Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Blue-light Induced Iron-Catalyzed Chemoselective α-Alkylation and α-Olefination of Arylacetonitriles with Alcohols

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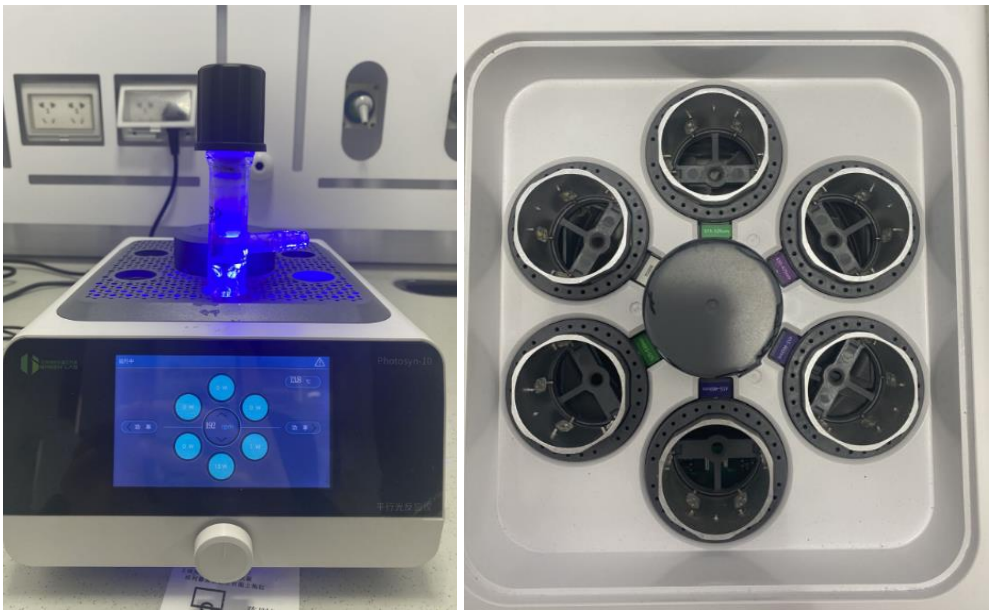
1. General information

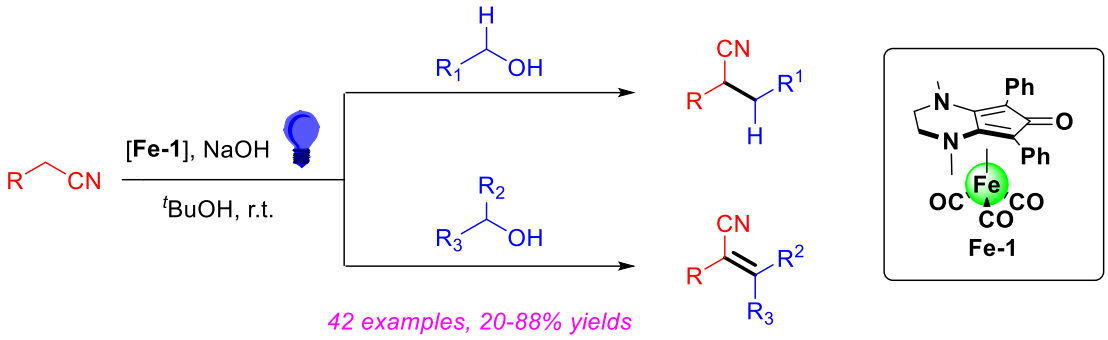
NMR spectra were recorded with tetramethylsilane (TMS) as the internal standard. ^{1}H NMR spectra were recorded at 400 MHz, ^{13}C NMR spectra were recorded at 100 MHz and ^{19}F NMR (376 MHz) spectra were recorded at 376 MHz on Bruker AV ANCE II instruments. ^{1}H NMR chemical shifts (δ) are reported in ppm relative to tetramethylsilane (TMS) with the solvent signal as the internal standard ($CDCl_3$ at 7.26 ppm). ^{13}C NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.16 ppm). Data are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (double of doublet) or m (multiplets), coupling constants (Hz) and integration. High resolution mass spectra were obtained with the Q-TOF-Premier mass spectrometer (Agilent 1200HPLC-6210TOFMS). Reactions were monitored by TLC and visualized with ultraviolet light. All the solvents were used directly without any purification.

The photocatalysed reactions were carried out in an Photosyn-10 irradiated with (1) a 0-18 W Diall Blue LED lamp (455- 460 nm); (2) a 0-18 W Diall purple LED lamp (430 - 435 nm); (3) a 0-18 W Diall green LED lamp (515 - 525 nm or 525 – 530 nm); (4) a 0-18 W Diall white LED lamp (5500 K).

Experimental setup for the photocatalytic reactions:



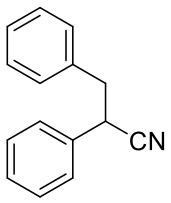
2. General Procedure for the Synthesis of α- alkylation/olefinated of nitrile



To a mixture of **Fe-1** catalyst (2.5 mol %), NaOH (0.4 eq.), nitriles (0.5 mmol) and primary/ secondary alcohol (0.75 mmol), 1.0 mL of ^{t}BuOH was added. Then, the reaction was stirred under Ar in a pressure tube (ACE pressure tube, 15 mL). The mixture was stirred at room temperature and exposed to blue light for 12 hours. The reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layers were washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1-10:1) to give the desired product α- alkylation/olefinated of nitrile.

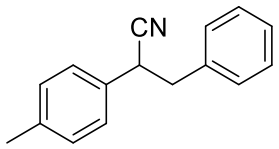
3.Spectra data of products

2,3-Diphenylpropanenitrile (3a):



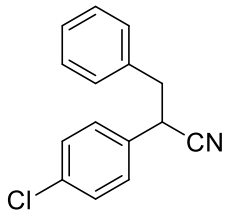
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 88 mg, 85% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.42 – 7.35 (m, 3H), 7.34 – 7.28 (m, 5H), 7.19 – 7.15 (m, 2H), 4.03 (dd, J = 8.5, 6.4 Hz, 1H), 3.26 – 3.13 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.3, 135.3, 129.2, 129.0, 128.7, 128.2, 127.5, 127.4, 120.4, 42.2, 39.8.; HRMS-ESI (m/z): calcd for $C_{15}H_{13}N$ $[M+H]^+$ 208.1121, found 208.1023.

3-Phenyl-2-(*p*-tolyl) propanenitrile (3b):



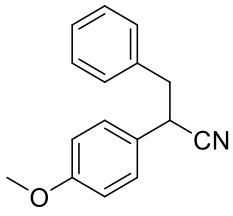
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 92 mg, 83% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.31 – 7.35 （m, 3H）, 7.19 – 7.24 (m, 6H), 3.99 – 4.03 (dd, *J* = 6.4, 6.4 Hz, 1H), 3.16 – 3.21 (m, 2H), 2.4 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 138.0, 163.5, 132.3, 129.8, 129.7, 129.3, 129.1, 128.6, 128.3, 127.8, 127.4, 127.4, 120.6, 42.2, 39.4, 21.1.; HRMS-ESI (m/z): calcd for $C_{16}H_{16}N$ $[M+H]^+$ 222.1277, found 222.1280.

2-(4-Chlorophenyl)-3-phenylpropanenitrile (3c):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 100 mg, 83% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.34 – 7.25 (m, 5H), 7.19 – 7.14 (m, 2H), 7.10 (dd, *J* = 7.2, 2.0 Hz, 2H), 4.01 – 3.96 (m, 1H), 3.22 – 3.06 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.8, 134.2, 133.6, 129.3, 129.2, 128.9, 128.7, 127.6, 120.0, 42.0, 39.2; HRMS-ESI (m/z): calcd for $C_{15}H_{13}ClN$ $[M+H]^+$ 242.0731, found 242.0728.

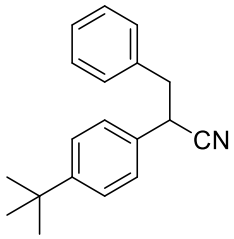
2-(4-Methoxyphenyl)-3-phenylpropanenitrile (3d):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 104 mg, 88% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.31 – 7.23 (m, 3H), 7.18 – 7.10 (m, 4H), 6.88 – 6.84 (m, 2H), 3.94 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.79 (s, 3H), 3.12 (qd, *J* = 13.6, 7.2 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.4, 136.4, 129.3,

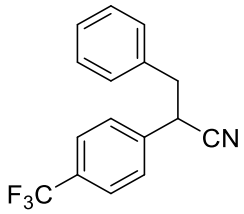
128.7, 128.6, 127.4, 127.2, 120.7, 114.4, 55.4, 42.3, 39.0.; HRMS-ESI (m/z): calcd for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1226, found 238.1225.

2-(4-(Tert-butyl) phenyl)-3-phenylpropanenitrile (3e):



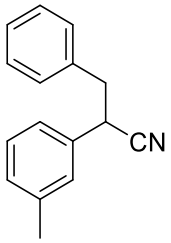
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 105 mg, 80% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.41 – 7.36 (m, 2H), 7.30 (dq, *J* = 6.8, 5.6, 5.2 Hz, 3H), 7.25 – 7.17 (m, 4H), 3.97 (dd, *J* = 8.8, 6.4 Hz, 1H), 3.20 – 3.08 (m, 2H), 1.32 (s, 9H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 151.3, 136.6, 132.3, 129.2, 128.7, 127.4, 127.1, 126.0, 120.6, 42.3, 39.5, 34.6, 31.3.; HRMS-ESI (m/z): calcd for $C_{19}H_{22}N$ $[M+H]^+$ 264.1747, found 264.1743.

3-Phenyl-2-(4-(trifluoromethyl) phenyl) propanenitrile (3f):



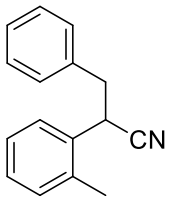
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 28 mg, 20% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.65 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.18 – 7.13 (m, 2H), 4.11 (dd, *J* = 8.0, 6.4 Hz, 1H), 3.30 – 3.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 139.1 (d, *J* = 1.5 Hz), 135.6, 130.6 (q, *J* = 32.8 Hz), 129.2, 128.8, 127.7, 126.0 (q, *J* = 3.8 Hz), 123.82(d, *J* = 272.3 Hz), 119.7, 41.9, 39.6.; HRMS-ESI (m/z): calcd for $C_{16}H_{13}F_3N$ $[M+H]^+$ 276.0995, found 276.0990.

3-Phenyl-2-(*m*-tolyl) propanenitrile (3g):



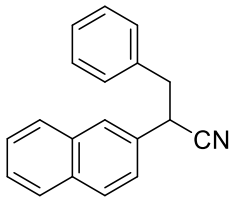
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 88 mg, 80% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.44 – 7.31 (m, 4H), 7.27 – 7.18 (m, 4H), 7.14 (dt, *J* = 7.6, 1.6 Hz, 1H), 4.02 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.21 (t, *J* = 7.2 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.9, 136.6, 135.3, 129.3, 129.0, 129.0, 128.7, 128.2, 127.5, 124.6, 120.6, 42.3, 39.9, 21.5; HRMS-ESI (m/z): calcd for $C_{16}H_{16}N$ $[M+H]^+$ 222.1277 found 222.1270.

3-Phenyl-2-(*o*-tolyl) propanenitrile (3h):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 83 mg, 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.54 – 7.47 (m, 1H), 7.41 – 7.34 (m, 3H), 7.33 – 7.28 (m, 2H), 7.27 – 7.20 (m, 3H), 4.21 (dd, *J* = 8.8, 6.0 Hz, 1H), 3.25 – 3.10 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.6, 135.1, 133.8, 131.0, 129.2, 128.8, 128.4, 127.7, 127.5, 127.0, 120.9, 41.0, 36.7, 19.1; HRMS-ESI (m/z): calcd for $C_{16}H_{16}N$ $[M+H]^+$ 222.1277 found 222.1262.

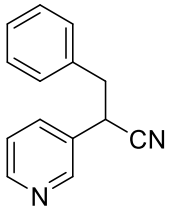
2-(Naphthalen-2-yl)-3-phenylpropanenitrile (3i):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 100 mg, 78% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.92 – 7.81 (m, 3H), 7.77 (d, *J* = 1.8 Hz, 1H), 7.55 (dt, *J* = 6.4, 3.6 Hz, 2H), 7.39 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.23 – 7.17 (m, 2H), 4.20 (dd, *J* = 8.0, 6.4 Hz, 1H), 3.37 – 3.20 (m,

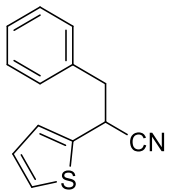
2H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.3, 133.2, 132.9, 132.5, 129.28, 129.0, 128.7, 127.9, 127.8, 127.46, 126.7, 126.7, 126.6, 125.0, 120.4, 42.2, 40.0.; HRMS-ESI (m/z): calcd for $C_{19}H_{16}N$ $[M+H]^+$ 258.1277, found 258.1282.

3-Phenyl-2-(pyridin-3-yl) propanenitrile (3j):



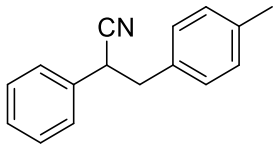
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:10) mixture as eluent. Colorless oil; 68 mg, 65% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.58 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.46 (d, *J* = 2.4 Hz, 1H), 7.57 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.28 (dqt, *J* = 4.0, 2.8, 1.6 Hz, 4H), 7.14 – 7.05 (m, 2H), 4.06 (dd, *J* = 8.0, 6.8 Hz, 1H), 3.25 – 3.09 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 149.7, 148.8, 135.4, 135.1, 131.0, 129.3, 128.8, 127.7, 123.8, 119.5, 41.8, 37.2.; HRMS-ESI (m/z): calcd for $C_{14}H_{13}N_2$ $[M+H]^+$ 209.1073, found 209.1079.

3-Phenyl-2-(thiophen-2-yl) propanenitrile (3k):



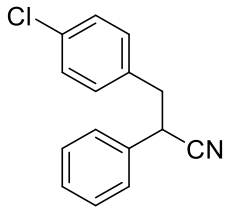
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:10) mixture as eluent. Colorless oil; 64 mg, 60% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.34 – 7.26 (m, 4H), 7.17 – 7.12 (m, 3H), 6.98 (dd, *J* = 5.2, 1.2 Hz, 1H), 4.11 (t, *J* = 7.2 Hz, 1H), 3.16 (dd, *J* = 7.2, 2.0 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.3, 135.1, 129.2, 128.7, 127.5, 127.1, 126.4, 123.0, 120.2, 41.1, 35.0.; HRMS-ESI (m/z): calcd for $C_{13}H_{12}NS$ $[M+H]^+$ 214.0685, found 214.0680.

2-Phenyl-3-(*p*-tolyl) propanenitrile (3l):



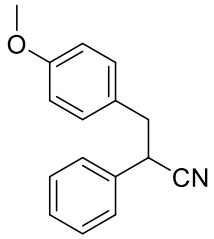
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 81 mg, 73% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.33 – 7.42 (m, 3H), 7.17 – 7.19 (d, *J* = 8Hz, 2H), 7.10 – 7.12 (d, *J* = 4Hz, 2H), 4.04 (dd, *J* = 5.6, 6.4 Hz, 1H), 3.16 – 3.20 (m, 2H), 2.40 (s,3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 137.0, 135.5, 133.4, 129.4, 129.2, 129.1, 128.2, 127.6, 120.5, 41.8, 39.9, 21.1. HRMS-ESI (m/z): calcd for $C_{16}H_{16}N$ $[M+H]^+$ 222.1277, found 222.1279.

3-(4-Chlorophenyl)-2-phenylpropanenitrile (3m):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 88 mg, 73% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38 (qt, *J* = 5.2, 2.0 Hz, 3H), 7.31 – 7.25 (m, 4H), 7.09 – 7.04 (m, 2H), 4.01 (dd, *J* = 8.0, 6.4 Hz, 1H), 3.22 – 3.11 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 134.7, 134.6, 133.4, 130.7, 129.1, 128.8, 128.4, 127.5, 120.1, 41.5, 39.6.; HRMS-ESI (m/z): calcd for $C_{16}H_{16}N$ $[M+H]^+$ 242.0731 found 242.0730.

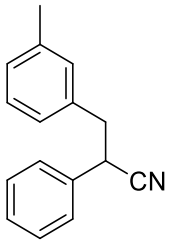
3-(4-Methoxyphenyl)-2-phenylpropanenitrile (3n):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 95 mg, 80% yield, ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.40 – 7.34 (m, 3H), 7.30 (d, J = 6.6 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.02 – 3.99 (m, 1H), 3.81 (s, 3H), 3.18 – 3.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 158.9, 135.3, 130.4,

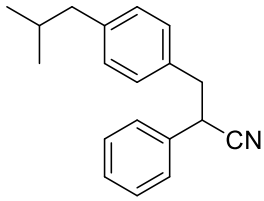
129.0, 128.4, 128.2, 127.6, 120.6, 114.0, 55.3, 41.4, 40.1.; HRMS-ESI (m/z): calcd for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1226, found 238.1229.

2-Phenyl-3-(*m*-tolyl) propanenitrile (3o):



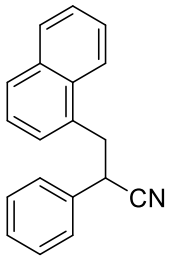
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 89 mg, 80% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ7.49 – 7.37 (m, 3H), 7.36 – 7.30 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.05 – 6.92 (m, 2H), 4.03 (dd, *J* = 8.6, 6.3 Hz, 1H), 3.17 (qd, *J* = 13.6, 7.5 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 138.3, 136.3, 135.4, 130.0, 129.1, 128.6, 128.2, 128.2, 127.5, 126.3, 120.5, 42.3, 39.9, 21.4; HRMS-ESI (m/z): calcd for $C_{16}H_{16}N$ $[M+H]^+$ 222.1277 found 222.1272.

3-(4-Isobutylphenyl)-2-phenylpropanenitrile (3p):



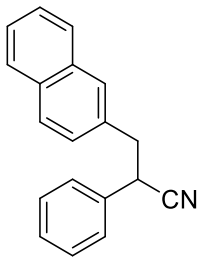
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 103 mg, 78% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38 (tdt, *J* = 7.2, 5.2, 1.8 Hz, 3H), 7.30 (dd, *J* = 7.8, 1.8 Hz, 2H), 7.15 – 7.07 (m, 4H), 4.02 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.17 (qd, *J* = 13.6, 7.2 Hz, 2H), 2.49 (d, *J* = 7.2 Hz, 2H), 1.88 (dh, *J* = 13.6, 6.8 Hz, 1H), 0.94 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 140.9, 135.4, 133.6, 129.4, 129.0, 129.0, 128.2, 127.5, 120.6, 45.1, 42.0, 40.0, 30.3, 22.4; HRMS-ESI (m/z): calcd for $C_{19}H_{22}N$ $[M+H]^+$ 264.1747 found 264.1759.

3-(Naphthalen-1-yl)-2-phenylpropanenitrile (3q):



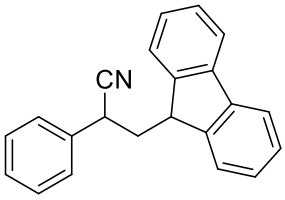
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 96 mg, 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.01 – 7.93 (m, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.59 (dddd, *J* = 17.2, 8.0, 6.8, 1.2 Hz, 2H), 7.47 – 7.34 (m, 7H), 4.21 (dd, *J* = 8.8, 6.8 Hz, 1H), 3.74 – 3.61 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.7, 134.0, 132.3, 131.3, 129.3, 129.2, 128.4, 128.4, 128.2, 127.4, 126.6, 125.9, 125.6, 122.7, 120.6, 39.6, 38.9.; HRMS-ESI (m/z): calcd for $C_{19}H_{16}N$ $[M+H]^+$ 258.1277, found 258.1279.

3-(Naphthalen-2-yl)-2-phenylpropanenitrile (3r):



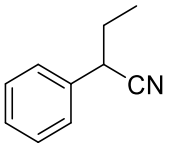
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 96 mg, 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.83 (dddd, *J* = 15.2, 6.8, 4.8 2.4 Hz, 3H), 7.64 (s, 1H), 7.50 (dt, *J* = 7.2, 2.4 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.32 (dt, *J* = 7.2, 1.6 Hz, 2H), 7.29 – 7.25 (m, 1H), 4.13 (dd, *J* = 8.4, 6.4 Hz, 1H), 3.36 (qd, *J* = 13.6, 7.6 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.2, 133.8, 133.4, 132.6, 129.1, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 127.2, 126.3, 126.0, 120.5, 42.4, 39.8.; HRMS-ESI (m/z): calcd for $C_{19}H_{16}N$ $[M+H]^+$ 258.1277, found 258.1272.

3-(9H-fluoren-9-yl)-2-phenylpropanenitrile (3s):



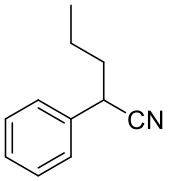
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 109 mg, 74% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.79 – 7.86 (m, 2H), 7.69 – 7.71 (d, *J* = 8.0Hz, 1H), 7.48 – 7.52 (t, *J* = 7.6Hz, 1H), 7.37 – 7.45 (m, 5H), 7.26 – 7.34 (m, 4H), 4.26 (dd, *J* = 6.4, 6.4Hz, 1H), 3.88 – 3.92 (m, 1H), 2.76 – 2.83 (m, 1H), 2.21 – 2.28 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 145.6, 145.0, 141.4, 141.0, 136.1, 129.2, 129.2, 128.2, 128.0, 128.0, 127.7, 127.3, 127.3, 127.3, 125.0, 124.2, 120.6, 120.4, 120.2, 45.6, 40.2, 35.0. HRMS-ESI (m/z): calcd for $C_{22}H_{18}N$ $[M+H]^+$ 296.1434 found 296.1436.

2-Phenylbutanenitrile (3t):



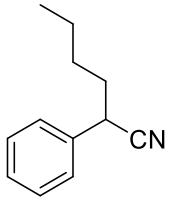
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 61 mg, 85% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43 – 7.38 (m, 2H), 7.38 – 7.32 (m, 3H), 3.81 (dd, *J* = 8.8, 6.4 Hz, 1H), 2.00 – 1.80 (m, 2H), 1.59 – 1.47 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 135.8, 129.0, 128.0, 127.3, 120.7, 38.9, 29.2, 11.5.; HRMS-ESI (m/z): calcd for $C_{10}H_{12}N$ $[M+H]^+$ 146.0964, found 146.0970.

2-Phenylpentanenitrile (3u):



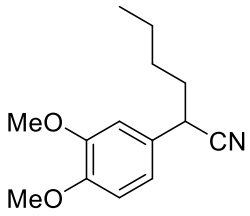
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 63 mg, 80% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.30 – 7.25 (m, 2H), 7.24 – 7.19 (m, 3H), 3.68 (dd, *J* = 8.8, 6.4 Hz, 1H), 1.86 – 1.66 (m, 2H), 1.41 (dddd, *J* = 11.6, 10.0, 7.2, 6.0 Hz, 2H), 0.86 (t, *J* = 7.2 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.1, 129.1, 128.0, 127.3, 120.9, 37.9, 37.2, 20.3, 13.4.; HRMS-ESI (m/z): calcd for $C_{11}H_{14}N$ $[M+H]^+$ 160.1121, found 160.1128.

2-Phenylhexanenitrile (3v):



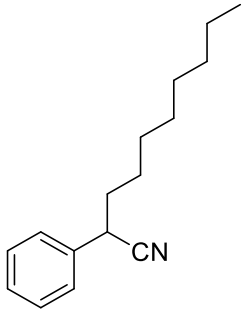
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 71 mg, 82% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.43 – 7.38 (m, 2H), 7.37 – 7.33 (m, 3H), 3.79 (dd, *J* = 8.6, 6.3 Hz, 1H), 2.01 – 1.85 (m, 2H), 1.52 – 1.33 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.1, 129.0, 128.0, 127.2, 120.9, 37.4, 35.6, 29.1, 22.1, 13.8.; HRMS-ESI (m/z): calcd for $C_{12}H_{16}N$ $[M+H]^+$ 174.1277, found 174.1280.

2-(3,4-Dimethoxyphenyl) hexanenitrile (3w):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 88 mg, 76% yield, ^{1}H NMR (400 MHz, CDCl3, ppm) δ 6.86 (d, J = 2.0 Hz, 2H), 6.82 (d, J = 1.6 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.72 (dd, J = 8.4, 6.4 Hz, 1H), 1.94 – 1.81 (m, 2H), 1.49 – 1.31 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H).; ^{13}C NMR (100 MHz, CDCl3, ppm) δ 149.4, 148.8, 128.5, 121.1, 119.6, 111.5, 110.3, 56.0, 55.9, 36.9, 35.6, 29.1, 22.0, 13.8.8.; HRMS-ESI (m/z): calcd for C14H20NO2 [M+H]+ 234.1489, found 234.1495.

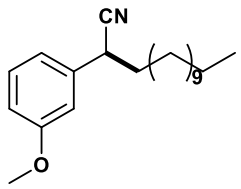
2-Phenyldecanenitrile (3x):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 85 mg, 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.44

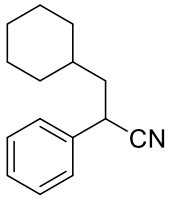
– 7.38 (m, 2H), 7.38 – 7.29 (m, 3H), 3.79 (dd, *J* = 8.6, 6.3 Hz, 1H), 1.99 – 1.84 (m, 2H), 1.56 – 1.45 (m, 2H), 1.38 – 1.25 (m, 10H), 0.91 (t, *J* = 6.8 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 136.1, 129.0, 128.0, 127.2, 120.9, 37.4, 35.9, 31.8, 29.3, 29.1, 23.0, 27.0, 22.6, 14.1.; HRMS-ESI (m/z): calcd for $C_{16}H_{24}N$ $[M+H]^+$ 230.1903, found 230.1909.

2-(3-Methoxyphenyl) tetradecanenitrile (3y):



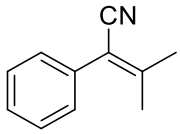
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 114 mg, 72%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.19 – 7.15 (m, 1H), 6.80 – 6.72 (m, 3H), 3.71 (s, 3H), 3.64 – 3.60 (m, 1H), 1.82 – 1.69 (m, 2H), 1.39 – 1.35 (m, 2H), 1.14 (s, 18H), 0.77 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 160.0, 137.6, 130.1, 120.9, 119.5, 113.3, 113.1, 55.3, 37.4, 35.8, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.0, 27.1, 22.7, 14.1. HRMS (ESI) m/z: calcd for $C_{21}H_{34}NO$ $[M+H]^+$: 316.2635, found: 316.2641.

2-Cyclohexyl-2-phenylacetonitrile (3z):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless oil; 81 mg, 76% yield, ^{1}H NMR (600 MHz, $CDCl_3$, ppm): δ 7.31 – 7.28 (m, 2H), 7.24 (d, J = 6.0 Hz, 3H), 3.78 – 3.75 (m, 1H), 1.83 – 1.74 (m, 2H), 1.65 – 1.55 (m, 5H), 1.47 – 1.43 (m, 1H), 1.23 – 1.16 (m, 2H), 1.12 – 1.07 (m, 1H), 0.93 – 0.84 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, ppm): δ 136.5, 129.1, 128.0, 127.2, 121.1, 43.7, 35.3, 34.8, 33.3, 32.4, 26.3, 26.0, 25.9.; HRMS-ESI (m/z): calcd for $C_{15}H_{20}N$ [M+H]+ 214.1590, found 214.1585.

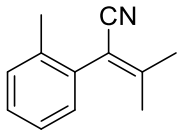
3-Methyl-2-phenylbut-2-enenitrile (5a):



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 51 mg, 65%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.43

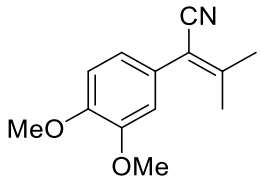
– 7.28 (m, 5H), 2.28 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 155.6, 136.8, 133.4, 130.5, 129.9, 128.7, 126.2, 118.1, 110.0, 24.0, 21.3, 19.5. HRMS-ESI (m/z): calcd for $C_{11}H_{12}N$ $[M+H]^+$: 158.0964, found: 158.0966.

3-Methyl-2-(o-tolyl) but-2-enenitrile (5b) :



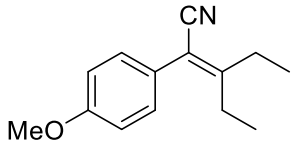
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 52 mg, 61%. ^{1}H NMR (400 MHz, CDCl3, ppm): δ 7.28 – 7.20 (m, 3H), 7.11 (d, J = 7.2 Hz, 1H), 2.29 (d, J = 8.4 Hz, 6H), 1.72 (s, 3H). 13C NMR (100 MHz, CDCl3, ppm): δ 155.6, 136.8, 133.4, 130.5, 129.9, 128.7, 126.2, 118.1, 110.0, 24.1, 21.3, 19.5. HRMS-ESI (m/z): calcd for $C_{12}H_{18}NO$ $[M+H]^+$: 172.1126, found: 172.1124.

2-(3,4-Dimethoxyphenyl)-3-methylbut-2-enenitrile (5c) :



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:10) mixture as eluent. Colorless liquid. Yield: 65 mg, 60%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.82 – 6.74 (m, 3H), 3.81 (d, J = 2.0 Hz, 6H), 2.16 (s, 3H), 1.85 (s, 3H).^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.0, 148.9, 148.8, 126.6, 121.8, 118.9, 112.0, 111.0, 110.5, 55.9, 55.8, 24.8, 21.6. HRMS-ESI (m/z): calcd for $C_{13}H_{16}NO_2$ $[M+H]^+$: 218.1176, found: 218.1181.

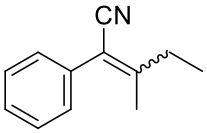
3-Ethyl-2-(4-methoxyphenyl)pent-2-enenitrile (5d) :



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:10) mixture as eluent. Colorless liquid. Yield: 61 mg, 56%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.24 – 7.21 (m, 2H), 6.94 – 6.92 (m, 2H), 3.85 (s, 3H), 2.60 (q, *J* = 7.6 Hz, 2H), 2.26 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H), 1.05 (t, *J* = 7.6 Hz, 3H).^{13}C NMR (100 MHz,

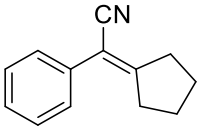
$CDCl_3$, ppm): δ 164.8, 159.4, 130.2, 126.5, 118.9, 114.1, 109.8, 55.3, 28.2, 24.6, 12.9, 12.6. HRMS-ESI (m/z): calcd for $C_{14}H_{18}NO$ $[M+H]^+$: 216.1383, found: 216.1377.

3-Methyl-2-phenylpent-2-enenitrile (5e) :



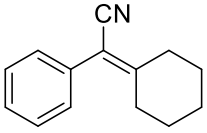
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:40) mixture as eluent. Colorless liquid (Z/E = 52:48). Yield: 43 mg, 50%.^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.42 – 7.28 (m, 5H), 2.62 (q, *J* = 7.6 Hz, 1H), 2.23 (d, *J* = 7.6 Hz, 2H), 1.91 (s, 1H), 1.22 (d, *J* = 7.6 Hz, 1H), 1.07 (t, *J* = 7.6 Hz, 1H) .^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 159.9, 134.2, 134.1, 129.1, 128.9, 128.7, 128.6, 128.3, 128.2, 118.9, 118.6, 110.7, 110.2, 31.8, 27.5, 21.8, 19.1, 12.6, 12.4. HRMS-ESI (m/z): calcd for $C_{12}H_{13}N$ $[M+H]^+$: 172.1048, found: 172.1053.

2-Cyclopentylidene-2-phenylacetonitrile (5f) :



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 72 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm):δ 7.45 – 7.40 (m, 4H), 7.35 – 7.33 (m, 1H), 2.84 (t, J = 4.8 Hz, 2H), 2.63 – 2.61 (m, 2H), 1.89 – 1.81 (m, 4H).^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 167.0, 134.3, 128.9, 128.6, 128.0, 127.9, 127.6, 118.7, 35.9, 33.9, 27.0, 25.5. HRMS-ESI (m/z): calcd for $C_{13}H_{14}N$ $[M+H]^+$: 184.1121, found: 184.1128.

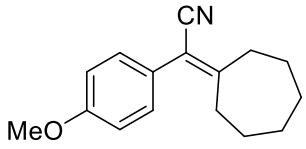
2-Cyclohexylidene-2-phenylacetonitrile (5g) :



Colorless liquid. Yield: 81 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.35 – 7.43 (m, 3H), 7.28 – 7.32 (m, 2H), 2.71 (t, *J* = 6.4Hz, 2H), 2.34 (t, *J* = 6.4Hz, 2H), 1.78 – 1.82 (m, 2H), 1.61 – 1.70 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.0, 133.9, 129.3, 128.7, 128.2,

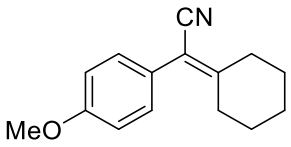
35.4, 31.3, 28.1, 28.0, 25.9. HRMS-ESI (m/z): calcd for $C_{14}H_{16}N$ $[M+H]^+$: 198.1277, found: 198.1280.

2-Cycloheptylidene-2-(4-methoxyphenyl)acetonitrile (5h) :



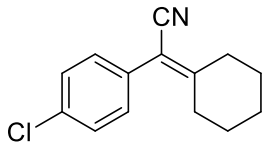
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 94 mg, 78%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.21 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 2.79 – 2.76 (m, 2H), 2.43 – 2.40 (m, 2H), 1.82 – 1.76 (m, 2H), 1.65 – 1.58 (m, 4H), 1.54 – 1.49 (m, 2H).^{13}C NMR (100 MHz, $CDCl_3$, ppm):δ 163.7, 159.4, 130.3, 129.0, 126.7, 119.0, 114.2, 114.0, 110.0, 55.3, 36.1, 32.8, 29.6, 28.8, 27.3, 27.0. HRMS-ESI (m/z): calcd for $C_{16}H_{20}NO$ $[M+H]^+$: 242.1539, found: 242.1545.

2-Cyclohexylidene-2-(4-methoxyphenyl) acetonitrile (5i) :



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 97 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.20 – 7.23 (m, 2H), 6.92 – 6.94 (m, 2H), 3.84 (s, 3H), 2.67 – 2.70 (m, 2H), 2.32 – 3.35 (m, 2H), 1.77 – 1.81 (m, 2H), 1.60 – 1.66 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.1, 159.4, 130.5, 126.2, 118.9, 114.0, 107.3, 55.3, 35.3, 31.2, 28.1, 27.9, 26.0. HRMS-ESI (m/z): calcd for $C_{15}H_{18}NO$ $[M+H]^+$: 228.1383, found: 228.1384.

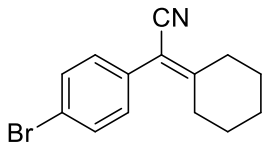
2-(4-Chlorophenyl)-2-cyclohexylideneacetonitrile (5j) :



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 99 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.23 – 7.40 (m, 4H), 2.68 – 2.72 (t, *J* = 6.0Hz, 2H), 2.30-2.33 (t, *J* = 5.6Hz, 2H), 1.79 – 1.82 (t, *J* = 6.0Hz, 2H), 1.66 – 1.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.7, 134.3, 132.3, 130.6,

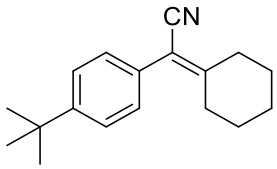
128.9, 118.3, 106.7, 35.4, 31.3, 28.1, 27.9, 25.8. HRMS-ESI (m/z): calcd for $C_{15}H_{15}ClN$ $[M+H]^+$: 232.0888, found: 232.0885.

2-(4-Bromophenyl)-2-cyclohexylideneacetonitrile (5k) :



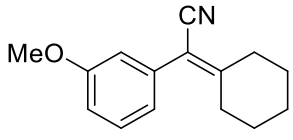
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 113 mg, 82%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.63 – 2.60 (m, 2H), 2.24 – 2.21 (m, 2H), 1.75 – 1.69 (m, 2H), 1.61 – 1.49 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.7, 132.8, 131.9, 130.9, 122.4, 118.2, 106.8, 35.4, 31.3, 28.1, 27.9, 25.8. HRMS (ESI) m/z caled for $C_{14}H_{14}BrN$ $[M+H]^+$: 277.1770, found: 277.1774.

2-(4-(Tert-butyl) phenyl)-2-cyclohexylideneacetonitrile (5l) :



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 95 mg, 75%. 1H NMR (400 MHz, CDCl3, ppm): δ 7.41 - 7.43 (m, 2H), 7.23 – 7.25（m, 2H）, 2.69 – 2.72 (t, *J* = 6.0Hz, 2H), 2.35 – 2.38 (t, *J* = 6.0Hz, 2H), 1.79 – 1.82 (t, *J* = 6.0Hz, 2H), 1.63 – 1.67 (m, 4H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.4, 151.2, 130.9, 128.9, 127.7, 126.1, 125.6, 118.9, 107.6, 35.4, 34.7, 31.3, 31.3, 28.1, 28.0. 26.0. HRMS-ESI (m/z): calcd for $C_{18}H_{24}N$ $[M+H]^+$: 254.1903, found: 254.1905.

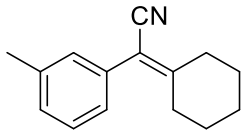
2-Cyclohexylidene-2-(3-methoxyphenyl) acetonitrile (5m) :



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 93 mg, 82%. 1H NMR (400 MHz, CDCl3, ppm): δ 7.28 – 7.32 (m, 2H), 6.83 – 6.91（m, 2H）, 3.84 (s, 3H), 2.70 (t, *J* = 5.6Hz, 2H), 2.35 (t, *J* = 4.8Hz, 2H), 1.78 – 1.82 (m, 2H), 1.61 – 1.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.1,

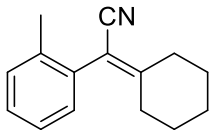
159.4, 130.5, 126.2, 118.9, 114.0, 107.2, 55.3, 35.3, 35.3, 31.2，28.1, 27.9, 26.0. HRMS-ESI (m/z): calcd for $C_{15}H_{18}N$ $[M+H]^+$: 228.1383, found: 212.1387.

2-Cyclohexylidene-2-(*m*-tolyl) acetonitrile (5n) :



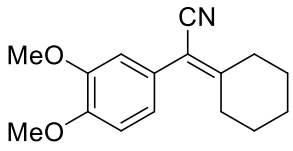
Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 83 mg, 78%. ^{1}H NMR (400 MHz, CDCl3, ppm): δ 7.27 – 7.31 (m, 1H), 7.07 – 7.17 (m, 3H), 2.69 – 2.72 (t, J = 6.4Hz, 2H), 2.39 (s, 3H), 2.33 – 2.36 (t, *J* = 6.4 Hz, 2H), 1.79 – 1.82 (t, *J* = 6.4Hz, 2H), 1.60 – 1.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.7, 138.4, 133.8, 129.8, 128.9, 128.5, 126.4, 118.8, 107.8, 35.4, 31.3, 38.1, 27.9, 25.9, 21.4. HRMS-ESI (m/z): calcd for $C_{15}H_{18}N$ $[M+H]^+$: 212.1434, found: 212.1437.

2-Cyclohexylidene-2-(*o*-tolyl) acetonitrile (5o) :



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 80 mg, 75%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.19 – 7.28 (m, 3H), 7.10 – 7.12 (d, *J* = 5.4Hz, 1H), 2.70 – 2.73 (t, *J* = 6.0Hz, 2H), 2.32 (s, 3H), 2.07 – 2.09 (t, *J* = 7.2Hz, 2H), 1.79 – 1.82 (t, *J* = 6.4Hz, 2H), 1.62 – 1.67 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.7, 136.9, 133.1, 130.5, 130.0, 128.7, 126.1, 117.9, 34.6, 31.3, 28.2, 27.8, 25.9, 19.6. HRMS-ESI (m/z): calcd for $C_{15}H_{18}N$ $[M+H]^+$: 213.1434, found: 213.1440.

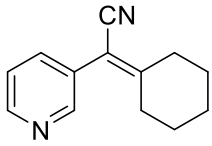
2-Cyclohexylidene-2-(3,4-dimethylphenyl) acetonitrile (5p) :



Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 103 mg, 80%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 6.81 – 6.90 (m, 3H), 3.91 (s, 6H), 2.67 – 2.71 (t, *J* = 6.4Hz, 2H), 2.34 – 2.37 (t, *J* = 6.0Hz, 2H), 1.78 – 1.81 (t, *J* = 6.0Hz, 2H), 1.59 – 1.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.4,

149.0, 148.9, 126.4, 121.9, 118.8, 112.2, 111.0, 107.4, 56.0, 55.9, 35.3, 31.4, 28.1, 28.0, 25.9. HRMS-ESI (m/z): calcd for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1489, found: 258.1492.

2-Cyclohexylidene-2-(pyridin-3-yl)acetonitrile (5q) :

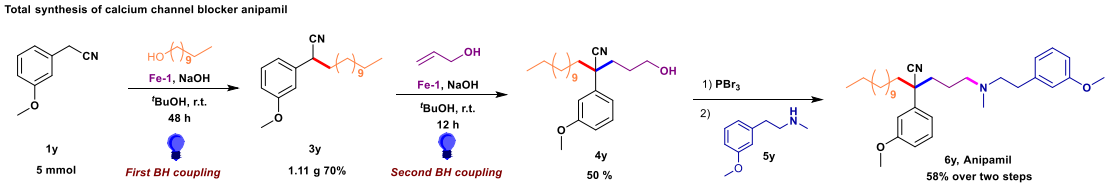


Purified by silica-gel column chromatography using ethyl acetate/hexane (1:20) mixture as eluent. Colorless liquid. Yield: 68 mg, 69%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.50 (d, *J* = 22.5 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.28 (m, 1H), 2.67 – 2.63 (m, 2H), 2.27 – 2.22 (m, 2H), 1.74 (q, *J* = 5.6 Hz, 2H), 1.63 – 1.52 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ164.4, 149.9, 149.2, 136.8, 130.1, 123.6, 117.9, 104.4, 35.5, 31.4, 28.1, 28.0, 25.8. HRMS-ESI (m/z): calcd for $C_{13}H_{15}N_2$ $[M+H]^+$: 199.1230, found: 199.1244.

