Supporting Information

Electrochemical oxidative thiocyanation and amination of enaminones towards the synthesis of multi-substituted alkenes

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General information

Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis was dual display potentiostat (DJS-292B) (made in China). The anodic electrode was graphite rod (ϕ 6 mm) and cathodic electrode was platinum plate (15 mm×15 mm×0.3 mm). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 300-400 mesh silica gel in petroleum (boiling point was between 60-90 ^{o}C). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum to the indicated solvent, and they were listed as volume/volume ratios. NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR), 376 MHz (^{19}F NMR). Chemical shifts were reported relative to tetramethylsilane, dimethyl sulfoxide (2.50 ppm for ^{1}H, 39.6 ppm for ^{13}C), respectively. And all ^{1}H, ^{13}C and ^{19}F NMR data spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants were reported in Hertz (Hz). GC-MS spectra were recorded on a Shimadzu GC-MS QP2010 Ultra.

Experimental procedure

General procedure for the preparation of 3：

In an oven-dried undivided three-necked bottle (25 mL) equipped with a stir bar, enaminones **1** (0.5 mmol), ammonium thiocyanate **2a** (3.5 mmol, 266.4 mg), MeCN/HFIP/H_2O (11 mL, v/v/v = 9/1/1) was added. The bottle was equipped with graphite rod (ϕ 6 mm, about 15 mm immersion depth in solution) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 18 mA under N_2 atmosphere at room temperature for 4 h. After completion of the reaction, as indicated by TLC and GC-MS, the crude mixture product was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 2 : 1). The crude product follow by recrystallization from dichloromethane and n-hexane afforded pure product

Procedure for gram scale synthesis of 3a:

In an oven-dried undivided beaker (100 mL) equipped with a stir bar, (*E*)-3-(dimethylamino)-1-phenylprop-2-en-1-one **1a** (5.0 mmol, 876.2 mg), ammonium thiocyanate **2a** (35.0 mmol, 2664.2 mg), MeCN/H_2O/HFIP (110 mL, v/v/v = 90/10/10) was added. The bottle was equipped with graphite rod (ϕ 6 mm, about 15 mm immersion depth in solution) as the anode and platinum plate (15 mm×15 mm×0.3 mm) as the cathode. The reaction mixture was stirred and electrolyzed at a constant current of 25 mA under N_2 atmosphere at room temperature for 22 h, After completion of the reaction, as indicated by TLC and GC-MS, The pure product (yield 62%, yellow solid, 0.76 g) was obtained by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 2 : 1).

A **B** **C** **D**

Figure S1. The experimental setup for electrolysis. (A: The electrodes used in the reaction. B, C and D: The electrochemical reaction apparatus used.)

General procedure for cyclic voltammetry(CV):

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under air at room temperature. The working electrode was a glassy carbon electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. 10 mL of CH_3CN containing 0.01 M $^nBu_4NBF_4$ were poured into the electrochemical cell in all experiments. The scan rate is 0.1 V/s, ranging from 0 V to 3.0 V. The peak potentials *vs*. Ag/AgCl for used. An obvious oxidation peak of **1a** was observed at 1.59 V. The oxidation peak of **2a** could also be observed at 1.49 V.

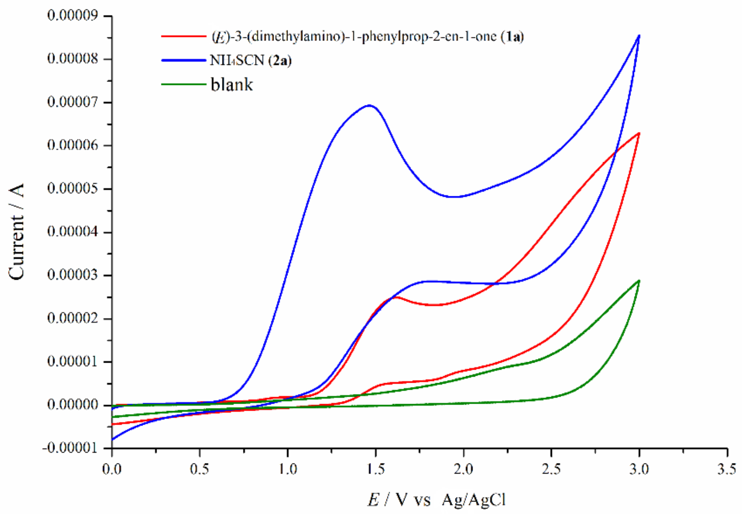
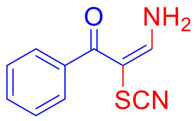


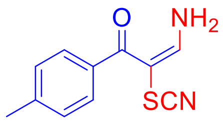
Figure S1 Cyclic voltammetry

Detail descriptions for products



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 84% isolated yield (E/Z>20/1), 85.8 mg).

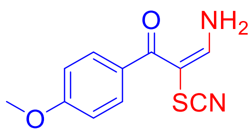
(*E*)-3-amino-1-phenyl-2-thiocyanatoprop-2-en-1-one (3a).[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.27 - 8.23 (m, 2H), 7.68 - 7.62 (m, 1H), 7.54 - 7.44 (m, 5H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.90, 158.99, 140.07, 130.76, 128.80, 128.32, 112.69, 89.99.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 76% isolated yield (E/Z>20/1), 82.9 mg).

(*E*)-3-amino-2-thiocyanato-1-(*p*-tolyl)prop-2-en-1-one (3b).[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.13 - 8.05 (m, 2H), 7.63 - 7.56 (m, 1H), 7.29 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.76, 158.71, 140.67, 137.18, 129.28, 128.51, 112.68, 89.95, 21.41.

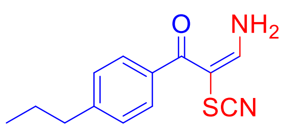
HRMS (ESI) calcd for $C_{11}H_{10}N_2OS$: 241.0406 (M+Na$^+$), found: 241.0406.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 85% isolated yield (E/Z=14/1), 99.6 mg).

(*E*)-3-amino-1-(4-methoxyphenyl)-2-thiocyanatoprop-2-en-1-one (3c).[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 - 8.08 (m, 2H), 7.75 - 7.69 (m, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.06, 161.54, 158.41, 132.07, 130.59, 114.05, 112.75, 89.72, 55.78.

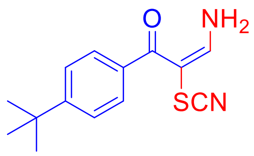
HRMS (ESI) calcd for $C_{11}H_{10}N_2O_2S$: 257.0355 (M+Na$^+$), found: 257.0357.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 67% isolated yield (E/Z=12/1), 87.2 mg).

(*E*)-3-amino-1-(4-propylphenyl)-2-thiocyanatoprop-2-en-1-one (3d). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10 - 8.07 (m, 2H), 7.63 - 7.58 (m, 1H), 7.31 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 2.53 (t, J = 8.0 Hz, 2H), 1.54 (q, J = 8.0 Hz, 2H), 0.83 (t, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.75, 158.74, 145.24, 137.45, 128.68, 128.50, 112.66, 89.96, 37.50, 24.30, 14.07.

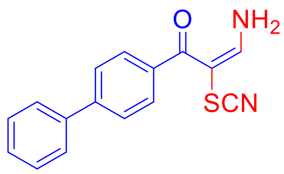
HRMS (ESI) calcd for $C_{13}H_{14}N_2OS$: 269.0719 (M+Na$^+$), found: 269.0728.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 69% isolated yield (E/Z=14/1), 89.7 mg).

(*E*)-3-amino-1-(4-(tert-butyl)phenyl)-2-thiocyanatoprop-2-en-1-one (3e). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.19 - 8.16 (m, 2H), 7.72 - 7.66 (m, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 2H), 1.31 (s, 9H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.71, 158.81, 153.56, 137.21, 128.35, 125.54, 112.68, 89.94, 35.04, 31.43.

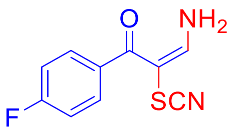
HRMS (ESI) calcd for $C_{14}H_{16}N_2OS$: 283.0876 (M+Na$^+$), found: 283.0886.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 45% isolated yield (E/Z=2/1), 63.1 mg).

(*E*)-1-([1,1'-biphenyl]-4-yl)-3-amino-2-thiocyanatoprop-2-en-1-one (3f). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 - 8.24 (m, 2H), 7.79 - 7.71 (m, 5H), 7.56 (d, J = 8.0 Hz, 2H), 7.50 (t, J = 8.0 Hz, 2H), 7.41 (t, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.52, 158.96, 142.45, 139.70, 138.92, 129.52, 129.16, 128.46, 127.29, 127.03, 112.72, 89.99.

HRMS (ESI) calcd for $C_{16}H_{12}N_2OS$: 303.0563 (M+Na$^+$), found:303.0565.

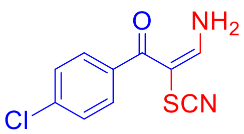


The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 79% isolated yield (E/Z=1/1.4), 87.8 mg).

(*E*)-3-amino-1-(4-fluorophenyl)-2-thiocyanatoprop-2-en-1-one (3g) ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.31 - 8.27 (s, 2H), 7.84 - 7.82 (m, 1H), 7.70 (t, J = 8.0 Hz, 1H), 7.57 - 7.55 (m, 1H), 7.36 - 7.30 (m, 2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 188.72, 164.50 (d, J = 250.5 Hz), 158.98, 135.19 (d, J = 3.0 Hz), 130.98 (d, J = 9.1 Hz), 116.02 (d, J = 22.2 Hz), 112.65, 89.83. ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -108.26.

(*Z*)-3-amino-1-(4-fluorophenyl)-2-thiocyanatoprop-2-en-1-one (3g) ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.22 (s, 2H), 7.81 - 7.79 (m, 1H), 7.66 (s, 1H), 7.54 - 7.51 (m, 1H), 7.30 - 7.25 (m, 2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 184.44, 175.23, 163.62 (d, J = 248.5 Hz), 151.54, 136.44 (d, J = 3.0 Hz), 131.38 (d, J = 9.1 Hz), 127.14, 115.71 (d, J = 22.2 Hz). ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -110.12.

HRMS (ESI) calcd for $C_{10}H_7FN_2OS$: 245.0155 (M+Na$^+$), found: 245.0159.

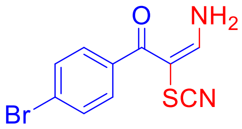


The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 74% isolated yield (E/Z=2/1), 88.3 mg).

(*E*)-3-amino-1-(4-chlorophenyl)-2-thiocyanatoprop-2-en-1-one (3h).[1] ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.34 - 8.32 (m, 2H), 7.77 - 7.68 (m, 1H), 7.57 - 7.51 (m, 4H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 188.79, 159.16, 138.75, 135.50, 130.28, 128.86, 112.63, 89.88.

(*Z*)-3-amino-1-(4-chlorophenyl)-2-thiocyanatoprop-2-en-1-one (3h). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.27 (s, 2H), 7.66 (s, 1H), 7.50 - 7.48 (m, 4H); ^{13}C NMR (101 MHz, DMSO-*d*^{6}) 184.57, 175.38, 151.86, 137.30, 136.91, 130.56, 129.15, 127.04.

HRMS (ESI) calcd for $C_{10}H_7ClN_2OS$: 239.0040 (M+H$^+$), found: 239.0048.

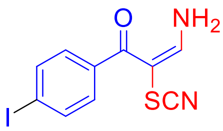


The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 75% isolated yield (E/Z=2.7/1), 106.2 mg).

(*E*)-3-amino-1-(4-bromophenyl)-2-thiocyanatoprop-2-en-1-one (3i).[1] ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 - 8.29 (m, 2H), 7.63 (s, 2H), 7.41 (d, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 188.82, 159.12, 139.16, 131.76, 130.45, 124.28, 112.57, 89.89.

(*Z*)-3-amino-1-(4-bromophenyl)-2-thiocyanatoprop-2-en-1-one (3i). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.25 (s, 2H), 7.73 - 7.65 (m, 5H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.63, 175.41, 151.83, 137.68, 132.05, 130.70, 127.05, 125.84.

HRMS (ESI) calcd for $C_{10}H_7BrN_2OS$: 282.9535 (M+H$^+$), found: 282.9533.

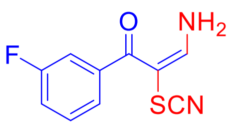


The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 80% isolated yield (E/Z=1/1), 132.1 mg).

(*E*)-3-amino-1-(4-iodophenyl)-2-thiocyanatoprop-2-en-1-one (3j). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 - 8.29 (m, 2H), 7.83 (d, J = 8.0 Hz, 3H), 7.71 - 7.65 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.06, 159.10, 139.47, 130.54, 129.41, 112.57, 97.87, 89.85.

(*Z*)-3-amino-1-(4-iodophenyl)-2-thiocyanatoprop-2-en-1-one (3j). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 (s, 2H), 7.89 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.91, 175.36, 151.76, 137.92, 137.61, 130.34, 127.05, 99.82.

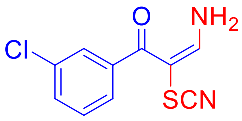
HRMS (ESI) calcd for $C_{10}H_7IN_2OS$: 352.9216 (M+Na$^+$), found: 352.9227.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 87% isolated yield (E/Z=10/1), 96.6 mg).

(*E*)-3-amino-1-(3-fluorophenyl)-2-thiocyanatoprop-2-en-1-one (3k). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.35 - 8.27 (m, 2H), 7.74 - 7.68 (m, 1H), 7.57 - 7.48 (m, 1H), 7.36 - 7.27 (m, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 188.38, 162.21 (d, J = 247.5 Hz), 159.26, 142.41 (d, J = 6.1 Hz), 130.93 (d, J = 8.1 Hz), 124.41 (d, J = 2.0 Hz), 117.53 (d, J = 20.2 Hz), 115.13 (d, J = 22.2 Hz), 112.54, 89.80. ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.42.

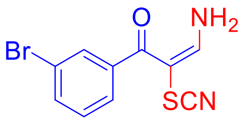
HRMS (ESI) calcd for $C_{10}H_7FN_2OSNa$: 245.0155 (M+Na$^+$), found: 245.0159.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 75% isolated yield (E/Z=11/1), 89.5 mg).

(*E*)-3-amino-1-(3-chlorophenyl)-2-thiocyanatoprop-2-en-1-one (3l). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.34 - 8.28 (m, 2H), 7.73 - 7.65 (m, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.49 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 1H) ; ^{13}C NMR (101 MHz, DMSO-d_6) δ 188.30, 159.29, 142.16, 133.58, 130.74, 130.53, 127.95, 126.93, 112.53, 89.81.

HRMS (ESI) calcd for $C_{10}H_8ClN_2OS$: 239.0040 (M+H$^+$), found: 239.0048.

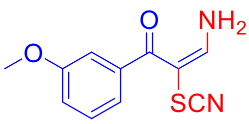


The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 66% isolated yield (E/Z=5/1), 93.4 mg).

(*E*)-3-amino-1-(3-bromophenyl)-2-thiocyanatoprop-2-en-1-one (3m). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.37 - 8.31 (m, 2H), 7.83 - 7.67 (m, 2H), 7.61 (s, 1H), 7.47 - 7.41 (m, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 188.21, 159.29, 142.36, 133.43, 131.23, 130.78, 127.30, 122.08, 112.54, 89.82.

(*Z*)-3-amino-1-(3-bromophenyl)-2-thiocyanatoprop-2-en-1-one (3m). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.29 (s, 2H), 7.66 - 7.61 (m, 4H), 7.39 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.09, 175.56, 152.21, 140.82, 134.71, 130.99, 127.70, 126.81, 126.24, 122.34.

HRMS (ESI) calcd for $C_{10}H_7BrN_2OS$: 282.9535 (M+H$^+$), found: 282.9533.

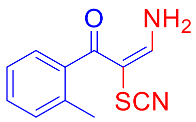


The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in

82% isolated yield (E/Z=8/1), 95.9 mg).

(*E*)-3-amino-1-(3-methoxyphenyl)-2-thiocyanatoprop-2-en-1-one (3n). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.25 - 8.21 (m, 2H), 7.73 - 7.66 (m, 1H), 7.45 - 7.35 (m, 1H), 7.21 - 6.98 (m, 3H), 3.79 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.62, 159.48, 159.06, 141.47, 129.93, 120.49, 116.54, 113.39, 112.68, 89.94, 55.70.

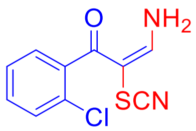
HRMS (ESI) calcd for $C_{11}H_{10}N_2O_2S$: 235.0536 (M+H$^+$), found: 235.0535.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 60% isolated yield (E/Z=20/1), 61.2 mg).

(*E*)-3-amino-2-thiocyanato-1-(o-tolyl)prop-2-en-1-one (3o). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 - 8.20 (m, 2H), 7.40 - 7.31 (m, 2H), 7.28 - 7.22 (m, 2H), 7.12 (d, J = 8.0 Hz, 3H), 2.14 (s, 3H) ; ^{13}C NMR (101 MHz, DMSO-d_6) δ 190.93, 158.83, 140.45, 134.84, 130.83, 129.29, 126.85, 125.97, 112.56, 91.16, 18.97.

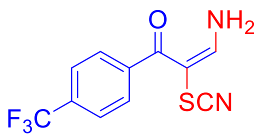
HRMS (ESI) calcd for $C_{11}H_{10}N_2OS$: 241.0406 (M+Na$^+$), found: 241.0413.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 75% isolated yield (E/Z>20/1), 89.5 mg).

(*E*)-3-amino-1-(2-chlorophenyl)-2-thiocyanatoprop-2-en-1-one (3p). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (s, 2H), 7.56 - 7.42 (m, 4H), 7.29 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.34, 176.13, 153.19, 138.58, 131.70, 130.33, 130.23, 129.38, 127.58, 127.03.

HRMS (ESI) calcd for $C_{10}H_7ClN_2OS$: 260.9860 (M+Na$^+$), found: 260.9869.



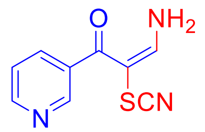
The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 80% isolated yield (E/Z=1.5/1), 108.8 mg).

(*E*)-3-amino-2-thiocyanato-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (3q). ^{1}H NMR (400

MHz, DMSO-d_6) δ 8.40 - 8.36 (m, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.71 - 7.67 (m, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 188.77, 159.51, 144.12, 130.63 (q, J = 32.3 Hz), 128.99, 125.97 (q, J = 4.0 Hz), 124.26 (q, J = 248.5 Hz), 112.53, 89.99. ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.40.

