SUPPORTING INFORMATION

Ferrocene catalyzed carbohydroxylation of alkenes using H_2O and cycloketone oxime esters

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1. General Information

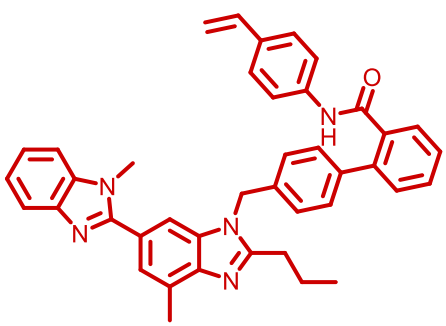
Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using 100-200 mesh silica gel. ^{1}H NMR spectra were recorded on 400 or 500 MHz spectrometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 101 or 126 MHz with complete proton decoupling spectrometers. ^{19}F NMR spectra were recorded on 376 MHz spectrometer. The high resolution mass spectra (HRMS) were measured by using ESI-TOF techniques. Melting points of solids were recorded using Electrothermal (IA9100) melting point apparatus. UV-vis studies were performed on a SHIMADZU UV-Spectrophotometer (UV-1800).

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Alkenes 1a-1k are commercially available. Alkenes 1l-1r,[1] oxime esters 1a-1m[2] were synthesized from the known procedures available in the literature.

2. Analytical data of the newly synthesized alkene 1r:

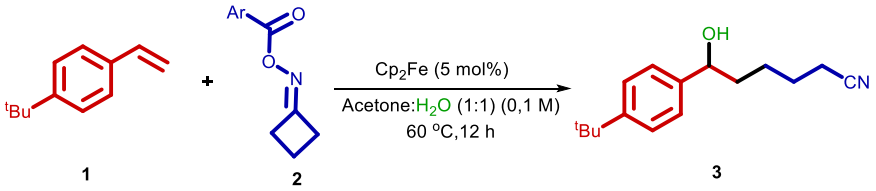
4'-((1,7'-Dimethyl-2'-propyl-1H,3'H-[2,5'-bibenzo[d]imidazol]-3'-yl)methyl)-N-(4-vinylphenyl)-[1,1'-biphenyl]-2-carboxamide (1r)



3ra

White solid (67% yield); Mp = 142 – 144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 2H), 7.53 – 7.47 (m, 2H), 7.46 – 7.38 (m, 4H), 7.38 – 7.33 (m, 2H), 7.33 – 7.26 (m, 2H), 7.20 – 7.05 (m, 7H), 6.53 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.59 (d, *J* = 17.6 Hz, 1H), 5.40 (s, 2H), 5.14 (d, *J* = 11.0 Hz, 1H), 3.78 (s, 3H), 2.85 (t, *J* = 7.8 Hz, 2H), 2.76 (s, 3H), 1.84 – 1.80 (m, 2H), 1.00 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 156.4, 154.6, 143.2, 142.8, 139.7, 138.7, 137.2, 136.6, 136.0, 135.6, 135.6, 135.1, 133.9, 130.7, 130.3, 129.5, 129.4, 129.1, 128.0, 126.7, 124.0, 123.9, 122.6, 122.4, 119.7, 119.5, 113.2, 109.6, 108.8, 46.9, 31.8, 29.8, 21.8, 16.9, 14.1; HRMS (ESI) calcd for $C_{41}H_{38}N_5O^+$ $[M+H]^+$ = 616.3071, found = 616.3066.

3. General experimental procedure for the ferrocene catalysed direct carbohydroxylation of aryl alkenes



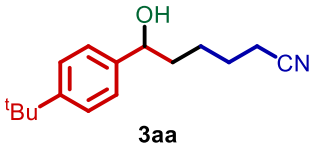
1 2 3

Ar = 4-$CF_3C_6H_4$

An oven dried 5.0 mL vial equipped with a magnetic stir bar was charged with alkene **1** (0.3 mmol, 1.0 equiv.), oxime ester **2** (0.45 mmol, 1.5 equiv.), Cp_2Fe (0.015 mmol, 5 mol%) followed by 1:1 ratio of acetone/water (3.0 mL). The mixture was stirred at 60 °C for 12 h. After completion of reaction, the resulting mixture was cooled to room temperature and concentrated under reduced pressure to remove acetone completely. Then the residue was diluted with ethyl acetate (15 mL), and washed successively with 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 compounds **3**.

4. Characterization data of the distal hydroxyl-nitriles 3:

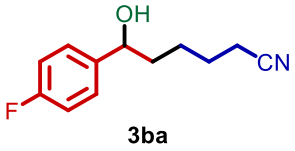
6-(4-(tert-Butyl)phenyl)-6-hydroxyhexanenitrile (3aa)



3aa

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (70.7 mg, 96% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 2H), 7.28 – 7.23 (m, 2H), 4.63 (dd, *J* = 7.5, 5.5 Hz, 1H), 2.31 (t, *J* = 7.1 Hz, 2H), 2.04 (brs, 1H), 1.87 – 1.75 (m, 1H), 1.75 – 1.62 (m, 3H), 1.62 – 1.52 (m, 1H), 1.52 – 1.38 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 141.5, 125.6, 125.6, 119.8, 74.1, 38.1, 34.6, 31.5, 25.5, 25.2, 17.2; HRMS(ESI) calcd for $C_{16}H_{23}NNaO^+$ $[M+Na]^+$ = 268.1672, found = 268.1671.

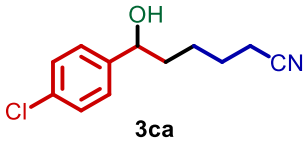
6-(4-Fluorophenyl)-6-hydroxyhexanenitrile (3ba)



3ba

Column chromatography eluent - hexane/ethyl acetate 88:12; Pale yellow liquid (28.0 mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.08 – 7.00 (m, 2H), 4.67 (dd, *J* = 7.4, 5.6 Hz, 1H), 2.33 (t, *J* = 7.0 Hz, 2H), 1.95 (brs, 1H), 1.86 – 1.76 (m, 1H), 1.75 – 1.64 (m, 3H), 1.62 – 1.53 (m, 1H), 1.51 – 1.38 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.2 (d, *J* = 246.0 Hz), 140.3 (d, *J* = 2.1 Hz), 127.6 (d, *J* = 8.1 Hz), 119.7, 115.5 (d, *J* = 21.5 Hz), 73.7, 38.3, 25.4, 25.1, 17.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.76; HRMS(ESI) calcd for $C_{12}H_{13}FN^+$ $[M+H-H_2O]^+$ = 190.1026, found = 190.1026.

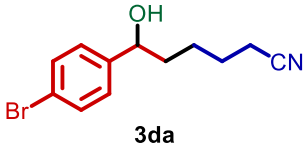
6-(4-Chlorophenyl)-6-hydroxyhexanenitrile (3ca)



3ca

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (60.4 mg, 90% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.30 (m, 2H), 7.28 – 7.25 (m, 2H), 4.67 (dd, *J* = 7.5, 5.5 Hz, 1H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.02 (brs, 1H), 1.84 – 1.74 (m, 1H), 1.73 – 1.64 (m, 3H), 1.63 – 1.53 (m, 1H), 1.49 – 1.39 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 133.5, 128.8, 127.3, 119.7, 73.6, 38.3, 25.4, 25.0, 17.2; HRMS(ESI) calcd for $C_{12}H_{14}{}^{35}ClNNaO^+$ $[M+Na]^+$ = 246.0656, found = 246.0656; calcd for $C_{12}H_{14}{}^{37}ClNNaO^+$ $[M+Na]^+$ = 248.0627, found = 248.0627.

6-(4-Bromophenyl)-6-hydroxyhexanenitrile (3da)

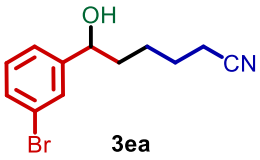


3da

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (51.5 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 2H), 7.18 – 7.11 (m, 2H), 4.59 (t, *J* = 5.9 Hz, 1H), 2.26 (t, *J* = 6.7 Hz, 2H), 1.82 (brs, 1H), 1.77 – 1.68 (m, 1H), 1.67 – 1.56 (m, 3H), 1.55 – 1.45 (m, 1H), 1.45 – 1.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 131.7, 127.6, 121.5, 119.7,

73.6, 38.2, 25.4, 25.0, 17.3; HRMS(ESI) calcd for $C_{12}H_{13}{}^{79}BrN^+$ $[M+H-H_2O]^+$ = 250.0226, found = 250.0225; calcd for $C_{12}H_{13}{}^{81}BrN^+$ $[M+H-H_2O]^+$ = 252.0205, found = 252.0205.

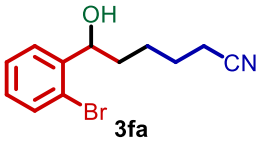
6-(3-Bromophenyl)-6-hydroxyhexanenitrile (3ea)



3ea

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (32.2 mg, 40% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (t, *J* = 1.6, 1H), 7.34 (dt, *J* = 7.2, 1.7 Hz, 1H), 7.20 – 7.13 (m, 2H), 4.60 (dd, *J* = 7.4, 5.3 Hz, 1H), 2.27 (t, *J* = 7.0 Hz, 2H), 1.79 – 1.69 (m, 2H), 1.68 – 1.58 (m, 3H), 1.57 – 1.47 (m, 1H), 1.46 – 1.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 130.9, 130.3, 129.0, 124.6, 122.8, 119.7, 73.7, 38.3, 25.4, 25.0, 17.3; HRMS(ESI) calcd for $C_{12}H_{13}{}^{79}BrN^+$ $[M+H-H_2O]^+$ = 250.0226, found = 250.0226; calcd for $C_{12}H_{13}{}^{81}BrN^+$ $[M+H-H_2O]^+$ = 252.0205, found = 252.0205.

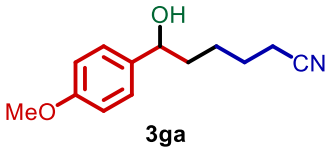
6-(2-Bromophenyl)-6-hydroxyhexanenitrile (3fa)



3fa

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (28.2 mg, 35% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (ddd, *J* = 14.1, 7.8, 1.1 Hz, 2H), 7.28 (t, *J* = 7.1 Hz, 1H), 7.07 (td, *J* = 7.9, 1.4 Hz, 1H), 5.01 (dd, *J* = 7.7, 3.8 Hz, 1H), 2.29 (t, *J* = 6.9 Hz, 2H), 1.96 (brs, 1H), 1.74 – 1.52 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 132.8, 129.1, 128.0, 127.3, 121.9, 119.8, 72.6, 36.7, 25.4, 25.1, 17.3; HRMS(ESI) calcd for $C_{12}H_{18}{}^{79}BrN_2O^+$ $[M+NH_4]^+$ = 285.0597, found = 285.0597; calcd for $C_{12}H_{18}{}^{81}BrN_2O^+$ $[M+NH_4]^+$ = 287.0577, found = 287.0576.

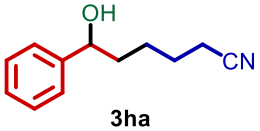
6-Hydroxy-6-(4-methoxyphenyl)hexanenitrile (3ga)



3ga

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (44.7 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.19 (m, 2H), 6.96 – 6.83 (m, 2H), 4.62 (dd, *J* = 7.2, 6.0 Hz, 1H), 3.80 (s, 3H), 2.32 (t, *J* = 7.1 Hz, 2H), 2.02 (brs, 1H), 1.89 – 1.76 (m, 1H), 1.75 – 1.63 (m, 3H), 1.61 – 1.51 (m, 1H), 1.50 – 1.35 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 136.6, 127.2, 119.8, 114.1, 74.0, 55.4, 38.1, 25.5, 25.2, 17.2; HRMS(ESI) calcd for $C_{13}H_{17}NNaO_2^+$ $[M+Na]^+$ = 242.1151, found = 242.1148.

6-Hydroxy-6-phenylhexanenitrile (3ha)

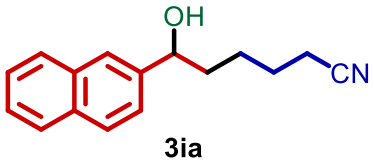


3ha

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (49.4 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33

– 7.18 (m, 5H), 4.61 (dd, J = 7.3, 5.7 Hz, 1H), 2.25 (t, J = 7.0 Hz, 2H), 1.82 – 1.69 (m, 2H), 1.68 – 1.58 (m, 3H), 1.56 – 1.46 (m, 1H), 1.45 – 1.32 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 128.7, 127.9, 125.9, 119.8, 74.3, 38.2, 25.5, 25.1, 17.2; HRMS(ESI) calcd for $C_{12}H_{15}NNaO^+$ $[M+Na]^+$ = 212.1046, found = 212.1045.

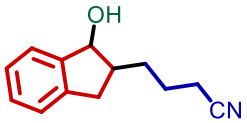
6-Hydroxy-6-(naphthalen-2-yl)hexanenitrile (3ia)



3ia

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (50.3 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.71 (m, 3H), 7.68 (s, 1H), 7.46 – 7.34 (m, 3H), 4.76 (t, J = 6.4 Hz, 1H), 2.22 (t, J = 7.0 Hz, 2H), 1.91 (brs, 1H), 1.87 – 1.67 (m, 2H), 1.65 – 1.46 (m, 3H), 1.45 – 1.32 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9, 133.4, 133.2, 128.6, 128.0, 127.8, 126.4, 126.1, 124.7, 124.0, 119.8, 74.4, 38.1, 25.5, 25.2, 17.2; HRMS(ESI) calcd for $C_{16}H_{17}NNaO^+$ $[M+Na]^+$ = 262.1202, found = 262.1202.

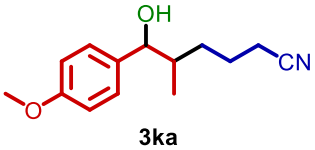
4-(1-Hydroxy-2,3-dihydro-1H-inden-2-yl)butanenitrile (3ja) (1.1:1 diastereomers)



3ja

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (16.3 mg, 27% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 1H), 7.29 – 7.18 (m, 3H), 5.01 (d, J = 5.6 Hz, 0.5H), 4.83 (d, J = 7.0 Hz, 0.5H), 3.12 (dd, J = 15.7, 8.0 Hz, 0.5H), 2.95 (dd, J = 15.7, 7.6 Hz, 0.5H), 2.76 (dd, J = 15.7, 9.0 Hz, 0.5H), 2.50 (dd, J = 15.6, 8.9 Hz, 0.5H), 2.45 – 2.39 (m, 2H), 2.38 – 2.30 (m, 0.5H), 2.23 – 2.13 (m, 0.5H), 1.99 – 1.76 (m, 4H), 1.75 – 1.64 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 144.8, 143.3, 141.3, 129.0, 128.4, 127.0, 125.2, 124.9, 124.9, 123.9, 119.9, 119.8, 81.6, 76.3, 50.2, 44.6, 36.2, 36.1, 32.7, 28.4, 24.4, 24.3, 17.7, 17.5; HRMS(ESI) calcd for $C_{13}H_{15}NNaO^+$ $[M+Na]^+$ = 224.1046, found = 224.1045.

6-Hydroxy-6-(4-methoxyphenyl)-5-methylhexanenitrile (3ka) (1:1 diastereomers)

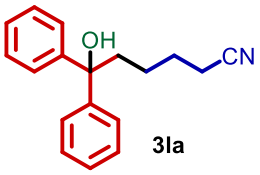


3ka

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (31.5 mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 2H), 6.84 – 6.76 (m, 2H), 4.38 (d, J = 6.1 Hz, 0.5H), 4.27 (d, J = 7.2 Hz, 0.5H), 3.73 (s, 3H), 2.29 – 2.13 (m, 2H), 1.85 (brs, 1H), 1.77 – 1.58 (m, 3H), 1.56 – 1.34 (m, 1H), 1.27 – 1.07 (m, 1H), 0.88 (d, J = 6.7 Hz, 1.5H), 0.67 (d, J = 6.7 Hz, 1.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.21, 159.1, 135.6, 135.4, 127.8, 127.6, 120.0, 119.8,

113.8, 78.5, 77.8, 55.4, 39.8, 39.8, 32.3, 31.9, 23.4, 23.4, 17.6, 17.5, 15.9, 14.9; HRMS(ESI) calcd for $C_{14}H_{19}NNaO_2^+$ $[M+Na]^+$ = 256.1308, found = 256.1306.

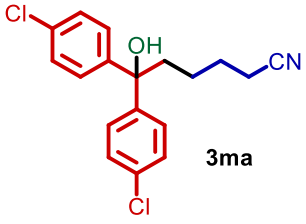
6-Hydroxy-6,6-diphenylhexanenitrile (3la)



3la

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (50.2 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 4H), 7.35 – 7.27 (m, 4H), 7.27 – 7.19 (m, 2H), 2.35 – 2.22 (m, 4H), 2.14 (brs, 1H), 1.67 (p, *J* = 7.7 Hz, 2H), 1.49 – 1.38 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 128.4, 127.1, 126.1, 119.8, 78.1, 41.2, 25.9, 23.4, 17.3; HRMS(ESI) calcd for $C_{18}H_{19}NNaO^+$ $[M+Na]^+$ = 288.1359, found = 288.1359.

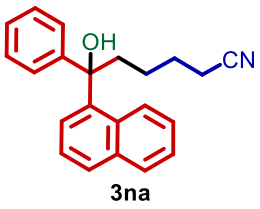
6,6-Bis(4-chlorophenyl)-6-hydroxyhexanenitrile (3ma)



3ma

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (64.2 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 8H), 2.30 (t, *J* = 7.1 Hz, 2H), 2.27 – 2.22 (m, 2H), 2.13 (brs, 1H), 1.67 (p, *J* = 7.8 Hz, 2H), 1.47 – 1.36 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 133.3, 128.6, 127.5, 119.7, 77.5, 41.1, 25.8, 23.2, 17.3; HRMS(ESI) calcd for $C_{18}H_{17}Cl_2NNaO^+$ $[M+Na]^+$ = 356.0579, found = 356.0578.

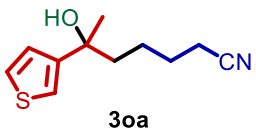
6-Hydroxy-6-(naphthalen-1-yl)-6-phenylhexanenitrile (3na)



3na

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (85.2 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.2 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.80 – 7.71 (m, 2H), 7.50 – 7.44 (m, 2H), 7.44 – 7.39 (m, 2H), 7.35 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.26 – 7.20 (m, 1H), 2.39 (t, *J* = 8.1 Hz, 2H), 2.28 – 2.21 (m, 3H), 1.72 – 1.62 (p, *J* = 7.4 Hz, 2H), 1.54 – 1.35 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 144.0, 133.1, 132.5, 128.4, 128.4, 128.2, 127.6, 127.3, 126.3, 126.2, 126.2, 124.9, 124.2, 119.8, 78.2, 41.0, 26.0, 23.4, 17.2; HRMS(ESI) calcd for $C_{22}H_{21}NNaO^+$ $[M+Na]^+$ = 338.1515, found = 338.1515.

6-Hydroxy-6-(thiophen-3-yl)heptanenitrile (3oa)

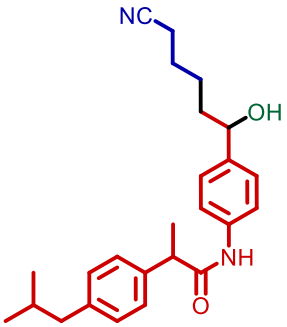


3oa

Column chromatography eluent - hexane/ethyl acetate 85:15; Pale yellow liquid (47.7 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.15 (dd, *J* = 3.0, 1.4 Hz, 1H), 7.03 (dd, *J* =

5.0, 1.3 Hz, 1H), 2.29 (t, *J* = 7.2 Hz, 2H), 1.90 (brs, 1H), 1.83 – 1.76 (m, 2H), 1.66 – 1.58 (m, 2H), 1.57 (s, 3H), 1.50 – 1.31 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 126.2, 125.6, 119.8, 119.6, 73.5, 43.1, 29.9, 25.7, 23.6, 17.2; HRMS(ESI) calcd for $C_{11}H_{15}NNaOS^+$ $[M+Na]^+$ = 232.0766, found = 232.0766.

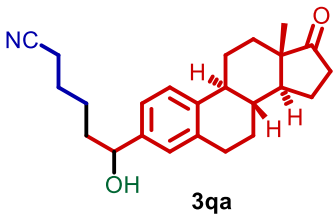
N-(4-(5-Cyano-1-hydroxypentyl)phenyl)-2-(4-isobutylphenyl)propenamide (3pa)



3pa

Column chromatography eluent - hexane/ethyl acetate 50:50; Pale yellow liquid (71.8 mg, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.21 – 7.13 (m, 4H), 7.10 – 7.05 (m, 3H), 4.53 (t, *J* = 6.2 Hz, 1H), 3.61 (q, *J* = 6.8 Hz, 1H), 2.40 (d, *J* = 7.1 Hz, 2H), 2.22 (t, *J* = 7.0 Hz, 2H), 1.94 (brs, 1H), 1.80 (h, *J* = 6.7 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.63 – 1.54 (m, 3H), 1.54 – 1.39 (m, 4H), 1.37 – 1.25 (m, 1H), 0.83 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 141.2, 140.4, 138.1, 137.5, 130.0, 127.5, 126.5, 120.0, 119.8, 73.8, 47.8, 45.1, 38.1, 30.3, 25.4, 25.1, 22.5, 18.6, 17.2; HRMS(ESI) calcd for $C_{25}H_{33}N_2O_2^+$ $[M+H]^+$ = 393.2536, found = 393.2538.

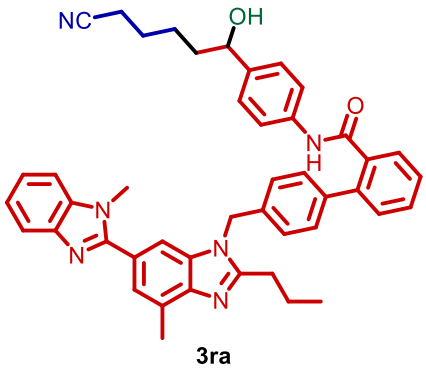
6-Hydroxy-6-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)hexanenitrile (3qa) (1:1 diastereomers)



3qa

Column chromatography eluent - hexane/ethyl acetate 80:20; Pale yellow liquid (85.5 mg, 78% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.16 (m, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 7.00 (s, 1H), 4.55 (t, *J* = 6.0 Hz, 1H), 2.85 (d, *J* = 4.7 Hz, 2H), 2.50 – 2.30 (m, 2H), 2.30 – 2.15 (m, 3H), 2.14 – 1.84 (m, 5H), 1.80 – 1.69 (m, 1H), 1.68 – 1.60 (m, 3H), 1.59 – 1.49 (m, 3H), 1.49 – 1.31 (m, 5H), 0.84 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 220.8, 142.1, 139.4, 136.8, 126.5, 126.5, 125.6, 123.3, 119.7, 74.1, 74.0, 50.6, 48.1, 44.5, 38.3, 38.1, 35.9, 31.7, 29.6, 26.6, 25.8, 25.5, 25.2, 21.7, 17.2, 13.9; HRMS(ESI) calcd for $C_{24}H_{31}NNaO_2^+$ $[M+Na]^+$ = 388.2247, found = 388.2246.

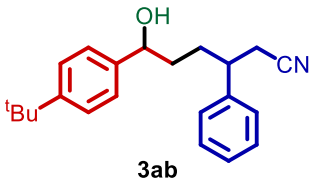
N-(4-(5-Cyano-1-hydroxypentyl)phenyl)-4'-((1,7'-dimethyl-2'-propyl-1H,3'H-[2,5'-bibenzo[d]imidazol]-3'-yl)methyl)-[1,1'-biphenyl]-2-carboxamide (3ra)



3ra

Column chromatography eluent - hexane/ethyl acetate 30:70; Pale yellow liquid (46.3 mg, 22% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.85 (d, *J* = 7.3 Hz, 1H), 7.66 (d, *J* = 7.5 Hz, 1H), 7.43 – 7.29 (m, 9H), 7.19 – 7.14 (m, 2H), 6.95 (s, 1H), 6.92 – 6.84 (m, 4H), 5.39 (s, 2H), 4.45 (dd, *J* = 7.4, 5.0 Hz, 1H), 3.89 (s, 3H), 2.74 – 2.65 (m, 5H), 2.23 (t, *J* = 7.0 Hz, 2H), 1.82 – 1.73 (m, 2H), 1.64 – 1.51 (m, 4H), 1.37 – 1.26 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 157.3, 141.3, 140.2, 138.9, 136.7, 136.0, 135.3, 135.1, 130.8, 130.1, 129.9, 129.6, 129.2, 128.2, 127.5, 126.5, 124.3, 123.9, 119.9, 119.8, 110.4, 110.0, 73.5, 47.4, 38.1, 32.6, 29.8, 29.6, 25.5, 25.2, 21.7, 17.3, 17.1, 14.2; HRMS(ESI) calcd for $C_{45}H_{45}N_6O_2^+$ $[M+H]^+$ = 701.3598, found = 701.3593.

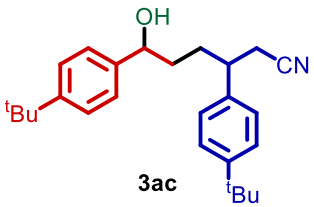
6-(4-(tert-Butyl)phenyl)-6-hydroxy-3-phenylhexanenitrile (3ab) (1.1:1 diastereomers)



3ab

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (68.5 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.29 – 7.22 (m, 1H), 7.21 – 7.12 (m, 4H), 4.62 (t, *J* = 6.3 Hz, 0.5H), 4.57 (t, *J* = 6.3 Hz, 0.5H), 3.00 – 2.85 (m, 1H), 2.57 (d, *J* = 7.2 Hz, 2H), 2.03 – 1.83 (m, 2H), 1.78 – 1.68 (m, 1H), 1.68 – 1.49 (m, 2H), 1.30 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.9, 150.8, 141.5, 141.3, 129.1, 129.0, 127.6, 127.3, 125.7, 125.6, 118.6, 74.3, 74.0, 42.4, 42.2, 36.5, 36.5, 34.7, 31.5, 31.4, 31.3, 25.5; HRMS(ESI) calcd for $C_{22}H_{27}NNaO^+$ $[M+Na]^+$ = 344.1985, found = 344.1985.

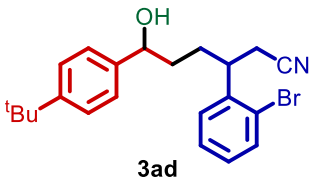
3,6-Bis(4-(tert-butyl)phenyl)-6-hydroxyhexanenitrile (3ac) (1.5:1 diastereomers)



3ac

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (90.6 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30 (m, 4H), 7.24 – 7.17 (m, 2H), 7.14 – 7.05 (m, 2H), 4.63 (t, *J* = 6.3 Hz, 0.6H), 4.58 (t, *J* = 6.3 Hz, 0.4H), 2.98 – 2.86 (m, 1H), 2.56 (d, *J* = 6.8 Hz, 2H), 2.06 – 1.87 (m, 1H), 1.87 – 1.70 (m, 2H), 1.70 – 1.58 (m, 2H), 1.31 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 150.8, 150.4, 141.5, 141.4, 138.4, 138.4, 127.0, 125.9, 125.9, 125.8, 125.6, 125.6, 125.6, 118.8, 118.8, 74.4, 74.1, 41.9, 41.7, 36.5, 36.4, 34.7, 34.6, 31.5, 31.3, 25.5; HRMS(ESI) calcd for $C_{26}H_{34}N^+$ $[M+H-H_2O]^+$ = 360.2686, found = 360.2686.

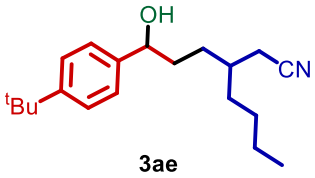
3-(2-Bromophenyl)-6-(4-(tert-butyl)phenyl)-6-hydroxyhexanenitrile (3ad) (1:1 diastereomers)



3ad

Column chromatography eluent - hexane/ethyl acetate 85:15; Pale yellow liquid (78.1 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (ddd, *J* = 8.0, 2.8, 1.2 Hz, 1H), 7.40 – 7.26 (m, 4H), 7.23 – 7.19 (m, 2H), 7.16 – 7.09 (m, 1H), 4.66 (dd, *J* = 7.3, 5.8 Hz, 0.5H), 4.61 (dd, *J* = 6.3, 5.8 Hz, 0.5H), 3.68 – 3.53 (m, 1H), 2.68 – 2.53 (m, 2H), 2.12 – 2.00 (m, 1H), 1.98 – 1.86 (m, 1H), 1.85 – 1.72 (m, 1H), 1.71 – 1.51 (m, 2H), 1.31 (s, 5H), 1.30 (s, 4H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 150.9, 141.5, 141.2, 140.1, 140.1, 133.5, 133.5, 129.0, 128.3, 128.2, 127.8, 127.7, 125.7, 125.6, 125.6, 125.6, 125.2, 118.1, 118.0, 74.2, 73.9, 40.0, 39.7, 36.2, 36.1, 34.7, 31.5, 30.0, 24.2, 24.1; HRMS(ESI) calcd for $C_{22}H_{25}{}^{79}BrN^+$ $[M+H-H_2O]^+$ = 382.1165, found = 382.1164; calcd for $C_{22}H_{25}{}^{81}BrN^+$ $[M+H-H_2O]^+$ = 384.1144, found = 384.1142.

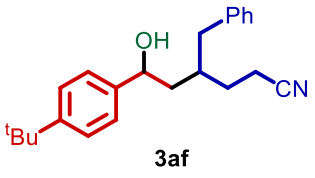
3-(3-(4-(tert-Butyl)phenyl)-3-hydroxypropyl)heptanenitrile (3ae) (1:1 diastereomers)



3ae

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (75.1 mg, 83% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 7.23 – 7.15 (m, 2H), 4.55 (dd, *J* = 7.5, 5.4 Hz, 1H), 2.29 – 2.21 (m, 2H), 1.91 (brs, 1H), 1.79 – 1.67 (m, 1H), 1.66 – 1.59 (m, 2H), 1.58 – 1.46 (m, 1H), 1.40 – 1.28 (m, 3H), 1.25 (s, 9H), 1.23 – 1.12 (m, 4H), 0.84 – 0.79 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.9, 141.6, 141.5, 125.7, 125.6, 118.9, 74.5, 74.4, 36.0, 35.9, 35.2, 34.6, 33.1, 33.1, 31.5, 30.0, 30.0, 28.8, 28.8, 22.8, 21.9, 14.1; HRMS(ESI) calcd for $C_{20}H_{31}NNaO^+$ $[M+Na]^+$ = 324.2298, found = 324.2297.

4-Benzyl-6-(4-(tert-butyl)phenyl)-6-hydroxyhexanenitrile (3af) (1.2:1 diastereomers)

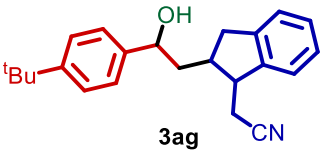


3af

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (61.4 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.33 (m, 2H), 7.32 – 7.23 (m, 3H), 7.23 – 7.17 (m, 2H), 7.16 – 7.08 (m, 2H),), 4.74 (dd, *J* = 8.5, 5.1 Hz, 0.5H), 4.65 (dd, *J* = 9.0, 4.5 Hz, 0.5H), 2.80 – 2.66 (m, 1H), 2.63 – 2.48 (m, 1H), 2.37 – 2.21 (m, 2H), 2.11 – 1.93 (m, 1H), 1.91 – 1.82 (m, 1H), 1.81 – 1.69 (m, 2H), 1.68 – 1.58 (m, 2H), 1.32 (s, 4H), 1.31 (s, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 150.9, 141.8, 141.7, 139.8, 139.8, 129.3, 129.2, 128.6, 126.4, 125.7, 125.6, 125.5, 120.1, 120.0, 72.4, 72.2, 42.8, 42.3, 40.6, 40.4, 36.2, 36.0, 34.7,

31.5, 30.1, 29.1, 14.; HRMS(ESI) calcd for $C_{23}H_{29}NNaO^+$ $[M+Na]^+$ = 358.2141, found = 358.2142.

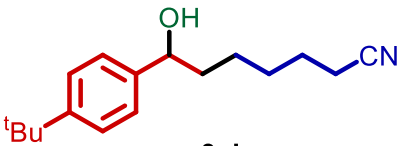
2-(2-(2-(4-(tert-Butyl)phenyl)-2-hydroxyethyl)-2,3-dihydro-1H-inden-1-yl)acetonitrile (3ag) (1.2:1 diastereomers)



3ag

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (83.0 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.25 – 7.18 (m, 3H), 7.15 – 7.08 (m, 3H), 4.74 – 4.67 (m, 1H), 3.20 – 3.02 (m, 2H), 2.69 – 2.34 (m, 4H), 2.16 – 1.99 (m, 2H), 1.97 – 1.85 (m, 1H), 1.24 (s, 5H), 1.23 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.0, 150.9, 142.9, 142.7, 142.7, 142.5, 141.9, 141.2, 127.8, 127.8, 126.9, 125.7, 125.7, 125.6, 125.5, 124.9, 123.7, 123.7, 119.1, 119.0, 73.2, 73.0, 47.3, 46.9, 44.1, 43.7, 43.0, 42.8, 38.3, 37.8, 34.6, 31.5, 22.1, 21.8; HRMS(ESI) calcd for $C_{23}H_{27}NNaO^+$ $[M+Na]^+$ = 356.1985, found = 356.1984.

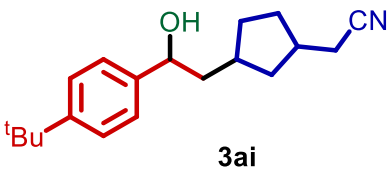
7-(4-(tert-Butyl)phenyl)-7-hydroxyheptanenitrile (3ah)



3ah

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (17.1 mg, 22% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.21 – 7.18 (m, 2H), 4.58 (dd, J = 7.5, 5.7 Hz, 1H), 2.25 (t, J = 7.1 Hz, 2H), 1.79 – 1.71 (m, 1H), 1.69 – 1.54 (m, 4H), 1.46 – 1.38 (m, 3H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 141.8, 125.7, 125.6, 119.9, 74.3, 38.6, 34.7, 31.5, 28.7, 25.4, 25.2, 17.2; HRMS(ESI) calcd for $C_{17}H_{25}NNaO^+$ $[M+Na]^+$ = 282.1828, found = 282.1828.

2-(3-(2-(4-(tert-Butyl)phenyl)-2-hydroxyethyl)cyclopentyl)acetonitrile (3ai) (1.2:1 diastereomers)

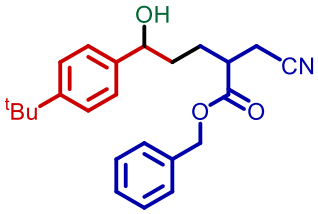


3ai

Column chromatography eluent - hexane/ethyl acetate 90:10; Pale yellow liquid (44.5 mg, 52% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.34 (m, 2H), 7.29 – 7.24 (m, 2H), 4.67 – 4.61 (m, 1H), 2.39 – 2.34 (m, 1H), 2.34 – 2.29 (m, 1H), 2.28 – 2.03 (m, 2H), 2.02 – 1.92 (m, 2H), 1.91 – 1.76 (m, 3H), 1.75 – 1.47 (m, 3H), 1.47 – 1.35 (m, 1H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 141.9, 125.7, 125.7, 125.6, 119.5, 119.3, 74.5, 73.7, 73.6, 45.4, 45.3, 40.1, 40.0, 39.7, 38.2, 38.0, 38.0, 37.9, 37.0, 37.0, 36.2, 36.1, 35.6,

35.5, 35.4, 35.3, 34.7, 33.2, 32.7, 32.4, 32.2, 31.7, 31.5, 31.0, 30.9, 30.5, 27.5, 23.4, 23.2; HRMS(ESI) calcd for $C_{19}H_{27}NNaO^+$ $[M+Na]^+$ = 308.1985, found = 308.1983.

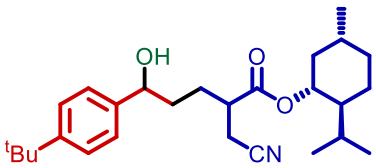
Benzyl 5-(4-(tert-butyl)phenyl)-2-(cyanomethyl)-5-hydroxypentanoate (3aj) (1:1 diastereomers)



3aj

Column chromatography eluent - hexane/ethyl acetate 85:15; Pale yellow liquid (74.0 mg, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 7H), 7.21 – 7.17 (m, 2H), 5.16 (q, *J* = 12.2 Hz, 2H), 4.65 – 4.56 (m, 1H), 2.89 – 2.78 (m, 1H), 2.65 (ddd, *J* = 16.9, 7.1, 1.6 Hz, 1H), 2.54 (ddd, *J* = 16.8, 10.0, 6.7 Hz, 1H), 2.01 – 1.84 (m, 2H), 1.82 – 1.63 (m, 3H), 1.31 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 150.9, 141.1, 141.1, 135.3, 128.8, 128.7, 128.6, 125.6, 125.6, 117.8, 117.8, 73.9, 73.7, 67.3, 41.6, 41.4, 35.6, 35.5, 34.6, 31.5, 28.0, 27.9, 19.5, 19.5; HRMS(ESI) calcd for $C_{24}H_{29}NNaO_3^+$ $[M+Na]^+$ = 402.2039, found = 402.2038.

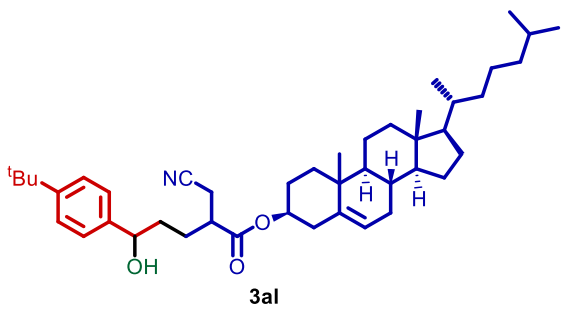
2-Isopropyl-5-methylcyclohexyl 5-(4-(tert-butyl)phenyl)-2-(cyanomethyl)-5-hydroxypentanoate (3ak) (1:1 diastereomers)



3ak

Column chromatography eluent - hexane/ethyl acetate 80:20; Pale yellow liquid (87.2 mg, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.27 – 7.23 (m, 2H), 4.77 – 4.69 (m, 1H), 4.69 – 4.62 (m, 1H), 2.84 – 2.69 (m, 1H), 2.64 (dd, *J* = 16.8, 7.2 Hz, 1H), 2.59 – 2.44 (m, 1H), 2.05 – 1.92 (m, 2H), 1.90 – 1.81 (m, 2H), 1.80 – 1.73 (m, 2H), 1.73 – 1.64 (m, 3H), 1.54 – 1.37 (m, 2H), 1.32 (s, 9H), 1.11 – 0.95 (m, 2H), 0.92 – 0.85 (m, 6H), 0.76 – 0.66 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.3, 172.2, 151.0, 141.3, 125.7, 125.6, 125.6, 125.5, 117.8, 75.8, 75.7, 75.6, 74.1, 73.9, 73.8, 47.0, 47.0, 46.9, 42.0, 42.0, 41.8, 41.7, 40.9, 40.9, 36.0, 35.8, 35.7, 35.6, 34.7, 34.3, 31.5, 31.5, 28.2, 28.1, 28.1, 27.9, 26.3, 26.2, 26.2, 23.4, 23.1, 22.1, 21.0, 20.9, 20.9, 19.7, 19.7, 19.6, 16.3, 16.0, 16.0; HRMS(ESI) calcd for $C_{27}H_{45}N_2O_3^+$ $[M+NH_4]^+$ = 445.3425, found = 445.3424.

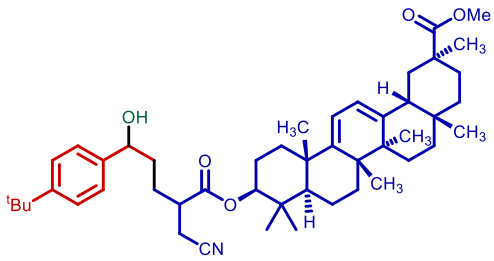
10,13-Dimethyl-17-(6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-2-yl 5-(4-(tert-butyl)phenyl)-2-(cyanomethyl)-5-hydroxypentanoate (3al) (1:1 diastereomers)



3al

Column chromatography eluent - hexane/ethyl acetate 85:15; Pale yellow liquid (148.1 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 2H), 7.28 – 7.24 (m, 2H), 5.38 (dd, *J* = 3.2, 1.2 Hz, 1H), 4.71 – 4.61 (m, 2H), 2.82 – 2.68 (m, 1H), 2.69 – 2.45 (m, 2H), 2.37 – 2.26 (m, 2H), 2.05 – 1.92 (m, 3H), 1.91 – 1.77 (m, 6H), 1.76 – 1.63 (m, 2H), 1.64 – 1.53 (m, 6H), 1.53 – 1.41 (m, 5H), 1.32 (s, 9H), 1.21 – 1.05 (m, 8H), 1.02 (s, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.87 (dd, *J* = 6.6, 1.8 Hz, 6H), 0.68 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.1, 151.1, 141.2, 141.1, 139.4, 139.4, 125.7, 125.7, 123.2, 117.9, 117.9, 75.4, 74.0, 73.9, 56.8, 56.3, 50.2, 42.5, 41.8, 41.5, 39.9, 39.7, 38.1, 37.1, 36.7, 36.3, 35.9, 35.7, 35.6, 34.7, 32.1, 32.0, 31.5, 28.4, 28.2, 28.0, 27.9, 27.9, 24.4, 24.0, 23.0, 22.7, 21.2, 19.7, 19.6, 19.5, 18.9, 12.0; HRMS(ESI) calcd for $C_{44}H_{67}NNaO_3^+$ $[M+Na]^+$ = 680.5019, found = 680.5013.