4. General Procedure for the Synthesis of Biologically Active Molecules

General Procedure for the Synthesis of Anipamil

Synthesis of Anipamil (**5y**):



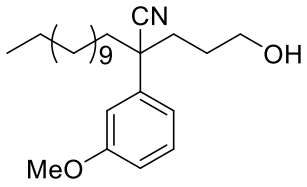
Experimental Procedure for Synthesis of 2-(3-Methoxyphenyl) tetradecanenitrile (3y):

To a mixture of **Fe-1** catalyst (0.125 mmol), NaOH (2.0 mmol), 3-methoxy phenyl acetonitrile (5 mmol) and 1-dodecanol (10 mmol), 10 mL of ^{t}BuOH was added. Then, the reaction was stirred under Ar in a pressure tube (ACE pressure tube, 75 mL). The mixture was stirred at room temperature and exposed to blue light for 48 hours. The reaction was diluted with ethyl acetate and water. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. The combined organic layers were washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1-10:1) to give the desired product **3y** (711 mg, 70% yield).

Experimental Procedure for Synthesis of 2-(3-Hydroxypropyl)-2-(3-methoxyphenyl) tetradecanenitrile (4y):

To a mixture of **Fe-1** catalyst (0.088 mmol), NaOH (1.4 mmol), 2-(3-methoxyphenyl) tetradecanenitrile (**3y**, 3.5 mmol) and allyl alcohol (7 mmol), 7 mL of ^{t}BuOH was added. Then, the reaction was stirred under Ar in a pressure tube (ACE pressure tube, 75 mL). The mixture was stirred at room temperature and exposed to blue light for 24 hours. A Schlenk flask (50 mL) was equipped with a stir bar, Then, the solvent was evaporated, and the resulted residue was purified by silica-gel (100-200 mesh) column chromatography using ethyl acetate/hexane (20:80) mixture as eluent. **4y** was isolated in 501 mg, 50 %.

2-(3-Hydroxypropyl)-2-(3-methoxyphenyl) tetradecanenitrile (4y) :



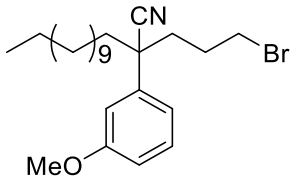
Colorless oil;510 mg 50% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30 (t, *J* = 8.0 Hz, 1H), 7.99 – 6.95 (m, 2H), 6.84 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.83 (s, 3H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.12 – 1.83 (m, 6H), 1.75 – 1.64 (m, 1H), 1.50 – 1.08 (m, 22H), 0.88 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 159.9, 140.1, 129.9, 122.5, 118.2, 112.4, 112.4, 62.1, 55.3, 48.1, 41.2, 37.4, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 28.5, 25.3, 22.7, 14.1. HRMS-ESI (m/z): calcd for $C_{24}H_{40}NO_2$ $[M+H]^+$: 374.3054, found: 374.3059.

Experimental Procedure for Synthesis of Anipamil (6y)[2]:

Step 1: To a round bottom flask, a magnetic stir bar, 2-(3-hydroxypropyl)-2-(3-methoxyphenyl) tetradecanenitrile (**4y**, 0.5 mmol, 1 equiv) and toluene (1 mL) were added under nitrogen atmosphere and cooled to -5 °C. To this solution, PBr_3 (0.6 mmol, 1.1 equiv) was added dropwise and stirred for 30 minutes. The reaction mixture was allowed to warm to room temperature and then heated at 100 °C for 2 h. Upon completion, reaction mixture was cooled to room temperature, poured into ice, and the resulted aqueous solution was extracted using diethyl ether (2 × 10 mL). The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure using a rotavapor, and the residue was used directly in next step.

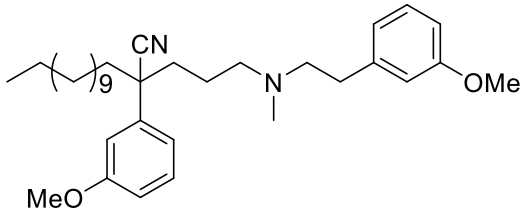
Step two: Residue (above), 2-(3-methoxyphenyl)-*N*-methylethan-1-amine[1] (**5y**, 0.3 mmol, 1 equiv.) and acetonitrile (1 mL) were charged in a round bottom flask. Freshly ground anhydrous Na_2CO_3 (0.9 mmol, 3 equiv.) was added as one portion, and the solution was heated at 80 °C for 6 h. Upon completion of the reaction, the solvent was removed under reduced pressure using a rotavapor, and the residue obtained was dissolved in water (2 mL). The aqueous solution was extracted using ethyl acetate (3 × 10 mL), the combined organic layer washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed, and resulted residue purified by silica gel column chromatography using DCM/MeOH (95:5) mixture as eluent. Yields were calculated for pure isolated products. The aqueous solution was extracted using ethyl acetate (3 × 10 mL), the combined organic layer washed with brine, and dried over anhydrous Na_2SO_4. The solvent was removed, and the resulted residue was purified by silica gel column chromatography using DCM/MeOH (90:10) mixture as eluent. Anipamil (**6y**) was isolated in 151 mg, 58% yield.

2-(3-Bromopropyl)-2-(3-methoxyphenyl) hexanenitrile (5y):



Colorless oil, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.32 (t, *J* = 8.0 Hz, 1H), 7.01 – 6.85 (m, 3H), 3.85 (s, 3H), 3.36 (dd, *J* = 6.7, 5.6 Hz, 2H), 2.18 – 1.85 (m, 5H), 1.70 – 1.64 (m, 1H), 1.52 – 1.12 (m, 20H), 0.90 (t, *J* = 6.8 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.1, 139.7, 130.0, 122.2, 118.1, 112.8, 112.2, 55.3, 47.8, 41.3, 39.5, 32.9, 31.9, 29.6, 29.6, 29.5, 29.4, 29.3, 29.2, 28.4, 25.2, 22.7, 14.1.; HRMS-ESI (m/z): calcd for $C_{24}H_{39}BrNO$ $[M+H]^+$ 436.2210, found 436.2220.

Anipamil (6y):

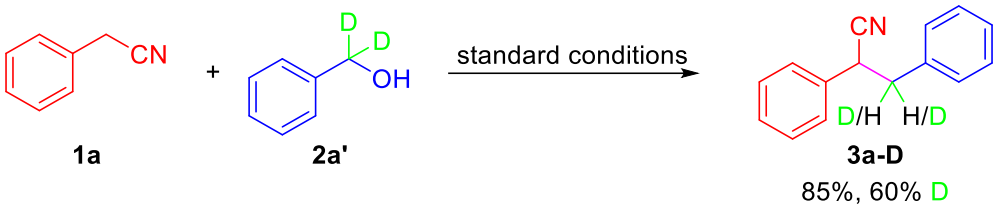


Colorless oil; 529mg 58% yield, ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.32 – 7.28 (m, 1H), 7.23 – 7.19 (m, 1H), 6.98 – 6.96 (m, 2H), 6.88 – 6.75 (m,

4H), 3.82 (d, J = 10.8 Hz, 6H), 2.74 – 2.70 (m, 2H), 2.58 – 2.54 (m, 2H), 2.37 (td, J = 6.8, 2.0 Hz, 2H), 2.23 (s, 3H), 2.99 – 1.90 (m, 4H), 1.70 – 1.46 (m, 2H), 1.26 (dd, J = 11.6, 4.8 Hz, 21H), 0.90 (t, J = 6.8 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.0, 159.7, 142.1, 140.3, 129.9, 129.3, 122.6, 121.1, 118.2, 114.6, 112.5, 111.4, 111.3,59.1, 56.8, 55.3, 55.1, 48.2, 41.9, 41.2, 38.7, 33.7, 31.9, 29.6, 29.6, 29.5, 29.5, 29.3, 29.3, 25.2, 23.0, 22.7, 14.1.; HRMS-ESI (m/z): calcd for $C_{34}H_{53}N_2O_2$ $[M+H]^+$ 521.4102, found 521.4105.

5. Mechanism Studies

Synthesis of Products 3a-D

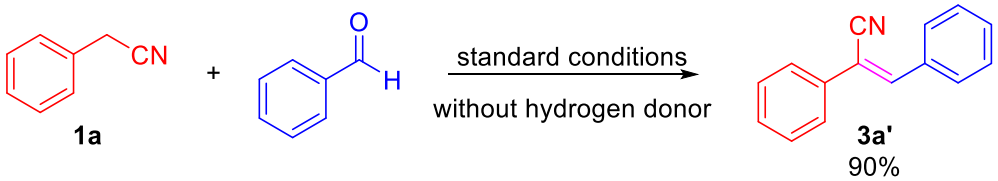


1a **2a'** **3a-D**

85%, 60% D

To a mixture of **Fe-1** catalyst (2.5 mol %), NaOH (0.4 eq.), nitriles **1a** (0.5 mmol) and alcohol **2a'** (0.75 mmol), 1.0 mL of ^{t}BuOH was added. Then, the reaction was stirred under Ar in a pressure tube (ACE pressure tube, 15 mL). The mixture was stirred at room temperature and exposed to blue light for 12 hours. The reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layers were washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1-10:1) to give the desired product **3a-D** (109 mg, 85%).

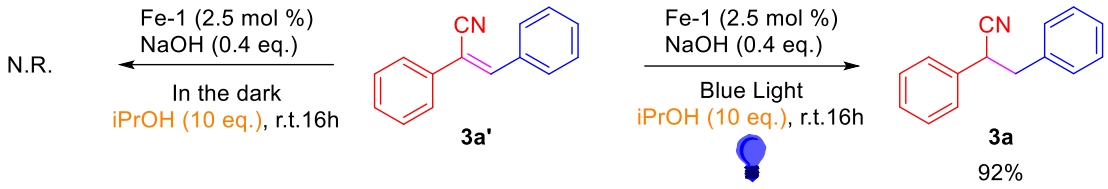
Synthesis of Products 3a'



1a **3a'**

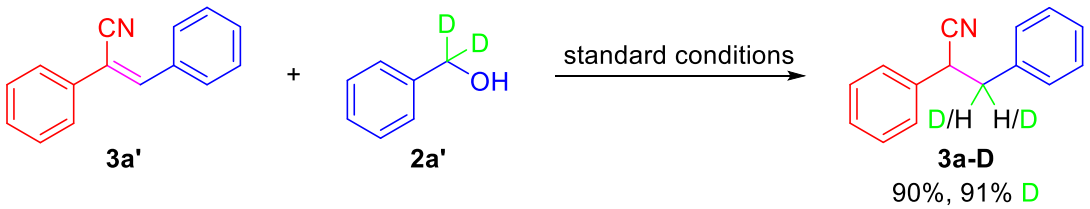
90%

To a mixture of **Fe-1** catalyst (2.5 mol %), NaOH (0.4 eq.), nitriles **1a** (1 mmol) and benzaldehyde (1.5 mmol), 1.5 mL of ^{t}BuOH was added. Then, the reaction was stirred under Ar in a pressure tube (ACE pressure tube, 15 mL). The mixture was stirred at room temperature and exposed to blue light for 12 hours. The reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layers were washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1-10:1) to give the desired product **3a'** (232 mg, 90%).



To a mixture of **Fe-1** catalyst (2.5 mol %), NaOH (0.4 eq.), **3a'** (0.5 mmol) and 0.5 mL of ^{t}BuOH was added. Then, the reaction was stirred under Ar in a pressure tube (ACE pressure tube, 15 mL). The mixture was stirred at room temperature and exposed to blue light / in the dark for 16 hours. The reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layers were washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1-10:1) to give the desired product **3a**.

Synthesis of Products 3a-D



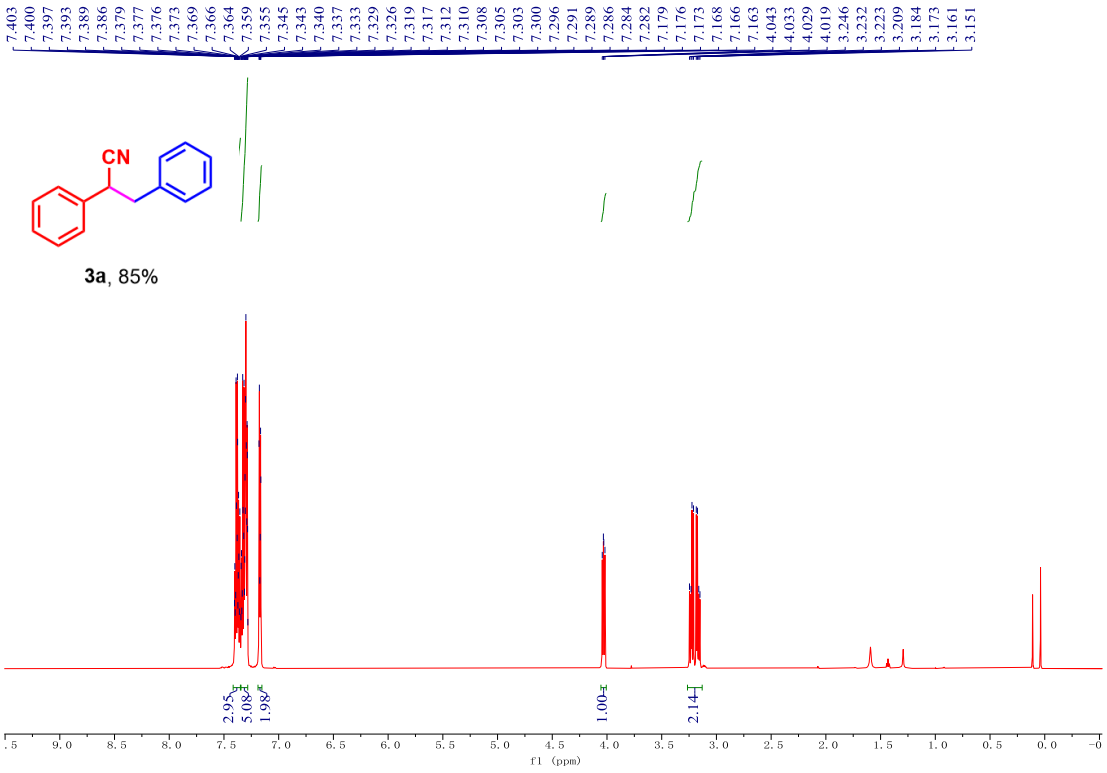
To a mixture of **Fe-1** catalyst (2.5 mol %), NaOH (0.4 eq.), 3**a'** (0.5 mmol) and alcohol **2a'** (0.75 mmol), 1.0 mL of ^{t}BuOH was added. Then, the reaction was stirred under Ar in a pressure tube (ACE pressure tube, 15 mL). The mixture was stirred at room temperature and exposed to blue light for 12 hours. The reaction was diluted with ethyl acetate (10 mL) and water (10 mL). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layers were washed by brine and dried over magnesium sulfate and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1-10:1) to give the desired product **3a-D** (115 mg, 90%).

6. Reference

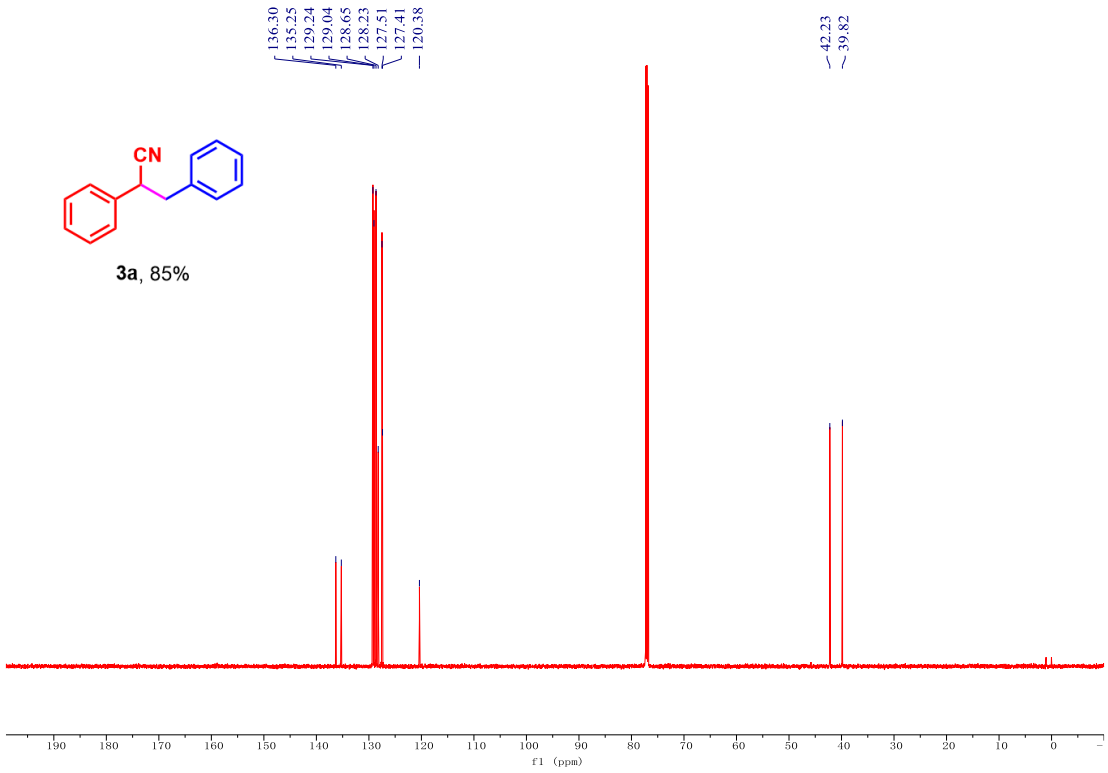
1. J. H. Schrittwieser, V. Resch, J. H. Sattler, W. D. Lienhart, K. Durchschein, A. Winkler, K. Gruber, P. Macheroux and W. Kroutil, *Angew. Chem., Int. Ed.*, 2011, **50**, 1068-1071.
2. S. Thiyagarajan, R. V. Sankar, P. K. Anjalikrishna, C. H. Suresh and C. Gunanathan, Catalytic Formal Conjugate Addition: Direct Synthesis of δ-Hydroxynitriles from Nitriles and Allylic Alcohols. *ACS Catalysis*, 2022, **12**, 2191-2204.

7. NMR spectra

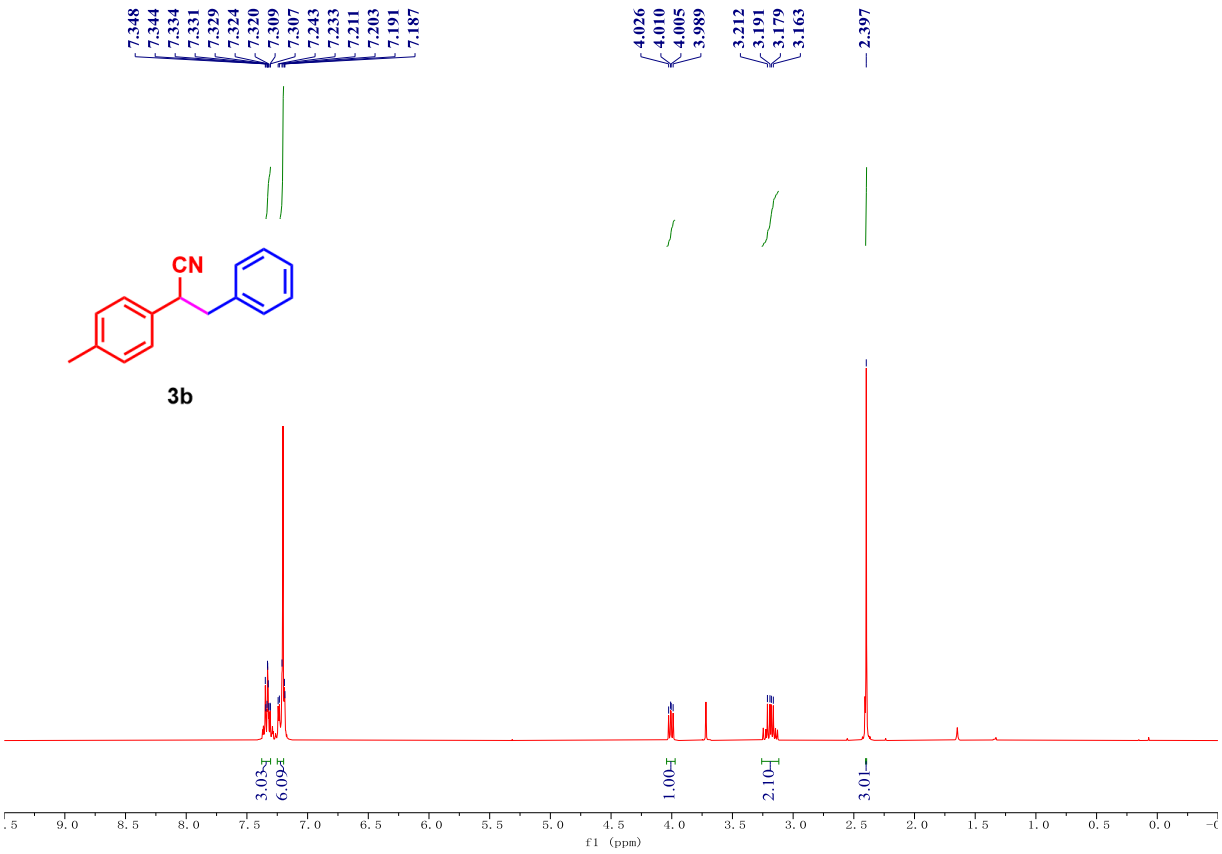
^{1}H NMR spectrum of 2,3-diphenylpropanenitrile (**3a**, 400 MHz, $CDCl_3$):



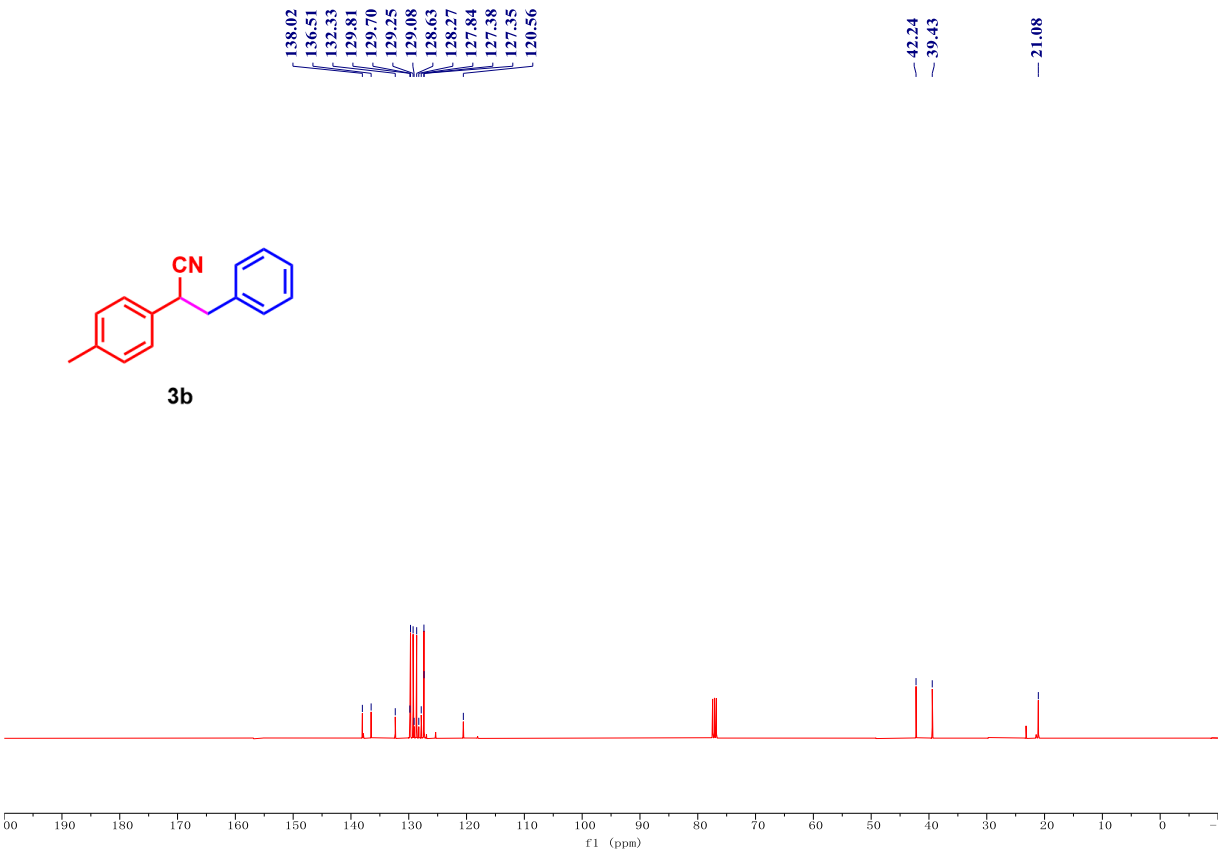
^{13}C NMR spectrum of 2,3-diphenylpropanenitrile (**3a**, 100 MHz, $CDCl_3$):



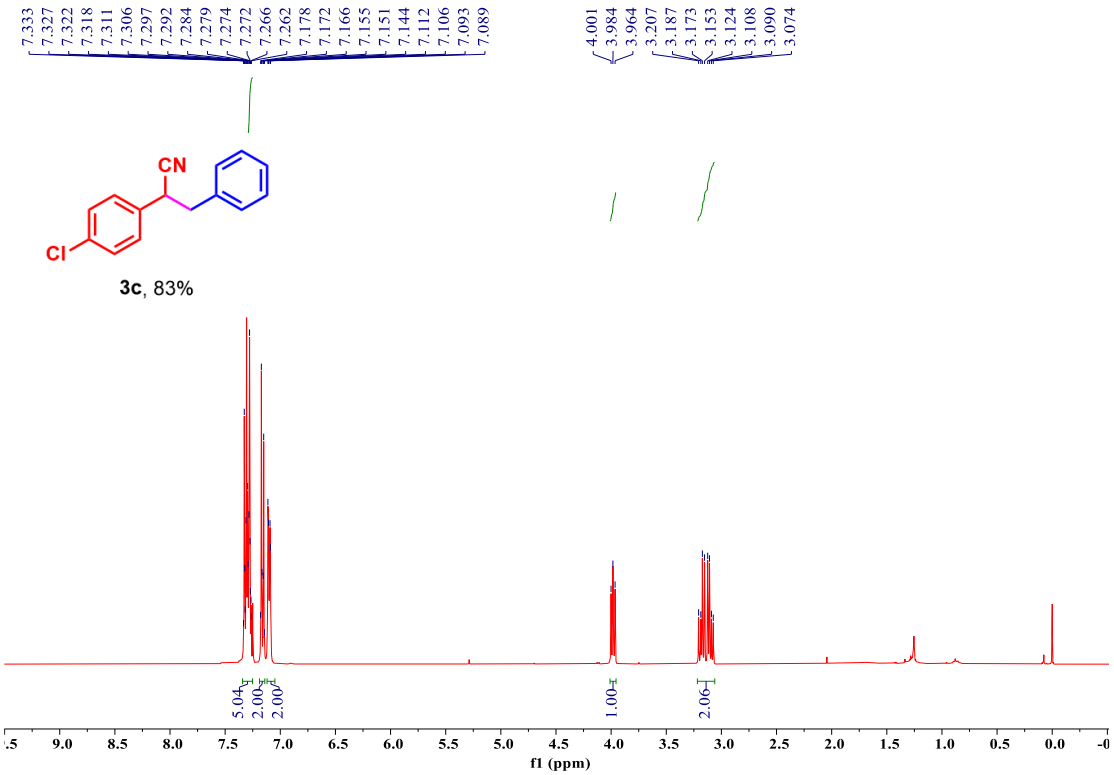
^{1}H NMR spectrum of 3-phenyl-2-(p-tolyl) propanenitrile (**3b**, 400 MHz, $CDCl_3$):



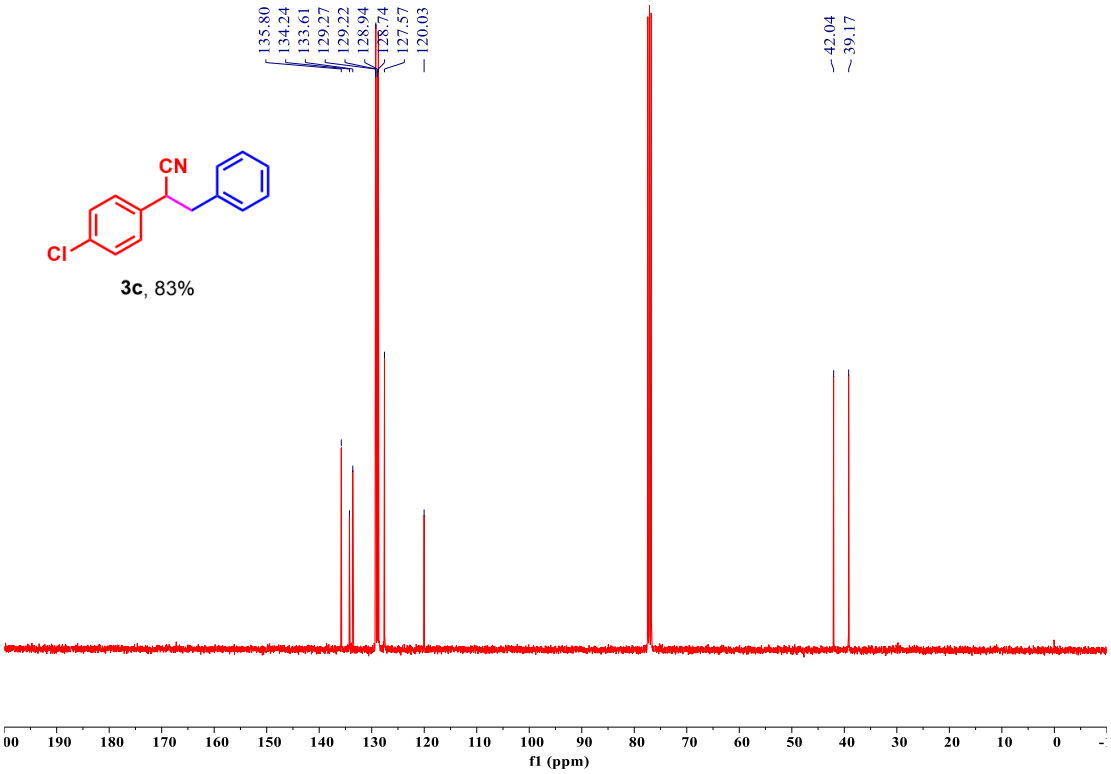
^{13}C NMR spectrum of 3-phenyl-2-(p-tolyl) propanenitrile (**3b**, 100 MHz, $CDCl_3$):



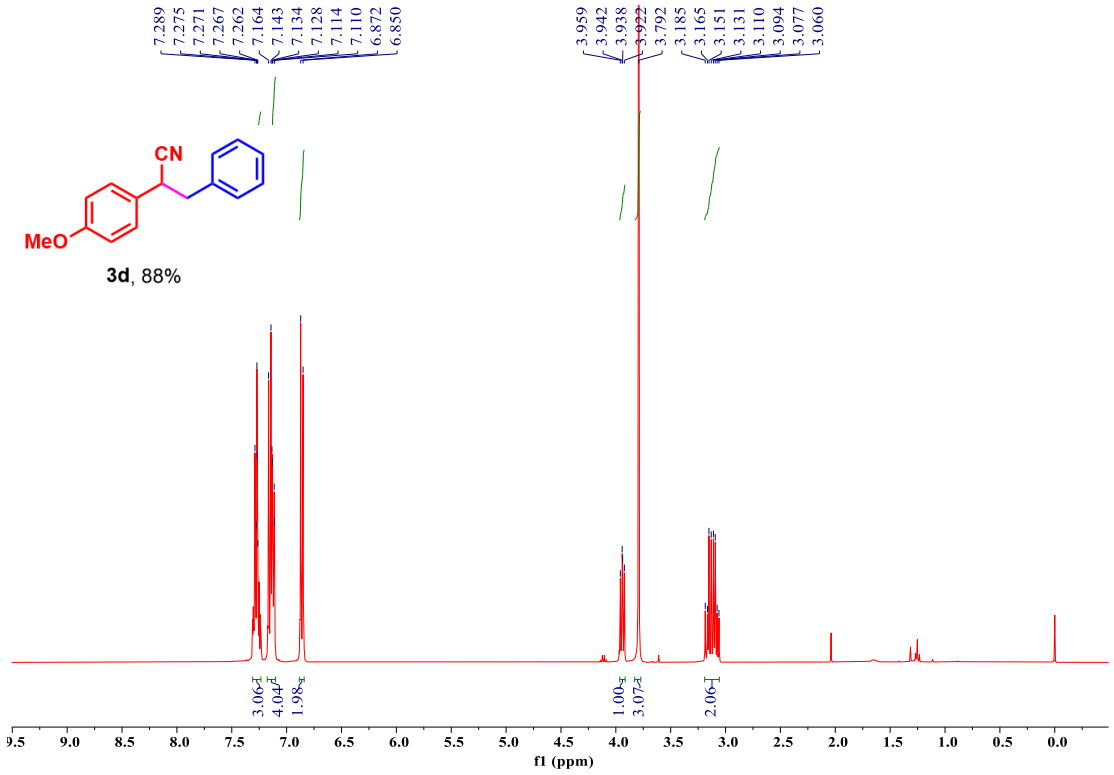
^{1}H NMR spectrum of 2-(4-chlorophenyl)-3-phenylpropanenitrile (**3c**, 400 MHz, $CDCl_3$):



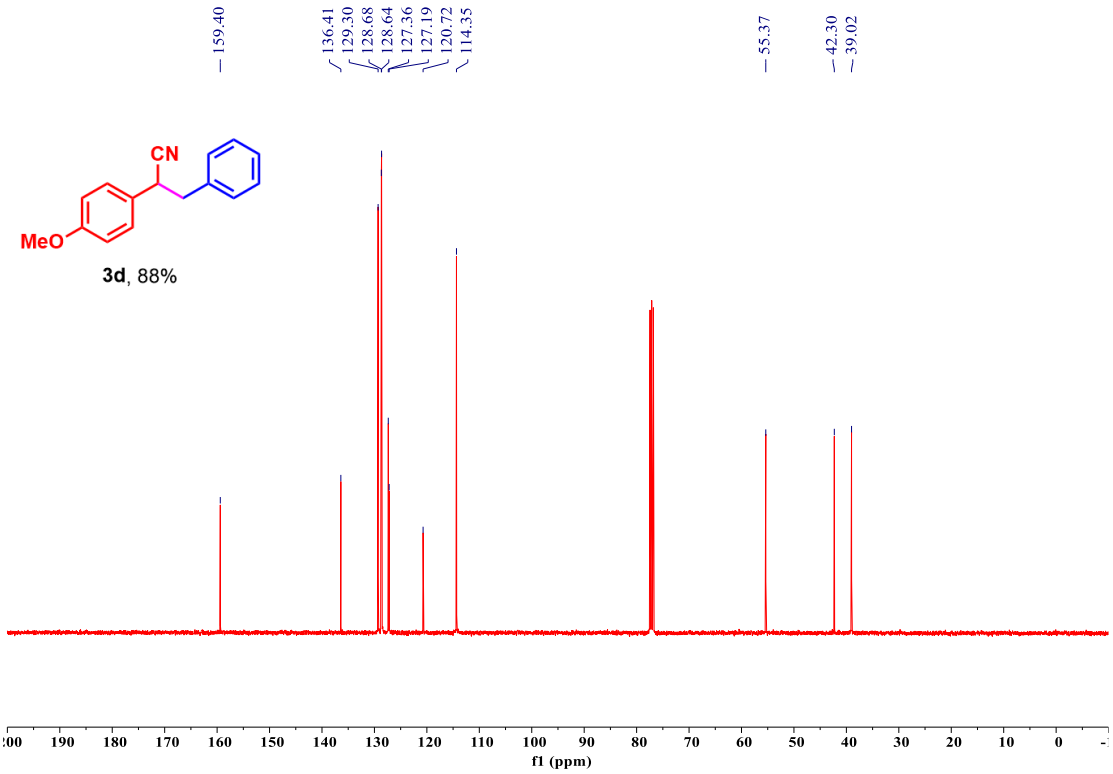
^{13}C NMR spectrum of 2-(4-chlorophenyl)-3-phenylpropanenitrile (**3c**, 100 MHz, $CDCl_3$):



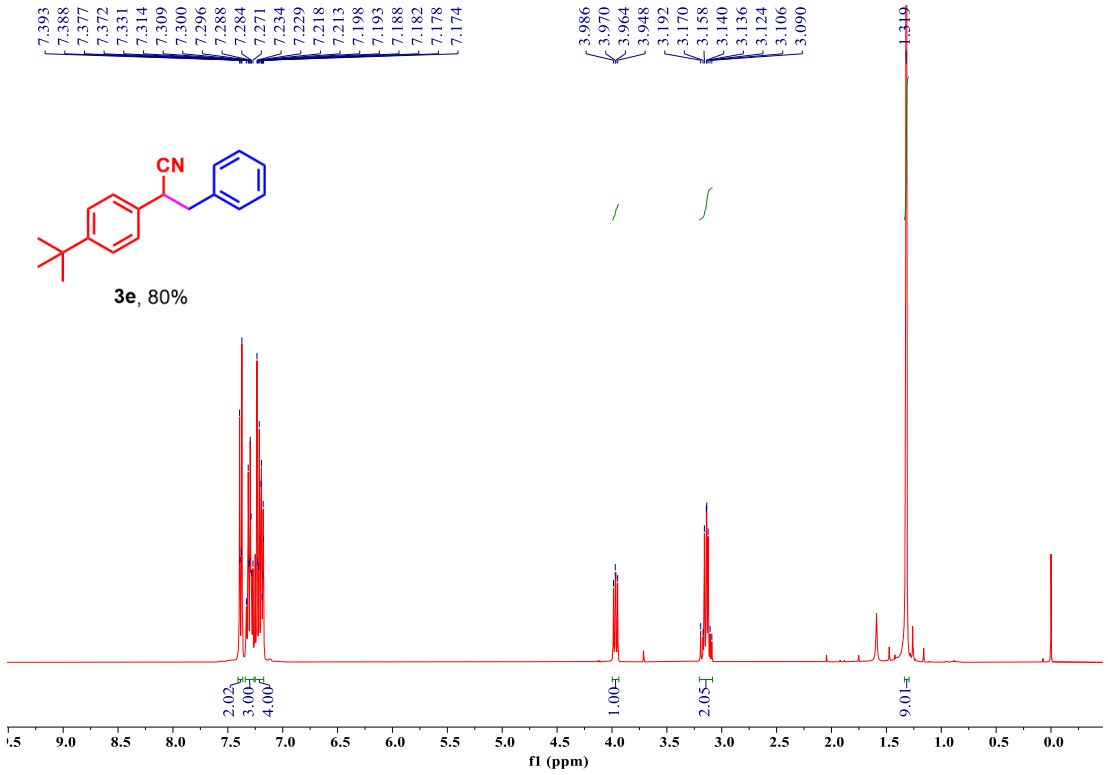
^{1}H NMR spectrum of 2-(4-methoxyphenyl)-3-phenylpropanenitrile (**3d**, 400 MHz, $CDCl_3$):



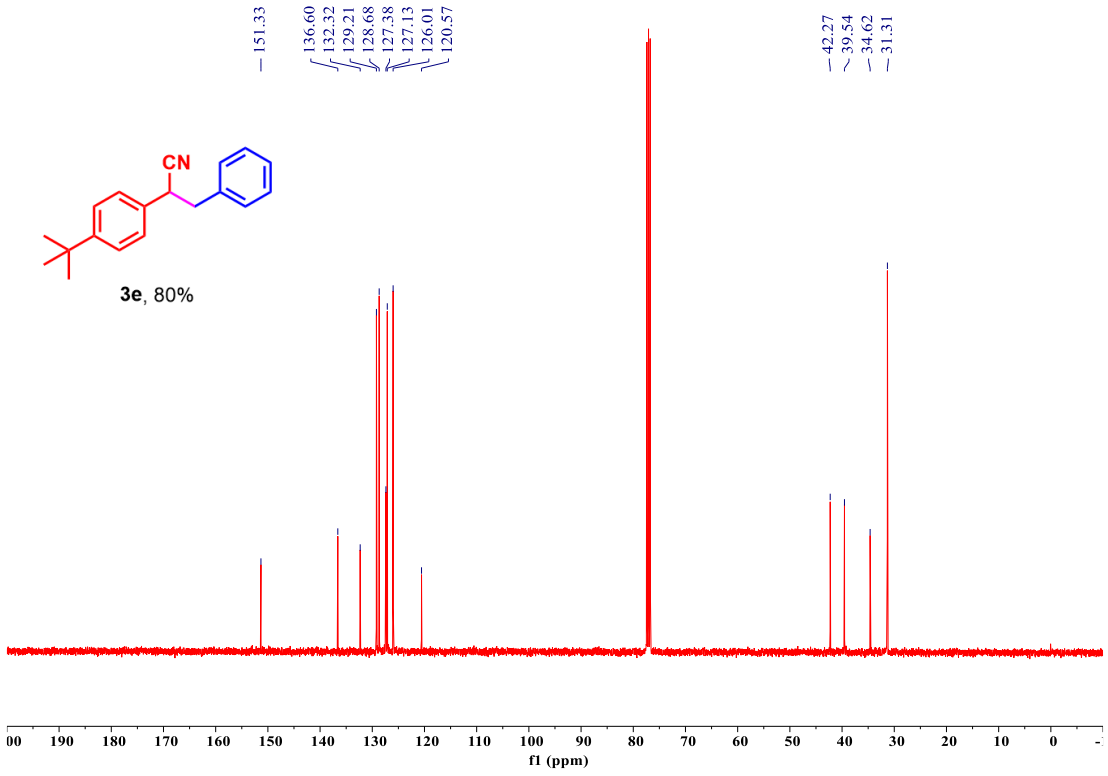
^{13}C NMR spectrum of 2-(4-methoxyphenyl)-3-phenylpropanenitrile (**3d**, 100 MHz, $CDCl_3$):



