SUPPORTING INFORMATION

Ferrocene Catalyzed Redox-Neutral Difunctionalization of Alkenes using Cycloketone Oxime Esters: Access to Distal Imido-Nitriles

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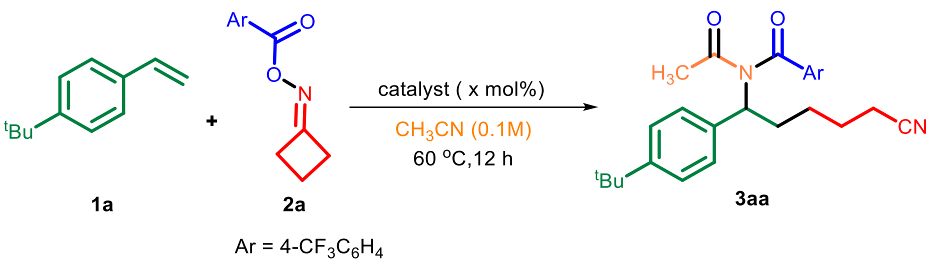
1. General Information

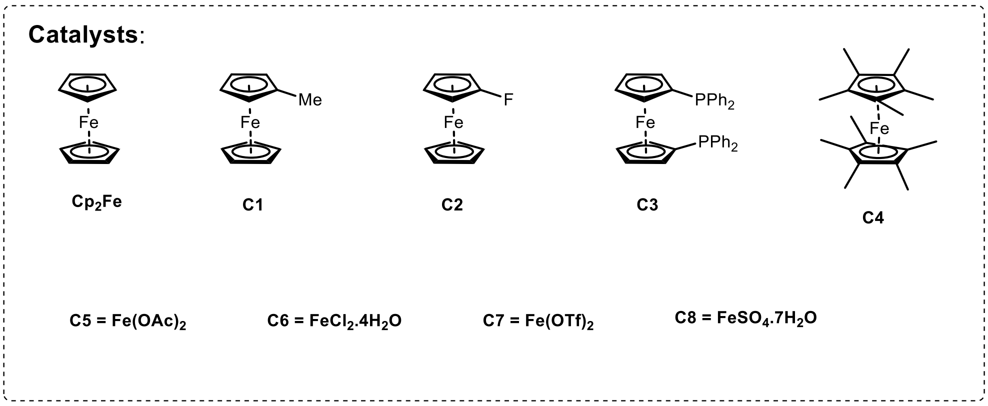
Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All solvents were dried and distilled according to standard procedures. Flash column chromatography was performed using 100-200 mesh silica gel. ^{1}H NMR spectra were recorded on 400 or 500 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 101 or 126 or 176 MHz with complete proton decoupling spectrophotometers. ^{19}F NMR spectra were recorded on 376 or 471 MHz spectrophotometers. The high resolution mass spectra (HRMS) were measured by using ESI-TOF techniques. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

Alkenes 1a-1j and 1n are commercially available. Alkenes 1k-1m and 1o-1p[1], oxime esters 1a-1q[2] and substituted ferrocene catalysts C1 and C2[3] were synthesized following the known procedures available in the literature.

2. Detailed Optimization of Reaction Conditions

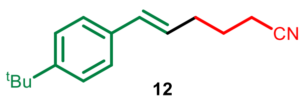
Table S1. Identification of suitable catalyst and its optimal loading





Entry[a]	Catalyst (x mol%)	Yield[b] [%]
1	Cp_2Fe (5 mol%)	71%
2	C1 (5 mol%)	58%
5	C2 (5 mol%)	40%
6	C3 (5 mol%)	0
7	C4 (5 mol%)	0
8	C5 (5 mol%)	0
9	C6 (5 mol%)	0
10	[c]C7 (5 mol%)	0
15	C8 (5 mol%)	0
16	Cp_2Fe (2 mol%)	57%
17	Cp_2Fe (10 mol%)	56%
18	No catalyst	0

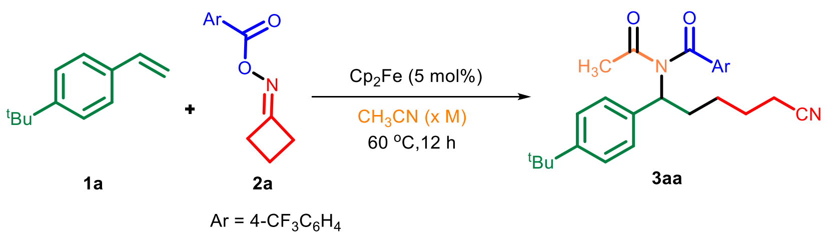
[a] Reaction conditions; **1a** (0.1 mmol), **2a** (0.2 mmol), catalyst (x mmol) in CH_3CN (1.0 mL) at 60 °C. [b] Isolated yields. [c] Heck type product **12** was observed in 18% yield.



12

As shown in Table S1, among all the catalysts tested, $FeCp_2$ on 5 mol% loading turned out to be the best condition for this transformation.

Table S2. Optimization of concentration of the reaction mixture

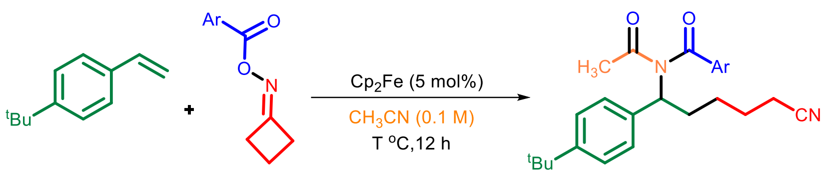


Entry[a]	Concentration	Yield[b] [%]
1	0.1 M	71%
2	0.2 M	43%
3	0.05 M	60%

[a] Reaction conditions; **1a** (0.1 mmol), **2a** (0.2 mmol), Cp_2Fe (0.005 mmol) in CH_3CN (x M) at 60 °C. [b] Isolated yields.

As shown in Table S2, 0.1 M turned out to be the optimal concentration for this transformation.

Table S3. Identification of optimal reaction temperature

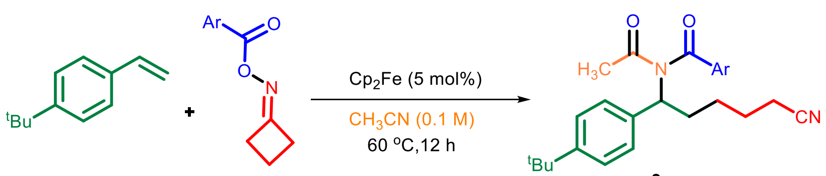


Entry[a]	Temperature (T °C)	Yield[b] [%]
1	Room temperature	0
2	40 °C	35%
3	60 °C	71%
4	80 °C	58%
5	100 °C	48%

[a] Reaction conditions; **1a** (0.1 mmol), **2a** (0.2 mmol), Cp_2Fe (0.005 mmol) in CH_3CN (0.1 M) at T °C. [b] Isolated yields.

As shown in Table S3, 60 °C turned out to be the optimal temperature for this transformation.

Table S4. Optimization of stoichiometry of the reaction partners

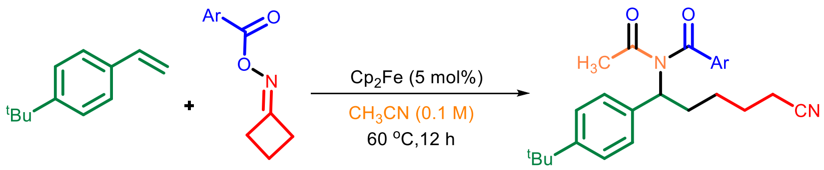


Entry[a]	1a (equiv.)	2a (equiv.)	Yield[b] [%]
1	1	1	50%
2	1	1.5	68%
3	1	2	71%

[a] Reaction conditions; **1a** (0.1 mmol), **2a** (x mmol), Cp_2Fe (0.005 mmol) in CH_3CN (0.1 M) at 60 °C. [b] Isolated yields.

As shown in Table S4, among the equivalents tested, 1:2 ratio of **1a** and **2a** gave the best result in terms of yield.

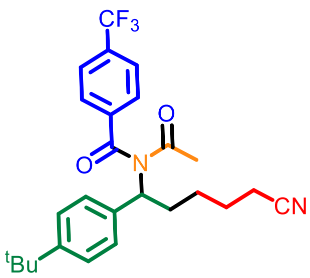
3. General Experimental Procedure for the synthesis of 3-9



In an oven dried 5.0 mL vial equipped with a magnetic stir bar was charged with alkene **1** (0.1 mmol, 1.0 equiv.), oxime ester **2** (0.2 mmol, 2.0 equiv.), Cp_2Fe (0.005 mmol, 5 mol%) followed by the addition of CH_3CN (1.0 mL) under nitrogen atmosphere. Then the mixture was stirred at 60 °C for 12 h. After completion of reaction, the resulting mixture was cooled to room temperature and concentrated under reduced pressure. Then the residue was diluted with ethyl acetate (15 mL), and washed successively with aq. $NaHCO_3$ solution (10 mL×2) and brine solution (10 mL×2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to get the desired compounds **3-9**.

4. Characterization Data of Products

N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-5-cyanopentyl)-4-(trifluoromethyl)benzamide (3aa)

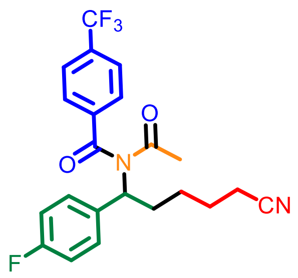


3aa

Pale yellow liquid (32.6 mg, 71% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.60 (m, 4H), 7.37 – 7.28 (m, 4H), 5.67 (dd, J = 8.5, 7.2 Hz, 1H), 2.45 – 2.39 (m, 1H), 2.36 (t, J = 7.0 Hz, 2H), 2.31 – 2.20 (m, 1H), 1.91 (s, 3H), 1.81 – 1.68 (m, 2H), 1.54 (p, J = 7.8 Hz, 2H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 173.1, 151.0, 139.9, 135.8, 134.3 (q, J = 33.7 Hz), 129.1, 127.8, 126.0 (q, J = 3.4 Hz), 125.5, 123.5 (q, J = 273.3 Hz), 119.6, 59.9, 34.6, 31.4, 27.6, 26.2, 25.2, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.16; HRMS(ESI) calcd for $C_{26}H_{30}F_3N_2O_2^+$ $[M+H]^+$ = 459.2259, found = 459.2245.

For the synthesis on 1.6 mmol scale, the reaction mixture was stirred at 60 °C for 48 hours. The desired product was isolated as a pale yellow liquid with a yield of 53% (388 mg).

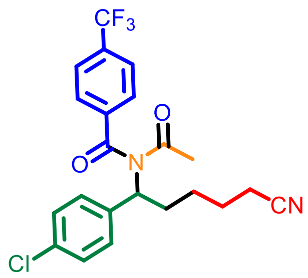
N-Acetyl-N-(5-cyano-1-(4-fluorophenyl)pentyl)-4-(trifluoromethyl)benzamide (3ba)



3ba

Pale yellow liquid (27.3 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.63 (m, 4H), 7.49 – 7.40 (m, 2H), 7.07 – 6.91 (m, 2H), 5.70 (t, *J* = 8.2 Hz, 1H), 2.49 – 2.40 (m, 1H), 2.37 (t, *J* = 7.0 Hz, 2H), 2.30 – 2.19 (m, 1H), 1.86 (s, 3H), 1.81 – 1.68 (m, 2H), 1.53 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.1, 172.9, 1632.3 (d, *J* = 247.8 Hz), 139.8, 134.8 (d, *J* = 2.8 Hz), 134.6 (q, *J* = 33.3 Hz), 130.2 (d, *J* = 8.1 Hz), 129.1, 126.2 (q, *J* = 3.6 Hz), 123.4 (q, *J* = 272.5 Hz), 119.5, 115.5 (d, *J* = 21.5 Hz), 59.6, 31.5, 27.9, 26.2, 25.1, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.19, -113.90; HRMS(ESI) calcd for $C_{22}H_{21}F_4N_2O_2^+$ $[M+H]^+$ = 421.1539, found = 421.1535.

N-Acetyl-N-(1-(4-chlorophenyl)-5-cyanopentyl)-4-(trifluoromethyl)benzamide (3ca)

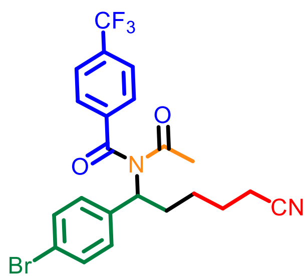


3ca

Pale yellow liquid (31.5 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 4H), 7.43 – 7.37 (m, 2H), 7.32 – 7.27 (m, 2H), 5.68 (t, *J* = 7.5 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.37 (t, *J* = 7.0 Hz, 2H), 2.30 – 2.18 (m, 1H), 1.86 (s, 3H), 1.80 – 1.66 (m, 2H), 1.52 (p, *J* = 7.9 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.0, 173.0, 139.8, 137.5, 134.6 (q, *J* = 33.1 Hz), 133.9, 129.8, 129.1, 128.8, 126.3 (q, *J* = 3.3 Hz), 123.4 (q, *J* = 271.3 Hz), 119.5, 59.6, 31.2, 27.9, 26.2, 25.1, 17.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.18; HRMS(ESI) calcd for $C_{22}H_{21}ClF_3N_2O_2^+$ $[M+H]^+$ = 437.1244, found = 437.1236.

For the synthesis on 0.5 mmol scale, the reaction mixture was stirred at 60 °C for 24 hours. The desired product was isolated as a pale yellow liquid with a yield of 67% (146 mg).

N-Acetyl-N-(1-(4-bromophenyl)-5-cyanopentyl)-4-(trifluoromethyl)benzamide (3da)

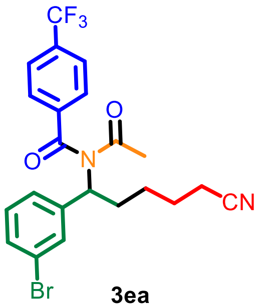


3da

Pale yellow liquid (24.1 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.66 (m, 4H), 7.47 – 7.43 (m, 2H), 7.36 – 7.32 (m, 2H), 5.66 (t, *J* = 7.5 Hz, 1H), 2.48 – 2.39 (m, 1H), 2.37 (t, *J* = 7.0 Hz, 2H), 2.30 – 2.17 (m, 1H), 1.86 (s, 3H), 1.80 – 1.69 (m, 2H), 1.52 (p, *J* = 7.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 172.9, 139.7, 138.0, 134.6 (q, *J* = 33.1 Hz), 131.7, 130.0, 129.0, 126.2 (q, *J*

= 3.4 Hz), 123.3 (q, J = 273.4 Hz), 122.0, 119.4, 59.6, 31.1, 27.9, 26.1, 25.0, 17.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.18; HRMS(ESI) calcd for $C_{22}H_{21}BrF_3N_2O_2^+$ $[M+H]^+$ = 481.0739, found = 481.0730.

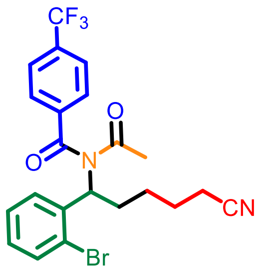
N-Acetyl-N-(1-(3-bromophenyl)-5-cyanopentyl)-4-(trifluoromethyl)benzamide (3ea)



3ea

Pale yellow liquid (24.5 mg, 51% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.66 (m, 4H), 7.61 (s, 1H), 7.43 – 7.36 (m, 2H), 7.20 (t, J = 7.9 Hz, 1H), 5.67 (dd, J = 8.6, 7.1 Hz, 1H), 2.48 – 2.41 (m, 1H), 2.37 (t, J = 7.0 Hz, 2H), 2.27 – 2.15 (m, 1H), 1.88 (s, 3H), 1.82 – 1.66 (m, 2H), 1.53 (p, J =7.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 141.5, 139.7, 134.6 (q, J = 32.7 Hz), 131.4, 131.2, 130.2, 129.1, 126.9, 126.3 (q, J = 3.3 Hz), 123.4 (q, J = 273.1 Hz), 122.8, 119.5, 59.7, 31.2, 27.9, 26.1, 25.1, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.18; ; HRMS(ESI) calcd for $C_{22}H_{21}BrF_3N_2O_2^+$ $[M+H]^+$ = 481.0739, found = 481.0737.

N-Acetyl-N-(1-(2-bromophenyl)-5-cyanopentyl)-4-(trifluoromethyl)benzamide (3fa)

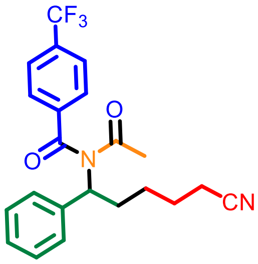


3fa

Pale yellow liquid (27.9 mg, 58% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 7.7 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.63 (dd, J = 7.9, 1.5 Hz, 1H), 7.55 (dd, J = 8.0, 1.3 Hz, 1H), 7.29 (td, J = 7.8, 1.3 Hz, 1H), 7.12 (td, J = 7.7, 1.6 Hz, 1H), 5.88 (t, J = 7.7 Hz, 1H), 2.46 – 2.26 (m, 4H), 1.95 (s, 3H), 1.86 – 1.68 (m, 2H), 1.65 – 1.41 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 172.0, 139.7, 137.0, 134.5 (q, J = 32.3 Hz), 133.3, 131.0, 129.8, 129.3, 127.5, 126.1 (q, J = 3.4 Hz), 125.0, 123.5 (q, J = 272.9 Hz), 119.5, 59.9, 31.3, 27.1, 26.0, 25.1, 17.2; ^{19}F NMR (471 MHz, CDC13) δ -63.18; HRMS(ESI) calcd for $C_{22}H_{21}BrF_3N_2O_2^+$ $[M+H]^+$ = 481.0739, found = 481.0737

For the synthesis on 0.5 mmol scale, the reaction mixture was stirred at 60 ºC for 24 hours. The desired product was isolated as a pale yellow liquid with a yield of 55% (132 mg).

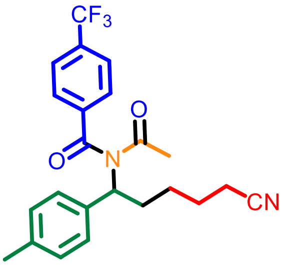
N-Acetyl-N-(5-cyano-1-phenylpentyl)-4-(trifluoromethyl)benzamide (3ga)



3ga

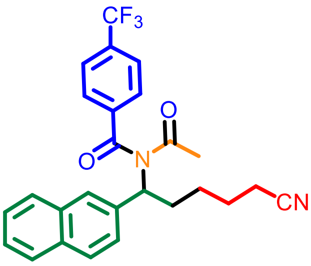
Pale yellow liquid (24.5 mg, 61% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.62 (m, 4H), 7.46 – 7.40 (m, 2H), 7.35 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 5.71 (t, J = 7.8 Hz, 1H), 2.50 – 2.40 (m, 1H), 2.37 (t, J = 7.0 Hz, 2H), 2.34 – 2.22 (m, 1H), 1.89 (s, 3H), 1.83 – 1.68 (m, 2H), 1.55 (p, J = 7.5, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 173.0, 139.9, 139.0, 134.2 (q, J = 33.2 Hz), 129.0, 128.6, 128.2, 128.1, 126.1 (q, J = 3.3 Hz), 123.4 (q, J = 273.0 Hz), 119.5, 60.2, 31.3, 27.7, 26.2, 25.2, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.16; HRMS(ESI) calcd for $C_{22}H_{22}F_3N_2O_2^+$ $[M+H]^+$ = 403.1633, found = 403.1624.

N-Acetyl-N-(5-cyano-1-(p-tolyl)pentyl)-4-(trifluoromethyl)benzamide (3ha)



3ha

Pale yellow liquid (26.2 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 4H), 7.24 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 5.59 (t, J = 7.8 Hz, 1H), 2.39 – 2.30 (m, 1H), 2.28 (t, J = 7.0 Hz, 2H), 2.24 – 2.14 (m, 4H), 1.81 (s, 3H), 1.73 – 1.60 (m, 2H), 1.45 (p, J = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 173.0, 139.9, 137.8, 135.8, 134.3 (q, J = 33.2 Hz), 129.3, 129.0, 128.1, 126.0 (q, J = 3.2 Hz), 123.5 (q, J = 273.0 Hz), 119.5, 60.0, 31.4, 27.6, 26.2, 25.1, 21.1, 17.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.16; HRMS(ESI) calcd for $C_{23}H_{24}F_3N_2O_2^+$ $[M+H]^+$ = 417.1790, found = 417.1781.

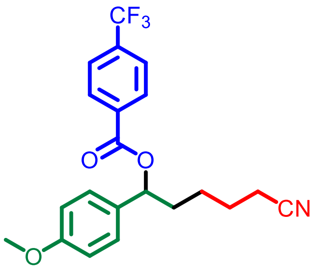


3ia

N-Acetyl-N-(5-cyano-1-(naphthalen-2-yl)pentyl)-4-(trifluoromethyl)benzamide (3ia) Pale yellow liquid (29.0 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.85 – 7.77 (m, 3H), 7.69 – 7.62 (m, 4H), 7.58 (dd, J = 8.6, 1.7 Hz, 1H), 7.50 – 7.44 (m, 2H), 5.89 (t, J = 7.8 Hz, 1H), 2.61 – 2.48 (m, 1H), 2.45 – 2.35 (m, 3H), 1.89 (s, 3H), 1.86 – 1.72 (m, 2H), 1.59 (p, J = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.3, 173.2, 139.9, 136.3, 134.4 (q, J = 33.4 Hz), 133.2, 133.0, 129.1, 128.5, 128.3, 127.7, 127.4, 126.4, 126.2, 123.4 (q, J = 33.4 Hz), 119.6, 60.3, 31.4, 27.8, 26.3, 25.2, 17.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.19; HRMS(ESI) calcd for $C_{26}H_{23}F_3N_2NaO_2^+$ $[M+Na]^+$ = 475.1609, found = 475.1624.

For the synthesis on 0.5 mmol scale; the reaction mixture was stirred at 60 °C for 24 hours. The desired product was isolated as a pale yellow liquid with a yield of 61% (144.6 mg).

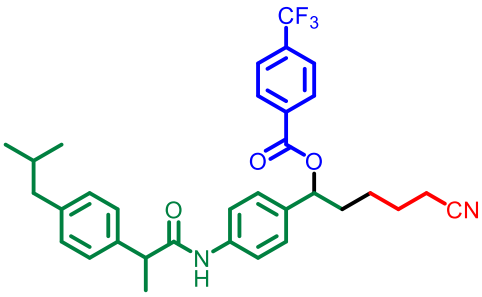
5-Cyano-1-(4-methoxyphenyl)pentyl 4-(trifluoromethyl)benzoate (3'ja)



3'ja

Pale yellow liquid (33.6 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 6.94 – 6.87 (m, 2H), 5.96 (t, *J* = 7.0 Hz, 1H), 3.79 (s, 3H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.19 – 2.07 (m, 1H), 2.01 – 1.89 (m, 1H), 1.71 (p, *J* = 7.6 Hz, 2H), 1.64 – 1.53 (m, 1H), 1.52 – 1.43 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 159.7, 134.6 (q, *J* = 32.7 Hz), 133.7, 131.9, 130.1, 128.0, 125.5 (q, *J* = 3.5 Hz), 123.7 (q, *J* = 273.1 Hz), 119.50, 114.2, 76.7, 55.4, 35.4, 25.2, 24.9, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.11; HRMS(ESI) calcd for $C_{21}H_{20}F_3NNaO_3^+$ $[M+Na]^+$ = 414.1293, found = 414.1284.

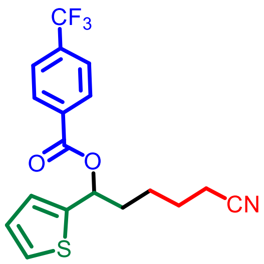
5-Cyano-1-(4-(2-(4-isobutylphenyl)propanamido)phenyl)pentyl 4-(trifluoromethyl) benzoate (3'ka)



3'ka

Pale yellow liquid (51.6 mg, 56% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.39 – 7.33 (m, 2H), 7.26 – 7.22 (m, 2H), 7.17 (d, *J* = 7.7 Hz, 2H), 7.07 (d, *J* = 7.8 Hz, 2H), 7.00 (s, 1H), 5.84 (t, *J* = 6.9 Hz, 1H), 3.61 (q, *J* = 7.1 Hz, 1H), 2.39 (d, *J* = 7.2 Hz, 2H), 2.28 – 2.21 (m, 2H), 2.07 – 1.95 (m, 1H), 1.89 – 1.74 (m, 2H), 1.62 (p, *J* = 7.6 Hz, 2H), 1.50 (d, *J* = 7.2 Hz, 3H), 1.49 – 1.43 (m, 1H), 1.41 – 1.31 (m, 1H), 0.83 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 164.7, 141.3, 138.1, 138.0, 135.5, 134.7 (q, *J* = 32.9 Hz), 133.5, 130.1, 130.0, 127.5, 127.3, 125.6 (q, *J* = 3.4 Hz), 123.7 (q, *J* = 271.9 Hz), 119.9, 119.5, 76.6, 47.9, 45.1, 35.4, 30.3, 25.2, 24.8, 22.5, 18.6, 17.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.14; HRMS(ESI) calcd for $C_{33}H_{35}F_3N_2NaO_3^+$ $[M+Na]^+$ = 587.2497, found = 587.2509.

5-Cyano-1-(thiophen-2-yl)pentyl 4-(trifluoromethyl)benzoate (3'la)

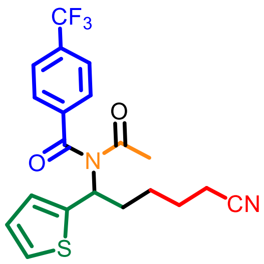


(3'la)

Pale yellow liquid (15.4 mg, 42% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 5.1 Hz, 1H), 7.14 (d, *J* = 3.4 Hz, 1H), 7.04 – 6.94 (m, 1H), 6.31 (t, *J* = 6.9 Hz, 1H), 2.36 (t, *J* = 6.9 Hz, 2H), 2.27 – 2.16 (m, 1H), 2.13 – 2.00 (m, 1H), 1.74 (p, *J* = 7.3 Hz, 2H), 1.63 – 1.53 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.7, 142.5, 134.8 (q, *J* = 33.2 Hz), 133.4, 130.2, 126.9, 126.4, 125.9, 125.6 (q, *J* = 3.4 Hz), 123.7 (q, *J* = 272.3 Hz), 119.4, 72.2, 35.8, 25.1, 24.9, 17.2;

^{19}F NMR (377 MHz, $CDCl_3$) δ -63.16; HRMS(ESI) calcd for $C_{18}H_{16}F_3NNaO_2S^+$ $[M+Na]^+$ = 390.0751, found = 390.0747.

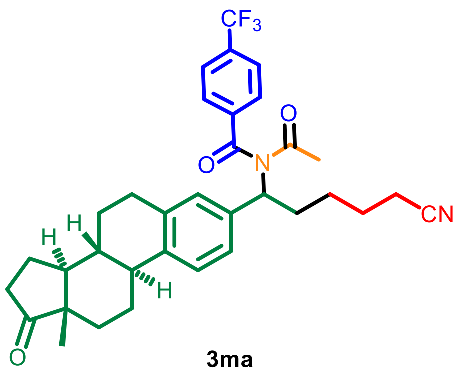
N-Acetyl-N-(5-cyano-1-(thiophen-2-yl)pentyl)-4-(trifluoromethyl)benzamide (3la)



(**3la**)

Pale yellow liquid (3.7 mg, 9% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 4H), 7.22 (dd, J = 5.1, 1.0 Hz, 1H), 7.04 (d, J = 3.5 Hz, 1H), 6.92 (dd, J = 5.1, 3.6 Hz, 1H), 5.86 (t, J = 7.8 Hz, 1H), 2.51 – 2.40 (m, 1H), 2.37 (t, J = 7.0 Hz, 2H), 2.34 – 2.23 (m, 1H), 1.93 (s, 3H), 1.79 – 1.69 (m, 2H), 1.55 (p, J = 7.6 Hz, 2H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 173.1, 172.7, 142.2, 139.7, 134.6 (q, J = 33.5 Hz), 129.2, 126.9, 126.7, 126.2, 125.7, 1243.4 (q, J = 274.1 Hz), 119.5, 56.3, 33.5, 27.7, 26.2, 25.0, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.18; HRMS(ESI) calcd for $C_{20}H_{19}F_3N_2NaO_2S^+$ $[M+Na]^+$ = 431.1017, found = 431.1018.

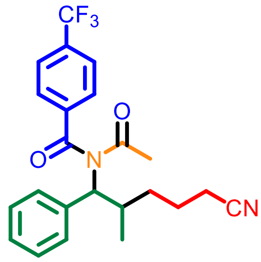
N-Acetyl-N-(5-cyano-1-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)pentyl)-4-(trifluoromethyl)benzamide (3ma)



3ma

Pale yellow liquid (31.2 mg, 54% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 1.1 Hz, 4H), 7.18 – 7.10 (m, 2H), 7.04 (s, 1H), 5.60 – 5.52 (m, 1H), 2.84 – 2.75 (m, 2H), 2.49 – 2.27 (m, 5H), 2.24 – 2.15 (m, 2H), 2.14 – 1.86 (m, 5H), 1.84 (s, 3H), 1.75 – 1.62 (m, 2H), 1.59 – 1.52 (m, 1H), 1.51 – 1.33 (m, 6H), 0.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.0, 173.3, 173.1, 140.0, 139.6, 136.7, 136.7, 136.4, 136.3, 134.3 (q, J = 32.7 Hz), 130.6, 129.1, 128.8, 128.7, 126.1, 125.6, 125.5, 124.8 (q, J = 273.3 Hz), 119.6, 60.0, 50.6, 48.1, 44.4, 38.1, 36.0, 31.7, 31.4, 31.3, 29.8, 29.6, 27.7, 26.6, 26.2, 25.8, 25.7, 25.2, 21.7, 17.2, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.12; HRMS(ESI) calcd for $C_{34}H_{38}F_3N_2O_3^+$ $[M+H]^+$ = 579.2835, found = 579.2826.

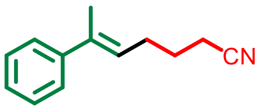
N-Acetyl-N-(5-cyano-2-methyl-1-phenylpentyl)-4-(trifluoromethyl)benzamide (3na) (1.8:1 diastereomers)



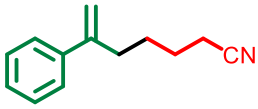
3na

Pale yellow liquid (22.9 mg, 55% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 2H), 7.55 – 7.42 (m, 4H), 7.36 – 7.22 (m, 3H), 5.50 – 5.37 (m, 1H), 3.54 – 3.41 (m, 0.7H), 3.12 – 2.99 (m, 0.3H), 2.70 – 2.49 (m, 1.3H), 2.47 – 2.40 (m, 0.7H), 2.22 – 2.05 (m, 0.3H), 1.93 – 1.67 (m, 1.6H), 1.87 (s, 1.8H), 1.81(s, 1.2H) 1.46 – 1.25 (m, 1.8H), 1.07 (d, *J* = 6.7 Hz, 1.9H), 0.87 (d, *J* = 6.6 Hz, 1.2H); ^{13}C NMR (176 MHz, CDCl3) δ 173.8, 173.5, 173.0, 172.7, 140.1, 139.6, 138.2, 137.1, 134.2 (q, *J* = 33.6 Hz), 129.2, 129.1, 129.0, 129.0, 128.8, 128.7, 128.2, 126.1 (q, *J* = 3.2 Hz), 123.3 (q, *J* = 272.8 Hz), 119.8, 118.5, 66.3, 65.2, 33.3, 32.6, 32.2, 27.9, 27.4, 22.6, 22.5, 18.4, 17.6, 17.5; ^{19}F NMR (376 MHz, CDCl3) δ -63.19, -63.25; HRMS(ESI) calcd for $C_{23}H_{24}F_3N_2O_2^+$ $[M+H]^+$ = 417.1790, found = 417.1791.

(E)-6-Phenylhept-5-enenitrile (3oa) (T:L = 60:40)



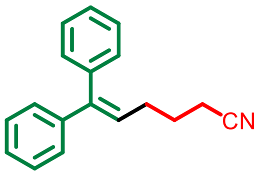
3oa - L



3oa - T

Pale yellow liquid (4.4 mg, 24% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.07 (m, 5H), 5.70 – 5.67 (m, 0.4H), 5.29 (brs, 0.6H), 5.07 (brs, 0.6H), 2.60 – 2.50 (m, 1H), 2.45 – 2.25 (m, 3H), 2.07 (s, 1H), 1.84 (p, *J* = 7.2 Hz, 1H), 1.68 – 1.54 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 143.4, 140.8, 137.2, 128.4, 128.3, 127.6, 127.0, 126.1, 125.7, 125.4, 119.7, 113.1, 34.5, 27.6, 27.1, 25.4, 25.0, 17.1, 16.7, 16.0; HRMS(ESI) calcd for $C_{13}H_{16}N^+$ $[M+H]^+$ = 186.1238, found = 186.1238.

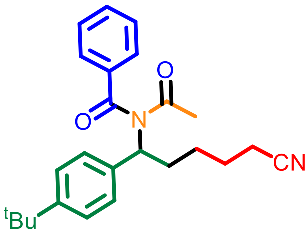
6,6-Diphenylhex-5-enenitrile (3pa)



3pa

Pale yellow liquid (10.1 mg, 41% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 2H), 7.35 – 7.30 (m, 1H), 7.29 – 7.23 (m, 3H), 7.23 – 7.19 (m, 2H), 7.17 – 7.13 (m, 2H), 6.01 (t, *J* = 7.4 Hz, 1H), 2.32 – 2.23 (m, 4H), 1.79 (p, *J* = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 142.2, 139.7, 129.8, 128.5, 128.3, 127.4, 127.3, 126.7, 119.6, 28.8, 25.9, 16.8; HRMS(ESI) calcd for $C_{18}H_{18}N^+$ $[M+H]^+$ = 248.1439, found = 248.1437.

N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-5-cyanopentyl)benzamide (3ab)

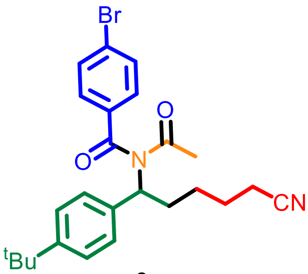


3ab

Pale yellow liquid (25.0 mg, 64% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 2H), 7.45 (dt, *J* = 2.6, 1.6 Hz, 1H), 7.36 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 5.62 (dd, *J* = 8.3, 7.4 Hz, 1H), 2.42 – 2.31 (m, 1H), 2.28 (t, *J* = 7.1 Hz, 2H), 2.23 – 2.12 (m, 1H), 1.76 (s, 3H), 1.72 – 1.61 (m, 2H), 1.46 (p, *J* = 7.8 Hz, 2H), 1.20 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 173.2, 150.7, 136.8, 136.3, 133.1, 129.1, 129.0, 128.0, 125.4, 119.6, 59.7, 35.0, 31.4, 27.7, 26.3, 25.3, 17.2; HRMS(ESI) calcd for $C_{25}H_{30}N_2NaO_2^+$ $[M+Na]^+$ = 413.2205, found = 413.2205.

For the synthesis on 0.5 mmol scale; the reaction mixture was stirred at 60 ºC for 24 h. The desired product was isolated as a pale yellow liquid with an yield of 62% (121 mg).

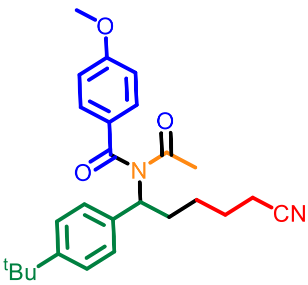
N-Acetyl-4-bromo-N-(1-(4-(tert-butyl)phenyl)-5-cyanopentyl)benzamide (3ac)



3ac

Pale yellow liquid (24.9 mg, 53% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.44 – 7.39 (m, 2H), 7.34 – 7.28 (m, 4H), 5.66 (dd, *J* = 8.5, 7.2 Hz, 1H), 2.45 – 2.38 (m, 1H), 2.35 (t, *J* = 7.1 Hz, 2H), 2.28 – 2.17 (m, 1H), 1.88 (s, 3H), 1.81 – 1.67 (m, 2H), 1.52 (p, *J* = 7.7 Hz, 2H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 172.8, 150.9, 136.0, 135.5, 132.4, 130.5, 128.2, 127.9, 125.5, 119.6, 59.8, 34.6, 31.5, 31.4, 27.6, 26.3, 25.2, 17.2; HRMS(ESI) calcd for $C_{25}H_{29}BrN_2NaO_2^+$ $[M+Na]^+$ = 491.1310, found = 491.1307.

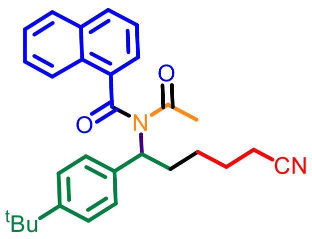
N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-5-cyanopentyl)-4-methoxybenzamide (3ad)



3ad

Pale yellow liquid (17.7 mg, 42% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.52 (m, 2H), 7.37 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 6.89 – 6.83 (m, 2H), 5.67 (t, *J* = 7.9 Hz, 1H), 3.84 (s, 3H), 2.46 – 2.37 (m, 1H), 2.34 (t, *J* = 7.1 Hz, 2H), 2.26 – 2.15 (m, 1H), 1.85 (s, 3H), 1.79 – 1.68 (m, 2H), 1.52 (p, *J* = 8.4 Hz, 2H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.1, 172.5, 163.8, 150.6, 136.3, 131.7, 128.9, 128.1, 125.3, 119.7, 114.3, 59.6, 55.7, 34.6, 31.6, 31.4, 27.2, 26.3, 25.3, 17.2; HRMS(ESI) calcd for $C_{26}H_{33}N_2O_3^+$ $[M+H]^+$ = 421.2491, found = 421.2488.

N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-5-cyanopentyl)-1-naphthamide (3ae)

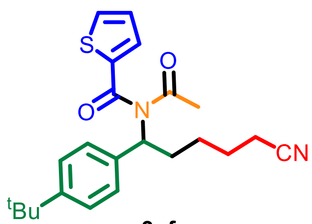


3ae

Pale yellow liquid (26.0 mg, 59% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.3 Hz, 1H), 7.95 (d, J = 7.7 Hz, 1H), 7.91 – 7.84 (m, 1H), 7.63 – 7.51 (m, 2H), 7.43 – 7.35 (m, 4H), 7.35 – 7.30 (m, 2H), 5.75 (t, J = 7.8 Hz, 1H), 2.54 – 2.42 (m, 1H), 2.41 – 2.29 (m, 3H), 1.79 (s, 3H), 1.78 – 1.68 (m, 2H), 1.56 (p, J = 7.9 Hz, 2H), 1.29 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 150.7, 136.1, 134.5, 134.0, 132.6, 130.5, 128.7, 128.3, 127.2, 127.1, 125.4, 125.0, 124.6, 119.7, 59.5, 34.6, 31.4, 31.3, 27.7, 26.4, 25.3, 17.2; HRMS(ESI) calcd for $C_{29}H_{33}N_2O_2^+$ $[M+H]^+$ = 441.2542, found = 441.2537.

For the synthesis on 0.5 mmol scale, the reaction mixture was stirred at 60 °C for 24 hours. The desired product was isolated as a pale yellow liquid with a yield of 54% (119 mg).

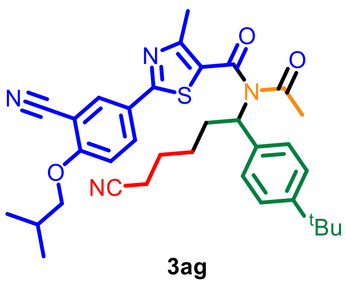
N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-5-cyanopentyl)thiophene-2-carboxamide (3af)



3af

Pale yellow liquid (28.2 mg, 71% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, J = 5.0, 1.2 Hz, 1H), 7.28 – 7.23 (m, 3H), 7.23 – 7.19 (m, 2H), 6.94 (dd, J = 4.9, 3.8 Hz, 1H), 5.57 (t, J = 7.9 Hz, 1H), 2.34 – 2.29 (m, 1H), 2.27 (t, J = 7.1 Hz, 2H), 2.16 – 2.07 (m, 1H), 1.92 (s, 3H), 1.71 – 1.60 (m, 2H), 1.51 – 1.39 (m, 2H), 1.19 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.6, 168.1, 150.8, 140.7, 136.0, 134.9, 134.1, 128.2, 128.0, 125.4, 119.6, 59.8, 34.6, 31.6, 31.4, 26.6, 26.2, 25.2, 17.2; HRMS(ESI) calcd for $C_{23}H_{29}N_2O_2S^+$ $[M+H]^+$ = 397.1950, found = 397.1942

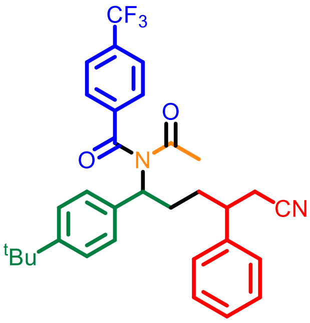
N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-5-cyanopentyl)-2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxamide (3ag)



3ag

Pale yellow liquid (42.1 mg, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 2.1 Hz, 1H), 7.94 (dd, J = 8.8, 2.1 Hz, 1H), 7.29 – 7.22 (m, 4H), 6.93 (d, J = 8.9 Hz, 1H), 5.50 (t, J = 7.8 Hz, 1H), 3.83 (d, J = 6.5 Hz, 2H), 2.49 (s, 3H), 2.29 (t, J = 7.1 Hz, 2H), 2.27 – 2.22 (m, 1H), 2.20 – 2.10 (m, 2H), 2.01 (s, 3H), 1.72 – 1.62 (m, 2H), 1.51 – 1.40 (m, 2H), 1.18 (s, 9H), 1.02 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 168.3, 167.3, 162.9, 160.8, 151.2, 135.5, 132.7, 132.2, 128.9, 128.2, 125.5, 119.6, 115.3, 112.8, 103.2 75.8, 60.1, 34.6, 31.9, 31.3, 28.2, 26.2, 26.0, 25.2, 19.1, 17.5, 17.2; HRMS(ESI) calcd for $C_{34}H_{41}N_4O_3S^+$ $[M+H]^+$ = 585.2899, found = 585.2899.

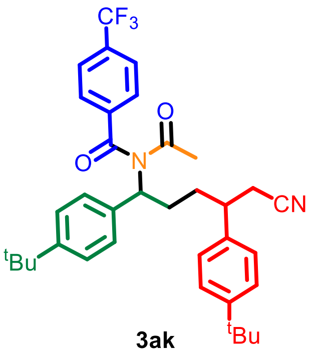
N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-5-cyano-4-phenylpentyl)-4-(trifluoromethyl) benzamide (3aj) (1.2:1 diastereomers)



3aj

Pale yellow liquid (48.7 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.53 (m, 4H), 7.37 – 7.31 (m, 2H), 7.31 - 7.17 (m, 7H), 5.74 – 5.61 (m, 1H), 3.12 – 2.93 (m, 1H), 2.73 – 2.48 (m, 2H), 2.43 – 2.19 (m, 1H), 2.17 – 2.02 (m, 1H), 1.99 – 1.80 (m, 5H), 1.26 (s, 5H), 1.25 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 173.1, 173.0, 172.8, 151.6, 150.9, 141.2, 141.0, 139.9, 139.8, 135.9, 135.6, 134.2 (q, *J* = 25.3 Hz), 129.2, 129.0, 129.0, 127.9, 127.8, 127.7, 127.3, 127.3, 126.0 (q, *J* = 3.0 Hz), 125.8, 125.5, 125.5, 123.4 (q, *J* = 272.0 Hz), 118.5, 118.5, 59.9, 59.3, 59.2, 42.3, 41.7, 34.6, 32.4, 32.0, 31.3, 30.0, 29.4, 28.3, 27.6, 27.5, 27.4, 25.4, 15.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.13, -63.17; HRMS(ESI) calcd for $C_{32}H_{34}F_3N_2O_2^+$ $[M+H]^+$ = 535.2572, found = 535.2580

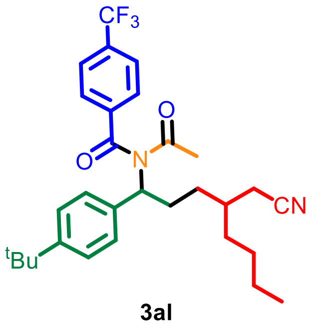
N-Acetyl-N-(1,4-bis(4-(tert-butyl)phenyl)-5-cyanopentyl)-4-(trifluoromethyl)benzamide (3ak) (1.2:1 diastereomers)



3ak

Pale yellow liquid (44.9 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.53 (m, 3H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.30 – 7.20 (m, 4H), 7.12 (dd, *J* = 8.4, 2.3 Hz, 2H), 5.72 – 5.60 (m, 1H), 3.12 – 2.91 (m, 1H), 2.67 – 2.51 (m, 2H), 2.40 – 2.20 (m, 1H), 2.15 – 2.04 (m, 1H), 1.98 – 1.76 (m, 5H), 1.31 (s, 9H), 1.26 (s, 5H), 1.26 (s, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 173.5, 173.2, 173.1, 150.9, 150.9, 150.6, 140.0, 139.9, 138.2, 138.0, 136.0, 135.8, 134.0 (q, *J* = 32.3 Hz), 129.1, 129.0, 127.9, 127.7, 126.9, 126.9, 126.0, 125.5, 125.5, 123.5 (q, *J* = 272.8 Hz), 118.7, 118.7, 60.1, 59.3, 41.8, 41.2, 34.6, 32.4, 32.0, 31.5, 31.4, 30.0, 29.8, 29.3, 27.7, 27.5, 25.5, 25.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.14; HRMS(ESI) calcd for $C_{36}H_{42}F_3N_2O_2^+$ $[M+H]^+$ = 591.3198, found = 591.3193.

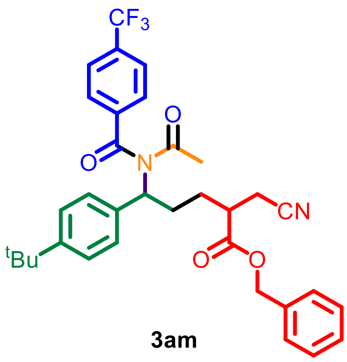
N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-4-(cyanomethyl)octyl)-4-(trifluoromethyl) benzamide (3al) (1:1 diastereomers)



3al

Pale yellow liquid (30.9 mg, 60% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 4H), 7.35 – 7.29 (m, 4H), 5.66 – 5.60 (m, 1H), 2.47 – 2.33 (m, 3H), 2.30 – 2.17 (m, 1H), 1.91 (2×s, 3H), 1.82 – 1.73 (m, 1H), 1.56 – 1.34 (m, 5H), 1.34 – 1.30 (m, 2H), 1.28 (brs, 9H), 1.25 – 1.18 (m, 1H), 0.88 (q, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 173.2, 173.1, 151.0, 139.9, 136.0, 135.9, 134.3 (q, J = 32.8 Hz), 129.1, 127.9, 127.8, 126.0, 125.5, 123.5 (q, J = 273.5 Hz), 118.8, 118.7, 60.4, 60.3, 35.2, 35.0, 34.6, 33.3, 33.0, 31.4, 31.0, 30.8, 29.4, 29.0, 28.8, 27.7, 27.6, 22.8, 21.9, 21.8, 14.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.16; HRMS(ESI) calcd for $C_{30}H_{38}F_3N_2O_2^+$ $[M+H]^+$ = 515.2885, found = 515.2876.

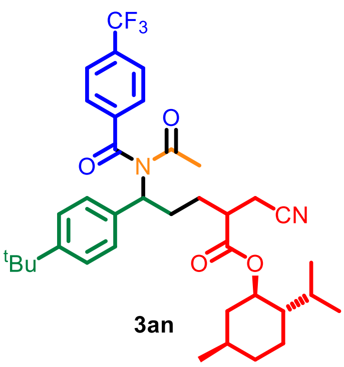
Benzyl 5-(N-acetyl-4-(trifluoromethyl)benzamido)-5-(4-(tert-butyl)phenyl)-2-(cyanomethyl) pentanoate (3am) (1:1 diastereomers)



3am

Pale yellow liquid (26.7mg, 45% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 4H), 7.29 – 7.24 (m, 5H), 7.23 – 7.15 (m, 4H), 5.61 – 5.52 (m, 1H), 5.17 – 5.04 (m, 2H), 2.89 – 2.75 (m, 1H), 2.69 – 2.50 (m, 2H), 2.44 – 2.29 (m, 1H), 2.27 – 2.05 (m, 1H), 1.88 – 1.67 (m, 5H), 1.20 (s, 9H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 173.4, 173.3, 173.0, 172.2, 151.1, 151.1, 139.8, 135.5, 135.4, 135.2, 135.2, 134.3 (q, J = 33.2 Hz), 134.2, 129.1, 128.8, 128.8, 128.7, 128.7, 128.6, 127.8, 126.1, 125.6, 125.7, 123.4 (q, J = 272.7 Hz), 117.7, 117.6, 67.6, 67.5, 59.8, 59.4, 41.4, 41.1, 34.6, 31.4, 29.1, 28.7, 28.6, 27.7, 27.7, 19.5, 19.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.15; HRMS(ESI) calcd for $C_{34}H_{36}F_3N_2O_4^+$ $[M+H]^+$ = 593.2627, found = 593.2623.

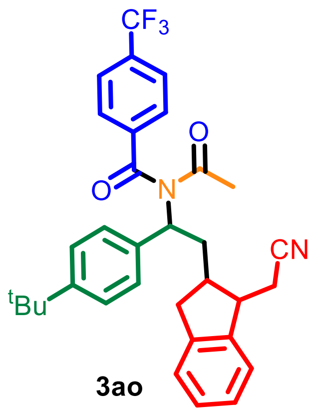
(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 5-(N-acetyl-4-(trifluoromethyl)benzamido)-5-(4-(tert-butyl)phenyl)-2-(cyanomethyl)pentanoate (3an) (1:1 diastereomers)



3an

Pale yellow liquid (41.7 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 4H), 7.27 – 7.21 (m, 4H), 5.66 – 5.54 (m, 1H), 4.72 – 4.59 (m, 1H), 2.81 – 2.66 (m, 1H), 2.65 – 2.47 (m, 2H), 2.46 – 2.23 (m, 1H), 2.23 – 2.06 (m, 1H), 1.97 – 1.84 (m, 1H), 1.82 (d, J = 3.1 Hz, 3H), 1.79 – 1.66 (m, 3H), 1.65 – 1.56 (m, 2H), 1.47 – 1.36 (m, 1H), 1.36 – 1.27 (m, 1H), 1.20 (s, 4.5H), 1.20 (s, 4.5H), 1.05 – 0.87 (m, 2H), 0.86 – 0.78 (m, 6H), 0.75 (d, J = 7.0 Hz, 1H), 0.69 – 0.59 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 173.0, 172.0, 171.9, 151.0, 139.9, 135.6, 134.3 (q, J = 33.9 Hz), 129.1, 127.8, 127.8, 126.1, 125.5, 123.4 (q, J = 273.0 Hz), 117.8, 117.7, 75.9, 75.8, 59.9, 59.6, 59.5, 47.0, 46.9, 41.9, 41.7, 41.5, 41.3, 40.9, 40.8, 34.6, 34.2, 31.5, 31.5, 31.4, 29.3, 29.1, 28.9, 28.9, 28.8, 27.7, 27.6, 26.4, 26.3, 23.3, 23.2, 23.1, 22.1, 20.9, 19.8, 19.6, 19.6, 16.2, 16.0, 15.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.16; HRMS(ESI) calcd for $C_{37}H_{48}F_3N_2O_4^+$ $[M+H]^+$ = 641.3566, found = 641.3571.

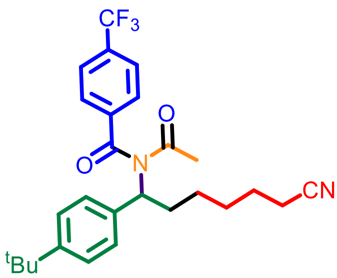
N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-2-(1-(cyanomethyl)-2,3-dihydro-1H-inden-2-yl)ethyl)-4-(trifluoromethyl)benzamide (3ao) (1.6:1 diastereomers)



3ao

Pale yellow liquid (47.6 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 4H), 7.34 – 7.19 (m, 5H), 7.16 – 7.09 (m, 3H), 5.92 – 5.76 (m, 1H), 3.24 – 3.09 (m, 2H), 2.99 (ddd, J = 14.1, 11.3, 3.1 Hz, 1H), 2.80 – 2.55 (m, 3H), 2.28 – 2.17 (m, 1H), 2.14 – 2.00 (m, 1H), 1.83 (s, 1.2H), 1.78 (s, 1.8H), 1.21 (s, 5.5H), 1.18 (s, 3.5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.6, 173.4, 172.5, 151.2, 151.1, 142.4, 142.4, 142.1, 139.9, 136.4, 134.8, 134.4 (q, J = 32.8 Hz), 129.2, 128.3, 128.0, 127.7, 127.1, 126.1 (q, J = 3.8 Hz), 125.6, 125.1, 123.9, 123.4, 123.4 (q, J = 272.9 Hz), 118.8, 118.6, 58.5, 58.3, 47.1, 43.3, 42.8, 37.9, 37.6, 37.1, 36.4, 34.6, 31.4, 28.0, 27.6, 22.3, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.14; HRMS(ESI) calcd for $C_{33}H_{34}F_3N_2O_2^+$ $[M+H]^+$ = 547.2572, found = 547.2584.

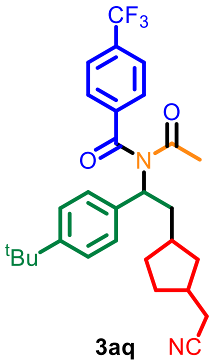
N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-6-cyanohexyl)-4-(trifluoromethyl)benzamide (3ap)



3ap

Pale yellow liquid (11.3 mg, 24% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.26 – 7.21 (m, 4H), 5.57 (t, J = 7.8 Hz, 1H), 2.31 – 2.23 (m, 3H), 2.22 – 2.11 (m, 1H), 1.85 (s, 3H), 1.59 (p, J = 7.2 Hz, 2H), 1.52 – 1.41 (m, 2H), 1.35 (p, J = 7.7 Hz, 2H)), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 173.1, 150.9, 140.0, 136.1, 134.2 (q, J = 33.4 Hz), 134.38, 129.0, 127.8, 126.0 (q, J = 3.3 Hz), 125.5, 123.4 (q, J = 272.5 Hz), 119.7, 60.2, 34.6, 32.0, 32.4, 28.6, 27.5, 26.4, 25.3, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.15 ; HRMS(ESI) calcd for $C_{27}H_{32}F_3N_2O_2^+$ $[M+H]^+$ = 473.2416, found = 473.2411.

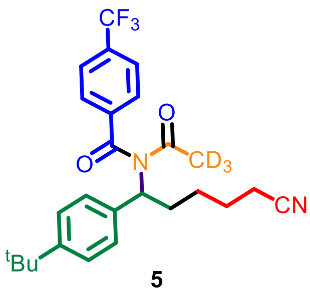
N-Acetyl-N-(1-(4-(tert-butyl)phenyl)-2-(3-(cyanomethyl)cyclopentyl)ethyl)-4-(trifluoromethyl)benzamide (3aq) (1:1 diastereomers)



3aq

Pale yellow liquid (30.9 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.29 – 7.21 (m, 4H), 5.66 – 5.57 (m, 1H), 2.37 – 2.21 (m, 4H), 2.19 – 2.01 (m, 2H), 2.00 – 1.86 (m, 2H), 1.86 – 1.76 (m, 5H), 1.62 – 1.49 (m, 2H), 1.20 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5, 173.1, 173.0, 150.9, 140.1, 136.1, 136.1, 134.2 (q, *J* = 32.8 Hz), 129.0, 128.0, 127.9, 127.9, 126.0, 125.5, 124.83, 123.5 (q, *J* = 273.0 Hz), 119.3, 119.2, 119.1, 59.3, 59.2, 40.0, 39.7, 39.6, 38.6, 38.4, 37.9, 37.7, 37.5, 36.2, 36.1, 35.2, 35.2, 34.6, 32.9, 32.9, 32.4, 32.2, 31.4, 30.9, 30.9, 29.8, 27.7, 27.6, 23.3, 23.3, 23.1, 23.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.15; HRMS(ESI) calcd for $C_{29}H_{33}F_3N_2NaO_2^+$ $[M+Na]^+$ = 521.2392, found = 521.2388.

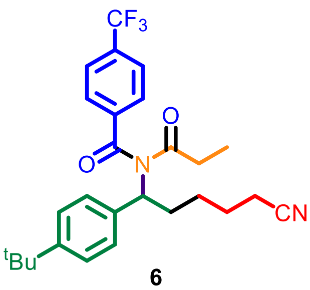
N-(Acetyl-d3)-N-(1-(4-(tert-butyl)phenyl)-5-cyanopentyl)-4-(trifluoromethyl)benzamide (5)



5

Pale yellow liquid (29.1 mg, 63% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.53 (m, 4H), 7.31 – 7.21 (m, 4H), 5.59 (t, *J* = 7.7 Hz, 1H), 2.41 – 2.32 (m, 1H), 2.29 (t, *J* = 6.8 Hz, 2H), 2.24 – 2.12 (m, 1H), 1.76 – 1.60 (m, 2H), 1.47 (p, *J* = 7.1 Hz, 2H), 1.20 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 173.1, 150.9, 139.9, 135.9, 134.3 (q, *J* = 32.3 Hz), 129.1, 127.8, 126.0 (q, *J* = 3.2 Hz), 125.5, 123.5 (q, *J* = 272.4 Hz), 119.6, 59.9, 34.6, 31.4, 26.6 (h, *J* = 19.5 Hz) 26.2, 25.2, 17.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.15; HRMS(ESI) calcd for $C_{26}H_{27}D_3F_3N_2O_2^+$ $[M+H]^+$= 462.2448, found = 462.2445.

