3$, 101 MHz)



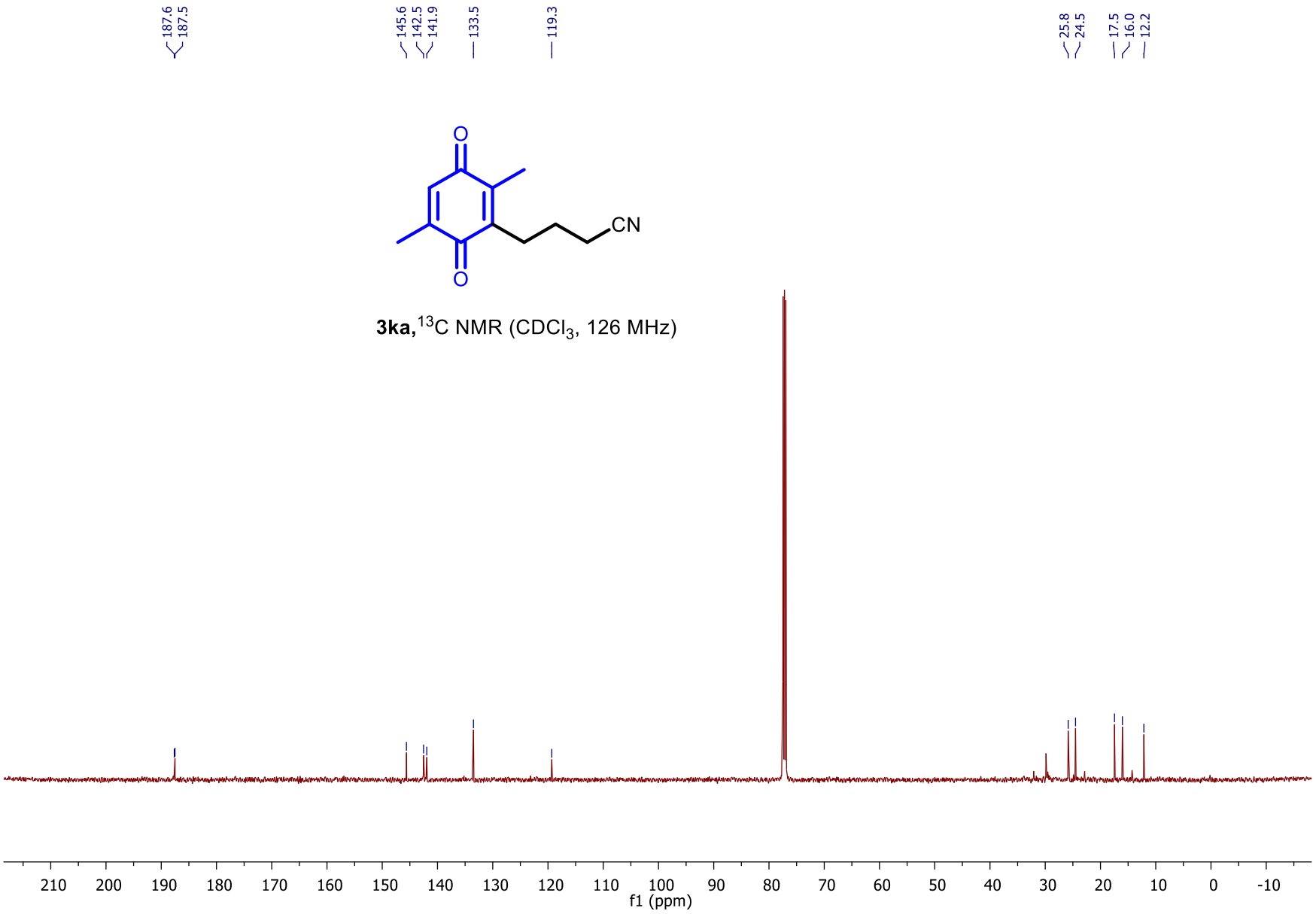
3ja,^{1}H NMR ($CDCl_3$, 400 MHz)



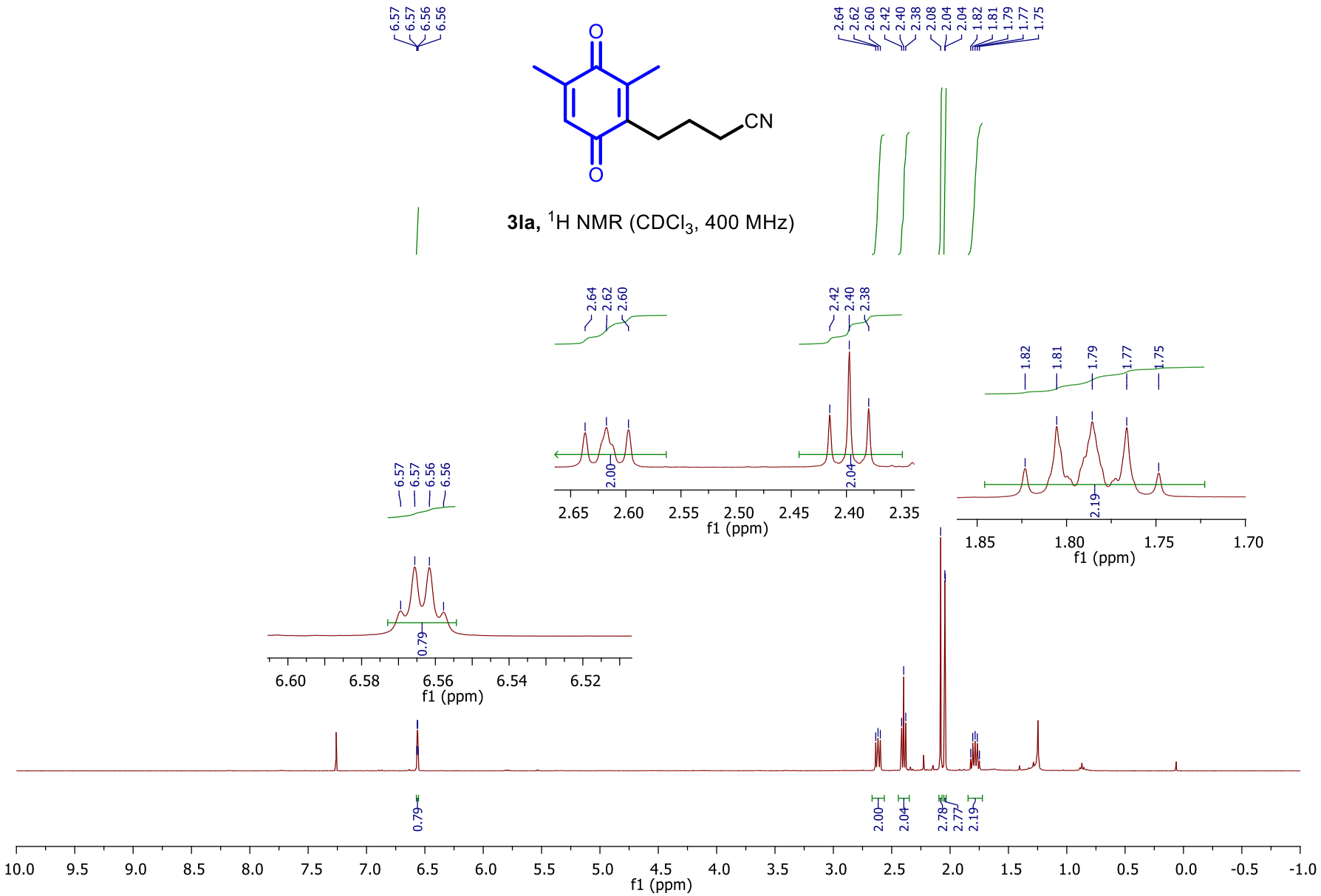
3ja,^{13}C NMR ($CDCl_3$, 126 MHz)



3ka,^{1}H NMR ($CDCl_3$, 400 MHz)



