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Mn-catalyzed syngas-assisted reductive Knoevenagel condensation

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List of sections

General information

Unless otherwise stated, all substrates and reagents were purchased from commercial suppliers and used without further purification.

Isolation of products was performed using preparative flash chromatograph InterChim PuriFlash; hexane-ethyl acetate binary system was used as an eluent. All details about particular chromatographic parameters are provided with the description of each compound.

^{1}H NMR spectra were recorded in $CDCl_3$ or acetone-d_6 on Varian Inova-400 spectrometer. $^{13}C\{^{1}H\}$ NMR spectra were recorded in $CDCl_3$ or acetone-d_6 on Varian Inova-400 or Bruker Avance 400 spectrometers at 101 MHz. Chemical shifts are reported in parts per million relative to $CHCl_3$ (7.26 and 77.16 ppm for ^{1}H and ^{13}C respectively) or acetone (2.05 and 29.84, 206.26 ppm for ^{1}H and $^{13}C\{^{1}H\}$ respectively). The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet; coupling constants are given in Hertz (Hz).

Analytical gas chromatography (GC) was performed using a Chromatec Crystal 5000.2NP gas chromatograph fitted with a flame ionization detector (He was used as the carrier gas) and a MS detector. Chromatec CR-5MS (30 meters) capillary columns were used.

GC settings for the yield determination using FID detector:

The injector temperature was 250 °C, split ratio of 10:1 at the moment of injection, the FID temperature was 250 °C. Column compartment temperature program: 100°C for 2 min, 100 °C →290 °C at 30 °C/min. Flow rate 1.5 mL/min, column CR5MS.

GC settings for the qualitative analysis using MS detector:

The injector temperature was 250 °C, split ratio of 40:1 at the moment of injection. Column compartment temperature program: 60°C for 2 min, 60°C → 250°C at 30°C/min, 250°C for 1 min. Flow rate 1 mL/min. MSD parameters: ion source temperature 200°C, transfer line temperature 290°C. Retention times (t_R) and integrated ratios were obtained using Chromatec Analytic Software.

All catalytic reactions were carried out using 300 mL stainless steel autoclave. A metal bracket, placed onto a heating plate, was used to ensure proper heating of the autoclave. The reactions were carried out without stirring. The reagents were loaded into glass vials, closed with teflon caps with a small hole and placed into the autoclave.

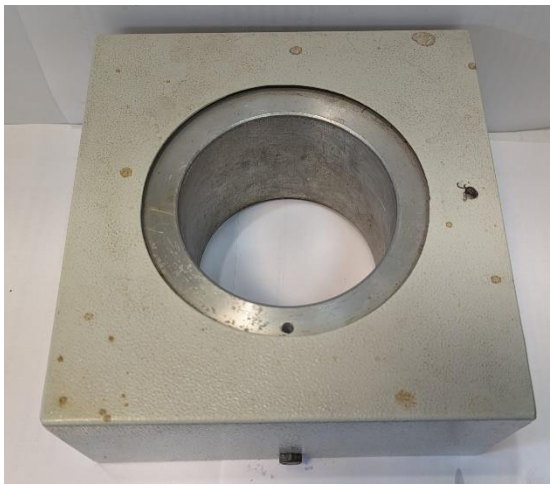


Figure S1. Metal bracket used for proper heating of the autoclave

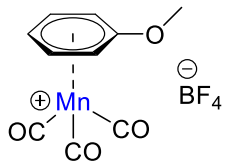
Figure S2. Teflon caps with a small hole

Syngas preparation: to a gas tank with ca. 40 bar of carbon monoxide ca. 40 bar of hydrogen were added (to achieve a total pressure of 80 bar). The tank was equilibrated at room temperature for 24 hours, and the resulting gas mixture was analyzed by GC. The gas was used if H_2:CO ratio was 1-1.2:1. The analysis was repeated periodically, if the ratio was outside the above-mentioned range, it was adjusted by addition of the corresponding gas followed by equilibration and GC analysis.

Experimental section

Synthesis of manganese complex

[(η^6-anisole)Mn(CO)$_3$][BF$_4$] (Mn-1)



Mn-1 complex was synthesized according to the procedure described in the literature, which was modified to obtain the BF_4^- complex[S1].

A mixture of $Mn(CO)_5Br$ (713 mg, 2.6 mmol), $AlCl_3$ (777 mg, 5.8 mmol) and anisole (7 mL) was placed under Ar atmosphere into a foil-wrapped 100 mL round bottom flask, prepared by Schlenk technique. The mixture was heated to 100 °C with reflux condenser equipped with check valve for 4 hours. Then mixture was cooled down to room temperature, transferred into a separatory funnel and 15 mL of ice were added. The funnel was shaken and 20 mL of toluene were added. The mixture was shaken for 3 minutes and the lower aqueous layer was collected. Then it was washed with 15 mL of petroleum ether and an excess of 40% HBF_4 (1.2 mL) was added dropwise under strong stirring, so a yellow precipitate formed. This mixture was cooled down to 5 °C overnight. The resulting precipitate was collected, air-dried without an access of light and washed with 3x5 mL of diethyl ether. The yellow powder was dried under reduced pressure, dissolved in acetone, and this solution was decanted to get rid of undissolved waste. The solution was then placed into a slightly opened 5 mL vial. After 24 h, orange crystals were obtained from the completely evaporated solution (325 mg, 37%).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.15 (dd seems as t, J = 6.7 Hz, 2H), 6.46 (d, J = 7.1 Hz, 2H), 6.29 (t, J = 6.3 Hz, 1H), 4.18 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Acetone-d_6) δ 216.6, 150.9, 106.3, 90.8, 84.0, 58.8.

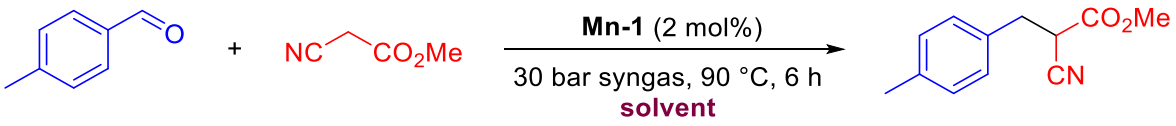
The obtained NMR data are in agreement with the literature report[S2].

Conditions optimization

General procedure for conditions optimization reactions

A glass vial was charged with the corresponding amount of the catalyst (2 mol%), methyl cyanoacetate (100 mol%), carbonyl compound (100 mol%) and solvent. Then the vial was closed with teflon cap with a small hole. Six vials were placed into a 300 ml stainless steel autoclave. The autoclave was sealed, flushed three times with 10 bar of syngas, and then charged with the 30 bar of syngas and placed into a preheated metal bracket. After the indicated time, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane to 5 mL, and then a sample of the resulting solution was analyzed by GC. The yields were determined by GC.

Table S1. Screening of solvents

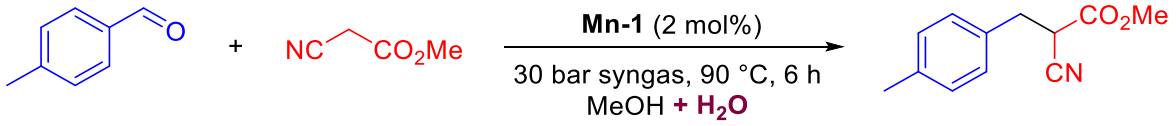


Solvent	Yield, %
Neat	0
Acetone	0
Methyl *tert*-butyl ether	0
Ethyl acetate	0
Dichloromethane	3
Methanol	23[a]

Manganese catalyst **Mn-1** 1.33 mg (4.0 µmol), 17.6 µL (0.2 mmol) methyl cyanoacetate, 23.5 µL (0.2 mmol) 4-methylbenzaldehyde, 100 µL of the corresponding solvent, 30 bar syngas, 90°C inside the reactor, 6 h.

[a]4 experiments

Table S2. Screening of added H_2O amount



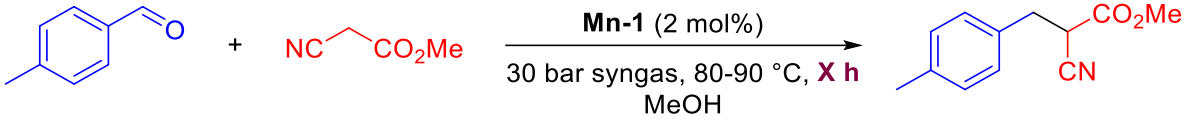
H_2O amount, mol%	Yield, %
0.24[a]	23[b]
200	24
300	25
400	21

Manganese catalyst **Mn-1** 1.33 mg (4.0 µmol), 17.6 µL (0.2 mmol) methyl cyanoacetate, 23.5 µL (0.2 mmol) 4-methylbenzaldehyde, 100 µL of methanol, corresponding amount of water, 30 bar syngas, 90°C inside the reactor, 6 h.

[a]The proportion of water in methanol was measured by Fischer titration

[b]4 experiments

Table S3. Optimization of time of reaction



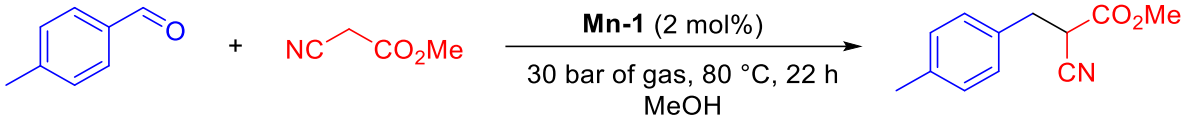
Time, h	Temperature, °C	Yield, %
6	90	23[a]
22	80	48
22	80	49[b]

Manganese catalyst **Mn-1** 1.33 mg (4.0 µmol), 17.6 µL (0.2 mmol) methyl cyanoacetate, 23.5 µL (0.2 mmol) 4-methylbenzaldehyde, 100 µL of methanol, 30 bar syngas, 80-90°C inside the reactor, 6-22 h.

[a]4 experiments

[b]200 mol% of water was added

Table S4. Reaction with other gases instead of syngas



Gas	Yield, %
15 atm H_2 + 15 atm CO	48
H_2	7
CO	2

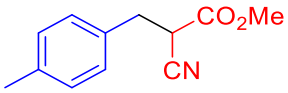
Manganese catalyst **Mn-1** 1.33 mg (4.0 µmol), 17.6 µL (0.2 mmol) methyl cyanoacetate, 23.5 µL (0.2 mmol) 4-methylbenzaldehyde, 100 µL of methanol, 30 bar of gas, 80°C inside the reactor, 22 h.

Characterization of products

General procedure of reductive alkylation by cyanoacetate

A glass vial was charged with corresponding amount of the catalyst (5 mol%), methyl cyanoacetate (100 mol%), carbonyl compound (100 mol%) and solvent. Then vial was closed with teflon cap with a small hole. Six vials were placed into a 300 ml stainless steel autoclave. The autoclave was sealed, flushed three times with 10 bar of syngas, and then charged with the 30 bar of syngas and placed into a preheated metal bracket. After 22 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a measuring flask and diluted with dichloromethane. In order to get rid of catalyst reaction mixture was passed through a small pad of silica gel; combined solvents were removed on a rotary evaporator. The yield of the product was determined by ^{1}H NMR. The residue was purified using preparative flash chromatograph InterChim PuriFlash or standard column chromatography.

Methyl 2-cyano-3-(*p*-tolyl)propanoate (1)



1

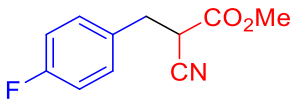
Catalyst **Mn-1** (3.34 mg, 5 mol%, 0.01 mmol), methyl cyanoacetate (17.6 µL, 100 mol%, 0.2 mmol), 4-methylbenzaldehyde (23.6 µL, 100 mol%, 0.2 mmol) and 150 µL of methanol were added into the glass vial. Then the vial was closed with teflon cap with a small hole and placed into a 300 mL stainless steel autoclave. The autoclave then was sealed, flushed three times with 10 atm of syngas and then charged with 30 atm of syngas and placed into a preheated to 110°C metal bracket (to achieve 90°C inside autoclave). After 22 h of heating, the reactor was cooled from 90°C to room temperature and depressurized. The reaction mixture was then diluted with 2 mL of dichloromethane. In order to get rid of catalyst reaction mixture was passed through a small pad of silica gel and washed with 4 mL of 5:1 (hexane-ethyl acetate) mixture. Combined solvents were removed on a rotary evaporator. NMR yield of methyl 2-cyano-3-(*p*-tolyl)propanoate was 63%. The residue was purified using column chromatography in 7:1 (hexane-ethyl acetate) binary system (Rf = 0.2) to afford 21 mg (53%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.15 (s, 4H), 3.79 (s, 3H), 3.74 – 3.68 (m, 1H), 3.24 (dd, *J* = 13.6, 5.7 Hz, 1H), 3.16 (dd, *J* = 13.6, 8.4 Hz, 1H), 2.34 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ 166.2, 137.7, 132.3, 129.7, 129.0, 116.2, 53.6, 39.8, 35.6, 21.2.