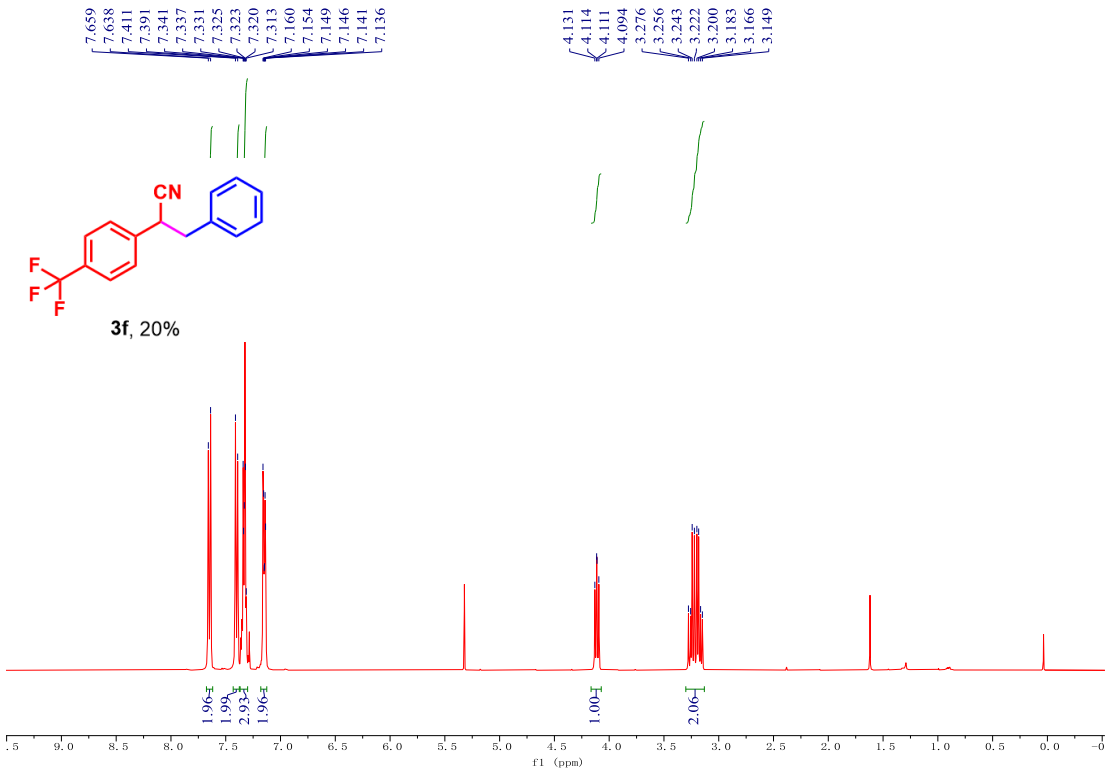
^{1}H NMR spectrum of 2-(4-(tert-butyl) phenyl)-3-phenylpropanenitrile (**3e**, 400 MHz, $CDCl_3$):



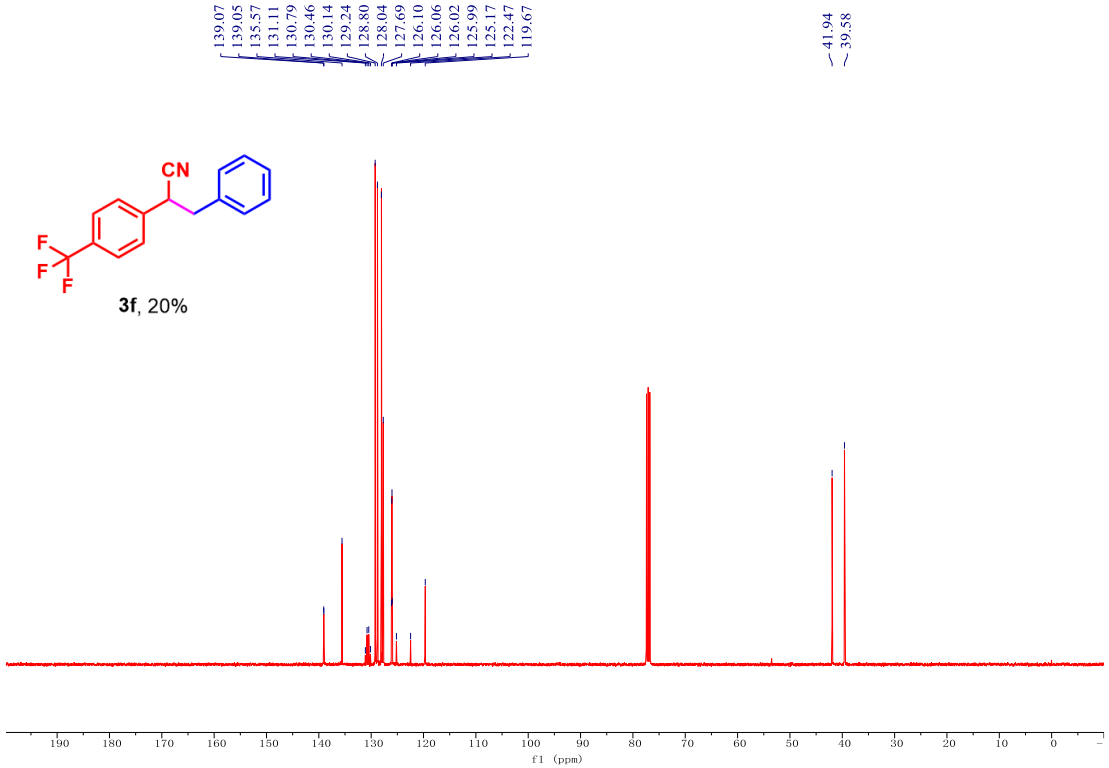
^{13}C NMR spectrum of 2-(4-(tert-butyl) phenyl)-3-phenylpropanenitrile (**3e**, 100 MHz, $CDCl_3$):



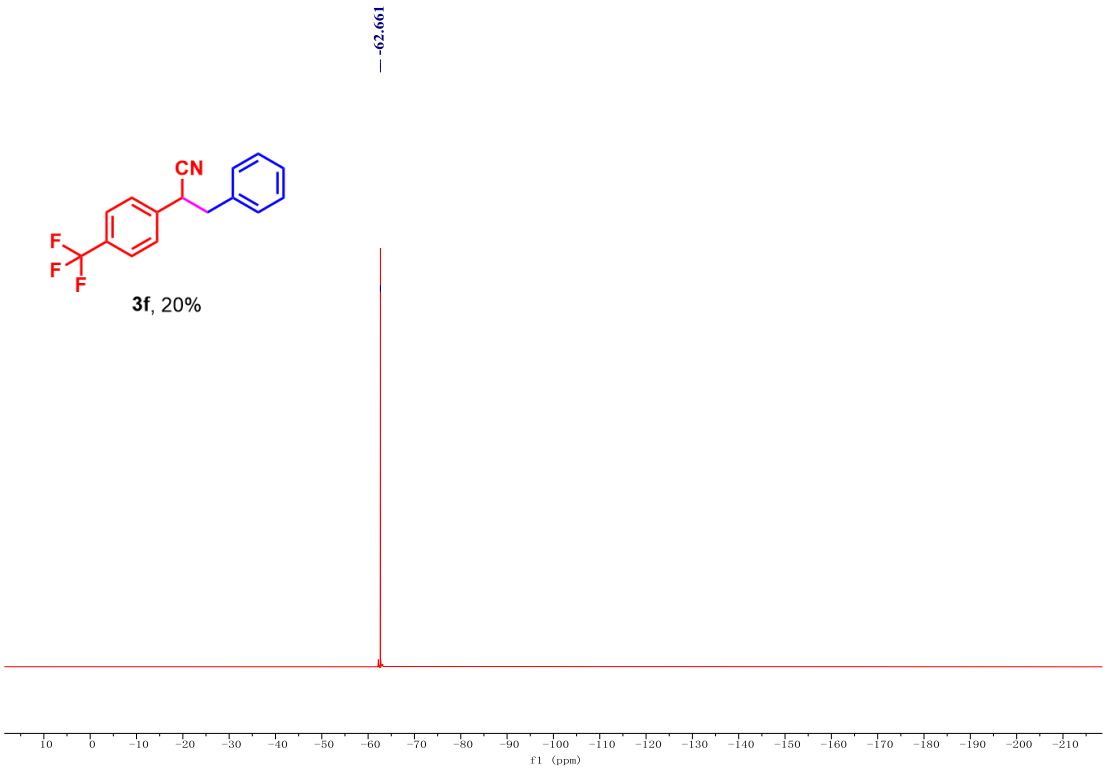
^{1}H NMR spectrum of 3-phenyl-2-(4-(trifluoromethyl) phenyl) propanenitrile (**3f**, 400 MHz, $CDCl_3$):



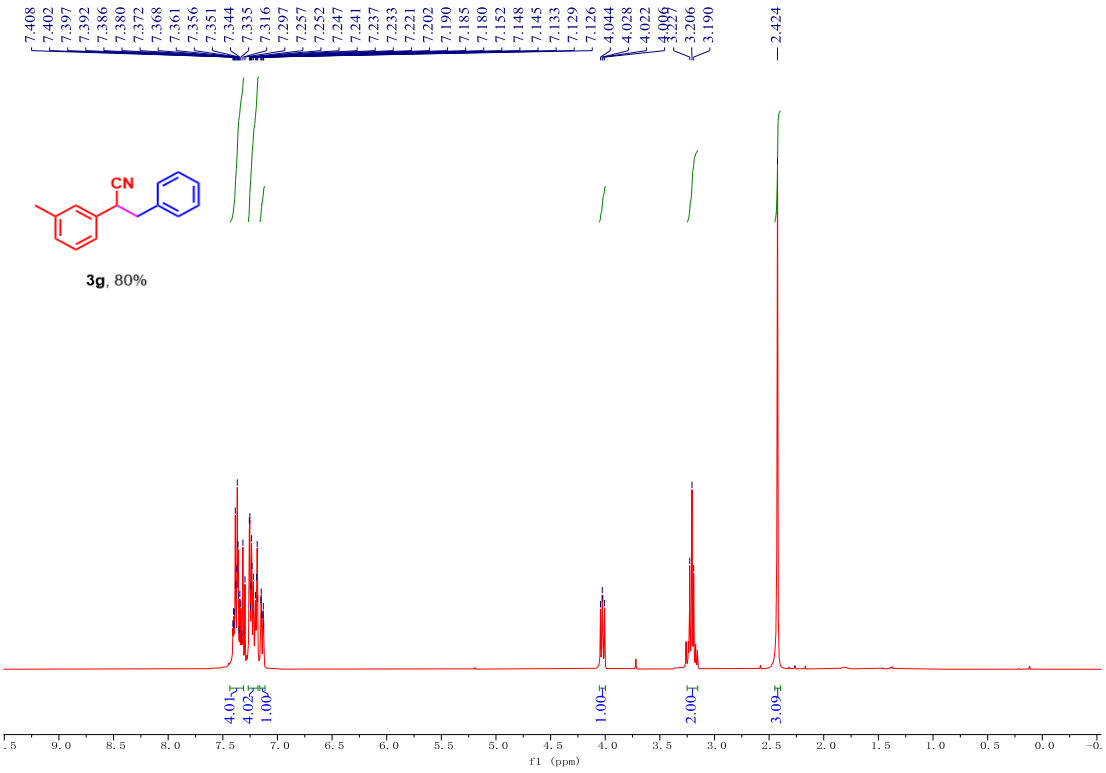
^{13}C NMR spectrum of 3-phenyl-2-(4-(trifluoromethyl) phenyl) propanenitrile (**3f**, 100 MHz, $CDCl_3$):



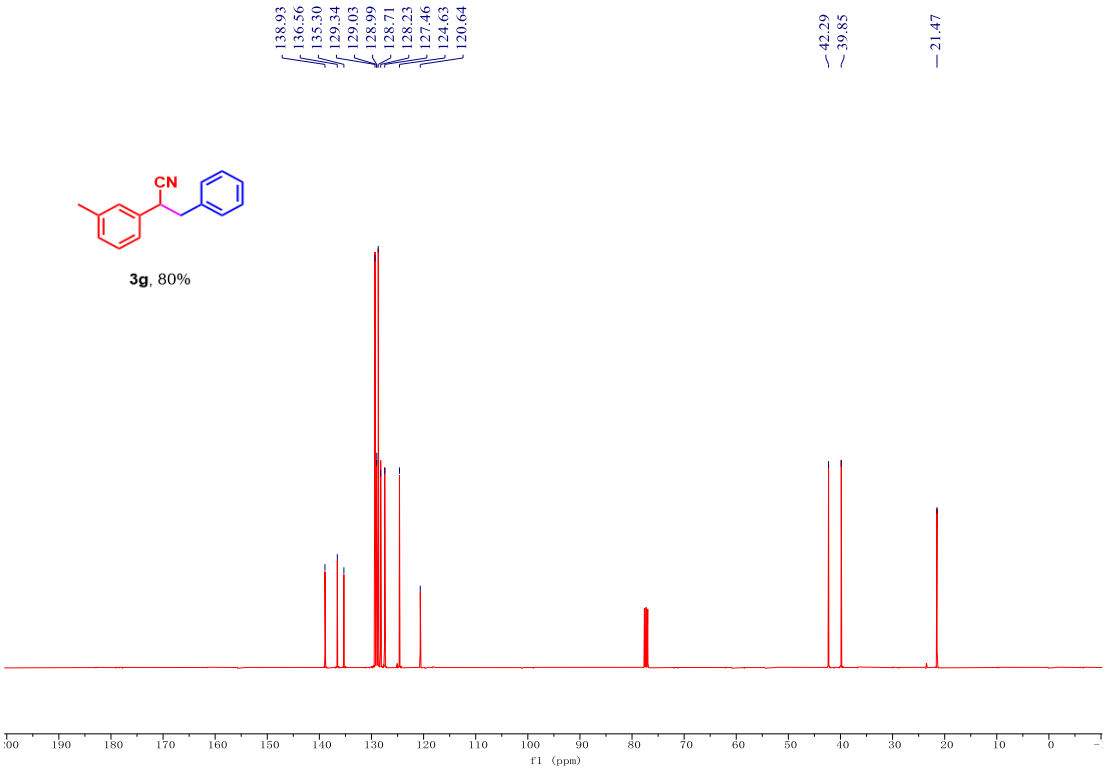
^{19}F NMR spectrum of 3-phenyl-2-(4-(trifluoromethyl) phenyl) propanenitrile (**3f**, 376 MHz, $CDCl_3$):



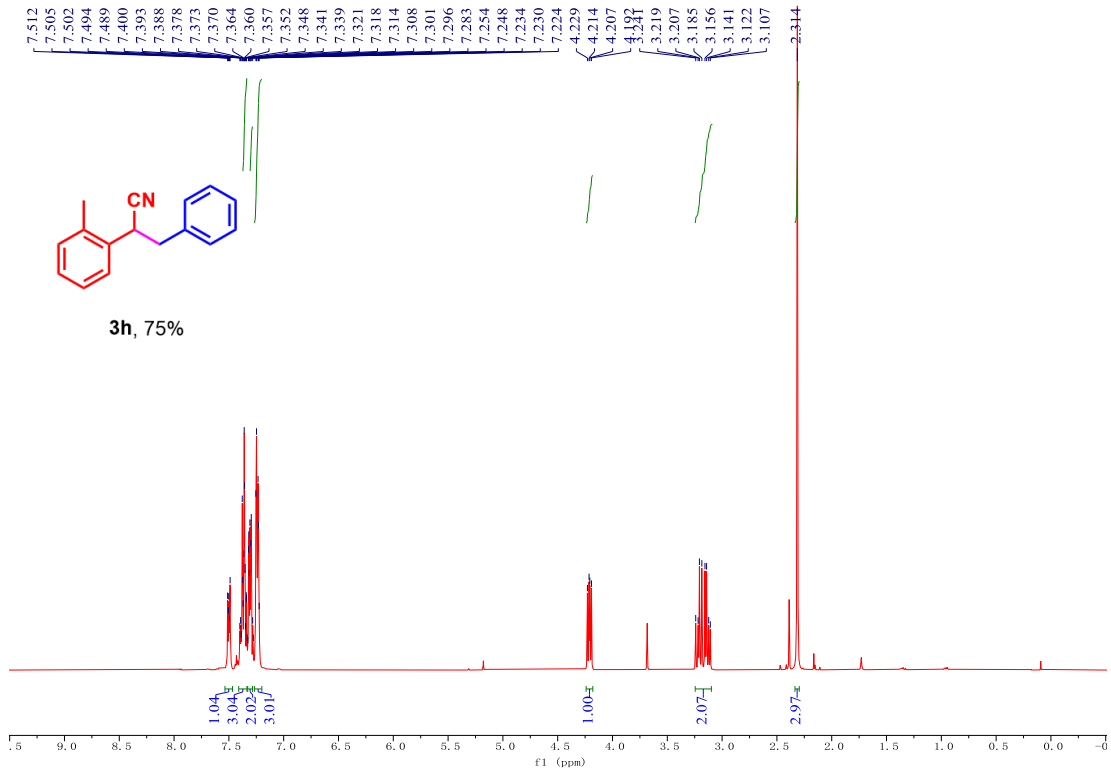
^{1}H NMR spectrum of 3-phenyl-2-(m-tolyl) propanenitrile (**3g**, 400 MHz, $CDCl_3$) :



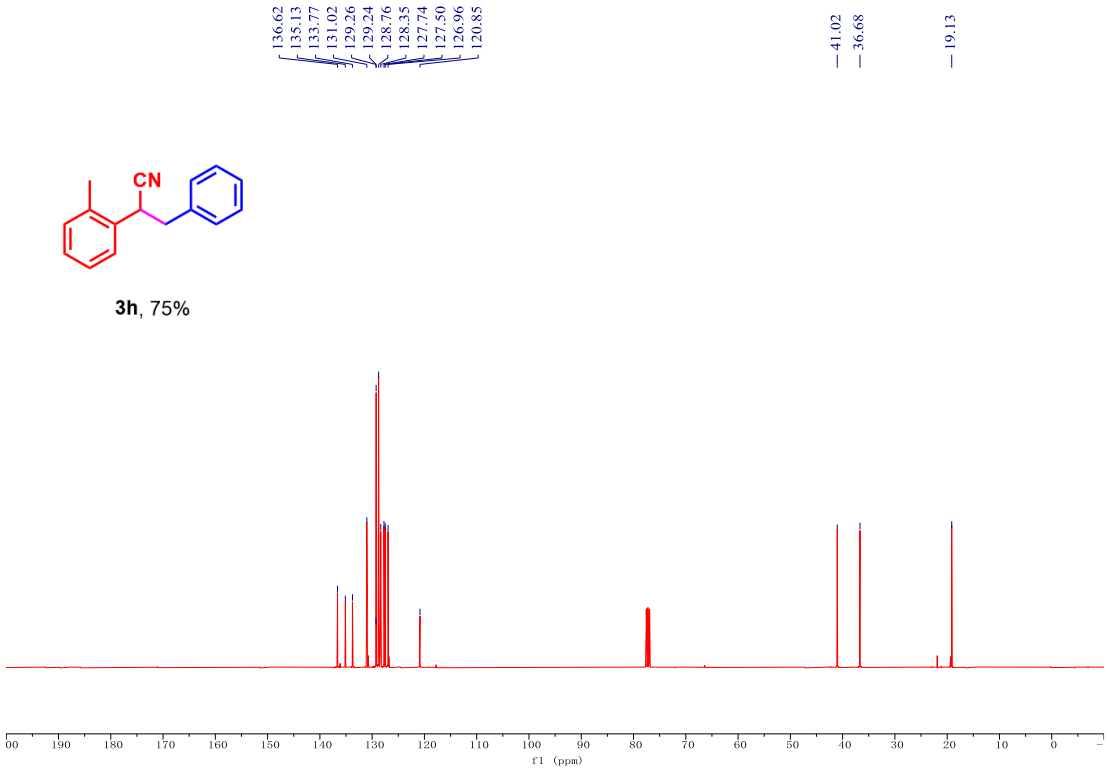
^{13}C NMR spectrum of 3-phenyl-2-(m-tolyl) propanenitrile (**3g**, 100 MHz, $CDCl_3$):



^{1}H NMR spectrum of 3-phenyl-2-(p-tolyl) propanenitrile (**3h**, 400 MHz, $CDCl_3$) :

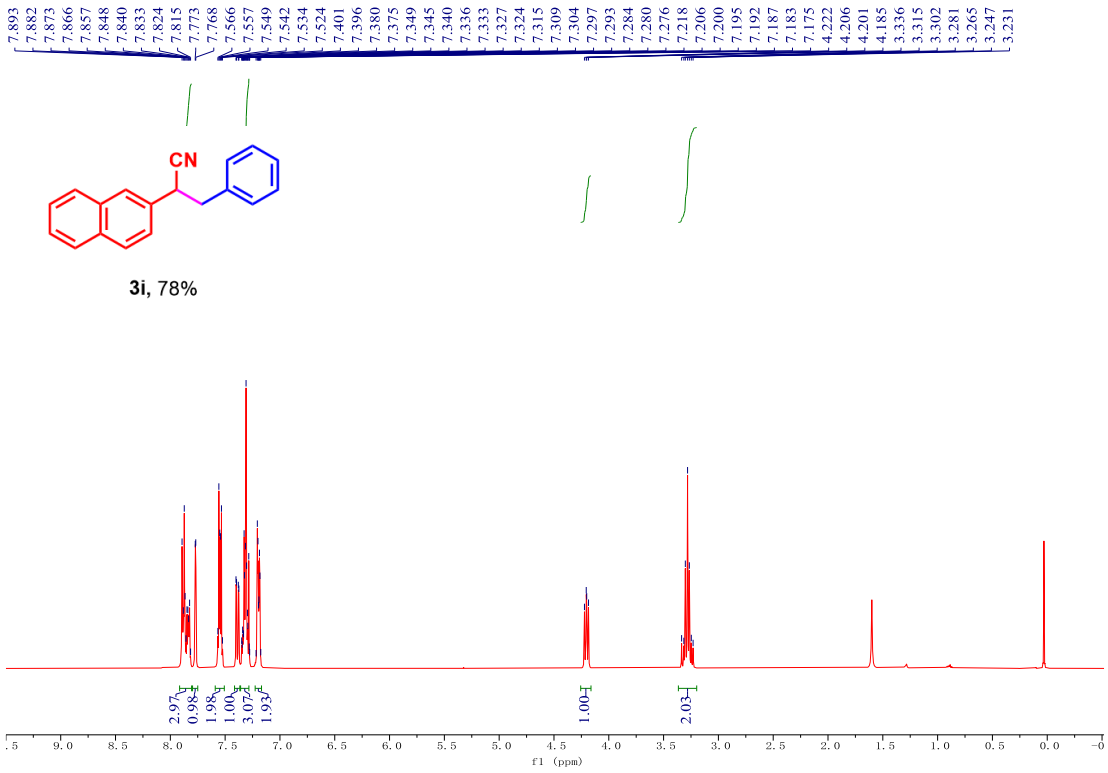


^{13}C NMR spectrum of 3-phenyl-2-(p-tolyl) propanenitrile (**3h**, 100 MHz, $CDCl_3$):



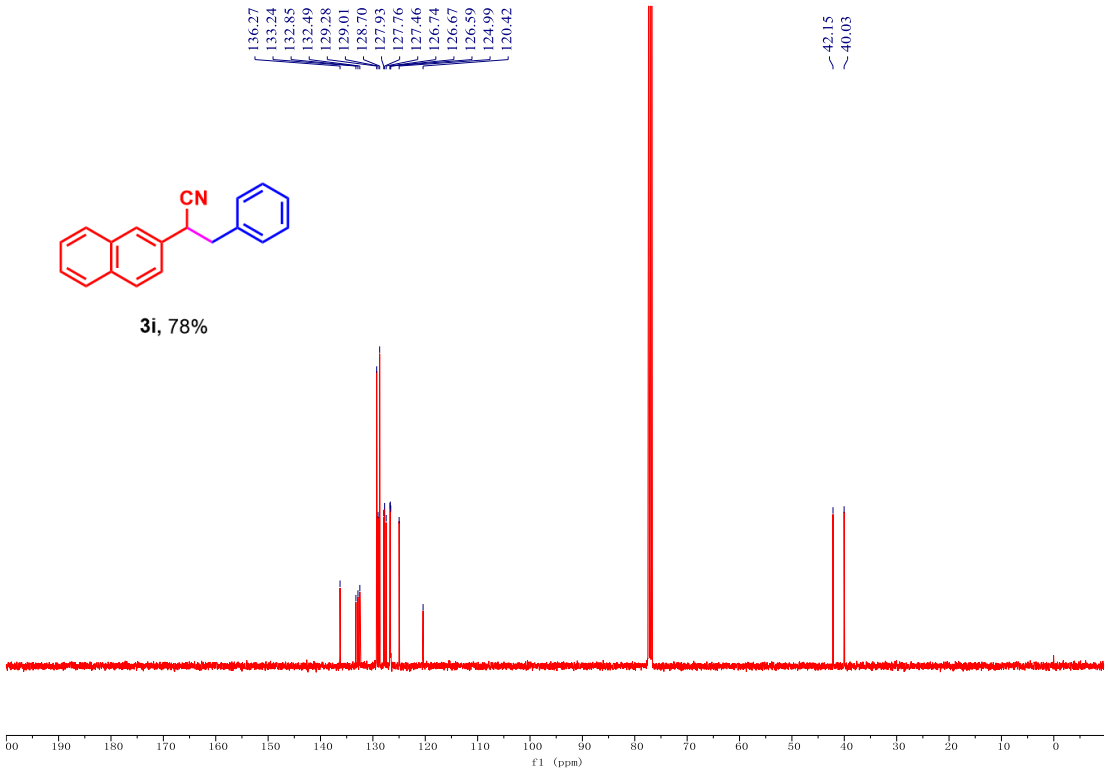
3h, 75%

^{1}H NMR spectrum of 2-(naphthalen-2-yl)-3-phenylpropanenitrile (**3i**, 400 MHz, $CDCl_3$) :

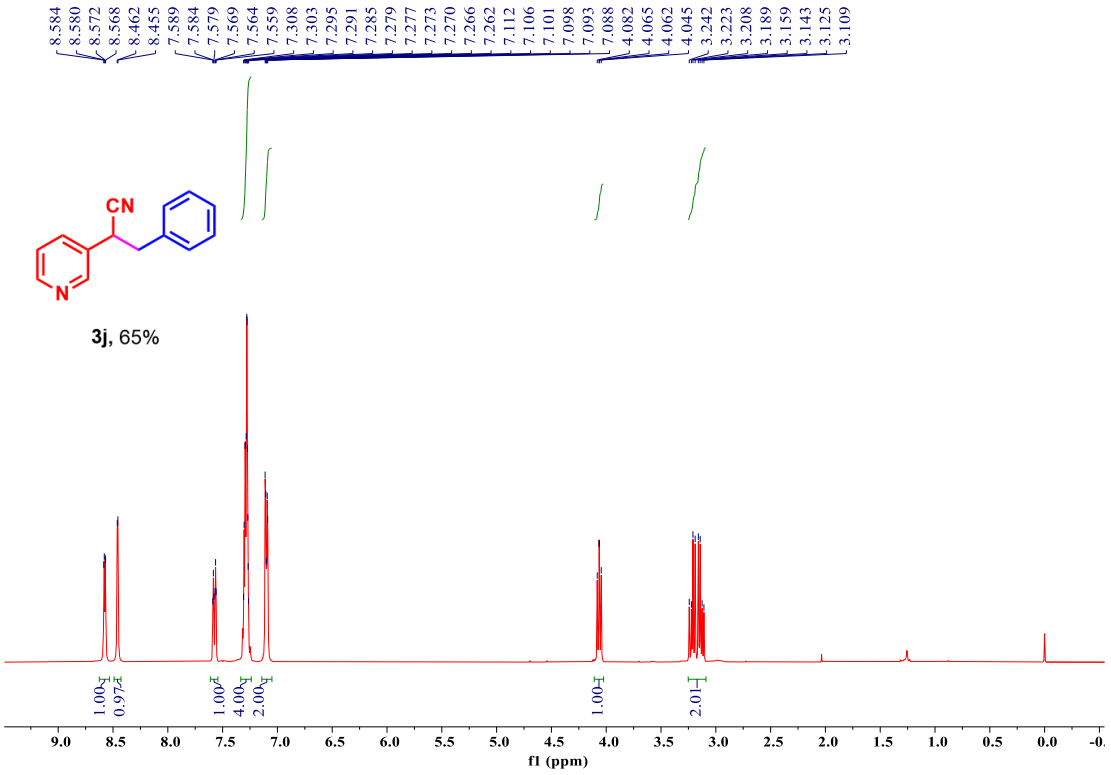


3i, 78%

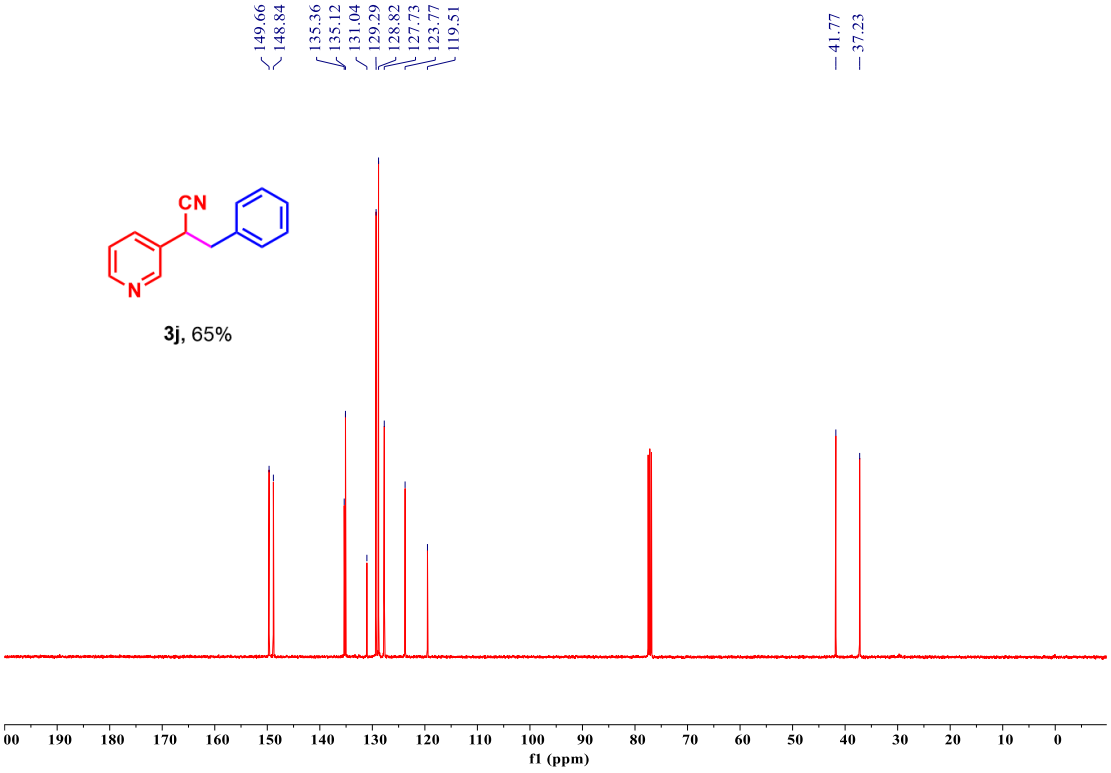
^{13}C NMR spectrum of 2-(naphthalen-2-yl)-3-phenylpropanenitrile (**3i**, 100 MHz, $CDCl_3$):



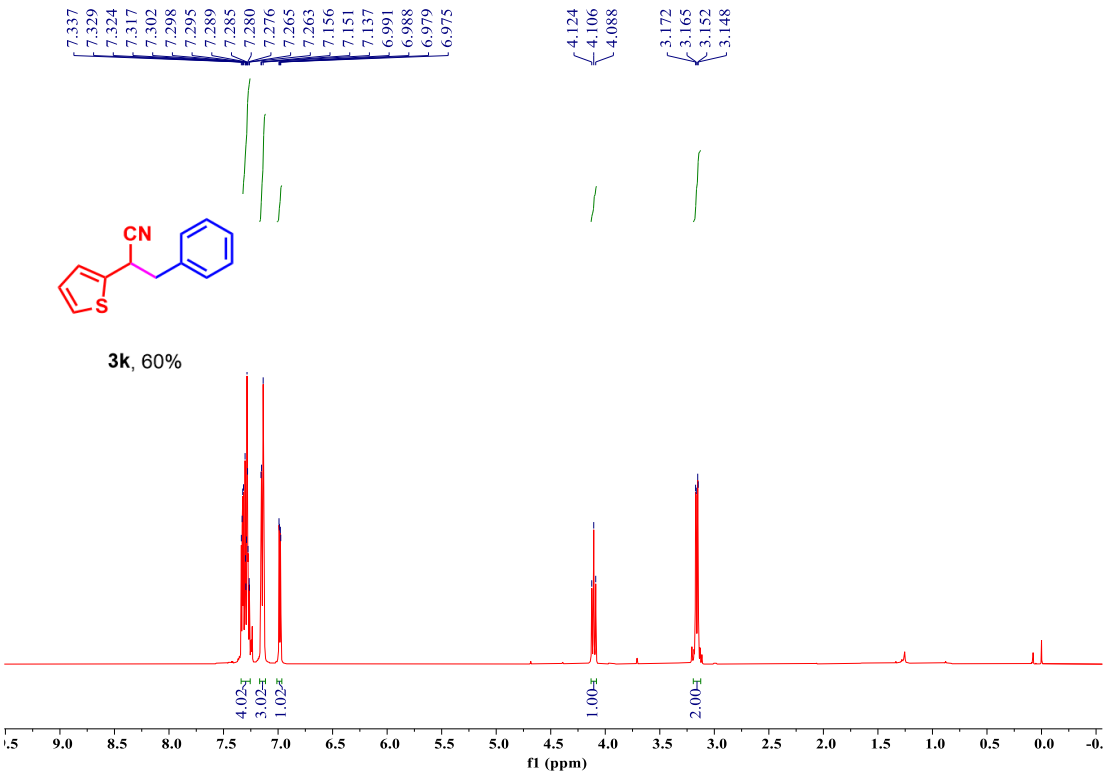
^{1}H NMR spectrum of 3-phenyl-2-(pyridin-3-yl) propanenitrile (**3j**, 400 MHz, $CDCl_3$):



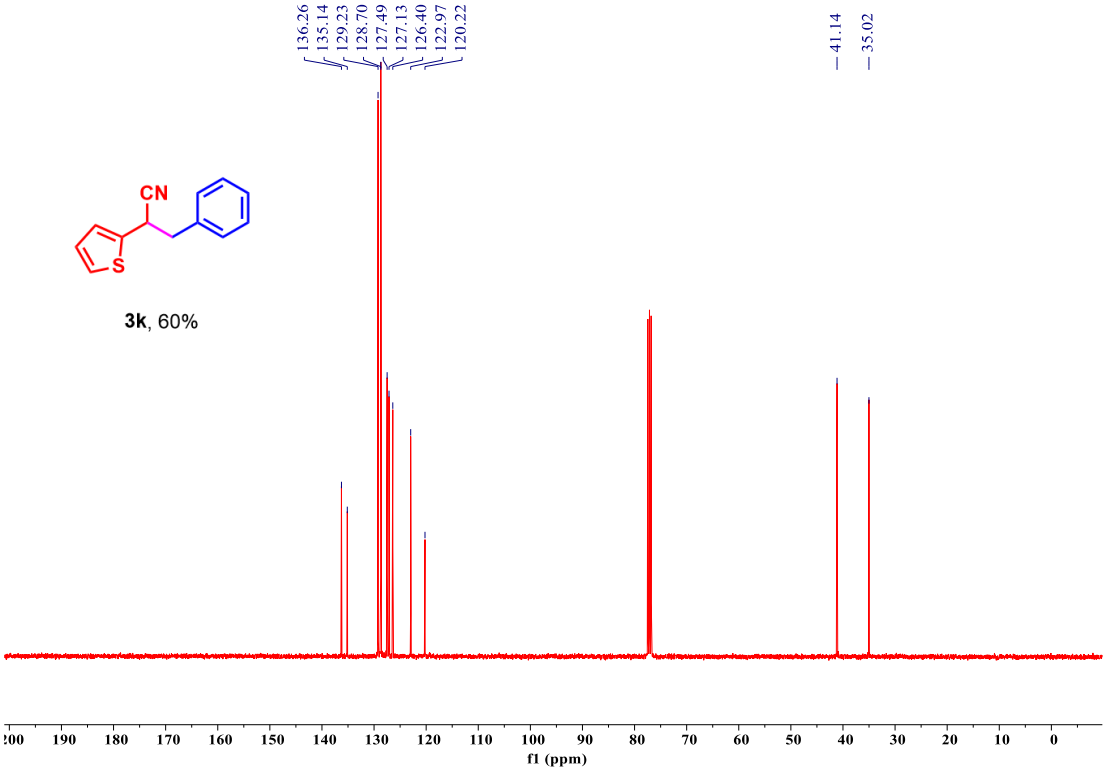
^{13}C NMR spectrum of 3-phenyl-2-(pyridin-3-yl) propanenitrile (**3j**, 100 MHz, $CDCl_3$):



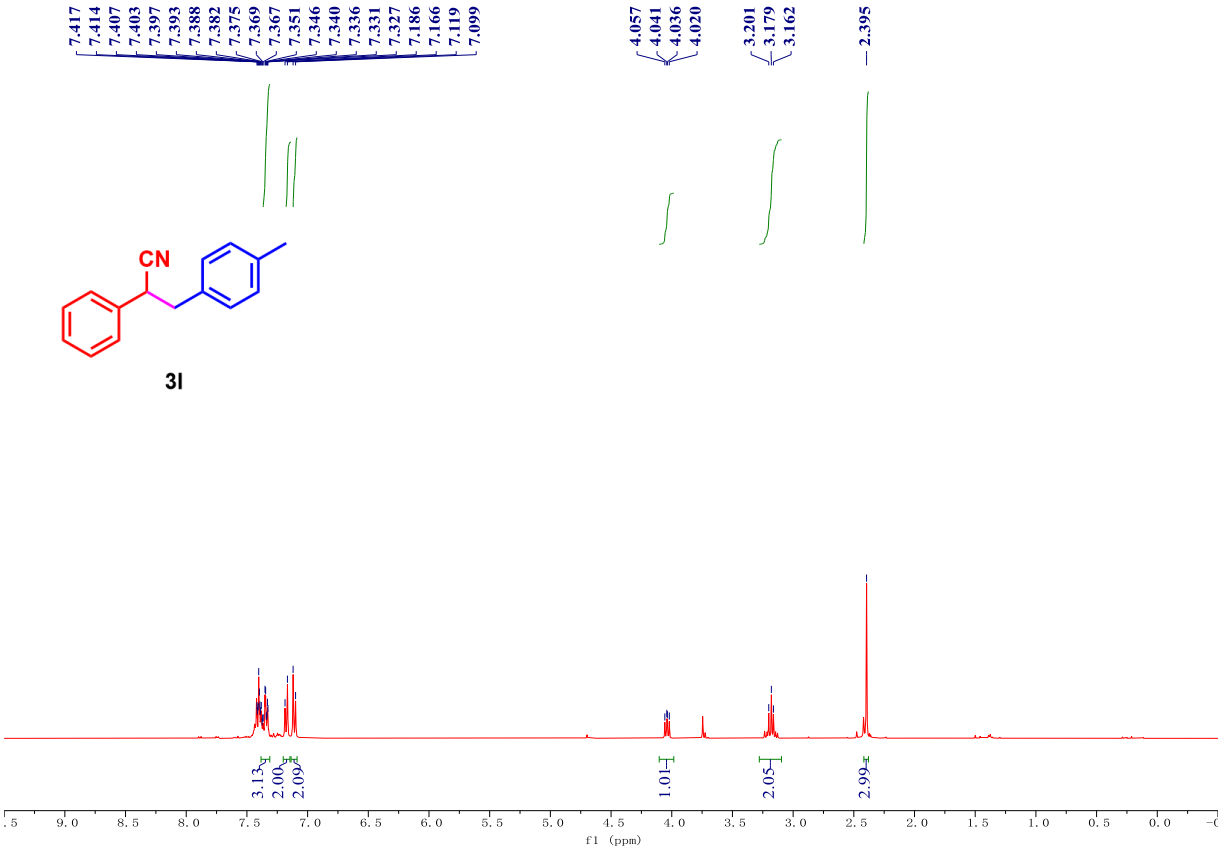
^{1}H NMR spectrum of 3-phenyl-2-(thiophen-2-yl) propanenitrile (**3k**, 400 MHz, $CDCl_3$):



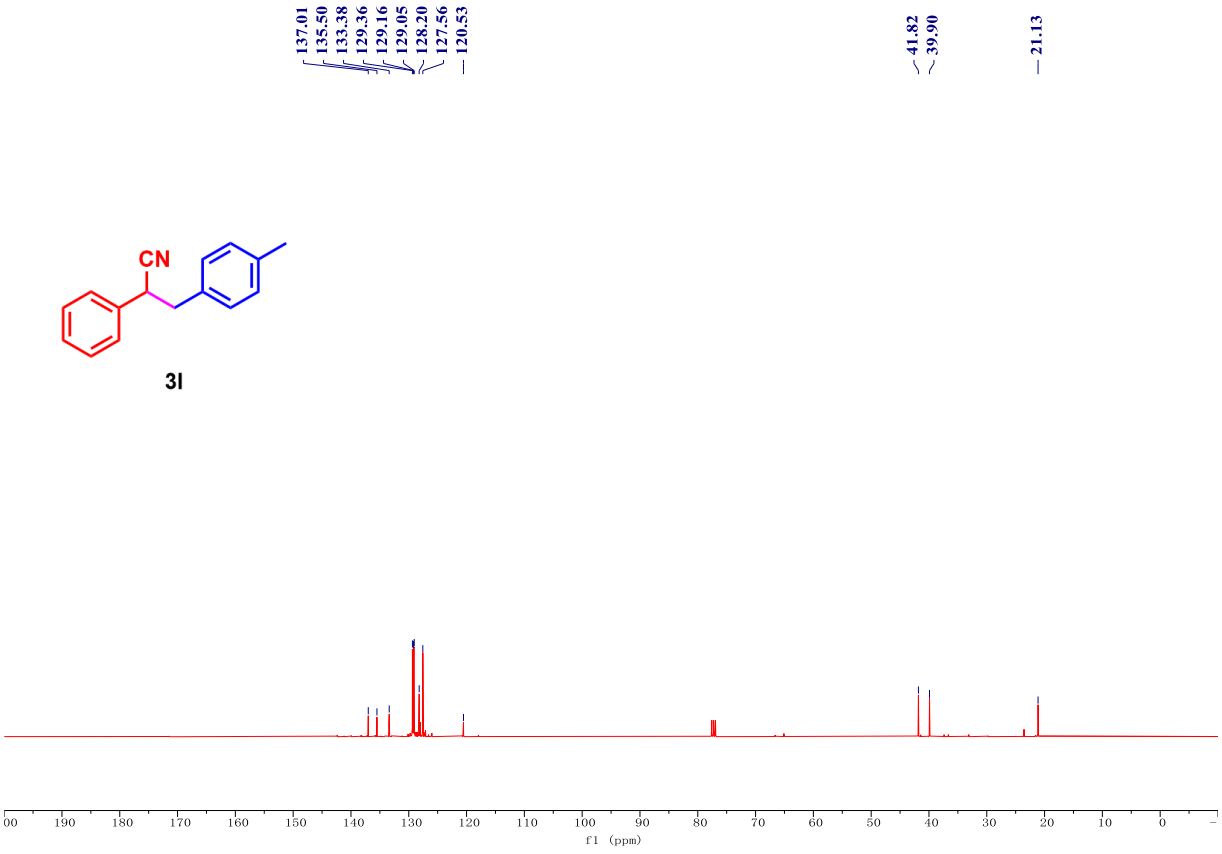
^{13}C NMR spectrum of 3-phenyl-2-(thiophen-2-yl) propanenitrile (**3k**, 100 MHz, $CDCl_3$):