3ka, ^{13}C NMR ($CDCl_3$, 126 MHz)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1.79
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CN
O
O
3la, 1H NMR (CDCl3, 400 MHz)
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2.04
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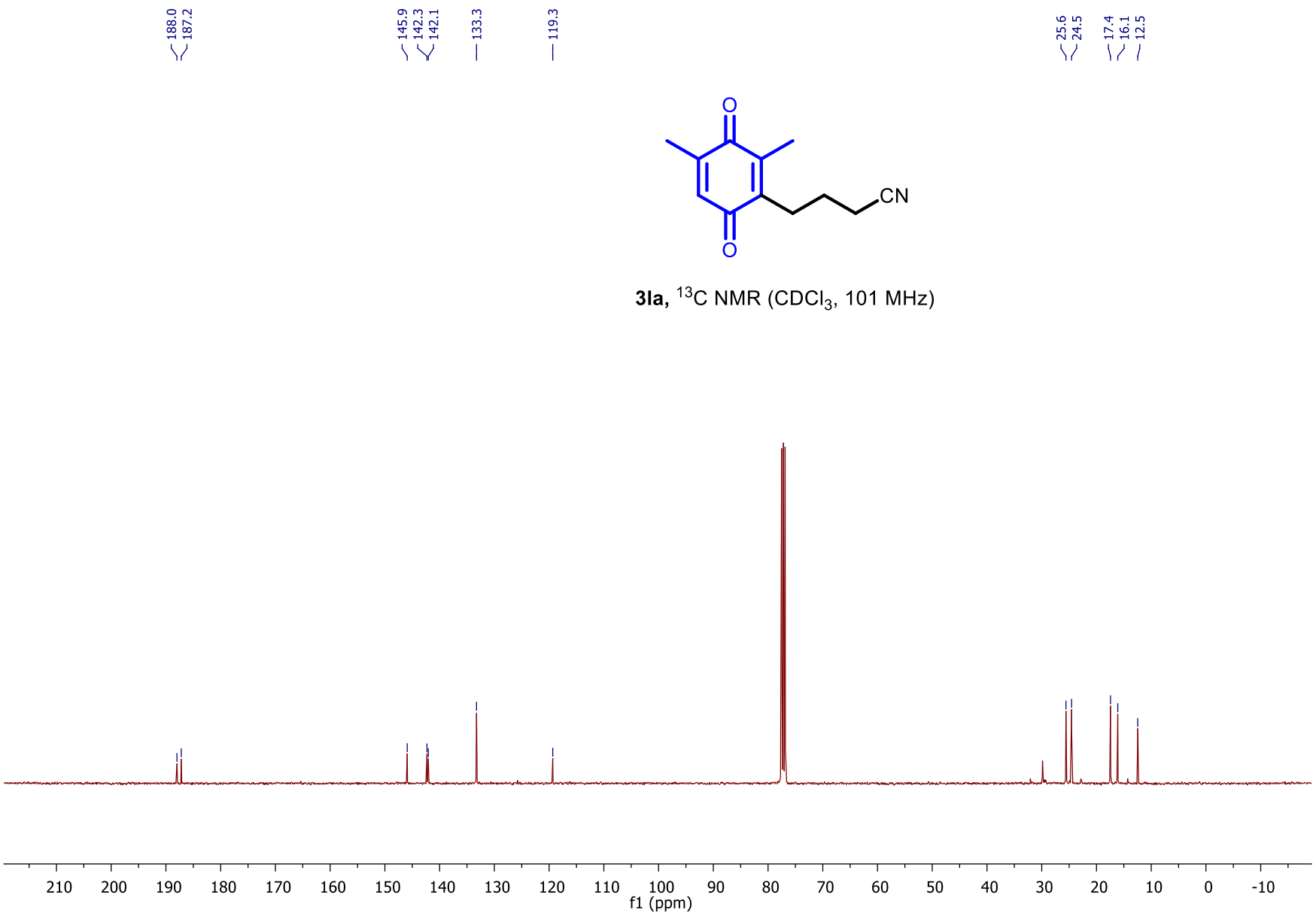
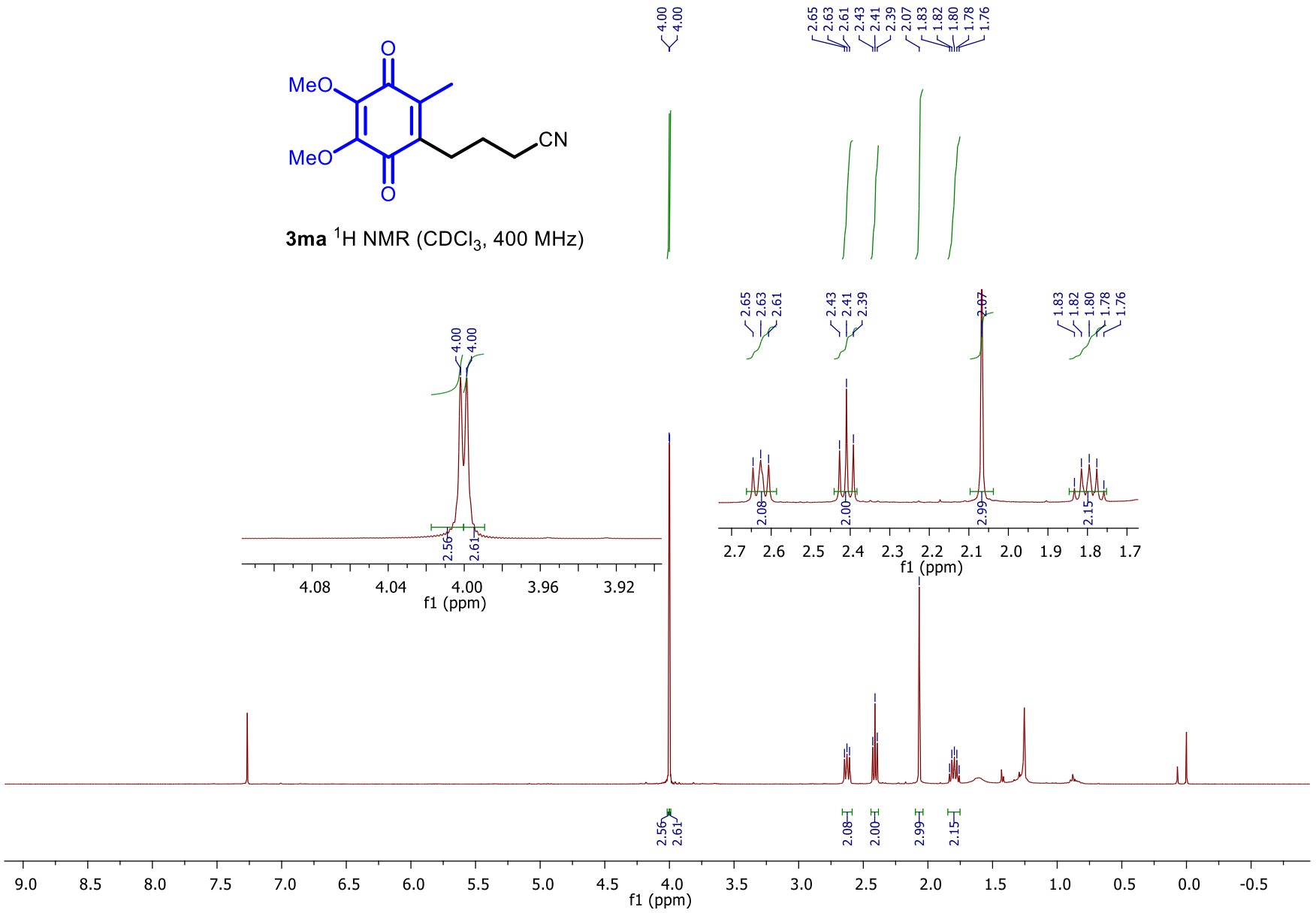
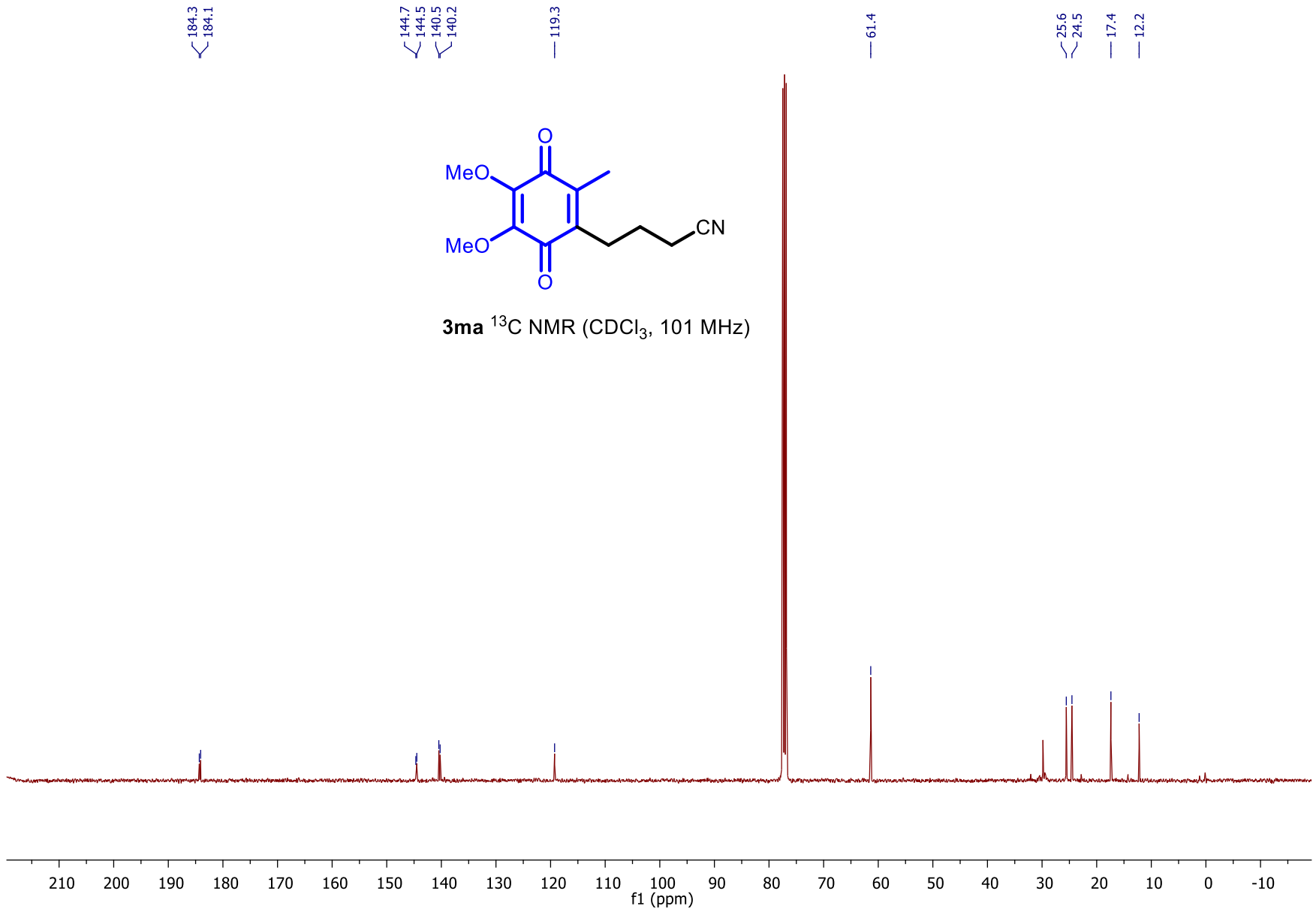
0.79
f1 (ppm)
0.79
2.00
2.04
2.78
2.77
2.19
f1 (ppm)



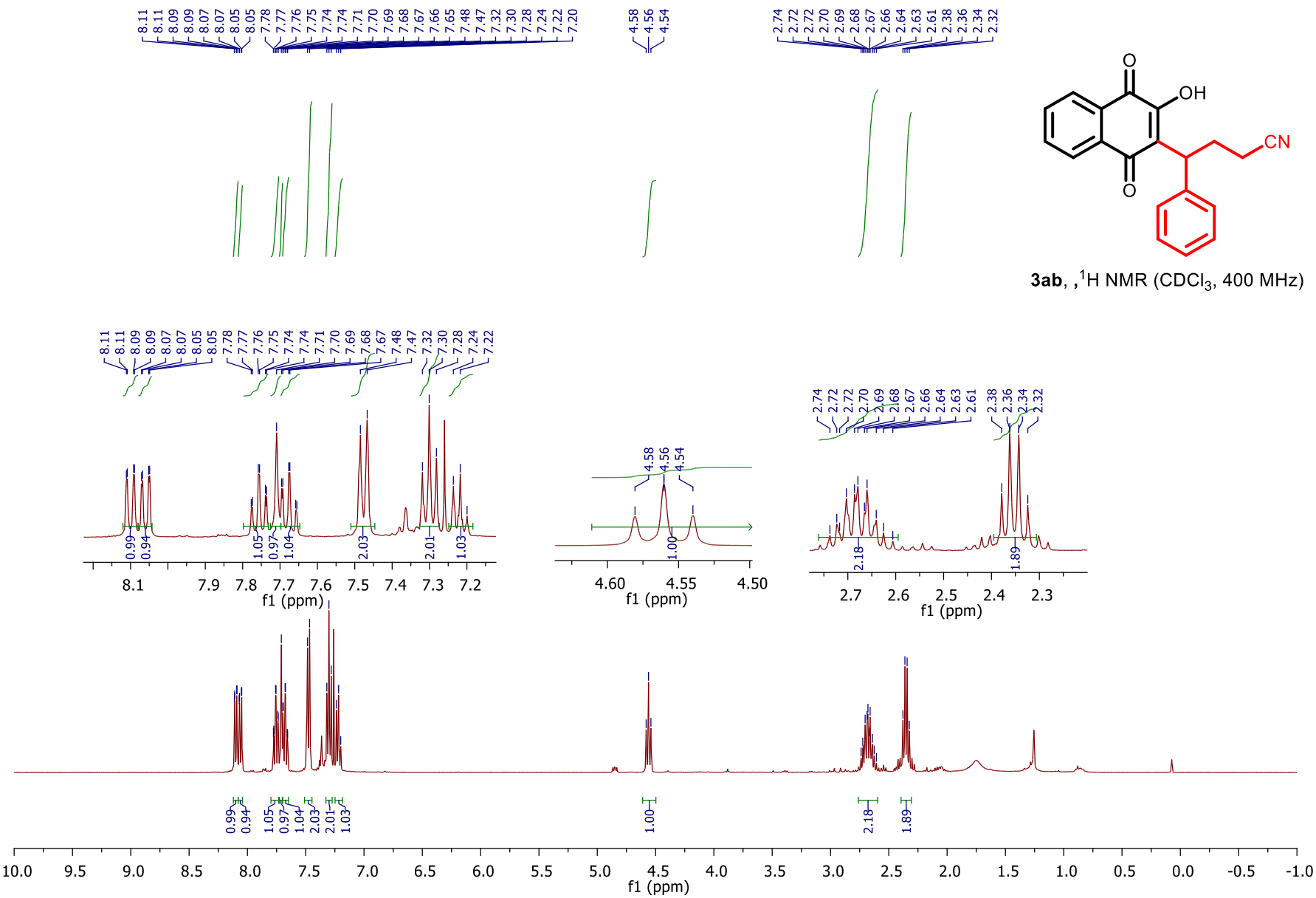
3la, ^{13}C NMR ($CDCl_3$, 101 MHz)



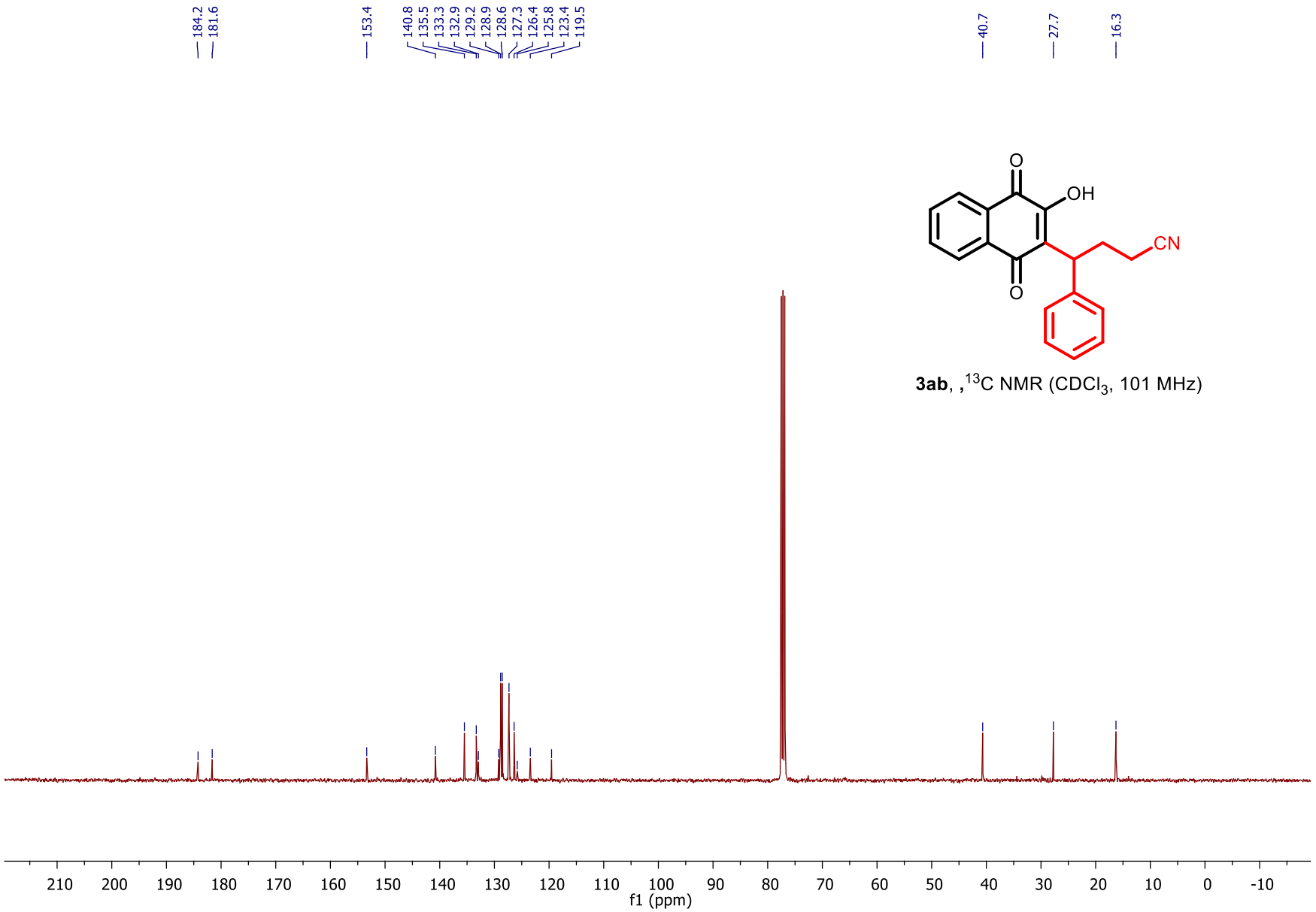
3ma ^{1}H NMR ($CDCl_3$, 400 MHz)