NMR spectra are in agreement with the literature date[53].

Methyl 2-cyano-3-(4-fluorophenyl)propanoate (2)



2

Catalyst **Mn-1** (6.68 mg, 5 mol%, 0.02 mmol), methyl cyanoacetate (35.3 µL, 100 mol%, 0.4 mmol), 4-fluorobenzaldehyde (42.2 µL, 100 mol%, 0.4 mmol) and 300 µL of methanol were added into the glass vial. Then the vial was closed with teflon cap with a small hole and placed into a 300 mL stainless steel autoclave. The autoclave then was sealed, flushed three times with 10 atm of syngas and then charged with 30 atm of syngas and placed into a preheated to 110°C metal bracket (to achieve 90°C inside

autoclave). After 22 h of heating, the reactor was cooled from 90°C to room temperature and depressurized. The reaction mixture was then diluted with 2 mL of dichloromethane. In order to get rid of catalyst reaction mixture was passed through a small pad of silica gel and washed with 4 mL of 5:1 (hexane-ethyl acetate) mixture. Combined solvents were removed on a rotary evaporator. NMR yield of methyl 2-cyano-3-(4-fluorophenyl)propanoate was 61%. The residue was purified using column chromatography in 7:1 (hexane-ethyl acetate) binary system (Rf = 0.11) to afford 50 mg (60%) as a colorless oil.

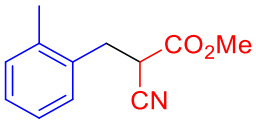
^{1}H NMR (400 MHz, Chloroform-d) δ 7.24 (dd, *J* = 8.5, 5.6 Hz, 2H), 7.03 (t, *J* = 8.5 Hz, 2H), 3.79 (s, 2H), 3.72 (dd, *J* = 8.0, 5.9 Hz, 1H), 3.25 (dd, *J* = 14.0, 5.9 Hz, 1H), 3.17 (dd, *J* = 14.0, 8.0 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ 164.8 (d, *J* = 222.6 Hz), 161.3, 131.0 (d, *J* = 3.3 Hz), 130.8 (d, *J* = 8.5 Hz), 116.0, 115.9 (d, *J* = 21.5 Hz), 53.7, 39.6, 35.0.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.4 (tt, *J* = 8.7, 5.3, 4.4 Hz)

NMR spectra are in agreement with the literature date[S3].

Methyl 2-cyano-3-(*o*-tolyl)propanoate (3)



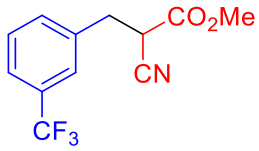
3

Catalyst **Mn-1** (6.68 mg, 5 mol%, 0.02 mmol), methyl cyanoacetate (35.3 µL, 100 mol%, 0.4 mmol), 2-methylbenzaldehyde (46.6 µL, 100 mol%, 0.4 mmol) and 300 µL of methanol were added into the glass vial. Then the vial was closed with teflon cap with a small hole and placed into a 300 mL stainless steel autoclave. The autoclave then was sealed, flushed three times with 10 atm of syngas and then charged with 30 atm of syngas and placed into a preheated to 110°C metal bracket (to achieve 90°C inside autoclave). After 22 h of heating, the reactor was cooled from 90°C to room temperature and depressurized. The reaction mixture was then diluted with 2 mL of dichloromethane. In order to get rid of catalyst reaction mixture was passed through a small pad of silica gel and washed with 4 mL of 5:1 (hexane-ethyl acetate) mixture. Combined solvents were removed on a rotary evaporator. NMR yield of methyl 2-cyano-3-(o-tolyl)propanoate was 59%. The residue was purified using column chromatography in 9:1 (hexane-ethyl acetate) binary system (Rf = 0.15) to afford 37 mg (46%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.20 (s, 4H), 3.82 (s, 3H), 3.70 (dd, *J* = 9.6, 5.8 Hz, 1H), 3.35 (dd, *J* = 14.1, 5.8 Hz, 1H), 3.19 (dd, *J* = 14.1, 9.6 Hz, 1H), 2.37 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ 166.3, 136.3, 133.7, 130.9, 129.7, 128.0, 126.6, 116.2, 53.7, 38.4, 33.2, 19.3.

Methyl 2-cyano-3-[3-(trifluoromethyl)phenyl]propanoate (4)



4

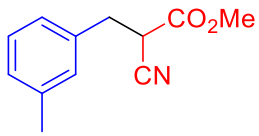
Catalyst **Mn-1** (6.68 mg, 5 mol%, 0.02 mmol), methyl cyanoacetate (35.3 µL, 100 mol%, 0.4 mmol), 3-(trifluoromethyl)benzaldehyde (53.5 µL, 100 mol%, 0.4 mmol) and 300 µL of methanol were added into the glass vial. Then the vial was closed with teflon cap with a small hole and placed into a 300 mL stainless steel autoclave. The autoclave then was sealed, flushed three times with 10 atm of syngas and then charged with 30 atm of syngas and placed into a preheated to 110°C metal bracket (to achieve 90°C inside autoclave). After 22 h of heating, the reactor was cooled from 90°C to room temperature and depressurized. The reaction mixture was then diluted with 2 mL of dichloromethane. In order to get rid of catalyst reaction mixture was passed through a small pad of silica gel and washed with 4 mL of 5:1 (hexane-ethyl acetate) mixture. Combined solvents were removed on a rotary evaporator. NMR yield of methyl 2-cyano-3-(3-(trifluoromethyl)phenyl)propanoate was 70%. The residue was purified using column chromatography in 9:1 (hexane-ethyl acetate) binary system (Rf = 0.14) to afford 57 mg (55%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.61 – 7.55 (m, 1H), 7.54 – 7.45 (m, 3H), 3.82 – 3.75 (m, 4H), 3.34 (dd, *J* = 14.0, 5.8 Hz, 1H), 3.27 (dd, *J* = 14.0, 8.2 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ 165.7, 136.2, 132.7 (d, *J* = 1.6 Hz), 131.4 (q, *J* = 32.5 Hz), 129.6, 126.0 (q, *J* = 3.8 Hz), 124.9 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.3 Hz), 115.7, 53.8, 39.3, 35.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.8.

Methyl 2-cyano-3-(*m*-tolyl)propanoate (5)



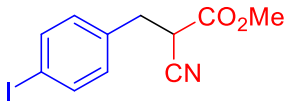
5

Catalyst **Mn-1** (6.68 mg, 5 mol%, 0.02 mmol), methyl cyanoacetate (35.3 µL, 100 mol%, 0.4 mmol), 3-methylbenzaldehyde (47.1 µL, 100 mol%, 0.4 mmol) and 300 µL of methanol were added into the glass vial. Then the vial was closed with teflon cap with a small hole and placed into a 300 mL stainless steel autoclave. The autoclave then was sealed, flushed three times with 10 atm of syngas and then charged with 30 atm of syngas and placed into a preheated to 110°C metal bracket (to achieve 90°C inside autoclave). After 22 h of heating, the reactor was cooled from 90°C to room temperature and depressurized. The reaction mixture was then diluted with 2 mL of dichloromethane. In order to get rid of catalyst reaction mixture was passed through a small pad of silica gel and washed with 4 mL of 5:1 (hexane-ethyl acetate) mixture. Combined solvents were removed on a rotary evaporator. NMR yield of methyl 2-cyano-3-(m-tolyl)propanoate was 51%. The residue was purified using column chromatography in 9:1 (hexane-ethyl acetate) binary system (Rf = 0.28) to afford 40 mg (49%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.22 (t, *J* = 7.6 Hz, 1H), 7.13 – 7.01 (m, 3H), 3.78 (s, 3H), 3.72 (t, *J* = 5.6 Hz, 1H), 3.23 (dd, *J* = 13.8, 5.6 Hz, 1H), 3.13 (dd, *J* = 13.8, 8.9 Hz, 1H), 2.34 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-d) δ 166.2, 138.7, 135.3, 129.8, 128.9, 128.7, 126.1, 116.2, 53.6, 39.7, 35.8, 21.5.

Methyl 2-cyano-3-(4-iodophenyl)propanoate (6)



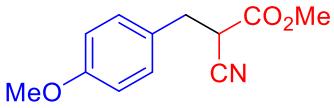
6

Catalyst **Mn-1** (3.34 mg, 5 mol%, 0.01 mmol), methyl cyanoacetate (17.6 µL, 100 mol%, 0.2 mmol), 4-iodobenzaldehyde (46.2 mg, 100 mol%, 0.2 mmol) and 150 µL of methanol were added into the glass vial. Then the vial was closed with teflon cap with a small hole and placed into a 300 mL stainless steel autoclave. The autoclave then was sealed, flushed three times with 10 atm of syngas and then charged with 30 atm of syngas and placed into a preheated to 110°C metal bracket (to achieve 90°C inside autoclave). After 22 h of heating, the reactor was cooled from 90°C to room temperature and depressurized. The reaction mixture was then diluted with 2 mL of dichloromethane. In order to get rid of catalyst reaction mixture was passed through a small pad of silica gel and washed with 3 mL of 5:1 (hexane-ethyl acetate) mixture. Combined solvents were removed on a rotary evaporator. NMR yield of methyl 2-cyano-3-(4-iodophenyl)propanoate was 70%. The residue was purified using column chromatography in hexane-ethyl acetate binary system (gradient 6:1 hexane-ethyl acetate to 4:1 hexane-ethyl acetate for 30 min, Rf 0.19 in 6:1 hexane-ethyl acetate) to afford 37 mg (59%) as a colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.2 Hz, 2H), 3.79 (s, 3H), 3.72 (dd, *J* = 8.2, 5.7 Hz, 1H), 3.21 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.14 (dd, *J* = 13.9, 8.2 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, Chloroform-d) δ 165.8, 138.1, 134.9, 131.1, 115.9, 93.7, 53.8, 39.3, 35.2.

Methyl 2-cyano-3-(4-methoxyphenyl)propanoate (7)



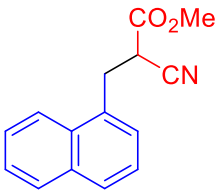
7

Catalyst **Mn-1** (6.68 mg, 5 mol%, 0.02 mmol), methyl cyanoacetate (35.3 µL, 100 mol%, 0.4 mmol), 4-methoxybenzaldehyde (48.6 mg, 100 mol%, 0.4 mmol) and 300 µL of methanol were added into the glass vial. Then the vial was closed with teflon cap with a small hole and placed into a 300 mL stainless steel autoclave. The autoclave then was sealed, flushed three times with 10 atm of syngas and then charged with 30 atm of syngas and placed into a preheated to 110°C metal bracket (to achieve 90°C inside autoclave). After 22 h of heating, the reactor was cooled from 90°C to room temperature and depressurized. The reaction mixture was then diluted with 2 mL of dichloromethane. In order to get rid of catalyst reaction mixture was passed through a small pad of silica gel and washed with 4 mL of 5:1 (hexane-ethyl acetate) mixture. Combined solvents were removed on a rotary evaporator. NMR yield of methyl 2-cyano-3-(4-methoxyphenyl)propanoate was 39%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 3.79 (s, 3H), 3.78 (s, 3H), 3.70 (dd, *J* = 8.2, 5.7 Hz, 1H), 3.22 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.14 (dd, *J* = 13.9, 8.2 Hz, 1H).

NMR spectra are in agreement with the literature date[S4].

Methyl 2-cyano-3-(naphthalen-1-yl)propanoate (8)



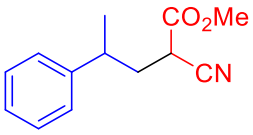
8

Catalyst **Mn-1** (6.68 mg, 5 mol%, 0.02 mmol), methyl cyanoacetate (35.3 µL, 100 mol%, 0.4 mmol), 1-naphthaldehyde (54.3 mg, 100 mol%, 0.4 mmol) and 300 µL of methanol were added into the glass vial. Then the vial was closed with teflon cap with a small hole and placed into a 300 mL stainless steel autoclave. The autoclave then was sealed, flushed three times with 10 atm of syngas and then charged with 30 atm of syngas and placed into a preheated to 110°C metal bracket (to achieve 90°C inside autoclave). After 22 h of heating, the reactor was cooled from 90°C to room temperature and depressurized. The reaction mixture was then diluted with 2 mL of dichloromethane. In order to get rid of catalyst reaction mixture was passed through a small pad of silica gel and washed with 4 mL of 5:1 (hexane-ethyl acetate) mixture. Combined solvents were removed on a rotary evaporator. NMR yield of methyl 2-cyano-3-(naphthalen-1-yl)propanoate was 39%.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.87 (m, 2H), 7.83 (dd, *J* = 8.1 Hz, 1H), 7.67 – 7.42 (m, 4H), 3.95 – 3.88 (m, 2H), 3.82 (s, 3H), 3.53 (dd, *J* = 15.4, 10.8 Hz, 1H).

