Aminative Annulation of Cyano-Enynyl Esters Leading to Functionalized Cyclopentenones

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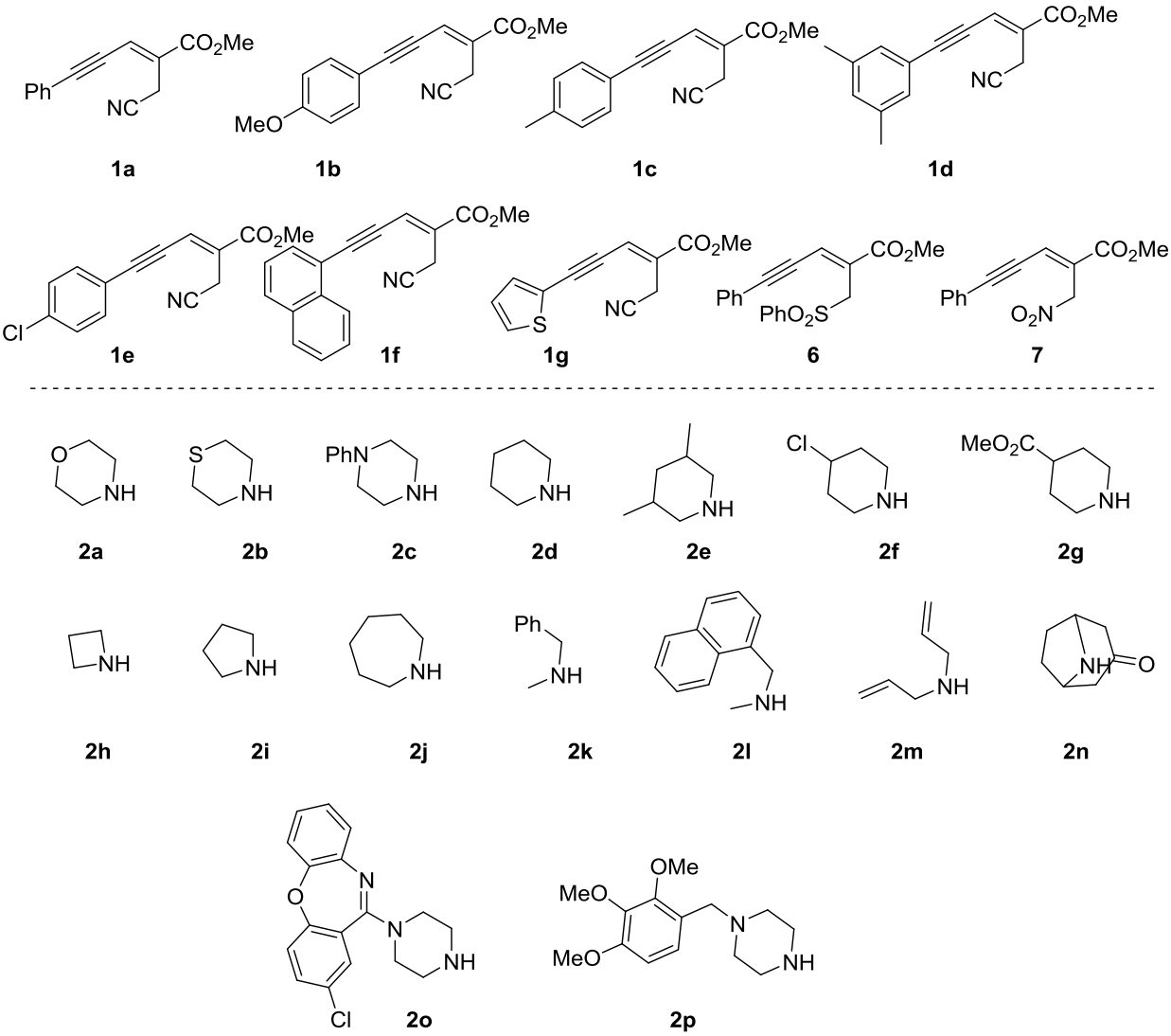
1. General information:

All the reactions were performed in oven-dried glass apparatus, the air and moisture sensitive reactions were carried out under inert atmosphere (nitrogen) using freshly distilled anhydrous solvents. Commercially available reagents were used as such without further purification. All reactions were monitored by thin-layer chromatography carried out on silica plates using UV-light and anisaldehyde for visualization. Column chromatography was peRf ormed on silica gel (100-200 mesh) using hexane and ethyl acetate as eluent. ^{1}H NMR was recorded in $CDCl_3$ on 500 MHz, 400 MHz and 300 MHz and ^{13}C NMR was recorded on 125 MHz, 100 MHz and 75 MHz. δ7.26 and δ77 are corresponding to $CDCl_3$ in ^{1}H NMR and ^{13}C NMR respectively, δ1.56 is related to moisture present in $CDCl_3$. Chemical shifts were reported in δ (ppm) relative to TMS as an internal standard and *J* values were given in Hz (hertz). Multiplicity is indicated as, s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets), etc. FTIR spectra were recorded on Alpha (Bruker) Infrared Spectrophotometer. High resolution mass spectra (HRMS) [ESI+] were obtain using either a TOF or a double focusing spectrometer. All the 2-en-4-ynyl cyanides were synthesized by using previous report.[1]

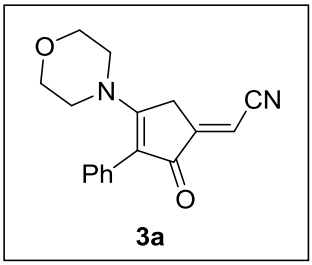
2. Structures of starting materials



3. General reaction and characterization data of compounds

General procedure for the synthesis of cyclopentenones: To a stirred solution of 2-en-4-ynyl cyanide [1] (0.2 mmol) in 1 mL acetonitrile were added amine (0.4 mmol, 2.0 equiv), K_2CO_3 (55 mg, 0.4 mmol, 2.0 equiv). Then reaction mixture was heated to 80 °C and stirred for 2-4 h. The reaction progress was monitored by TLC. After completion of the reaction, mixture was cooled to room temperature, and filtered through a pad of Celite. The filtrate was concentrated in vacuo to afford crude products, which was purified by flash column chromatography on silica gel (Hexane/EtOAc=70:30) to give the pure products.

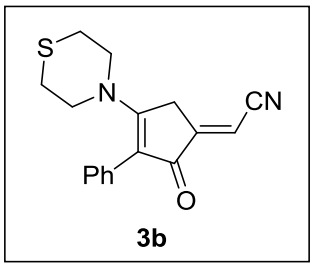
(*E*)-2-(4-Morpholino-2-oxo-3-phenylcyclopent-3-en-1-ylidene)acetonitrile (3a):



3a

Orange solid, 45 mg, 73% yield, m.p. 220−222 °C, Rf = 0.5 (hexane/ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 1H), 7.24 – 7.20 (m, 2H), 6.13 (t, *J* = 2.0 Hz, 1H), 3.67 (s, 4H), 3.58 (d, *J* = 2.0 Hz, 2H), 3.42 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 165.4, 154.3, 133.4, 129.8, 128.6, 127.7, 118.2, 116.9, 94.5, 66.5, 49.5, 33.2; IR (KBr): νmax = 2922, 2217, 1723, 1550, 1441, 1272, 1112, 750 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{17}N_2O_2$ $[M + H]^+$: 281.1285, found: 281.1286.

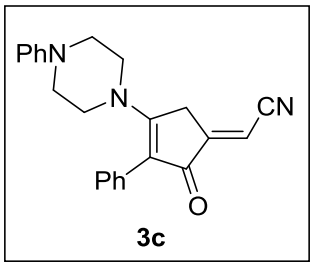
(*E*)-2-(2-Oxo-3-phenyl-4-thiomorpholinocyclopent-3-en-1-ylidene)acetonitrile (3b):



3b

Pale yellow solid, 46 mg, 71% yield, m.p. 201−203 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.2 Hz, 2H), 6.13 (s, 1H), 3.70 (s, 4H), 3.58 (d, *J* = 1.6 Hz, 2H), 2.62 (s, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.1, 165.3, 154.2, 133.8, 129.7, 128.7, 127.8, 118.6, 116.9, 94.5, 51.1, 33.4, 27.5 ; IR (KBr): νmax = 2922, 2217, 1660, 1545, 1499, 1282, 947, 748 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{17}N_2SO$ $[M + H]^+$: 297.1056, found: 297.1056.

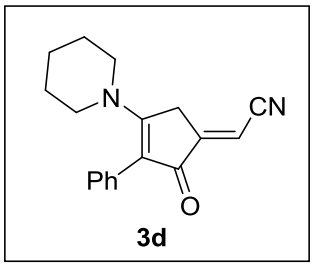
(*E*)-2-(2-Oxo-3-phenyl-4-(4-phenylpiperazin-1-yl)cyclopent-3-en-1-ylidene)acetonitrile (3c):



3c

Orange solid, 59 mg, 75% yield, m.p. 202−204 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 7.4 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.26 – 7.23 (m, 2H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.14 (t, *J* = 2.0 Hz, 1H), 3.64 (d, *J* = 2.0 Hz, 2H), 3.59 (s, 4H), 3.17 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.4, 162.8, 151.1, 147.7, 131.0, 127.3, 126.8, 126.0, 125.1, 118.6, 115.7, 114.4, 114.1, 91.9, 46.9, 46.5, 30.8.; IR (KBr): νmax = 2921, 2216, 1610, 1547, 1227, 882, 752, 694 cm^{-1}; HRMS (ESI): m/z calcd for $C_{23}H_{22}N_3O$ $[M + H]^+$: 356.1757, found: 356.1757.

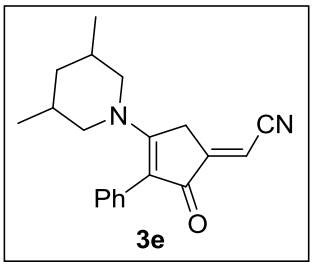
(*E*)-2-(2-Oxo-3-phenyl-4-(piperidin-1-yl)cyclopent-3-en-1-ylidene)acetonitrile (3d):



3d

Yellow solid, 42 mg, 69% yield, m.p. 172−174 °C, R_f = 0.5 (hexane/ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (t, *J* = 7.4 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.24 – 7.21 (m, 2H), 6.10 (t, *J* = 1.7 Hz, 1H), 3.57 (d, *J* = 1.9 Hz, 2H), 3.37 (s, 4H), 1.62 (s, 6H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 165.6, 155.2, 134.2, 129.7, 128.4, 127.4, 117.6, 117.2, 93.6, 50.7, 33.4, 26.2, 23.8; IR (KBr): νmax = 2925, 2214, 1537, 1443, 1297, 1022, 965, 721 cm^{-1}; HRMS (ESI): m/z calcd for $C_{18}H_{19}N_2O$ $[M + H]^+$: 279.1492, found: 279.1496.

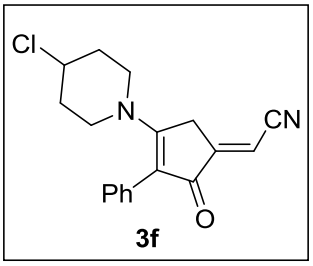
(*E*)-2-(4-(3,5-Dimethylpiperidin-1-yl)-2-oxo-3-phenylcyclopent-3-en-1-ylidene)acetonitrile (3e):



3e

Pale Yellow solid, 49 mg, 72% yield, m.p. 204−206 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.38 (t, J = 7.1 Hz, 2H), 7.35 – 7.24 (m, 1H), 7.18 (d, J = 7.1 Hz, 2H), 6.05 (s, 1H), 3.77 (s, 3H), 3.38 (s, 1H), 2.67 (s, 1H), 2.27 (s, 1H), 1.74 (d, J = 12.1 Hz, 2H), 1.57 (s, 1H), 0.89 (s, 3H), 0.77 (dd, J = 24.2, 12.2 Hz, 1H), 0.45 (s, 3H).; ^{13}C NMR (100 MHz, DMSO-d_6) δ 184.8, 166.5, 156.9, 135.7, 130.1, 128.5, 127.3, 117.9, 116.4, 92.7, 56.3, 55.7, 41.3, 33.1, 32.1, 31.0, 18.7; IR (KBr): νmax = 2923, 2216, 1660, 1547, 1287, 1250, 748, 667 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{23}N_2O$ $[M + H]^+$: 307.1805, found: 307.1808.

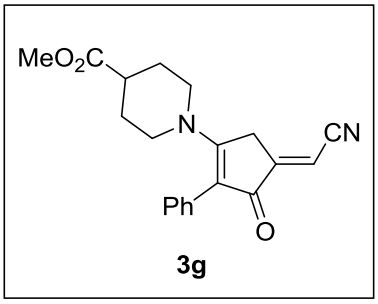
(*E*)-2-(4-(4-Chloropiperidin-1-yl)-2-oxo-3-phenylcyclopent-3-en-1-ylidene)acetonitrile (3f):



3f

Brown solid, 47 mg, 68% yield, m.p. 143−145 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 6.7 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.22 (d, J = 7.3 Hz, 2H), 6.13 (s, 1H), 4.32 (s, 1H), 3.59 (s, 4H), 3.41 (s, 2H), 2.06 (s, 2H), 1.88 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.9, 165.4, 154.5, 133.6, 129.7, 128.6, 127.7, 118.2, 116.9, 94.4, 54.9, 46.1, 34.8, 33.5.; IR (KBr): νmax = 2925, 2216, 1596, 1287, 1253, 1126, 750, 761, 708 cm^{-1}; HRMS (ESI): m/z calcd for $C_{18}H_{18}ClN_2O$ $[M + H]^+$: 313.1102, found: 313.1103.

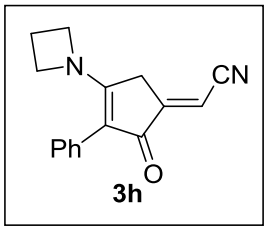
Methyl(*E*)-1-(4-(cyanomethylene)-3-oxo-2-phenylcyclopent-1-en-1-yl)piperidine-4-carboxylate (3g):



3g

Brown solid, 55 mg, 75% yield, m.p. 132−134 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.0 Hz, 2H), 6.12 (s, 1H), 3.74 (s, 2H), 3.70 (s, 3H), 3.58 (d, *J* = 1.7 Hz, 2H), 3.09 (s, 2H), 2.64 – 2.54 (m, 1H), 1.90 (s, 2H), 1.76 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.8, 173.8, 165.5, 154.7, 133.8, 129.7, 128.6, 127.6, 118.0, 117.0, 94.1, 52.1, 48.6, 39.9, 33.4, 28.1; IR (KBr): νmax = 2952, 2216, 1728, 1542, 1442, 1913, 1037, 749, 696 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{21}N_2O_3$ $[M + H]^+$: 337.1547, found: 337.1542.

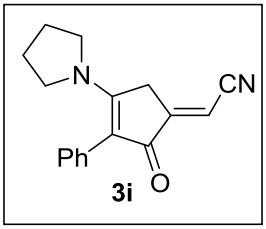
(*E*)-2-(4-(Azetidin-1-yl)-2-oxo-3-phenylcyclopent-3-en-1-ylidene)acetonitrile (3h):



3h

Pale Yellow solid, 35 mg, 63% yield, m.p. 180−182 °C, R_f = 0.3 (hexane/ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.32 (m, 2H), 7.28 – 7.25 (m, 1H), 7.25 – 7.22 (m, 2H), 6.12 (t, *J* = 2.0 Hz, 1H), 4.36 (t, *J* = 7.7 Hz, 2H), 3.83 (t, *J* = 7.7 Hz, 2H), 3.38 (d, *J* = 2.0 Hz, 2H), 2.43 – 2.36 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.3, 165.4, 155.3, 131.2, 130.2, 127.8, 127.3, 117.0, 116.7, 94.3, 55.0, 53.0, 30.3, 16.8.; IR (KBr): νmax = 2926, 2215, 1657, 1541, 1441, 1278, 747, 693 cm^{-1}; HRMS (ESI): m/z calcd for $C_{16}H_{15}N_2O$ $[M + H]^+$: 251.1179, found: 251.1181.

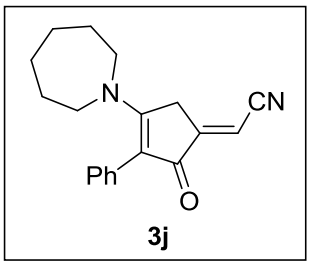
(*E*)-2-(2-Oxo-3-phenyl-4-(pyrrolidin-1-yl)cyclopent-3-en-1-ylidene)acetonitrile (3i):



3i

Brown solid, 43 mg, 74% yield, m.p. 150−152 °C, R_f = 0.5 (hexane/ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 3H), 7.24 – 7.17 (m, 2H), 6.12 (s, 1H), 3.67 (t, *J* = 6.2 Hz, 2H), 3.60 (s, 2H), 3.01 (t, *J* = 6.0 Hz, 2H), 2.00 – 1.92 (m, 2H), 1.88 – 1.79 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.2, 166.1, 154.6, 133.9, 129.8, 128.6, 127.6, 118.0, 117.0, 94.2, 50.1, 33.7, 23.8.; IR (KBr): νmax = 2877, 2216, 1546, 1445, 1287, 750 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{17}N_2O$ $[M + H]^+$: 265.1335, found: 265.1338.

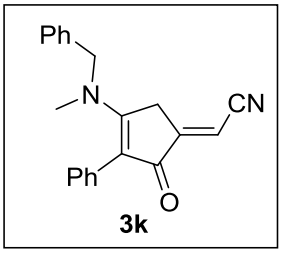
(*E*)-2-(4-(Azepan-1-yl)-2-oxo-3-phenylcyclopent-3-en-1-ylidene)acetonitrile (3j):



3j

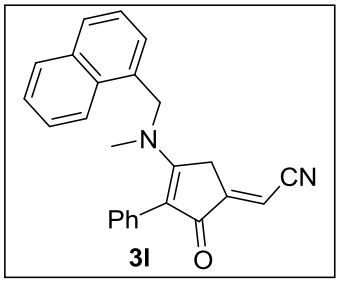
Pale Yellow solid, 46 mg, 71% yield, m.p. 146−148 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.30 – 7.27 (m, 1H), 7.20 – 7.18 (m, 2H), 6.10 (t, *J* = 2.0 Hz, 1H), 3.62 (d, *J* = 2.0 Hz, 2H), 3.60 (s, 2H), 3.28 (s, 2H), 1.83 (s, 2H), 1.68 (s, 2H), 1.52 (s, 2H), 1.36 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.6, 166.2, 155.0, 134.4, 130.4, 128.2, 127.4, 118.4, 117.2, 93.6, 52.5, 33.2, 29.2, 27.4, 26.6, 26.4; IR (KBr): νmax = 2925, 2215, 1659, 1535, 1438, 1274, 743, 617 cm^{-1}; HRMS (ESI): m/z calcd for $C_{19}H_{21}N_2O$ $[M + H]^+$: 293.1648, found: 293.1652.

(*E*)-2-(4-(Benzyl(methyl)amino)-2-oxo-3-phenylcyclopent-3-en-1-ylidene)acetonitrile (3k):



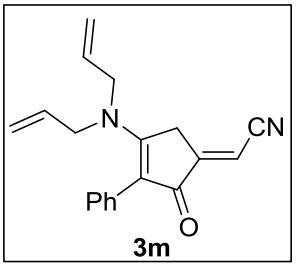
Yellow syrup, 50 mg, 72% yield, R_f = 0.4 (hexane/ethyl acetate = 7:3) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.10 (m, 10H), 6.14 (s, 1H), 4.58 (s, 2H), 3.68 (s, 2H), 2.82 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 165.4, 154.3, 133.4(3C), 129.8(3C), 128.6, 127.7, 118.2, 116.9, 94.5, 66.5, 49.5, 33.2; IR (KBr neat): νmax 3016, 2858, 2217, 1551, 1410, 1215, 1155, 746, 696 cm^{-1}; HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O$ $[M + H]^+$: 315.1492, found: 315.1492.

(*E*)-2-(4-(Methyl(naphthalen-1-ylmethyl)amino)-2-oxo-3-phenylcyclopent-3-en-1-ylidene)acetonitrile (3l):



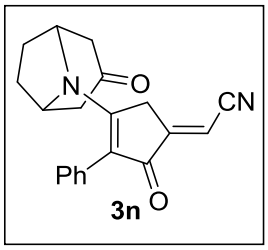
Pale Yellow solid, 53 mg, 66% yield, m.p. 156−158 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.82 (m, 2H), 7.51 (d, *J* = 28.1 Hz, 3H), 7.31 – 7.16 (m, 7H), 6.15 (s, 1H), 5.04 (s, 2H), 3.70 (s, 2H), 2.91 (s, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 167.4, 154.7, 133.9, 133.5, 130.7, 130.3, 129.2, 129.0, 128.2, 127.4, 126.1, 126.4, 125.3, 121.9, 118.9, 116.9, 94.4, 55.7, 33.4.; IR (KBr): νmax = 3011, 2216, 1545, 795, 747, 696 cm^{-1}; HRMS (ESI): m/z calcd for $C_{25}H_{21}N_2O$ $[M + H]^+$: 365.1648, found: 365.1638.

(*E*)-2-(4-(Diallylamino)-2-oxo-3-phenylcyclopent-3-en-1-ylidene)acetonitrile (3m):



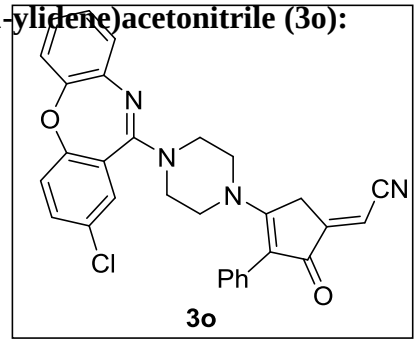
Brown solid, 48 mg, 75% yield, m.p. 87−89 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.30 (m, 1H), 7.20 – 7.18 (m, 2H), 6.11 (t, *J* = 2.0 Hz, 1H), 5.61 (s, 2H), 5.25 (s, 4H), 3.88 (d, *J* = 3.4 Hz, 4H), 3.64 (d, *J* = 2.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.1, 166.7, 154.4, 133.6, 131.4, 130.3, 128.4, 127.8, 118.8, 118.5, 116.9, 94.5, 52.2, 33.3.; IR (KBr): νmax = 3017, 2926, 2217, 1664, 1543, 1290, 926, 747, 701 cm^{-1};HRMS (ESI): m/z calcd for $C_{19}H_{19}N_2O$ $[M + H]^+$: 291.1492, found: 291.1497.

(*E*)-2-(2-Oxo-4-(3-oxo-8-azabicyclo[3.2.1]octan-8-yl)-3-phenylcyclopent-3-en-1-ylidene)acetonitrile (3n):



Pale Yellow solid, 47 mg, 67% yield, m.p. 189−191 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 3H), 7.26 – 7.19 (m, 2H), 6.17 (s, 1H), 4.57 (s, 1H), 4.21 (s, 1H), 3.70 (s, 2H), 2.62 (d, *J* = 60.8 Hz, 4H), 2.17 – 1.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 185.9, 161.5, 154.2, 133.2, 129.9, 128.8, 128.2, 118.9, 116.8, 95.0, 57.1, 54.7, 49.7, 48.3, 33.1, 28.3.; IR (KBr): νmax = 2924, 2217, 1715, 1543, 1496, 1285, 1198, 997, 750, 614cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{19}N_2O_2$ $[M + H]^+$: 319.1441, found: 319.1434.

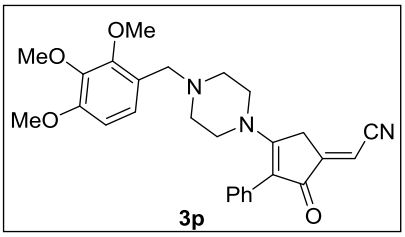
(*E*)-2-(4-(4-(2-Chlorodibenzo[*b,f*][1,4]oxazepin-11-yl)piperazin-1-yl)-2-oxo-3-phenylcyclopent-3-en-1-ylidene)acetonitrile (3o):



3o

Light Orange solid, 82 mg, 73% yield, m.p. 213−215 °C, R_f = 0.3 (hexane/ethyl acetate = 7:3) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (t, J = 7.4 Hz, 3H), 7.31 (d, J = 7.0 Hz, 1H), 7.21 (dd, J = 17.7, 8.1 Hz, 4H), 7.11 (d, J = 6.8 Hz, 3H), 7.04 (d, J = 8.4 Hz, 1H), 6.15 (s, 1H), 3.63 (s, 2H), 3.54 (s, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.0, 165.5, 159.4, 158.3, 154.3, 151.7, 139.4, 133.5, 133.1, 130.6, 129.8, 128.7, 128.6, 127.7, 127.1, 126.0, 125.4, 124.4, 123.0, 120.3, 118.4, 116.9, 94.6, 48.7, 47.4, 33.3.; IR (KBr): νmax = 3058, 2924, 2217, 1662, 1548, 1443, 1228, 750, 671 cm^{-1}; HRMS (ESI): m/z calcd for $C_{30}H_{24}ClN_4O_2$ $[M + H]^+$: 507.1582, found: 507.1578

(*E*)-2-(2-Oxo-3-phenyl-4-(4-(2,3,4-trimethoxybenzyl)piperazin-1-yl)cyclopent-3-en-1-ylidene)acetonitrile (3p):

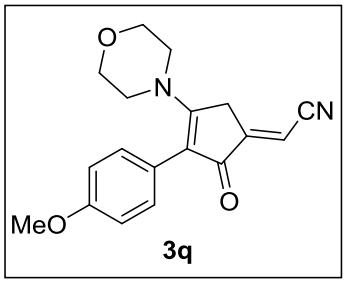


3p

Brown solid, 69 mg, 68% yield, m.p. 110−112 °C, R_f = 0.3 (hexane/ethyl acetate = 7:3) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.4 Hz, 2H), 7.29 – 7.24 (m, 1H), 7.20 (d, J = 7.1 Hz, 2H), 6.91 (d, J = 8.5 Hz, 2H), 6.62 (d, J = 8.5 Hz, 2H), 6.11 (s, 1H), 3.86 (s, 6H), 3.84 (s, 3H), 3.56 (d, J = 1.6 Hz, 2H), 3.47 (s, 2H), 3.40 (s, 4H), 2.46 (s, 4H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.8, 165.4, 154.8, 153.3, 152.6, 142.3, 133.7, 129.8, 128.5, 127.5, 125.1, 122.72, 117.9, 117.0, 107.0, 94.0, 61.2, 60.8, 56.2, 56.0, 52.5, 49.4, 33.3; IR (KBr): νmax = 2931,

2216, 1549, 1497, 1278, 1095, 751, 697 cm^{-1}; HRMS (ESI): m/z calcd for $C_{27}H_{30}N_3O_4$ $[M + H]^+$: 460.2231, found: 460.2223.

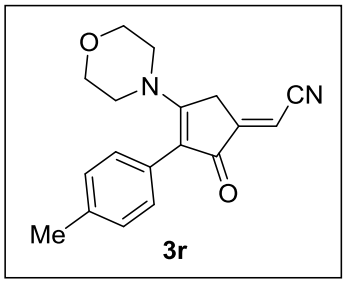
(*E*)-2-(3-(4-Methoxyphenyl)-4-morpholino-2-oxocyclopent-3-en-1-ylidene)acetonitrile (3q):



3q

Orange solid, 51 mg, 75% yield, m.p. 203−205 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 6.12 (s, 1H), 3.82 (s, 3H), 3.68 (s, 4H), 3.56 (d, J = 1.8 Hz, 2H), 3.44 (s, 4H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.3, 165.3, 159.0, 154.3, 130.1, 125.3, 117.1, 116.9, 114.1, 94.3, 66.5, 55.3, 49.4, 33.2.; IR (KBr): νmax = 2922, 2216, 1659, 1547, 1242, 748 cm^{-1}; HRMS (ESI): m/z calcd for $C_{18}H_{19}N_2O_3$ $[M + H]^+$: 311.1390, found: 311.1382.

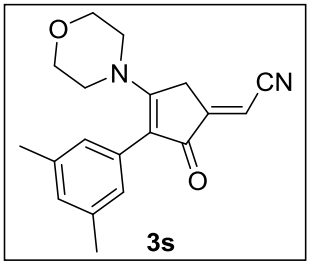
(*E*)-2-(4-Morpholino-2-oxo-3-(p-tolyl)cyclopent-3-en-1-ylidene)acetonitrile (3r):



3r

Brown solid, 46 mg, 71% yield, m.p. 199−201 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, J = 7.8 Hz, 2H), 7.10 (d, J = 7.9 Hz, 2H), 6.12 (s, 1H), 3.68 (s, 4H), 3.56 (d, J = 1.6 Hz, 2H), 3.43 (s, 4H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.2, 165.3, 154.4, 137.5, 130.3, 129.7, 129.3, 118.3, 116.9, 94.4, 66.5, 49.4, 33.8, 21.3; IR (KBr): νmax = 2922, 2856, 2216, 1660, 1546, 1441, 744, 663 cm^{-1}; HRMS (ESI): m/z calcd for $C_{18}H_{19}N_2O_2$ $[M + H]^+$: 295.1441, found: 295.1436.

