## Supporting Information

# Divergent cyanoalkylation/cyanoalkylsulfonylation of enamides under organophotoredox catalytic conditions

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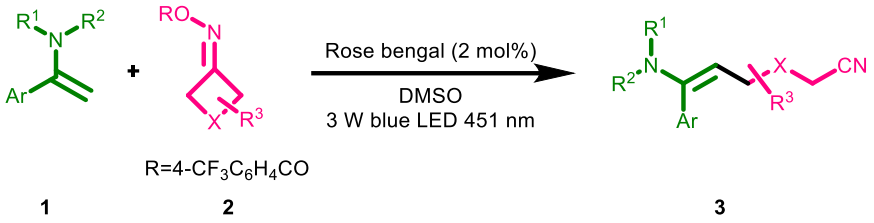
## 1. General information:

Unless otherwise noted, reagents obtained from commercial suppliers were used without further purification. All solvents were dried and distilled according to standard procedures. Reactions were monitored by silica gel thin-layer chromatography (TLC). Silica gel (100-200 mesh) packed in glass column was used for the column chromatography. NMR spectra were recorded at 400, 500 MHz (H), at 101, 125 MHz (C) and at 376 MHz (F) respectively. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (H: δ = 7.26 and C: δ = 77.0 ppm) as internal standard, and coupling constants (J) are measured in hertz (Hz). High-resolution mass spectra (HRMS) were recorded using ESI-TOF techniques. Melting points of solids were recorded using Electrothermal (IA9100) melting point apparatus. All photoredox-catalyzed reactions were carried out in *Penn PhD Photoreactor M2* (3W blue LED, 451nm) purchased from Sigma-Aldrich. Fluorescent quenching studies were performed on Agilent Cary Eclipse fluorescence spectrophotometer. All enamides[1] and oxime esters[2] were prepared using existing methods.

## 2. Experimental procedures:

### 2.1) General procedure for the visible-light promoted cyanoalkylation of enamides:




An oven dried vial equipped with a magnetic stir bar was charged with enamide **1** (0.3 mmol), oxime ester **2** (0.36 mmol) and Rose bengal (0.006 mmol). The vial was sealed with a septum, evacuated and backfilled with nitrogen three times. 1.0 mL of DMSO was then added via syringe with gentle stirring under $N_2$ atmosphere. The vial was introduced into *Penn PhD Photoreactor M2* (3W blue LED, 451nm) and allowed to stir for 6 h. After completion of reaction, the reaction mixture was diluted with ethyl acetate (15 mL), and washed successively with water (10 mL×2), 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 compound **3**.

**Analytical data for the cyanoalkylated compounds 3:**

**(*E*)-N-Benzyl-N-(5-cyano-1-phenylpent-1-en-1-yl)acetamide (3aa)**

Yellow syrup (78.3 mg, 82% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.36 (m, 3H), 7.31-7.21 (m, 5H), 7.20 – 7.15 (m, 2H), 5.20 (t, *J* = 7.6 Hz, 1H), 4.50 (s, 2H), 2.31 (q, *J* = 7.6 Hz, 2H), 2.22 (s, 3H), 2.15 (t, *J* = 7.1 Hz, 2H), 1.63 (p, *J* = 7.4 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.5, 140.1, 137.5, 134.5, 129.7, 129.0, 128.9, 128.6, 128.4, 127.4, 119.0, 48.9, 27.4, 25.2, 22.3, 16.5; HRMS (ESI) calcd for $C_{21}H_{23}N_2O^+$ $[M+H]^+$ = 319.1805, found = 319.1796.

**(*E*)-N-Benzyl-N-(5-cyano-1-(2-methoxyphenyl)pent-1-en-1-yl)acetamide (3ba)**

Pale-yellow syrup (74.2 mg, 71% yield); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 1H), 7.29 – 7.15 (m, 5H), 7.04 – 6.89 (m, 3H), 5.29 (t, *J* = 7.5 Hz, 1H), 4.47 (s, 2H), 3.79 (s, 3H),

2.31 (s, 3H), 2.15 (t, *J* = 7.2 Hz, 2H), 2.08 (q, *J* = 7.2 Hz, 2H), 1.62 (p, *J* = 7.2 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.2, 157.6, 138.4, 138.0, 131.6, 130.6, 130.1, 128.8, 128.2, 127.1, 123.2, 120.6, 119.3, 111.3, 55.4, 48.5, 27.5, 25.0, 22.5, 16.6; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_2^+$ $[M+H]^+$ = 349.1910, found = 349.1895.

**(*E*)-N-Benzyl-N-(5-cyano-1-(3-methoxyphenyl)pent-1-en-1-yl)acetamide (3ca)**

Brown syrup (81.5 mg, 78% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 4H), 7.22 – 7.16 (m, 2H), 6.92 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.73 (s, 1H), 5.19 (t, *J* = 7.5 Hz, 1H), 4.52 (s, 2H), 3.80 (s, 3H), 2.32 (q, *J* = 7.6 Hz, 2H), 2.21 (s, 3H), 2.15 (t, *J* = 7.2 Hz, 2H), 1.63 (p, *J* = 7.2Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 159.9, 140.1, 137.6, 136.0, 129.9, 129.9, 129.1, 128.4, 127.5, 121.1, 119.1, 114.5, 114.1, 55.5, 49.1, 27.5, 25.3, 22.4, 16.7; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_2^+$ $[M+H]^+$ = 349.1911, found = 349.1907.

**(*E*)-N-Benzyl-N-(1-(3-chlorophenyl)-5-cyanopent-1-en-1-yl)acetamide (3da)**

Brown syrup (59.2 mg, 56% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.33 (m, 2H), 7.30 – 7.24 (m, 3H), 7.20 - 7.14 (m, 3H), 7.11 (ddd, *J* = 5.3, 3.0, 1.7 Hz, 1H), 5.25 (t, *J* = 7.6 Hz, 1H), 4.51 (s, 2H), 2.30 (q, *J* = 7.6 Hz, 2H), 2.21 (s, 3H), 2.17 (t, *J* = 7.1 Hz, 2H), 1.64 (p, *J* = 7.2 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 139.1, 137.4, 136.6, 135.1, 130.9, 130.2, 129.3, 129.1, 128.6, 127.7, 126.9, 118.9, 49.3, 27.4, 25.3, 22.4, 16.7; HRMS (ESI) calcd for $C_{21}H_{22}ClN_2O^+$ $[M+H]^+$ = 353.1415, found = 353.1411.

**(*E*)-N-Benzyl-N-(5-cyano-1-(4-fluorophenyl)pent-1-en-1-yl)acetamide (3ea)**

Red syrup (67.6 mg, 67% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 3H), 7.22 – 7.15 (m, 4H), 7.11 (t, *J* = 8.5 Hz, 2H), 5.20 (t, *J* = 7.5 Hz, 1H), 4.50 (s, 2H), 2.29 (q, *J* = 7.6 Hz, 2H), 2.20 (s, 3H), 2.15 (t, *J* = 7.1 Hz, 2H), 1.63 (p, *J* = 7.6 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.46, 162.9 (d, *J* = 250.5Hz), 139.37, 137.48, 130.7, 130.5 (d, *J* = 8.2 Hz), 129.8, 129.1, 128.5, 127.6, 119.0, 116.0 (d, *J* = 21.7 Hz), 49.1, 27.4, 25.3, 22.4, 16.7; $^{19}$F NMR (376

MHz, $CDCl_3$) δ -111.5; HRMS (ESI) calcd for $C_{21}H_{22}FN_2O^+$ $[M+H]^+$ = 337.1711, found = 337.1707.

**(*E*)-N-Benzyl-N-(1-(4-chlorophenyl)-5-cyanopent-1-en-1-yl)acetamide (3fa)**

Brown syrup (76.1 mg, 72% yield); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.31 – 7.23 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 4H), 5.22 (t, *J* = 7.3 Hz, 1H), 4.51 (s, 2H), 2.35 – 2.25 (m, 2H), 2.24 – 2.10 (m, 5H), 1.63 (p, *J* = 7.4 Hz, 2H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.6, 139.2, 137.4, 135.0, 133.1, 130.4, 129.9, 129.2, 129.1, 128.5, 127.6, 119.0, 49.1, 27.4, 25.2, 22.4, 16.7; HRMS (ESI) calcd for $C_{21}H_{22}ClN_2O^+$ $[M+H]^+$ = 353.1415, found = 353.1402.

**(*E*)-N-Benzyl-N-(1-(4-bromophenyl)-5-cyanopent-1-en-1-yl)acetamideacetamide (3ga)**

Brown syrup (78.4 mg, 66% yield); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.23 (m, 3H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.23 (t, *J* = 7.2 Hz, 1H), 4.50 (s, 2H), 2.29 (q, *J* = 7.2 Hz, 2H), 2.23 – 2.10 (m, 5H), 1.63 (p, *J* = 7.2 Hz, 2H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.5, 139.3, 137.4, 133.6, 132.2, 130.4, 130.2, 129.1, 128.5, 127.6, 123.3, 119.0, 49.1, 27.5, 25.2, 22.4, 16.7; HRMS (ESI) calcd for $C_{21}H_{22}BrN_2O^+$ $[M+H]^+$ = 397.0910, found = 397.0899.

**(*E*)-N-Benzyl-N-(5-cyano-1-(4-(trifluoromethyl)phenyl)pent-1-en-1-yl)acetamide (3ha)**

Brown syrup (83.4 mg, 72% yield); $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.27 (m, 5H), 7.17 (d, *J* = 5.3 Hz, 2H), 5.31 (s, 1H), 4.57 (s, 2H), 2.33 (d, *J* = 6.1 Hz, 2H), 2.27 – 2.12 (m, 5H), 1.71 – 1.60 (m, 2H); $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 170.4, 139.1, 138.4, 137.3, 131.6, 131.1 (q, *J* = 32.5) , 129.1, 129.0, 128.6, 127.7, 126.0, 123.8 (q, *J* = 272.5 Hz), 118.9, 49.2, 27.4, 25.2, 22.4, 16.7; $^{19}F$ NMR (376 MHz, $CDCl_3$) δ -62.8; HRMS (ESI) calcd for $C_{22}H_{22}F_3N_2O^+$ $[M+H]^+$ = 387.1679, found = 386.1672.

**(*E*)-N-Benzyl-N-(5-cyano-1-(*p*-tolyl)pent-1-en-1-yl)acetamide (3ia)**

Yellow syrup (58.8 mg, 59% yield); $^1H$ NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.19 – 7.16 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 5.14 (t, *J* = 7.6 Hz, 1H), 4.49

(s, 2H), 2.39 (s, 3H), 2.30 (q, *J* = 7.5 Hz, 2H), 2.20 (s, 3H), 2.15 (t, *J* = 7.2 Hz, 2H), 1.62 (p, *J* = 7.2 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 140.2, 139.2, 137.7, 131.6, 129.6, 129.2, 129.1, 128.5, 128.4, 127.5, 119.2, 48.9, 27.5, 25.4, 22.4, 21.4, 16.7; HRMS (ESI) calcd for $C_{22}H_{25}N_2O^+$ $[M+H]^+$ = 333.1962, found = 333.1964.

**(*E*)-N-Benzyl-N-(5-cyano-1-(2,4-dichlorophenyl)pent-1-en-1-yl)acetamide (3ja)**

Brown syrup (80.0 mg, 69% yield); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.30 – 7.19 (m, 4H), 7.15 (d, *J* = 5.9 Hz, 2H), 7.00 (s, 1H), 5.48 (s, 1H), 4.47 (s, 2H), 2.33 (s, 3H), 2.26 – 2.16 (m, 2H), 2.13 – 2.02 (m, 2H), 1.68 (p, *J* = 7.4 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.8, 137.4, 135.8, 134.7, 132.7, 132.2, 131.8, 130.8, 130.4, 128.4, 127.5, 127.4, 118.9, 48.8, 27.8, 24.8, 22.7, 16.9; HRMS (ESI) calcd for $C_{21}H_{21}Cl_2N_2O^+$ $[M+H]^+$ = 387.1026, found = 387.1017.

**(*E*)-N-Benzyl-N-(5-cyano-1-(2,4-difluorophenyl)pent-1-en-1-yl)acetamide (3ka)**

Yellow syrup (67.0 mg, 63% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.7 Hz, 3H), 7.20 – 7.16 (m, 2H), 7.09 (q, *J* = 7.6 Hz, 1H), 6.96 – 6.84 (m, 2H), 5.36 (t, *J* = 7.4 Hz, 1H), 4.49 (s, 2H), 2.24 (s, 3H), 2.17 (t, *J* = 7.14 Hz, 2H), 2.10 (q, *J* = 7.14 Hz, 2H), 1.64 (p, *J* = 7.14 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 163.2 (dd, *J* = 240.0, 17.0 Hz), 160.5 (dd, *J* = 250.6, 11.4 Hz), 137.3, 134.0, 132.5, 131.8 (d, *J* = 8.3 Hz), 128.9, 128.5, 127.5, 119.0, 118.8, 112.1 (dd, *J* = 21.4, 2.0 Hz), 112.0, 112.0, 104.9 (t, *J* = 26.6 Hz), 48.9, 27.6, 24.6, 22.3, 16.7; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -107.4, -107.9; HRMS (ESI) calcd for $C_{21}H_{21}F_2N_2O^+$ $[M+H]^+$ = 355.1617, found = 355.1604.

**(*E*)-N-Benzyl-N-(5-cyano-1-(3,4-dichlorophenyl)pent-1-en-1-yl)acetamide (3la)**

Brown syrup (62.5 mg, 54% yield); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.2 Hz, 1H), 7.32 – 7.24 (m, 4H), 7.16 (d, *J* = 6.8 Hz, 2H), 7.05 (dd, *J* = 8.3, 2.0 Hz, 1H), 5.27 (t, *J* = 7.5 Hz, 1H), 4.51 (s, 2H), 2.29 (q, *J* = 7.6 Hz, 2H), 2.17 (d, *J* = 7.9 Hz, 5H ), 1.64 (p, *J* = 7.6 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.3, 138.2, 137.1, 134.6, 133.3, 131.2, 130.9, 130.2,

128.9, 128.5, 127.8, 127.6, 118.8, 49.2, 27.3, 25.1, 22.3, 16.6; HRMS (ESI) calcd for $C_{21}H_{21}Cl_2N_2O^+$ $[M+H]^+$ = 387.1026, found = 387.1017.

**(*E*)-N-Benzyl-N-(5-cyano-1-(naphthalen-2-yl)pent-1-en-1-yl)acetamide (3ma)**

Yellow syrup (89.5 mg, 81% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 3H), 7.61 (s, 1H), 7.49 – 7.42 (m, 2H), 7.25 – 7.16 (m, 4H), 7.13 – 7.11 (m, 2H), 5.21 (t, *J* = 7.5 Hz, 1H), 4.47 (s, 2H), 2.31 (q, *J* = 7.3 Hz, 2H), 2.20 (s, 3H), 2.08 (t, *J* = 7.0 Hz, 2H), 1.59 (p, *J* = 7.4 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 140.4, 137.7, 133.4, 133.2, 131.9, 130.1, 129.2, 128.8, 128.5, 128.4, 127.9, 127.5, 127.1, 126.9, 125.7, 119.2, 77.4, 49.2, 27.6, 25.4, 22.5, 16.7; HRMS (ESI) calcd for $C_{25}H_{25}N_2O^+$ $[M+H]^+$ = 369.1962, found = 369.1962.

**(*E*)-N-Benzyl-N-(5-cyano-1-(thiophen-2-yl)pent-1-en-1-yl)acetamide (3na)**

Yellow oil (60.3 mg, 62% yield); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 4.9, 0.9 Hz, 1H), 7.32 – 7.26 (m, 3H), 7.25 – 7.20 (m, 2H), 7.10 – 7.04 (m, 2H), 5.06 (t, *J* = 7.6 Hz, 1H), 4.66 (s, 2H), 2.46 (q, *J* = 7.5 Hz, 2H), 2.15 – 2.08 (m, 5H), 1.65 (p, *J* = 7.3 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.6, 138.0, 137.7, 134.4, 130.4, 129.4, 128.5, 127.7, 127.6, 127.6, 127.1, 119.1, 49.6, 27.4, 25.0, 21.9, 16.6; HRMS(ESI) calcd for $C_{19}H_{20}N_2NaOS^+$ $[M+Na]^+$ = 347.1194, found = 347.1187.

**(*E*)-N-(5-Cyano-1-phenylpent-1-en-1-yl)-N-methylacetamide (3oa)**

Yellow syrup (25.4 mg, 35% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.34 (m, 3H), 7.29 – 7.24 (m, 2H), 5.60 (t, *J* = 7.3 Hz, 1H), 2.97 (s, 3H), 2.45 (q, *J* = 7.4 Hz, 2H), 2.37 (t, *J* = 7.4 Hz, 2H), 2.11 (s, 3H), 1.84 (p, *J* = 7.4 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 143.1, 134.9, 129.1, 128.9, 128.5, 127.1, 119.1, 35.4, 27.7, 25.5, 22.2, 17.1; HRMS (ESI) calcd for $C_{15}H_{18}N_2NaO^+$ $[M+Na]^+$ = 265.1311, found = 265.1306.

**(*E*)-N-Allyl-N-(5-cyano-1-phenylpent-1-en-1-yl)acetamide (3pa)**

Yellow syrup (64.4 mg, 80% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.25 (m, 3H), 7.21 – 7.16 (m, 2H), 5.70 (ddt, *J* = 16.7, 10.2, 6.4 Hz, 1H), 5.47 (t, *J* = 7.5 Hz, 1H), 4.99 (dd, *J* =

35.9, 13.6 Hz, 2H), 3.87 (d, *J* = 6.2 Hz, 2H), 2.37 (q, *J* = 7.8 Hz, 2H), 2.29 (t, *J* = 7.1 Hz, 2H), 2.08 (s, 3H), 1.73 (p, *J* = 7.2 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.3, 140.3, 134.5, 129.3, 129.2, 128.9, 128.7, 119.2, 79.2, 71.9, 36.0, 27.7, 25.5, 22.3, 16.9; HRMS (ESI) calcd for $C_{17}H_{21}N_2O^+$ $[M+H]^+$ = 269.1648, found = 269.1690.

**(*E*)-N-(5-Cyano-1-phenylpent-1-en-1-yl)-N-(prop-2-yn-1-yl)acetamide (3qa)**

Yellow syrup (58.3 mg, 73% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 3H), 7.32 – 7.27 (m, 2H), 5.72 (t, *J* = 7.6 Hz, 1H), 4.20 (d, *J* = 1.7 Hz, 2H), 2.48 (q, *J* = 7.6 Hz, 2H), 2.38 (t, *J* = 7.1 Hz, 2H), 2.19 (s, 1H), 2.11 (s, 3H), 1.83 (p, *J* = 7.4 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.4, 140.9, 134.9, 133.3, 129.0, 128.8, 128.6, 119.1, 117.9, 49.1, 27.7, 25.5, 22.4, 16.9; HRMS (ESI) calcd for $C_{17}H_{19}N_2O^+$ $[M+H]^+$ = 267.1492, found = 267.1532.

**(*E*)-N-Benzyl-N-(4-(cyanomethyl)-1-phenyloct-1-en-1-yl)acetamide (3ab)**

Orange syrup (79.7 mg, 71% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 3H), 7.30 – 7.22 (m, 5H), 7.21 – 7.18 (m, 2H), 5.19 (t, *J* = 7.6 Hz, 1H), 4.52 (dd, *J* = 35.9, 14.4 Hz, 2H), 2.33 – 2.21 (m, 5H), 2.14 – 1.96 (m, 1H), 1.65 (dt, *J* = 12.8, 6.4 Hz, 1H), 1.30 – 1.06 (m, 7H), 0.85 (t, *J* = 7.1 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 140.4, 137.7, 134.7, 129.2, 129.1, 129.1, 128.9, 128.7, 128.5, 127.5, 118.3, 49.0, 35.9, 33.0, 32.3, 28.7, 22.7, 22.5, 21.5, 14.1.; HRMS (ESI) calcd for $C_{25}H_{31}N_2O^+$ $[M+H]^+$ = 375.2431, found = 375.2432.

**(*E*)-N-Benzyl-N-(5-cyano-1,4-diphenylpent-1-en-1-yl)acetamide (3ac)**

Yellow syrup (81.6 mg, 69% yield); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 3H), 7.29 – 7.21 (m, 6H), 7.15 – 7.11 (m, 2H), 7.09 (dd, *J* = 7.1, 2.2 Hz, 2H), 6.96 – 6.90 (m, 2H), 5.09 (t, *J* = 8.0 Hz, 1H), 4.71 (d, *J* = 14.4 Hz, 1H), 4.06 (d, *J* = 14.4 Hz, 1H), 2.97 – 2.88 (m, 1H), 2.66 (tdd, *J* = 9.9, 7.7, 3.6 Hz, 2H), 2.50 – 2.36 (m, 2H), 1.76 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 140.7, 140.3, 137.5, 134.6, 129.1, 129.1, 128.9, 128.9, 128.7, 128.4, 127.9, 127.4, 127.3, 118.1, 48.9, 42.4, 33.6, 25.0, 21.7; HRMS (ESI) calcd for $C_{27}H_{27}N_2O^+$ $[M+H]^+$ = 395.2118, found = 395.2125.

**(*E*)-N-Benzyl-N-(4-(4-(tert-butyl)phenyl)-5-cyano-1-phenylpent-1-en-1-yl)acetamide (3ad)**

Yellow syrup (114.8 mg, 85% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 3H), 7.28 – 7.21 (m, 5H), 7.15 – 7.06 (m, 4H), 6.86 (d, *J* = 8.3 Hz, 2H), 5.07 (dd, *J* = 8.4, 6.1 Hz, 1H), 4.73 (d, *J* = 14.4 Hz, 1H), 4.01 (d, *J* = 14.4 Hz, 1H), 2.92 (td, *J* = 12.1, 7.0 Hz, 1H), 2.76 – 2.67 (m, 1H), 2.65 – 2.54 (m, 1H), 2.51 – 2.36 (m, 2H), 1.68 (s, 3H), 1.28 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.8, 150.9, 140.5, 137.6, 137.2, 134.7, 129.1, 128.9, 128.9, 128.8, 128.4, 127.4, 126.9, 126.0, 118.3, 48.9, 41.9, 34.6, 33.7, 31.4, 25.1, 21.6; HRMS (ESI) calcd for $C_{31}H_{35}N_2O^+$ $[M+H]^+$ = 451.2744, found = 451.2742.

**(*E*)-N-Benzyl-N-(4-(2-bromophenyl)-5-cyano-1-phenylpent-1-en-1-yl)acetamide (3ae)**

Yellow syrup (96.3 mg, 68% yield); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.9, 1.1, 1H), 7.46 – 7.38 (m, 3H), 7.28 – 7.22 (m, 3H), 7.20 – 7.15 (m, 3H), 7.14 – 7.06 (m, 3H), 6.86 (d, *J* = 7.5, 1H), 5.11 (dd, *J* = 8.2, 6.5, 1H), 4.66 (d, *J* = 14.4, 1H), 4.15 (d, *J* = 14.4, 1H), 3.58 (dq, *J* = 12.4, 6.1, 1H), 2.83 – 2.66 (m, 2H), 2.53 – 2.35 (m, 2H), 1.77 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 141.3, 138.9, 137.5, 134.7, 133.6, 129.4, 129.2, 128.9, 128.8, 128.5, 128.8, 127.9, 127.7, 127.4, 124.9, 117.6, 49.2, 40.3, 32.1, 23.7, 21.8; HRMS(ESI) calcd for $C_{27}H_{26}BrN_2O^+$ $[M+H]^+$ = 473.1223, found = 473.1220.

**(*E*)-N-Benzyl-N-(4-(4-bromophenyl)-5-cyano-1-phenylpent-1-en-1-yl)acetamide (3af)**

Yellow syrup (72.2 mg, 51% yield); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.34 (m, 5H), 7.30 – 7.25 (m, 3H), 7.16 – 7.12 (m, 2H), 7.09 (dd, *J* = 6.5, 2.9, 2H), 6.81 (d, *J* = 8.2, 2H), 5.06 (t, *J* = 7.3, 1H), 4.70 (d, *J* = 14.4, 1H), 4.11 (d, *J* = 14.5, 1H), 2.89 (td, *J* = 12.3, 6.9, 1H), 2.72 – 2.52 (m, 2H), 2.41 (d, *J* = 6.9, 2H), 1.84 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 141.1, 139.2, 137.5, 134.5, 132.3, 129.2, 128.9, 128.9, 128.7, 128.5, 127.8, 127.4, 121.8, 117.7, 49.1, 42.0, 33.5, 24.8, 21.8; HRMS (ESI) calcd for $C_{27}H_{26}BrN_2O^+$ $[M+H]^+$ = 473.1223, found = 473.1227.

**(*E*)-N-Benzyl-N-(4-(benzyloxy)-5-cyano-1-phenylpent-1-en-1-yl)acetamide (3ag)**

Brown syrup (54.7 mg, 43% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.41 (dt, *J* = 11.1, 3.9 Hz, 3H), 7.35 – 7.30 (m, 3H), 7.29 – 7.20 (m, 7H), 7.20 – 7.16 (m, 2H), 5.31 (t, *J* = 7.5 Hz, 1H), 4.51 (dd, *J* = 30.3, 8.4 Hz, 2H), 4.44 – 4.30 (m, 2H), 3.66 – 3.56 (m, 1H), 2.59 – 2.45 (m, 2H), 2.32 (d, *J* = 5.6 Hz, 2H), 2.17 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 141.4, 137.6, 137.1, 134.5, 129.2, 129.0, 128.9, 128.7, 128.5, 128.3, 127.9, 127.5, 126.1, 117.1, 74.1, 72.0, 48.9, 33.2, 22.8, 22.3; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_2^+$ $[M+H]^+$ = 425.2224, found = 425.2225.

**(*E*)-N-Benzyl-N-(3-benzyl-5-cyano-1-phenylpent-1-en-1-yl)acetamide (3ah)**

Yellow syrup (75.9 mg, 62% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 6H), 7.20 – 7.11 (m, 5H), 7.00 (s, 2H), 6.80 (dd, *J* = 6.4, 2.6 Hz, 2H), 4.91 (dd, *J* = 43.9, 12.6 Hz, 2H), 4.08 (d, *J* = 14.4 Hz, 1H), 2.84 (s, 1H), 2.60 (dd, *J* = 13.8, 6.1 Hz, 1H), 2.48 (dd, *J* = 13.7, 8.2 Hz, 1H), 2.02 (s, 3H), 1.87 (dtd, *J* = 25.0, 16.7, 8.4 Hz, 2H), 1.75 – 1.61 (m, 1H), 1.42 (td, *J* = 14.1, 8.5 Hz, 1H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.2, 140.7, 138.2, 137.6, 134.6, 134.1, 129.0, 128.8, 128.5, 127.6, 126.6, 119.2, 48.5, 41.2, 38.4, 30.7, 22.2, 14.8; HRMS (ESI) calcd for $C_{28}H_{29}N_2O^+$ $[M+H]^+$ = 409.2275, found = 409.2264.

**(*E*)-N-Benzyl-N-(2-(1-(cyanomethyl)-2,3-dihydro-1H-inden-2-yl)-1-phenylvinyl)acetamide (3ai)**

Black syrup (79.2 mg, 65% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.37 (m, 3H), 7.30 – 7.25 (m, 5H), 7.23 – 7.13 (m, 6H), 5.29 (d, *J* = 9.7 Hz, 1H), 4.56 (q, *J* = 14.4 Hz, 2H), 3.14 – 2.98 (m, 3H), 2.62 (dd, *J* = 14.9, 6.9 Hz, 1H), 2.50 (dd, *J* = 16.9, 5.1 Hz, 1H), 2.37 (dd, *J* = 16.9, 6.5 Hz, 1H), 2.27 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.3, 141.9, 141.6, 140.5, 137.6, 134.7, 133.5, 129.2, 129.0, 128.7, 128.4, 128.1, 127.5, 127.3, 124.8, 123.4, 118.1, 49.0, 47.6, 45.1, 38.2, 22.7, 20.9; HRMS (ESI) calcd for $C_{28}H_{27}N_2O^+$ $[M+H]^+$ = 407.2118, found = 407.2141.

**(*E*)-N-Benzyl-N-(3-(cyanomethoxy)-1-phenylprop-1-en-1-yl)acetamide (3aj)**

Yellow syrup (60.5 mg, 63% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 3H), 7.33 – 7.25 (m, 3H), 7.23 – 7.15 (m, 4H), 5.49 (t, *J* = 6.5 Hz, 1H), 4.55 (s, 2H), 4.17 (d, *J* = 7.0 Hz, 2H), 4.10 (s, 2H), 2.22 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 144.2, 137.3, 134.1, 129.9, 129.1, 128.9, 128.7, 128.6, 127.6, 125.0, 115.7, 67.7, 55.5, 49.5, 22.6; HRMS(ESI) calcd for $C_{20}H_{21}N_2O_2^+$ $[M+H]^+$ = 321.1598, found = 321.1594.

**(*E*)-N-Benzyl-N-(5-cyano-1,4,4-triphenylpent-1-en-1-yl)acetamide (3ak)**

Red syrup (22.6 mg, 16% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 3H), 7.34 – 7.28 (m, 4H), 7.26 – 7.19 (m, 8H), 7.12 – 7.08 (m, 2H), 6.96 – 6.92 (m, 3H), 4.95 (t, *J* = 6.8 Hz, 1H), 4.44 (s, 2H), 3.17 (d, *J* = 6.8 Hz, 2H), 2.80 (s, 2H), 2.17 (s, 3H).$^{13}$C NMR (151 MHz, $CDCl_3$) δ 170.6, 143.9, 141.3, 137.7, 134.8, 129.2, 128.9, 128.9, 128.7, 128.7, 128.6, 127.4, 126.7, 117.6, 49.2, 48.8, 48.6, 37.7, 31.1, 21.9; HRMS (ESI) calcd for $C_{33}H_{31}N_2O^+$ $[M+H]^+$ = 471.2431, found = 471.2441.

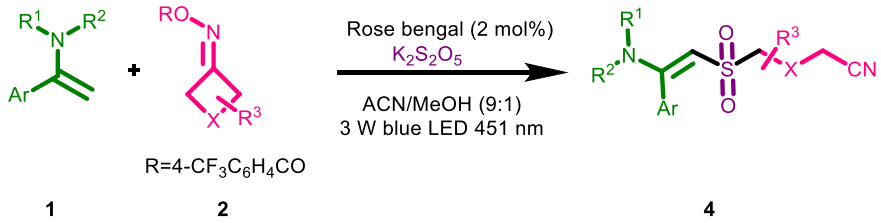
**Table S1: Optimization of reaction conditions for cyanoalkylsulfonylation[a]**


| S.No. | Solvent (M) | $SO_2$ Source (equiv) | Yield of 4aa (%) |
|---|---|---|---|
| 1 | DMSO(0.3M) | $K_2S_2O_5$ (1.2eq) | 0 |
| 2 | DMF(0.3M) | $K_2S_2O_5$ (1.2eq) | 0 |
| 3 | ACN(0.3M) | $K_2S_2O_5$ (1.2eq) | 0 |
| 4 | Dimethylcarbonate(0.3M) | $K_2S_2O_5$ (1.2eq) | 0 |
| 5 | ACN/MeOH (1:1) (0.3M) | $K_2S_2O_5$ (1.2eq) | 13 |
| 6 | ACN/MeOH (4:1)(0.3M) | $K_2S_2O_5$ (1.2eq) | 26 |
| 7 | ACN/MeOH (9:1)(0.3M) | $K_2S_2O_5$ (1.2eq) | 58 |
| 8 | ACN/MeOH (9:1)(0.3M) | $K_2S_2O_5$ (3eq) | 73 |

| | | | |
|---|---|---|---|
| 9 | ACN/MeOH (9:1)(0.3M) | $Na_2S_2O_5$ (1.2eq) | 0 |
| 10 | ACN/MeOH (9:1)(0.3M) | DABSO (1.2eq) | 36 |

[a]Reaction conditions: Enamide **1a** (0.3 mmol), oxime ester **2a** (0.36 mmol), Rose bengal (0.006 mmol), $SO_2$ source (0.9 mmol) and 1.0 mL of solvent under blue LEDs at room temperature for 6 h.

**2.2) General procedure for the visible-light promoted cyanoalkylsulfonylation of enamides:**




An oven dried vial equipped with a magnetic stir bar was charged with enamide **1** (0.3 mmol), oxime ester **2** (0.36 mmol), $K_2S_2O_5$ (0.9 mmol) and Rose Bengal (0.006 mmol). The vial was sealed with a septum, evacuated and backfilled with nitrogen three times. 1 mL of $CH_3CN$/MeOH (9:1) was then added via syringe with gentle stirring under $N_2$ atmosphere. The vial was introduced into *Penn PhD Photoreactor M2* (3W blue LED, 451nm) and allowed to stir for 6 h. After completion of reaction, the resulting mixture was concentrated under reduced pressure then the residue was diluted with ethyl acetate (15 mL), and washed successively with aq. $NaHCO_3$ solution (10mL×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 compound **4**.

**Analytical data for the cyanoalkylsulfonylated compounds 4:**

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (4aa)**

Yellow oil (83.8 mg, 73% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.51 (m, 1H), 7.50 – 7.43 (m, 4H), 7.39 – 7.28 (m, 3H), 7.20 – 7.15 (m, 2H), 6.18 (s, 1H), 4.65 (s, 2H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.19 (s, 3H), 1.97 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 153.3, 136.4, 132.3, 131.9, 129.9, 129.1, 128.9, 128.3, 128.2, 125.2, 118.1, 53.3, 51.1, 23.7, 18.6, 16.3; HRMS (ESI) calcd for $C_{21}H_{23}N_2O_3S^+$ $[M+H]^+$ = 383.1424, found = 383.1434.

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-(2-methoxyphenyl)vinyl)acetamide (4ba)**

Yellow oil (66.8 mg, 54% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.46 (ddd, *J* = 8.4, 7.5, 1.7 Hz, 1H), 7.33 – 7.21 (m, 3H), 7.19 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.12 – 7.06 (m, 2H), 7.00 (td, *J* = 7.5, 0.9 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.21 (s, 1H), 4.57 (s, 2H), 3.81 (s, 3H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.32 (s, 3H), 2.01 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 157.3, 151.8, 136.8, 132.8, 132.4, 128.6, 127.8, 127.6, 124.8, 120.4, 120.3, 118.2, 111.1, 55.7, 53.2, 50.0, 23.2, 18.5, 16.2; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_4S^+$ $[M+H]^+$ = 413.1530, found =413.1535.

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-(3-methoxyphenyl)vinyl)acetamide (4ca)**

Yellow oil (94.1 mg, 76% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 4H), 7.23 – 7.15 (m, 2H), 7.10 – 7.00 (m, 2H), 7.01 – 6.94 (m, 1H), 6.19 (s, 1H), 4.67 (s, 2H), 3.81 (s, 3H), 2.81 (t, *J* = 7.3 Hz, 2H), 2.42 (t, *J* = 7.0 Hz, 2H), 2.18 (s, 3H), 1.96 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 159.8, 152.9, 136.4, 133.6, 130.1, 129.0, 128.3, 128.2, 125.4, 122.0, 118.1, 117.8, 115.3, 55.6, 53.1, 51.2, 23.6, 18.7, 16.3; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_4S^+$ $[M+H]^+$ = 413.1530, found =413.1533.

**(*E*)-N-Benzyl-N-(1-(3-chlorophenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetamide (4da)**

Pale brown oil (55.0 mg, 44% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.48 (m, 1H), 7.43 – 7.31 (m, 6H), 7.17 – 7.12 (m, 2H), 6.23 (s, 1H), 4.63 (s, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.48 (t, *J* = 7.0 Hz, 2H), 2.23 (s, 3H), 2.03 (p, *J* = 7.0 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5,

151.7, 136.1, 135.0, 133.9, 131.9, 130.0, 129.5, 129.2, 128.5, 128.3, 128.1, 125.9, 118.1, 53.6, 51.2, 23.6, 18.6, 16.3; HRMS (ESI) calcd for $C_{21}H_{22}ClN_2O_3S^+$ $[M+H]^+$ = 417.1034, found =417.1035.

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-(4-fluorophenyl)vinyl)acetamide (4ea)**

Yellow oil (79.3 mg, 66% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.8, 5.4 Hz, 2H), 7.40 – 7.28 (m, 3H), 7.22 – 7.07(m, 4H), 6.17 (s, 1H), 4.64 (s, 2H), 2.89 (t, *J* = 7.2 Hz, 2H), 2.47 (t, *J* = 7.0 Hz, 2H), 2.20 (s, 3H), 2.01 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 164.7 (d, *J* = 254.1 Hz), 152.3, 136.2, 132.3 (d, *J* = 8.8 Hz), 129.1, 128.3, 128.2, 125.0, 118.1, 116.2 (d, *J* = 22.1 Hz), 53.4, 51.2, 23.6, 18.6, 16.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -106.5; HRMS (ESI) calcd for $C_{21}H_{22}FN_2O_3S^+$ $[M+H]^+$ = 401.1330, found =401.1336.

**(*E*)-N-Benzyl-N-(1-(4-chlorophenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetamide (4fa)**

Brown oil (72.5 mg, 58% yield); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.22 (m, 5H), 7.08 (d, *J* = 7.0 Hz, 2H), 6.12 (s, 1H), 4.56 (s, 2H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.40 (t, *J* = 6.9 Hz, 2H), 2.14 (s, 3H), 1.95 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.6, 152.1, 138.3, 136.2, 131.3, 130.6, 129.2, 129.2, 128.3, 128.2, 125.4, 118.1, 53.5, 51.2, 23.6, 18.6, 16.3; HRMS (ESI) calcd for $C_{21}H_{22}ClN_2O_3S^+$ $[M+H]^+$ = 417.1034, found =417.1037.

**(*E*)-N-Benzyl-N-(1-(4-bromophenyl)-2-((3-cyanopropyl)sulfonyl)vinyl)acetamide (4ga)**

Brown oil (72.0 mg, 52% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.50 (m, 2H), 7.45 – 7.22 (m, 5H), 7.17 – 7.12 (m, 2H), 6.19 (s, 1H), 4.63 (s, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 2.48 (t, *J* = 7.0 Hz, 2H), 2.21 (s, 3H), 2.02 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.6, 152.2, 136.2, 132.2, 131.5, 131.0, 129.2, 128.3, 128.1, 126.7, 125.4, 118.1, 53.5, 51.2, 23.6, 18.6, 16.3; HRMS (ESI) calcd for $C_{21}H_{22}BrN_2O_3S^+$ $[M+H]^+$ = 461.0529, found =461.0532.

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-(4-(trifluoromethyl)phenyl)vinyl) acetamide (4ha)**

Yellow oil (73.0 mg, 54% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.44 – 7.30 (m, 3H), 7.21 – 7.07 (m, 2H), 6.31 (s, 1H), 4.61 (s, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 2.48 (t, *J* = 7.0 Hz, 2H), 2.25 (s, 3H), 2.03 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.5, 151.7, 136.0, 133.34 (q, *J* = 32.9 Hz), 133.0, 130.4, 129.2, 128.4, 128.0, 126.1, 125.7 (q, *J* = 3.3 Hz), 123.6(q, *J* = 273.0 Hz),118.1, 53.7, 51.3, 23.6, 18.6, 16.3;$^{19}$F NMR (376 MHz, $CDCl_3$) δ -63.0; HRMS (ESI) calcd for $C_{22}H_{22}F_3N_2O_3S^+$ $[M+H]^+$ = 451.1298, found =451.1306.

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-(p-tolyl)vinyl)acetamide (4ia)**

Colorless oil (57.1 mg, 48% yield); $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 4H), 7.31 – 7.25 (m, 3H), 7.19 – 7.14 (m, 2H), 6.09 (s, 1H), 4.64 (s, 2H), 2.80 (t, *J* = 7.3 Hz, 2H), 2.50 – 2.34 (m, 5H), 2.15 (s, 3H), 1.95 (p, *J* = 7.1 Hz, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.7, 153.4, 142.8, 136.5, 129.9, 129.7, 129.3, 129.0, 128.3, 128.1, 124.6, 118.1, 53.2, 51.1, 23.7, 21.7, 18.6, 16.3; HRMS (ESI) calcd for $C_{22}H_{25}N_2O_3S^+$ $[M+H]^+$ = 397.1580, found =397.1579.

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-(2,4-dichlorophenyl)vinyl)acetamide (4ja)**

Yellow oil (52.8 mg, 39% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.0 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.28 – 7.24 (m, 1H), 7.14 (d, *J* = 8.3 Hz, 1H), 7.09 – 7.02 (m, 2H), 6.55 (s, 1H), 4.58 (s, 2H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.52 (t, *J* = 7.0 Hz, 2H), 2.34 (s, 3H), 2.15 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 171.1, 150.1, 137.8, 136.1, 134.6, 133.4,130.0, 129.2, 129.1, 128.1, 127.1, 126.8, 123.9, 118.2, 54.0, 51.2, 23.8, 18.8, 16.3; HRMS (ESI) calcd for $C_{21}H_{21}Cl_2N_2O_3S^+$ $[M+H]^+$ = 451.0644, found =451.0650.

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-(2,4-difluorophenyl)vinyl)acetamide (4ka)**

Yellow oil (72.8 mg, 58% yield); $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 3H), 7.26 – 7.19 (m, 1H), 7.16 – 7.10 (m, 2H), 7.00 – 6.83 (m, 2H), 6.28 (s, 1H), 4.62 (s, 2H), 3.04 (t, *J* =

7.3 Hz, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.29 (s, 3H), 2.05 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.5, 164.89 (dd, *J* = 255.6, 12.4 Hz), 160.71 (dd, *J* = 252.9, 12.3 Hz), 147.2, 136.1, 132.88 (dd, *J* = 10.1, 3.1 Hz), 129.1, 128.2, 127.9, 125.6, 118.1, 116.3 (dd, *J* = 13.9, 3.7 Hz), 112.1 (dd, *J* = 21.7, 2.8 Hz), 104.8 (t, *J* = 25.6 Hz), 53.4, 50.7, 23.3, 18.52, 16.3; $^{19}$F NMR (376 MHz, $CDCl_3$) δ -103.5, -107.9; HRMS (ESI) calcd for $C_{21}H_{21}F_2N_2O_3S^+$ $[M+H]^+$ = 419.1235, found =419.1237.

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-(3,4-dichlorophenyl)vinyl)acetamide (4la)**

Yellow oil (62.3 mg, 46% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 1H), 7.45 (d, *J* = 2.1 Hz, 1H), 7.40 – 7.31 (m, 3H), 7.29 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.17 – 7.10 (m, 2H), 6.24 (s, 1H), 4.62 (s, 2H), 2.96 (t, *J* = 7.3 Hz, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.24 (s, 3H), 2.05 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 150.8, 136.3, 135.9, 133.4, 132.0, 131.3, 130.7, 129.4, 129.2, 128.4, 128.0, 126.0, 118.1, 53.7, 51.3, 23.5, 18.6, 16.3; HRMS (ESI) calcd for $C_{21}H_{21}Cl_2N_2O_3S^+$$[M+H]^+$ = 451.0644, found =451.0649.

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-(naphthalen-2-yl)vinyl)acetamide (4ma)**

Yellow oil (54.5 mg, 42% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 1H), 7.95 – 7.86 (m, 3H), 7.64 – 7.54 (m, 2H), 7.47 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.21 – 7.16 (m, 2H), 6.26 (s, 1H), 4.67 (s, 2H), 2.85 (t, *J* = 7.3 Hz, 2H), 2.39 (t, *J* = 7.0 Hz, 2H), 2.23 (s, 3H), 1.97 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.7, 153.3, 136.4, 134.6, 132.5, 131.2, 129.4, 129.1, 128.9, 128.5, 128.3, 128.2, 128.0, 127.4, 125.6, 125.4, 118.1, 53.4, 51.2, 23.7, 18.7, 16.2; HRMS (ESI) calcd for $C_{25}H_{25}N_2O_3S^+$ $[M+H]^+$ = 433.1580, found =433.1577.

**(*E*)-N-Benzyl-N-(2-((3-cyanopropyl)sulfonyl)-1-(thiophen-2-yl)vinyl)acetamide (4na)**

Yellow oil (42 mg, 36% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.67 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.36 – 7.32 (m, 3H), 7.26 – 7.24 (m, 2H), 7.19 – 7.15 (m, 1H),

5.95 (s, 1H), 4.77 (s, 2H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.46 (t, *J* = 7.0 Hz, 2H), 1.95 (p, *J* = 7.3 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.0, 145.5, 136.3, 134.8, 134.7, 132.3, 128.9, 128.8, 128.8, 128.3, 125.3, 117.9, 52.4, 51.4, 22.8, 18.5, 16.2; HRMS(ESI) calcd for $C_{19}H_{20}N_2NaO_3S_2^+$ $[M+Na]^+$ = 411.0813, found = 411.0805.

**(*E*)-N-(2-((3-Cyanopropyl)sulfonyl)-1-phenylvinyl)-N-methylacetamide (4oa)**

Red oil (31.3 mg, 34% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.43 (m, 5H), 6.41 (s, 1H), 3.02 (s, 3H), 2.97 (t, *J* = 7.2 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.17 (s, 3H), 2.13 (p, *J* = 14.3, 7.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.9, 154.4, 132.3, 131.8, 129.8, 128.9, 123.4, 118.2, 53.3, 36.7, 23.5, 18.8, 16.3; HRMS (ESI) calcd for $C_{15}H_{19}N_2O_3S^+$ $[M+H]^+$ = 307.1111, found =307.1109.

**(*E*)-N-Allyl-N-(2-((3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (4pa)**

Red oil (38.9 mg, 39% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.40 (m, 5H), 6.40 (s, 1H), 5.84 – 5.67 (m, 1H), 5.22 (dd, *J* = 10.3, 1.1 Hz, 1H), 5.09 (dd, *J* = 17.1, 1.2 Hz, 1H), 4.05 (dt, *J* = 5.8, 1.3 Hz, 2H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.50 (t, *J* = 7.0 Hz, 2H), 2.15 (s, 3H), 2.12 (p, *J* = 7.1 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.5, 153.6, 132.5, 132.3, 131.8, 129.9, 128.8, 124.6, 118.8, 118.2, 53.3, 51.0, 23.5, 18.8, 16.3; HRMS (ESI) calcd for $C_{17}H_{20}N_2NaO_3S^+$ $[M+Na]^+$ = 355.1087, found =355.1084.

**(*E*)-N-(2-((3-Cyanopropyl)sulfonyl)-1-phenylvinyl)-N-(prop-2-yn-1-yl)acetamide (4qa)**

Red oil (30.7 mg, 31% yield); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.53 (m, 3H), 7.52-7.45 (m, 2H), 6.51 (s, 1H), 4.34 (d, *J* = 2.4 Hz, 2H), 3.00 (t, *J* = 7.3 Hz, 2H), 2.51 (t, *J* = 7.0 Hz, 2H), 2.36 (t, *J* = 2.5 Hz, 1H), 2.15 (p, *J* = 7.1 Hz, 2H), 2.08 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.2, 153.0, 132.3, 132.1, 130.1, 128.9, 124.8, 118.2, 78.0, 73.6, 53.3, 37.8, 23.6, 18.8, 16.3; HRMS(ESI) calcd for $C_{17}H_{19}N_2O_3S^+$ $[M+H]^+$ = 331.1111, found =331.1108.

**(*E*)-N-Benzyl-N-(2-((2-(cyanomethyl)hexyl)sulfonyl)-1-phenylvinyl)acetamide (4ab)**

Pale yellow oil (56.6 mg, 43% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.50 (m, 1H), 7.49 – 7.44 (m, 4H), 7.37 – 7.27 (m, 3H), 7.19 – 7.13 (m, 2H), 6.19 (s, 1H), 4.76 – 4.47 (m, 2H), 2.80 – 2.69 (m, 2H), 2.65 (dd, *J* = 17.1, 5.6 Hz, 1H), 2.49 (dd, *J* = 17.1, 4.3 Hz, 1H), 2.29 – 2.21 (m, 1H), 2.19 (s, 3H), 1.49 – 1.32 (m, 2H), 1.25 (p, *J* = 7.2 Hz, 2H), 1.19 – 1.05 (m, 2H), 0.87 (t, *J* = 7.3 Hz, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 153.1, 136.4, 132.3, 131.9, 130.0, 129.0, 128.9, 128.3, 128.2, 126.1, 117.4, 57.3, 51.1, 33.3, 29.8, 28.4, 23.6, 22.4, 21.7, 14.0; HRMS (ESI) calcd for $C_{25}H_{31}N_2O_3S^+$ $[M+H]^+$ = 439.2050, found =439.2048.

**(*E*)-N-Benzyl-N-(2-((3-cyano-2-phenylpropyl)sulfonyl)-1-phenylvinyl)acetamide (4ac)**

Pale yellow oil (67.4 mg, 49% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.48 (m, 1H), 7.47 – 7.39 (m, 4H), 7.38 – 7.27 (m, 6H), 7.18-7.07 (m, 4H), 6.10 (s, 1H), 4.59 (q, *J* = 15.3 Hz, 2H), 3.64 – 3.48 (m, 1H), 3.21 (dd, *J* = 14.2, 9.4 Hz, 1H), 3.04 (dd, *J* = 14.2, 4.1 Hz, 1H), 2.81 (d, *J* = 6.1 Hz, 2H), 2.14 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.7, 153.3, 139.3, 136.3, 132.3, 131.9, 130.0, 129.4, 129.0, 128.9, 128.6, 128.1, 127.1, 125.2, 117.3, 58.6, 51.2, 36.0, 24.4, 23.6; HRMS (ESI) calcd for $C_{27}H_{27}N_2O_3S^+$ $[M+H]^+$ = 459.1737, found =459.1736.

**(*E*)-N-Benzyl-N-(2-((2-(4-(tert-butyl)phenyl)-3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (4ad)**

Pale yellow oil (78.7 mg, 51% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.48 (m, 1H), 7.47 – 7.40 (m, 4H), 7.37 – 7.27 (m, 5H), 7.16 – 7.10 (m, 2H), 7.06 –7.01 (m, 2H), 6.09 (s, 1H), 4.58 (q, *J* = 15.3 Hz, 2H), 3.62 – 3.43 (m, 1H), 3.22 (dd, *J* = 14.2, 9.4 Hz, 1H), 3.06 (dd, *J* = 14.2, 4.0 Hz, 1H), 2.80 (dd, *J* = 6.0, 2.5 Hz, 2H), 2.14 (s, 3H), 1.30 (s, 9H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 153.3, 151.6, 136.4, 136.2, 132.2, 131.9, 130.0, 129.0, 128.8, 128.2, 128.1, 126.8, 126.3, 125.3, 117.4, 58.7, 51.1, 35.5, 34.7, 31.4, 24.4, 23.6; HRMS (ESI) calcd for $C_{31}H_{35}N_2O_3S^+$ $[M+H]^+$ = 515.2363, found =515.2364.

**(*E*)-N-Benzyl-N-(2-((2-(2-bromophenyl)-3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (4ae)**

Pale yellow oil (85.5 mg, 53% yield); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.53-7.48 (m, 1H), 7.47 – 7.40 (m, 4H), 7.34-7.26 (m, 4H), 7.18 (td, *J* = 7.8, 1.5 Hz, 1H), 7.15 – 7.12 (m, 2H), 7.08 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.17 (s, 1H), 4.80 – 4.50 (m, 2H), 4.19 – 3.92 (m, 1H), 3.28 (dd, *J* = 14.2, 9.9 Hz, 1H), 3.03 (ddd, *J* = 24.0, 15.7, 5.1 Hz, 2H), 2.83 (dd, *J* = 17.1, 4.3 Hz, 1H), 2.16 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 153.8, 137.8, 136.4, 133.8, 132.2, 131.9, 130.0, 130.0, 129.0, 128.9, 128.4, 128.3, 128.1, 124.8, 123.8, 116.9, 57.2, 51.3, 34.8, 23.7, 22.7; HRMS (ESI) calcd for $C_{27}H_{26}BrN_2O_3S^+$ $[M+H]^+$ = 537.0842, found =537.0842.

**(*E*)-N-Benzyl-N-(2-((2-(4-bromophenyl)-3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (4af)**

Pale yellow oil (103.2 mg, 64% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.49 (m, 1H), 7.48 – 7.39 (m, 6H), 7.37 – 7.27 (m, 3H), 7.17 – 7.11 (m, 2H), 7.00 – 6.93 (m, 2H), 6.18 (s, 1H), 4.74 – 4.50 (m, 2H), 3.56-3.45 (m, 1H), 3.15 (dd, *J* = 14.2, 9.4 Hz, 1H), 2.96 (dd, *J* = 14.2, 4.1 Hz, 1H), 2.77 (d, *J* = 6.3 Hz, 2H), 2.15 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.8, 153.4, 138.3, 136.3, 132.5, 132.2, 131.9, 130.0, 129.1, 128.9, 128.8, 128.2, 128.0, 125.1, 122.6, 117.0, 58.2, 51.3, 35.4, 24.2, 23.7. HRMS (ESI) calcd for $C_{27}H_{26}BrN_2O_3S^+$ $[M+H]^+$ = 537.0842, found =537.0843.

**(*E*)-N-Benzyl-N-(2-((2-(benzyloxy)-3-cyanopropyl)sulfonyl)-1-phenylvinyl)acetamide (4ag)**

Pale yellow oil (89.4 mg, 61% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.48 – 7.40 (m, 4H), 7.39 – 7.32 (m, 4H), 7.32 – 7.26 (m, 4H), 7.13 – 7.09 (m, 2H), 6.24 (s, 1H), 4.65 (d, *J* = 15.2 Hz, 1H), 4.53 (d, *J* = 11.2 Hz, 1H), 4.44 (dd, *J* = 13.2, 5.6 Hz, 2H), 4.23 – 4.11 (m, 1H), 3.22 (dd, *J* = 14.6, 6.7 Hz, 1H), 2.96 (dd, *J* = 14.6, 5.5 Hz, 1H), 2.70 (dd, *J* = 17.1, 4.8 Hz, 1H), 2.52 (dd, *J* = 17.1, 4.8 Hz, 1H), 2.10 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.6, 153.0, 136.4, 136.2, 132.4, 131.8, 130.0, 128.9, 128.9, 128.8, 128.5, 128.3, 128.3,

128.1, 125.9, 116.1, 72.7, 69.6, 58.8, 50.9, 23.5, 23.3.HRMS (ESI) calcd for $C_{28}H_{29}N_2O_4S^+$ $[M+H]^+$ = 489.1843, found =489.1840.

**(*E*)-N-Benzyl-N-(2-((1-(cyanomethyl)-2,3-dihydro-1H-inden-2-yl)sulfonyl)-1-phenylvinyl)acetamide (4ai)**

Pale yellow oil (36.7 mg, 26% yield); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.43 (m, 5H), 7.39 – 7.27 (m, 5H), 7.24 – 7.11 (m, 4H), 6.20 (s, 1H), 4.64 (s, 2H), 3.94 (dd, *J* = 12.1, 5.2 Hz, 1H), 3.56 – 3.37 (m, 1H), 3.17 (dd, *J* = 16.3, 7.8 Hz, 1H), 3.02 (dd, *J* = 16.4, 9.2 Hz, 1H), 2.86 (qd, *J* = 17.1, 4.9 Hz, 2H), 2.18 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.8, 153.9, 139.5, 139.0, 136.5, 132.4, 132.0, 129.9, 129.1, 128.9, 128.9, 128.1, 125.0, 123.6, 123.6, 117.2, 66.8, 51.3, 41.3, 33.5, 23.7, 22.8, 9.9; HRMS (ESI) calcd for $C_{28}H_{27}N_2O_3S^+$ $[M+H]^+$ = 471.1737, found = 471.1736.

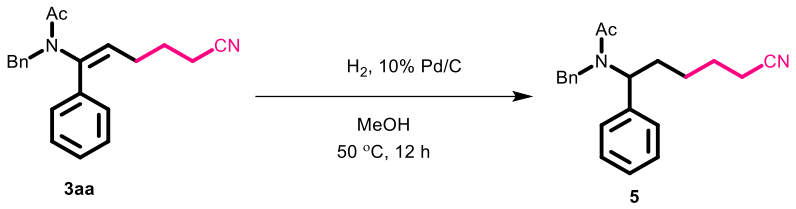
**3. Gram-scale experiment:**

An oven dried 25mL vial equipped with a magnetic stir bar was charged with enamide **1a** (1.02 g, 4.0 mmol), oxime ester **2a** (1.23 g, 4.8 mmol) and Rose bengal (81.4 mg, 0.08 mmol). The vial was sealed with a septum, evacuated and backfilled with nitrogen three times. 13.3 mL of DMSO was then added via syringe with gentle stirring under $N_2$ atmosphere. The vial was introduced into *Penn PhD Photoreactor M2* (3W blue LED, 451nm) and allowed to stir for 8 h. After completion of reaction, the reaction mixture was diluted with ethyl acetate (25 mL), and washed successively with water (25 mL×2), aq.$NaHCO_3$ solution (25 mL×2) and brine solution (25 mL×2). The organic layer was dried over anhydrous sodium sulfate, concentrated and purified via flash chromatography on silica gel to get the desired compound **3aa** (0.94 g, 74%).

**4. Synthetic applications :**

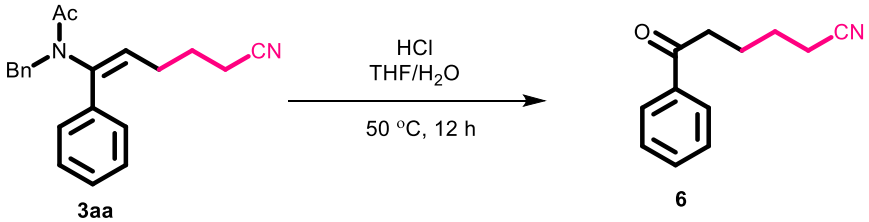
**4.1) Synthetic applications of cyanoalkylated Enamides:**

**N-Benzyl-N-(5-cyano-1-phenylpentyl)acetamide (5)**




Enamide **3aa** (31.8 mg, 0.1mmol) in methanol (2.0 mL) was hydrogenated at 50 °C under hydrogen balloon in the presence of palladium/charcoal (4.0 mg) for 12 h. Upon completion, the reaction mixture was filtered over Celite bed and the solvent was removed under vacuum. The residue was purified by flash chromatography (petroleum ether/ethylacetate) to afford the desired product **5** in 66% yield (21.1 mg) as a green oil. $^{1}$H NMR (400 MHz, $CDCl_3$) for two conformers: δ 7.42 – 7.15 (m, 9H), 6.97 (d, $J$ = 7.1 Hz, 1H), 5.92 and 4.95 (2 × t, $J_{5.92}$ = 7.7 Hz and $J_{4.95}$ = 7.2 Hz, 1H ), 5.03 and 4.40 (2 × d, $J_{5.03}$ = 15.3 Hz and $J_{4.40}$ = 17.5 Hz, 1H), 4.23 and 3.74 (2 × d, $J_{4.23}$ = 17.5 Hz and $J_{3.74}$ = 15.3 Hz, 1H), 2.36 and 2.07 (2 × s, 3H), 2.25 (t, $J$ = 6.9 Hz 2H), 1.96 – 1.77 (m, 2H), 1.70 – 1.60 (m, 1H), 1.60 – 1.50 (m, 1H), 1.49 – 1.38 (m, 2H); $^{13}$C NMR for two conformers (126 MHz, $CDCl_3$) δ 172.1, 139.2, 137.9, 129.8, 129.1, 129.0, 128.9, 128.7, 128.7, 128.6, 128.4, 128.1, 128.0, 127.9, 127.5, 127.3, 127.0, 126.2, 125.7, 119.7, 61.9, 60.5, 56.3, 49.0, 48.2, 45.7, 31.7, 31.3, 30.1, 27.4, 26.1, 25.9, 25.3, 25.1, 22.8, 22.7, 22.7, 22.3, 21.1, 17.1, 16.7, 16.6, 14.3, 14.2; HRMS(ESI) calcd for $C_{21}H_{25}N_2O^+$ $[M+H]^+$ = 321.1961, found = 321.1967.

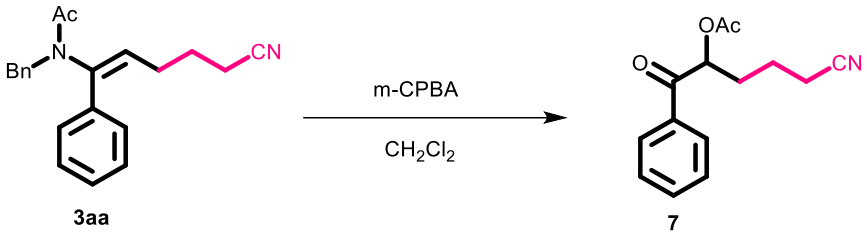
**6-Oxo-6-phenylhexanenitrile (6)**




To a solution of **3aa** (31.8 mg, 0.1 mmol) in a mixed solvent of THF/$H_2O$ (1:1, 2.0 mL) was added concentrated hydrochloric acid (1.0 mL), and the vial was heated at 50 °C for 24 h. Upon completion of the reaction, the mixture was diluted with EtOAc. The solvent was then removed

under vacuo. The residue was purified by flash chromatography (petroleum ether/ethylacetate) to afford the desired product **6** in 82% yield (15.3 mg) as white solid. mp = 77 – 79 °C; $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.92 (m, 2H), 7.60 – 7.54 (m, 1H), 7.49 – 7.42 (m, 2H), 3.03 (t, *J* = 7.0 Hz, 2H), 2.40 (t, *J* = 7.1 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.81 – 1.70 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.2, 136.8, 133.3, 128.7, 128.0, 119.6, 37.4, 25.1, 23.2, 17.3; HRMS (ESI) calcd for $C_{12}H_{14}NO^+$ $[M+H]^+$ = 188.1070, found = 188.1075.

**5-Cyano-1-oxo-1-phenylpentan-2-yl acetate (7)**

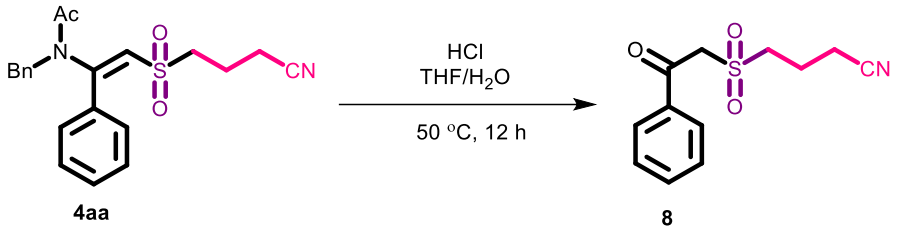



**3aa** **7**

Enamide **3aa** (31.8 mg, 0.1 mmol) was added into a tube. Then 70% m-CPBA (74 mg, 0.3 mmol) was added to the stirred solution of the enamide in $CH_2Cl_2$ (3.0 mL) at 0 °C and the resultant suspension stirred for 30 min before warming to room temperature. The resulting mixture was stirred at room temperature for 24 hours as monitored by TLC. Upon completion, the solvent was then removed under vacuum. The residue was purified by flash chromatography (petroleum ether/ethylacetate) to afford the desired product **7** in 87% yield (21.3 mg) as yellow syrup. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.92 (m, 2H), 7.65 – 7.57 (m, 1H), 7.54 – 7.43 (m, 2H), 5.92 (dd, *J* = 8.0, 4.2 Hz, 1H), 2.48 – 2.35 (m, 2H), 2.17 (s, 3H), 2.14 – 2.04 (m, 1H), 2.04 – 1.93 (m, 1H), 1.88 – 1.77 (m, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 195.8, 170.5, 134.5, 134.1, 129.1, 128.5, 119.1, 74.1, 30.1, 21.5, 20.8, 17.1; HRMS (ESI) calcd for $C_{14}H_{16}NO_3^+$ $[M+H]^+$ = 246.1125, found = 246.1114.

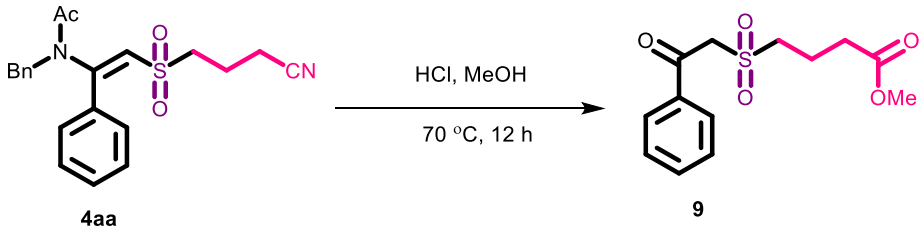
**4.2) Synthetic applications of cyanoalkylsulfonylated Enamides:**

**4-((2-Oxo-2-phenylethyl)sulfonyl)butanenitrile (8)**




To a solution of 3aa (38.2 mg, 0.1 mmol) in a mixed solvent of THF/$H_2O$ (1:1, 2.0 mL) was added concentrated hydrochloric acid (1.0 mL), and the vial was heated at 50 °C for 24 h. Upon completion of the reaction, the mixture was diluted with EtOAc (20 mL). The solvent was then removed under vacuo. The residue was purified by flash chromatography (petroleum ether/ethylacetate) to afford the desired product **8** in 79% yield (19.8 mg) as colourless oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 4.65 (s, 2H), 3.45 (t, *J* = 7.4 Hz, 2H), 2.63 (t, *J* = 7.1 Hz, 2H), 2.29 (p, *J* = 7.2 Hz, 2H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ 189.1, 135.6, 135.0, 129.3, 129.2, 118.3, 60.1, 51.9, 18.4, 16.4; HRMS(ESI) calcd for $C_{12}H_{14}NO_3S^+$ $[M+H]^+$ = 252.0689, found = 252.0681.

**Methyl 4-((2-oxo-2-phenylethyl)sulfonyl)butanoate (9)**

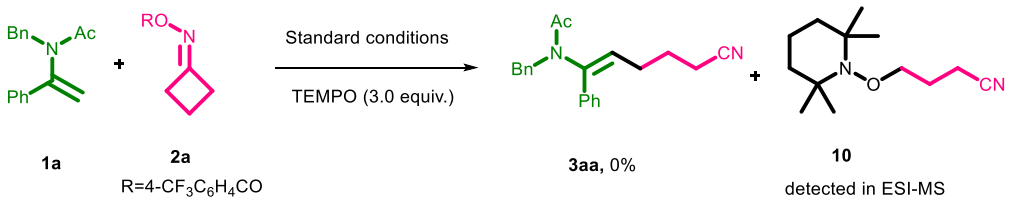



To a Schlenk tube were added 3aa (38.2 mg, 0.1 mmol), 1.0 mL conc. HCl and 1.0 mL MeOH. Then the mixture was heated at 70 °C and stirred overnight under reflux conditions. After cooling to room temperature, the reaction mixture was quenched with 10 mL of $H_2O$, and

extracted with EtOAc (10 mL×3). The combined organic layer was washed with brine (15 mL), dried over anhydrous $Na_2SO_4$, filtered, and concentrated in vacuum. The residue was purified by flash chromatography (petroleum ether/ethylacetate) to afford the desired product **9** in 72 % yield (20.5 mg) as a colourless oil. $^1$H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 4.60 (s, 2H), 3.70 (s, 3H), 3.37 (t, *J* = 8.1 Hz, 2H), 2.55 (t, *J* = 7.1 Hz, 2H), 2.23 (p, *J* = 7.6 Hz, 2H); $^{13}$C NMR (126 MHz, $CDCl_3$) δ 189.3, 172.6, 135.8, 134.8, 129.4, 129.1, 59.7, 52.8, 52.0, 32.2, 17.7; HRMS(ESI) calcd for $C_{13}H_{17}O_5S^+$ $[M+H]^+$ = 285.0791, found = 285.0783

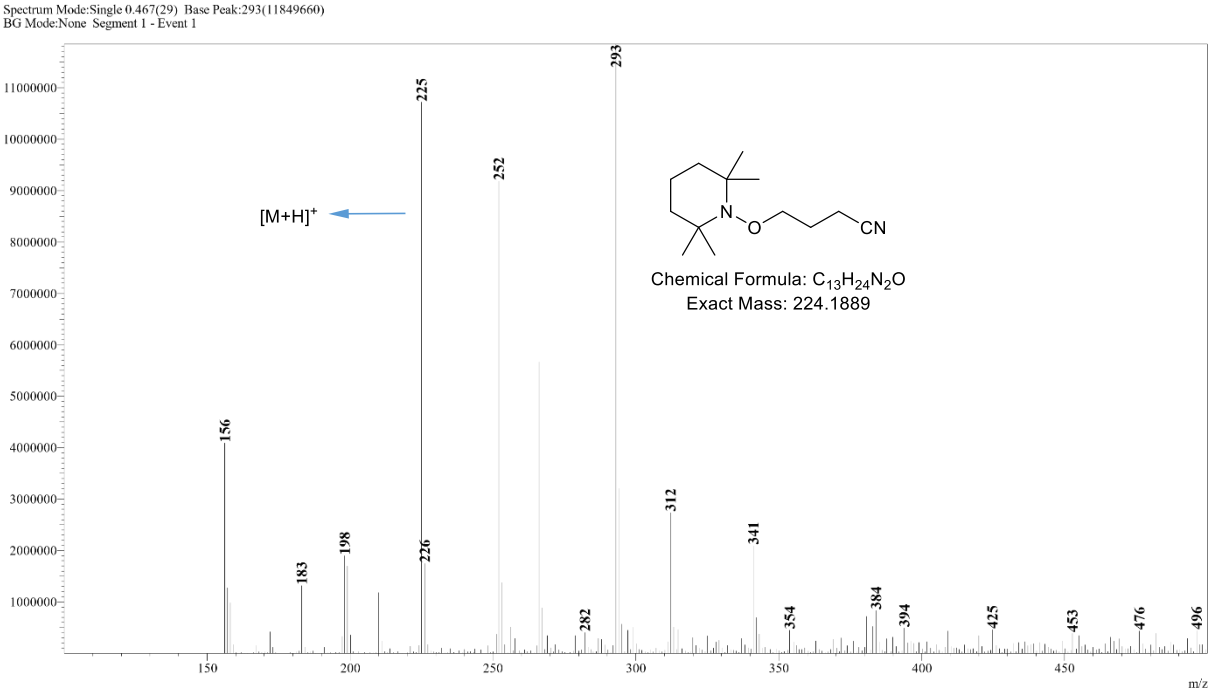
## 5. Control experiments for mechanistic studies:

### 5.1) Radical inhibition/trapping experiments:

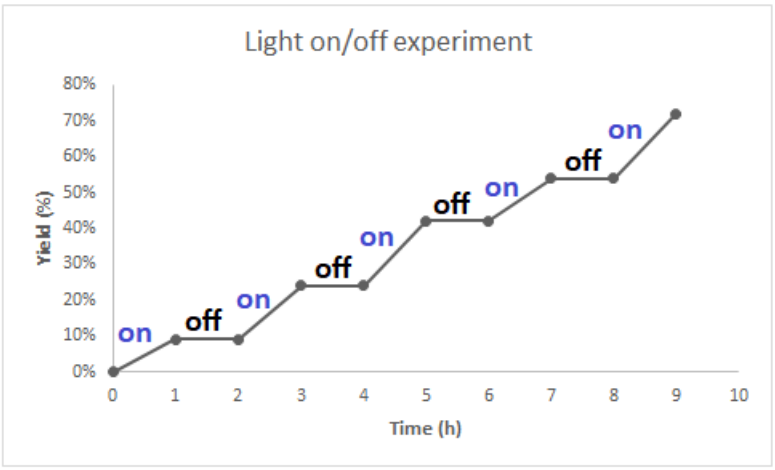



**1a** **2a** R=4-$CF_3C_6H_4CO$ **3aa**, 0% **10** detected in ESI-MS

An oven dried vial equipped with a magnetic stir bar was charged with enamide **1a** (93.6 mg, 0.3 mmol), oxime ester **2a** (92.5 mg, 0.36 mmol), Rose bengal (6.1 mg, 0.006 mmol) and TEMPO (140.6 mg, 0.9 mmol). The vial was sealed with a septum, evacuated and backfilled with nitrogen three times. 1.0 mL of DMSO was then added via syringe with gentle stirring under $N_2$ atmosphere. The vial was introduced into *Penn PhD Photoreactor M2* (3W blue LED, 451nm) and allowed to stir for 6 h. After completion of reaction, the reaction mixture was diluted with ethyl acetate (15 mL), and washed successively with water (10 mL×2), aq. $NaHCO_3$ solution (10 mL×2) and brine solution (10 mL×2). The organic layer was dried over anhydrous sodium sulfate, concentrated. In this reaction, the formation of product 3aa was completely suppressed. The cyanoalkyl-TEMPO adduct **10** was characterized by ESI-MS.




