Copper-Catalyzed Selective Radical-Radical Cross-coupling for C-S Bond Formation: An Access to α-alkylthionitriles

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General Information

All reagents were obtained from commercial suppliers unless otherwise stated. The solvents were dried and distilled prior to use by the literature methods. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum ether (boiling point is between 60-90 ^{0}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they are listed as volume/volume ratios. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 100 MHz (^{13}C NMR). Tetramethylsilane was used as an internal standard. All ^{1}H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). Selective ratios were recorded with a Varian GC 2000 gas chromatography instrument with a FID detector. GC-Ms spectra were recorded on Varian GC-Ms 3900-2100T and Shimadzu GCMS-QP2010SE.

EPR experiments

EPR spectra was recorded at 298 K on EPR spectrometer operated at 9.4158 GHz. Typical spectrometer parameters are shown as follows, scan range: 100 G; center field set: 3359.8 G; time constant: 163.84 ms; scan time: 30.72 s; modulation amplitude: 1.0 G; modulation frequency: 100 kHz; receiver gain: 1.00×105; microwave power: 19.05 mW.

The reaction between 1a (*p*-toluenethiol) and $Cu(OTf)_2$ was investigated by electron paramagnetic resonance (EPR) (X band, 9.4 GHz, RT): In an oven-dried Schlenk tube equipped with a stir bar, *p*-toluenethiol (**1a**, 0.30 mmol), $Cu(OTf)_2$ (0.015 mmol), 1,10-phen (0.06 mmol) was combined. Then, DMF (2.0 mL) were added in the tube via syringe. The reaction mixture was allowed to stir vigorously at 80 °C for 5 mintues. Thereafter, 10 uL of DMPO (5,5-dimethyl-1-pyrroline N-oxide) was added and well mixed. Afterwards, 20 uL of the mixture was quickly taken out into a small tube and analyzed by EPR.

XANES and EXAFS Data Collection and Analysis

X-ray absorption measurements were acquired on the insertion device beam line of the Materials Research Collaborative Access Team (MRCAT) at the Advanced Photon Source, Argonne National Laboratory. The data were collected in transmission quick scan mode. Insertion device experiments utilized a cryogenically cooled double-crystal monochromator in conjunction with an uncoated glass mirror to minimize the presence of harmonics. The monochromator was scanned continuously during the measurements with data points integrated over 0.5 eV for 0.03 s per data point. The ionization chambers were optimized for the maximum current with linear response (~1010 photons detected/sec) with 10% absorption (N_2) in the incident ion chamber and 70% absorption (50% N_2 and 50% Ar) in the transmission

detector. A Cu foil spectrum (edge energy 8979 eV) was acquired simultaneously with each measurement for energy calibration and multiple scans were taken to ensure spectrum reproducibility.

All of the solution samples were prepared in a glove box and placed in a sample holder made of PEEK (polyether ether ketone) equipped with a screw top and O-ring fitting to prevent exposure to air and water. The path length of the cell is 3.5 mm and the Cu concentration was adjusted to be about 0.07 M. The edge energy of the X-Ray absorption near edge structure (XANES) spectrum was determined from the inflection point in the edge, i.e., the maximum in the first derivative of the XANES spectrum. The pre-edge energy was determined from the maximum of the pre-edge peak. Background removal and normalization procedures were carried out using the Athena software package using standard methods. Standard procedures based on Artemis software (Demeter 0.9.20) were used to extract the extended X-ray absorption fine structure (EXAFS) data. The coordination parameters were obtained by the least square fit in R-space of the nearest neighbor, k^2 weighted Fourier transform data. The data fit equally well with both k^1 and k^3 weightings.

DMF solution of $Cu(OTf)_2$: $Cu(OTf)_2$ (72.3 mg, 0.2 mmol) was dissolved in 3 mL dry DMF, and then the solution was transferred into the XAS solution cell and sealed with the screw top. The XAS spectrum of $Cu(OTf)_2$ (in DMF solution) was measured at room temperature.

Reaction of 1a and $Cu(OTf)_2$ under nitrogen: **1a** (248 mg, 2.0 mmol) and $Cu(OTf)_2$ (72.3 mg, 0.2 mmol) was mixed in 3 mL dry DMF under nitrogen at 80 °C for 1 mintues, and then the solution was transferred into the XAS solution cell and sealed with the screw top. The XAS spectrum was measured at room temperature.

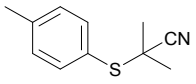
Reaction of 1a and $Cu(OTf)_2$ under air: **1a** (248 mg, 2.0 mmol) and $Cu(OTf)_2$ (72.3 mg, 0.2 mmol) was mixed in 3 mL dry DMF under air at 80 °C for 1h, and then the solution was transferred into the XAS solution cell and sealed with the screw top. The XAS spectrum was measured at room temperature.

General Procedures

2-methyl-2-(p-tolylthio)propanenitrile (3a):

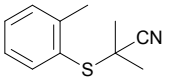
$Cu(OTf)_2$ (0.015 mmol, 5.5 mg), 1,10-Phenanthroline hydrate (0.06 mmol, 10.8 mg), p-methylthi ophen-ol (0.3 mmol, 37.2 mg), AIBN (0.6 mmol, 98.4 mg) were added into an oven-dried Schlenk tube equipped with a magnetic stirred bar. And DCE (3 mL) injected into the Schlenk tube. The Schlenk tube was then heated up to 80 °C and kept stirring for 12 hours. After completion of the reaction, as indicated byTLC and GC-MS, The pure product (yield 85%, 48.7 mg) was obtained by flash column chromatographyon silica gel (petroleumether : ethyl acetate = 200 : 1).

Detailed descriptions for products:



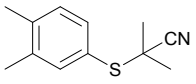
2-methyl-2-(p-tolylthio)propanenitrile (3a) :

(Isolated yield: 85%, colorless oil, 48.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 2.38 (s, 3H), 1.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.7, 136.8, 130.1, 126.5, 122.6, 39.9, 27.5, 21.4. HRMS (ESI) calcd for $C_{11}H_{13}NSNa^+$ 214.0661, found $[(M+Na)]^+$ 214.0666.



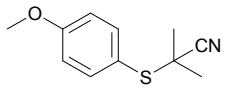
2-methyl-2-(o-tolylthio)propanenitrile (3b):

(Isolated yield: 77%, colorless oil, 44.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (t, J = 8.0 Hz, 1H), 7.29-7.32 (m, 2H), 7.22(s, 1H), 2.55 (d, J = 8.0 Hz, 3H), 1.60 (d, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 138.1, 130.9, 130.5, 129.3, 126.8, 122.7, 40.1, 27.8, 21.5.



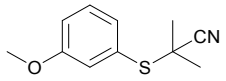
2-(3,4-dimethylphenylthio)-2-methylpropanenitrile (3c):

(Isolated yield: 65%, yellow oil, 40.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 8.0 Hz, 2H), 7.16 (d, J = 8.0 Hz, 1H), 2.28 (s, 6H), 1.59 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 137.8, 137.7, 134.4, 130.5, 126.6, 122.7, 39.8, 27.6, 19.7. HRMS (ESI) calcd for $C_{12}H_{15}NSNa^+$ 228.0817, found $[(M+Na)]^+$ 228.0821.



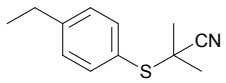
2-(4-methoxyphenylthio)-2-methylpropanenitrile (3d):

(Isolated yield: 72%, Colorless oil, 44.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 8.0 Hz, 2H), 6.93 (d, J = 8.0 Hz, 2H), 3.83 (s, 3H), 1.58 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5, 138.6, 122.6, 120.7, 114.7, 55.4, 40.1, 27.4. HRMS (ESI) calcd for $C_{11}H_{13}NOSNa^+$ 230.0610, found $[(M+Na)]^+$ 230.0614.



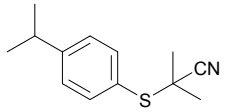
2-(3-methoxyphenylthio)-2-methylpropanenitrile (3e):

(Isolated yield: 72%, yellow oil, 44.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 8.0 Hz, 1H), 7.24-7.27 (m, 2H), 7.00 (d, J = 8.0 Hz, 1H), 3.83 (s, 3H), 1.61 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 130.9, 130.0., 128.8, 122.7, 121.3, 116.6, 55.5, 39.8, 27.6. HRMS (ESI) calcd for $C_{11}H_{13}NOSNa^+$ 230.0610, found $[(M+Na)]^+$ 230.0610.



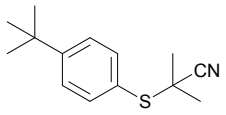
2-(4-ethylphenylthio)-2-methylpropanenitrile (3f) :

(Isolated yield: 83%, yellow oil, 51.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 2.70-2.65 (m, 2H), 1.59 (s, 6H), 1.25 (t, J = 8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.9, 136.9, 128.9, 126.7, 122.6, 39.8, 28.7, 27.6, 15.3.



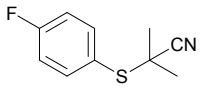
2-(4-isopropylphenylthio)-2-methylpropanenitrile (3g):

(Isolated yield: 74%, colorless oil, 48.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 2.94 (d, J = 8.0 Hz, 1H), 1.60 (s, 6H), 1.26 (d, J = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.4, 136.9, 127.4, 126.8, 122.6, 39.8, 34.0, 27.6, 23.8. HRMS (ESI) calcd for $C_{13}H_{17}NSNa^+$ 242.0974, found $[(M+Na)]^+$ 242.0983.



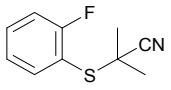
2-(4-tert-butylphenylthio)-2-methylpropanenitrile (3h):

(Isolated yield: 95%, yellow oil, 66.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 1.60 (s, 6H), 1.33 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.7, 136.6, 126.5, 126.3, 122.7, 39.8, 34.8, 31.2, 27.6. HRMS (ESI) calcd for $C_{14}H_{19}NSNa^+$ 256.1130, found $[(M+Na)]^+$ 256.1133.



2-((4-fluorophenyl)thio)-2-methylpropanenitrile (3i):

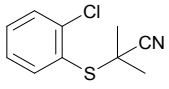
(Isolated yield: 50%, yellow oil, 29.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 - 7.65 (m, 2H), 7.12 (t, J = 8.0Hz, 2H), 1.60 (s, 6H). ^{13}C NMR (100 MHz, CDCl3): δ 164.3 (d, J = 250.0 Hz), 139.1 (d, J = 9.0 Hz), 125.3 (d, J = 4.0 Hz), 122.29, 116.6 (d, J = 22.0 Hz), 40.1, 27.4. HRMS (ESI) calcd for $C_{10}H_{10}FNSNa^+$ 218.0410, found $[(M+Na)]^+$ 218.0418.



2-((2-fluorophenyl)thio)-2-methylpropanenitrile (3j):

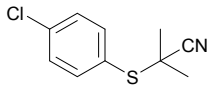
(Isolated yield: 90%, yellow oil, 52.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (t, J = 8.0 Hz, 1H), 7.51-7.45 (m, 1H), 7.27-7.16 (m, 2H), 1.65 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8 (d, J = 248.0 Hz), 139.5, 133.0 (d, J =

8.0 Hz), 125.0 (d, J = 4.0 Hz), 122.1, 116.9 (d, J = 18.0 Hz), 116.3 (d, J = 23.0 Hz), 40.6, 27.6. HRMS (ESI) calcd for $C_{10}H_{10}FNSNa^+$ 218.0410, found $[(M+Na)]^+$ 218.0412.



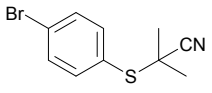
2-((2-chlorophenyl)thio)-2-methylpropanenitrile (3k):

(Isolated yield: 78%, yellow oil, 48.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82-7.80 (m, 1H), 7.44 (d, J = 8.0 Hz, 1H), 7.30-7.25 (m, J = 8.0 Hz, 2H), 1.58 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.5, 138.9, 131.6, 130.4, 129.3, 127.7, 122.2, 41.1, 27.6. HRMS (ESI) calcd for $C_{10}H_{10}ClNSNa^+$ 234.0115, found $[(M+Na)]^+$ 234.0117.



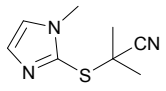
2-((4-chlorophenyl)thio)-2-methylpropanenitrile (3l):

(Isolated yield: 71%, colorless oil, 44.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.60 (m, 2H), 7.40-7.38 (m, 2H), 1.60 (s, 6H). ^{13}C NMR (100 MHz, CDCl3): δ 138.1, 137.0, 129.6, 128.4, 122.2, 40.0, 27.5.



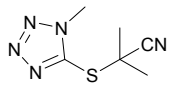
2-((4-bromophenyl)thio)-2-methylpropanenitrile (3m):

(Isolated yield: 84%, yellow oil, 64.5 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 4H), 1.61 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.3, 132.6, 129.0, 125.4, 122.2, 40.0, 27.5.



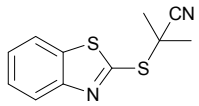
2-methyl-2-((1-methyl-1H-imidazol-2-yl)thio)propanenitrile (3n):

(Isolated yield: 89%, yellow oil, 48.3 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (s, 1H), 7.16 (s,1H), 3.9 (s, 3H), 1.73 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.6, 130.9, 125.1, 122.4, 40.6, 34.4, 27.7. HRMS (ESI) calcd for $C_{14}H_{19}N_3SNa^+$ 204.0566, found $[(M+Na)]^+$ 204.0570.



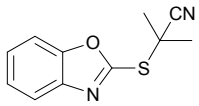
2-methyl-2-((1-methyl-1H-tetrazol-5-yl)thio)propanenitrile (3o):

(Isolated yield: 90%, yellow oil, 49.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.19 (s, 3H), 1.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 120.7, 41.2, 34.7, 27.9. HRMS (ESI) calcd for $C_6H_9N_5SNa^+$ 206.0471, found $[(M+Na)]^+$ 206.0472.



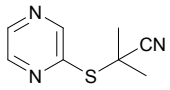
2-(benzo[d]thiazol-2-ylthio)-2-methylpropanenitrile (3p):

(Isolated yield: 94%, yellow oil, 66.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, J = 8.0 Hz, 1H), 7.85 (d, J = 8.0 Hz, 1H), 7.52 - 7.48 (m, 1H), 7.43-7.39 (m, 1H), 1.89 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 153.3, 136.8, 126.6, 125.8, 123.3, 121.3, 41.2, 28.1. HRMS (ESI) calcd for $C_{11}H_{10}N_2S_2Na^+$ 257.0178, found $[(M+Na)]^+$ 257.0189.



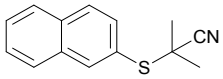
2-(benzo[d]oxazol-2-yl)-2-methylpropanenitrile (3q):

(Isolated yield: 81%, yellow oil, 53.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.72 (m, 1H), 7.54-7.52 (m, 1H), 7.35-7.33 (m, 2H), 1.96 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 151.7, 141.6, 125.2, 124.2, 121.1, 119.8, 110.4, 39.8, 28.2. HRMS (ESI) calcd for $C_{11}H_{10}N_2OSNa^+$ 241.0406, found $[(M+Na)]^+$ 241.0407.



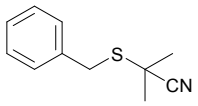
2-(4-tert-butylphenylthio)-2-methylpropanenitrile (3r):

(Isolated yield: 52%, yellow oil, 27.9 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, J = 8.0 Hz, 2H), 8.34 (s, 1H), 1.79 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.2, 145.4, 144.3, 141.9, 121.7, 38.4, 28.0.



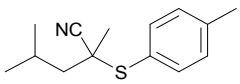
2-methyl-2-(naphthalen-2-ylthio)propanenitrile (3s):

(Isolated yield: 78%, colorless oil, 53.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 7.89-7.85 (m, 3H), 7.74-7.71 (m, 1H), 7.56-7.53 (m, 2H), 1.63 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.2, 133.8, 133.5, 132.7, 128.9, 128.3, 127.8, 127.6, 127.2, 126.8, 122.7, 40.0, 27.7. HRMS (ESI) calcd for C14H13NSNa+ 256.661, found $[(M+Na)]^{+}$ 250.0661.



2-(benzylthio)-2-methylpropanenitrile (3t):

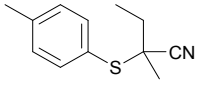
(Isolated yield: 81%, yellow oil, 46.4 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.0 Hz, 2H), 7.33 (t, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 1H), 4.03 (s, 2H), 1.63 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 129.2, 128.8, 127.6, 122.0, 37.4, 36.2, 28.1. HRMS (ESI) calcd for $C_{11}H_{13}NSNa^{+}$ 214.0661, found $[(M+Na)]^{+}$ 214.0666.



2,4-dimethyl-2-(p-tolylthio)pentanenitrile (3u):

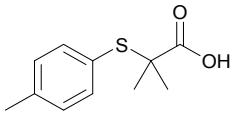
(Isolated yield: 97%, colorless oil, 67.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H), 2.07-1.98 (m, 1H), 1.78-1.67 (m, 2H), 1.51(s, 3H), 1.06-1.03 (m, 6H). ^{13}C NMR (100

MHz, $CDCl_3$): δ 140.6, 137.1, 130.0, 126.1, 122.3, 48.1, 43.6, 26.3, 25.8, 23.9, 23.6, 21.4. HRMS (ESI) calcd for $C_{14}H_{19}NSNa^+$ 256.1130, found $[(M+Na)]^+$ 256.1132.



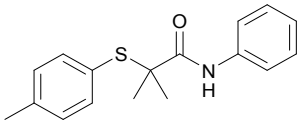
2-methyl-2-(p-tolylthio)butanenitrile (3v):

(Isolated yield: 54%, colorless oil, 33.2 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H), 1.91-1.72 (m, 2H), 1.50 (s, 3H), 1.15 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 137.0, 130.0, 126.1, 121.2, 45.2, 32.8, 24.8, 21.3, 9.6. HRMS (ESI) calcd for $C_{11}H_{13}NSNa^+$ 228.0817, found $[(M+Na)]^+$ 228.0821.



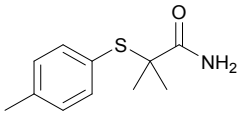
2-methyl-2-(p-tolylthio)propanoic acid (4a):

(Isolated yield: 85%, white solid, 89.2 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 9.64 (s, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H), 1.48 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.3, 139.9, 136.9, 129.6, 127.6, 50.6, 25.4, 21.3(d, J = 3.0 Hz).



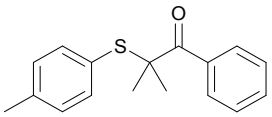
2-methyl-N-phenyl-2-(p-tolylthio)propanamide (4b):

(Isolated yield: 43%, white solid, 61.3 mg); ^1H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.37-7.31 (m, 4H), 7.15-7.08 (m, 3H), 2.31 (s, 3H), 1.57 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 139.4, 137.9, 134.8, 130.0, 129.1, 127.7, 124.3, 119.6, 53.6, 26.7, 21.2.