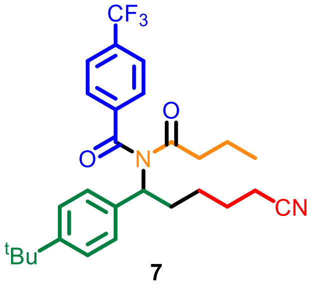
N-(1-(4-(tert-Butyl)phenyl)-5-cyanopentyl)-N-propionyl-4-(trifluoromethyl)benzamide (6)



6

Pale yellow liquid (19.4 mg, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 4H), 7.28 – 7.21 (m, 4H), 5.60 (dd, *J* = 8.7, 7.0 Hz, 1H), 2.42 – 2.32 (m, 1H), 2.29 (t, *J* = 7.0 Hz, 2H), 2.23 – 2.12 (m, 1H), 1.98 (q, *J* = 7.3 Hz, 2H), 1.75 – 1.61 (m, 2H), 1.47 (p, *J* = 7.4 Hz, 2H), 1.20 (s, 9H), 0.83 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (176 MHz, $CDCl_3$) δ 177.8, 173.2, 151.0, 140.1, 135.9, 134.2 (q, *J* = 33.2 Hz), 129.0, 127.8, 126.0, 125.5, 123.5 (q, *J* = 271.4 Hz), 119.6, 59.9, 34.6, 33.7, 31.4, 31.4, 26.3, 25.2, 17.2, 9.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.14; HRMS(ESI) calcd for $C_{27}H_{32}F_3N_2O_2^+$ $[M+H]^+$ = 473.2416, found = 473.2418.

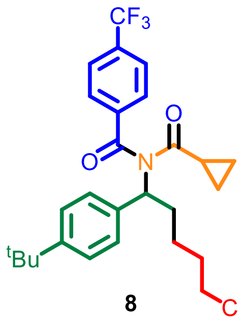
N-(1-(4-(tert-Butyl)phenyl)-5-cyanopentyl)-N-butyryl-4-(trifluoromethyl)benzamide (7)



7

Pale yellow liquid (27.2 mg, 56% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 4H), 7.29 – 7.21 (m, 4H), 5.60 (dd, *J* = 8.4, 7.3 Hz, 1H), 2.40 – 2.32 (m, 1H), 2.29 (t, *J* = 7.1 Hz, 2H), 2.25 – 2.14 (m, 1H), 1.96 – 1.89 (m, 2H), 1.76 – 1.61 (m, 2H), 1.47 (p, *J* = 7.6 Hz, 2H), 1.40 – 1.32 (m, 2H), 1.20 (s, 9H), 0.58 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.7, 173.3, 151.0, 140.1, 135.9, 134.2 (q, *J* = 33.4 Hz), 129.1, 128.0, 126.0 (q, *J* = 3.2 Hz), 125.5, 123.5 (q, *J* = 273.1 Hz), 119.6, 59.9, 42.1, 34.6, 31.6, 31.4, 26.3, 25.3, 19.2, 17.2, 13.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.14; HRMS(ESI) calcd for $C_{28}H_{34}F_3N_2O_2^+$ $[M+H]^+$ = 487.2572, found = 487.2569.

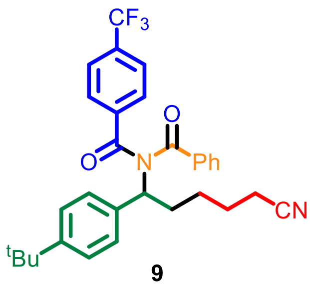
N-(1-(4-(tert-Butyl)phenyl)-5-cyanopentyl)-N-(cyclopropanecarbonyl)-4-(trifluoromethyl) benzamide (8)



8

Pale yellow liquid (27.6mg, 57% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.56 (m, 4H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 5.72 (dd, *J* = 9.4, 6.4 Hz, 1H), 2.49 – 2.38 (m, 1H), 2.30 (t, *J* = 7.0 Hz, 2H), 2.20 – 2.09 (m, 1H), 1.78 – 1.61 (m, 2H), 1.54 – 1.48 (m, 2H), 1.21 (s, 9H), 1.10 – 1.03 (m, 1H), 0.94 – 0.82 (m, 2H), 0.51 – 0.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 172.5, 150.8, 140.4, 136.4, 134.0 (q, *J* = 32.8 Hz), 129.3, 127.8, 125.8 (q, *J* = 3.4 Hz), 125.5, 123.5 (q, *J* = 272.4 Hz), 119.6, 59.7, 34.6, 31.4, 31.0, 26.2, 25.2, 20.9, 17.3, 12.8, 12.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.13; HRMS(ESI) calcd for $C_{28}H_{32}F_3N_2O_2^+$ $[M+H]^+$ = 485.2416, found = 485.2417.

N-Benzoyl-N-(1-(4-(tert-butyl)phenyl)-5-cyanopentyl)-4-(trifluoromethyl)benzamide (9)

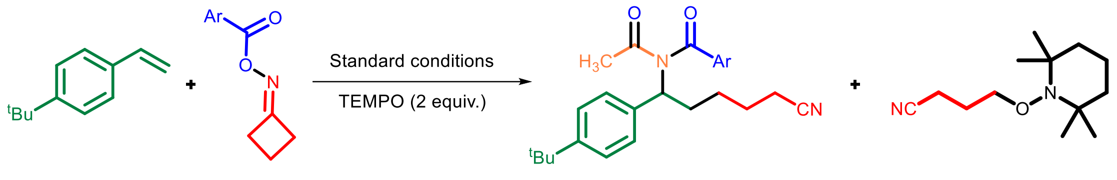


9

Pale yellow liquid (33.8 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.27 – 7.23 (m, 4H), 7.21 – 7.10 (m, 3H), 7.02 (t, *J* = 7.7 Hz, 2H), 5.81 (dd, *J* = 8.9, 6.9 Hz, 1H), 2.67 – 2.52 (m, 1H), 2.37 – 2.24 (m, 3H), 1.80 – 1.67 (m, 2H), 1.67 – 1.55 (m, 2H), 1.21 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.2, 173.0, 151.1, 141.0, 137.6, 136.1, 133.0 (q, *J* = 32.7 Hz), 132.3, 128.8, 128.8, 128.6, 128.2, 125.6, 125.3 (q, *J* = 3.3 Hz), 123.3 (q, *J* = 273.2 Hz), 119.6, 61.1, 34.7, 31.5, 31.4, 26.5, 25.3, 17.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.37; HRMS(ESI) calcd for $C_{31}H_{32}F_3N_2O_2^+$ $[M+H]^+$ = 521.2416, found = 521.2414.

5. The Mechanism Studies:

5.1 Radical inhibition/trapping experiments:



In an oven dried 5.0 mL vial equipped with a magnetic stir bar was charged with alkene **1a** (16.0 mg, 0.1 mmol, 1.0 equiv.), oxime ester **2a** (51.4 mg, 0.2 mmol, 2.0 equiv.), Cp_2Fe (0.9 mg, 0.005 mmol, 5 mol%), TEMPO (31.3 mg, 0.2 mmol, 2.0 equiv.) followed by the addition of CH_3CN (1.0 mL) under nitrogen atmosphere. Then the mixture was stirred at 60 ºC for 12 h. After completion of reaction, the resulting mixture was cooled to room temperature and concentrated under reduced pressure. Then the residue was diluted with ethyl acetate (15 mL), and washed successively with aq. NaHCO3 solution (10 mL×2) and brine solution (10 mL×2). The organic layer was dried over anhydrous sodium sulfate and concentrated. In this reaction, the formation of product 3aa was completely suppressed. The cyanoalkyl-TEMPO adduct **10** was characterized by ESI-MS.

This clearly indicates that the reaction involves a cyanoalkyl radical reaction pathway.

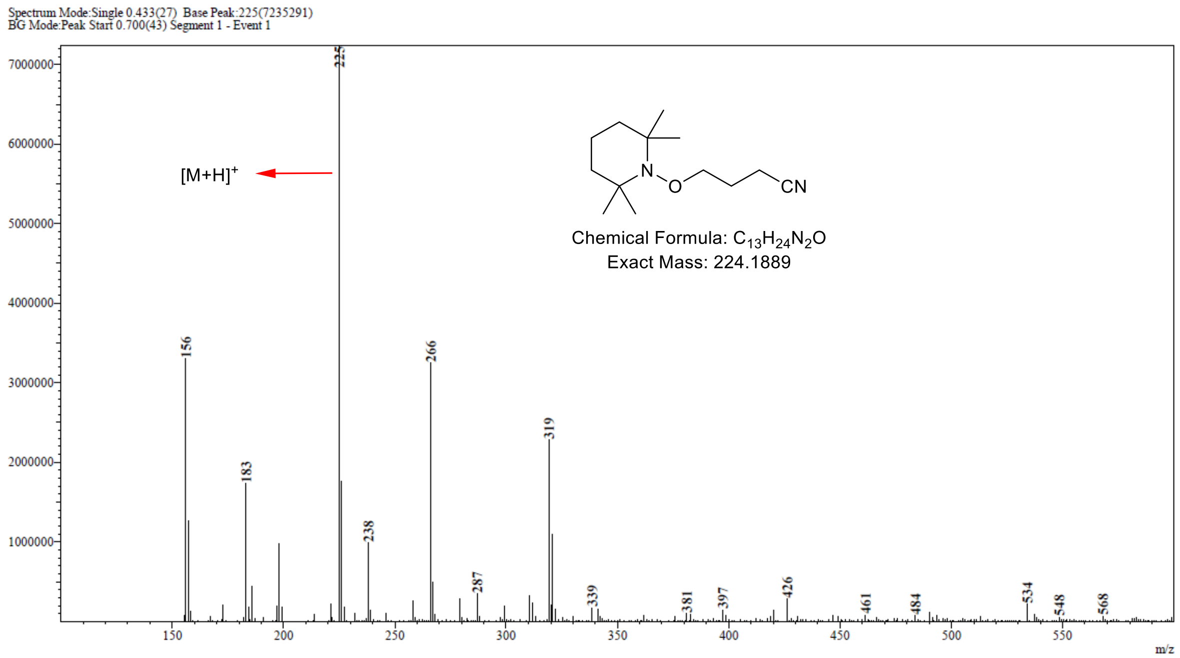


Figure S1

5.2 Mechanistic investigation by ^{1}H NMR studies:

To investigate the interaction of Cp_2Fe with reactants, the following ^{1}H NMR studies were executed.

The NMR spectra of Cp_2Fe in CD_3CN (I), **2a** in CD_3CN (II) and **1a** in CD_3CN (V) were collected.

Later Cp_2Fe (55.8 mg, 0.3 mmol, 1.0 equiv.), oxime ester **2a** (154.2mg, 0.6 mmol, 2.0 equiv.) were dissolved in CD_3CN (3.0 mL). The resulting mixture was evacuated with nitrogen for 3 times. After that, the solution was stirred at room temperature for 12 h. An aliquot of this solution subjected to ^{1}H NMR (III).

The same experiment was conducted at 60 ºC. Cp_2Fe (55.8 mg, 0.3 mmol, 1.0 equiv.), oxime ester **2a** (154.2mg, 0.6 mmol, 2.0 equiv.) were dissolved in CD_3CN (3.0 mL). The resulting mixture was evacuated with nitrogen for 3 times. After that, the solution was stirred at 60 ºC for 12 hours. After cooling to room temperature an aliquot of this reaction mixture subjected to ^{1}H NMR (IV) and the data was collected.

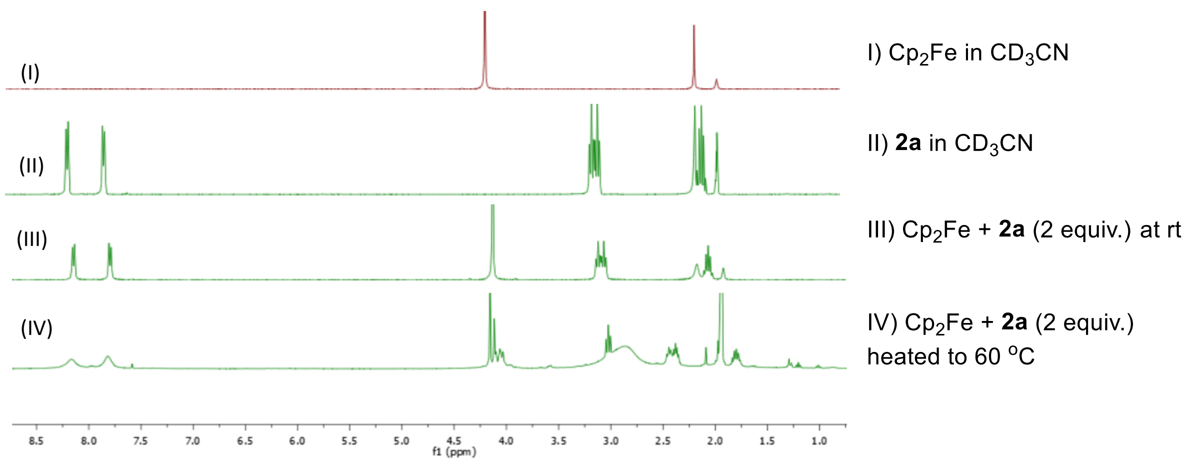
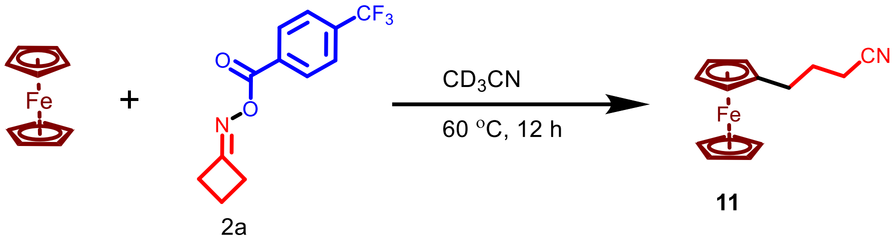
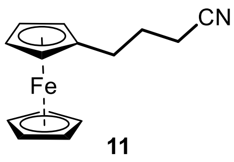


Figure S2

There is no change in the ferrocene and oxime ester signals at room temperature (III, Figure S2). But after heating to 60 ºC, new ferrocene signals were observed (IV, Figure S2). The new spot was isolated and characterized.



COMPOUND 11:



Red liquid (16.7 mg, 22% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.12 (s, 5H), 4.09 (s, 4H), 2.51 (t, J = 7.5 Hz, 2H), 2.33 (t, J = 7.1 Hz, 2H), 1.87 – 1.79 (p, J = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.8, 69.8, 69.2, 68.6, 28.6, 26.9, 16.9; HRMS(ESI) calcd for $C_{14}H_{15}FeN^{+}$ $[M]^{+}$ = 253.0553, found = 253.0551.

Similarly, Cp_2Fe (55.8 mg, 0.3 mmol, 1.0 equiv.), Styrene **1a** (96.2 mg, 0.6 mmol, 2.0 equiv.) were dissolved in CD_3CN (3.0 mL). The resulting mixture was evacuated with nitrogen for 3 times. After that, the solution was stirred at room temperature for 12 h. An aliquot of this solution subjected to ^{1}H NMR (VI).

The same experiment was conducted at 60°C. Cp_2Fe (55.8 mg, 0.3 mmol, 1.0 equiv.), Styrene **1a** (96.2 mg, 0.6 mmol, 2.0 equiv.) were dissolved in CD_3CN (3.0 mL). The resulting mixture was evacuated with nitrogen for 3times. After that, the solution was stirred at 60 °C for 12 hours. After cooling to room temperature an aliquot of this reaction mixture subjected to ^{1}H NMR (VII) and the data was collected.

No change in the ferrocene and styrene signals was observed at room temperature as well as at 60 °C (VI and VII of Figure S3).

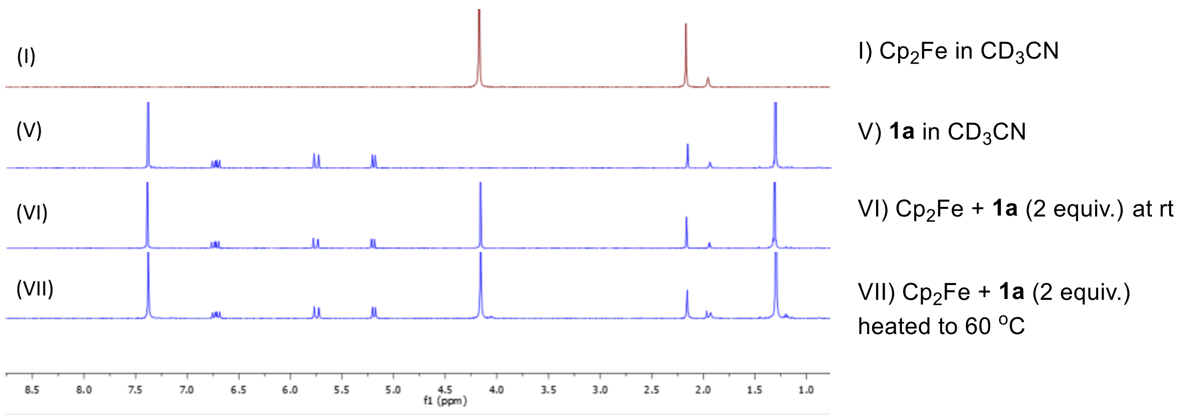
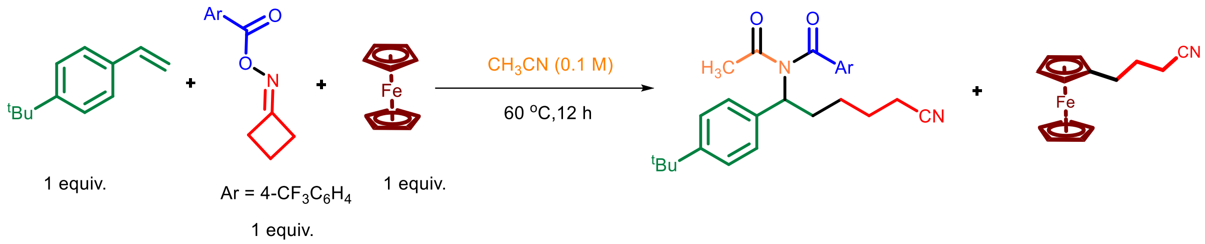


Figure S3

These results suggest that Cp_2Fe is interacting with oxime ester **2a** rather than styrene **1a**.

5.3 Competitive experiment between styrene and ferrocene for cyanoalkyl radical addition:



1a **2a** **3aa (46%)** **11 (0%)**

In an oven dried 5.0 mL vial equipped with a magnetic stir bar was charged with alkene **1a** (16.0 mg, 0.1 mmol, 1.0 equiv.), oxime ester **2a** (25.7 mg, 0.1 mmol, 1.0 equiv.), Cp_2Fe (18.6 mg, 0.1 mmol, 1 equiv.) followed by the addition of CH_3CN (1.0 mL) under nitrogen atmosphere. Then the mixture was stirred at 60 ºC for about 12 h. After completion of reaction, the resulting mixture was cooled to room temperature and concentrated under reduced pressure. Then the residue was diluted with ethyl acetate (15 mL), and washed successively with aq. NaHCO3 solution (10 mL×2) and brine solution (10 mL×2). The organic layer was dried over anhydrous sodium sulfate, concentrated and and purified via flash chromatography on silica gel. In this reaction **3aa** was isolated in 46% yield and compound **11** was not formed.

In this reaction the cyanoalkyl radical preferentially added on styrene (**1a**) over ferrocene. This observation clearly rules out the possibility that **11** might be a catalyst for this transformation.

6. **References**

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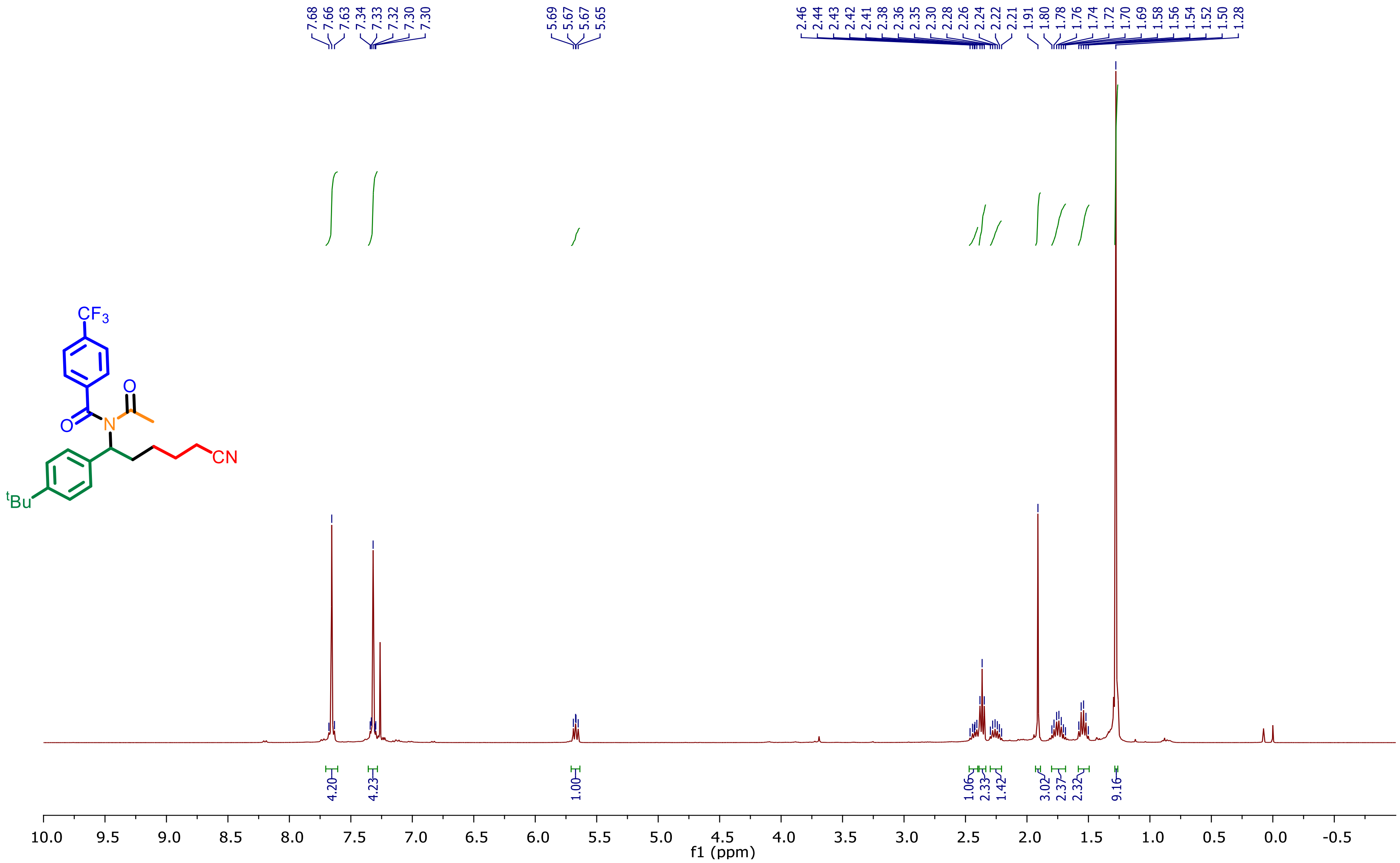
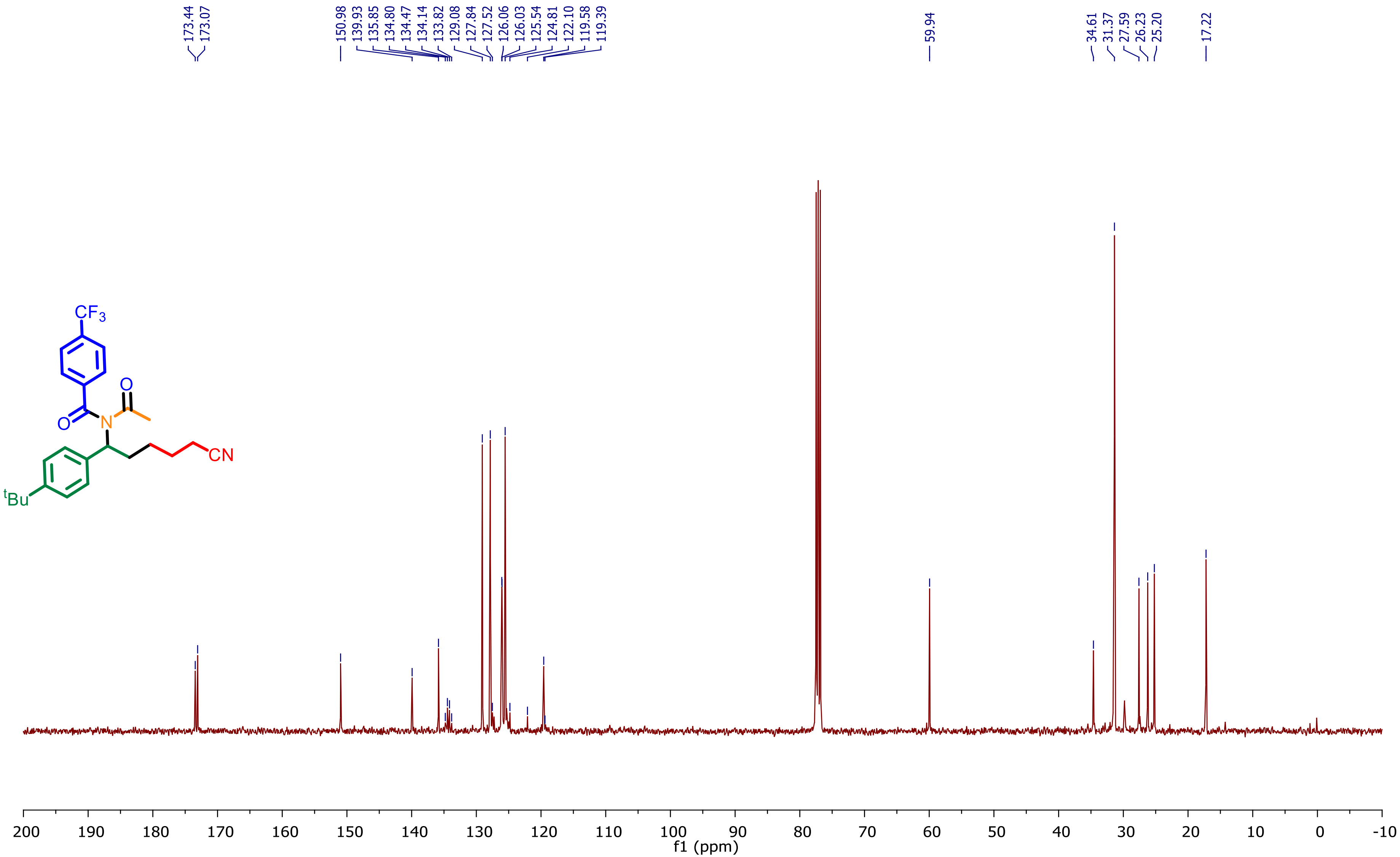
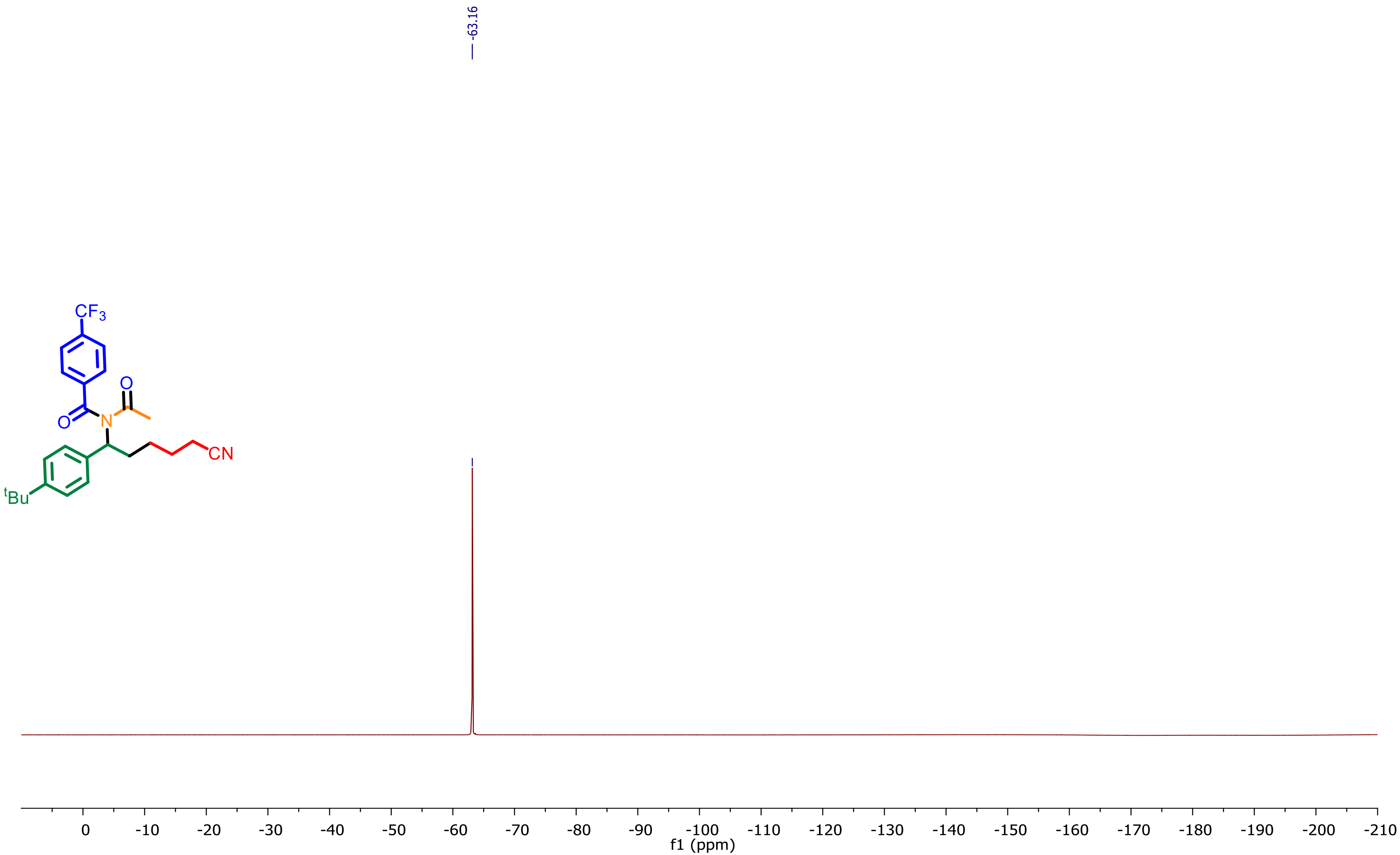
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3aa)**



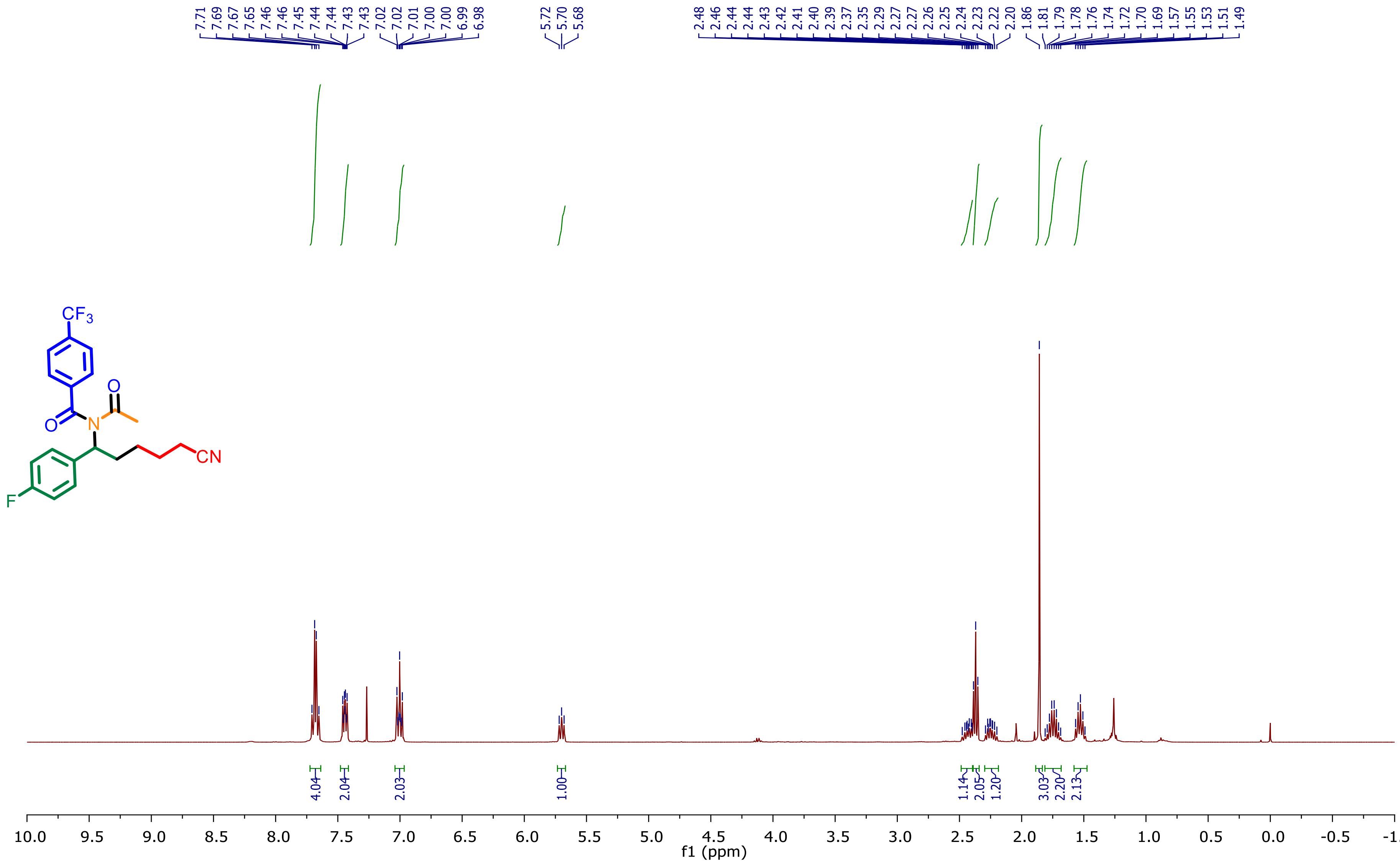
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3aa)**



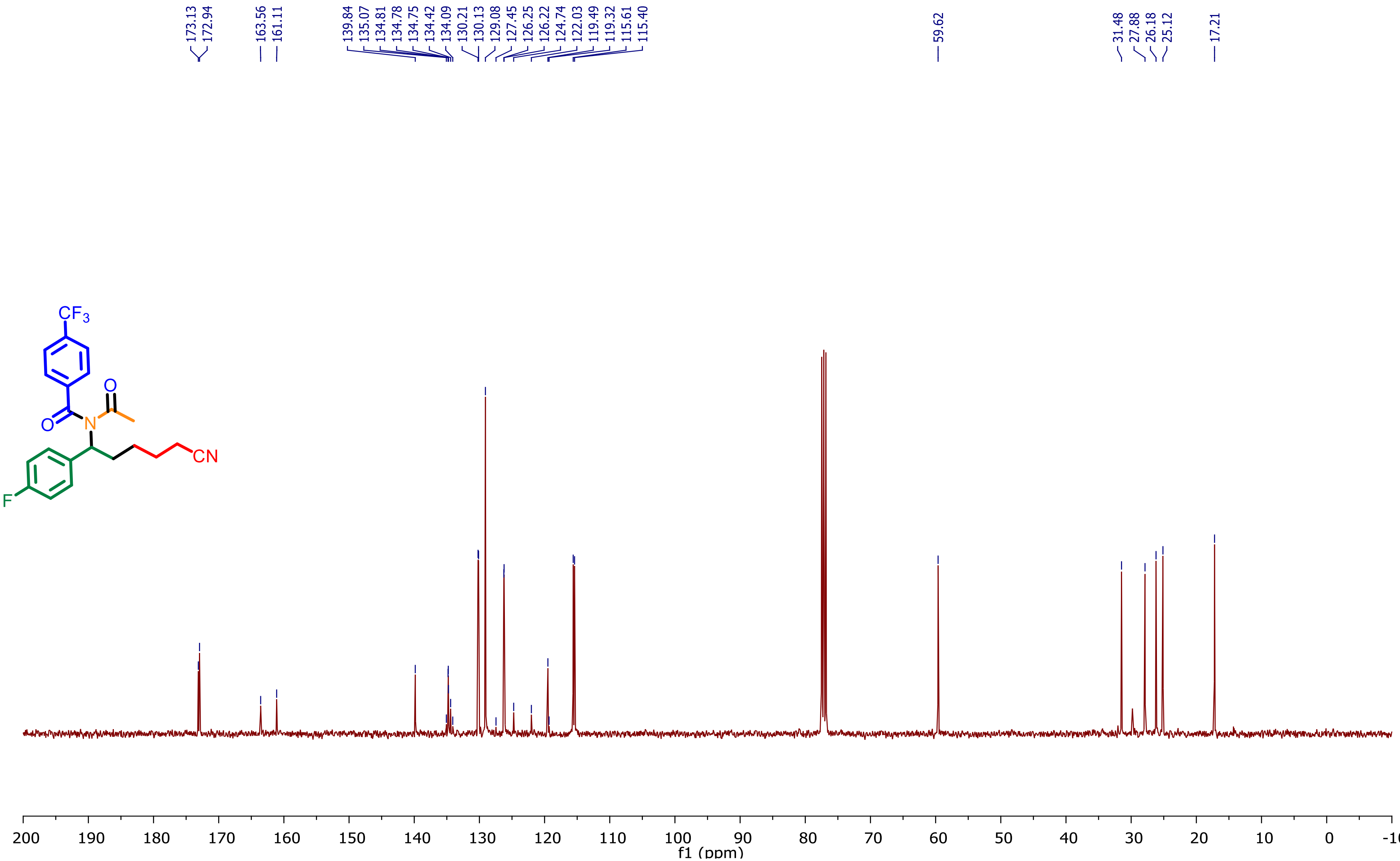
[19]F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3aa)**



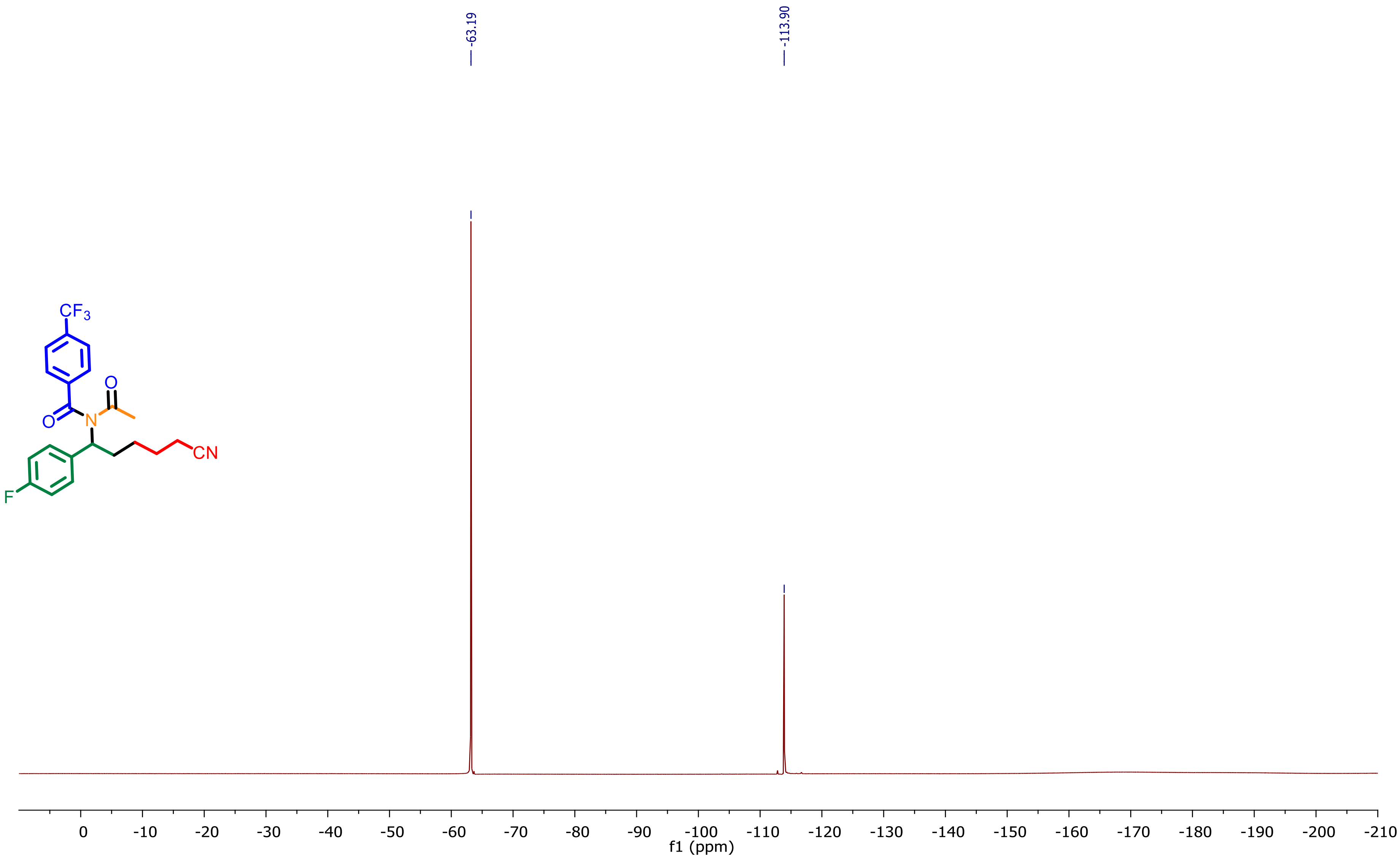
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ba)**



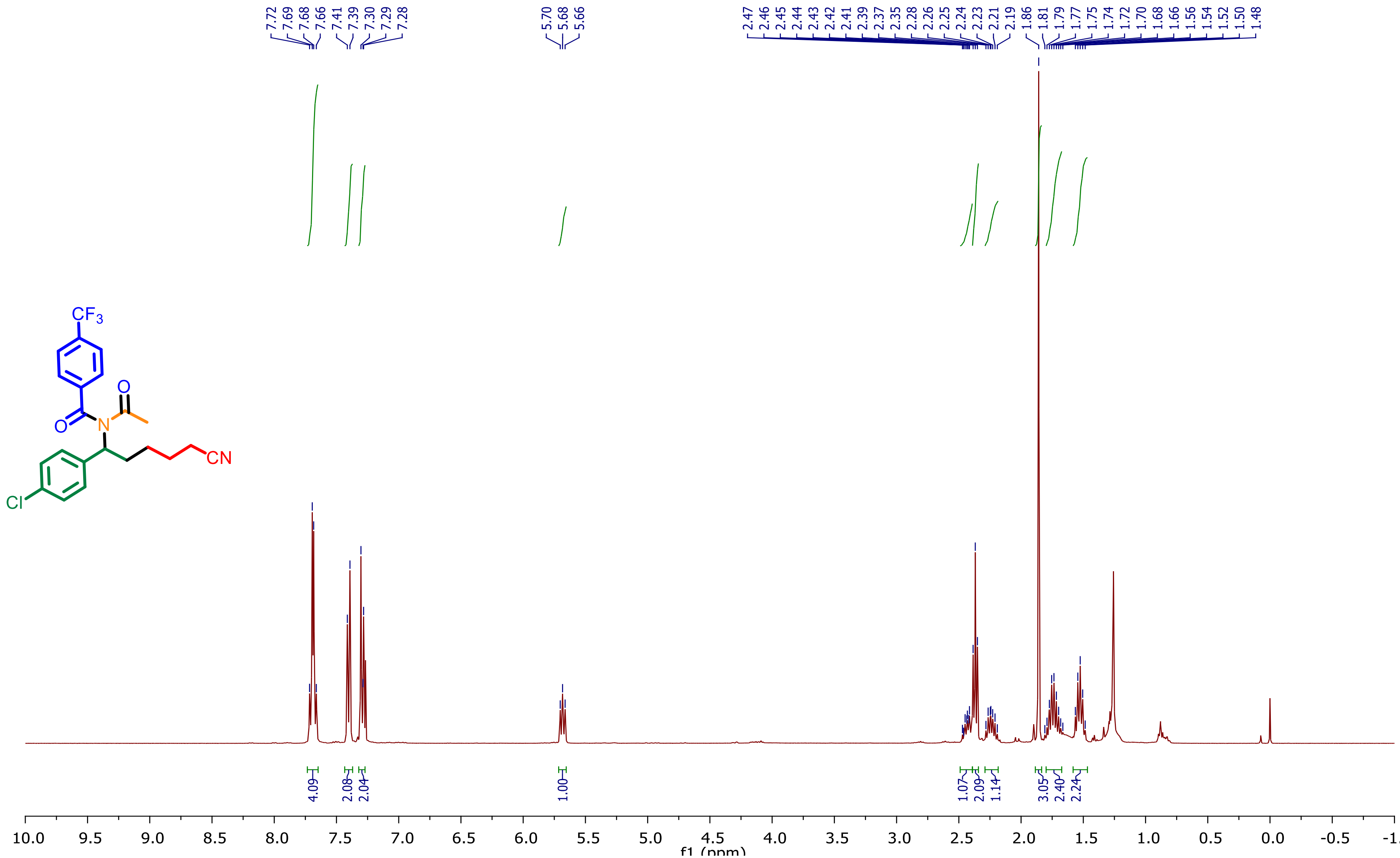
[13]C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ba)**



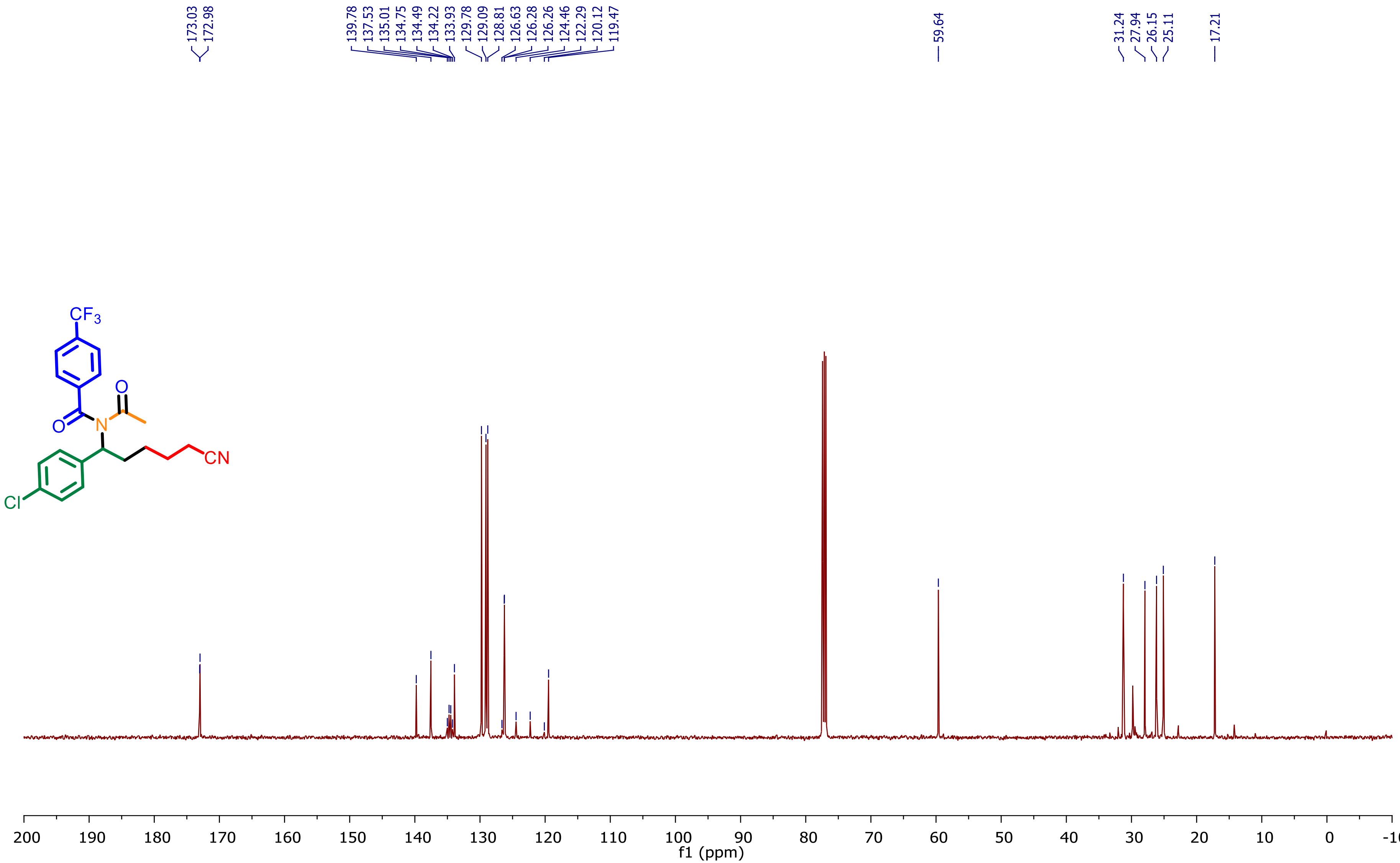
[19]F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3ba)**



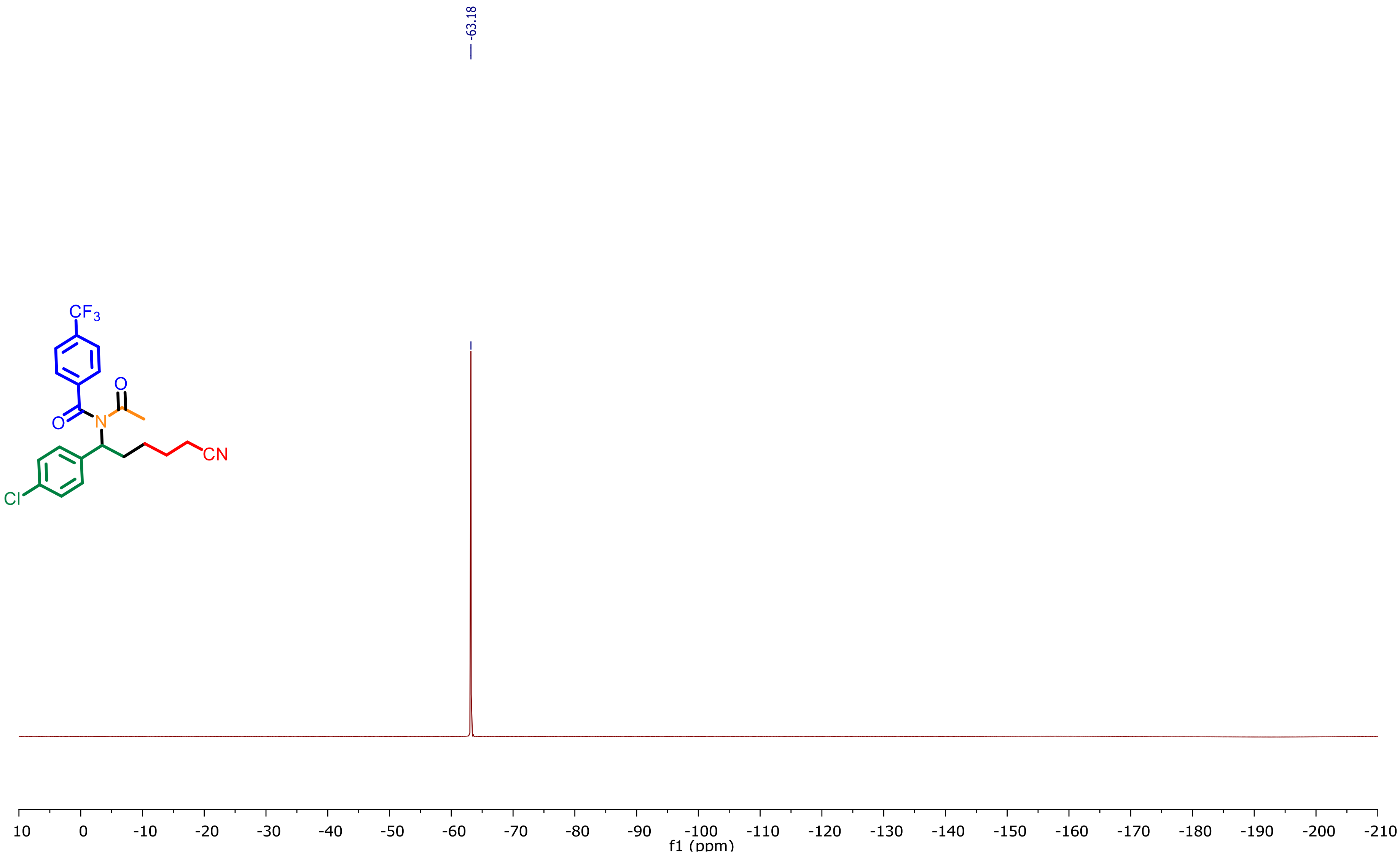
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ca)**



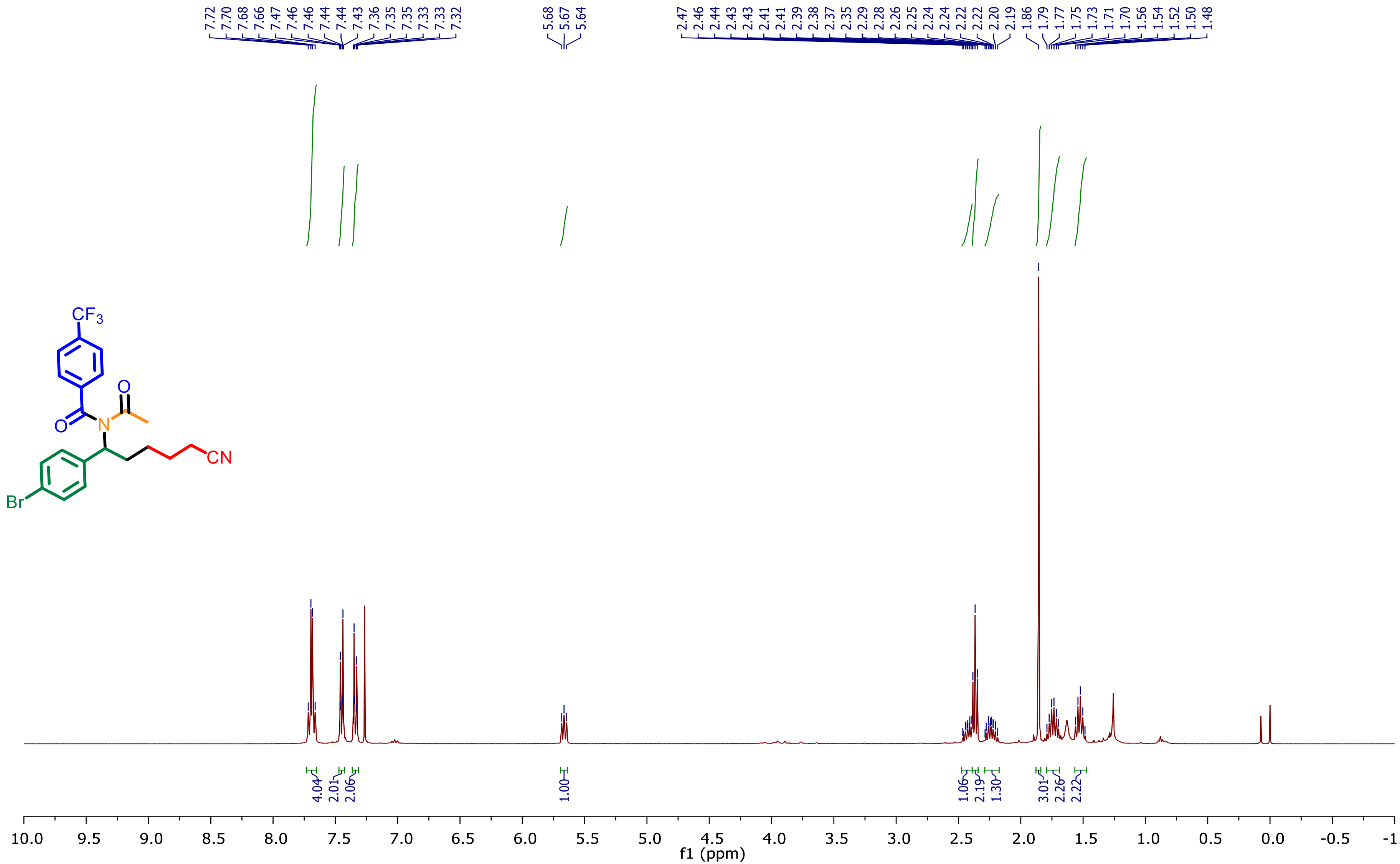
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ca)**