NMR spectra are in agreement with the literature date[S5].

Methyl 2-cyano-4-phenylpentanoate (9)



9

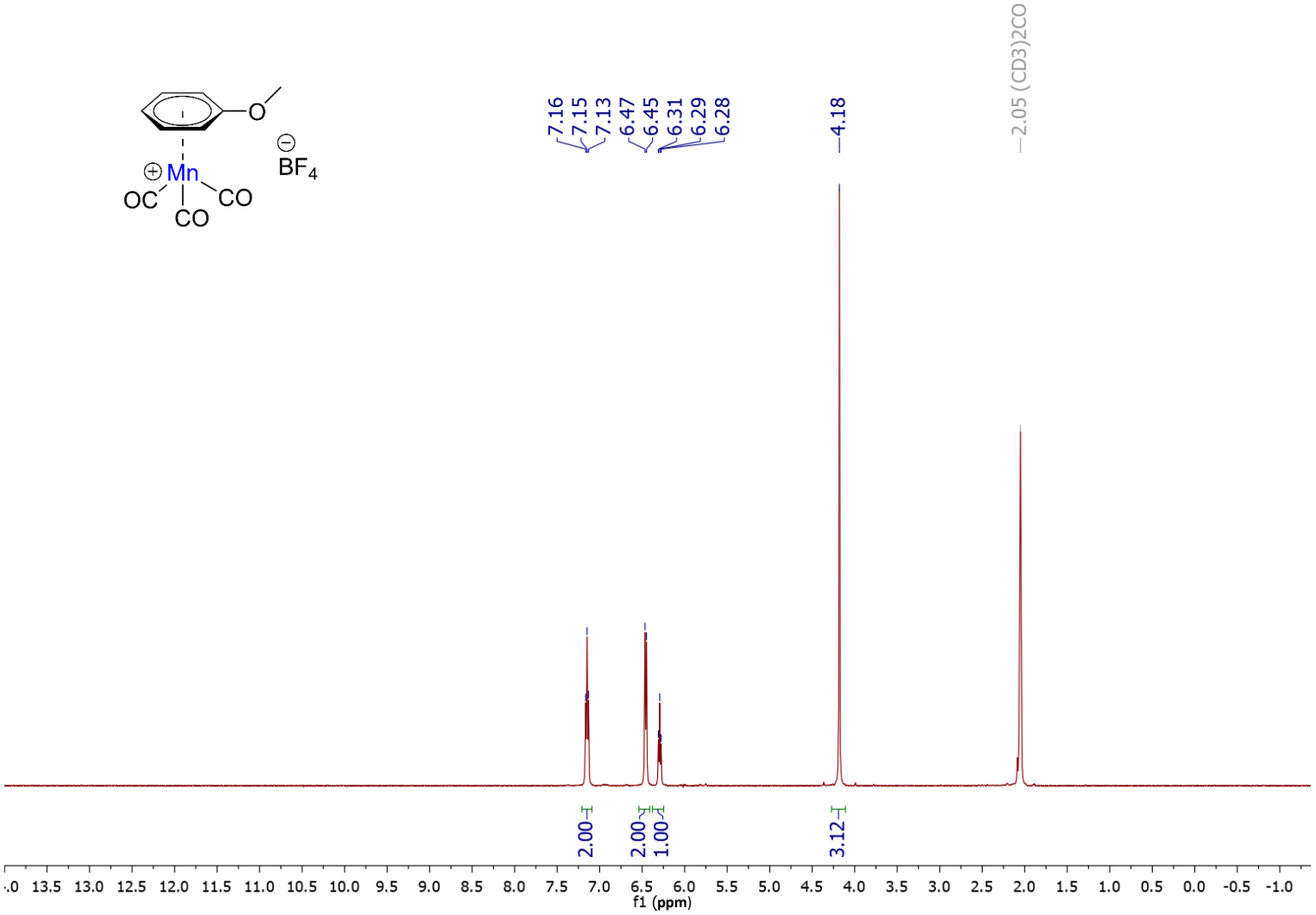
Catalyst **Mn-1** (6.68 mg, 5 mol%, 0.02 mmol), methyl cyanoacetate (35.3 µL, 100 mol%, 0.4 mmol), 2-phenylpropanal (53.6 µL, 100 mol%, 0.4 mmol) and 300 µL of methanol were added into the glass vial. Then the vial was closed with teflon cap with a small hole and placed into a 300 mL stainless steel autoclave. The autoclave then was sealed, flushed three times with 10 atm of syngas and then charged with 30 atm of syngas and placed into a preheated to 110°C metal bracket (to achieve 90°C inside autoclave). After 22 h of heating, the reactor was cooled from 90°C to room temperature and depressurized. The reaction mixture was then diluted with 2 mL of dichloromethane. In order to get rid of catalyst reaction mixture was passed through a small pad of silica gel and washed with 4 mL of 5:1 (hexane-ethyl acetate) mixture. Combined solvents were removed on a rotary evaporator. NMR yield of methyl 2-cyano-4-phenylpentanoate was 42% with diastereomeric ratio 1:1.4.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.18 (m, 5H), 3.74 (s, 3H), 3.40 (dd seems as t, *J* = 7.2 Hz, 1H) 3.14 – 2.90 (m, 1H), 2.27 – 2.15 (m, 2H), 1.34 (d, *J* = 6.9 Hz, 3H).

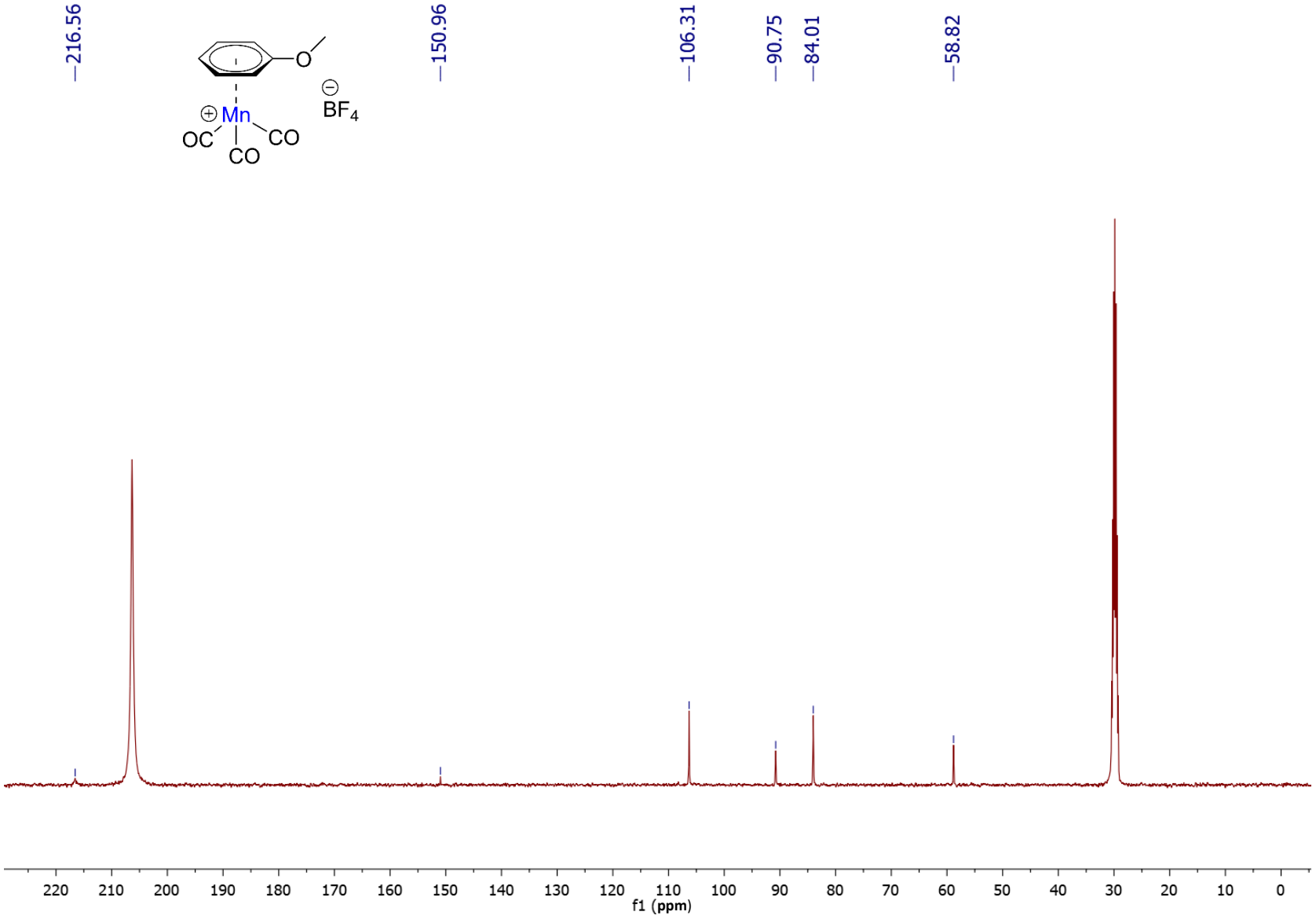
^{1}H, ^{13}C, ^{19}F NMR spectra of obtained compounds

NMR spectra of manganese complexes

^{1}H spectrum of [(η^{6}-anisole)Mn(CO)$_3$][BF$_4$] (Mn-1) (Acetone-d_6, 400 MHz)

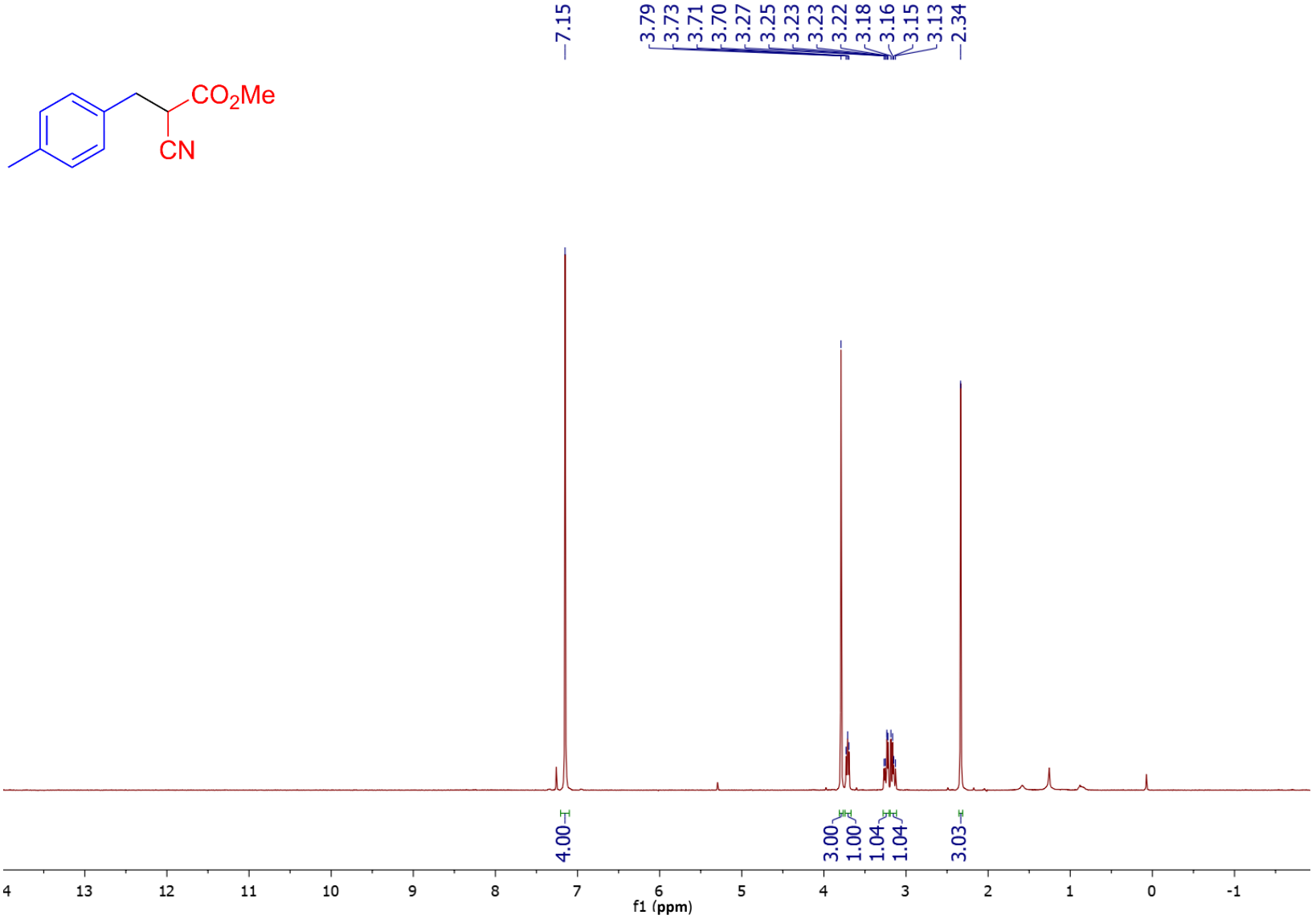


$^{13}C\{^{1}H\}$ spectrum of [(η^6-anisole)Mn(CO)$_3$][BF_4] (Mn-1) (Acetone-d_6, 101 MHz)

