Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting information

Deconjugative alkylation "pairing" as a simple platform for carbocycle synthesis

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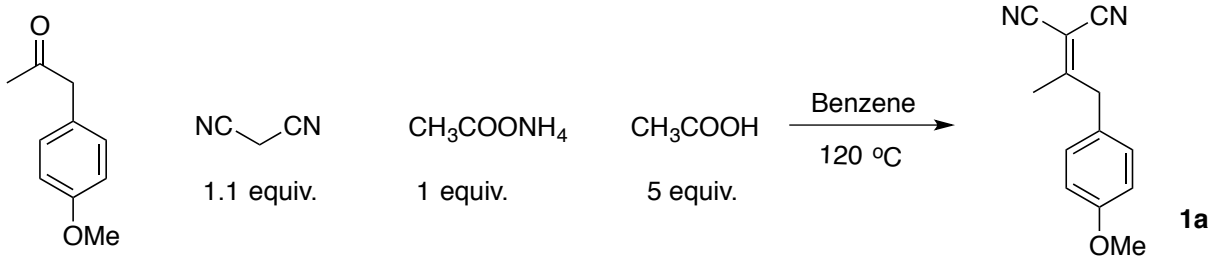
Experimental section

All commercial materials were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ (with $CHCl_3$ residual peak as an internal standard) or toluene-d_8 using a 500 MHz spectrometer. All ^{13}C NMR spectra were recorded with complete proton decoupling. HRMS data were recorded on Agilent Time of Flight 6200 spectrometer. Reaction progress was monitored by thin-layer chromatography (TLC) and visualized by UV light, phosphomolybdic acid stain, and $KMnO_4$ stain. All reactions were carried out using anhydrous solvents obtained dried by passing through activated alumina columns.

General procedure for Knoevenagel-condensation

All reaction components were dissolved in benzene and refluxed using a Dean-Stark apparatus until completion. The mixture was then cooled down, and the solvents were evaporated. The pure products were isolated *via* column chromatography (hexanes – ethyl acetate).

2-(1-(4-methoxyphenyl)propan-2-ylidene)malononitrile (1a)



Yellow oil, 8.3 g, 98% yield

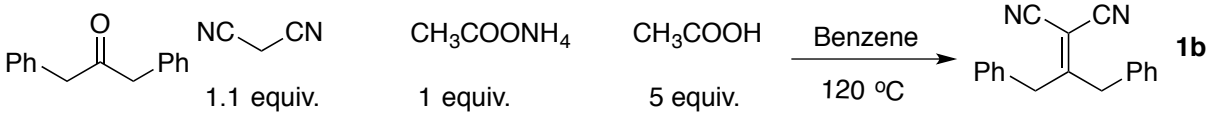
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 3.81 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.2, 159.5, 130.1, 126.4, 114.8, 112.2, 112.0, 86.1, 55.5, 43.0, 22.3.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{12}N_2O$ 235.0842; Found 235.0846.

R_f: 0.43 (hexanes – ethyl acetate 8:2).

2-(1,3-diphenylpropan-2-ylidene)malononitrile (1b)



Orange solid, 6 g, 99% yield

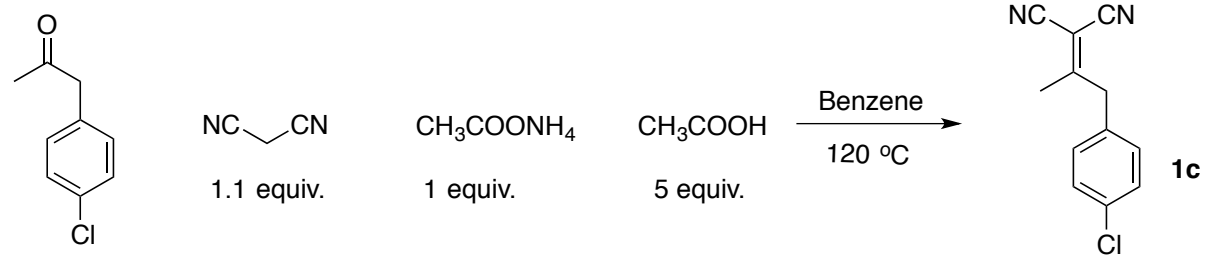
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 6H), 7.19 – 7.15 (m, 4H), 3.77 (s, 4H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.8, 134.5, 129.5, 129.1, 128.2, 112.2, 86.9, 40.5.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{14}N_2$ 281.1049; Found 281.1057.

R_f: 0.50 (hexanes – ethyl acetate 8:2), m.p 50-51 °C

2-(1-(4-chlorophenyl)propan-2-ylidene)malononitrile (1c)



Orange solid, 3.7 g, 96% yield

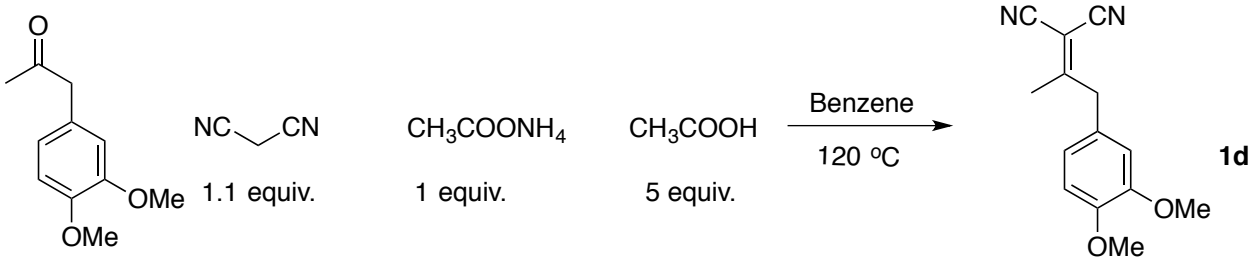
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 3.84 (s, 2H), 2.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 178.9, 134.4, 132.9, 130.3, 129.7, 112.0, 111.7, 87.0, 43.0, 22.3.

HRMS (ESI – TOF) m/z: $[M + NH_4]^+$ Calcd for $C_{12}H_9ClN_2$ 234.0793; Found 234.0793.

R_f: 0.45 (hexanes – ethyl acetate 9:1), m.p: 53-54 ºC

2-(1-(3,4-dimethoxyphenyl)propan-2-ylidene)malononitrile (1d)



Yellow crystals, 3.6 g, 97% yield

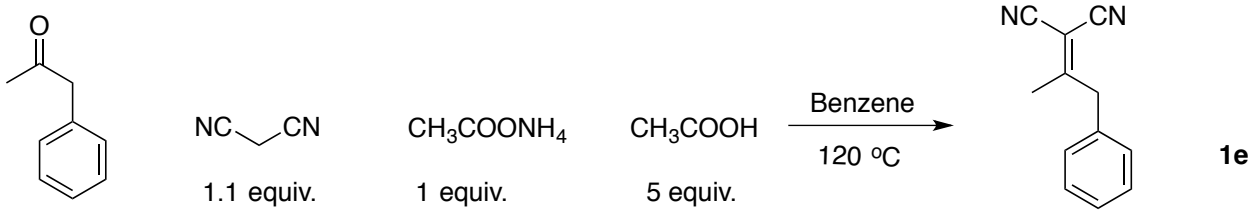
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.84 (d, *J* = 8.2 Hz, 1H), 6.74 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.68 (d, *J* = 2.0 Hz, 1H), 3.88 (s, 3H), 3.88 (s, 3H), 3.80 (s, 2H), 2.20 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 180.1, 149.7, 126.8, 121.4, 112.3, 112.0, 111.8, 86.1, 56.1, 56.1, 43.4, 22.4.

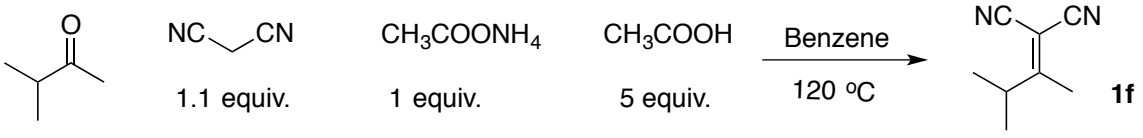
HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{14}N_2O_2$ 265.0947; Found 265.0943.

R_f: 0.40 (hexanes – ethyl acetate 7:3), m.p.:76-77 ºC

2-(1-phenylpropan-2-ylidene)malononitrile[1] (1e)



2-(3-methylbutan-2-ylidene)malononitrile (1f)



Colorless oil, 4.0 g, 86% yield

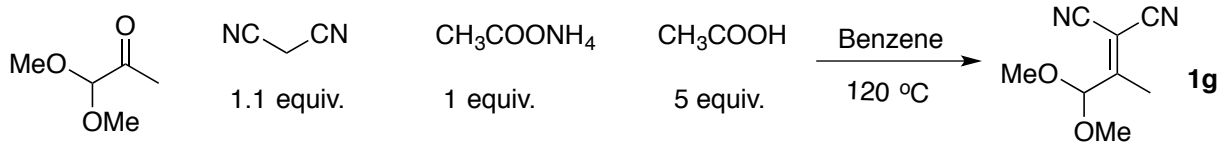
^{1}H NMR (500 MHz, $CDCl_3$) δ 3.24 (h, *J* = 6.7 Hz, 1H), 2.19 (s, 3H), 1.15 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 187.3, 112.1, 111.5, 84.7, 35.7, 20.2, 17.7.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_8H_{10}N_2$ 135.0917; Found 135.0917.

R_f: 0.65 (hexanes – ethyl acetate 85:15).

2-(1,1-dimethoxypropan-2-ylidene)malononitrile (1g)



Yellow oil, 2.7 g, 98% yield

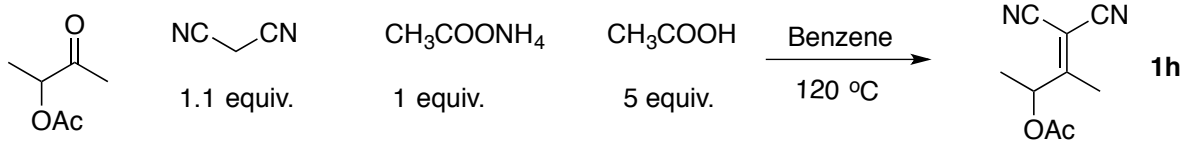
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.08 (s, 1H), 3.45 (s, 6H), 2.23 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 111.1, 110.7, 102.8, 87.5, 55.9, 17.3.

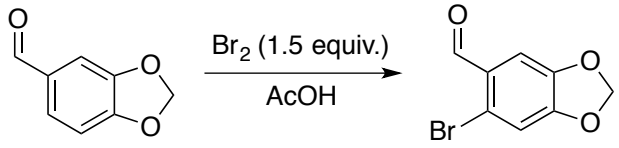
HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_8H_{10}N_2O_2$ 167.0815; Found 167.0812.

R_f: 0.55 (hexanes – ethyl acetate 85:15).

4,4-dicyano-3-methylbut-3-en-2-yl acetate[2] (1h)



Bromination of piperinal



To an oven dried 250 ml flask, piperinal (5g, 33 mmol, 1 equiv.) and 10 ml of glacial acetic acid was added. Initially 2 ml of Br_2 was added at room temperature, then after 24 hours 0.6 ml of Br_2 was added and stirred for 2 days. Upon completion *via* TLC, the solution was transferred to a separatory funnel. Ethyl acetate (150 mL) was added, and washed with 2x100 mL 10% $Na_2S_2O_3$ aqueous solution and brine. The organic phase was

evaporated and the solid product was recrystallized using ethanol. The product 6-bromobenzo[*d*][1,3]dioxole-5-carbaldehyde (5 g, 65%) appeared as white needle like crystals.

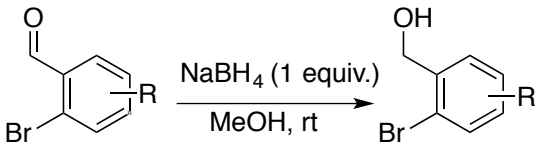
^{1}H NMR (500 MHz, $CDCl_3$) δ10.18 (s, 1H), 7.36 (s, 1H), 7.06 (s, 1H), 6.08 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.5, 153.5, 148.3, 128.2, 121.7, 113.4, 108.3, 102.9.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_8H_5BrO_3$ 228.9495; Found 228.9495.

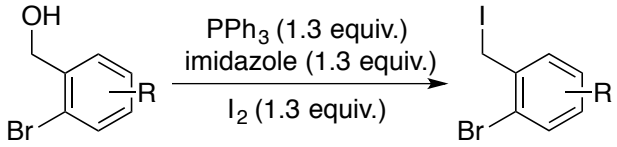
R_f: 0.70 (hexanes – ethyl acetate 9:1).

General procedure for reduction of aryl aldehydes

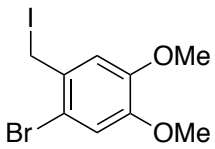


To an oven dried Schlenk flask, aryl aldehyde (1 equiv.) and Methanol (0.5 M concentration of the aldehyde) was added at 0 °C, which was followed by addition of $NaBH_4$ (1 equiv.) while blanketing with an inert gas. The ice bath was removed and stirred further (15-30 minutes) at room temperature. Upon completion *via* TLC the solution was transferred to a separatory funnel and ethyl acetate was added, then washed twice with brine. The organic phase was evaporated and purification was done using flash column chromatography.

General procedure for iodation of benzyl alcohol[3]



1-bromo-2-(iodomethyl)-4,5-dimethoxybenzene (2a)



Yellow solid, 5.8 g, 61%

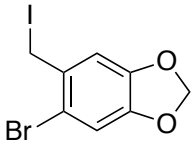
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.89 (s, 1H), 4.52 (s, 2H), 3.87 (s, 3H), 3.85 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 148.8, 130.1, 116.0, 114.6, 112.8, 56.4, 56.3, 7.2.

HRMS (ESI – TOF) m/z: $[M + NH_4]^+$ Calcd for $C_9H_{10}BrIO_2$ 373.9247; Found 373.9245.

R_f: 0.75 (hexanes – ethyl acetate 9:1), m.p.: 79-80 ºC

5-bromo-6-(iodomethyl)benzo[*d*][1,3]dioxole[4] (2b)



Orange solid, 1.2 g, 61%

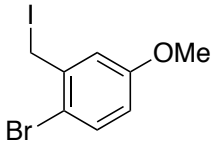
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.89 (s, 1H), 5.97 (s, 2H), 4.49 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.5, 147.8, 131.3, 115.3, 113.4, 110.0, 102.2, 7.21.

HRMS (ESI – TOF) m/z: $[M + NH_4]^+$ Calcd for $C_8H_6BrIO_2$ 357.8934; Found 357.8910.

R_f: 0.75 (hexanes – ethyl acetate 9:1), m.p.: 93-94 ºC

1-bromo-2-(iodomethyl)-4-methoxybenzene[5] (2c)



White solid, 1.5 g, 51%

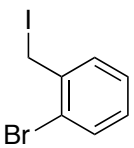
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 3.0 Hz, 1H), 6.70 (dd, *J* = 8.8, 3.0 Hz, 1H), 4.49 (s, 2H), 3.79 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 139.3, 134.2, 115.8, 115.9, 114.5, 55.7, 6.0.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for C_8H_8BrIO 325.8798; Found 325.8794.

R_f: 0.70 (hexanes – ethyl acetate 9:1), m.p. 83-84 ºC.

1-bromo-2-(iodomethyl)benzene (2d)



White solid, 7.1 g, 90%

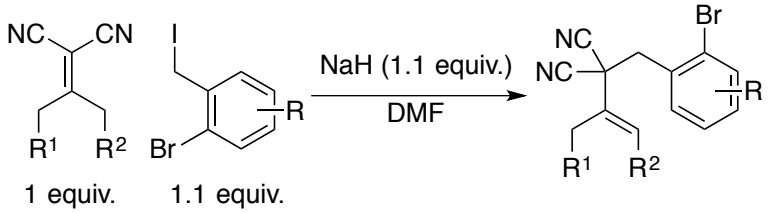
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 4.55 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 138.5, 133.7, 130.8, 129.7, 128.2, 124.2, 5.9.

HRMS (ESI – TOF) m/z: $[M + NH_4]^+$ Calcd for C_7H_6BrI 313.9036; Found 313.9048.

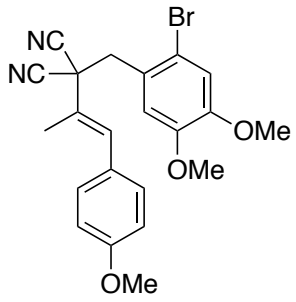
R_f: 0.75 (hexanes – ethyl acetate 9:1), m.p.: 82-81 ºC

General procedure for α-alkylation of Knoevenagel adducts



To an oven dried Schlenk flask, dry sodium hydride (1 equiv.) and dry dimethyl formamide (1M with respect to Knoevenagel adduct) was added and stirred at room temperature. First the Knoevenagel adduct (1 equiv., 1 g - 200 mg) and then, iodomethyl benzene (1.1 equiv.) was transferred immediately and stirred at room temperature. Upon completion *via* TLC the solution was transferred to a separatory funnel and ethyl acetate was added, and then washed twice with brine. The organic phase was evaporated and purification was done using flash column chromatography.

(*E*)-2-(2-bromo-4,5-dimethoxybenzyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile (3a)



Yellow semi-solid, 2.0 g, 99%

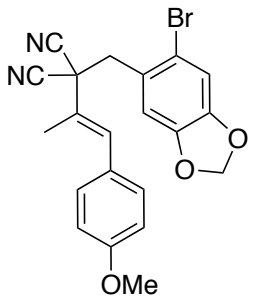
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.3 Hz, 2H), 7.05 (s, 2H), 6.90 (d, *J* = 8.3 Hz, 2H), 6.80 (s, 1H), 3.86 (s, 6H), 3.80 (s, 3H), 3.55 (s, 2H), 2.16 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 149.8, 148.4, 131.4, 130.4, 127.6, 125.4, 123.5, 116.3, 115.7, 114.5, 114.0, 113.9, 56.2, 56.1, 55.3, 46.2, 42.4, 15.5.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{21}BrN_2O_3$ 463.0628; Found 463.0621.

R_f: 0.45 (hexanes – ethyl acetate 7:3).

(*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile (3b)



Orange solid, 1.4 g, 70%

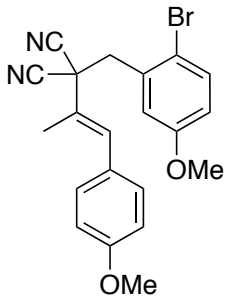
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.7 Hz, 2H), 7.08 (s, 1H), 7.04 (s, 1H), 6.92 (d, *J* = 8.7 Hz, 2H), 6.86 (s, 1H), 6.03 (s, 2H), 3.83 (s, 3H), 3.53 (s, 2H), 2.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 149.1, 147.9, 131.6, 130.5, 127.8, 125.7, 124.8, 117.2, 114.4, 114.1, 113.4, 111.2, 102.4, 55.5, 46.2, 42.7, 15.6.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{17}BrN_2O_3$ 447.0315; Found 447.0345.

R_f: 0.55 (hexanes – ethyl acetate 70:30), m.p.: 117-118 ºC

(*E*)-2-(2-bromo-5-methoxybenzyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile (3c)



White semi-solid, 353 mg, 91%

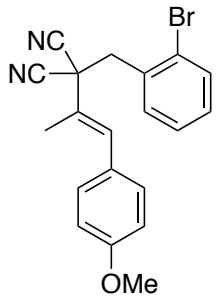
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.8 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 2H), 7.13 (s, 1H), 6.92 (d, *J* = 8.3 Hz, 2H), 6.83 (s, 1H), 6.81 (s, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.60 (s, 2H), 2.19 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 159.1, 134.1, 132.8, 131.7, 130.5, 127.7, 125.6, 117.1, 116.9, 116.5, 114.5, 114.0, 55.7, 55.5, 46.0, 42.7, 15.7.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{19}BrN_2O_2$ 433.0601; Found 433.0566.

R_f: 0.44 (hexanes – ethyl acetate 85:15).

(*E*)-2-(2-bromobenzyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile (3d)



Yellow semi-solid, 280 mg, 78%

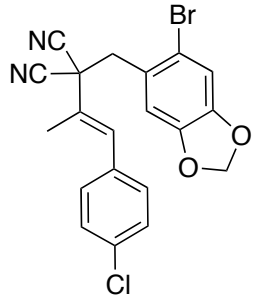
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 7.8, 1.7 Hz, 1H), 7.44 – 7.36 (m, 1H), 7.30 – 7.22 (m, 1H), 7.21 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.82 (s, 1H), 3.84 (s, 3H), 3.65 (s, 2H), 2.21 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 133.5, 132.0, 131.9, 131.6, 130.4, 130.4, 127.9, 127.6, 126.3, 125.4, 114.3, 114.0, 55.4, 45.9, 42.3, 15.6.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{17}BrN_2O$ 403.0416; Found 403.0431.

R_f: 0.60 (hexanes – ethyl acetate 85:15).

(*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1-(4-chlorophenyl)prop-1-en-2-yl)malononitrile (3e)



Pale white semi-solid, 531 mg, 67%

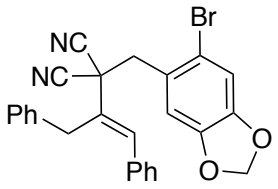
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.07 (s, 1H), 7.03 (s, 1H), 6.84 (s, 1H), 6.03 (s, 2H), 3.55 (s, 2H), 2.15 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 147.9, 134.1, 133.6, 130.9, 130.3, 128.8, 128.2, 124.4, 117.1, 114.1, 113.3, 111.1, 102.4, 45.9, 42.5, 15.6.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{14}BrClN_2O_2$ 450.9819; Found 450.9839.

R_f: 0.57 (hexanes – ethyl acetate 85:15).

(*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1,3-diphenylprop-1-en-2-yl)malononitrile (3f)



White semi-solid, 255 mg, 70%

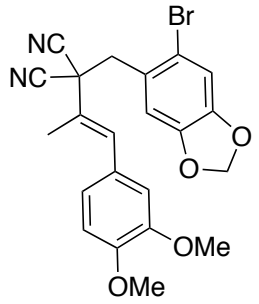
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.24 (m, 10H), 7.23 (s, 1H), 7.05 (s, 1H), 6.99 (s, 1H), 6.03 (s, 2H), 4.02 (s, 2H), 3.38 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 147.9, 136.9, 135.2, 134.7, 130.0, 129.1, 128.9, 128.7, 128.6, 127.3, 124.8, 117.3, 114.5, 113.3, 111.1, 102.4, 45.7, 44.3, 35.4.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{19}BrN_2O_2$ 493.0522; Found 493.0529.

R_f: 0.4 (hexanes – ethyl acetate 85:15).

(*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1-(3,4-dimethoxyphenyl)prop-1-en-2-yl)malononitrile (3g)



Yellow semi-solid, 300.7 mg, 80%

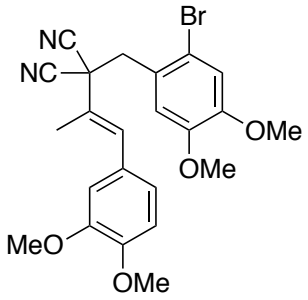
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (s, 1H), 7.04 (s, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 6.2 Hz, 2H), 6.76 (s, 1H), 6.03 (s, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 3.54 (s, 2H), 2.19 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 148.7, 147.7, 131.6, 127.8, 125.8, 124.4, 121.6, 117.0, 114.1, 113.1, 112.1, 112.1, 110.9, 110.9, 102.1, 55.8, 45.9, 42.4, 15.4.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{19}BrN_2O_4$ 477.0420; Found 477.0424.

R_f: 0.55 (hexanes – ethyl acetate 7:3).

(*E*)-2-(2-bromo-4,5-dimethoxybenzyl)-2-(1-(3,4-dimethoxyphenyl)prop-1-en-2-yl)malononitrile (3h)



Yellow solid, 3.0 g, 95%

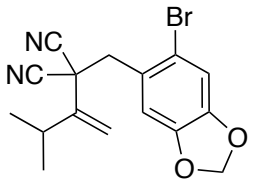
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, *J* = 2.7 Hz, 2H), 6.92 – 6.86 (m, 2H), 6.85 (s, 1H), 6.78 (s, 1H), 3.93 (s, 3H), 3.93 – 3.91 (m, 9H), 3.60 (s, 2H), 2.22 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7, 148.8, 148.6, 148.4, 131.5, 127.8, 125.7, 123.4, 121.7, 116.2, 115.6, 114.4, 114.0, 112.1, 110.9, 56.1, 56.0, 55.8, 55.8, 46.1, 42.3, 15.5.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{23}BrN_2O_4$ 471.0914; Found 471.0931.

R_f: 0.45 (hexanes – ethyl acetate 70:30), m.p.: 128-129 ºC

2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(3-methylbut-1-en-2-yl)malononitrile (3k)



White semi-solid, 35 mg, 54%

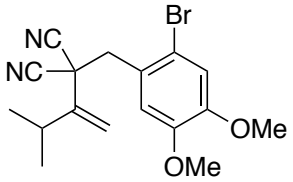
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 1H), 7.05 (s, 1H), 6.03 (s, 2H), 5.69 (s, 1H), 5.43 (s, 1H), 3.42 (s, 2H), 2.64 (hept, *J* = 6.9 Hz, 1H), 1.29 (s, 3H), 1.27 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.1, 147.9, 147.6, 124.8, 116.9, 115.1, 114.2, 113.4, 110.8, 102.4, 45.1, 43.2, 31.1, 24.6.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{15}BrN_2O_2$ 369.0209; Found 369.0203.

R_f: 0.65 (hexanes – ethyl acetate 9:1).

2-(2-bromo-4,5-dimethoxybenzyl)-2-(3-methylbut-1-en-2-yl)malononitrile (3l)



White semi-solid, 93 mg, 69%

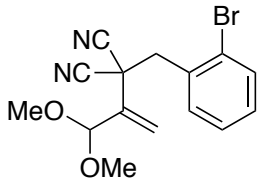
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 1H), 7.07 (s, 1H), 5.67 (s, 1H), 5.41 (s, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.43 (s, 2H), 2.63 (p, *J* = 6.8 Hz, 1H), 1.27 (s, 3H), 1.26 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 148.6, 147.5, 123.7, 116.1, 115.8, 115.0, 114.4, 113.7, 56.2, 56.2, 45.2, 43.1, 31.1, 24.5.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{19}BrN_2O_2$ 385.0522; Found 385.0523.

R_f: 0.70 (hexanes – ethyl acetate 9:1).

2-(2-bromobenzyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile (3m)



Colorless oil, 1.2 g, 58%

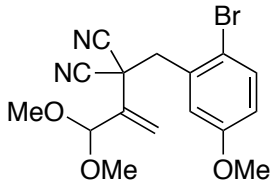
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.26 (t, *J* = 7.7 Hz, 1H), 5.88 (s, 1H), 5.85 (s, 1H), 5.07 (s, 1H), 3.72 (s, 2H), 3.51 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 133.5, 132.3, 132.0, 130.2, 127.7, 125.9, 120.7, 113.8, 102.5, 54.8, 43.1, 41.4.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{15}BrN_2O_2$ 357.0209; Found 357.0213.

R_f: 0.75 (hexanes – ethyl acetate 85:15).

2-(2-bromo-5-methoxybenzyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile (3n)



Yellow semi-solid, 323 mg, 42%

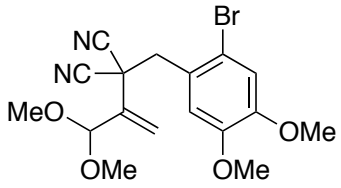
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.8 Hz, 1H), 7.12 (d, *J* = 3.0 Hz, 1H), 6.80 (dd, *J* = 8.8, 3.1 Hz, 1H), 5.84 (d, *J* = 19.4 Hz, 2H), 5.03 (s, 1H), 3.81 (s, 3H), 3.64 (s, 2H), 3.48 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 136.6, 134.0, 133.1, 120.8, 117.2, 116.6, 116.1, 113.9, 102.6, 55.6, 54.8, 43.4, 41.5.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{17}BrN_2O_3$ 387.0315; Found 387.0321.

R_f: 0.55 (hexanes – ethyl acetate 85:15).

2-(2-bromo-4,5-dimethoxybenzyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile (3o)



Yellow semi-solid, 214 mg, 45%

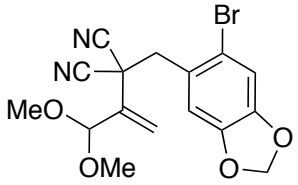
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (d, *J* = 2.3 Hz, 2H), 5.82 (d, *J* = 14.8 Hz, 2H), 5.01 (s, 1H), 3.88 (d, *J* = 6.7 Hz, 6H), 3.60 (s, 2H), 3.47 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 148.4, 136.7, 124.1, 120.8, 116.2, 115.9, 114.2, 114.2, 102.6, 56.2, 56.2, 55.0, 43.4, 41.9.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{19}BrN_2O_4$ 417.0420; Found 417.0433.

R_f: 0.65 (hexanes – ethyl acetate 8:2).

2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile (3p)



Yellow semi-solid, 1.0 g, 44%

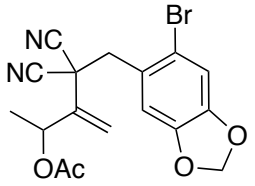
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (s, 1H), 7.03 (s, 1H), 6.02 (s, 2H), 5.85 (s, 1H), 5.82 (s, 1H), 5.03 (s, 1H), 3.59 (s, 2H), 3.48 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 147.6, 136.6, 125.0, 120.7, 116.8, 113.9, 113.2, 111.1, 102.6, 102.2, 54.8, 43.3, 41.6.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{15}BrN_2O_4$401.0107; Found 401.0116.

R_f: 0.55 (hexanes – ethyl acetate 85:15).

5-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-4,4-dicyano-3-methylenepentan-2-yl acetate (3q)



Yellow semi-solid, 223 mg, 51%

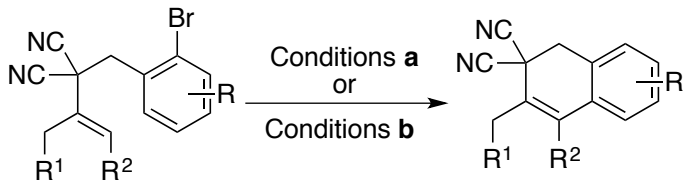
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.07 (s, 1H), 7.00 (s, 1H), 6.01 (s, 2H), 5.77 (s, 1H), 5.72 (s, 1H), 5.53 (q, *J* = 6.5 Hz, 1H), 3.77 (d, *J* = 14.2 Hz, 1H), 3.38 (d, *J* = 14.3 Hz, 1H), 2.12 (s, 3H), 1.57 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.7, 148.9, 147.6, 141.2, 124.4, 119.0, 116.9, 113.7, 113.5, 113.2, 110.8, 102.1, 68.2, 43.5, 42.5, 21.1, 20.7.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{15}BrN_2O_4$ 413.0107; Found 413.0095.

R_f: 0.6 (hexanes – ethyl acetate 7:3).

General procedure for Heck cyclization of α-alkylated Knoevenagel adducts



[a] $Pd(OAc)_2$ (0.1 equiv.), KOAc (5 equiv.), TBAI (2 equiv.), THF, 130 °C (sealed vessels), 15 hr
[b] $PdCl_2$ (0.05 equiv.), KOAc (5 equiv.), TBAI (2 equiv.), THF, 130 °C (pressure vessels), 3-5 hr

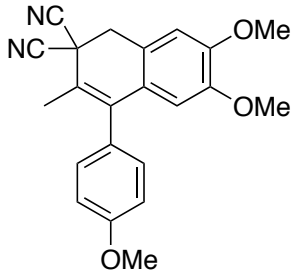
Condition A: To an oven dried pressure vessel, potassium acetate (5 equiv.), tetra-*n*-butyl ammonium bromide (2 equiv.), α-alkylated product (1 equiv.) and dry tetrahydrofuran (0.5 M with respect to the α-alkylated product) was transferred and stirred at room temperature while blanketing with an inert gas. Then palladium(II) acetate (0.1 equiv.) was added and sealed the pressure vessel with a screw cap, and stirred at 130 °C for 15 hours.

Condition B: To an oven dried pressure vessel, potassium acetate (5 equiv.), tetra-*n*-butyl ammonium bromide (2 equiv.), α-alkylated product (1 equiv.) and dry tetrahydrofuran (0.5 M with respect to the α-alkylated product) was transferred and stirred at room temperature while blanketing with an inert gas. Then palladium(II)

chloride (0.05 equiv.) was added and sealed the pressure vessel with a screw cap, and stirred at 130 °C for 3-5 hours.

Upon completion *via* TLC the solution was transferred to a separatory funnel and ethyl acetate was added, then washed twice with brine. The organic phase was evaporated and purification was done using flash column chromatography.

6,7-dimethoxy-4-(4-methoxyphenyl)-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile (4a)



White semi-solid, 91 mg, 54%

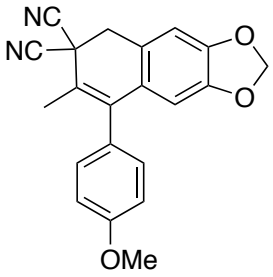
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.77 (s, 1H), 6.25 (s, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.59 (s, 3H), 3.51 (s, 2H), 2.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 149.2, 148.7, 139.4, 130.5, 129.2, 127.1, 120.4, 119.8, 115.1, 114.3, 111.2, 111.0, 56.2, 56.0, 55.4, 38.0, 37.5, 18.3.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{20}N_2O_3$ 383.1366; Found 383.1385.

R_f: 0.55 (hexanes – ethyl acetate 8:2).

8-(4-methoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile (4b)



Yellow semi-solid, 180 mg, 73%

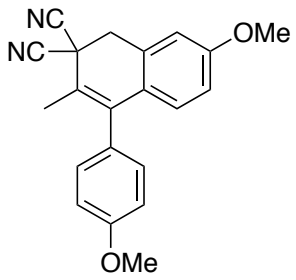
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.2 Hz, 2H), 6.98 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 1H), 6.22 (s, 1H), 5.93 (s, 2H), 3.87 (s, 3H), 3.48 (s, 2H), 2.03 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 147.7, 147.5, 139.3, 130.3, 129.1, 128.5, 121.7, 120.1, 114.8, 114.3, 108.4, 108.2, 101.5, 55.4, 38.2, 37.4, 18.2.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{16}N_2O_3$ 367.1053; Found 367.1045.

R_f: 0.5 (hexanes – ethyl acetate 70:30).

7-methoxy-4-(4-methoxyphenyl)-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile (4c)



White semi-solid, 67 mg, 73%

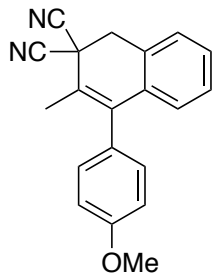
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.6 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.71 – 6.65 (m, 2H), 3.87 (s, 3H), 3.81 (s, 3H), 3.55 (s, 2H), 2.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 159.4, 139.4, 130.5, 129.4, 129.3, 129.1, 127.1, 119.3, 115.0, 114.3, 114.0, 113.3, 55.6, 55.5, 38.6, 37.3, 18.2.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{18}N_2O_2$ 353.1260; Found 353.1257.

R_f: 0.38 (hexanes – ethyl acetate 85:15).

4-(4-methoxyphenyl)-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile (4d)



Yellow semi-solid, 9 mg, 37%

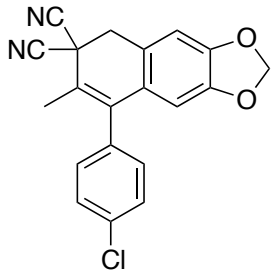
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 4.1 Hz, 2H), 7.22 – 7.16 (m, 1H), 7.08 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 6.75 (d, *J* = 7.8 Hz, 1H), 3.87 (s, 3H), 3.59 (s, 2H), 2.08 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 139.6, 133.9, 130.4, 128.9, 128.6, 128.5, 127.7, 127.5, 127.4, 122.1, 114.8, 114.3, 55.3, 38.1, 37.2, 18.3.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{16}N_2O$ 323.1155; Found 323.1168.

R_f: 0.60 (hexanes – ethyl acetate 85:15).

8-(4-chlorophenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile (4e)



White semi-solid, 227 mg, 39%

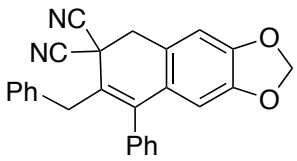
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.77 (s, 1H), 6.15 (s, 1H), 5.94 (s, 2H), 3.49 (s, 2H), 2.02 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.9, 147.9, 138.7, 135.6, 134.3, 130.7, 129.4, 127.8, 121.8, 120.7, 114.7, 108.6, 108.0, 101.8, 38.2, 37.4, 18.2.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{13}ClN_2O_2$ 371.0558; Found 371.0559.

R_f: 0.57 (hexanes – ethyl acetate 85:15).

7-benzyl-8-phenylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile (4f)



Yellow semi-solid, 87 mg, 56%

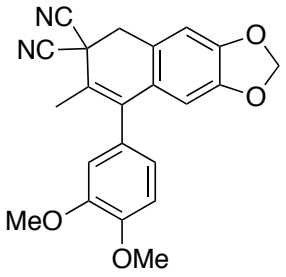
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.26 (m, 10H), 6.78 (s, 1H), 6.31 (s, 1H), 5.95 (s, 2H), 3.77 (s, 2H), 3.50 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 1478.0, 147.9, 141.6, 137.0, 135.5, 129.6, 129.1, 129.1, 129.1, 128.8, 128.4, 128.3, 127.4, 122.7, 122.5, 114.7, 108.6, 108.5, 101.7, 39.6, 38.3, 35.7.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{18}N_2O_2$ 413.1260; Found 413.1259.

R_f: 0.50 (hexanes – ethyl acetate 85:15).

8-(3,4-dimethoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile (4g)



Yellow semi-solid, 62.7 mg, 61%

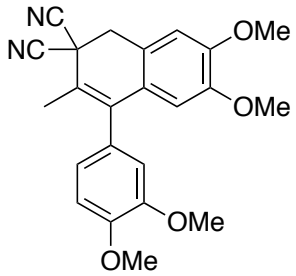
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.1 Hz, 1H), 6.75 (s, 1H), 6.68 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.60 (d, *J* = 1.9 Hz, 1H), 6.24 (s, 1H), 5.93 (s, 2H), 3.94 (s, 3H), 3.87 (s, 3H), 3.48 (s, 2H), 2.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 148.6, 147.6, 147.4, 139.3, 129.3, 128.2, 121.4, 121.4, 120.0, 114.6, 111.8, 111.3, 108.2, 108.0, 101.4, 55.9, 55.8, 38.1, 37.2, 18.1.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{18}N_2O_4$ 375.1339; Found 375.1337.

R_f: 0.55 (hexanes – ethyl acetate 7:3).

4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile (4h)



Yellow semi-solid, 2.3 g, 92%

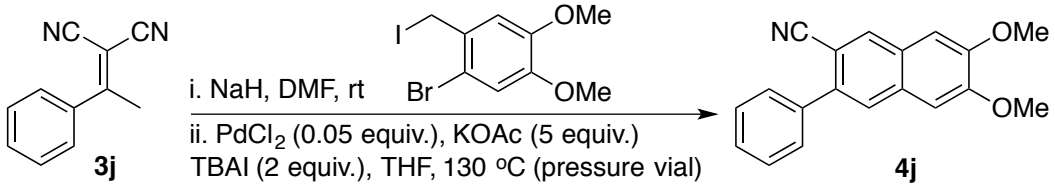
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.94 (d, *J* = 8.2 Hz, 1H), 6.77 (s, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 6.63 (s, 1H), 6.27 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 3.85 (s, 3H), 3.58 (s, 3H), 3.50 (s, 2H), 2.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.2, 149.2, 148.7, 139.4, 129.4, 126.9, 121.7, 120.3, 119.8, 115.0, 112.1, 111.3, 111.0, 111.0, 56.2, 56.1, 56.0, 56.0, 37.9, 37.4, 18.2.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{22}H_{22}N_2O_4$ 413.1472; Found 413.1465.

R_f: 0.26 (hexanes – ethyl acetate 7:3).

6,7-dimethoxy-3-phenyl-2-naphthonitrile (4j)



3j **4j**

Yellow semi-solid, 26 mg, 30%

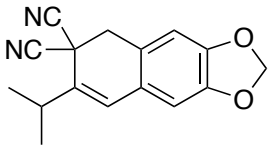
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.77 (s, 1H), 7.63 (d, *J* = 7.5 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.15 (s, 2H), 4.04 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.2, 150.8, 138.6, 138.6, 133.7, 131.4, 129.0, 128.6, 128.2, 127.4, 127.3, 119.4, 107.3, 106.2, 106.0, 56.1.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{15}NO_2$290.1176; Found 290.1177.

R_f: 0.6 (hexanes – ethyl acetate 85:15).

7-isopropylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile (4k)



Yellow semi-solid, 37 mg, 29%

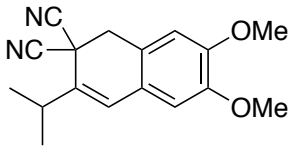
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.73 (s, 1H), 6.68 (s, 1H), 6.44 (s, 1H), 5.99 (s, 2H), 3.38 (s, 2H), 2.87 (h, *J* = 6.7 Hz, 1H), 1.32 (s, 3H), 1.31 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 134.1, 125.9, 125.6, 121.6, 115.0, 108.7, 107.9, 101.6, 39.3, 35.6, 32.4, 21.5.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{14}N_2O_2$ 289.0947; Found 289.0954.

R_f: 0.45 (hexanes – ethyl acetate 85:15).

3-isopropyl-6,7-dimethoxynaphthalene-2,2(1*H*)-dicarbonitrile (4l)



Yellow semi-solid, 47 mg, 55%

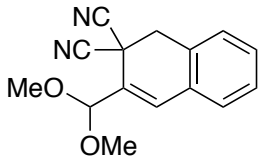
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.78 (d, *J* = 9.4 Hz, 2H), 6.55 (s, 1H), 3.94 (d, *J* = 10.3 Hz, 6H), 3.46 (s, 2H), 2.93 (p, *J* = 6.8 Hz, 1H), 1.37 (d, *J* = 6.7 Hz, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 149.1, 133.7, 125.5, 124.5, 120.1, 115.2, 111.1, 110.7, 56.2, 56.2, 39.1, 35.7, 32.4, 21.5.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}N_2O_2$ 305.1260; Found 305.1255.

R_f: 0.45 (hexanes – ethyl acetate 85:15).

3-(dimethoxymethyl)naphthalene-2,2(1*H*)-dicarbonitrile (4m)



Yellow semi-solid, 32 mg, 83%

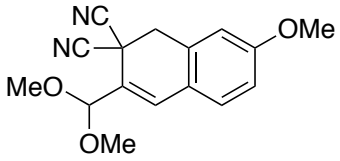
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 2H), 7.21 – 7.17 (m, 2H), 6.90 (s, 1H), 5.14 (s, 1H), 3.46 (s, 2H), 3.41 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 130.6, 130.3, 130.2, 129.1, 128.5, 128.4, 128.2, 125.5, 114.4, 101.4, 54.2, 39.3, 32.5.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{14}N_2O_2$ 277.0947; Found 277.0938

R_f: 0.75 (hexanes – ethyl acetate 85:15).

3-(dimethoxymethyl)-7-methoxynaphthalene-2,2(1*H*)-dicarbonitrile (4n)



Yellow semi-solid, 87.2 mg, 64%

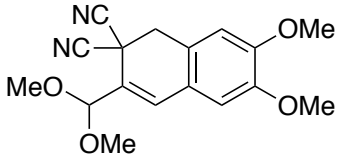
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.4 Hz, 1H), 6.92 (s, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.80 (s, 1H), 5.18 (s, 1H), 3.82 (s, 3H), 3.49 (s, 2H), 3.47 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7, 129.9, 129.7, 122.8, 122.2, 114.2, 114.1, 113.5, 101.3, 55.3, 53.9, 39.3, 32.2.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}N_2O_3$ 307.1053; Found 307.1063.

R_f: 0.65 (hexanes – ethyl acetate 85:15).

3-(dimethoxymethyl)-6,7-dimethoxynaphthalene-2,2(1*H*)-dicarbonitrile (4o)



White semi-solid, 91 mg, 54%

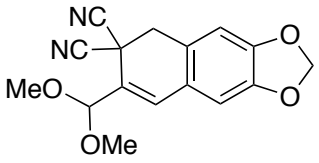
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.90 (s, 1H), 6.77 (d, *J* = 6.5 Hz, 2H), 5.20 (s, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.48 (s, 6H), 3.47 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.4, 149.2, 130.3, 123.2, 123.1, 121.3, 114.6, 111.5, 111.3, 101.5, 56.3, 56.3, 54.2, 39.2, 32.7.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{18}N_2O_4$ 337.1159; Found 337.1160.

R_f: 0.50 (hexanes – ethyl acetate 8:2).

7-(dimethoxymethyl)naphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile (4p)



Yellow semi-solid, 415 mg, 61%

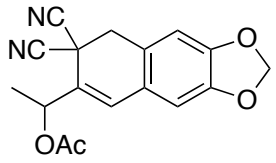
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.74 (s, 1H), 6.73 (s, 1H), 5.99 (s, 2H), 5.17 (s, 1H), 3.46 (s, 6H), 3.42 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 148.0, 130.2, 124.4, 123.3, 122.8, 114.4, 108.9, 108.6, 101.8, 101.4, 54.1, 39.2, 32.6.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{14}N_2O_4$ 321.0846; Found 321.0856.

R_f: 0.70 (hexanes – ethyl acetate 85:15).

1-(7,7-dicyano-7,8-dihydronaphtho[2,3-*d*][1,3]dioxol-6-yl)ethyl acetate (4q)



White semi-solid, 56 mg, 40%

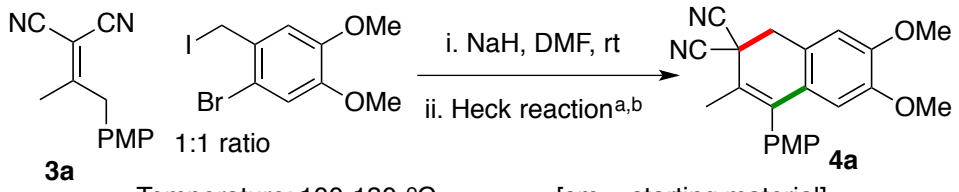
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.75 (s, 1H), 6.72 (s, 1H), 6.69 (s, 1H), 6.01 (s, 2H), 5.75 (q, J = 6.8, 6.4 Hz, 1H), 3.43 (s, 2H), 2.15 (s, 3H), 1.63 (d, J = 6.5 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 148.8, 147.9, 129.5, 126.6, 124.3, 122.2, 114.2, 108.6, 108.2, 101.6, 69.8, 38.9, 33.0, 20.9, 18.2.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{14}N_2O_4$ 333.0846; Found 333.0861.

R_f: 0.70 (hexanes – ethyl acetate 85:15).

Optimization of the 6-*endo-trig* Heck cyclization



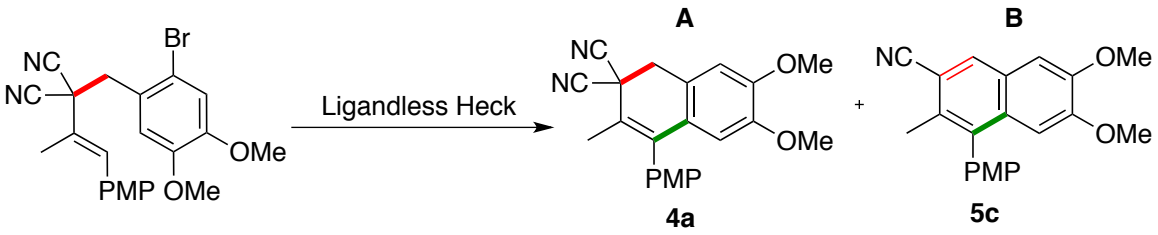
Temperature: 100-130 °C [sm = starting material]

Catalyst	Base	Ligand	Additives	solvents	Yield
10 mol% $Pd(PPh_3)_4$	Et_3N			THF, DMF, CH_3CN	sm
10 mol% $Pd(PPh_3)_4$	K_2CO_3			THF, DMF, CH_3CN	sm
10 mol% $Pd(OAc)_2$	KOAc	PPh_3	Bu_4NI	THF, DMF, CH_3CN	sm
10 mol% $Pd(OAc)_2$	NaOAc	TTBP	Bu_4NI	DMP	27%
10 mol% $Pd(OAc)_2$	Et_3N	DPPF		THF, DMF, CH_3CN	sm
10 mol% $Pd(OAc)_2$	KOAc	DPEPhos	Bu_4NI	DMP	sm
10 mol% $Pd(PPh_3)Cl_2$	KOAc		Bu_4NI	THF	sm
1 mol% $PdCl_2$	KOAc		Bu_4NI	THF	1%
10 mol% $Pd(OAc)_2$	KOAc		Bu_4NI	THF	32%
20 mol% $PdCl_2$	KOAc		Bu_4NI	THF	51%
5 mol% $PdCl_2$	KOAc		Bu_4NI	THF	71%
			Bu_4NBr		
			Bu_4NCl		

Procedure: Refer page 10 and 17

^{1}H NMR, ^{13}C NMR, HRMS: Refer page 23.

Base study for the 6-endo-trig Heck cyclization



Conditions : $PdCl_2$ (0.05 equiv.), **Base** (5 equiv.), TBAI (2 equiv.), THF, 130 °C (pressure vial)

Base	Yields	Time	NMR (ratio of A:B)
K_2CO_3	A = 56% B = 22%	18 hrs	(7:3)
K_3PO_4	A = 28%	18 hrs	~20:1
Cs_2CO_3	A = 27%	18 hrs	~7:3
Na_2CO_3	A = 50%	18 hrs	~8:2
KOAc	A =56%	18 hrs	98:2
KOAc	A = 71%	5 hrs	100%

Procedure: Refer page 10 and 17

^{1}H NMR, ^{13}C NMR, HRMS of product A: Refer page 23.

Product B:

Yellow semi-solid, 7 mg, 22%

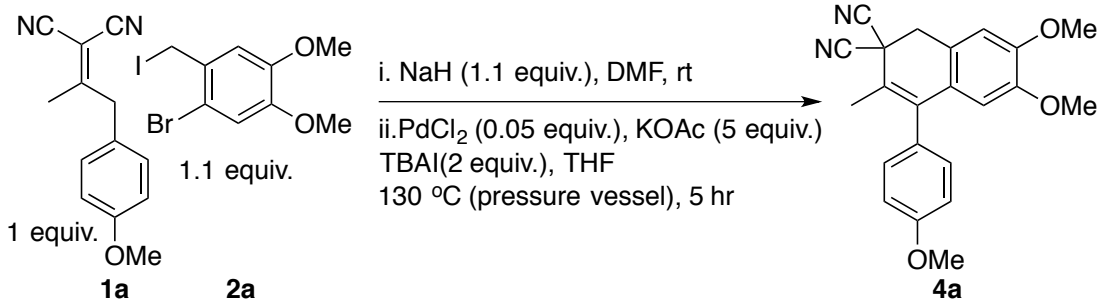
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.84 (s, 1H), 4.15 (s, 3H), 4.06 (s, 3H), 3.87 (s, 3H), 2.50 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 151.6, 149.8, 138.3, 132.2, 131.8, 131.4, 130.9, 130.7, 126.9, 119.4, 114.3, 109.4, 106.3, 105.3, 56.1, 55.8, 55.4, 19.1.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{19}NO_3$ 334.1438; Found 356.1264.

R_f: 0.53 (hexanes – ethyl acetate 85:15).

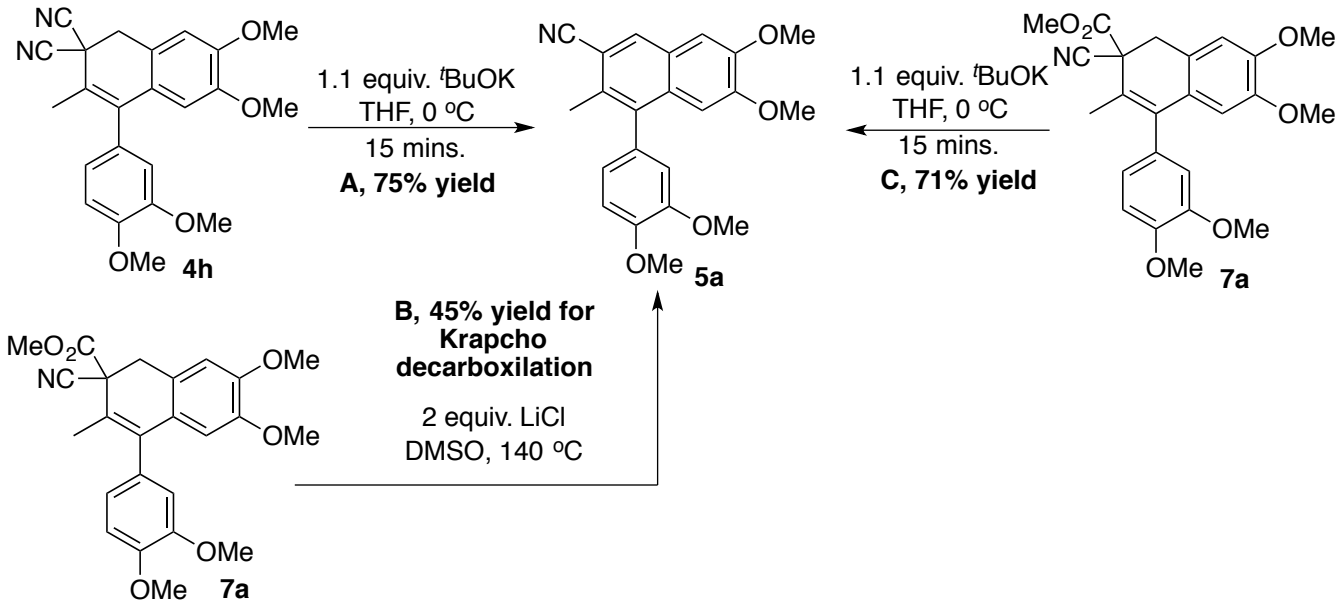
One-pot synthesis



To an oven dried 25 ml Schlenk flask, dry sodium hydride (1 equiv., 25 mg) and dry dimethyl formamide (1M with respect to Knoevenagel adduct, 942 µl) was added and stirred at room temperature. First the Knoevenagel adduct (1 equiv., 200 mg) and then, iodomethyl benzene (1.1 equiv., 370 mg) was transferred immediately and stirred at room temperature for 20 minutes. Upon completion *via* TLC, the mixture was transferred to a separatory funnel and ethyl acetate (150 mL) was added, followed by 2×100 mL of brine, to remove dimethyl formamide. Then the mixture was transferred to an oven dried 15 ml pressure vessel. Next, potassium acetate (5 equiv., 462 mg), tetra-*n*-butyl ammonium bromide (2 equiv., 696 mg) and dry tetrahydrofuran (0.5 M with respect to the Knoevenagel product) was transferred to the pressure vessel and stirred at room temperature while blanketing with an inert gas. Next palladium(II) chloride (0.05 equiv., 8 mg) was added and sealed the pressure vessel with a screw cap, and stirred at 130 °C for 5 hours. Upon completion *via* TLC, the solution was transferred to a separatory funnel. Then ethyl acetate (150 mL) was added, and washed with 2×100 mL of brine. The organic phase was evaporated and purification was done using flash column chromatography (2:8 ethyl acetate to hexane), which yielded 56% (190 mg) of 6,7-dimethoxy-4-(4-methoxyphenyl)-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile.

Decyanation of *gem-di*nitrile

General procedures for 4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-2-naphthonitrile (5a)



Conditions A and C: To an oven dried Schlenk flask, the Heck product (**A**) or ester (**C**) (1 equiv.), potassium *tert*-butoxide (1.1 equiv.) and tetrahydrofuran (0.2 M with respect to the Heck or ester product) was transferred and stirred at 0 °C. Upon completion *via* TLC the solution was transferred to a separatory funnel and ethyl acetate was added, then washed twice with brine. The organic phase was evaporated and purification was done using flash column chromatography.

Conditions B: To an oven dried Schlenk flask, ester (**B**) (1 equiv.), lithium chloride (2 equiv.) and DMSO (0.2 M with respect to theester product) was transferred and stirred at 140 °C. Upon completion *via* TLC the solution was transferred to a separatory funnel and ethyl acetate was added, then washed twice with brine. The organic phase was evaporated and purification was done using flash column chromatography.

Yellow solid, 29 mg, 60% (**A**); 35 mg, 45% (**B**); 30 mg, 71% (**C**)

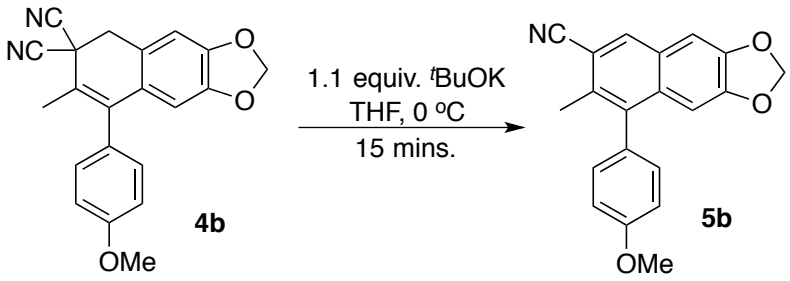
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.11 (s, 1H), 7.02 (d, J = 8.1 Hz, 1H), 6.78 (d, J = 8.2 Hz, 1H), 6.73 (s, 1H), 6.71 (s, 1H), 3.99 (s, 3H), 3.98 (s, 3H), 3.86 (s, 3H), 3.72 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 149.9, 149.2, 148.5, 138.4, 132.3, 131.9, 131.4, 131.1, 126.9, 122.1, 119.4, 112.8, 111.5, 109.5, 106.3, 105.3, 56.1, 56.1, 56.0, 55.9, 19.1.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{21}NO_4$ 364.1543; Found 364.1553.

R_f: 0.50 (hexanes – ethyl acetate 7:3).

8-(4-methoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile (5b)



White semi-solid, 5.8 mg, 69%

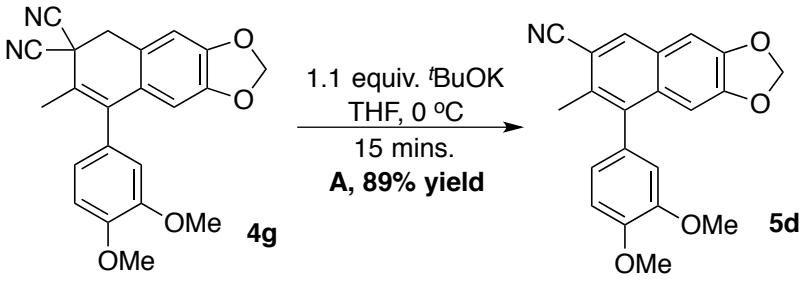
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.13 – 7.08 (m, 3H), 7.04 (d, *J* = 8.5 Hz, 2H), 6.70 (s, 1H), 6.02 (s, 2H), 3.90 (s, 3H), 2.34 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 150.2, 148.0, 139.1, 133.2, 132.8, 132.4, 131.0, 130.8, 128.2, 119.3, 114.4, 109.8, 103.9, 103.3, 101.7, 55.5, 19.2.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{15}NO_3$ 318.1125; Found 318.1118.

R_f: 0.55 (hexanes – ethyl acetate 85:15).

8-(3,4-dimethoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile (5d)



Pale white semi-solid, 25 mg, 89%

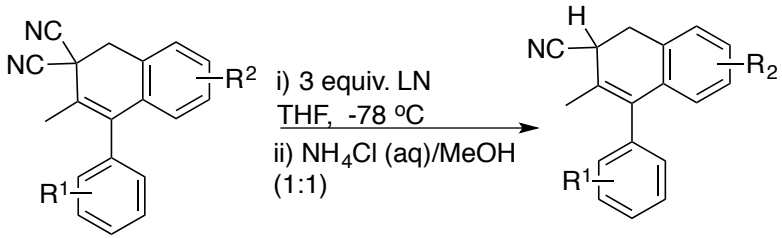
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.11 (s, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.76 – 6.71 (m, 2H), 6.69 (s, 1H), 6.03 (s, 2H), 3.97 (s, 3H), 3.86 (s, 3H), 2.35 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 149.3, 148.6, 148.0, 139.2, 133.1, 132.7, 132.3, 131.1, 128.2, 122.1, 119.2, 112.8, 111.6, 109.8, 103.9, 103.2, 101.7, 56.1, 19.1.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{17}NO_4$ 348.1230; Found 348.1230.

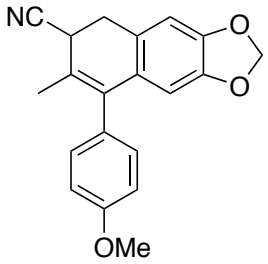
R_f: 0.45 (hexanes – ethyl acetate 85:15).

General procedure for reductive decyanation of *gem*-dinitriles



To an oven dried Schlenk flask, the Heck product (1 equiv.) and dry tetrahydrofuran (0.1 M with respect to the Heck product) was transferred and stirred at -78 °C for 10 minutes, while blanketing with an inert gas. Then lithium naphthalinide[6] (LN) was added and quenched immediately (after 10 seconds) with methanol: saturated ammonium chloride solution (1:1) at -78 °C. The solution was transferred to a separatory funnel and ethyl acetate was added. Then washed twice with brine. The organic phase was evaporated and purification was done using flash column chromatography.

8-(4-methoxyphenyl)-7-methyl-5,6-dihydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile (SI1)



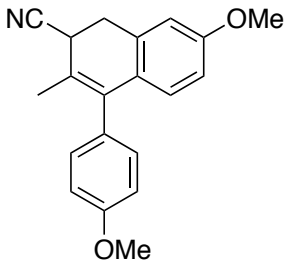
White semi-solid, 25 mg, 51%

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.05 (d, *J* = 7.6 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.70 (s, 1H), 6.20 (s, 1H), 5.88 (s, 2H), 3.85 (s, 3H), 3.46 (t, *J* = 6.6 Hz, 1H), 3.13 (dd, *J* = 15.4, 6.2 Hz, 1H), 3.04 (dd, *J* = 15.4, 6.9 Hz, 1H), 1.88 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 146.8, 146.4, 136.7, 130.9, 130.6, 129.9, 124.8, 124.0, 120.4, 114.1, 108.3, 107.6, 101.2, 55.4, 32.3, 32.1, 19.9.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{17}NO_3$ 342.1101; Found 342.1101.

7-methoxy-4-(4-methoxyphenyl)-3-methyl-1,2-dihydronaphthalene-2-carbonitrile (6b)



White semi-solid, 15 mg, 39%

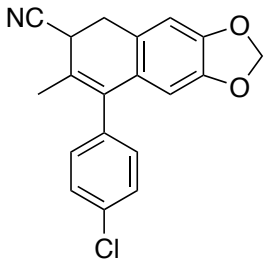
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 – 7.04 (m, 2H), 6.97 (s, 1H), 6.95 (s, 1H), 6.76 (s, 1H), 6.61 (s, 2H), 3.86 (s, 3H), 3.79 (s, 3H), 3.50 (t, *J* = 6.6 Hz, 1H), 3.20 (dd, *J* = 15.4, 6.3 Hz, 1H), 3.12 (dd, *J* = 15.4, 6.9 Hz, 1H), 1.88 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 158.9, 136.6, 132.6, 131.0, 130.7, 128.7, 127.9, 123.2, 120.5, 114.0, 113.8, 112.1, 55.4, 55.4, 32.4, 32.1, 19.8.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}NO_2$ 306.1489; Found 306.1480.

R_f: 0.53 (hexanes – ethyl acetate 85:15).

8-(4-chlorophenyl)-7-methyl-5,6-dihydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile (6c)



Pale orange semi-solid, 7 mg, 33%

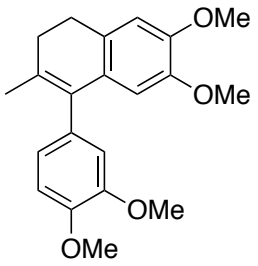
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.12 – 7.04 (m, 2H), 6.73 – 6.70 (m, 1H), 6.12 (s, 1H), 5.89 (s, 2H), 3.47 (t, *J* = 6.6 Hz, 1H), 3.13 (dd, *J* = 15.4, 6.3 Hz, 1H), 3.05 (dd, *J* = 15.4, 6.9 Hz, 1H), 1.87 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 146.7, 136.9, 136.1, 133.6, 131.2, 129.1, 124.8, 124.6, 120.1, 108.5, 107.3, 101.3, 32.2, 32.0, 19.9.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{14}ClNO_2$ 346.0605; Found 346.0591.

R_f: 0.43 (hexanes – ethyl acetate 85:15).

4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene (6d)



White semi-solid, 12 mg, 24%

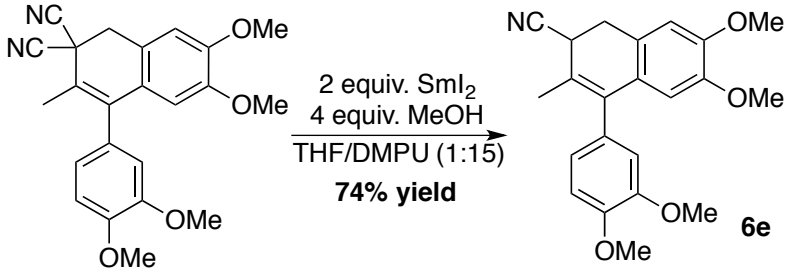
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.91 (d, *J* = 8.1 Hz, 1H), 6.74 – 6.68 (m, 3H), 6.25 (s, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.59 (s, 3H), 2.81 (t, *J* = 8.1 Hz, 2H), 2.36 (t, *J* = 8.1 Hz, 2H), 1.75 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 147.7, 147.1, 147.1, 132.9, 132.7, 132.1, 130.1, 127.6, 122.6, 113.4, 111.2, 111.1, 110.0, 56.2, 56.1, 56.0, 56.0, 30.6, 28.1, 21.5.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{24}O_4$ 363.1567; Found 363.1575

R_f: 0.53 (hexanes – ethyl acetate 85:15).

