Supplementary Information

Ketenes as dienophiles in *aza*-Diels-Alder reactions with dicyanohydrazones for access to pyridazin-3(2*H*)-ones

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Contents

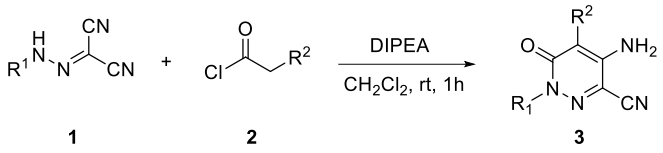
1. General information

Unless stated otherwise, reagents were used directly as obtained commercially. Reactions were monitored by TLC using silica gel GF254 plates. Flash column chromatography was performed using silica gel. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) spectra were recorded on Bruker AV III 400MHz or 600MHz NMR spectrometers. Chemical shifts are reported in ppm using tetramethylsilane or the residual solvent peak as a reference. Infrared spectra were recorded on a Bruker Tensor 27 FT-IR. HRMS were recorded on a Waters Xevo G2-XS TOF mass spectrometer. Computational studies were carried out with Spartan'24 and Gaussian 16 platform. Single crystal X-ray diffraction data was collected using a Bruker D8 Quest diffractometer (Cu Kα, λ= 1.54178 Å).

Dicyanohydrazones[1], and aminomethylene malononitriles[2] were prepared according to previously reported procedures.

2. Preparation and characterization of pyridazin-3(2H)-ones 3

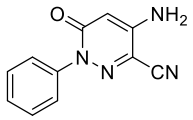
General procedure



1 **2** **3**

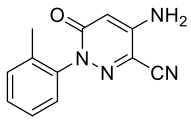
To a stirred solution of **1** (0.20 mmol, 1 equiv.) and acid chloride **2** (0.24 mmol, 1.2 equiv.) in dichloromethane (2 mL) were added DIPEA (0.40 mmol, 2 equiv.). The reaction mixture was stirred for 1 h at room temperature and then extracted with ethyl acetate. The combined organic layer was washed with saturated brine, dried over Na_2SO_4, and concentrated in vacuo to give the crude product which was purified by column chromatography (petroleum ether:ethyl acetate = 2:1) to afford the desired product **3**.

4-amino-6-oxo-1-phenyl-1,6-dihydropyridazine-3-carbonitrile (3a)



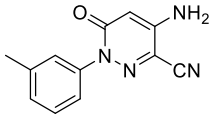
Following the general procedure with **1a** (34.0 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3a** was obtained as a faint yellow solid (39.0 mg, 92% yield). **Gram scale**: Following the general procedure with **1a** (1.35 g, 8.00 mmol) acetyl chloride (752mg, 9.60 mmol) and DIPEA (2.06g， 16.00 mmol), **3a** was obtained as a faint yellow solid (1.58 g, 93% yield); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.51 –7.46 (m,4H), 7.46 –7.41 (m, 1H), 7.00 (s, 2H), 5.83 (s, 1H) ppm; **^{13}C NMR** (151 MHz, DMSO) δ 159.6, 149.3, 141.1, 129.0, 128.8, 126.2, 116.9, 113.7, 98.8 ppm; **IR** (KBr): v = 3400, 3368, 3193, 2238, 1660, 1584, 1331, 1200, 832, 748, 683 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{11}H_9N_4O$ 213.0776, found 213.0779.

4-amino-6-oxo-1-(o-tolyl)-1,6-dihydropyridazine-3-carbonitrile (3b)



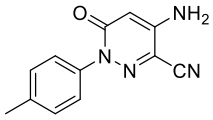
Following the general procedure with **1b** (36.6 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3b** was obtained as a faint yellow solid (23.5mg, 52% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.36 (m, 1H), 7.34 –7.30 (m, 2H), 7.22-7.19 (m, 1H), 6.07 (s, 1H), 4.92 (s, 2H), 2.16 (s, 3H) ppm; **^{13}C NMR** (151 MHz, DMSO-d_6) δ 159.6, 149.5, 140.6, 135.2, 131.03, 129.6, 127.8, 127.1, 116.8, 113.6, 98.7, 17.3 ppm; **IR** (KBr): v = 3418, 3175, 2921, 1666, 1618, 1330, 1208, 830, 748, 620 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{11}N_4O$ 227.0933, found 227.0936.

4-**amino-6-oxo-1-(m-tolyl)-1,6-dihydropyridazine-3-carbonitrile (3c)**



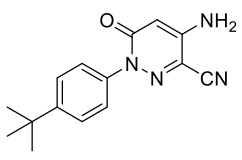
Following the general procedure with **1c** (36.6 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3c** was obtained as a faint yellow solid (26.2 mg, 58% yield); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.39 –7.33 (m,1H), 7.30 –7.22 (m, 3H), 6.99 (s, 2H), 5.82 (s, 1H), 2.35 (s, 3H) ppm; **^{13}C NMR** (151 MHz, DMSO) δ 159.6, 149.3, 141.1, 138.6, 129.5, 128.8, 126.6, 123.4, 116.7, 113.7, 98.8, 21.2 ppm; **IR** (KBr): v = 3391, 3200, 1643, 1615, 1443, 1208, 1199, 861, 748, 620 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{11}N_4O$ 227.0933, found 227.0933.

4-amino-6-oxo-1-(p-tolyl)-1,6-dihydropyridazine-3-carbonitrile (3d)



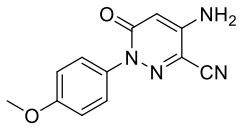
Following the general procedure with **1d** (36.6 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3d** was obtained as a faint yellow solid (27.6 mg, 61% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.28 –7.27 (m,2H), 6.11 (s, 1H), 4.85 (s, 2H), 2.40 (s, 3H) ppm; **^{13}C NMR** (151 MHz, DMSO-d_6) δ 159.6, 149.3, 138.7, 138.4, 129.4, 126.0, 116.7, 113.79, 98.8, 21.1 ppm; **IR** (KBr): v = 3406, 3336, 3208, 2239, 1629, 1330, 1198, 822, 638 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{11}N_4O$ 227.0933, found 227.0936.

4-amino-1-(4-(tert-butyl)phenyl)-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3e)



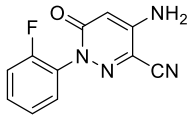
Following the general procedure with **1e** (45.0 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3e** was obtained as a faint yellow solid (38.6 mg, 72% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50-7.41 (m, 4H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.06 (s, 1H), 4.98 (s, 2H), 1.34 (s, 9H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.2, 152.2, 147.2, 137.8, 125.9, 124.8, 116.4, 112.4, 101.2, 34.81, 31.2 ppm; **IR** (KBr): v = 3352, 3191, 2964, 1621, 1454, 1337, 1207, 839, 752 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{15}H_{17}N_4O$ 269.1402, found 269.1409.

4-amino-1-(4-methoxyphenyl)-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3f)



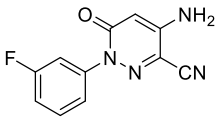
Following the general procedure with **1f** (40.0 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3f** was obtained as a faint yellow solid (37.8 mg, 78% yield); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.38 (d, *J* = 9.1 Hz, 2H), 7.00 (d, *J* = 9.1 Hz, 2H), 6.95 (s, 2H), 5.80 (s, 1H), 3.79 (s, 3H) ppm; **^{13}C NMR** (151 MHz, DMSO) δ 158.6, 158.3, 148.2, 133.0, 126.4, 115.4, 113.0, 112.7, 97.7, 54.8 ppm; **IR** (KBr): v = 3402, 3327, 3182, 2920, 2234, 1660, 1616, 1509, 1242, 1022, 829 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{11}N_4O_2$ 243.0882, found 243.0886.

4-amino-1-(2-fluorophenyl)-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3g)



Following the general procedure with **1g** (37.6 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3g** was obtained as a faint yellow solid (31.3 mg, 68% yield); **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.50-7.44 (m, 1H), 7.42 – 7.36 (m, 1H), 7.3 - 7.27 (m, 1H), 7.25 -7.21 (m, 1H), 6.06 (s, 1H), 4.88 (s, 2H) ppm; **^{13}C NMR** (151 MHz, CDCl3) δ 158.6 (d, J = 256.6 Hz), 131.3 (d, J = 7.8 Hz), 128.1 (d, *J* = 13.0 Hz), 124.7 (d, *J* = 3.5 Hz), 116.7 (d, *J* = 19.5 Hz),156.1, 147.2, 128.3, 117.3, 112.1, 100.9 ppm; **IR** (KBr): v = 3414, 3173, 1672, 1622, 1494, 1228, 1102, 1003, 829, 756, 621 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{11}H_8N_4OF$ 231.0682, found 231.0685.

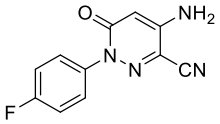
4-amino-1-(3-fluorophenyl)-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3h)



Following the general procedure with **1h** (37.6 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3h** was obtained as a faint yellow solid (33.1 mg, 72% yield); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.57 –7.50 (m, 1H), 7.47 – 7.42 (m, 1H), 7.40 –7.36 (m, 1H), 7.33 – 7.28 (m, 1H), 7.06 (s, 2H), 5.83 (s, 1H) ppm; **^{13}C NMR** (151 MHz, DMSO)

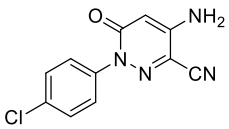
δ 161.9 (d, *J* = 244.1 Hz), 142.3 (d, *J* = 11.1 Hz), 130.7 (d, *J* = 9.0 Hz), 115.8 (d, *J* = 21.3 Hz), 113.6 (d, *J* = 13.7 Hz).159.4, 149.3, 122.4, 117.3, 113.8, 98.7 ppm; **IR** (KBr): v = 3397, 3214, 2242, 1662, 1589, 1484, 1238, 827, 685 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{11}H_8N_4OF$ 231.0682, found 231.0685.

4-amino-1-(4-fluorophenyl)-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3i)



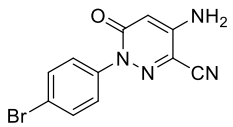
Following the general procedure with **1i** (37.6 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3i** was obtained as a faint yellow solid (37.7 mg, 82% yield); **^{1}H NMR** (600 MHz, DMSO-d_6) (δ, ppm): 7.55 –7.50 (m, 2H), 7.32 –7.30 (m, 2H), 7.02 (s, 2H), 5.82 (s, 1H) ppm; **^{13}C NMR** (151 MHz, DMSO-d_6) δ 161.8 (d, *J* = 245.3 Hz), 159.6, 149.4, 137.4 (d, *J* = 3.4 Hz), 128.5 (d, *J* = 8.4 Hz), 117.0, 115.9 (d, *J* = 22.7 Hz), 113.7, 98.8 ; **IR** (KBr): v = 3406, 3337, 3196, 2238, 1660, 1501, 1332, 1226, 834, 632 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{11}H_8N_4OF$ 231.0682, found 231.0686.

4-amino-1-(4-chlorophenyl)-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3j)



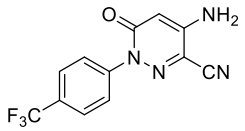
Following the general procedure with **1j** (40.8 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3j** was obtained as a faint yellow solid (44.3 mg, 90% yield); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.63 (s, 1H), 7.53 – 7.48 (m, 3H), 7.06 (s, 2H), 5.83 (s, 1H) ppm; **^{13}C NMR** (151 MHz, DMSO) δ 159.5, 149.4, 139.9, 133.3, 129.1, 128.0, 117.3, 113.6, 98.7 ppm; **IR** (KBr): v = 3402, 3330, 3200, 2239, 1659, 1583, 1471, 1331, 1198, 1027, 836, 682 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{11}H_8N_4OCl$ 247.0387, found 247.0389.

4-amino-1-(4-bromophenyl)-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3k)



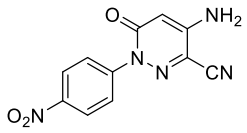
Following the general procedure with **1k** (49.6 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3k** was obtained as a faint yellow solid (49.9 mg, 86% yield); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.03 (s, 2H), 5.80 (s, 1H) ppm; **^{13}C NMR** (151 MHz, DMSO) δ 159.46, 149.40, 140.34, 132.03, 128.30, 121.76, 117.32, 113.64, 98.71 ppm; **IR** (KBr): v = 3407, 3332, 3221, 1671, 1458, 1331, 1196, 999, 827, 711cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{11}H_8N_4OBr$ 290.9881, found 290.9879.

4-amino-6-oxo-1-(4-(trifluoromethyl)phenyl)-1,6-dihydropyridazine-3-carbonitrile (3l)



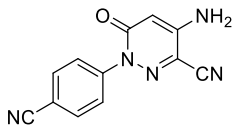
Following the general procedure with **1l** (47.6 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3l** was obtained as a faint yellow solid (53.2 mg, 95% yield);**^{1}H NMR** (600 MHz, DMSO-d_6) (δ, ppm): 7.82 (s, 4H), 7.11 (s, 2H), 5.85 (s, 1H) ppm; **^{13}C NMR** (151 MHz, DMSO) δ 159.4, 149.4, 144.2, 128.9 (q, J = 32.1 Hz), 127.0, 126.2 (q, J = 3.8 Hz), 124.3 (d, J = 272.0 Hz), 117.8, 113.6, 98.7 ppm; **IR** (KBr): v = 3404, 3332, 3220, 1671, 1590, 1322, 1109, 1068, 844 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* [M+H]$^+$ Calcd for $C_{11}H_8N_4OF$ 281.0650, found 281.0656 $C_{12}H_8N_4OF_3$

4-amino-1-(4-nitrophenyl)-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3m)



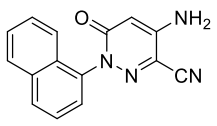
Following the general procedure with **1m** (43.0 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3m** was obtained as a faint yellow solid (47.8 mg, 93% yield); **^{1}H NMR** (600 MHz, DMSO-d_6) (δ, ppm): 8.33 (d, J = 9.0 Hz, 2H), 7.85 (d, J = 9.1 Hz, 2H), 7.15 (s, 2H), 5.84 (s, 1H) ppm; **^{13}C NMR** (151 MHz, DMSO) δ 159.3, 149.3, 146.9, 145.9, 127.0, 124.4, 118.2, 113.4, 98.5 ppm; **IR** (KBr): v = 3434, 3338, 3218, 2234, 1690, 1652, 1526, 1350, 1192, 855, 707 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* [M+H]$^+$ Calcd for $C_{11}H_8N_5O_3$ 258.0627, found 258.0631.

4-amino-1-(4-cyanophenyl)-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3n)



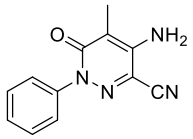
Following the general procedure with **1n** (39.0 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3n** was obtained as a faint yellow solid (45.1 mg, 95% yield); **^{1}H NMR** (600 MHz, DMSO-d_6) δ 7.98 (d, J = 8.5 Hz, 2H), 7.76 (d, J = 8.4 Hz, 2H), 7.12 (s, 2H), 5.83 (s, 1H) ppm; **^{13}C NMR** (151 MHz, DMSO) δ 159.3, 149.3, 144.5, 133.3, 126.9, 118.7, 118.0, 113.5, 111.2, 98.6 ppm; **IR** (KBr): v = 3388, 3321, 3215, 2921, 2236, 1632, 1590, 1451, 1330, 1196, 835, 737 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* [M+H]$^+$ Calcd for $C_{12}H_8N_5O$ 238.0729, found 238.0731.

4-amino-1-(naphthalen-2-yl)-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3o)



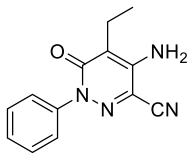
Following the general procedure with **1o** (44.0 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3o** was obtained as a faint yellow solid (37.2 mg, 71% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 8.14 – 7.93 (m, 4H), 7.65 – 7.53 (m, 3H), 7.05 (s, 2H), 5.88 (s, 1H) ppm; **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.77, 149.45, 138.77, 132.93, 132.70, 128.68, 128.60, 128.11, 127.48, 127.29, 124.70, 124.36, 117.15, 113.77, 98.86 ppm; **IR** (KBr): v = 3417, 3332, 3247, 1672, 1588, 1329, 1194, 847, 737 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_{15}H_{10}N_4ONa$ 285.0752, found 285.0756.

4-amino-5-methyl-6-oxo-1-phenyl-1,6-dihydropyridazine-3-carbonitrile (3p)



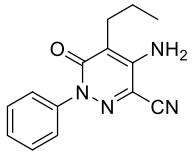
Following the general procedure with **1a** (34.0 mg, 0.20 mmol)，propionyl chloride (22.2 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3p** was obtained as a faint yellow solid (33.0 mg, 73% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.52 – 7.42 (m, 5H), 6.63 (s, 2H), 1.93 (s, 3H) ppm;**^{13}C NMR** (151 MHz, DMSO) δ 160.05, 145.28, 141.71, 129.07, 128.83, 126.38, 116.66, 114.11, 108.59, 10.33 ppm; **IR** (KBr): v = 3431, 3344, 3213, 1625, 1591, 1205, 763, 695 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{12}H_1N_4O$ 227.0933, found 227.0934.

4-amino-5-ethyl-6-oxo-1-phenyl-1,6-dihydropyridazine-3-carbonitrile (3q)



Following the general procedure with **1a** (34.0 mg, 0.20 mmol)，butyryl chloride (25.6 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3q** was obtained as a faint yellow solid (38.9 mg, 81% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.52 – 7.40 (m, 5H), 6.65 (s, 2H), 2.51 – 2.43 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO) δ 159.6, 144.5, 141.6, 129.0, 128.8, 126.3, 116.9, 114.1, 114.1, 17.3, 11.4 ppm; **IR** (KBr): v = 3446, 3328, 3214, 2963, 2237, 1619, 1422, 1204, 758, 699 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{13}H_{13}N_4O$ 241.1089, found 241.1093.

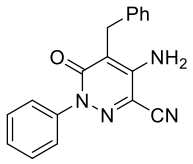
4-amino-6-oxo-1-phenyl-5-propyl-1,6-dihydropyridazine-3-carbonitrile (3r)



Following the general procedure with **1a** (34.0 mg, 0.20 mmol)，valeryl chloride (28.9 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3r** was obtained as a faint yellow solid (31.5 mg, 62% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.73 – 7.28 (m, 5H), 6.64 (s, 2H), 2.48 – 2.31 (m, 2H), 1.50 – 1.32 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, DMSO) δ 159.8, 144.9, 141.6, 129.0, 128.7, 126.3, 116.9, 114.1, 112.8, 25.8, 19.9, 14.3 ppm; **IR** (KBr): v =

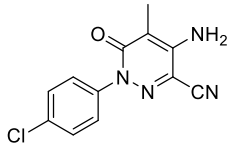
3448, 3325, 3210, 2962, 2233, 1624, 1439, 1205, 772, 700 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{14}H_{14}N_4ONa$ 227.1065, found 227.1061.

4-amino-5-benzyl-6-oxo-1-phenyl-1,6-dihydropyridazine-3-carbonitrile (3s)



Following the general procedure with **1a** (34.0 mg, 0.20 mmol)，hydrocinnamoyl chloride (40.5 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3s** was obtained as a faint yellow solid (51.4 mg, 85% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.54 – 7.39 (m, 5H), 7.33 – 7.12 (m, 5H), 6.80 (s, 2H), 3.84 (s, 2H) ppm; **^{13}C NMR** (101 MHz, DMSO) δ 159.9, 145.3, 141.5, 139.0, 129.0, 128.8, 128.6, 126.5, 126.3, 117.1, 114.0, 111.4, 29.1 ppm; **IR (KBr):** v = 3401, 3339, 3226, 2238, 1660, 1630, 1587, 1487, 1201,933, 768, 699 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{18}H_{15}N_4O$ 303.1246, found 303.1248.

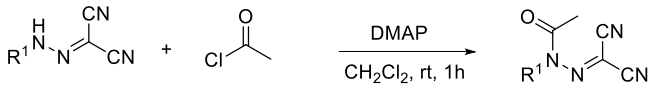
4-amino-1-(4-chlorophenyl)-5-methyl-6-oxo-1,6-dihydropyridazine-3-carbonitrile (3t)



Following the general procedure with **1j** (40.8 mg, 0.20 mmol)，propionyl chloride (22.2 mg, 0.24 mmol) and DIPEA (51.7 mg， 0.40 mmol)，**3t** was obtained as a faint yellow solid (37.4 mg, 72% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.55 (s, 4H), 6.68 (s, 2H), 1.92 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 159.93, 45.3, 140.4, 133.2, 129.0, 128.1, 116.9, 114.0, 108.4, 10.3 ppm; **IR** (KBr): v = 3414, 3355, 3251, 2241, 1664, 1601, 1513, 1407,1355, 1205, 1093, 831 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+H]^+$ Calcd for $C_{12}H_{10}N_4OCl$ 261.0543, found 261.0541.

3. Control experiments

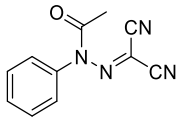
3.1 Preparation and characterization of 4a and 4b



1 **2** **4**

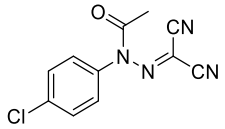
To a stirred solution of **1** (0.20 mmol, 1 equiv.) and acid chloride **2** (0.24 mmol, 1.2 equiv.) in dichloromethane (2 mL) were added DMAP (0.40 mmol, 2equiv.). The reaction mixture was stirred for 1h at room temperature and then extracted with ethyl acetate. The combined organic layer was washed with saturated brine, dried over Na_2SO_4, and concentrated in vacuo to give the crude product which was purified by column chromatography (petroleum ether:ethyl acetate = 4:1) to afford the desired product **4**.

***N*-acetyl-*N*-phenylcarbonohydrazonoyl dicyanide (4a)**



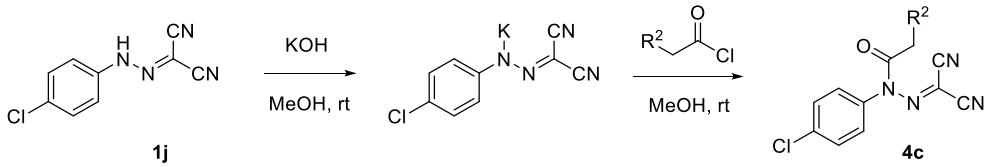
Following the general procedure with **1a** (34.0 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DMAP (48.9 mg， 0.40 mmol)，**4a** was obtained as a faint yellow solid (31.8mg, 75% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.78 – 6.96 (m, 5H), 2.49 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 172.7, 134.9, 132.3, 129.9, 129.8, 113.9, 107.4, 90.7, 21.7 ppm; **IR** (KBr): v = 3450, 3010, 2228, 1852, 1730, 1590, 1490, 1365, 1240, 1164, 953, 720 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_{11}H_8N_4O$ 235.0596, found 235.1392.

***N*-acetyl-*N*-(4-chlorophenyl)carbonohydrazonoyl dicyanide (4b)**



Following the general procedure with **1j** (34.0 mg, 0.20 mmol)，acetyl chloride (18.8 mg, 0.24 mmol) and DMAP (48.9 mg， 0.40 mmol)，**4b** was obtained as a faint yellow solid (38.4 mg, 78% yield); **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.65 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 2.48 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 172.7, 137.0, 133.7, 132.0, 129.9, 113.8, 107.6, 91.1, 21.7 ppm; **IR** (KBr): v = 3455, 2983, 2945, 2230, 1736, 1531, 1487, 1356, 1225, 1124, 905, 836 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_{11}H_8N_4OCl$ 247.0384, found 247.1301.

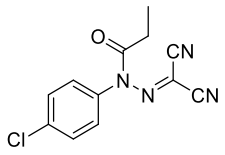
***3.2 Preparation and characterization of 4c* [3]**



1j **4c**

To a stirred solution of **1j** (1.00 mmol, 1 equiv.) and KOH(1.00 mmol, 1 equiv.) in methanol (15 mL). The reaction mixture was stirred for 3h at room temperature, the methanol is then largely distilled off in a vacuum, ether is added to the residue,and the formed potassium salt is filtered off with suction and dried at 60-90°C.in a vacuum. (0.20 mmol) of dry potassium salt of potassium 1-(4-chlorophenyl)-2-(dicyanomethylene)hydrazin-1-ide is suspended in 10 ml of dry acetonitrile, and a solution of (0.24 mmol) of propionyl chloride in 10 ml of acetonitrile is added dropwise at room temperature, with stirring, The mixture is stirred for 3 hours at room temperature and then heated for 5 hours to 50°C. The solvent is distilled off in a vacuum, and the residue is taken up with ether; filtration is effected and concentration is again carried out.

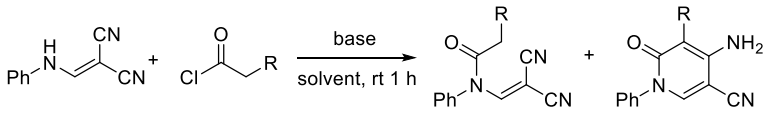
***N*-(4-chlorophenyl)-*N*-propionylcarbonohydrazonoyl dicyanide (4c)**



Following the general procedure with **1p** (1.00 mmol, 1 equiv.) ,KOH(1.00 mmol, 1 equiv.) and (0.24 mmol) of propionyl chloride, **4c** was obtained as a faint yellow solid of 65% yield; **^{1}H NMR** (400 MHz, DMSO-d_6) δ 7.65 (d, *J* = 8.7 Hz, 2H), 7.50 (d, J = 8.7 Hz, 2H), 2.89 (q, *J* = 7.3 Hz, 2H), 1.10 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 175.7, 137.0, 133.9, 132.0, 129.9, 113.8, 107.6, 90.8, 26.7, 8.7 ppm; **IR** (KBr): v = 3452, 3069, 2231, 1736, 1522, 1485, 1371, 1244, 1173, 1015, 944, 905, 731cm^{-1}; **HRMS** (ESI-QTOF) *m/z* $[M+Na]^+$ Calcd for $C_{12}H_9N_4ONaCl$ 283.0365, found 283.0363.