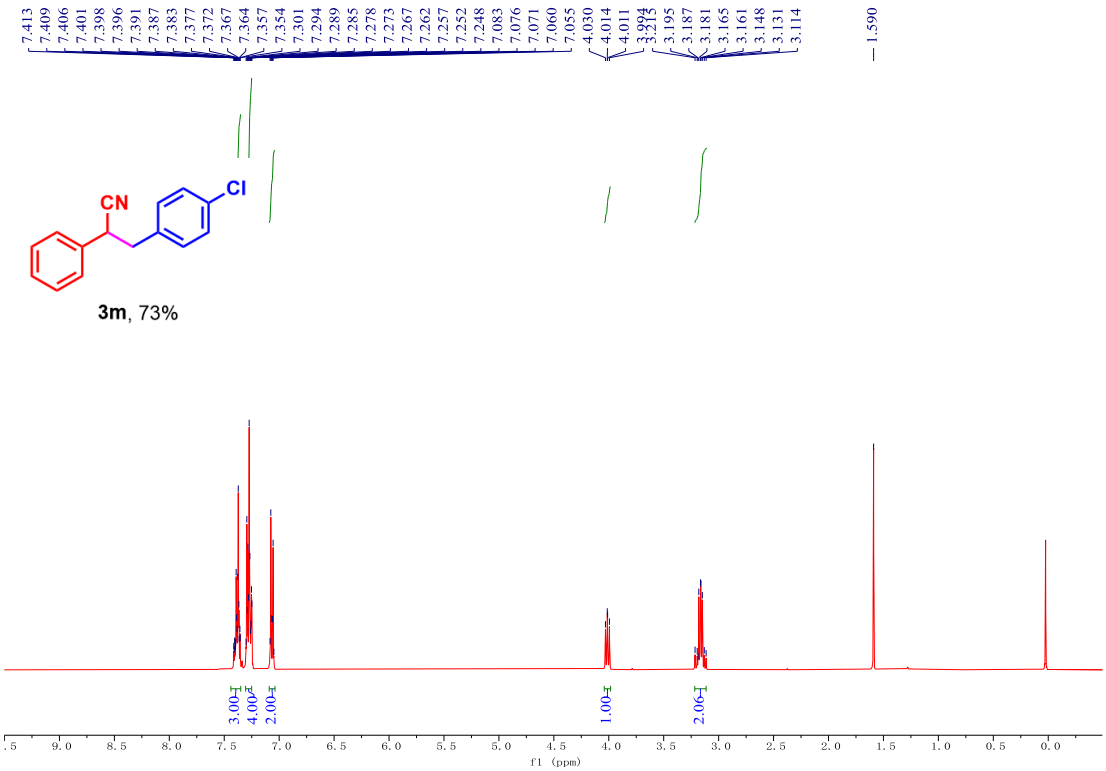
^{1}H NMR spectrum of 2-phenyl-3-(p-tolyl) propanenitrile (**3l**, 400 MHz, $CDCl_3$) :



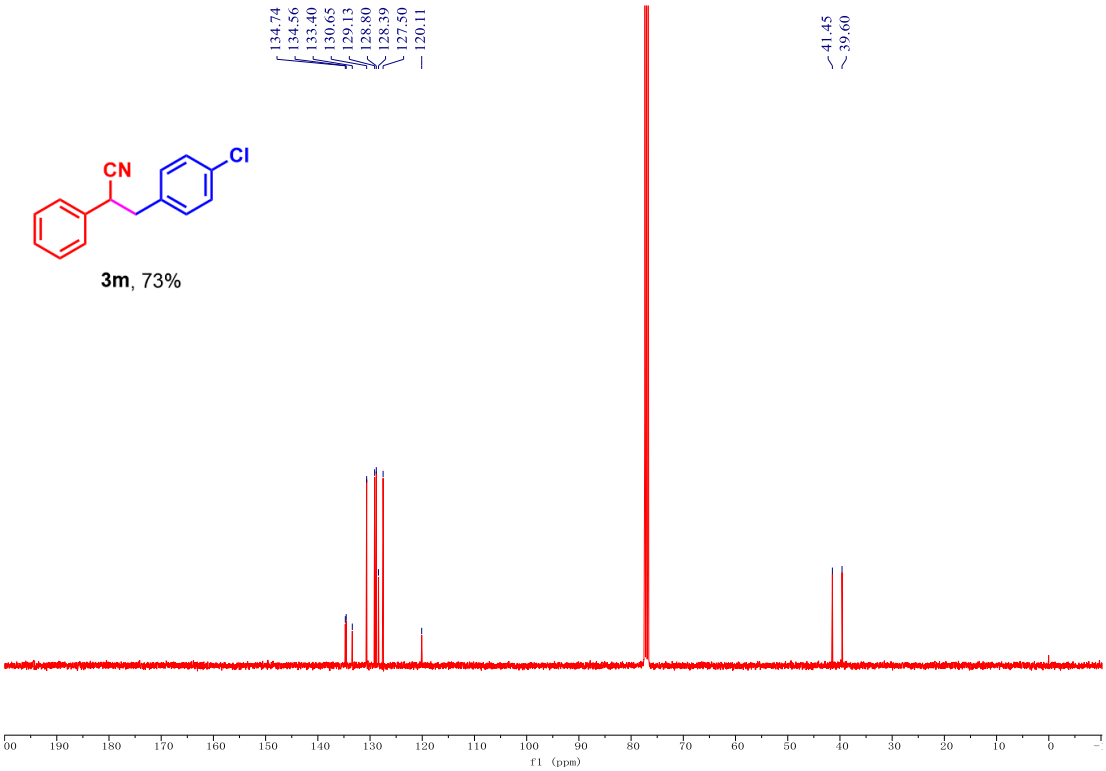
^{13}C NMR spectrum of 2-phenyl-3-(p-tolyl) propanenitrile (**3l**, 100 MHz, $CDCl_3$):



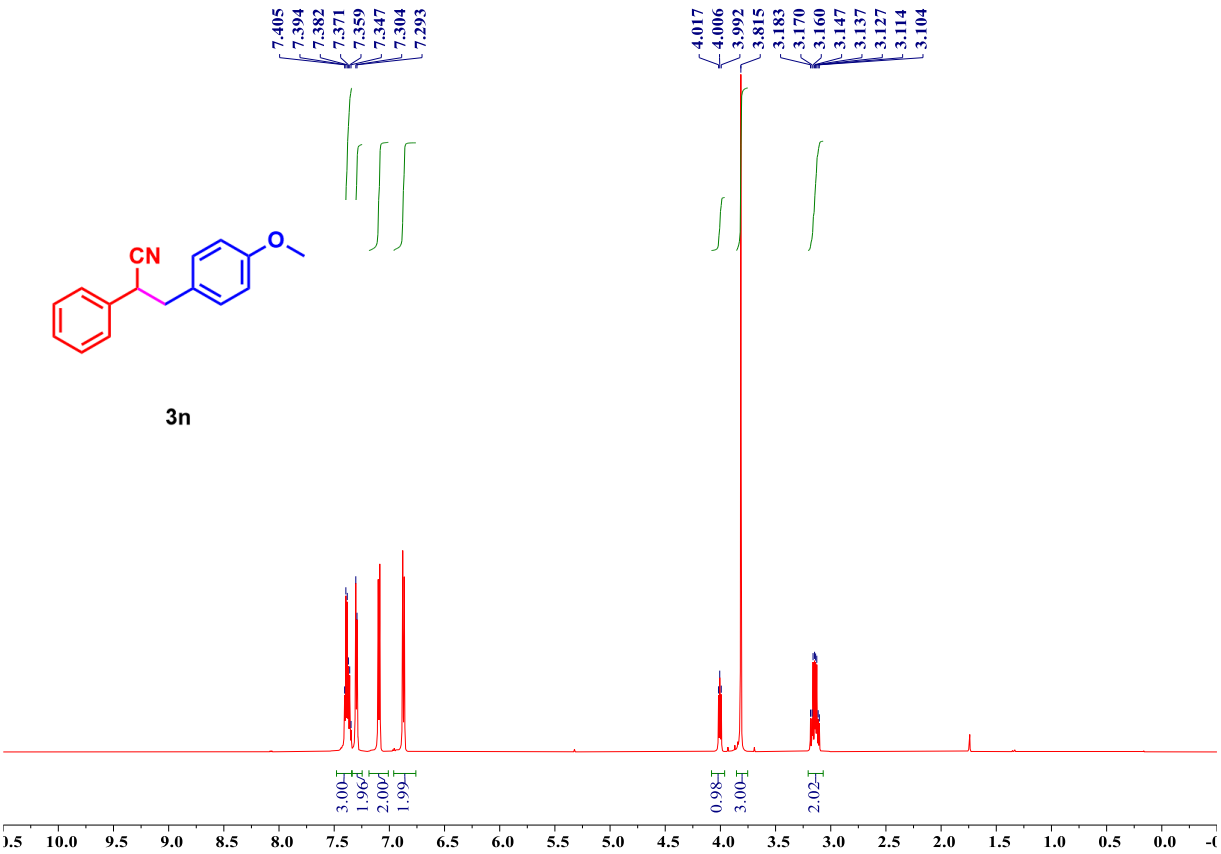
^{1}H NMR spectrum of 3-(4-chlorophenyl)-2-phenylpropanenitrile (**3m**, 400 MHz, $CDCl_3$) :



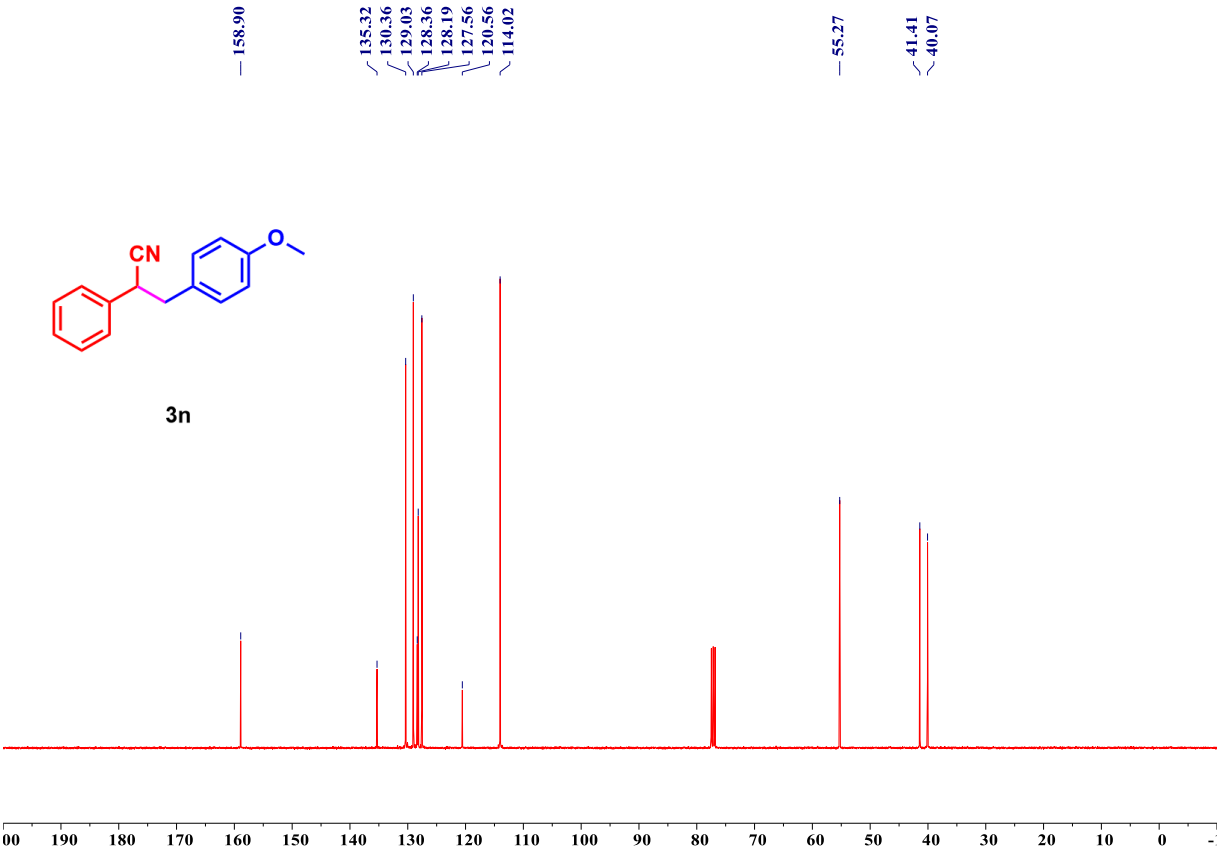
^{13}C NMR spectrum of 3-(4-chlorophenyl)-2-phenylpropanenitrile (**3m**, 100 MHz, $CDCl_3$):



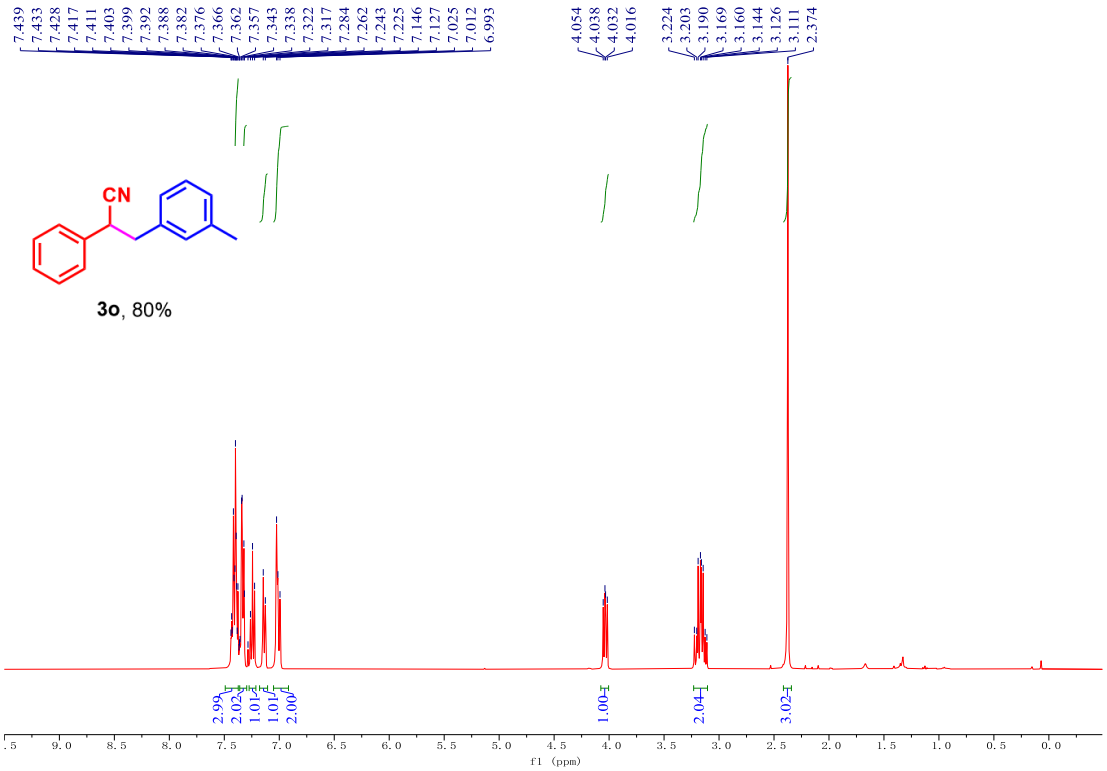
^{1}H NMR spectrum of 3-(4-methoxyphenyl)-2-phenylpropanenitrile (**3n**, 600 MHz, $CDCl_3$):



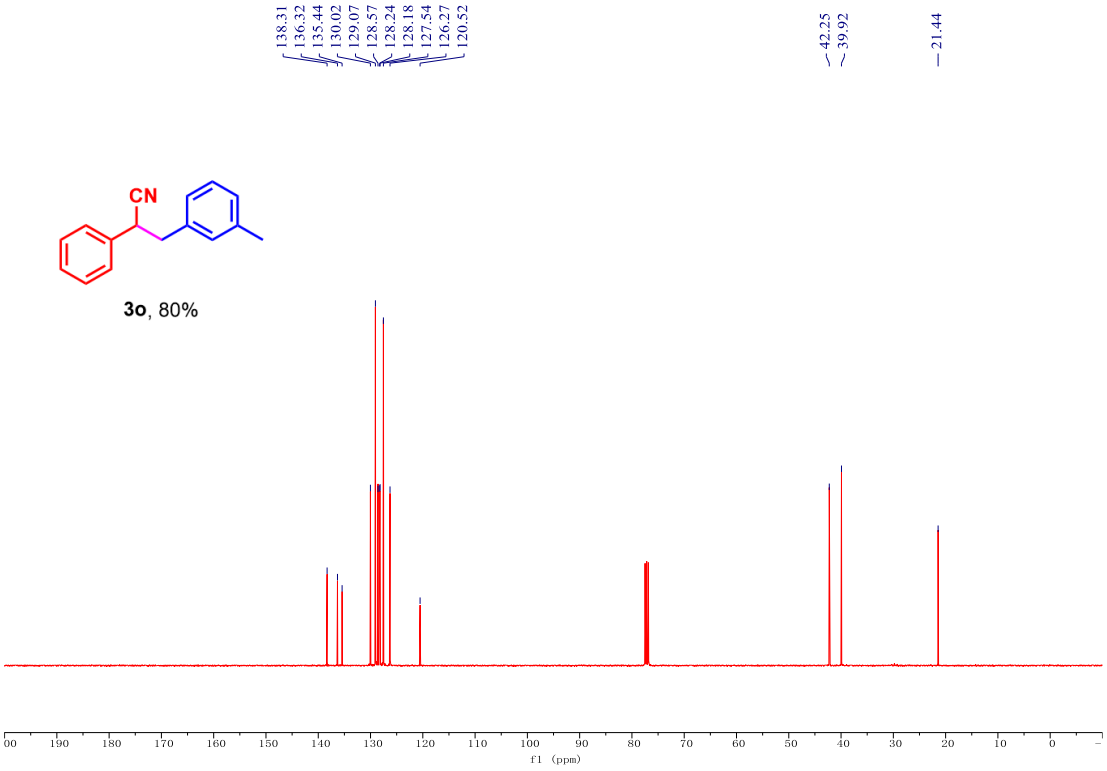
^{13}C NMR spectrum of 3-(4-methoxyphenyl)-2-phenylpropanenitrile (**3n**, 100 MHz, $CDCl_3$):



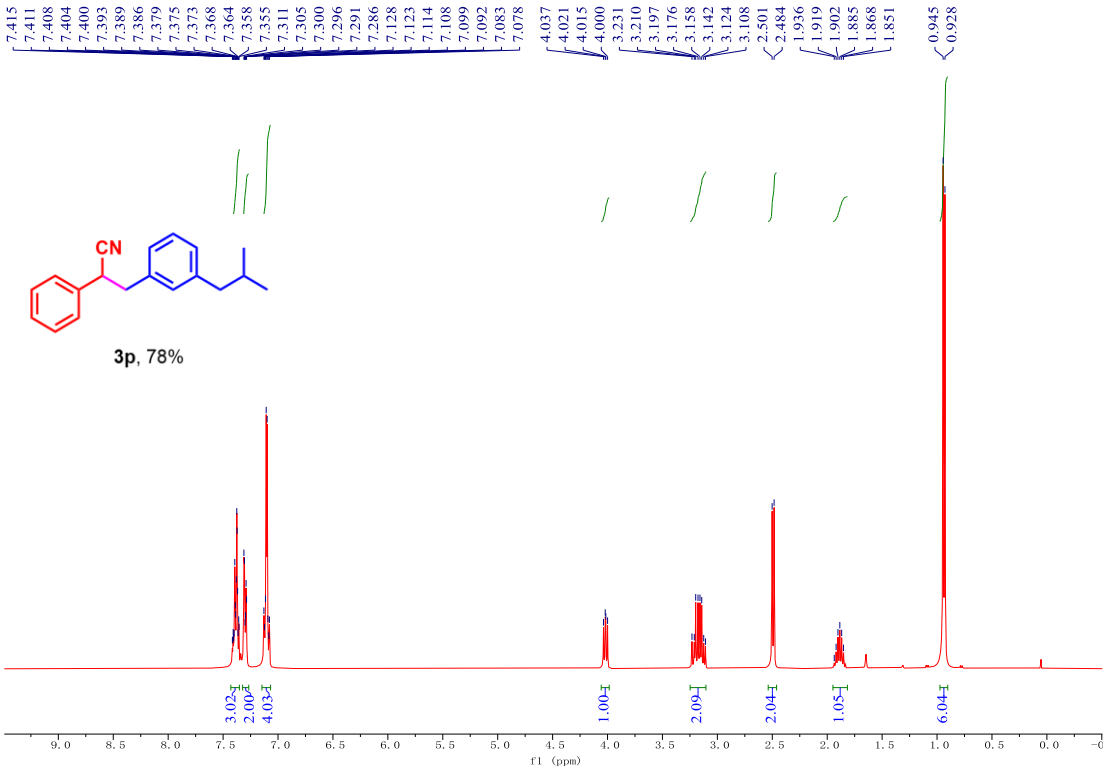
^{1}H NMR spectrum of 2-phenyl-3-(m-tolyl) propanenitrile (**3o**, 400 MHz, $CDCl_3$) :



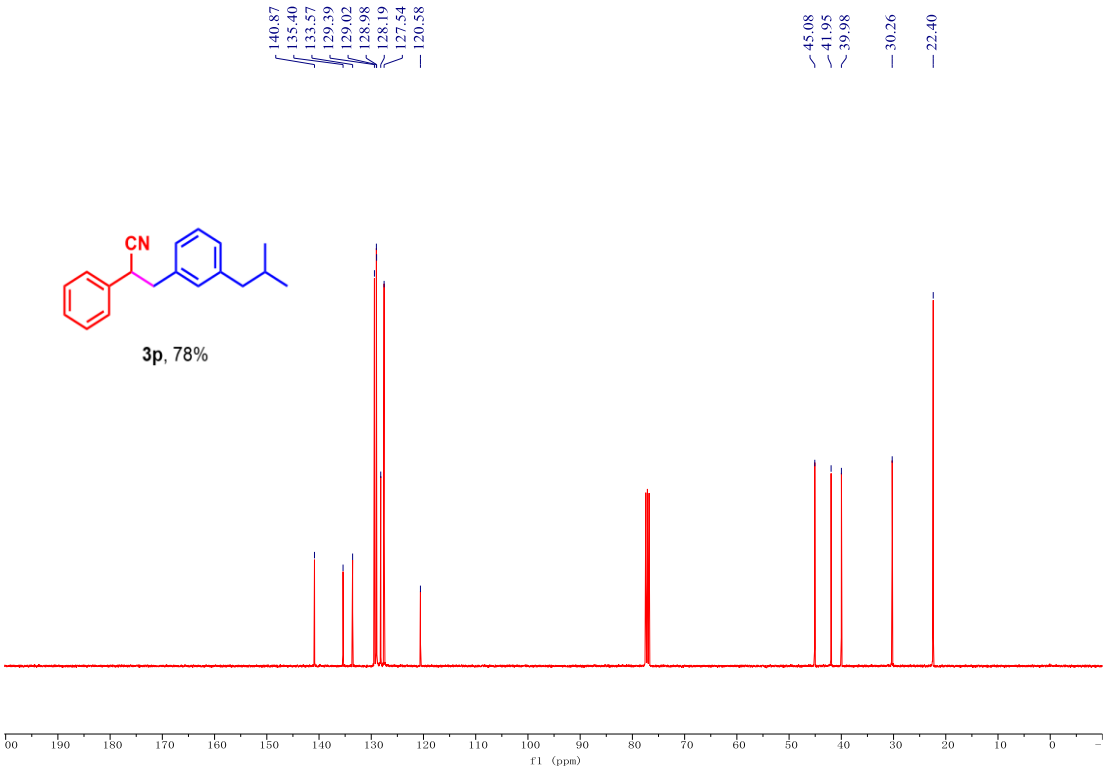
^{13}C NMR spectrum of 2-phenyl-3-(m-tolyl) propanenitrile (**3o**, 100 MHz, $CDCl_3$):



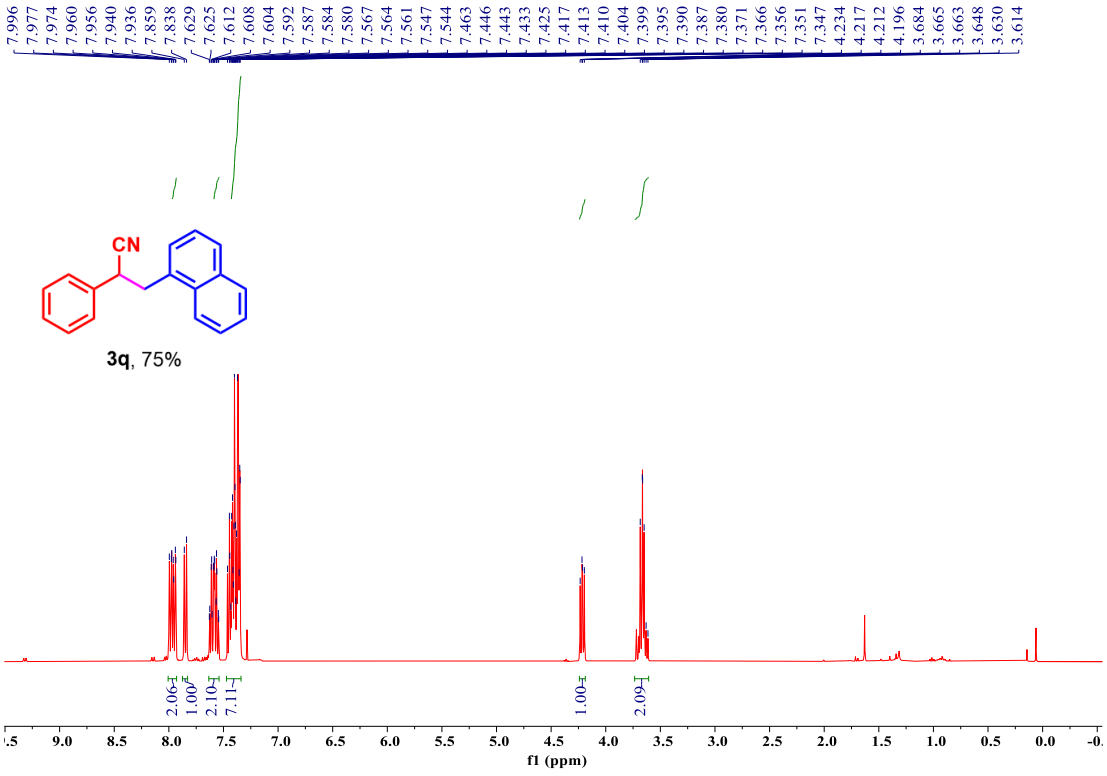
^{1}H NMR spectrum of 3-(4-isobutylphenyl)-2-phenylpropanenitrile (**3p**, 400 MHz, $CDCl_3$) :



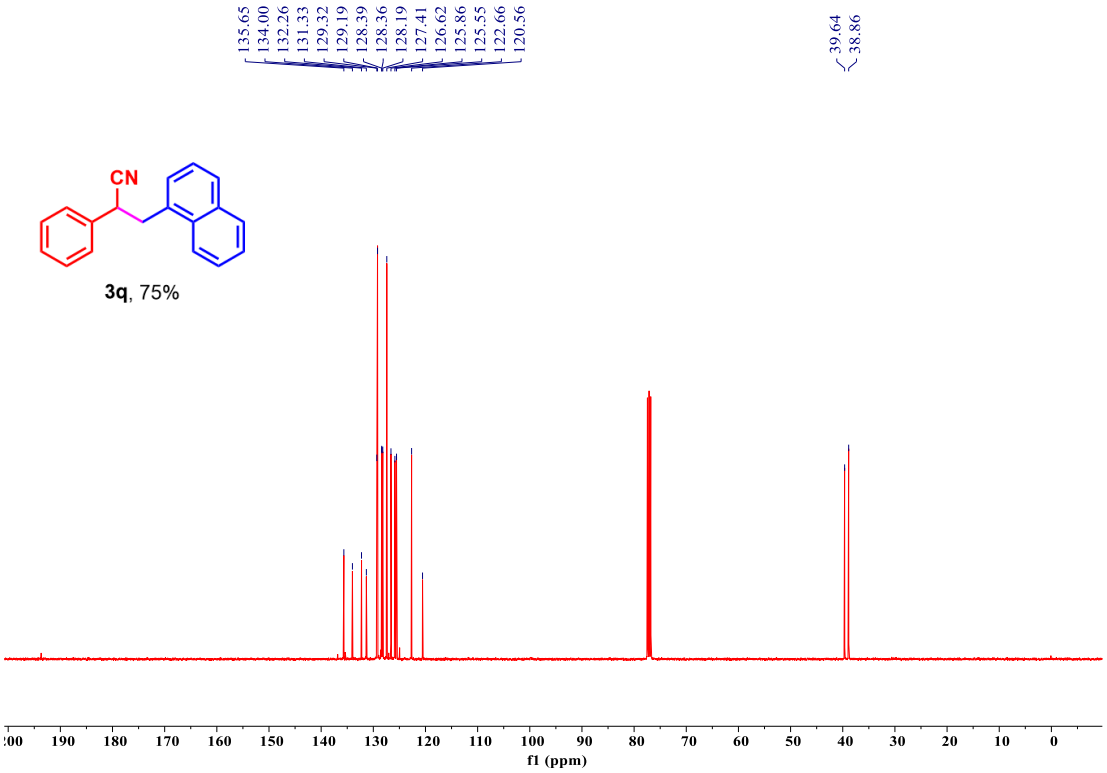
^{13}C NMR spectrum of 3-(4-isobutylphenyl)-2-phenylpropanenitrile (**3p**, 100 MHz, $CDCl_3$):



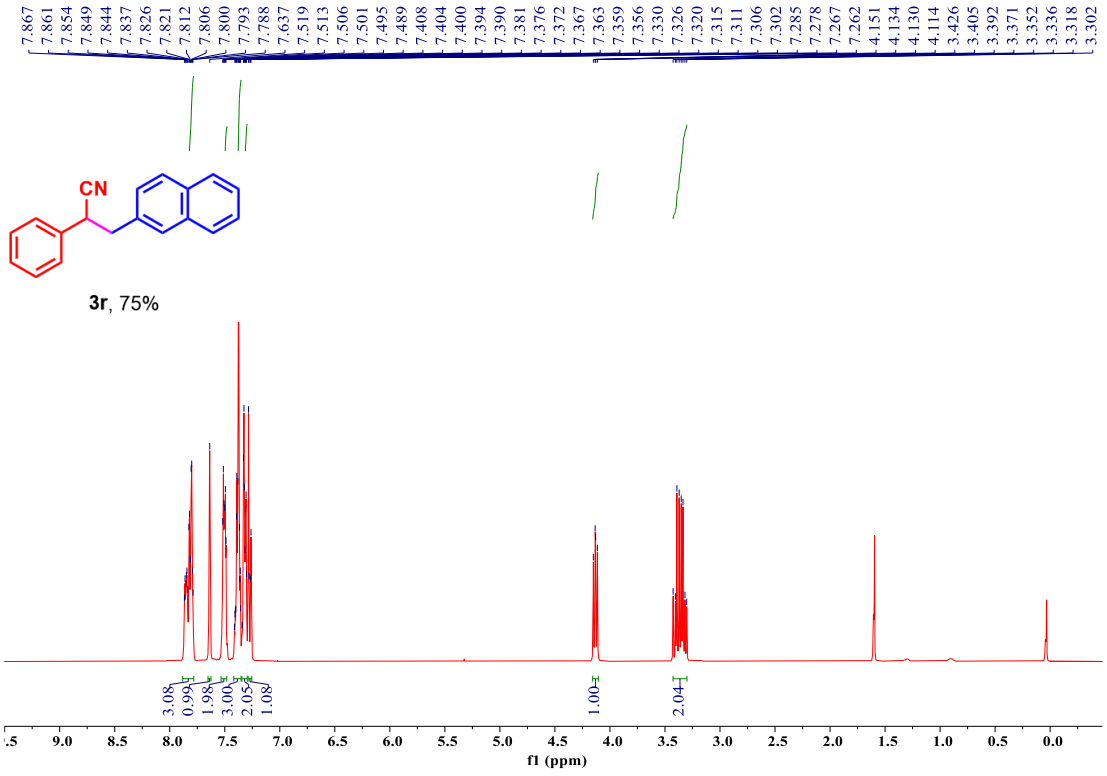
^{1}H NMR spectrum of 3-(naphthalen-1-yl)-2-phenylpropanenitrile (**3q**, 400 MHz, $CDCl_3$) :



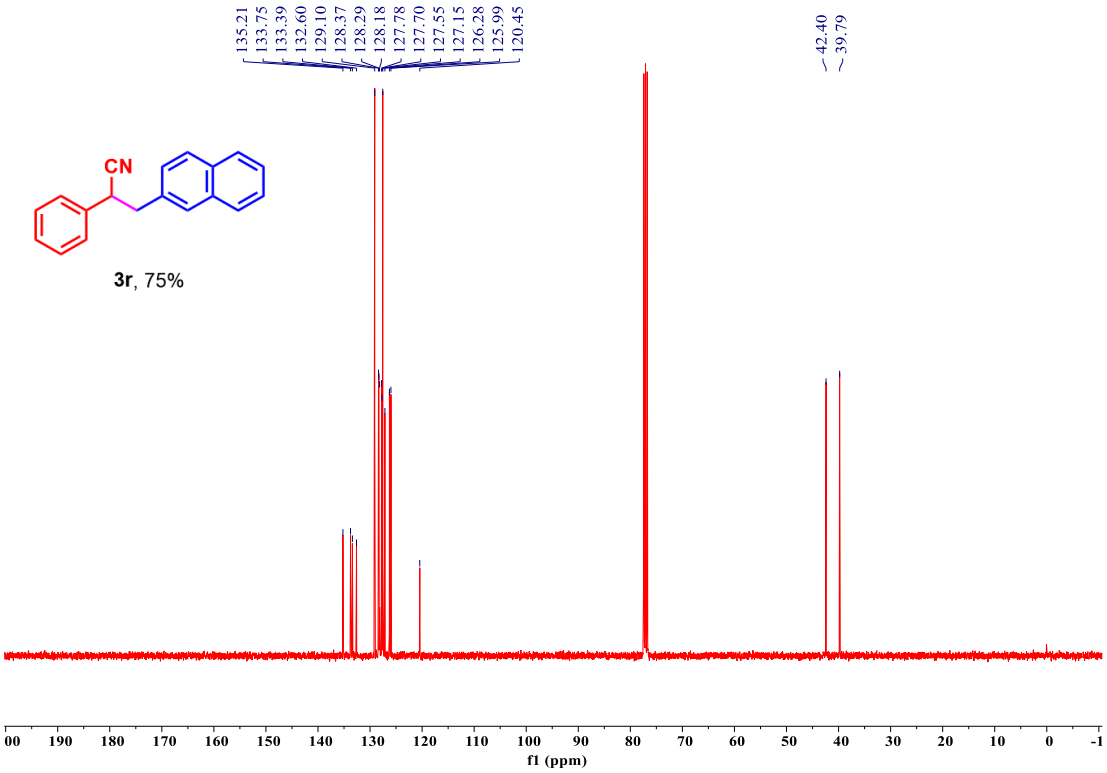
^{13}C NMR spectrum of 3-(naphthalen-1-yl)-2-phenylpropanenitrile (**3q**, 100 MHz, $CDCl_3$):



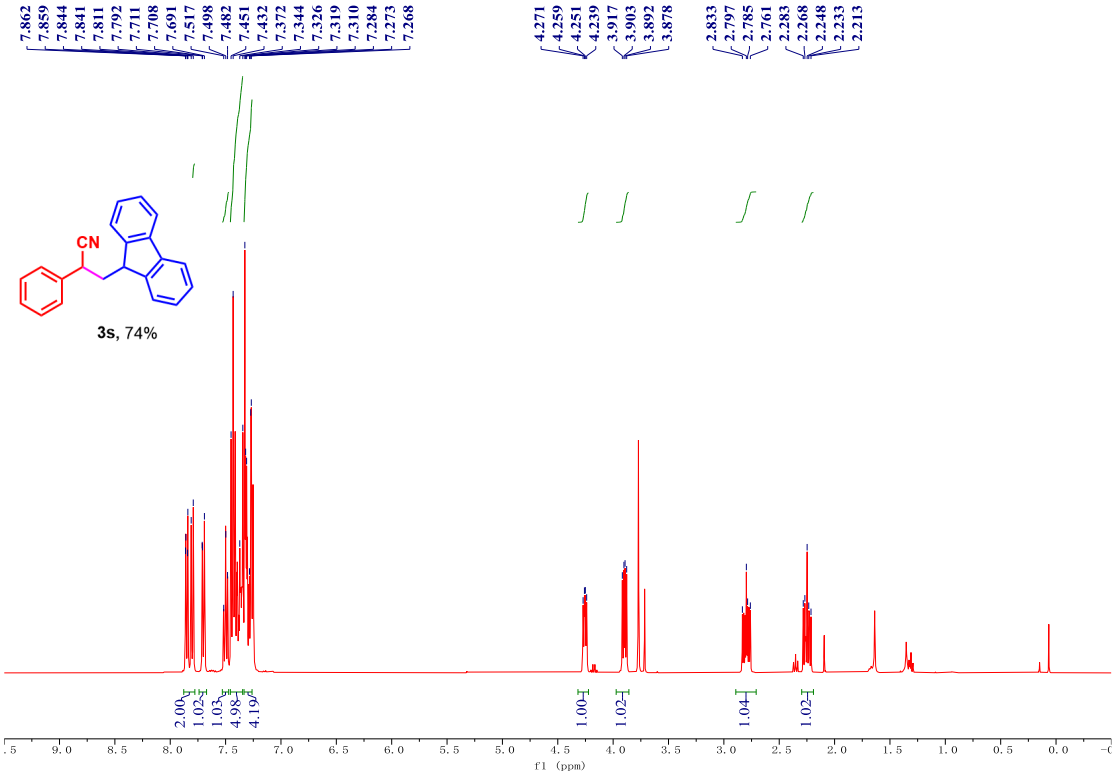
^{1}H NMR spectrum of 3-(naphthalen-2-yl)-2-phenylpropanenitrile (**3r**, 400 MHz, $CDCl_3$) :



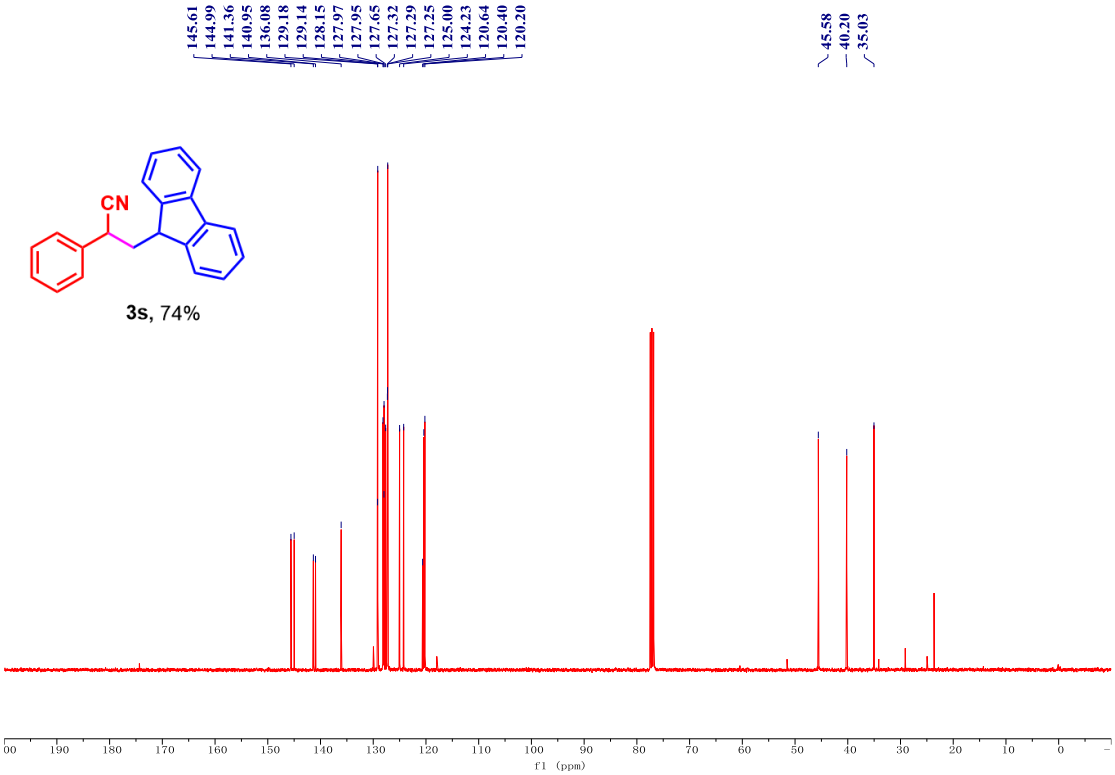
^{13}C NMR spectrum of 3-(naphthalen-2-yl)-2-phenylpropanenitrile (**3r**, 100 MHz, $CDCl_3$):



