# Supporting Information

## *for*

# Facile Synthesis of 1,2-Thiobenzonitriles via Cu-Catalyzed Denitrogenative Radical Coupling Reaction

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# 1. General information

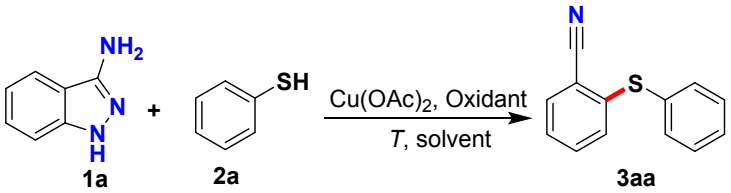
All chemicals were purchased from Adamas Reagent, Ltd, Energy chemical company, J&K Scientific Ltd, Alfa Aesa chemical company and so forth. $CH_3CN$ was dried by CaH prior to use. Unless otherwise stated, all experiments were conducted in a seal tube under air atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

$^1$H-NMR and $^{13}$C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 500 spectrometer (500 MHz $^1$H, 125 MHz $^{13}$C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ ($\delta$ = 7.26 for $^1$H-NMR , $\delta$ = 77.00 for $^{13}$C-NMR) or DMSO-$d_6$ ($\delta$ = 2.50 for $^1$H-NMR, $\delta$ = 39.60 for $^{13}$C-NMR) as an internal reference. High resolution mass spectra were recorded using Q-TOF time-of-flight mass spectrometer. Coupling constants (*J*) were reported in Hertz (Hz). The starting materials 1*H*-indazol-3-amine and 5-bromo-1*H*-indazol-3-amine were purchased from commercial suppliers. Other 1*H*-indazol-3-amines were synthetized according to methods reported by previous literatures.[1]

[1] (a) S. Antonysamy, G. Hirst, F. Park, P. Sprengeler, F. Stappenbeck, P. Steensma, M. Wilson, M. Wong, *Bioorg. Med. Chem. Lett.* 2009, **19**, 279; (b) D. N. Rao, Sk. Rasheed, R. A. Vishwakarm and P. Das. *Chem. Commun.,* 2014, **50**, 12911; (c) W. Kong, Y. Zhou and Q. Song, *Adv. Synth. Catal.* 2018, **360**, 1943.

## 2. Optimization of experiment conditions

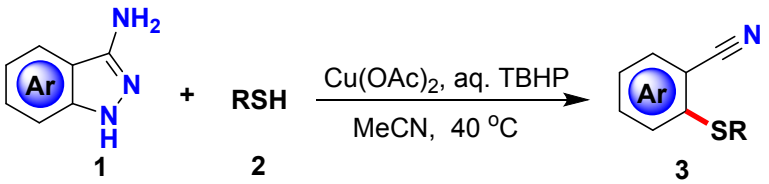
**Table S1.** Screening of conditions for the synthesis of 1,2-thiobenzonitriles




| Entry[a] | Oxidant | Solvent | Temperature | Yield of **3aa**[b] |
|---|---|---|---|---|
| 1 | DTBP | $CH_3CN$ | 60 °C | 53% |
| 2 | $O_2$ | $CH_3CN$ | 60 °C | 45% |
| 3 | aq.TBHP | $CH_3CN$ | 60 °C | 73% |
| 4 | PIFA | $CH_3CN$ | 60 °C | trace |
| 5 | *m*-CPBA | $CH_3CN$ | 60 °C | N.D. |
| 6 | BPO | $CH_3CN$ | 60 °C | N.D. |
| 7 | TBPB | $CH_3CN$ | 60 °C | 58% |
| 8 | aq.TBHP | $CH_3CN$ | 80 °C | 69% |
| 9 | aq.TBHP | $CH_3CN$ | 40 °C | (78%)[c] |
| 10 | aq.TBHP | DCM | 40 °C | 76% |
| 11 | aq.TBHP | EtOH | 40 °C | 21% |
| 12 | aq.TBHP | Dioxane | 40 °C | <10% |
| 13 | aq.TBHP | THF | 40 °C | trace |
| 14 | aq.TBHP | DMF | 40 °C | N.D. |
| 15 | aq.TBHP | EtOAc | 40 °C | 70% |
| 16[d] | aq.TBHP | $CH_3CN$ | 40 °C | 67% |
| 17[e] | aq.TBHP | $CH_3CN$ | 40 °C | 41% |
| 18[f] | aq. TBHP | $CH_3CN$ | 40 °C | N.D. |
| 19 | - | $CH_3CN$ | 40 °C | trace |

[a]All reactions unless otherwise stated were carried out with **1** (0.3 mmol), **2** (0.2 mmol), $Cu(OAc)_2$ (20 mol%) and Oxidant (2 equiv) in MeCN (1.0 mL) for 18 h. [b] GC yields. [c] Isolated yield. [d] $Cu(OAc)_2$ (10 mol%), [e] $Cu(OAc)_2$ (5 mol%). [f] without $Cu(OAc)_2$.

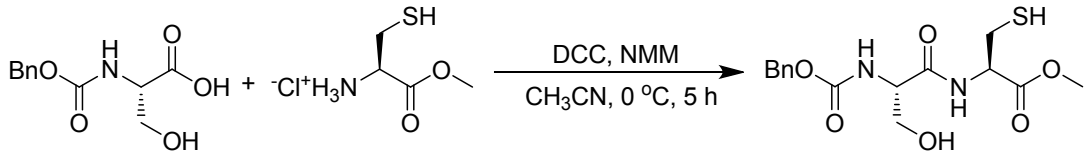
## 3. General procedure for the synthesis of 1,2-Thiobenzonitriles




TBHP (70% in water) (0.4 mmol, 2.0 equiv) was added to a mixture of $Cu(OAc)_2$ (7.4 mg, 20 mol%), 3-aminoindazoles **1** (0.3 mmol, 1.5 equiv) and thiols **2** (0.2 mmol, 1 equiv) in $CH_3CN$ (1 mL). Then the sealed tube was stirred at 40 °C for 18 h. Upon completion of the reaction, the solvent was evaporated under reduced

pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 50:1, v/v) to give the desired product **3**.

## 4. The Synthesis of (R)-Ethyl 2-((S)-2-(((benzyloxy)carbonyl)amino)-3-hydroxypropanamido)-3-mercaptopropanoate (6)

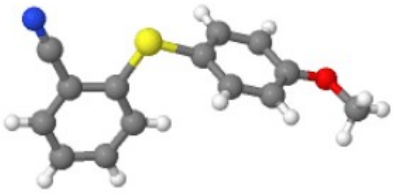



Following a slightly modified version of a reported procedure,[2] to a mixture of L-cysteine ethyl ester hydrochloride (1.90 g, 10.0 mmol) and N-carbobenzyloxy-L-serine (2.39 g, 10.0 mmol, 1.00 eq.) in $CH_3CN$ (25 mL) was added 4-Methylmorpholine (NMM) (1.12 mL, 10.0 mmol) at 0 °C. The mixture was stirred at room temperature until it became a light yellow solution and cooled back to 0 °C. Next was added DCC (2.08 g, 10.0 mmol) dissolved in $CH_3CN$ (20 mL) via a dropping funnel over a 5 minute time period. The reaction mixture quickly became a white suspension and was stirred at 0 °C for 5 hours. The suspension was filtered and the filtrate was concentrated in vacuo. The resulting colorless oil was taken up in EtOAc (50 mL) and extracted with 0.5 N aq. HCl (50 mL), 5% aq. $NaHCO_3$ (25 mL) and brine (25 mL). The organic layer was dried over MgSO4, filtered and concentrated in vacuo. The crude white solid was purified by flash chromatography (EtOAc:PE = 2:1, v/v), followed by recrystallization in $CH_2Cl_2$ affording **6** as a white solid.

[2] E. Gotschi, C. J. Jenny, R. Reindl, F. Ricklin, *Helv. Chim. Acta* 1996, **79**, 2219.

## 5. Crystal data of 3ad

Crystallographic data for compound **3ad** (CCDC-1842363) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



Bond precision: C-C = 0.0038 A Wavelength=0.71073

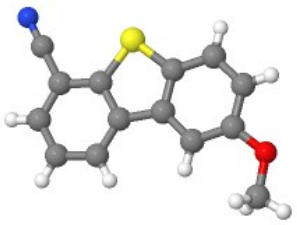
Cell: a=9.7200(19) b=17.845(2) c=7.7330(11)
alpha=90 beta=110.22(2) gamma=90

Temperature: 298 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1258.7(4) | 1258.7(4) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | C14 H11 N O S | C14 H11 N O S |
| Sum formula | C14 H11 N O S | C14 H11 N O S |
| Mr | 241.30 | 241.32 |
| Dx,g cm-3 | 1.273 | 1.273 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.239 | 0.239 |
| F000 | 504.0 | 504.7 |
| F000' | 504.68 | |
| h,k,lmax | 11,21,9 | 11,21,9 |
| Nref | 2216 | 2210 |
| Tmin,Tmax | | 0.382,1.000 |
| Tmin' | | |

Correction method= # Reported T Limits: Tmin=0.382 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.997 Theta(max)= 25.000
R(reflections)= 0.0440( 1416) wR2(reflections)= 0.1539( 2210)
S = 0.902 Npar= 155

Crystallographic data for compound **9** (CCDC-1863284) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email:deposit@ccdc.cam.ac.uk).



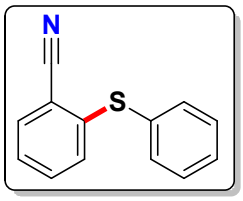
Bond precision: C-C = 0.0041 A Wavelength=0.71073
Cell: a=7.2127(8) b=13.0460(12) c=11.9273(15)
alpha=90 beta=99.535(10) gamma=90
Temperature: 298 K

| | Calculated | Reported |
|---|---|---|
| Volume | 1106.8(2) | 1106.8(2) |
| Space group | P 21/c | P 1 21/c 1 |
| Hall group | -P 2ybc | -P 2ybc |
| Moiety formula | C14 H9 N O S | C14 H9 N O S |
| Sum formula | C14 H9 N O S | C14 H9 N O S |
| Mr | 239.28 | 239.30 |
| Dx,g cm-3 | 1.436 | 1.436 |
| Z | 4 | 4 |
| Mu (mm-1) | 0.271 | 0.271 |
| F000 | 496.0 | 496.7 |
| F000' | 496.68 | |
| h,k,lmax | 8,15,14 | 8,15,14 |
| Nref | 1952 | 1945 |
| Tmin,Tmax | | 0.744,1.000 |
| Tmin' | | |

Correction method= # Reported T Limits: Tmin=0.744 Tmax=1.000 AbsCorr = MULTI-SCAN
Data completeness= 0.996 Theta(max)= 25.000
R(reflections)= 0.0499( 1309) wR2(reflections)= 0.1443( 1945)
S = 0.844 Npar= 155

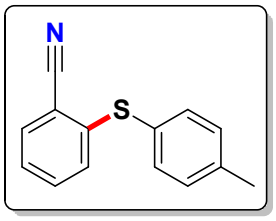
## 6. Characterization data for products

**2-(phenylthio)benzonitrile (3aa) (CAS Number: 91804-55-6)**



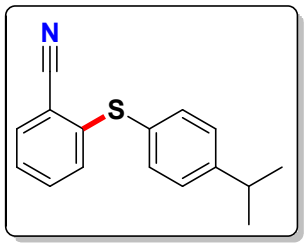
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a yellow oil (32.9 mg, 78%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 1H), 7.47 (ddd, *J* = 5.2, 2.9, 1.3 Hz, 2H), 7.43 – 7.36 (m, 4H), 7.25 (td, *J* = 7.6, 1.1 Hz, 1H), 7.12 (dd, *J* = 8.1, 0.6 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 142.1, 133.5, 133.4, 132.9, 131.6, 129.7, 129.6, 128.8, 126.4, 116.8, 112.6.

**2-(p-tolylthio)benzonitrile (3ab) (CAS Number: 162523-72-0)**



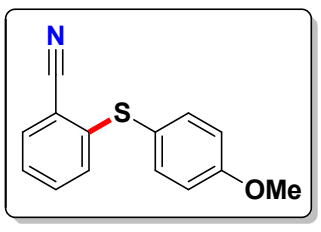
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a white solid (37.9 mg, 84%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.21 (ddd, *J* = 8.7, 5.9, 2.1 Hz, 3H), 7.03 (dd, *J* = 8.1, 0.6 Hz, 1H), 2.39 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 143.5, 139.5, 134.3, 133.4, 132.8, 130.6, 128.8, 127.5, 125.8, 116.9, 111.7, 21.2.

**2-((4-isopropylphenyl)thio)benzonitrile (3ac) (CAS Number: 1040330-02-6)**



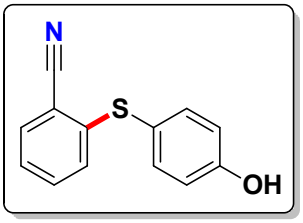
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a yellow oil (40.9 mg, 81%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.43 (dd, *J* = 8.4, 1.9 Hz, 2H), 7.38 (td, *J* = 8.0, 1.4 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 7.21 (td, *J* = 7.7, 0.8 Hz, 1H), 7.04 (d, *J* = 8.1 Hz, 1H), 3.00 – 2.89 (m, 1H), 1.27 (d, *J* = 6.9 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 150.3, 143.4, 134.2, 133.4, 132.8, 128.8, 127.9, 127.7, 125.8, 116.9, 111.7, 33.8, 23.8. HRMS (ESI, m/z) calcd for $C_{16}H_{16}NS[M+H]^+$: 254.0998; found: 254.1000.

**2-((4-methoxyphenyl)thio)benzonitrile (3ad) (CAS Number: 128958-95-2)**



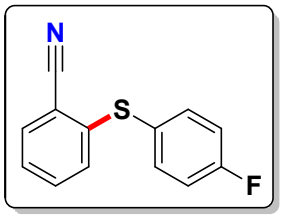
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 40:1, v/v) to give the product as a white solid (41.9 mg, 87%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.50 – 7.44 (m, 2H), 7.37 – 7.31 (m, 1H), 7.17 (td, *J* = 7.6, 1.1 Hz, 1H), 6.98 – 6.93 (m, 2H), 6.92 (d, *J* = 8.7 Hz, 1H), 3.84 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 160.7, 144.5, 136.7, 133.3, 132.8, 127.7, 125.4, 120.7, 116.9, 115.4, 110.7, 55.4.

**2-((4-hydroxyphenyl)thio)benzonitrile (3ae) (CAS Number: 1183982-86-6)**



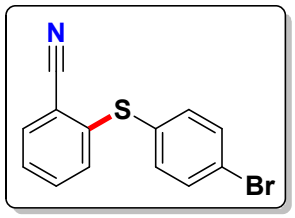

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 10:1, v/v) to give the product as a brown oil (31.8 mg, 70%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.39 – 7.32 (m, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 6.93 (dd, *J* = 6.6, 1.8 Hz, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 157.5, 144.8, 137.0, 133.4, 133.0, 127.8, 125.5, 120.4, 117.1, 117.0, 110.3.

**2-((4-fluorophenyl)thio)benzonitrile (3af) (CAS Number: 1021244-50-7)**



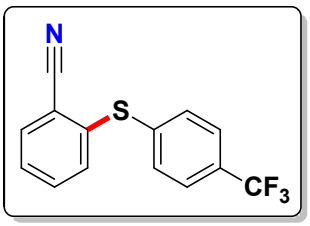

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a brown oil (31.4 mg, 68%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.41 (td, *J* = 7.8, 1.5 Hz, 1H), 7.29 – 7.23 (m, 1H), 7.15 – 7.08 (m, 2H), 7.06 (dd, *J* = 8.1, 0.6 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 163.3 (d, *J* = 251 Hz), 142.6, 136.2 (d, *J* = 8.5 Hz), 133.7, 133.0, 129.3, 126.6, 126.4, 117.1, 116.9 (d, *J* = 17.8 Hz), 112.4.

**2-((4-bromophenyl)thio)benzonitrile (3ag) (CAS Number: 1097168-13-2)**



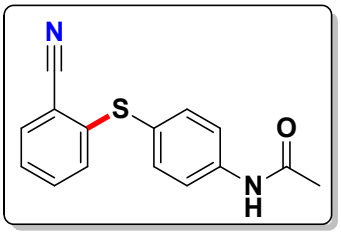

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a brown solid (32.9 mg, 57%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.45 (td, *J* = 7.8, 1.5 Hz, 1H), 7.33 – 7.28 (m, 3H), 7.20 (dd, *J* = 8.1, 0.6 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 141.0, 134.5, 133.8, 133.1, 132.8, 131.5, 130.7, 127.1, 123.1, 116.7, 113.6.

**2-((4-(trifluoromethyl)phenyl)thio)benzonitrile (3ah) (CAS Number: 1675712-66-9)**




The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 50:1, v/v) to give the product as a colourless oil (33.1 mg, 59%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.47 – 7.37 (m, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 138.8, 138.4, 134.1, 133.4, 130.9, 129.9, 128.3, 126.3 (q, *J* = 3.8 Hz), 124.9, 122.7, 116.7, 115.8.

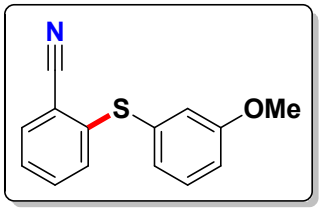
**N-(4-((2-cyanophenyl)thio)phenyl)acetamide (3ai) (CAS Number: 1021142-76-6)**




The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 2:1, v/v) to give the product as a yellowish-brown solid (41.3 mg, 77%). $^{1}$H NMR (500 MHz, DMSO) δ 10.20 (s, 1H),

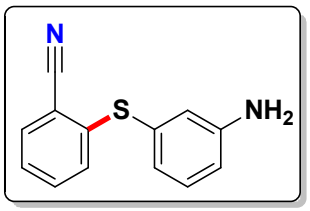
7.85 (dd, $J$ = 7.7, 1.2 Hz, 1H), 7.71 (d, $J$ = 8.6 Hz, 2H), 7.57 (td, $J$ = 8.0, 1.4 Hz, 1H), 7.47 (d, $J$ = 8.7 Hz, 2H), 7.36 (td, $J$ = 7.6, 0.9 Hz, 1H), 7.01 (d, $J$ = 8.0 Hz, 1H), 2.07 (s, 3H). $^{13}$C NMR (126 MHz, DMSO) δ 168.8, 142.4, 140.7, 135.1, 134.1, 134.0, 128.5, 126.8, 122.9, 120.3, 116.9, 110.5, 24.2. HRMS (ESI, m/z) calcd for $C_{15}H_{12}N_2OSNa$ $[M+Na]^+$: 291.0563; found: 291.0565.

**2-((3-methoxyphenyl)thio)benzonitrile (3aj) (CAS Number: 148901-63-7)**



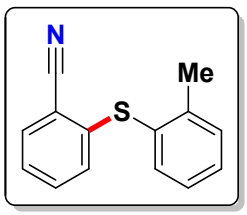

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 40:1, v/v) to give the product as a yellowish-brown solid (38.1 mg, 79%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, $J$ = 7.7, 1.4 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.33 – 7.29 (m, 1H), 7.27 (dt, $J$ = 7.6, 3.8 Hz, 1H), 7.17 (dd, $J$ = 8.1, 0.7 Hz, 1H), 7.04 (ddd, $J$ = 7.7, 1.6, 0.9 Hz, 1H), 7.02 – 6.98 (m, 1H), 6.91 (ddd, $J$ = 8.3, 2.5, 0.8 Hz, 1H), 3.80 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 160.3, 142.0, 133.6, 133.0, 130.5, 130.1, 126.5, 125.5, 118.4, 116.9, 114.7, 113.0, 110.0, 55.4.

**2-((3-aminophenyl)thio)benzonitrile (3ak) (CAS Number: 1994688-93-5)**



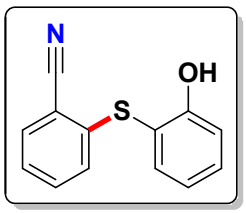

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 8:1, v/v) to give the product as a yellowish-brown solid (35.3 mg, 76%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.61 (dd, $J$ = 7.7, 1.3 Hz, 1H), 7.40 (td, $J$ = 7.9, 1.5 Hz, 1H), 7.23 (dt, $J$ = 7.6, 3.8 Hz, 1H), 7.16 (t, $J$ = 7.9 Hz, 2H), 6.87 – 6.82 (m, 1H), 6.79 (t, $J$ = 2.0 Hz, 1H), 6.69 (ddd, $J$ = 8.1, 2.3, 0.8 Hz, 1H), 3.77 (s, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 147.6, 142.7, 133.5, 132.9, 132.2, 130.5, 129.7, 126.2, 123.4, 119.5, 117.0, 115.6, 112.4.

**2-(o-tolylthio)benzonitrile (3al) (CAS Number: 162523-71-9)**




The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 70:1, v/v) to give the product as a pink oil (31.9 mg, 71%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, $J$ = 7.7, 1.4 Hz, 1H), 7.46 (d, $J$ = 7.5 Hz, 1H), 7.38 – 7.33 (m, 3H), 7.26 – 7.19 (m, 2H), 6.88 – 6.81 (m, 1H), 2.38 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 142.7, 141.9, 135.5, 133.5, 132.9, 131.1, 129.9, 129.7, 127.9, 127.2, 125.6, 116.8, 111.5, 20.6.

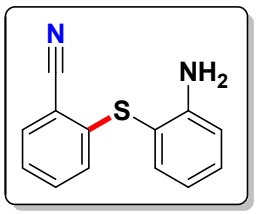
**2-((2-hydroxyphenyl)thio)benzonitrile (3am) (CAS Number: 1249046-12-5)**




The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 10:1, v/v) to give the product as a pink solid (25.4 mg, 56%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, $J$ = 7.7, 1.4 Hz, 1H), 7.53 (dd, $J$ = 7.7, 1.6 Hz, 1H), 7.44 (ddd, $J$ = 8.3, 7.5, 1.7 Hz, 1H), 7.37 (td, $J$ = 8.0, 1.5 Hz, 1H), 7.23 (td, $J$ = 7.6, 1.0 Hz, 1H), 7.11 (dd, $J$ = 8.2, 1.2 Hz, 1H), 7.01 (td, $J$ = 7.6, 1.3 Hz,

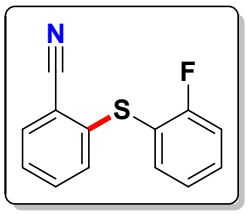
1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.39 (s, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 157.4, 141.2, 137.1, 133.6, 133.3, 133.2 126.8, 126.1, 121.7, 116.6, 116.2, 113.7, 110.9.

**2-((2-aminophenyl)thio)benzonitrile (3an) (CAS Number: 140425-65-6)**



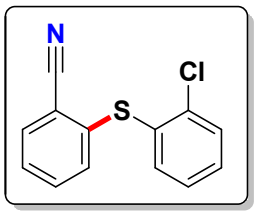

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 8:1, v/v) to give the product as a white solid (41.1 mg, 90%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.45 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.17 (td, *J* = 7.6, 1.0 Hz, 1H), 6.83 (dd, *J* = 8.1, 1.4 Hz, 2H), 6.79 (td, *J* = 7.5, 1.3 Hz, 1H), 4.35 (s, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 149.2, 142.4, 137.8, 133.4, 132.9, 132.1, 126.2, 125.3, 119.0, 116.9, 115.6, 111.3, 110.2.

**2-((2-fluorophenyl)thio)benzonitrile (3ao) (CAS Number: 1021142-73-3)**



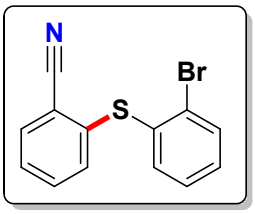

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a brown oil (27.4 mg, 60%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.48 (td, *J* = 7.4, 1.7 Hz, 1H), 7.45 – 7.38 (m, 2H), 7.28 (td, *J* = 7.6, 1.1 Hz, 1H), 7.23 – 7.12 (m, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 251 Hz), 140.3, 135.7, 133.7, 133.0, 131.5 (d, *J* = 7.9 Hz), 129.9, 126.8, 125.1 (d, *J* = 3.9 Hz), 118.8 (d, *J* = 17.9 Hz), 116.6 (d, *J* = 18.6 Hz), 116.4, 113.1.

**2-((2-chlorophenyl)thio)benzonitrile (3ap) (CAS Number: 148901-66-0)**



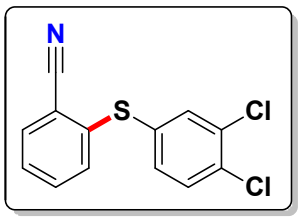

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a pink oil (25.9 mg, 53%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 1H), 7.48 (td, *J* = 7.9, 1.5 Hz, 2H), 7.32 (dddd, *J* = 13.7, 9.5, 7.7, 1.5 Hz, 3H), 7.26 – 7.22 (m, 1H), 7.20 (dd, *J* = 8.0, 0.7 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.5, 136.7, 133.9, 133.9, 133.1, 131.9, 131.3, 130.4, 129.8, 127.7, 127.3, 116.7, 114.3.

**2-((2-bromophenyl)thio)benzonitrile (3aq) (CAS Number: 537036-80-9)**



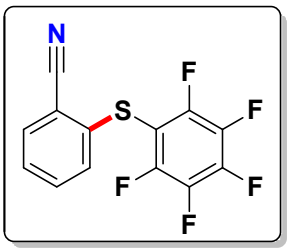

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a brown solid (28.3 mg, 49%).$^1$H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.48 (td, *J* = 7.8, 1.5 Hz, 1H), 7.35 (td, *J* = 7.6, 1.1 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.24 – 7.18 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.6, 134.2, 134.0, 133.8, 133.6, 133.2, 131.5, 129.7, 128.3, 127.4, 126.9, 116.7, 114.4.

**2-((3,4-dichlorophenyl)thio)benzonitrile (3ar) (CAS Number: 1479168-64-3)**



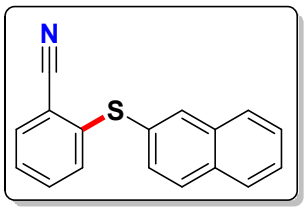
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a white solid (32.0 mg, 57%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.67 (m, 1H), 7.51 (td, *J* = 7.8, 1.5 Hz, 1H), 7.47 (d, *J* = 2.1 Hz, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.37 (td, *J* = 7.7, 1.2 Hz, 1H), 7.33 – 7.29 (m, 1H), 7.24 (dd, *J* = 8.4, 2.2 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 139.4, 134.0, 133.6, 133.5, 133.3, 132.9, 131.8, 131.4, 131.2, 130.9, 127.8, 116.6, 114.6.

**2-((perfluorophenyl)thio)benzonitrile (3as)**



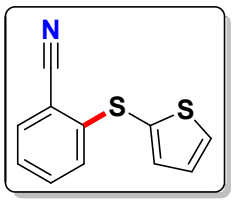
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 40:1, v/v) to give the product as a white solid (31.2 mg, 52%). m.p. 102-104 °C. IR (KBr, cm$^{-1}$): 2226, 1512, 1488, 1093, 980, 861, 757. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 1H), 7.52 (td, *J* = 7.8, 1.5 Hz, 1H), 7.40 (td, *J* = 7.7, 1.1 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 148.6 – 148.3(m), 146.7 – 146.3 (m), 143.7 – 143.5 (m), 141.5, 139.1– 138.8 (m), 137.1 – 136.9 (m), 136.8, 134.2, 133.4, 131.3, 128.3, 116.1, 114.5. HRMS (ESI, m/z) calcd for $C_{13}H_5F_5NS$ $[M+H]^+$: 302.0057; found: 302.0060.

**2-(naphthalen-2-ylthio)benzonitrile (3at) (CAS Number: 1154365-32-8)**



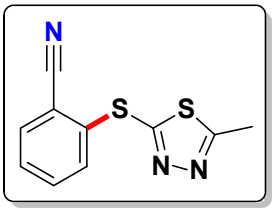
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a white solid (33.4 mg, 64%). $^1$H NMR (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.4 Hz, 1H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.83 – 7.80 (m, 1H), 7.66 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.59 – 7.52 (m, 2H), 7.47 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.26 (dd, *J* = 15.2, 1.1 Hz, 1H), 7.13 (dd, *J* = 8.1, 0.7 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 142.4, 133.8, 133.6, 133.3, 133.0, 133.0, 130.0, 129.9, 129.6, 128.9, 127.8, 127.7, 127.1, 126.9, 126.4, 117.0, 112.6.

**2-(thiophen-2-ylthio)benzonitrile (3au) (CAS Number: 1021238-32-3)**



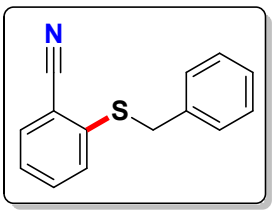
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a gray oil (32.1 mg, 76%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 2H), 7.43 – 7.37 (m, 2H), 7.22 (td, *J* = 7.6, 1.1 Hz, 1H), 7.14 (dd, *J* = 5.4, 3.6 Hz, 1H), 7.03 (dd, *J* = 8.2, 0.6 Hz, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 143.8, 137.7, 133.3, 133.1, 132.8, 128.4, 127.5, 127.4, 126.0, 116.6, 110.5.

**2-((5-methyl-1,3,4-thiadiazol-2-yl)thio)benzonitrile (3av) (CAS Number: 1179935-23-9)**



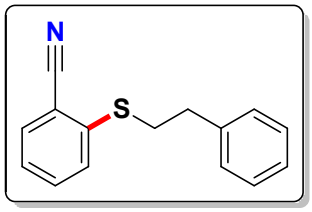
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a yellow solid (34.1 mg, 73%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.74 (ddd, *J* = 7.9, 2.9, 1.1 Hz, 2H), 7.61 (td, *J* = 7.8, 1.5 Hz, 1H), 7.51 (td, *J* = 7.7, 1.1 Hz, 1H), 2.72 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 167.5, 162.4, 134.7, 134.4, 134.2, 133.6, 129.9, 116.8, 116.3, 15.7.

**2-(benzylthio)benzonitrile (3aw) (CAS Number: 63216-04-6)**



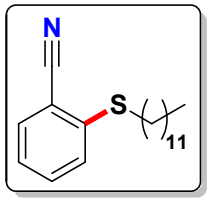
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a yellow oil (28.8 mg, 64%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 1H), 7.47 – 7.41 (m, 1H), 7.36 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.32 – 7.23 (m, 6H), 4.22 (s, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 140.6, 135.9, 133.6, 132.7, 130.5, 128.8, 128.6, 127.5, 126.6, 117.1, 114.4, 38.7.

**2-(phenethylthio)benzonitrile (3ax)**



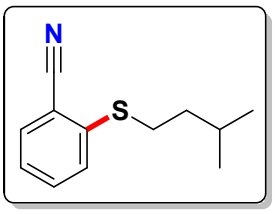
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a yellow oil (33.8 mg, 72%). IR (KBr, $cm^{-1}$): 3027, 2925, 2221, 1584, 1496, 1433, 1067, 1029, 753, 714, 696. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.42 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.29 – 7.20 (m, 4H), 3.32 – 3.24 (m, 2H), 3.01 – 2.94 (m, 2H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 141.4, 139.4, 133.6, 132.8, 129.0, 128.5, 128.4, 126.6, 126.0, 117.0, 113.6, 35.3, 34.9. HRMS (ESI, m/z) calcd for $C_{15}H_{13}NNaS[M+Na]^+$: 262.0061; found: 262.0065.

**2-(dodecylthio)benzonitrile (3ay) (CAS Number: 1621877-32-4)**



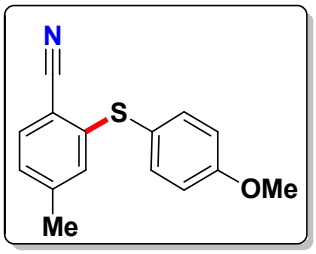
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a yellow oil (36.3 mg, 60%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.52 (td, *J* = 8.0, 1.5 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 1H), 7.25 (td, *J* = 7.6, 1.0 Hz, 1H), 3.08 – 3.00 (m, 2H), 1.70 (dt, *J* = 15.1, 7.5 Hz, 2H), 1.50 – 1.42 (m, 2H), 1.35 – 1.27 (m, 15H), 0.90 (t, *J* = 7.0 Hz, 4H).$^{13}$C NMR (126 MHz, $CDCl_3$) δ 142.3, 133.6, 132.8, 128.6, 125.7, 117.2, 113.3, 34.1, 33.5, 31.9, 29.6, 29.6, 29.5, 29.4, 29.1, 28.8, 28.0, 22.7, 14.1.