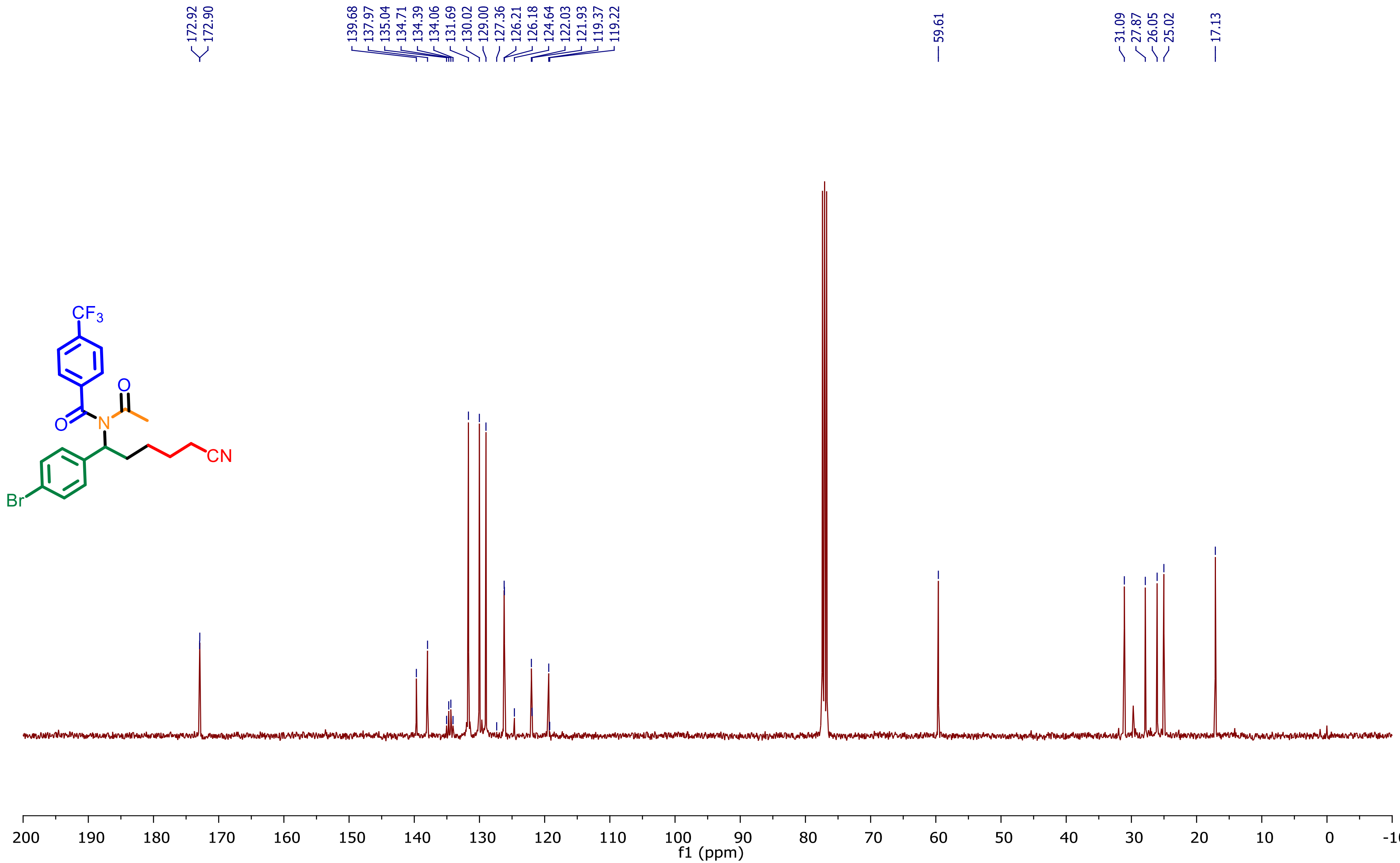
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **(3ca)**



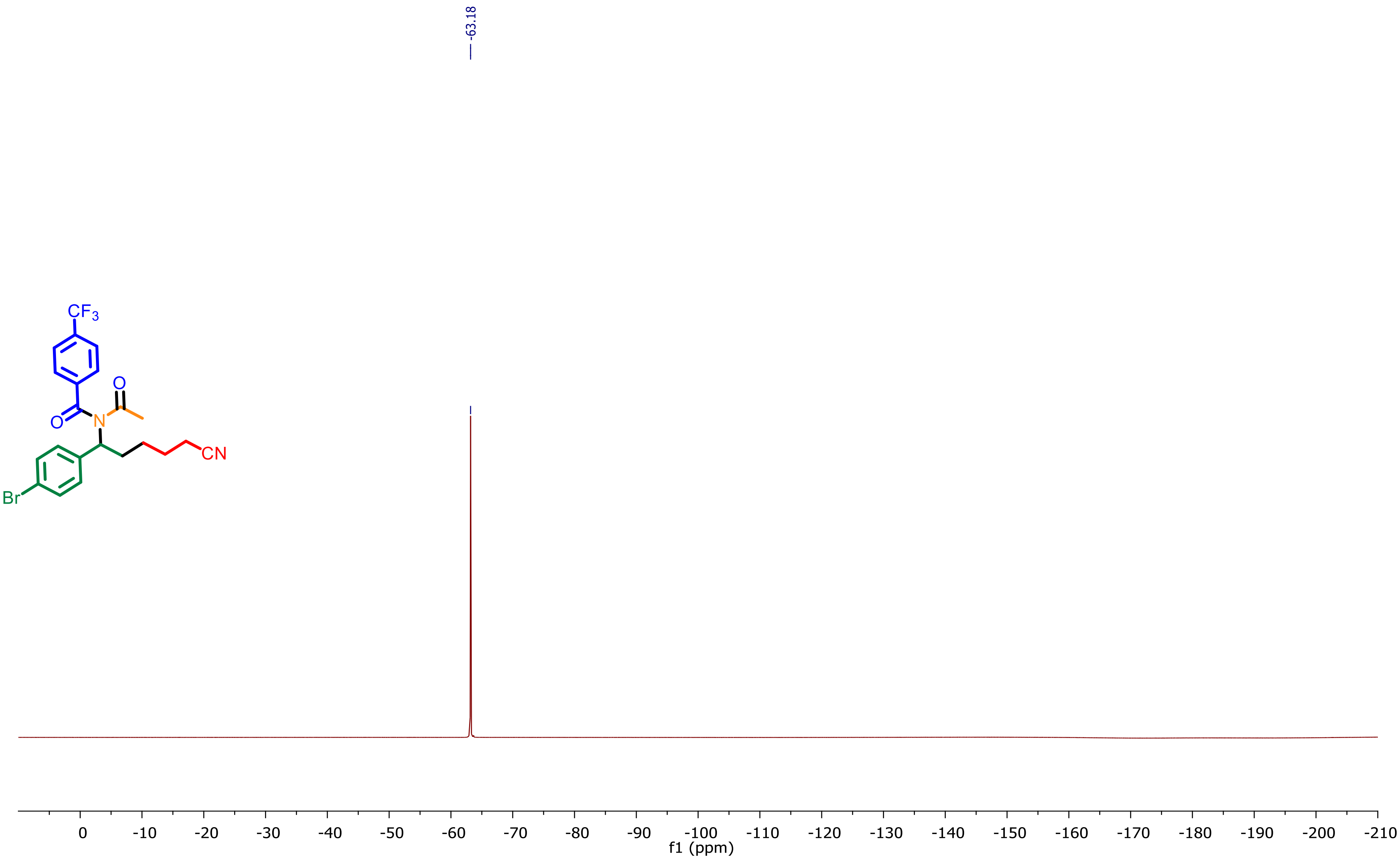
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3da)**



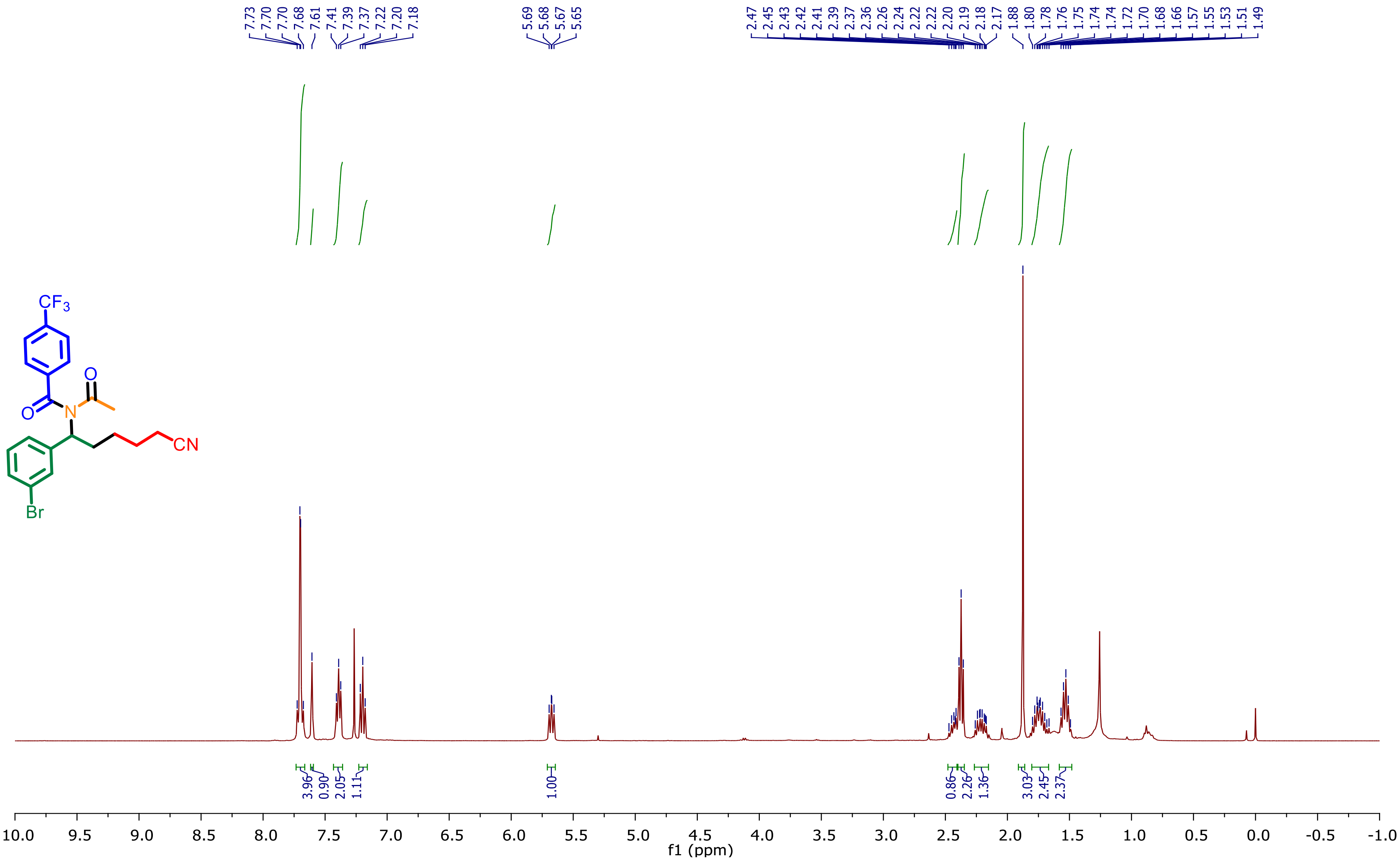
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3da)**



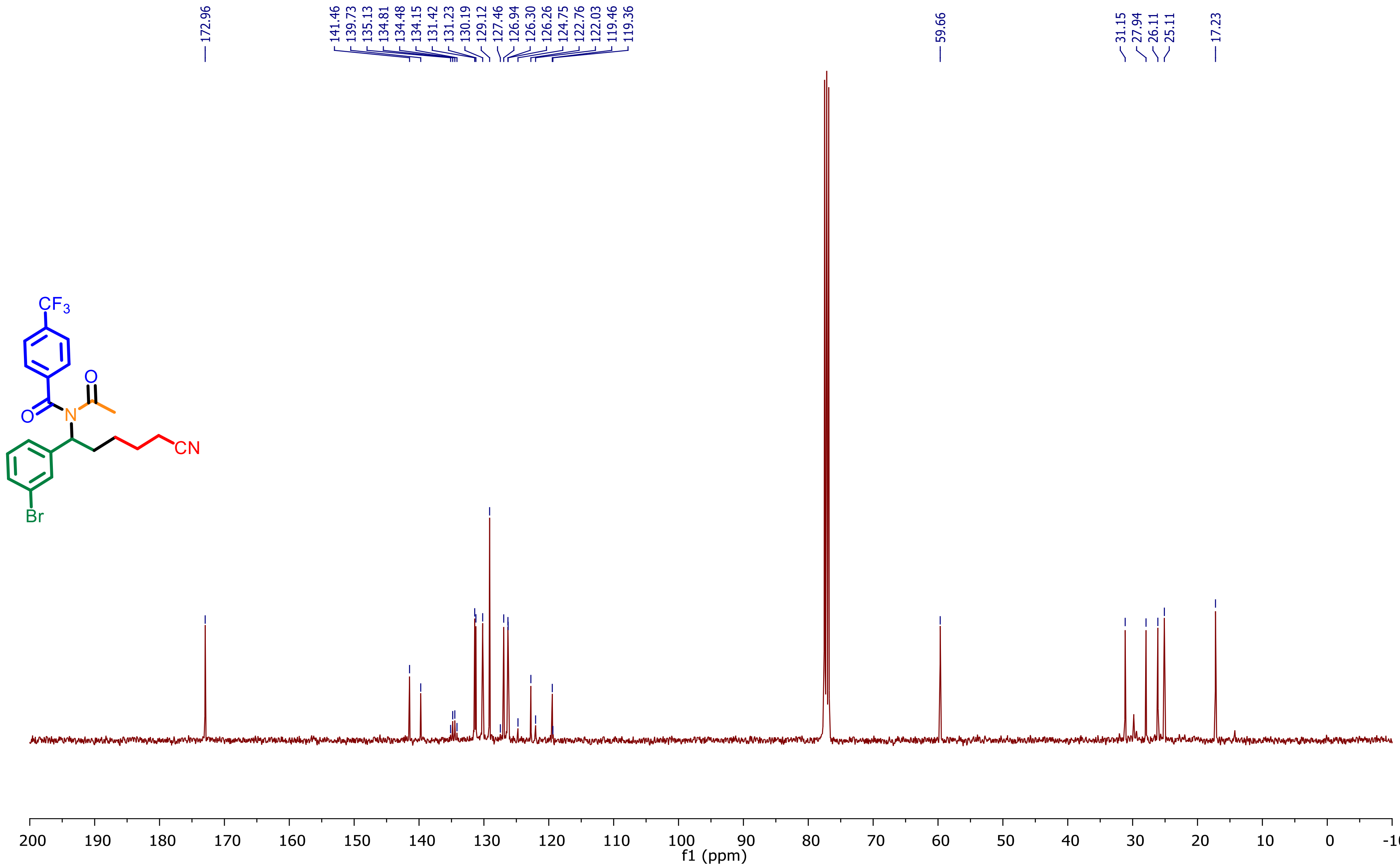
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3da)**



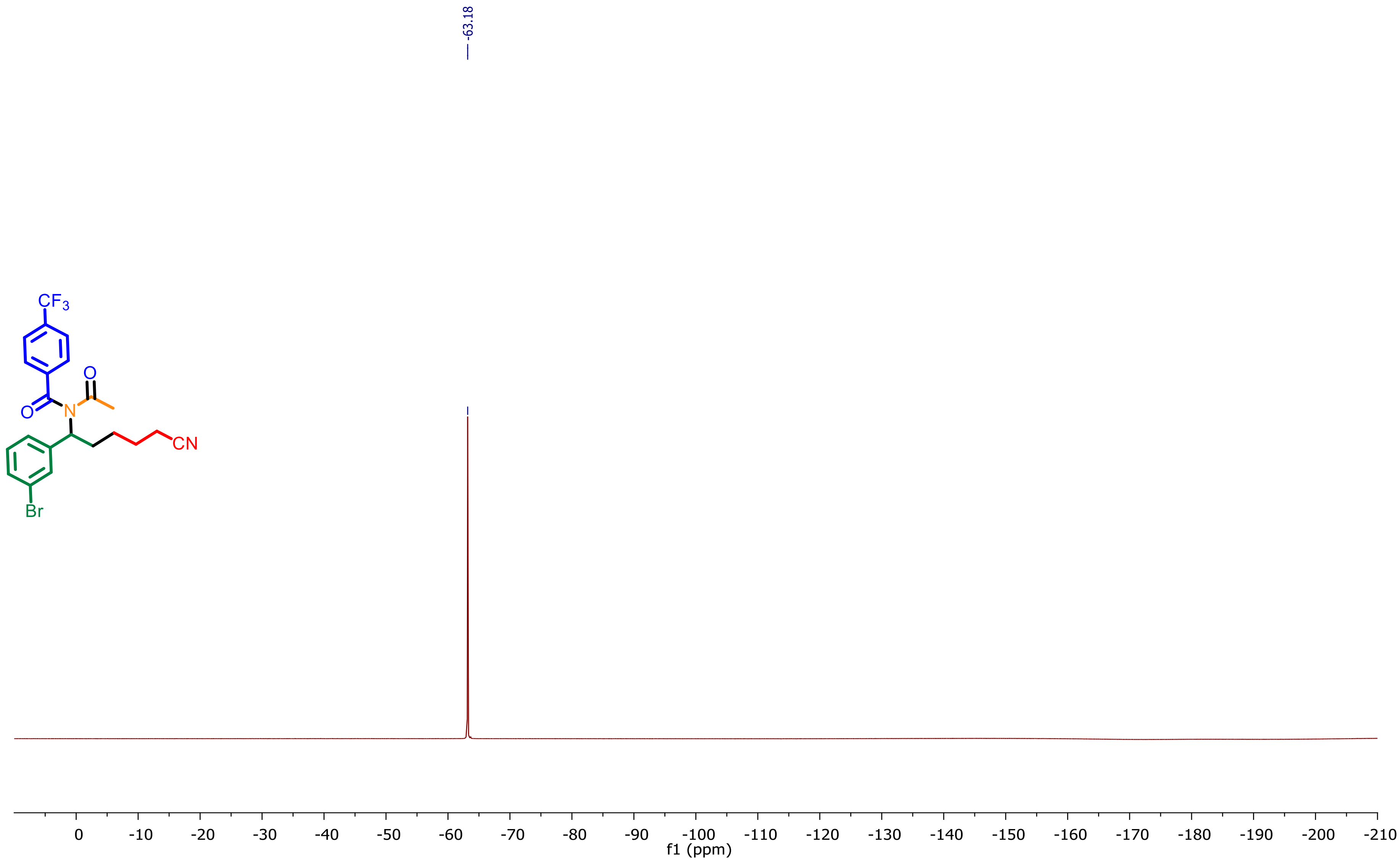
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ea)**



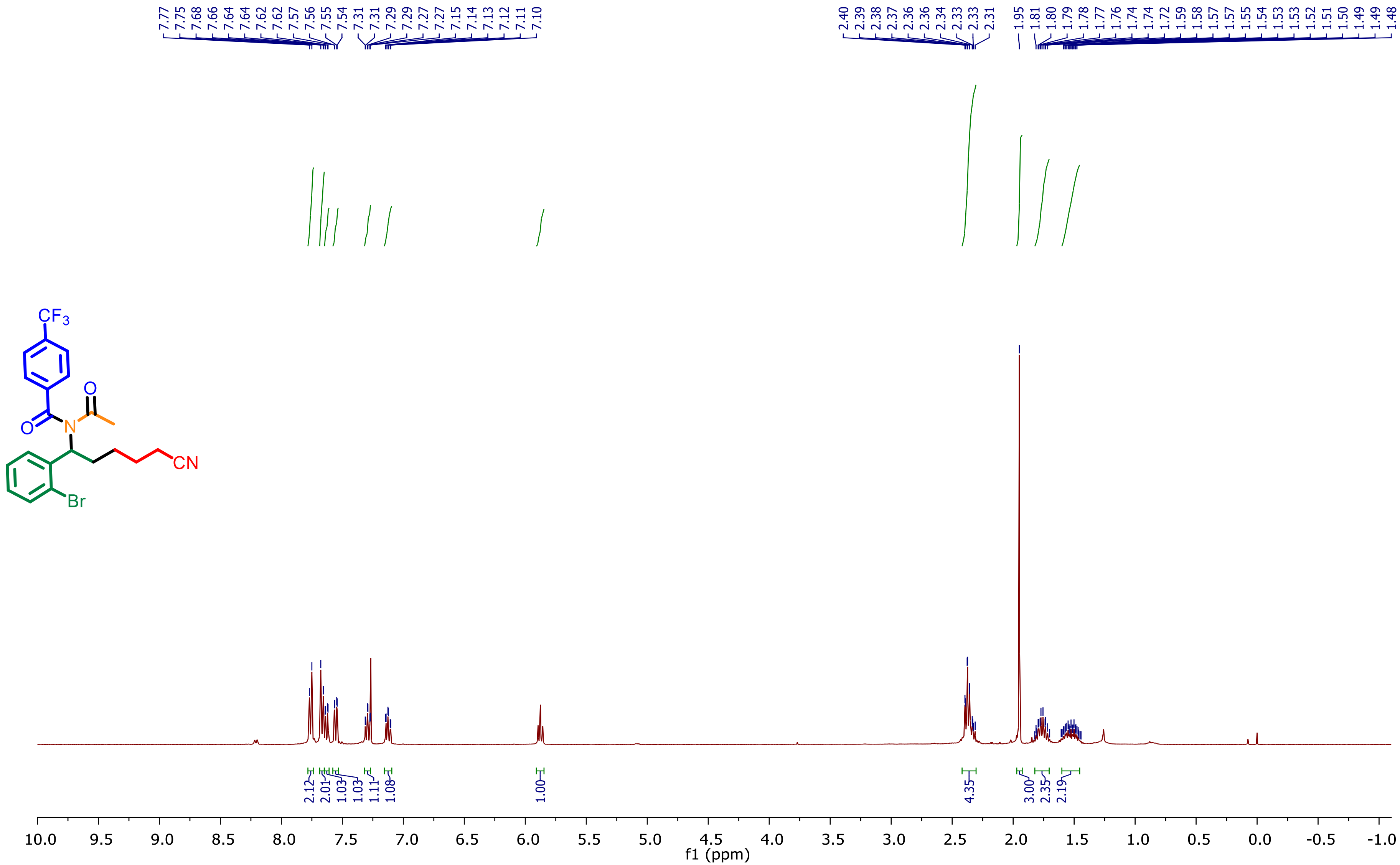
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ea)**



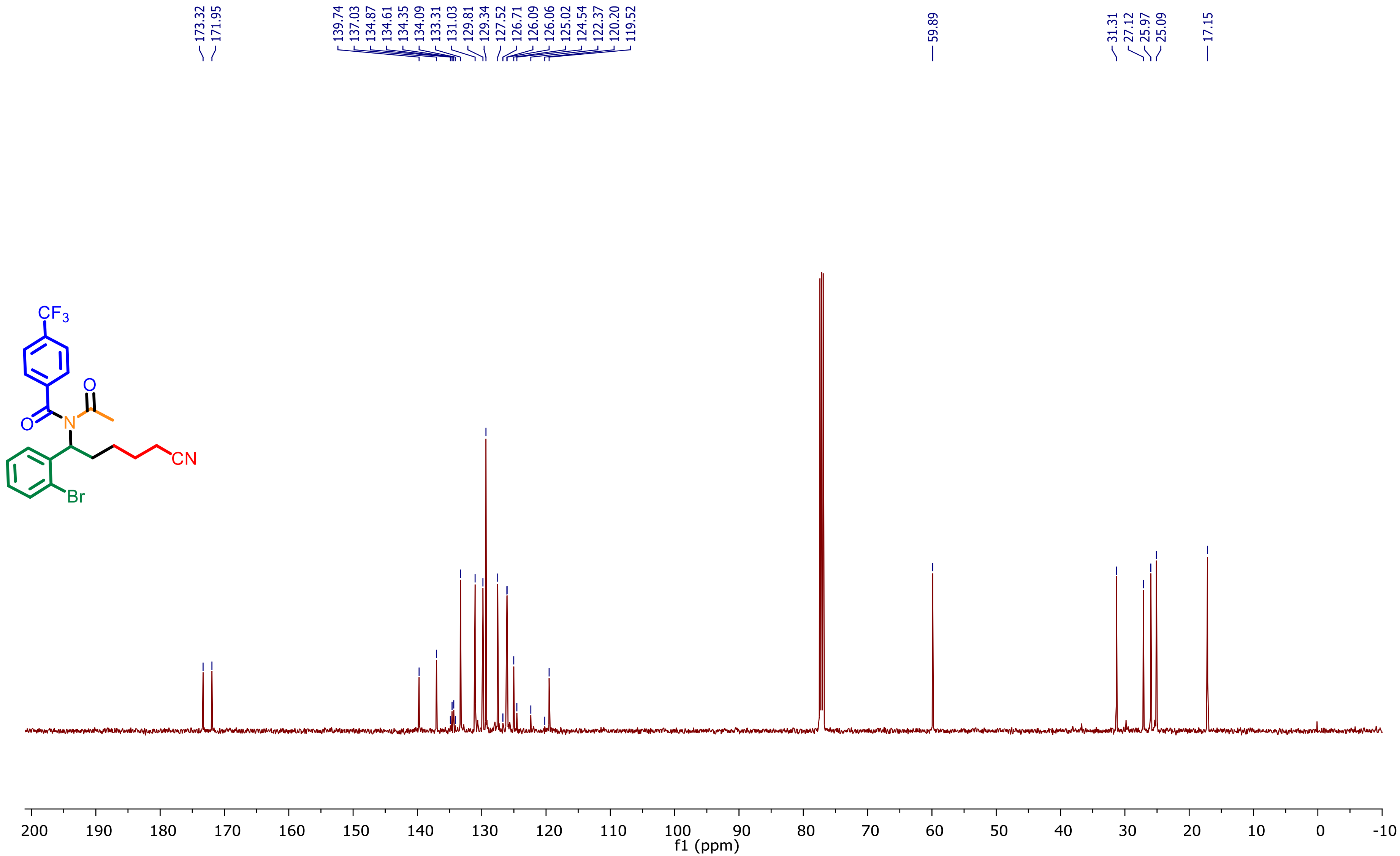
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3ea)**



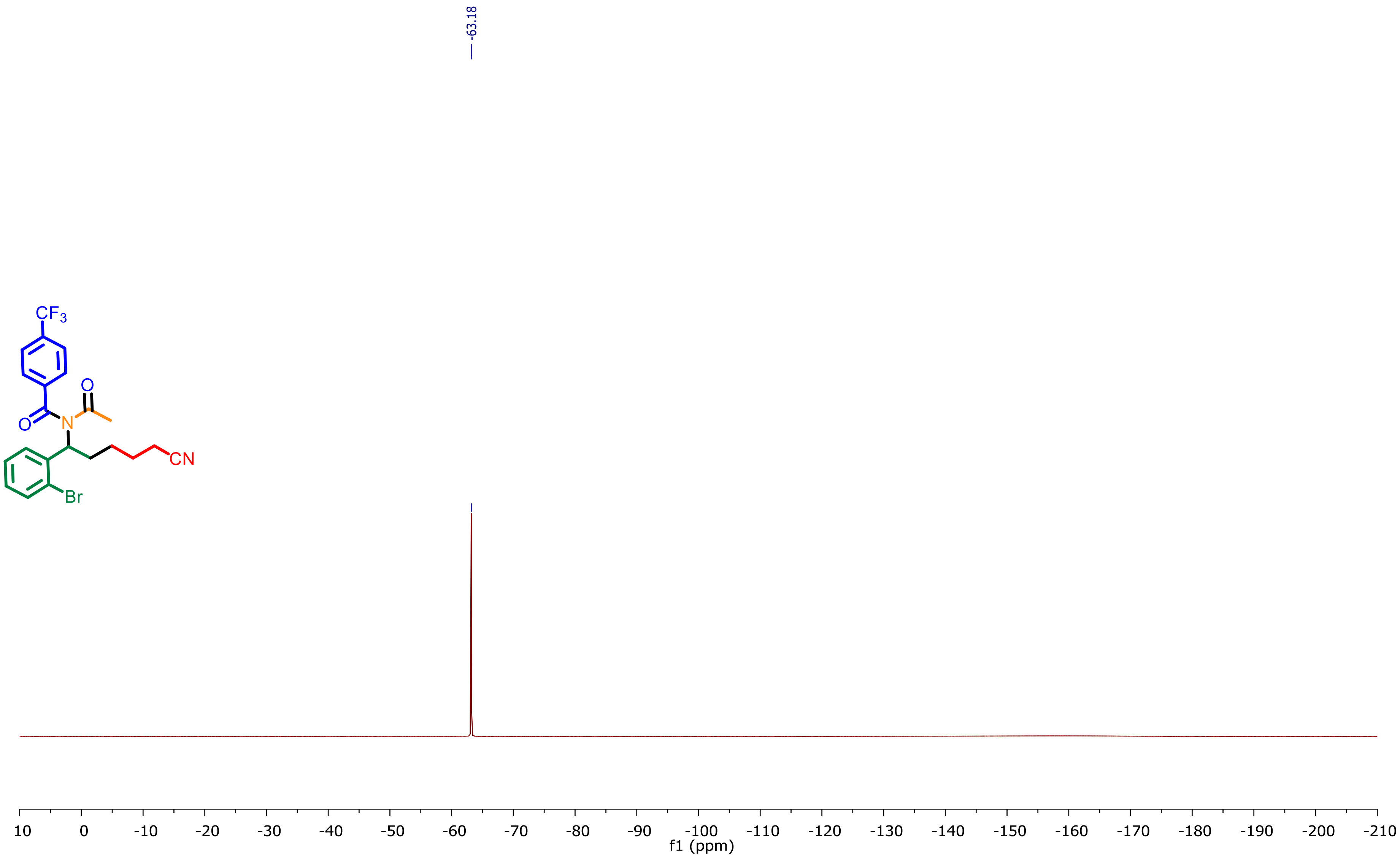
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3fa)**



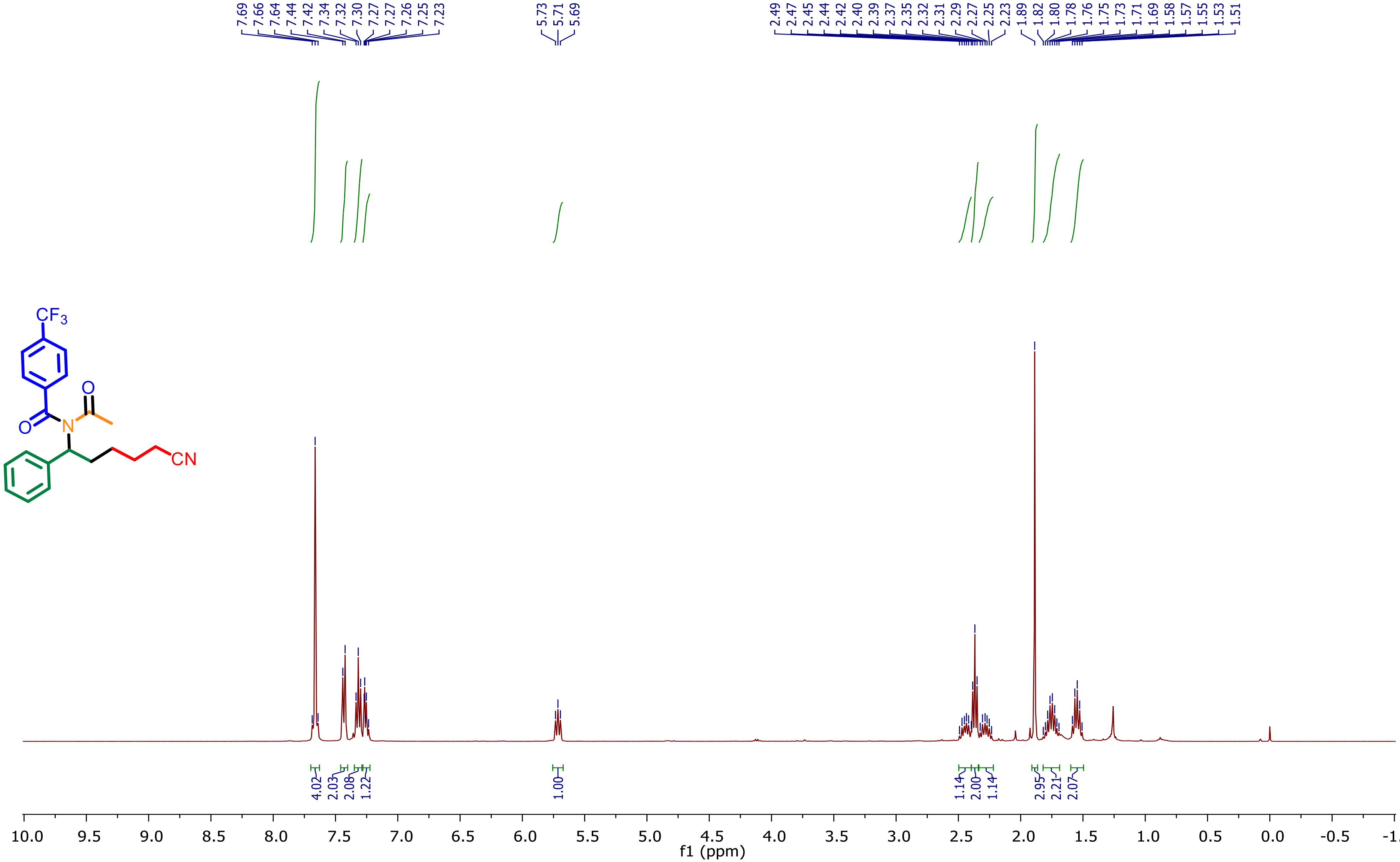
[13]C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3fa)**



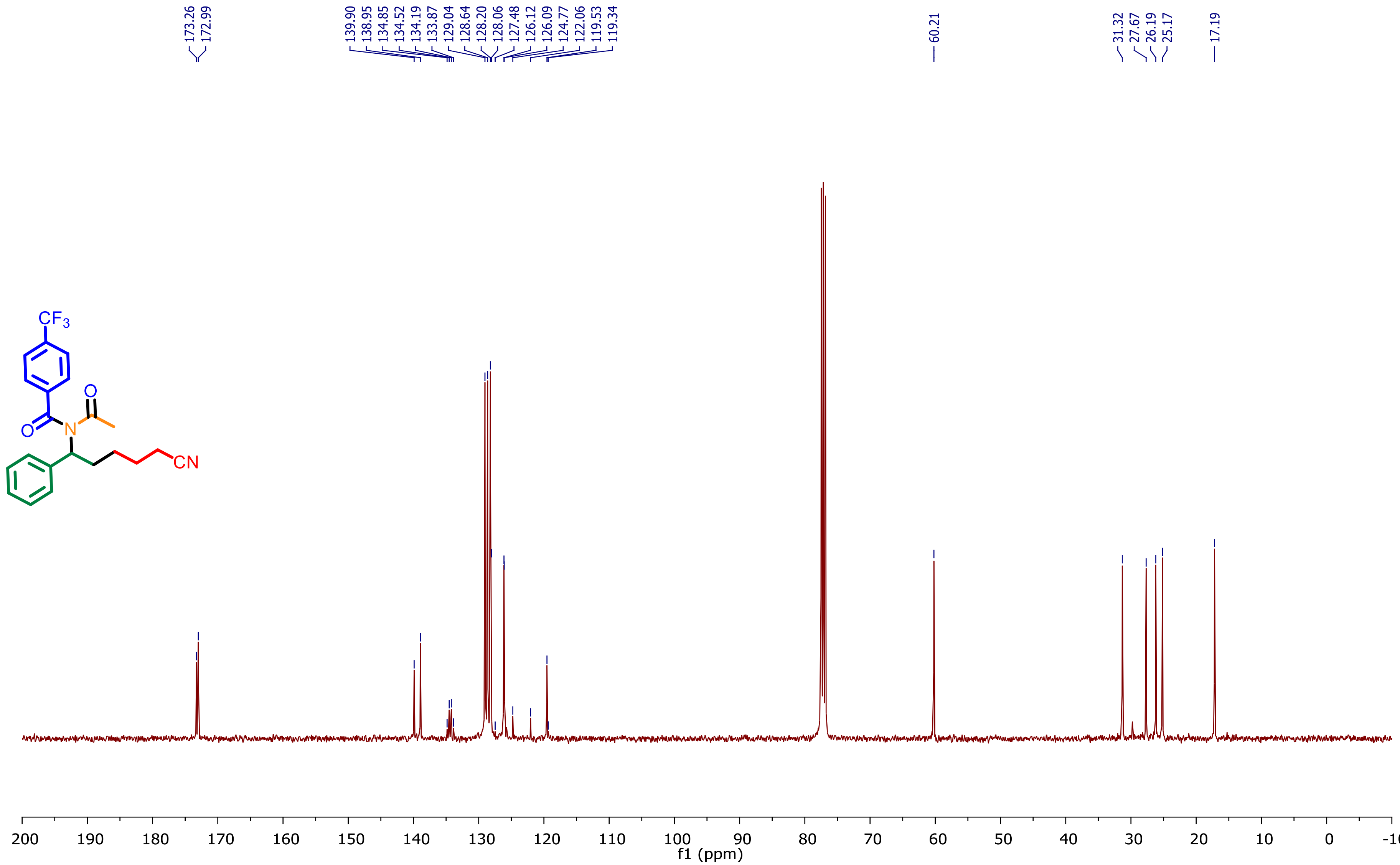
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **(3fa)**



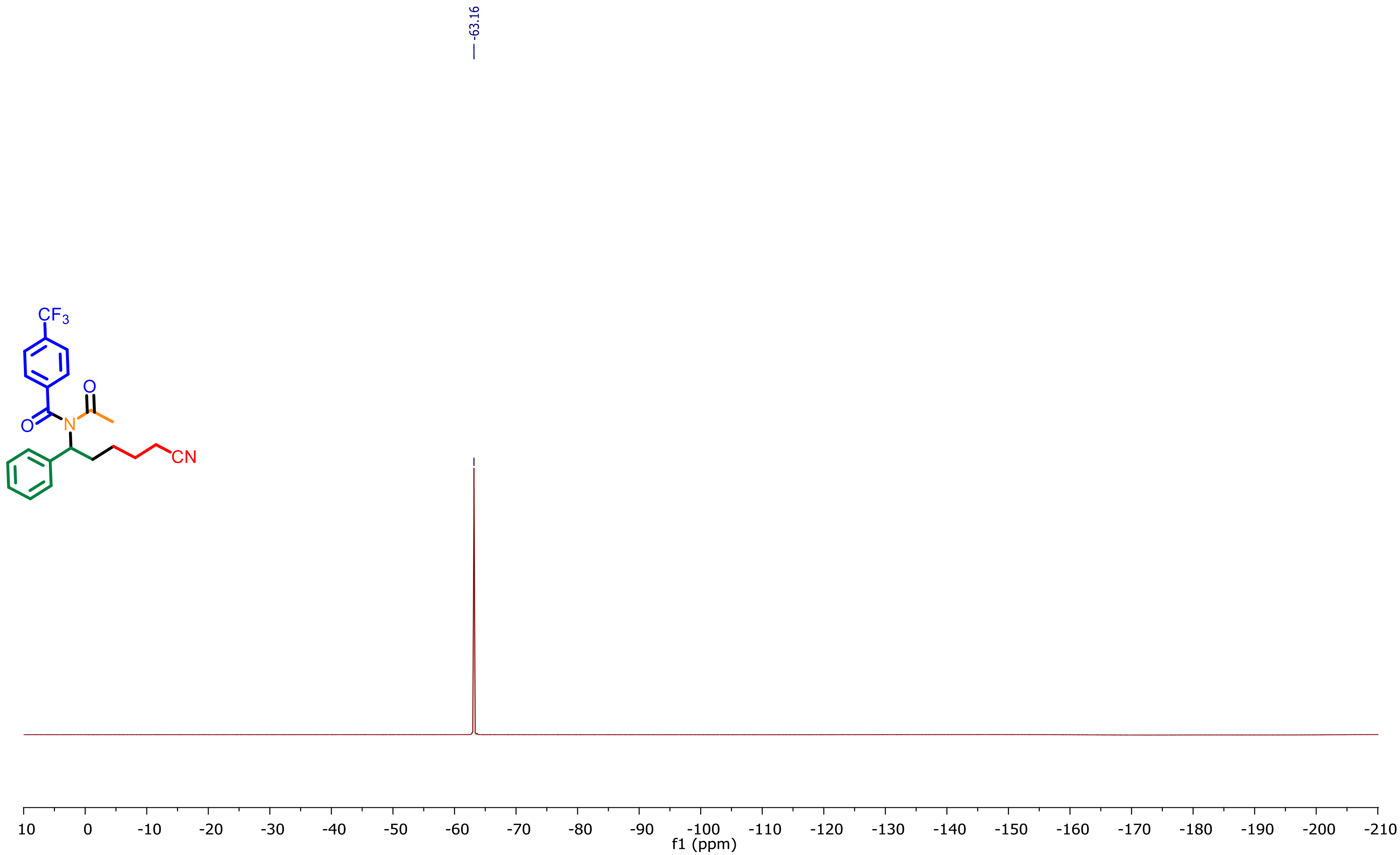
[1]H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ga)**



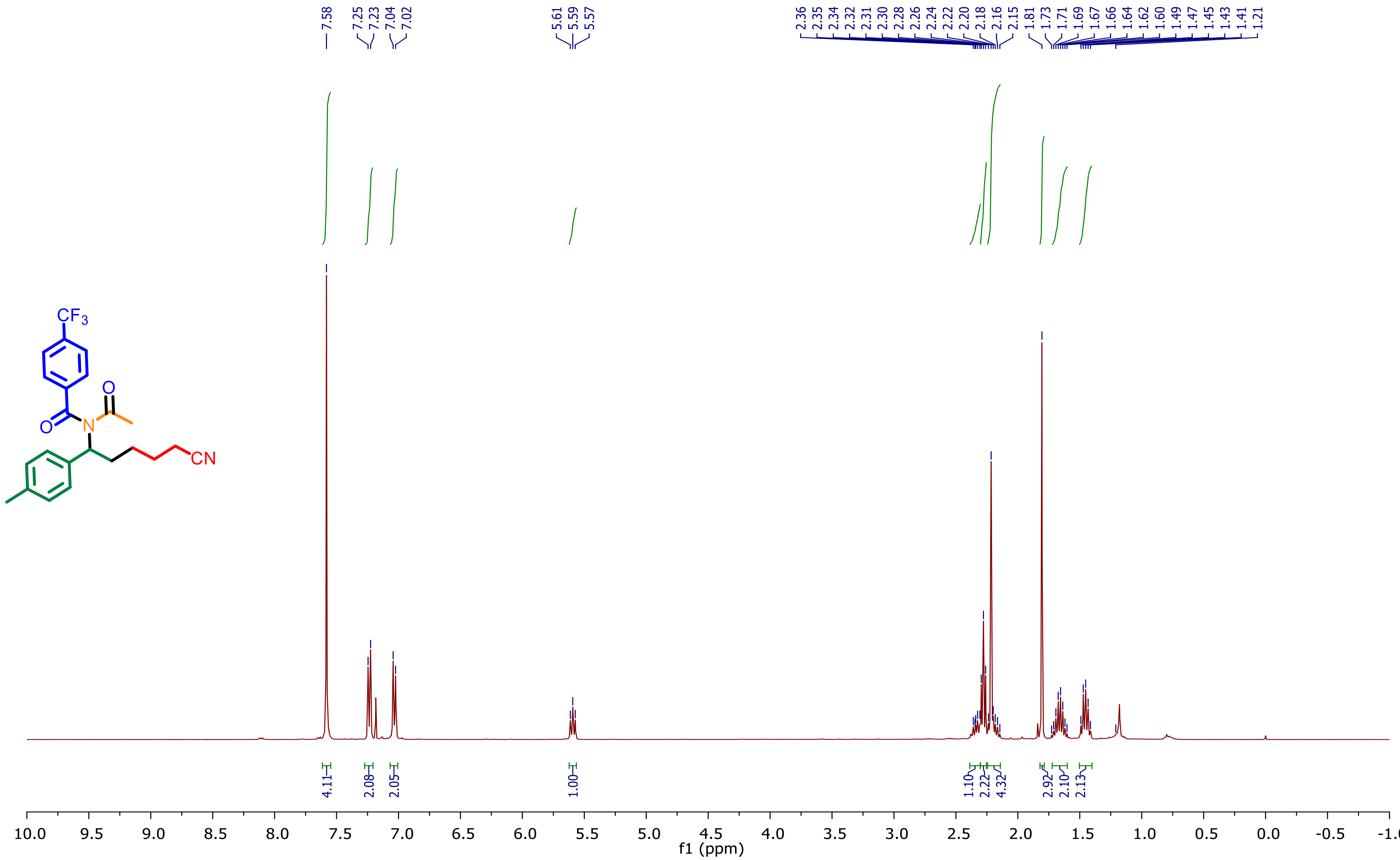
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ga)**



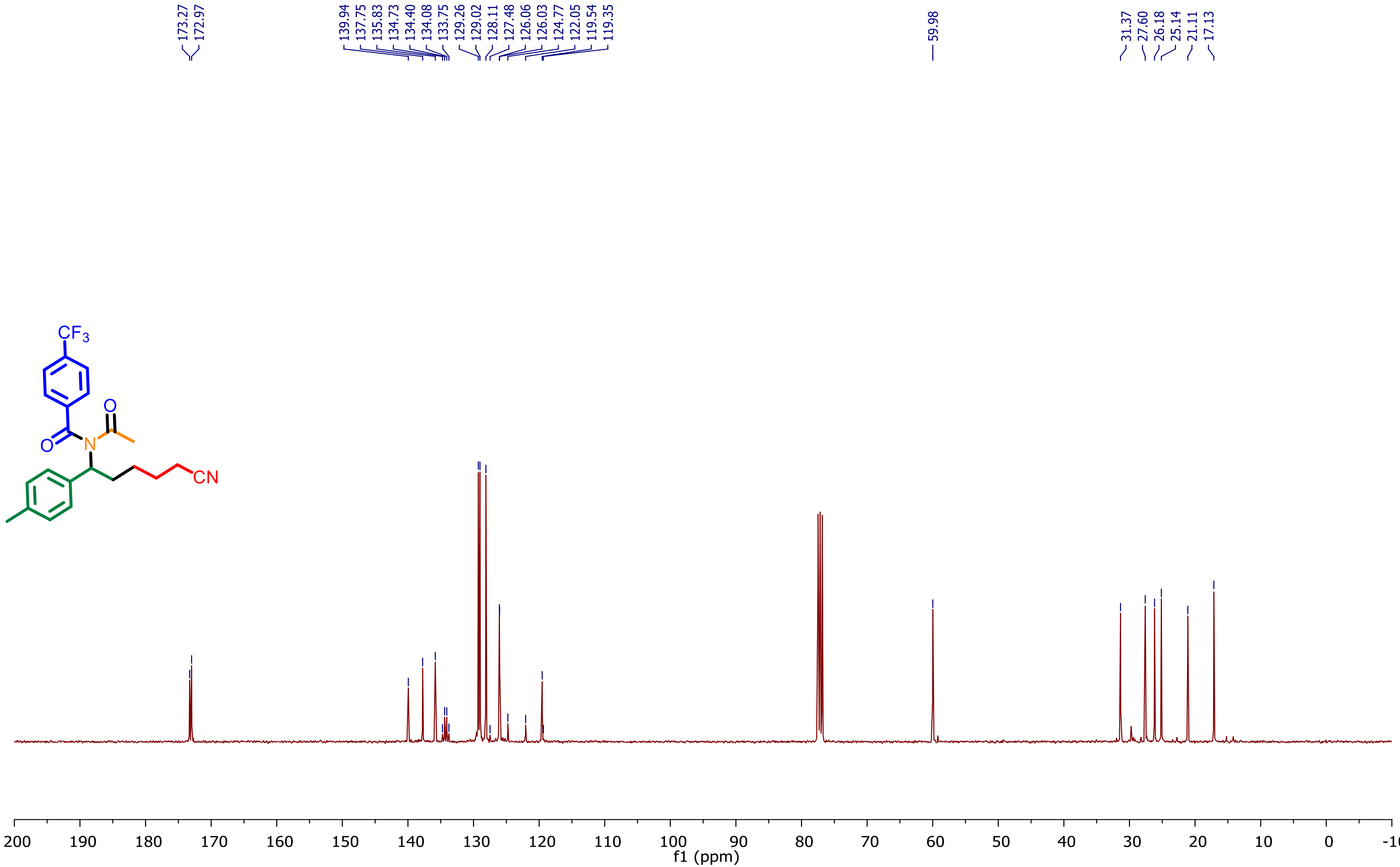
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3ga)**



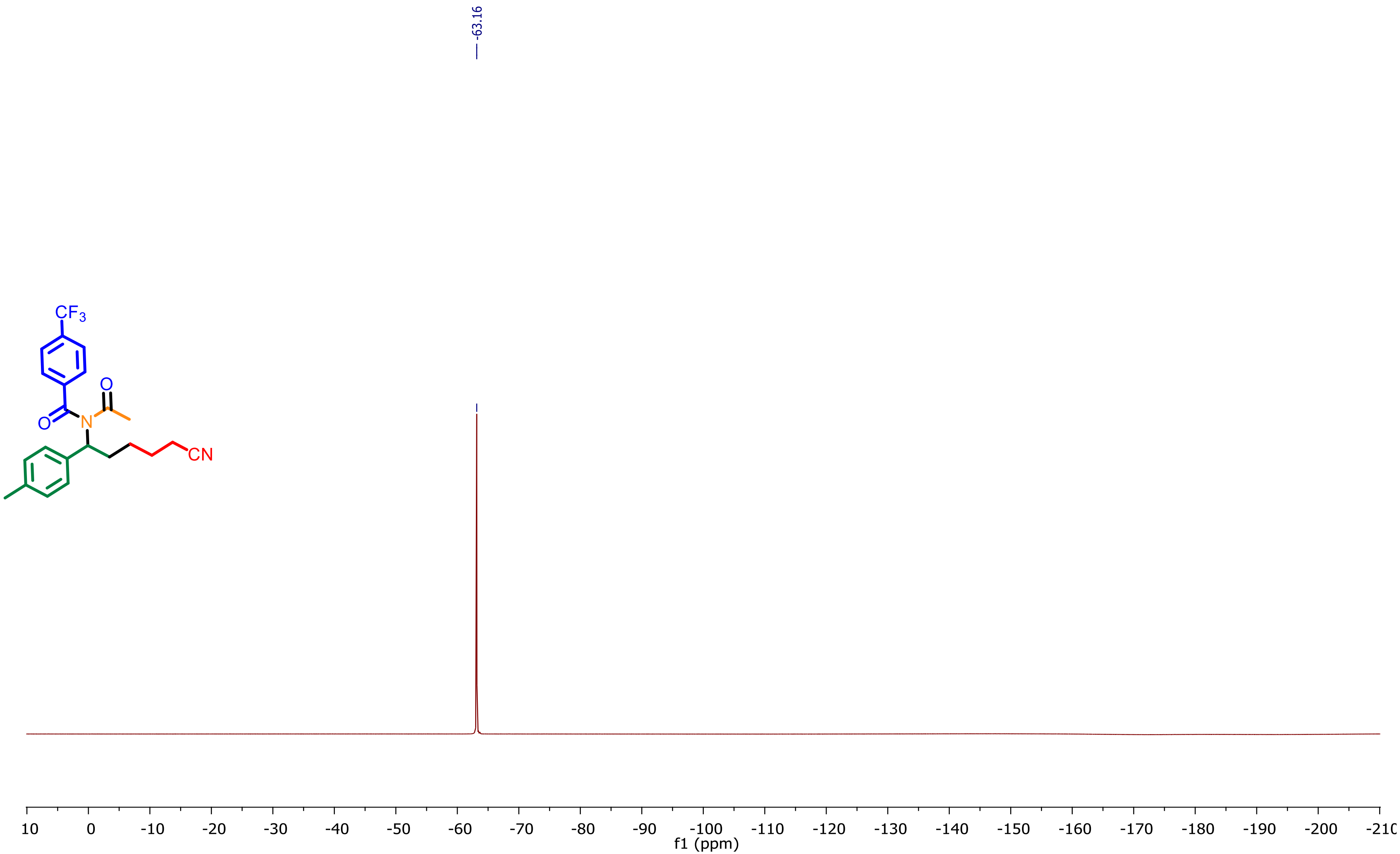
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ha)**



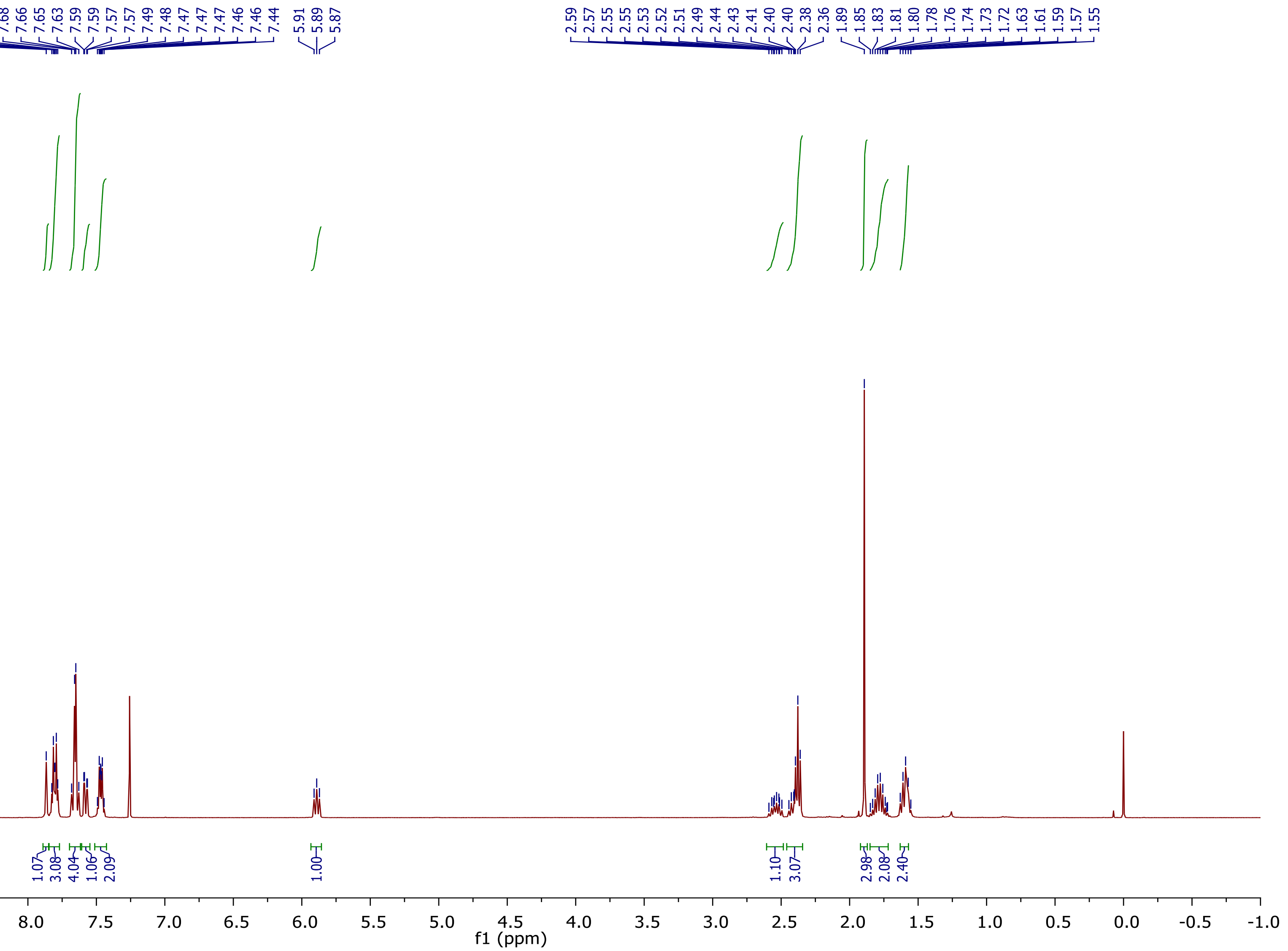
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ha)**