(*Z*)-3-amino-2-thiocyanato-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (3q). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.33 (s, 2H), 7.92 (d, J = 8.0 Hz, 2H), 7.87 (d, J = 8.0 Hz, 2H), 7.65 (s, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 184.60, 175.71, 152.62, 142.25, 131.71 (q, J = 31.3 Hz), 129.42, 126.89, 125.74 (q, J = 4.0 Hz), 124.20 (q, J = 247.5 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -61.50.

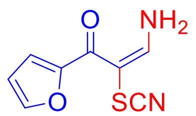
HRMS (ESI) calcd for $C_{11}H_7F_3N_2OS$: 295.0123 (M+Na$^+$), found: 295.0131.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 50% isolated yield (E/Z>20/1), 51.2 mg).

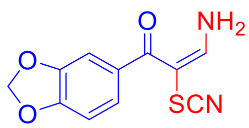
(*E*)-3-amino-1-(pyridin-3-yl)-2-thiocyanatoprop-2-en-1-one (3r). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.88 (s, 1H), 8.77 (d, J = 8.0 Hz, 1H), 8.31 (s, 2H), 8.11 (d, J = 8.0 Hz, 1H), 7.70 (s, 1H), 7.56 - 7.53 (m, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 183.95, 175.63, 152.53, 152.48, 149.06, 136.29, 134.37, 127.08, 124.18.

HRMS (ESI) calcd for $C_9H_7N_3OS$: 228.0202 (M+Na$^+$), found: 228.0209.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 72% isolated yield (E/Z>20/1), 75.7 mg).

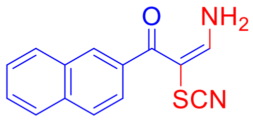
(*E*)-3-amino-1-(furan-2-yl)-2-thiocyanatoprop-2-en-1-one (3s). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.45 - 8.34 (m, 2H), 8.27 - 8.23 (m, 1H), 7.90 (s, 1H), 7.15 (d, J = 8.0 Hz, 1H), 6.67 (s, 1H) ; ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.39, 157.95, 152.21, 146.20, 117.00, 112.72, 112.25, 89.00. HRMS (ESI) calcd for $C_8H_6N_2O_2S$: 195.0223 (M+H$^+$), found: 195.0222.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 69% isolated yield (E/Z>20/1), 85.5 mg).

(*E*)-3-amino-1-(benzo[d][1,3]dioxol-5-yl)-2-thiocyanatoprop-2-en-1-one (3t). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 - 8.10 (m, 2H), 7.77 - 7.65 (m, 1H), 7.04 - 6.95 (m, 3H), 6.09 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 188.66, 158.60, 149.63, 147.67, 133.79, 123.51, 112.72, 108.90, 108.27, 102.04, 89.57.

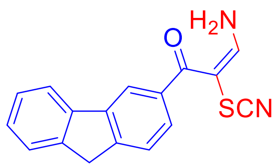
HRMS (ESI) calcd for $C_{11}H_8N_2O_3S$: 249.0328 (M+H$^+$), found: 249.0333



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 74% isolated yield (E/Z>20/1), 94.1 mg).

(*E*)-3-amino-1-(naphthalen-2-yl)-2-thiocyanatoprop-2-en-1-one (3u). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 - 8.22 (m, 2H), 8.02 - 7.95 (m, 4H), 7.83 - 7.77 (m, 1H), 7.60 - 7.55 (m, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 190.11, 159.34, 137.19, 134.07, 132.47, 129.09, 128.57, 128.22, 128.09, 127.91, 127.28, 125.58, 112.76, 90.34.

HRMS (ESI) calcd for $C_{14}H_{10}N_2OS$: 255.0587 (M+H$^+$), found: 255.0587.



The desired product was obtained as a pair of inseparable isomers (Yellow solid was obtained in 67% isolated yield (E/Z>20/1), 97.9 mg).

(*E*)-3-amino-1-(9H-fluoren-3-yl)-2-thiocyanatoprop-2-en-1-one (3v). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 - 8.19 (m, 2H), 7.96 (d, J = 8.0 Hz, 2H), 7.81 - 7.75 (m, 1H), 7.69 (s, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.44 - 7.35 (m, 2H), 3.97 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 189.97, 158.86, 144.18, 143.63, 143.42, 140.71, 138.36, 127.97, 127.53, 127.39, 125.72, 125.38, 121.05, 120.13, 112.75, 90.13, 36.94.

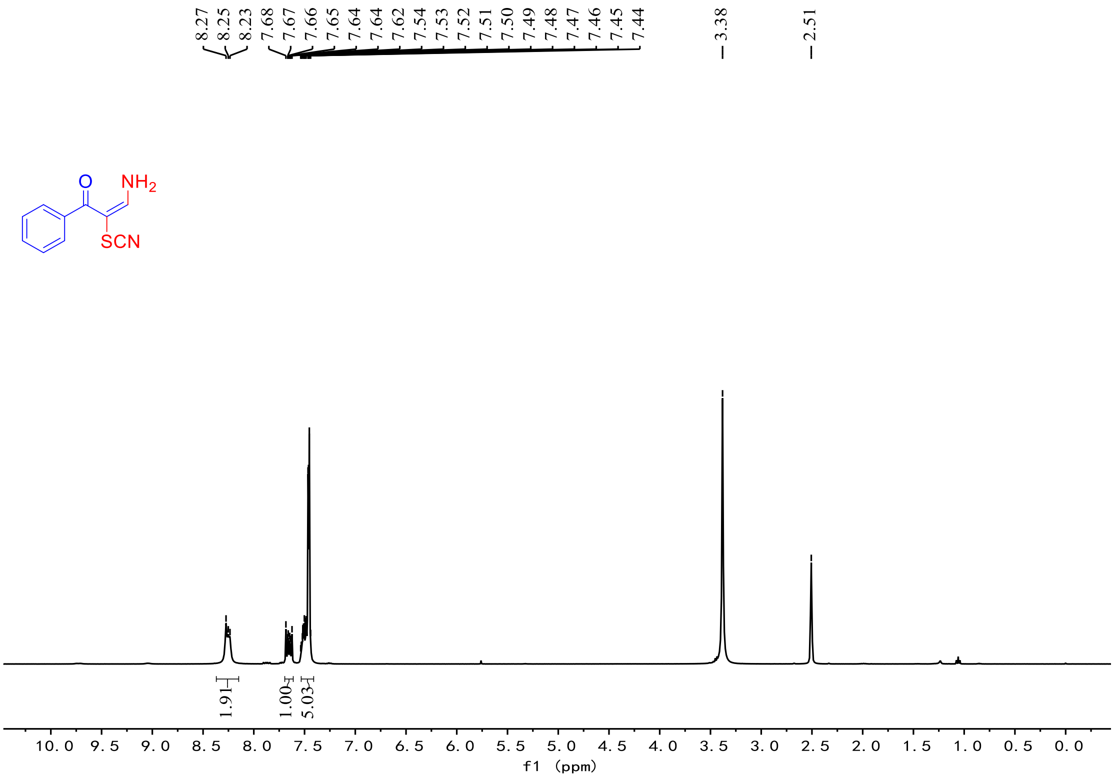
HRMS (ESI) calcd for $C_{17}H_{12}N_2OS$: 315.0563 (M+Na$^+$), found: 315.0574.

References

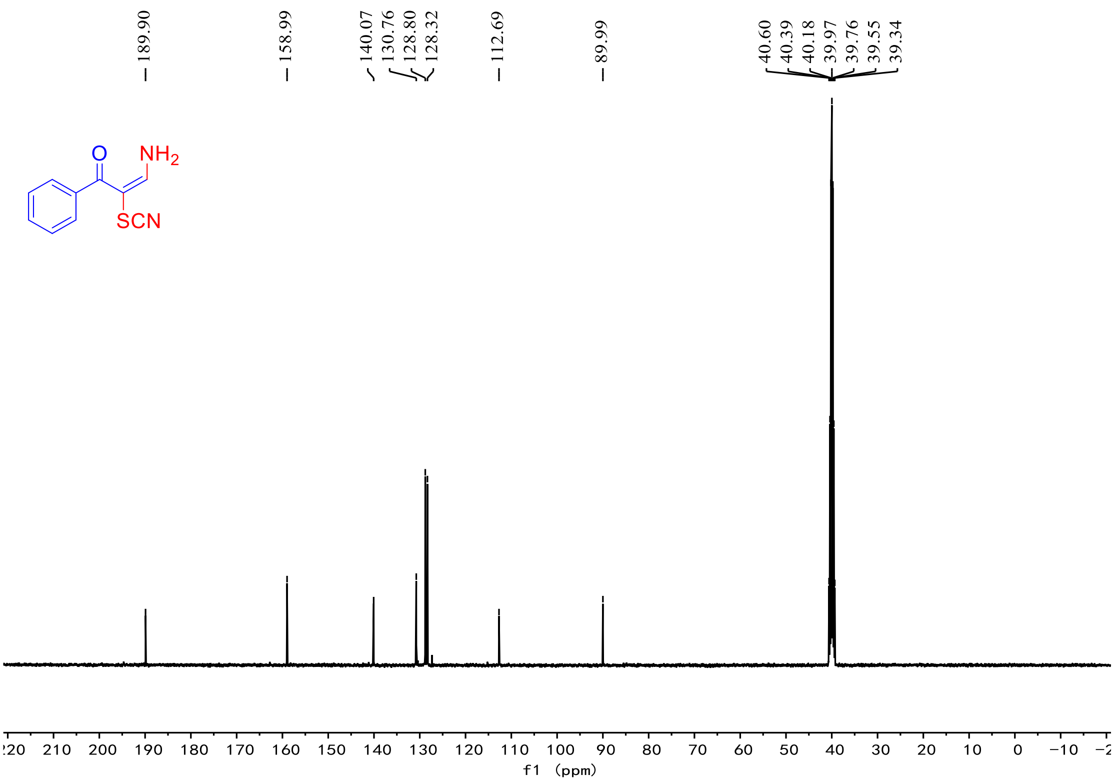
(1) Y. Gao, Y. Liu and J.-P. Wan, *J. Org. Chem.*, **2019**, *84*, 2243-2251;

Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra

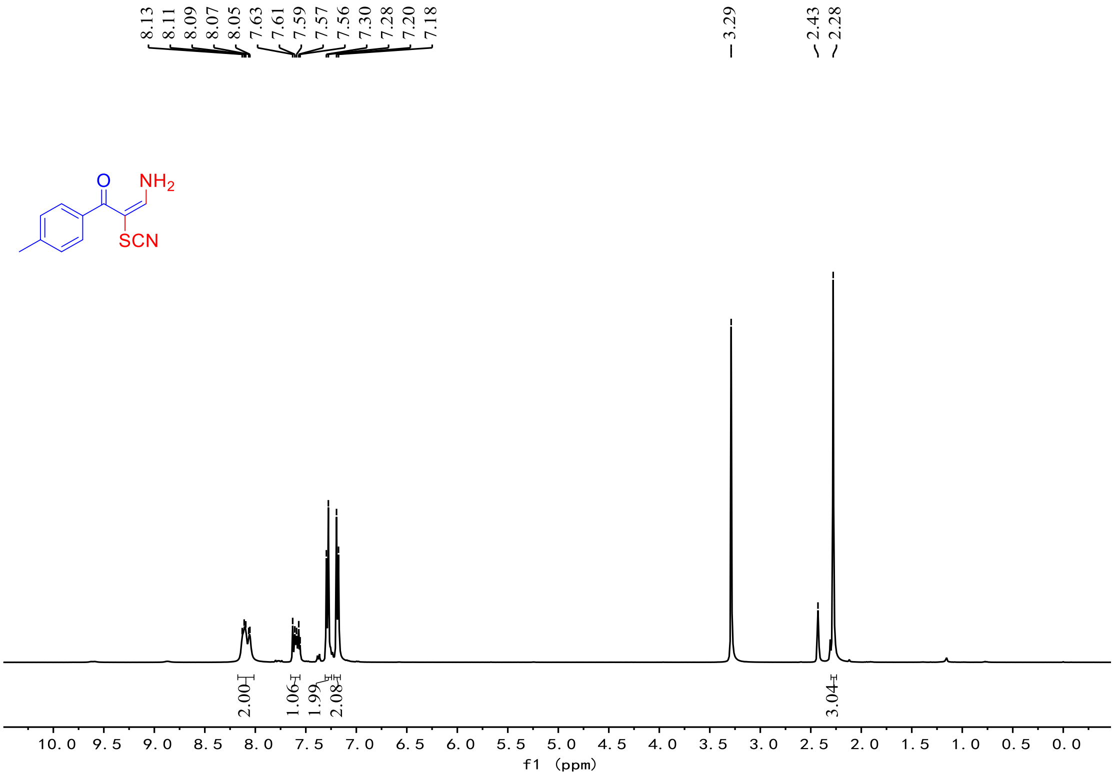
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3a**



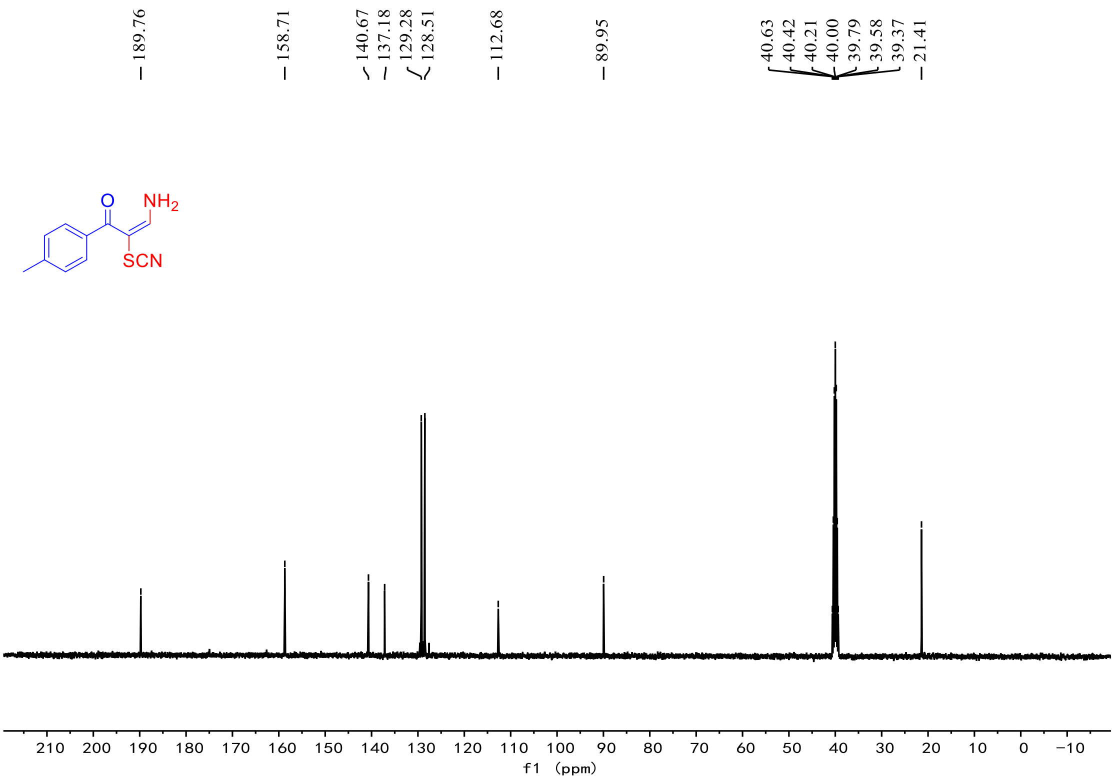
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3a**



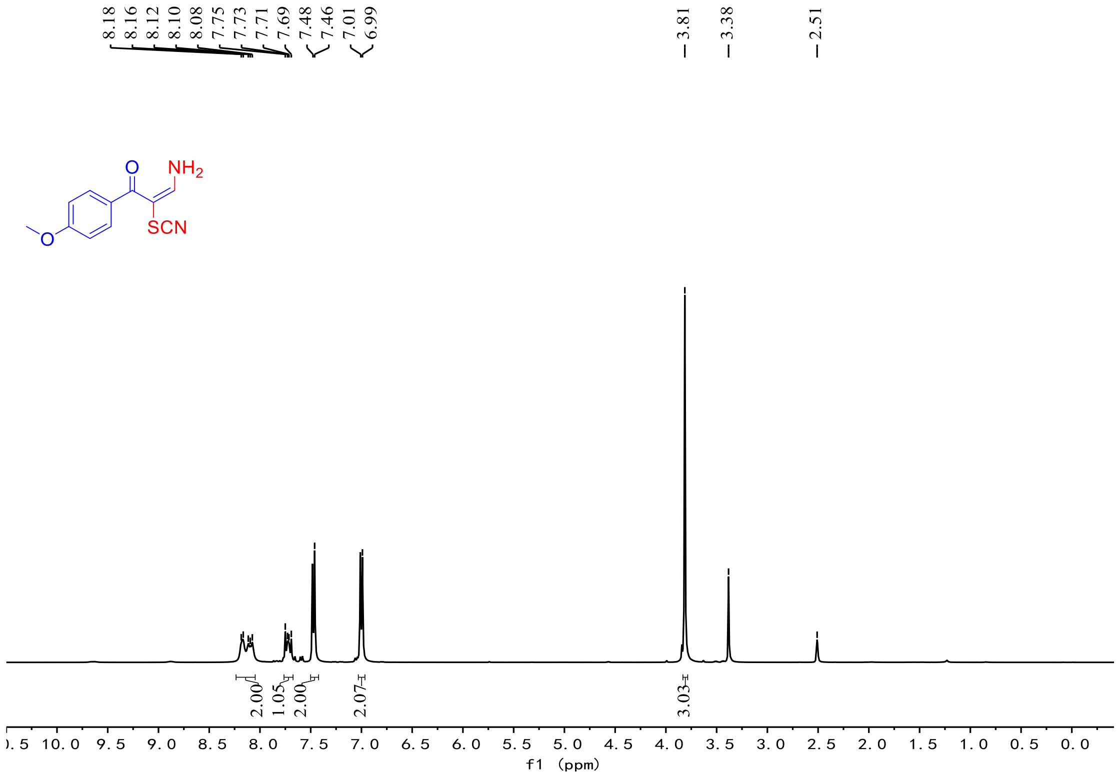
[1]H NMR (400 MHz, DMSO-d_6) of compound **3b**