**5.2) Light on/off experiment:**




Enamide **1a** (93.6 mg, 0.3 mmol), oxime ester **2a** (92.5 mg, 0.36 mmol), Rose bengal (6.1 mg, 0.006 mmol) and internal standard 1,3,5-trimethoxy benzene (50.5 mg, 0.3 mmol) were weighed in a vial. The vial was sealed with a septum, evacuated and backfilled with nitrogen three times. Later 1.0 mL of DMSO was added via syringe under $N_2$ atmosphere. Then this sealed vial was irradiated with blue LED alternately over 30 minutes (i.e. the reaction mixture was under light for 30 minutes followed by in the absence of light for the next 30 minutes).

After each 30 minutes of interval, some aliquot was removed from the reaction mixture and analyzed by $^{1}H$ nmr to determine the yield. As shown in the above graph, there was no progress in this transformation when the light was switched off. The results of this experiment indicate that continuous irradiation is necessary for this transformation, indicating that the possibility of a radical chain mechanism is highly unlikely in this scenario.

**5.3) Fluorescence quenching:**

Oxime ester **2a**: To a nitrogen degassed 2.5 mL solution of $2*10^{-5}$ M Rose bengal in DMSO placed in a quartz cuvett, was added 0.2 mL, 0.4 mL and 0.6 mL of 0.001 M oxime ester **2a** in DMSO consecutively at room temperature. These solutions were irradiated at 565 nm and fluorescence was measured from 530 nm to 800 nm.

Enamide **1a**: To a nitrogen degassed 2.5 mL solution of $2*10^{-5}$ M Rose bengal in DMSO placed in a quartz cuvett, was added 0.2 mL, 0.4 mL and 0.6 mL of 0.001 M enamide **1a** in DMSO consecutively at room temperature. These solutions were irradiated at 565 nm and fluorescence was measured from 530 nm to 800 nm.

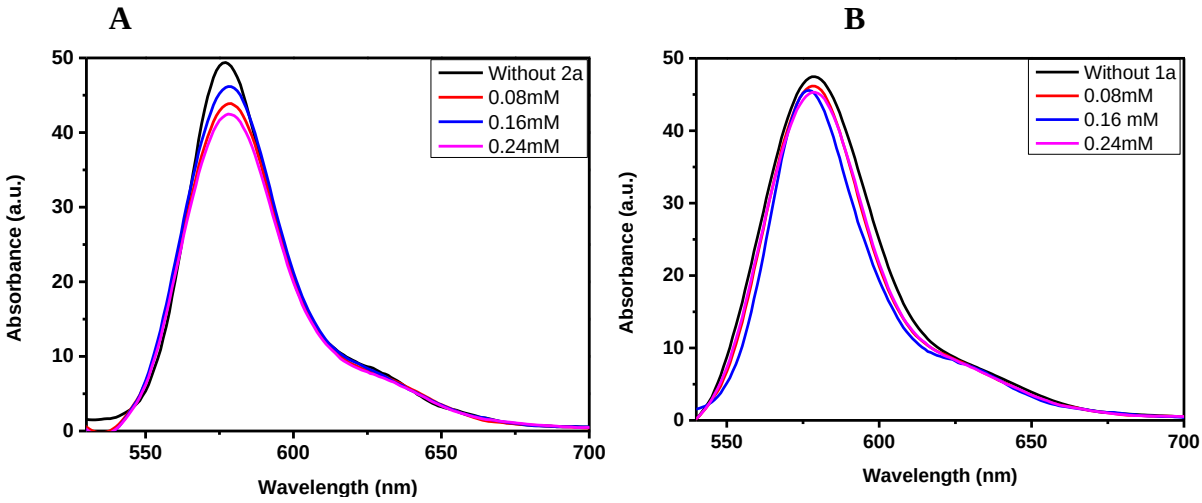



Figure S1. A) Fluorescence of Rose Bengal ($2*10^{-5}$ M) with oxime ester **2a** (0.08 – 0.24 mM) in DMSO. B) Fluorescence of Rose Bengal ($2*10^{-5}$ M) with enamide **1a** (0.08 – 0.24 mM) in DMSO.

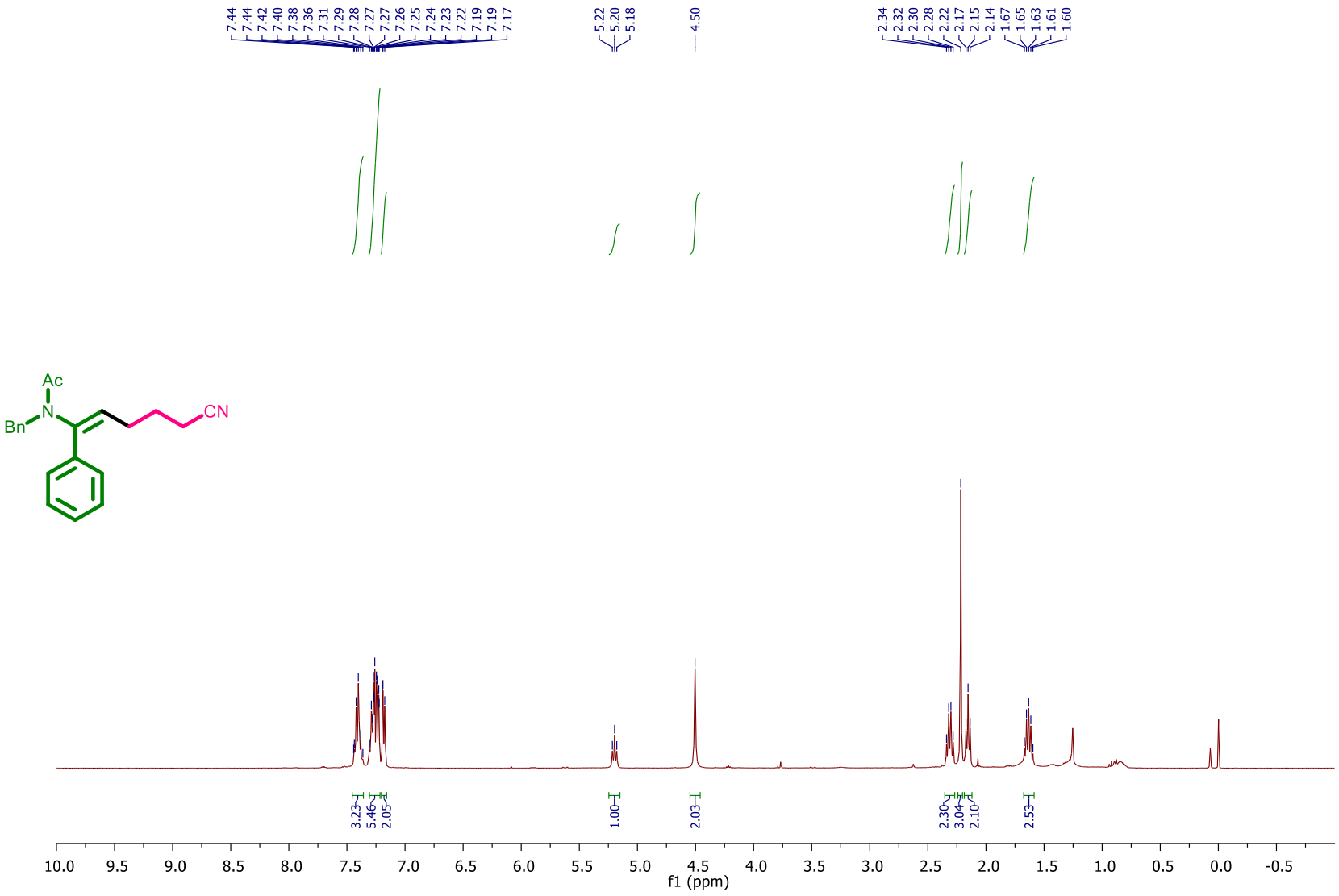
These results indicate that the luminescence quenching of Rose bengal was much more significant with oxime ester **2a** than enamide **1a**. So we hypothesized that reduction of oxime ester **2a** by photo-exited Rose Bengal was the initial step.

**References:**

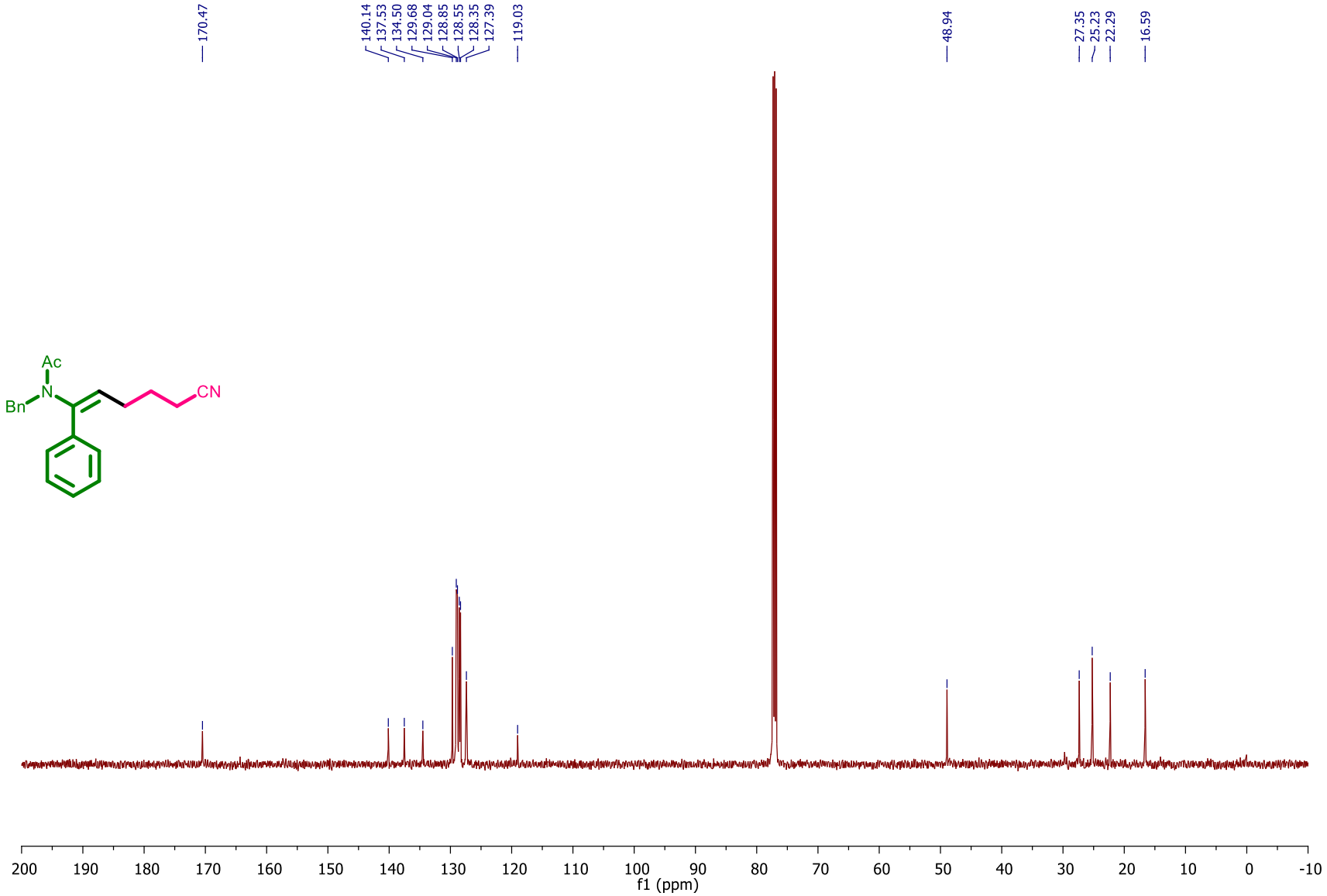

1. a) J. Y. Guo, Z. Y. Zhang, T. Guan, L. W. Mao, Q. Ban, K. Zhao and T. P. Loh, *Chem. Sci*., 2019, **10**, 8792–8798; b) T. H. Zhu, Z. Y. Zhang, J. Y. Tao, K. Zhao and T. P. Loh, *Org. Lett*., 2019, **21**, 6155–6159; c) T. H. Zhu, X. C. Zhang, X. L. Cui, Z. Y. Zhang, H. Jiang, S. S. Sun, L. L. Zhao, K. Zhao and T. P. Loh, *Adv. Synth. Catal*., 2019, **361**, 3593–3598; d) K. Zhao, Z. Y. Zhang, X. L. Cui, Y. X. Wang, X. D. Wu, W. M. Li, J. X. Wu, L. L. Zhao, J. Y. Guo and T. P. Loh, *Org. Lett*., 2020, **22**, 9029–9035; e) K. Zhao, X. C. Zhang, J. Y. Tao, X. D. Wu, J. X. Wu, W. M. Li, T. H. Zhu and T. P. Loh, *Green Chem*., 2020, **22**, 5497–5503; f) J.-Y. Tao, Y.-X. Wang, Q.-H. Zhang, K. Ni, T.-H. Zhu and K. Zhao, *Green Chem.*, 2022, **24**, 4004–4011.

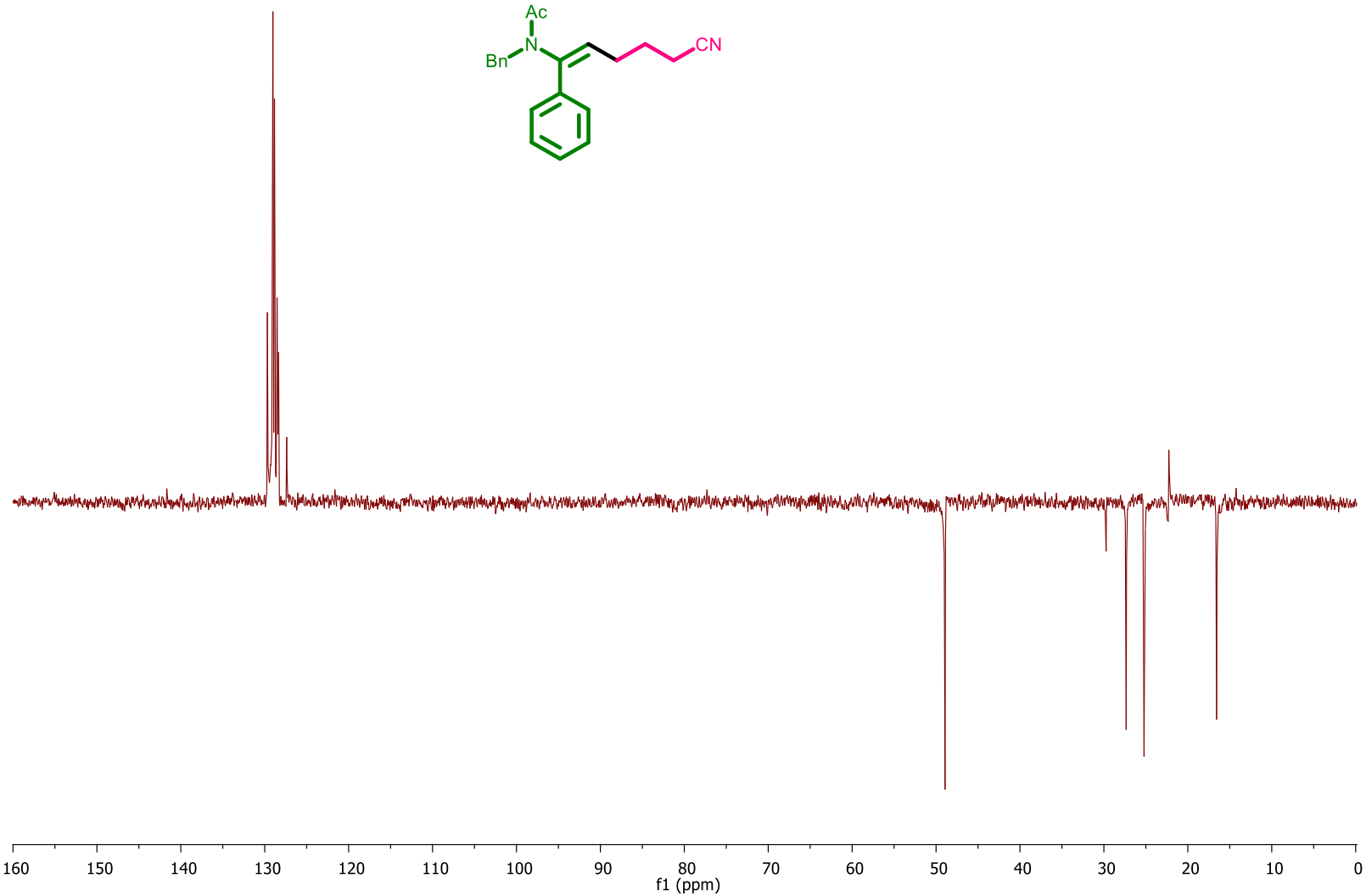
2. a) L. Li, H. Chen, M. Mei and L. Zhou, *Chem. Commun*, 2017, **53**, 11544-11547; b) X. Shen, J. J. Zhao and S. Yu, *Org. Lett.*, 2018, **20**, 5523–5527; c) X. Y. Yu, J. R. Chen, P. Z. Wang, M. N. Yang, D. Liang and W. J. Xiao, *Angew. Chem., Int. Ed.*, 2018, **57**, 738–743; d) Y. Liu, Q.-L. Wang, Z. Chen, H. Li, B.-Q. Xiong, P.-L. Zhang and K.-W. Tang, *Chem. Commun*, 2020, **56**, 3011; e) X. Zhao, L. Ji, Y. Gao, T. Sun, J. Qiao, A. Li and K. Lu, *J. Org. Chem.*, 2021, **86**, 11399–11406; f) N. Zhou, Z. Xia, S. Wu, K. Kuang, Q. Xu and M. Zhang, *J. Org. Chem.*, 2021, **86**, 15253–15262.

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

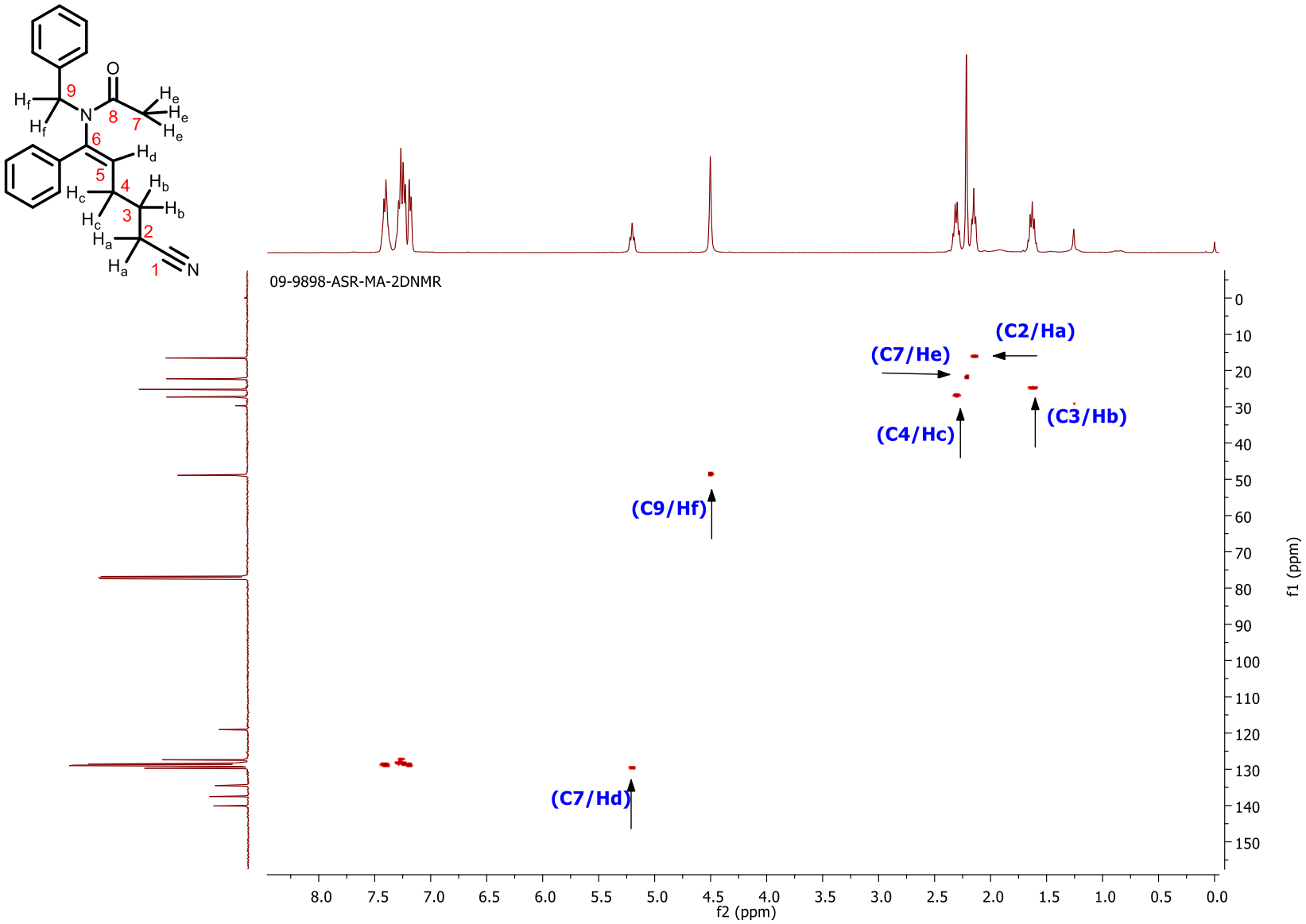


$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3aa)**

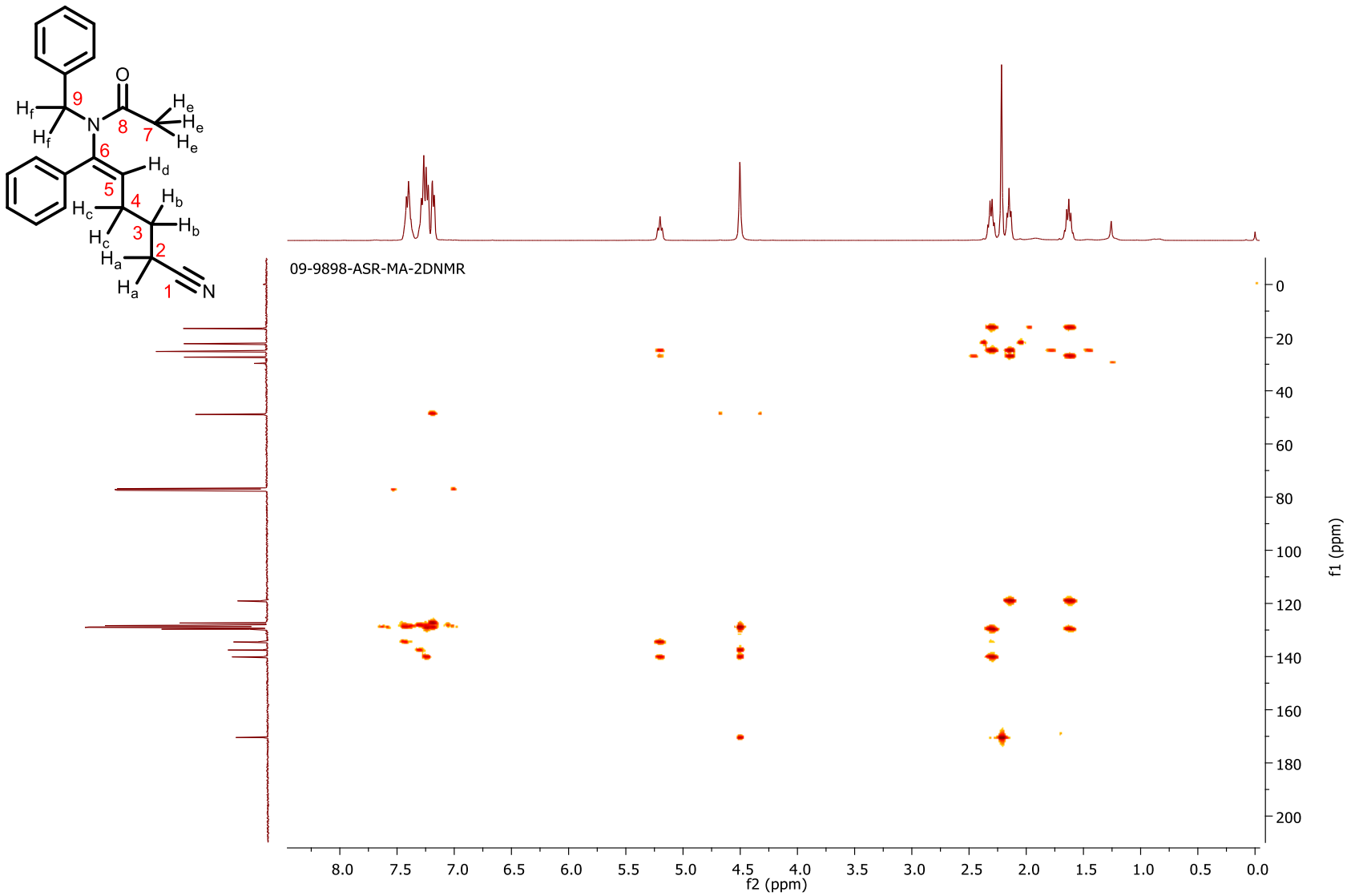




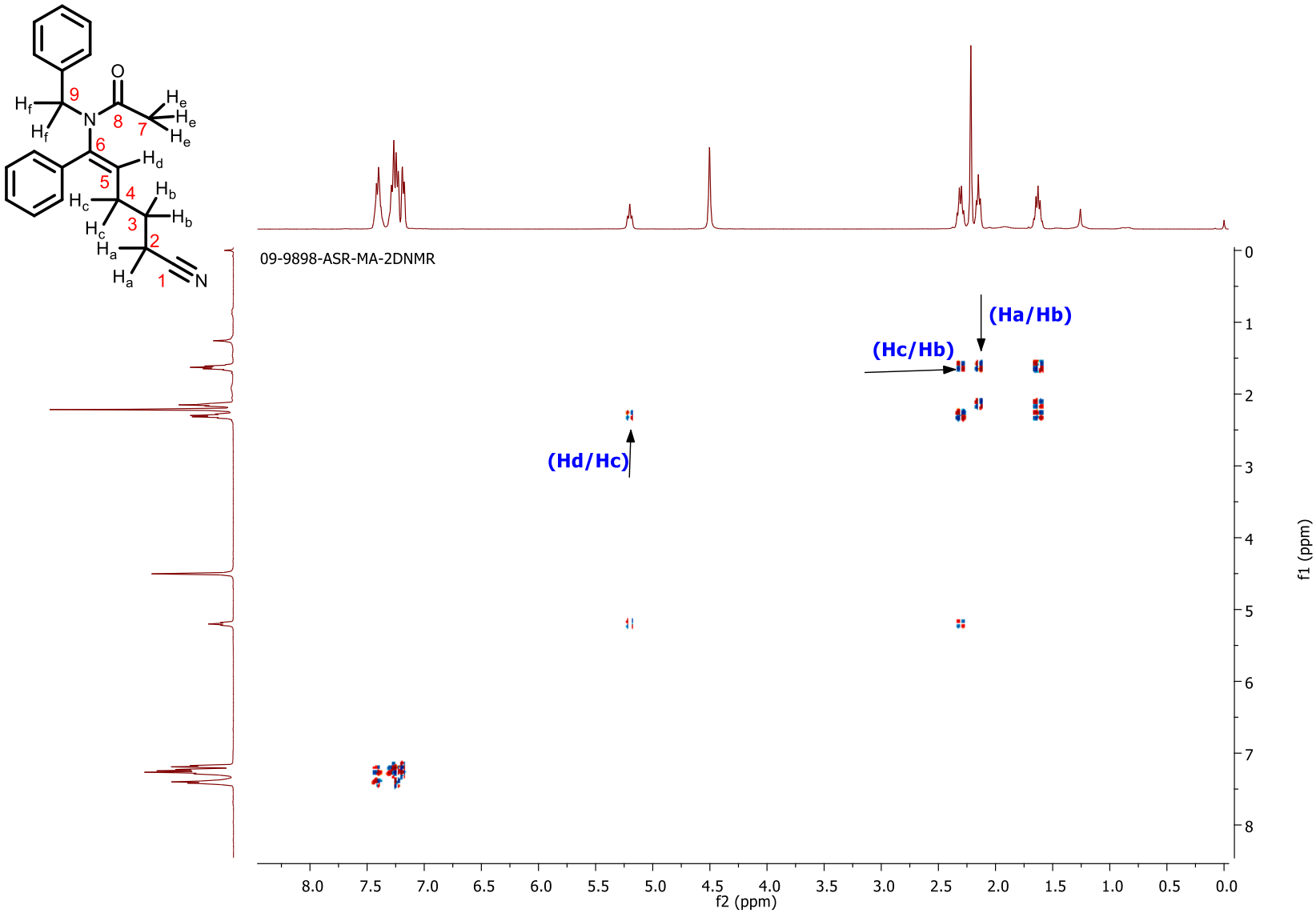

**DEPT spectrum of 3aa**



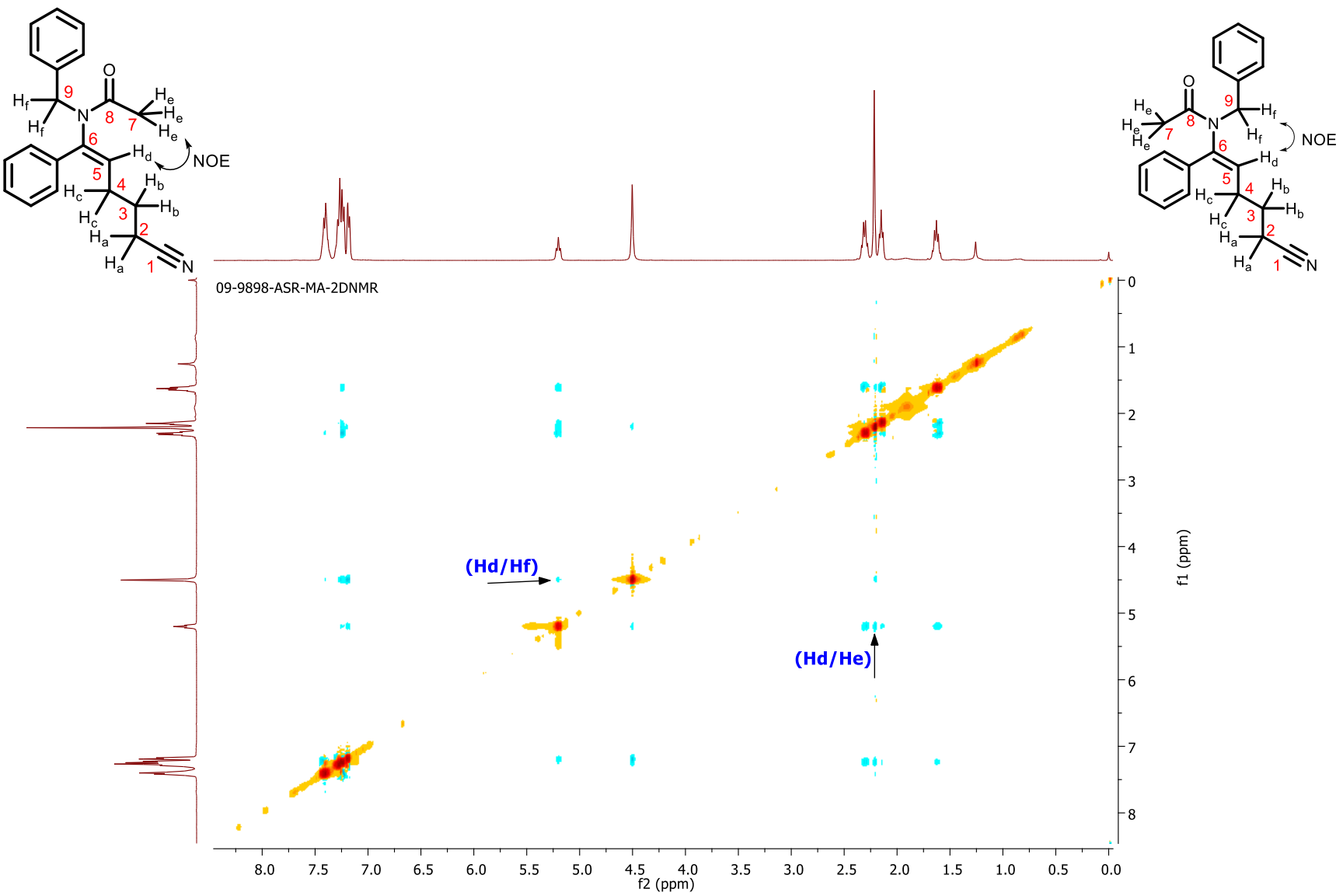

**$^{1}$H-$^{13}$C 2D-HSQC spectrum of 3aa**




**$^{1}$H-$^{13}$C 2D-HMBC spectrum of 3aa**

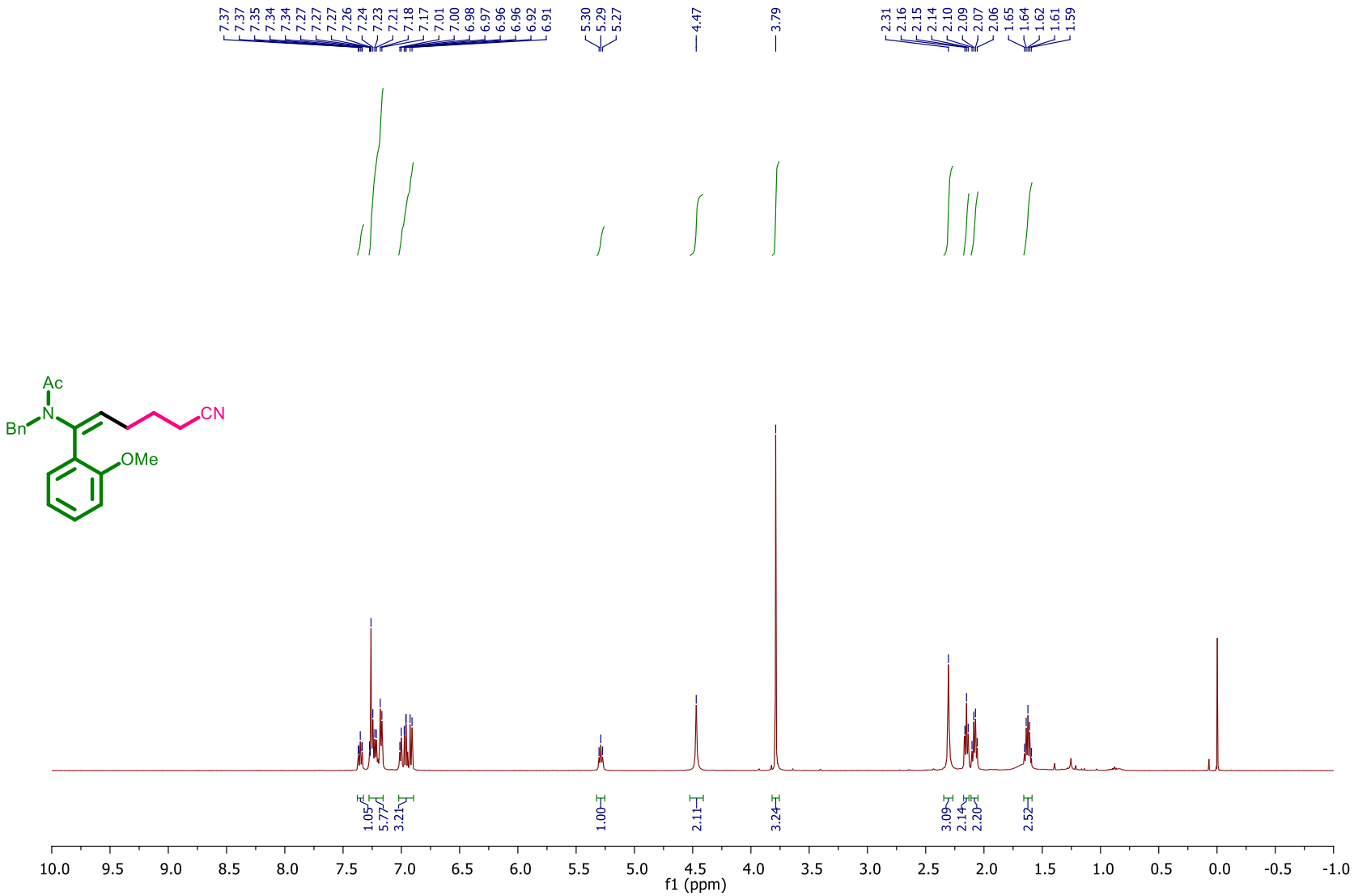



**$^{1}$H-$^{1}$H 2D-COSY spectrum of 3aa**

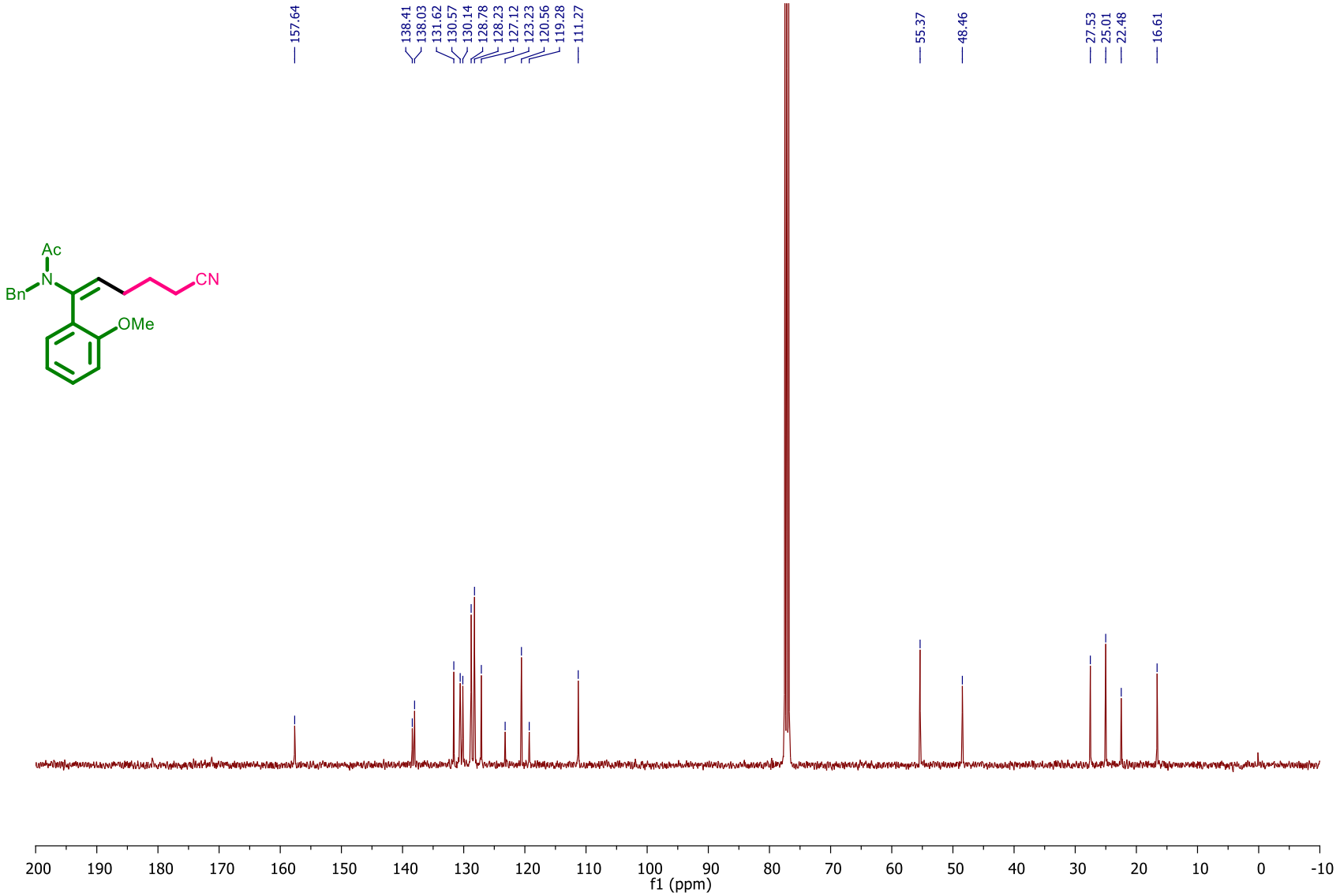



**$^{1}$H-$^{1}$H 2D-NOESY spectrum of 3aa**

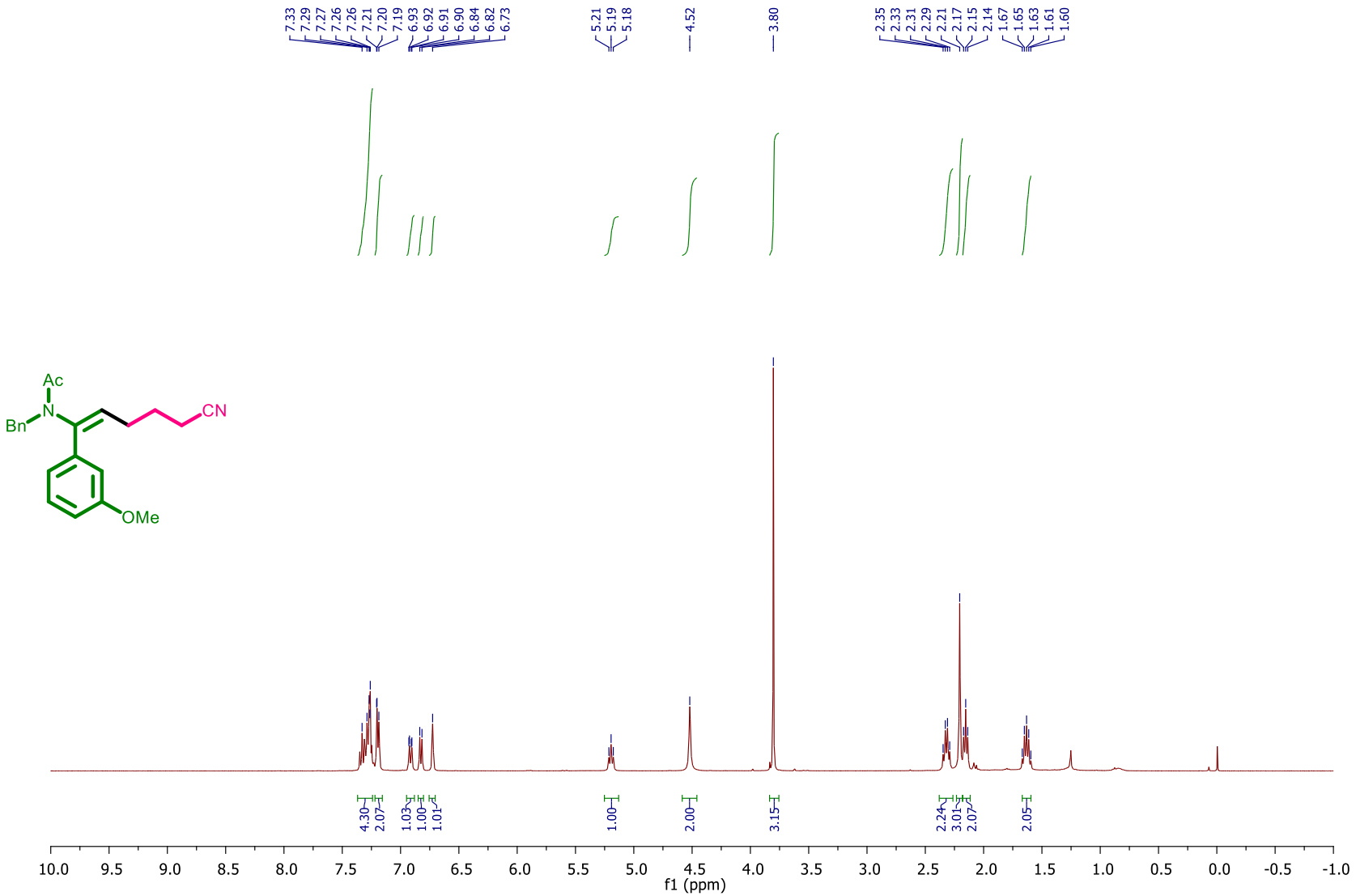
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3ba)**



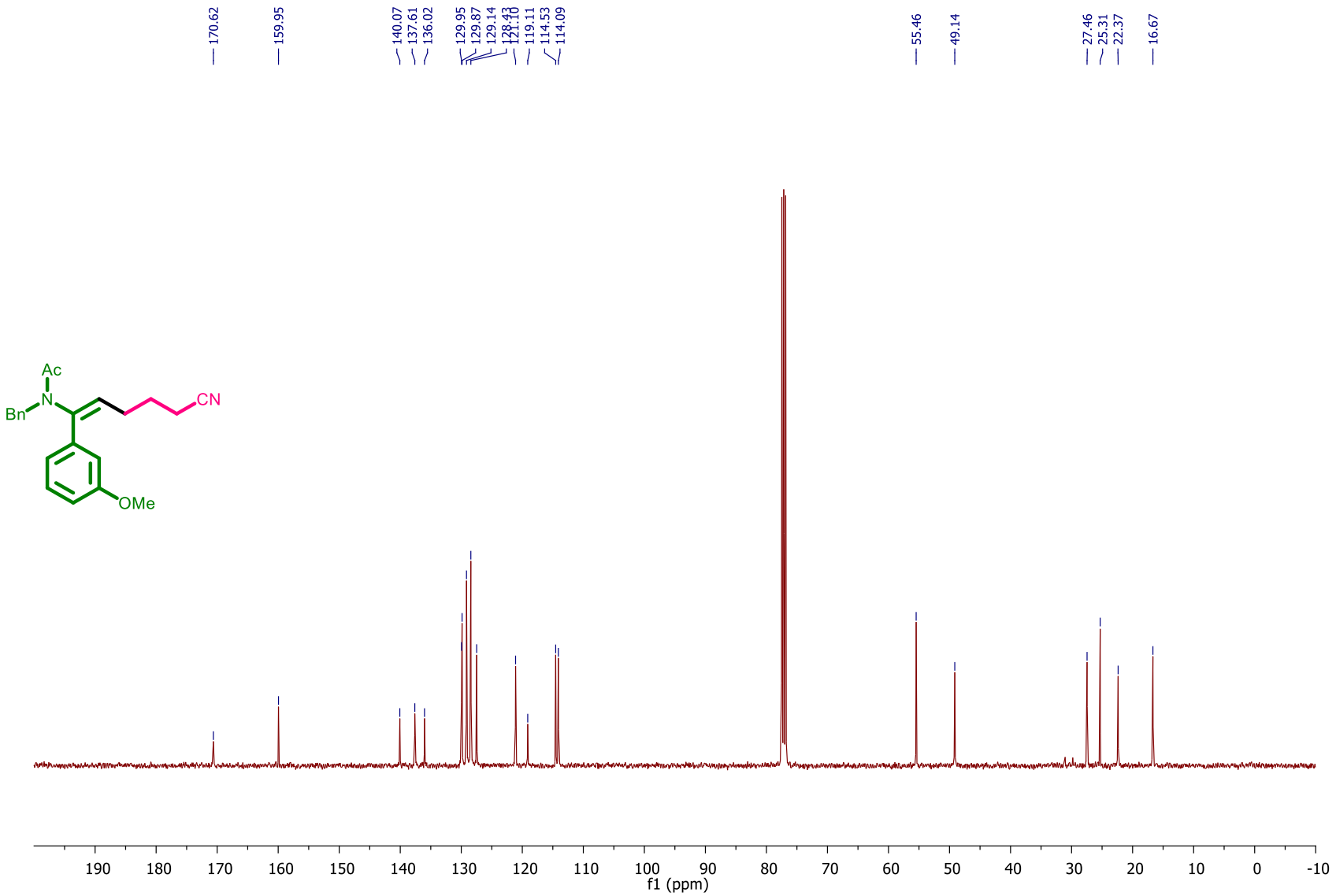
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ba)**



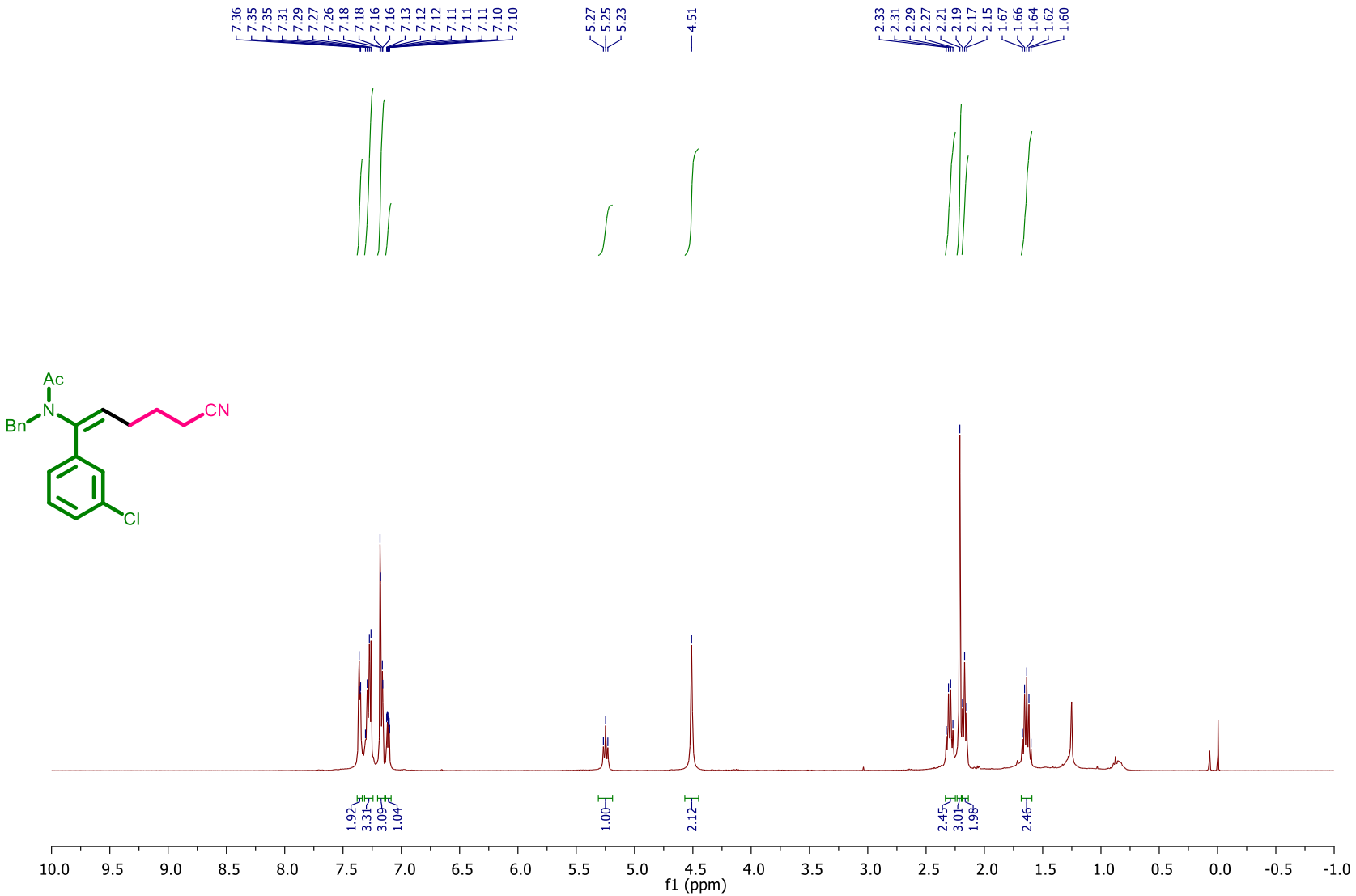
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ca)**



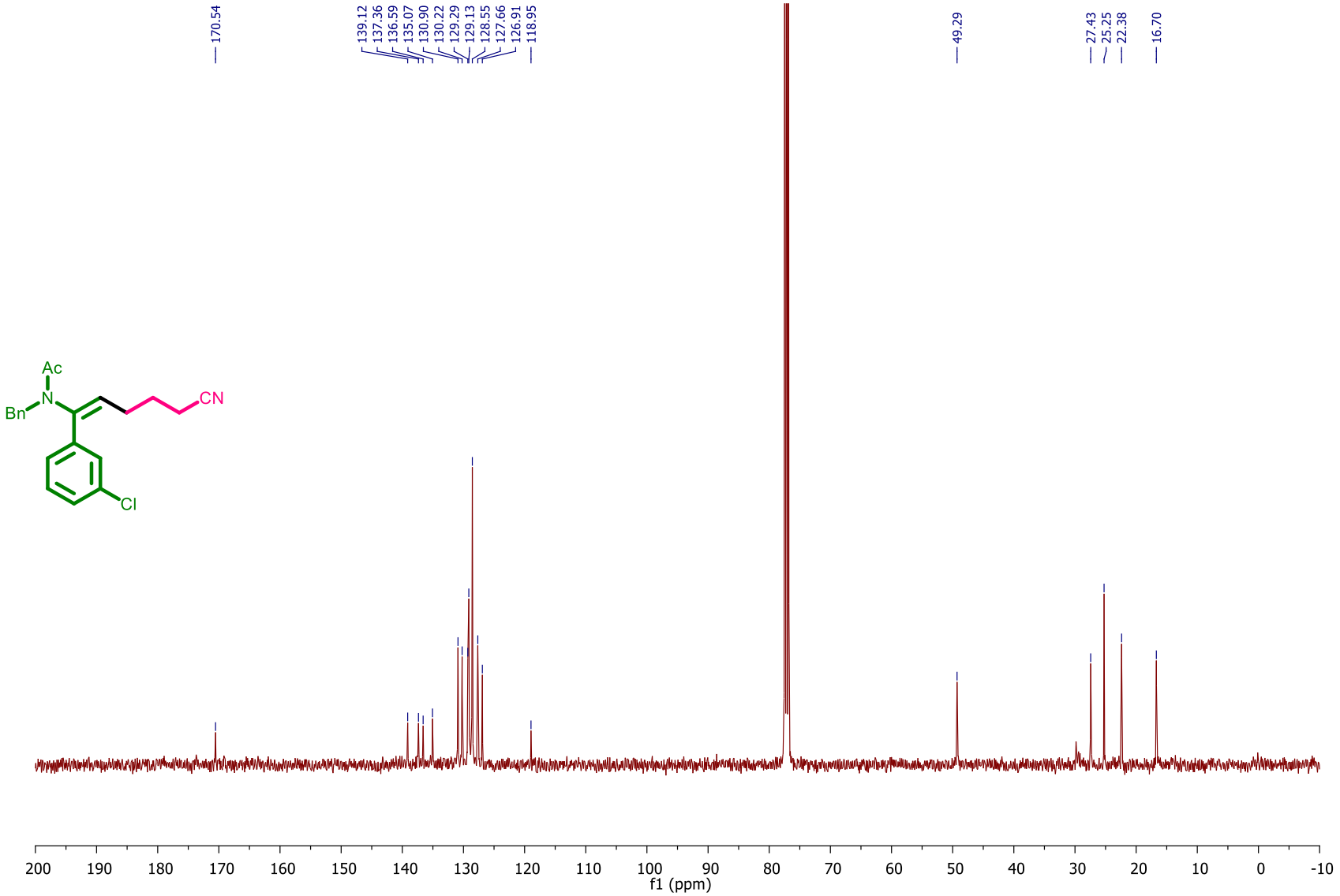
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ca)**



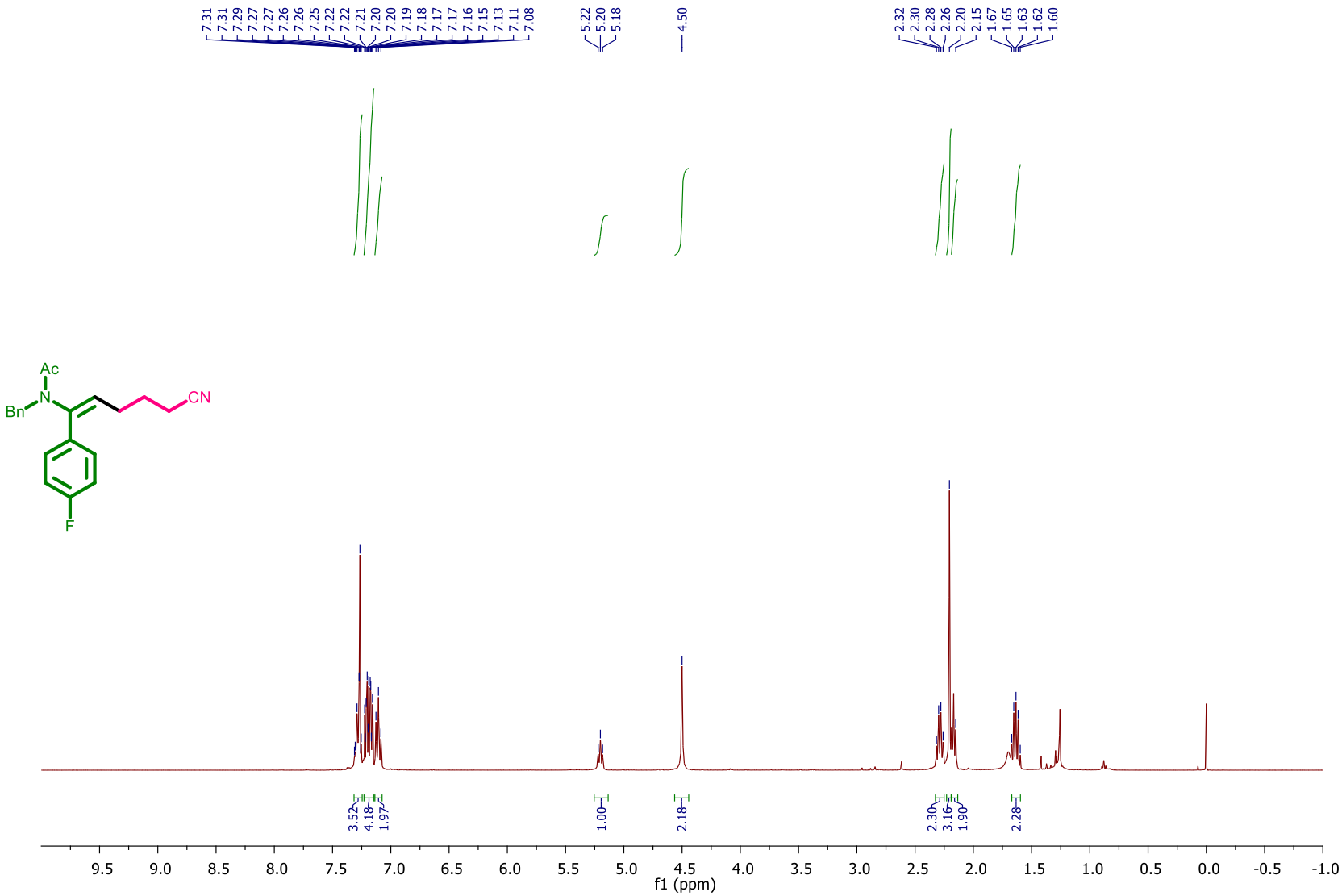
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3da)**



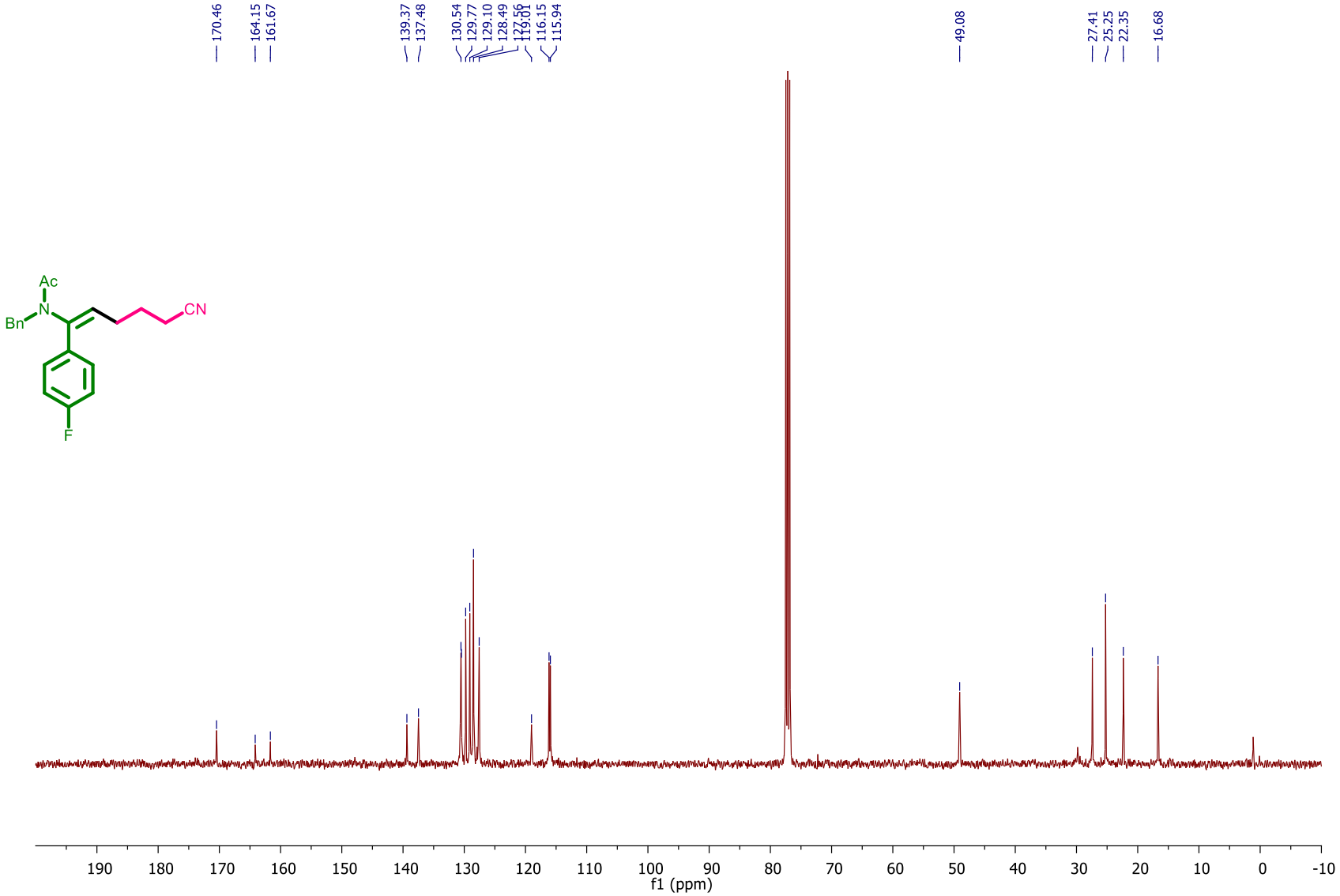
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3da)**



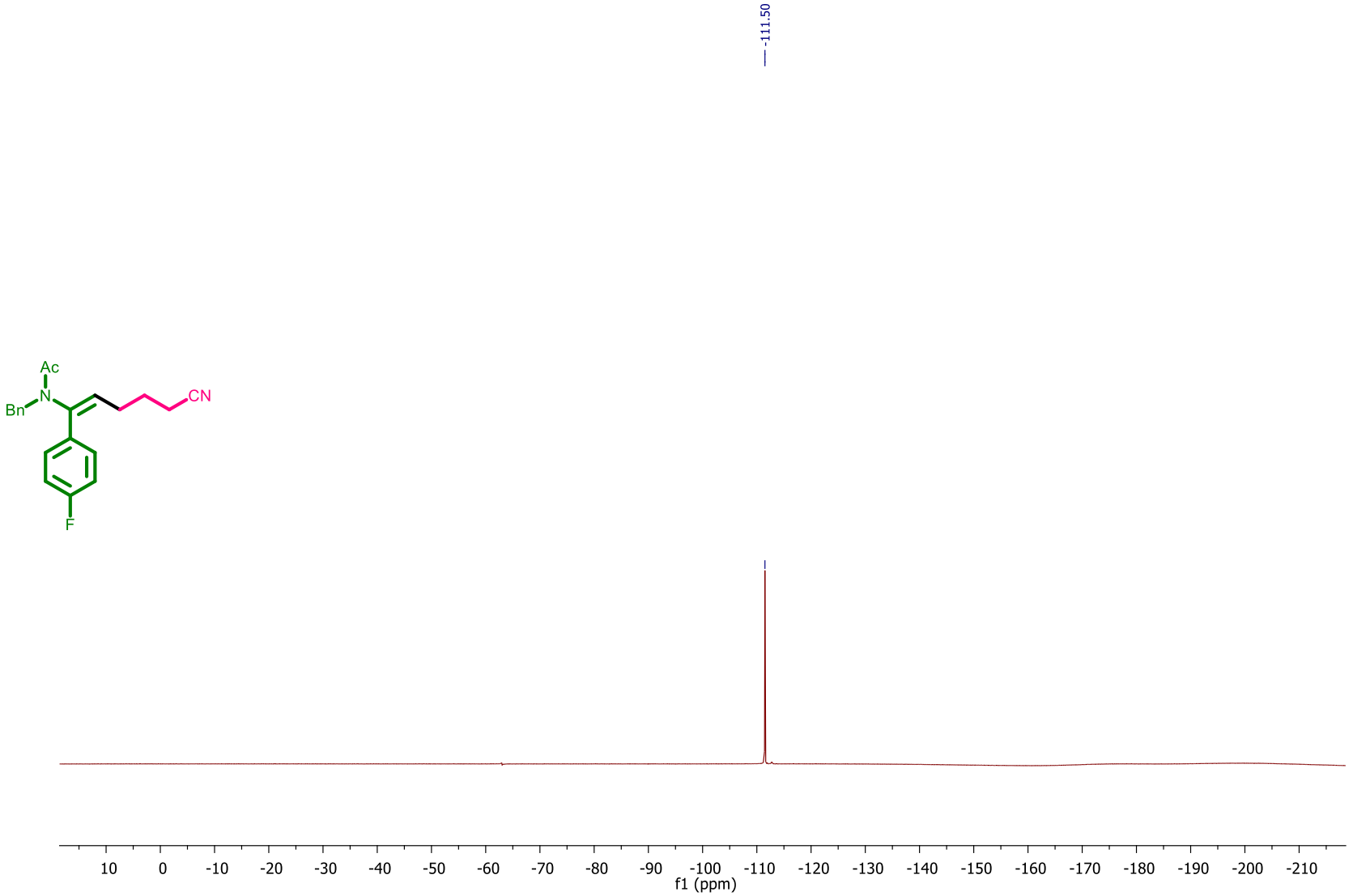
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ea)**