2-methyl-2-(p-tolylthio)propanamide (4c):

(Isolated yield: 80%, white solid, 83.6 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.67 (s, 1H), 6.11 (s, 1H), 2.34 (s, 3H), 1.49 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.6, 139.2, 135.1, 129.8, 128.0, 52.1, 26.7, 21.2.

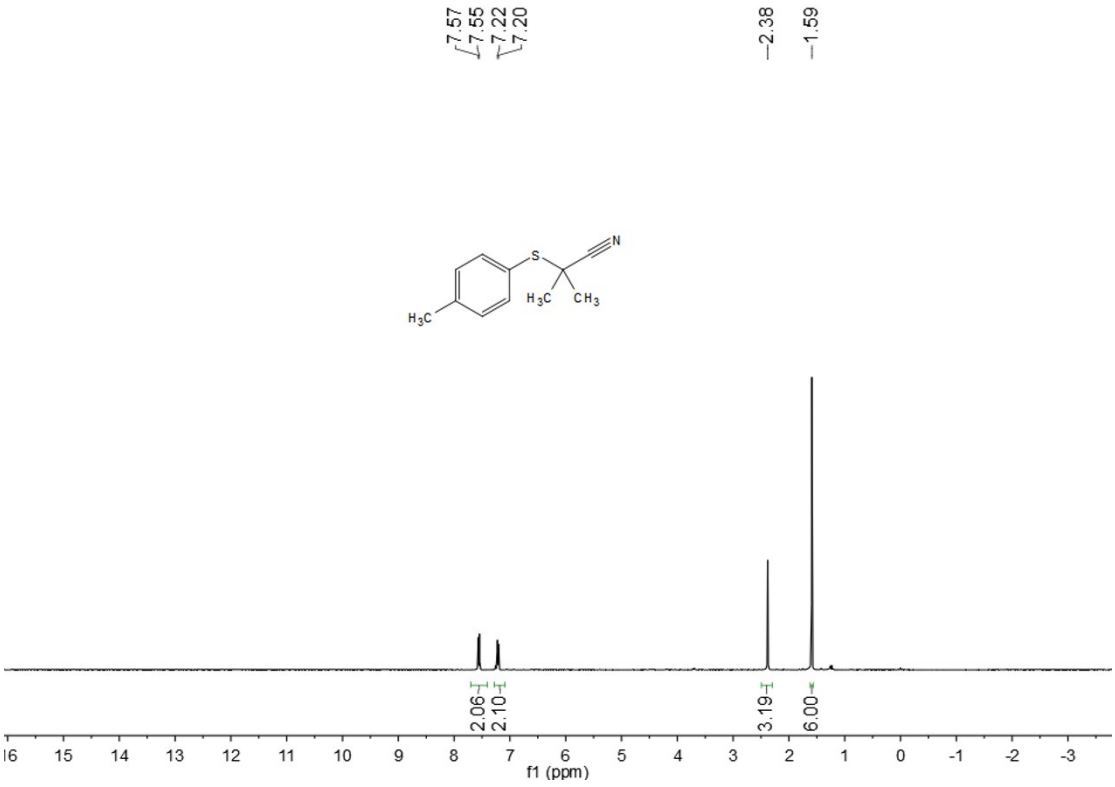


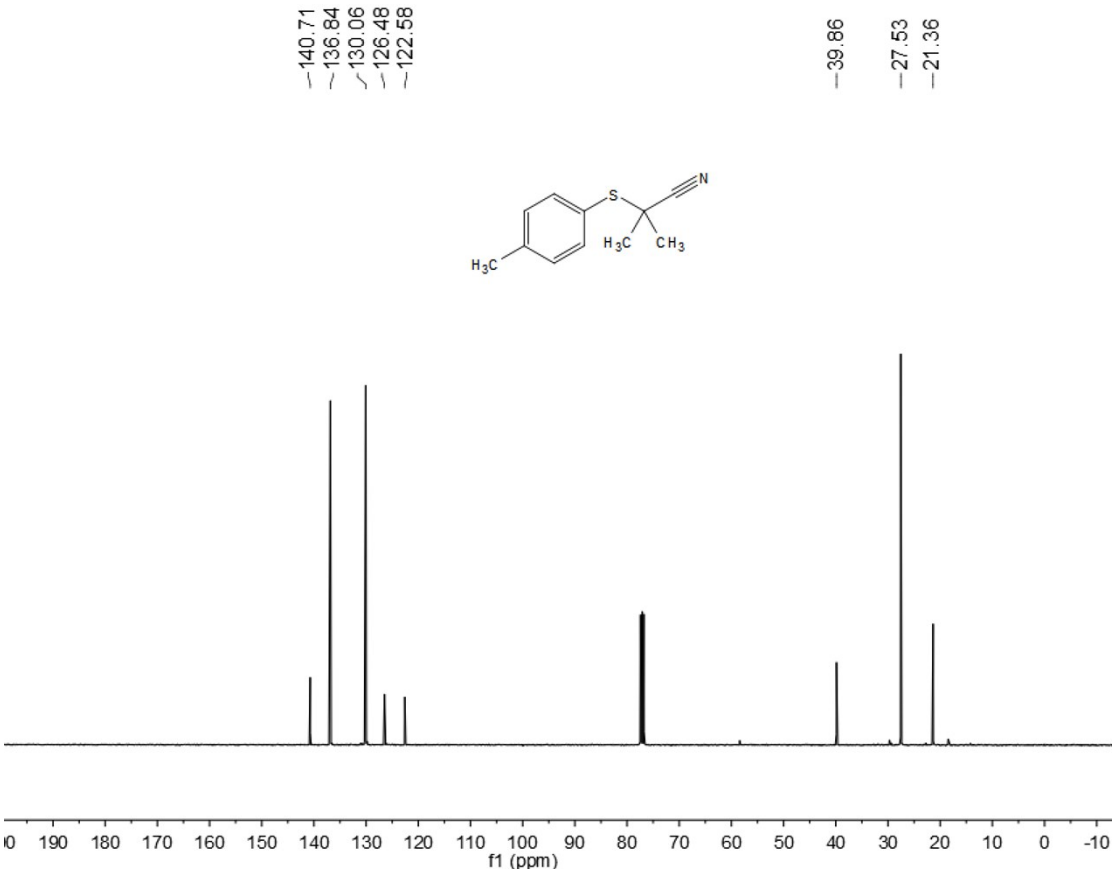
2-methyl-1-phenyl-2-(p-tolylthio)propan-1-one (4d):

(Isolated yield: 71%, white solid, 191.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, J = 8.0 Hz, 2H), 7.51 (m, 1H), 7.43 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 2.30 (s, 3H), 1.53 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.5, 139.7, 137.3, 136.5, 131.7, 129.7(d, J = 7.0 Hz), 128.1, 127.4, 54.9, 26.7, 21.3 (d, J = 2.0 Hz).

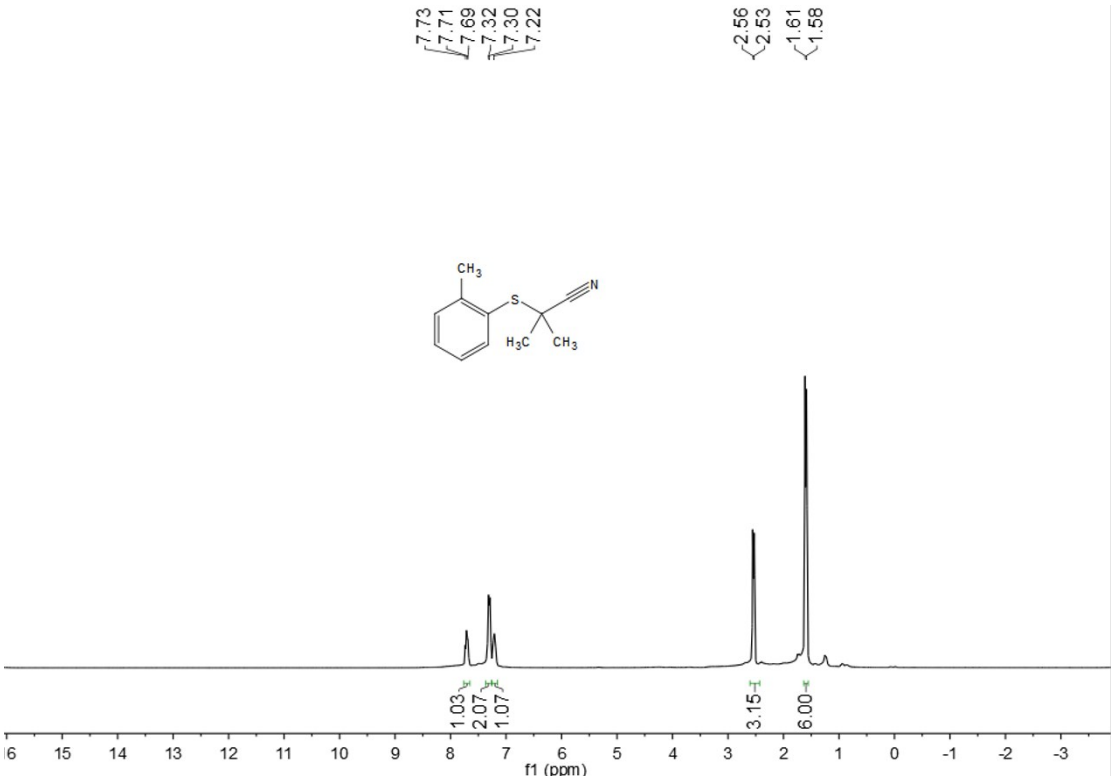
NMR Spectra of Products

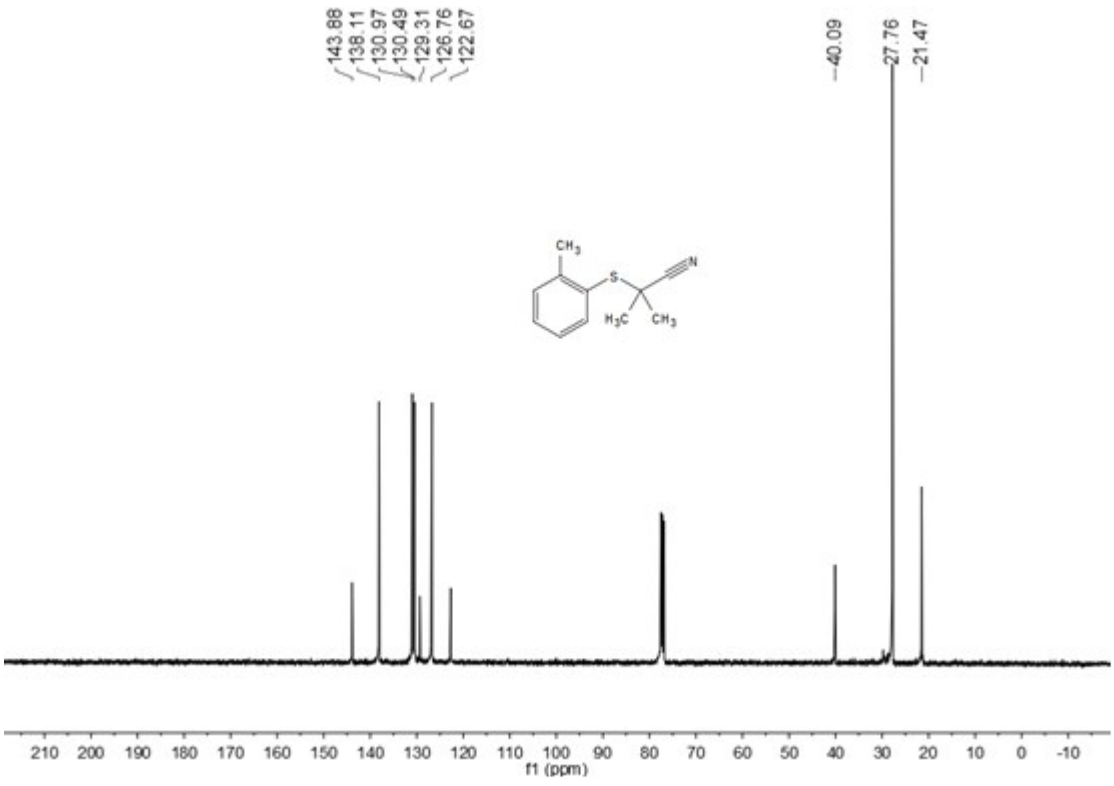
2-methyl-2-(p-tolylthio)propanenitrile (3a) :



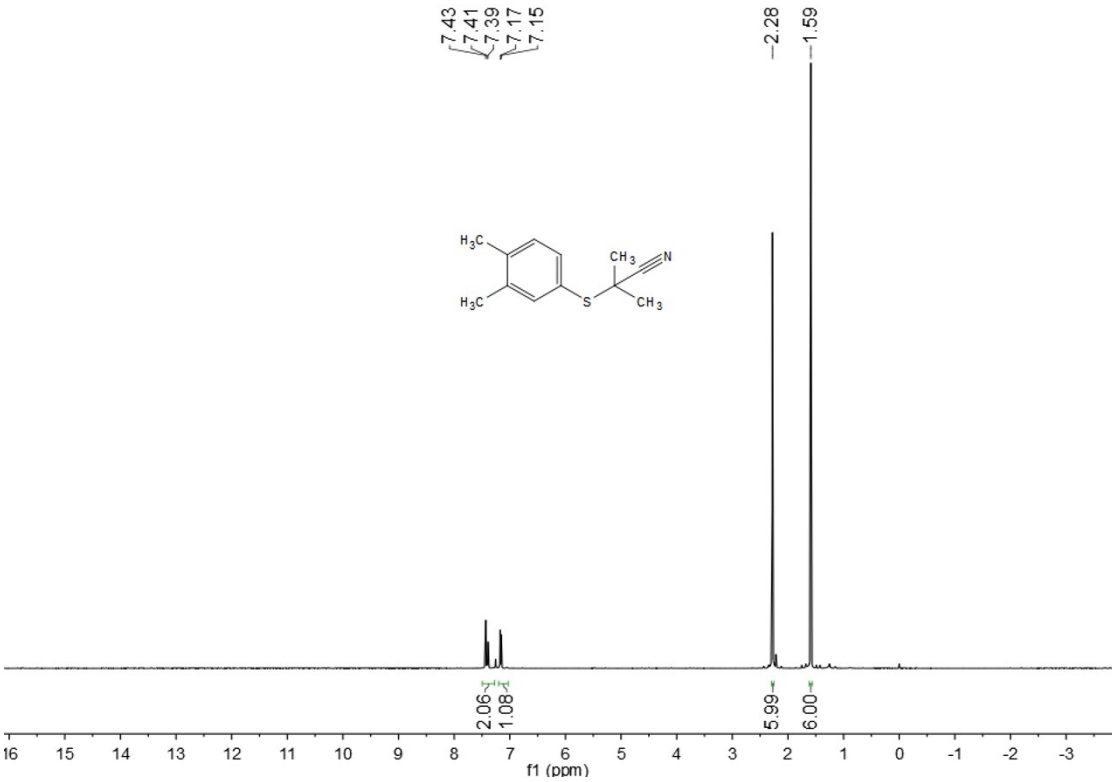


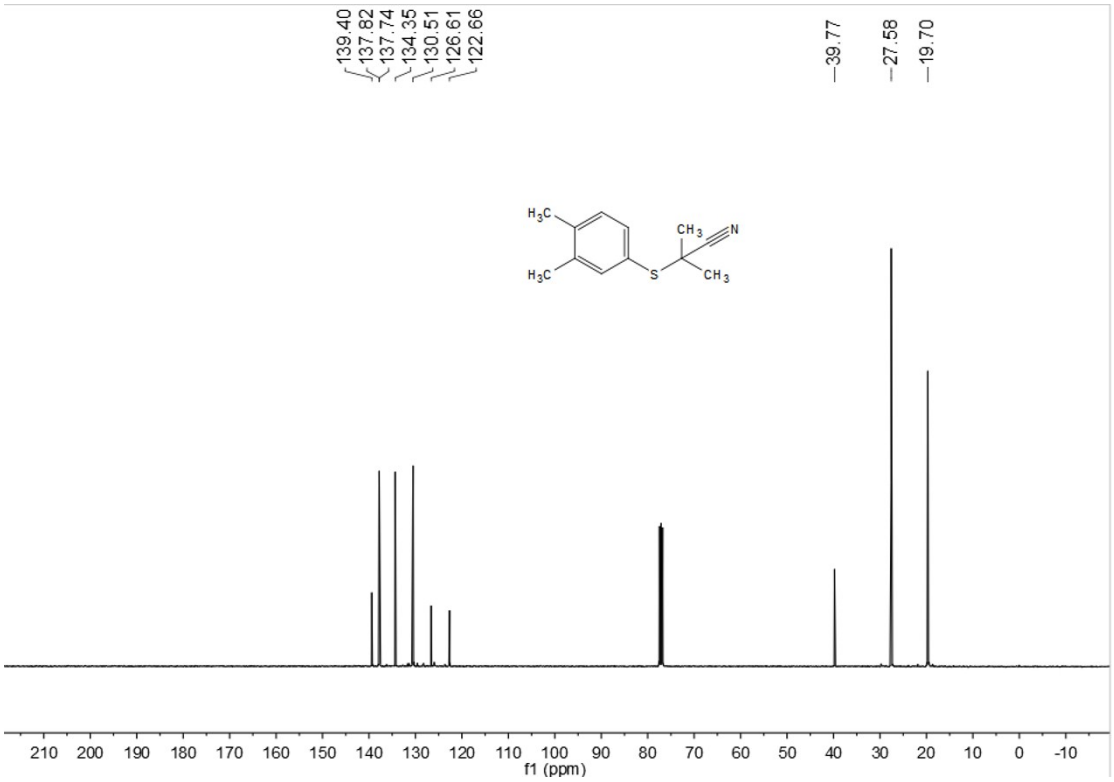
2-methyl-2-(o-tolylthio)propanenitrile (3b):