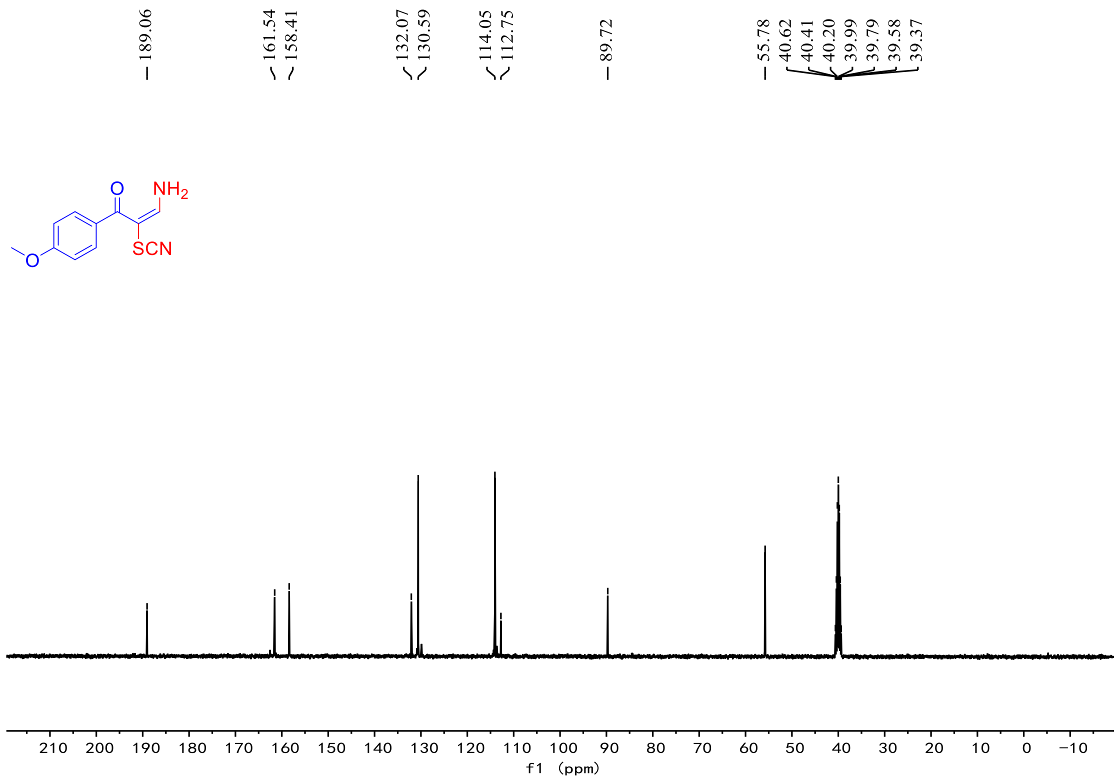
[13]C NMR (101 MHz, DMSO-d_6) of compound **3b**



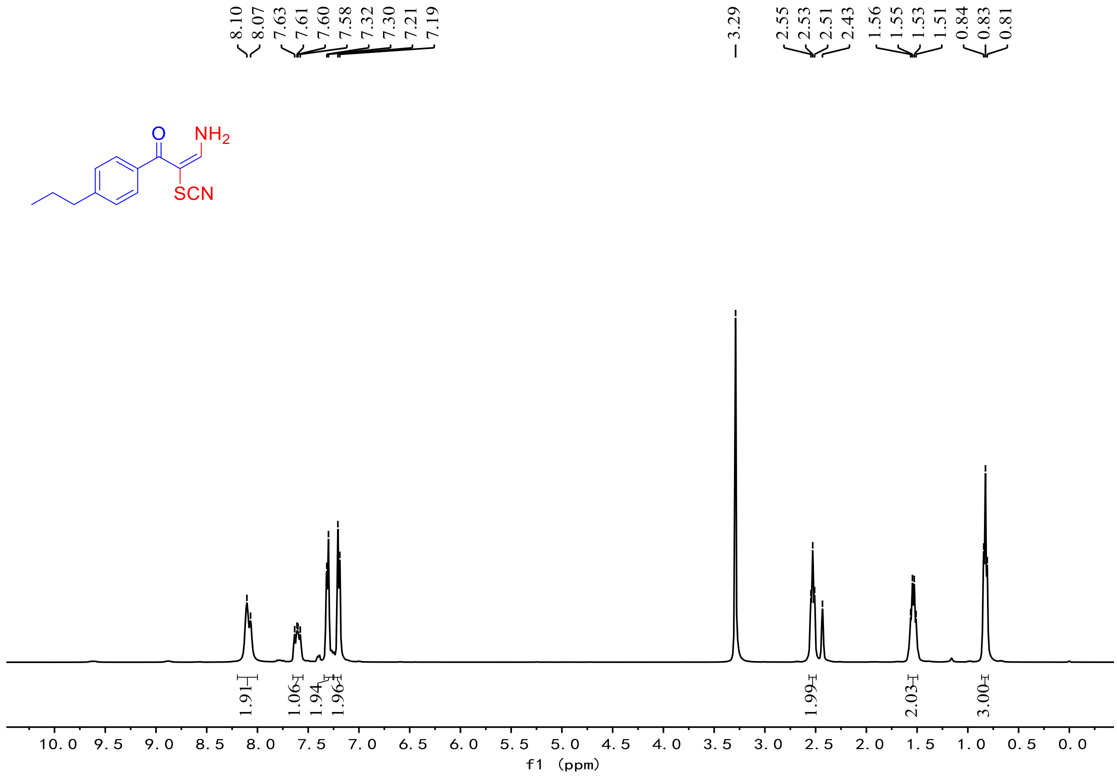
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3c**



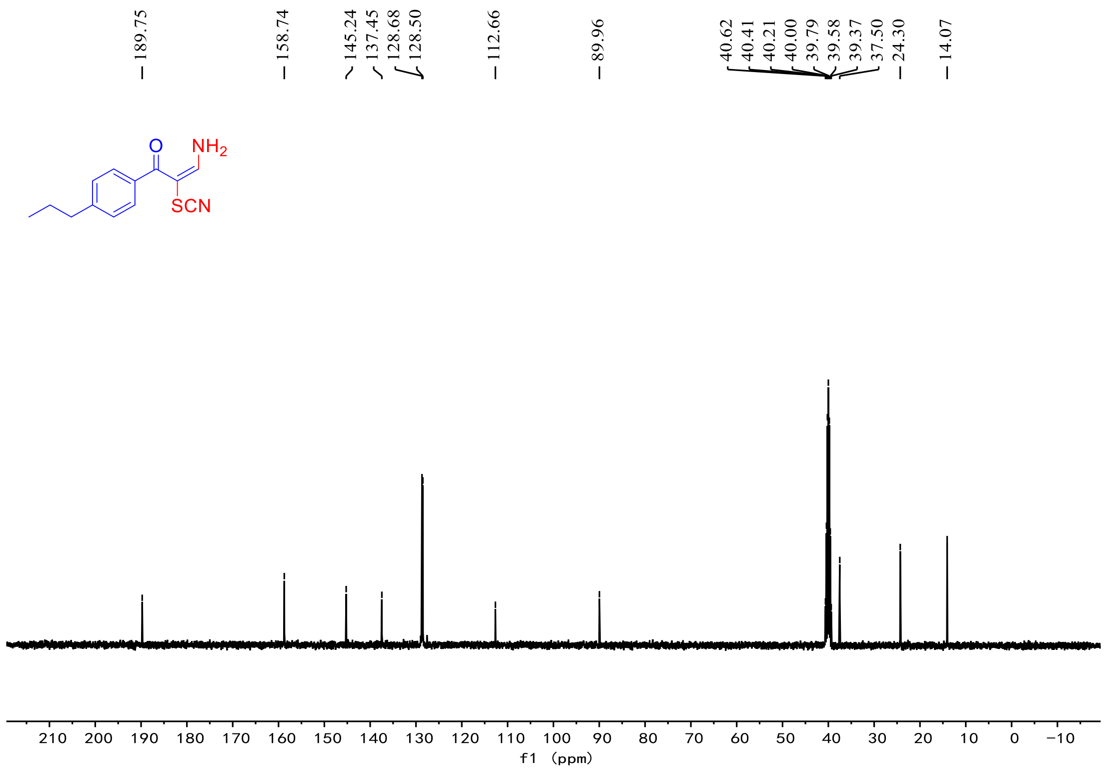
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3c**



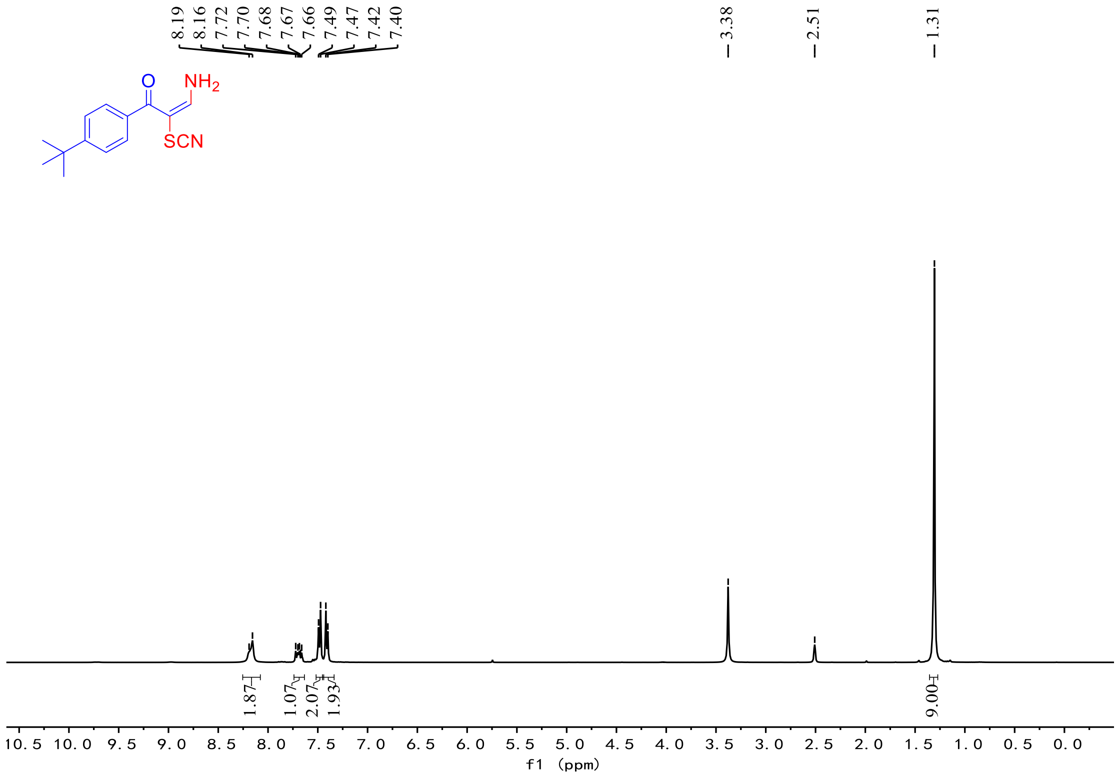
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3d**



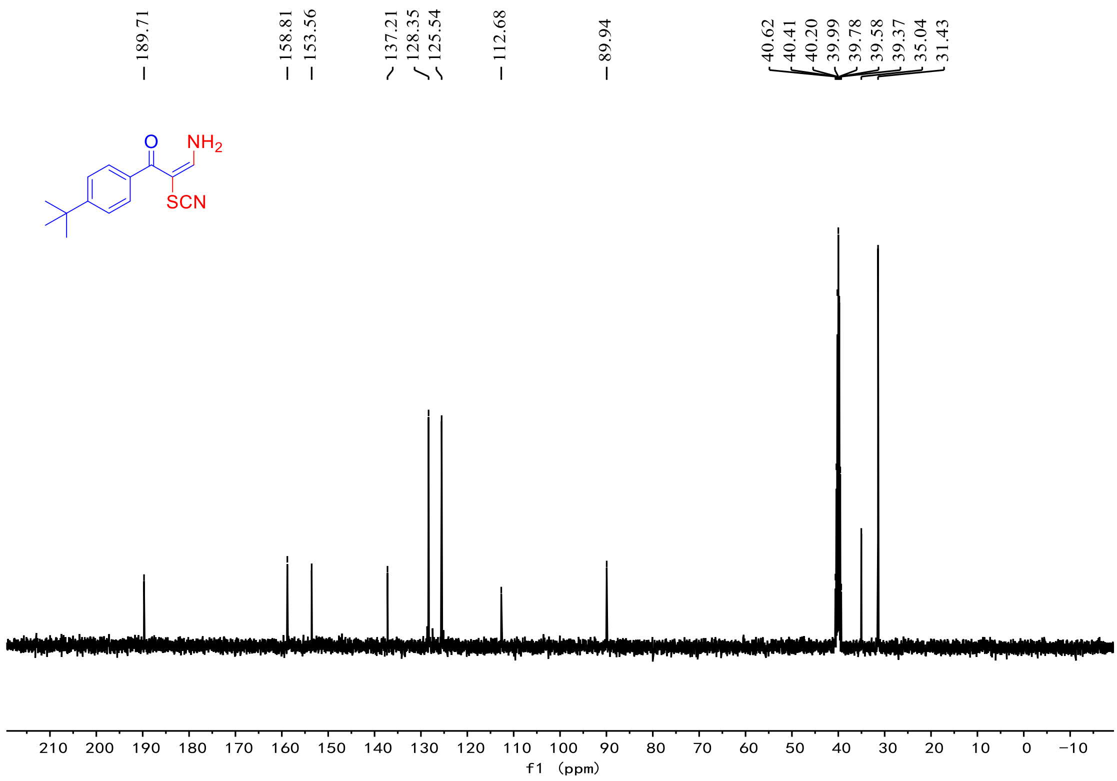
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3d**



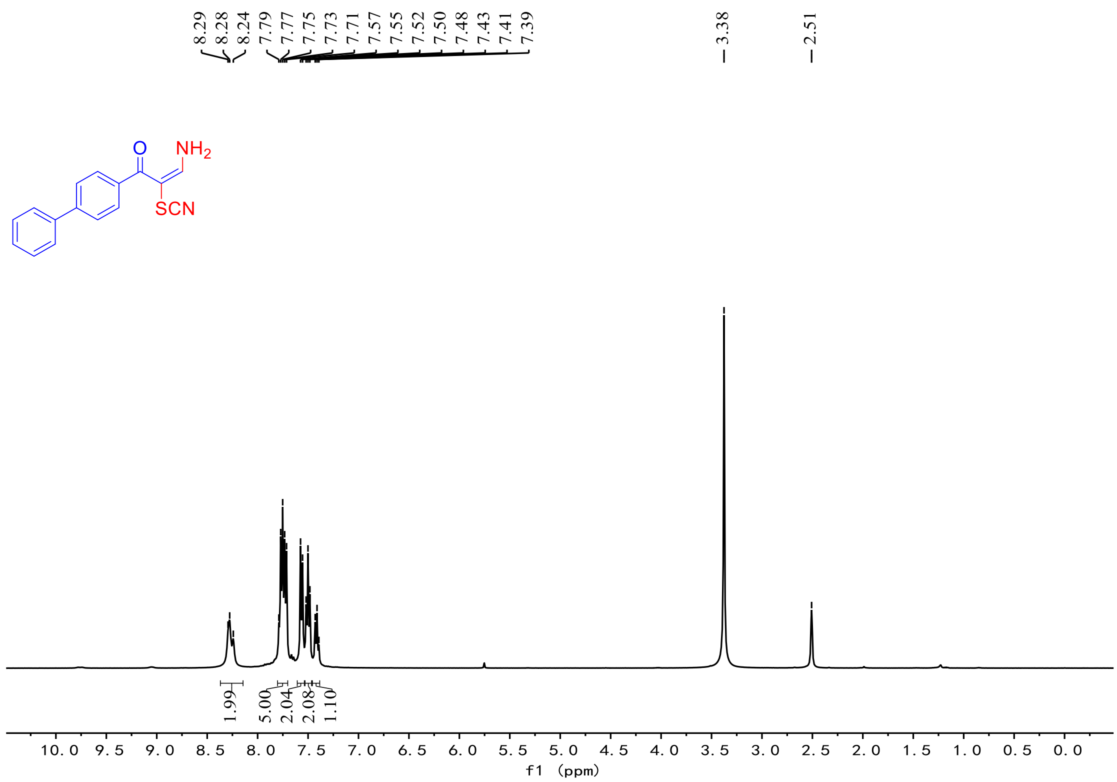
[1]H NMR (400 MHz, DMSO-d_6) of compound **3e**



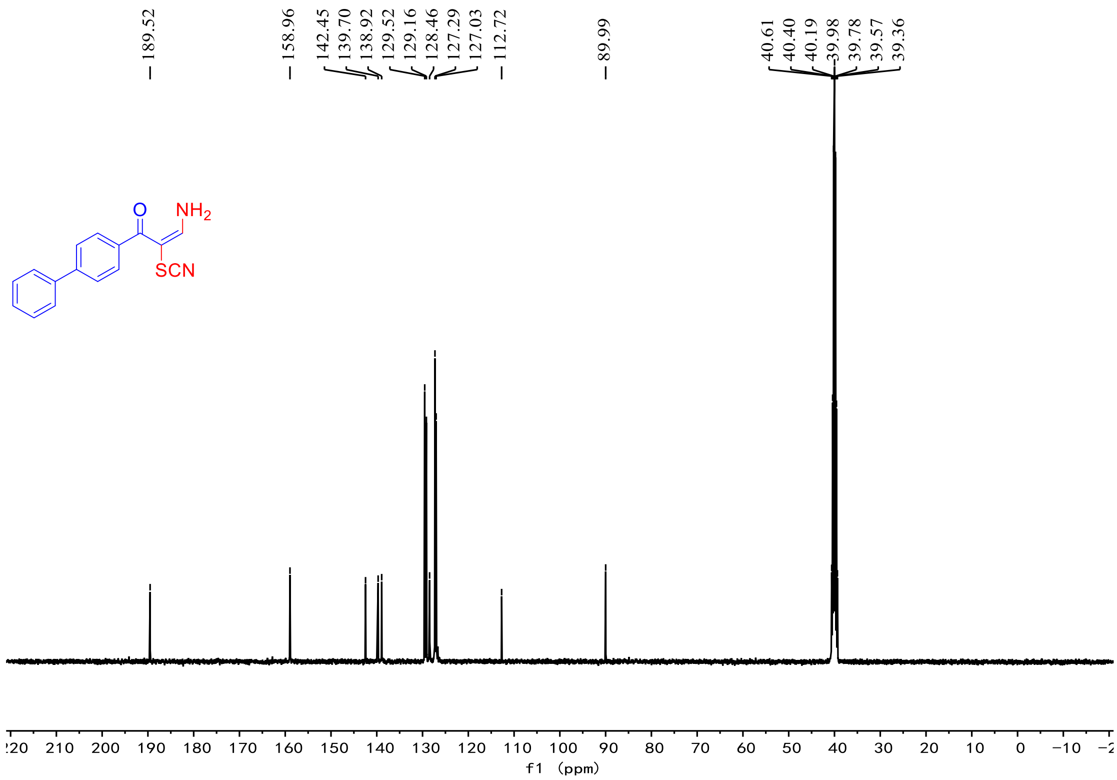
[13]C NMR (101 MHz, DMSO-d_6) of compound **3e**