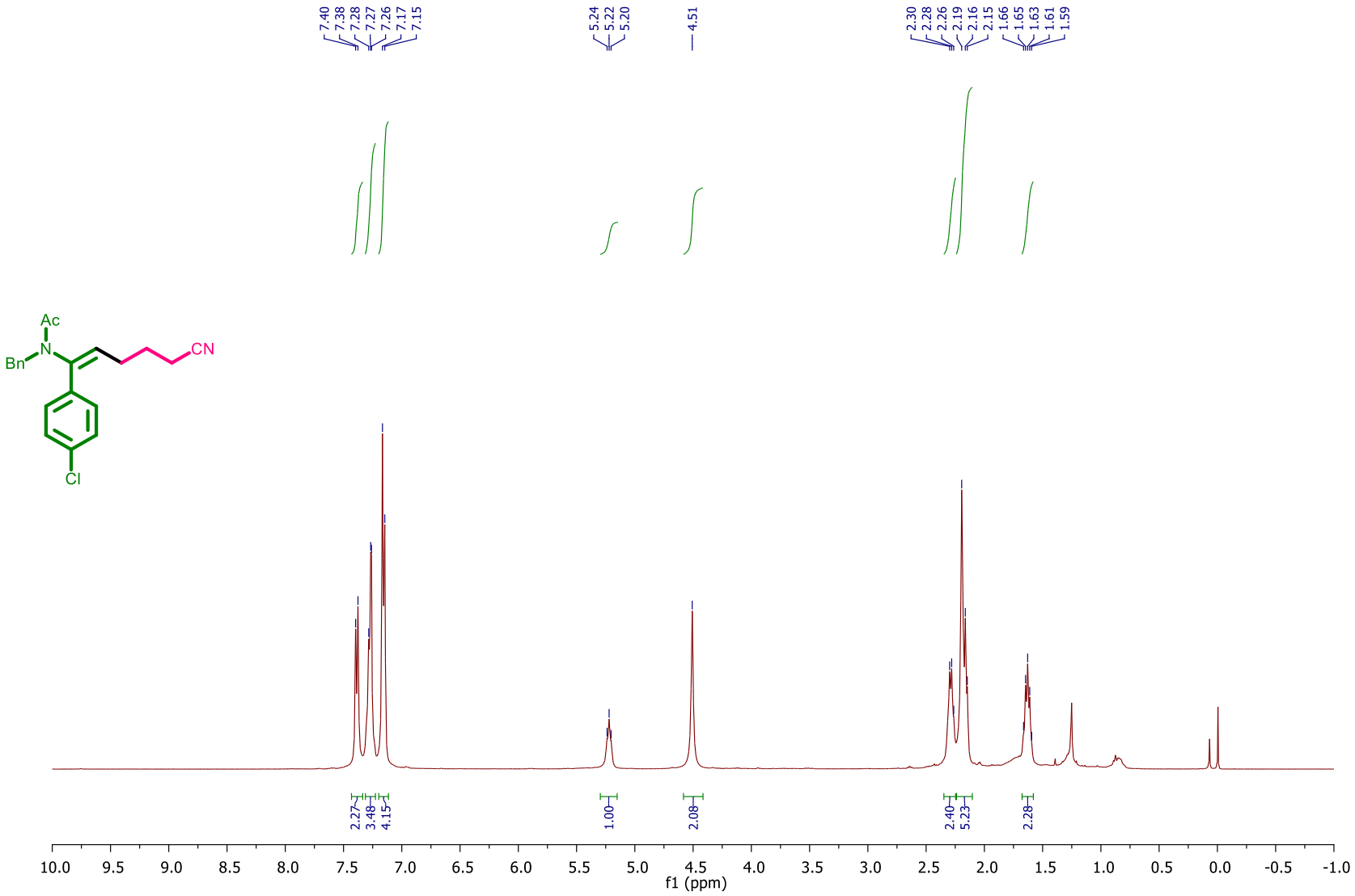
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ea)**



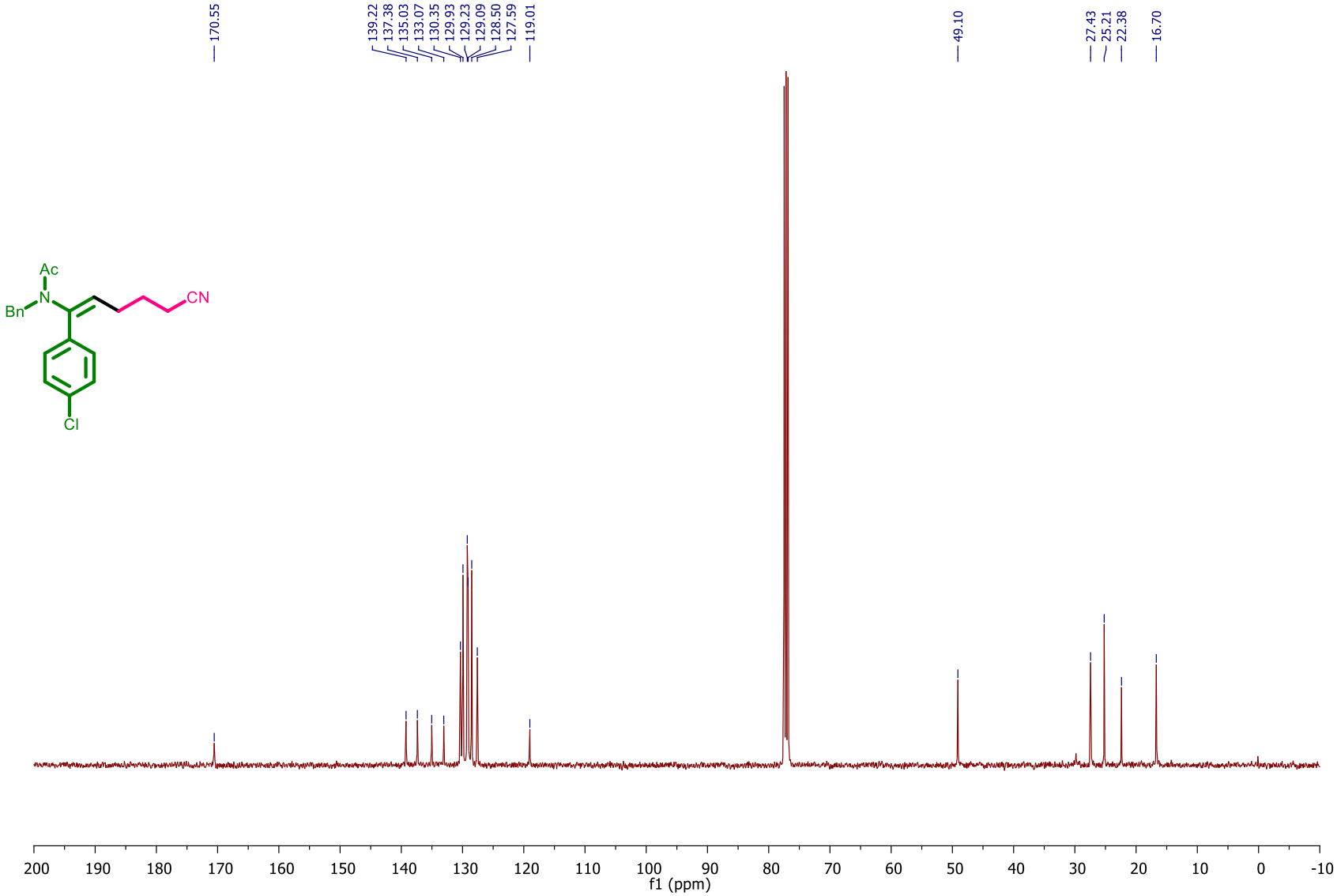
$^{19}F$ NMR (376 MHz, $CDCl_3$) Spectrum of compound **(3ea)**



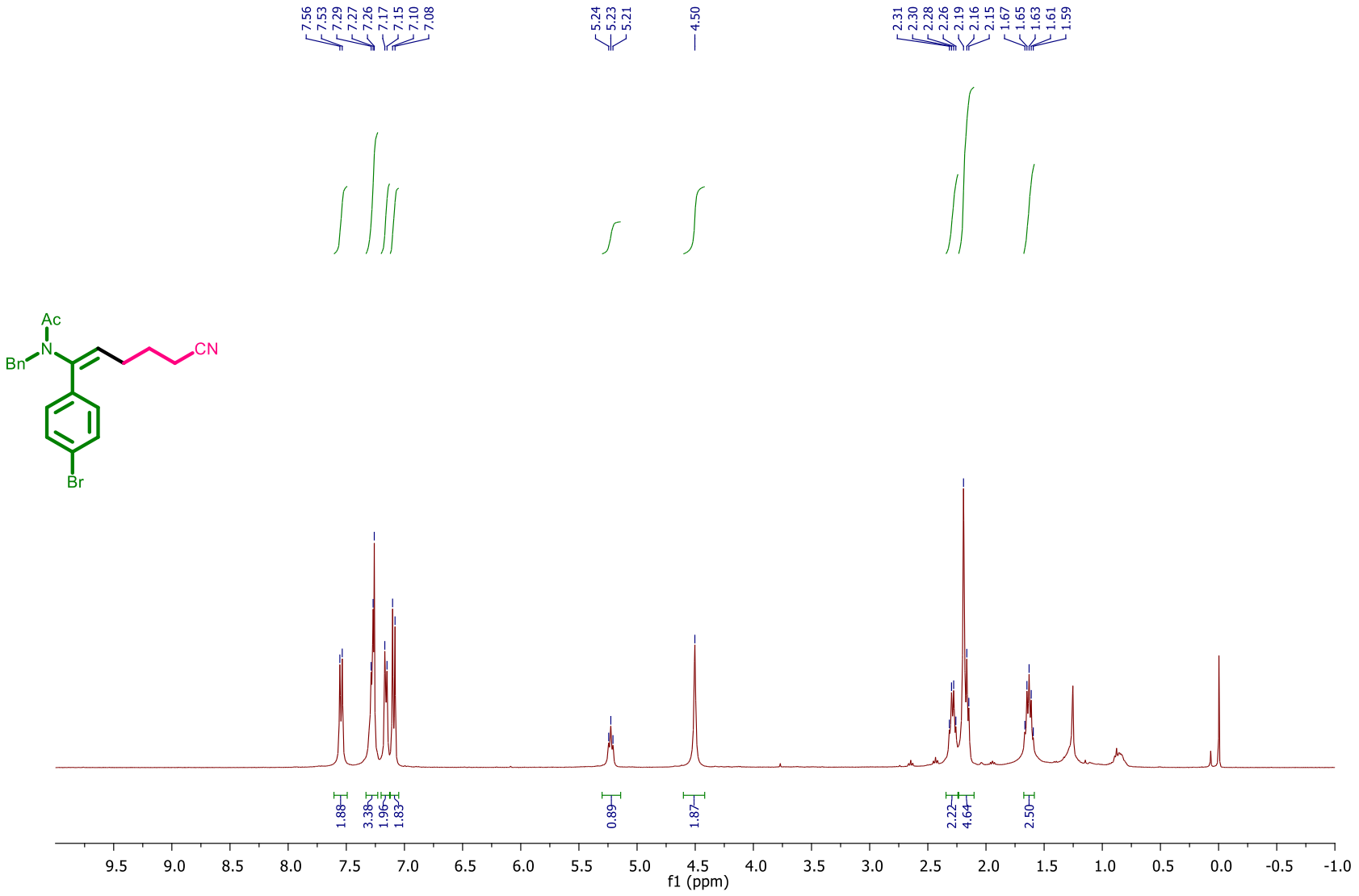
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3fa)**



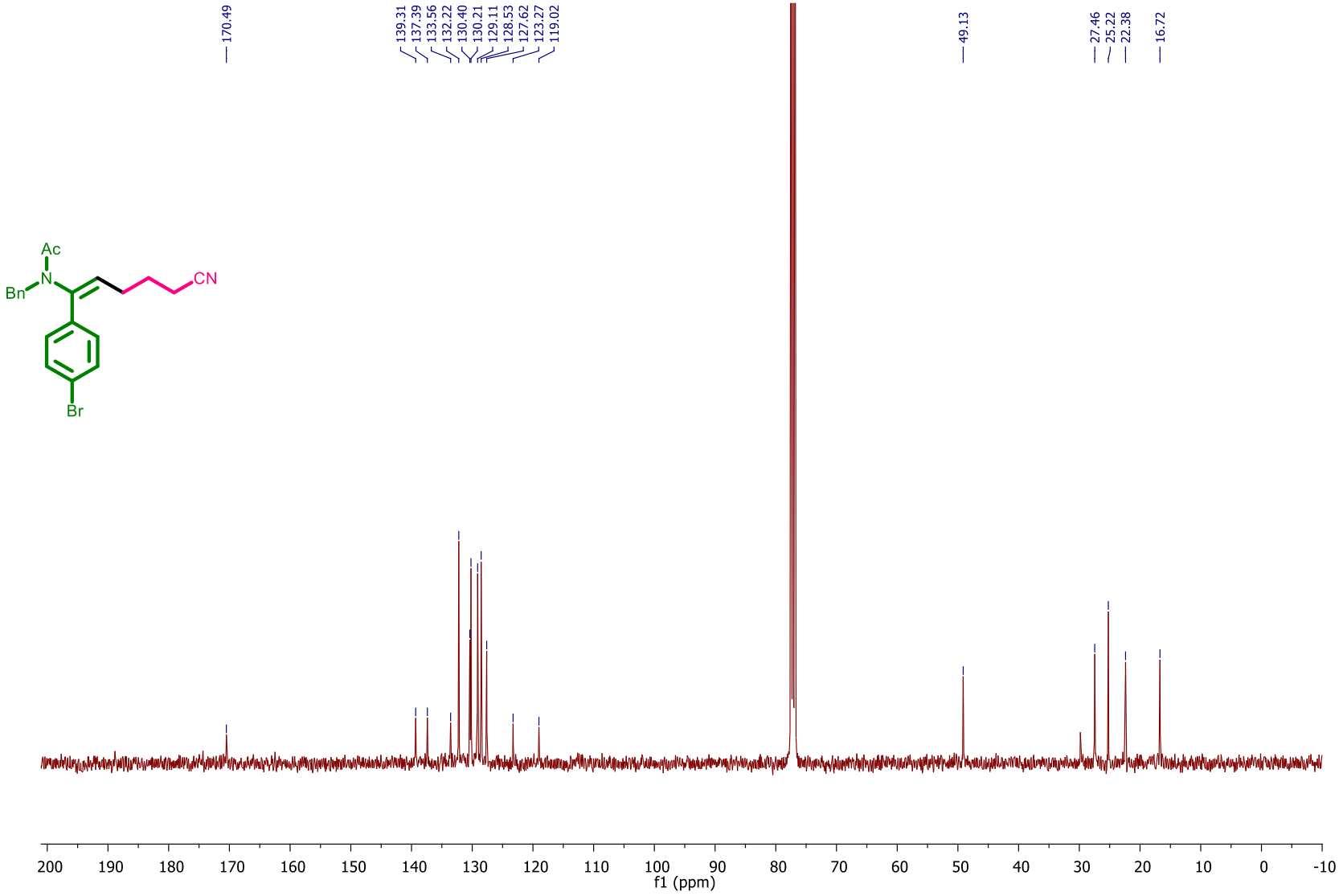
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3fa)**



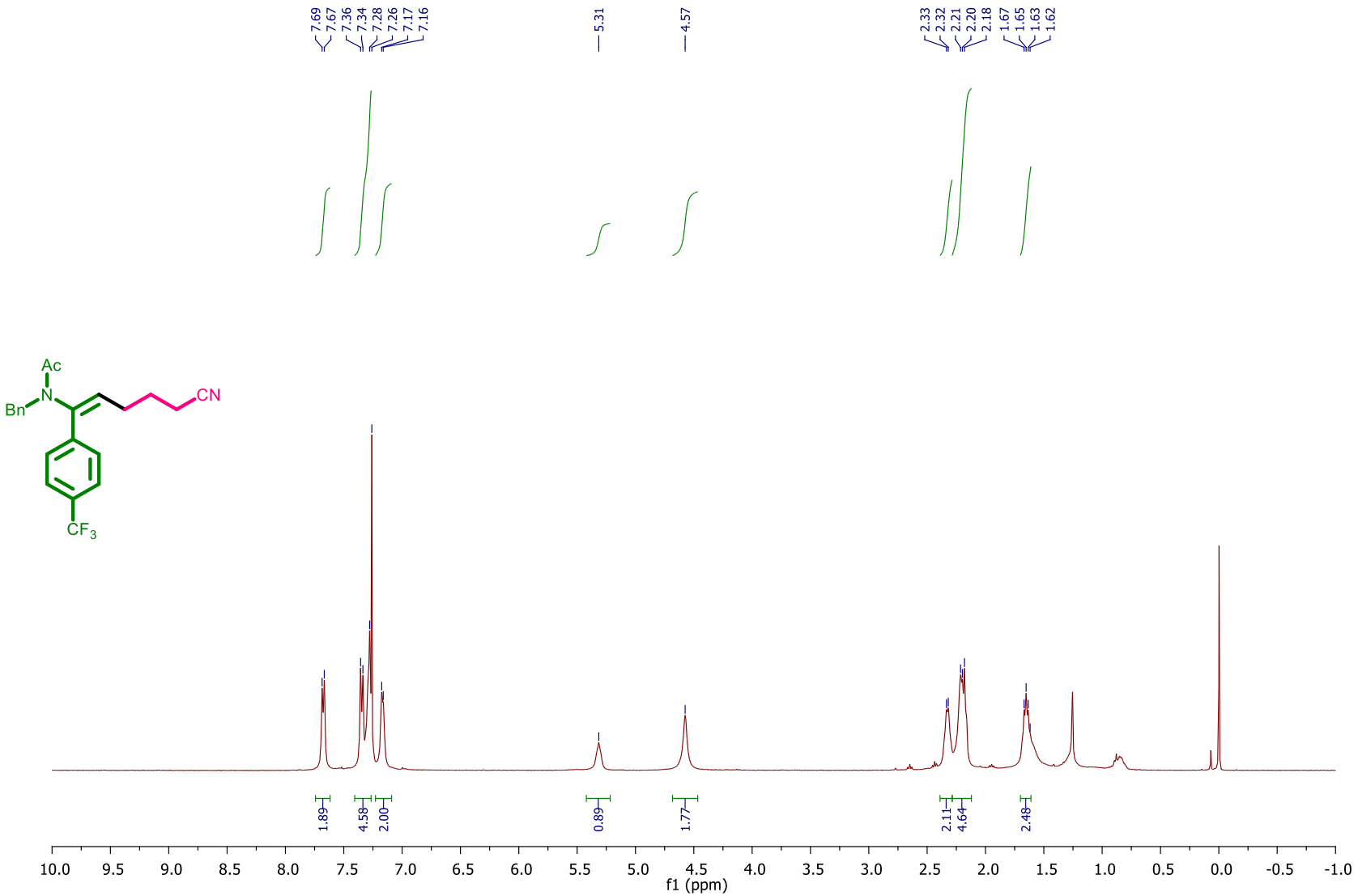
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ga)**



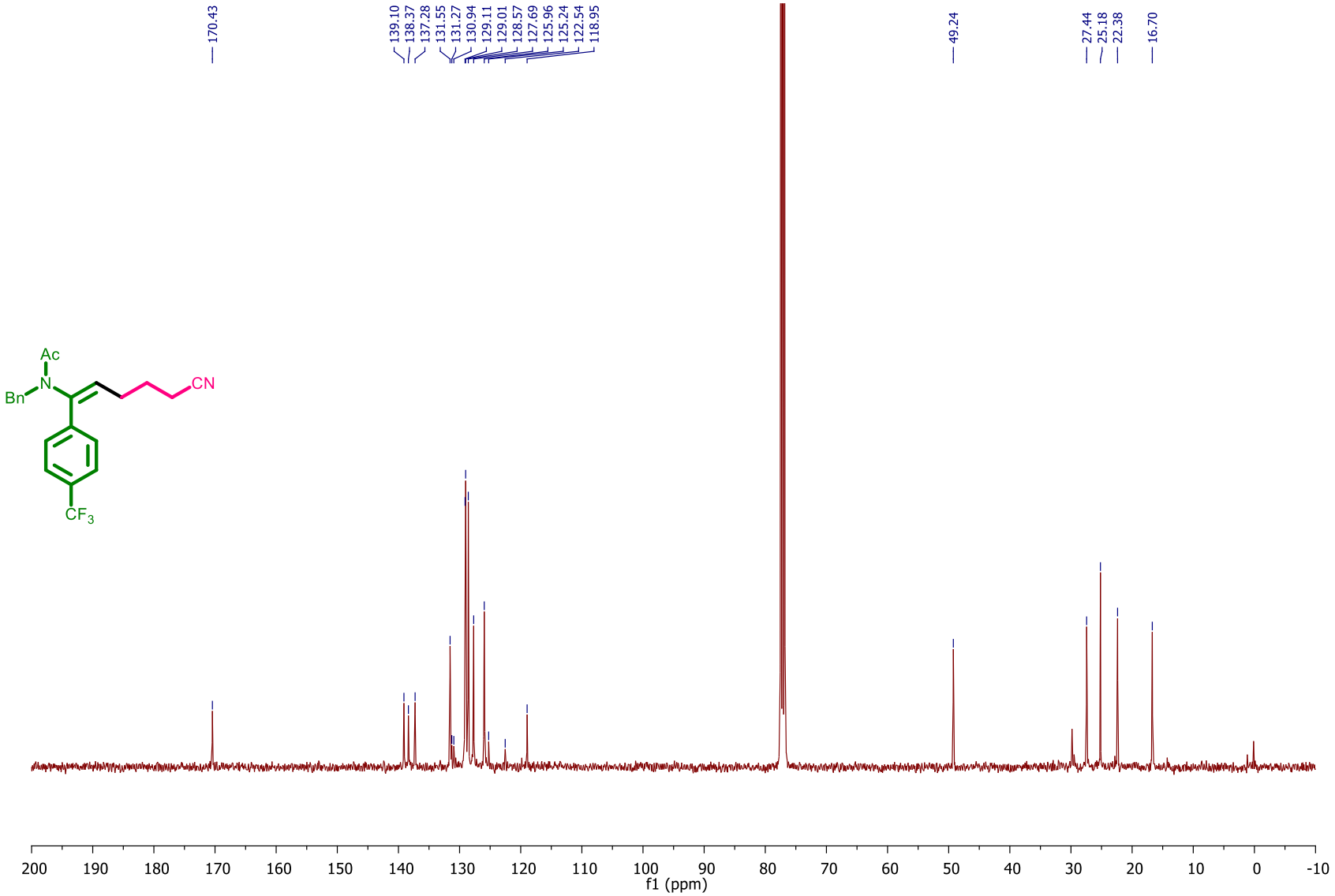
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ga)**



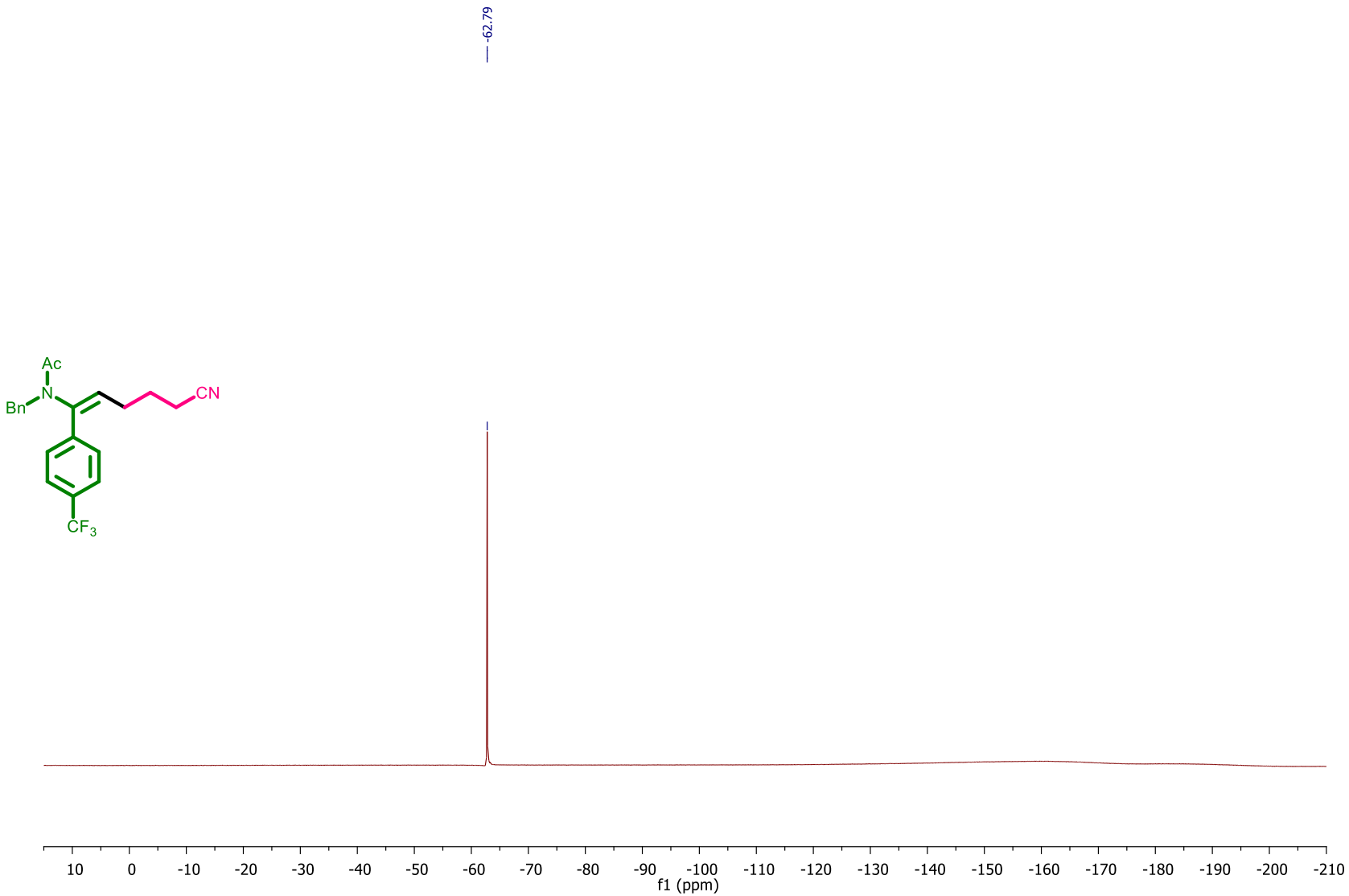
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ha)**



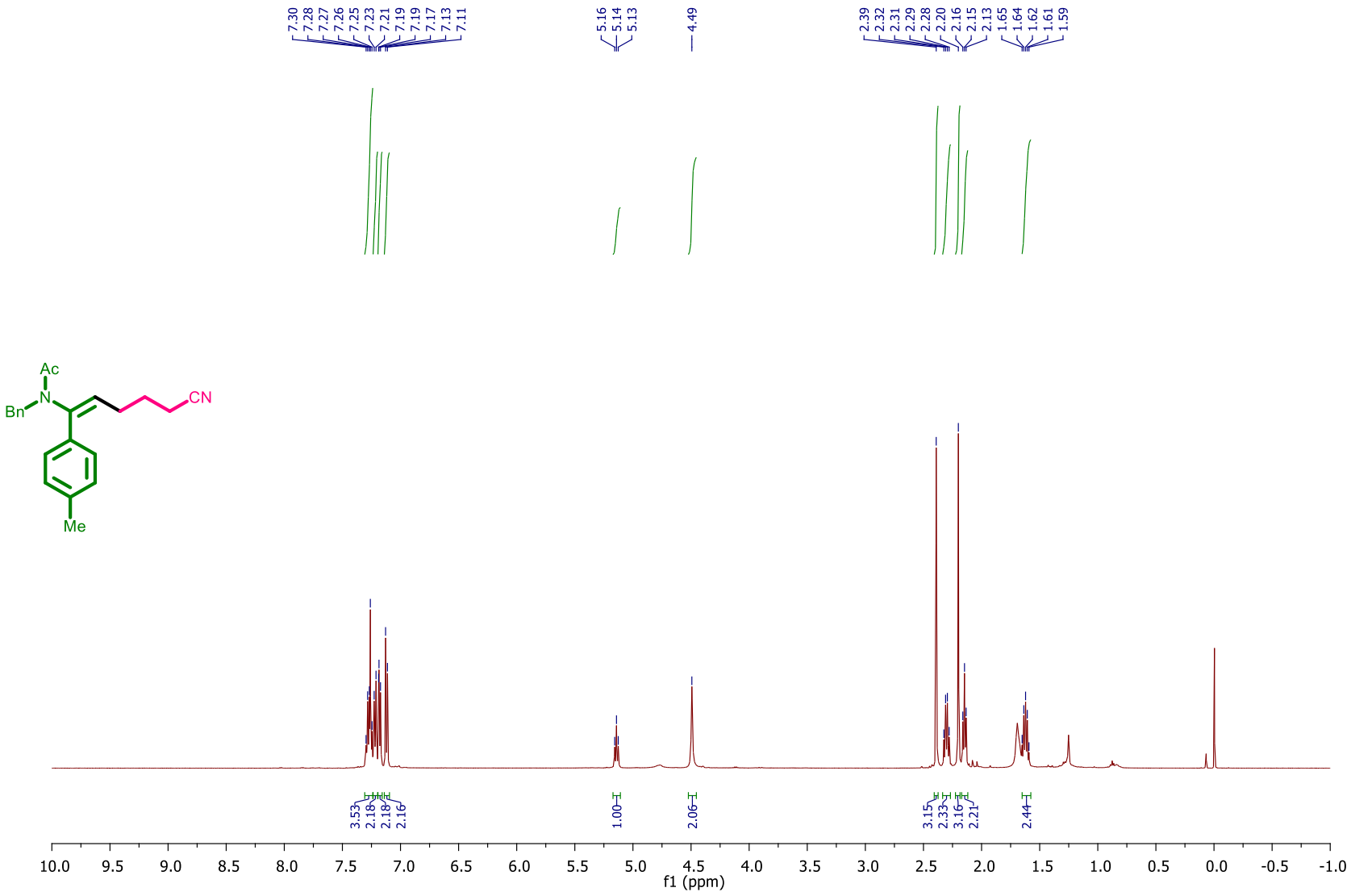
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ha)**



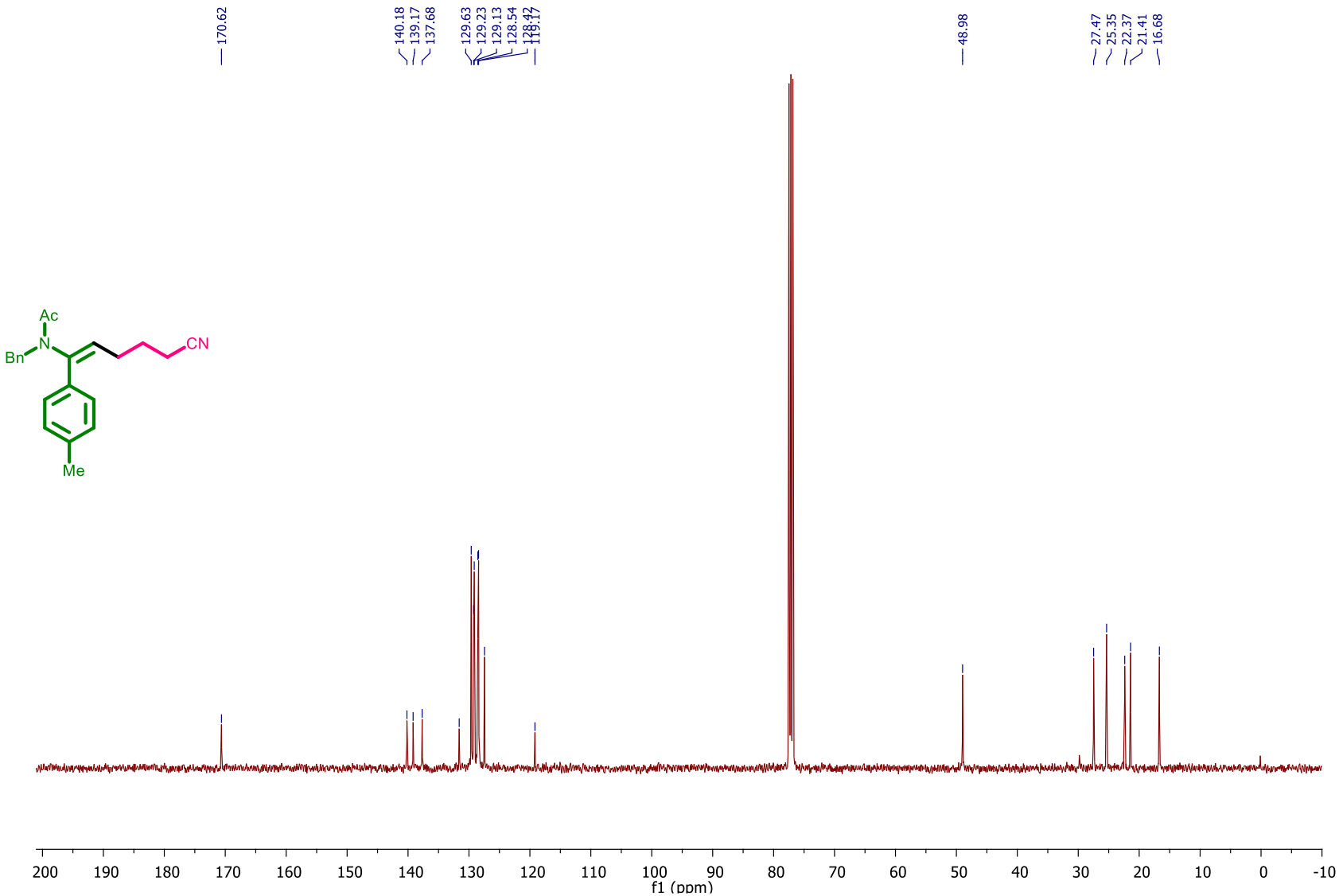
$^{19}F$ NMR (376 MHz, $CDCl_3$) Spectrum of compound **(3ha)**



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



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



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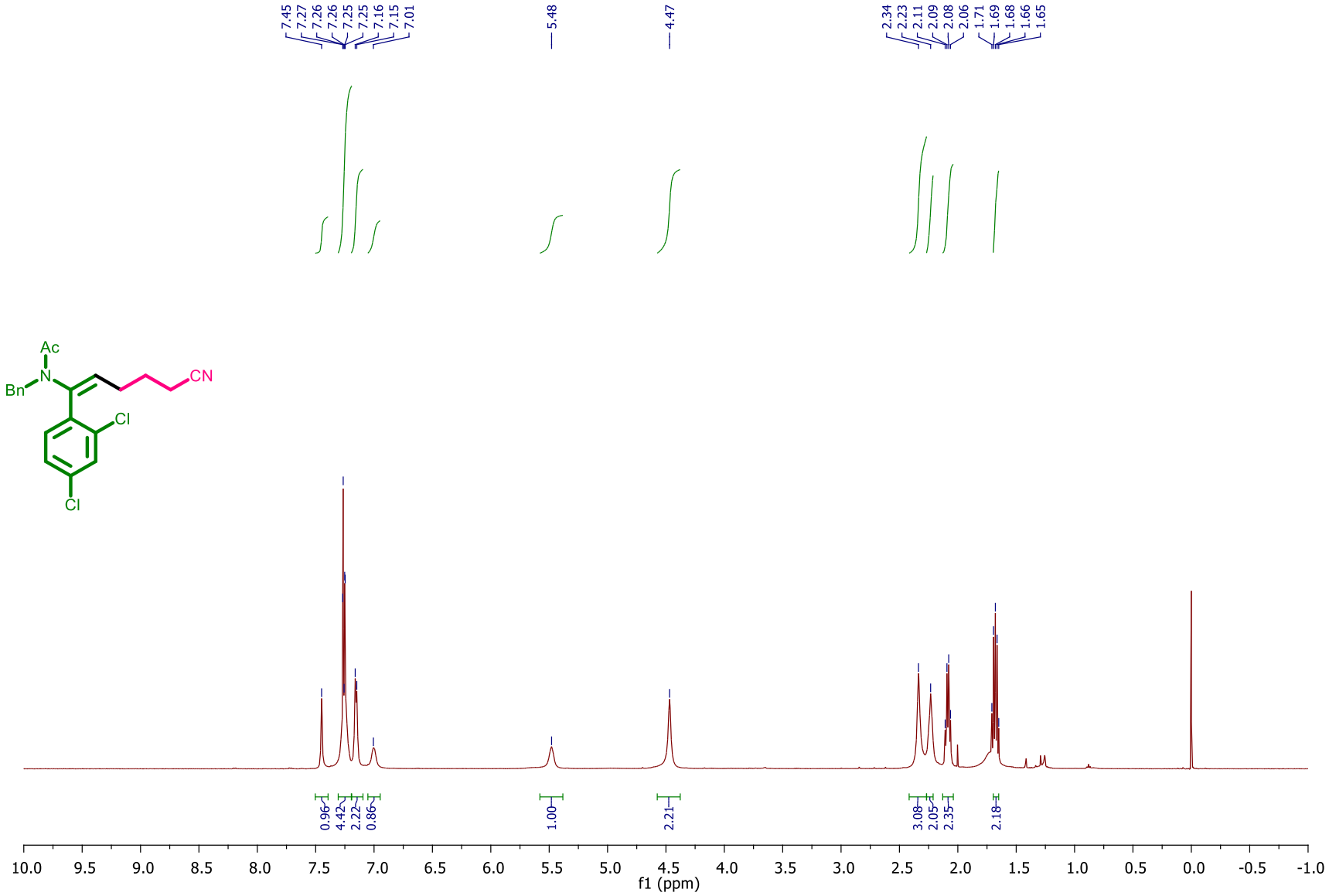
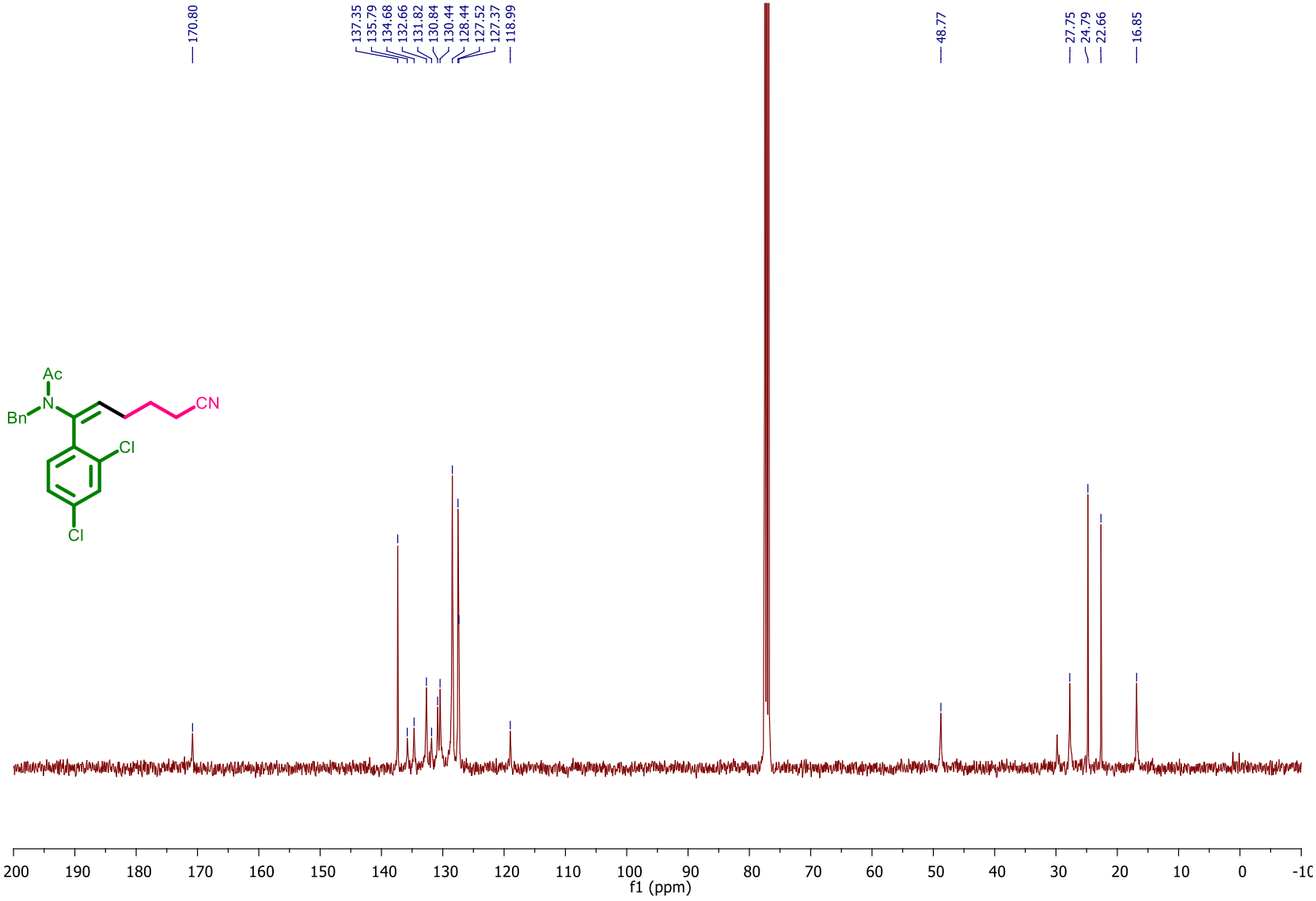
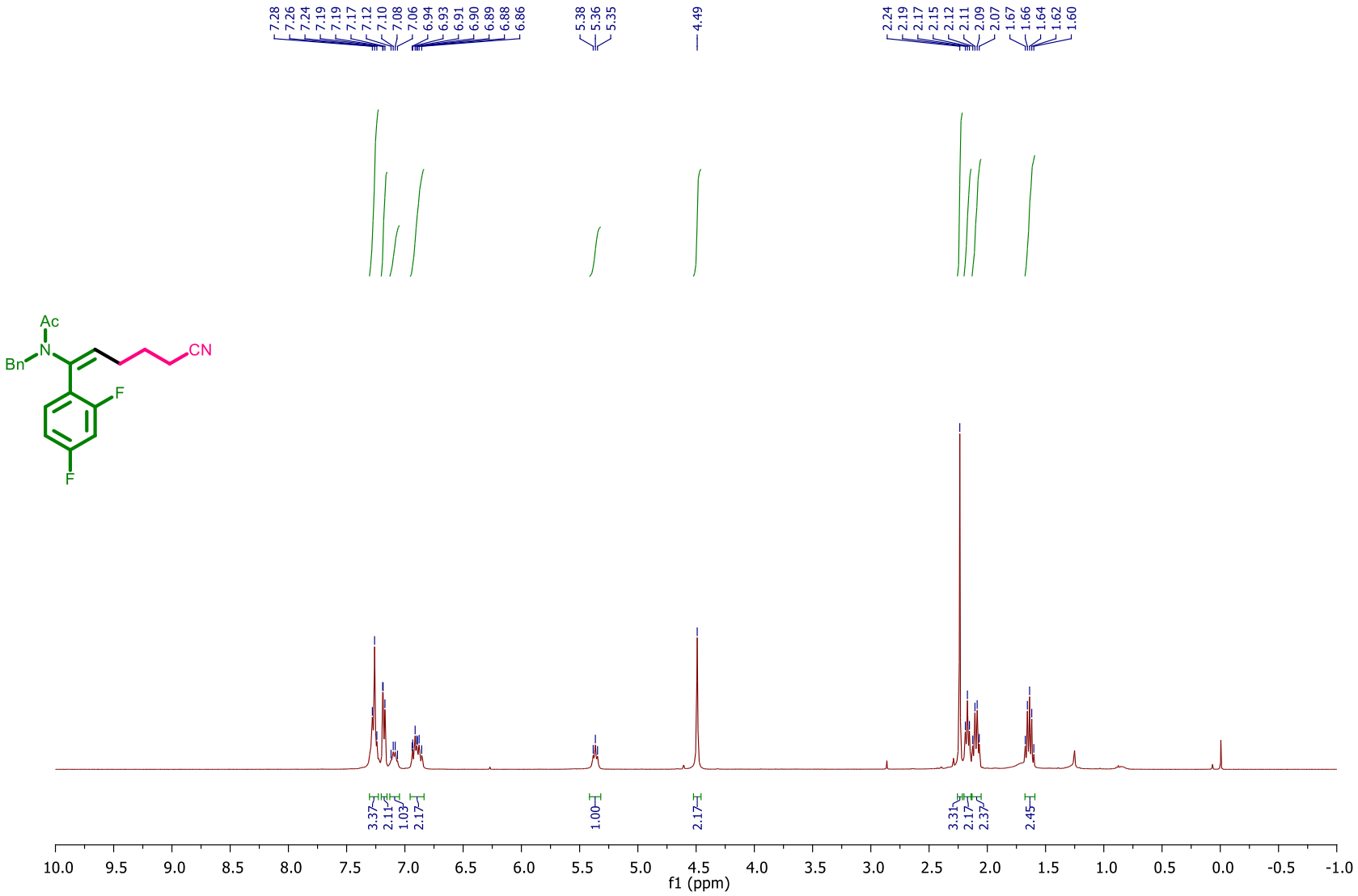


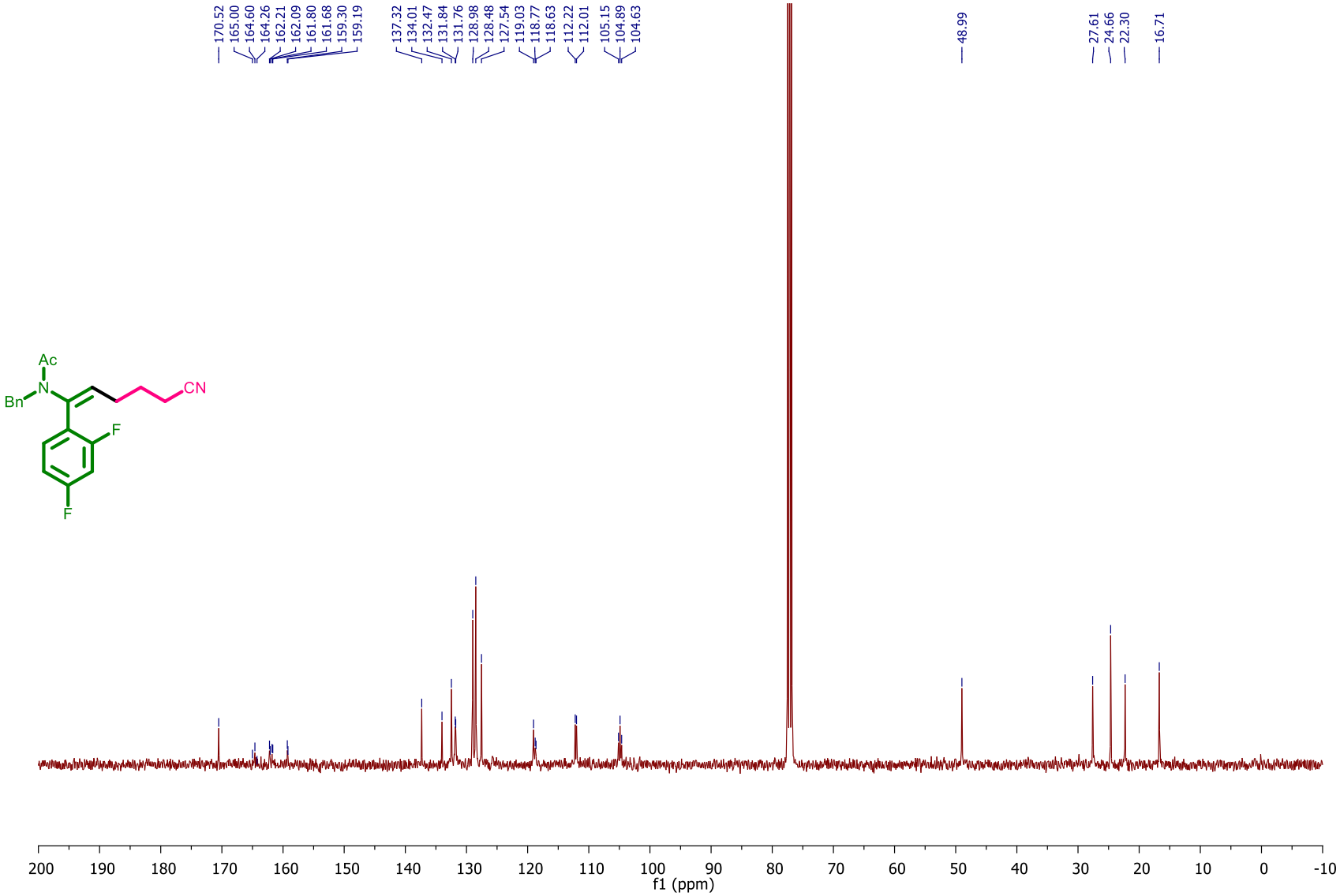
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ja)**



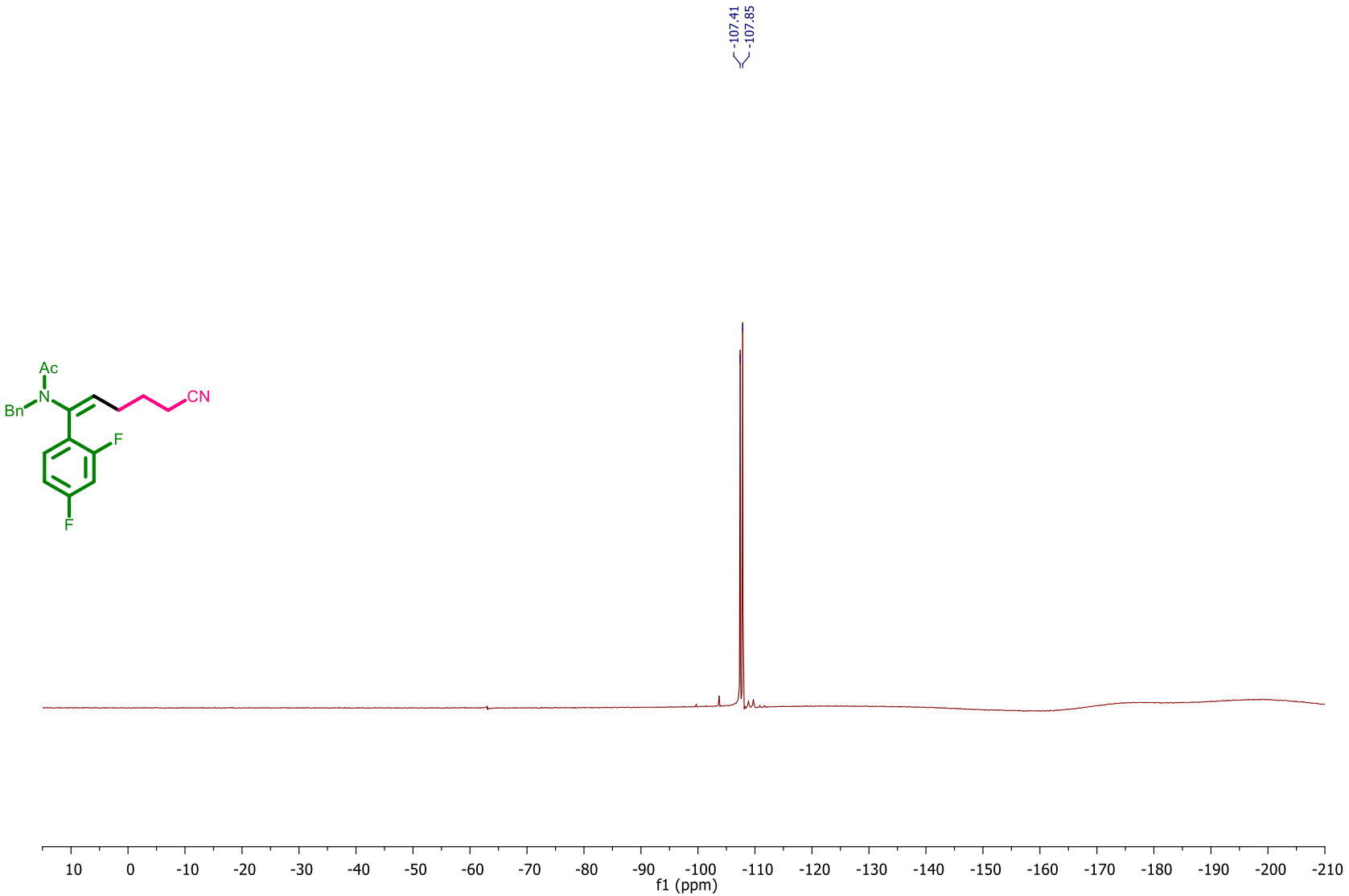
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ka)**



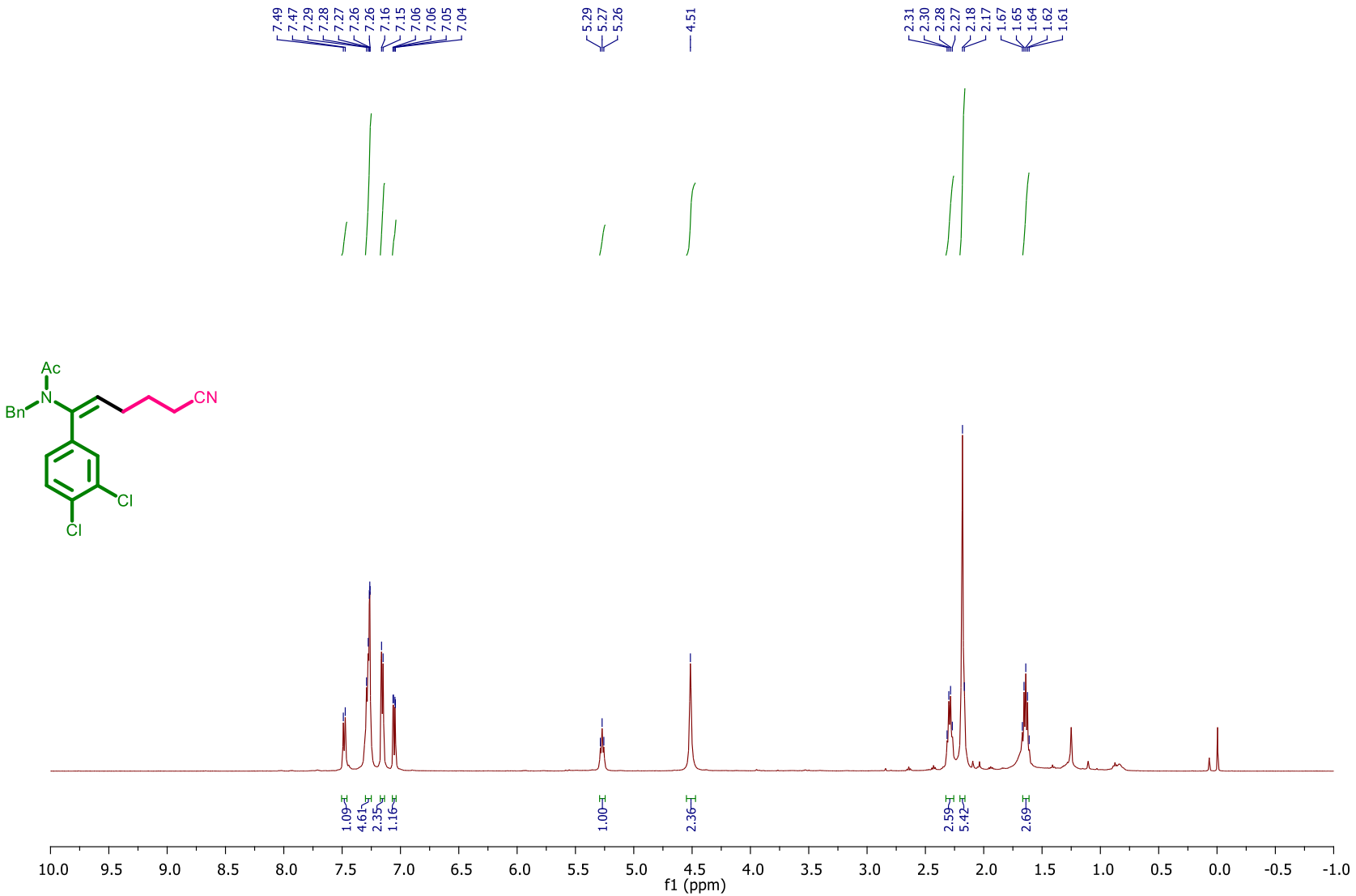
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ka)**



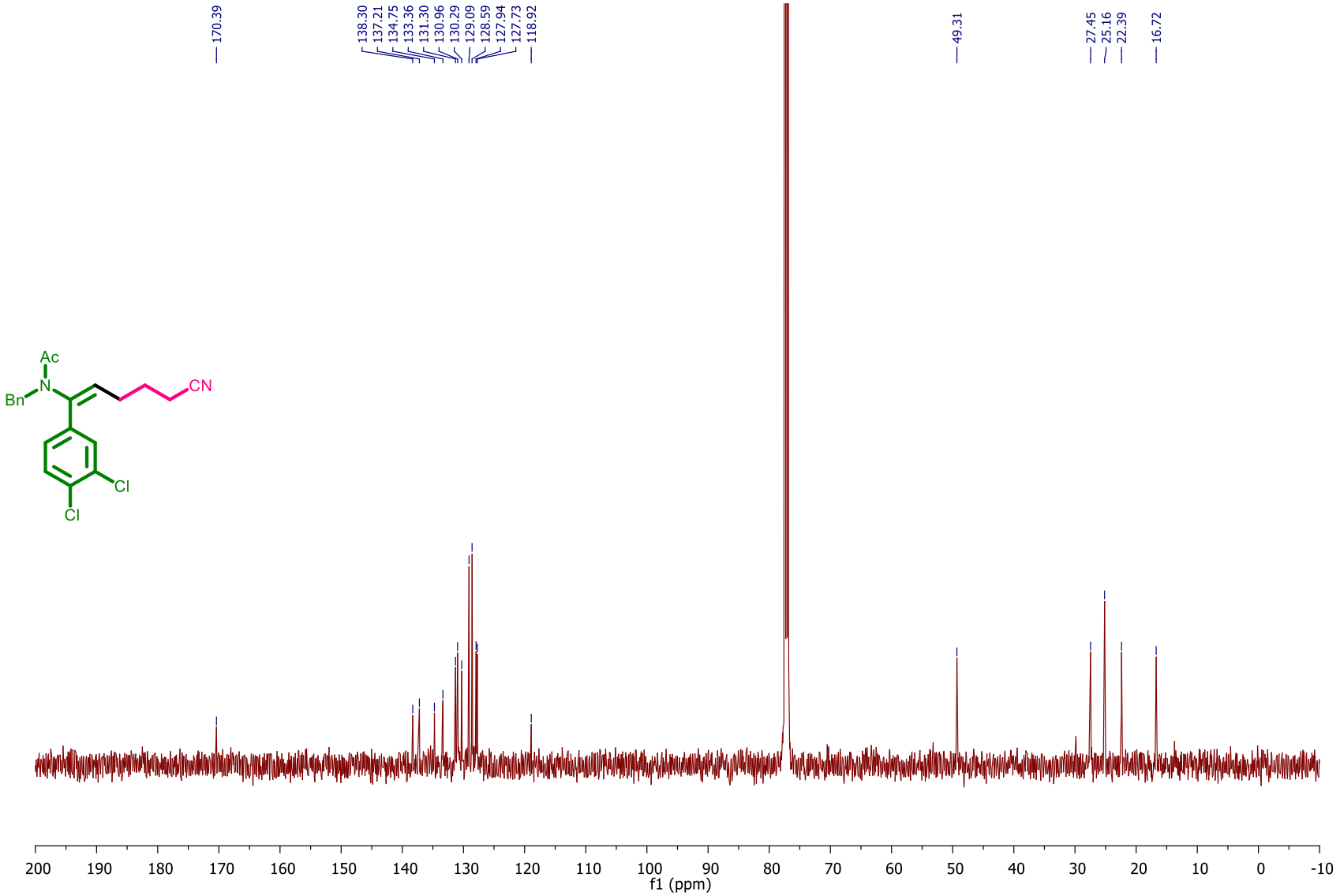
$^{19}F$ NMR (376 MHz, $CDCl_3$) Spectrum of compound **(3ka)**



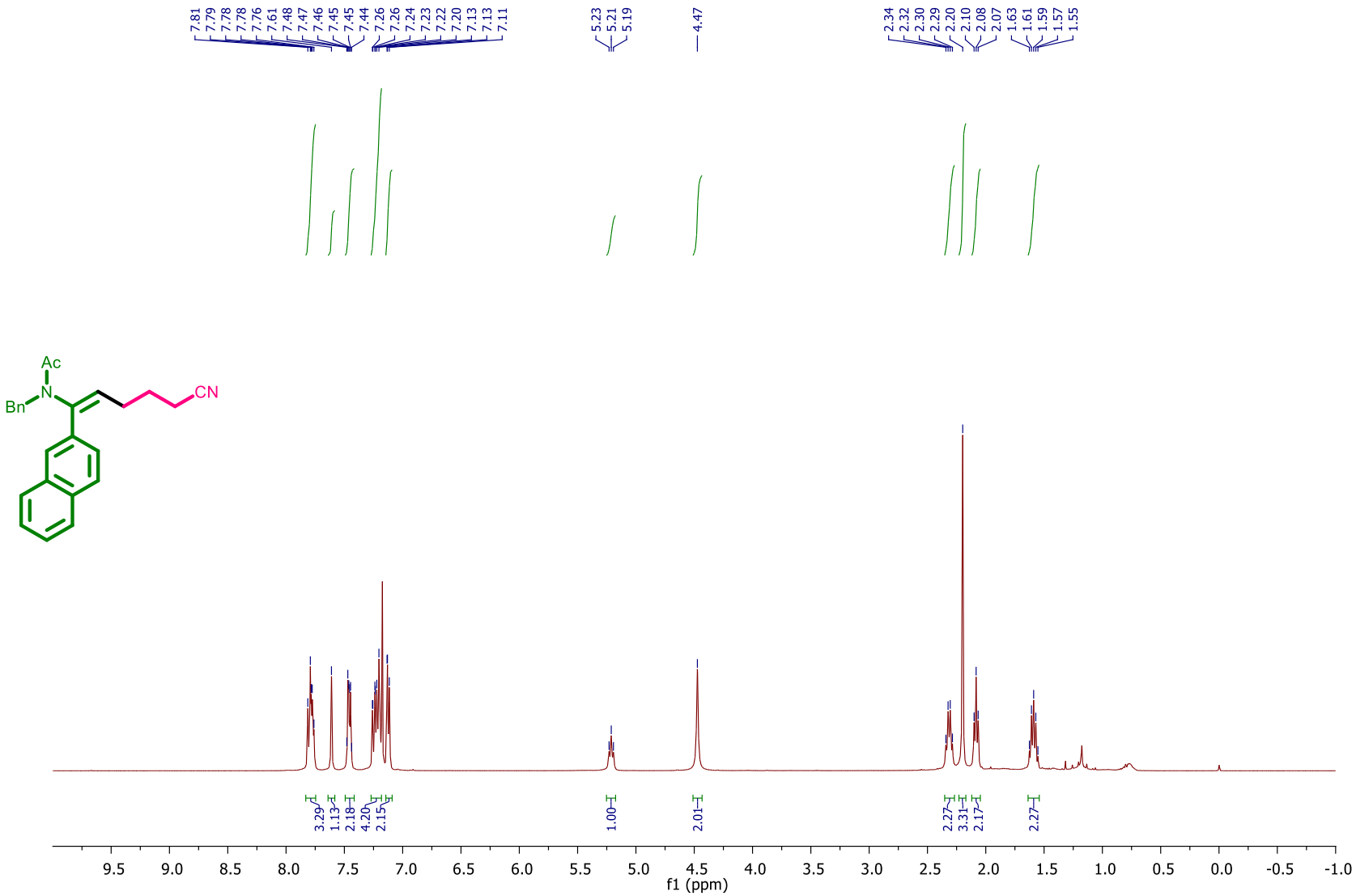
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3la)**



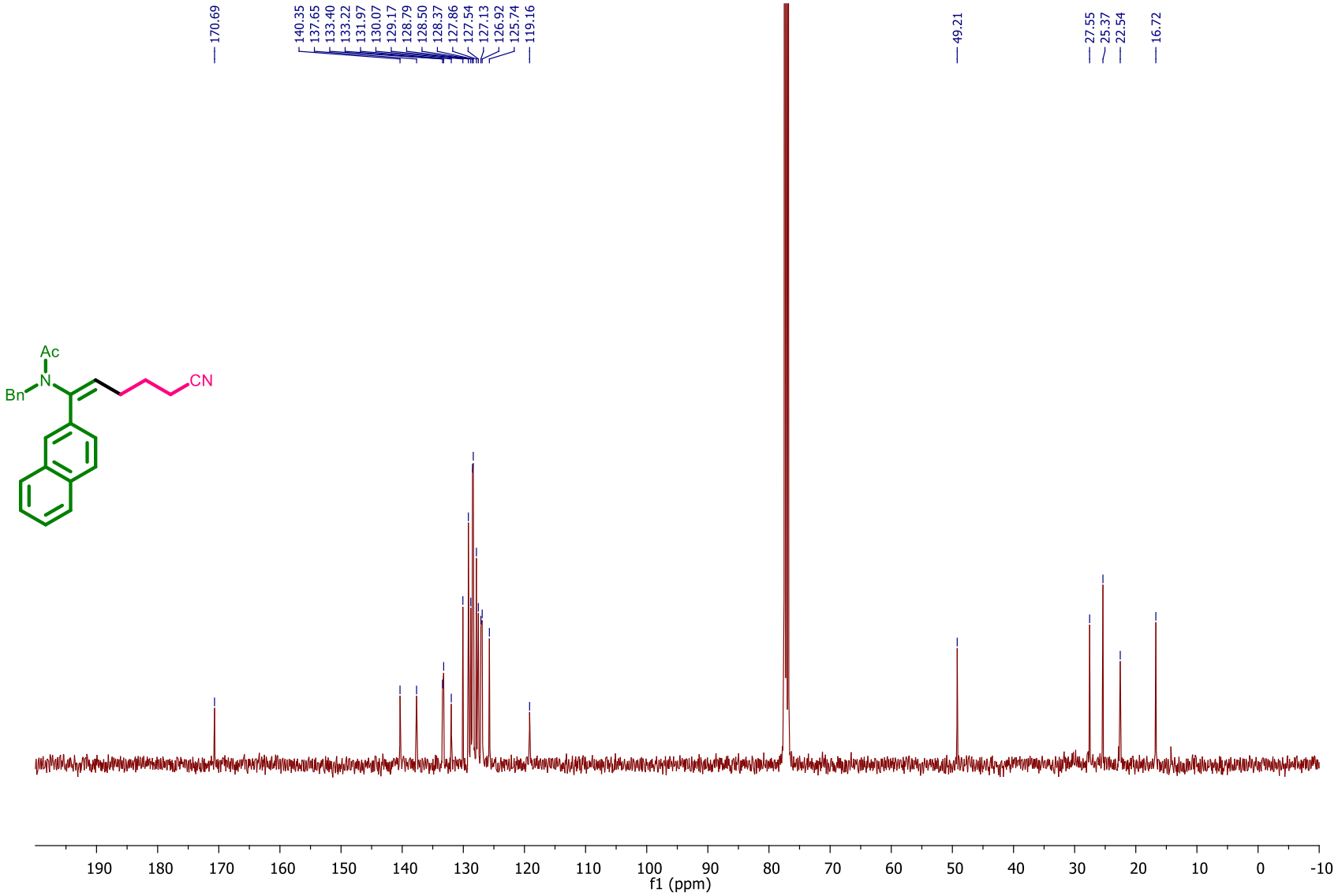
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3la)**



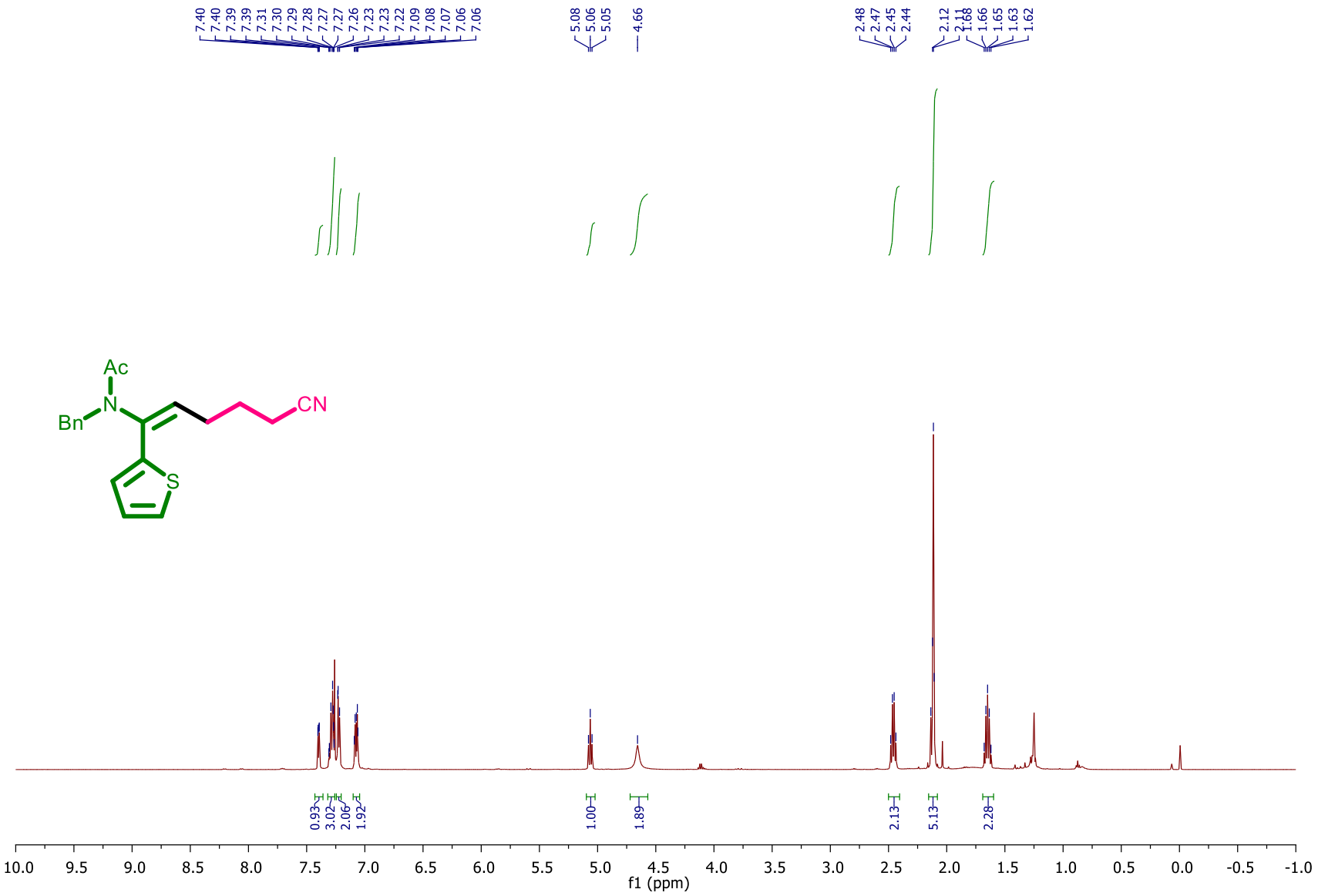
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ma)**