4. Preliminary exploration for the synthesis of 3-alkyl/unsubstituted 2-pyridones

4.1 Optimization of the reaction conditions



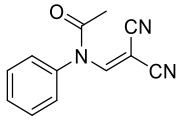
6 **2** (**2a**, R = H; **2b**, R = Me) **7** (**7a**, R = H; **7b**, R = Me) **8** (**8a**, R = H; **8b**, R = Me)

entry	**2**	base	solvent	**7**, yield (%)[b]	**8,** yield (%)[b]
1	**2b**	DIPEA	CH_2Cl_2	**7b**, 65	**8b**, 25
2	**2b**	Et_3N	CH_2Cl_2	**7b**, 43	**8b**, 48
3	**2b**	DBU	CH_2Cl_2	**7b**, 78	**8b**, 0
4	**2b**	KOH	CH_2Cl_2	**7b**, 60	**8b**, 0
5	**2b**	Et_3N	DMF	**7b**, 73	**8b**, 5
6	**2b**	Et_3N	PhCl	**7b**, 75	**8b**, 12
7	**2b**	Et_3N	ACN	**7b**, 72	**8b**, 10
8	**2b**	Et_3N	Acetone	**7b**, 80	**8b**, 8
9	**2b**	Et_3N	Toluene	**7b**, 75	**8b**, 6
10	**2a**	Et_3N	CH_2Cl_2	**7a**, 82	**8a**, 0

[a] Unless otherwise specified, the reactions were conducted using **6** (0.20 mmol), **2** (0.24 mmol), base (0.40 mmol) in 3 mL of solvent at 25 ℃ for 1 hour. [b] Isolated yields based on **6**.

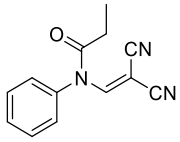
4.2 Characterization of compounds 7

_N_-(2,2-dicyanovinyl)-_N_-phenylacetamide (7a)



^{1}H NMR (400 MHz, DMSO-d6) δ 8.65 (s, 1H), 7.99 – 7.06 (m, 5H), 2.12 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 170.4, 153.8, 136.2, 131.4, 130.3, 129.6, 115.7, 110.5, 62.1, 23.0 ppm; **IR** (KBr): v = 3416, 3052, 2225, 1956, 1724, 1606, 1495, 1366, 1343, 1251, 1154, 983, 692 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* [M+Na]$^{+}$ Calcd for $C_{12}H_9N_3ONa$ 234.0643, found 234.0643.

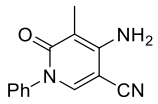
_N_-(2,2-dicyanovinyl)-_N_-phenylpropionamide (7b)



^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 1H), 7.73 – 6.90 (m, 5H), 2.32 (q, *J* = 7.1 Hz, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 173.5, 153.2, 135.8, 131.4, 130.3, 129.8, 115.7, 110.5, 61.9, 28.2, 8.7 ppm; **IR** (KBr): v = 3444, 3050, 2956, 2944, 2228, 1735, 1601, 1585, 1492, 1344, 1206, 1156, 1119, 1062, 968, 705 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* [M+Na]$^{+}$ Calcd for $C_{13}H_{11}N_3ONa$ 248.0800, found 248.1217.

4.3 Characterization of compound 8b

4-amino-5-methyl-6-oxo-1-phenyl-1,6-dihydropyridine-3-carbonitrile



^{1}H NMR (400 MHz, DMSO-d_6) δ 8.26 (s, 1H), 7.59 – 7.21 (m, 5H), 6.26 (s, 2H), 1.85 (s, 3H); **^{13}C NMR** (101 MHz, DMSO) δ 161.1, 150.5, 144.9, 140.7, 129.2, 128.6, 127.5, 116.2, 99.9, 84.2, 10.6 ppm; **IR** (KBr): v = 3329, 2922, 2852, 2220, 1673, 1456, 1377, 1261 cm^{-1}; **HRMS** (ESI-QTOF) *m/z* [M+H]$^{+}$ Calcd for $C_{13}H_{12}N_3O$ 226.0980, found 226.0982.

5. Computational studies

5.1 FMO maps and orbital energies of tautomerized dicyanohydrazones and ketene 2''

The calculations were performed using DFT (density functional theory) computations employing the ωB97X-D method with 6-311+G* basis set with Spartan'24 (Wavefunction, Inc.: Irvine, CA, USA, 2024) platform.

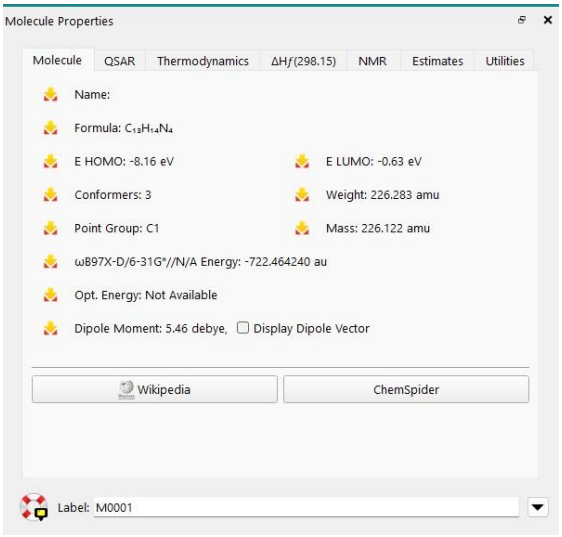
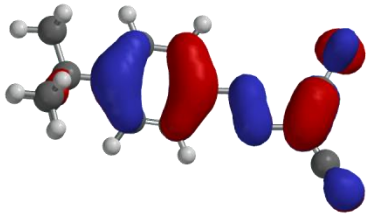
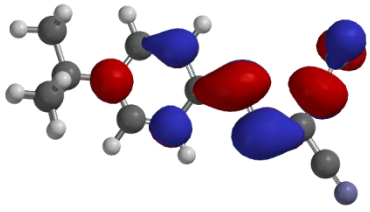


Figure S1 Calculated molecule properties of 1e''



-8.2 ev

Figure S2 HOMO map and orbital energy of 1e''



-0.6 ev

Figure S3 LUMO map and orbital energy of 1e''

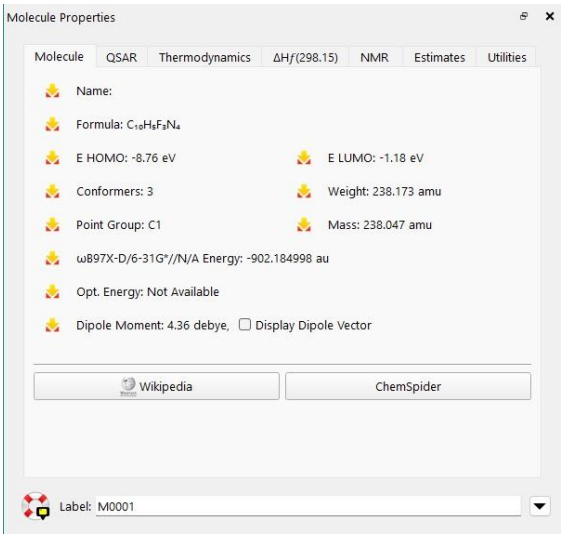
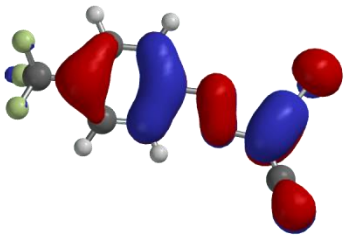
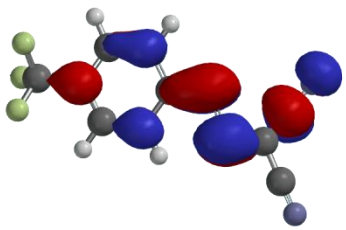


Figure S4 Calculated molecule properties of 1l'



-8.8 ev

Figure S5 HOMO map and orbital energy of 1l''



-1.2 ev

Figure S6 LUMO map and orbital energy of 1l''

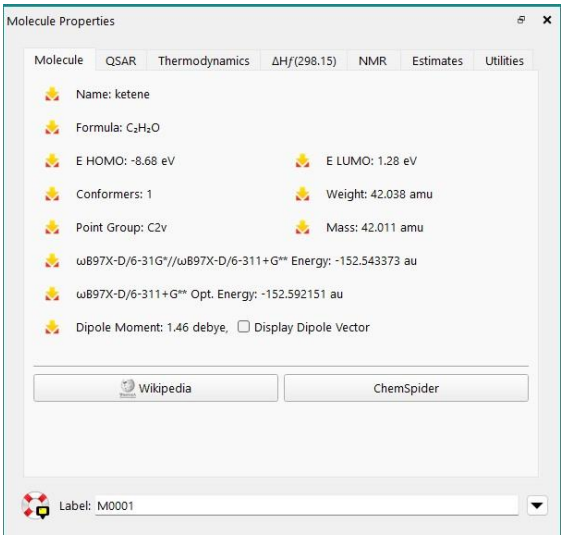


Figure S7 Calculated molecule properties of 2a'

-8.7 ev

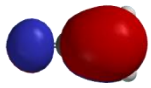
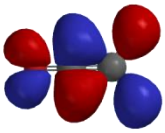


Figure S8 HOMO map and orbital energy of 2a'



1.3 ev

Figure S9 LUMO map and orbital energy of 2a'

5.2 Analysis of the possible interactions between the FMOs of 1'' and 2a'

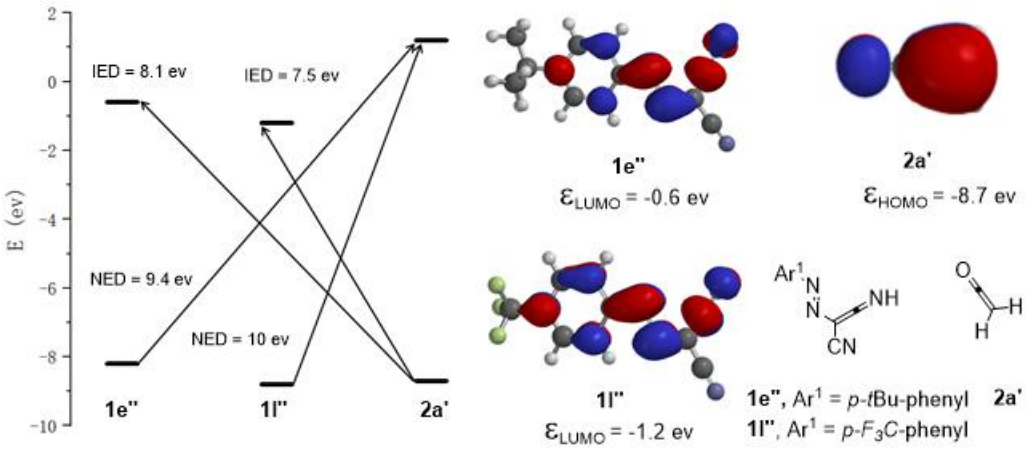


Figure S10 The possible interactions between the FMOs of 1'' and 2a'

5.3 Reaction profile for the reaction between 1a'' and 2a'

We collected the TS structure and energy profile in the reaction of **1a''** with **2a'**. All geometric structures were optimized using the Gaussian 16 program package[4].The geometry of all reactants and transition states were optimized using B3LYP hybrid functional[5,6]. The 6-31G (d) basis set [7] for C, O, N and H atoms. Harmonic vibrational frequency analysis was calculated at the same level to verify that reactants, intermediates, and products have positive frequencies, while transition states have and have only one imaginary frequency. Also, the intrinsic reaction coordinates (IRC) have been calculated to ensure that the transition states are connected to the corresponding reactants and products. To obtain more accurate energies, solution-phase single point energy calculations were performed at the ωB97X-D/def2-TZVP. A polarized continuum model based on the solute electron density (SMD) was utilized to simulate the solvent effect of CH_2Cl_2 solution.[8]

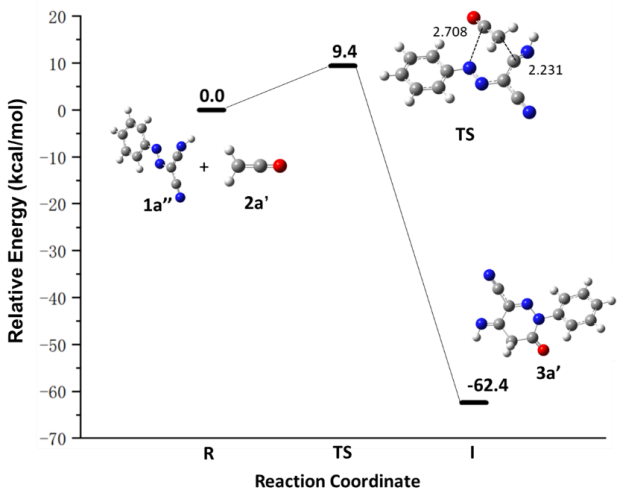


Figure S11. Calculataed energy profile for the annulation of 1a'' and 2a'

Table S1. Cartesian Coordinates of the TS structure.

C	1.97816200	-0.86321600	-0.22903800
C	2.61478000	0.37307800	-0.29754000
C	2.80886900	-2.00339400	-0.06417700
N	3.49819300	-2.93521300	0.06617000
N	0.62044800	1.07084600	-0.16547300
N	-0.10425700	-0.03656600	-0.35095600
C	-1.49114500	-0.26296200	-0.19540900
C	-2.04676700	-1.41039900	0.39791200
C	-2.33381500	0.76185800	-0.65128300
C	-3.42780100	-1.52560800	0.51594900
H	-1.38667300	-2.18873700	0.76438400
C	-3.71671300	0.63740300	-0.53093100
H	-1.88804500	1.63979100	-1.10755800
C	-4.26795700	-4.26795700	0.05259500
H	-3.85543200	-2.41097600	0.97847400
H	-4.36324400	1.43219600	-0.89185500
H	-5.34531400	-0.60109500	0.15290500
N	3.47793100	1.05112000	-0.83707800
H	3.85900800	1.88104700	-0.38020400
C	0.80706000	2.31043800	0.64503900
C	1.63387900	1.51992900	1.34531300
O	0.18530000	3.03346500	-0.01355300
H	2.52545600	2.00110200	1.74321900
H	1.17433700	0.72976200	1.92983300

5.4 FMO maps and orbital energies of 1a'', 6' and ketene 2b'

The calculations were performed using DFT (density functional theory) computations employing the ωB97X-D method with 6-311+G* basis set with Spartan'24 (Wavefunction, Inc.: Irvine, CA, USA, 2024) platform.

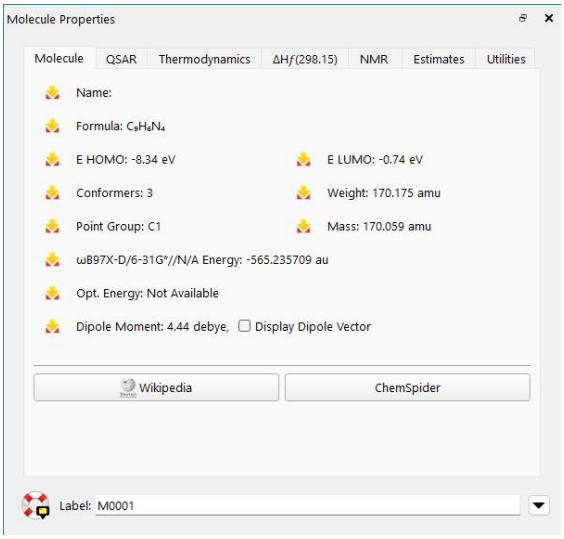


Figure S12 Calculated molecule properties of 1a''

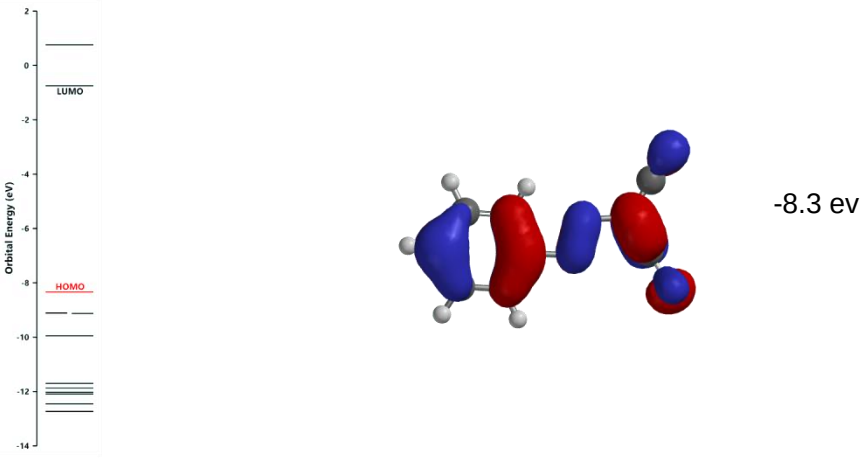


Figure S13 HOMO map and orbital energy of 1a''

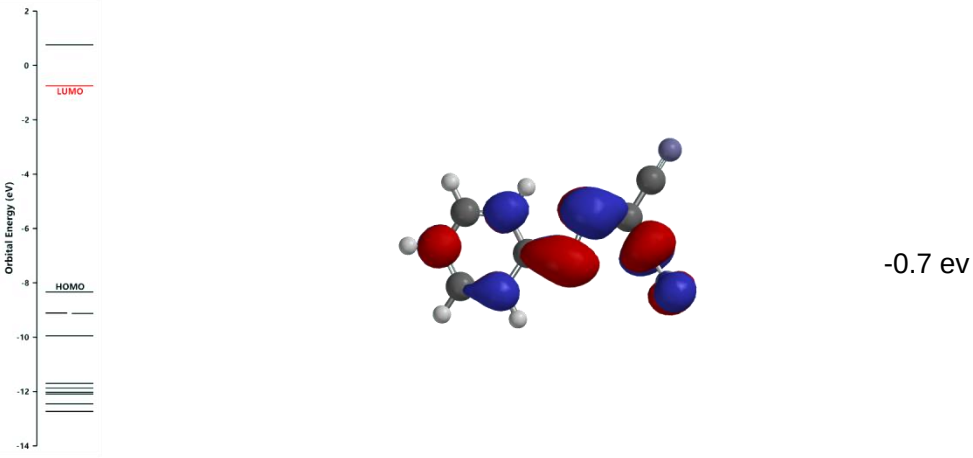


Figure S14 LUMO map and orbital energy of 1a''

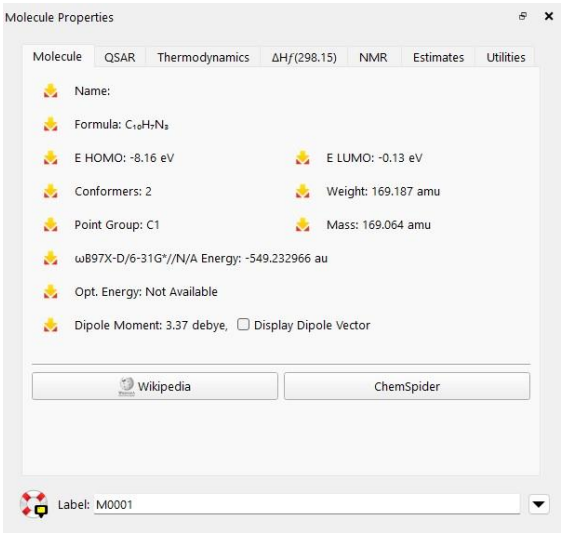
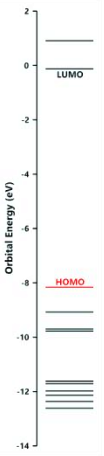
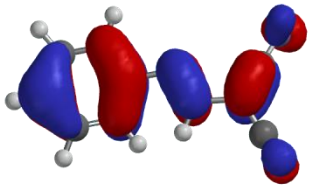


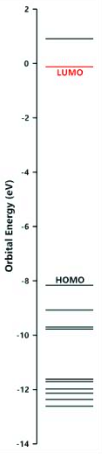
Figure S15 Calculated molecule properties of 6'

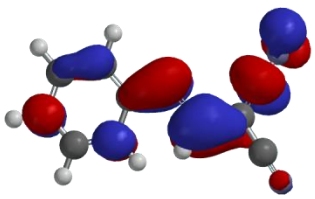




-8.2 ev

Figure S16 HOMO map and orbital energy of 6'





-0.1 ev

Figure S17 LUMO map and orbital energy of 6'

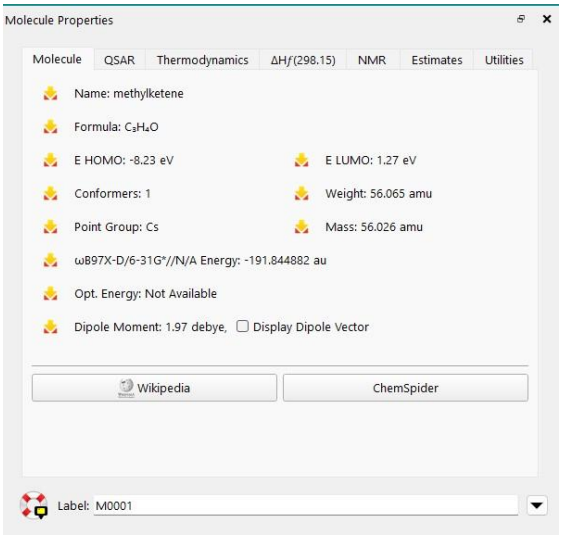


Figure S18 Calculated molecule properties of 2b'

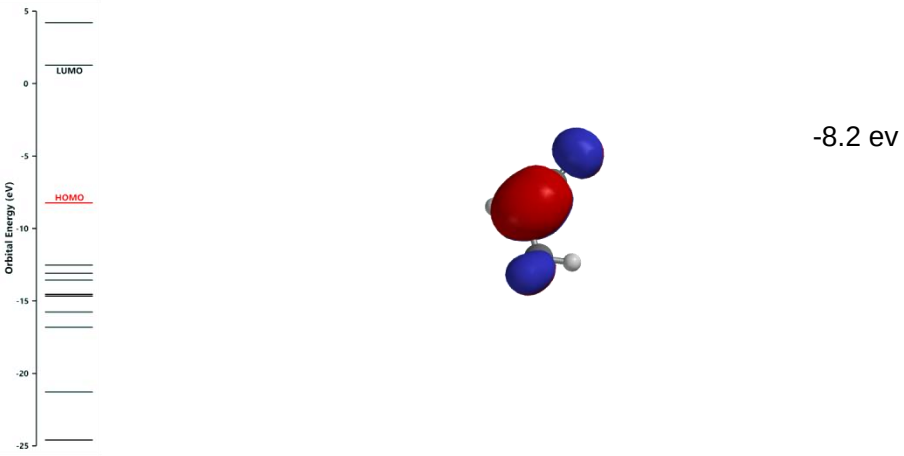


Figure S19 HOMO map and orbital energy of 2b'

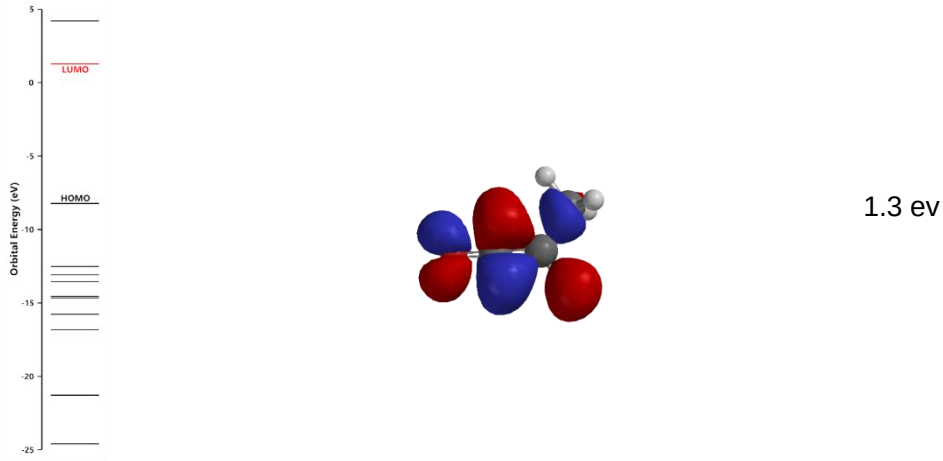


Figure S20 LUMO map and orbital energy of 2b'

5.5 Analysis of the possible interactions between the FMOs of 1a'', 6' and 2'

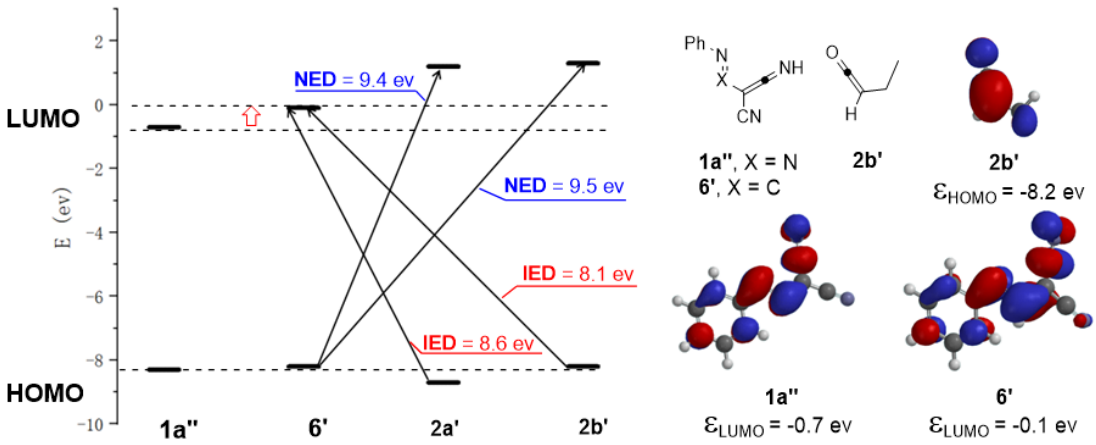


Figure S21 The possible interactions between the FMOs of 1a'', *6'* and 2'

6. X-ray crystal structure of 3e (CDCC 2379960)

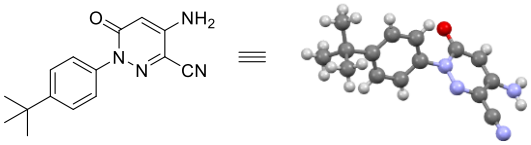
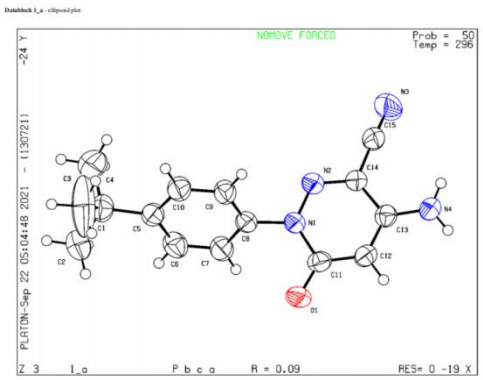


Figure S22. X-ray crystal structure of **3e**



Bond precision:	C-C = 0.0058 A	Wavelength=0.71073	
Cell:	a=11.6652(12)	b=11.4053(12)	c=22.148(2)
	alpha=90	beta=90	gamma=90
Temperature: 296 K			
Calculated	Reported		
Volume	2946.7(5)	2946.7(5)	
Space group	P b c a	P b c a	
Hall group	-P 2ac 2ab	-P 2ac 2ab	
Moiety formula	C15 H16 N4 O	?	
Sum formula	C15 H16 N4 O	C15 H16 N4 O	