4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carbonitrile[7] (6e)



White solid, 26 mg, 74%

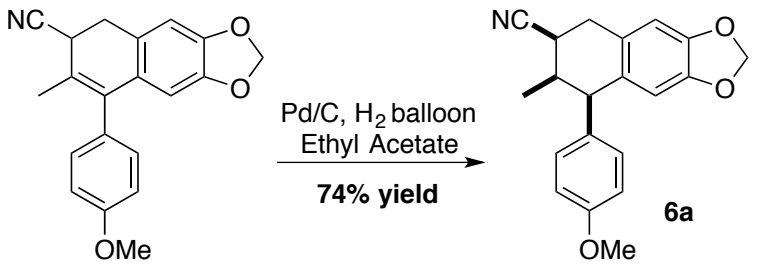
^{1}H NMR (500 MHz, Toluene-d8, 50 °C) δ 6.70 (d, *J* = 8.0 Hz, 1H), 6.67 – 6.61 (m, 2H), 6.49 (s, 1H), 6.44 (s, 1H), 3.52 (s, 6H), 3.46 (s, 3H), 3.32 (d, *J* = 1.2 Hz, 3H), 2.99 (t, *J* = 7.1 Hz, 1H), 2.79 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.75 (dd, *J* = 15.3, 6.7 Hz, 1H), 1.81 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 148.1, 148.1, 147.7, 136.6, 130.7, 128.1, 123.6, 123.4, 122.2, 120.5, 120.4, 112.6, 111.1, 110.5, 56.0, 56.0, 55.9, 55.8, 32.1, 31.5, 19.8.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}NO_4$ 366.1700; Found 366.1712.

R_f: 0.26 (hexanes – ethyl acetate 7:3).

Synthesis of (6*S*,7*R*,8*R*)-8-(4-methoxyphenyl)-7-methyl-5,6,7,8-tetrahydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile (6a)



To an oven dried Schlenk flask, the Heck product (1 equiv., 24 mg), palladium on carbon (0.1 equiv., 1mg) and ethyl acetate (1 M with respect to the Heck product, 75 µl) was transferred and stirred at room temperature, while subjecting to a positive pressure of hydrogen gas for 12 hours. Upon completion *via* TLC the mixture was passed through a celite plug and washed with 2×50 ml of ethyl acetate. The organic phase was evaporated and purification was done using flash column chromatography (2:8 ethyl actate to hexane), which yielded 74% of an orange solid (19mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.3 Hz, 2H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.58 (s, 1H), 6.40 (s, 1H), 5.88 (d, *J* = 11.3 Hz, 2H), 4.19 (d, *J* = 5.2 Hz, 1H), 3.82 (s, 3H), 3.21 – 3.11 (m, 2H), 2.99 (dd, *J* = 22.9, 11.7 Hz, 1H), 2.43 (p, *J* = 6.7 Hz, 1H), 0.91 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 146.6, 146.4, 133.9, 131.1, 129.5, 126.0, 121.6, 113.8, 109.8, 108.0, 101.1, 55.4, 49.3, 35.9, 31.8, 28.7, 11.0.

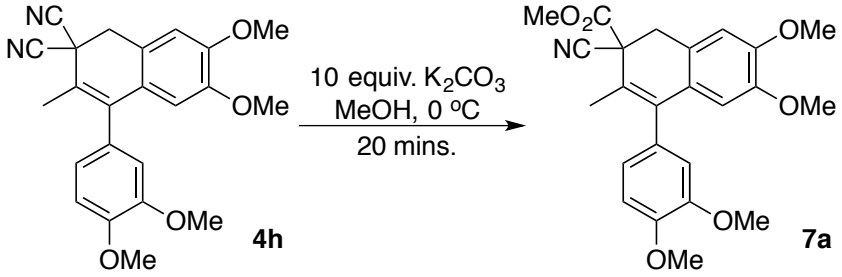
HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{19}NO_3$ 344.1257; Found 344.1264.

R_f: 0.33 (hexanes – ethyl acetate 85:15).

General procedure for ester formation of *gem-di*nitrile

To an oven dried Schlenk flask, the Heck product (1 equiv.), potassium carbonate (10 equiv.) and alcohol (0.1 M with respect to the Heck product) was transferred and stirred at 0 °C. Upon completion *via* TLC the solution was transferred to a separatory funnel and ethyl acetate was added, then washed twice with brine. The organic phase was evaporated and purification was done using flash column chromatography.

Methyl 2-cyano-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carboxylate (7a)



Yellow semi-solid, 125 mg, 91%

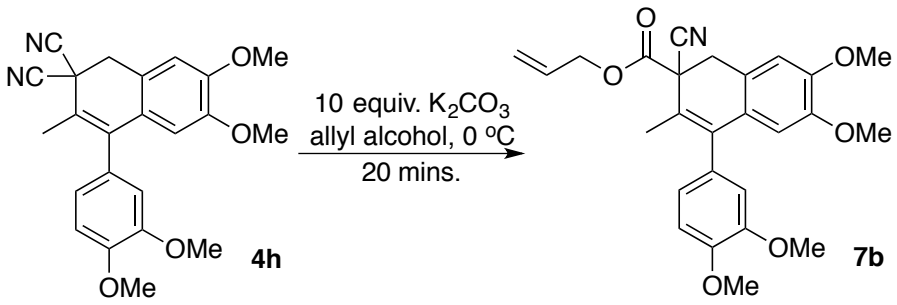
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.89 (d, *J* = 8.1 Hz, 1H), 6.70 – 6.66 (m, 2H), 6.61 (s, 1H), 6.18 (s, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.56 (d, *J* = 15.4 Hz, 1H), 3.52 (s, 3H), 3.28 (d, *J* = 15.4 Hz, 1H), 1.82 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 149.0, 148.5, 148.2, 147.9, 138.1, 130.4, 127.2, 123.0, 122.2, 121.8, 118.5, 112.4, 111.2, 110.8, 110.6, 56.0, 56.0, 55.8, 55.8, 53.8, 49.2, 36.7, 17.5.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{25}NO_6$ 446.1574; Found 446.1557.

R_f: 0.22 (hexanes – ethyl acetate 7:3).

Allyl 2-cyano-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carboxylate (7b)



Colorless liquid, 66 mg, 63%

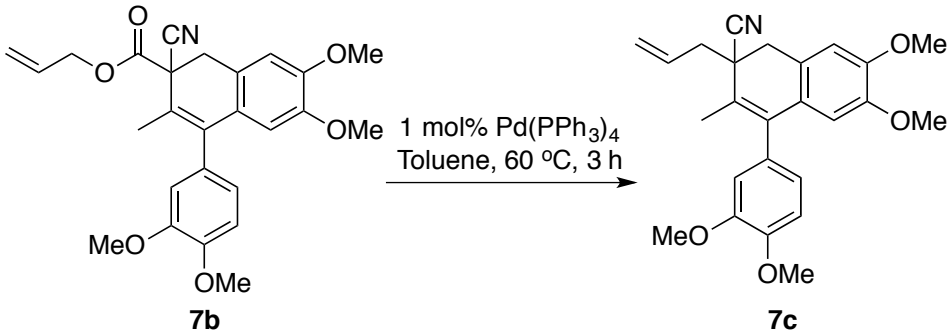
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.2 Hz, 1H), 6.73 – 6.68 (m, 2H), 6.64 (s, 1H), 6.21 (s, 1H), 5.88 (ddt, *J* = 16.5, 11.1, 5.7 Hz, 1H), 5.33 (d, *J* = 17.2 Hz, 1H), 5.26 (d, *J* = 10.6 Hz, 1H), 4.75 – 4.65 (m, 2H), 3.92 (s, 3H), 3.86 (d, *J* = 12.0 Hz, 6H), 3.61 (d, *J* = 15.4 Hz, 1H), 3.56 (s, 3H), 3.36 (d, *J* = 15.4 Hz, 1H), 1.89 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.4, 149.1, 148.6, 148.3, 148.0, 138.2, 130.8, 130.6, 127.3, 123.2, 122.4, 121.9, 119.4, 118.6, 112.4, 111.2, 110.8, 110.7, 67.3, 56.1, 56.1, 56.0, 55.9, 49.4, 36.8, 18.3.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{27}NO_6$ 450.1911; Found 450.1912

R_f: 0.35 (hexanes – ethyl acetate 7:3).

Synthesis of 2-allyl-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carbonitrile (7c)



To an oven dried 10 ml Schlenk flask, 2-allyl-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carbonitrile (1 equiv., 50 mg), tetrakis(triphenylphosphine)palladium(0) (0.01 equiv., 1.3

mg) and dry toluene (1 M with respect to the ester, 111 μl) was transferred and stirred at 60 °C , while blanketing with an inert gas. Upon completion *via* TLC the mixture was passed through a silica plug and washed with 2×50 ml of ethyl acetate. The organic phase was evaporated and purification was done using flash column chromatography (2:8 ethyl acetate to hexane), which yielded 71% of a colorless liquid (11mg).

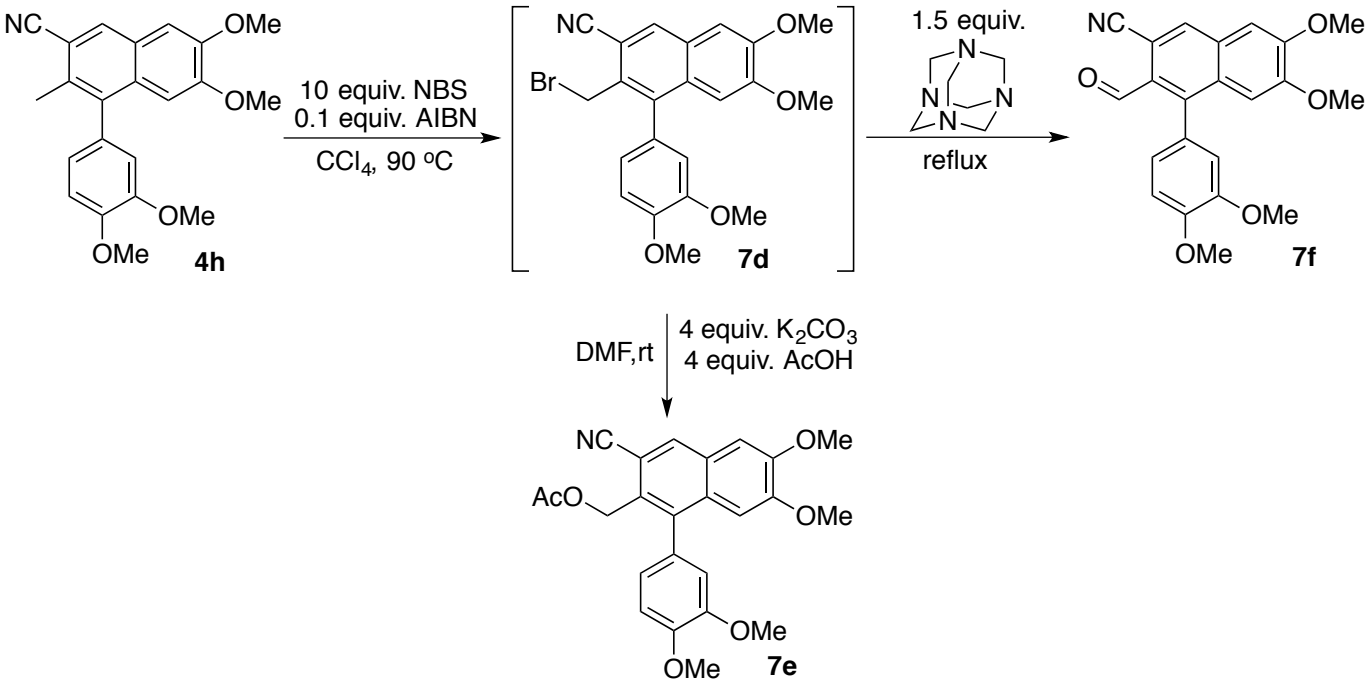
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.93 (d, *J* = 8.1 Hz, 1H), 6.70 – 6.65 (m, 2H), 6.61 (s, 1H), 6.21 (s, 1H), 5.99 – 5.87 (m, 1H), 5.25 (dd, *J* = 10.2, 1.9 Hz, 1H), 5.11 (d, *J* = 16.9 Hz, 1H), 3.93 (s, 3H), 3.88 (s, 6H), 3.58 (s, 3H), 6.64 – 6.60 (m, 1H), 3.34 (d, *J* = 15.3 Hz, 1H), 3.03 (d, *J* = 15.3 Hz, 1H), 2.51 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.27 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.91 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 148.4, 148.2, 147.8, 135.4, 132.2, 131.3, 128.4, 128.0, 122.8, 122.5, 122.2, 120.5, 111.4, 110.4, 56.2, 56.1, 56.0, 56.0, 42.6, 38.2, 36.5, 18.6.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{27}NO_4$ 428.1832; Found 428.1817.

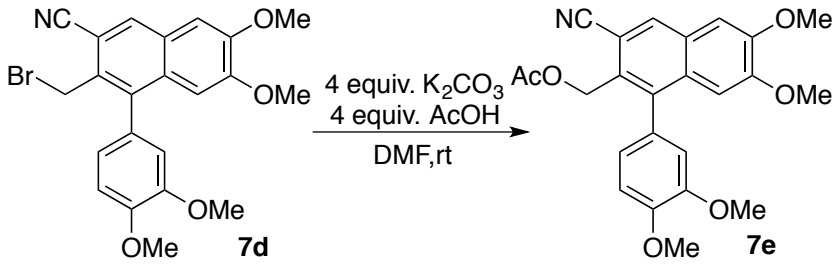
R_f: 0.40 (hexanes – ethyl acetate 7:3).

Further derivetization of -(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-2-naphthonitrile (4h)



To an oven dried 10 ml Schlenk flask, 4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-2-naphthonitrile (1 equiv., 400 mg), N-bromosuccinamide (10 equiv., 1.96 g), azobisisobutyronitrile (0.1 equiv., 18 mg) and carbontetrachloride (0.1 M with respect to the naphthonitrile, 10 ml) was transferred and stirred at 90 °C for 1 hour. Upon completion *via* TLC succinamide was filtered and washed with 2×10 ml of cold carbontetrachloride. The organic phase was evaporated and used, as it is to synthesize **7f** and **7e**. The brominated product yielded in 95% (463 mg) and appeared as a yellow liquid.

Synthesis of (3-cyano-1-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalen-2-yl)methyl acetate (7e)



To an oven dried 10 ml Schlenk flask, potassium carbonate (4 equiv., 63 mg), glacial acetic acid (4 equiv., 27 mg) and dry dimethyl formamide (0.5 M with respect to the naphthonitrile 280 µl) was transferred and stirred at room temperature. Then 3-(bromomethyl)-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-naphthonitrile (1 equiv., 50 mg) was added. Upon completion *via* TLC the solution was transferred to a separatory funnel. Then ethyl acetate (50 mL) was added, and washed with 2×100 mL of brine. The organic phase was evaporated and purification was done using flash column chromatography (20:70 ethyl acetate to hexane), which yielded 86% (41mg) of a yellow solid.

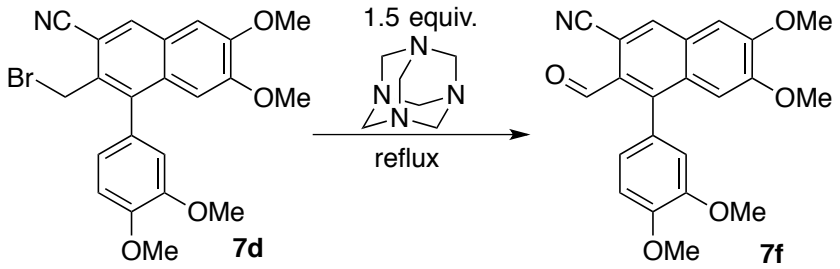
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.17 (s, 1H), 7.00 (d, *J* = 8.1 Hz, 1H), 6.82 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.80 – 6.78 (m, 2H), 5.09 (s, 2H), 4.03 (s, 3H), 3.98 (s, 3H), 3.85 (s, 3H), 3.74 (s, 3H), 2.06 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.5, 152.0, 151.0, 149.1, 149.0, 140.8, 133.0, 131.1, 129.3, 129.1, 128.5, 122.4, 118.4, 113.1, 111.3, 108.9, 106.5, 106.0, 63.2, 56.3, 56.1, 56.1, 56.0, 20.8.

HRMS (ESI – TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{23}NO_6$ 444.1418; Found 444.1414.

R_f: 0.45 (hexanes – ethyl acetate 7:3).

Synthesis of 4-(3,4-dimethoxyphenyl)-3-formyl-6,7-dimethoxy-2-naphthonitrile (7f)



To an oven dried 10 ml Schlenk flask, 3-(bromomethyl)-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2-naphthonitrile (1 equiv., 63 mg), hexamethylenetetramine (1.5 equiv., 30 mg) and chloroform (0.5 M with respect to the naphthonitrile) was transferred and refluxed at 63 °C for 30 minutes then 10 μl of acetic acid and 100 μl of water was added and stirred for another 10 minutes. Upon completion *via* TLC the solution was transferred to a separatory funnel. Then ethyl acetate (50 mL) was added, and washed with 2×100 mL of brine. The organic phase was evaporated and purification was done using flash column chromatography (20:70 ethyl acetate to hexane), which yielded 77% (42 mg) of a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.19 (s, 1H), 7.23 (s, 1H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.99 (s, 1H), 6.93 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.88 (d, *J* = 2.0 Hz, 1H), 4.07 (s, 3H), 4.00 (s, 3H), 3.88 (s, 3H), 3.79 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 190.2, 152.8, 152.4, 149.7, 149.2, 146.1, 135.3, 130.9, 130.2, 129.2, 126.7, 123.6, 118.7, 113.6, 111.3, 106.9, 106.3, 105.0, 56.5, 56.3, 56.2, 56.2.

HRMS (ESI – TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{19}NO_5$ 378.1336; Found 378.1317.

R_f: 0.35 (hexanes – ethyl acetate 7:3).

References

1) Gora, M., Kozik, B., Jamrozy, K., Luczynski, M., Brzuzan, P., Wozny, M. *Green Chem*. **2009**, *11*, 863.

2) Navaratne, P.V., Vertesaljai, P., Grenning, A.J. *Angew.Chem. Int .Ed*. **2016**, *55*,317.

3) Li, D.P., Pan, X.Q., Ani, L.T., Zou, J.P., Zhang, W. *J. Org. Chem*., **2014**, *79* (4), 1850.

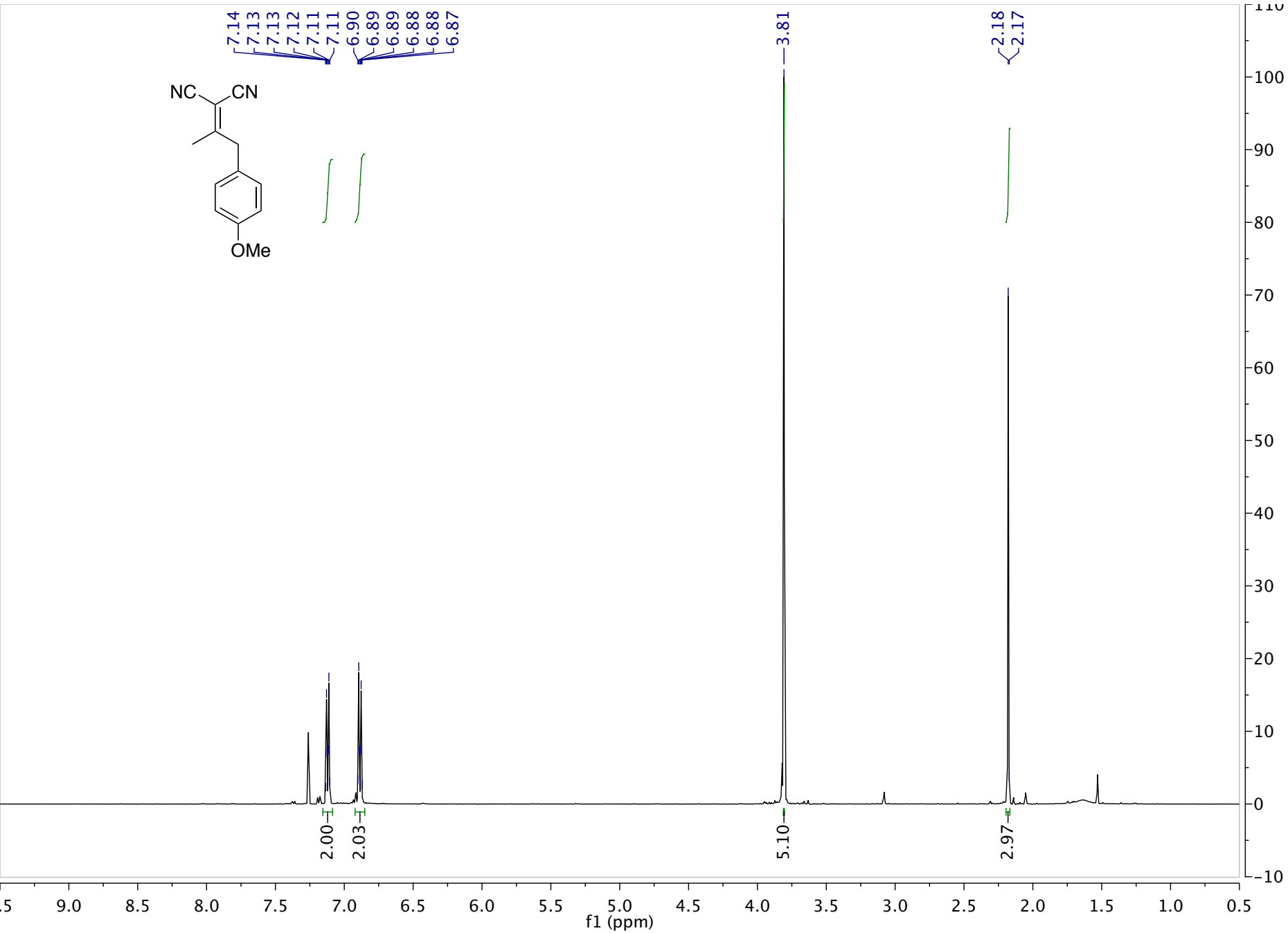
4) Weinreb, S. M., Jin, J. *J. Am. Chem. Soc*., **1997**, *119*(25), 5773.

5) Giorgi, G., Maiti, S., López-Alvarado, P., Menéndez, J. C. *Org. Biomol. Chem*. **2011**, *9*, 2722.

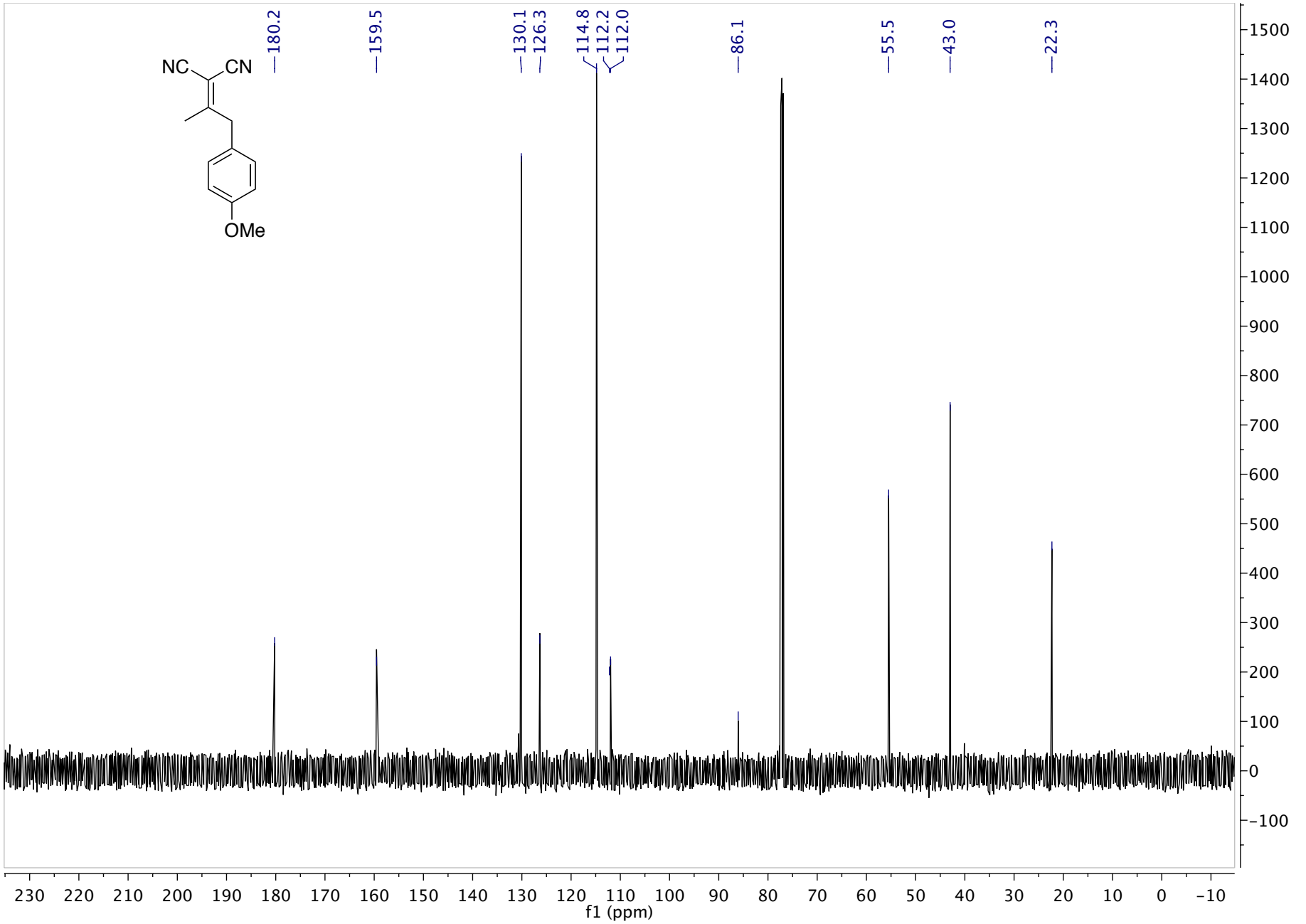
6) Liu, H.J., Shang, X. *Tet. Lett.* **1998**, *39*, 367.

7) Molander, G. A., Wolfe, J. P. *J. Braz. Chem. Soc.* **1996**, *7*, 335.

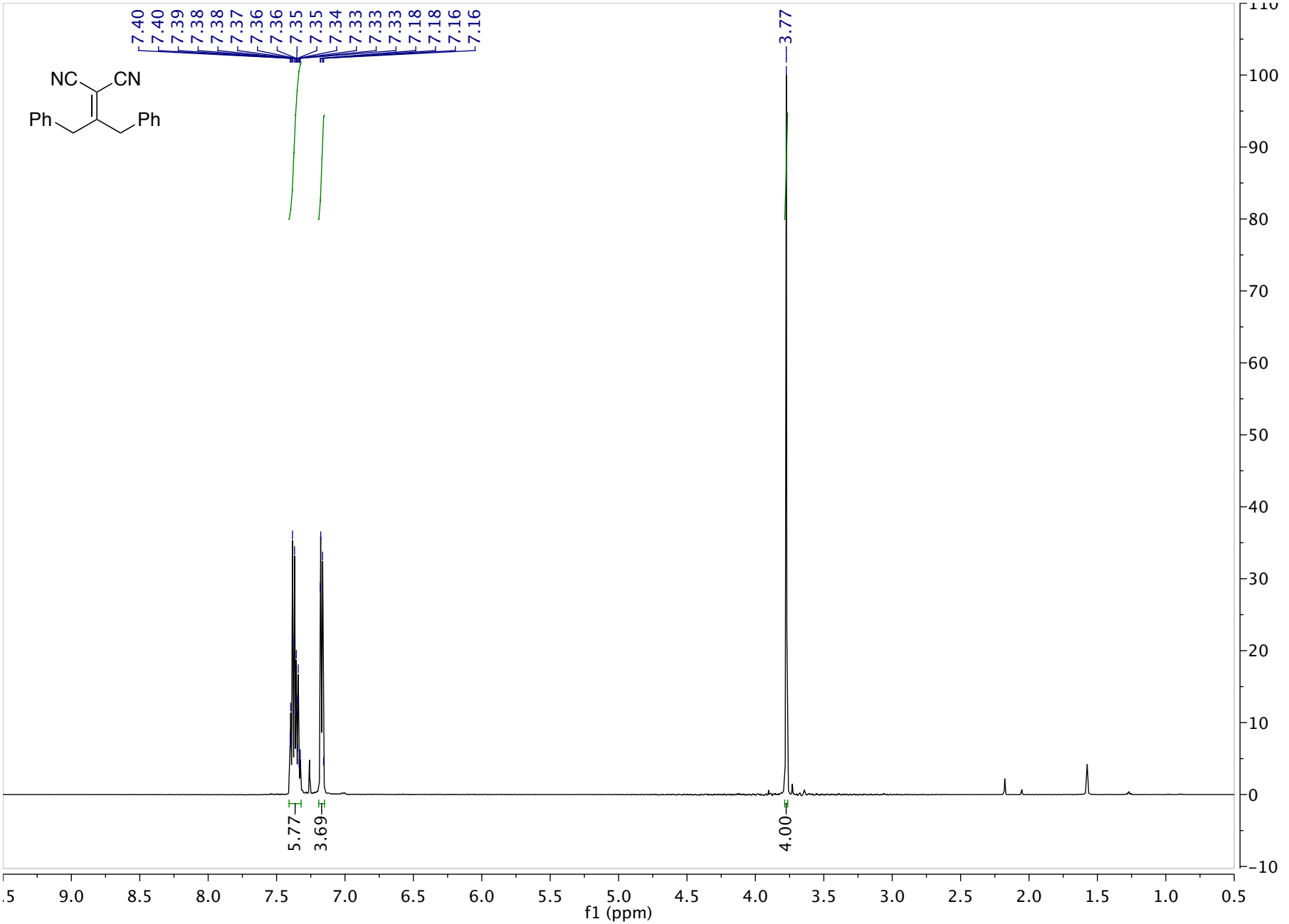
^{1}H spectrum of 2-(1-(4-methoxyphenyl)propan-2-ylidene)malononitrile 1a ($CDCl_3$)



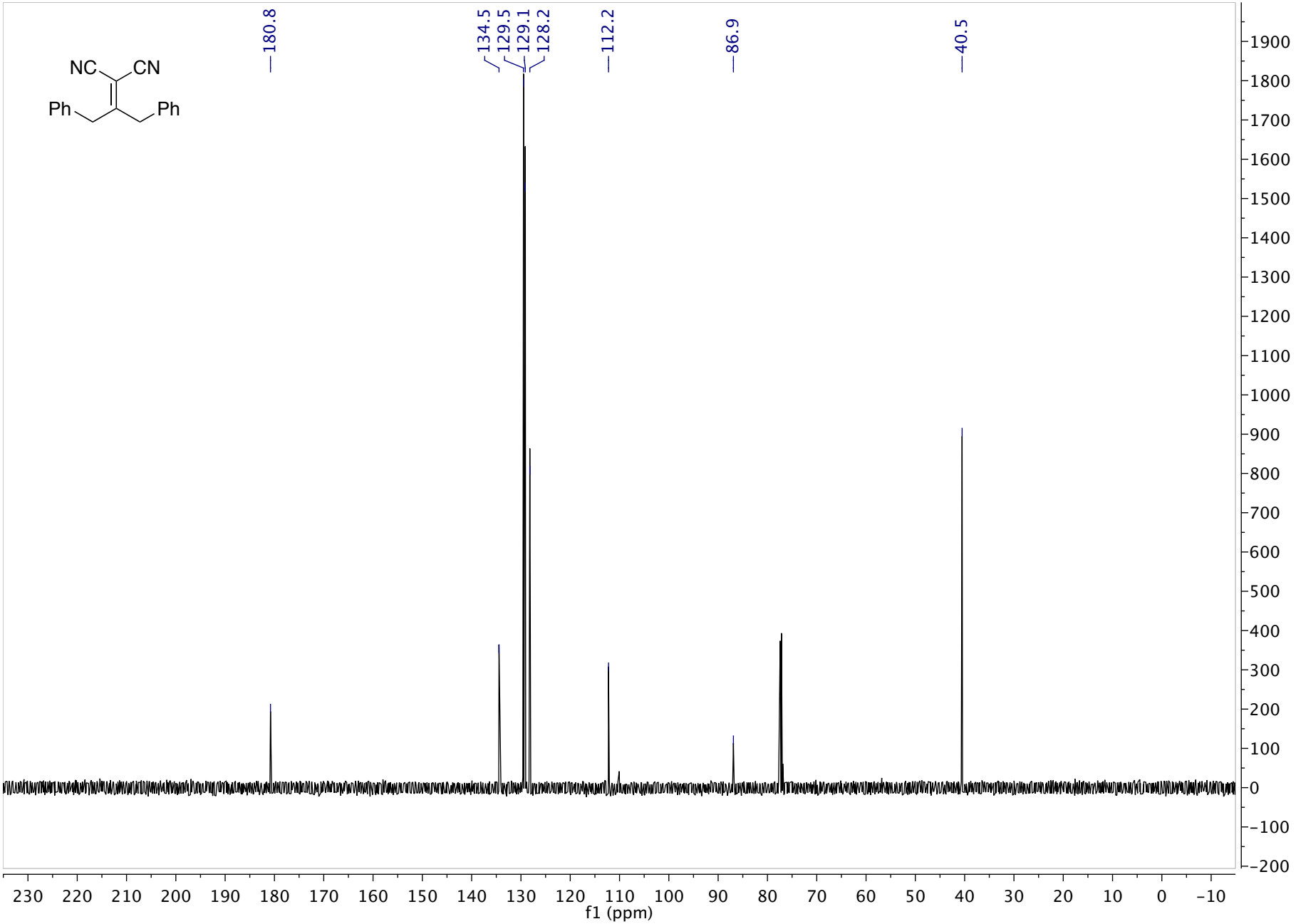
^{13}C spectrum of 2-(1-(4-methoxyphenyl)propan-2-ylidene)malononitrile 1a ($CDCl_3$)



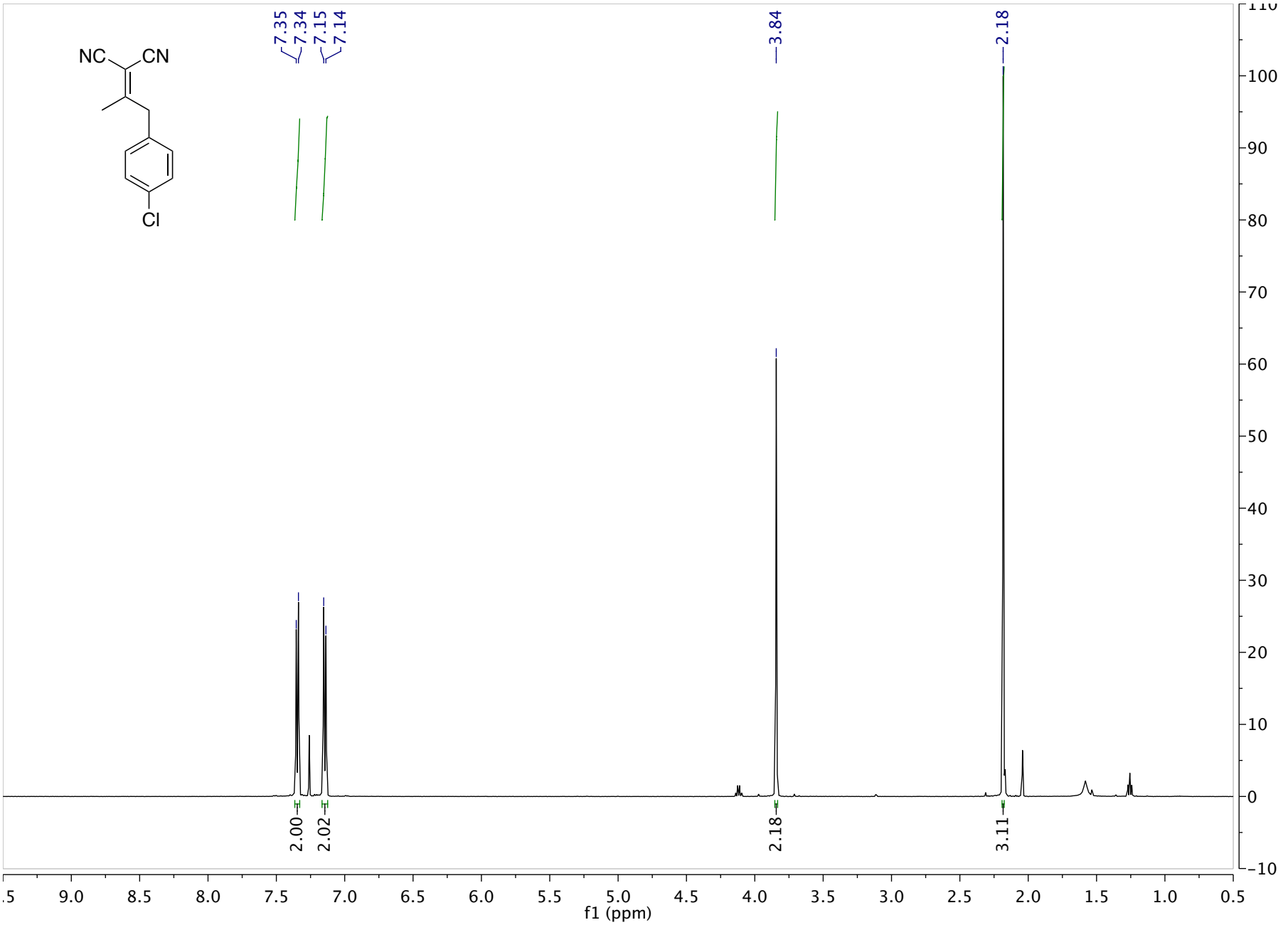
^{1}H spectrum of 2-(1,3-diphenylpropan-2-ylidene)malononitrile 1b ($CDCl_3$)



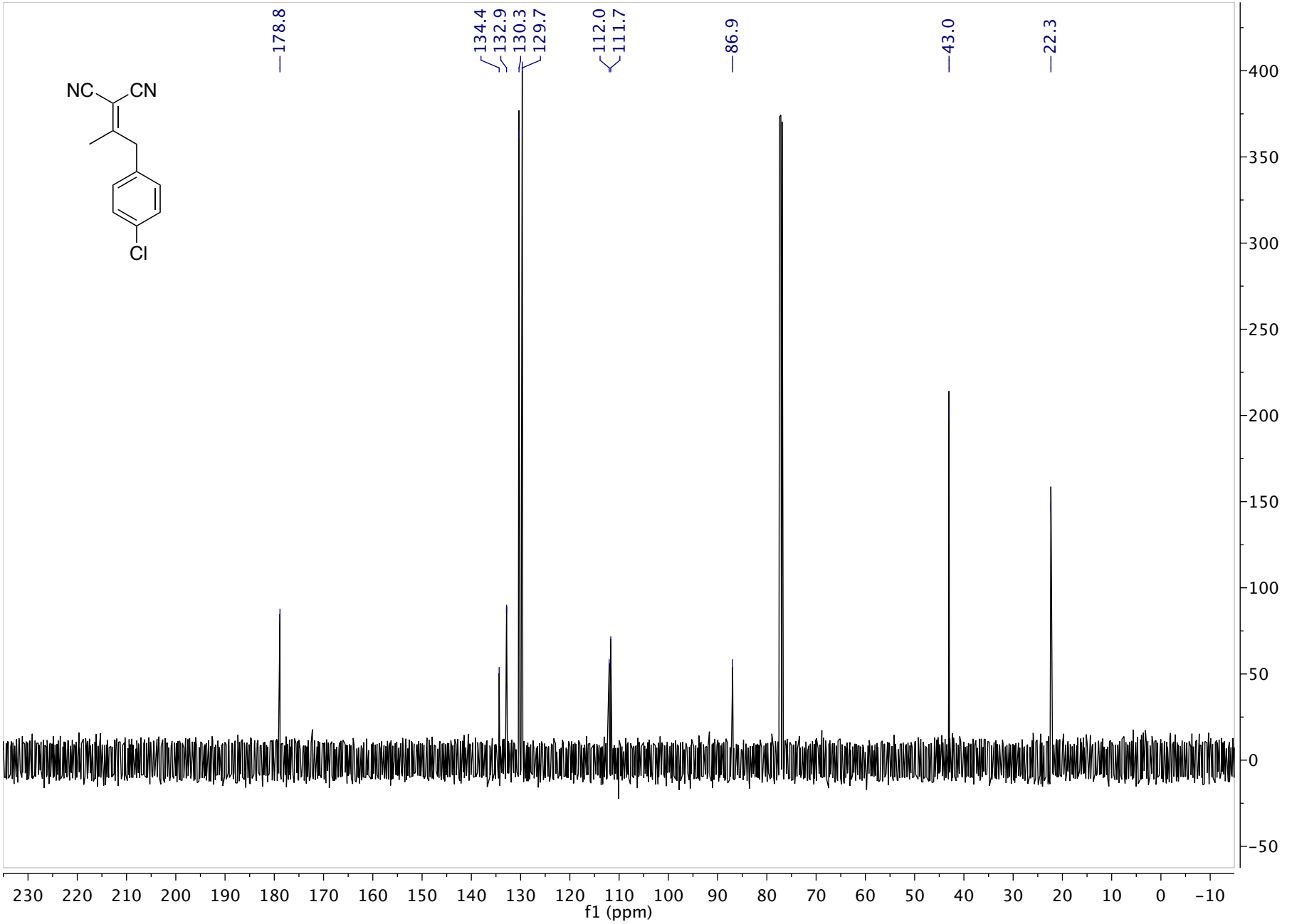
^{13}C spectrum of 2-(1,3-diphenylpropan-2-ylidene)malononitrile 1b ($CDCl_3$)



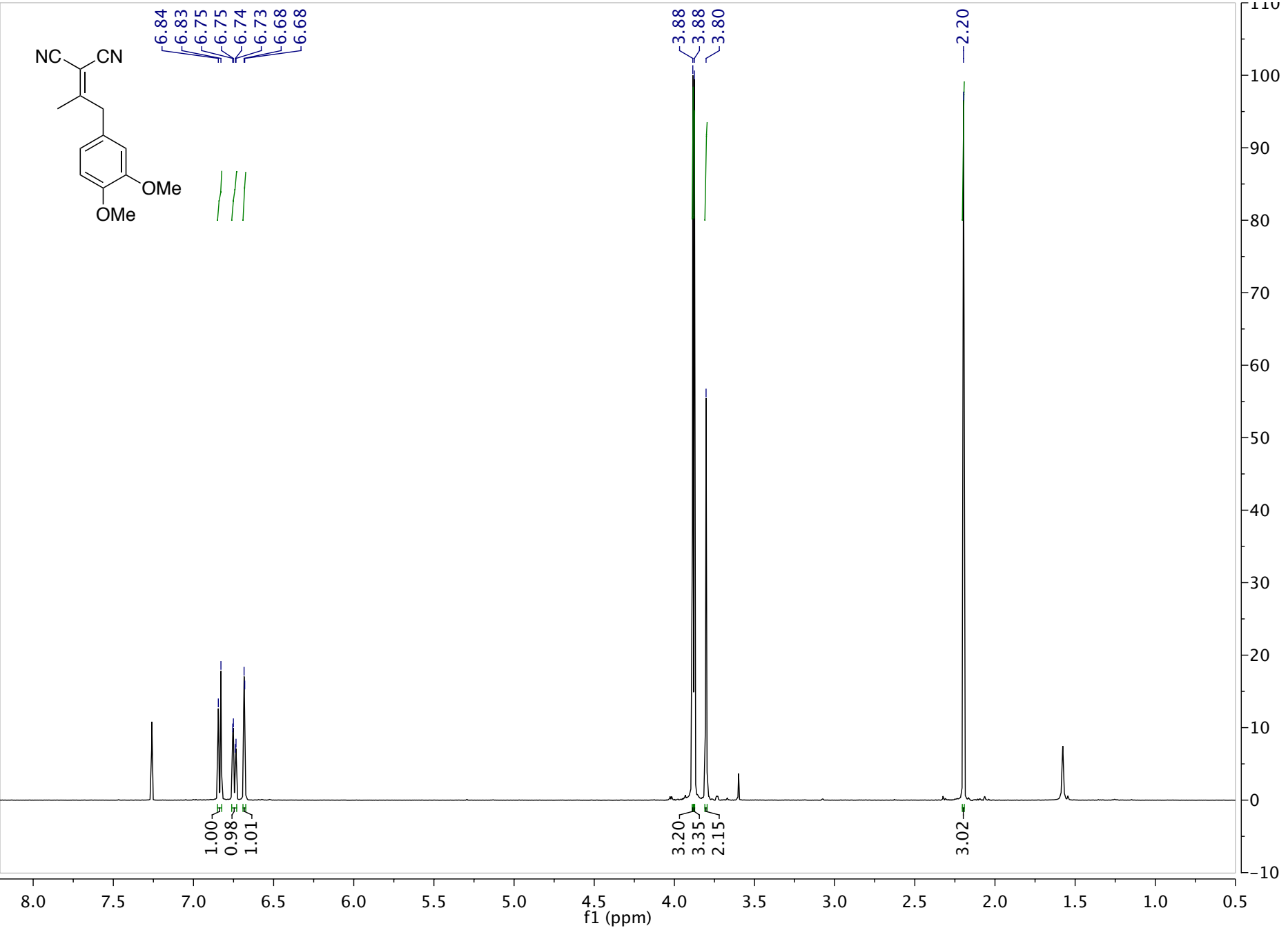
^{1}H spectrum of 2-(1-(4-chlorophenyl)propan-2-ylidene)malononitrile 1c ($CDCl_3$)



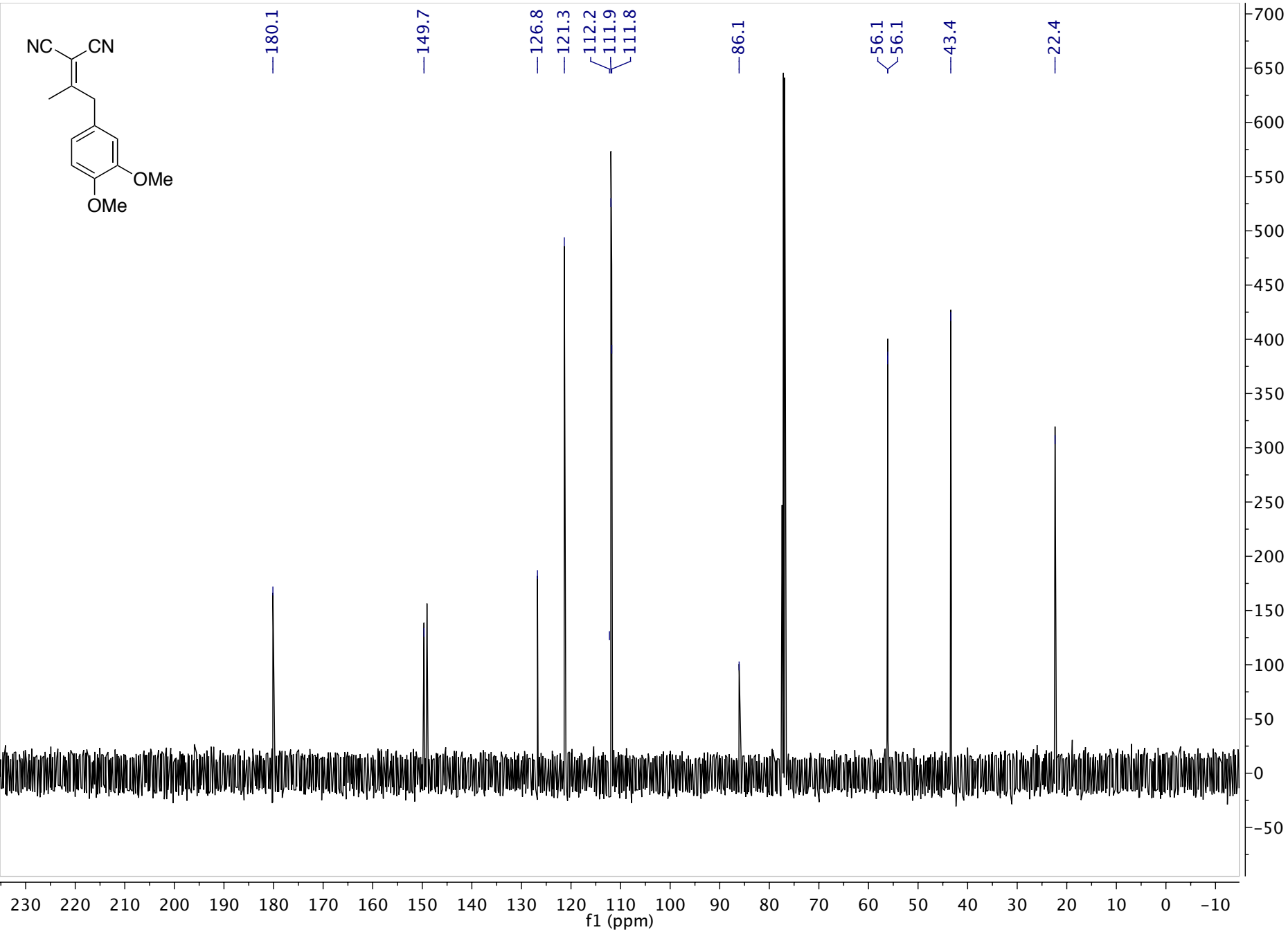
^{13}C spectrum of 2-(1-(4-chlorophenyl)propan-2-ylidene)malononitrile 1c ($CDCl_3$)



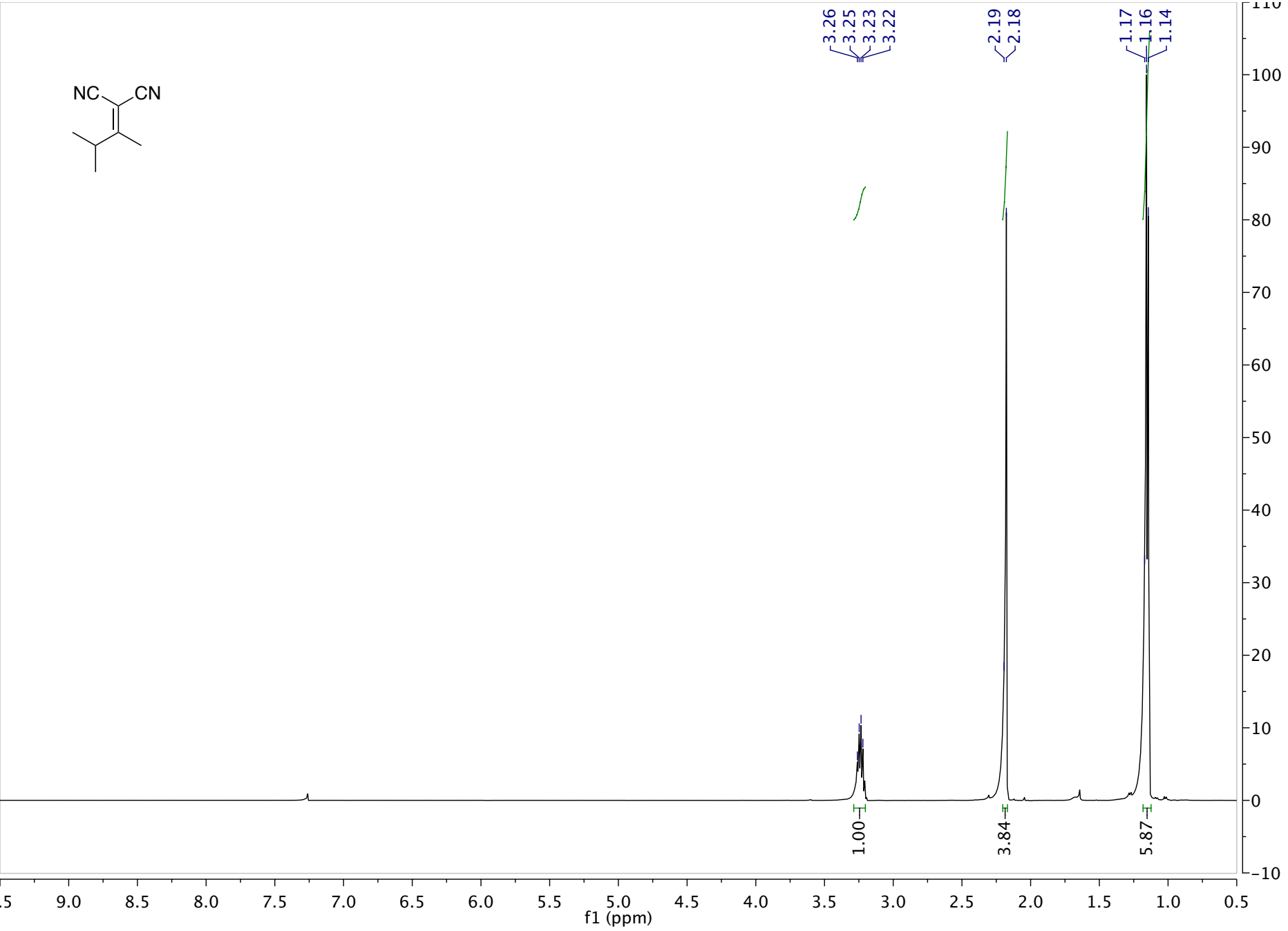
^{1}H spectrum of 2-(1-(3,4-dimethoxyphenyl)propan-2-ylidene)malononitrile 1d ($CDCl_3$)



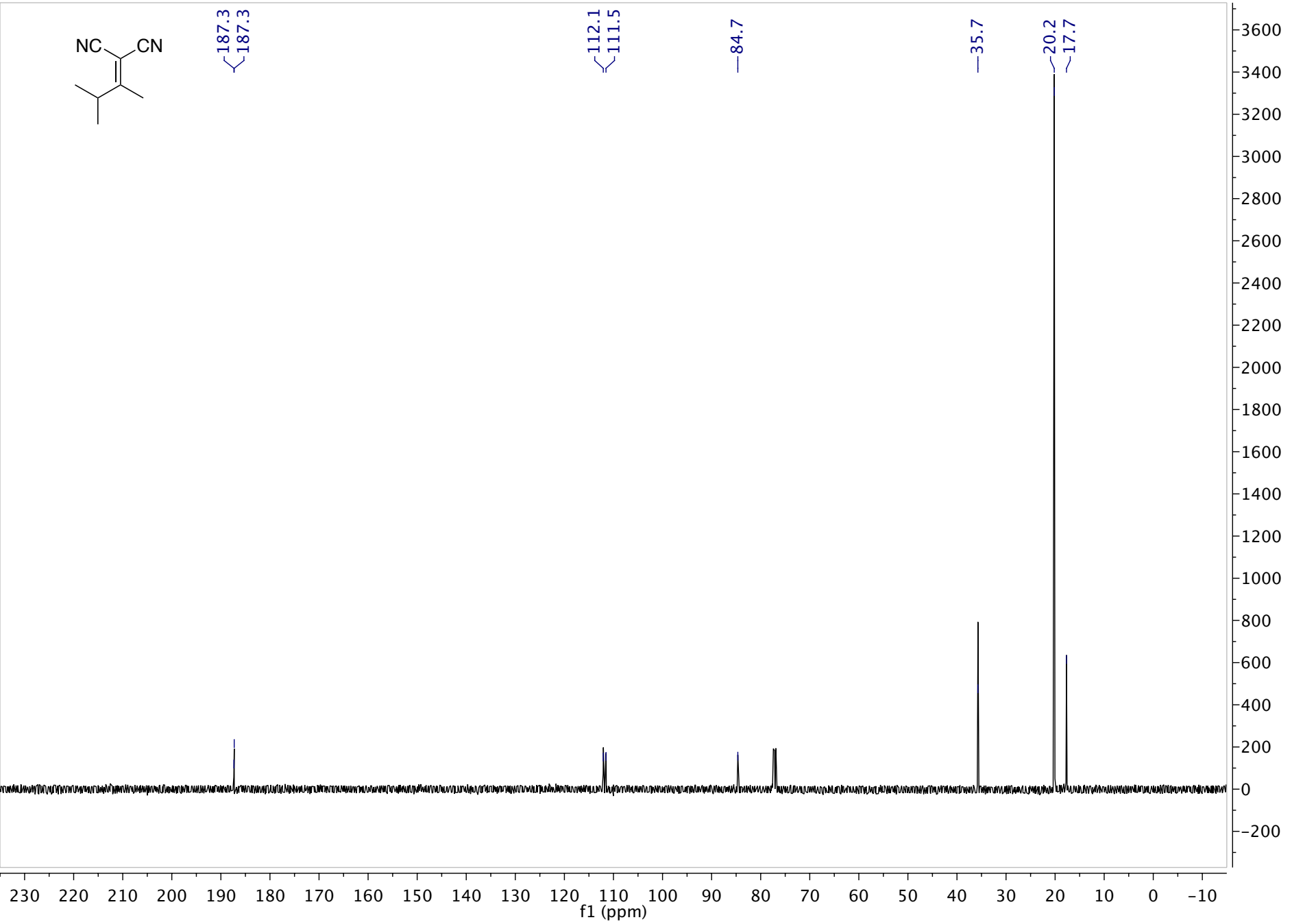
^{13}C spectrum of 2-(1-(3,4-dimethoxyphenyl)propan-2-ylidene)malononitrile 1d ($CDCl_3$)



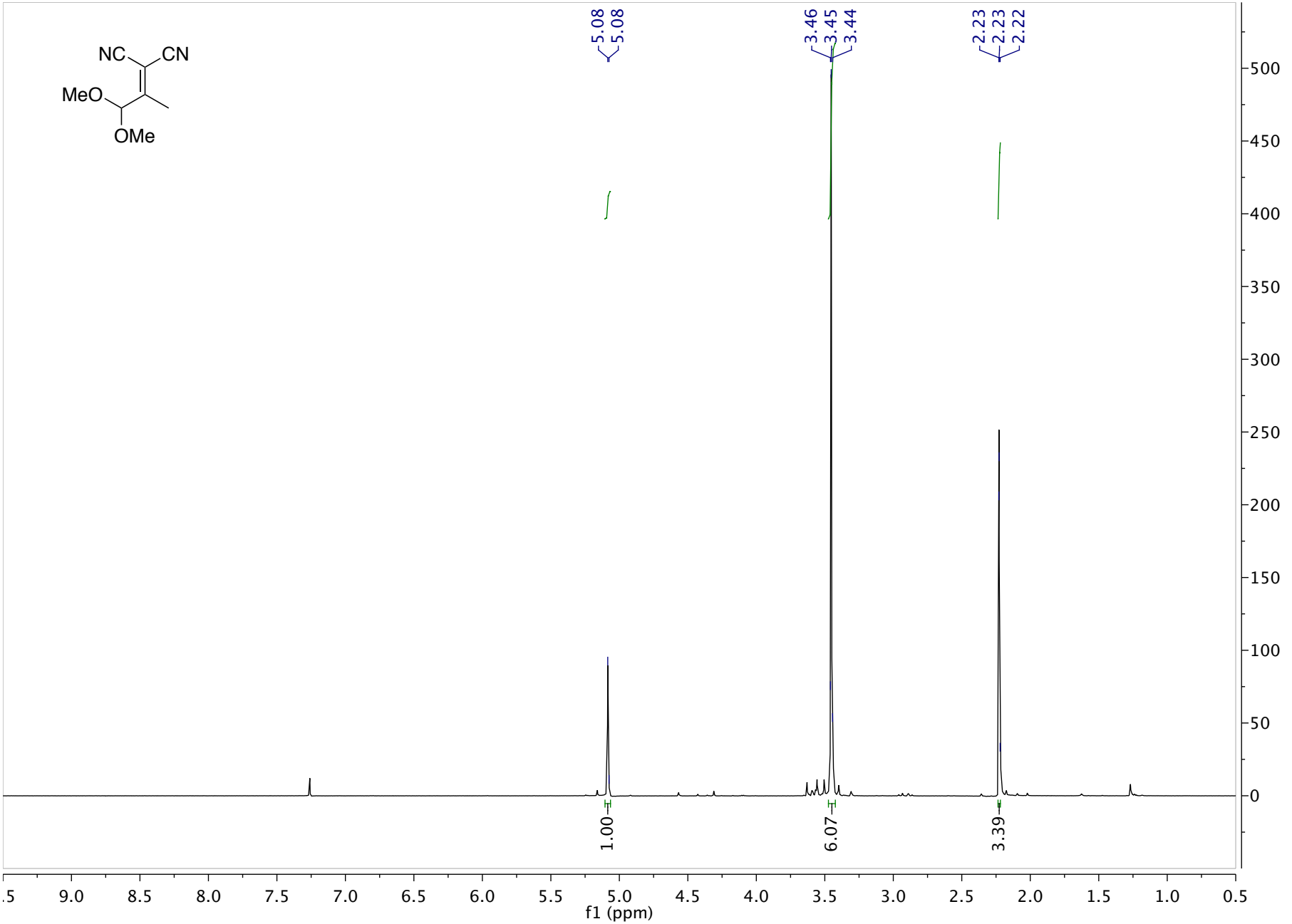
^{1}H spectrum of 2-(3-methylbutan-2-ylidene)malononitrile 1f ($CDCl_3$)



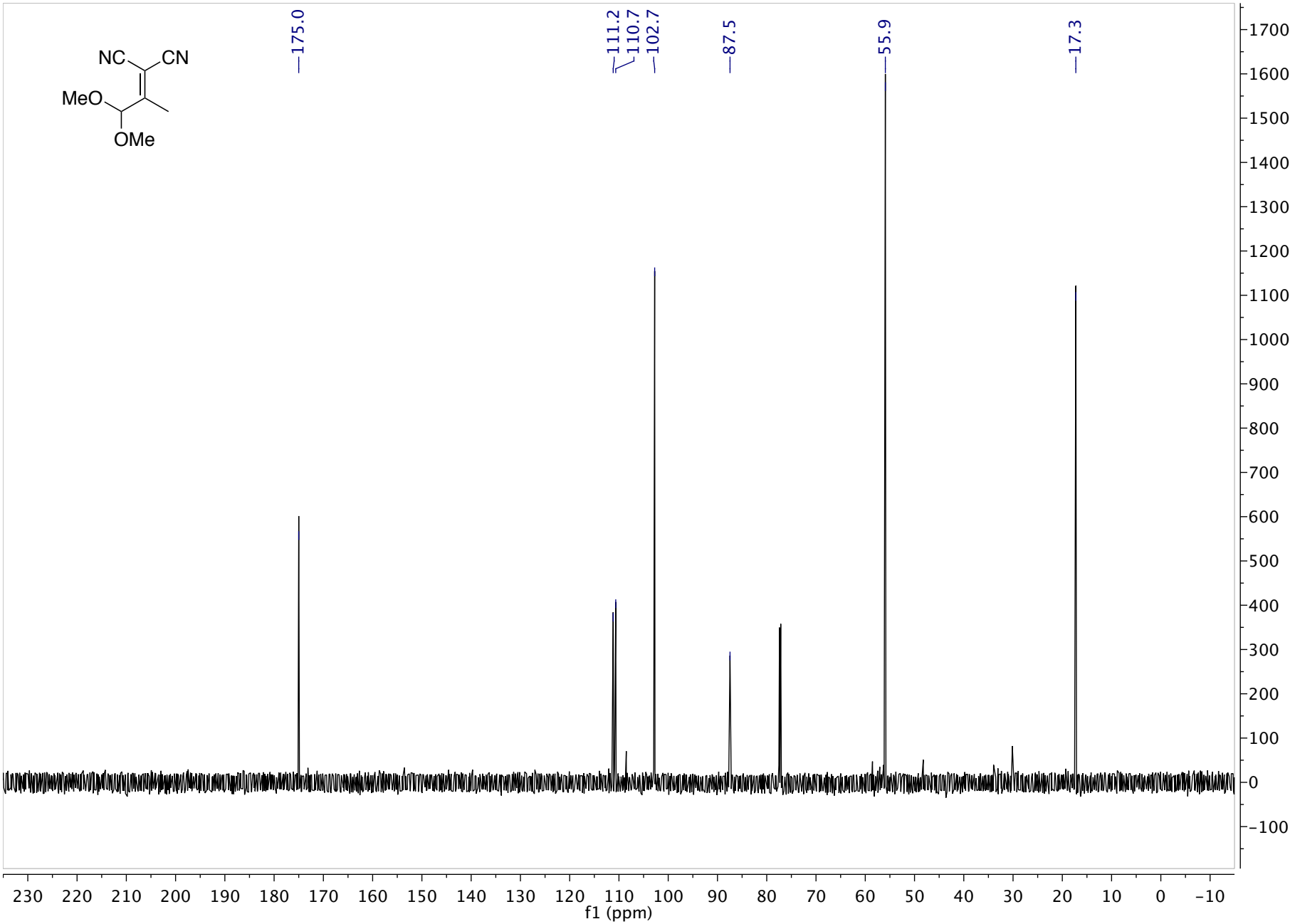
^{13}C spectrum of 2-(3-methylbutan-2-ylidene)malononitrile 1f ($CDCl_3$)