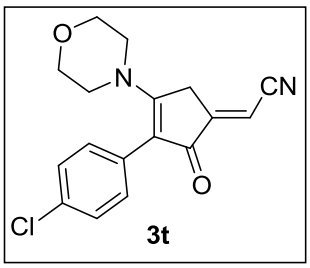
(*E*)-2-(3-(3,5-Dimethylphenyl)-4-morpholino-2-oxocyclopent-3-en-1-ylidene)acetonitrile (3s):



3s

Pale Yellow solid, 52 mg, 76% yield, m.p. 161−163 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (s, 1H), 6.82 (s, 2H), 6.12 (s, 1H), 3.68 (s, 4H), 3.56 (s, 2H), 3.42 (s, 4H), 2.30 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.1, 165.3, 154.4, 138.1, 133.1, 129.5, 127.5, 118.6, 116.9, 94.3, 66.5, 49.5, 33.1, 21.4.; IR (KBr): *ν*max =2919, 2216, 1661, 1544, 1114, 749, 667cm^{-1}; HRMS (ESI): m/z calcd for $C_{19}H_{21}N_2O_2$ $[M + H]^+$: 309.1598, found: 309.1598.

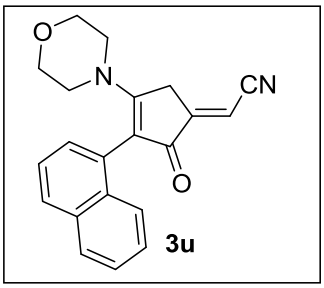
(*E*)-2-(3-(4-Chlorophenyl)-4-morpholino-2-oxocyclopent-3-en-1-ylidene)acetonitrile (3t):



3t

Brown solid, 51 mg, 73% yield, m.p. 223−225 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 6.13 (s, 1H), 3.69 (s, 4H), 3.58 (s, 2H), 3.43 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 185.8, 165.6, 153.1, 133.6, 131.8, 131.1, 128.8, 128.6, 116.7, 94.8, 66.4, 49.6, 33.2.; IR (KBr): νmax = 2923, 2217, 1663, 1548, 1496, 1284, 748, 666 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{16}ClN_2O_2$ $[M + H]^+$: 315.0895, found: 315.0896.

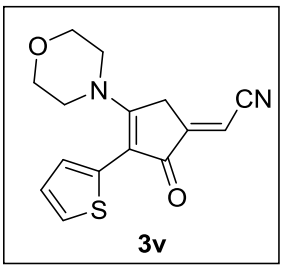
(*E*)-2-(4-Morpholino-3-(naphthalen-1-yl)-2-oxocyclopent-3-en-1-ylidene)acetonitrile (3u):



3u

Brown solid, 50 mg, 69% yield, m.p. 103−105 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3 ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.95 (d, J = 7.5 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.52 (dd, J = 15.3, 7.1 Hz, 3H), 7.31 (d, J = 6.6 Hz, 1H), 6.11 (t, J = 1.7 Hz, 1H), 3.93 (m, 2H), 3.75 – 3.56 (m, 4H), 3.23 – 2.74 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 185.6, 167.9, 156.6, 133.7, 132.8, 132.3, 128.8, 128.7, 128.27, 126.7, 126.6, 126.2, 126.1, 117.9, 114.5, 93.3, 66.7, 65.8, 49.7, 49.0, 33.1; IR (KBr): νmax = 2922, 2216, 1545, 1441, 1294, 749 cm^{-1}; HRMS (ESI): m/z calcd for $C_{21}H_{19}N_2O_2$ $[M + H]^+$: 331.1441, found: 331.1442.

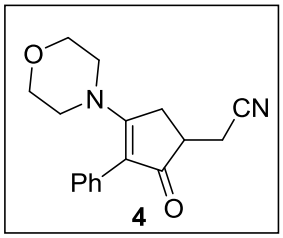
(*E*)-2-(4-Morpholino-2-oxo-3-(thiophen-2-yl)cyclopent-3-en-1-ylidene)acetonitrile (3v):



3v

Yellow solid, 44 mg, 70% yield, m.p. 208−210 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (dd, J = 5.1, 0.8 Hz, 1H), 7.06 (dd, J = 5.1, 3.5 Hz, 1H), 6.92 – 6.89 (m, 1H), 6.14 (s, 1H), 3.75 – 3.71 (m, 4H), 3.58 (d, J = 2.0 Hz, 2H), 3.56 – 3.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.8, 166.0, 153.4, 133.6, 128.2, 127.2, 126.9, 116.7, 110.8, 95.0, 66.5, 49.5, 33.3; IR (KBr): νmax = 2922, 2217, 1557, 1552, 1274, 1112, 745, 704cm^{-1}; HRMS (ESI): m/z calcd for $C_{15}H_{15}N_2O_2$ $[M + H]^+$: 287.0849, found: 287.0849.

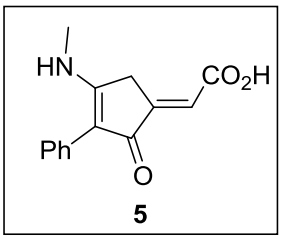
2-(4-Morpholino-2-oxo-3-phenylcyclopent-3-en-1-yl)acetonitrile (4):



4

A round-bottom flask was charged with cyclopentenone **3a** (30 mg, 0.17 mmol, 1 equiv) and EtOAc (2 mL) under a nitrogen atmosphere, and then 10% Pd−C catalyst (∼5 mg) was added. The reaction mixture was stirred at room temperature under hydrogen atmosphere (16 h) until consumption of starting material **3a** as monitored by thin layer chromatography (TLC). The reaction mixture was filtered through a pad of celite and concentrated under reduced pressure, and the residue was directly subjected to flash column chromatography on silica gel (30% EtOAc in hexanes; Rf = 0.4) to afford the desired product **4.** Half white solid, 24 mg, 80% yield, m.p. 157−159 °C, R_f = 0.4 (hexane/ethyl acetate = 7:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.4 Hz, 2H), 7.27 (t, J = 3.7 Hz, 1H), 7.19 – 7.16 (m, 2H), 3.64 (t, J = 4.7 Hz, 4H), 3.37 – 3.30 (m, 4H), 3.08 – 3.02 (m, 1H), 2.96 (dd, J = 16.8, 4.2 Hz, 1H), 2.89 – 2.83 (m, 1H), 2.63 – 2.50 (m, 2H).;^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 168.7, 133.9, 130.2, 128.4, 127.3, 118.4, 113.6, 66.4, 49.0, 39.9, 33.4, 20.0. IR (KBr): νmax = 2921, 2245, 1659, 1556, 1304, 752, 701cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{19}N_2O_2$ $[M + H]^+$: 283.1441, found: 282.1435.

(*E*)-(4-(methylamino)-2-oxo-3-phenylcyclopent-3-en-1-ylidene)methylformate (5):



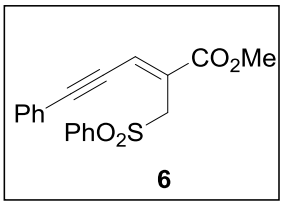
5

To a solution of cyclopentenone **3k** (32 mg, 0.10 mol, 1 equiv) in 2 mL of MeOH was added MeOH.HCL (2 mL). The reaction mixture was stirred for 16 h at reflux temperature. The

completion of the reaction was monitored by TLC followed by quenched with $NaHCO_3$ (5 mL), extracted with ethyl acetate (3 × 5 mL), dried over Na_2SO_4, concentrated under vacuo, and then purified by flash chromatography (5% MeOH in DCM; Rf = 0.3) to afford **5**. Brown solid, 19 mg, 78% yield, m.p. 168-170 °C, ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, J = 7.4 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.37 (t, J = 7.4 Hz, 1H), 6.37 (s, 1H), 3.80 (s, 3H), 3.52 (s, 2H) ; ^{13}C NMR (101 MHz, $CDCl_3$+DMSO-d_6) δ 202.1, 180.1, 171.2, 152.5, 135.3, 133.6, 132.8, 132.4, 126.9, 117.1, 56.4, 43.2.; IR (KBr): νmax = 2923, 2853, 1715, 1391, 1214, 767, 695 cm^{-1}; HRMS (ESI): m/z calcd for $C_{14}H_{14}N_2O_3$ $[M + H]^+$: 244.0968, found: 244.0961.

Methyl (*Z*)-5-phenyl-2-((phenylsulfonyl)methyl)pent-2-en-4-ynoate (6):

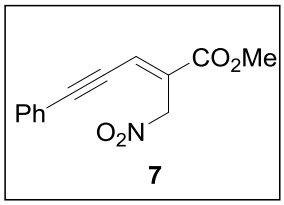
Reaction was conducted using modified condition,[4] To a stirred solution of corresponding MBH-alcohol [1] (1 equiv) in 5 mL of PEG 400 was added sodium phenylsulfinate (1.5 equiv) at room temperature and stirred for 1h at 80 ^{o}C. After completion of the reaction, the mixture was extracted with Et_2O (4 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc: hexanes) to afford the corresponding product.



6

Half white solid, 262 mg, 83% yield, m.p. 121−123 °C, Rf = 0.5 (hexane/ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.52 (d, J = 7.5 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.40- 7.37 (m, 5H), 7.04 (s, 1H), 4.52 (s, 2H), 3.69 (s, 3H).; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.37, 138.82, 133.80, 132.14, 129.92, 129.81, 129.06, 128.81, 128.49, 126.52, 121.66, 104.22, 84.62, 56.73, 52.64; IR (KBr): νmax = 2951, 2195, 1715, 1610, 1439, 1141, 1082, 728 cm−1; HRMS (ESI): m/z calcd for $C_{19}H_{17}SO_4$ $[M + H]^+$: 341.0842, found: 341.0848.

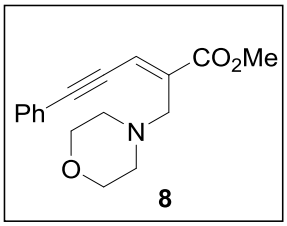
Methyl (E)-2-(nitromethyl)-5-phenylpent-2-en-4-ynoate (7): To a stirred solution of corresponding MBH-acetate [1] (1 equiv) in 10 mL of aqueous methanol (MeOH:water 9:1) was added sodium nitrate (1.5 equiv) at room temperature and stirred for given time. After completion of the reaction, the mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (3 x 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc: hexanes) to afford the corresponding product.



7

Half white solid, 195 mg, 78% yield, m.p. 58-60 °C, Rf = 0.5 (hexane/ethyl acetate = 7:3); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 2H), 7.44 – 7.36 (m, 3H), 7.29 (s, 1H), 5.48 (s, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.97, 132.20, 130.27, 130.07, 128.68, 128.31, 121.22, 106.35, 83.86, 72.07, 52.84.; IR (KBr): νmax = 2292, 2194, 1713, 1555, 1217, 752 cm−1; HRMS (ESI): m/z calcd for $C_{13}H_{10}NO_4$ $[M - H]^+$: 244.0607, found: 244.0604.

Methyl (*E*)-2-(morpholinomethyl)-5-phenylpent-2-en-4-ynoate (8):



8

Yellow solid, 47 mg, 81% yield, m.p. 123−125 °C, Rf = 0.4 (hexane/ethyl acetate = 7: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.36 (dt, *J* = 8.7, 4.2 Hz, 3H), 6.99 (s, 1H), 3.81 (s, 3H), 3.71 – 3.68 (m, 4H), 3.52 (s, 2H), 2.59 – 2.57 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.18, 138.17, 131.81, 129.42, 128.59, 123.03, 122.32, 101.91, 85.70,

67.02, 55.72, 53.74, 52.31; IR (KBr): νmax = 2946, 2855, 2196, 1715, 1608, 1240, 1117, 757 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{20}NO_3$ $[M + H]^+$: 286.1438, found: 286.1437.

X-ray Crystallography.

X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [2]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [3] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal structure determination of 3a

Crystal Data for $C_{17}H_{16}N_2O_2$ (*M* =280.32 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 10.2278(10) Å, *b* = 8.9747(9) Å, *c* = 15.8181(18) Å, *β* = 106.584(4)°, *V* = 1391.6(3) $Å^3$, *Z* = 4, *T* = 294(2) K, μ(MoKα) = 0.089 mm^{-1}, *Dcalc* = 1.338 g/cm^3, 19954 reflections measured (5.274° ≤ 2Θ ≤ 61.102°), 4257 unique (R_{int} = 0.0478, R_{sigma} = 0.0538) which were used in all calculations. The final R_1 was 0.0586 (I > 2σ(I)) and wR_2 was 0.1851 (all data).**CCDC 2242817** deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/

References:

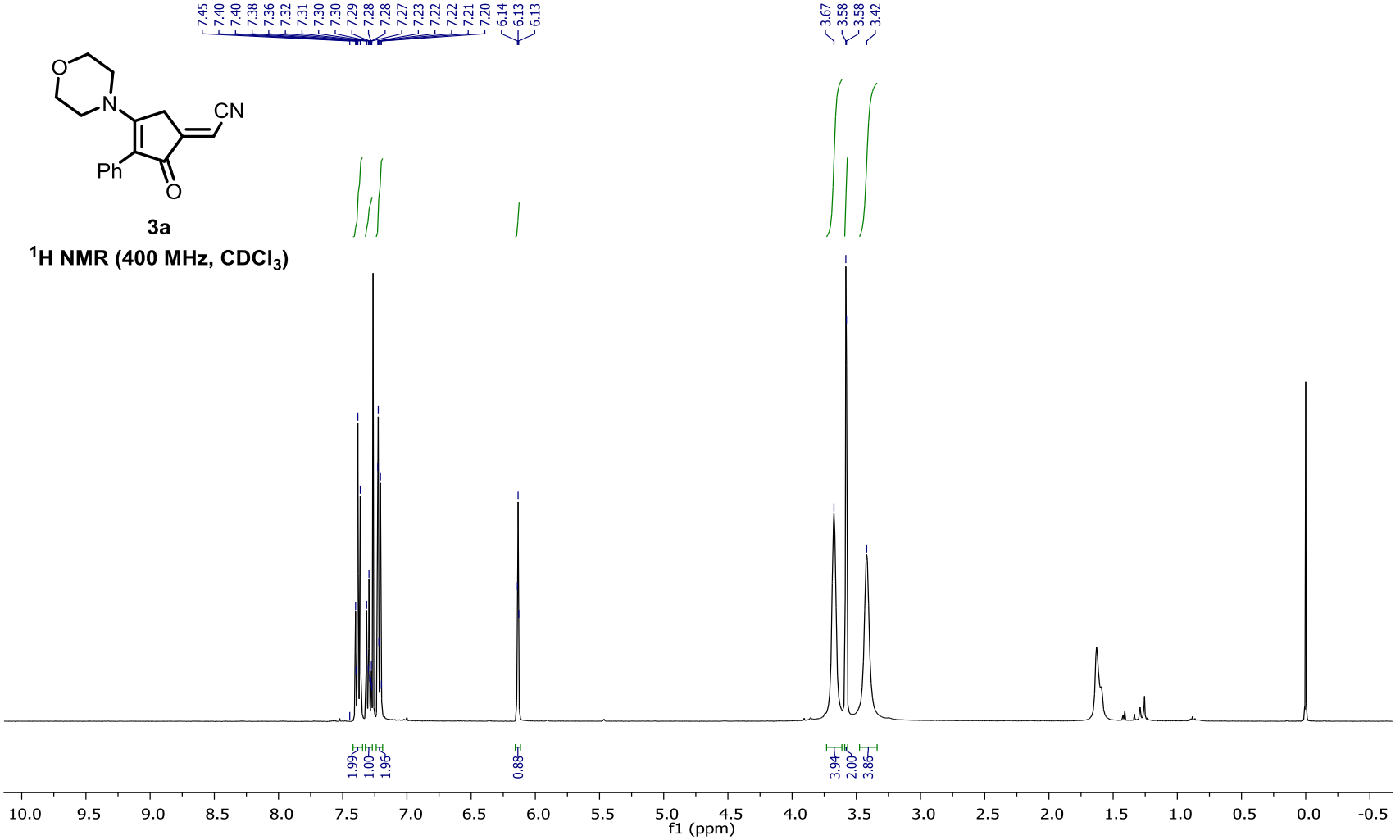
1) C. R. Reddy, V. Ganesh and N. Punna, *J. Org. Chem.*, 2022, ***87***, 11547.

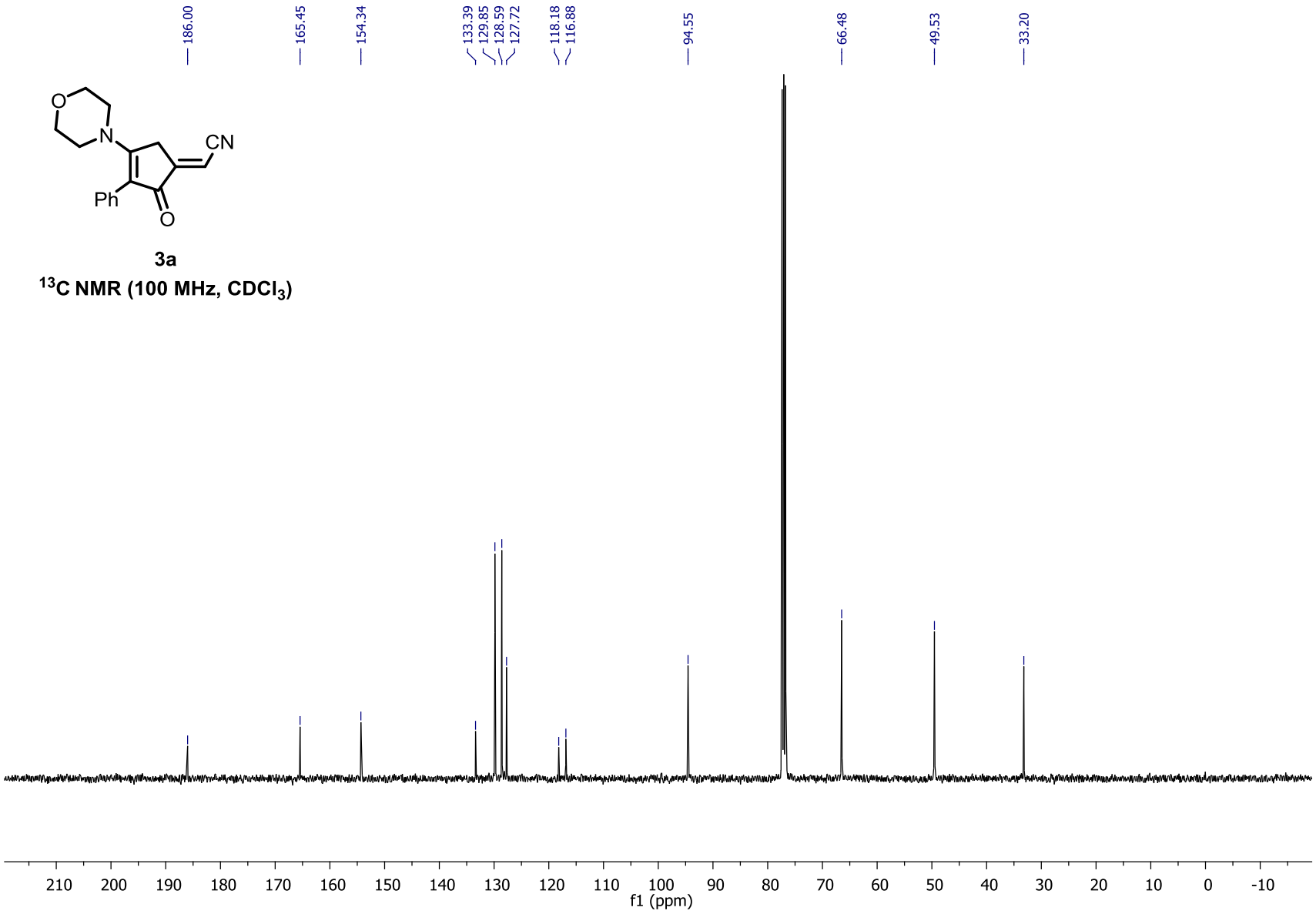
2) Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

3) Sheldrick G. M. (2015).Acta Crystallogr C71: 3-8.

4) S. Chandrasekhar, B. Saritha, V. Jagadeshwar, C. Narsihmulu, D. Vijay, G. D. Sarma and B. Jagadeesh, *Tetrahedron Lett.*, 2006, ***47***, 2981.

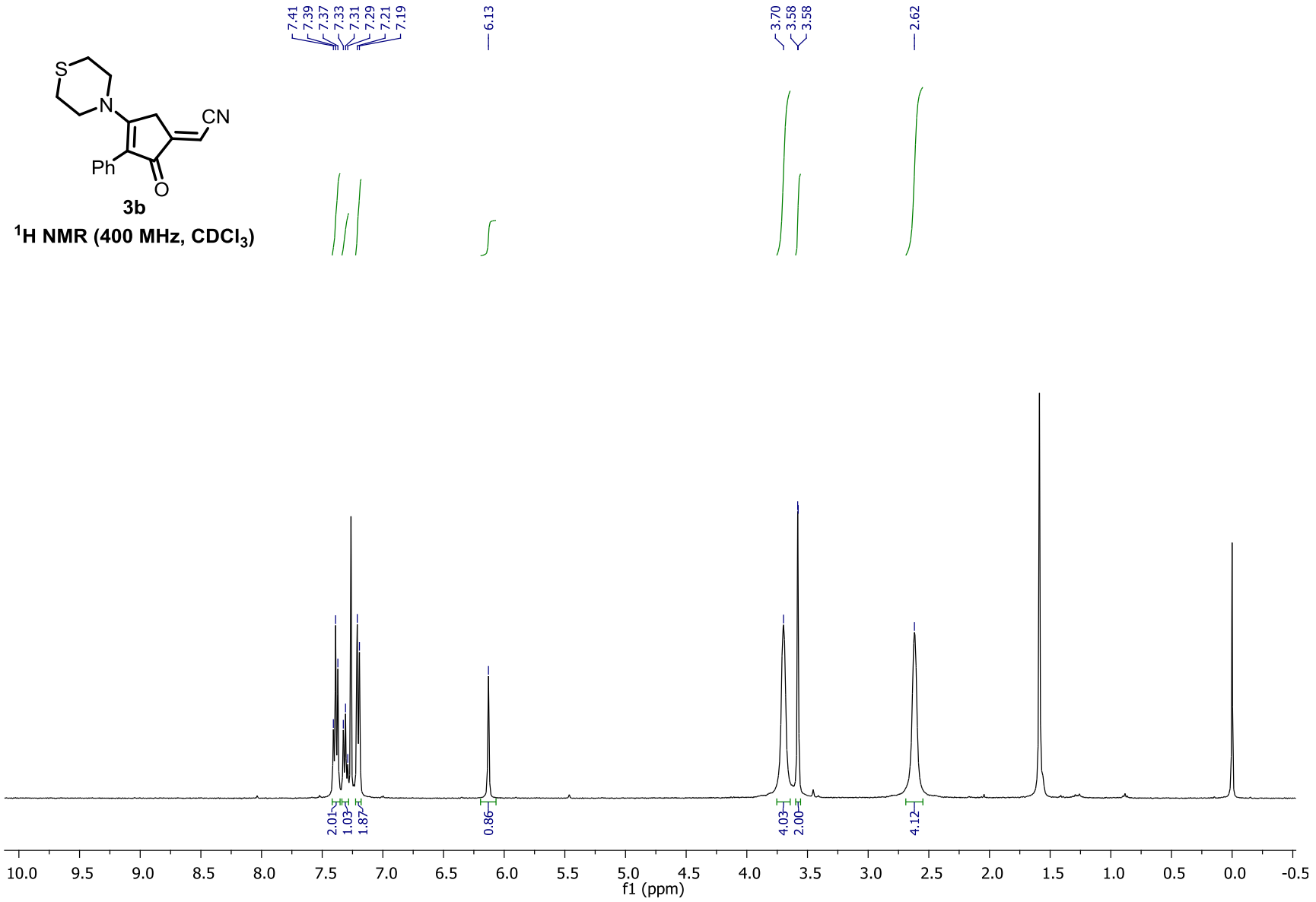
. 5. ^{1}H NMR and ^{13}C NMR spectral copies of compounds

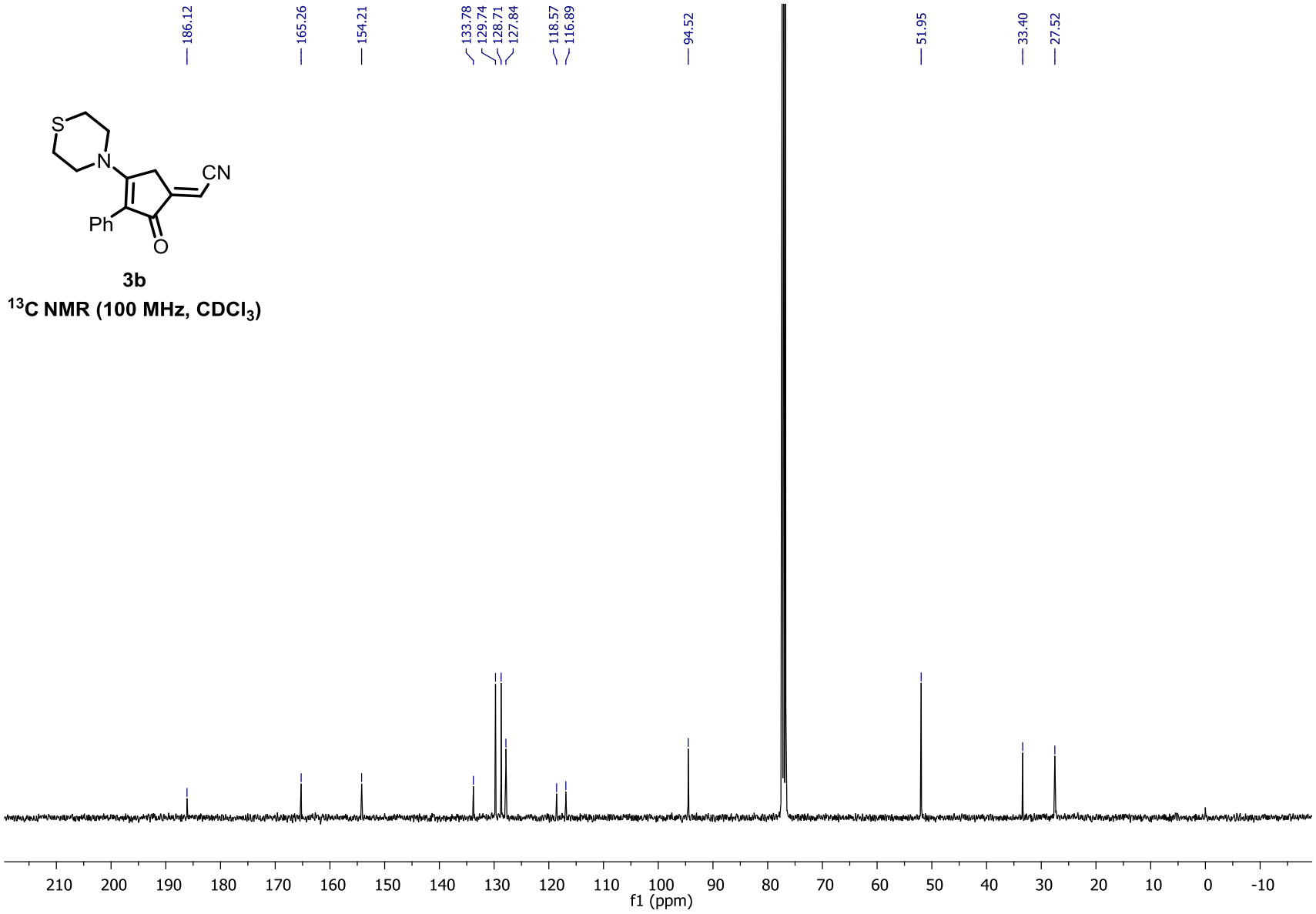




3a

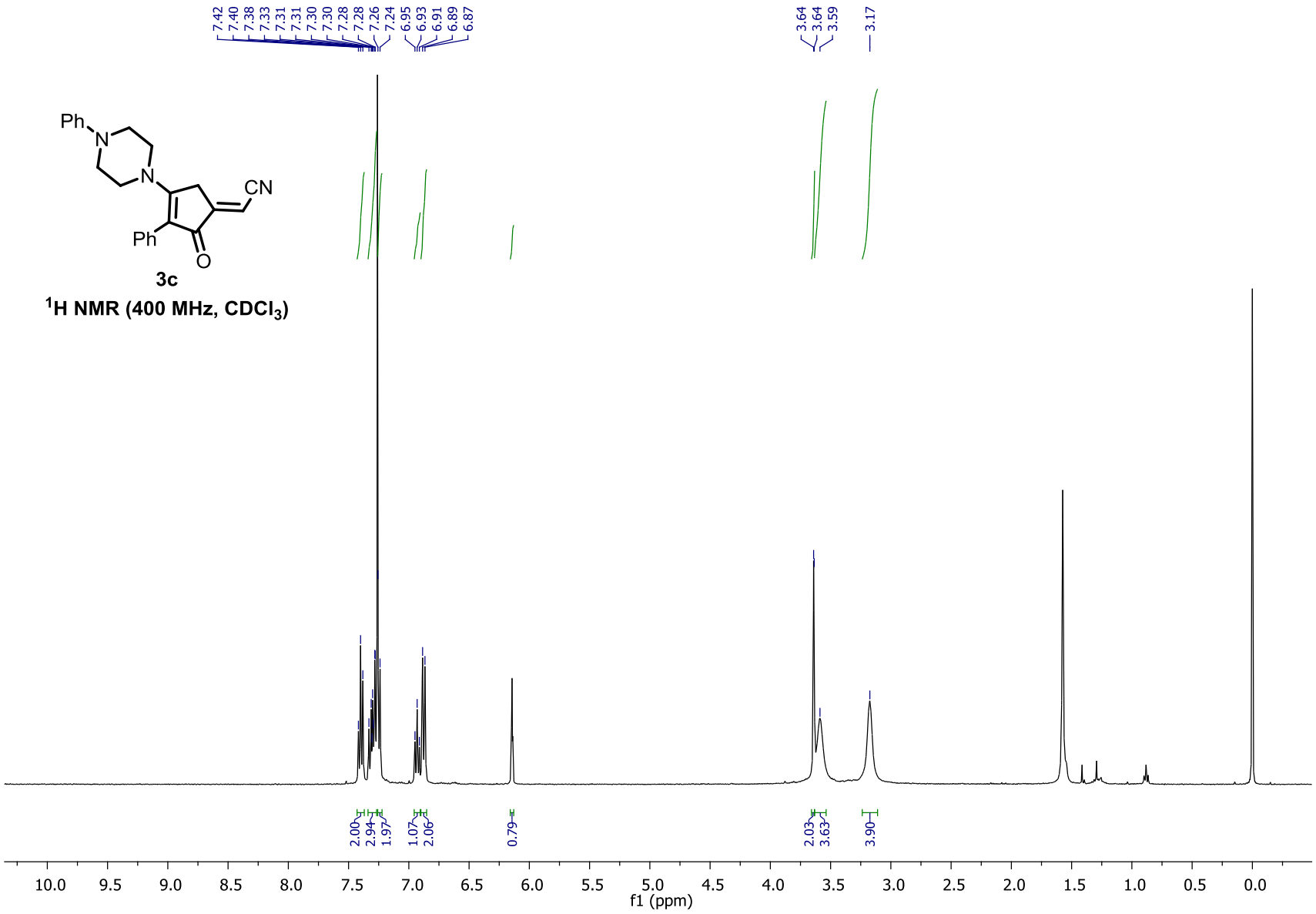
^{13}C NMR (100 MHz, $CDCl_3$)