Mr	268.32	268.32
Dx,g cm-3	1.210	1.210
Z	8	8
Mu (mm-1)	0.080	0.080
F000	1136.0	1136.0
F000’	1136.40	
h,k,lmax	13,13,26	13,13,26
Nref	2626 2620	
Tmin,Tmax	0.984,0.984	0.864,0.864
Tmin’	0.984	

Correction method= # Reported T Limits: Tmin=0.864 Tmax=0.864

AbsCorr = MULTI-SCAN

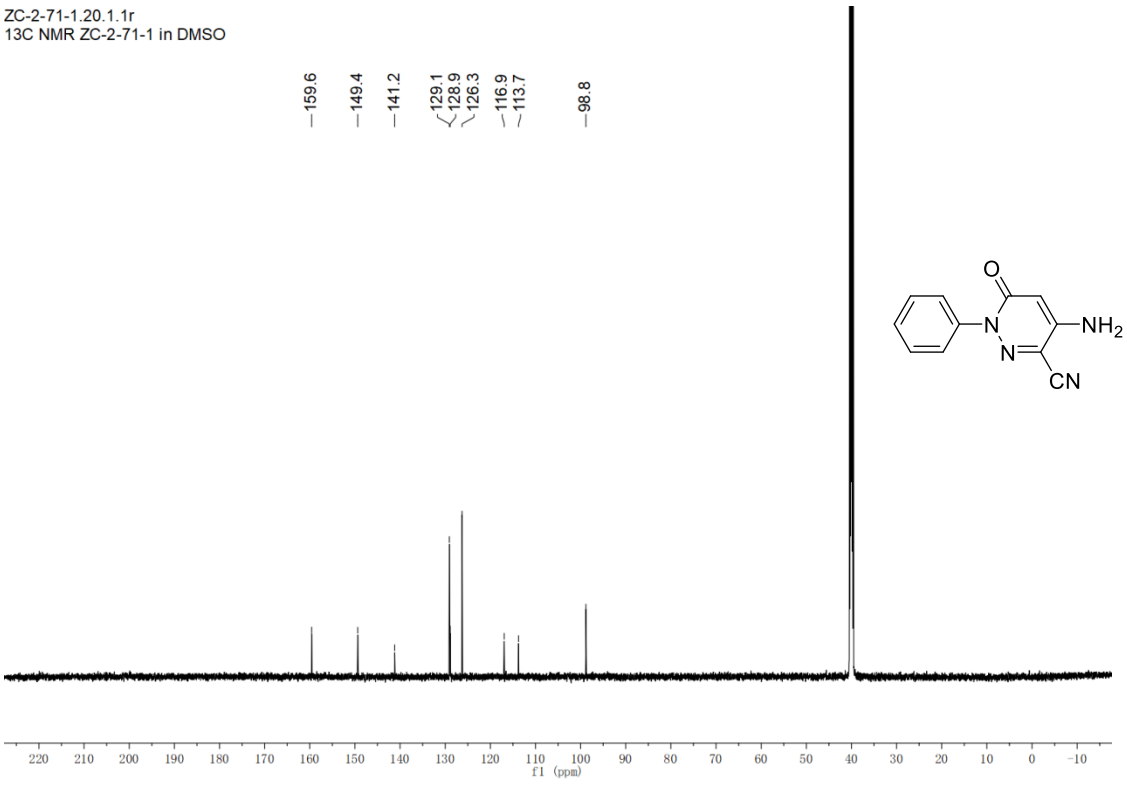
Data completeness= 0.998 Theta(max)= 25.101

R(reflections)= 0.0921(1718) wR2(reflections)= 0.2229(2620)

S = 1.158 Npar= 184

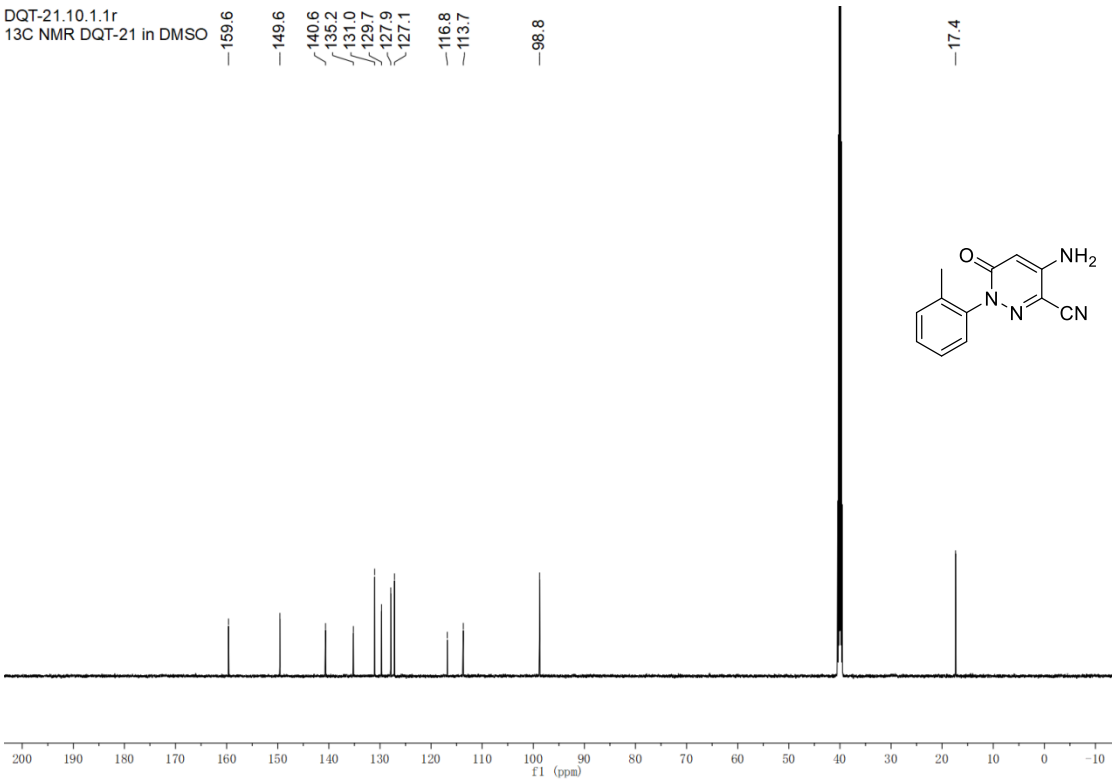
7.Copies of ^{1}H and ^{13}C NMR spectra

^{1}H NMR spectrum of compound **3a** (600 MHz, DMSO)

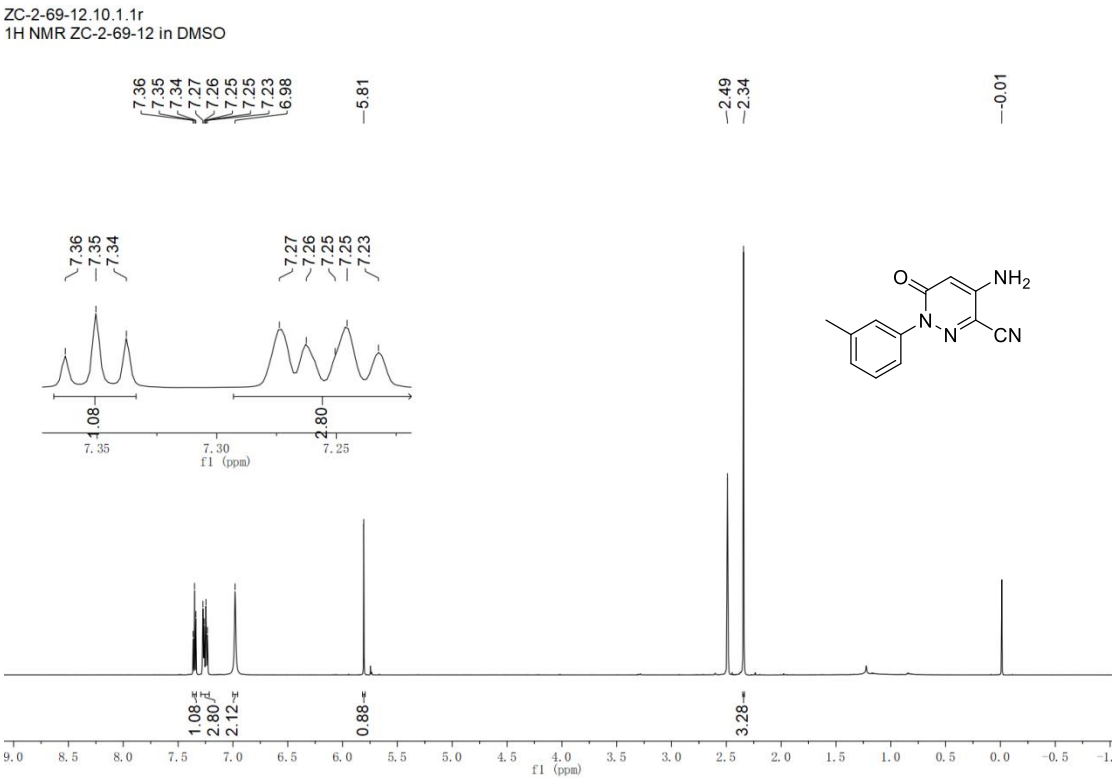


^{13}C NMR spectrum of compound **3a** (151 MHz, DMSO)

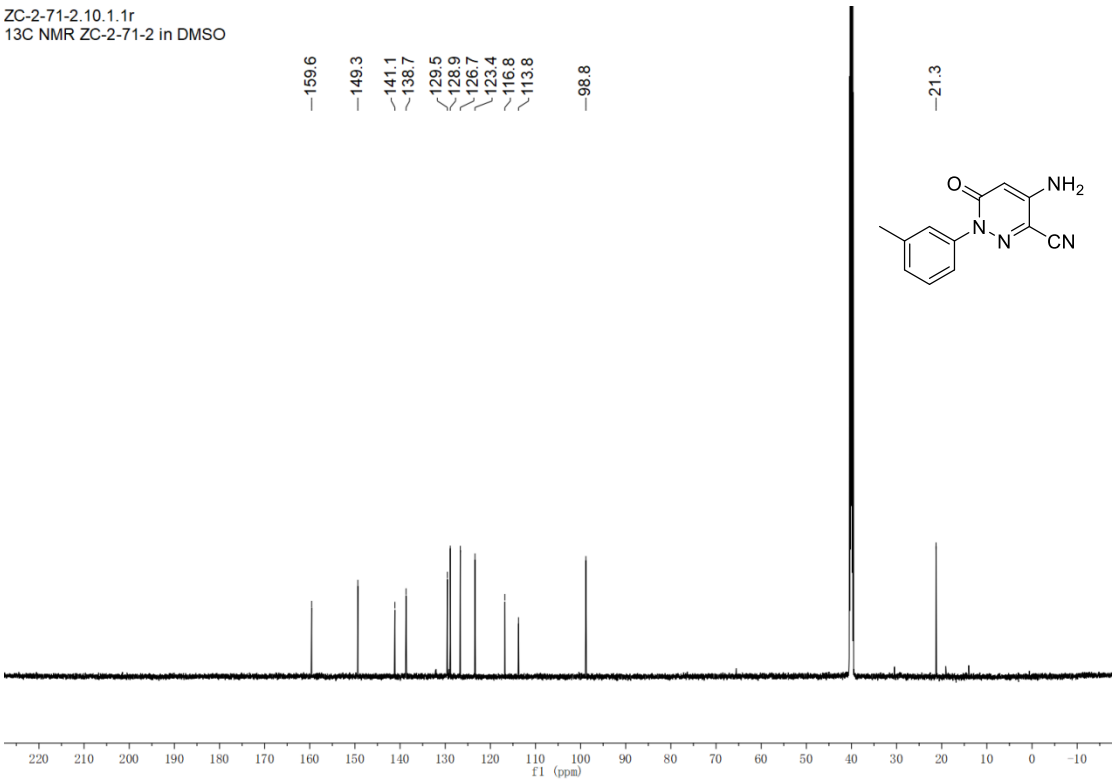
^{1}H NMR spectrum of compound **3b** (600 MHz, $CDCl_3$)



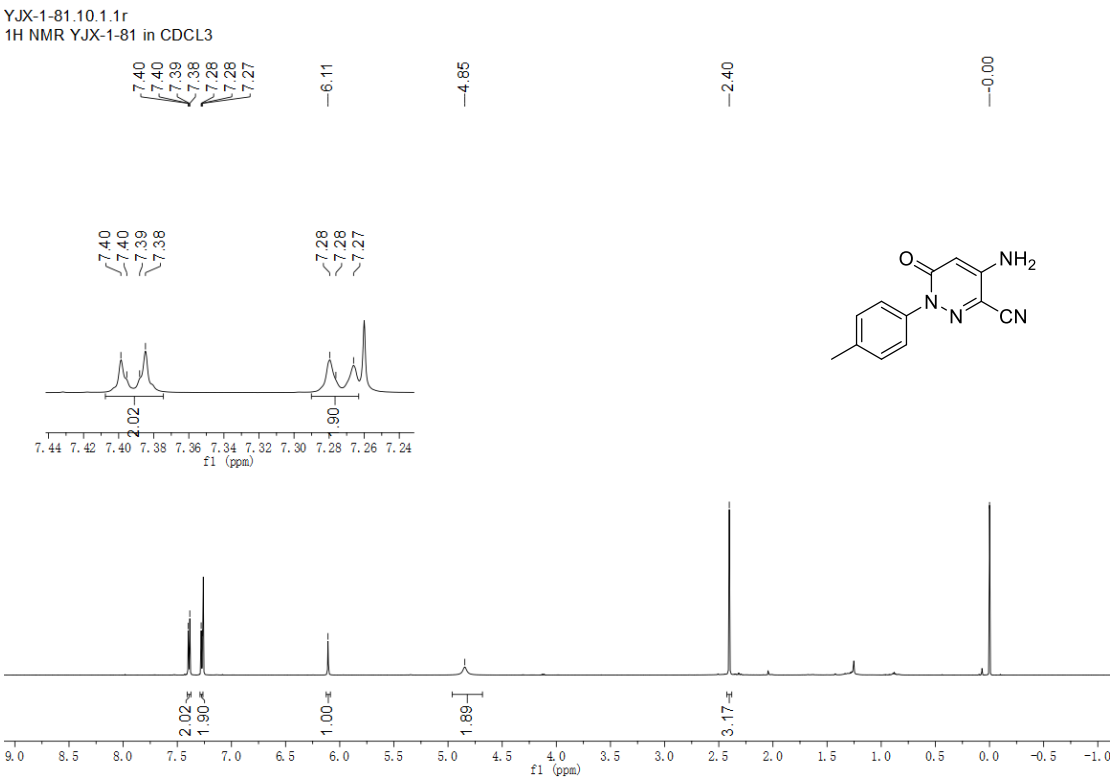
^{13}C NMR spectrum of compound **3b** (151 MHz, DMSO)



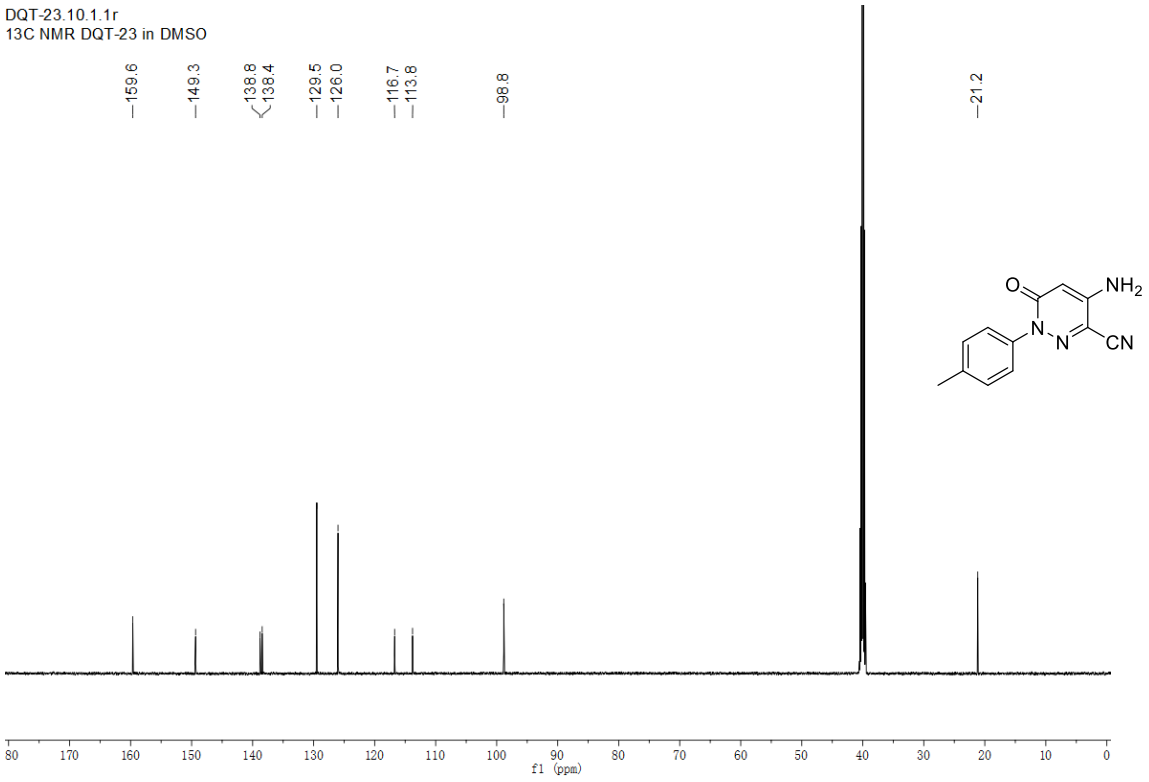
^{1}H NMR spectrum of compound **3c** (600 MHz, DMSO)



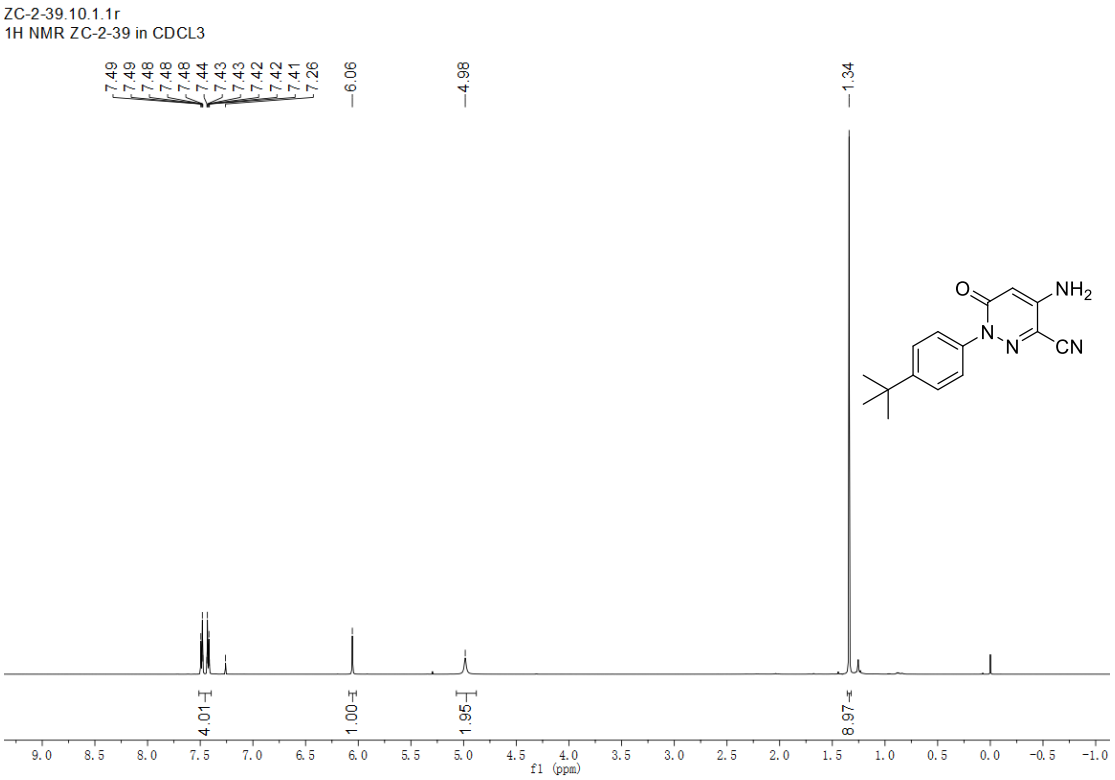
^{13}C NMR spectrum of compound **3c** (151 MHz, DMSO)



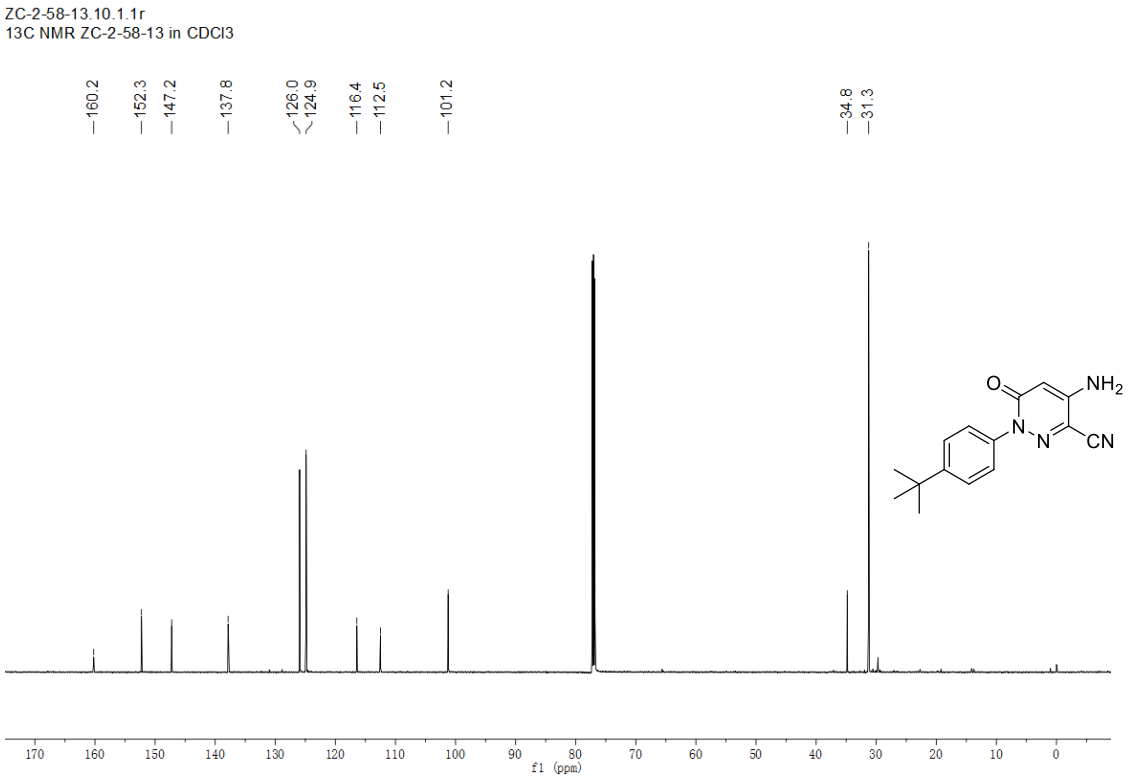
^{1}H NMR spectrum of compound **3d** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **3d** (151 MHz, DMSO)

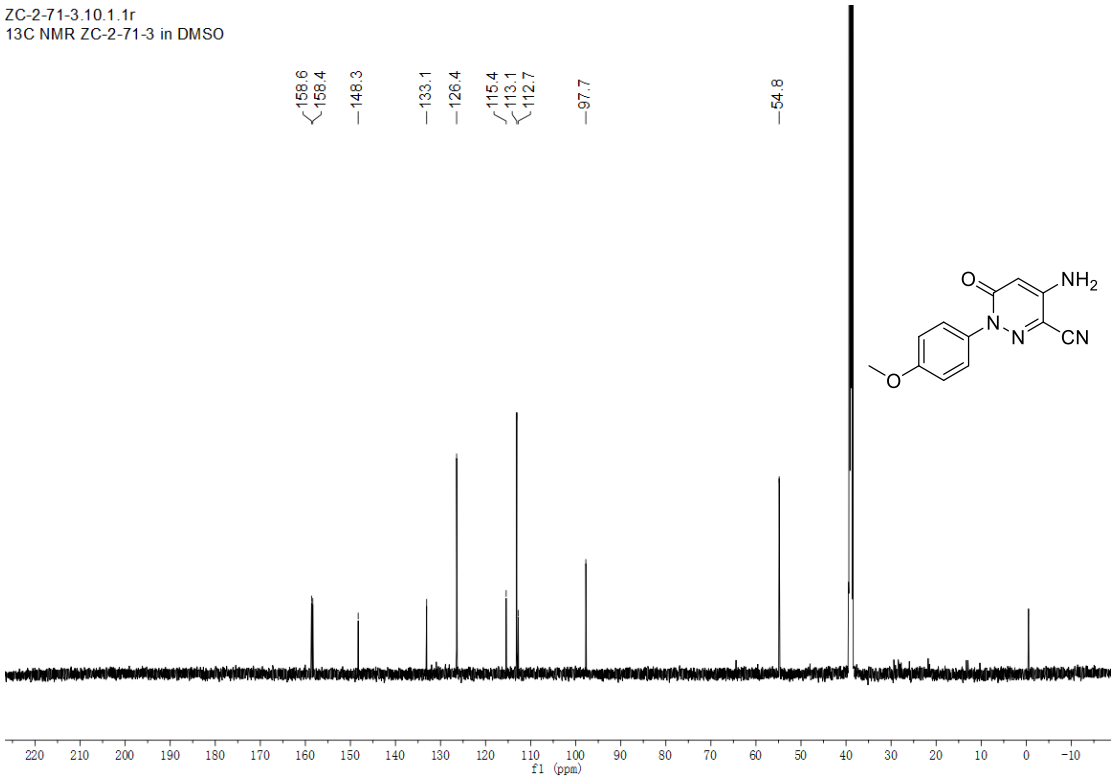


^{1}H NMR spectrum of compound **3e** (600 MHz, $CDCl_3$)