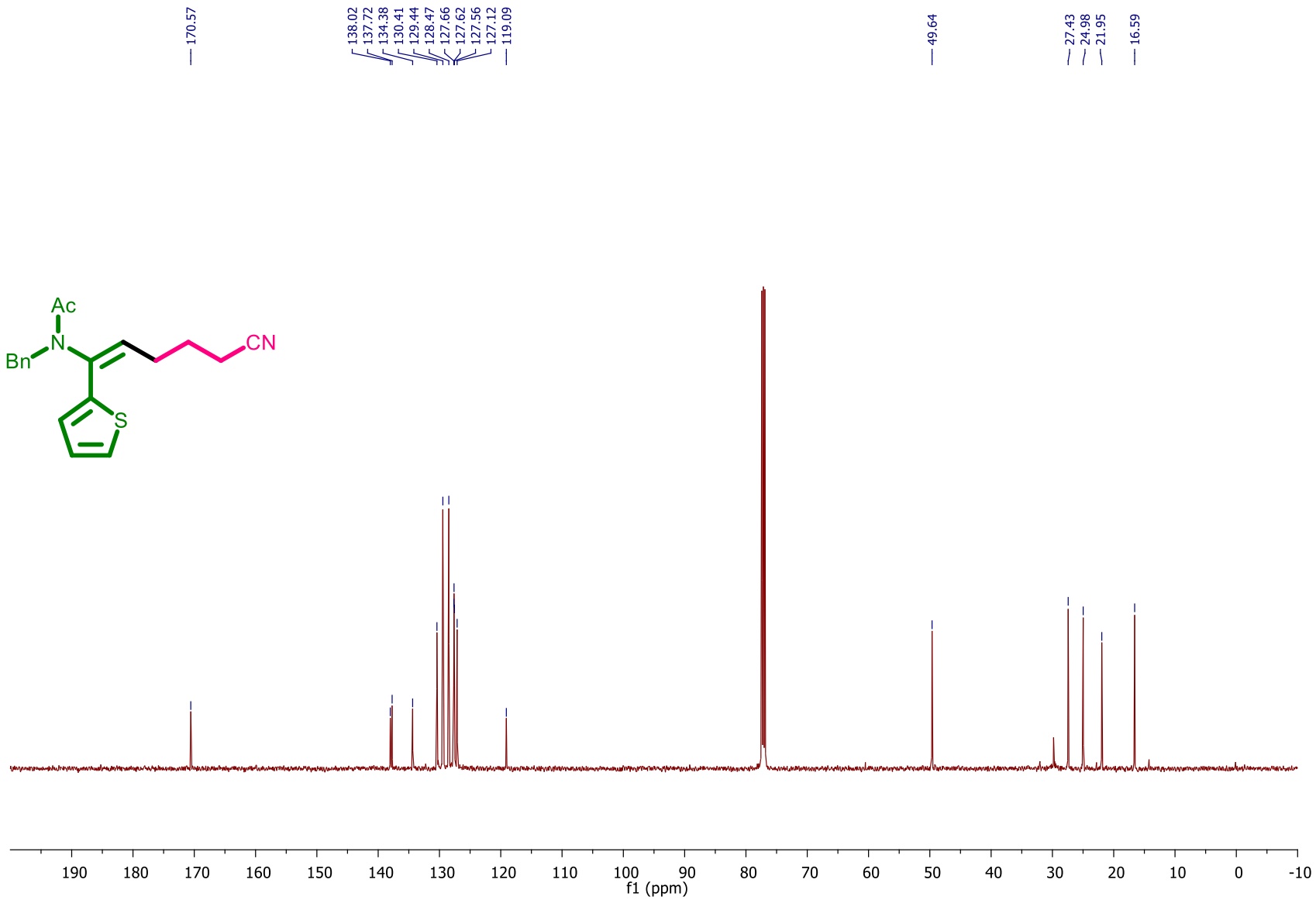
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3ma)**



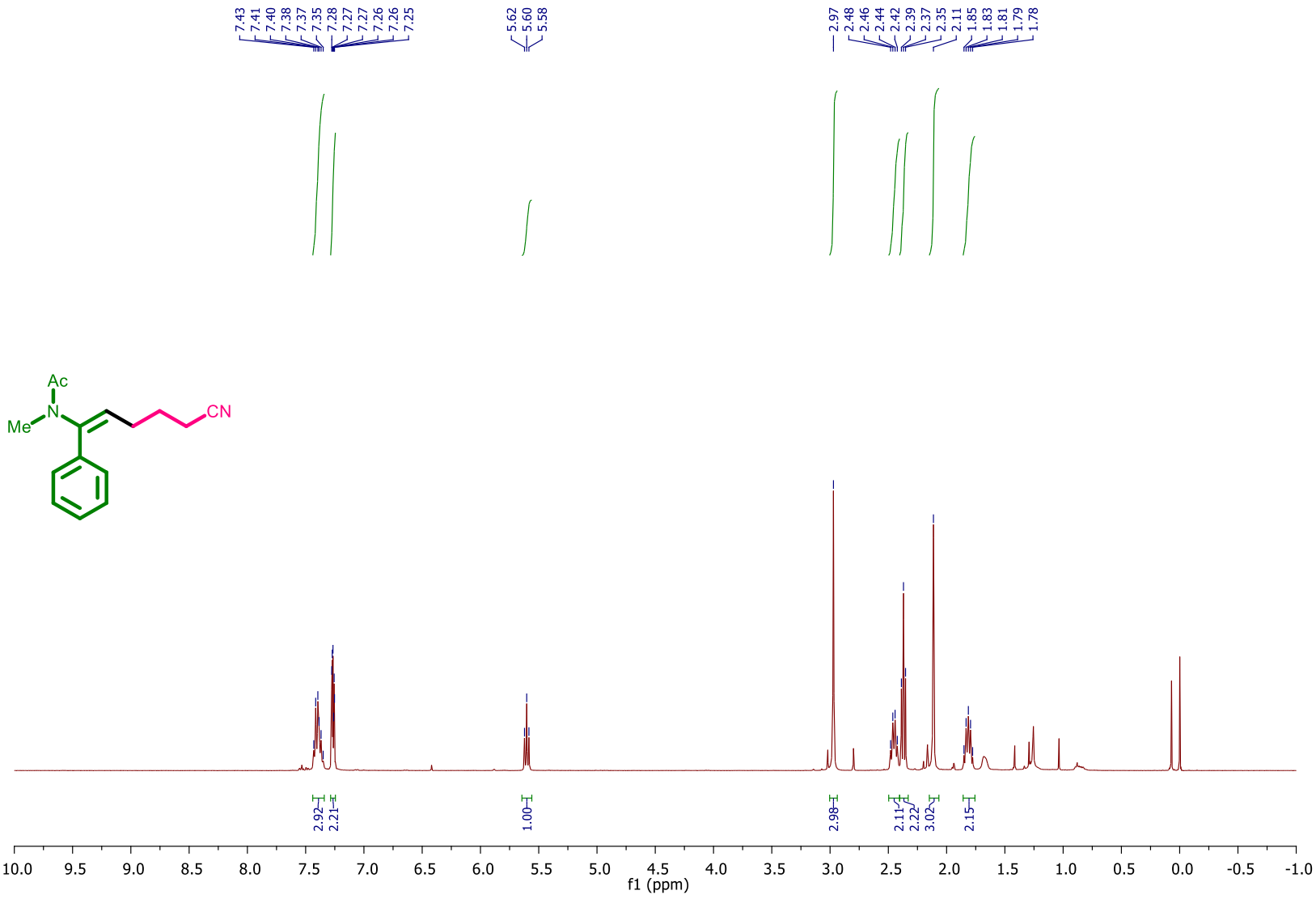
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3na)**



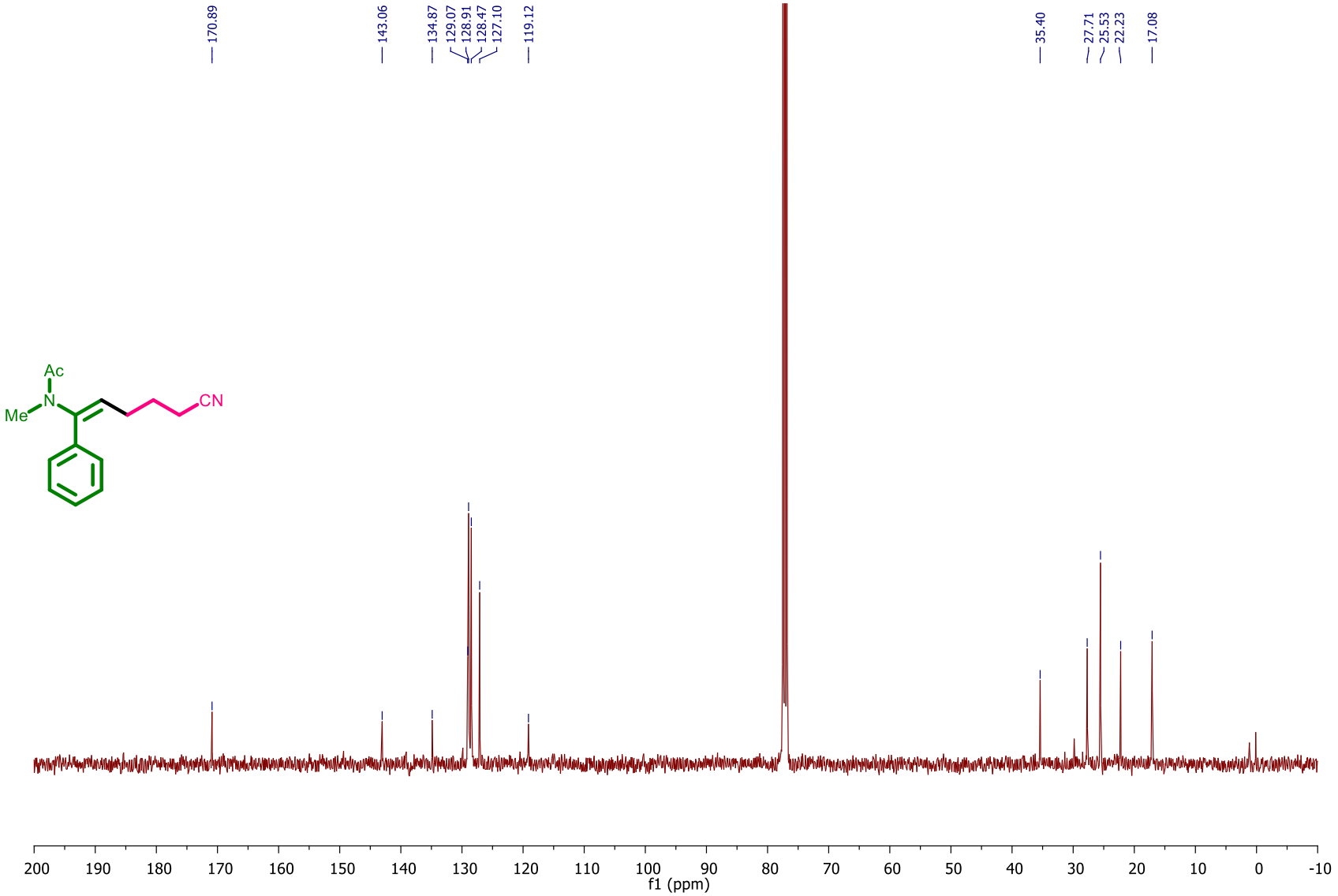
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3na)**



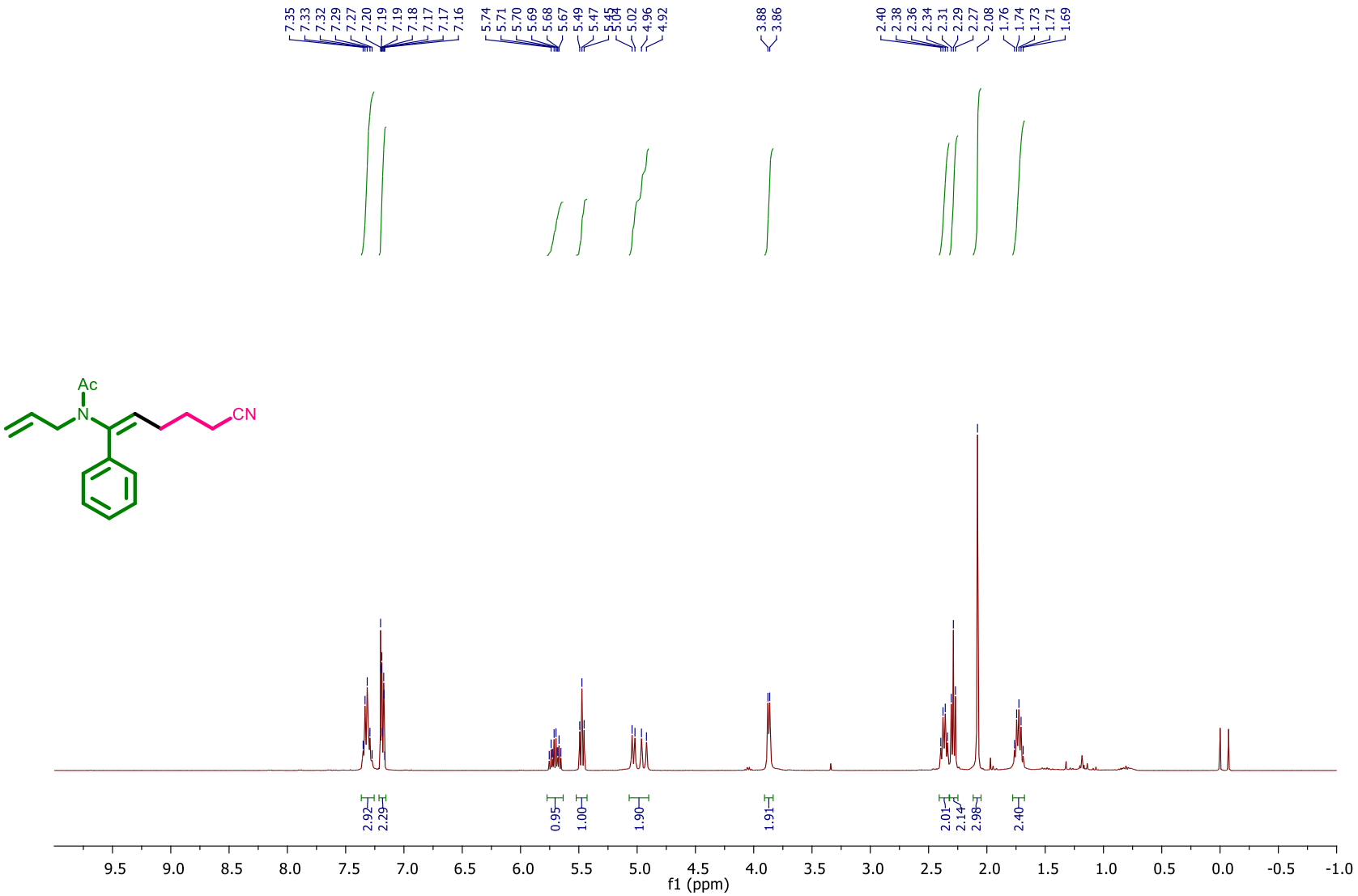
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3oa)**



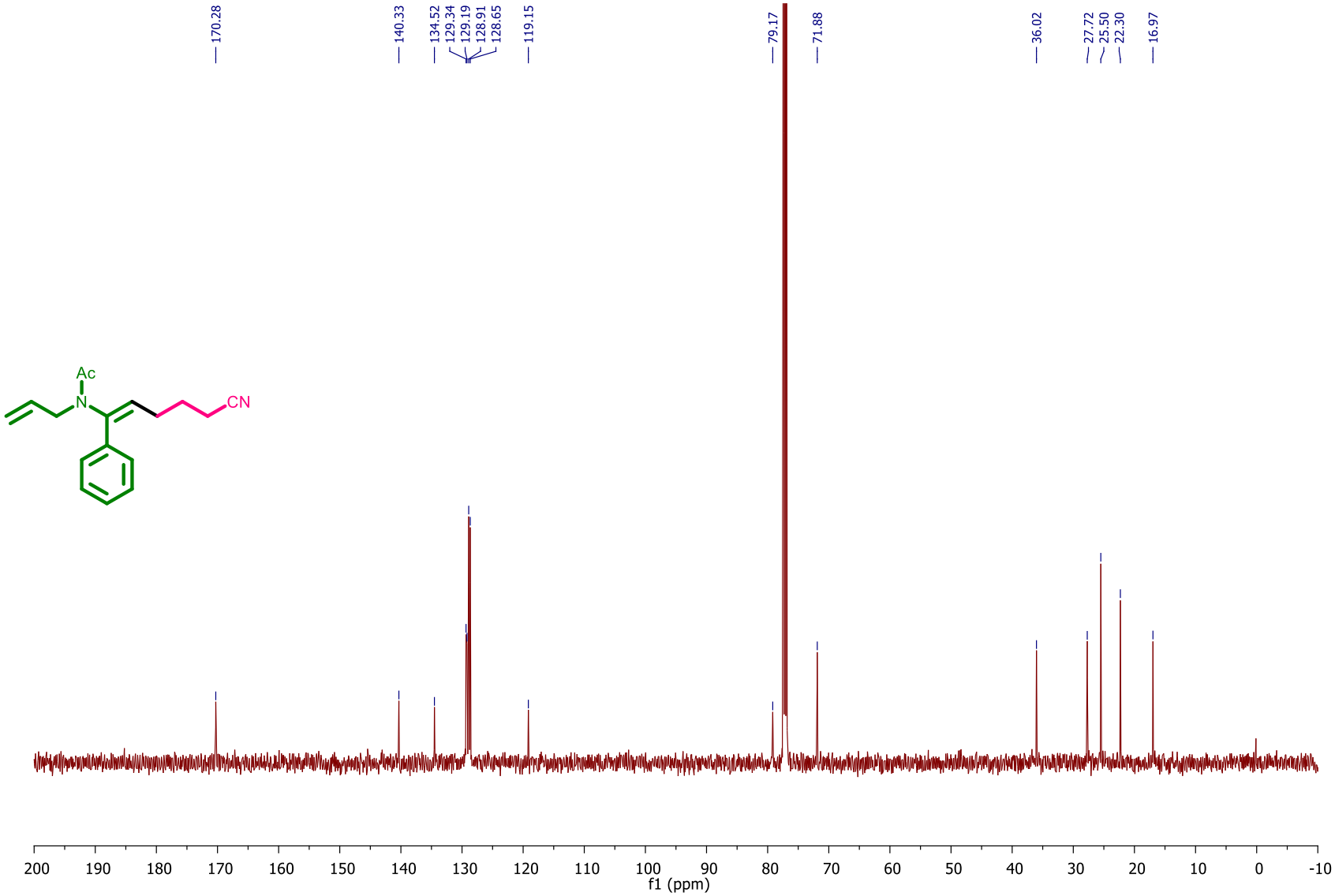
$^{13}C$ NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3oa)**



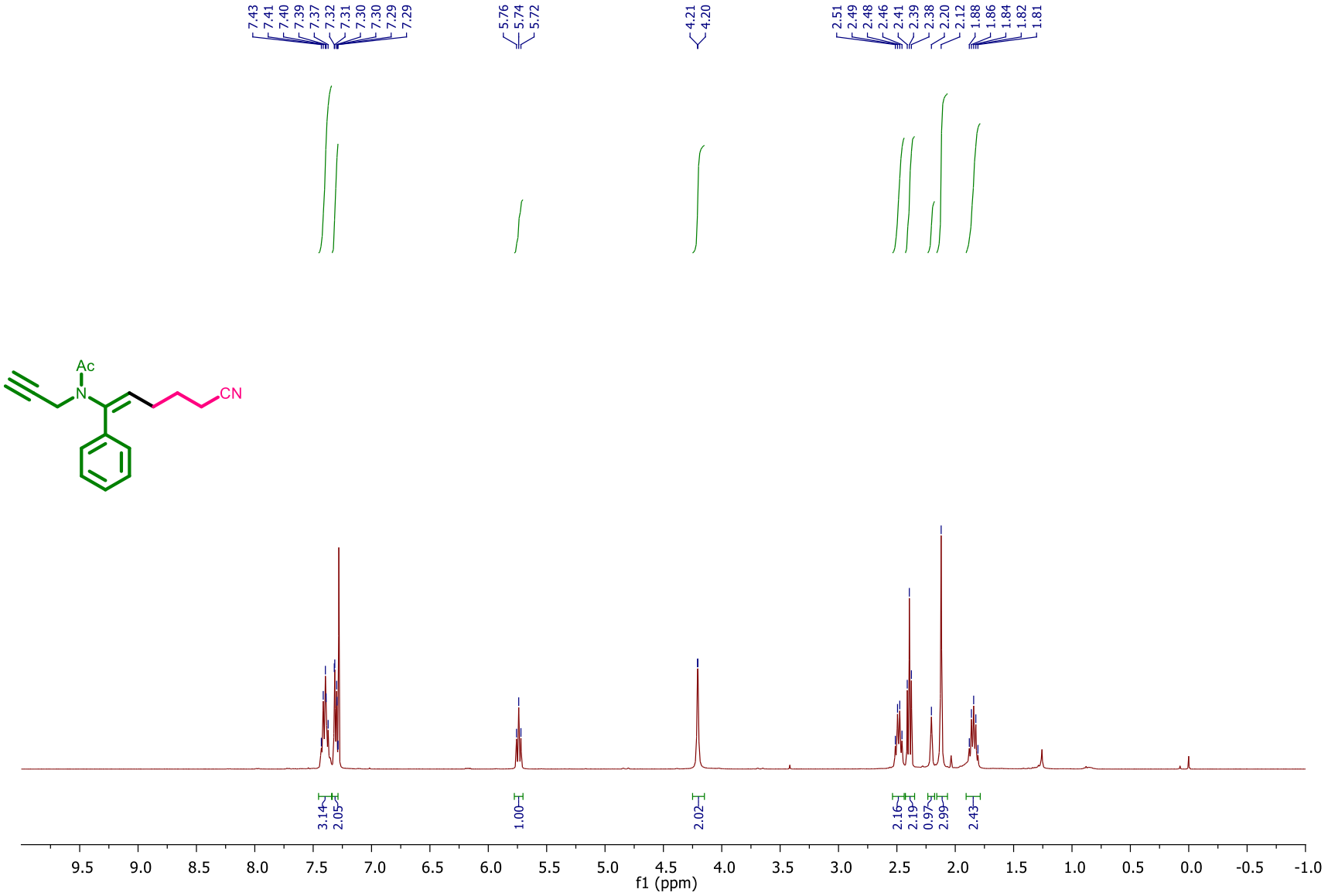
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3pa)**



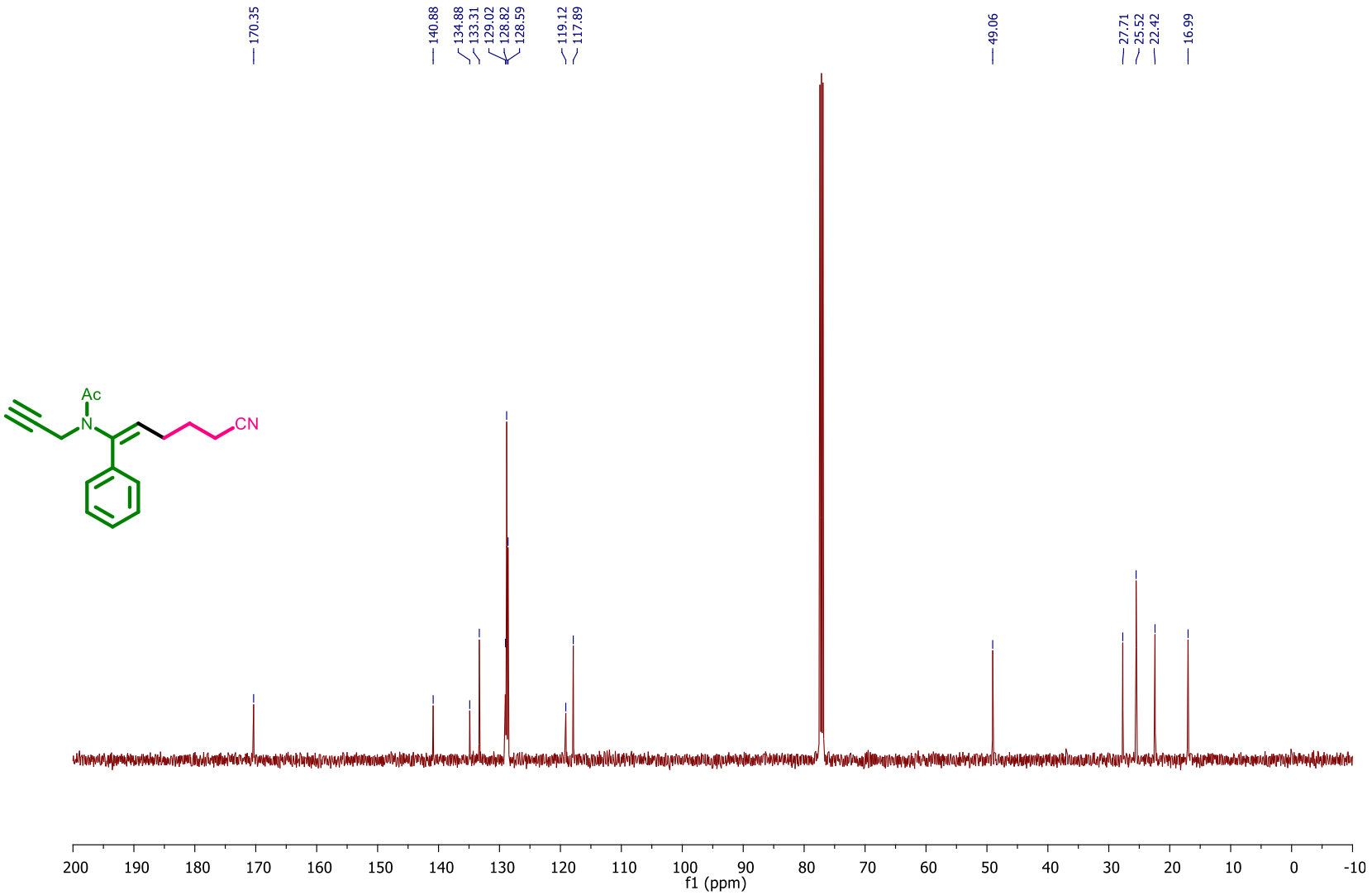
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3pa)**



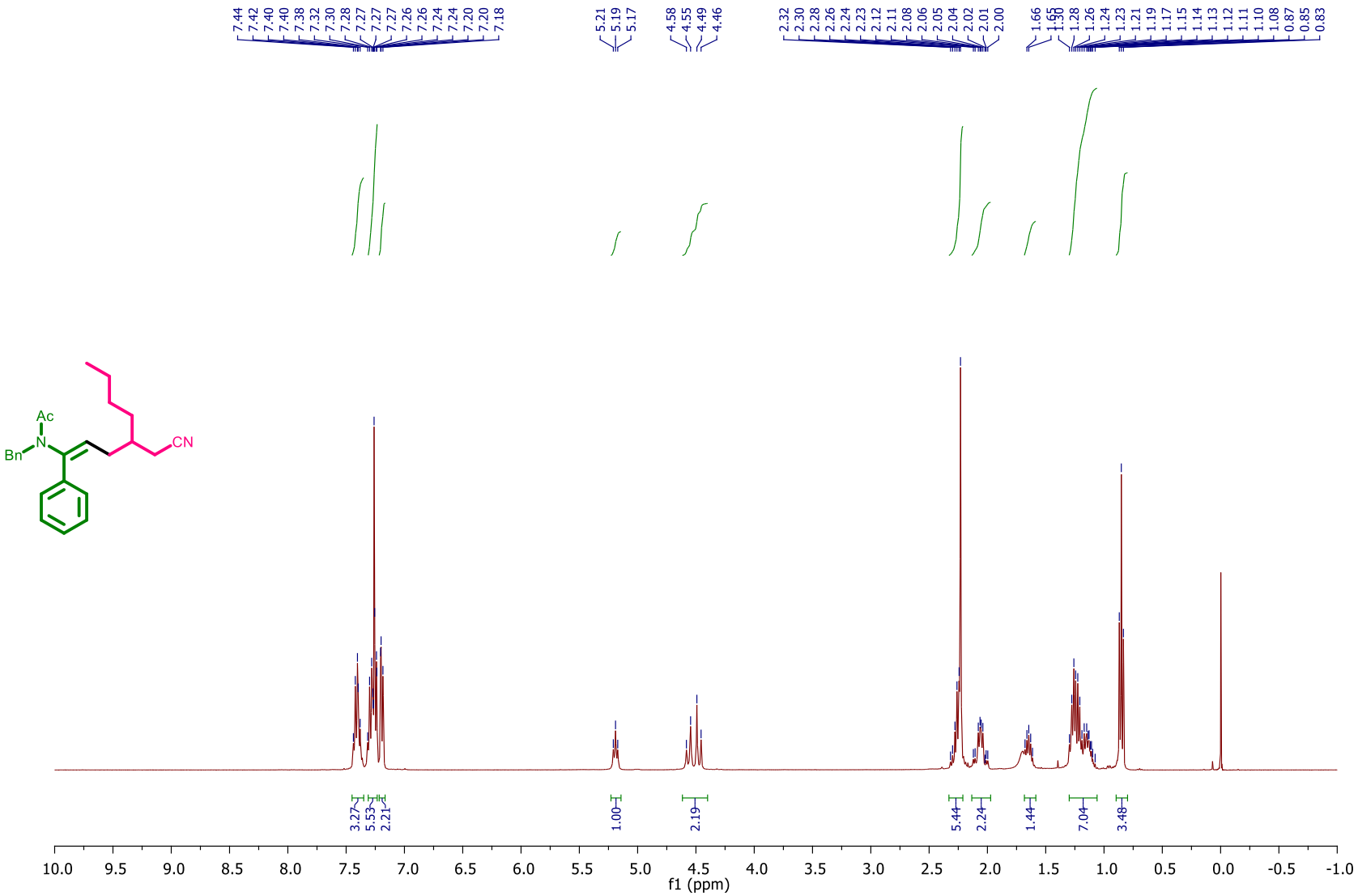
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3qa)**



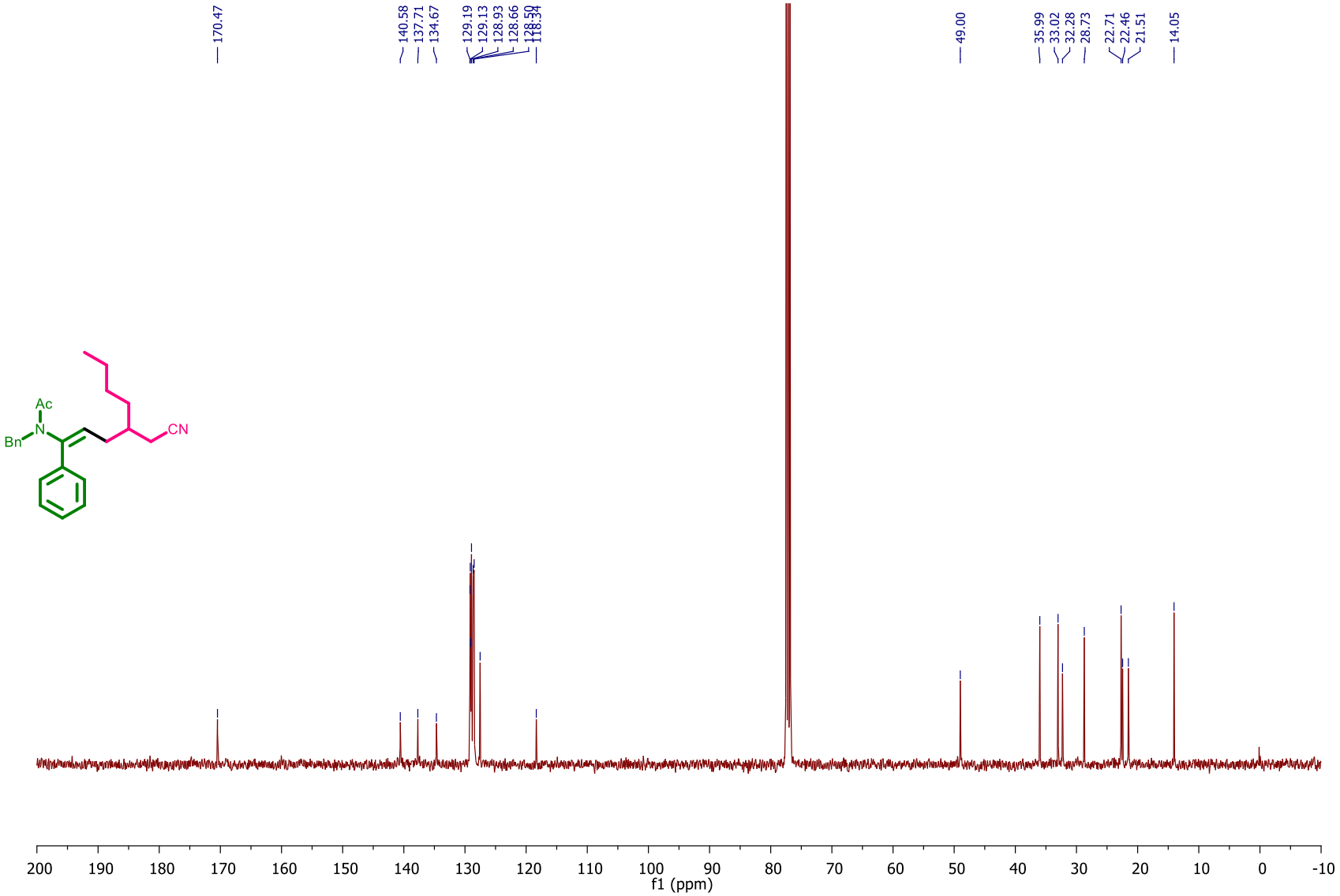
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3qa)**



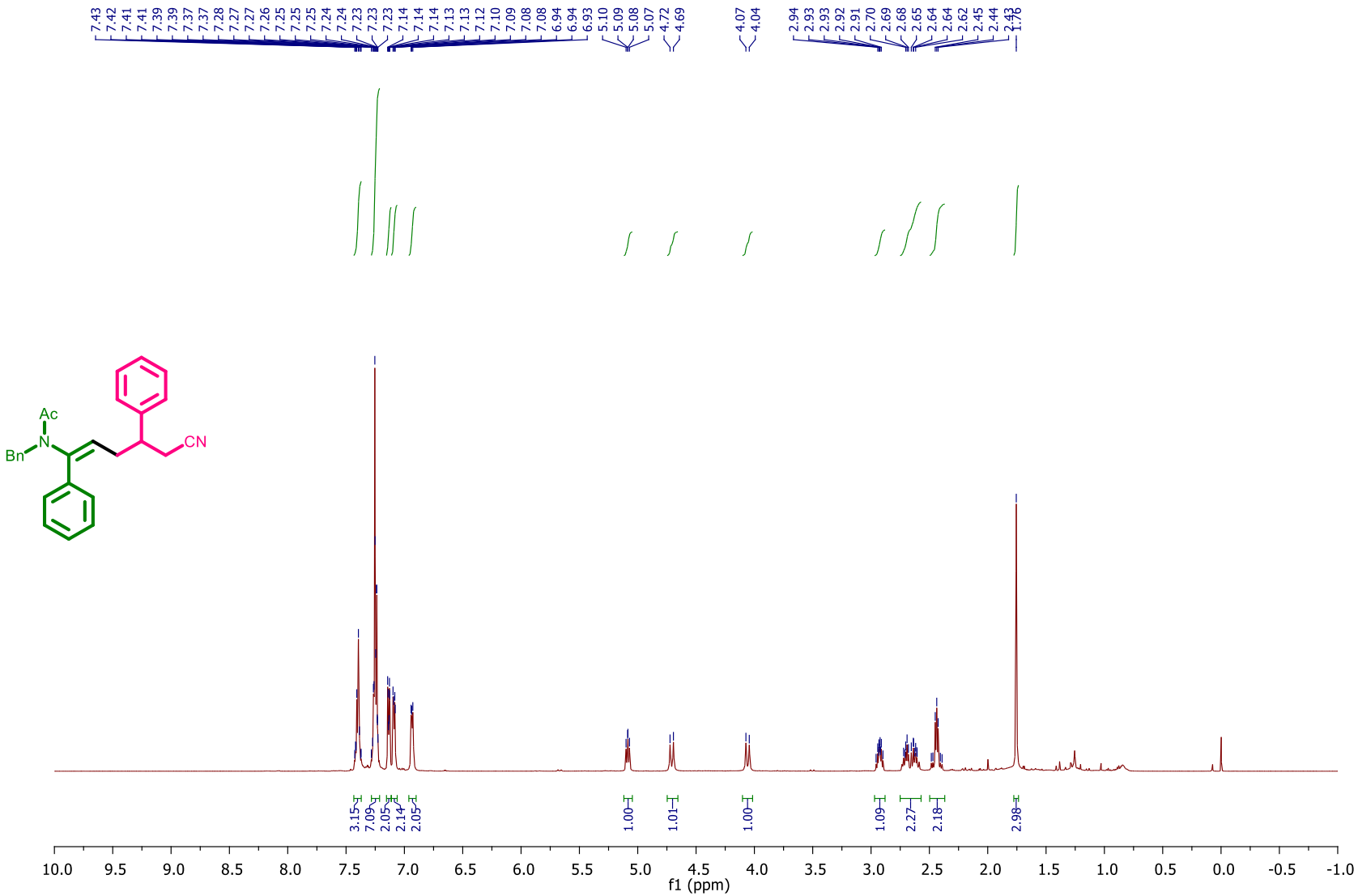
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ab)**



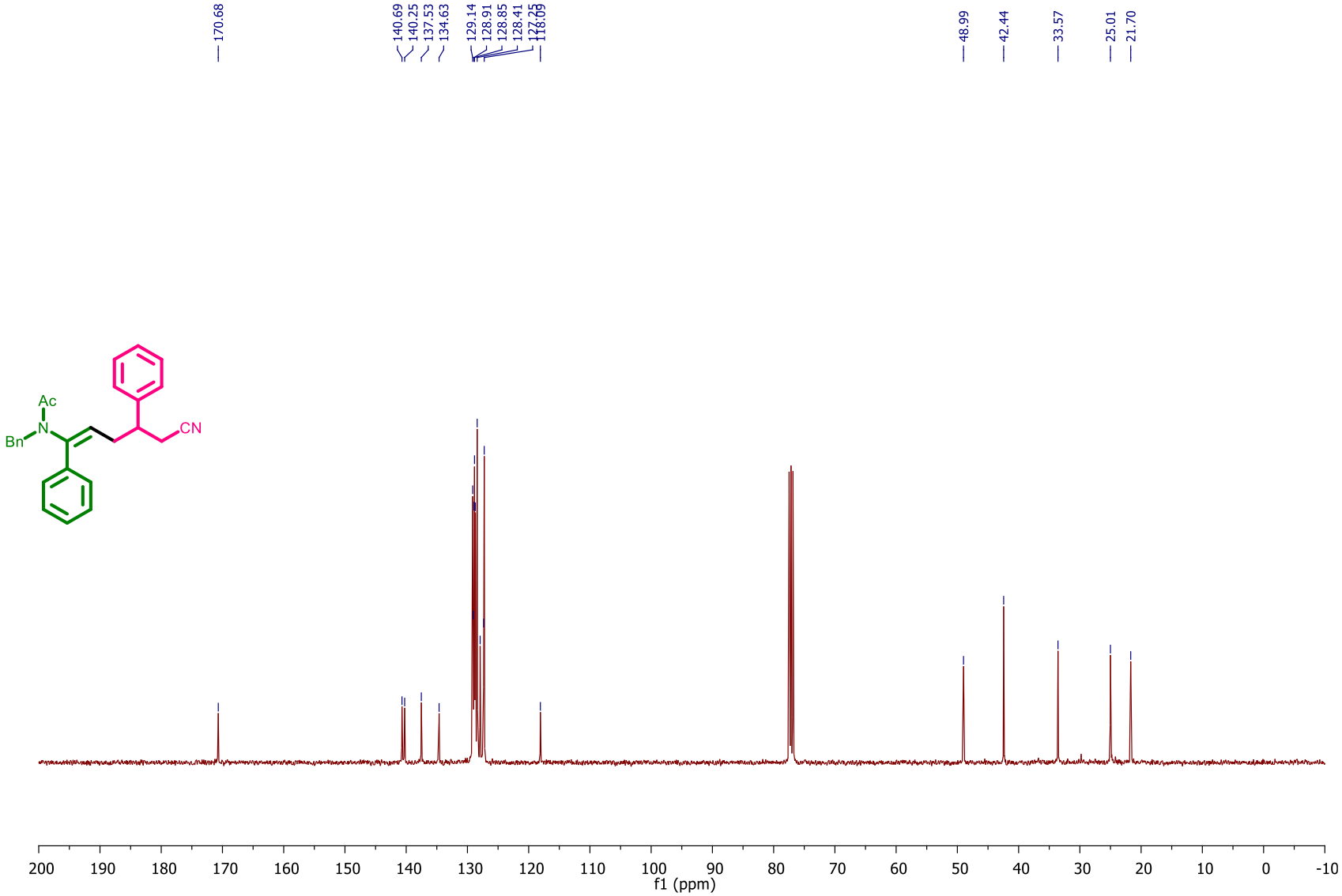
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ab)**



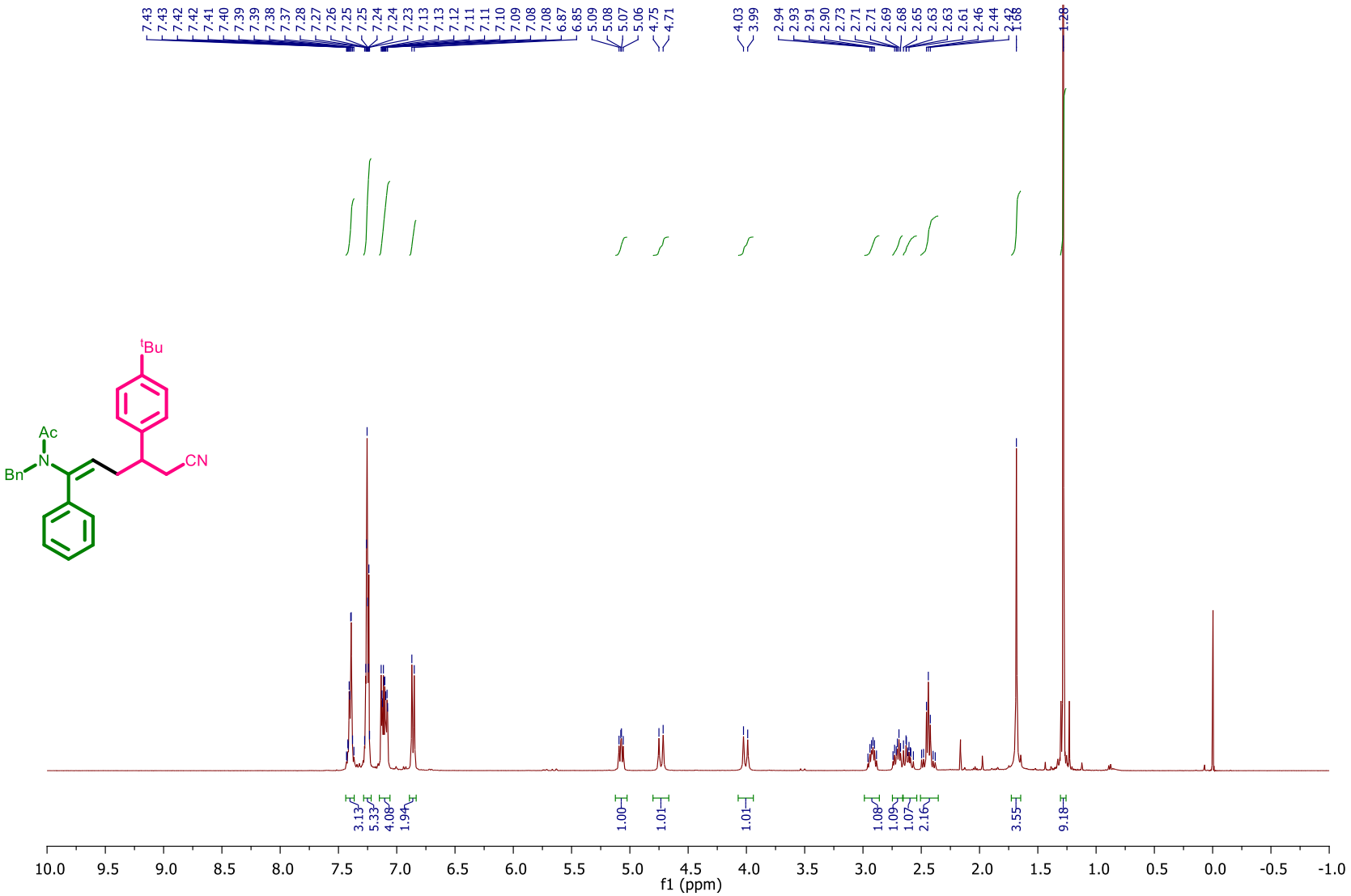
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3ac)**



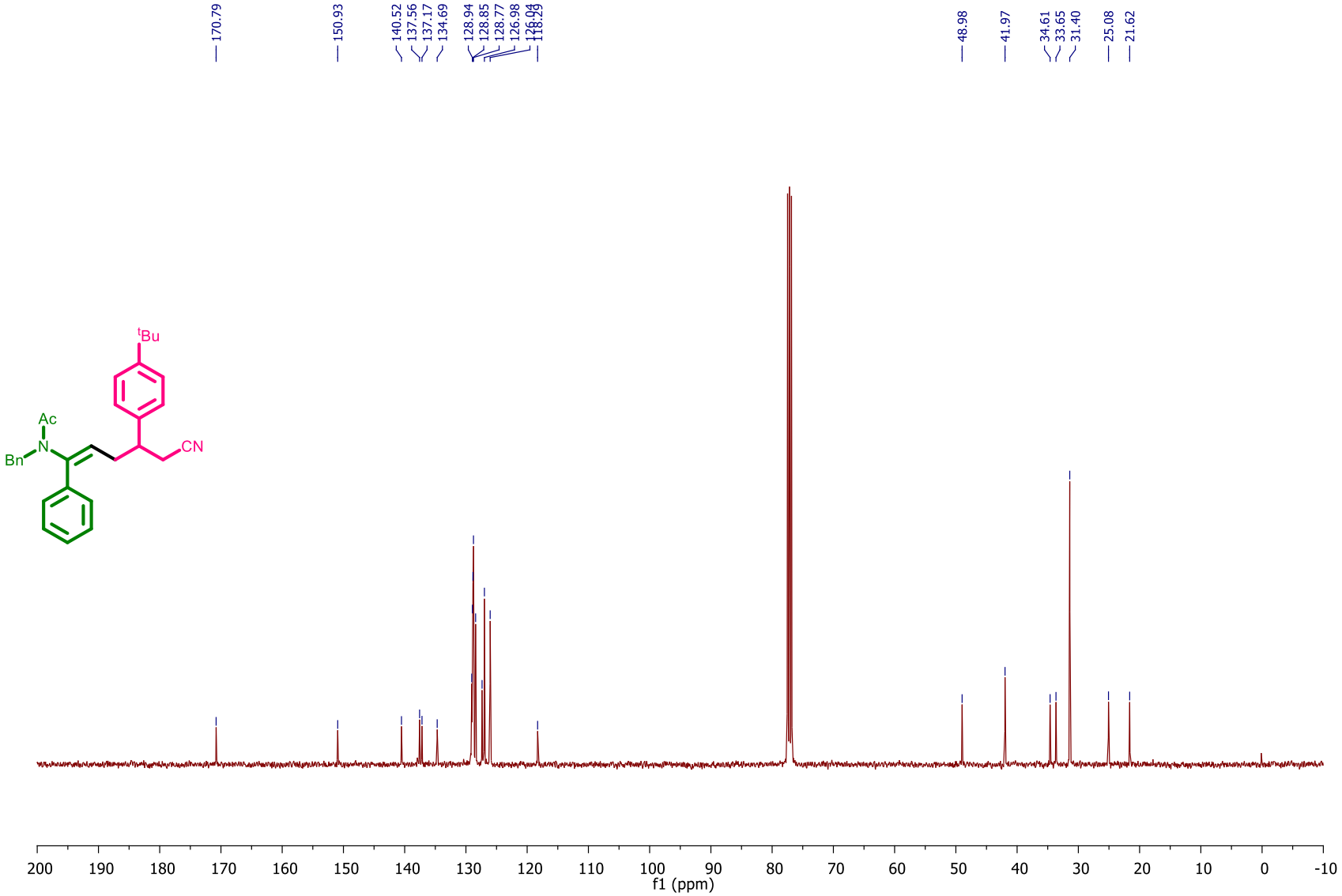
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ac)**



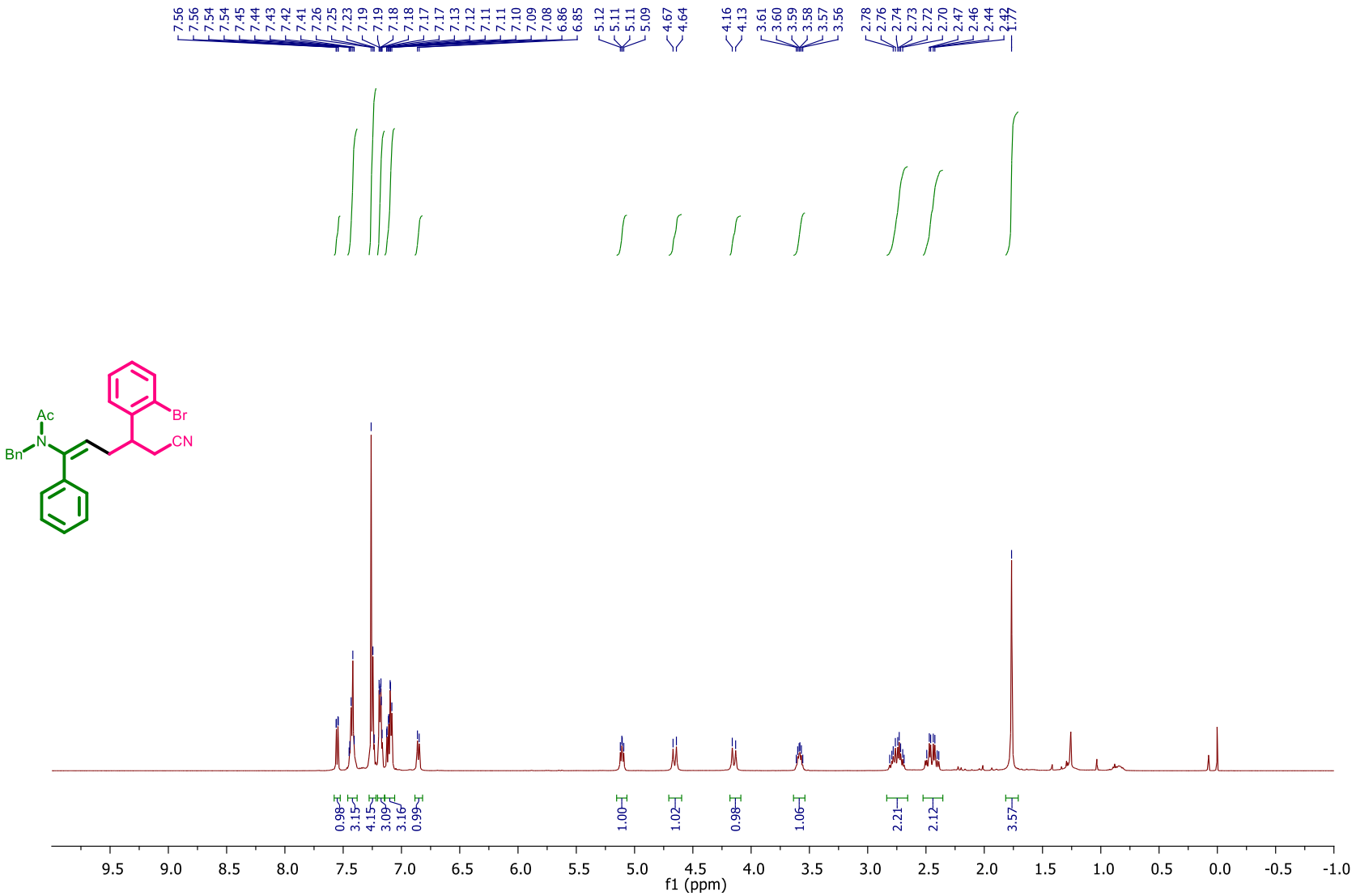
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ad)**



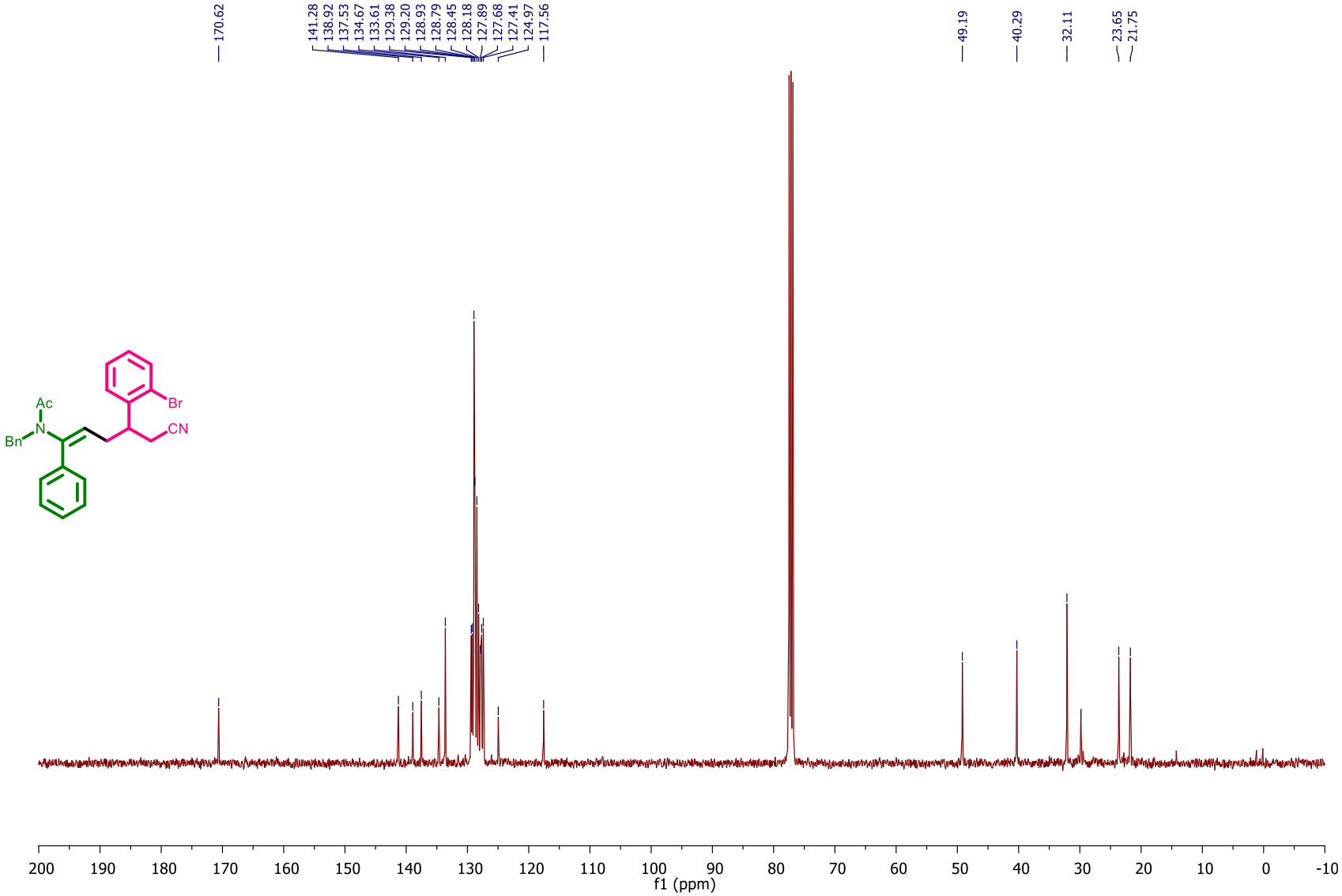
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ad)**



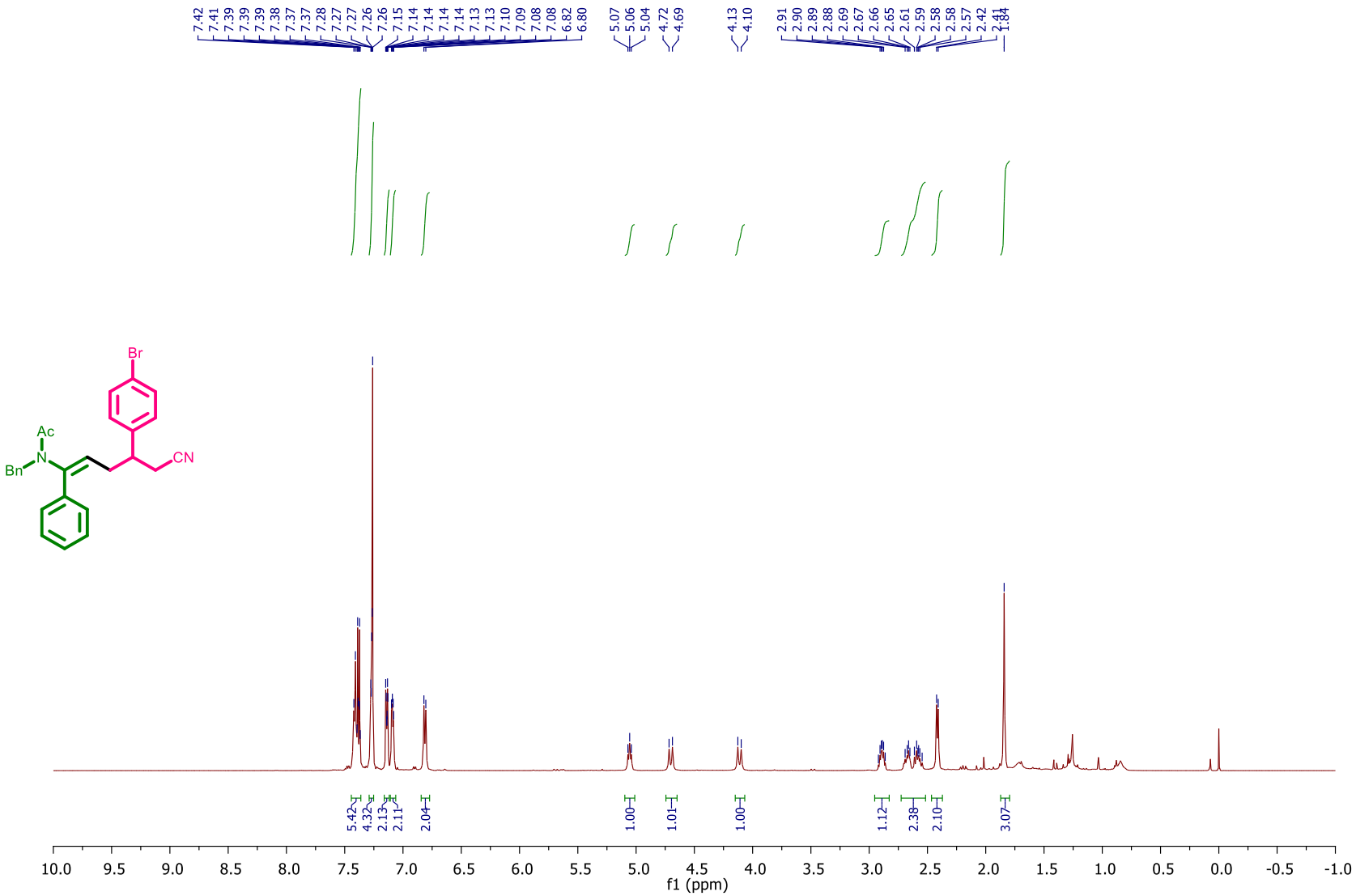
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3ae)**



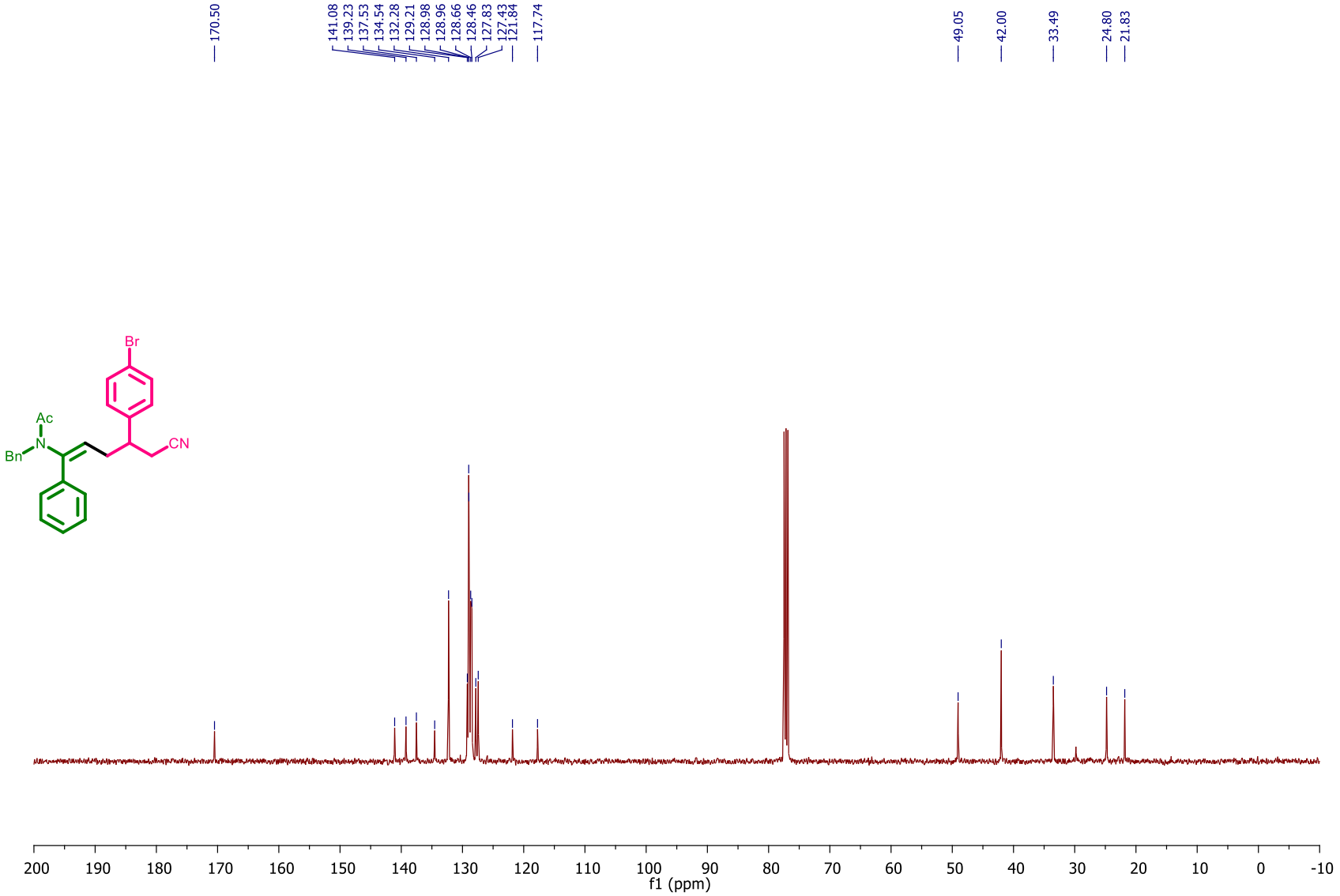
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ae)**



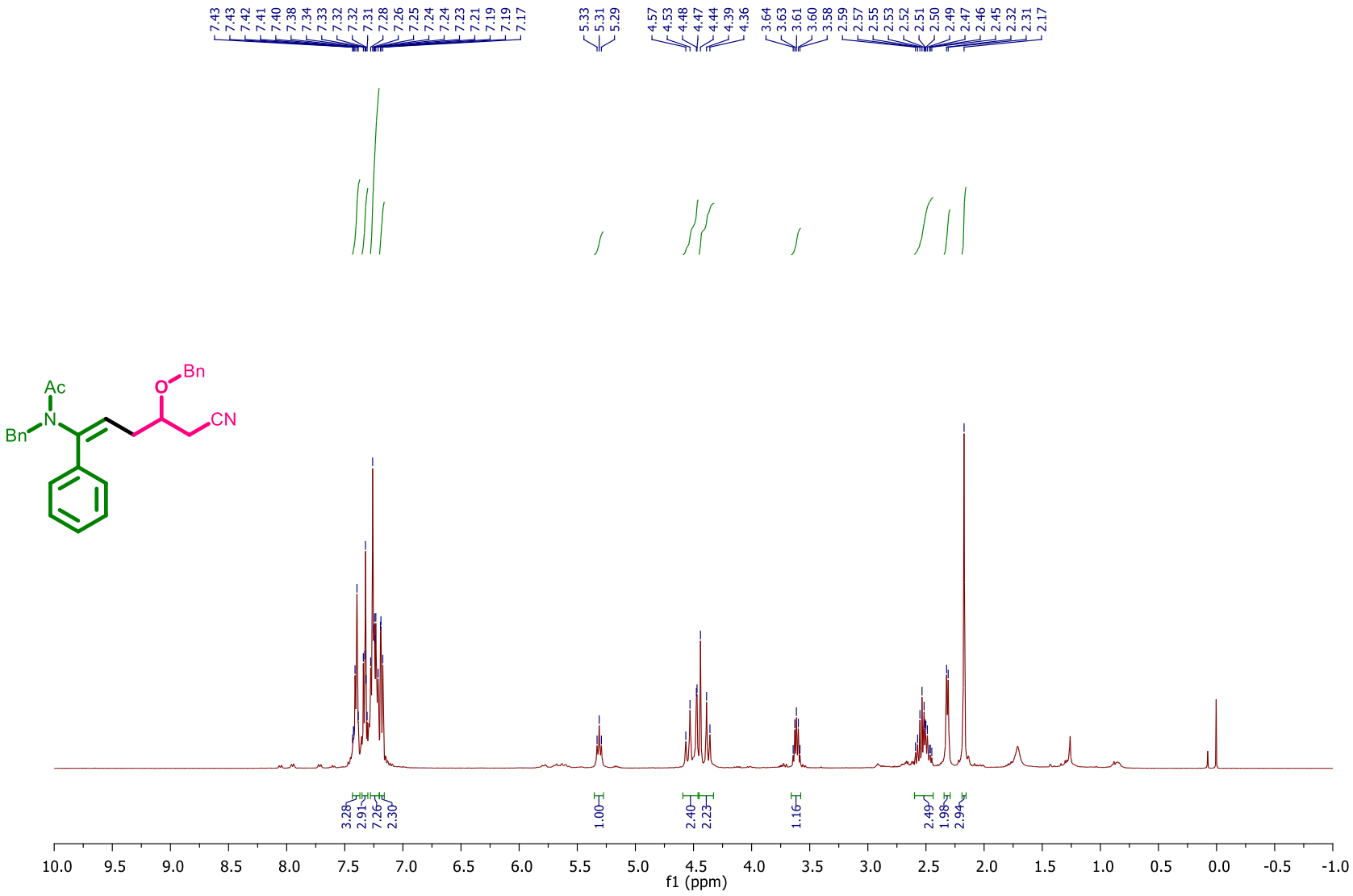
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(3af)**