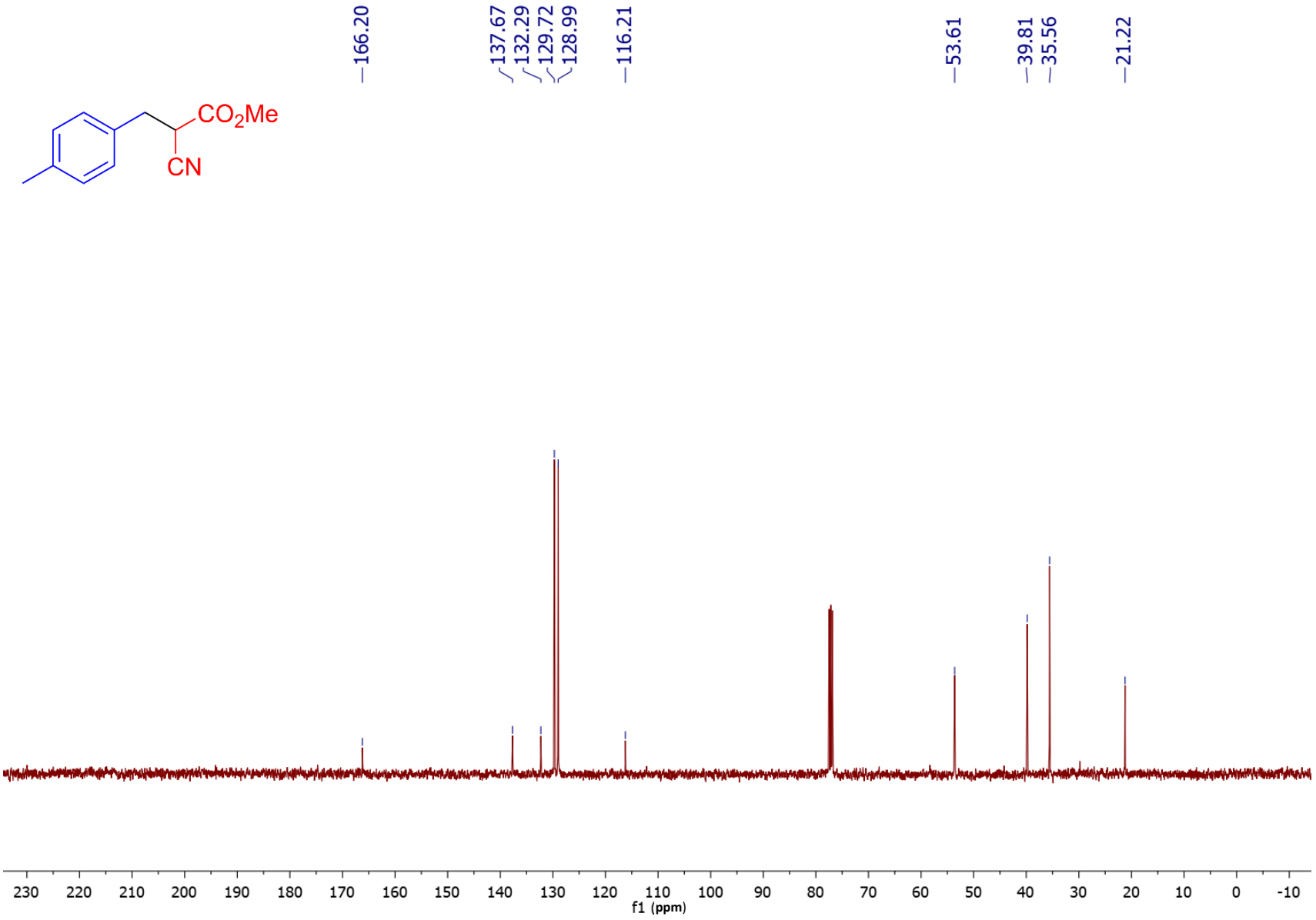


NMR spectra of products

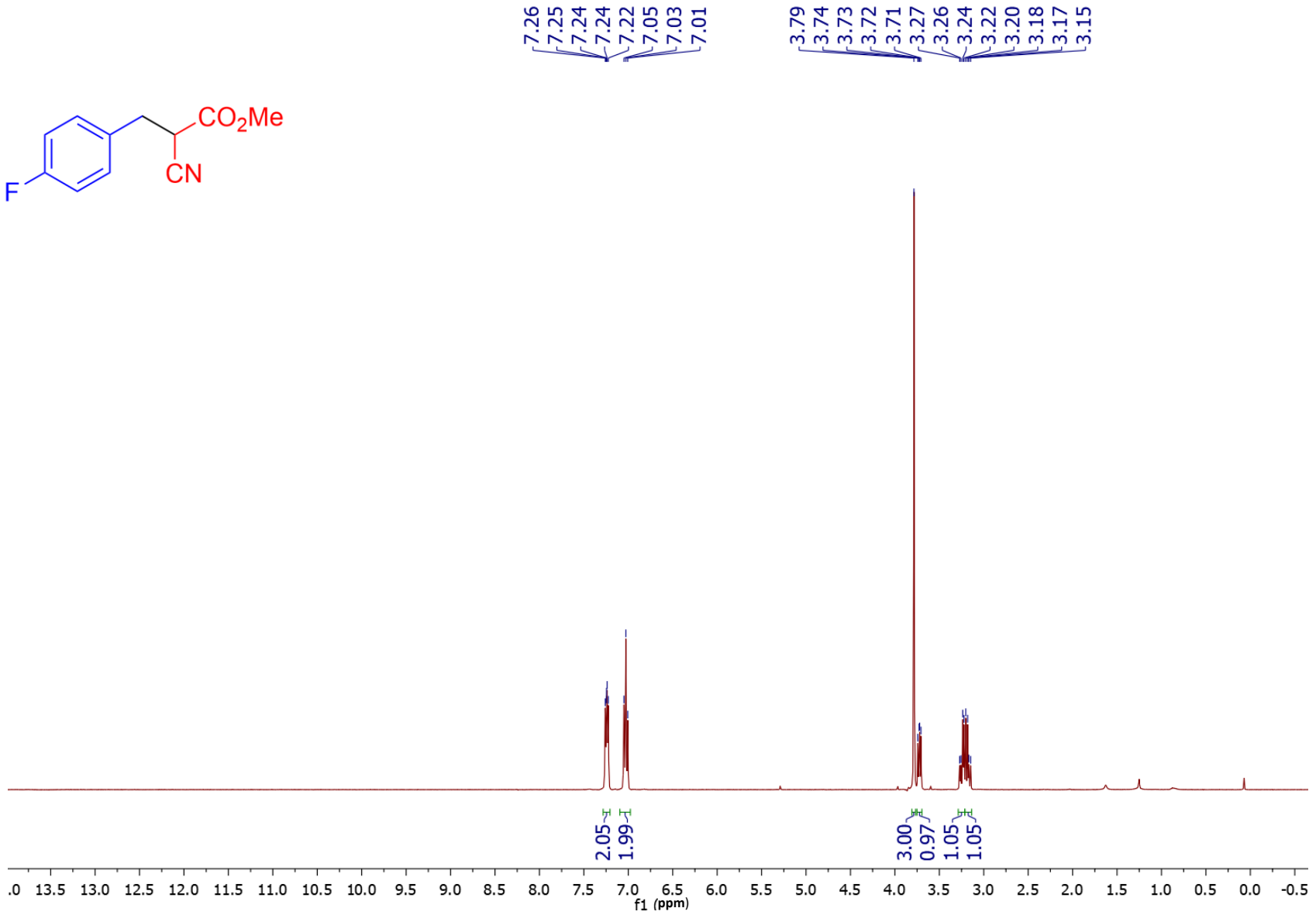
^{1}H spectrum of methyl 2-cyano-3-(*p*-tolyl)propanoate (1) ($CDCl_3$, 400 MHz)



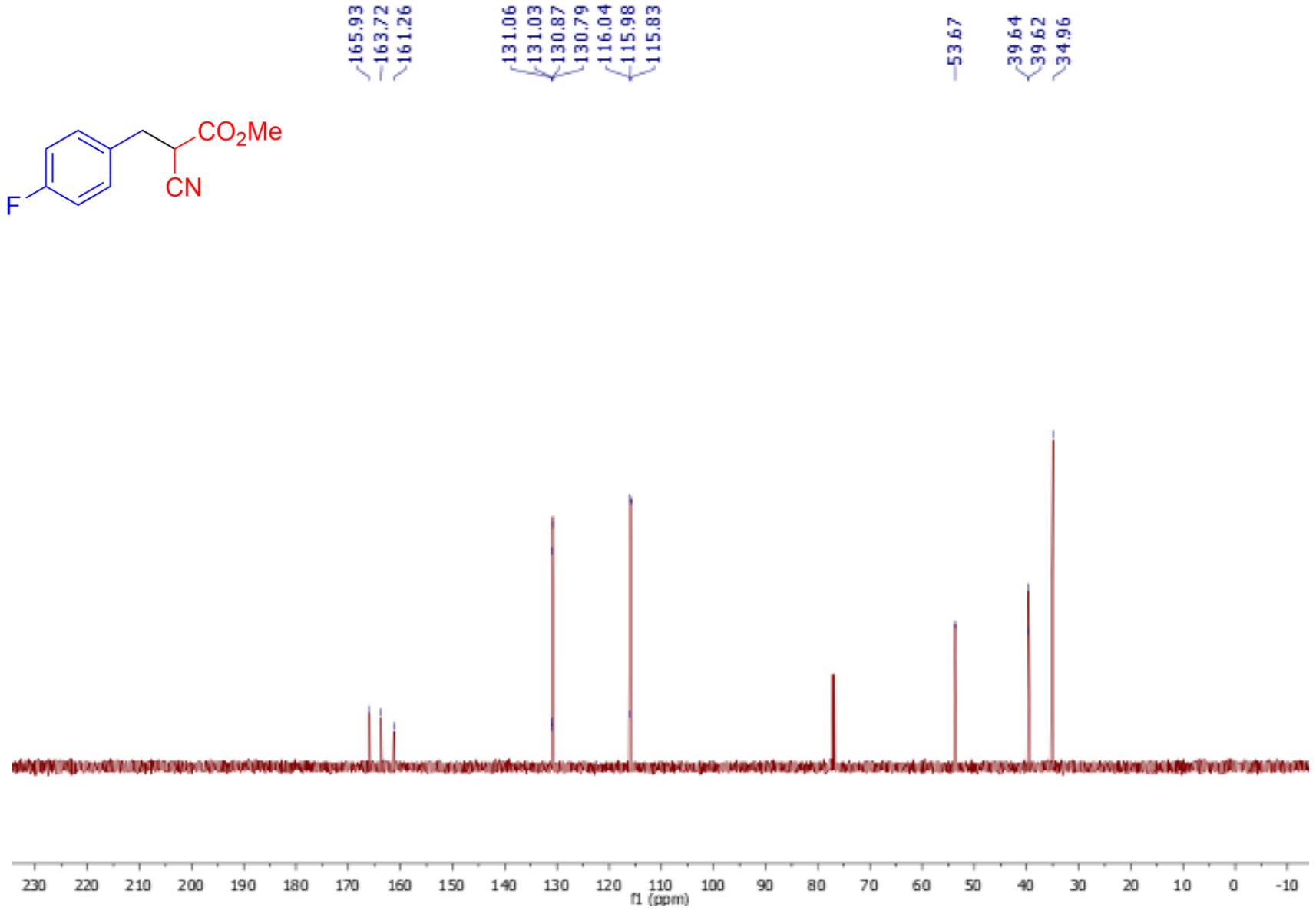
$^{13}C\{^{1}H\}$ spectrum of methyl 2-cyano-3-(*p*-tolyl)propanoate (1) ($CDCl_3$, 101 MHz)