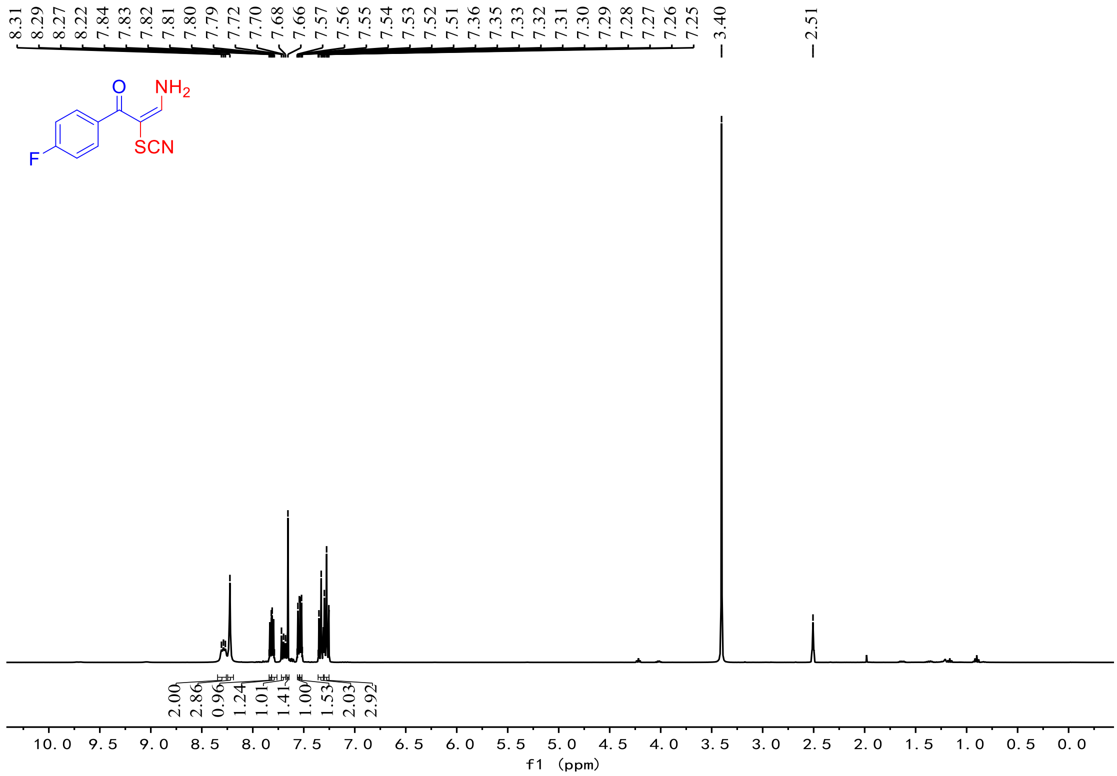
[1]H NMR (400 MHz, DMSO-d_6) of compound **3f**



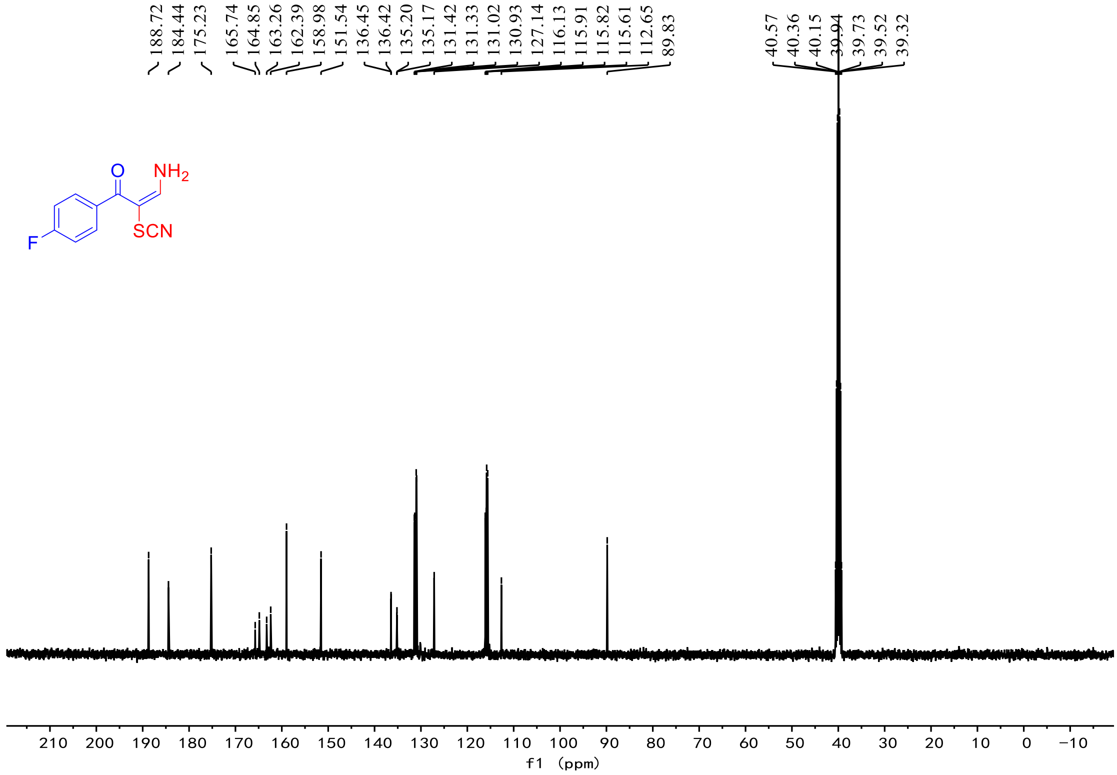
[13]C NMR (400 MHz, DMSO-d_6) of compound **3f**



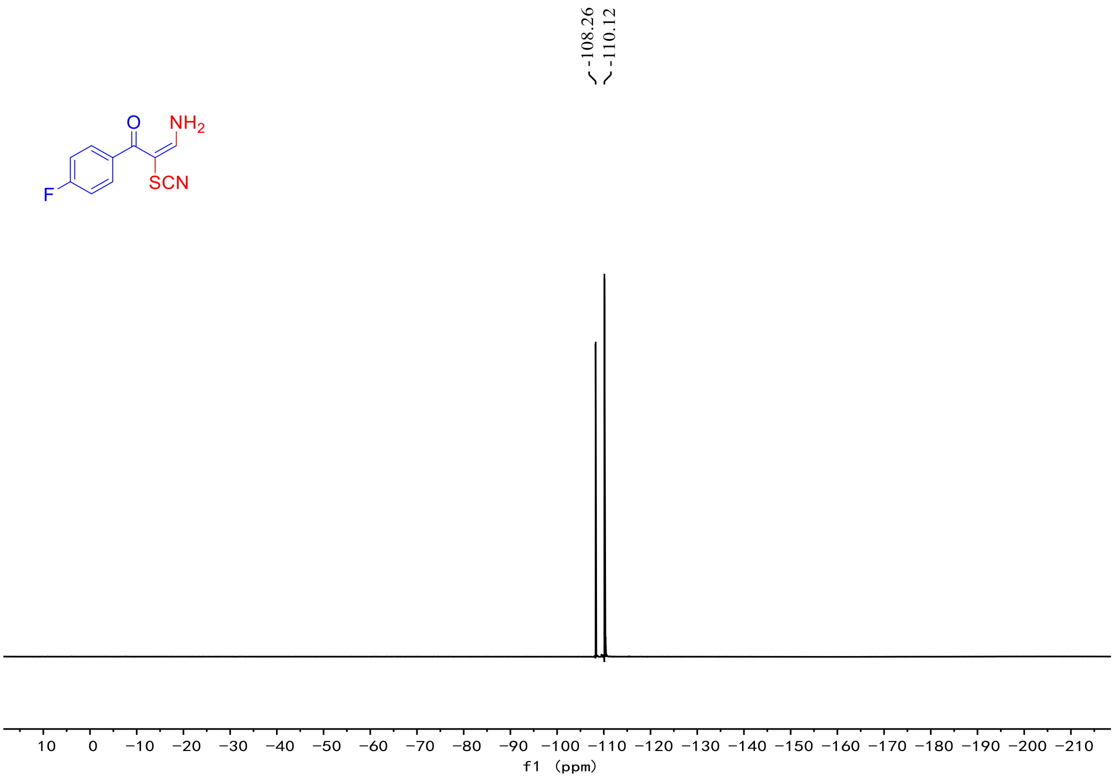
[1]H NMR (400 MHz, DMSO-d_6) of compound **3g**



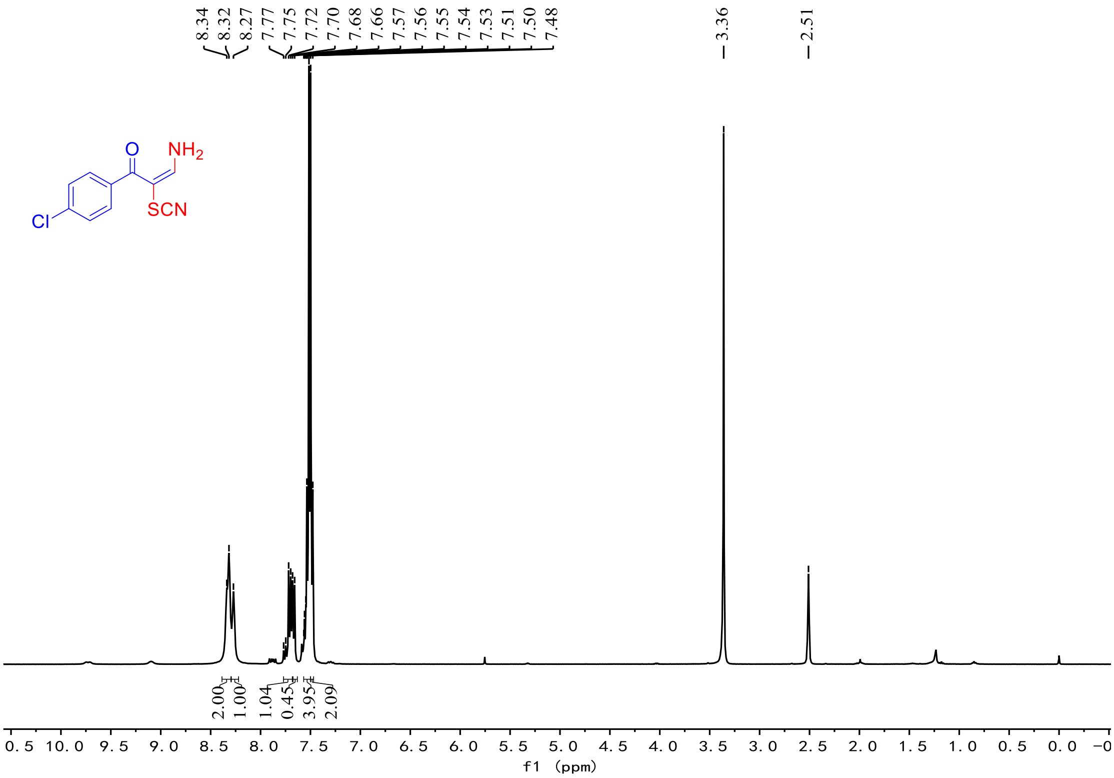
[13]C NMR (101 MHz, DMSO-d_6) of compound **3g**



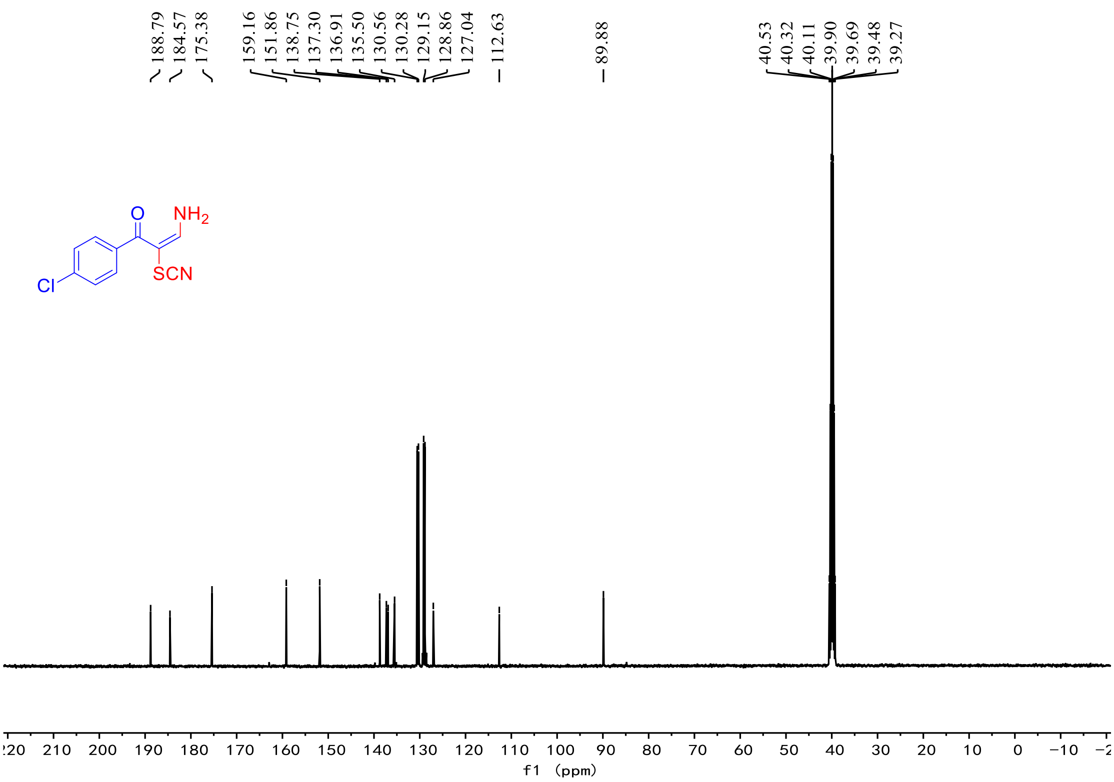
^{19}F NMR (376 MHz, DMSO-d_6) of compound **3g**



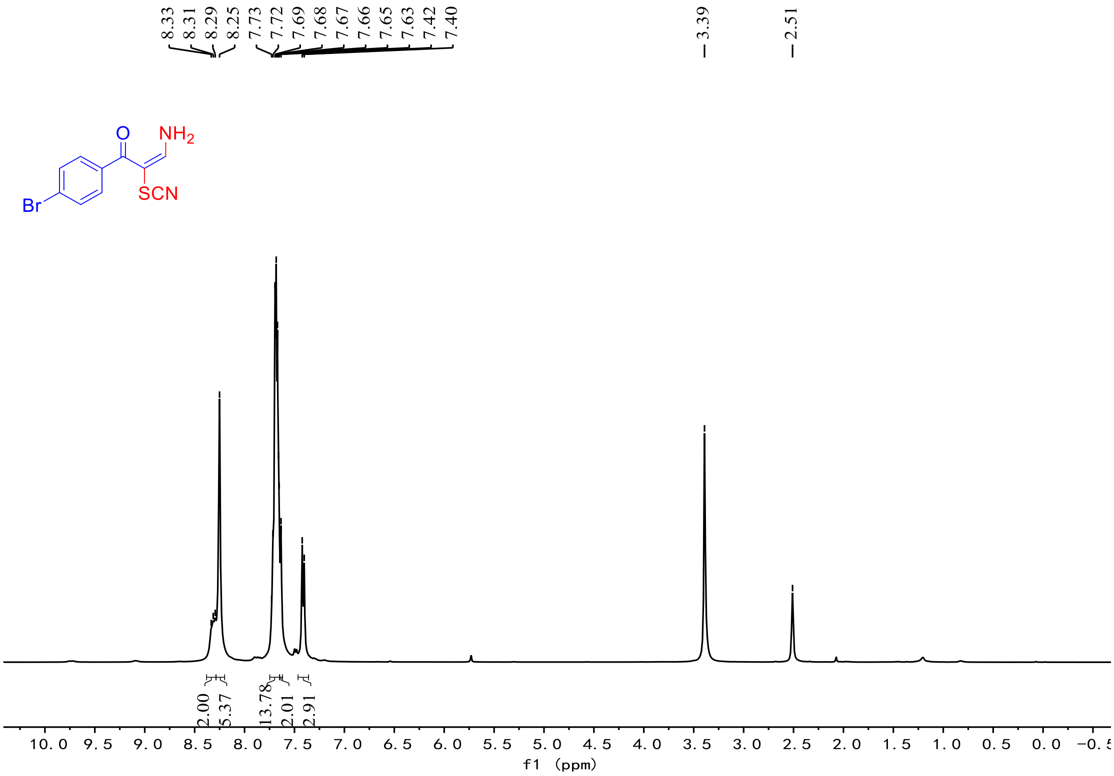
[1]H NMR (400 MHz, DMSO-d_6) of compound **3h**