Methyl 10-((5-(4-(tert-butyl)phenyl)-2-(cyanomethyl)-5-hydroxypentanoyl)oxy)-2,4a,6a,6b,9,9,12a-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14b-octadecahydropicene-2-carboxylate (3am) (1:1 diastereomers)



3am

Column chromatography eluent - hexane/ethyl acetate 80:20; Pale yellow liquid (155.4 mg, 70% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.20 – 7.18 (m, 2H), 5.53 (q, *J* = 5.9 Hz, 2H), 4.64 – 4.55 (m, 1H), 4.54 – 4.46 (m, 1H), 3.62 (s, 3H), 2.78 – 2.67 (m, 1H), 2.62 – 2.54 (m, 1H), 2.53 – 2.42 (m, 1H), 2.01 (dd, *J* = 13.3, 3.6 Hz, 1H), 1.93 (dt, *J* = 12.7, 3.0 Hz, 1H), 1.90 – 1.87 (m, 1H), 1.87 – 1.83 (m, 2H), 1.83 – 1.77 (m, 2H), 1.77 – 1.70 (m, 3H), 1.70 – 1.58 (m, 5H), 1.58 – 1.35 (m, 4H), 1.35 – 1.28 (m, 2H), 1.24 (s, 9H), 1.22 – 1.19 (m, 1H), 1.14 (s, 3H), 1.06 (s, 6H), 0.99 – 0.94 (m, 1H), 0.91 (s, 3H), 0.90 – 0.86 (m, 2H), 0.85 – 0.82 (m, 3H), 0.82 – 0.79 (m, 3H), 0.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.7, 172.3, 172.3, 154.1, 151.0, 151.0, 146.4, 146.4, 141.2, 141.1, 125.7, 121.5, 116.1, 82.2, 82.2, 82.1, 74.0, 74.0, 73.9, 73.8, 51.8, 51.4, 51.4, 46.5, 44.4, 42.9, 42.8, 42.1, 41.9, 41.8, 40.6, 38.7, 38.4, 38.0, 36.9, 35.8, 35.8, 35.6, 35.5, 34.7, 32.2, 31.7, 31.5, 31.3, 28.6, 28.5, 28.5, 28.4, 28.4, 28.4, 28.1, 27.9, 27.8, 27.4, 25.7, 25.4, 24.3, 21.1, 20.1, 19.8, 19.6, 19.6, 18.3, 17.0; HRMS(ESI) calcd for $C_{48}H_{73}N_2O_5^+$ $[M+NH_4]^+$ = 757.5496, found = 757.5514.

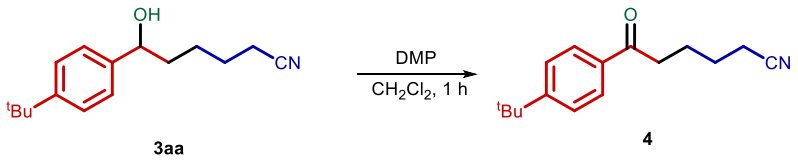
5. Gram scale experiment:

In an oven dried 100 mL vial equipped with a magnetic stir bar was charged with alkene **1a** (0.5 g, 3.2 mmol) oxime ester **2a** (1.2 g, 4.7 mmol), Cp_2Fe (29.3 mg, 0.16 mmol) followed by the addition of 1:1 ratio of acetone/water (32 mL) under nitrogen atmosphere. Then the mixture was stirred at 60 °C for 36 h. After completion of reaction, the resulting mixture was cooled to room temperature and concentrated under reduced pressure. Then the residue was diluted with ethyl acetate (25 mL), and washed successively with aq. $NaHCO_3$ solution (25 mL×2) and brine solution (25 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** (0.643 g, 82%).

6. Synthetic applications:

6-(4-(tert-Butyl)phenyl)-6-oxohexanenitrile (4)

To a solution of **3aa** (24.5 mg, 0.1 mmol) in CH_2Cl_2 (2.0 mL) was added Dess-Martin periodinane (51 mg, 0.12 mmol) at 0 °C and the reaction mixture is allowed to stir at room temperature. When the starting material was consumed completely (within 1 h), the reaction mixture was concentrated completely and purified via flash chromatography on silica gel to get the desired compound **4** in 86% yield.

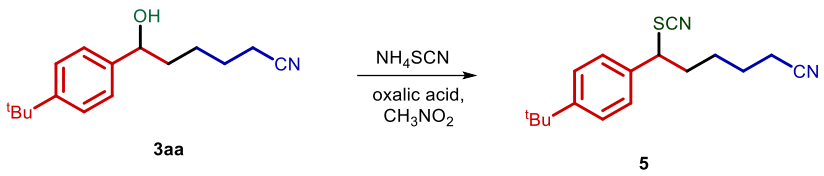


3aa **4**

Column chromatography eluent - hexane/ethyl acetate 95:5; Pale yellow oil (20.9 mg, 86%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.6 Hz, 2H), 7.48 (d, J = 8.6 Hz, 2H), 3.01 (t, J = 6.9 Hz, 2H), 2.40 (t, J = 7.1 Hz, 2H), 1.95 – 1.85 (m, 2H), 1.81 – 1.69 (m, 2H), 1.34 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8, 157.0, 134.2, 128.0, 125.6, 119.6, 37.3, 35.2, 31.1, 25.1, 23.2, 17.2. This spectroscopic data is consistent with that reported in the literature.[3]

6-(4-(*tert*-Butyl)phenyl)-6-thiocyanatohexanenitrile (5)

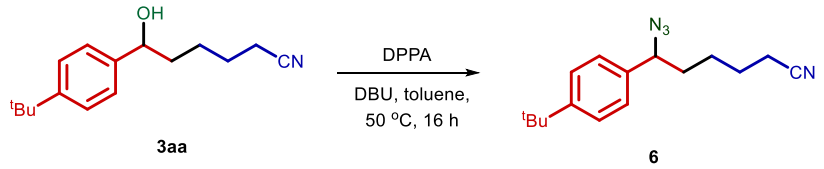
To a solution of **3aa** (24.5 mg, 0.1 mmol) in nitromethane (1 mL) oxalic acid (9.0 mg, 0.1mmol) and NaSCN (9.7 mg, 0.12 mmol) were added. The mixture was stirred at 60 °C for 8 hours. The mixture was poured into water and extracted with ethyl acetate. After concentration, the crude mixture was purified by column chromatography on silica gel to get **5** in 52% yield.



Column chromatography eluent - hexane/ethyl acetate 95:5; Yellow syrup (14.9 mg, 52%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.6 Hz, 2H), 4.32 (dd, J = 8.4, 6.9 Hz, 1H), 2.34 (t, J = 7.0 Hz, 2H), 2.27 – 2.14 (m, 2H), 1.77 – 1.65 (m, 2H), 1.58 – 1.41 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 134.4, 127.1, 126.2, 119.2, 111.7, 52.9, 35.1, 34.7, 31.2, 26.6, 24.9, 17.1; HRMS (ESI) calcd for $C_{17}H_{22}N_2SNa^+$ $[M+Na]^+$ = 309.1401, found = 309.1399.

6-Azido-6-(4-(*tert*-butyl)phenyl)hexanenitrile (6)

To a solution of **3aa** (24.5 mg, 0.1 mmol) in toluene (1 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (23 µL, 0.15 mmol) was added under N_2 atmosphere. To this, diphenylphosphoryl azide (DPPA) (32 µL, 0.15 mmol) was added and the resultant reaction mixture was heated to 50 °C for 16 h. The reaction mixture was cooled to room temperature and it was partitioned between ethyl acetate (10 mL) and brine solution (10 mL). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to get the desired compound **6** in 61% yield.

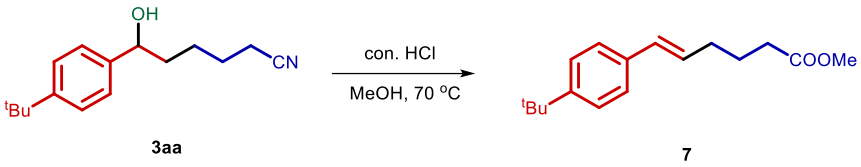


Column chromatography eluent - hexane/ethyl acetate 85:15; Yellow syrup (14.9 mg, 61%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 4.40 (dd, J = 7.6, 6.7 Hz, 1H), 2.33 (t, J = 7.0 Hz, 2H), 1.92 – 1.72 (m, 2H), 1.72 – 1.64 (m, 2H), 1.59 – 1.38 (m, 2H), 1.32 (s, J = 3.9 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 136.2, 126.5, 125.8, 119.5, 65.8, 35.4, 34.6, 31.3, 25.5, 25.2, 17.1; HRMS (ESI) calcd for $C_{16}H_{22}N^+$ $[M-N_3]^+$ = 228.1747, found = 228.1747.

Methyl (*E*)-6-(4-(*tert*-butyl)phenyl)hex-5-enoate (7)

To a solution of **3aa** (24.5 mg, 0.1 mmol) in MeOH (1 mL), con. HCl (1 mL) was added and heated to 70 °C under reflux conditions for 36 h. After cooling to room temperature, the reaction mixture was quenched with 10 mL of H_2O, and extracted with EtOAc (10 mL×3). The

combined organic layer was washed with brine (15 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by flash chromatography to afford the desired product **7** in 87% yield.

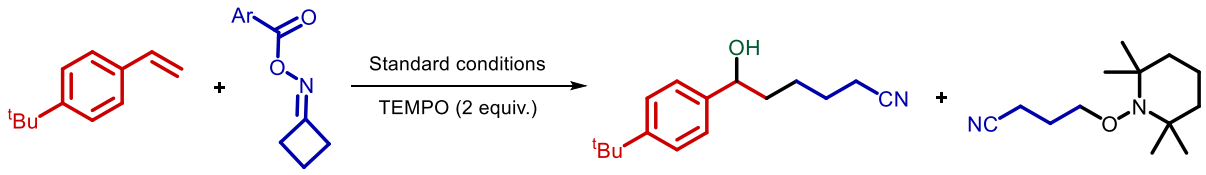


3aa **7**

Column chromatography eluent - hexane/ethyl acetate 95:5; Pale yellow oil (22.6 mg, 87%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 6.38 (d, J = 15.8 Hz, 1H), 6.13 (dt, J = 15.8, 7.0 Hz, 1H), 3.66 (s, 3H), 2.36 (t, J = 7.5 Hz, 2H), 2.26 – 2.22 (m, 2H), 1.81 (p, J = 7.5 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 150.1, 134.8, 130.5, 128.7, 125.7, 125.4, 51.56, 34.5, 33.4, 32.4, 31.3, 24.6. This spectral data is in consistent with the one reported in the literature.[4]

7. Mechanistic Studies:

A) Radical inhibition/trapping experiments:



1a **2a** **3aa (0%)** **8**, detected in ESI-MS

Ar = 4-$CF_3C_6H_4$

In an oven dried 5.0 mL vial equipped with a magnetic stir bar was charged with alkene **1a** (48.1 mg, 0.3 mmol), oxime ester **2a** (115.7 mg, 0.45 mmol), Cp_2Fe (2.8 mg, 0.015 mmol), TEMPO (93.8 mg, 0.6 mmol) followed by the addition of 1:1 ratio of acetone/water (3.0 mL) under nitrogen atmosphere. Then the mixture was stirred at 60 °C for 12 h. After completion of reaction, the resulting mixture was cooled to room temperature and concentrated under reduced pressure. Then the residue was diluted with ethyl acetate (15 mL), and washed successively with aq. $NaHCO_3$ solution (10 mL×2) and brine solution (10 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 **8** was characterized by ESI-MS.

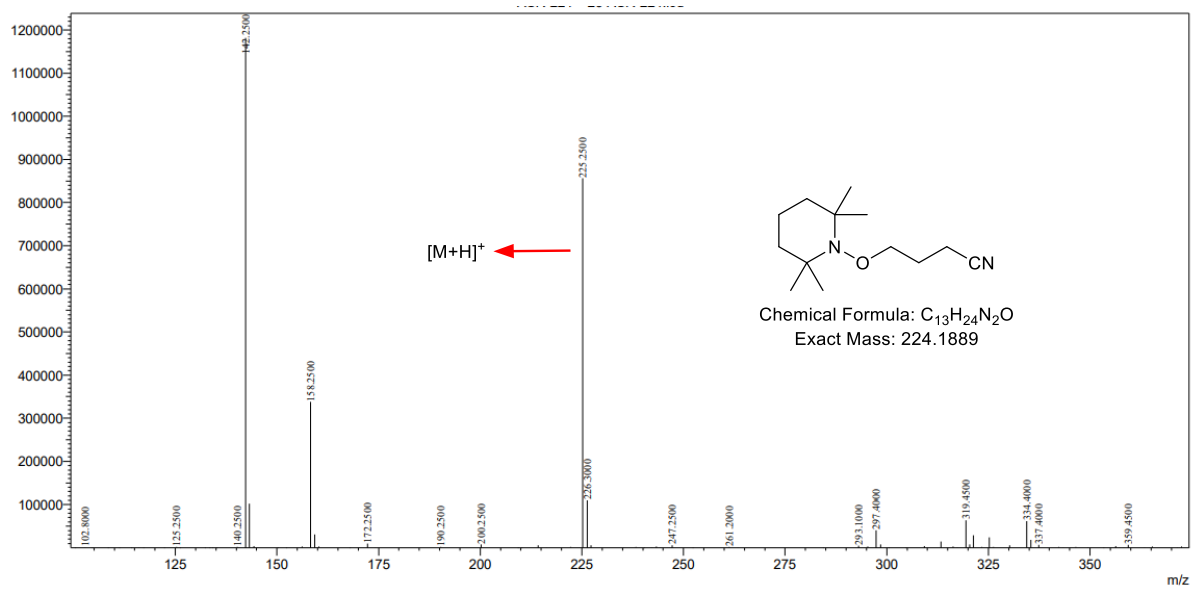


Figure S1: ESI-MS spectrum of the reaction with TEMPO

This observation suggests a cyanoalkyl radical reaction pathway.

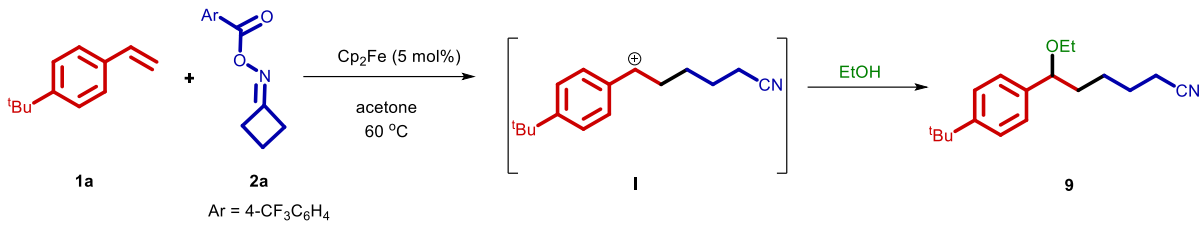
B) Reaction under oxygen atmosphere:

An oven dried 5.0 mL vial equipped with a magnetic stir bar was charged with alkene **1a** (48.1 mg, 0.3 mmol), oxime ester **2a** (115.7 mg, 0.45 mmol), Cp_2Fe (2.8 mg, 0.015 mmol), followed acetone (3.0 mL) that is dried over activated 4 Å molecular sieves for overnight. The mixture was stirred at 60 °C under oxygen balloon for 12 h. In this case, only 11% of **3aa** was isolated. This experiment clearly indicates H_2O is the source (not oxygen) for the –OH functionality of the desired carbohydroxylated compound **3aa**.

Note: The 11% of the product in the absence of water may be due to the presence of trace amounts of water in acetone as it is almost impossible to get 100% dry acetone.

C) Nucleophilic trapping experiment:

When the reaction between **1a** and **2a** was carried out using EtOH in the place of H_2O under the standard conditions, the ethyl ether product **9** was formed in 67% yield. The product **9** was resulted from the nucleophilic addition of EtOH on the carbocation intermediate I, which is generated during the oxidative transformation of radical that generated upon the addition of cyanoalkyl radical on **1a**. This observation clearly supports the participation of water as a nucleophile in this transformation.



6-(4-(*tert*-Butyl)phenyl)-6-ethoxyhexanenitrile (9)

Column chromatography eluent - hexane/ethyl acetate 95:5; Yellow syrup (55 mg, 67%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.17 (dd, J = 7.4, 4.4 Hz, 1H), 3.44 – 3.24 (m, 2H), 2.32 (t, J = 6.6 Hz, 2H), 1.87 – 1.74 (m, 1H), 1.72 – 1.57 (m, 4H), 1.48 – 1.40 (m, 1H), 1.32 (s, 9H), 1.17 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.3, 139.5, 126.1, 125.2, 119.8, 81.4, 64.1, 37.5, 34.5, 31.4, 25.4, 25.3, 17.1, 15.3; HRMS (ESI) calcd for $C_{16}H_{22}N^{+}$ $[M\text{-}OEt]^{+}$ = 228.1747, found = 228.1747.

D) UV-visible spectroscopic studies:

A 4.0 mL standard cuvette was charged with a 3.0 mL (1:1 acetone/ water) solution of Cp_2Fe (0.011 M) and its UV absorption spectrum was recorded. Absorption maximum at 442 nm was observed. Into that cuvett, styrene **1a** (69 mg) was added and it was monitored over six cycles for every 5 minutes with wavelength varying from 800–300 nm. In this case, no new ferrocene pattern was observed (Figure S2).

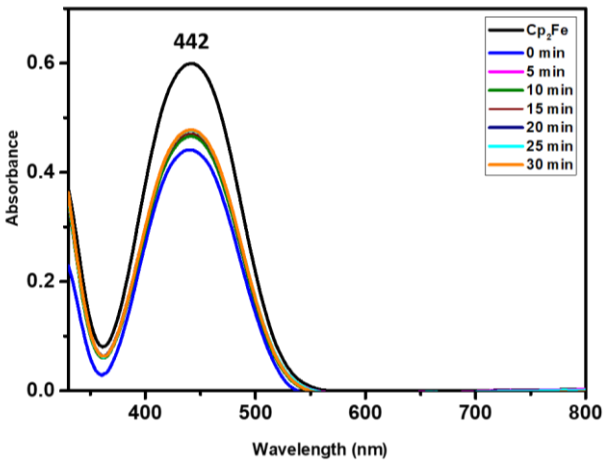


Figure S2: UV absorption spectra of Cp_2Fe and Cp_2Fe+**1a** mixture

Similarly, absorption spectra of Cp_2Fe (0.011 M) and oxime ester **2a** (110.5 mg) was also recorded over six cycles for every 5 minutes (Figure S3).

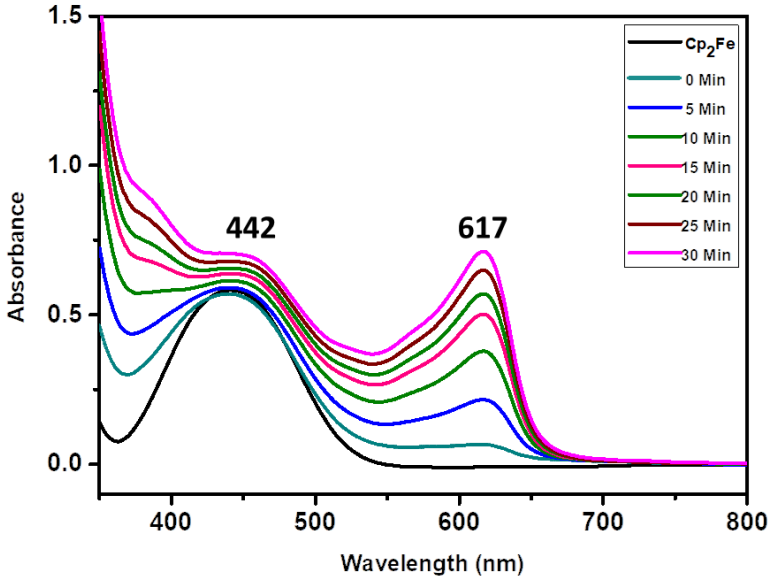


Figure S3: UV absorption spectra of Cp_2Fe and Cp_2Fe+**2a** mixture

In this case, there was an increase in the intensity of peak at 617 nm corresponding to ferrocenium ion. The colour of the solution was changed from light yellow to green After few minutes. This red shift was due to the formation of ferrocenium ions formed by the single electron transfer from ferrocene to oxime ester **2a**.

8. References

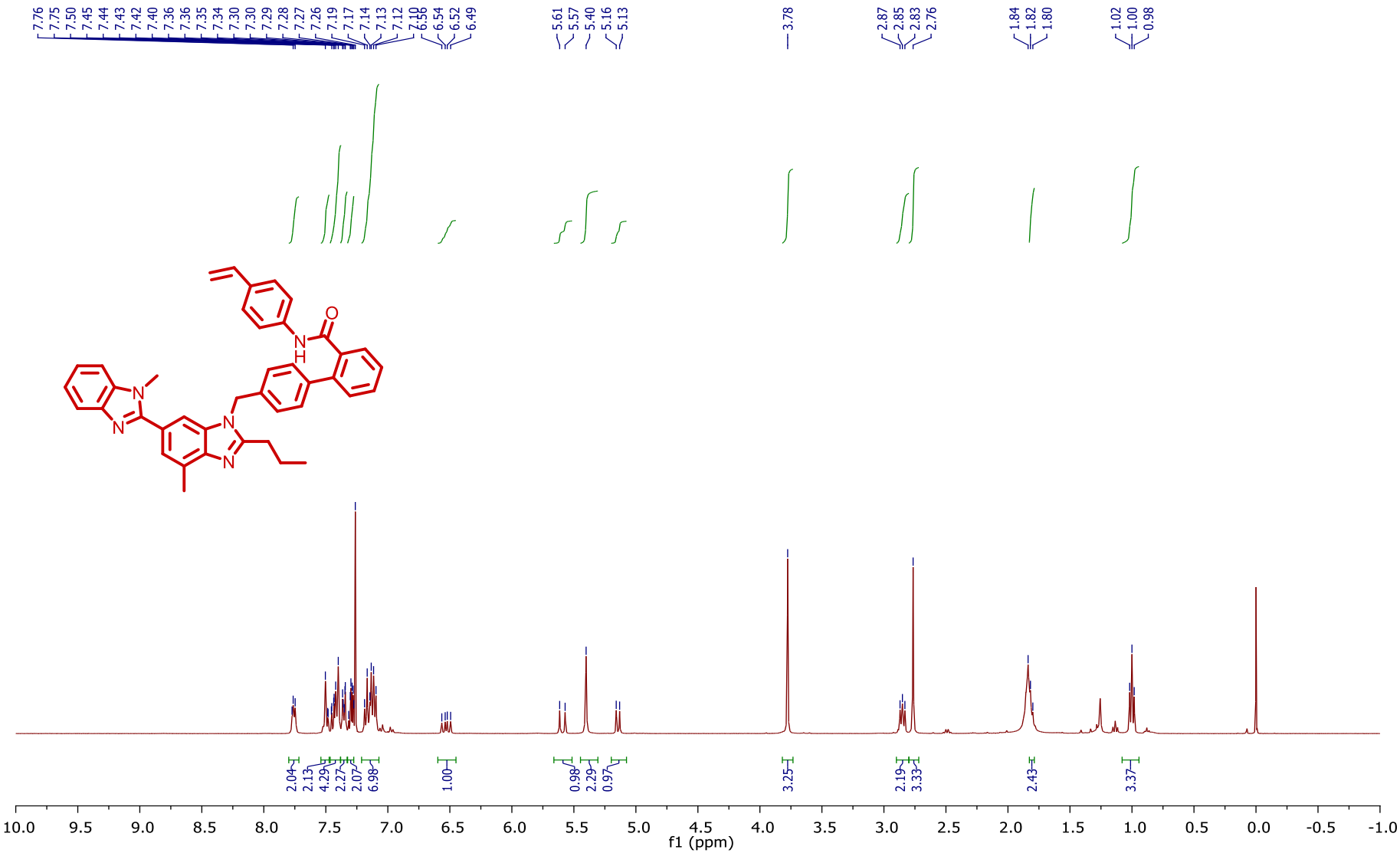
1. a) Y. Zhang, H. Liu, Q. Shi, X. Chen, X. Xie, *Green Chem.,* 2022, **24**, 7889-7893; b) M. Q. Tian, C. Wang, X. H. Hu, T. P. Loh, *Org. Lett.,* 2019, **21**, 1607–1611.

2. a) B. He, X. Yu, P. Wang, J. Chen, W. Xiao, *Chem. Commun.,* 2018, **54**, 12262–12265; b) Q. Min, G. Chen, F. Liu, *Org. Chem. Front*., 2019, **6**, 1200–1204; c) X. Y. Lu, Z. J. Xia, A. Gao, Q. L. Liu, R. C. Jiang, C. C. Liu, *J. Org. Chem*., 2021, **86**, 8829–8842; d) J. Chen, Y. J. Liang, P. Z. Wang, G. Q. Li, B. Zhang, H. Qian, X. D. Huan, W. Guan, W. J. Xiao, J. R. Chen, *J. Am. Chem. Soc*., 2021, **143**, 13382–13392; e) A. M. Ghouse, S. M. Akondi, *Org. Biomol. Chem.*, 2023, **21**, 5351–5355.

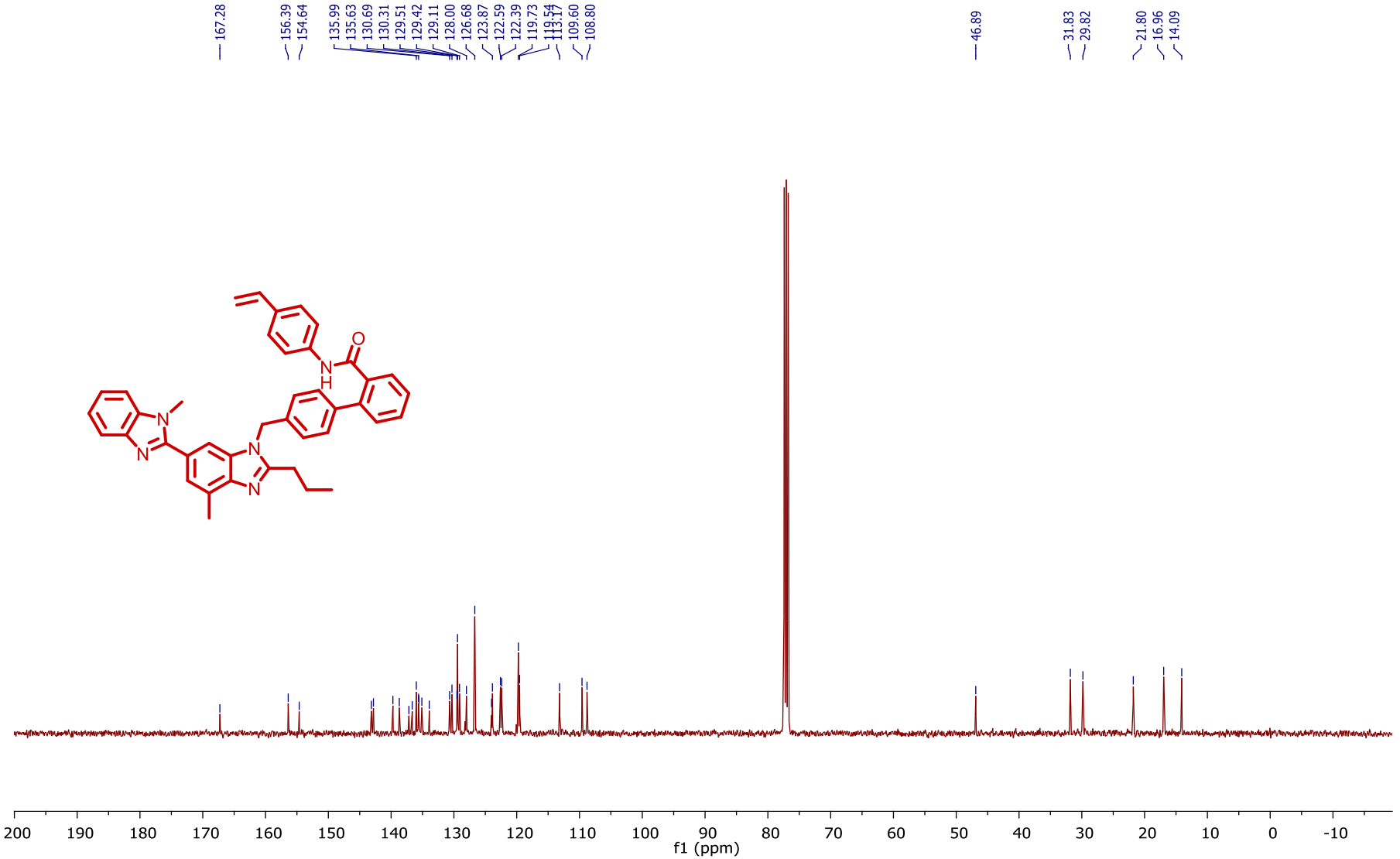
3. B.-Q. He, X.-Y. Yu, P.-Z. Wang, J.-R. Chen, W.-J. Xiao, *Chem. Commun.,* 2018, **54**, 12262–12265.

4. Z.-H. Xia, C.-L. Zhang, Z.-H. Gao, S. Ye, *Org. Lett.,* 2018, **20**, 3496–3499.

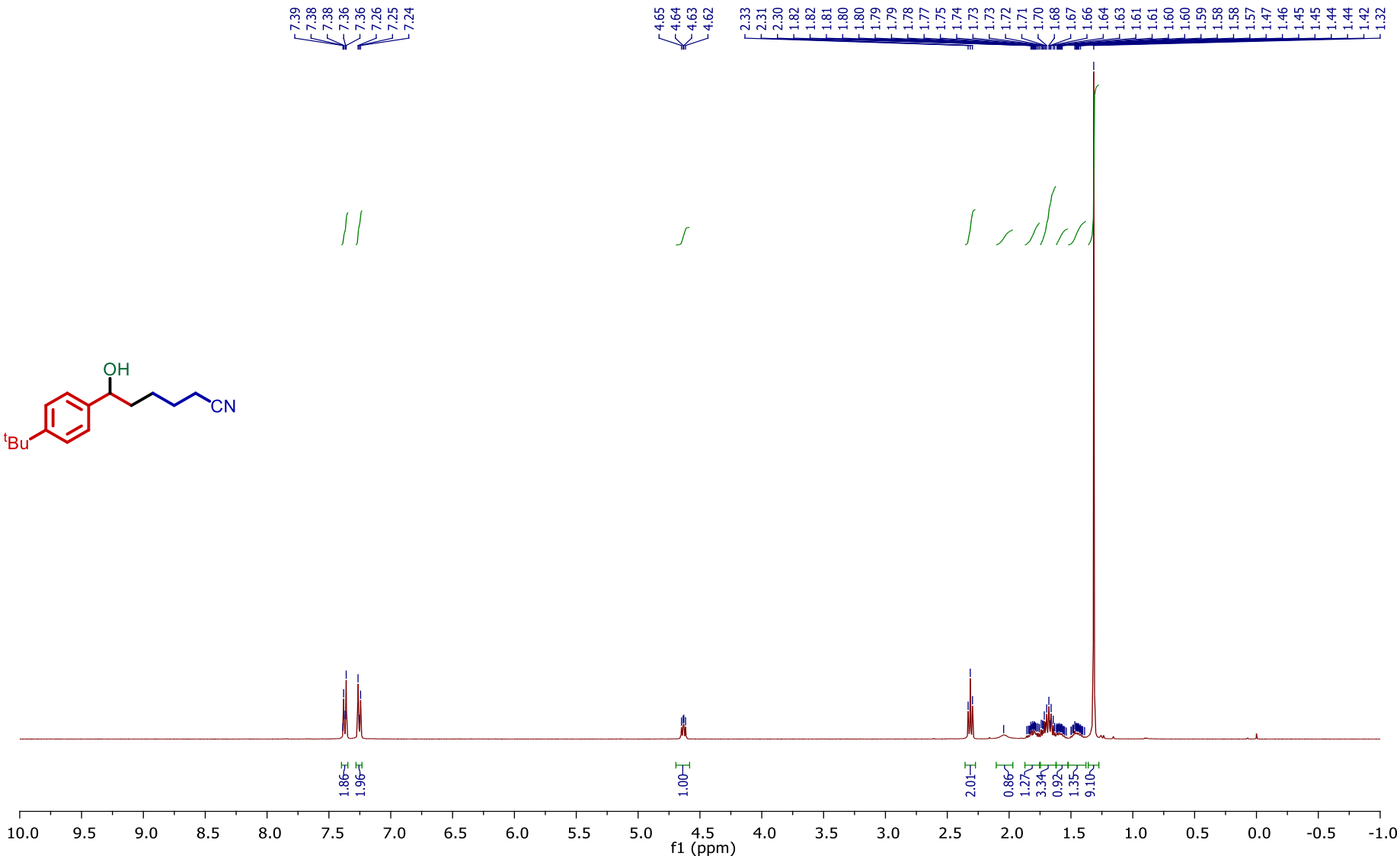
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(1r)**



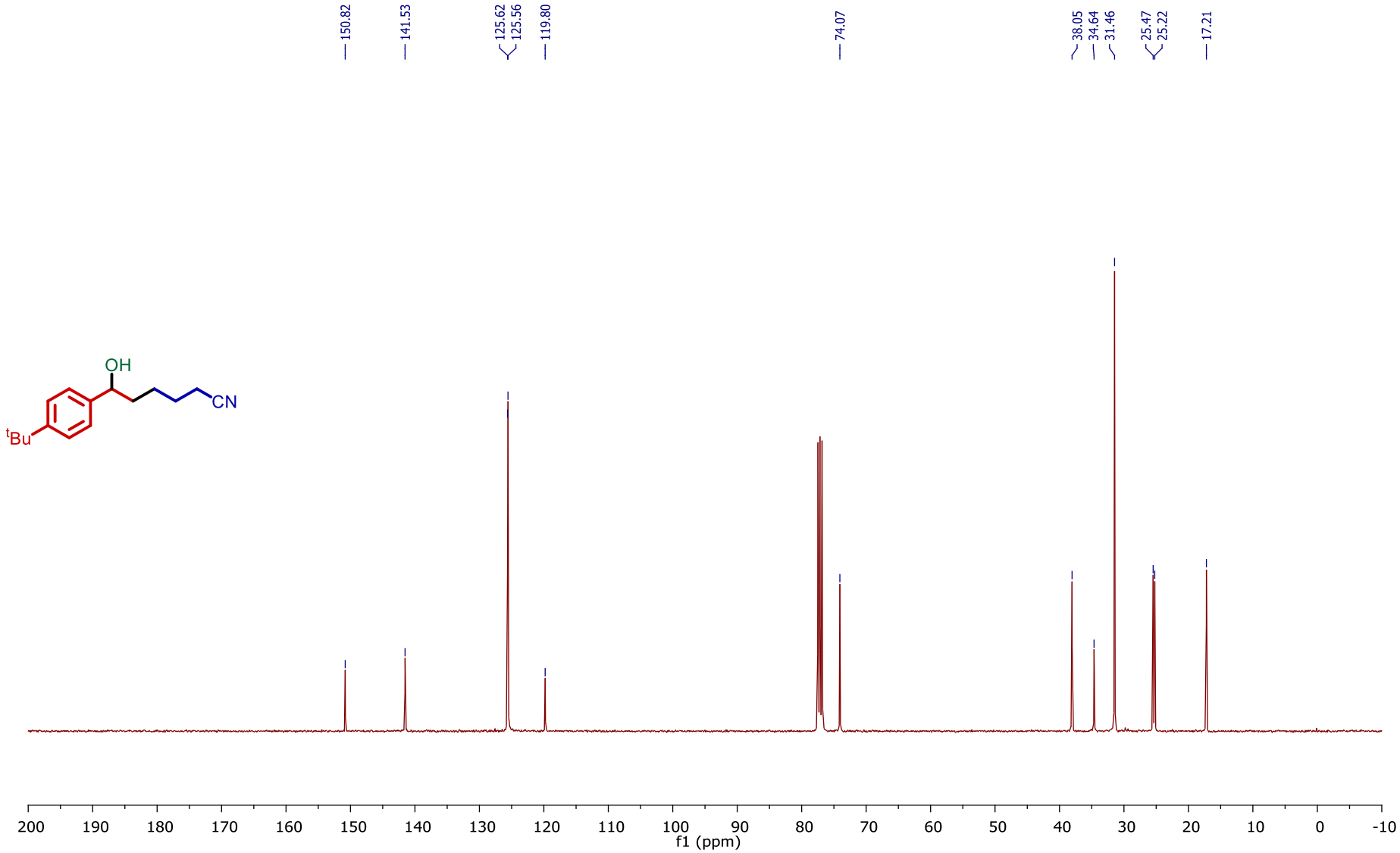
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(1r)**



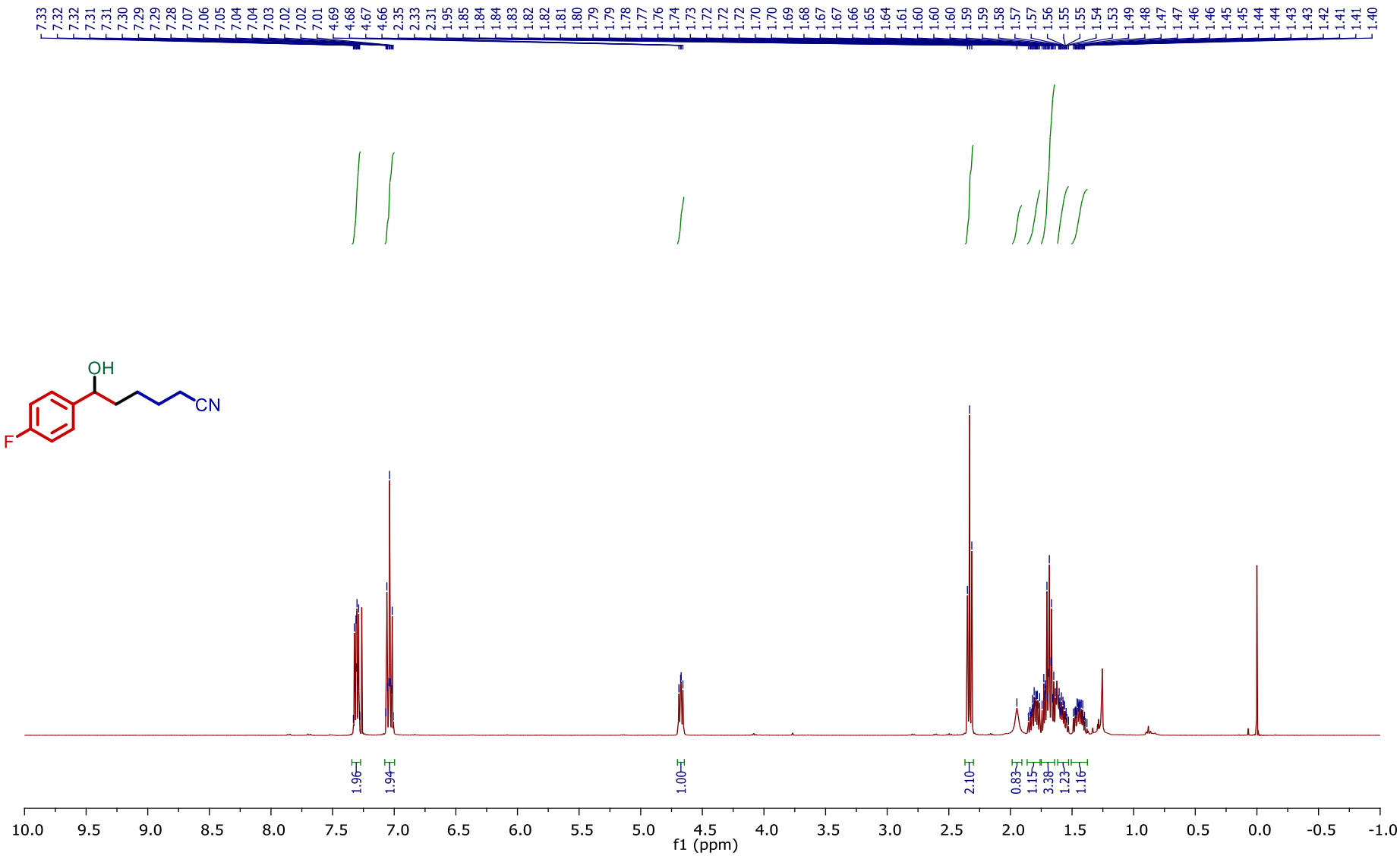
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3aa)**