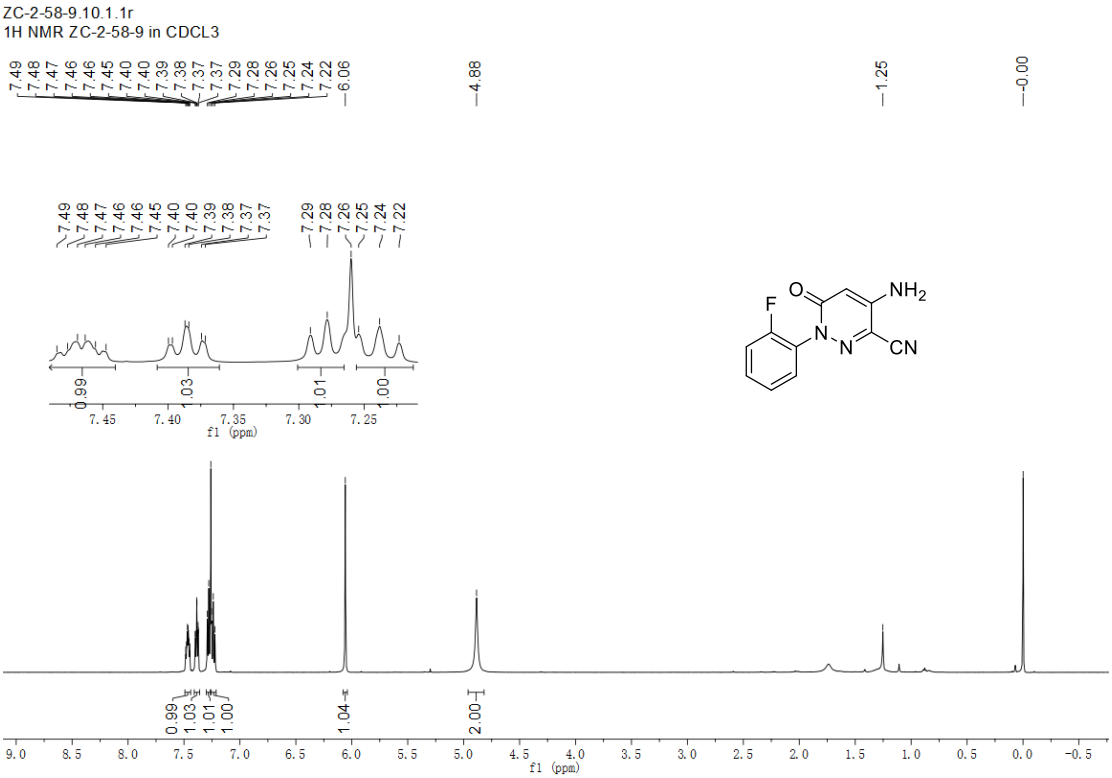


^{13}C NMR spectrum of compound **3e** (151 MHz, $CDCl_3$)

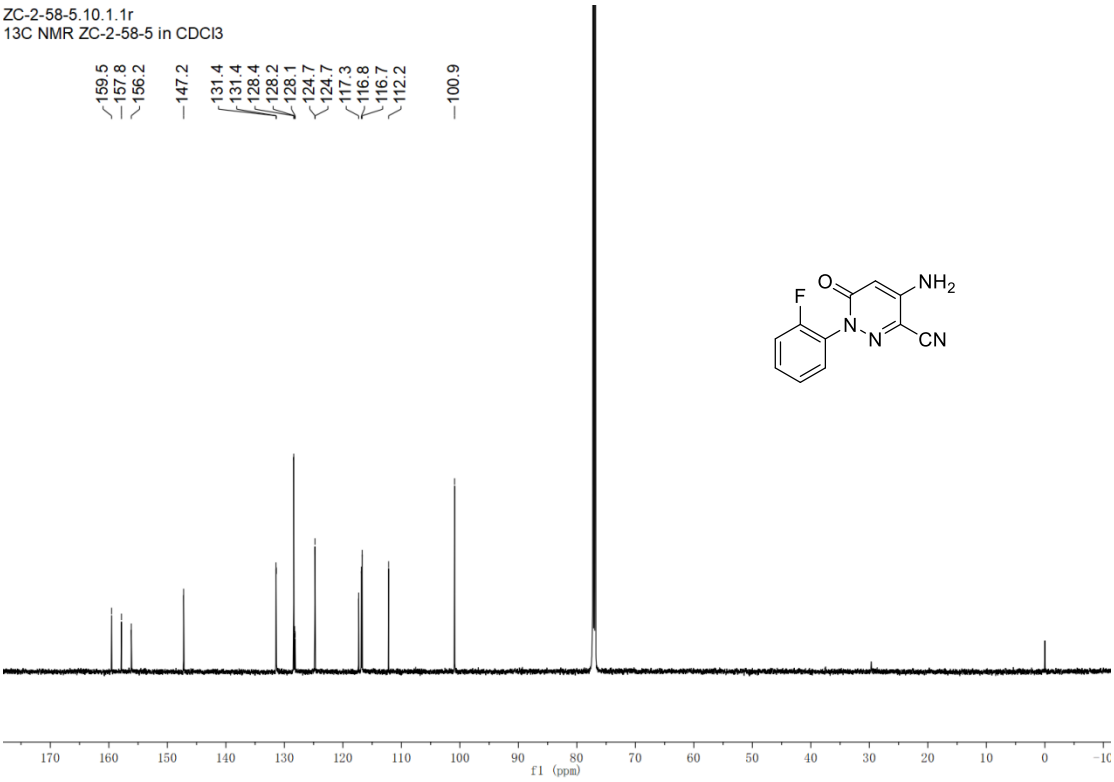
^{1}H NMR spectrum of compound **3f** (600 MHz, DMSO)



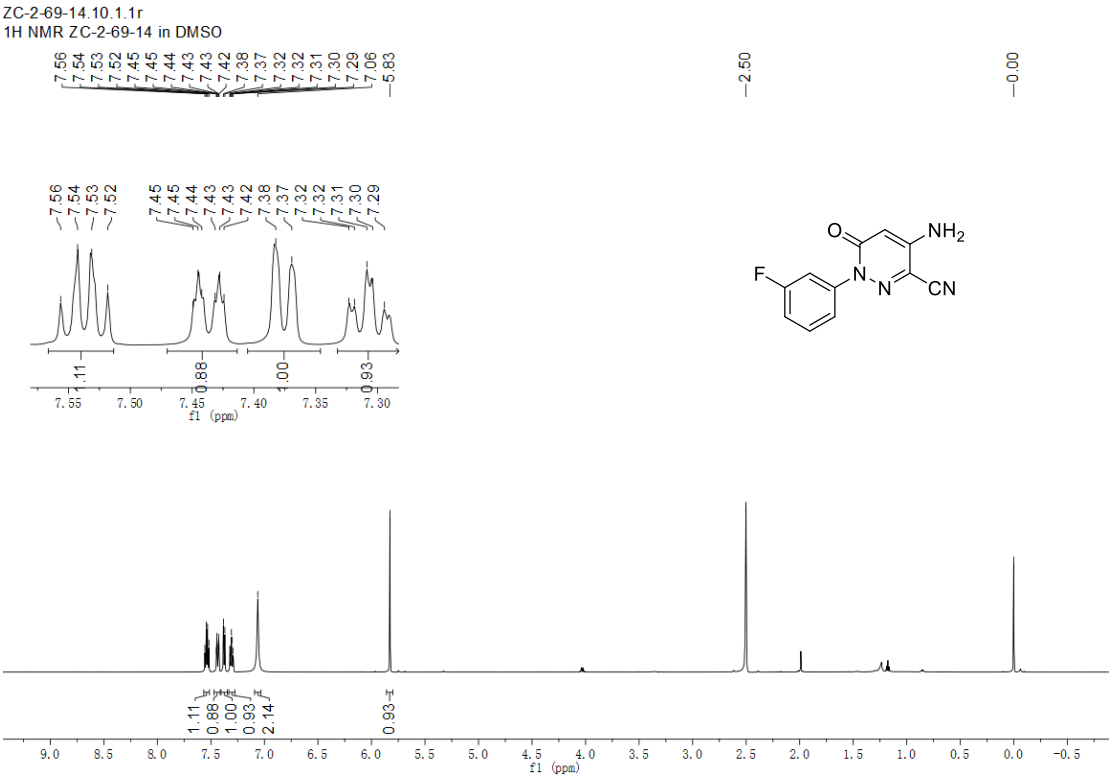
^{13}C NMR spectrum of compound **3f** (151 MHz, DMSO)



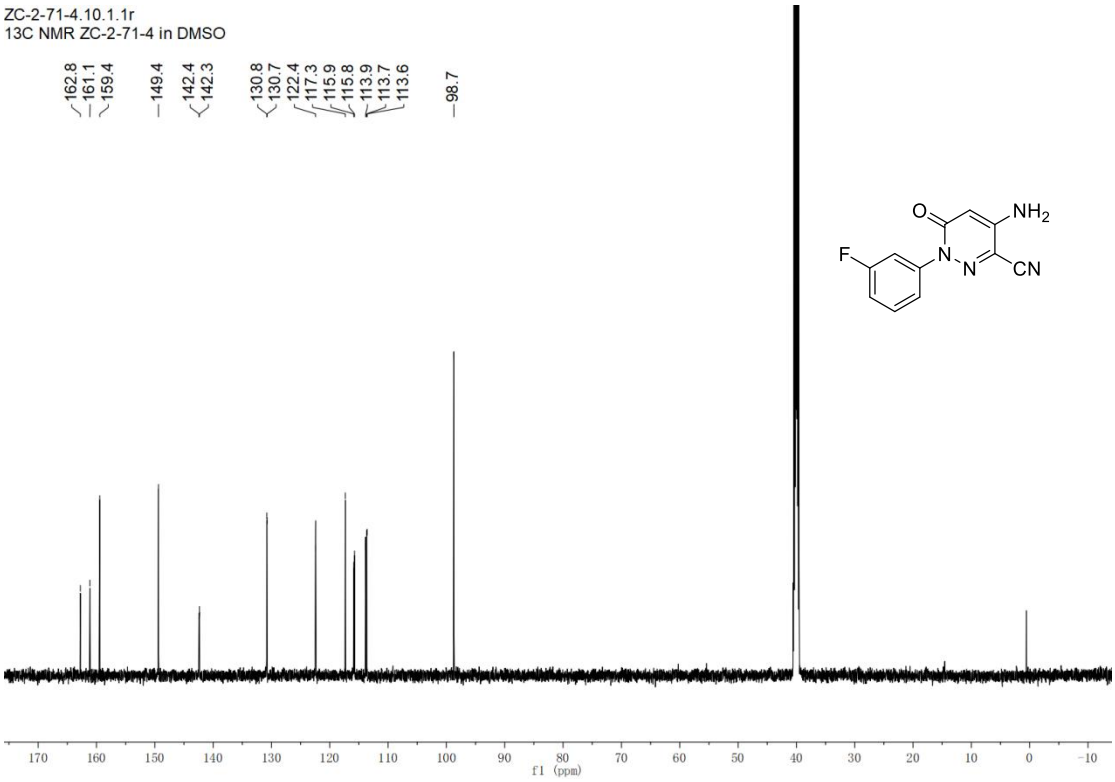
^{1}H NMR spectrum of compound **3g** (600 MHz, $CDCl_3$)



^{13}C NMR spectrum of compound **3g** (151 MHz, $CDCl_3$)

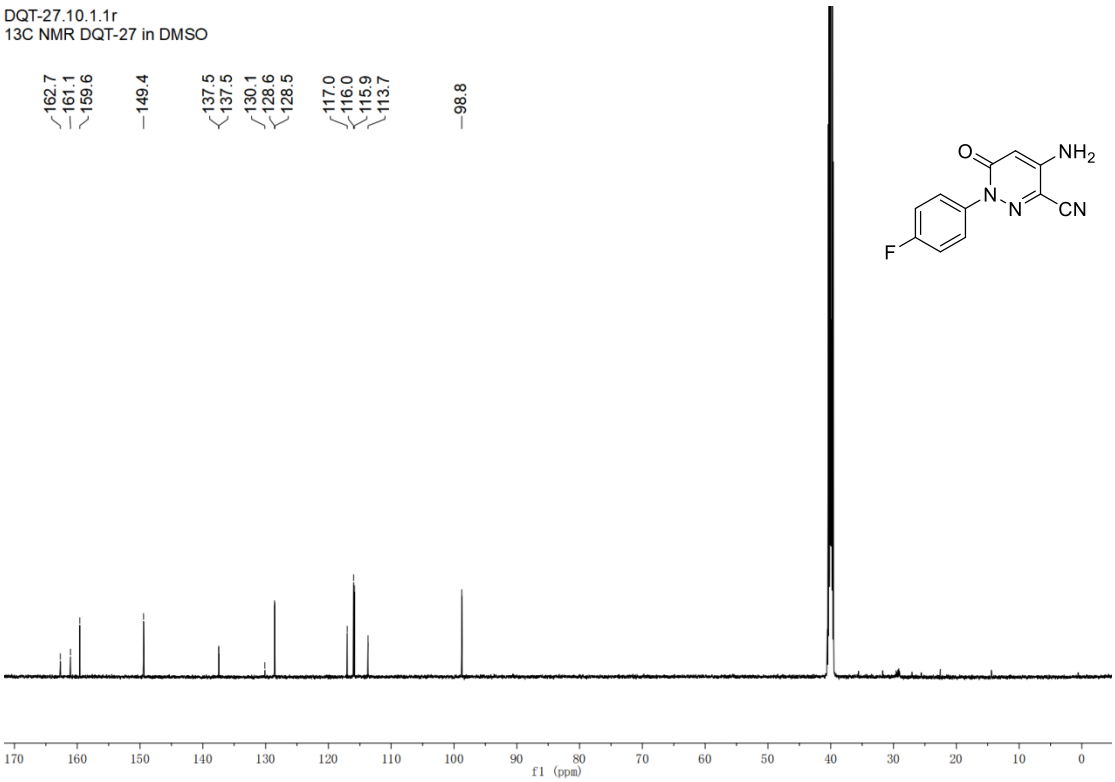


^{1}H NMR spectrum of compound **3h** (600 MHz,DMSO)

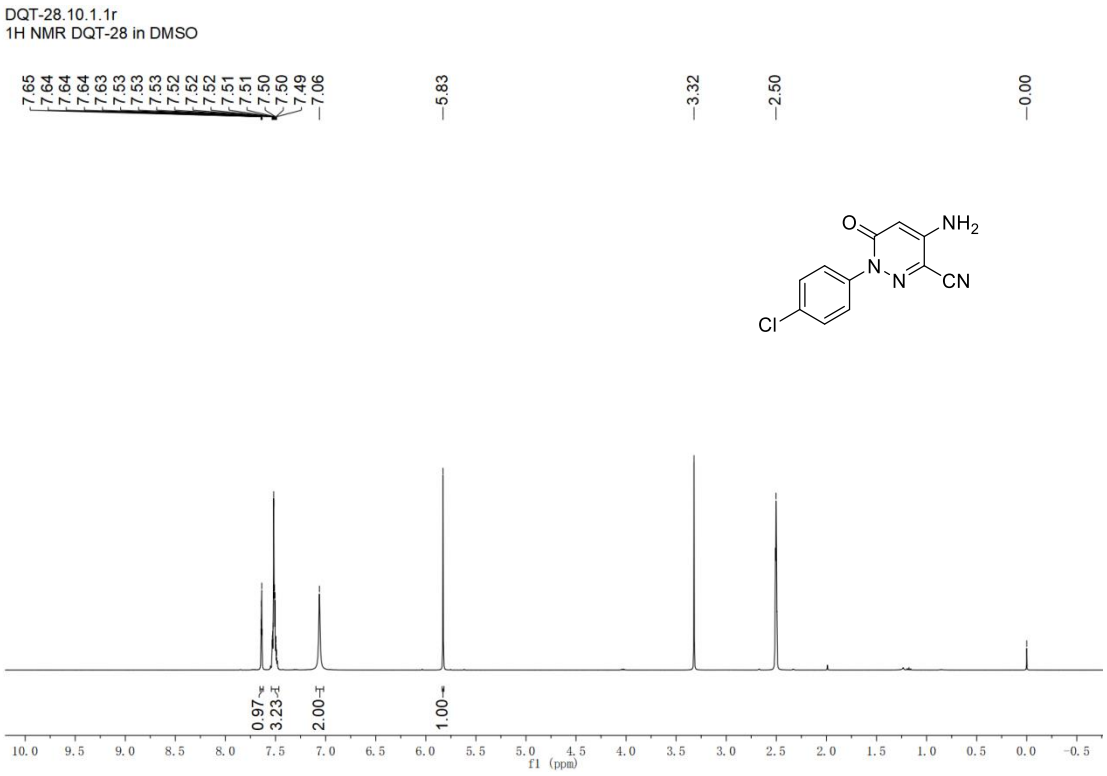


^{13}C NMR spectrum of compound **3h** (151 MHz, DMSO)

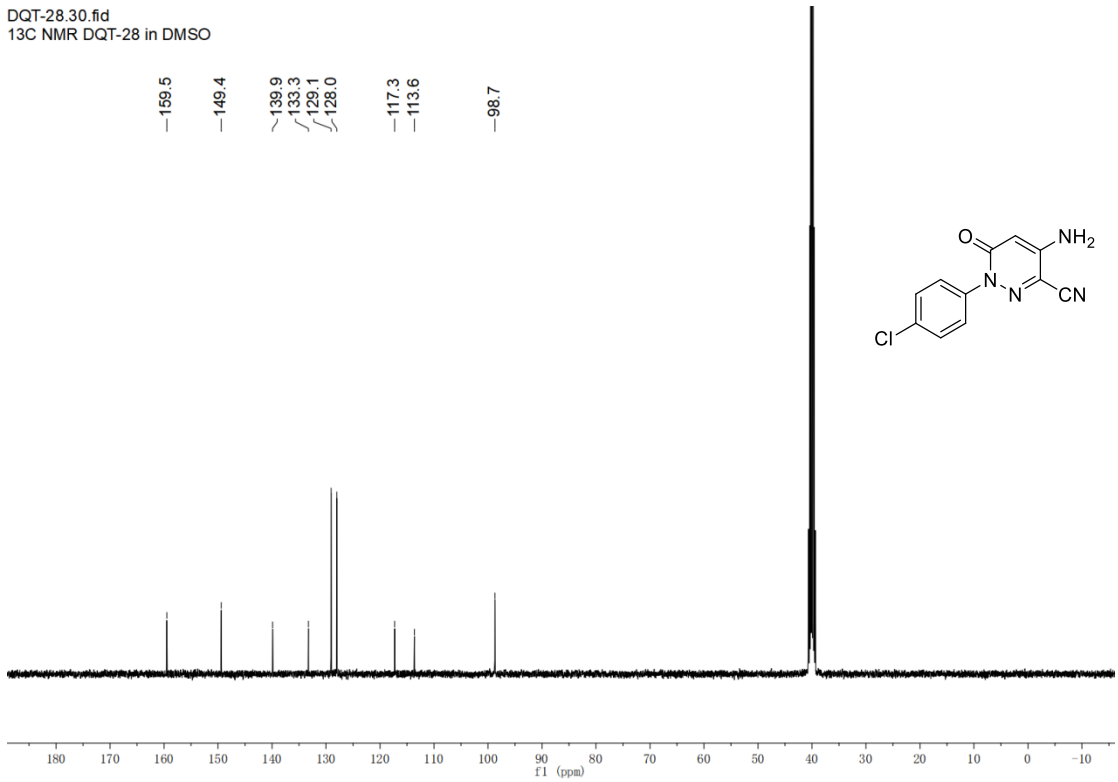
^{1}H NMR spectrum of compound **3i** (600 MHz, DMSO)



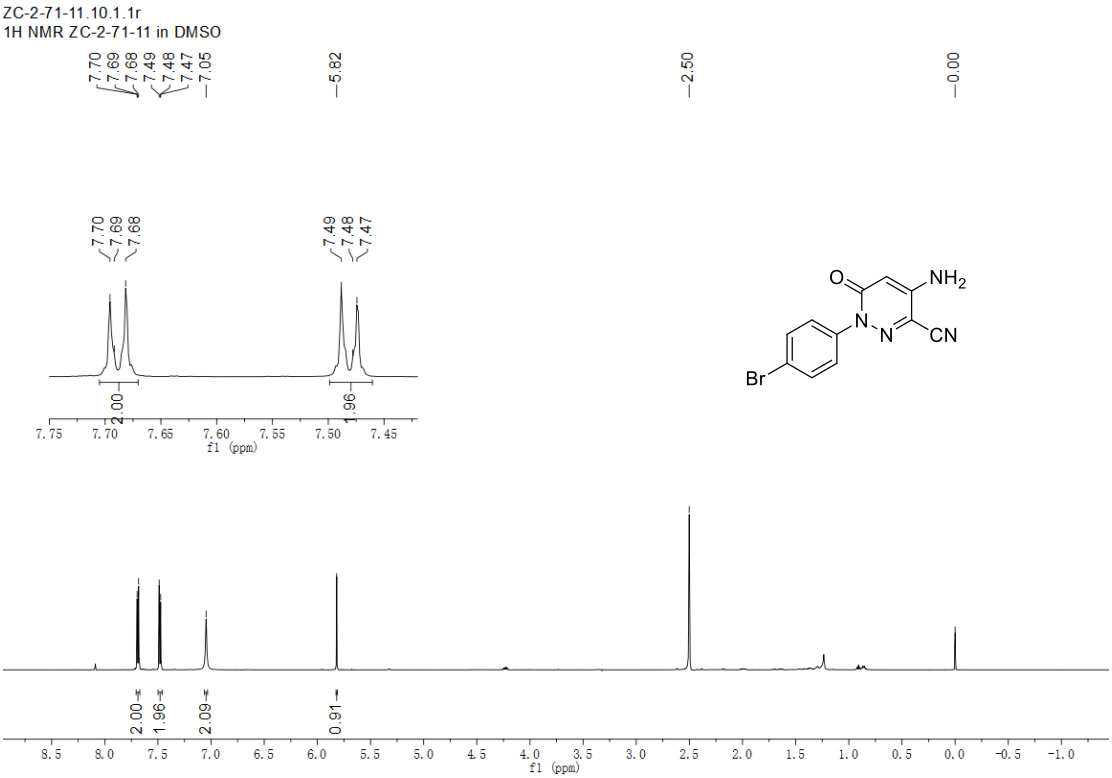
^{13}C NMR spectrum of compound **3i** (151 MHz, DMSO)



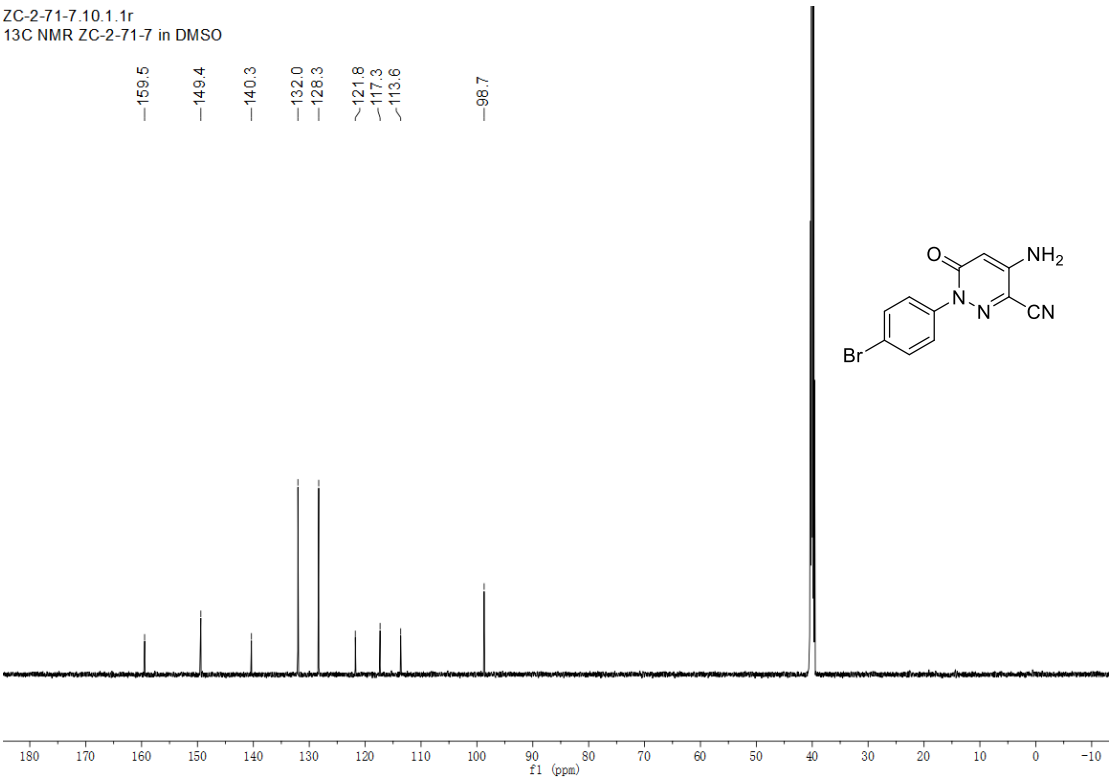
^{1}H NMR spectrum of compound **3j** (600 MHz, DMSO)



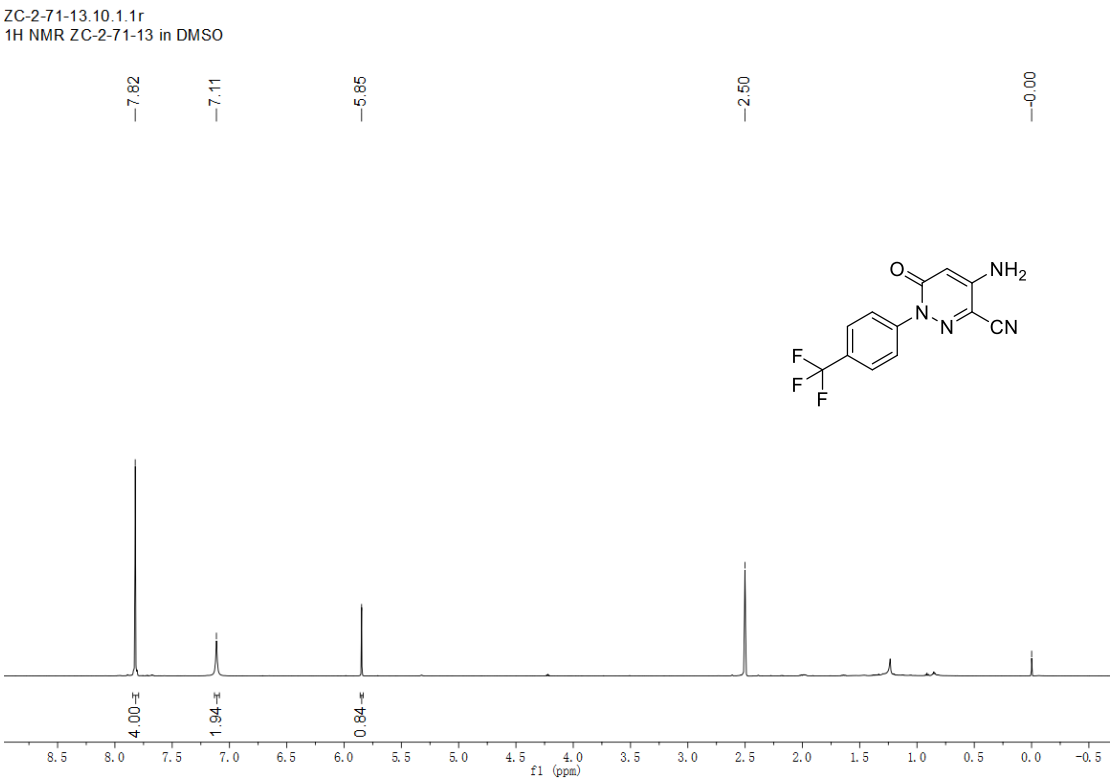
^{13}C NMR spectrum of compound **3j** (151 MHz, DMSO)