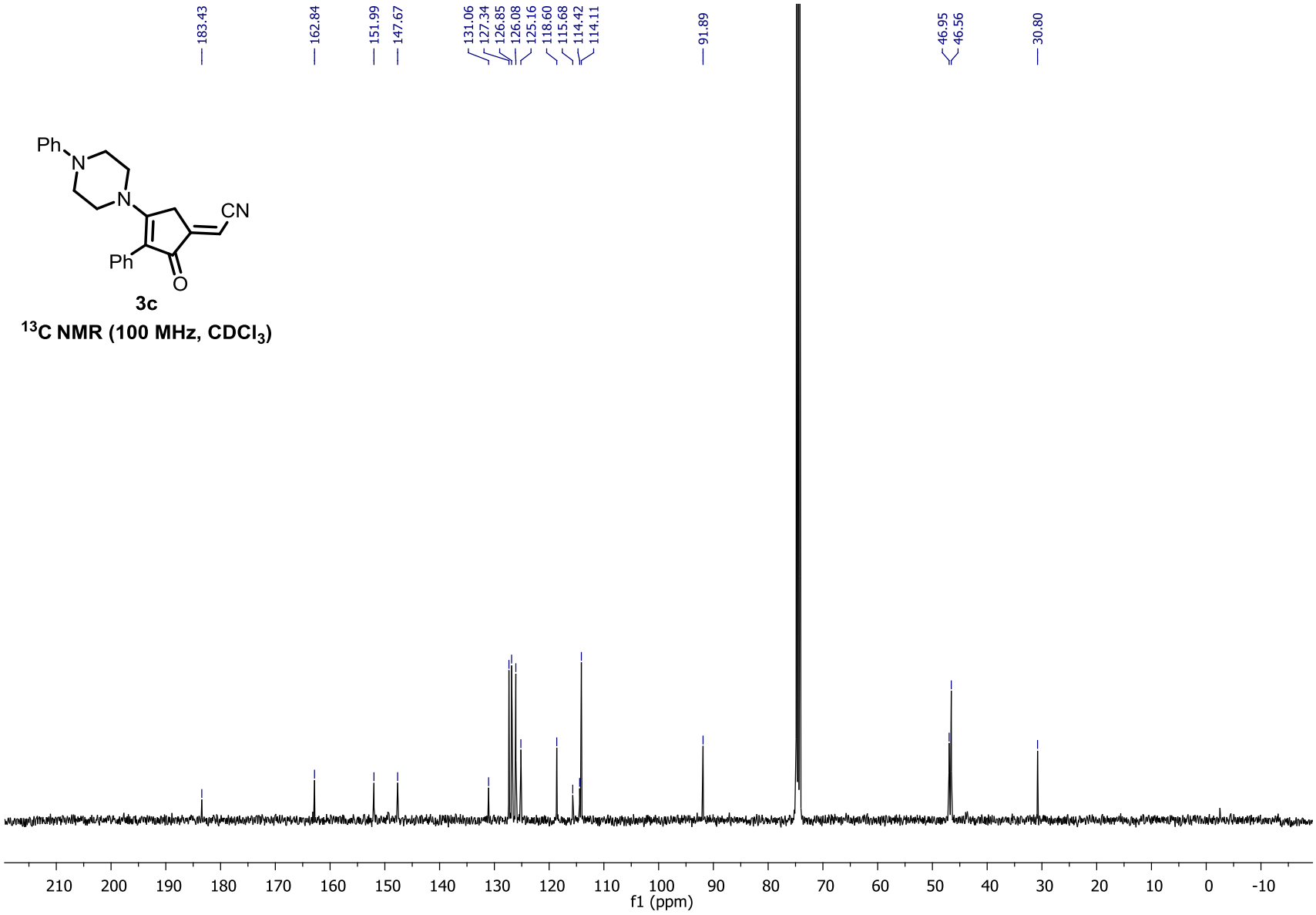

S
N
CN
Ph
O
3b
^{1}H NMR (400 MHz, CDCl$_3$)
7.41
7.39
7.37
7.33
7.31
7.29
7.21
7.19
6.13
3.70
3.58
3.58
2.62
2.01
1.03
1.87
0.86
4.03
2.00
4.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



3b

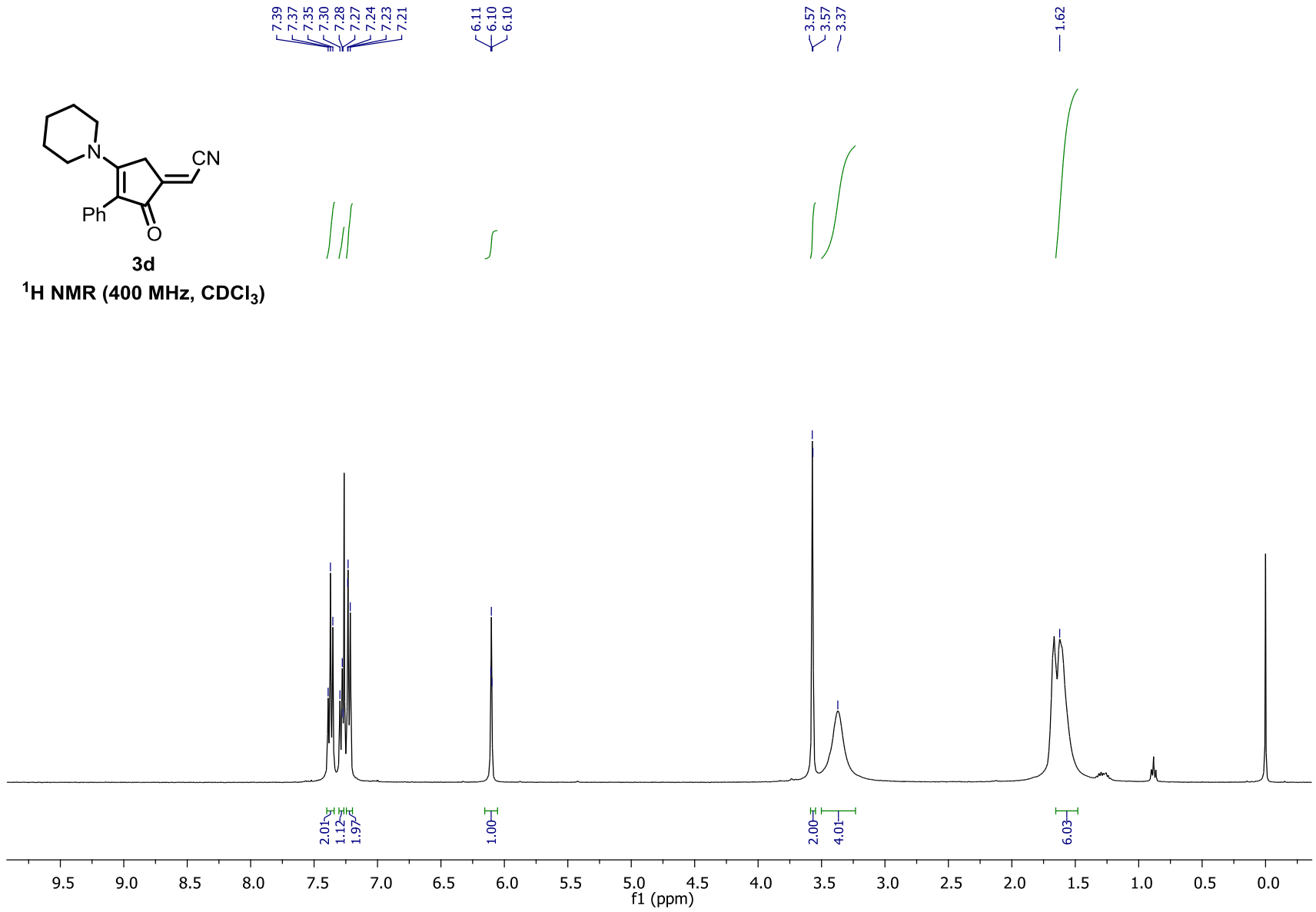
^{13}C NMR (100 MHz, $CDCl_3$)


7.42
7.40
7.38
7.33
7.31
7.31
7.30
7.30
7.28
7.28
7.26
7.24
6.95
6.93
6.91
6.89
6.87
3.64
3.64
3.59
3.17
Ph
N
N
CN
Ph
O
3c
1H NMR (400 MHz, CDCl3)
2.00
2.94
1.97
1.07
2.06
0.79
2.03
3.63
3.90
10.0
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
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



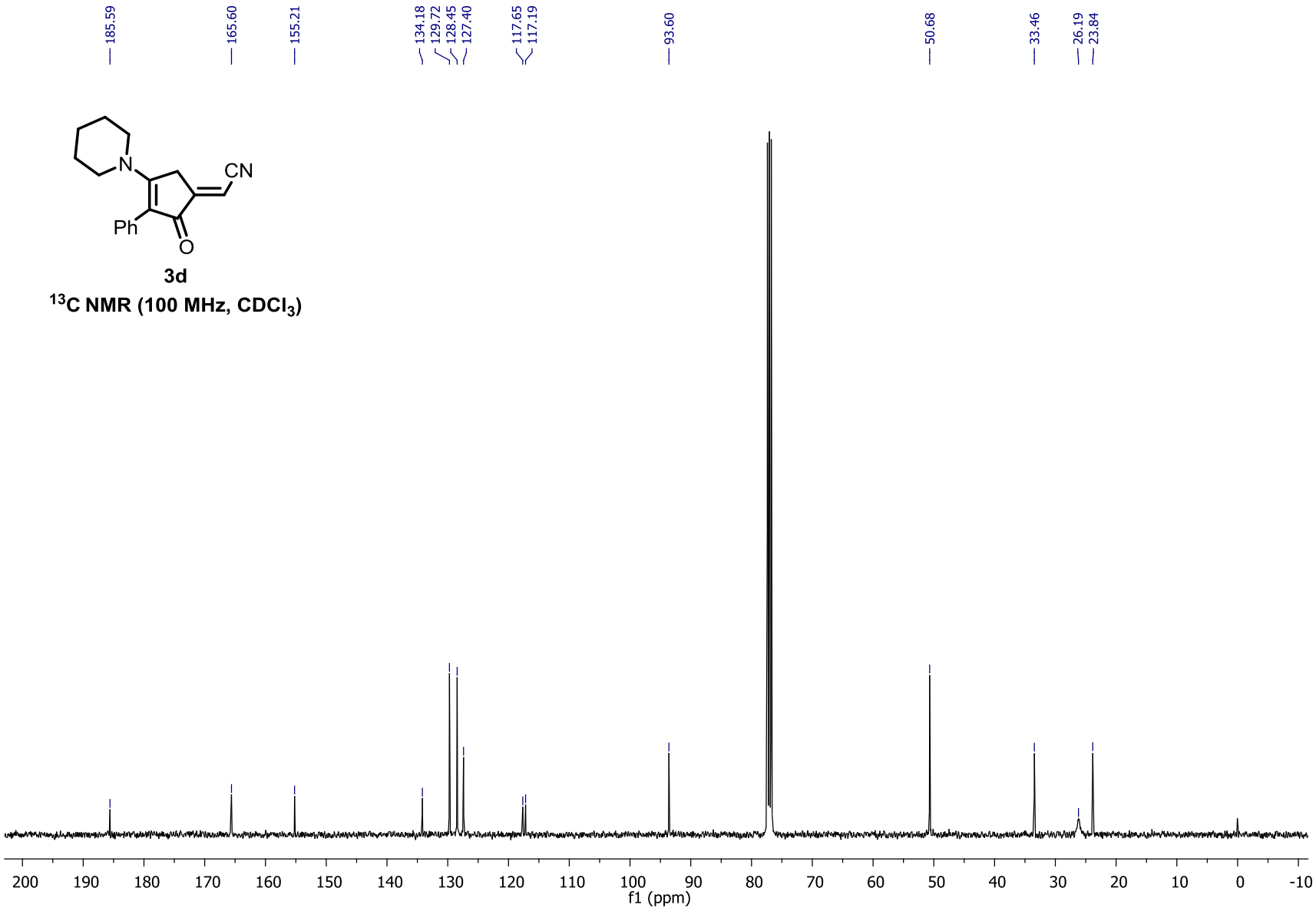
3c

^{13}C NMR (100 MHz, $CDCl_3$)



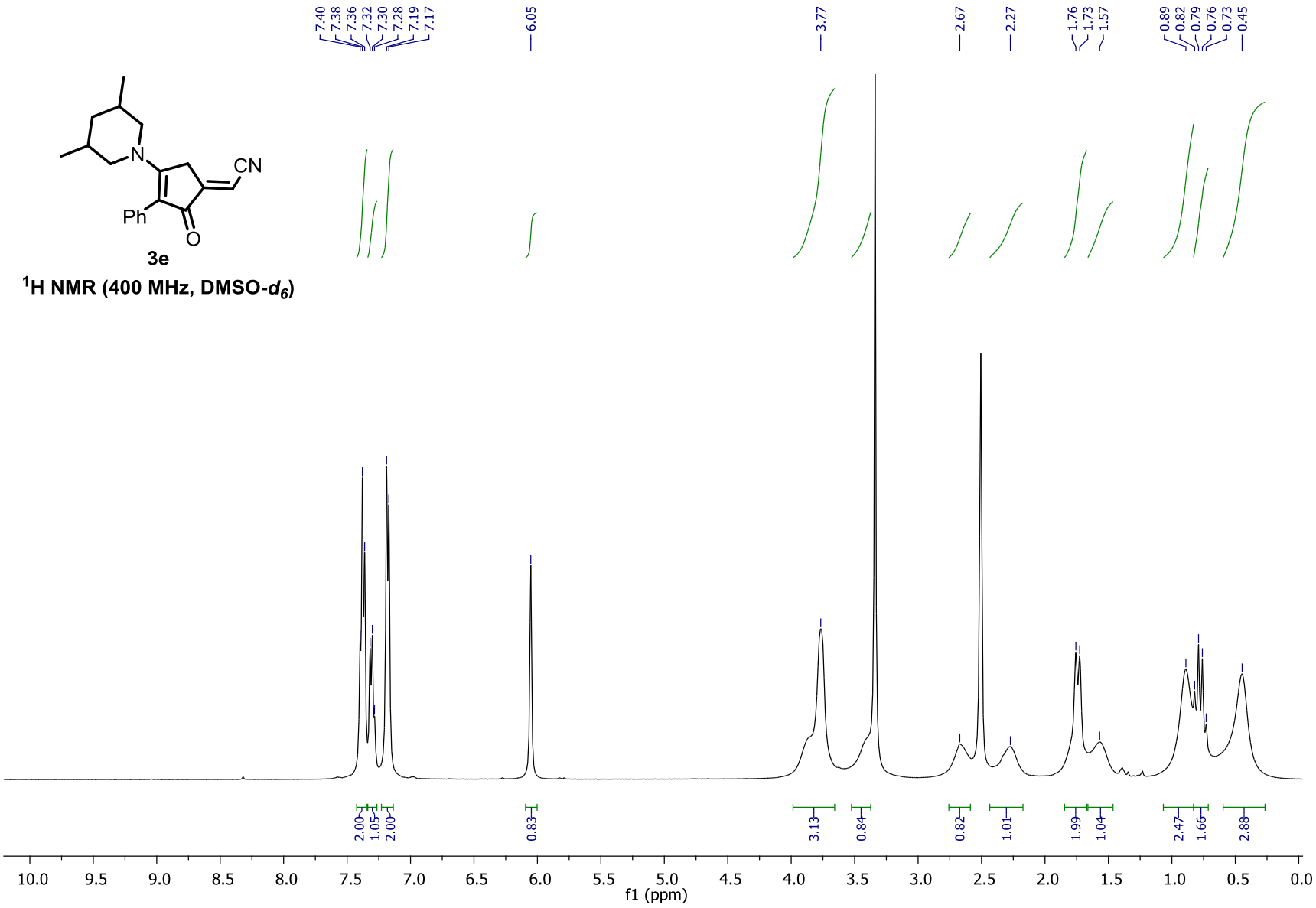
3d

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



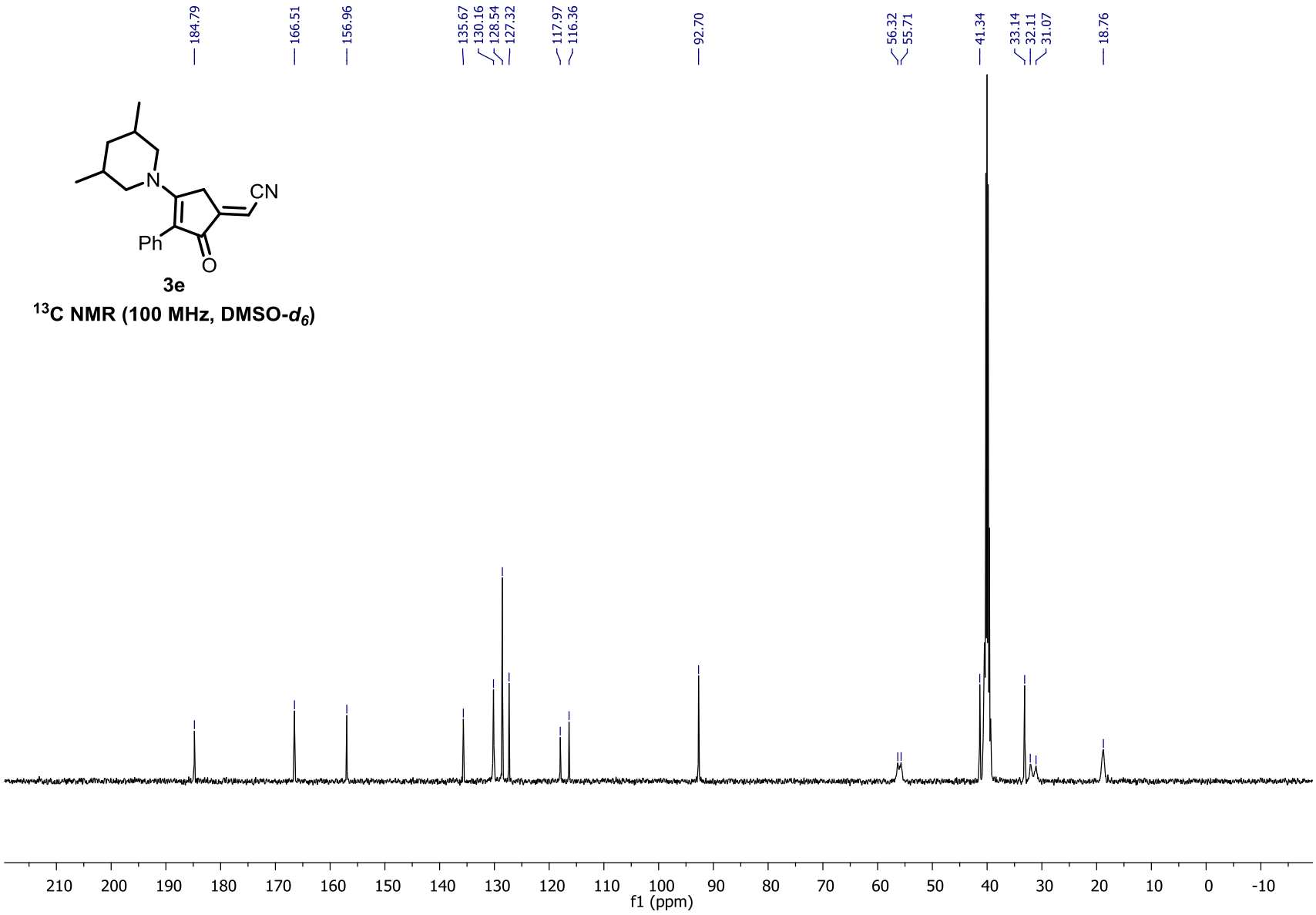
3d

^{13}C NMR (100 MHz, $CDCl_3$)



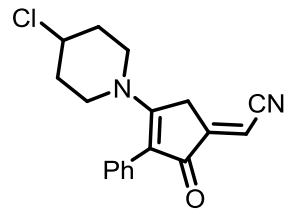
3e

^{1}H NMR (400 MHz, DMSO-d_6)



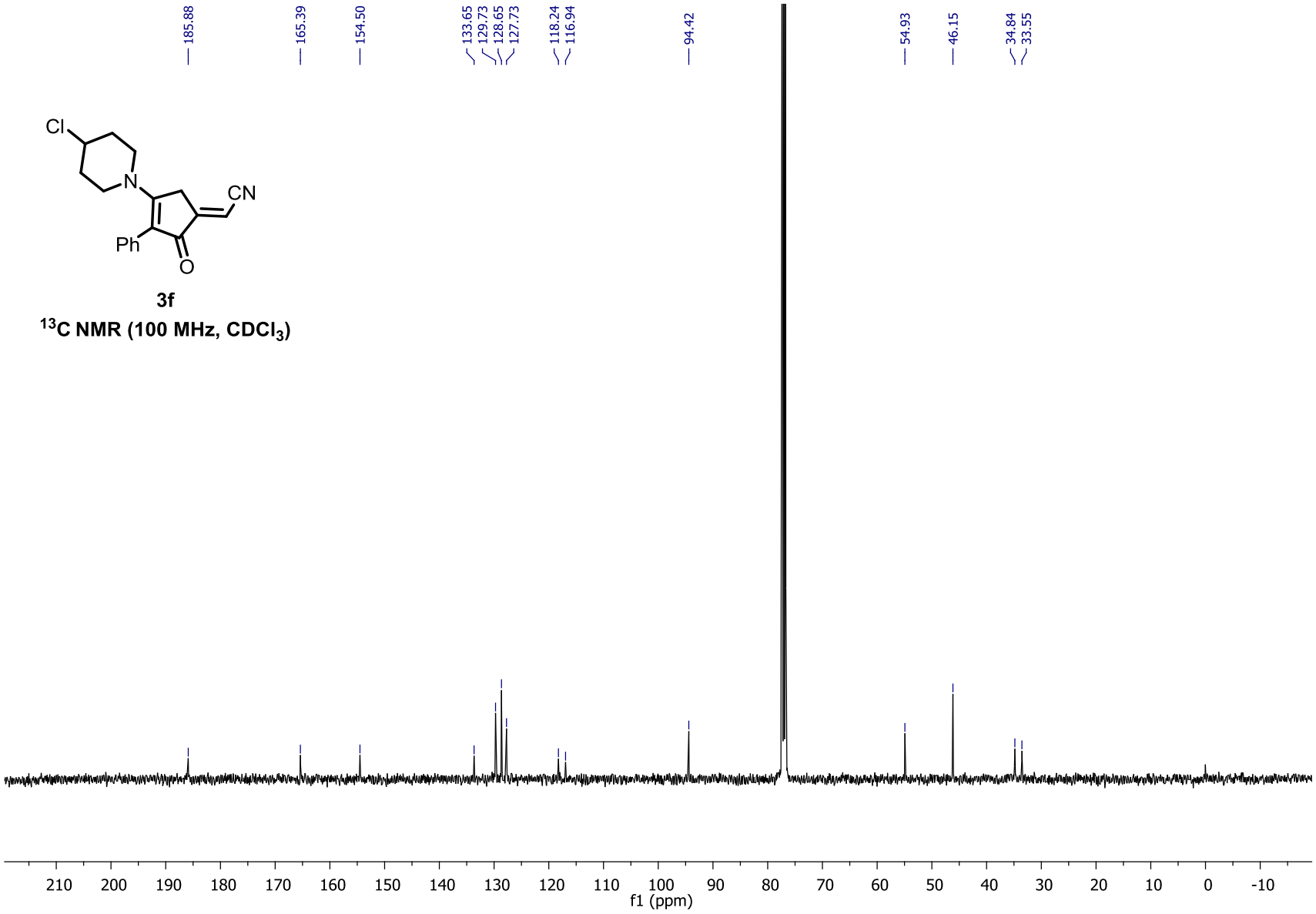
3e

^{13}C NMR (100 MHz, DMSO-d_6)