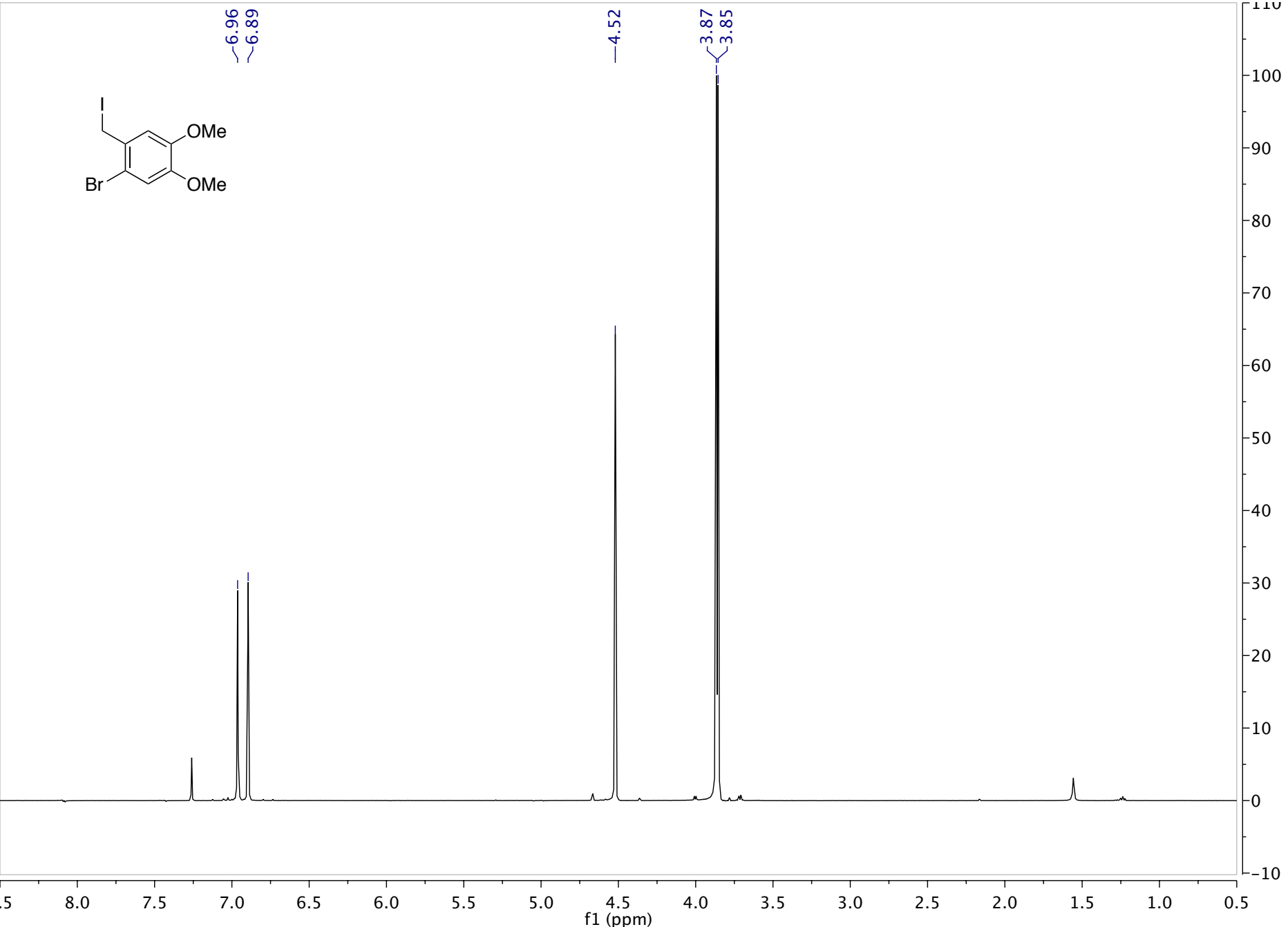
^{1}H spectrum of 2-(1,1-dimethoxypropan-2-ylidene)malononitrile 1g ($CDCl_3$)



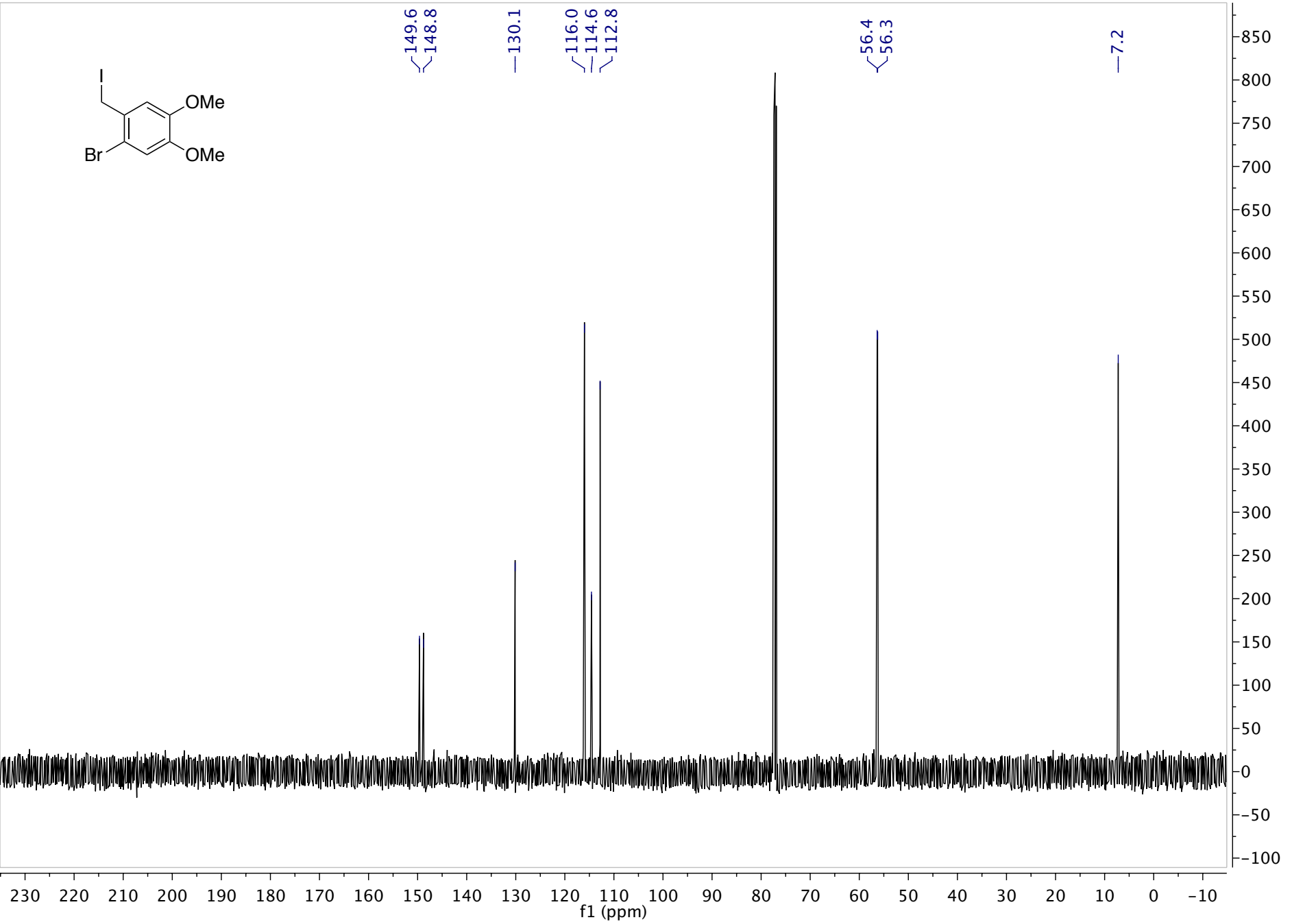
^{13}C spectrum of 2-(1,1-dimethoxypropan-2-ylidene)malononitrile 1g ($CDCl_3$)



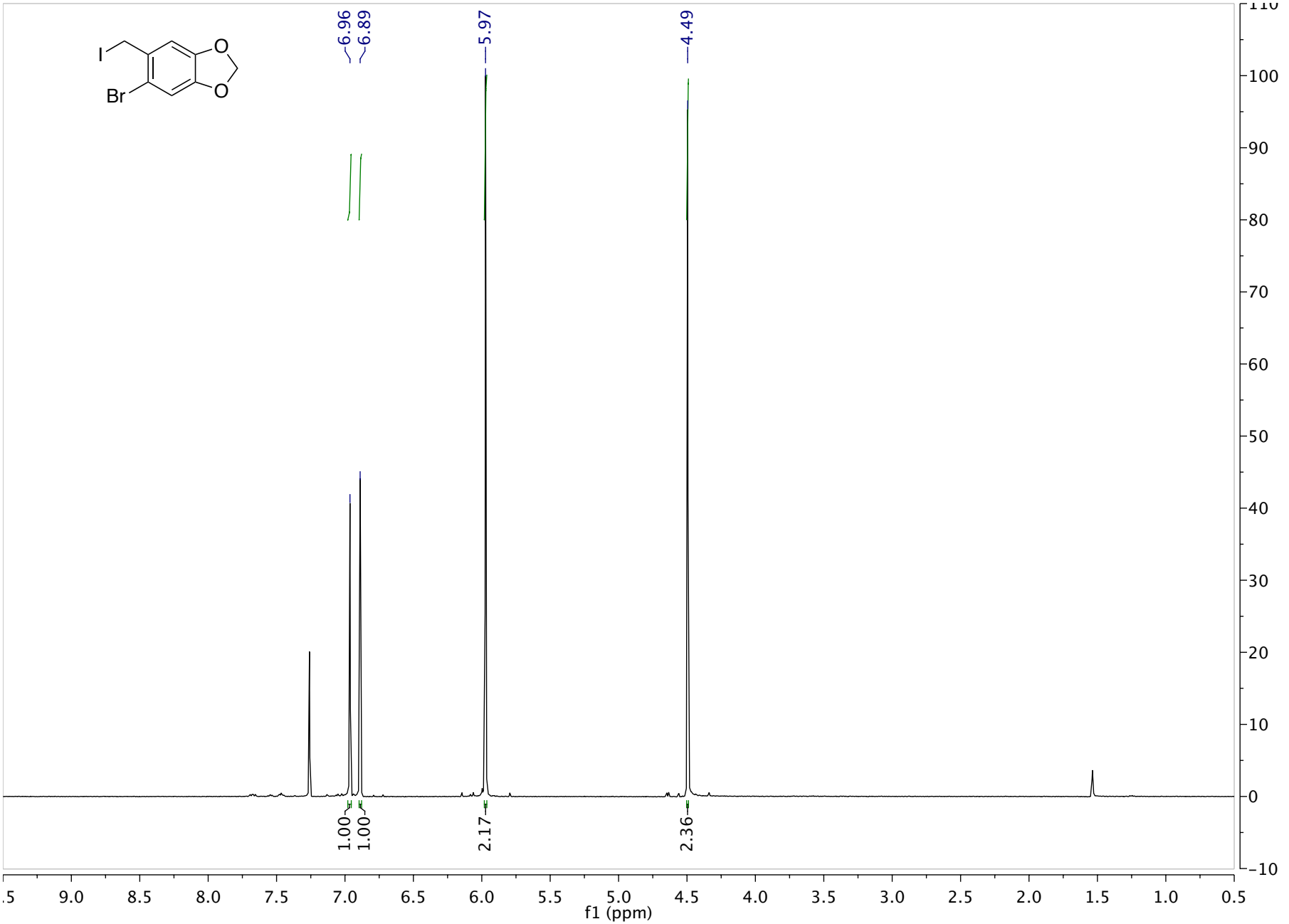
^{1}H spectrum of 1-bromo-2-(iodomethyl)-4,5-dimethoxybenzene 2a ($CDCl_3$)



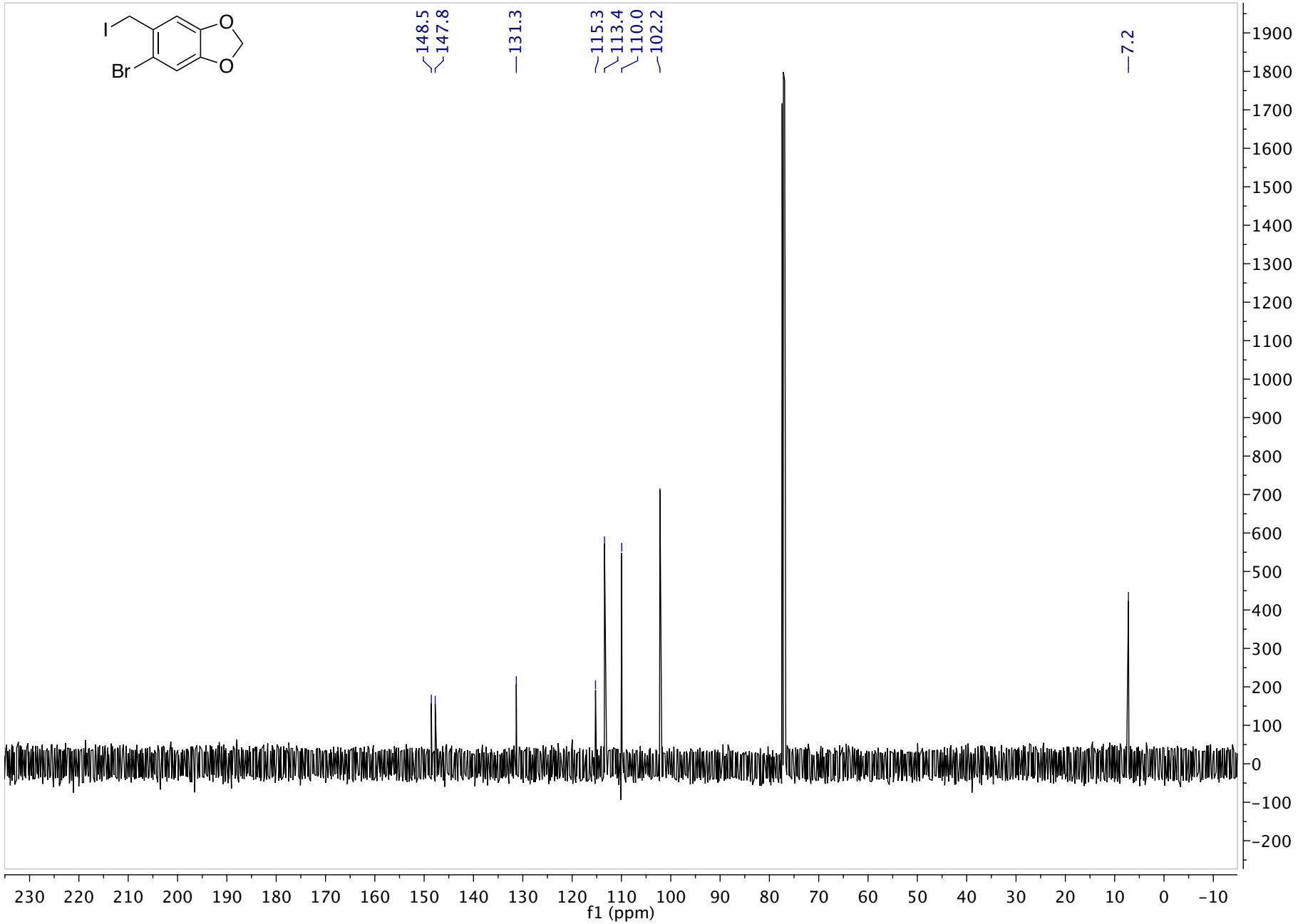
^{13}C spectrum of 1-bromo-2-(iodomethyl)-4,5-dimethoxybenzene 2a ($CDCl_3$)



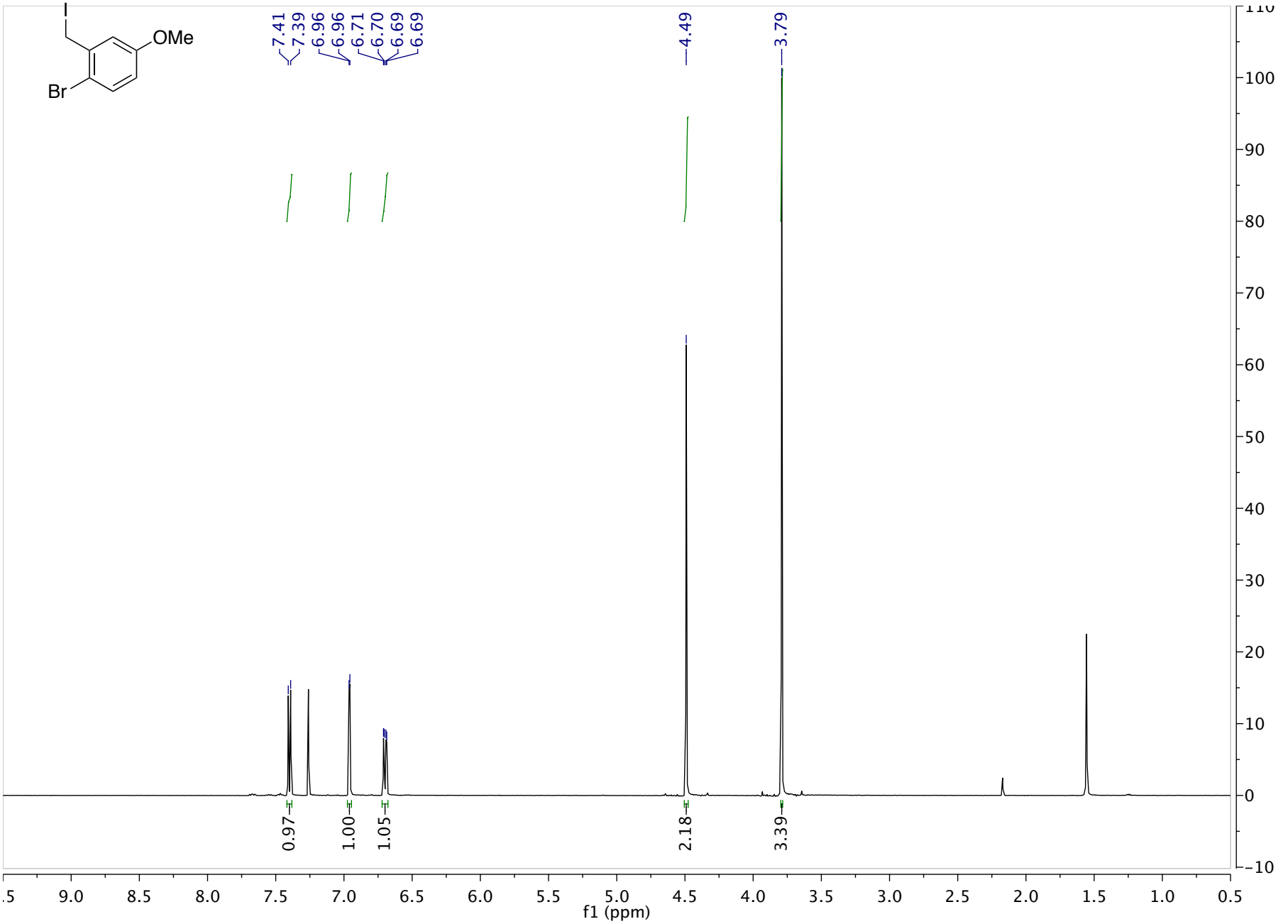
^{1}H spectrum of 5-bromo-6-(iodomethyl)benzo[*d*][1,3]dioxole 2b ($CDCl_3$)



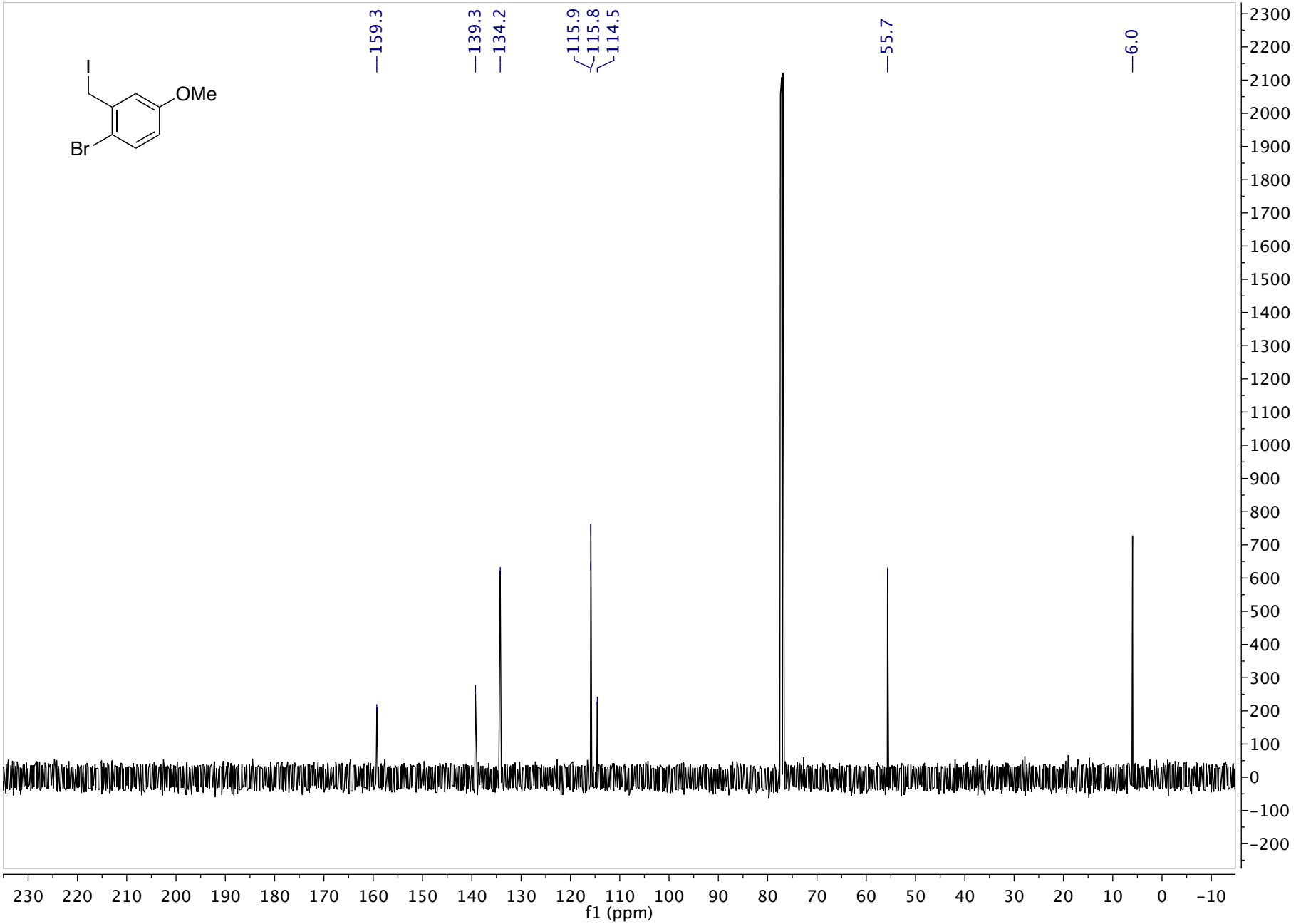
^{13}C spectrum of 5-bromo-6-(iodomethyl)benzo[*d*][1,3]dioxole 2b ($CDCl_3$)



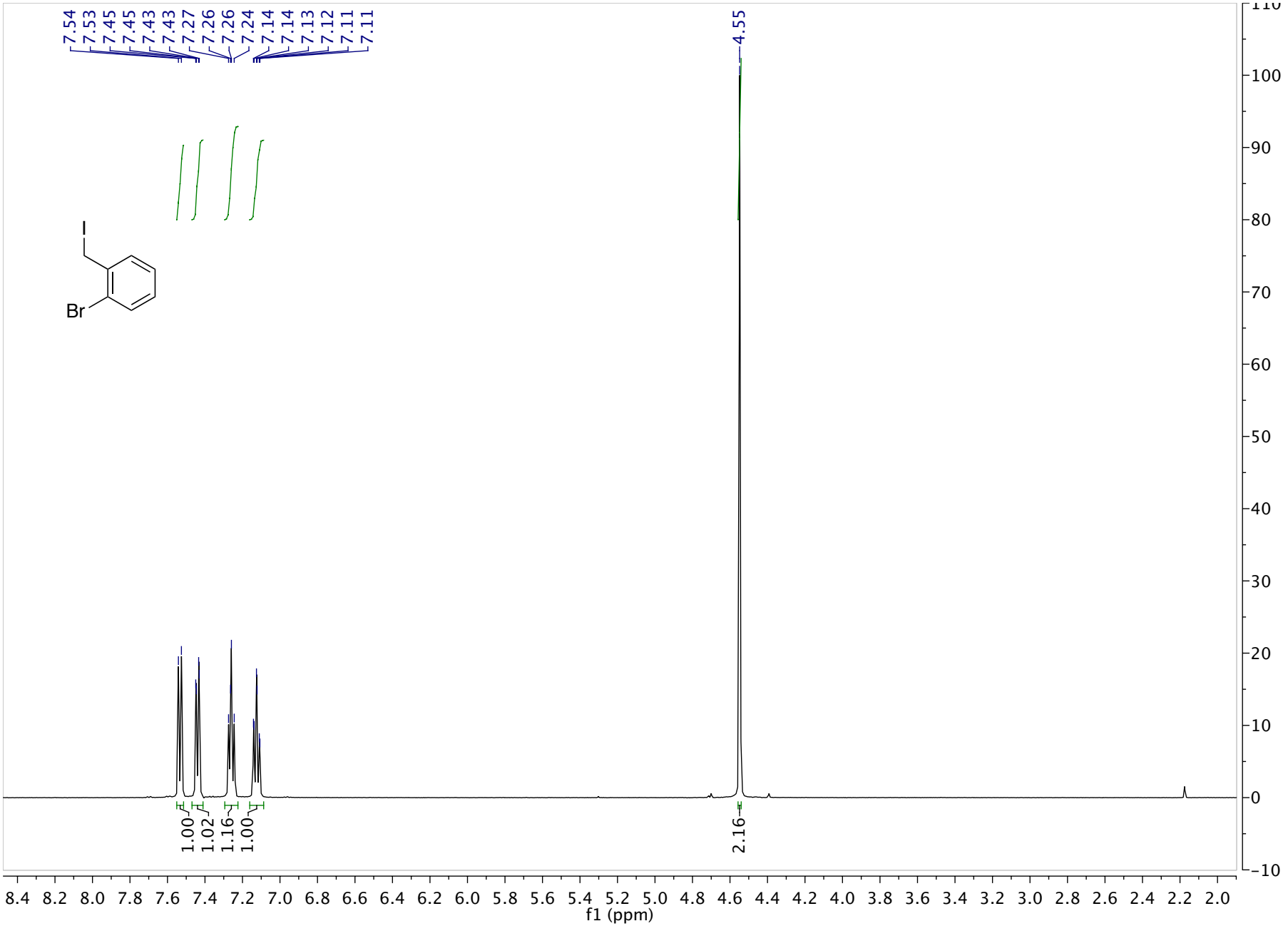
^{1}H spectrum of 1-bromo-2-(iodomethyl)-4-methoxybenzene 2c ($CDCl_3$)



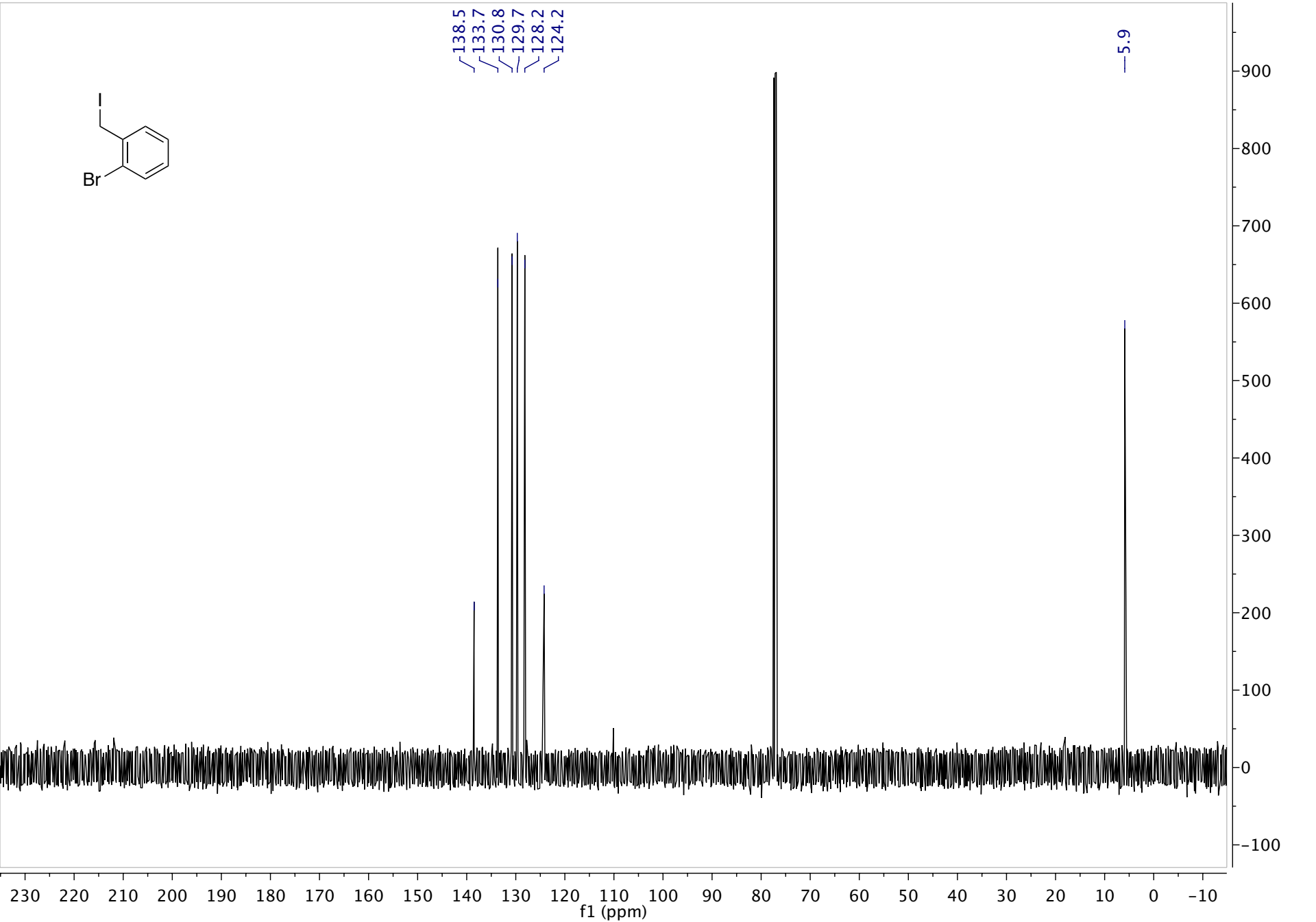
^{13}C spectrum of 1-bromo-2-(iodomethyl)-4-methoxybenzene 2c ($CDCl_3$)



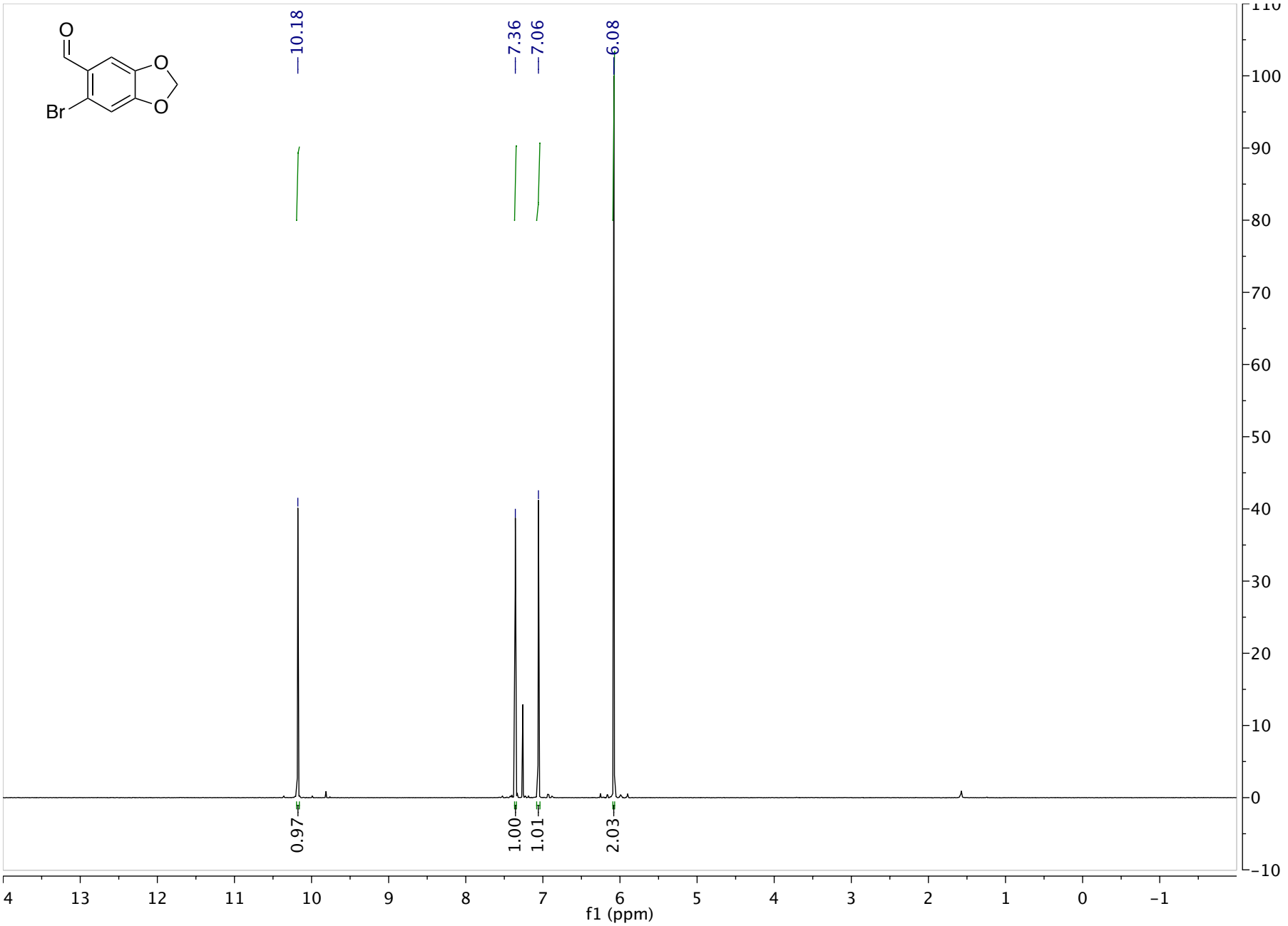
^{1}H spectrum of 1-bromo-2-(iodomethyl)benzene 2d ($CDCl_3$)



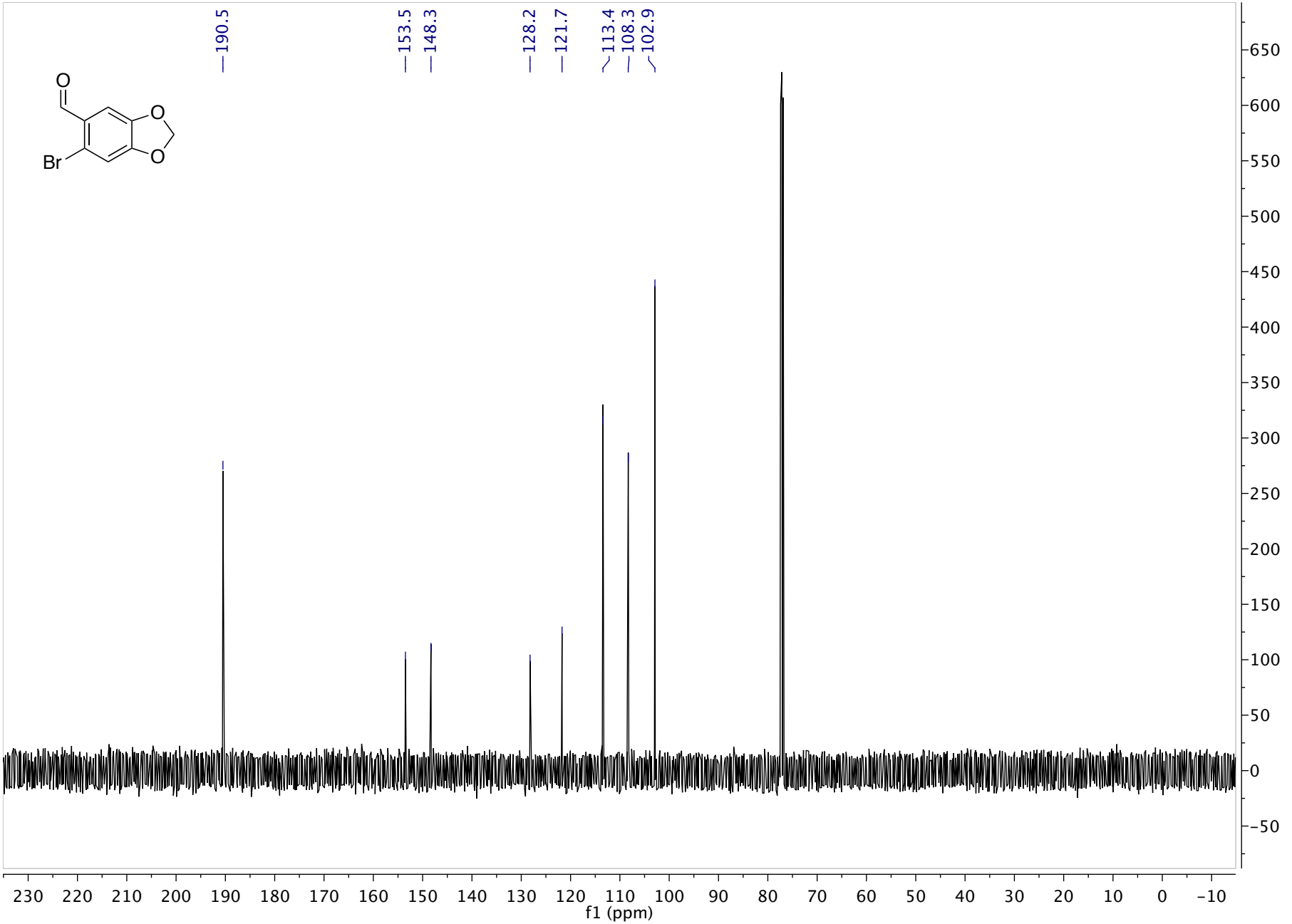
^{13}C spectrum of 1-bromo-2-(iodomethyl)benzene 2d ($CDCl_3$)



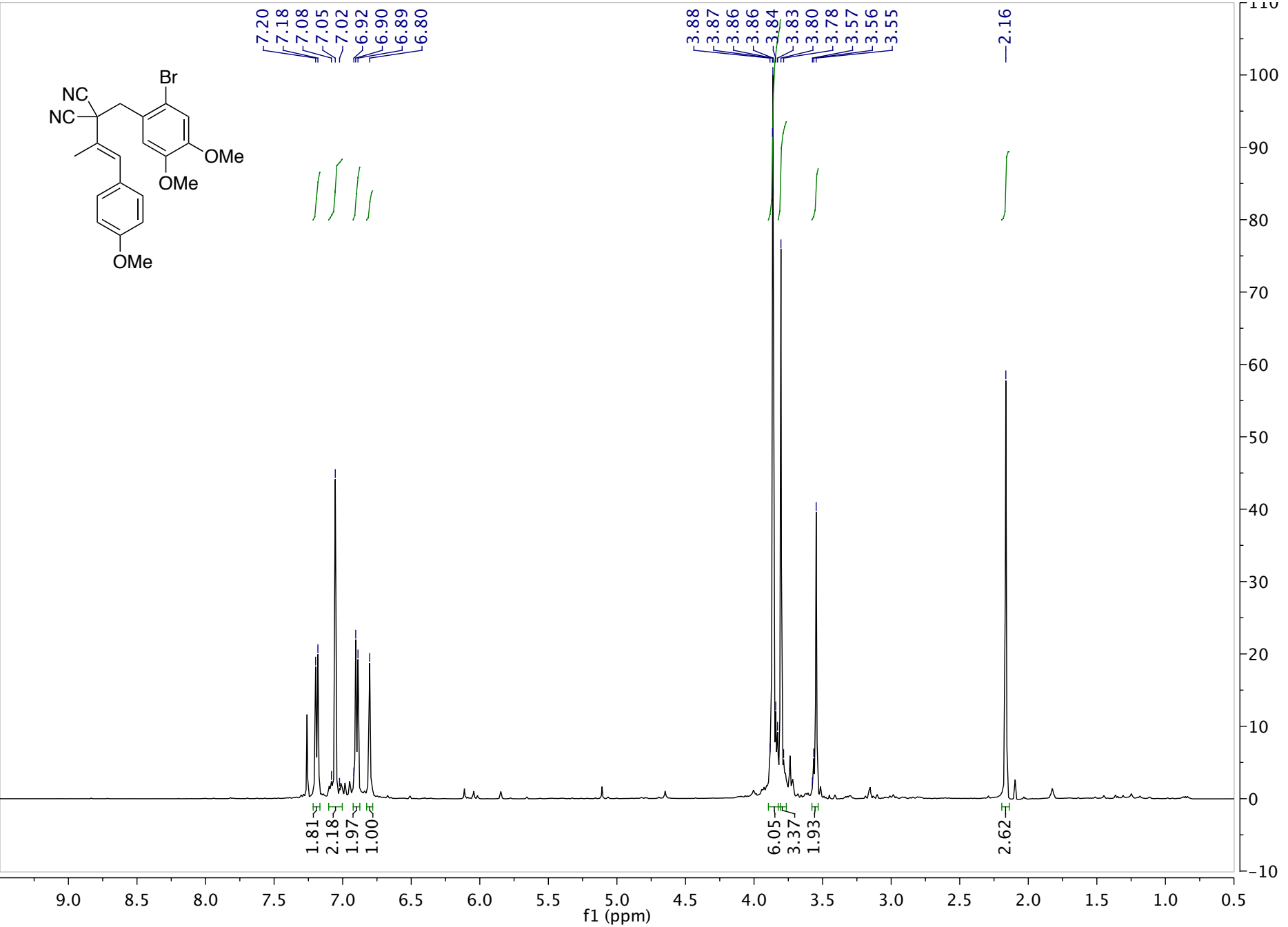
^{1}H spectrum of 6-bromobenzo[*d*][1,3]dioxole-5-carbaldehyde ($CDCl_3$)



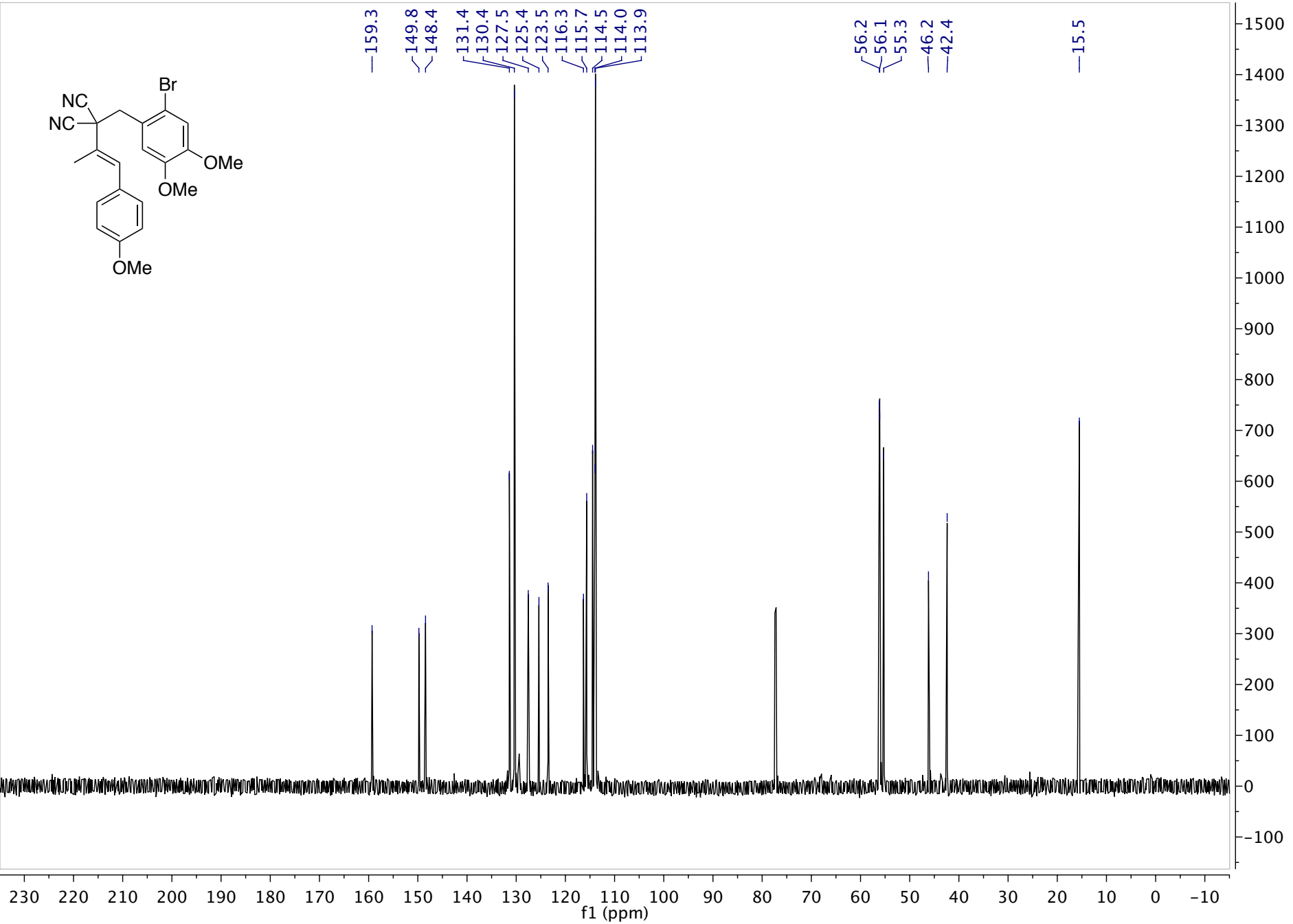
^{13}C spectrum of 6-bromobenzo[*d*][1,3]dioxole-5-carbaldehyde ($CDCl_3$)



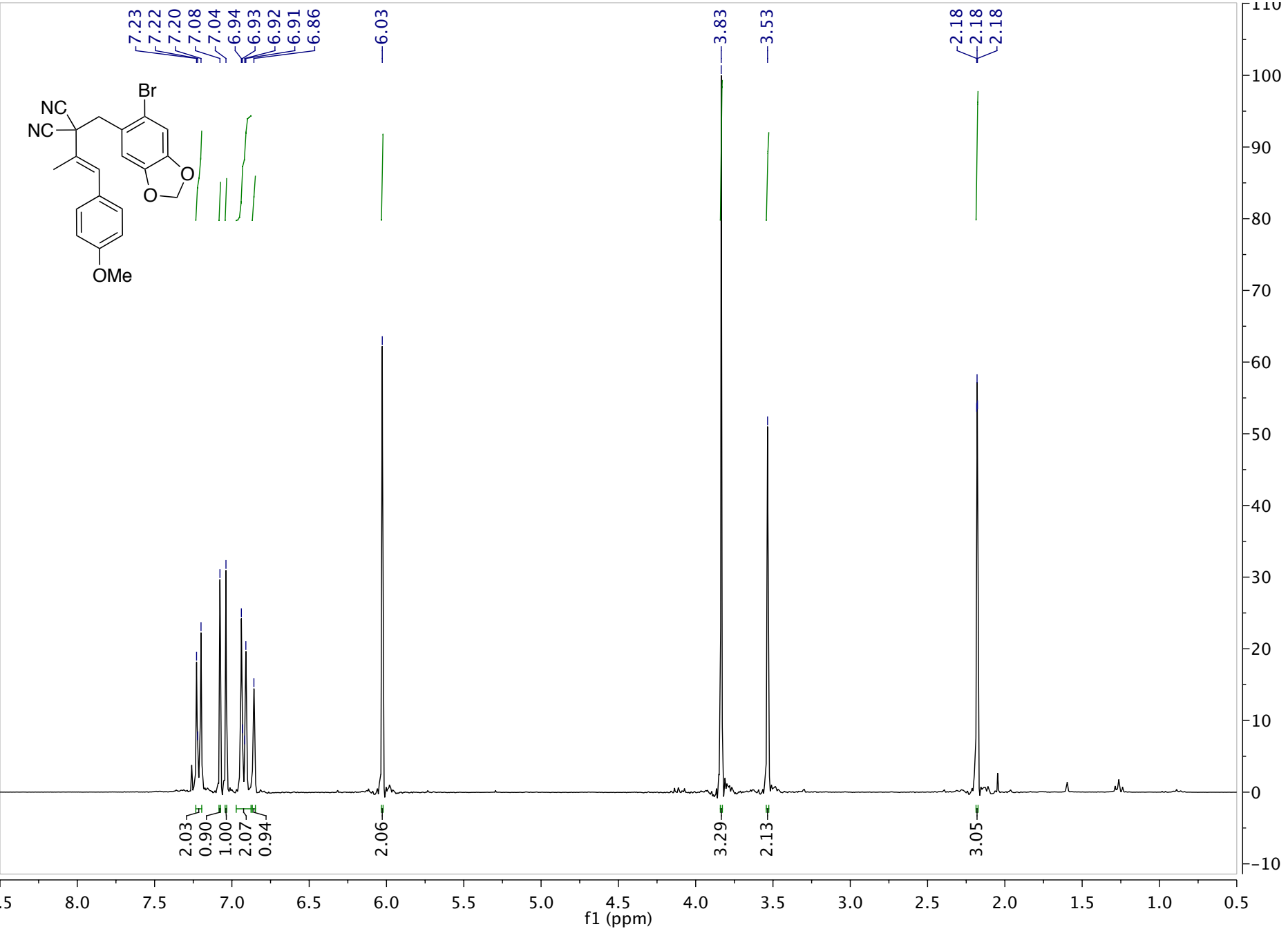
^{1}H spectrum of (*E*)-2-(2-bromo-4,5-dimethoxybenzyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile 3a ($CDCl_3$)



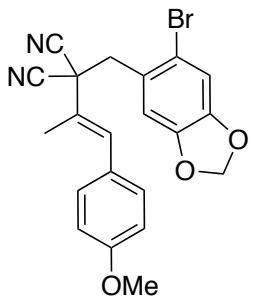
^{13}C spectrum of (*E*)-2-(2-bromo-4,5-dimethoxybenzyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile 3a ($CDCl_3$)



^{1}H spectrum of (*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile 3b ($CDCl_3$)



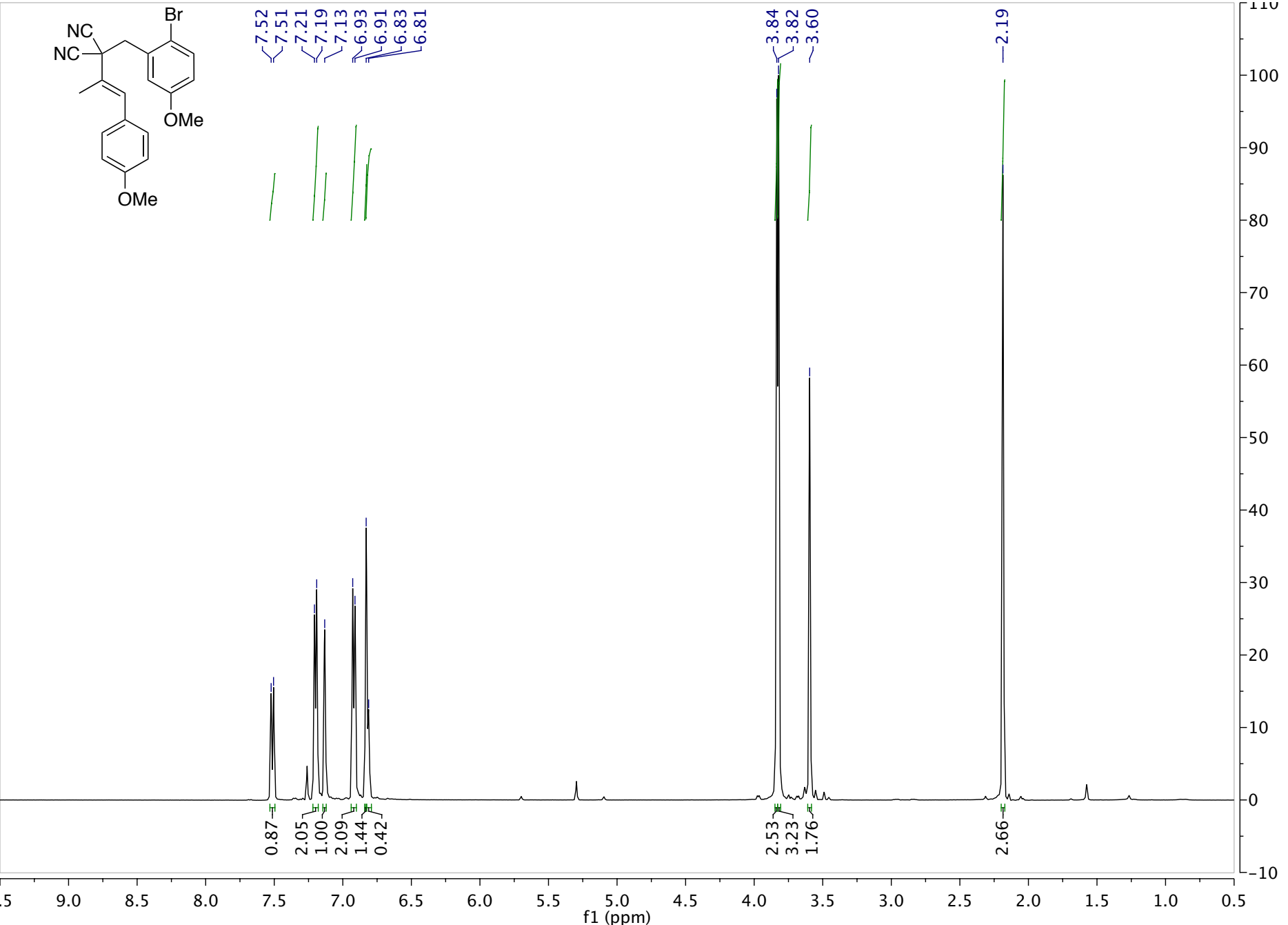
^{13}C spectrum of (*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile 3b ($CDCl_3$)



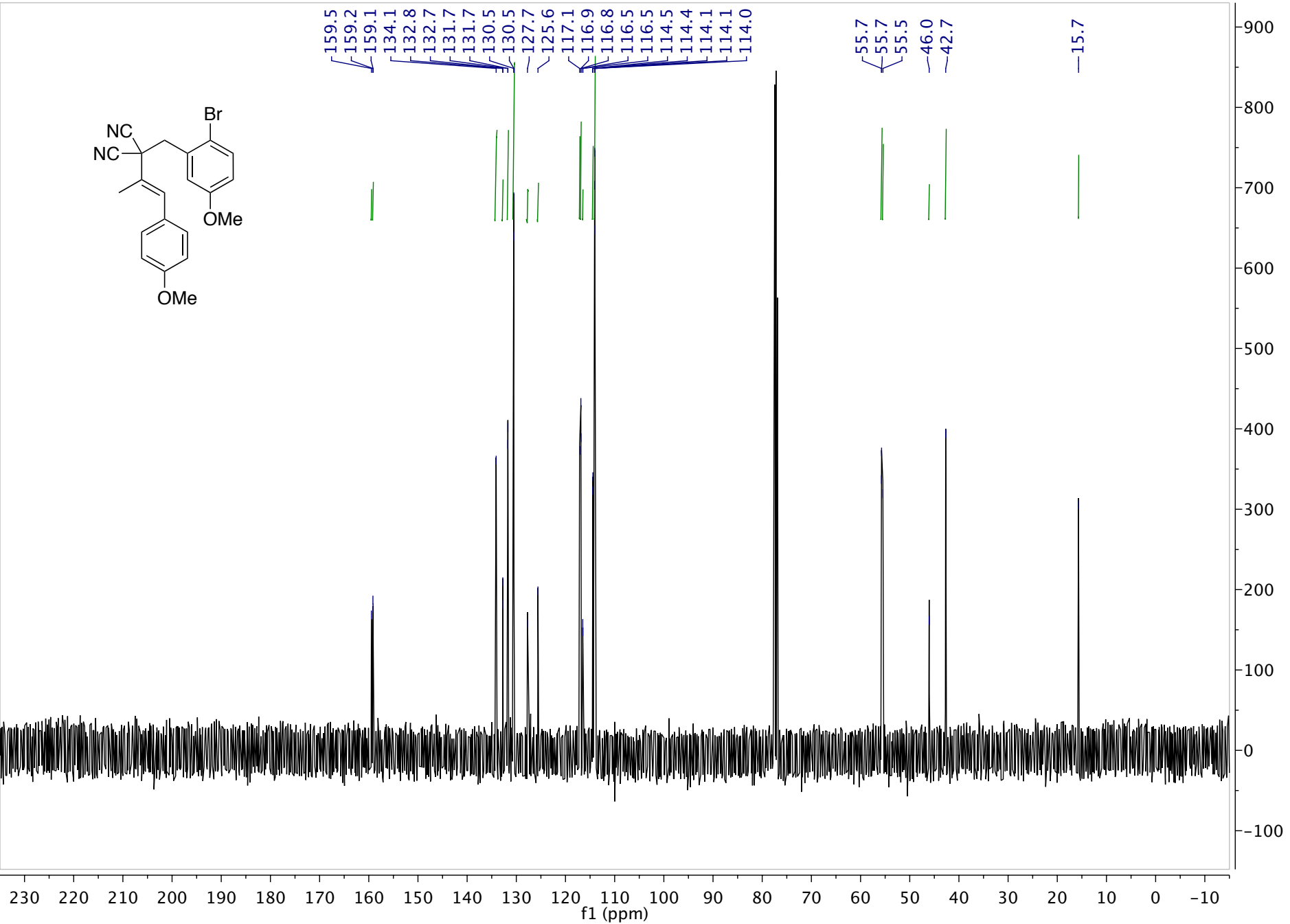
159.5
149.1
147.9
131.6
130.5
130.5
127.7
125.7
124.8
117.2
114.4
114.4
114.1
114.1
114.1
113.4
111.2
111.2
102.4
102.4
55.5
55.5
46.2
42.7
42.7
15.6

f1 (ppm)

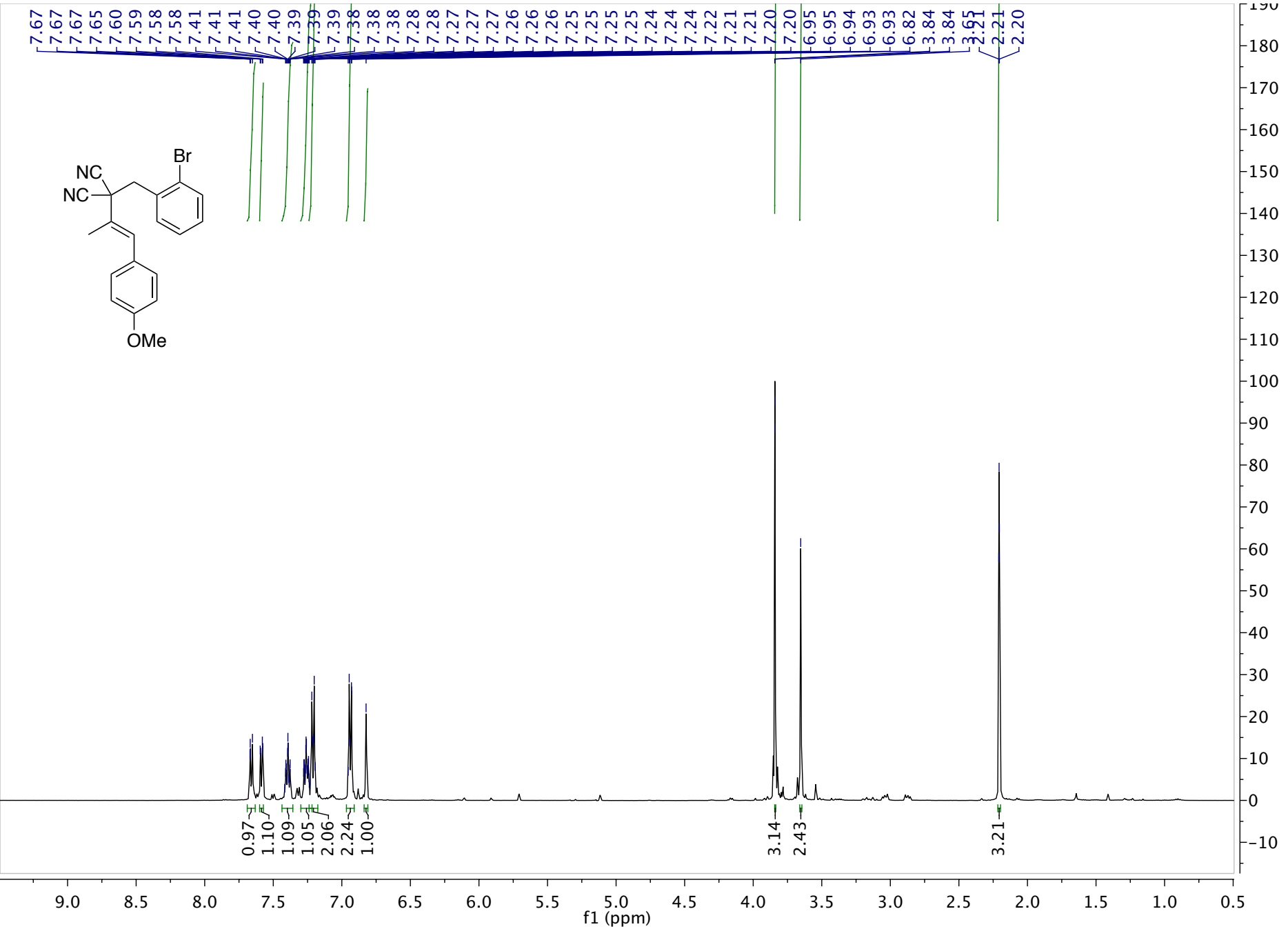
^{1}H spectrum of (*E*)-2-(2-bromo-5-methoxybenzyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile 3c ($CDCl_3$)



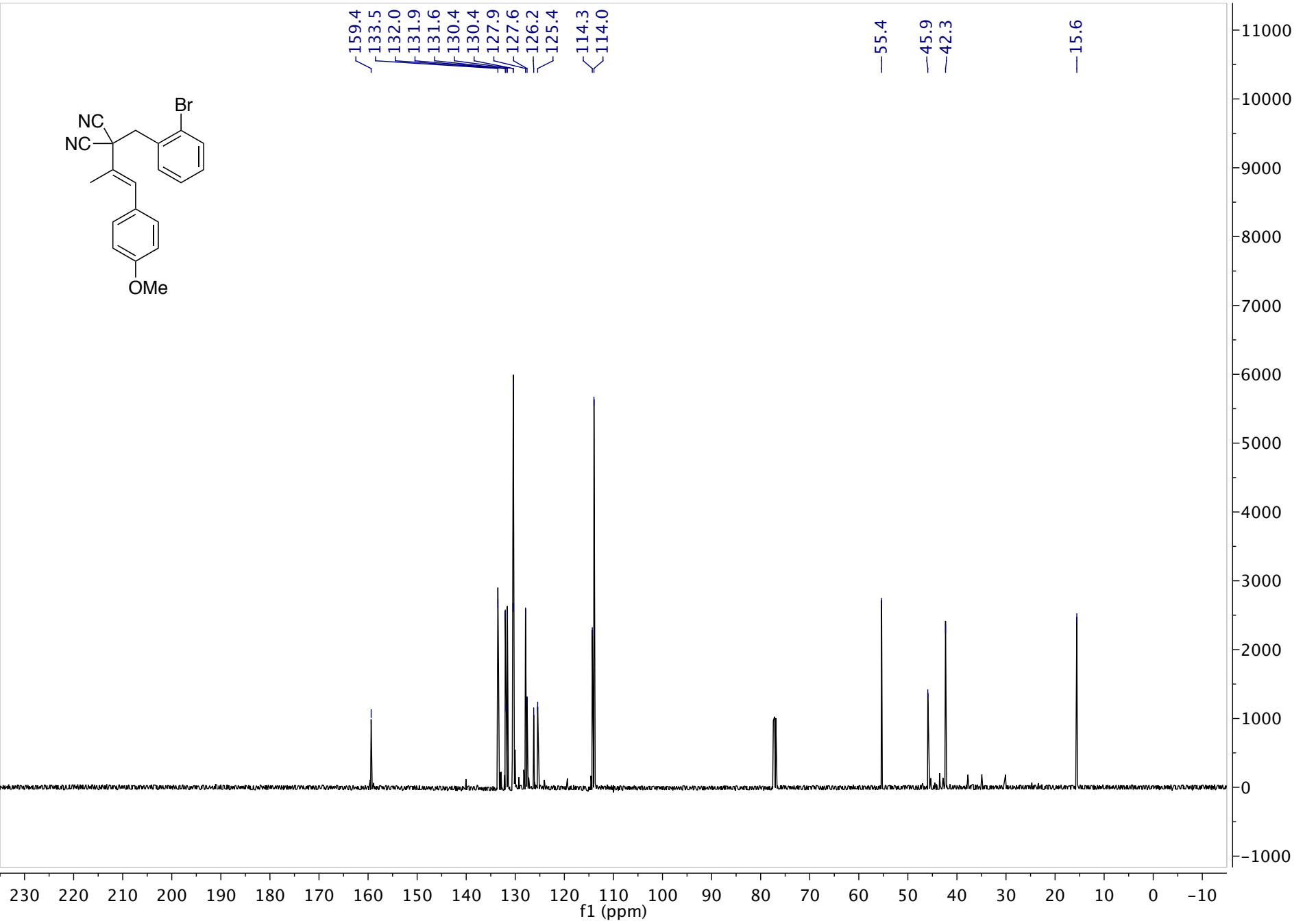
^{13}C spectrum of (*E*)-2-(2-bromo-5-methoxybenzyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile 3c ($CDCl_3$)