**2-((2-methylbutyl)thio)benzonitrile (3az) (CAS Number: 1697364-39-8)**



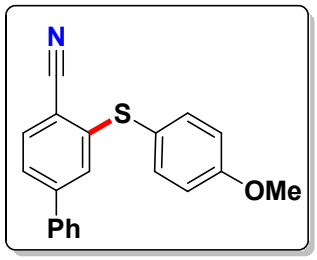

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 100:1, v/v) to give the product as a yellow oil (36.1 mg, 88%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.41 – 7.36 (m, 1H), 7.23 (td, *J* = 7.6, 1.1 Hz, 1H), 3.00 (dd, *J* = 8.3, 7.2 Hz, 2H), 1.74 (dp, *J* = 13.4, 6.7 Hz, 1H), 1.59 – 1.52 (m, 2H), 0.92 (d, *J* = 6.6 Hz, 6H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 142.1, 133.5, 132.7, 128.4, 125.6, 117.1, 113.1, 37.5, 31.4, 27.3, 22.1.

**2-((4-methoxyphenyl)thio)-4-methylbenzonitrile (3bd) (CAS Number: 1285207-40-0)**



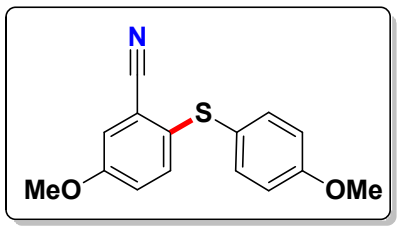

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a colourless oil (41.8 mg, 82%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 3H), 7.00 – 6.96 (m, 1H), 6.96 – 6.91 (m, 2H), 6.76 (s, 1H), 3.84 (s, 3H), 2.24 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 160.6, 143.9, 143.8, 136.4, 133.2, 128.6, 126.7, 121.2, 117.2, 115.3, 108.3, 55.3, 21.8.

**3-((4-methoxyphenyl)thio)-[1,1'-biphenyl]-4-carbonitrile (3cd)**



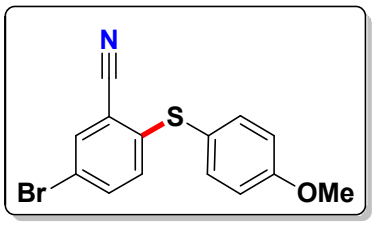

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a white solid (44.3 mg, 70%). m.p. 119-121 °C. IR (KBr, $cm^{-1}$): 2220, 1590, 1492, 1289, 1028, 966, 829, 763, 711. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.45 – 7.35 (m, 6H), 7.19 (d, *J* = 1.6 Hz, 1H), 7.00 – 6.93 (m, 2H), 3.85 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 160.7, 145.8, 144.7, 138.9, 136.5, 133.8, 129.0, 128.6, 127.1, 126.6, 124.5, 121.0, 117.1, 115.5, 109.7, 55.4. HRMS (ESI, m/z) calcd for $C_{20}H_{16}NOS$ $[M+H]^+$: 318.0947; found: 318.0949.

**5-methoxy-2-((4-methoxyphenyl)thio)benzonitrile (3dd)**



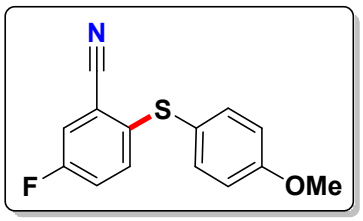

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a white solid (45.5 mg, 84%). m.p. 79-80 °C. IR (KBr, $cm^{-1}$): 2226, 1590, 1493, 1288, 1235, 1024, 922, 824, 712. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.34 (m, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.11 (d, *J* = 2.8 Hz, 1H), 6.97 (dd, *J* = 8.8, 2.9 Hz, 1H), 6.90 – 6.85 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 160.0, 158.2, 134.9, 133.2, 132.8, 123.9, 120.0, 117.9, 117.0, 115.1, 114.7, 55.7, 55.3. HRMS (ESI, m/z) calcd for $C_{15}H_{14}NO_2S$ $[M+H]^+$: 272.0740; found: 272.0741.

**5-bromo-2-((4-methoxyphenyl)thio)benzonitrile (3ed) (CAS Number: 1708105-51-4)**



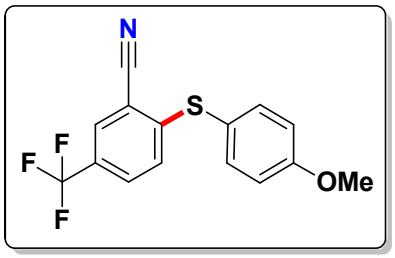

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a white solid (39.4 mg, 62%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.46 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 1H), 7.29 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.01 – 6.97 (m, 2H), 6.96 (d, *J* = 1.8 Hz, 1H), 3.86 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.2, 147.1, 137.0, 134.2, 129.8, 128.6, 128.2, 119.4, 116.2, 115.8, 109.0, 55.4.

**5-fluoro-2-((4-methoxyphenyl)thio)benzonitrile (CAS Number: 1467276-81-8)**



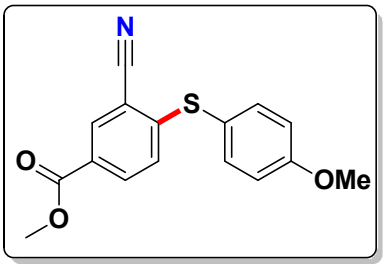

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a rufous oil (37.3 mg, 72%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.43 (m, 2H), 7.31 (dd, *J* = 7.9, 2.8 Hz, 1H), 7.11 (ddd, *J* = 8.8, 8.0, 2.8 Hz, 1H), 7.01 (dd, *J* = 8.9, 5.1 Hz, 1H), 6.96 – 6.91 (m, 2H), 3.83 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 160.2 (d, *J* = 249.5 Hz), 160.8, 159.2, 139.7 (d, *J* = 3.5 Hz), 136.3, 131.0 (d, *J* = 7.9 Hz), 121.6, 120.8 (d, *J* = 21.4 Hz), 120.1 (d, *J* = 25.0 Hz), 115.9 (d, *J* = 2.8 Hz), 115.5, 55.5.

**2-((4-methoxyphenyl)thio)-5-(trifluoromethyl)benzonitrile (3gd) (CAS Number: 212691-83-3)**




The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 30:1, v/v) to give the product as a pale yellow solid (37.1 mg, 60%). $^{1}$H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 1.0 Hz, 1H), 7.54 – 7.46 (m, 3H), 7.04 – 6.98 (m, 2H), 6.89 (d, *J* = 8.6 Hz, 1H), 3.87 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 161.5, 150.6, 137.4, 130.1 (q, *J* = 3.9 Hz), 129.2 (q, *J* = 3.4 Hz), 127.4 (q, *J* = 33.8 Hz), 126.7, 123.0 (q, *J* = 277.2 Hz), 118.6, 115.9, 115.5, 109.8, 55.5.

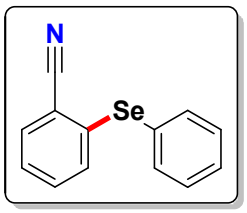
**methyl 3-cyano-4-((4-methoxyphenyl)thio)benzoate (3hd)**




The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 20:1, v/v) to give the product as a white solid (32.6 mg, 54%). m.p. 125-127 °C. IR (KBr, $cm^{-1}$): 2226, 1719, 1591, 1460, 1290, 1240, 1111, 1026, 981, 830, 799, 758. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.8 Hz, 1H), 7.92 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.52 – 7.45 (m, 2H), 7.02 – 6.97 (m, 2H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ

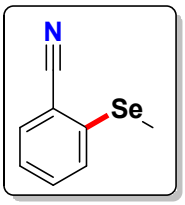
165.0, 161.4, 151.4, 137.3, 134.4, 133.3, 127.0, 126.1, 118.8, 116.0, 115.9, 109.5, 55.5, 52.5. HRMS (ESI, m/z) calcd for $C_{16}H_{14}NO_3S$ $[M+H]^+$: 300.0689; found: 300.0689.

**2-(phenylselanyl)benzonitrile (5a) (CAS Number: 107037-20-7)**



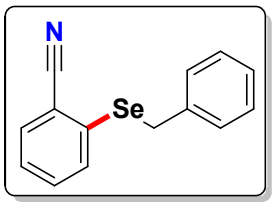

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a reddish brown oil (41.8 mg, 81%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.57 (m, 3H), 7.41 – 7.34 (m, 4H), 7.31 – 7.26 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 137.5, 135.2, 133.6, 133.0, 132.2, 129.8, 128.9, 127.9, 126.9, 117.5, 114.7.

**2-(methylselanyl)benzonitrile (5b) (CAS Number: 24845-06-5)**



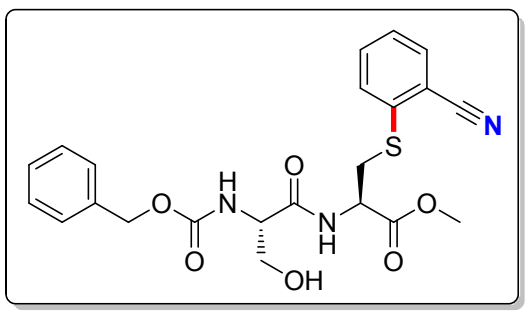

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as an amaranthine oil (27.1 mg, 69%). $^1$H NMR (500 MHz, $CDCl_3$) δ 7.59 (dd, $J$ = 4.7, 3.8 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.30 – 7.25 (m, 1H), 2.44 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 136.9, 133., 132.8, 130.4, 126.3, 117.6, 114.7, 7.7.

**2-(benzylselanyl)benzonitrile (5c)**



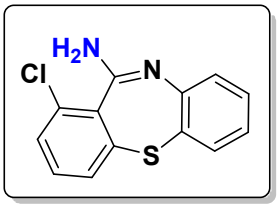

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:AcOEt = 60:1, v/v) to give the product as a pink oil (38.7 mg, 72%). IR (KBr, cm$^{-1}$): 2222, 1584, 1497, 1433, 1283, 1067, 1029, 754, 714, 695. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, $J$ = 7.6, 1.4 Hz, 1H), 7.52 (dd, $J$ = 7.8, 0.8 Hz, 1H), 7.41 (td, $J$ = 7.7, 1.5 Hz, 1H), 7.34 (td, $J$ = 7.6, 1.2 Hz, 1H), 7.28 – 7.20 (m, 5H), 4.24 (s, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 137.0, 134.7, 134.4, 133.6, 132.6, 128.9, 128.5, 127.7, 127.2, 117.9, 117.5, 32.4.

**(R) -methyl 2-((S)-2-(((benzyloxy)carbonyl)amino)-3-hydroxypropanamido)-3-((2-cyanophenyl)thio)propanoate (7)**



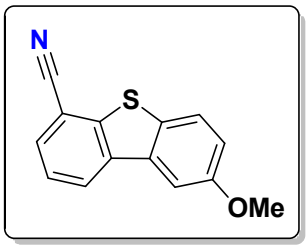

The reaction was performed following the general procedure. The residue was purified by flash column chromatograph by using EtOAc as eluent to give the product as a yellowish-brown oil. IR (KBr, cm$^{-1}$): 2226, 1717, 1675, 1507, 1294, 1251, 987, 732, 696. $^1$H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.55 (dd, $J$ = 15.8, 7.6 Hz, 2H), 7.47 (t, $J$ = 7.3 Hz, 1H), 7.37 – 7.24 (m, 8H), 6.04 (s, 1H), 5.10 (s, 3H), 4.76 (s, 1H), 4.29 (s, 1H), 3.96 (s, 1H), 3.80 – 3.65 (m, 3H), 3.57 (s, 3H), 3.51 – 3.33 (m, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 170.7, 170.1, 156.3, 138.6, 135.9, 133.6, 133.0, 131.8, 128.4, 128.0, 127.9, 127.5, 115.3, 67.0, 62.6, 55.7, 52.7, 51.9, 35.9. HRMS (ESI, m/z) calcd for $C_{22}H_{24}N_3O_6S[M+H]^+$: 458.1380; found: 458.1384.

**1-chlorodibenzo[b,f][1,4]thiazepin-11-amine (8)**




$^{t}$BuONa (0.4 mmol, 2 equiv) was added to 2-((2-aminophenyl)thio)-5-chlorobenzonitrile (**3im**) (0.2 mmol, 1 equiv) in anhydrous THF. The mixture was stirred at 70 $^{o}$C for 12 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 8:1, v/v) to give the desired product **8** as white solid (39.5 mg, 76%). m.p. 231-233 °C. IR (KBr, cm$^{-1}$): 3360, 1592, 1476, 1089, 837, 746, 717.$^{1}$H NMR (500 MHz, DMSO) δ 7.54 – 7.50 (m, 1H), 7.50 – 7.47 (m, 1H), 7.44 (tt, *J* = 9.4, 3.5 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.15 (brs, 2H), 6.93 (d, *J* = 2.3 Hz, 1H), 6.89 (dd, *J* = 8.3, 2.4 Hz, 1H). $^{13}$C NMR (126 MHz, DMSO) δ 160.8, 151.1, 137.7, 136.0, 133.6, 133.4, 131.6, 131.4, 129.1, 129.0, 125.9, 124.2, 121.7. HRMS (ESI, m/z) calcd for $C_{13}H_{10}ClN_2S[M+H]^+$: 261.0248; found: 261.0249.

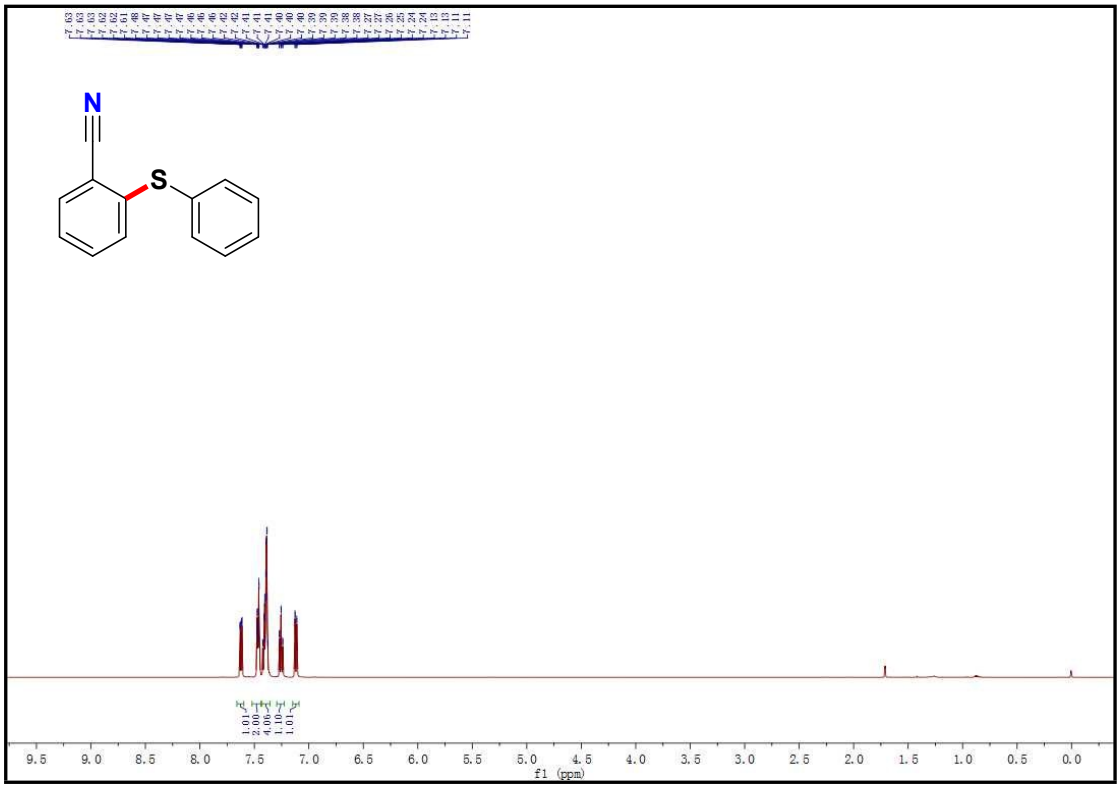
**8-methoxydibenzo[b,d]thiophene-4-carbonitrile (9)**

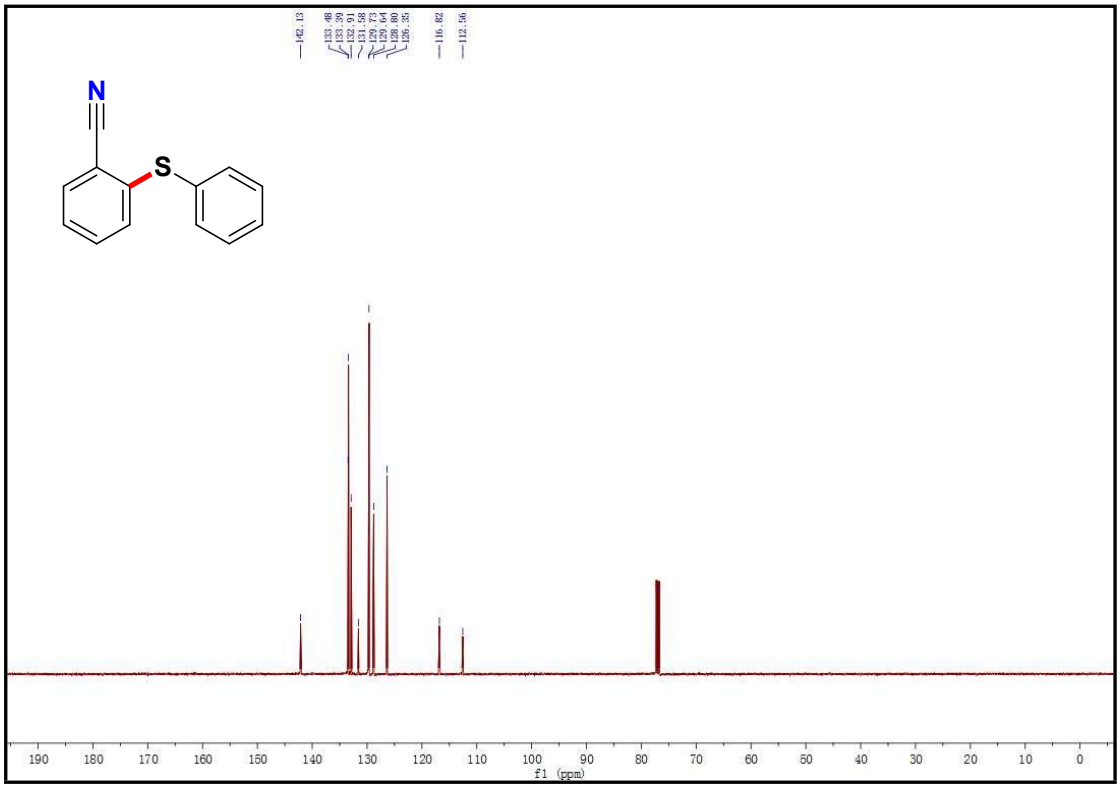



Under $N_2$, 1 mL DMA was added to the mixture of 3-bromo-2-((4-methoxyphenyl)thio)benzonitrile (**3jd**) (0.2 mmol, 1 equiv), $PdCl_2(PPh_3)_2$ (5 mol%) and CsOPiv (0.4 mmol, 2 equiv). The mixture was stirred at 140 $^{o}$C for 14 h. Upon completion of the reaction, ethyl acetate (20 mL) was added to the resulting solution, and then washed with aturated brine three times. The combined water layers were extracted with ethyl acetate (15 mL×2). The combined organic layers were dried over anhydrous $Na_2SO_4$. the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the desired product **9** as yellow solid (35.4 mg, 74%). m.p. 178-180 °C. IR (KBr, cm$^{-1}$): 2228, 1591, 1462, 1288, 1029, 826, 789, 712. $^{1}$H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.2 Hz, 1H), 7.73 (d, *J* = 7.1 Hz, 2H), 7.62 – 7.42 (m, 2H), 7.15 (d, *J* = 7.2 Hz, 1H), 3.93 (s, 3H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 158.0, 143.9, 136.3, 135.6, 130.9, 130.7,1 125.4, 124.2, 123.6, 117.1, 117.1, 106.9, 105.2, 55.7. HRMS (ESI, m/z) calcd for $C_{14}H_{10}ONS[M+H]^+$: 240.0478; found: 240.0481.

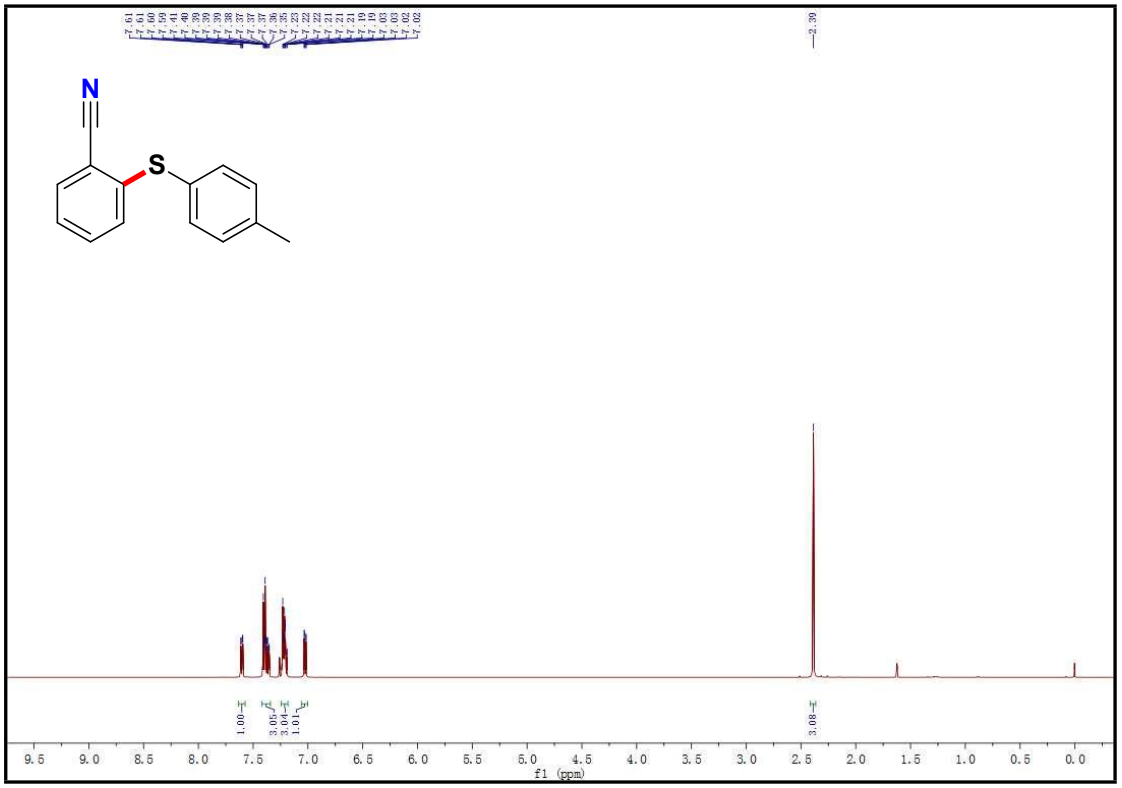
## 7.NMR spectroscopic data

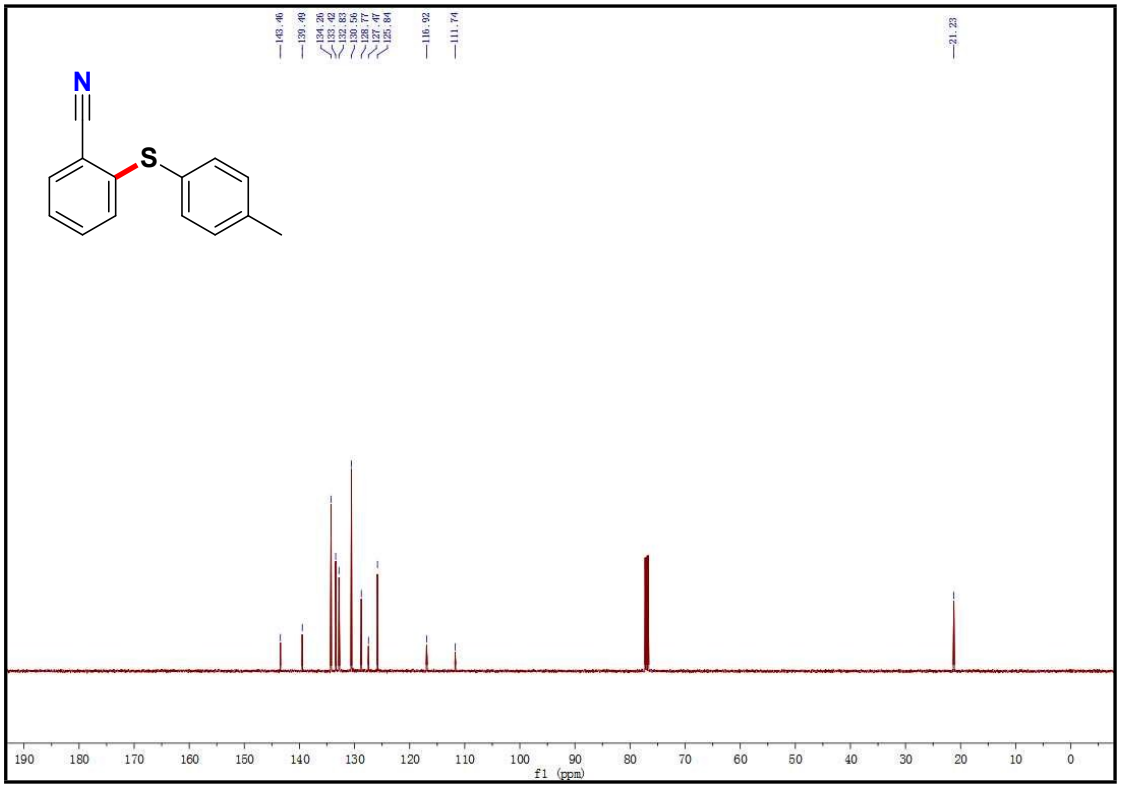
### 2-(phenylthio)benzonitrile (3aa)



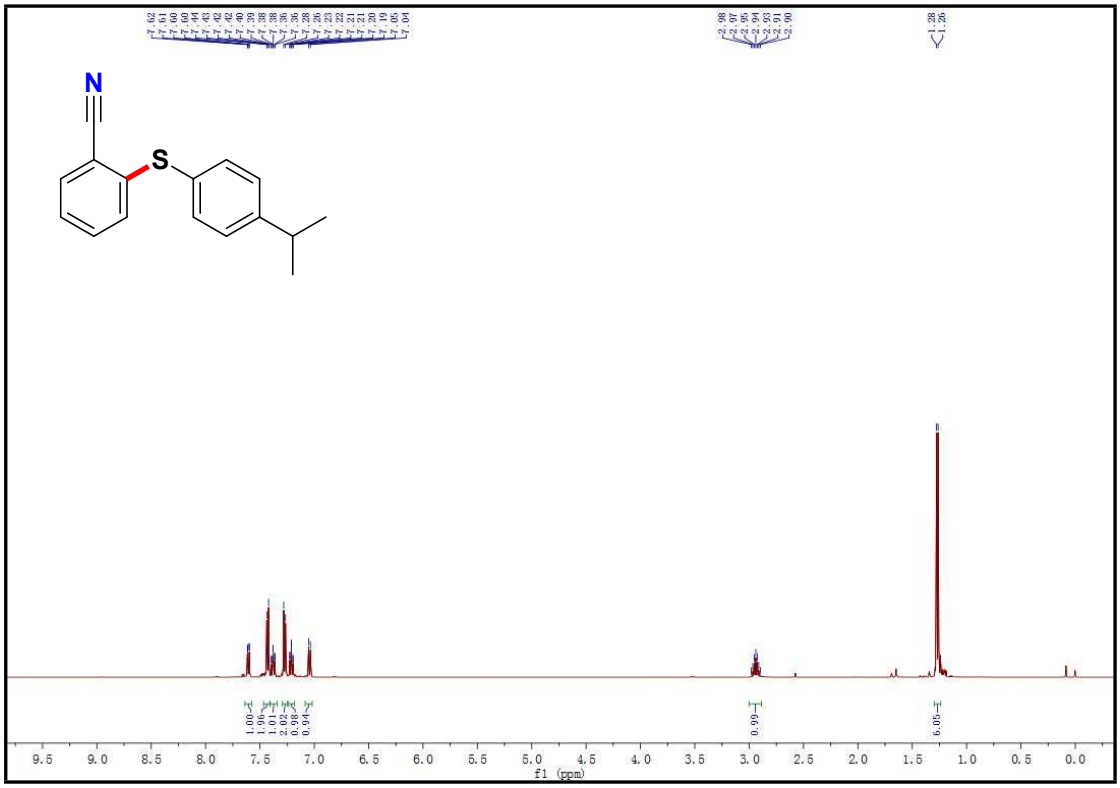



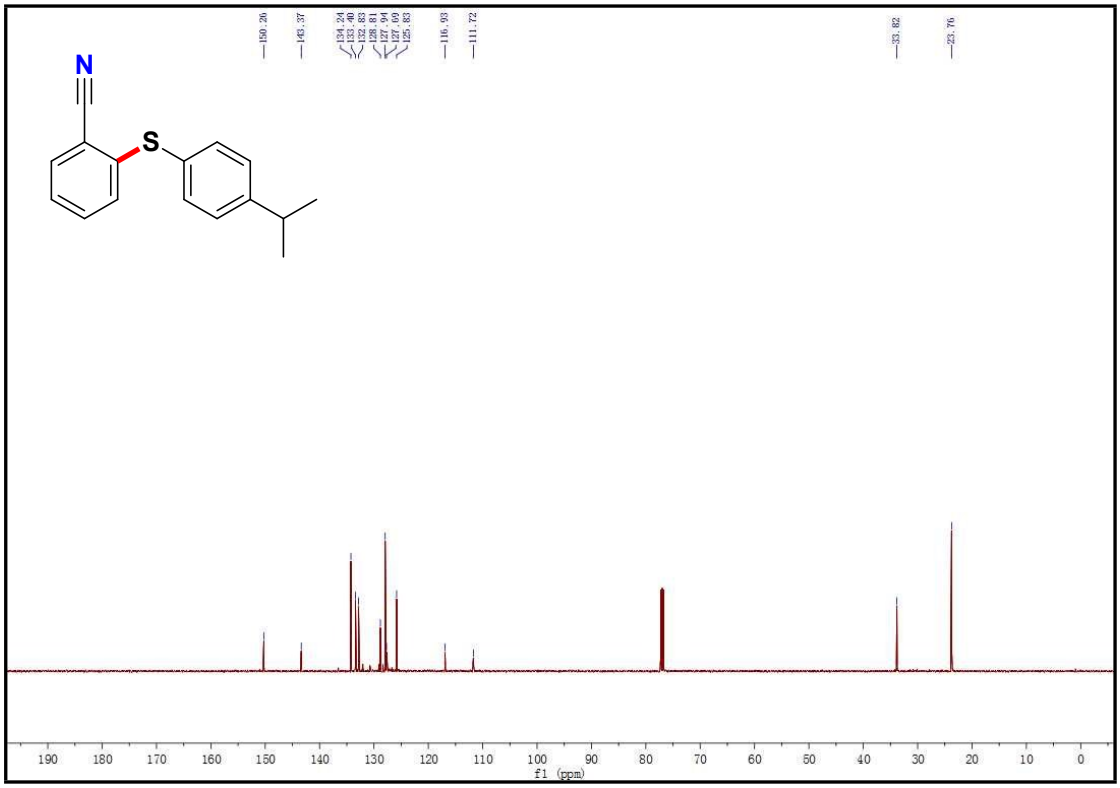
## 2-(p-tolylthio)benzonitrile (3ab)