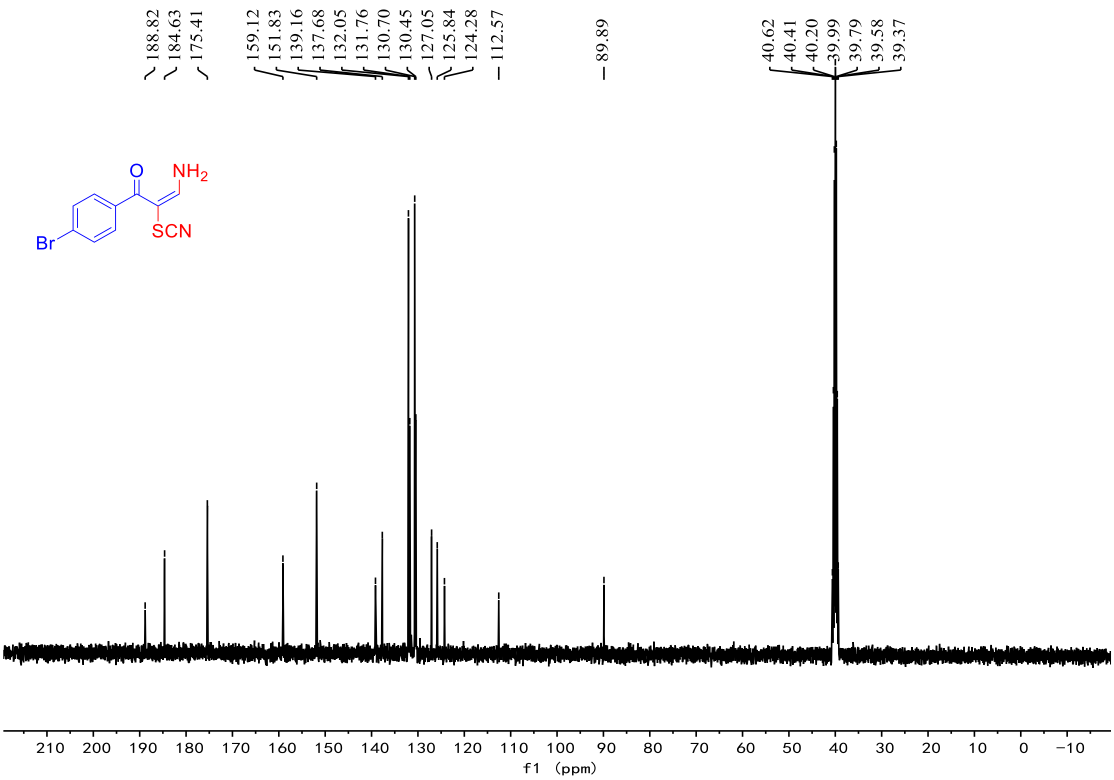
[13]C NMR (101 MHz, DMSO-d_6) of compound **3h**



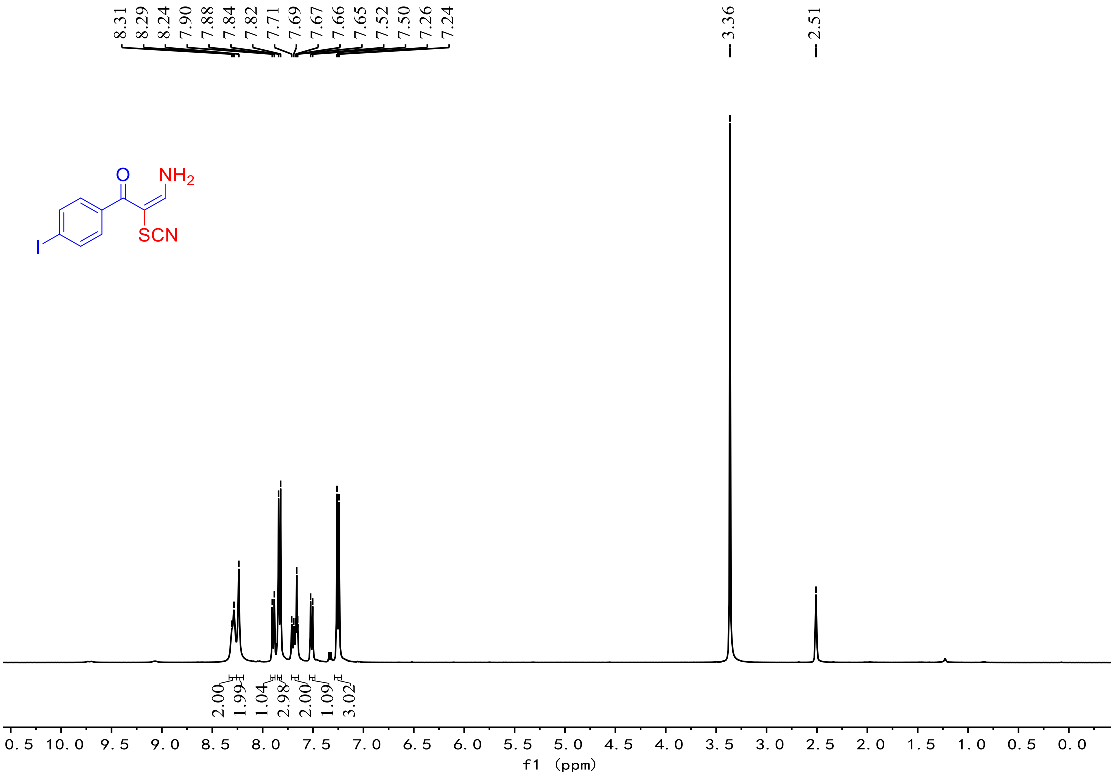
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3i**



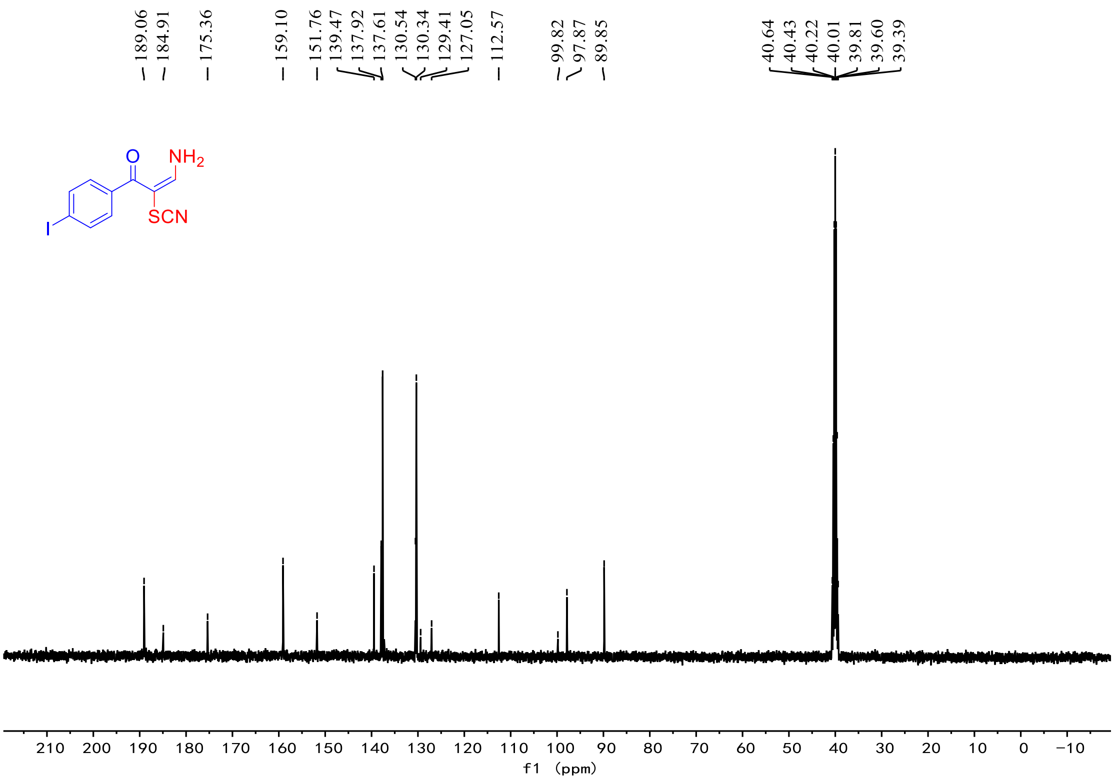
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3i**



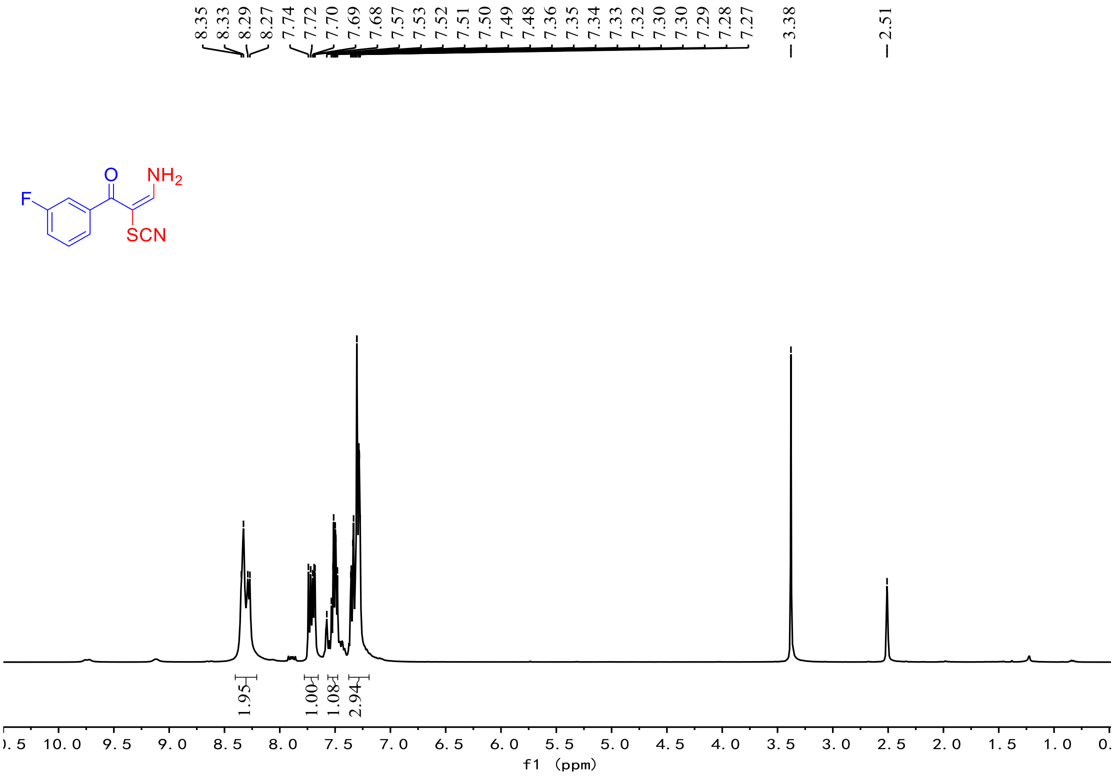
^1H NMR (400 MHz, DMSO-d_6) of compound **3j**



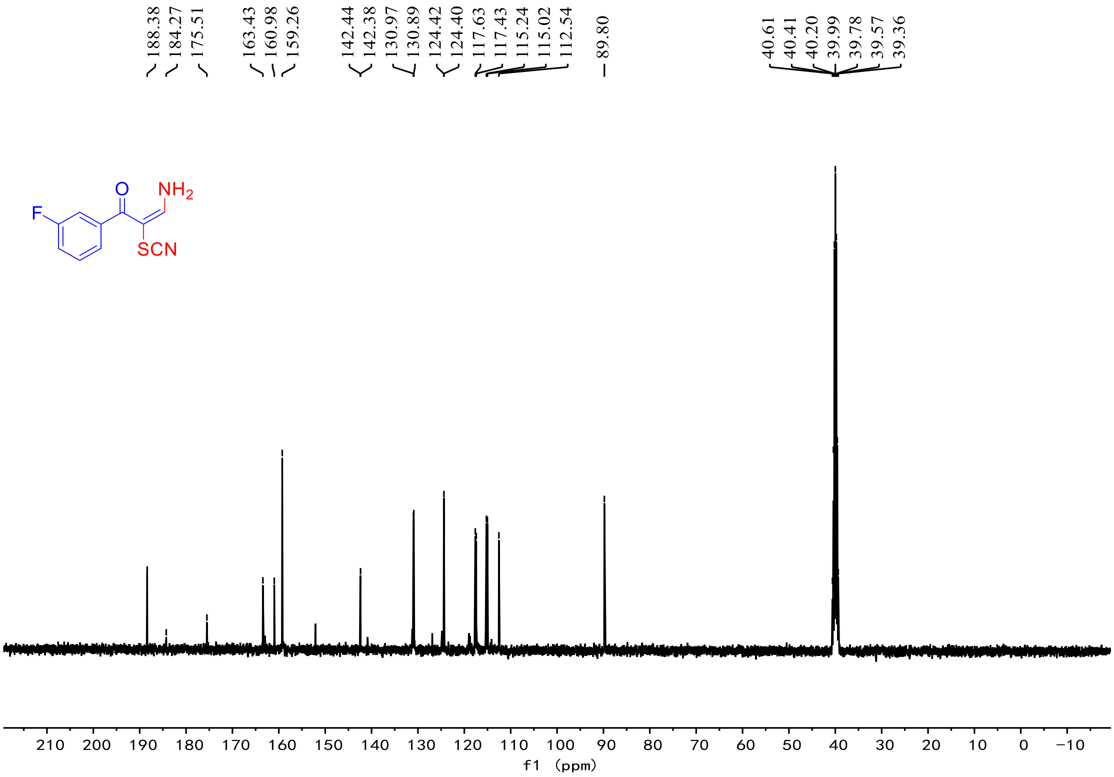
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3j**



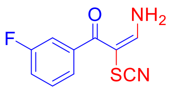
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3k**



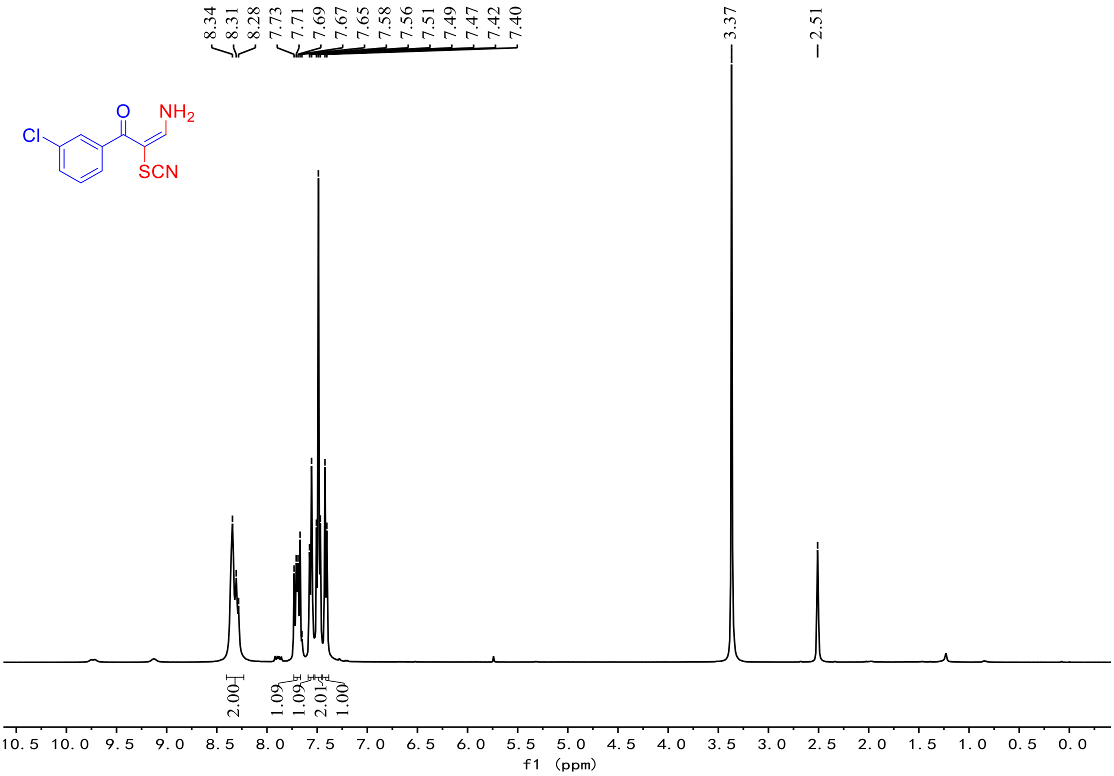
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3k**



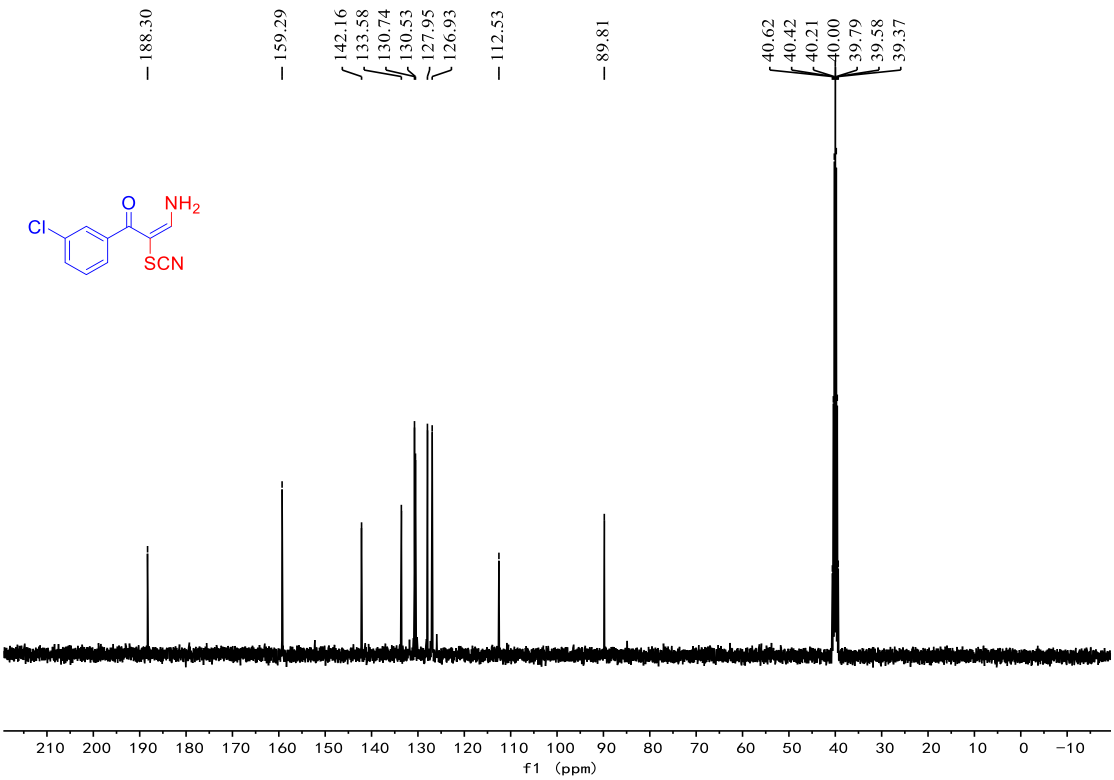
[19]F NMR (376 MHz, DMSO-d_6) of compound **3k**