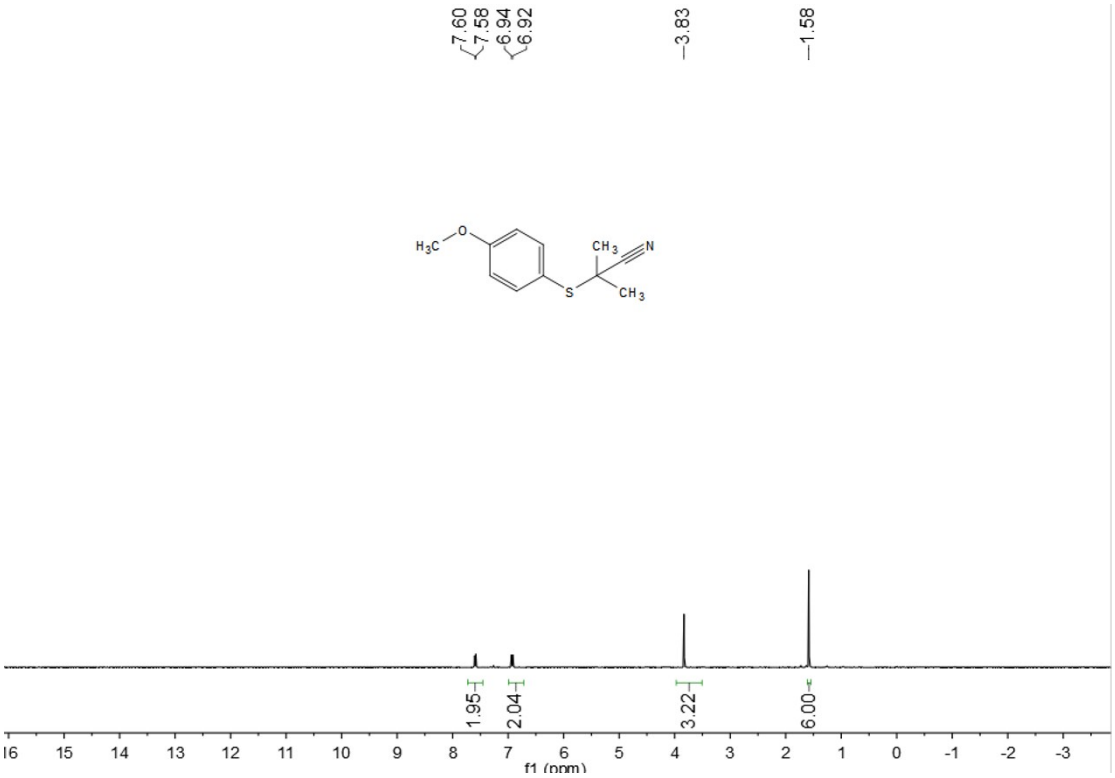


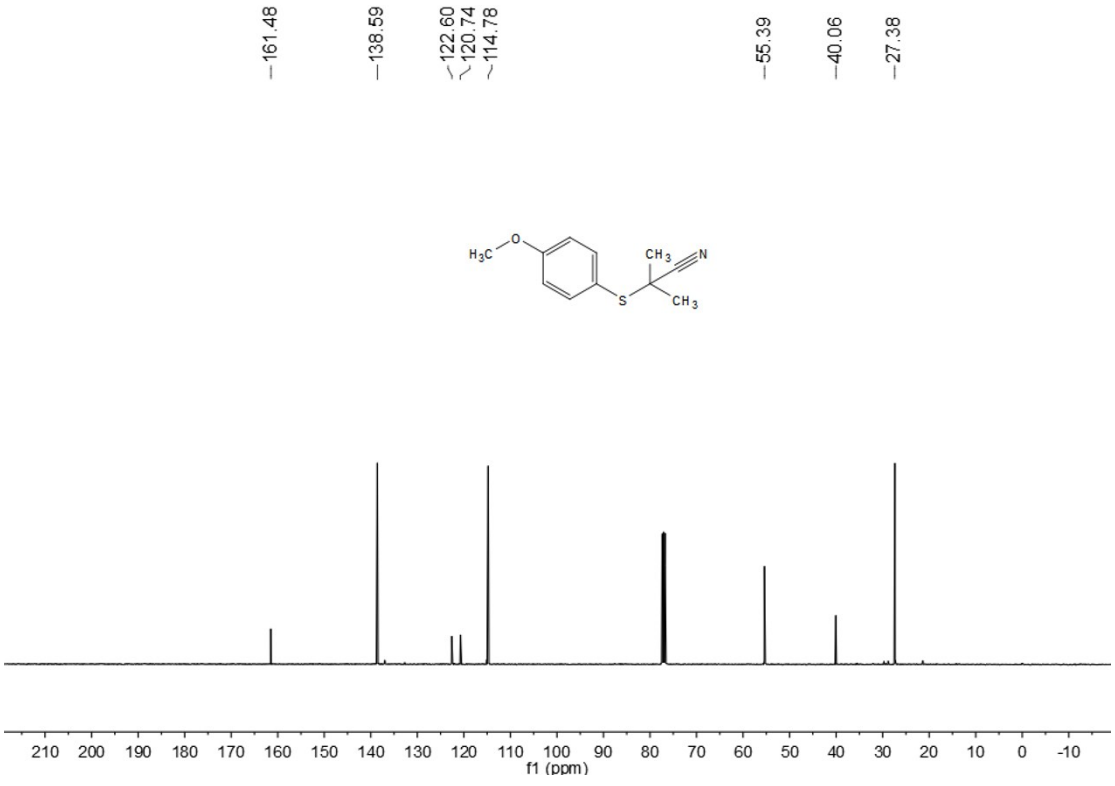
2-(3,4-dimethylphenylthio)-2-methylpropanenitrile (3c):



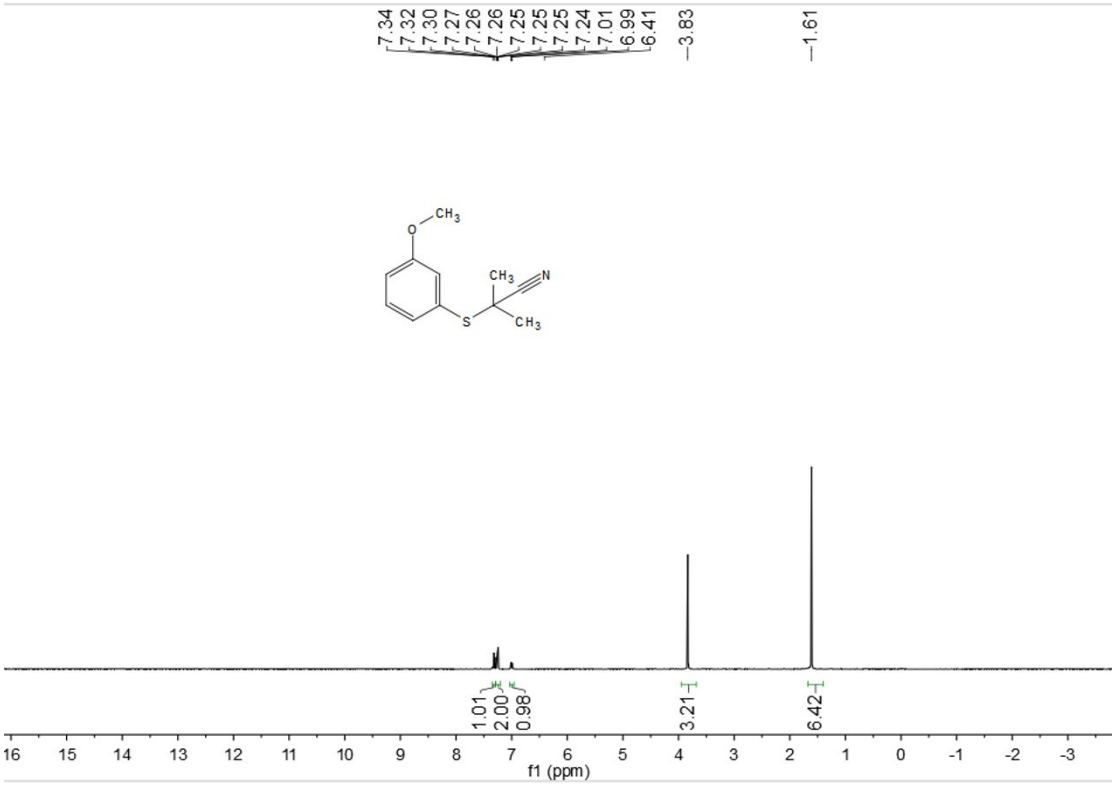


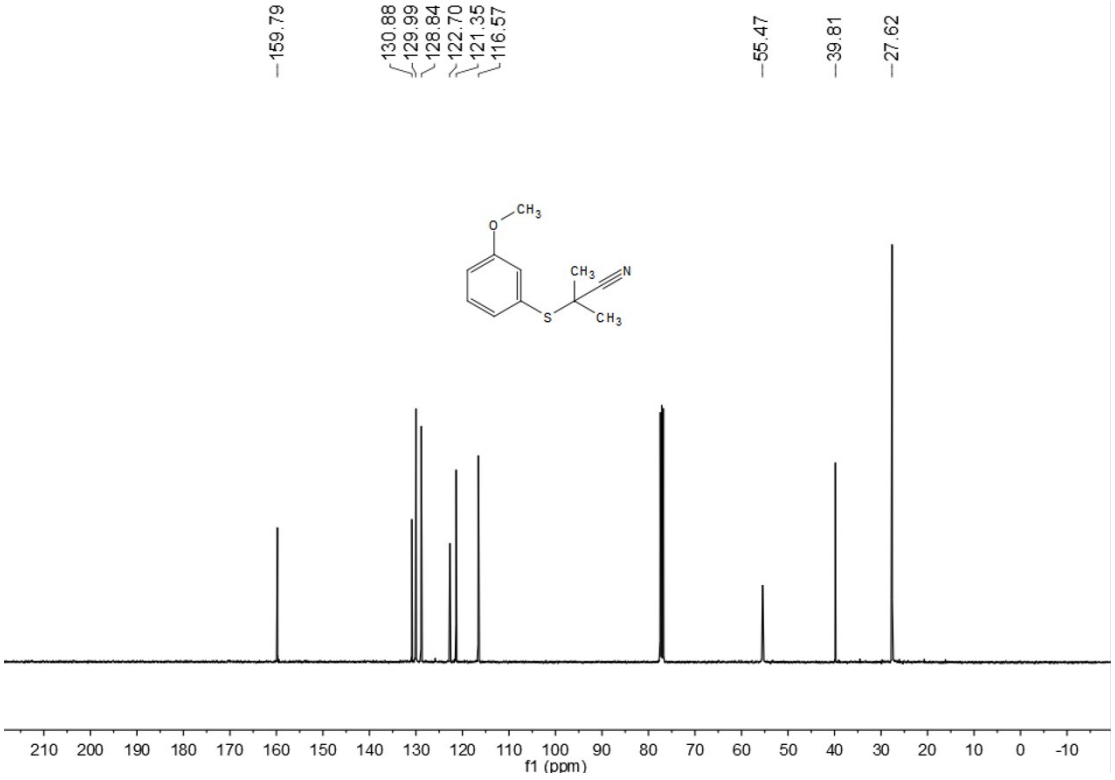
2-(4-methoxyphenylthio)-2-methylpropanenitrile (3d):



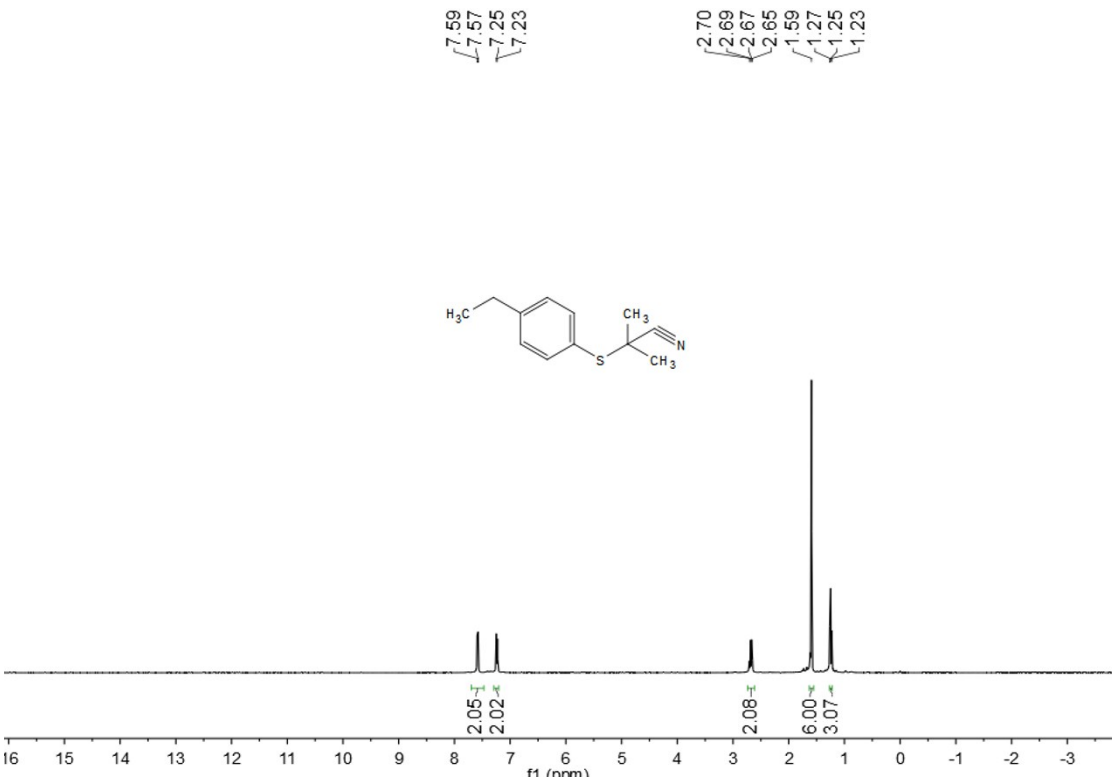


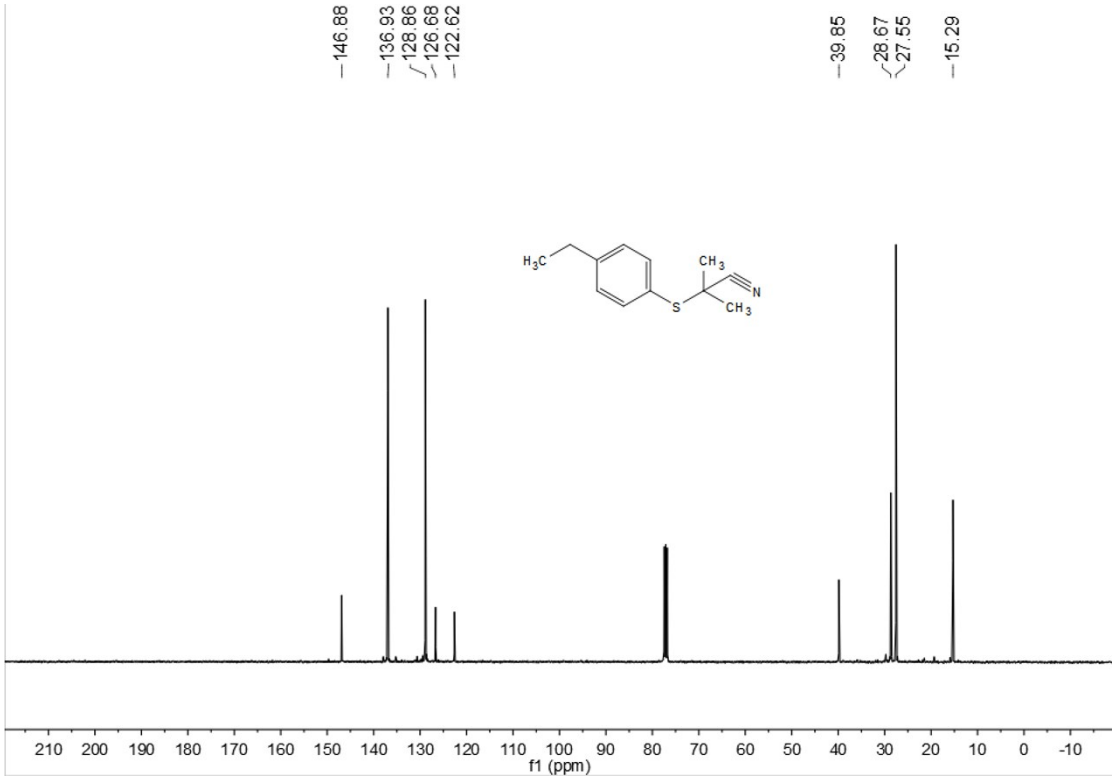
2-(3-methoxyphenylthio)-2-methylpropanenitrile (3e):