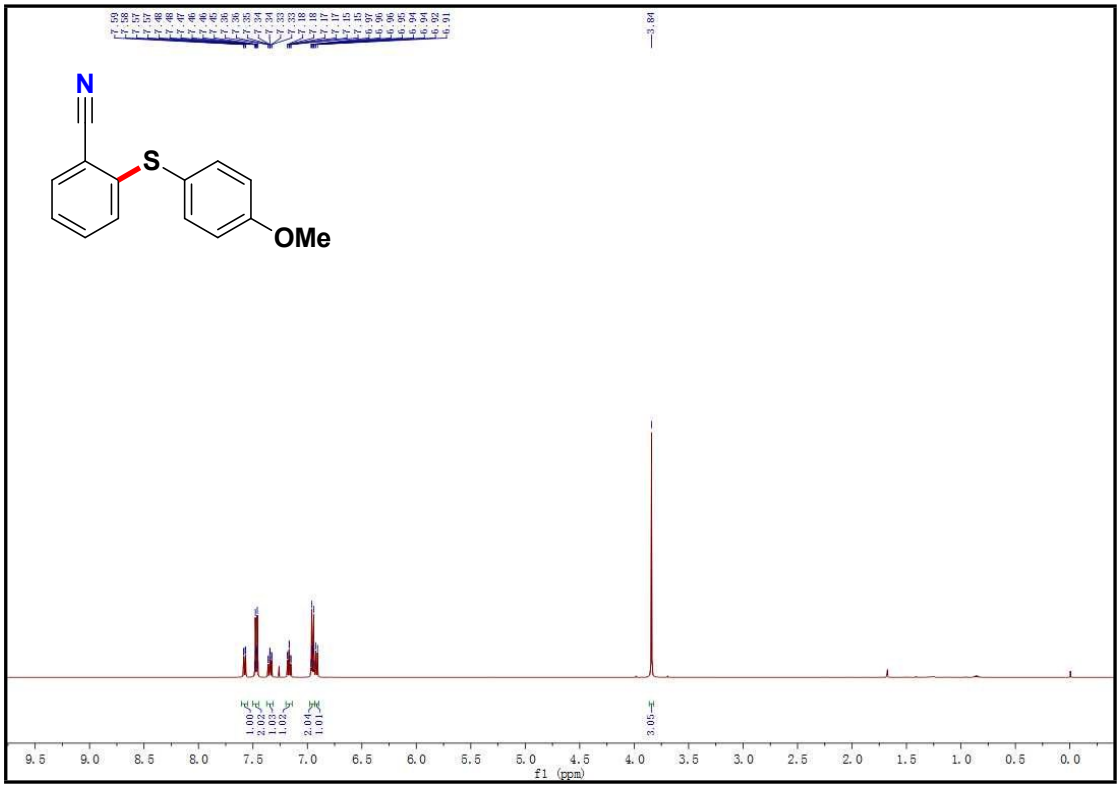



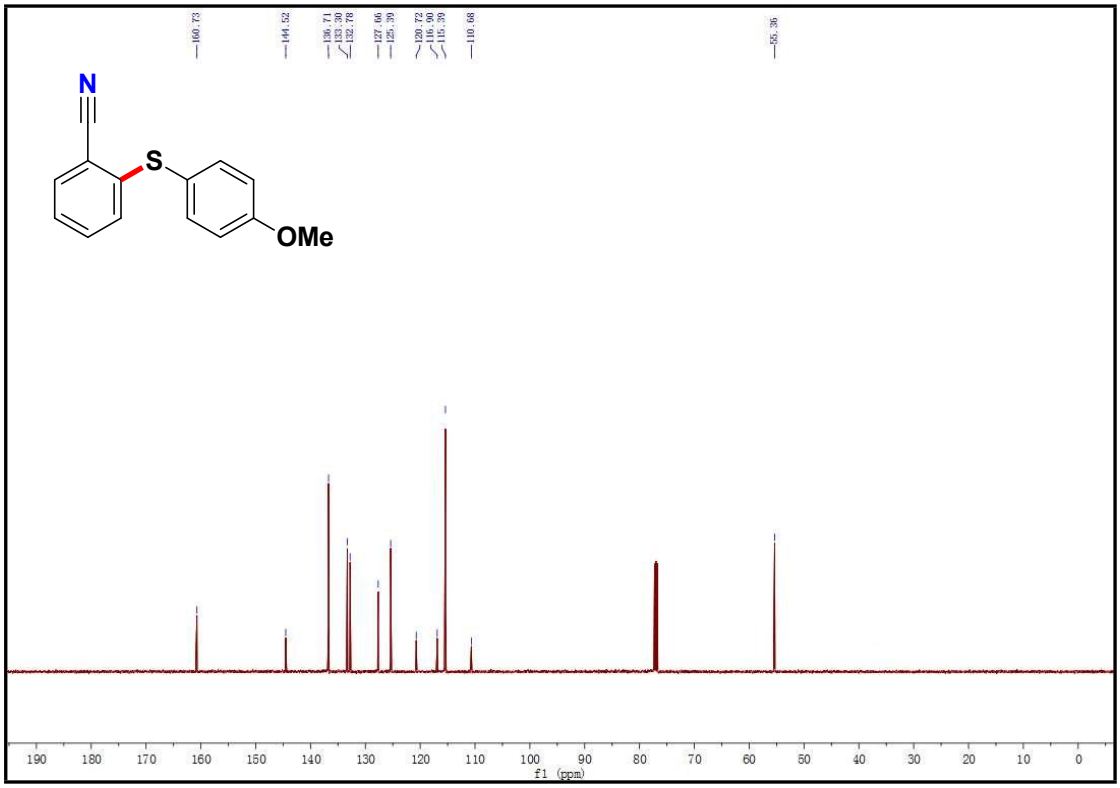
## 2-((4-isopropylphenyl)thio)benzonitrile (3ac)



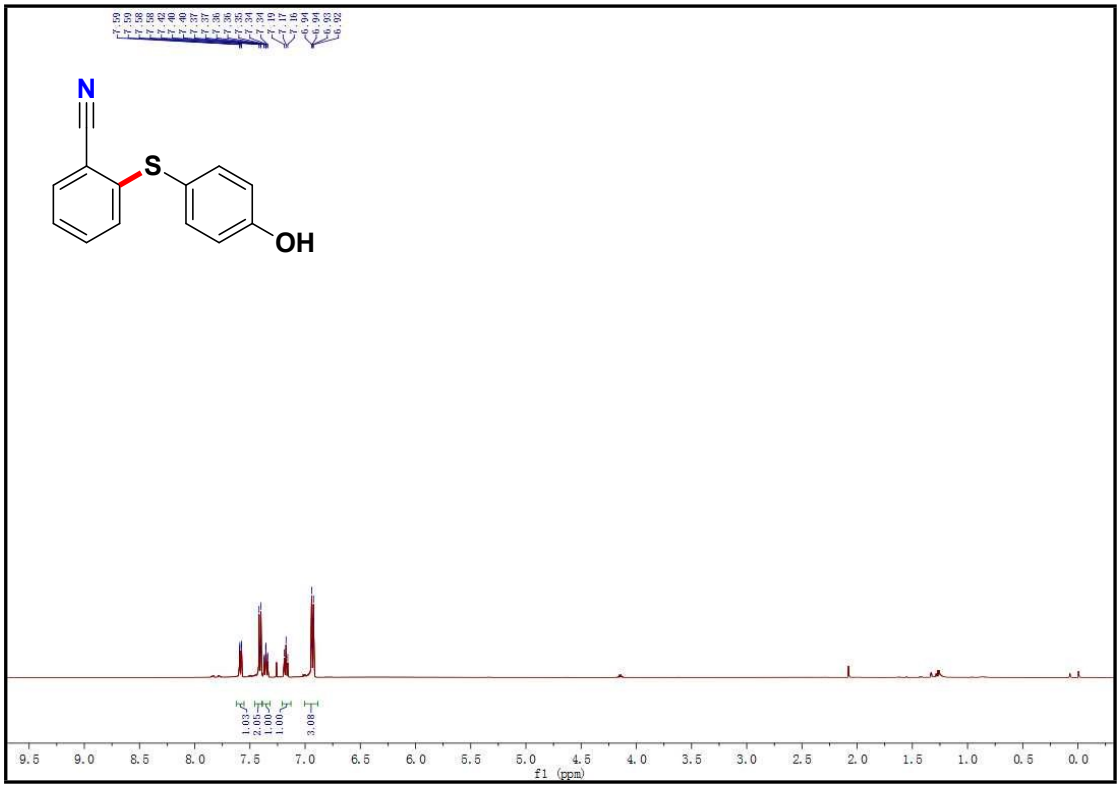



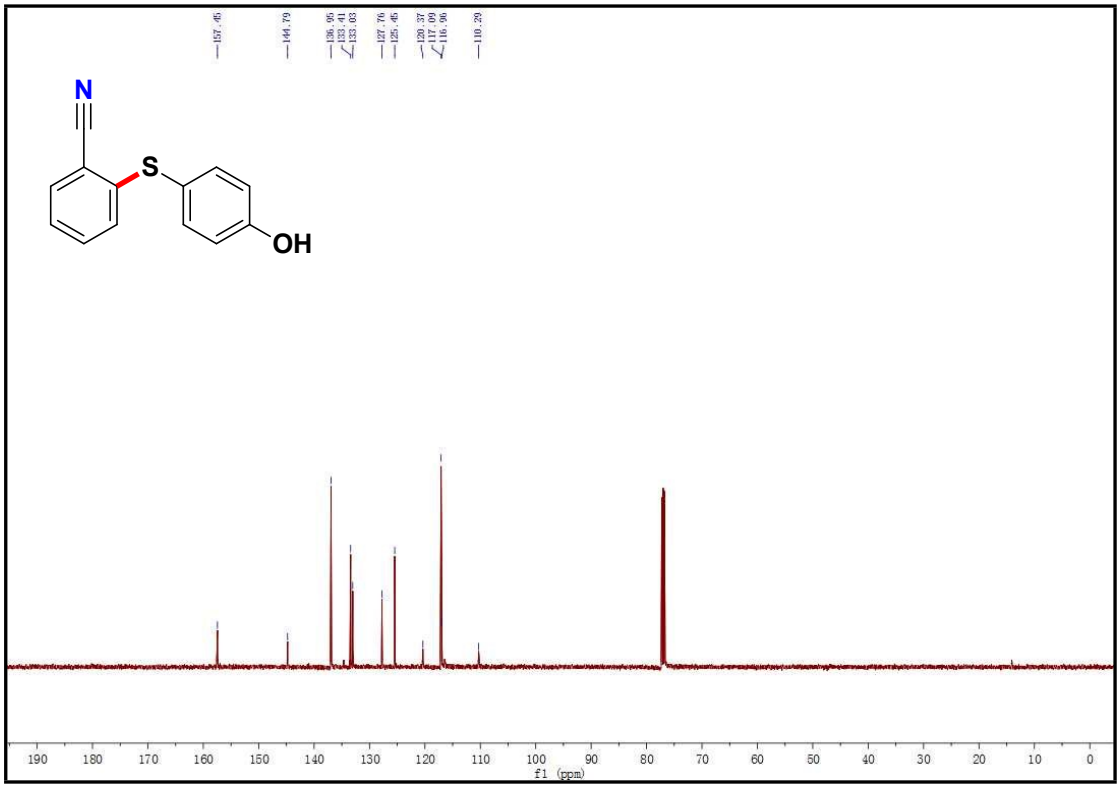
## 2-((4-methoxyphenyl)thio)benzonitrile (3ad)



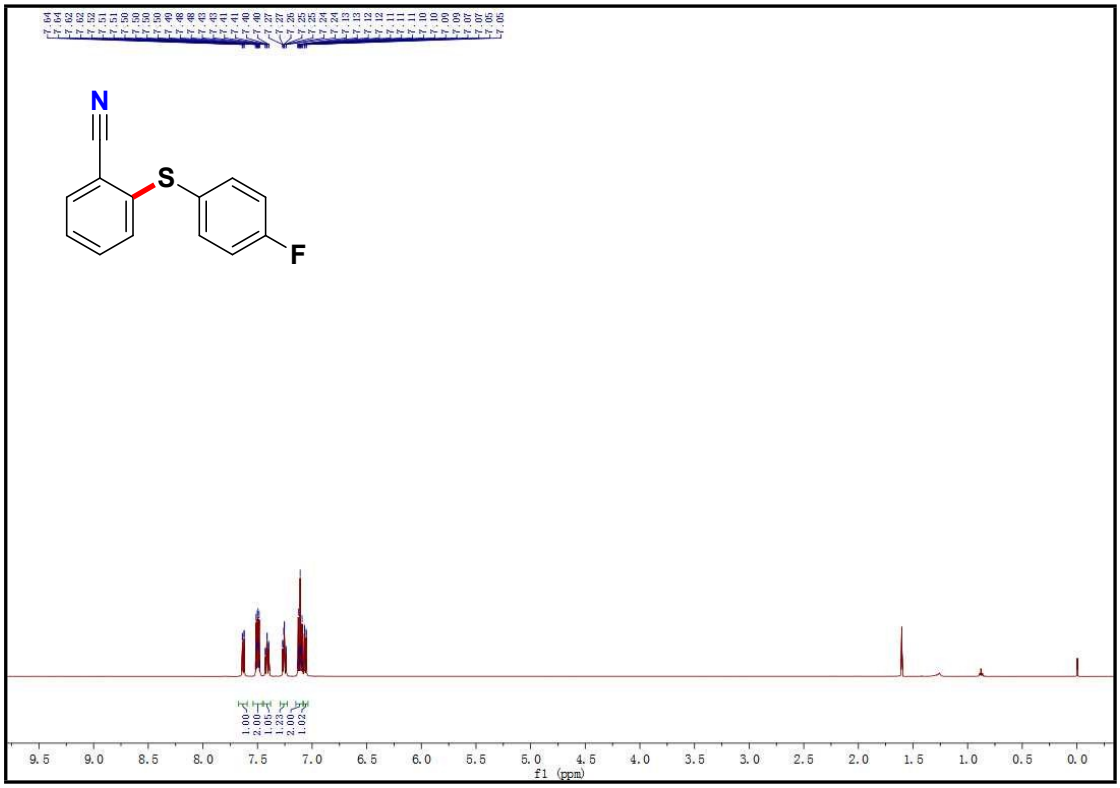



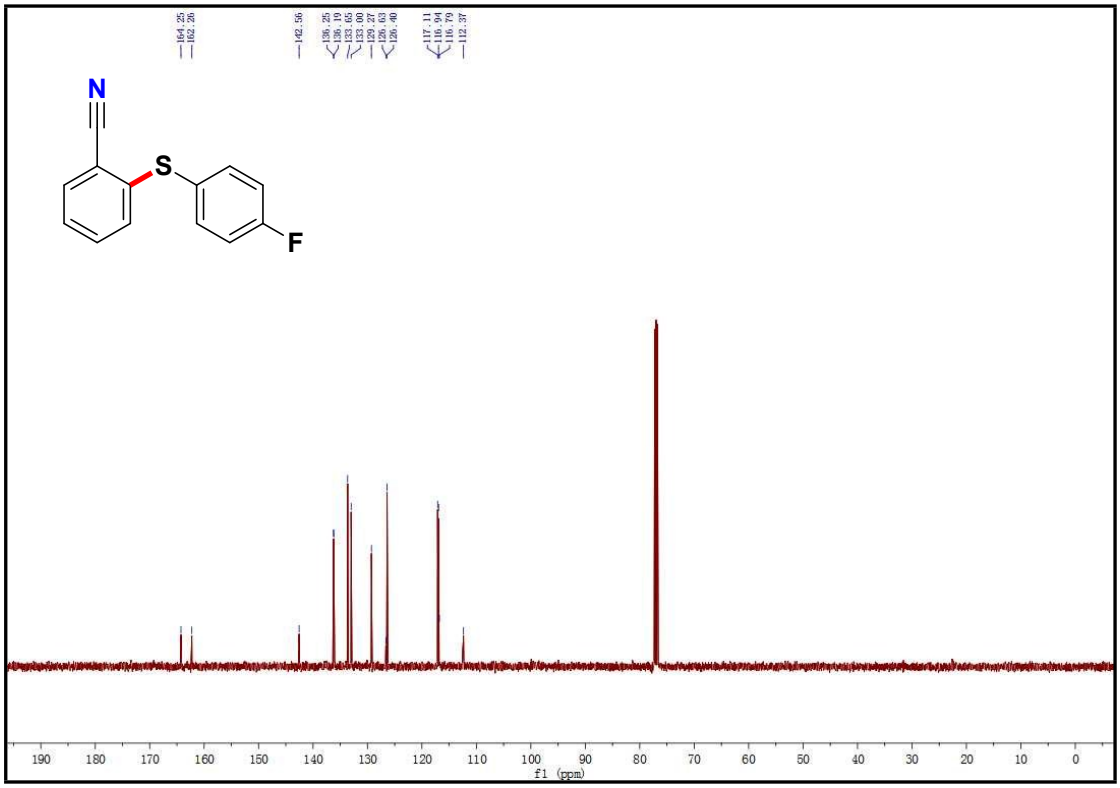
**2-((4-hydroxyphenyl)thio)benzonitrile (3ae)**



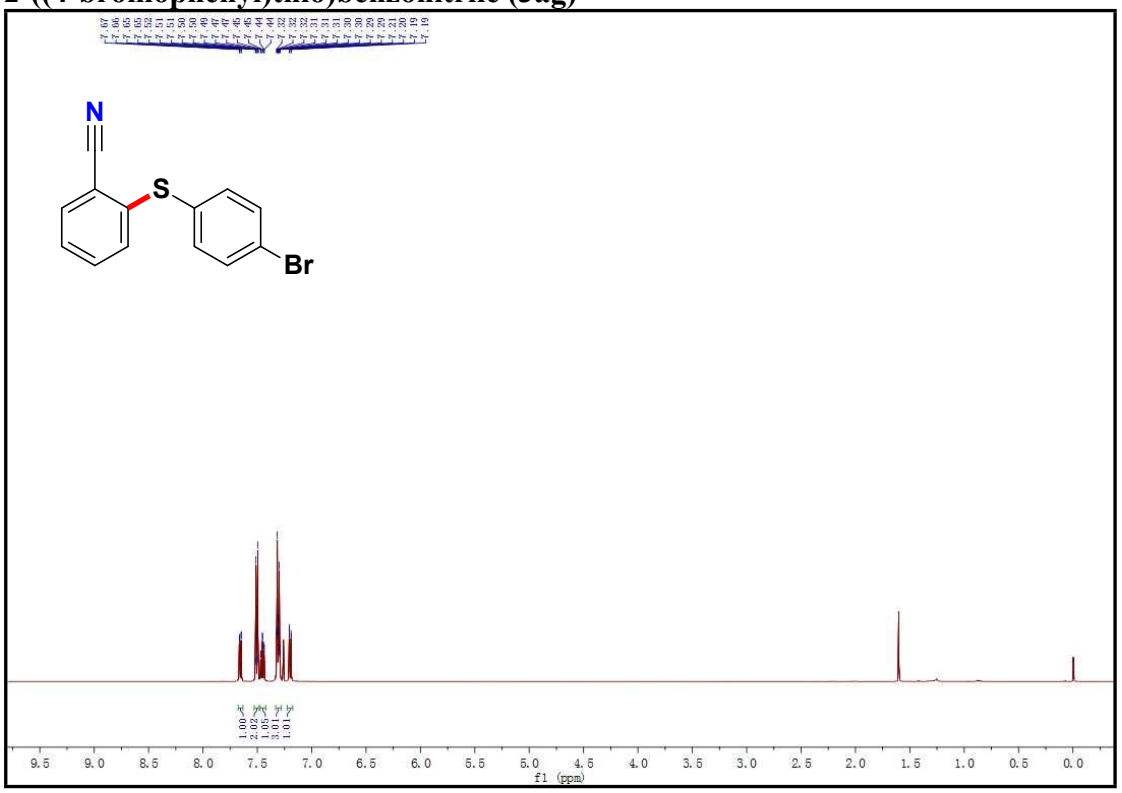



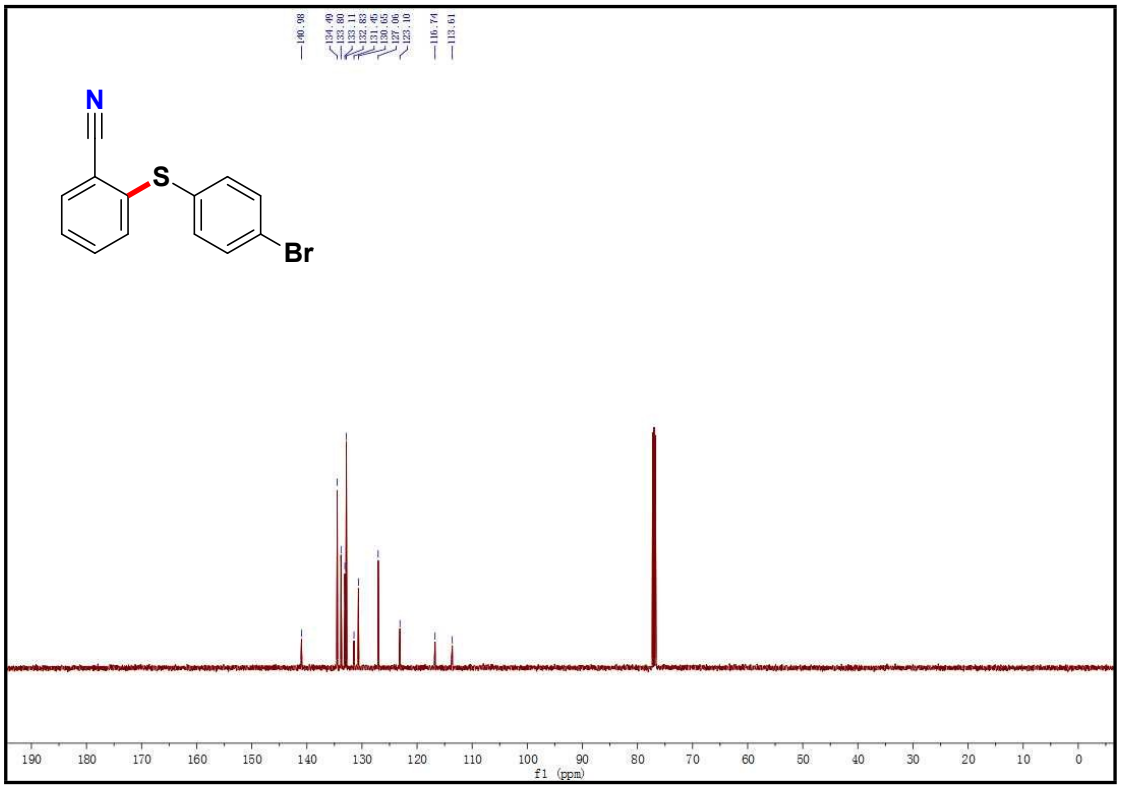
## 2-((4-fluorophenyl)thio)benzonitrile (3af)



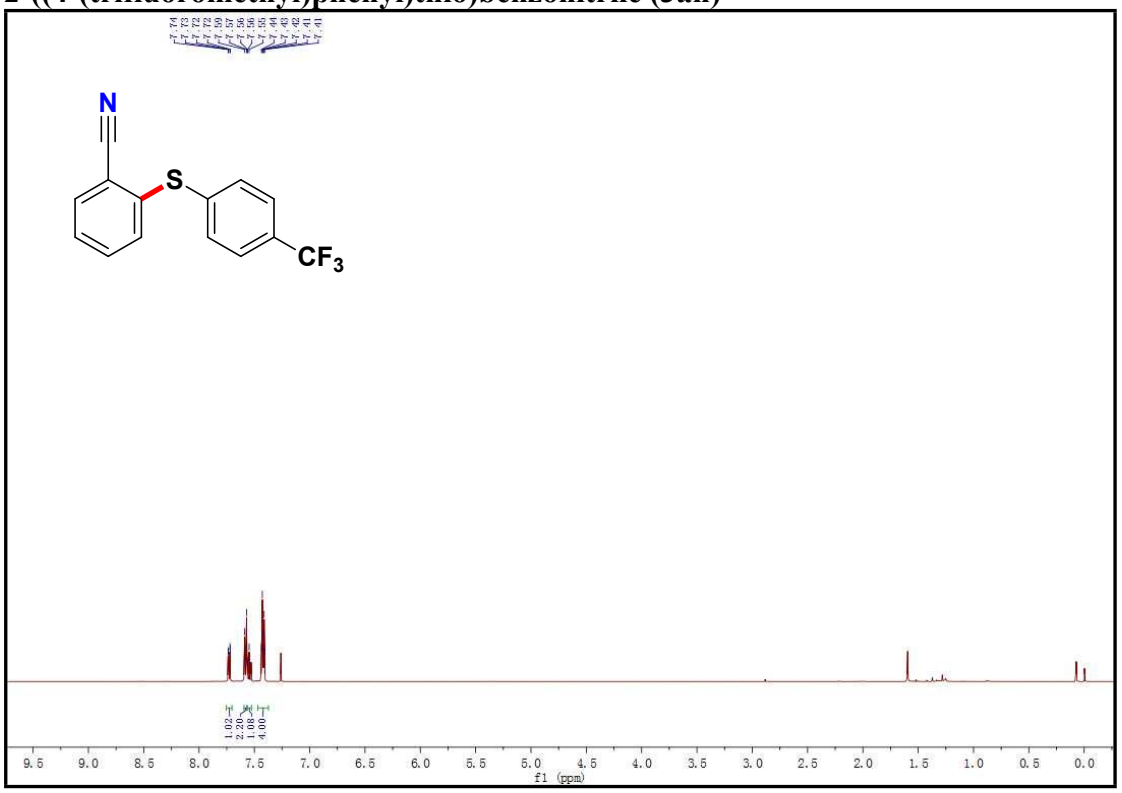



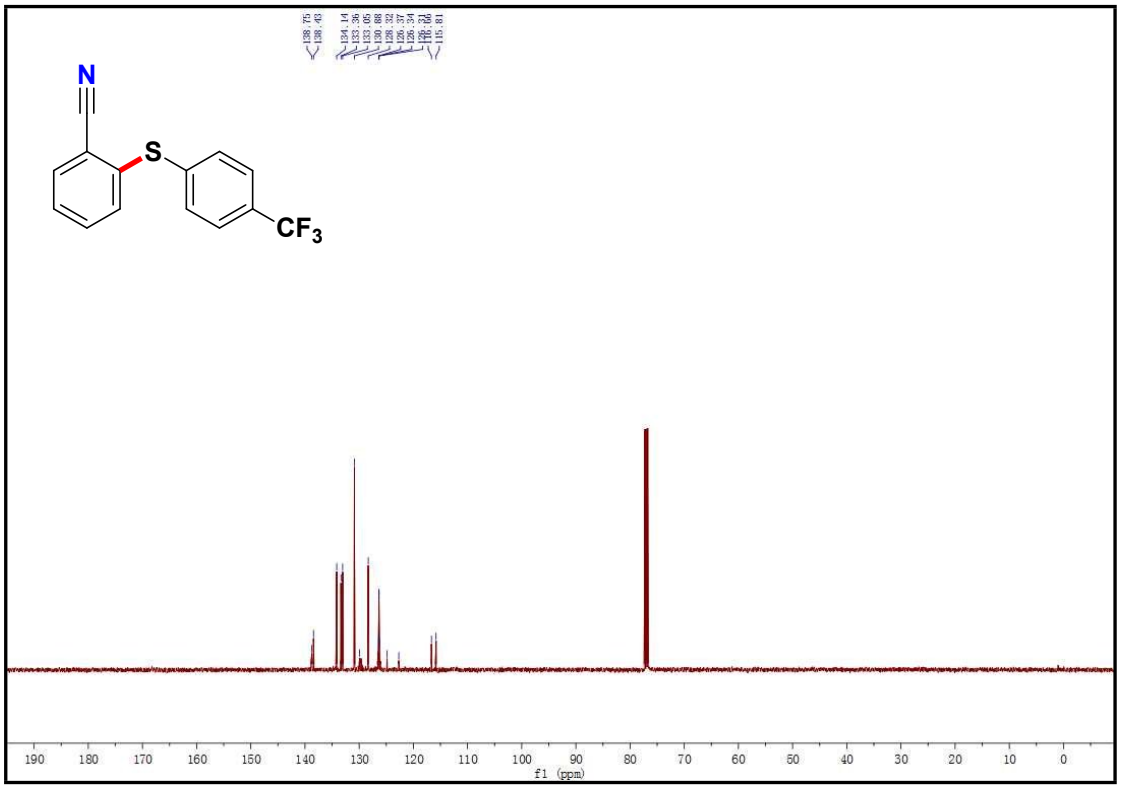
**2-((4-bromophenyl)thio)benzonitrile (3ag)**



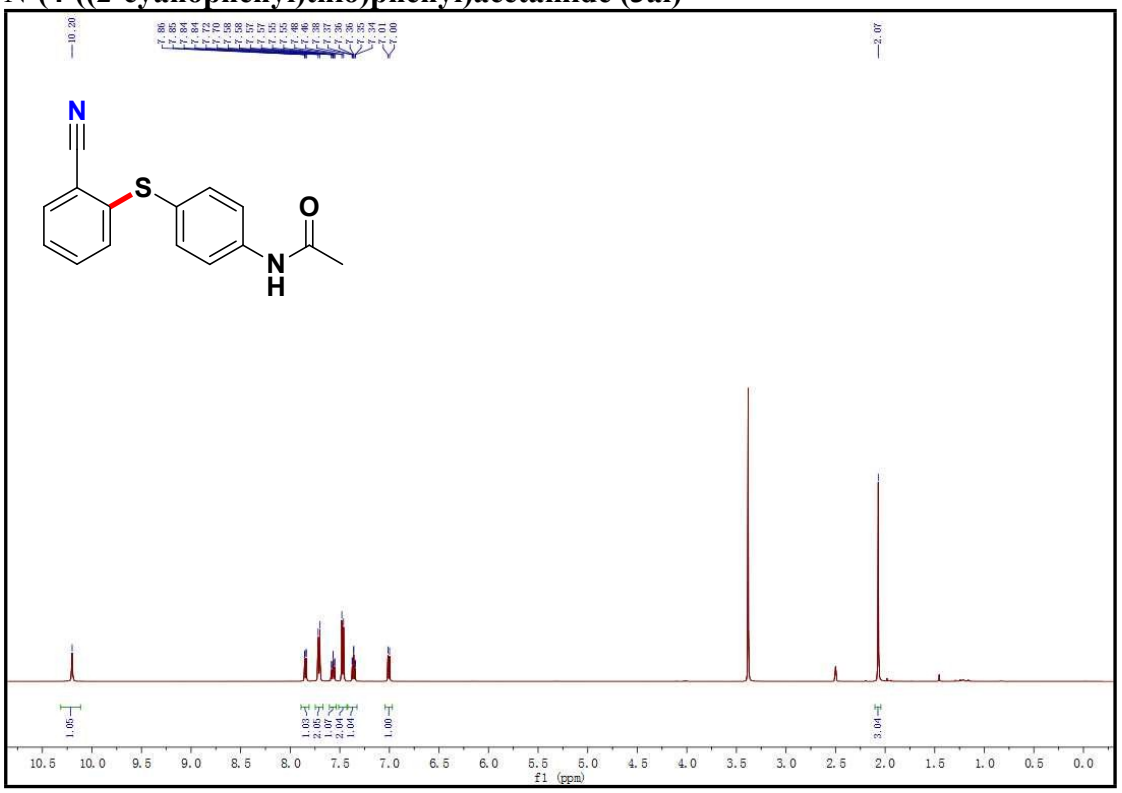



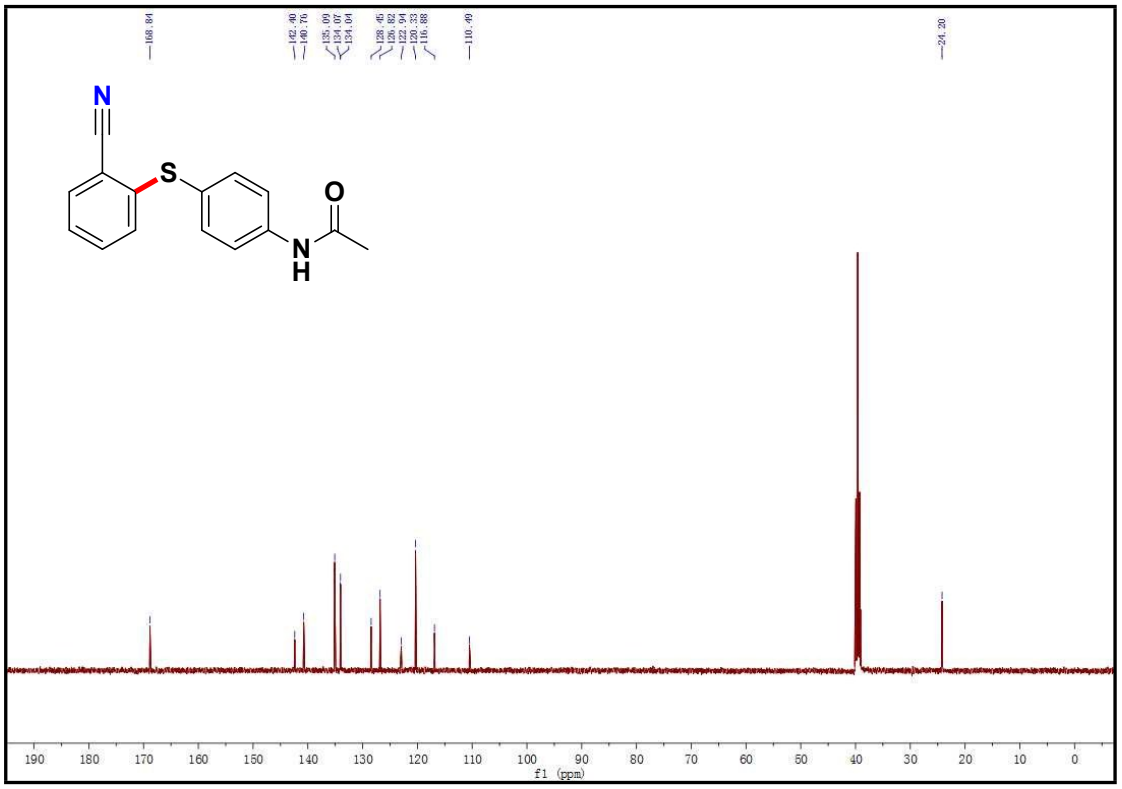
**2-((4-(trifluoromethyl)phenyl)thio)benzonitrile (3ah)**