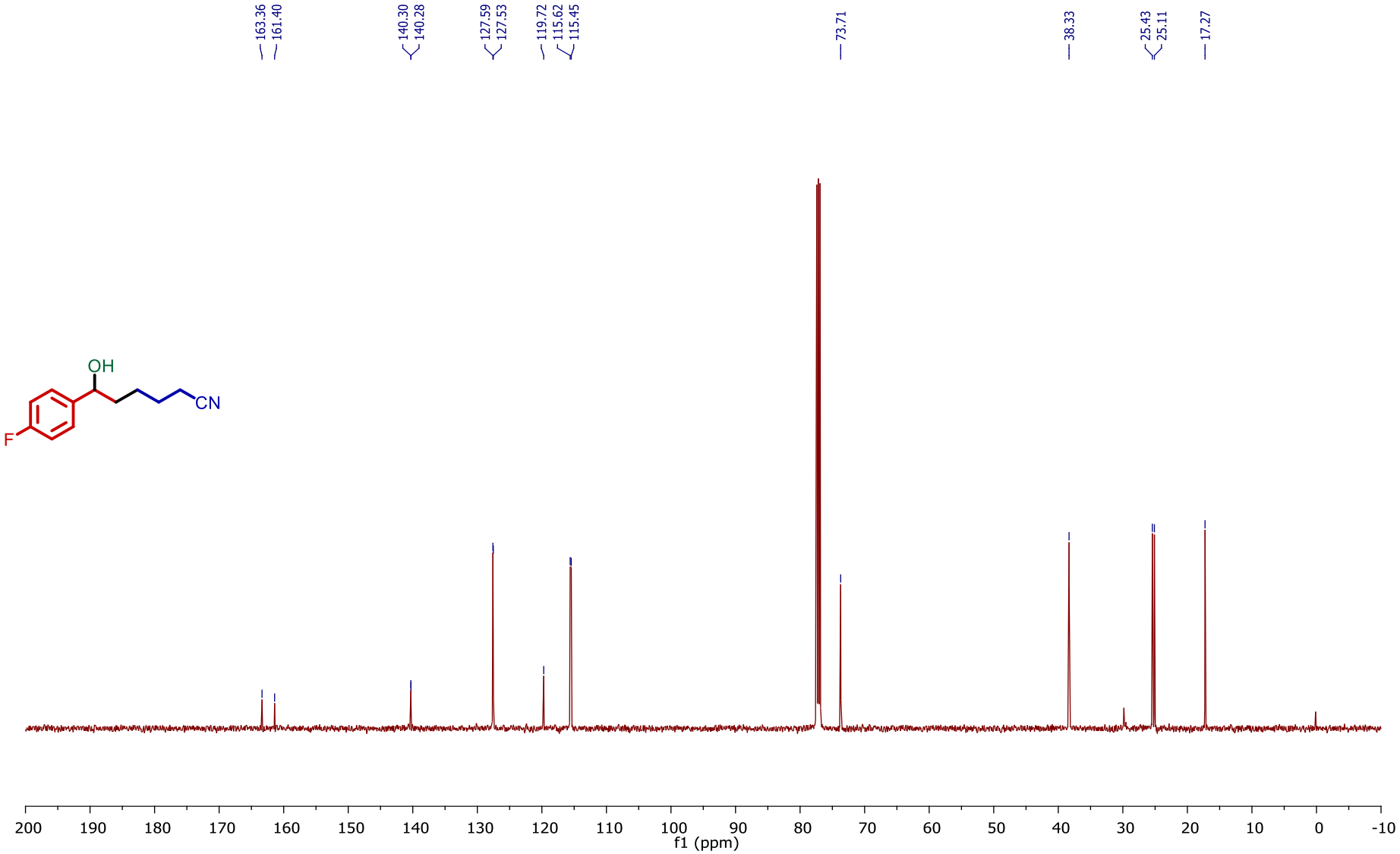
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3aa)**



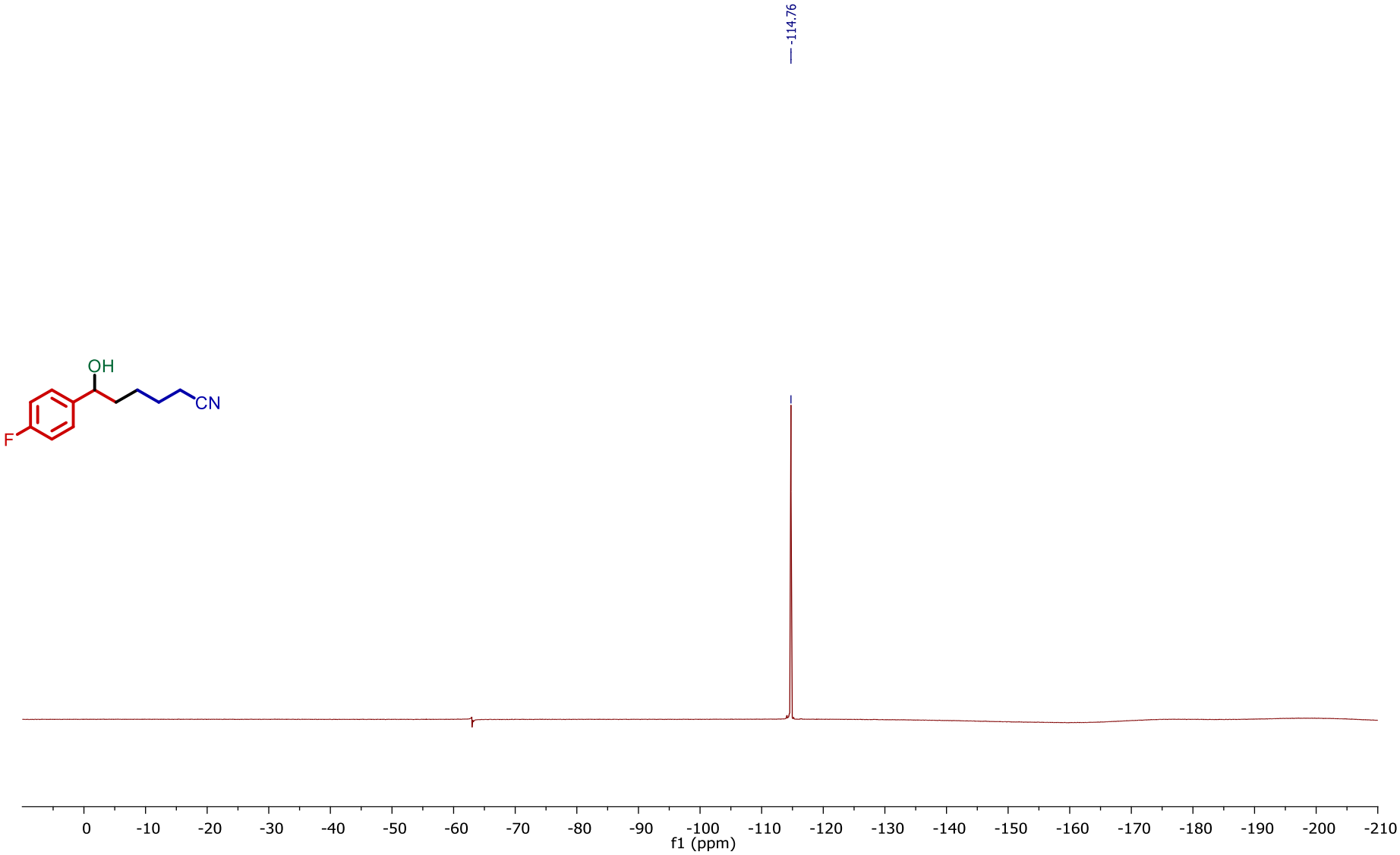
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ba)**



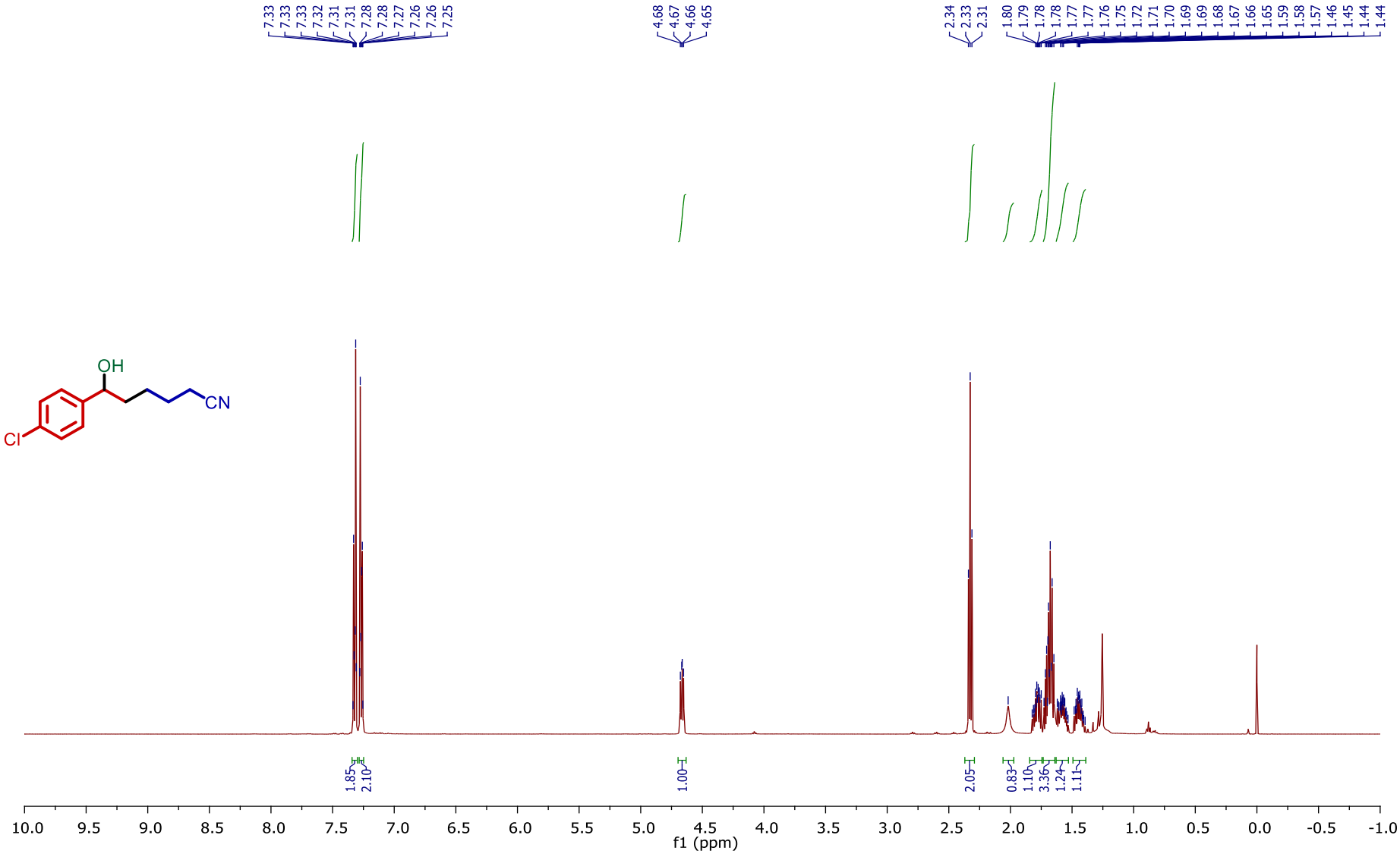
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ba)**



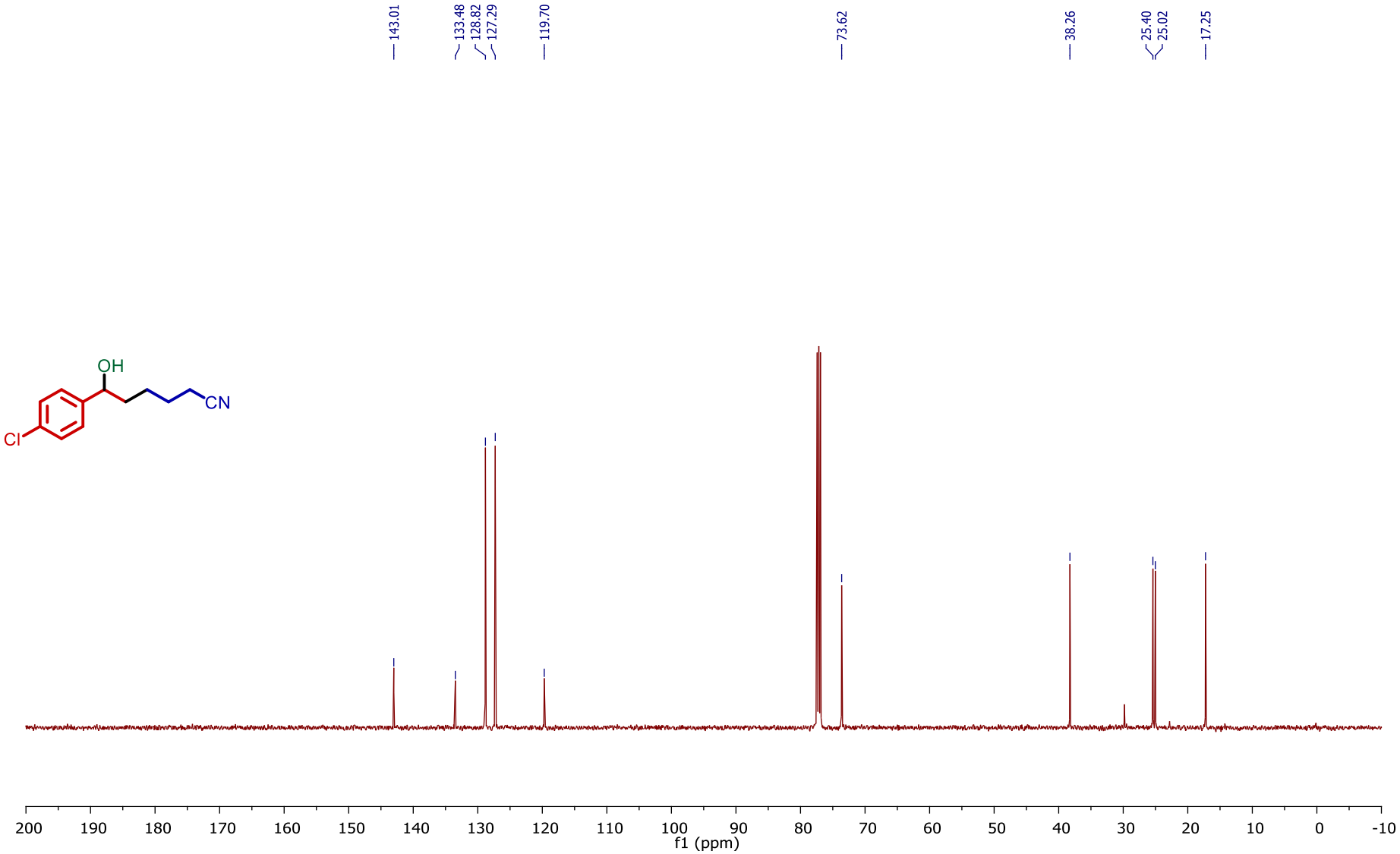
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3ba)**



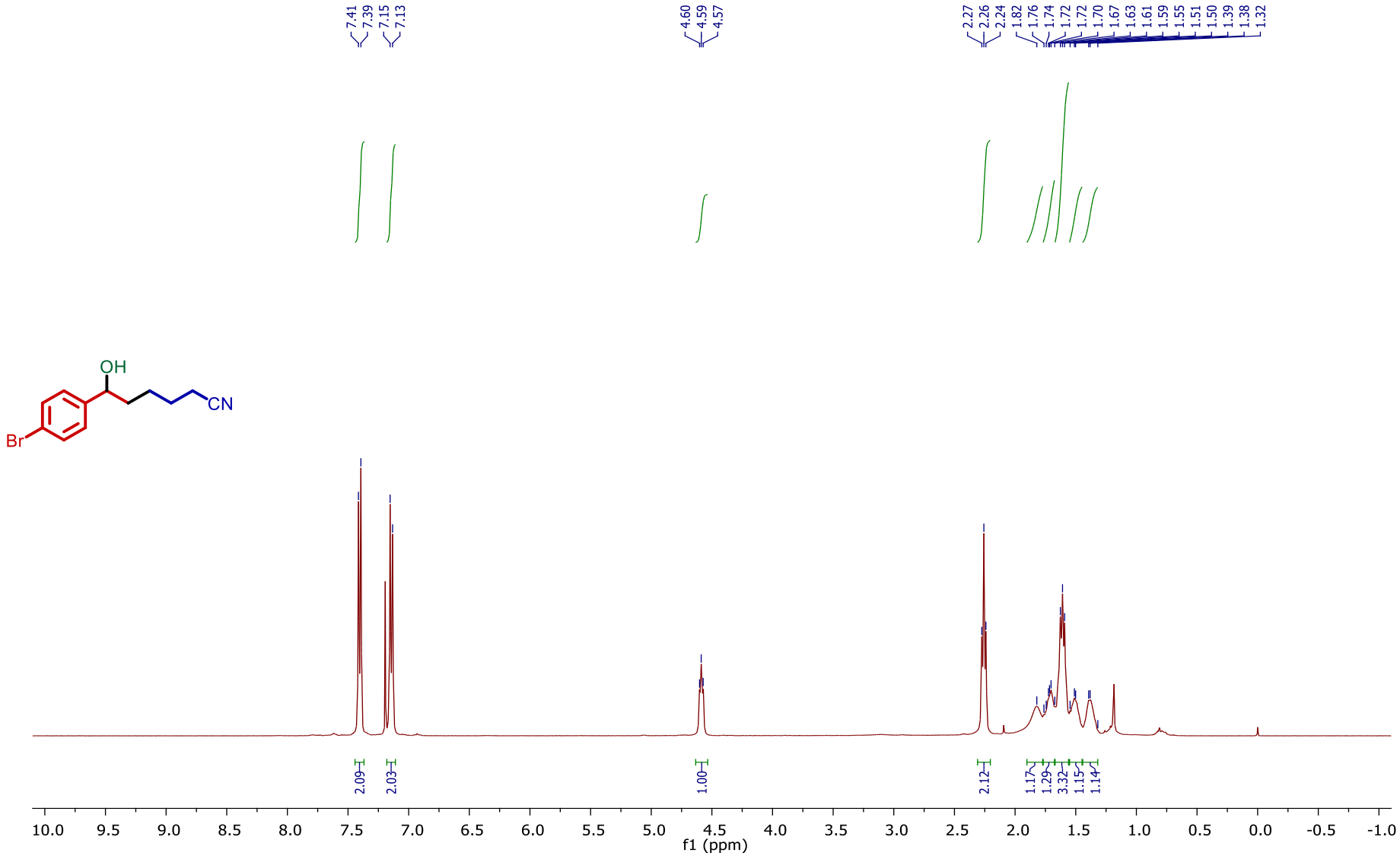
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3ca)**



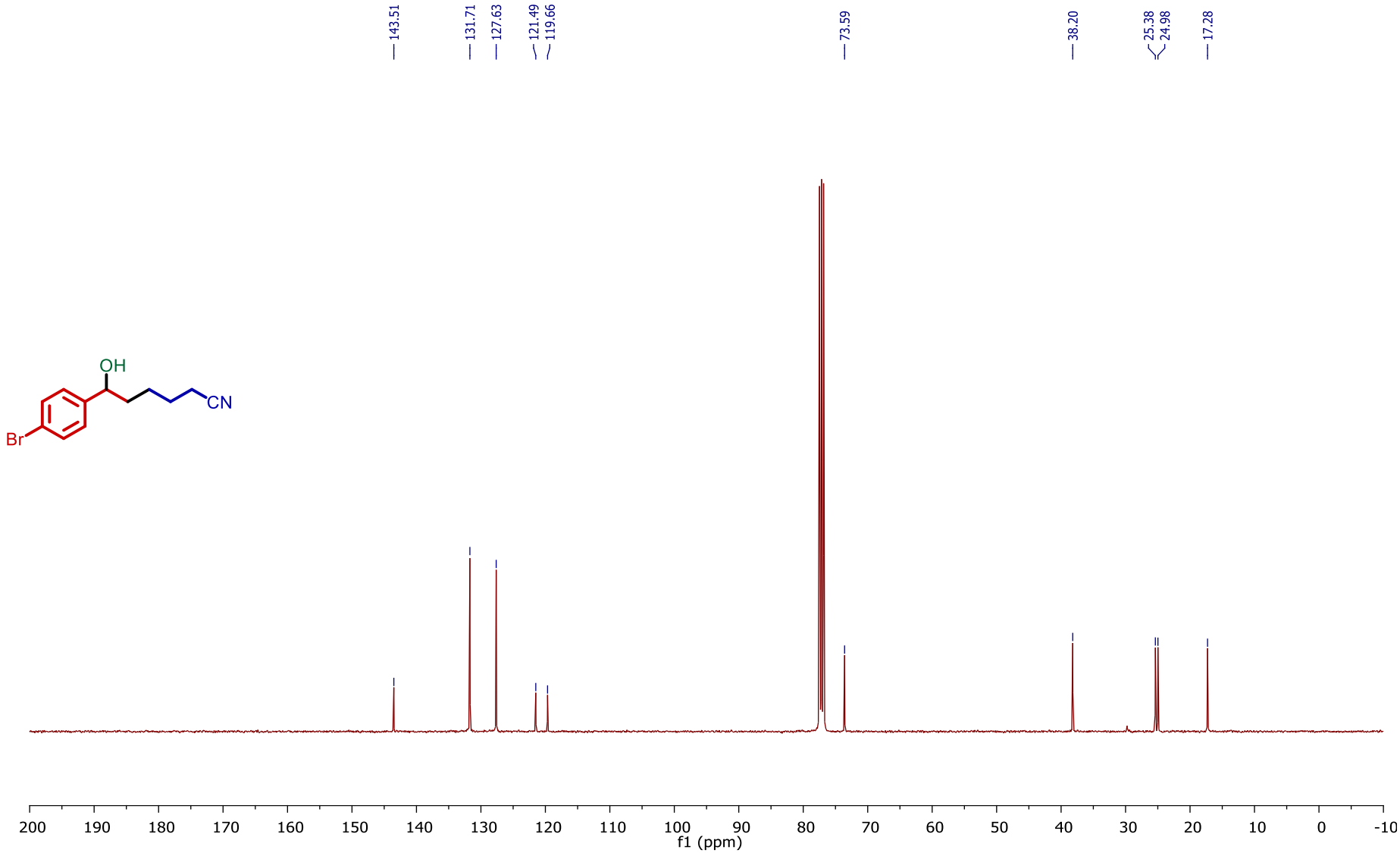
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ca)**



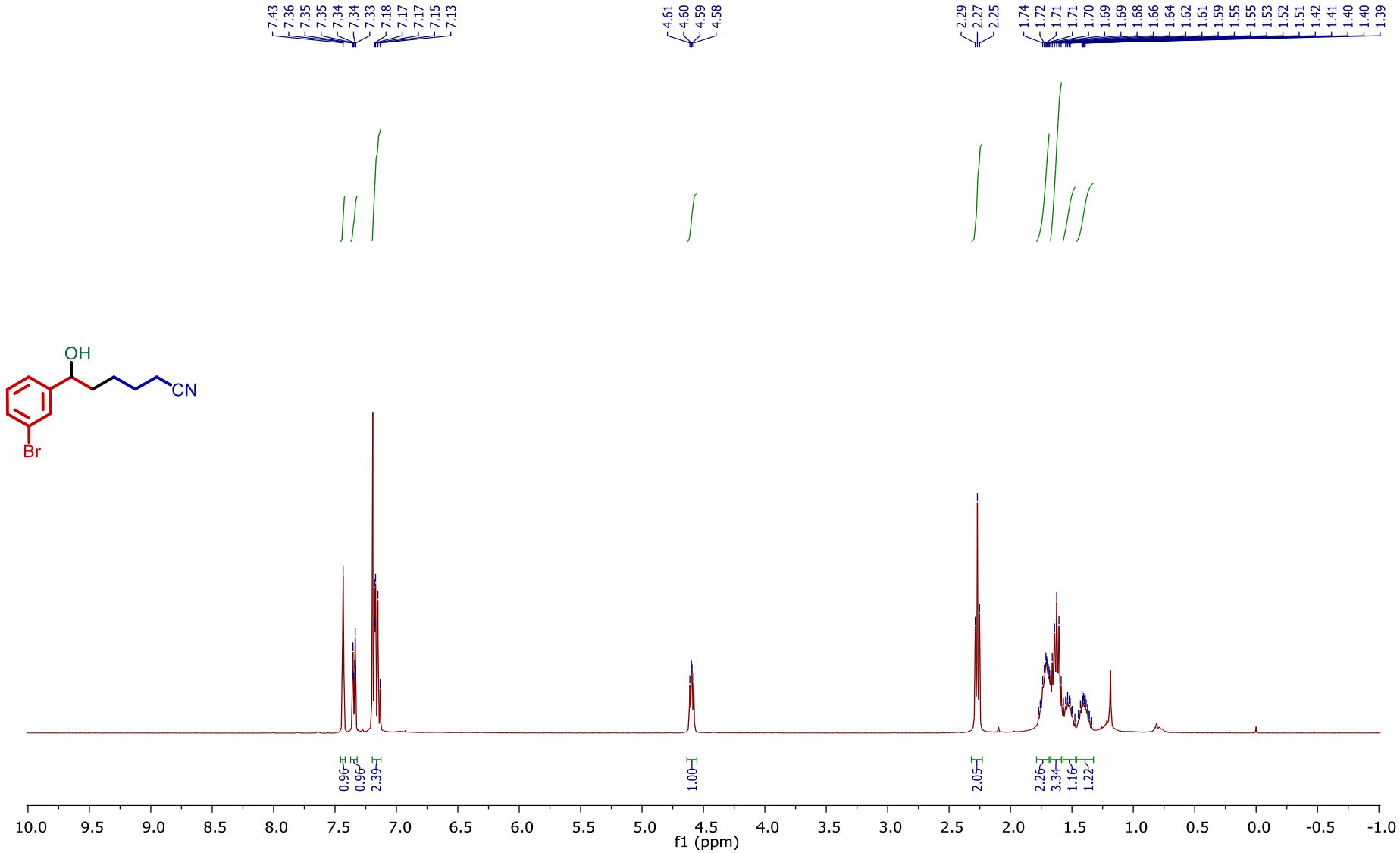
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3da)**



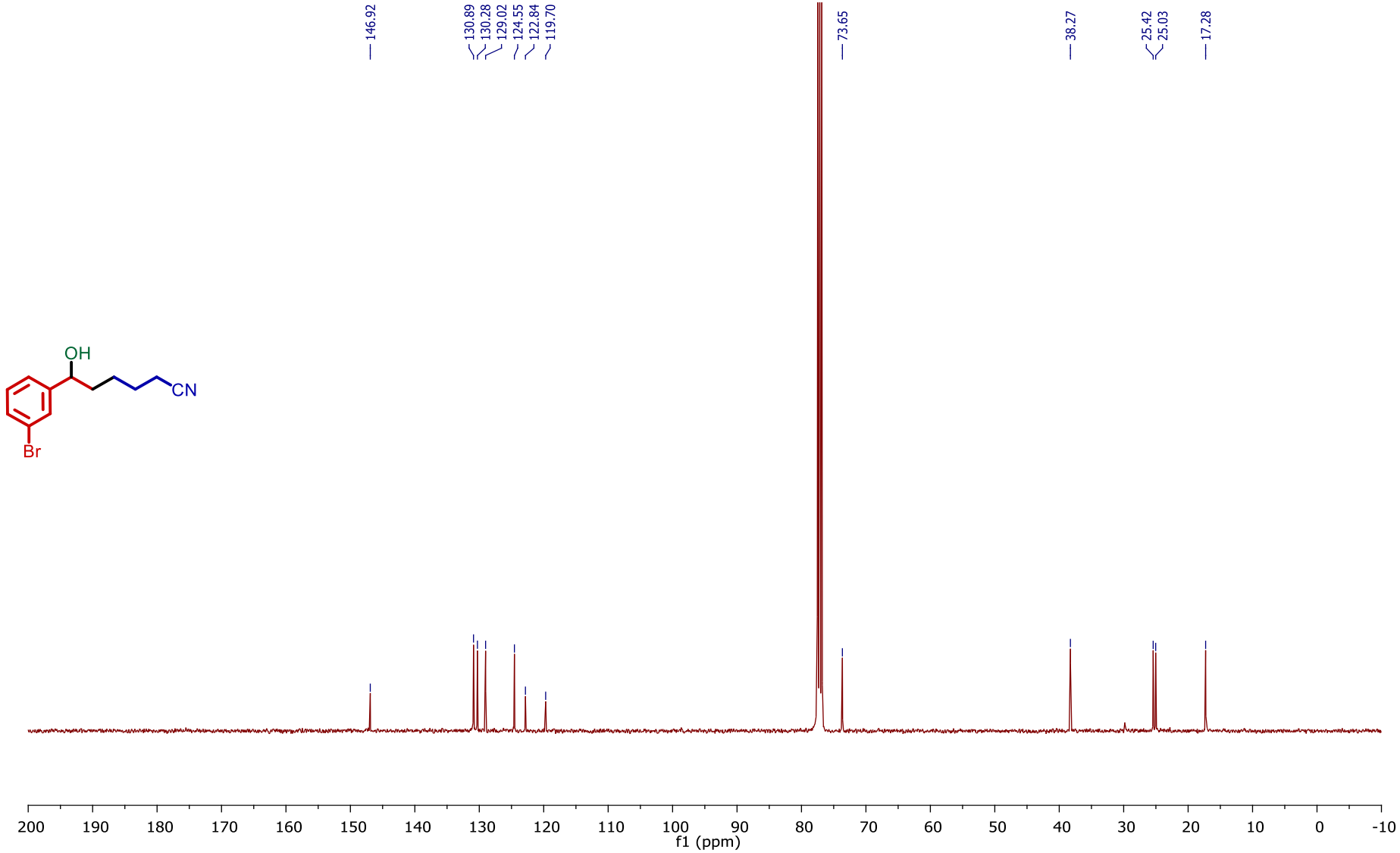
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3da)**



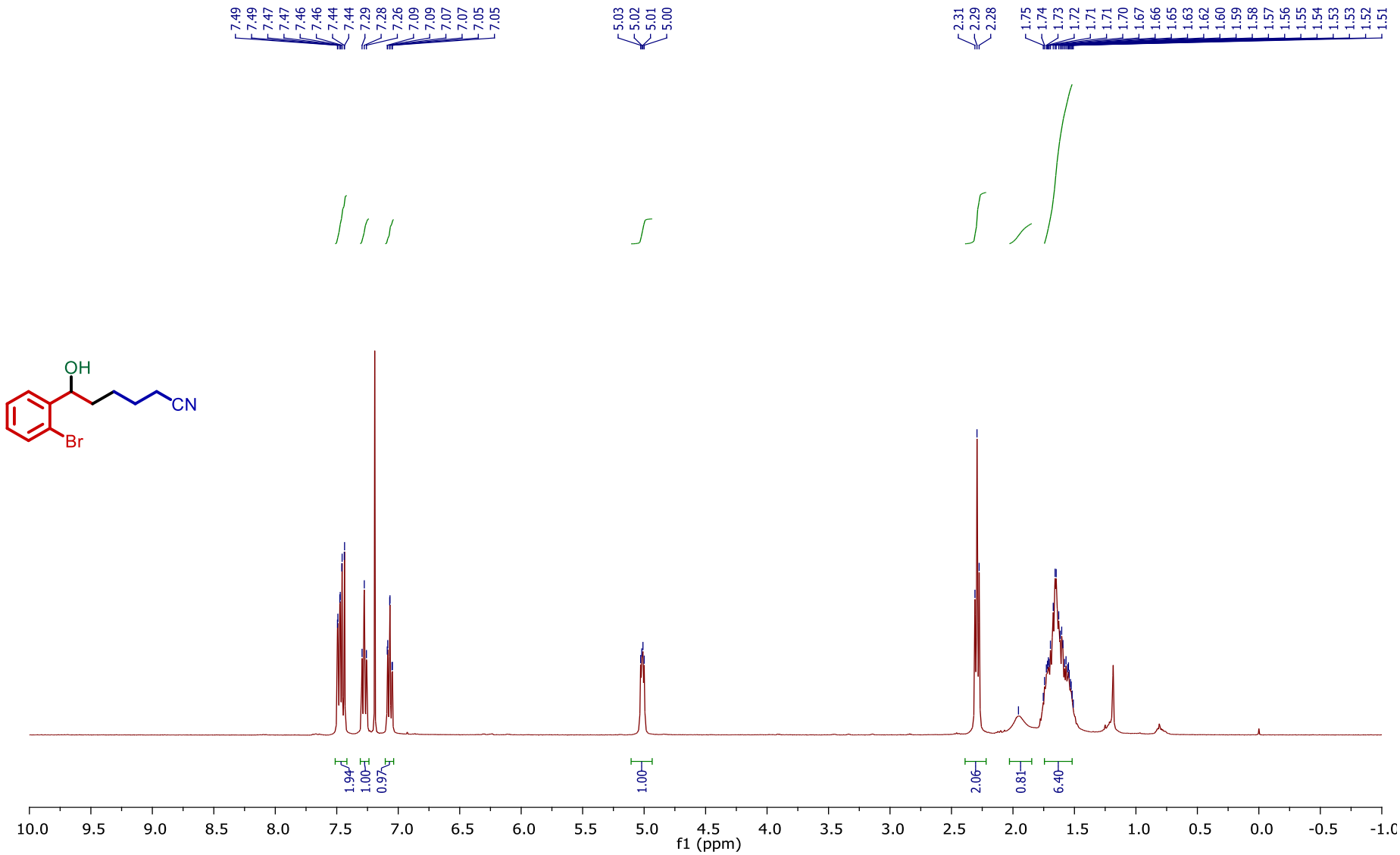
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ea)**



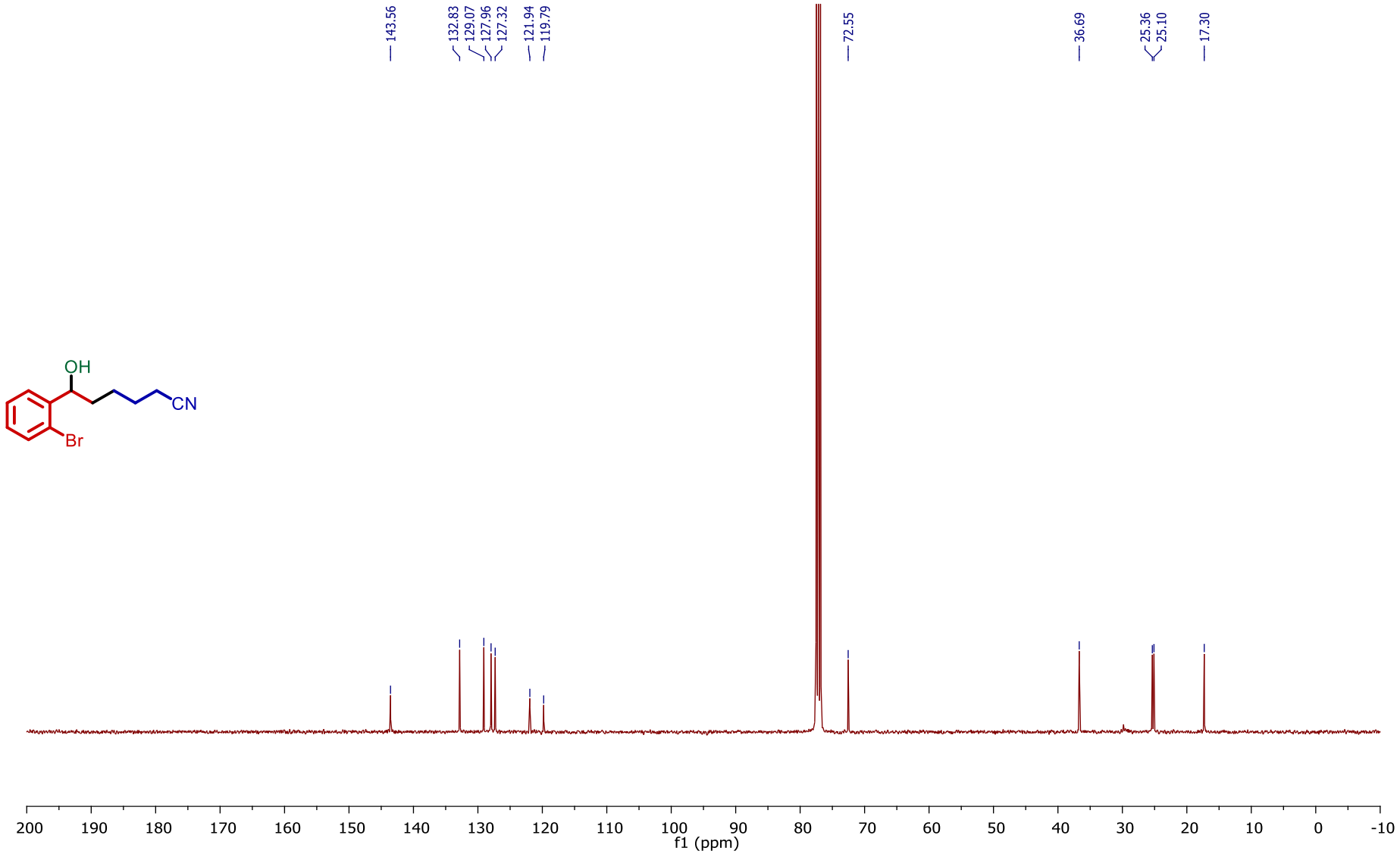
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ea)**



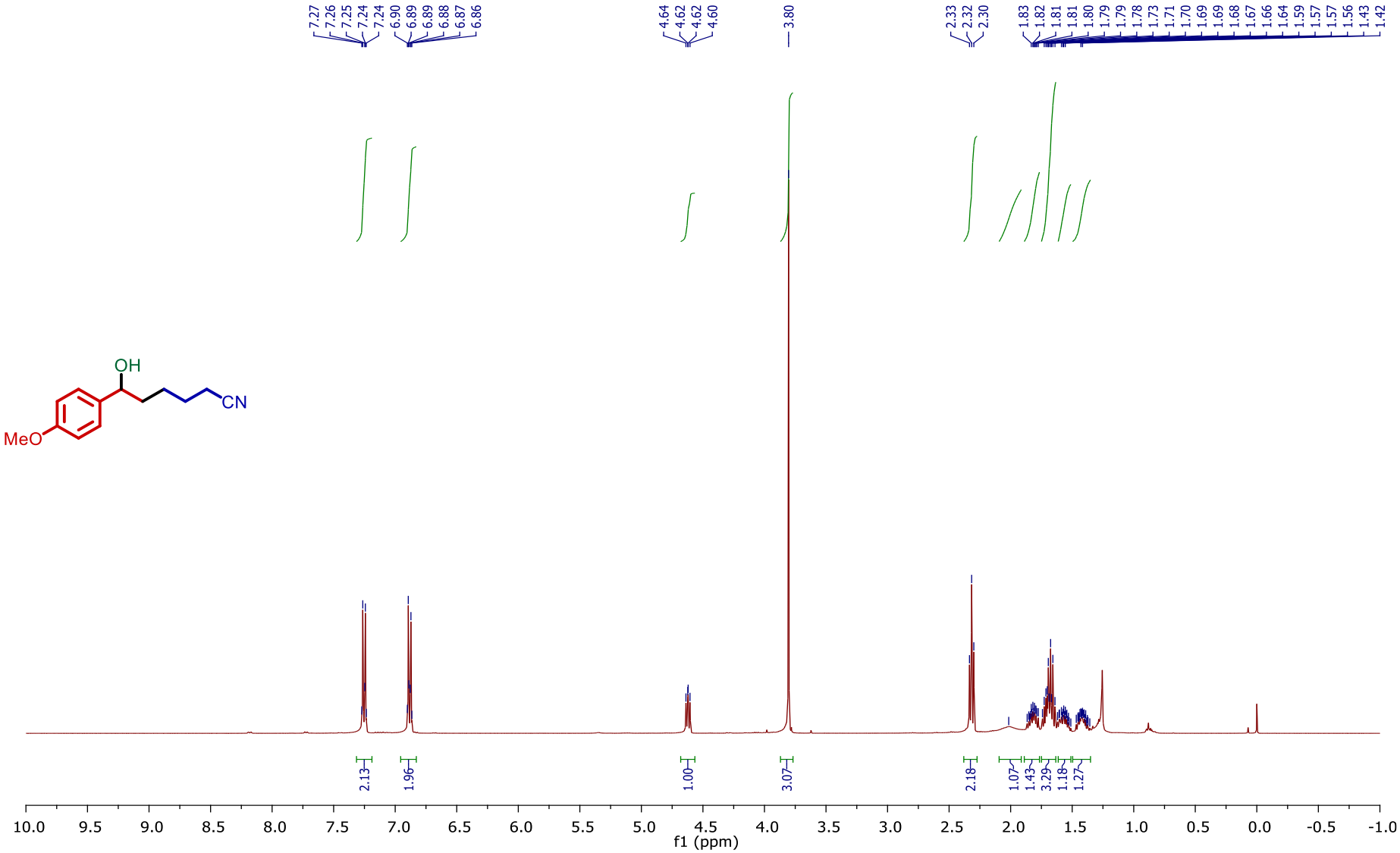
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3fa)**