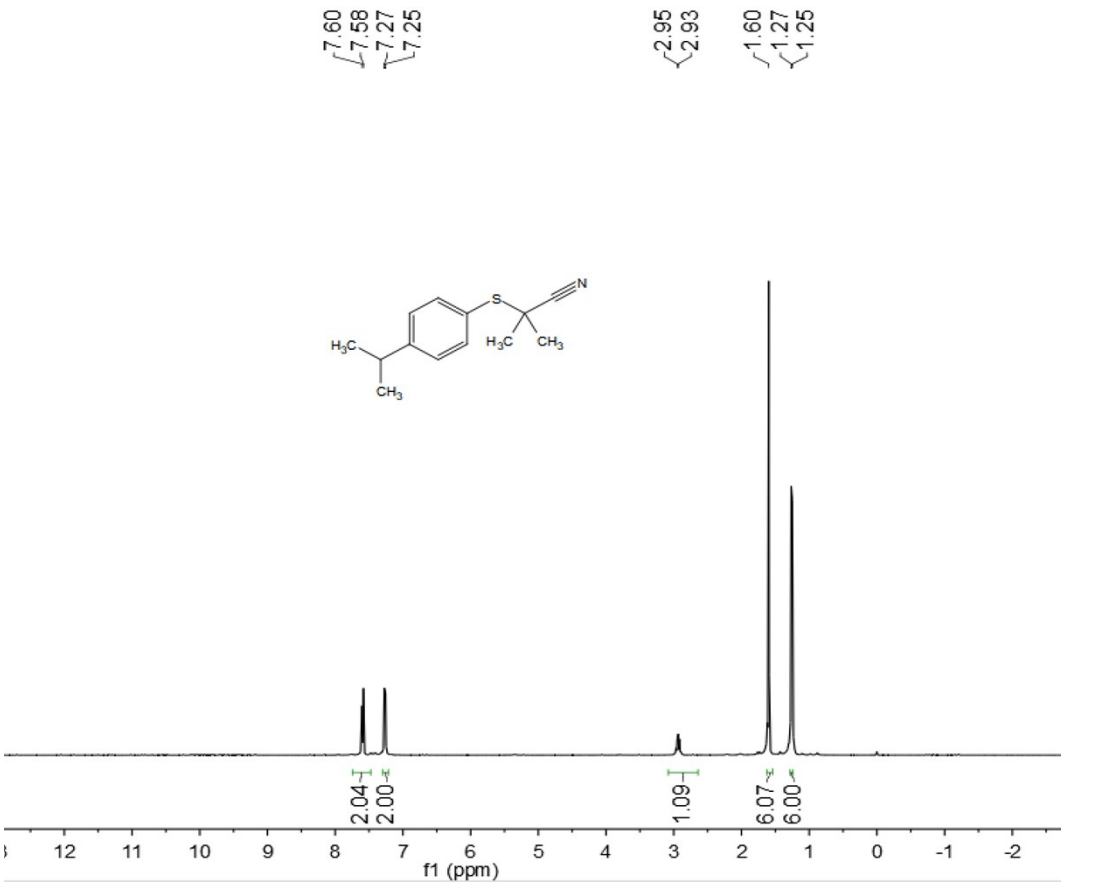


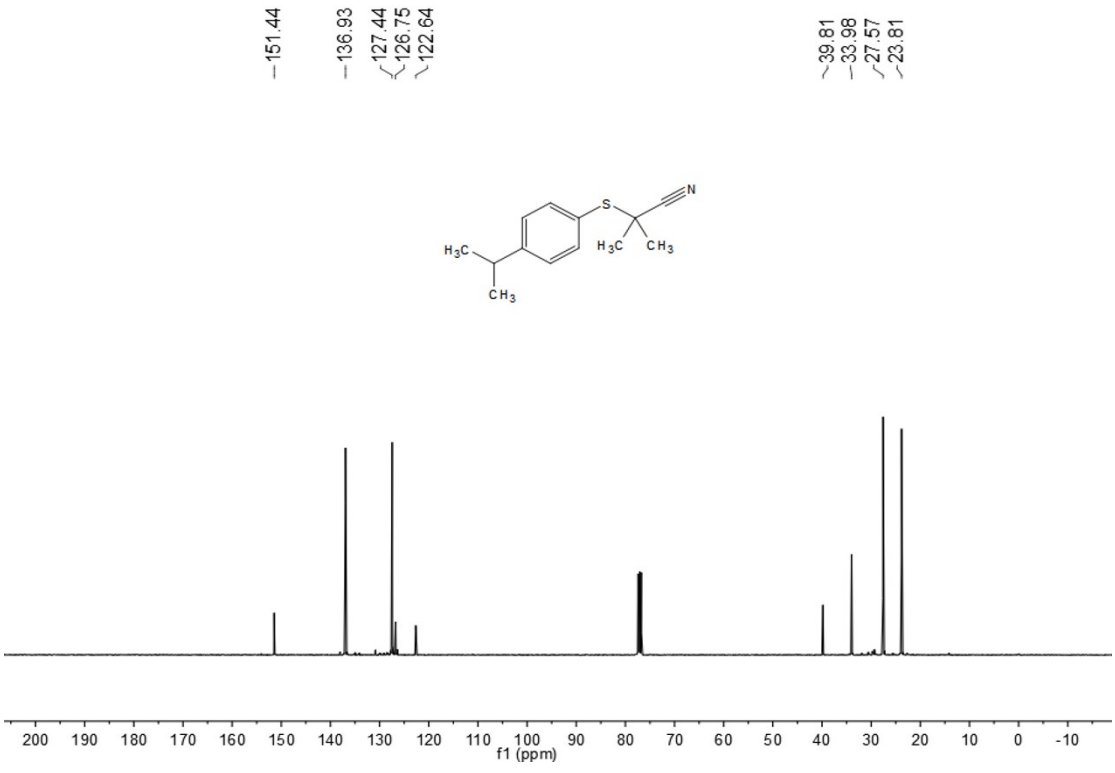
2-(4-ethylphenylthio)-2-methylpropanenitrile (3f) :



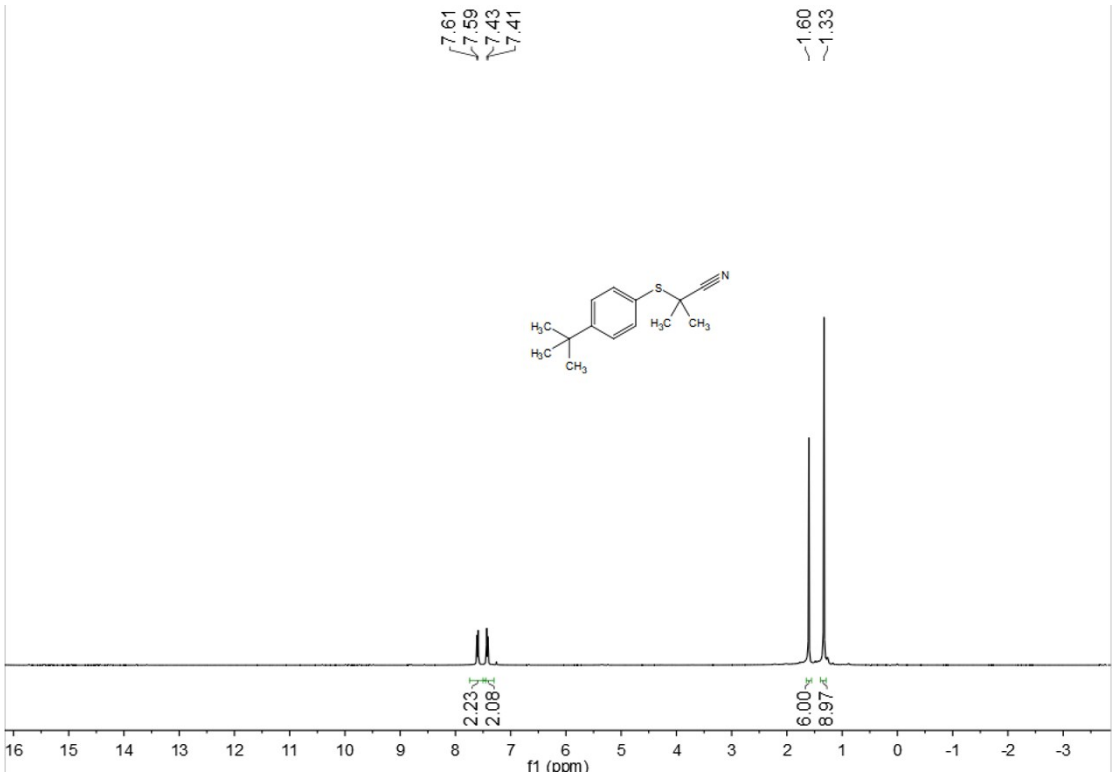


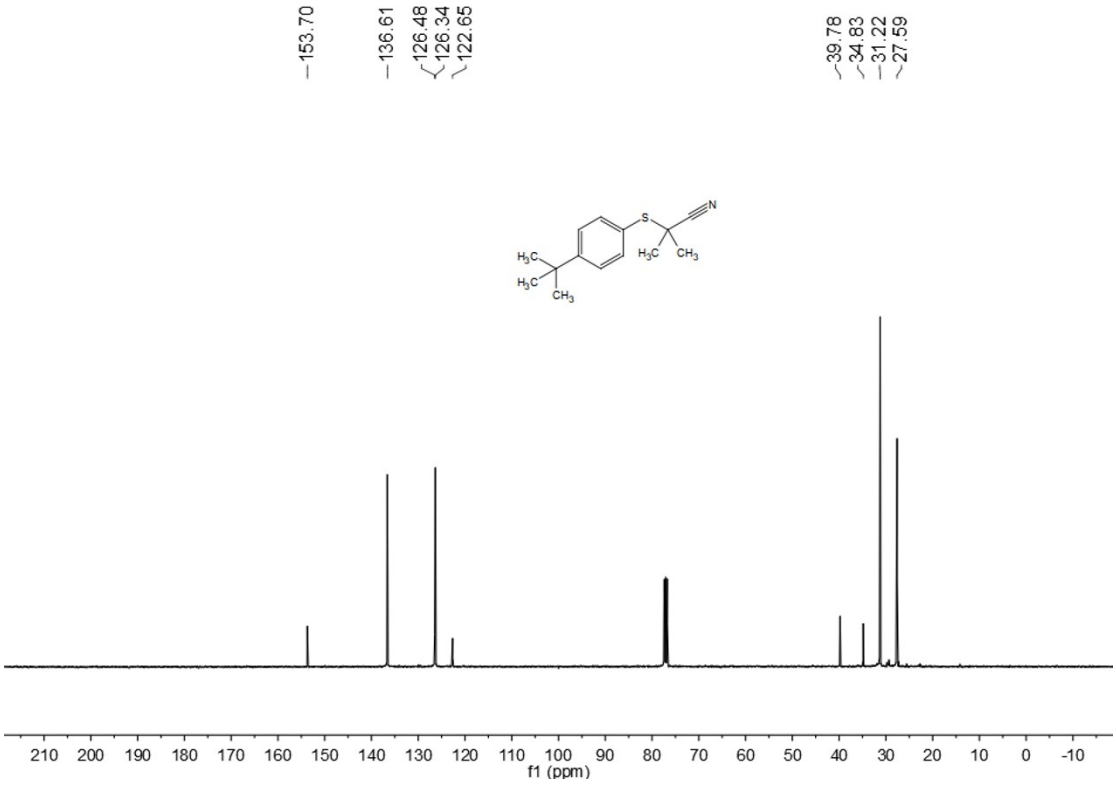
2-(4-isopropylphenylthio)-2-methylpropanenitrile (3g):


7.60
7.58
7.27
7.25
2.95
2.93
1.60
1.27
1.25
S
N
H3C
CH3
H3C
CH3
2.04
2.00
1.09
6.07
6.00
f1 (ppm)

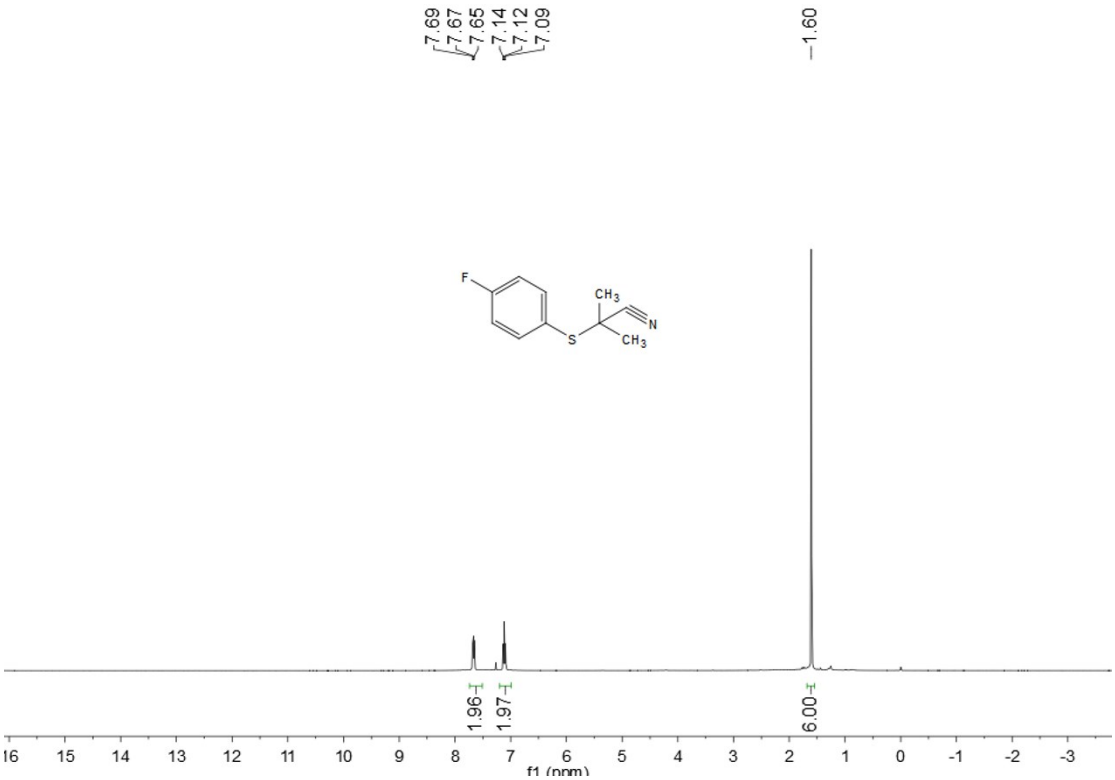

151.44
136.93
127.44
126.75
122.64
39.81
33.98
27.57
23.81
S
N
H3C
CH3
H3C
CH3
f1 (ppm)

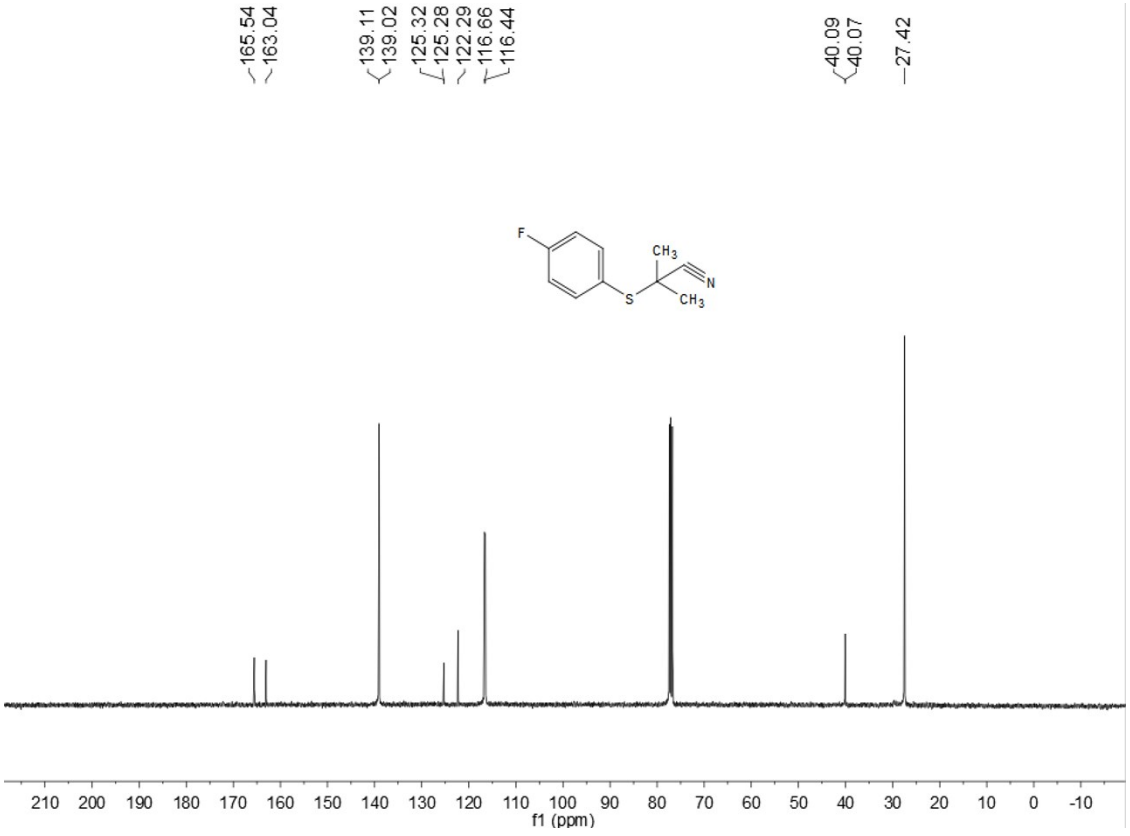
2-(4-tert-butylphenylthio)-2-methylpropanenitrile (3h):



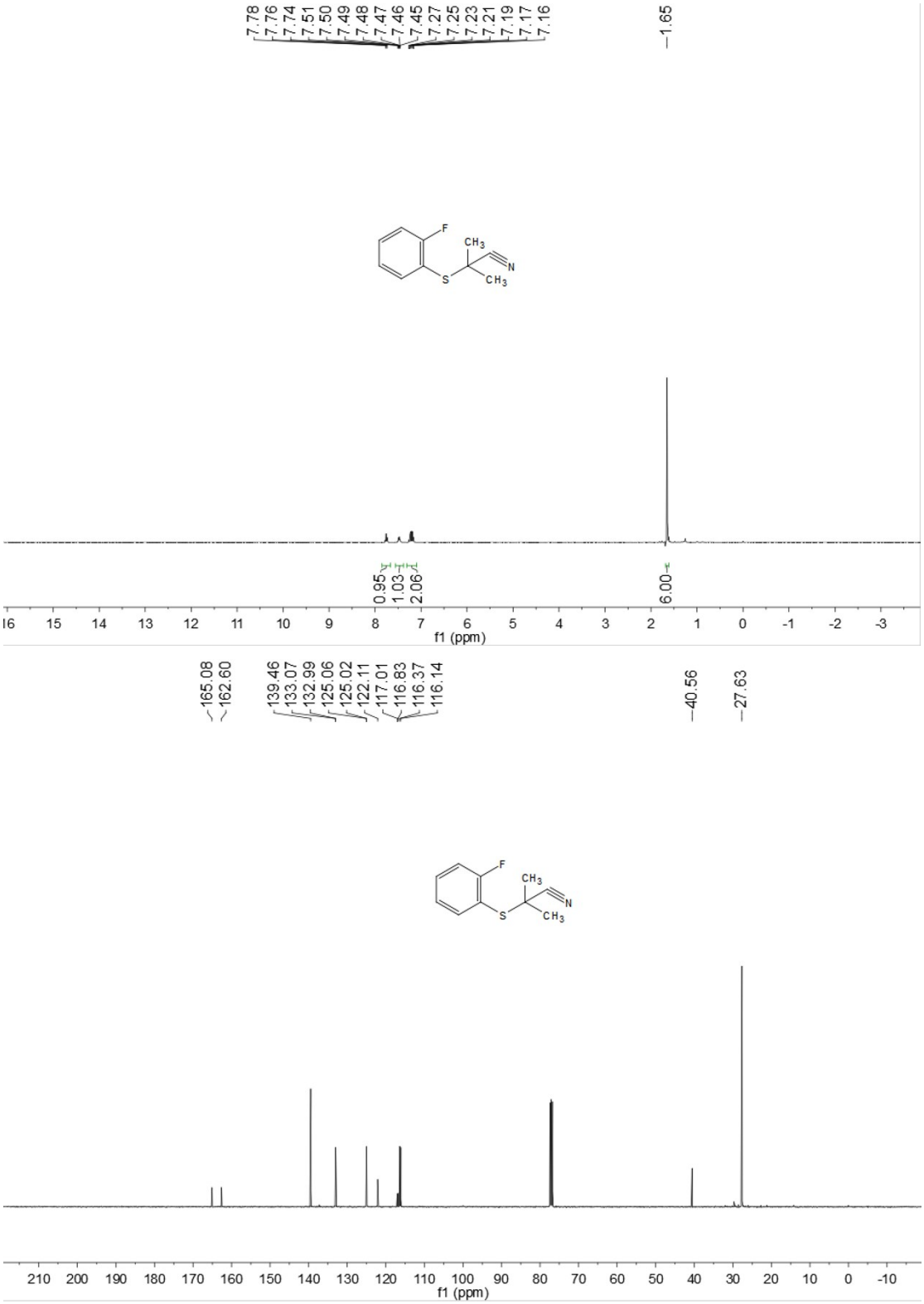


2-((4-fluorophenyl)thio)-2-methylpropanenitrile(3i)