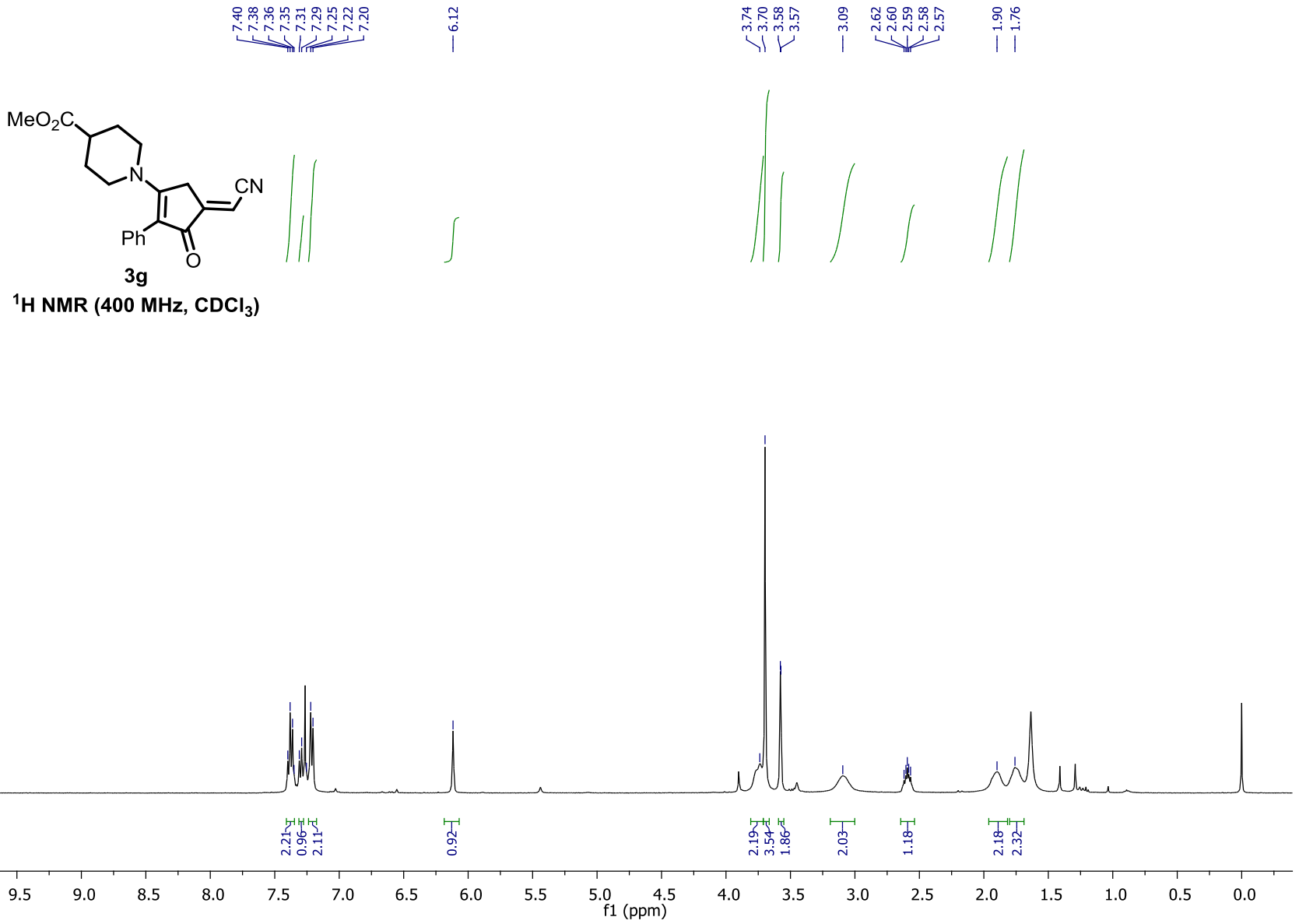
3f

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



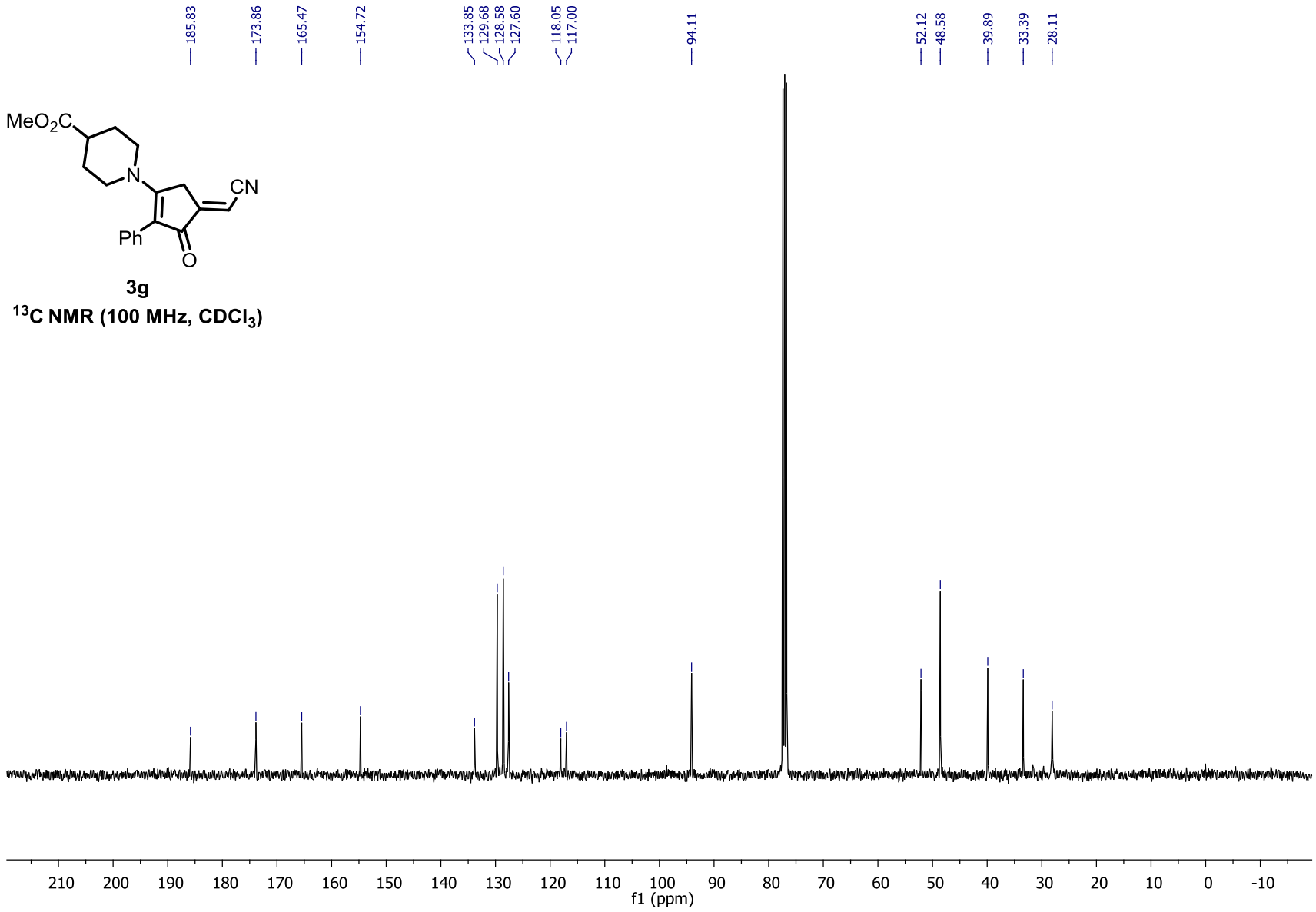
3f

^{13}C NMR (100 MHz, $CDCl_3$)



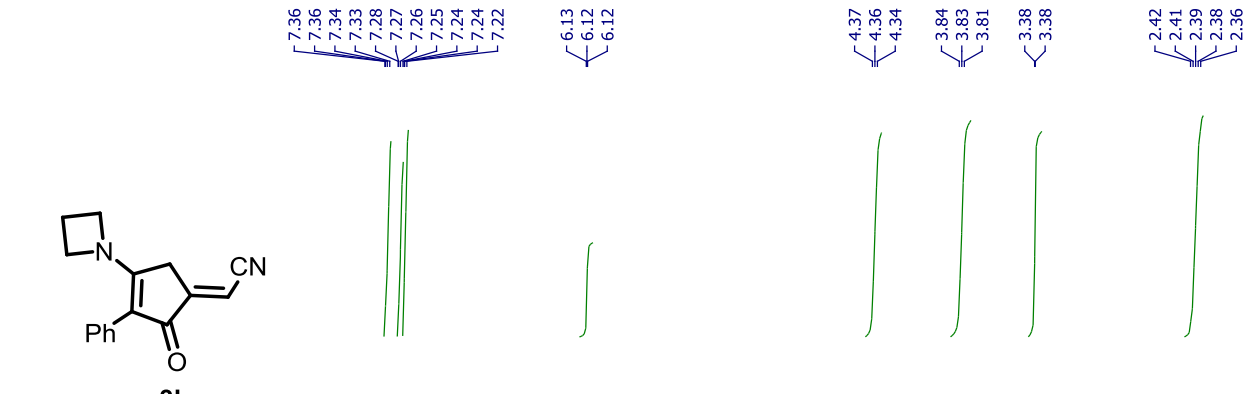
3g

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



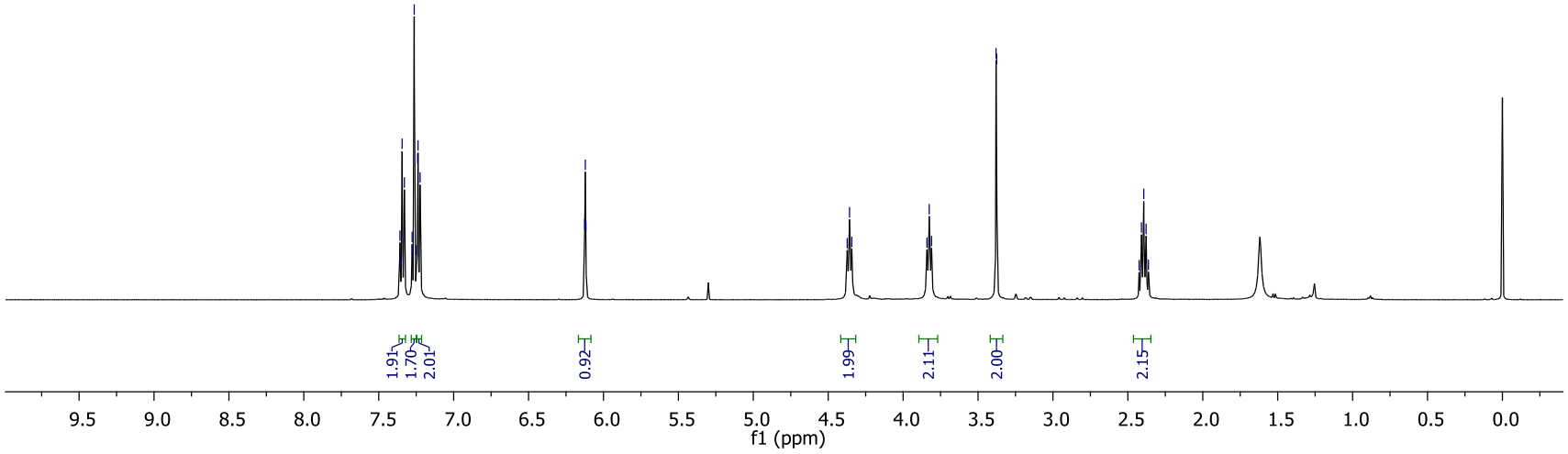
3g

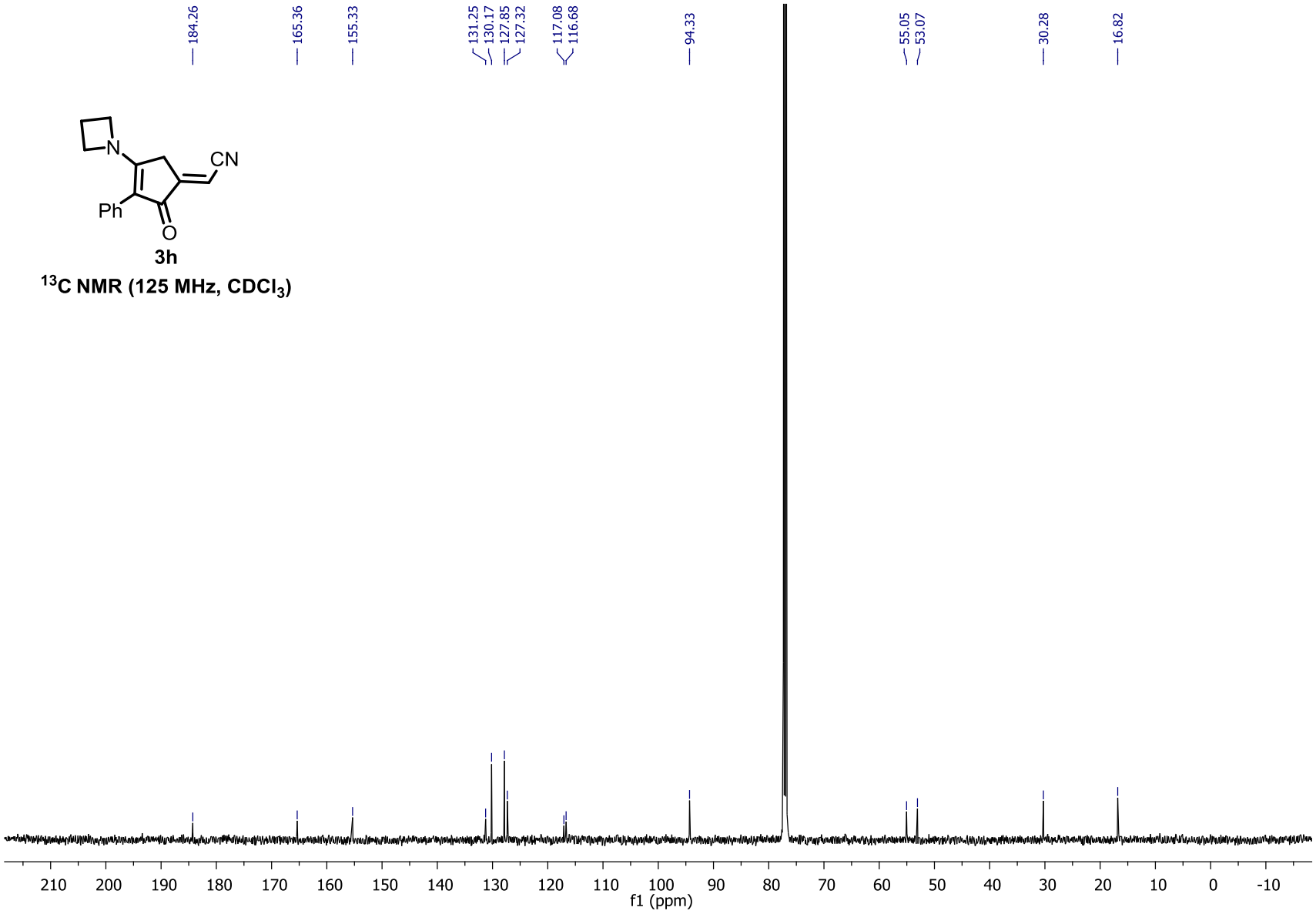
^{13}C NMR (100 MHz, $CDCl_3$)



3h

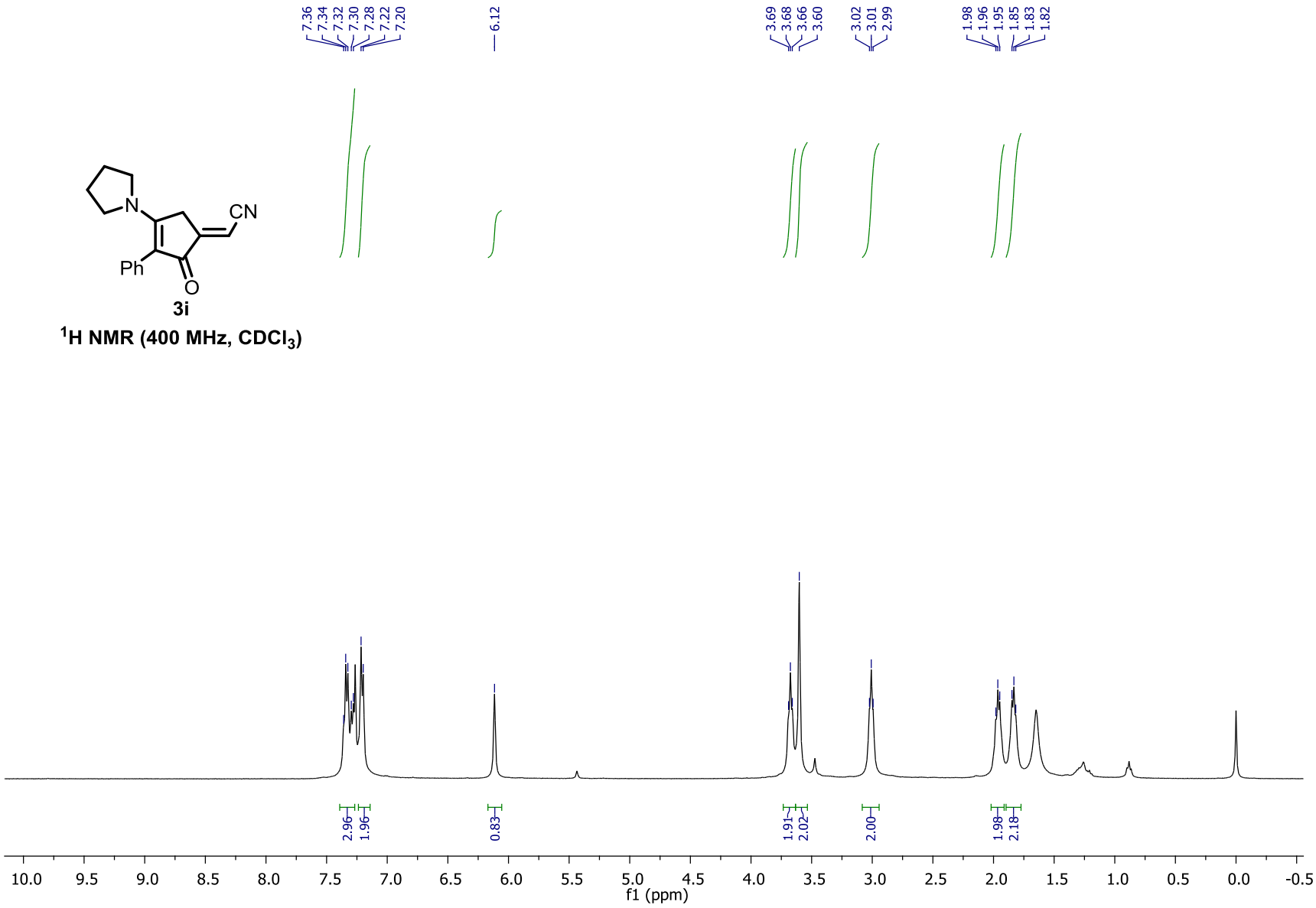
^{1}H NMR (500 MHz, $CDCl_3$)





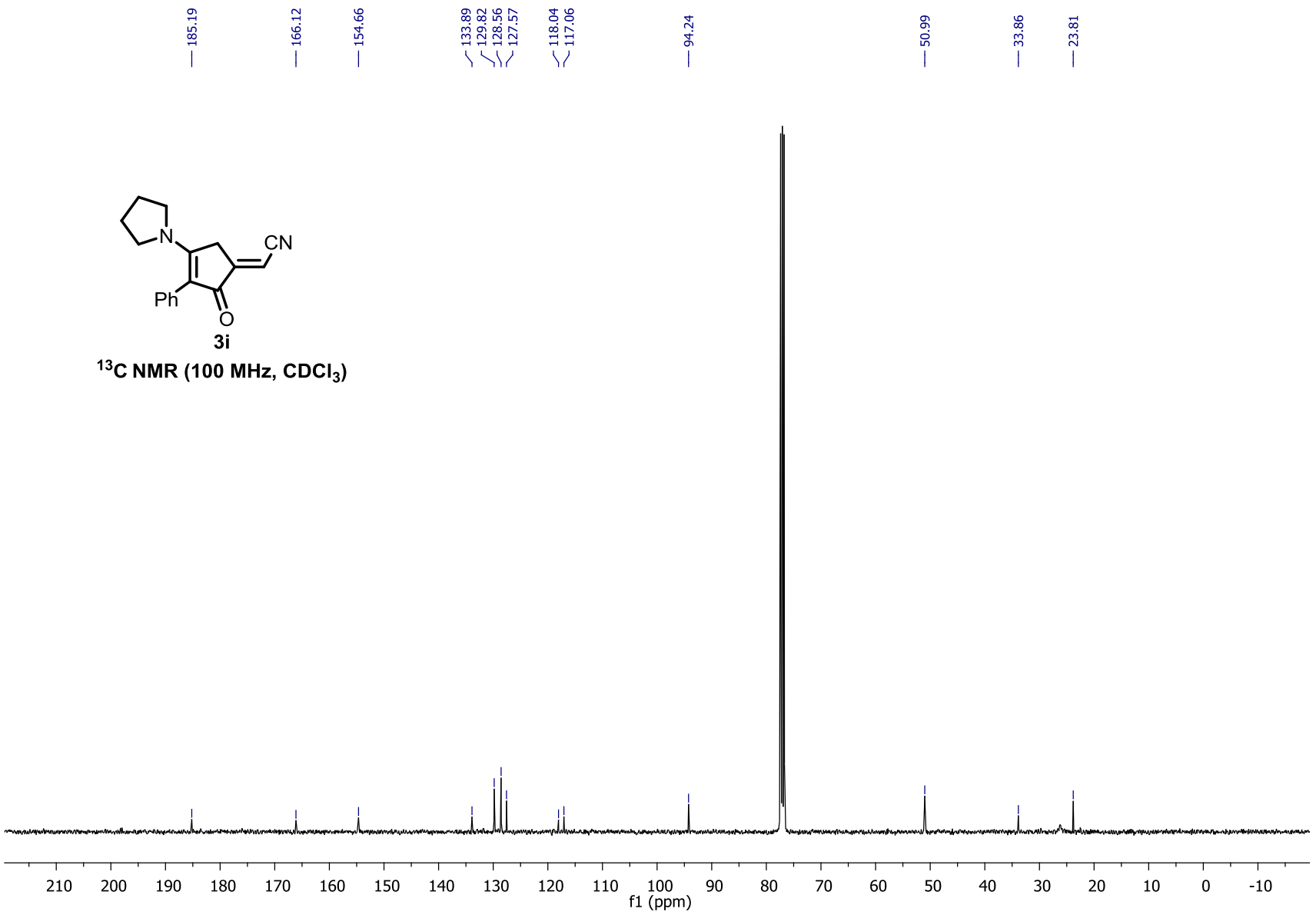
3h

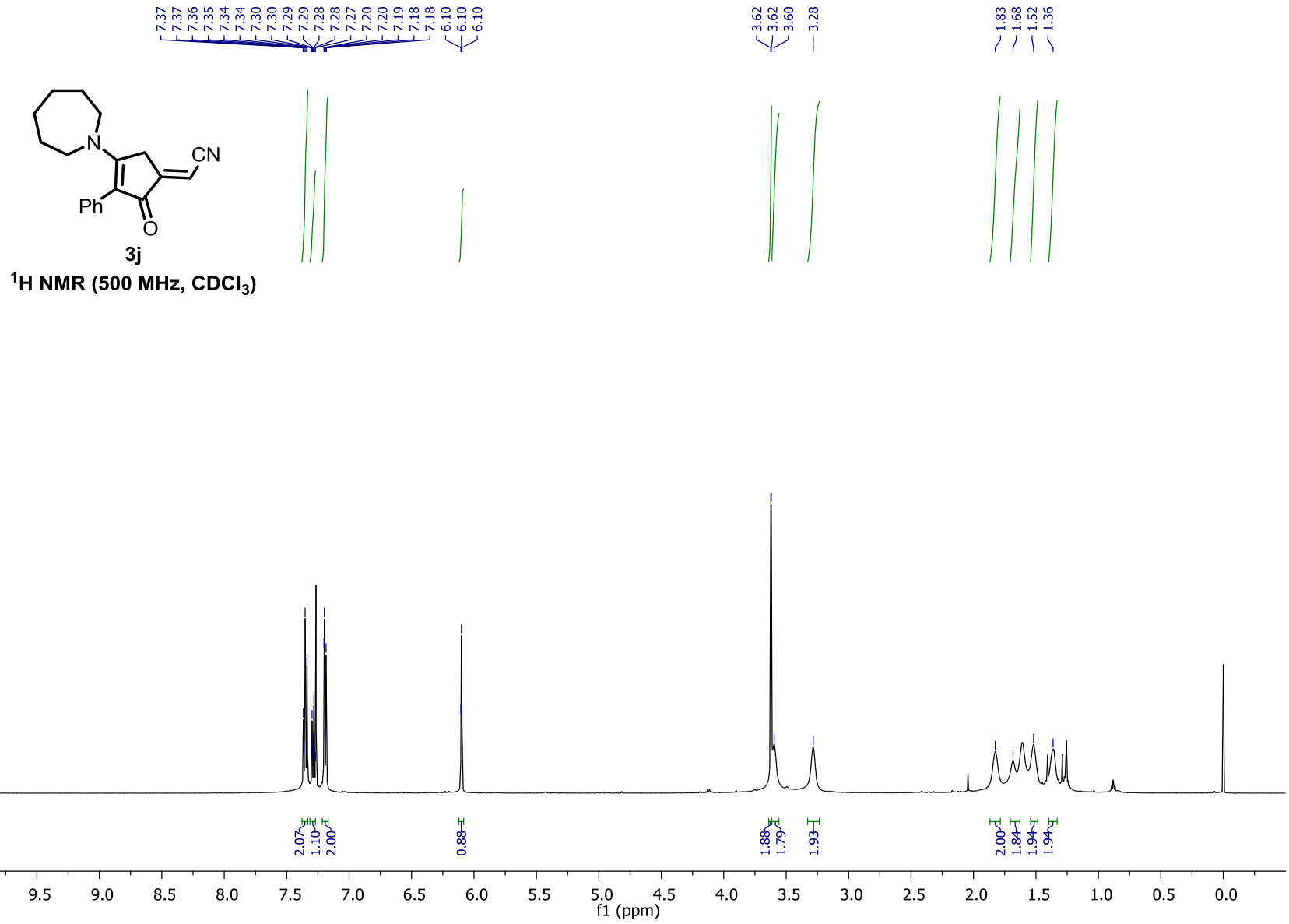
^{13}C NMR (125 MHz, $CDCl_3$)



3i

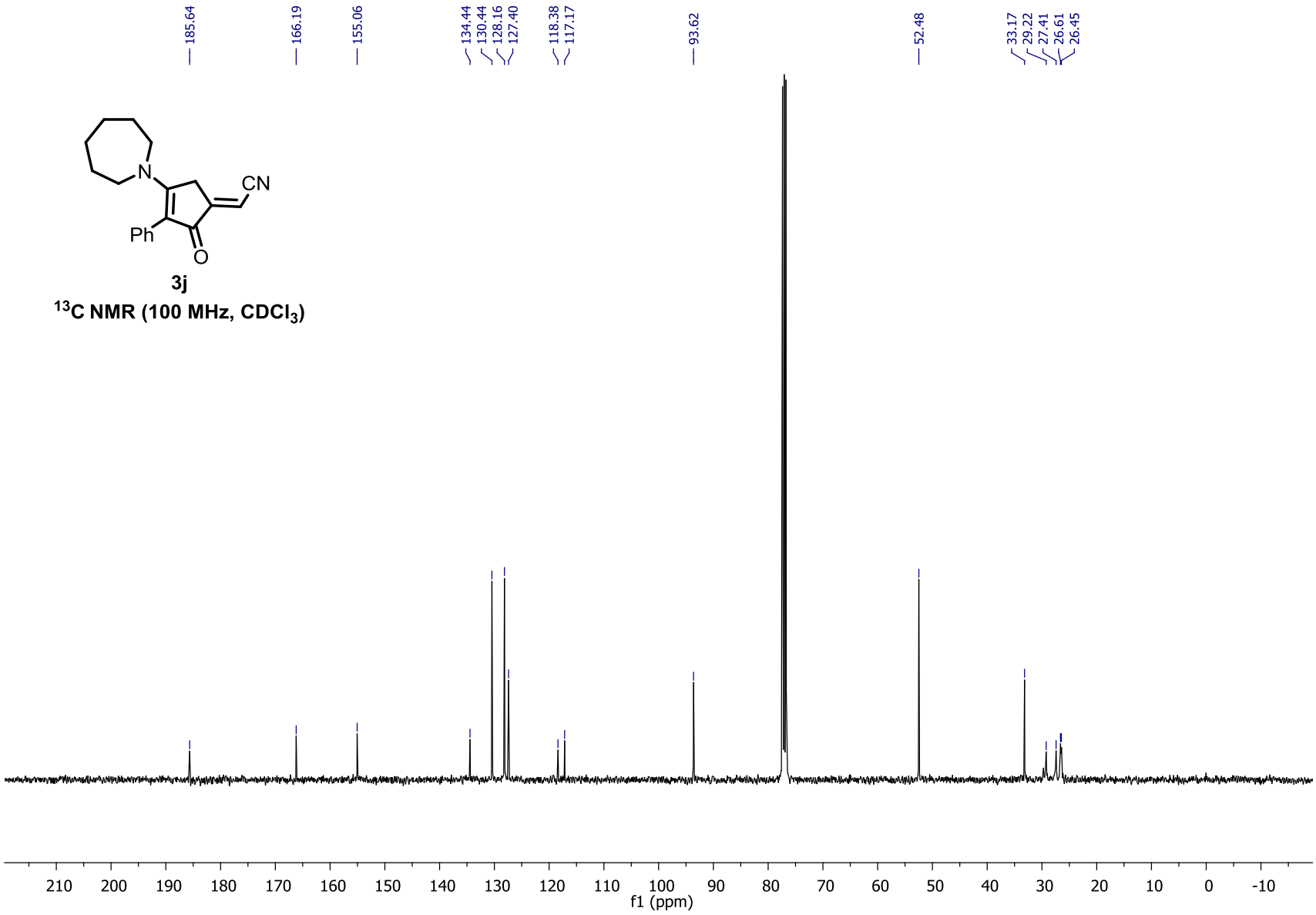
^{1}H NMR (400 MHz, $CDCl_3$)


185.19
166.12
154.66
133.89
129.82
128.56
127.57
118.04
117.06
94.24
50.99
33.86
23.81
N
CN
Ph
O
3i
^{13}C NMR (100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