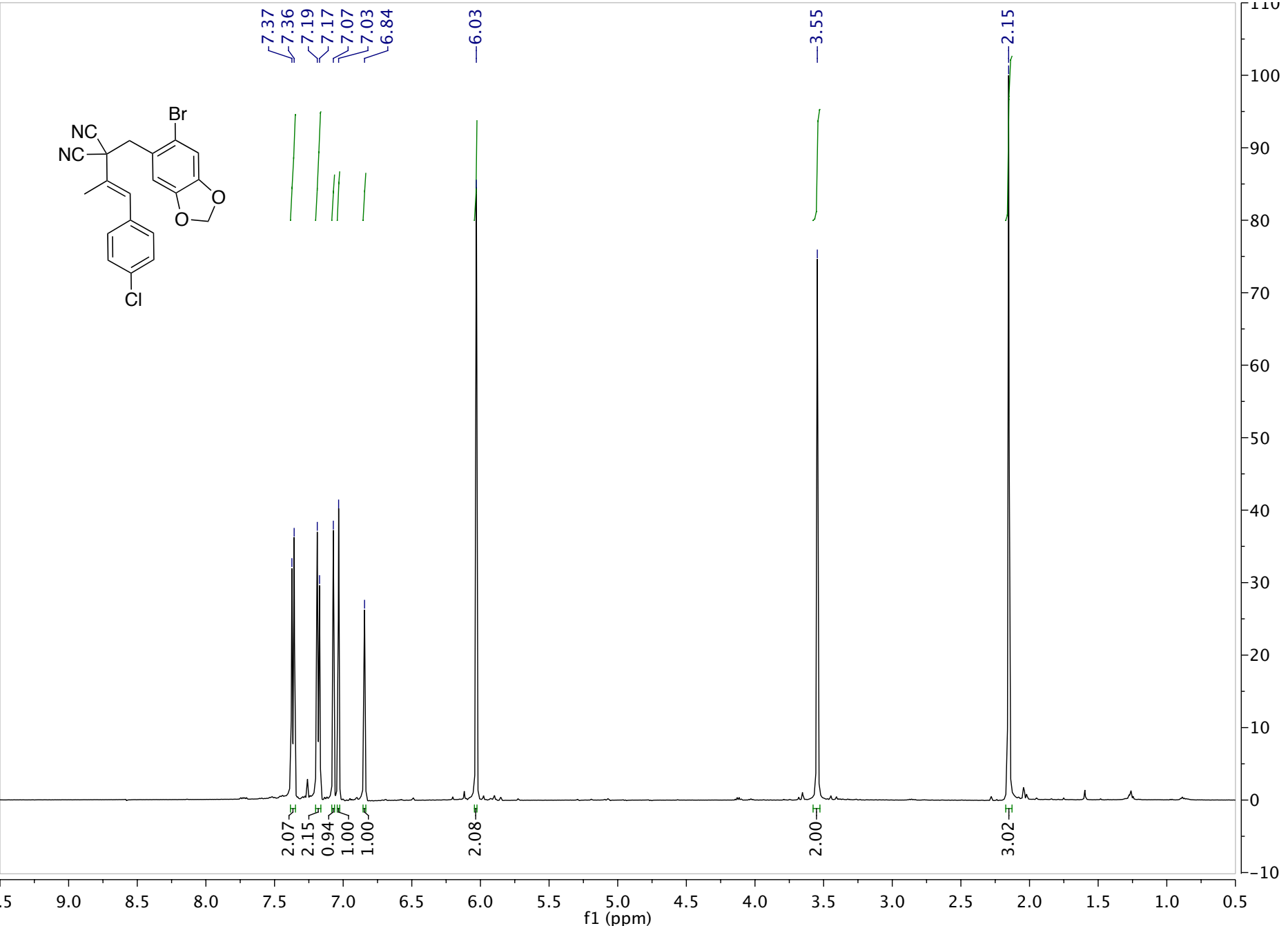
^{1}H spectrum of (*E*)-2-(2-bromobenzyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile 3d ($CDCl_3$)



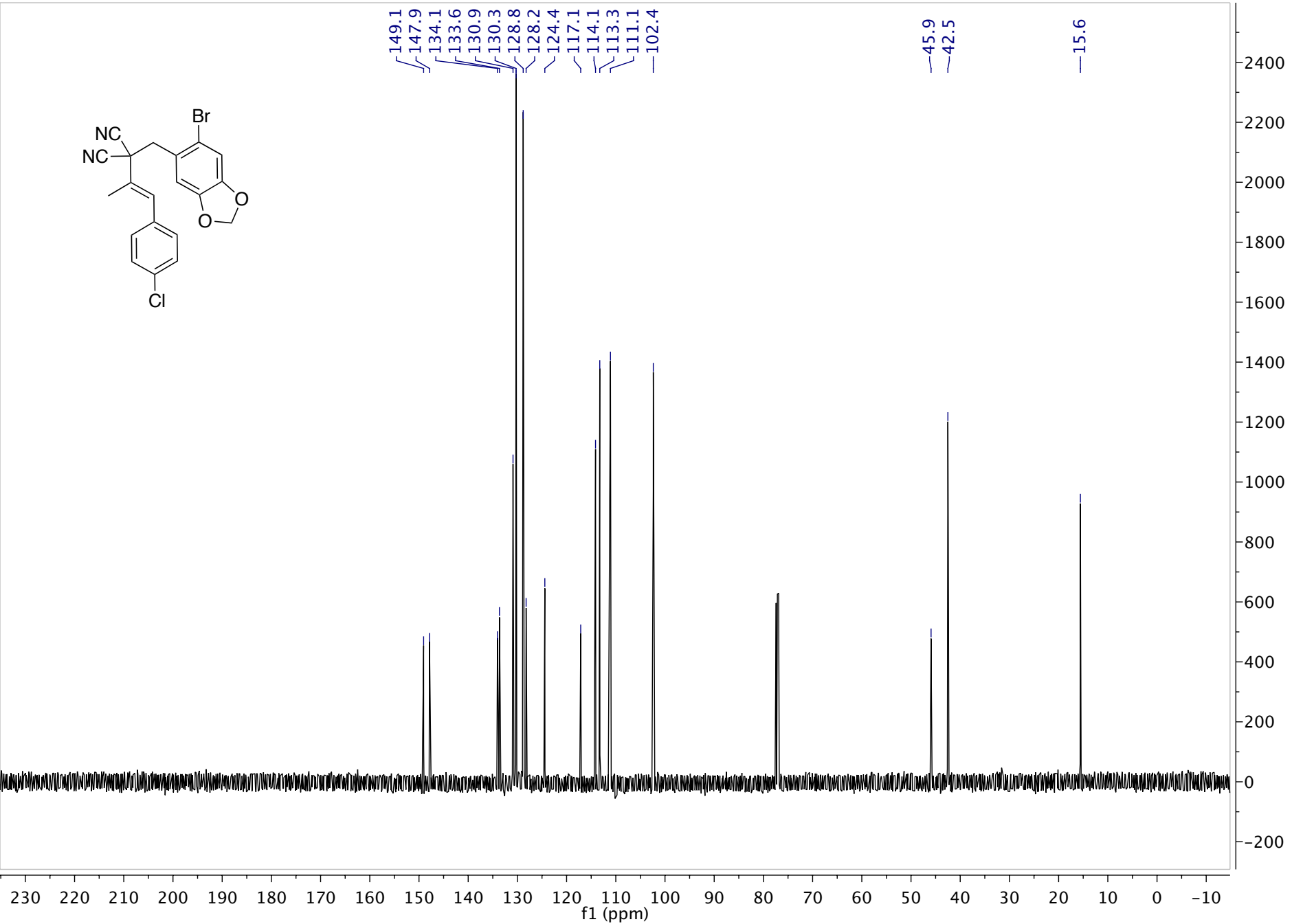
^{13}C spectrum of (*E*)-2-(2-bromobenzyl)-2-(1-(4-methoxyphenyl)prop-1-en-2-yl)malononitrile 3d ($CDCl_3$)



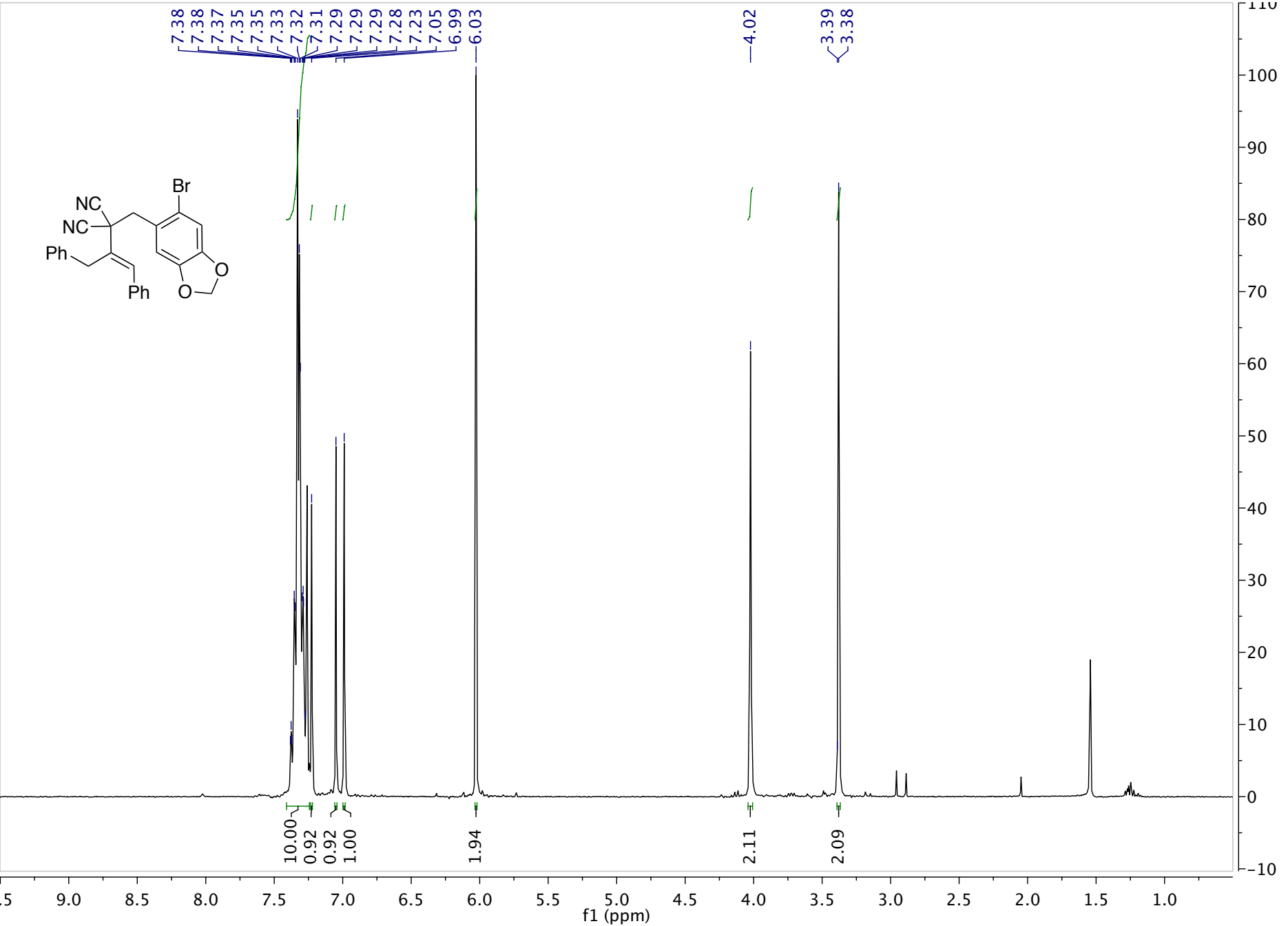
^{1}H spectrum of (*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1-(4-chlorophenyl)prop-1-en-2-yl)malononitrile 3e ($CDCl_3$)



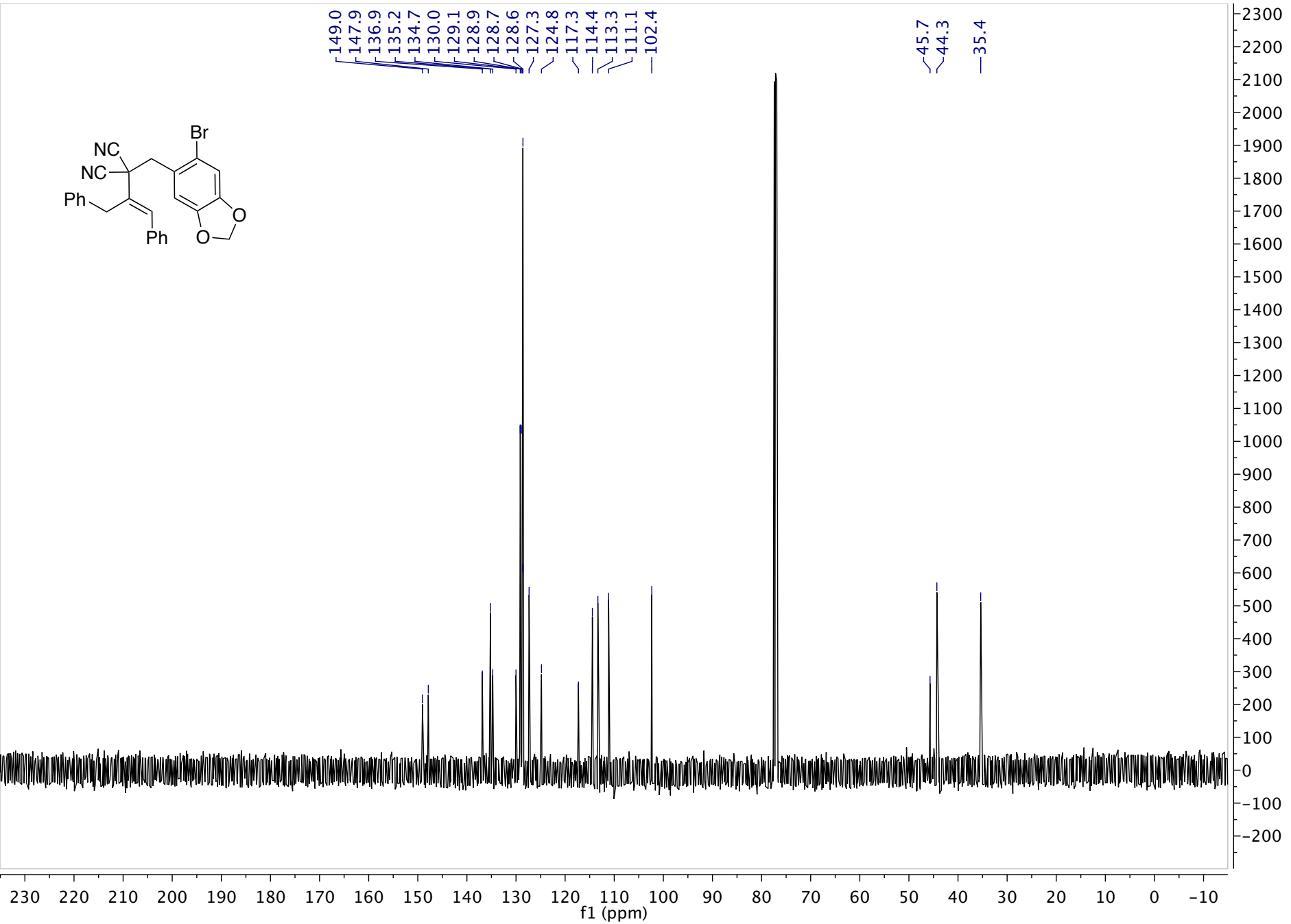
^{13}C spectrum of (*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1-(4-chlorophenyl)prop-1-en-2-yl)malononitrile 3e ($CDCl_3$)



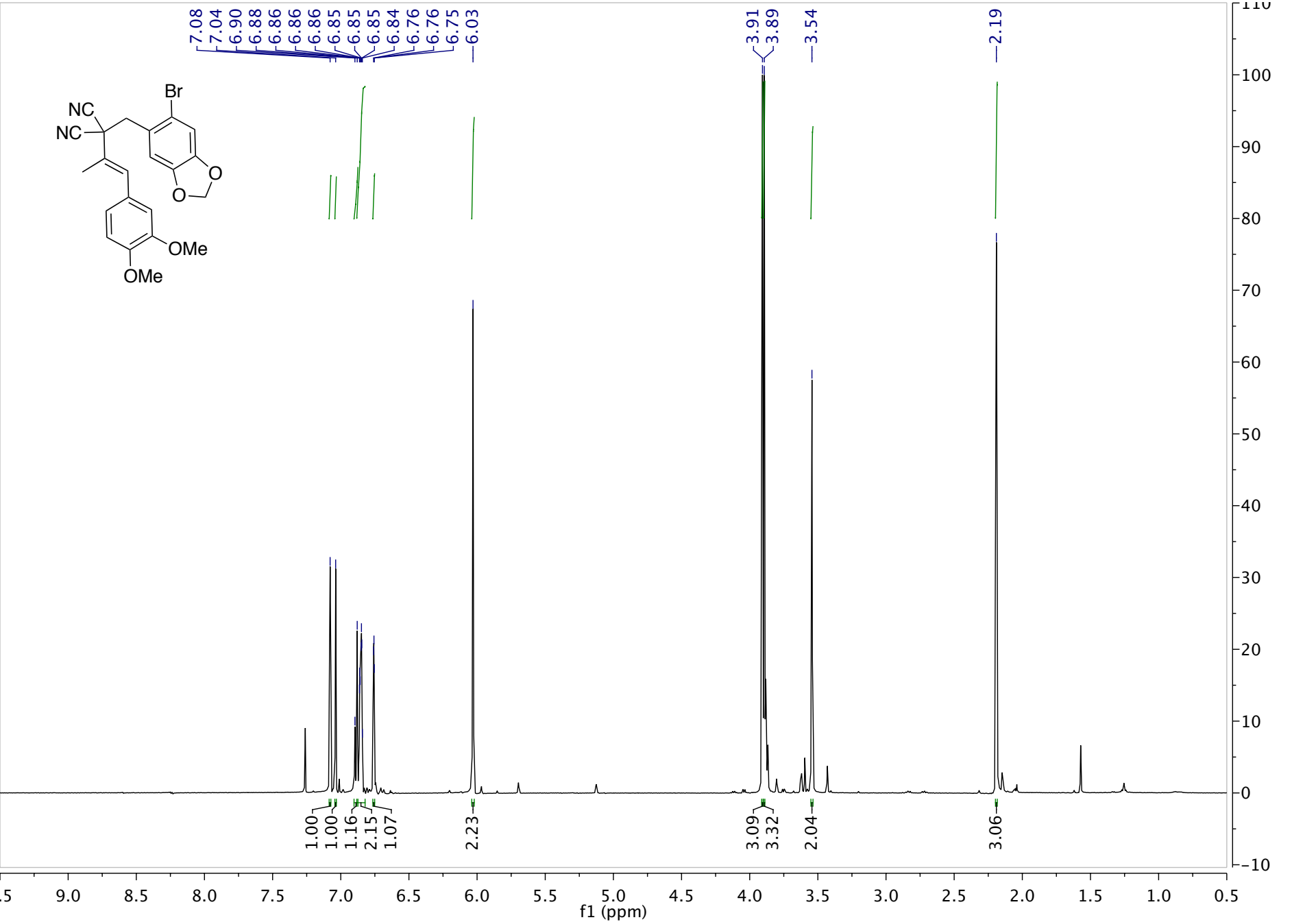
^{1}H spectrum of (*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1,3-diphenylprop-1-en-2-yl)malononitrile 3f ($CDCl_3$)



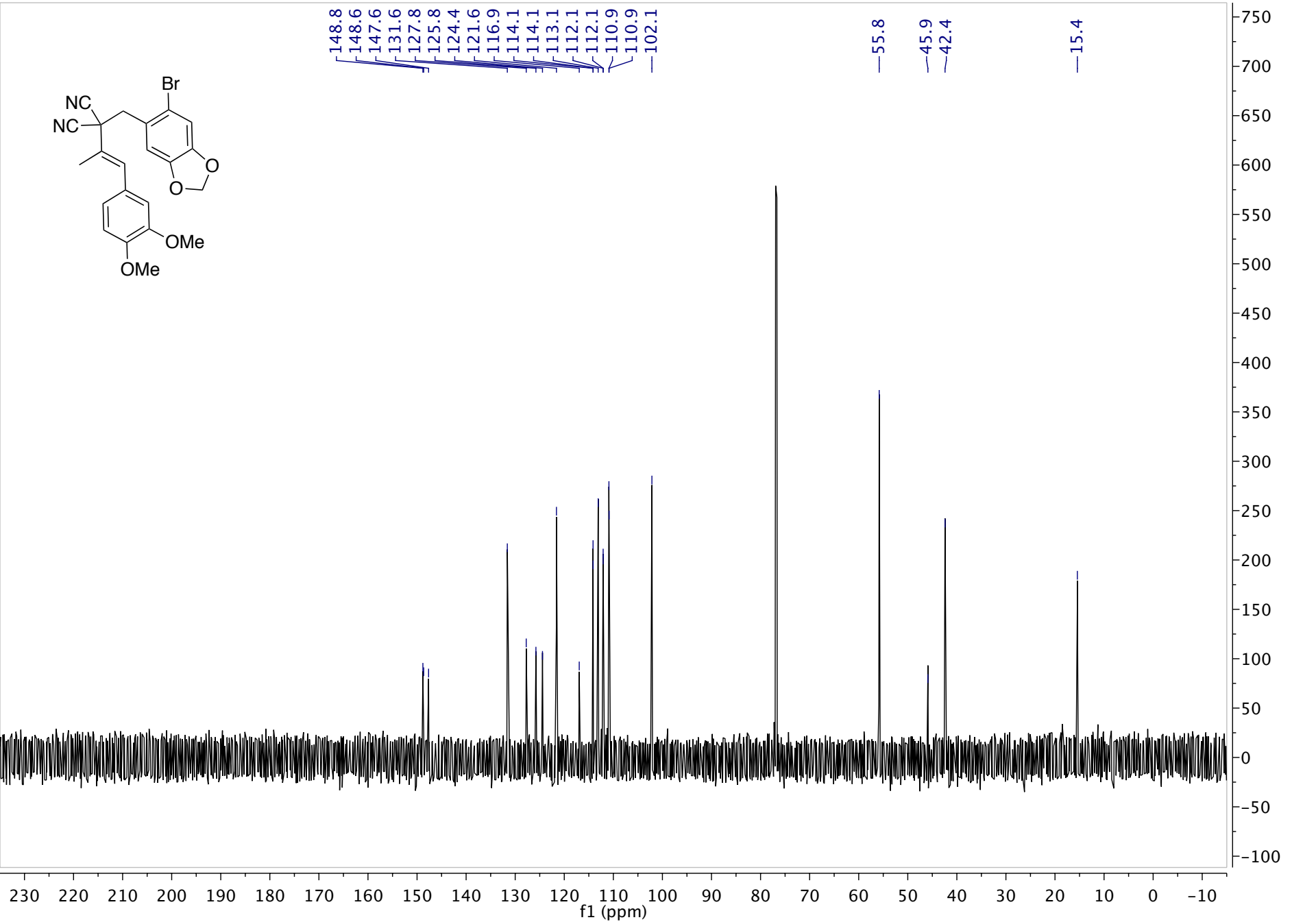
^{13}C spectrum of (*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1,3-diphenylprop-1-en-2-yl)malononitrile 3f ($CDCl_3$)



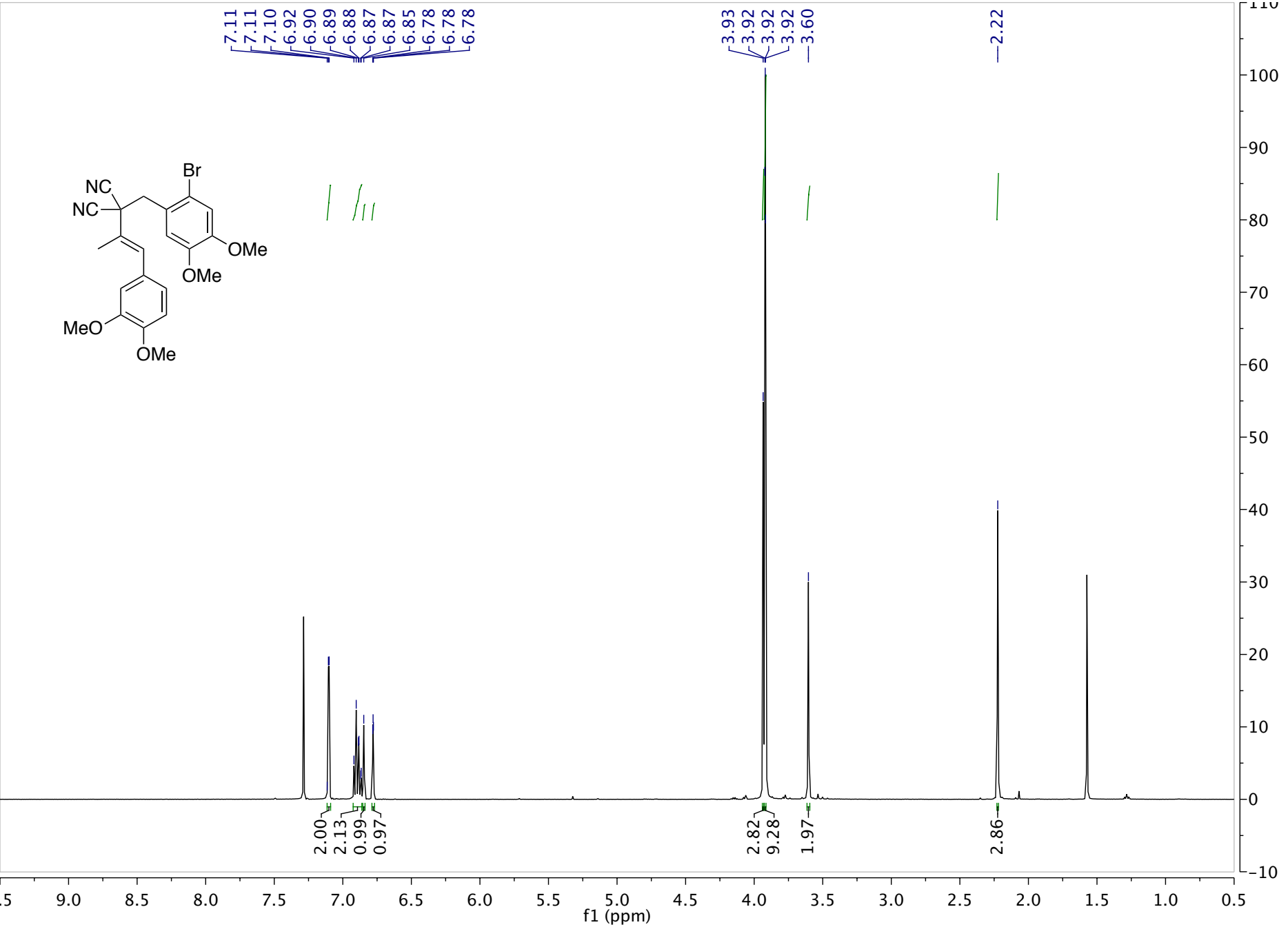
^{1}H spectrum of (*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1-(3,4-dimethoxyphenyl)prop-1-en-2-yl)malononitrile 3g ($CDCl_3$)



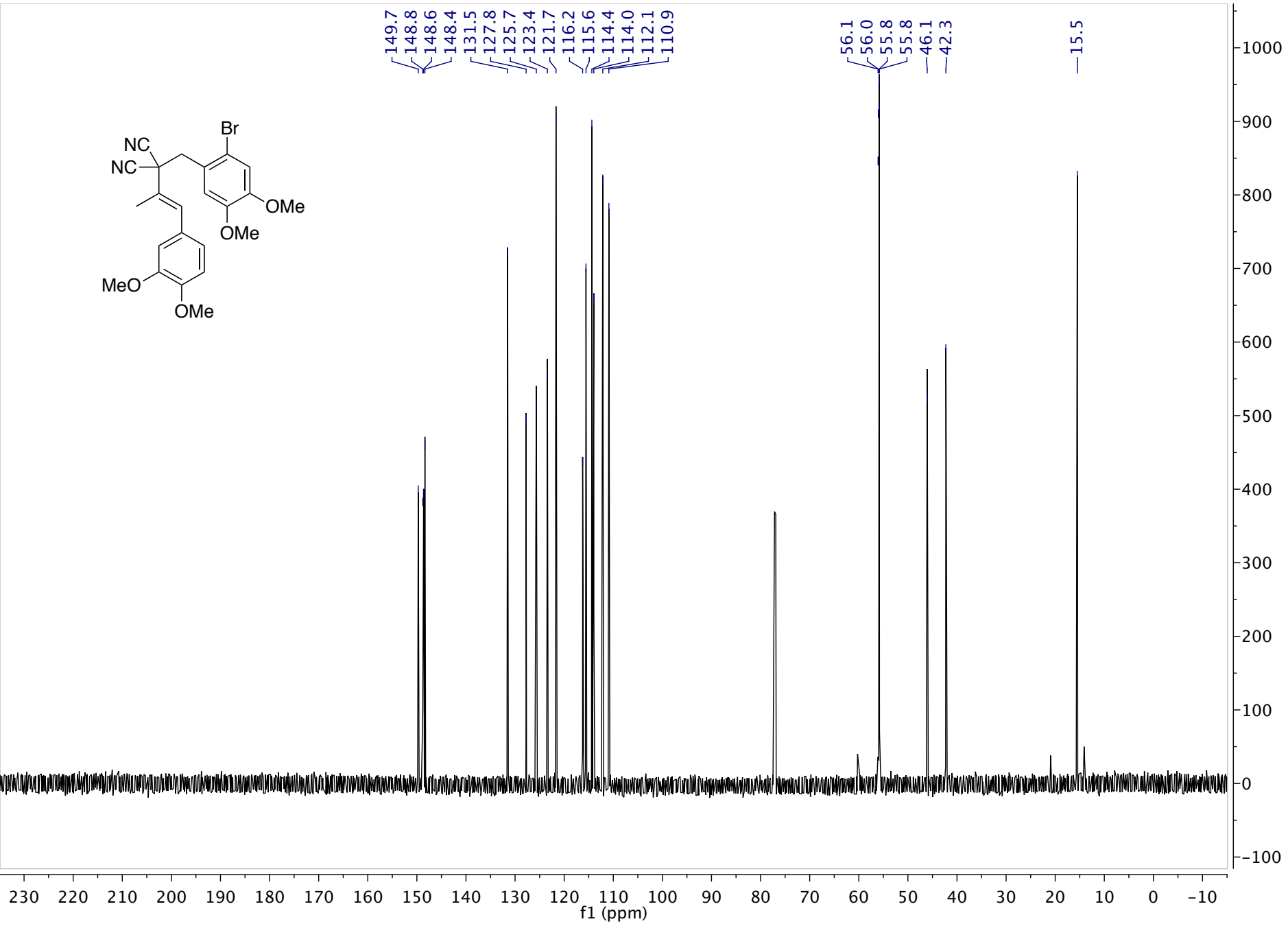
^{13}C spectrum of (*E*)-2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(1-(3,4-dimethoxyphenyl)prop-1-en-2-yl)malononitrile 3g ($CDCl_3$)



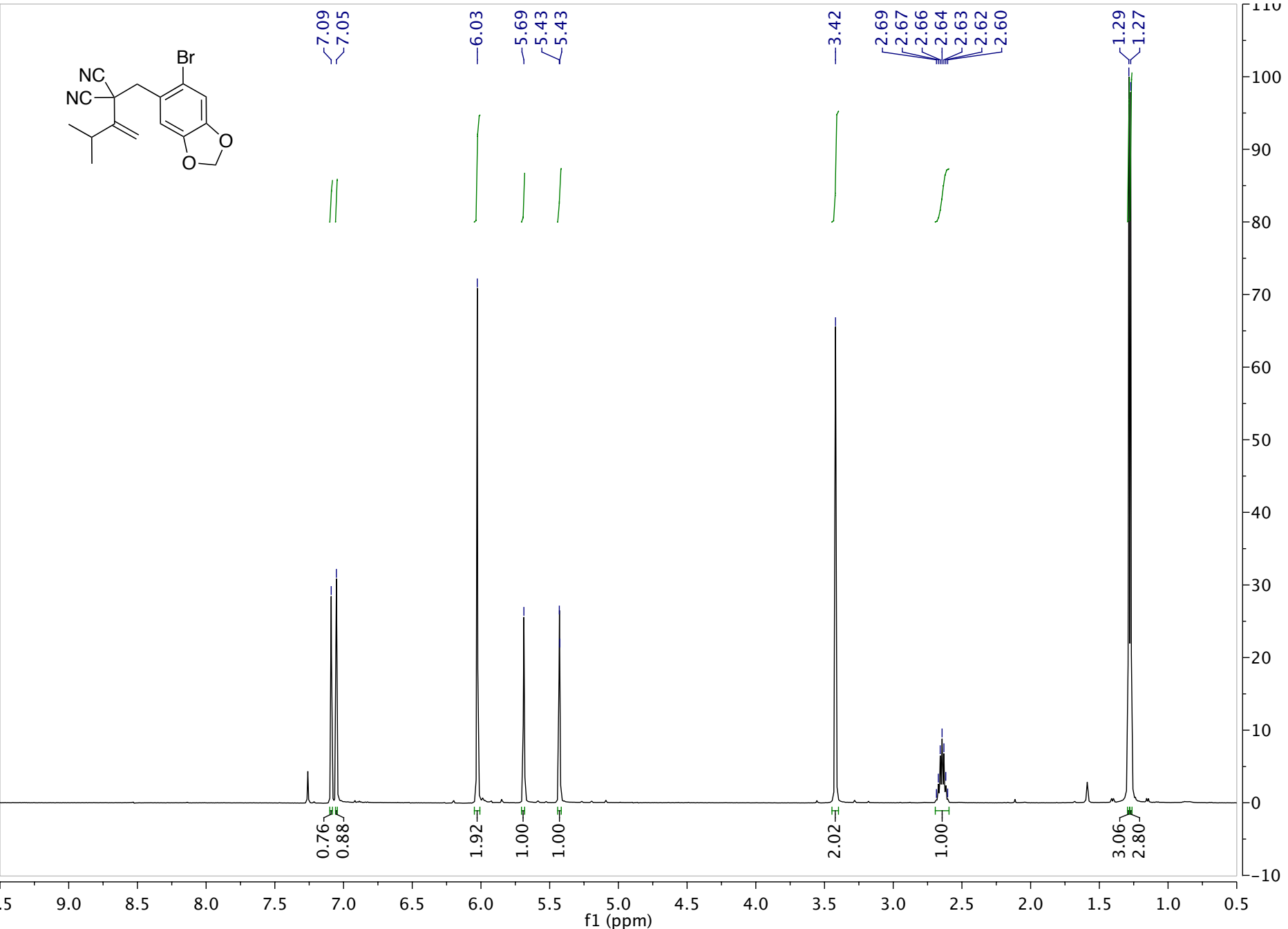
^{1}H spectrum of (*E*)-2-(2-bromo-4,5-dimethoxybenzyl)-2-(1-(3,4-dimethoxyphenyl)prop-1-en-2-yl)malononitrile 3h ($CDCl_3$)



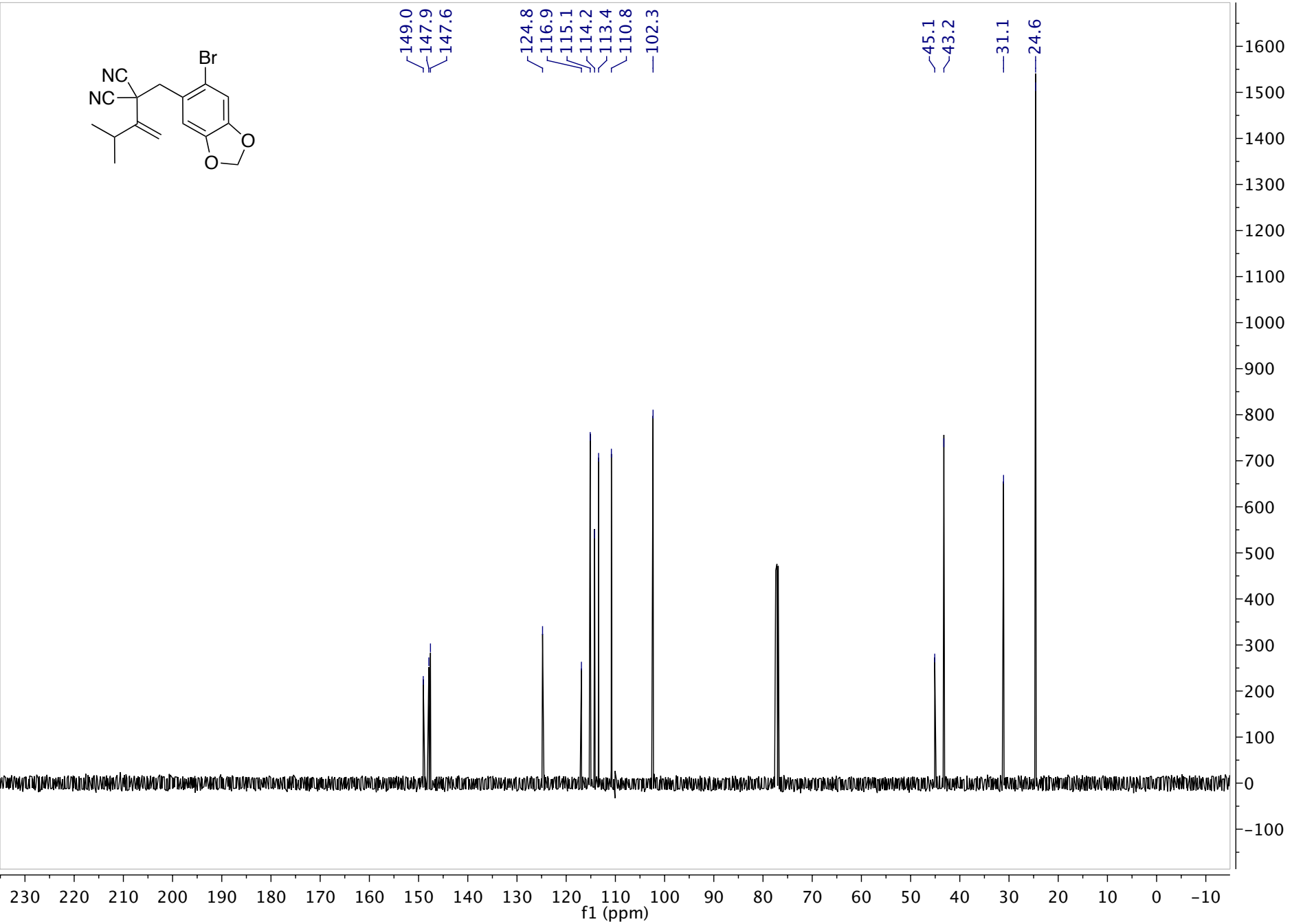
^{13}C spectrum of (*E*)-2-(2-bromo-4,5-dimethoxybenzyl)-2-(1-(3,4-dimethoxyphenyl)prop-1-en-2-yl)malononitrile 3h ($CDCl_3$)



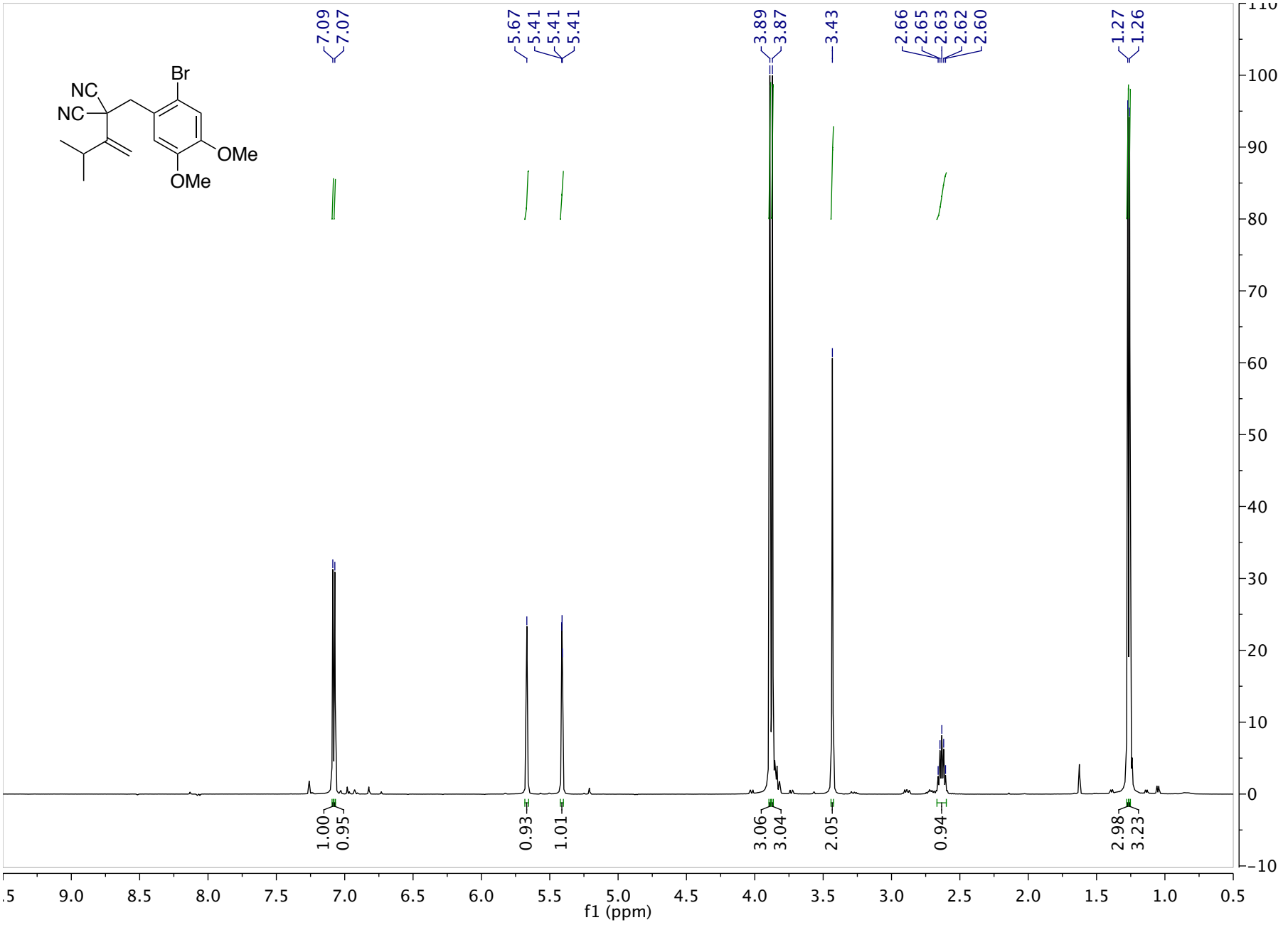
^{1}H spectrum of 2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(3-methylbut-1-en-2-yl)malononitrile 3k ($CDCl_3$)



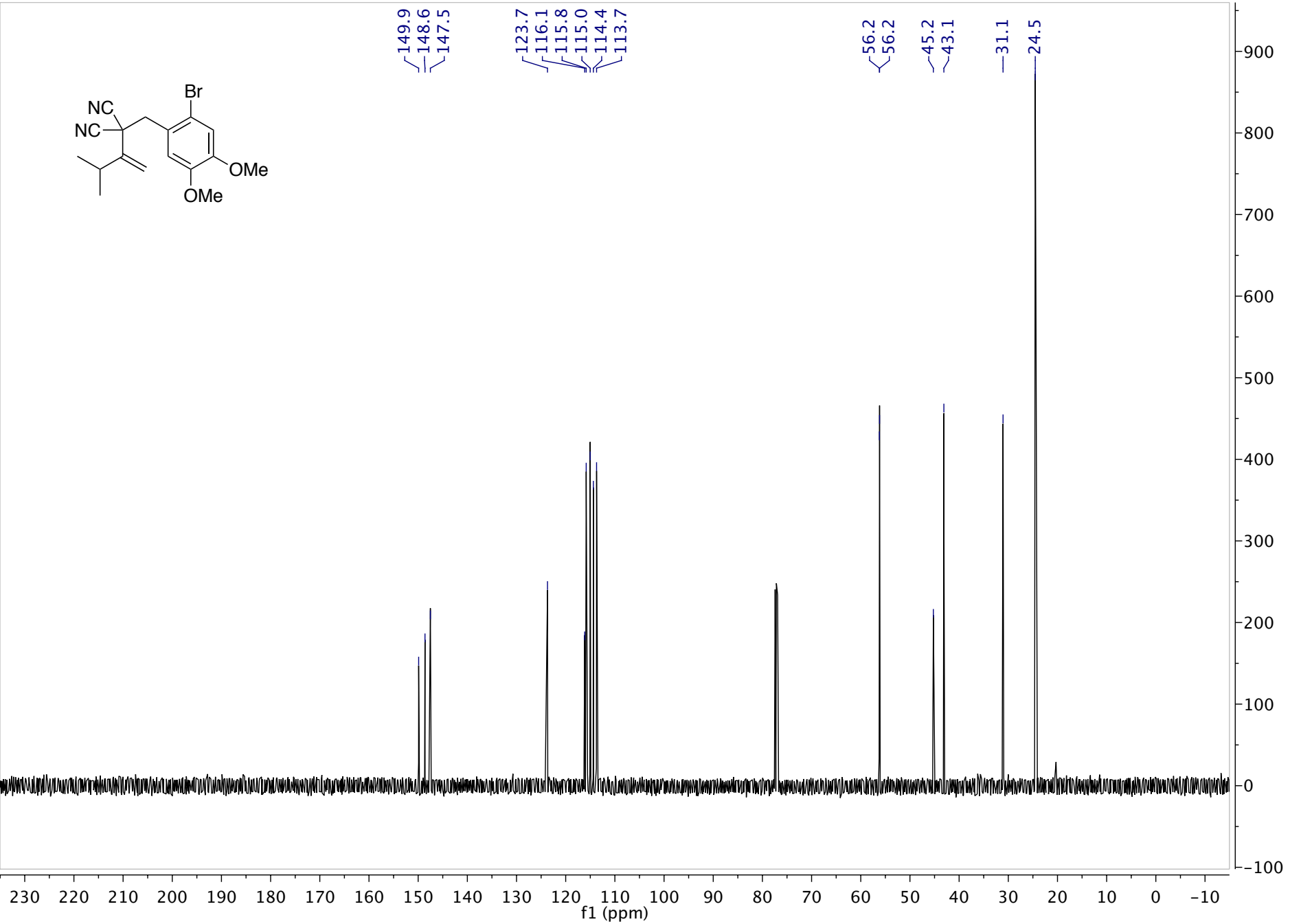
^{13}C spectrum of 2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(3-methylbut-1-en-2-yl)malononitrile 3k ($CDCl_3$)



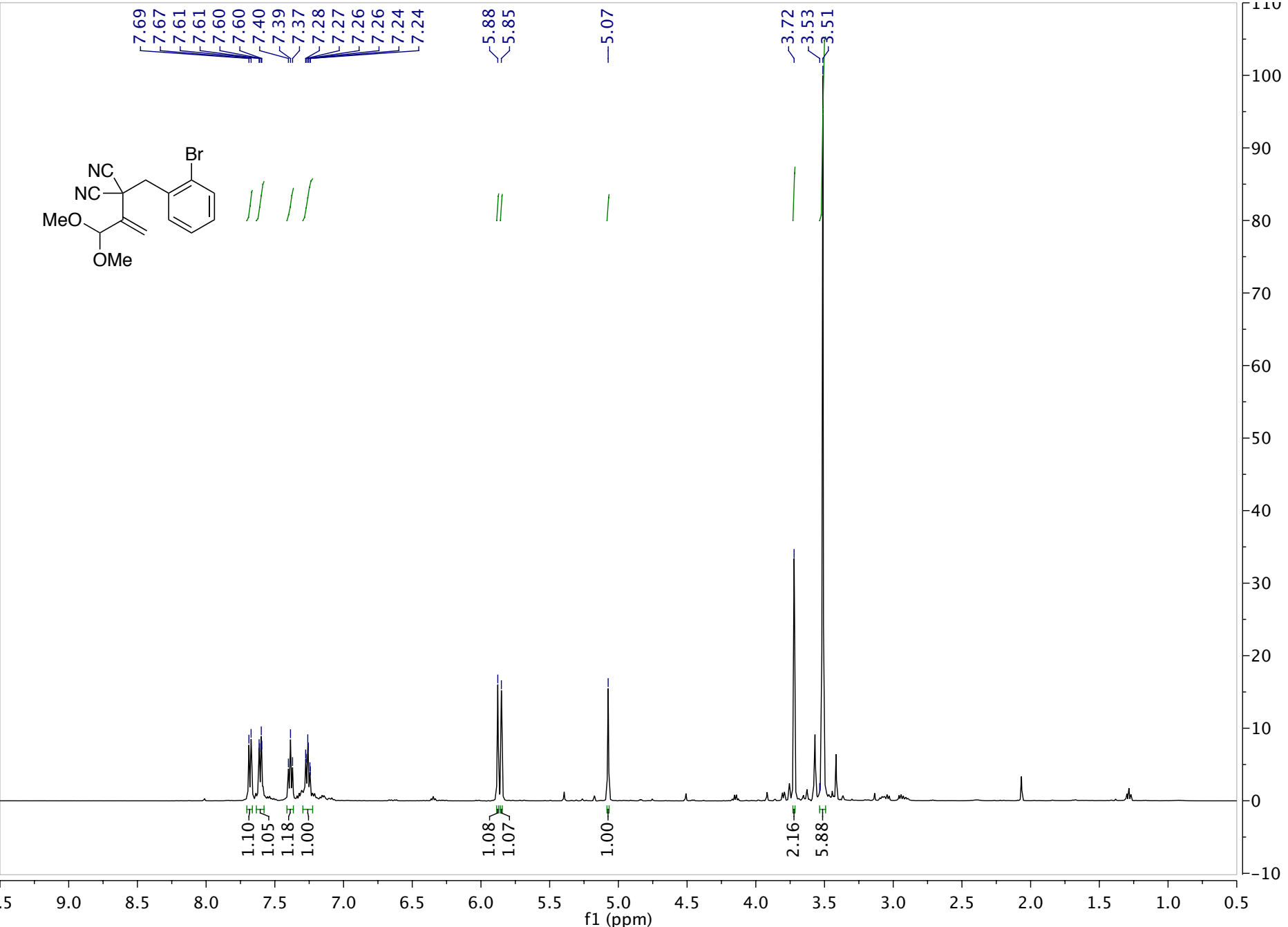
^{1}H spectrum of 2-(2-bromo-4,5-dimethoxybenzyl)-2-(3-methylbut-1-en-2-yl)malononitrile 3l ($CDCl_3$)



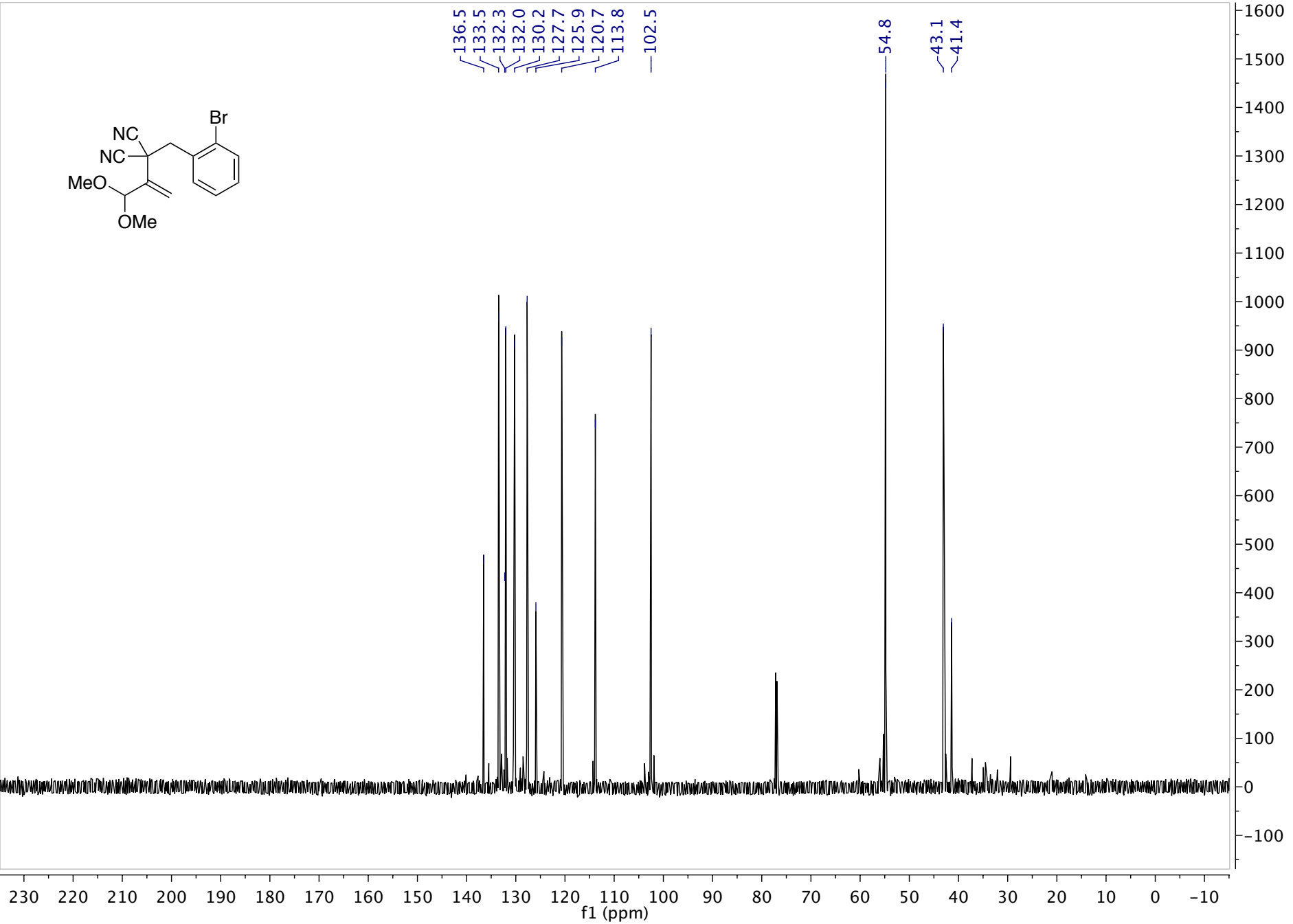
^{13}C spectrum of 2-(2-bromo-4,5-dimethoxybenzyl)-2-(3-methylbut-1-en-2-yl)malononitrile 3l ($CDCl_3$)



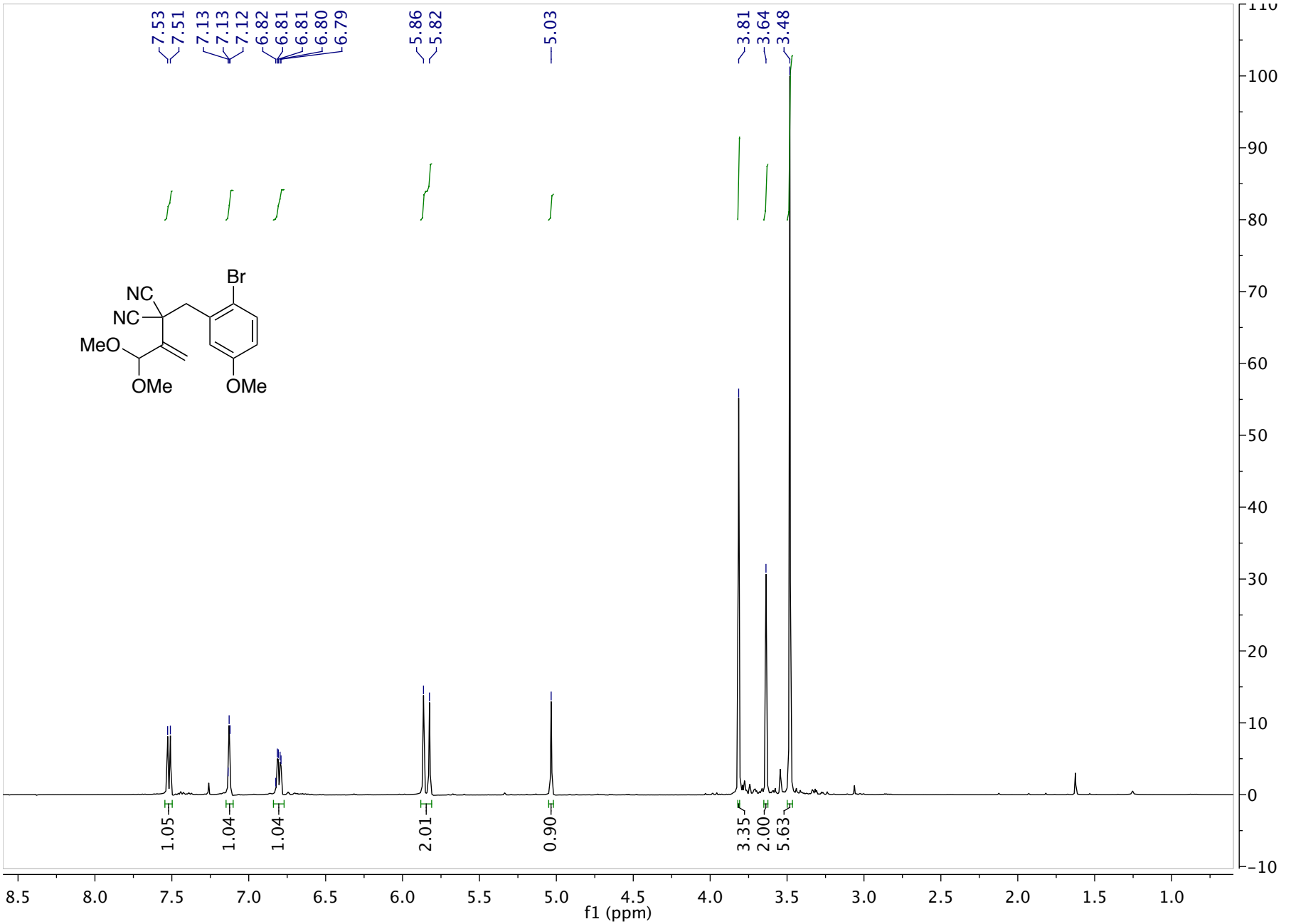
^{1}H spectrum of 2-(2-bromobenzyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile 3m ($CDCl_3$)



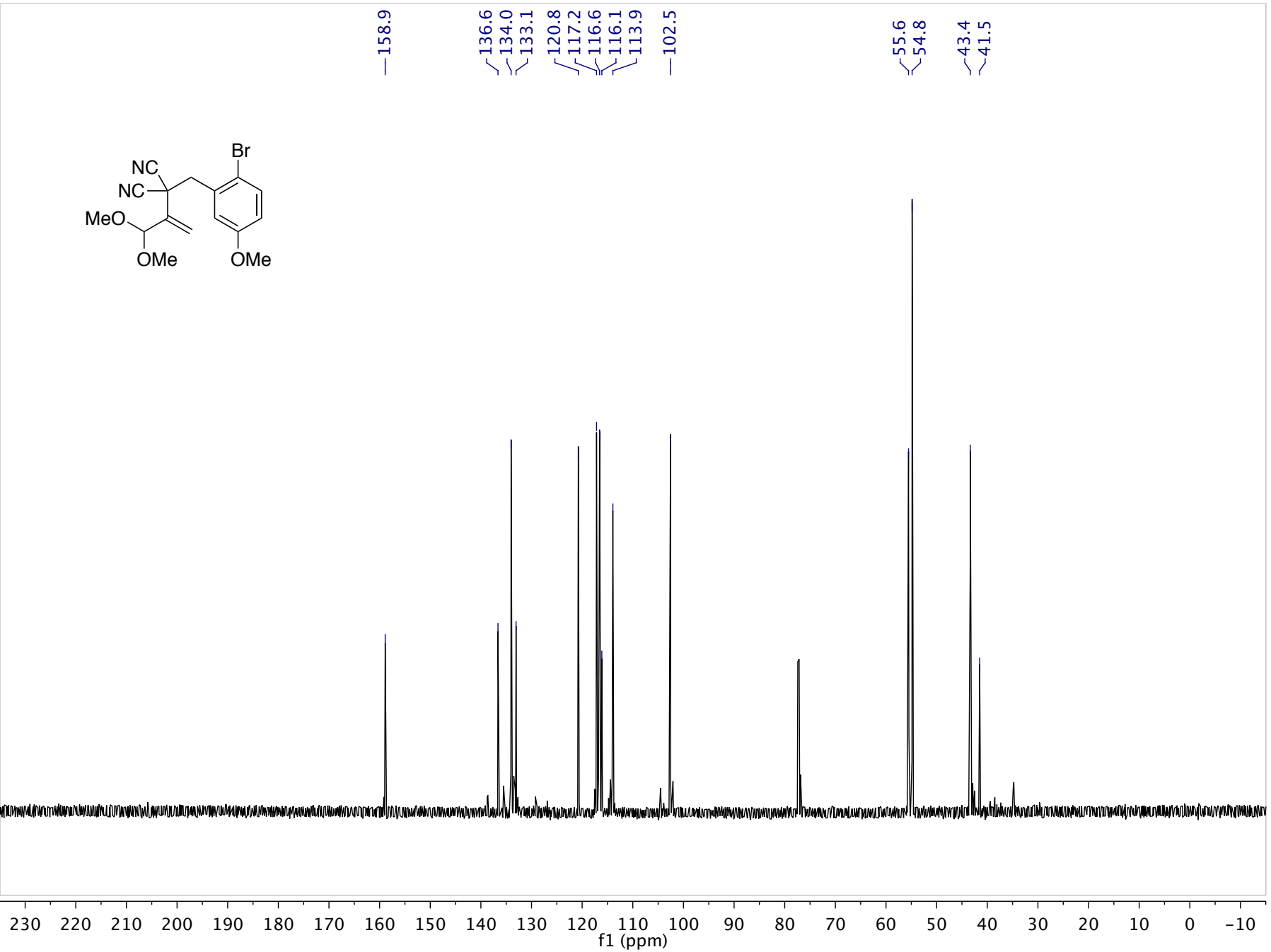
^{13}C spectrum of 2-(2-bromobenzyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile 3m ($CDCl_3$)



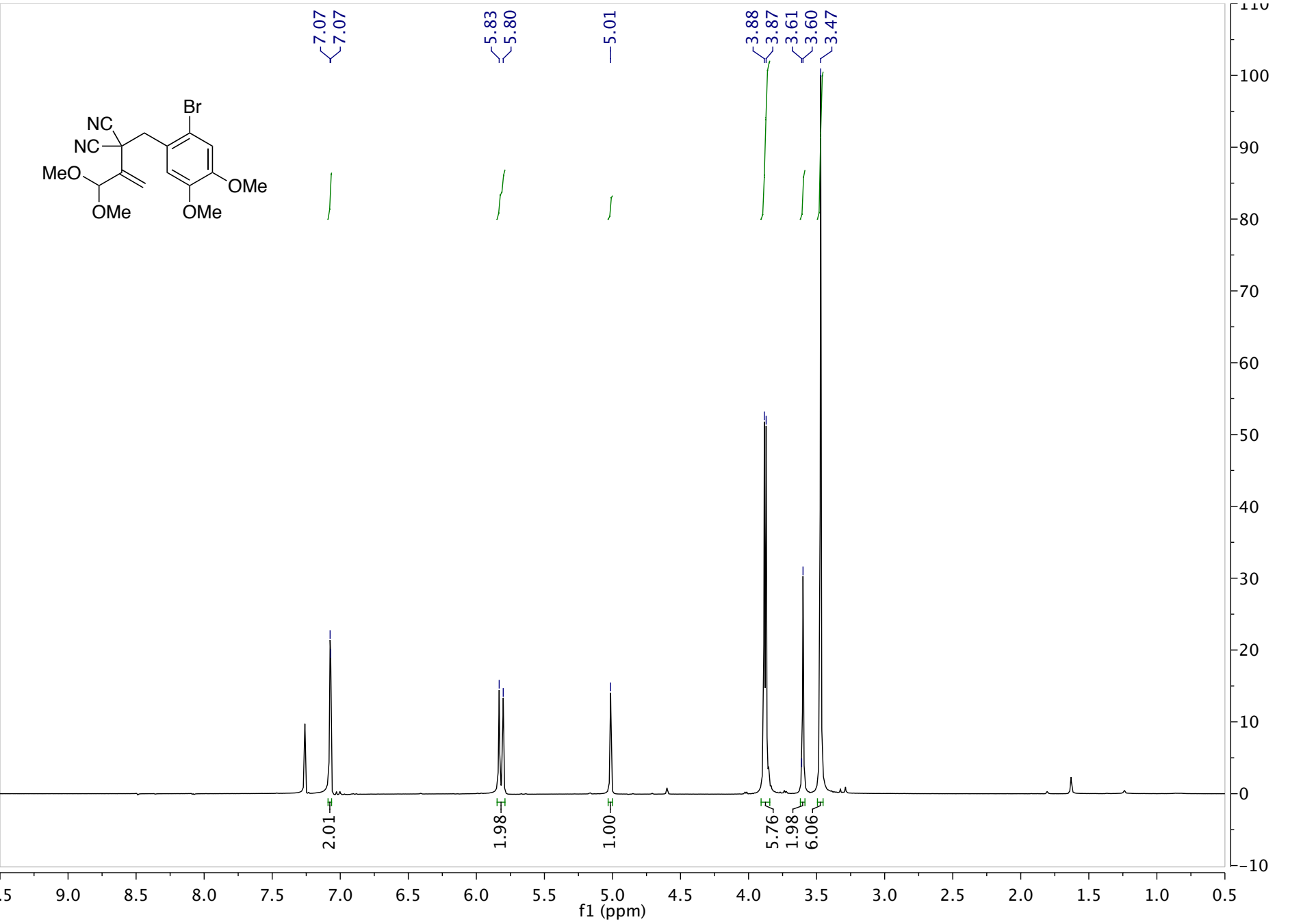
^{1}H spectrum of 2-(2-bromo-5-methoxybenzyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile 3n ($CDCl_3$)