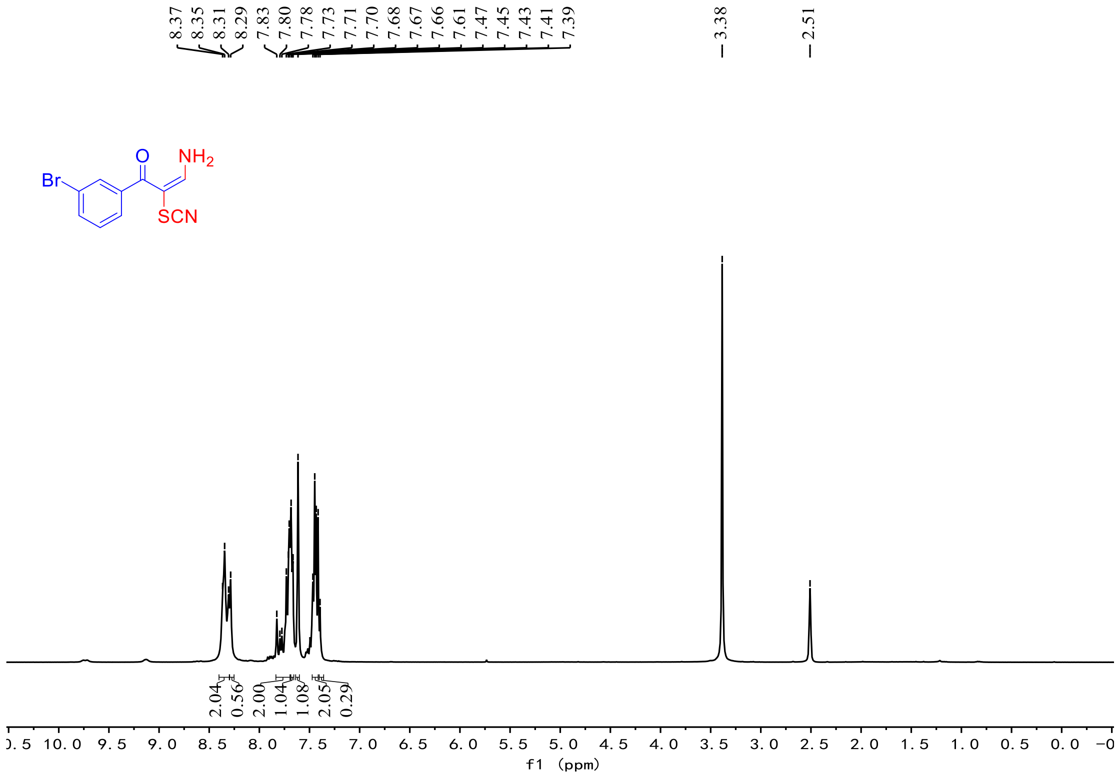
[1]H NMR (400 MHz, DMSO-d_6) of compound **3l**



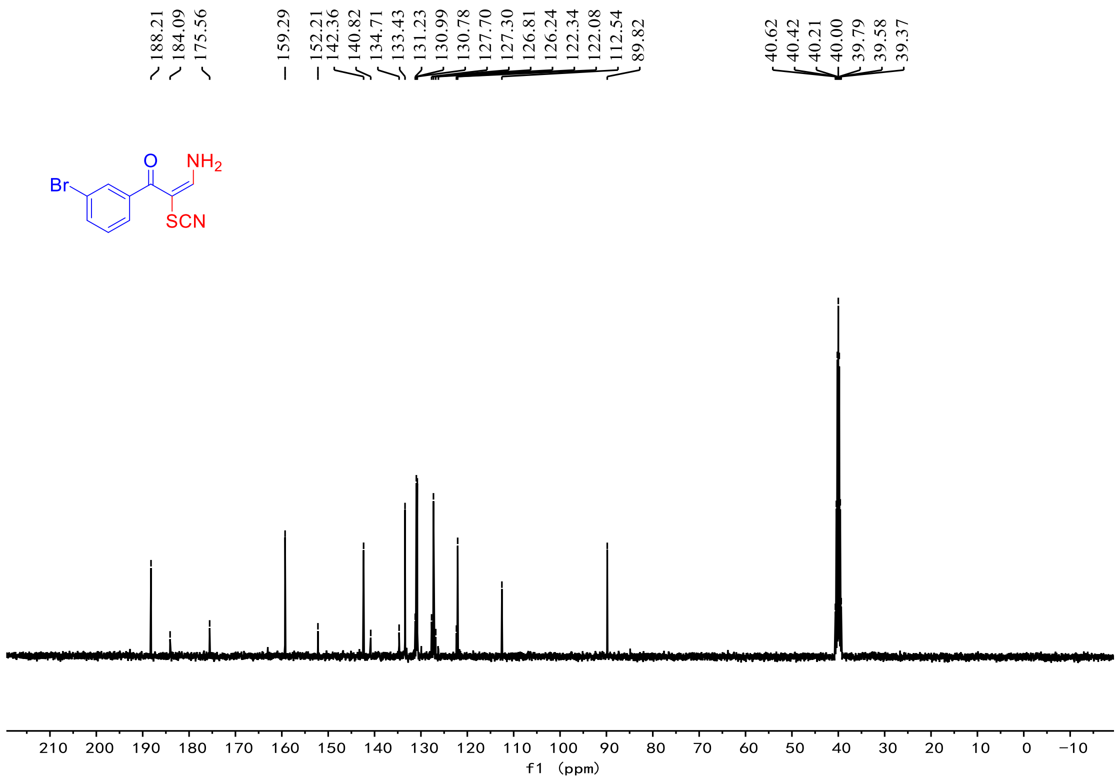
[13]C NMR (101 MHz, DMSO-d_6) of compound **3l**



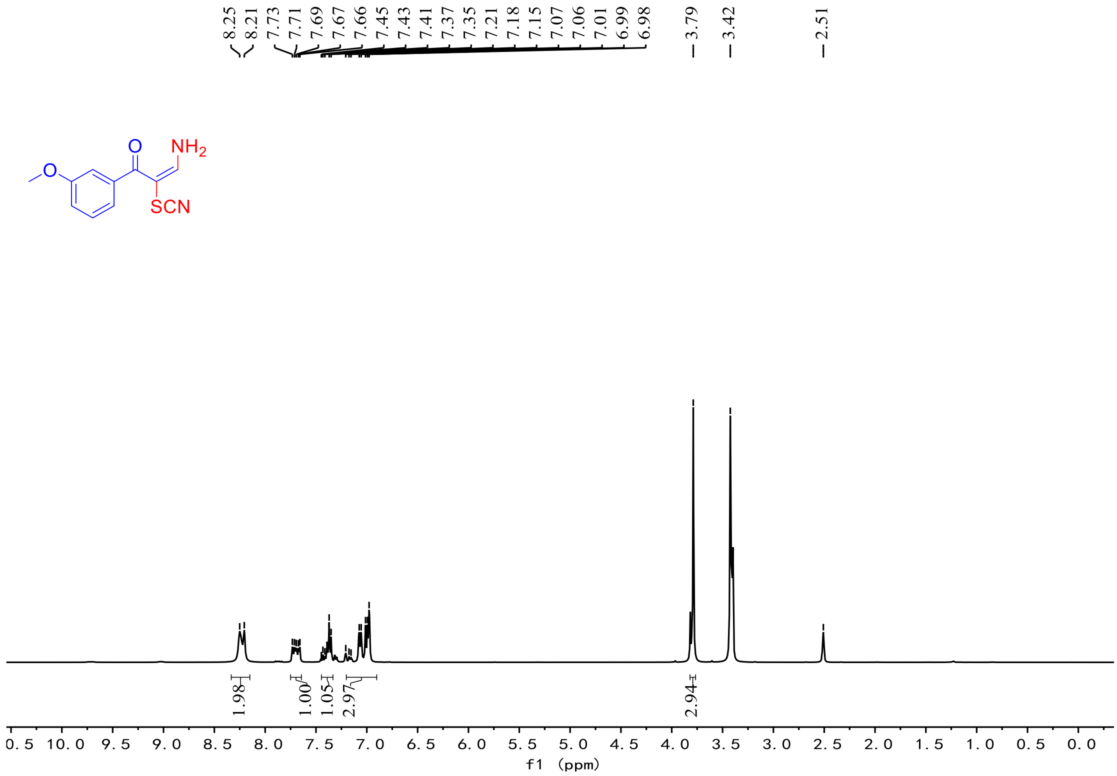
[1]H NMR (400 MHz, DMSO-d_6) of compound **3m**



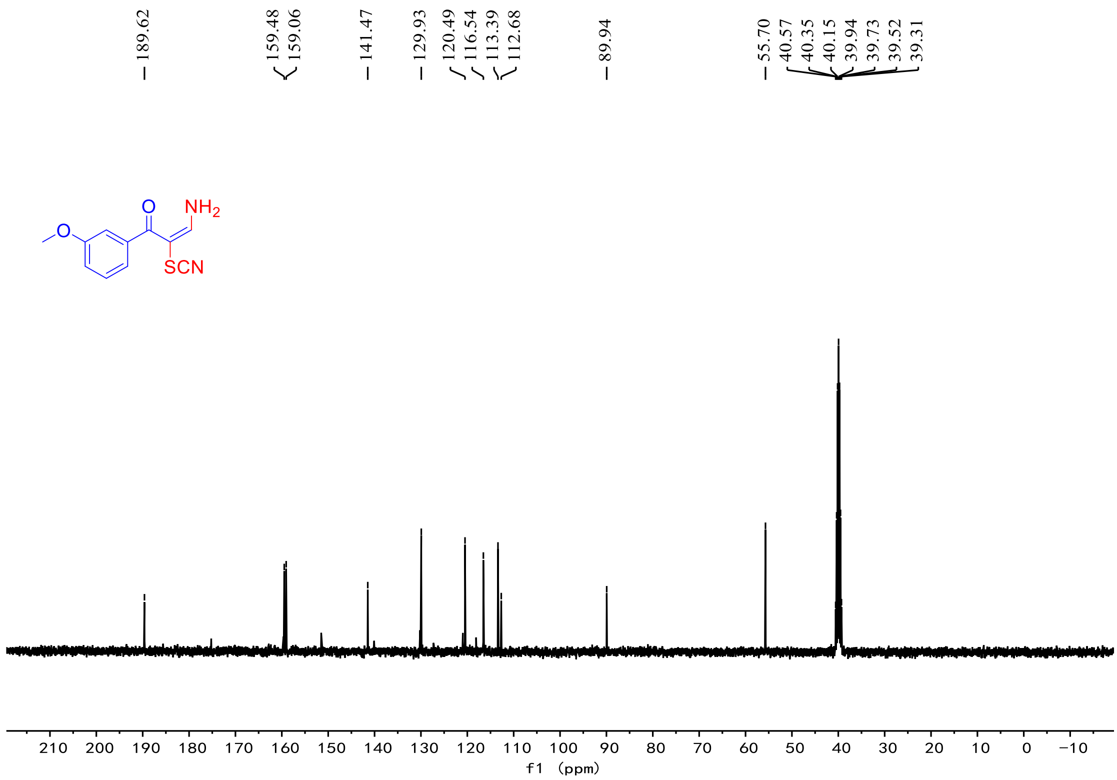
[13]C NMR (101 MHz, DMSO-d_6) of compound **3m**



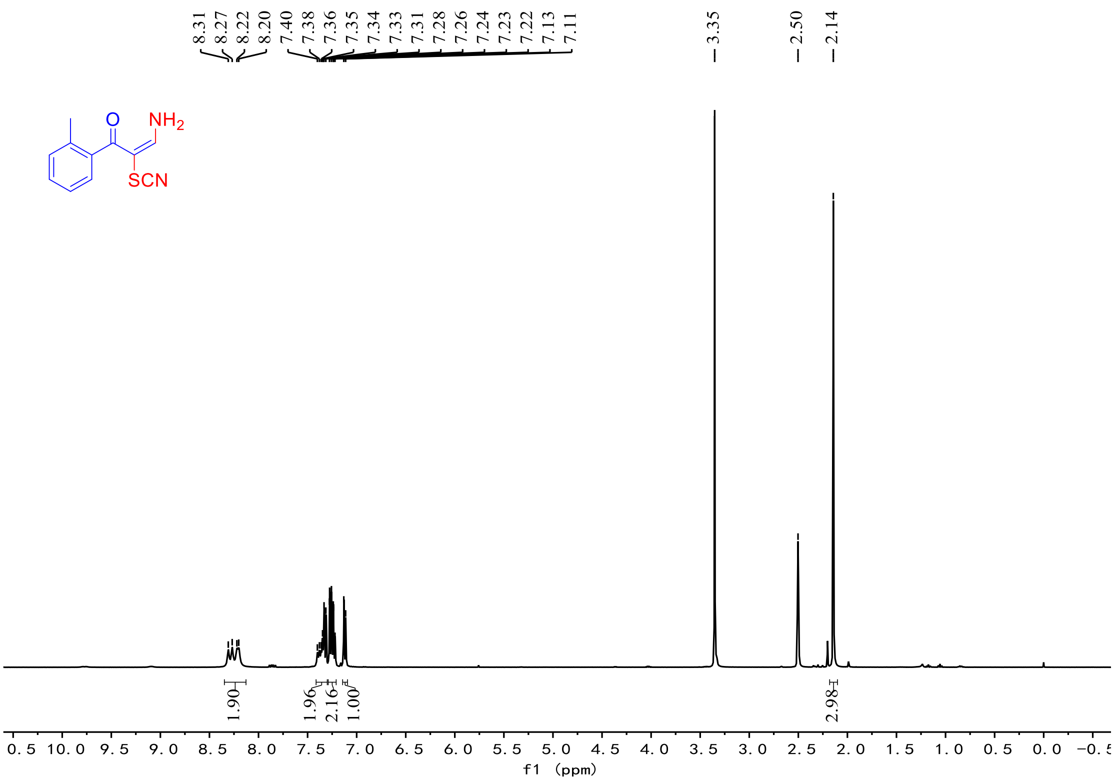
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3n**



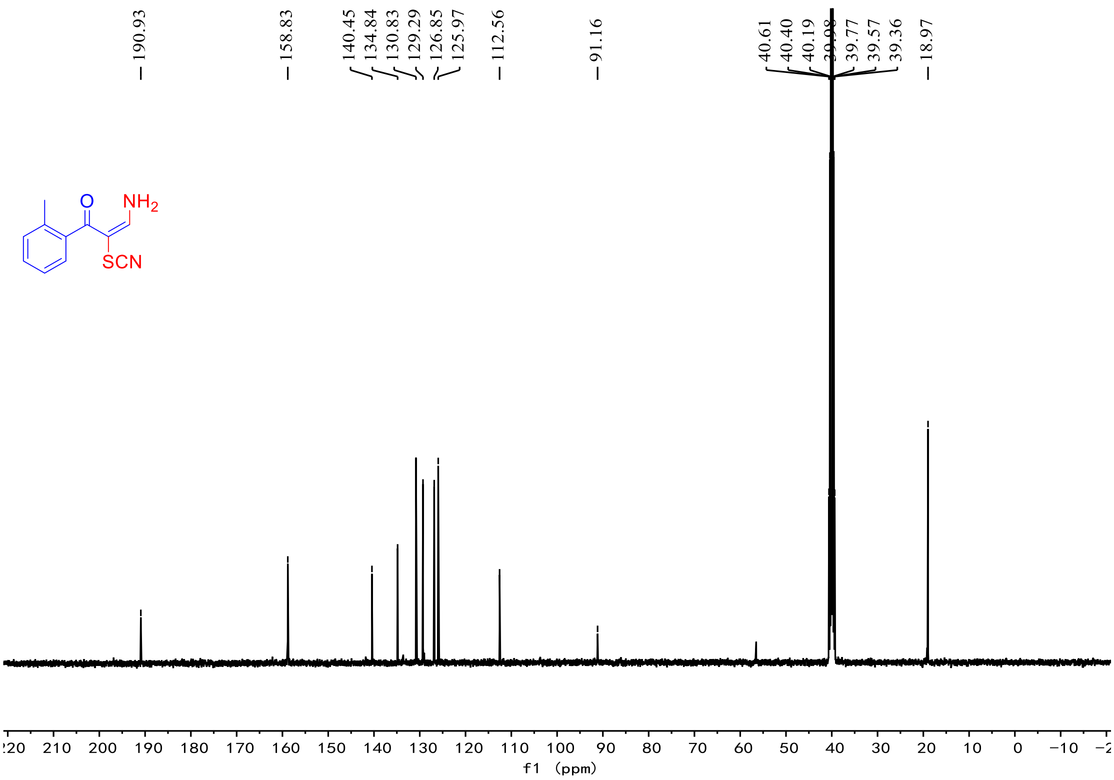
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3n**



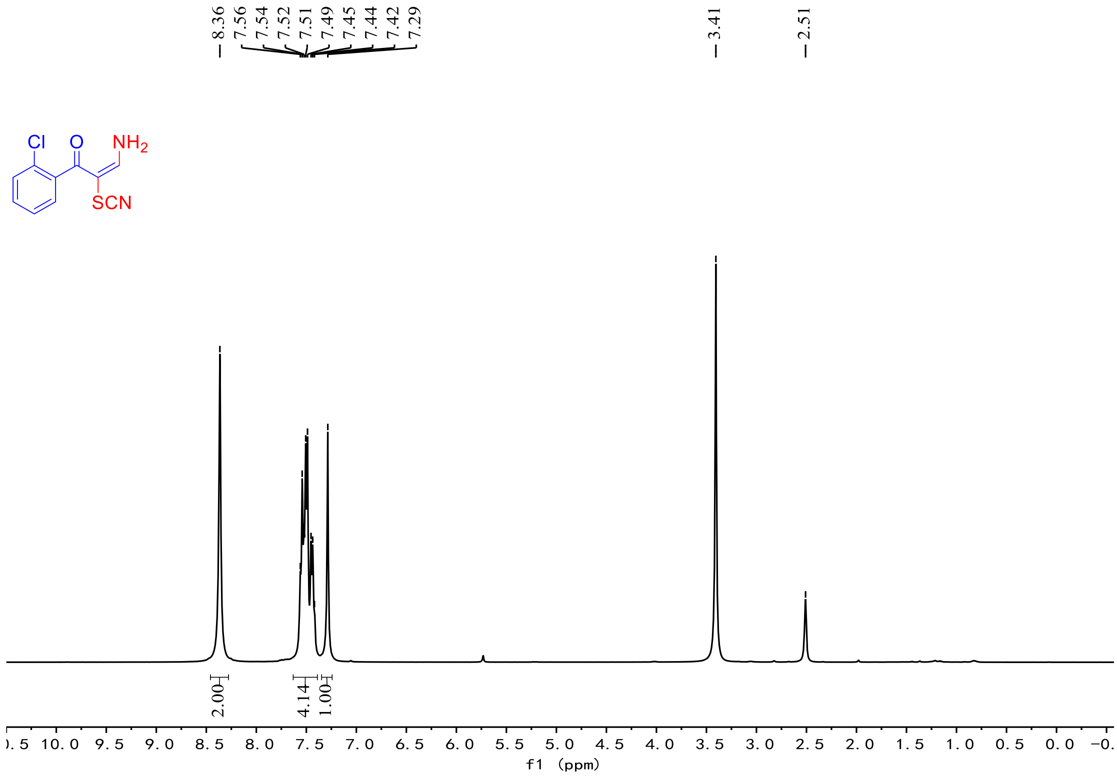
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3o**