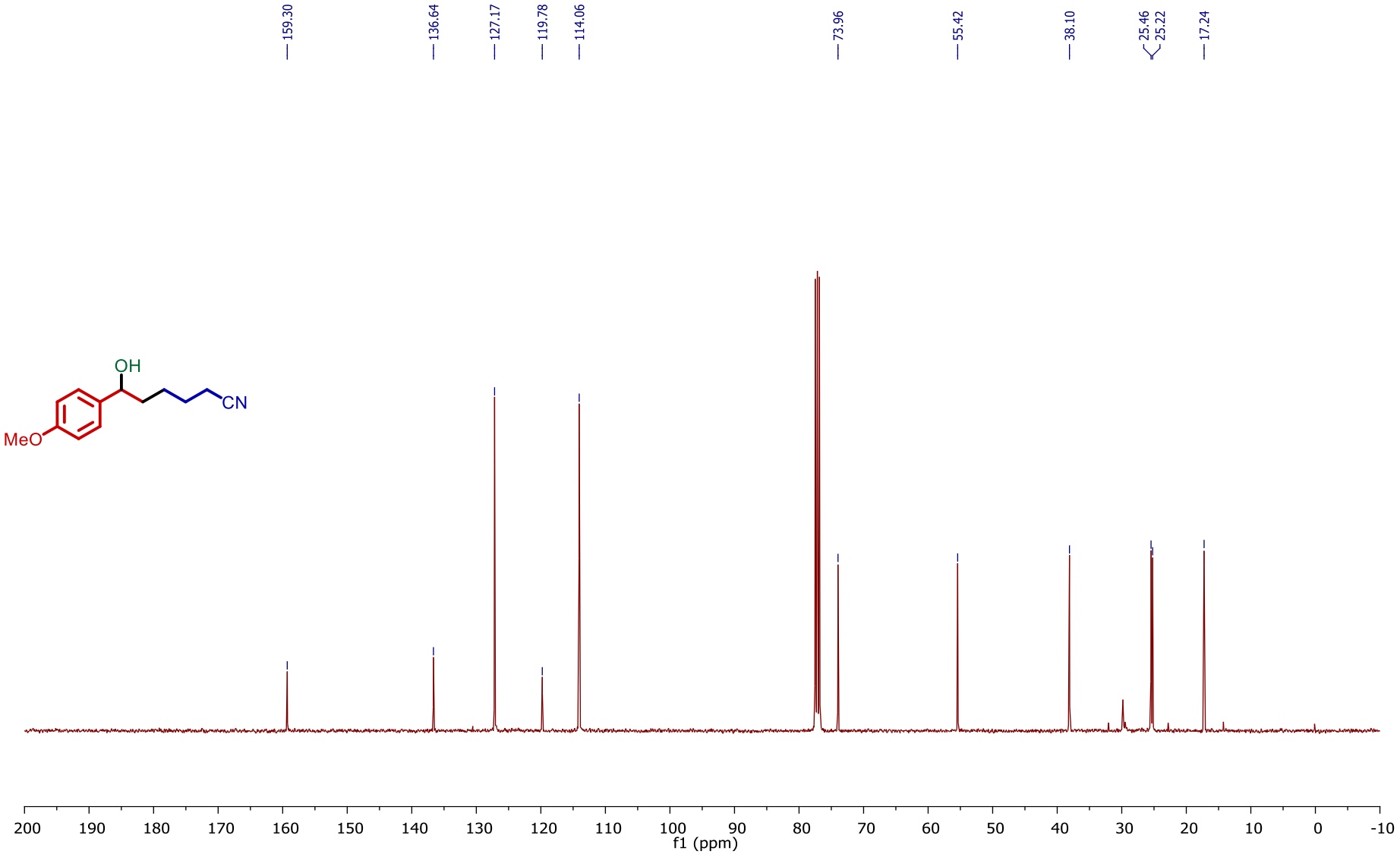
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3fa)**



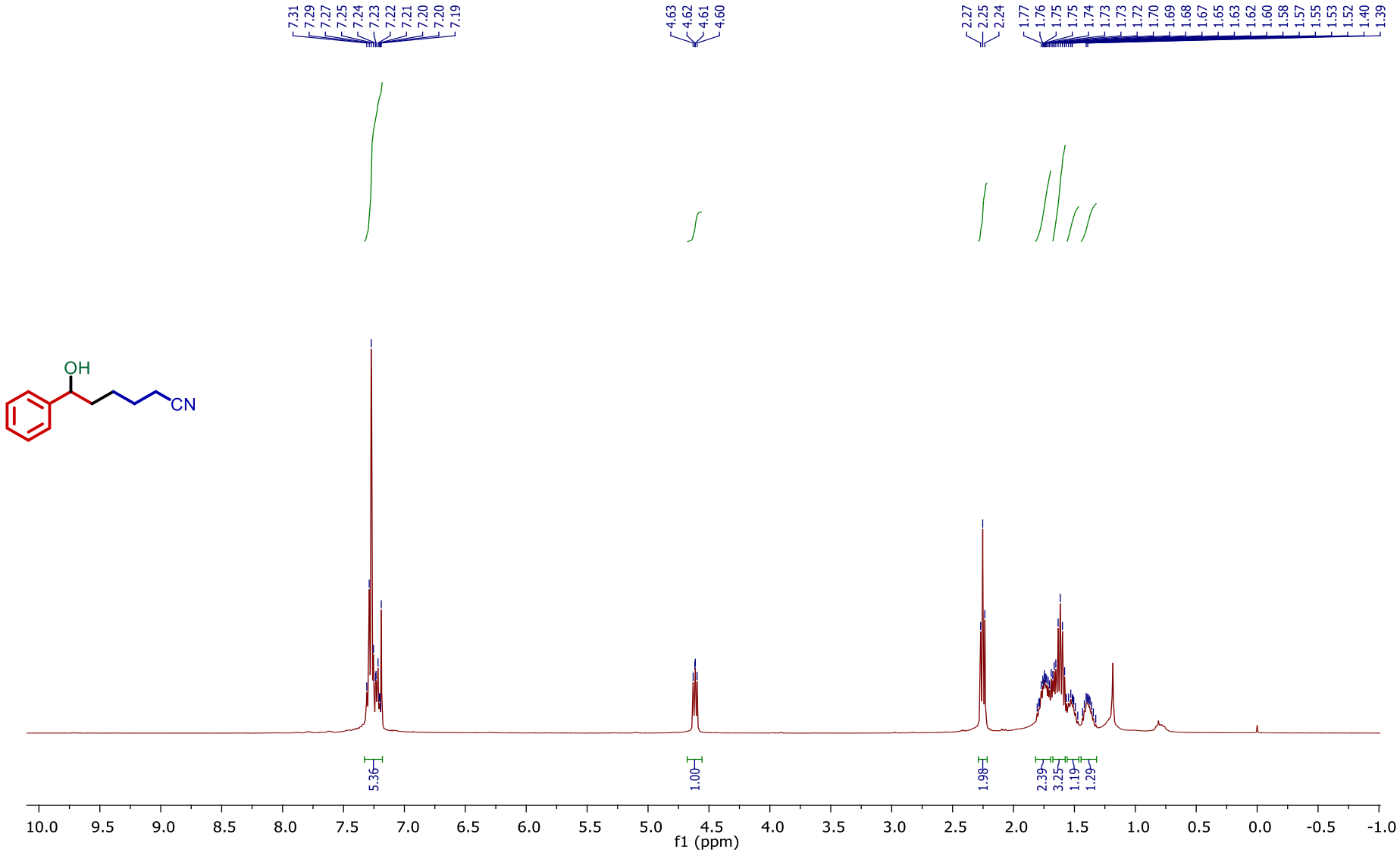
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ga)**



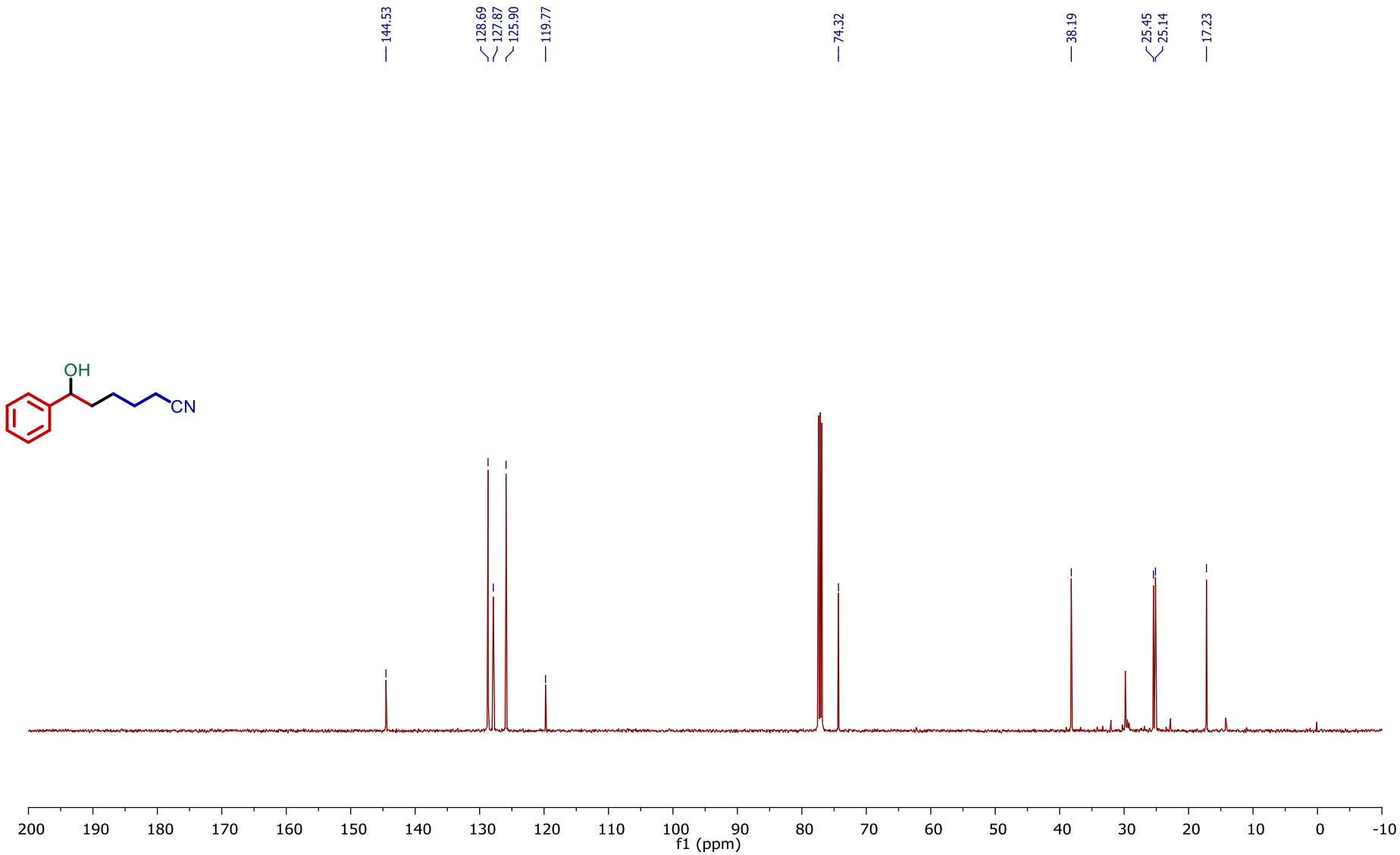
^{13}C NMR (101 Mz, $CDCl_3$) Spectrum of Compound **(3ga)**



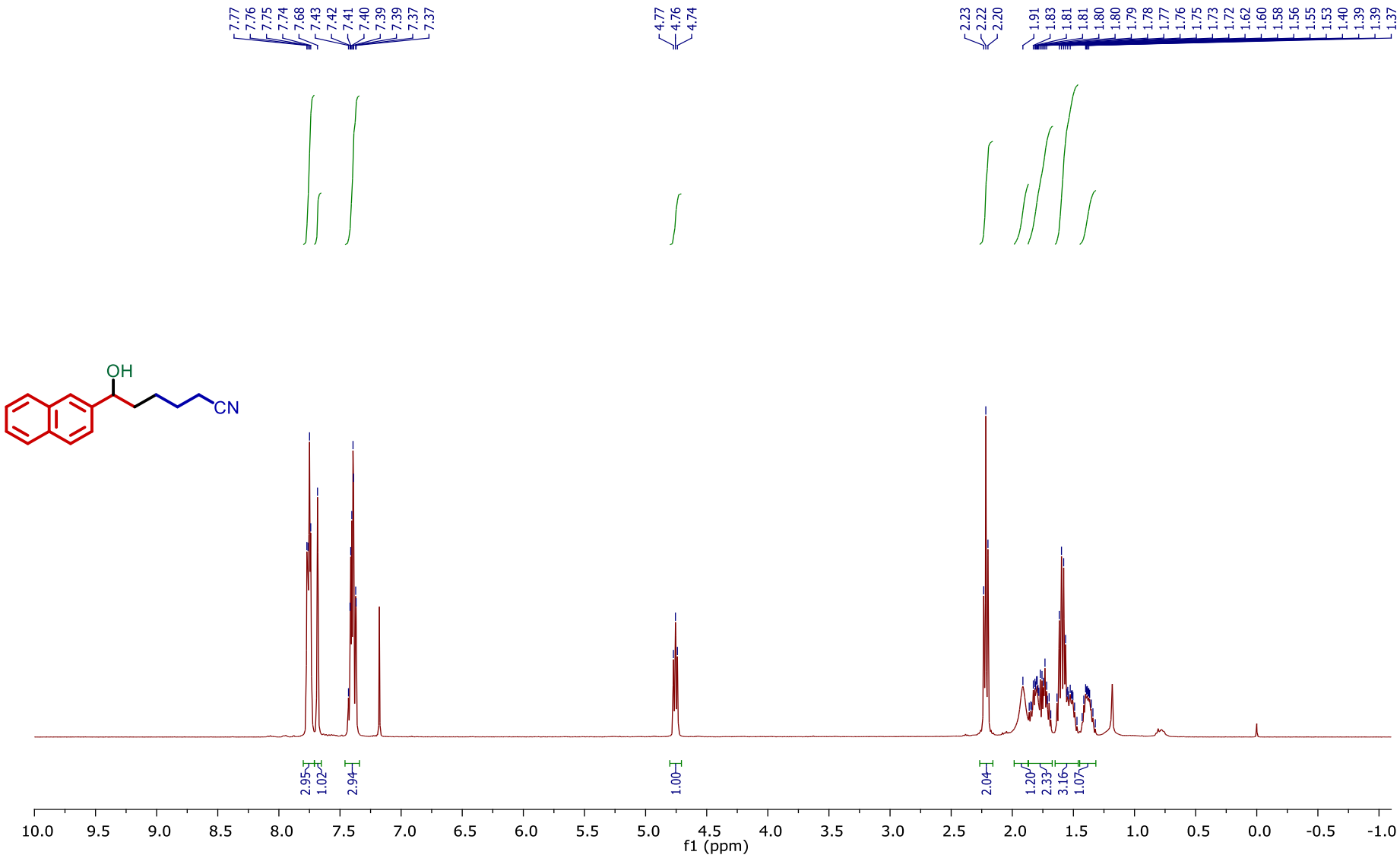
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ha)**



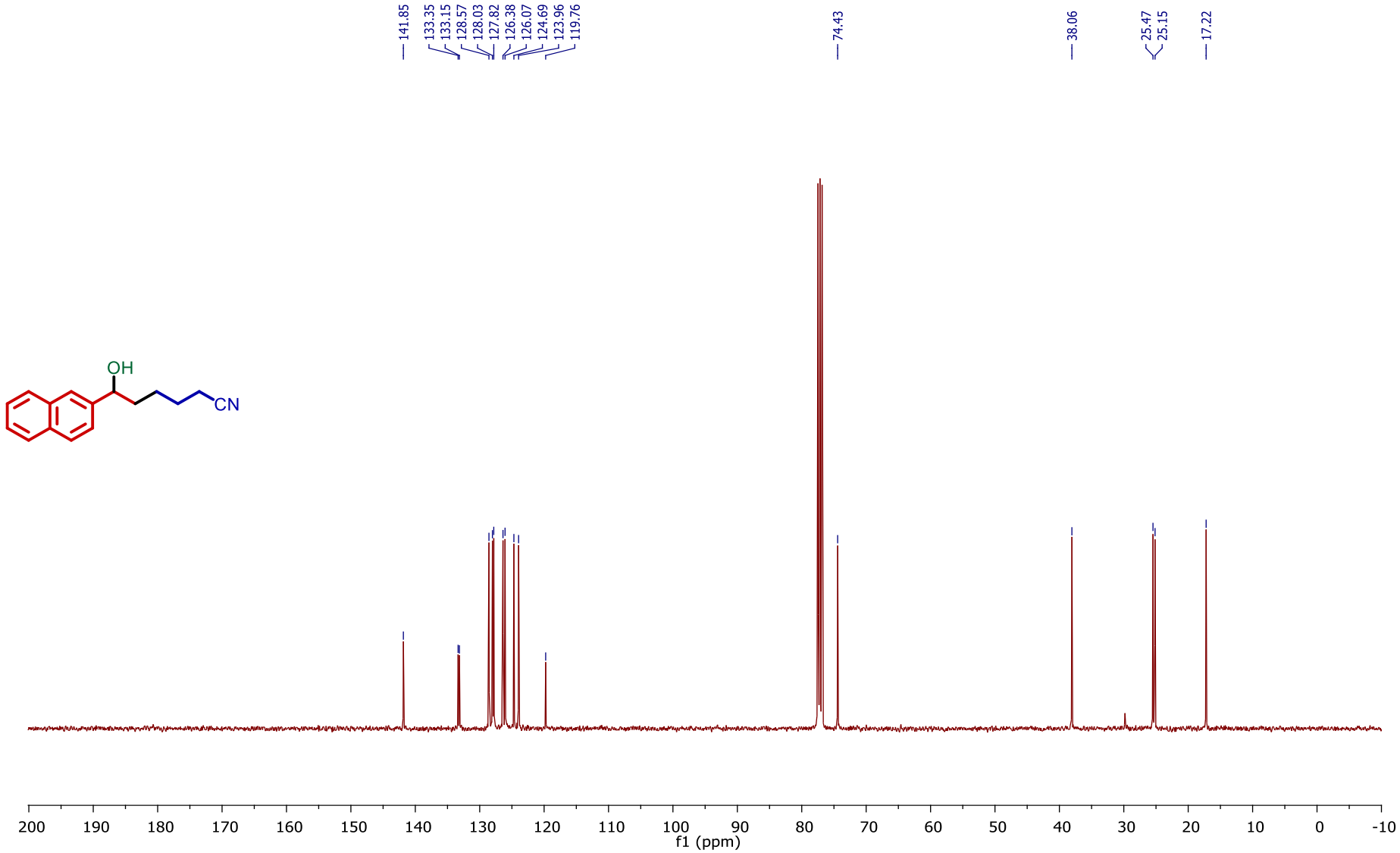
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ha)**



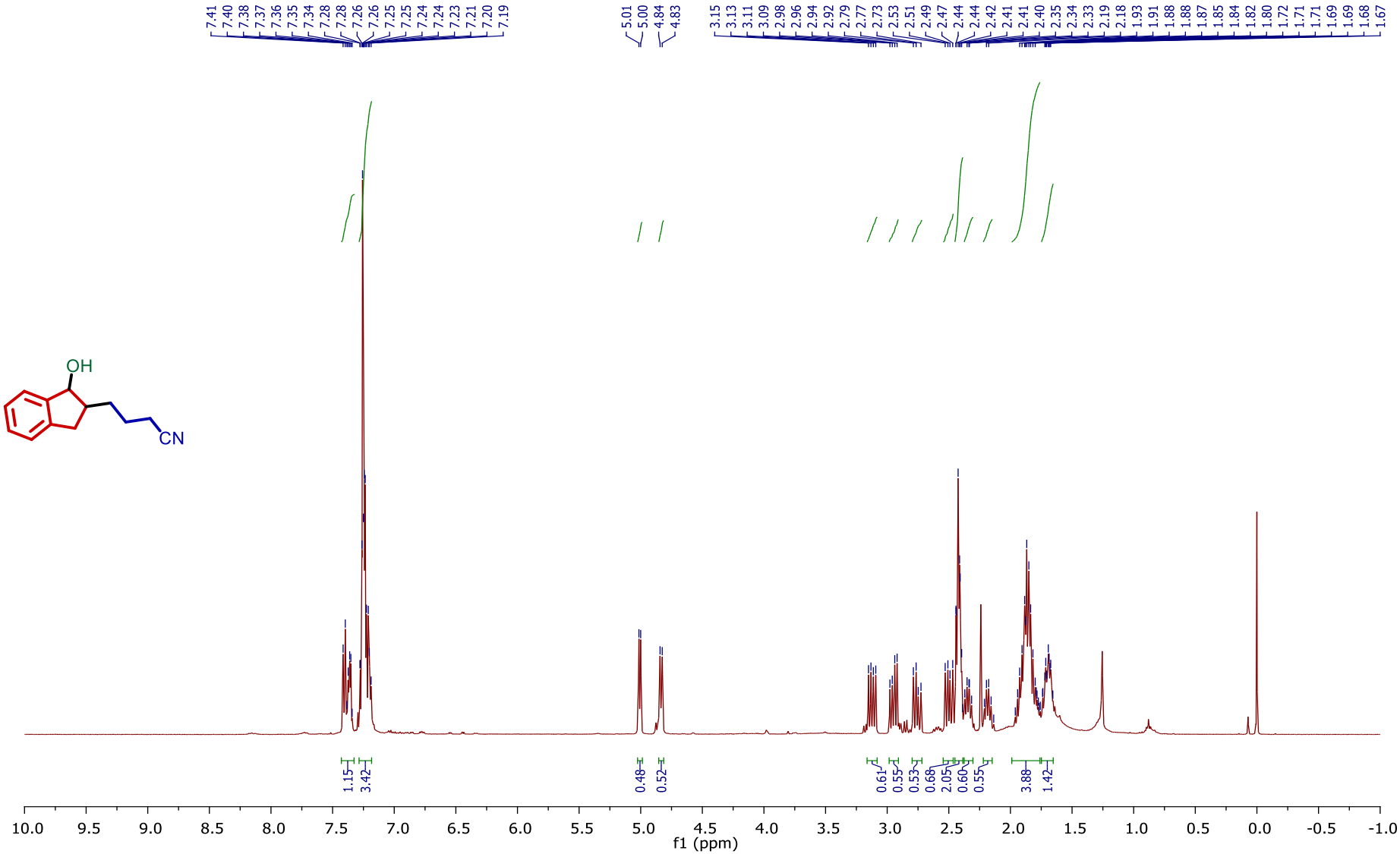
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ia)**



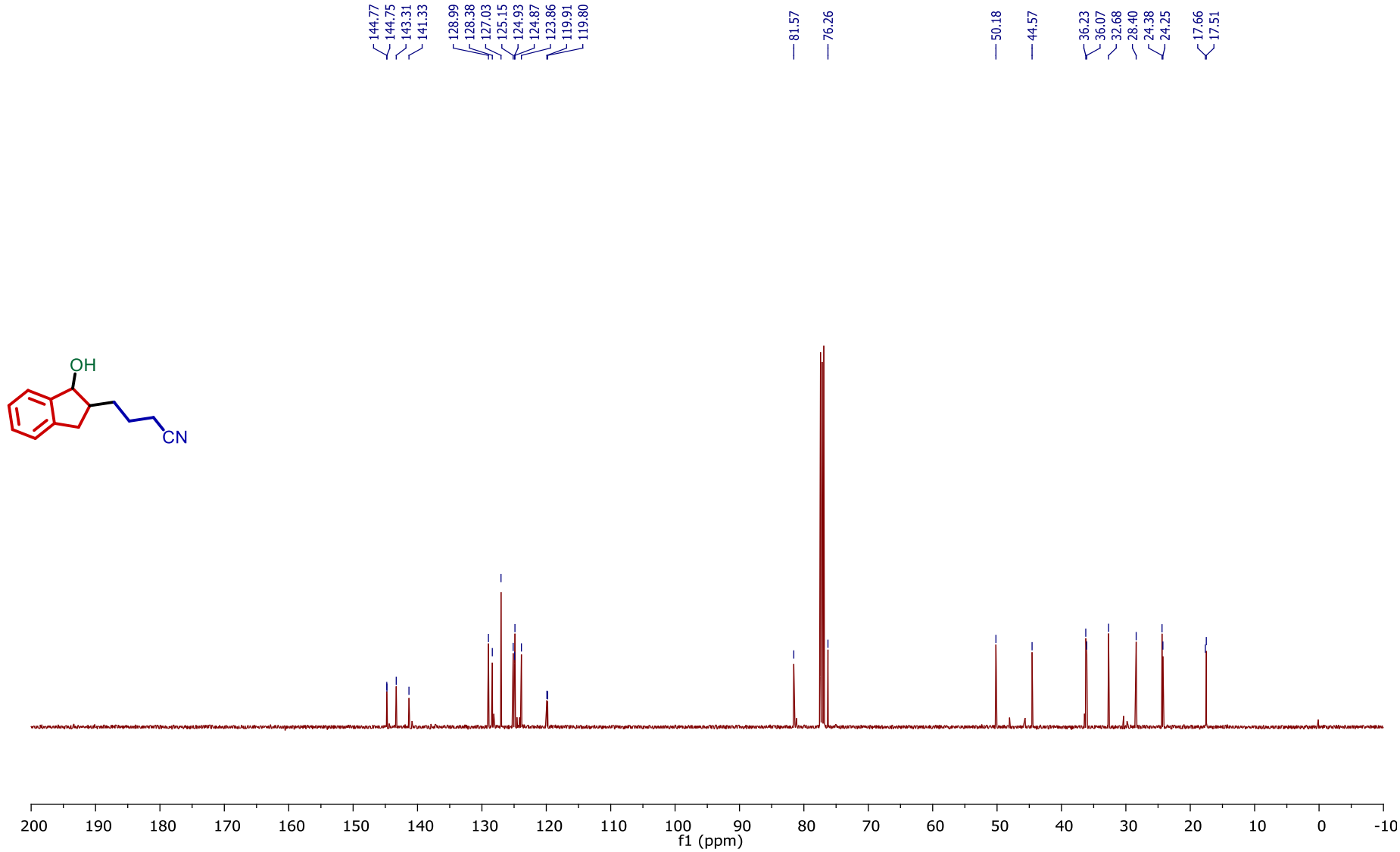
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ia)**



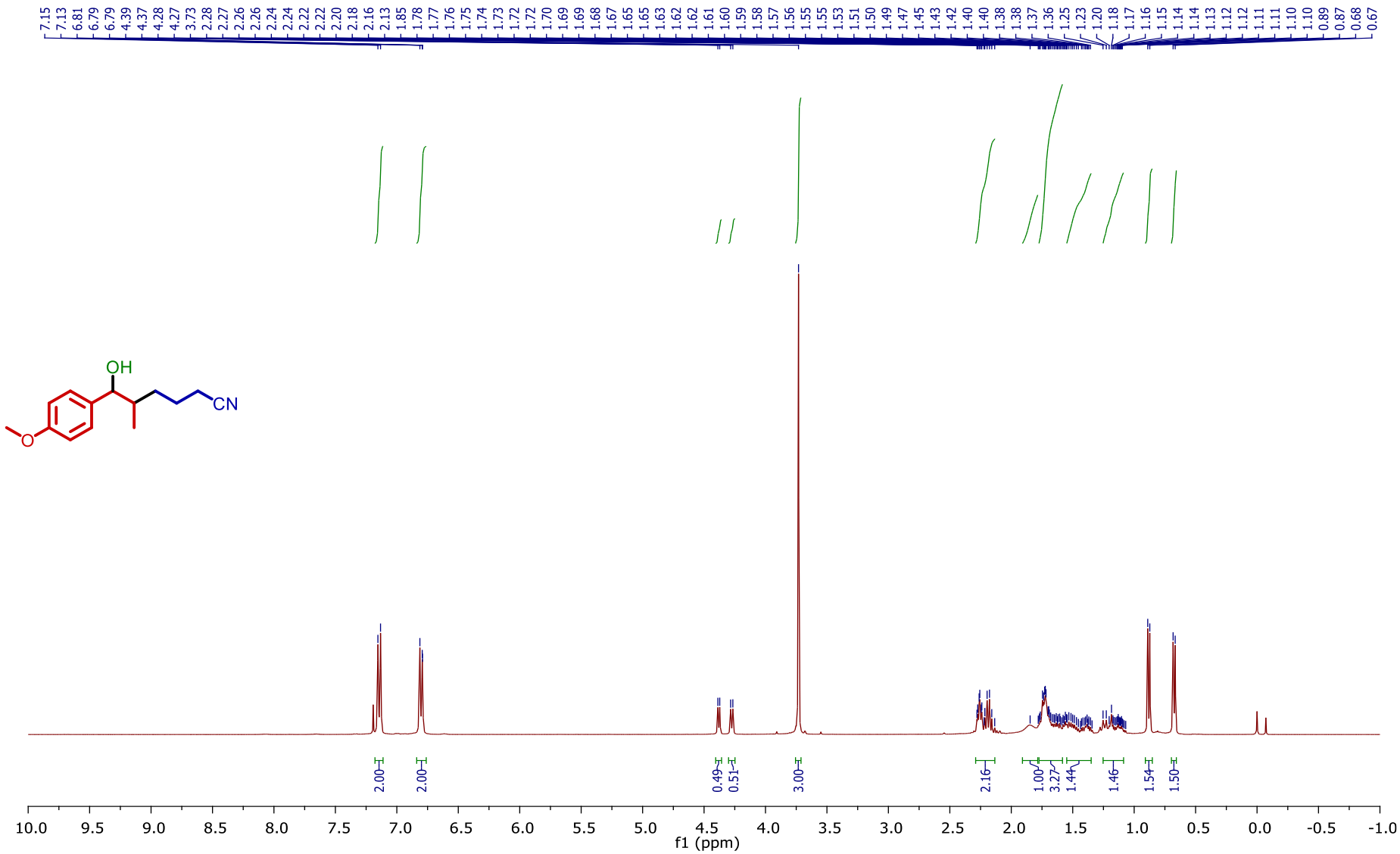
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ja)**



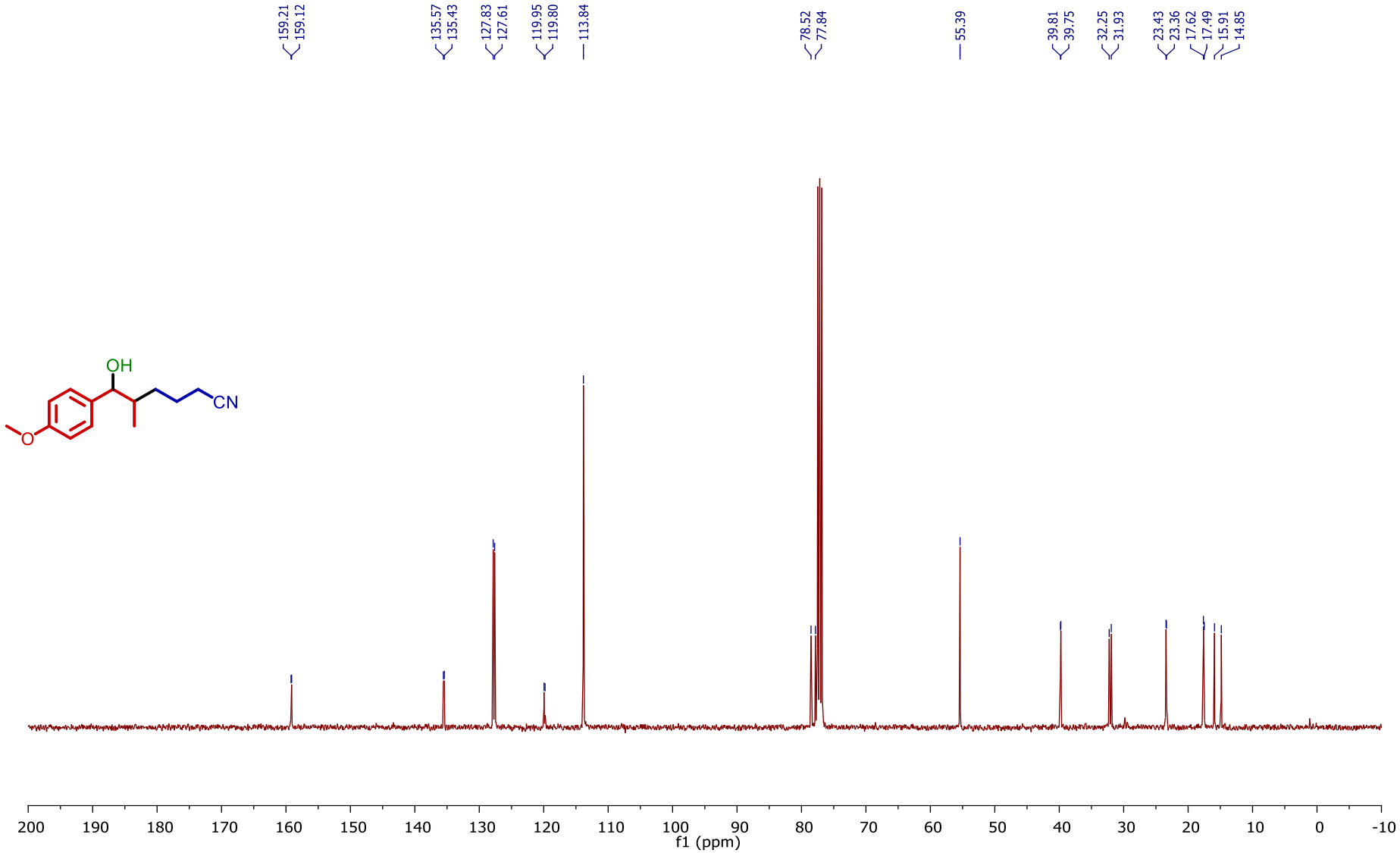
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ja)**



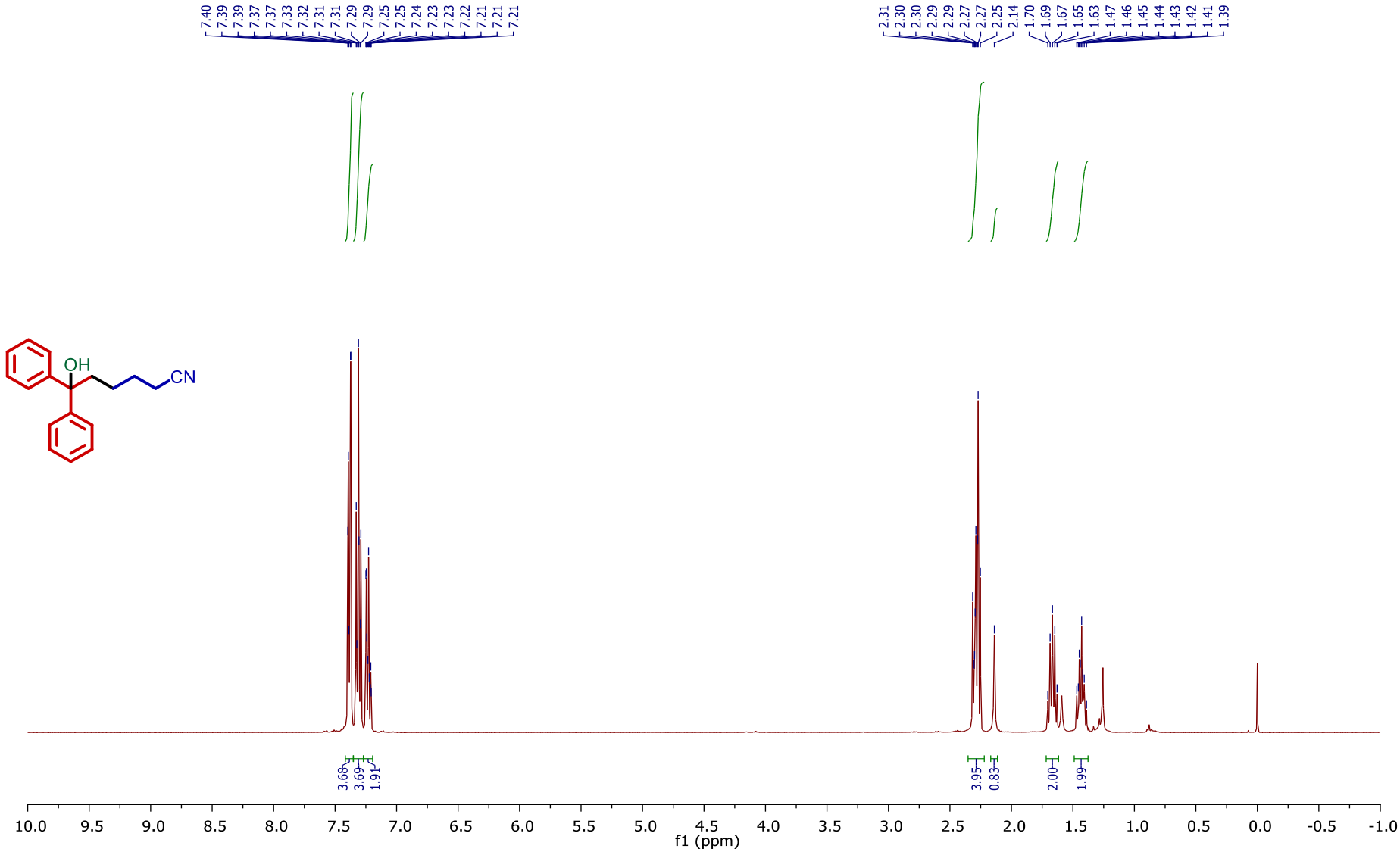
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ka)**



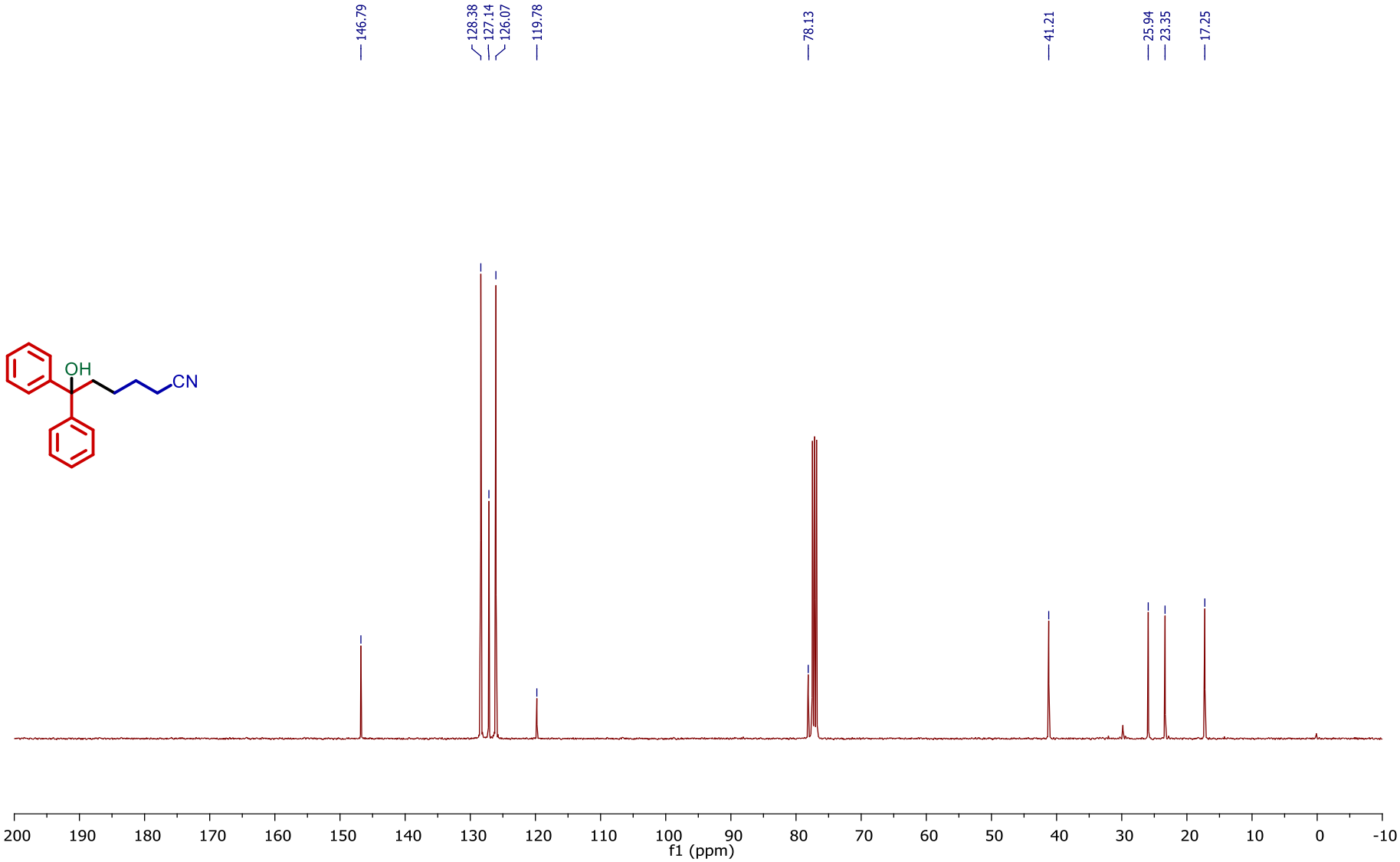
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ka)**



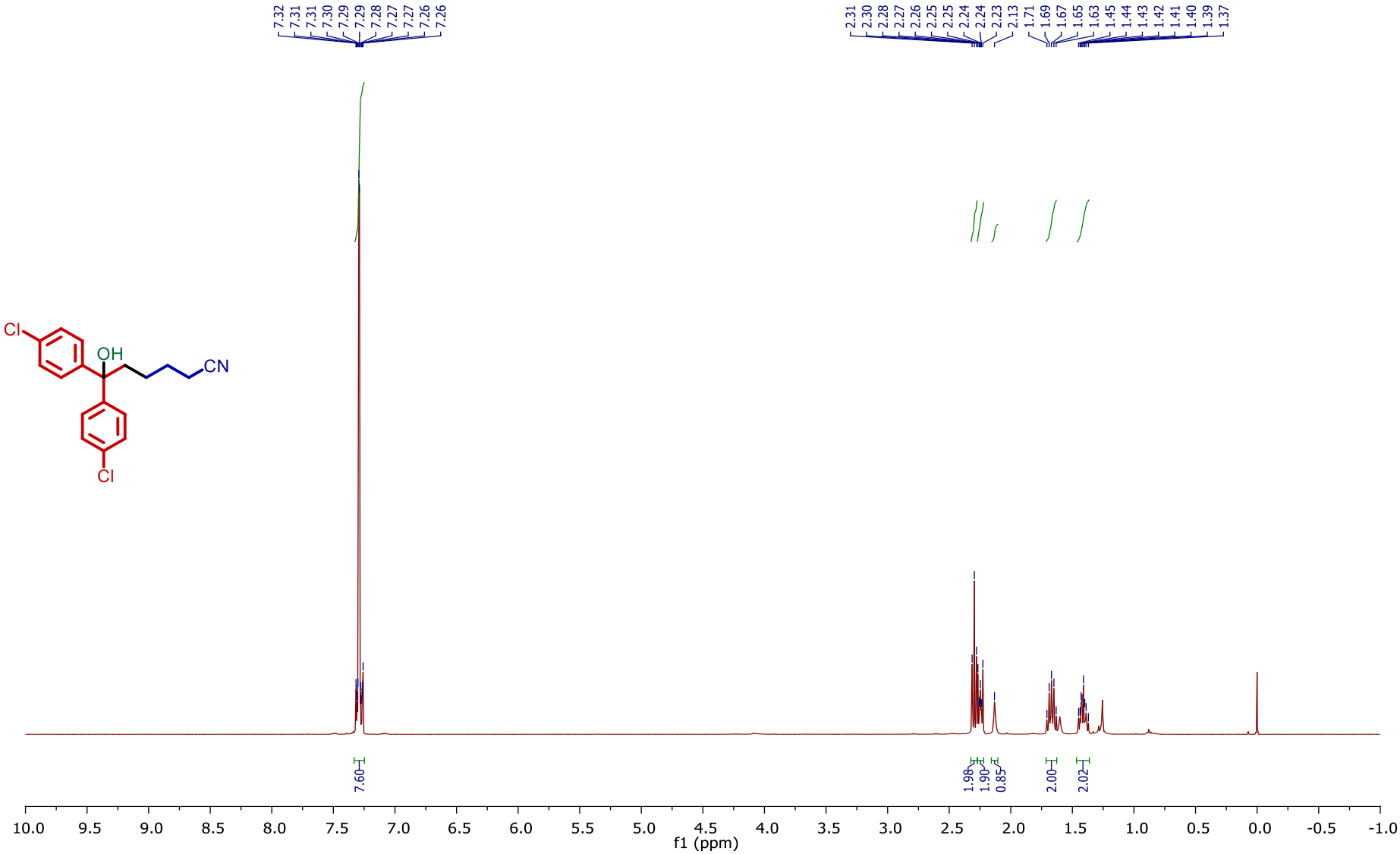
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3la)**