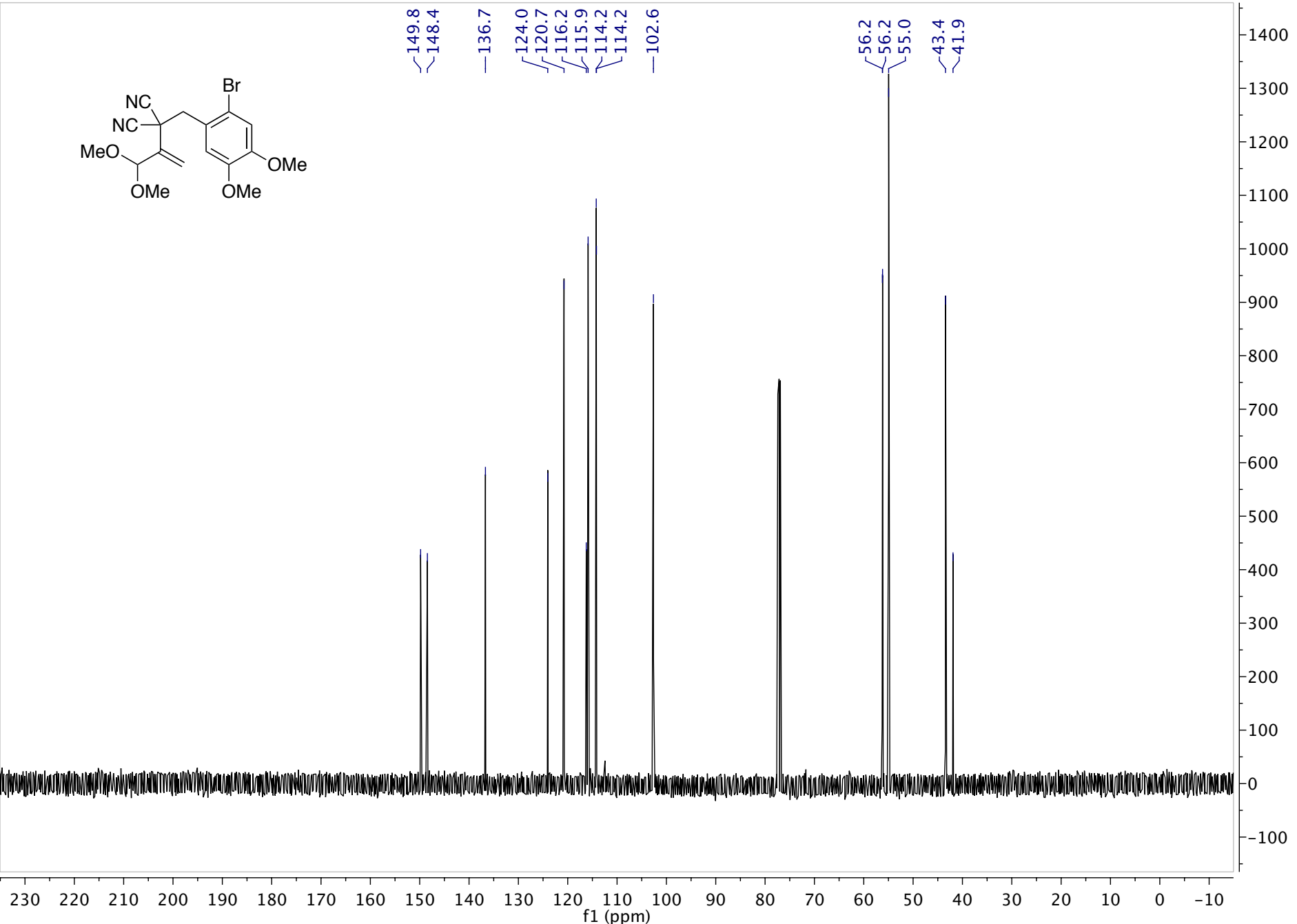
^{13}C spectrum of 2-(2-bromo-5-methoxybenzyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile 3n ($CDCl_3$)



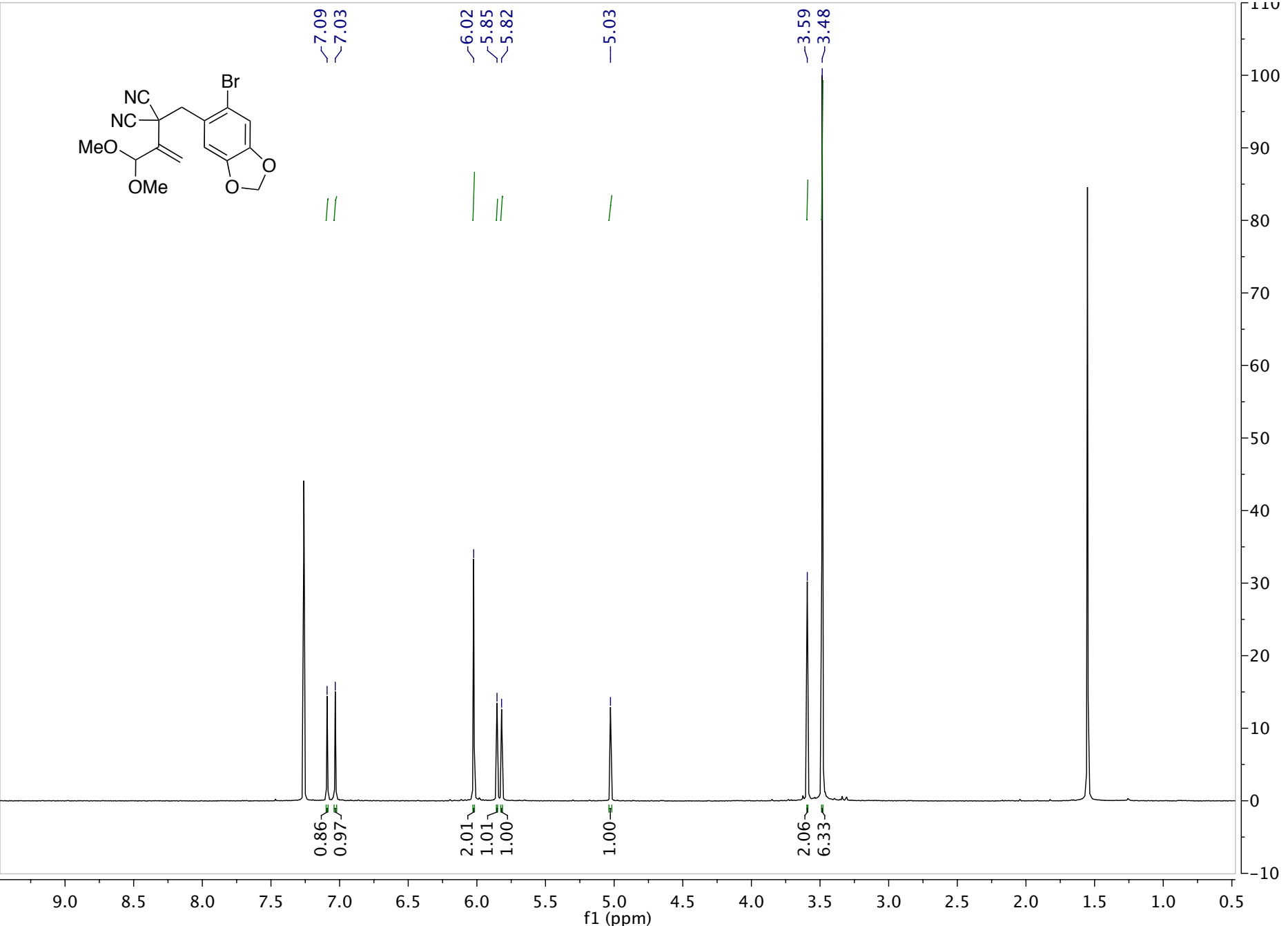
^{1}H spectrum of 2-(2-bromo-4,5-dimethoxybenzyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile 3o ($CDCl_3$)



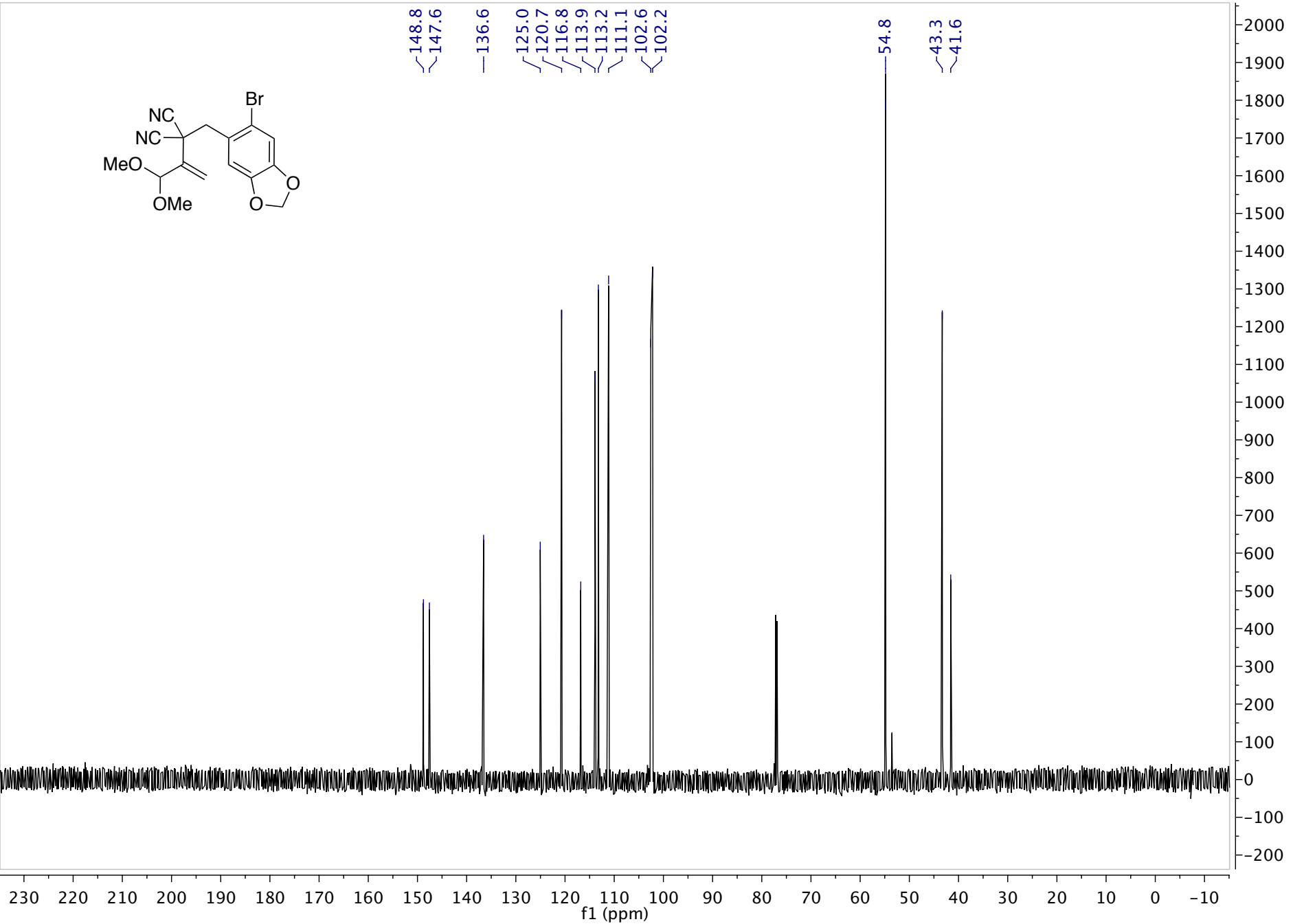
^{13}C spectrum of 2-(2-bromo-4,5-dimethoxybenzyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile 3o ($CDCl_3$)



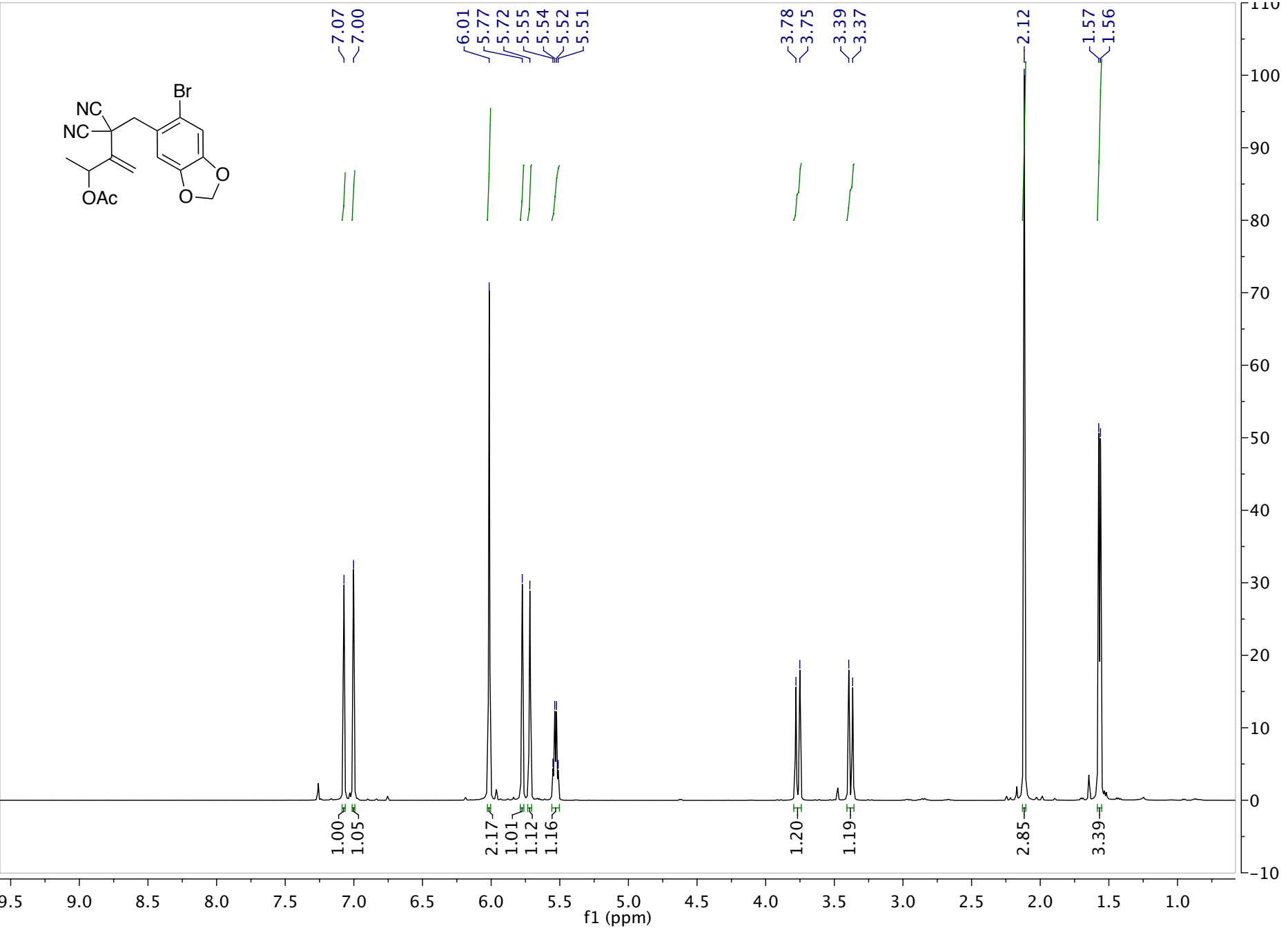
^{1}H spectrum of 2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile 3p ($CDCl_3$)



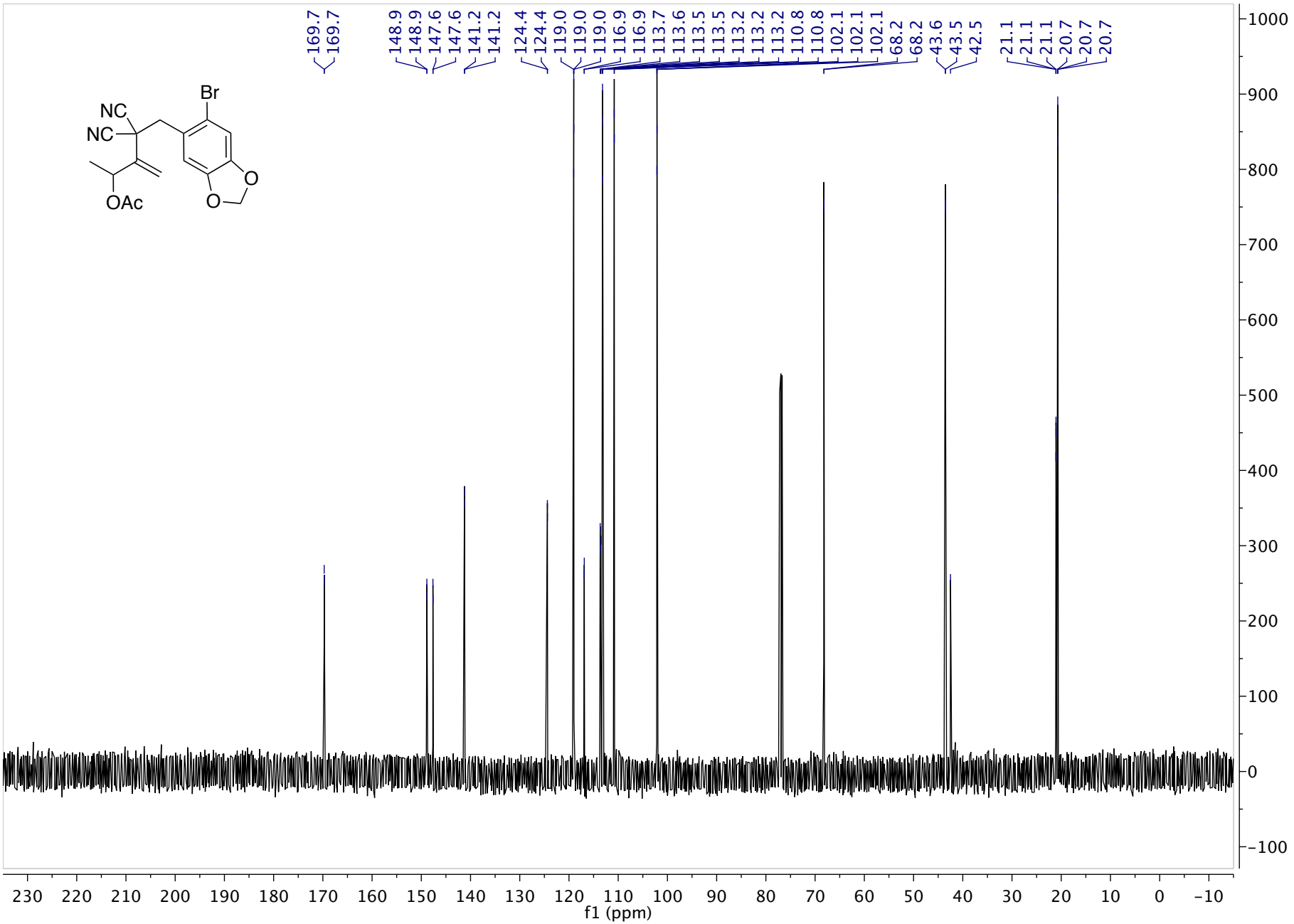
^{13}C spectrum of 2-((6-bromobenzo[*d*][1,3]dioxol-5-yl)methyl)-2-(3,3-dimethoxyprop-1-en-2-yl)malononitrile 3p ($CDCl_3$)



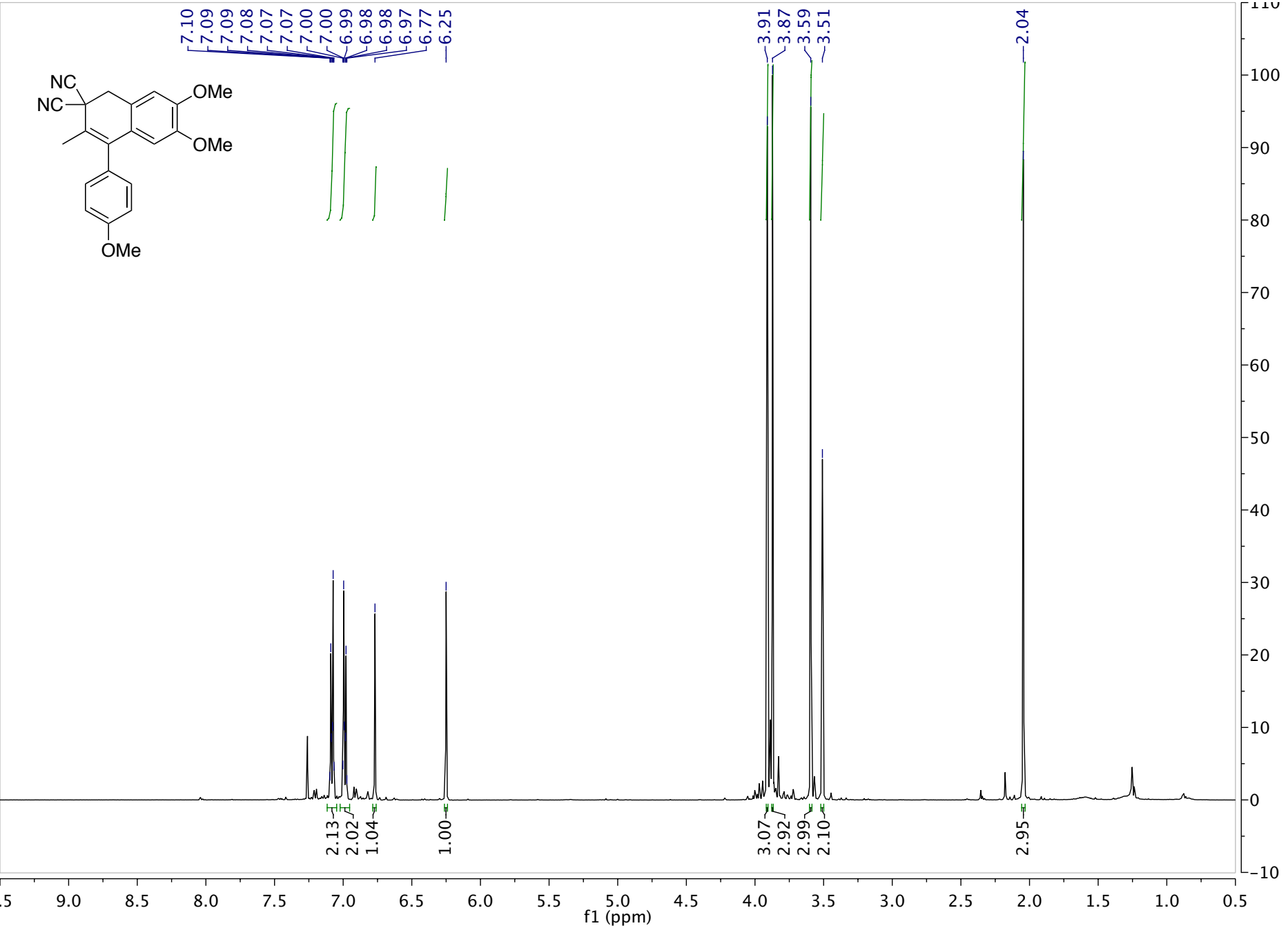
^{1}H spectrum of 5-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-4,4-dicyano-3-methylenepentan-2-yl acetate 3q ($CDCl_3$)



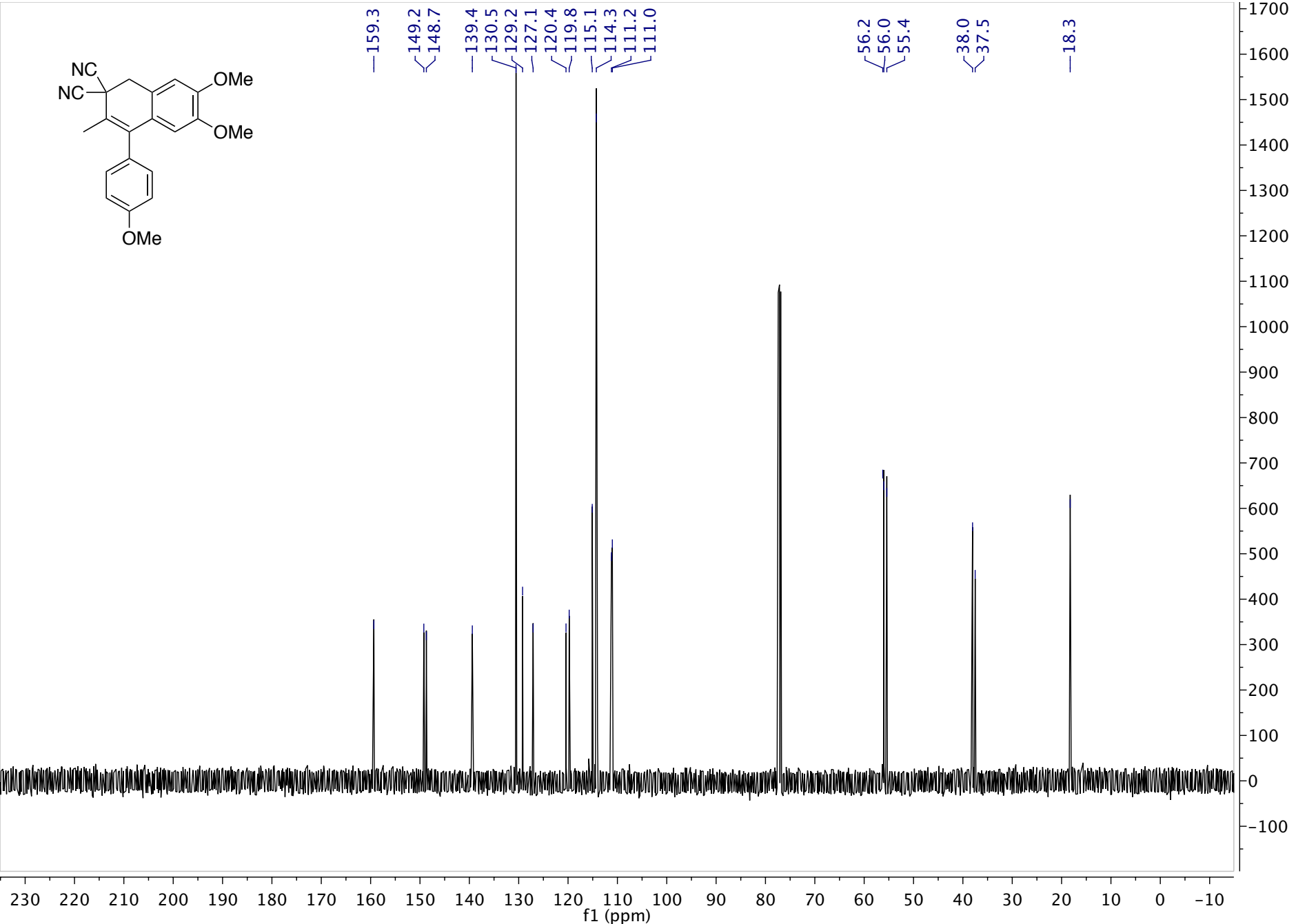
^{13}C spectrum of 5-(6-bromobenzo[*d*][1,3]dioxol-5-yl)-4,4-dicyano-3-methylenepentan-2-yl acetate 3q ($CDCl_3$)



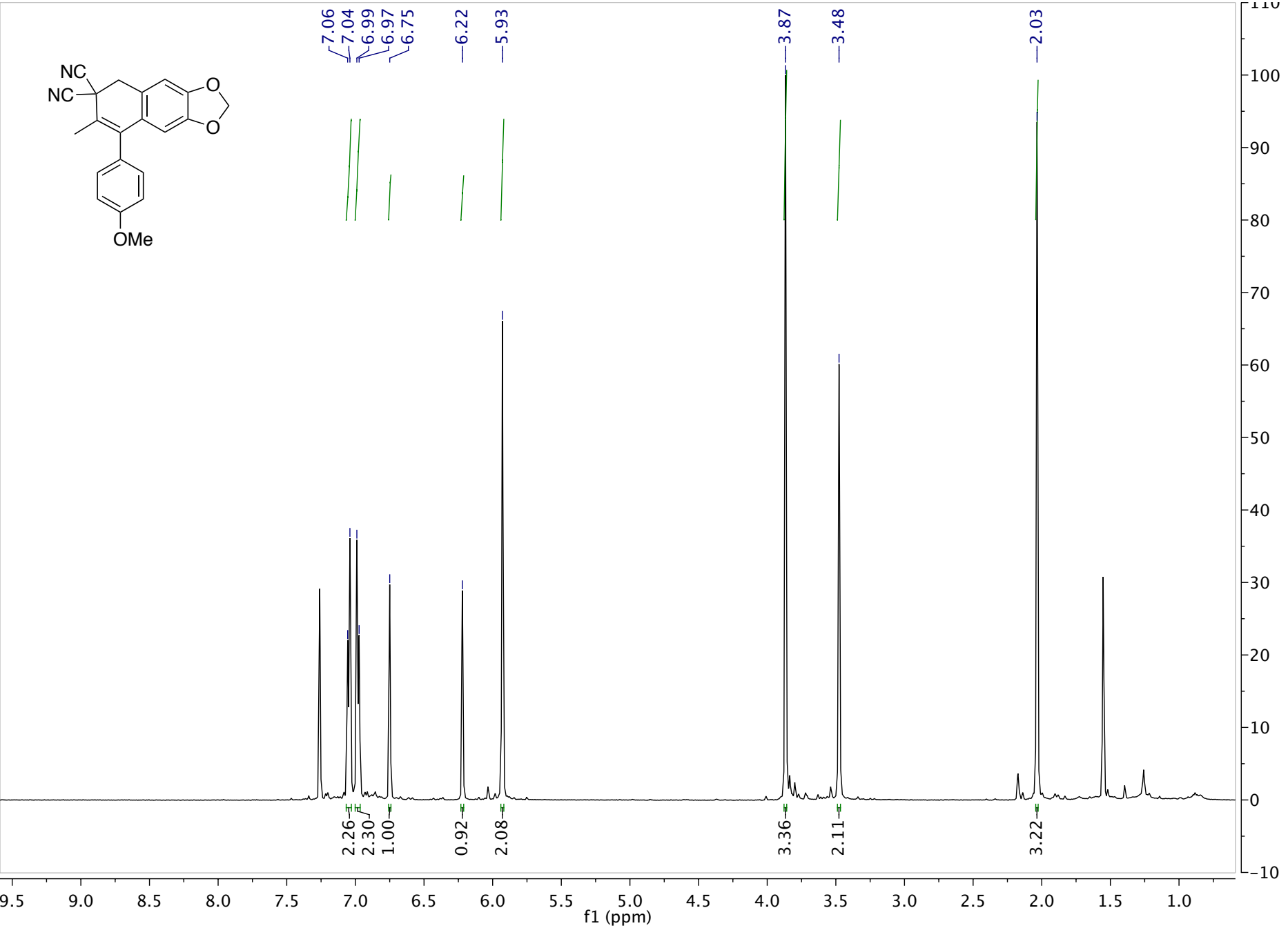
^{1}H spectrum of 6,7-dimethoxy-4-(4-methoxyphenyl)-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile 4a ($CDCl_3$)



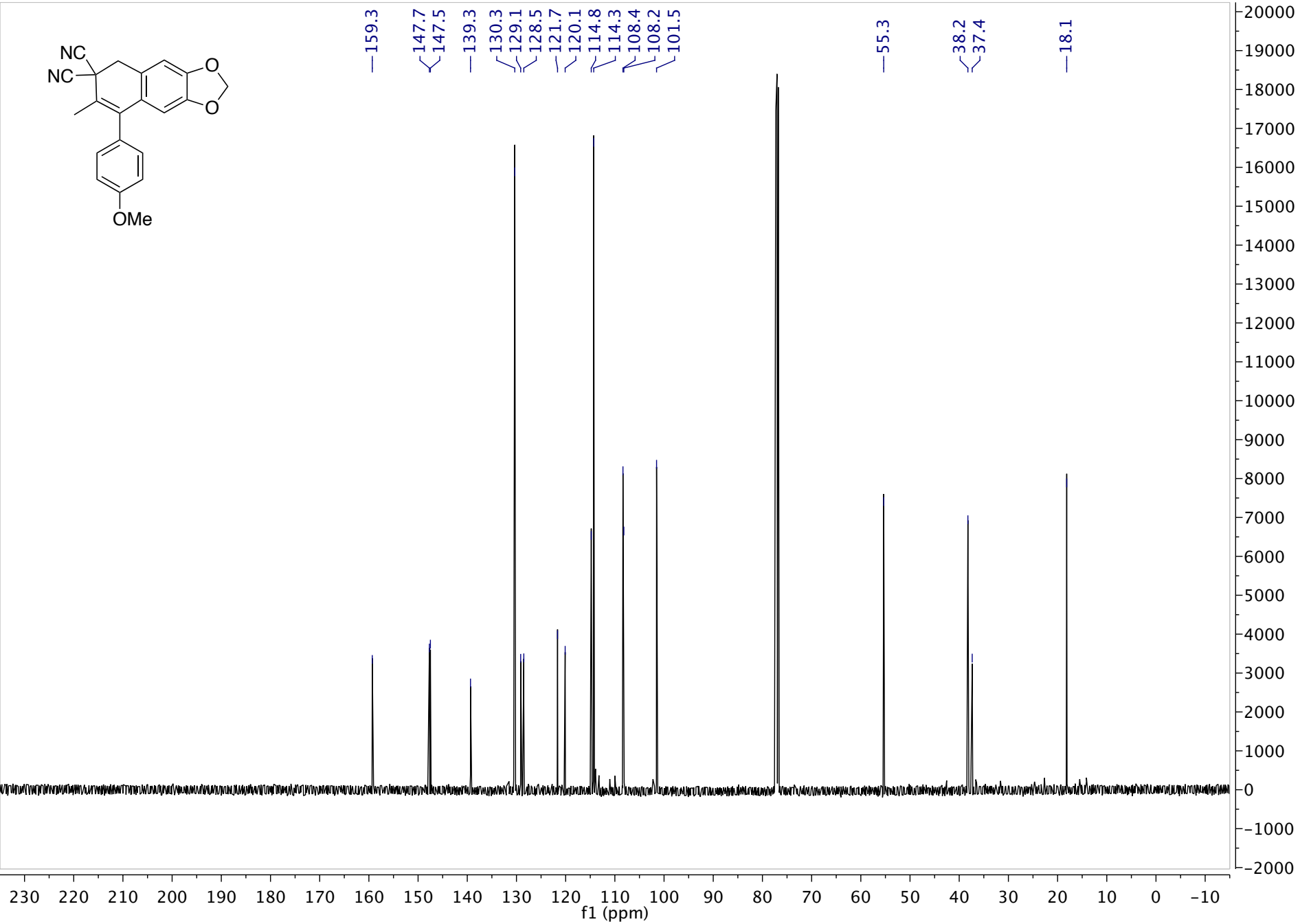
^{13}C spectrum of 6,7-dimethoxy-4-(4-methoxyphenyl)-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile 4a ($CDCl_3$)



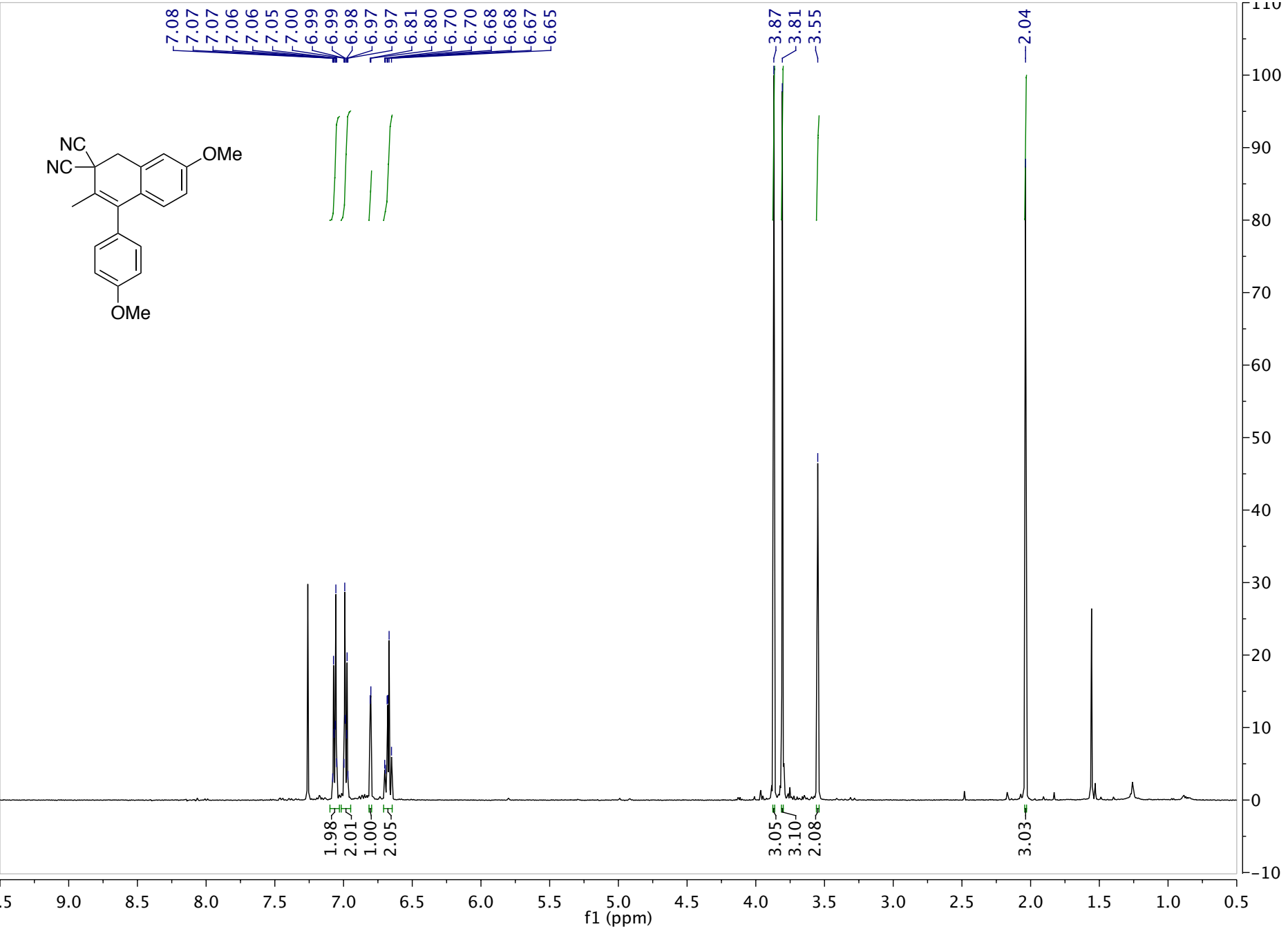
^{1}H spectrum of 8-(4-methoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4b ($CDCl_3$)



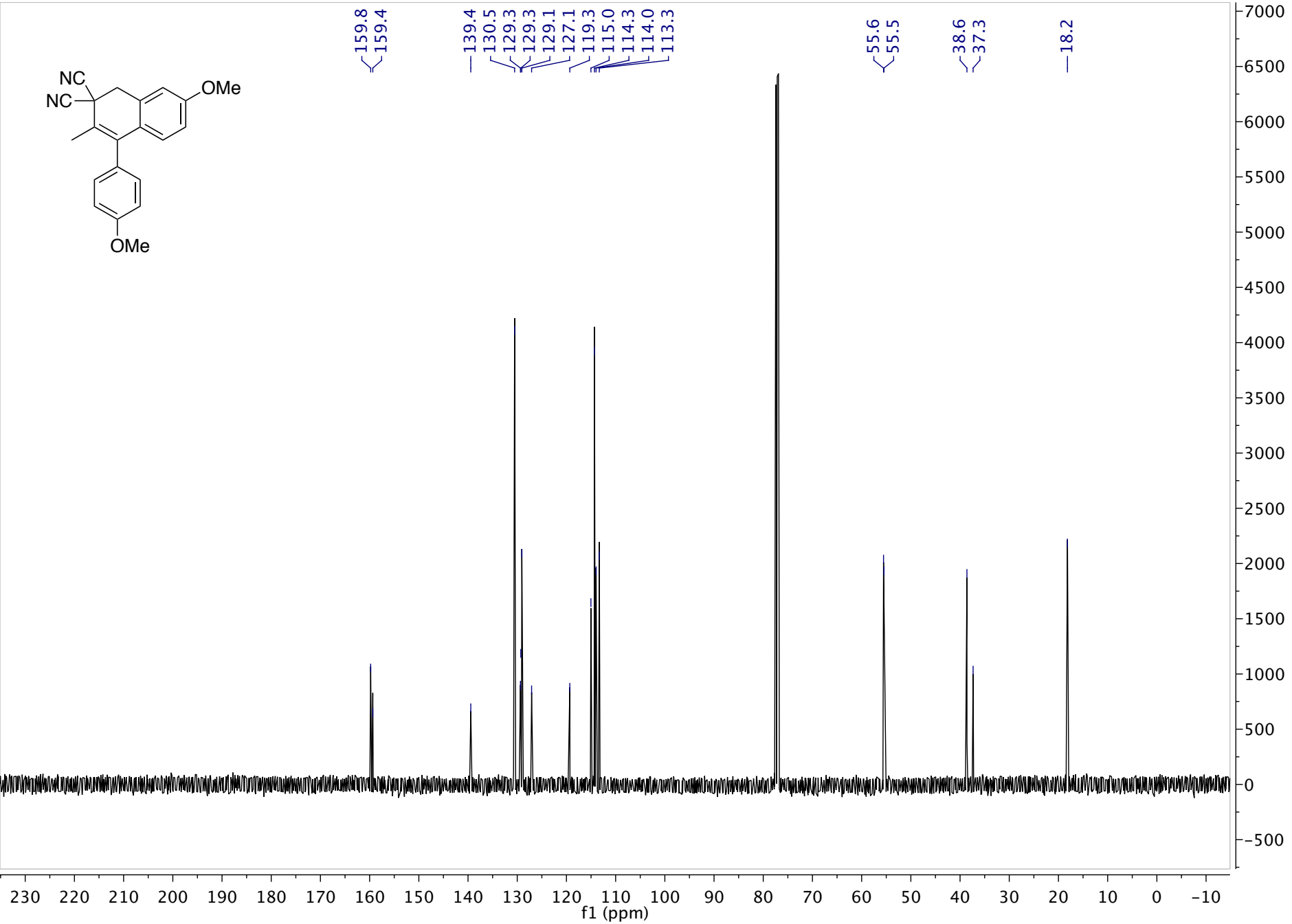
^{13}C spectrum of 8-(4-methoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4b ($CDCl_3$)



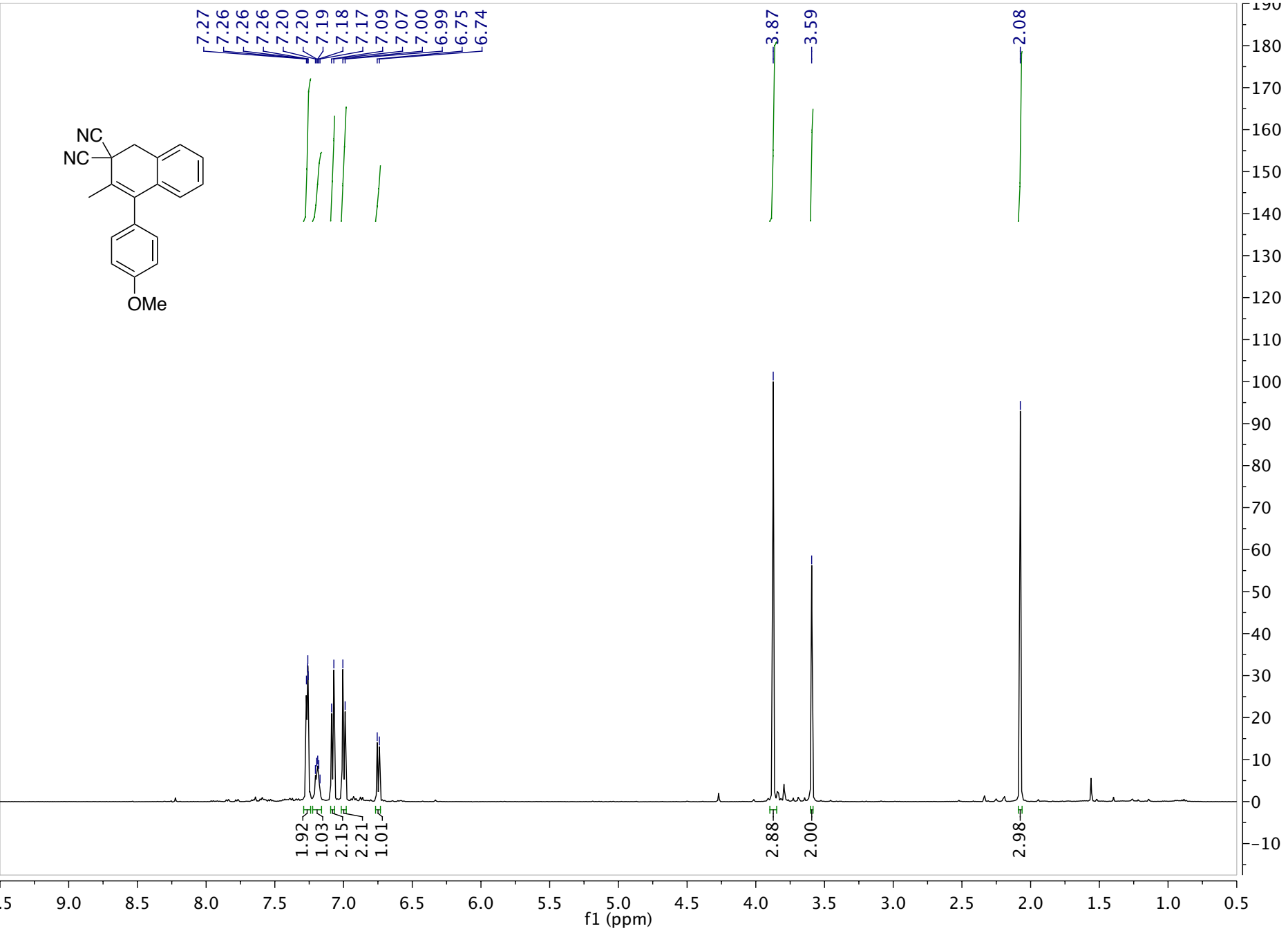
^{1}H spectrum of 7-methoxy-4-(4-methoxyphenyl)-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile 4c ($CDCl_3$)



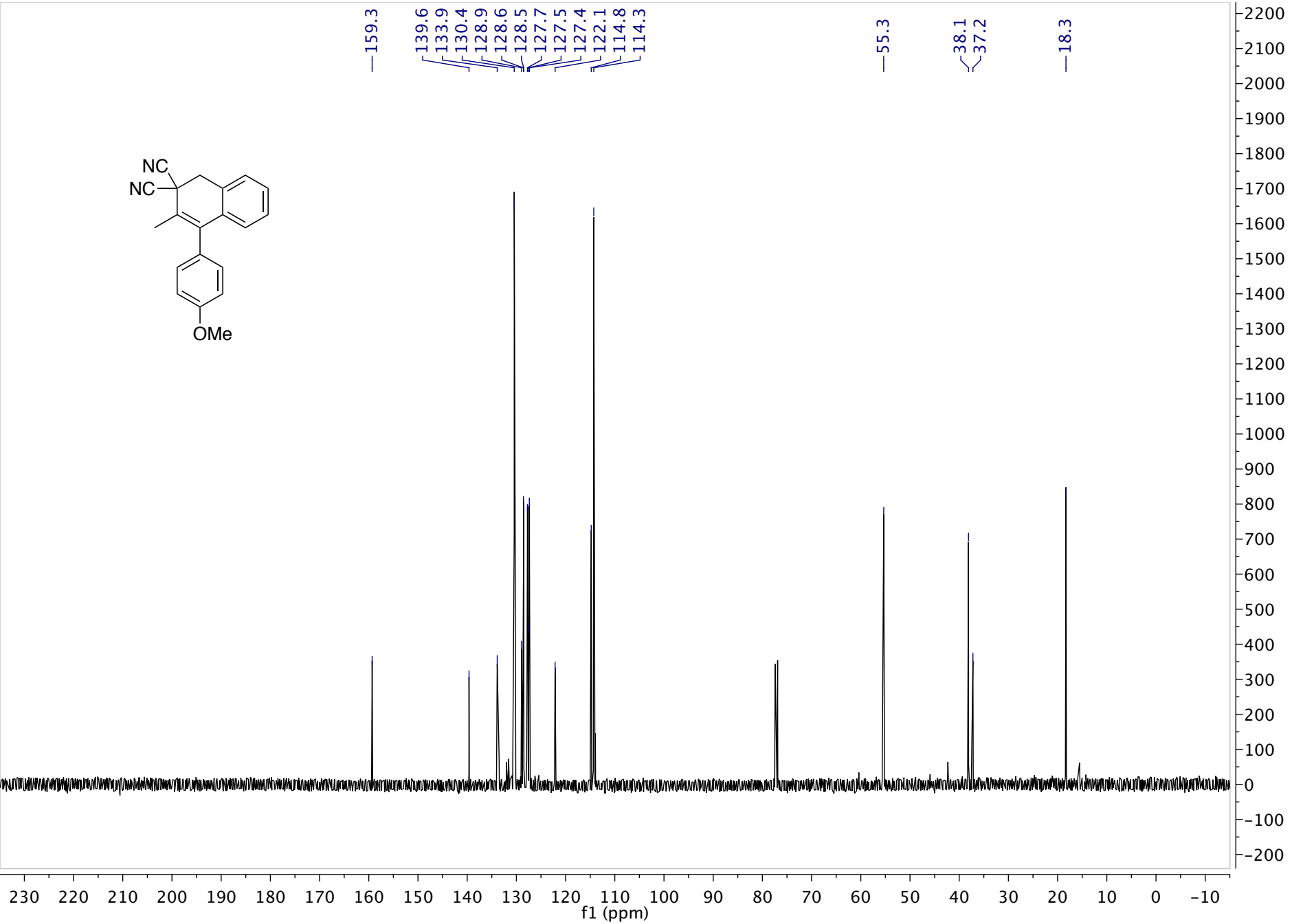
^{13}C spectrum of 7-methoxy-4-(4-methoxyphenyl)-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile 4c ($CDCl_3$)



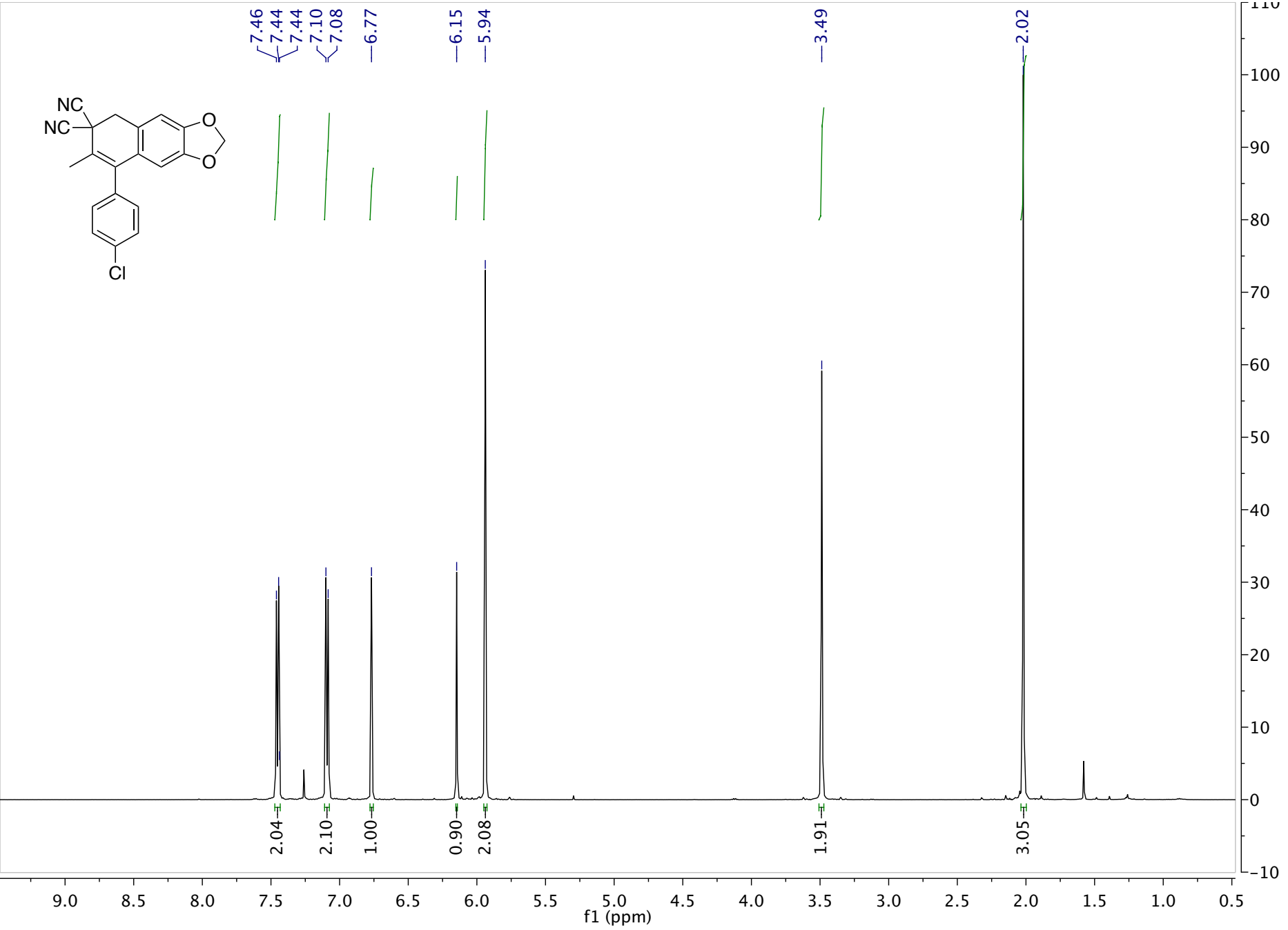
^{1}H spectrum of 4-(4-methoxyphenyl)-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile 4d ($CDCl_3$)



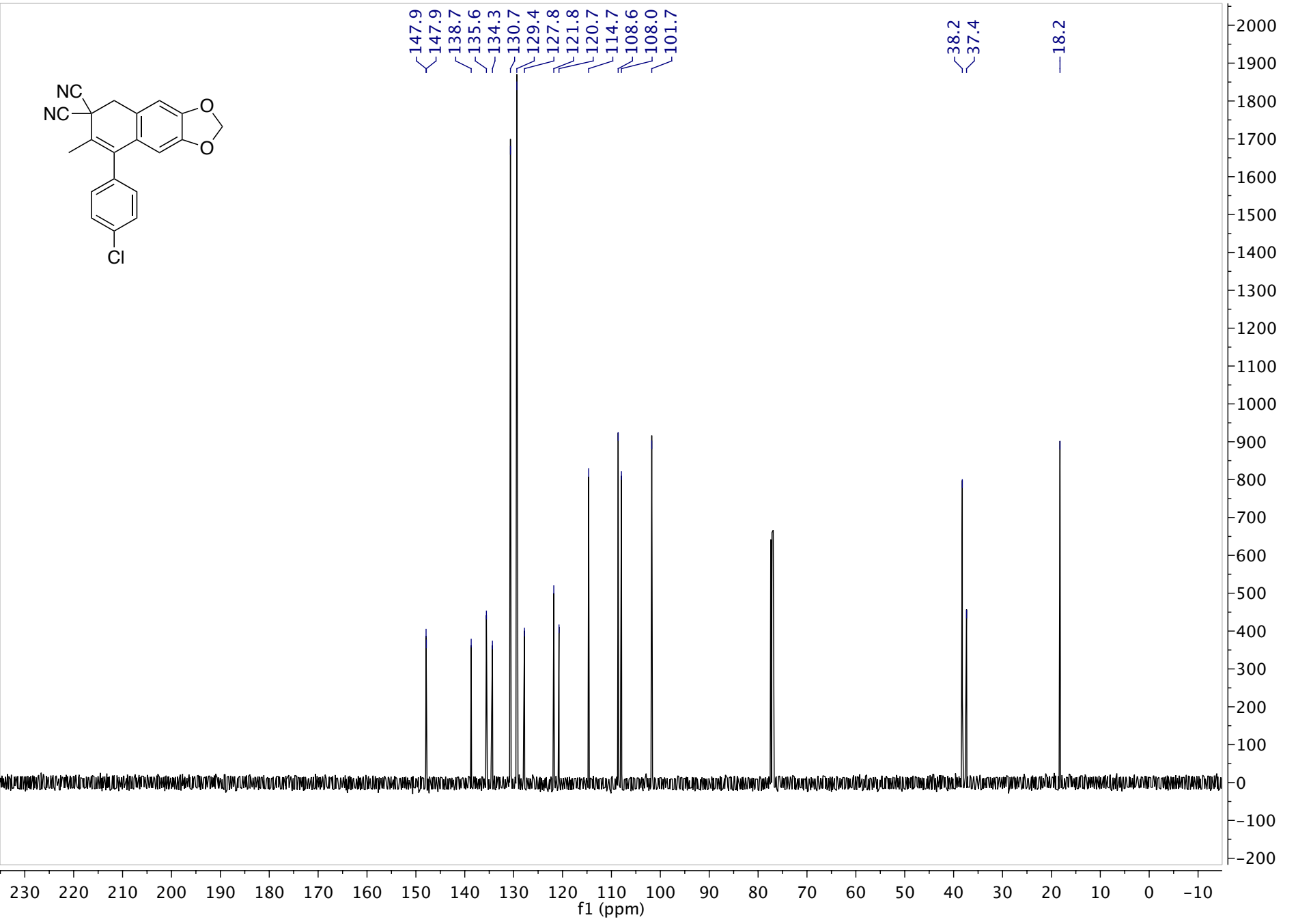
^{13}C spectrum of 4-(4-methoxyphenyl)-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile 4d ($CDCl_3$)



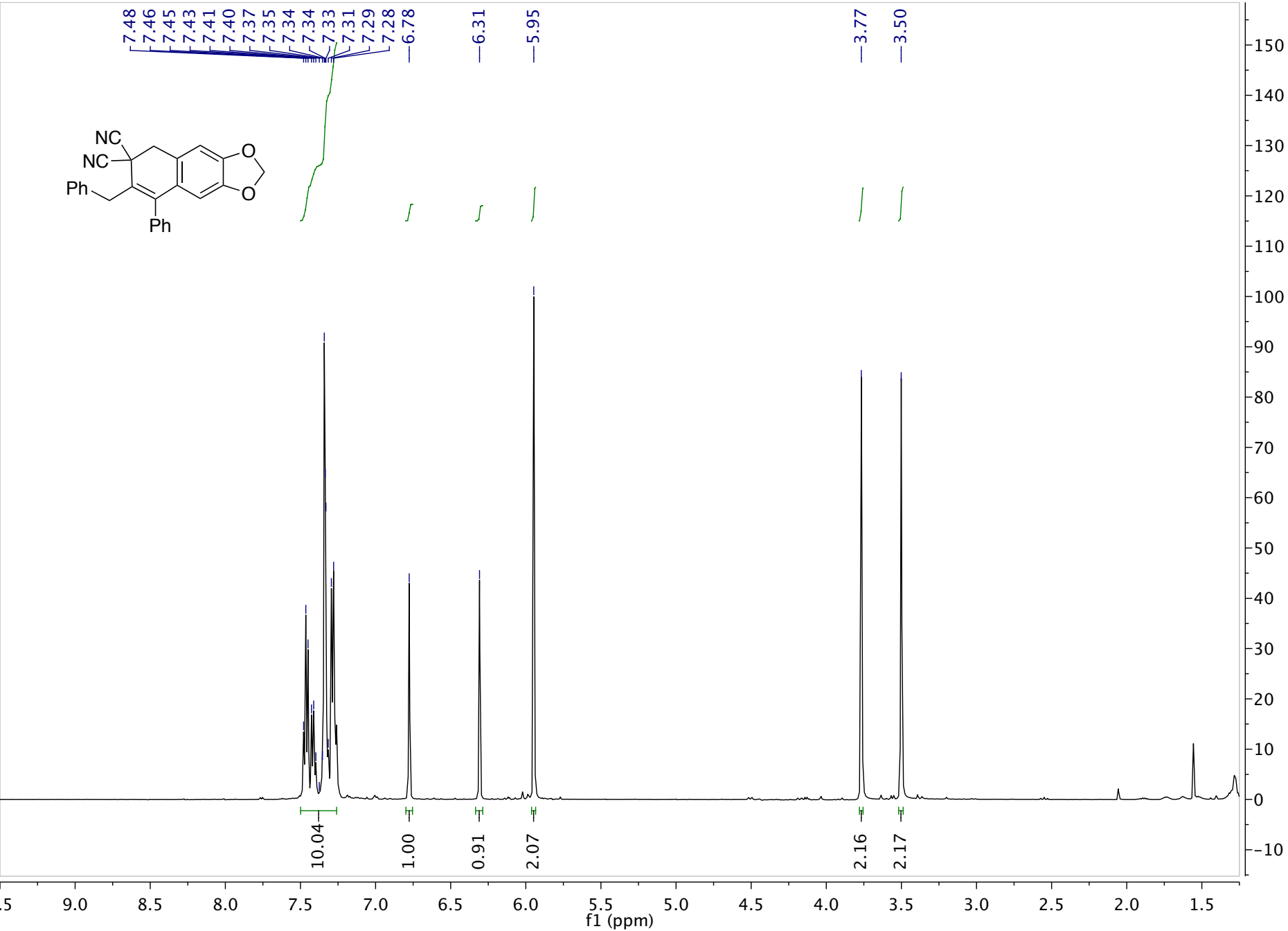
^{1}H spectrum of 8-(4-chlorophenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4e ($CDCl_3$)



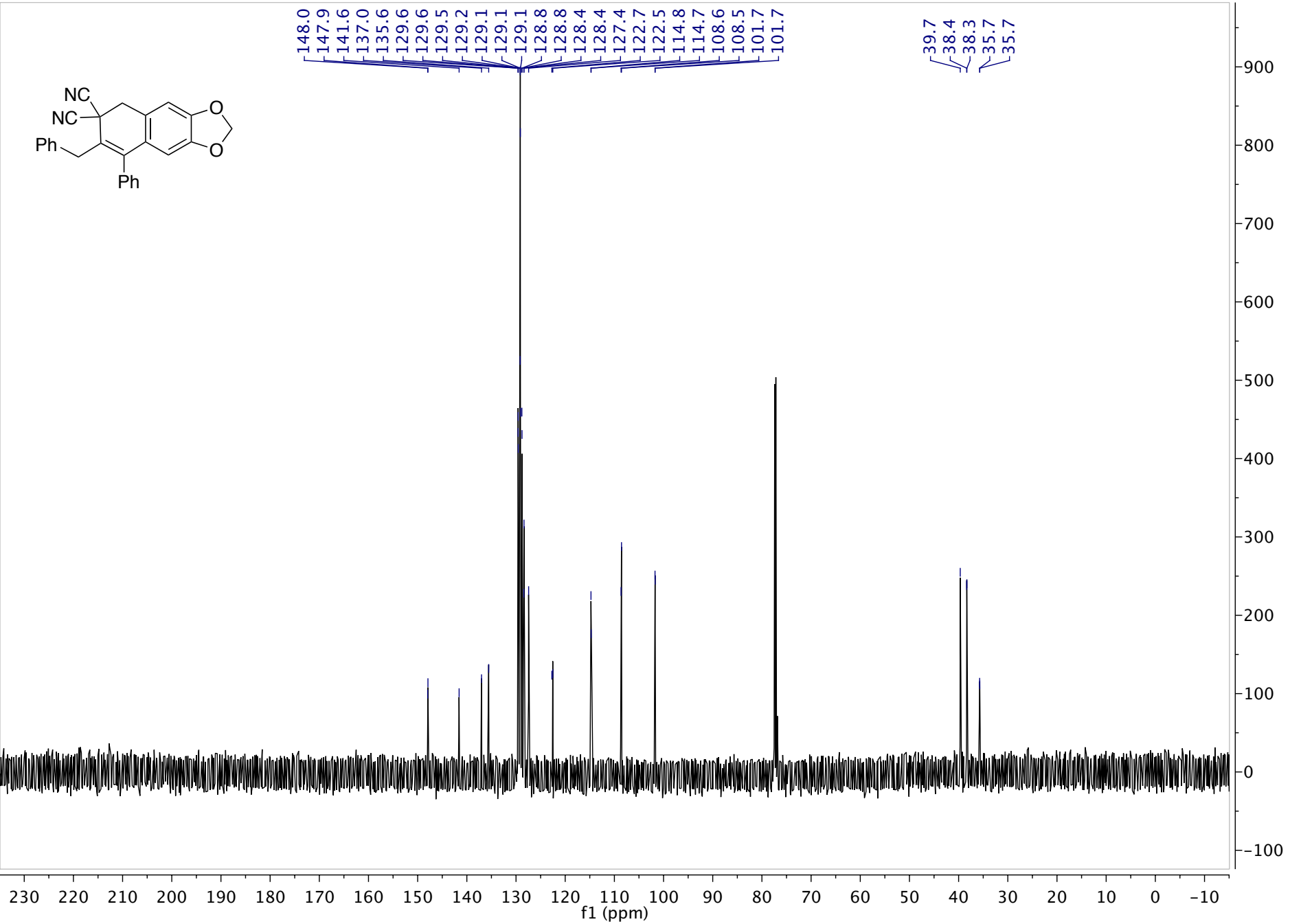
^{13}C spectrum of 8-(4-chlorophenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4e ($CDCl_3$)