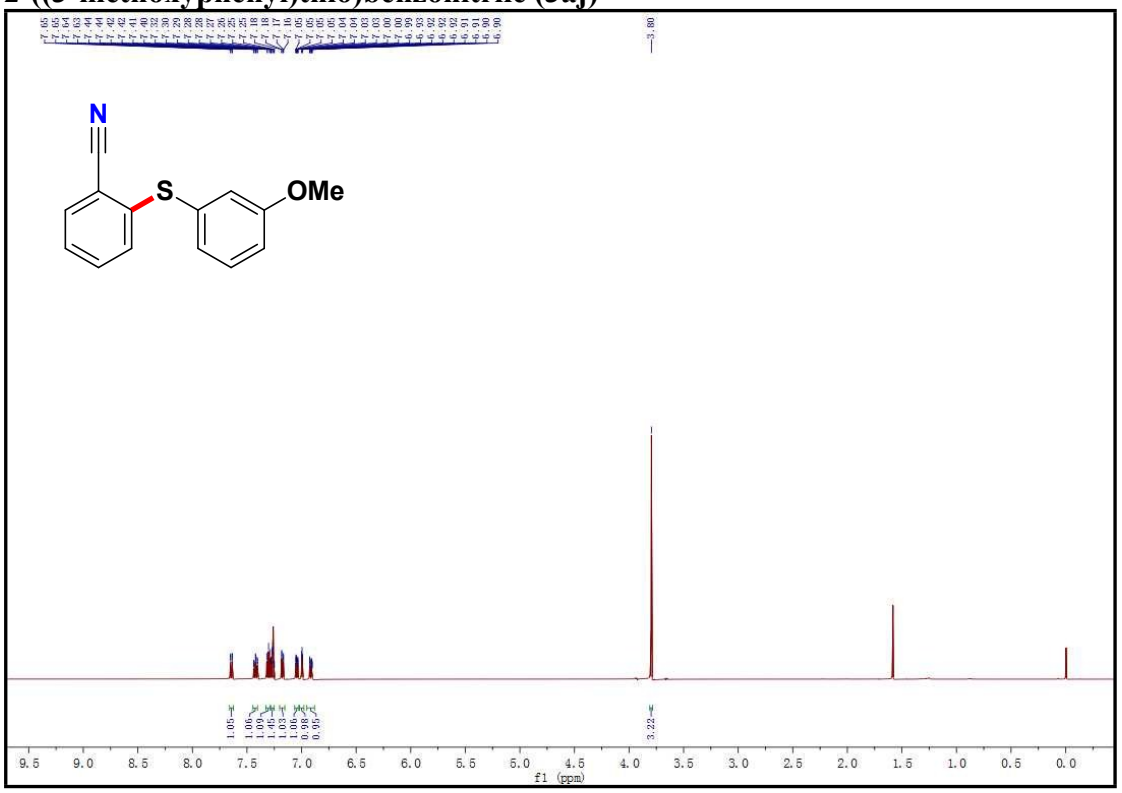



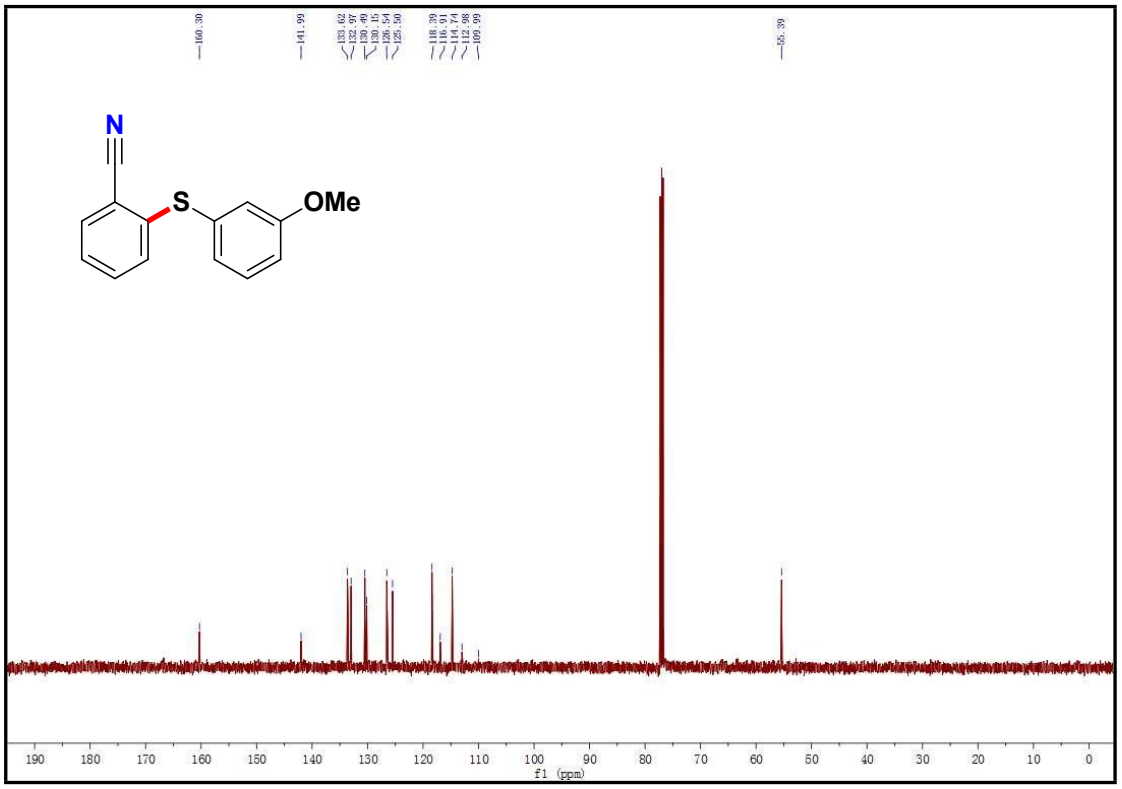
**N-(4-((2-cyanophenyl)thio)phenyl)acetamide (3ai)**



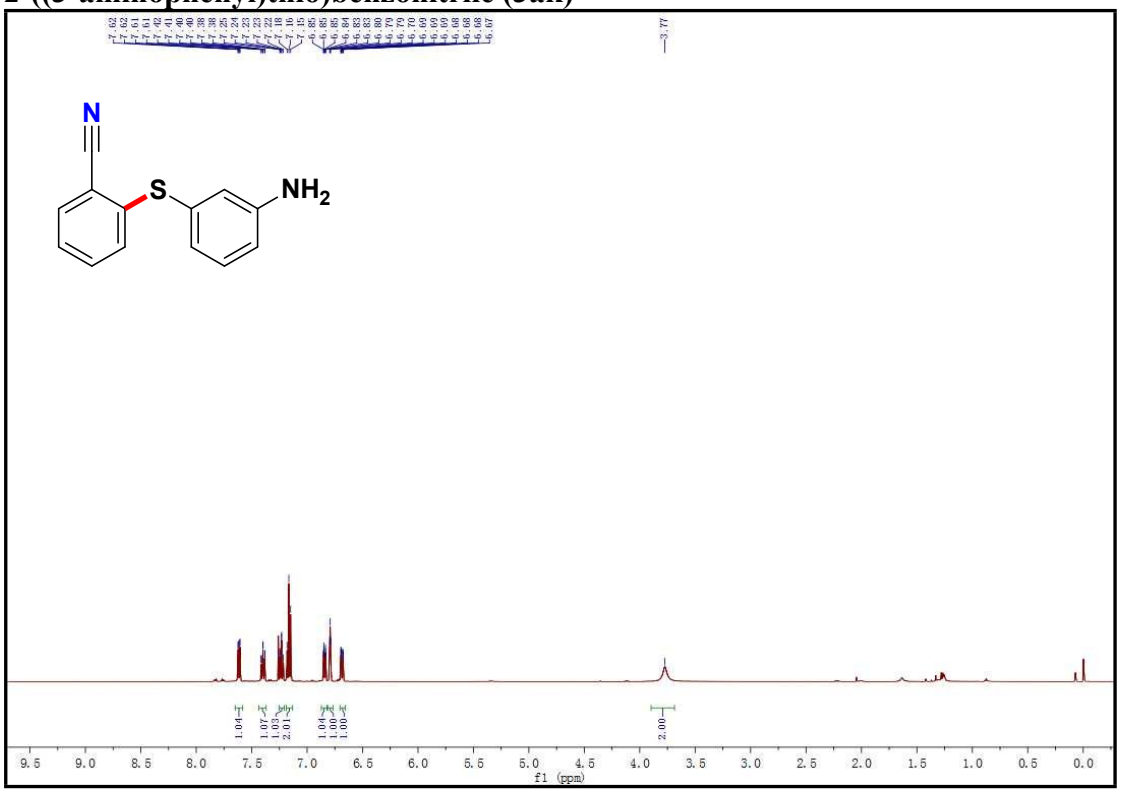



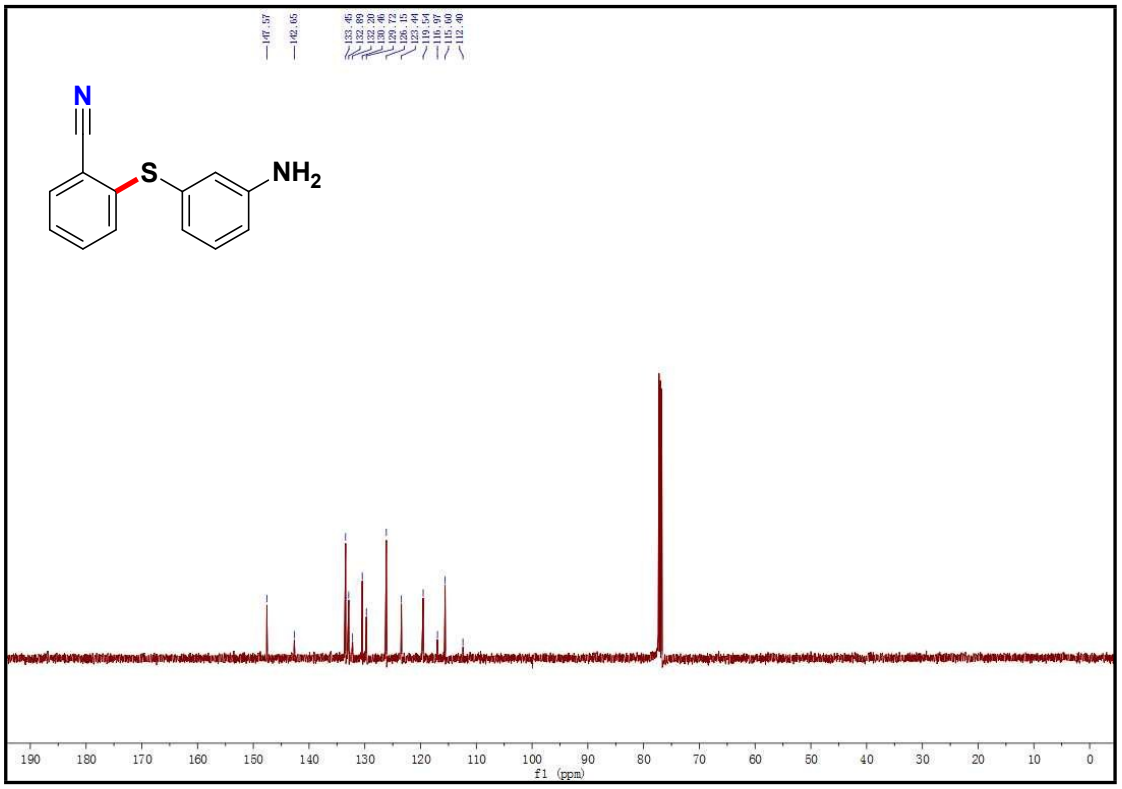
**2-((3-methoxyphenyl)thio)benzonitrile (3aj)**



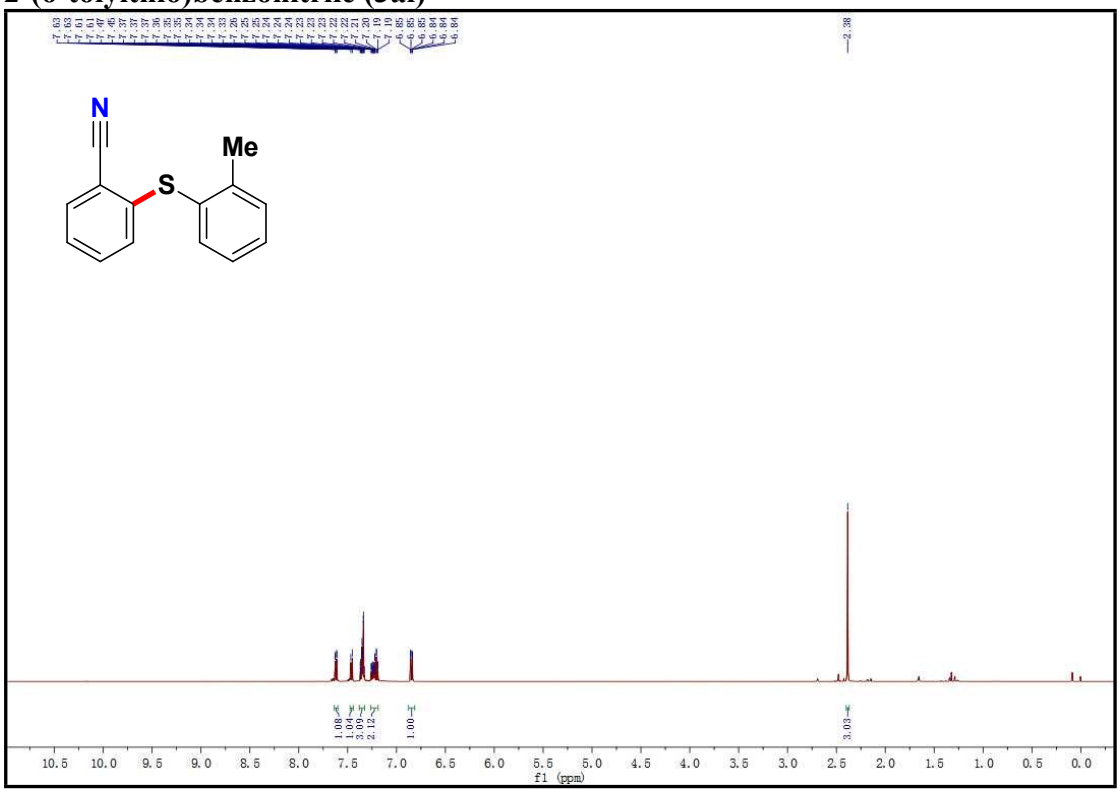



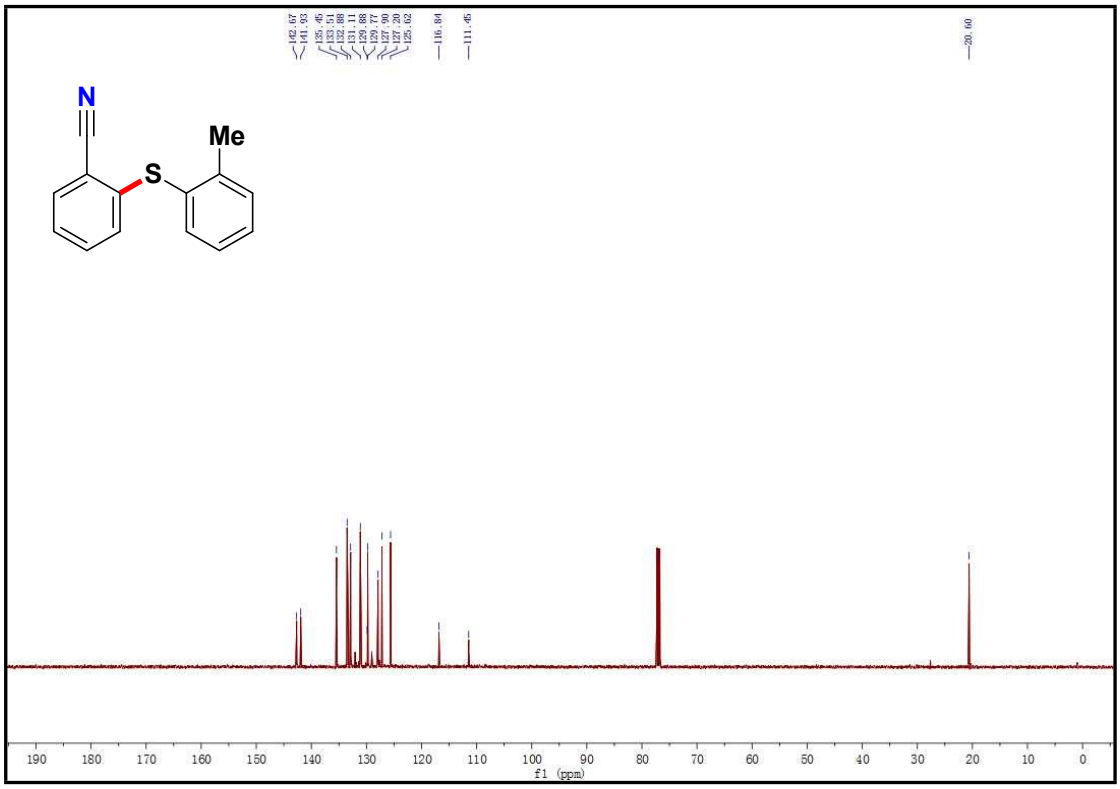
**2-((3-aminophenyl)thio)benzonitrile (3ak)**



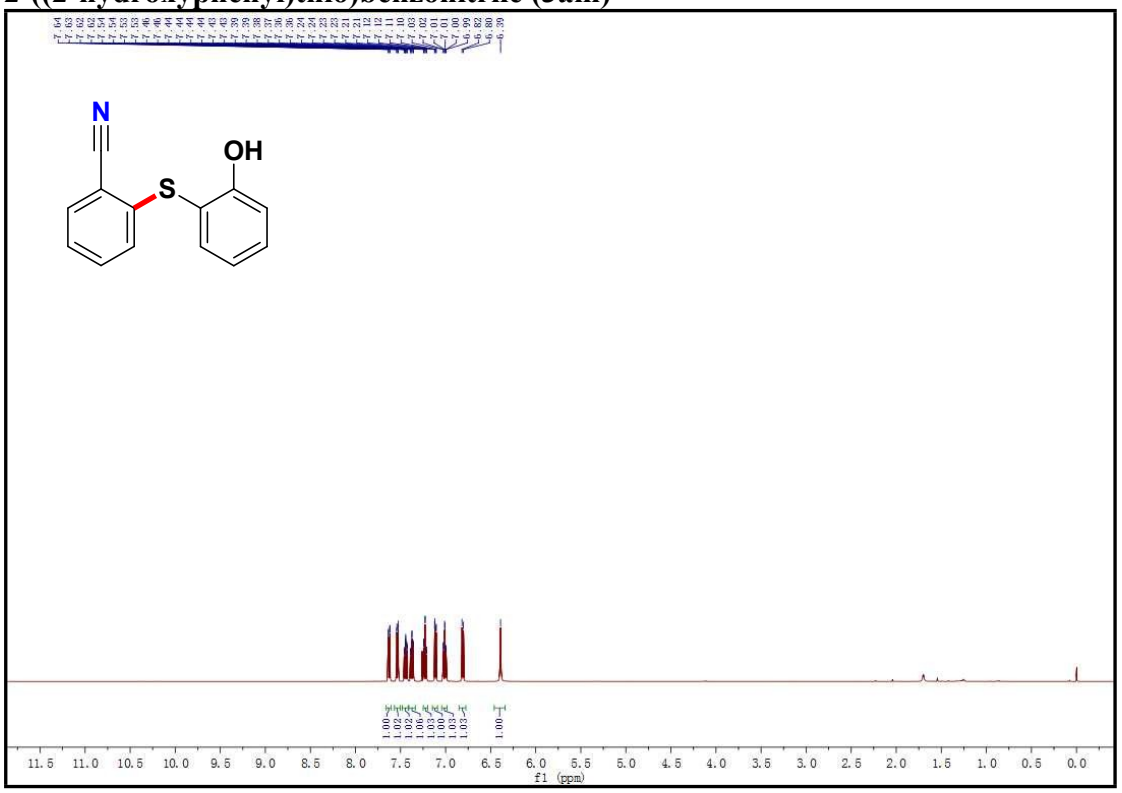



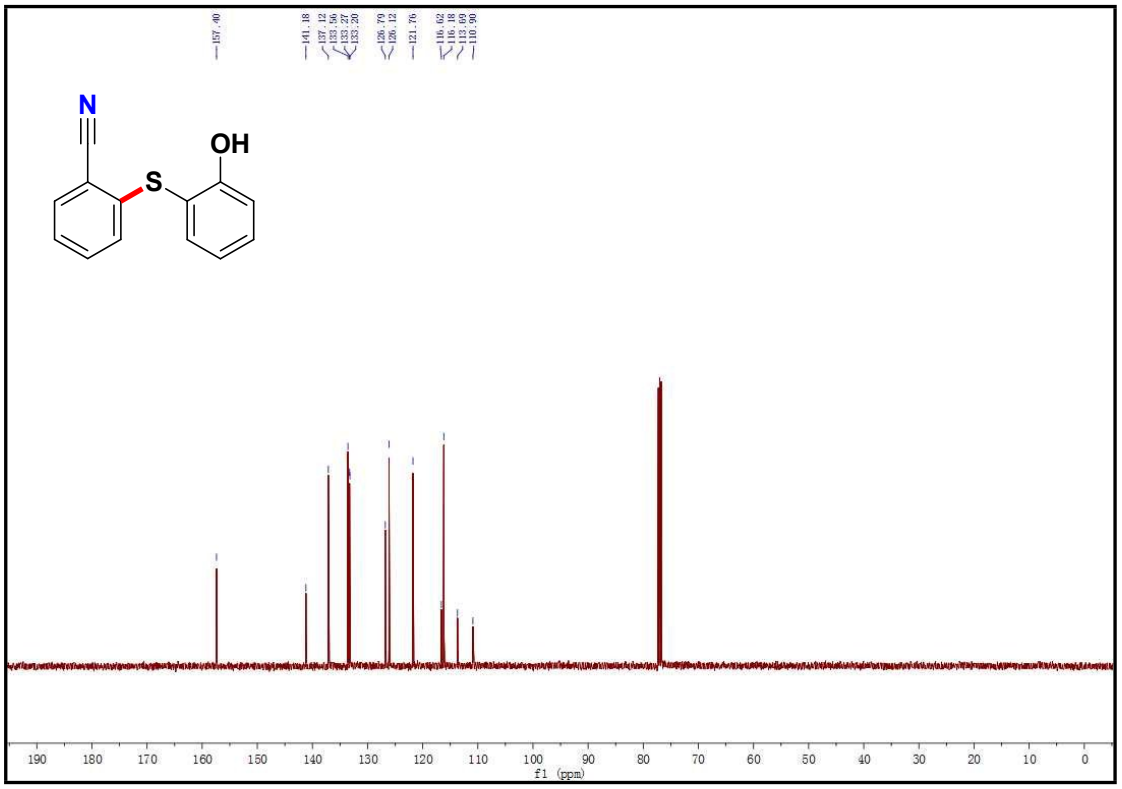
**2-(o-tolylthio)benzonitrile (3al)**



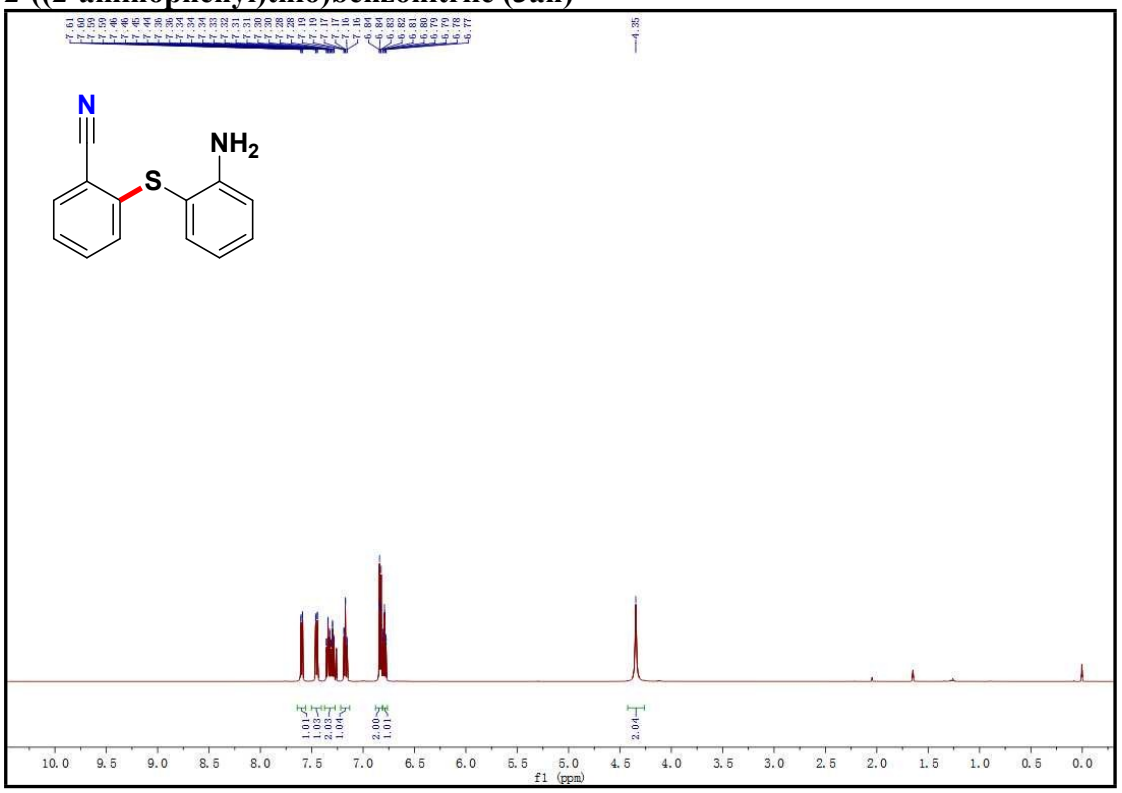



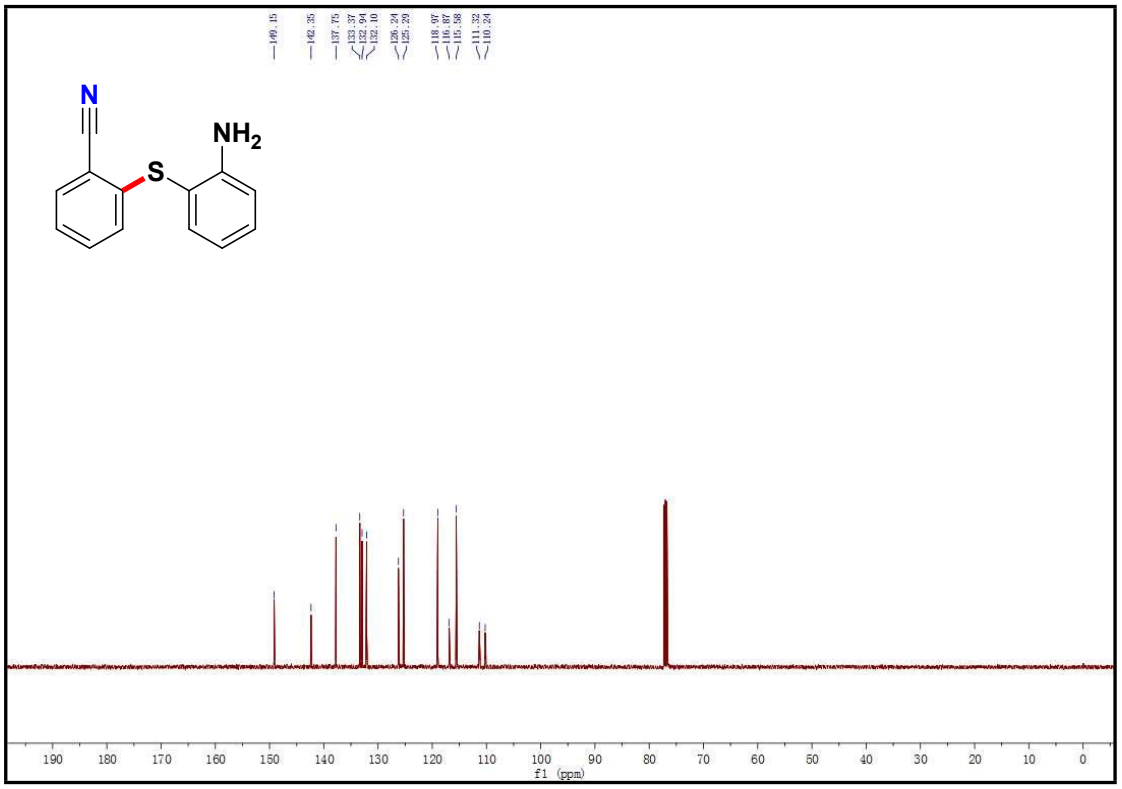
**2-((2-hydroxyphenyl)thio)benzonitrile (3am)**



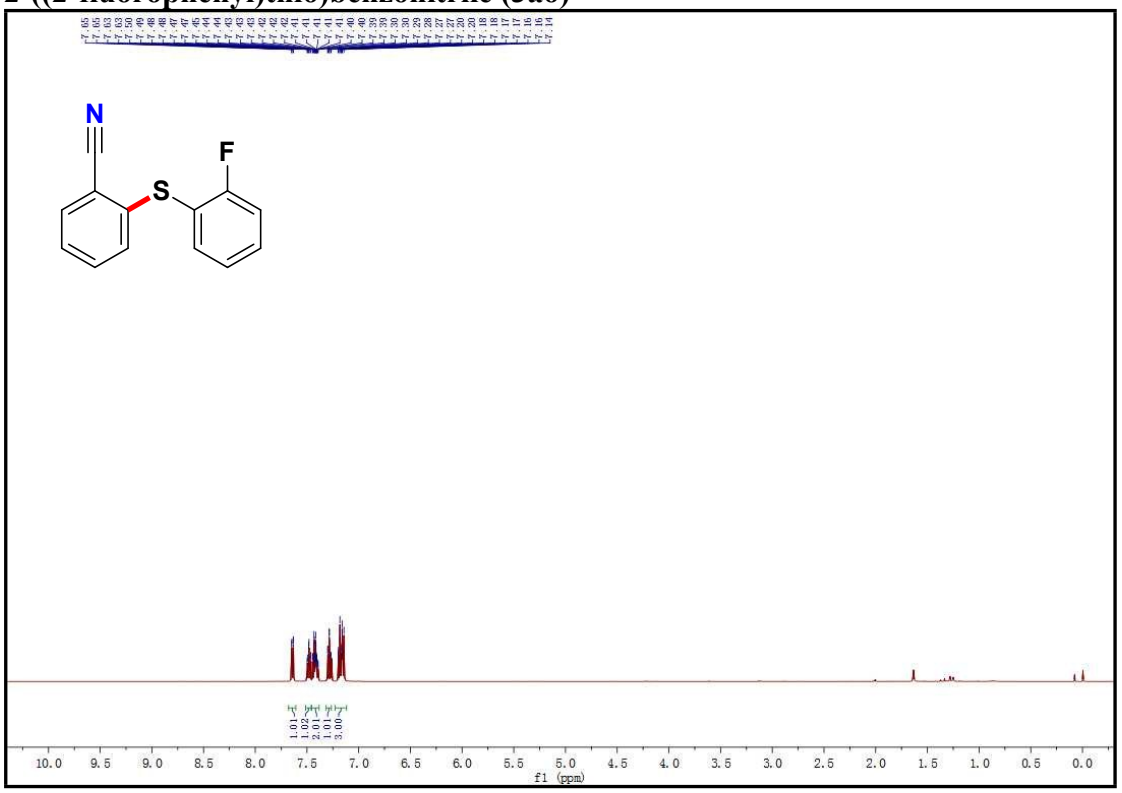



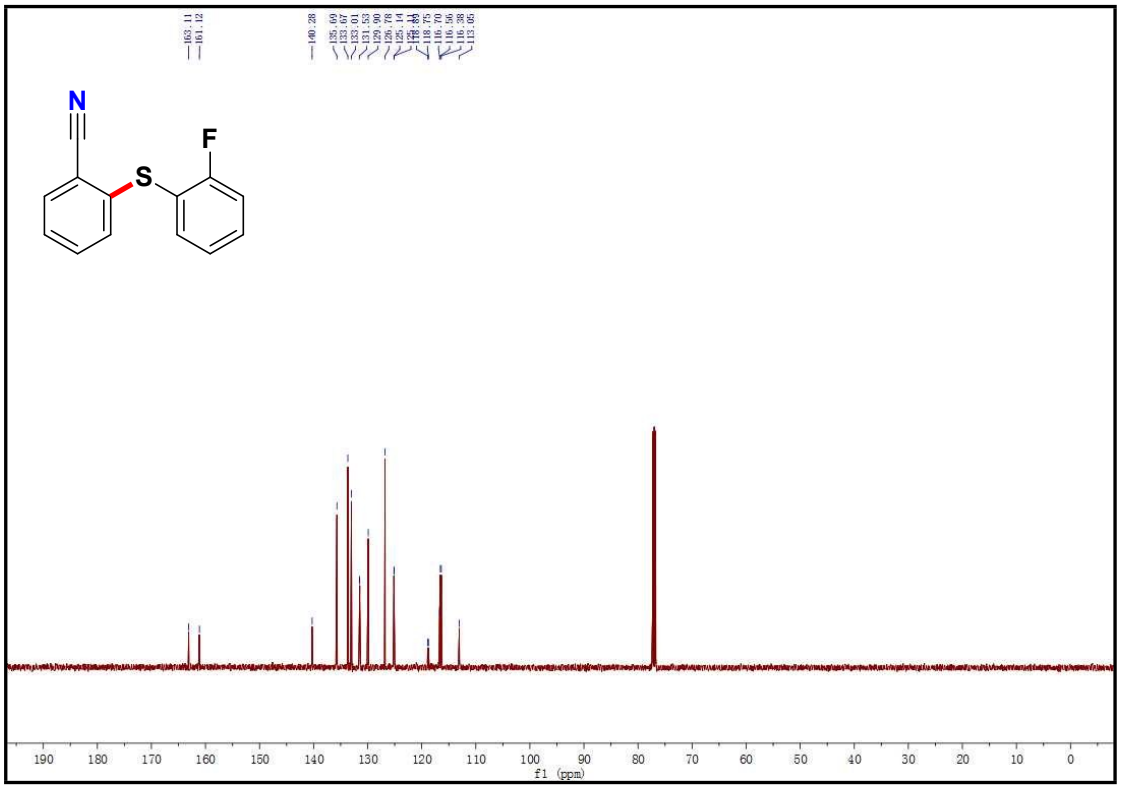
**2-((2-aminophenyl)thio)benzonitrile (3an)**