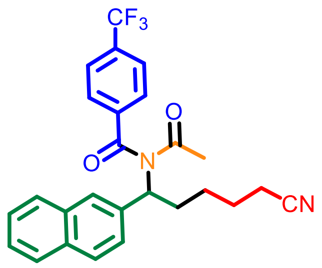


[19]F NMR (376 MHz, CDCl3) Spectrum of Compound **(3ha)**

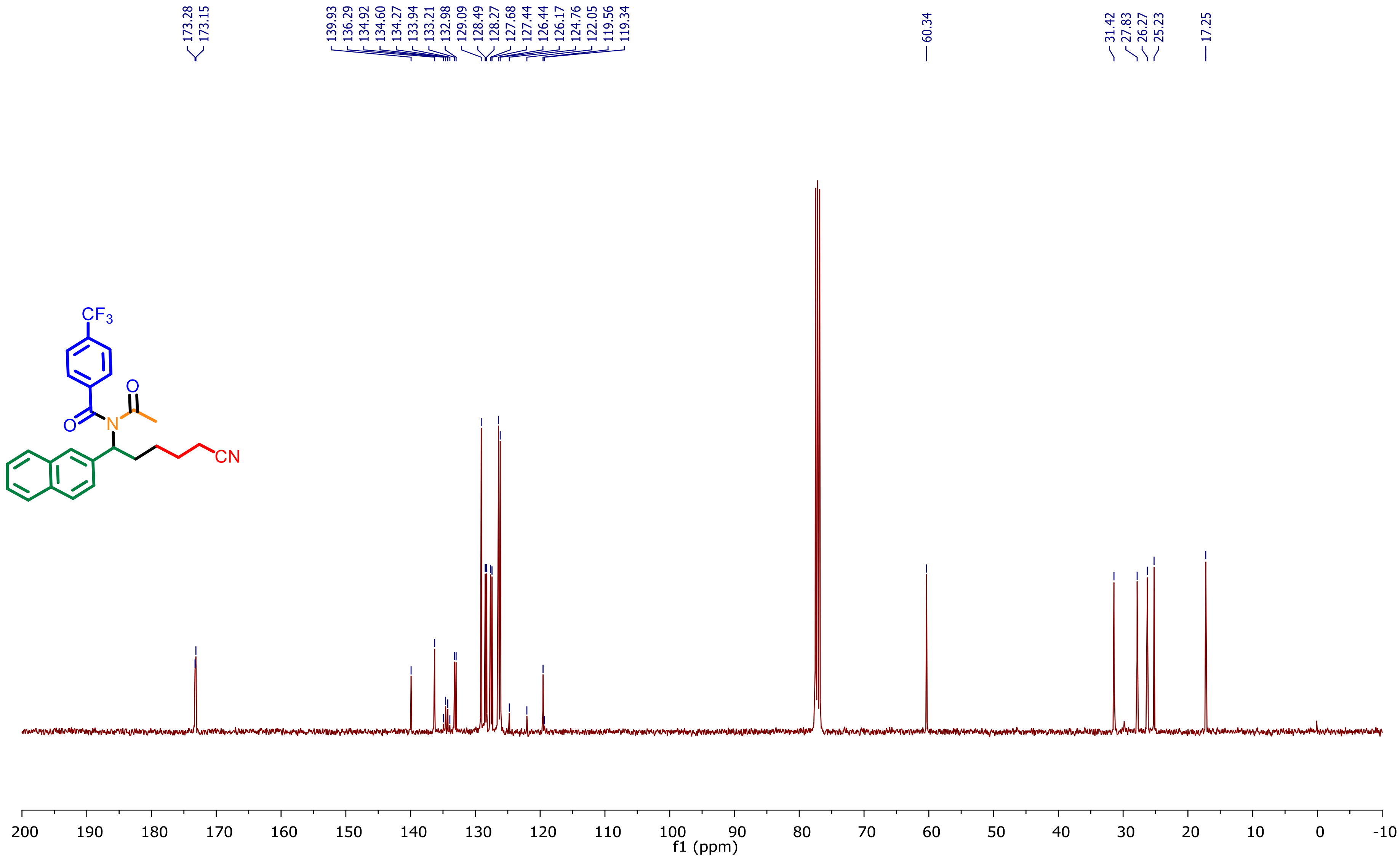


[1]H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ia)**

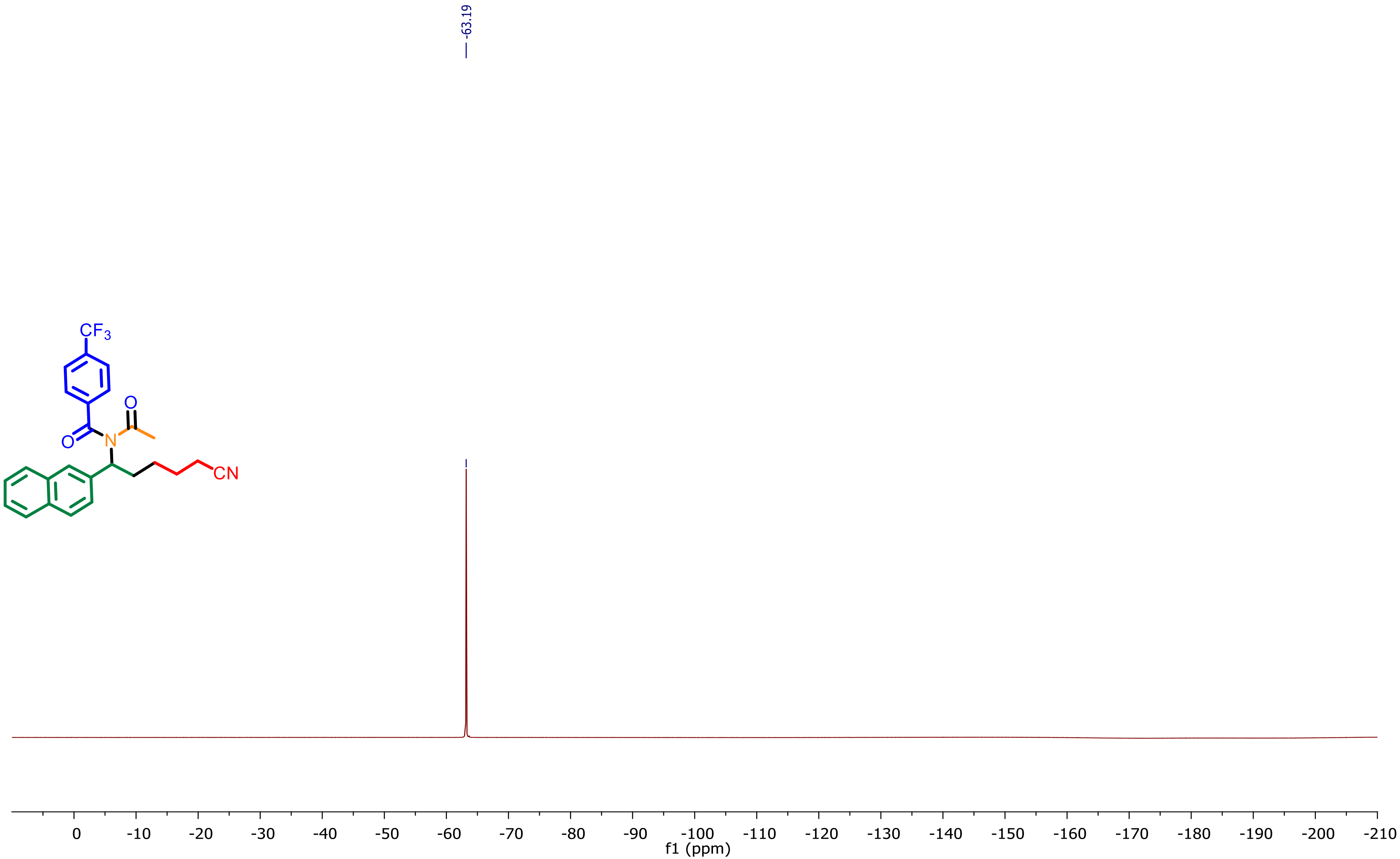




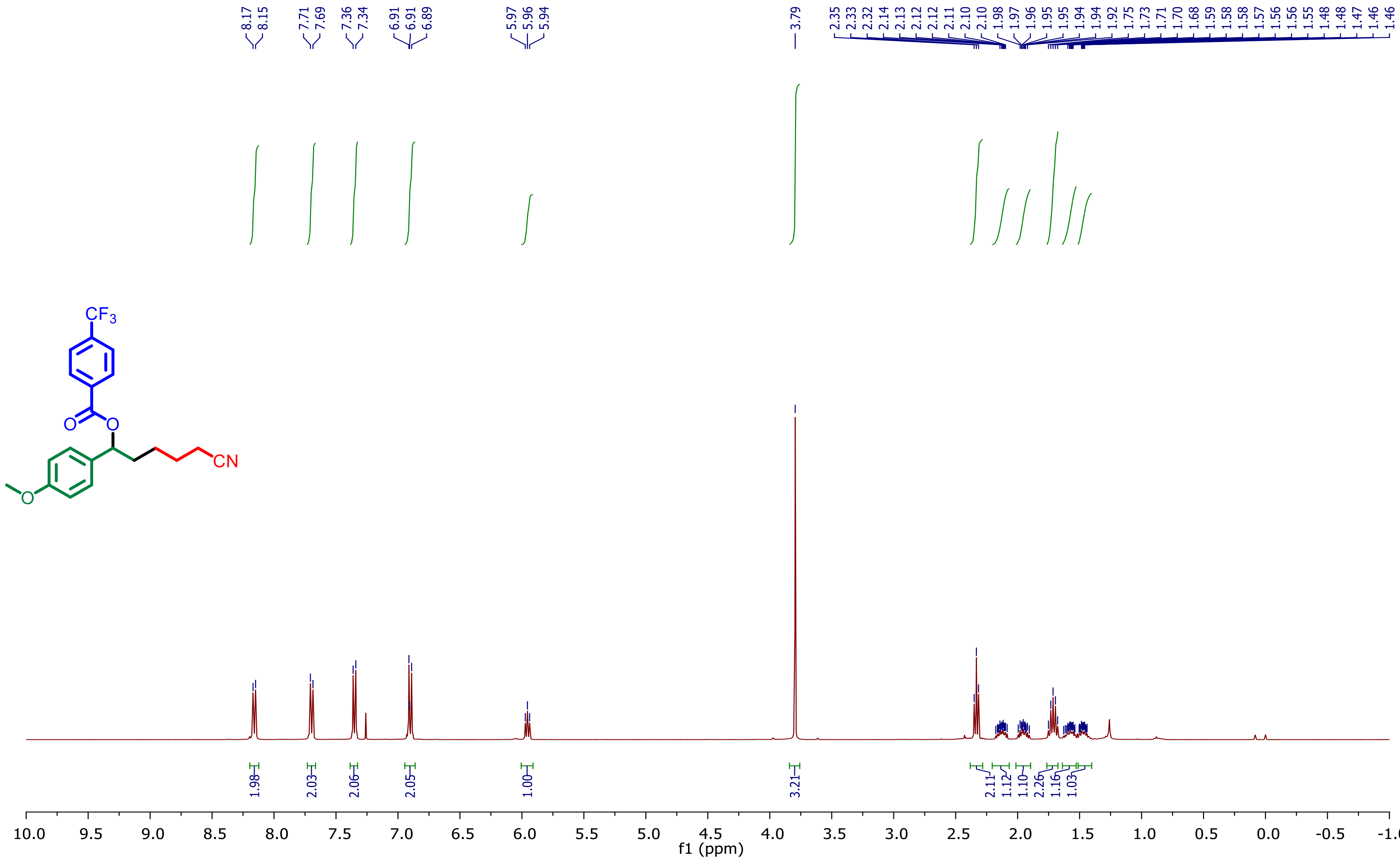
[13]C NMR (101 MHz, $CDCl_3$) Spectrum of Compoundk **(3ia)**



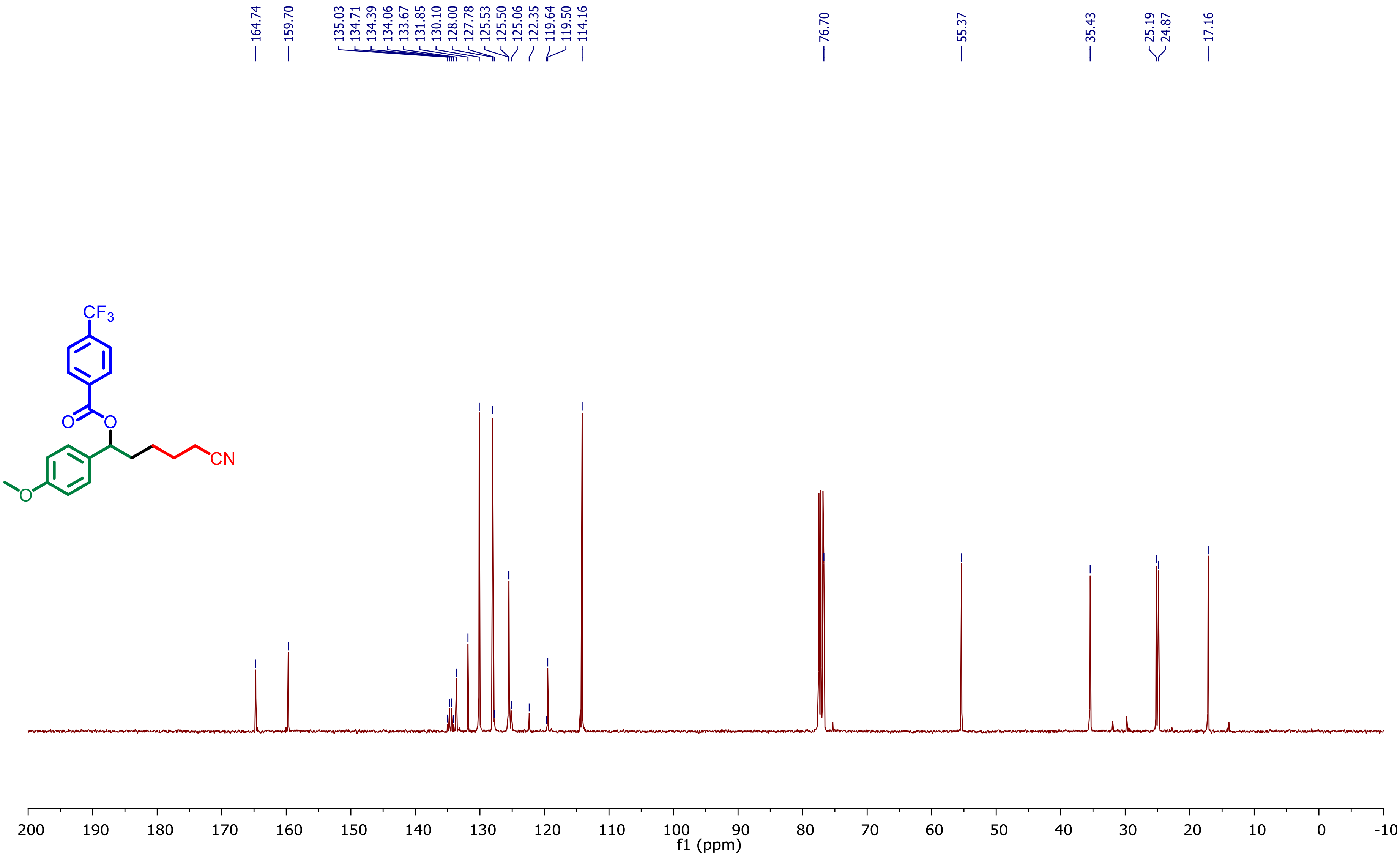
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3ia)**



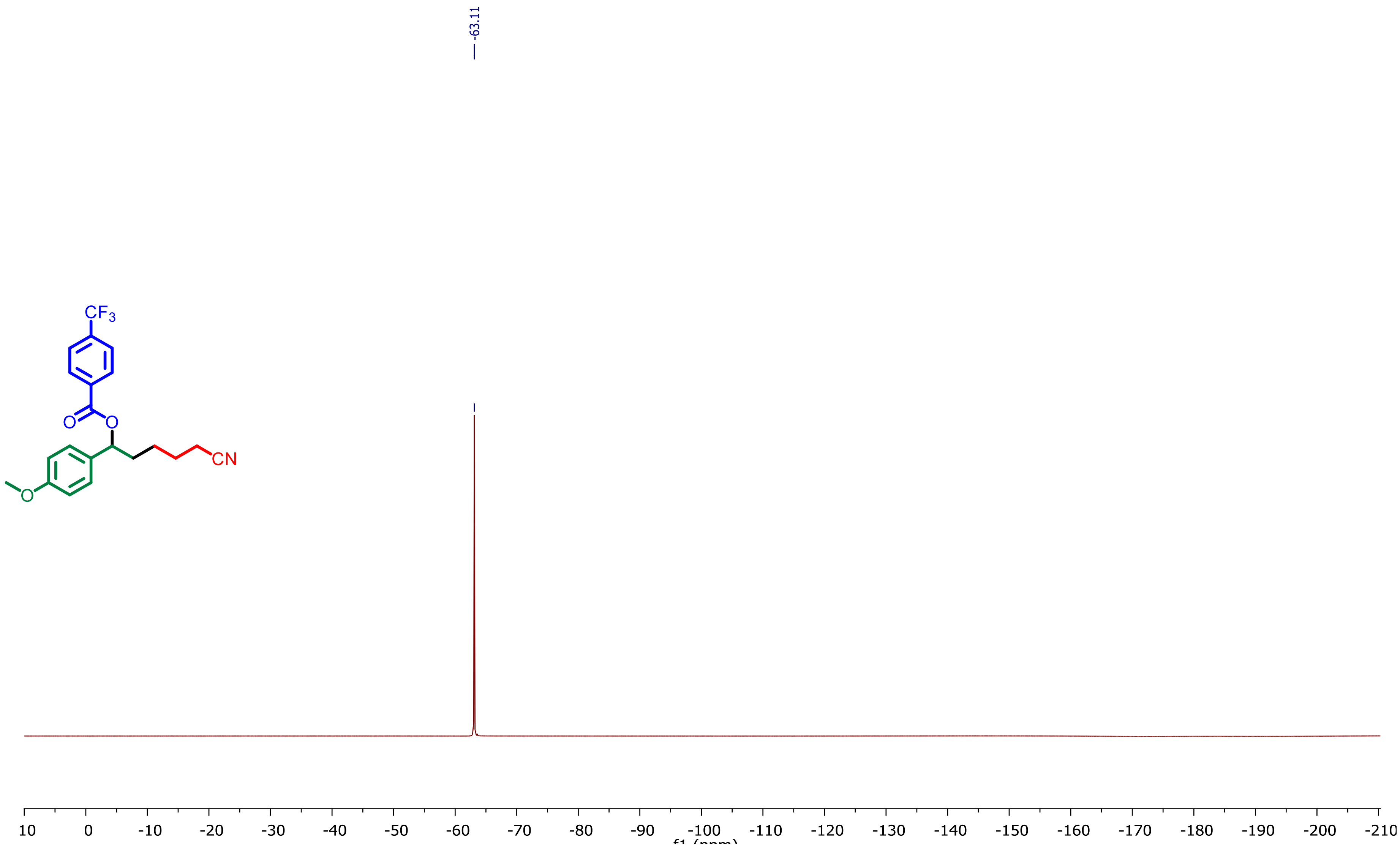
[1]H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3'ja)**



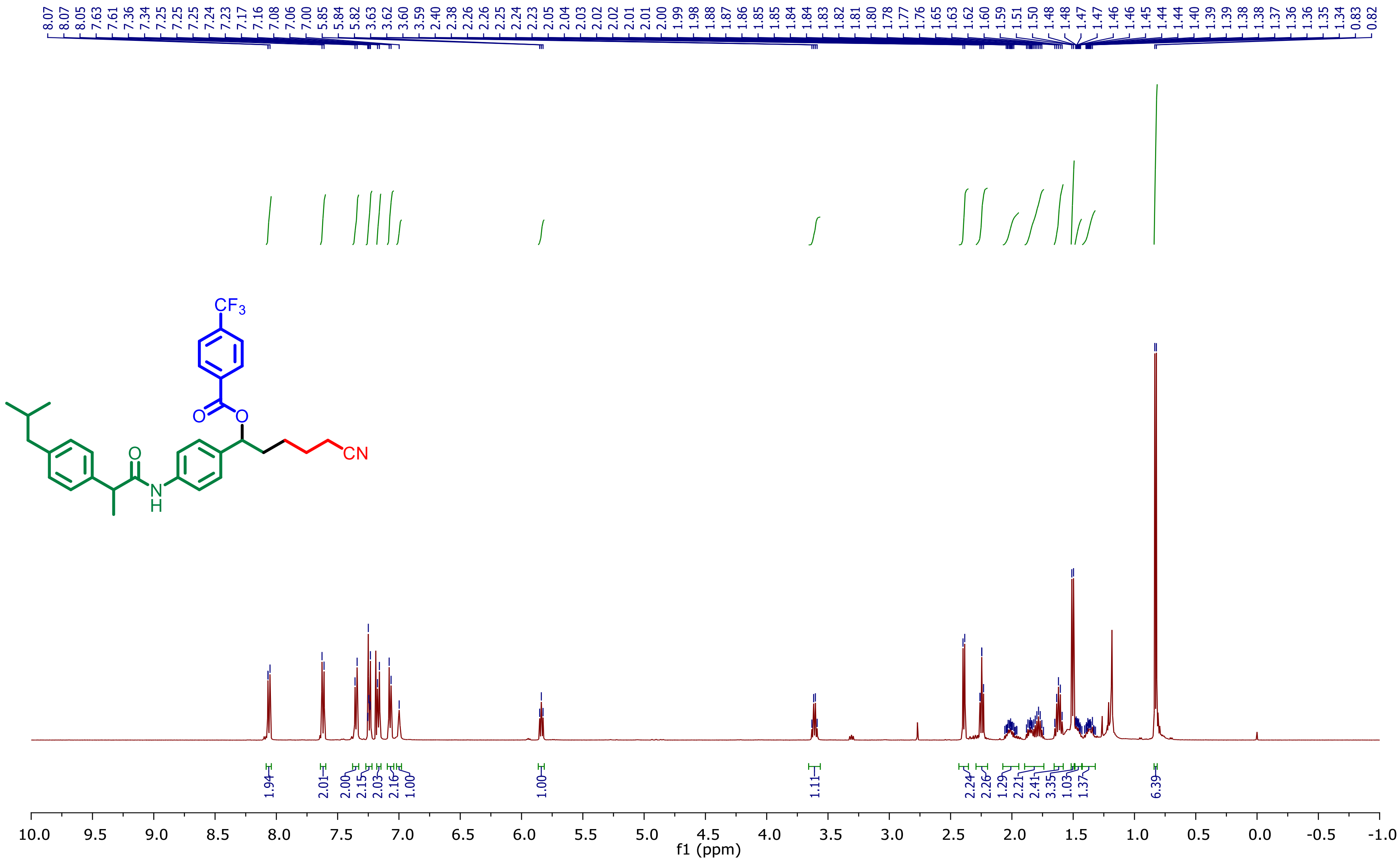
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3'ja)**



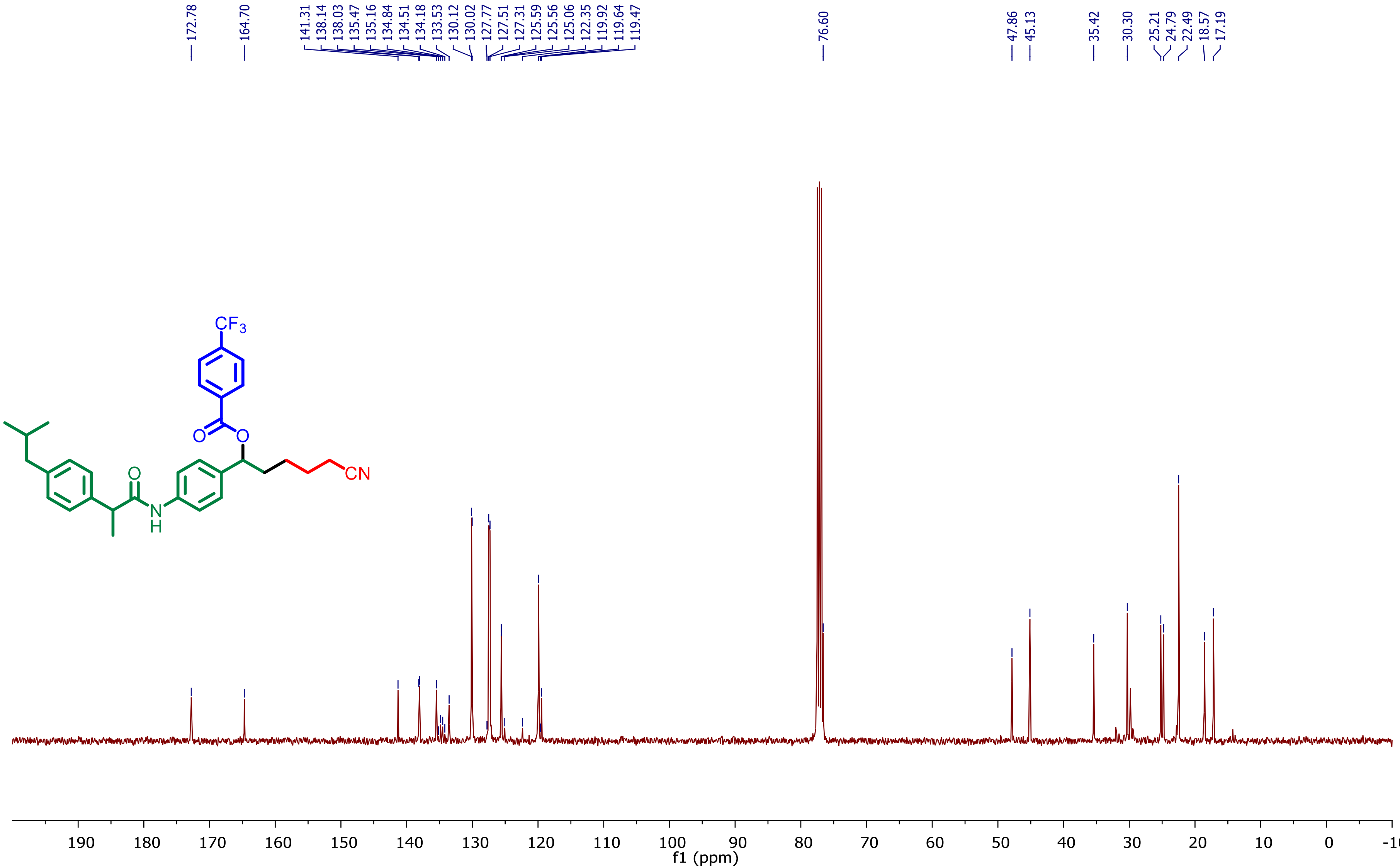
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3'ja)**



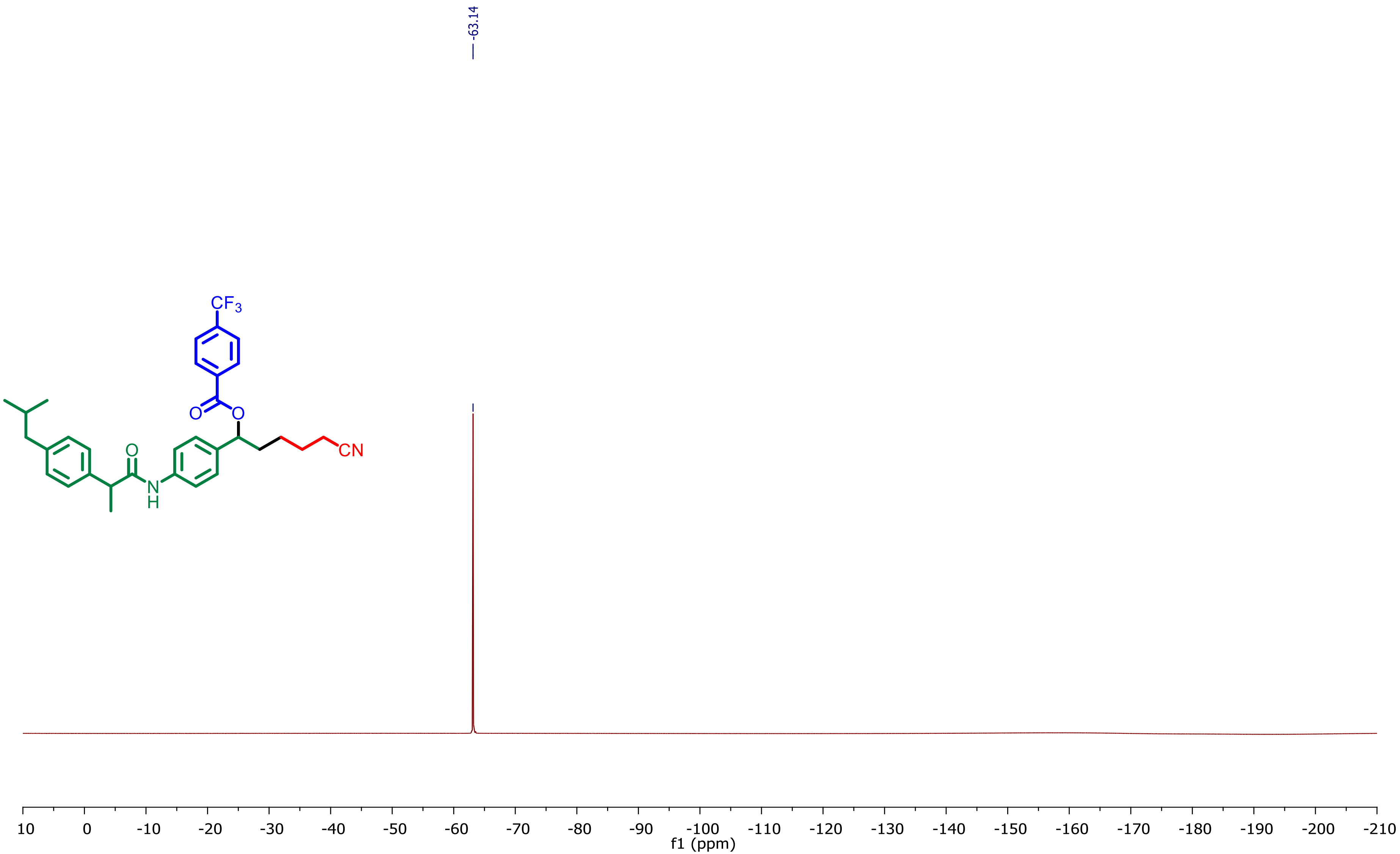
[1]H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3'ka)**



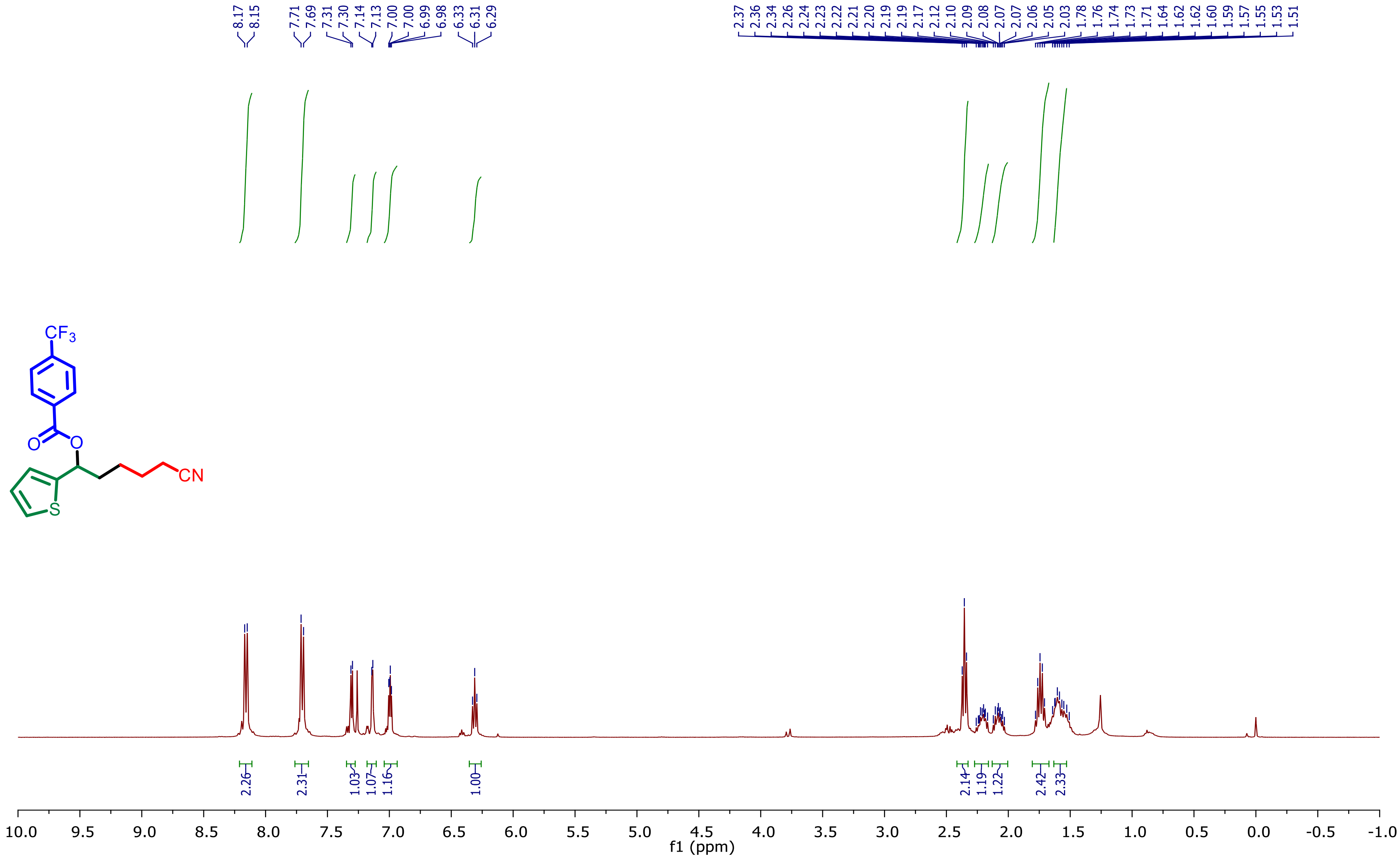
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3'ka)**



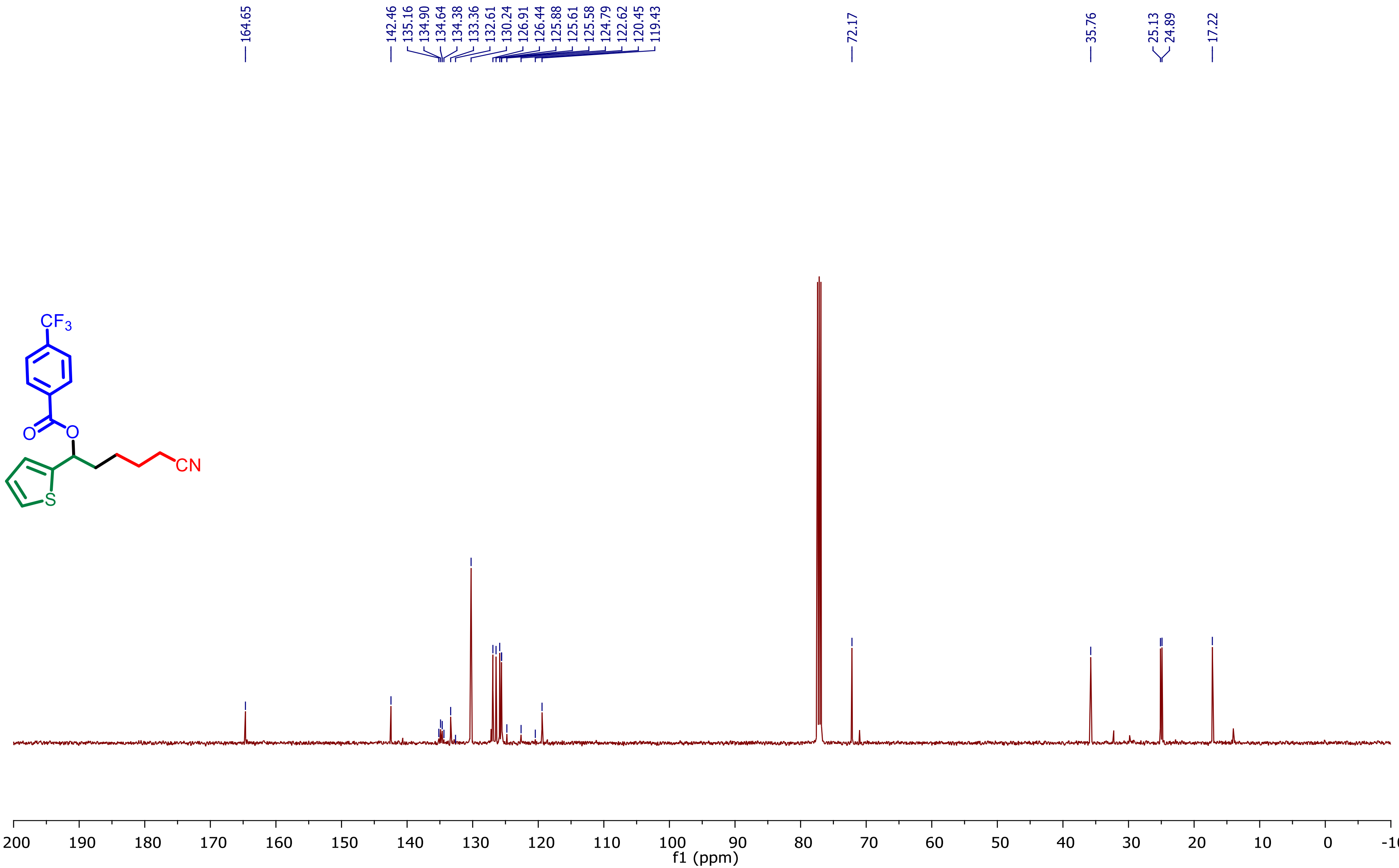
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **(3'ka)**



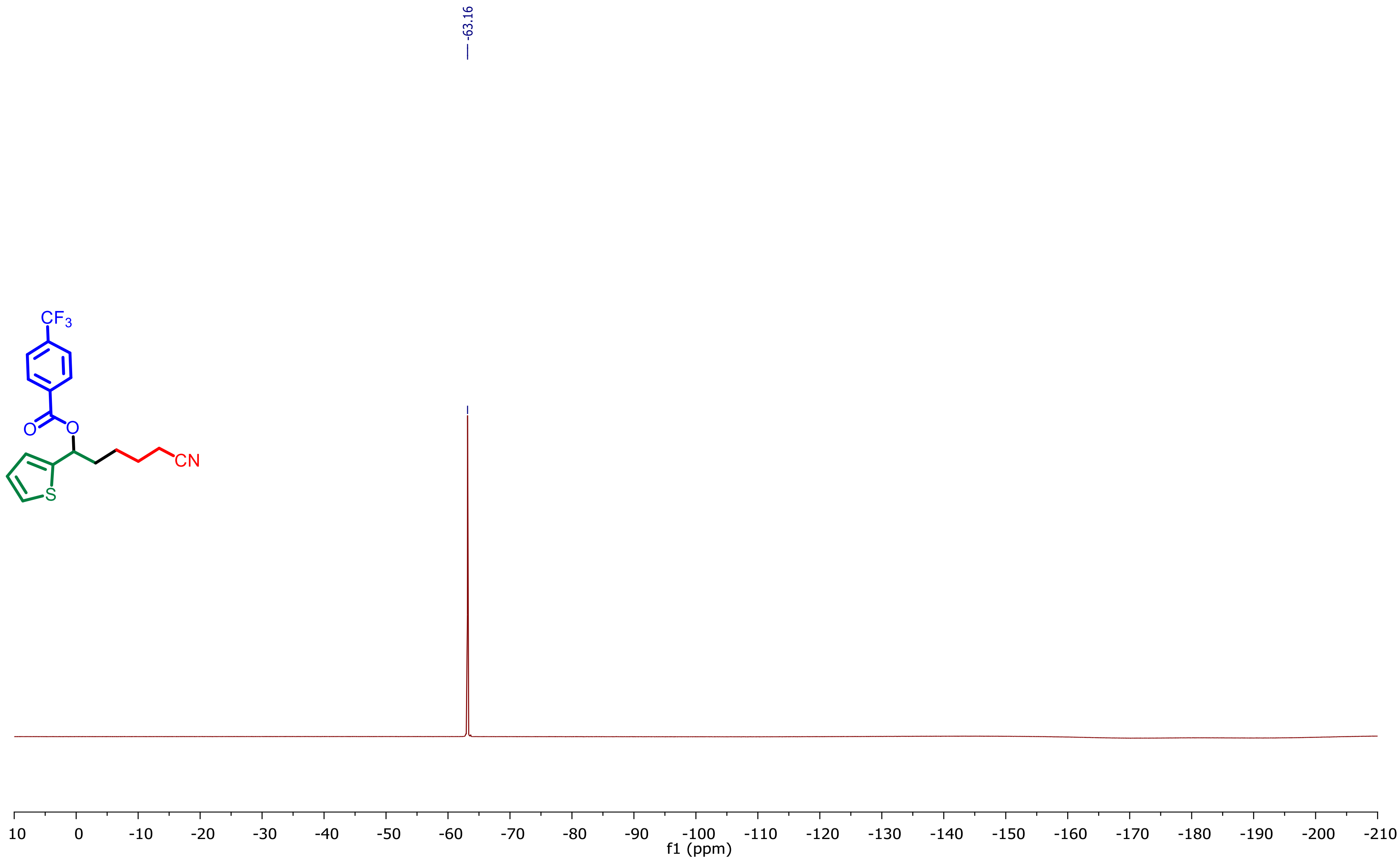
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3'la)**



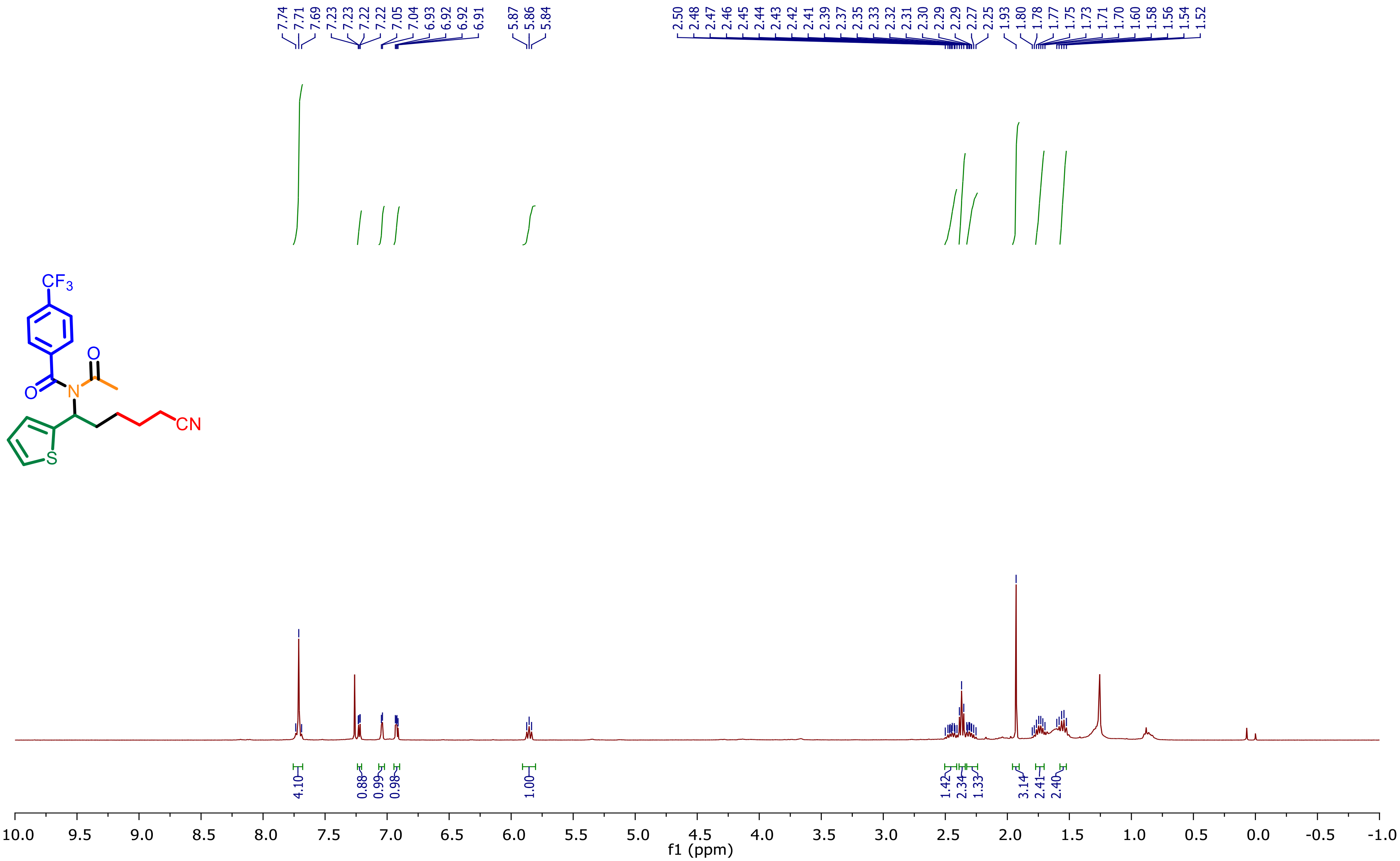
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3'la)**



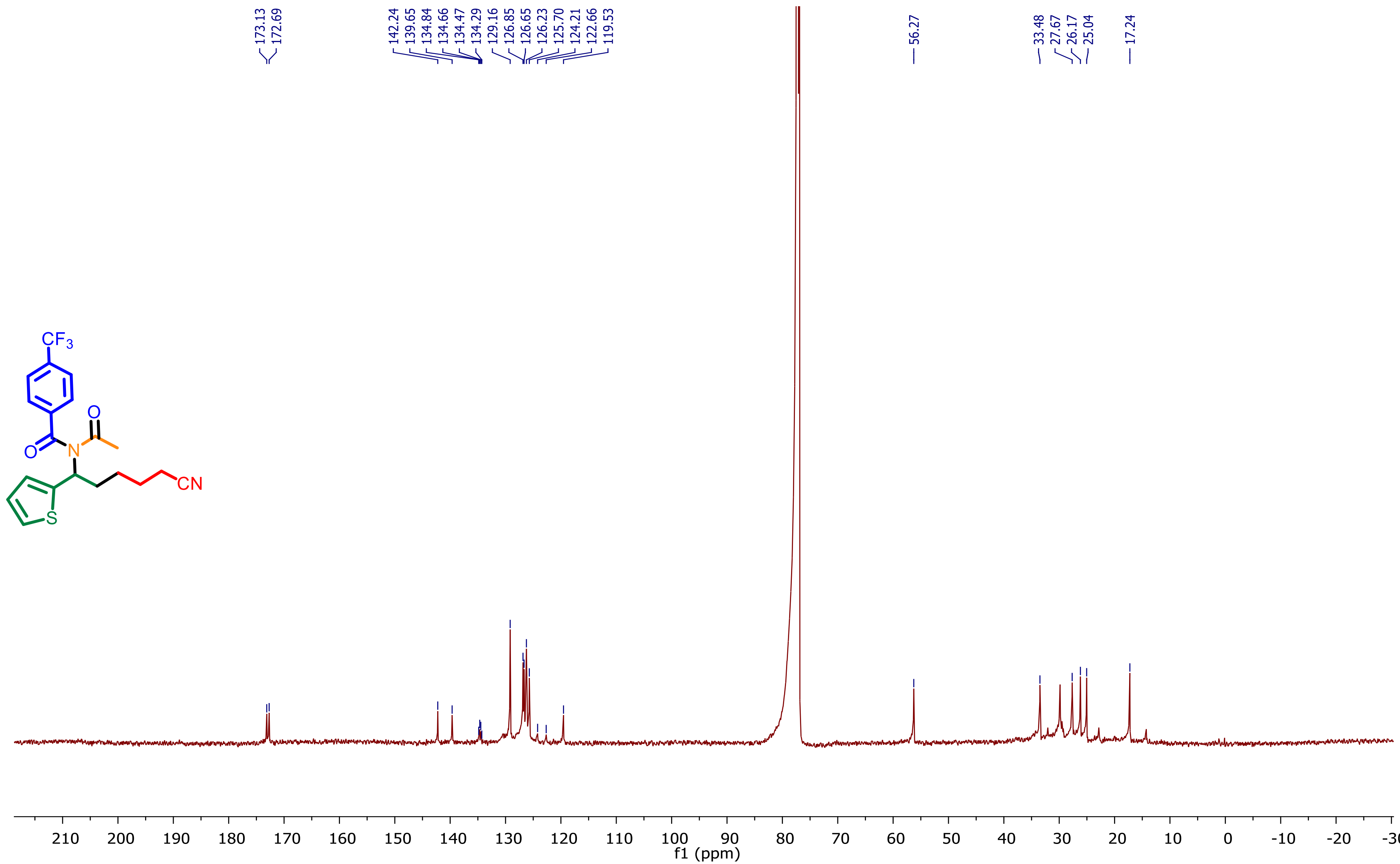
^{19}F NMR (377 MHz, $CDCl_3$) Spectrum of Compound **(3'la)**



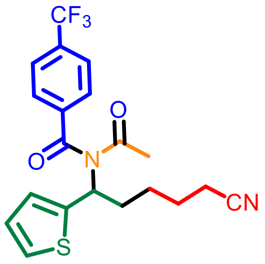
¹H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3la)**

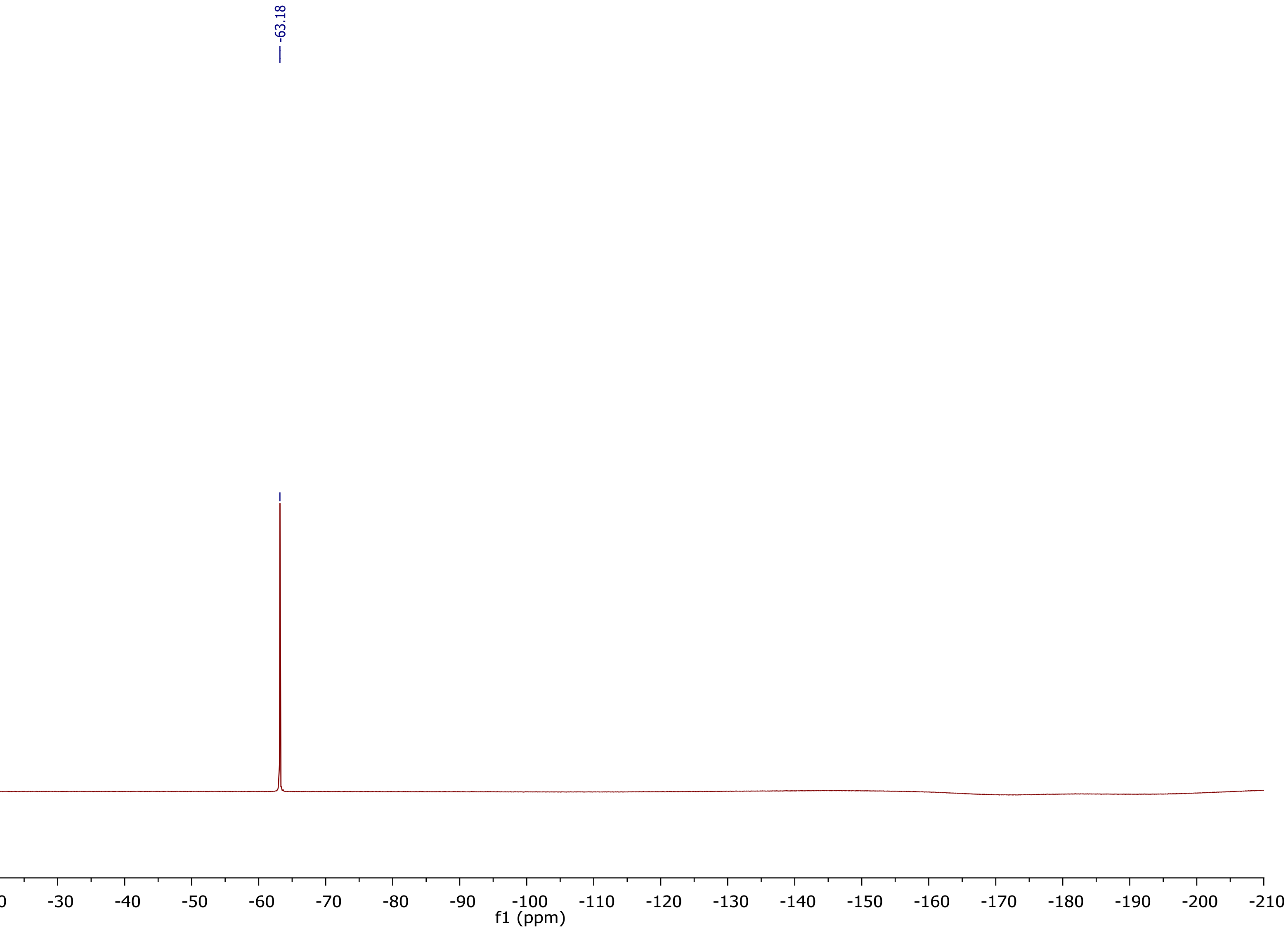


^{13}C NMR (176 MHz, $CDCl_3$) Spectrum of Compound **(3la)**

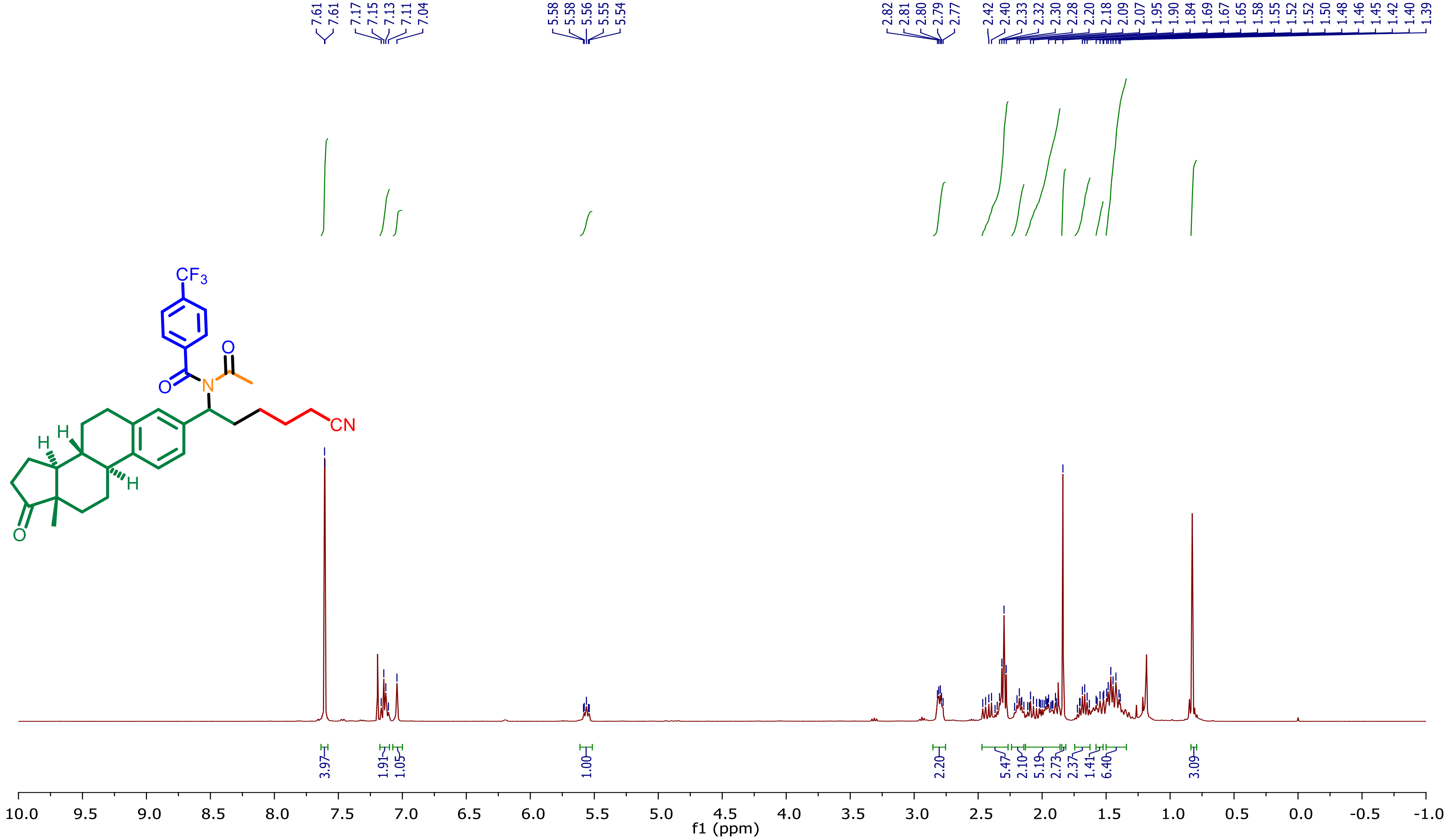


^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3la)**

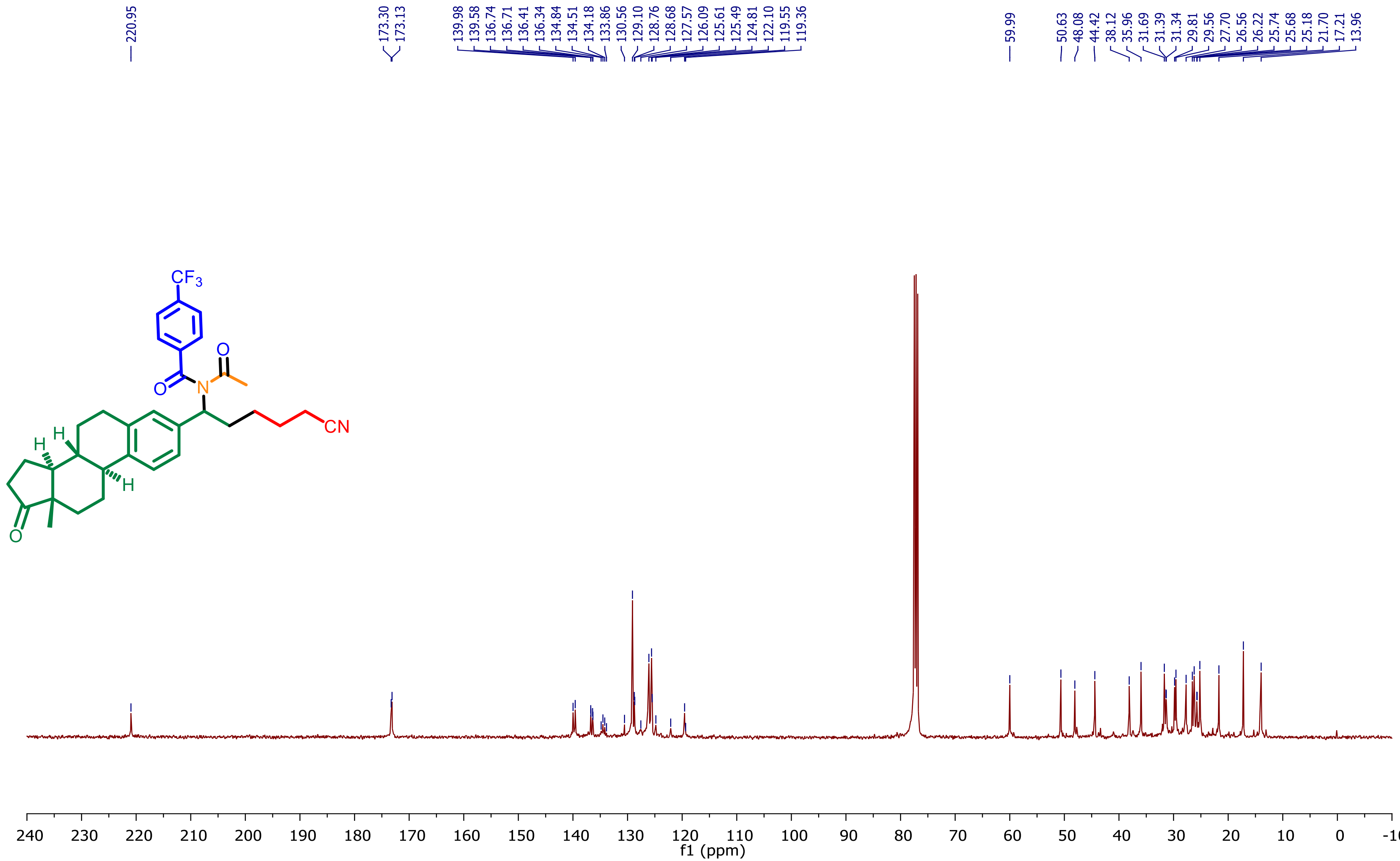




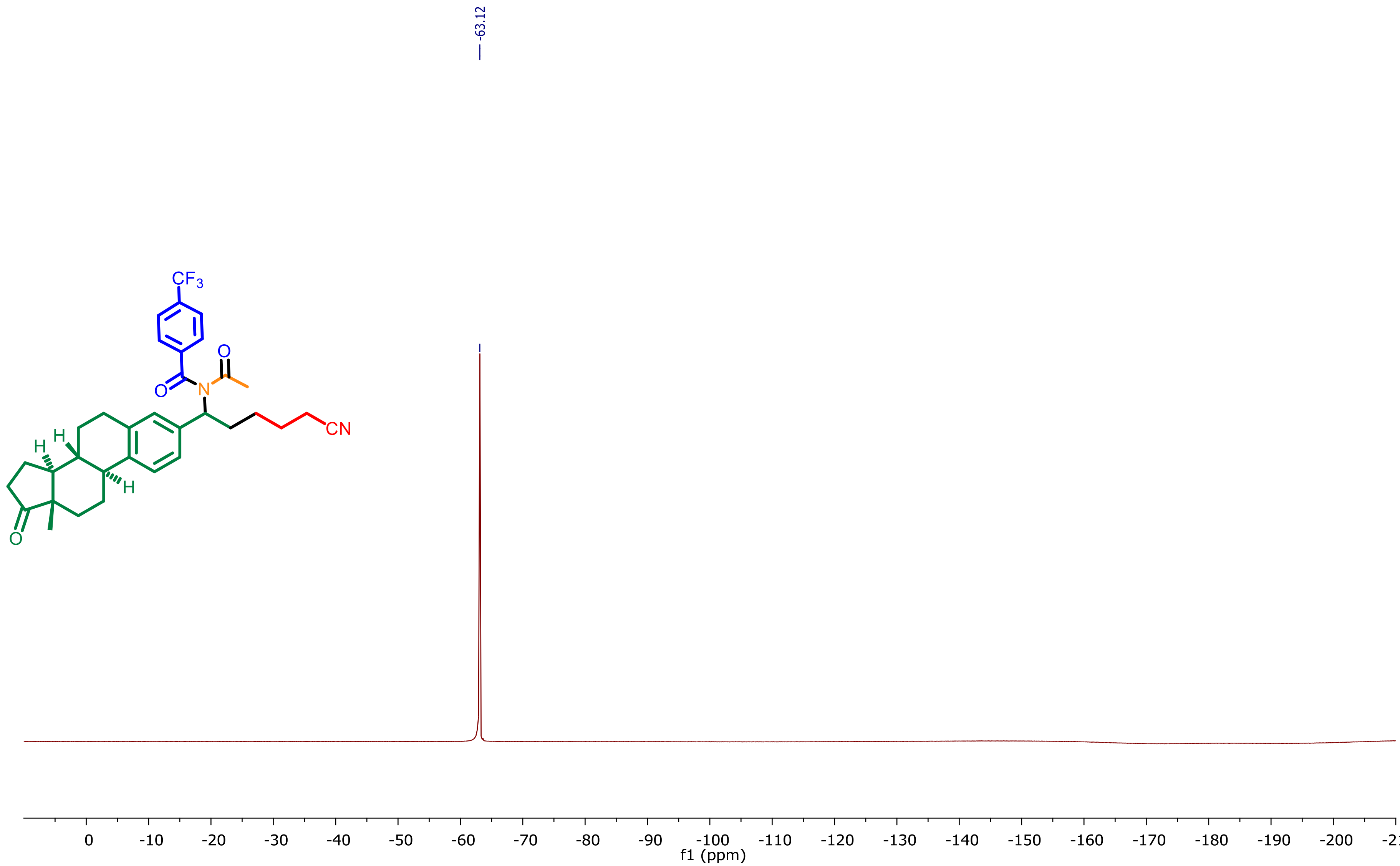
[1]H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ma)**