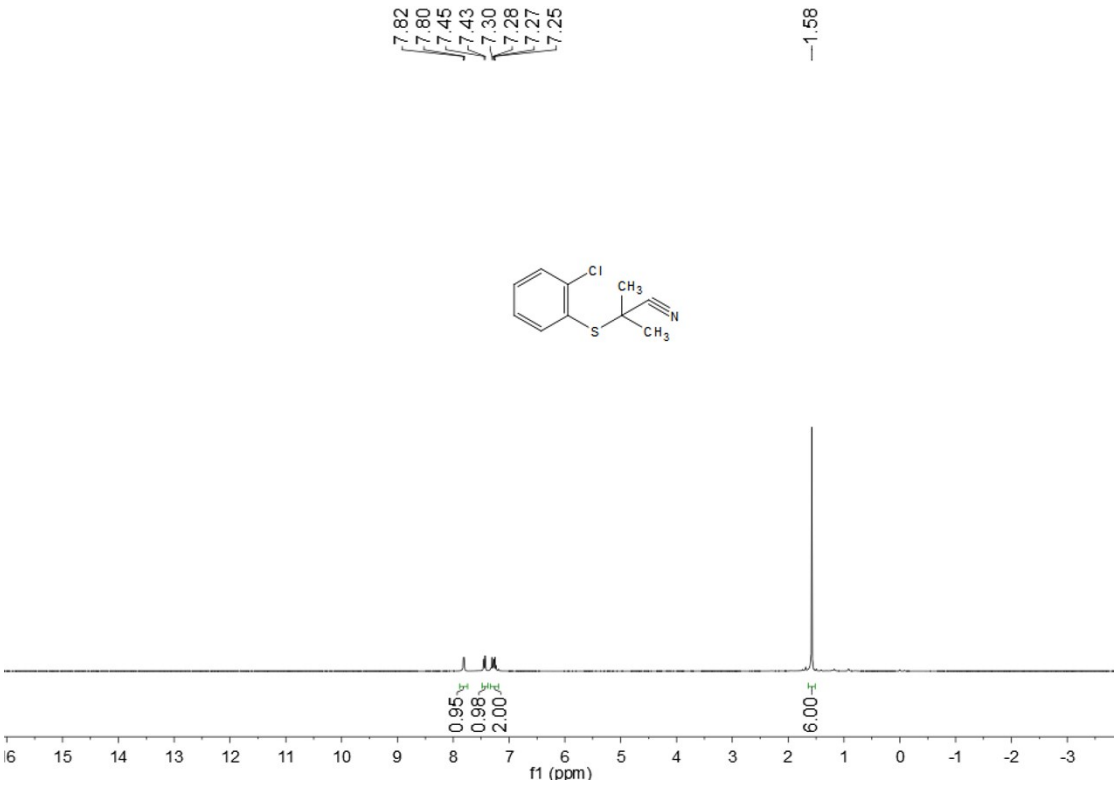


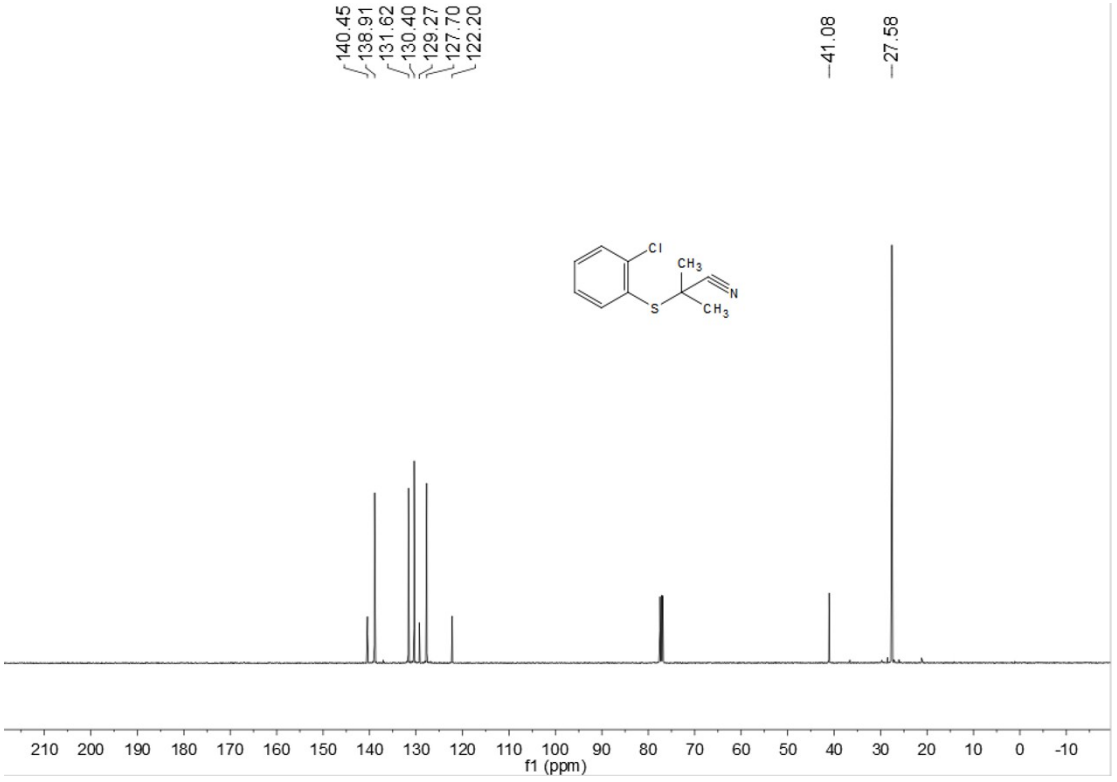


2-((2-fluorophenyl)thio)-2-methylpropanenitrile (3j):

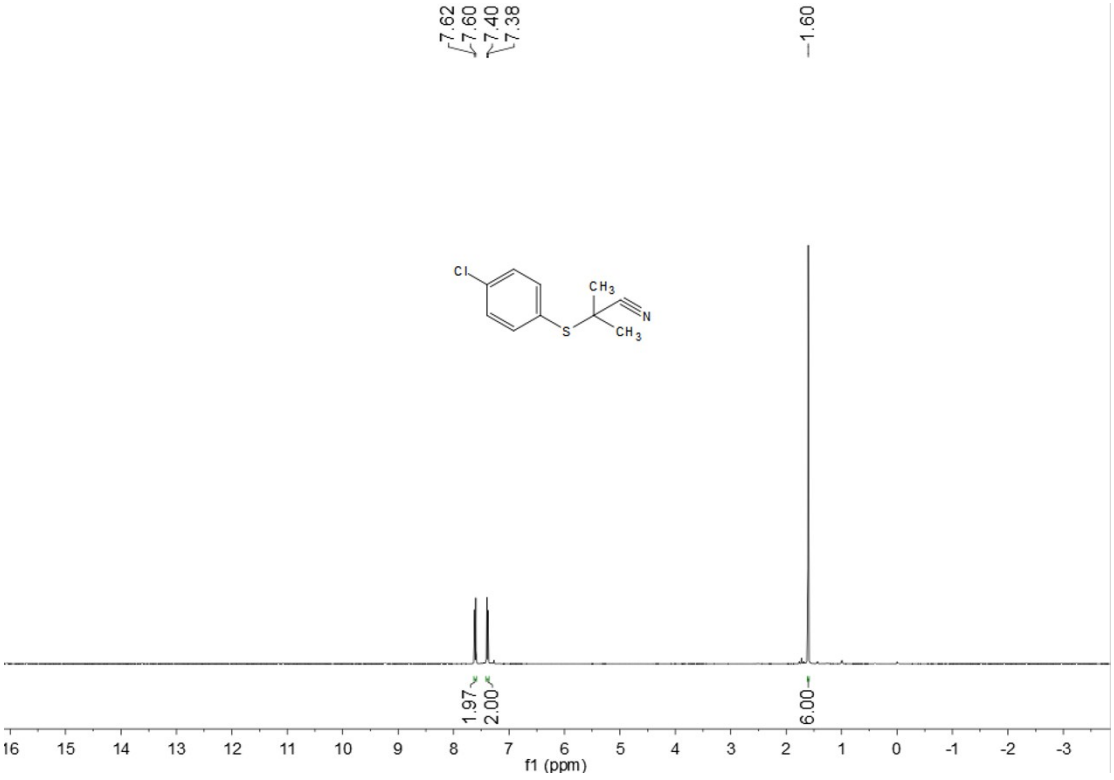


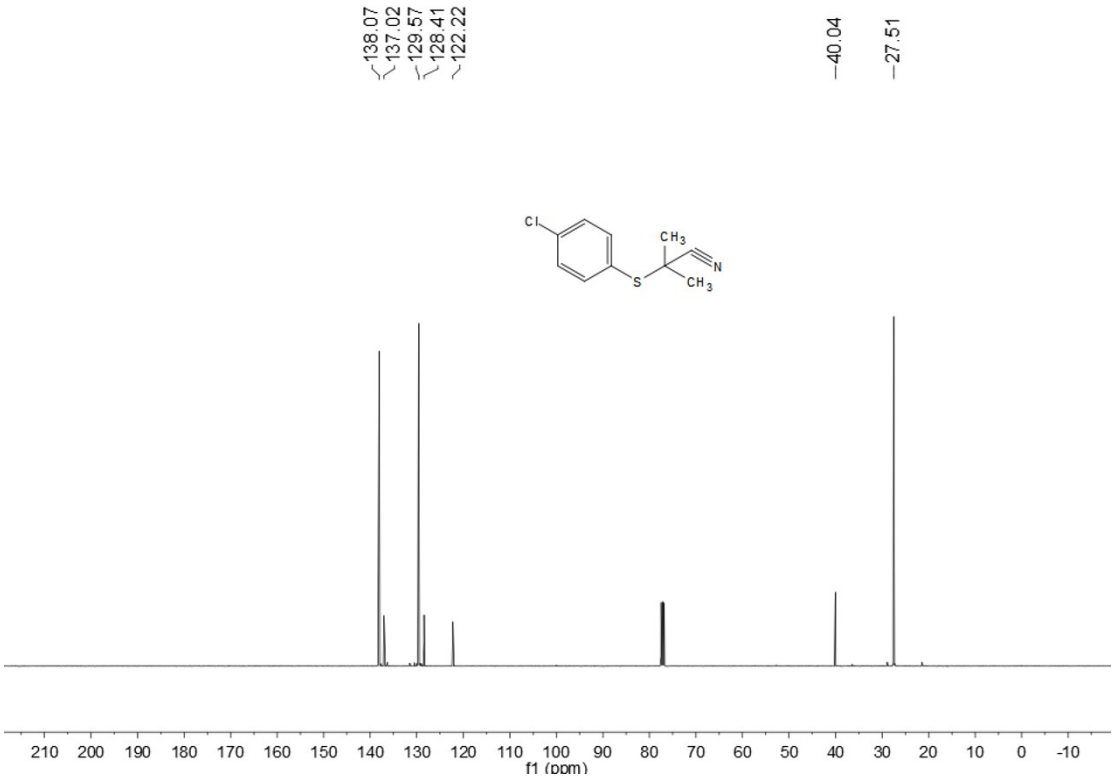
2-((2-chlorophenyl)thio)-2-methylpropanenitrile (3k):



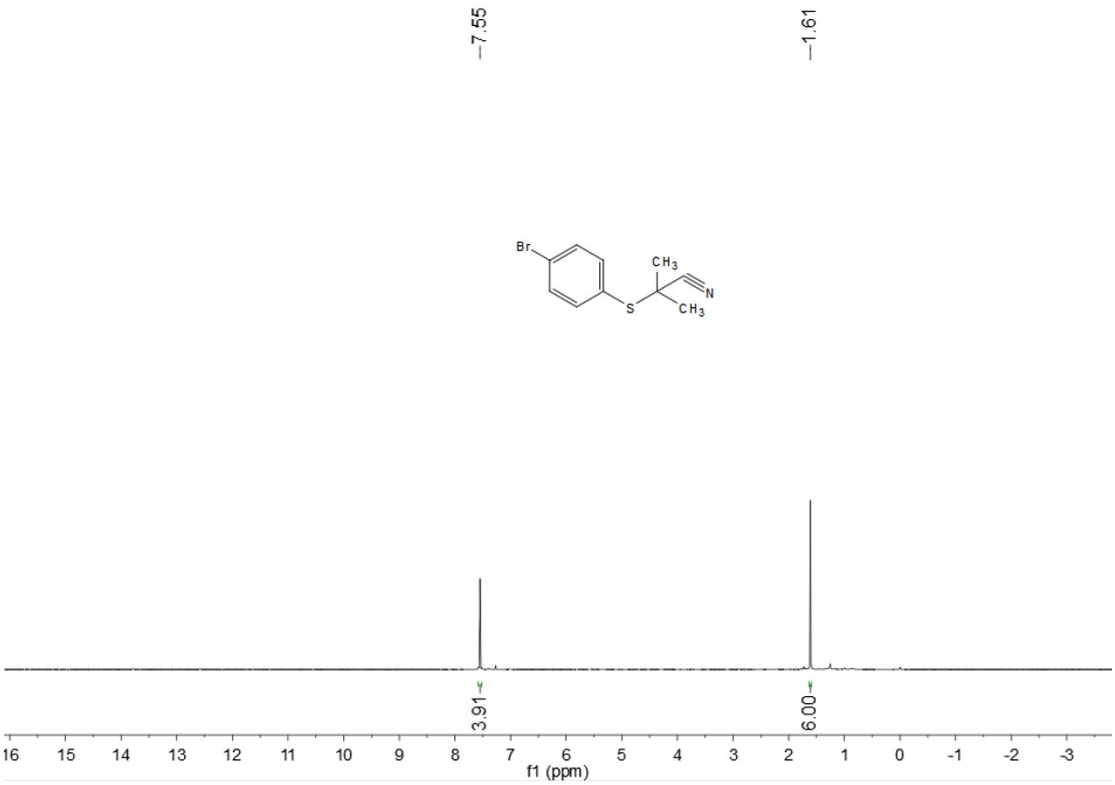


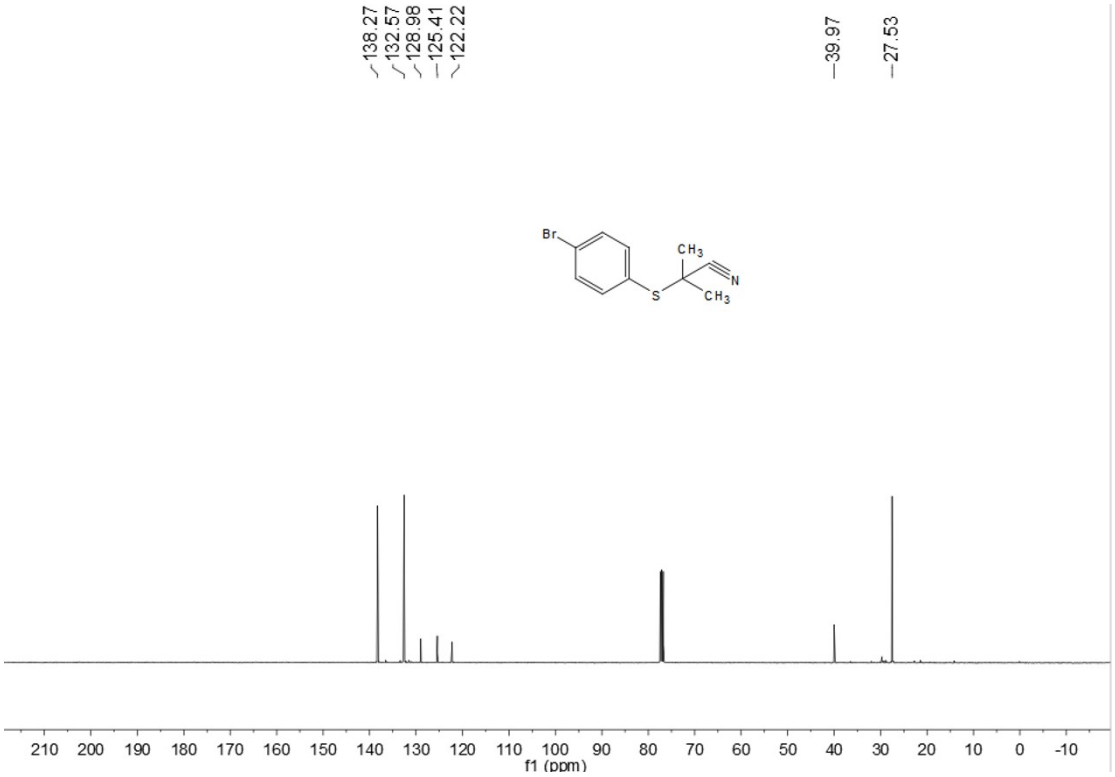
2-((4-chlorophenyl)thio)-2-methylpropanenitrile (3l):



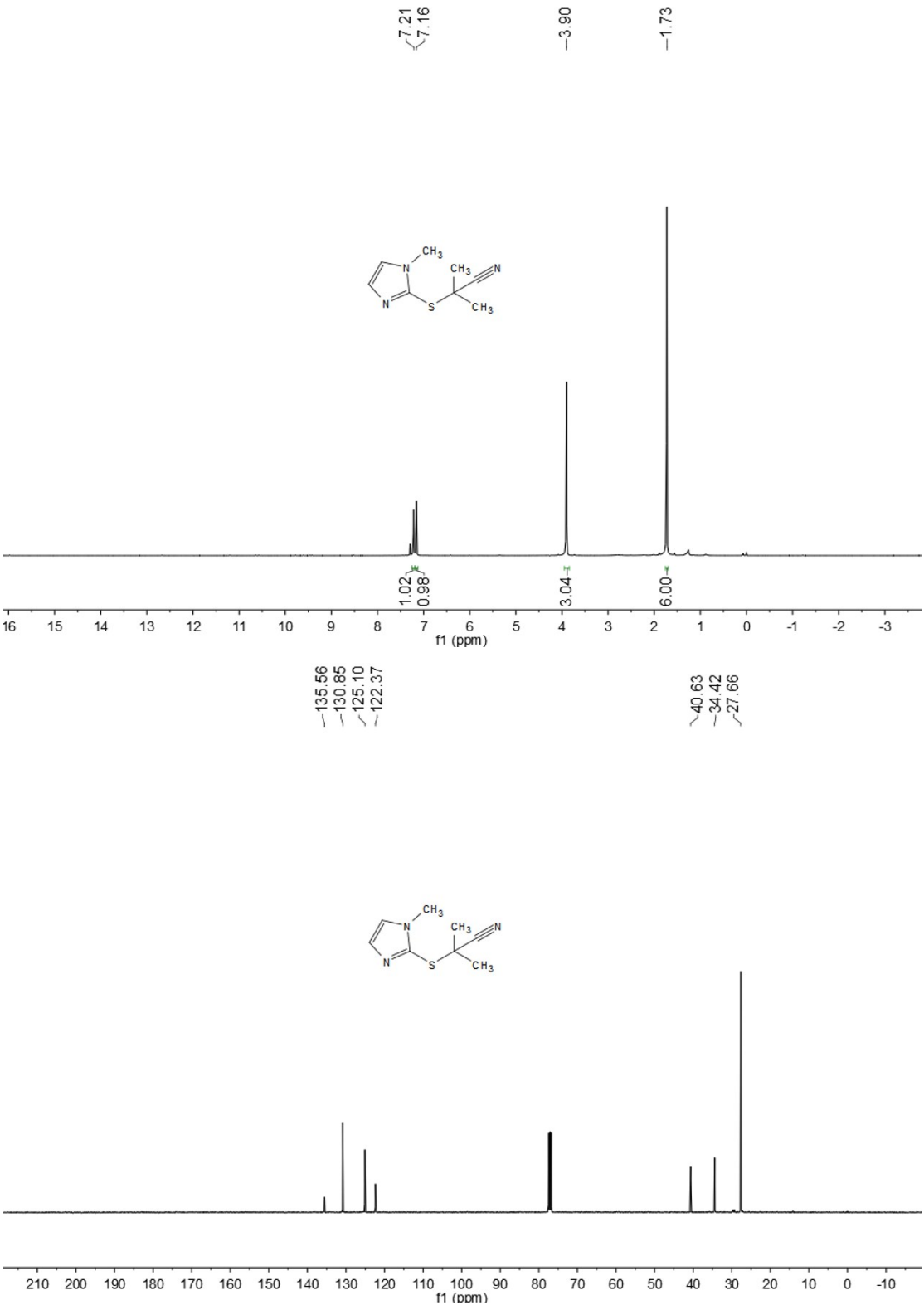


2-((4-bromophenyl)thio)-2-methylpropanenitrile (3m):