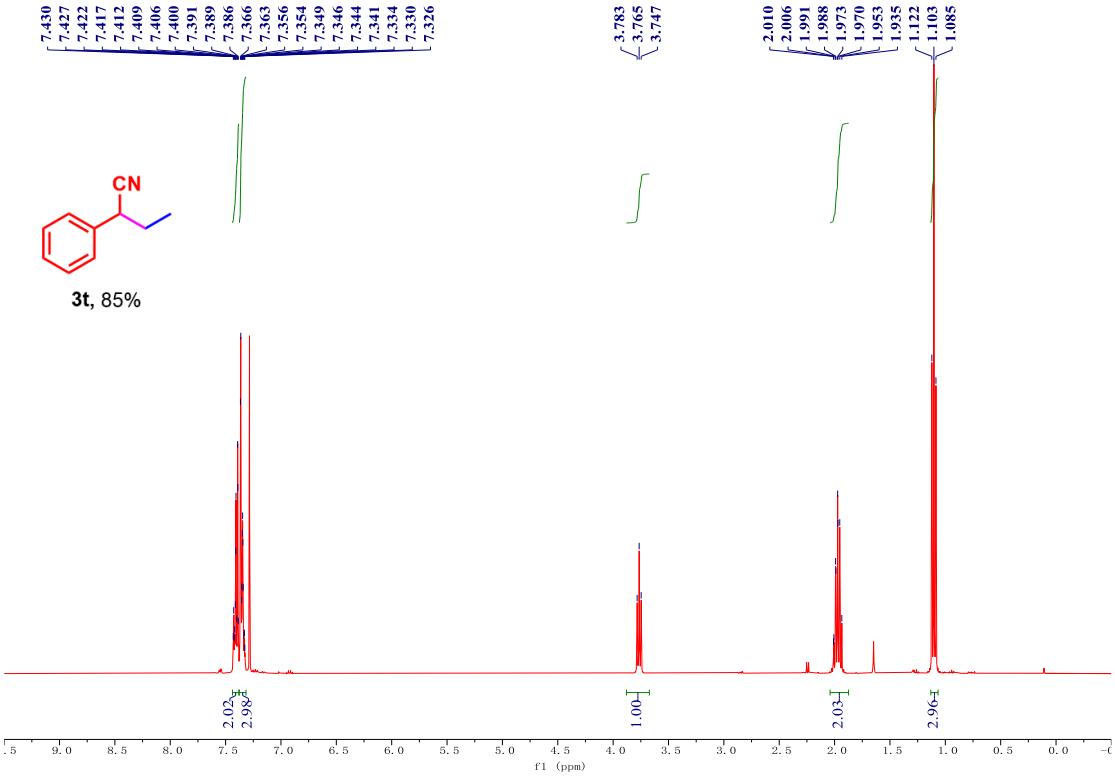
^{1}H NMR spectrum of 3-(9h-fluoren-9-yl)-2-phenylpropanenitrile (**3s**, 400 MHz, $CDCl_3$) :



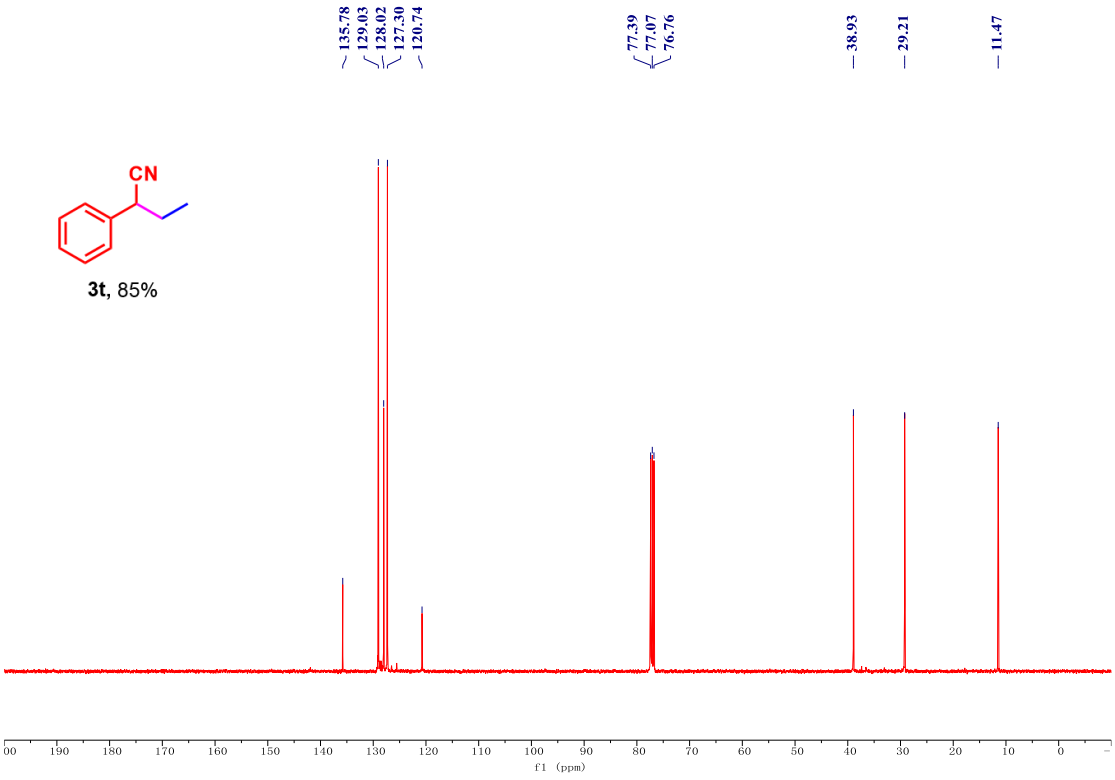
^{13}C NMR spectrum of 3-(9h-fluoren-9-yl)-2-phenylpropanenitrile (**3s**, 100 MHz, $CDCl_3$):



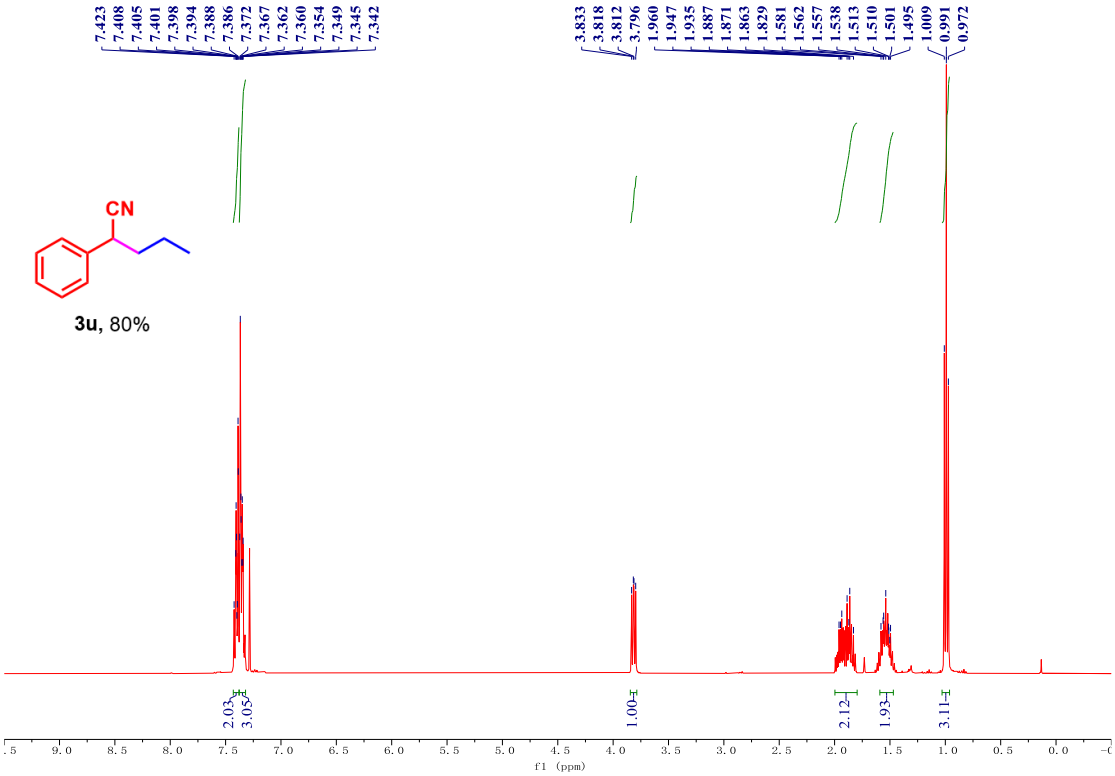
^{1}H NMR spectrum of 2-phenylbutanenitrile (**3t**, 400 MHz, $CDCl_3$) :



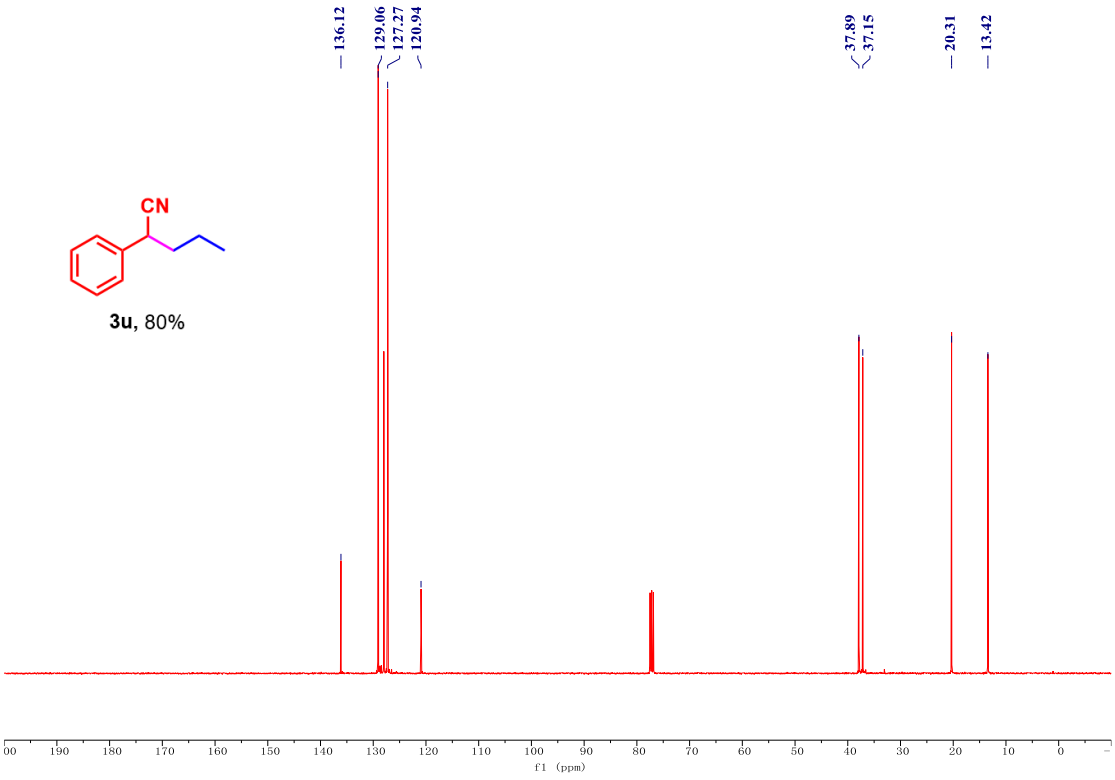
^{13}C NMR spectrum of 2-phenylbutanenitrile (**3t**, 100 MHz, $CDCl_3$):



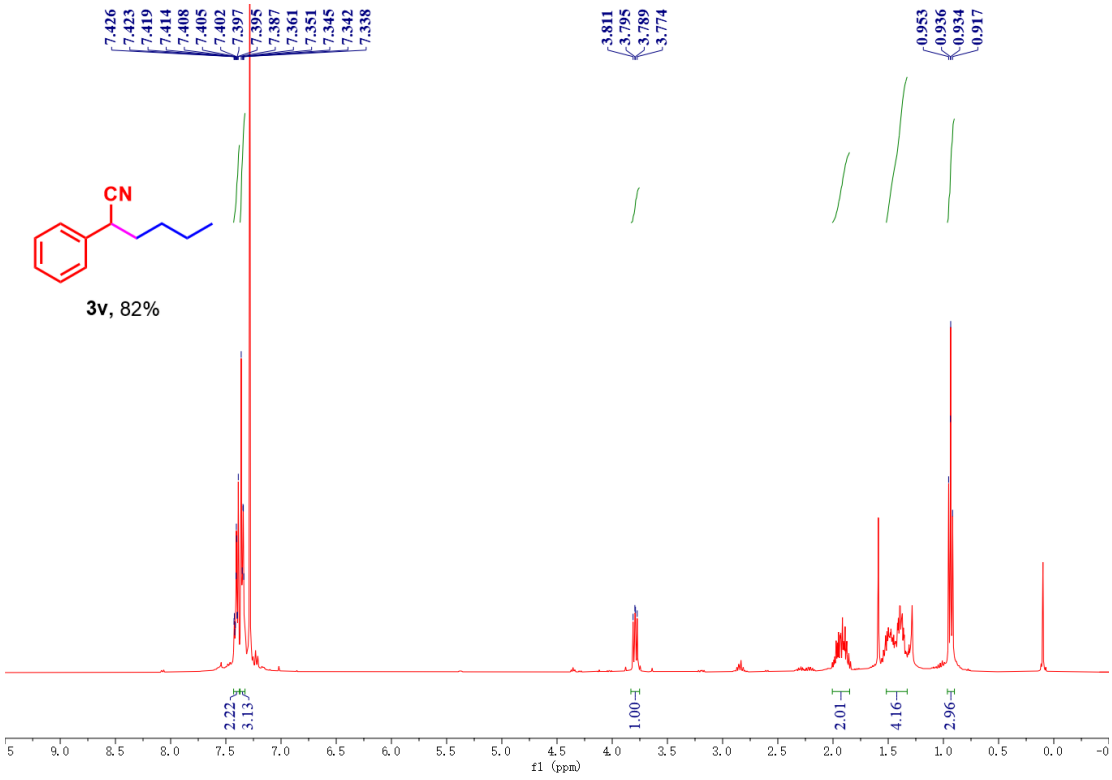
^{1}H NMR spectrum of 2-phenylpentanenitrile (**3u**, 400 MHz, $CDCl_3$) :



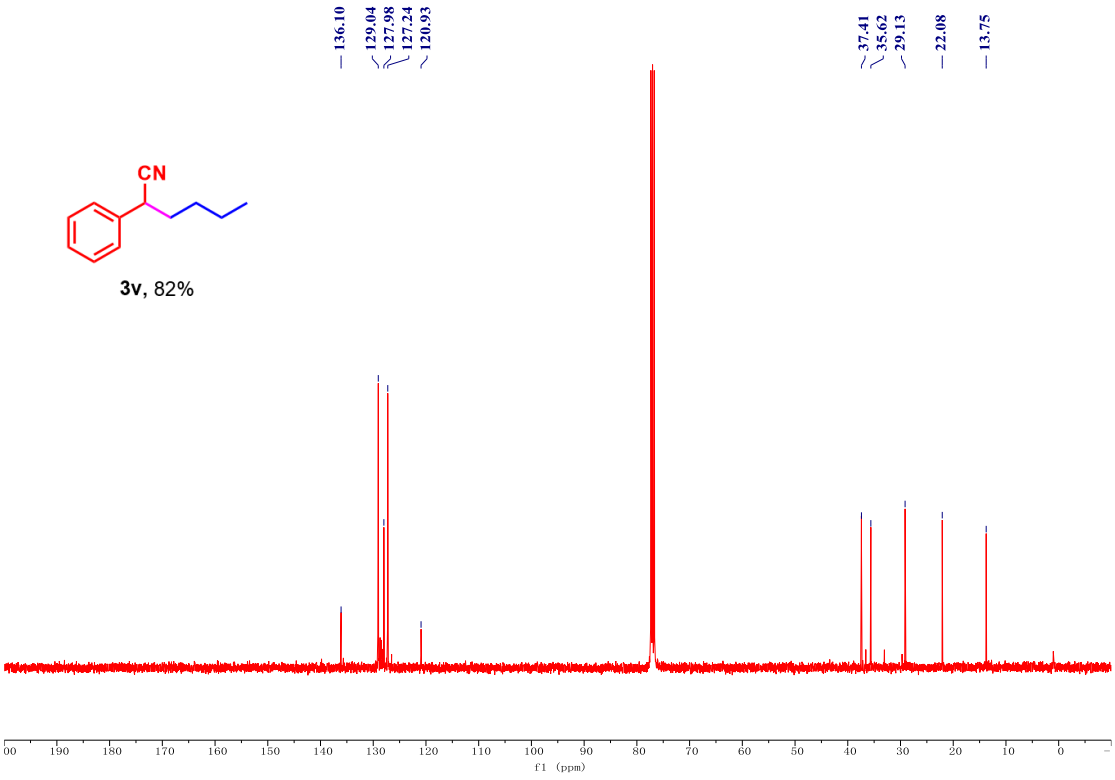
^{13}C NMR spectrum of 2-phenylpentanenitrile (**3u**, 100 MHz, $CDCl_3$):



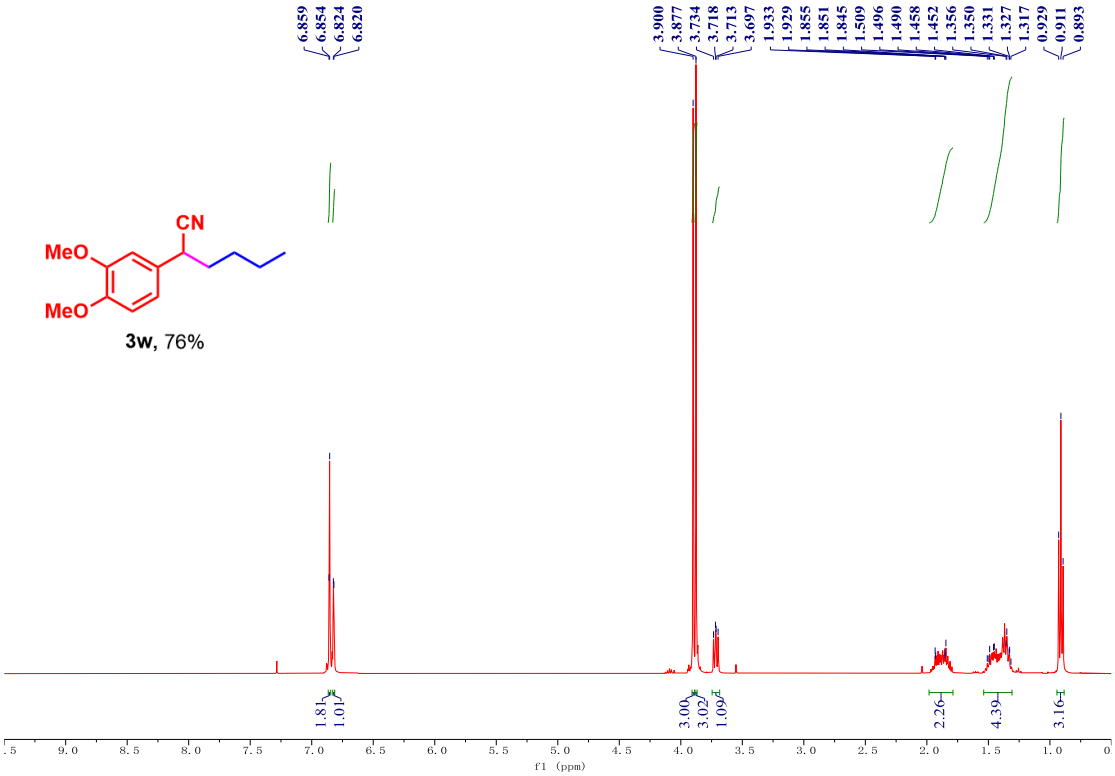
^{1}H NMR spectrum of 2-phenylhexanenitrile (**3v**, 400 MHz, $CDCl_3$) :



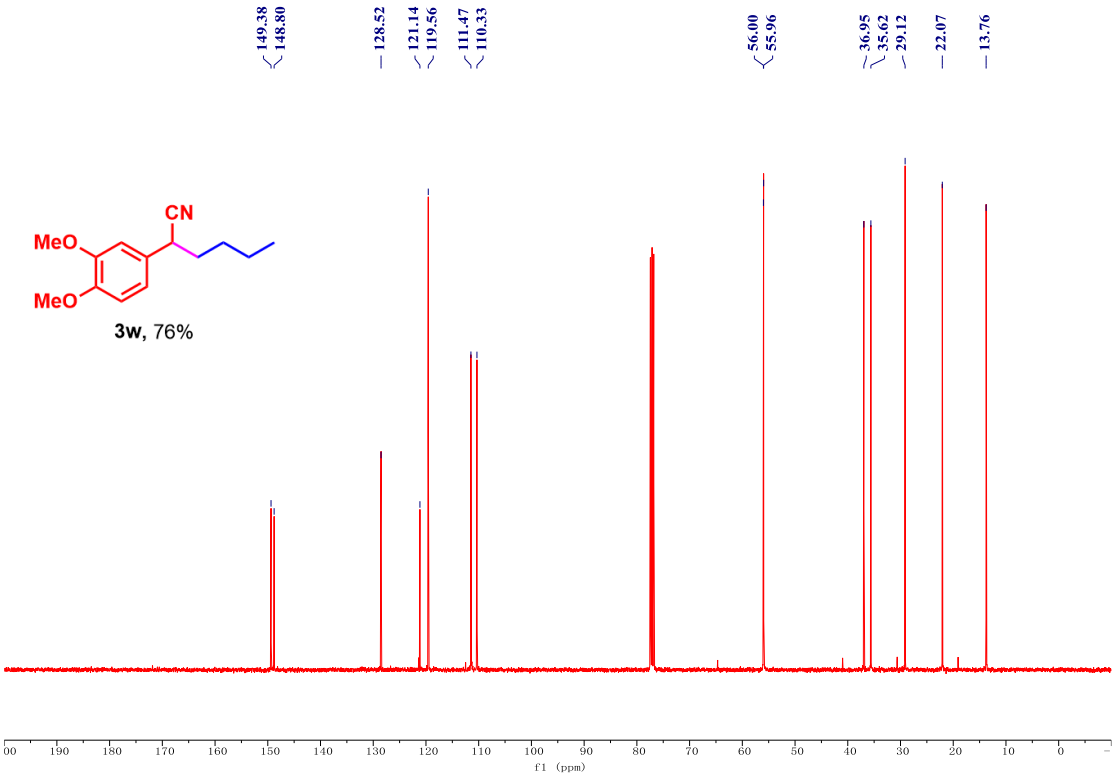
^{13}C NMR spectrum of 2-phenylhexanenitrile (**3v**, 100 MHz, $CDCl_3$):



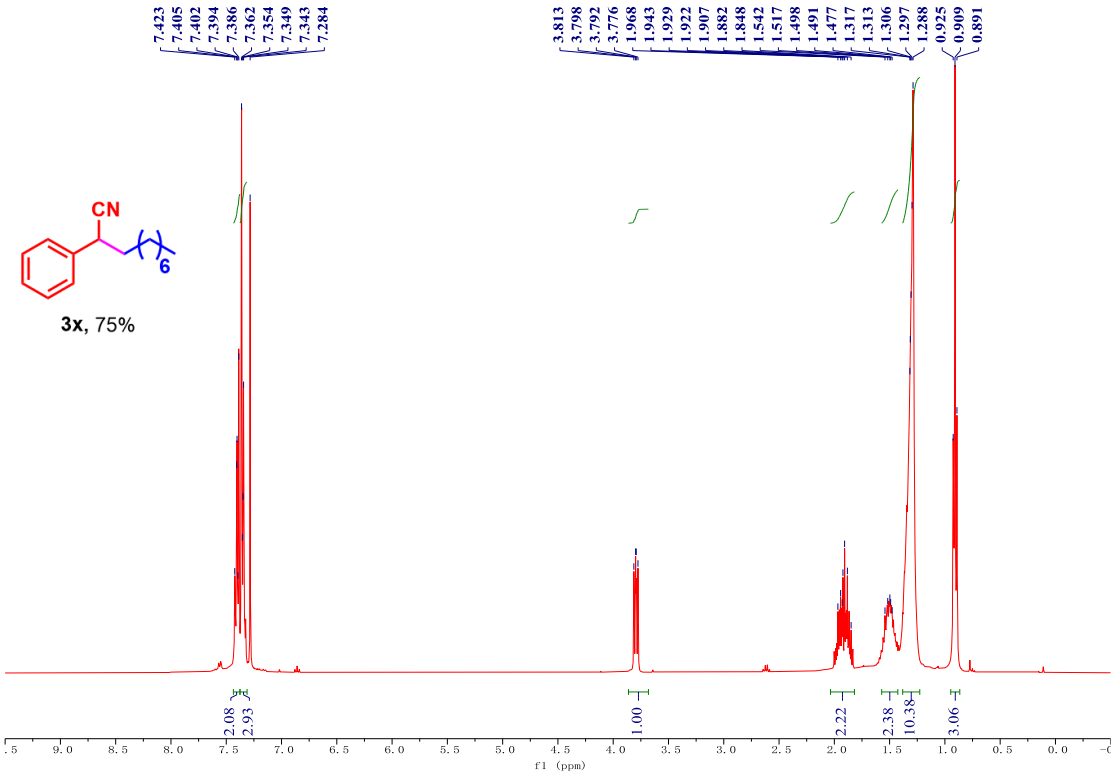
^{1}H NMR spectrum of 2-(3,4-dimethoxyphenyl) hexanenitrile (**3w**, 400 MHz, $CDCl_3$) :



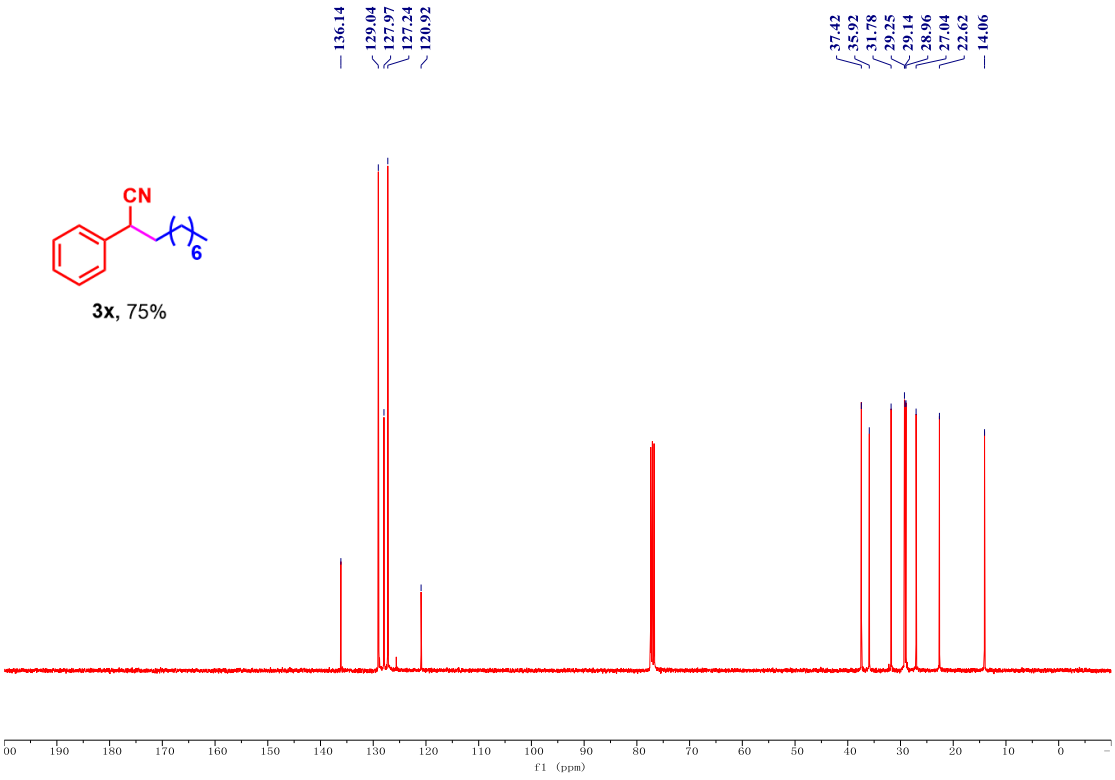
^{13}C NMR spectrum of 2-(3,4-dimethoxyphenyl) hexanenitrile (**3w**, 100 MHz, $CDCl_3$):



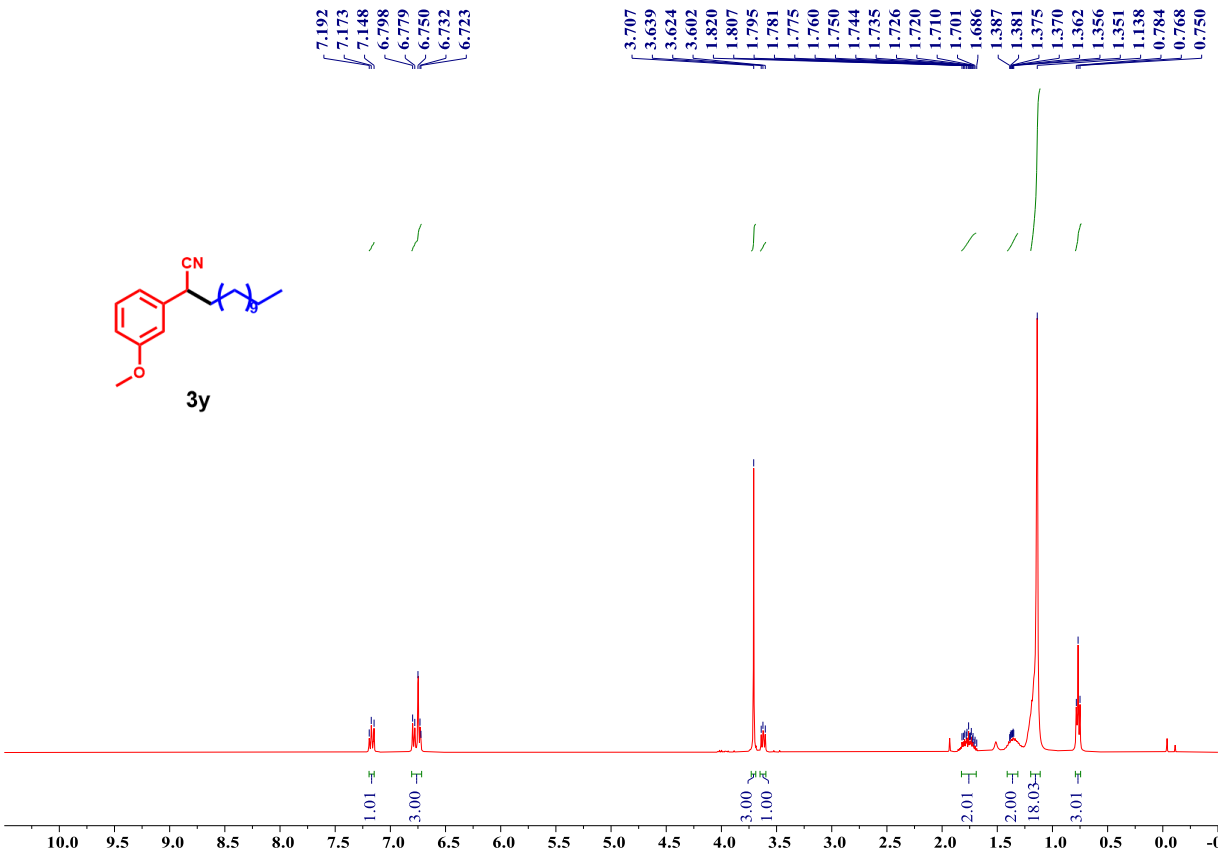
^{1}H NMR spectrum of 2-phenyldecanenitrile (**3x**, 400 MHz, $CDCl_3$) :



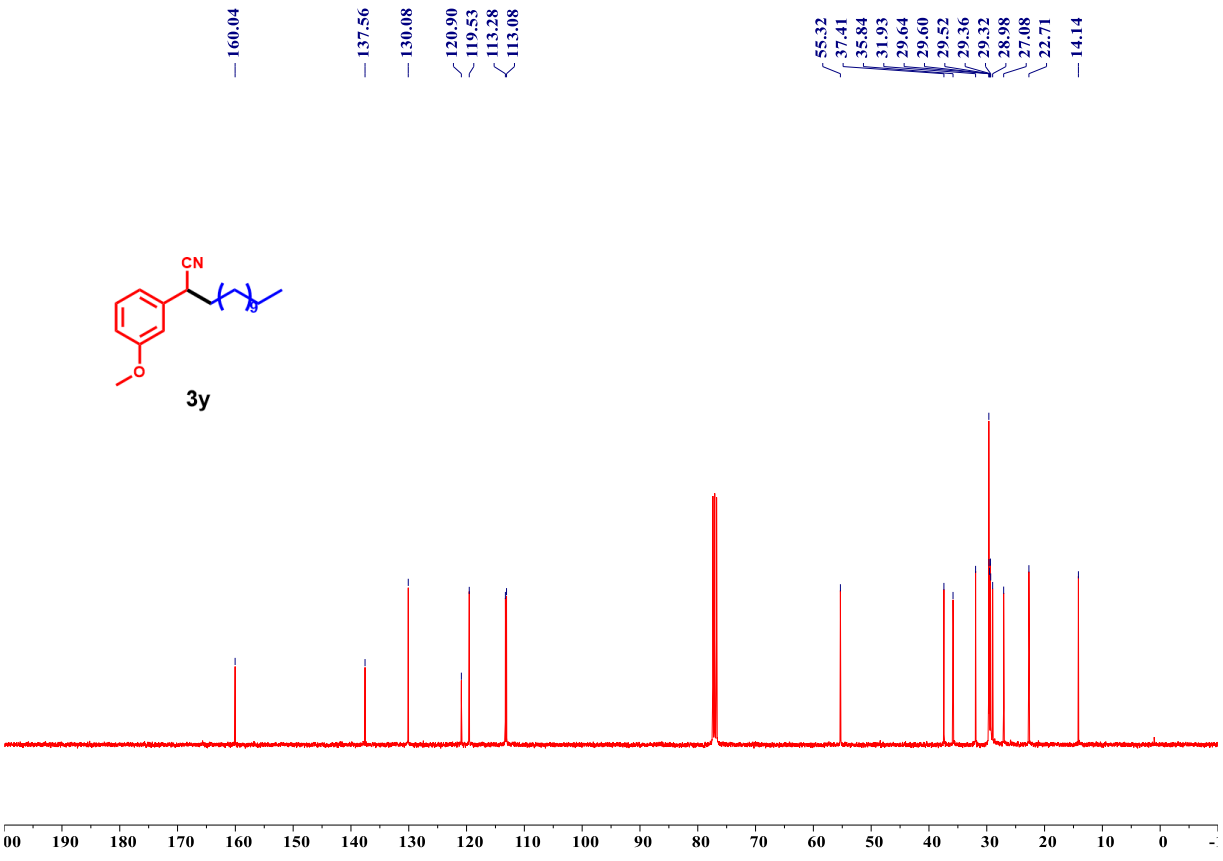
^{13}C NMR spectrum of 2-phenyldecanenitrile (**3x**, 100 MHz, $CDCl_3$):



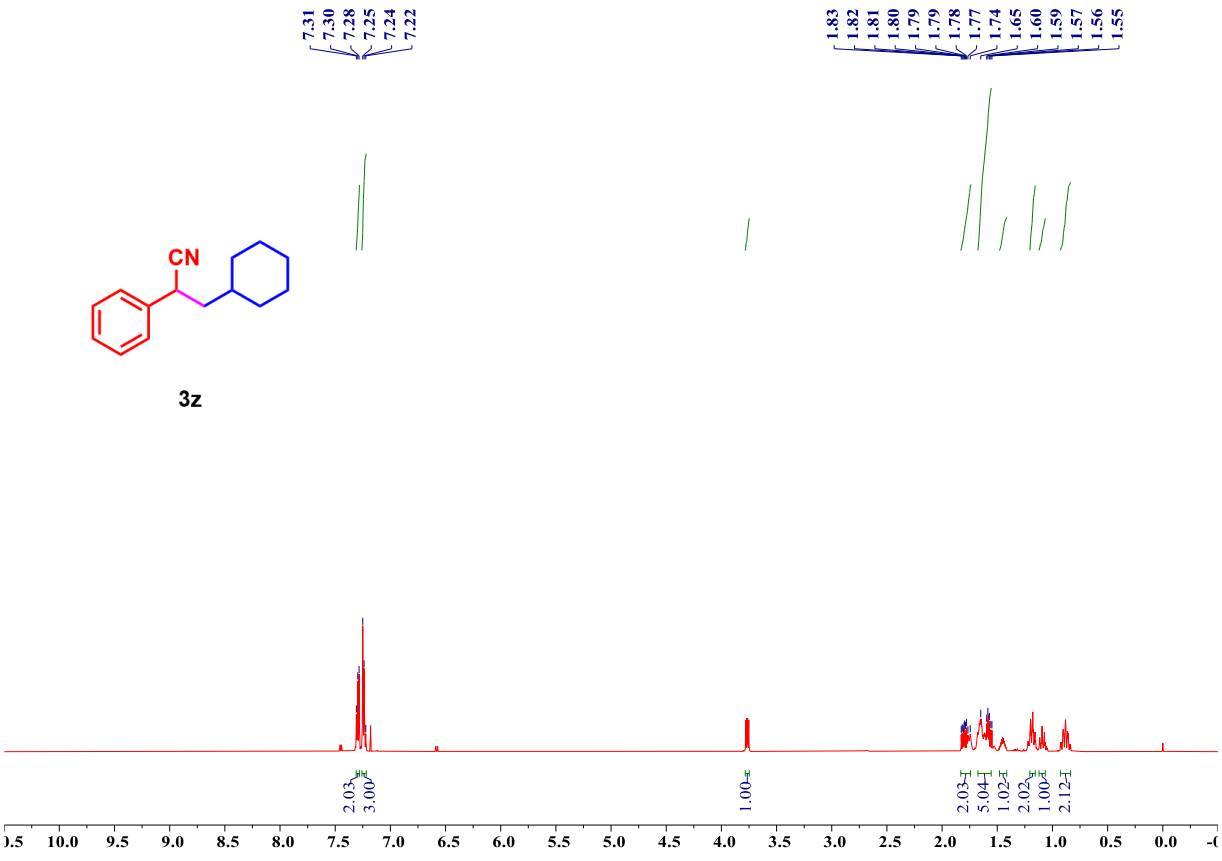
^{1}H NMR spectrum of 2-(3-methoxyphenyl) tetradecanenitrile (**3y**, 400 MHz, $CDCl_3$):



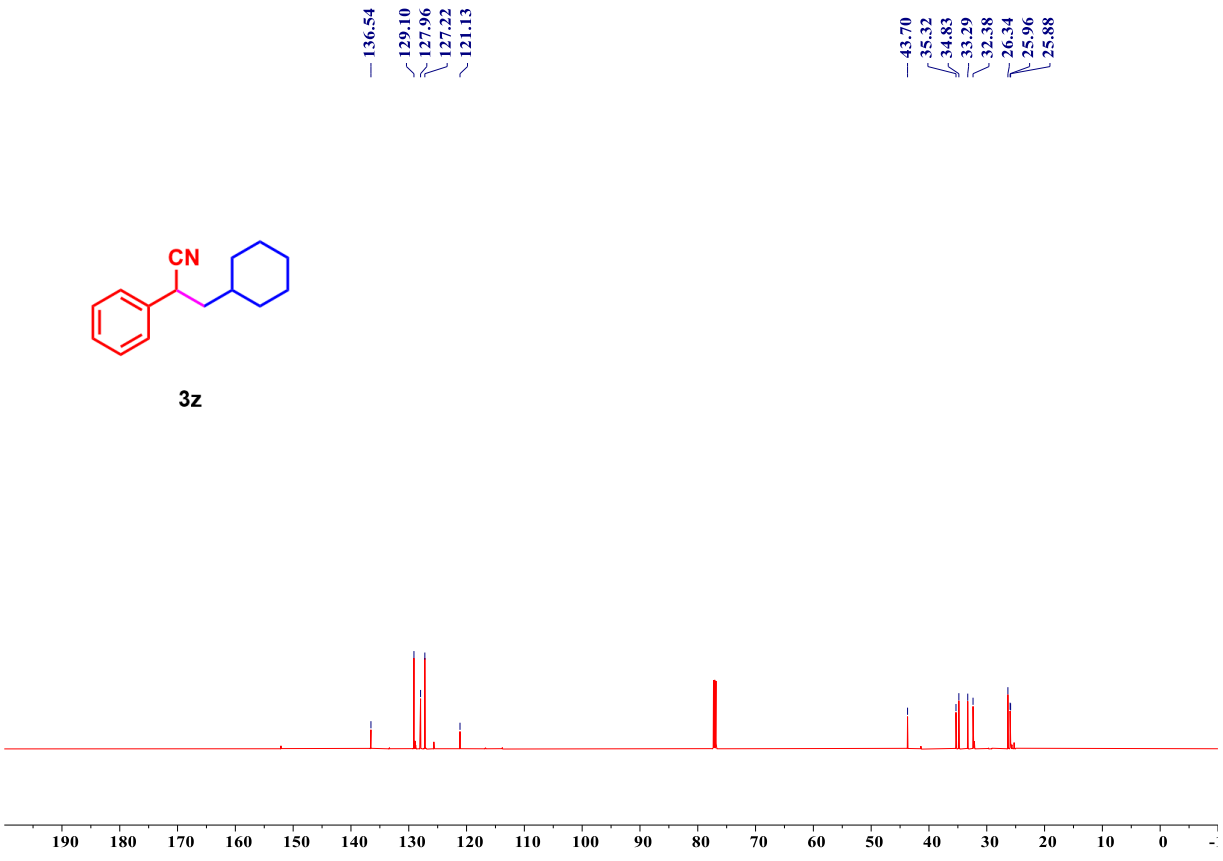
^{13}C NMR spectrum of 2-(3-methoxyphenyl) tetradecanenitrile (**3y**, 100 MHz, $CDCl_3$):