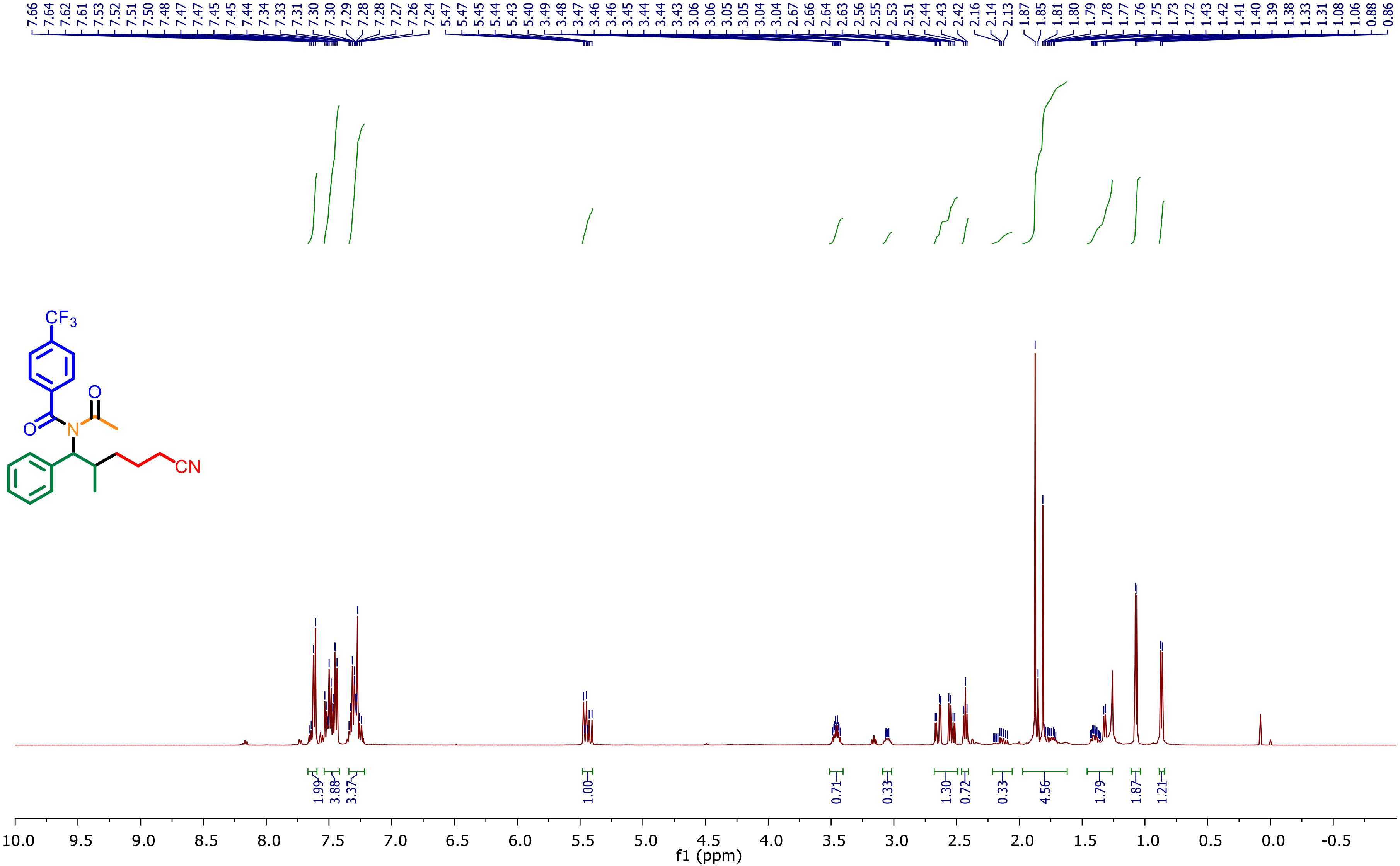
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ma)**



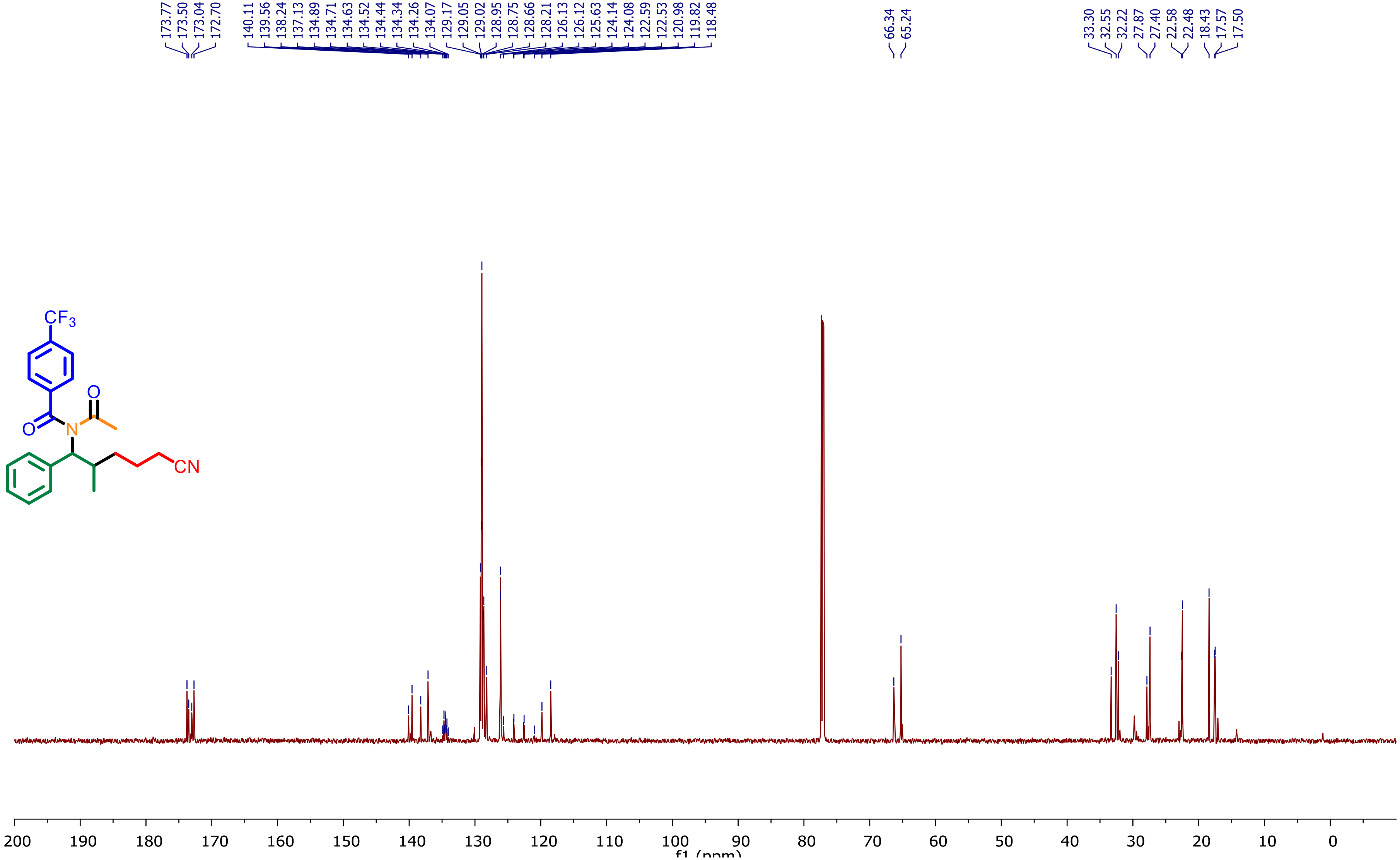
[19]F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3ma)**



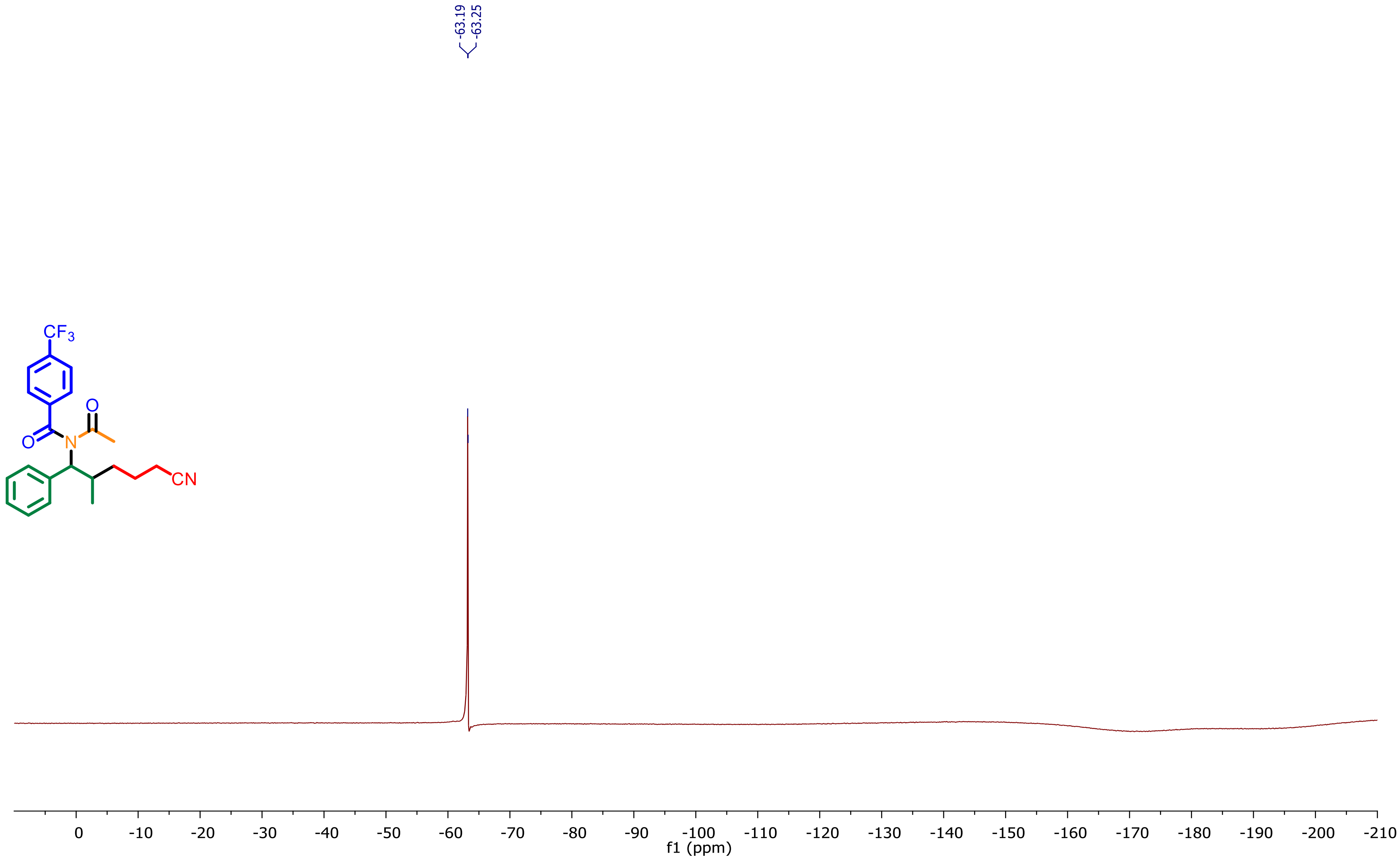
[1]H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3na)**



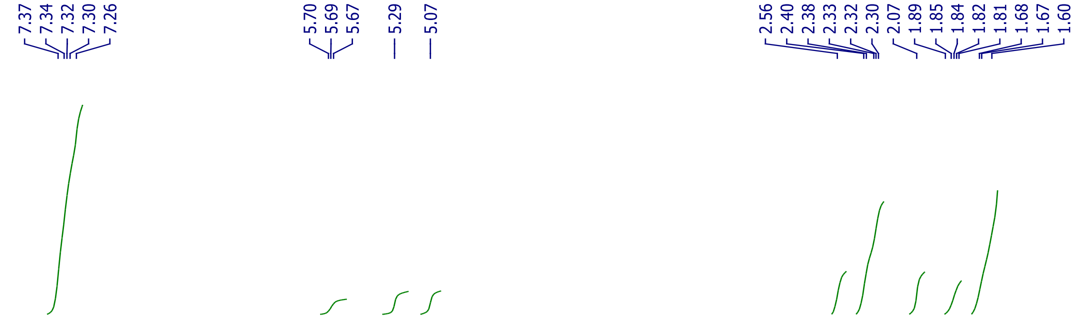
^{13}C NMR (176 MHz, $CDCl_3$) Spectrum of Compound **(3na)**

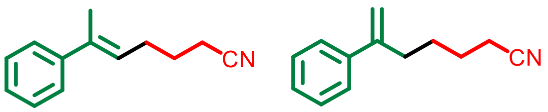


^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3na)**

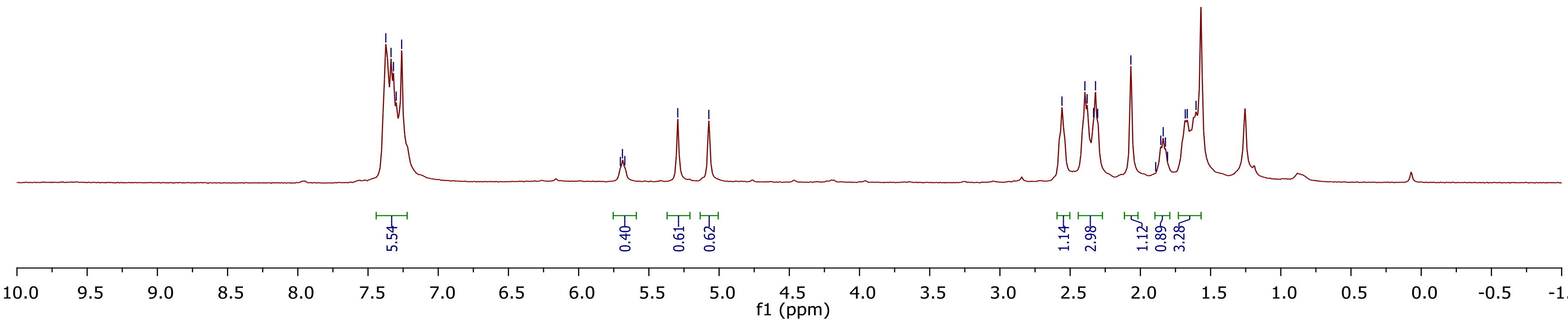


[1]H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3oa)**

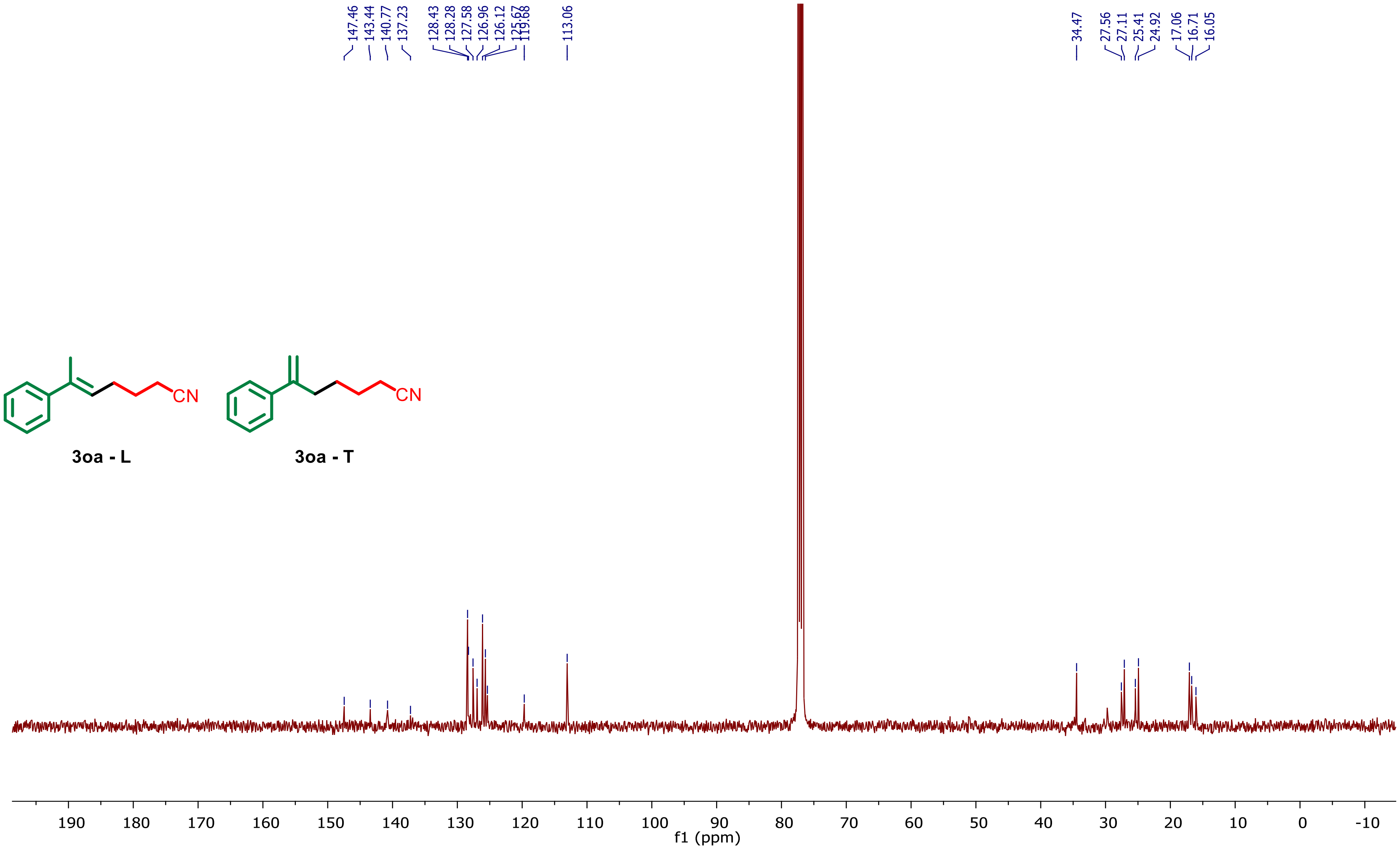




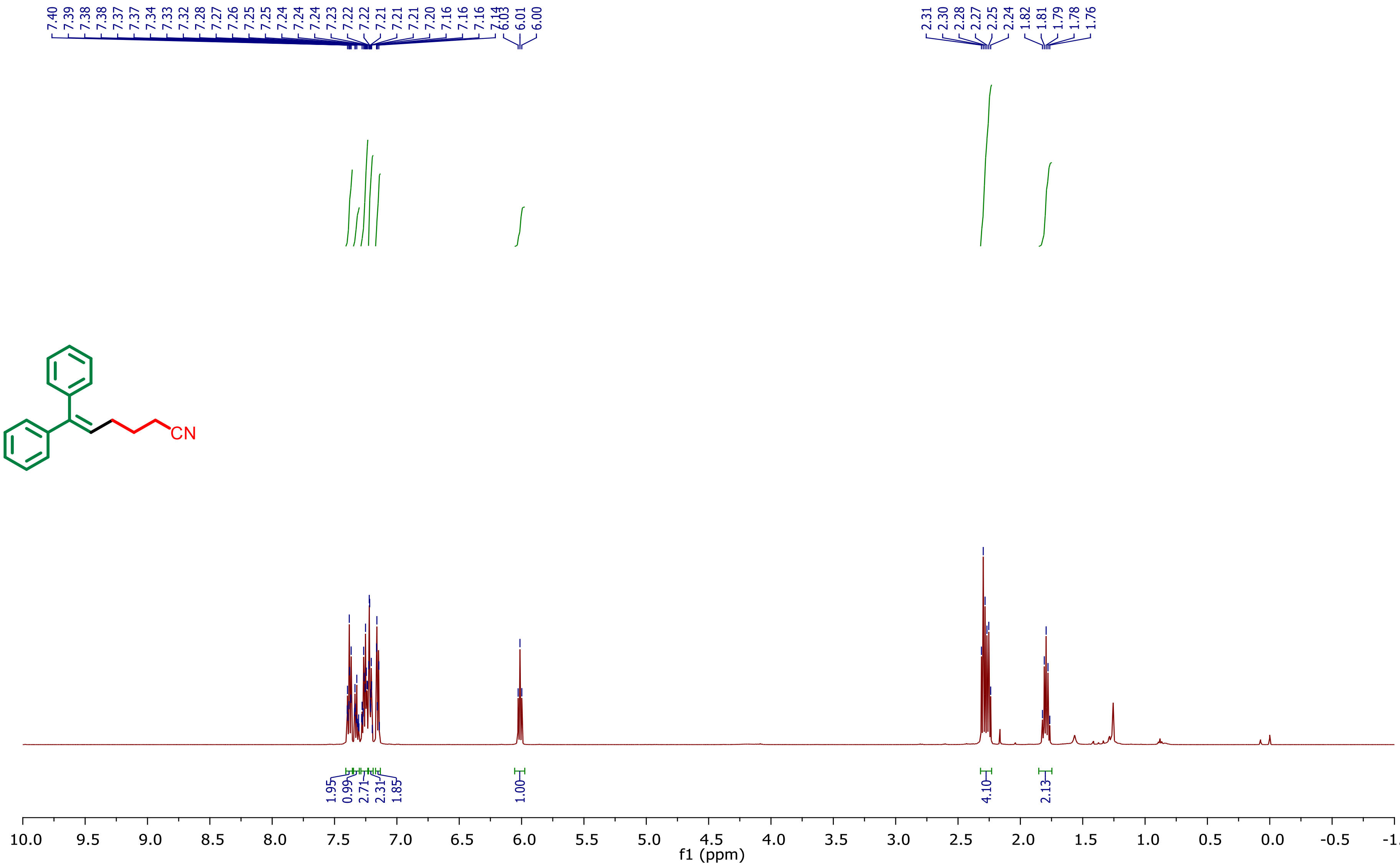
3oa - L **3oa - T**



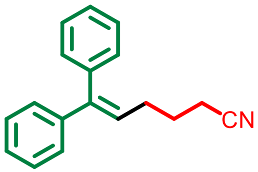
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3oa)**

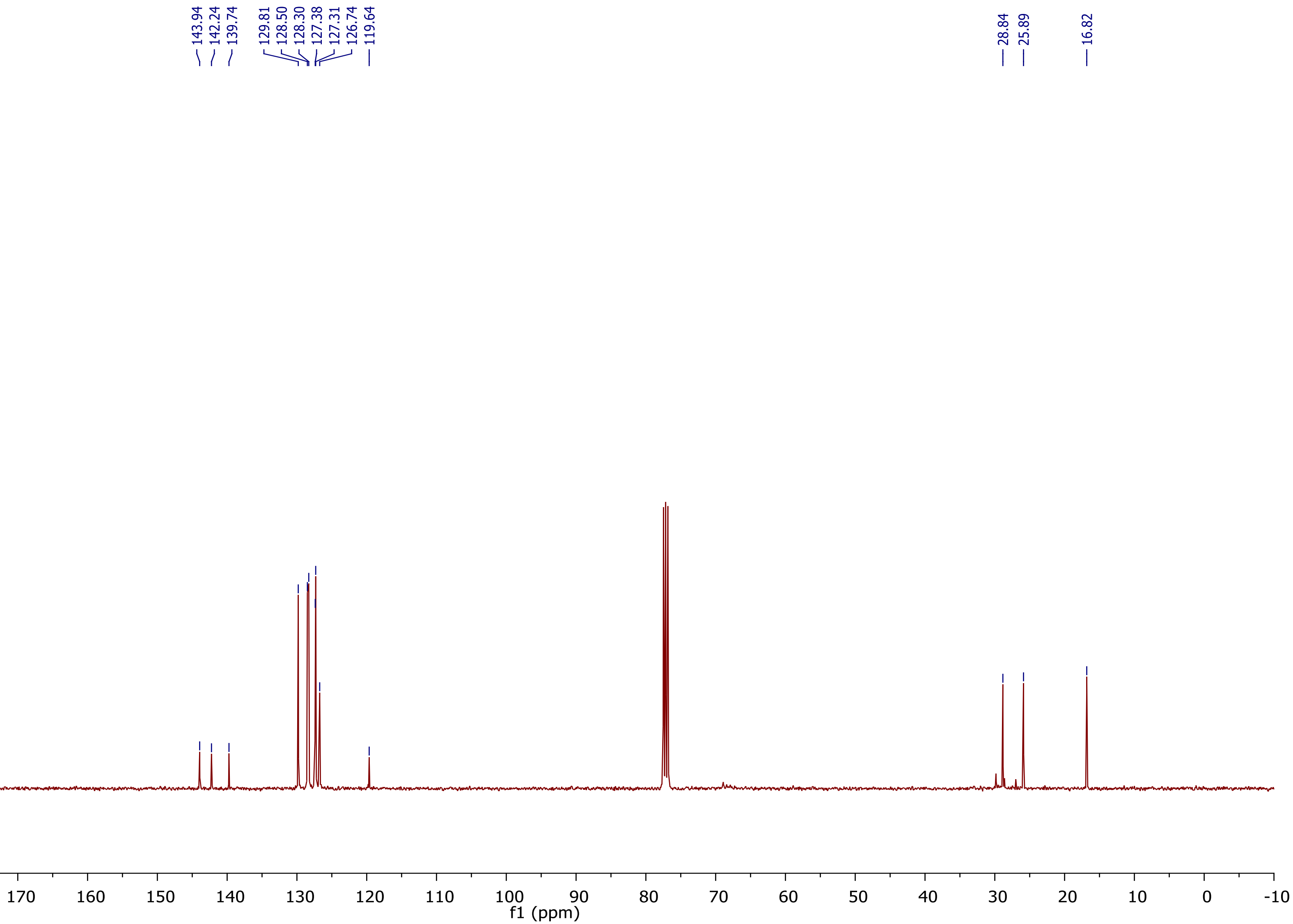


[1]H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3pa)**

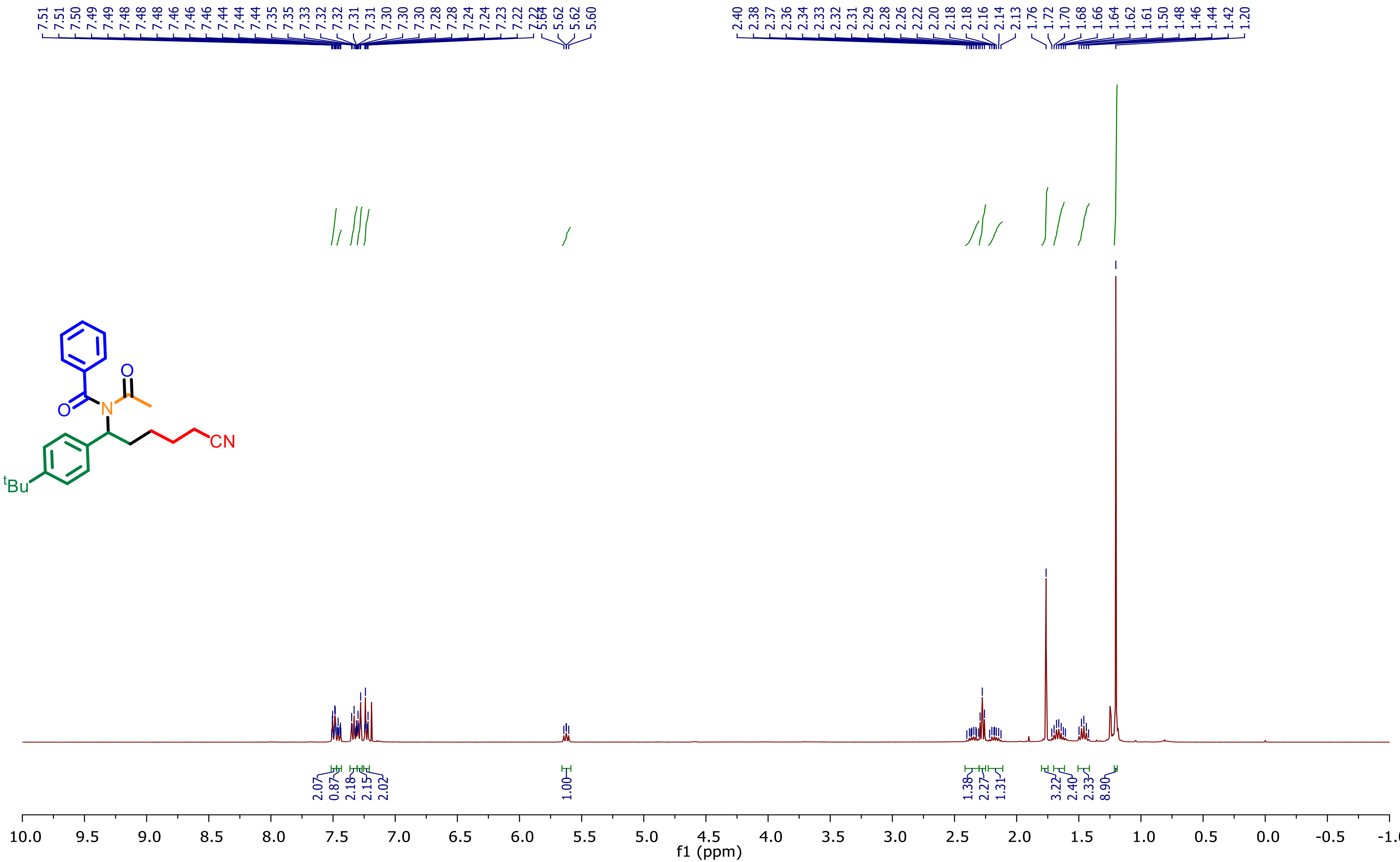


^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3pa)**

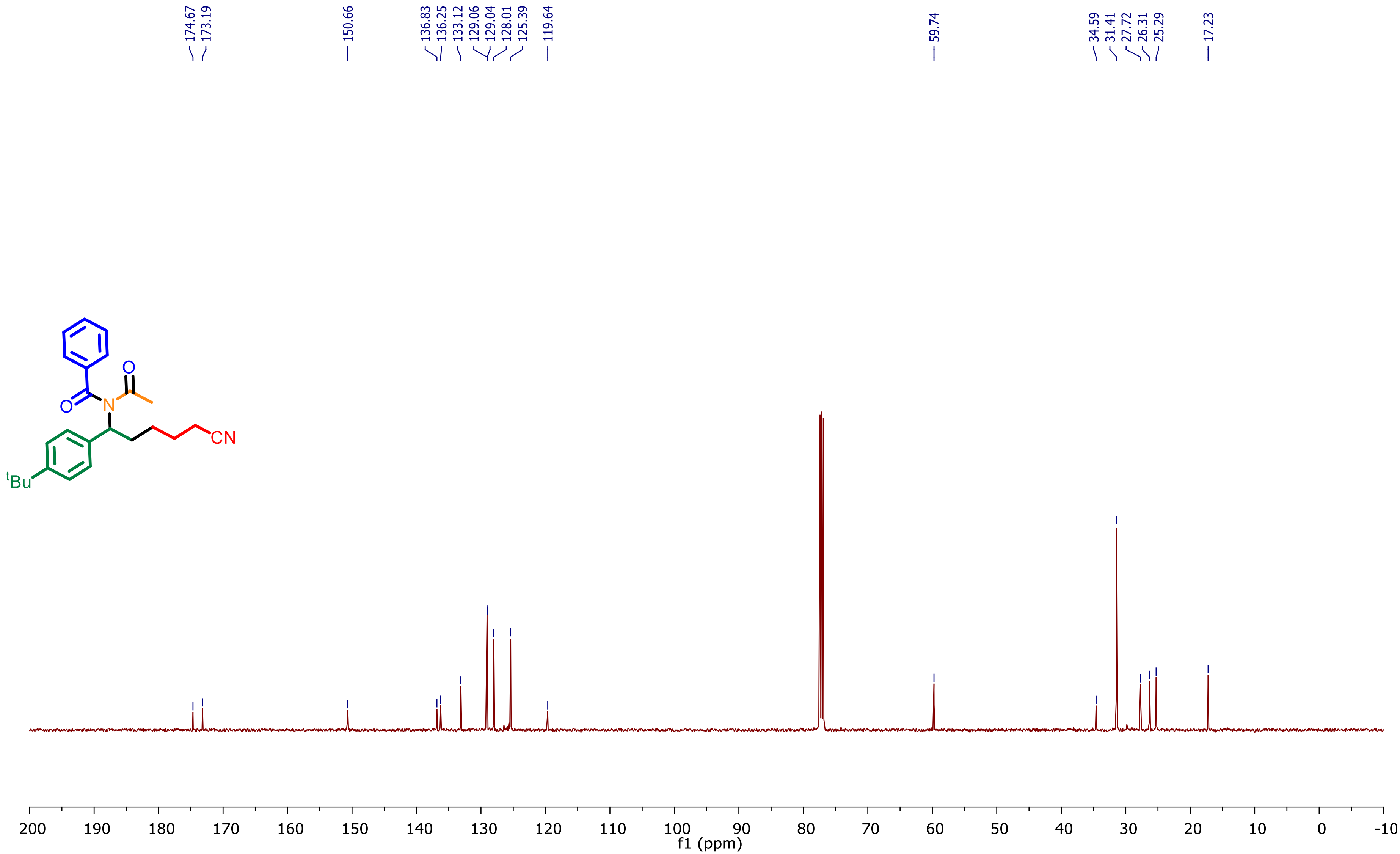




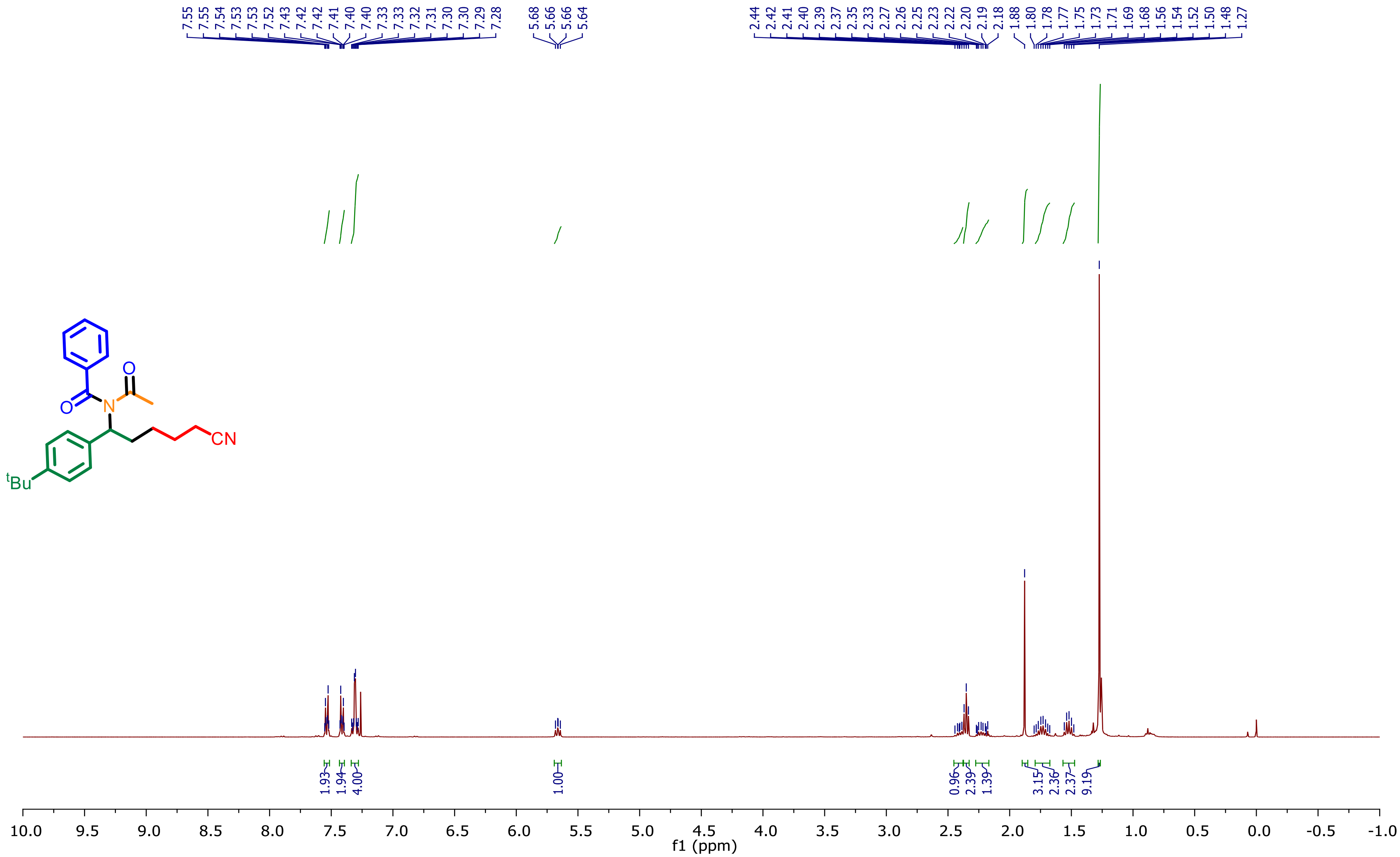
[1]H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ab)**



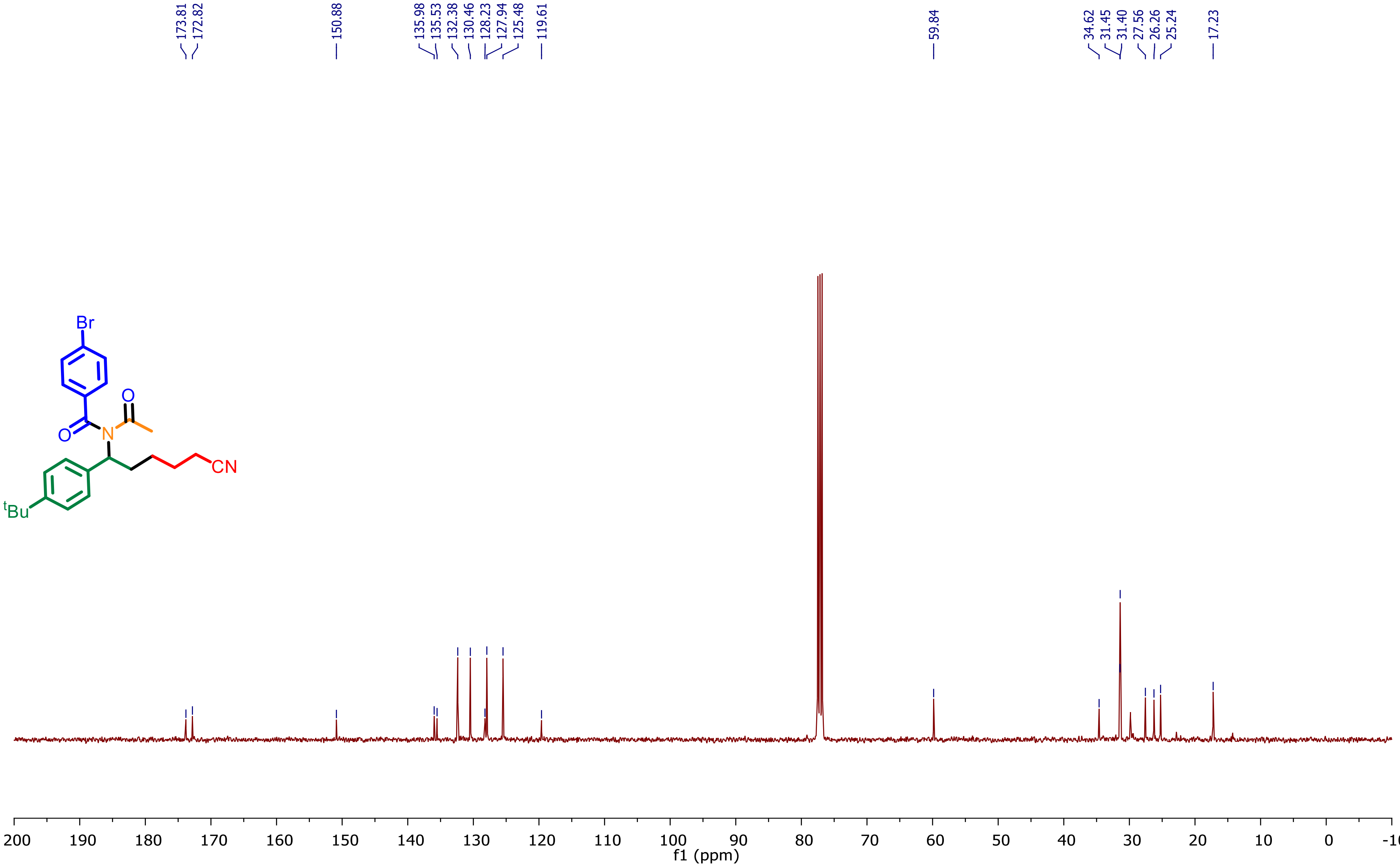
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ab)**



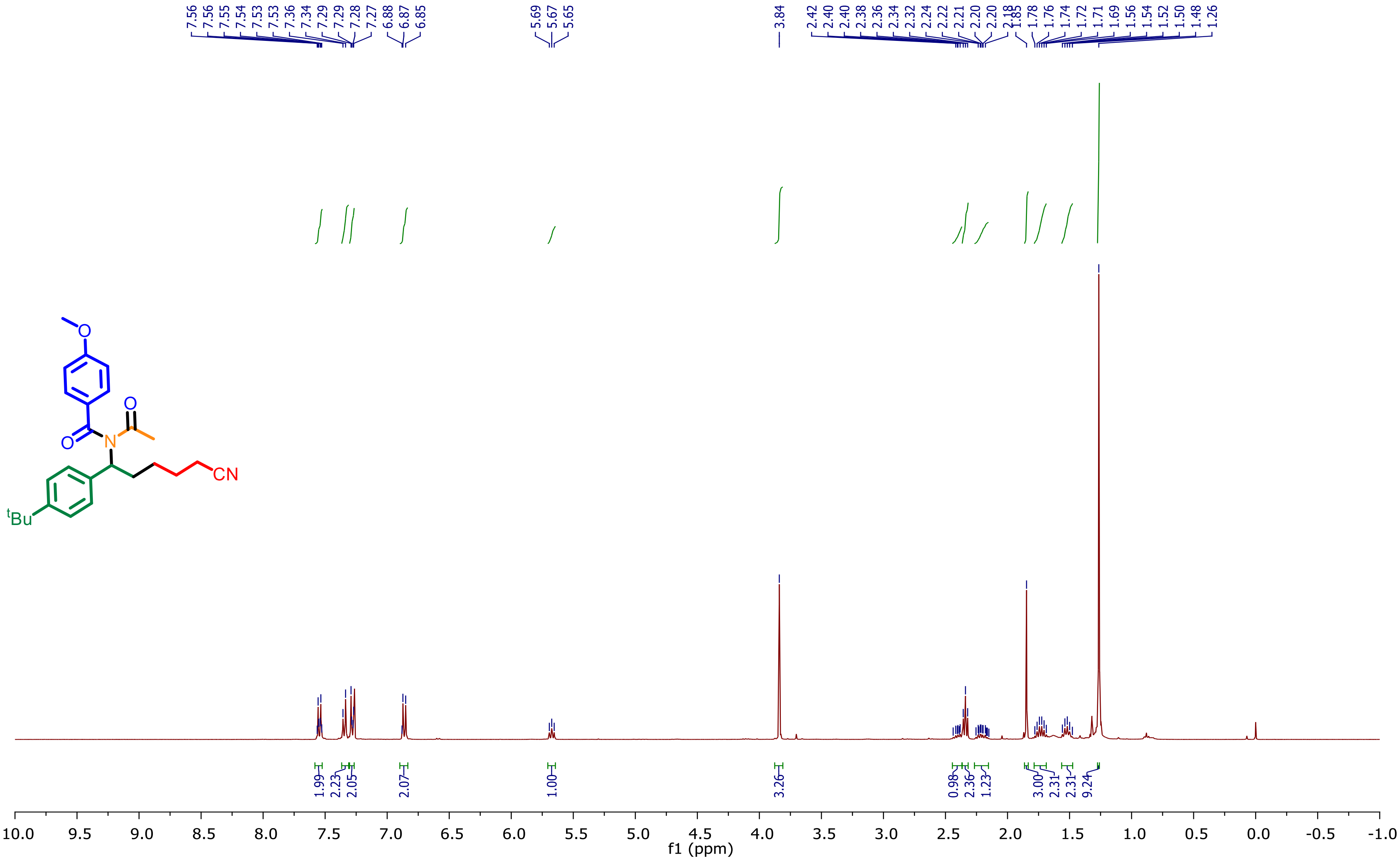
^1H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ac)**



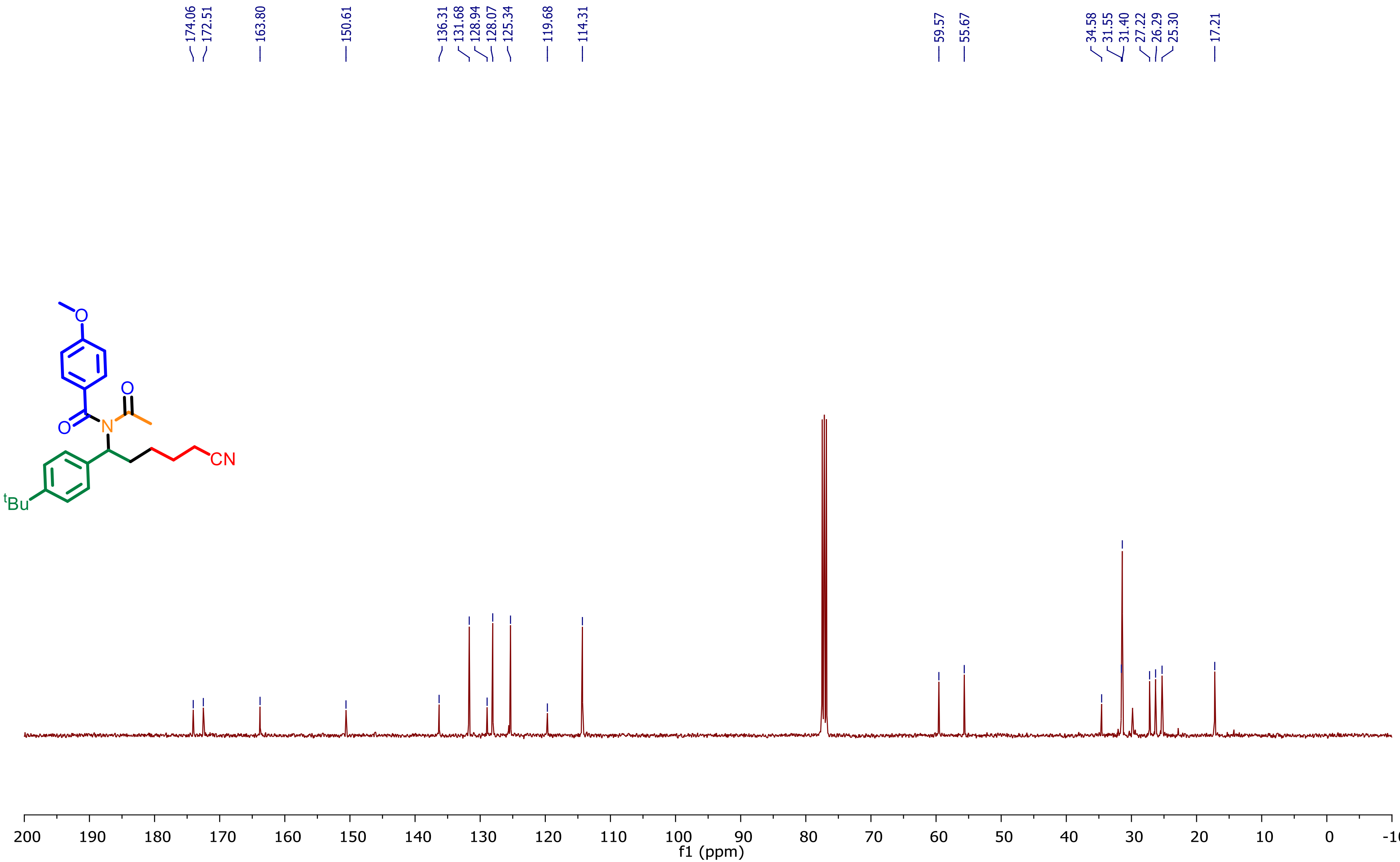
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ac)**



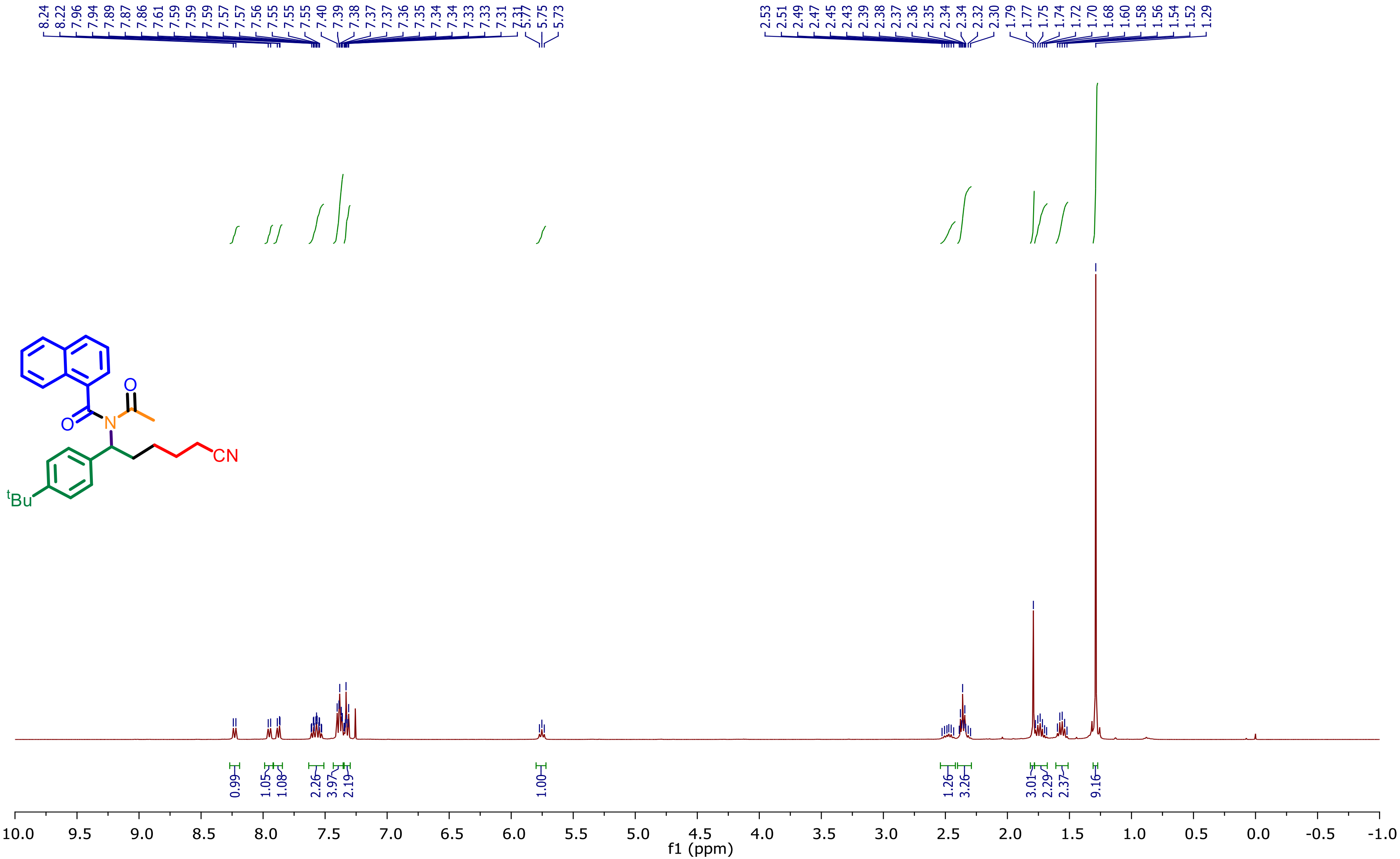
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ad)**