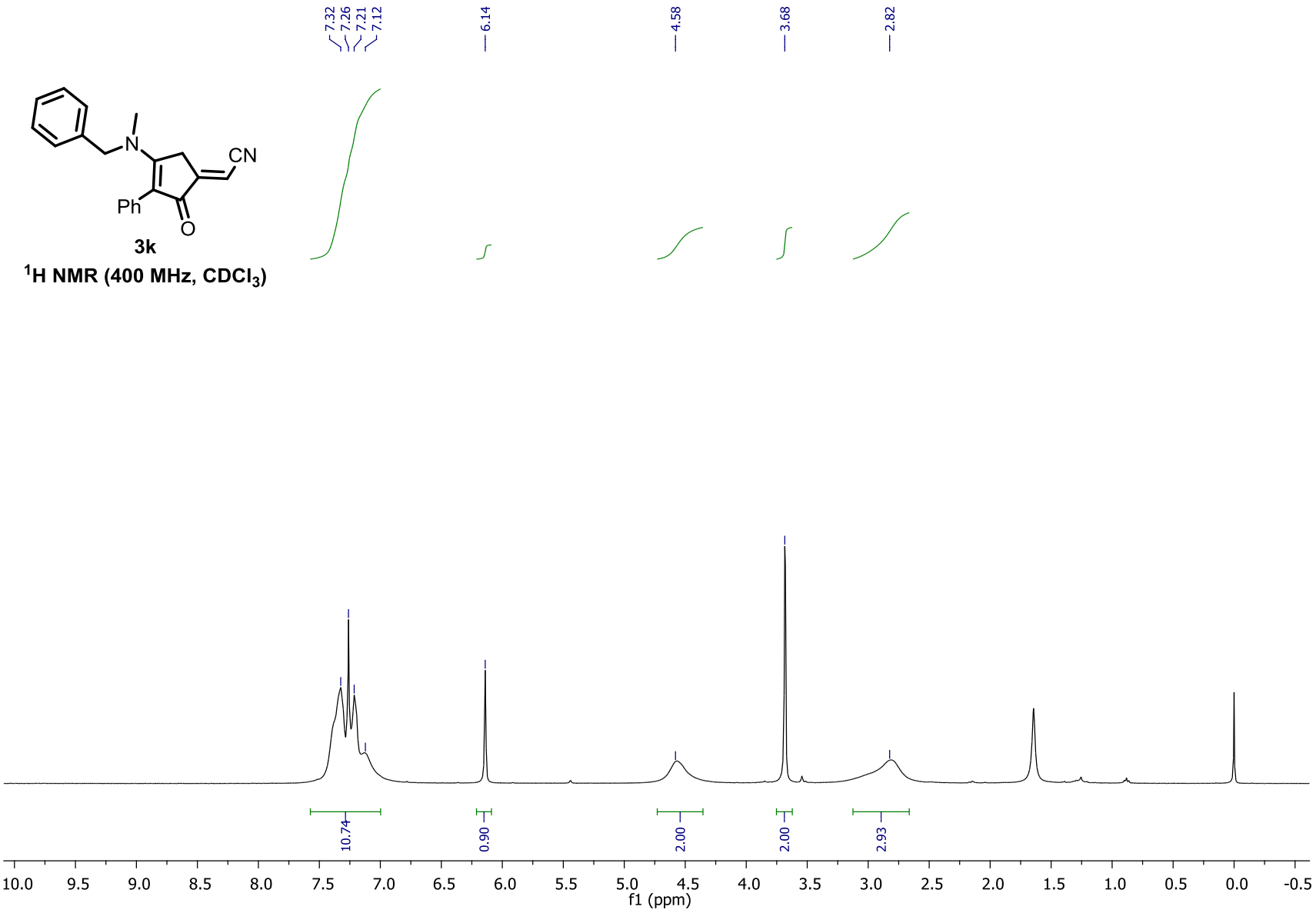
3j

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



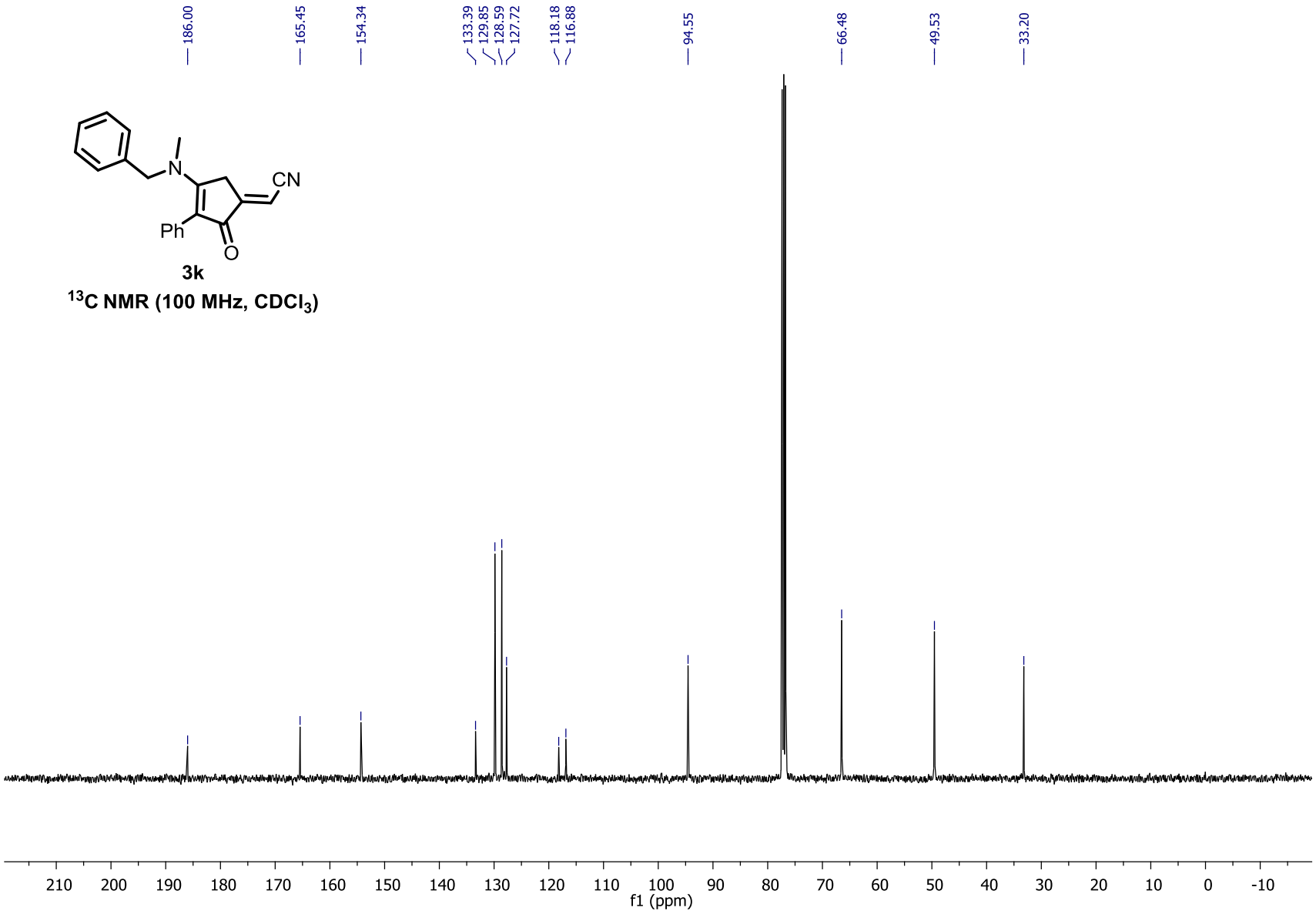
3j

^{13}C NMR (100 MHz, $CDCl_3$)



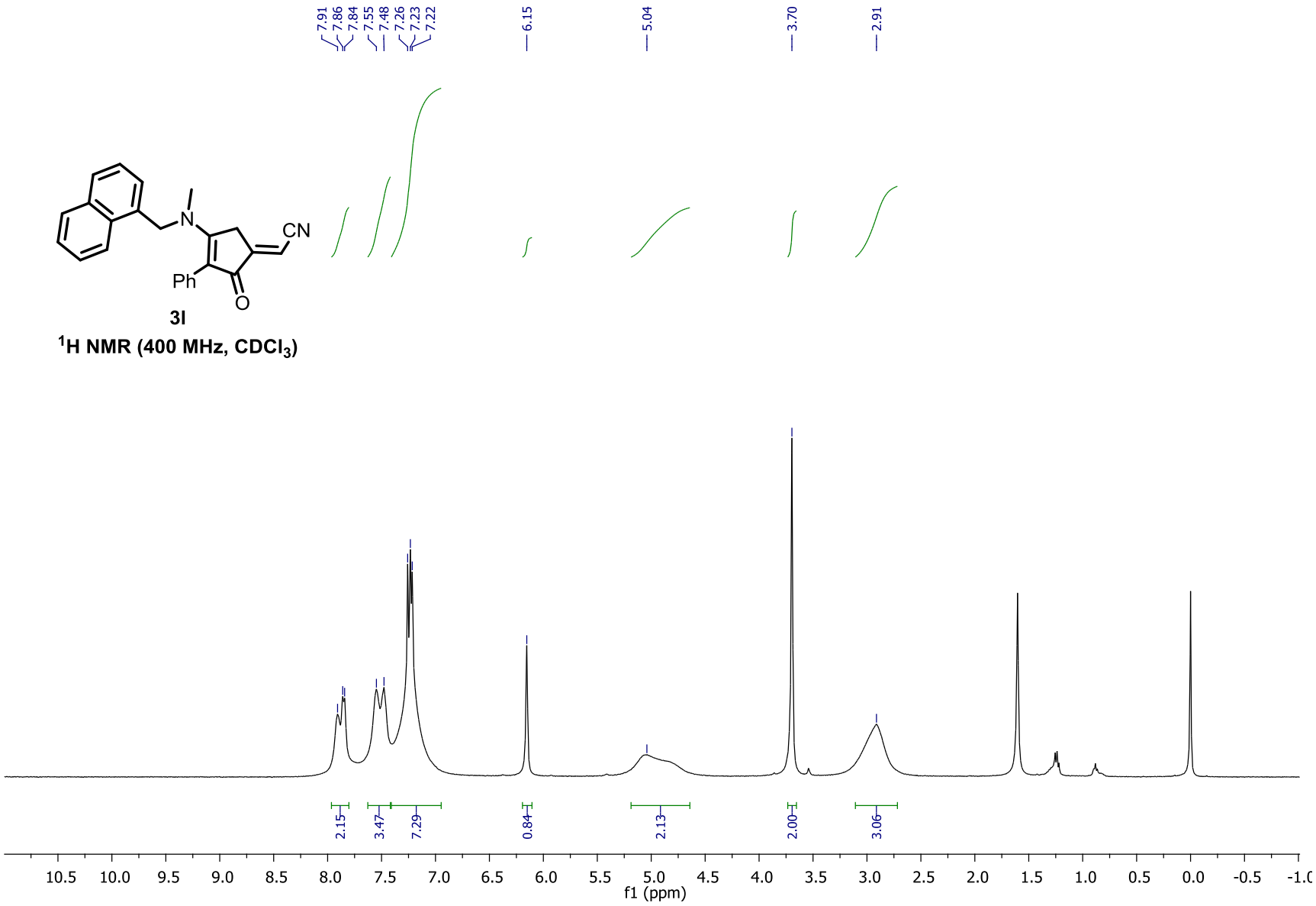
3k

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



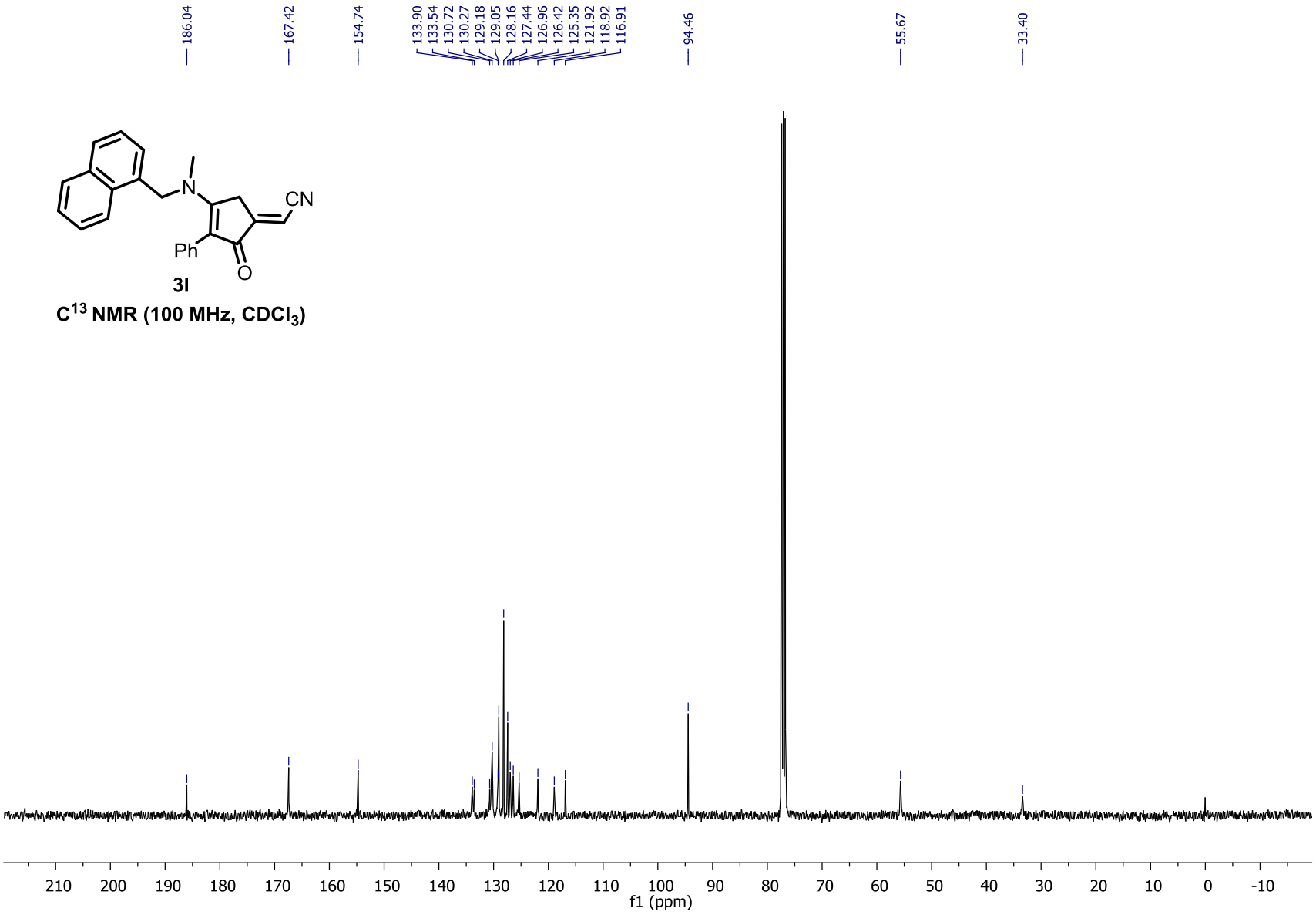
3k

^{13}C NMR (100 MHz, $CDCl_3$)



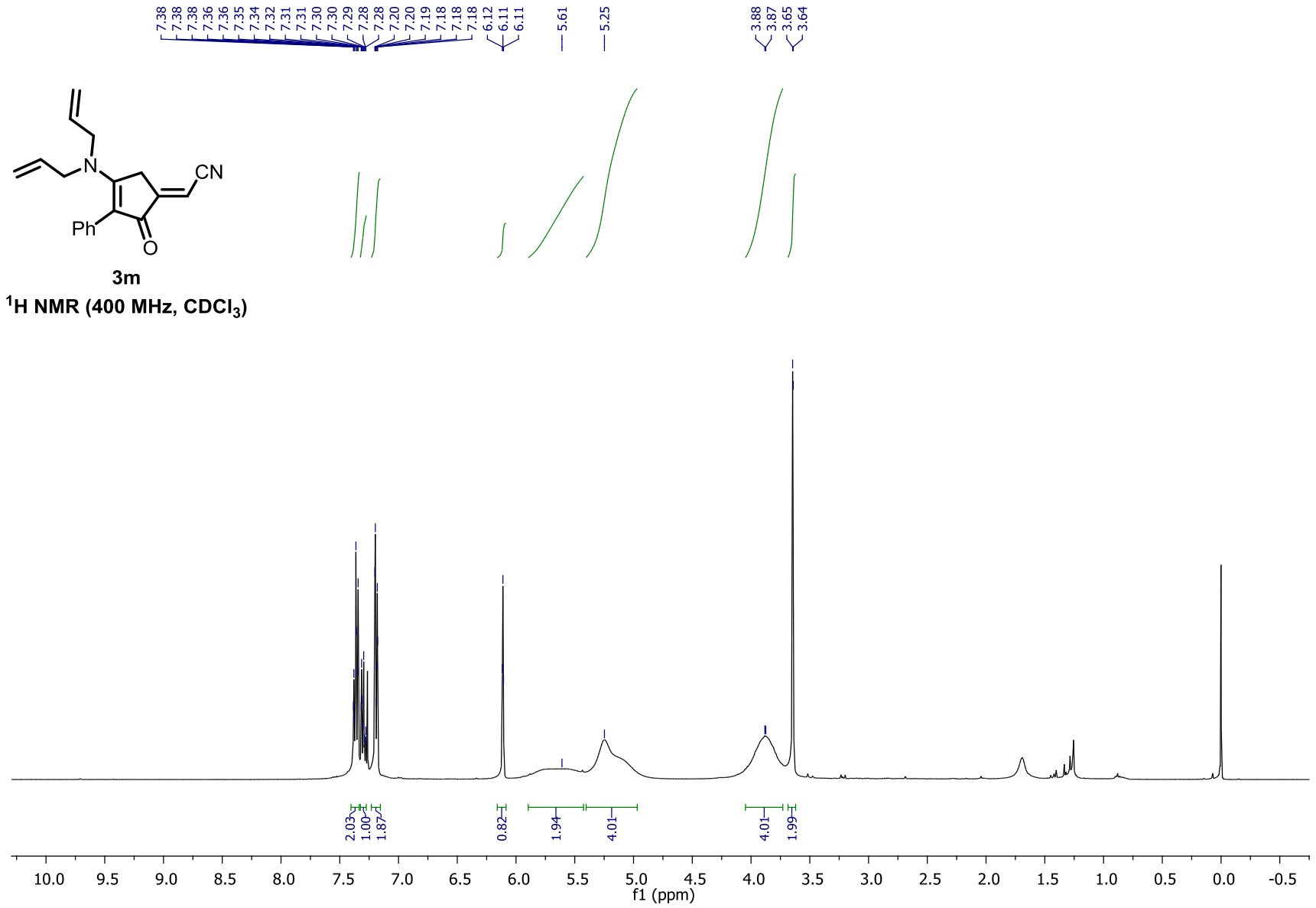
3l

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



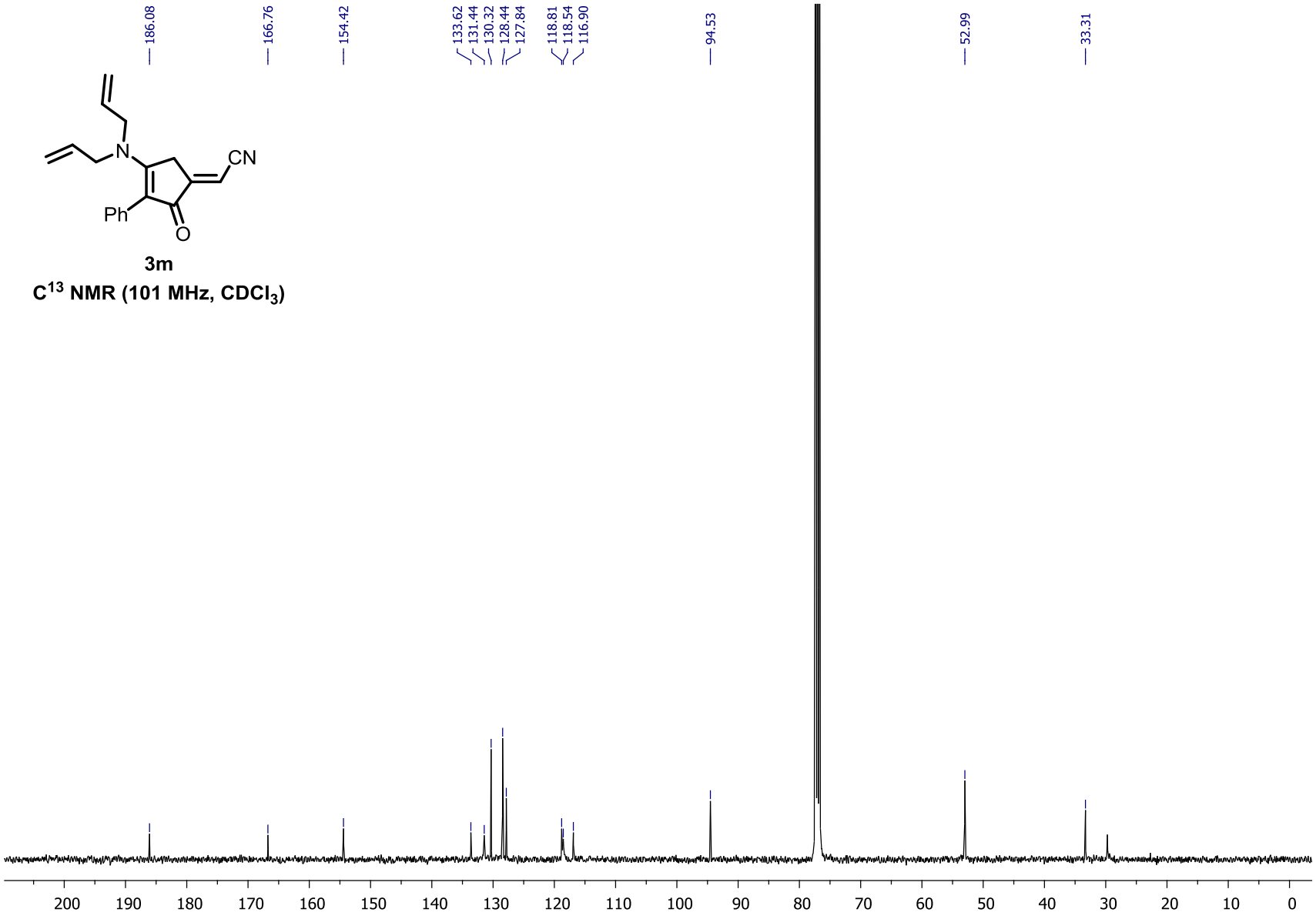
3l

C^{13} NMR (100 MHz, $CDCl_3$)



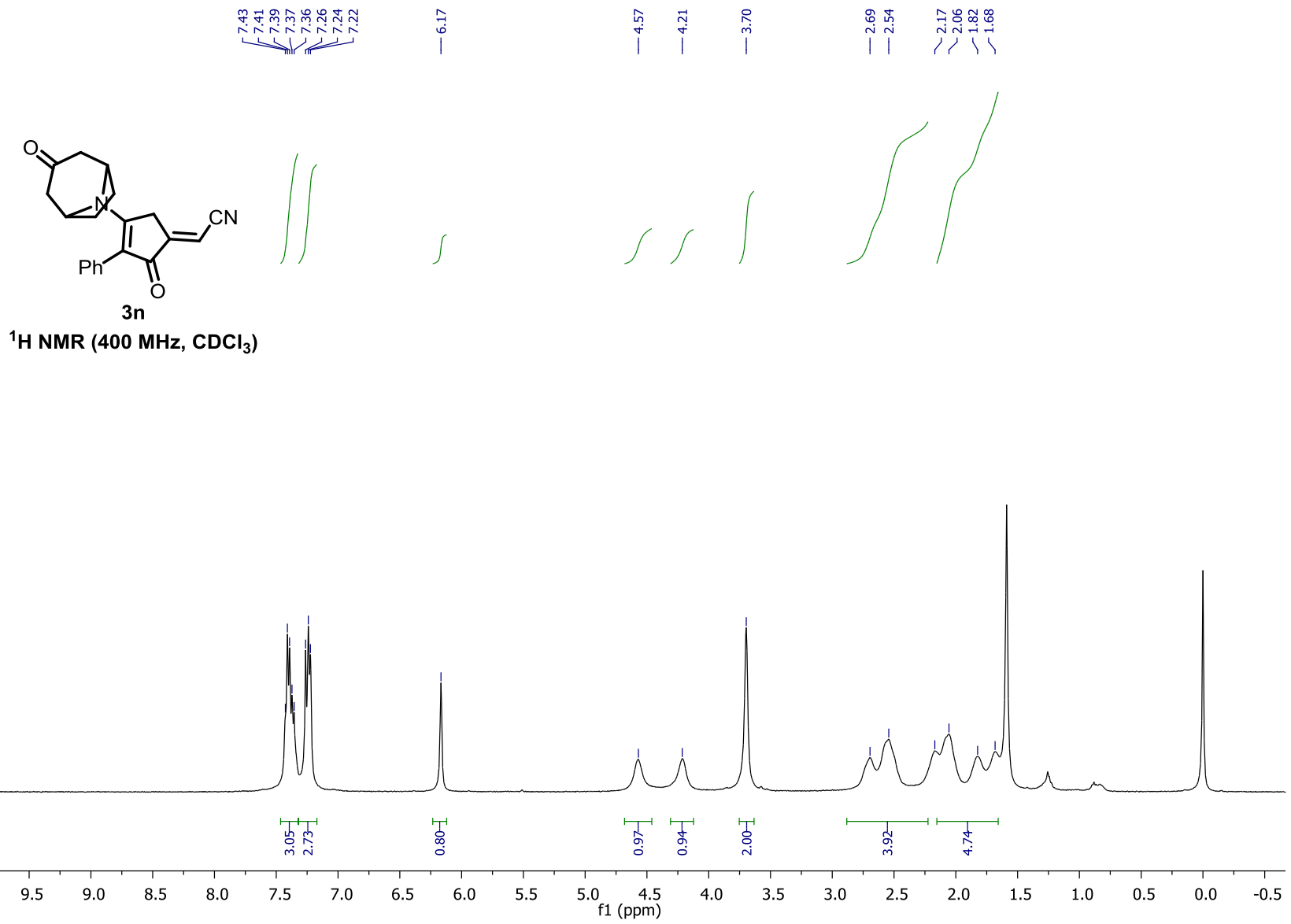
3m

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



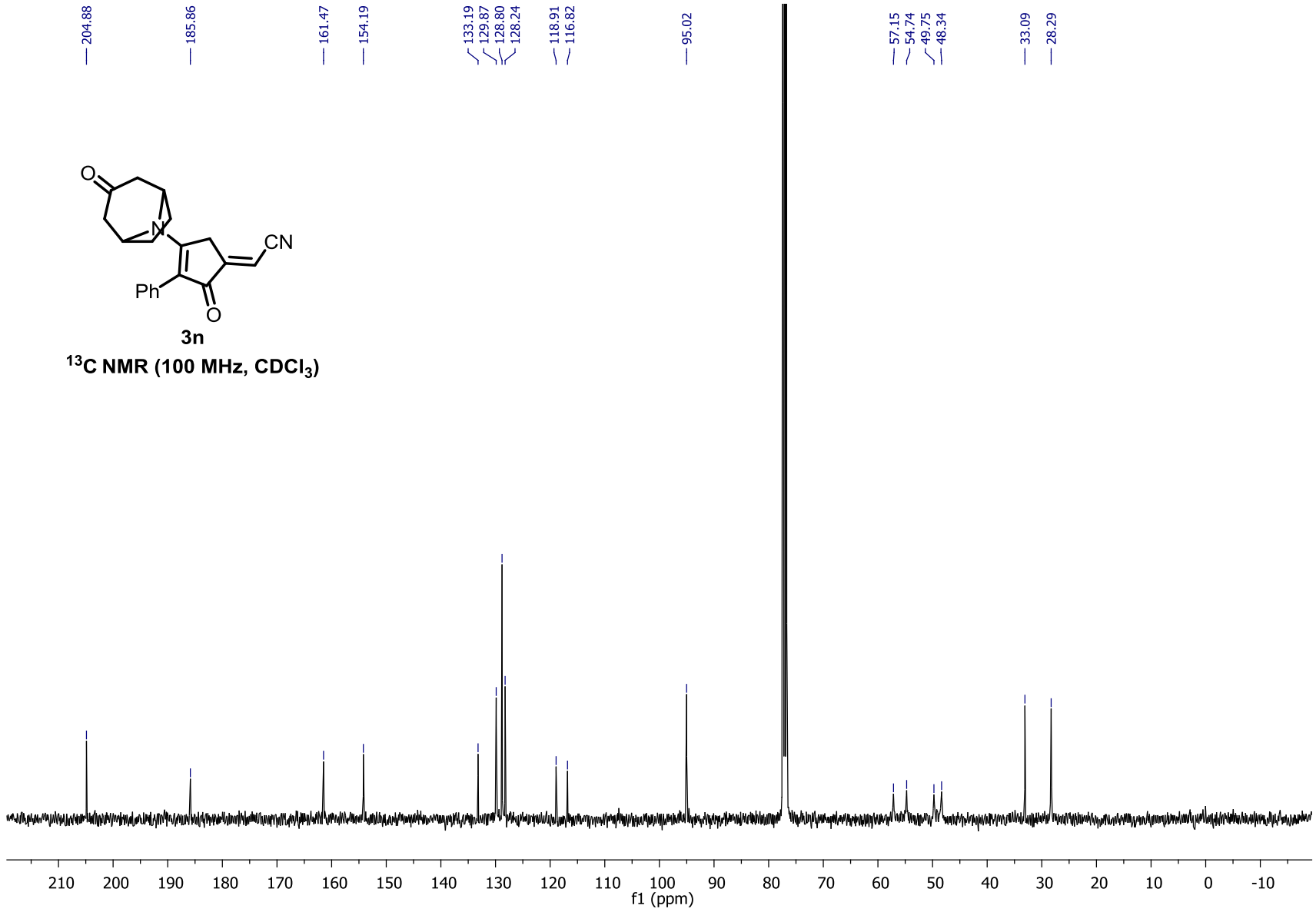
3m

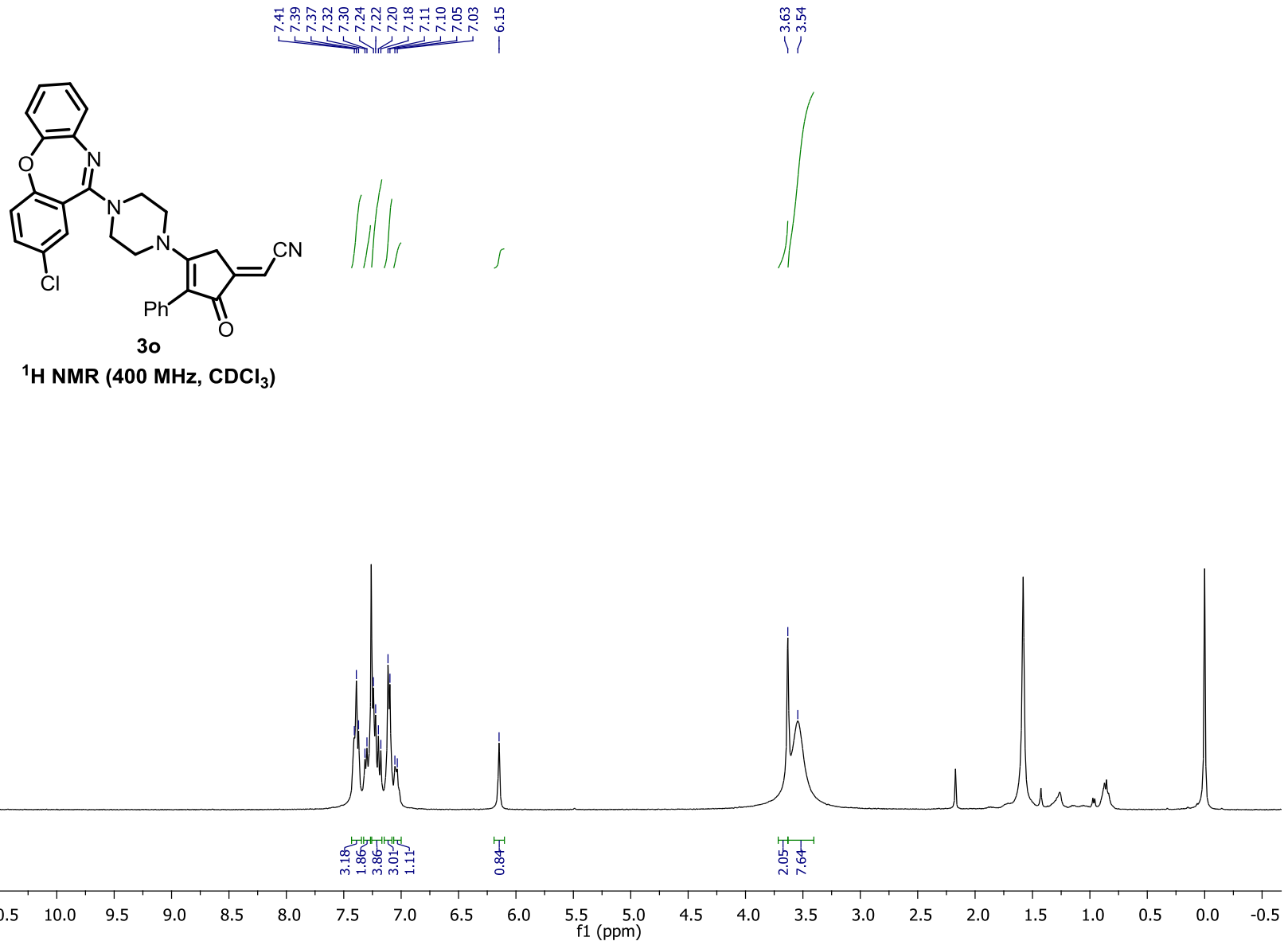
C^{13} NMR (101 MHz, $CDCl_3$)