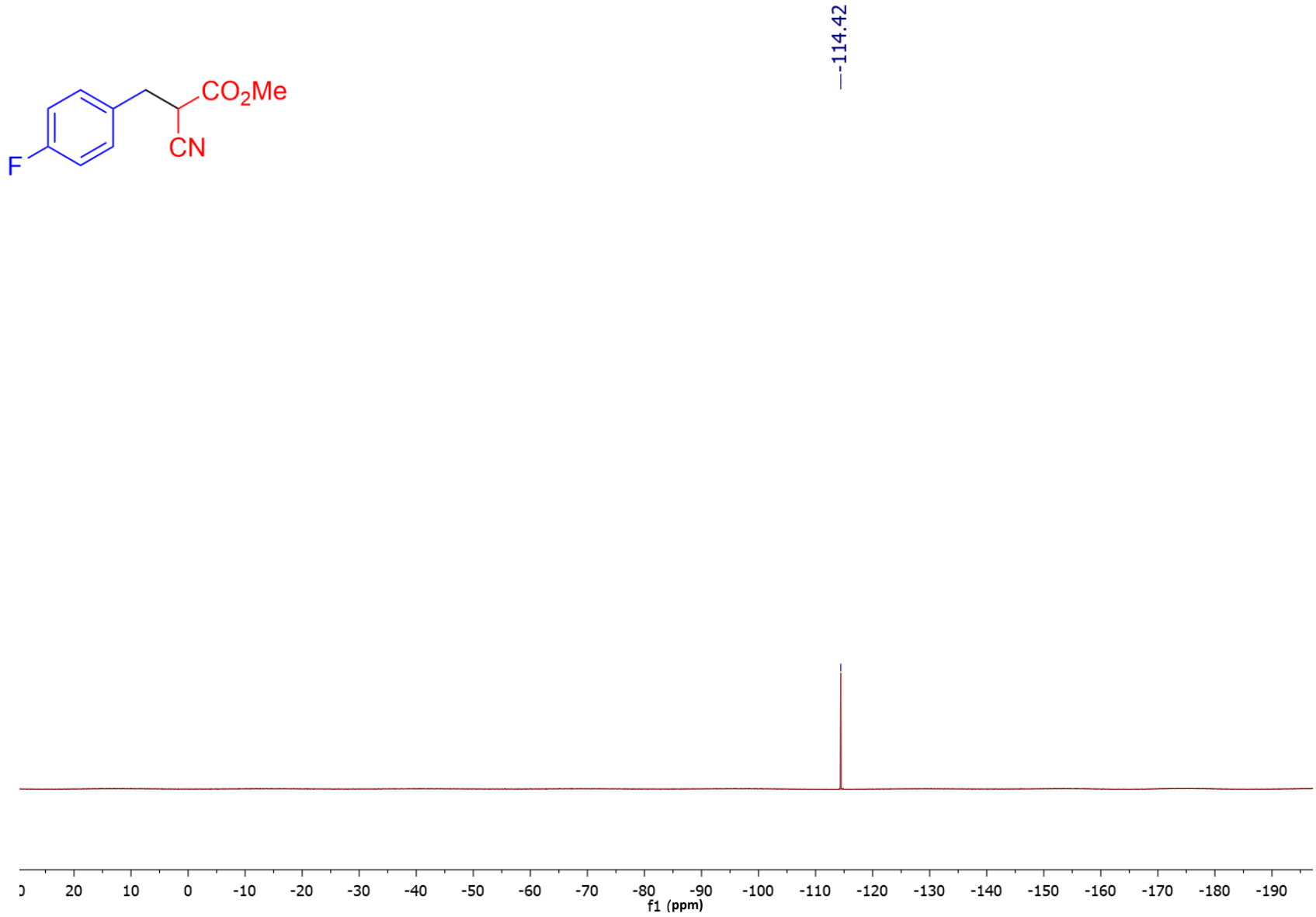
^{1}H spectrum of methyl 2-cyano-3-(4-fluorophenyl)propanoate (2) ($CDCl_3$, 400 MHz)



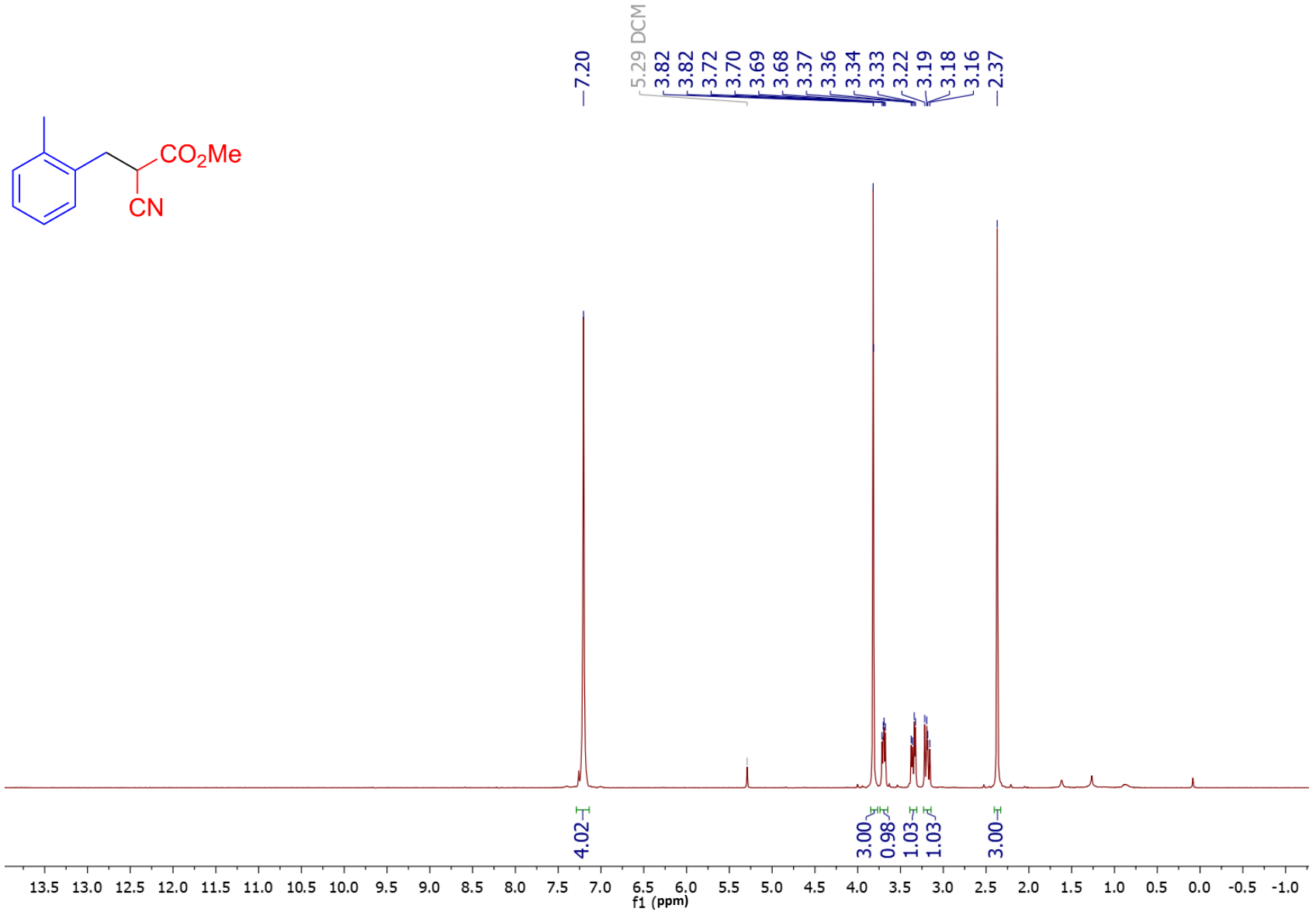
$^{13}C\{^{1}H\}$ spectrum of methyl 2-cyano-3-(4-fluorophenyl)propanoate (2) ($CDCl_3$, 101 MHz)



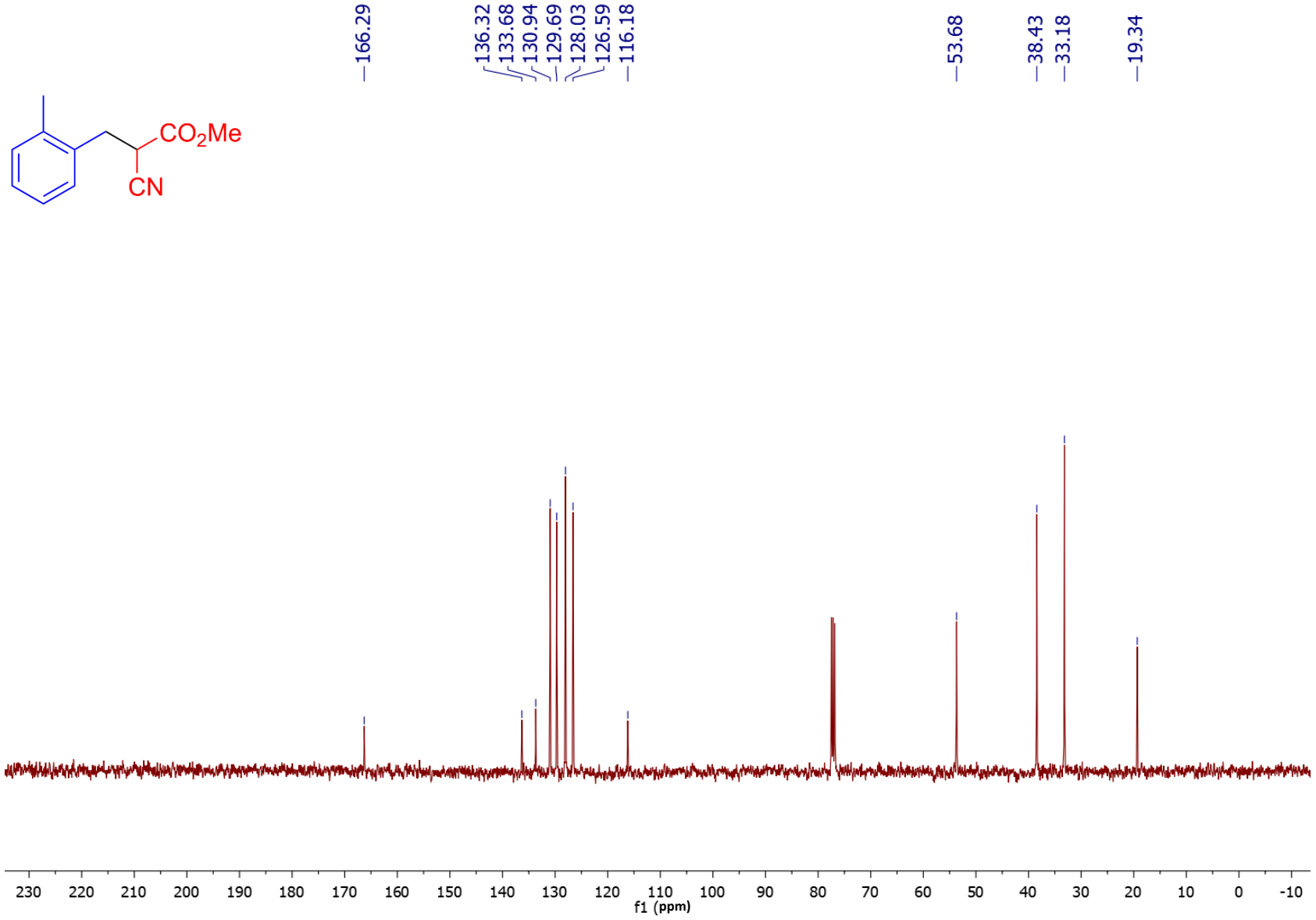
^{19}F spectrum of methyl 2-cyano-3-(4-fluorophenyl)propanoate (2) ($CDCl_3$, 376 MHz)