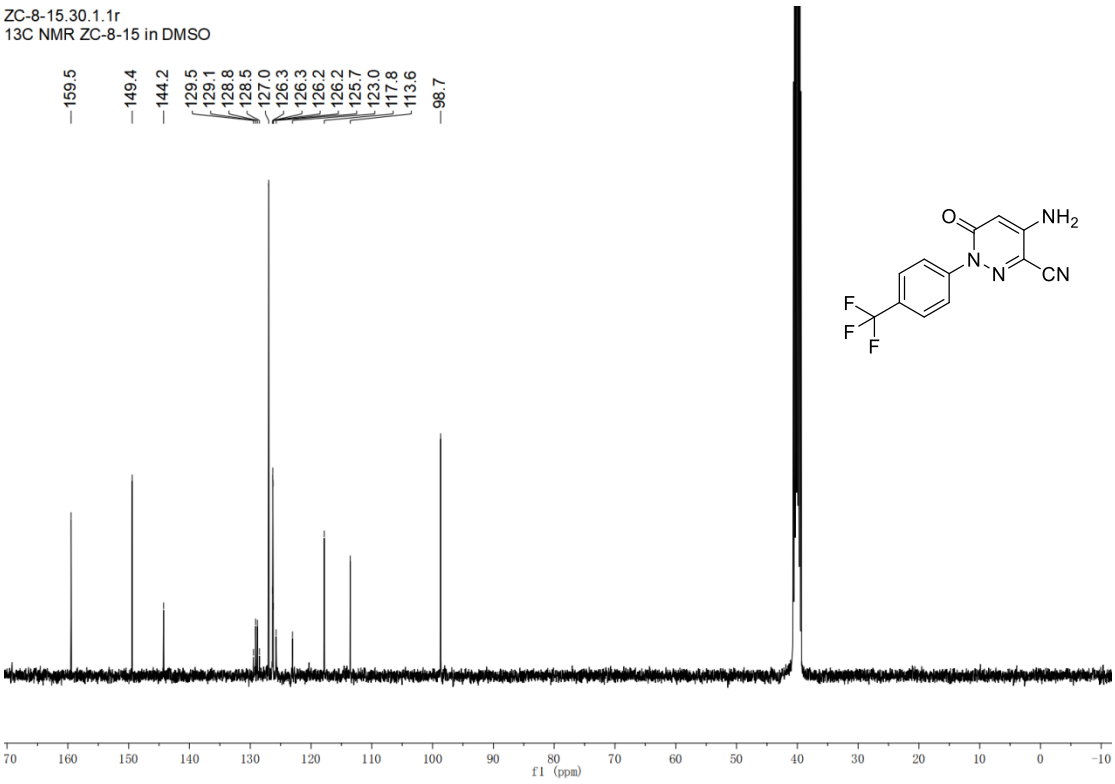
^{1}H NMR spectrum of compound **3k** (600 MHz, DMSO)



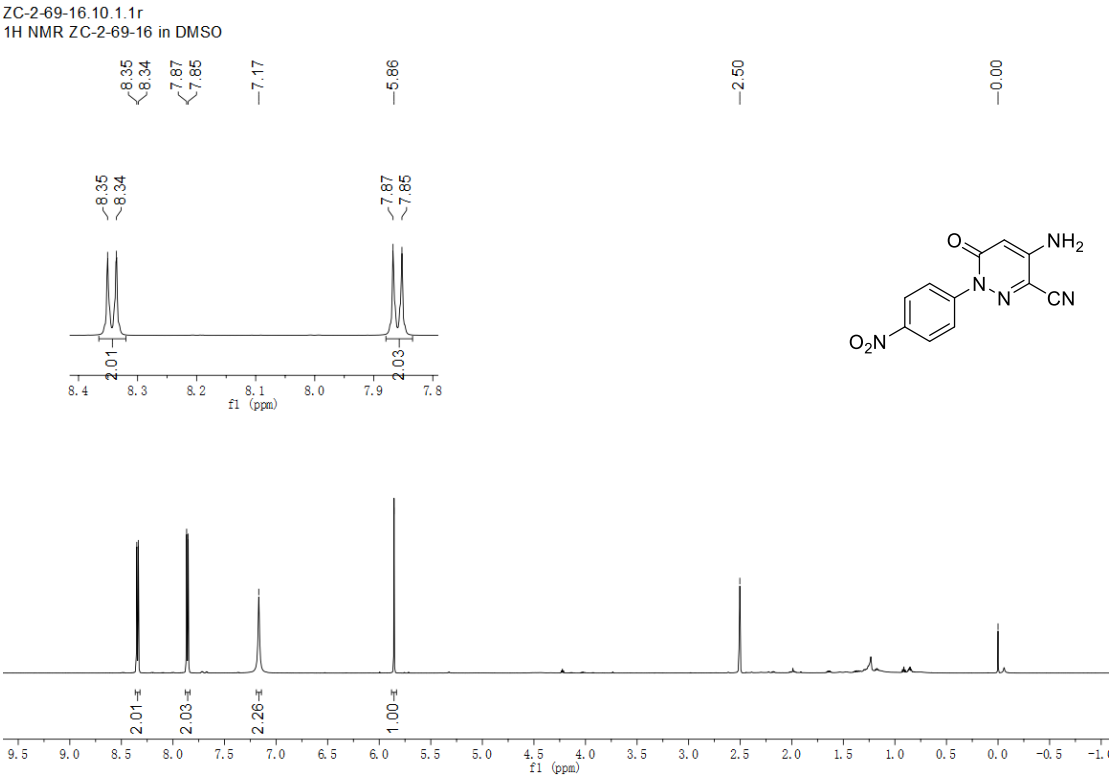
^{13}C NMR spectrum of compound **3k** (151 MHz, DMSO)



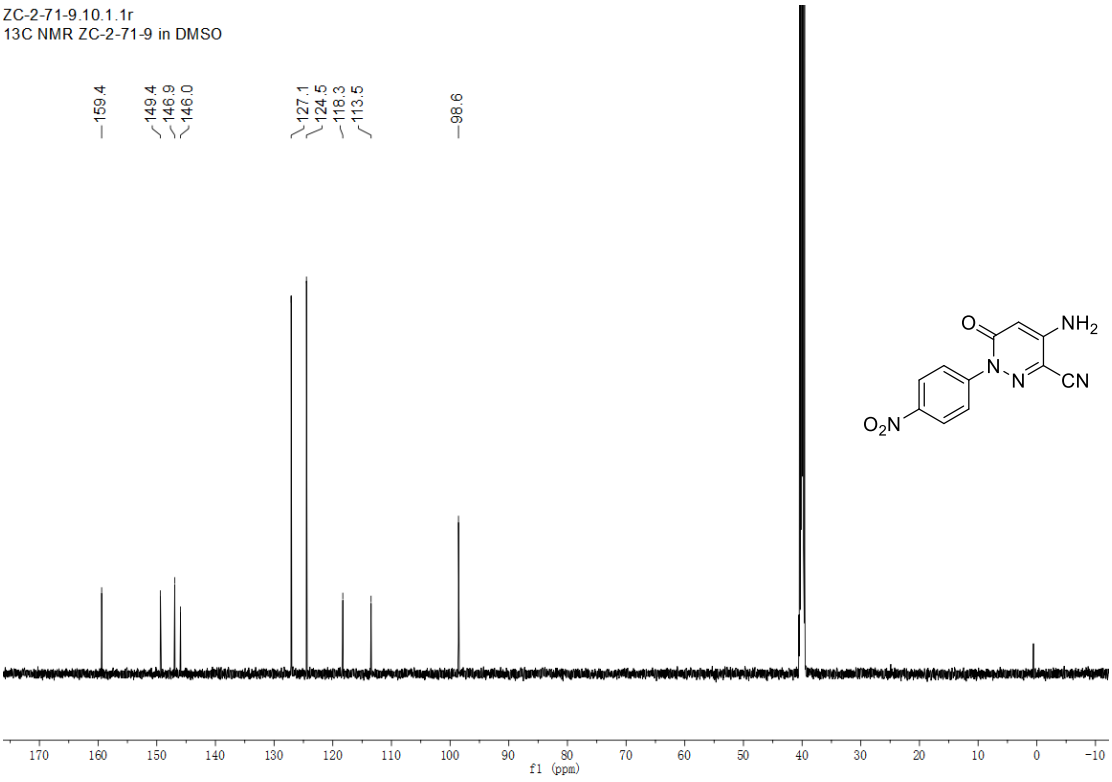
^{1}H NMR spectrum of compound **3l** (600 MHz, DMSO)



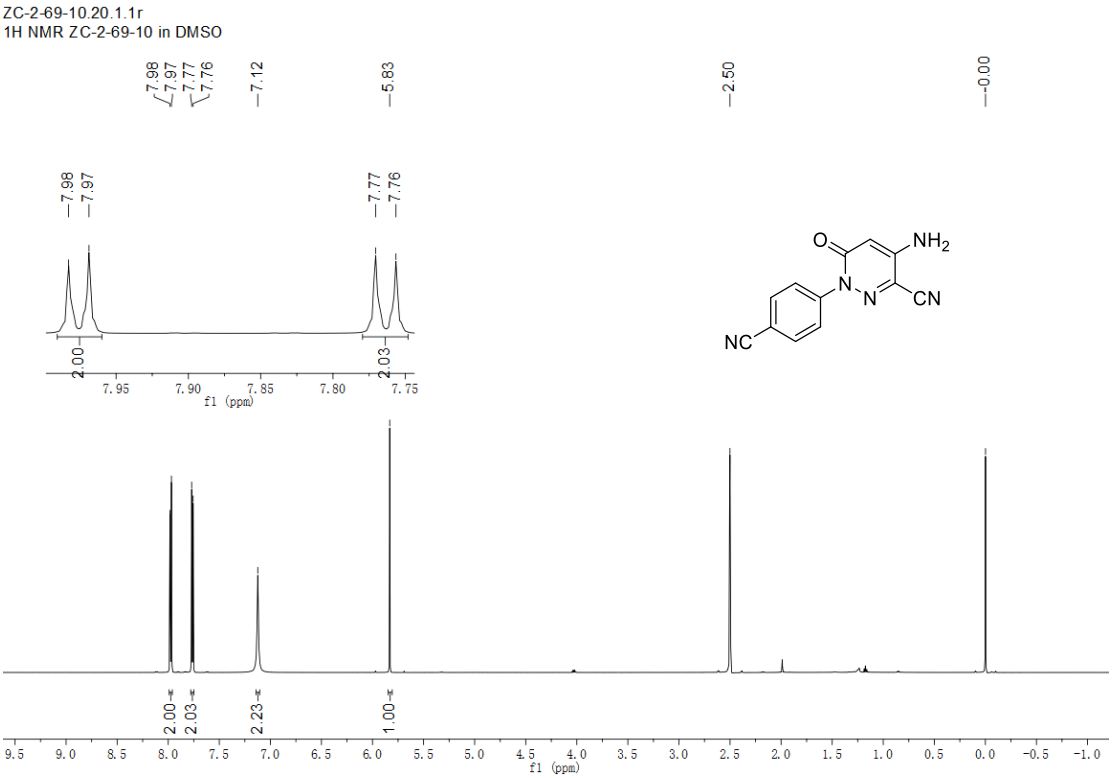
^{13}C NMR spectrum of compound **3l** (151 MHz, DMSO)



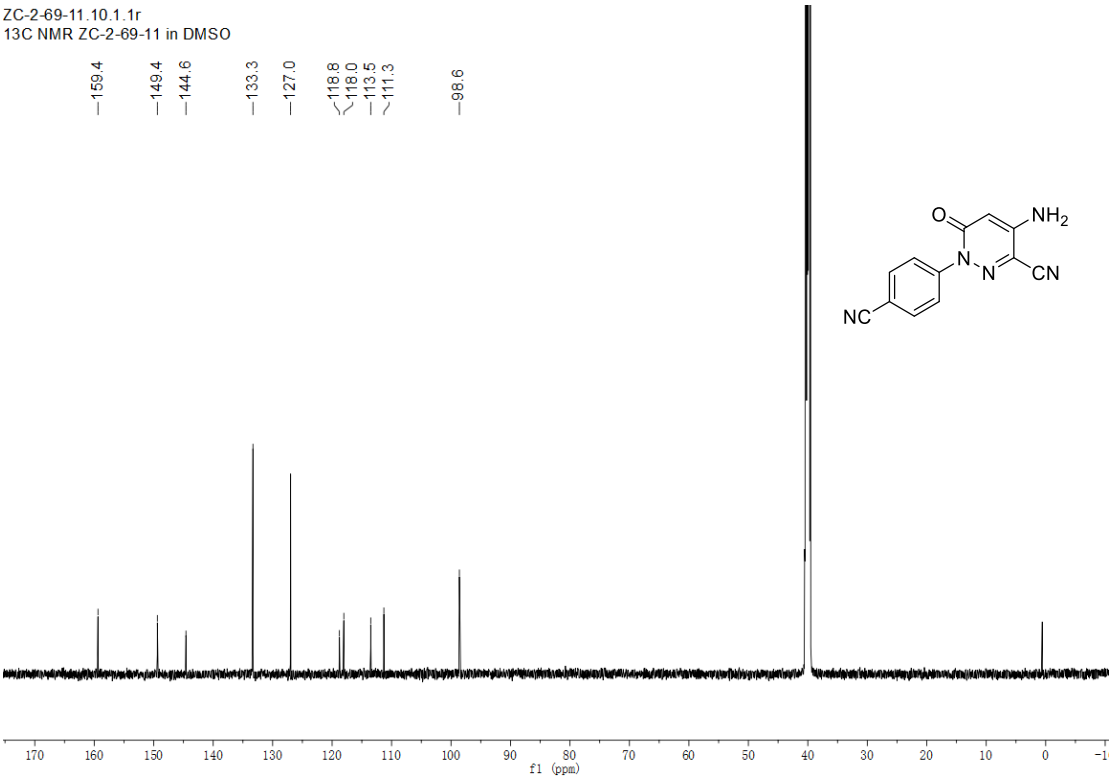
^{1}H NMR spectrum of compound **3m** (600 MHz, DMSO)



^{13}C NMR spectrum of compound **3m** (151 MHz, DMSO)

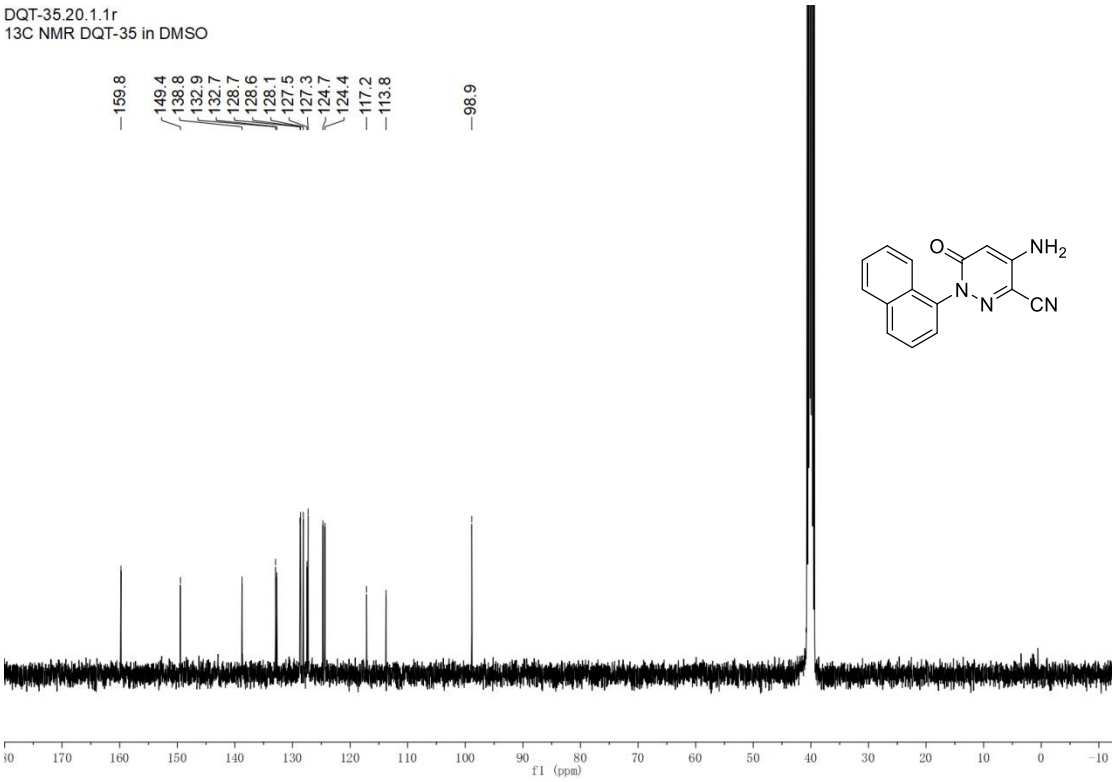


^{1}H NMR spectrum of compound **3n** (600 MHz, DMSO)

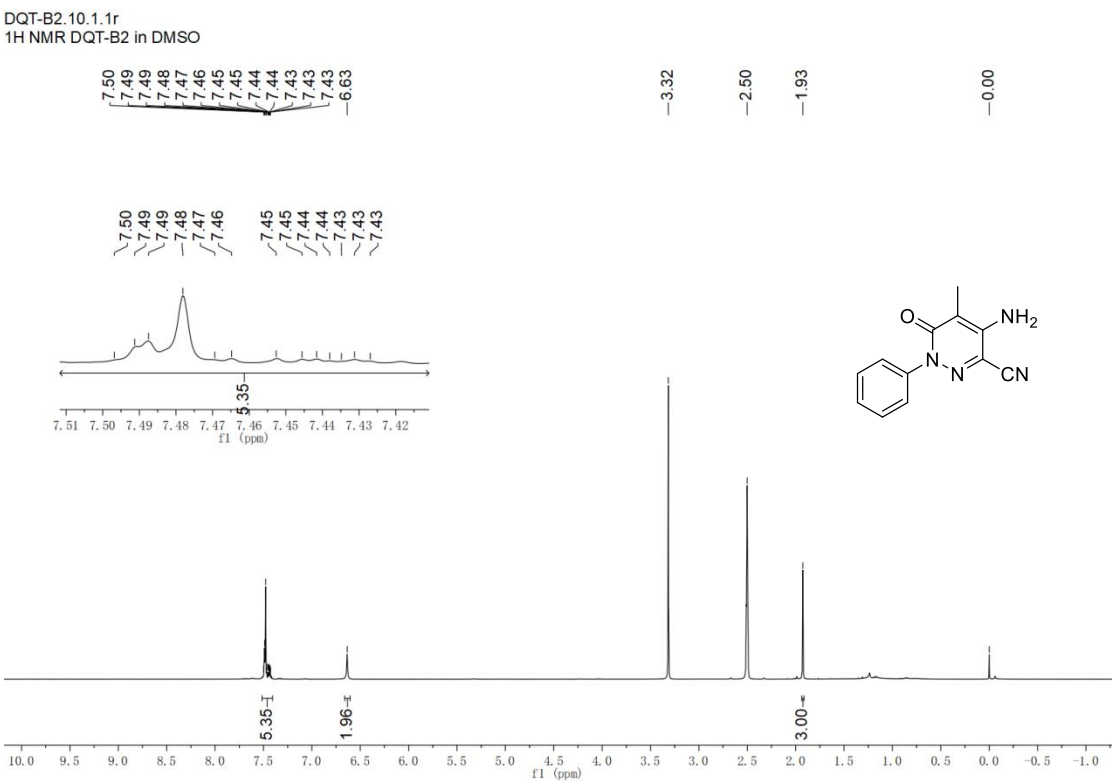


^{13}C NMR spectrum of compound **3n** (151 MHz, DMSO)

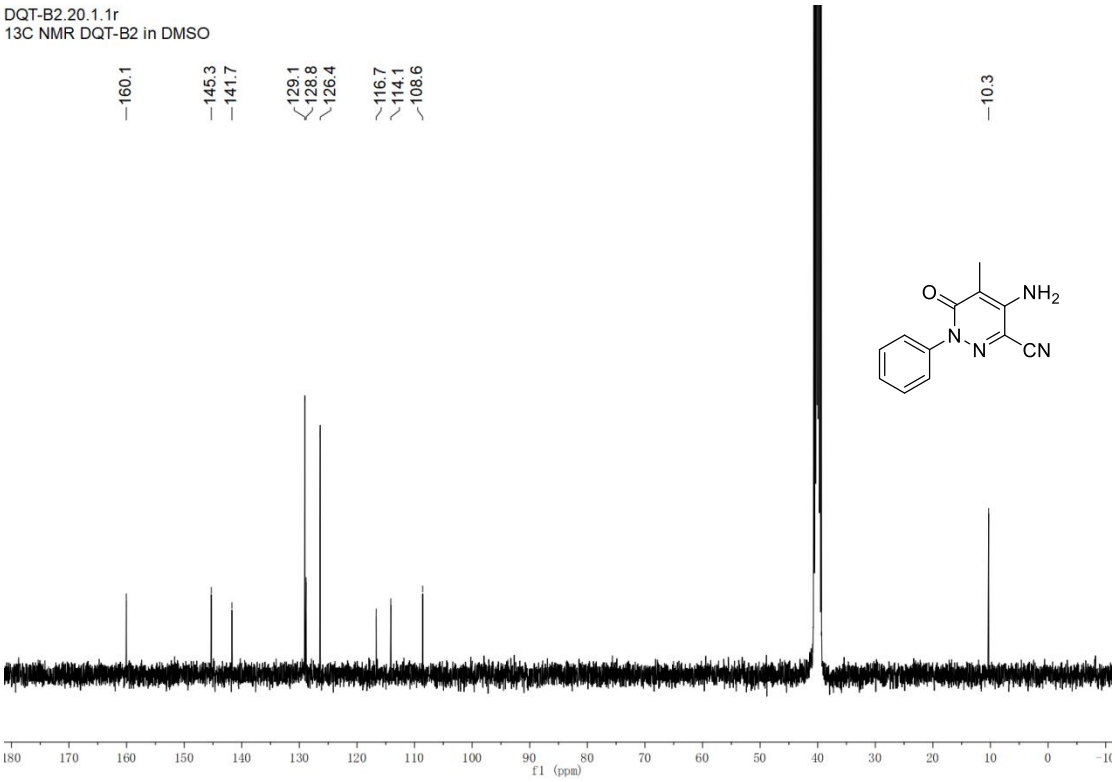
^{1}H NMR spectrum of compound **3o** (400 MHz, DMSO)



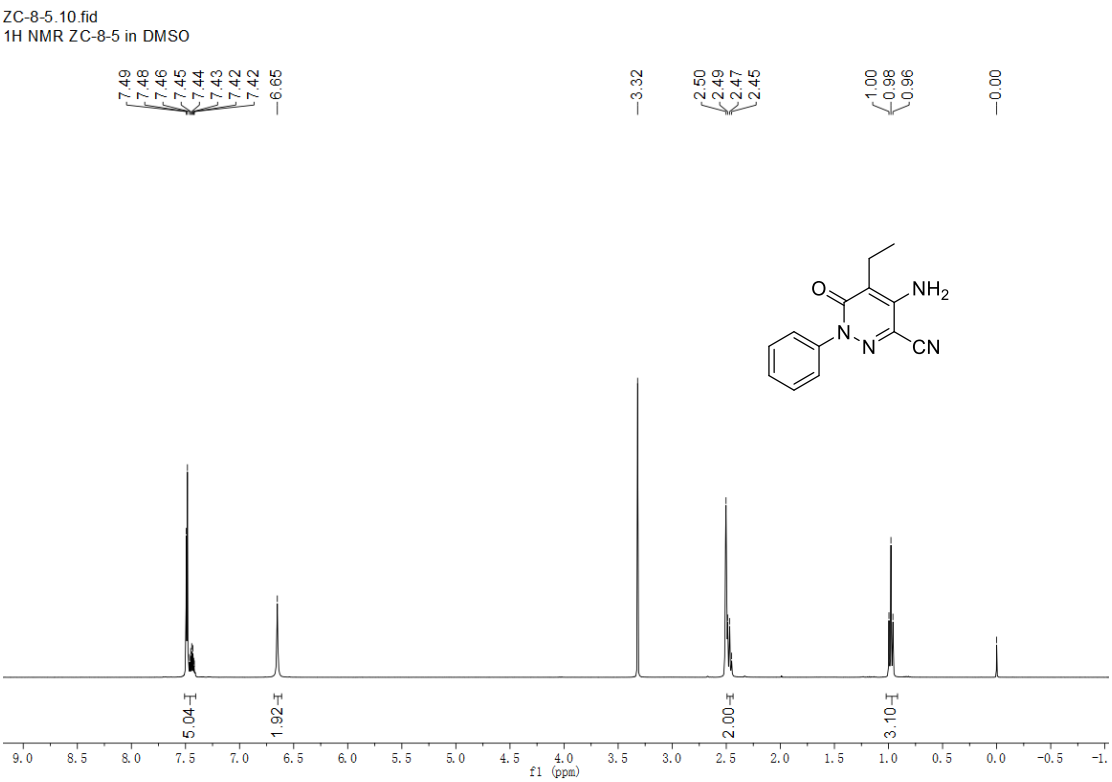
^{13}C NMR spectrum of compound **3o** (151 MHz, DMSO)