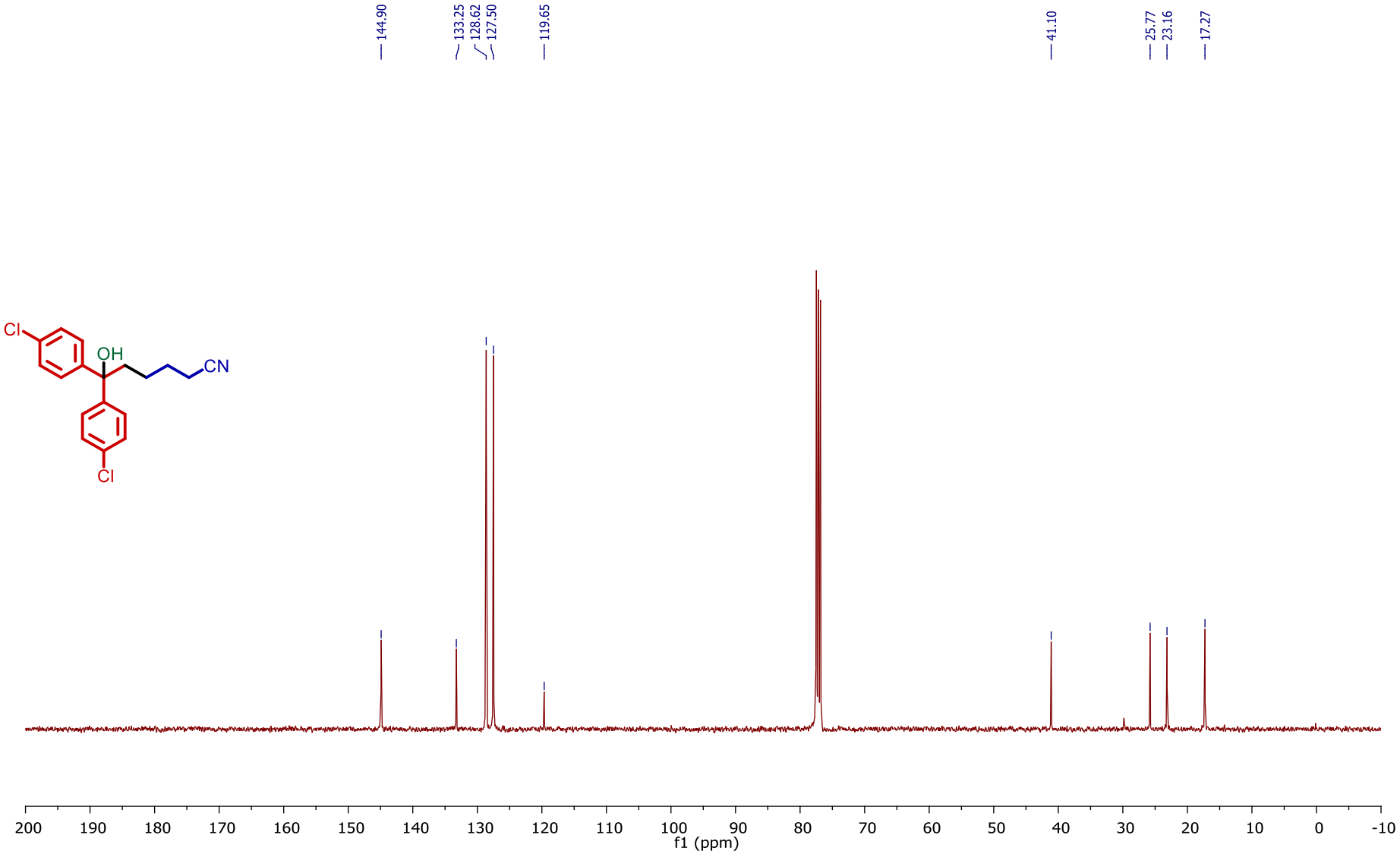
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3la)**



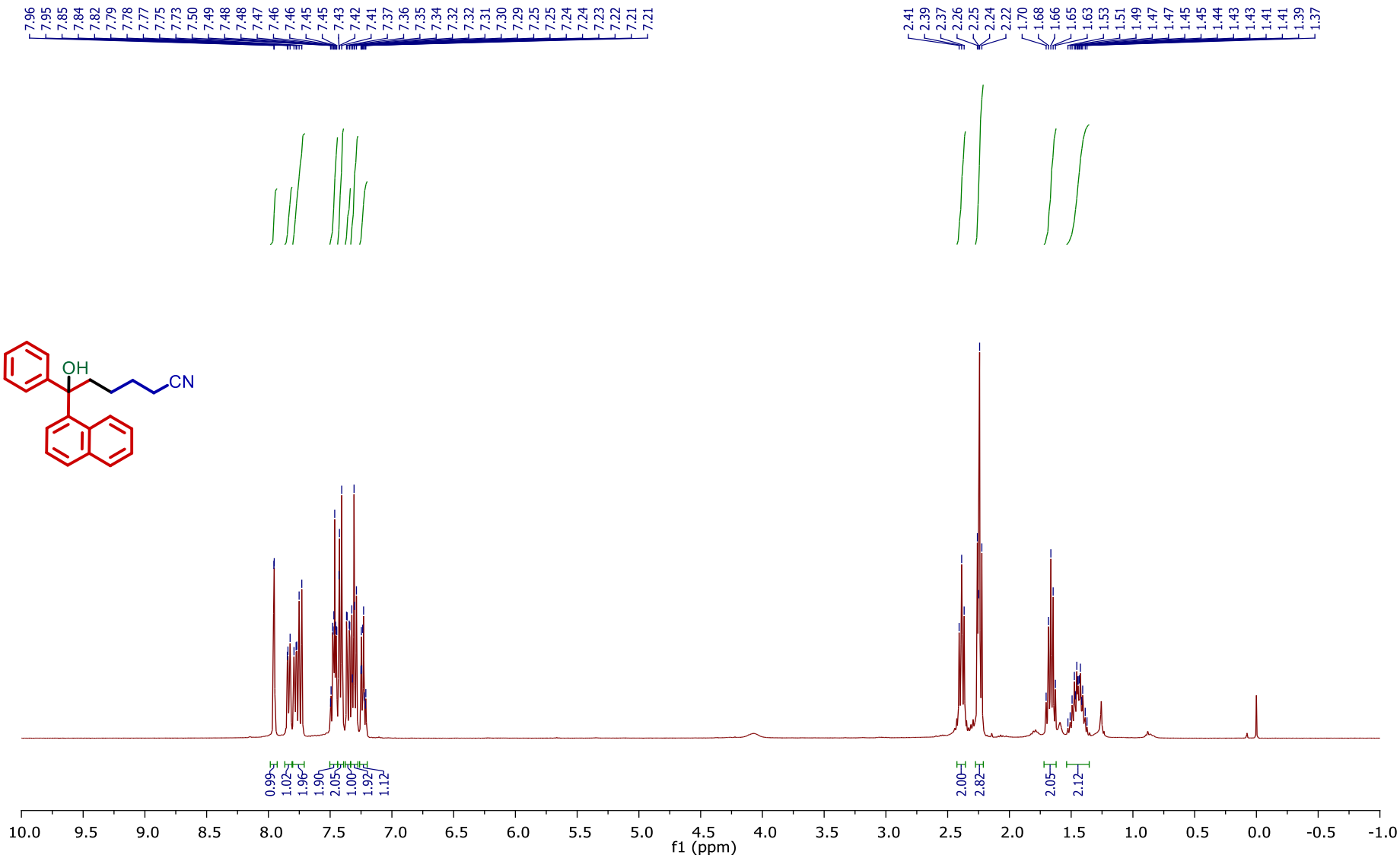
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ma)**



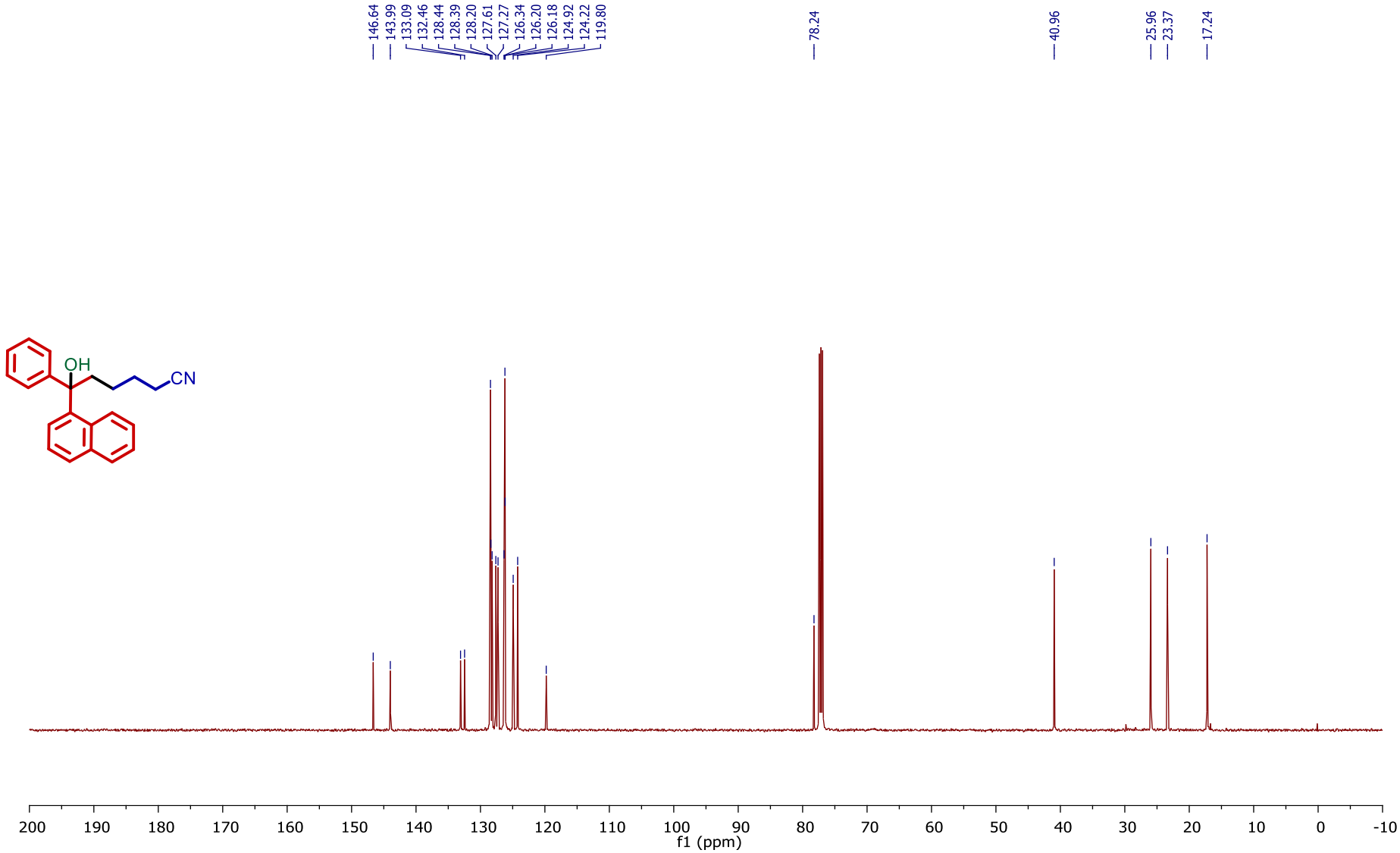
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ma)**



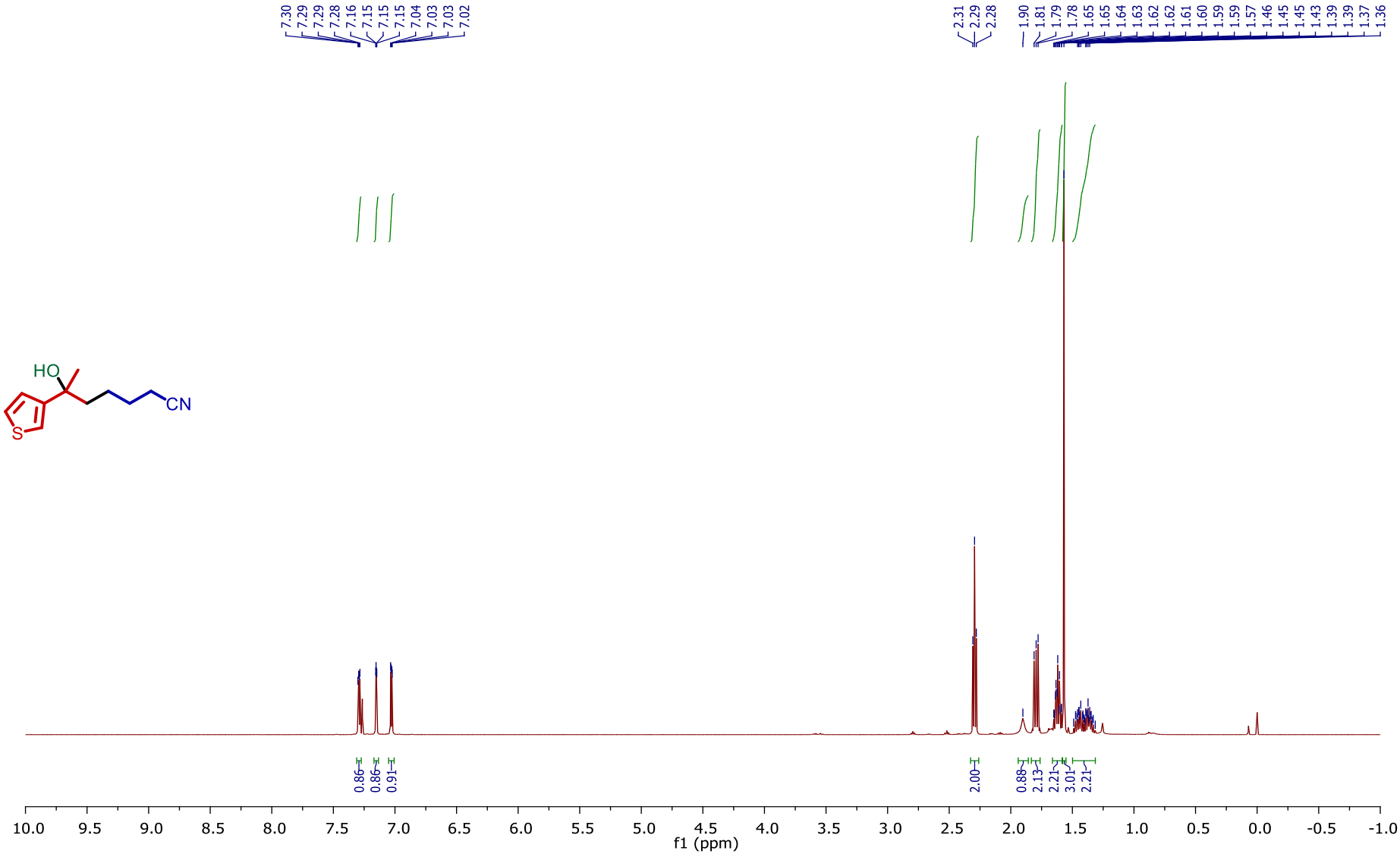
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3na)**



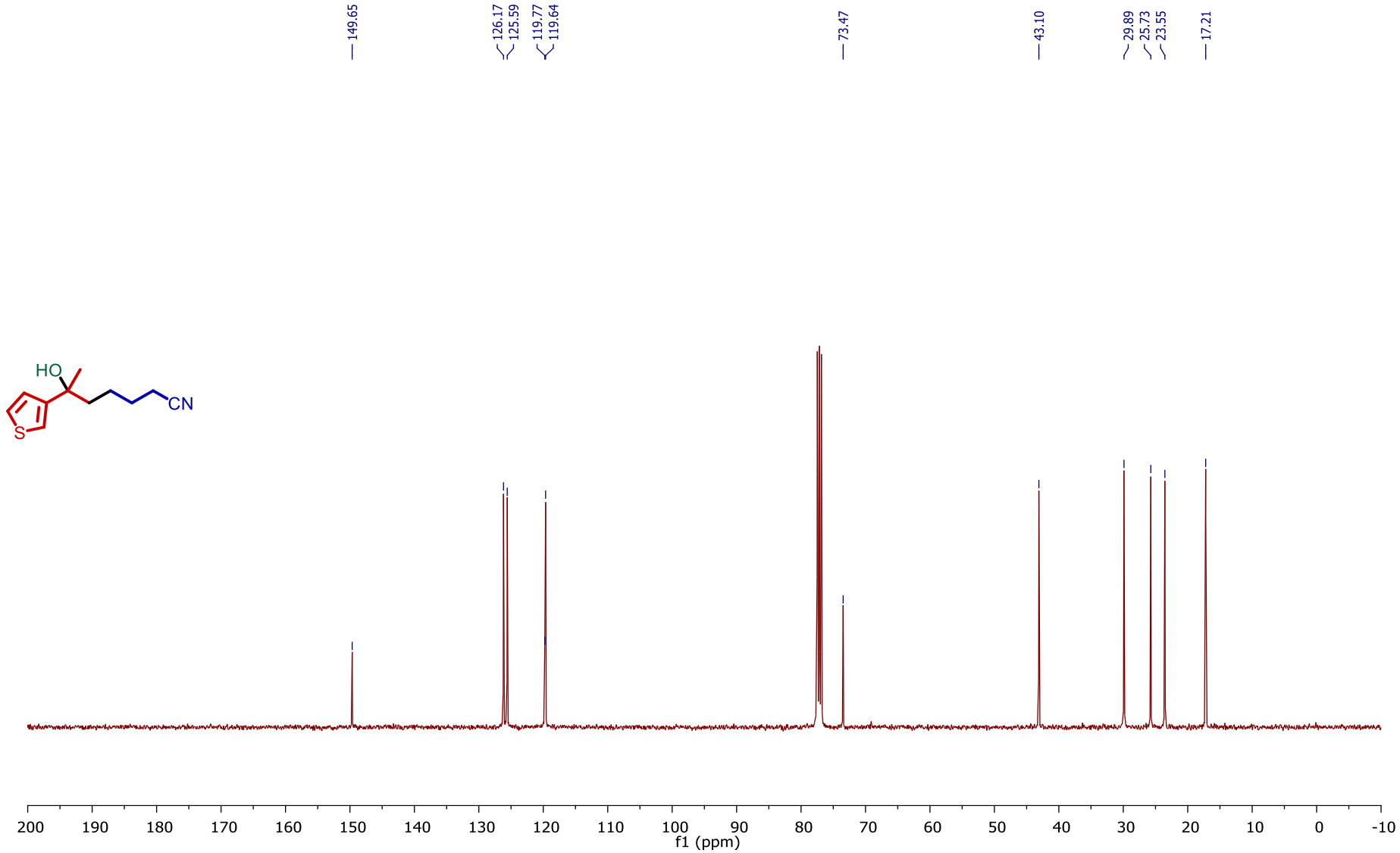
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3na)**



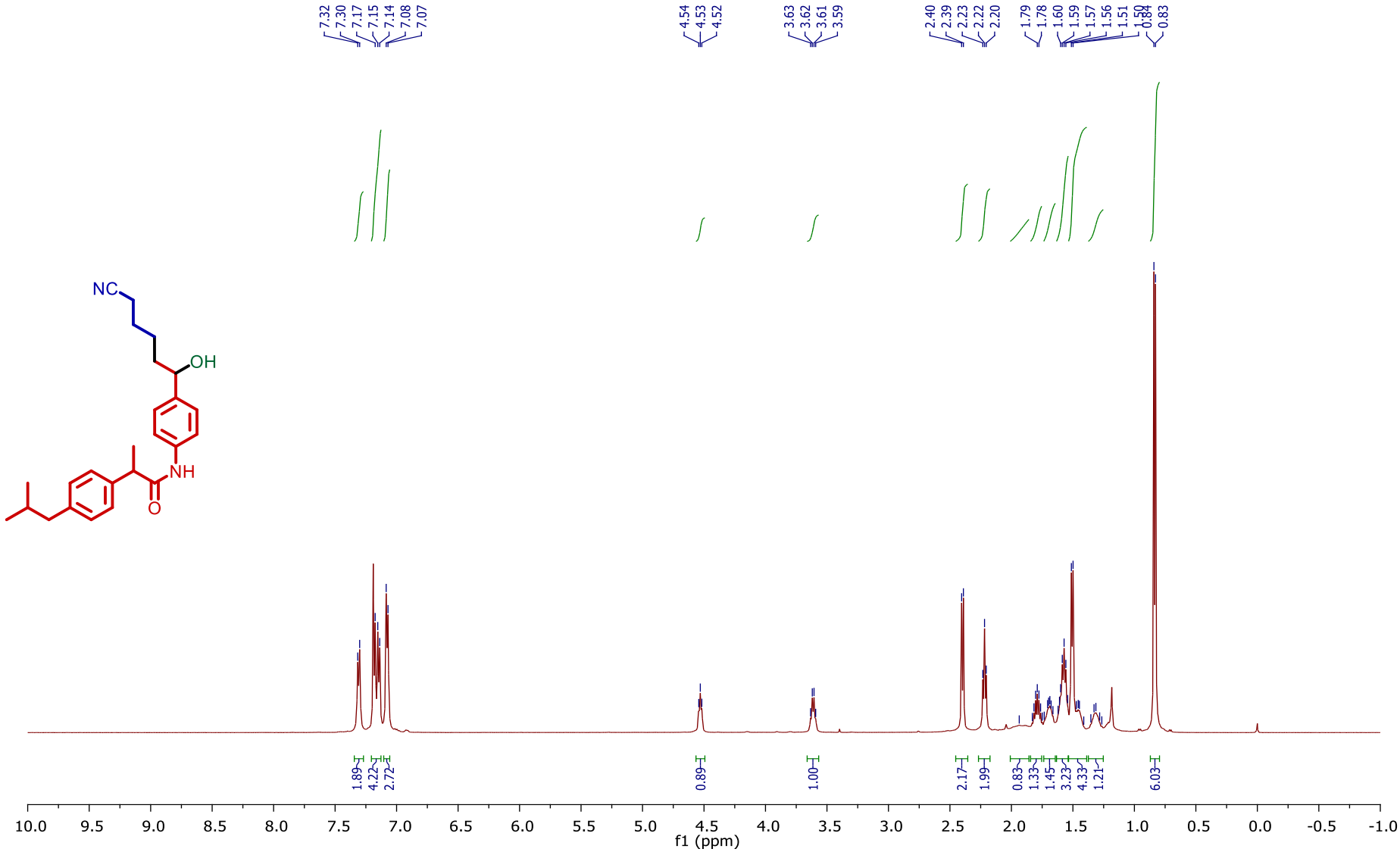
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3oa)**



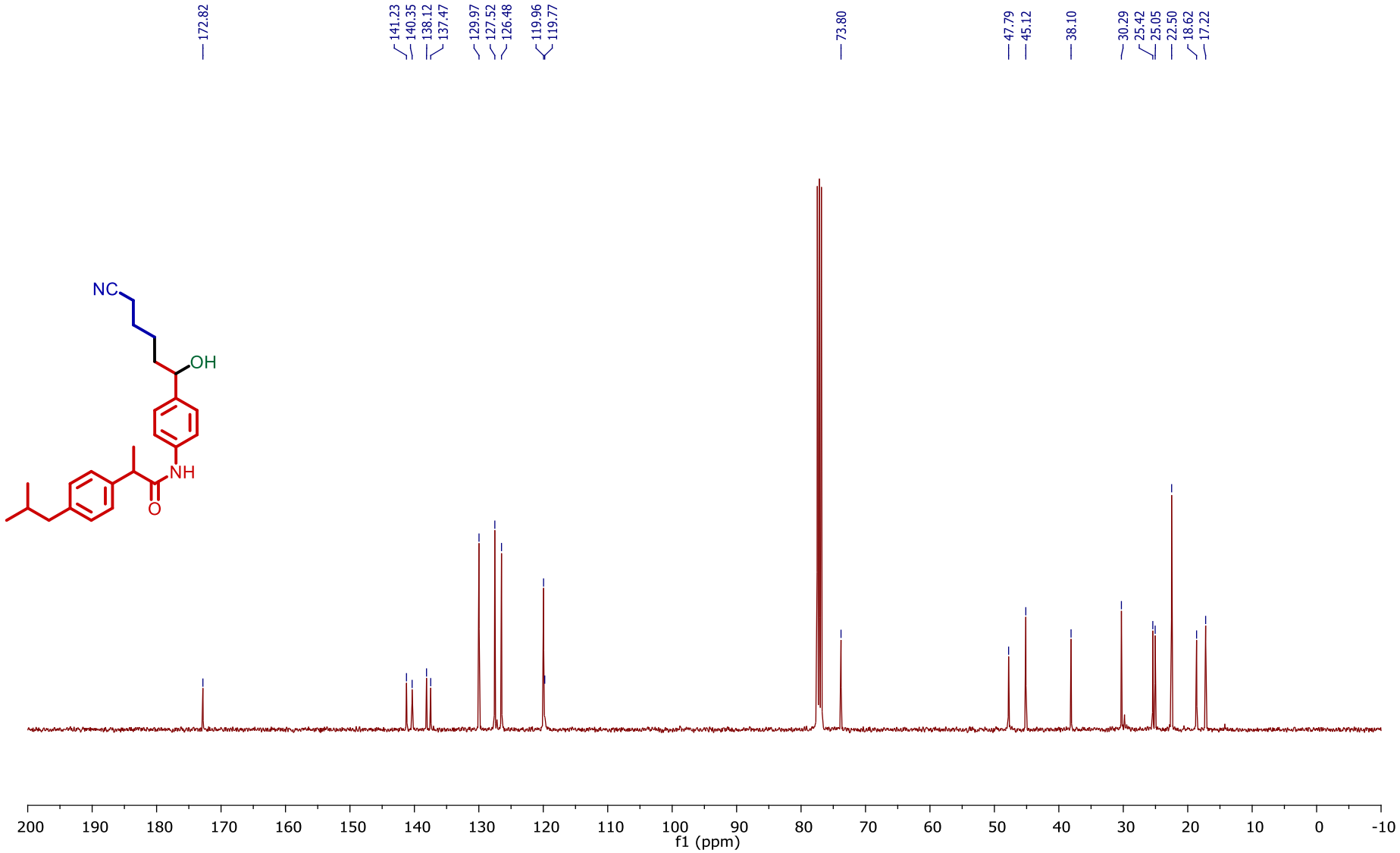
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3oa)**



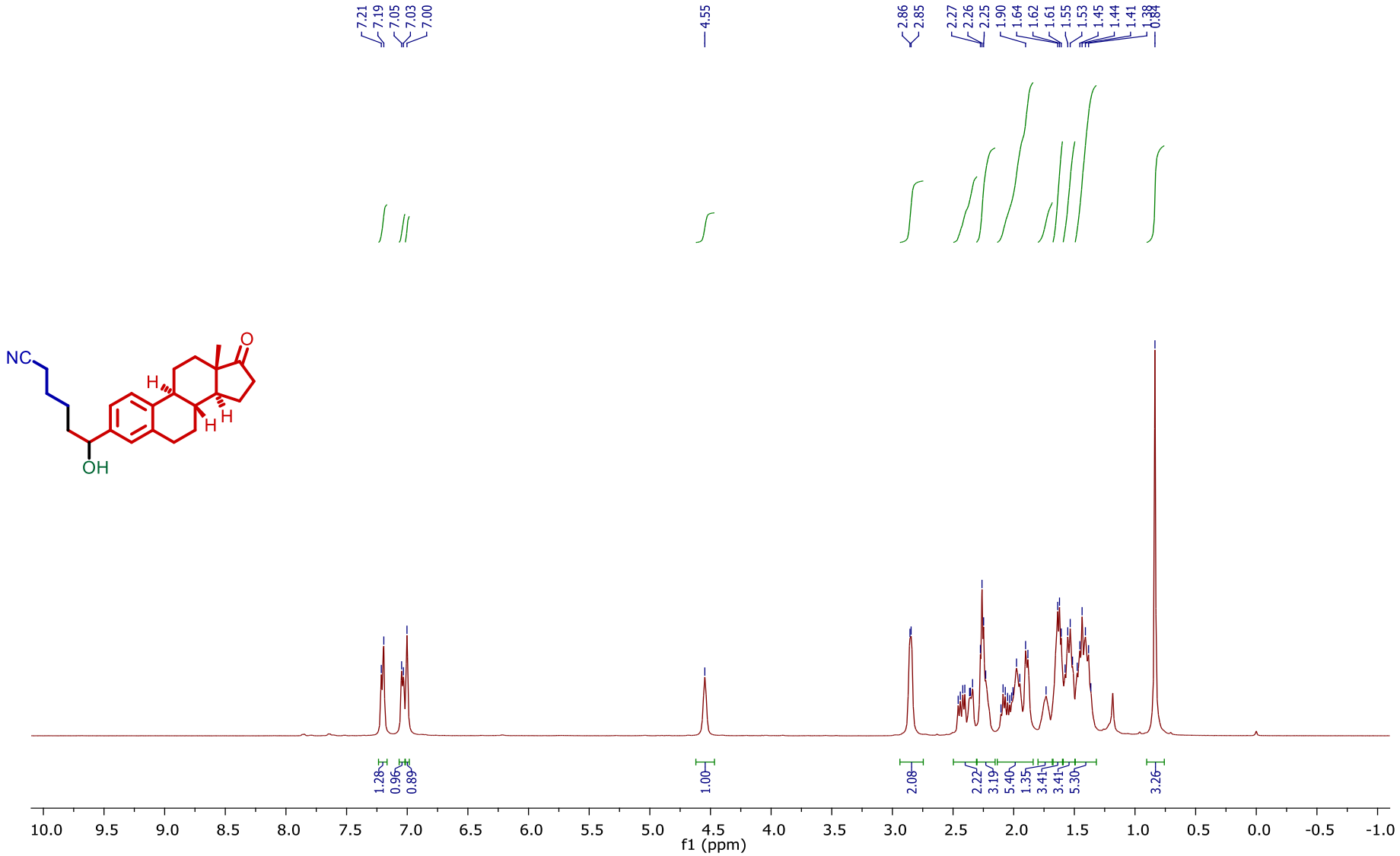
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3pa)**



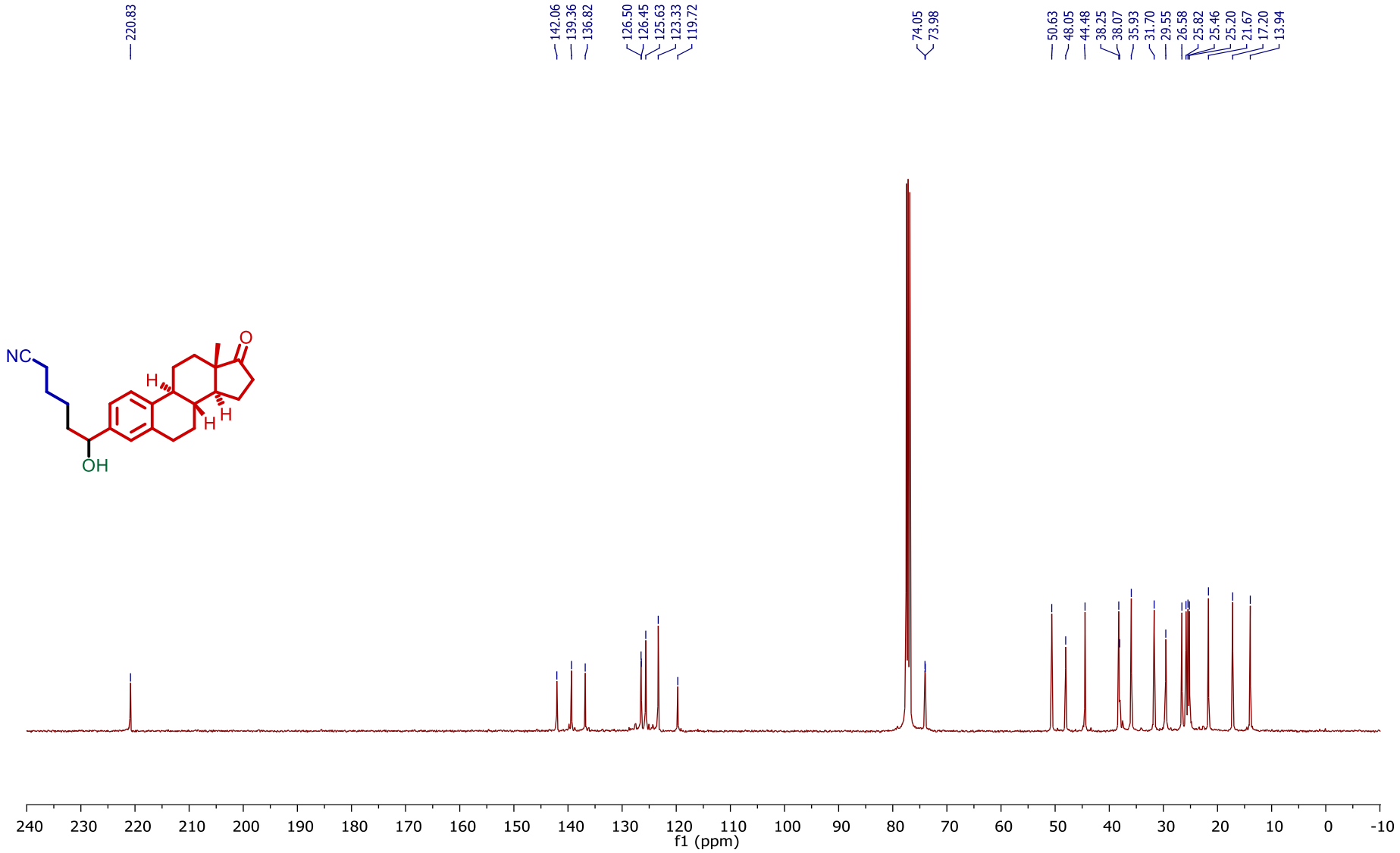
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3pa)**



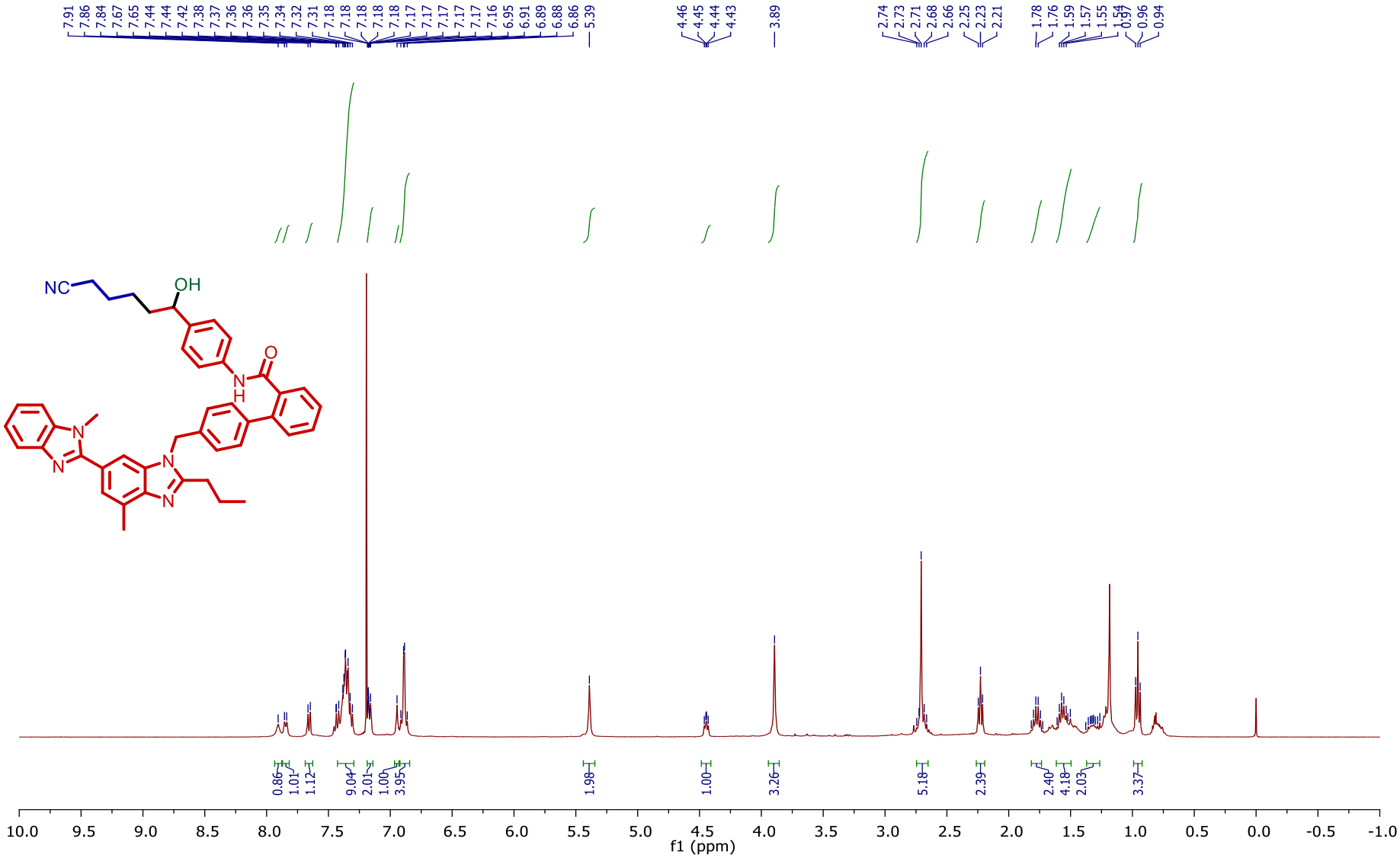
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3qa)**



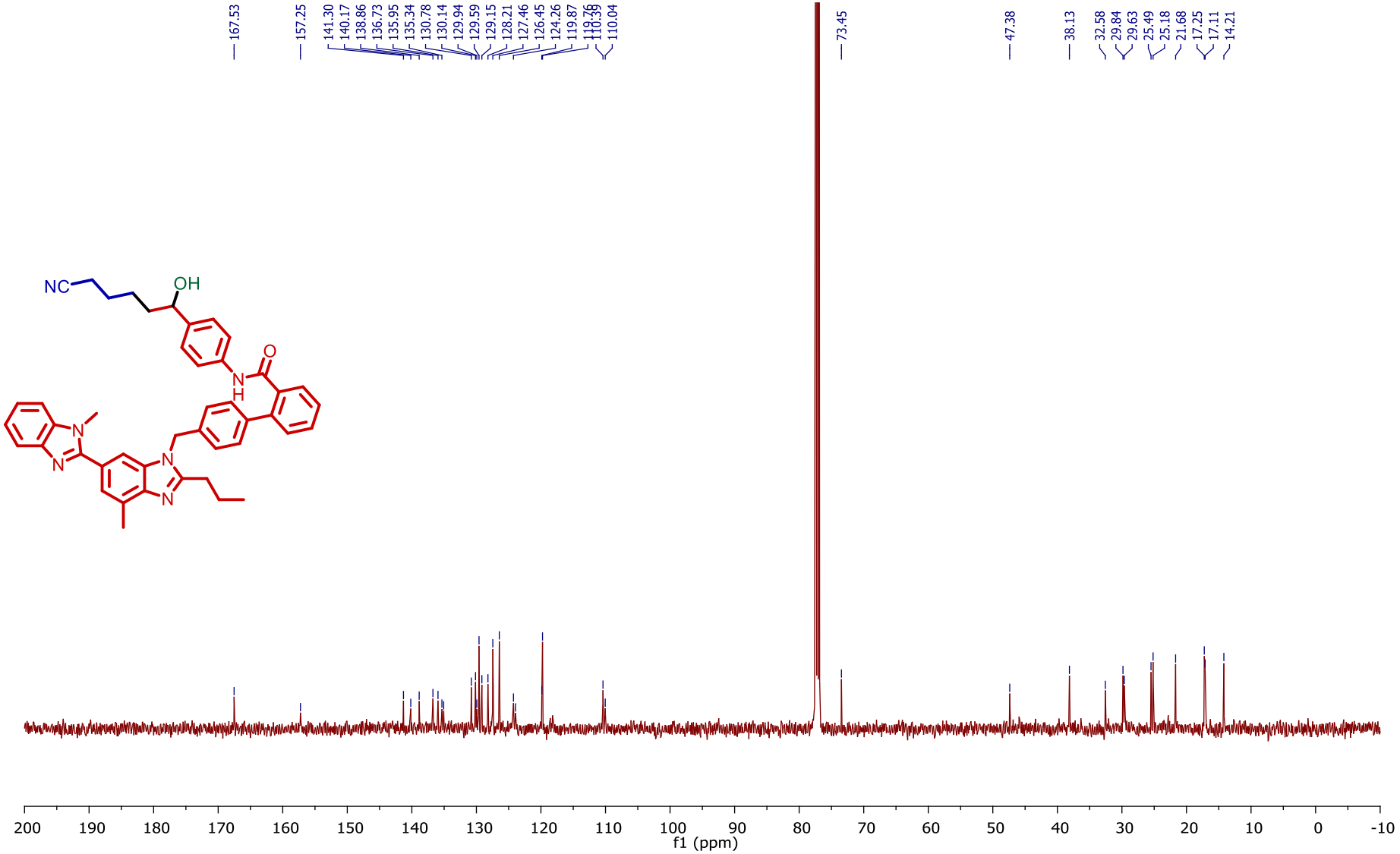
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3qa)**