3n

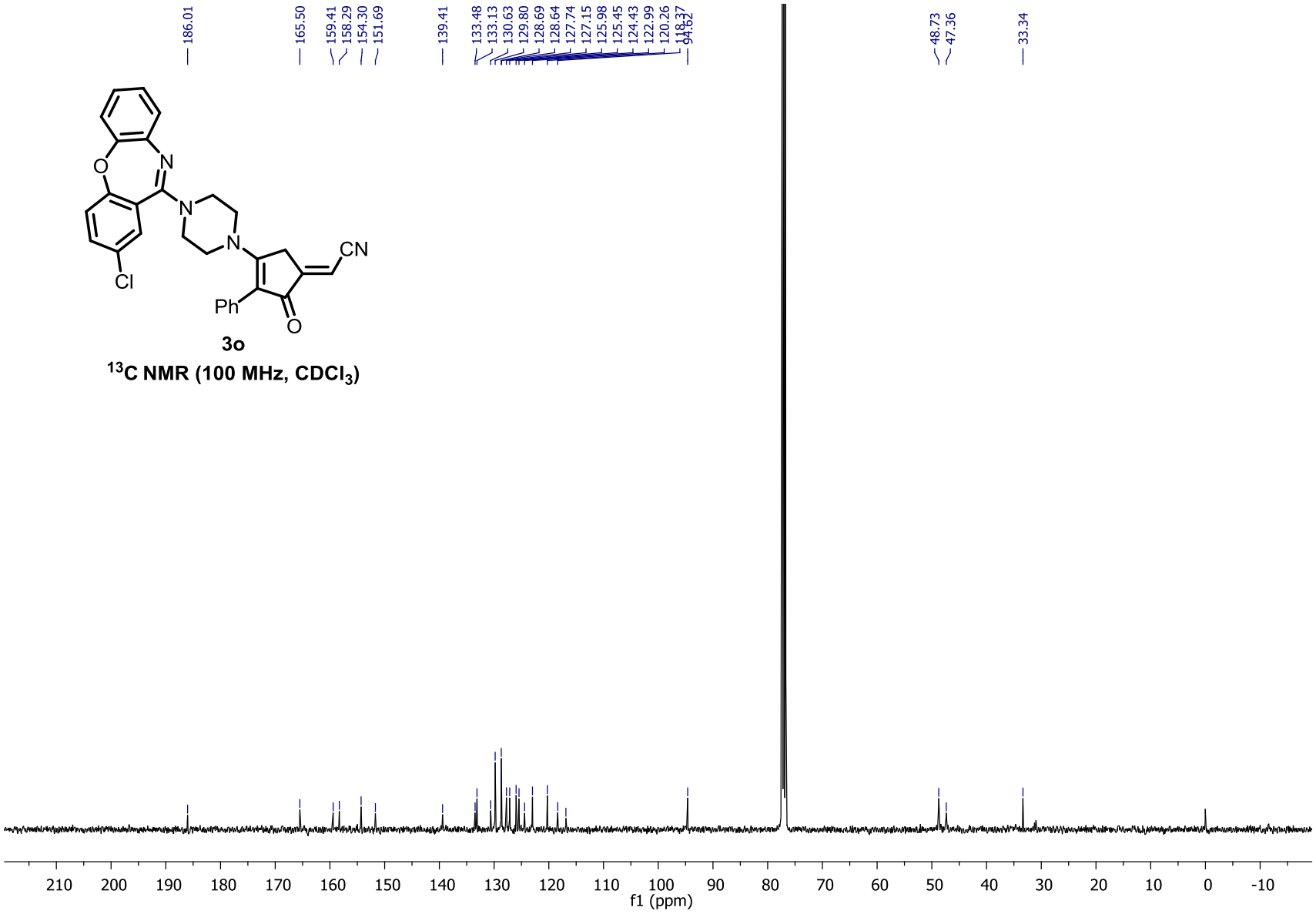
^{1}H NMR (400 MHz, $CDCl_3$)

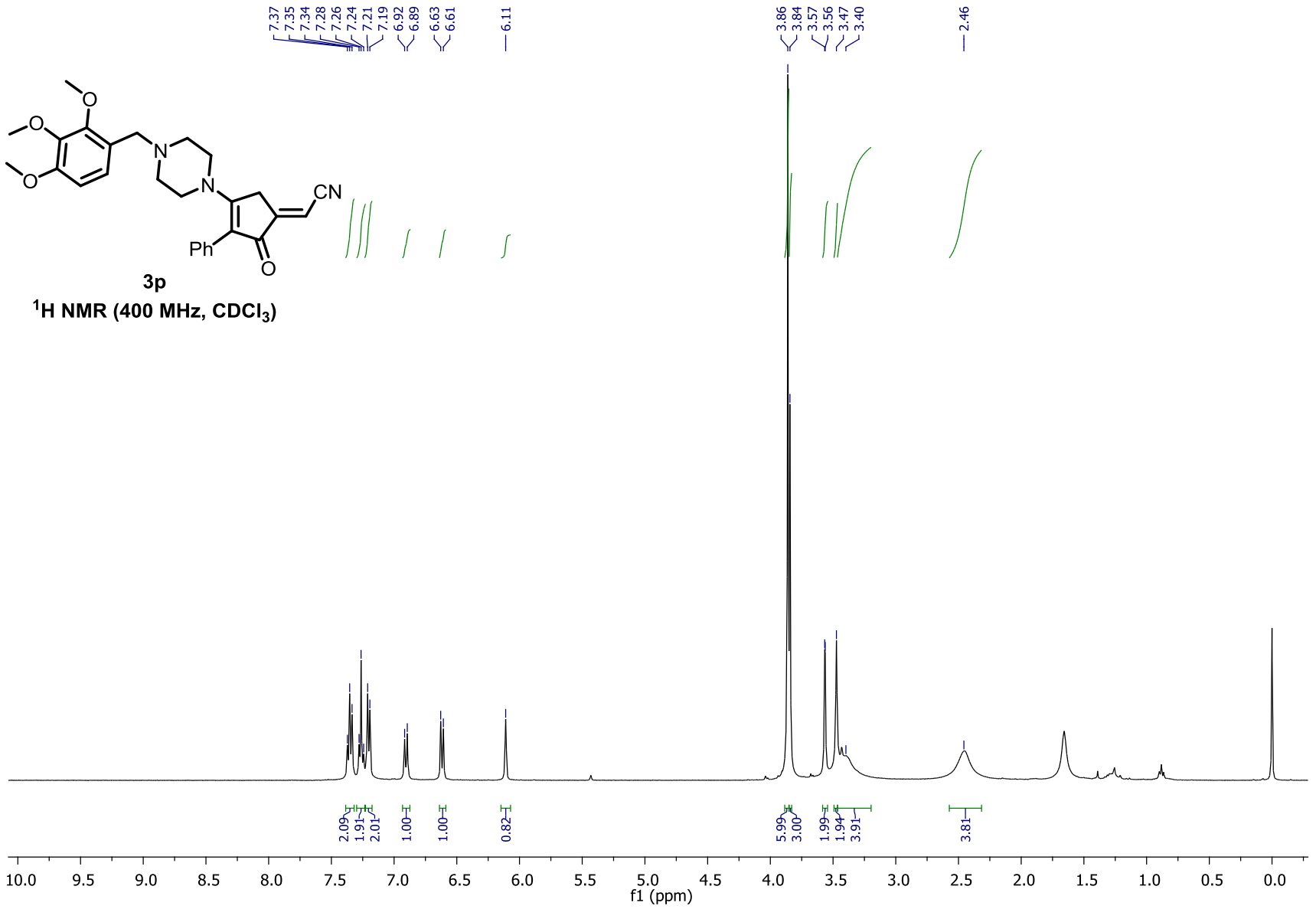

204.88
185.86
161.47
154.19
133.19
129.87
128.80
128.24
118.91
116.82
95.02
57.15
54.74
49.75
48.34
33.09
28.29
O
N
CN
Ph
O
3n
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3o

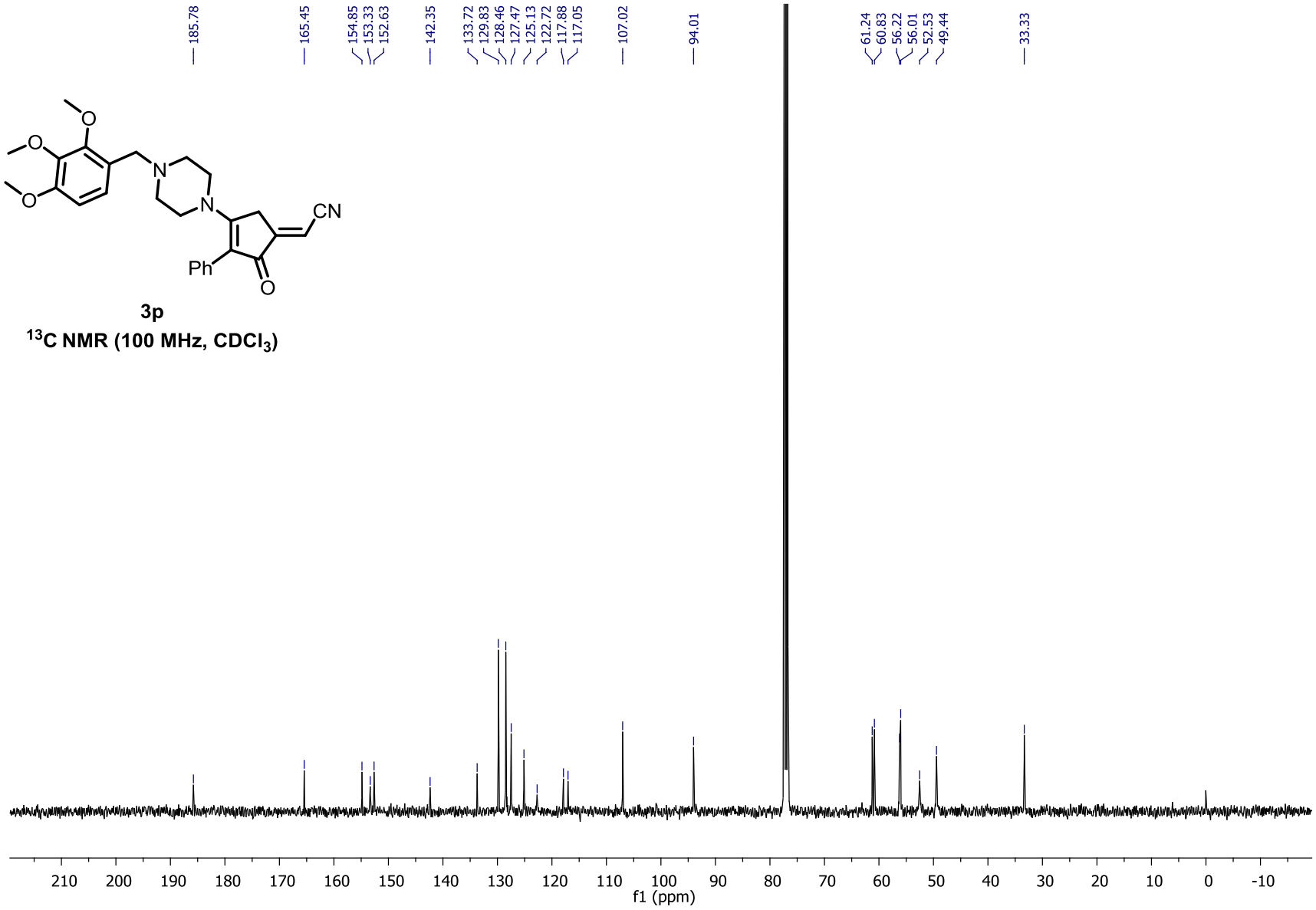
^{1}H NMR (400 MHz, $CDCl_3$)


186.01
165.50
159.41
158.29
154.30
151.69
139.41
133.48
133.13
130.63
129.80
128.69
128.64
127.74
127.15
125.98
125.45
124.43
122.99
120.26
118.37
94.62
48.73
47.36
33.34
O
N
N
N
Cl
CN
Ph
O
3o
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



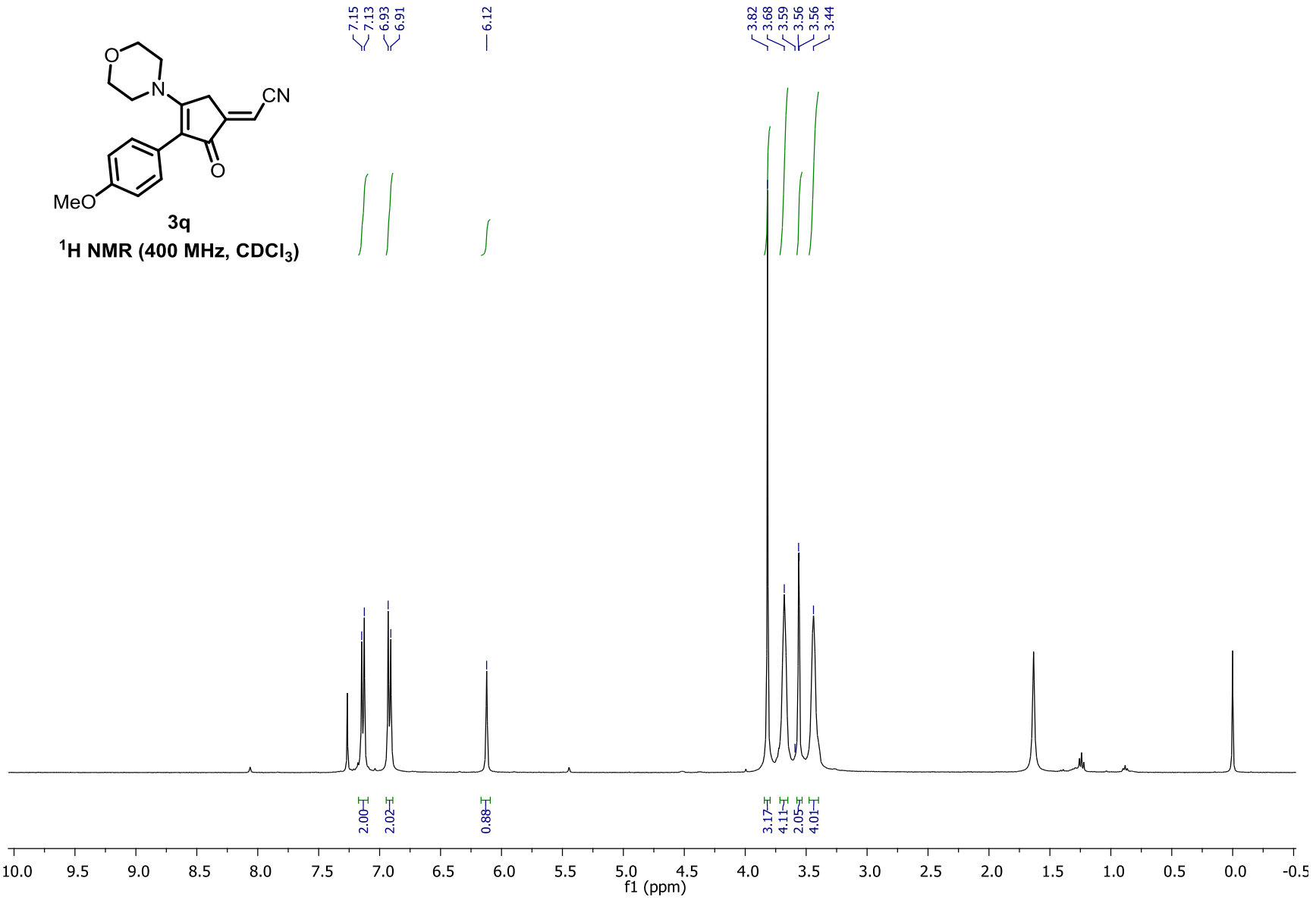
3p

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



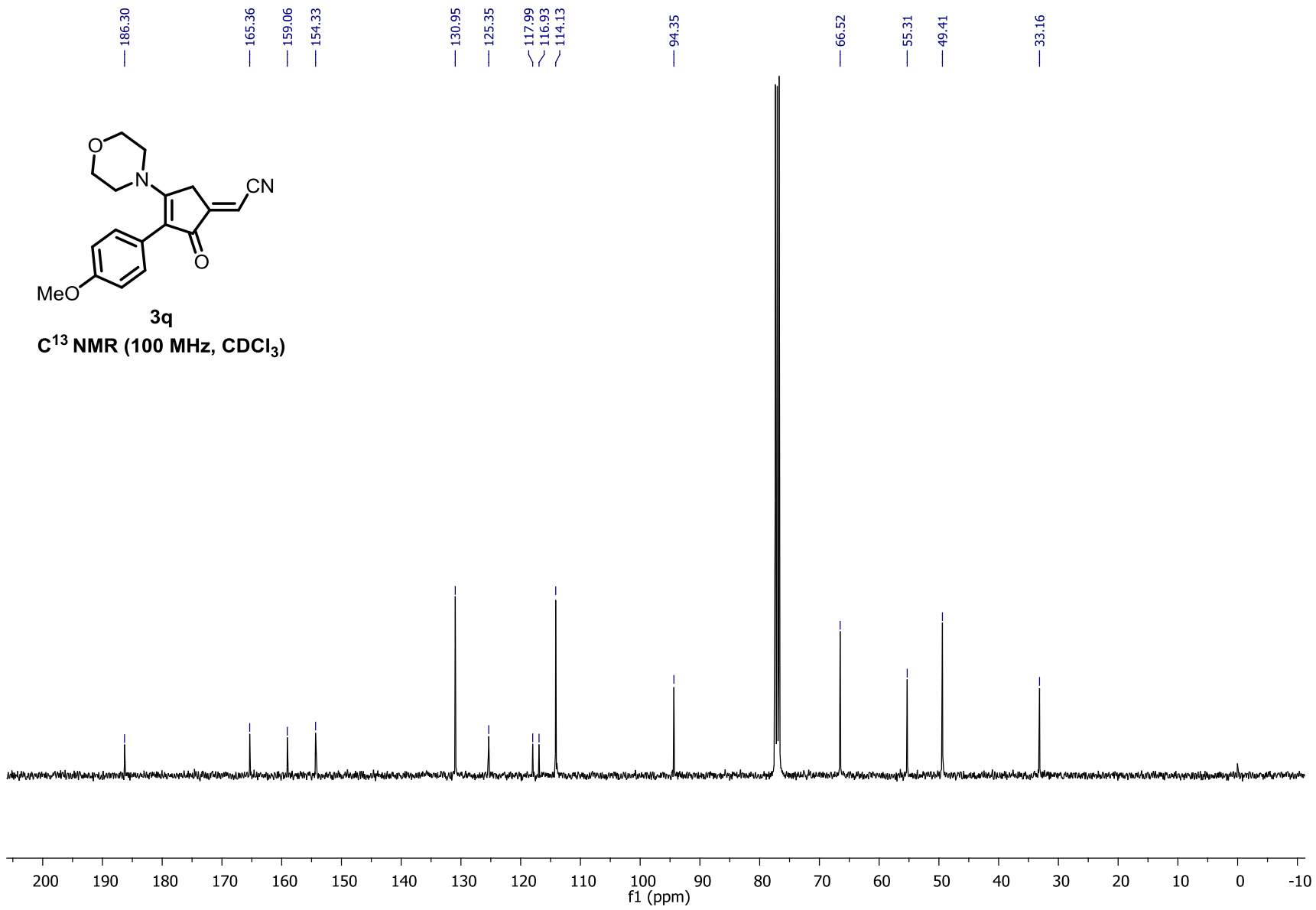
3p

^{13}C NMR (100 MHz, $CDCl_3$)



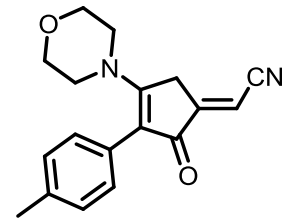
3q

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



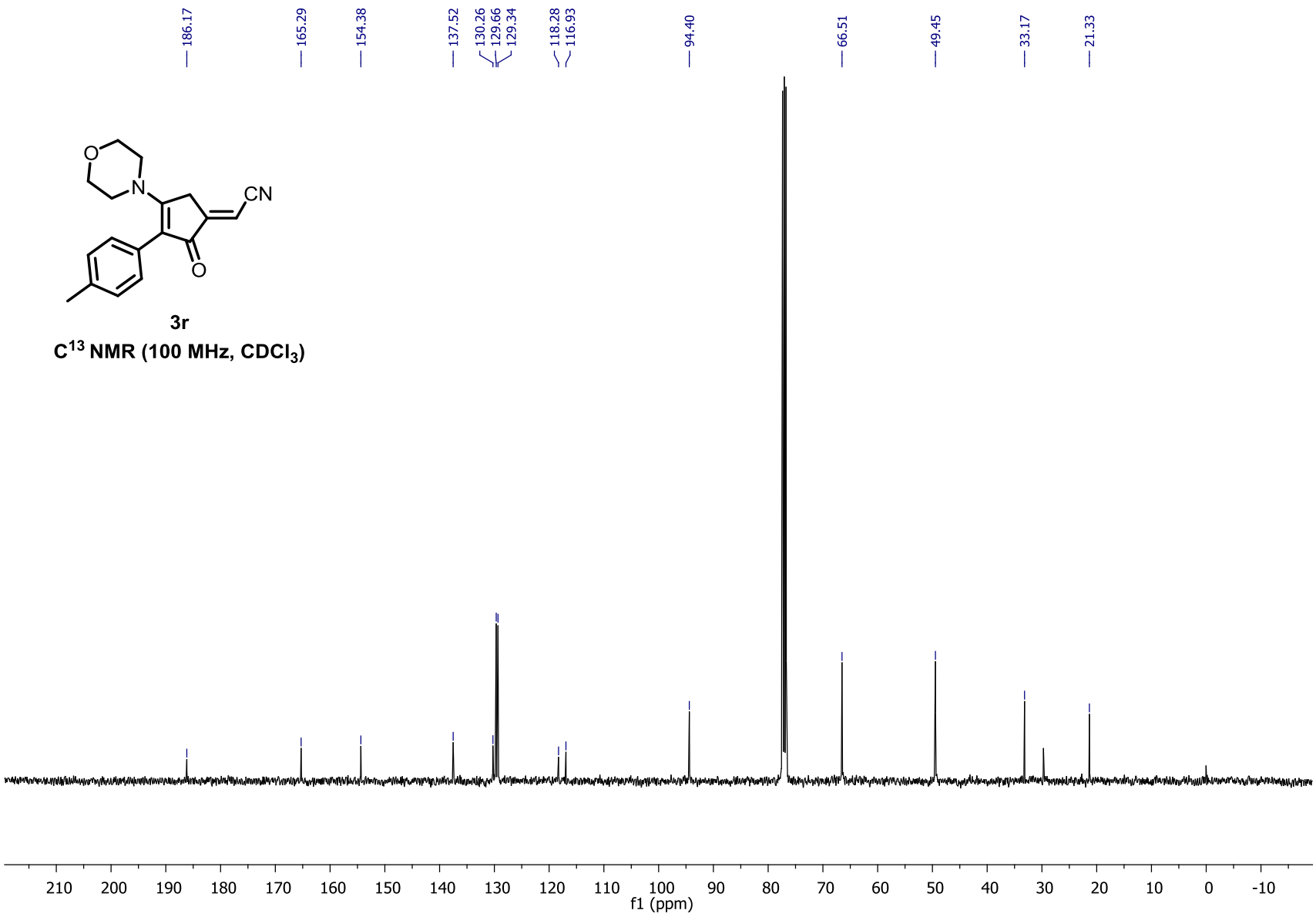
3q

C^{13} NMR (100 MHz, $CDCl_3$)