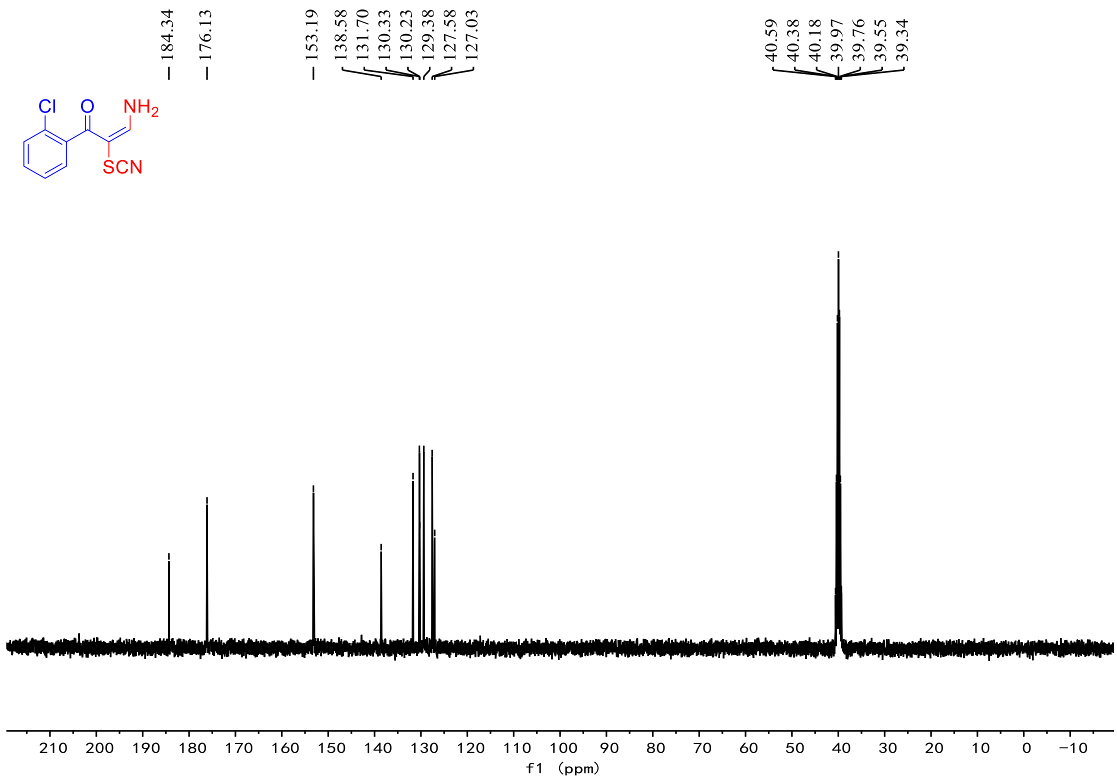
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3o**



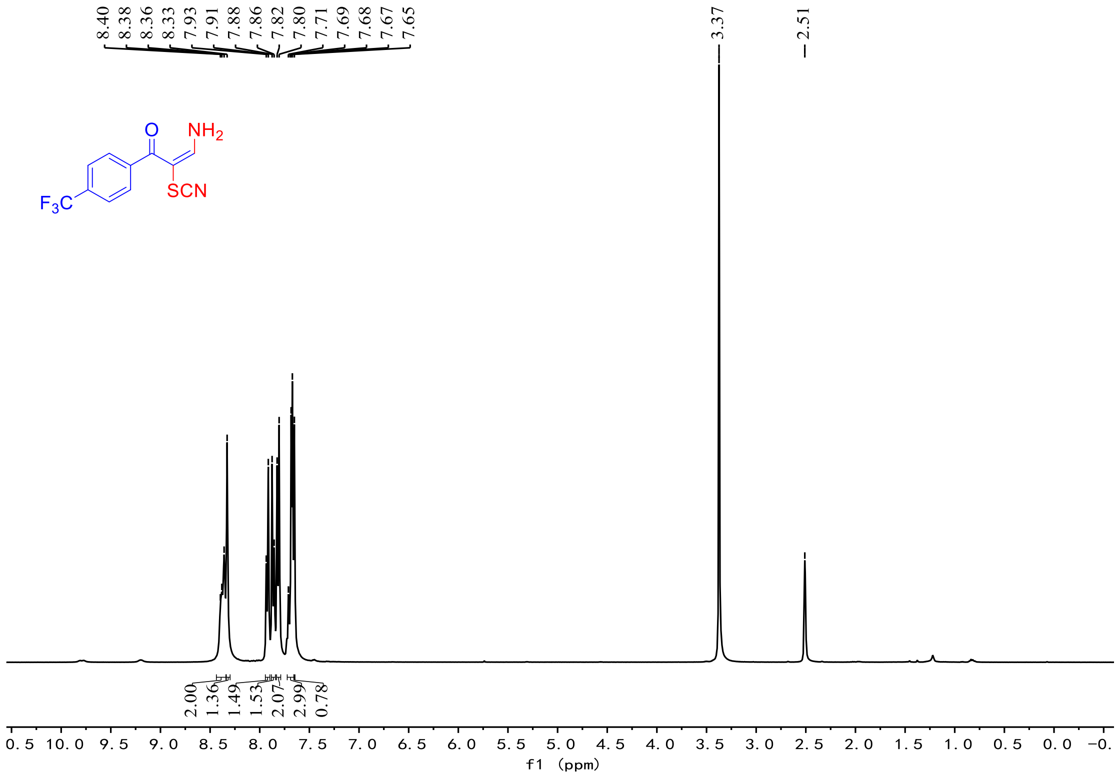
[1]H NMR (400 MHz, DMSO-d_6) of compound **3p**



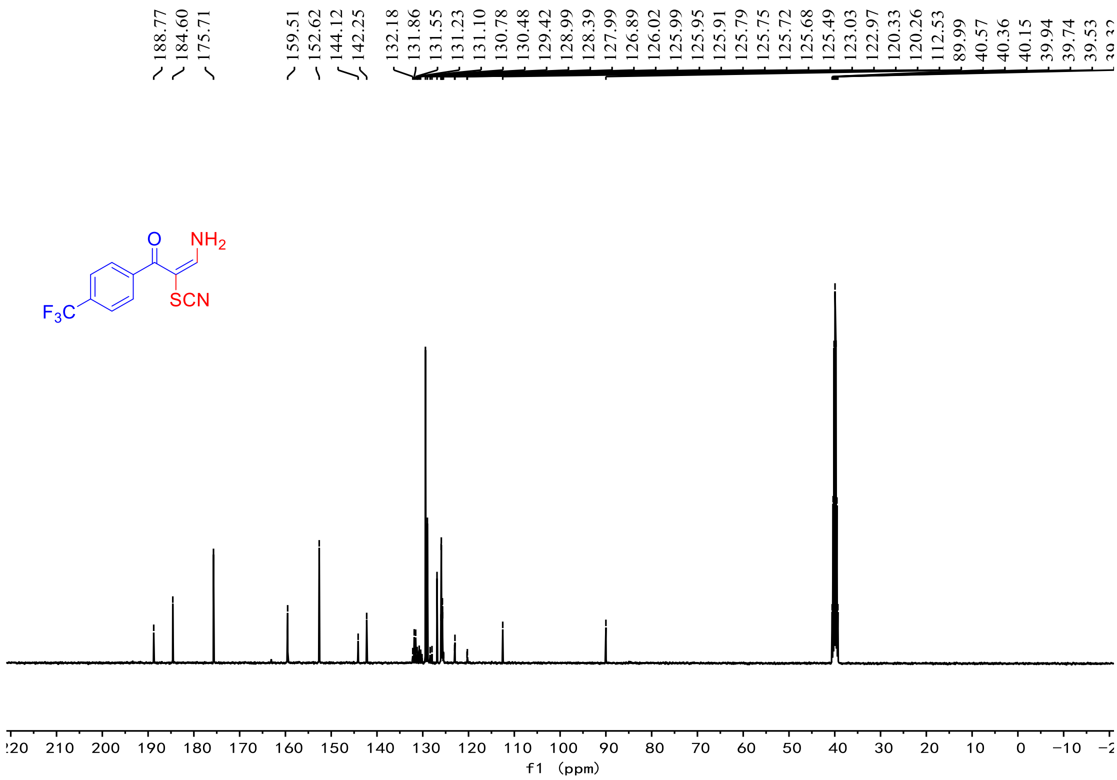
[13]C NMR (101 MHz, DMSO-d_6) of compound **3p**



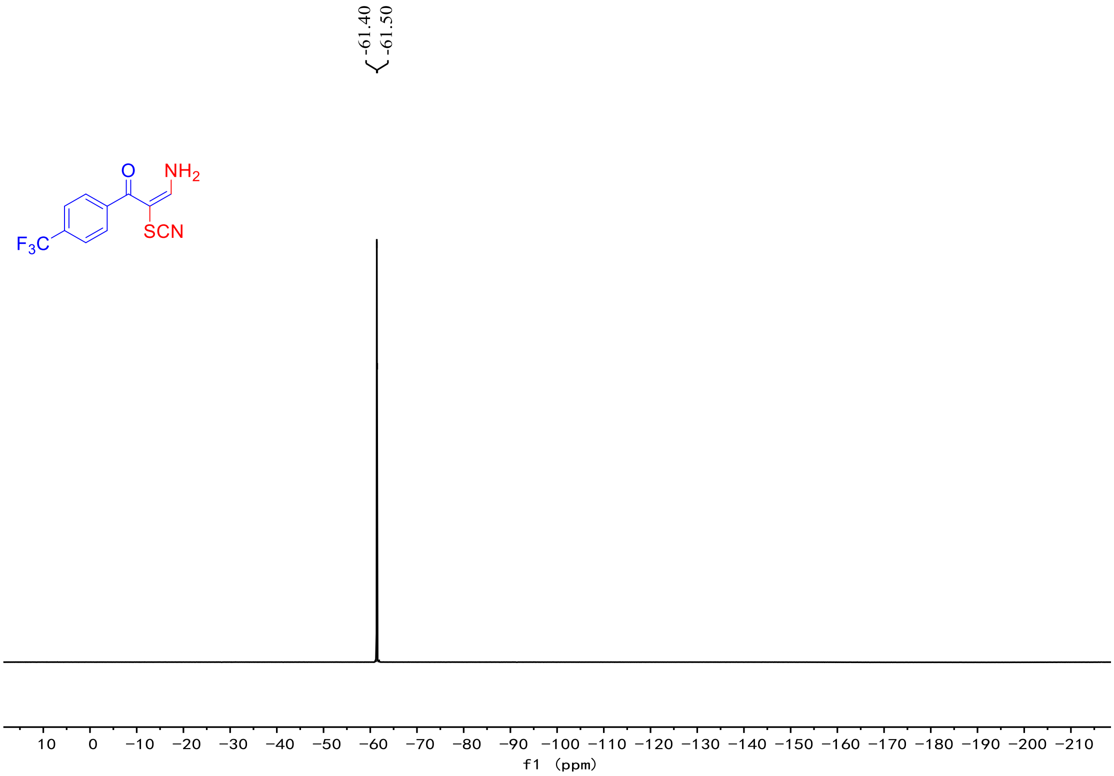
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3q**



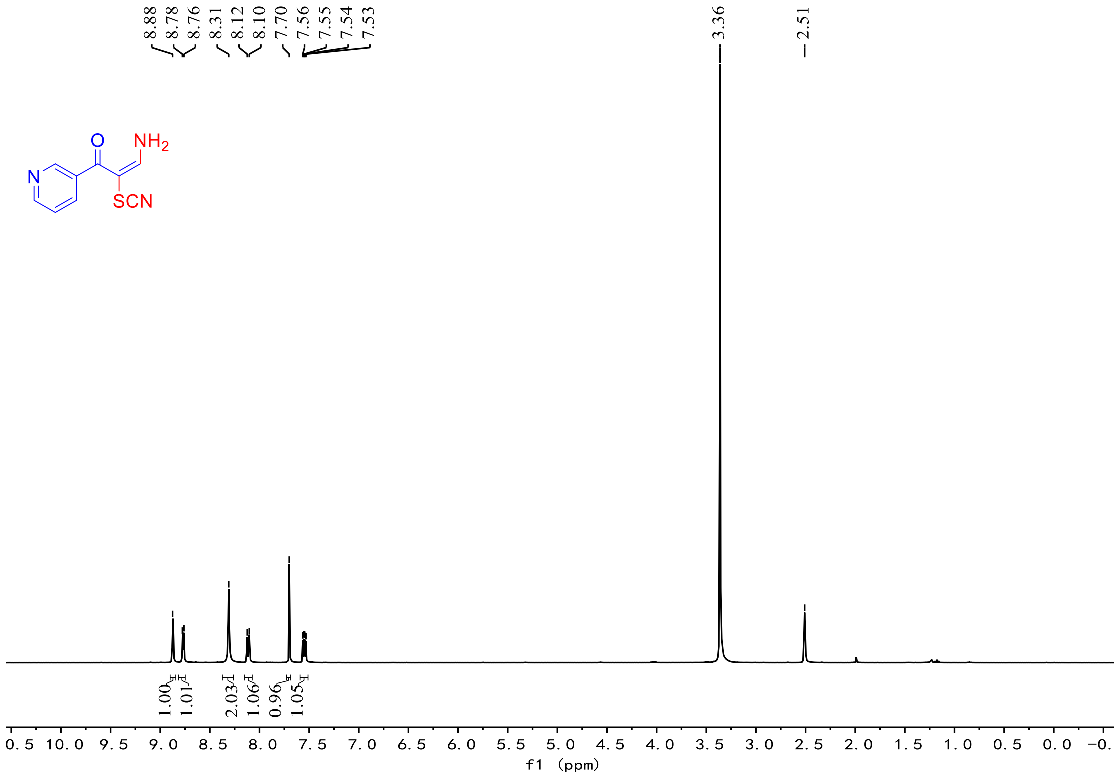
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3q**



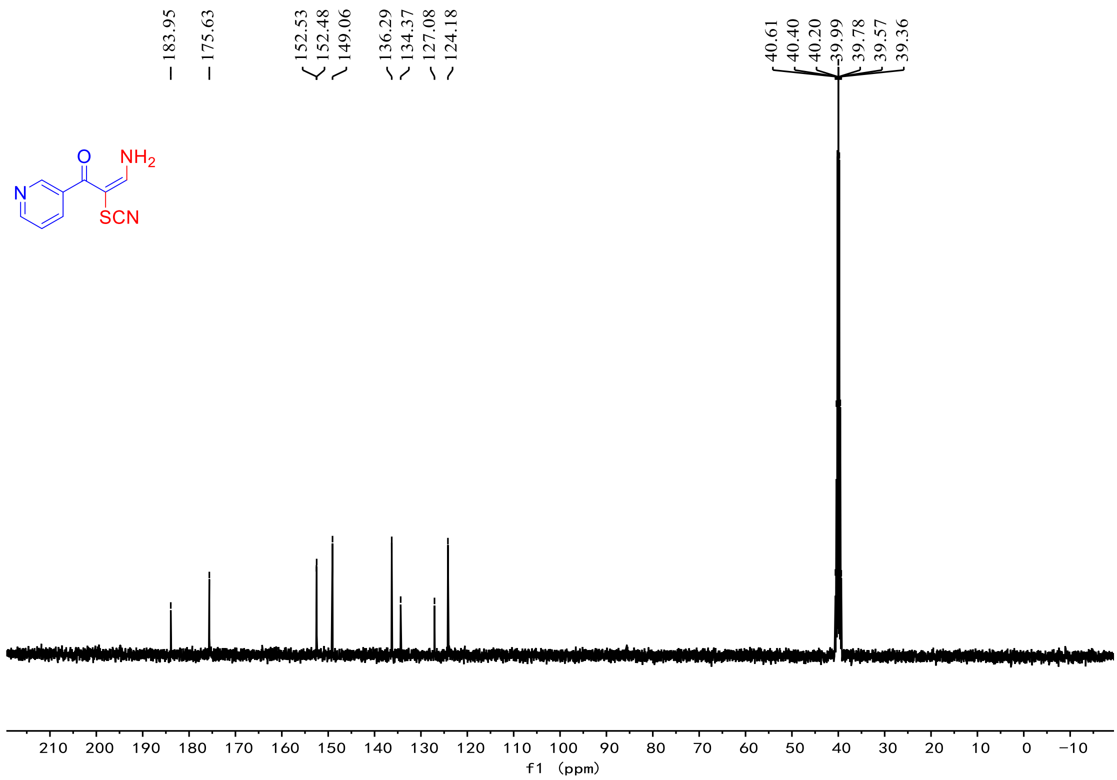
^{19}F NMR (376 MHz, DMSO-d_6) of compound **3q**