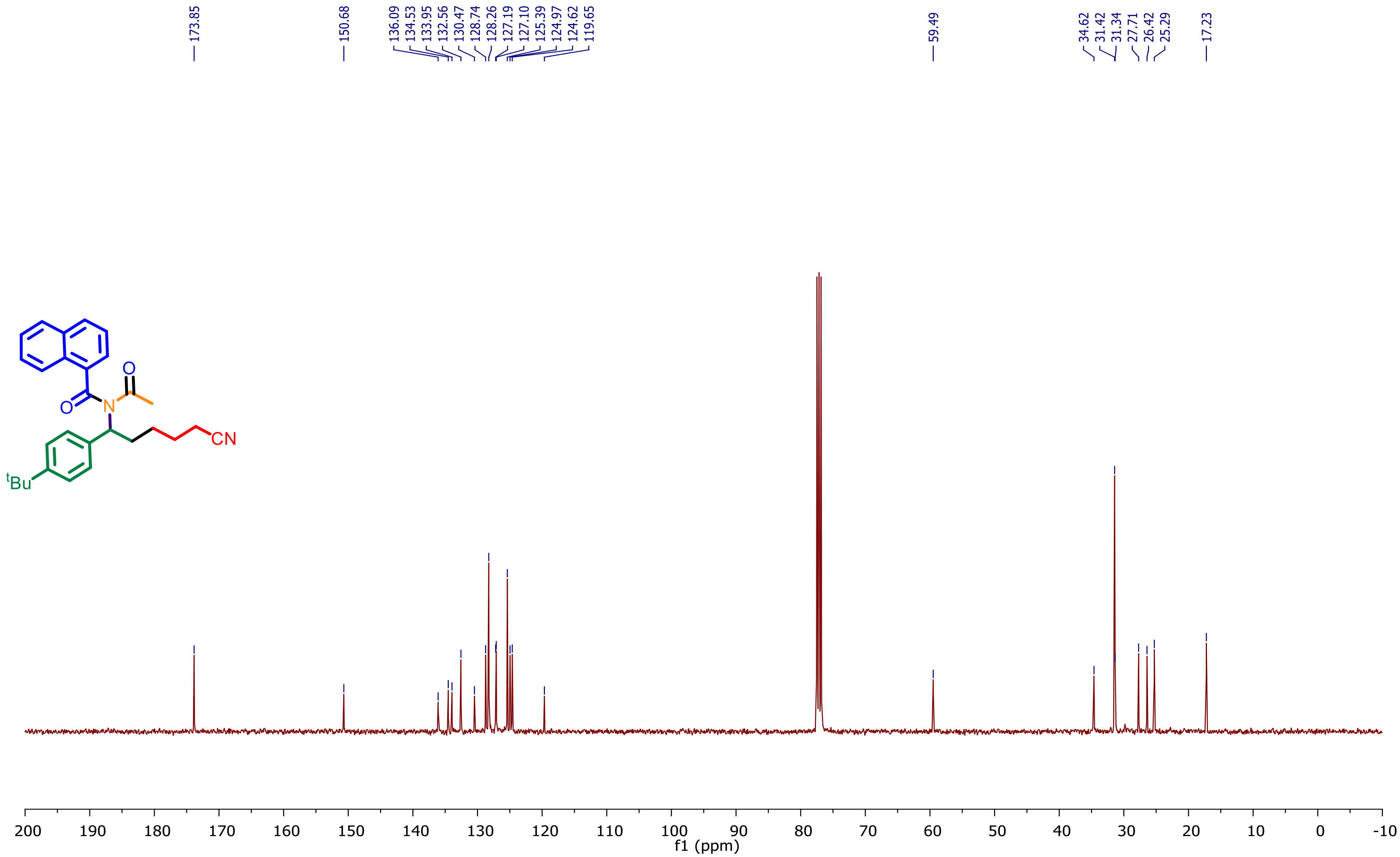
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ad)**



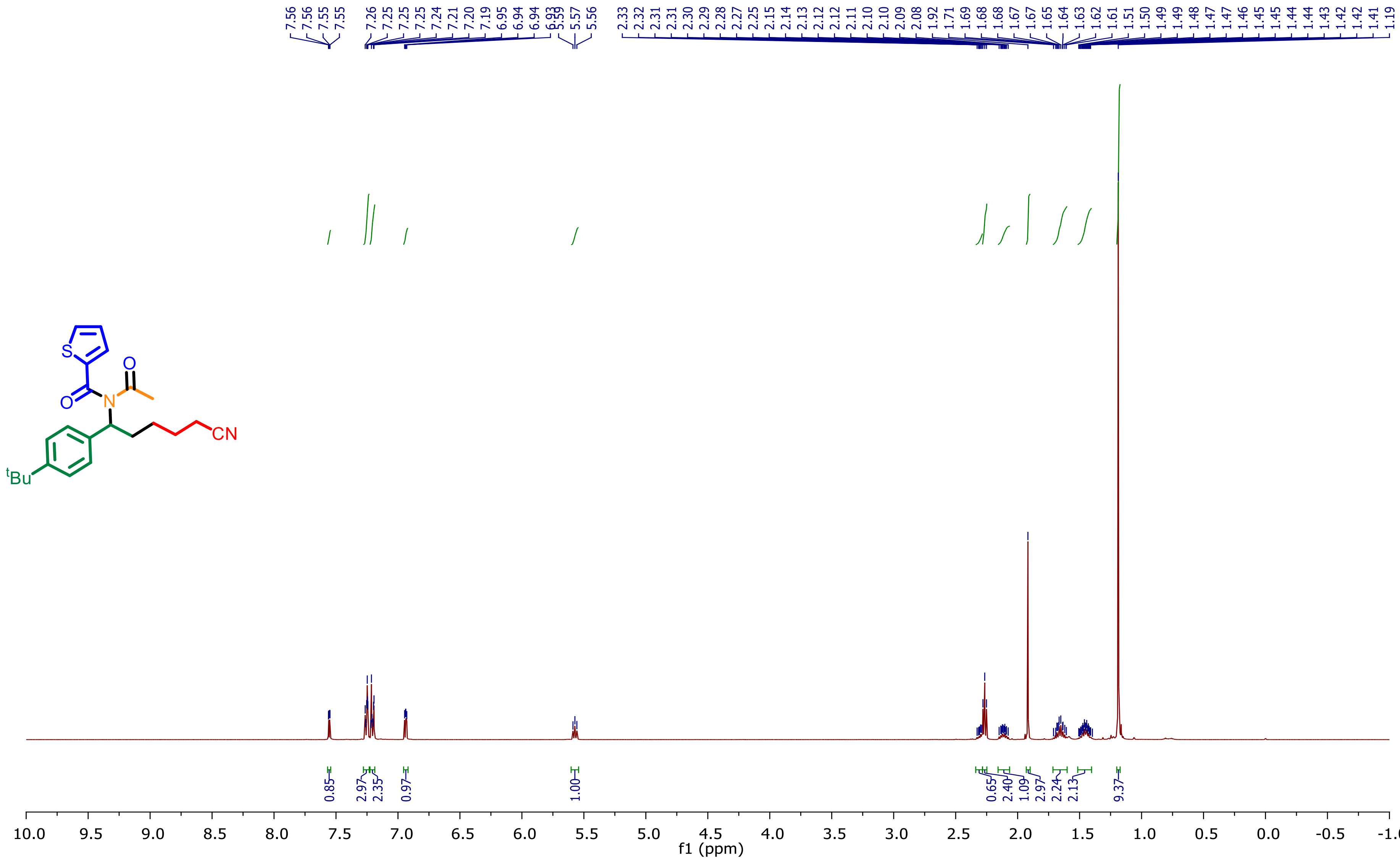
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ae)**



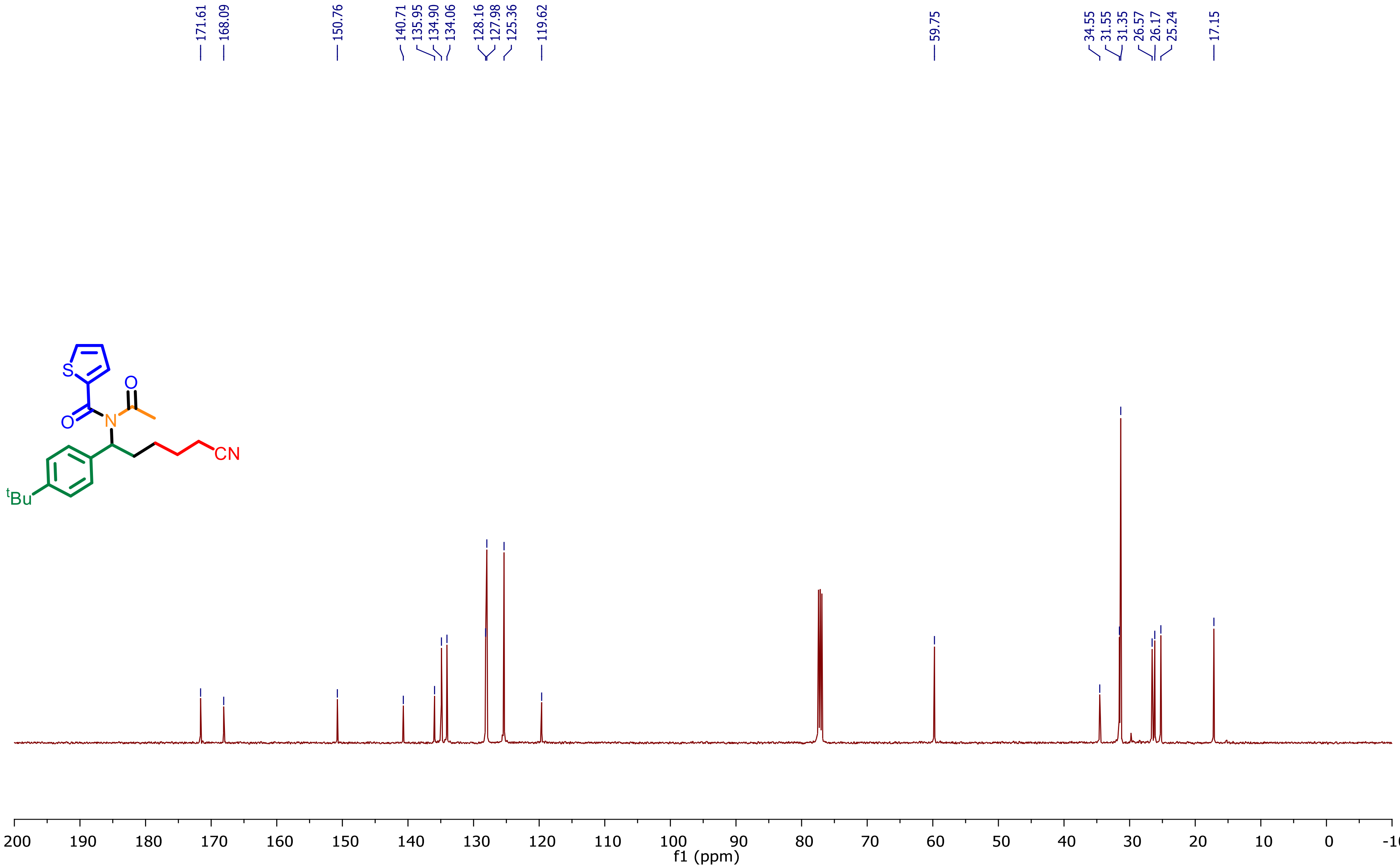
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ae)**



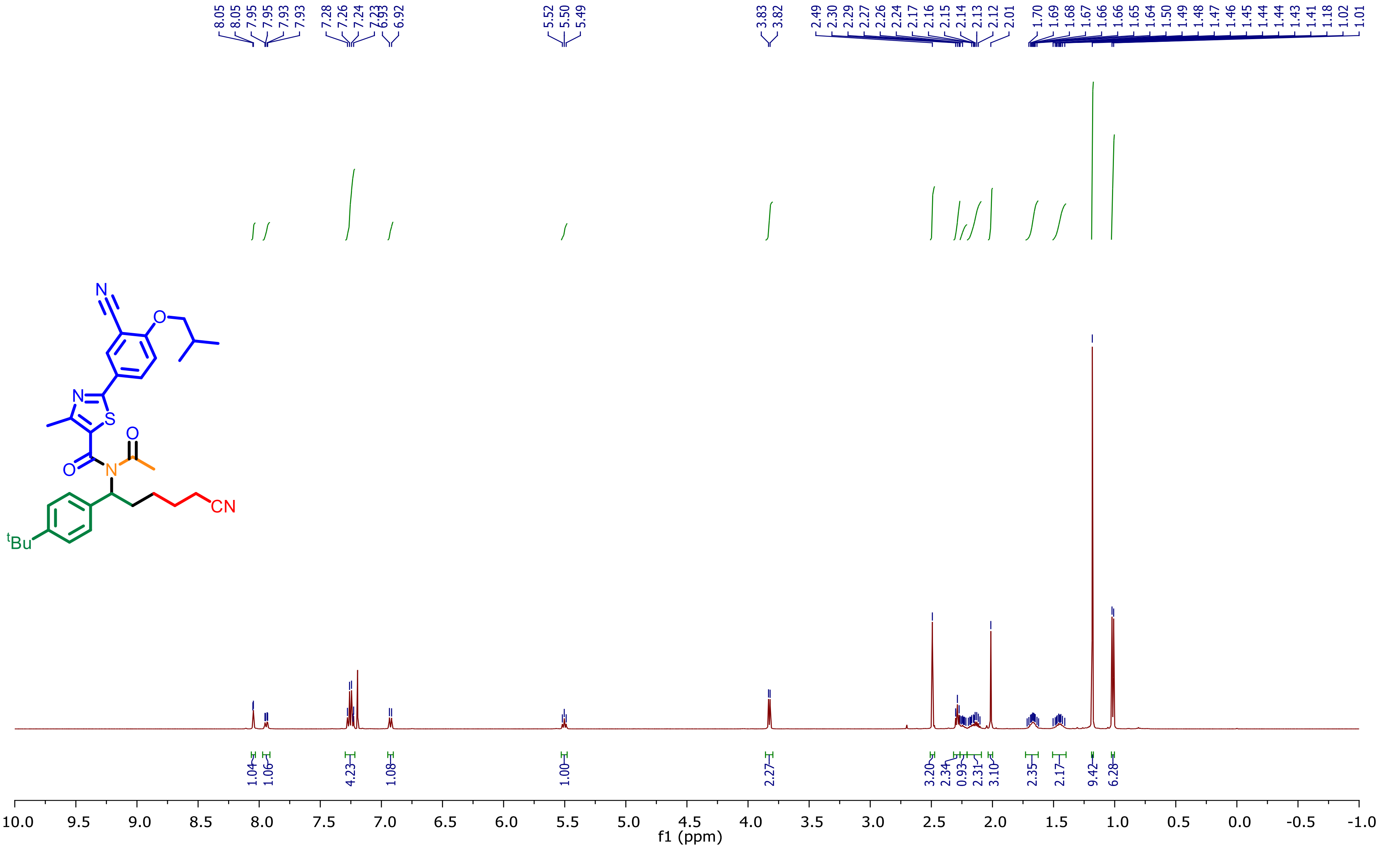
[1]H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3af)**



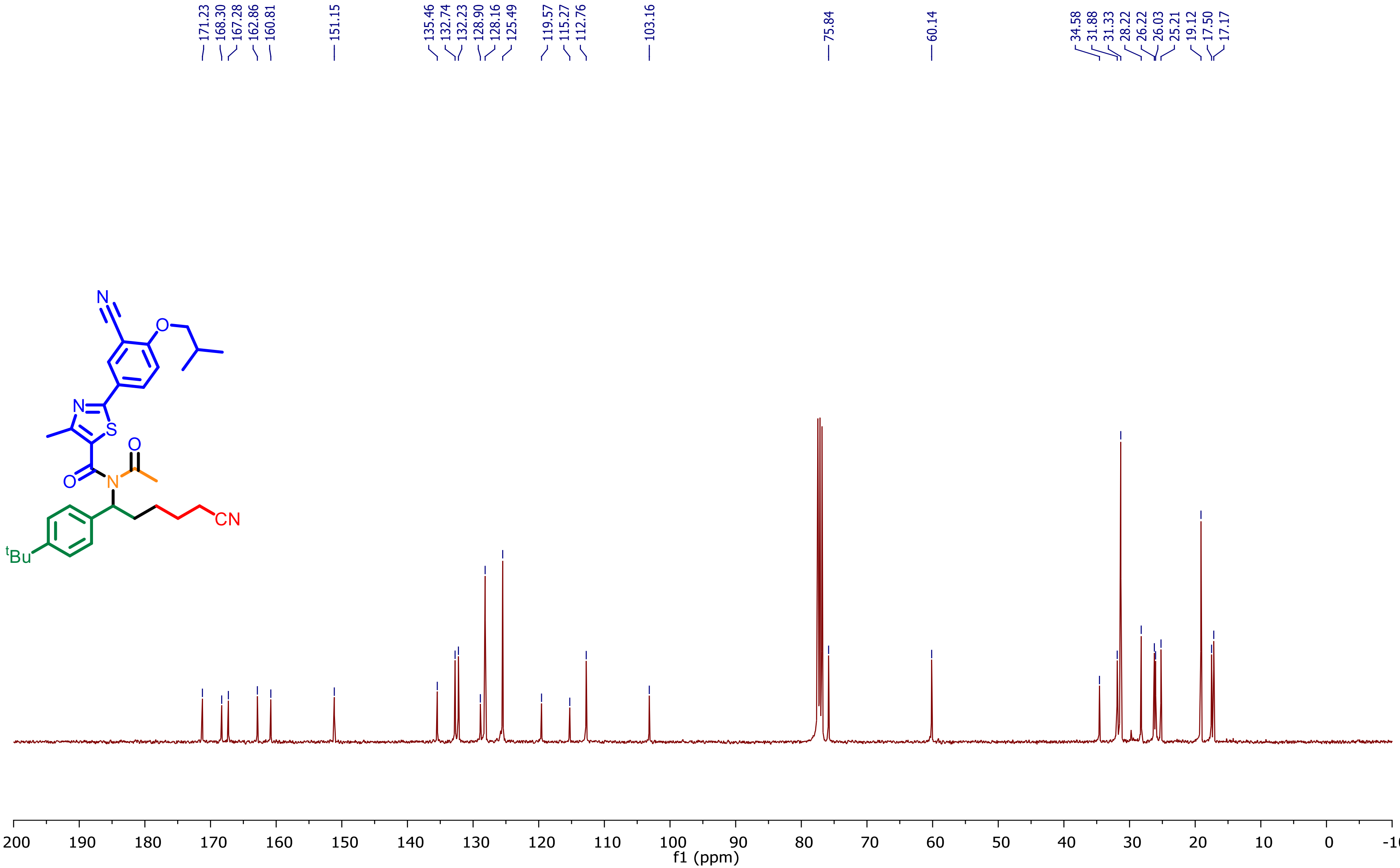
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3af)**



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



[13]C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ag)**



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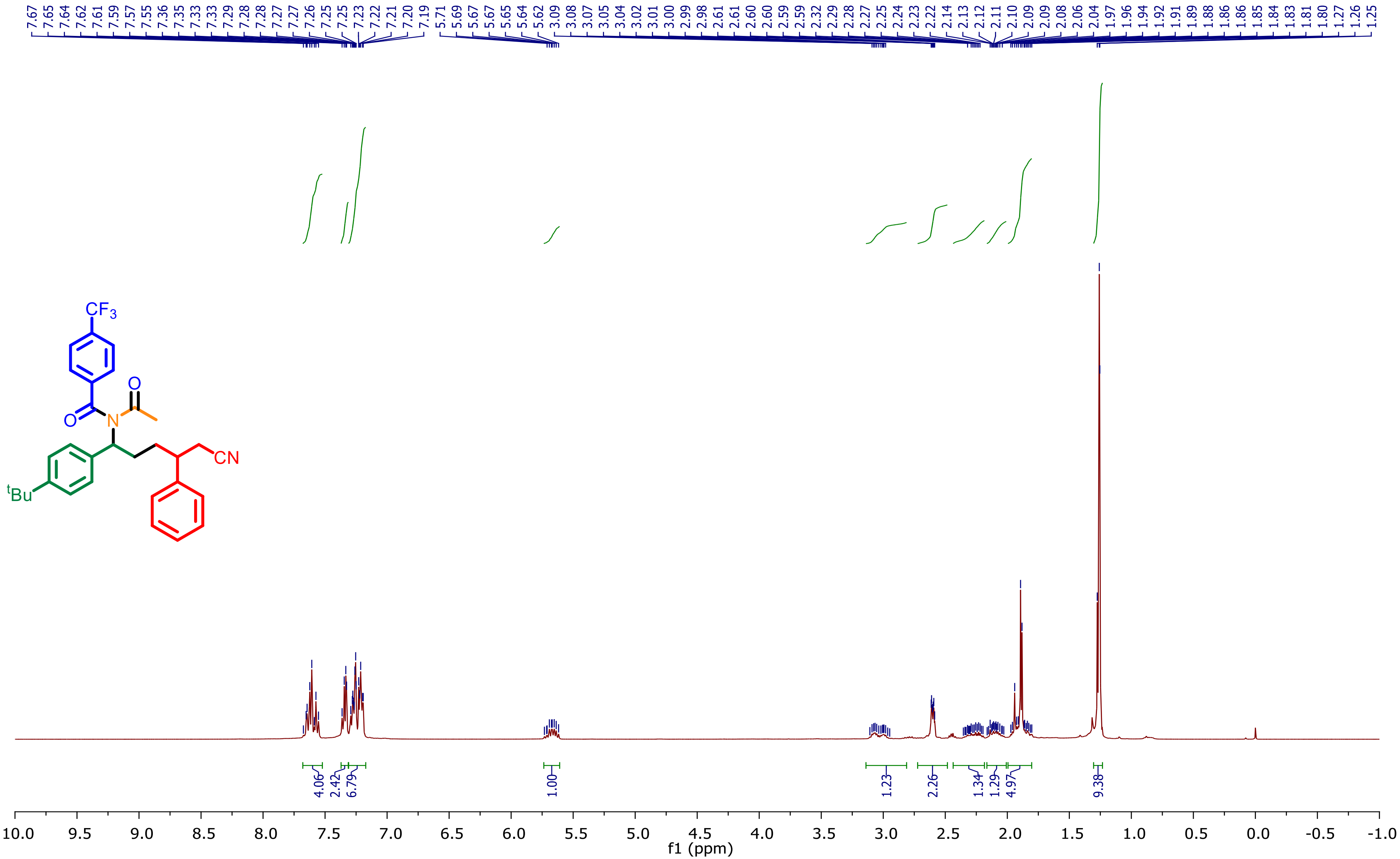
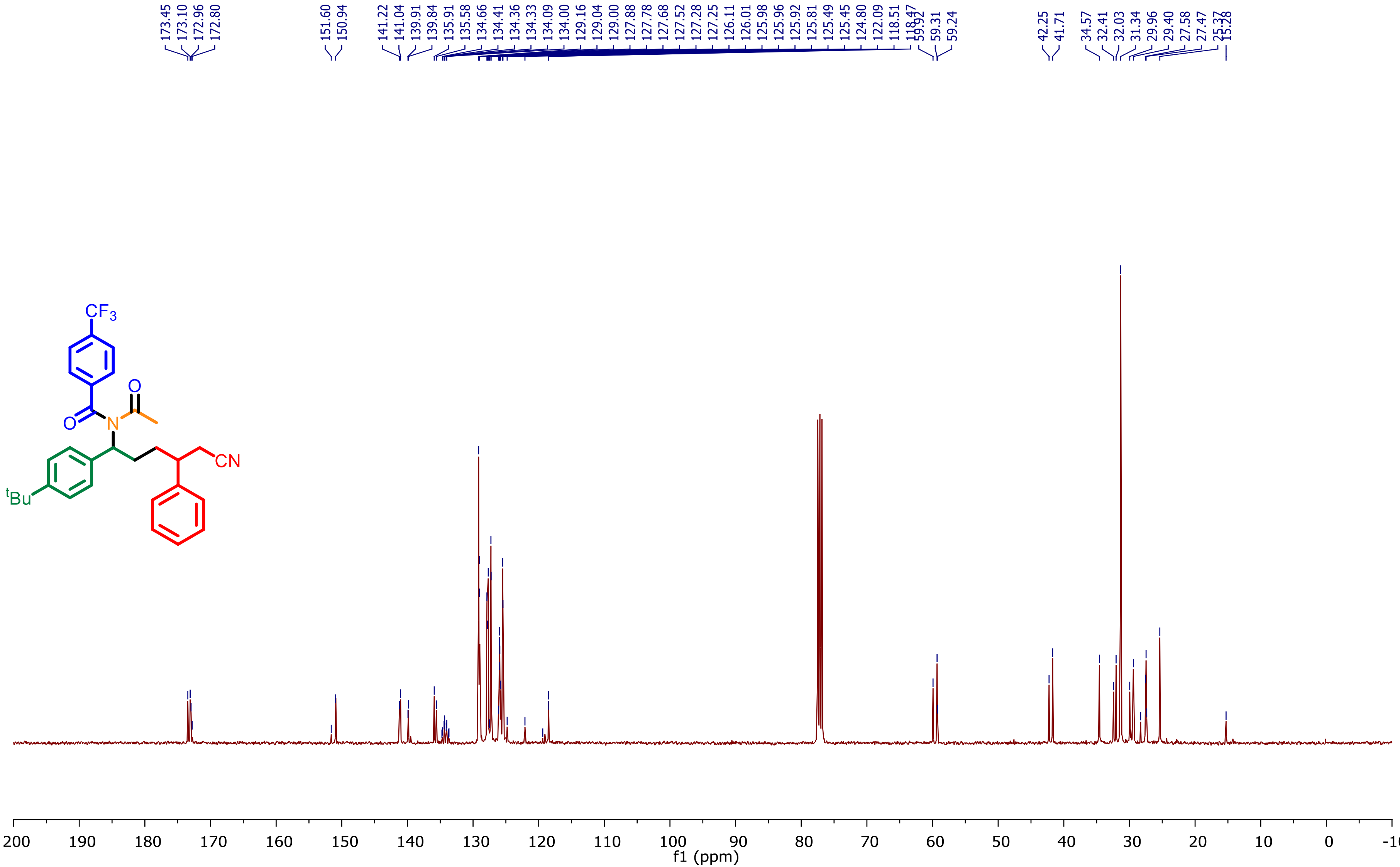
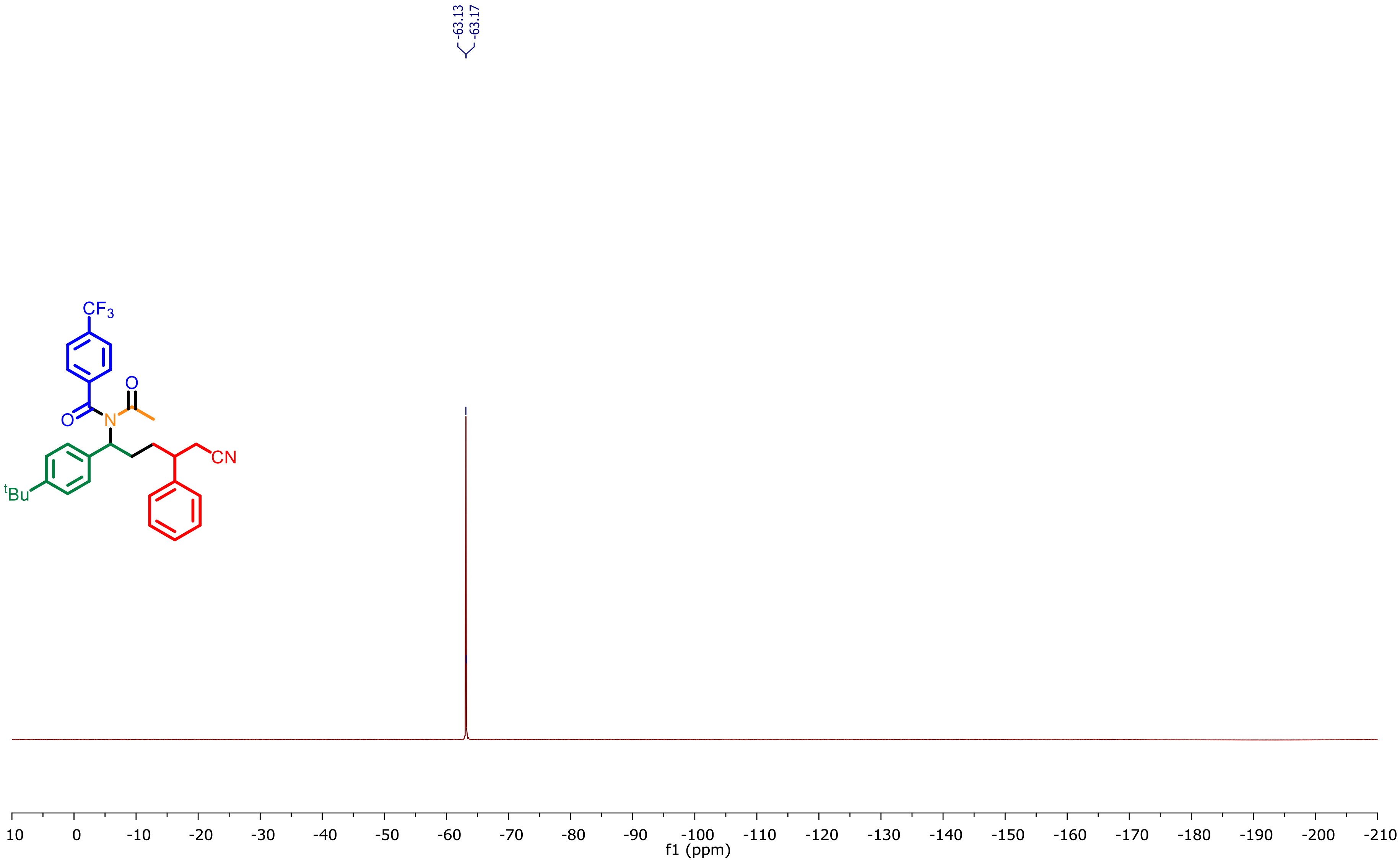
[1]H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3aj)**



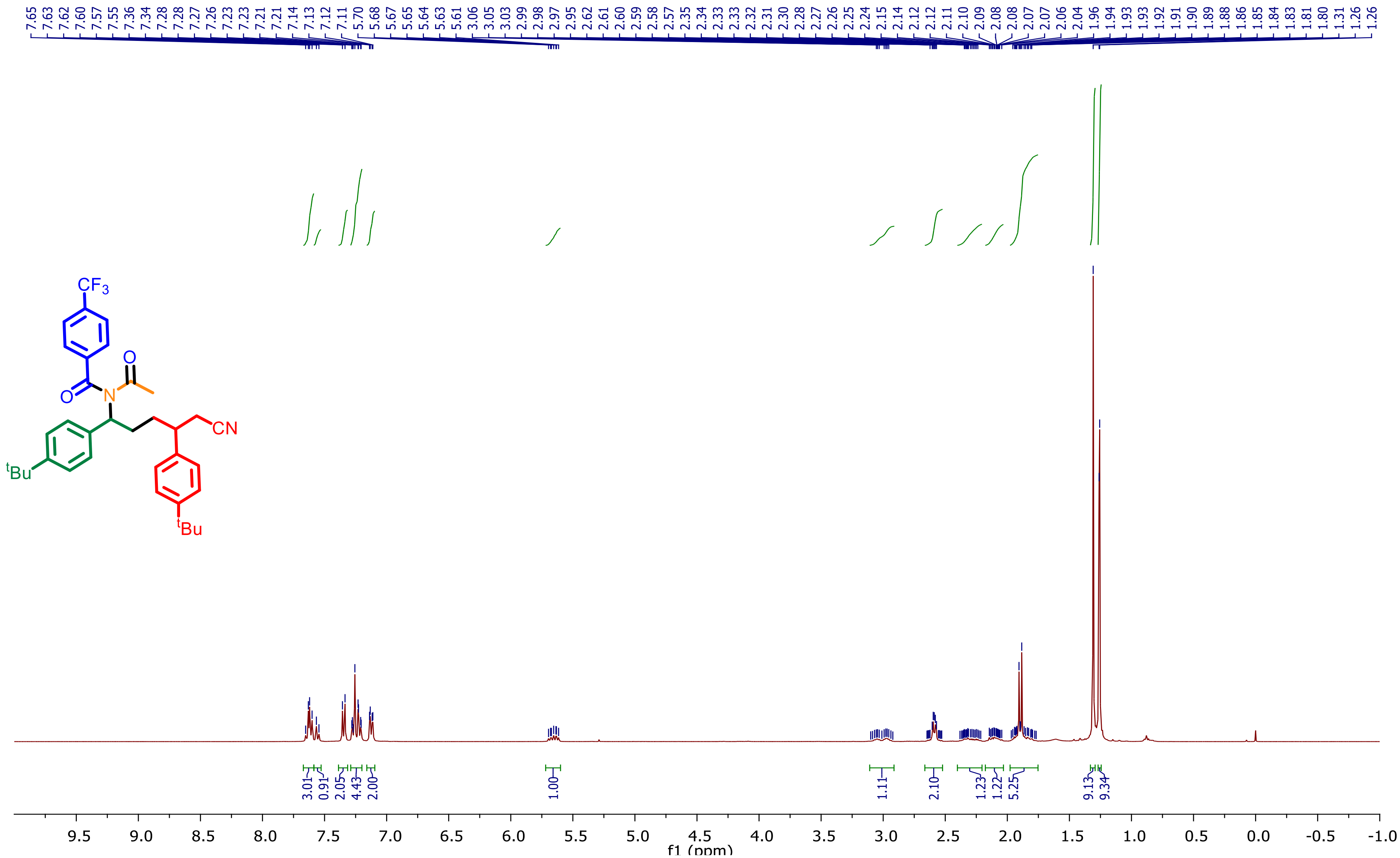
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3aj)**



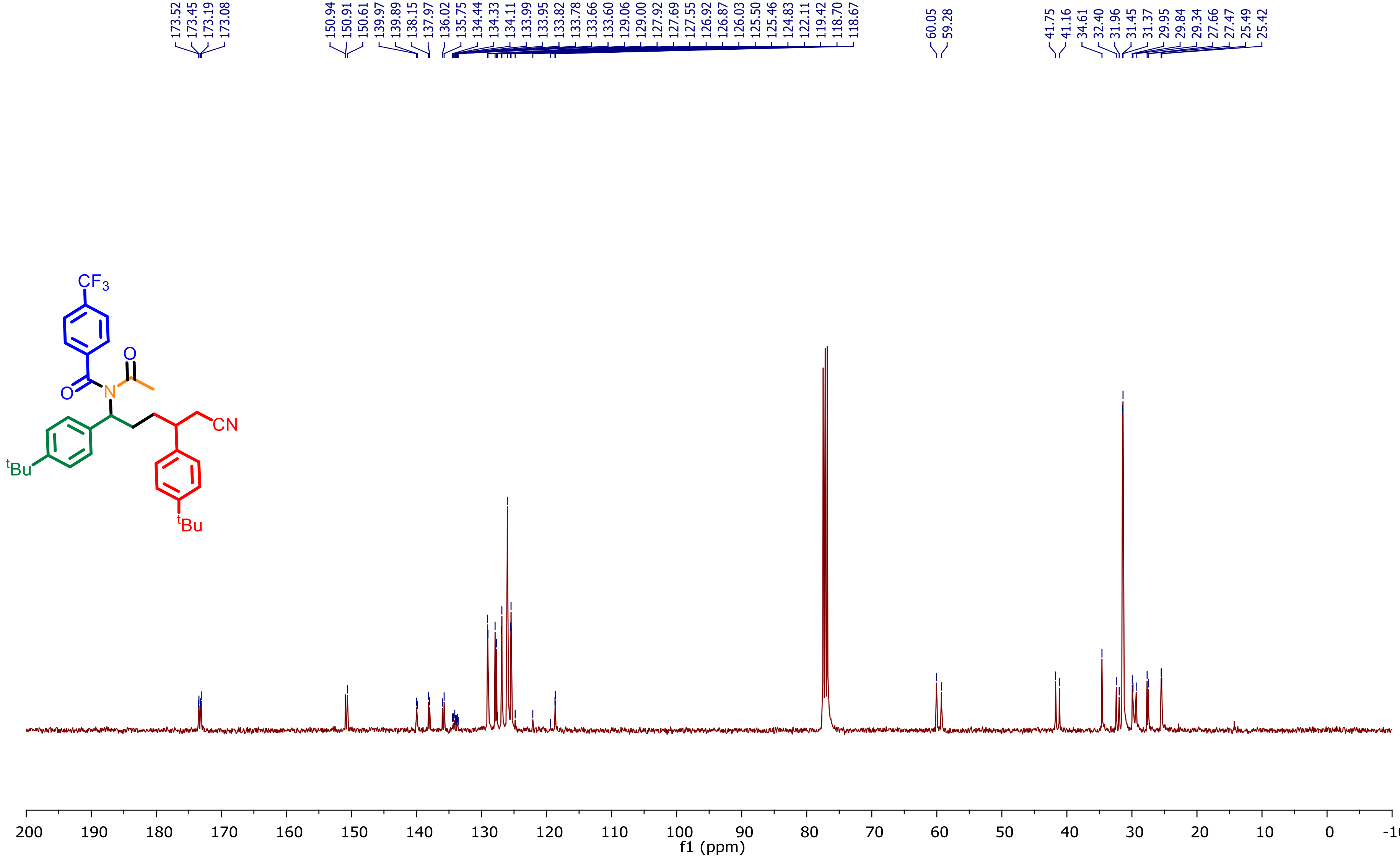
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **(3aj)**



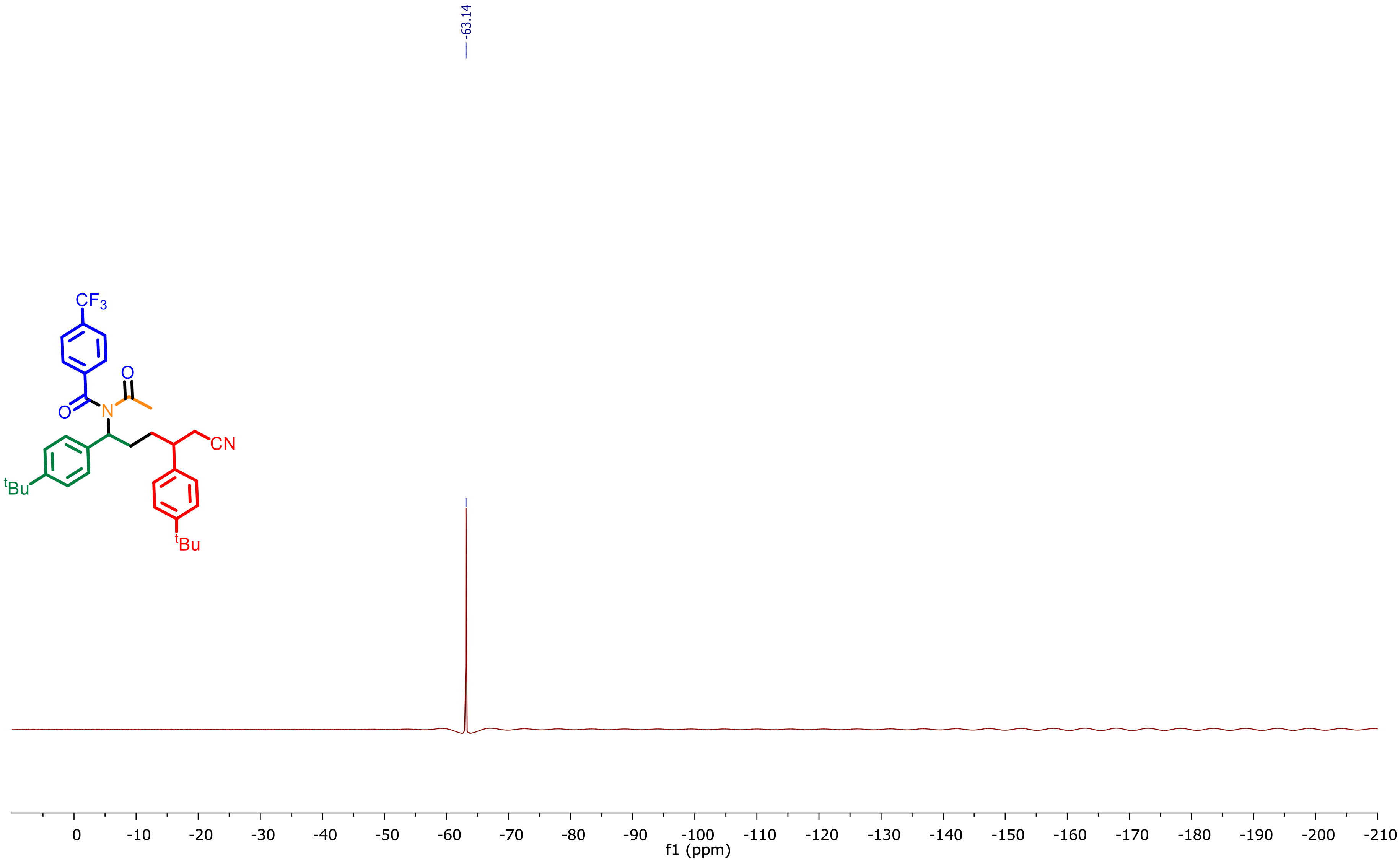
[1]H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ak)**



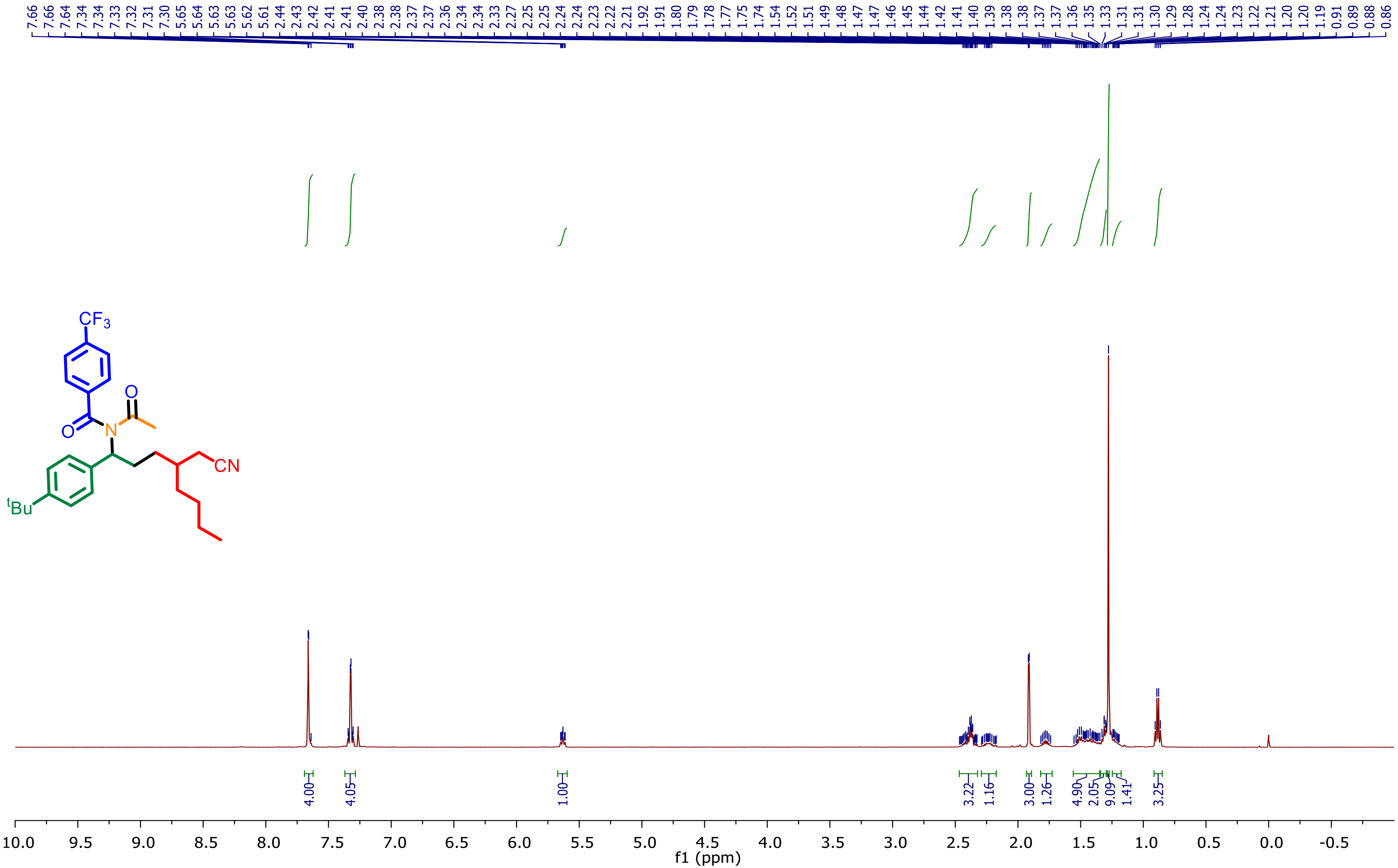
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ak)**



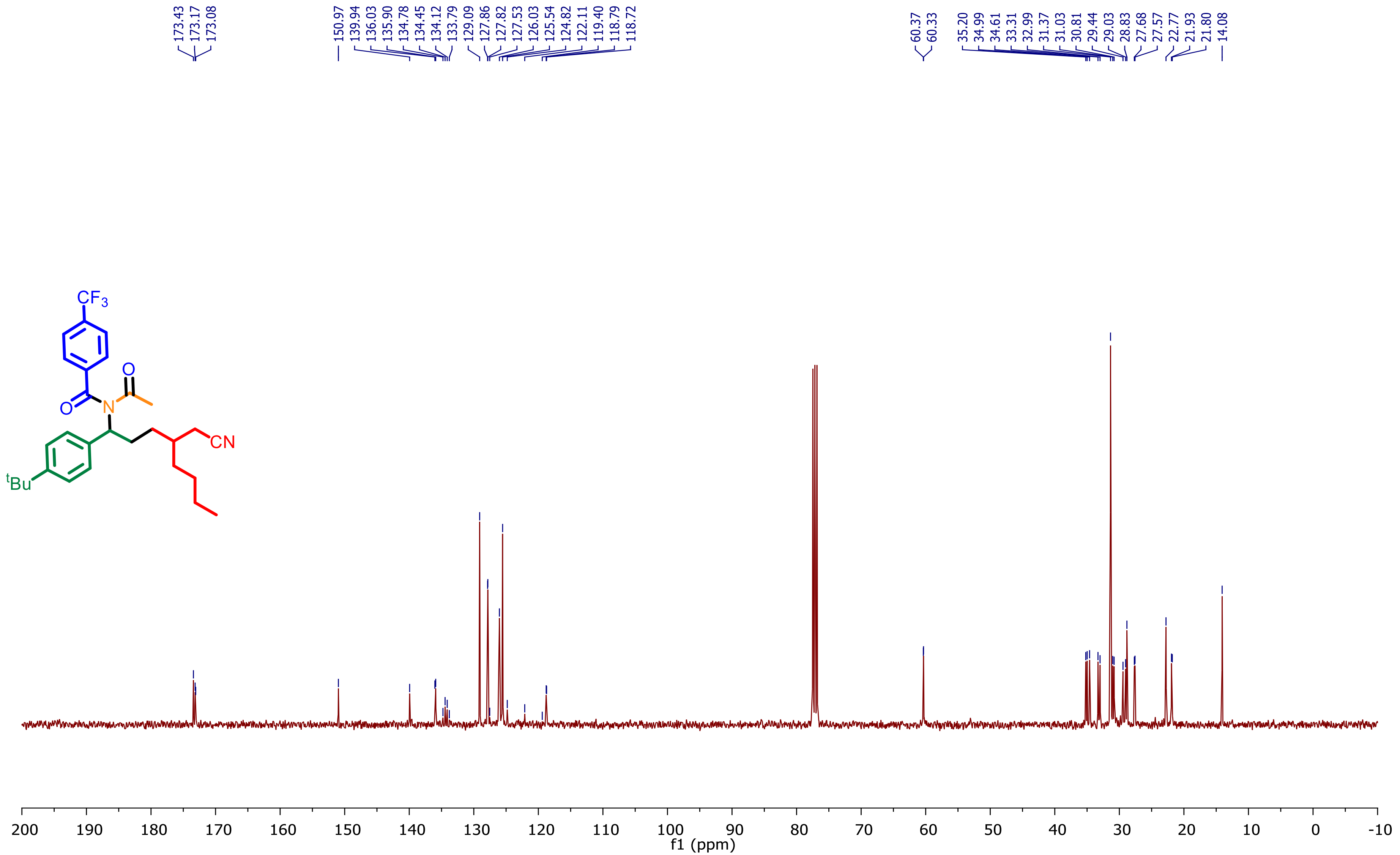
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3ak)**



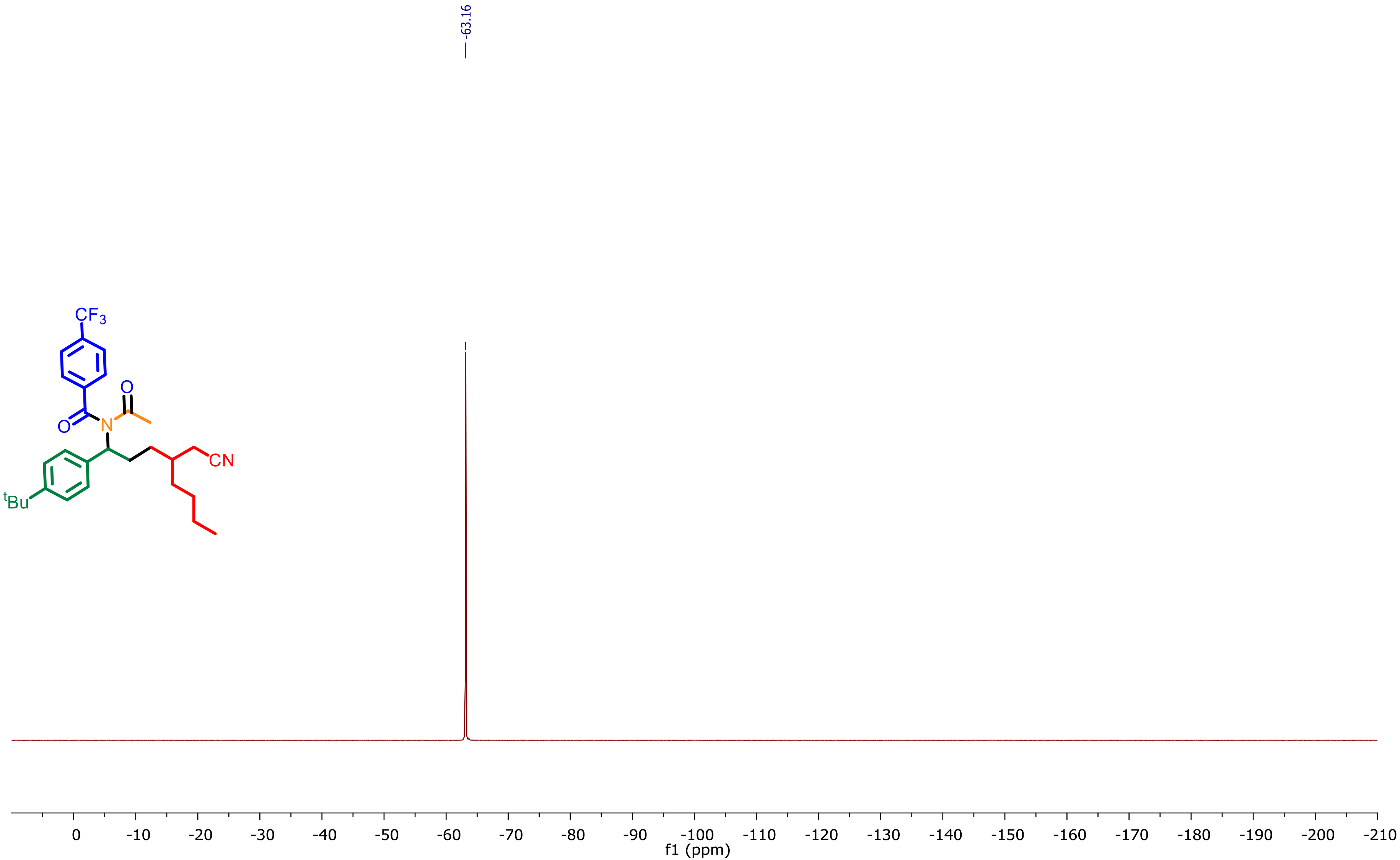
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3al)**



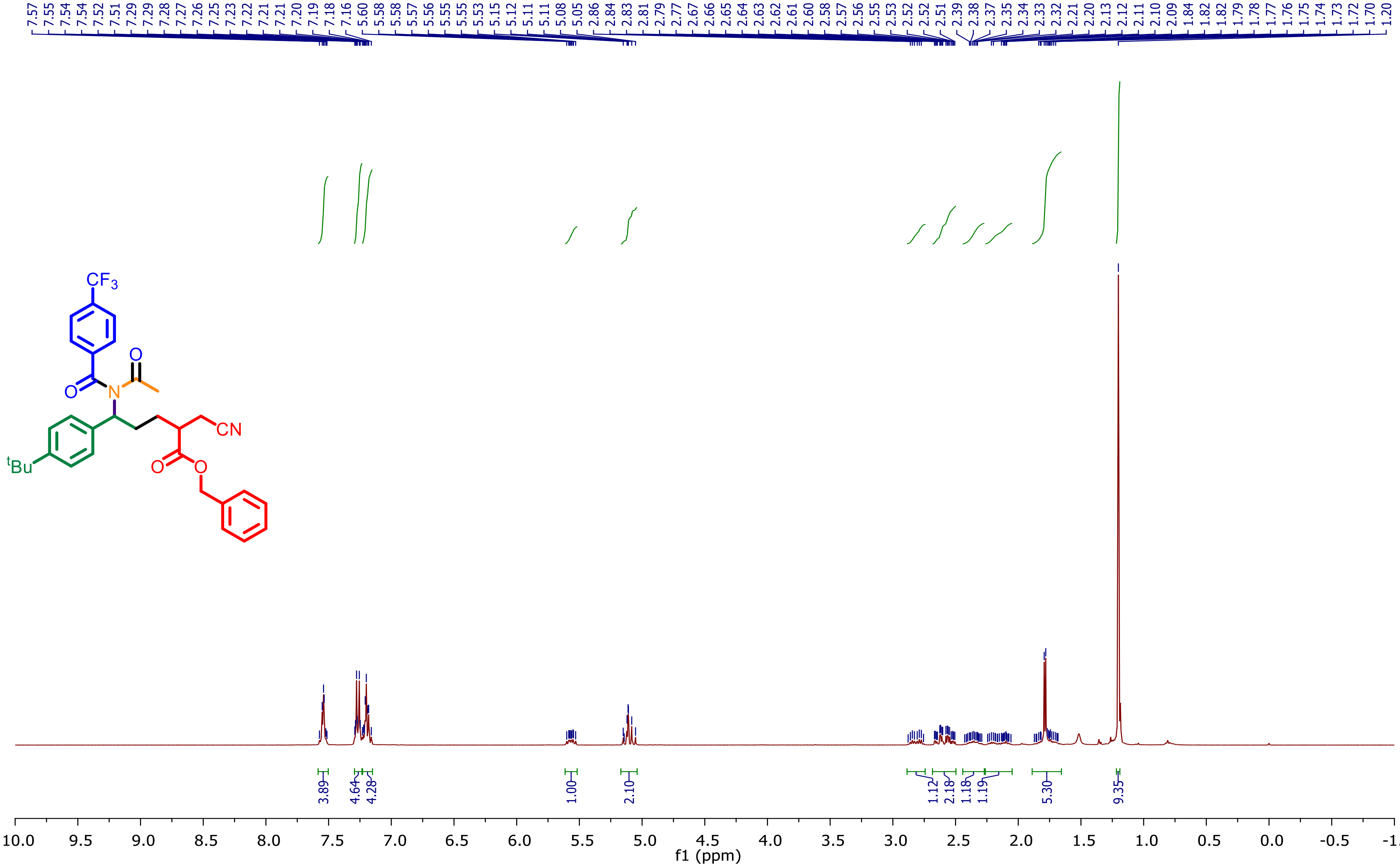
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3al)**