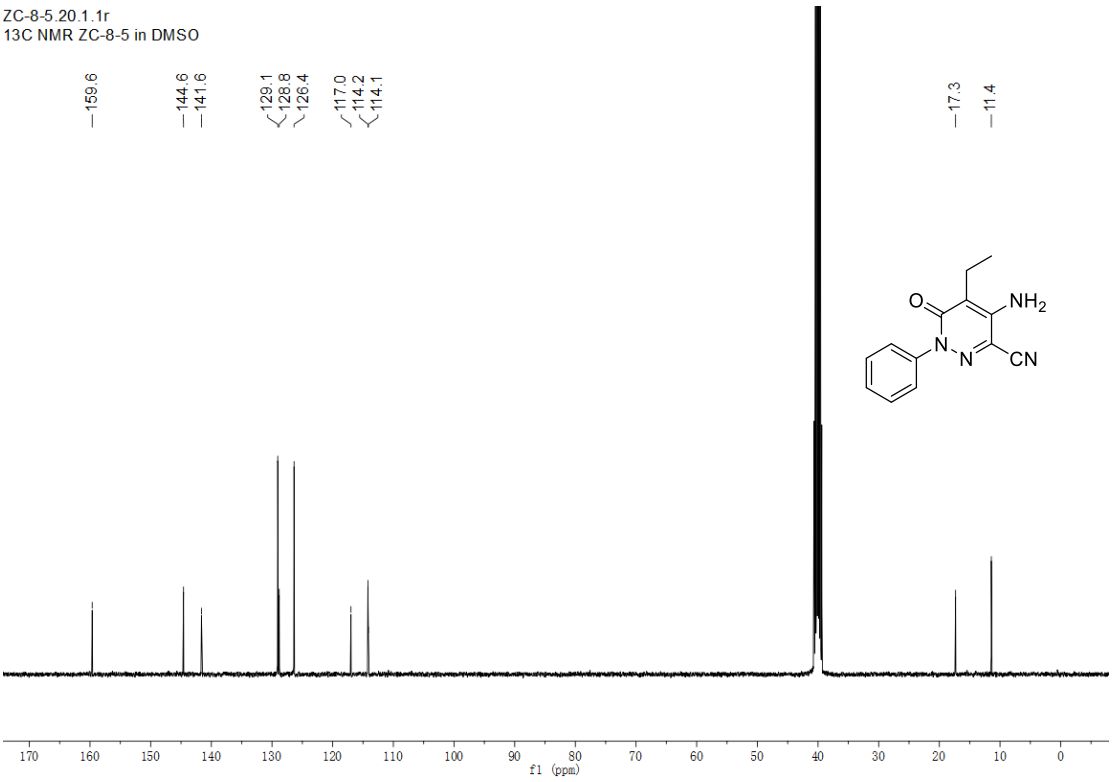
^{1}H NMR spectrum of compound **3p** (400 MHz, DMSO)



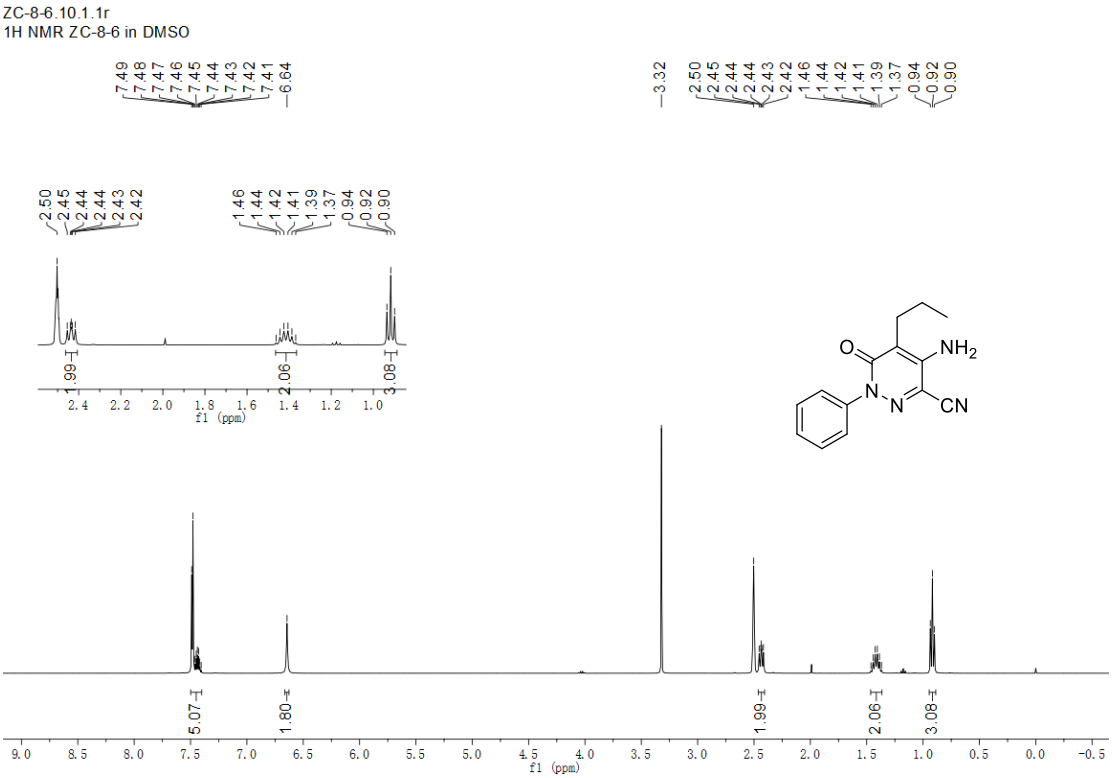
^{13}C NMR spectrum of compound **3p** (151 MHz, DMSO)



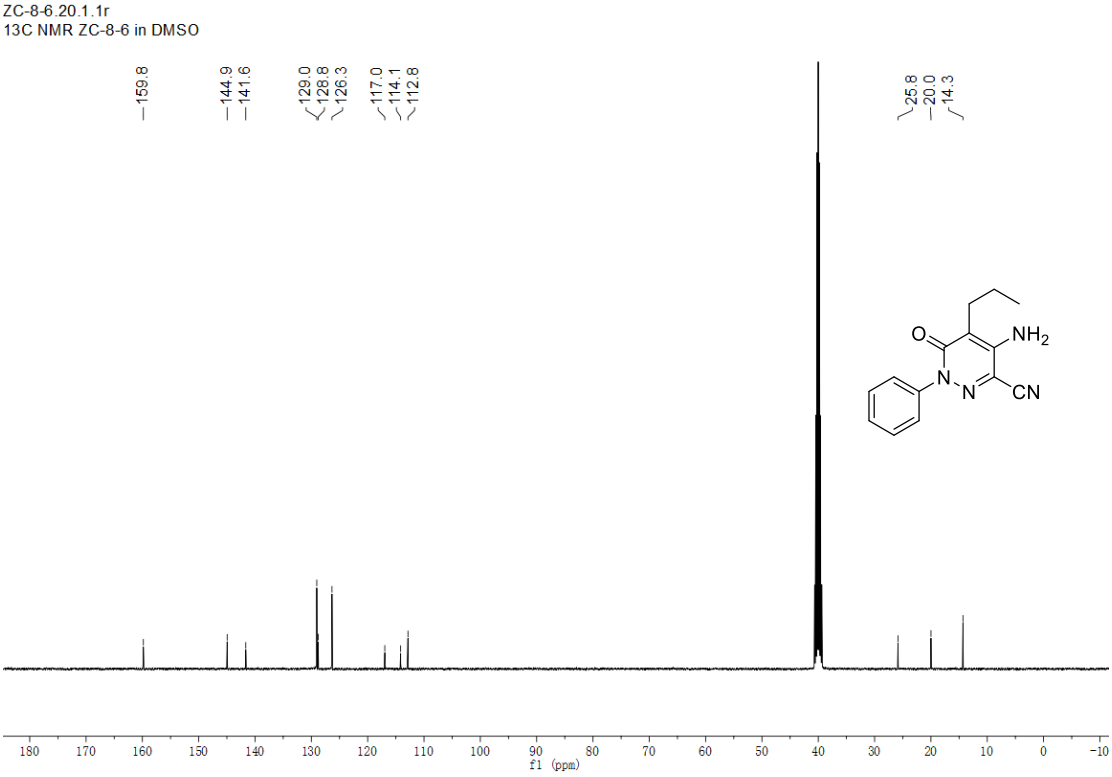
^{1}H NMR spectrum of compound **3q** (400 MHz, DMSO)



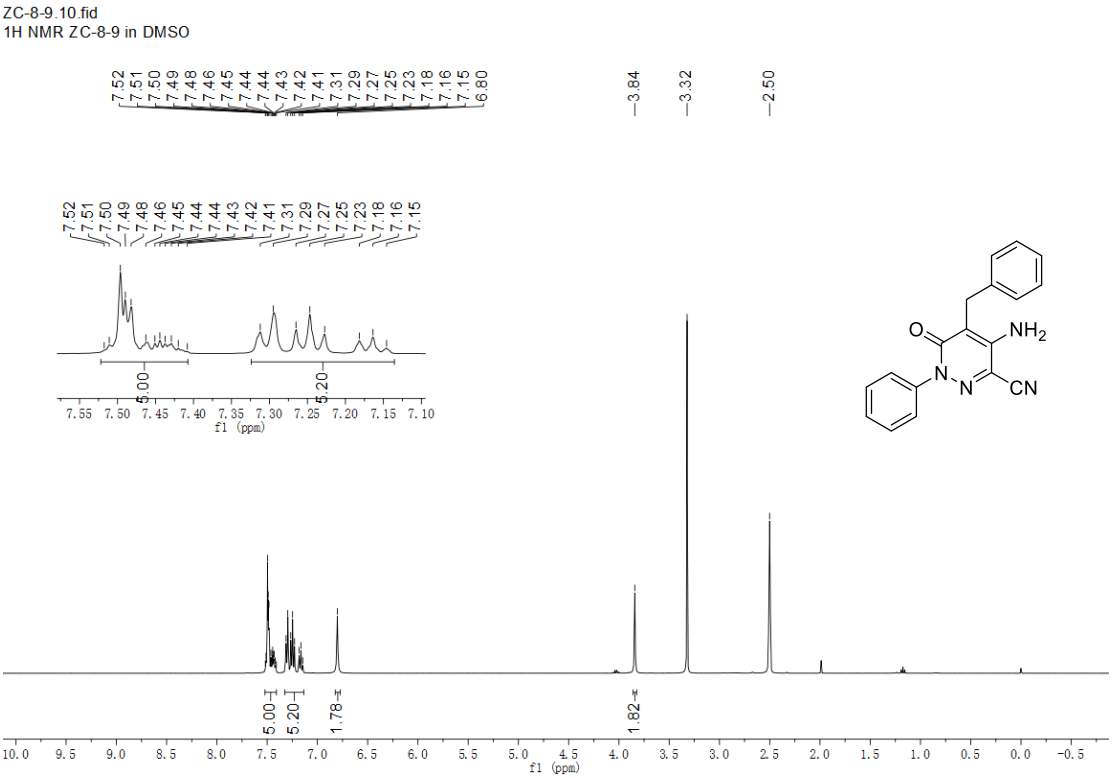
^{13}C NMR spectrum of compound **3q** (101 MHz, DMSO)



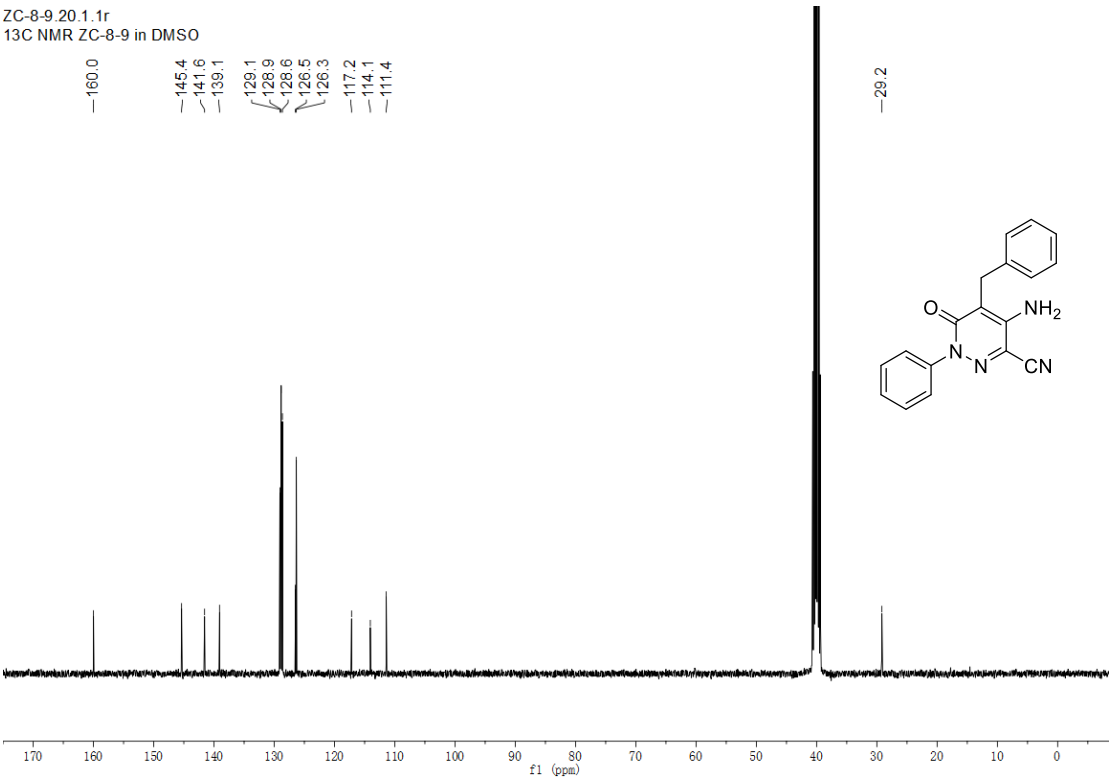
^{1}H NMR spectrum of compound **3r** (400 MHz, DMSO)



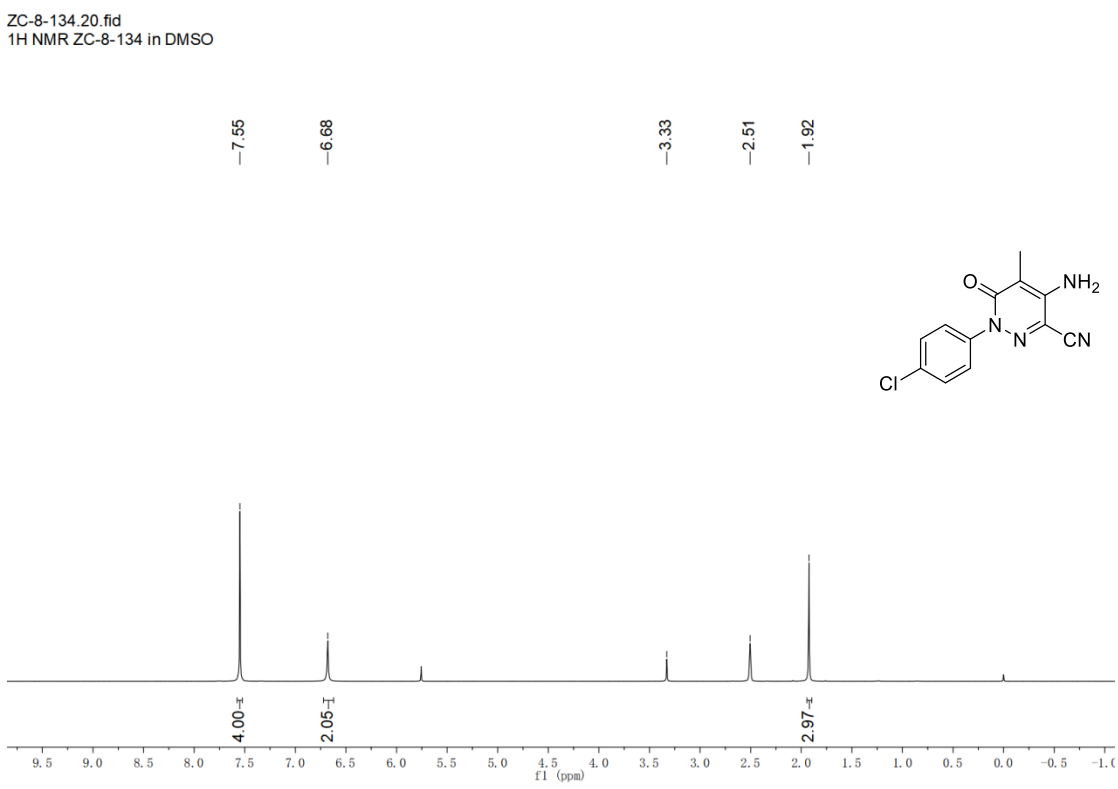
^{13}C NMR spectrum of compound **3r** (101 MHz, DMSO)



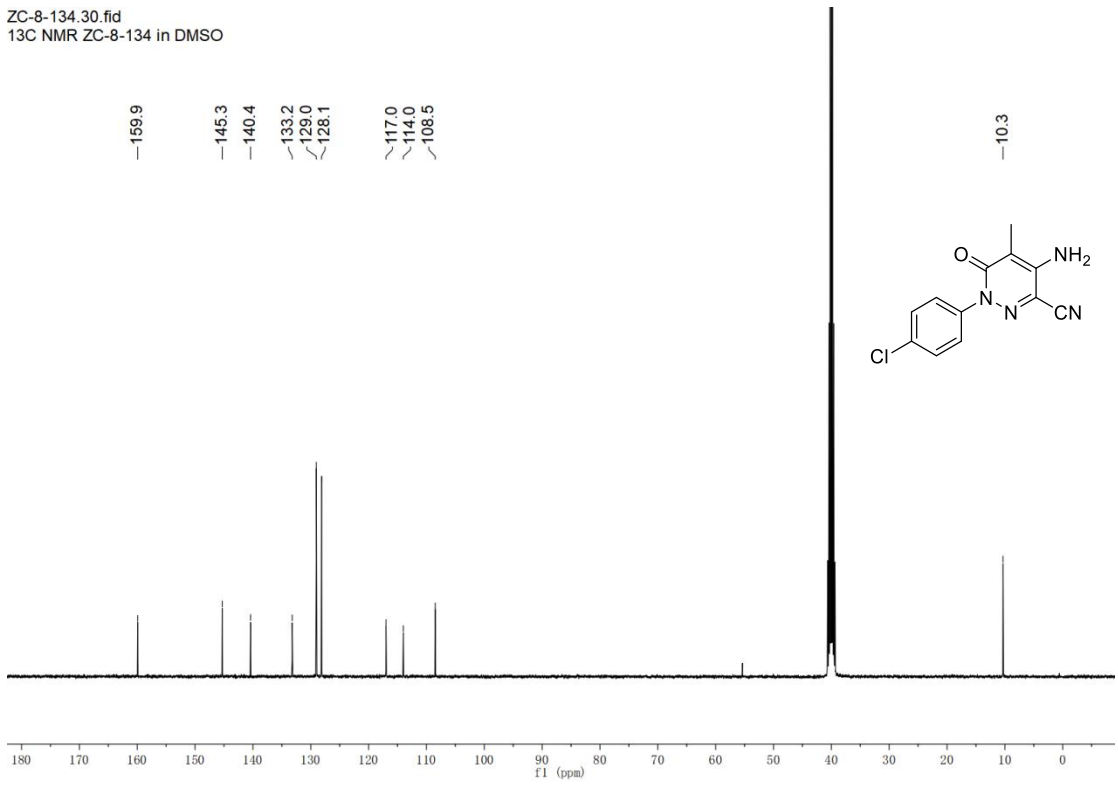
^{1}H NMR spectrum of compound **3s** (400 MHz, DMSO)



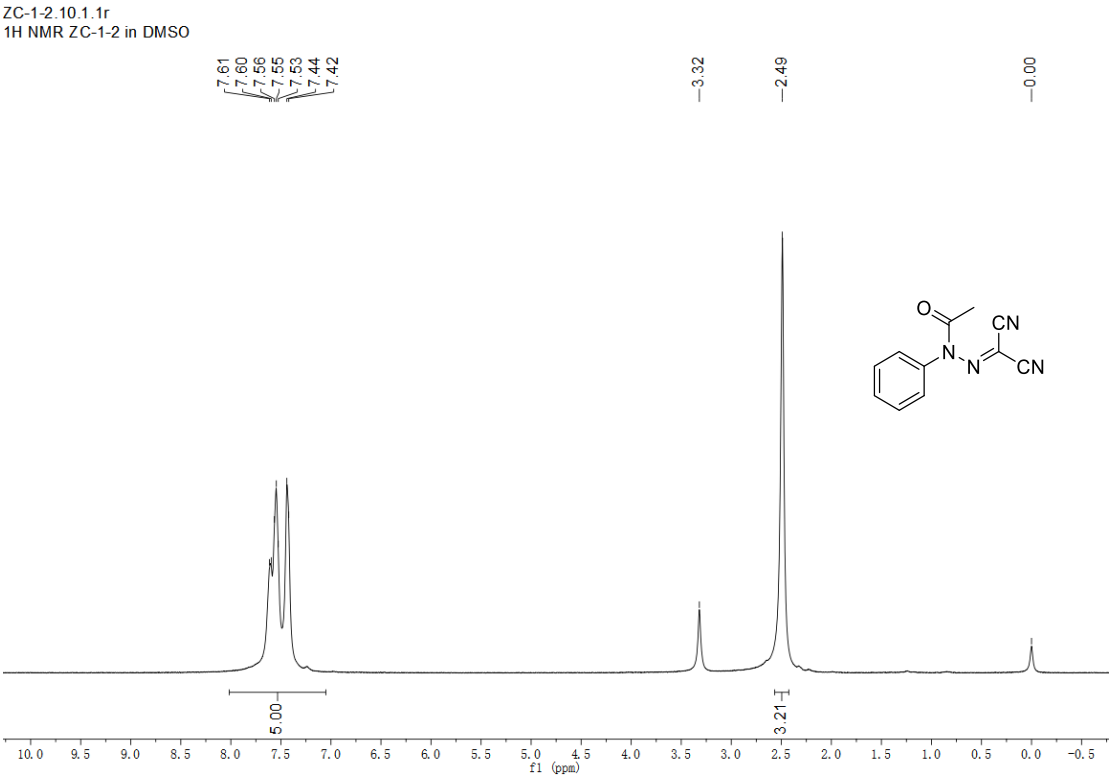
^{13}C NMR spectrum of compound **3s** (101 MHz, DMSO)



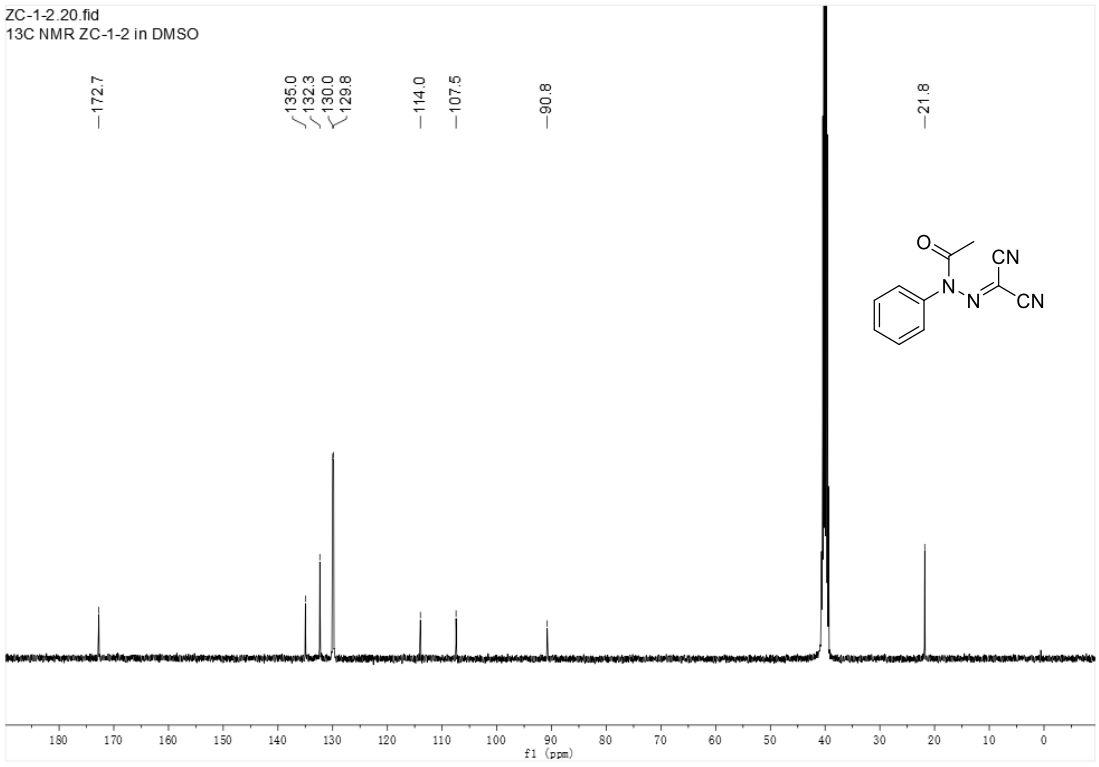
^{1}H NMR spectrum of compound **3t** (400 MHz, DMSO)



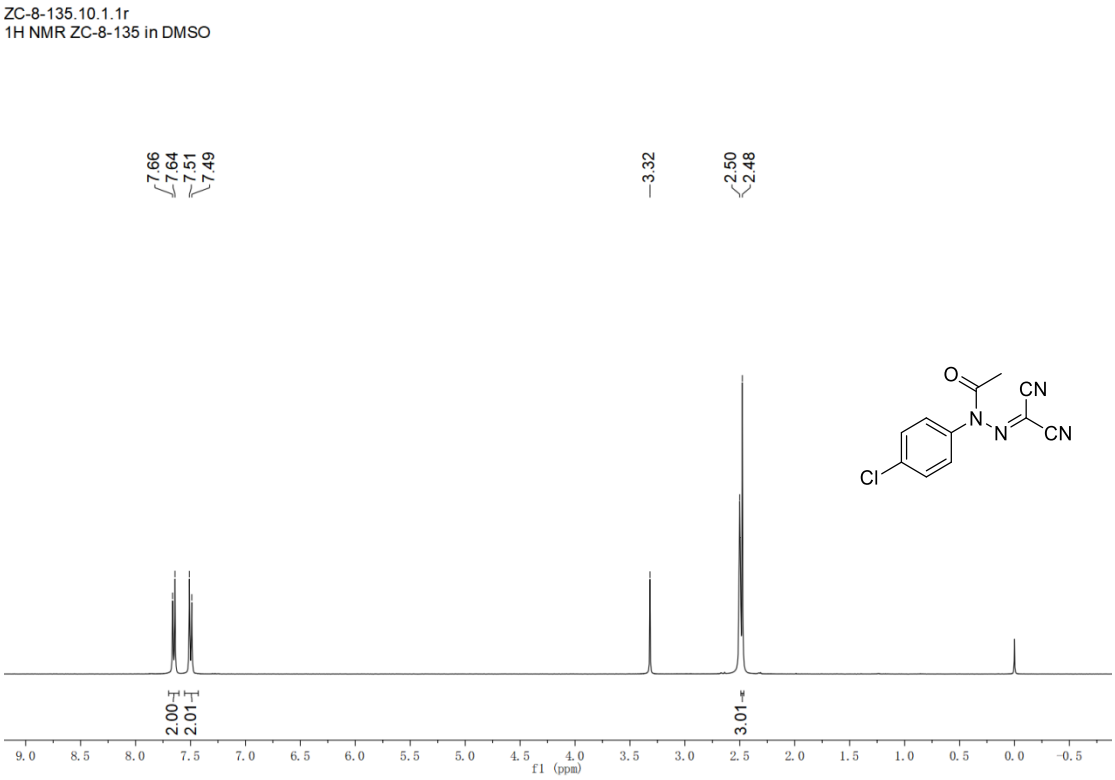
^{13}C NMR spectrum of compound **3t** (101 MHz, DMSO)