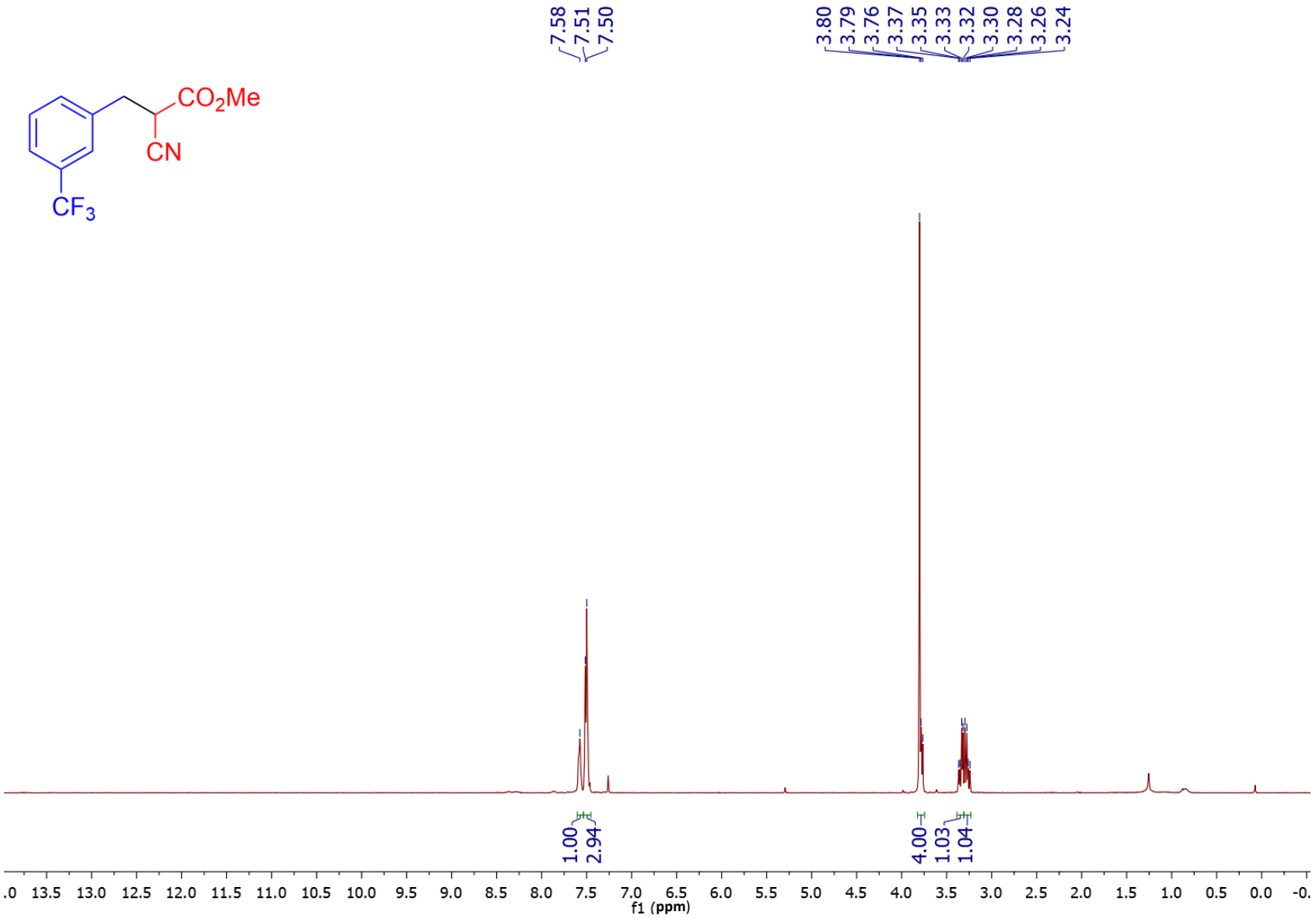
^{1}H spectrum of methyl 2-cyano-3-(*o*-tolyl)propanoate (3) ($CDCl_3$, 400 MHz)



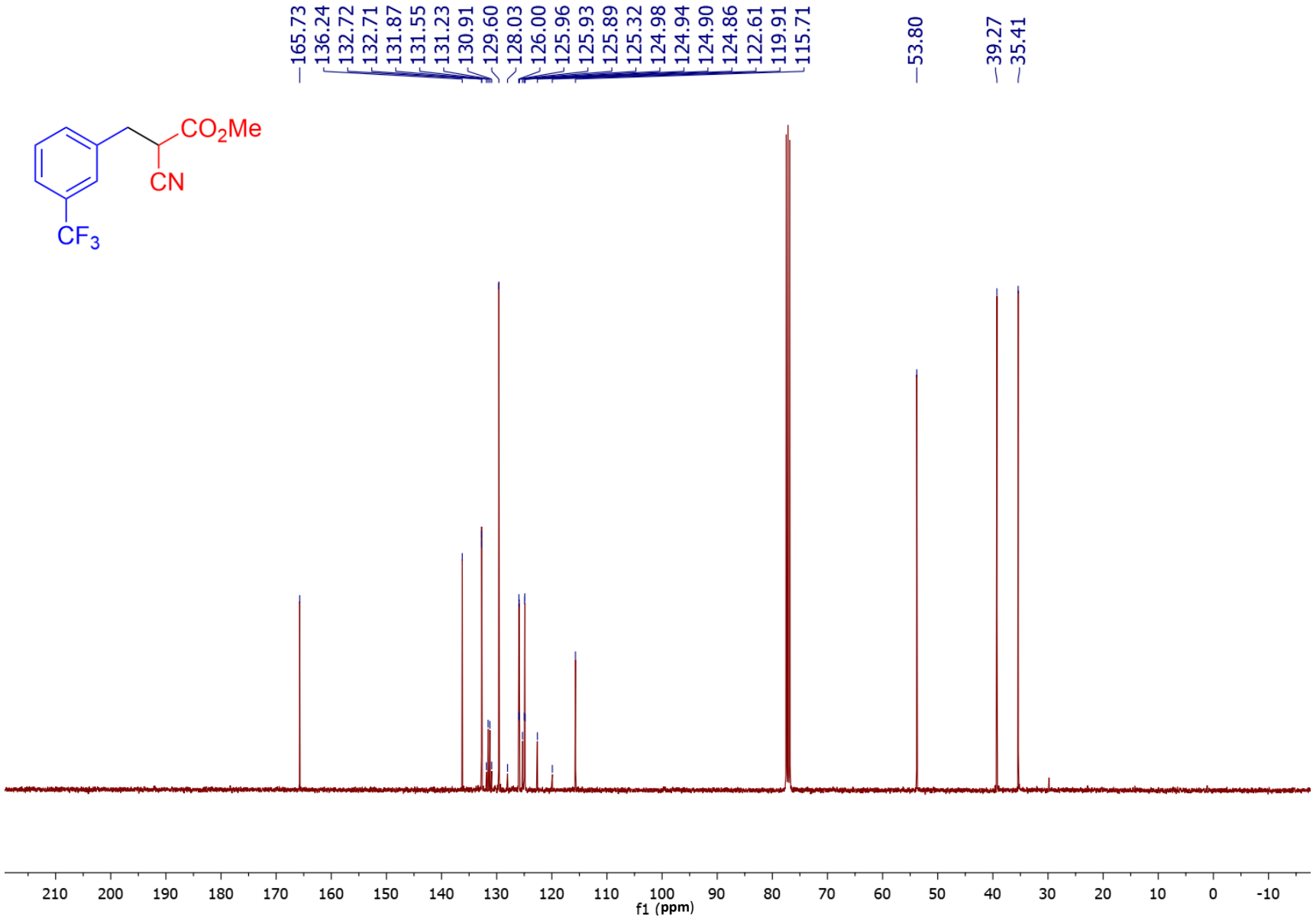
$^{13}C\{^{1}H\}$ spectrum of methyl 2-cyano-3-(*o*-tolyl)propanoate (3) ($CDCl_3$, 101 MHz)



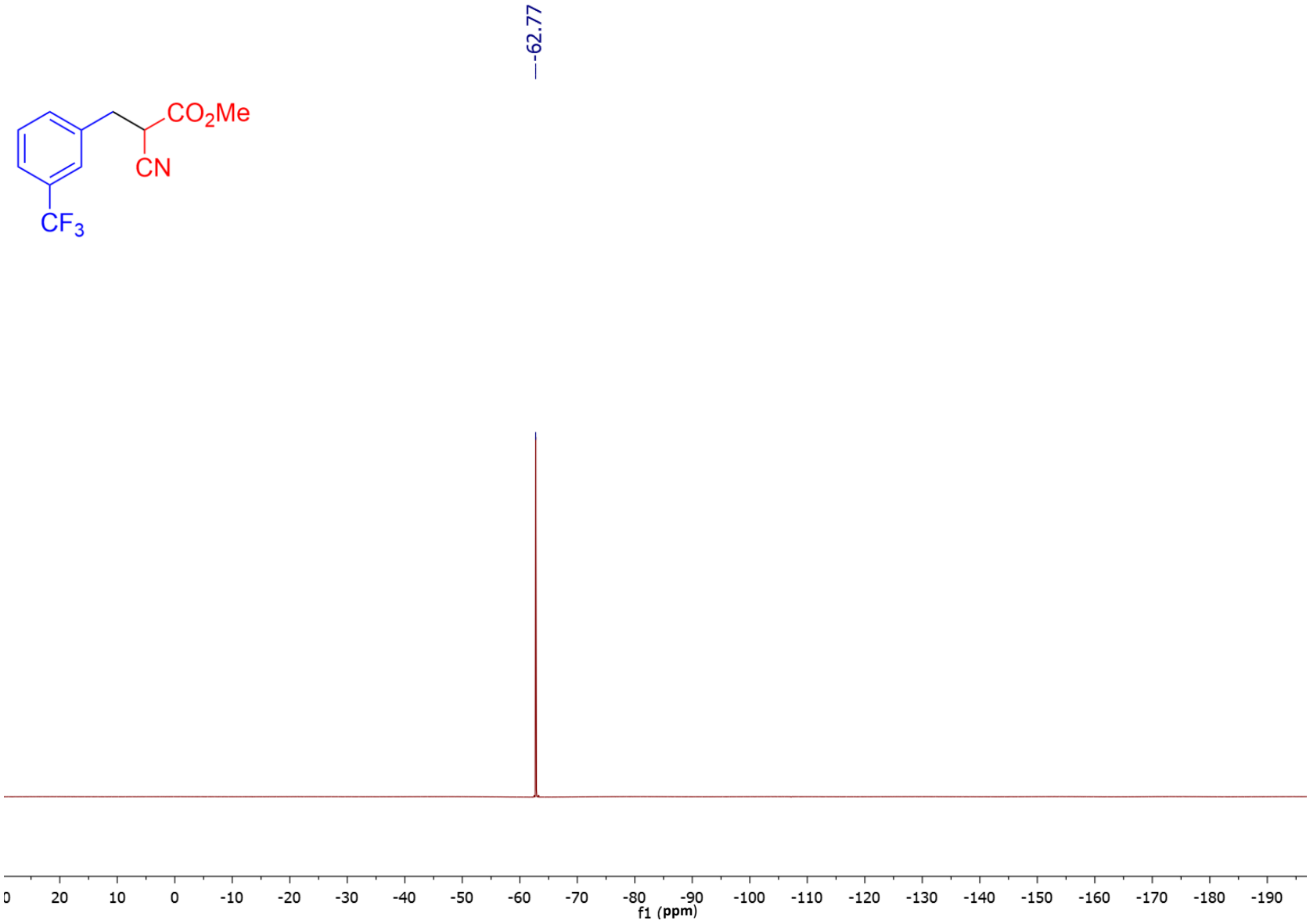
^{1}H spectrum of methyl 2-cyano-3-[3-(trifluoromethyl)phenyl]propanoate (4) ($CDCl_3$, 400 MHz)



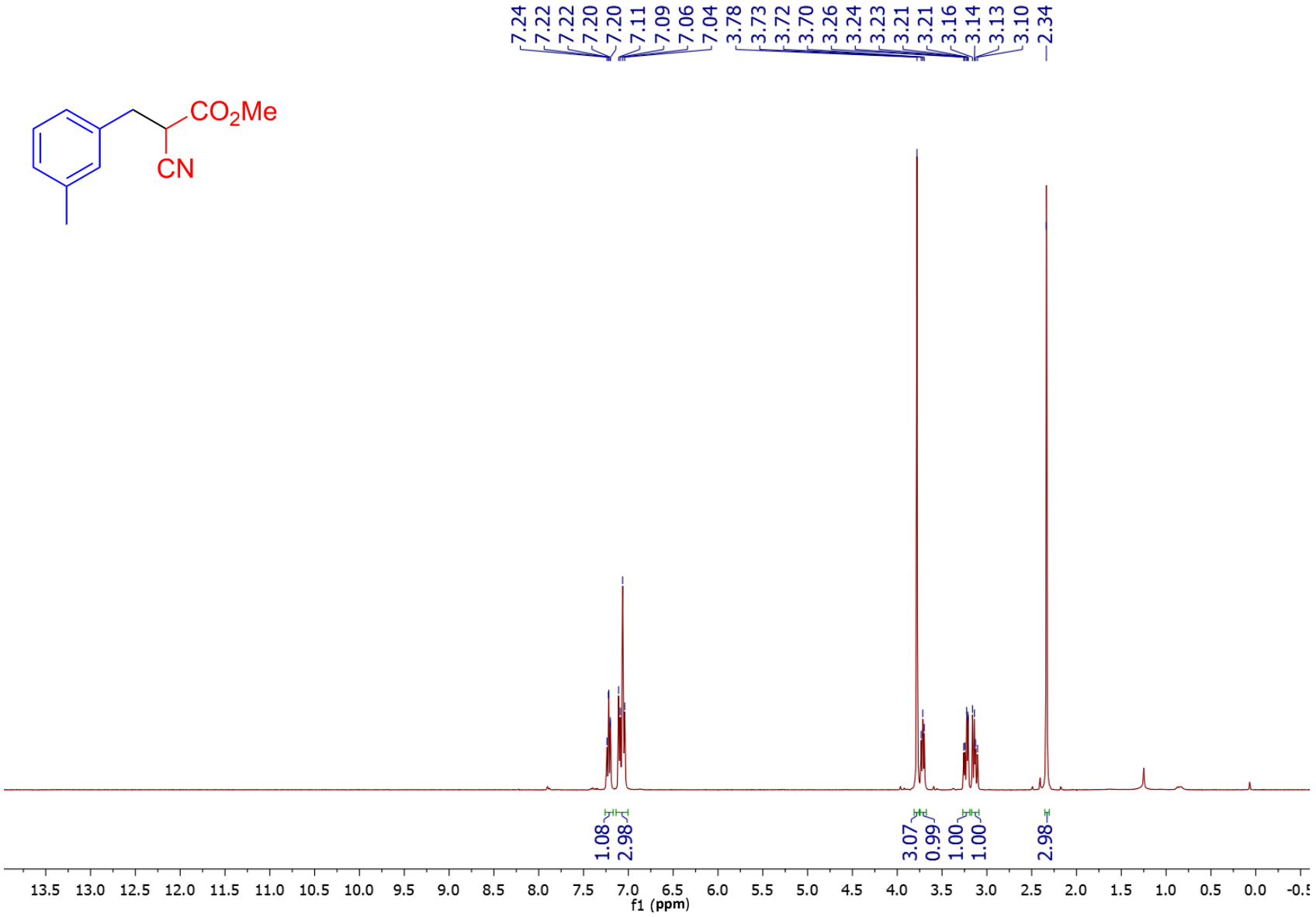
$^{13}C\{^{1}H\}$ spectrum of methyl 2-cyano-3-[3-(trifluoromethyl)phenyl]propanoate (4) ($CDCl_3$, 101 MHz)