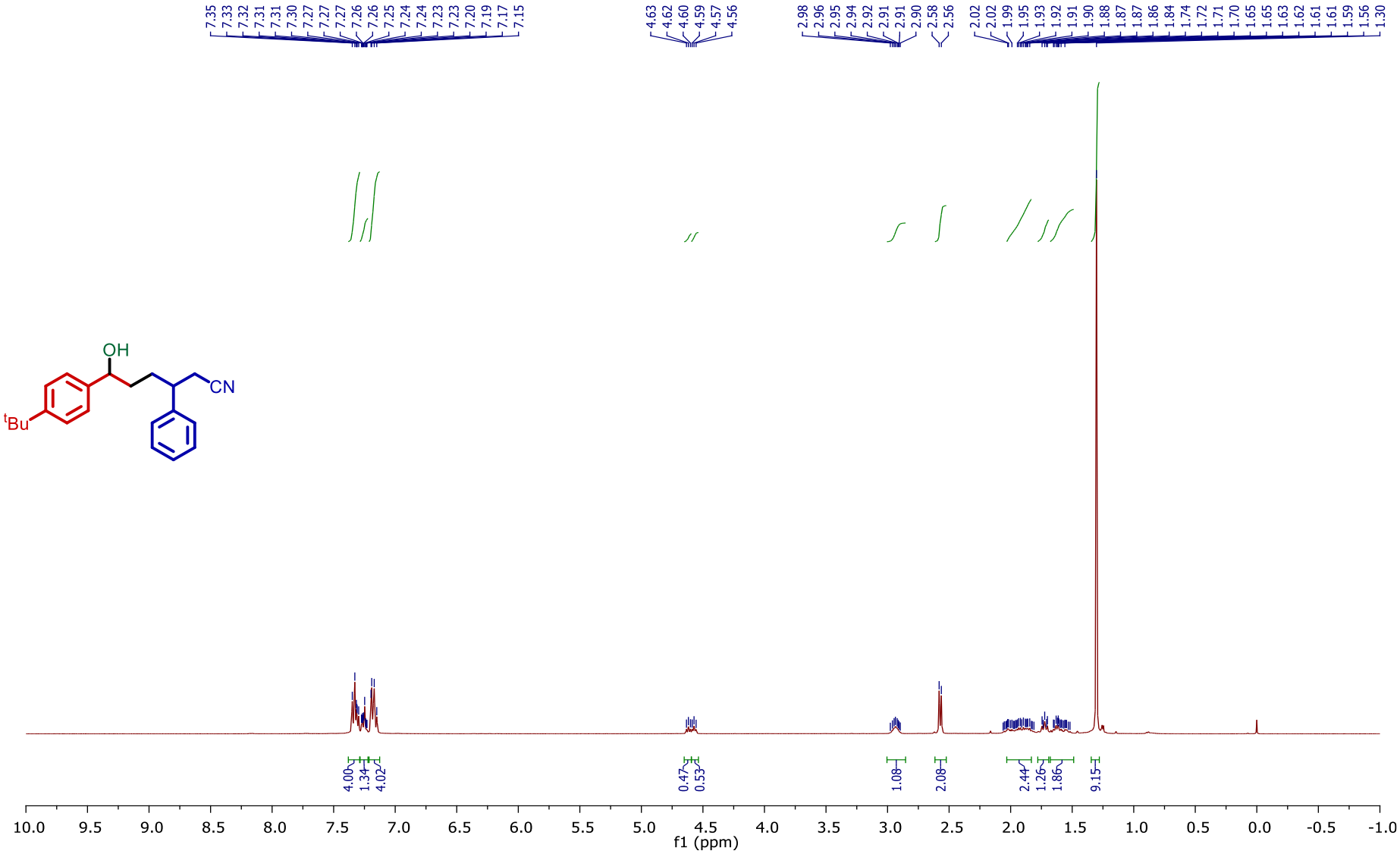
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ra)**



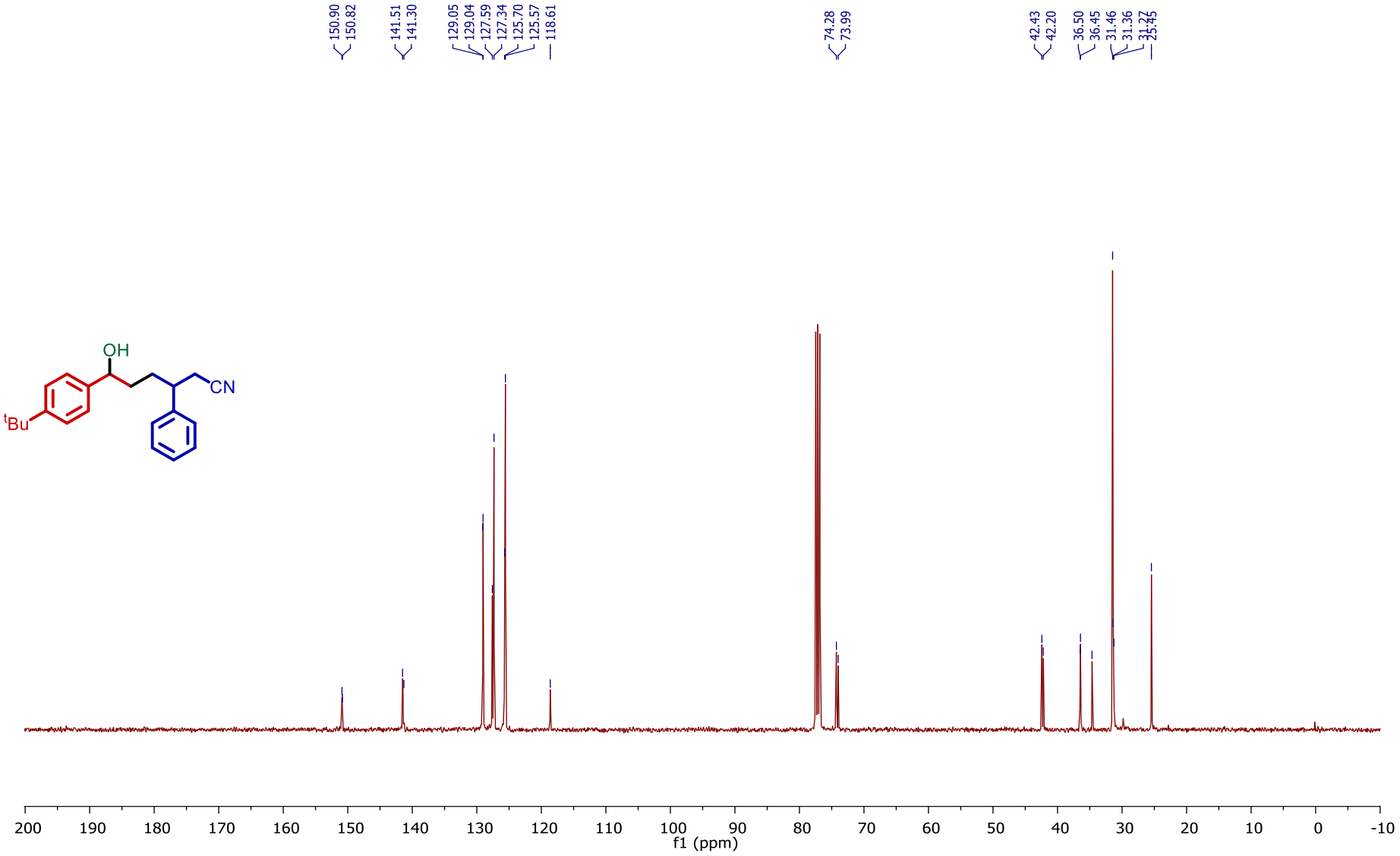
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ra)**



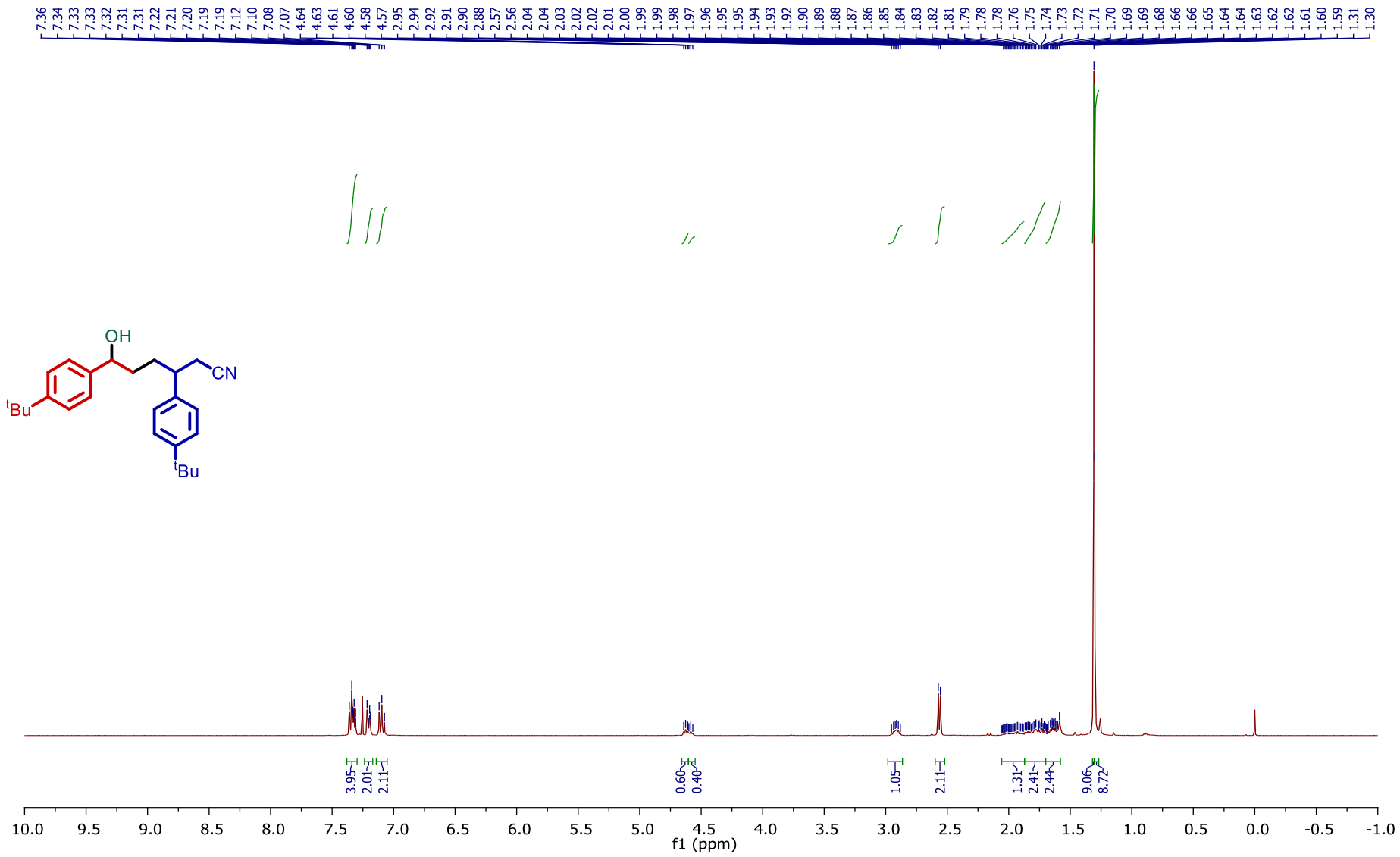
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ab)**



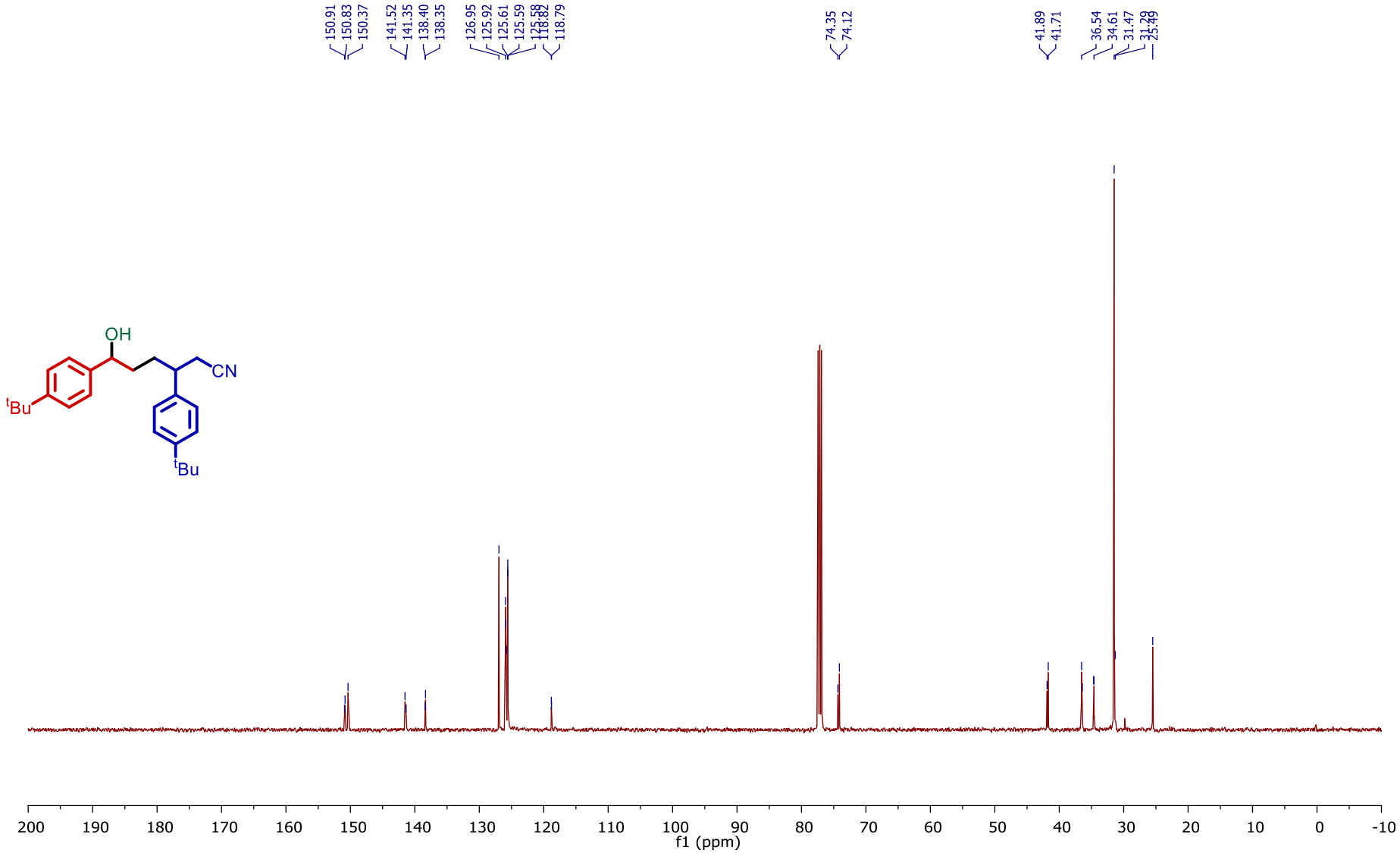
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ab)**



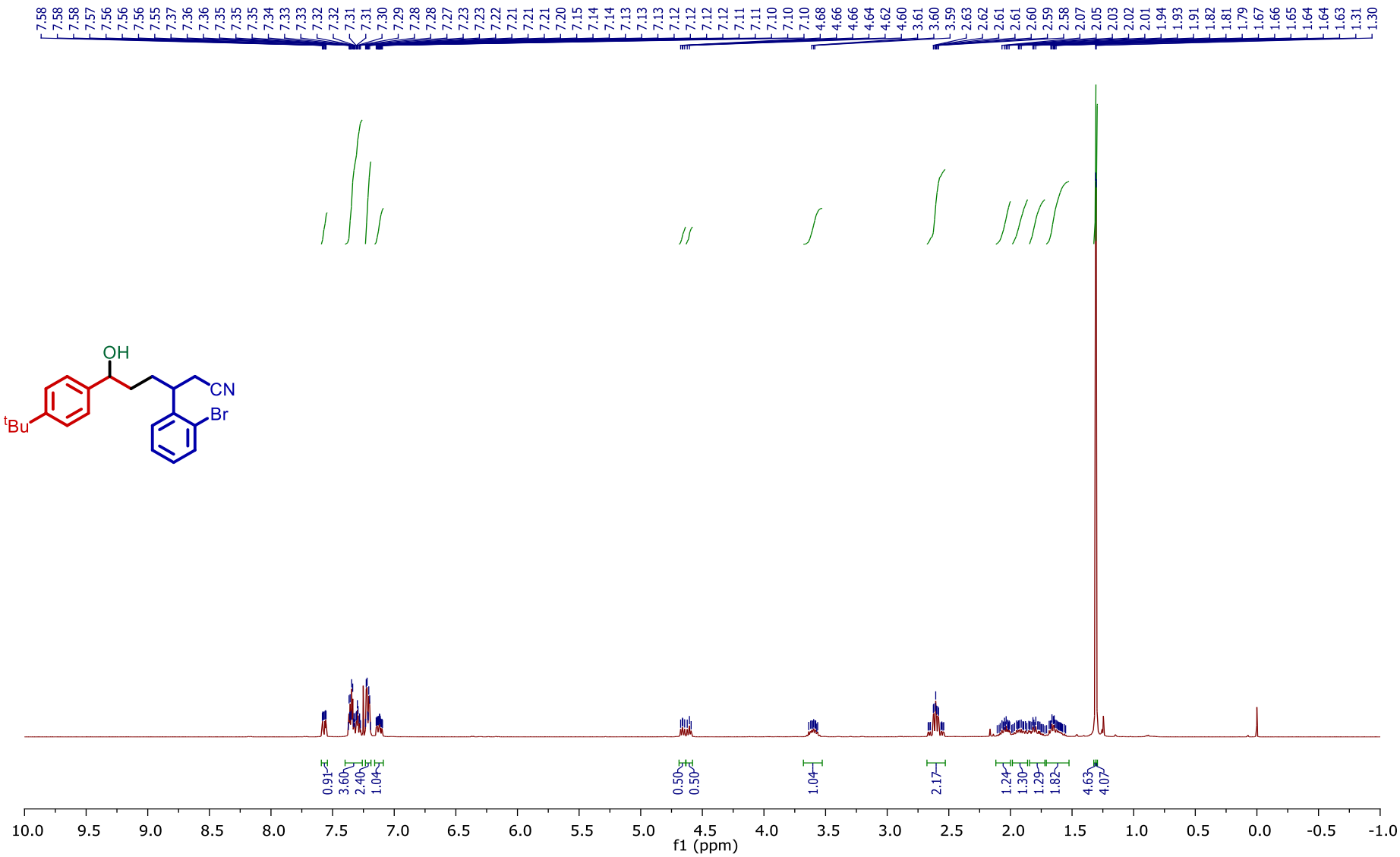
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ac)**



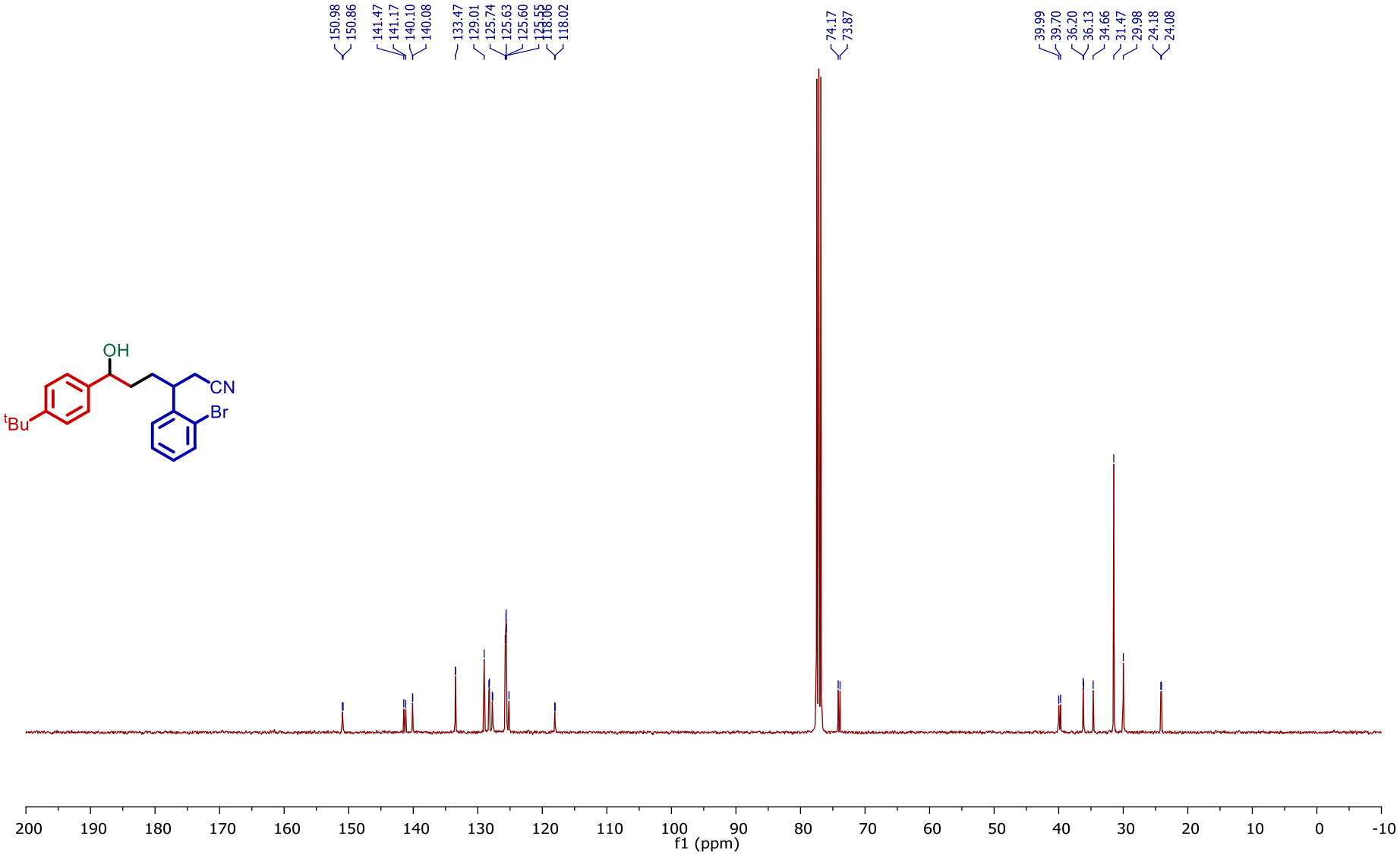
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ac)**



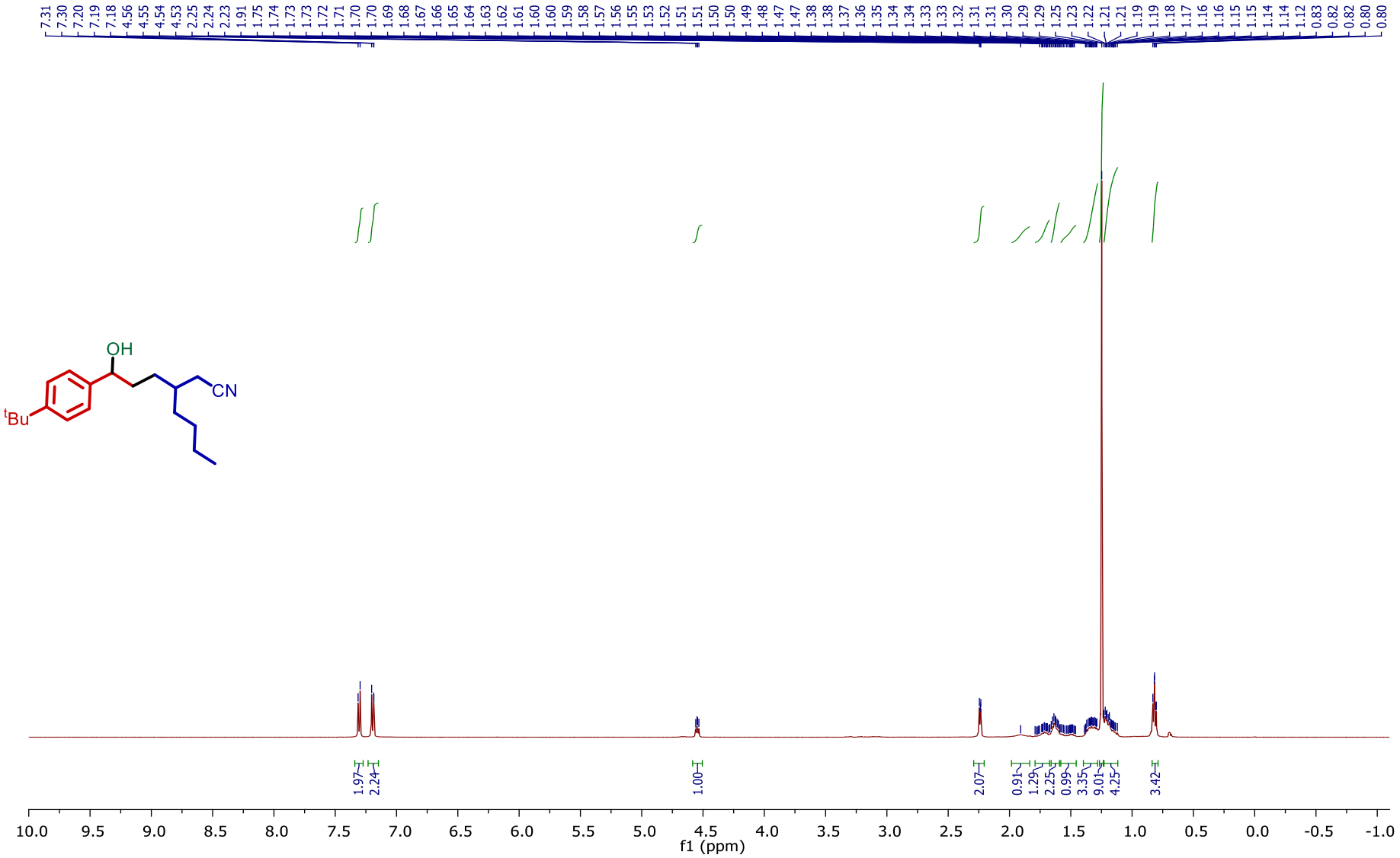
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ad)**



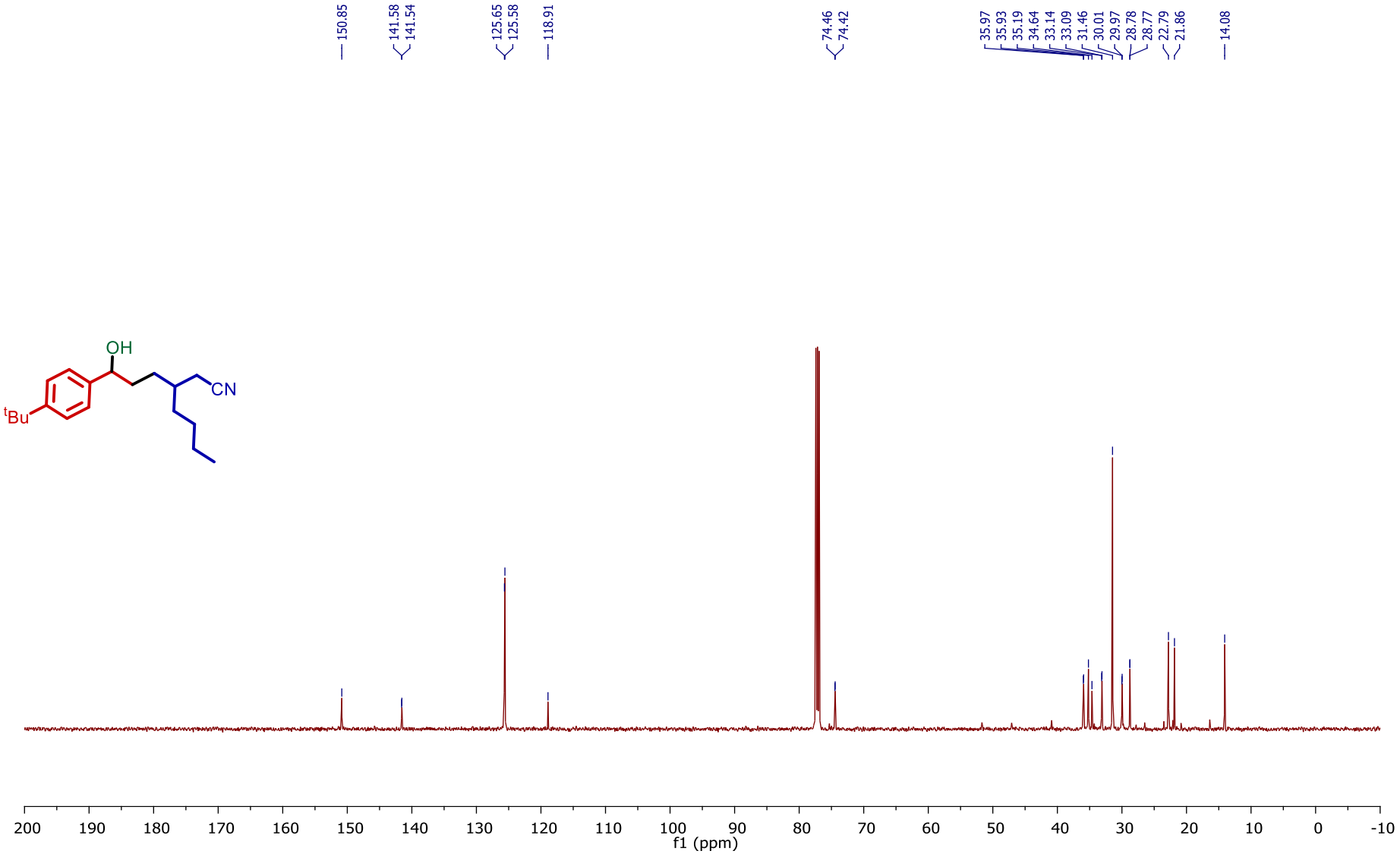
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ad)**



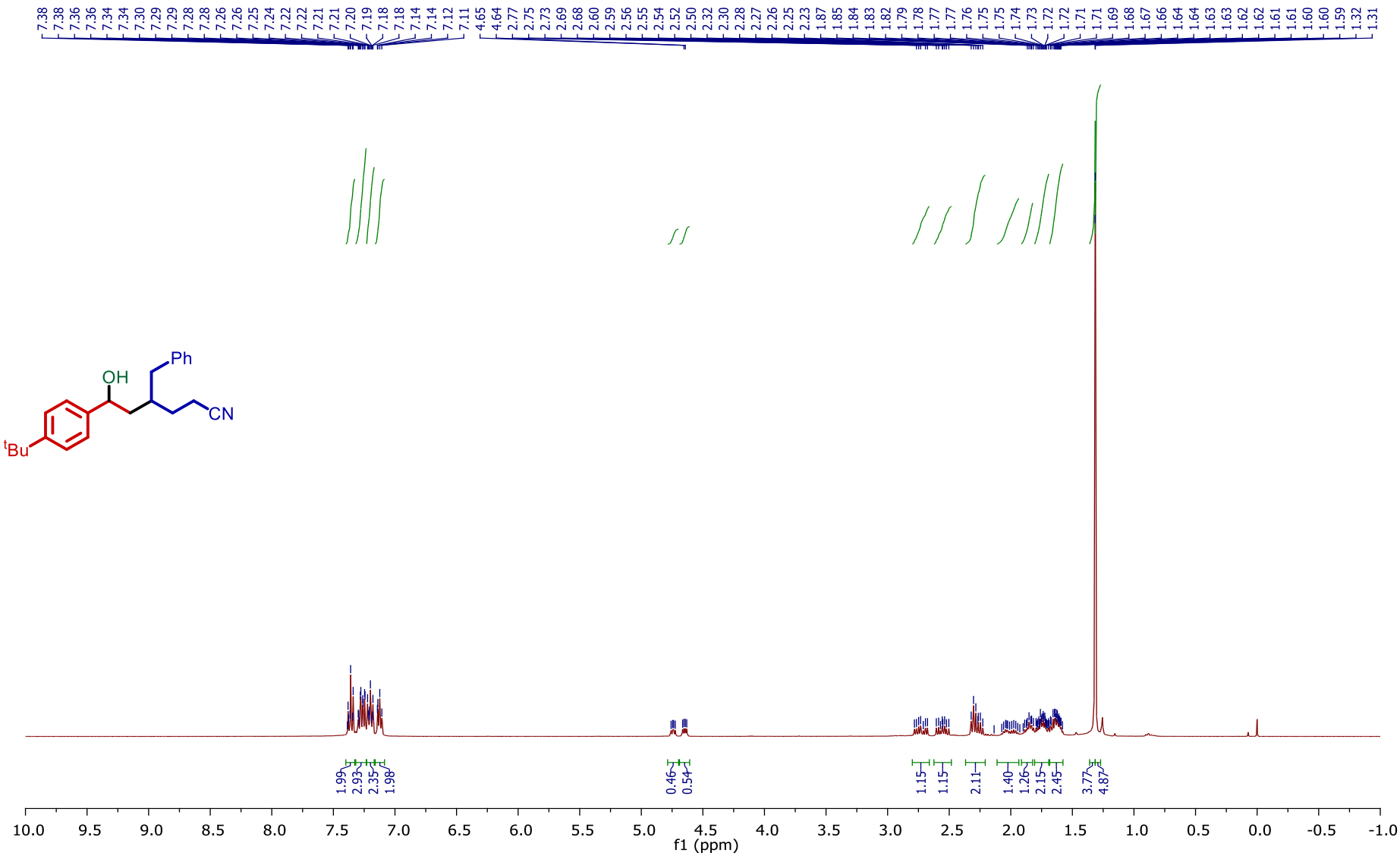
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3ae)**



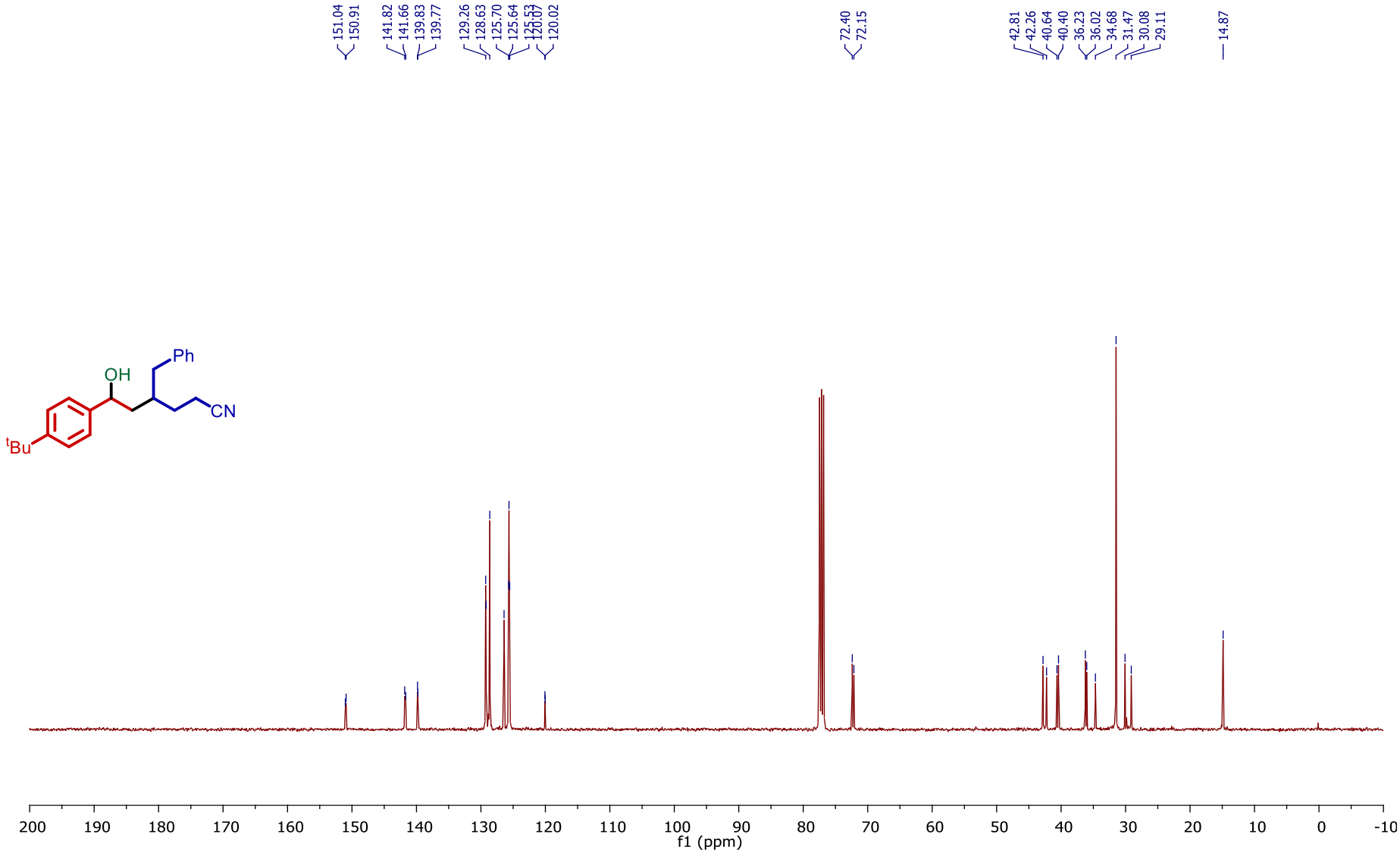
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ae)**



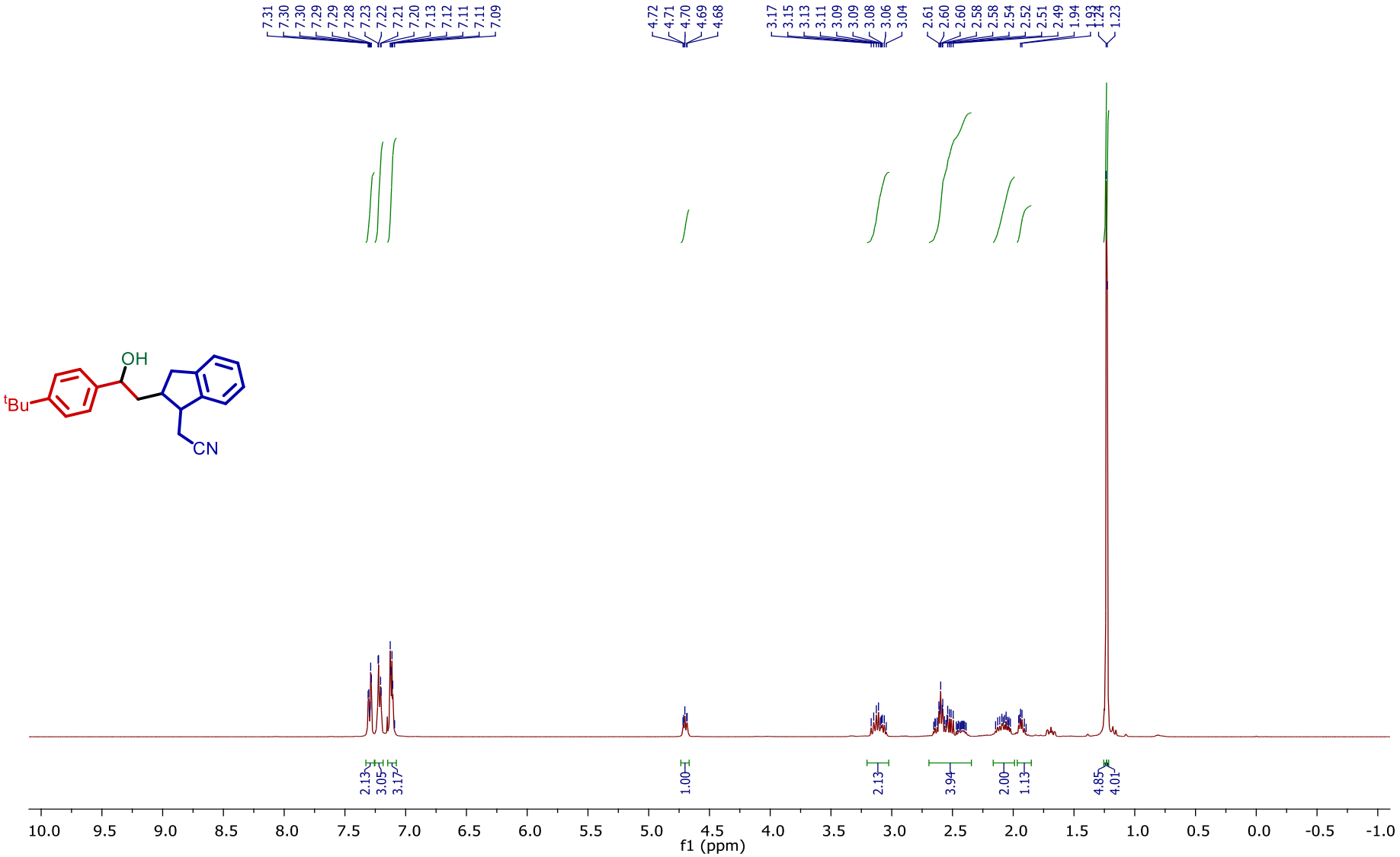
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3af)**