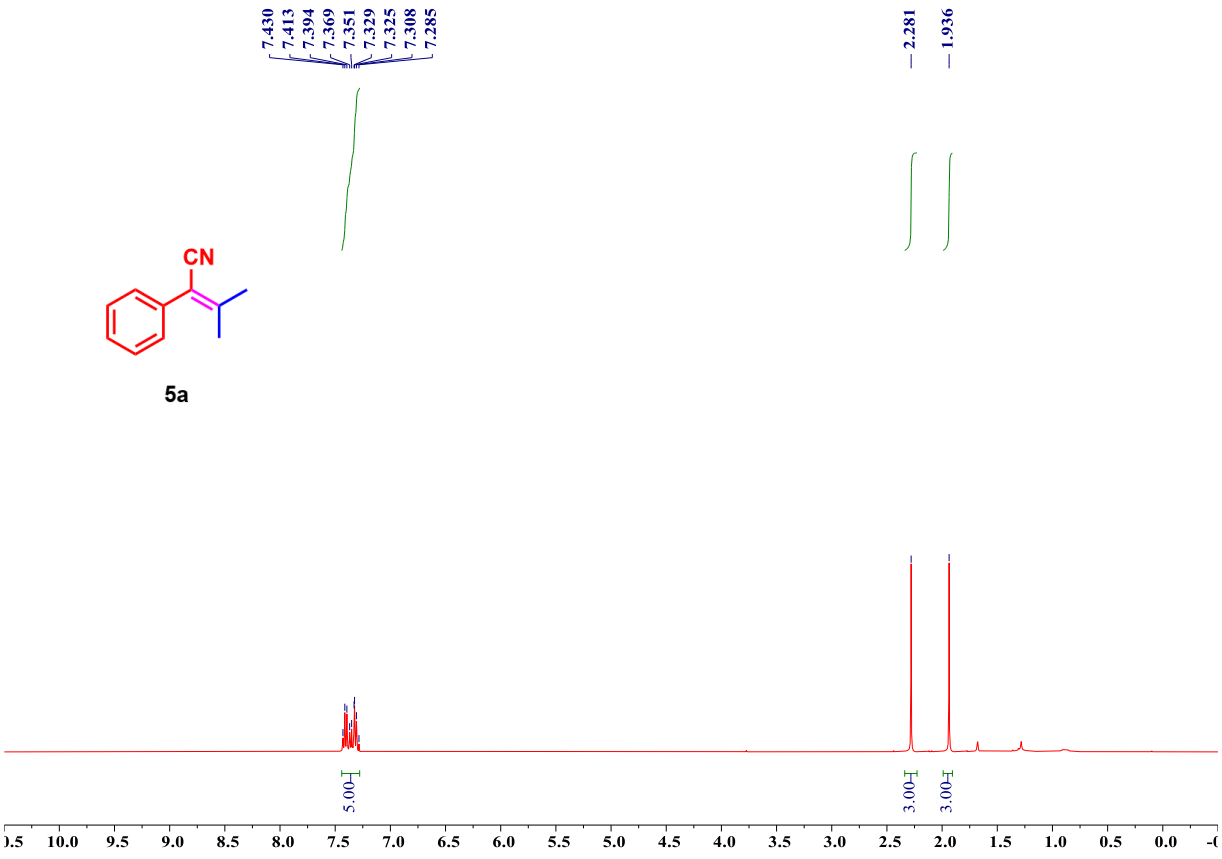
^{1}H NMR spectrum of 2-cyclohexyl-2-phenylacetonitrile (**3z**, 600 MHz, $CDCl_3$) :



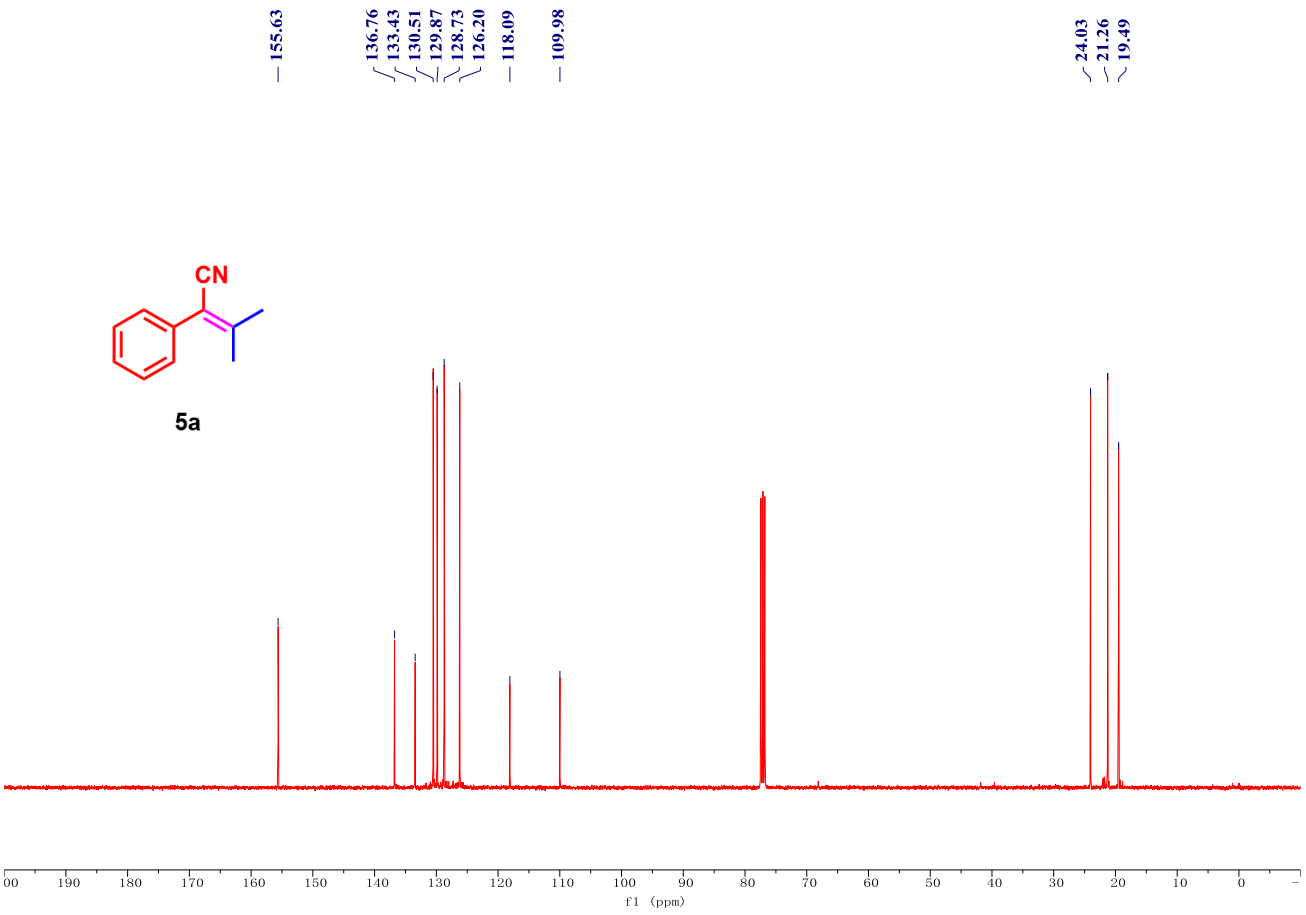
^{13}C NMR spectrum of 2-cyclohexyl-2-phenylacetonitrile (**3z**, 150 MHz, $CDCl_3$):



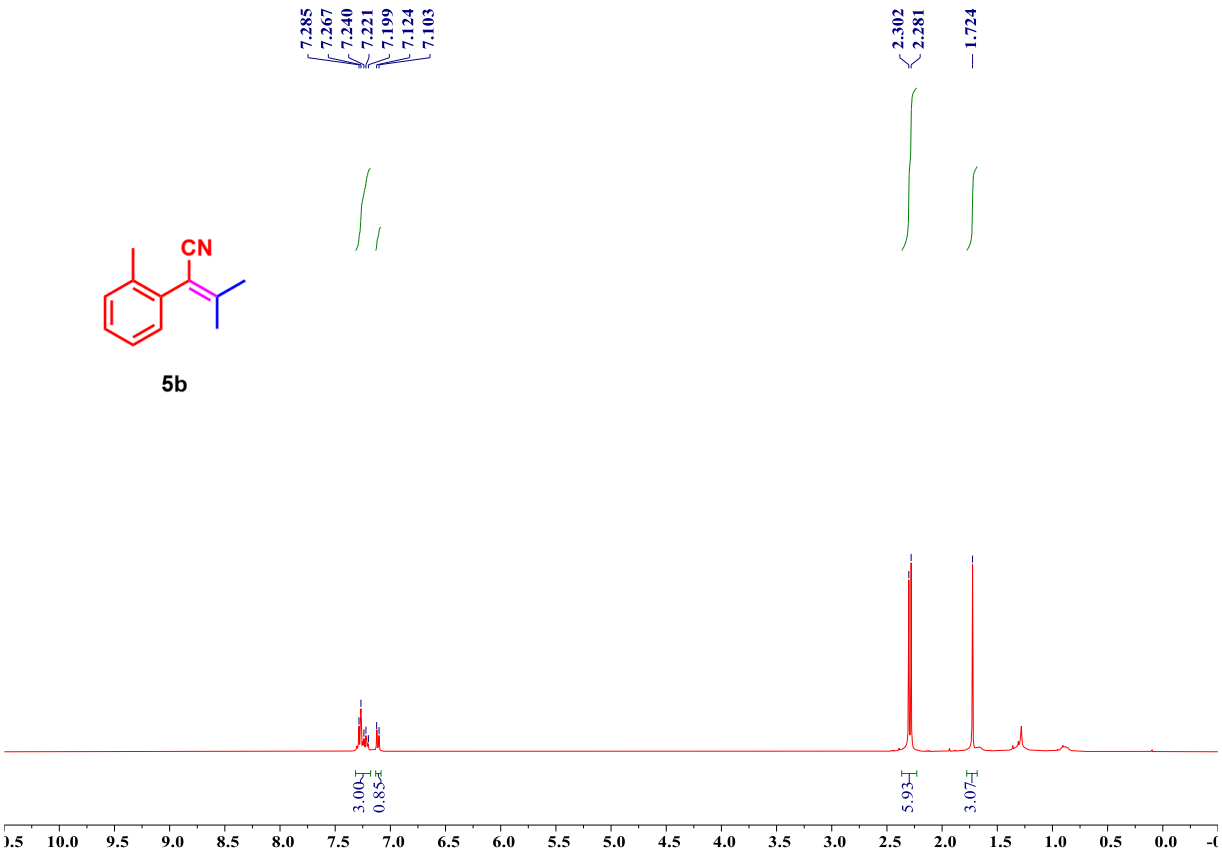
^{1}H NMR spectrum of 3-methyl-2-phenylbut-2-enenitrile (**5a**, 400 MHz, $CDCl_3$) :



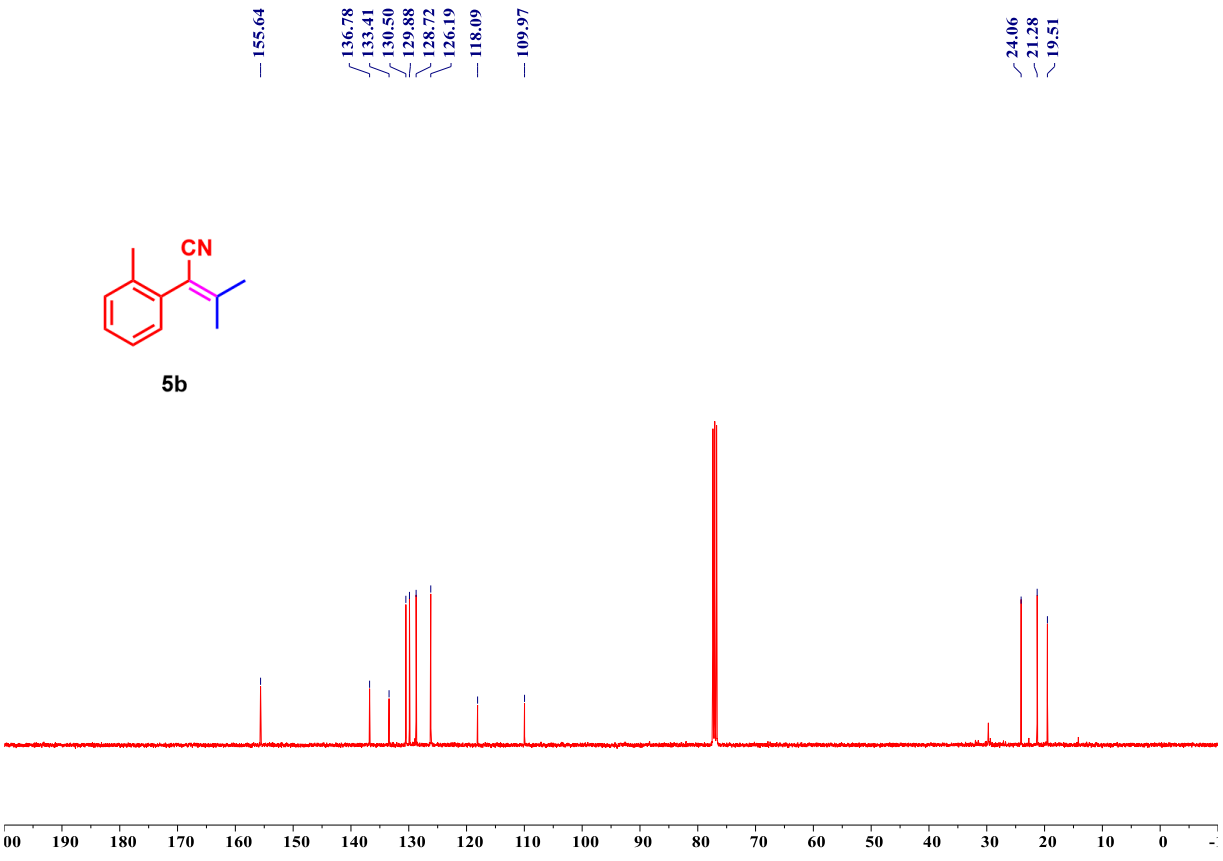
^{13}C NMR spectrum of 3-methyl-2-phenylbut-2-enenitrile (**5a**, 100 MHz, $CDCl_3$):



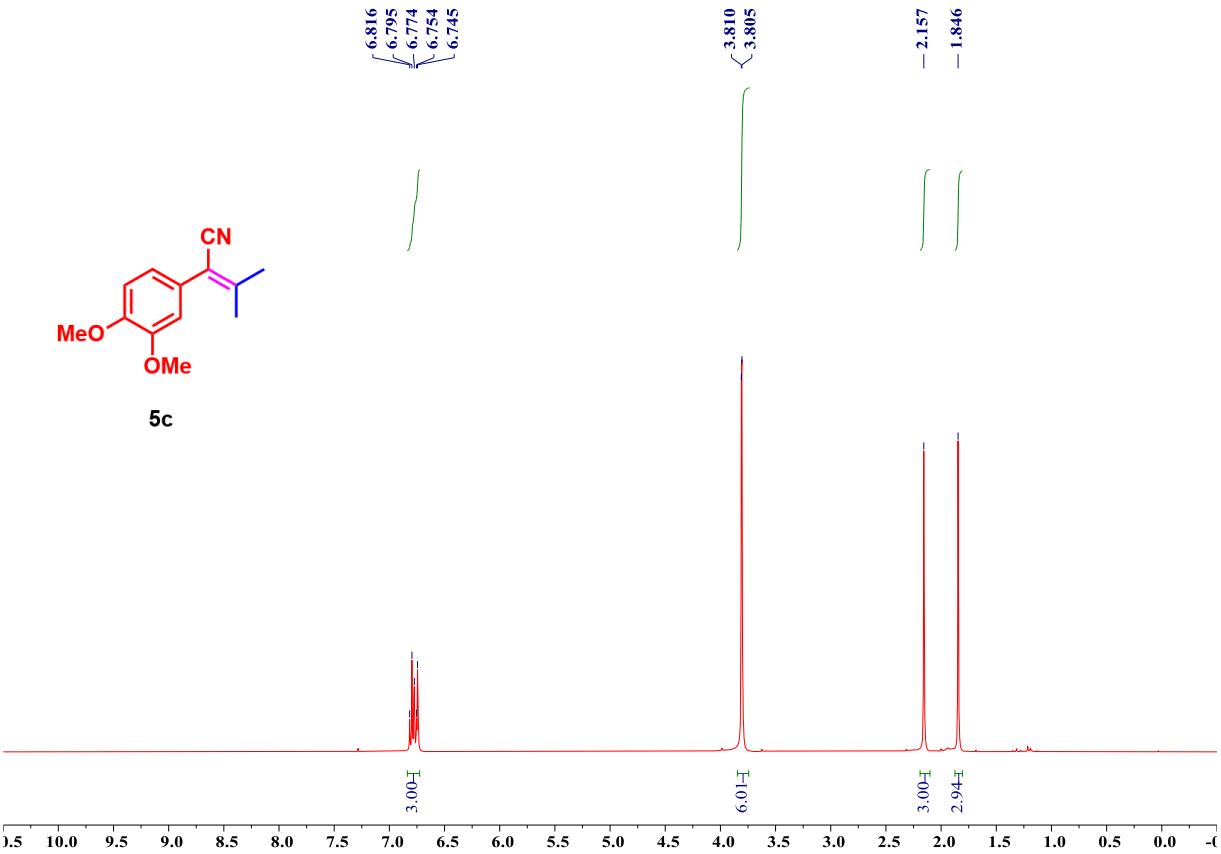
^{1}H NMR spectrum of 3-methyl-2-(o-tolyl) but-2-enenitrile (**5b**, 400 MHz, $CDCl_3$) :



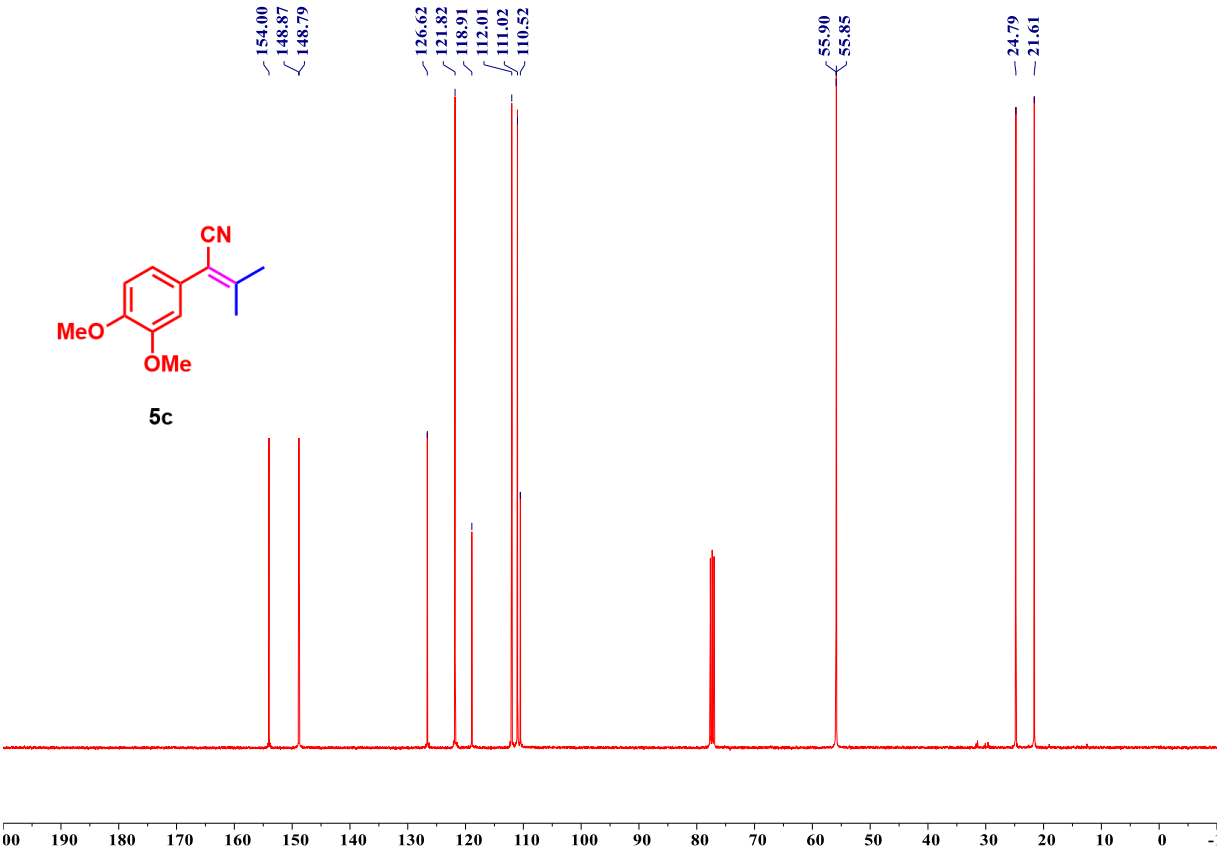
^{13}C NMR spectrum of 3-methyl-2-(o-tolyl) but-2-enenitrile (**5b**, 100 MHz, $CDCl_3$):



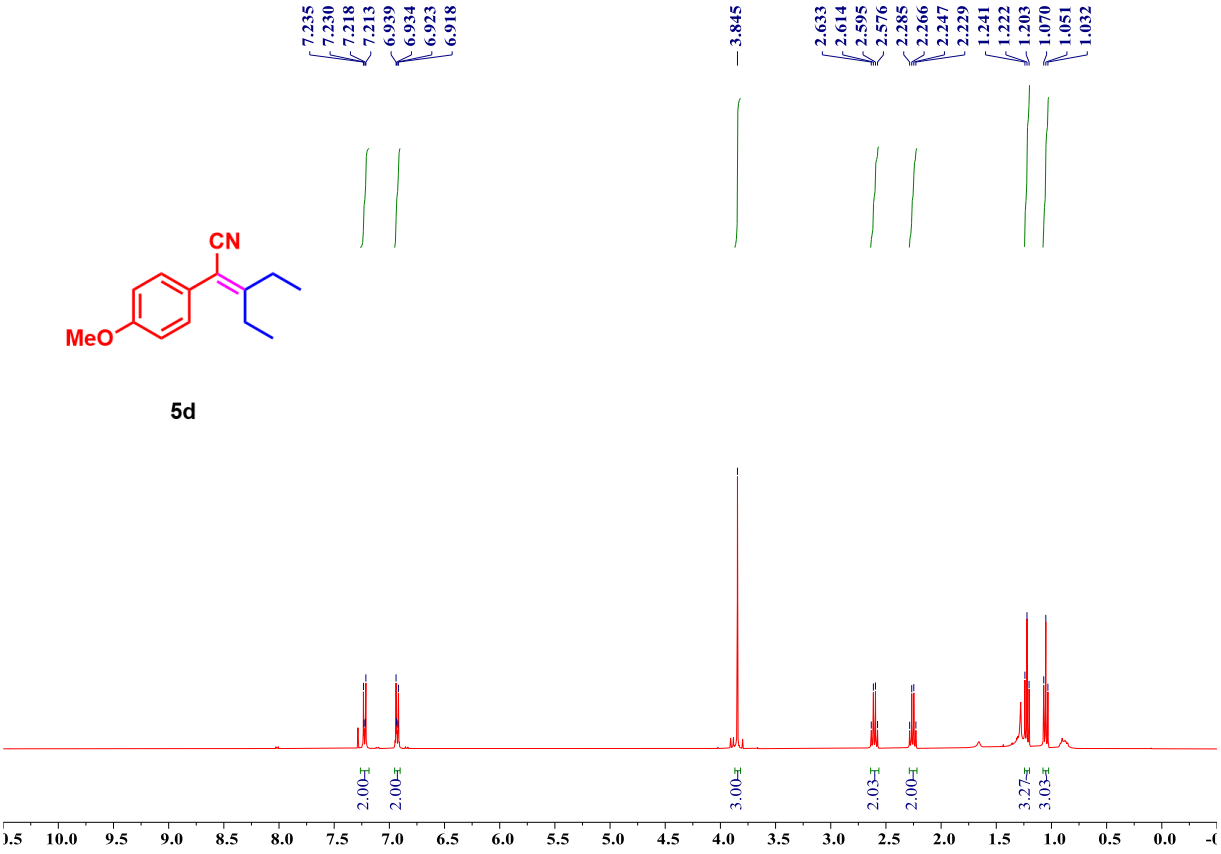
^{1}H NMR spectrum of 2-(3,4-dimethoxyphenyl)-3-methylbut-2-enenitrile (**5c**, 400 MHz, $CDCl_3$)



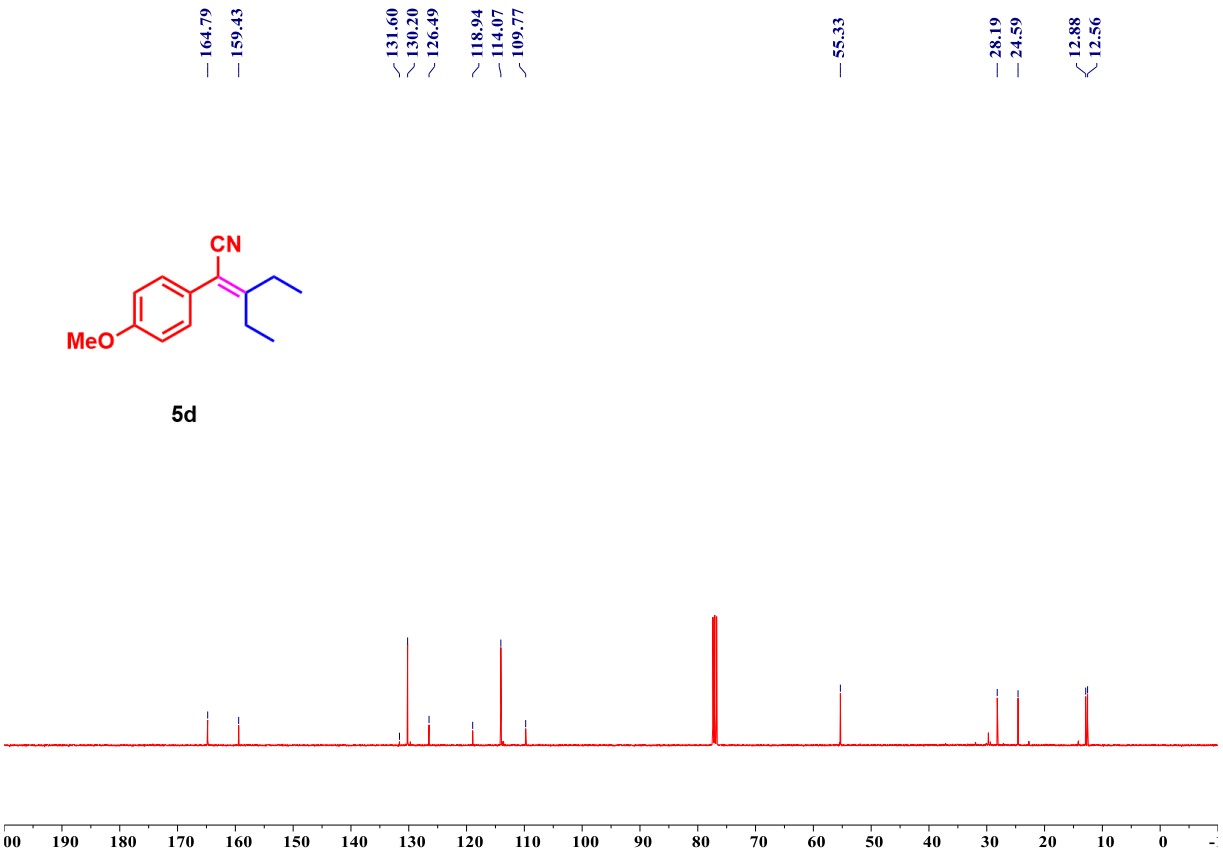
^{13}C NMR spectrum of 2-(3,4-dimethoxyphenyl)-3-methylbut-2-enenitrile (**5c**, 100 MHz, $CDCl_3$):



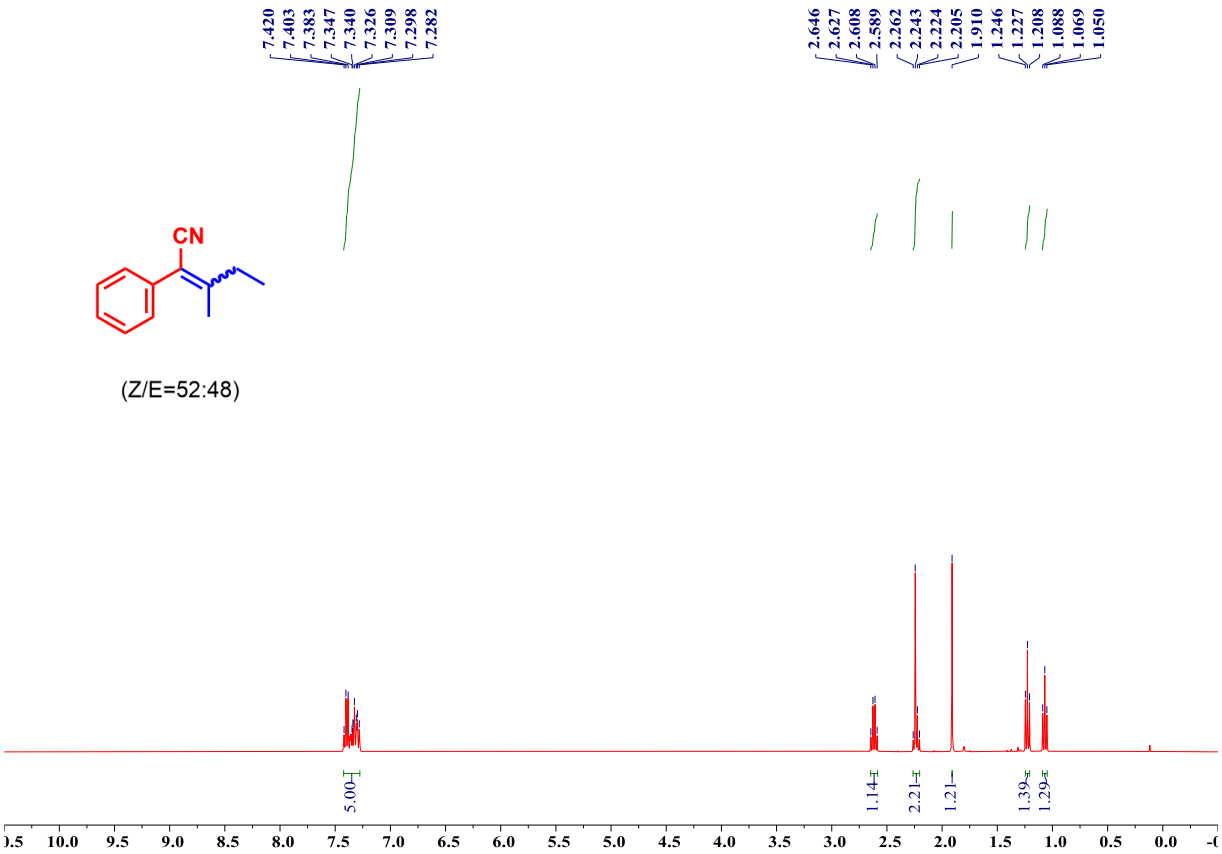
^{1}H NMR spectrum of 3-Ethyl-2-(4-methoxyphenyl)pent-2-enenitrile (**5d**, 100 MHz, $CDCl_3$):



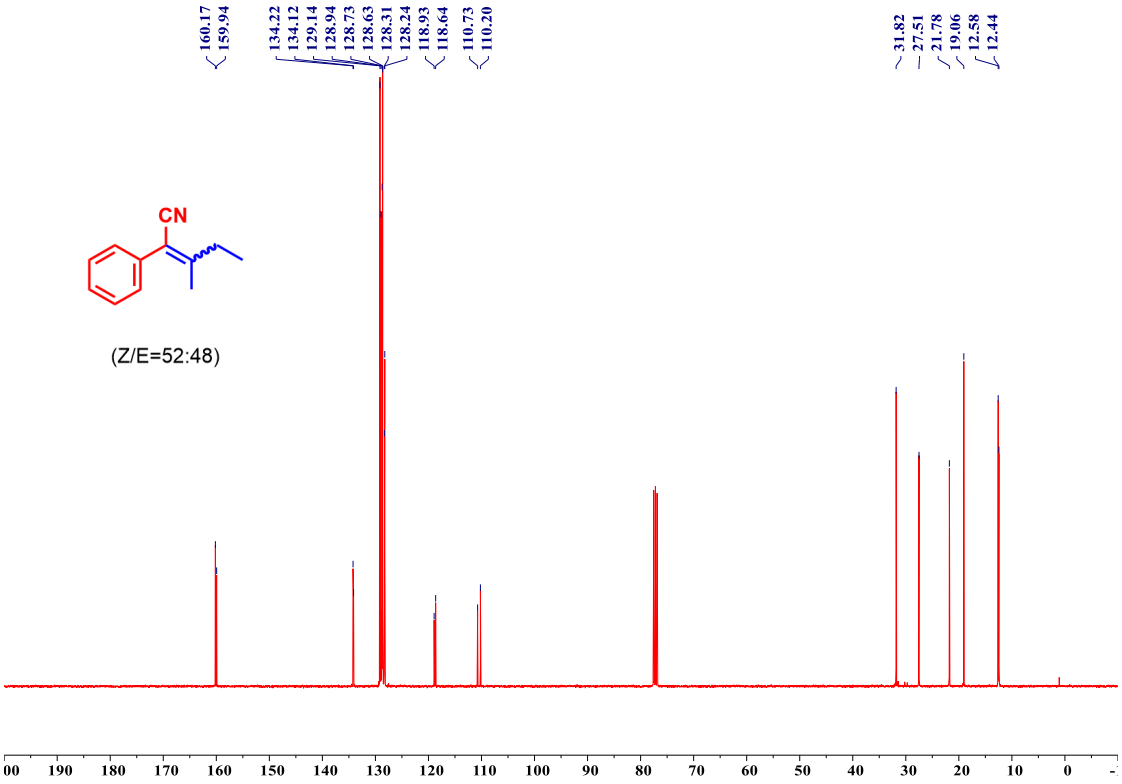
^{13}C NMR spectrum of 3-Ethyl-2-(4-methoxyphenyl)pent-2-enenitrile (**5d**, 100 MHz, $CDCl_3$):



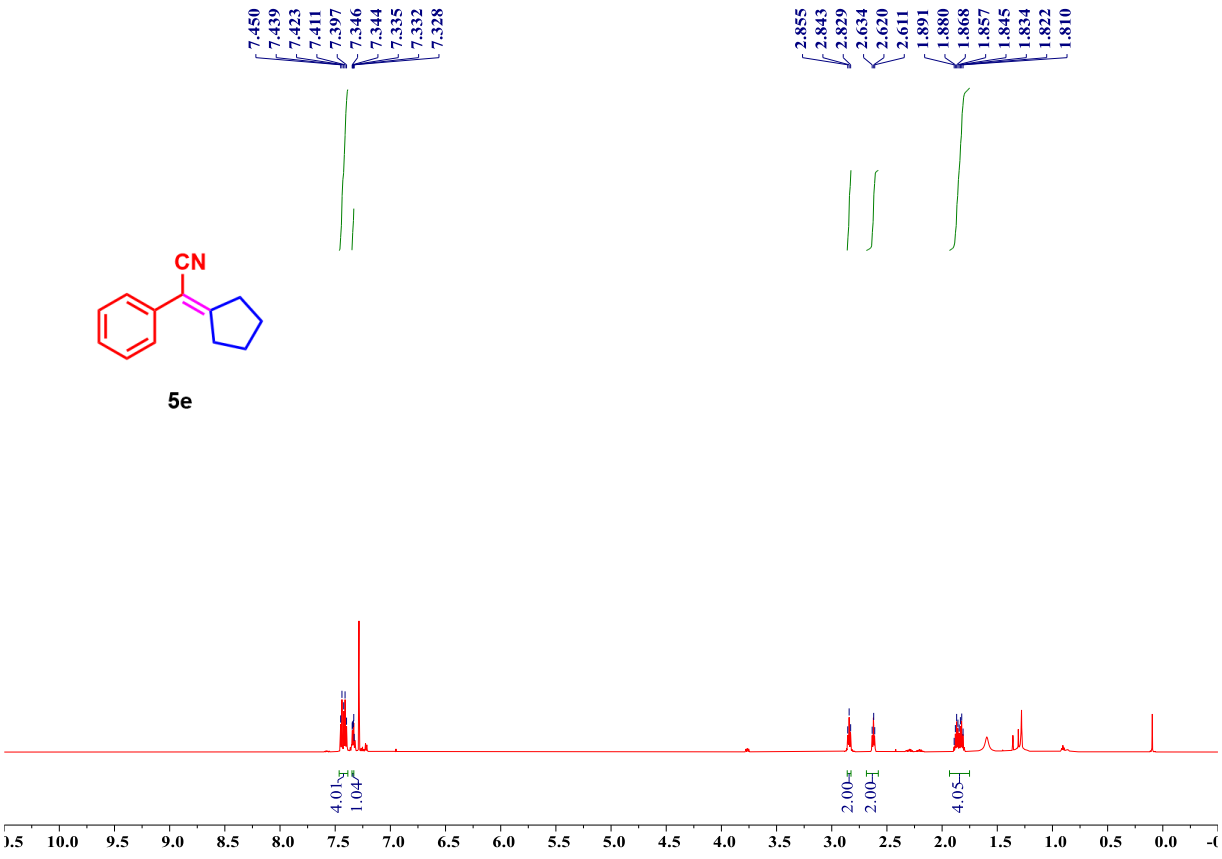
^{1}H NMR spectrum of 3-Methyl-2-phenylpent-2-enenitrile (**5q**, 100 MHz, $CDCl_3$):



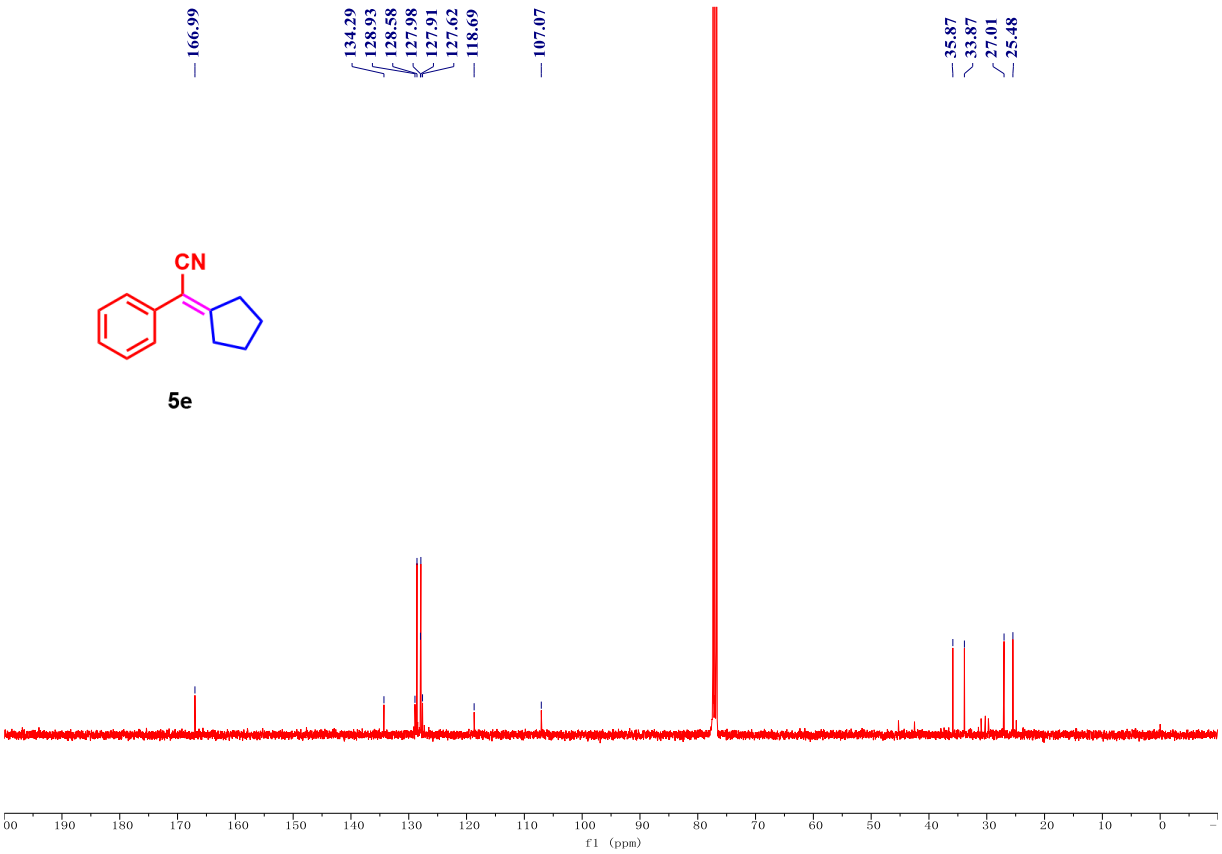
^{13}C NMR spectrum of 3-Methyl-2-phenylpent-2-enenitrile (**5q**, 100 MHz, $CDCl_3$):



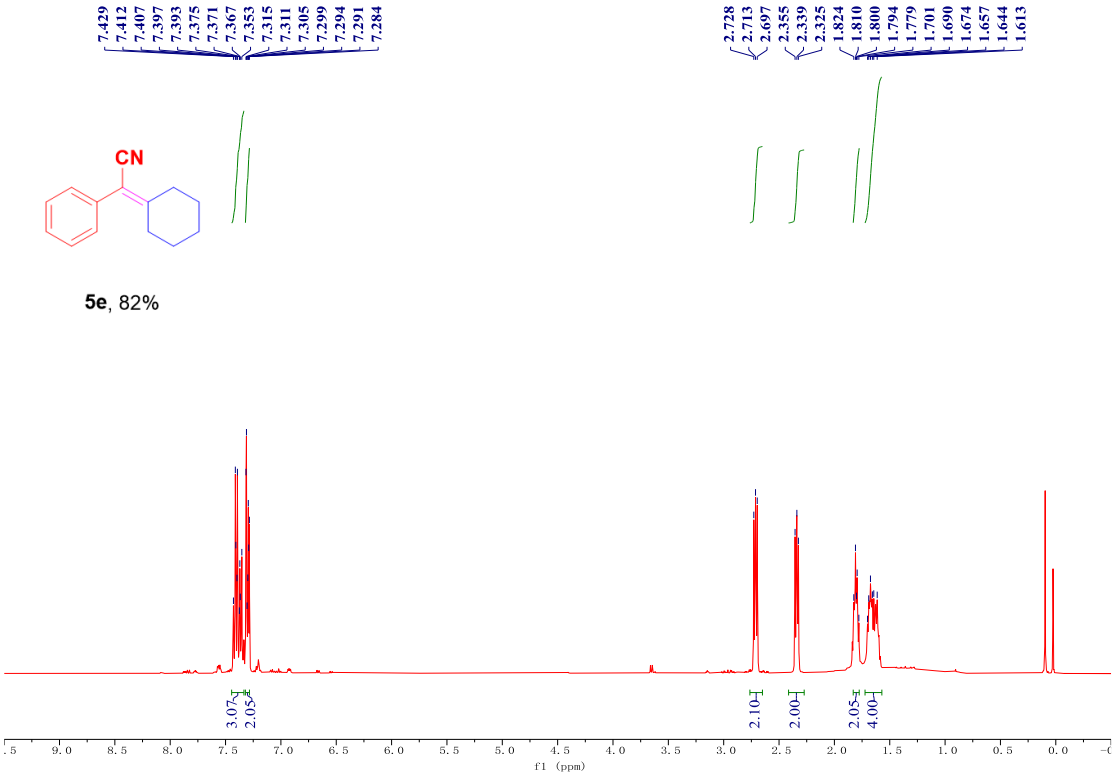
^{1}H NMR spectrum of 2-cyclopentylidene-2-phenylacetonitrile (**5f**, 400 MHz, $CDCl_3$) :