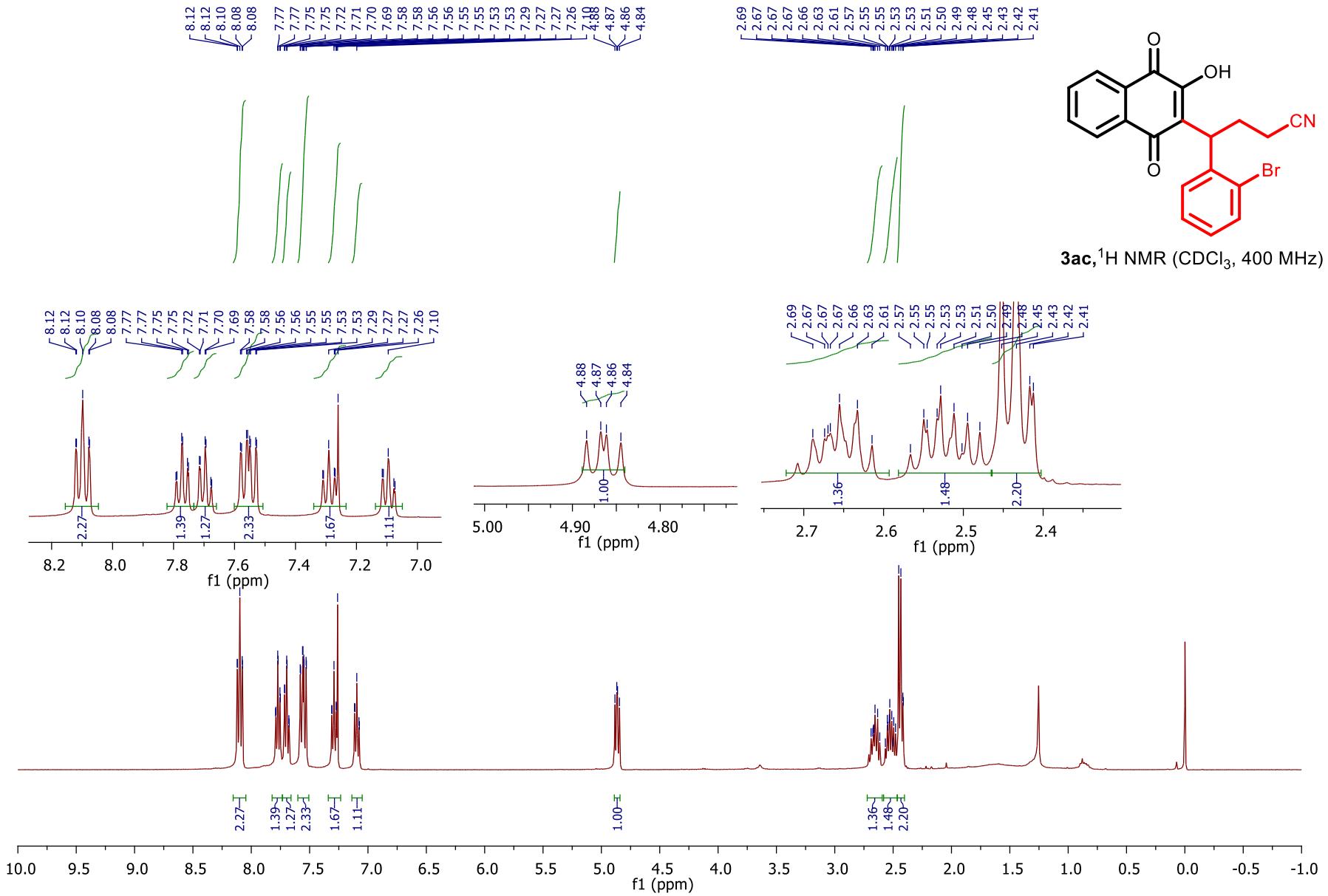
3ma ^{13}C NMR ($CDCl_3$, 101 MHz)

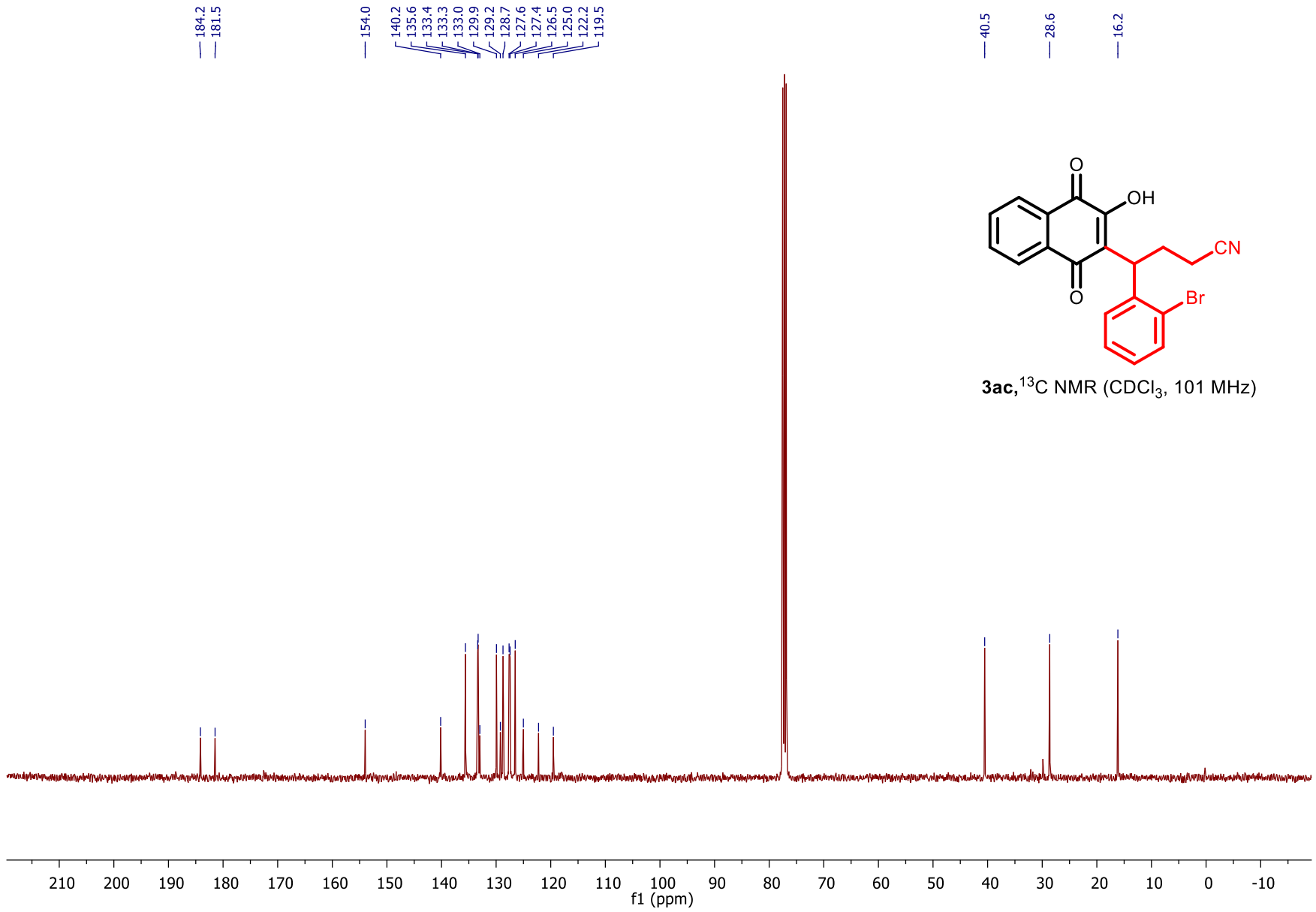


3ab, ,^{1}H NMR ($CDCl_3$, 400 MHz)

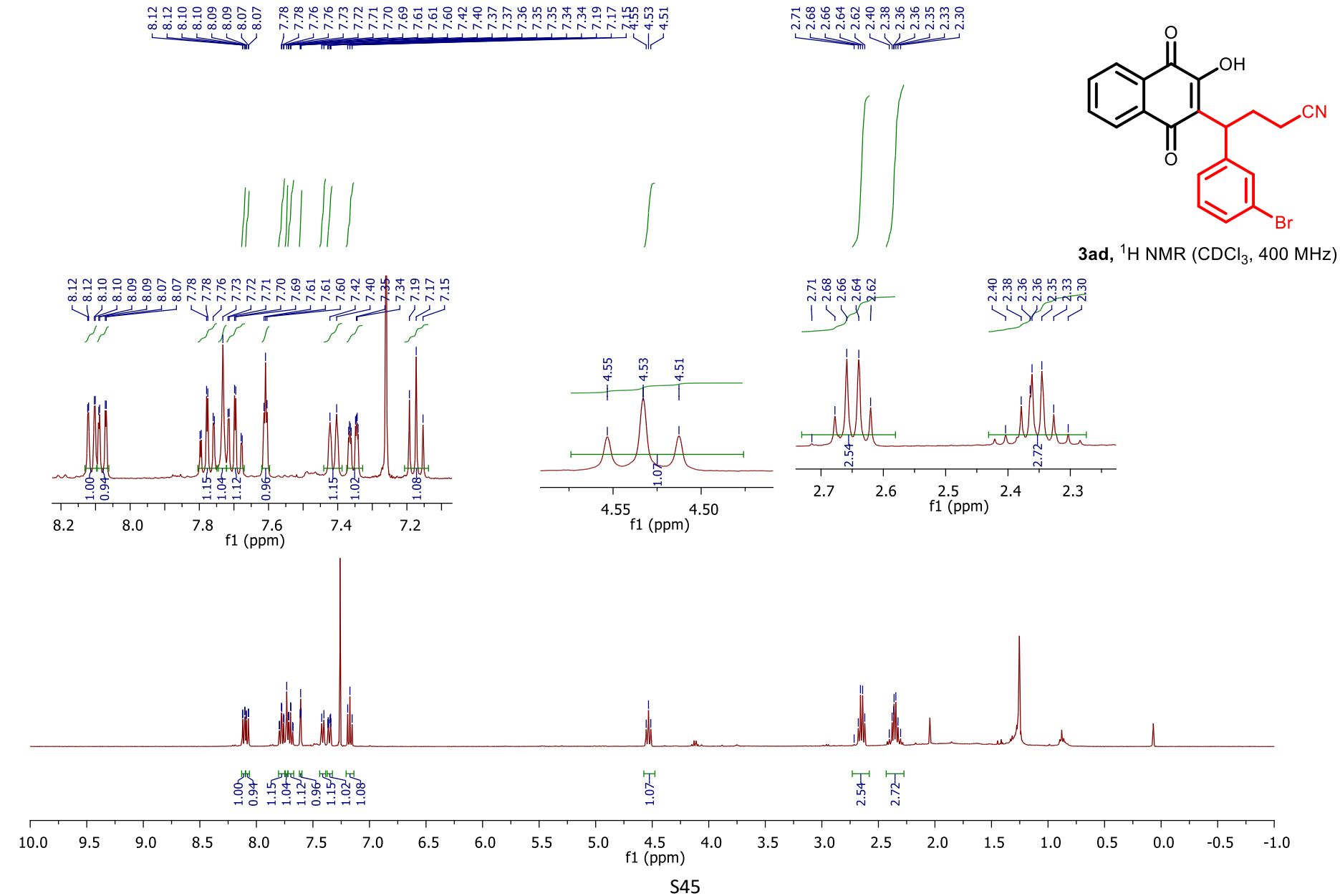


3ab, ,^{13}C NMR ($CDCl_3$, 101 MHz)