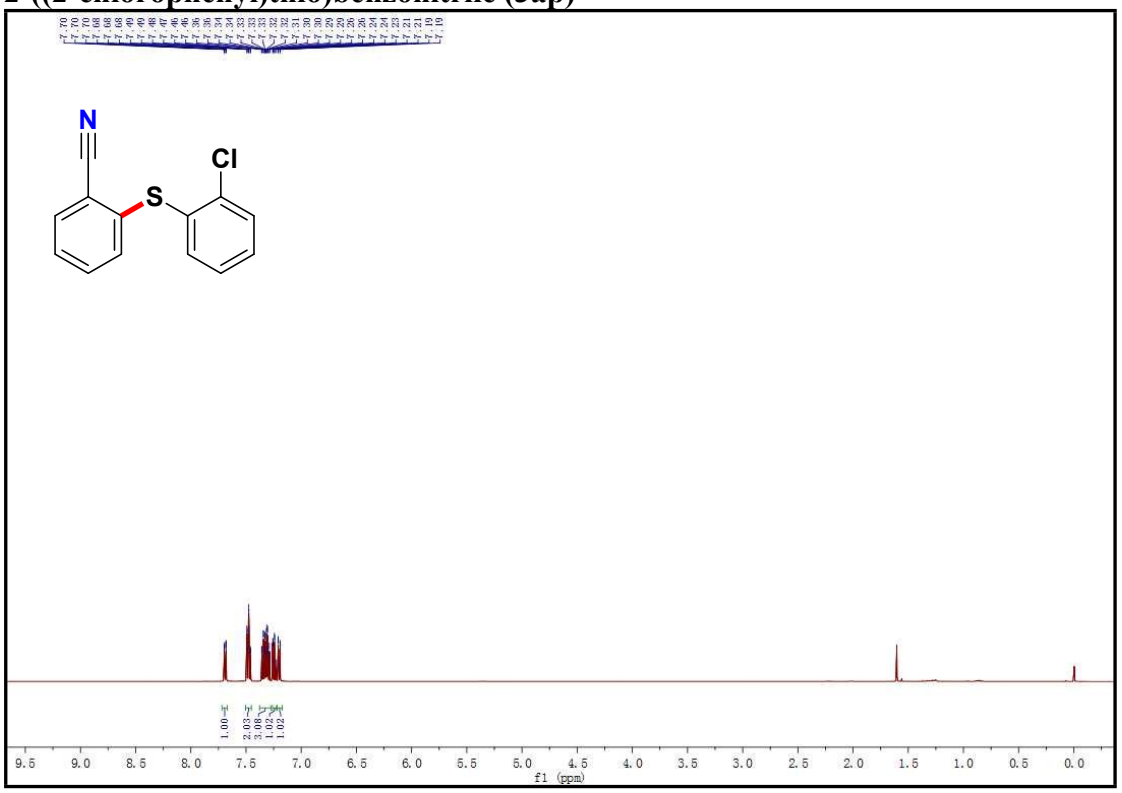



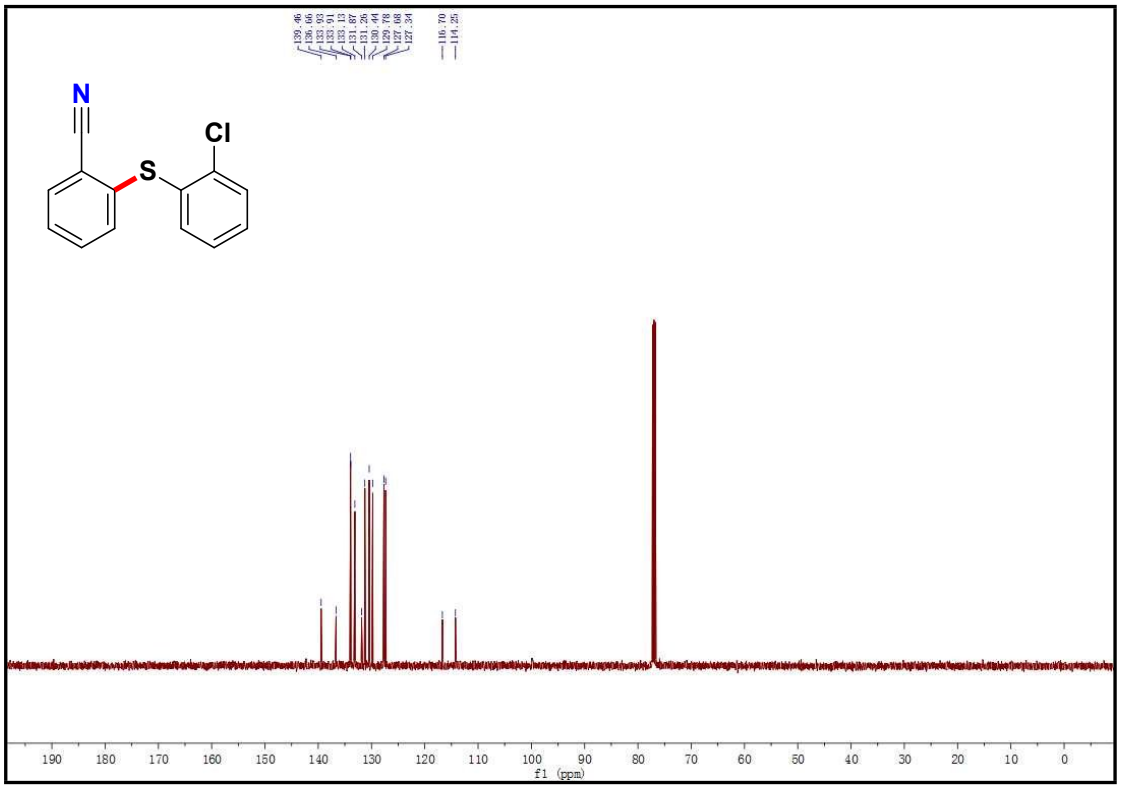
**2-((2-fluorophenyl)thio)benzonitrile (3ao)**



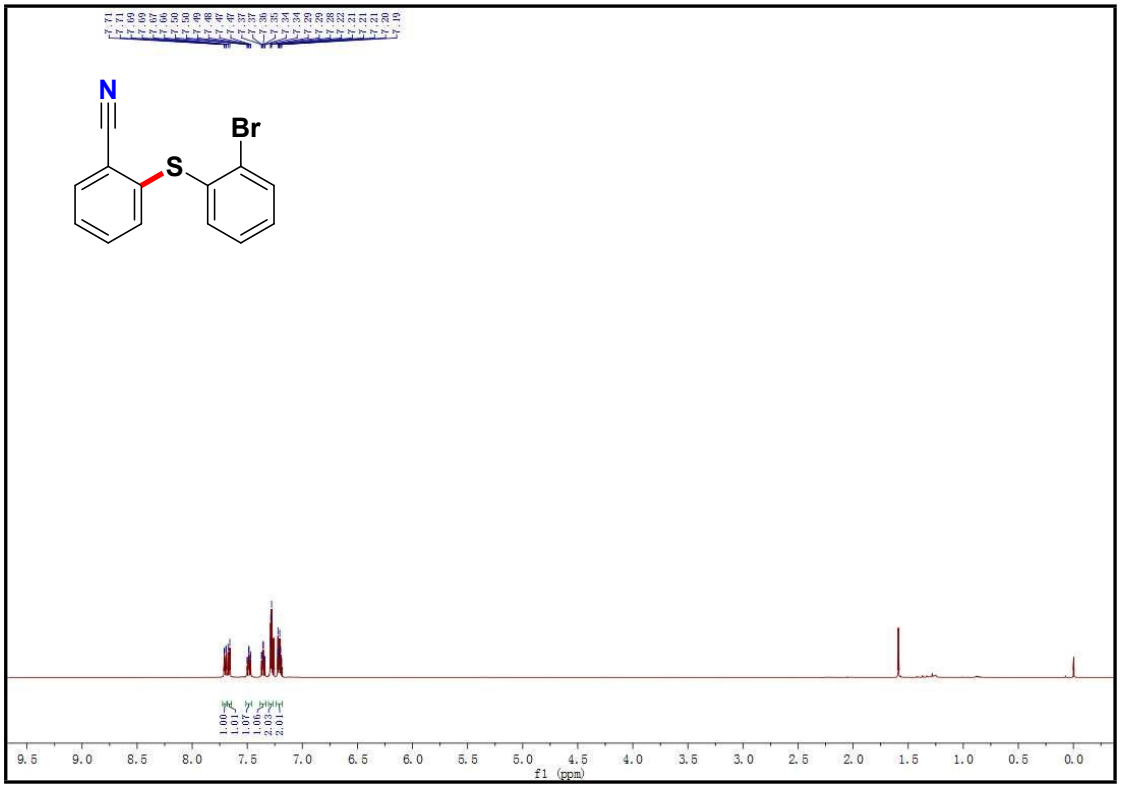



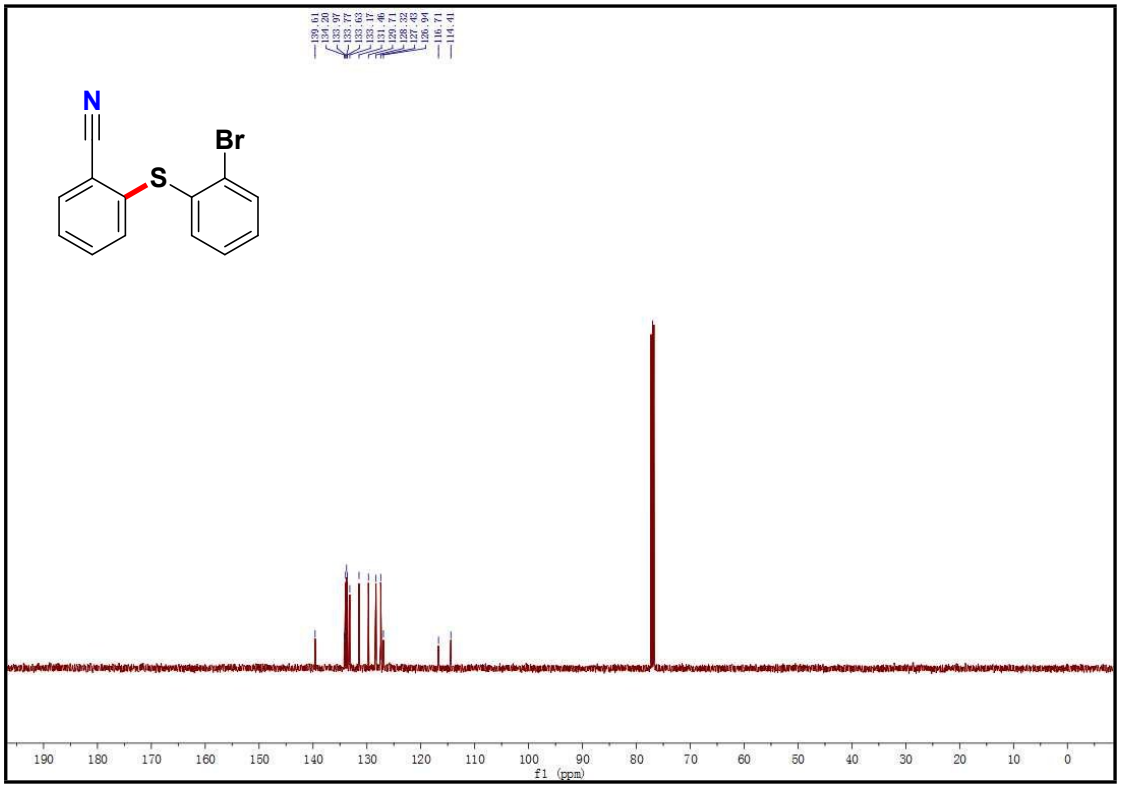
**2-((2-chlorophenyl)thio)benzonitrile (3ap)**



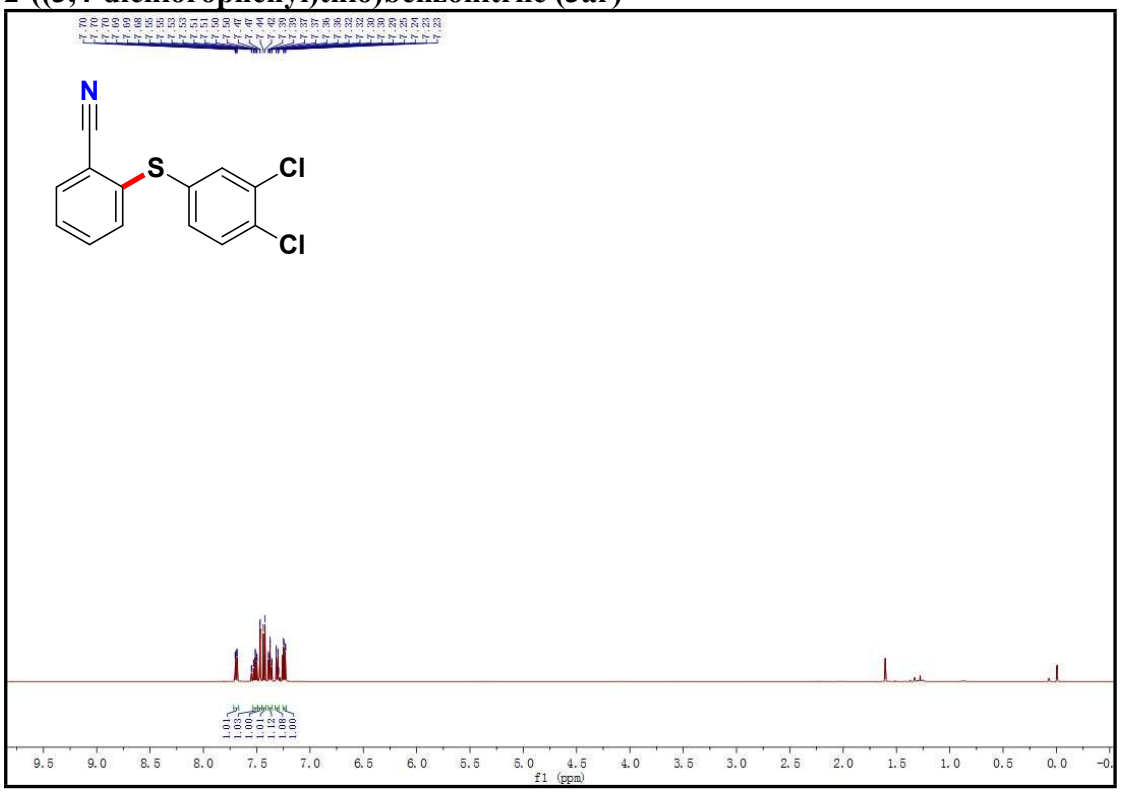



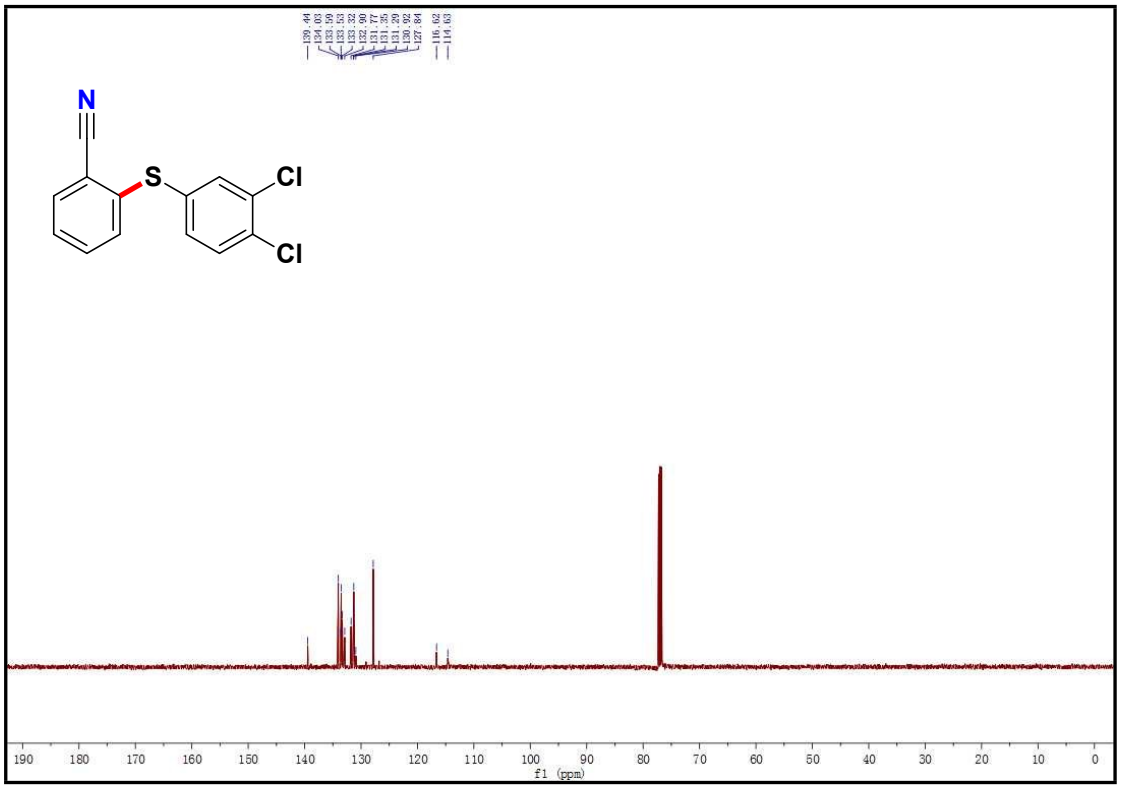
**2-((2-bromophenyl)thio)benzonitrile (3aq)**



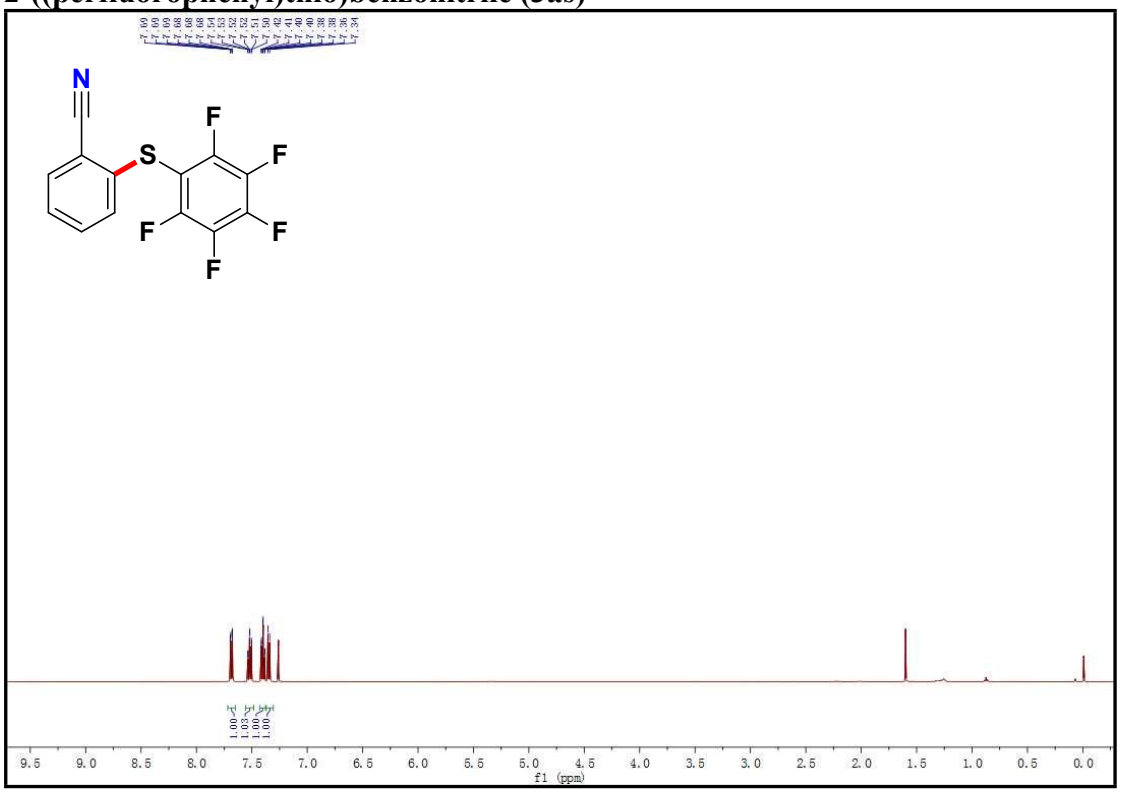



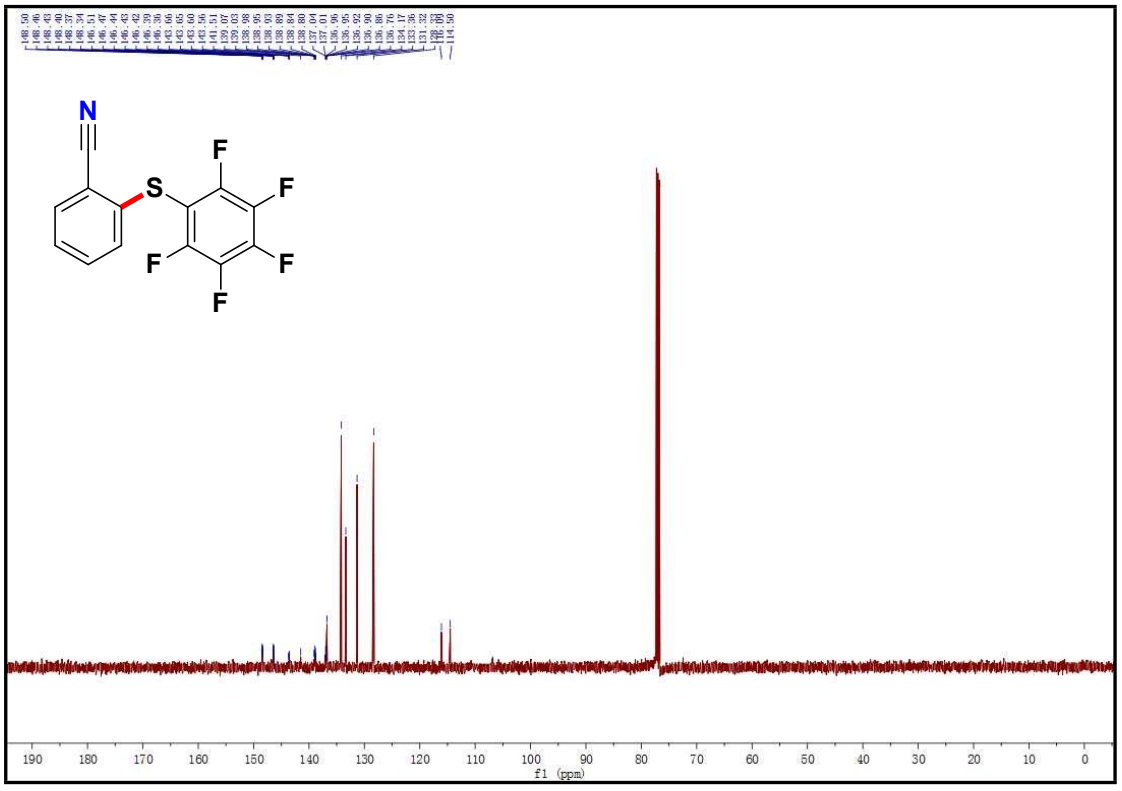
**2-((3,4-dichlorophenyl)thio)benzonitrile (3ar)**



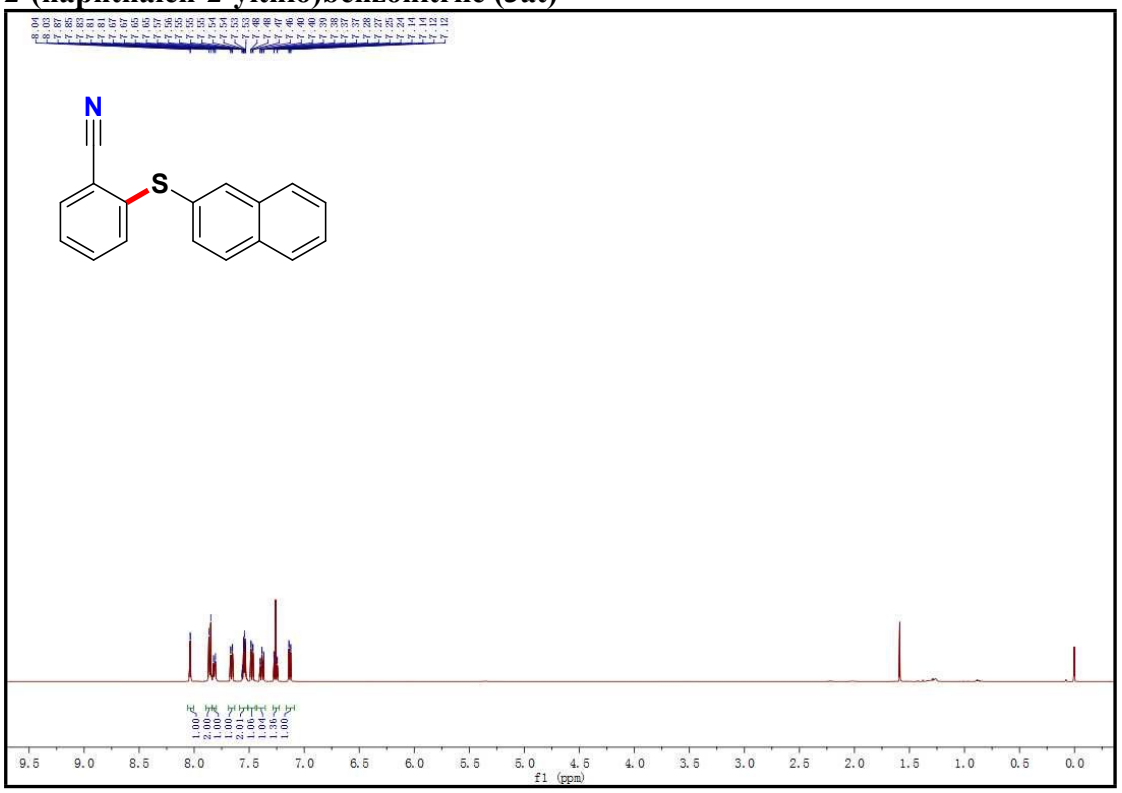



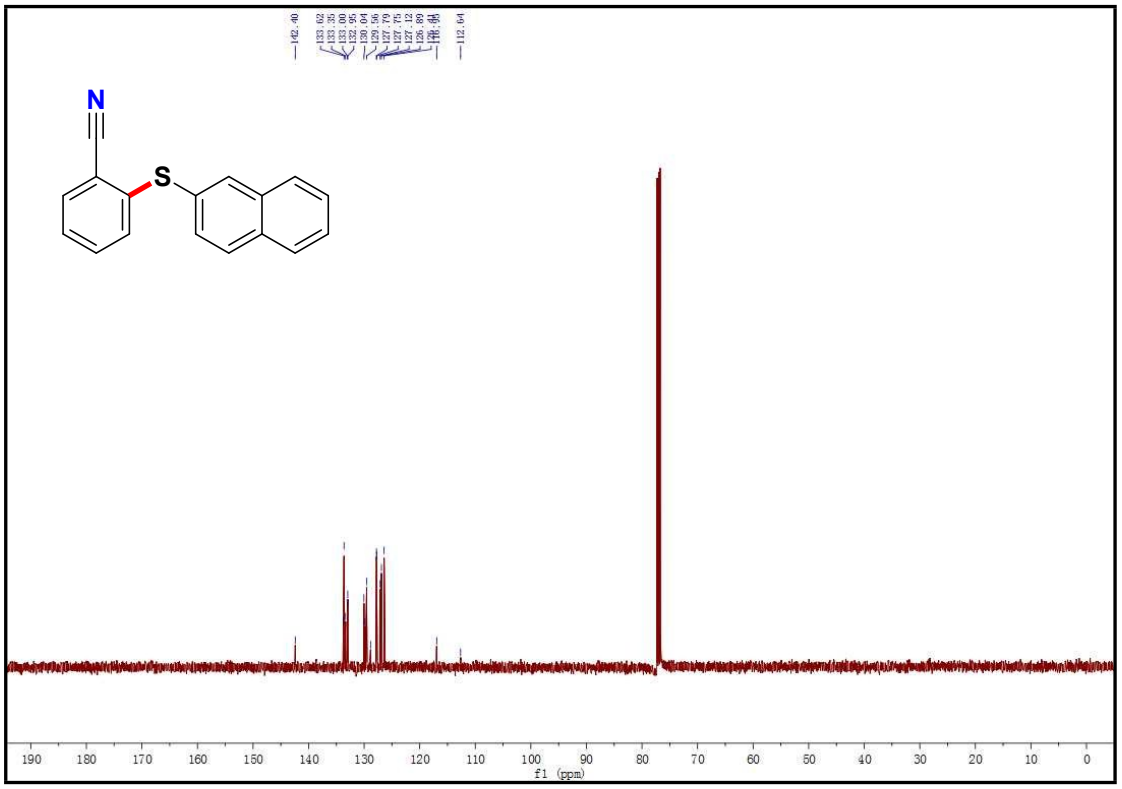
**2-((perfluorophenyl)thio)benzonitrile (3as)**