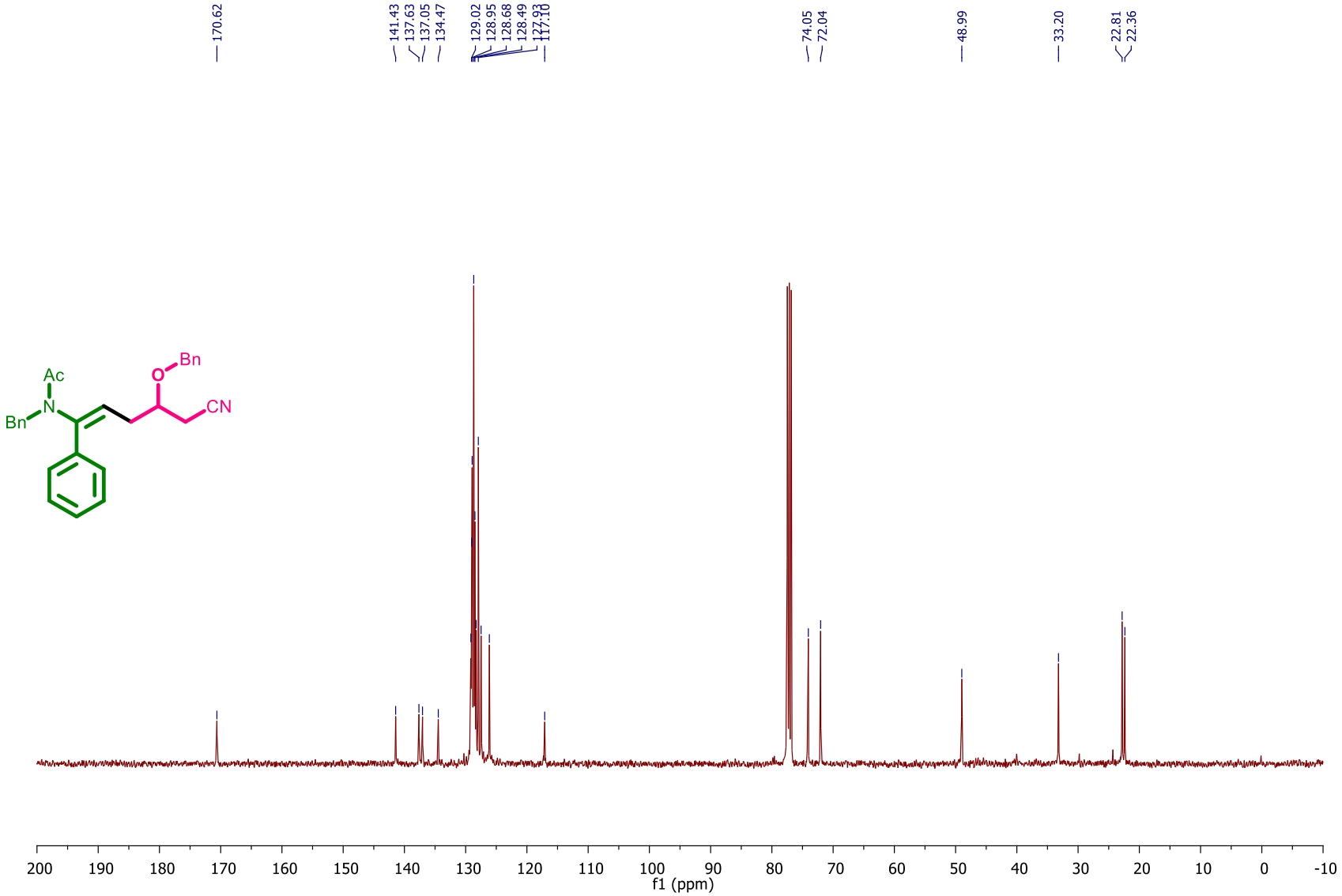
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3af)**



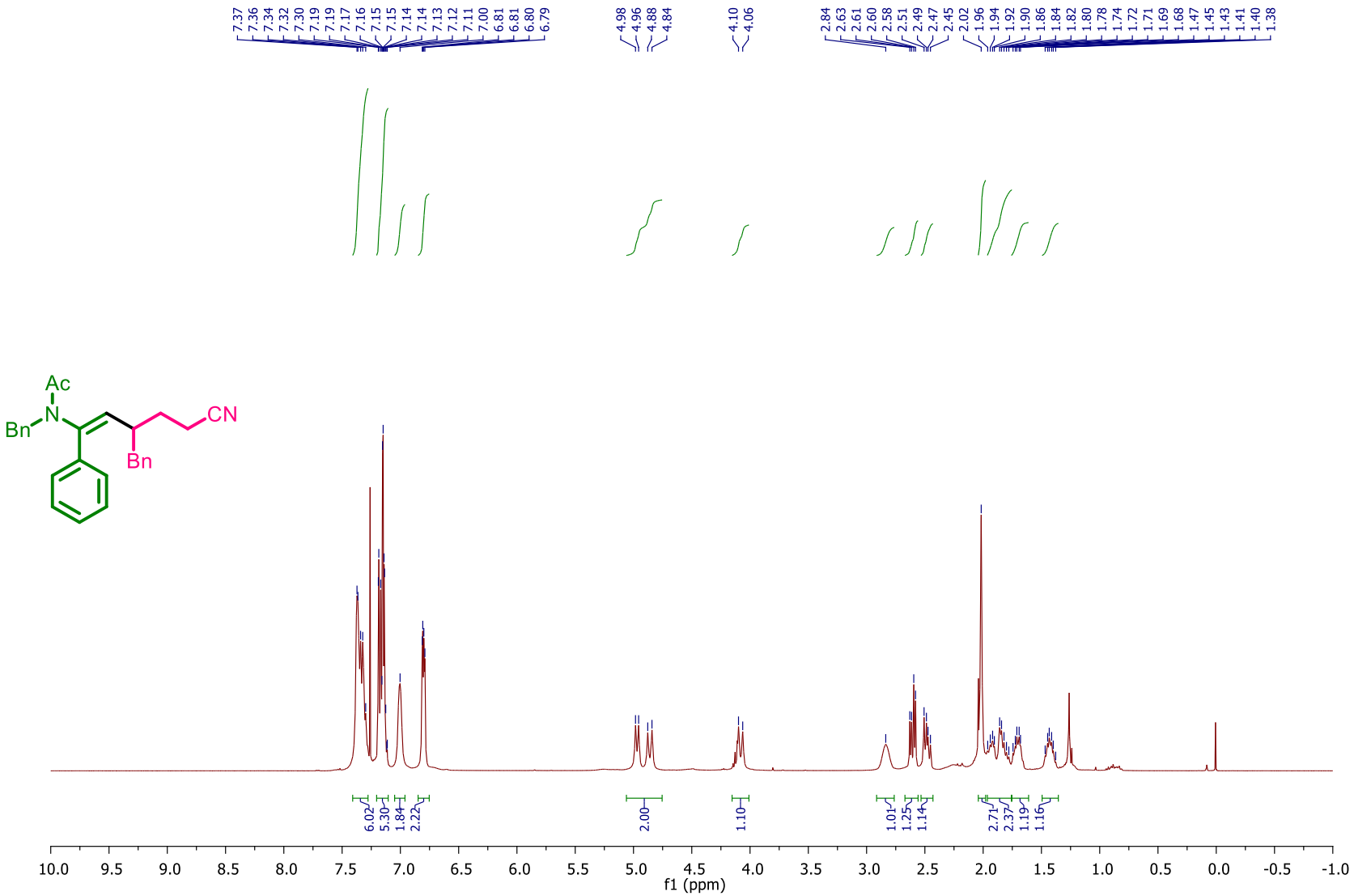
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ag)**



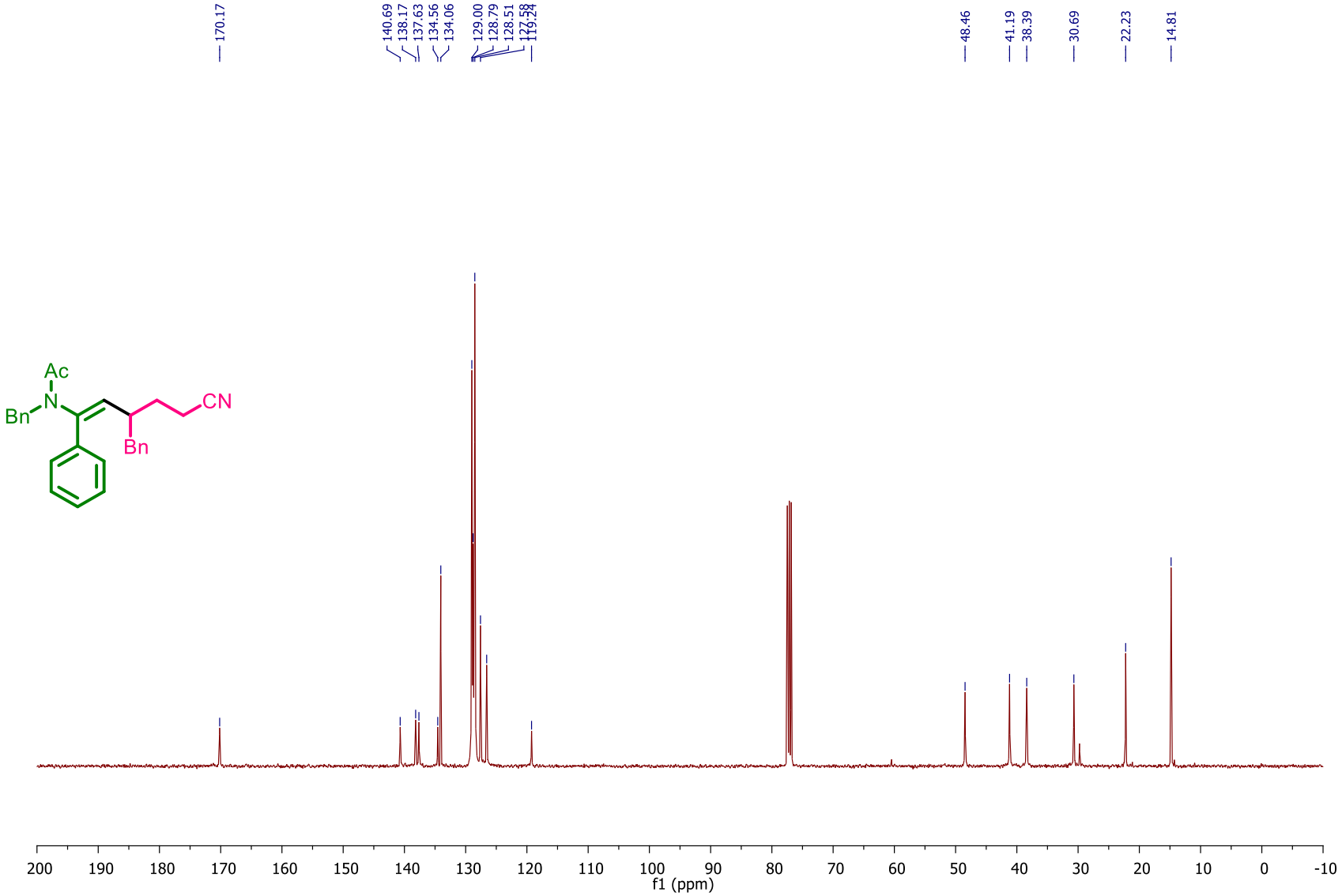
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ag)**



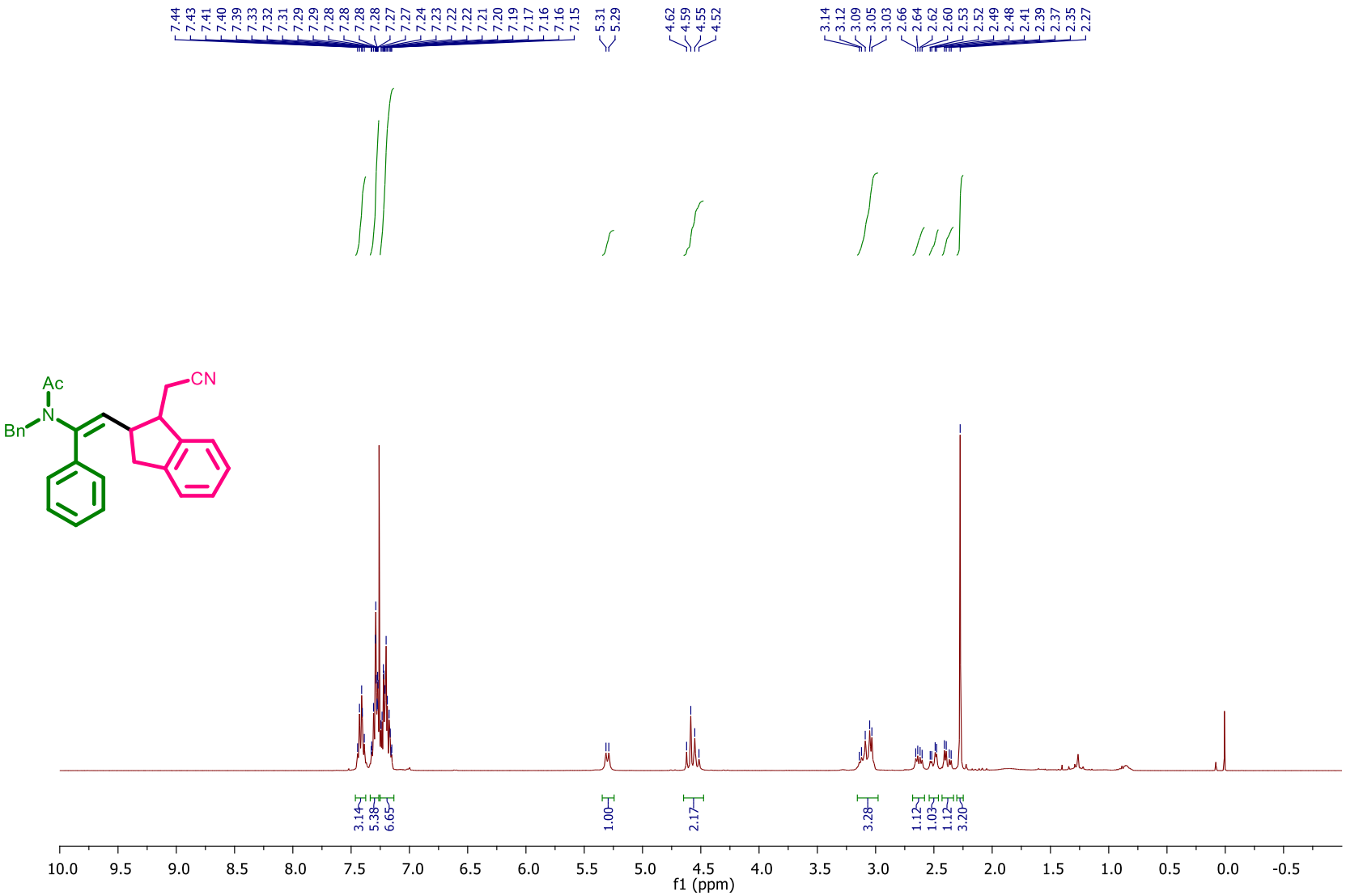
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ah)**



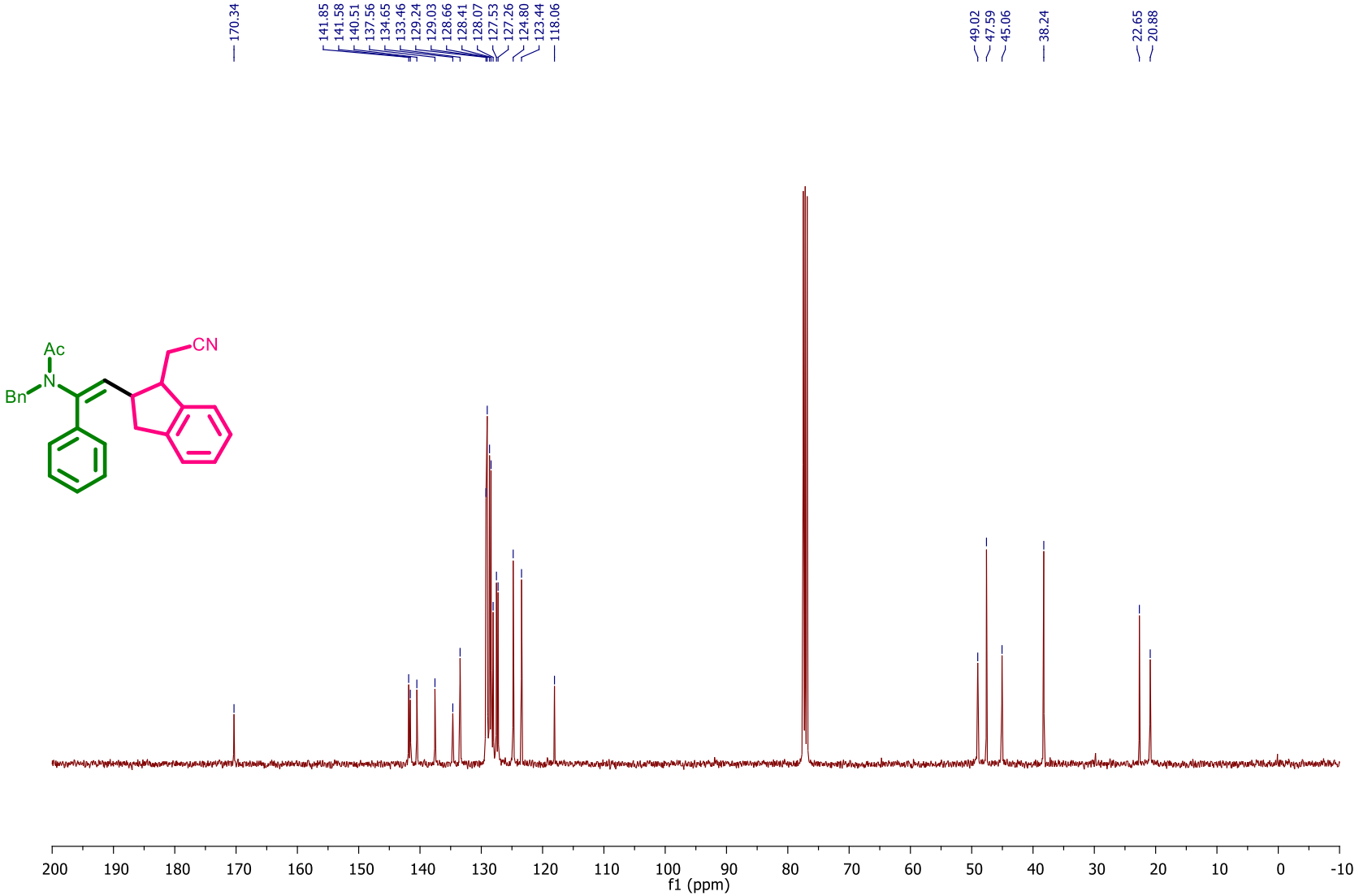
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ah)**



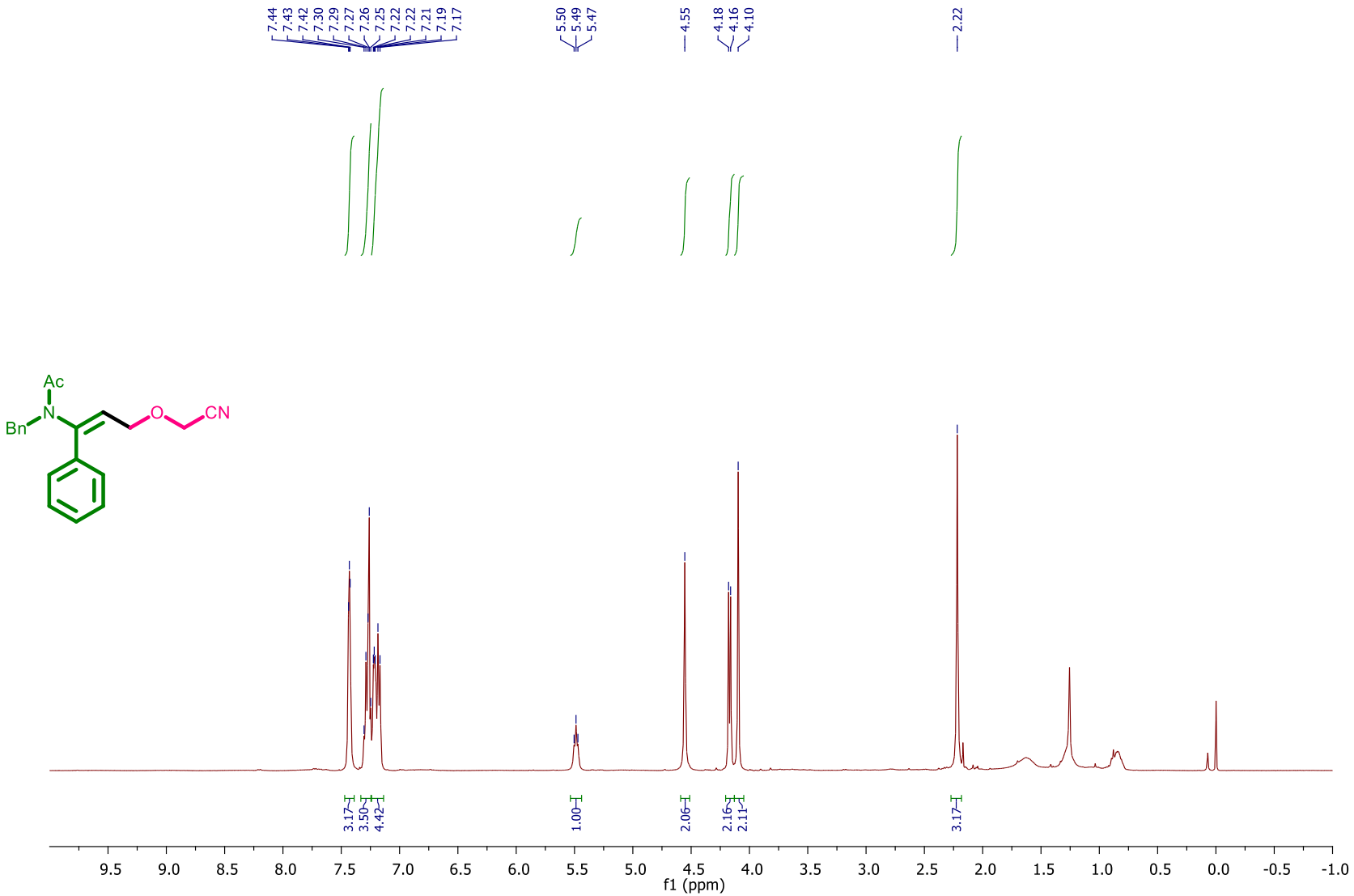
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ai)**



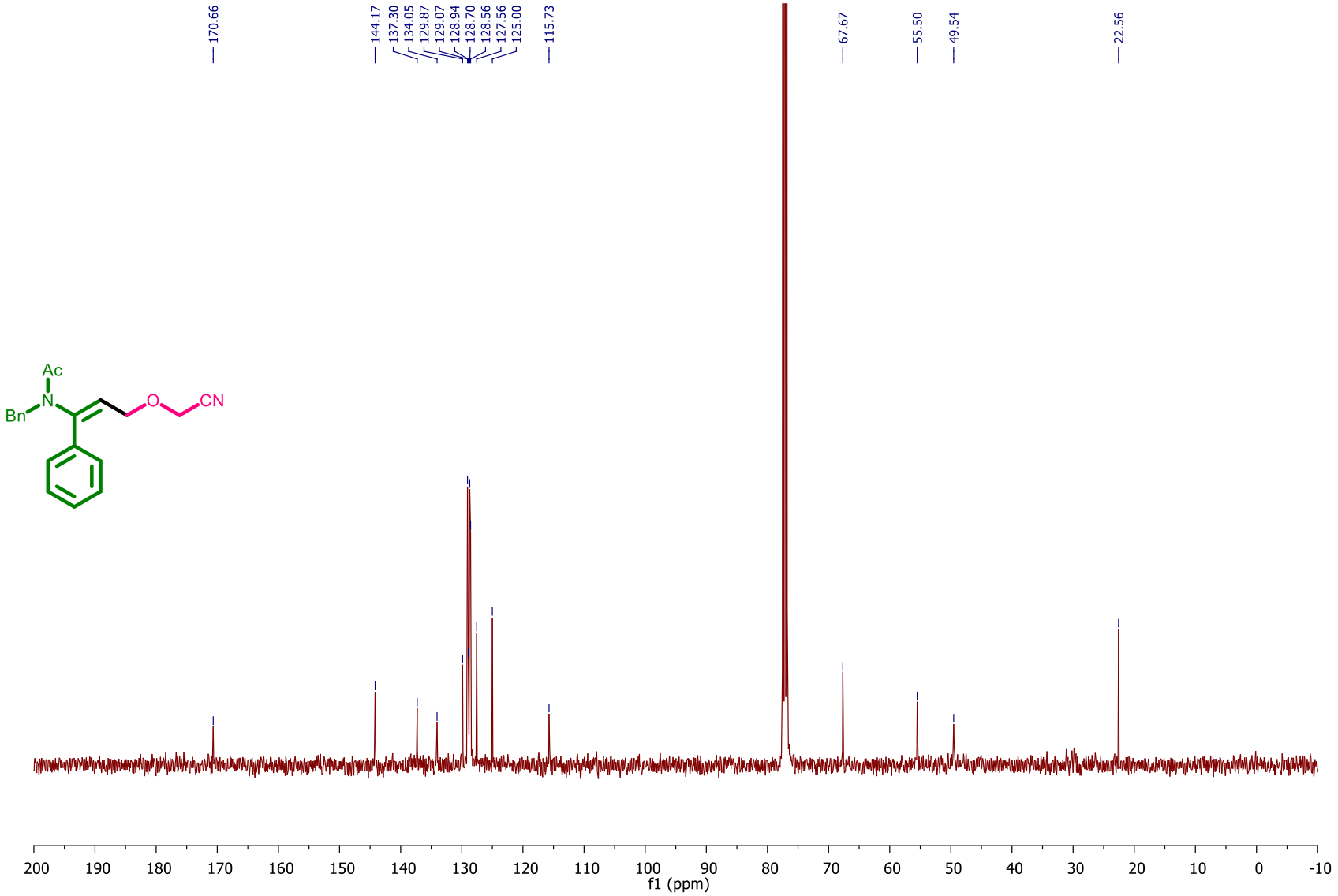
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ai)**



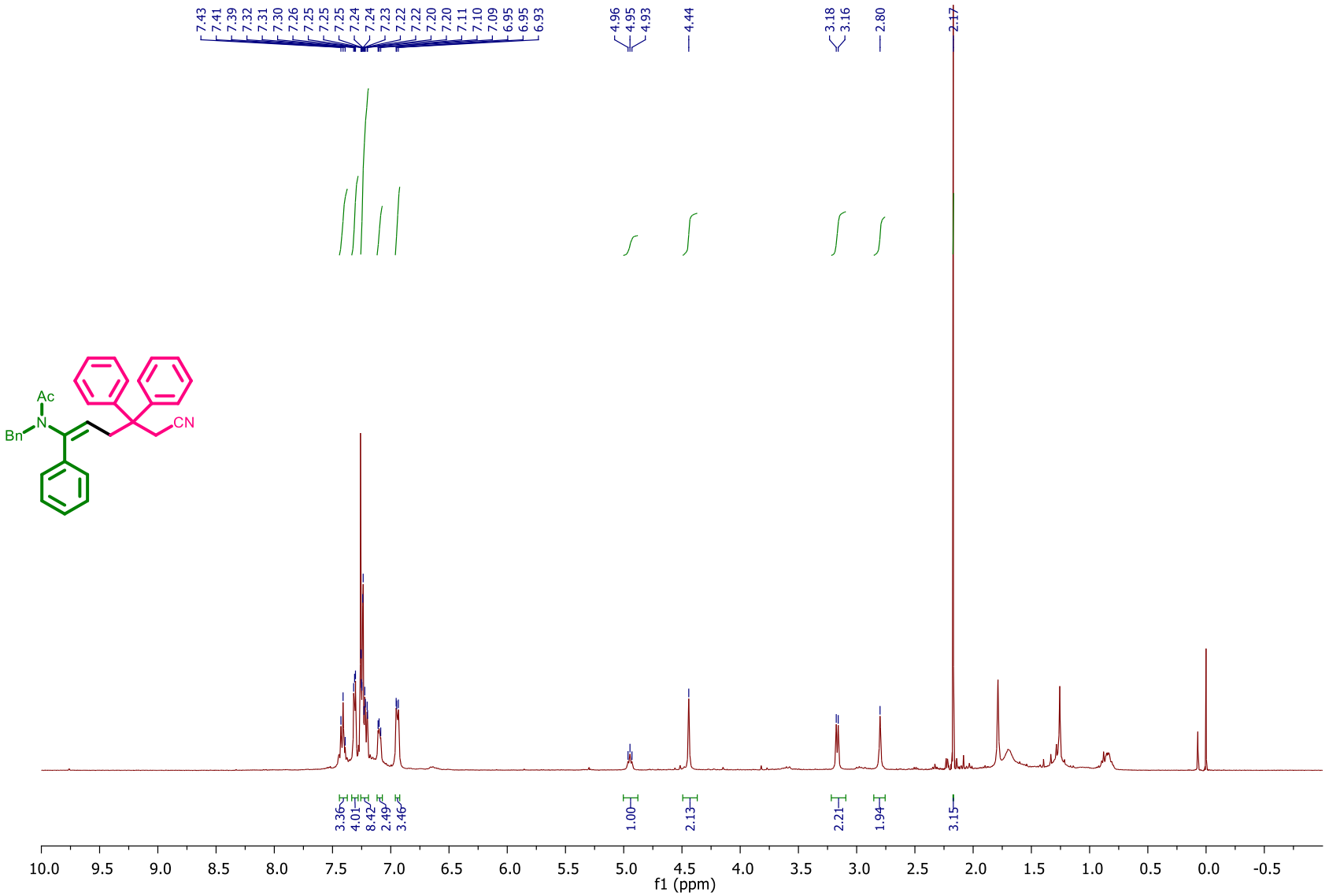
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3aj)**



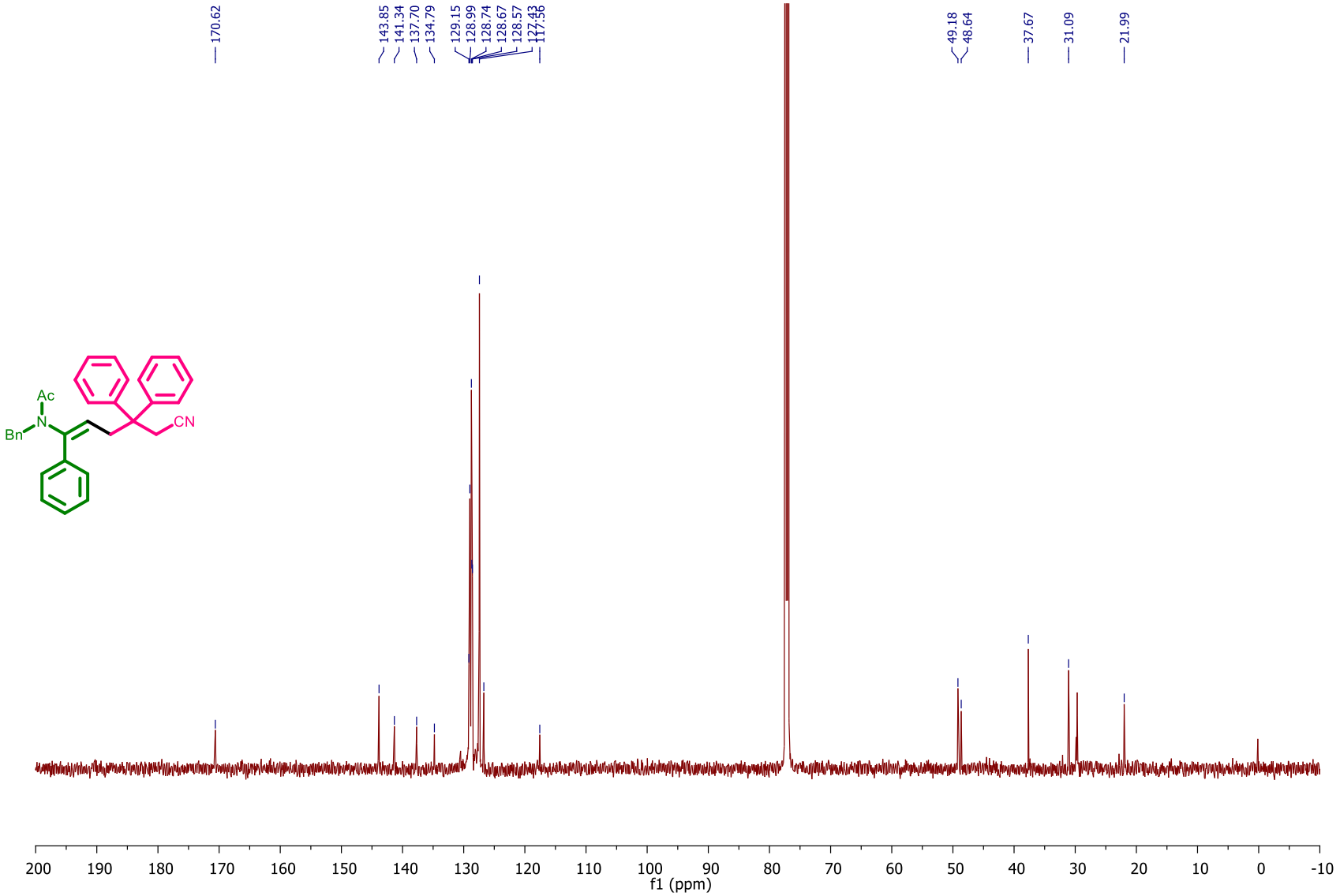
$^{13}C$ NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(3aj)**



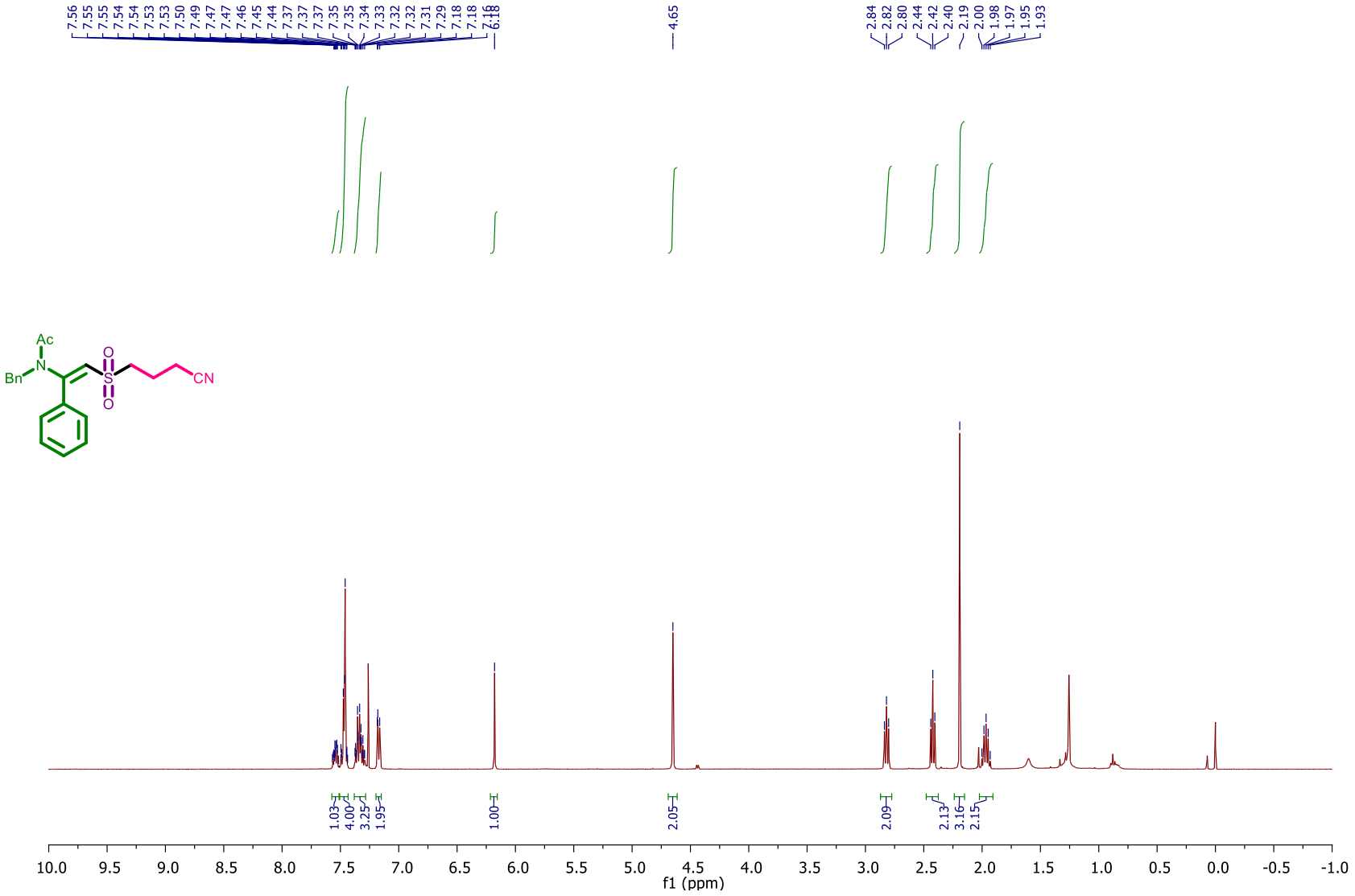
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(3ak)**



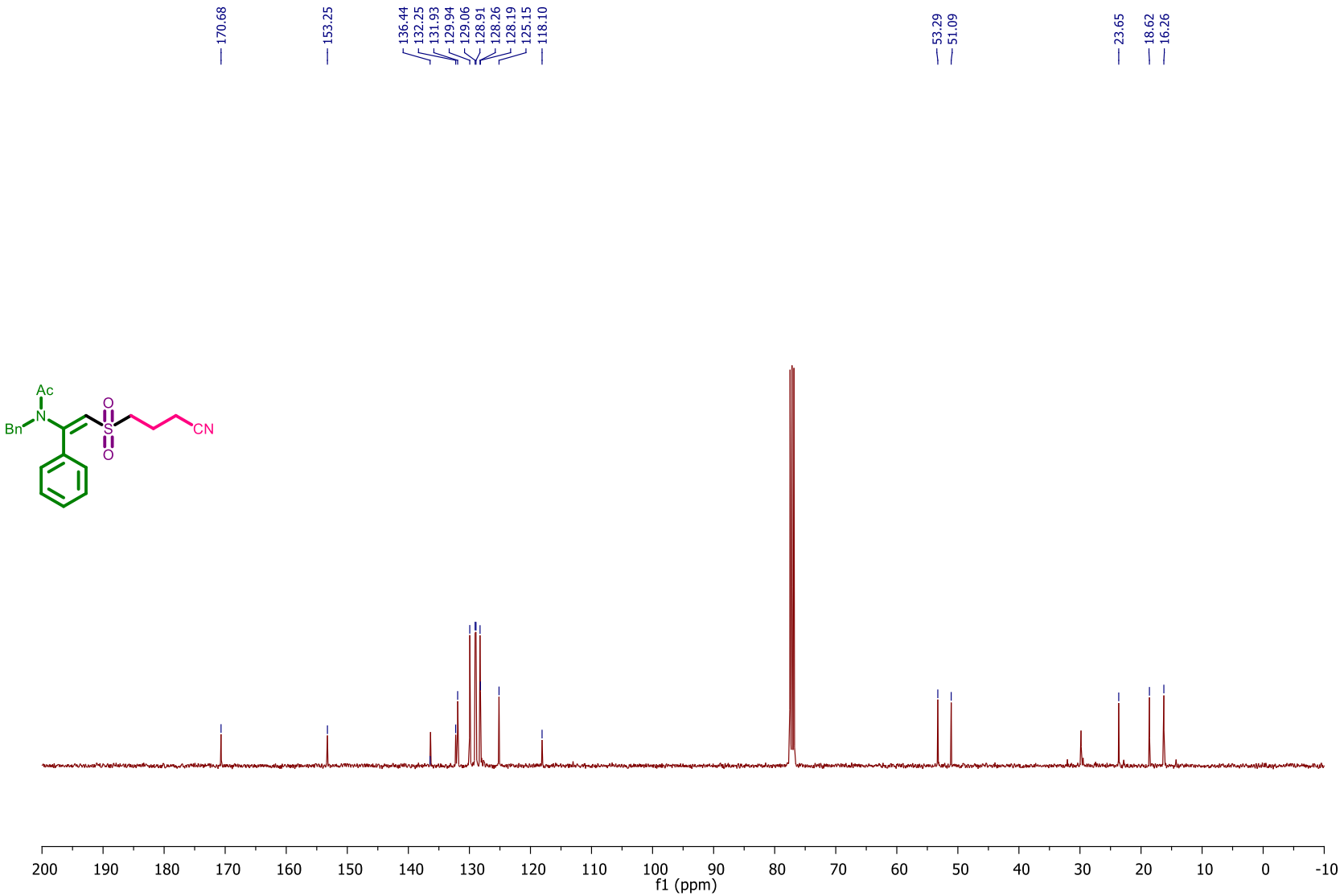
$^{13}C$ NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(3ak)**

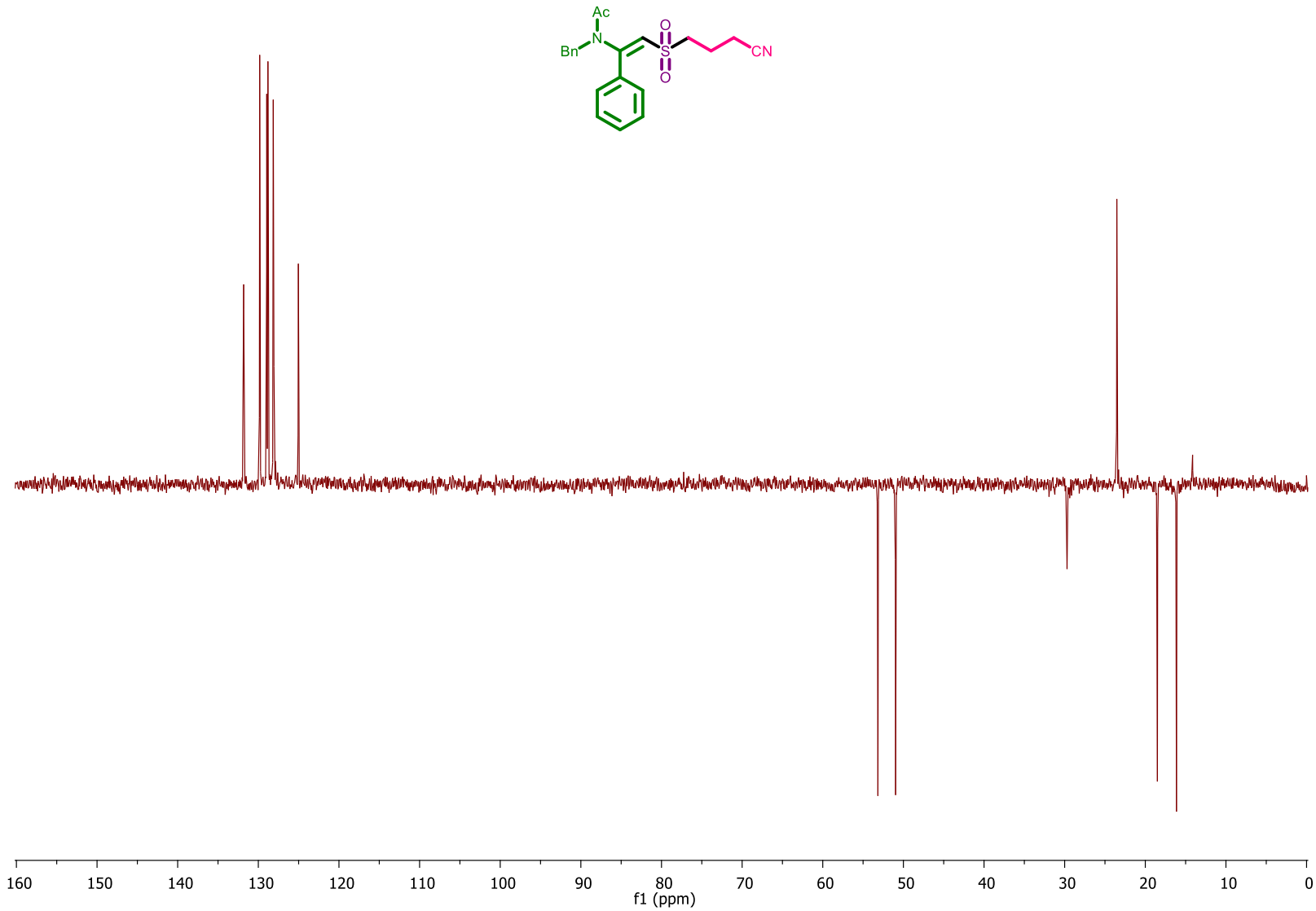


$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4aa)**

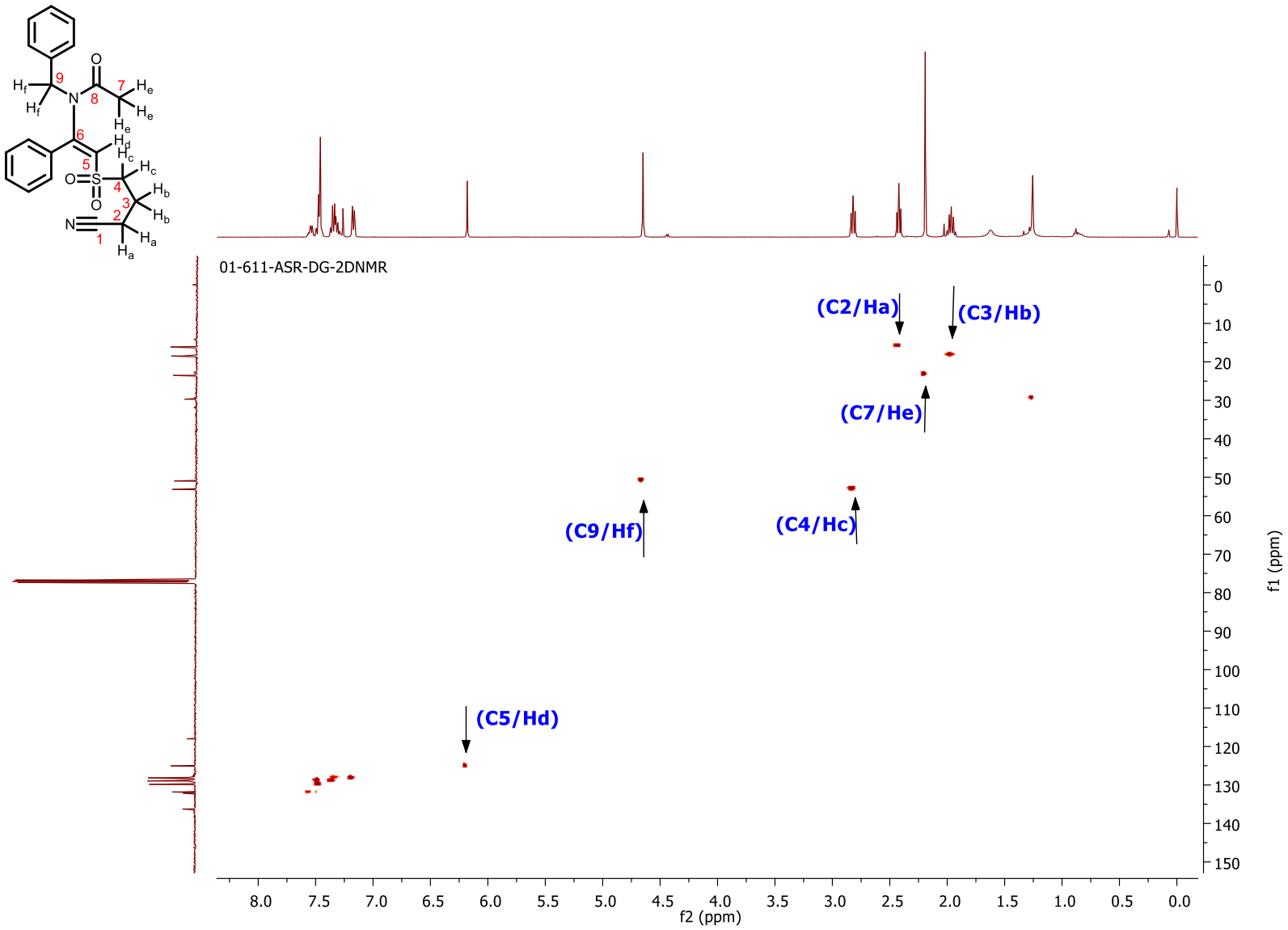


$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound (**4aa)**

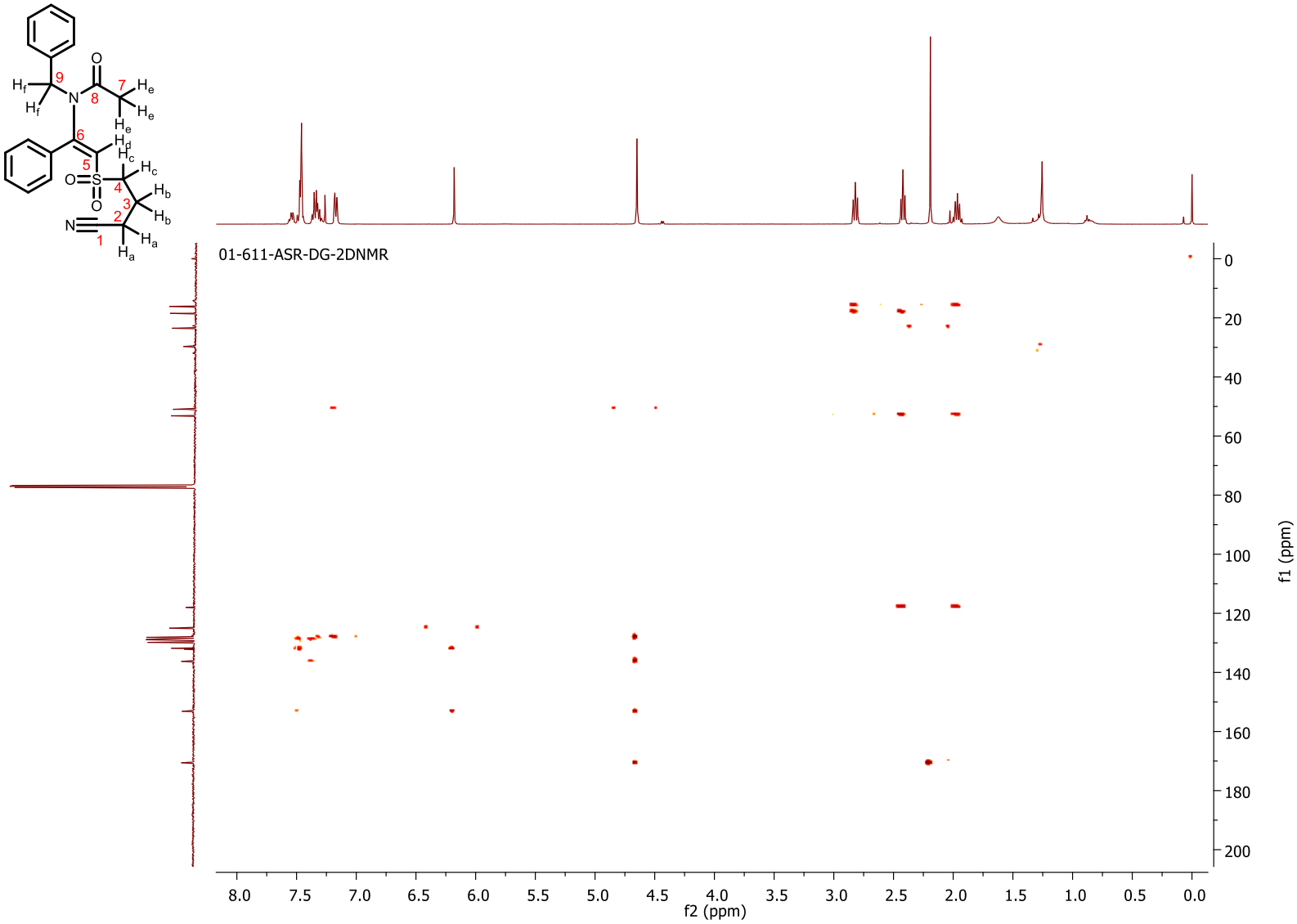




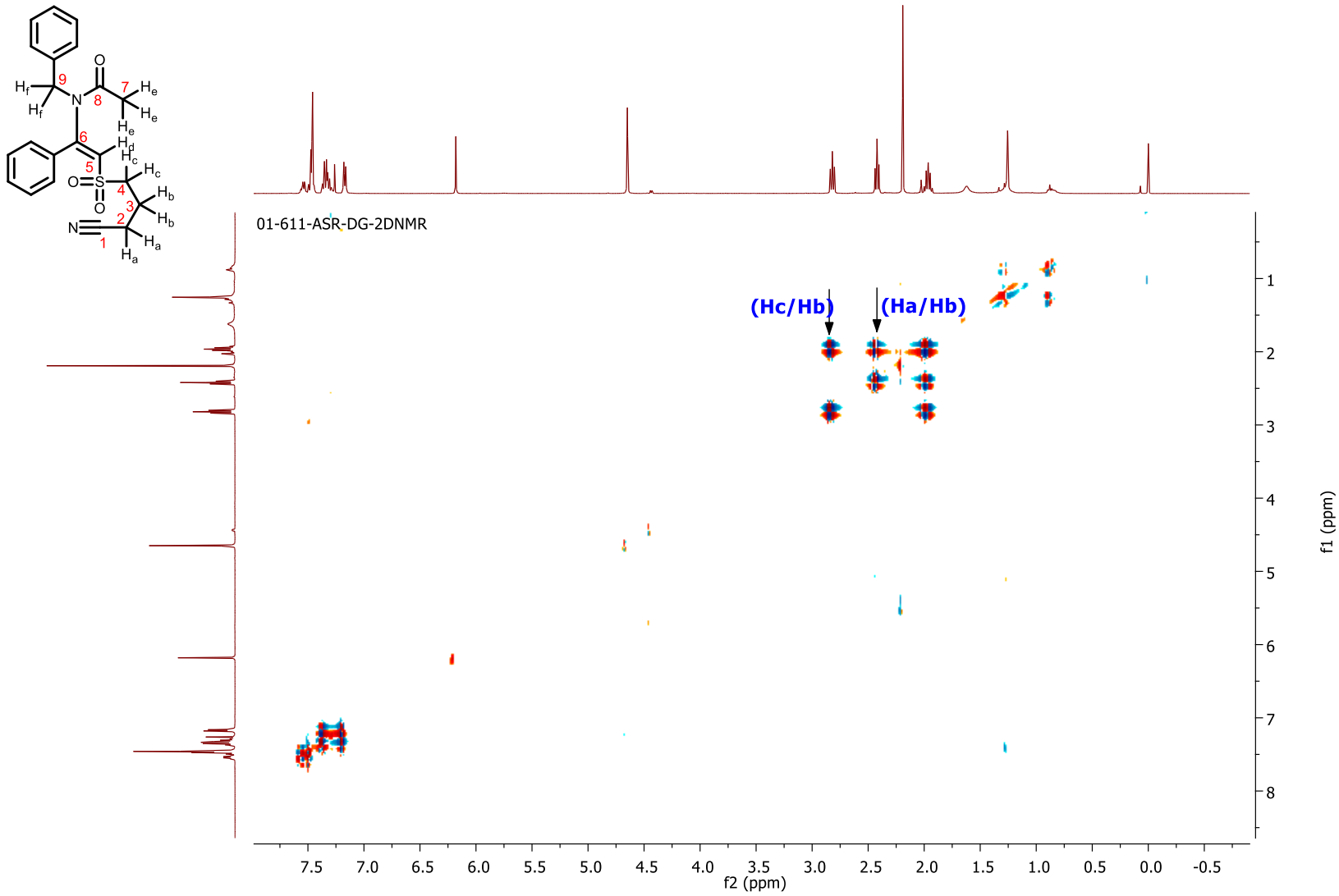

**DEPT spectrum of 4aa**



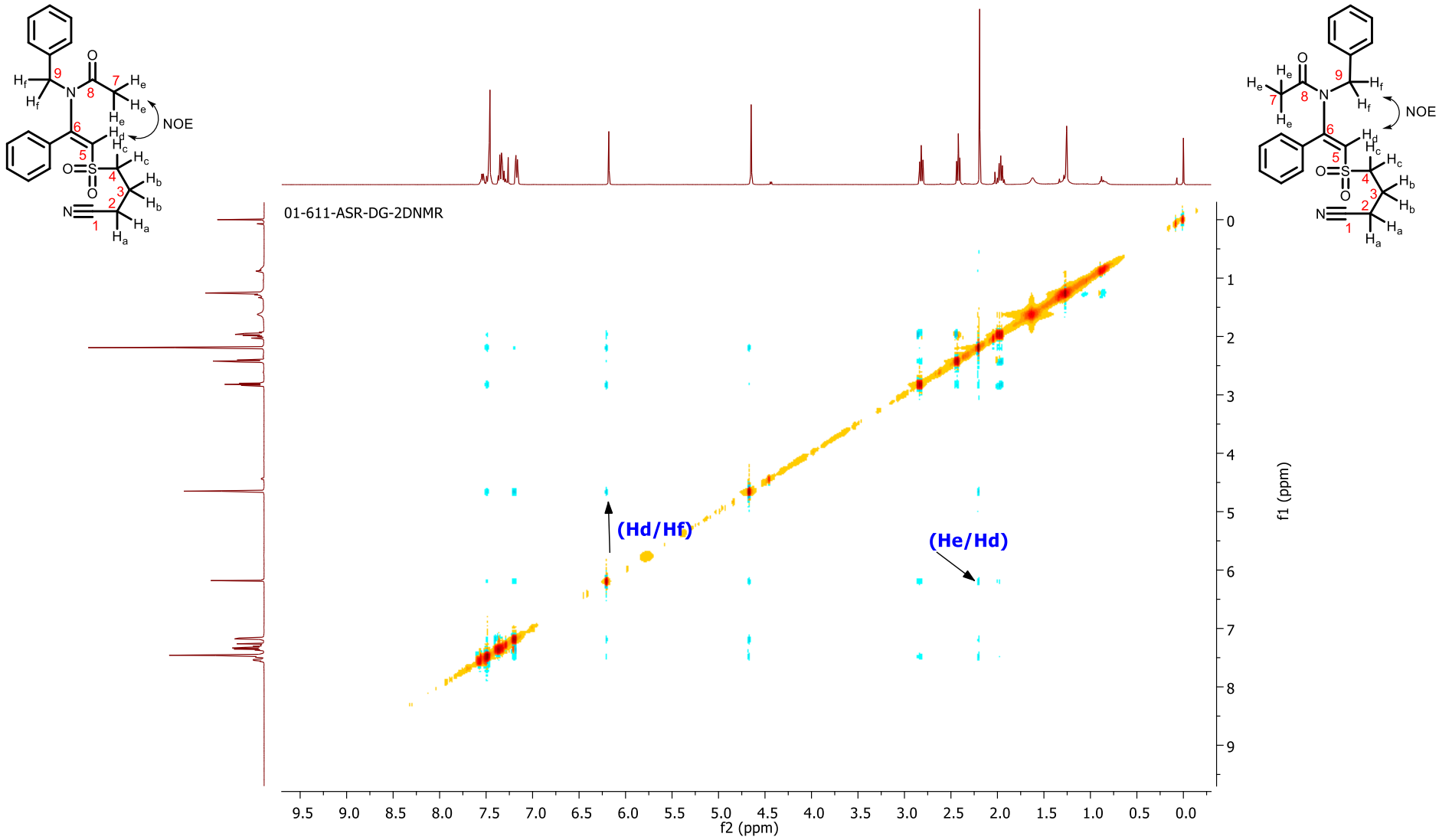

**$^{1}$H-$^{13}$C 2D-HSQC spectrum of 4aa**




**$^{1}$H-$^{13}$C 2D-HMBC spectrum of 4aa**

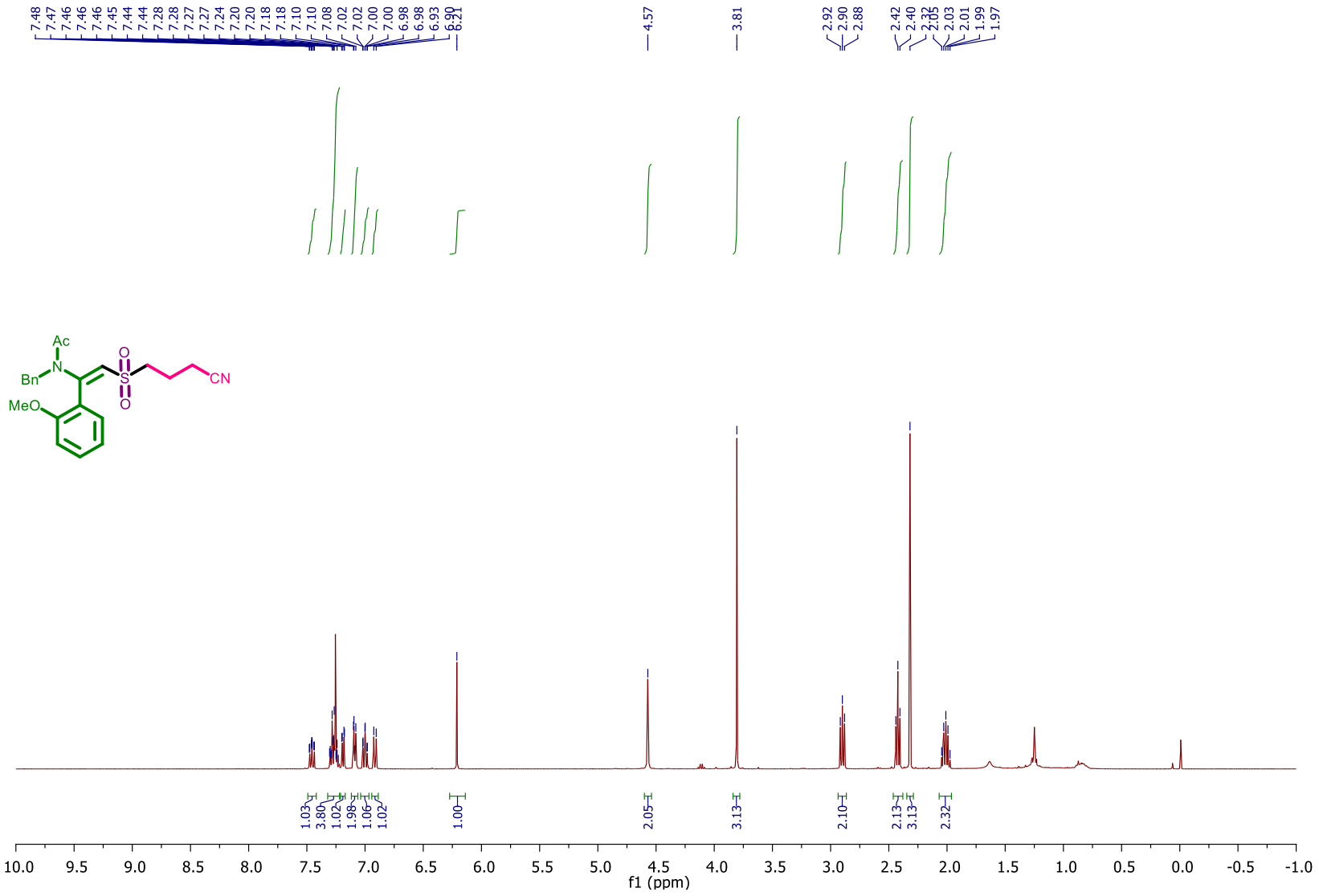



**$^{1}$H-$^{1}$H 2D-COSY spectrum of 4aa**

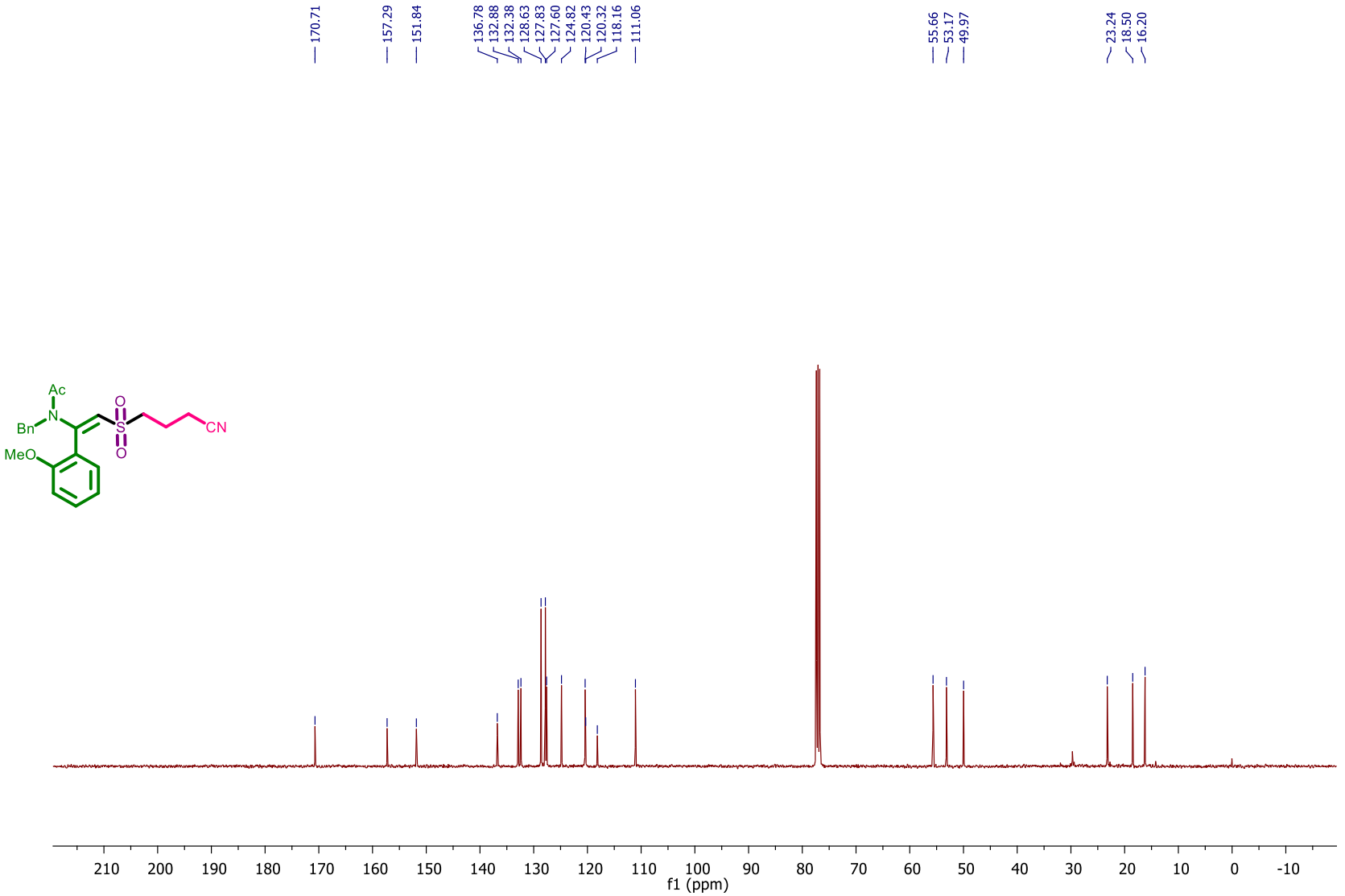



**$^{1}$H-$^{1}$H 2D-NOESY spectrum of 4aa**

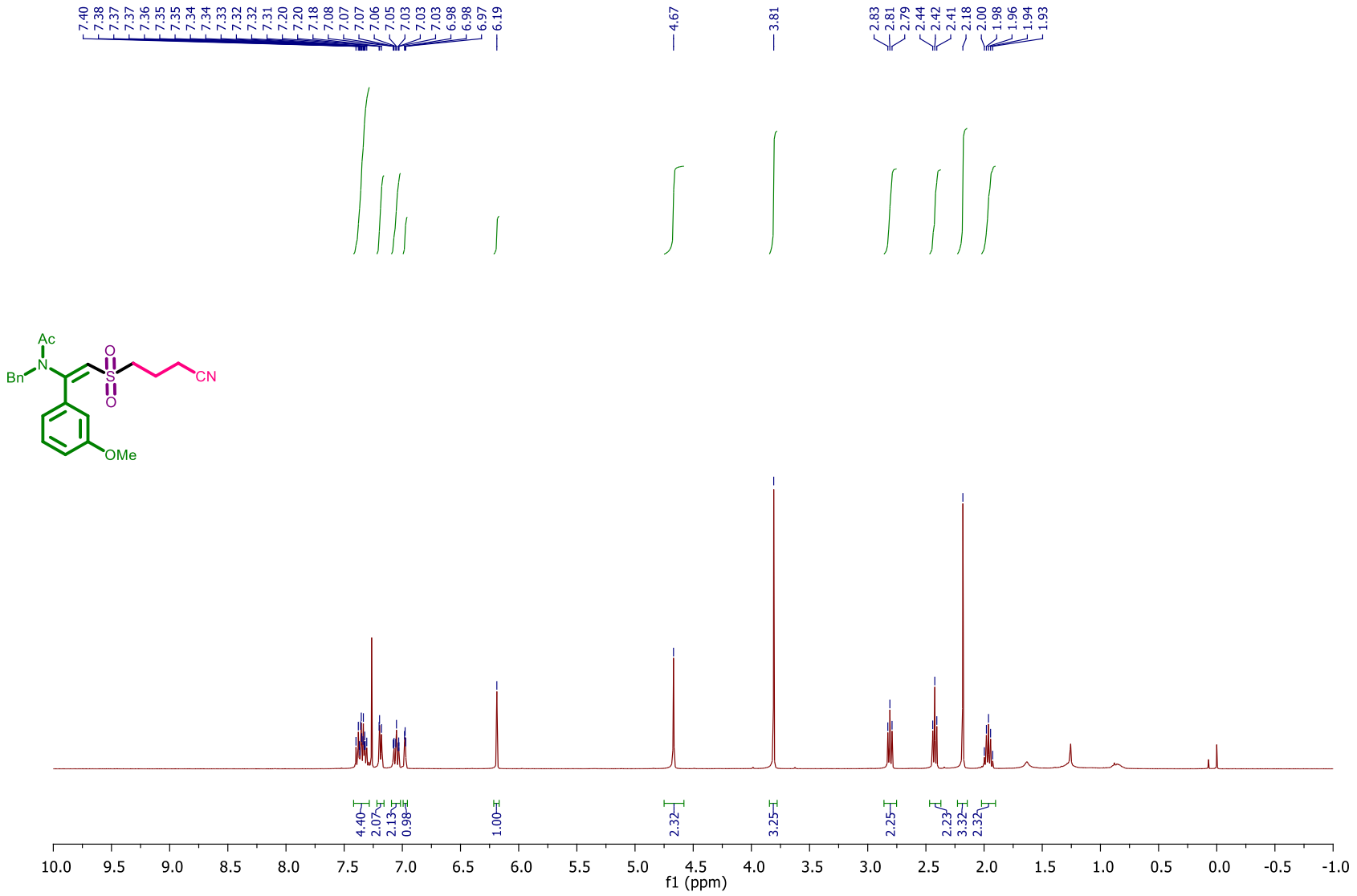
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ba)**