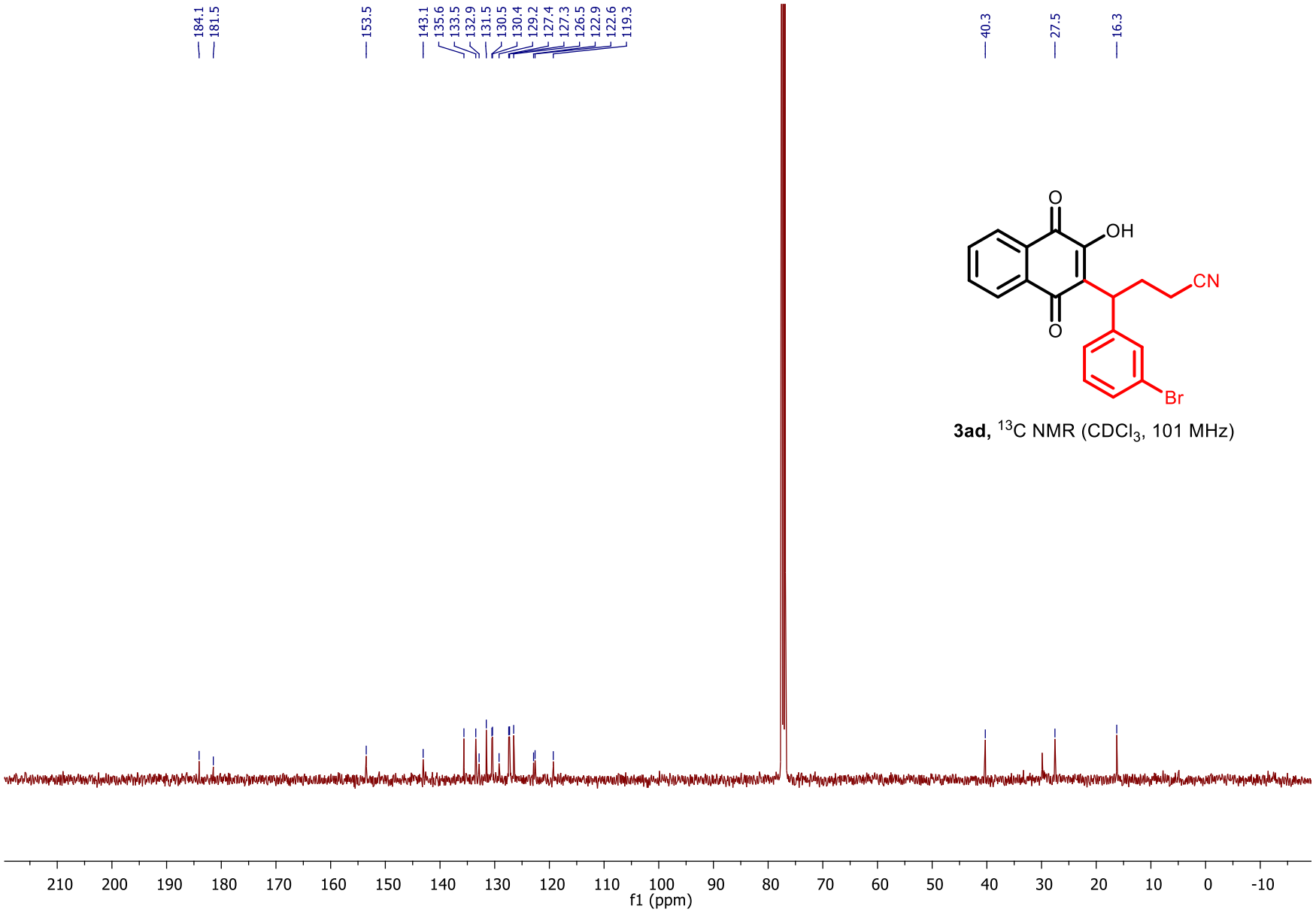

8.12 8.12 8.10 8.08 8.08 7.77 7.77 7.75 7.75 7.72 7.71 7.70 7.69 7.58 7.58 7.56 7.56 7.55 7.55 7.53 7.53 7.29 7.27 7.27 7.26 7.10 4.88 4.87 4.86 4.84
2.69 2.67 2.67 2.67 2.66 2.63 2.61 2.57 2.55 2.55 2.53 2.53 2.51 2.50 2.49 2.48 2.45 2.43 2.42 2.41
O
OH
CN
O
Br
3ac, 1H NMR (CDCl3, 400 MHz)
2.27 1.39 1.27 2.33 1.67 1.11
f1 (ppm)
1.00
f1 (ppm)
1.36 1.48 2.20
f1 (ppm)
2.27 1.39 1.27 2.33 1.67 1.11 1.00 1.36 1.48 2.20
f1 (ppm)



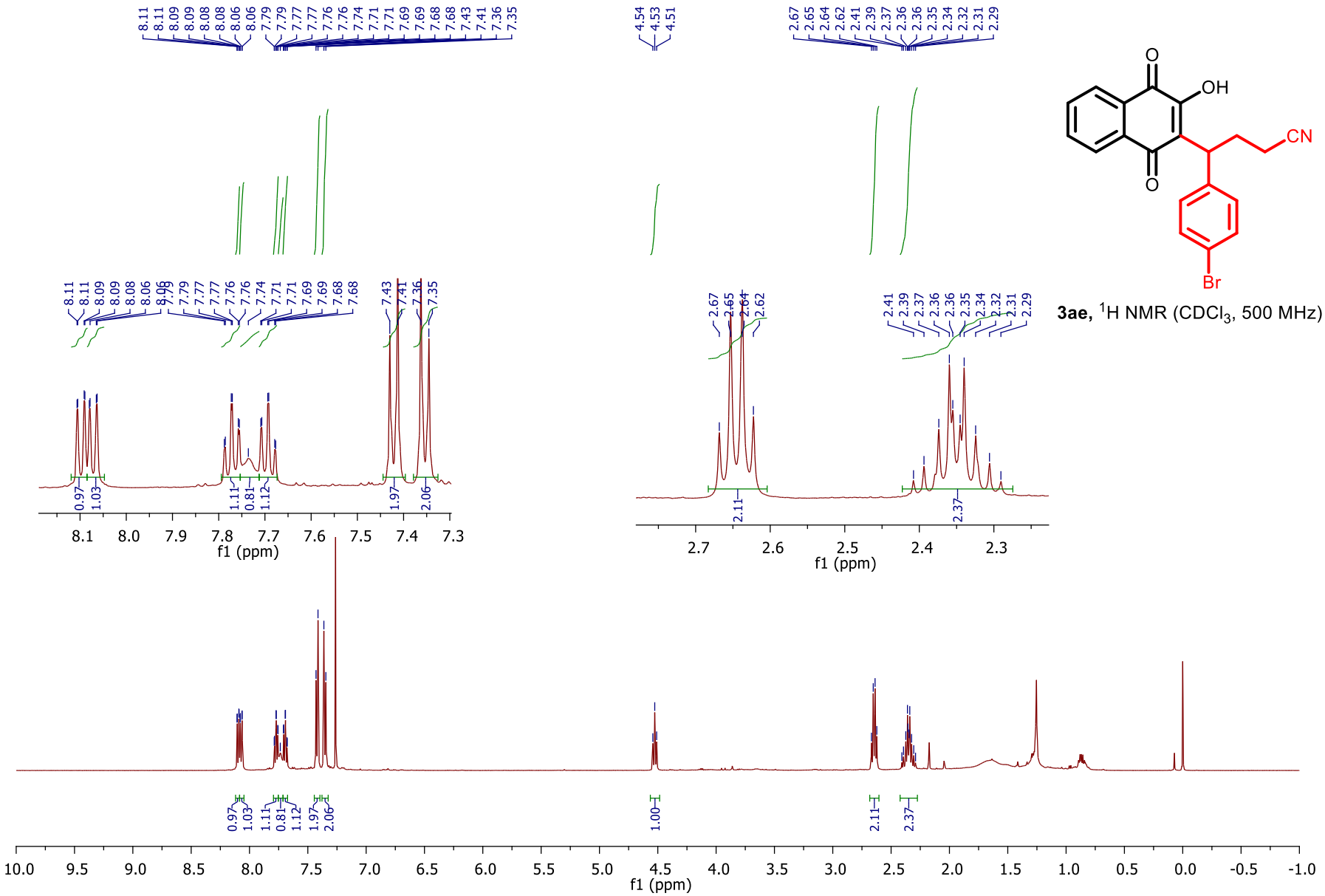
3ac, ^{13}C NMR ($CDCl_3$, 101 MHz)



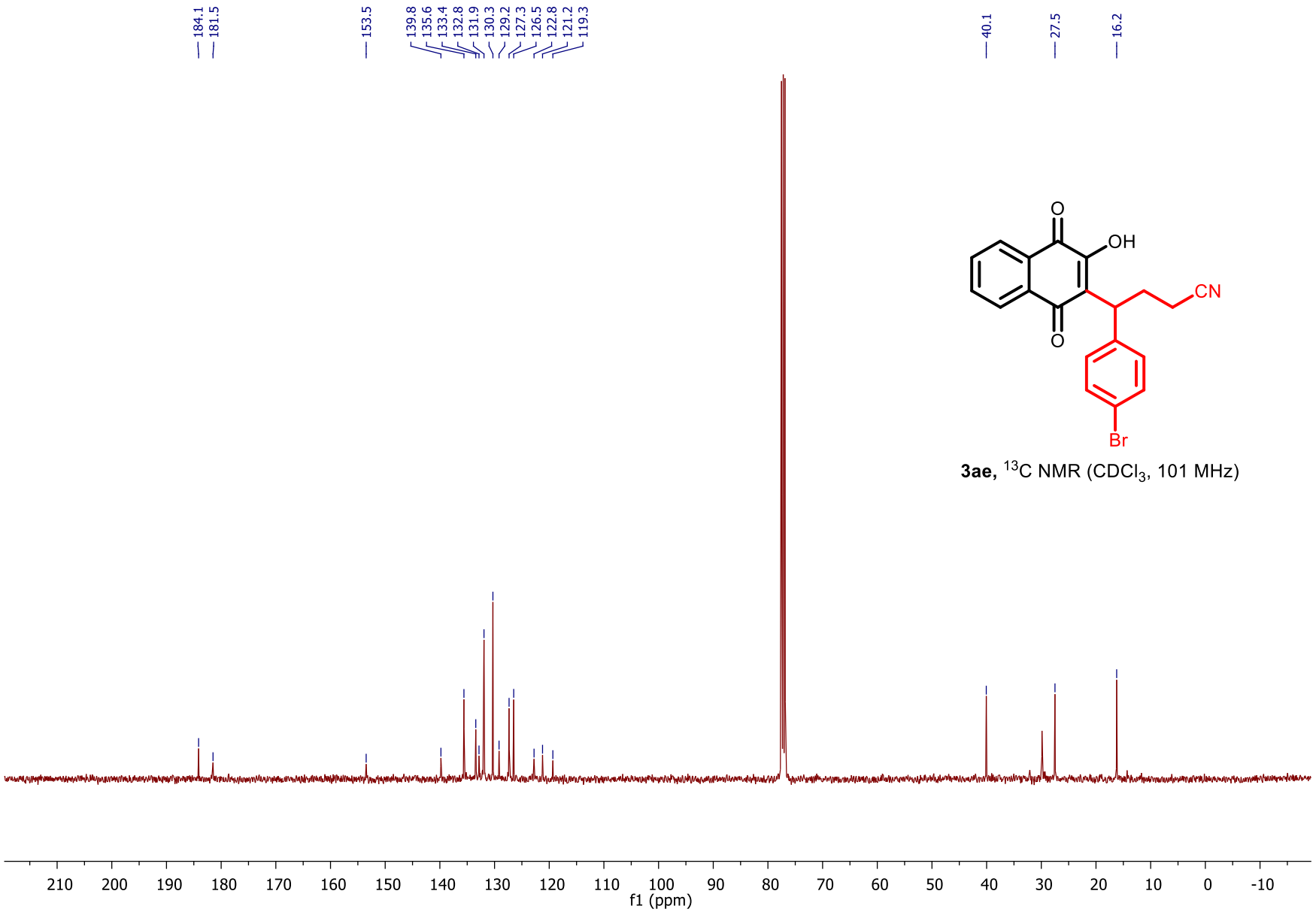
3ad, ^{1}H NMR ($CDCl_3$, 400 MHz)