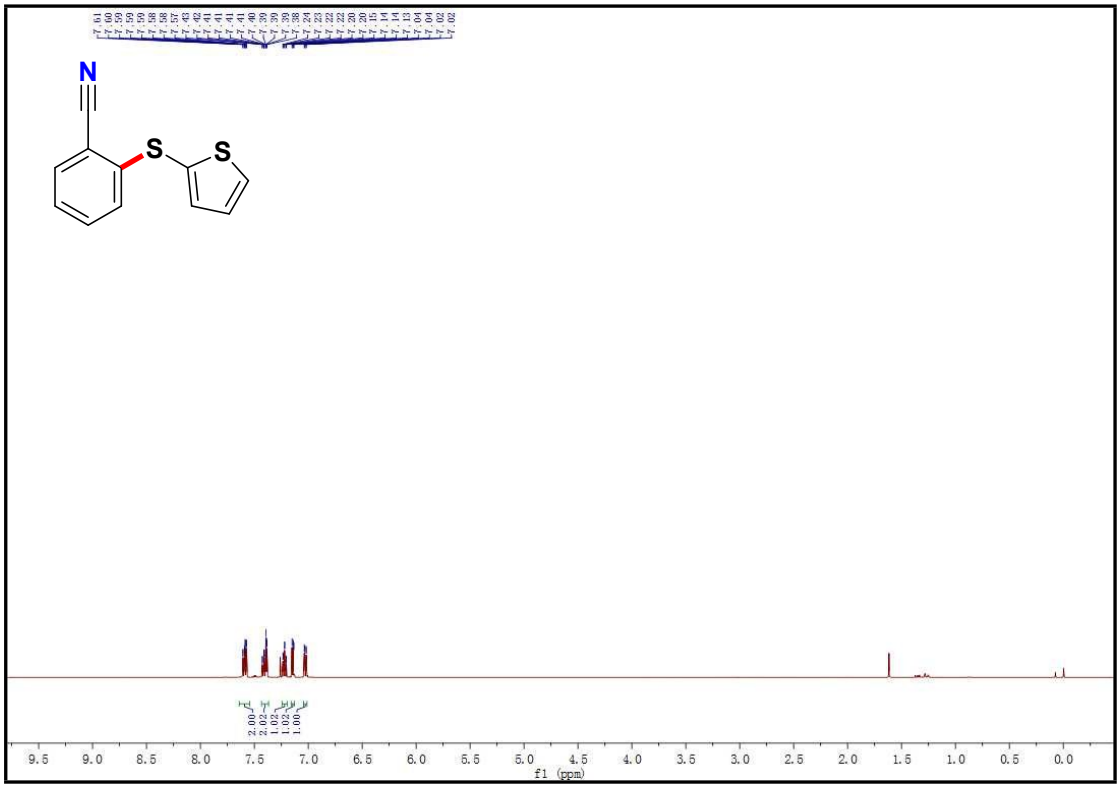



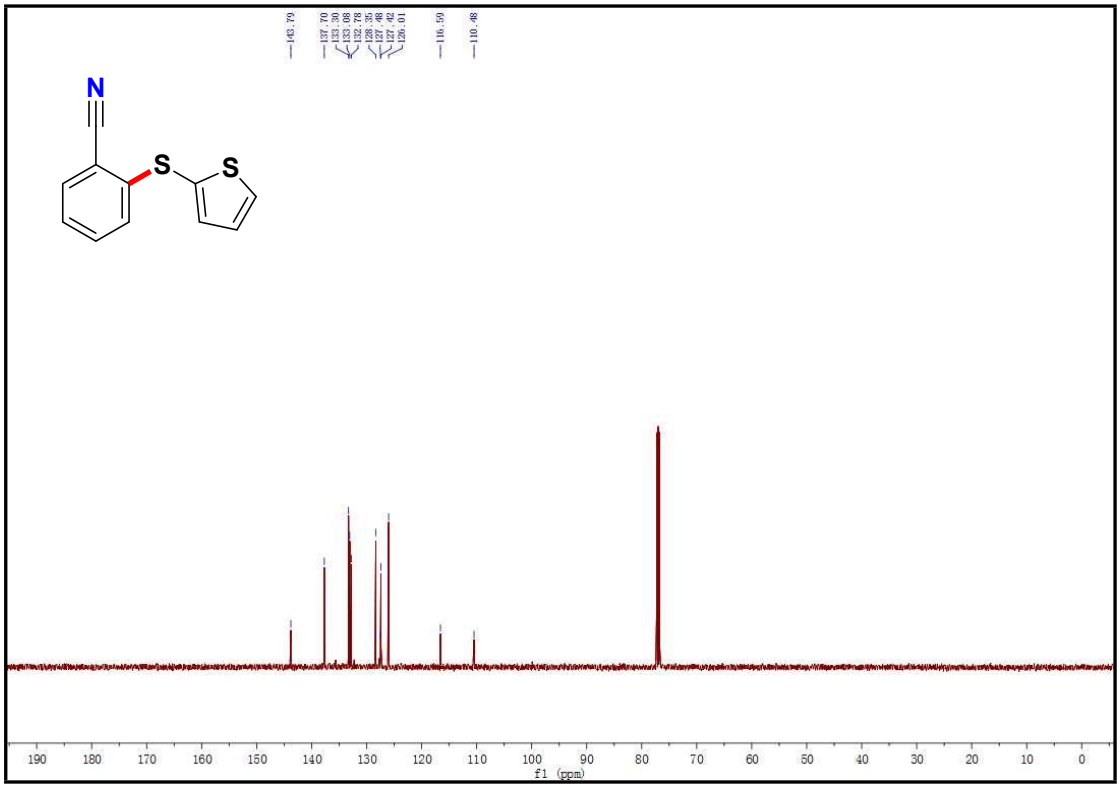
**2-(naphthalen-2-ylthio)benzonitrile (3at)**



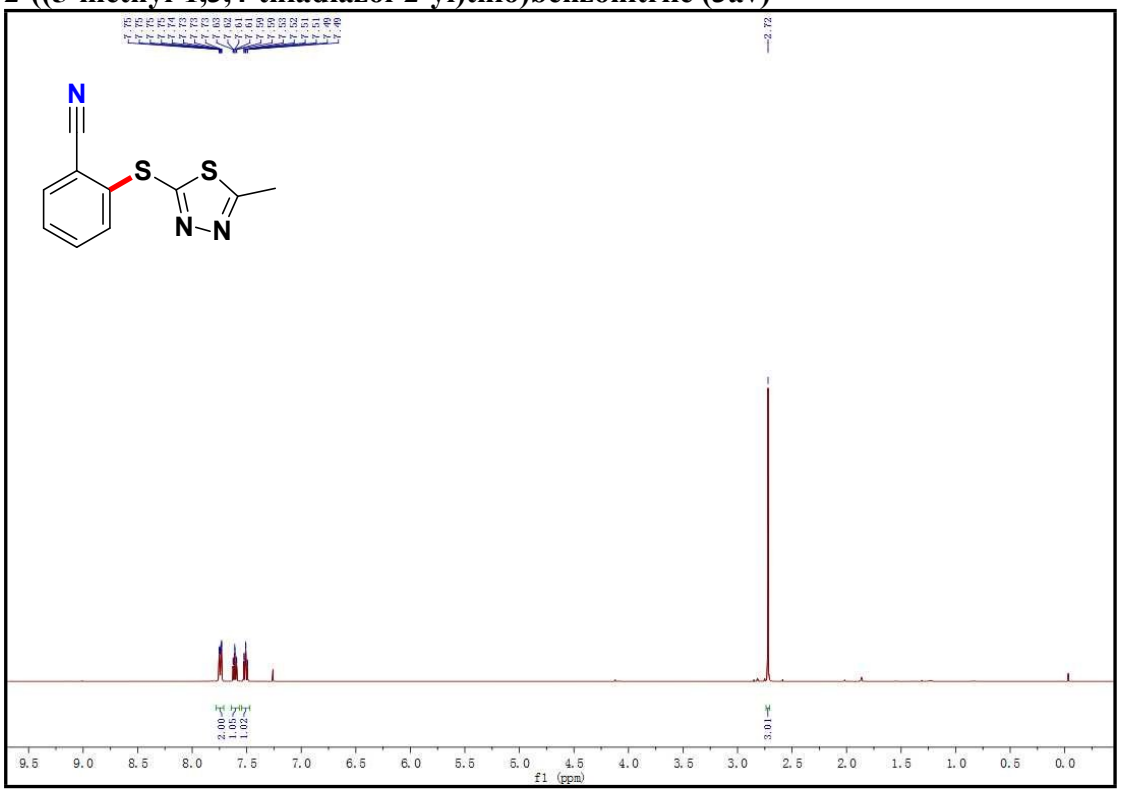



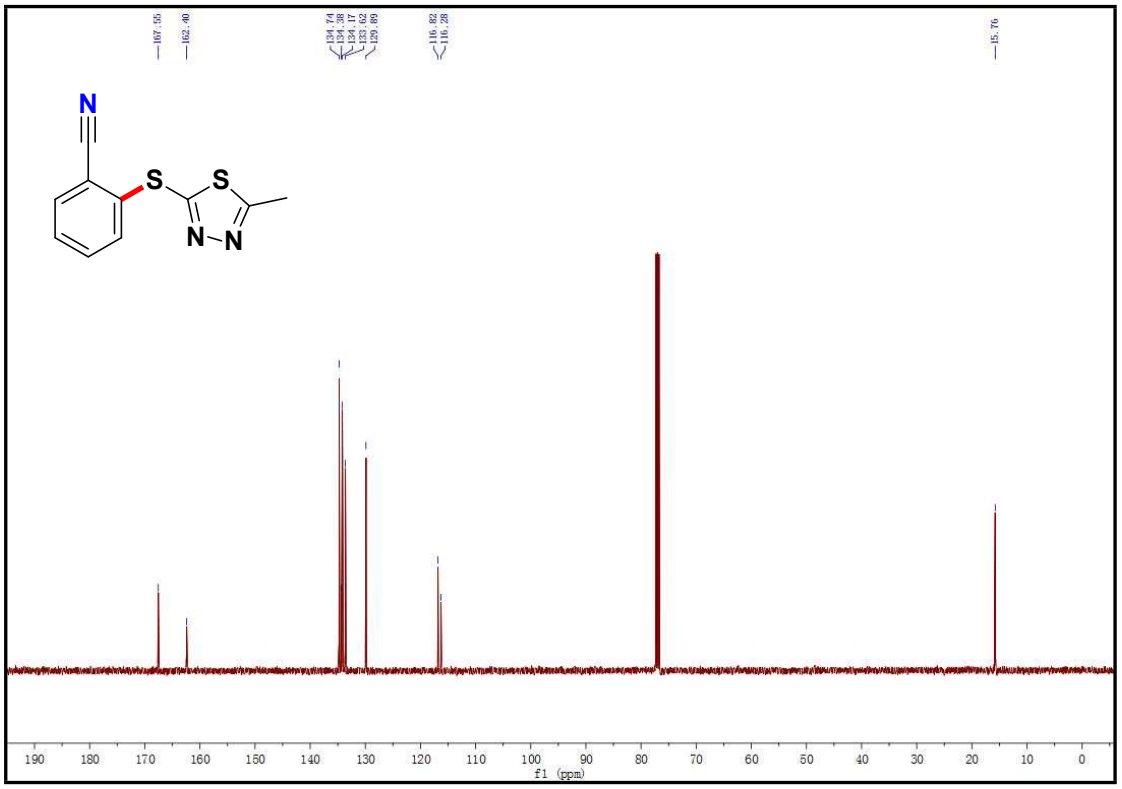
## 2-(thiophen-2-ylthio)benzonitrile (3au)



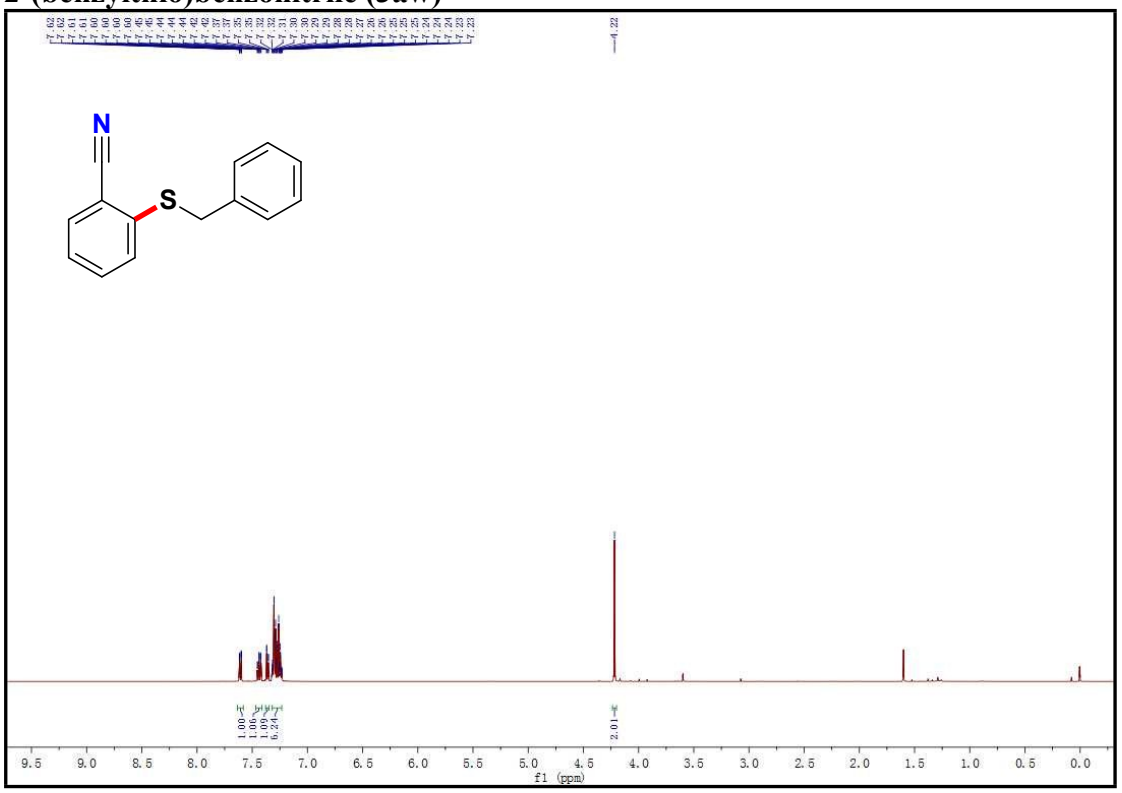



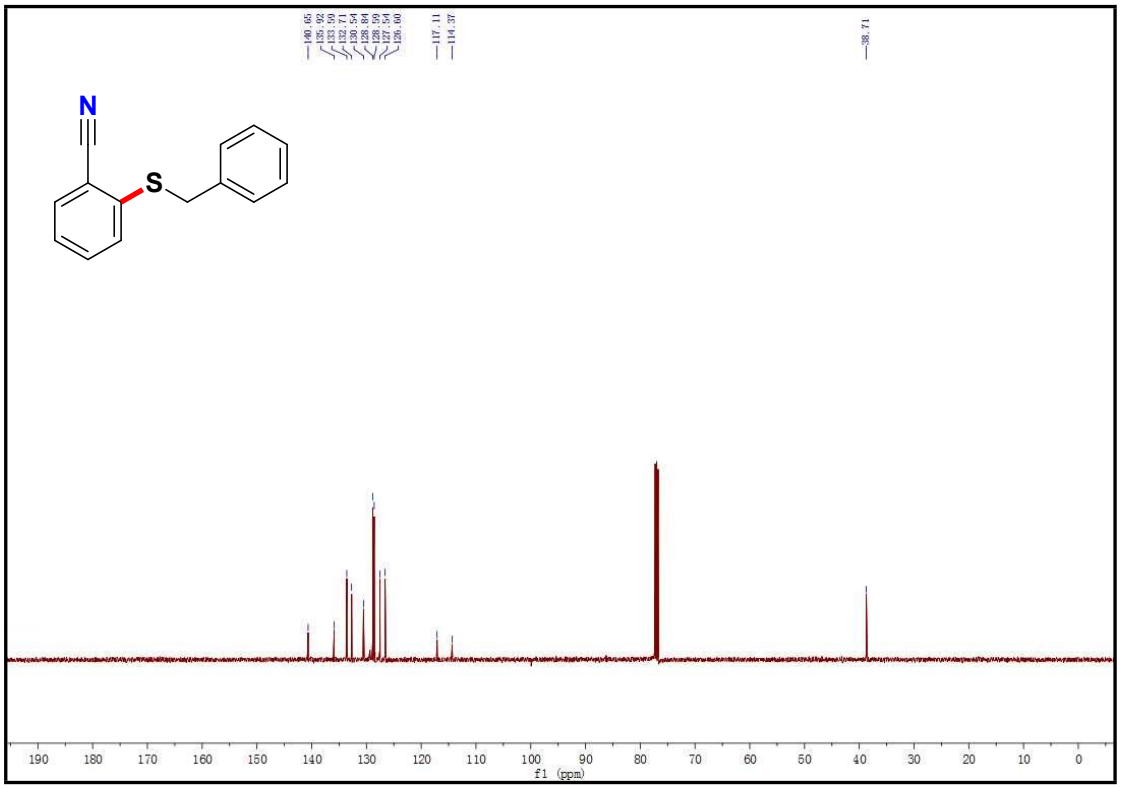
**2-((5-methyl-1,3,4-thiadiazol-2-yl)thio)benzonitrile (3av)**