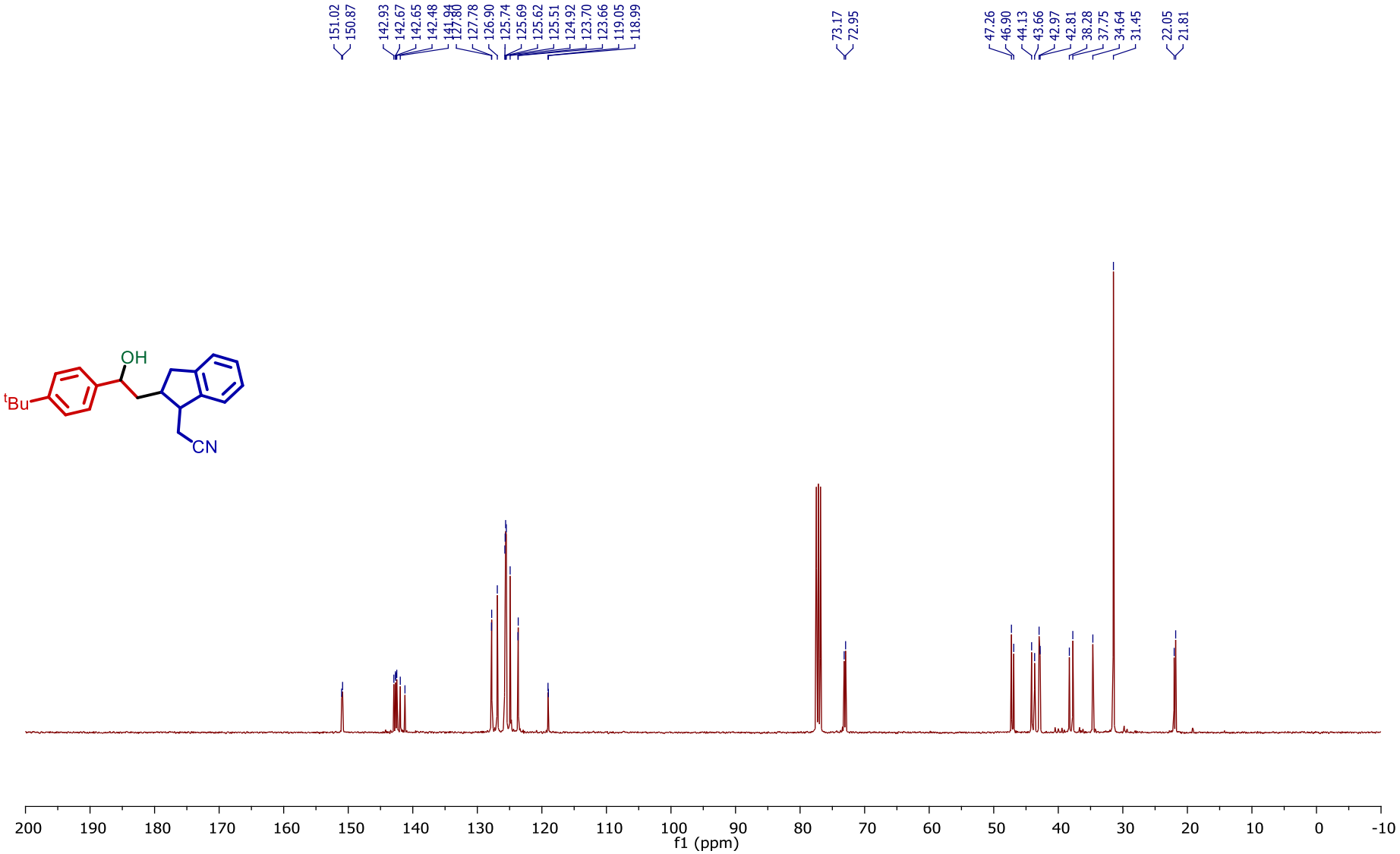
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3af)**



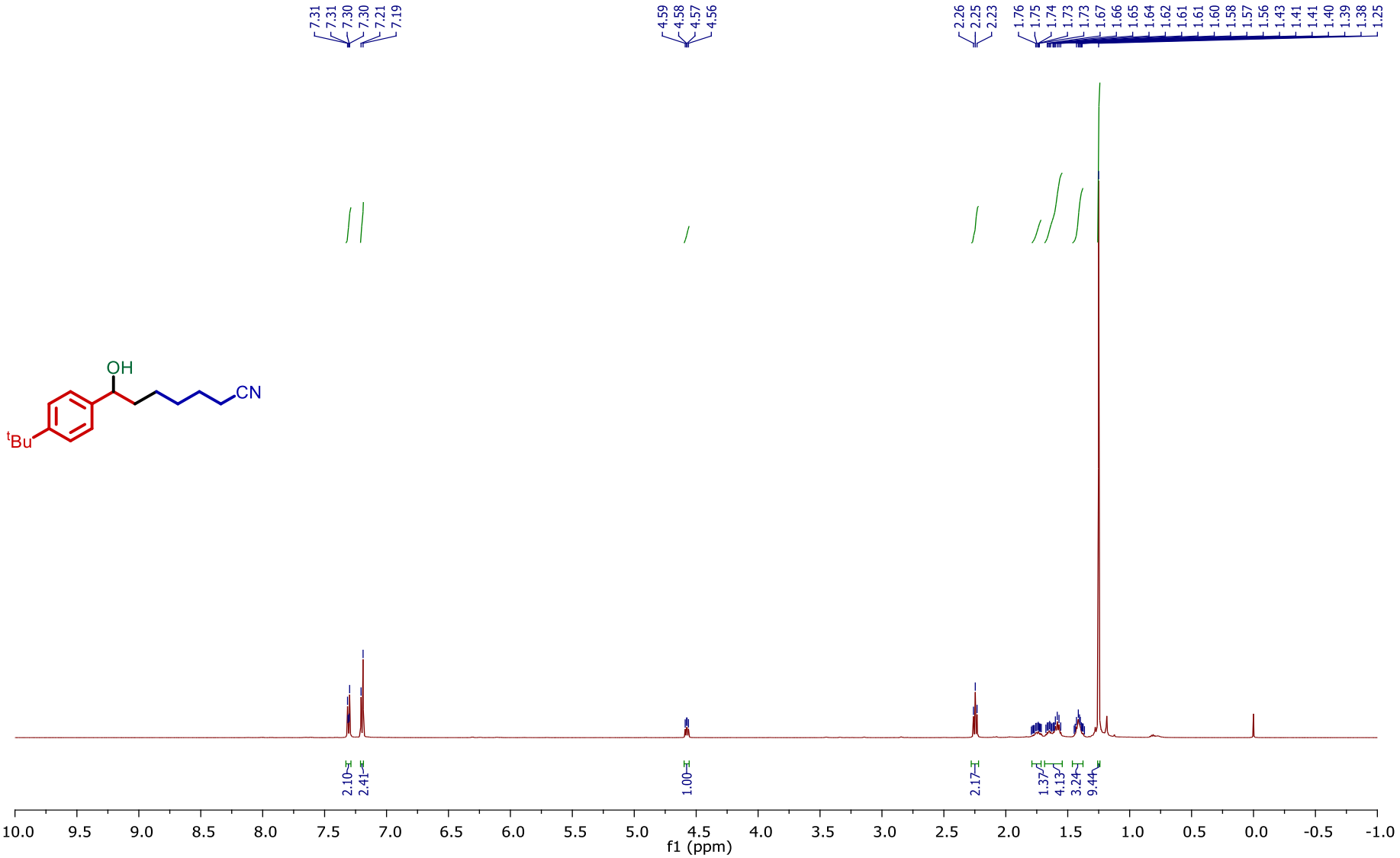
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ag)**



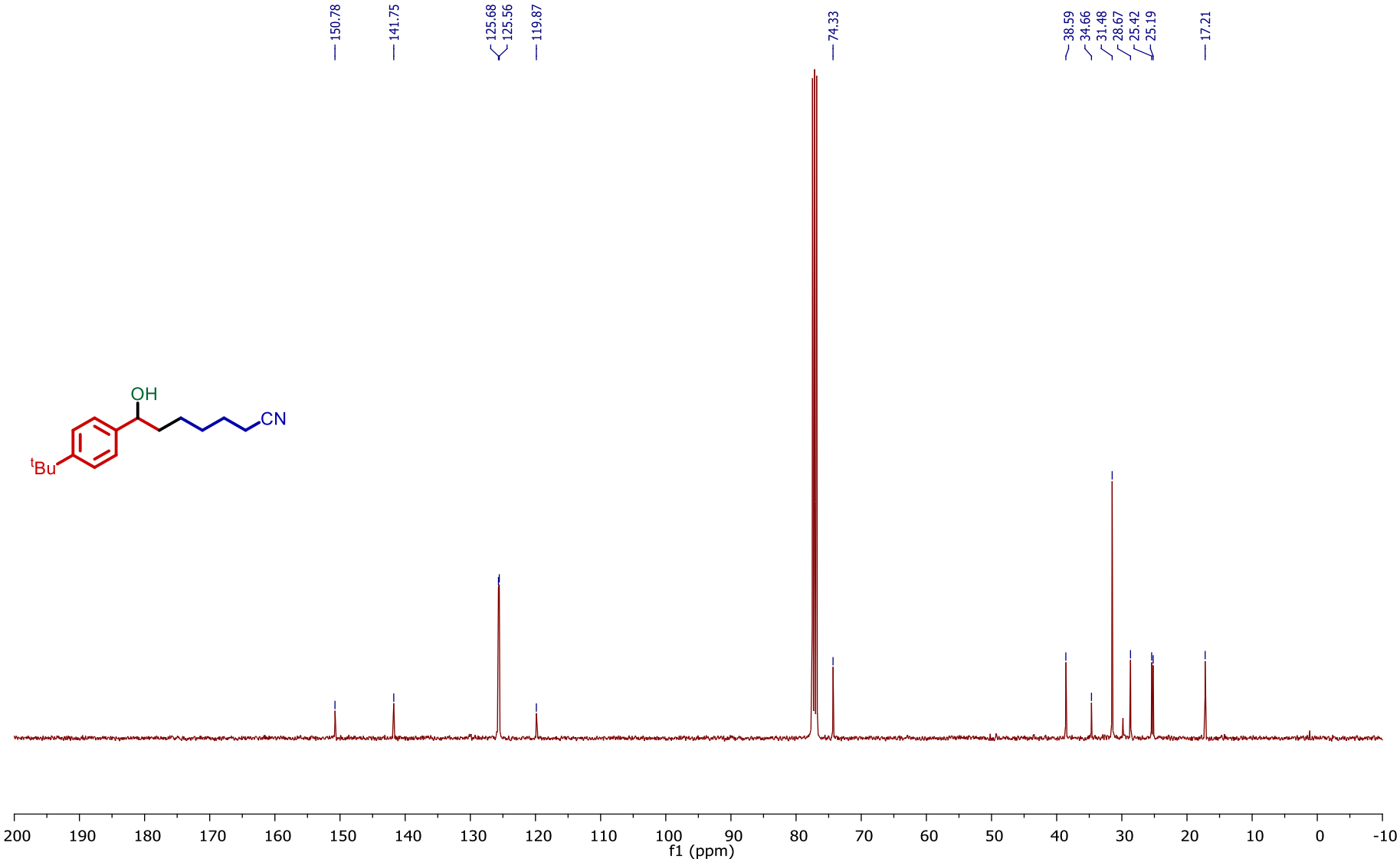
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ag)**



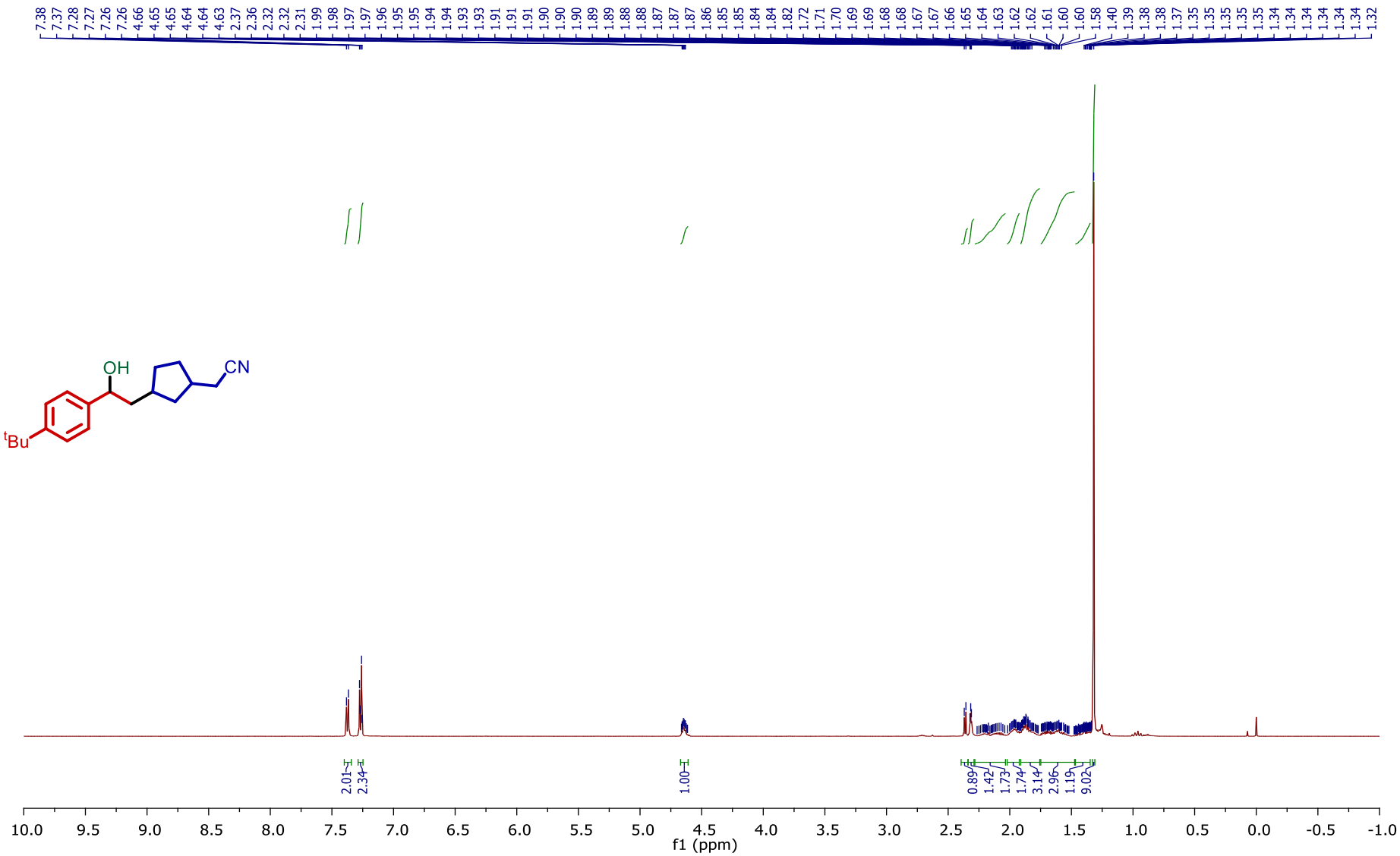
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3ah)**



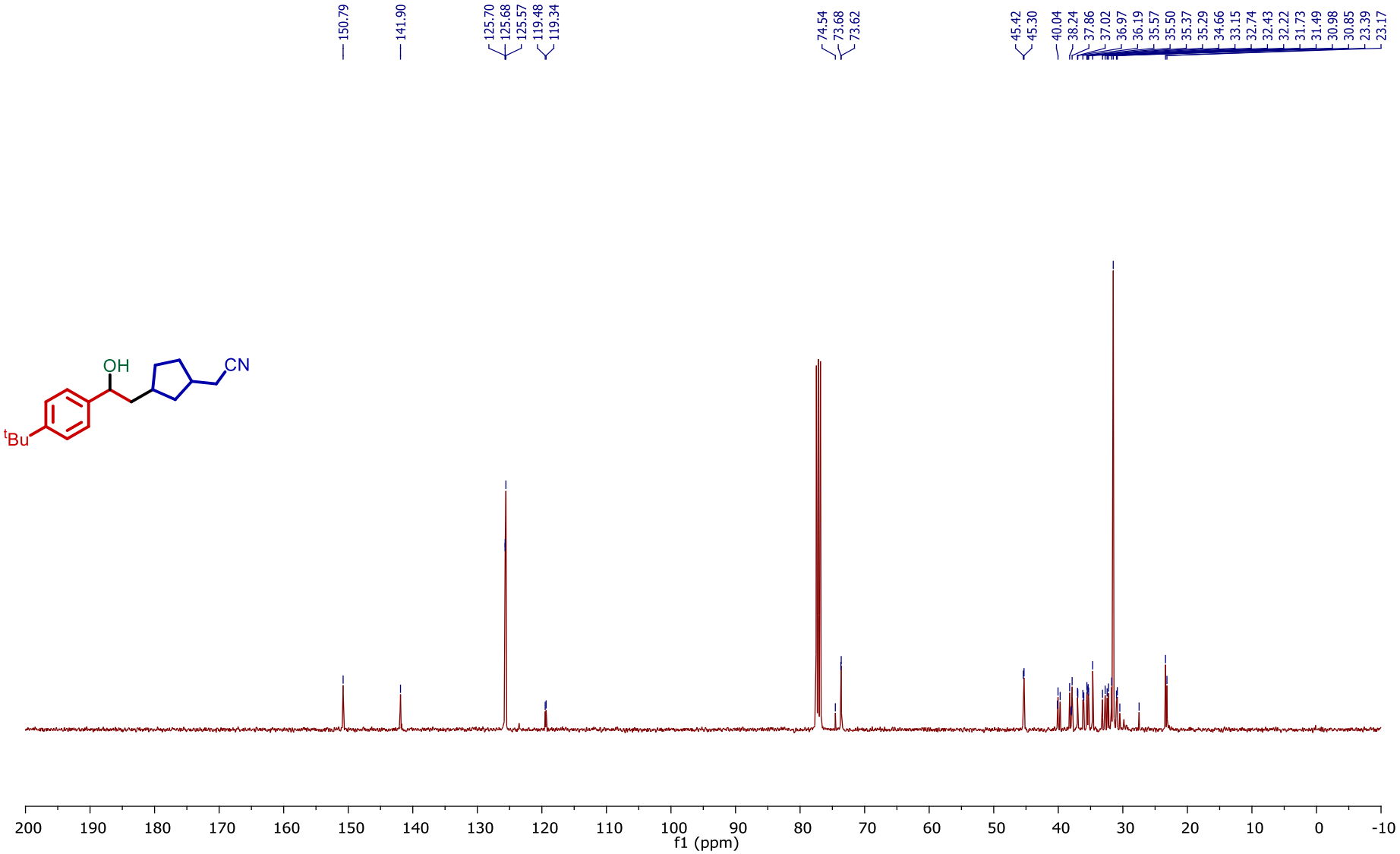
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ah)**



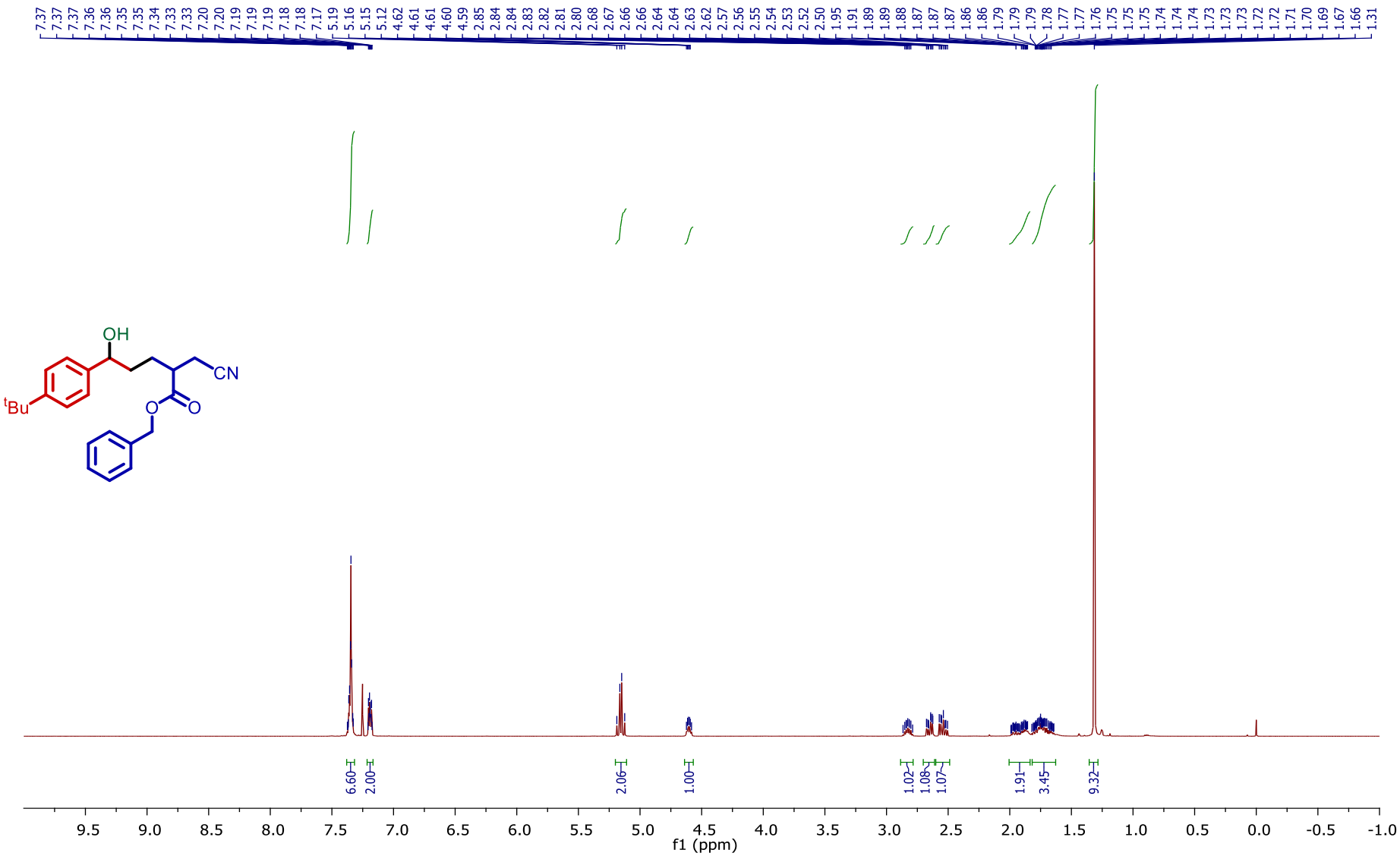
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3ai)**



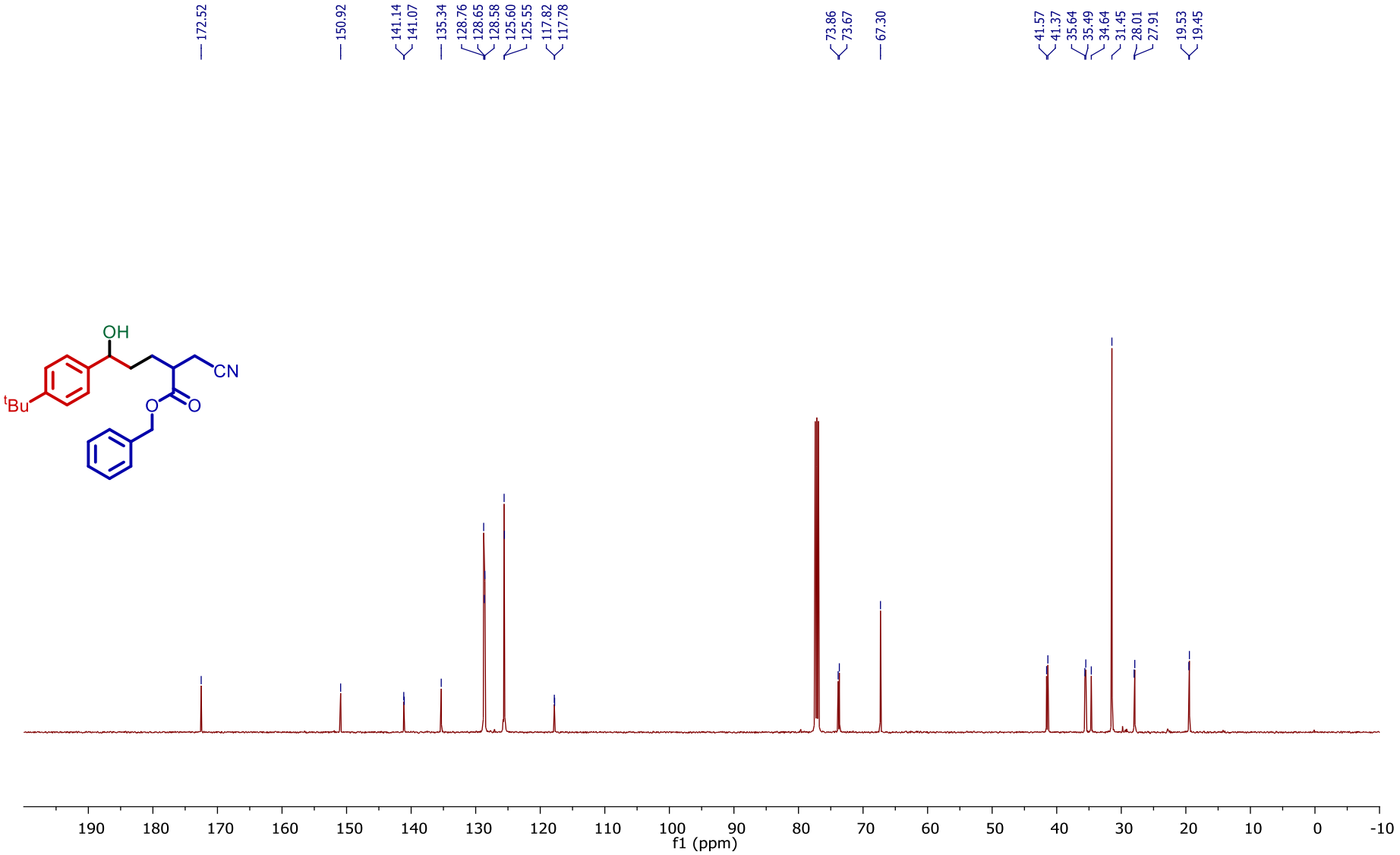
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ai)**



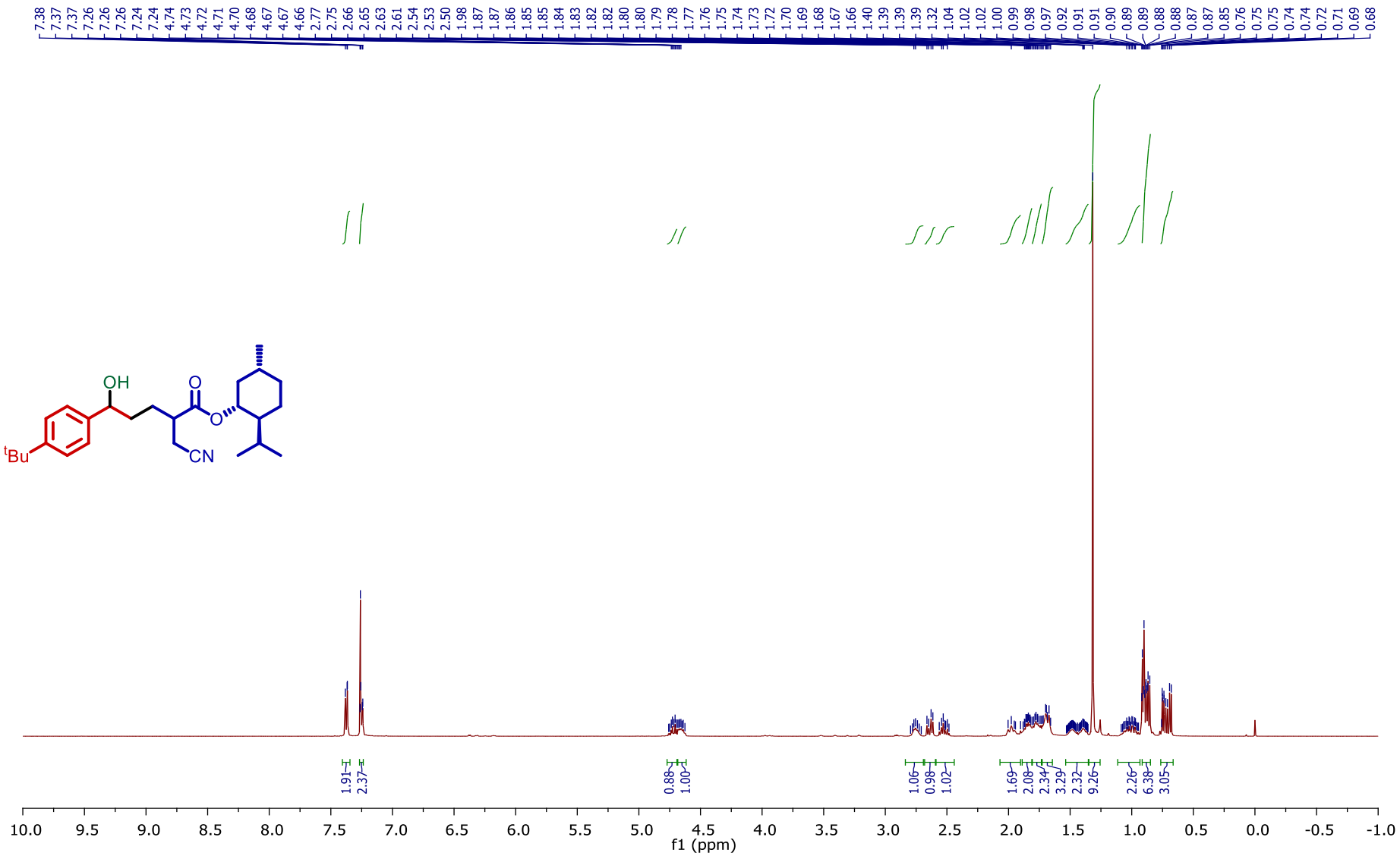
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3aj)**



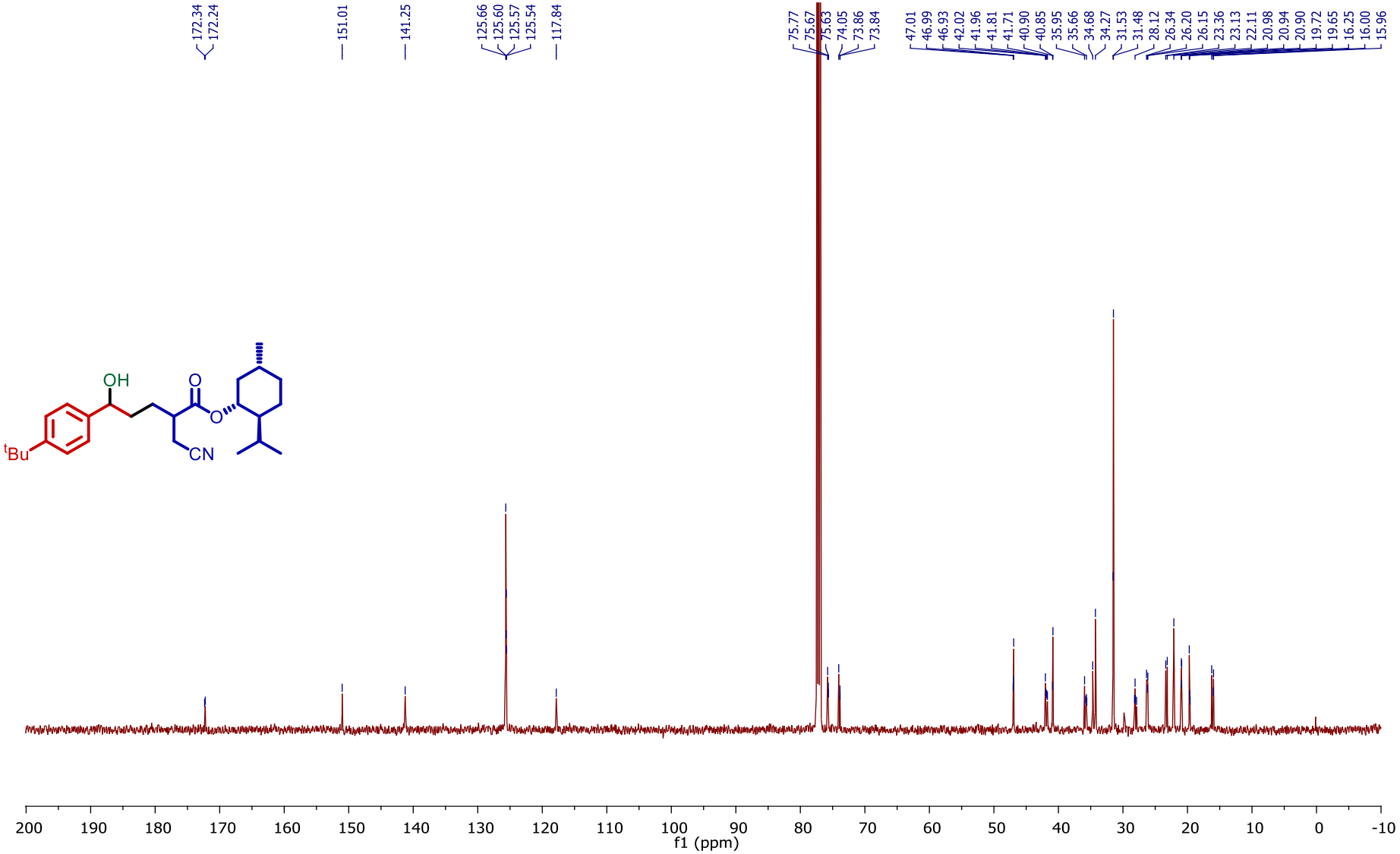
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3aj)**



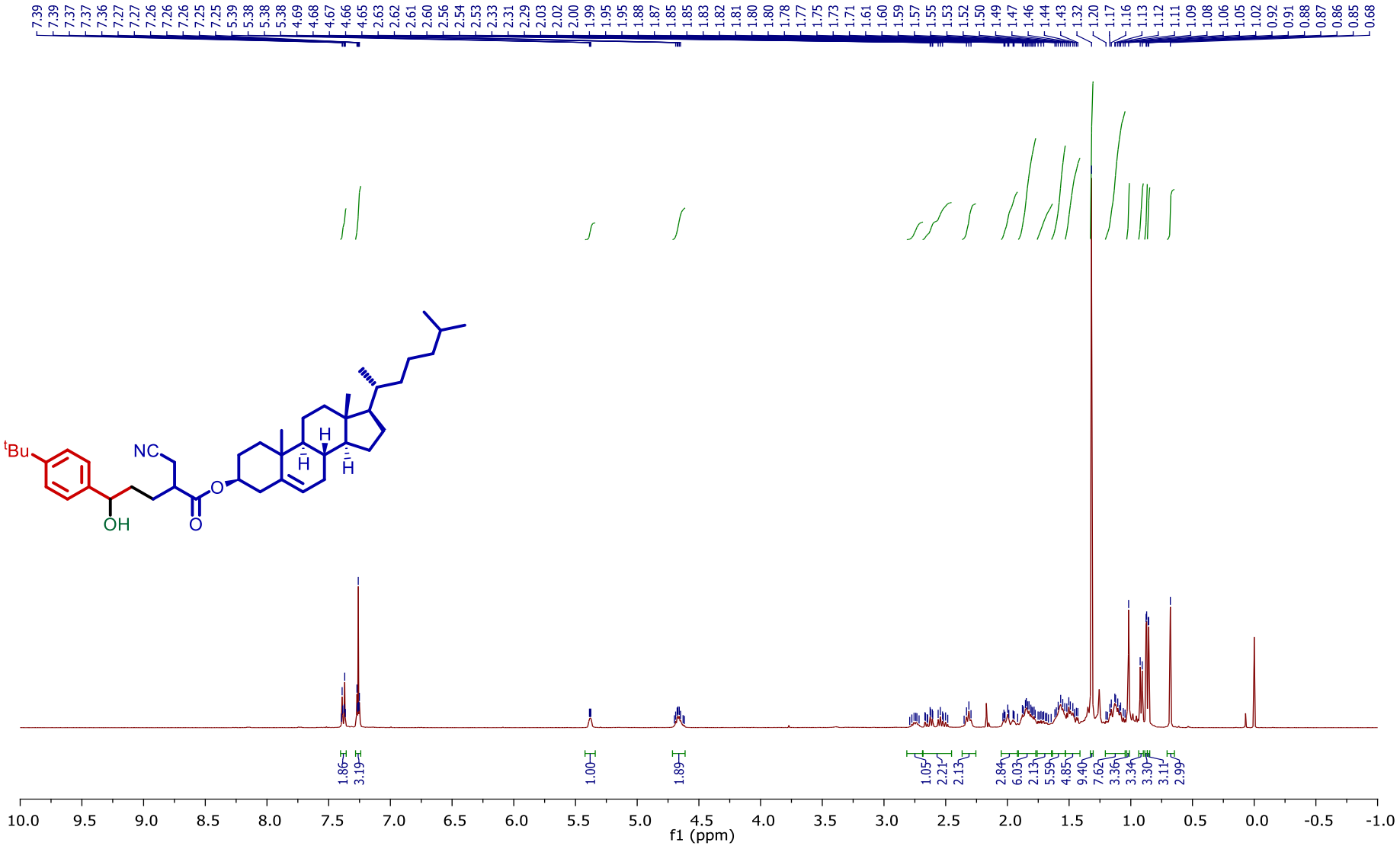
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3ak)**



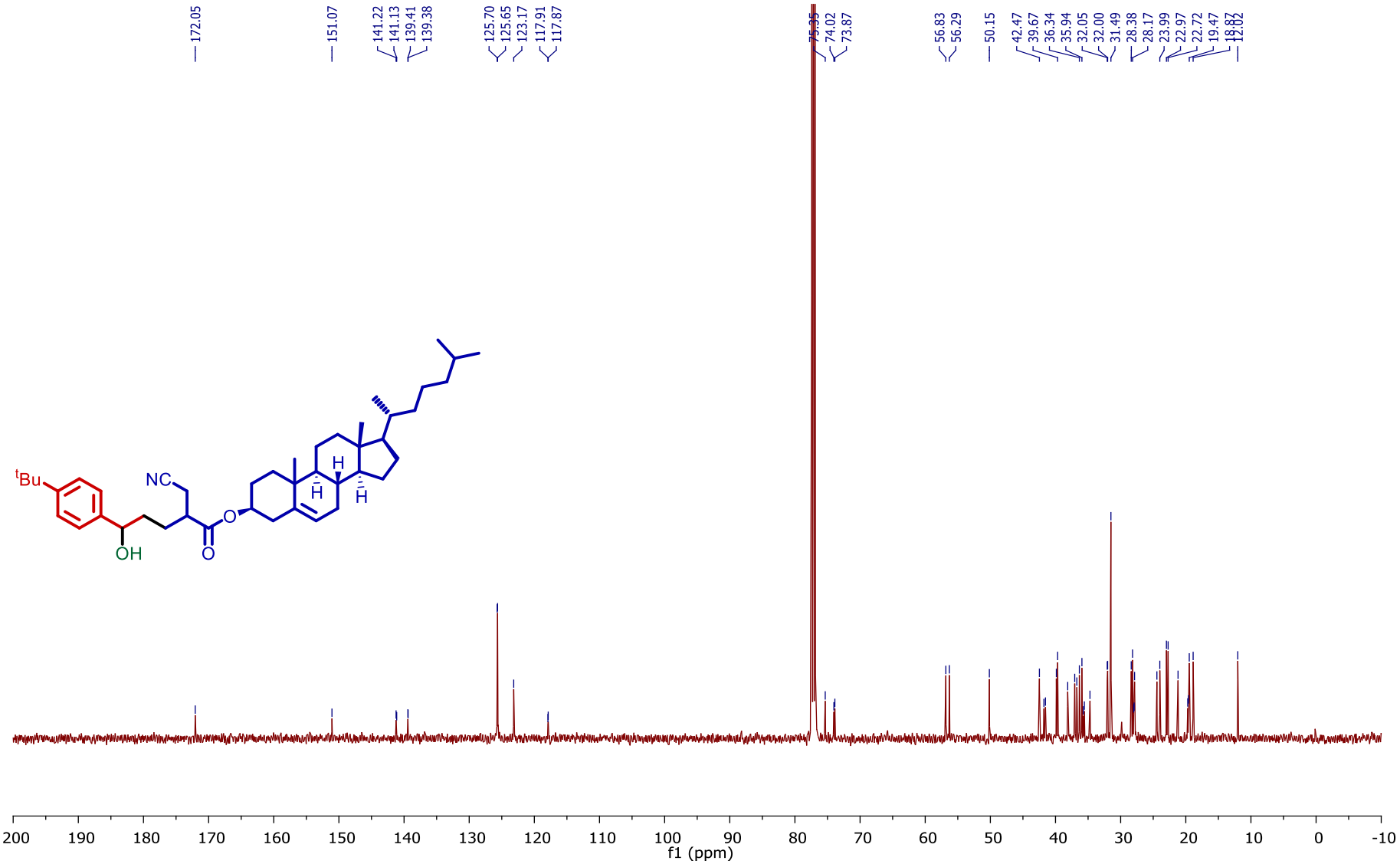
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ak)**