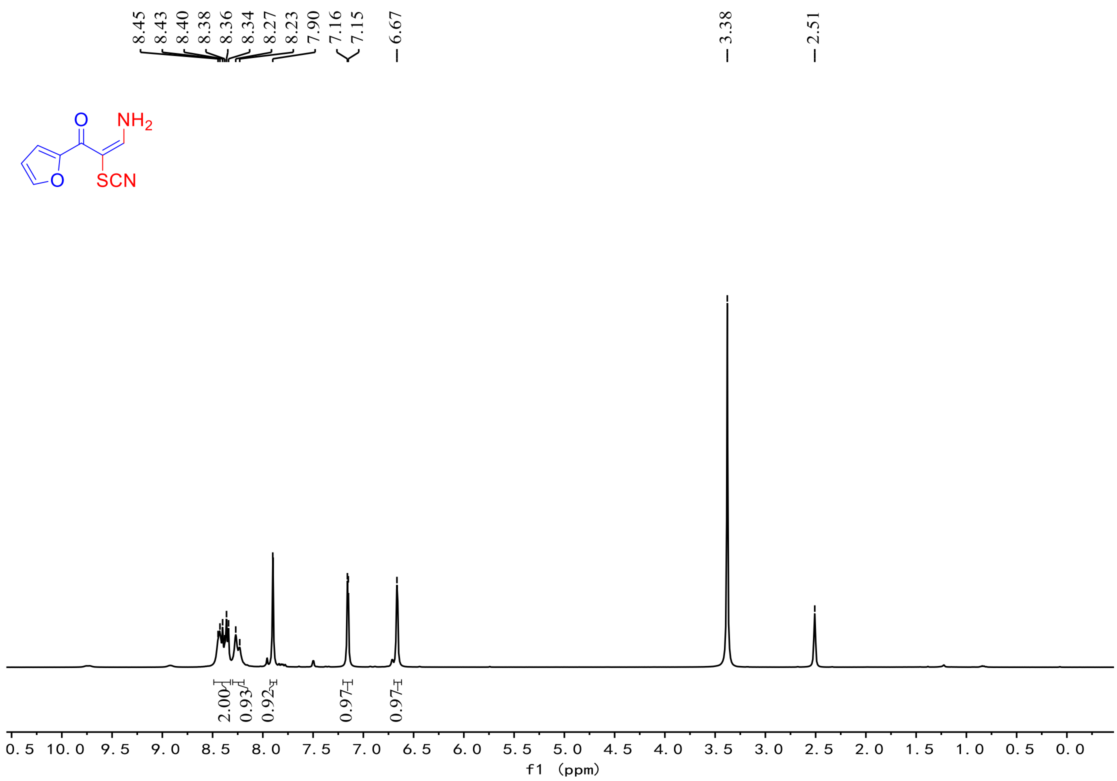
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3r**



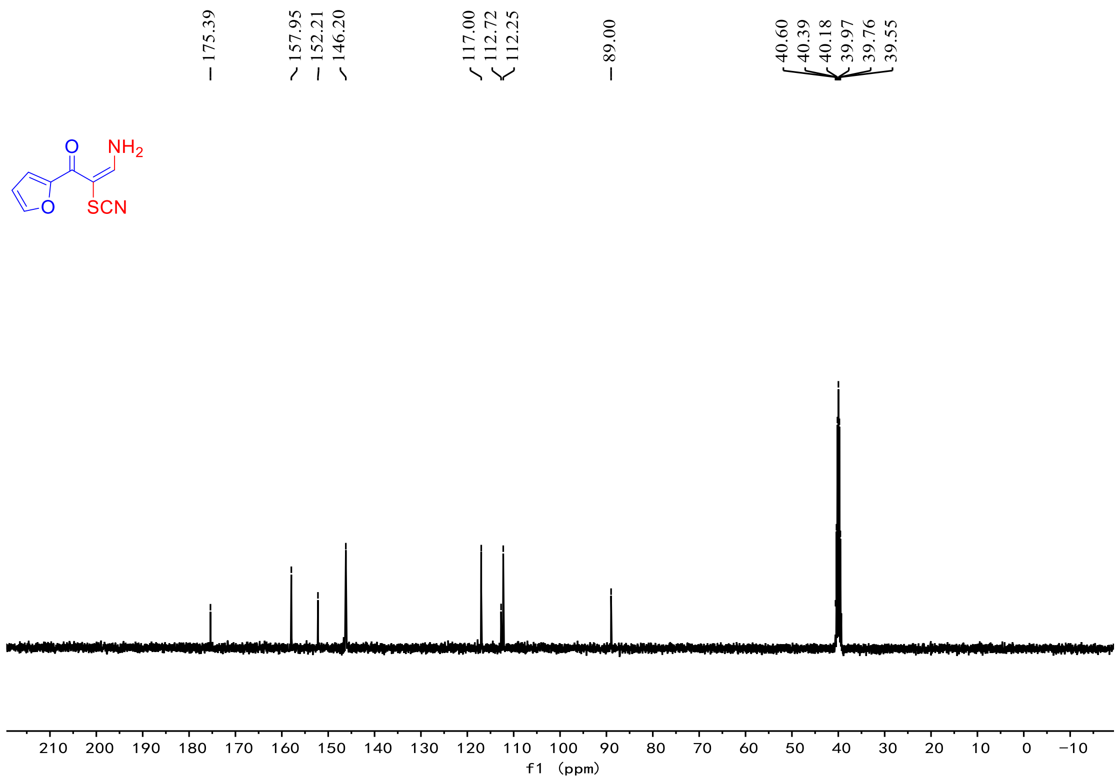
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3r**



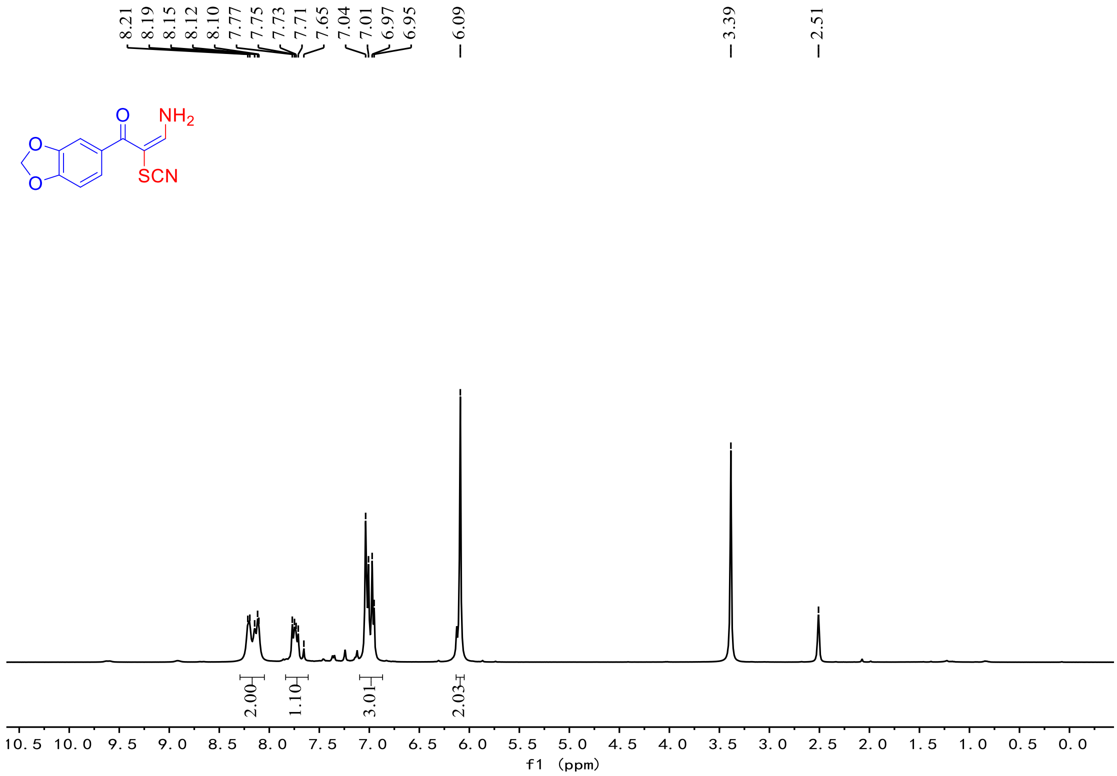
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3s**



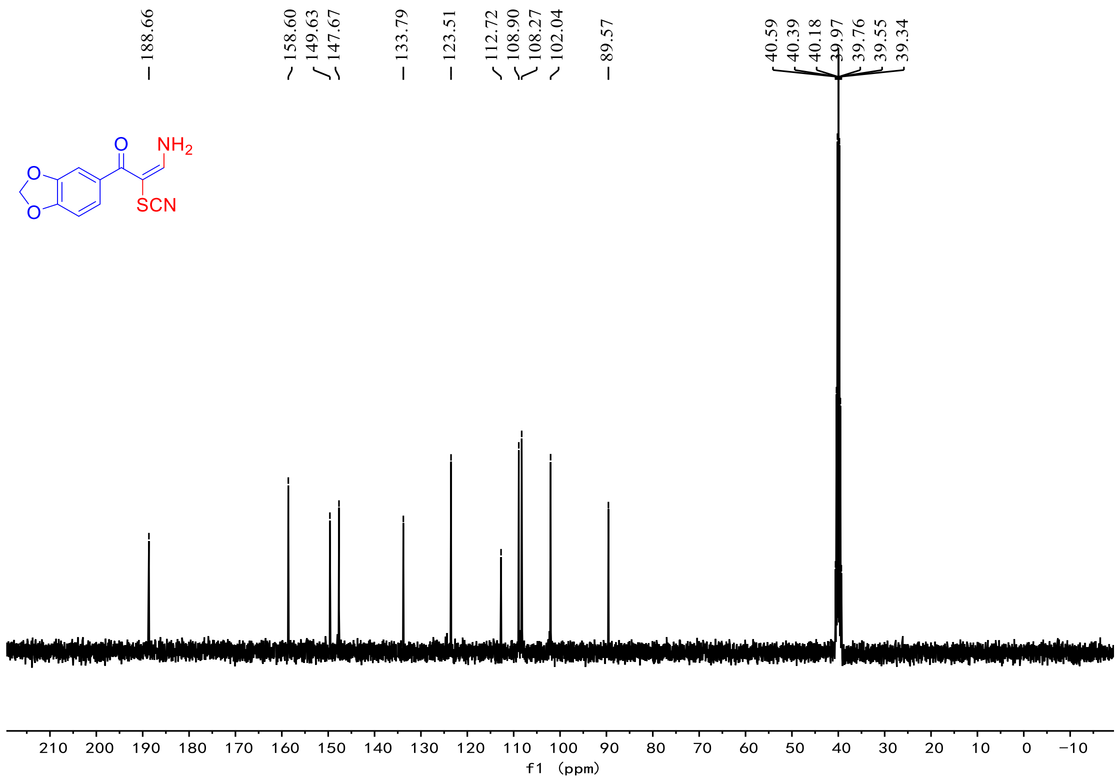
^{13}C NMR (101 MHz, DMSO-d_6) of compound **3s**



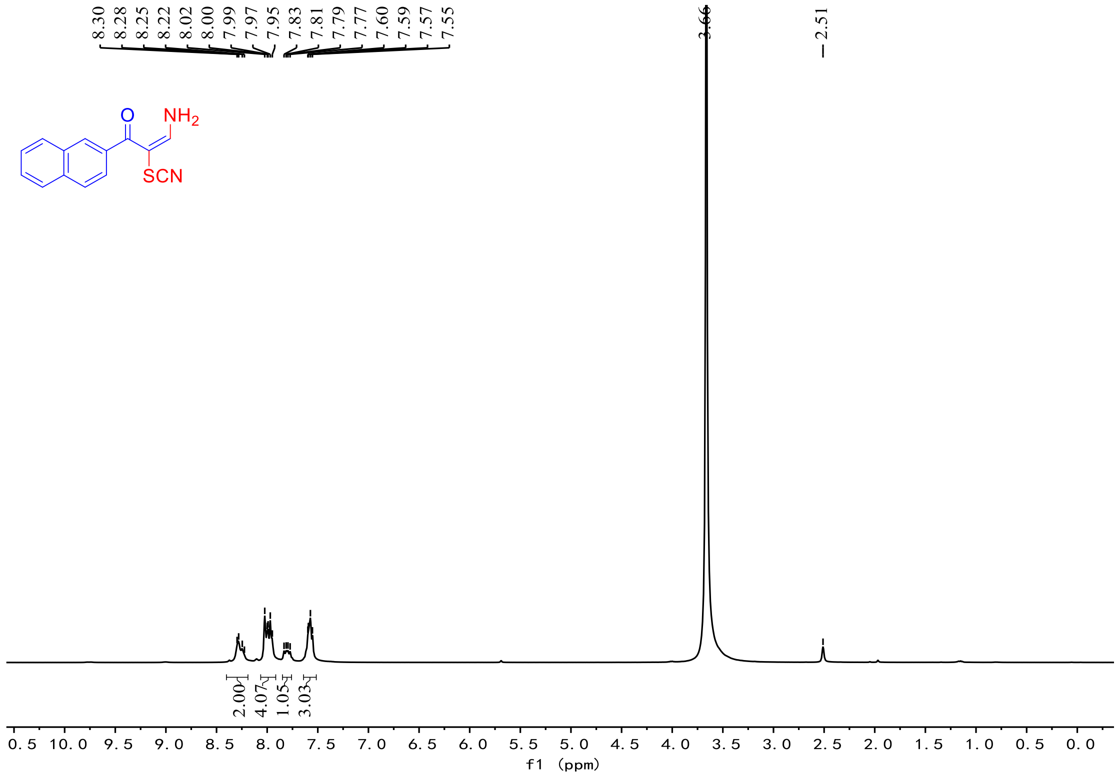
[1]H NMR (400 MHz, DMSO-d_6) of compound **3t**



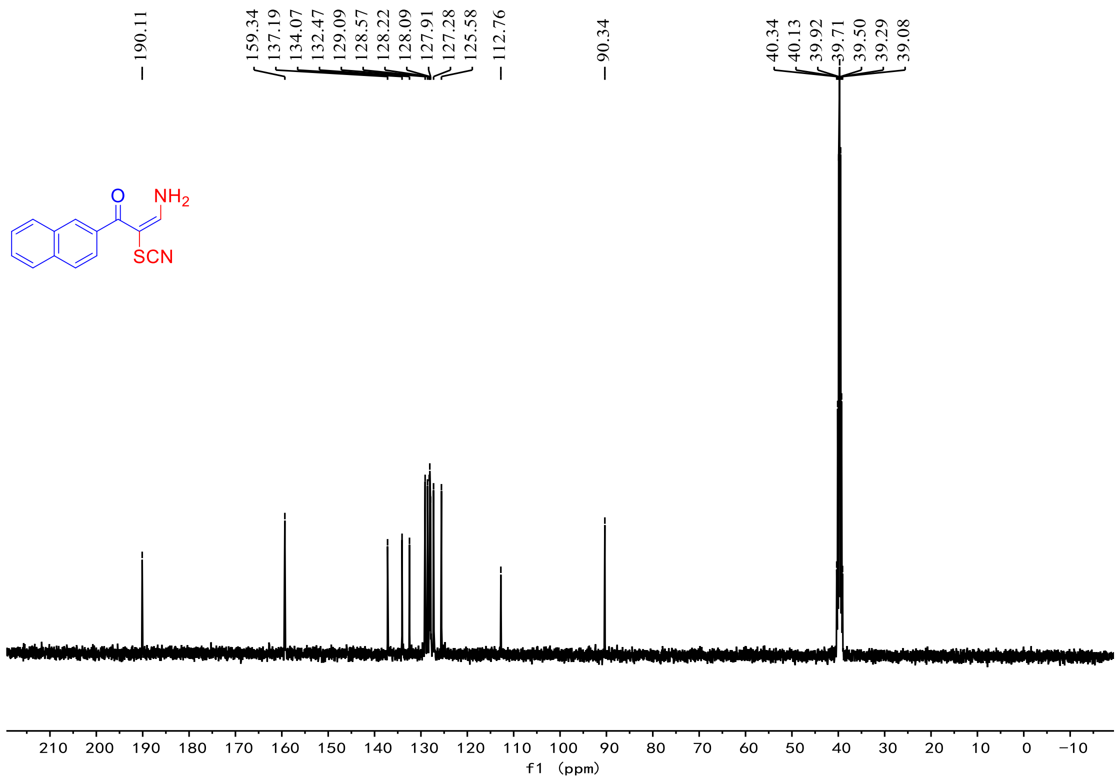
[13]C NMR (101 MHz, DMSO-d_6) of compound **3t**



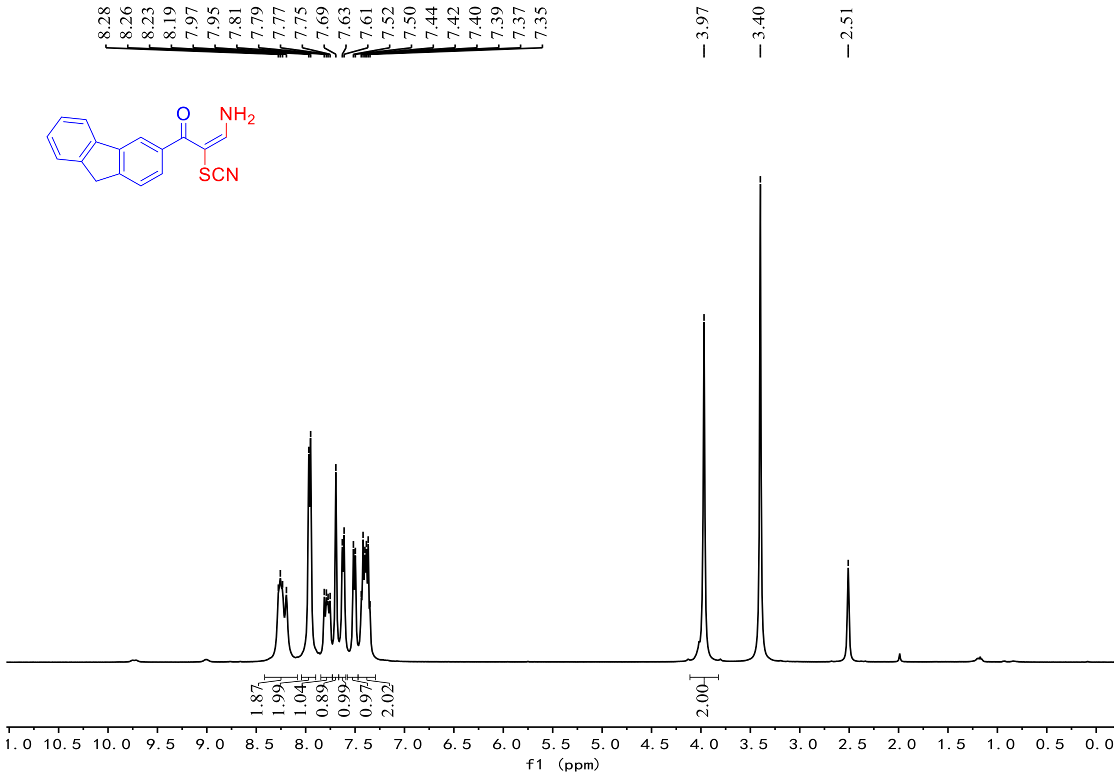
^{1}H NMR (400 MHz, DMSO-d_6) of compound **3u**



^{13}C NMR (101 MHz, DMSO-d_6) of compound **3u**



[1]H NMR (400 MHz, DMSO-d_6) of compound **3v**



[13]C NMR (101 MHz, DMSO-d_6) of compound **3v**