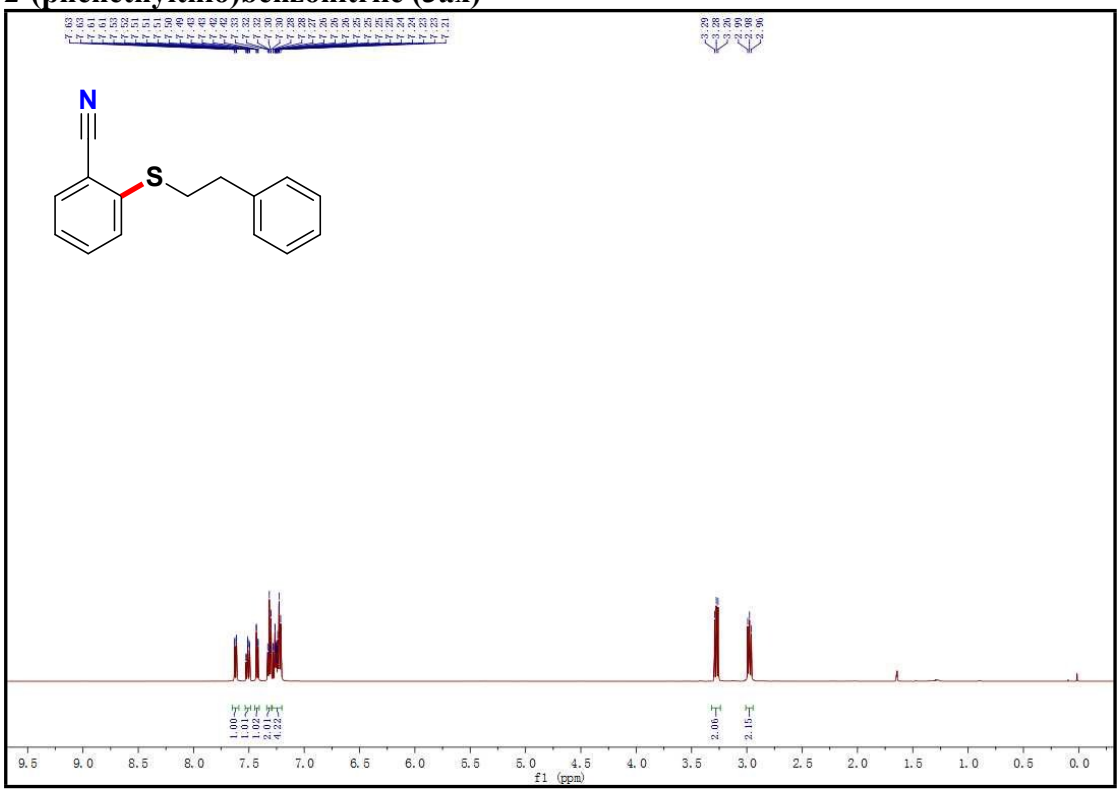



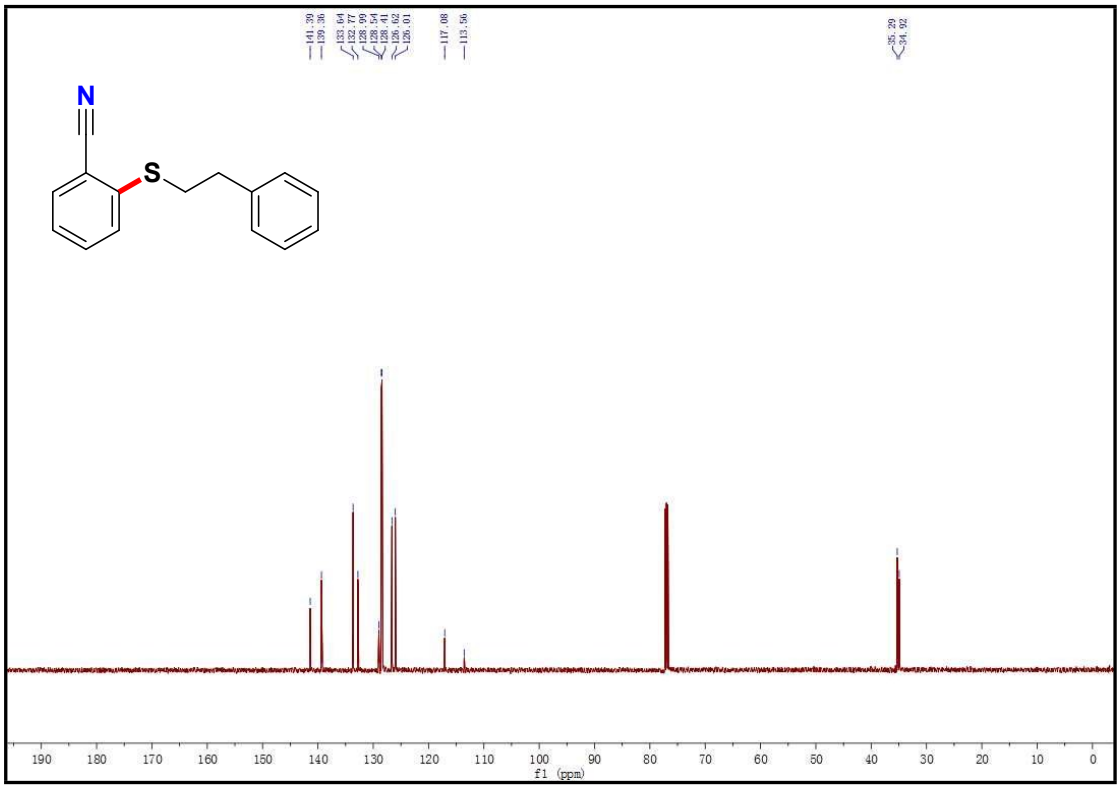
**2-(benzylthio)benzonitrile (3aw)**



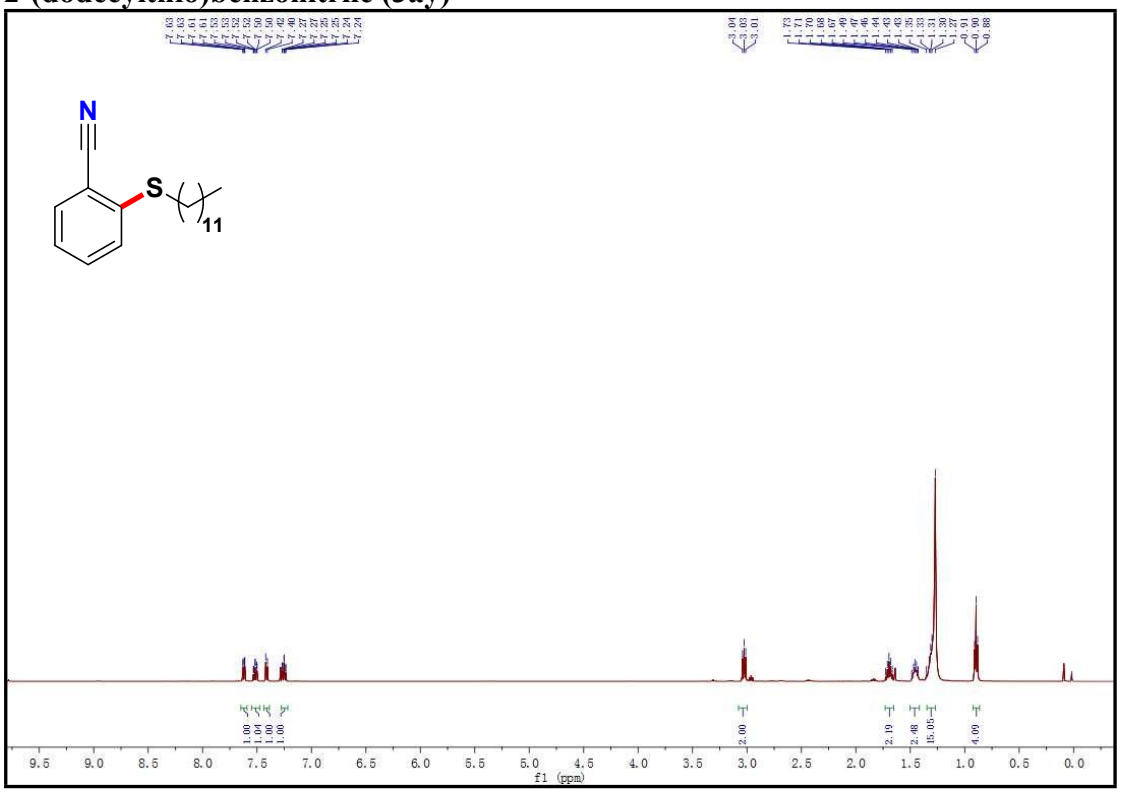



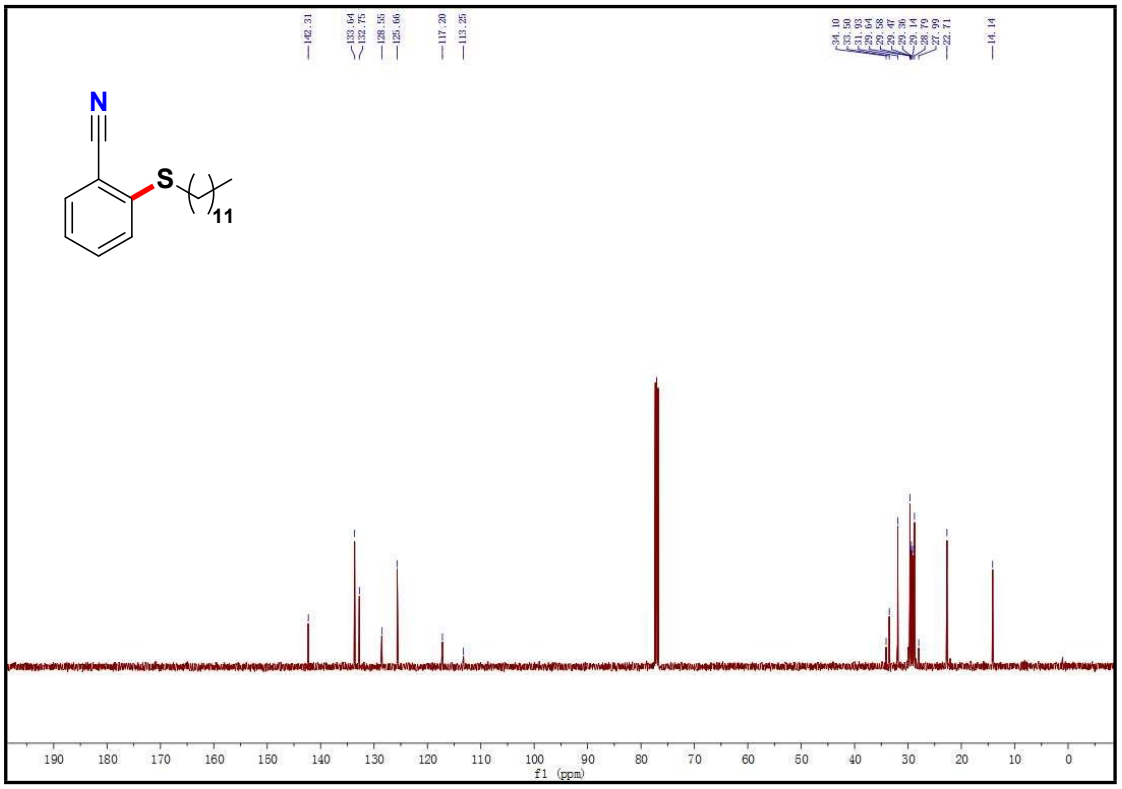
**2-(phenethylthio)benzonitrile (3ax)**



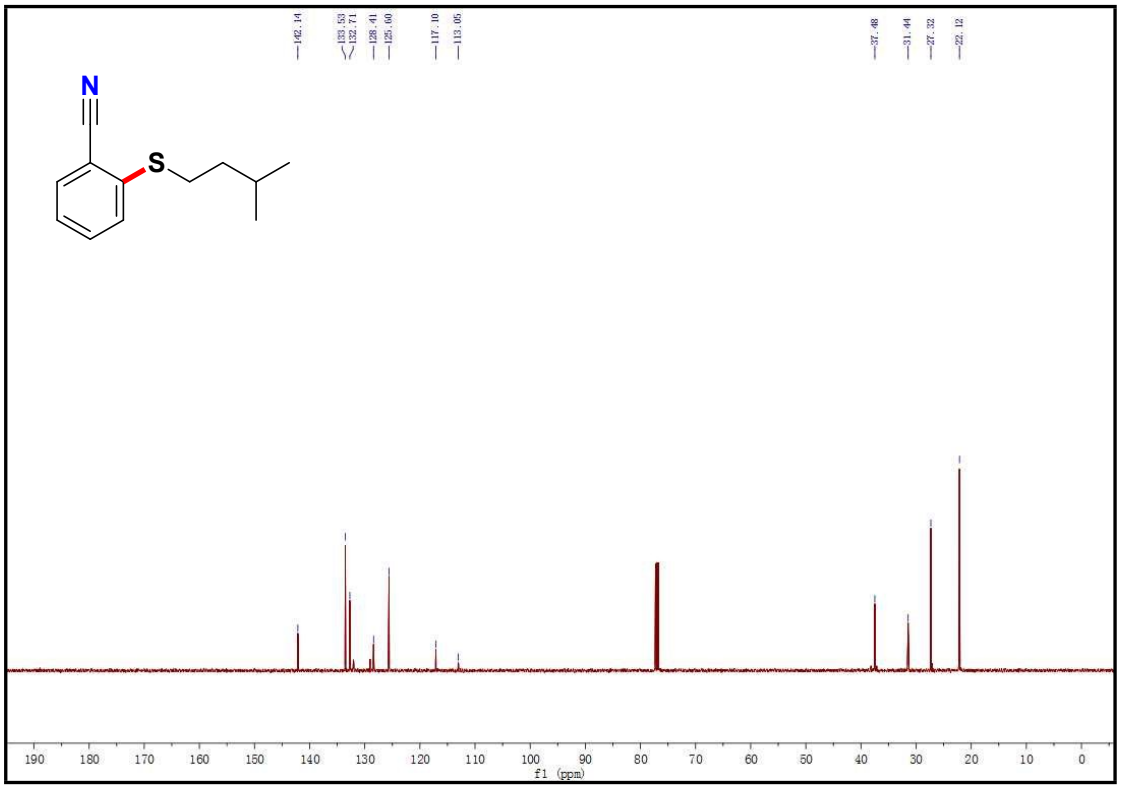



**2-(dodecylthio)benzonitrile (3ay)**

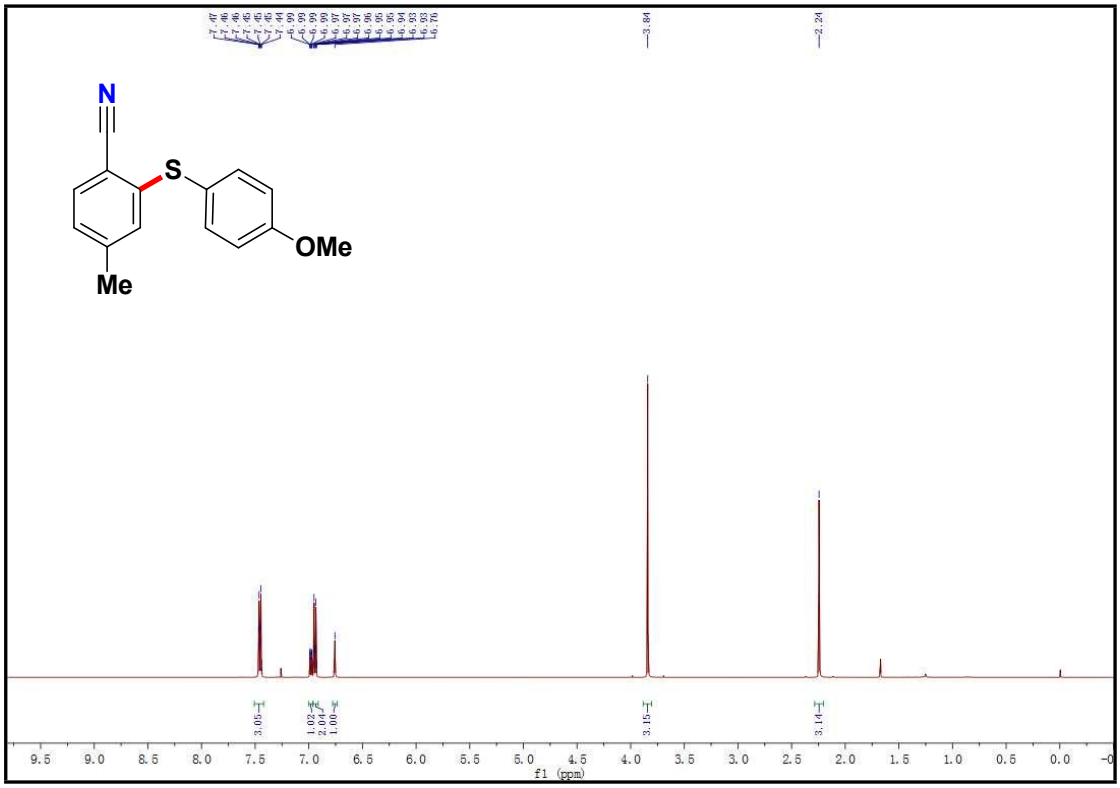


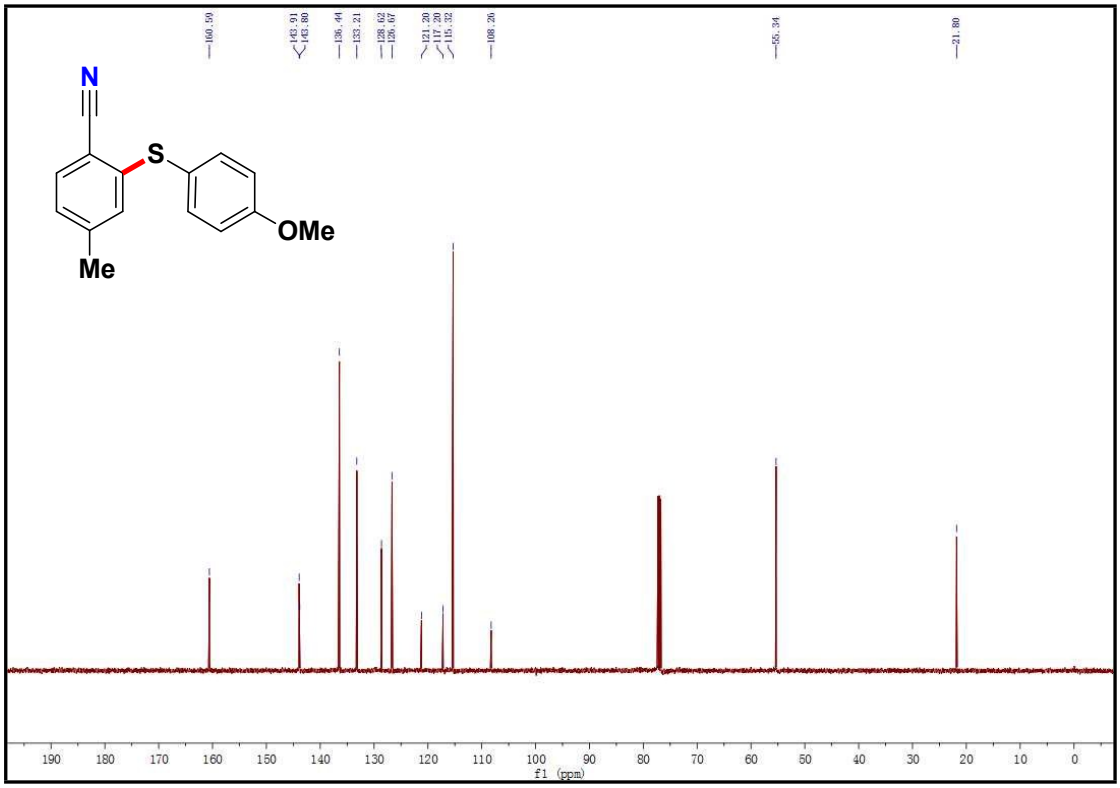



**2-((2-methylbutyl)thio)benzonitrile (3az)**

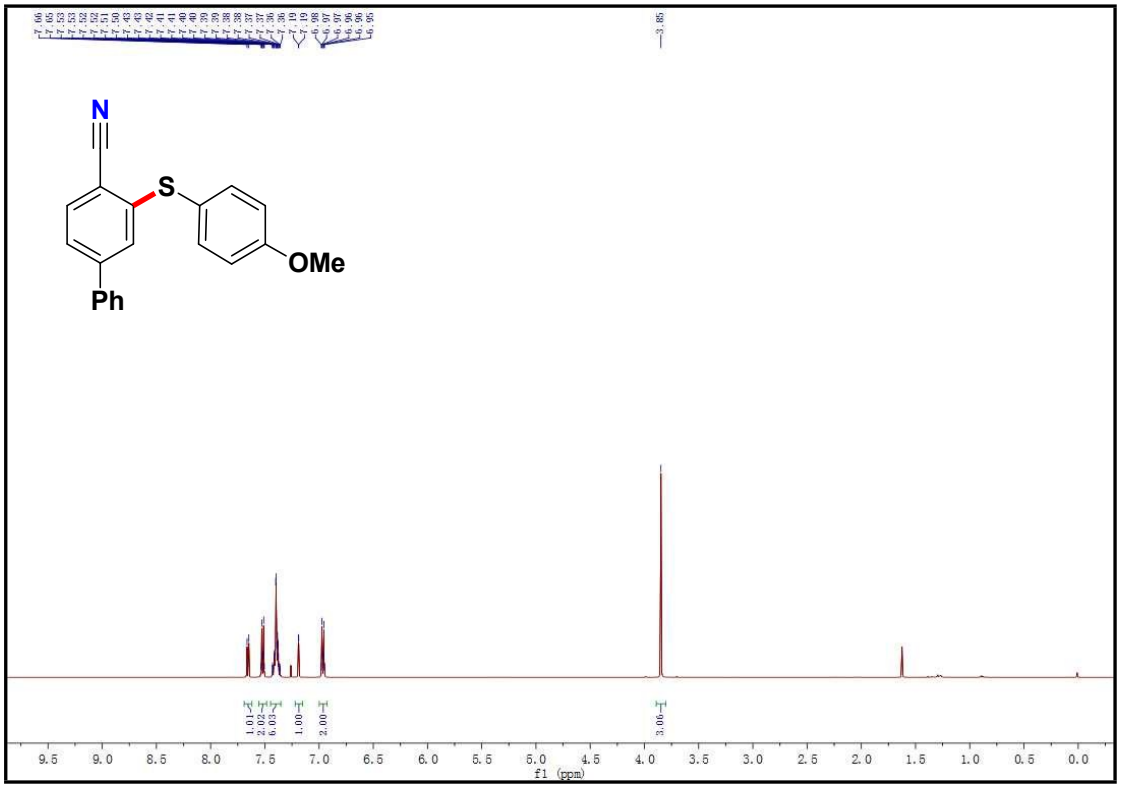



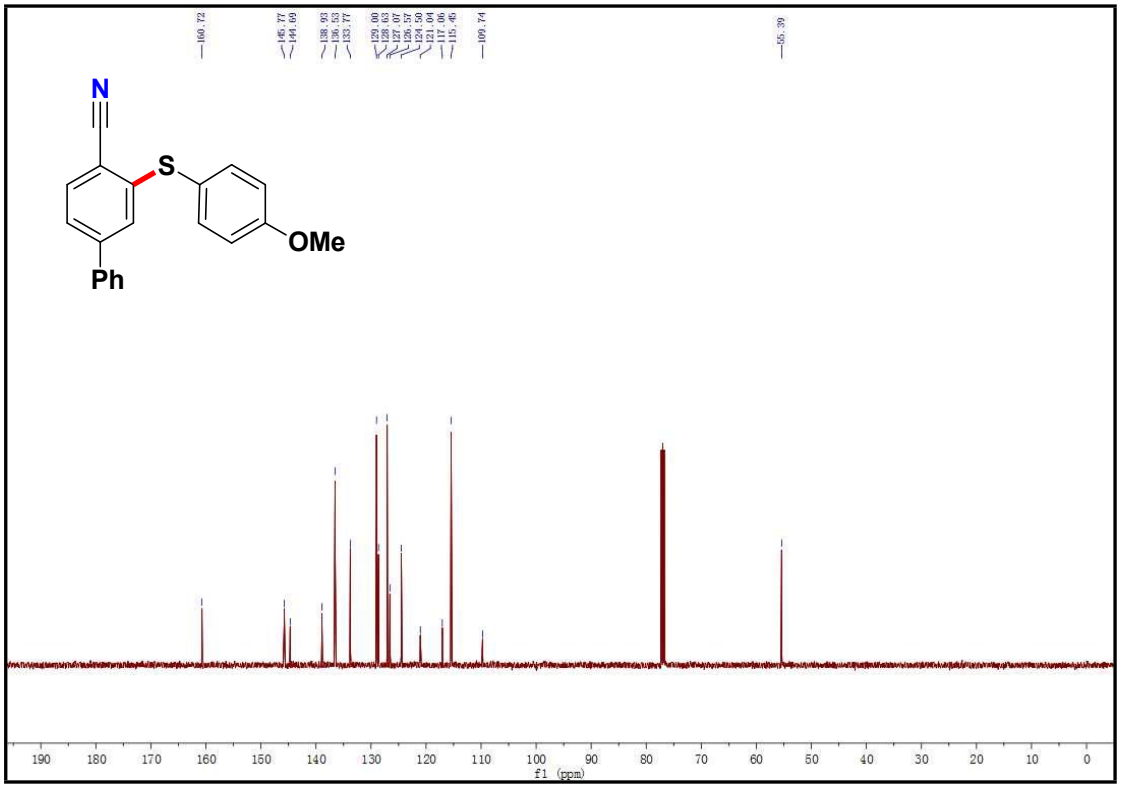
**2-((4-methoxyphenyl)thio)-4-methylbenzonitrile (3bd)**



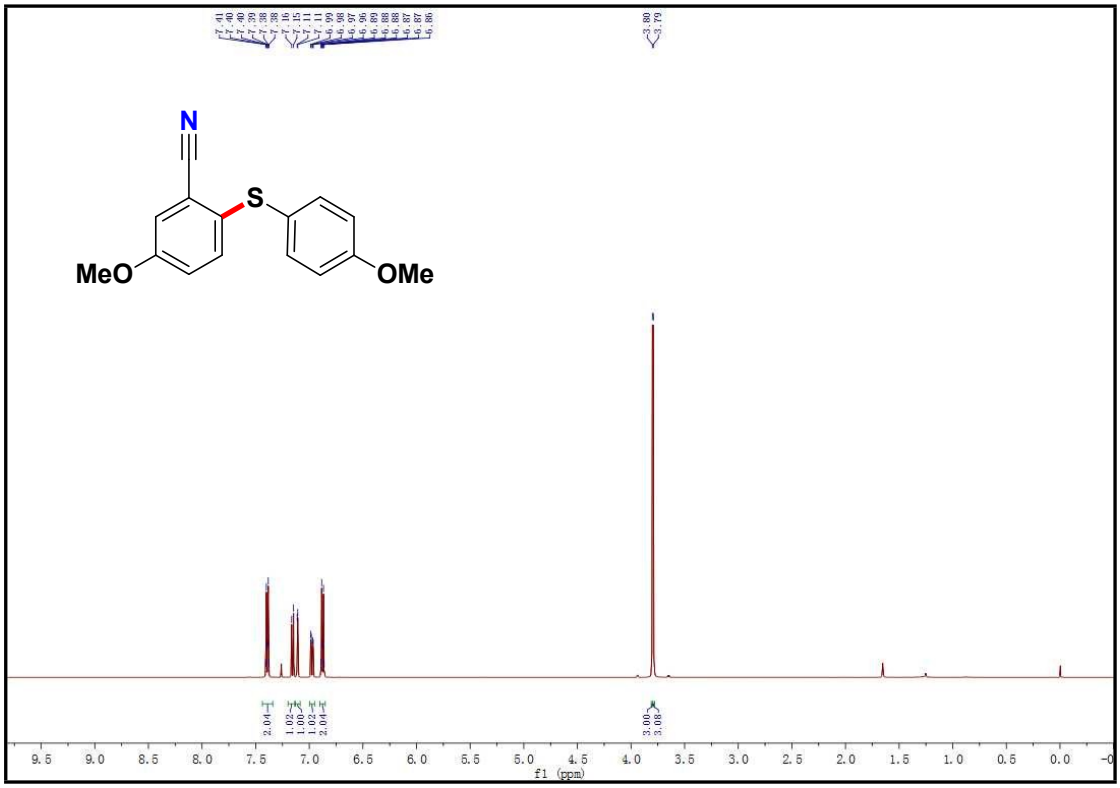



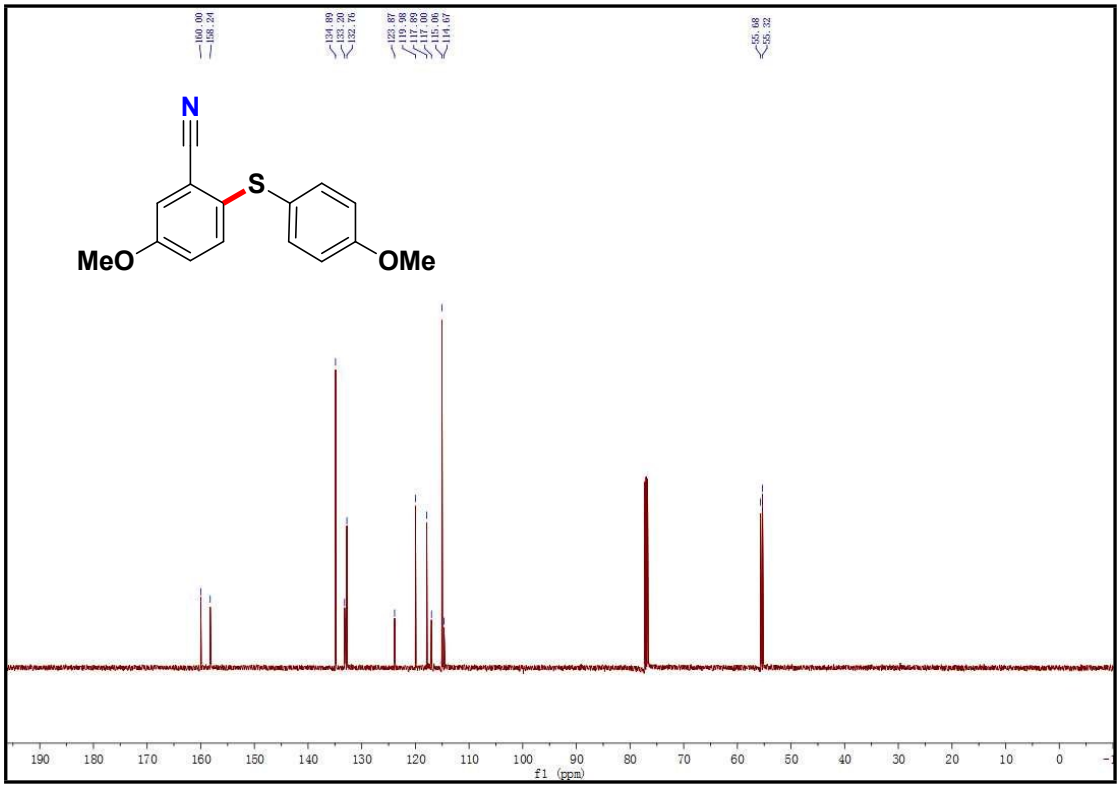
**3-((4-methoxyphenyl)thio)-[1,1'-biphenyl]-4-carbonitrile (3ed)**



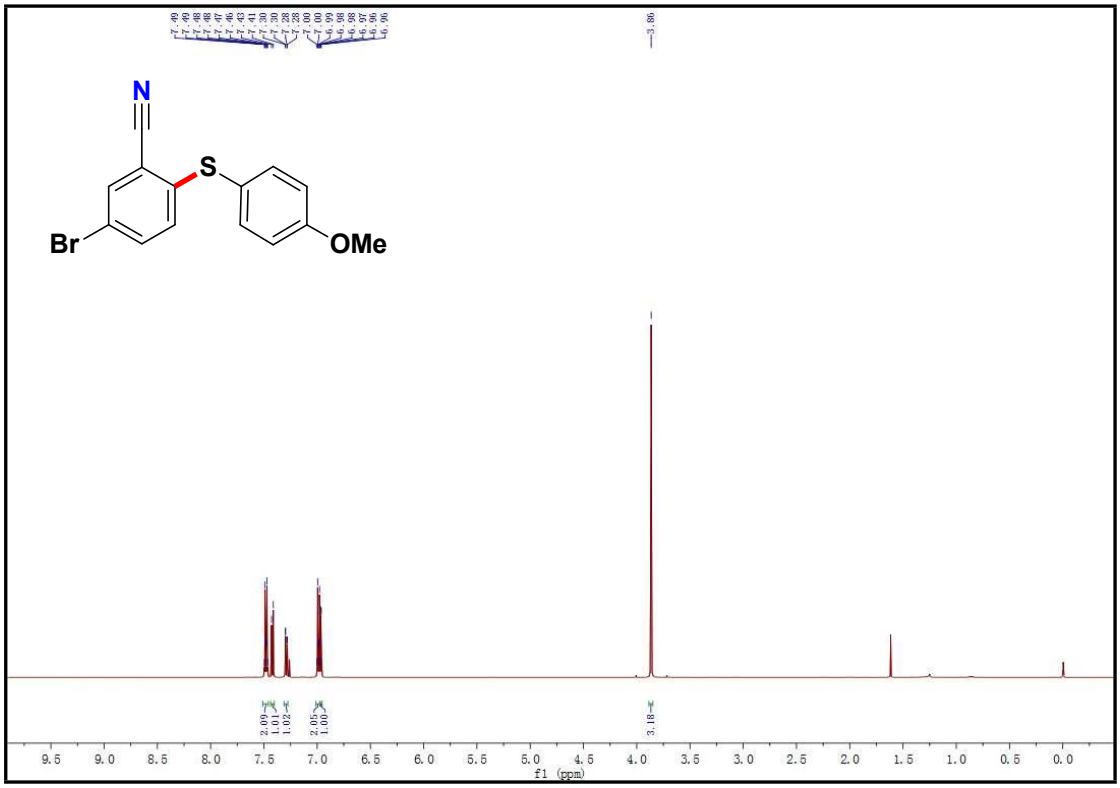



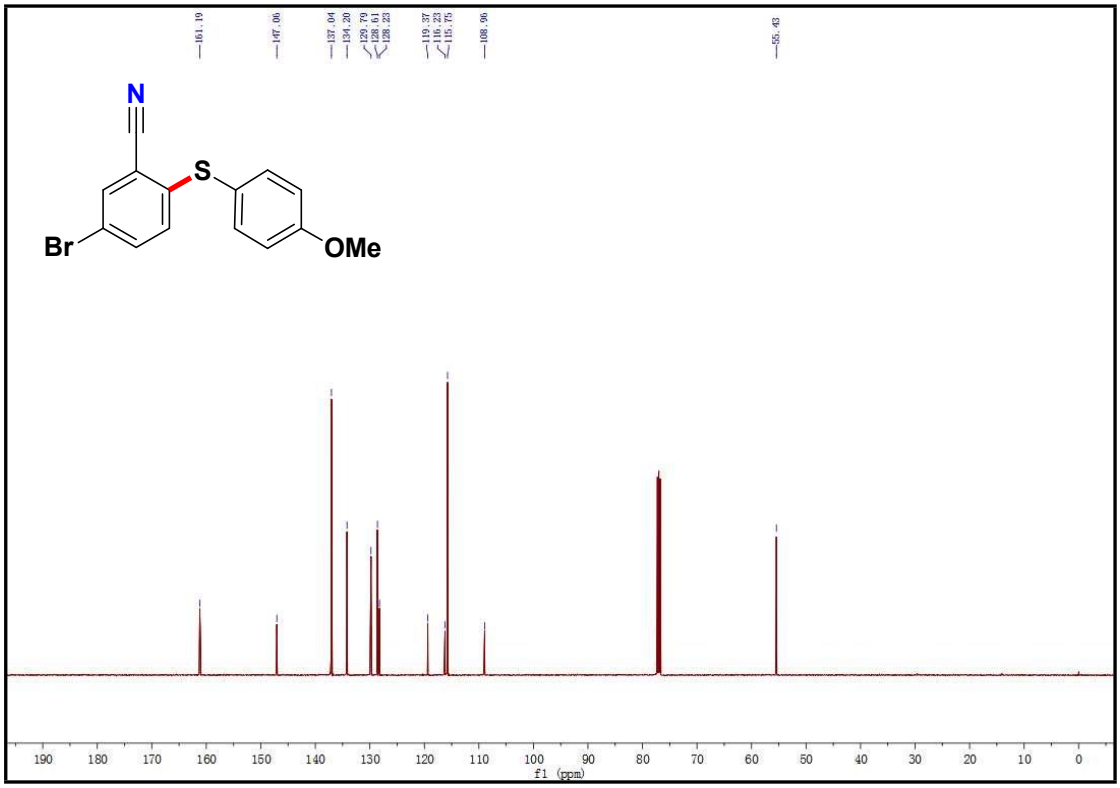
**3-((4-methoxyphenyl)thio)-4-methoxylbenzonitrile (3dd)**



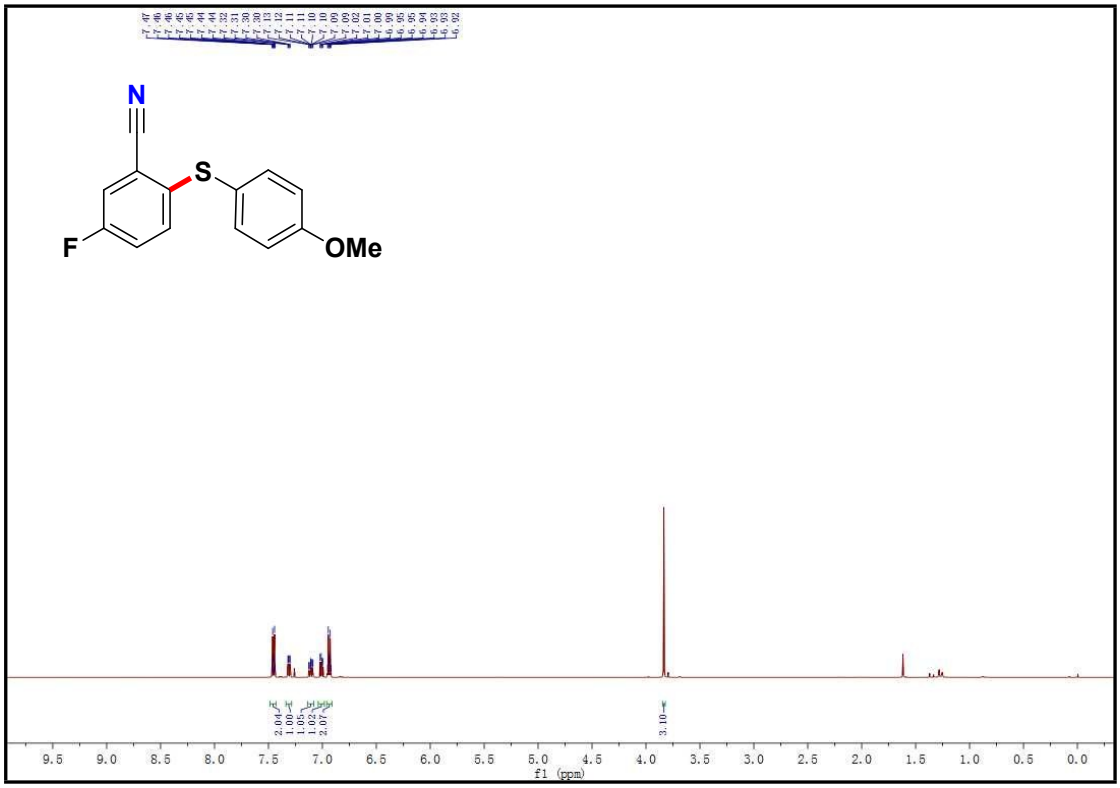



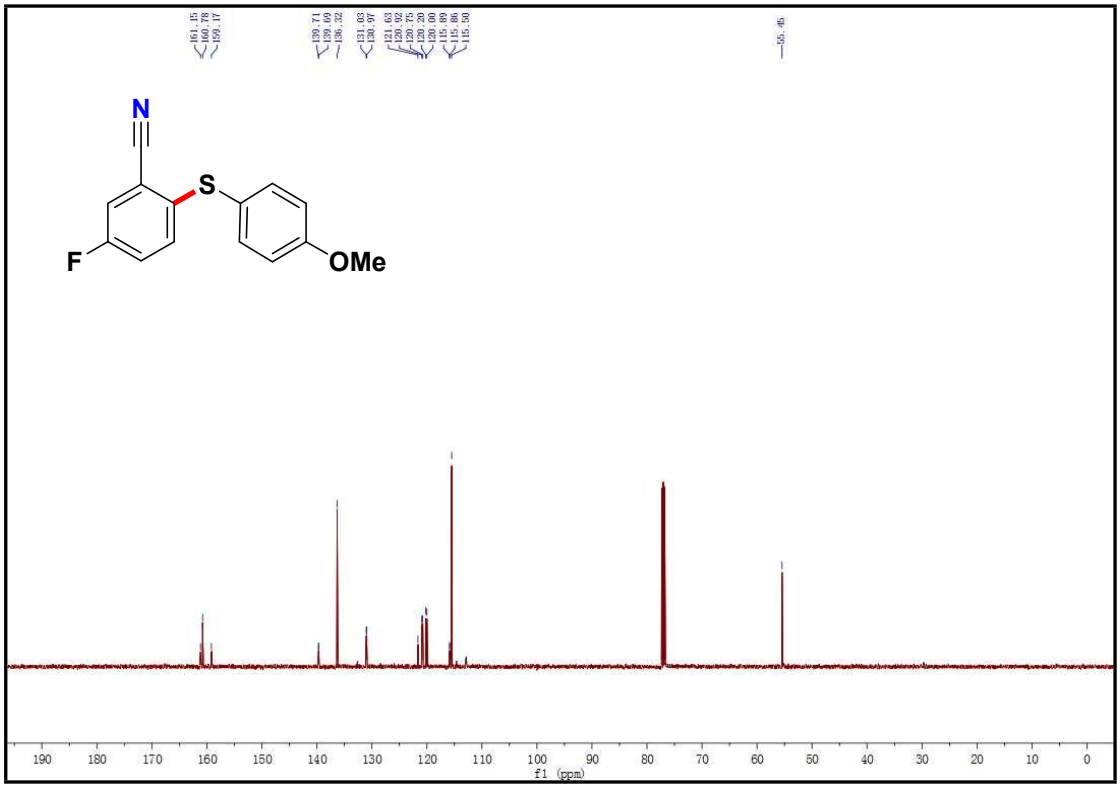
**5-bromo-2-((4-methoxyphenyl)thio)benzonitrile (3ed)**



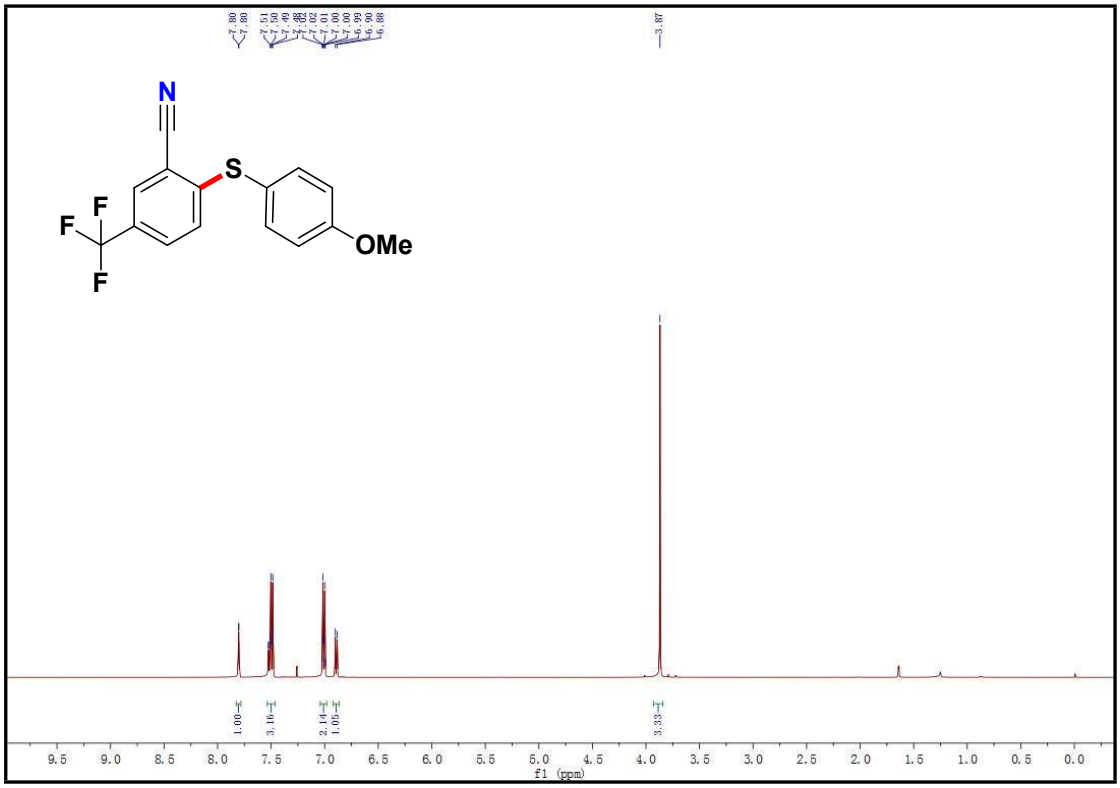



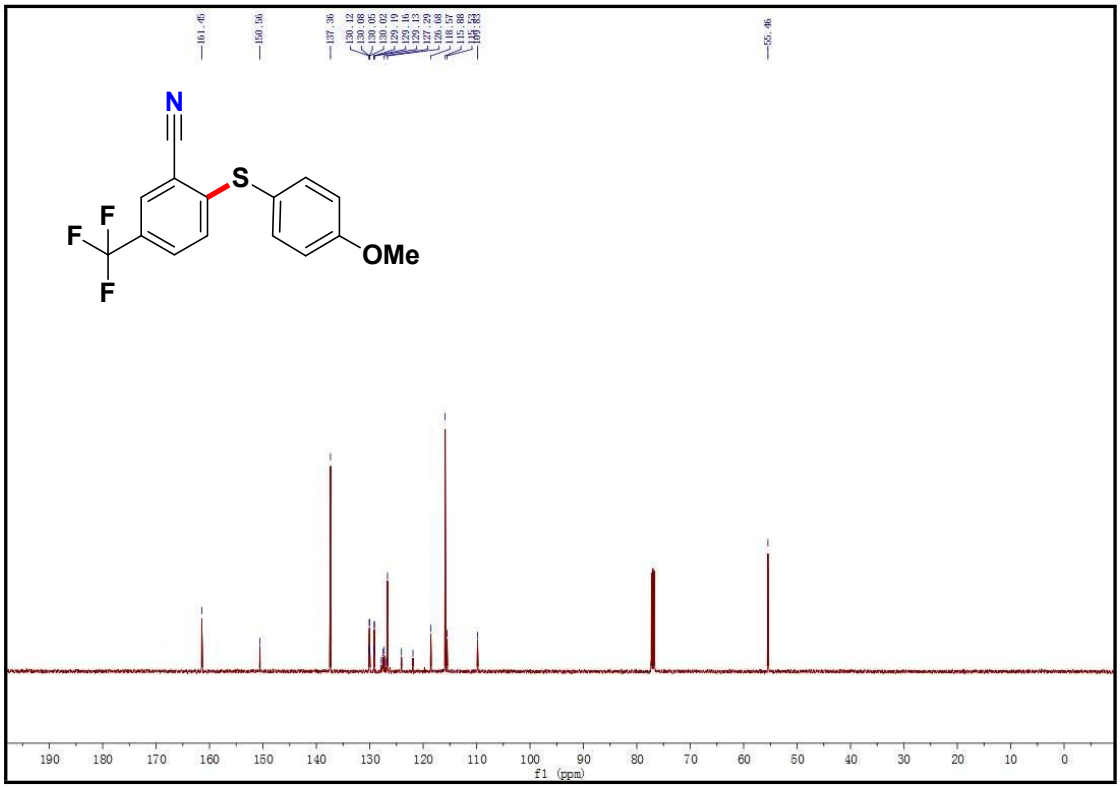
**5-fluoro-6-((4-methoxyphenyl)thio)benzonitrile (3fd)**