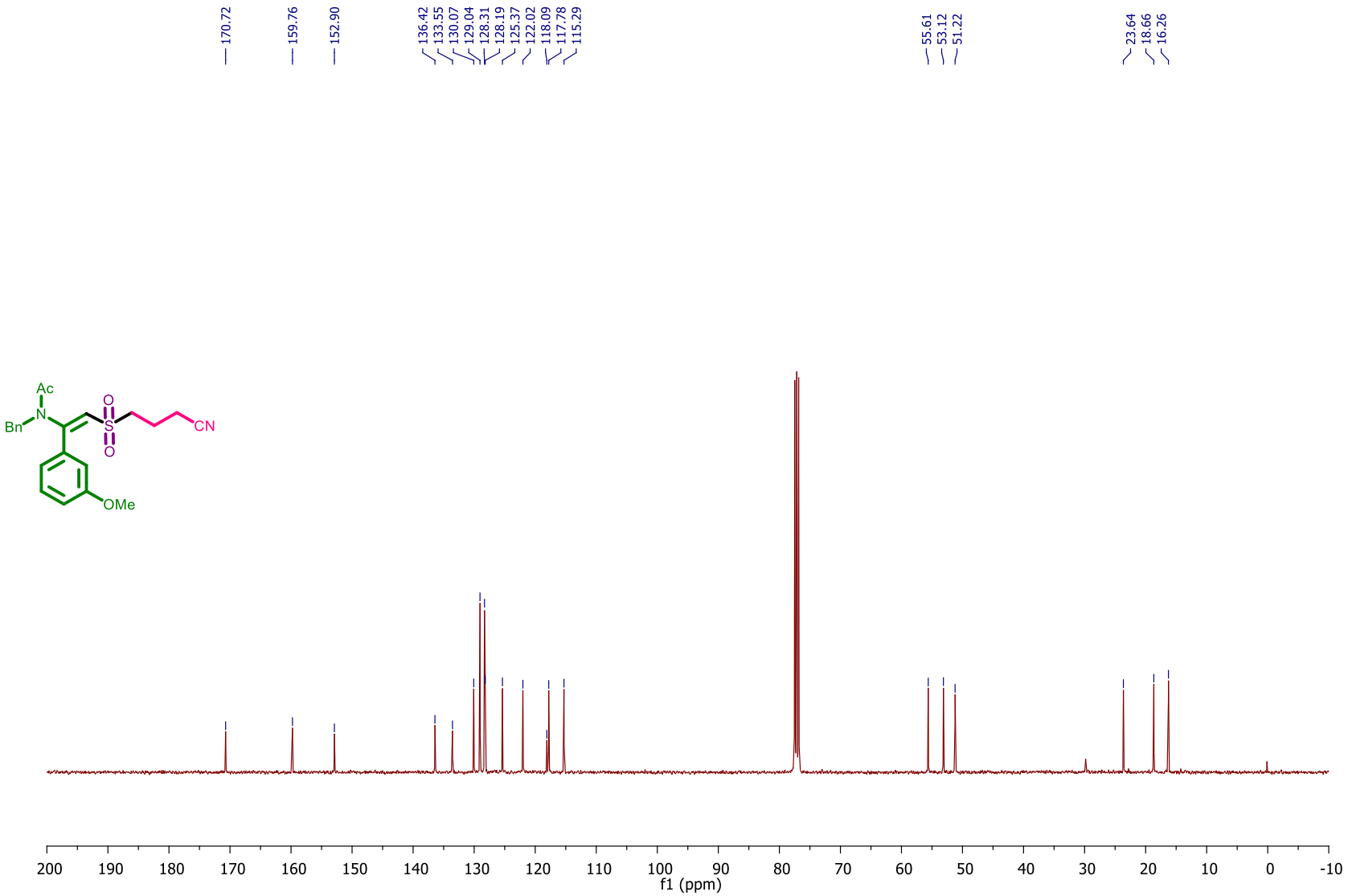
$^{13}C$ NMR (101 MHz, $CDCl_3$) Spectrum of Compound (**4ba)**



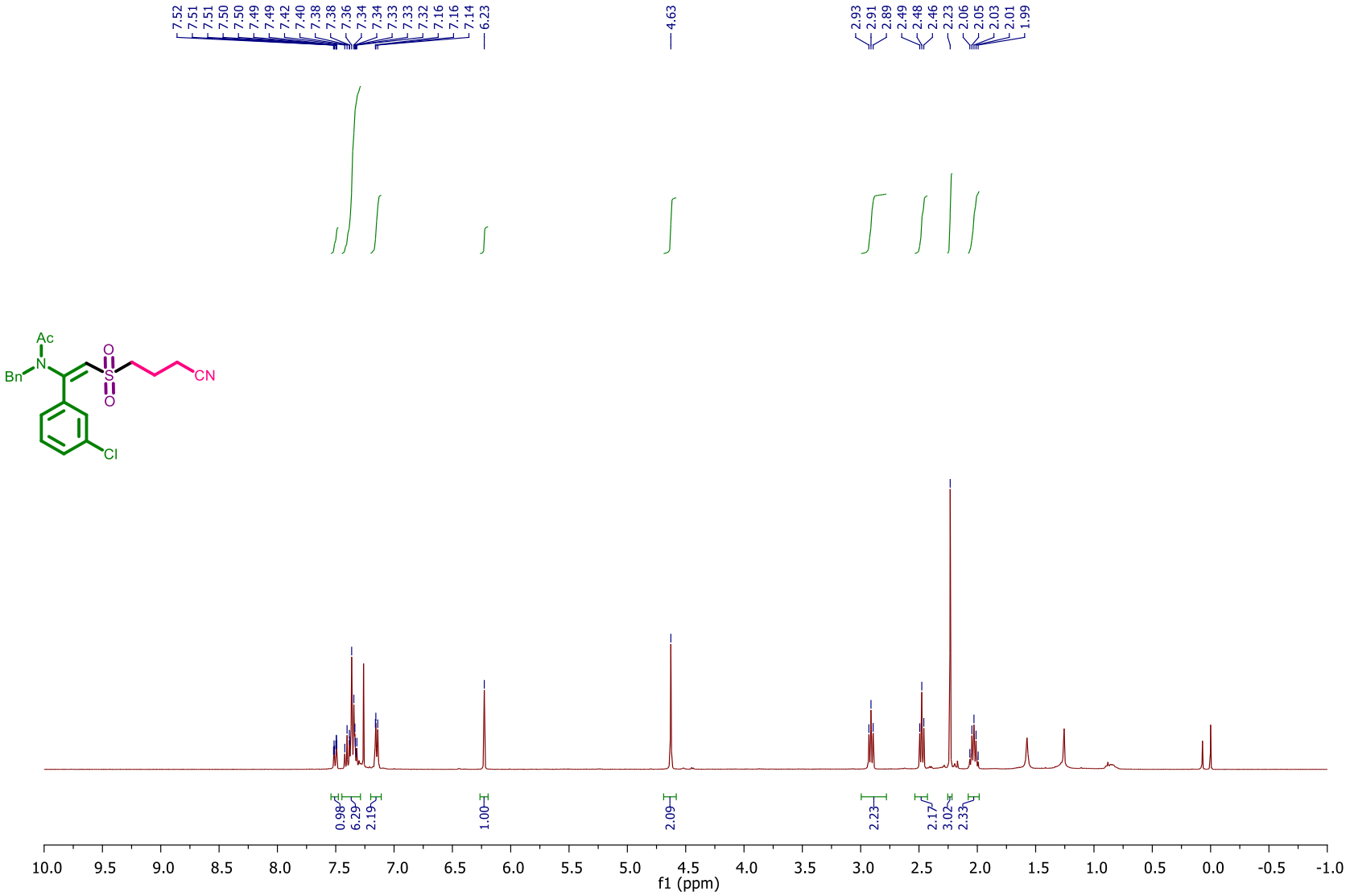
1H NMR (400 MHz, CDCl3) Spectrum of Compound **(4ca)**



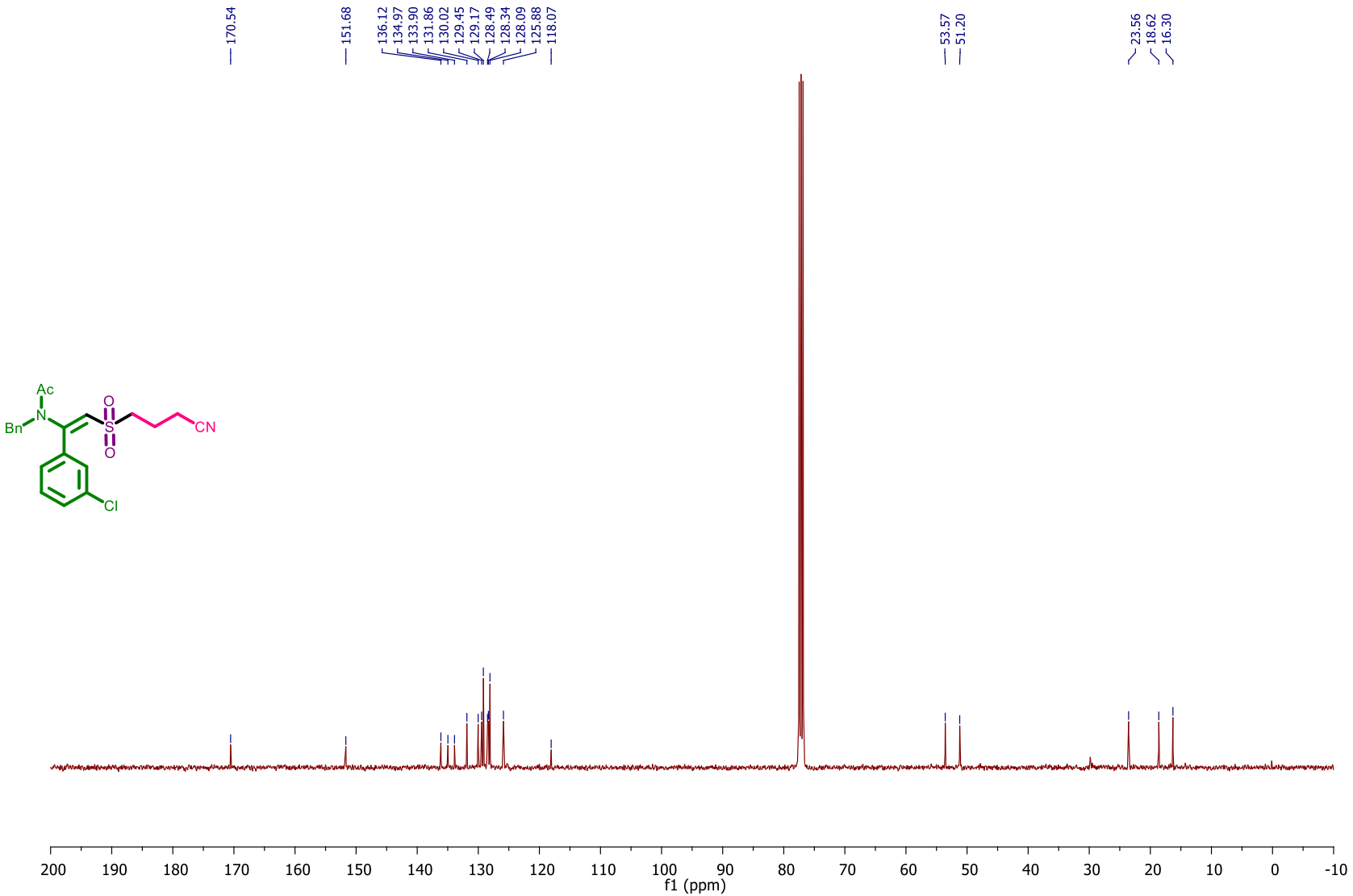
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4ca)**



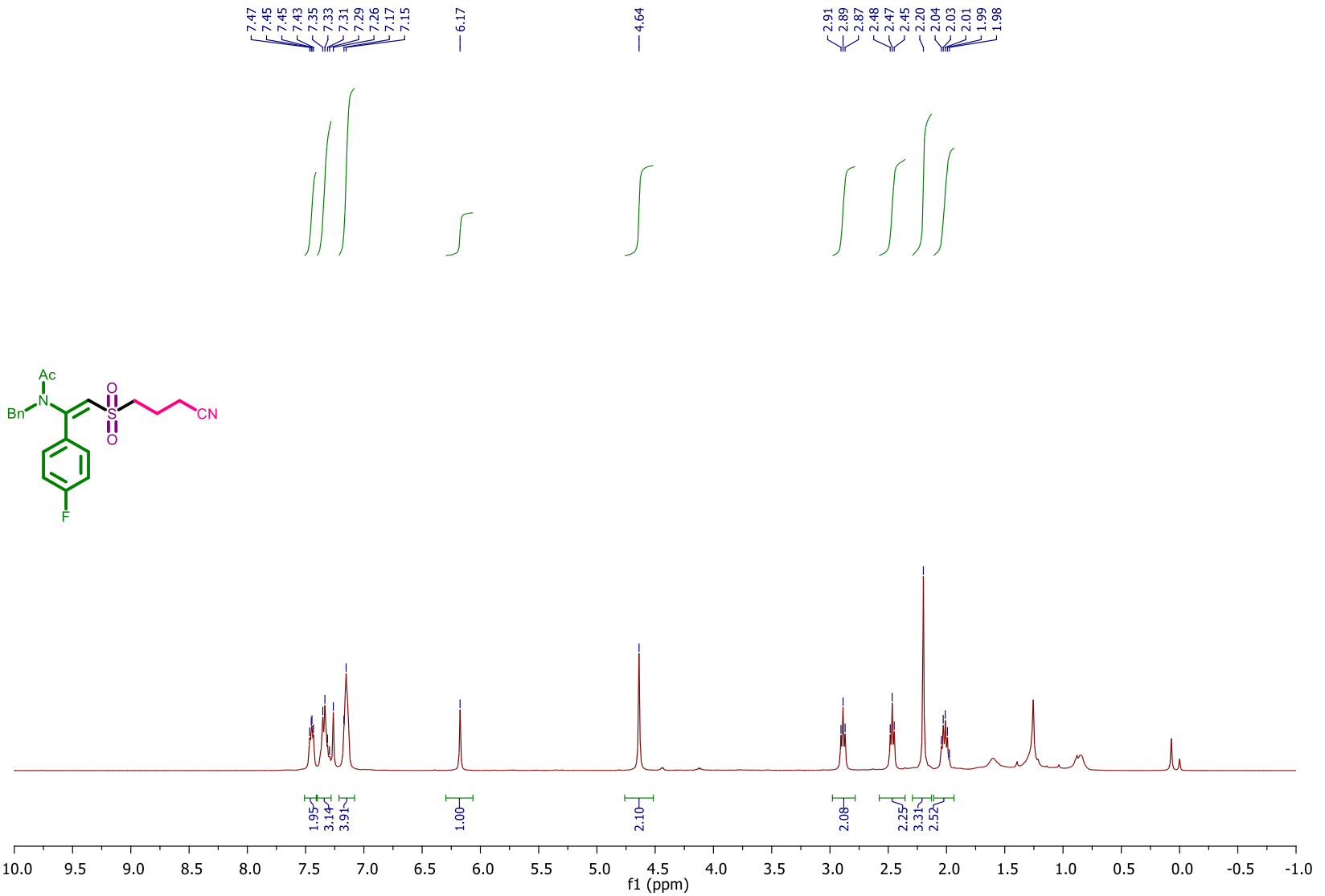
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4da)**



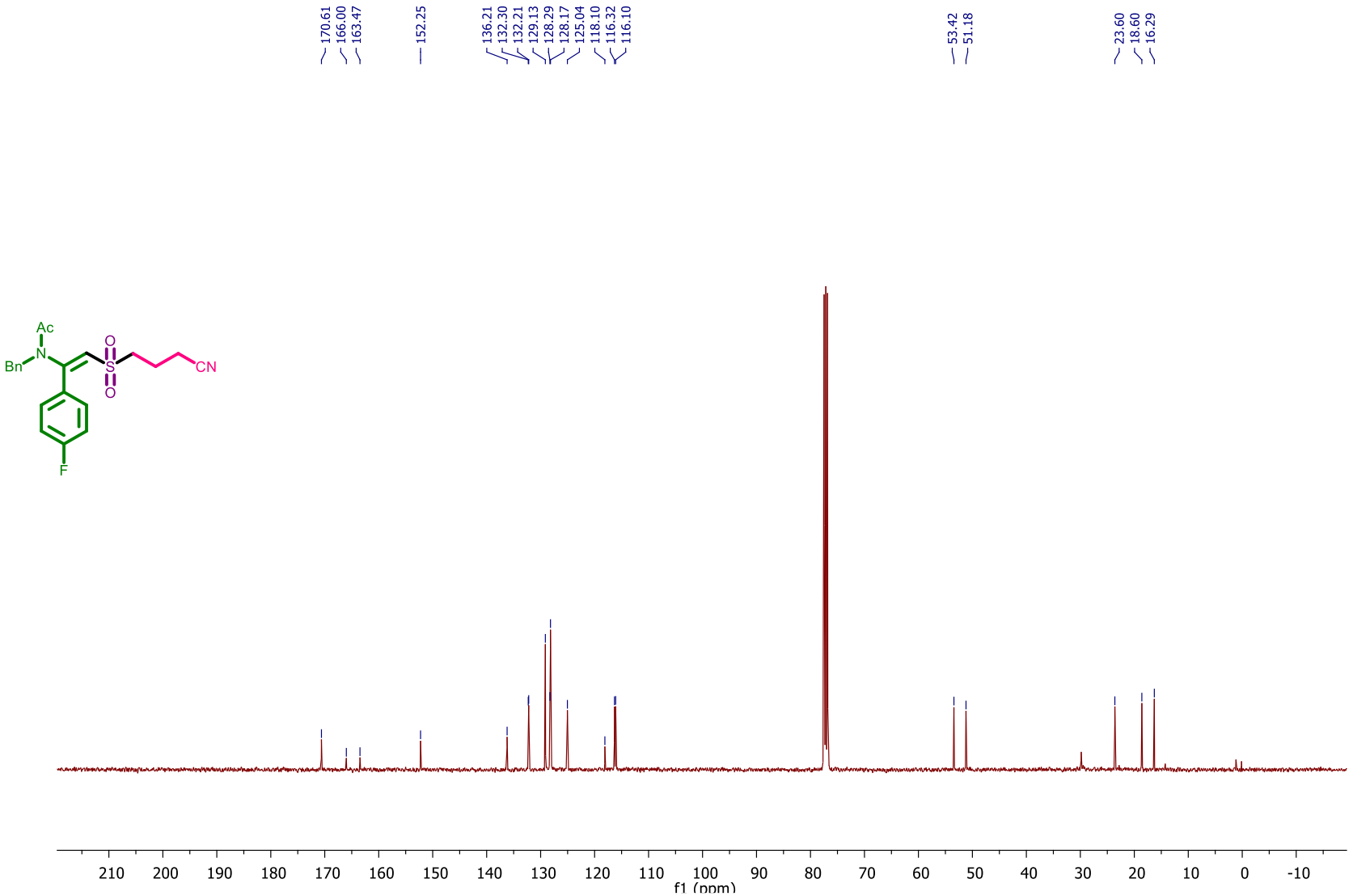
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4da)**



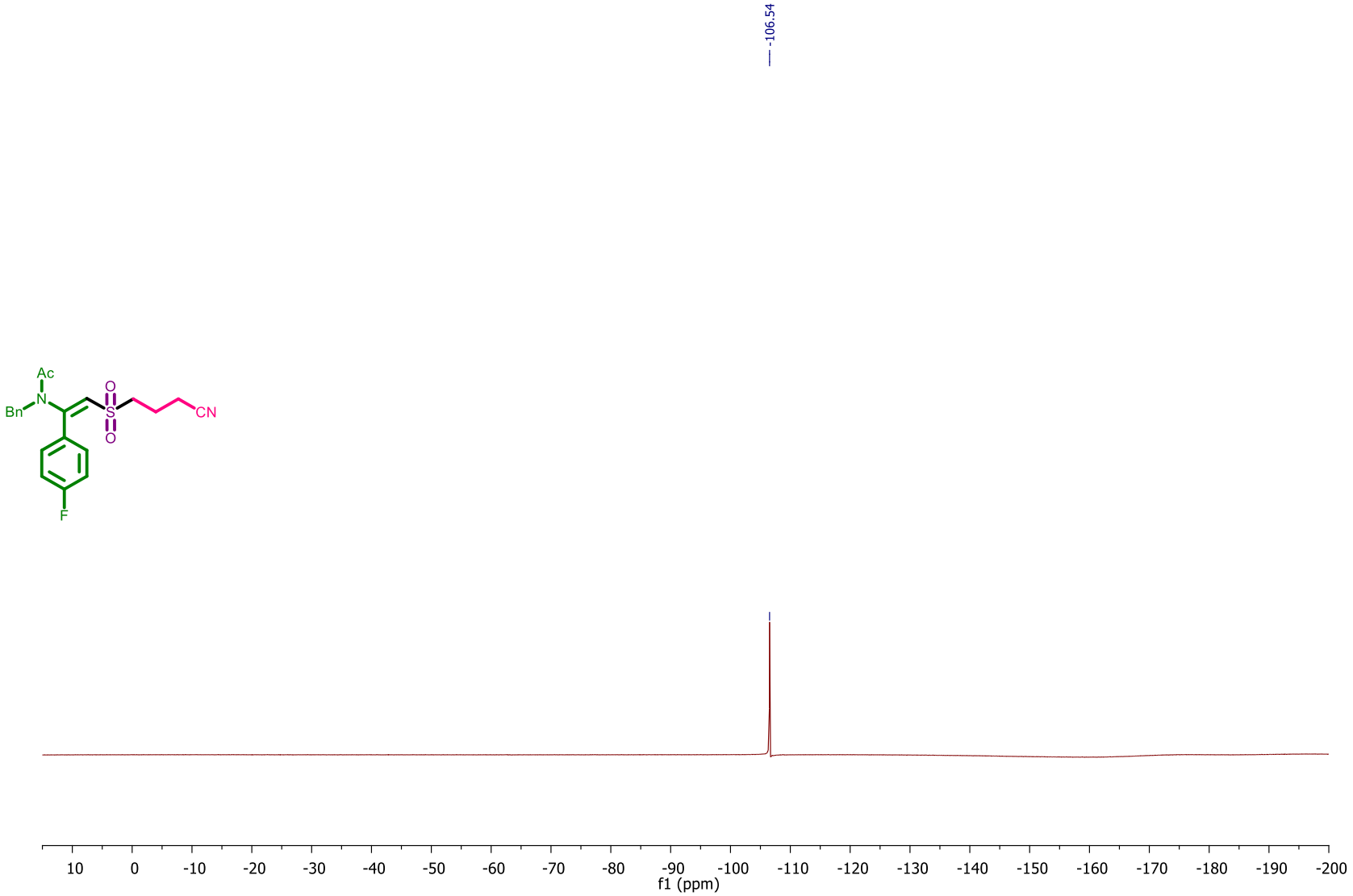
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ea)**



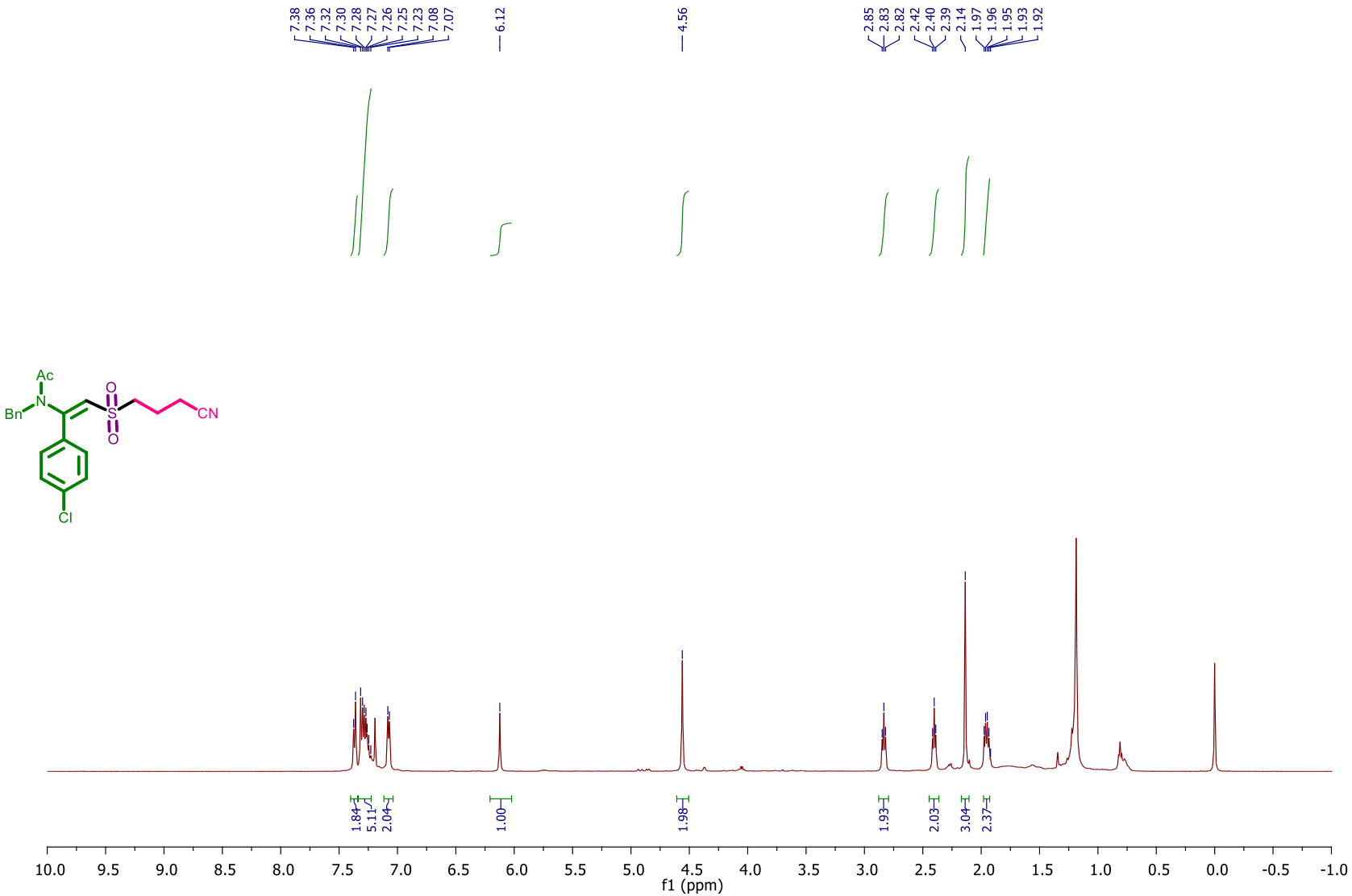
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4ea)**



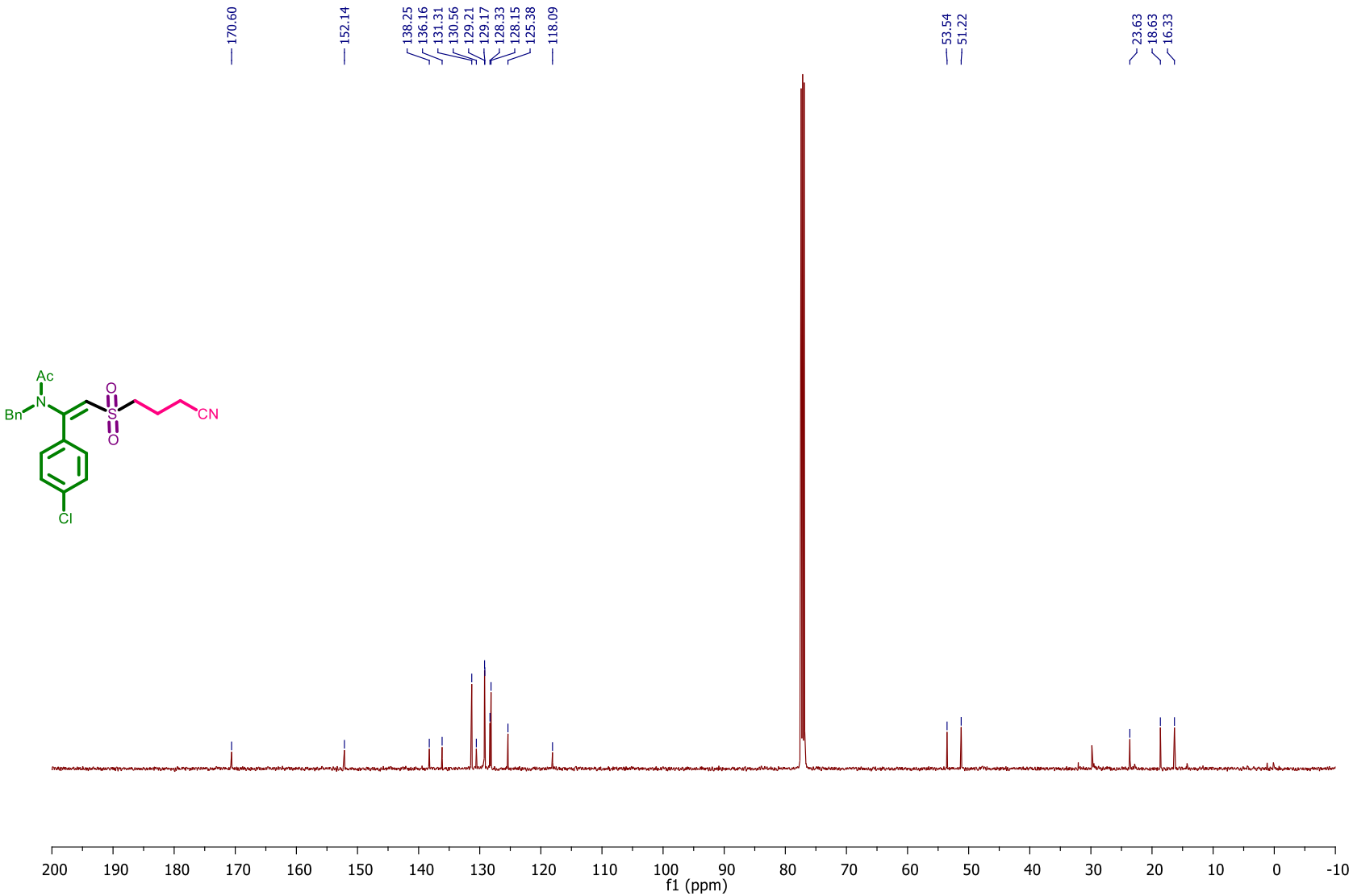
$^{19}F$ NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(4ea)**



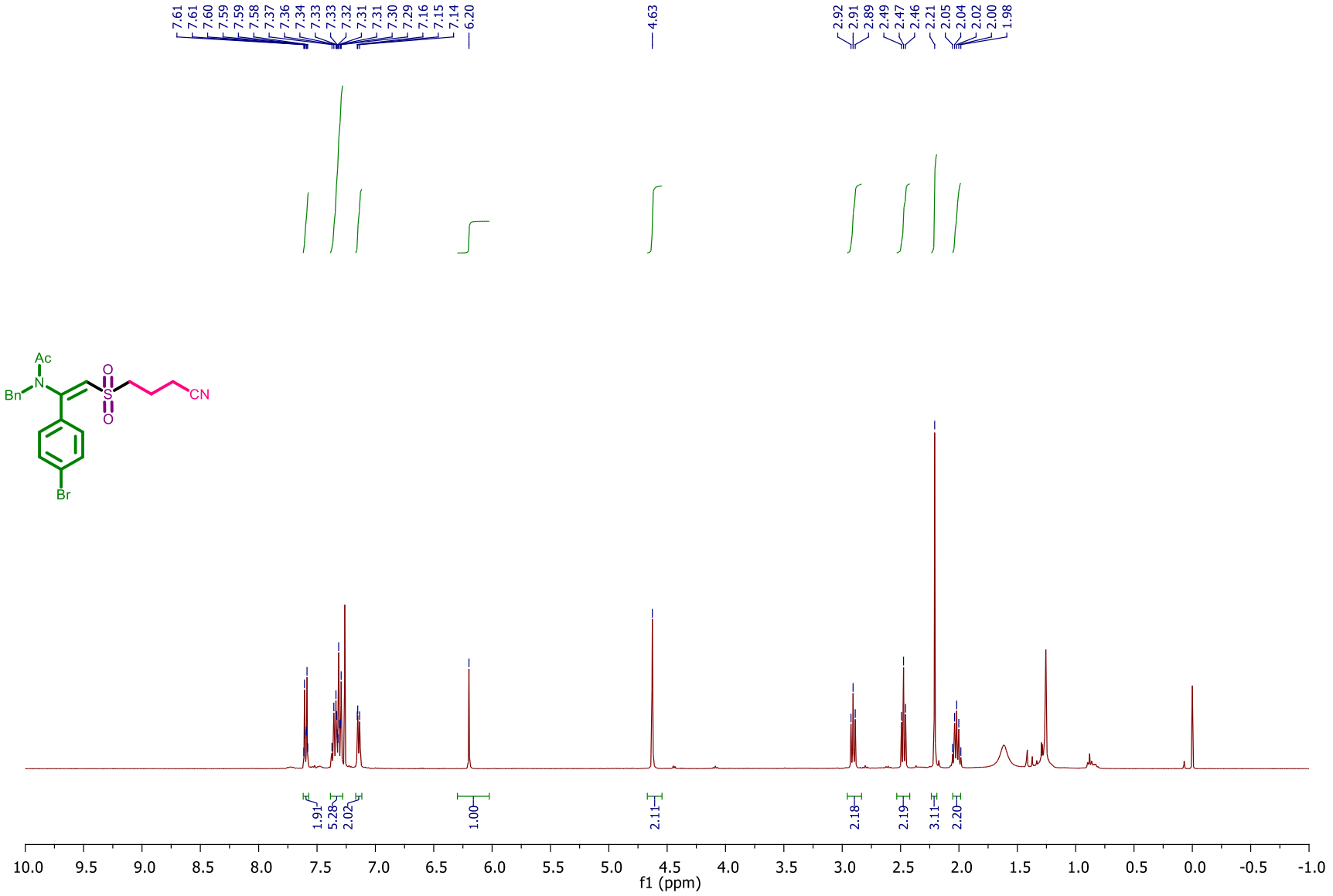
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(4fa)**



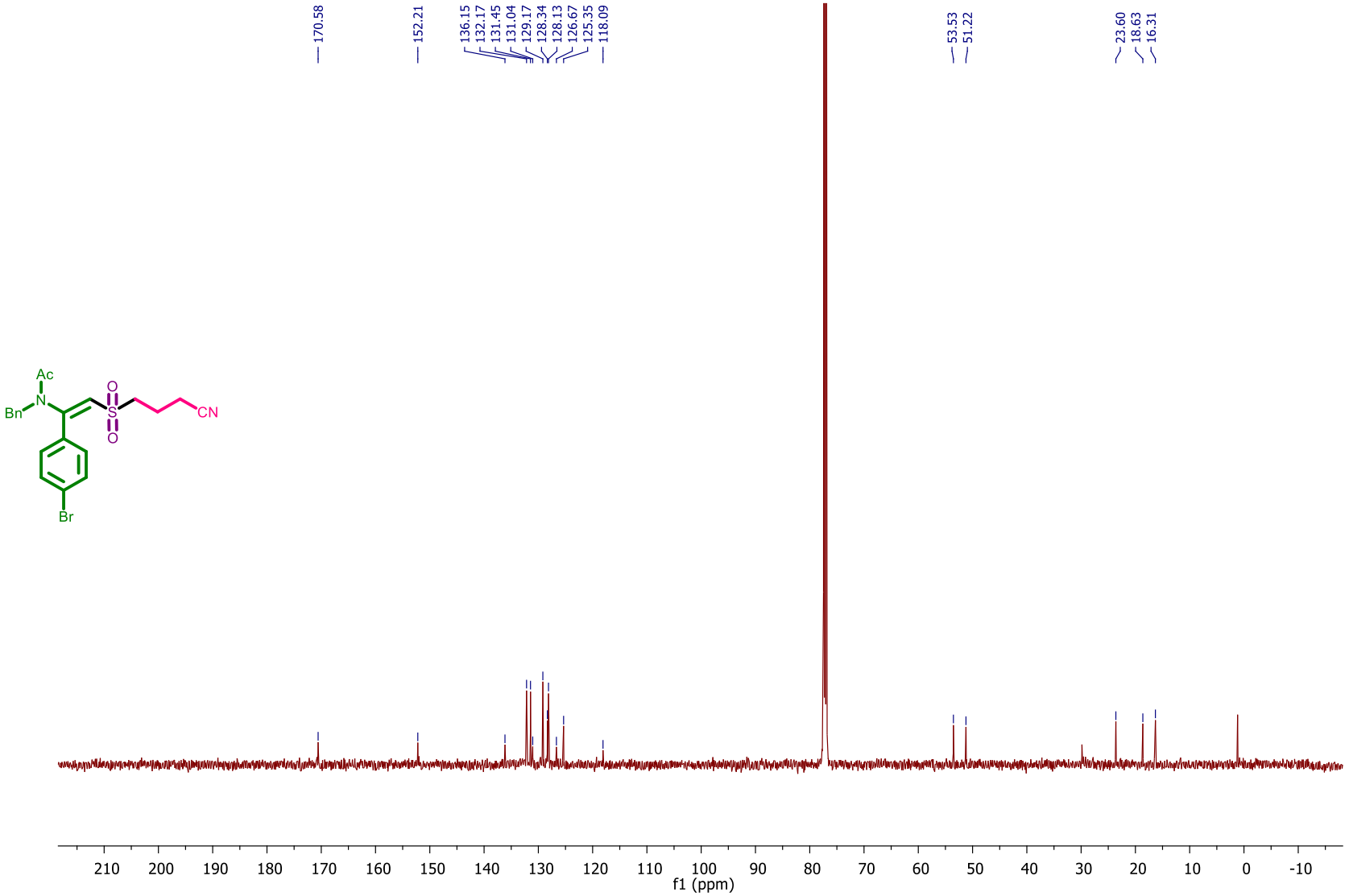
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(4fa)**



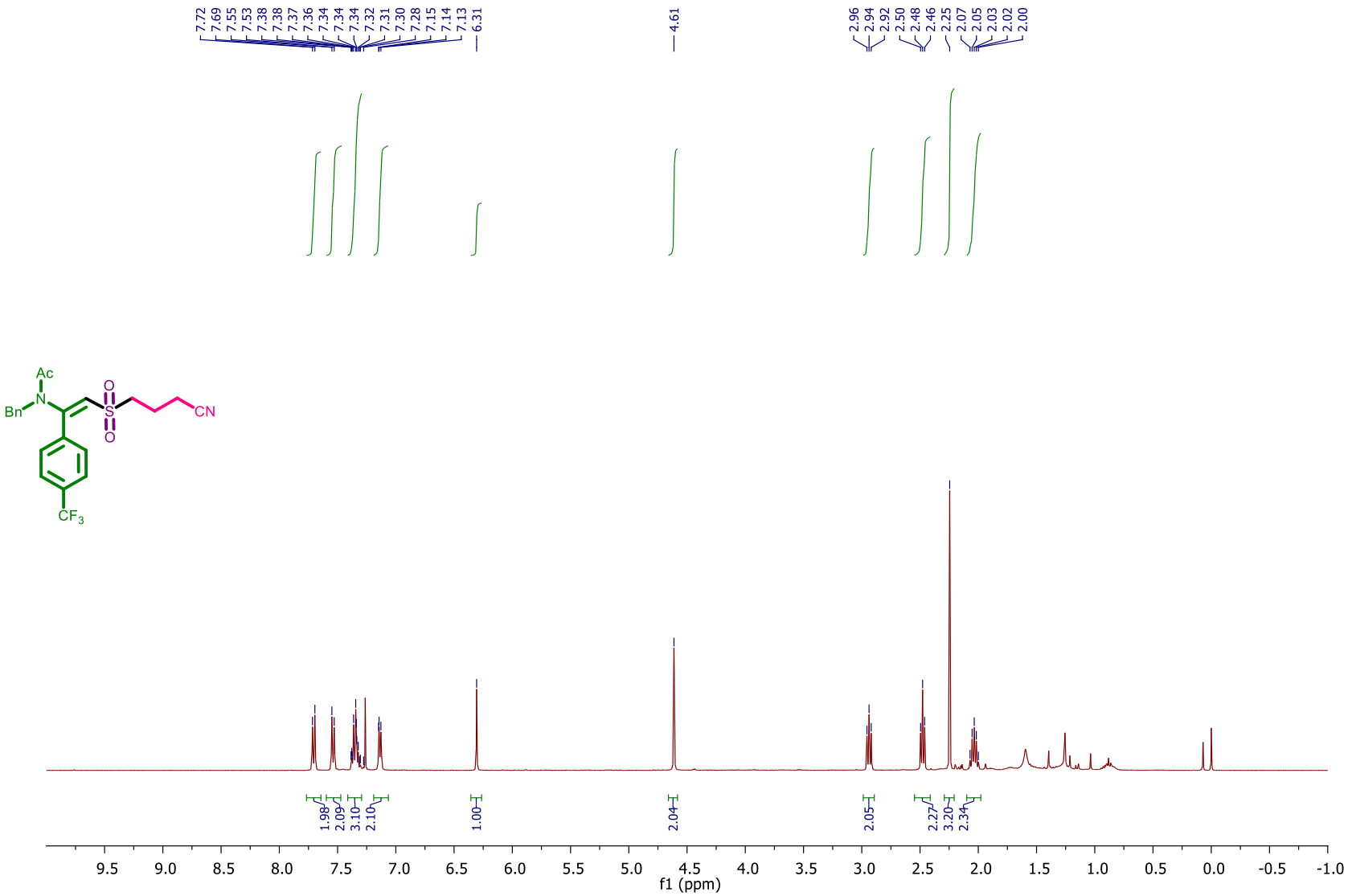
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ga)**



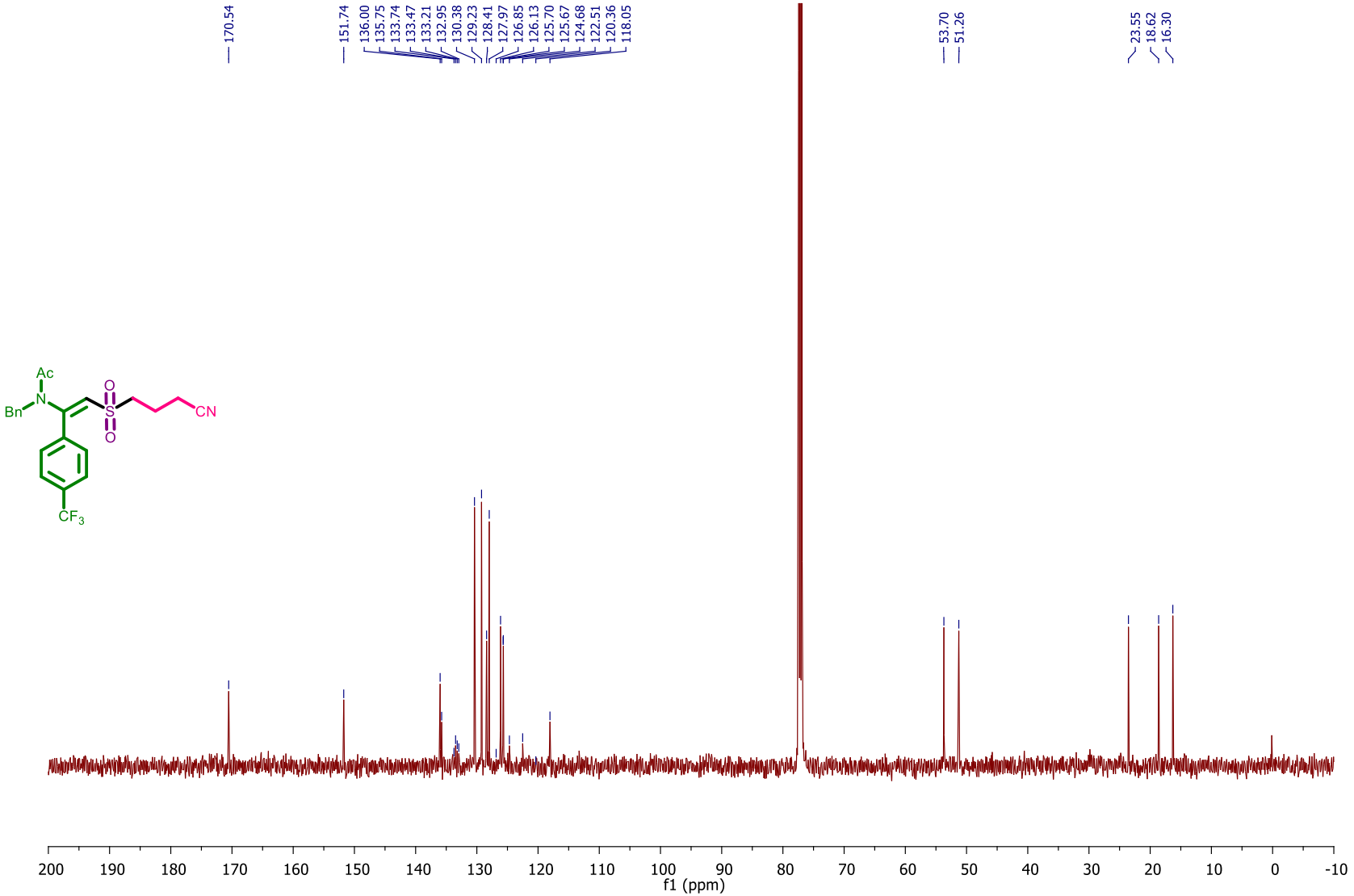
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(4ga)**



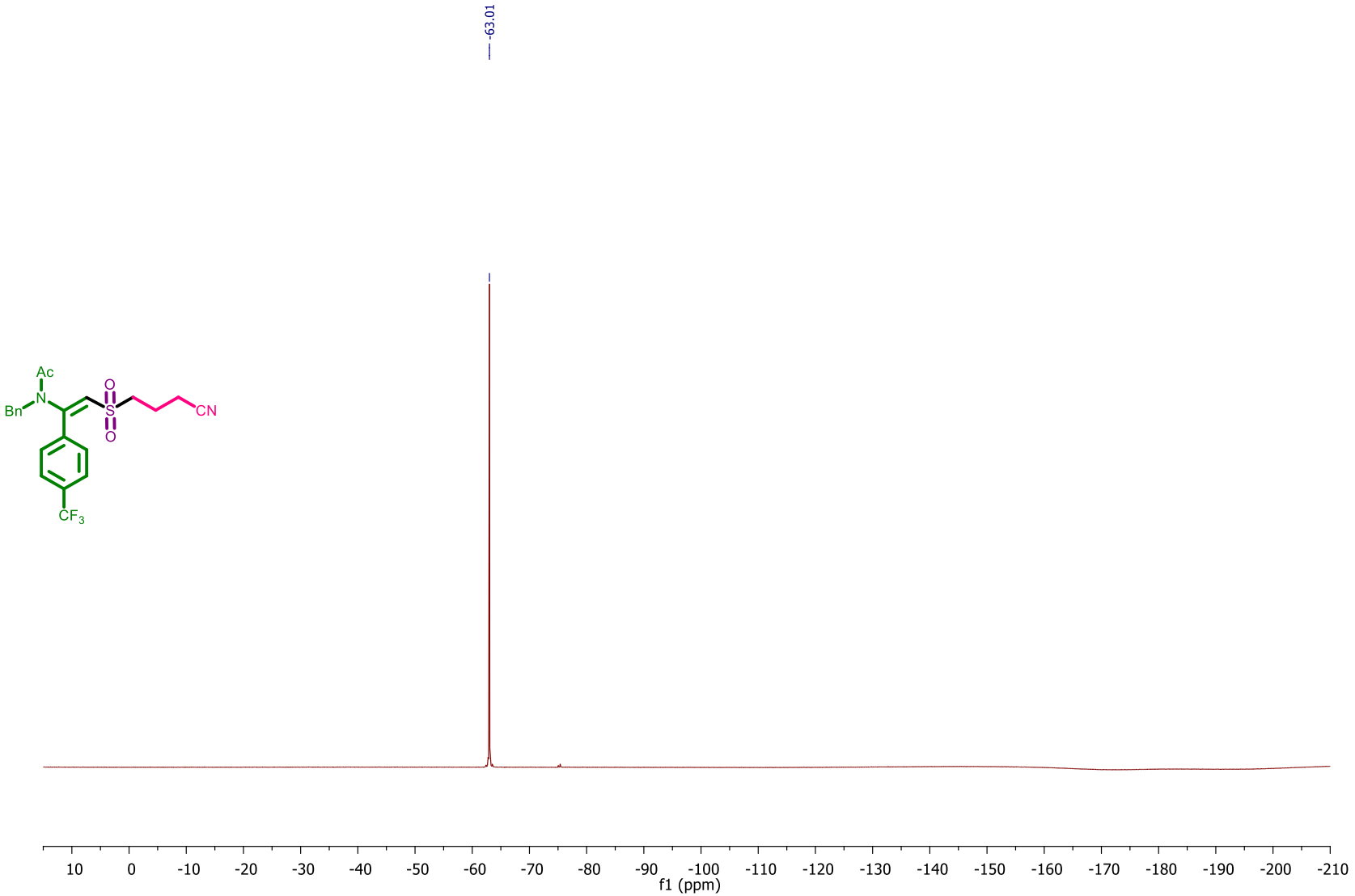
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ha)**



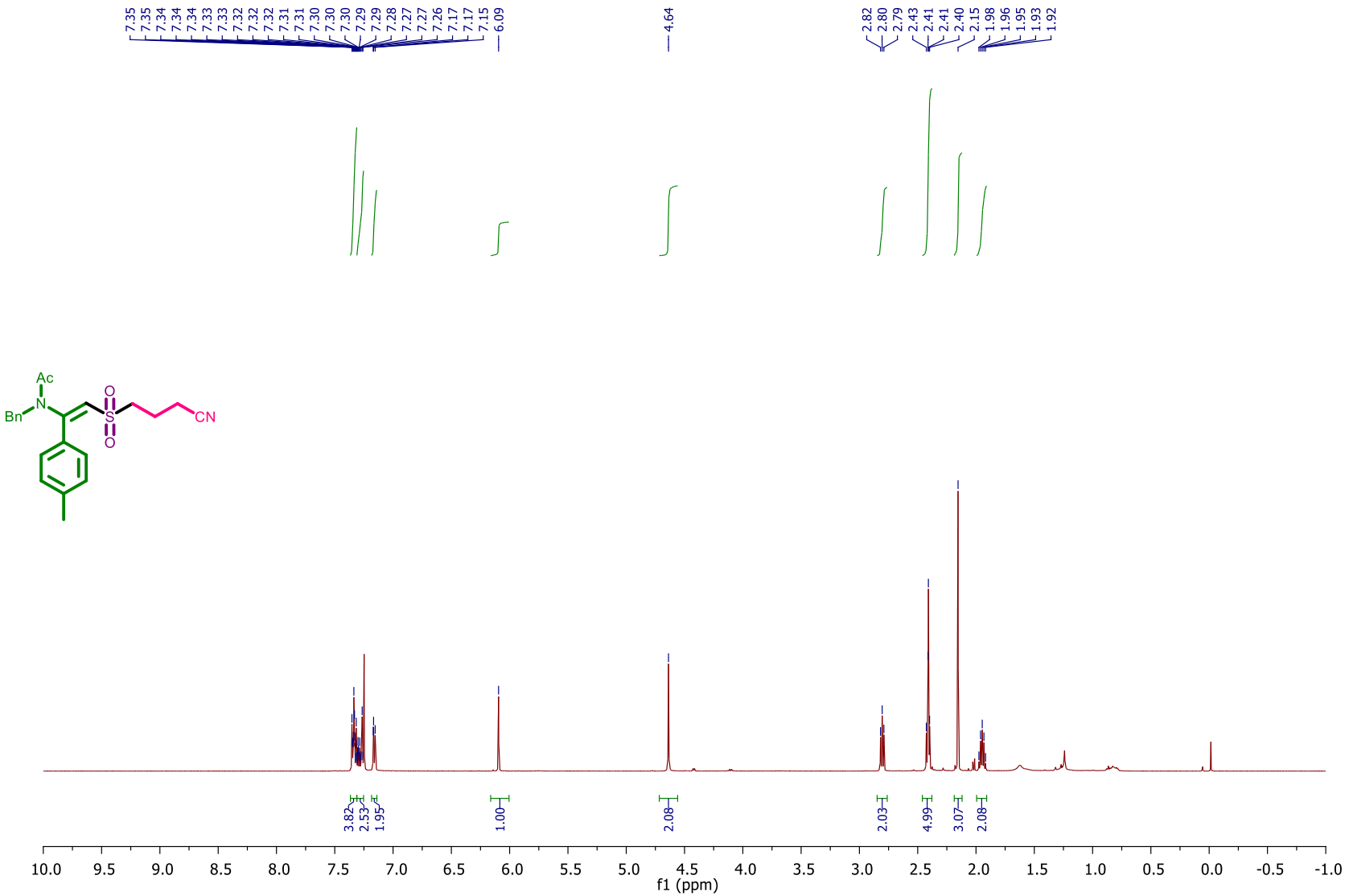
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(4ha)**



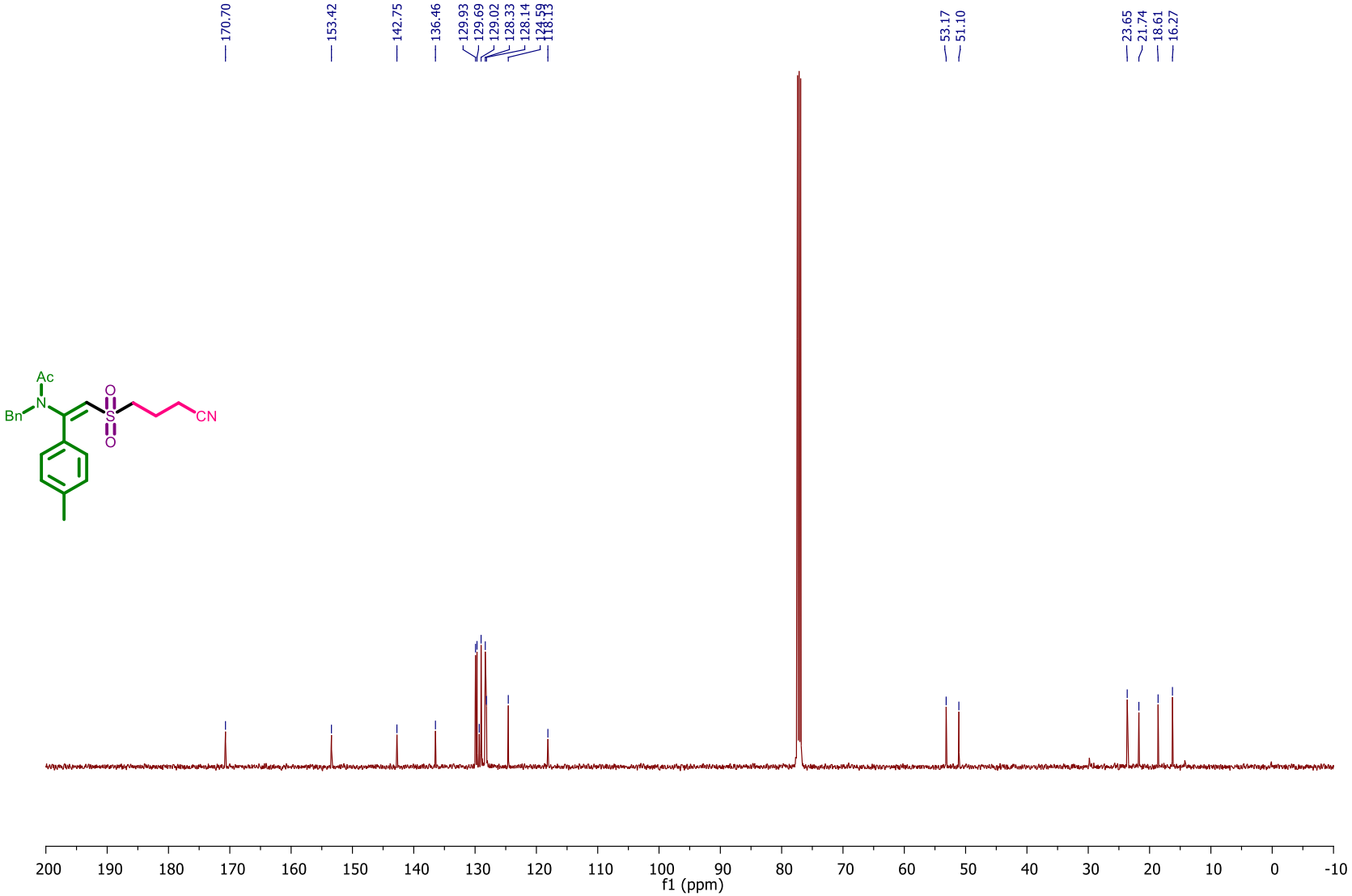
$^{19}F$ NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(4ha)**



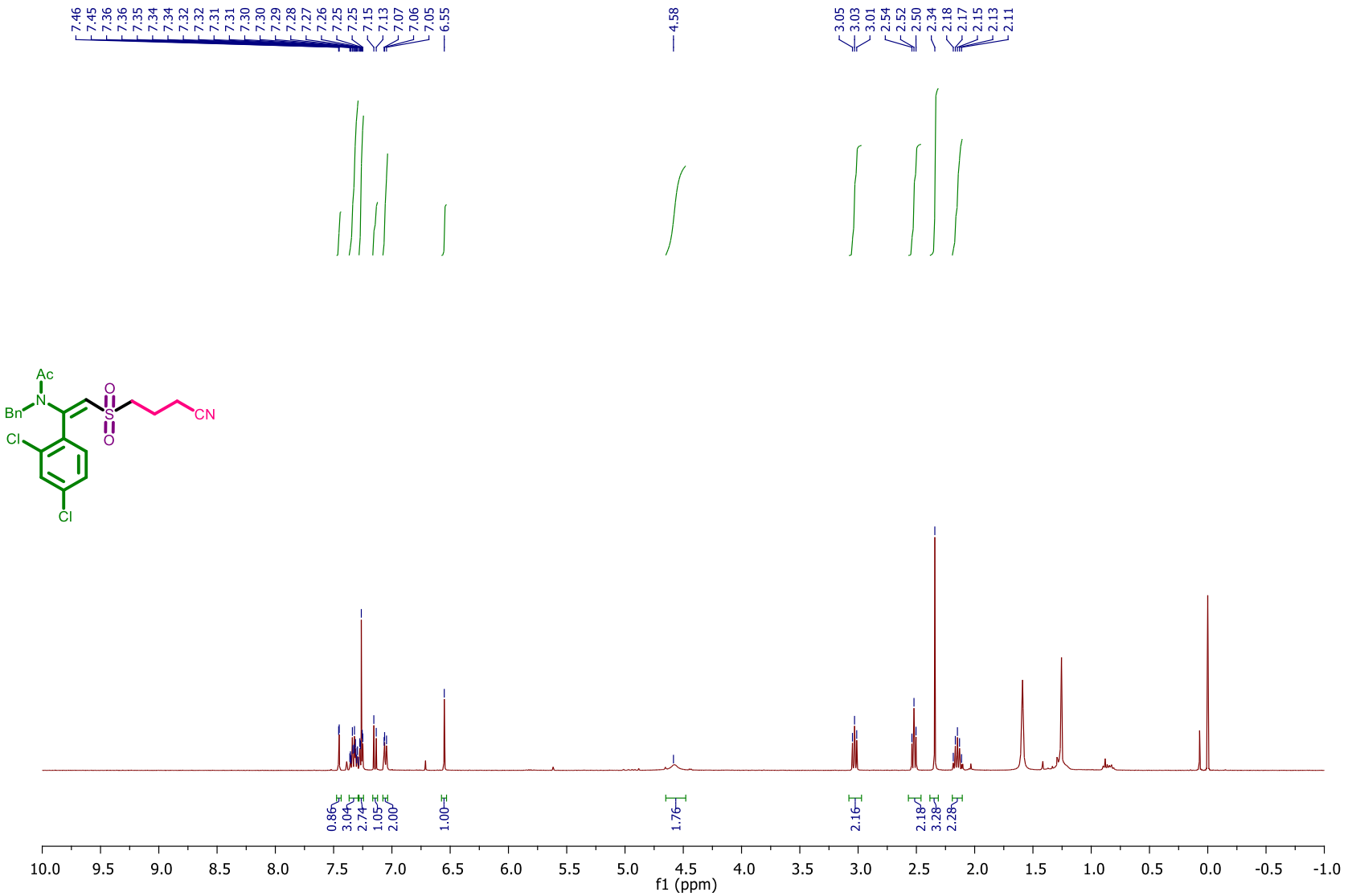
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(4ia)**



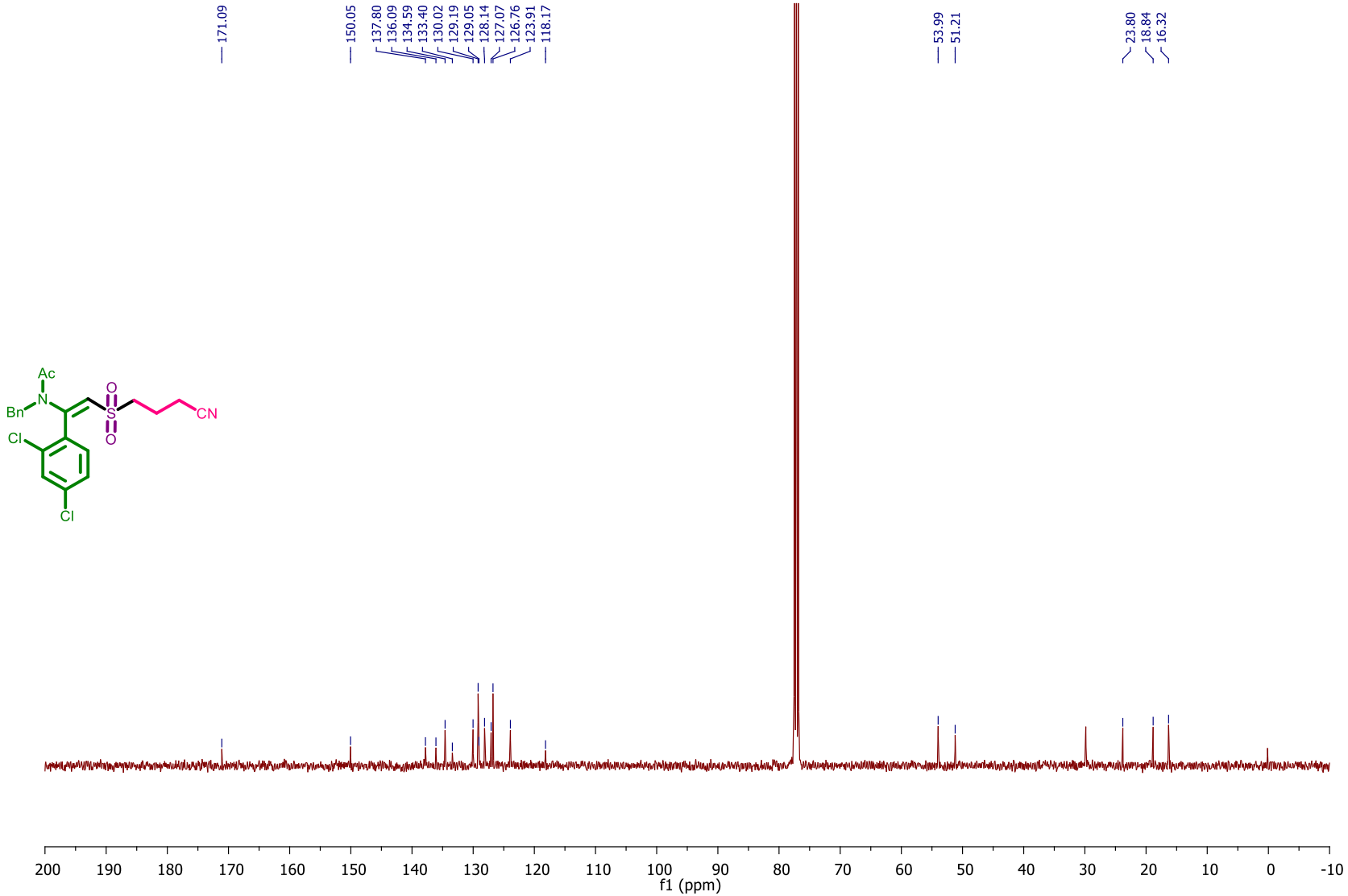
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(4ia)**



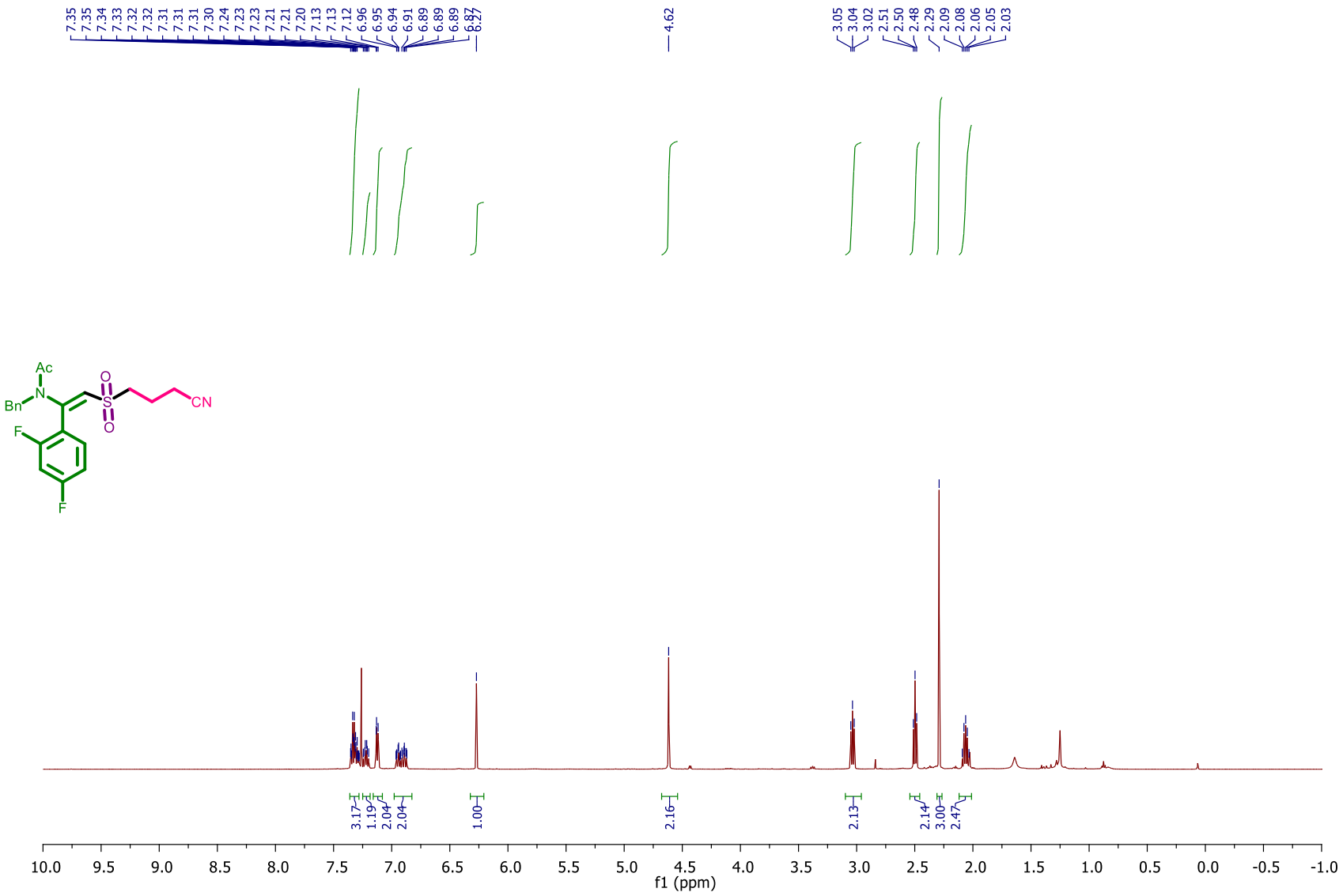
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ja)**