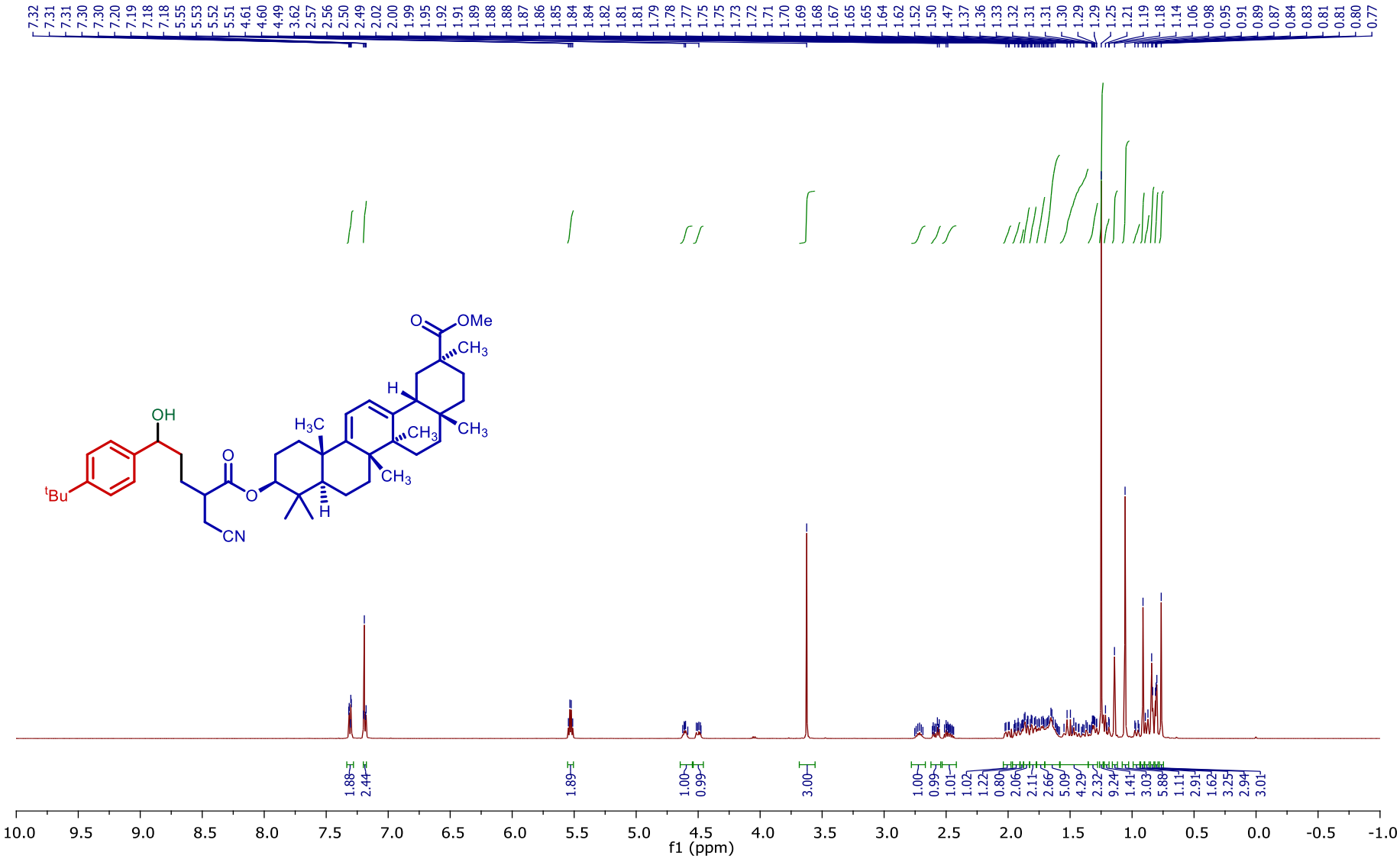
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3al)**



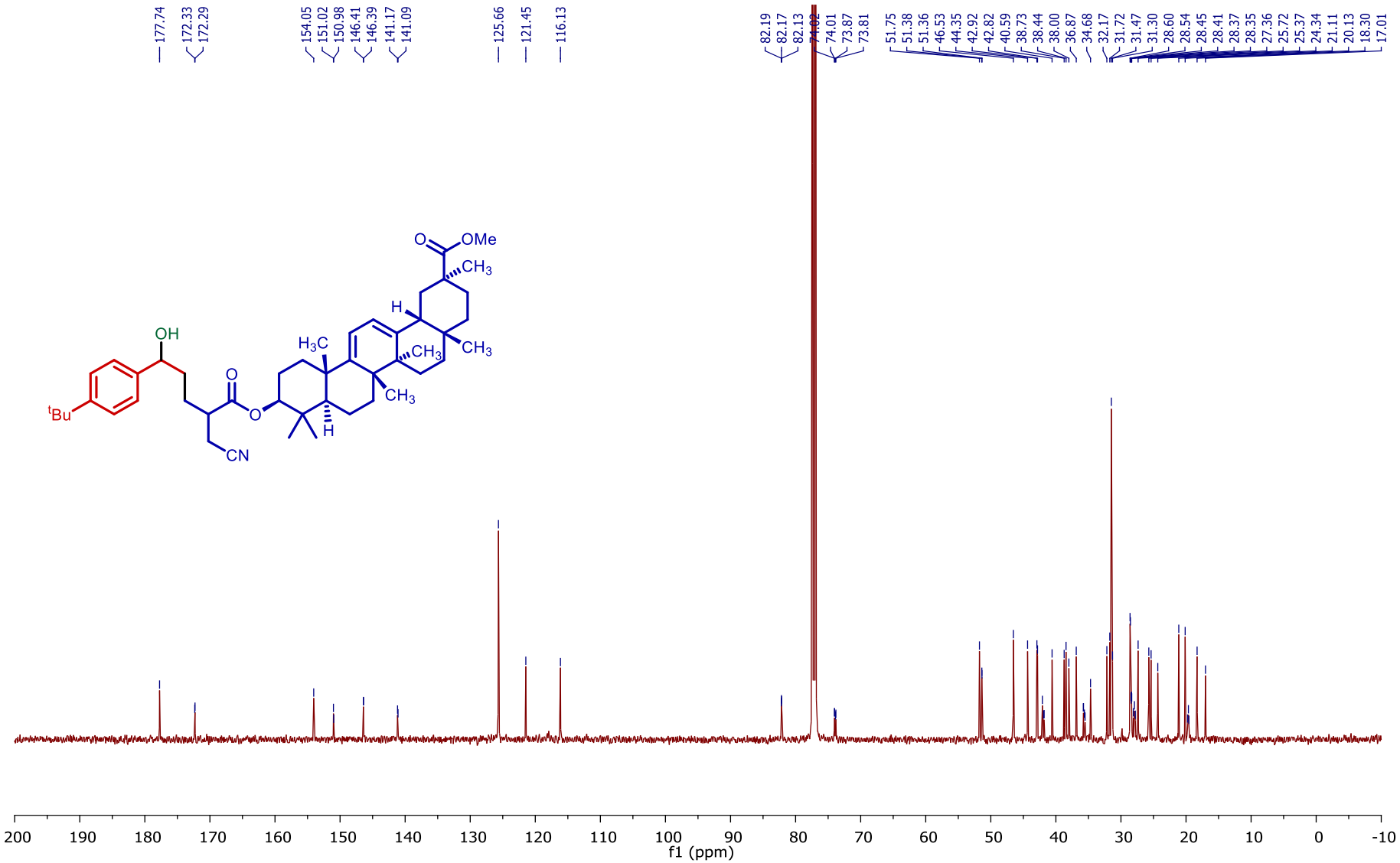
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3al)**



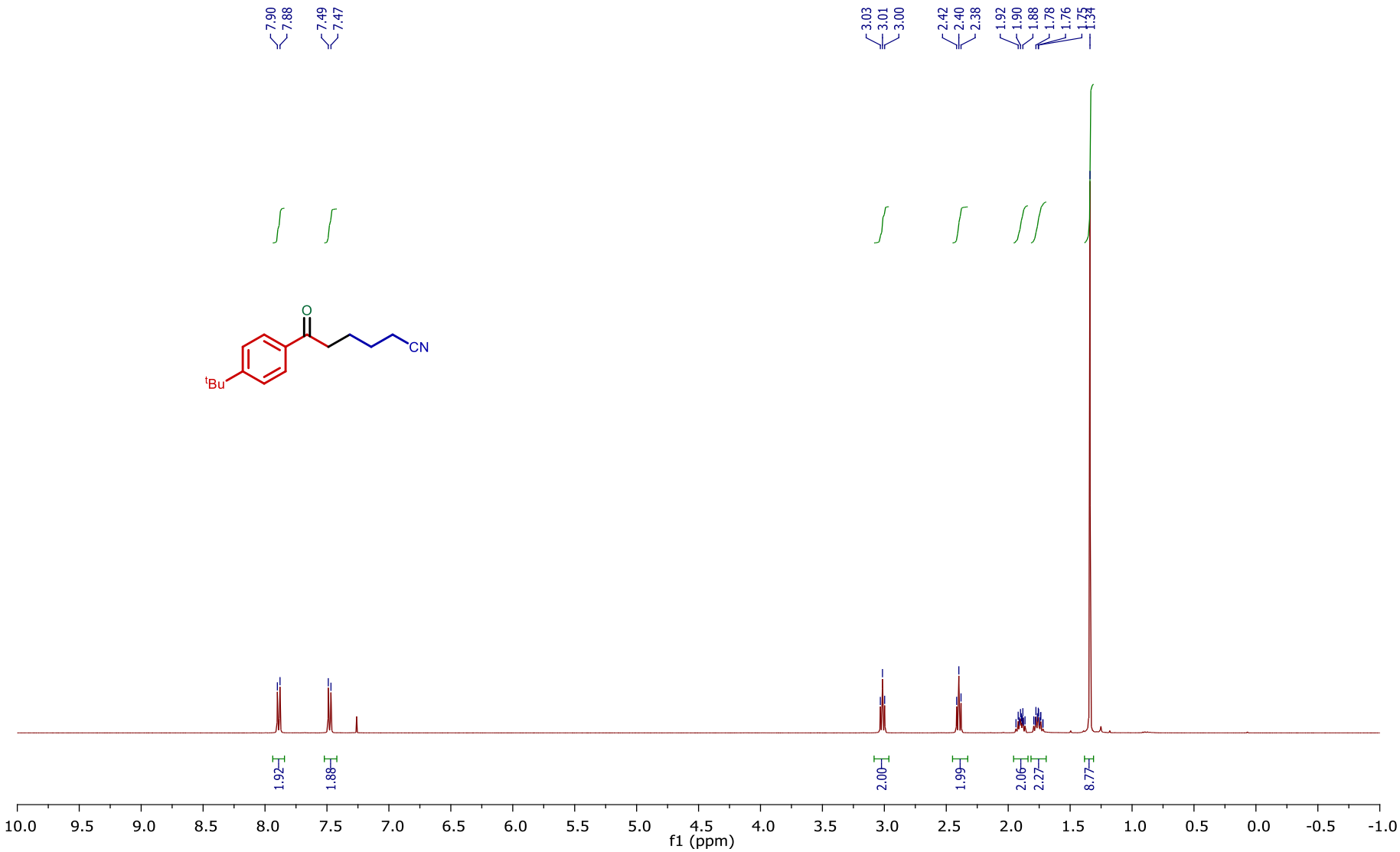
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3am)**



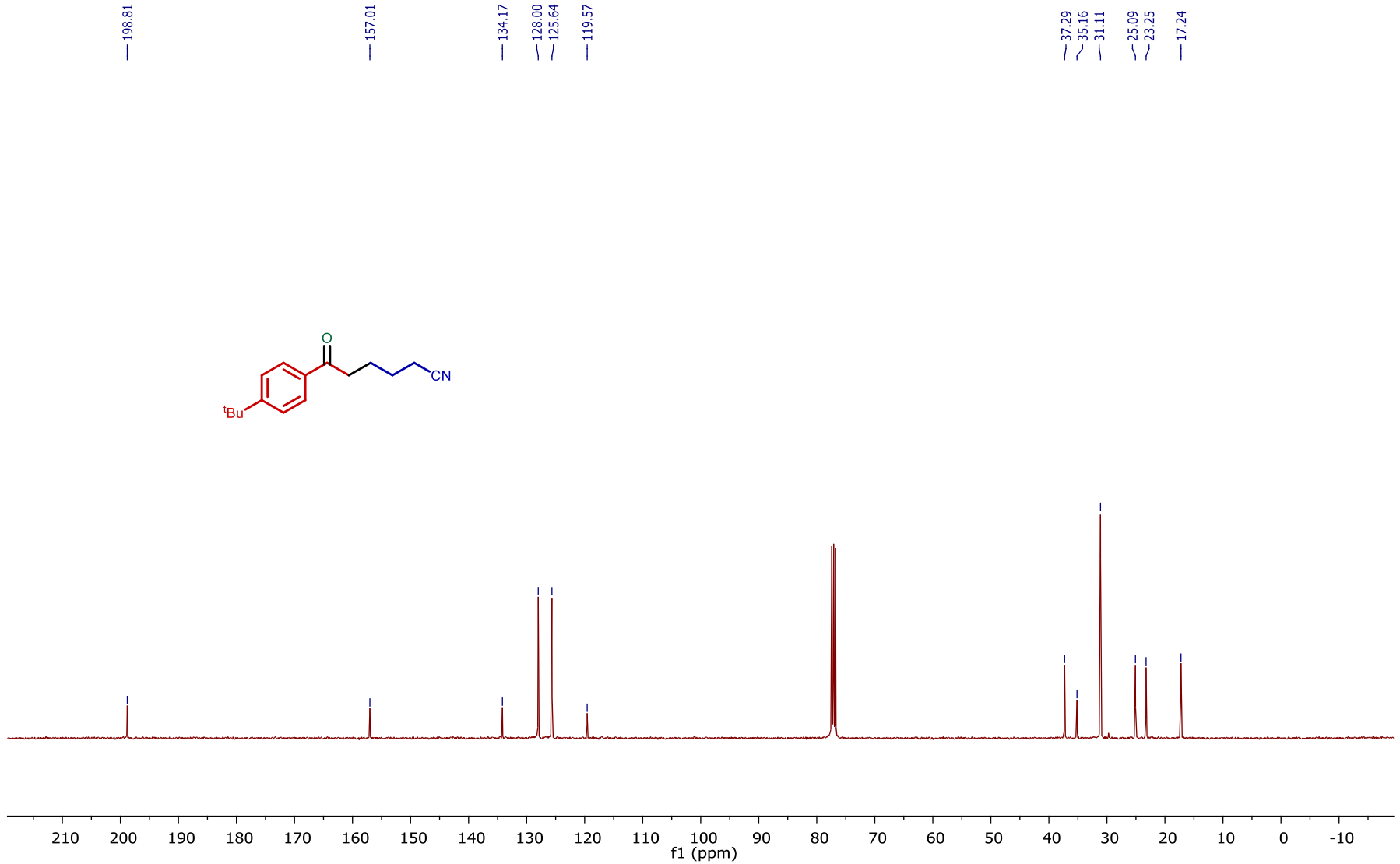
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3am)**



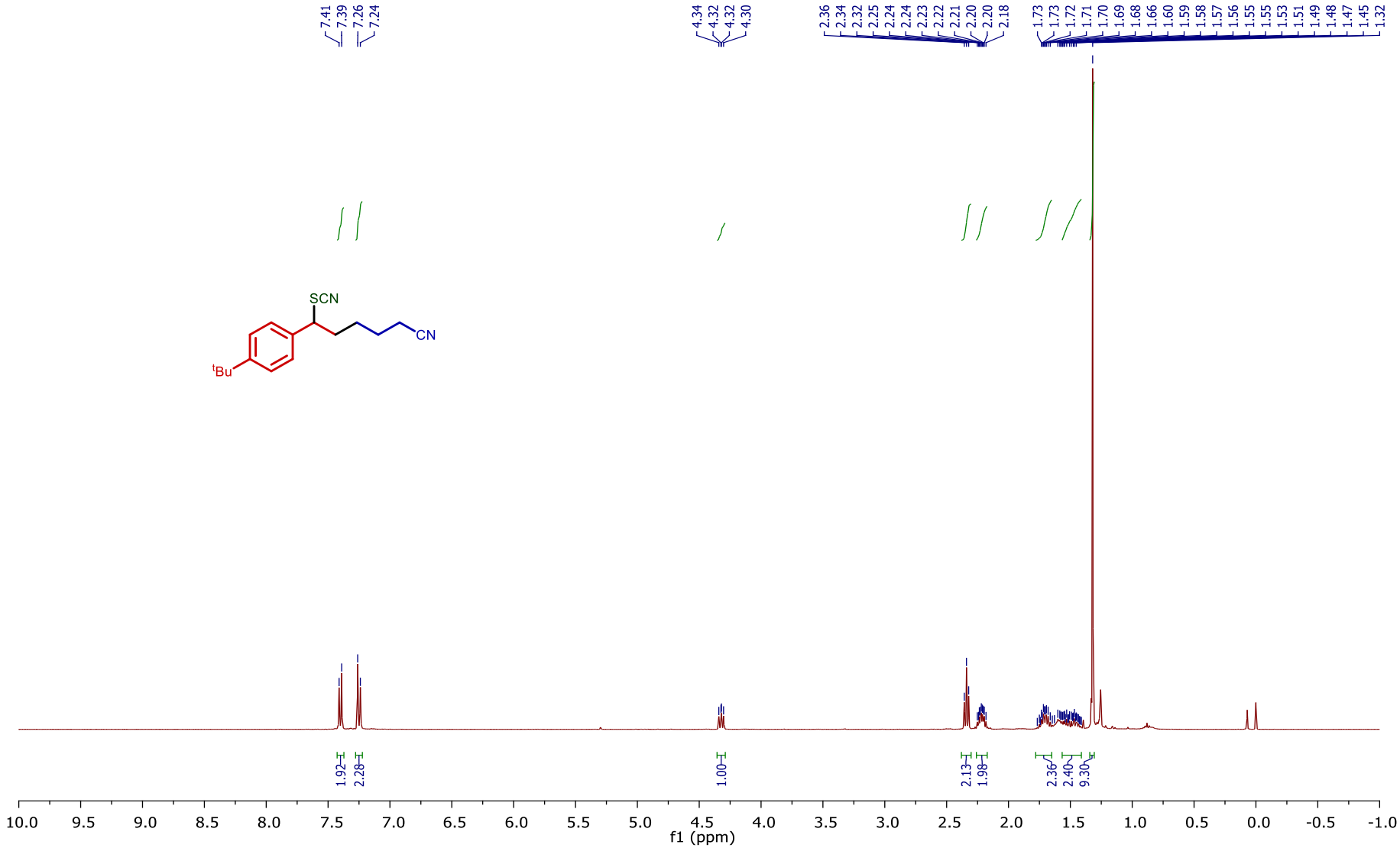
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4)**



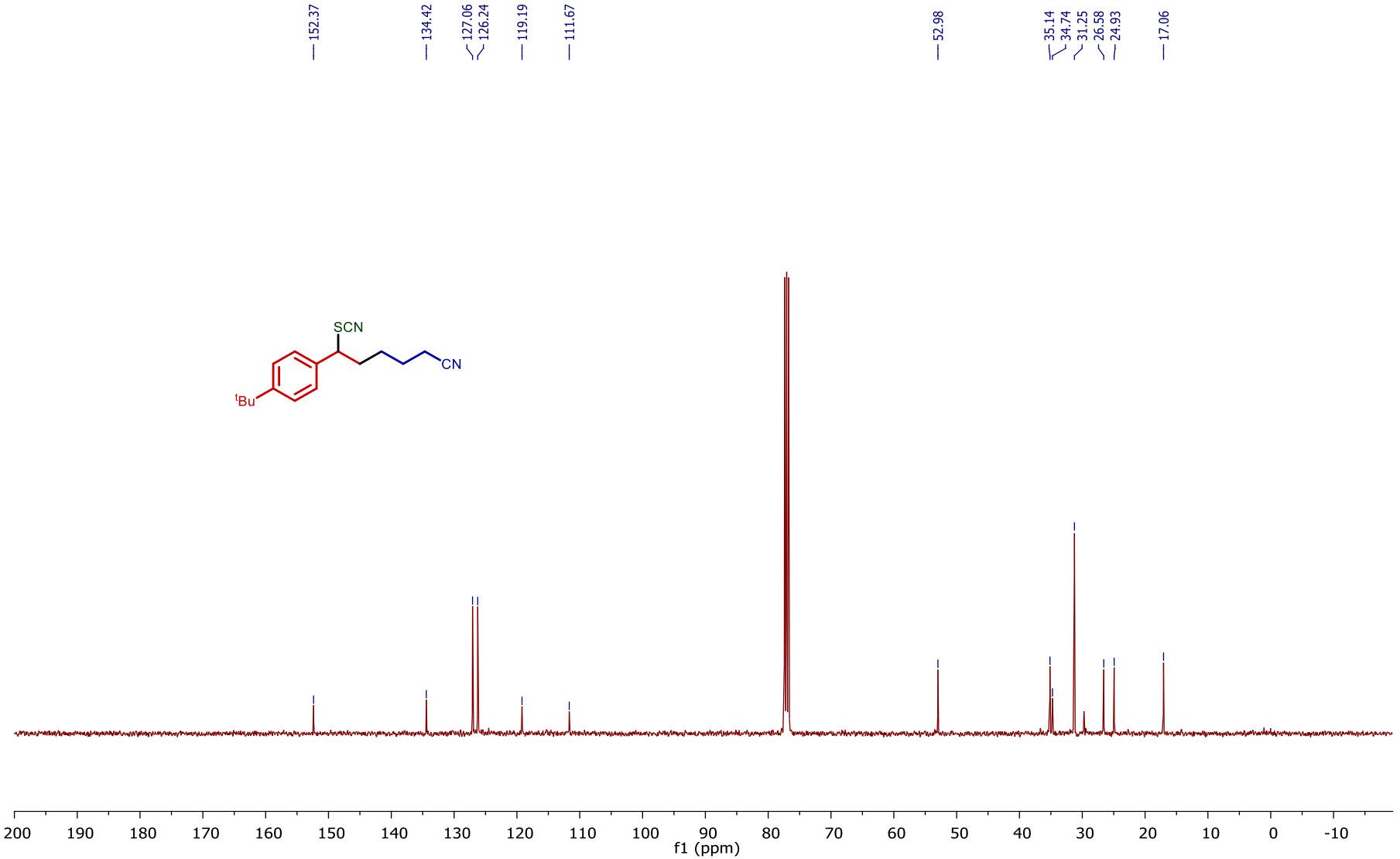
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4)**



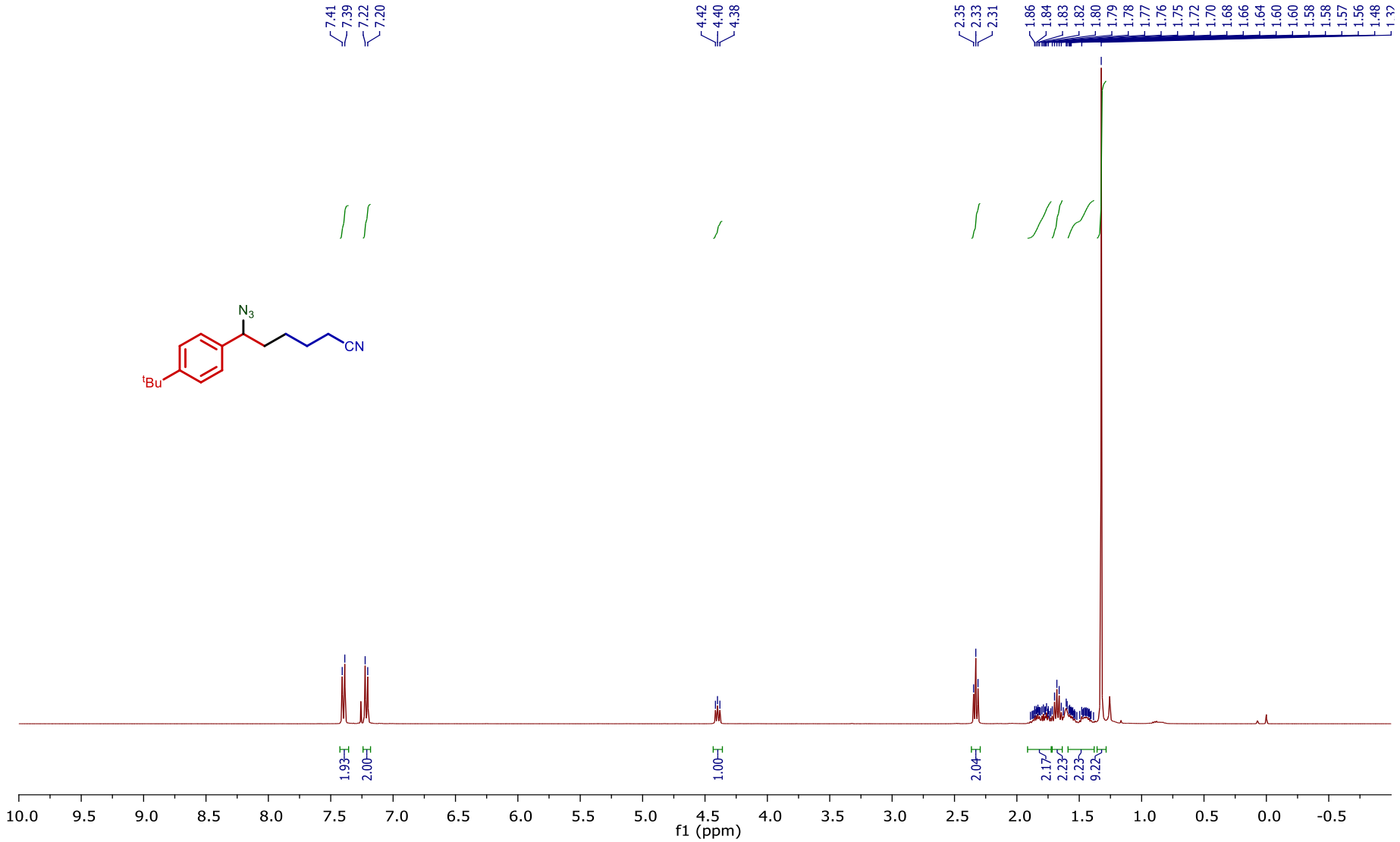
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(5)**



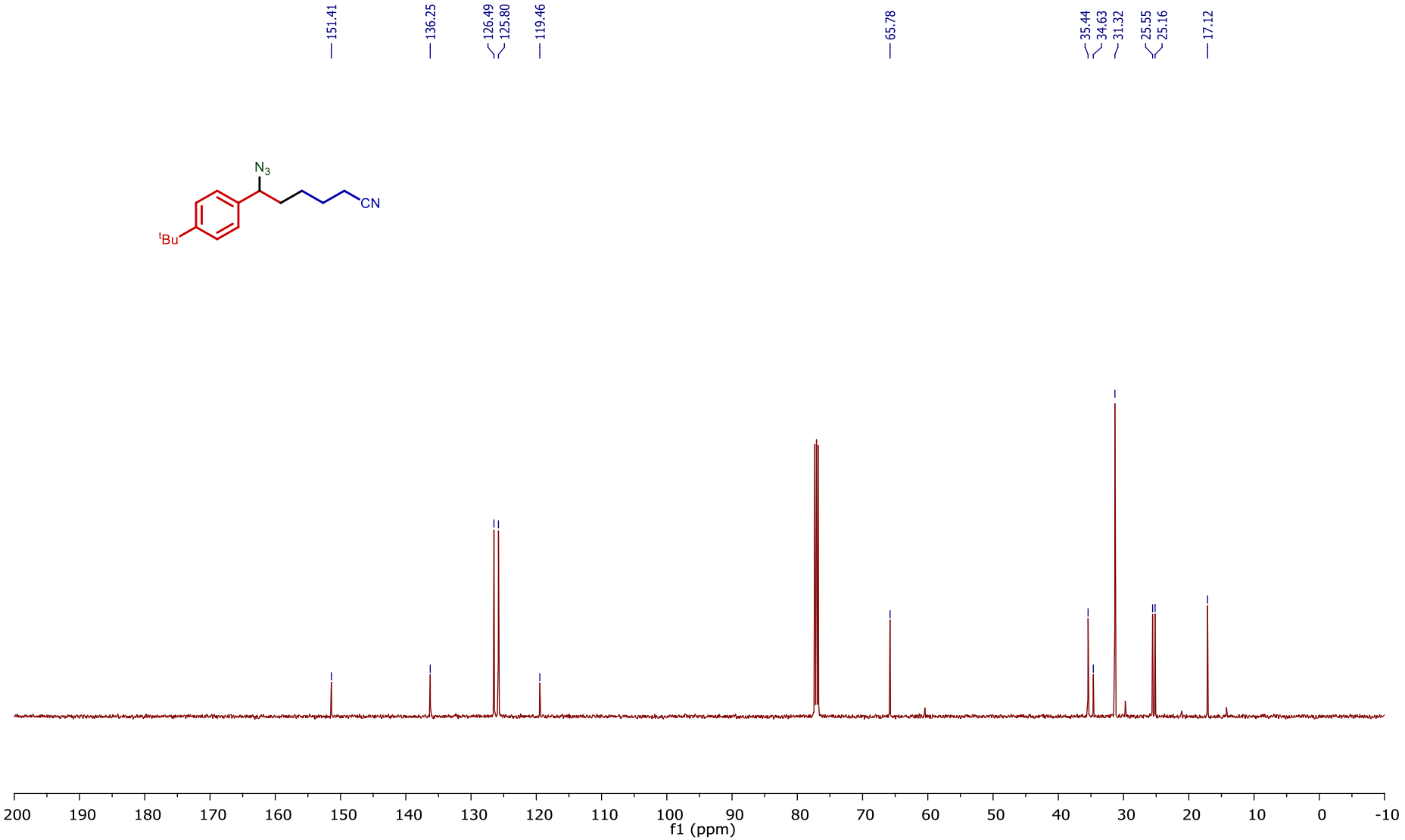
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(5)**



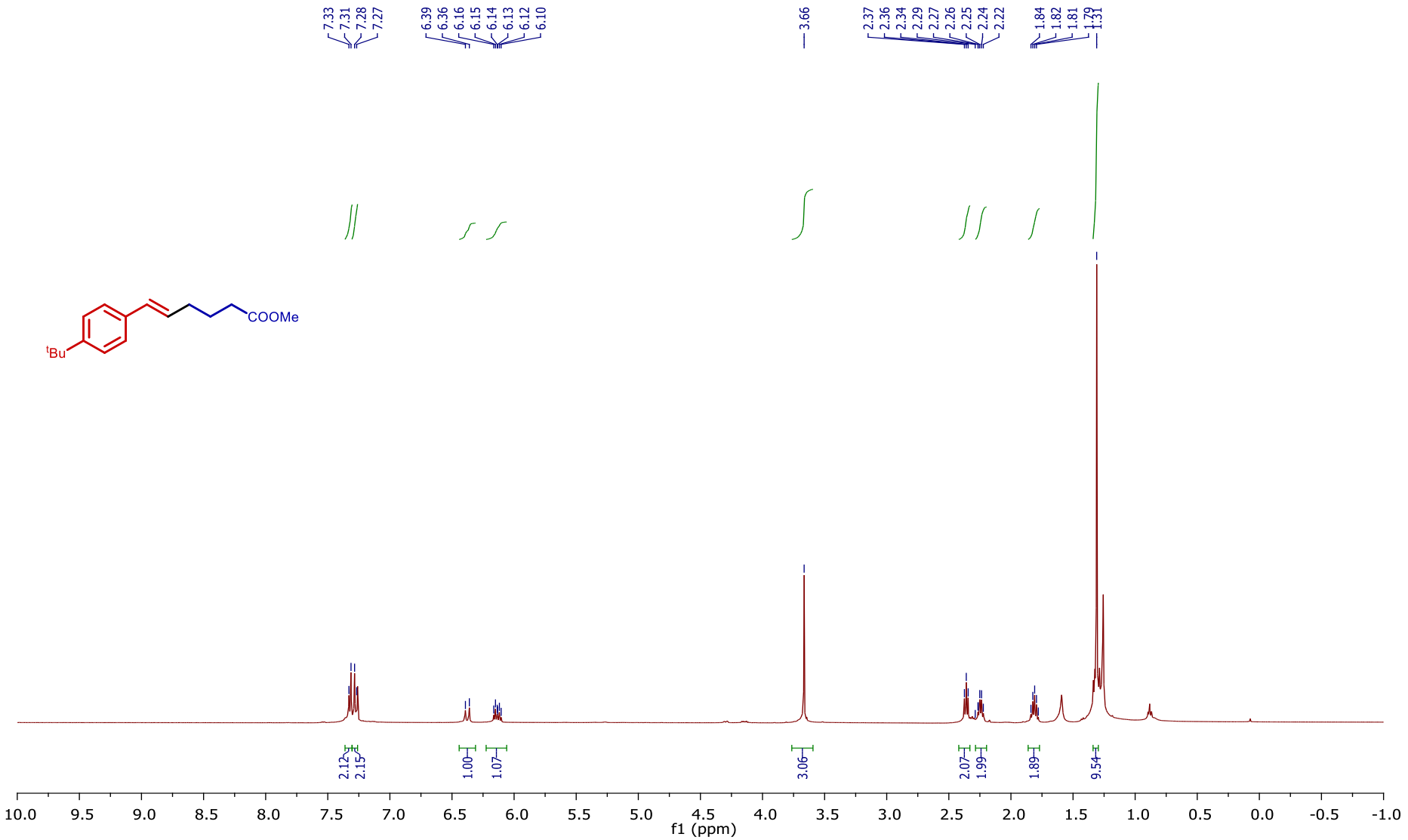
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(6)**



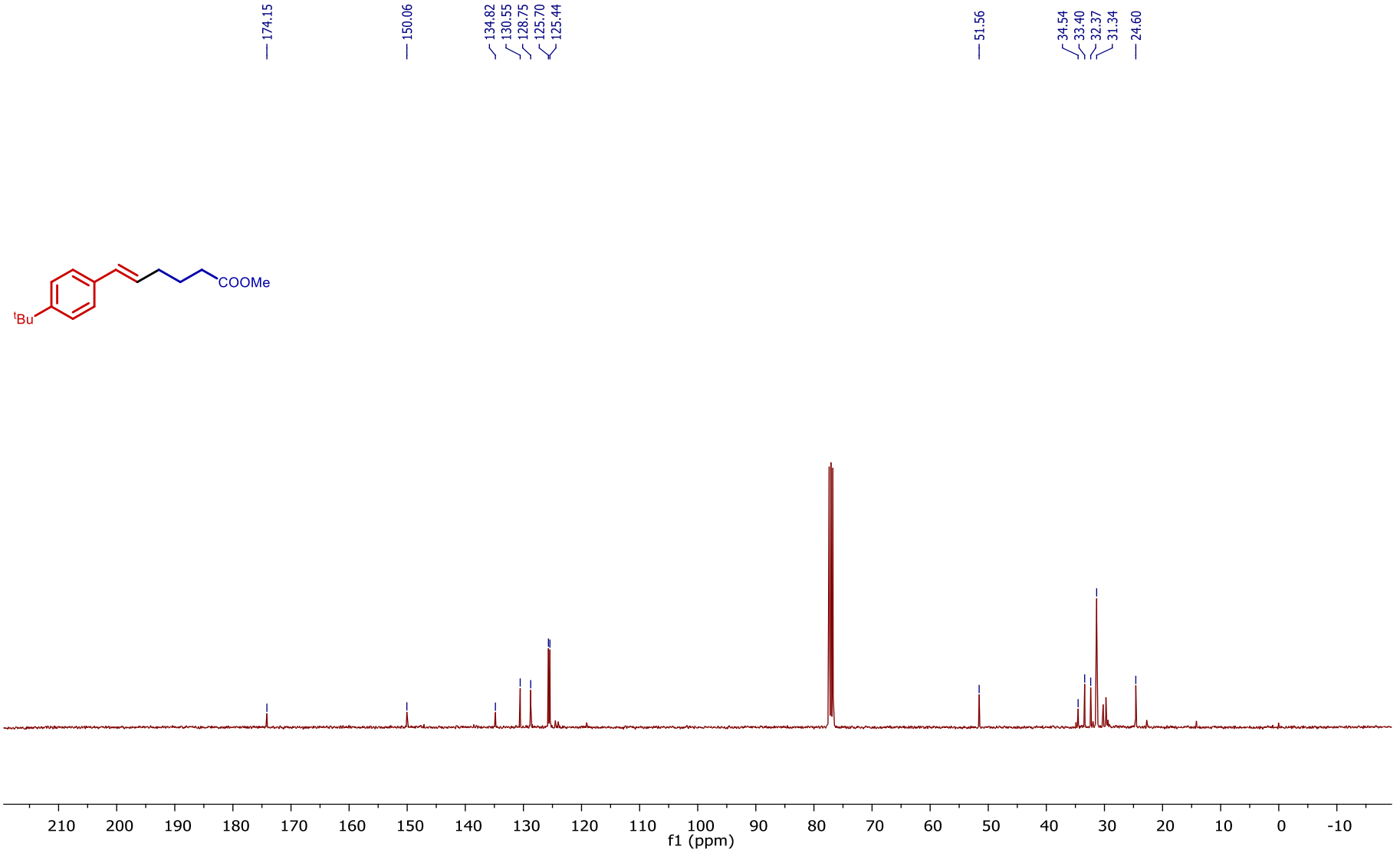
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(6)**



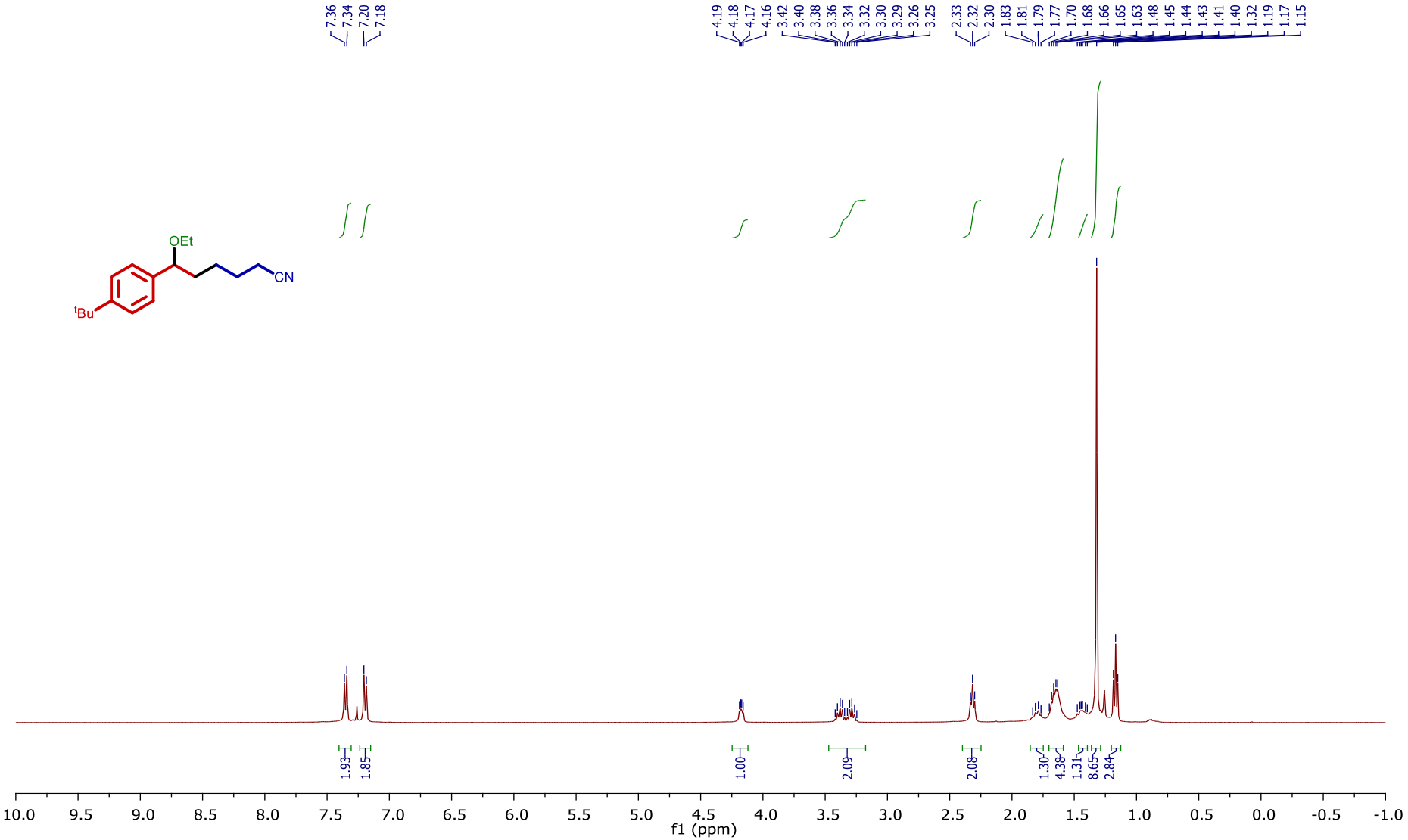
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(7)**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(7)**



^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(9)**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(9)**