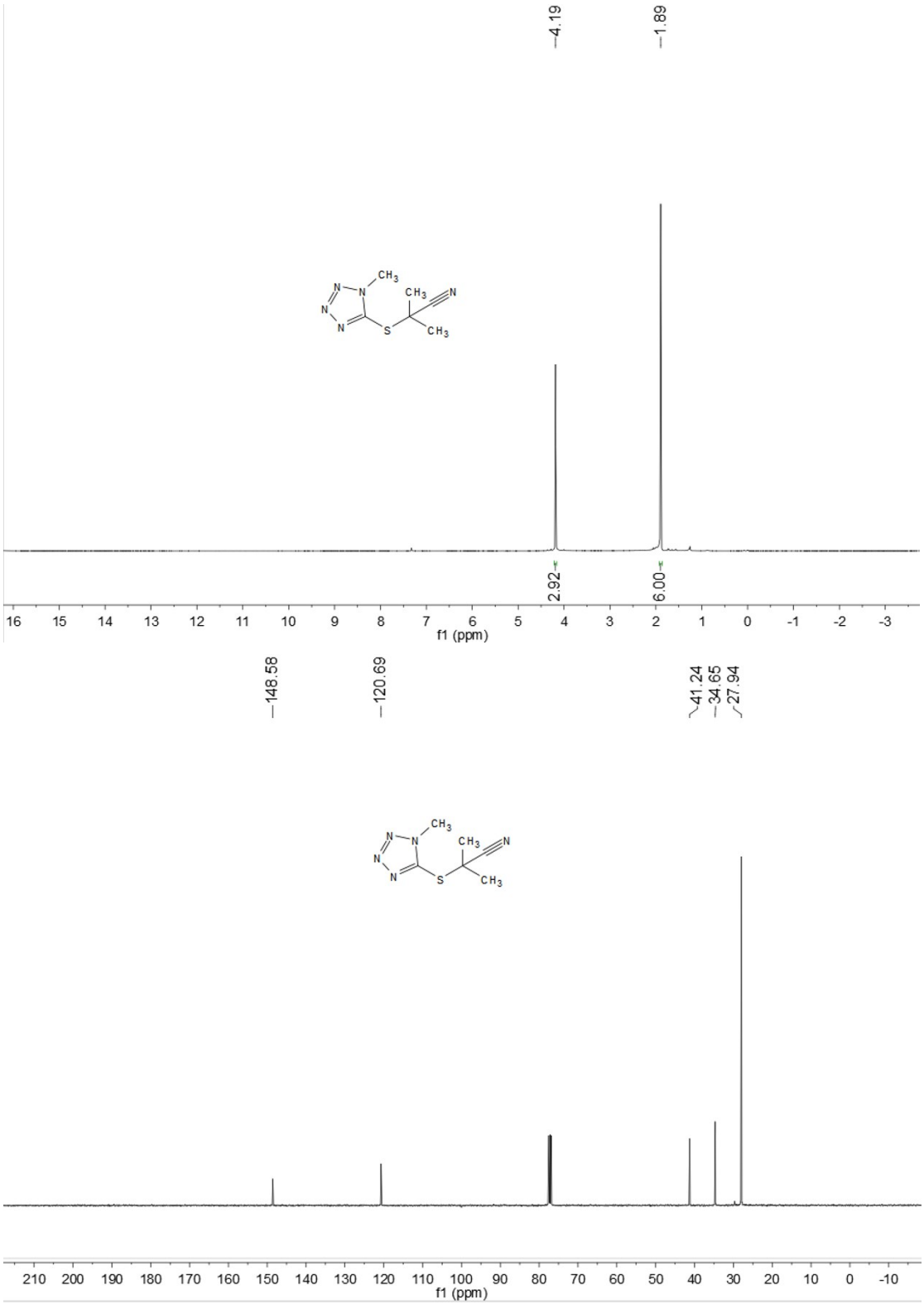




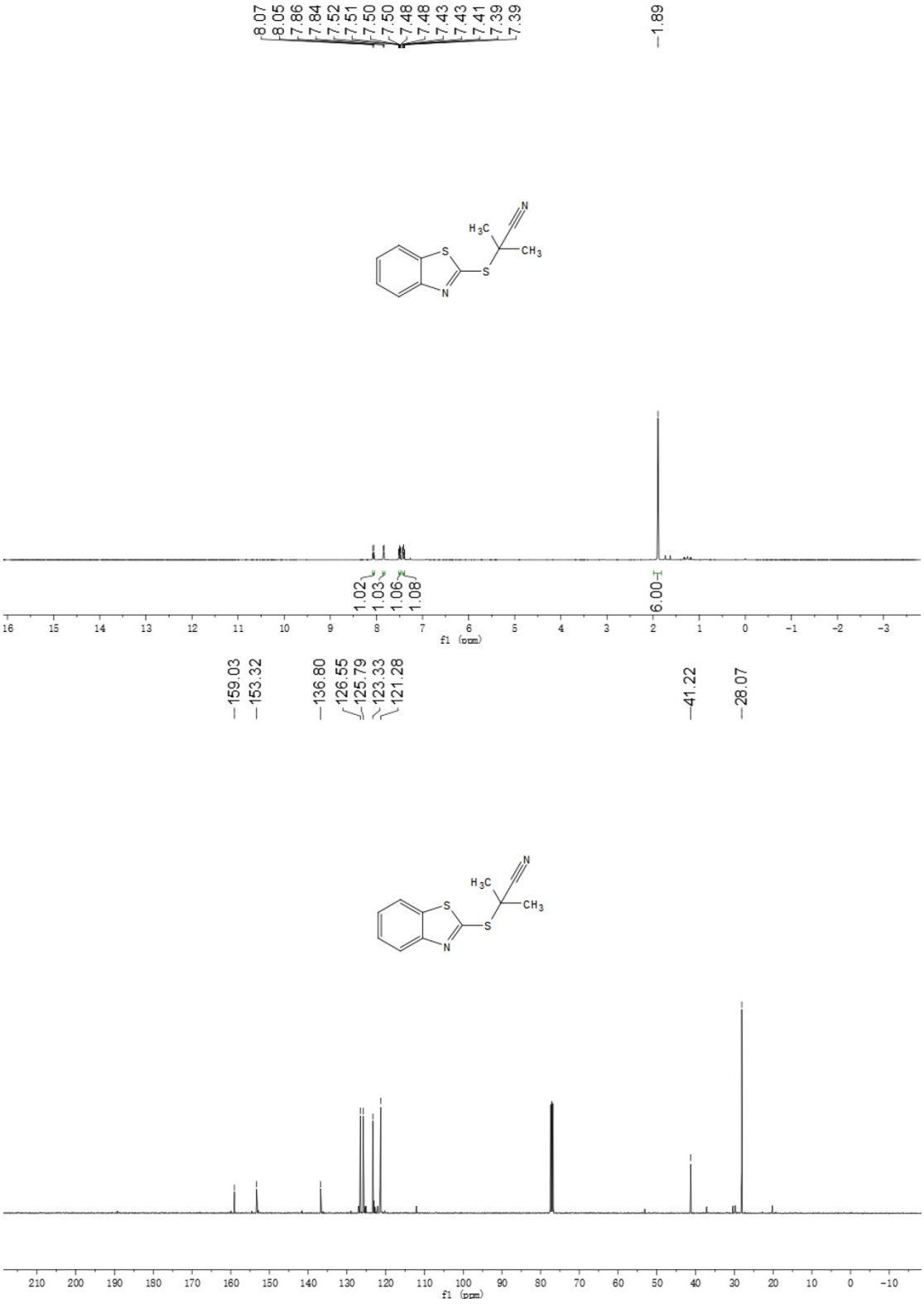
2-methyl-2-((1-methyl-1H-imidazol-2-yl)thio)propanenitrile (3n):



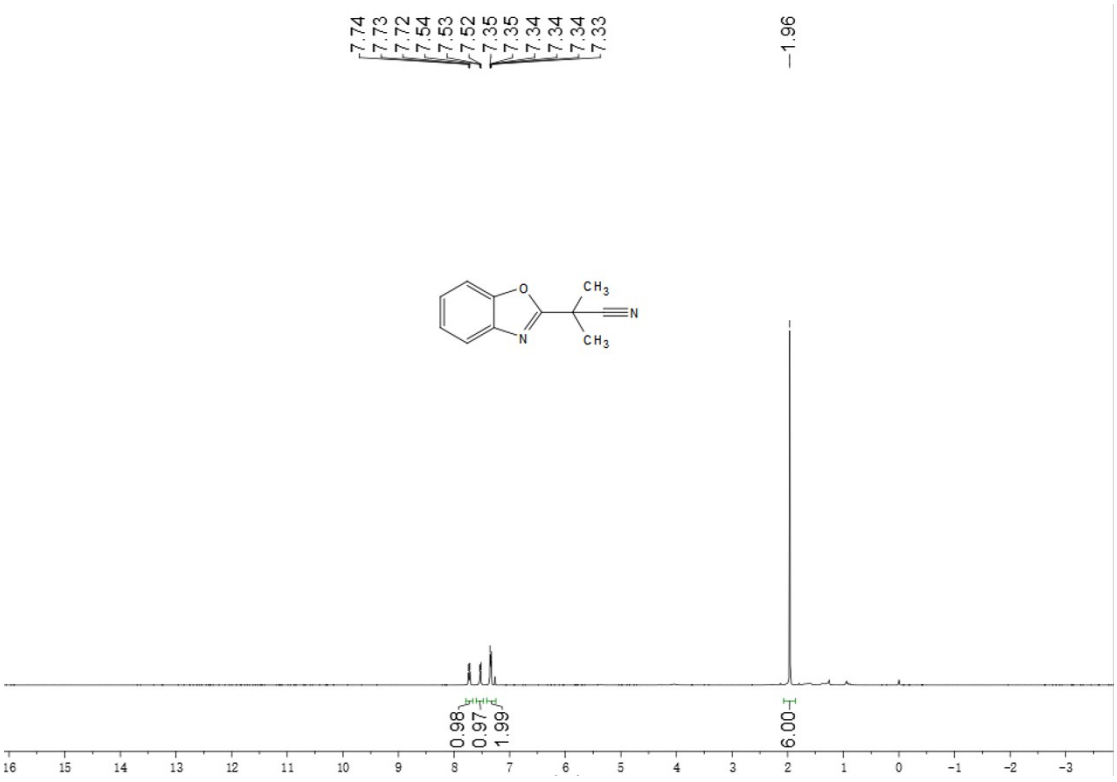
2-methyl-2-((1-methyl-1H-tetrazol-5-yl)thio)propanenitrile (30):

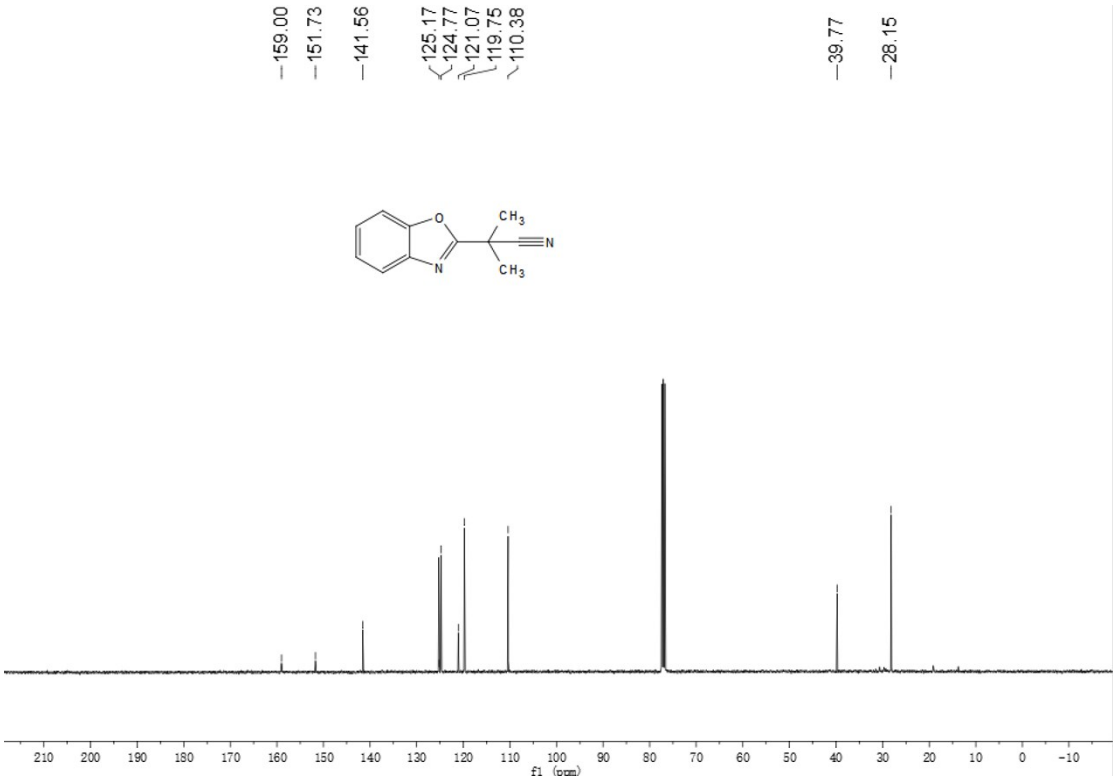


2-(benzo[d]thiazol-2-ylthio)-2-methylpropanenitrile (3p):

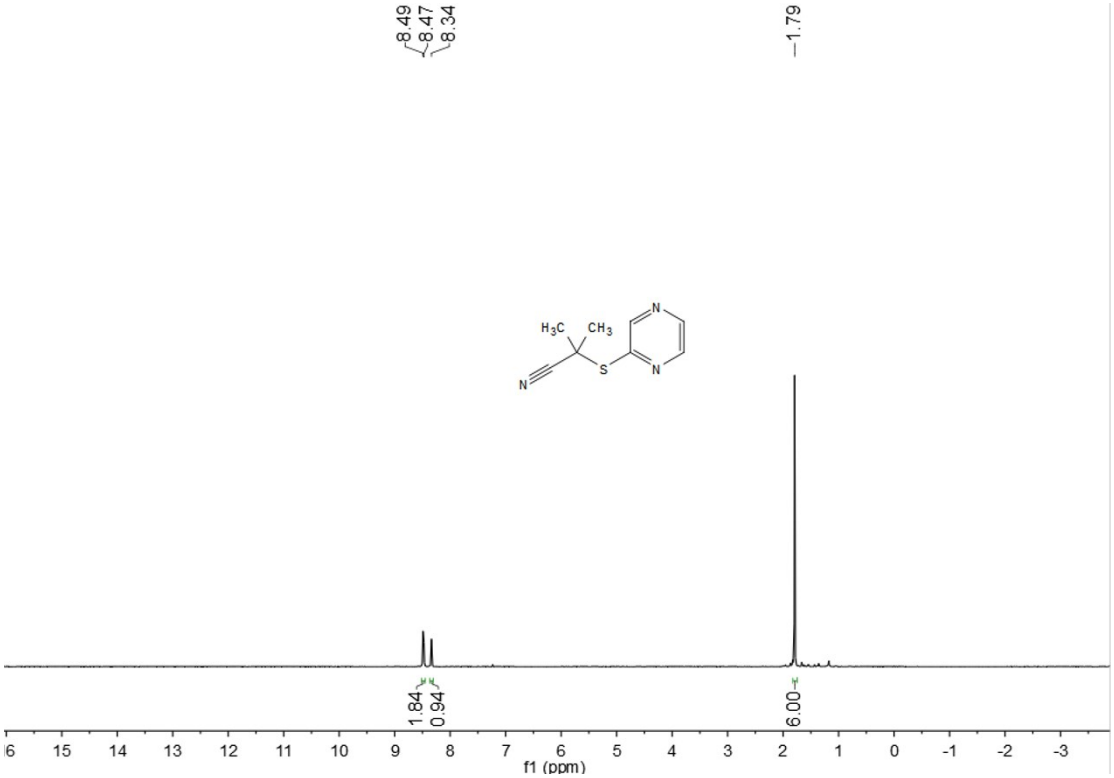


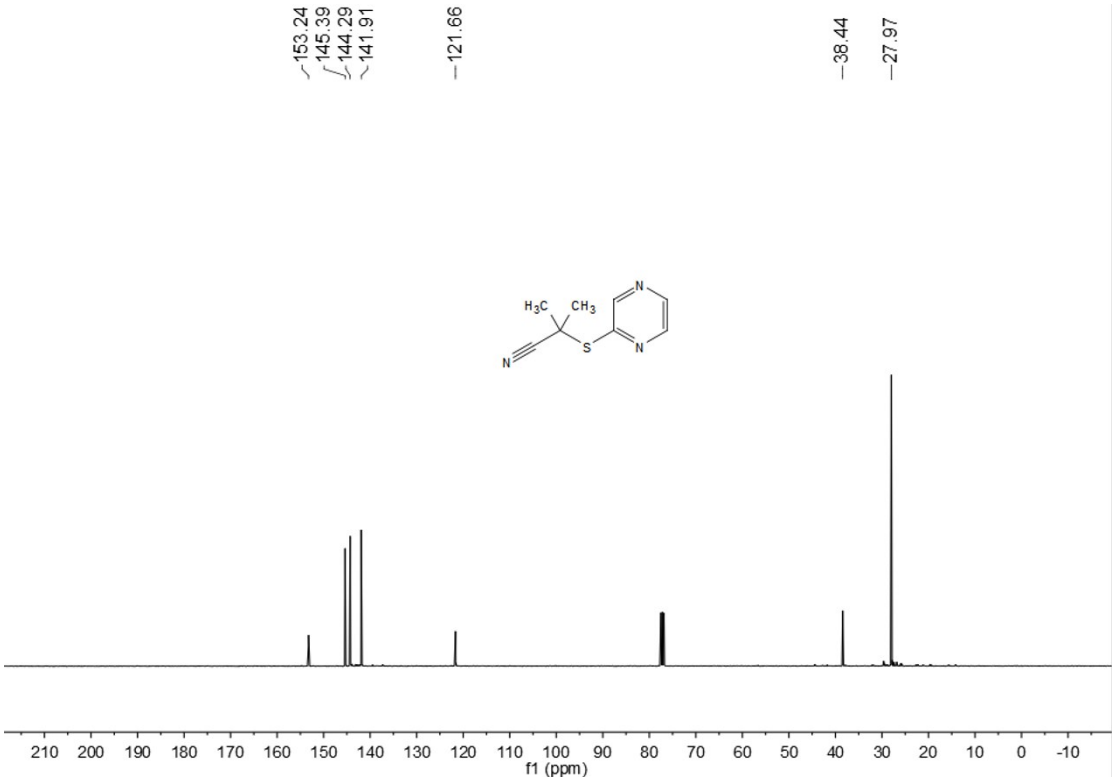
2-(benzo[d]oxazol-2-yl)-2-methylpropanenitrile (3q):