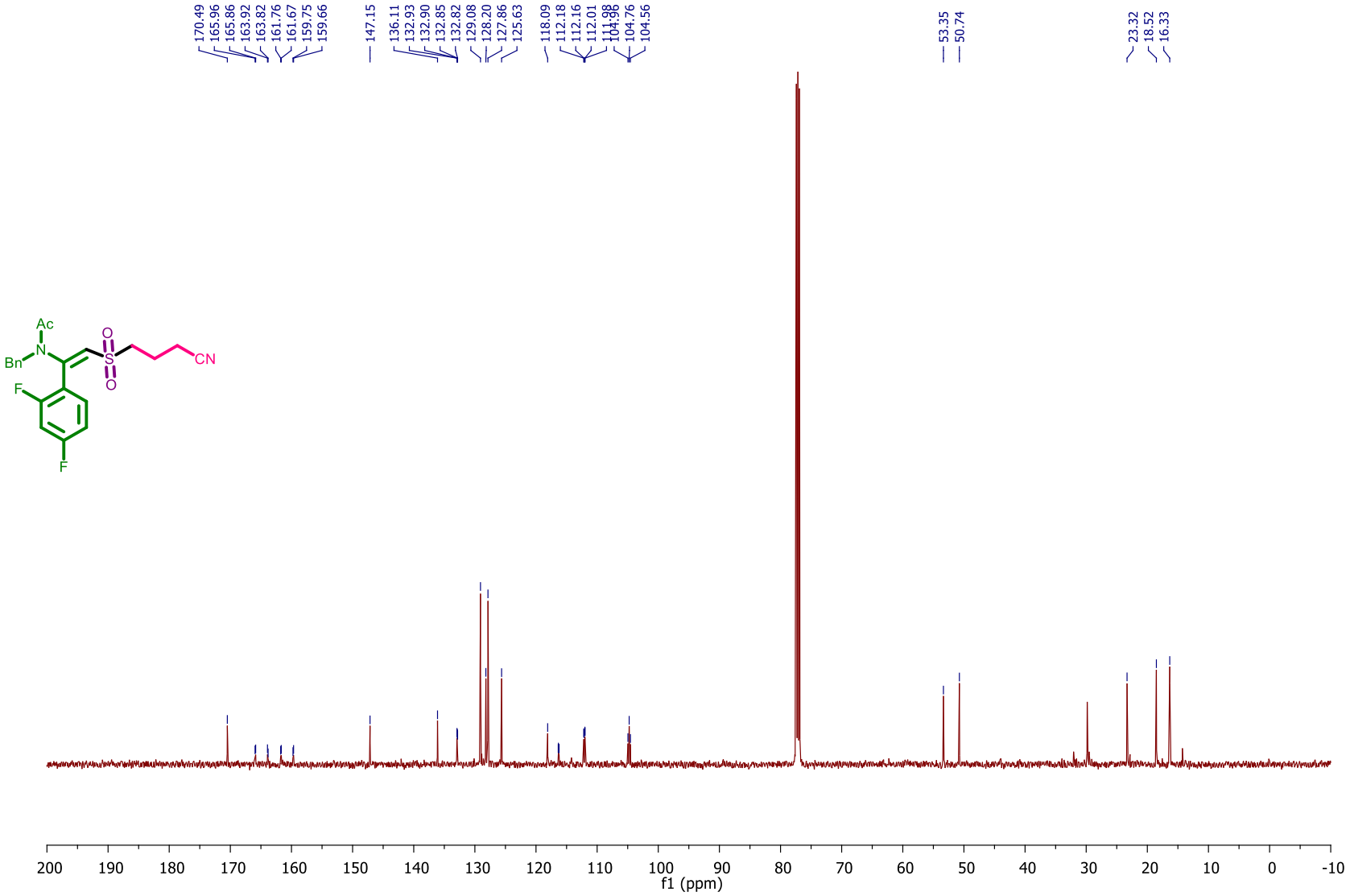
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4ja)**



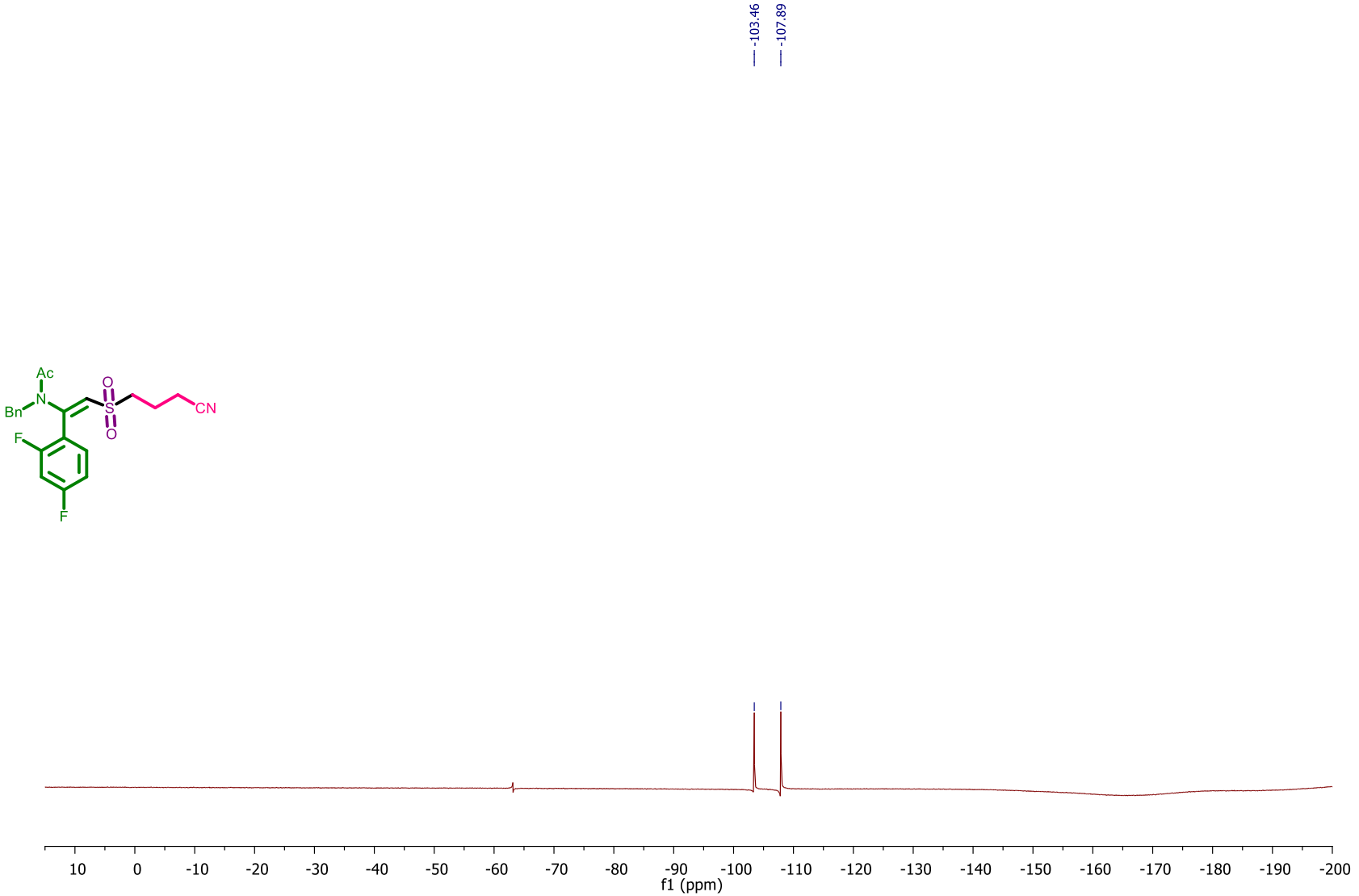
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ka)**



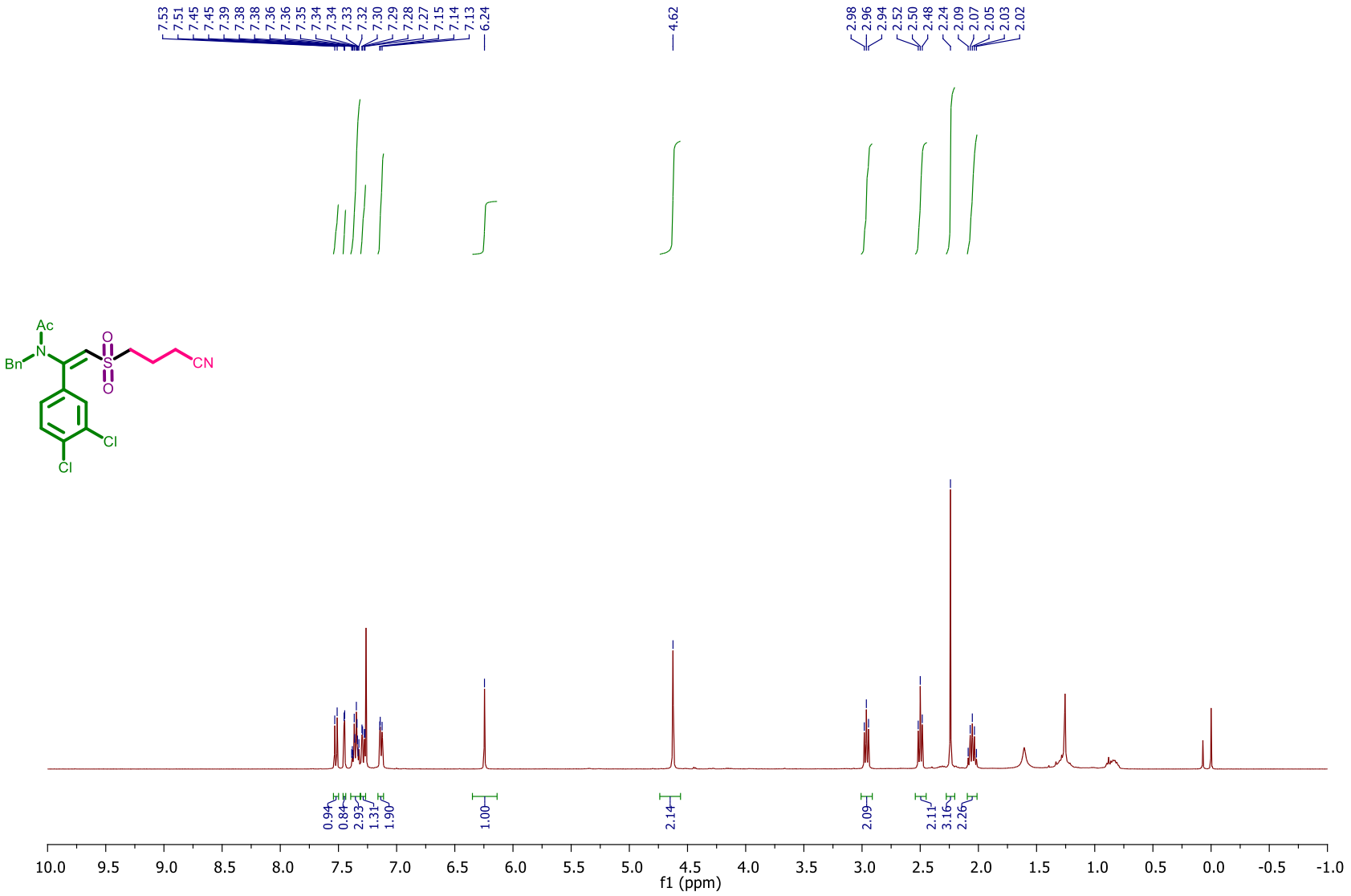
$^{13}C$ NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(4ka)**



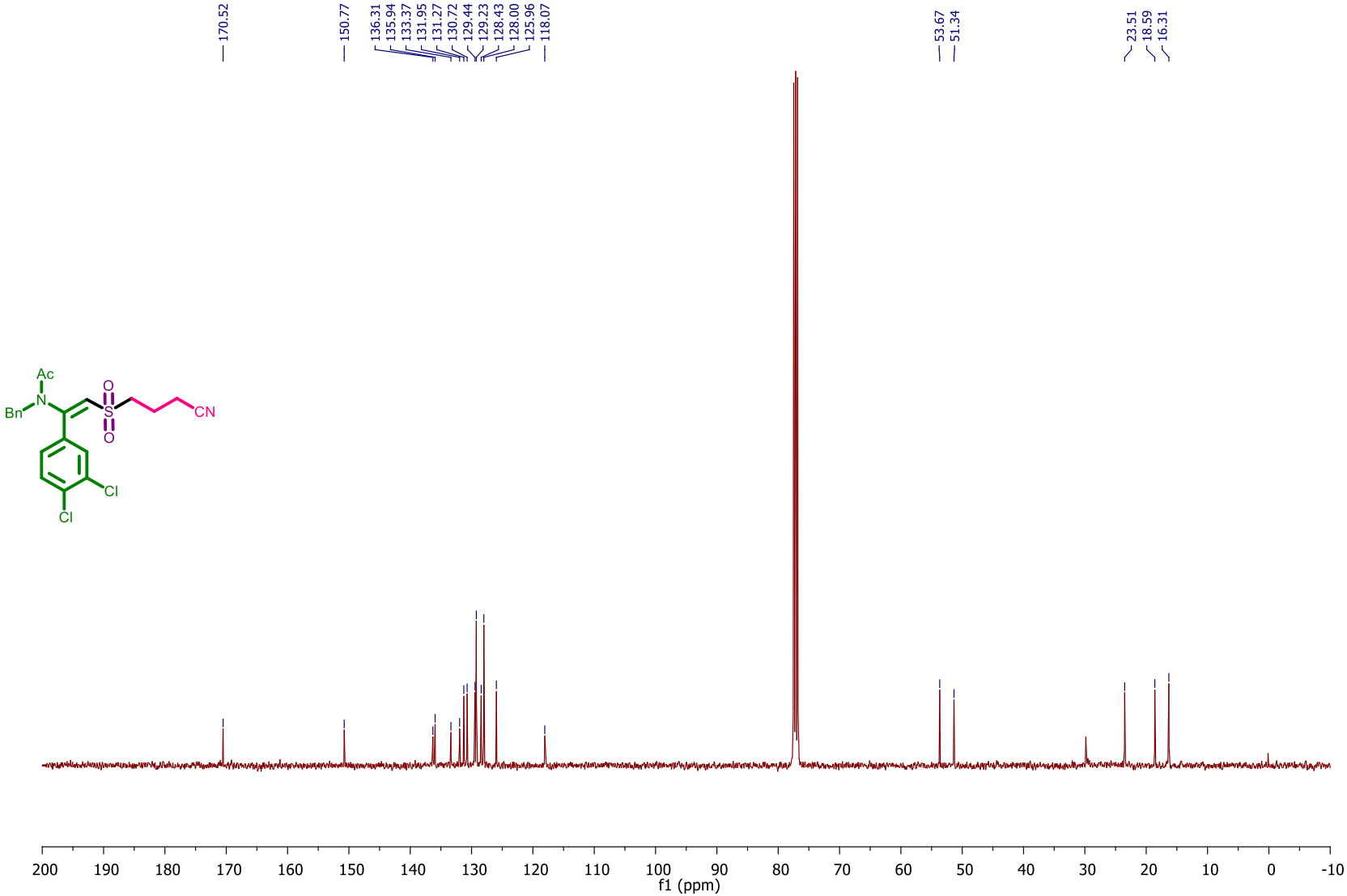
$^{19}F$ NMR (376 MHz, $CDCl_3$) Spectrum of Compound **(4ka)**



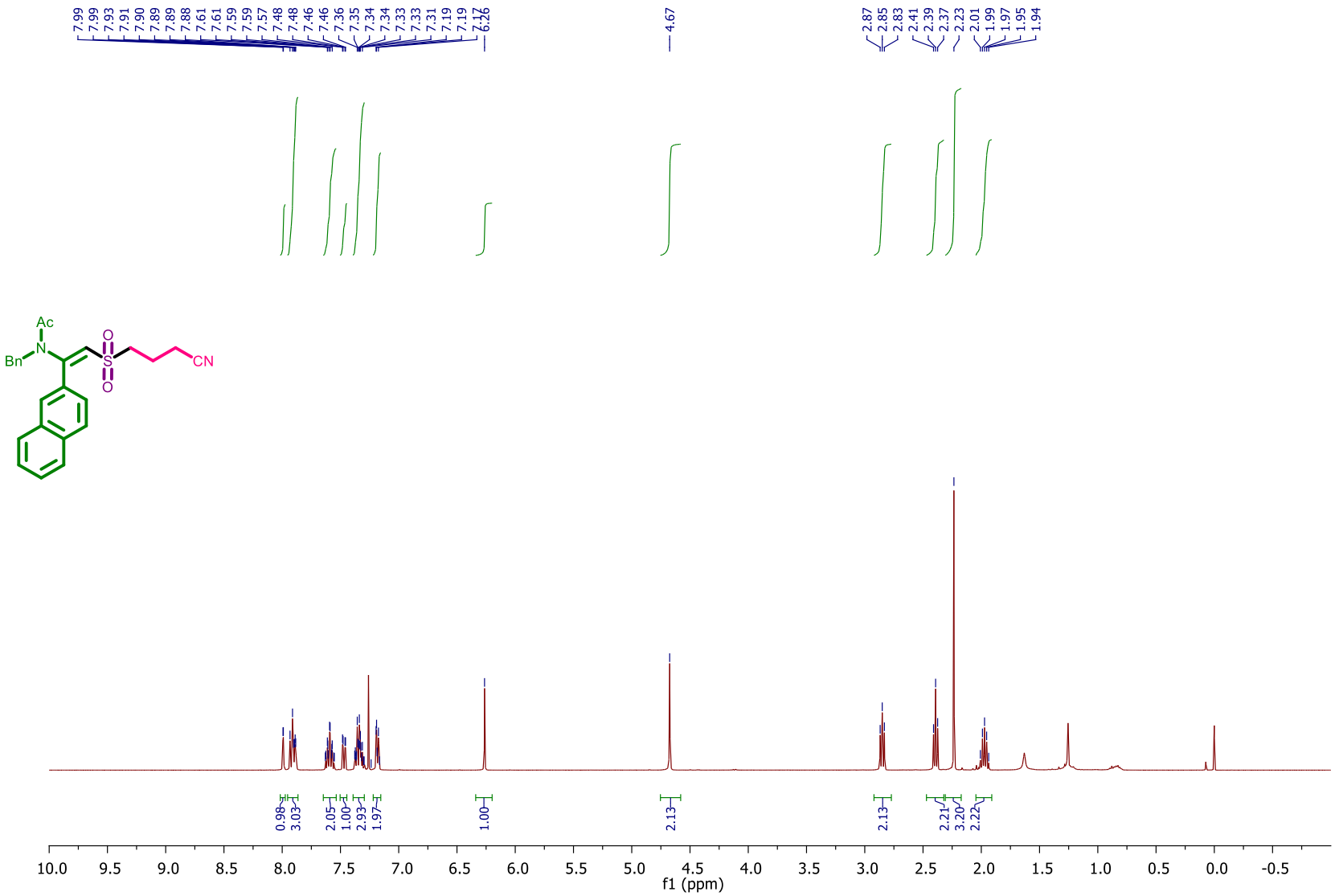
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4la)**



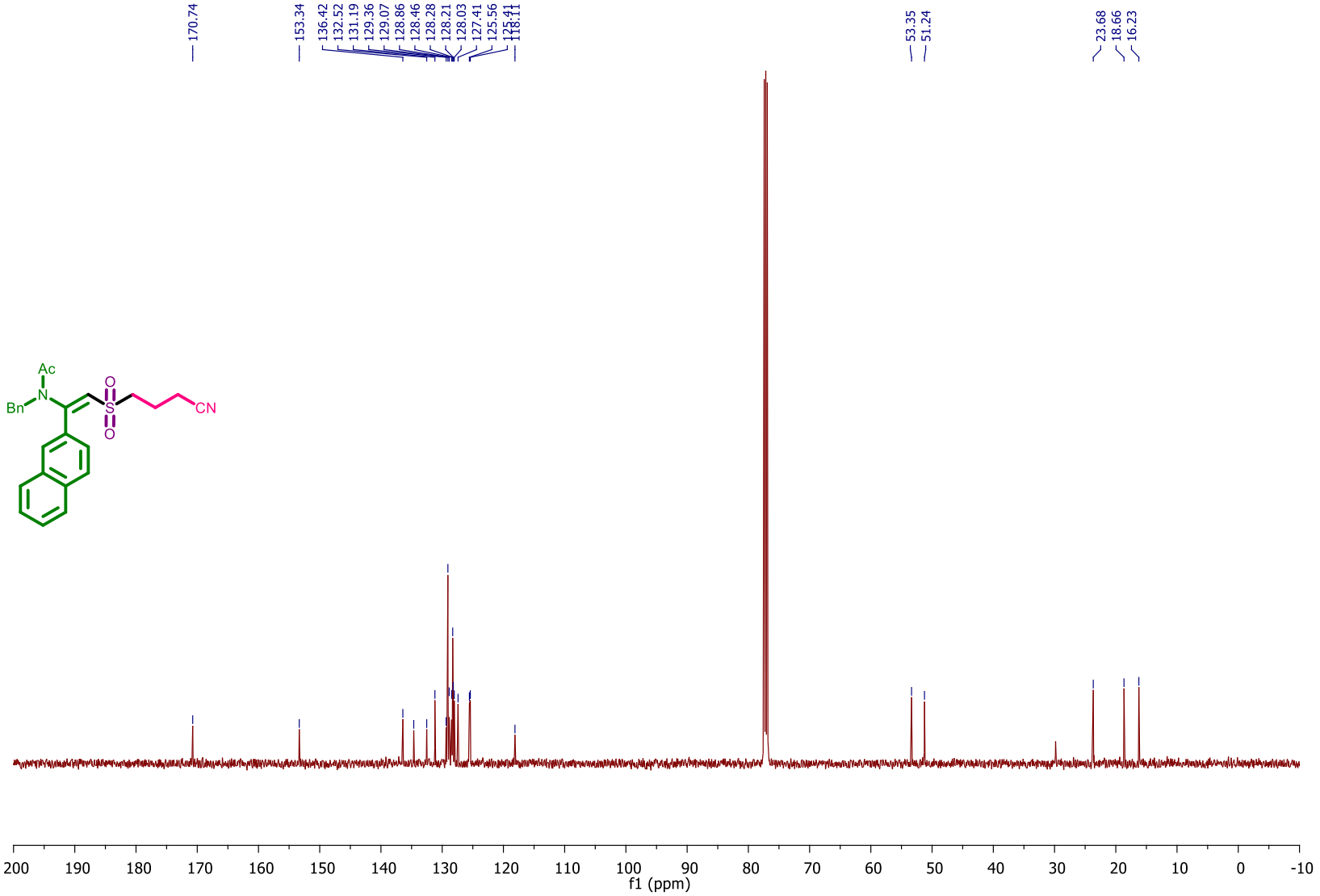
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4la)**



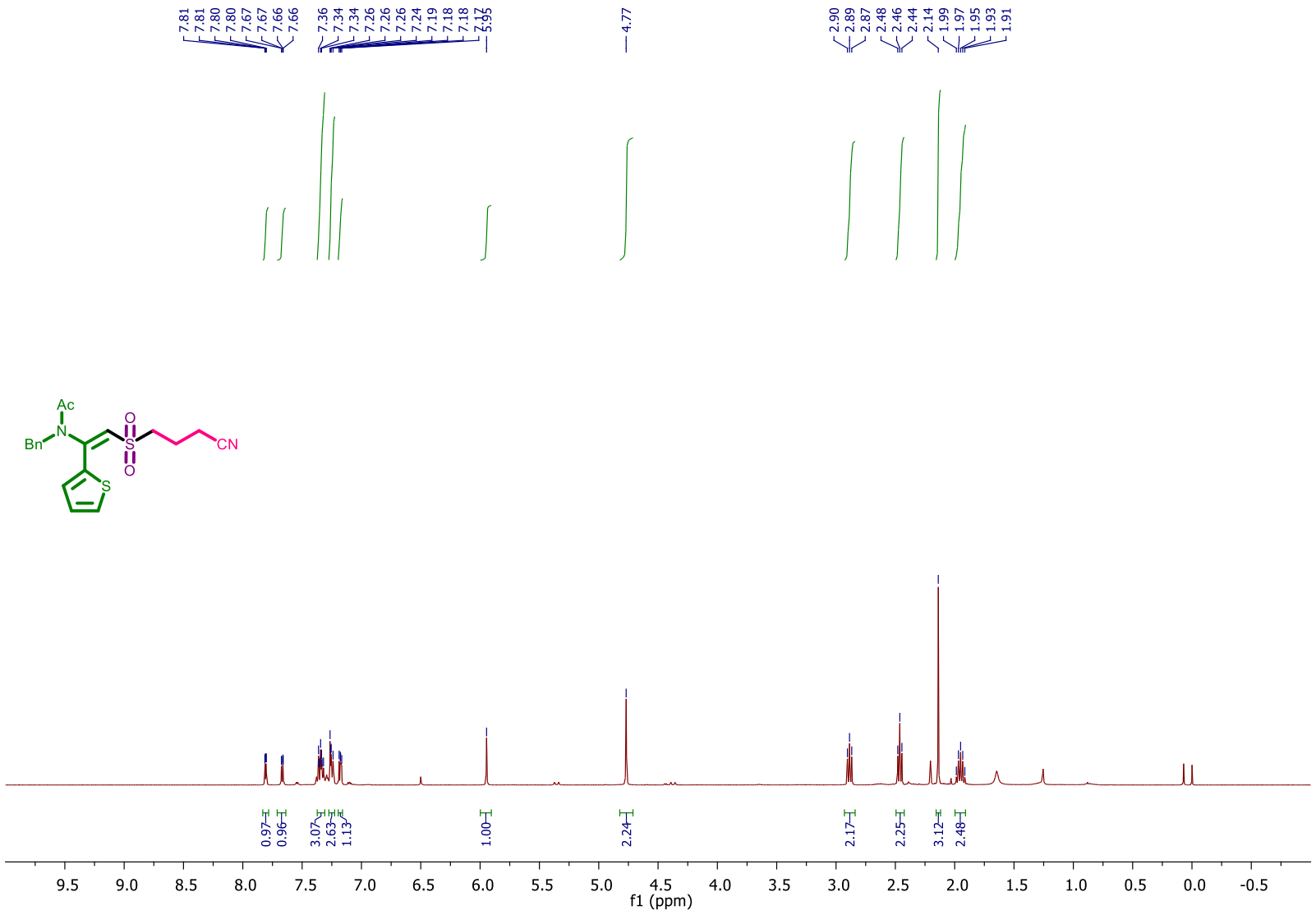
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ma)**



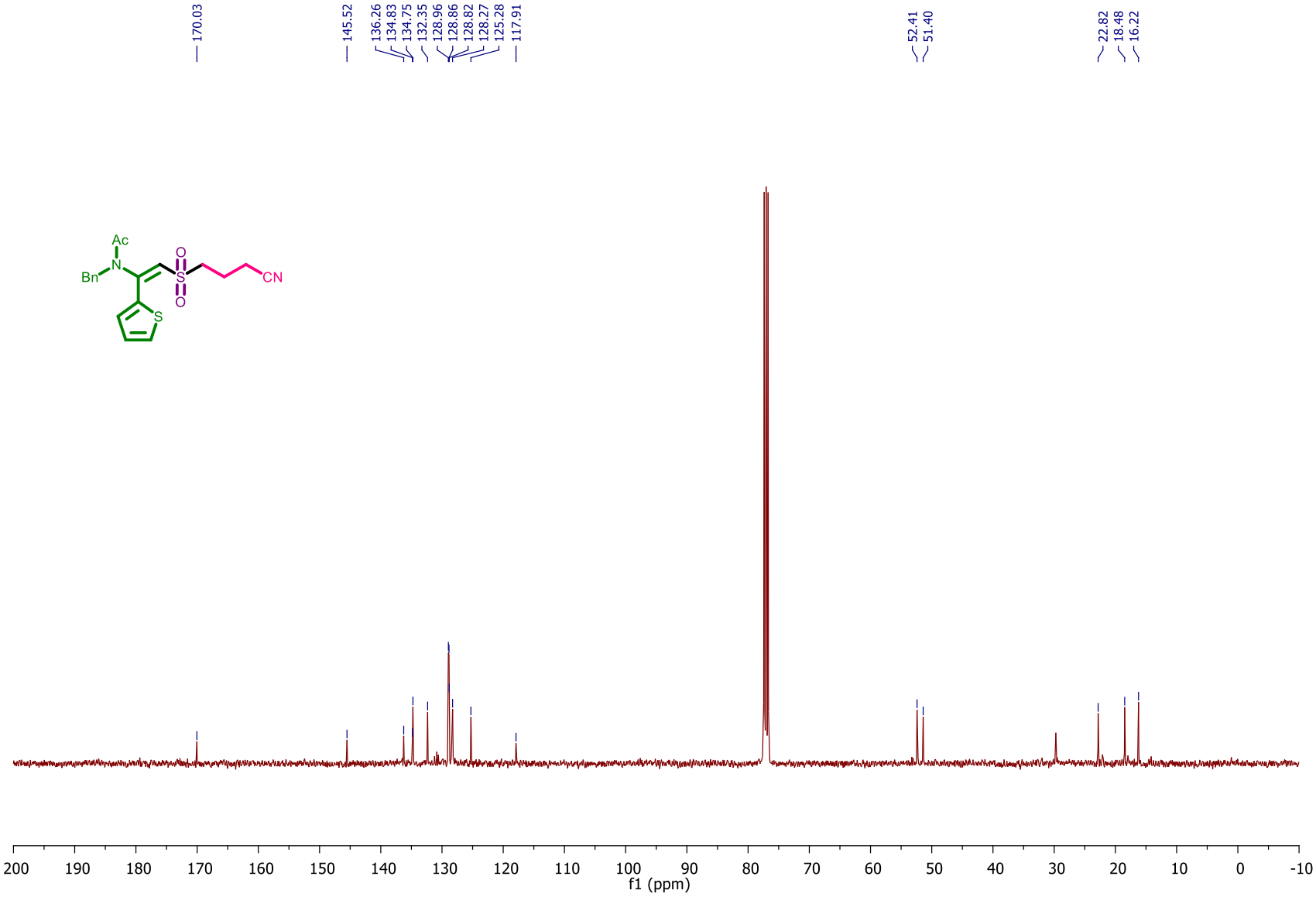
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(4ma)**



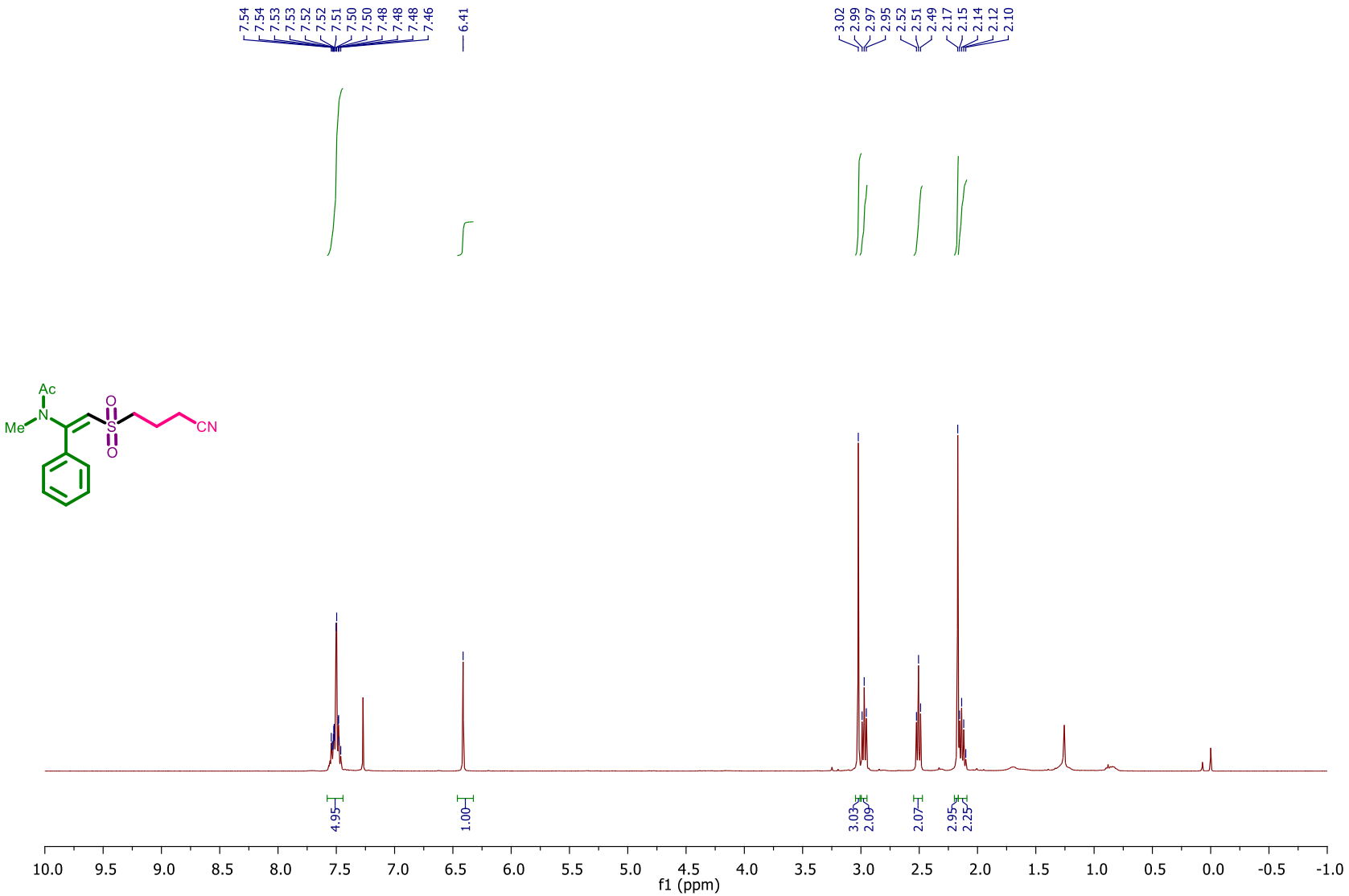
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4na)**



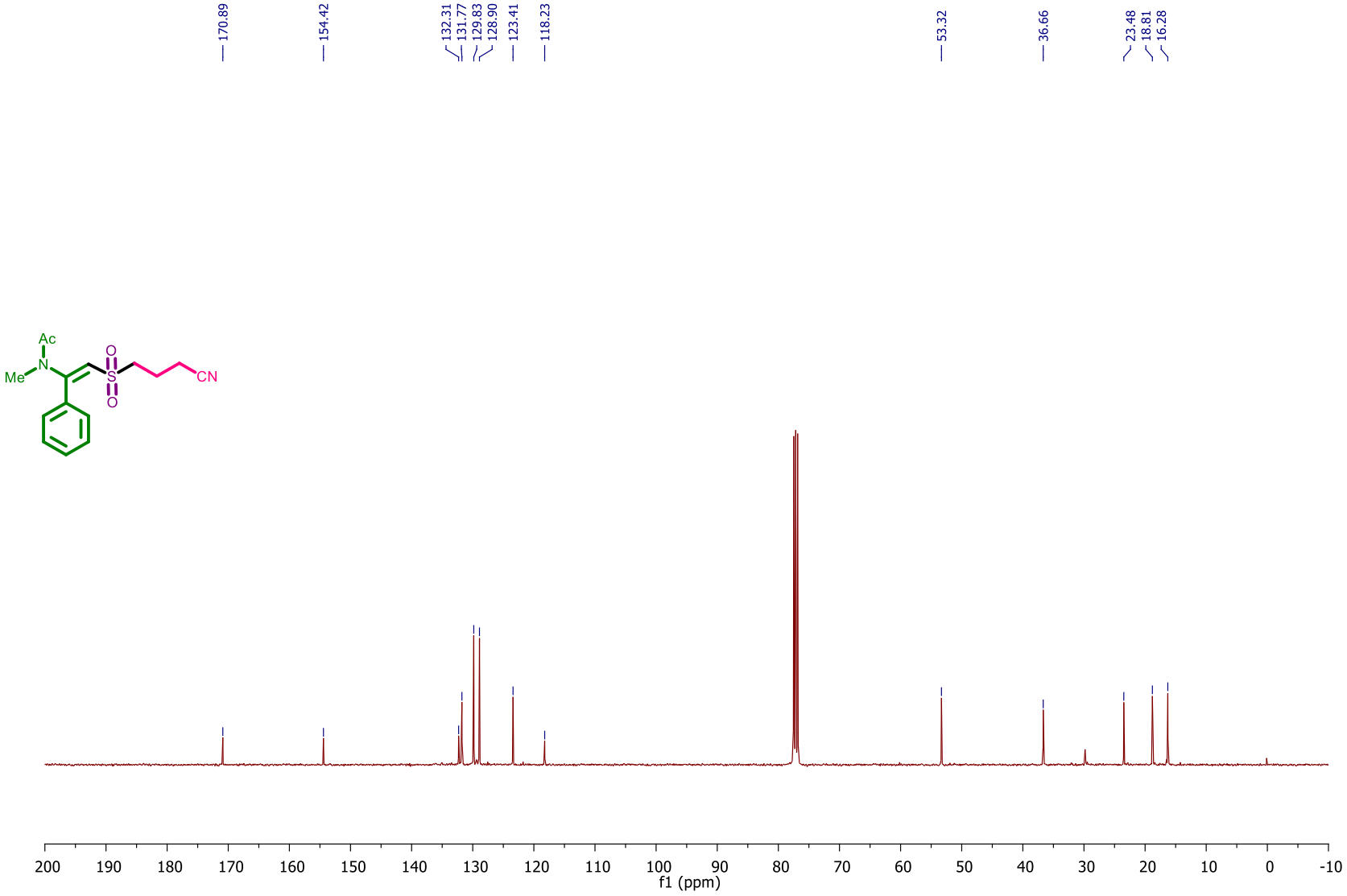
$^{13}C$ NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4na)**



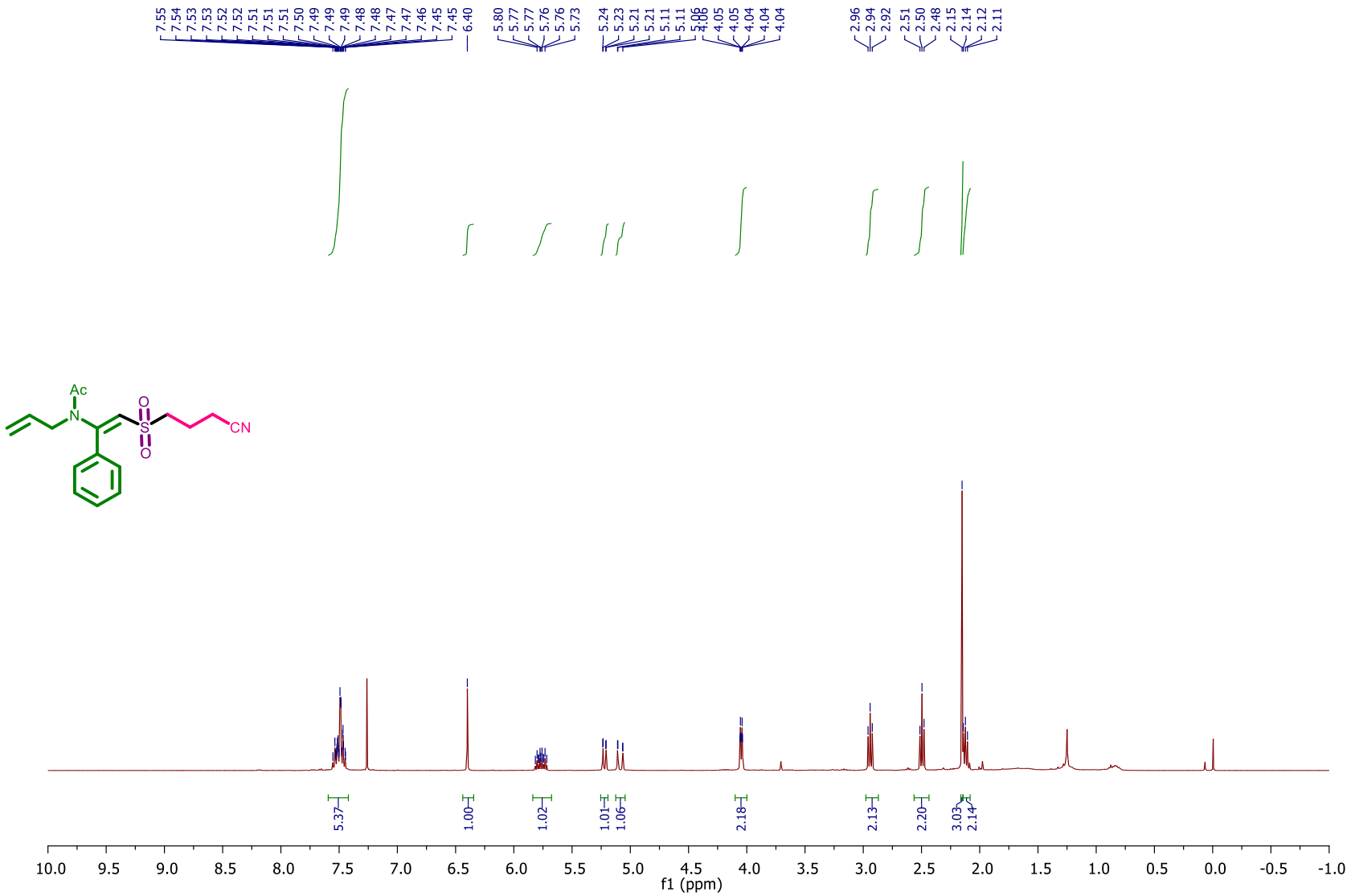
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4oa)**



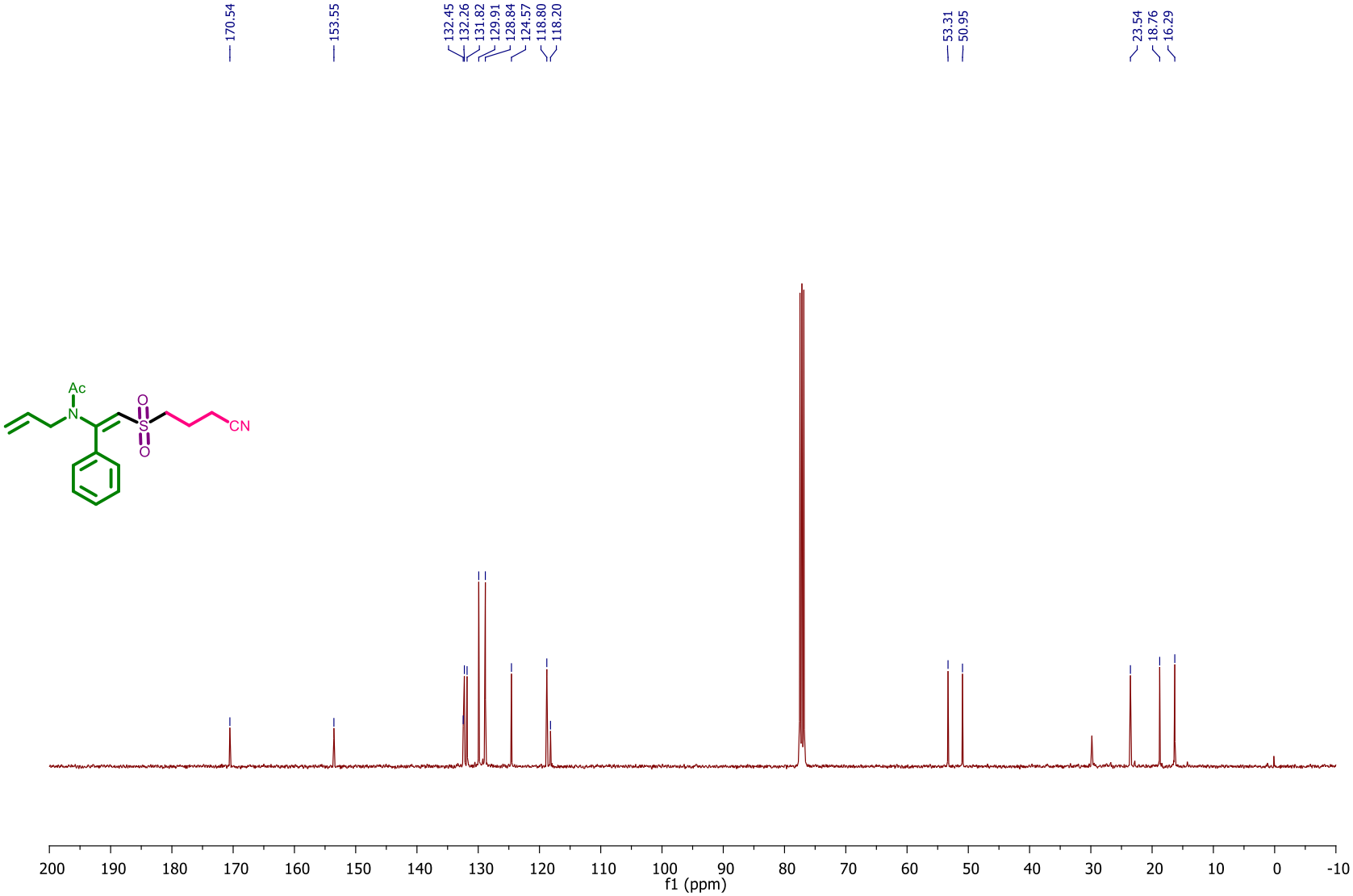
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4oa)**



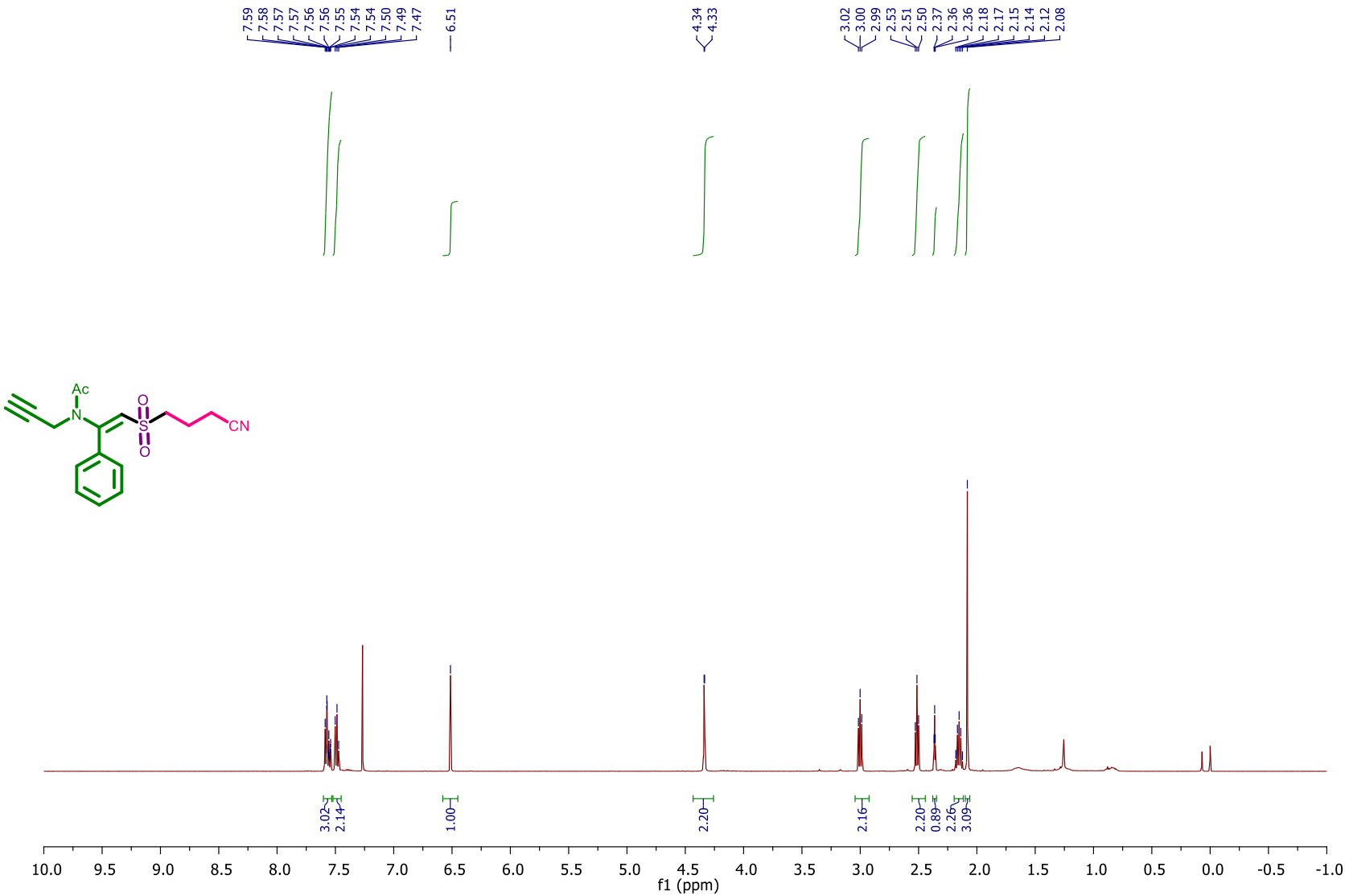
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(4pa)**



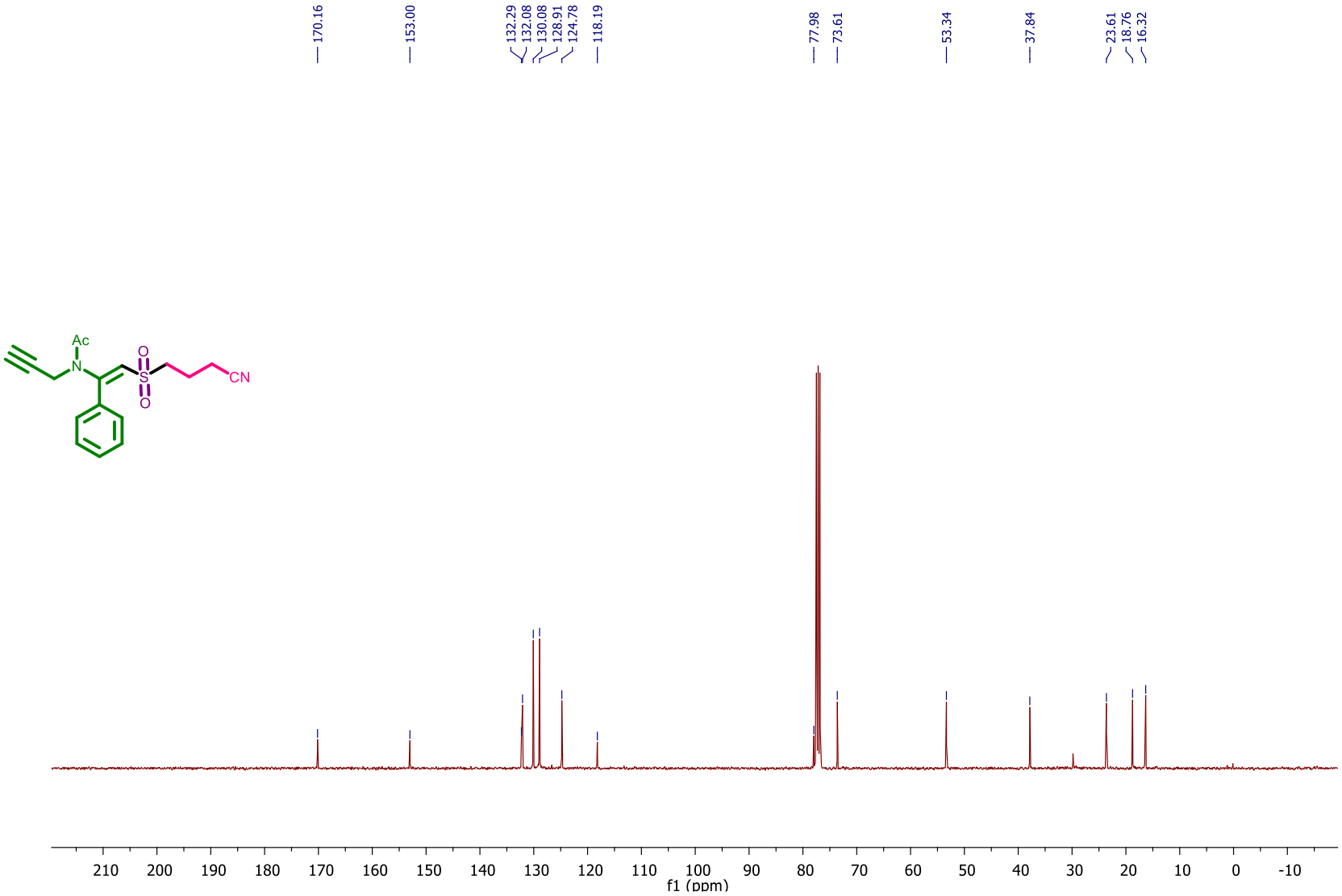
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4pa)**



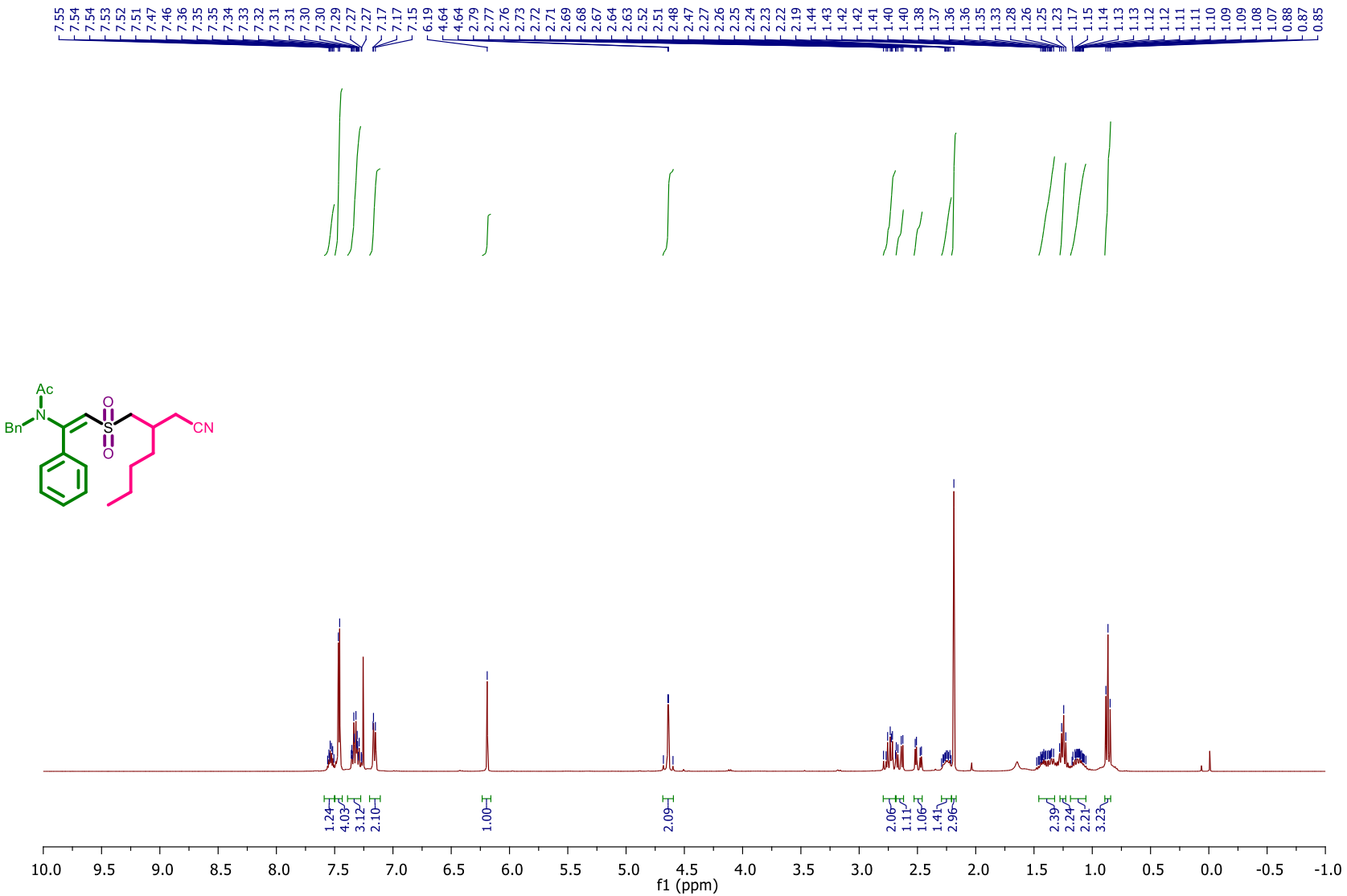
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(4qa)**



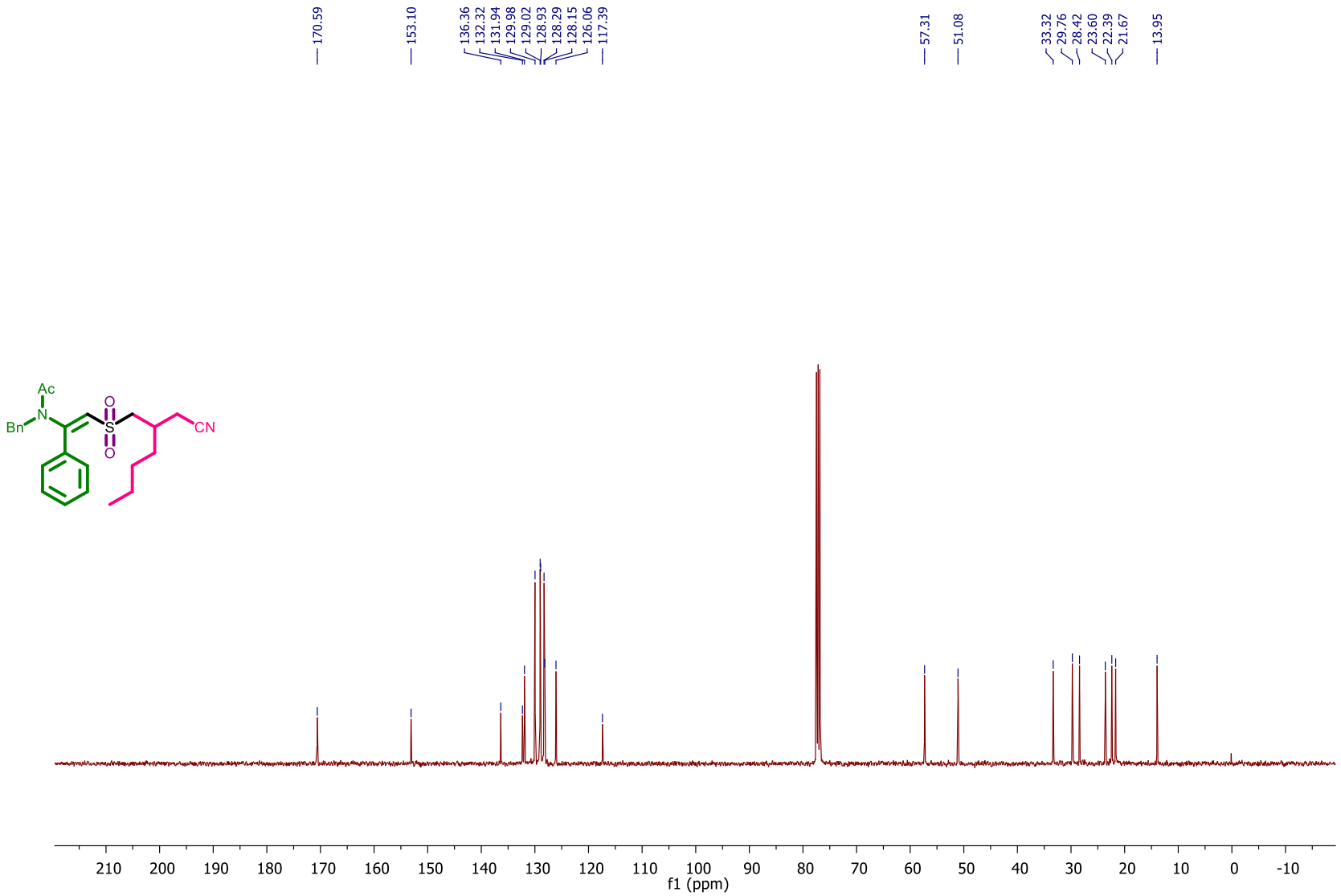
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4qa)**



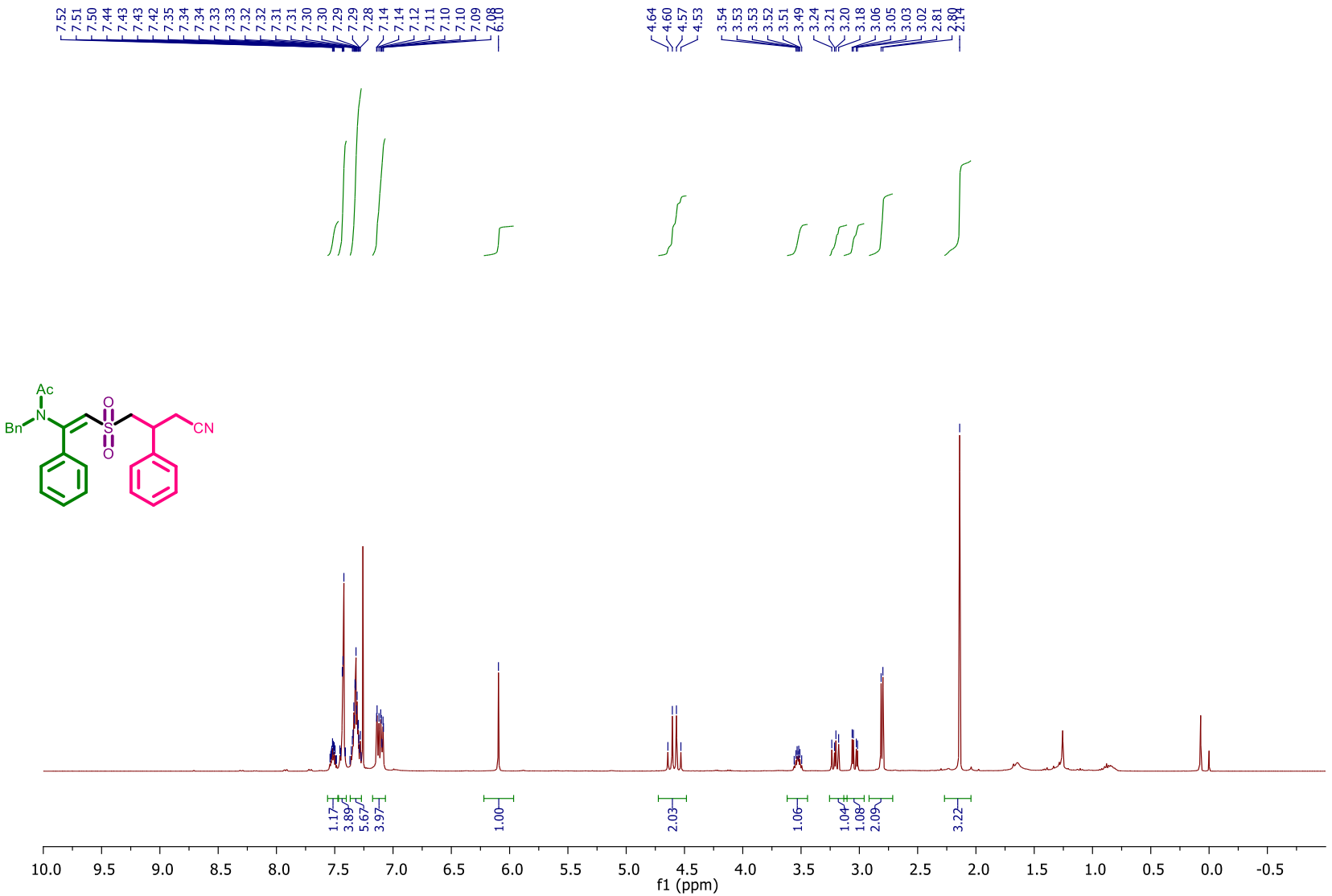
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ab)**



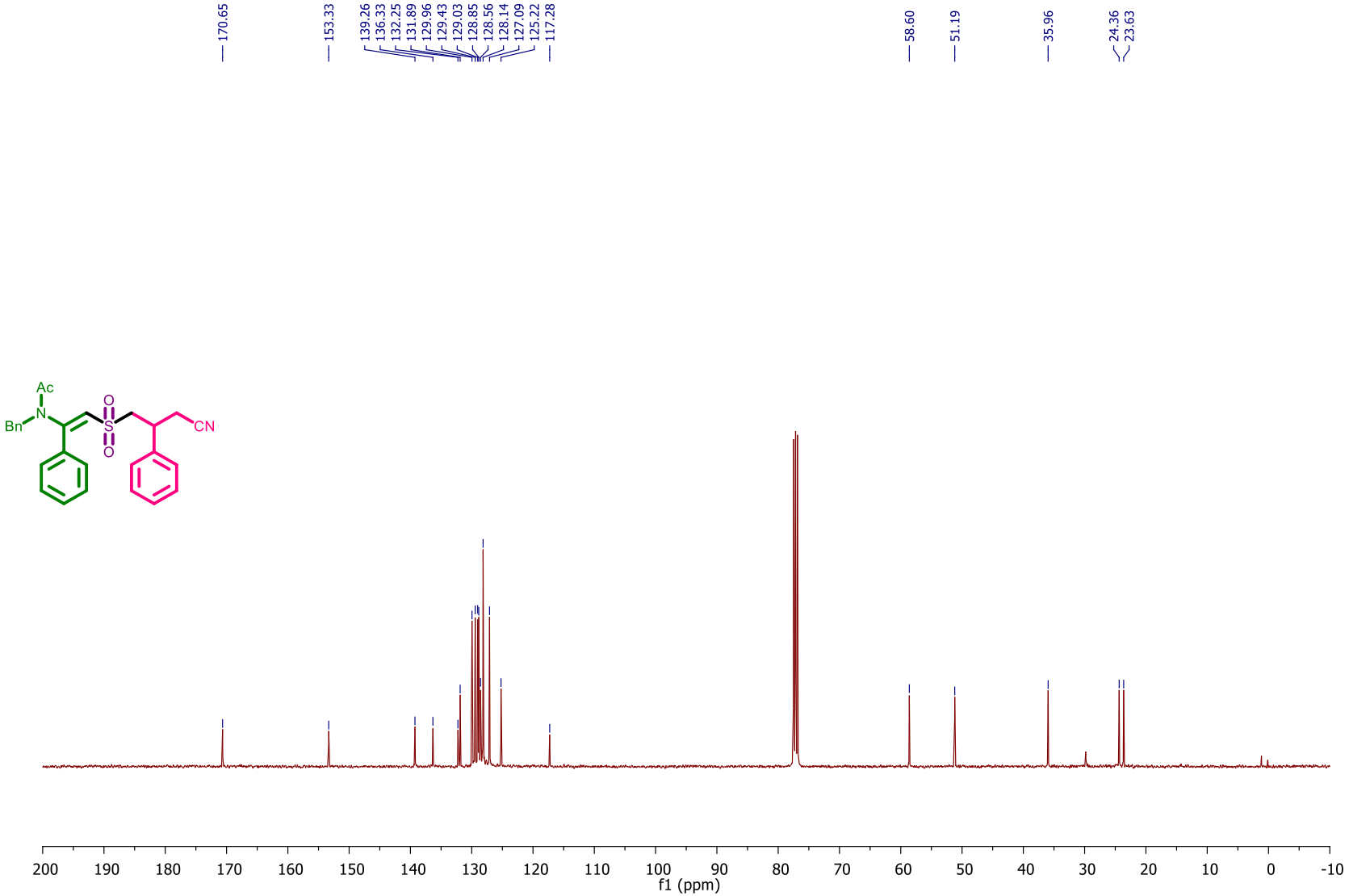
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4ab)**



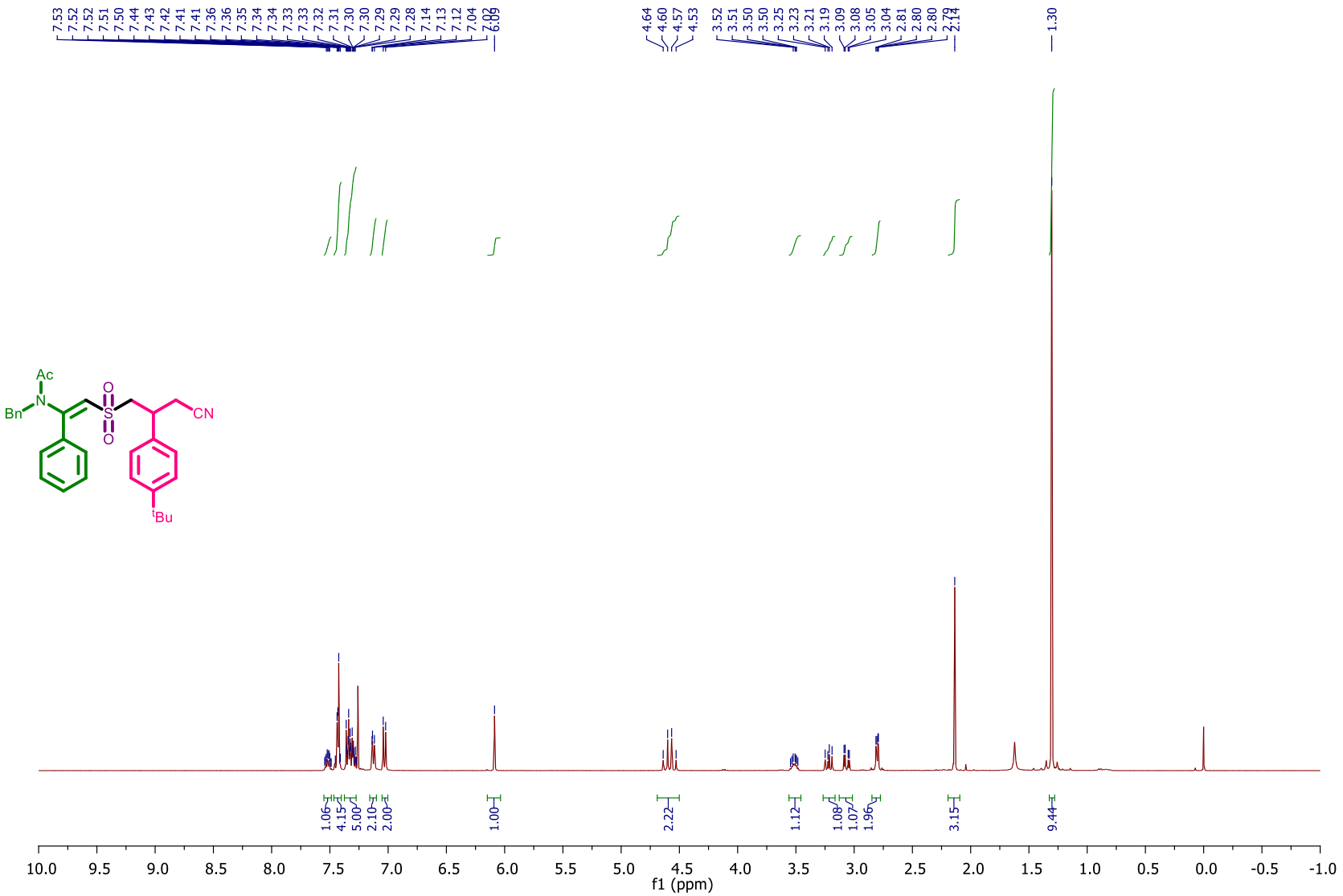
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ac)**