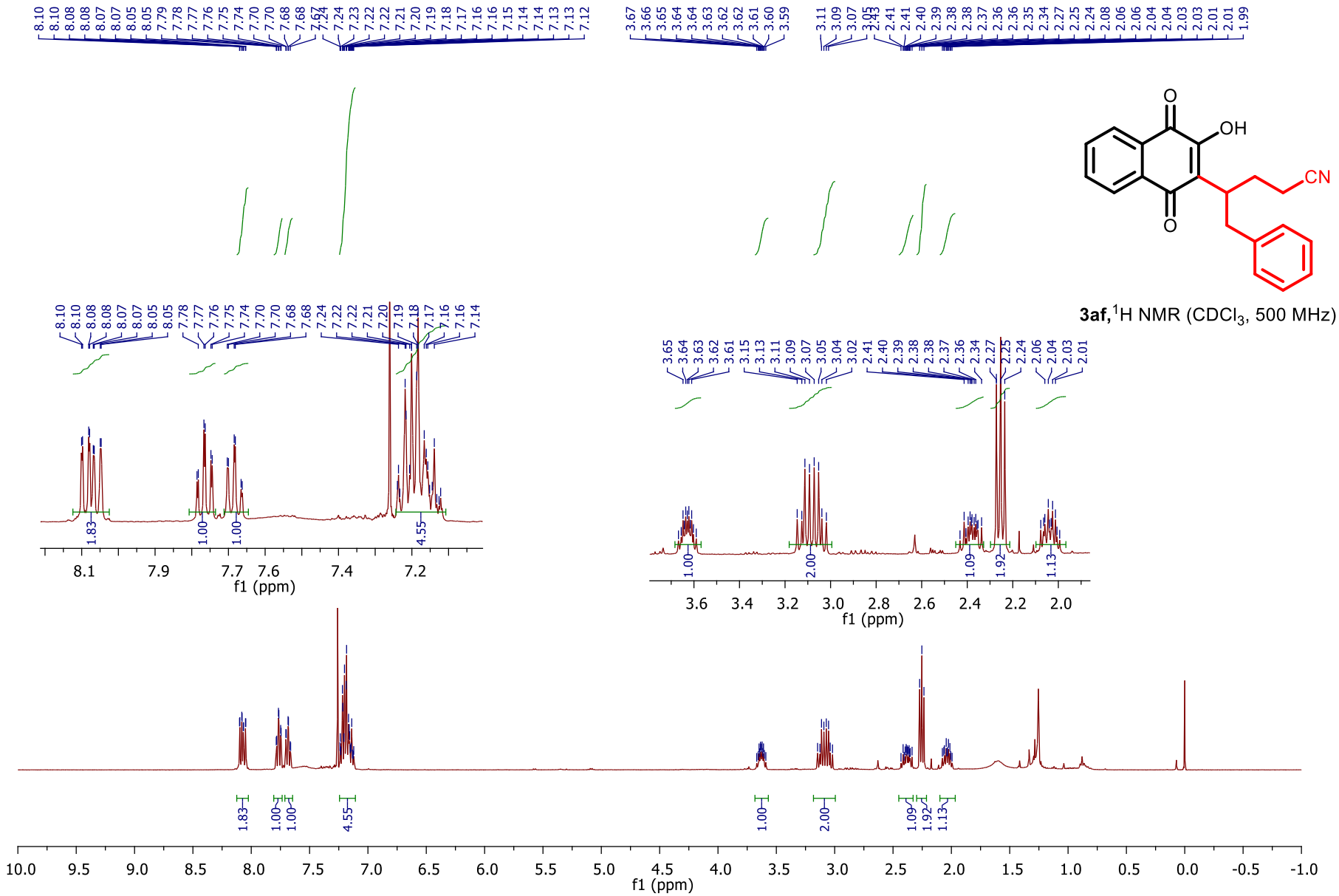
3ad, ^{13}C NMR ($CDCl_3$, 101 MHz)



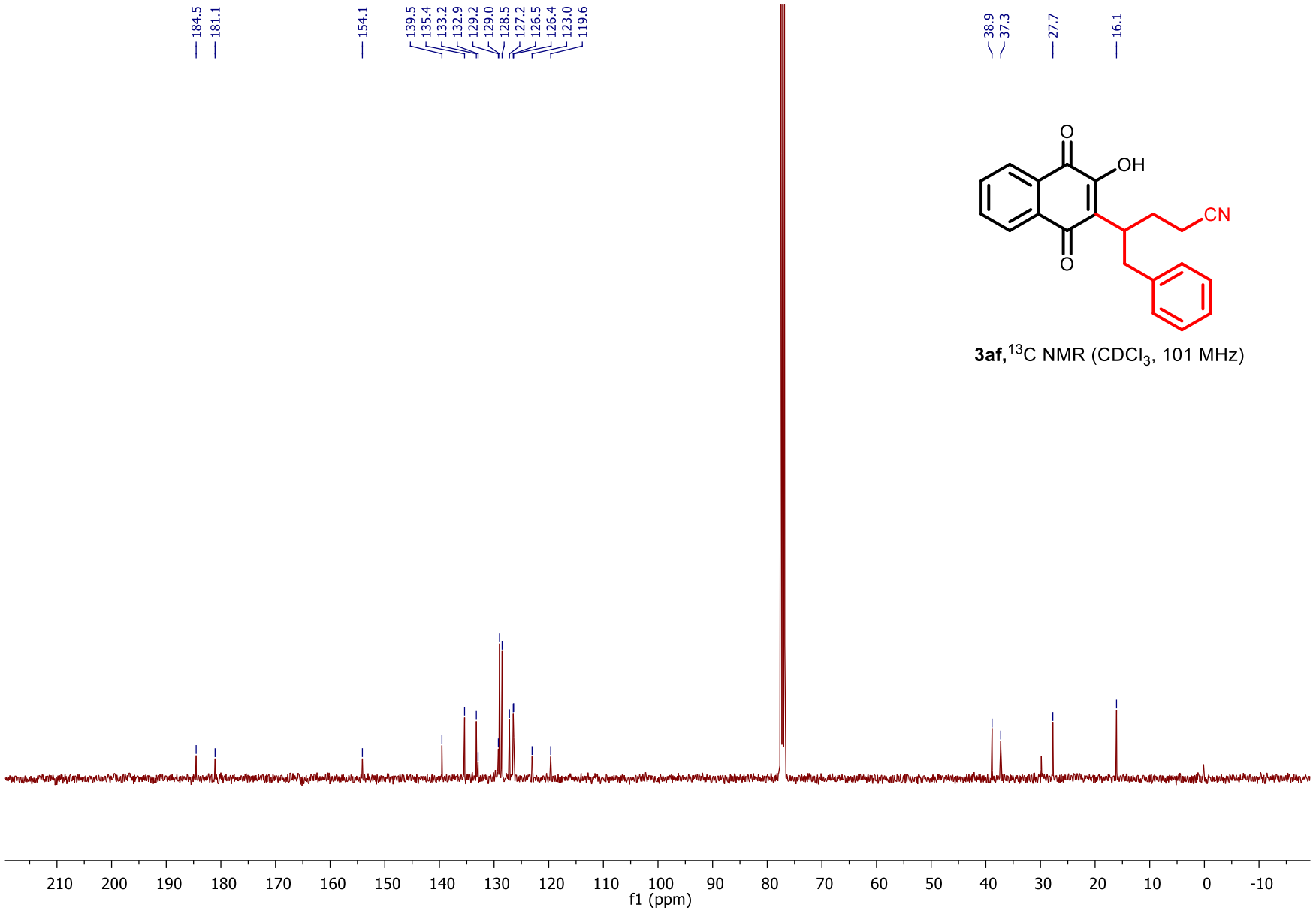
3ae, ^{1}H NMR ($CDCl_3$, 500 MHz)



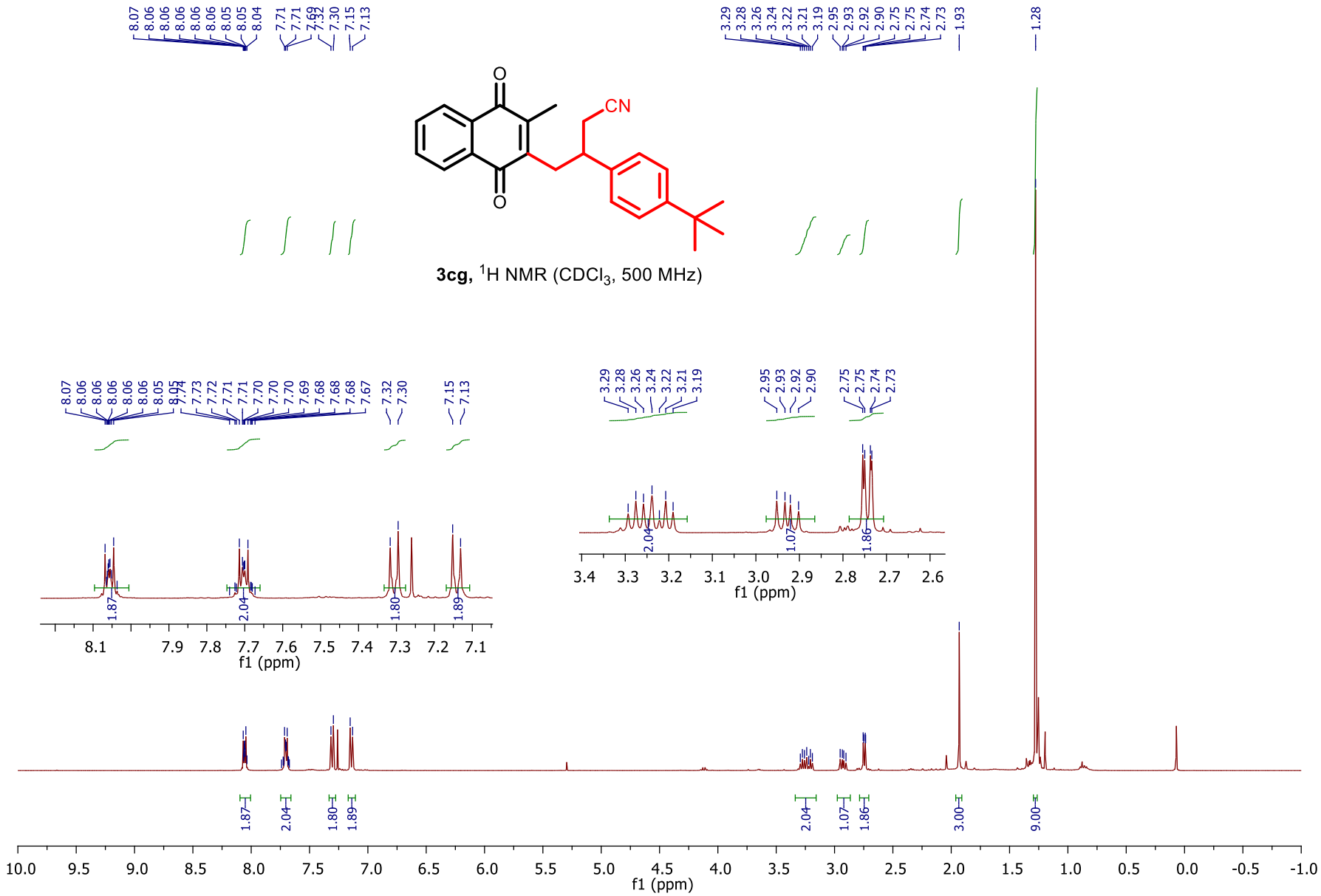
3ae, ^{13}C NMR ($CDCl_3$, 101 MHz)



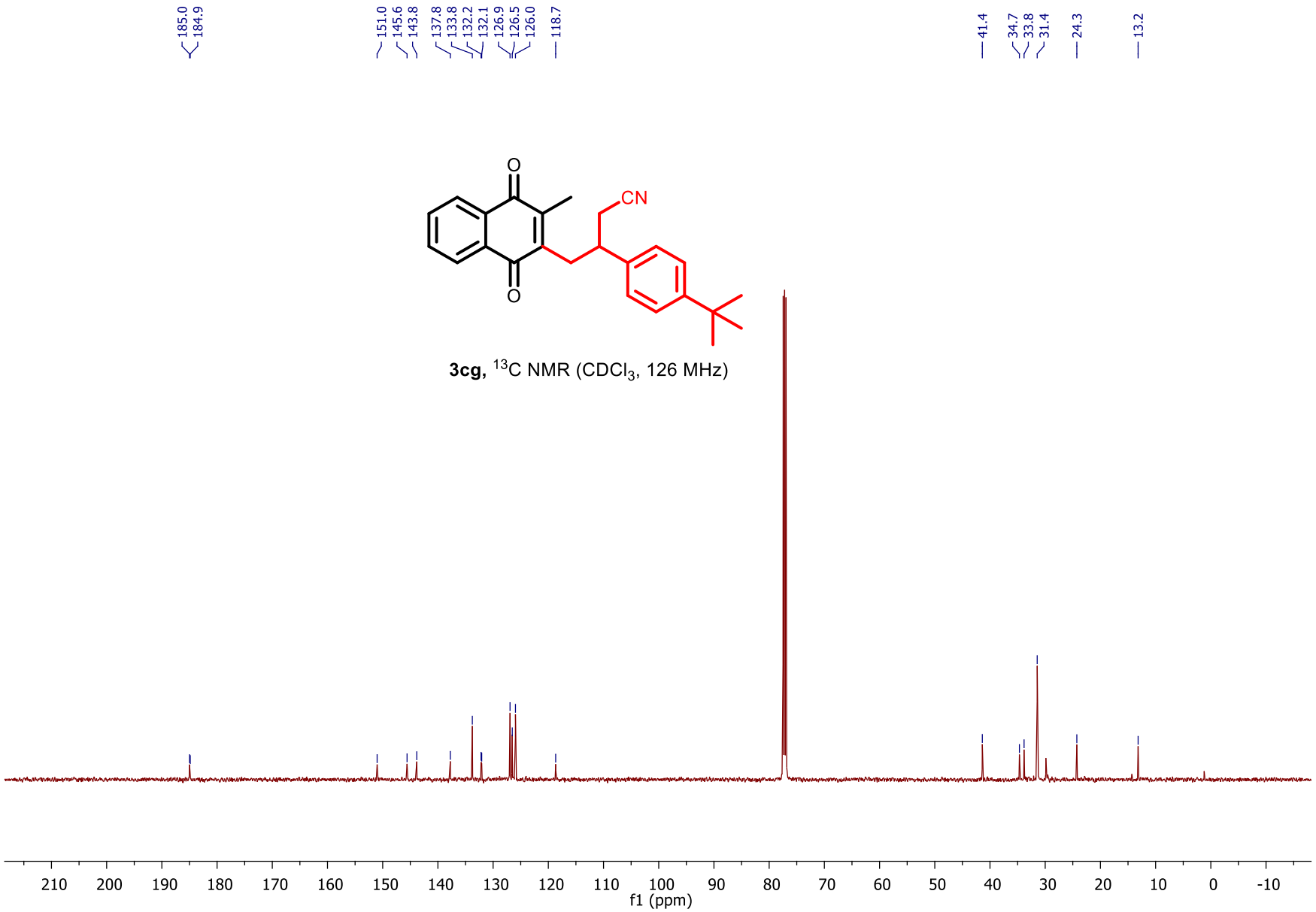
3af,^{1}H NMR ($CDCl_3$, 500 MHz)