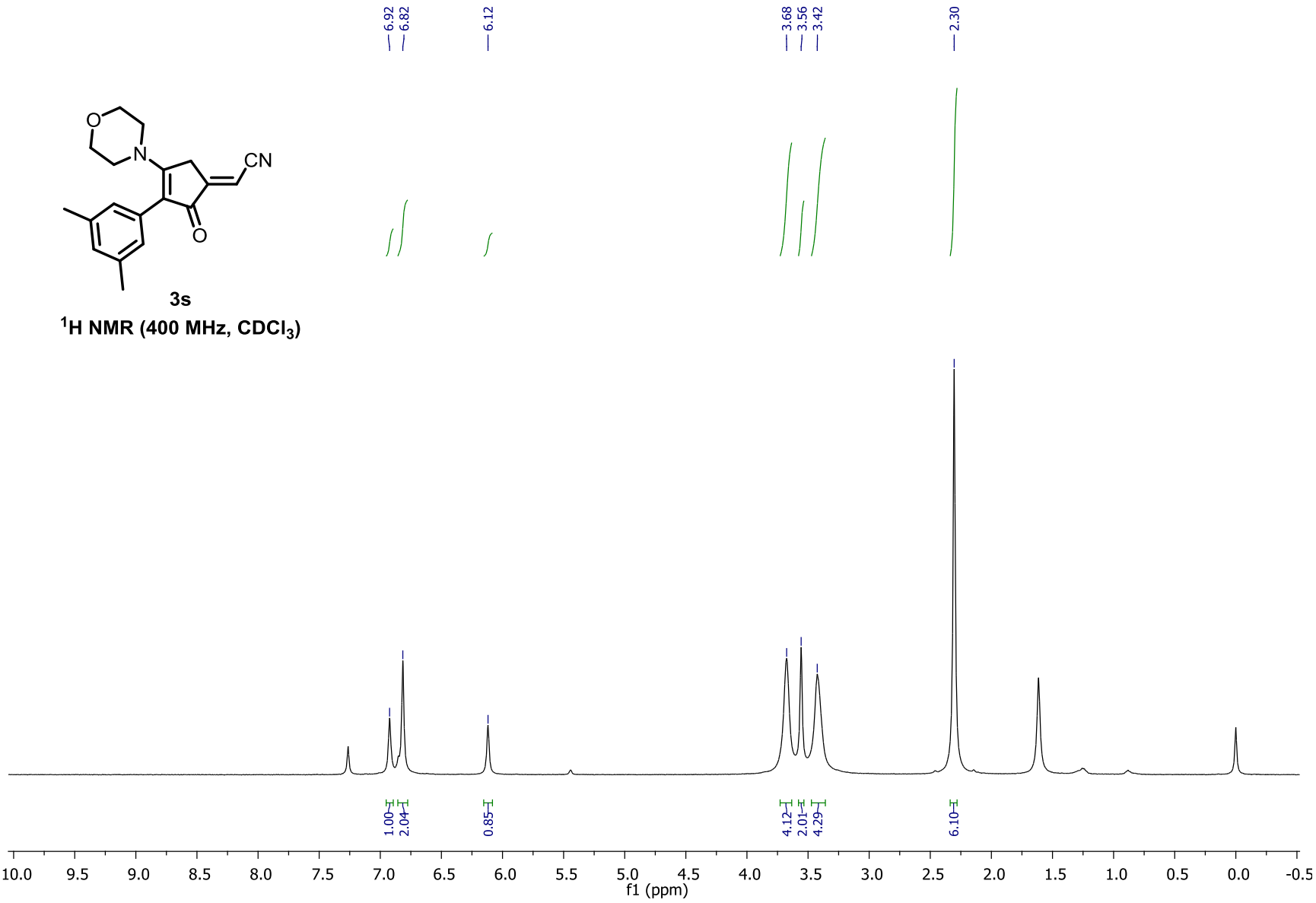
3r

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



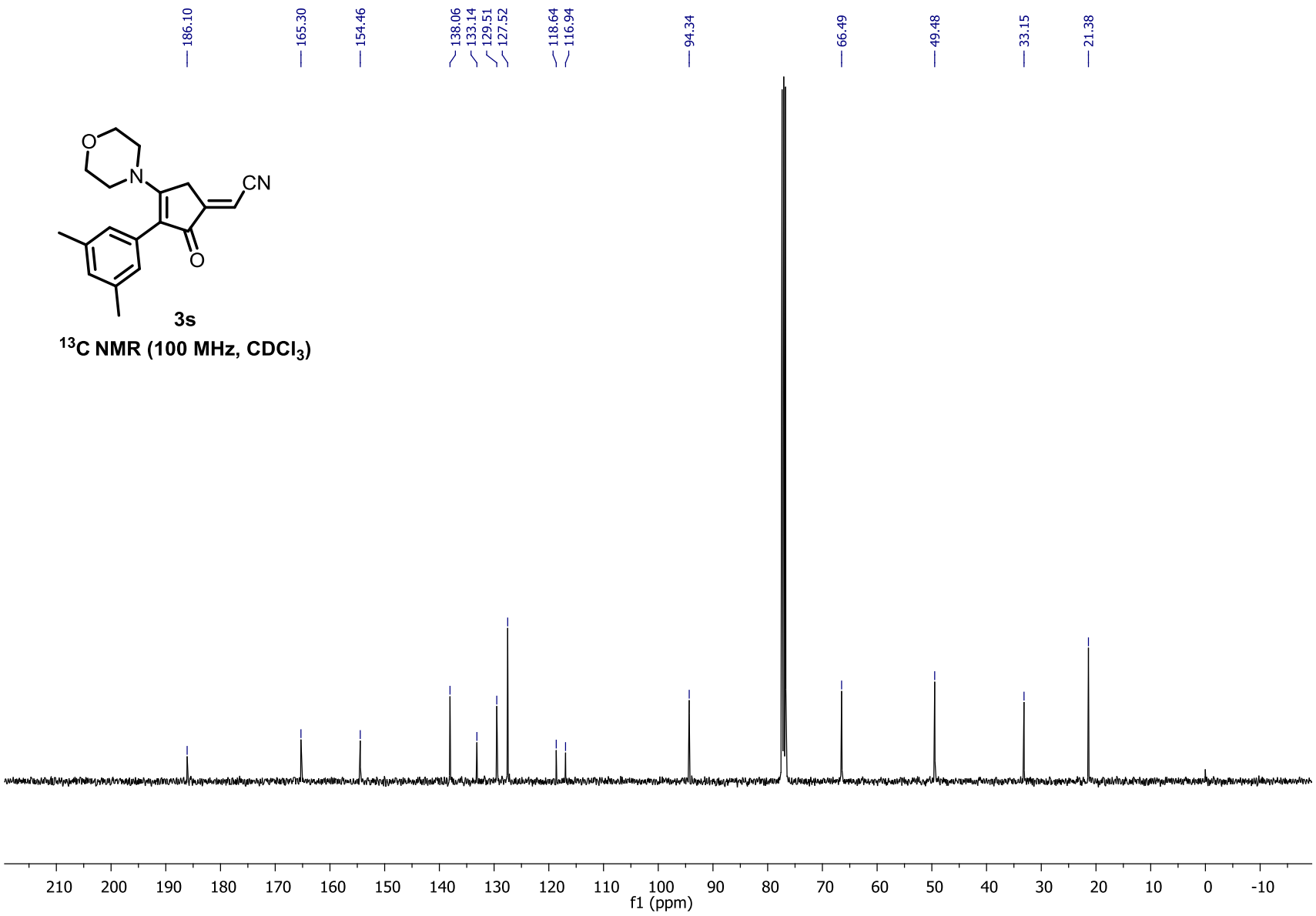
3r

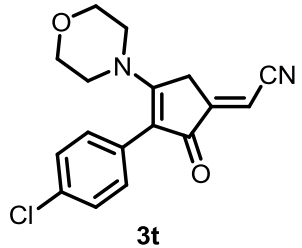
C^{13} NMR (100 MHz, $CDCl_3$)



3s

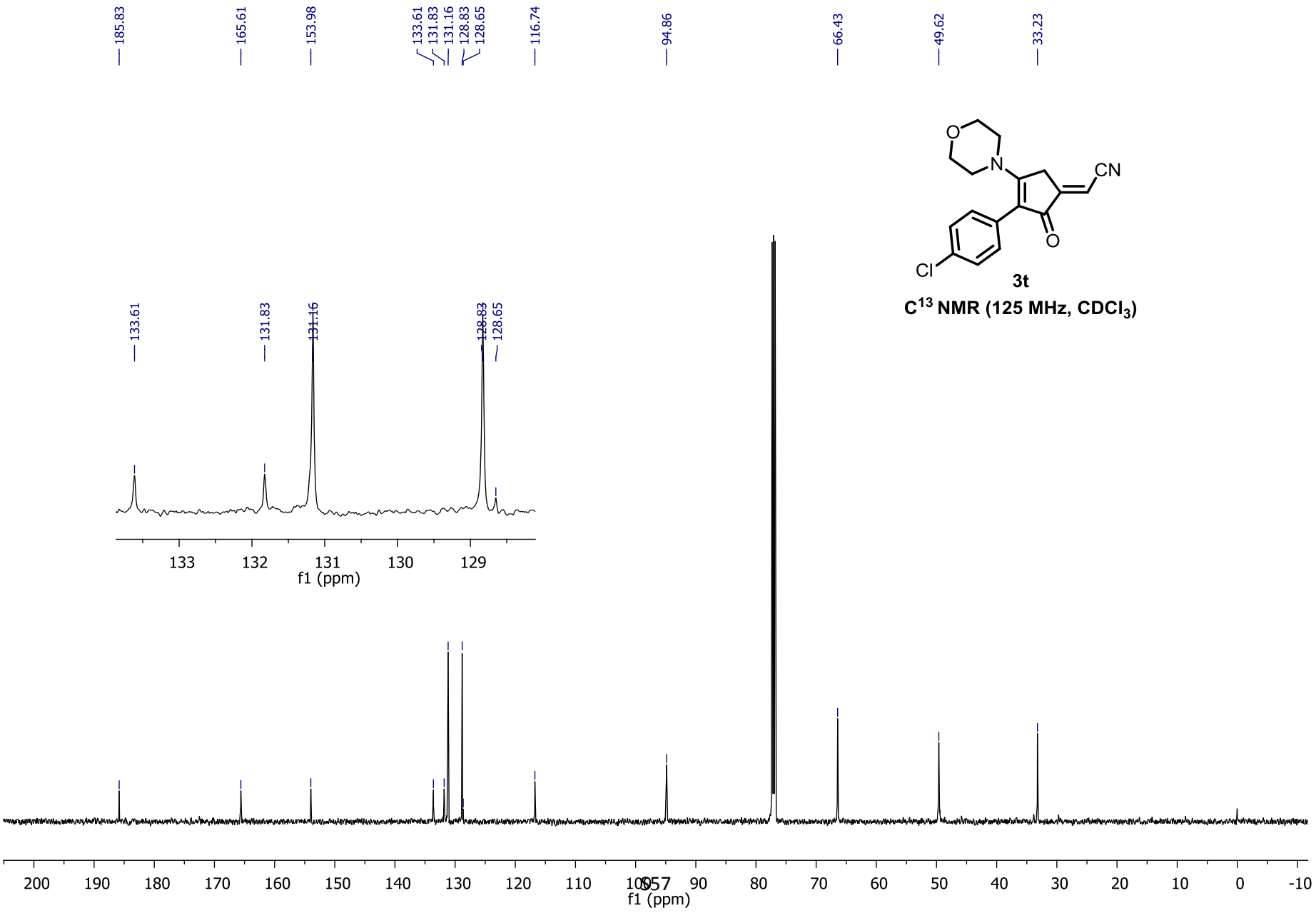
^{1}H NMR (400 MHz, $CDCl_3$)

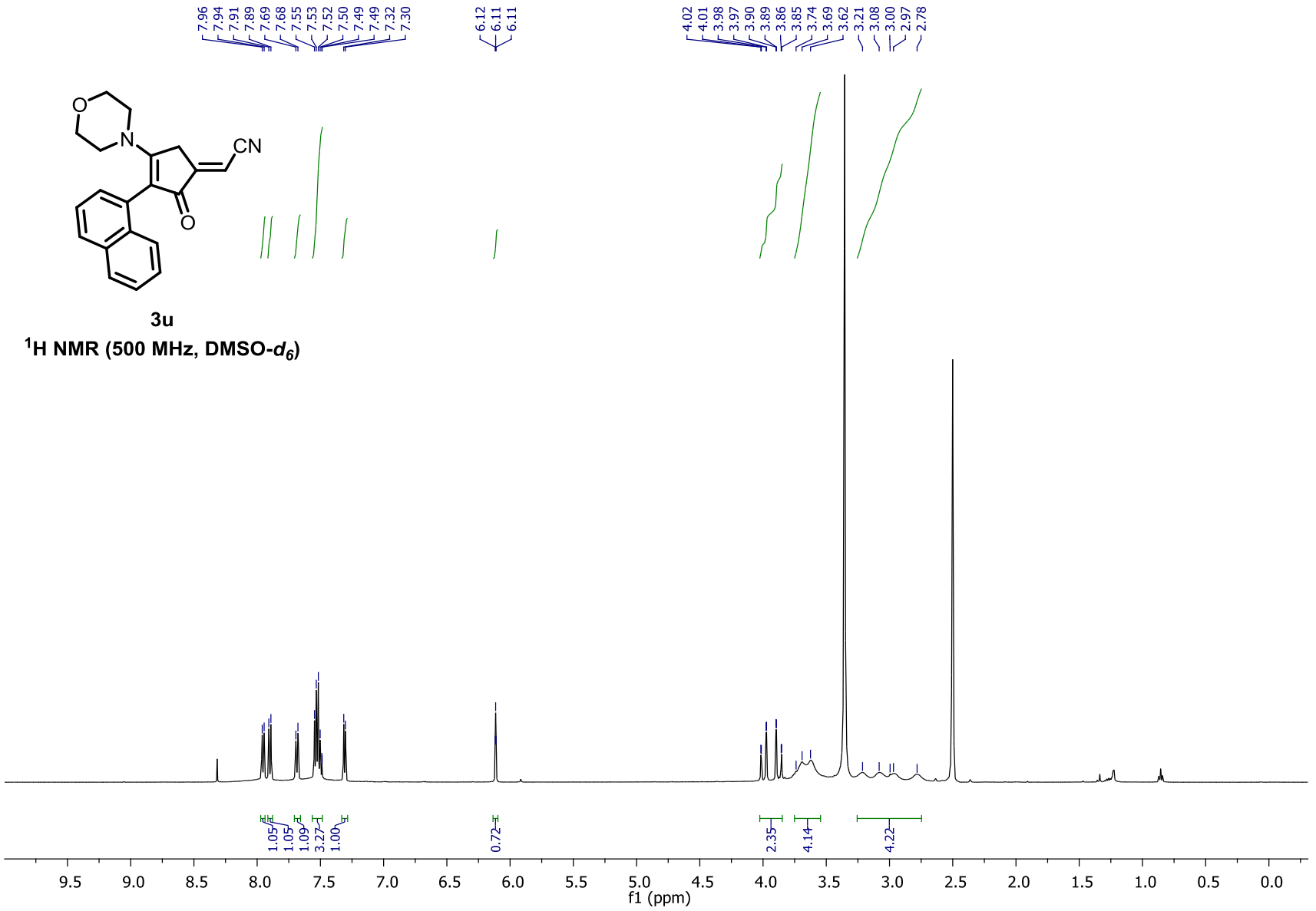

186.10
165.30
154.46
138.06
133.14
129.51
127.52
118.64
116.94
94.34
66.49
49.48
33.15
21.38
O
N
CN
O
3s
^{13}C NMR (100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3t

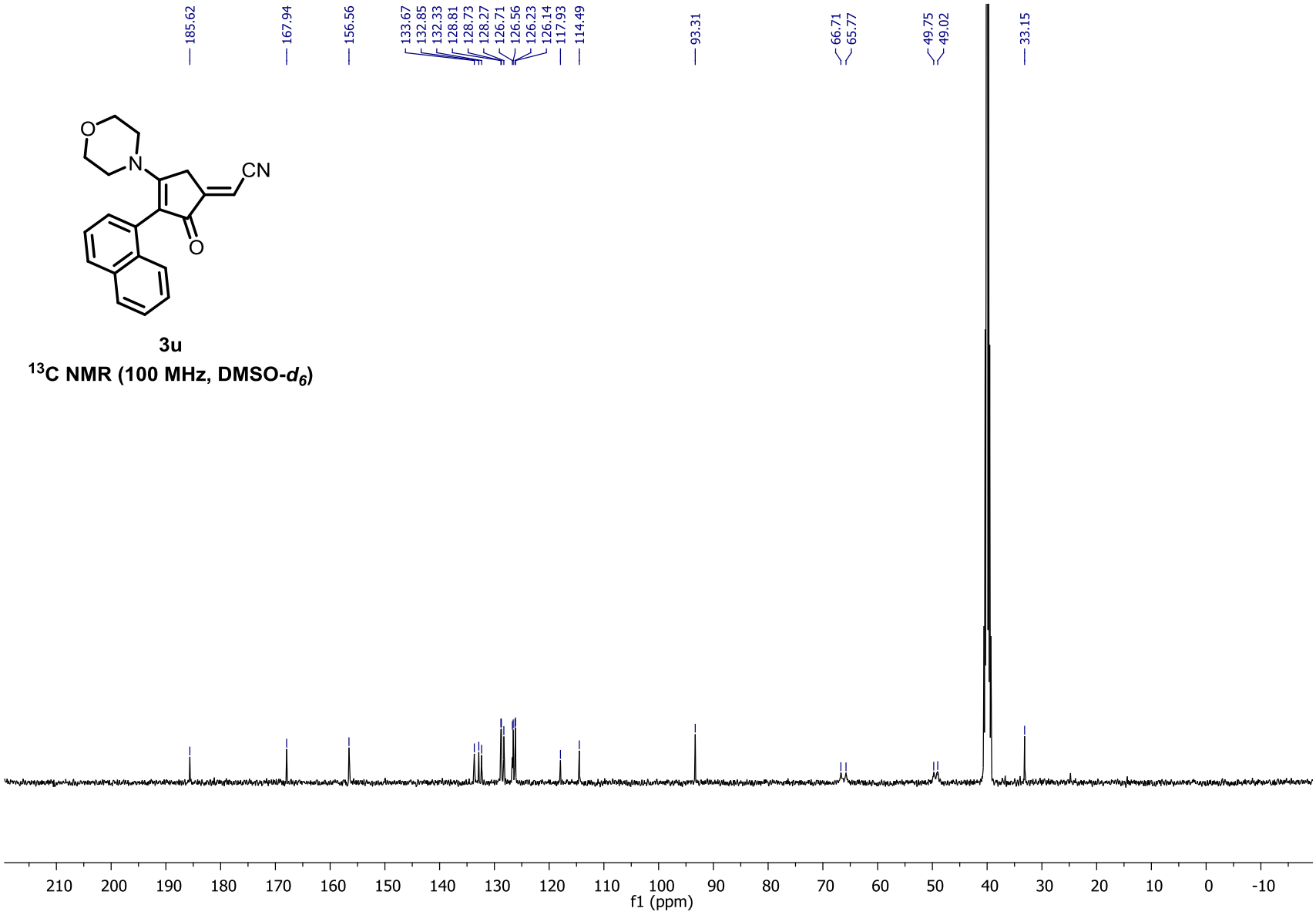
^{1}H NMR (400 MHz, $CDCl_3$)


185.83
165.61
153.98
133.61
131.83
131.16
128.83
128.65
116.74
94.86
66.43
49.62
33.23
O
N
CN
O
Cl
3t
C13 NMR (125 MHz, CDCl3)
133.61
131.83
131.16
128.83
128.65
133
132
131
130
129
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



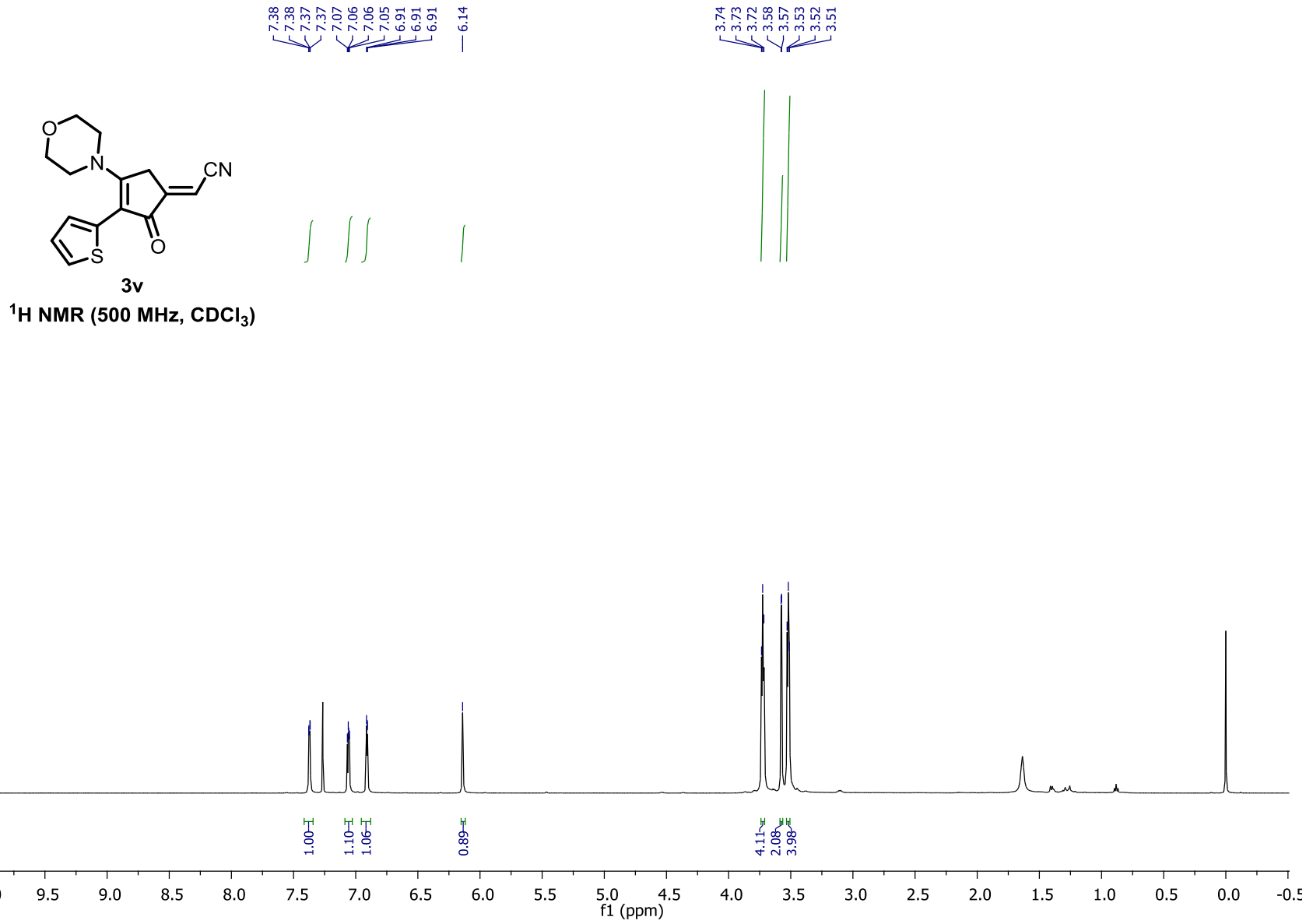
3u

^{1}H NMR (500 MHz, DMSO-d_6)



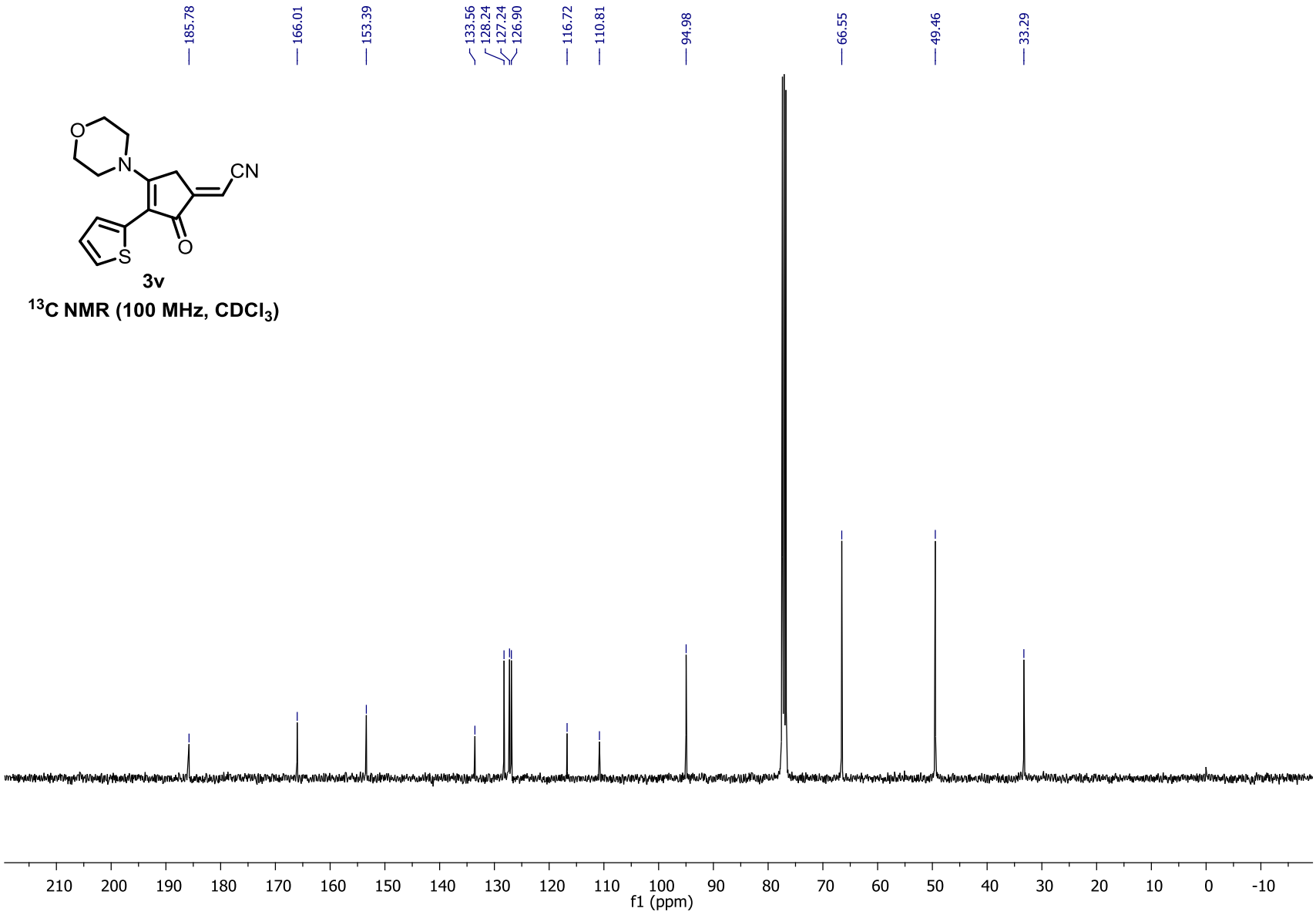
3u

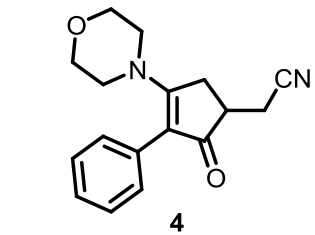
^{13}C NMR (100 MHz, DMSO-d_6)



3v

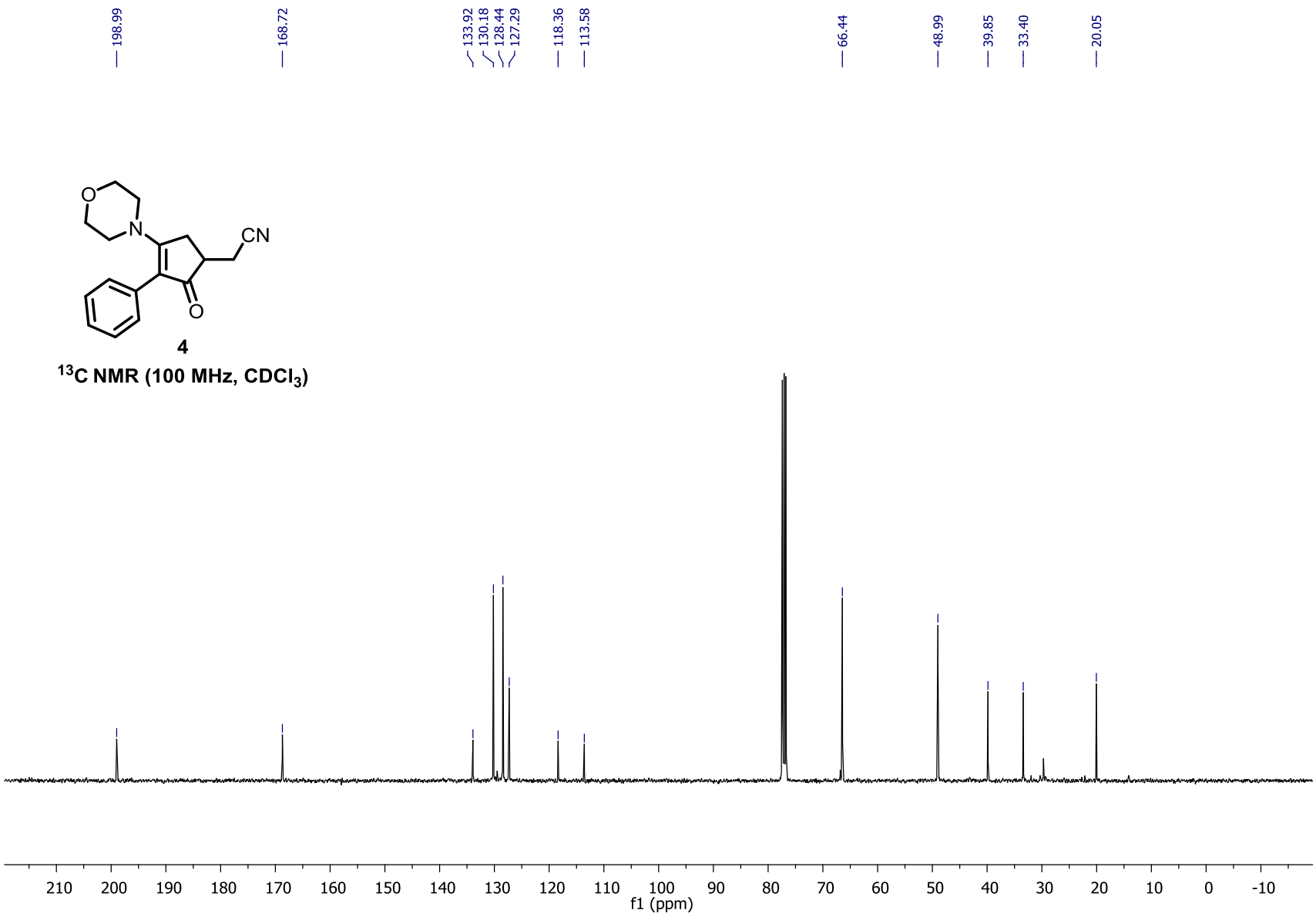
^{1}H NMR (500 MHz, $CDCl_3$)