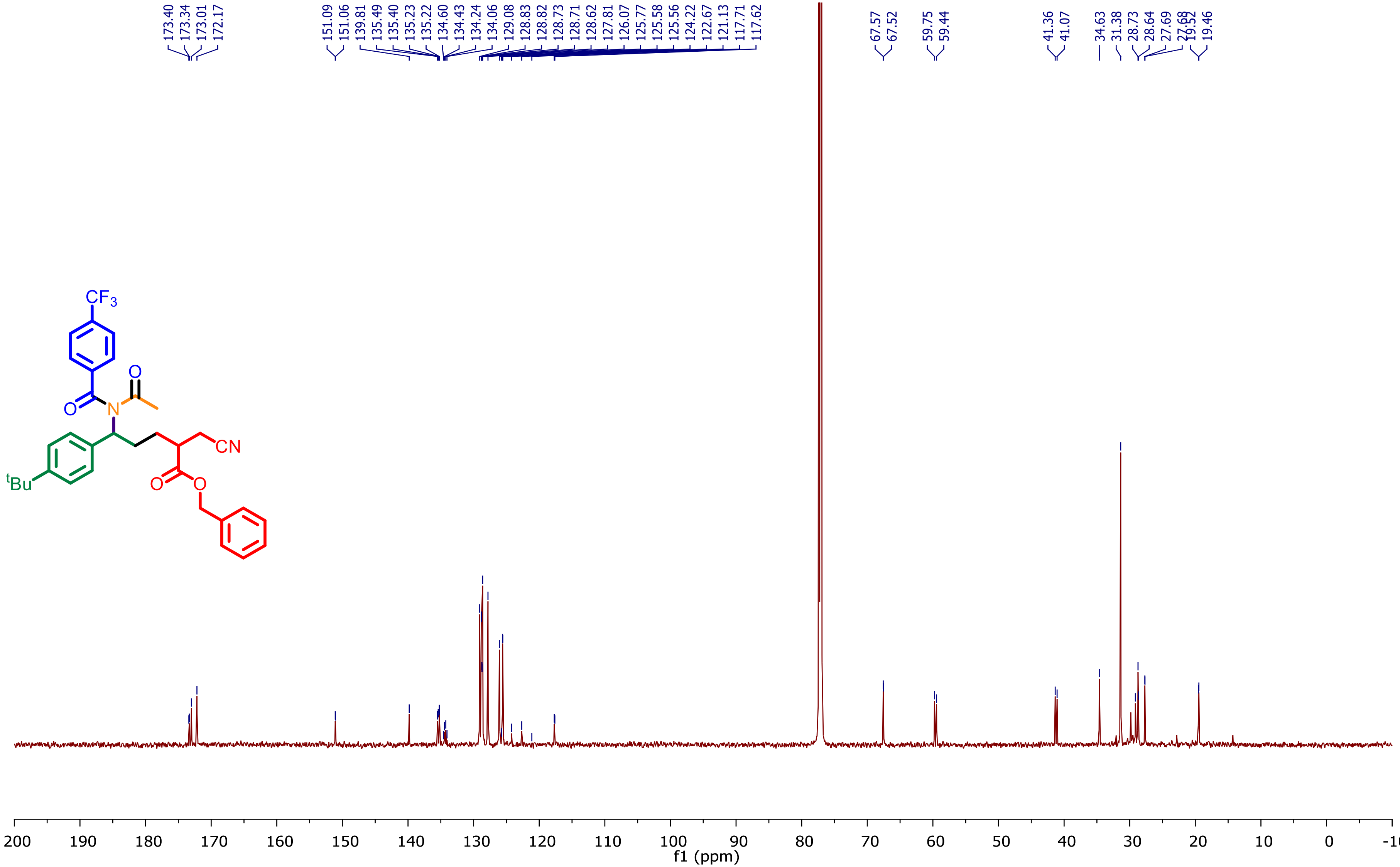
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3al)**



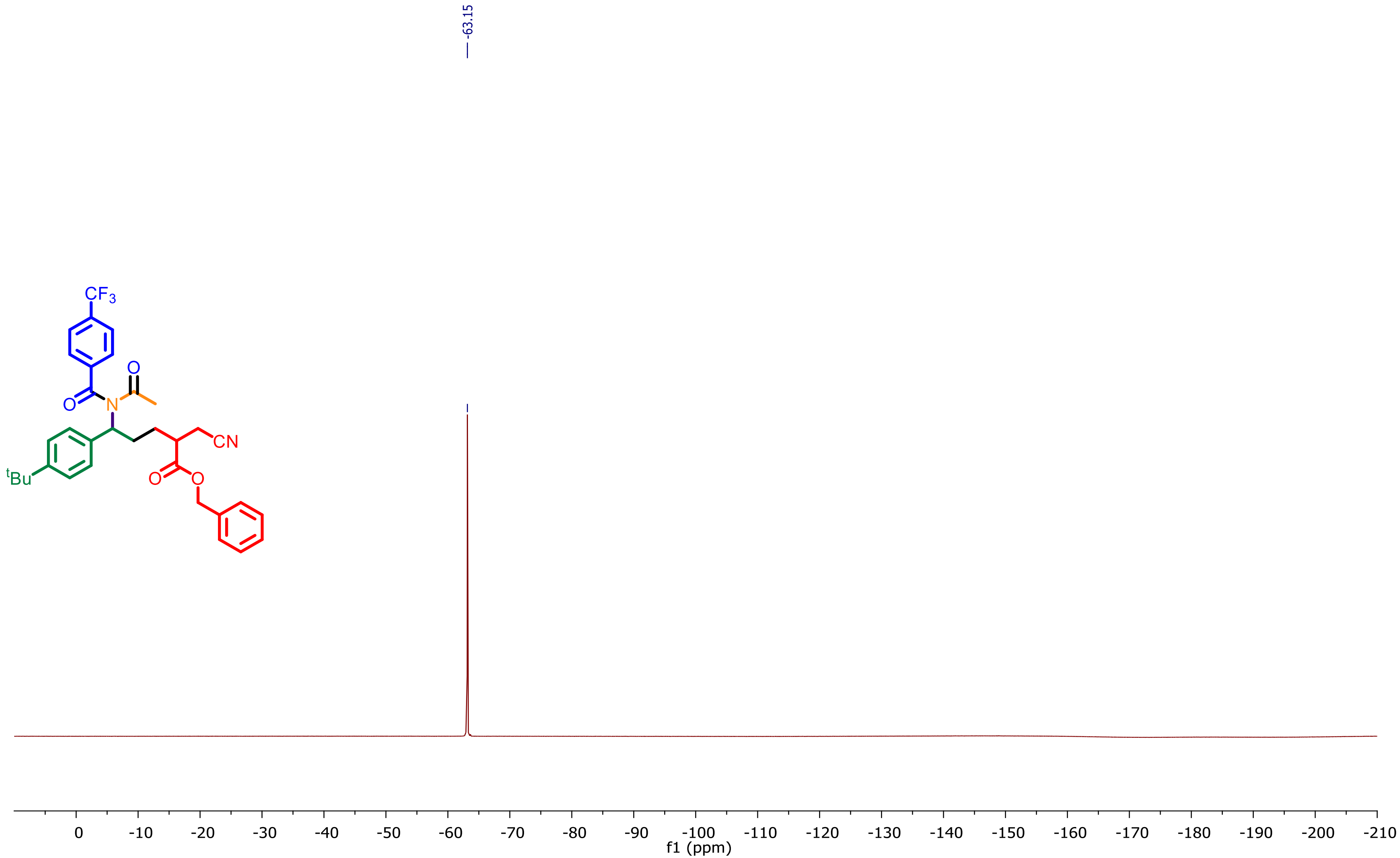
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3am)**



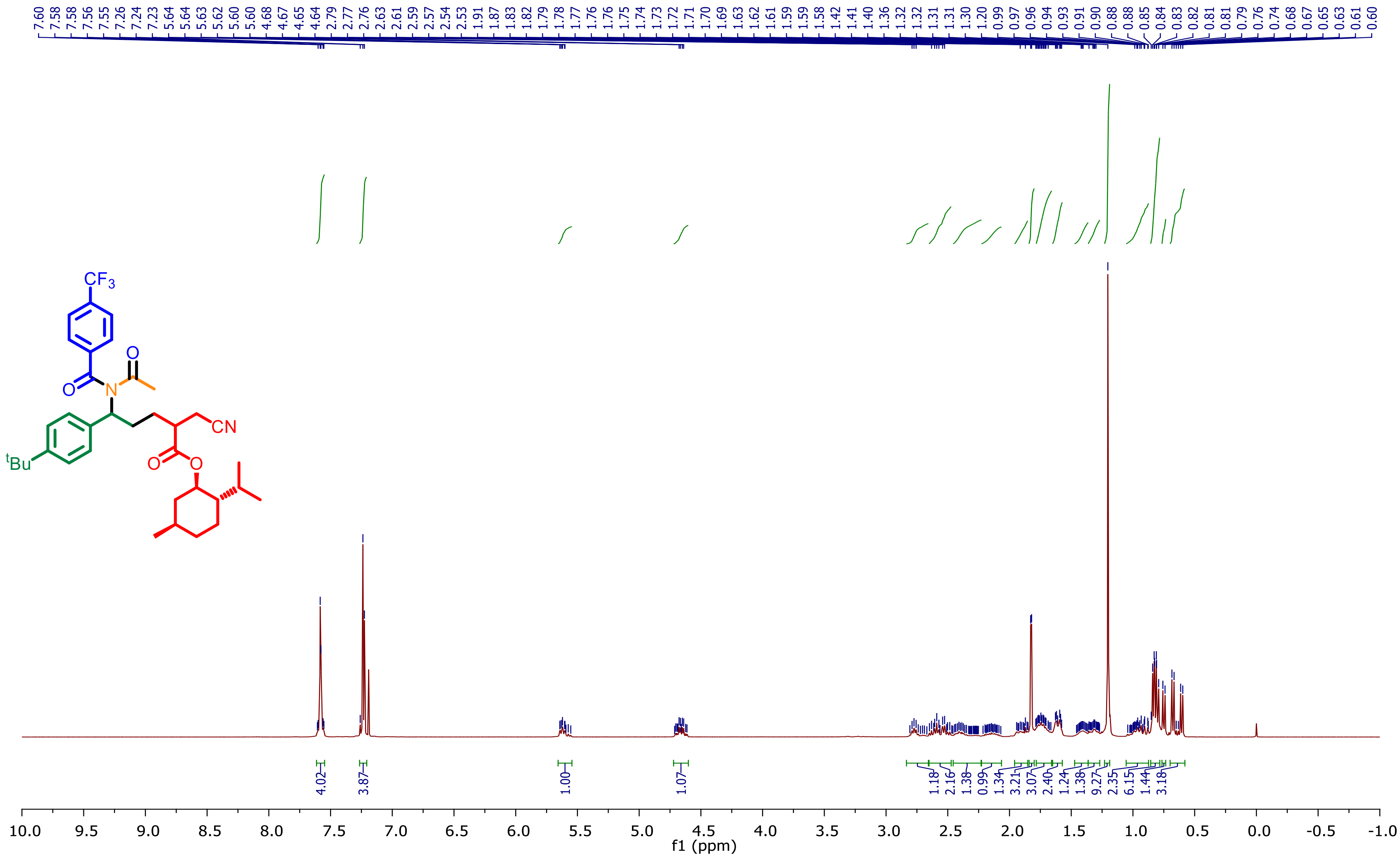
^{13}C NMR (176 MHz, $CDCl_3$) Spectrum of Compound **(3am)**



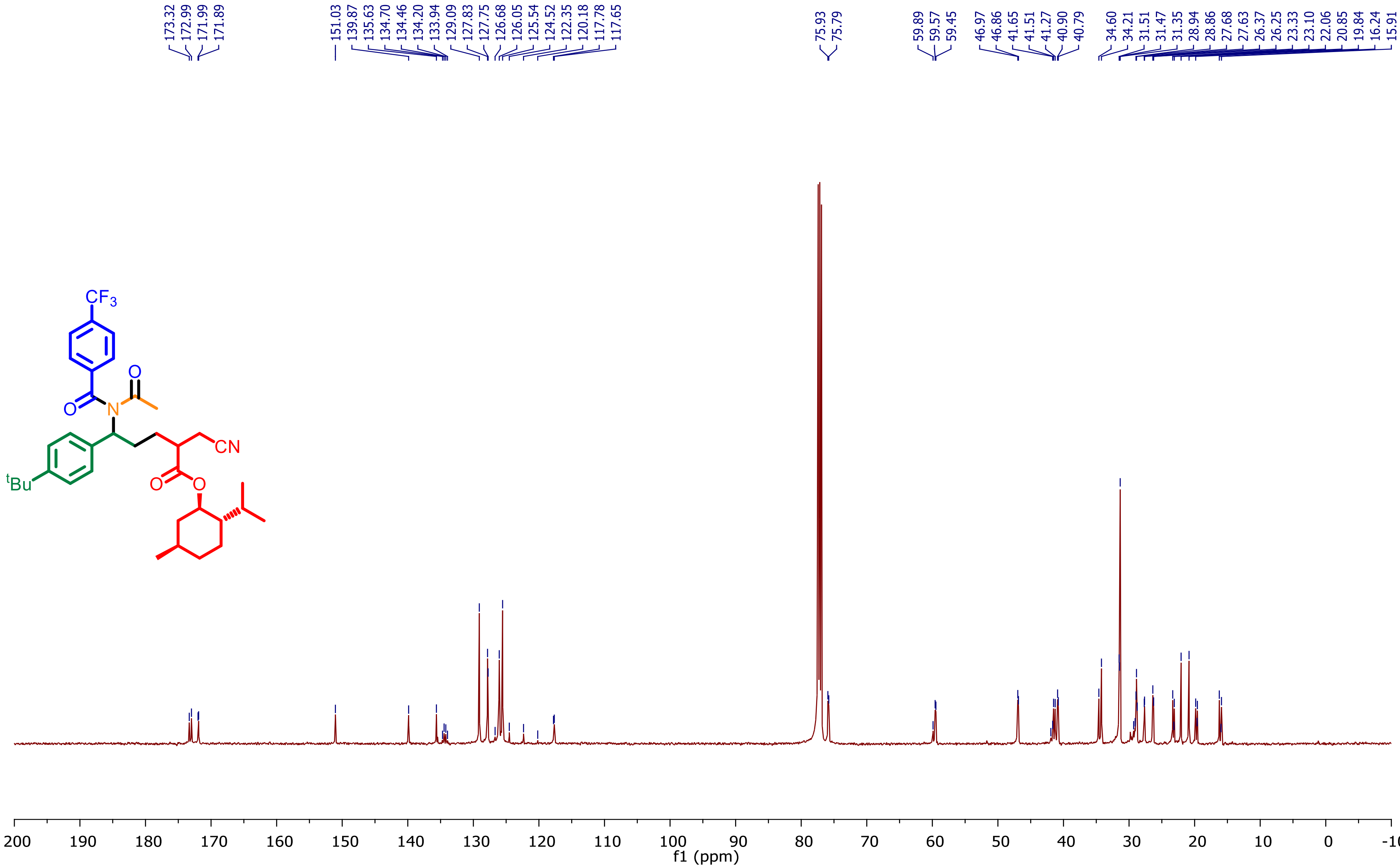
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3am)**



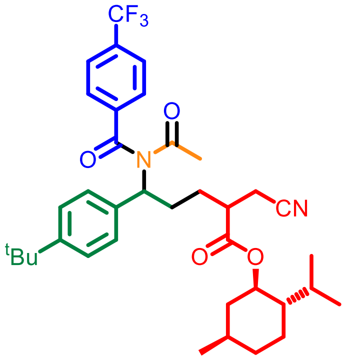
[1]H NMR (400 MHz, CDCl$_3$) Spectrum of Compound **(3an)**

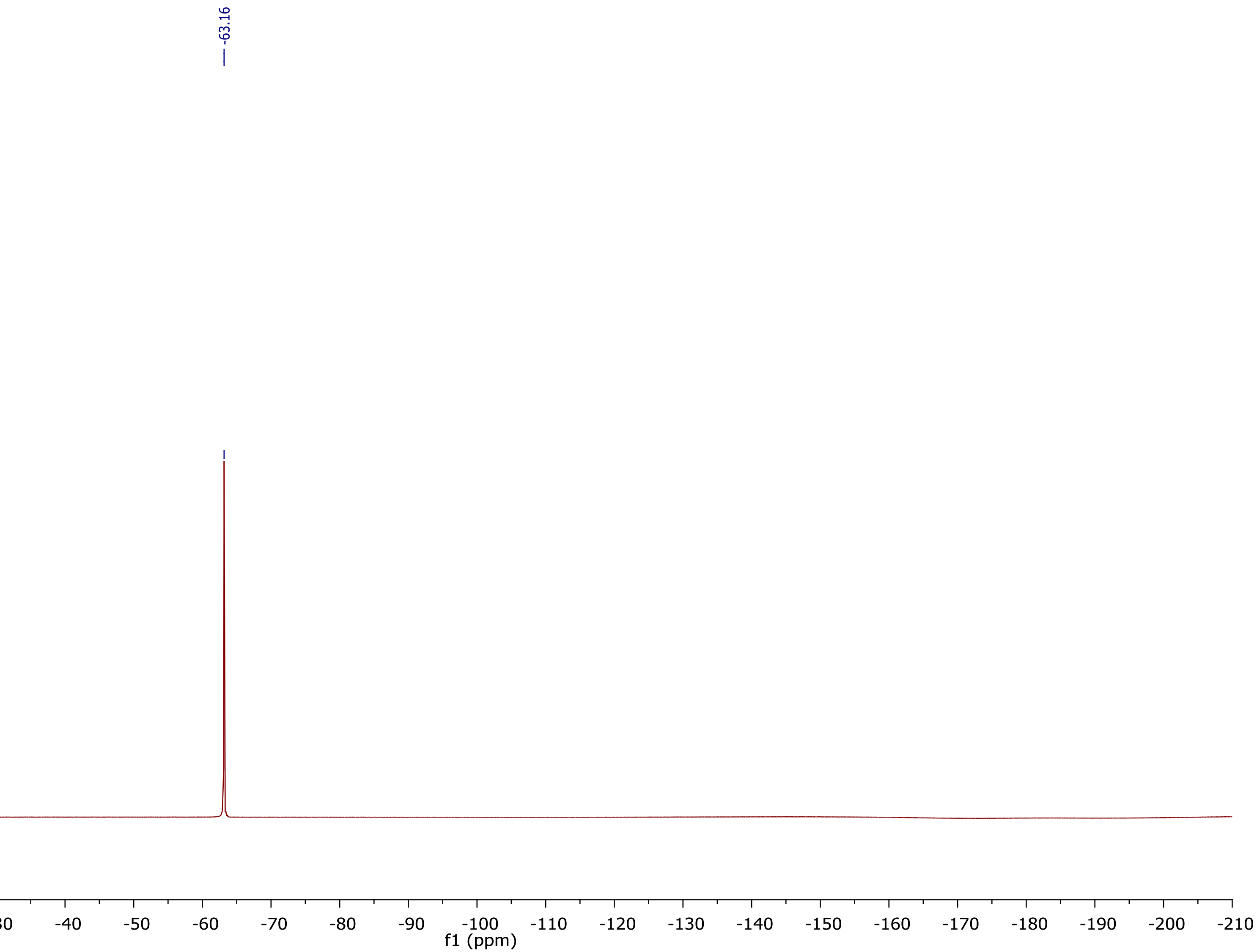


^{13}C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3an)**

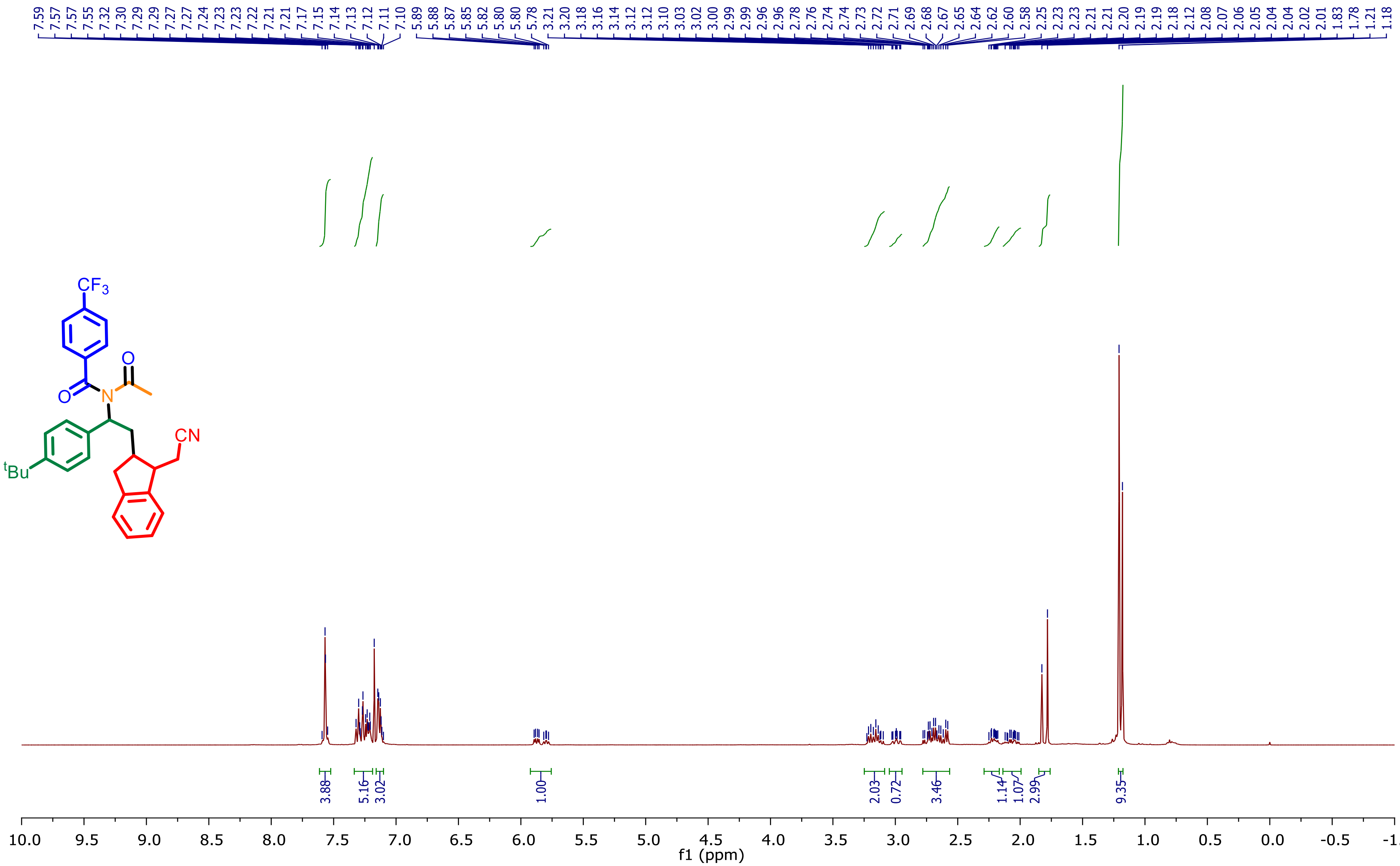


^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3an)**

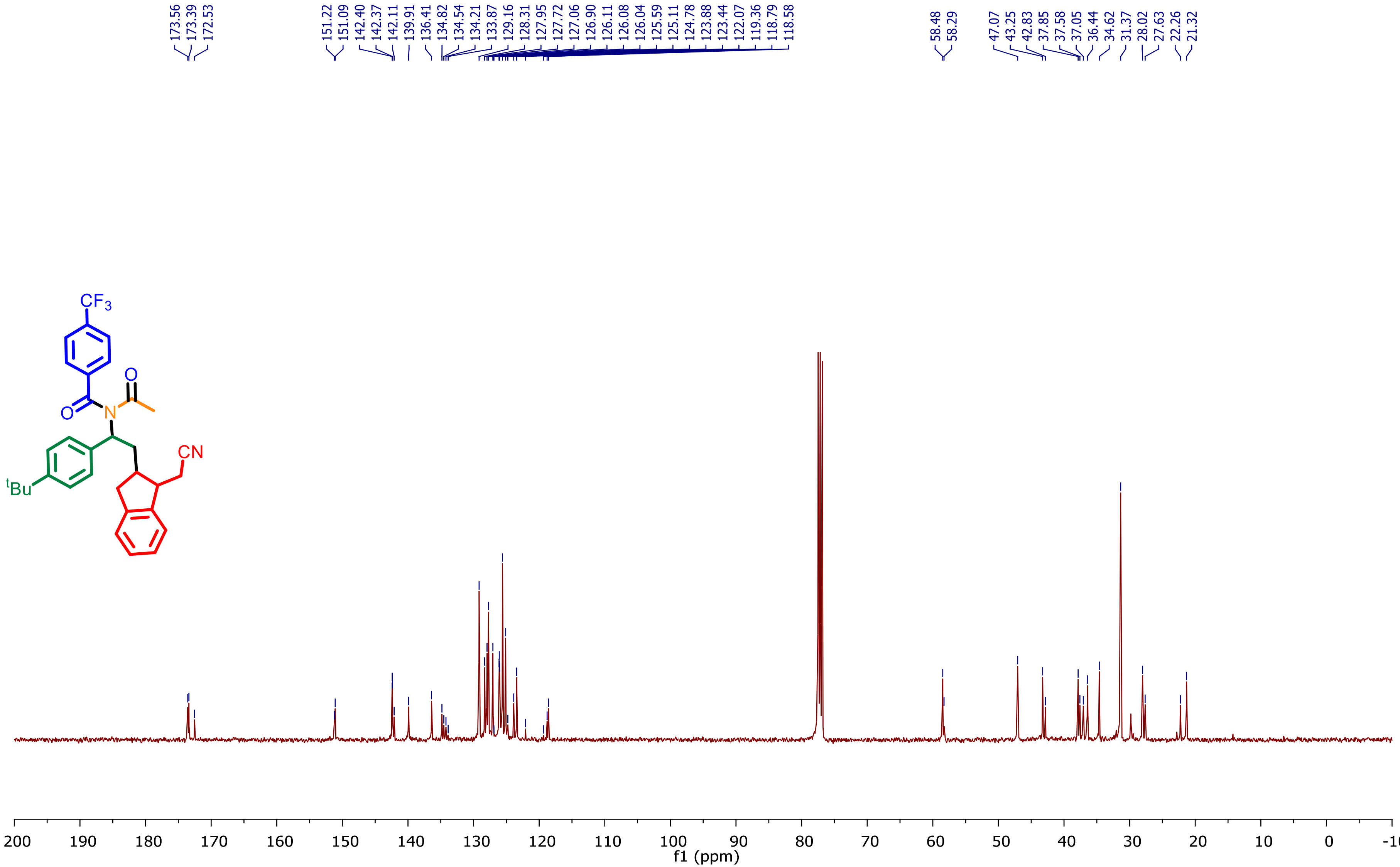




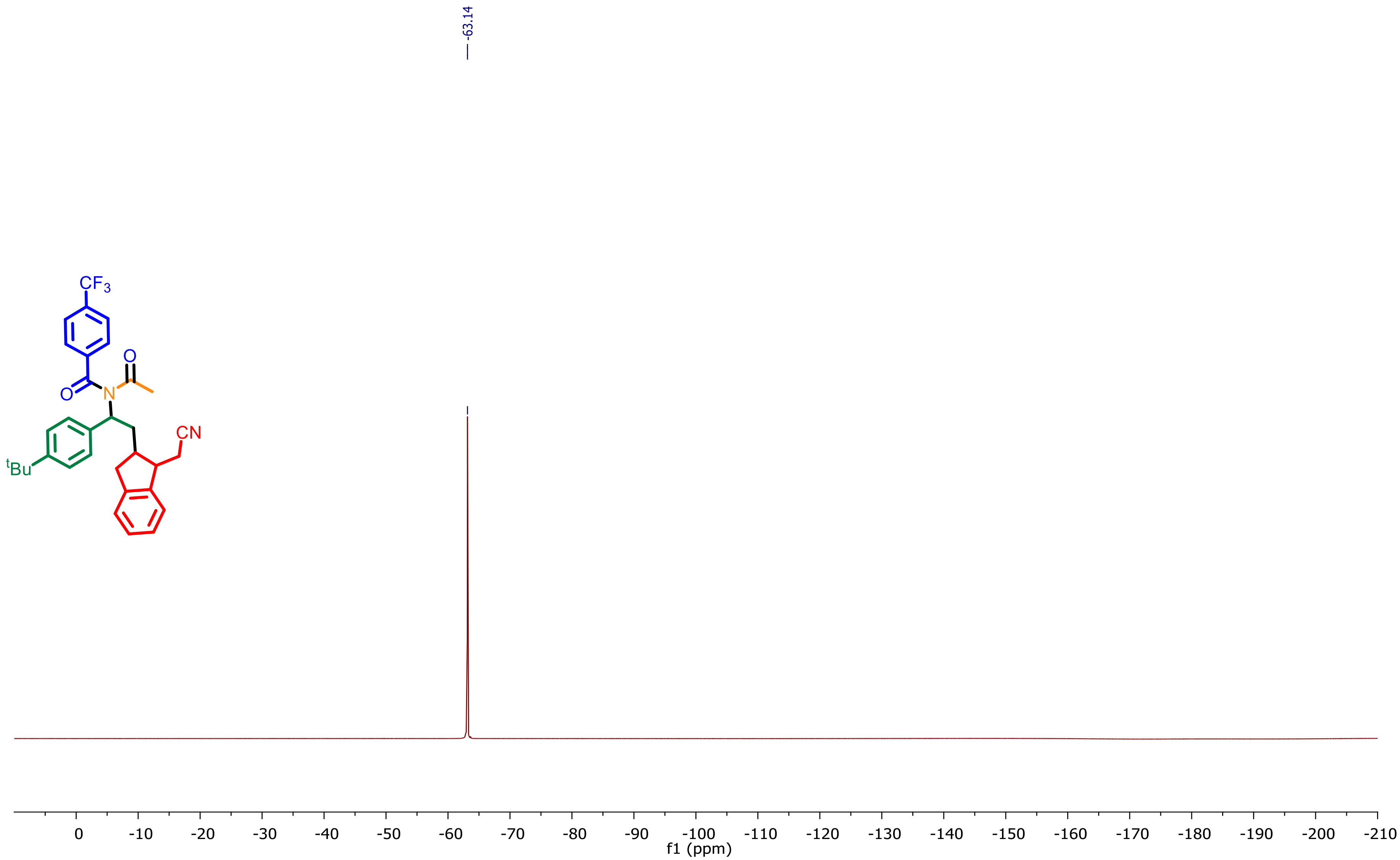
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ao)**



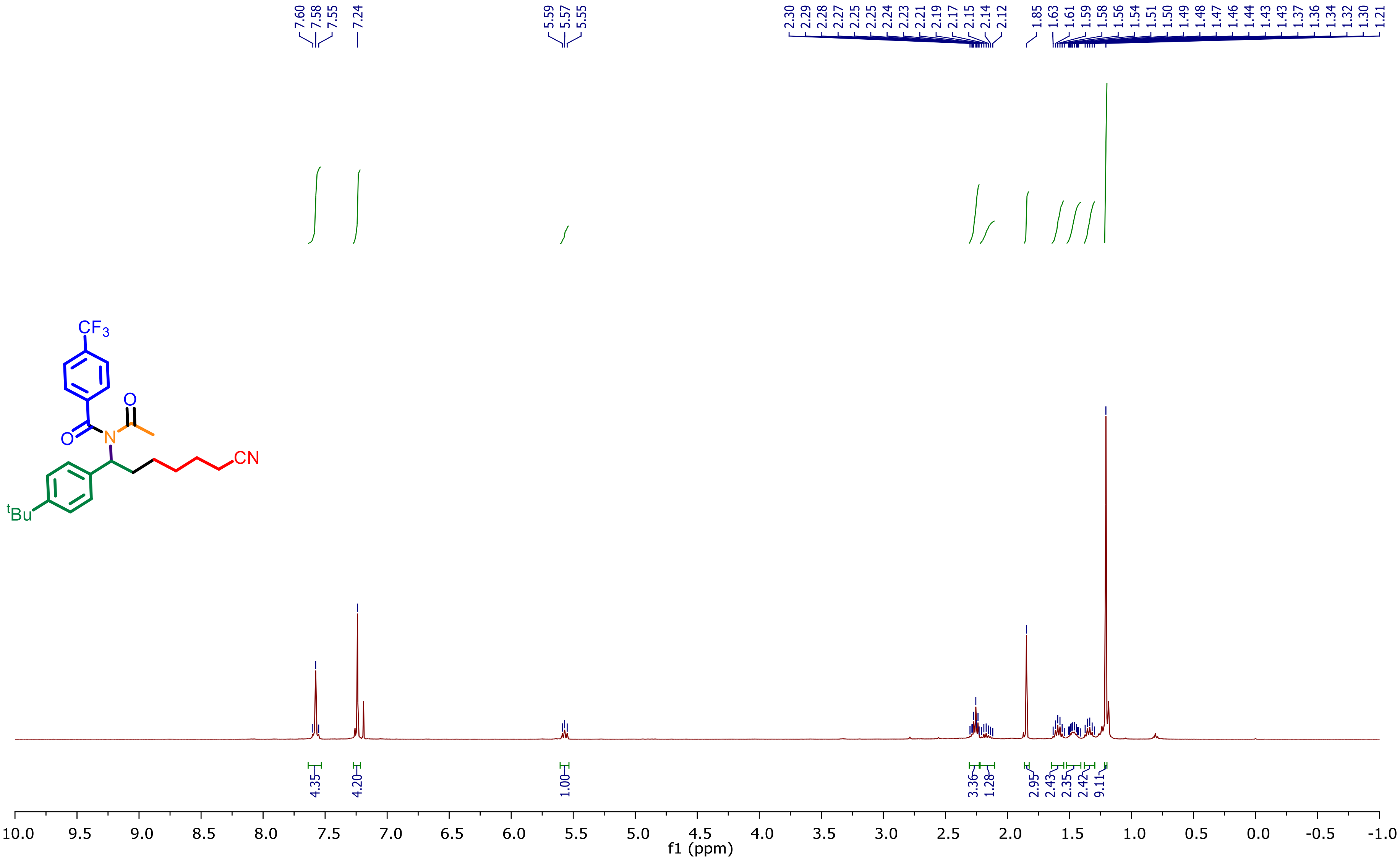
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ao)**



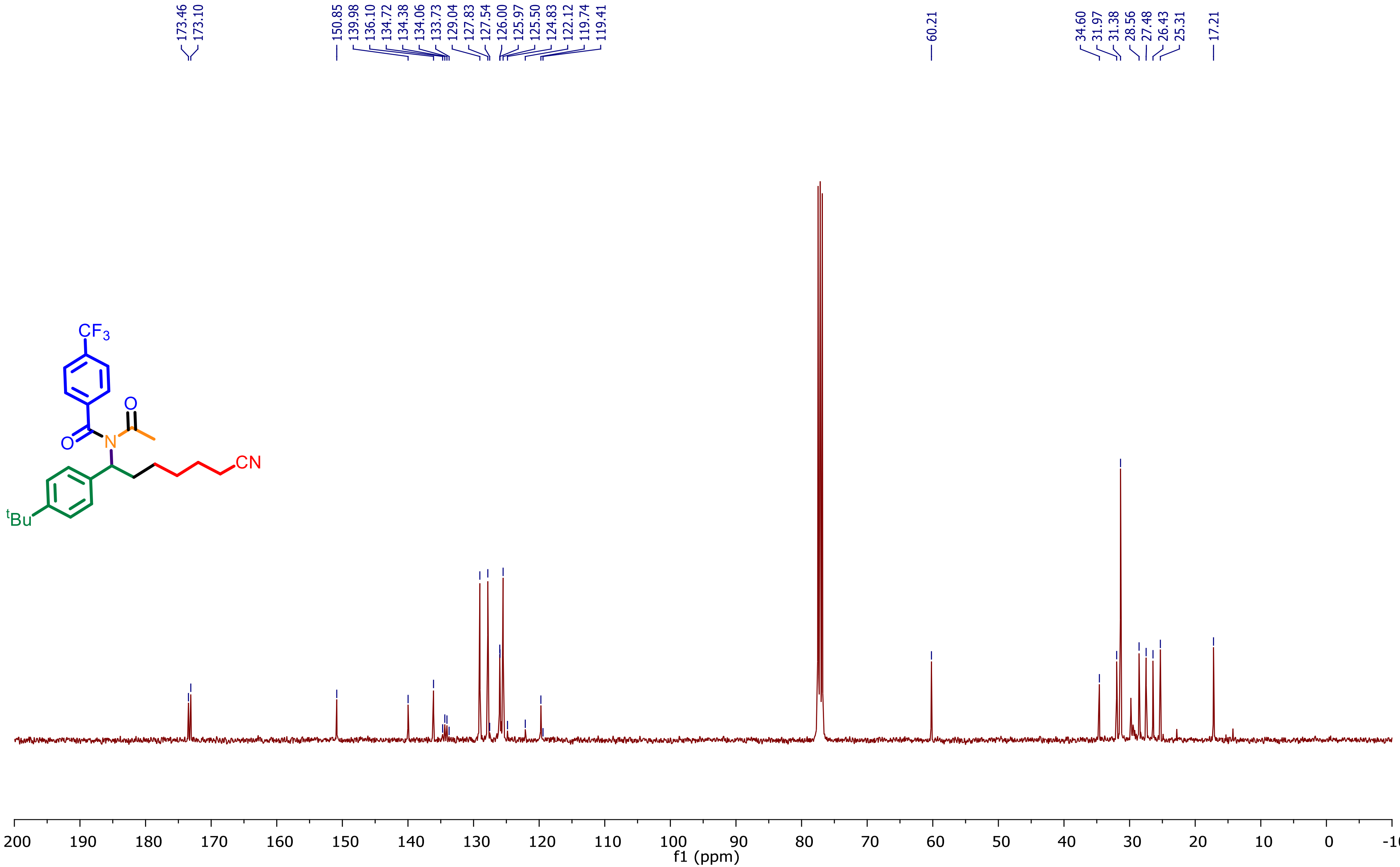
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3ao)**



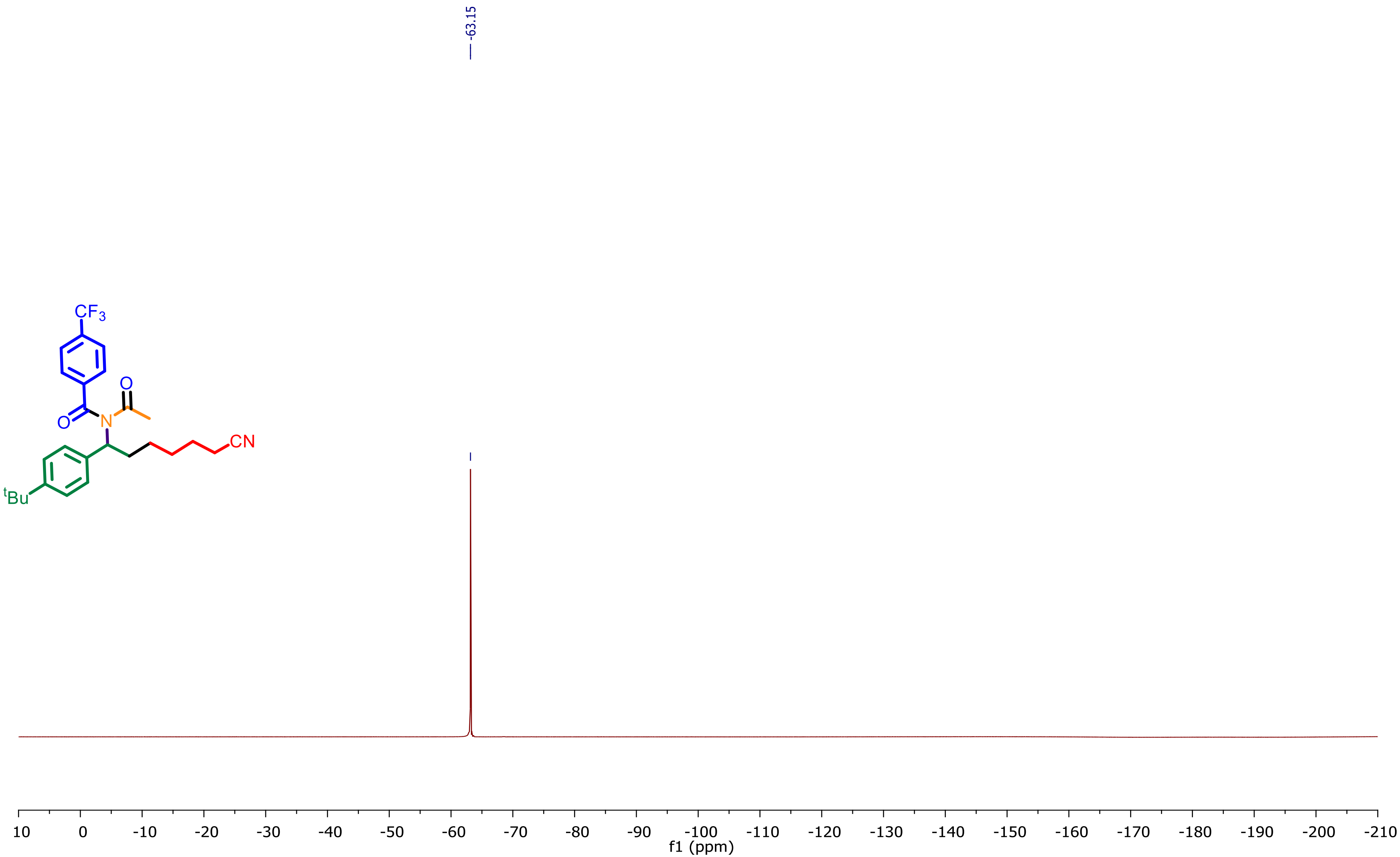
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ap)**



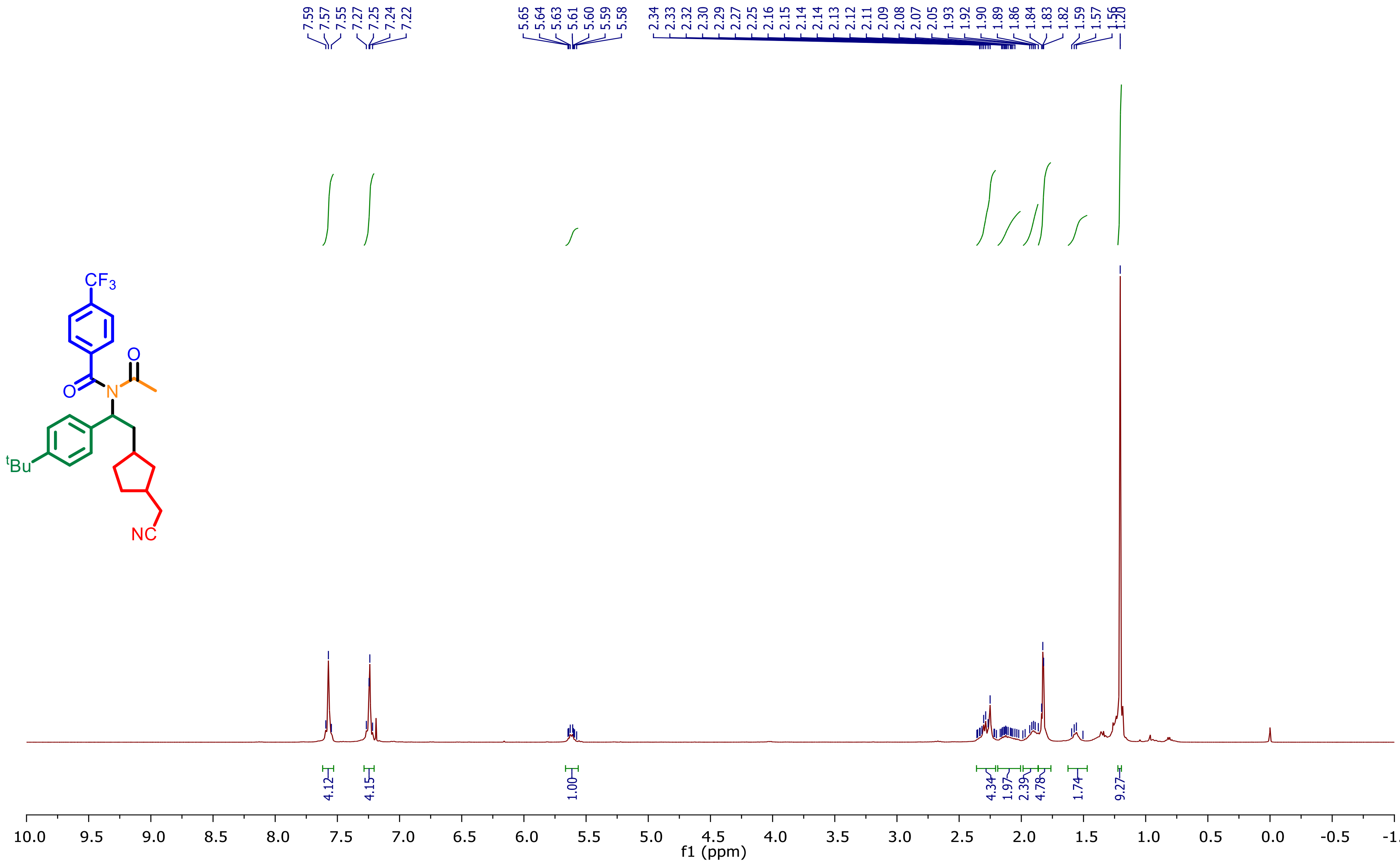
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ap)**



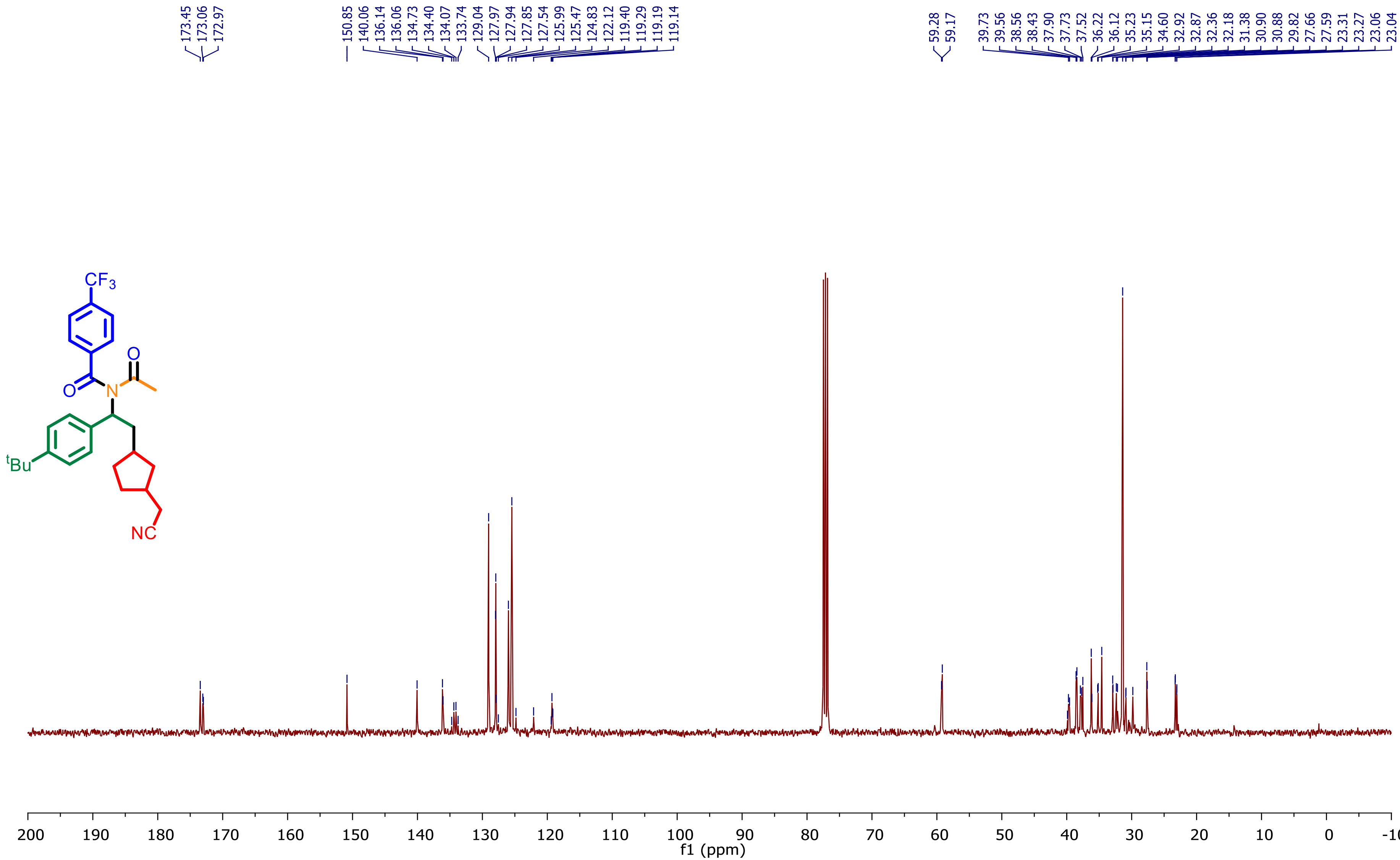
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3ap)**



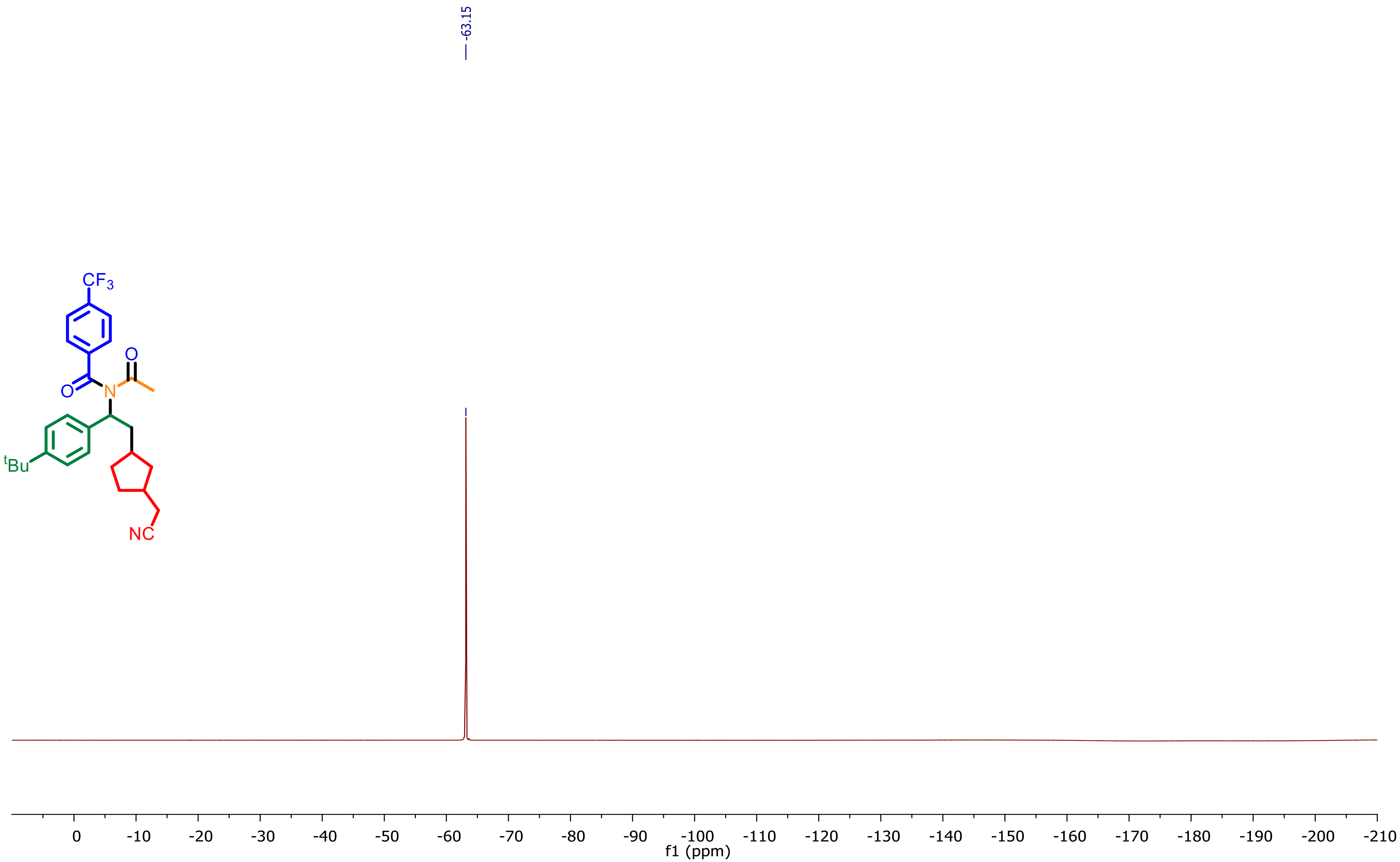
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3aq)**



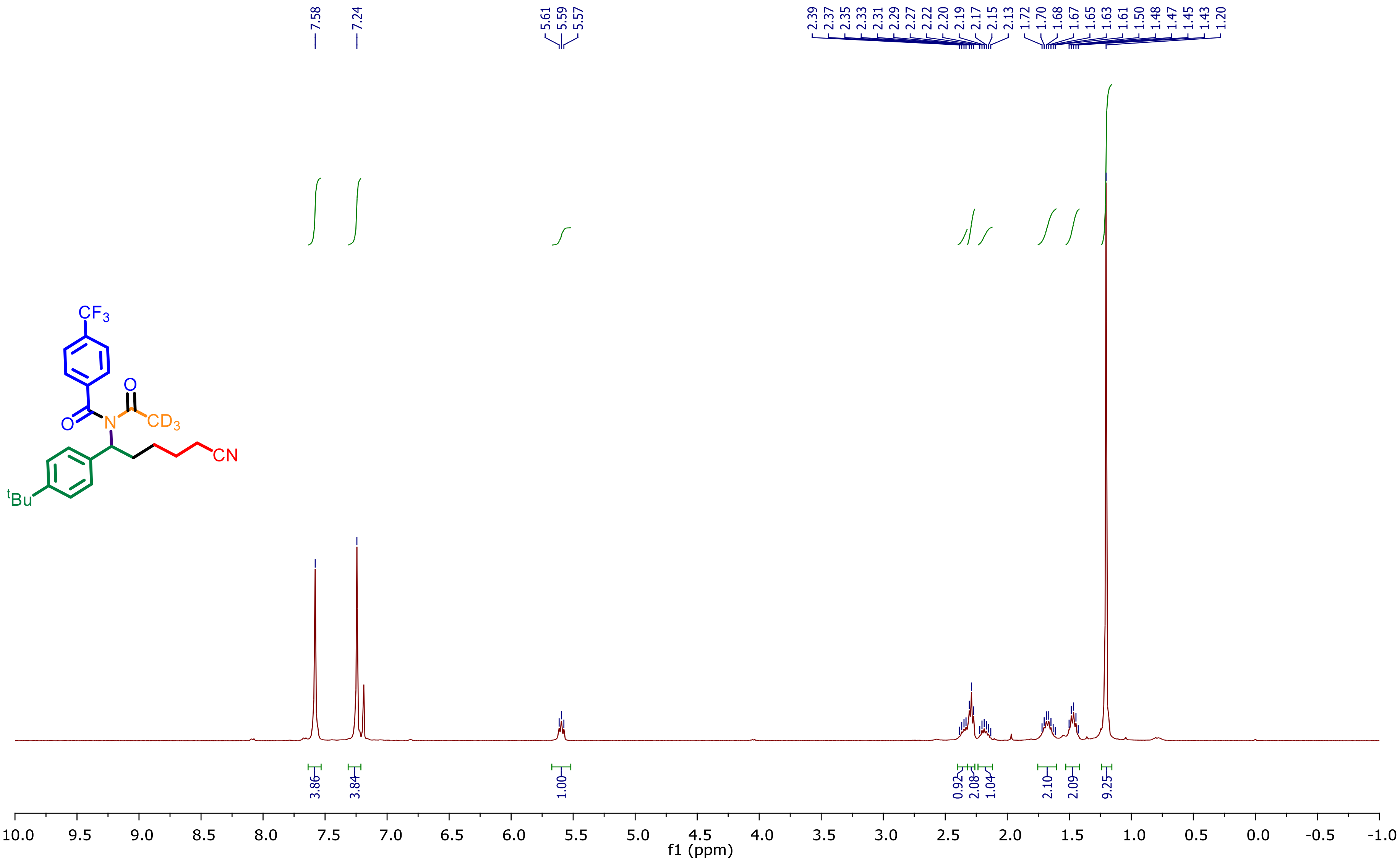
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3aq)**