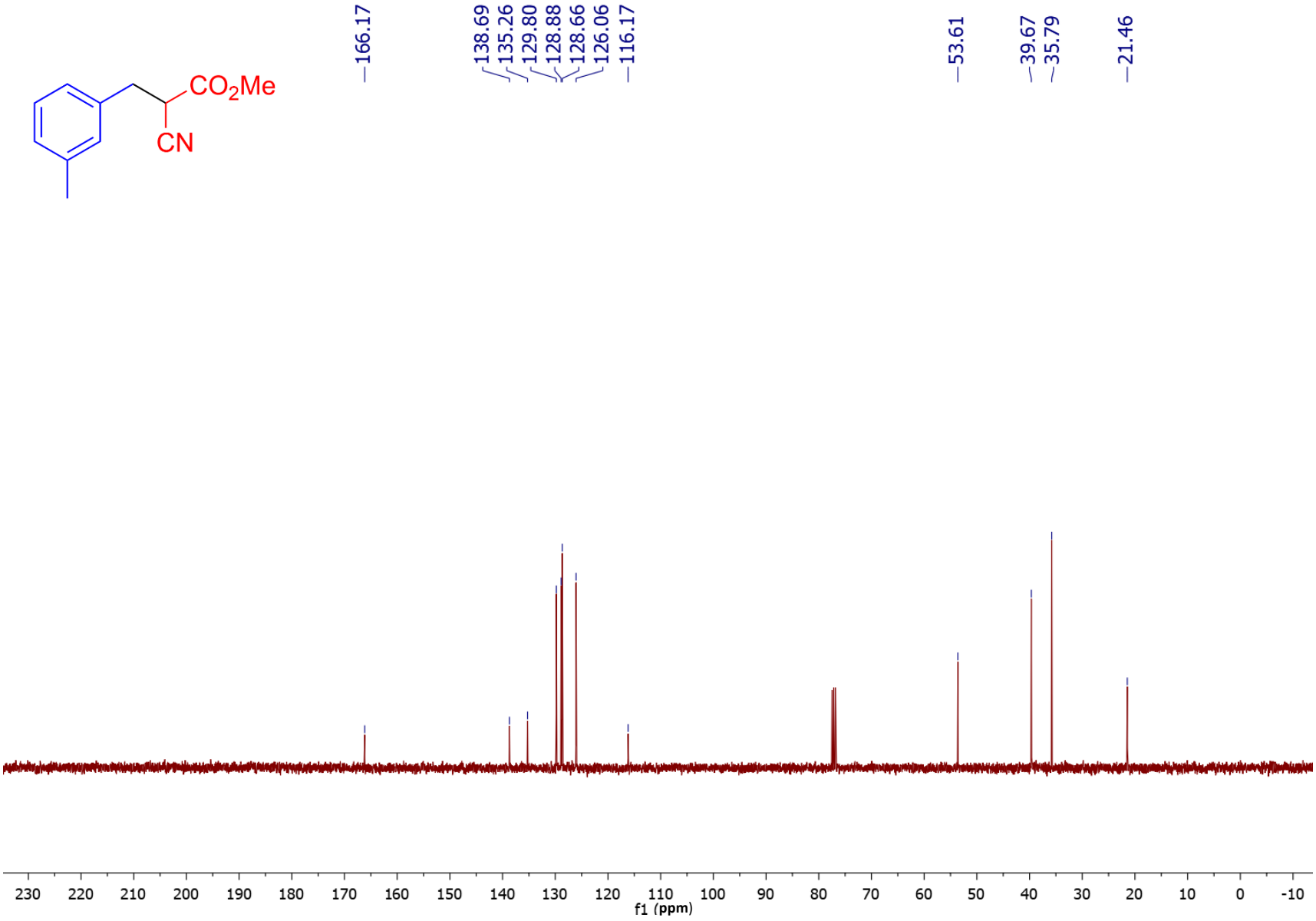
^{19}F spectrum of methyl 2-cyano-3-[3-(trifluoromethyl)phenyl]propanoate (4) ($CDCl_3$, 376 MHz)



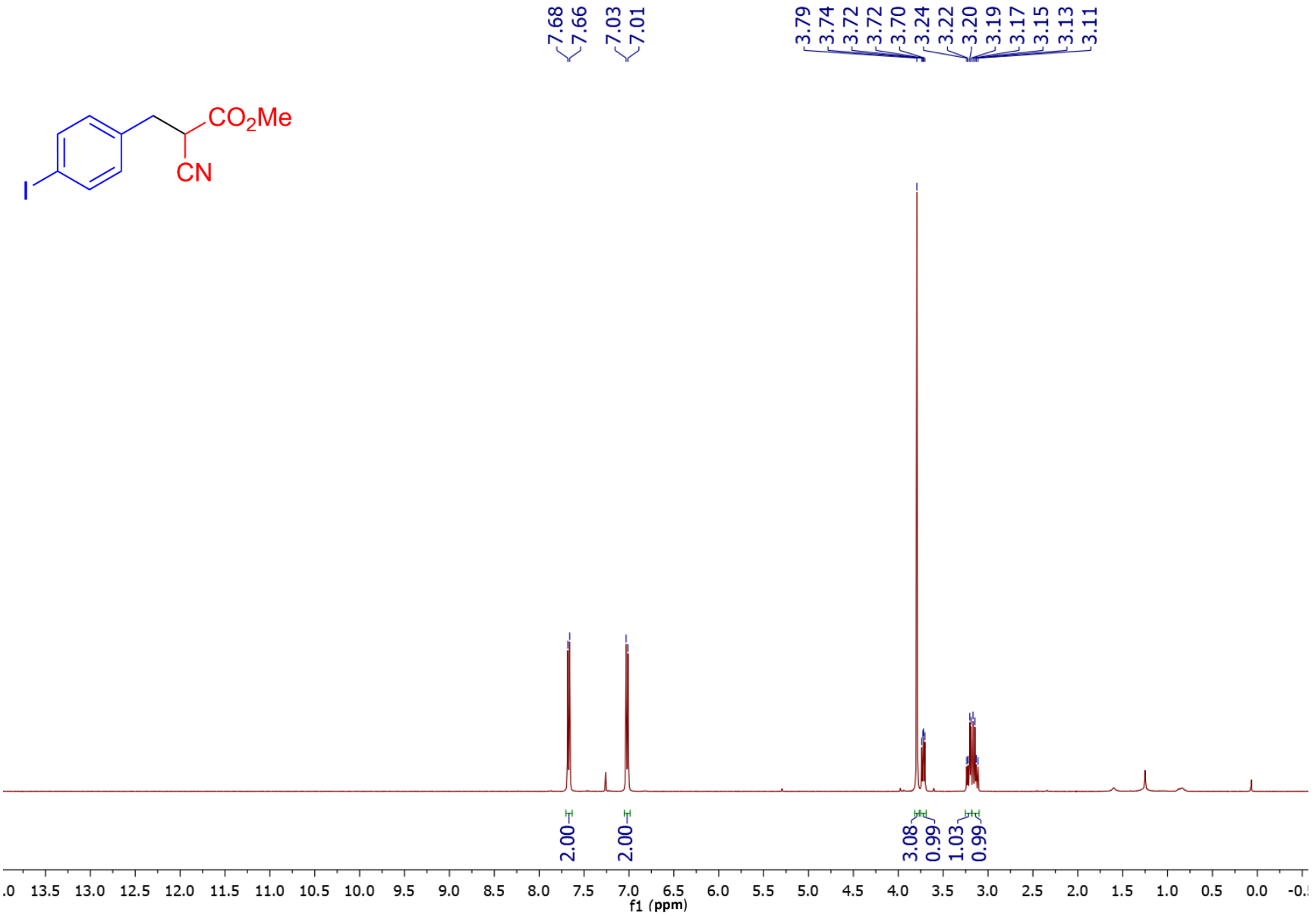
^{1}H spectrum of methyl 2-cyano-3-(*m*-tolyl)propanoate (5) ($CDCl_3$, 400 MHz)



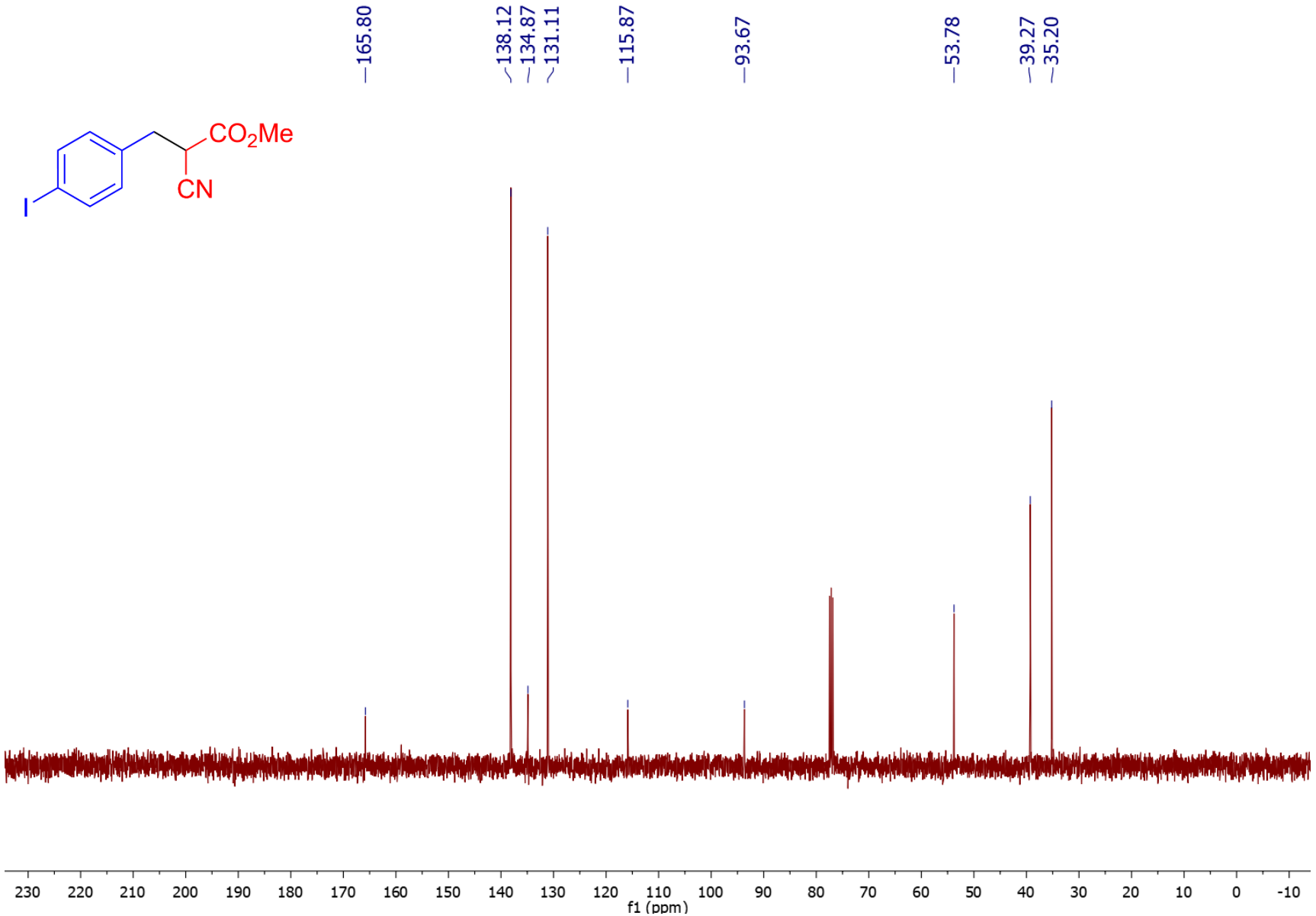
$^{13}C\{^{1}H\}$ spectrum of methyl 2-cyano-3-(*m*-tolyl)propanoate (5) ($CDCl_3$, 101 MHz)