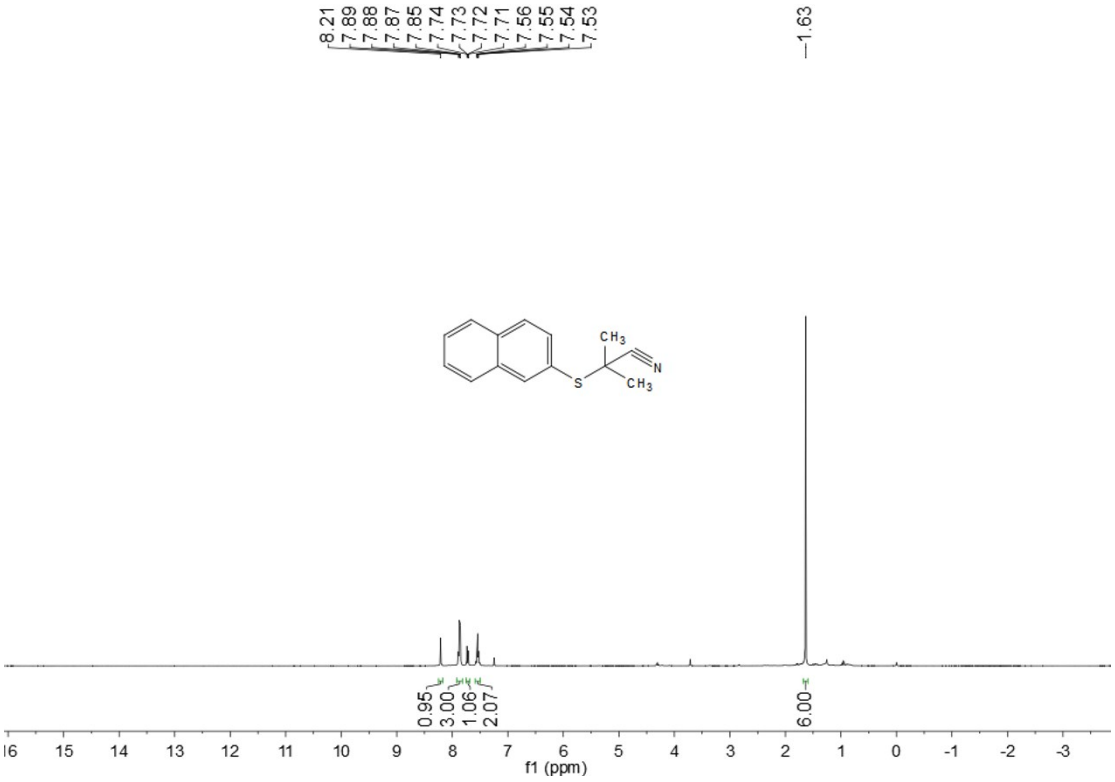


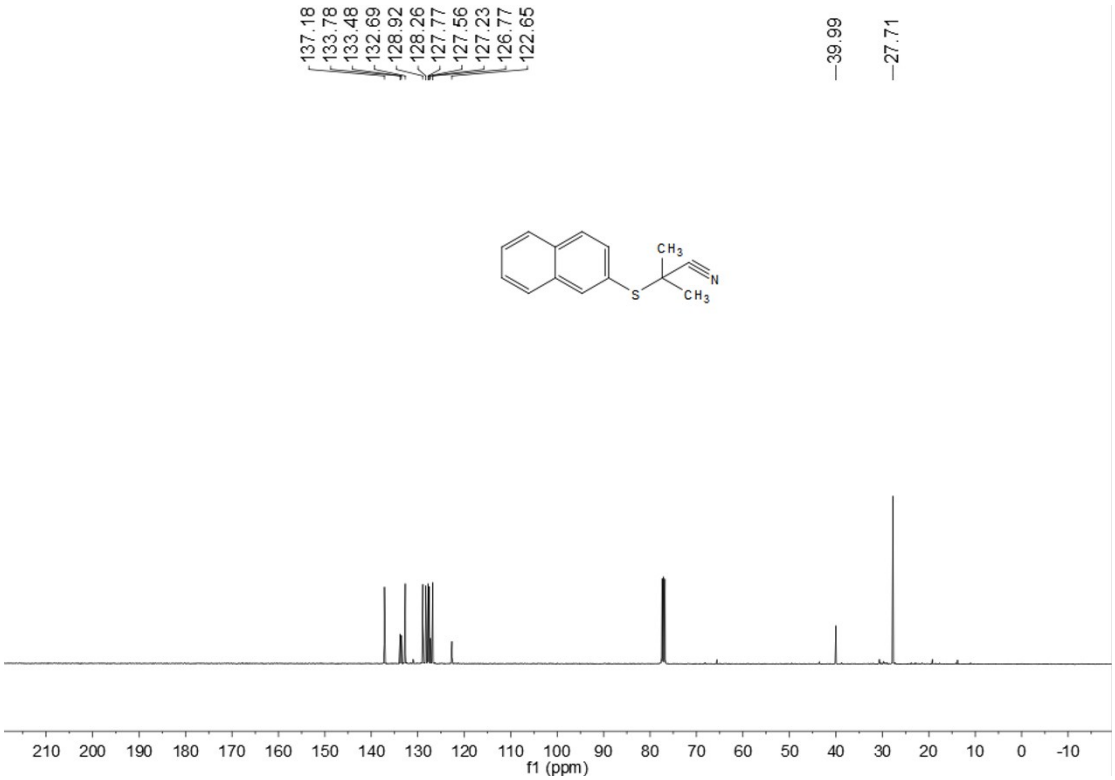
2-(4-tert-butylphenylthio)-2-methylpropanenitrile (3r):



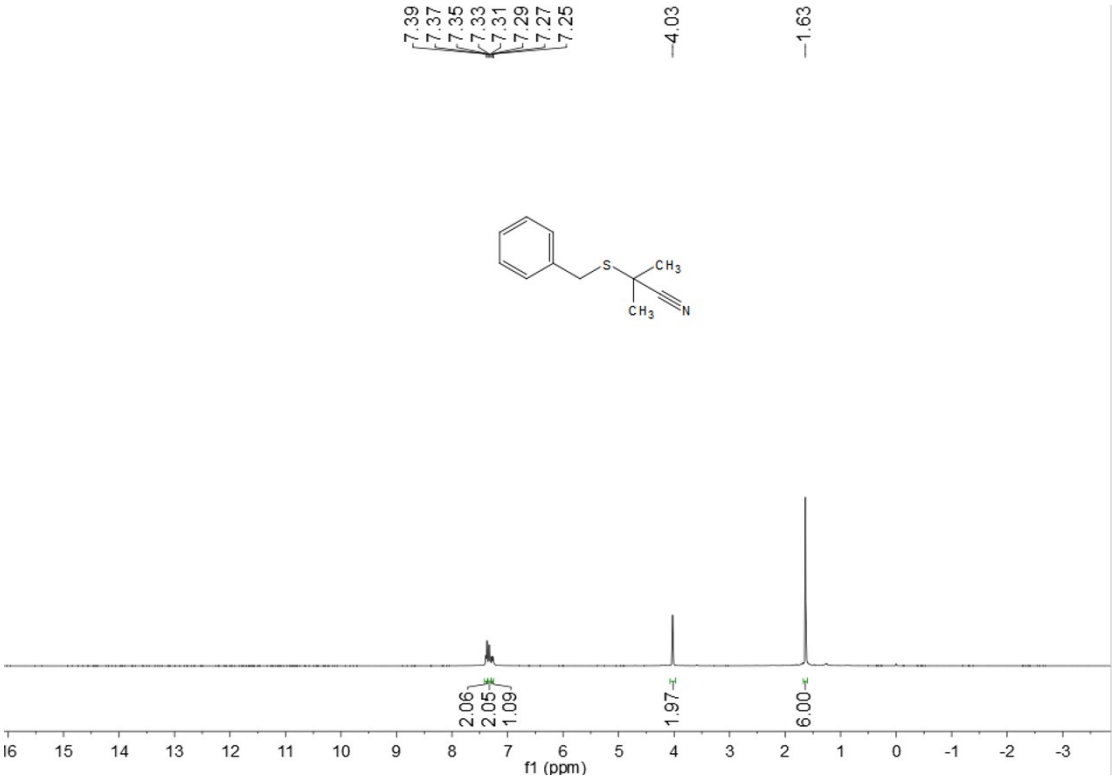


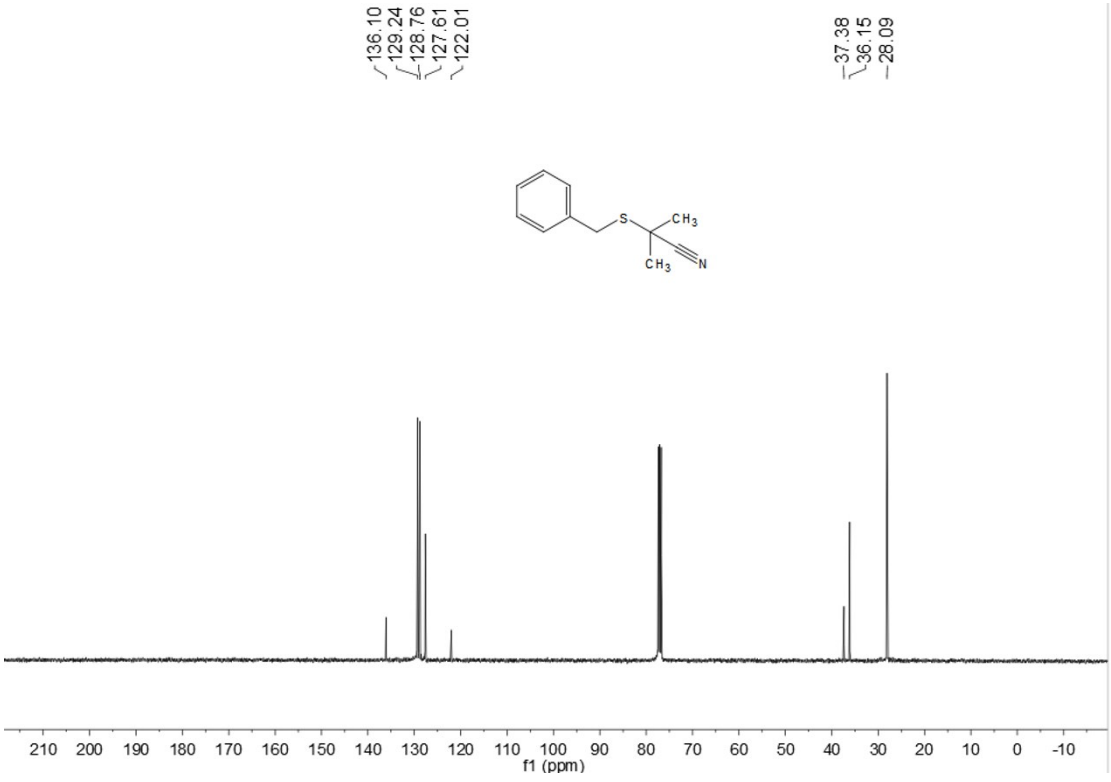
2-methyl-2-(naphthalen-2-ylthio)propanenitrile (3s):



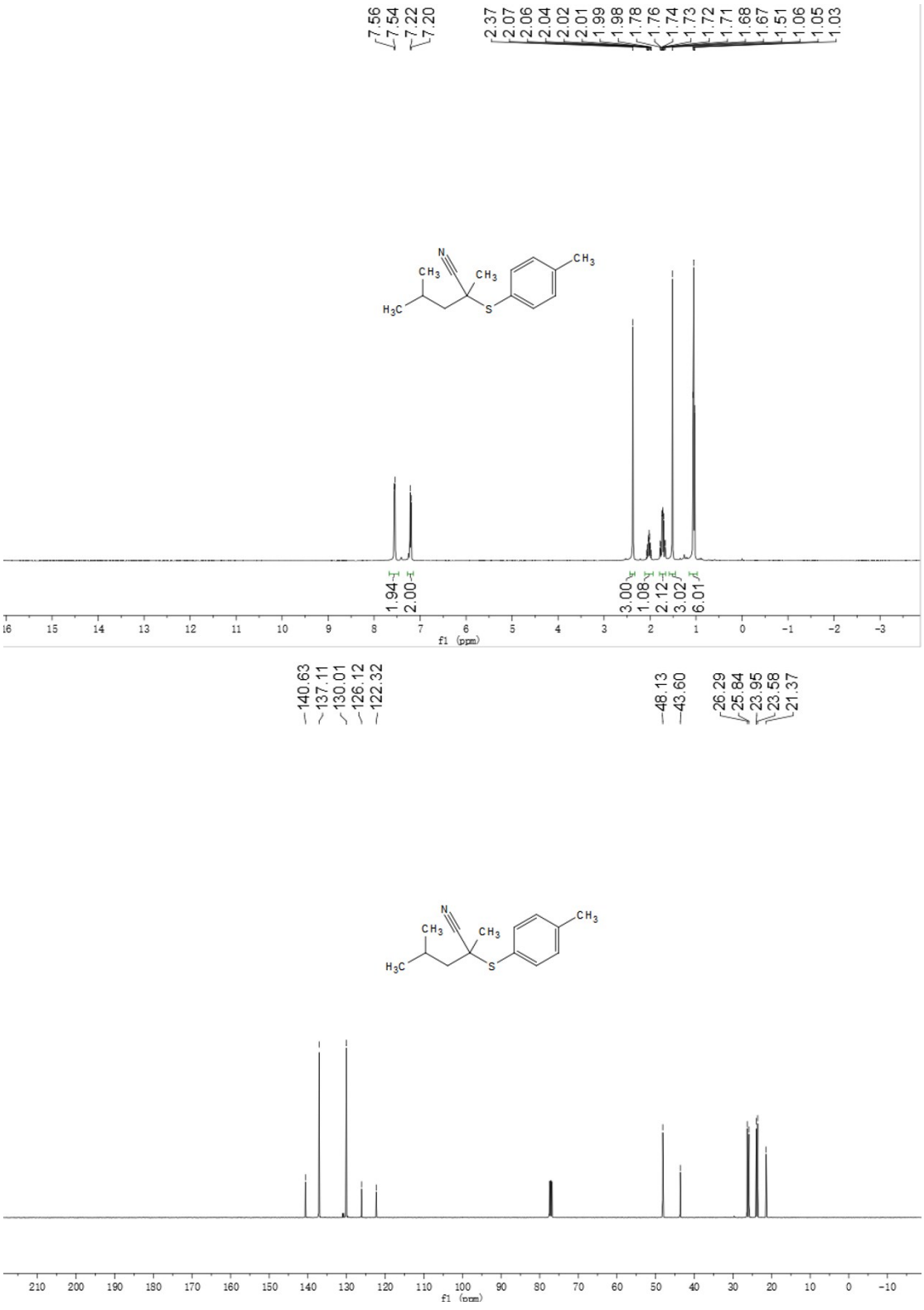


2-(benzylthio)-2-methylpropanenitrile (3t):