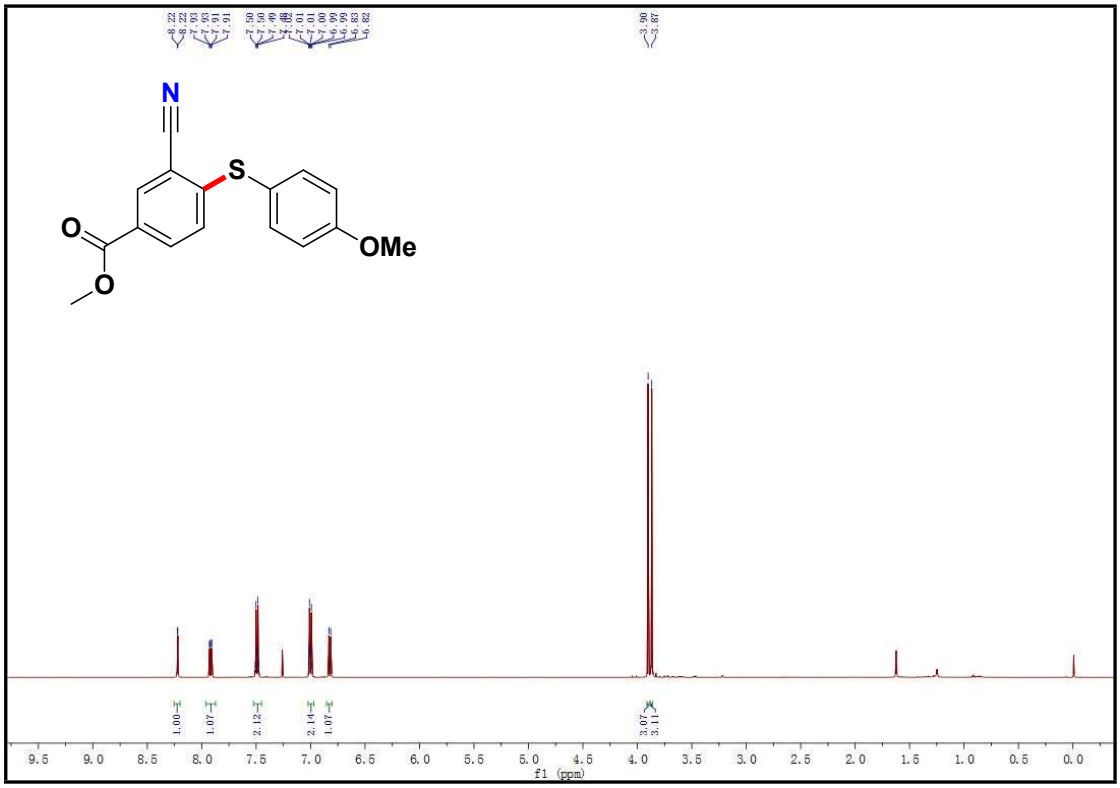



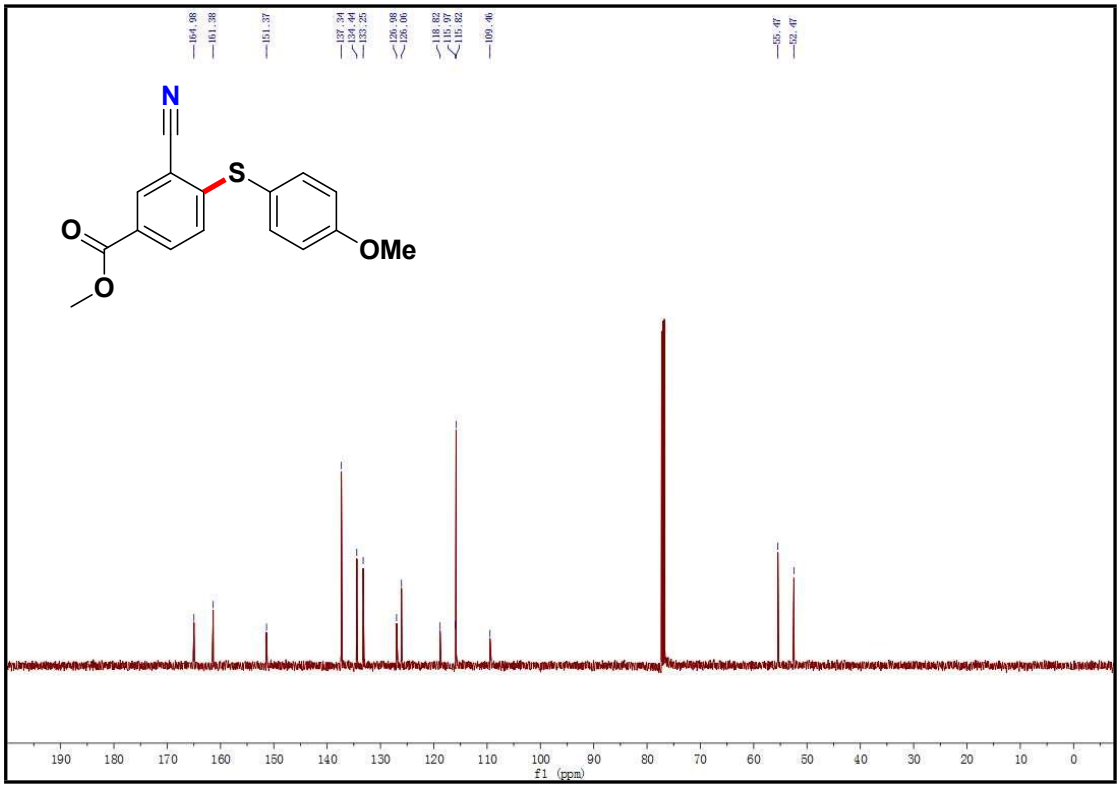
**2-((4-methoxyphenyl)thio)-5-(trifluoromethyl)benzonitrile (3gd)**



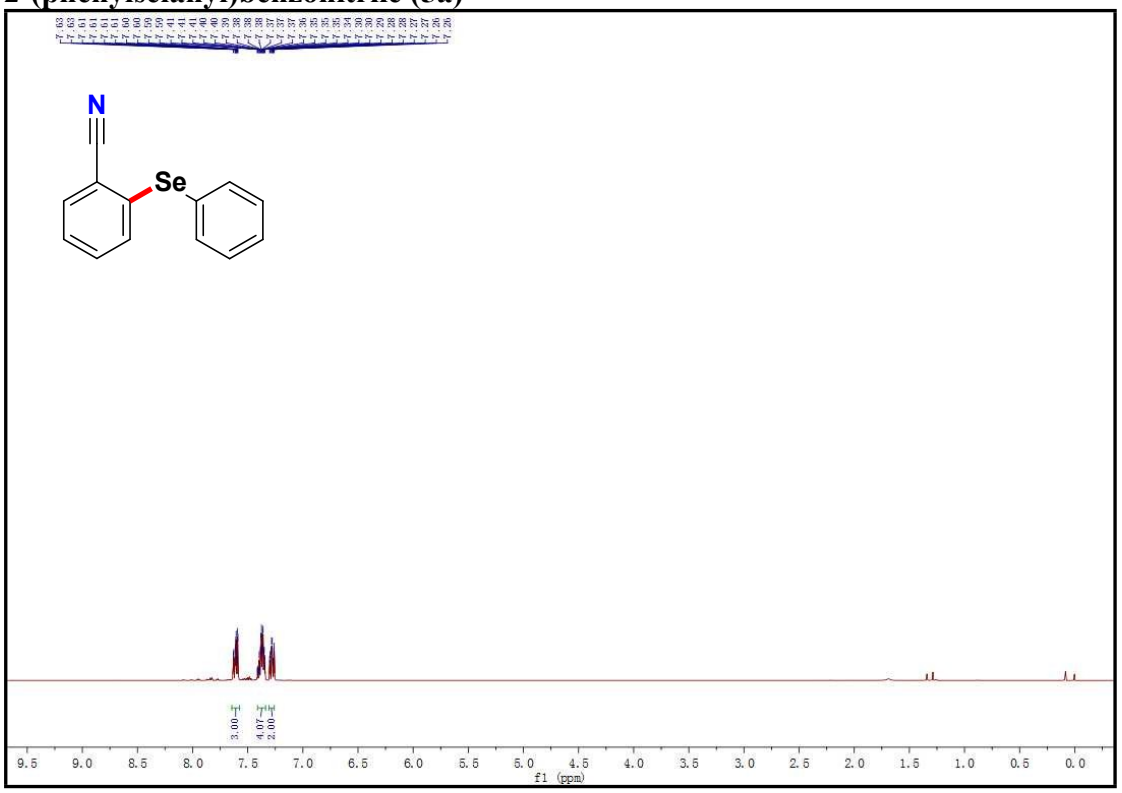



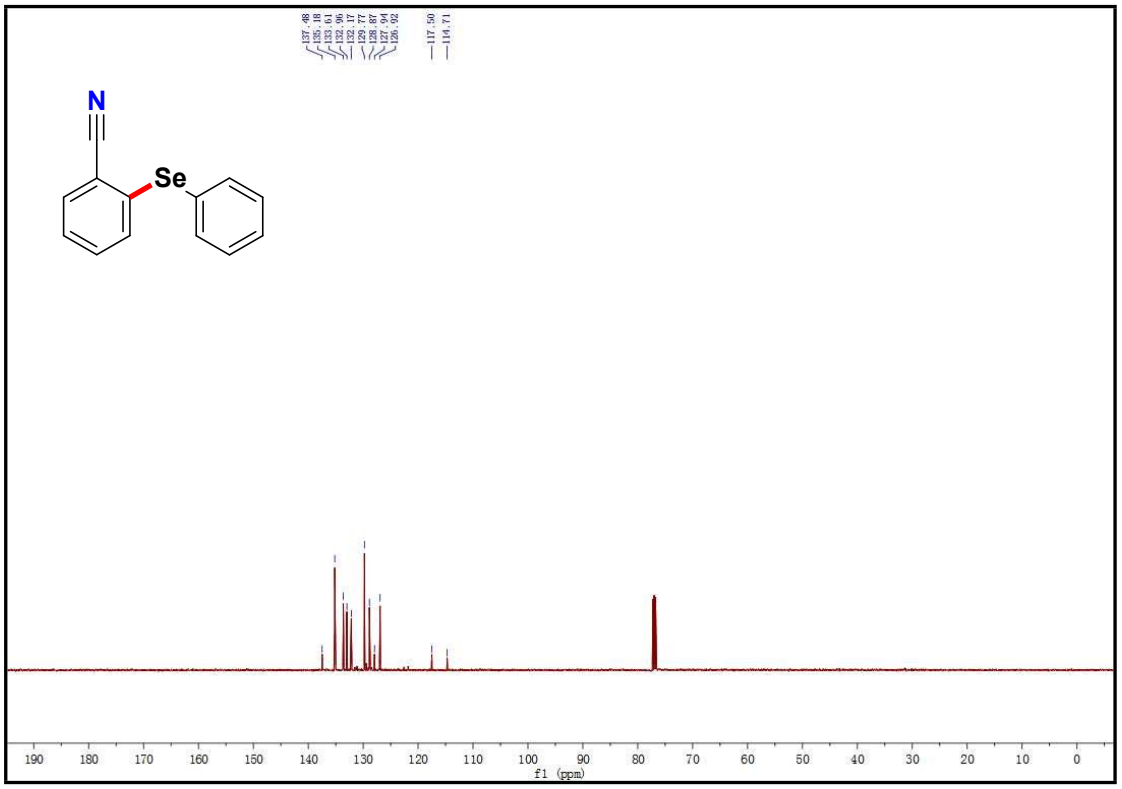
**methyl 3-cyano-4-((4-methoxyphenyl)thio)benzoate (3hd)**



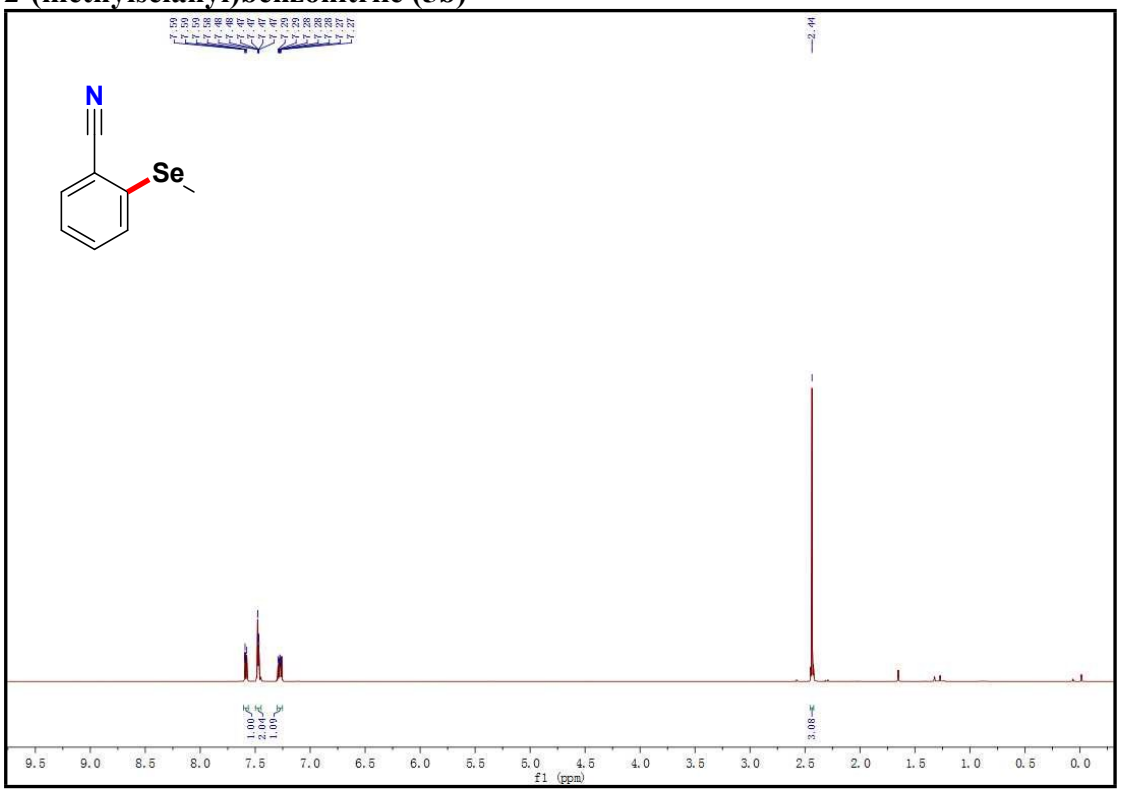



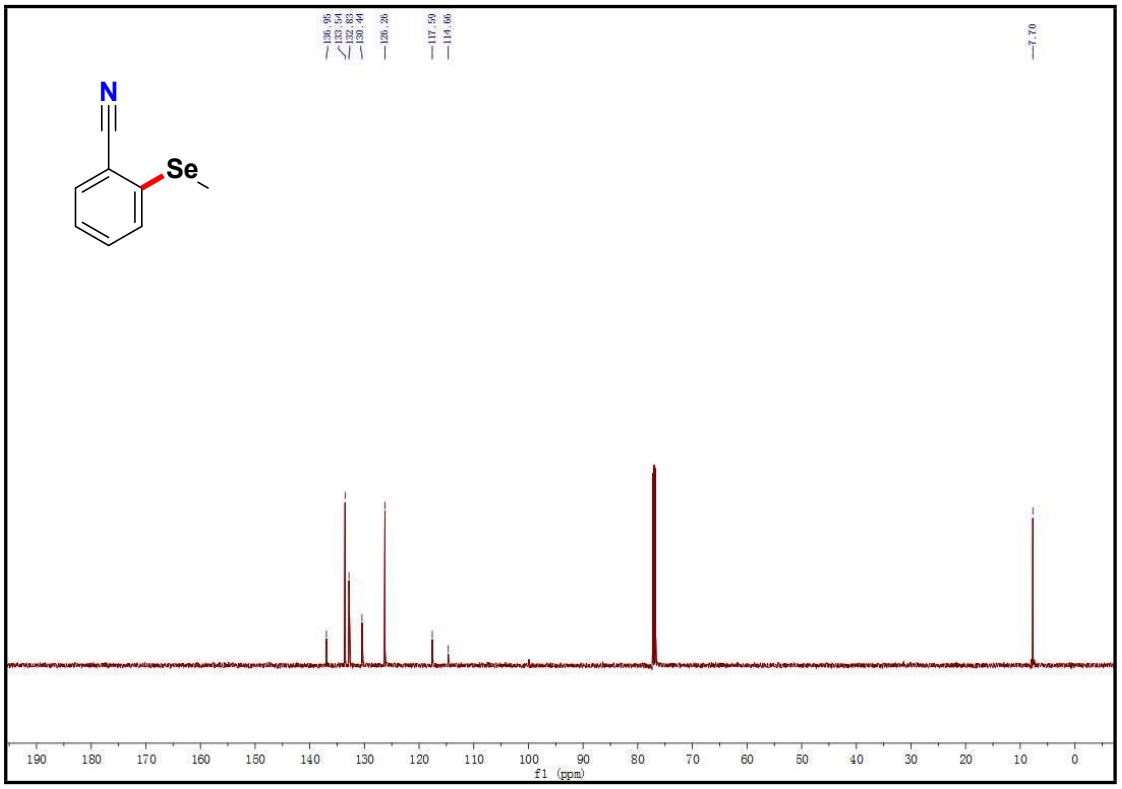
**2-(phenylselanyl)benzonitrile (5a)**



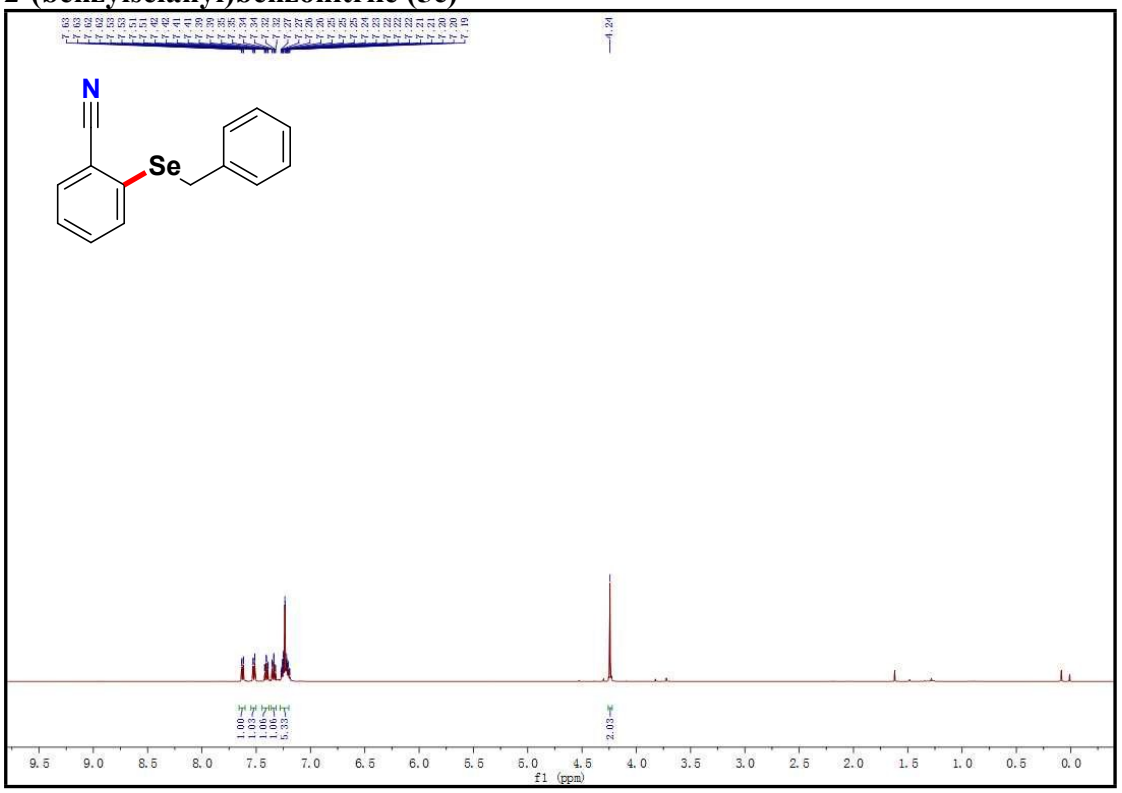



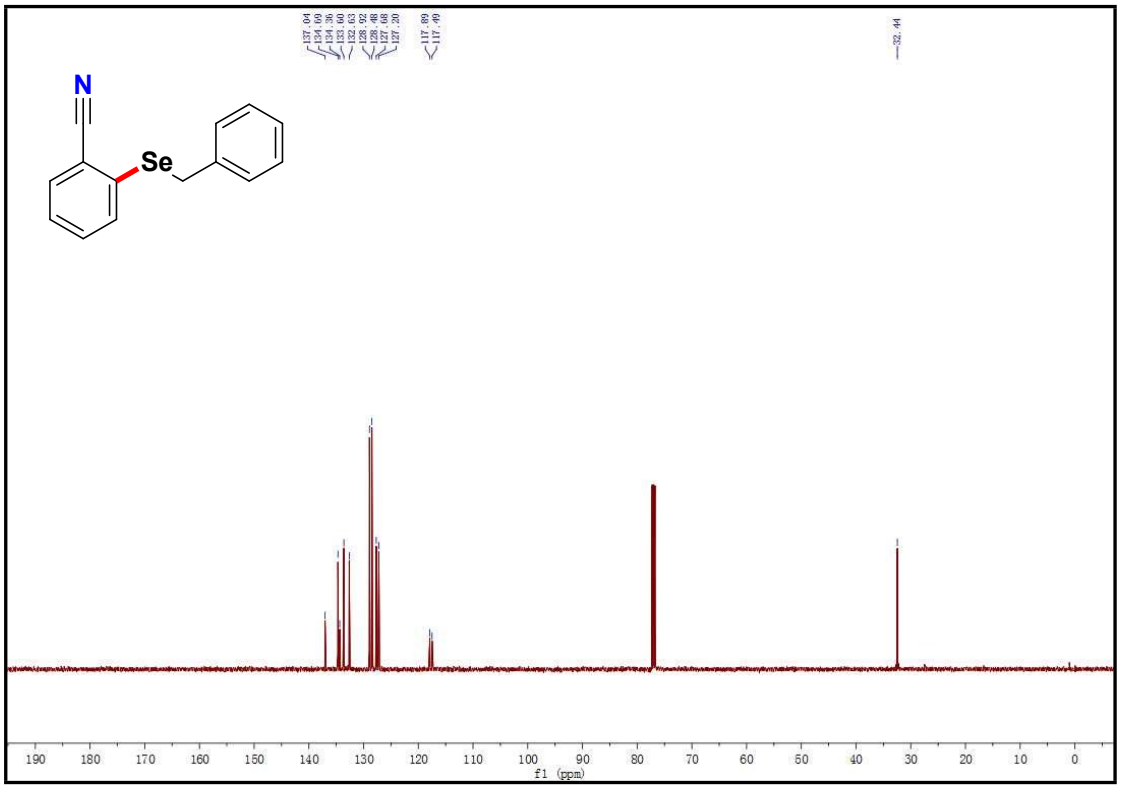
**2-(methylselanyl)benzonitrile (5b)**



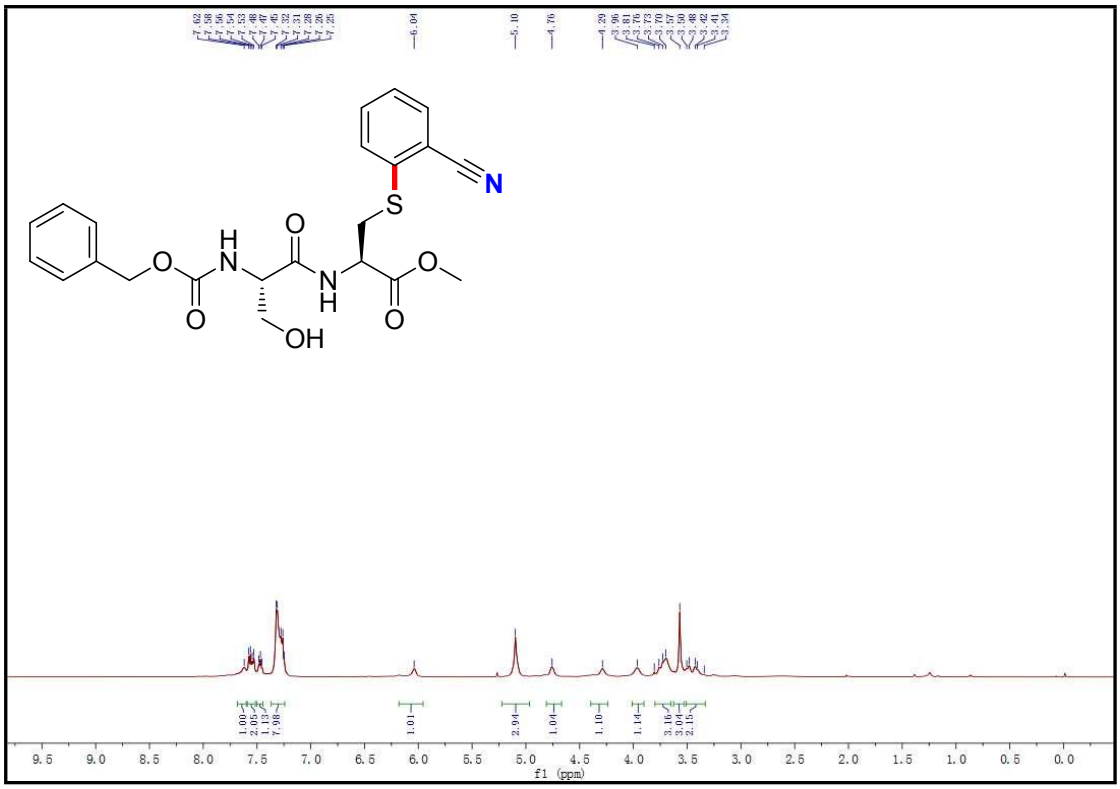



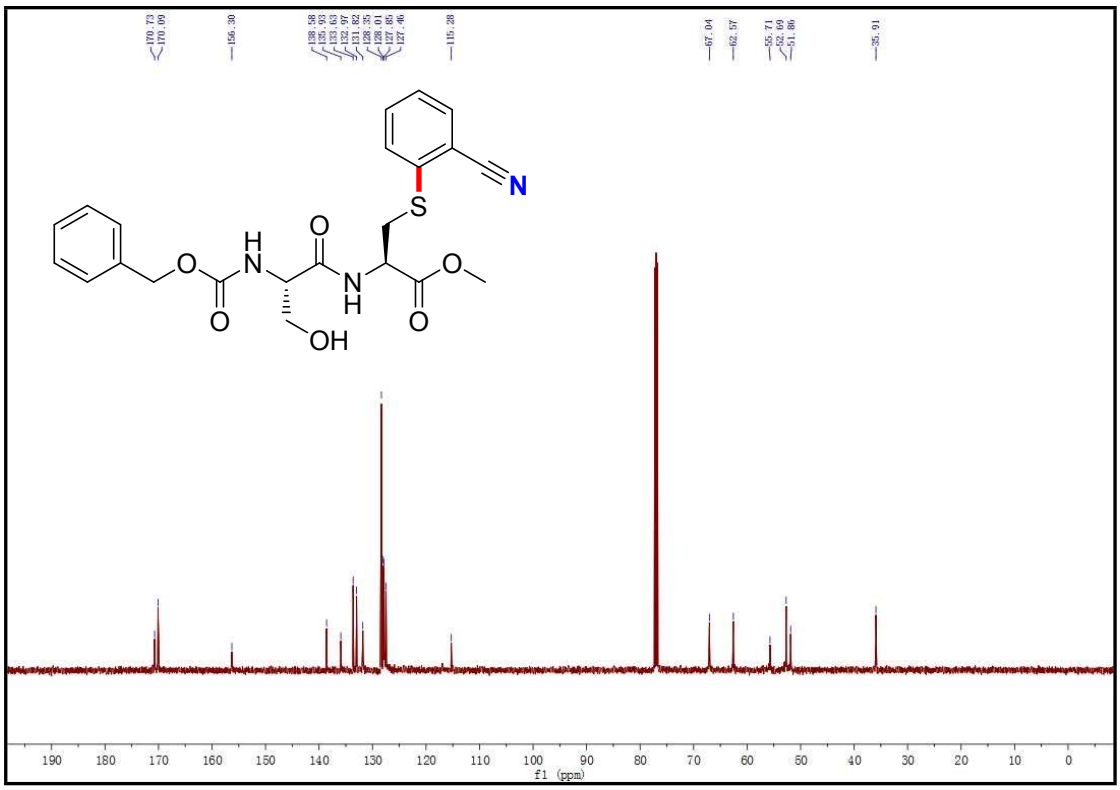
**2-(benzylselanyl)benzonitrile (5c)**



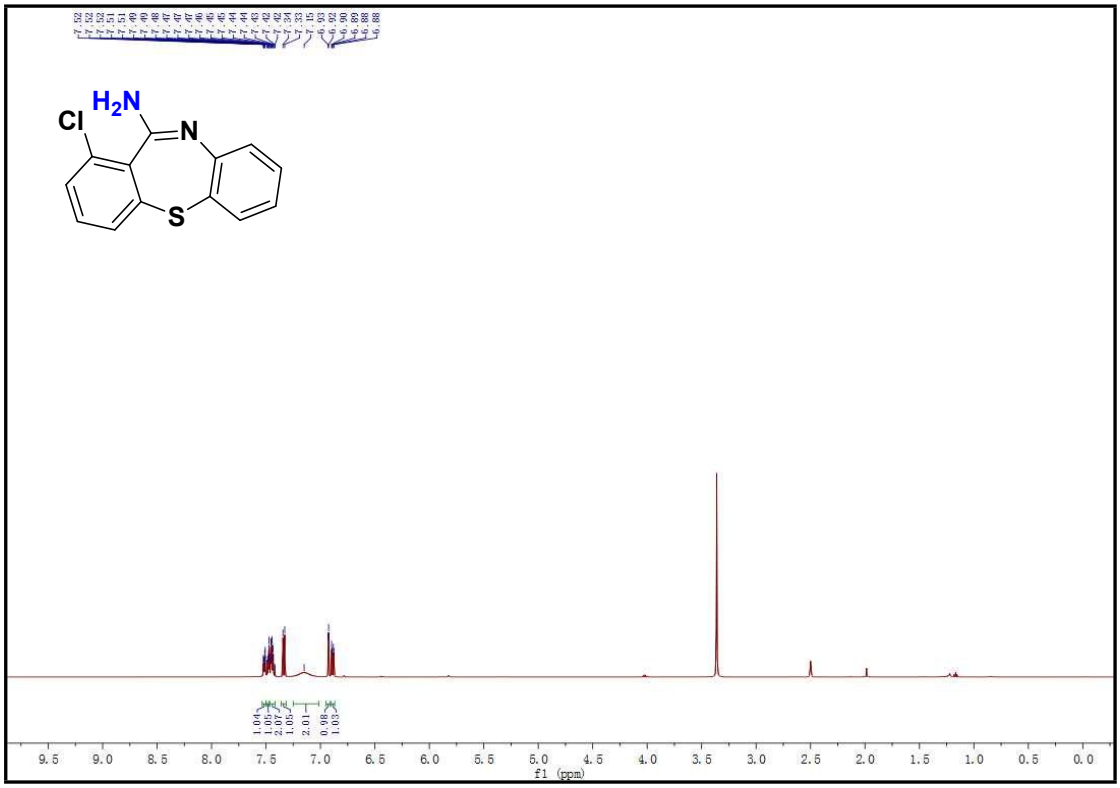



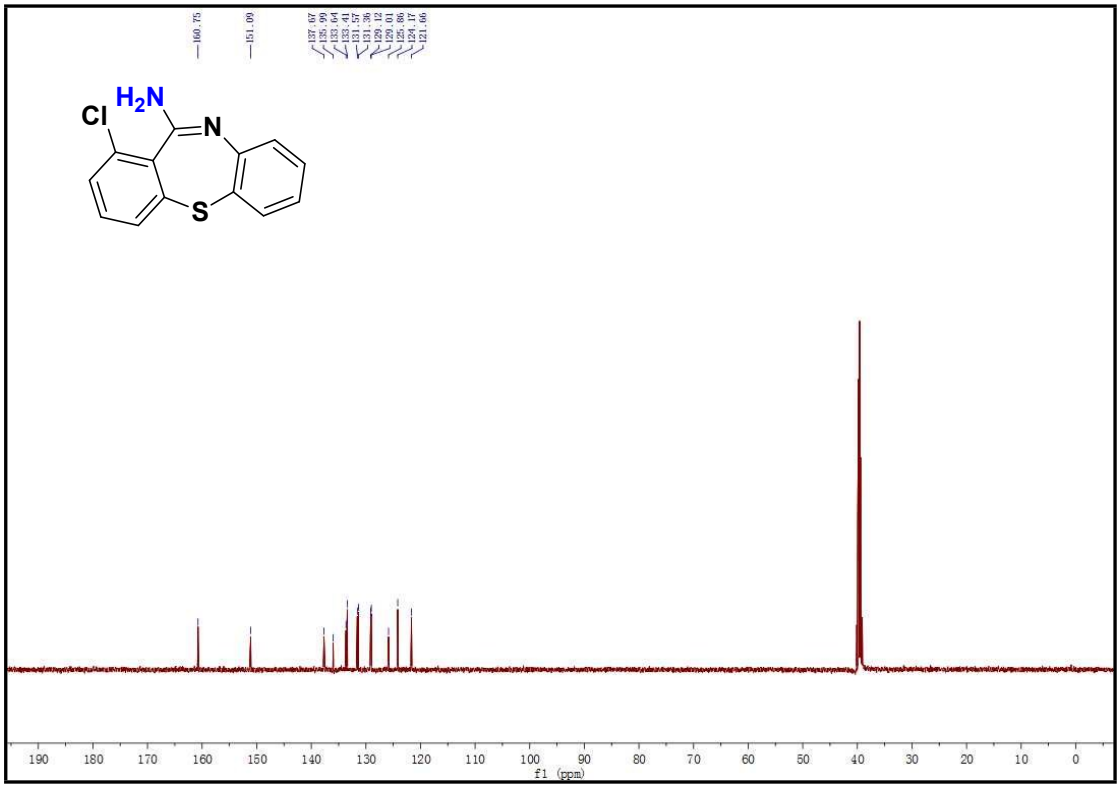
**(R)-methyl 2-((S)-2-(((benzyloxy)carbonyl)amino)-3-hydroxypropanamido)-3-((2-cyanophenyl)thio)propanoate (7)**



**1-chlorodibenzo[b,f][1,4]thiazepin-11-amine (8)**



**9-methoxydibenzo[b,d]thiophene-4-carbonitrile (9)**