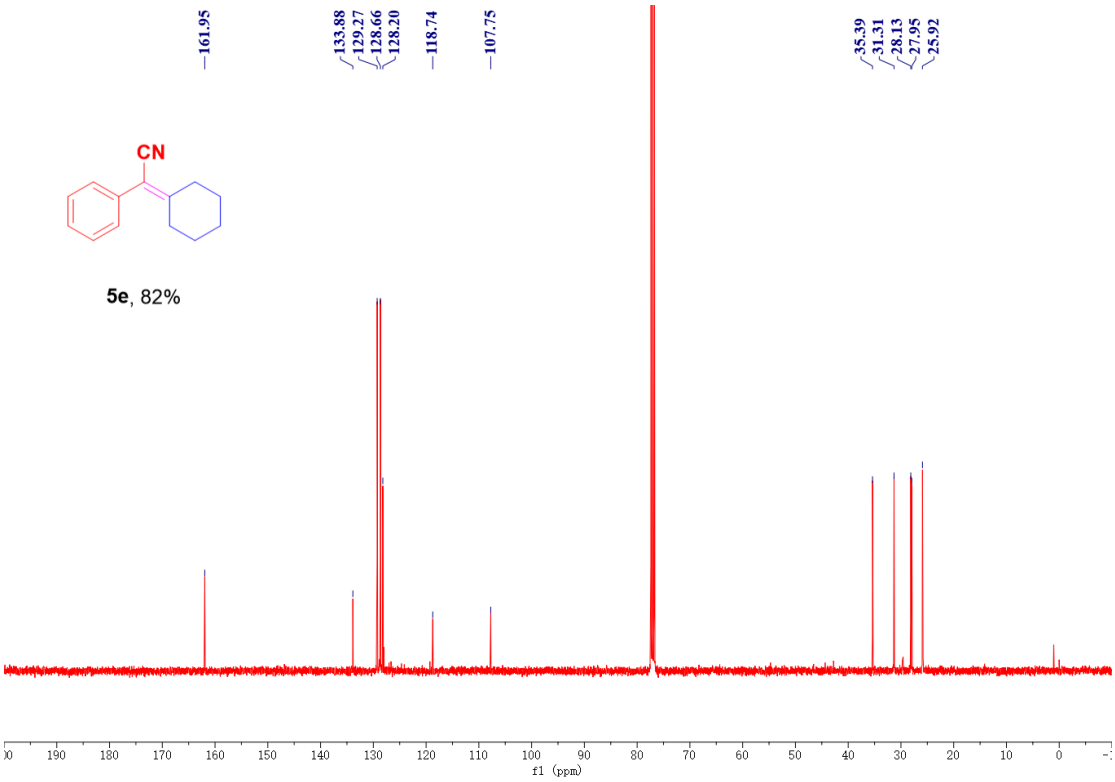
^{13}C NMR spectrum of 2-cyclopentylidene-2-phenylacetonitrile (**5f**, 100 MHz, $CDCl_3$):



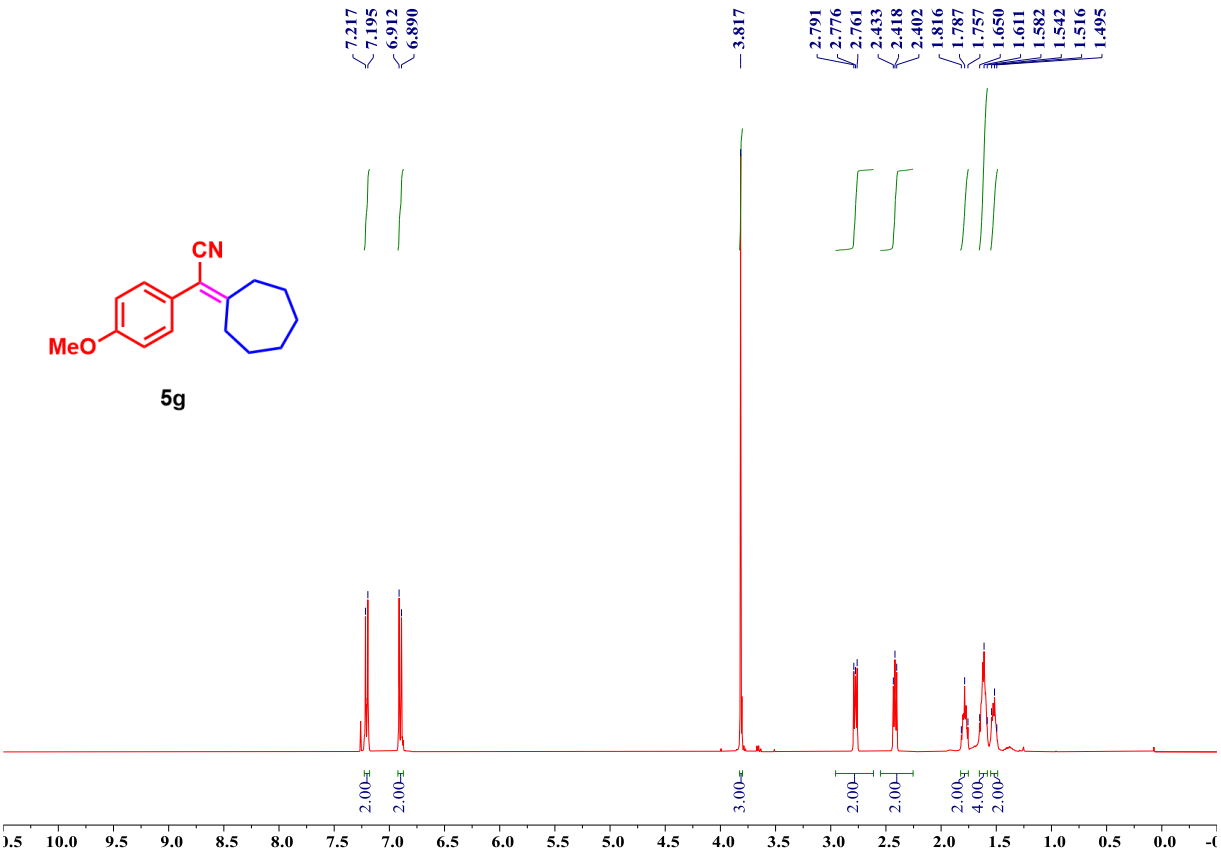
^{1}H NMR spectrum of 2-cyclohexylidene-2-phenylacetonitrile (**5g**, 400 MHz, $CDCl_3$) :



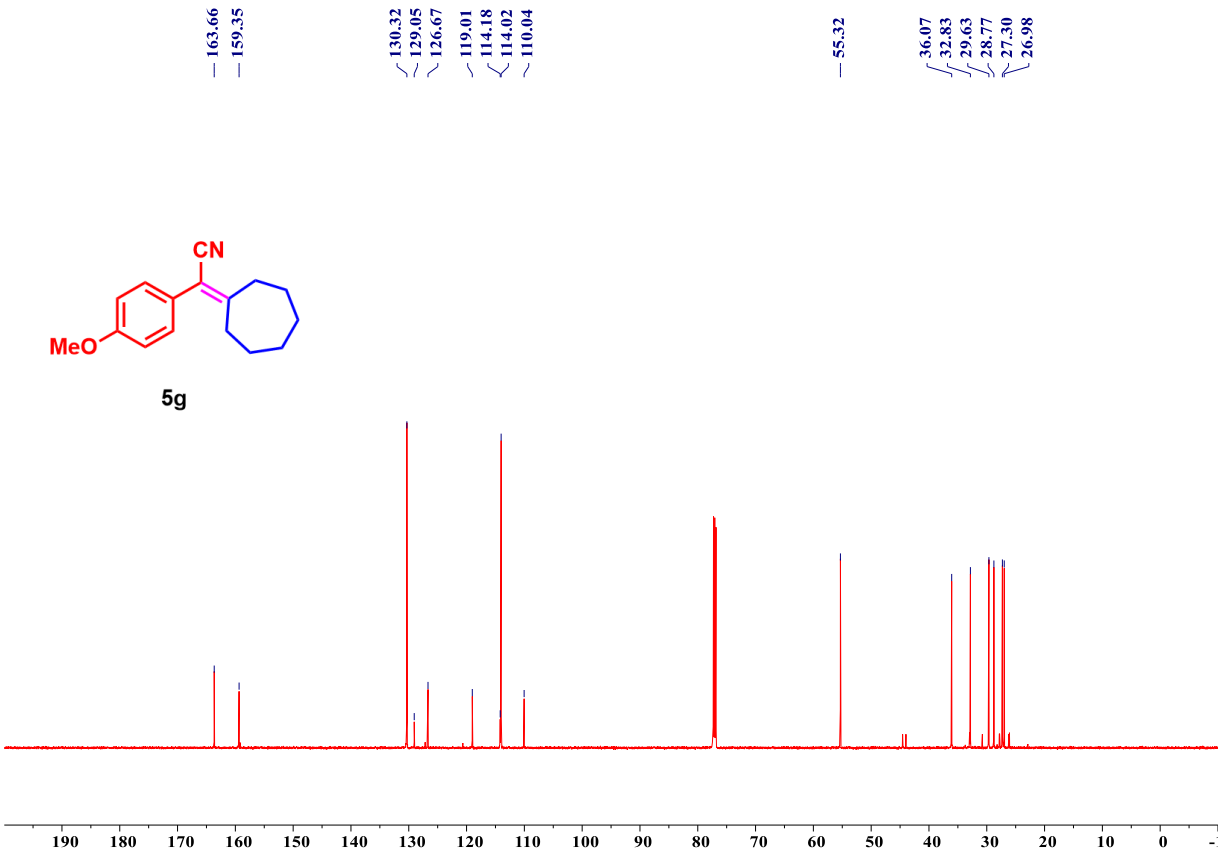
^{13}C NMR spectrum of 2-cyclohexylidene-2-phenylacetonitrile (**5g**, 100 MHz, $CDCl_3$):



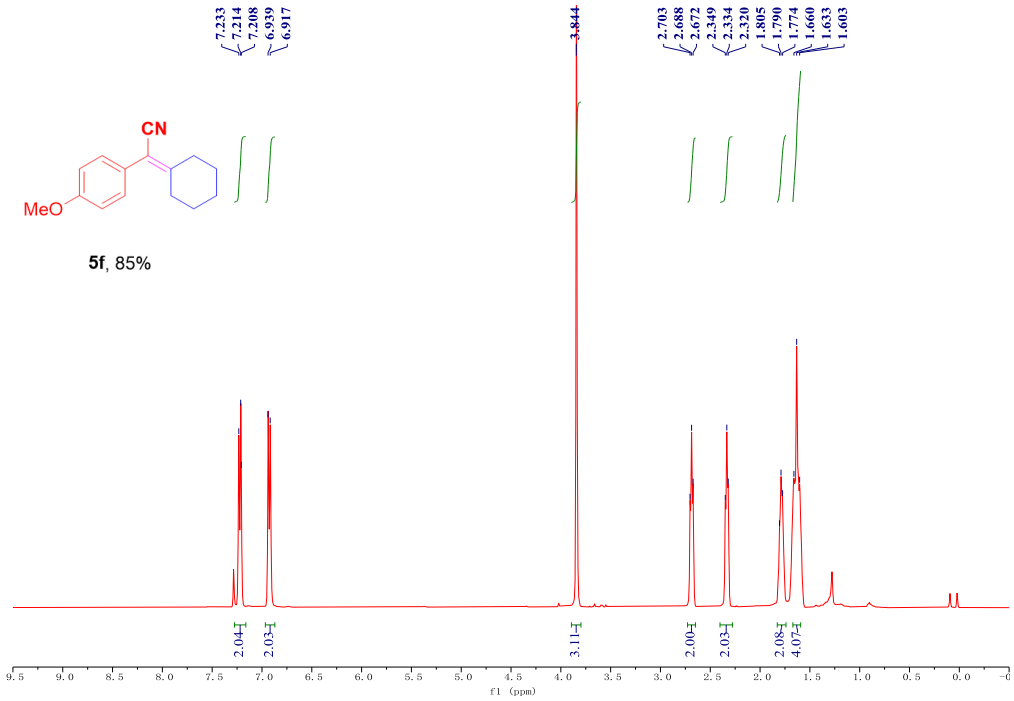
^{1}H NMR spectrum of 2-Cycloheptylidene-2-(4-methoxyphenyl)acetonitrile (**5h**, 400 MHz, $CDCl_3$) :



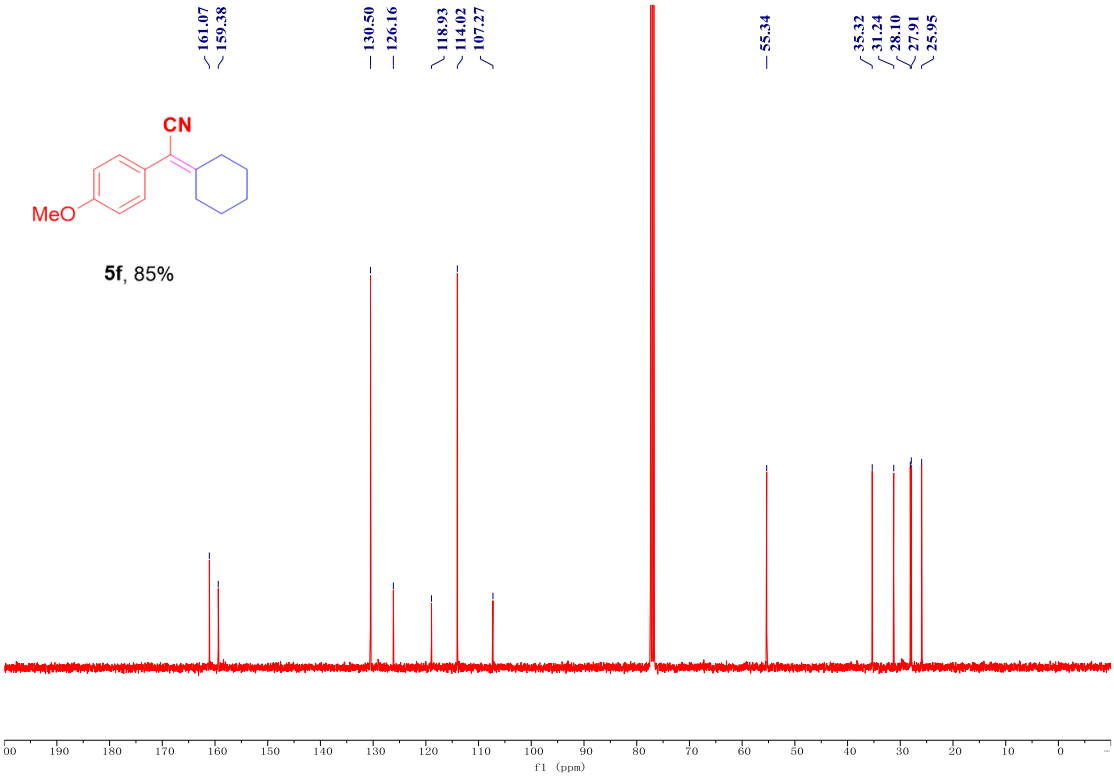
^{13}C NMR spectrum of 2-Cycloheptylidene-2-(4-methoxyphenyl)acetonitrile (**5h**, 100 MHz, $CDCl_3$):



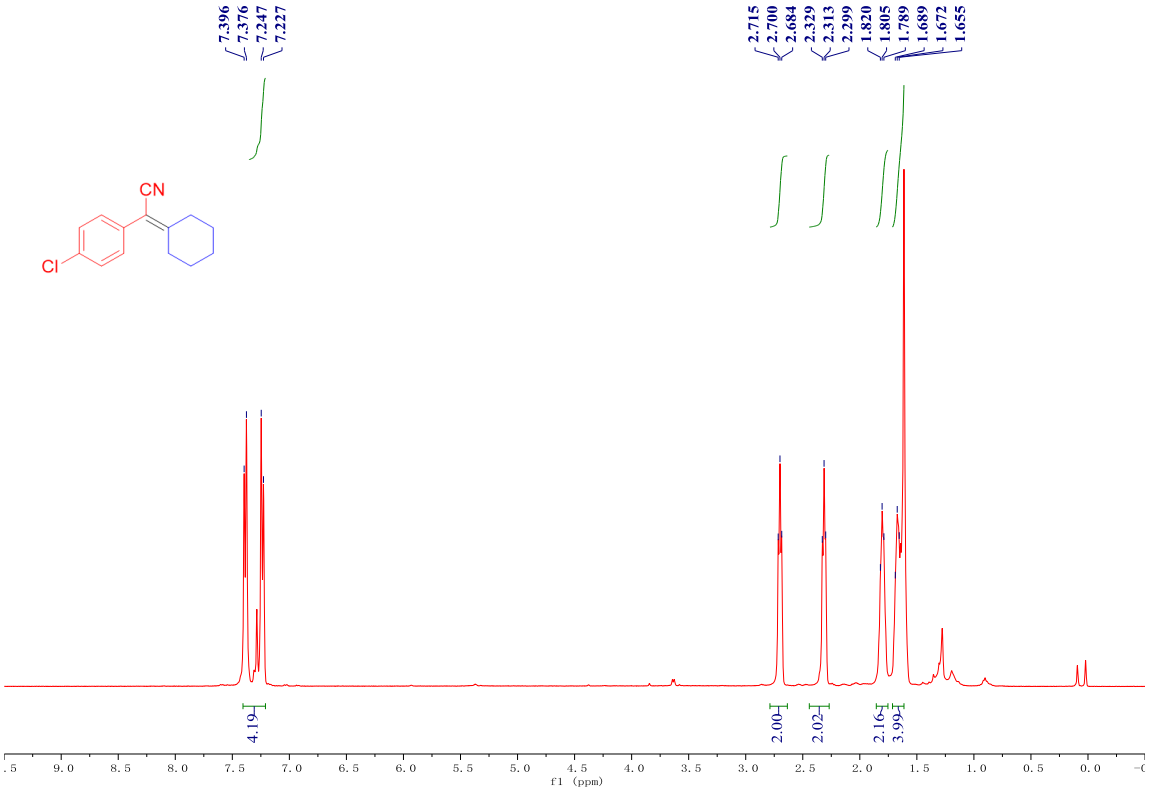
^{1}H NMR spectrum of 2-cyclohexylidene-2-(4-methoxyphenyl) acetonitrile (**5i**, 400 MHz, $CDCl_3$) :



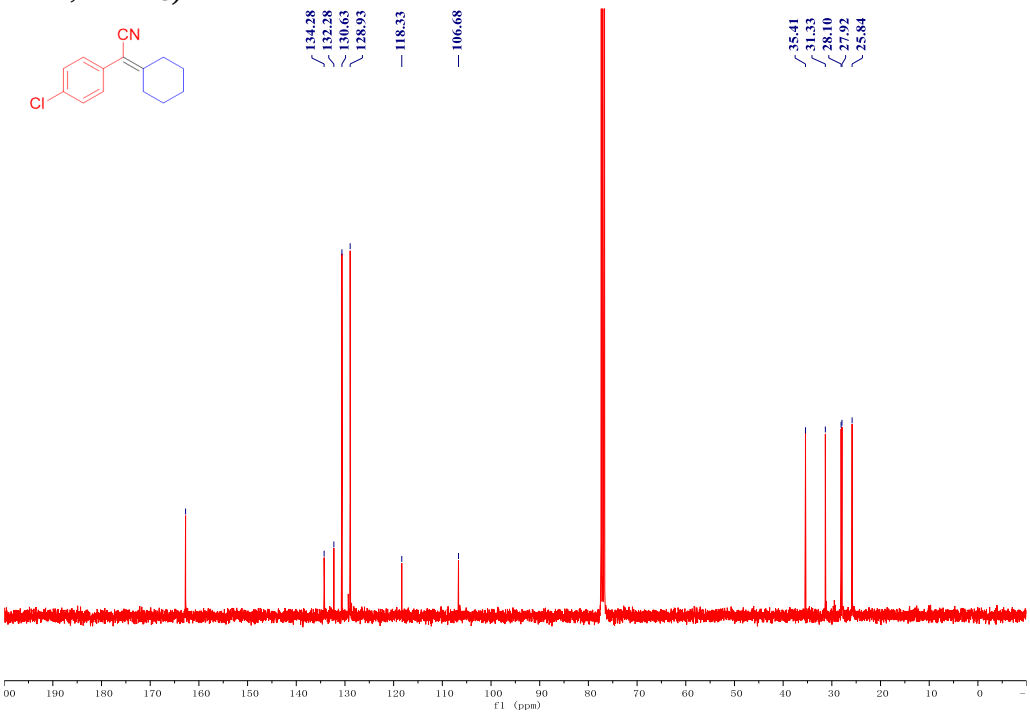
^{13}C NMR spectrum of 2-cyclohexylidene-2-(4-methoxyphenyl) acetonitrile (**5i**, 100 MHz, $CDCl_3$):



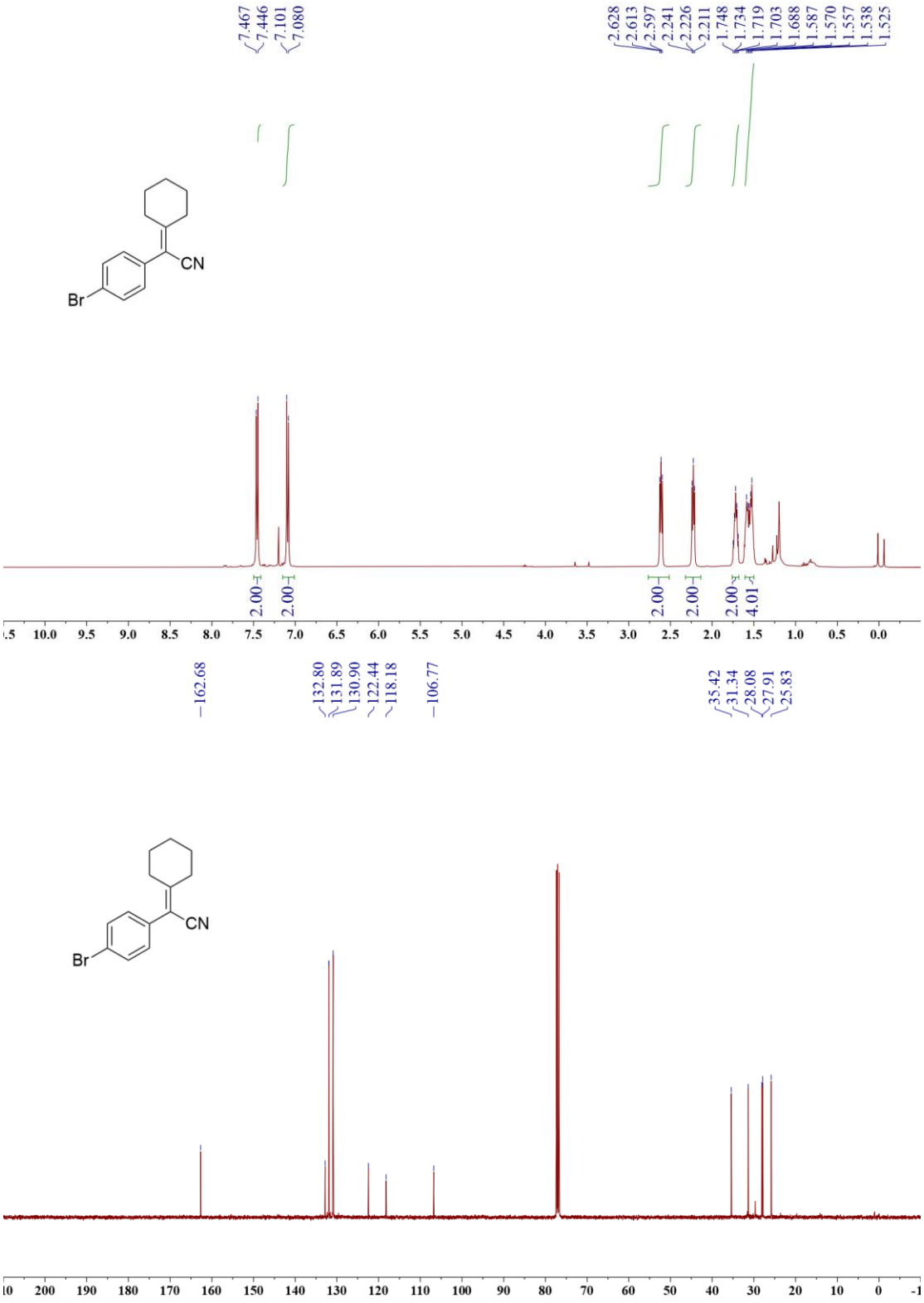
^{1}H NMR spectrum of 2-(4-chlorophenyl)-2-cyclohexylideneacetonitrile (**5j**, 400 MHz, $CDCl_3$) :



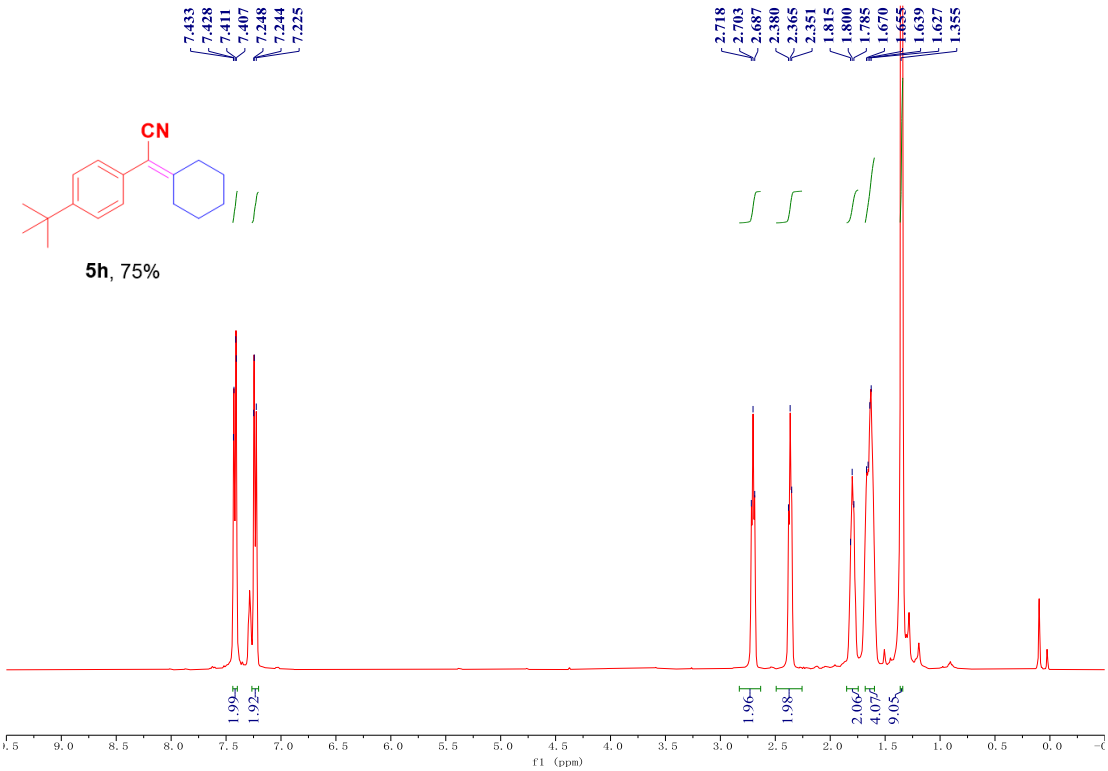
^{13}C NMR spectrum of 2-(4-chlorophenyl)-2-cyclohexylideneacetonitrile (**5j**, 100 MHz, $CDCl_3$):



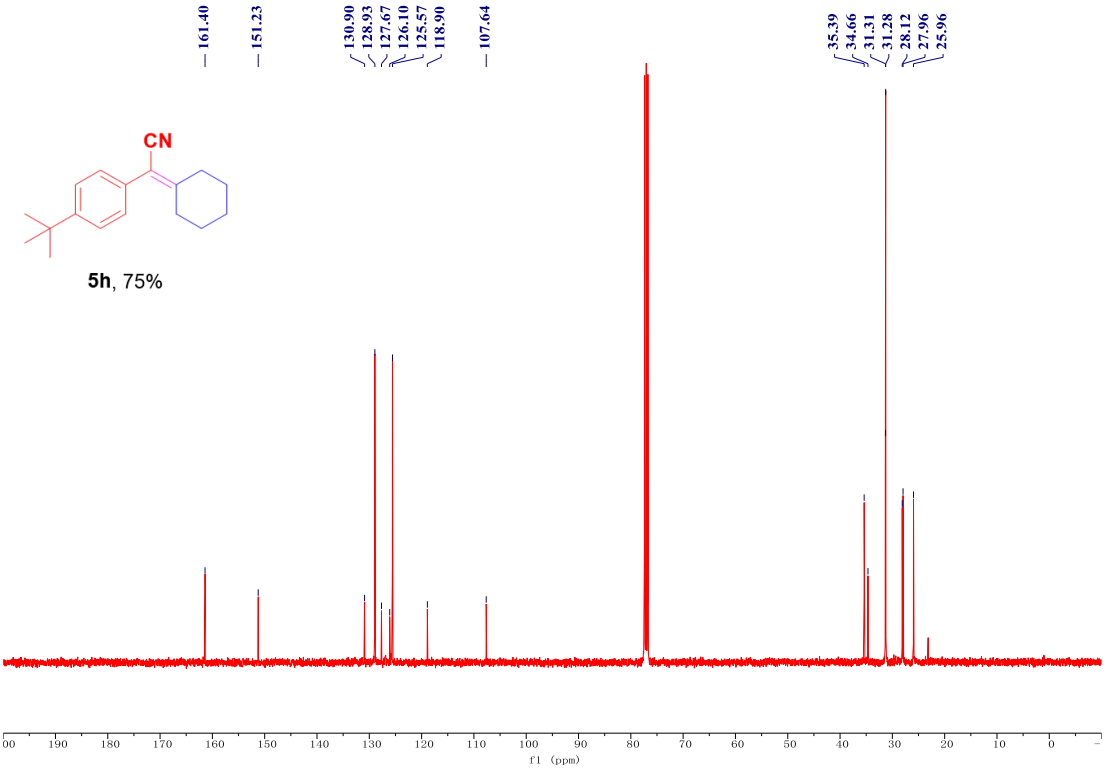
^{1}H NMR spectrum of 2-(4-chlorophenyl)-2-cyclohexylideneacetonitrile (**5k**, 400 MHz, $CDCl_3$) :



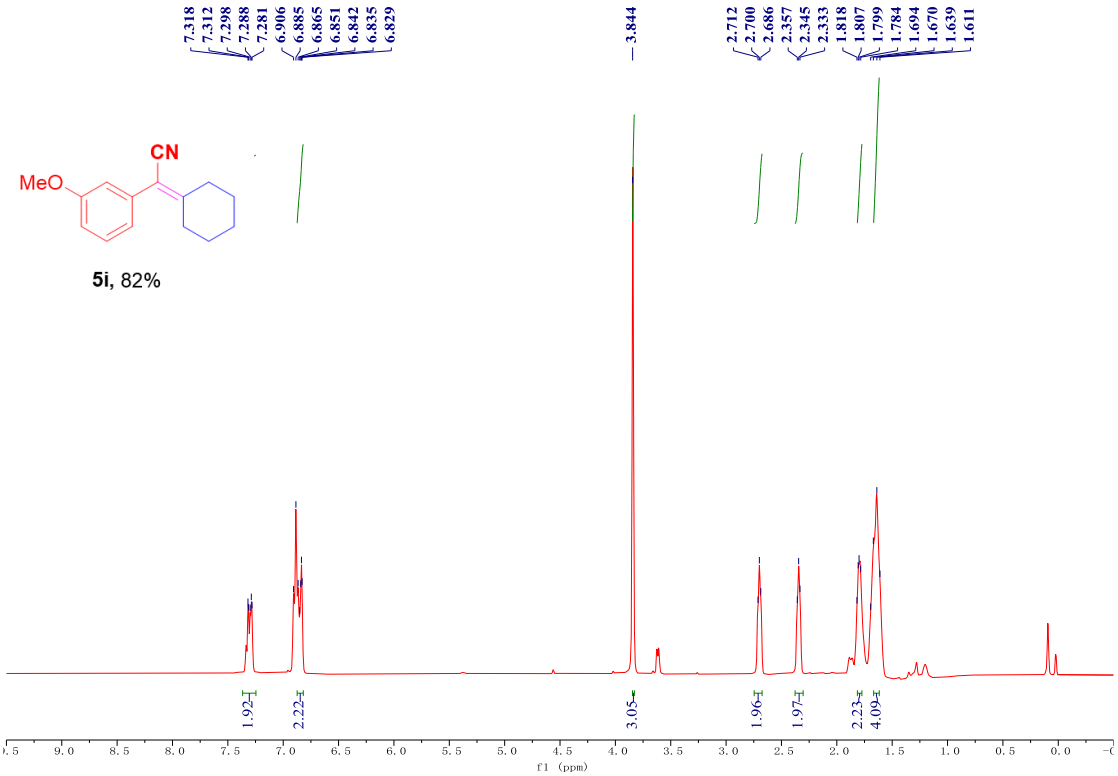
^{1}H NMR spectrum of 2-(4-(tert-butyl) phenyl)-2-cyclohexylideneacetonitrile (**5l**, 400 MHz, $CDCl_3$) :



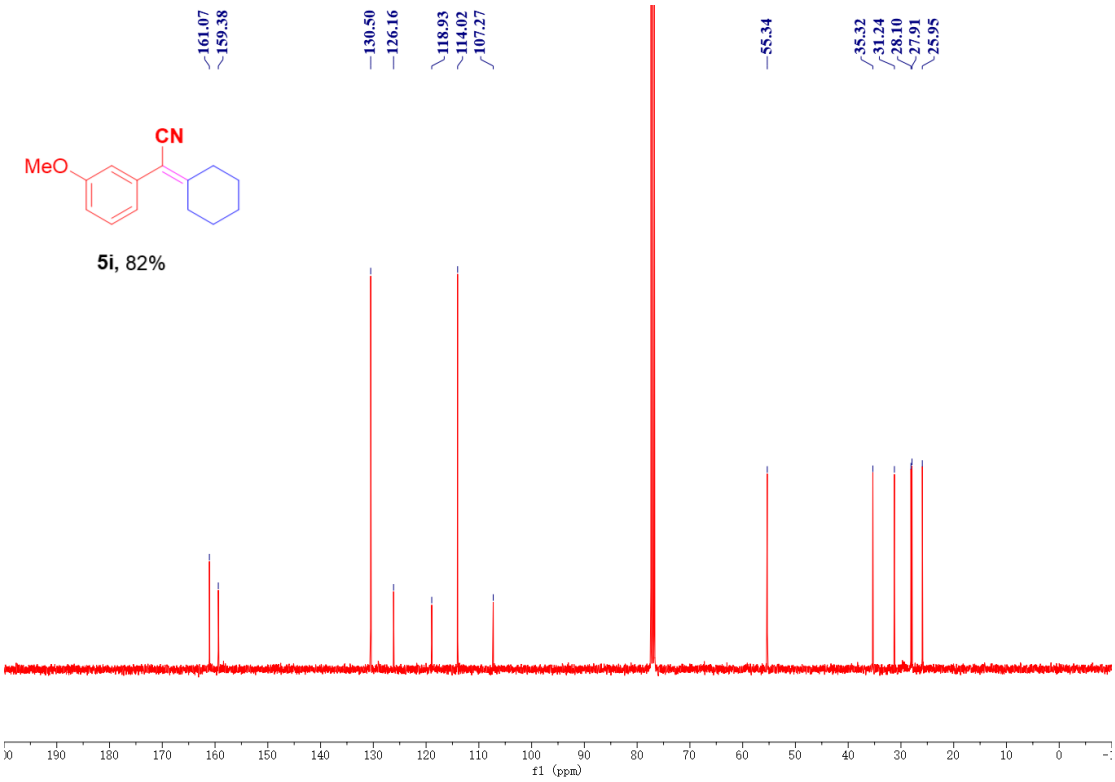
^{13}C NMR spectrum of 2-(4-(tert-butyl) phenyl)-2-cyclohexylideneacetonitrile (**5l**, 100 MHz, $CDCl_3$):



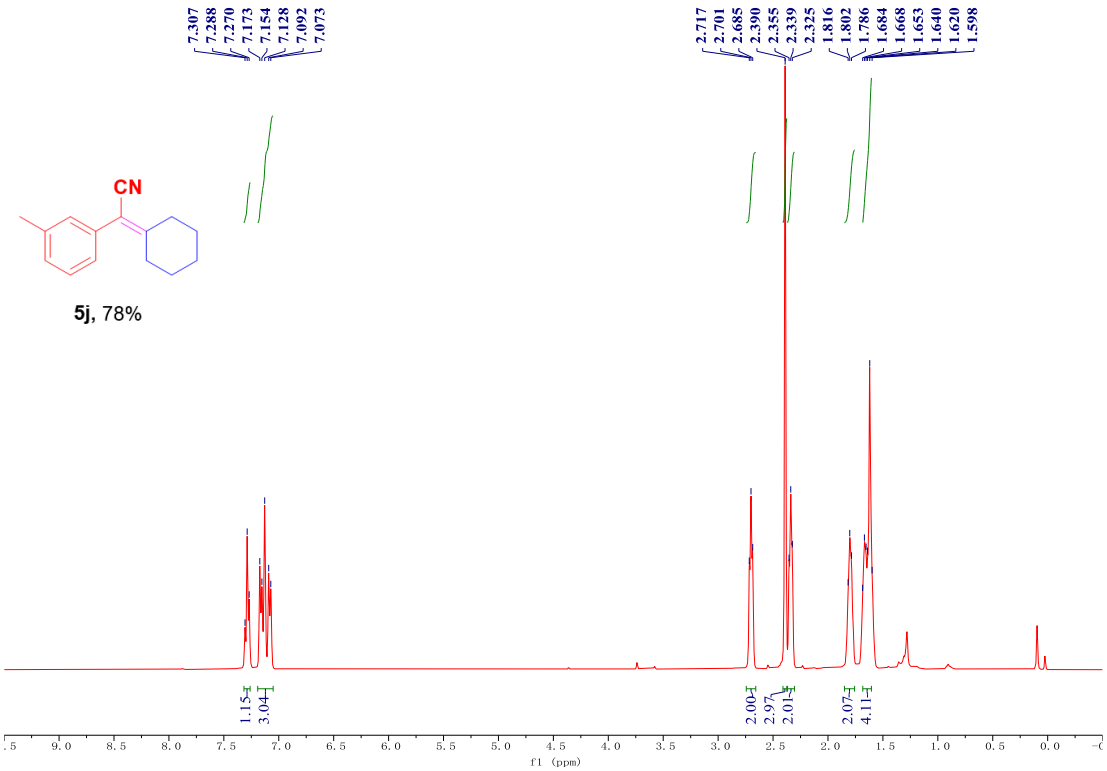
^{1}H NMR spectrum of 2-cyclohexylidene-2-(3-methoxyphenyl) acetonitrile (**5m**, 400 MHz, $CDCl_3$) :



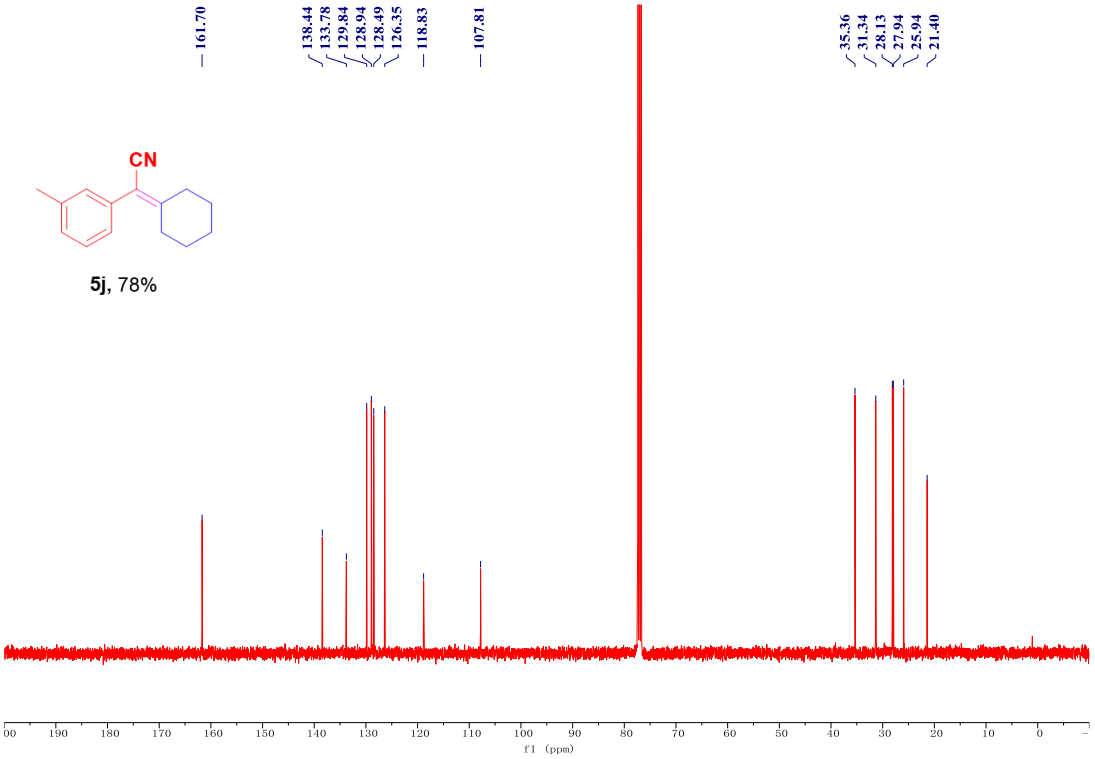
^{13}C NMR spectrum of 2-cyclohexylidene-2-(3-methoxyphenyl) acetonitrile (**5m**, 100 MHz, $CDCl_3$):