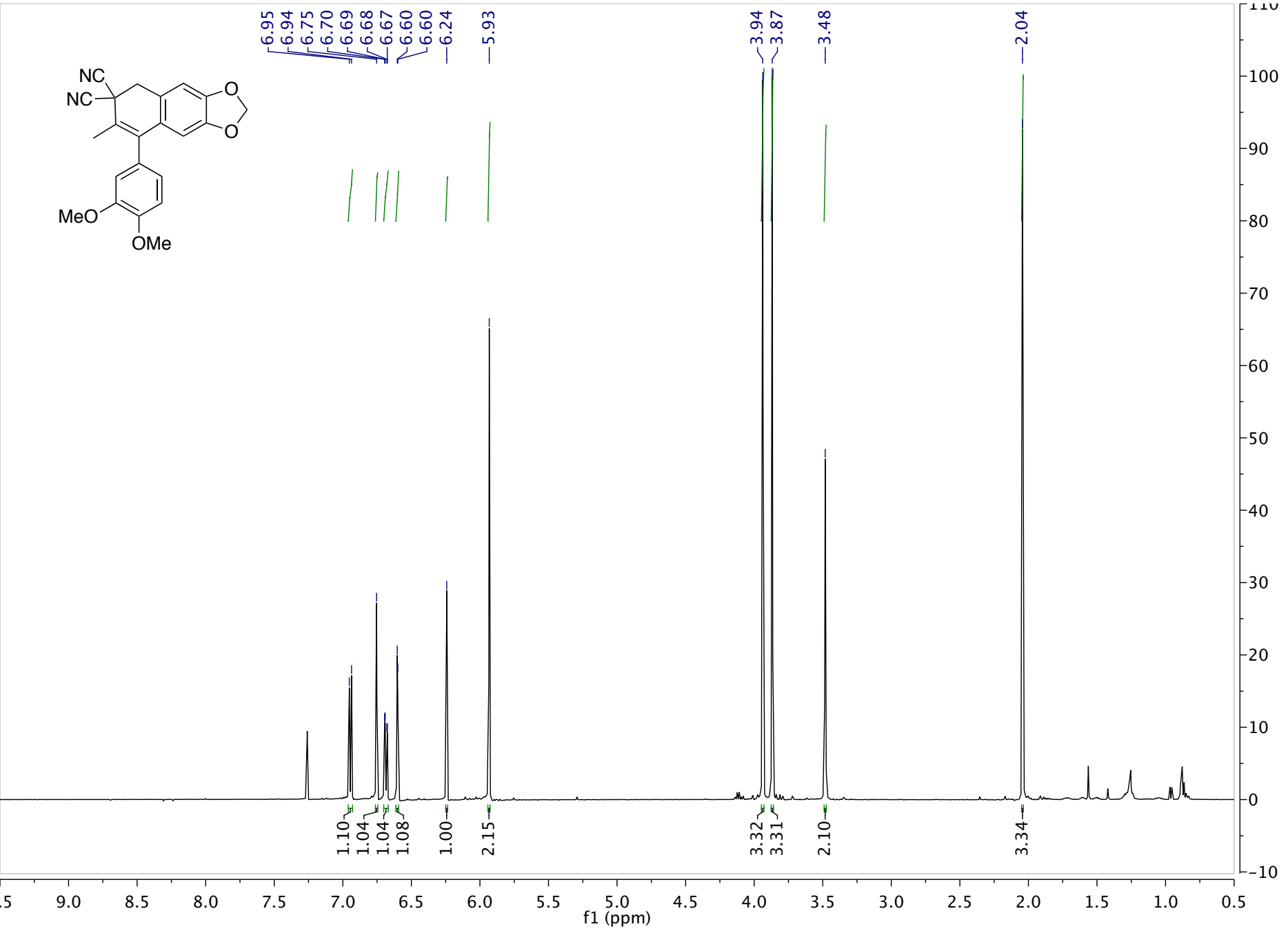
^{1}H spectrum of 7-benzyl-8-phenylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4f ($CDCl_3$)



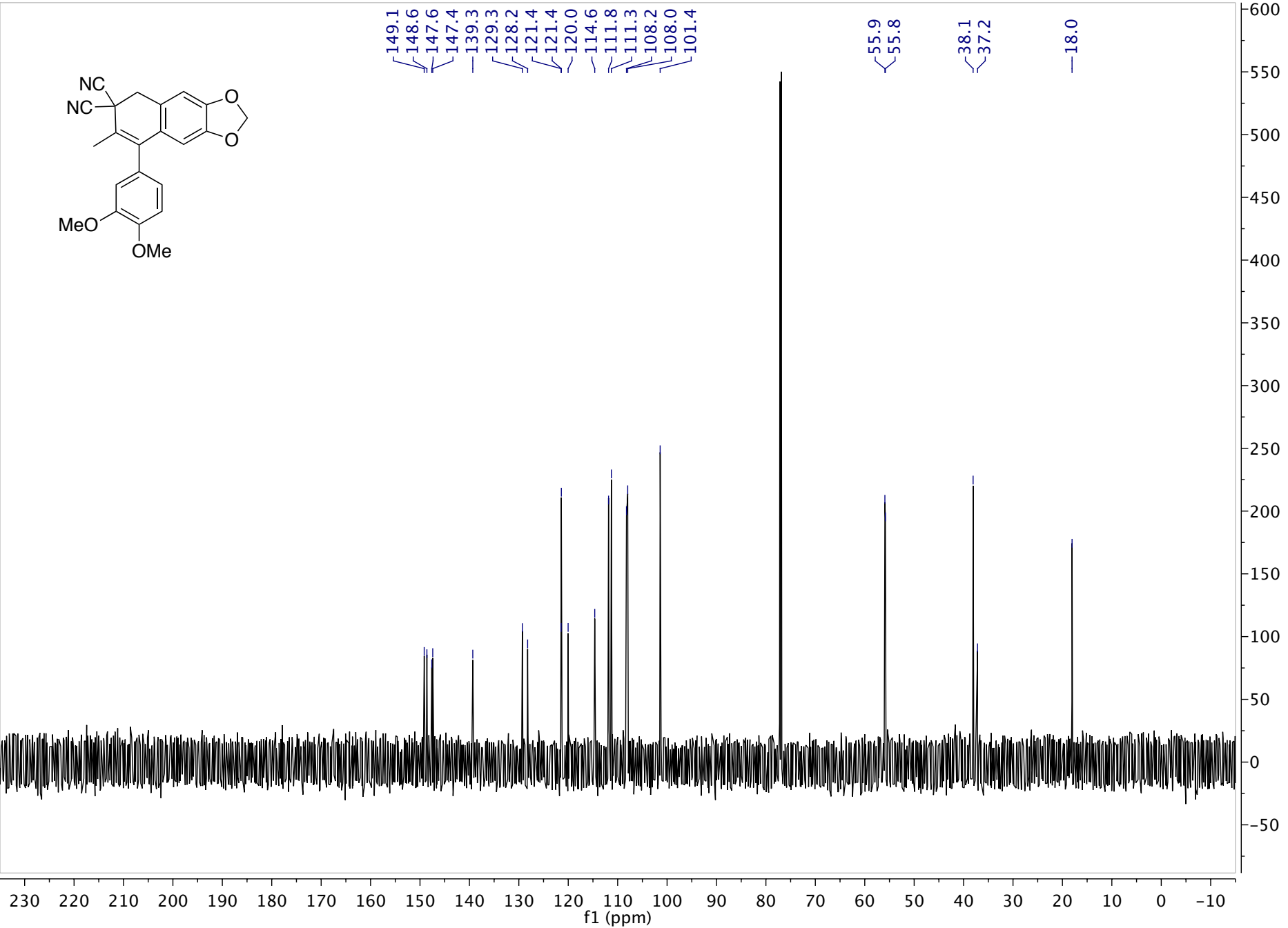
^{13}C spectrum of 7-benzyl-8-phenylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4f ($CDCl_3$)



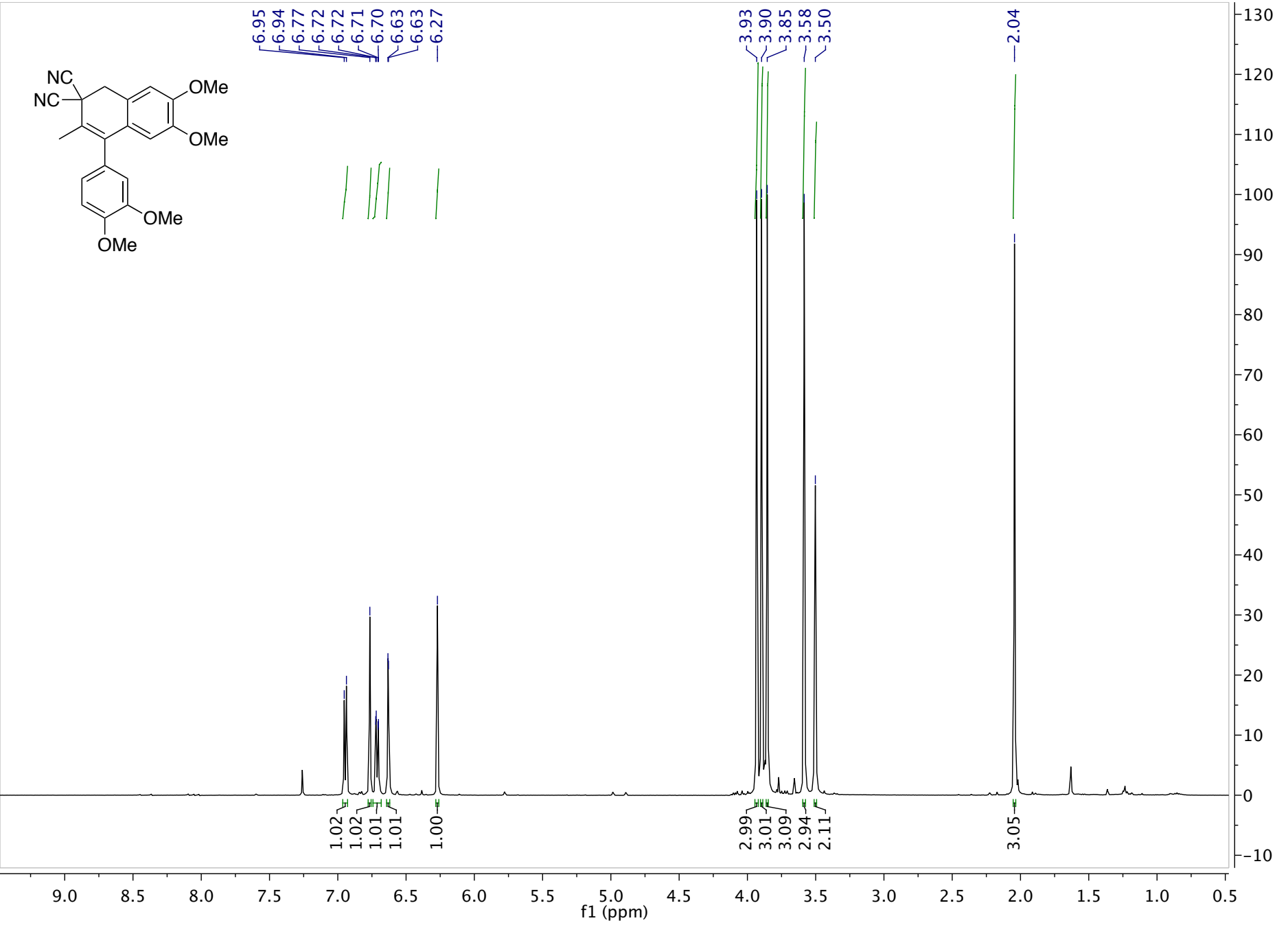
^{1}H spectrum of 8-(3,4-dimethoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4g ($CDCl_3$)



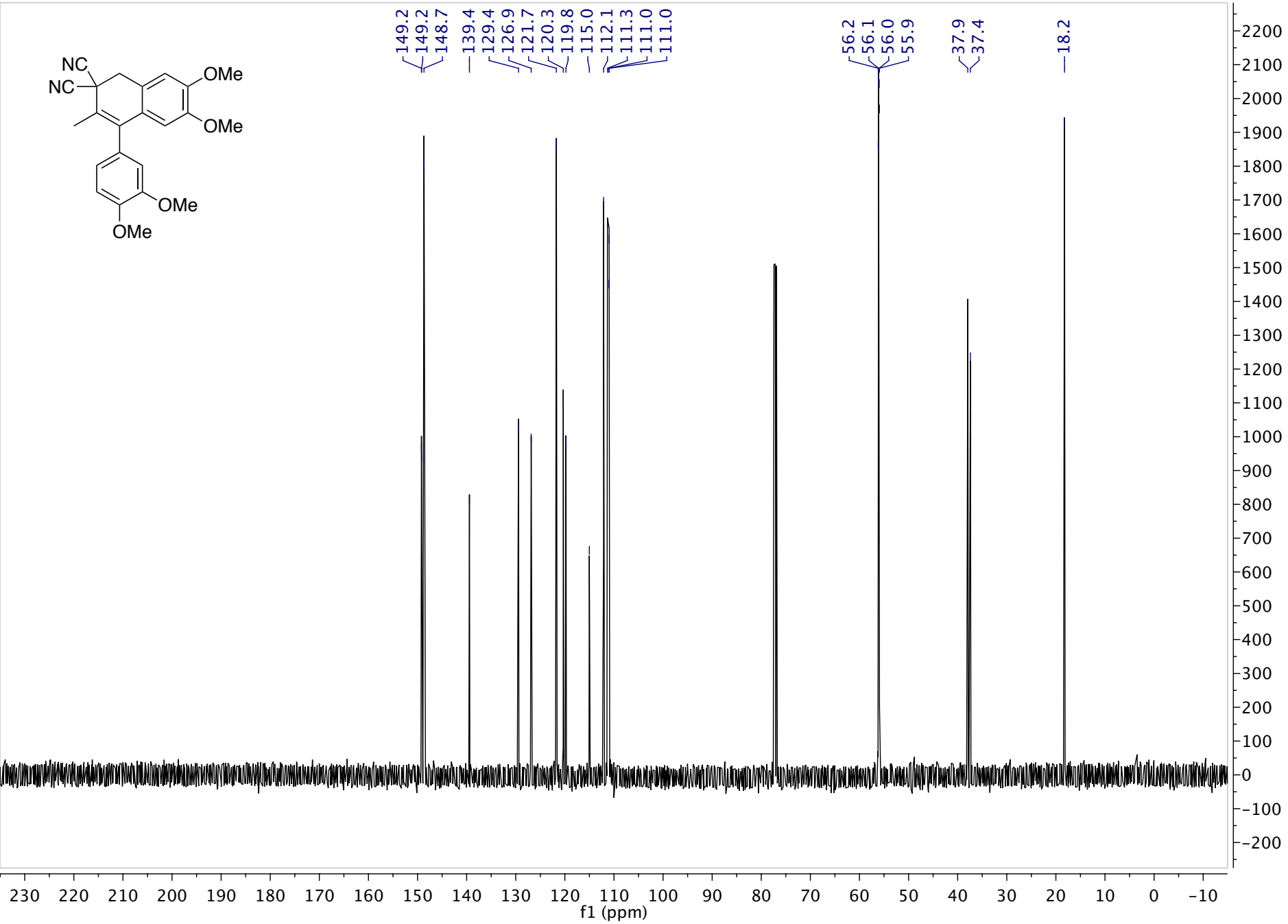
^{13}C spectrum of 8-(3,4-dimethoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4g ($CDCl_3$)



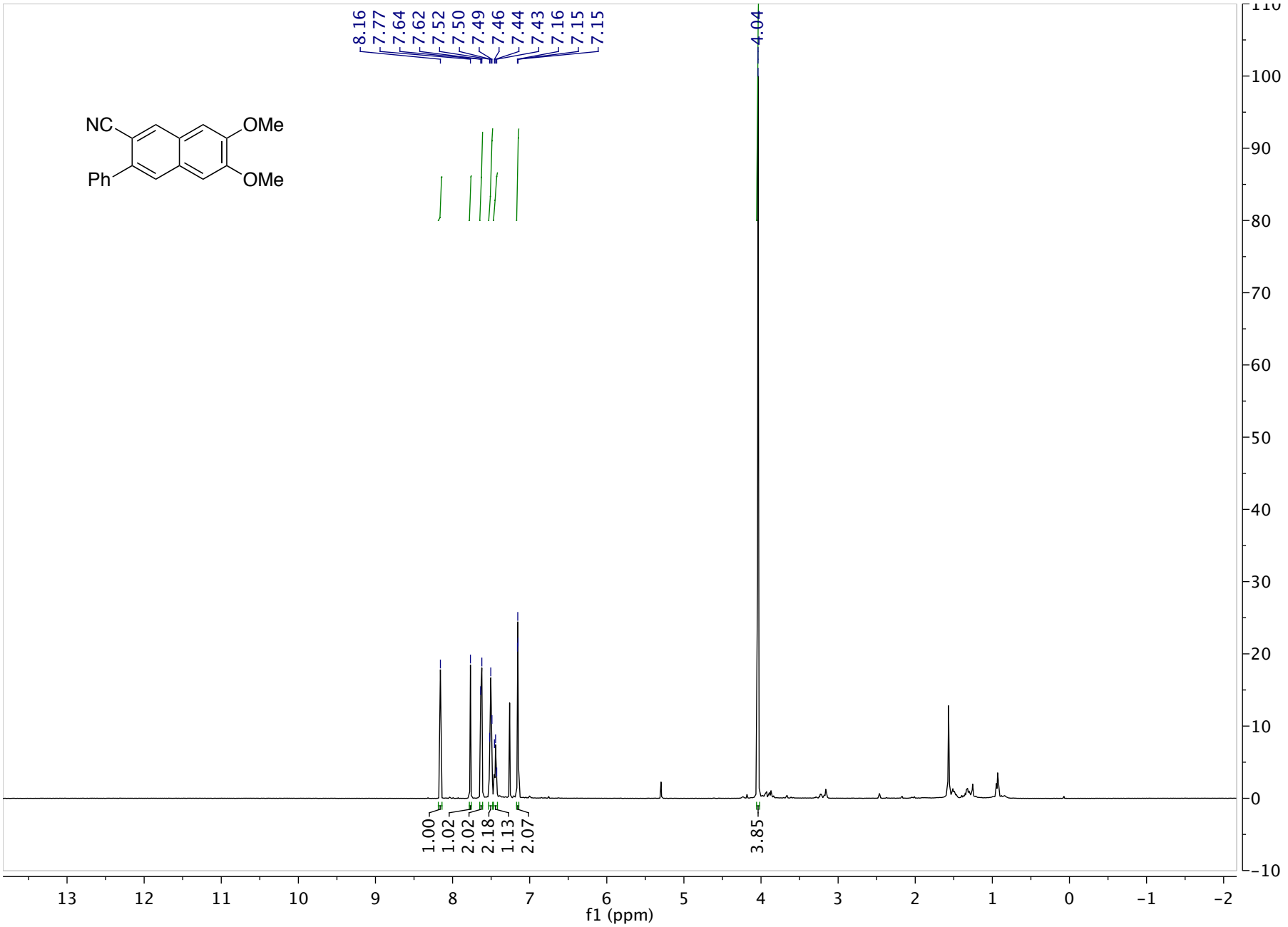
^{1}H spectrum of 4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile 4h ($CDCl_3$)



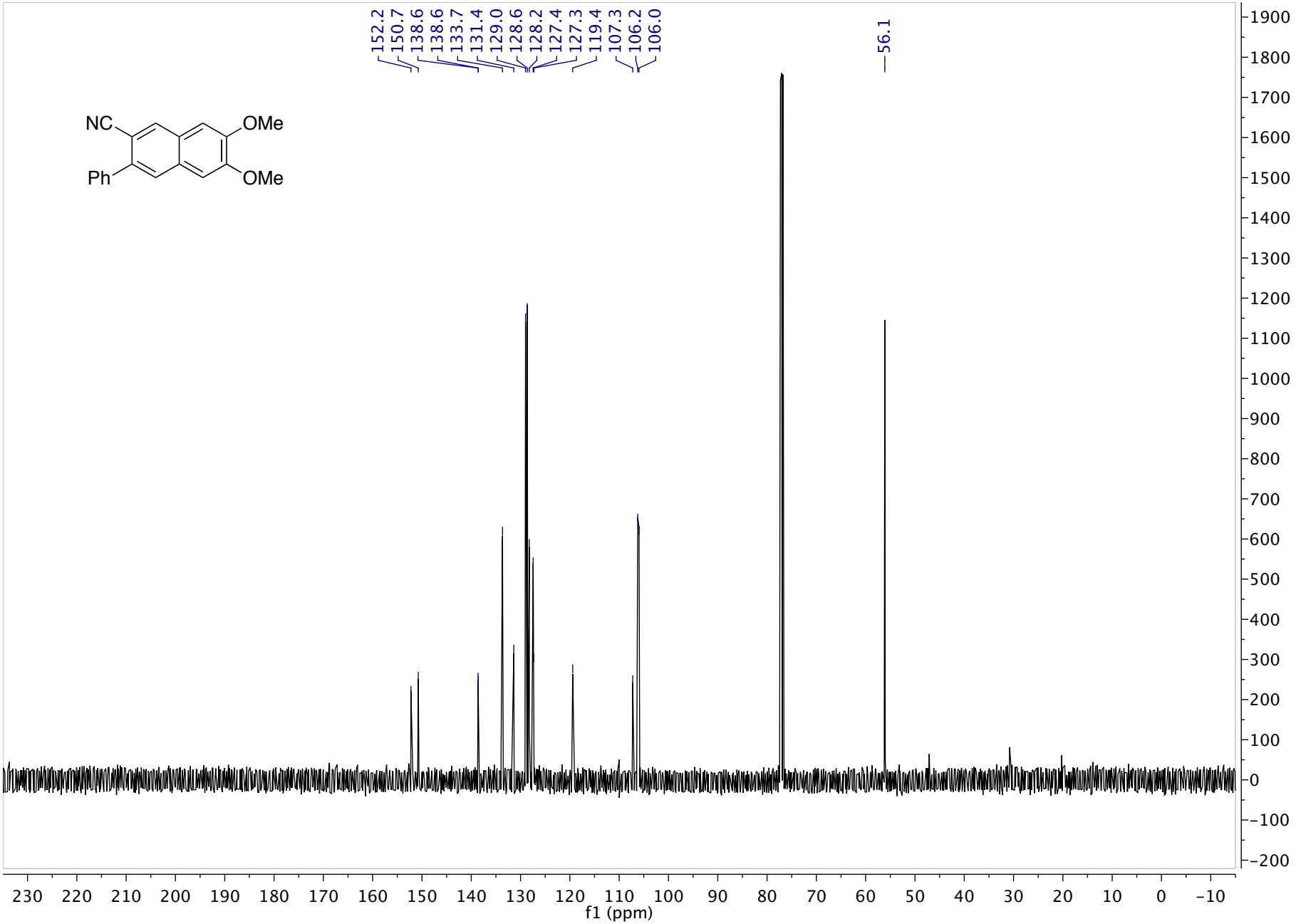
^{13}C spectrum of 4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methylnaphthalene-2,2(1*H*)-dicarbonitrile 4h ($CDCl_3$)



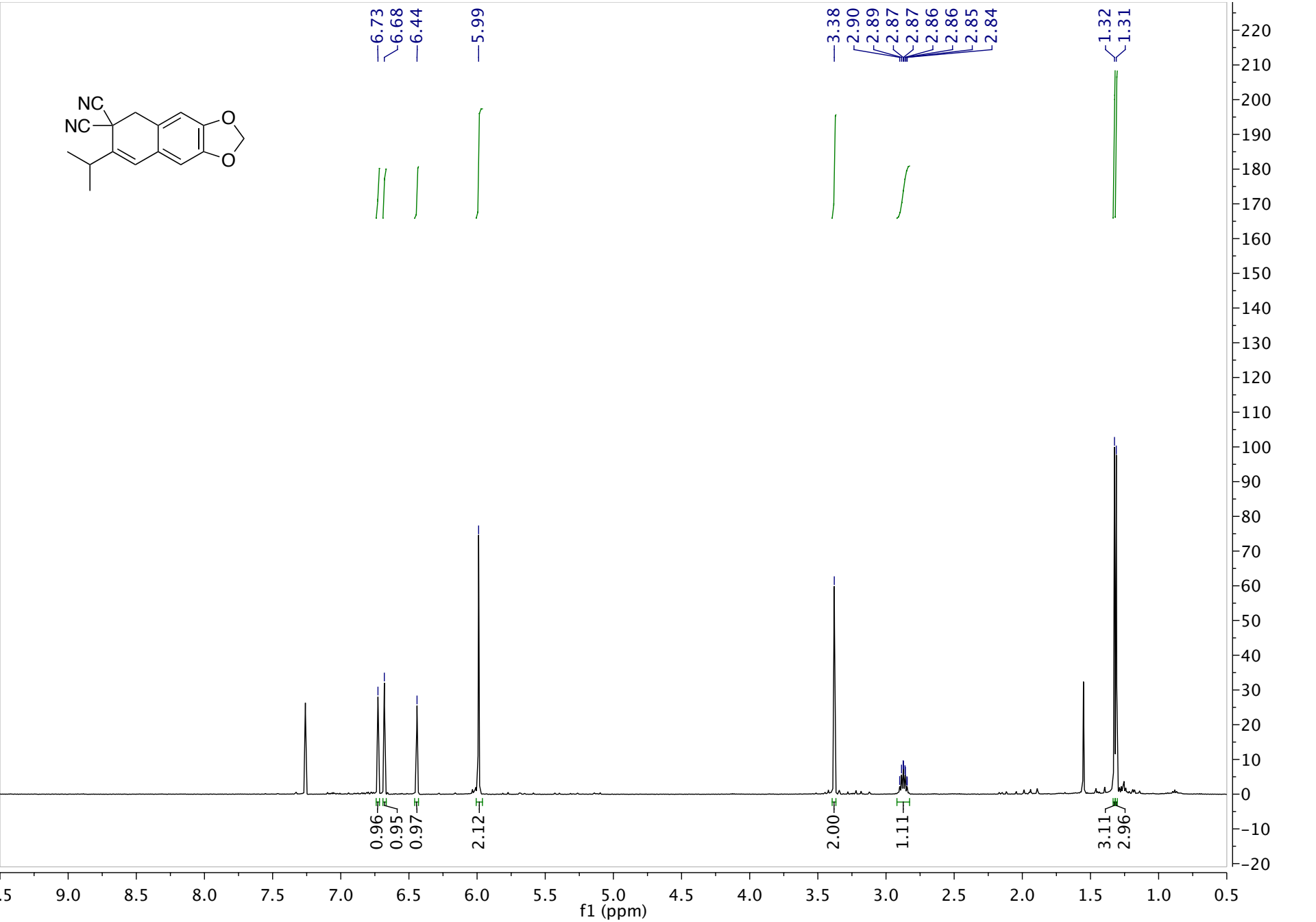
^{1}H spectrum of 6,7-dimethoxy-3-phenyl-2-naphthonitrile 4j ($CDCl_3$)



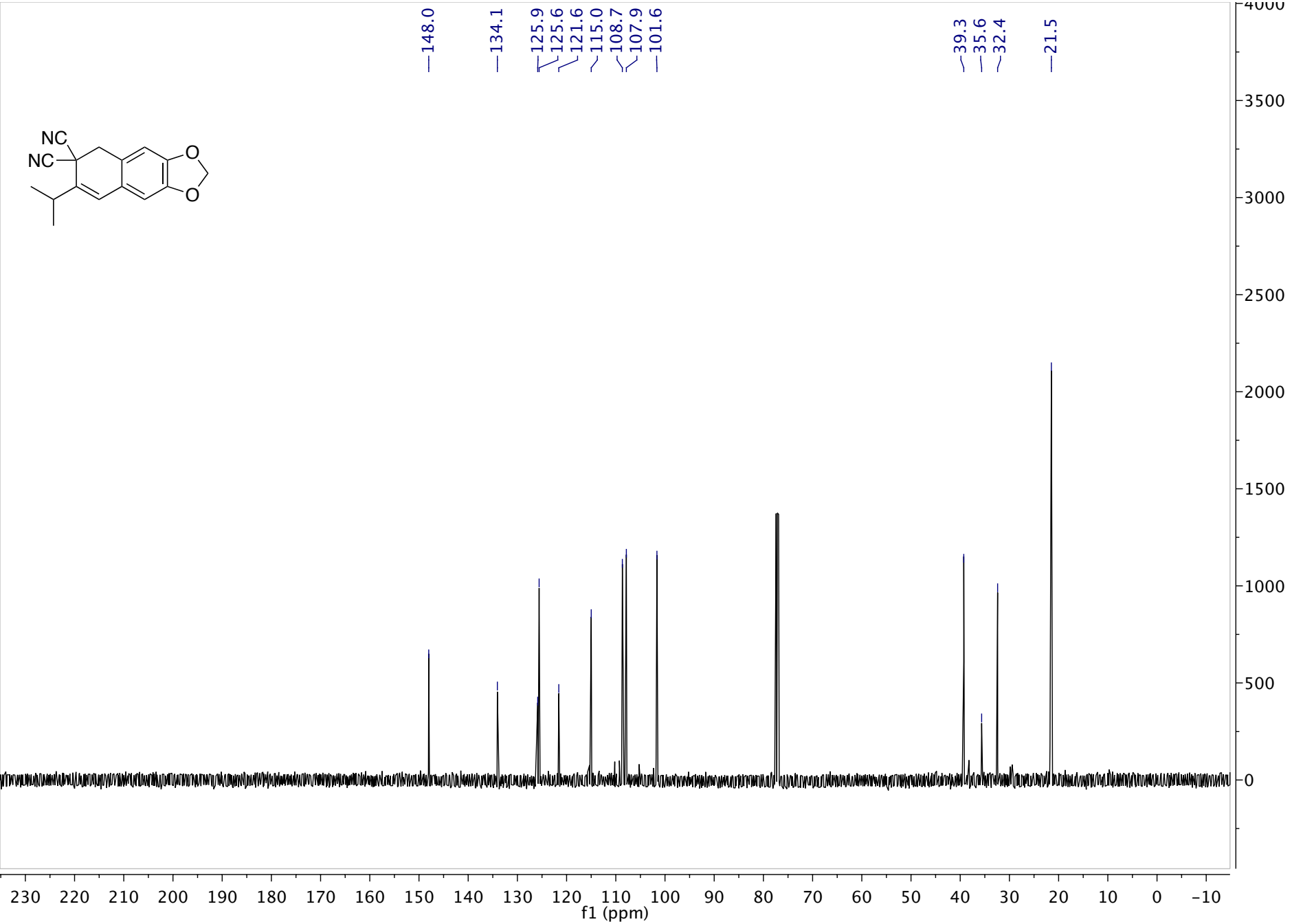
^{13}C spectrum of 6,7-dimethoxy-3-phenyl-2-naphthonitrile 4j ($CDCl_3$)



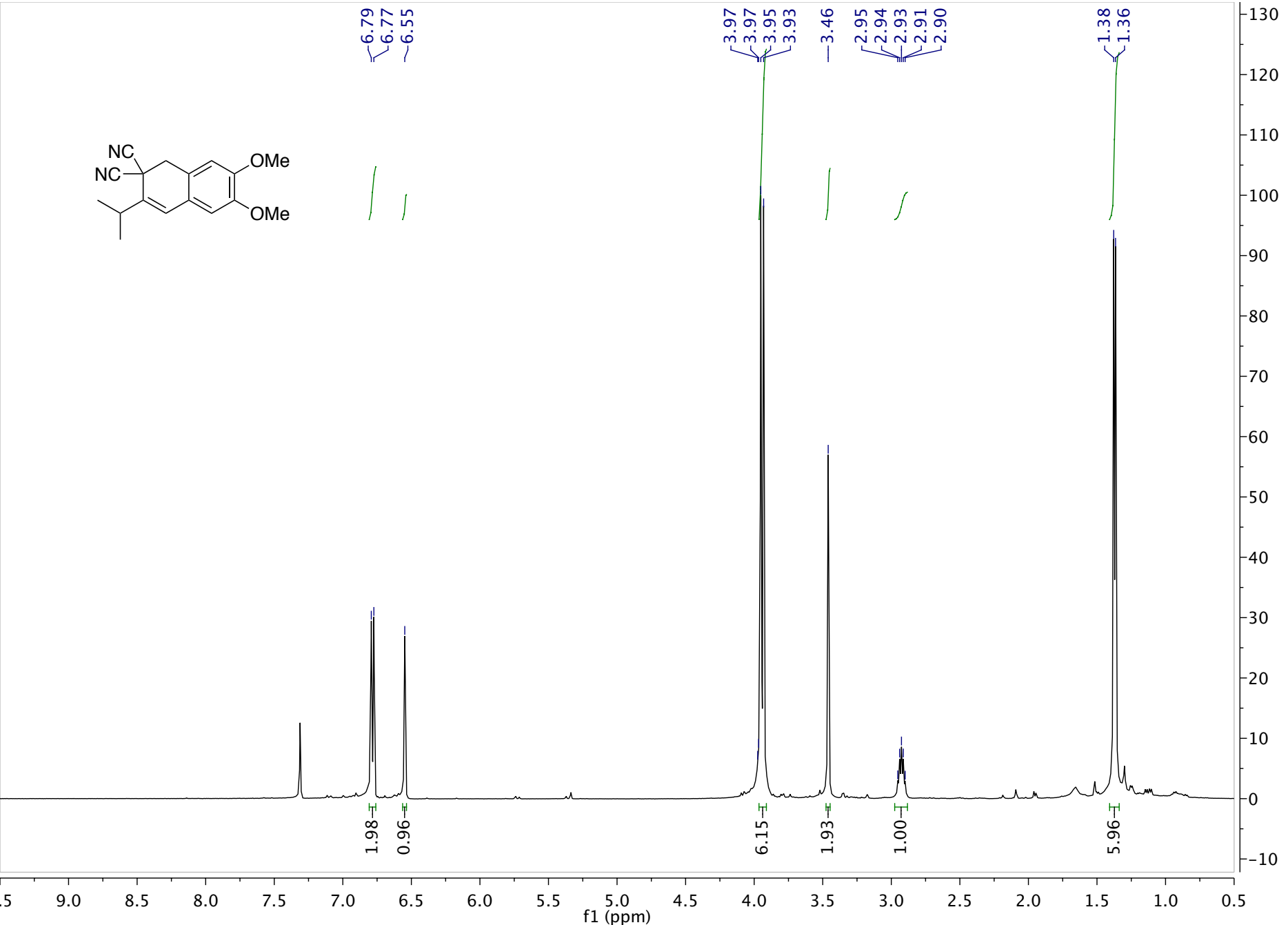
^{1}H spectrum of 7-isopropylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4k ($CDCl_3$)



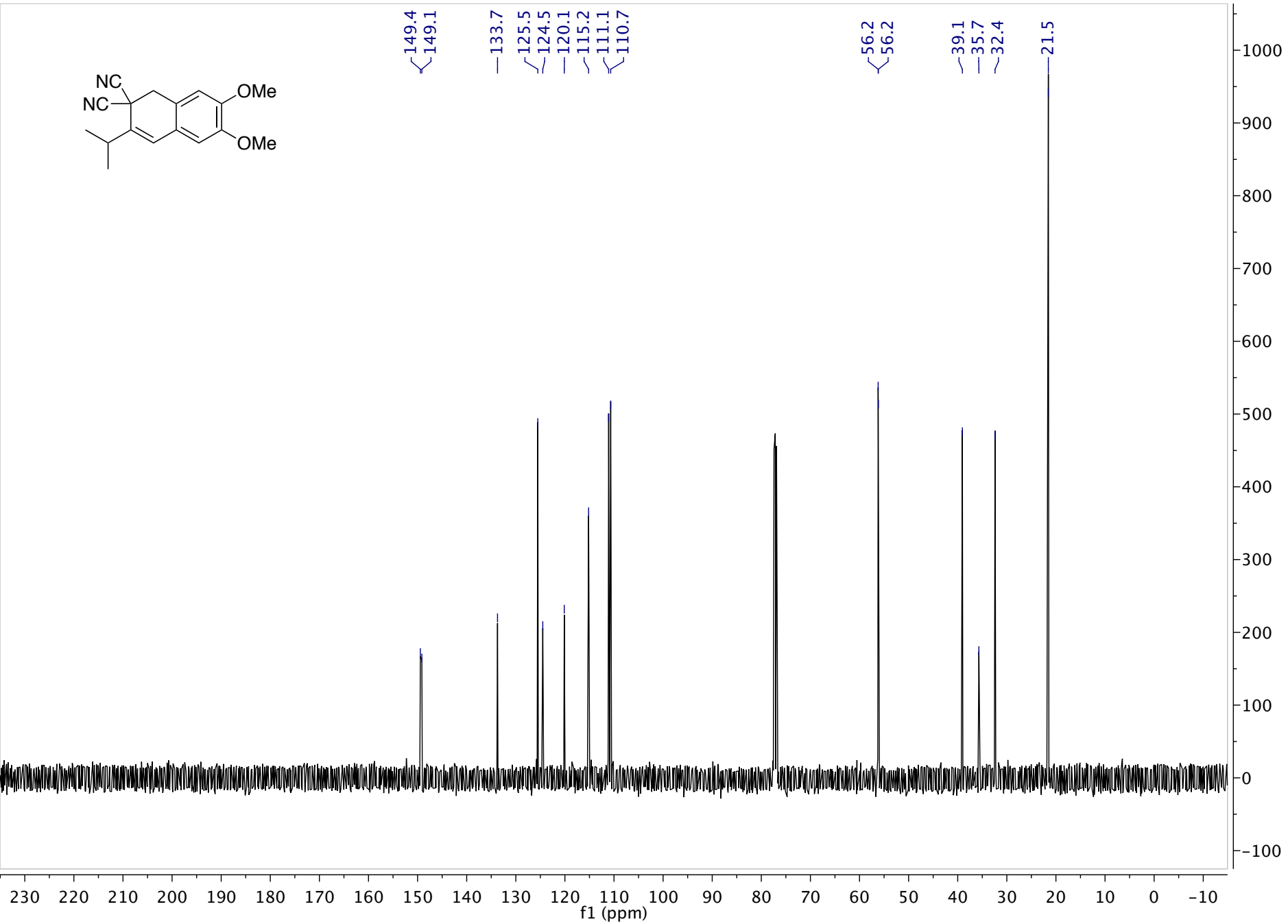
^{13}C spectrum of 7-isopropylnaphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4k ($CDCl_3$)



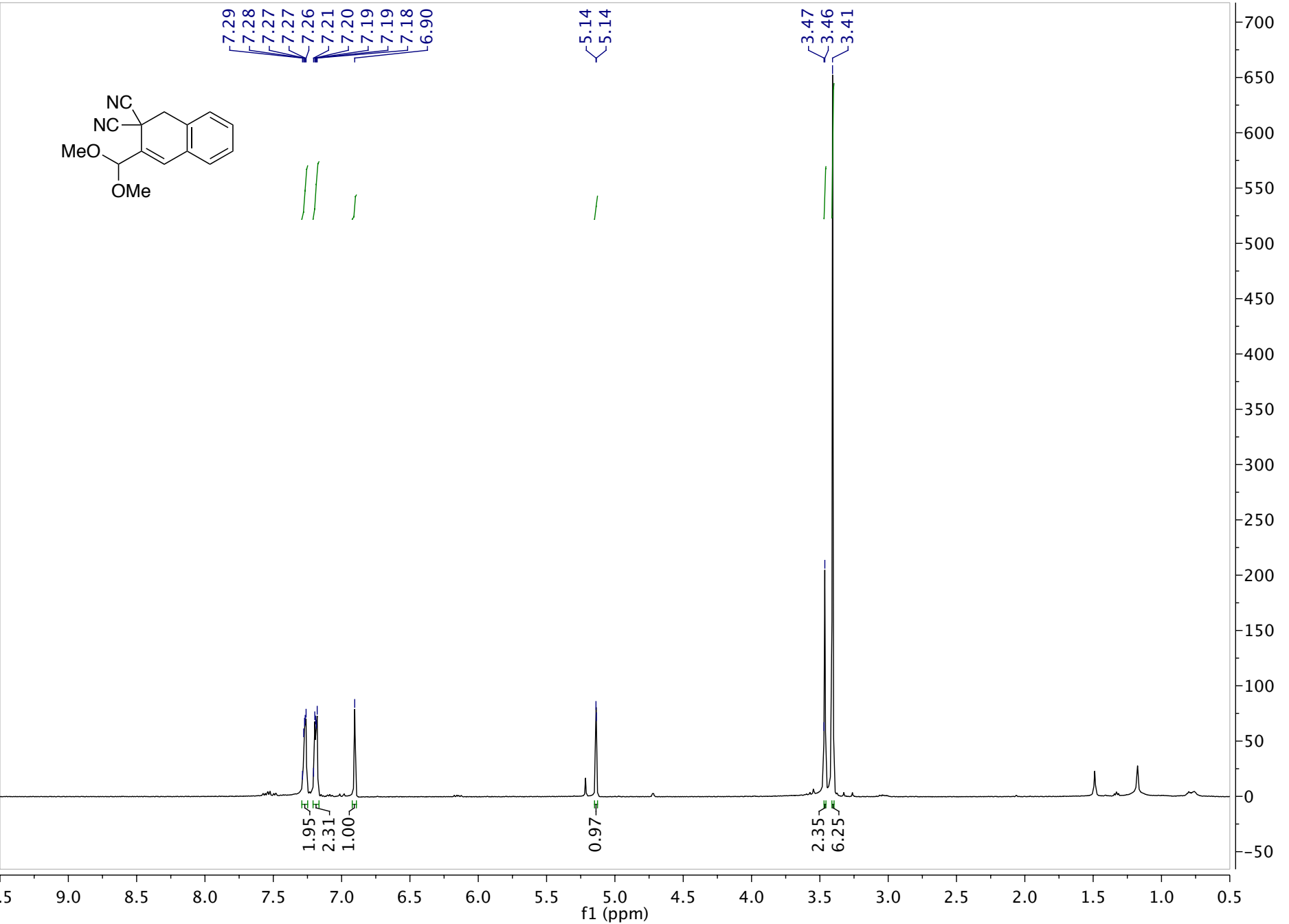
^{1}H spectrum of 3-isopropyl-6,7-dimethoxynaphthalene-2,2(1*H*)-dicarbonitrile 4l ($CDCl_3$)



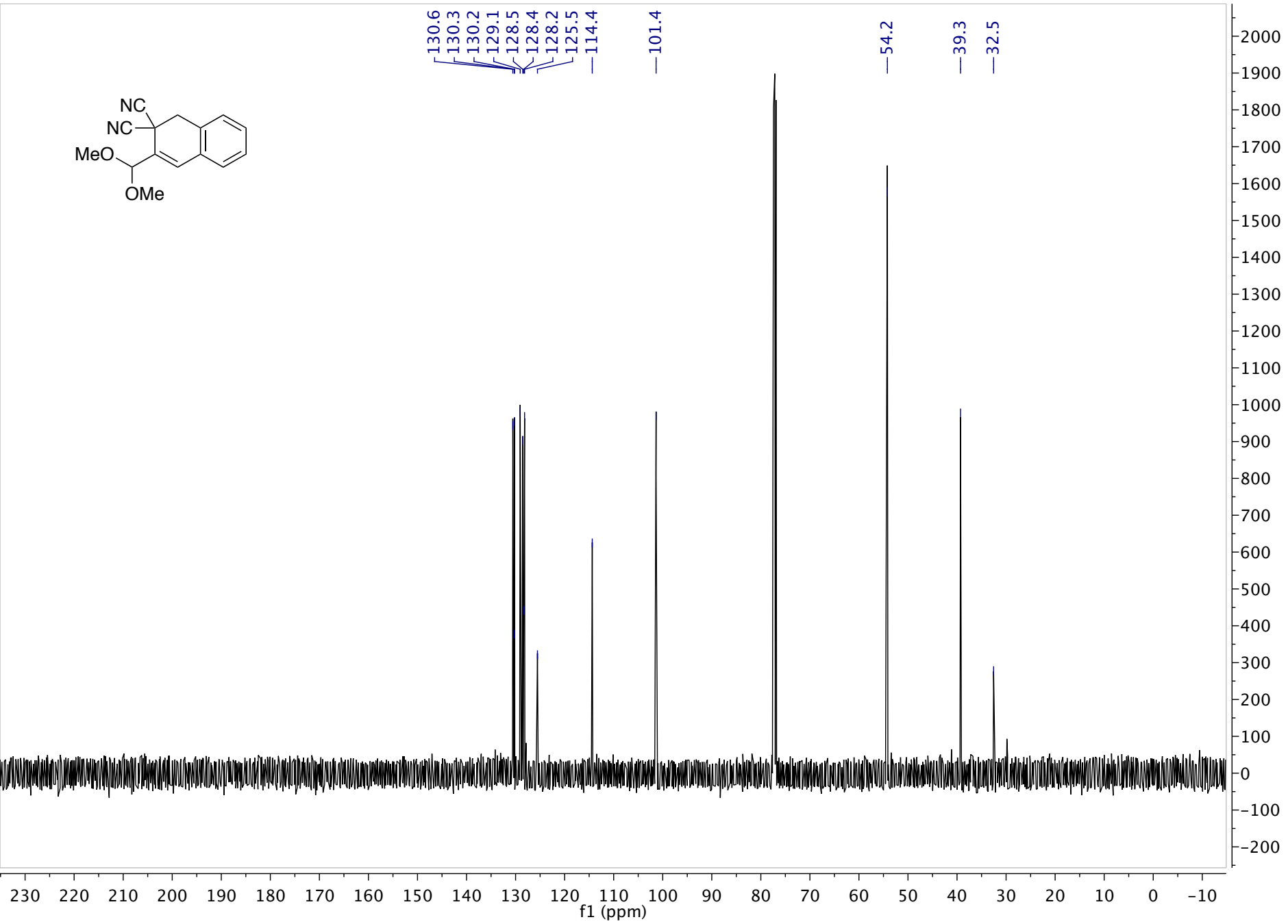
^{13}C spectrum of 3-isopropyl-6,7-dimethoxynaphthalene-2,2(1*H*)-dicarbonitrile 4l ($CDCl_3$)



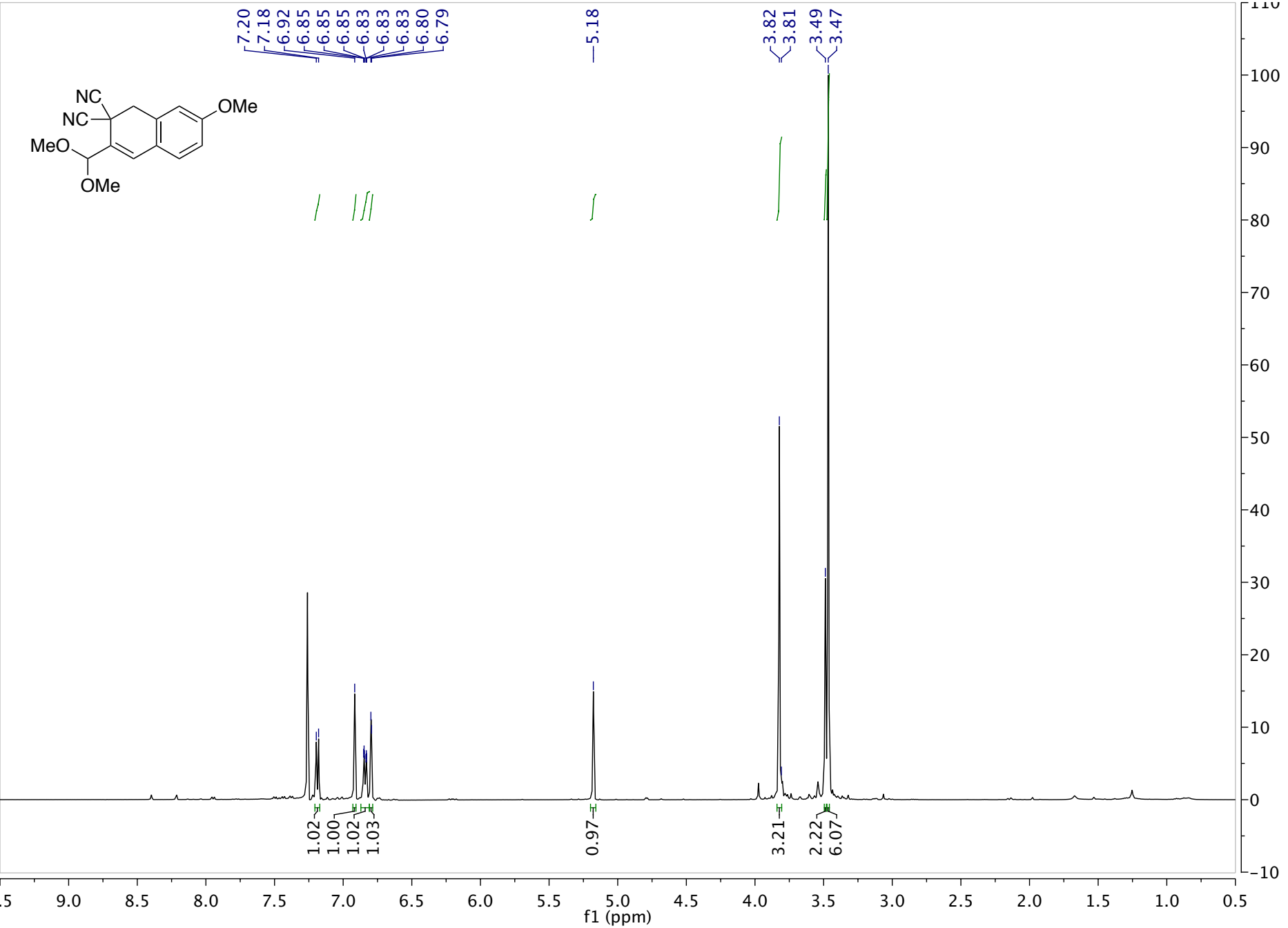
^{1}H spectrum of 3-(dimethoxymethyl)naphthalene-2,2(1*H*)-dicarbonitrile 4m ($CDCl_3$)



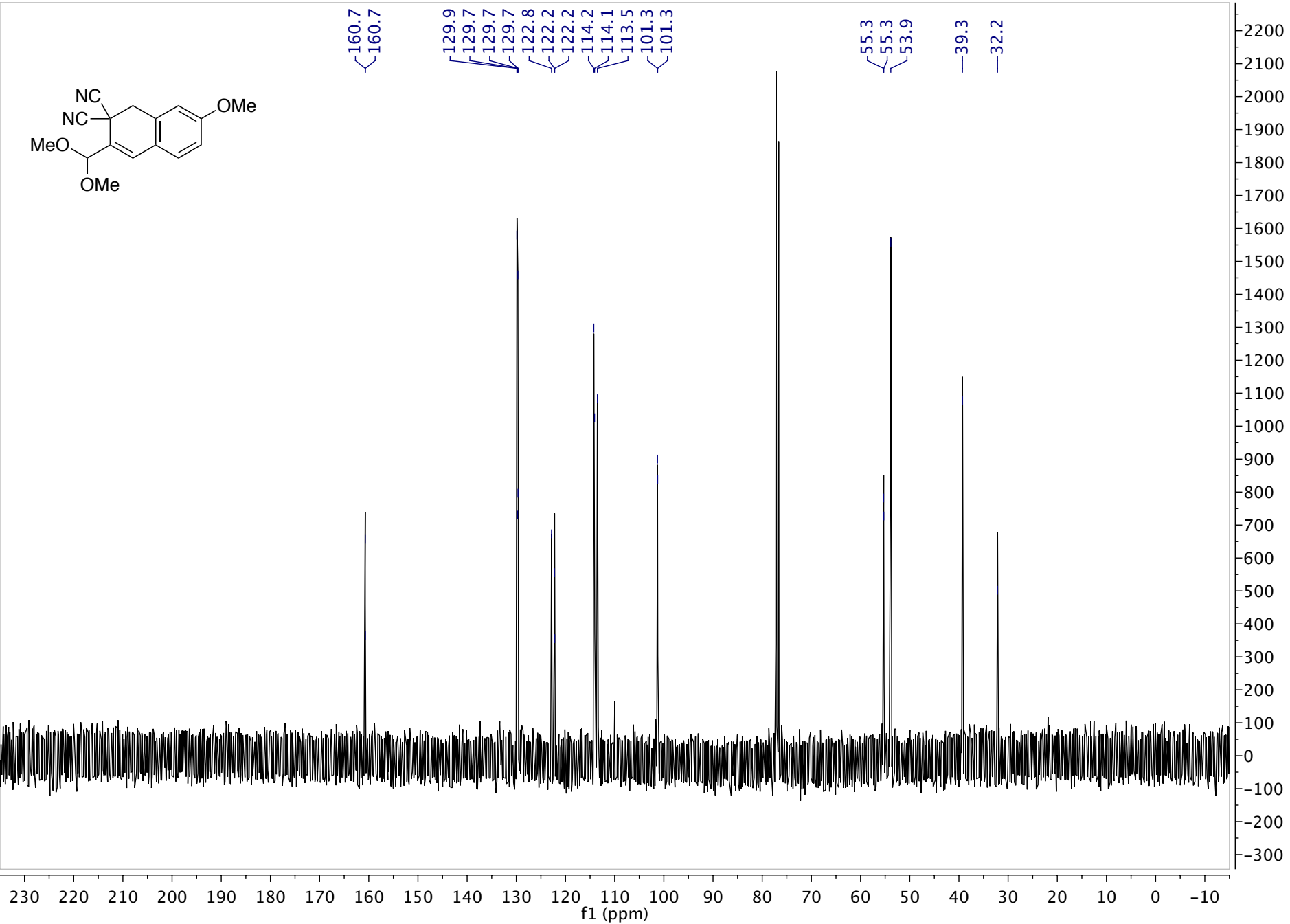
^{13}C spectrum of 3-(dimethoxymethyl)naphthalene-2,2(1*H*)-dicarbonitrile 4m ($CDCl_3$)



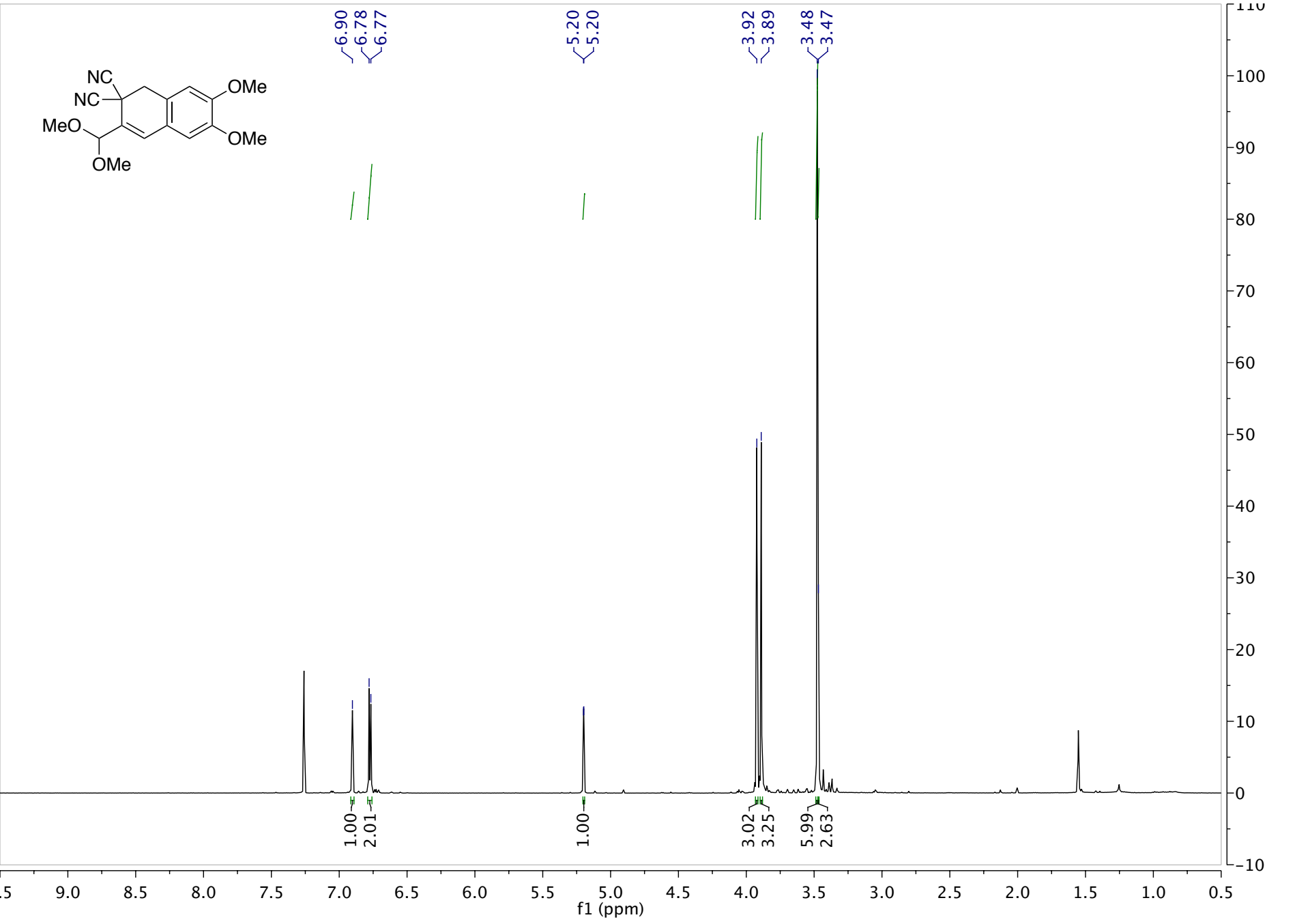
^{1}H spectrum of 3-(dimethoxymethyl)-7-methoxynaphthalene-2,2(1*H*)-dicarbonitrile 4n ($CDCl_3$)



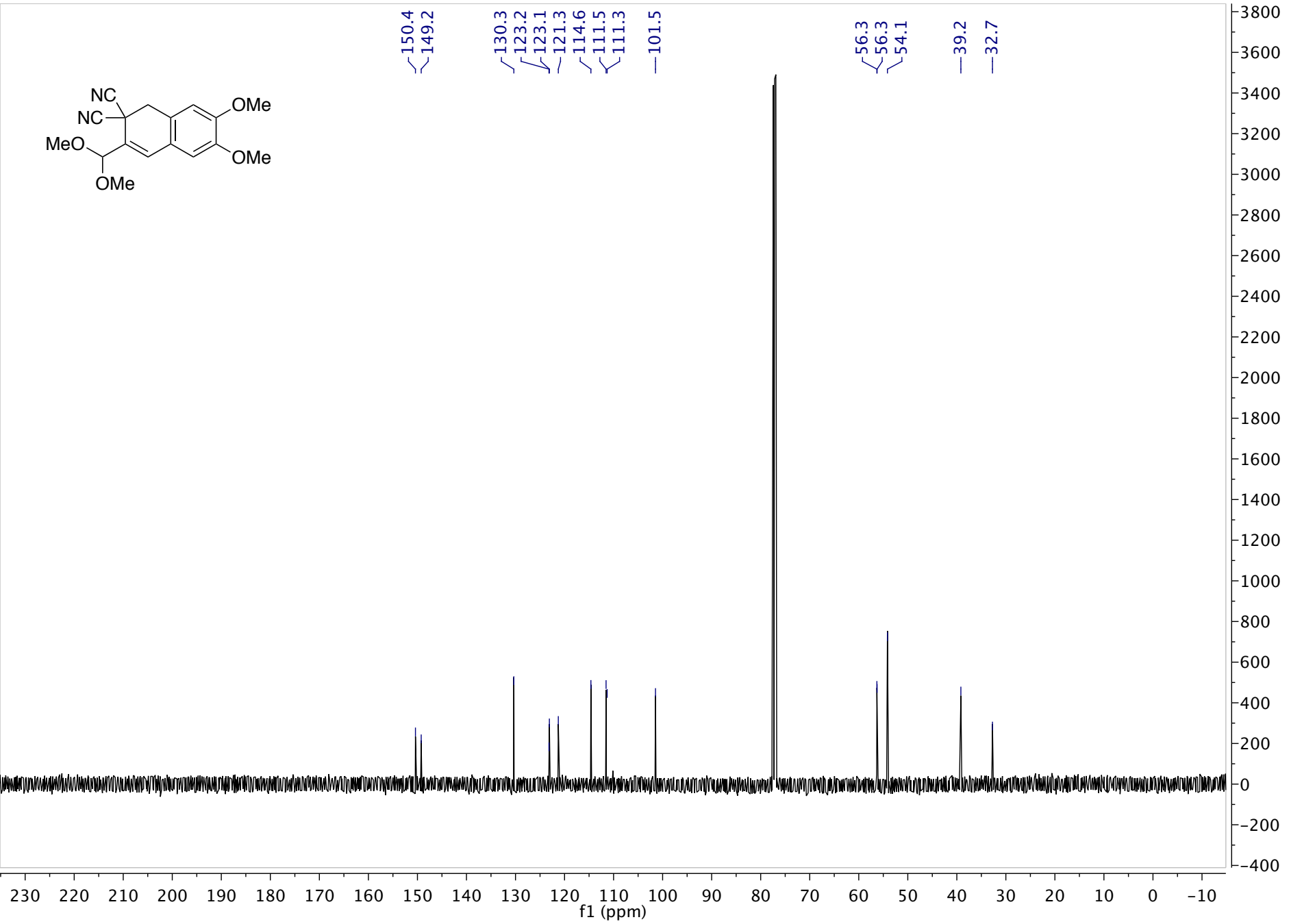
^{13}C spectrum of 3-(dimethoxymethyl)-7-methoxynaphthalene-2,2(1*H*)-dicarbonitrile 4n ($CDCl_3$)



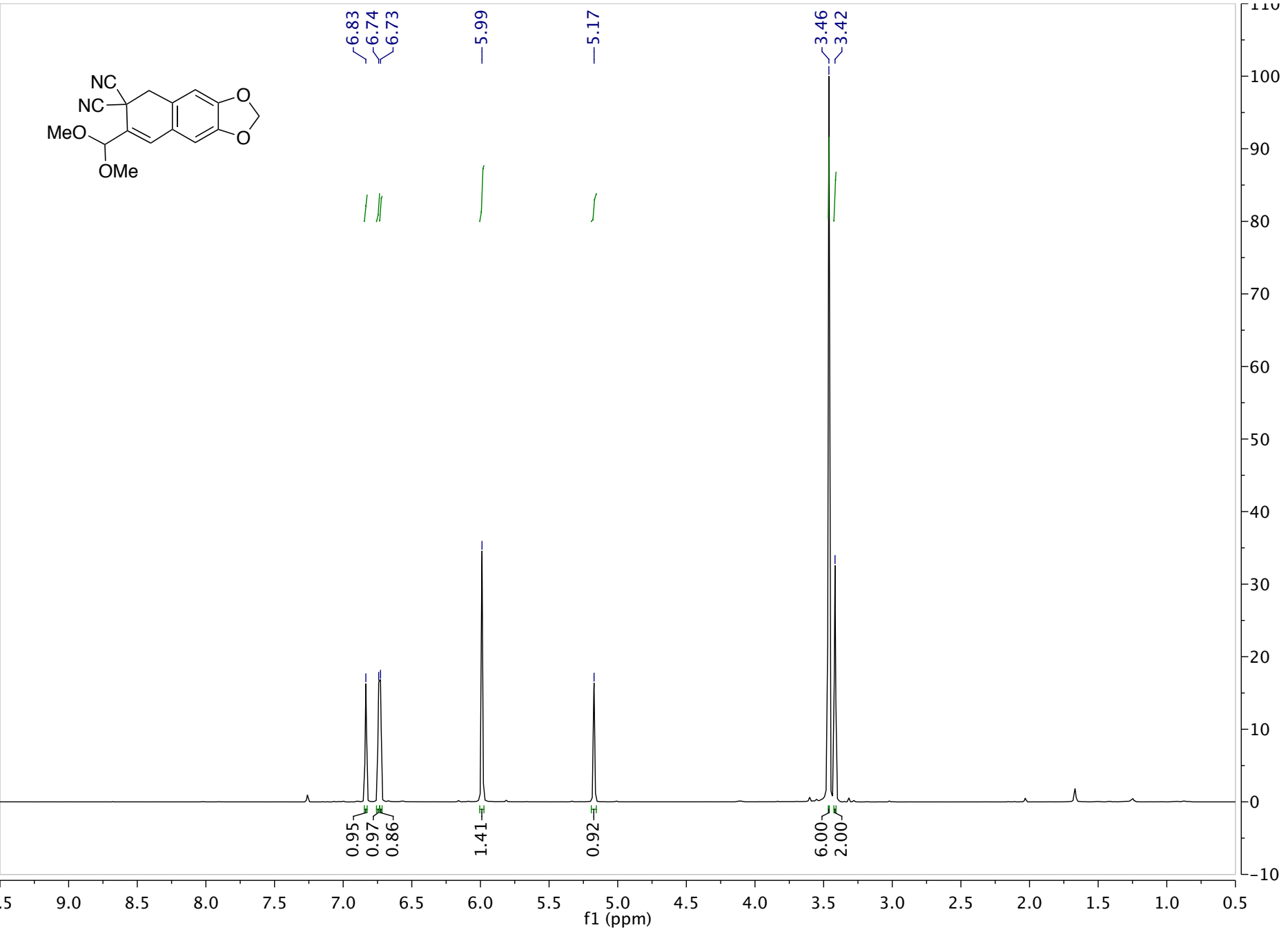
^{1}H spectrum of 3-(dimethoxymethyl)-6,7-dimethoxynaphthalene-2,2(1*H*)-dicarbonitrile 4o ($CDCl_3$)