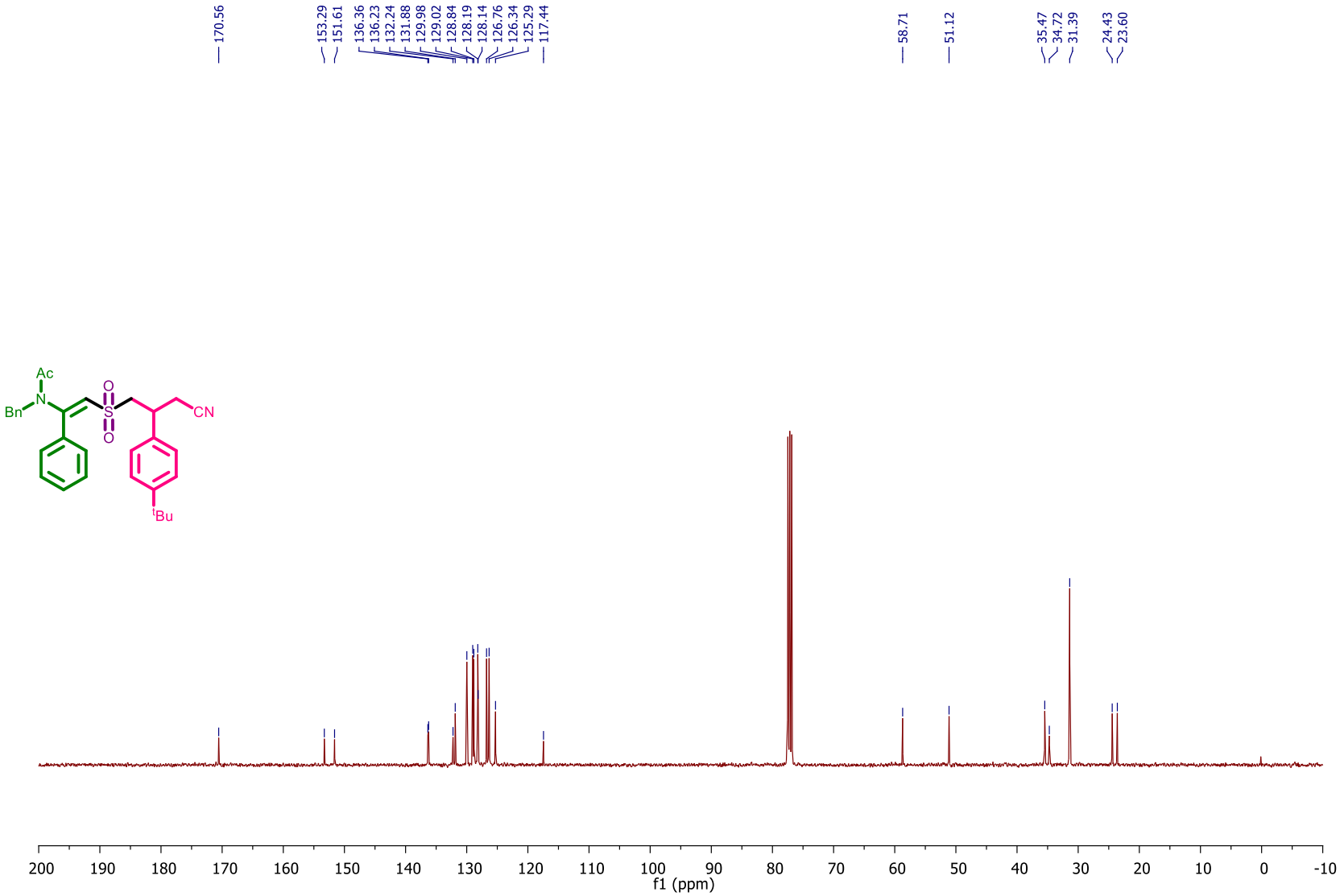
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4ac)**



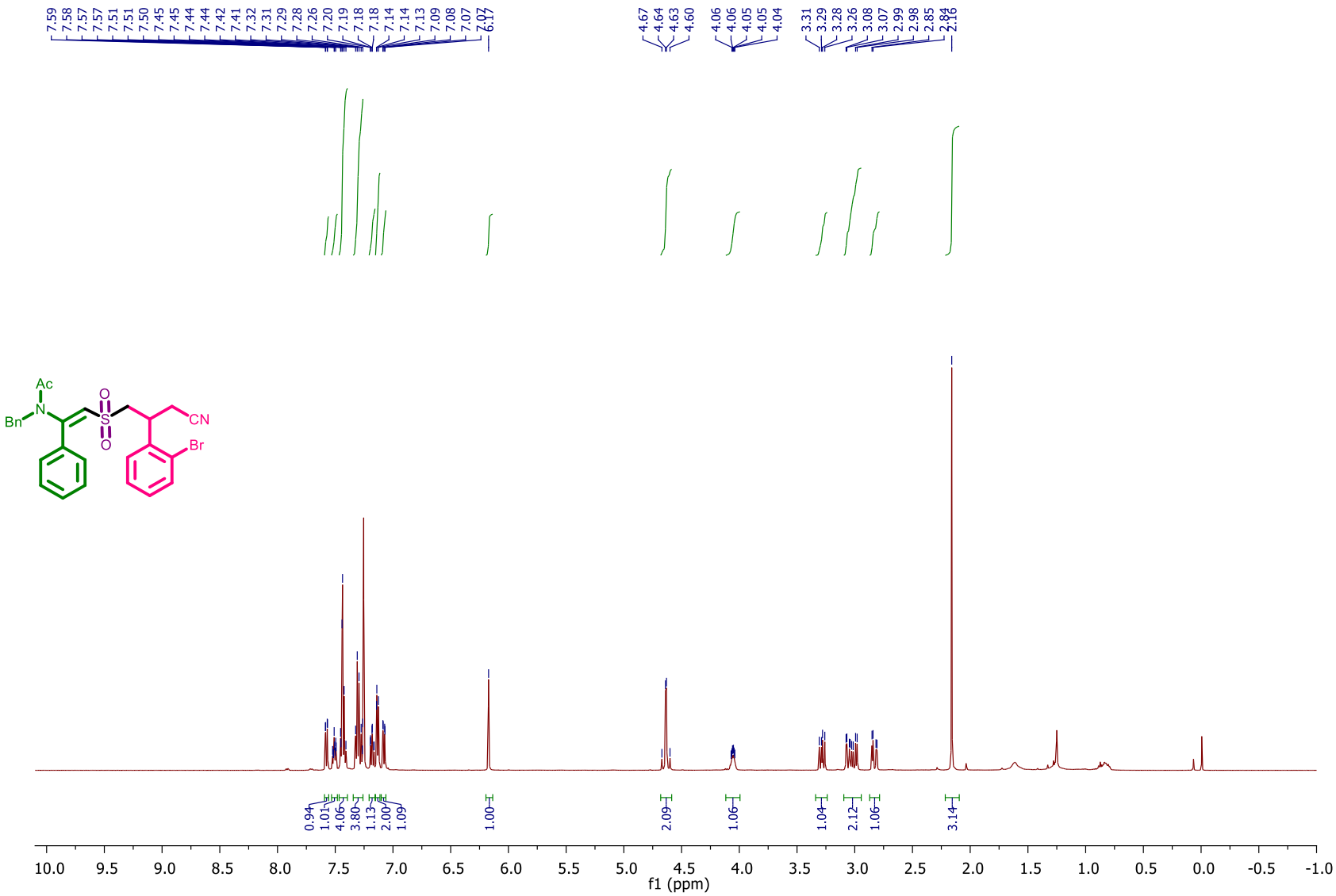
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ad)**



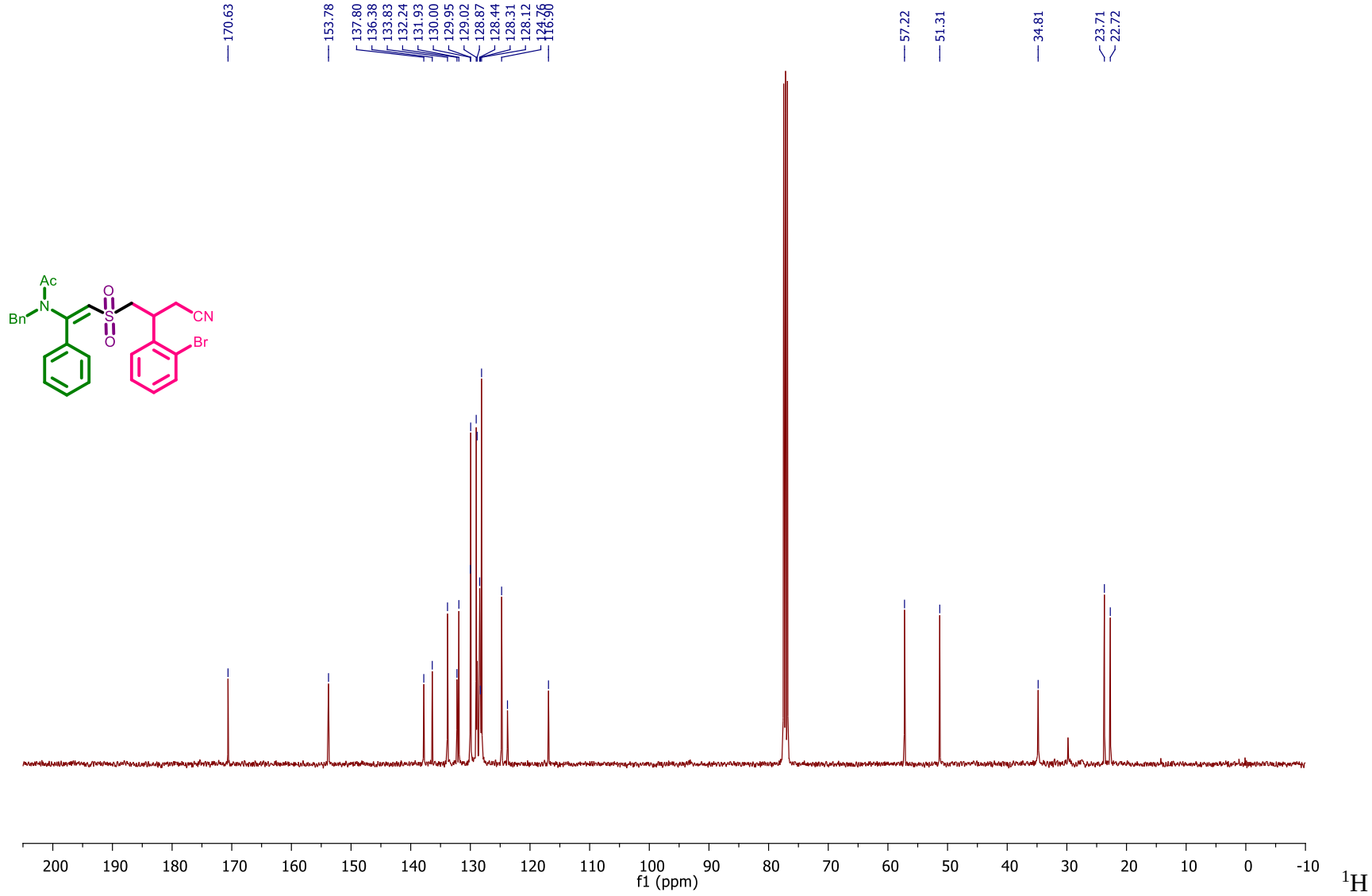
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4ad)**



$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(4ae)**

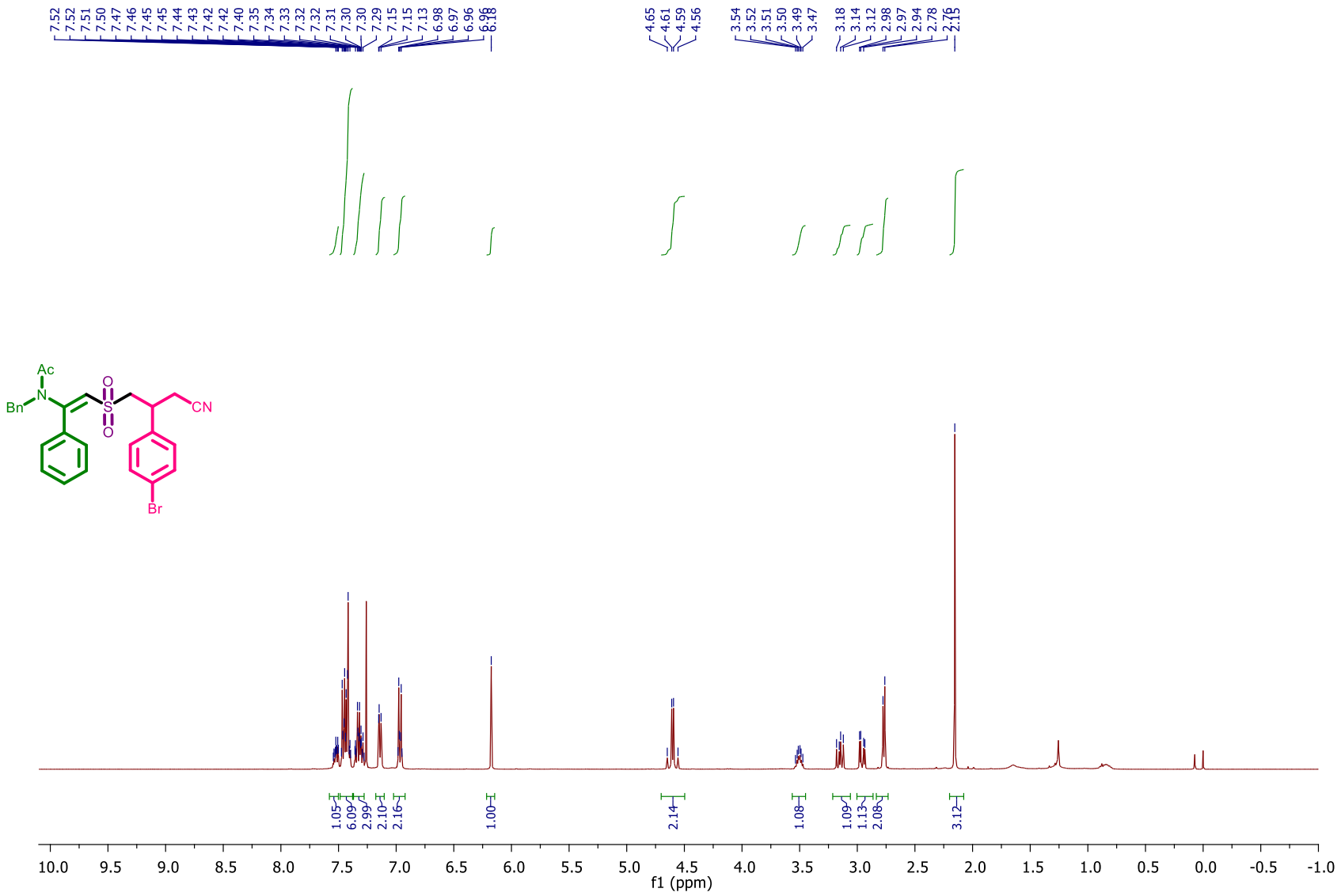


$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4ae)**

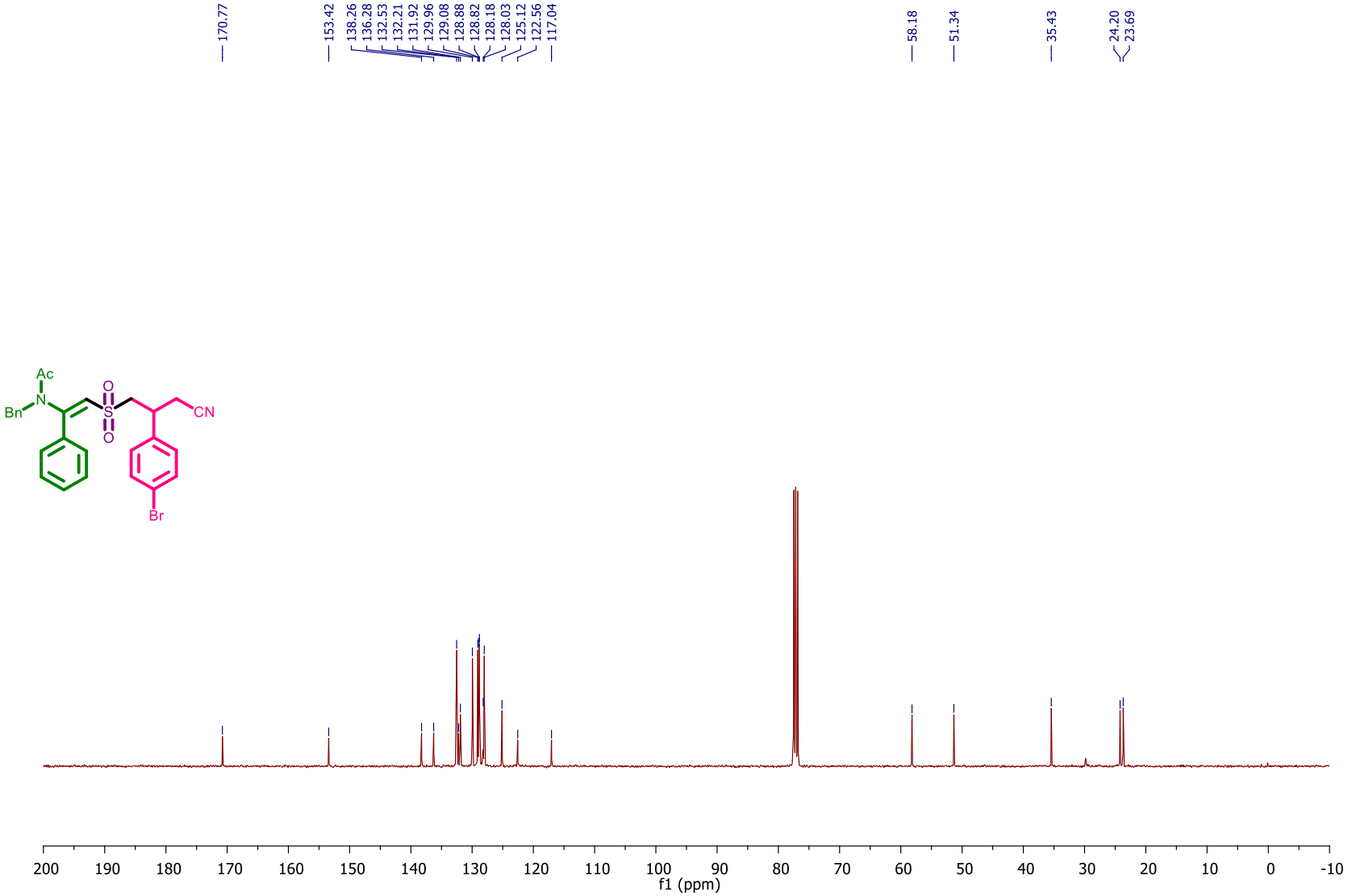



$^{1}$H

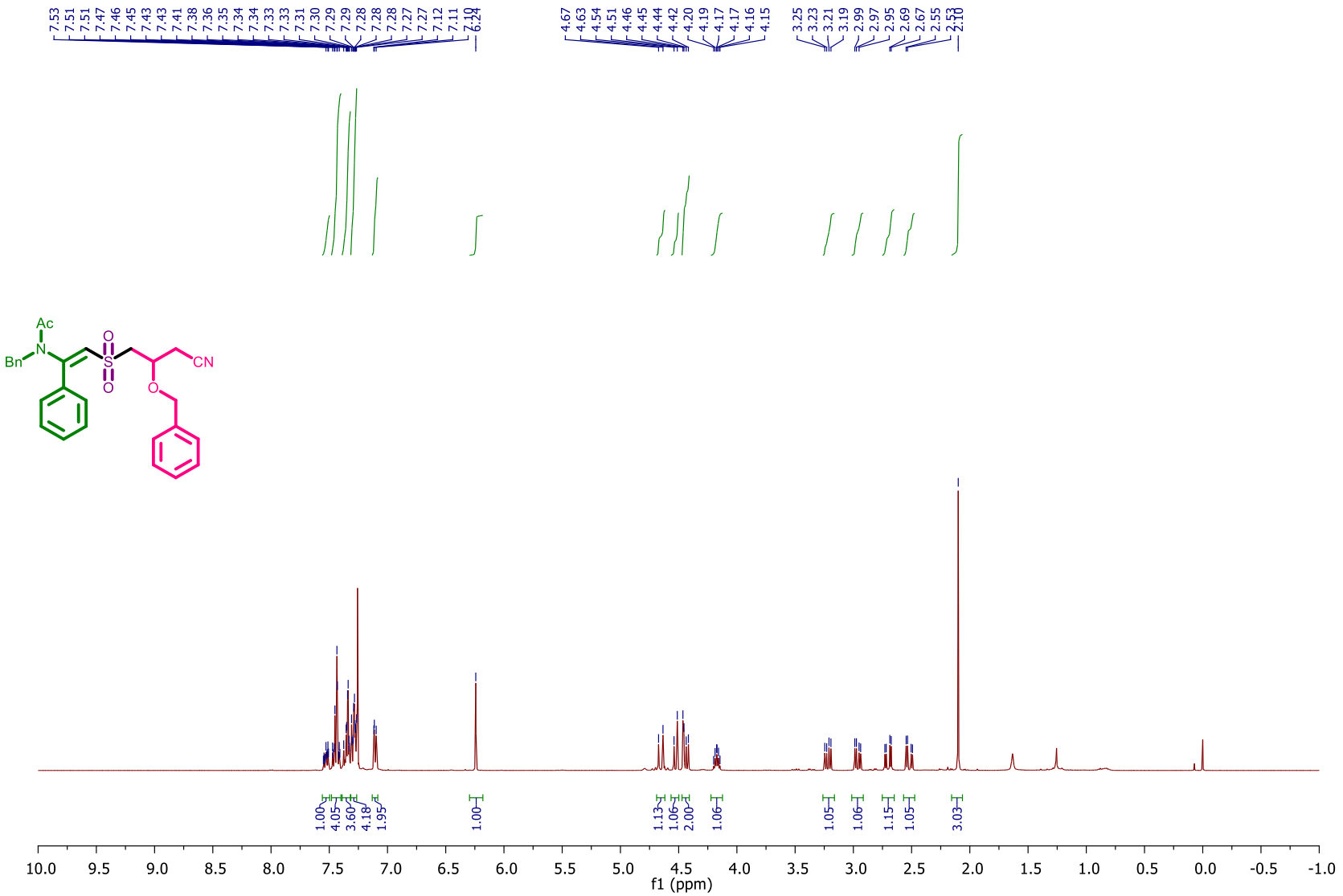
NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4af)**



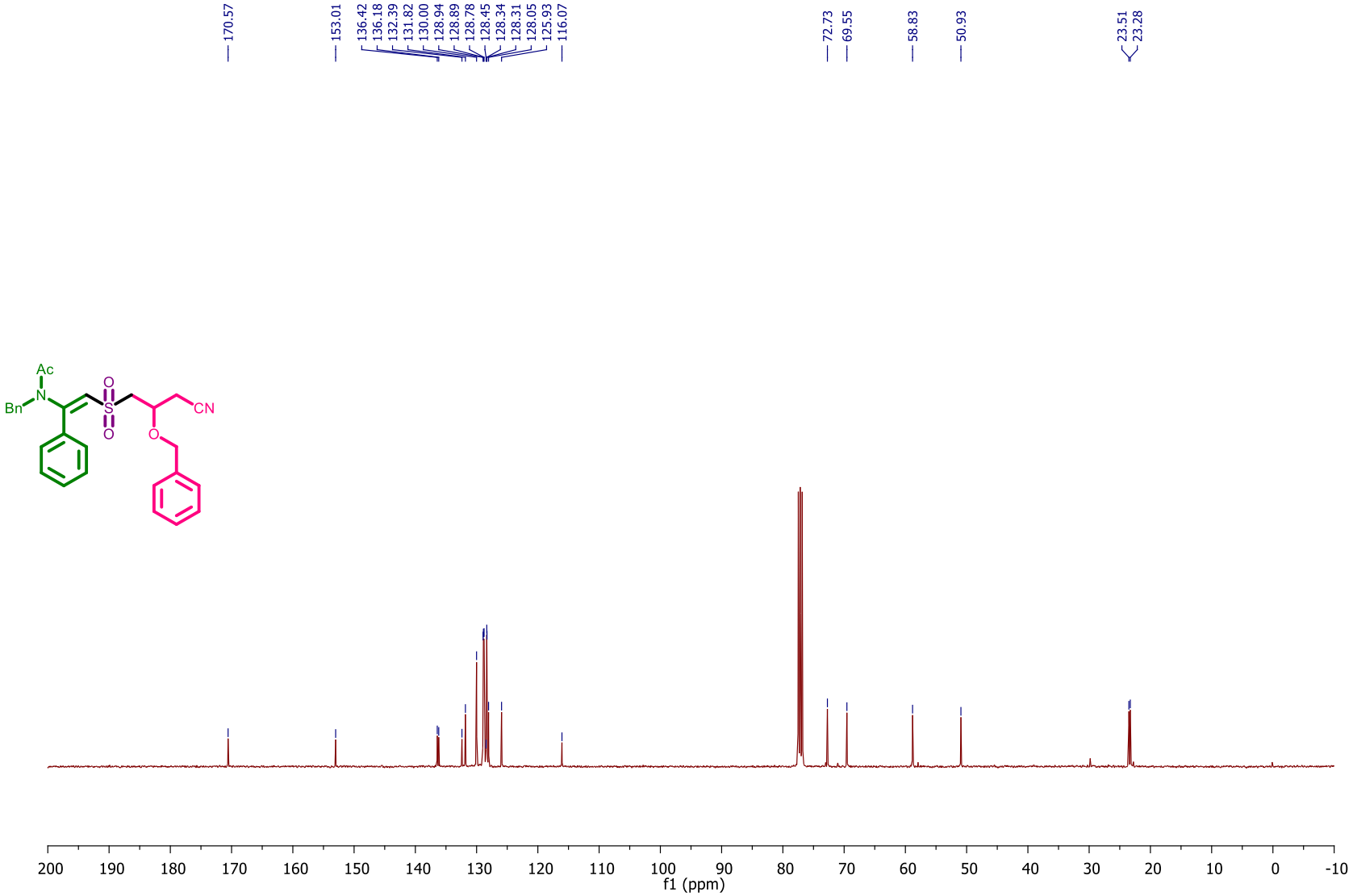
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4af)**



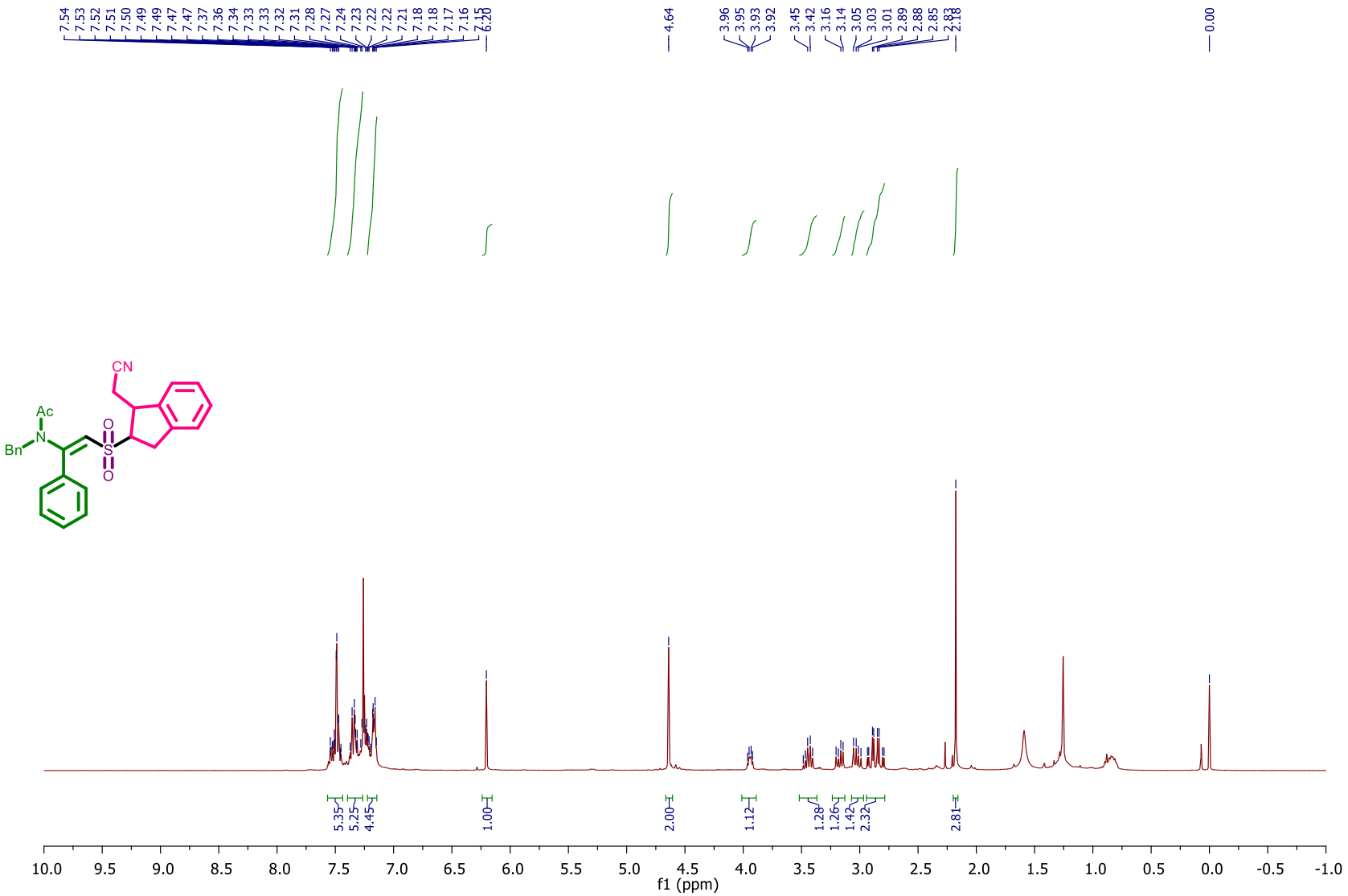
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ag)**



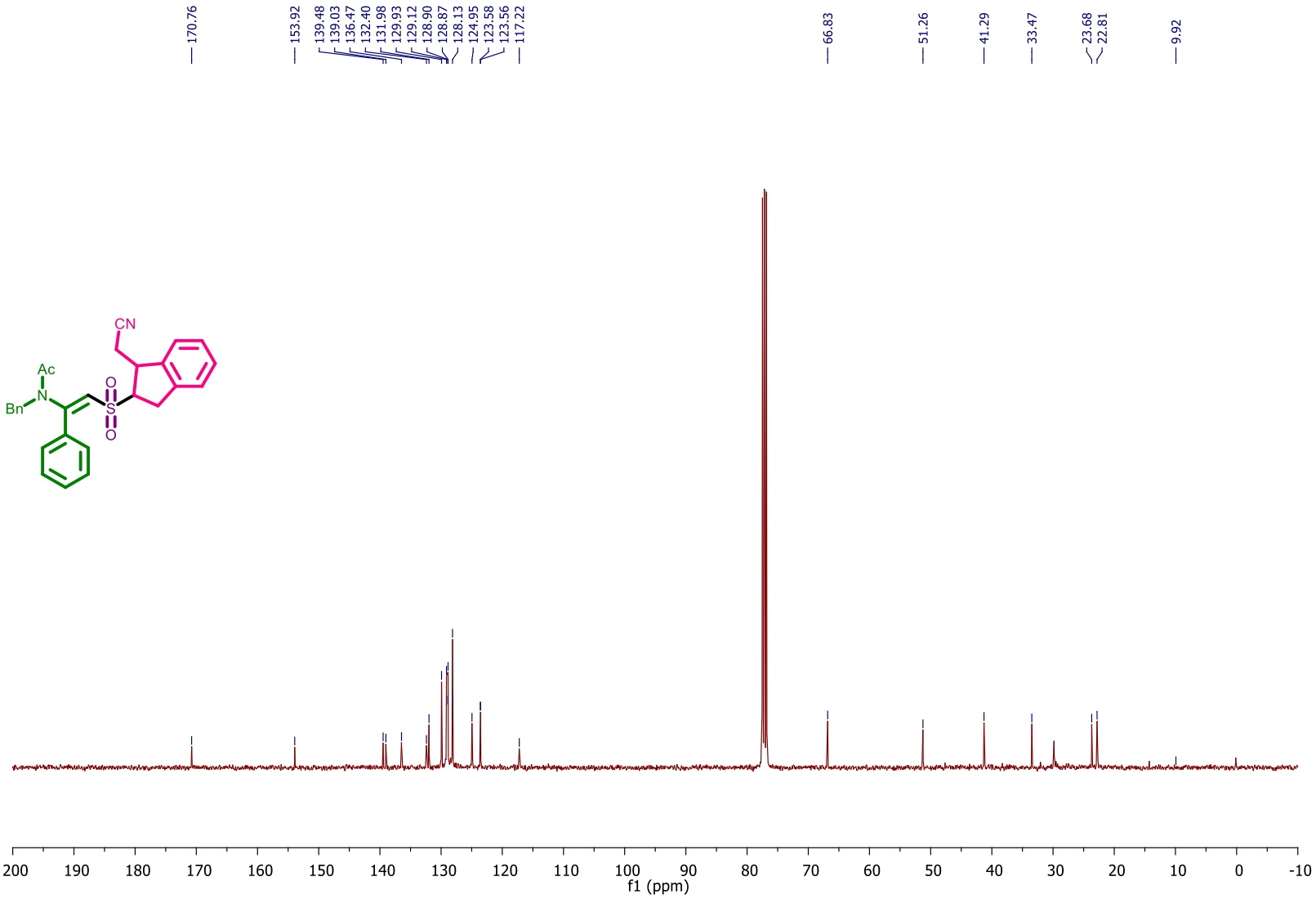
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4ag)**



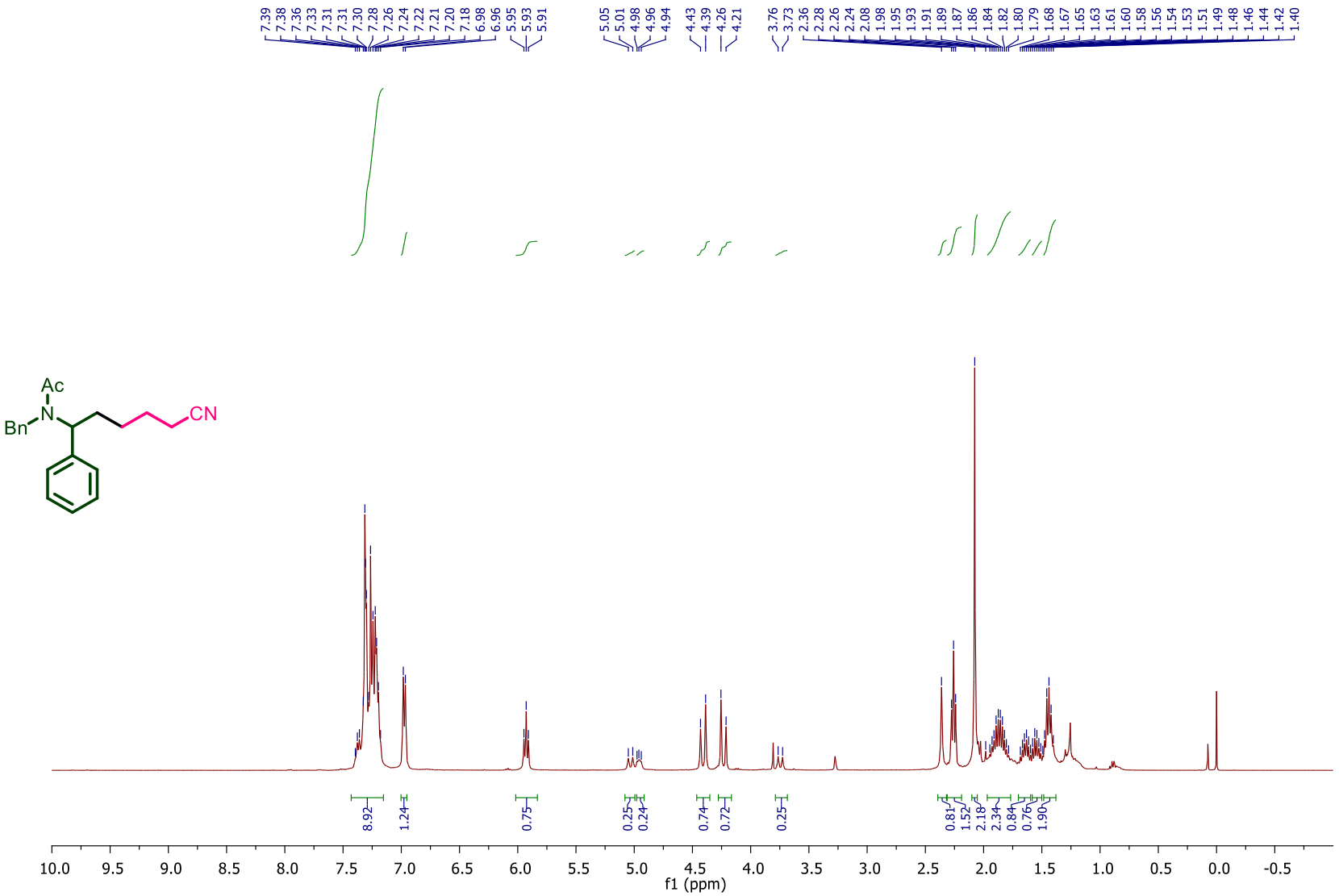
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(4ai)**



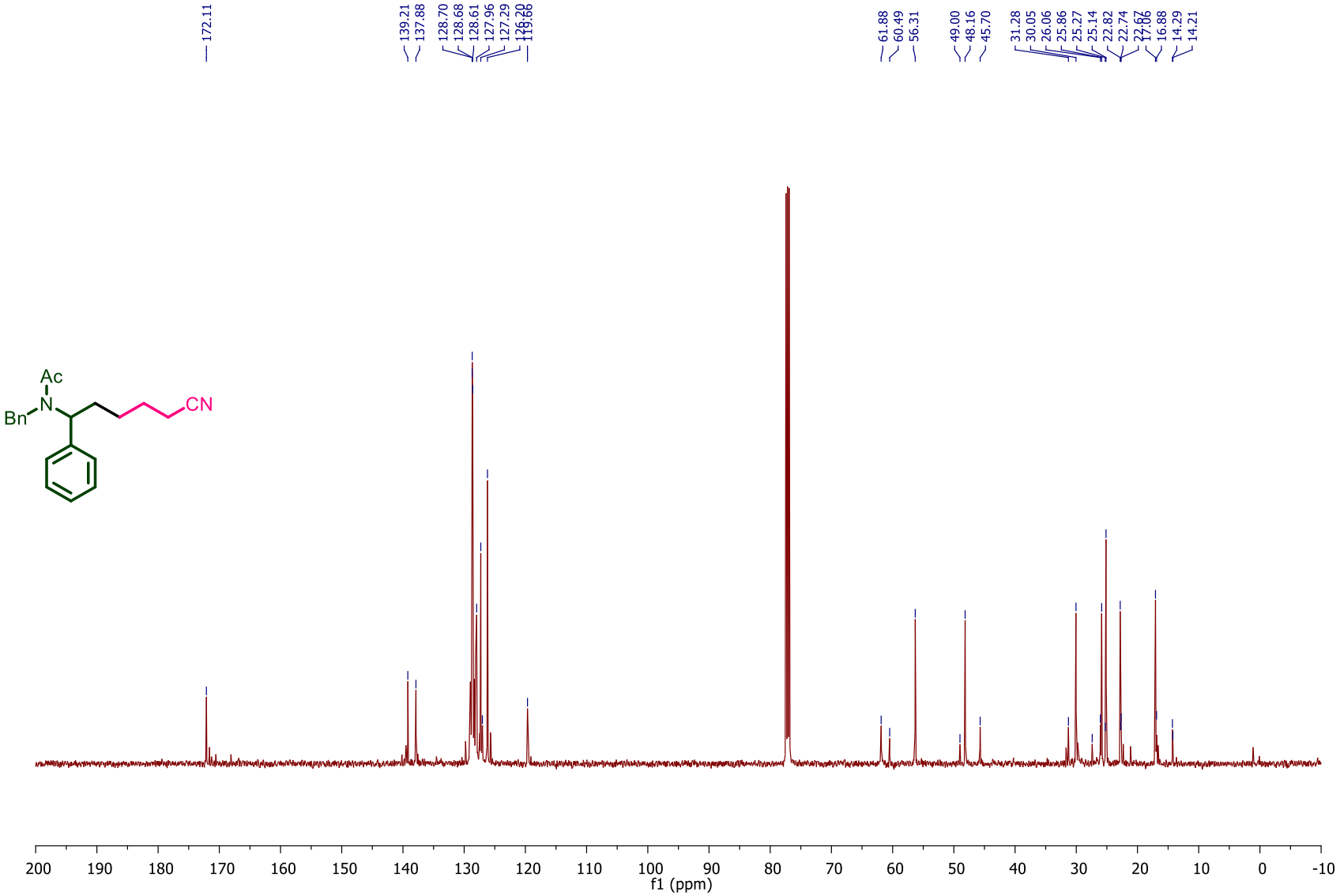
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(4ai)**



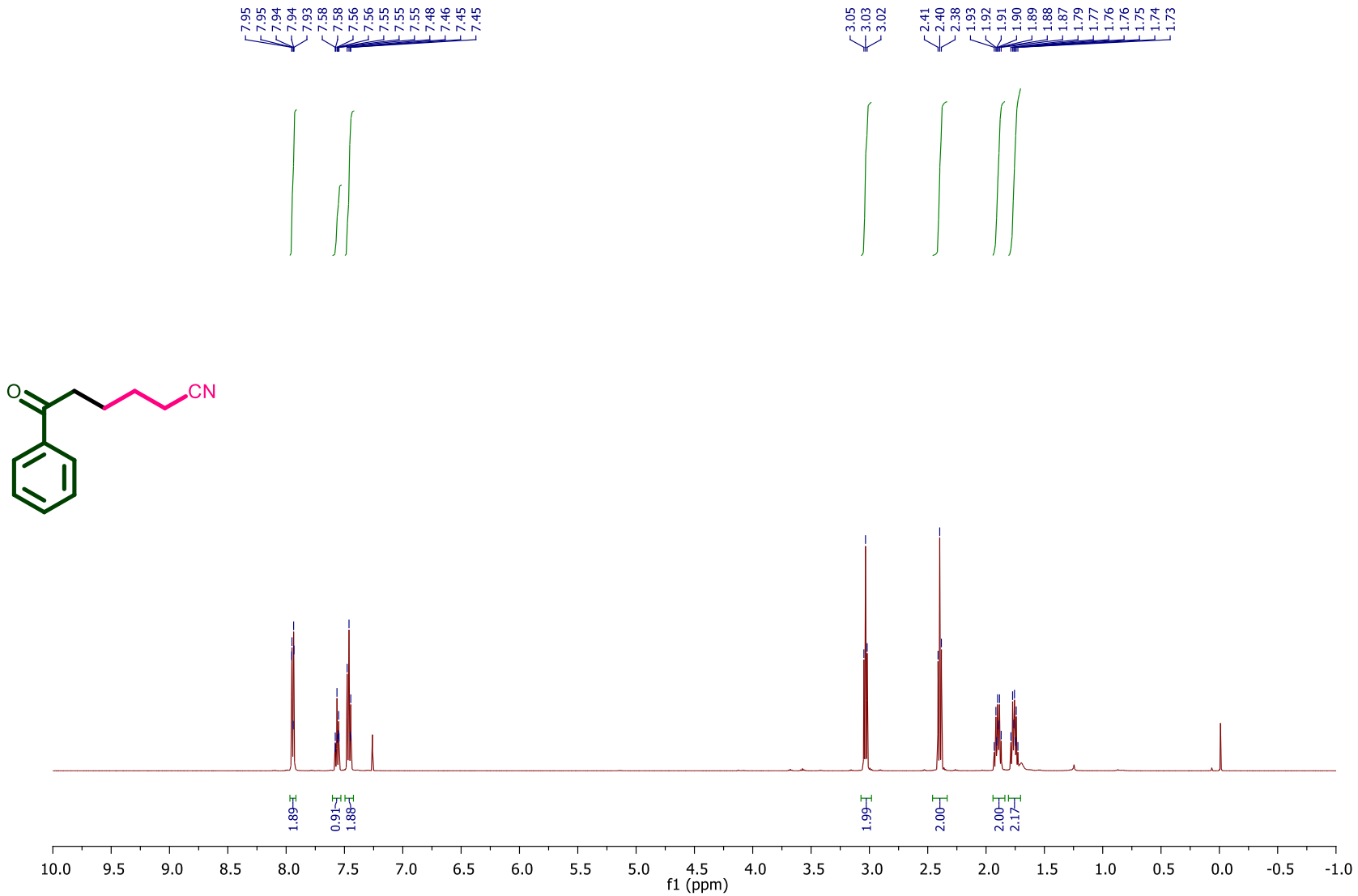
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(5)**



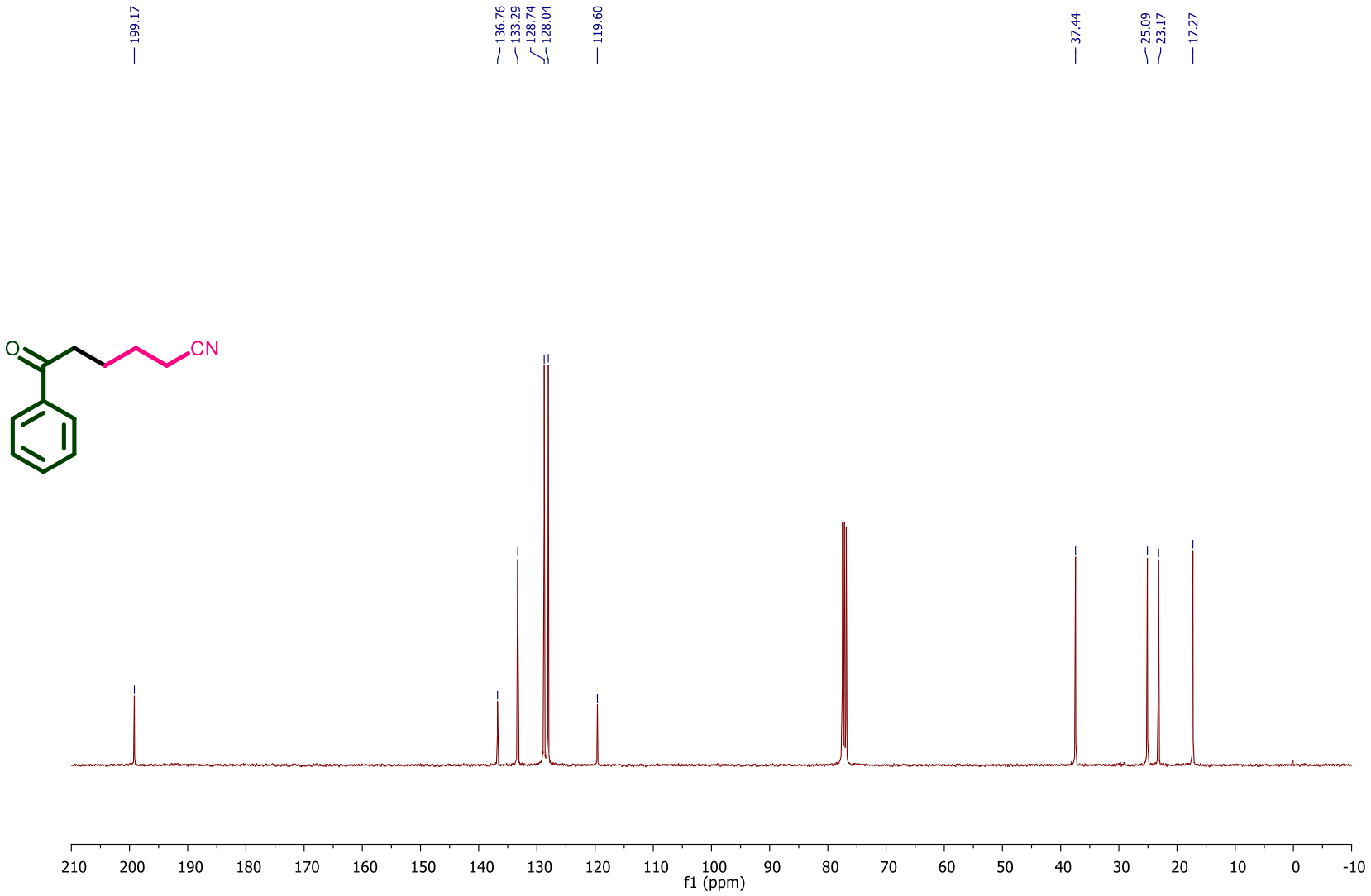
$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(5)**



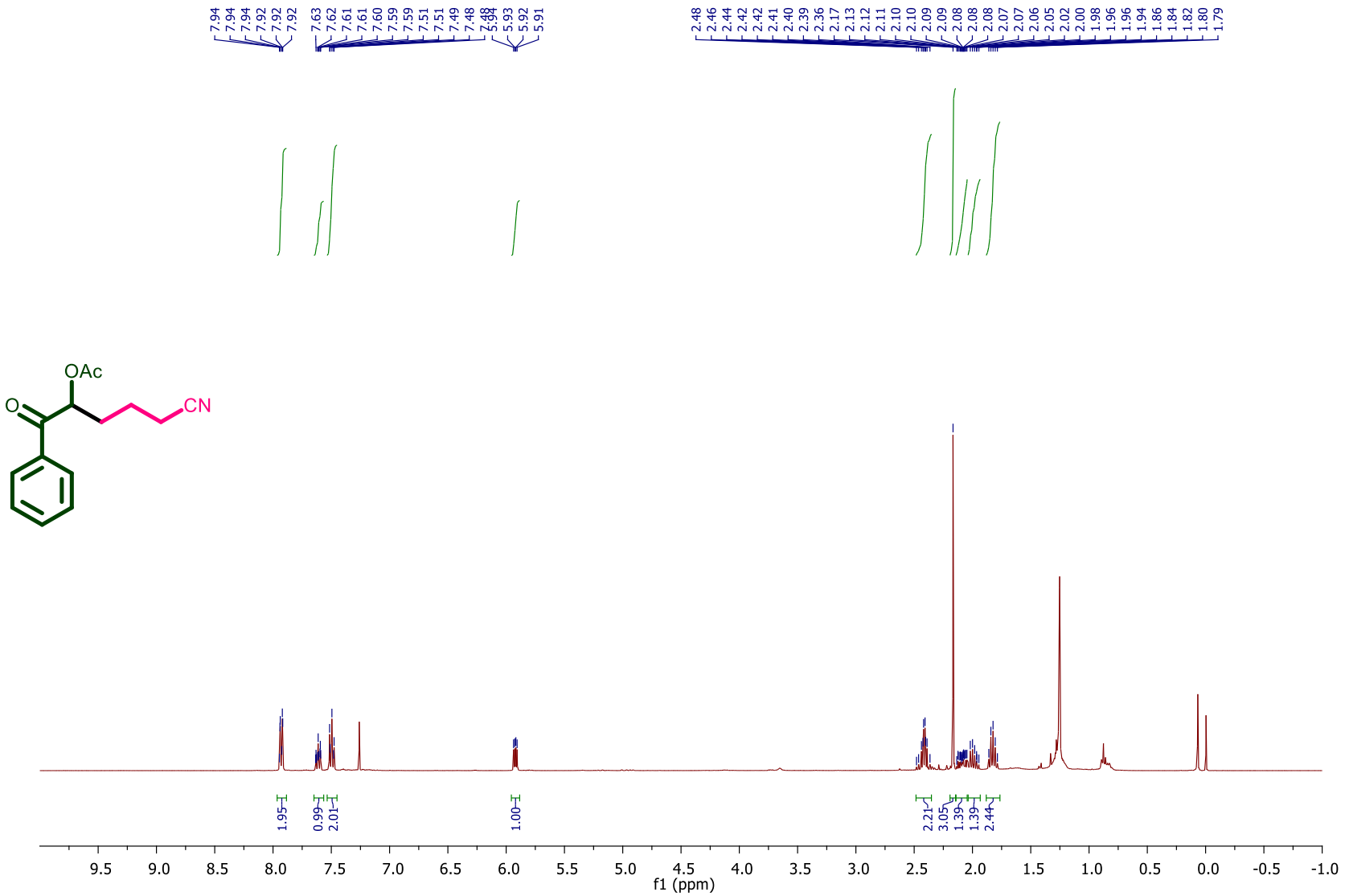
$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(6)**



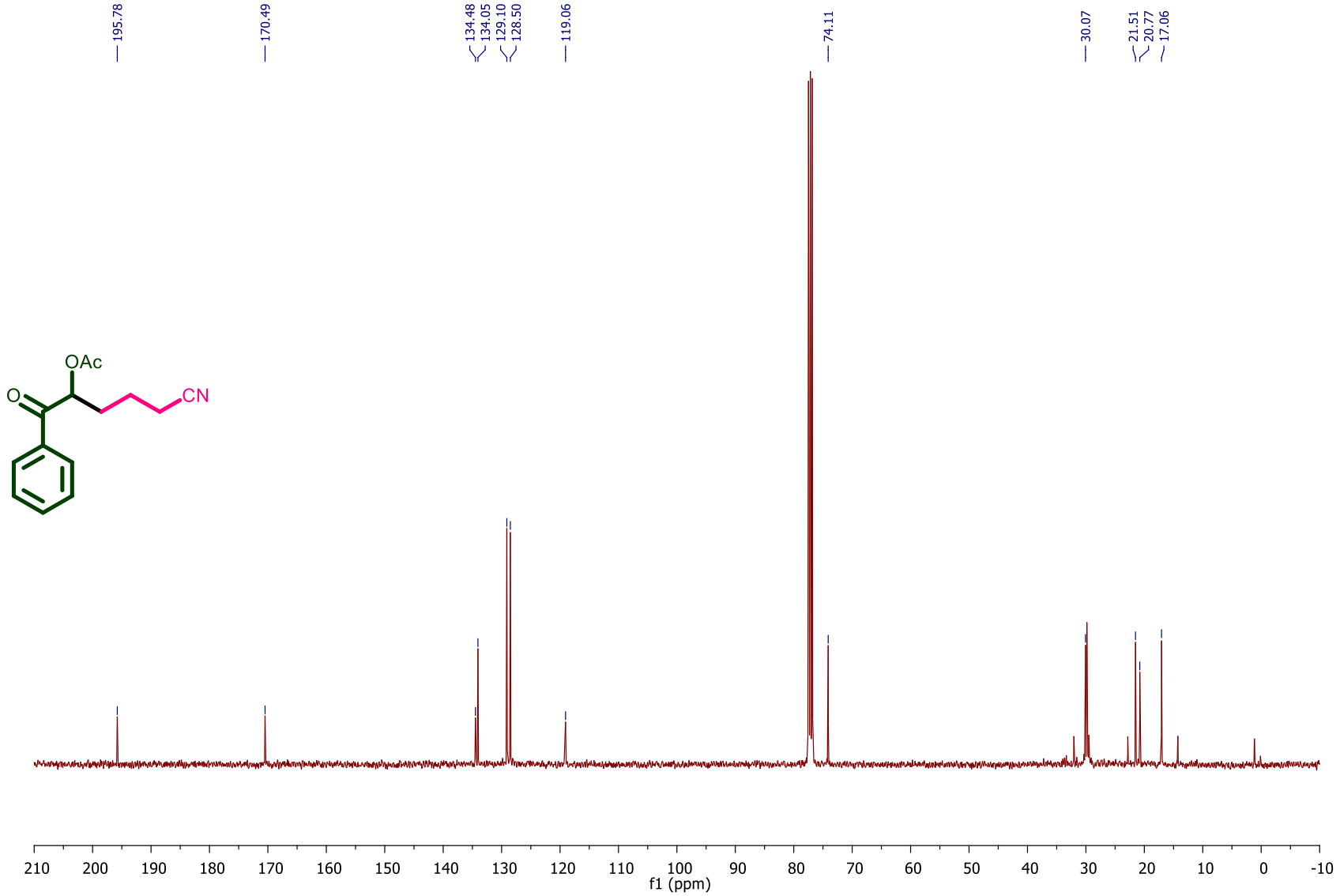
$^{13}C$ NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(6)**



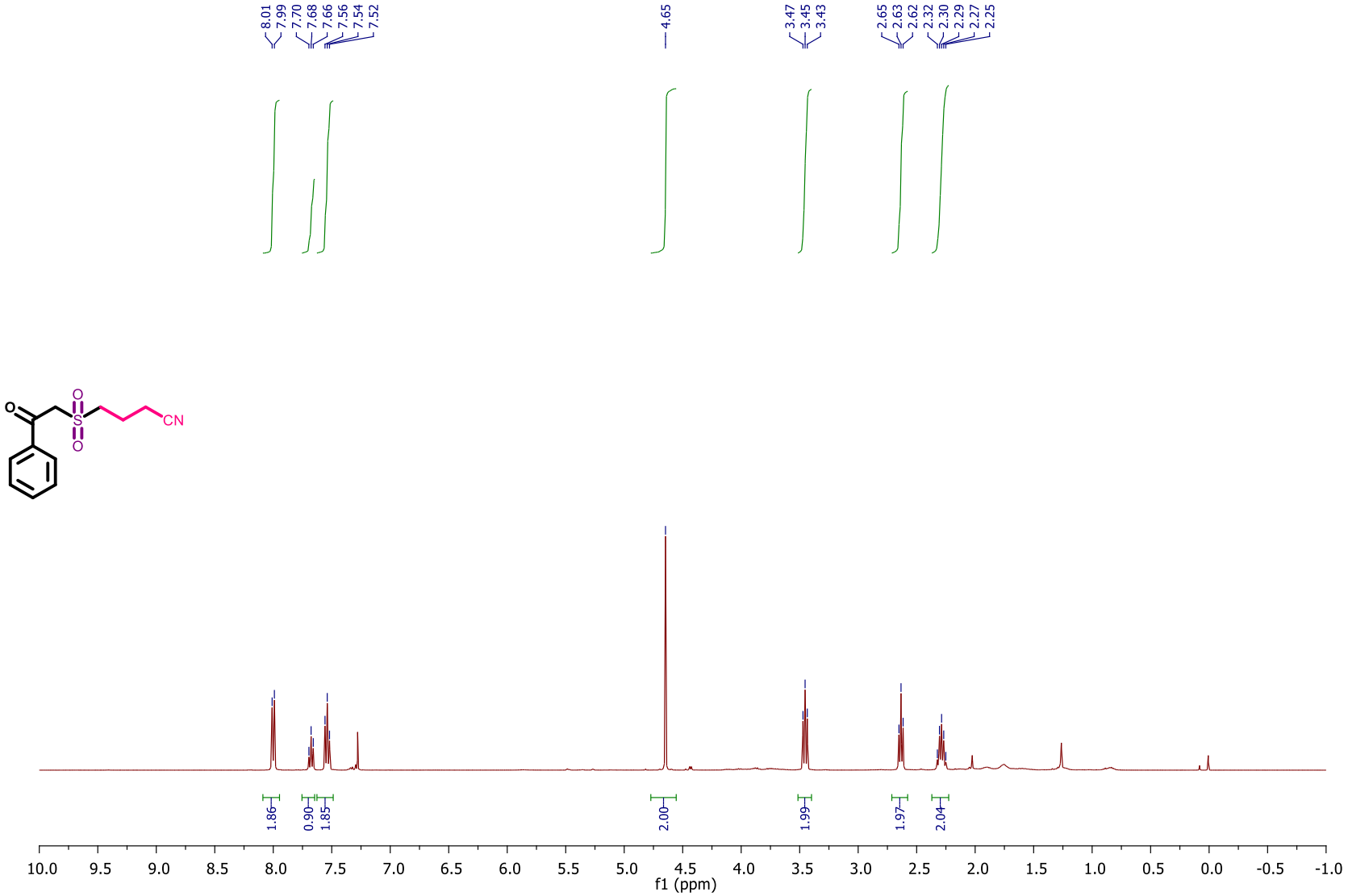
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound (7)



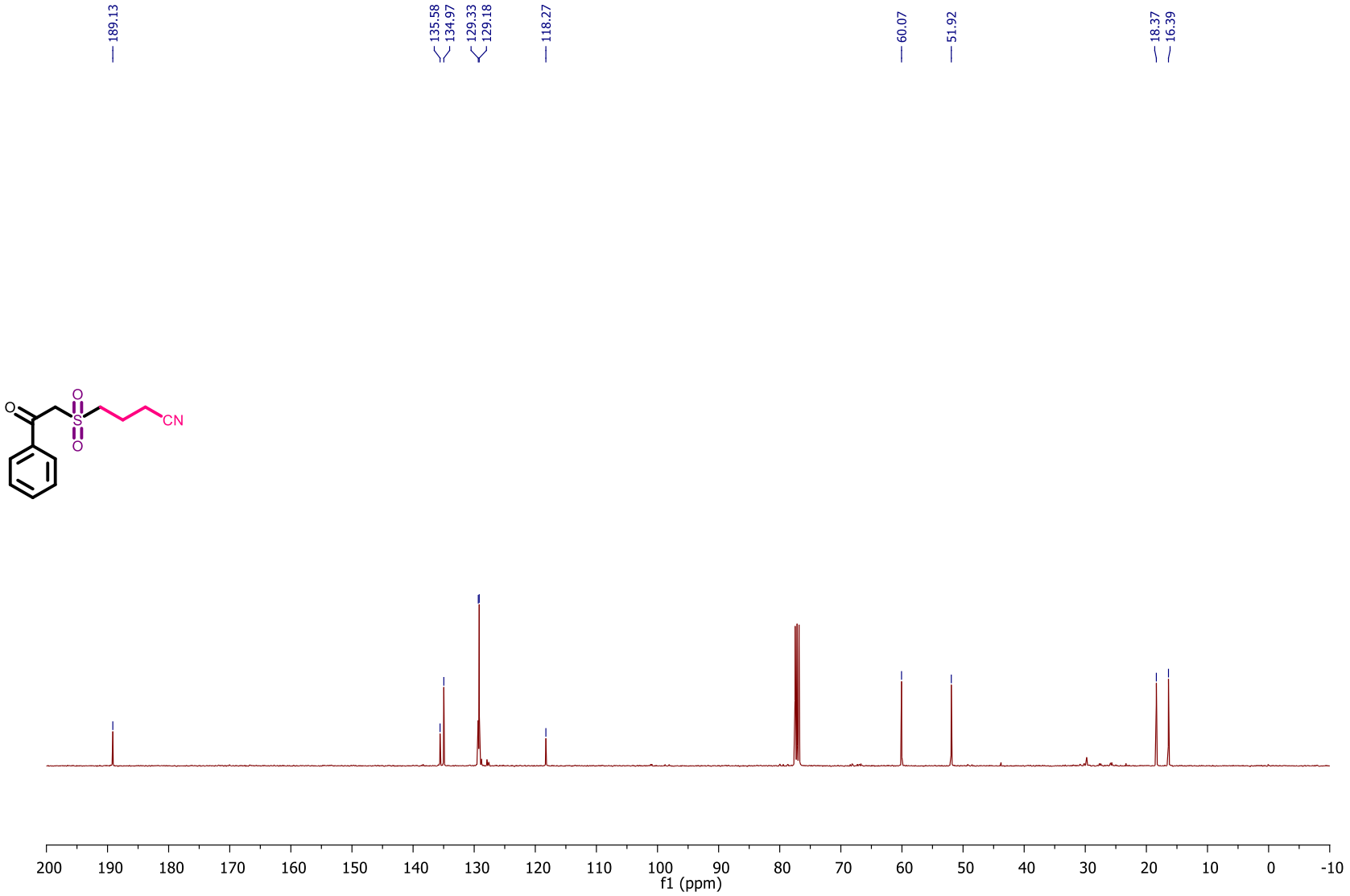
$^{13}$C NMR (101 MHz, $CDCl_3$) Spectrum of Compound **(7)**



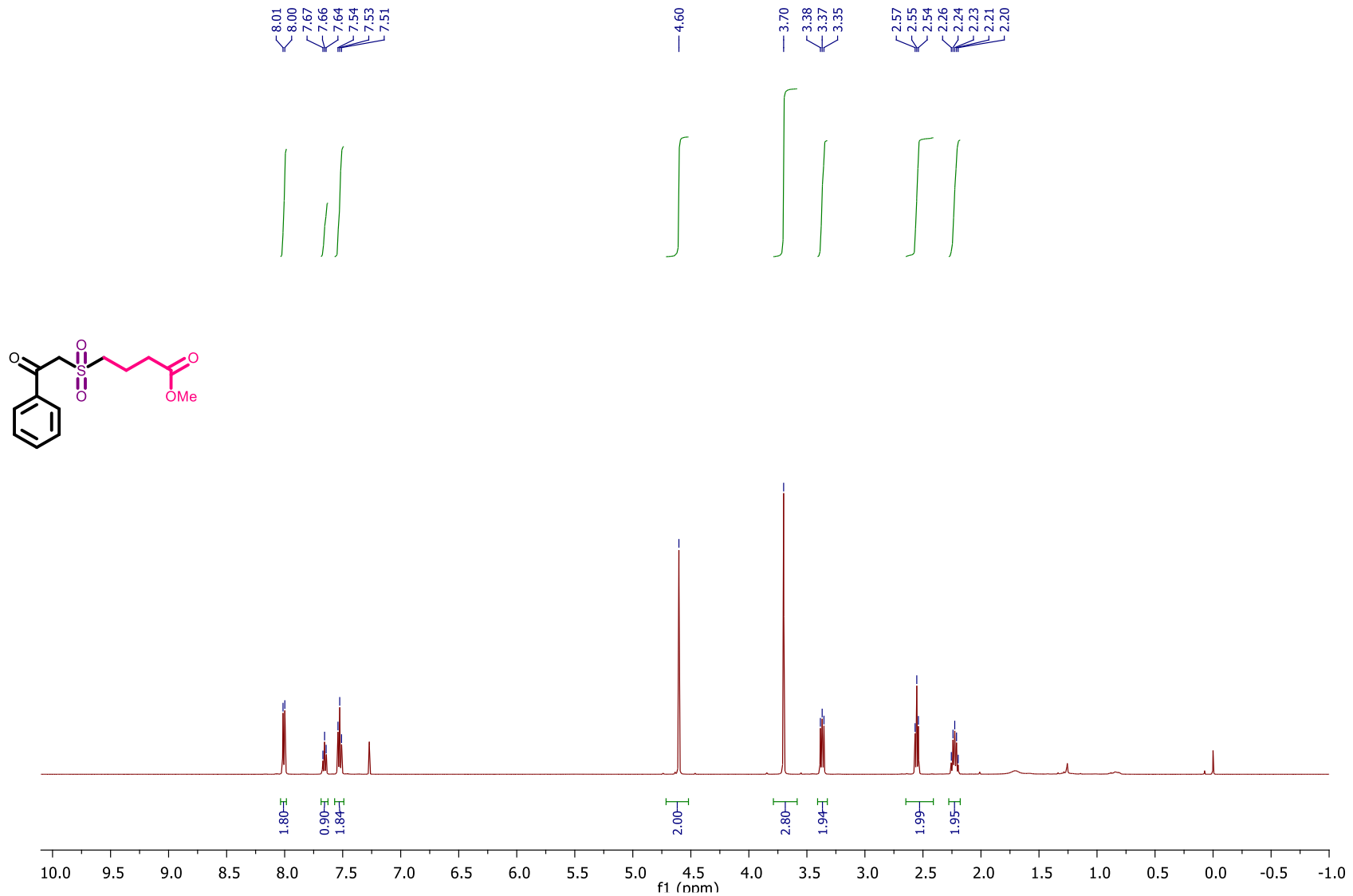
$^{1}$H NMR (400 MHz, $CDCl_3$) Spectrum of Compound **(8)**



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



$^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of Compound **(9)**



$^{13}$C NMR (126 MHz, $CDCl_3$) Spectrum of Compound **(9)**