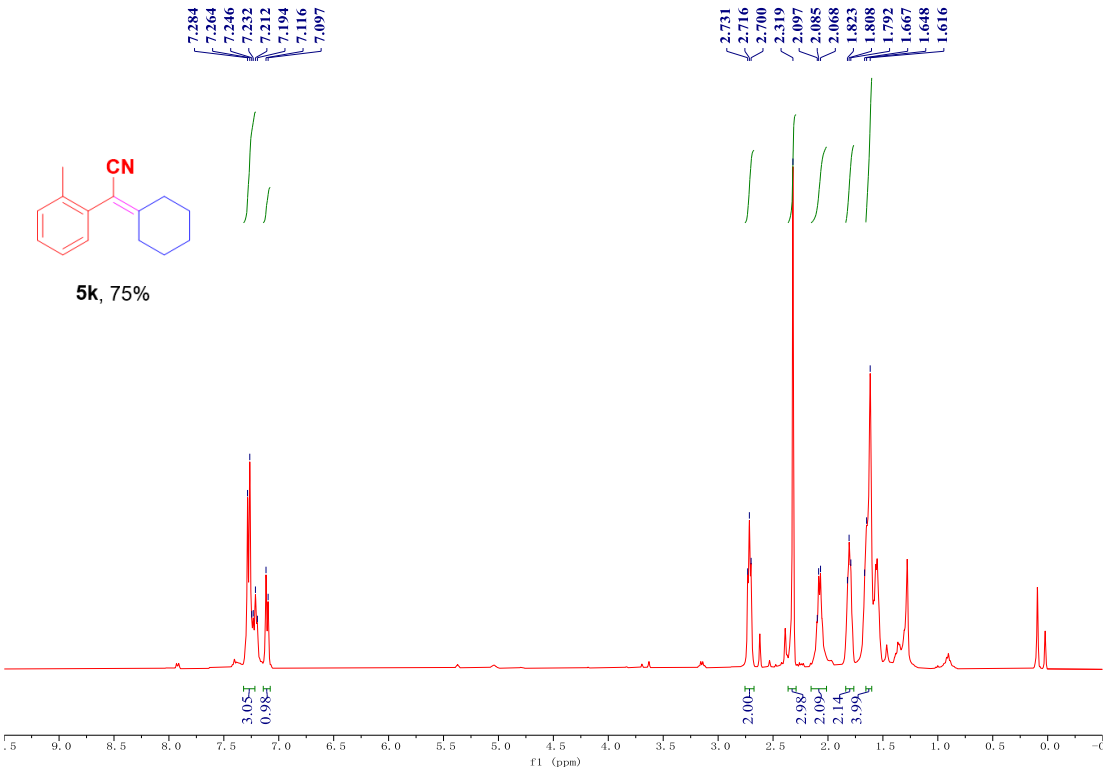
^{1}H NMR spectrum of 2-cyclohexylidene-2-(m-tolyl) acetonitrile (**5n**, 400 MHz, $CDCl_3$) :



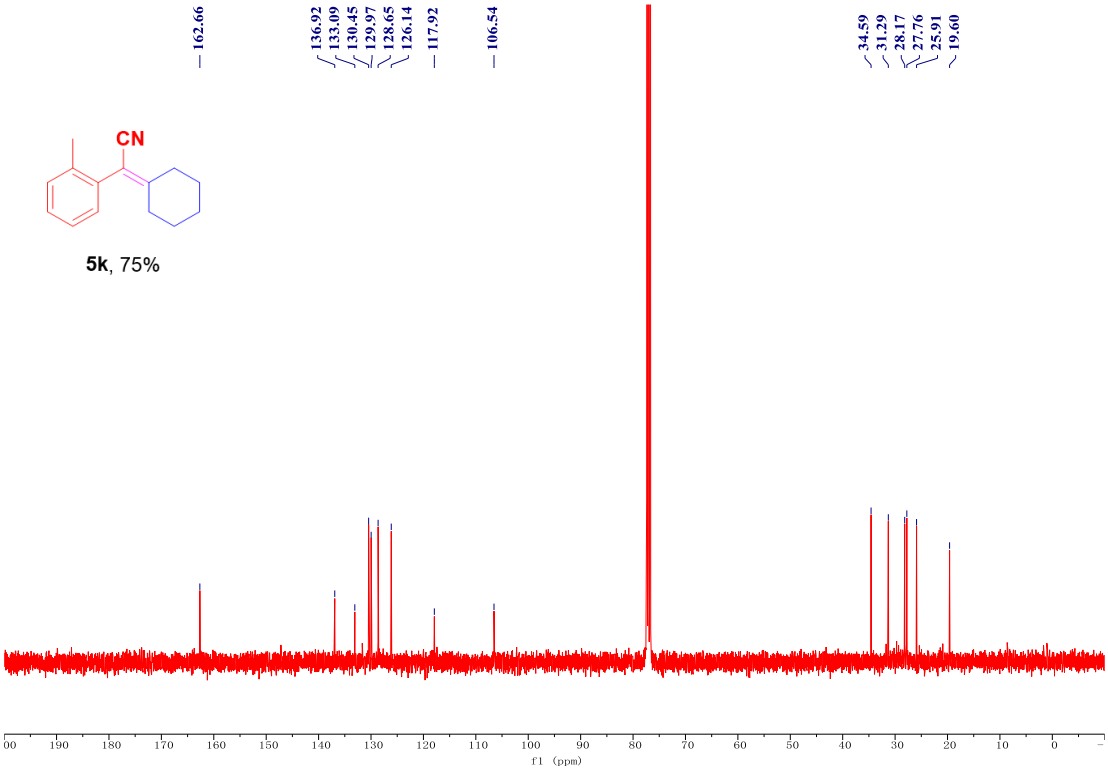
^{13}C NMR spectrum of 2-cyclohexylidene-2-(m-tolyl) acetonitrile (**5n**, 100 MHz, $CDCl_3$):



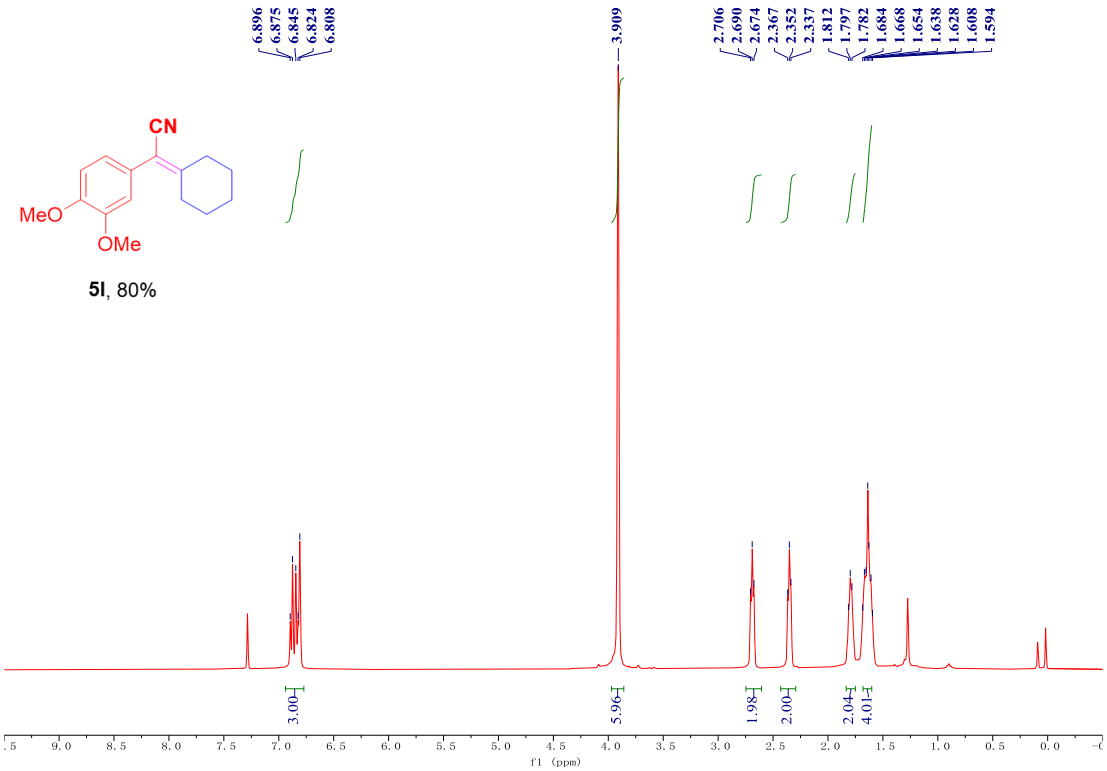
^{1}H NMR spectrum of 2-Cyclohexylidene-2-(*o*-tolyl) acetonitrile (**5o**, 400 MHz, $CDCl_3$) :



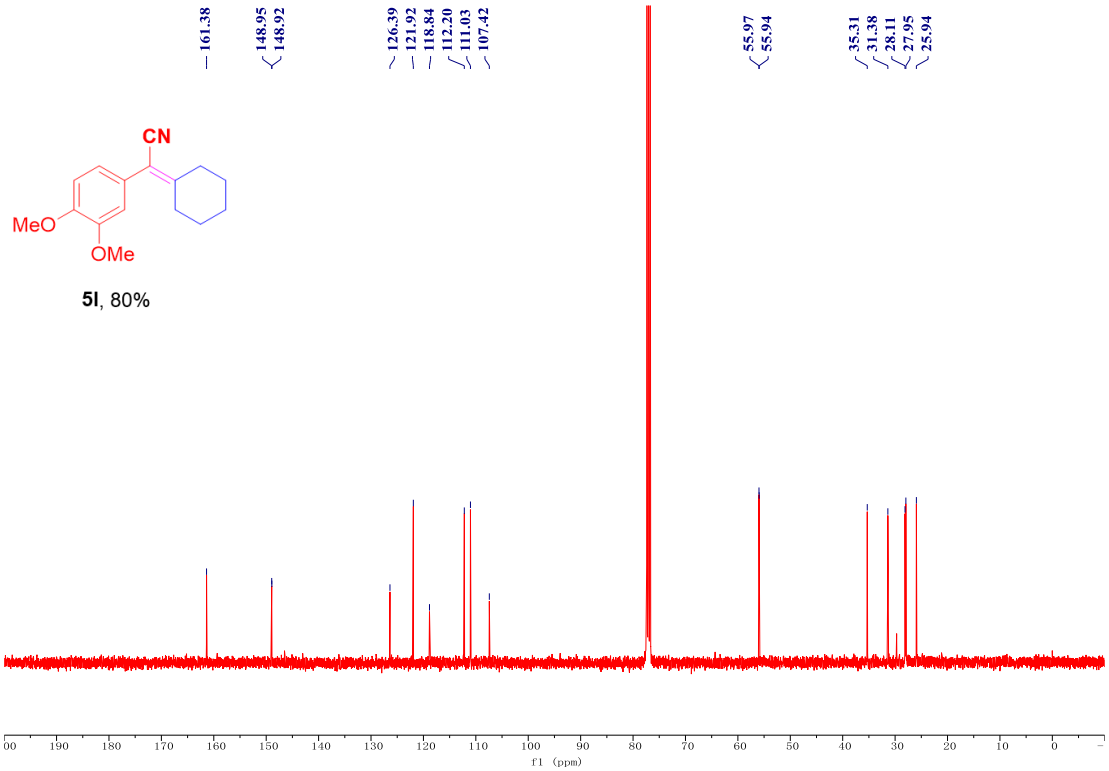
^{13}C NMR spectrum of 2-cyclohexylidene-2-(o-tolyl) acetonitrile (**5o**, 100 MHz, $CDCl_3$):



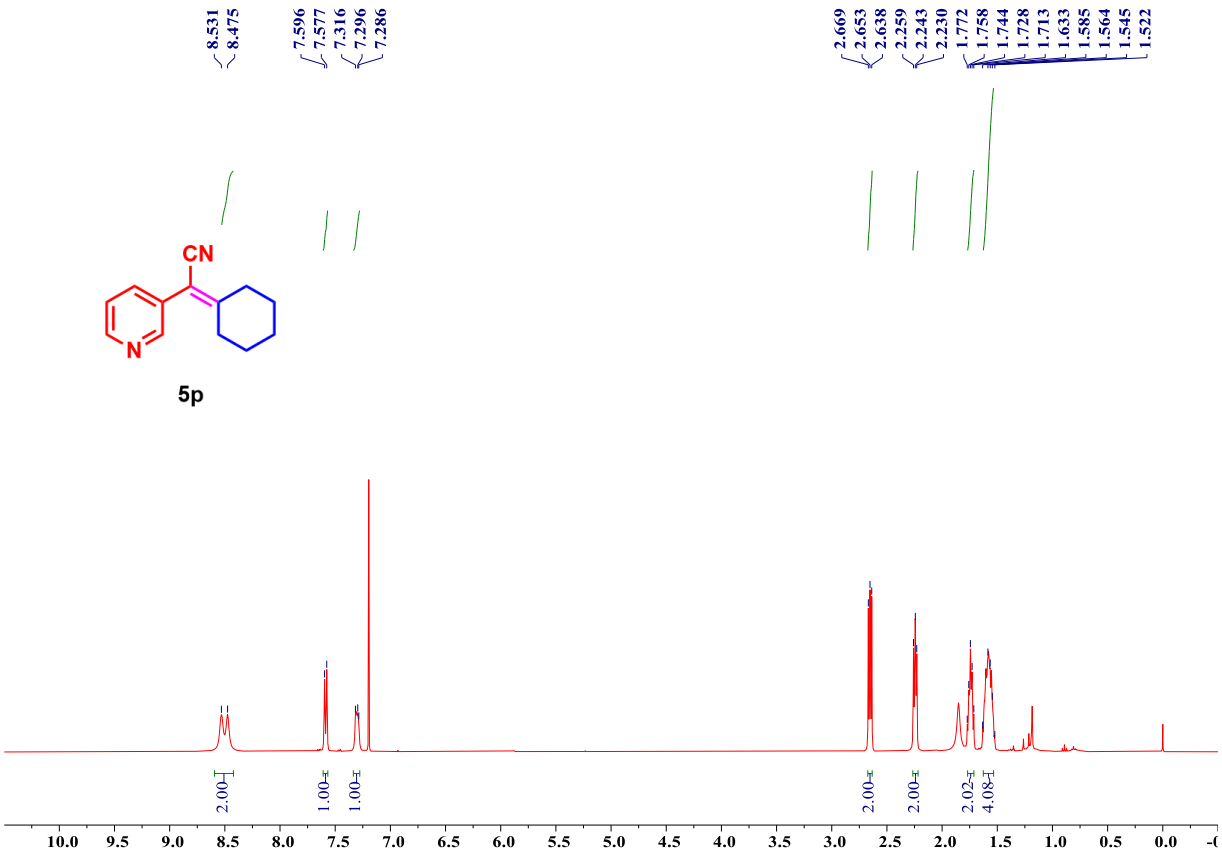
^{1}H NMR spectrum of 2-cyclohexylidene-2-(3,4-dimethylphenyl) acetonitrile (**5p**, 400 MHz, $CDCl_3$) :



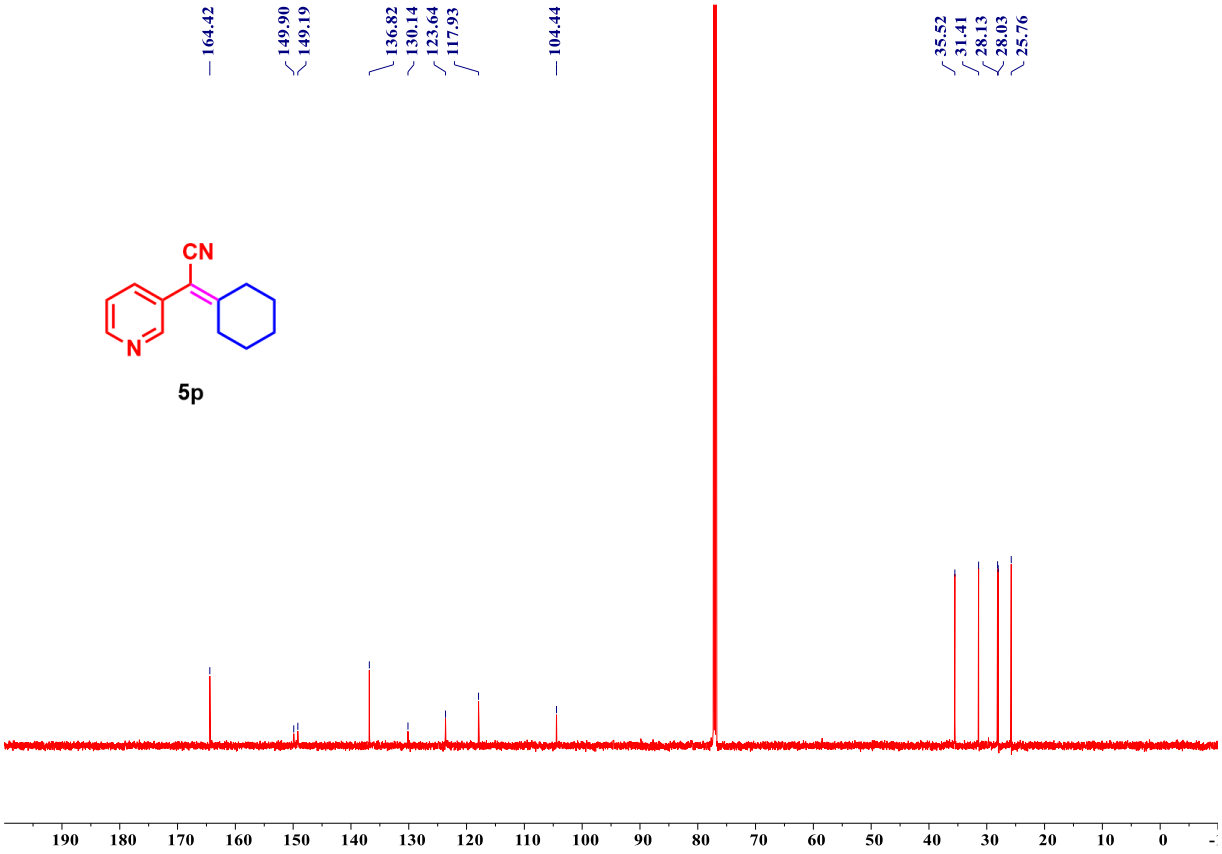
^{13}C NMR spectrum of 2-cyclohexylidene-2-(3,4-dimethylphenyl) acetonitrile (**5p**, 100 MHz, $CDCl_3$):



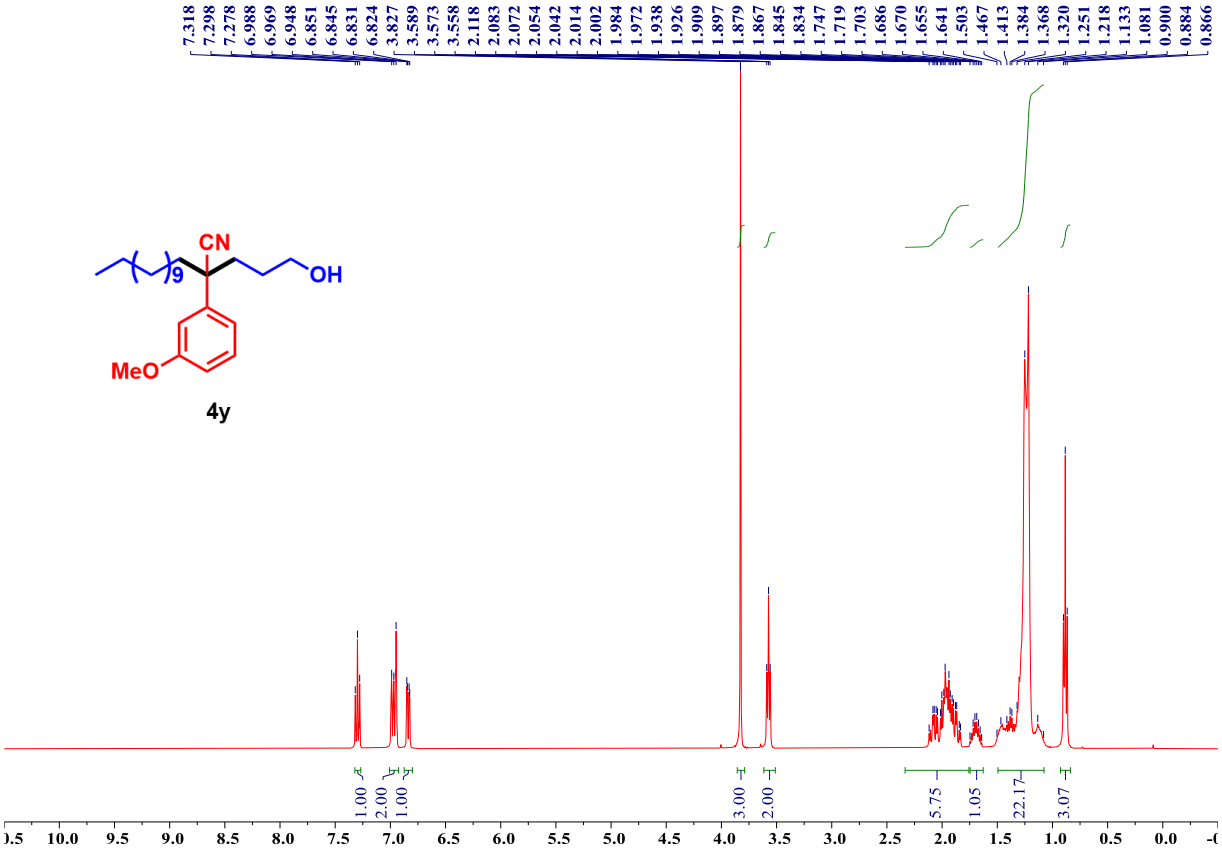
^{1}H NMR spectrum of 2-Cyclohexylidene-2-(pyridin-3-yl)acetonitrile (**5q**, 100 MHz, $CDCl_3$):



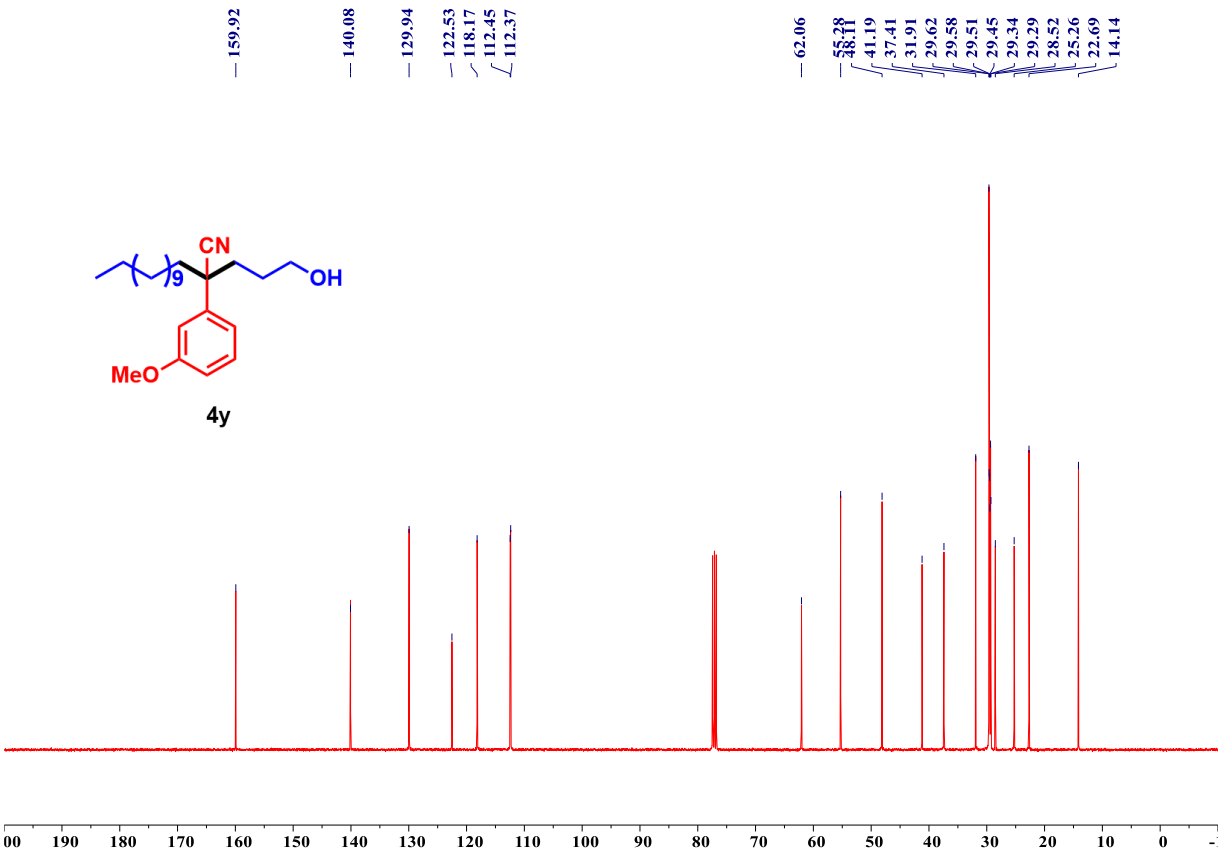
^{13}C NMR spectrum of 2-Cyclohexylidene-2-(pyridin-3-yl)acetonitrile (**5q**, 100 MHz, $CDCl_3$):



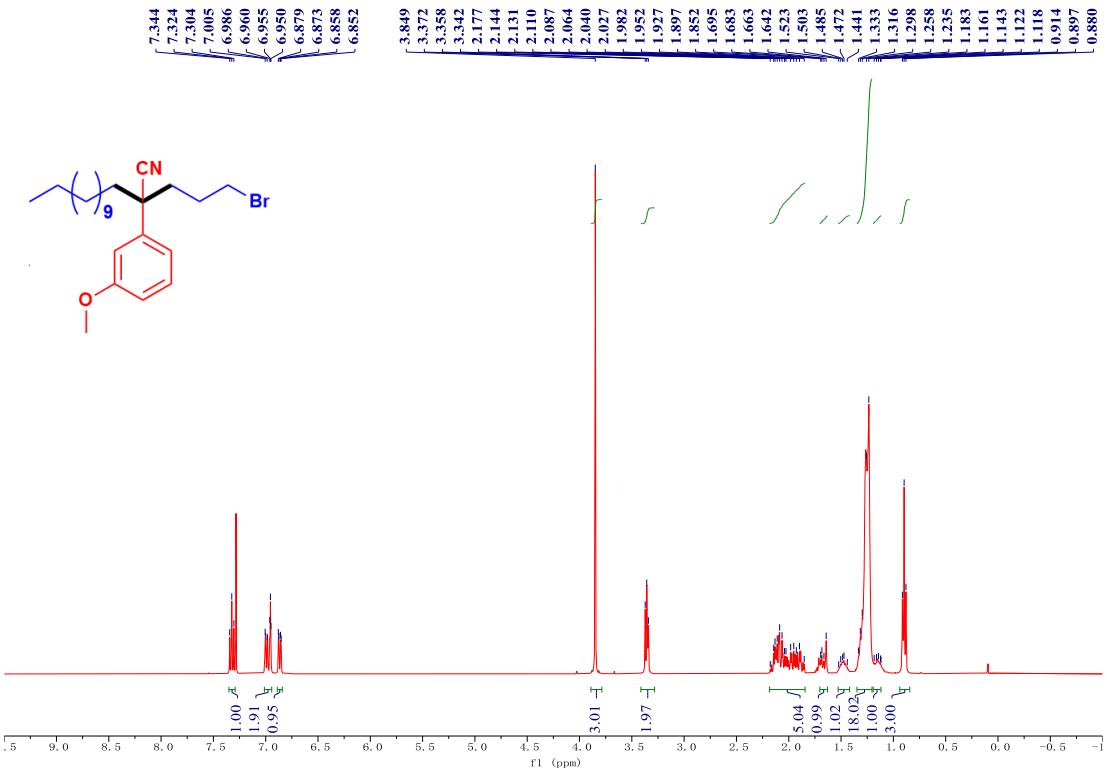
^{1}H NMR spectrum of 2-(3-hydroxypropyl)-2-(3-methoxyphenyl) tetradecanenitrile (**4y**, 400 MHz, $CDCl_3$):



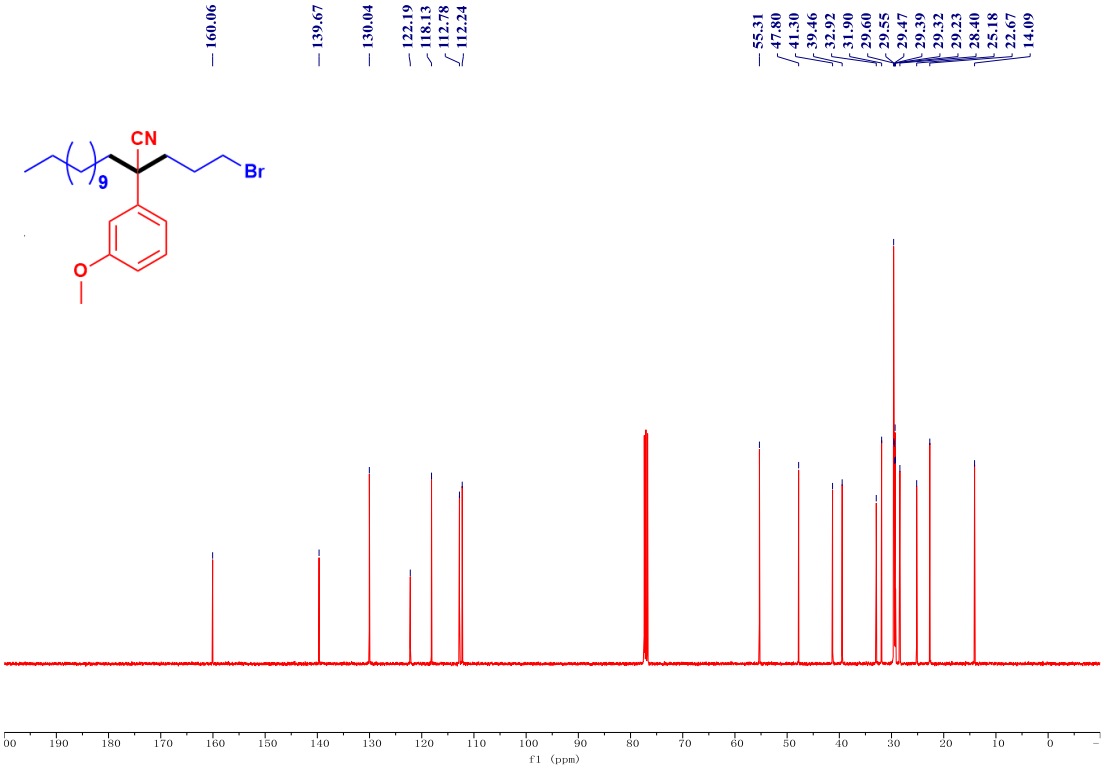
^{13}C NMR spectrum of 2-(3-hydroxypropyl)-2-(3-methoxyphenyl) tetradecanenitrile (**4y**, 100 MHz, $CDCl_3$):



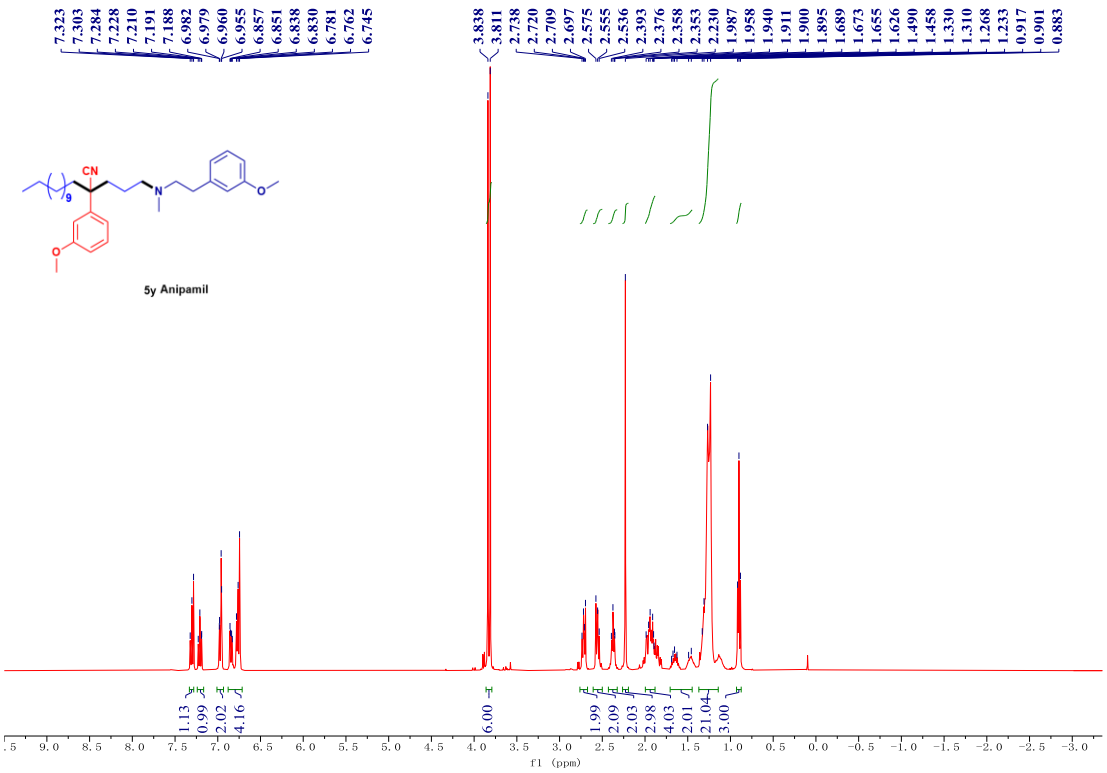
^{1}H NMR spectrum of 2-(3-bromopropyl)-2-(3-methoxyphenyl) tetradecanenitrile (**5y**, 400 MHz, $CDCl_3$):



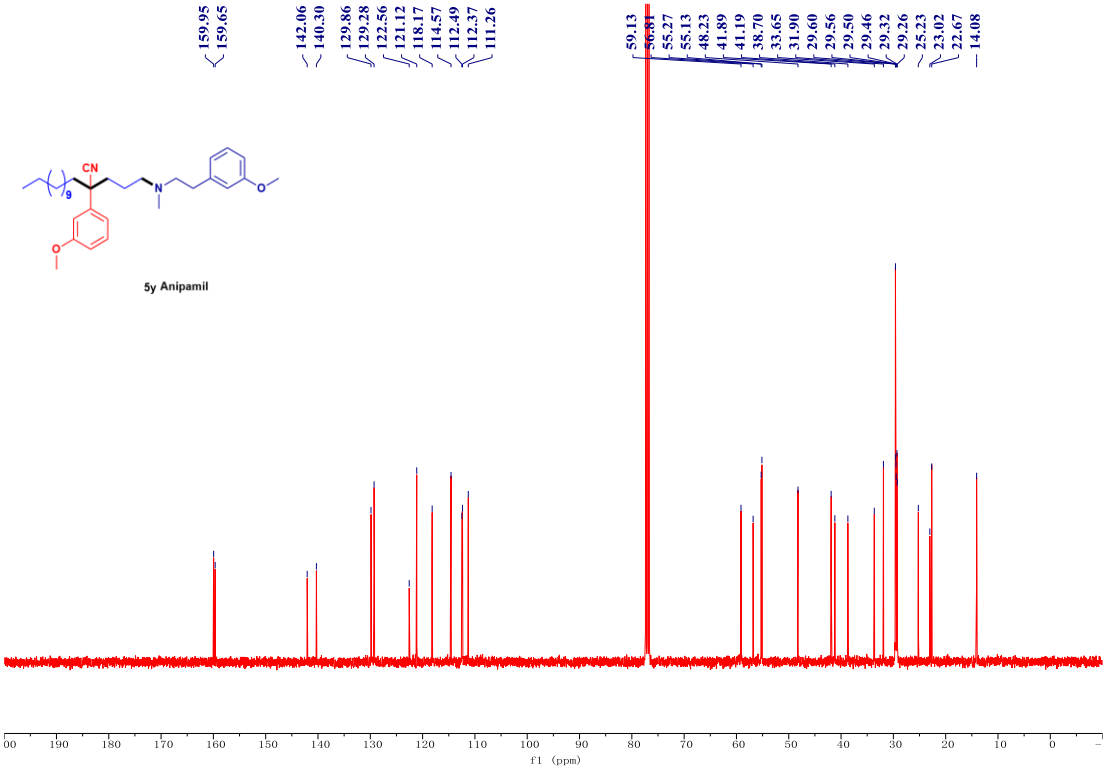
^{13}C NMR spectrum of 2-(3-bromopropyl)-2-(3-methoxyphenyl) tetradecanenitrile (**5y**, 100 MHz, $CDCl_3$):



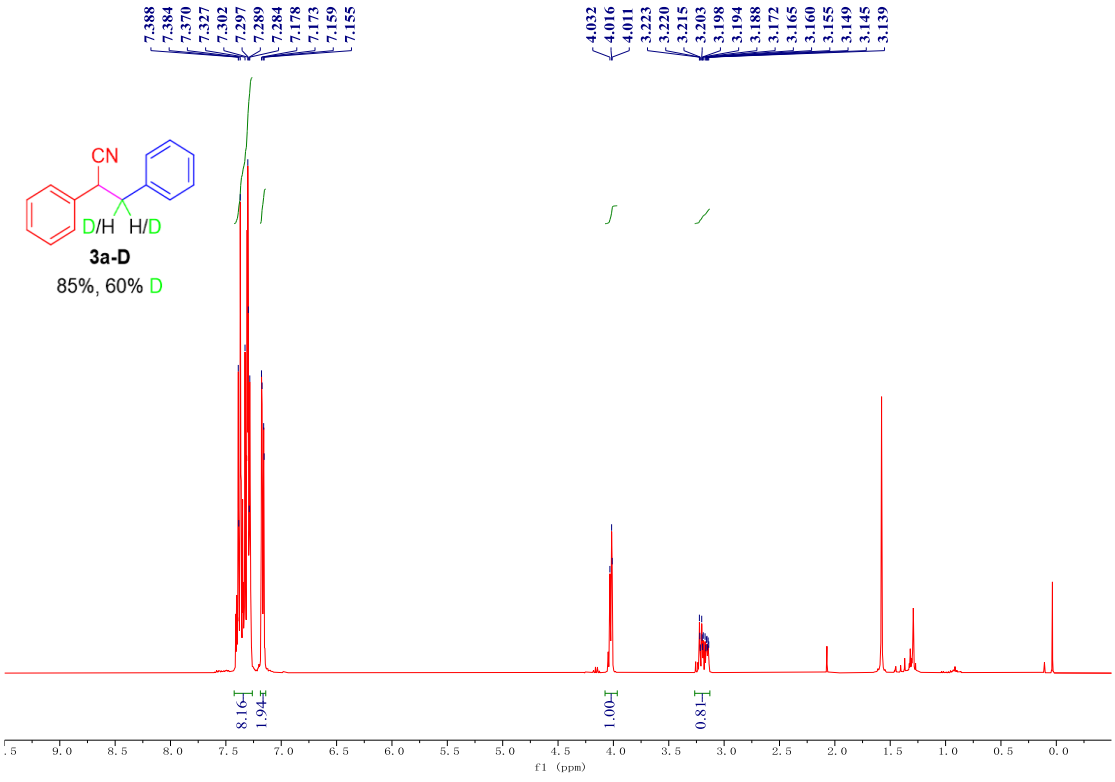
^{1}H NMR spectrum of 2-(3-((3-methoxyphenethyl) (methyl)amino) propyl)-2-(3-methoxyphenyl) tetradecanenitrile (**6y**, 400 MHz, $CDCl_3$):



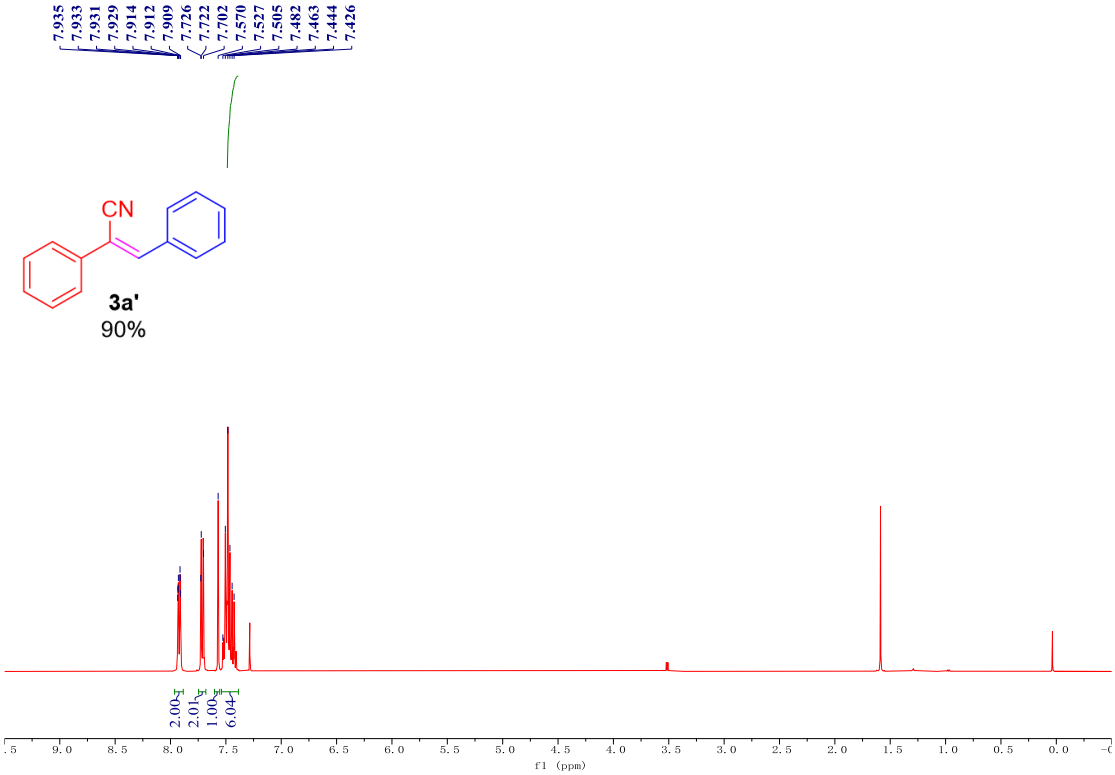
^{13}C NMR spectrum of 2-(3-((3-methoxyphenethyl) (methyl)amino) propyl)-2-(3-methoxyphenyl) tetradecanenitrile (**6y**, 100 MHz, $CDCl_3$):



^{1}H NMR spectrum of product (**3a-D**, 400 MHz, $CDCl_3$):



^{1}H NMR spectrum of product (**3a'**, 400 MHz, $CDCl_3$):



^{1}H NMR spectrum of product (**3a-D**, 400 MHz, $CDCl_3$):