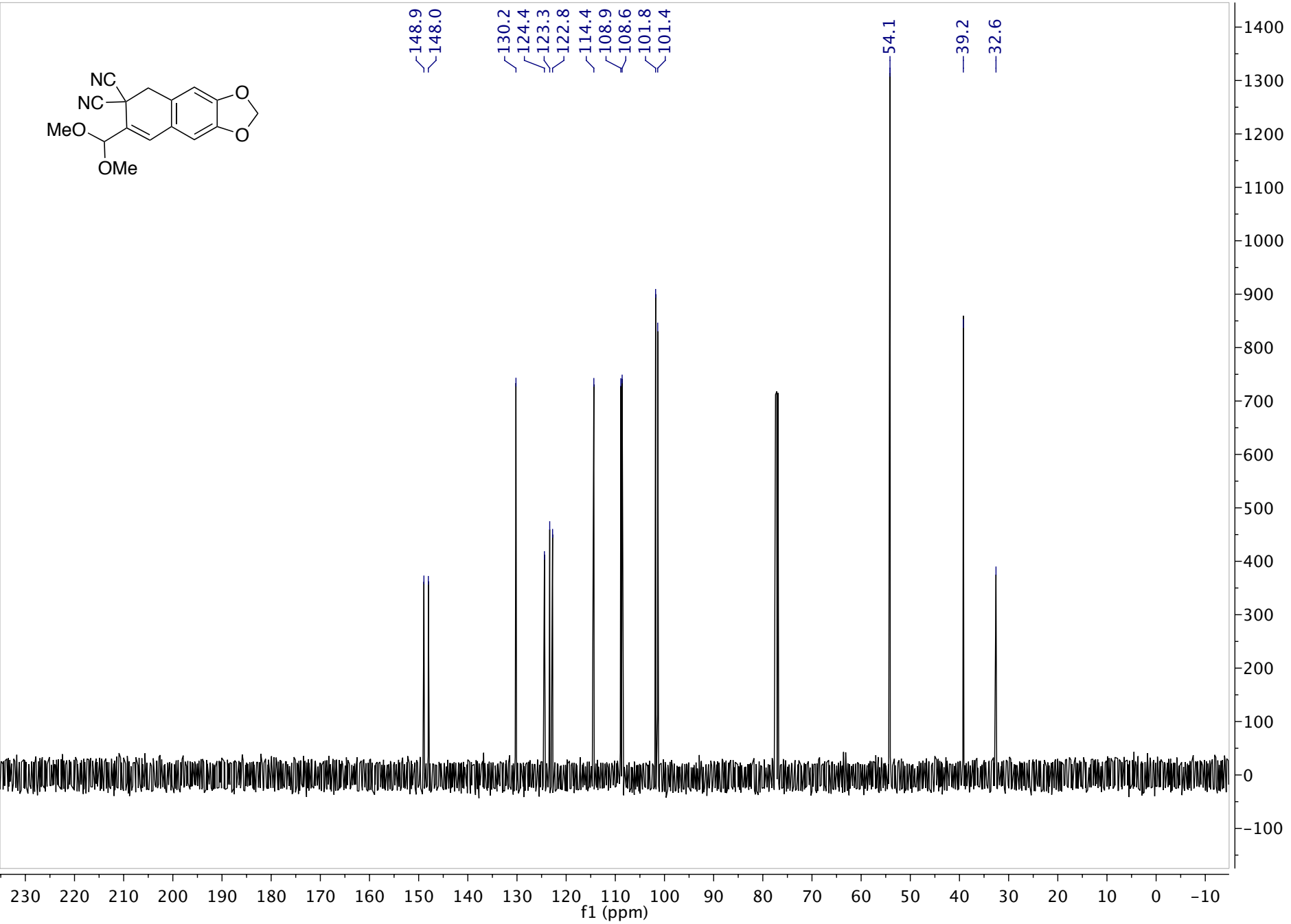
^{13}C spectrum of 3-(dimethoxymethyl)-6,7-dimethoxynaphthalene-2,2(1*H*)-dicarbonitrile 4o ($CDCl_3$)



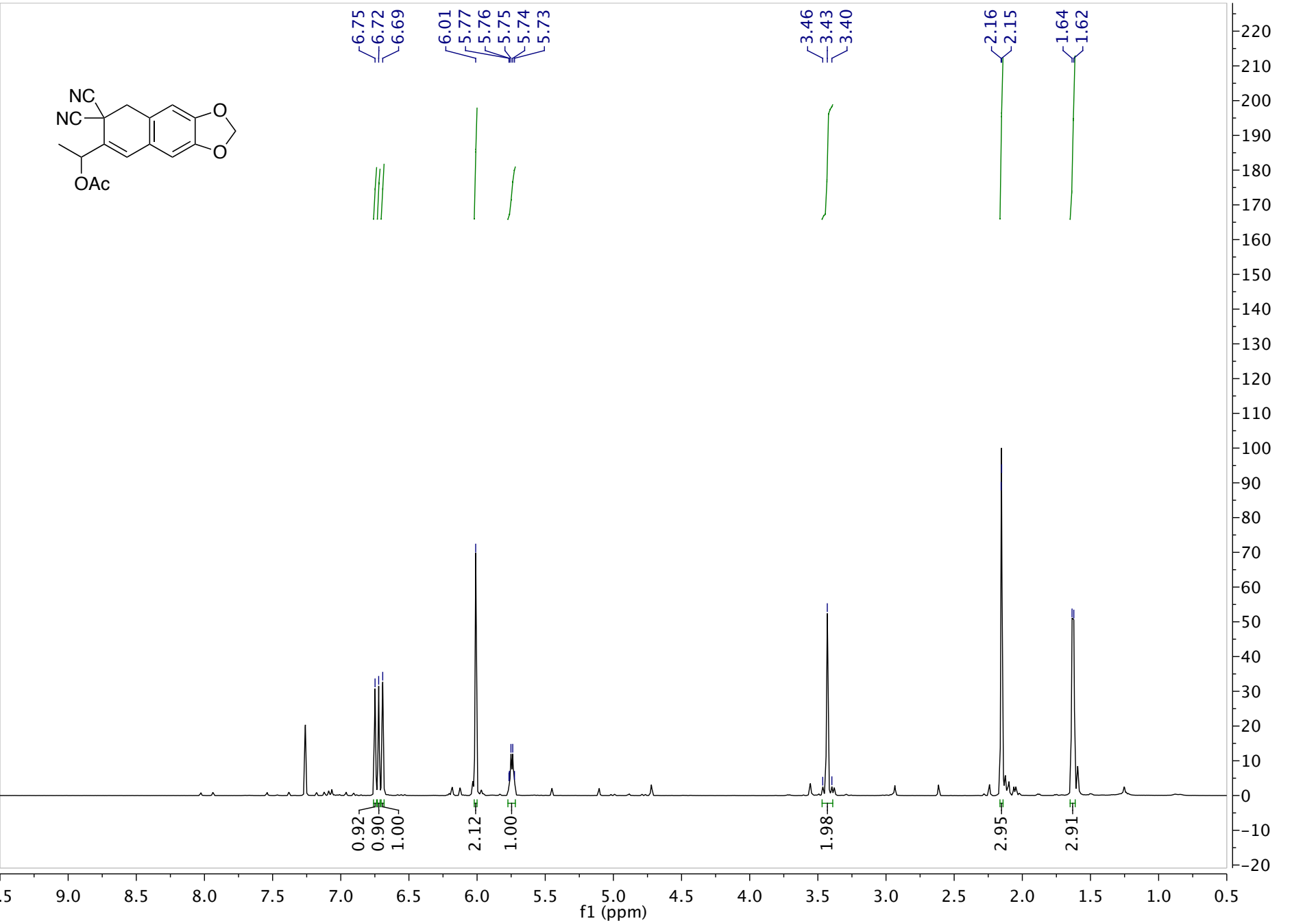
^{1}H spectrum of 7-(dimethoxymethyl)naphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4p ($CDCl_3$)



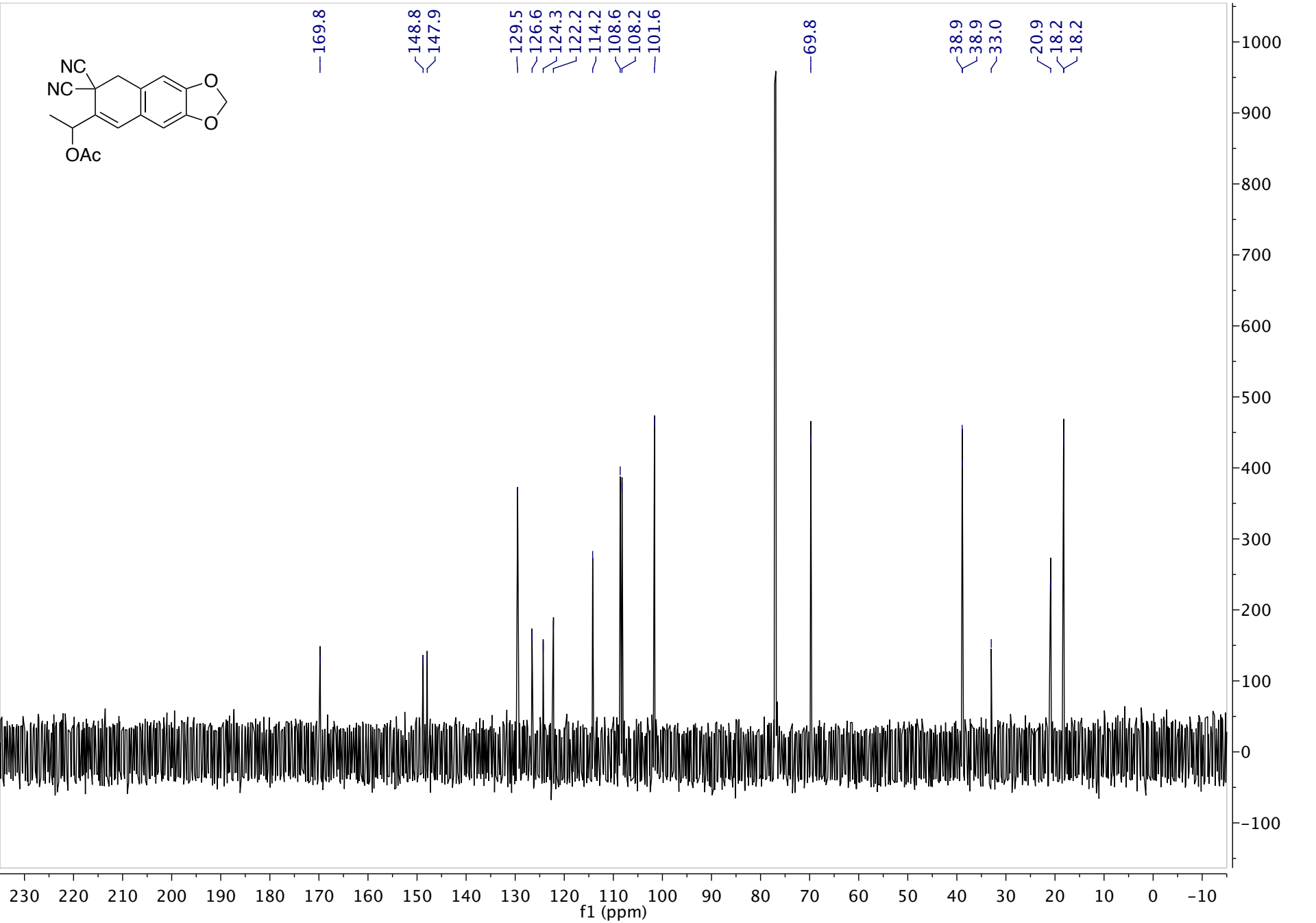
^{13}C spectrum of 7-(dimethoxymethyl)naphtho[2,3-*d*][1,3]dioxole-6,6(5*H*)-dicarbonitrile 4p ($CDCl_3$)



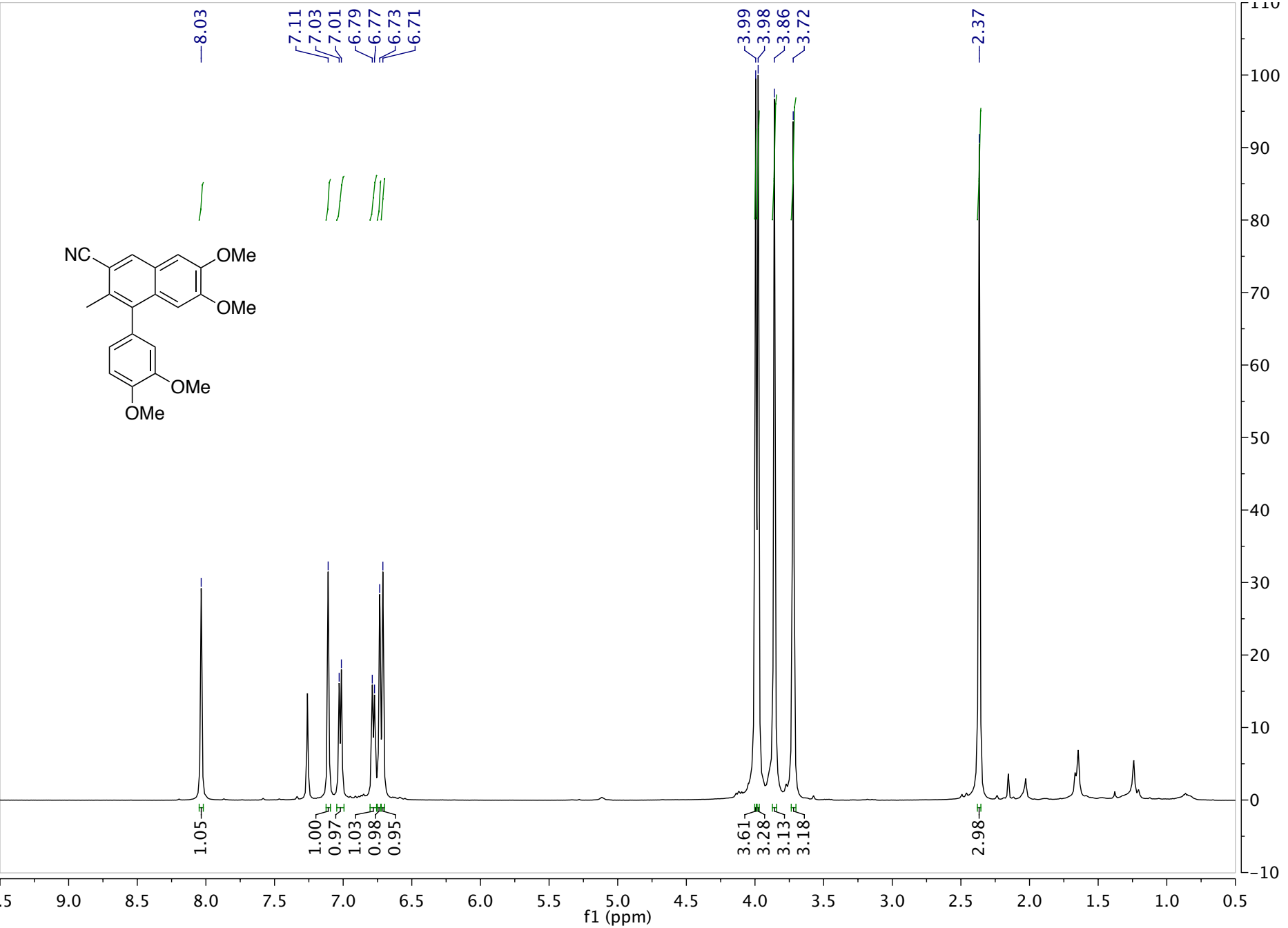
^{1}H spectrum of 1-(7,7-dicyano-7,8-dihydronaphtho[2,3-*d*][1,3]dioxol-6-yl)ethyl acetate 4q ($CDCl_3$)



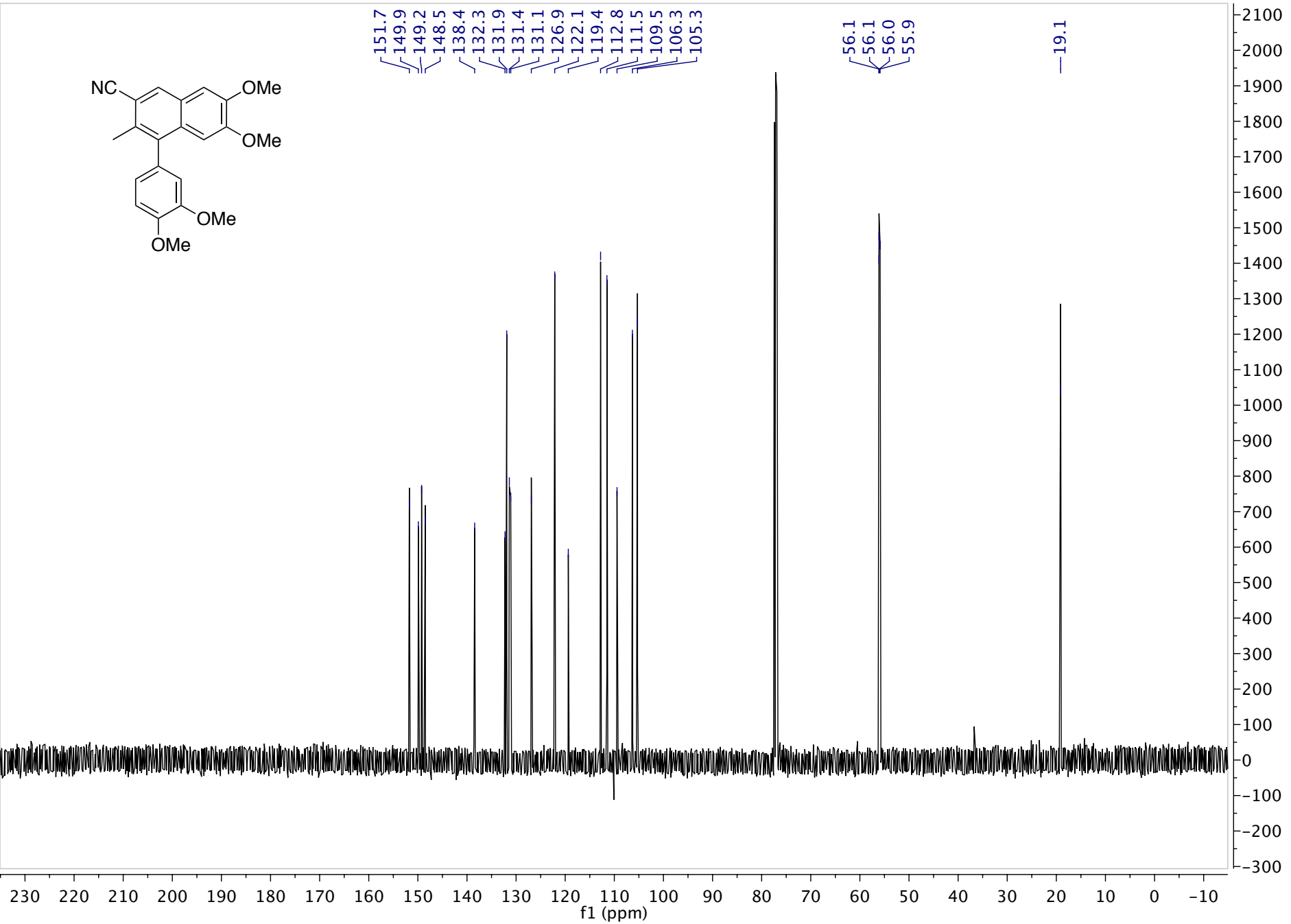
^{13}C spectrum of 1-(7,7-dicyano-7,8-dihydronaphtho[2,3-*d*][1,3]dioxol-6-yl)ethyl acetate 4q ($CDCl_3$)



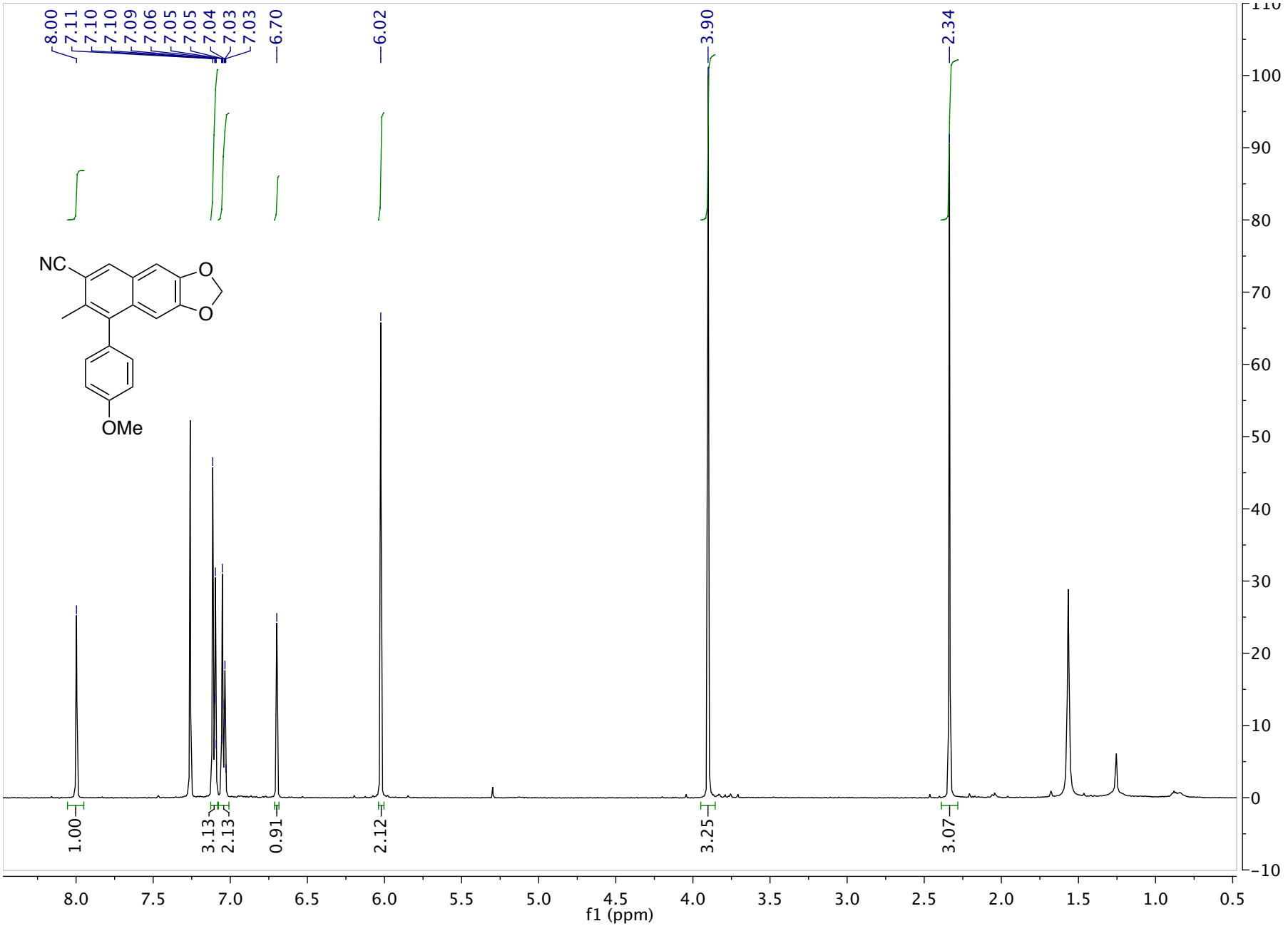
^{1}H spectrum of 8-(4-methoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 5a ($CDCl_3$)



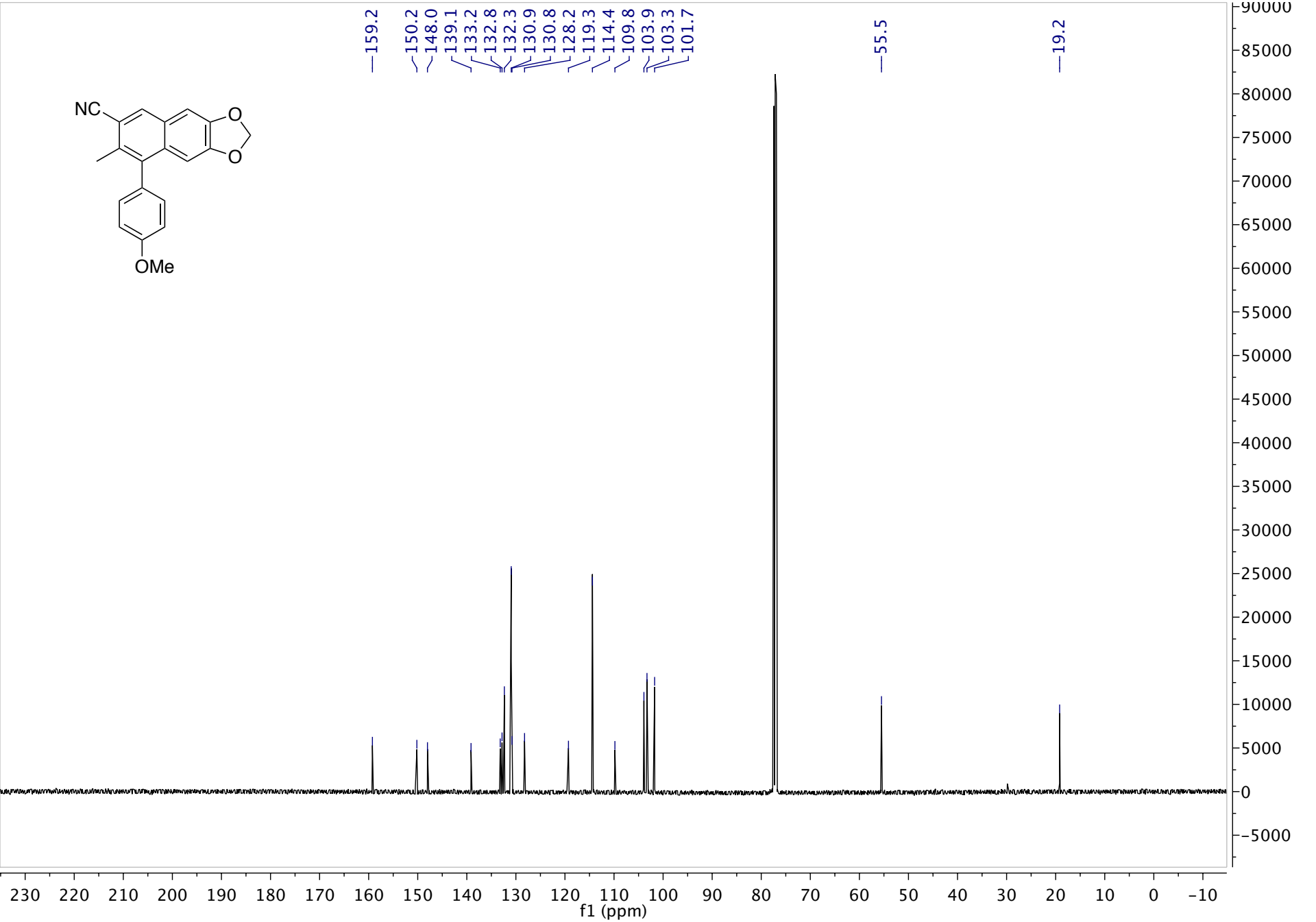
^{13}C spectrum of 8-(4-methoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 5a ($CDCl_3$)



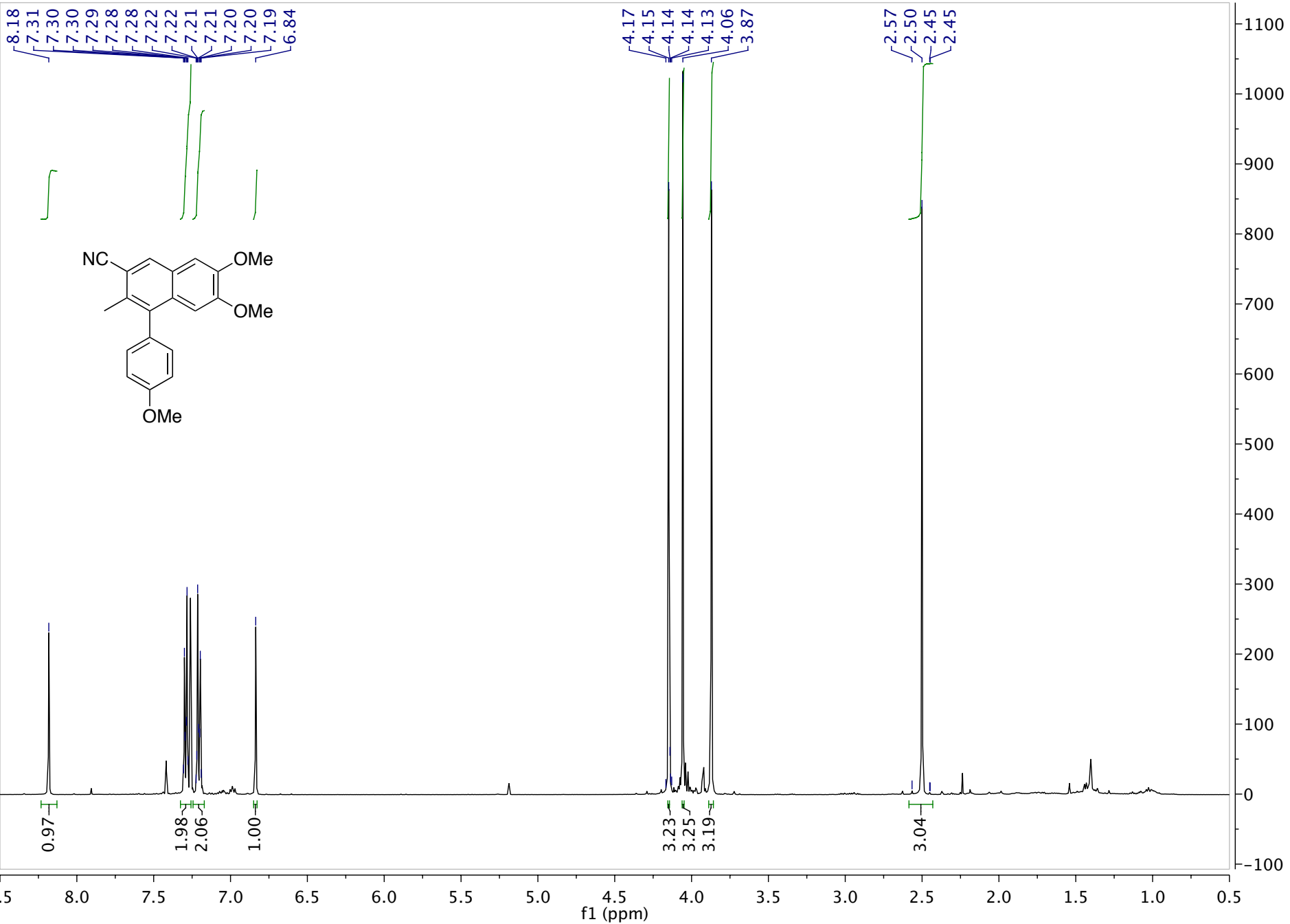
^{1}H spectrum of 8-(4-methoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 5b ($CDCl_3$)



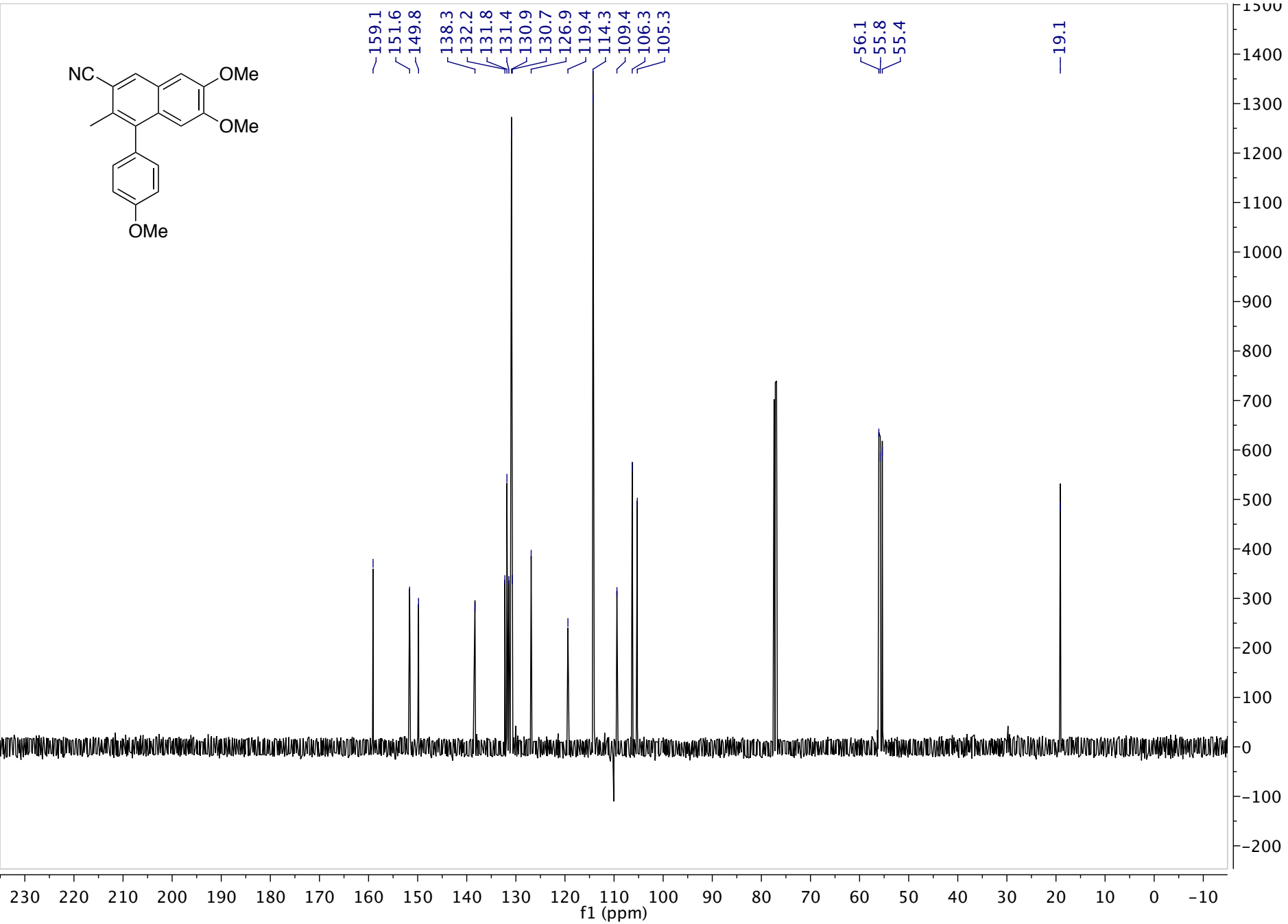
^{13}C spectrum of 8-(4-methoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 5b ($CDCl_3$)



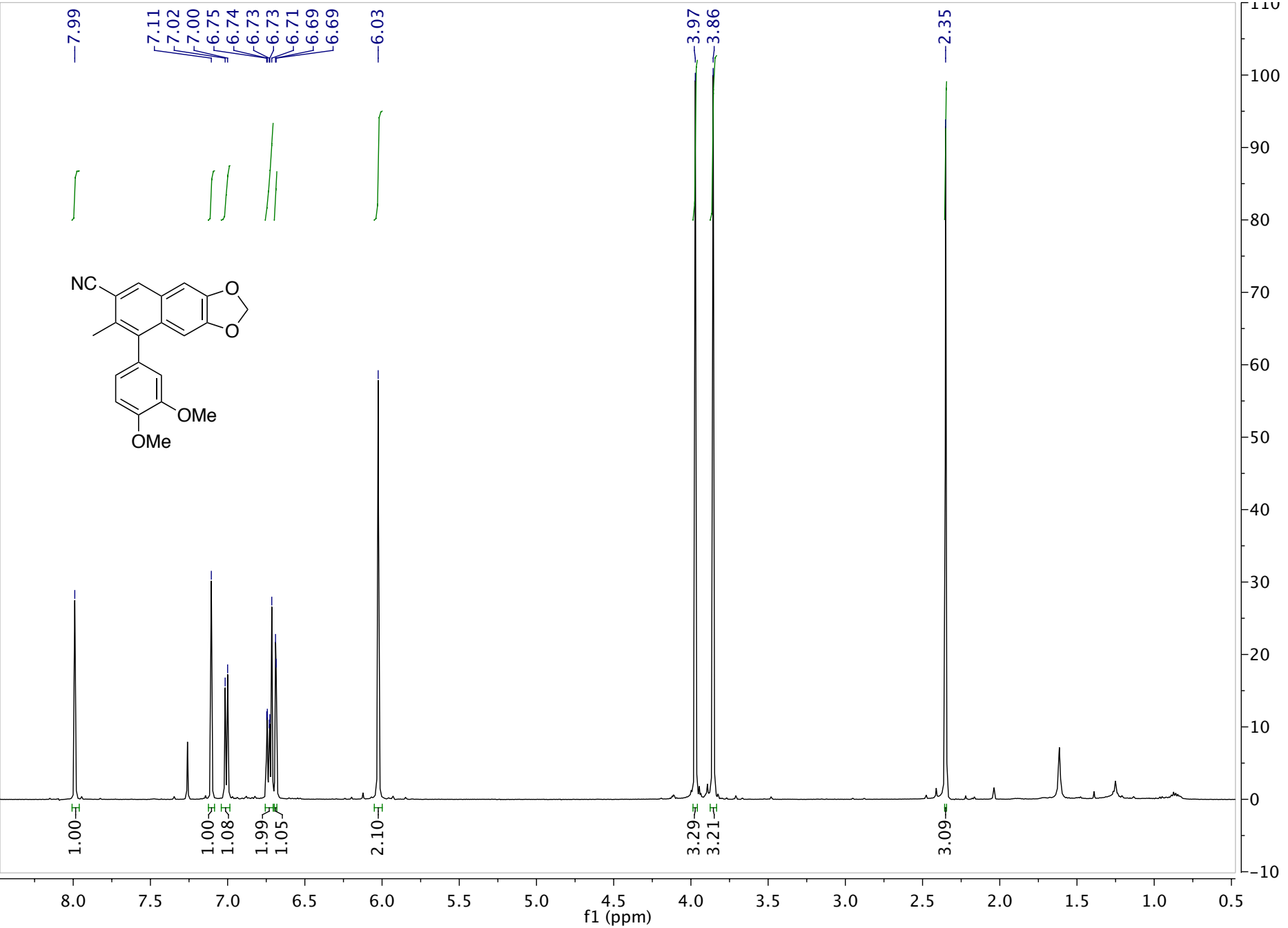
^{1}H spectrum of 6,7-dimethoxy-4-(4-methoxyphenyl)-3-methyl-2-naphthonitrile 5c ($CDCl_3$)



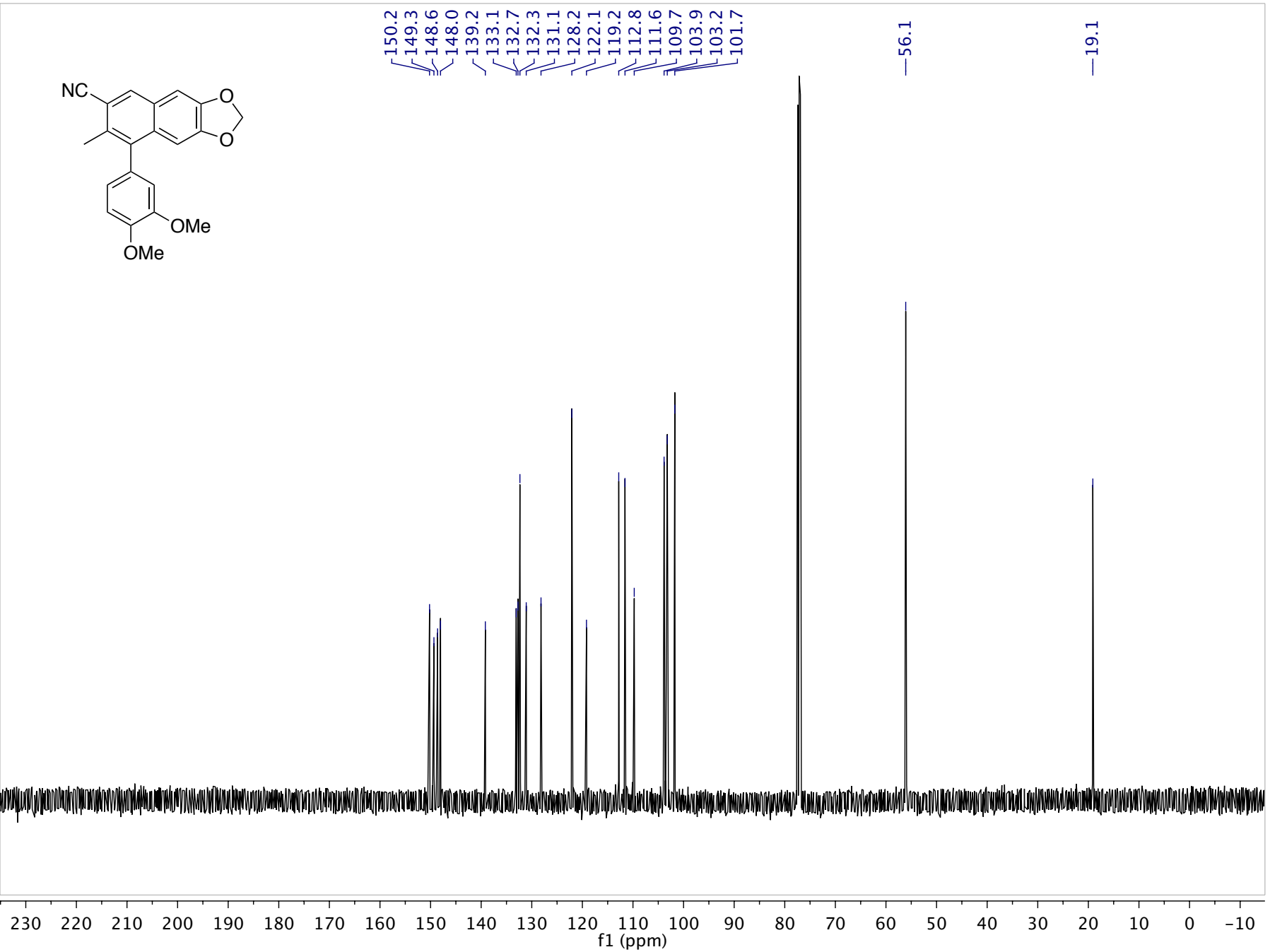
^{13}C spectrum of 6,7-dimethoxy-4-(4-methoxyphenyl)-3-methyl-2-naphthonitrile 5c ($CDCl_3$)



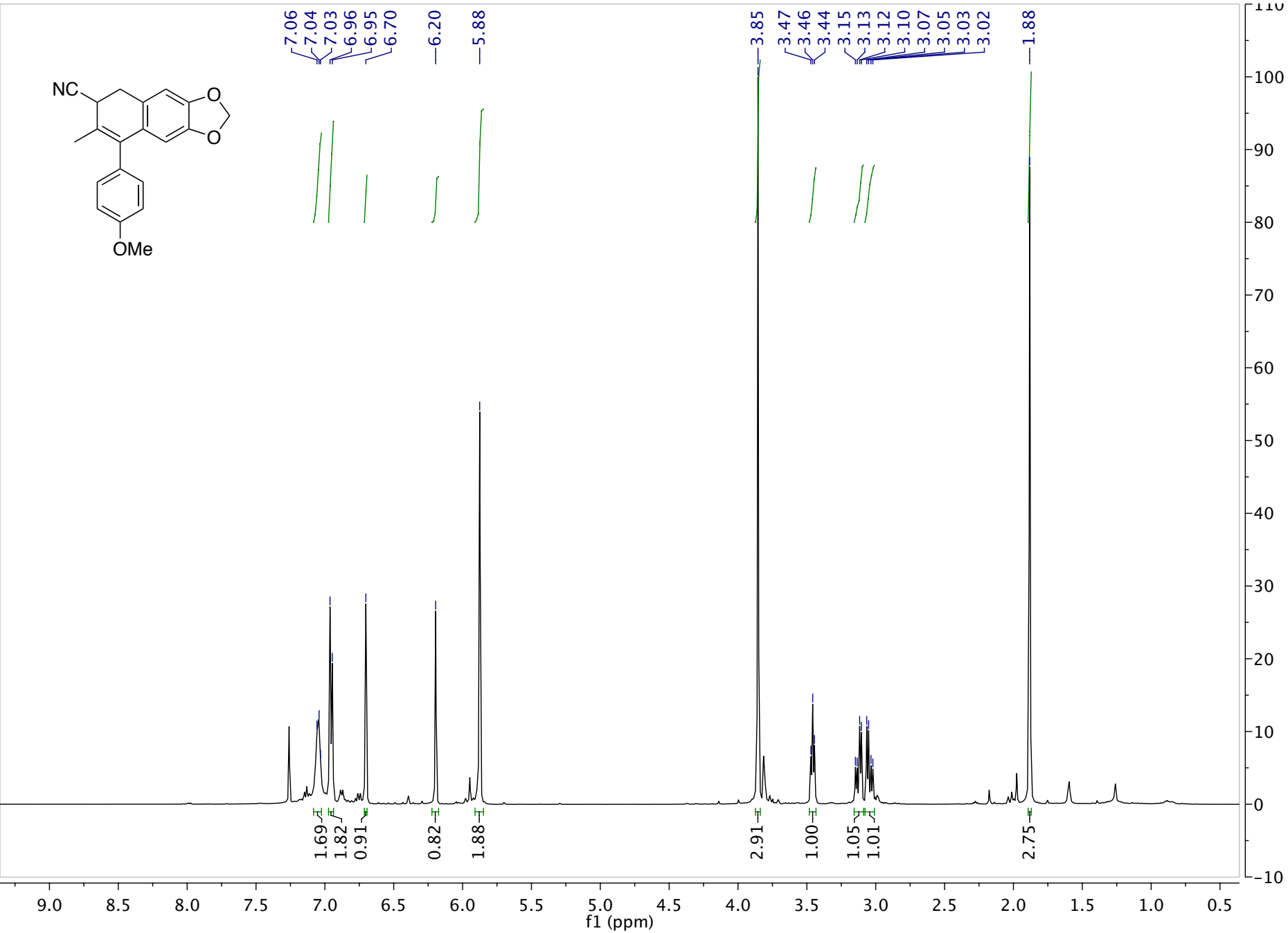
^{1}H spectrum of 8-(3,4-dimethoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 5d ($CDCl_3$)



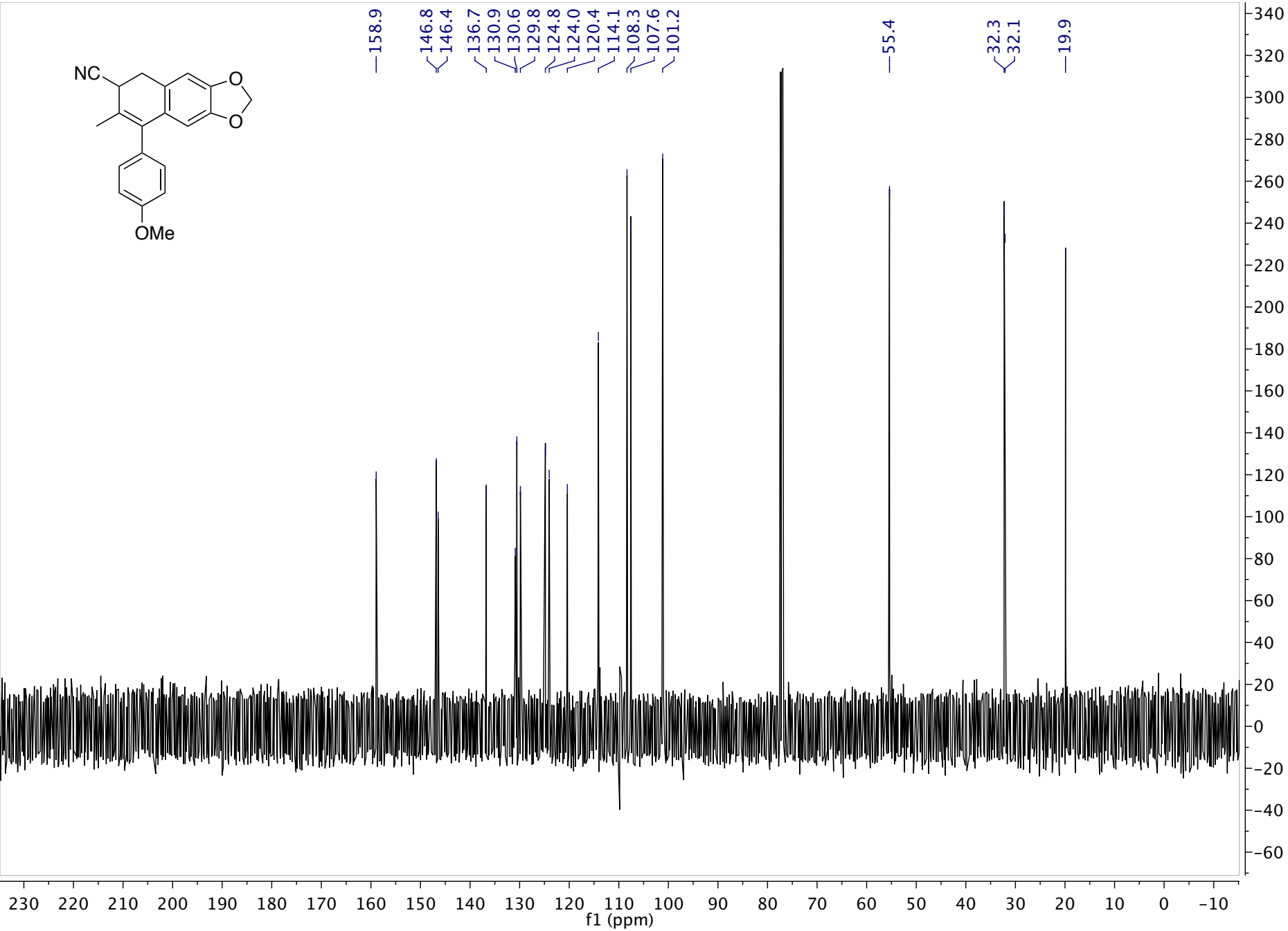
^{13}C spectrum of 8-(3,4-dimethoxyphenyl)-7-methylnaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 5d ($CDCl_3$)



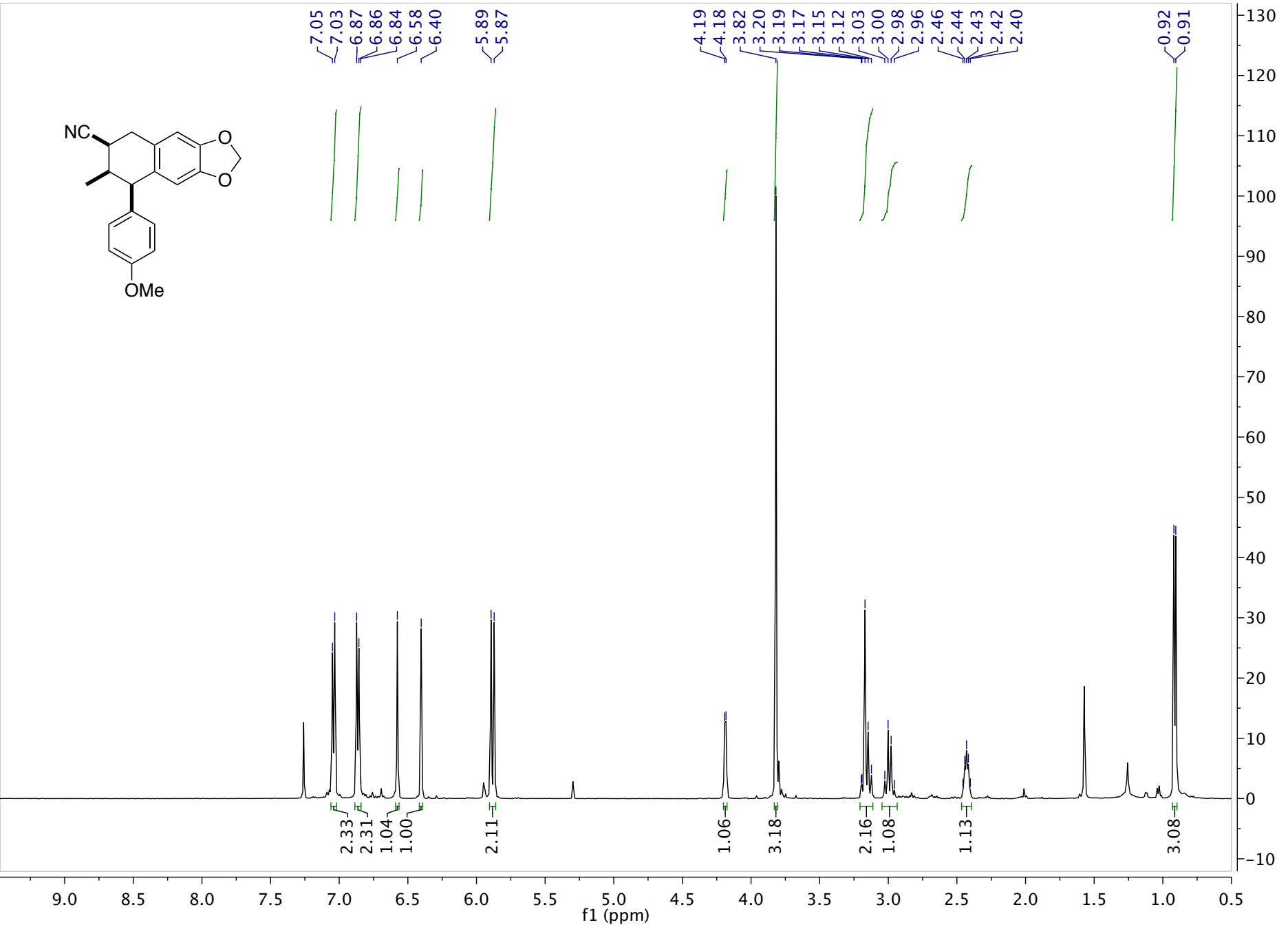
^{1}H spectrum of 8-(4-methoxyphenyl)-7-methyl-5,6-dihydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile SI1 ($CDCl_3$)



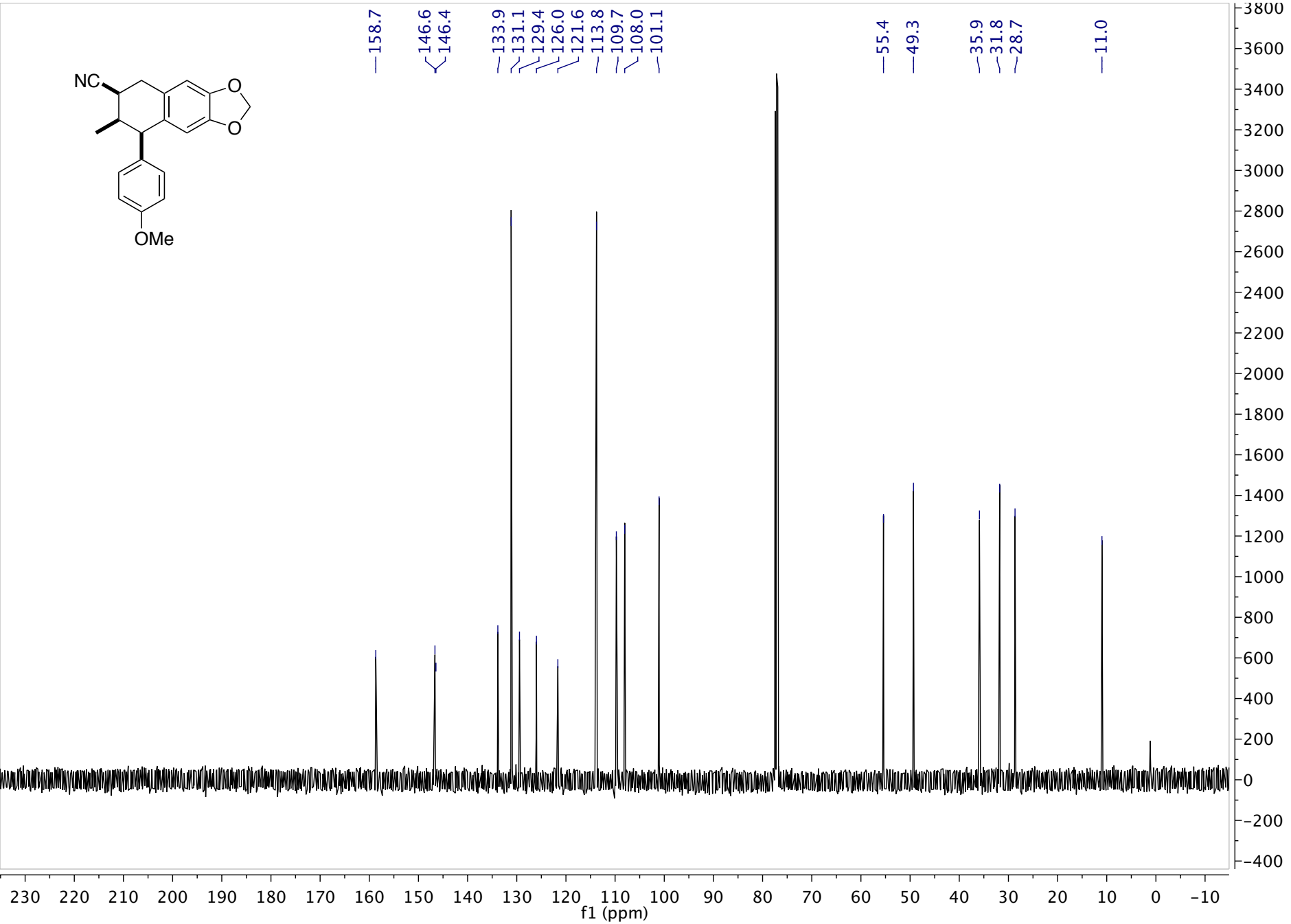
^{13}C spectrum of 8-(4-methoxyphenyl)-7-methyl-5,6-dihydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile SI1 ($CDCl_3$)



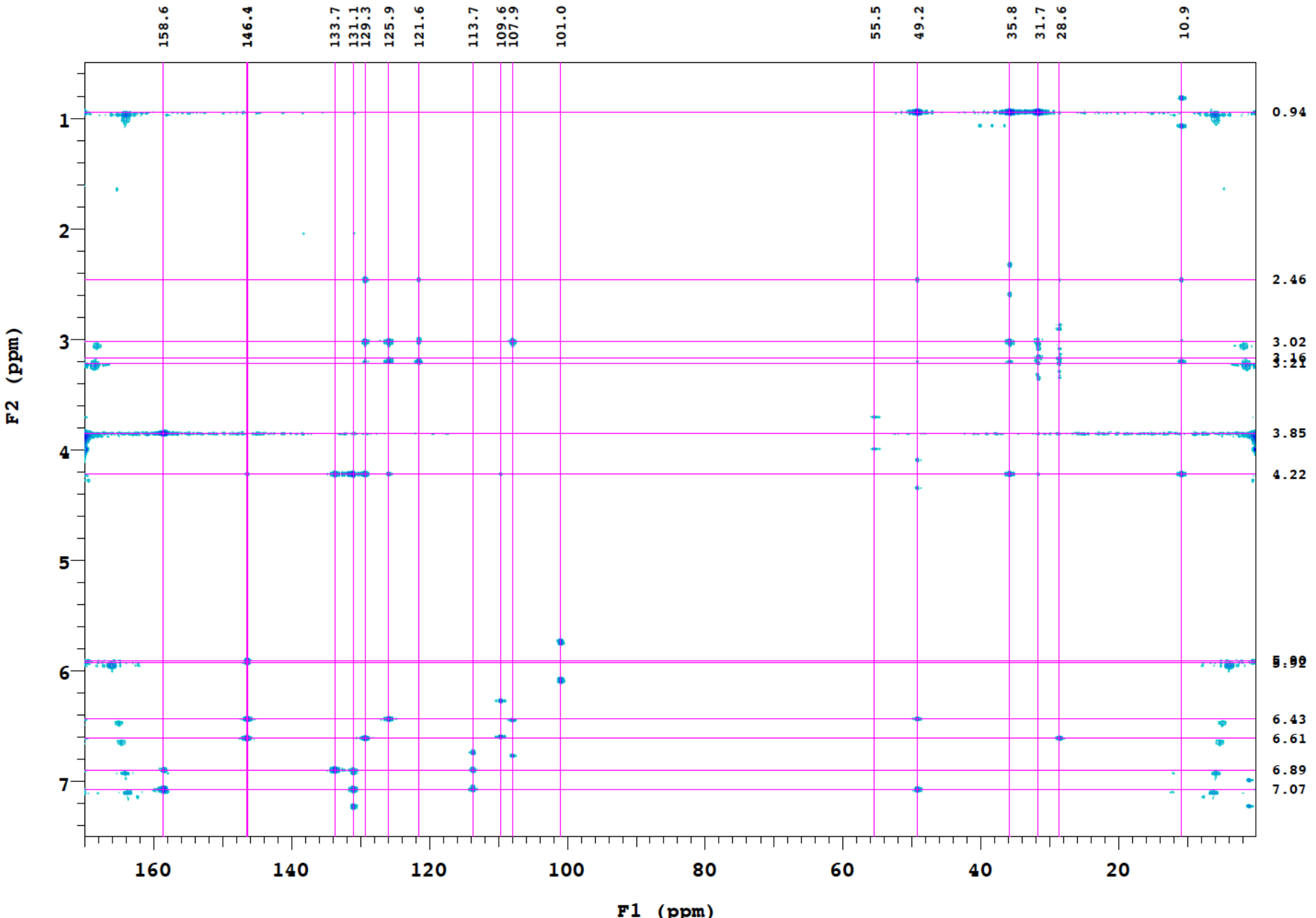
^{1}H spectrum of (6*S*,7*R*,8*R*)-8-(4-methoxyphenyl)-7-methyl-5,6,7,8-tetrahydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 6a ($CDCl_3$)



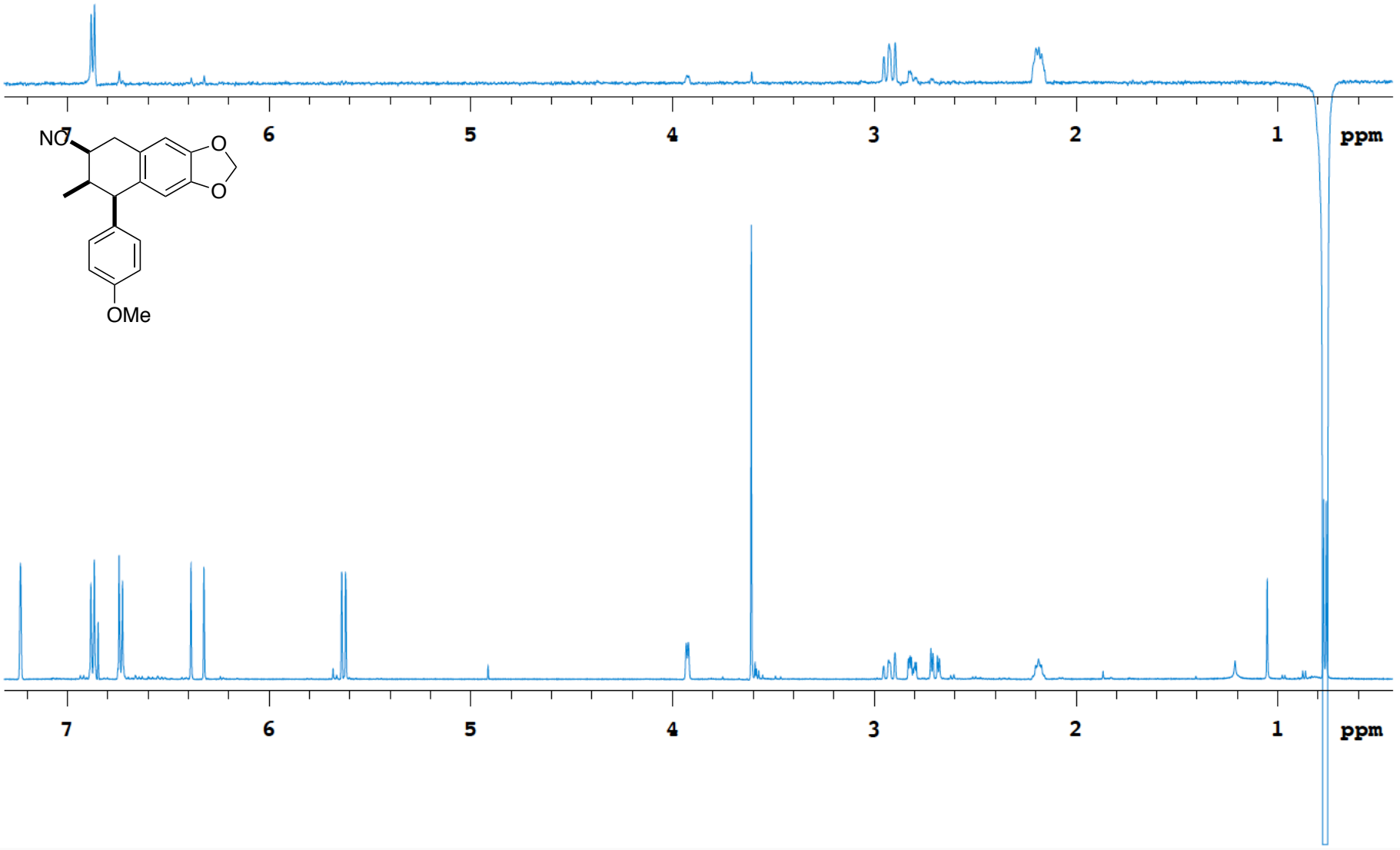
^{13}C spectrum of (6*S*,7*R*,8*R*)-8-(4-methoxyphenyl)-7-methyl-5,6,7,8-tetrahydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 6a ($CDCl_3$)