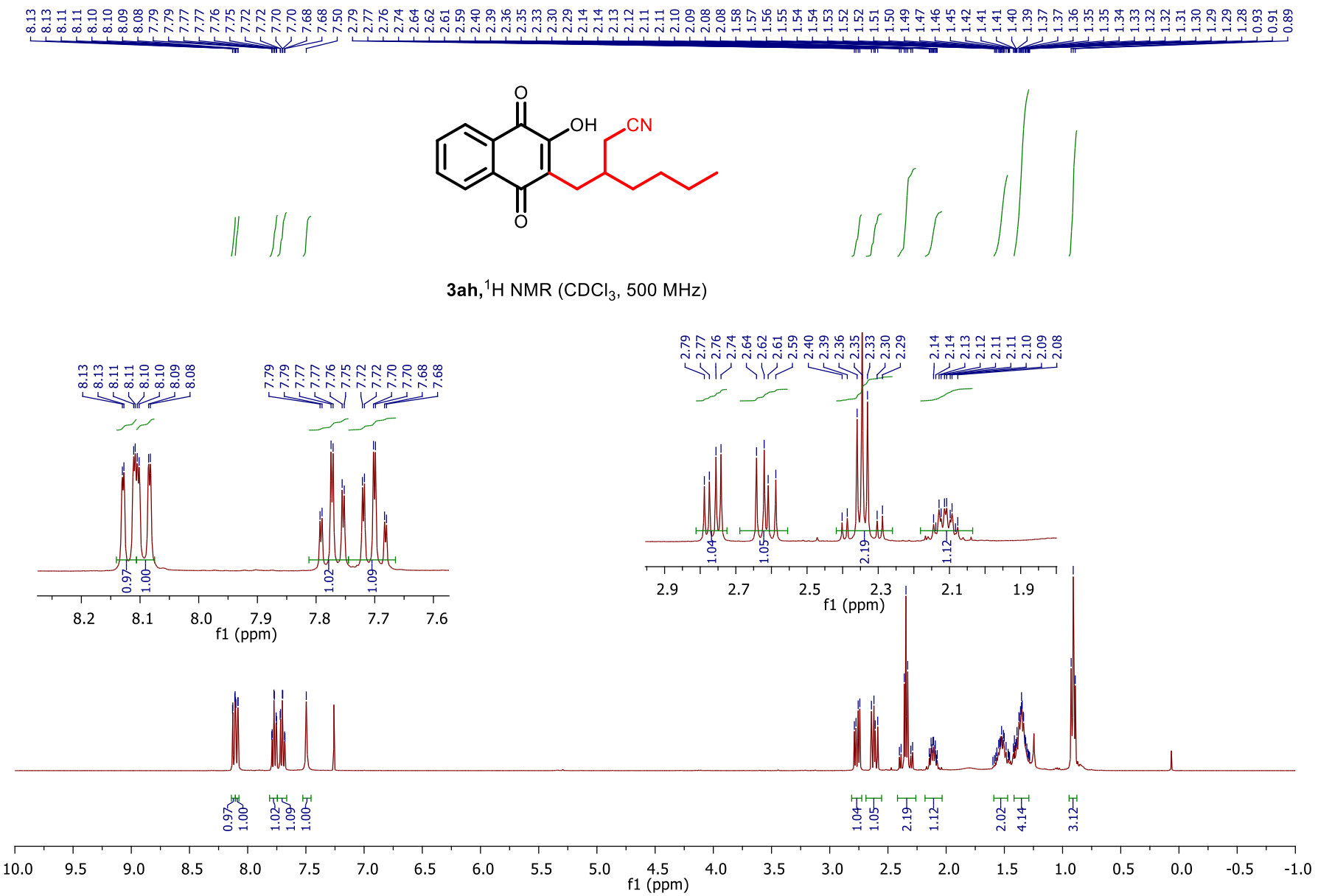
3af, ^{13}C NMR ($CDCl_3$, 101 MHz)



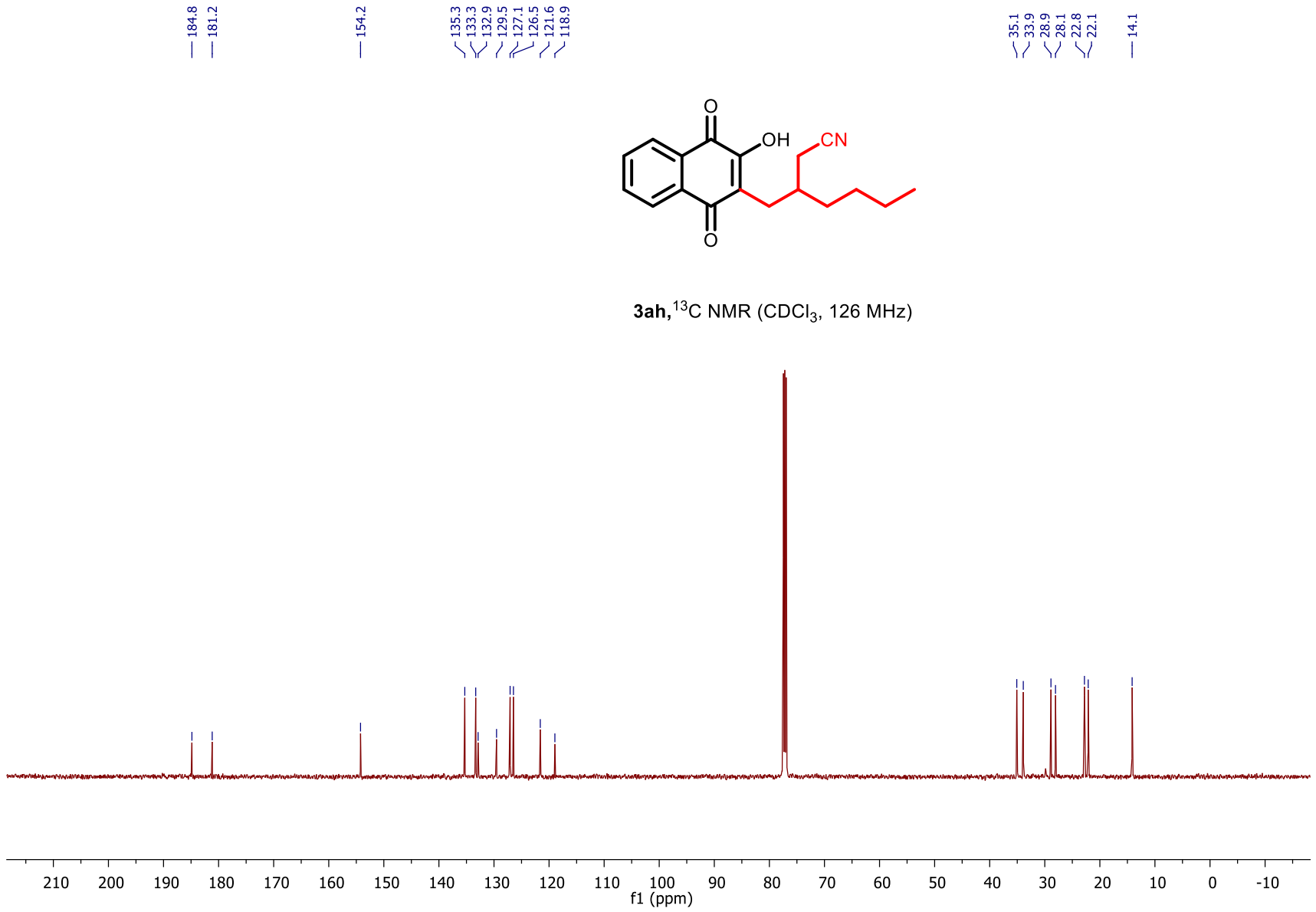
3cg, ^{1}H NMR ($CDCl_3$, 500 MHz)



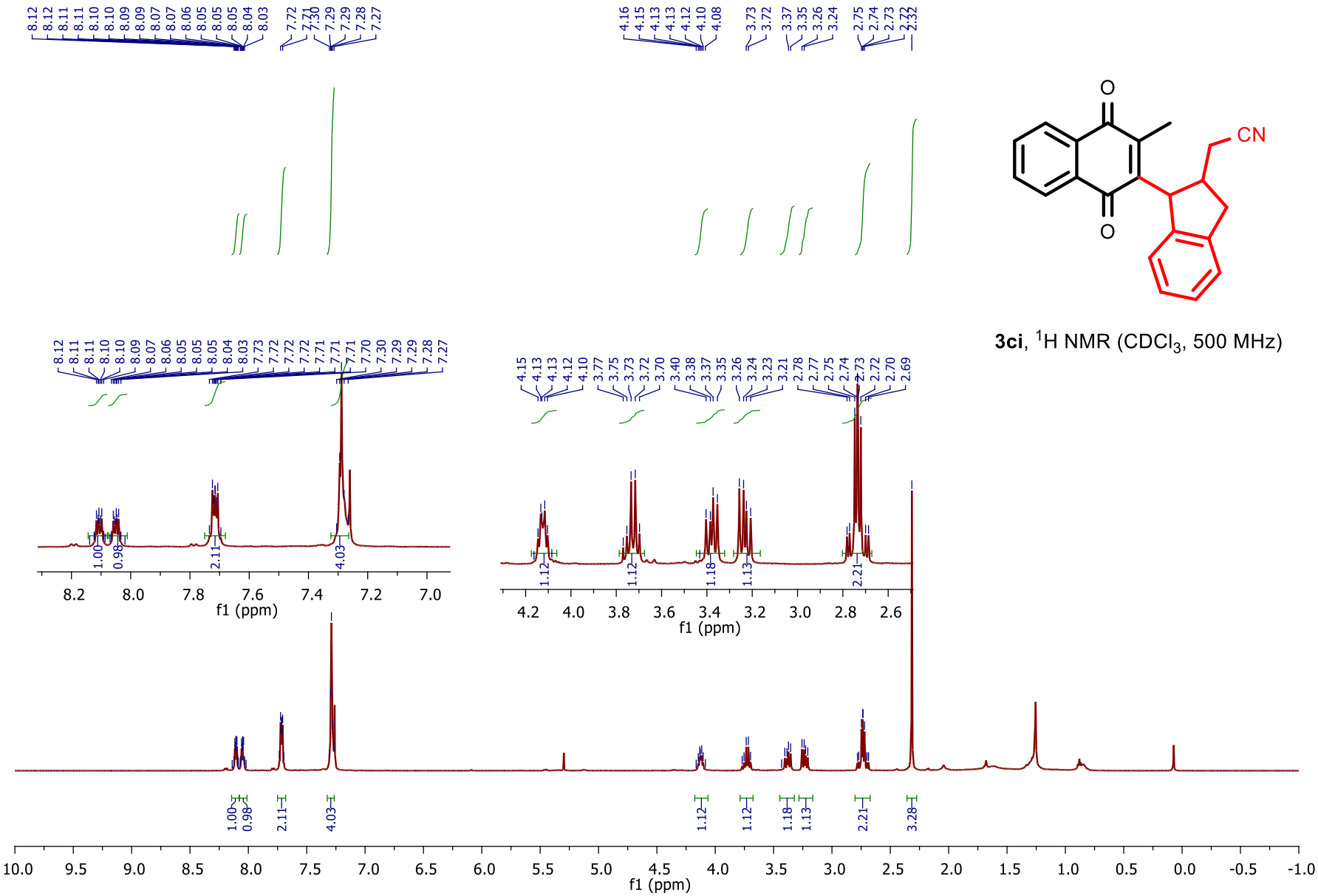
3cg, ^{13}C NMR ($CDCl_3$, 126 MHz)