185.78
166.01
153.39
133.56
128.24
127.24
126.90
116.72
110.81
94.98
66.55
49.46
33.29
O
N
CN
O
S
3v
^{13}C NMR (100 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



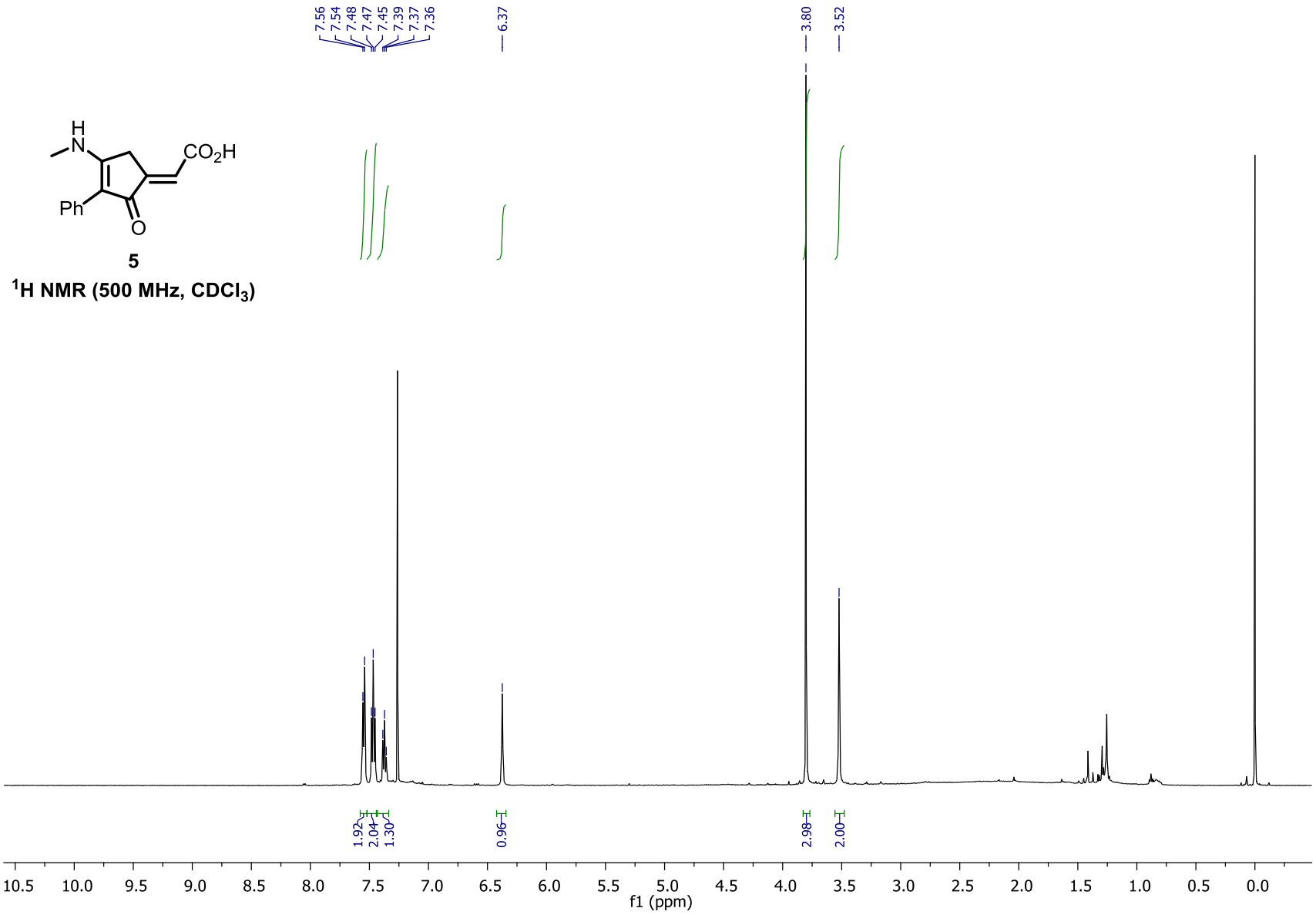
4

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



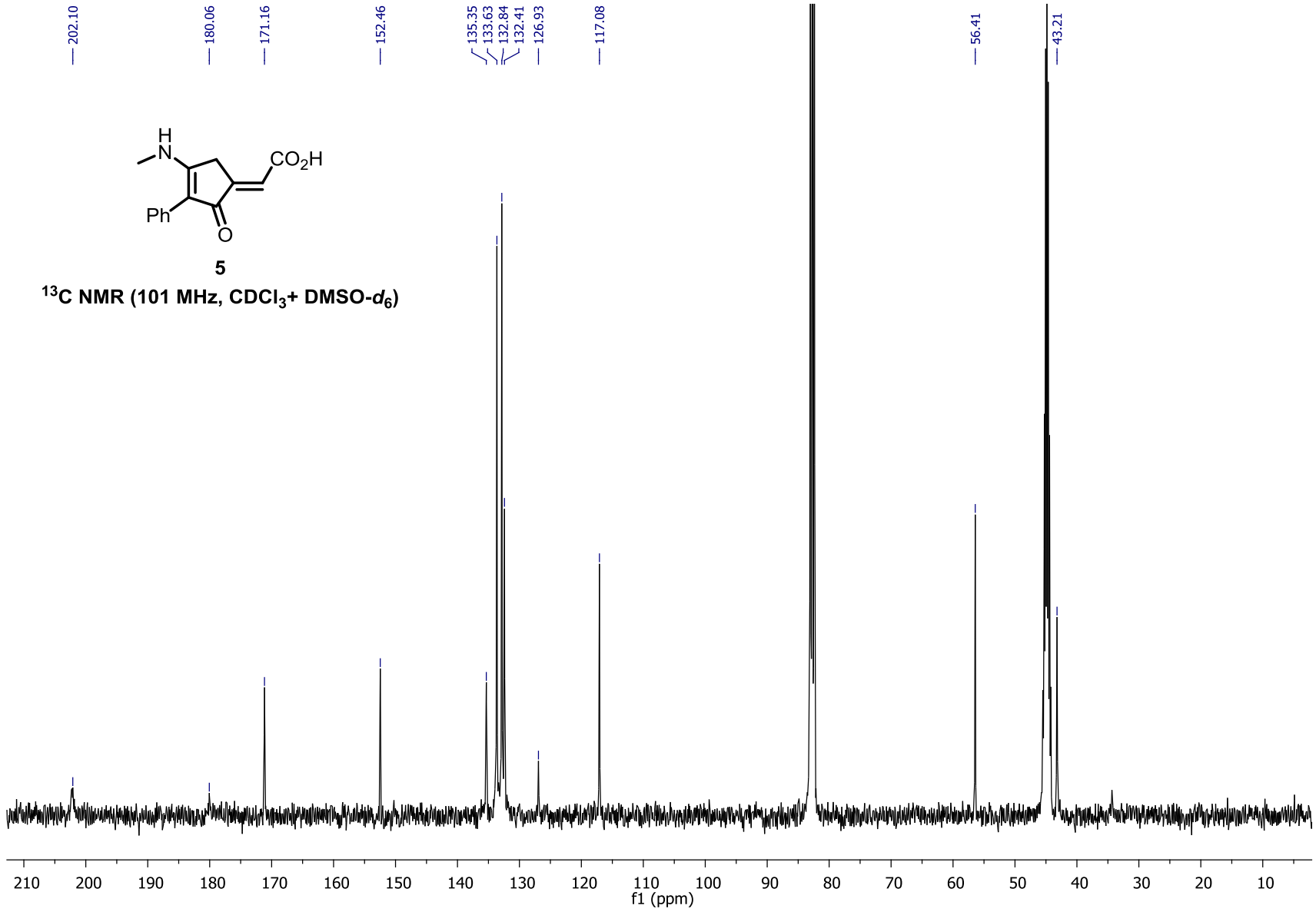
4

^{13}C NMR (100 MHz, $CDCl_3$)



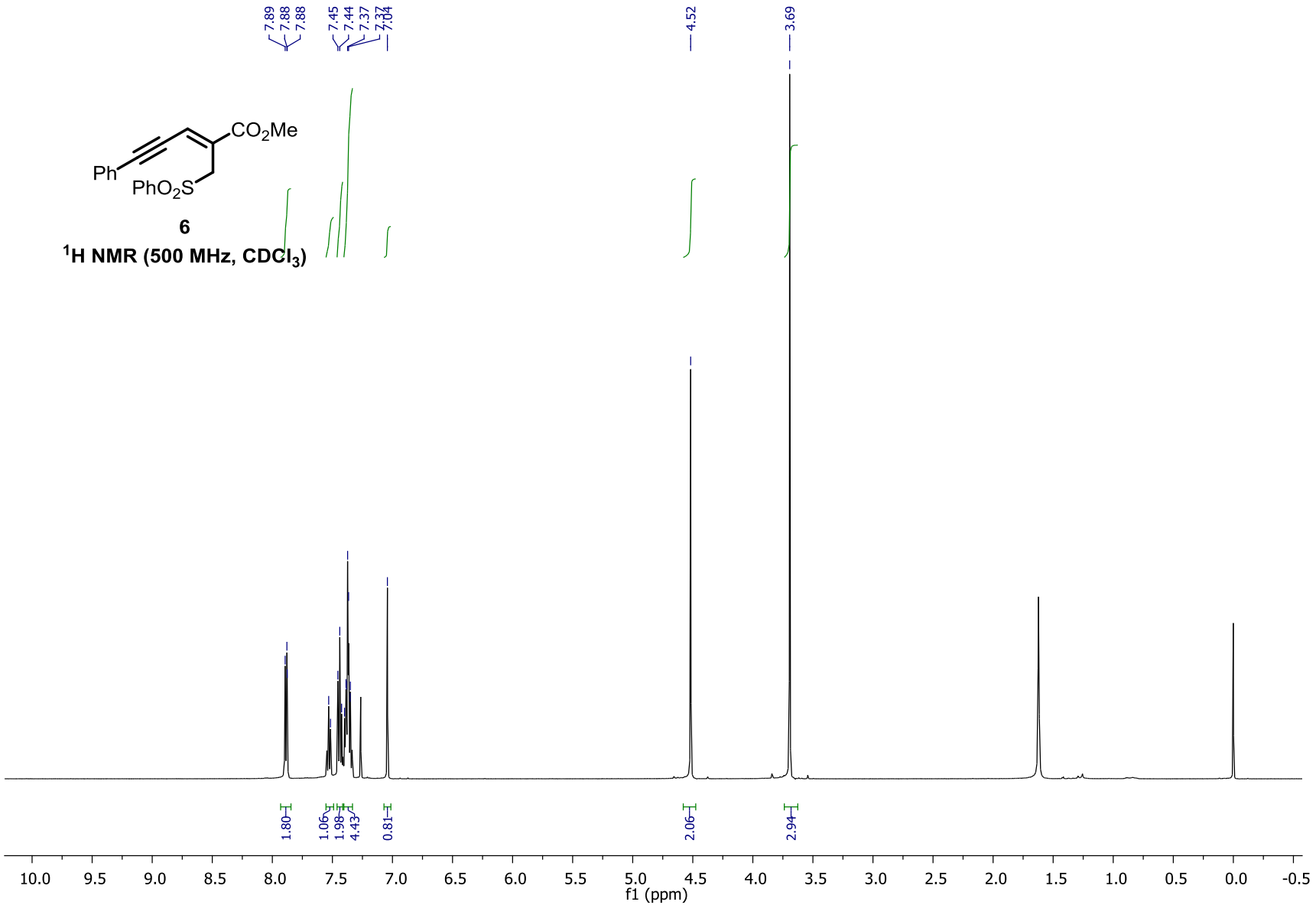
5

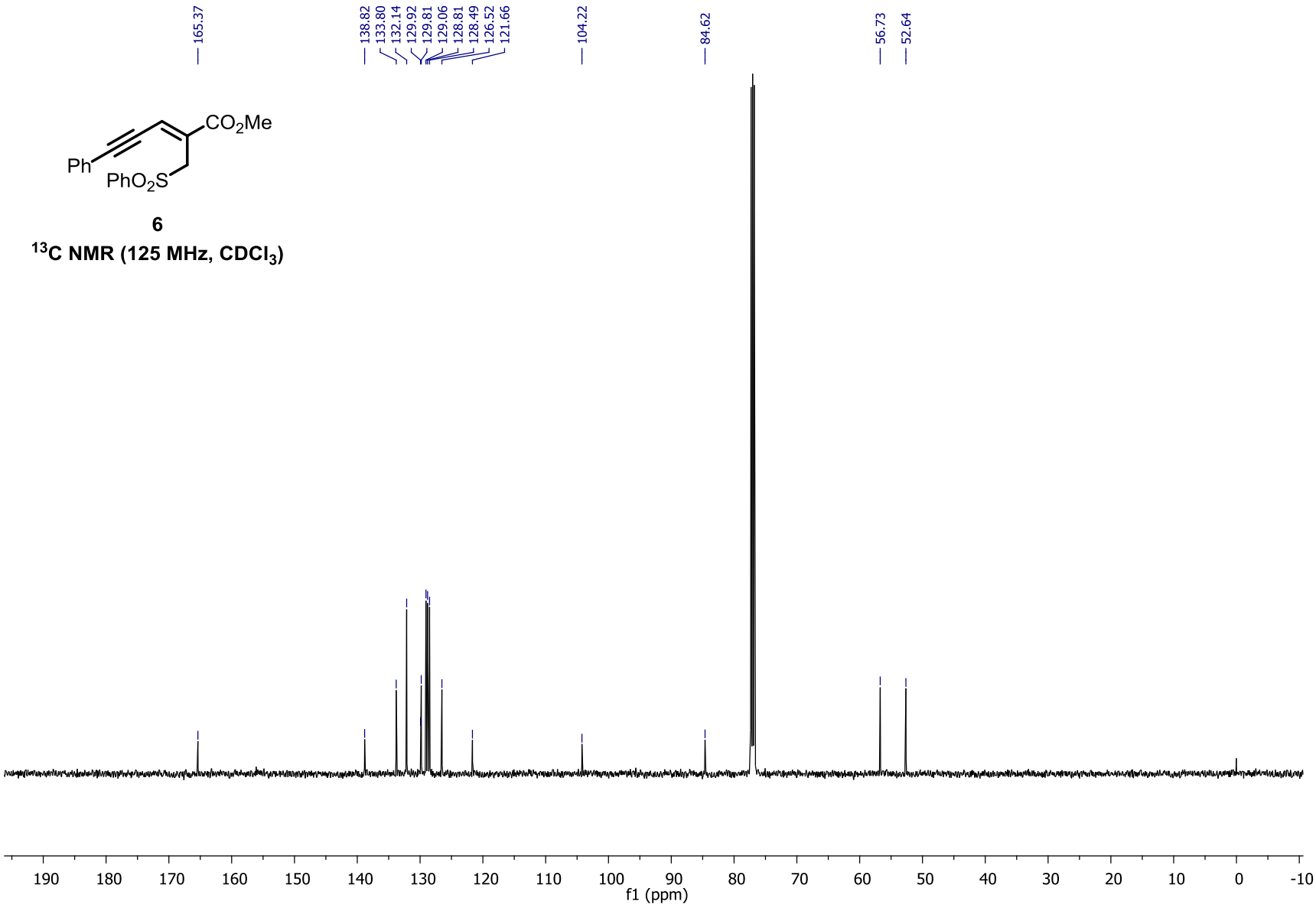
^{1}H NMR (500 MHz, $CDCl_3$)



5

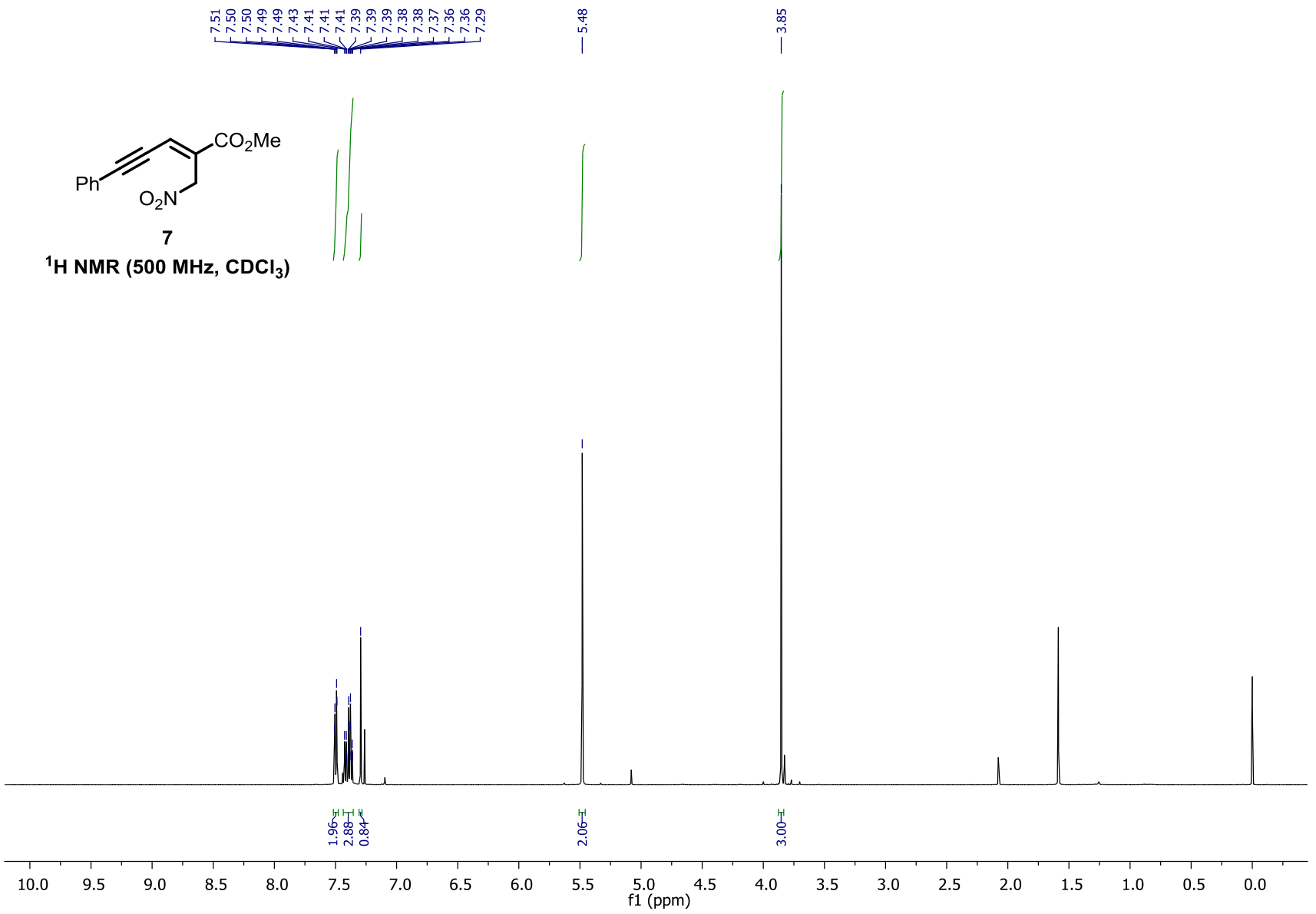
^{13}C NMR (101 MHz, $CDCl_3$+ DMSO-d_6)


7.89
7.88
7.88
7.45
7.44
7.37
7.04
4.52
3.69
CO2Me
Ph
PhO2S
6
1H NMR (500 MHz, CDCl3)
1.80
1.06
1.98
4.43
0.81
2.06
2.94
10.0
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
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)



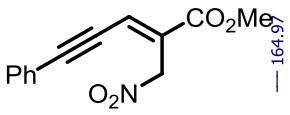
6

^{13}C NMR (125 MHz, $CDCl_3$)



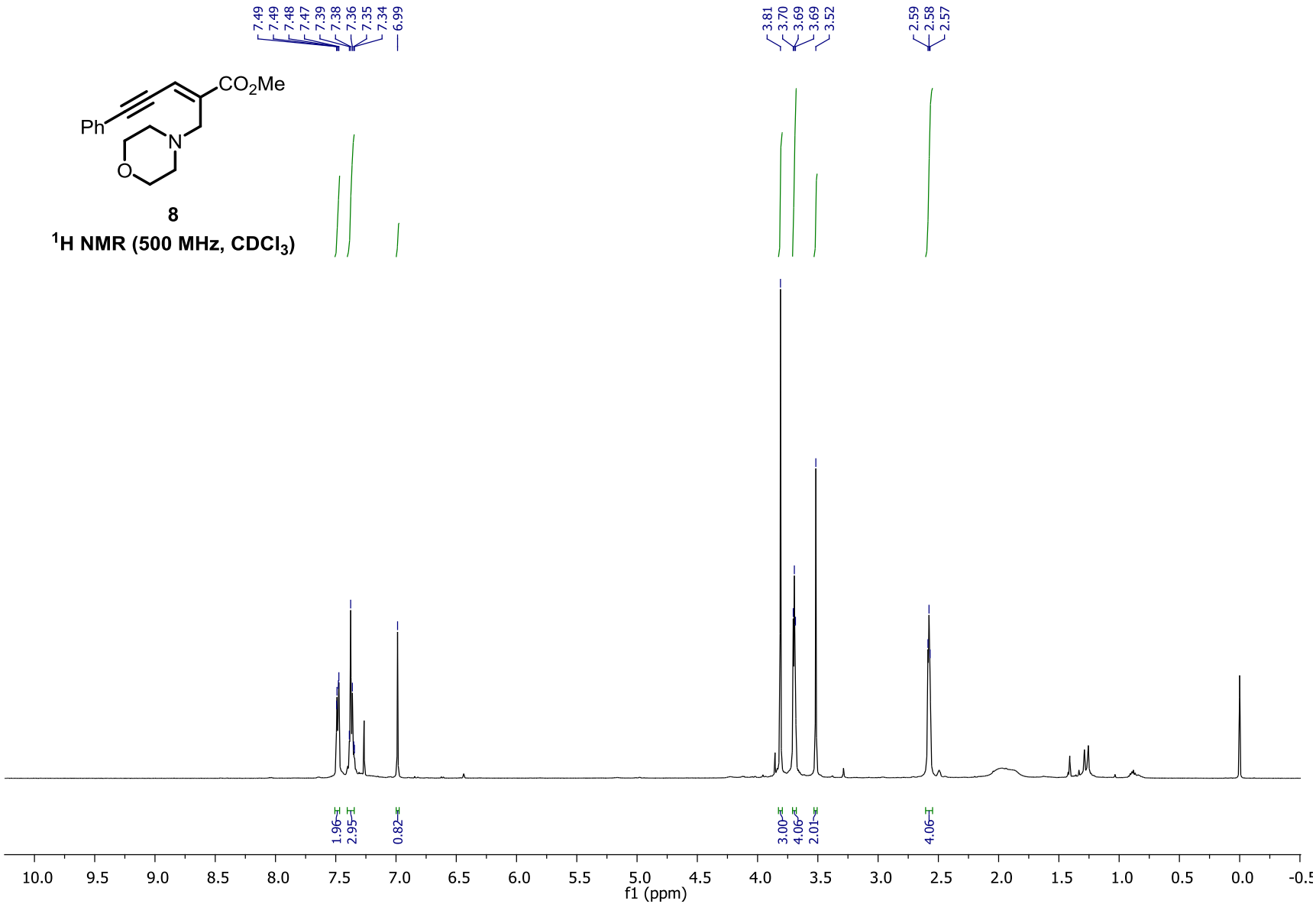
7

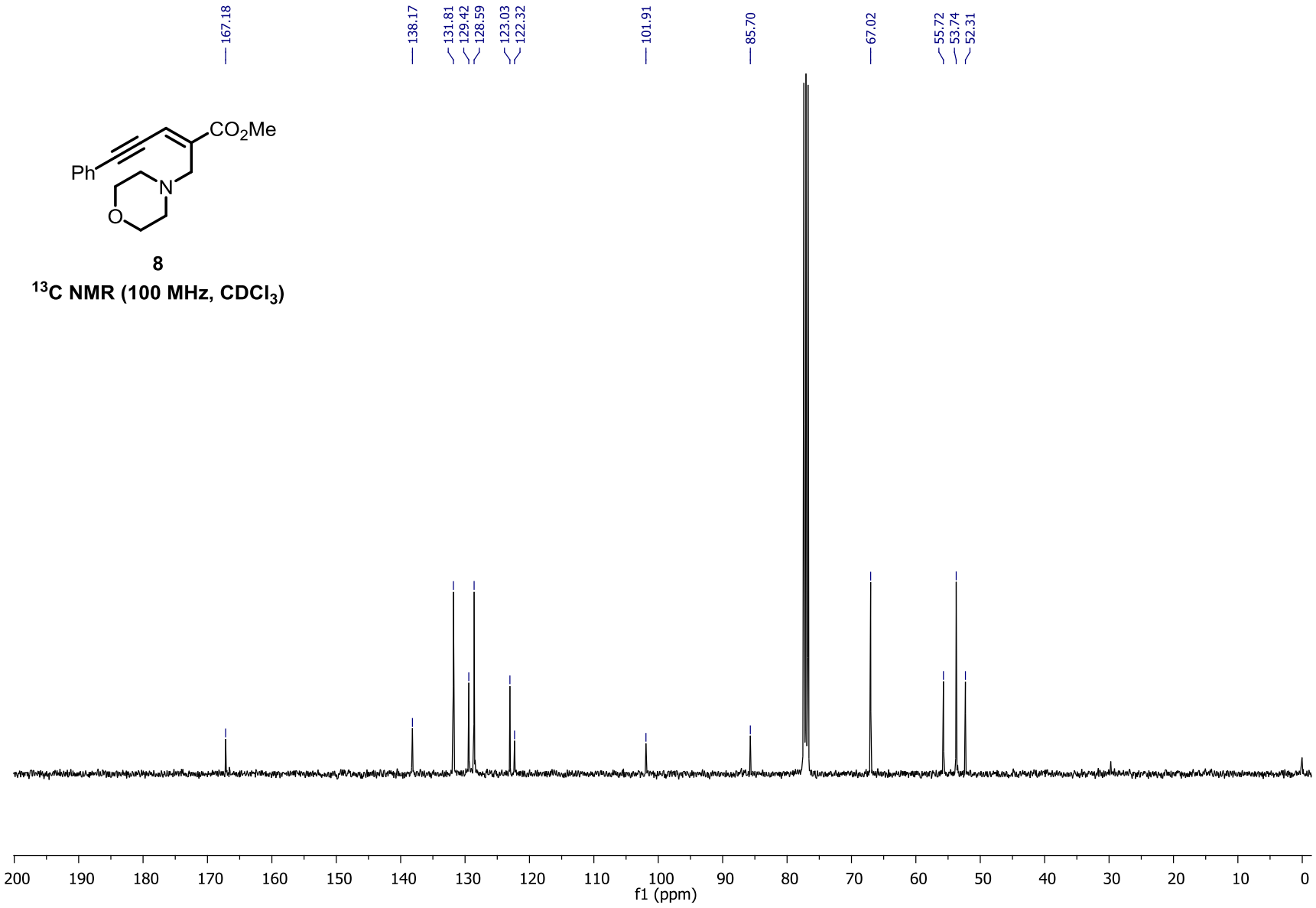
^{1}H NMR (500 MHz, $CDCl_3$)



7

^{13}C NMR (100 MHz, $CDCl_3$)


7.49
7.49
7.48
7.47
7.39
7.38
7.36
7.35
7.34
6.99
3.81
3.70
3.69
3.69
3.52
2.59
2.58
2.57
CO2Me
Ph
N
O
8
1H NMR (500 MHz, CDCl3)
1.96
2.95
0.82
3.00
4.06
2.01
4.06
10.0
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
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



8

^{13}C NMR (100 MHz, $CDCl_3$)