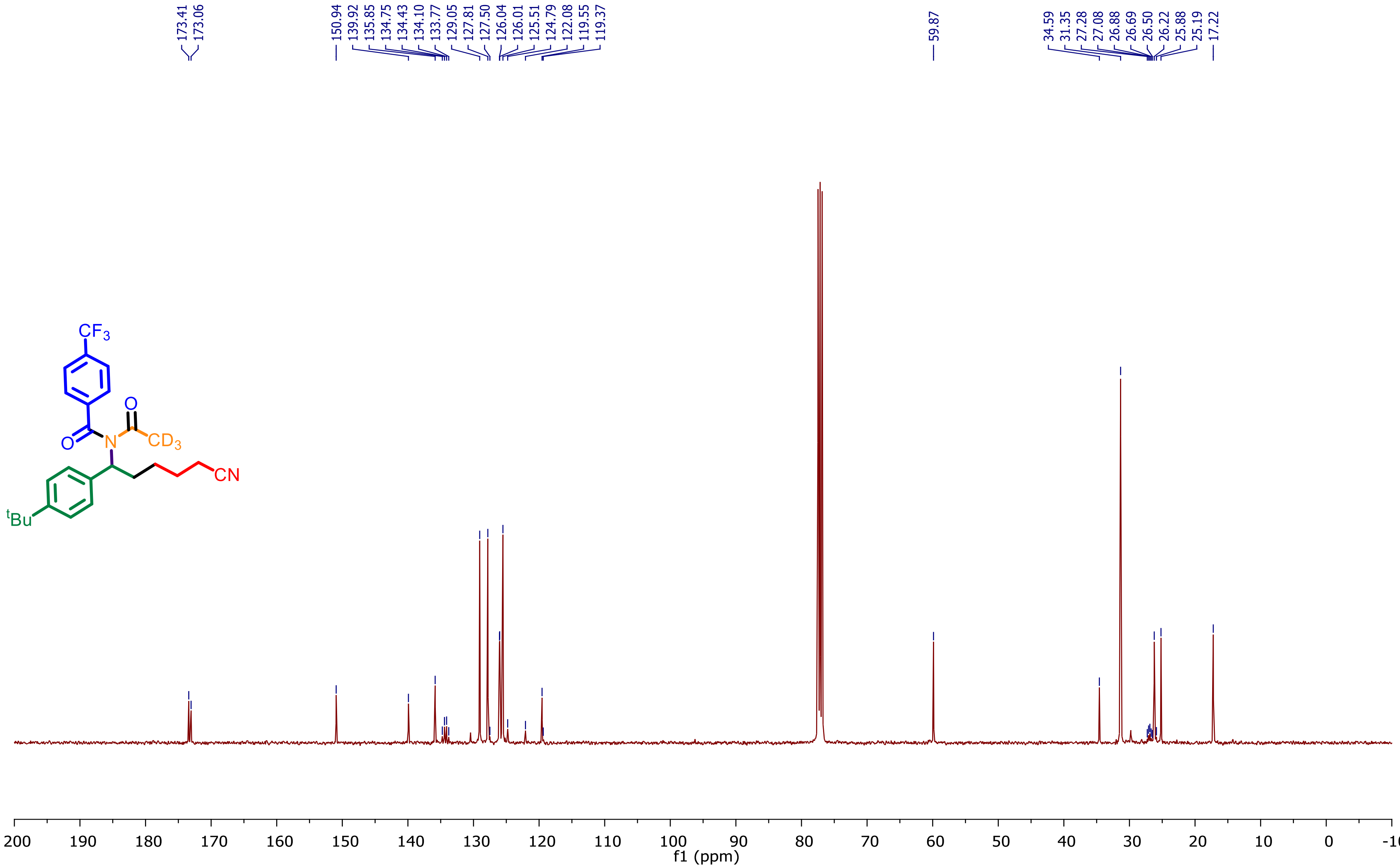
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(3aq)**



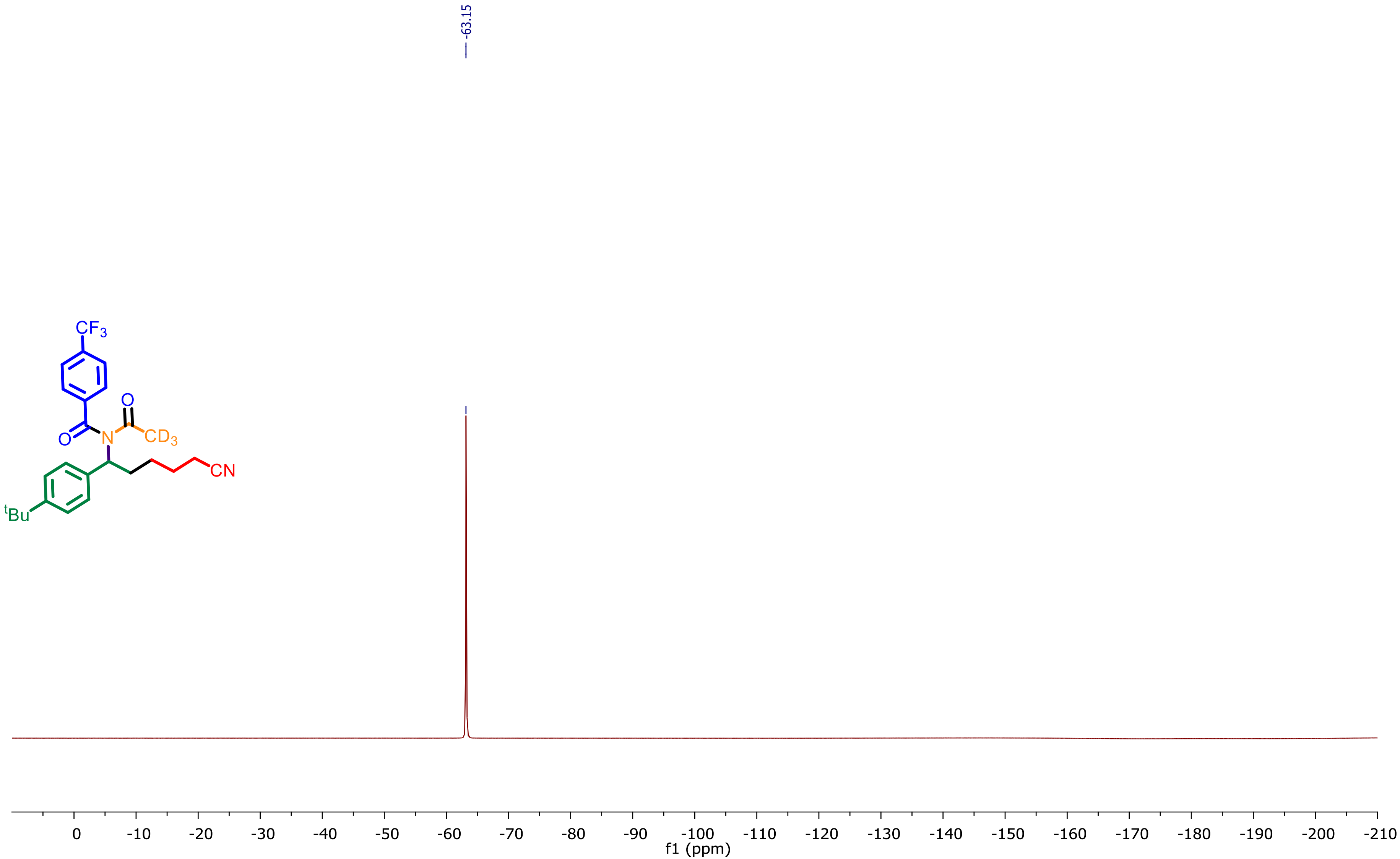
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(5)**



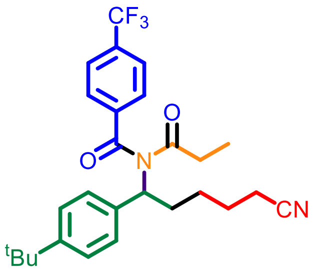
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(5)**

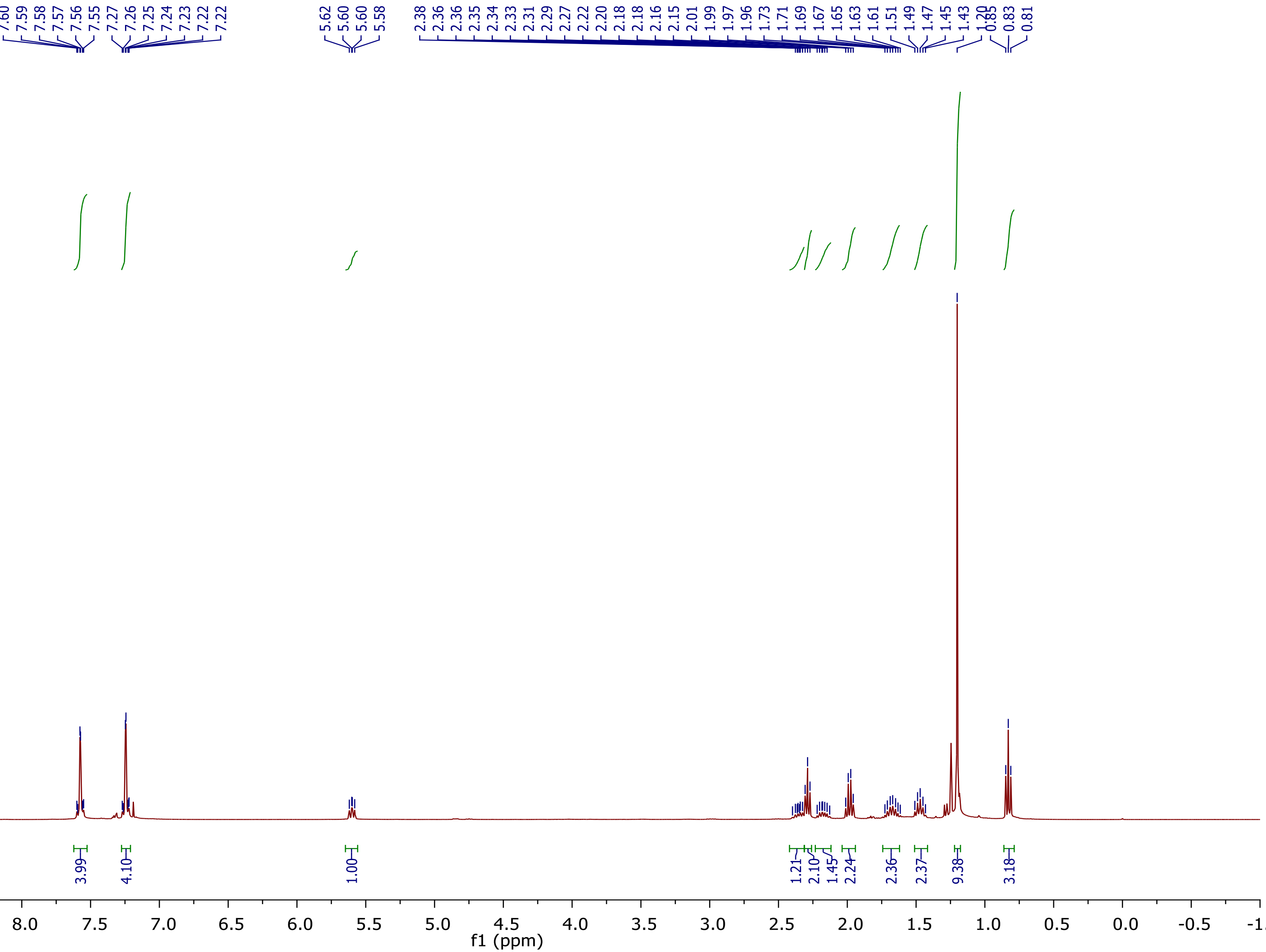


^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(5)**

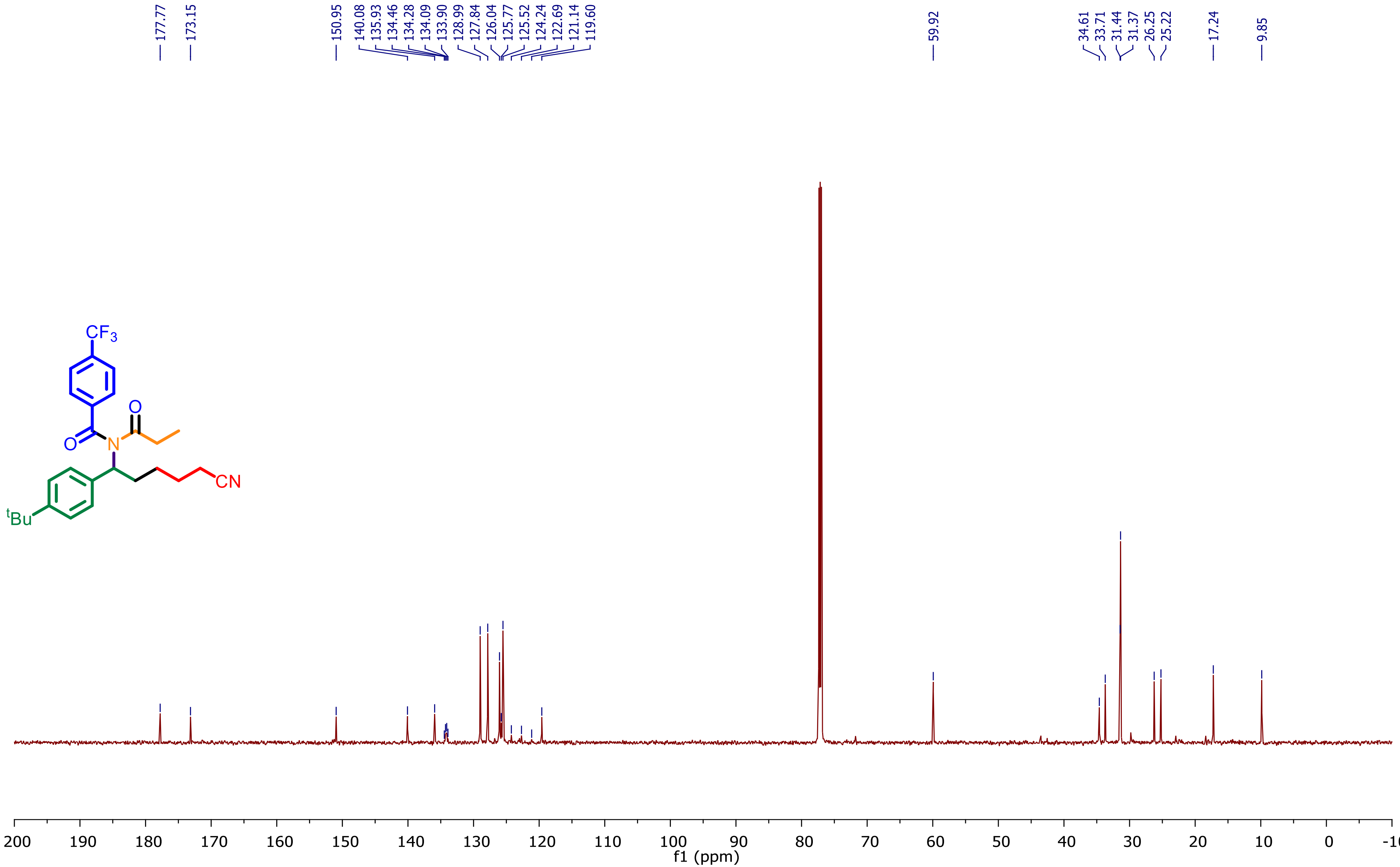


^1H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(6)**

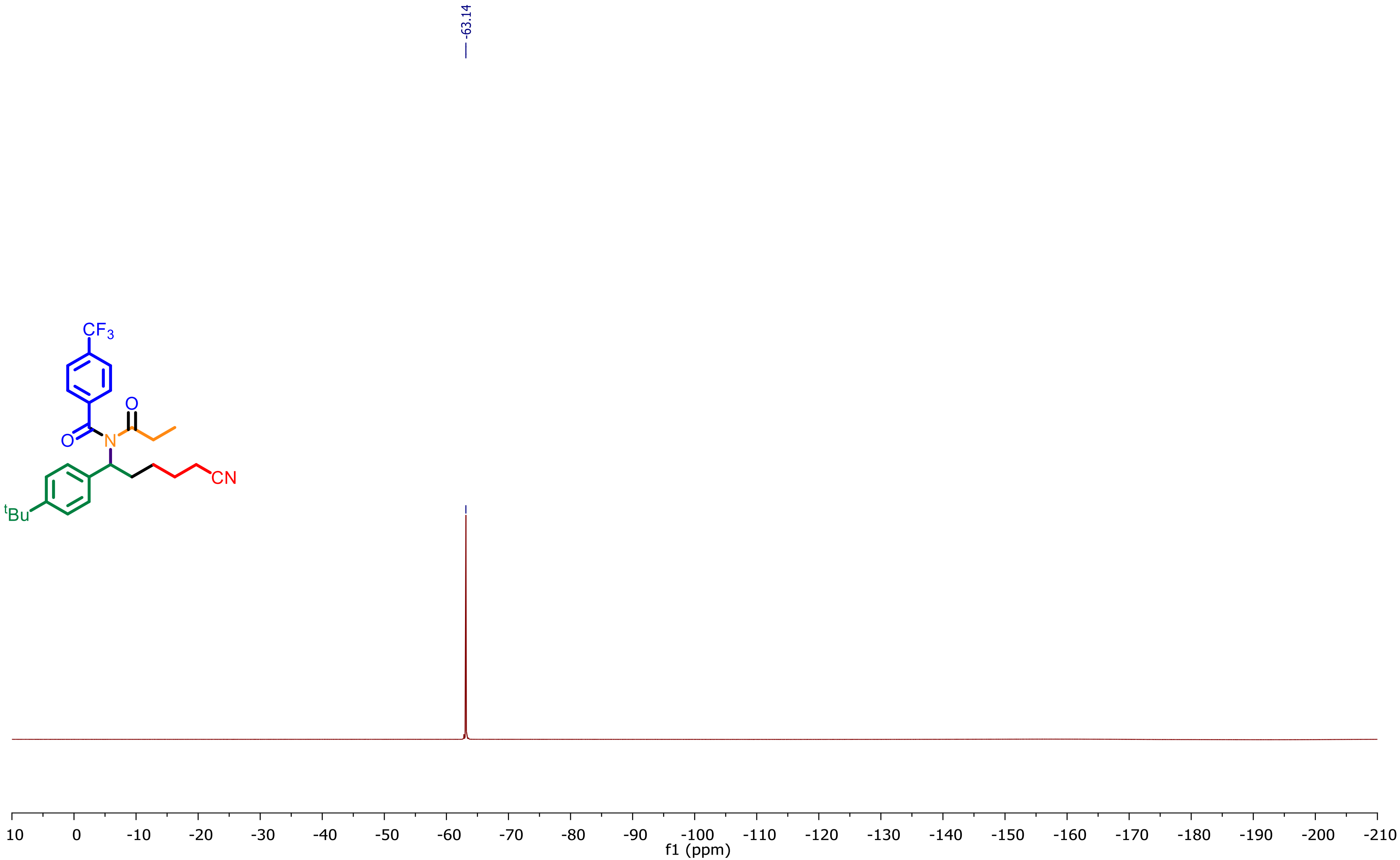




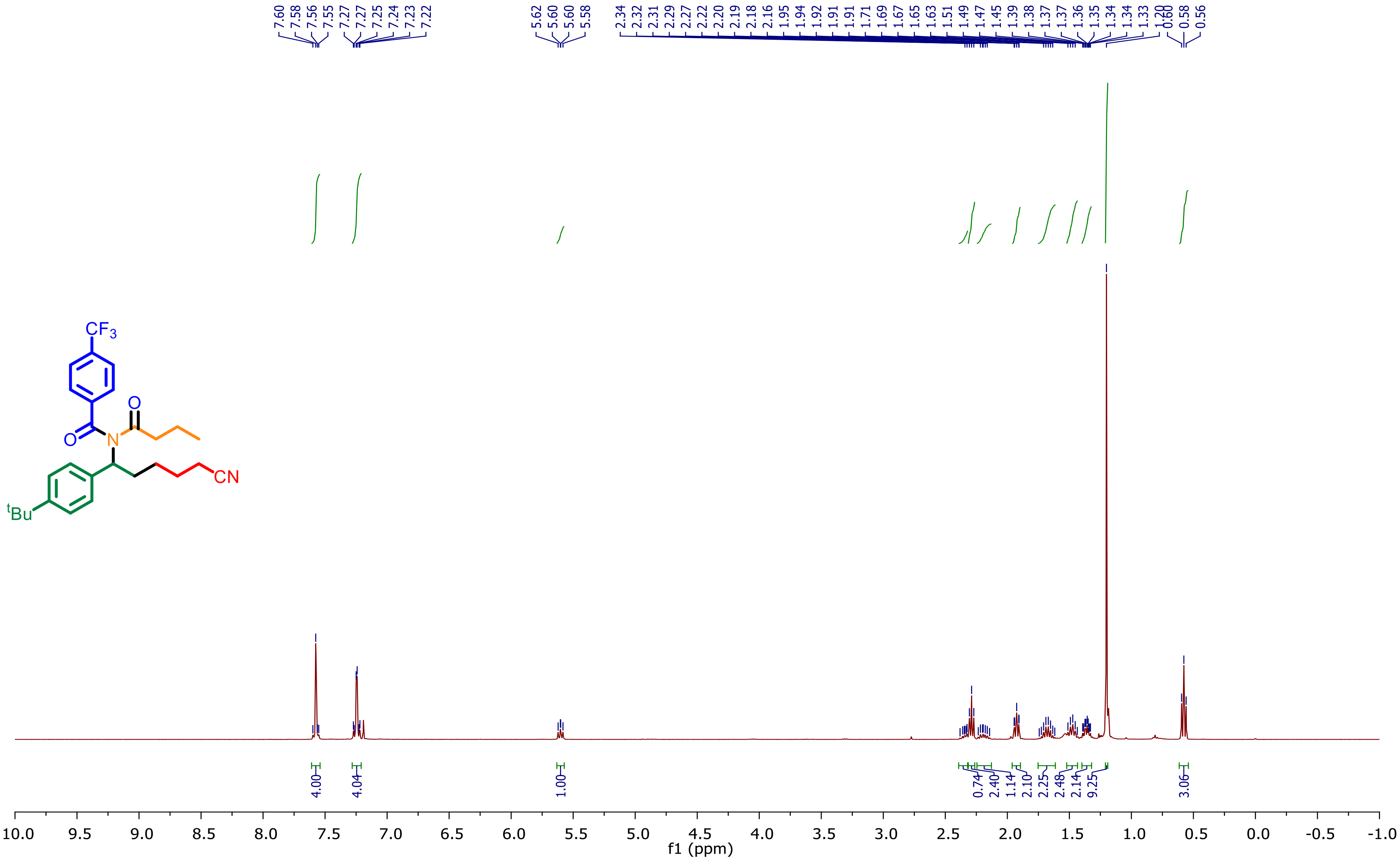
^{13}C NMR (176 MHz, $CDCl_3$) Spectrum of Compound **(6)**



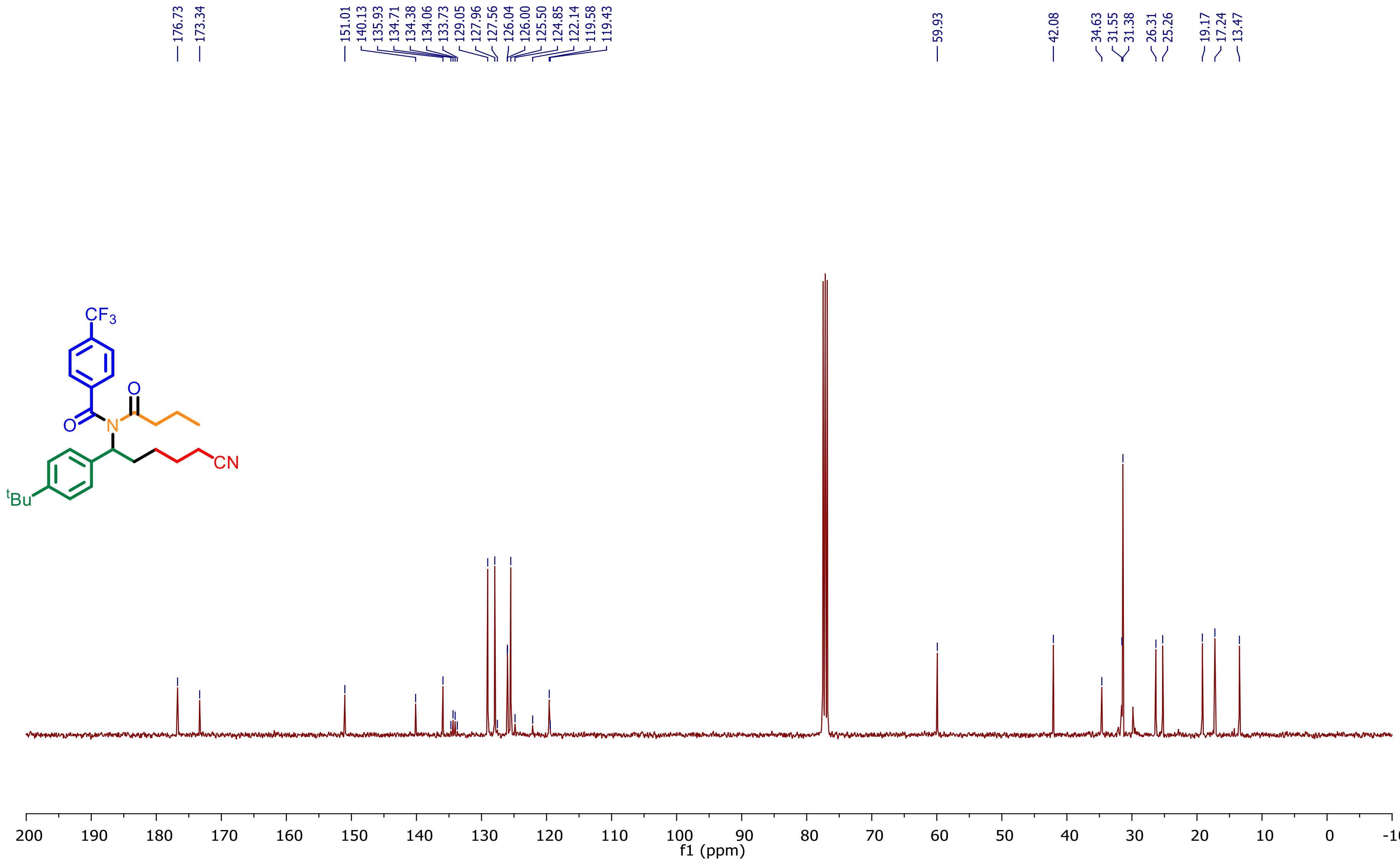
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **(6)**



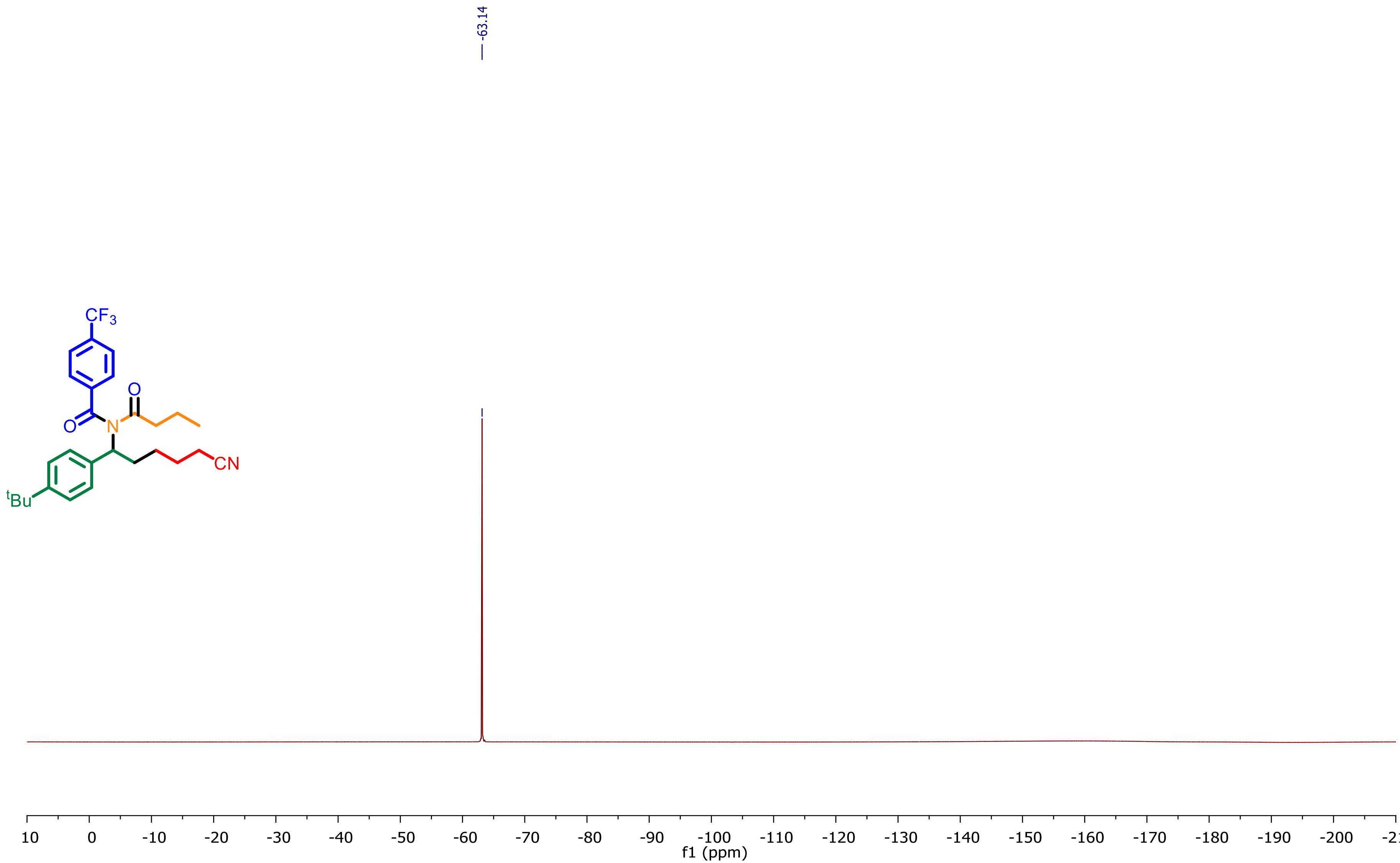
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(7)**



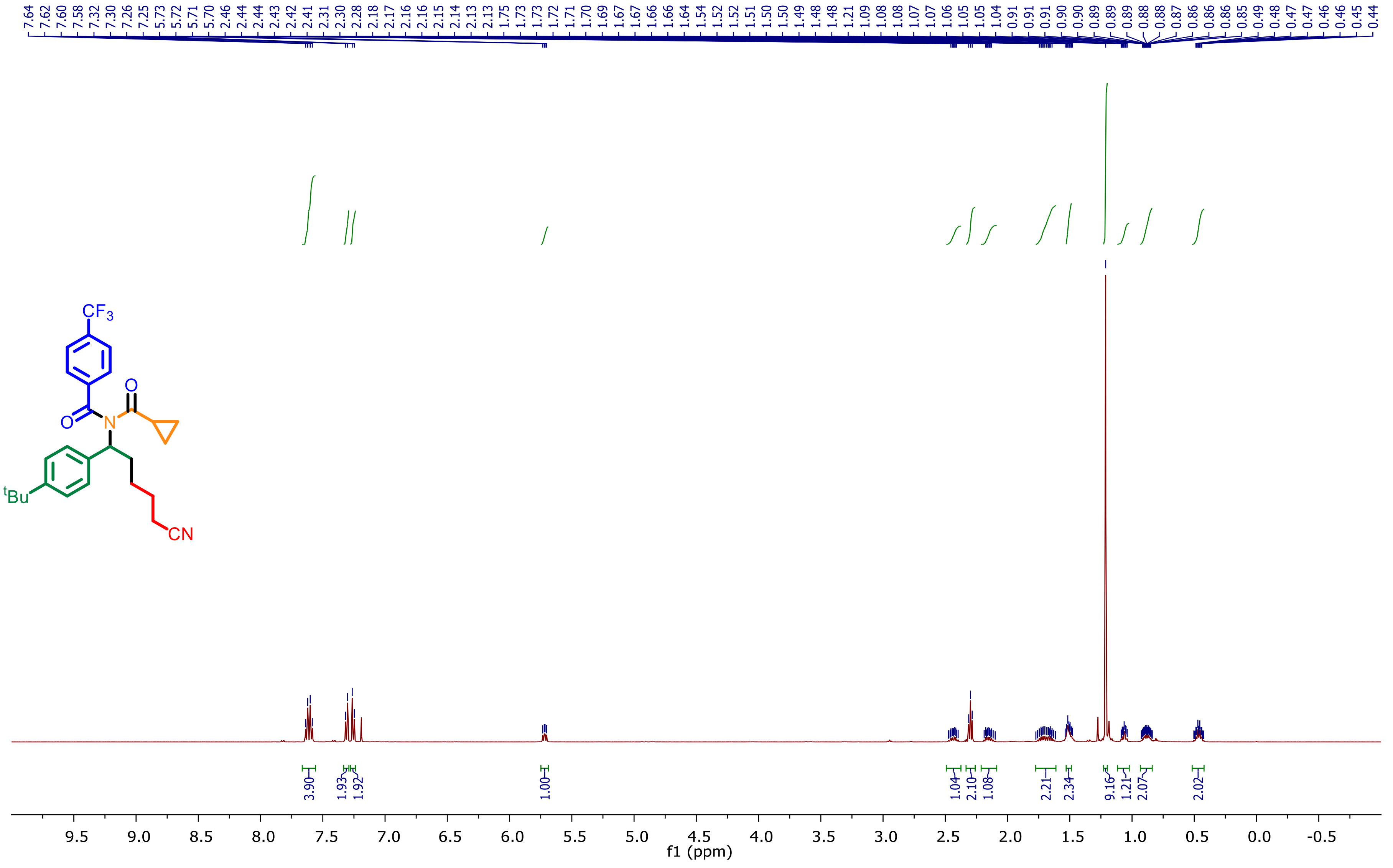
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(7)**



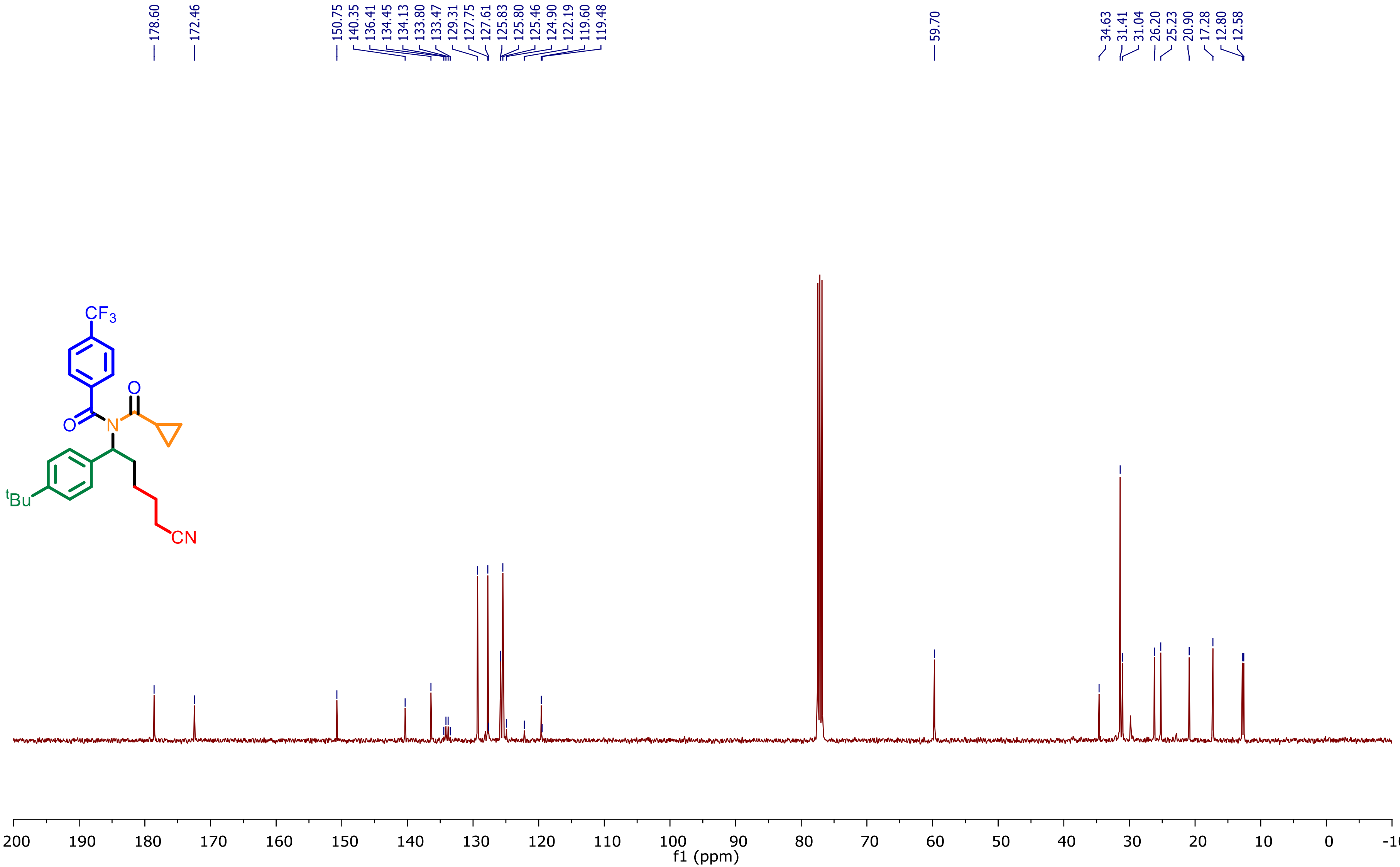
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **(7)**



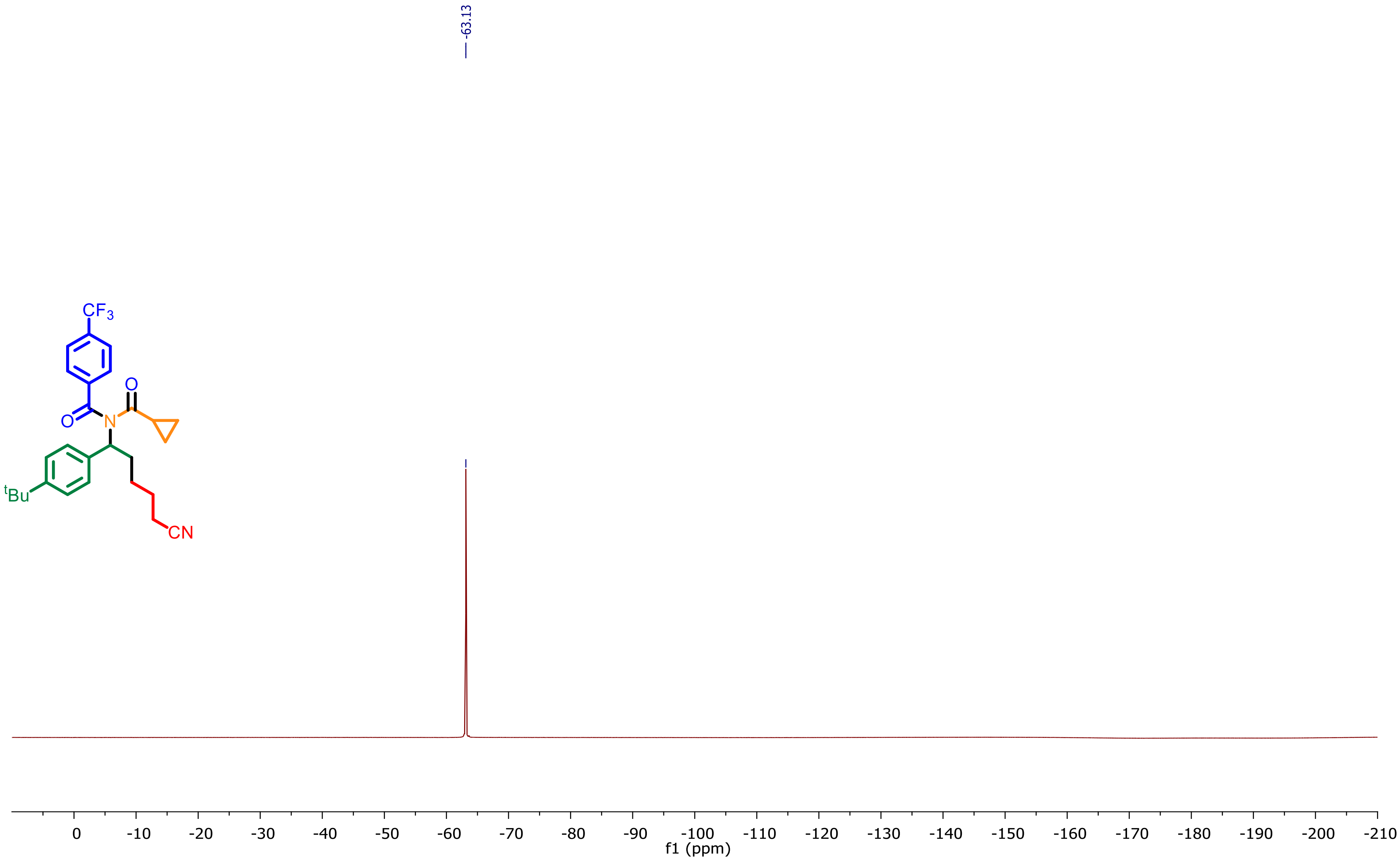
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(8)**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(8)**



^{19}F NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(8)**



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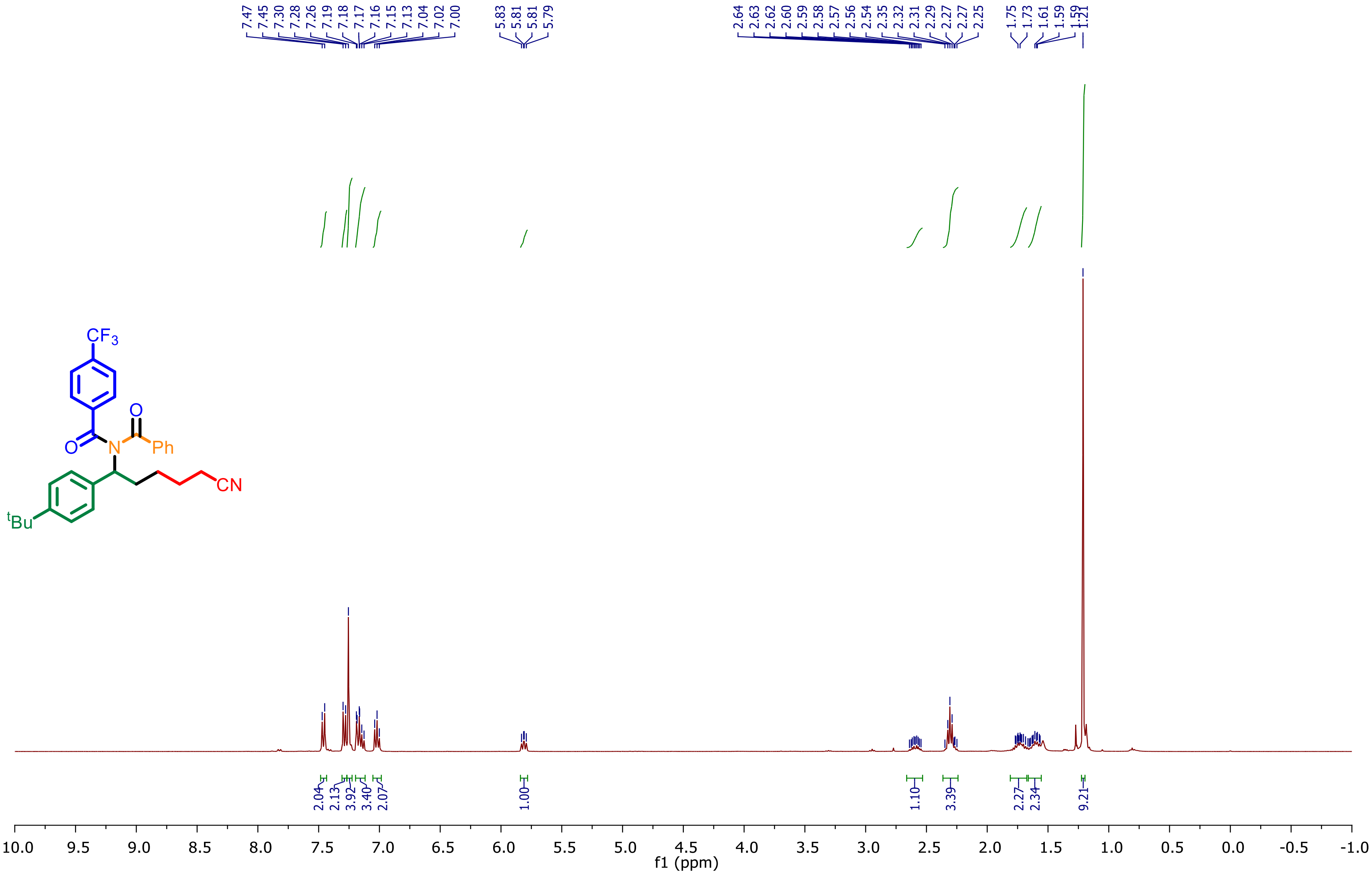
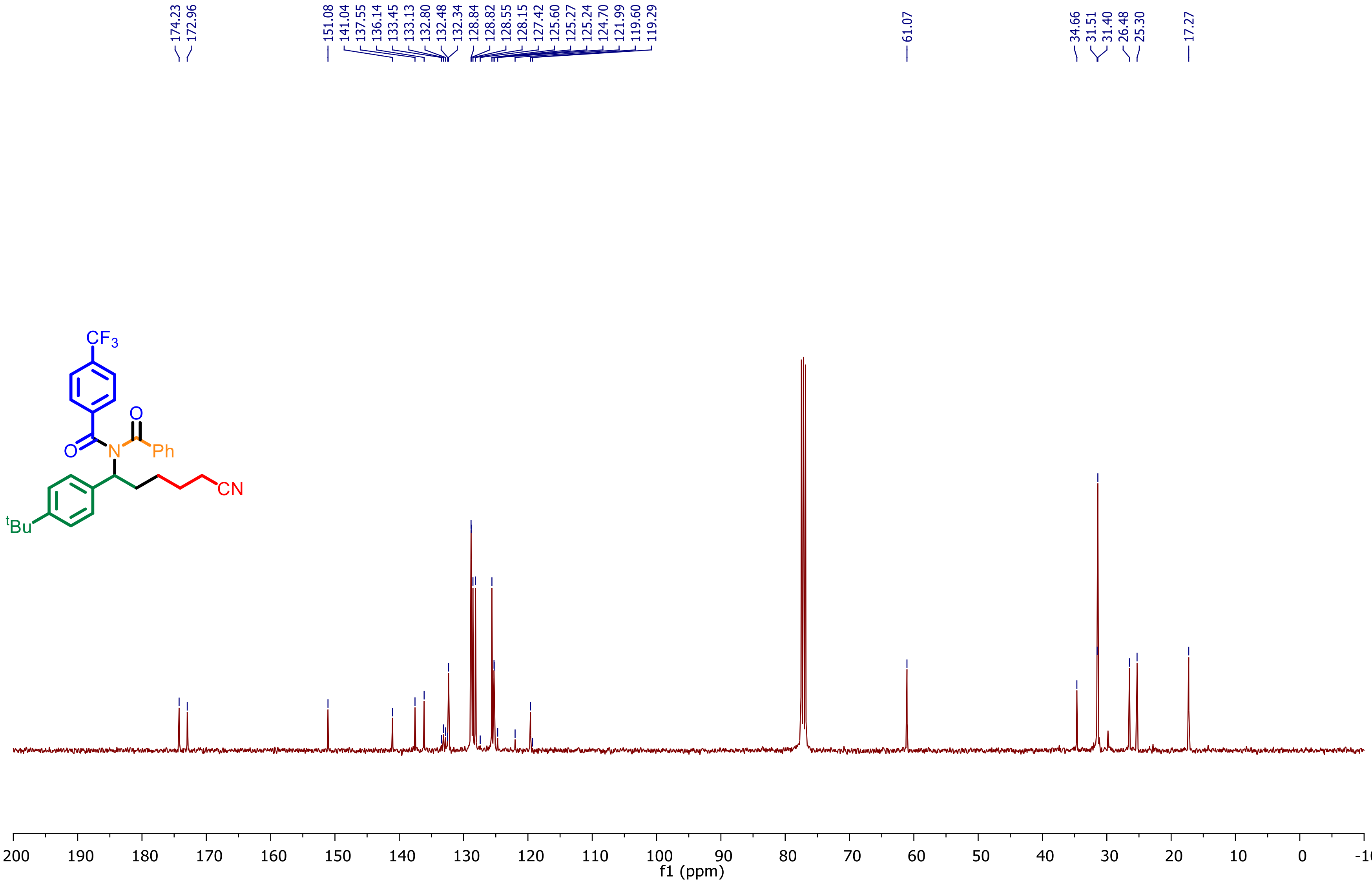
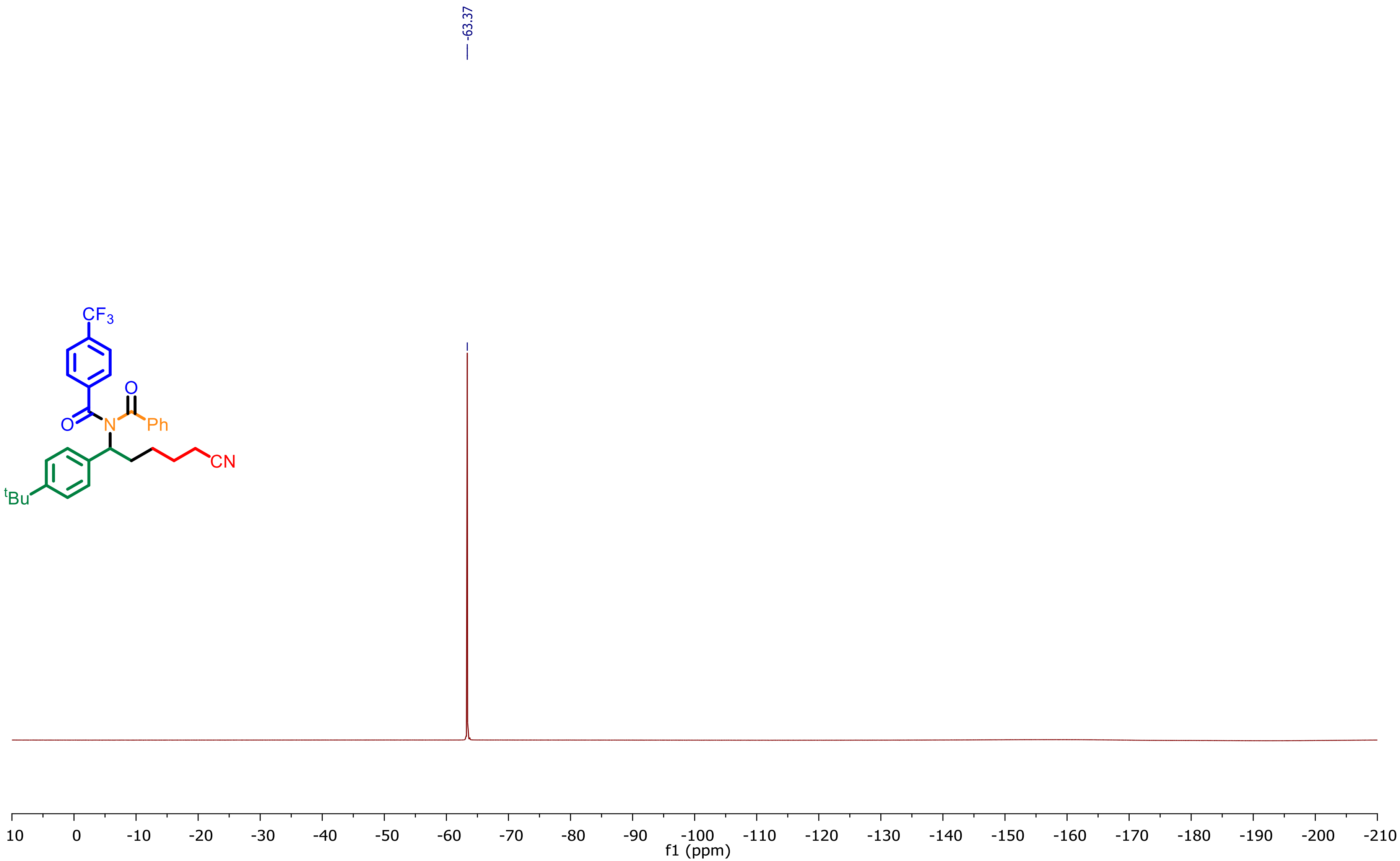
[1]H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(9)**



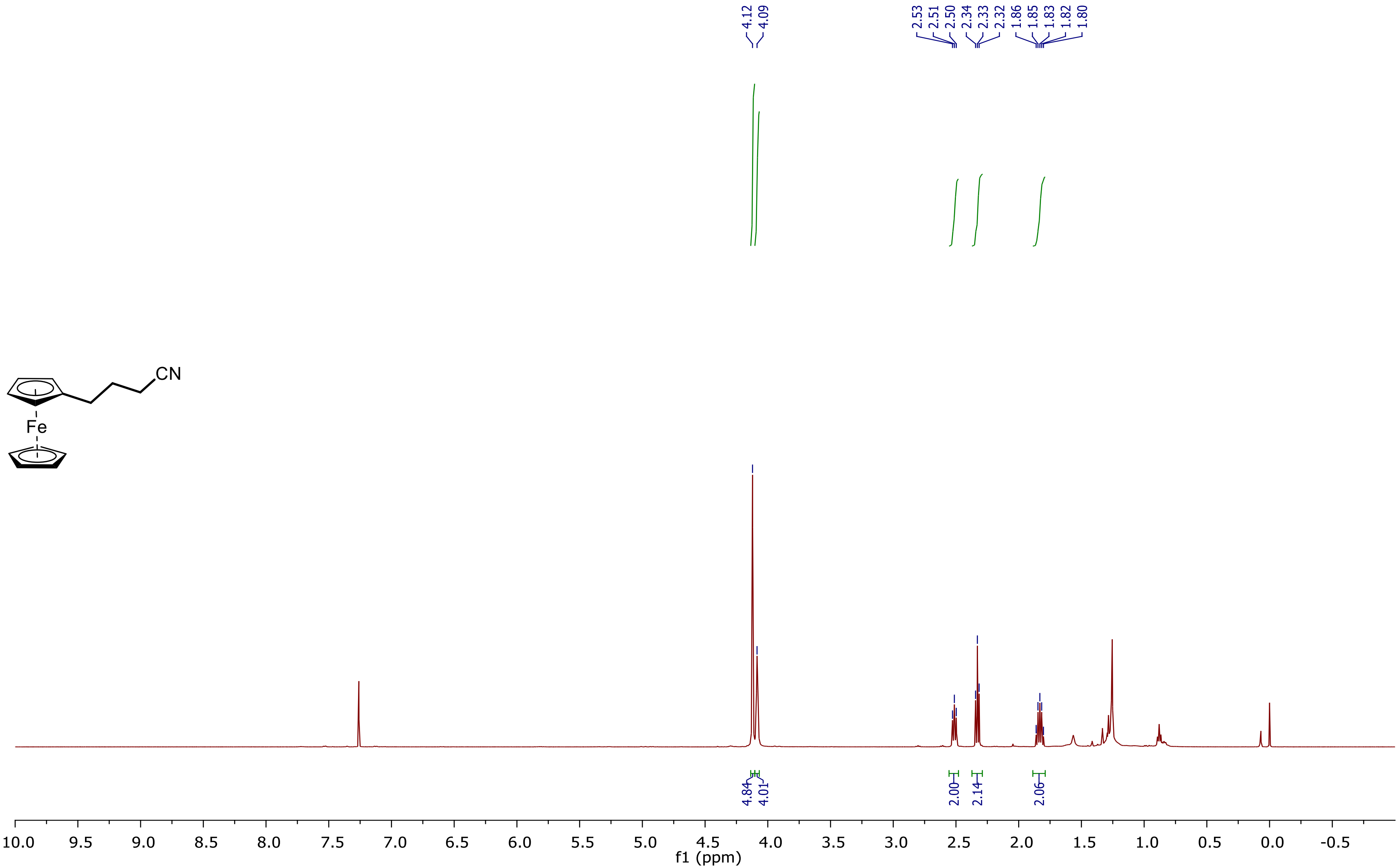
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(9)**



^{19}F NMR (471 MHz, $CDCl_3$) Spectrum of Compound **(9)**



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(11)**



^{13}C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(11)**