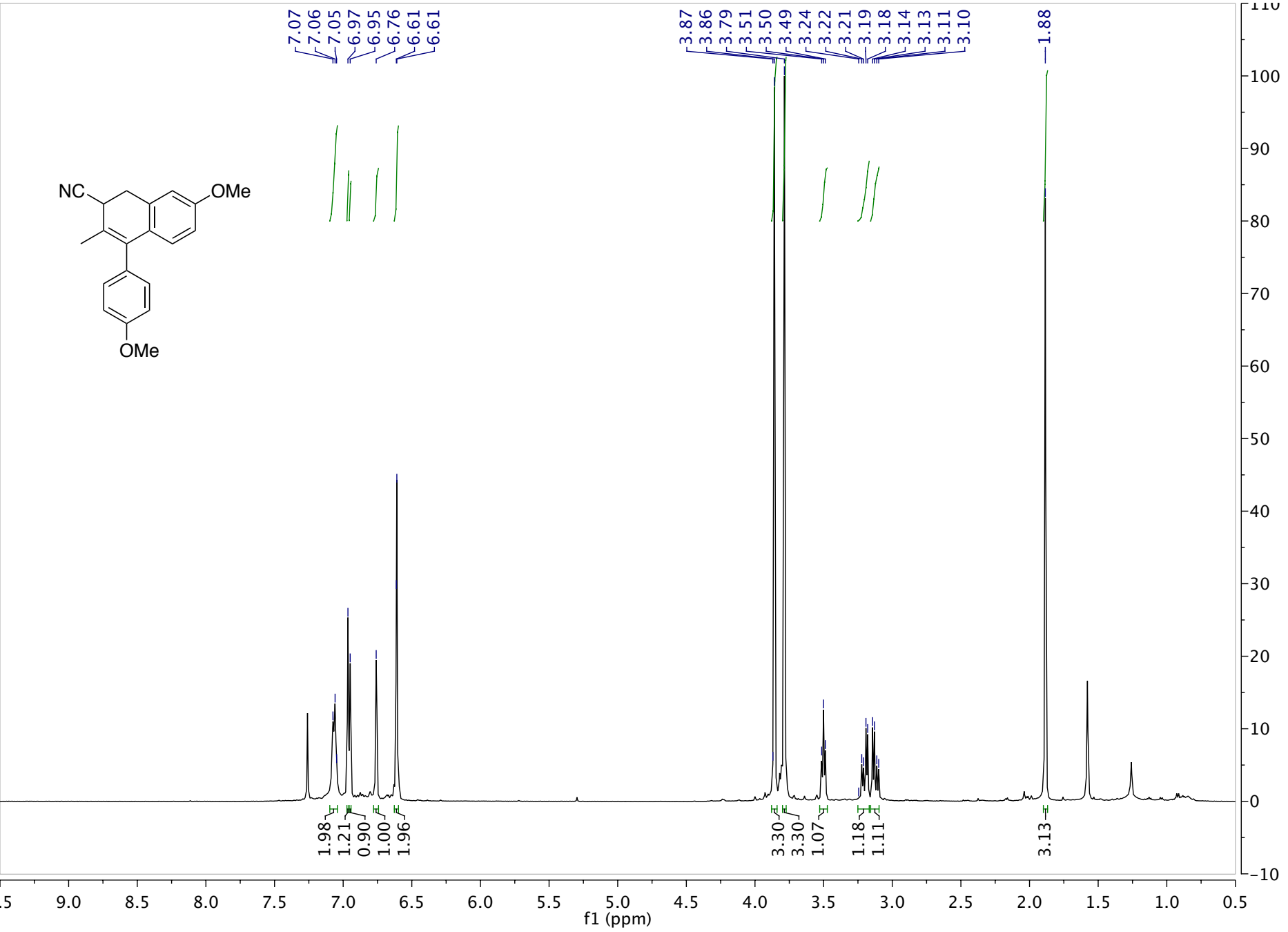
gHMBCAD of (6*S*,7*R*,8*R*)-8-(4-methoxyphenyl)-7-methyl-5,6,7,8-tetrahydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 6a ($CDCl_3$)



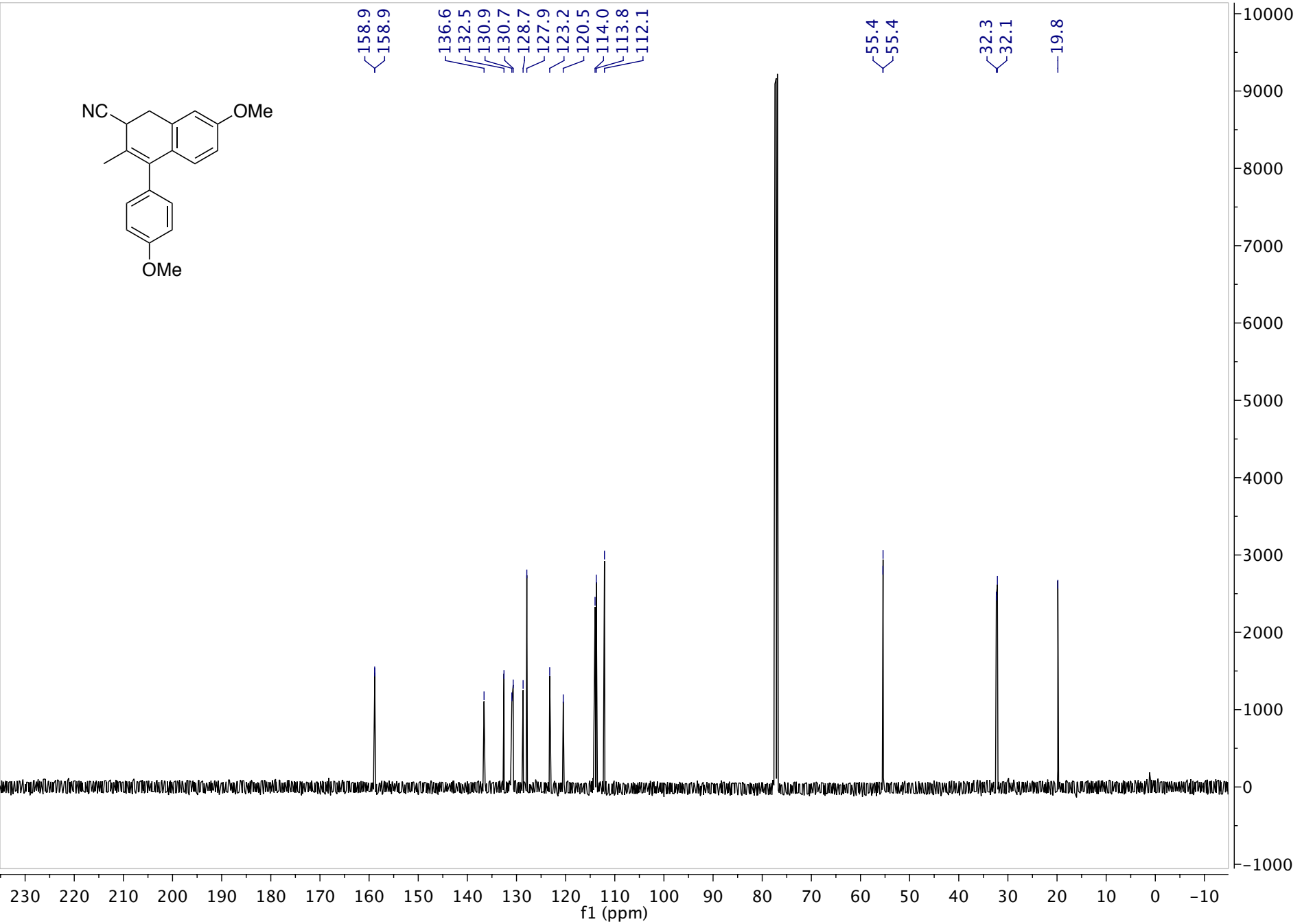
1D NOESY of (6*S*,7*R*,8*R*)-8-(4-methoxyphenyl)-7-methyl-5,6,7,8-tetrahydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 6a ($CDCl_3$)



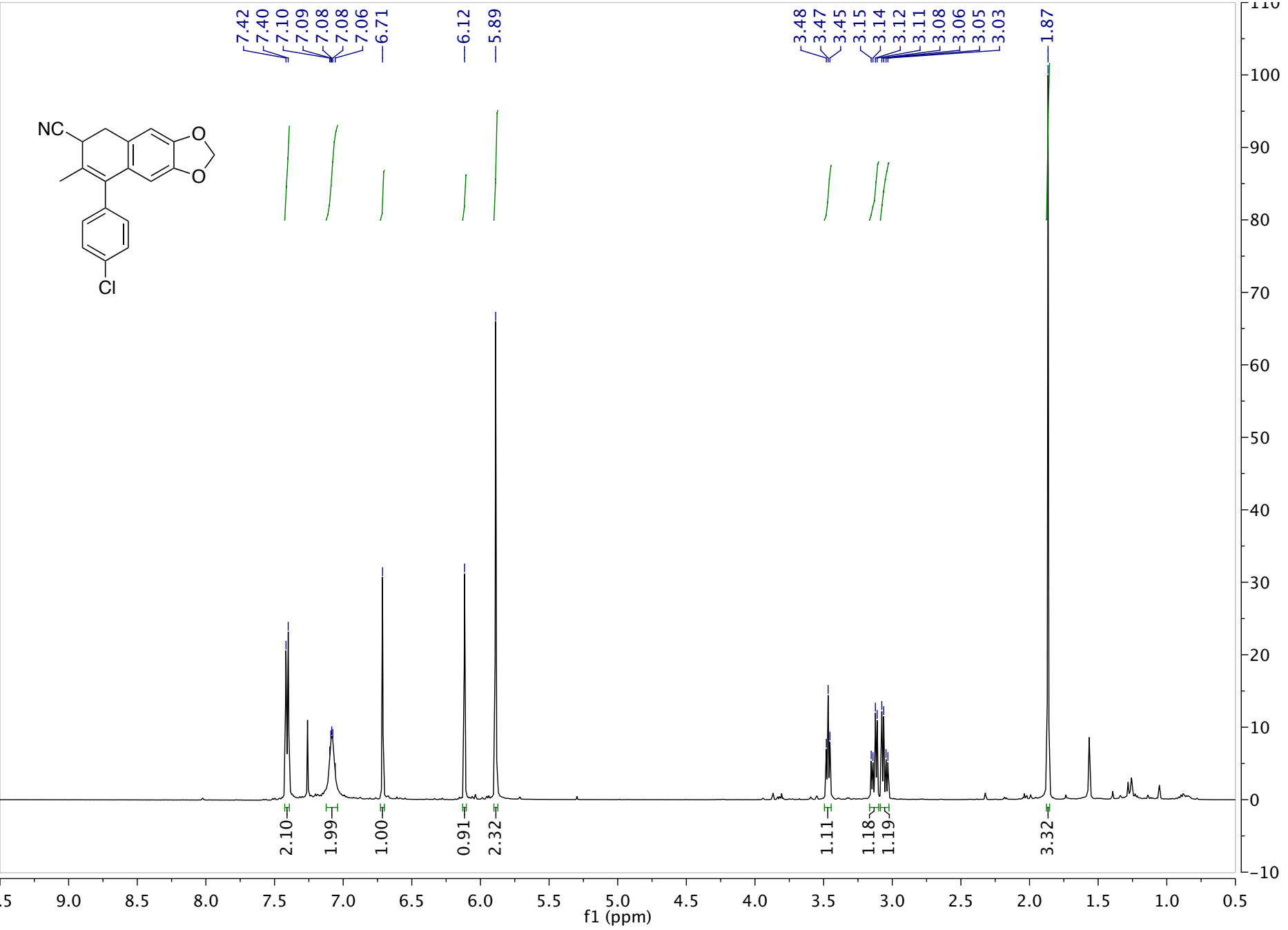
^{1}H spectrum of 7-methoxy-4-(4-methoxyphenyl)-3-methyl-1,2-dihydronaphthalene-2-carbonitrile 6b ($CDCl_3$)



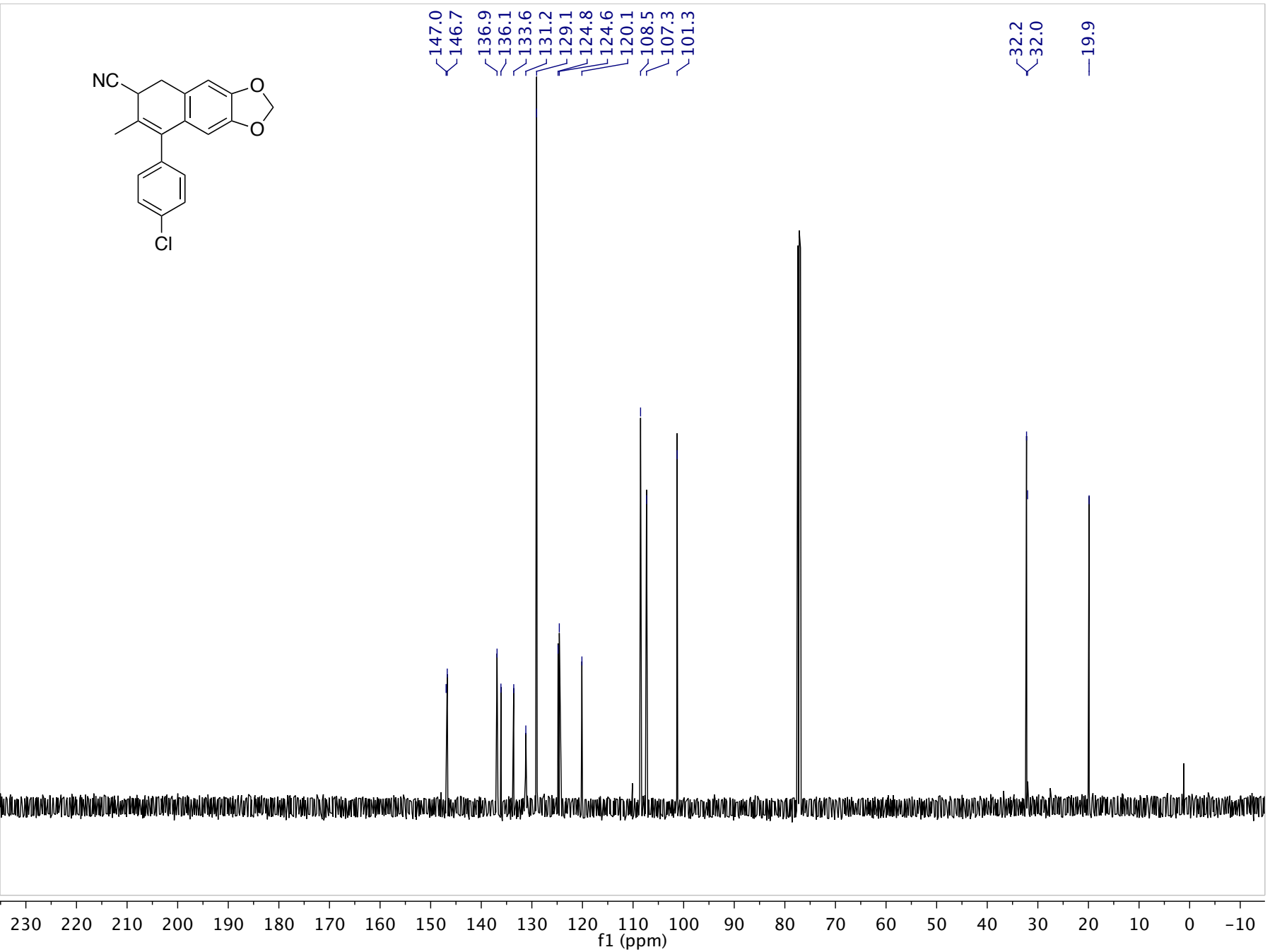
^{13}C spectrum of 7-methoxy-4-(4-methoxyphenyl)-3-methyl-1,2-dihydronaphthalene-2-carbonitrile 6b ($CDCl_3$)



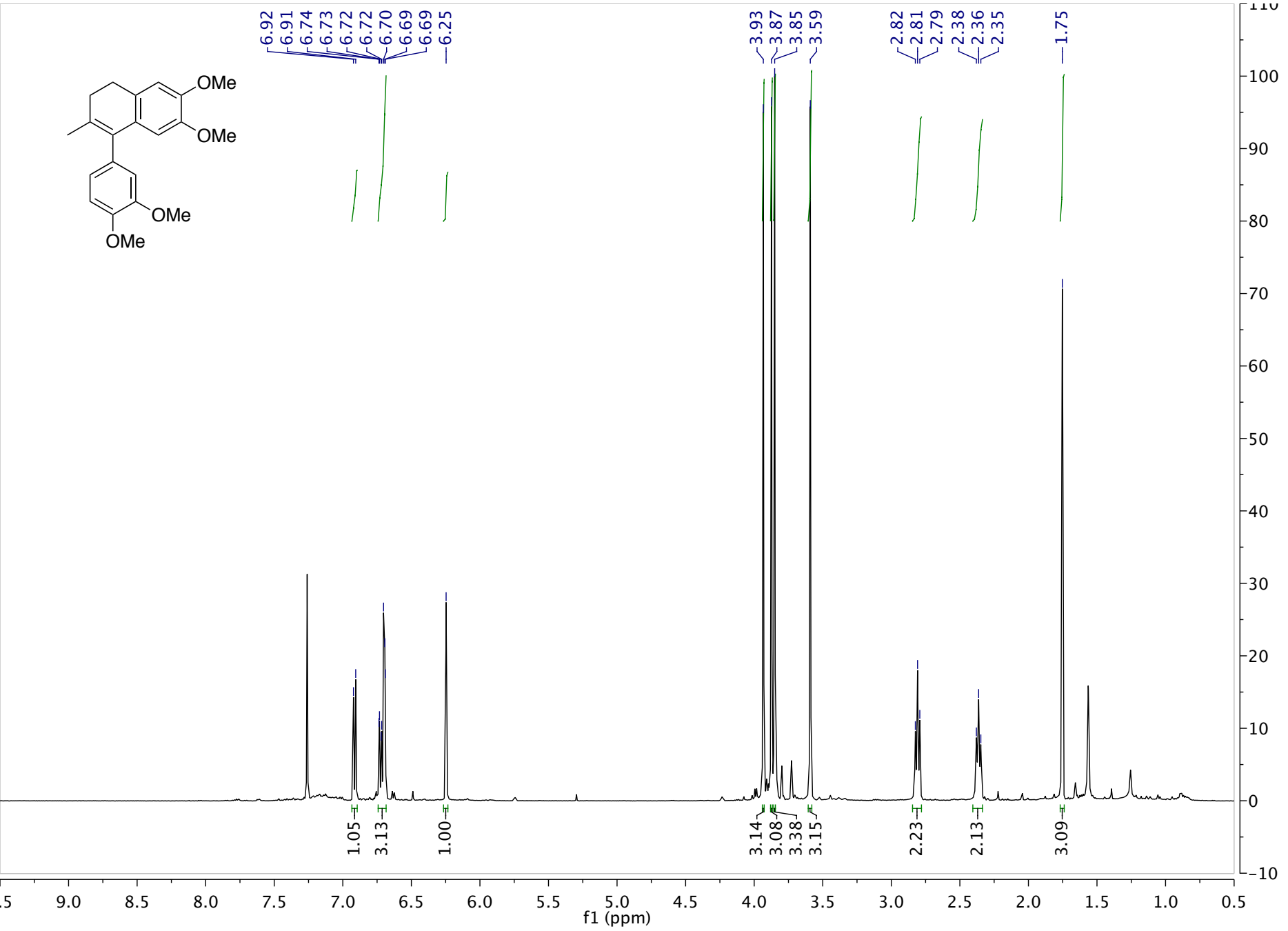
^{1}H spectrum of 8-(4-chlorophenyl)-7-methyl-5,6-dihydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 6c ($CDCl_3$)



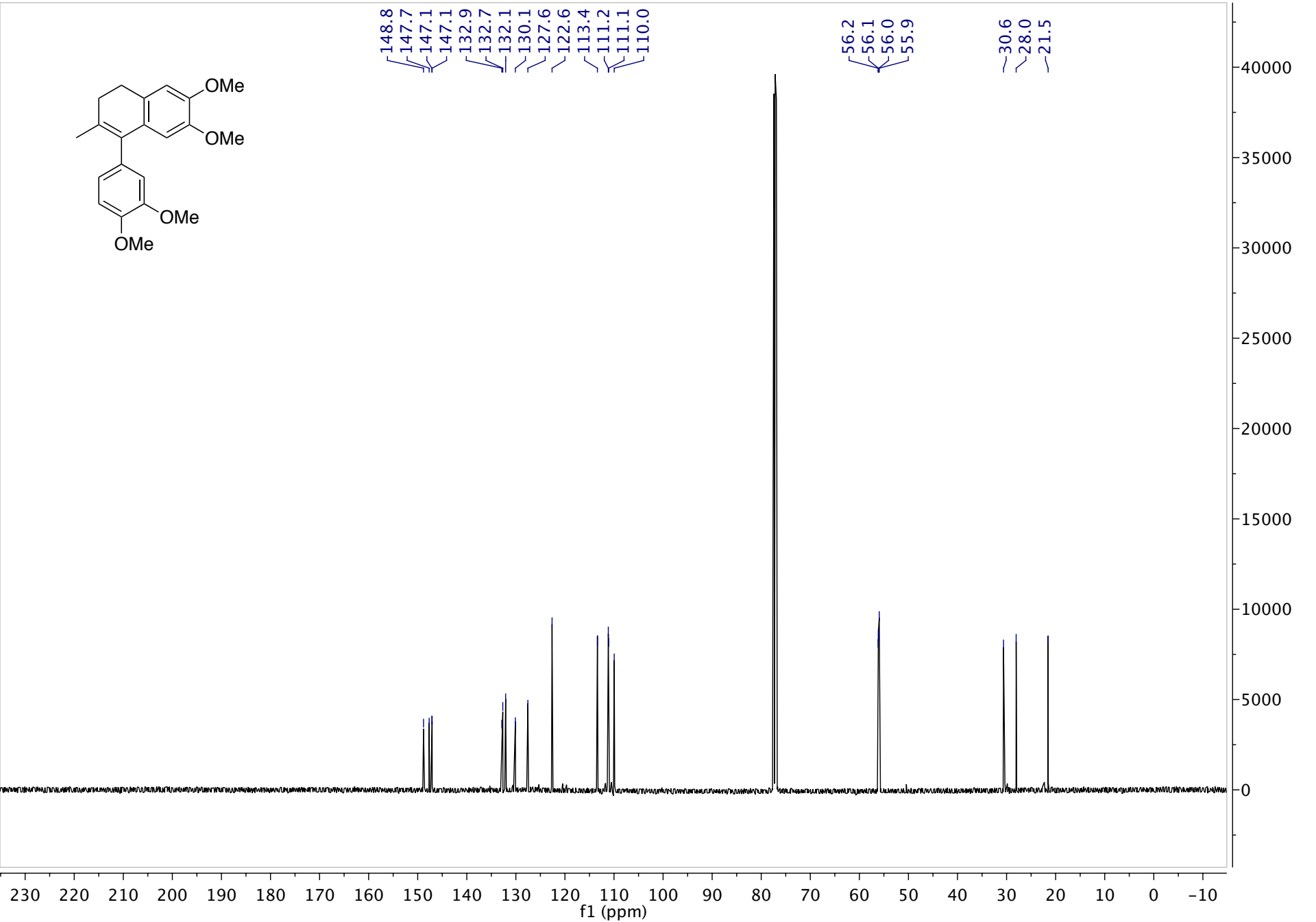
^{13}C spectrum of 8-(4-chlorophenyl)-7-methyl-5,6-dihydronaphtho[2,3-*d*][1,3]dioxole-6-carbonitrile 6c ($CDCl_3$)



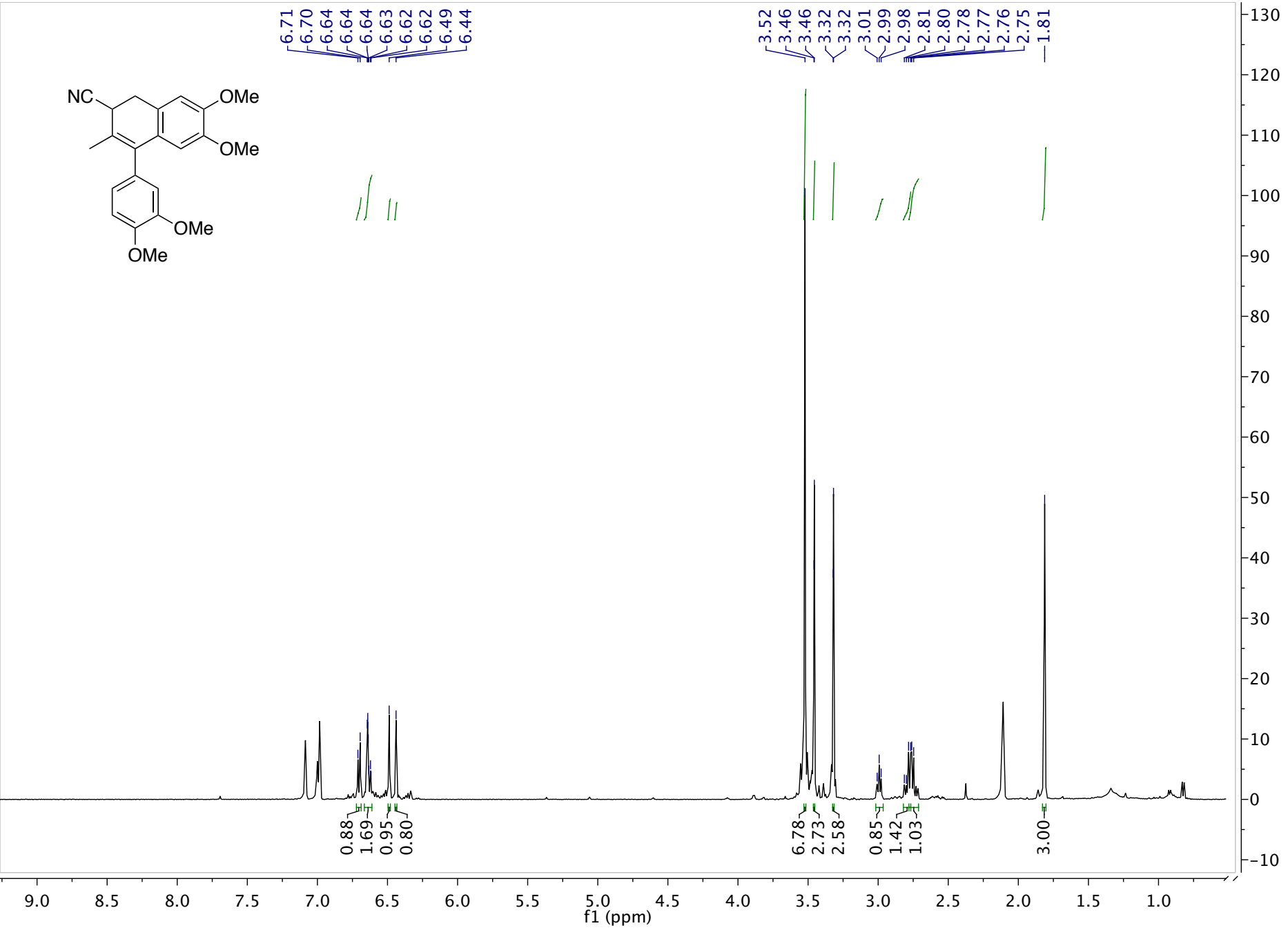
^{1}H spectrum of 4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene 6d ($CDCl_3$)



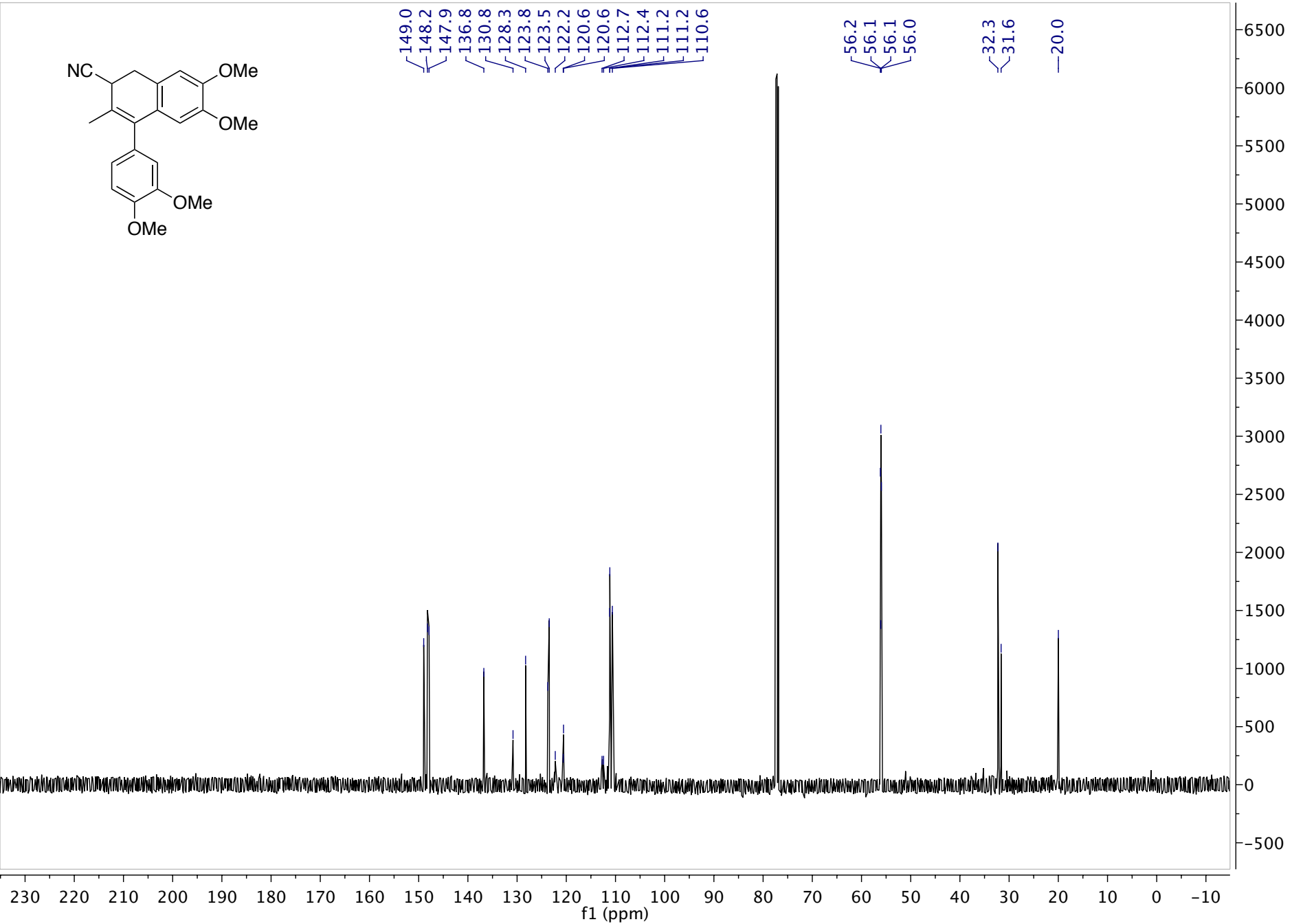
^{13}C spectrum of 4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene 6d ($CDCl_3$)



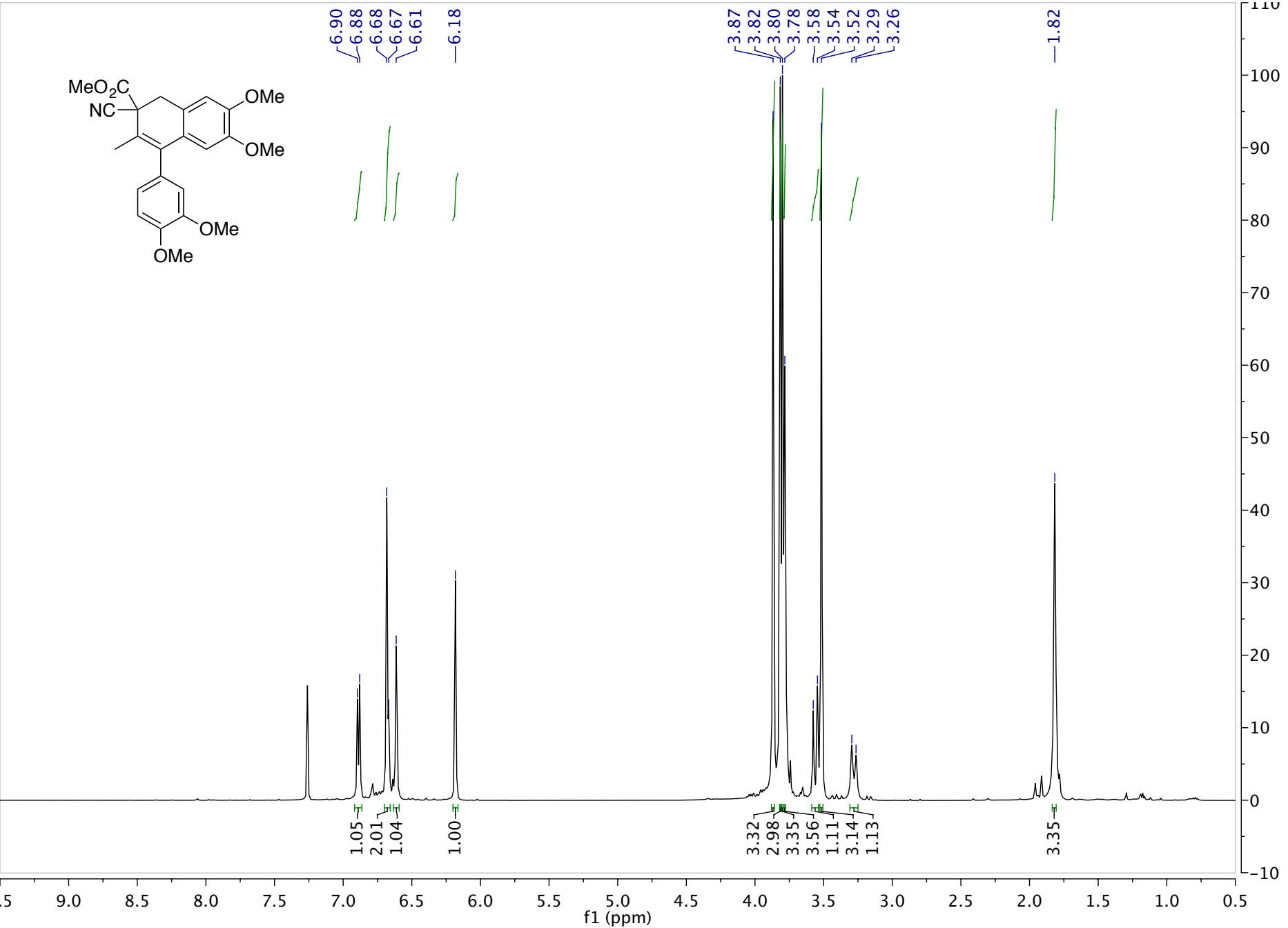
^{1}H spectrum of 4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carbonitrile 6e (Toluene-d_8)



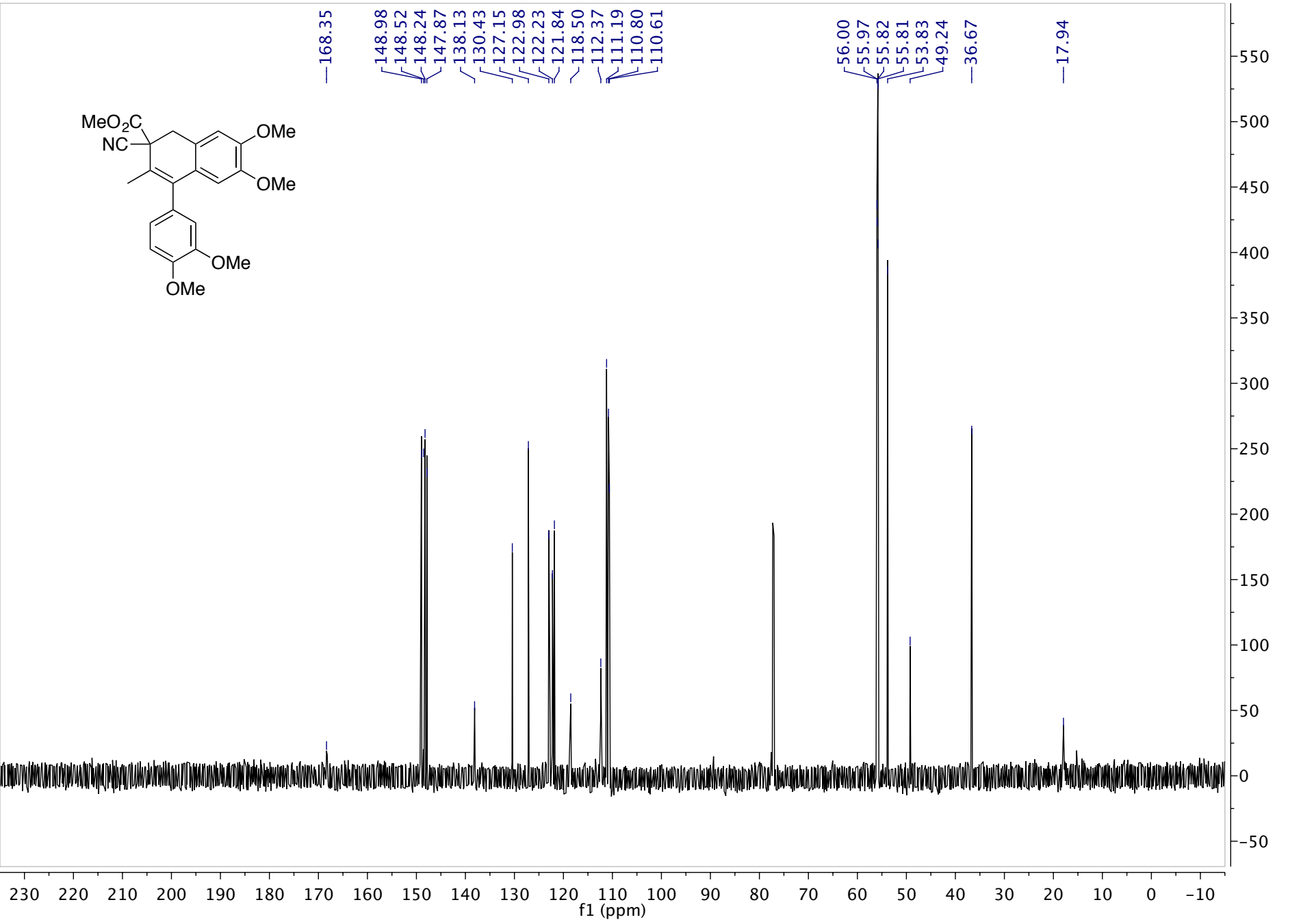
^{13}C spectrum of 4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carbonitrile 6e ($CDCl_3$)



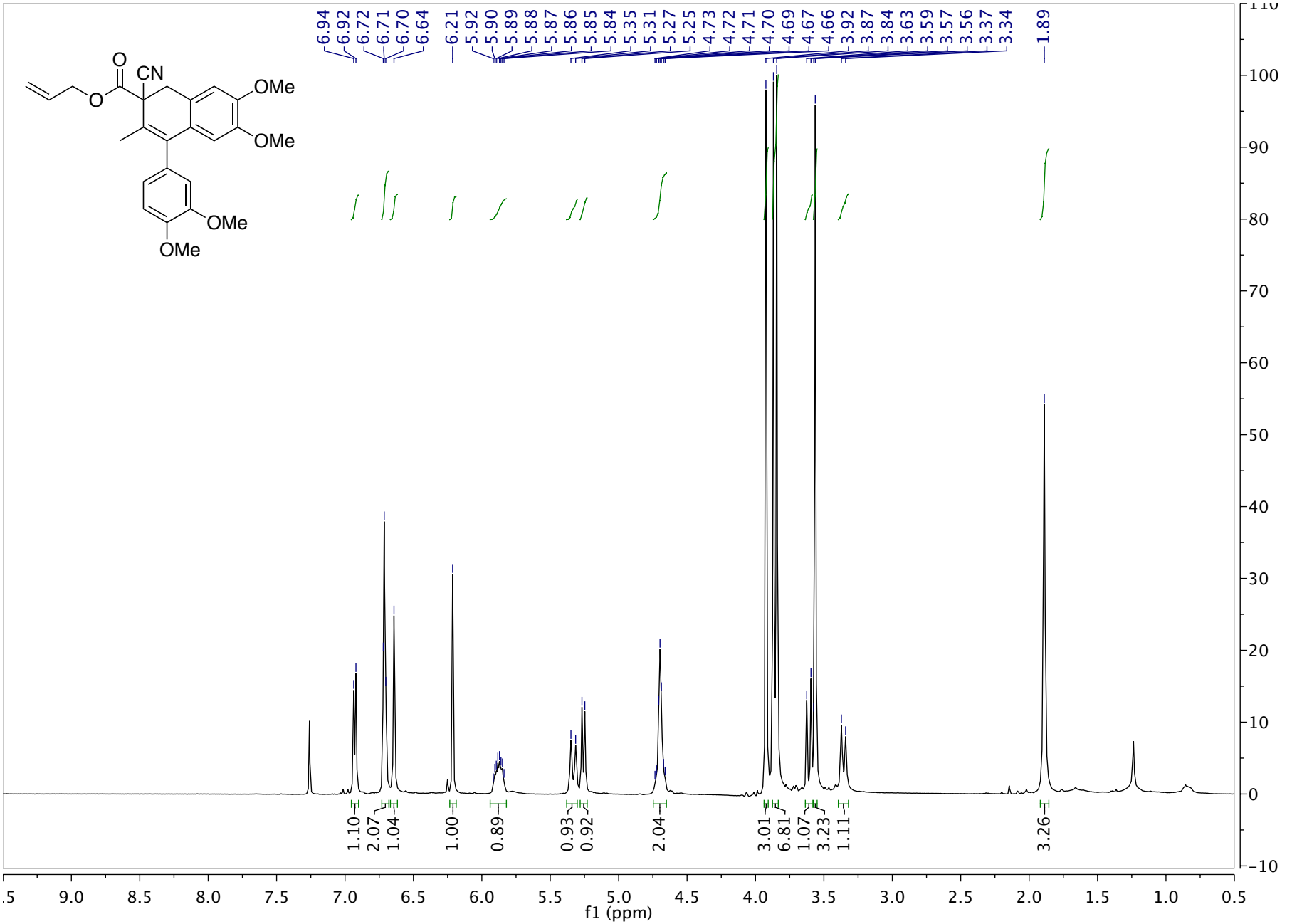
^{1}H spectrum of Methyl 2-cyano-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carboxylate($CDCl_3$)



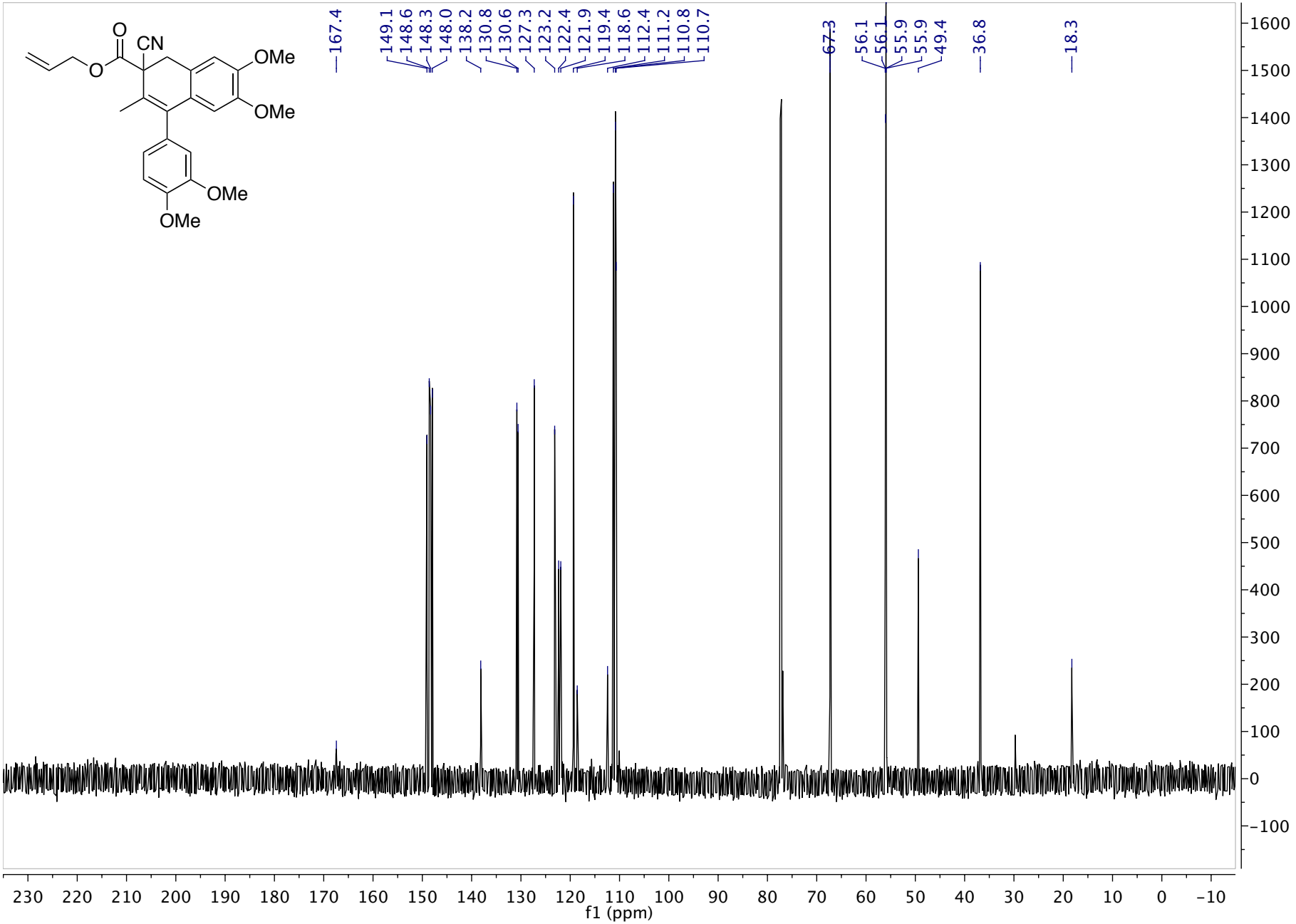
^{13}C spectrum of Methyl 2-cyano-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carboxylate 7a ($CDCl_3$)



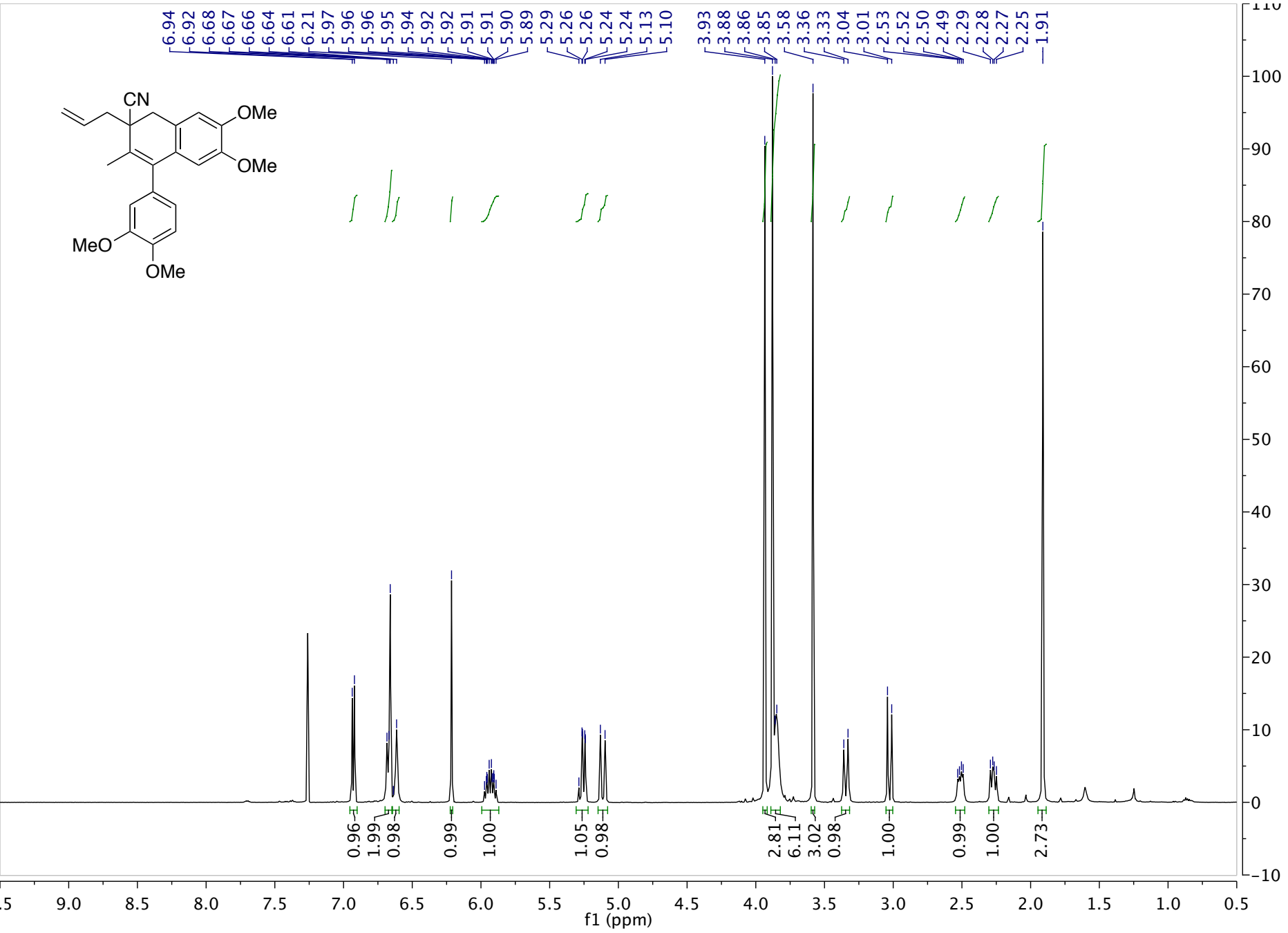
^{1}H spectrum of allyl 2-cyano-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carboxylate 7b ($CDCl_3$)



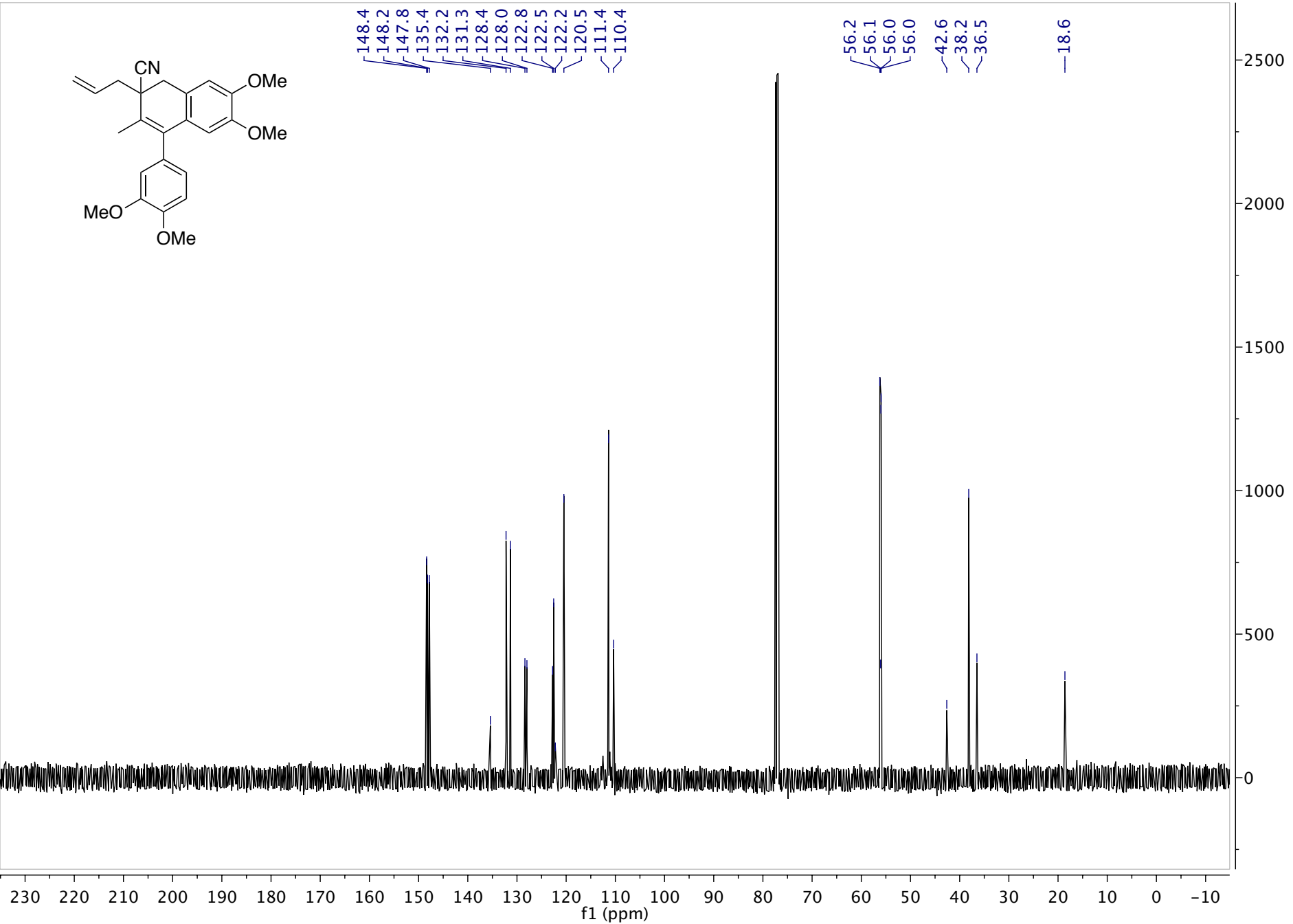
^{13}C spectrum of allyl 2-cyano-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carboxylate 7b ($CDCl_3$)



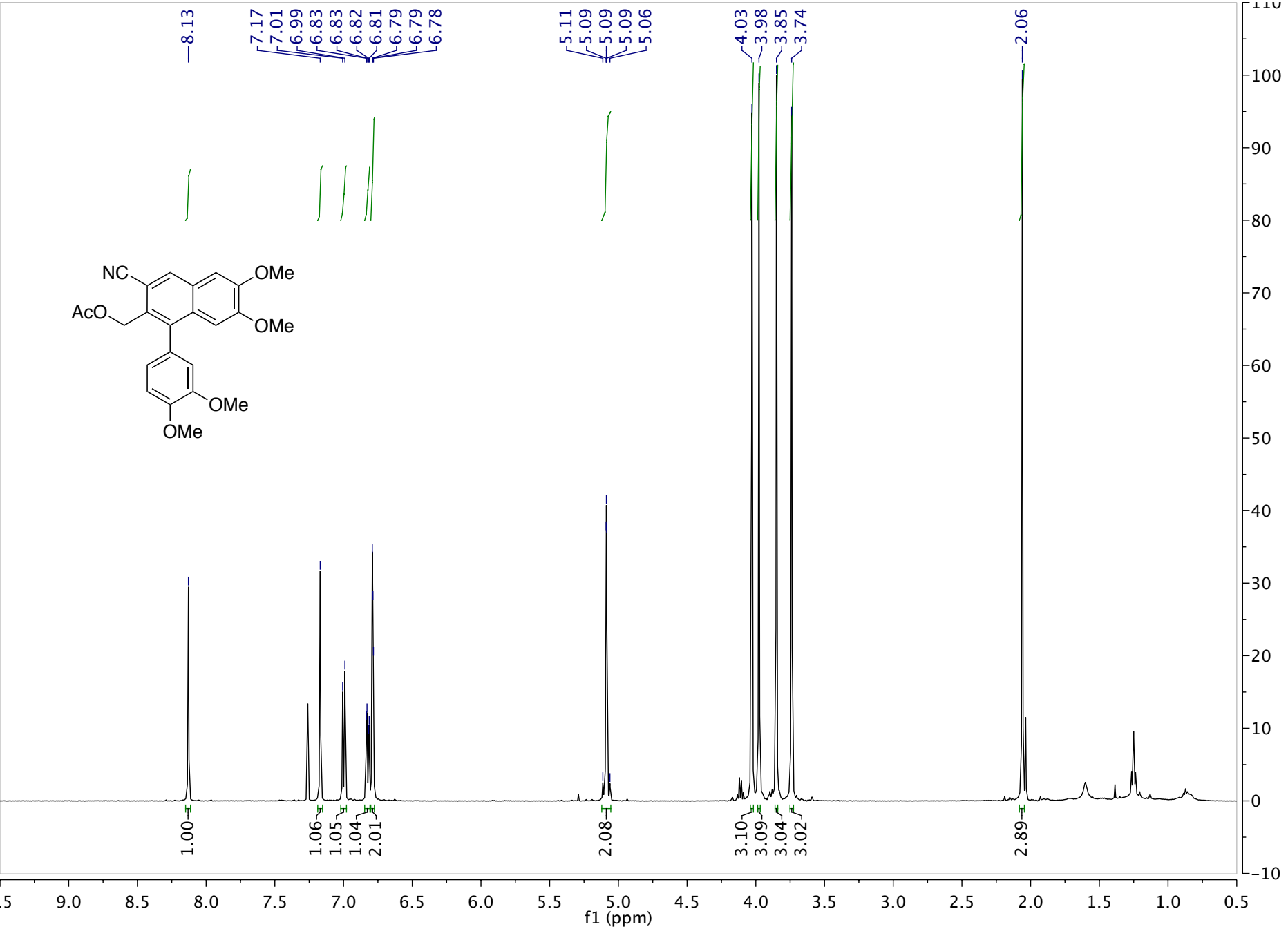
^{1}H spectrum of 2-allyl-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carbonitrile 7c ($CDCl_3$)



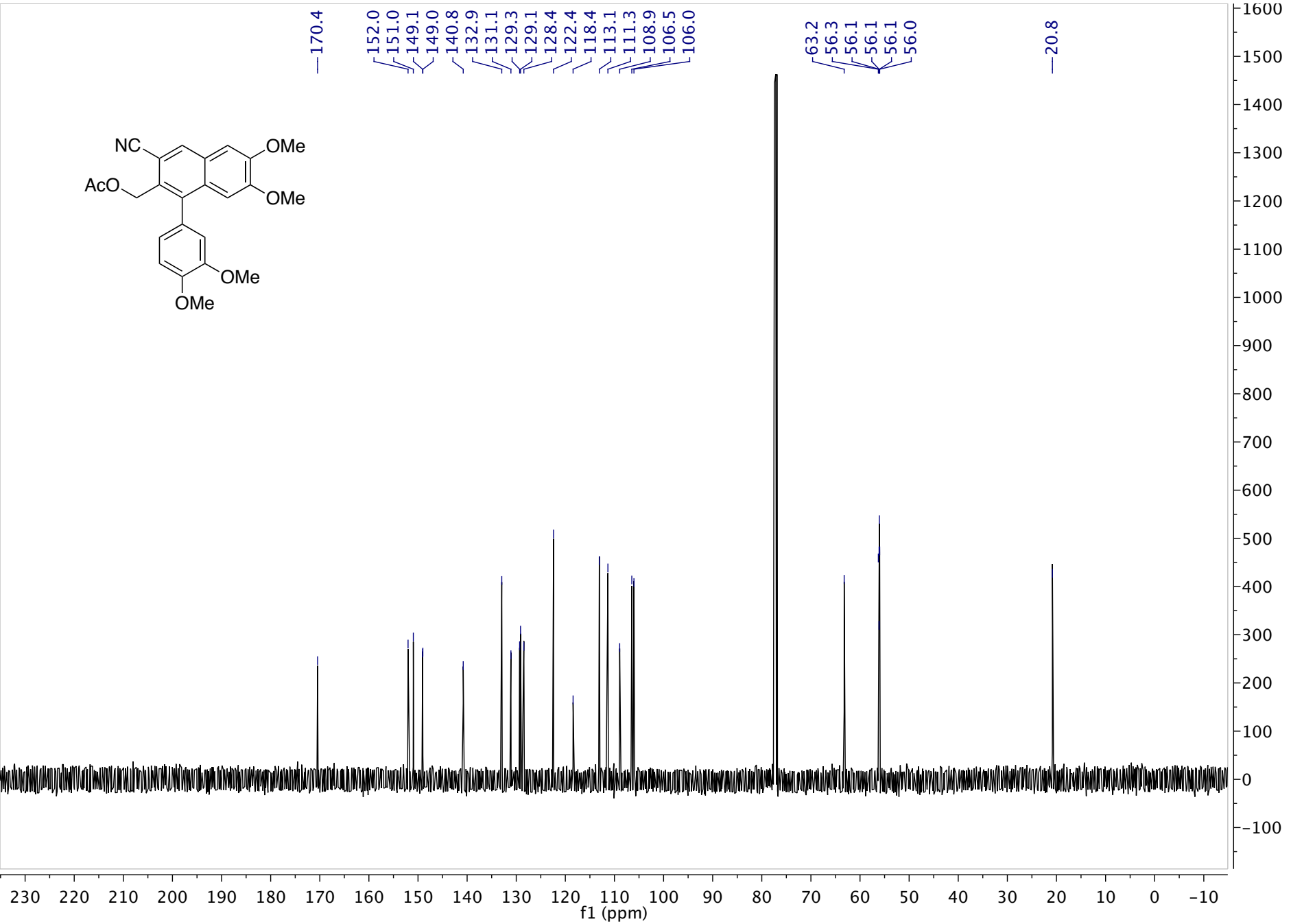
^{13}C spectrum of 2-allyl-4-(3,4-dimethoxyphenyl)-6,7-dimethoxy-3-methyl-1,2-dihydronaphthalene-2-carbonitrile 7c ($CDCl_3$)



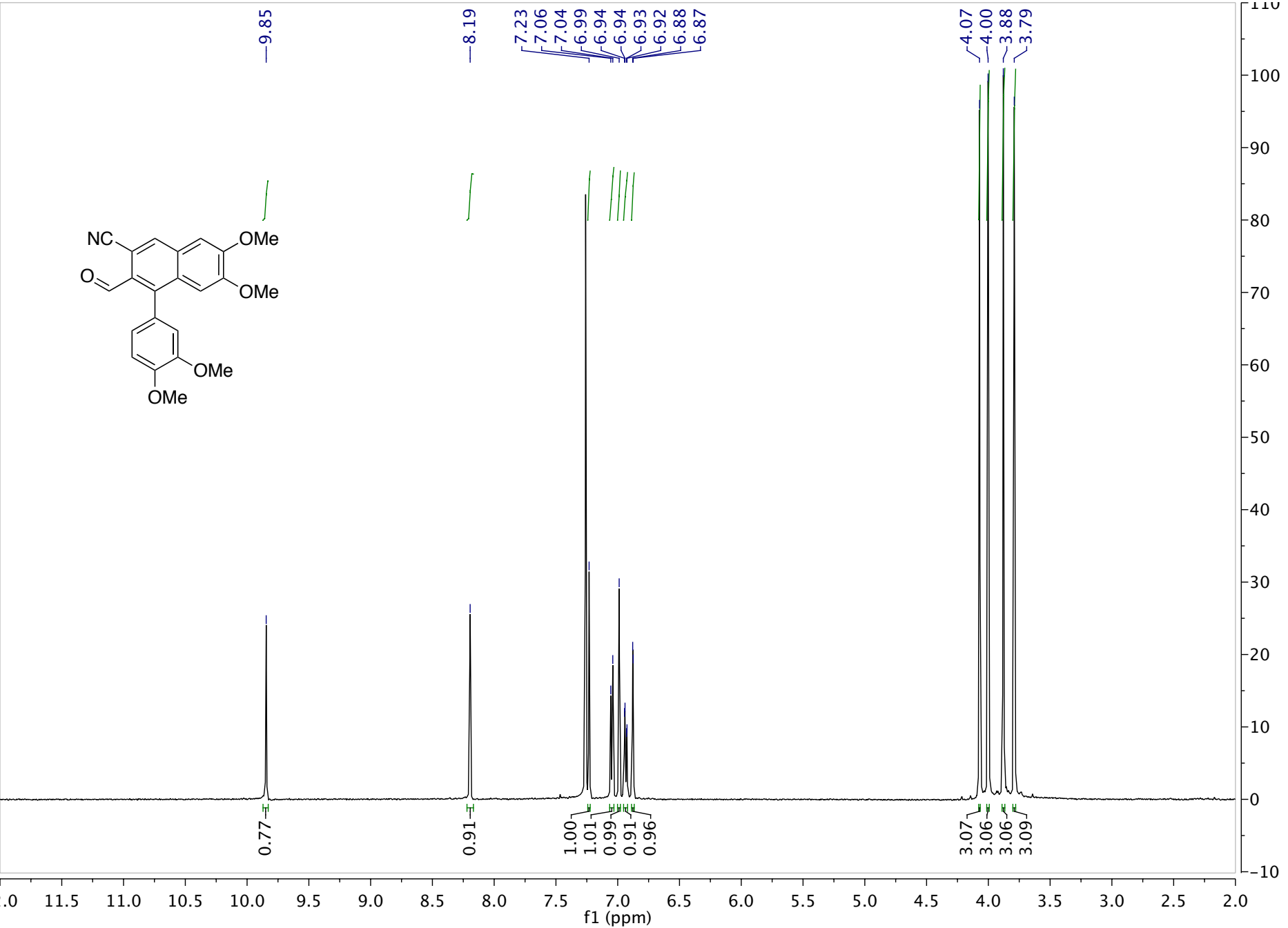
^{1}H spectrum of (3-cyano-1-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalen-2-yl)methyl acetate 7e ($CDCl_3$)



^{13}C spectrum of (3-cyano-1-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalen-2-yl)methyl acetate 7e ($CDCl_3$)



^{1}H spectrum of 4-(3,4-dimethoxyphenyl)-3-formyl-6,7-dimethoxy-2-naphthonitrile 7f ($CDCl_3$)



^{13}C spectrum of 4-(3,4-dimethoxyphenyl)-3-formyl-6,7-dimethoxy-2-naphthonitrile 7f ($CDCl_3$)