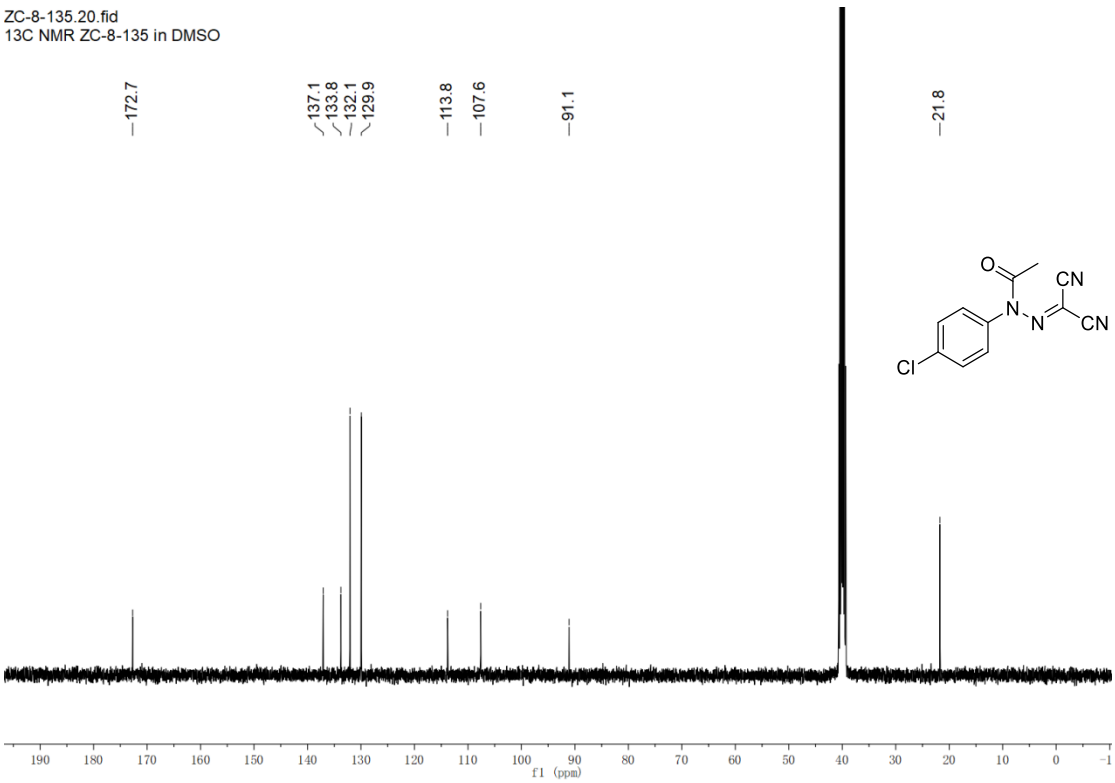
^{1}H NMR spectrum of compound **4a** (400 MHz, DMSO)



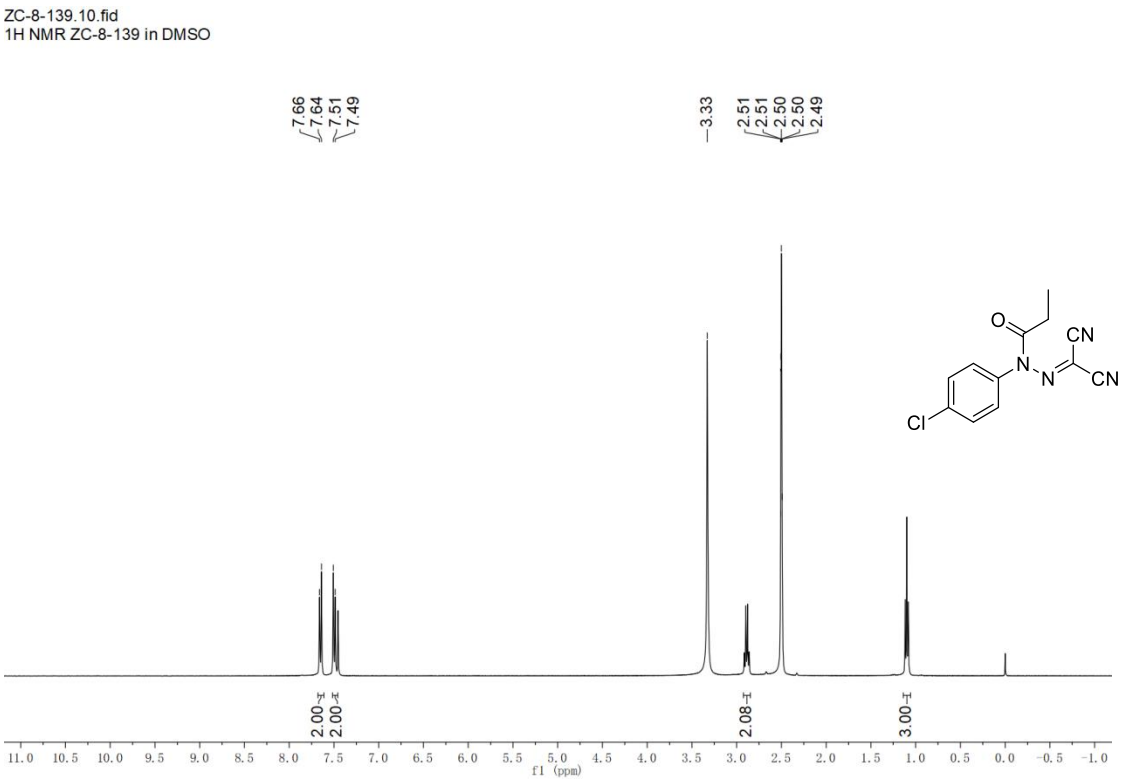
^{13}C NMR spectrum of compound **4a** (101 MHz, DMSO)



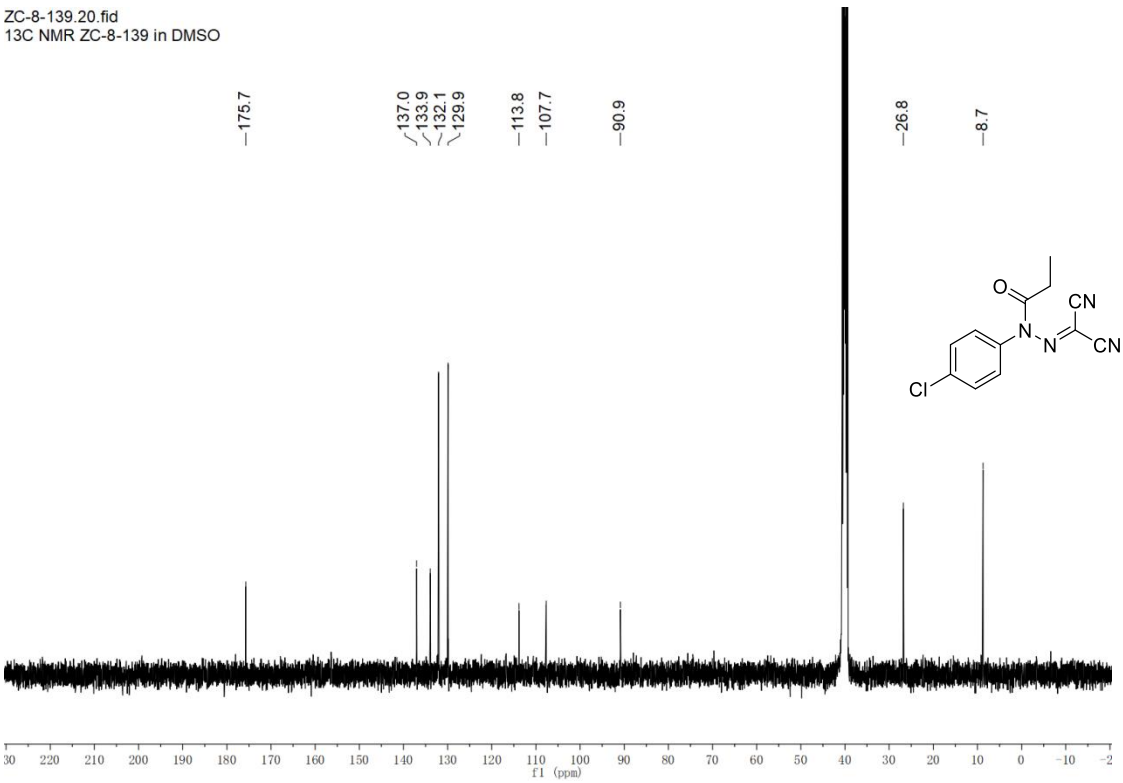
^{1}H NMR spectrum of compound **4b** (400 MHz, DMSO)



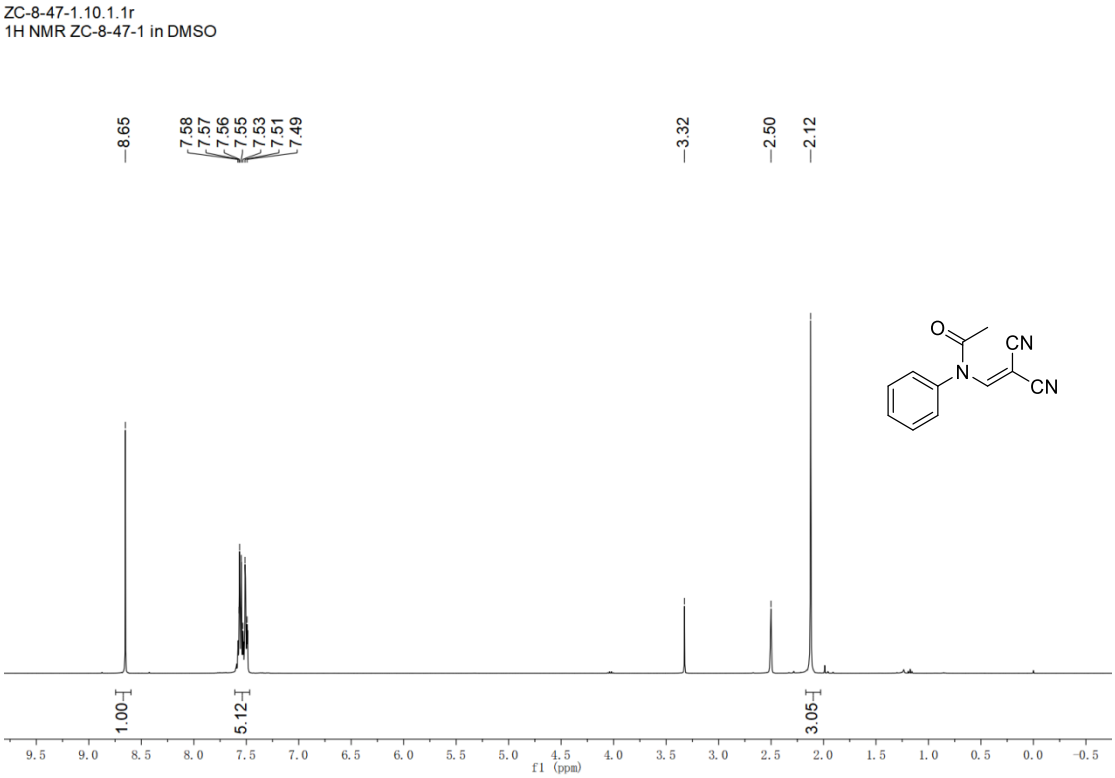
^{13}C NMR spectrum of compound **4b** (101 MHz, DMSO)



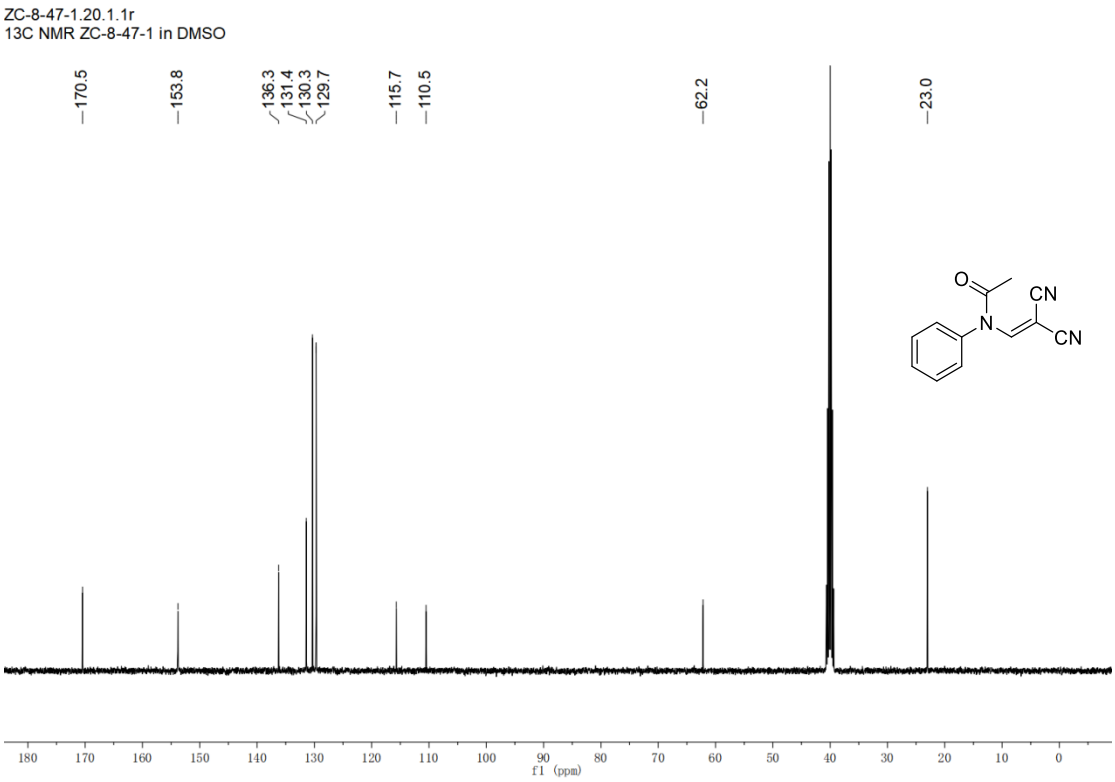
^{1}H NMR spectrum of compound **4c** (400 MHz, DMSO)



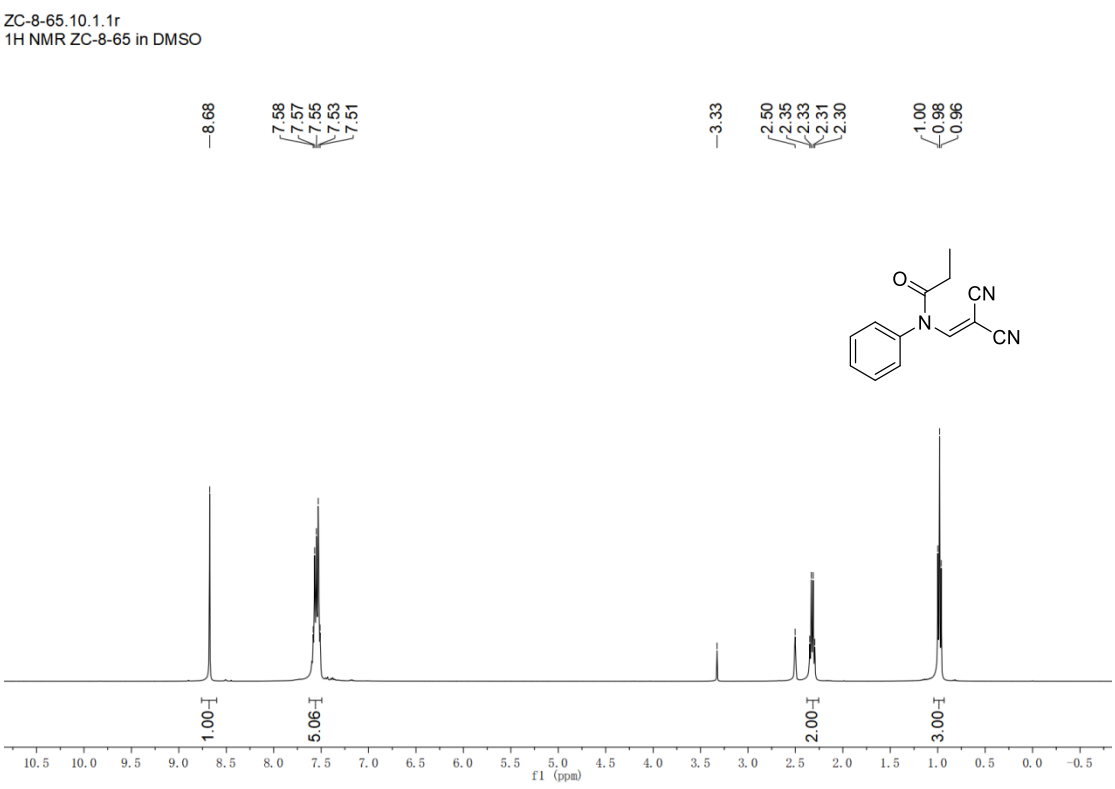
^{1}H NMR spectrum of compound **4c** (101 MHz, DMSO)



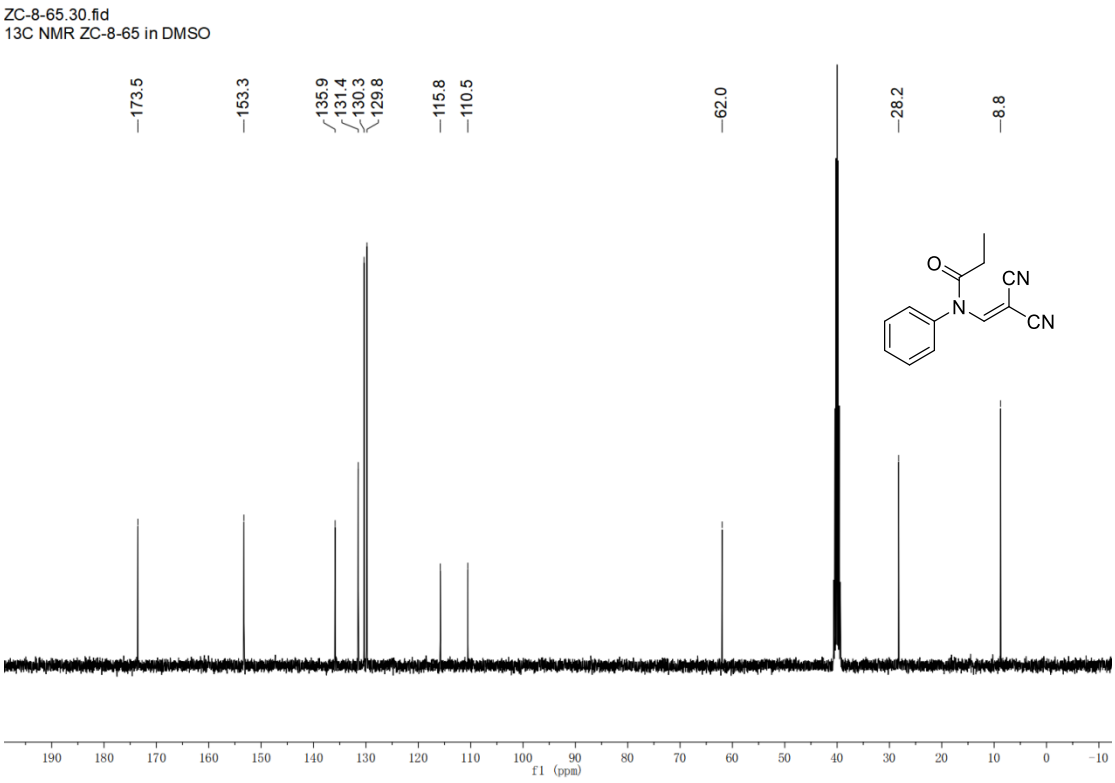
^{1}H NMR spectrum of compound **7a** (400 MHz, DMSO)



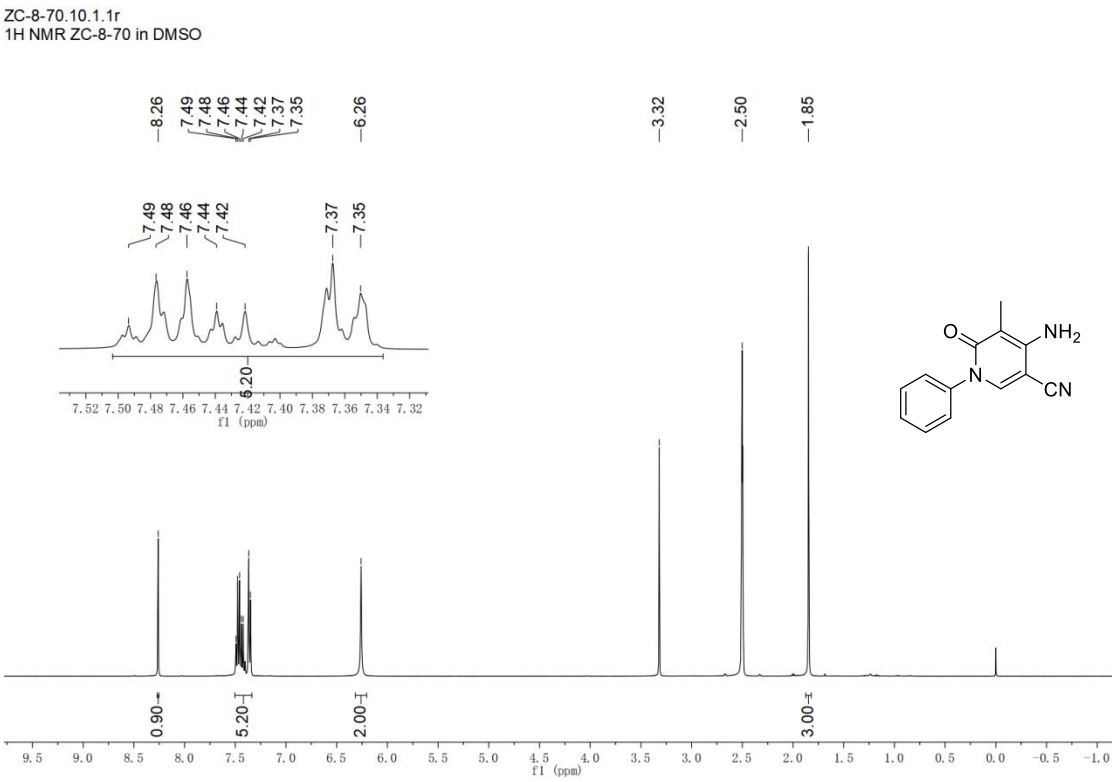
^{13}C NMR spectrum of compound **7a** (101 MHz, DMSO)



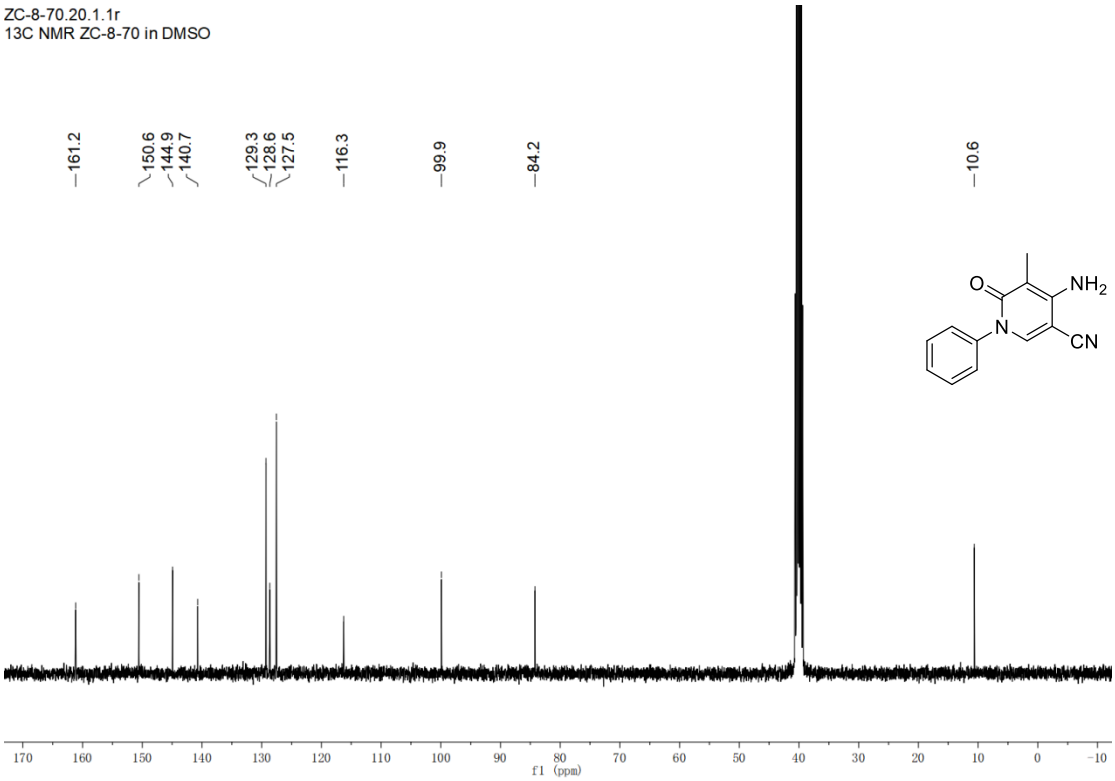
^{1}H NMR spectrum of compound **7b** (400 MHz, DMSO)



^{13}C NMR spectrum of compound **7b** (101 MHz, DMSO)



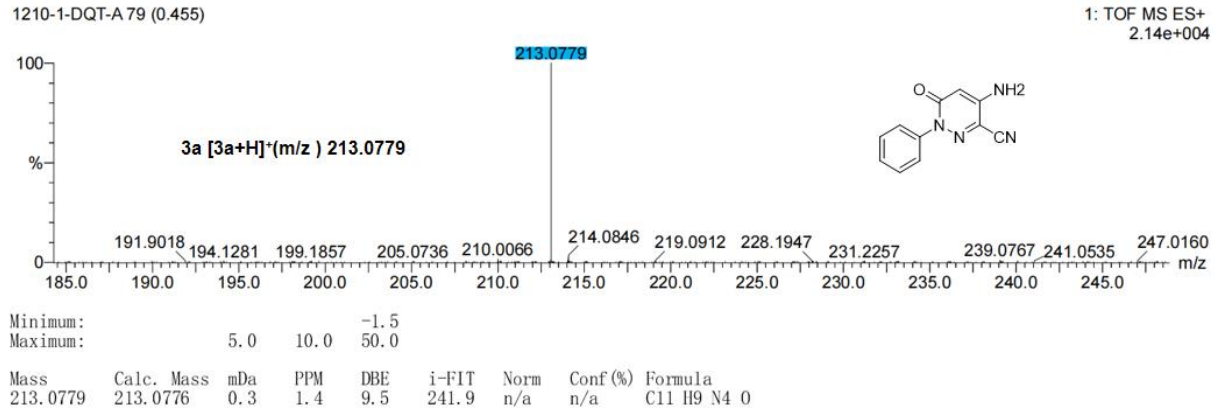
^{1}H NMR spectrum of compound **8b** (400 MHz, DMSO)



^{13}C NMR spectrum of compound **8b** (101 MHz, DMSO)

8. Copies of MS spectra

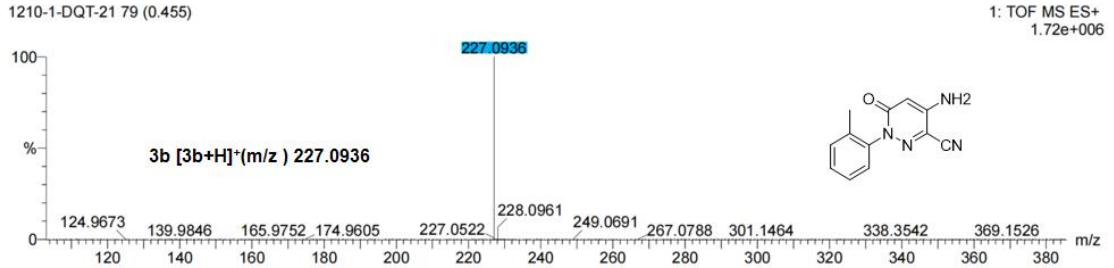
HRMS conditions: electrospray ionization source operating in the positive ion mode, capillary voltage: 3.5 kv, ion source temperature: 110℃, desolvation temperature: 400℃, nitrogen flow rate: 800 L/h.