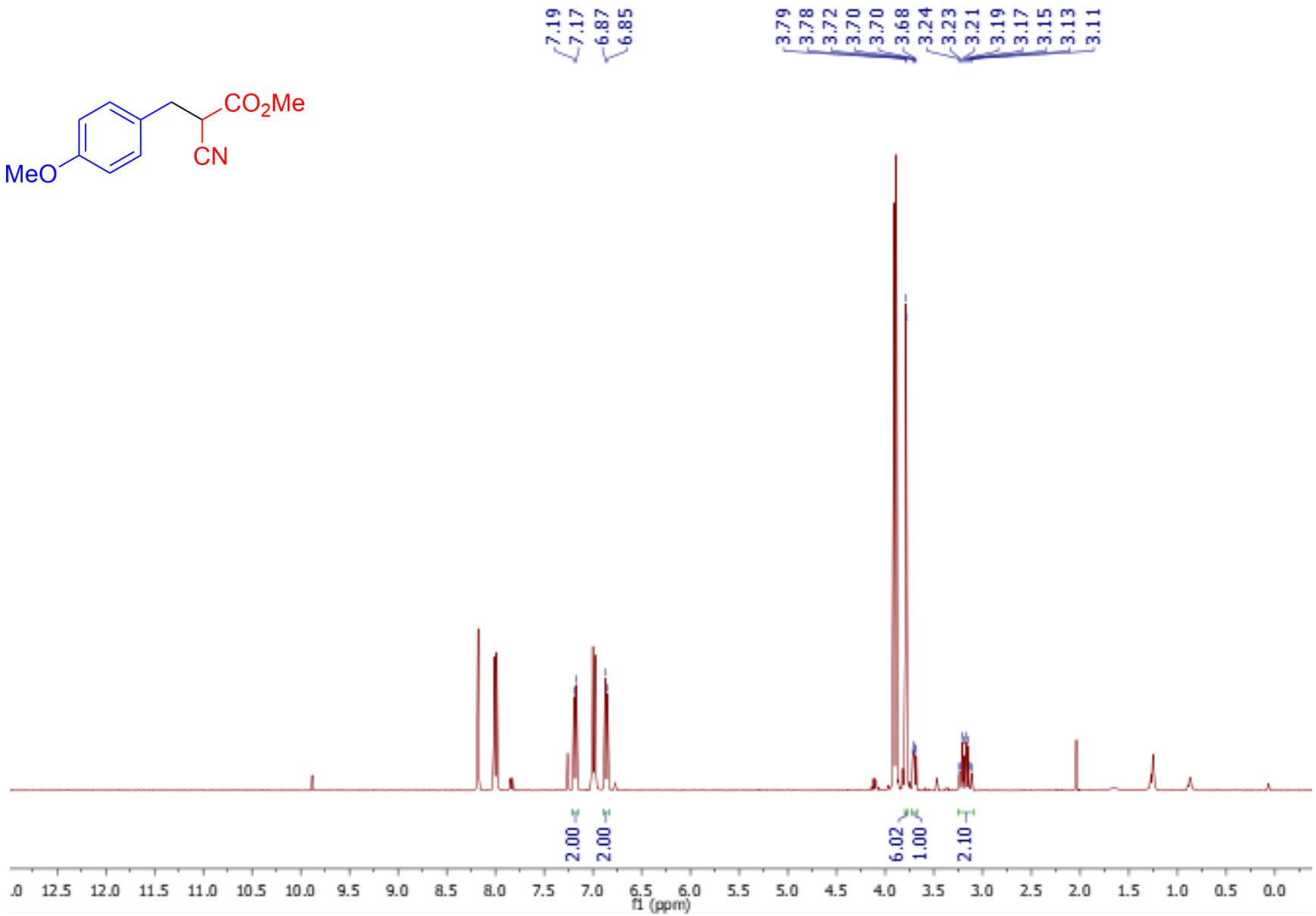
^{1}H spectrum of methyl 2-cyano-3-(4-iodophenyl)propanoate (6) ($CDCl_3$, 400 MHz)



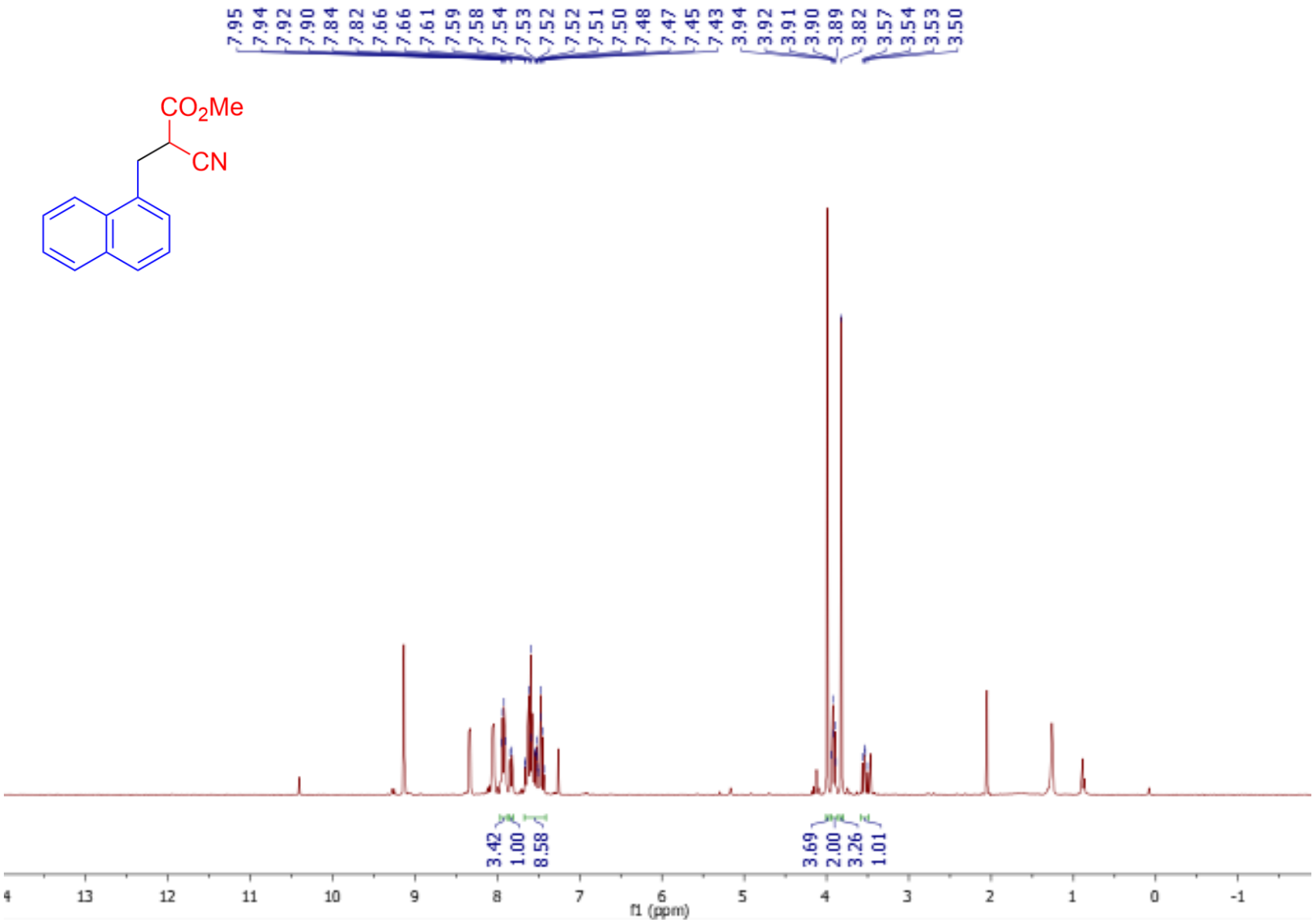
$^{13}C\{^{1}H\}$ spectrum of methyl 2-cyano-3-(4-iodophenyl)propanoate (6) ($CDCl_3$, 101 MHz)



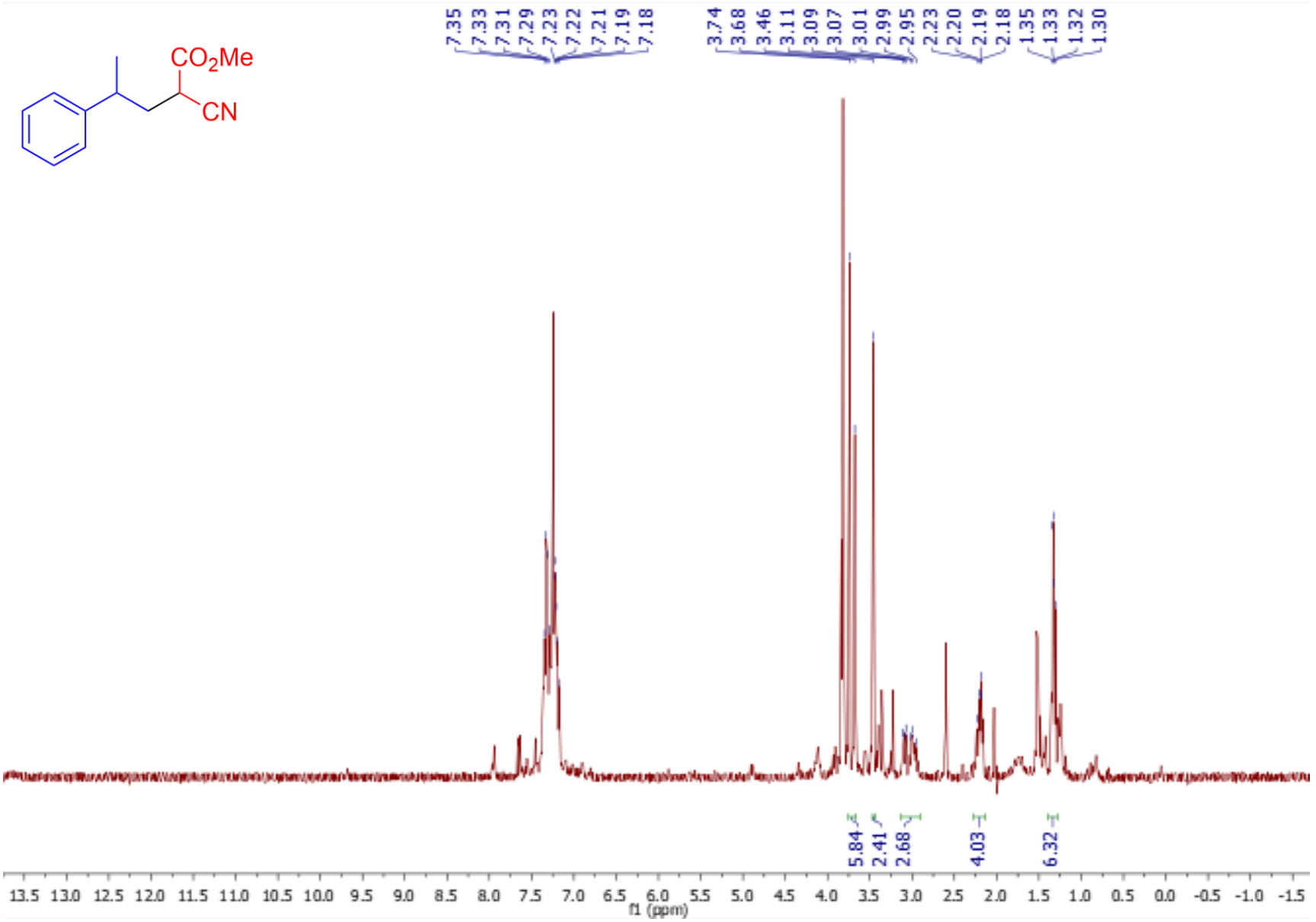
^{1}H spectrum of reaction mixture with methyl 2-cyano-3-(4-methoxyphenyl)propanoate (7) ($CDCl_3$, 400 MHz)



^{1}H spectrum of reaction mixture with methyl 2-cyano-3-(naphthalen-1-yl)propanoate (8) ($CDCl_3$, 400 MHz)



^{1}H spectrum of reaction mixture with methyl 2-cyano-4-phenylpentanoate (9) ($CDCl_3$, 400 MHz)



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