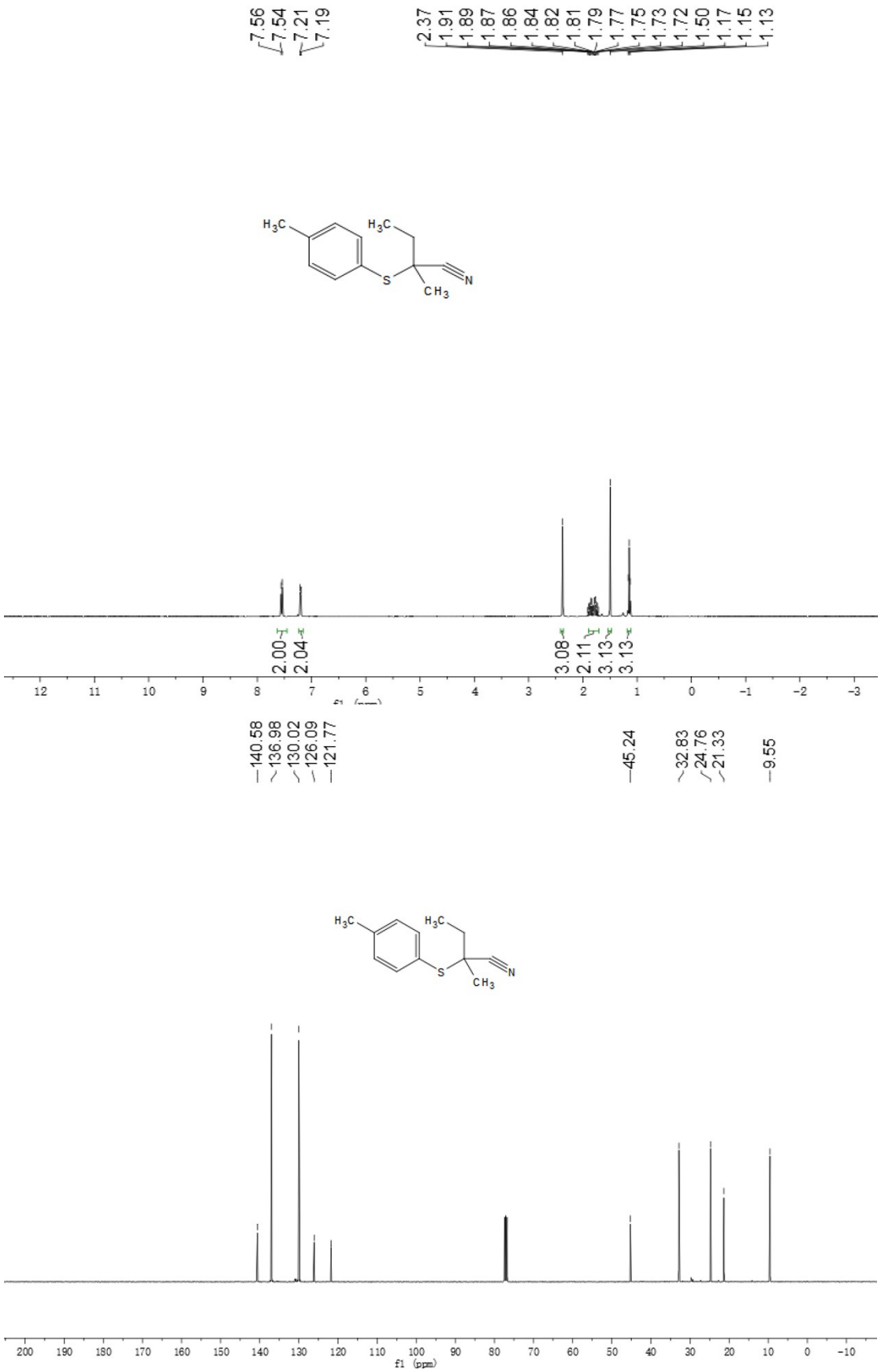




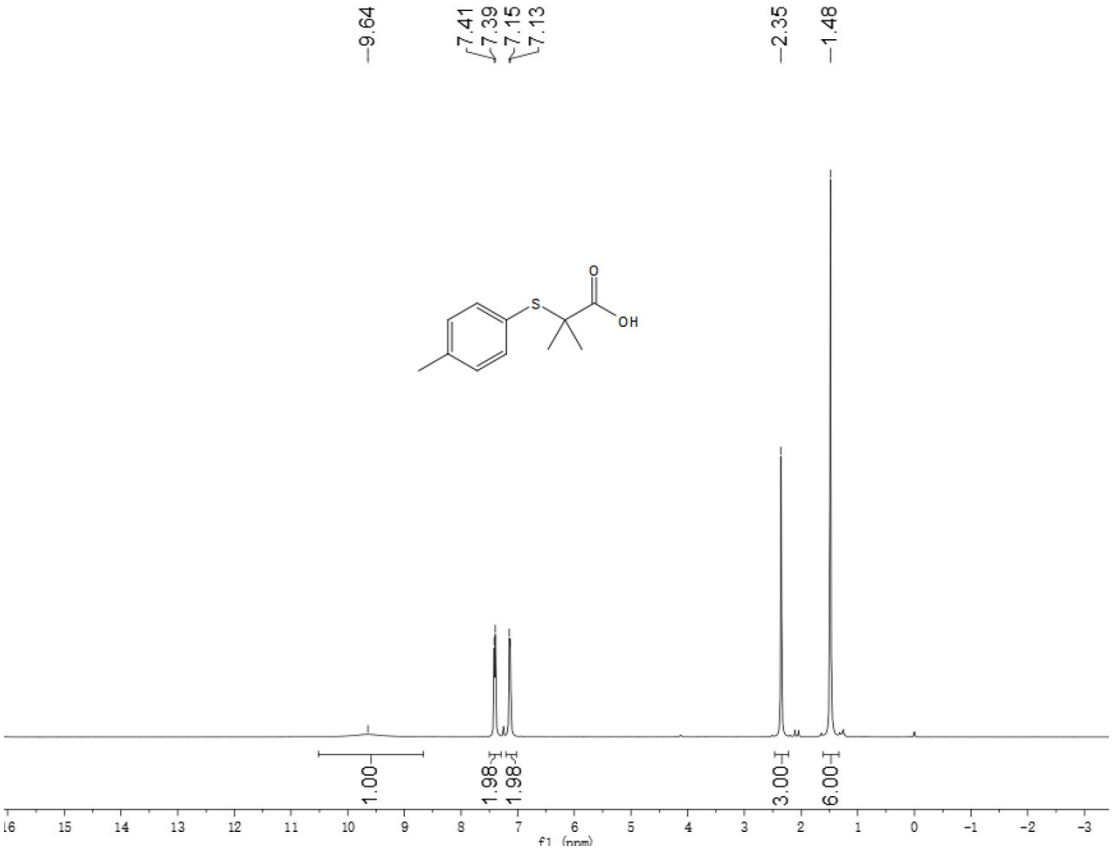
2,4-dimethyl-2-(p-tolylthio)pentanenitrile (3u):

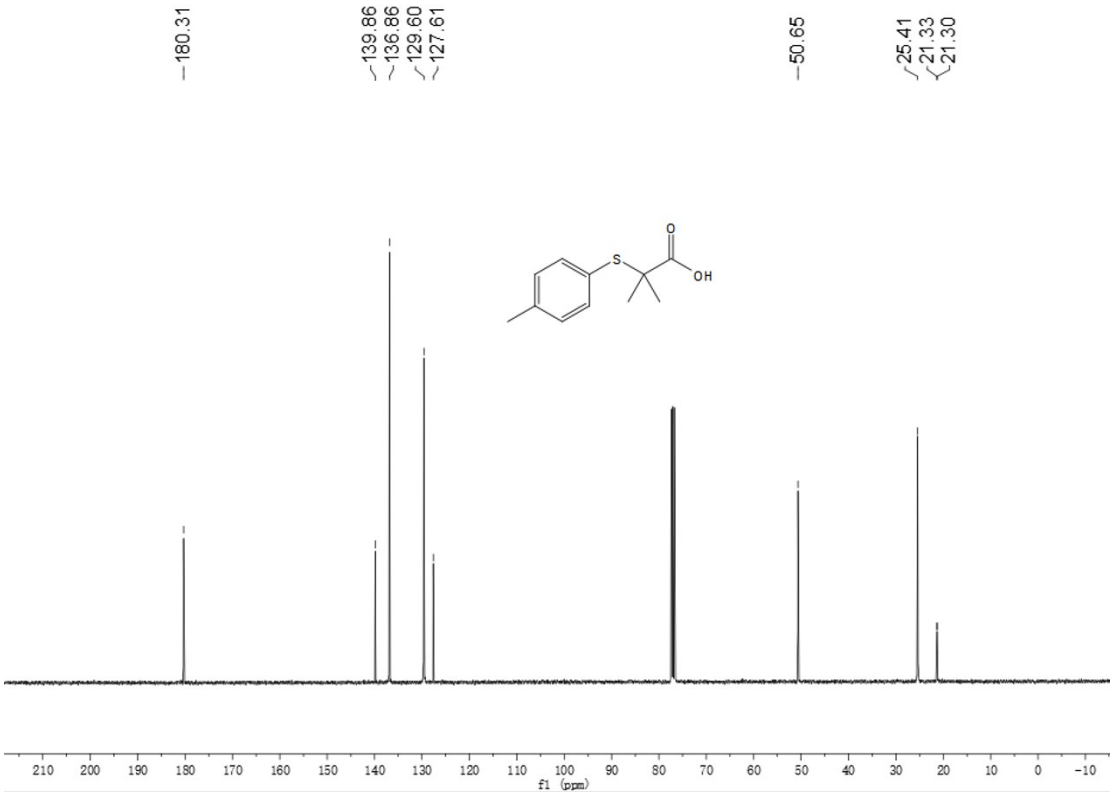


2-methyl-2-(p-tolylthio)butanenitrile (3v):

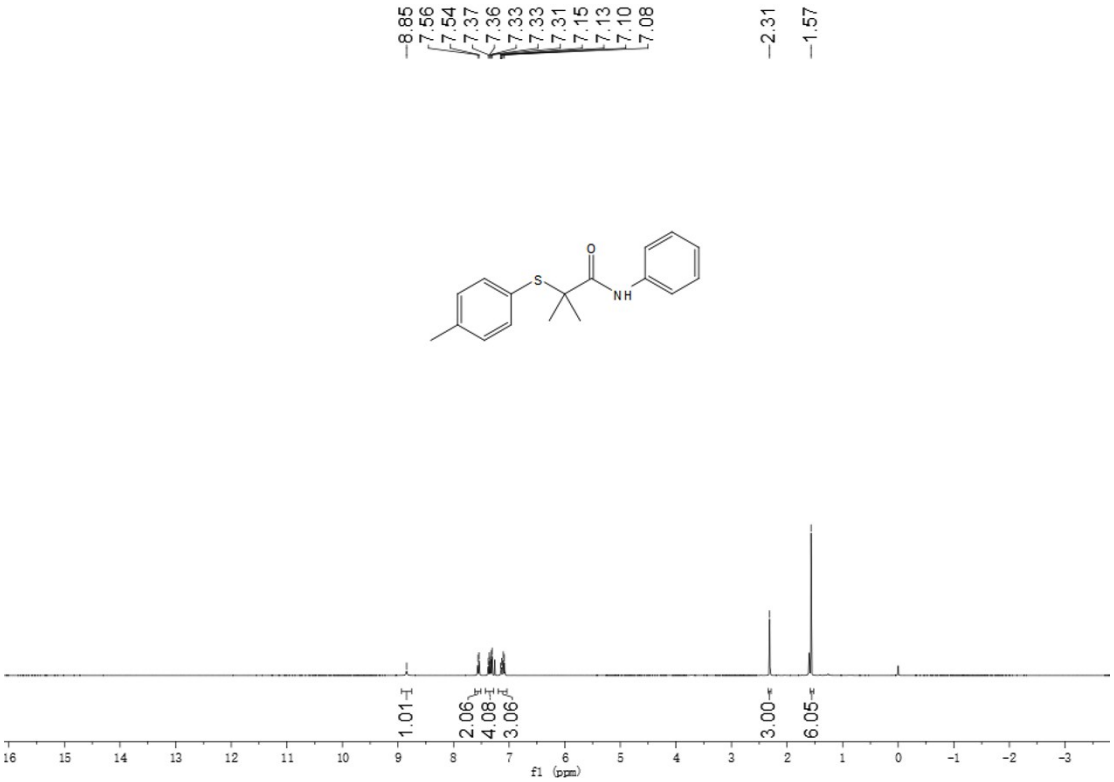


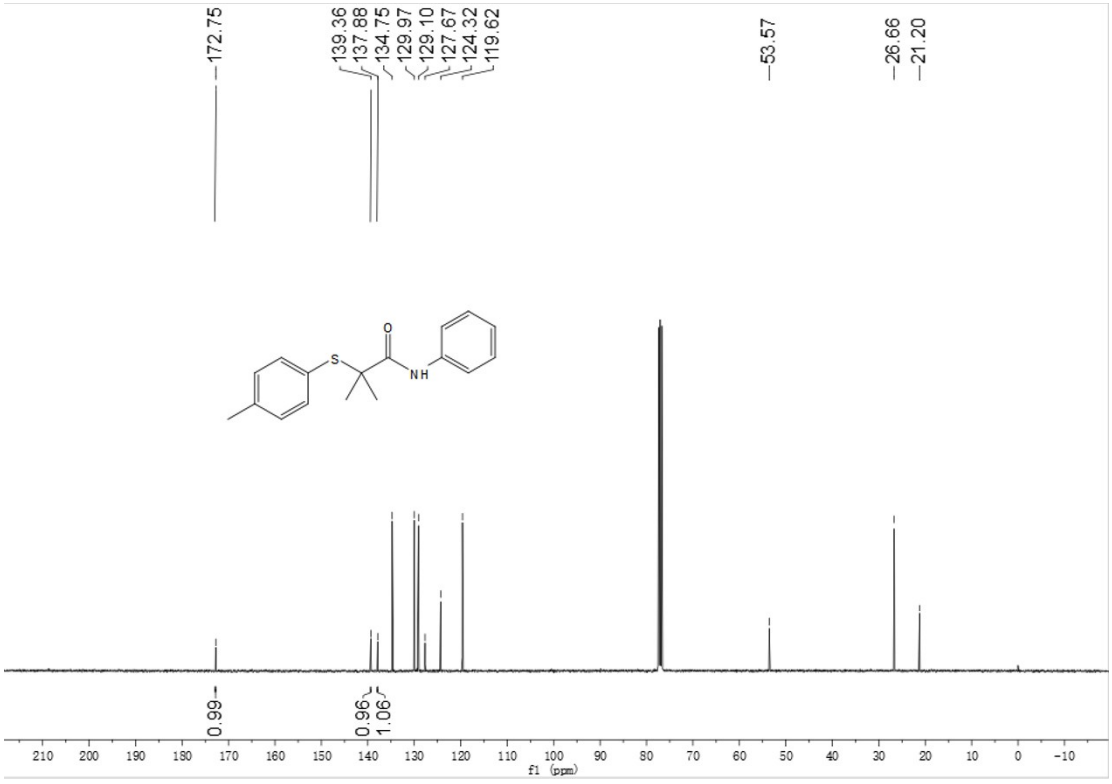
2-methyl-2-(p-tolylthio)propanoic acid (4a)



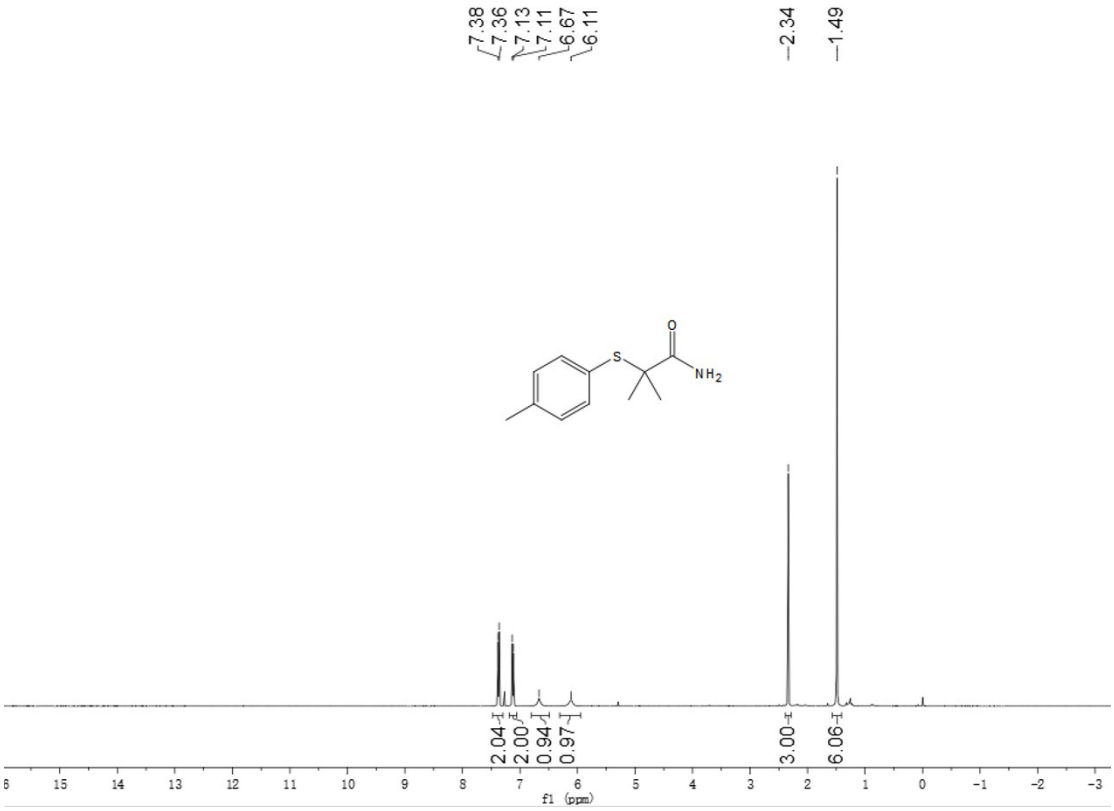


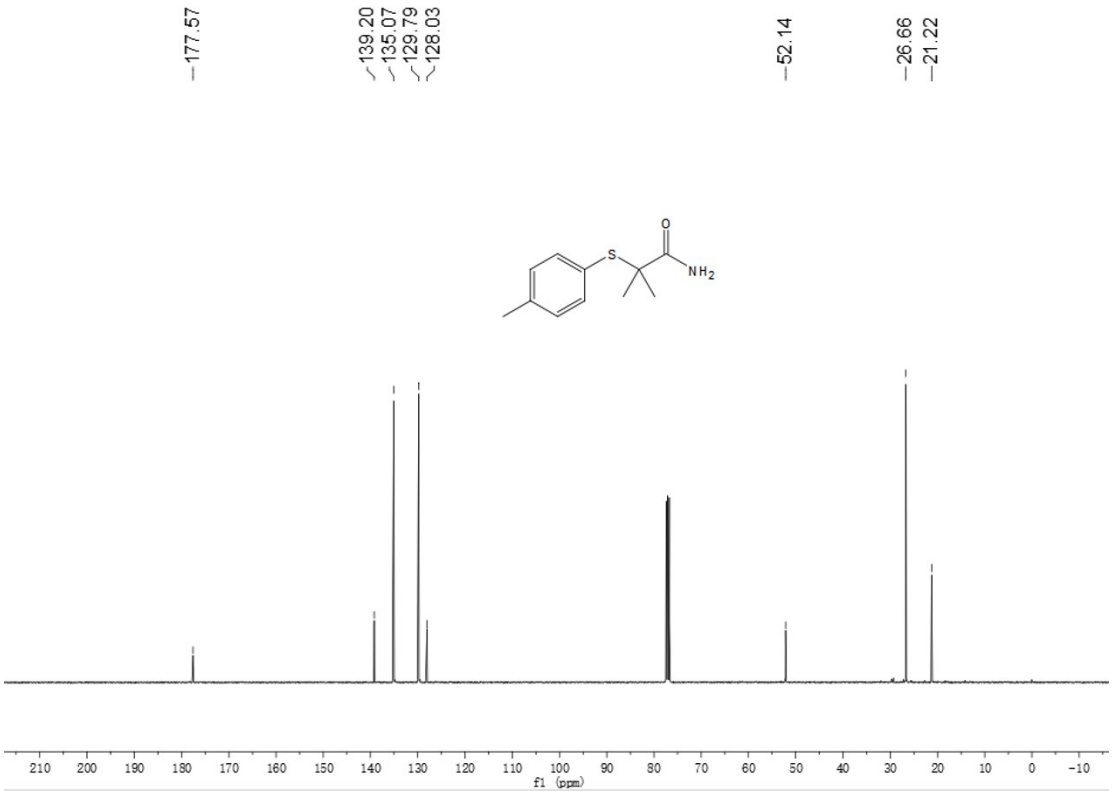
2-methyl-N-phenyl-2-(p-tolylthio)propanamide (4b)





2-methyl-2-(p-tolylthio)propanamide (4c)





2-methyl-1-phenyl-2-(p-tolylthio)propan-1-one (4d)