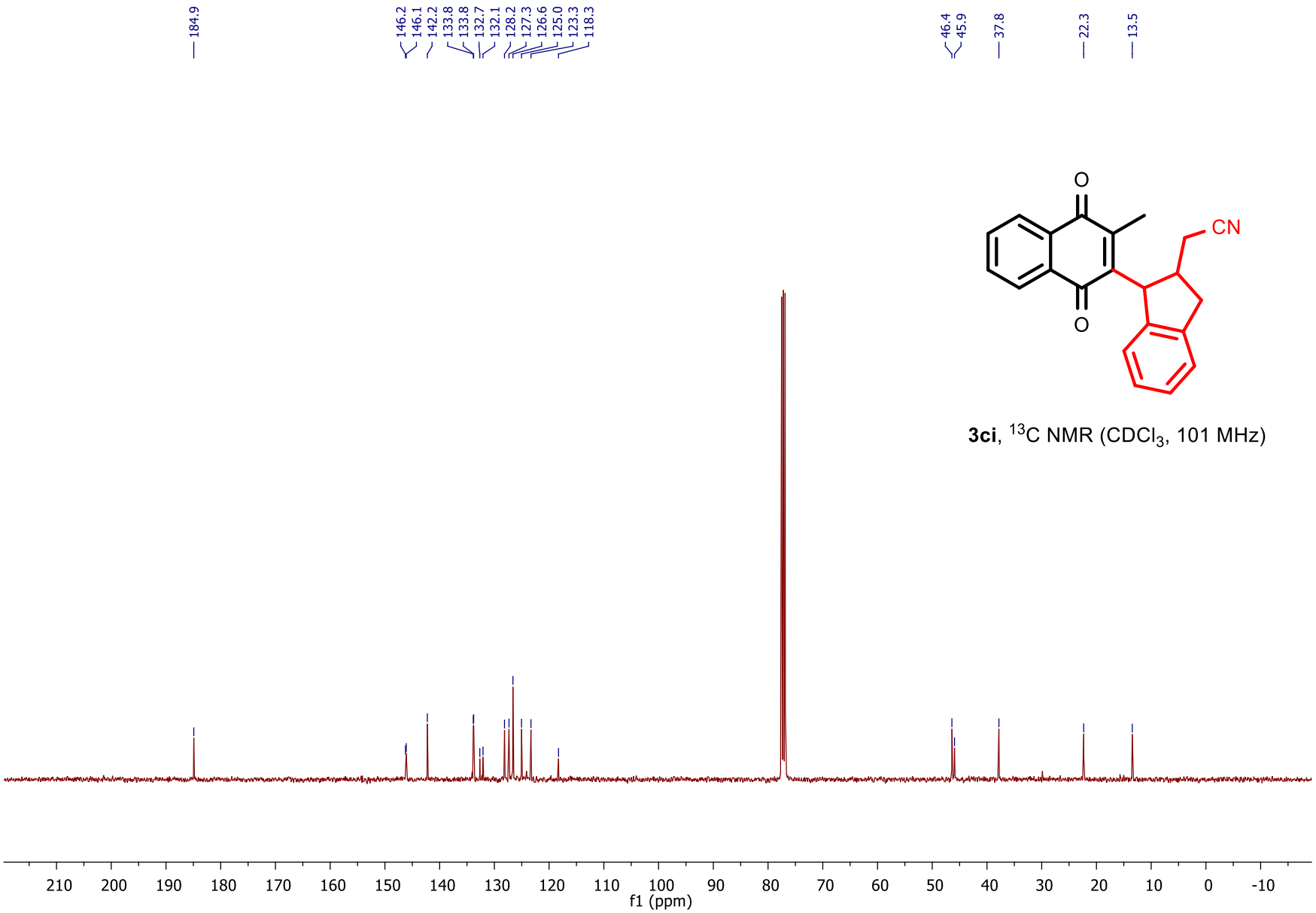
3ah,^{1}H NMR ($CDCl_3$, 500 MHz)



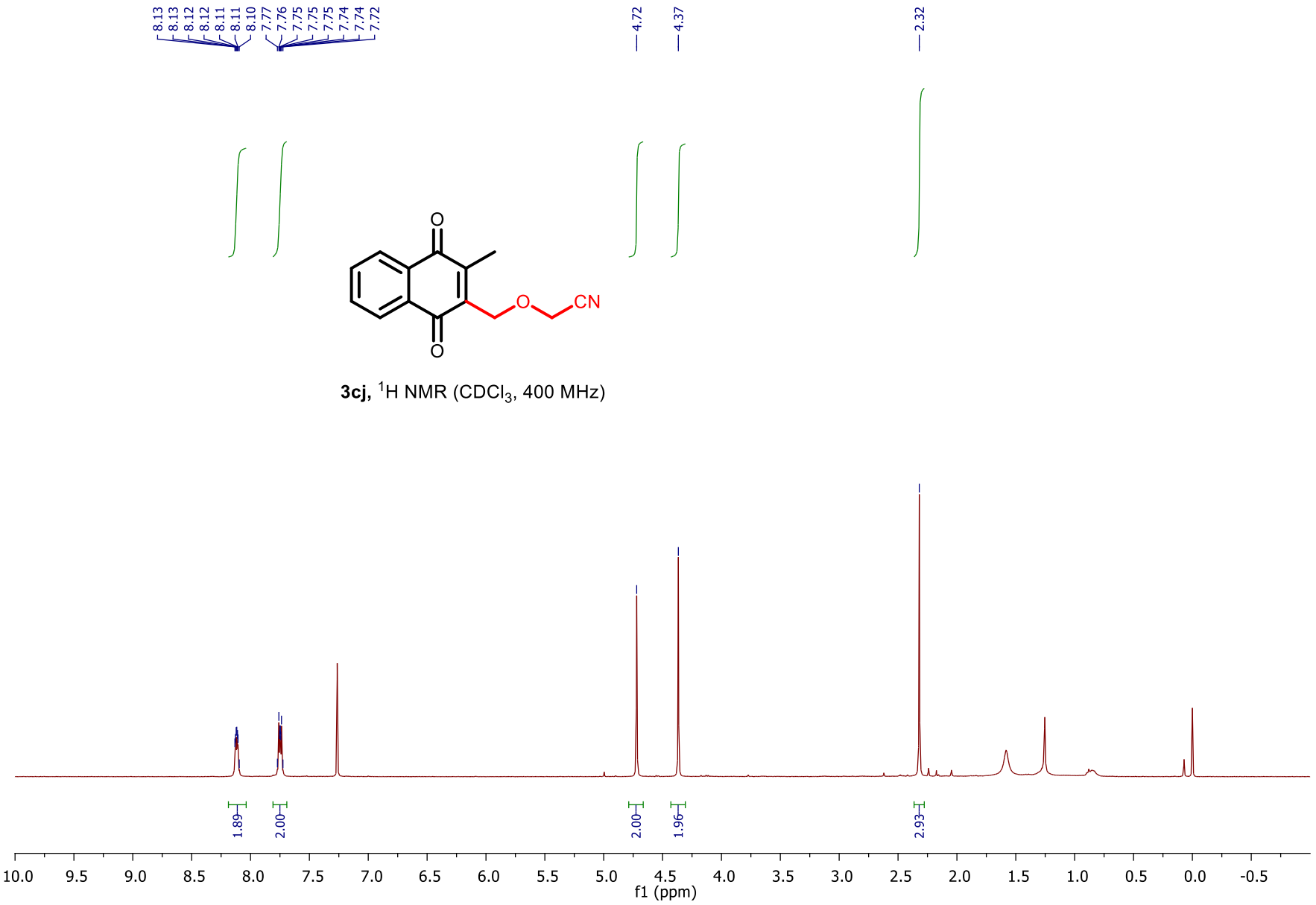
3ah, ^{13}C NMR ($CDCl_3$, 126 MHz)



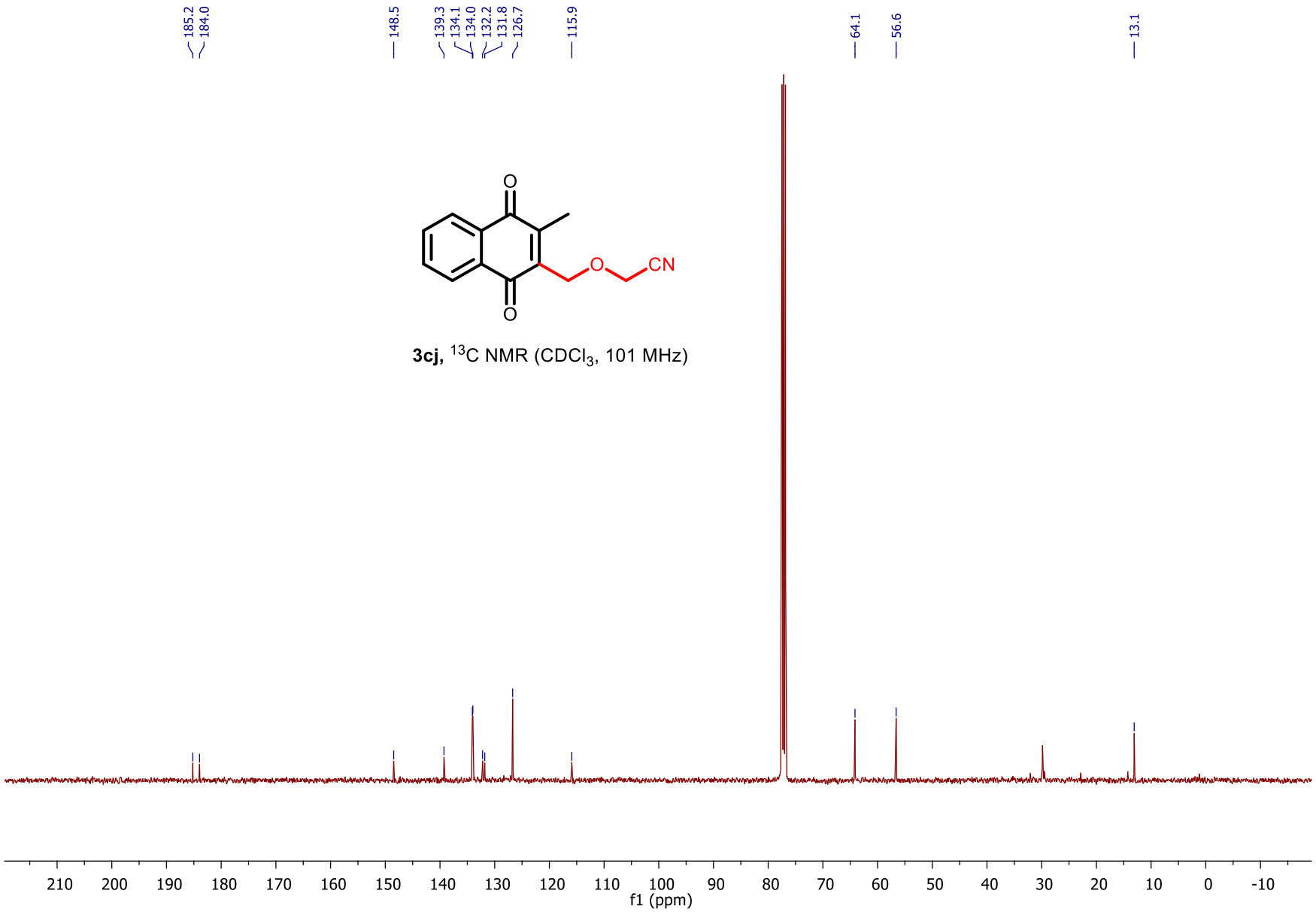
3ci, ^{1}H NMR ($CDCl_3$, 500 MHz)



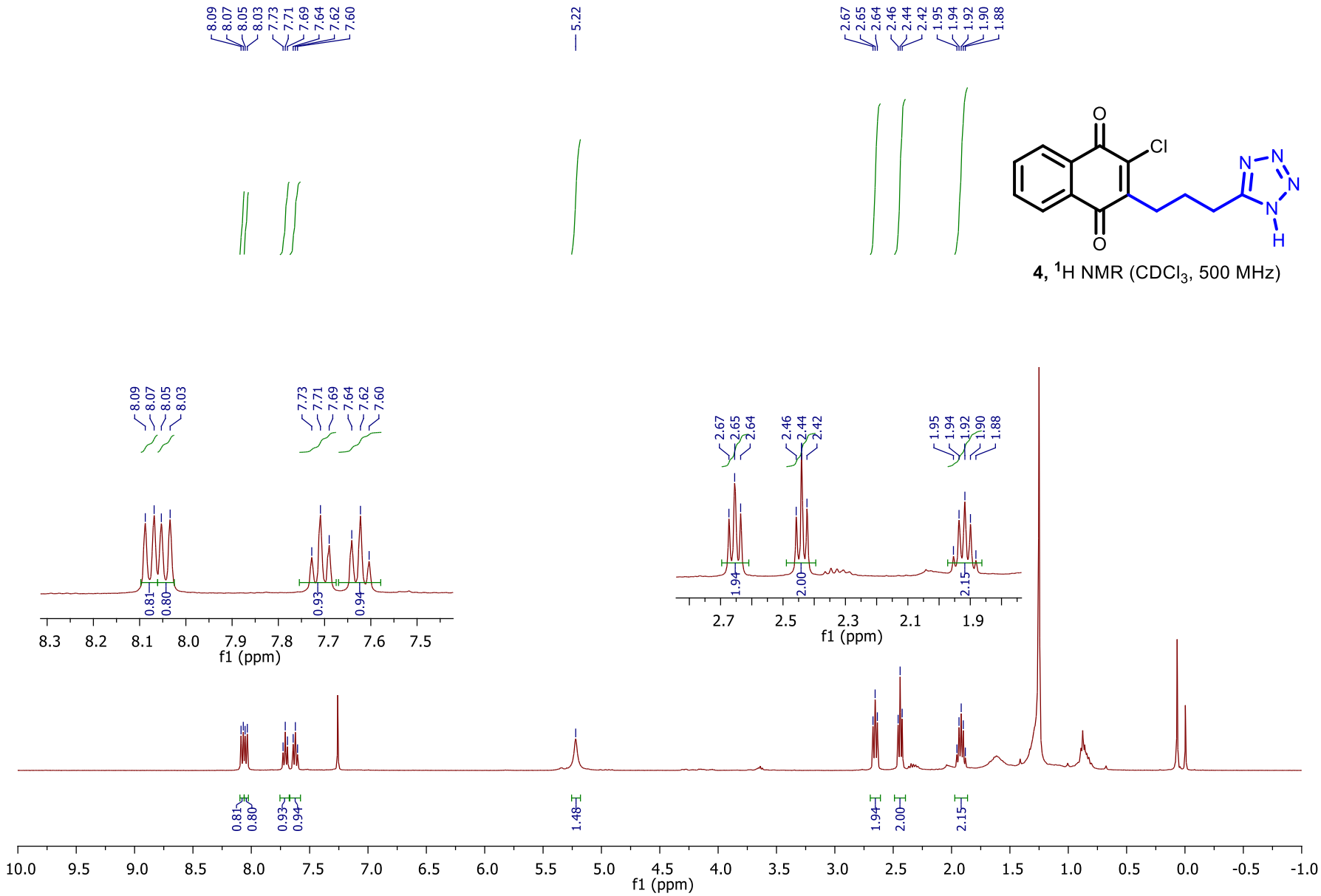
3ci, ^{13}C NMR ($CDCl_3$, 101 MHz)



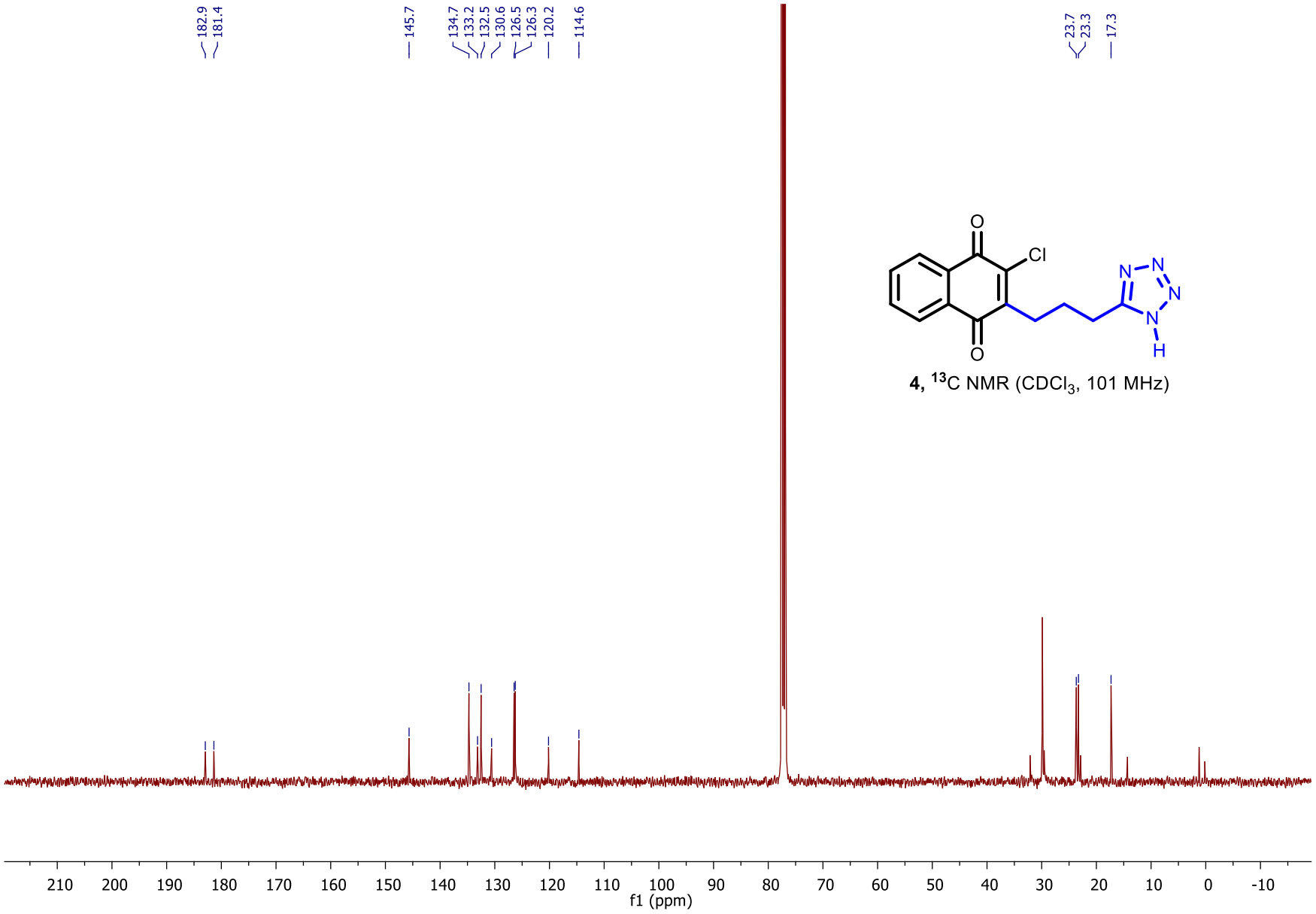
3cj, ^{1}H NMR ($CDCl_3$, 400 MHz)



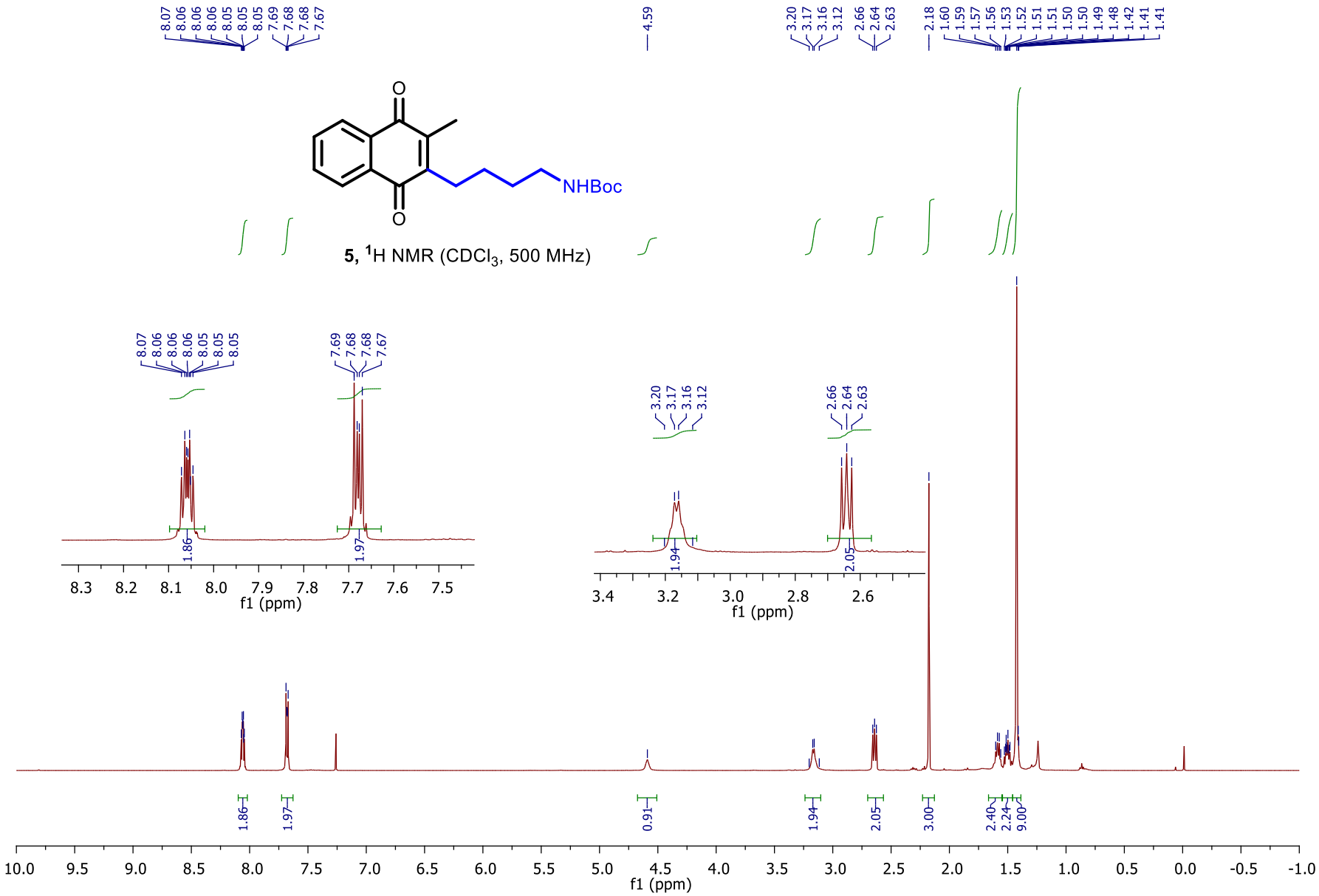
3cj, ^{13}C NMR ($CDCl_3$, 101 MHz)

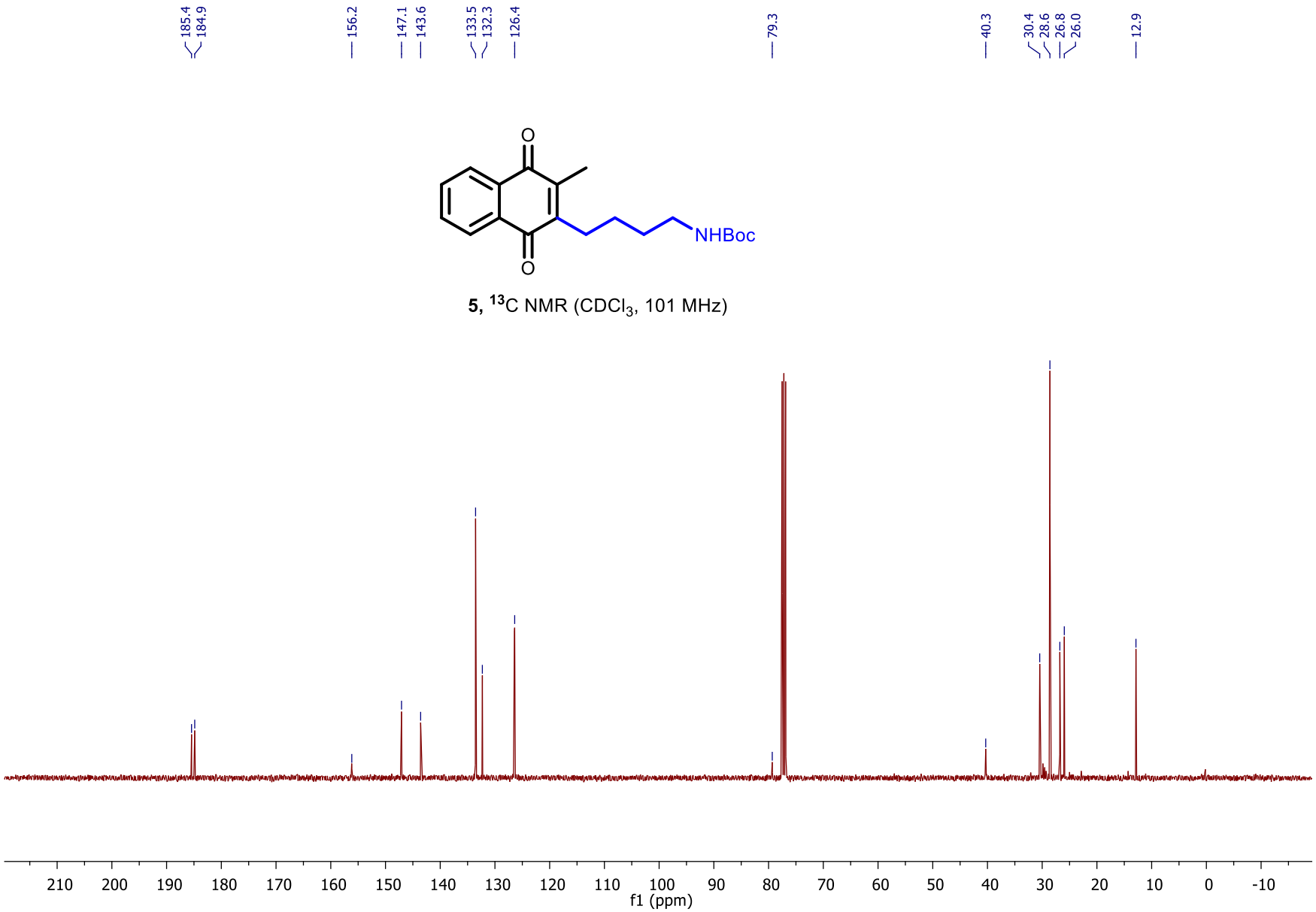


4, ^{1}H NMR ($CDCl_3$, 500 MHz)



4, ^{13}C NMR ($CDCl_3$, 101 MHz)


8.07
8.06
8.06
8.06
8.05
8.05
8.05
7.69
7.68
7.68
7.67
4.59
3.20
3.17
3.16
3.12
2.66
2.64
2.63
2.18
1.60
1.59
1.57
1.56
1.53
1.52
1.51
1.51
1.50
1.50
1.49
1.48
1.42
1.41
1.41
O
O
NHBoc
5, 1H NMR (CDCl3, 500 MHz)
1.86
1.97
1.94
2.05
f1 (ppm)
0.91
3.00
2.40
2.24
9.00



5, ^{13}C NMR ($CDCl_3$, 101 MHz)