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
213.0779	213.0776	0.3	1.4	9.5	241.9	n/a	n/a	C11 H9 N4 O

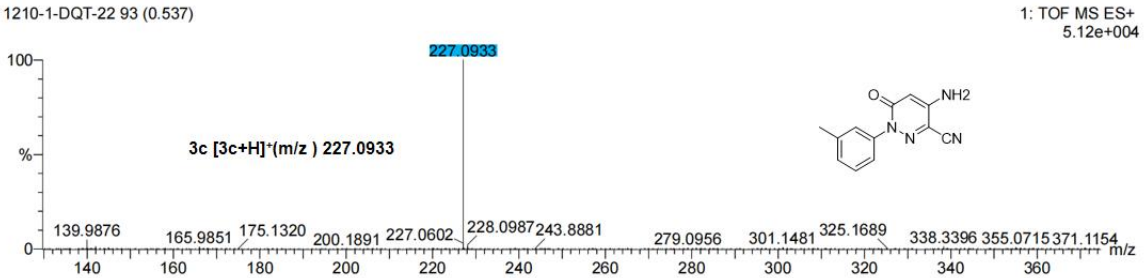
HRMS spectrum of **3a**



Minimum: -1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
227.0936	227.0933	0.3	1.3	9.5	770.2	n/a	n/a	C12 H11 N4 O

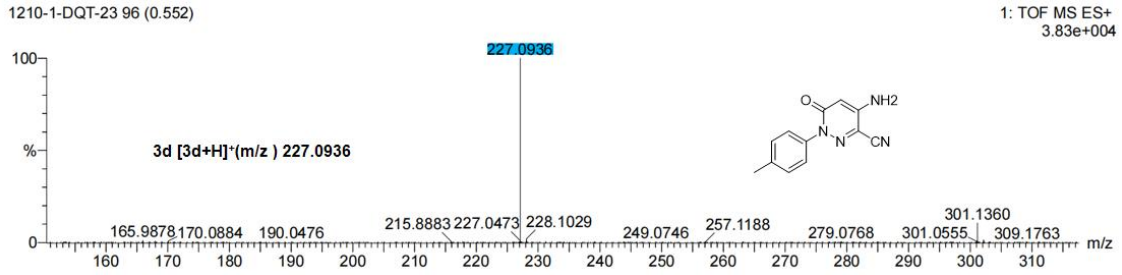
HRMS spectrum of **3b**



Minimum: -1.5
Maximum: 5.0 10.0 50.0

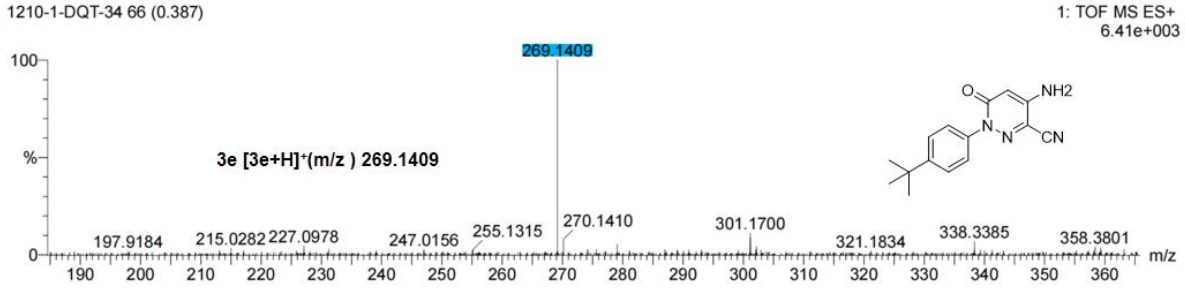
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
227.0933	227.0933	0.0	0.0	9.5	290.3	n/a	n/a	C12 H11 N4 O

HRMS spectrum of **3c**



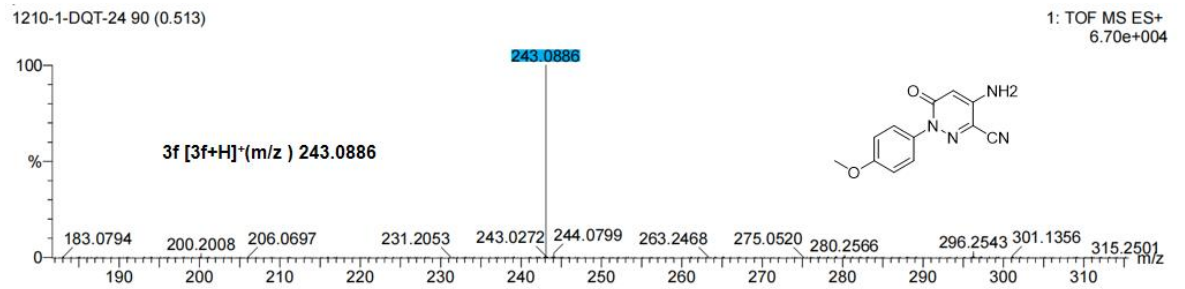
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
227.0936	227.0933	0.3	1.3	9.5	257.9	n/a	n/a	C12 H11 N4 O

HRMS spectrum of **3d**



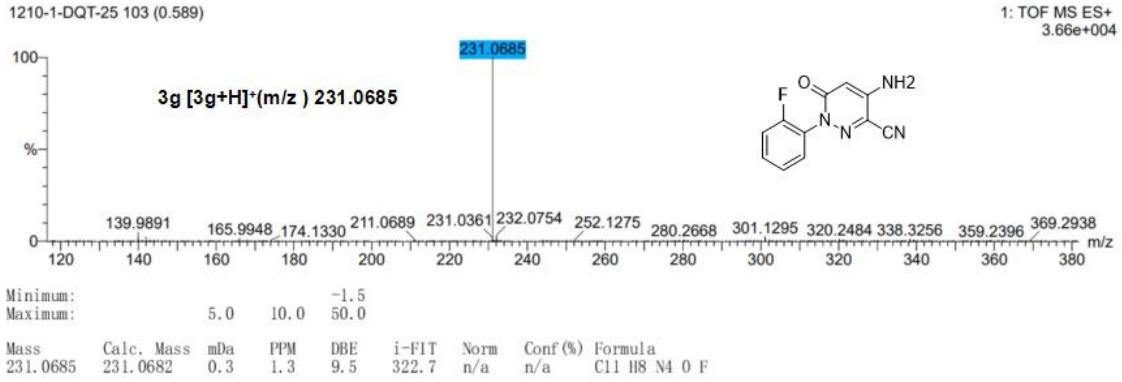
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
269.1409	269.1402	0.7	2.6	9.5	189.2	n/a	n/a	C15 H17 N4 O

HRMS spectrum of **3e**



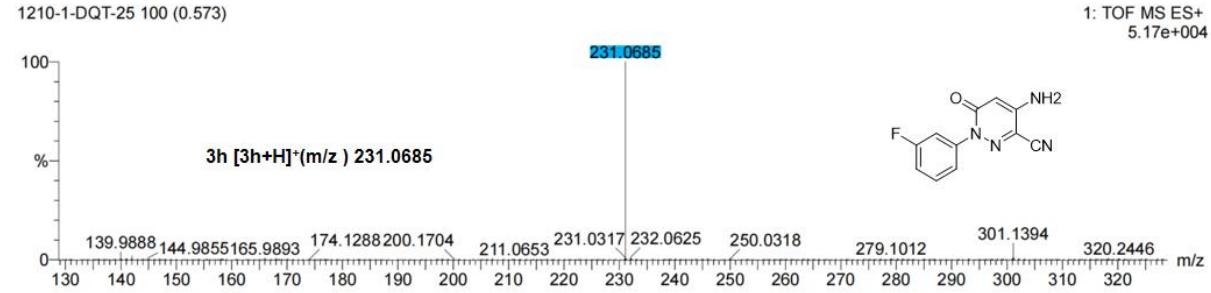
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
243.0886	243.0882	0.4	1.6	9.5	373.7	n/a	n/a	C12 H11 N4 O2

HRMS spectrum of **3f**



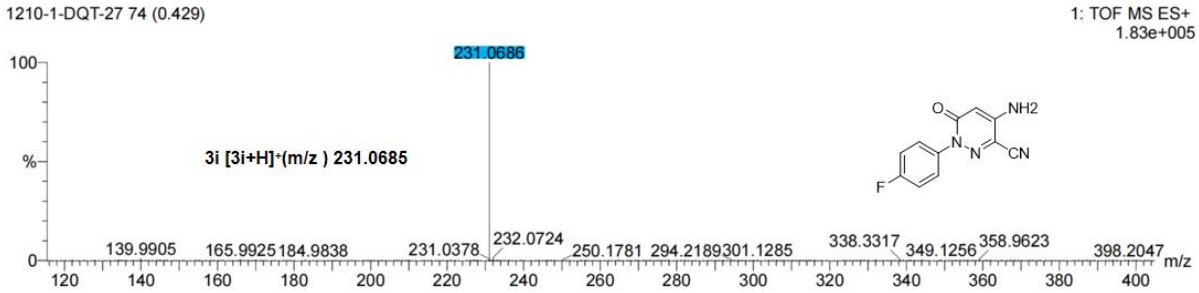
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
231.0685	231.0682	0.3	1.3	9.5	322.7	n/a	n/a	C11 H8 N4 O F

HRMS spectrum of **3g**



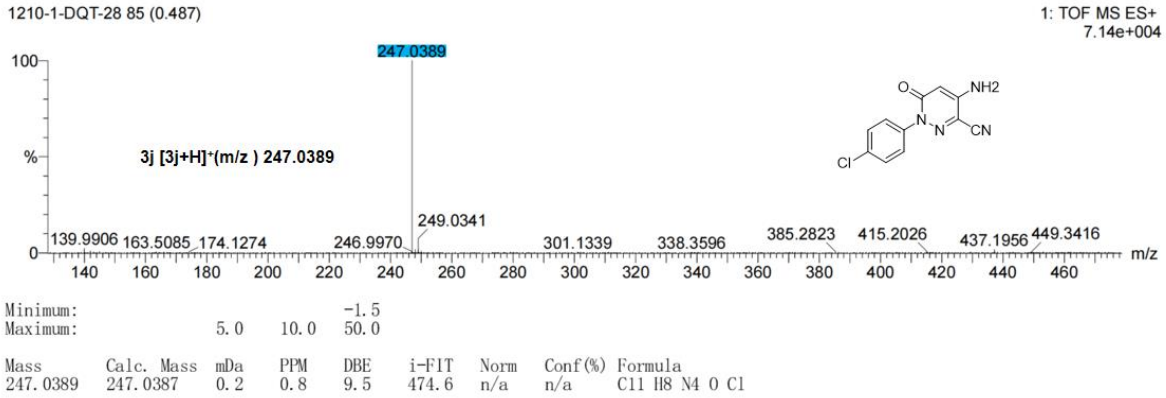
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
231.0685	231.0682	0.3	1.3	9.5	299.5	n/a	n/a	C11 H8 N4 O F

HRMS spectrum of **3h**

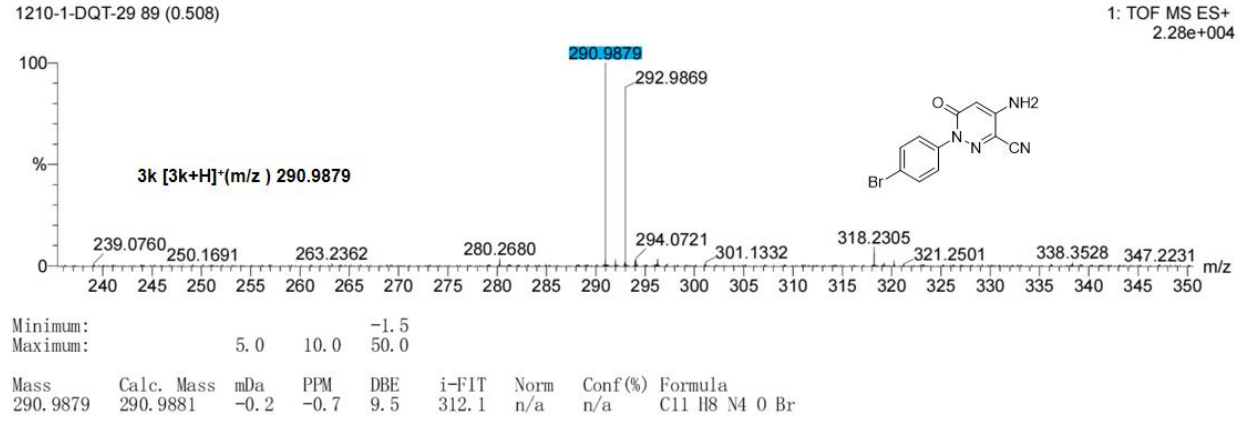


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
231.0686	231.0682	0.4	1.7	9.5	401.5	n/a	n/a	C11 H8 N4 O F

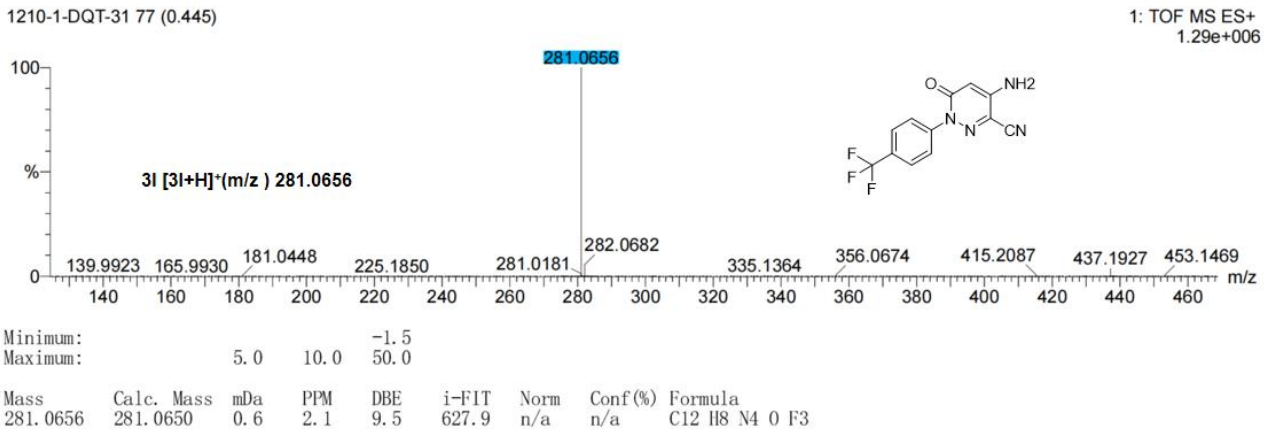
HRMS spectrum of **3i**



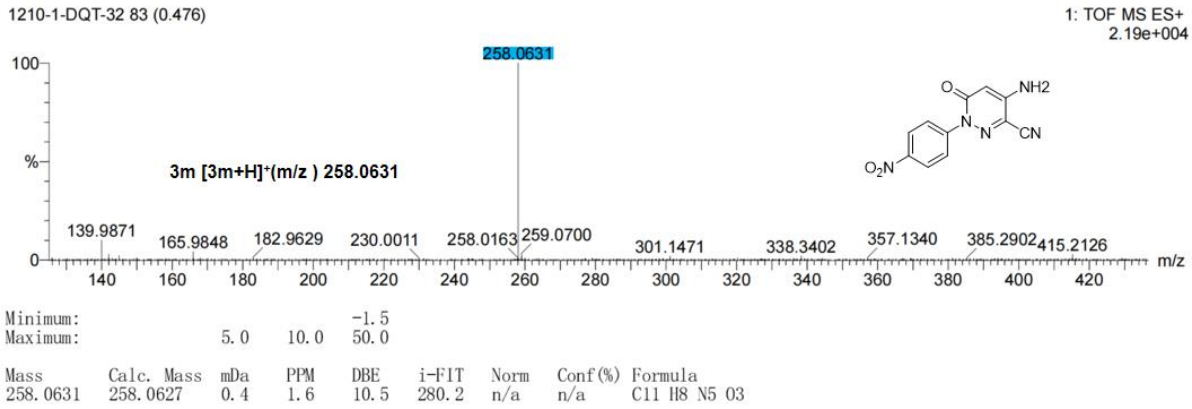
HRMS spectrum of **3j**



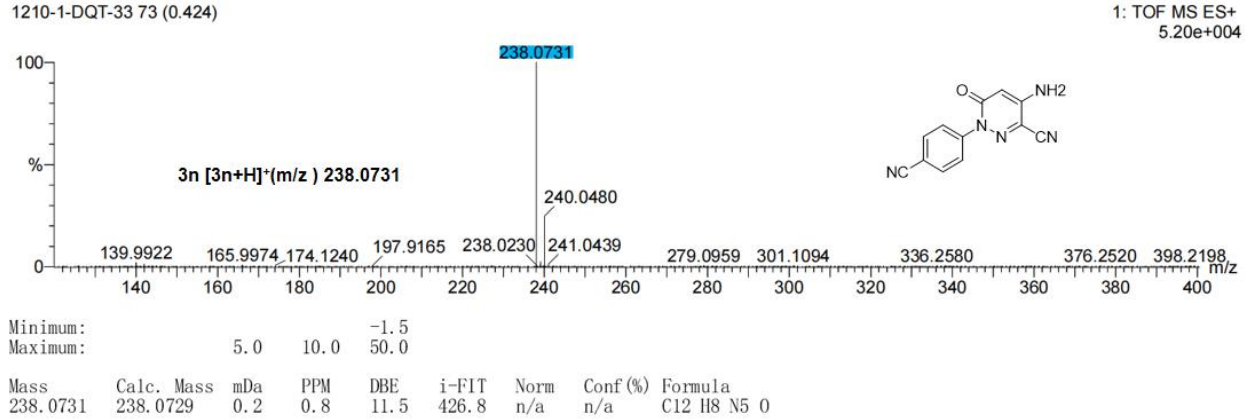
HRMS spectrum of **3k**



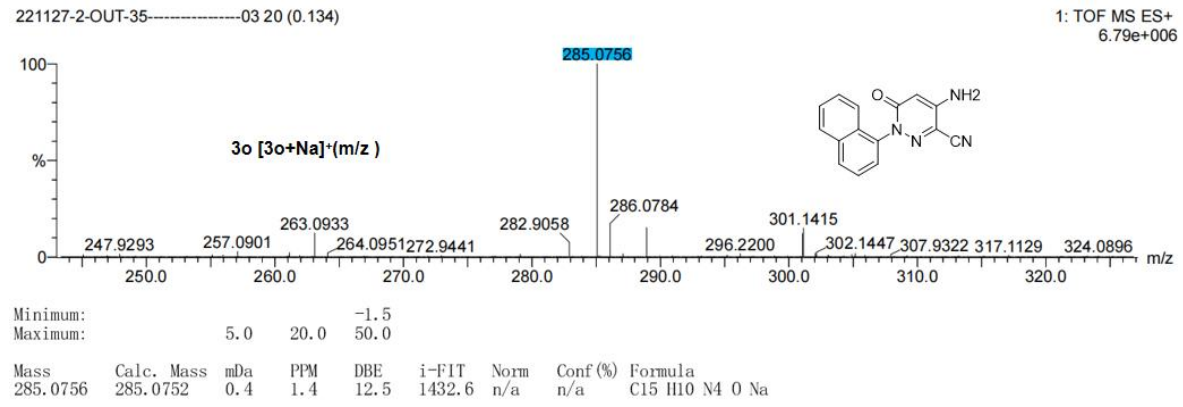
HRMS spectrum of **3l**



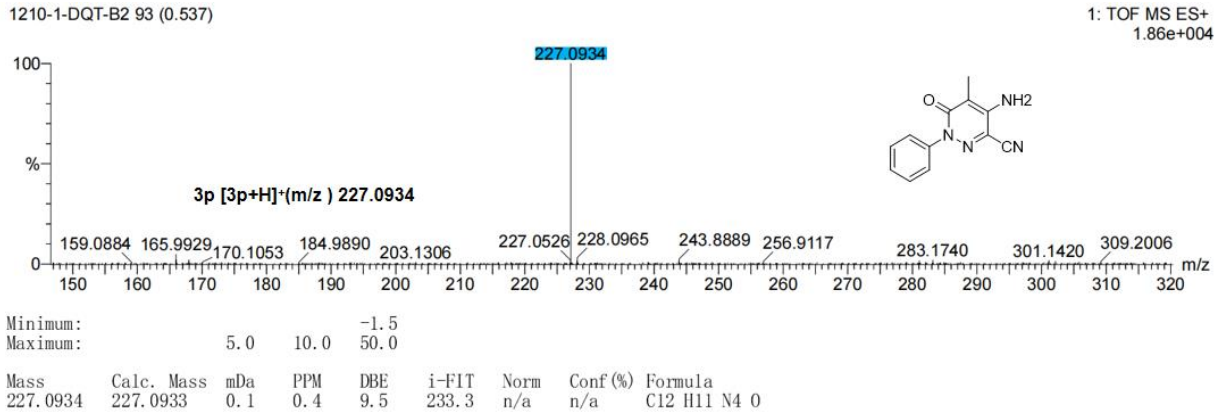
HRMS spectrum of **3m**



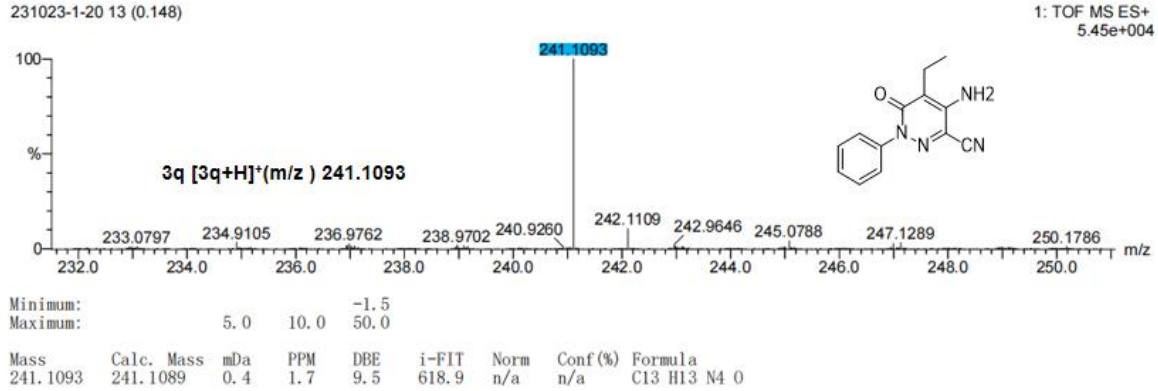
HRMS spectrum of **3n**



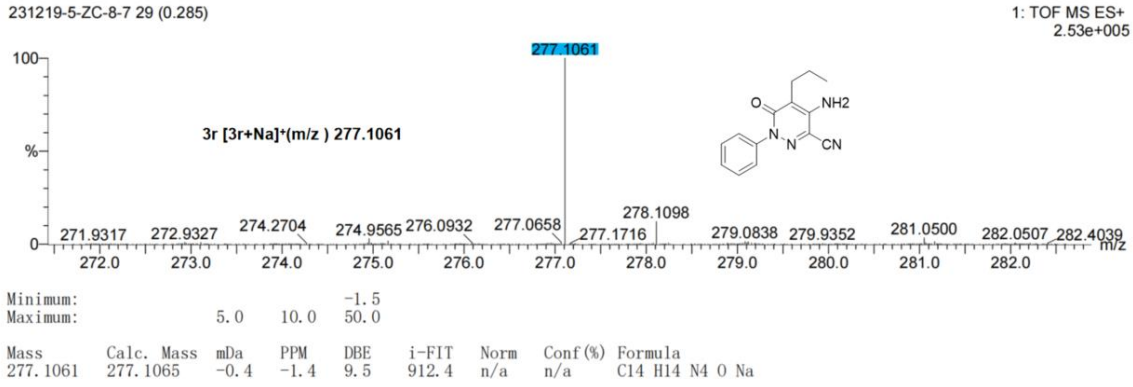
HRMS spectrum of **3o**



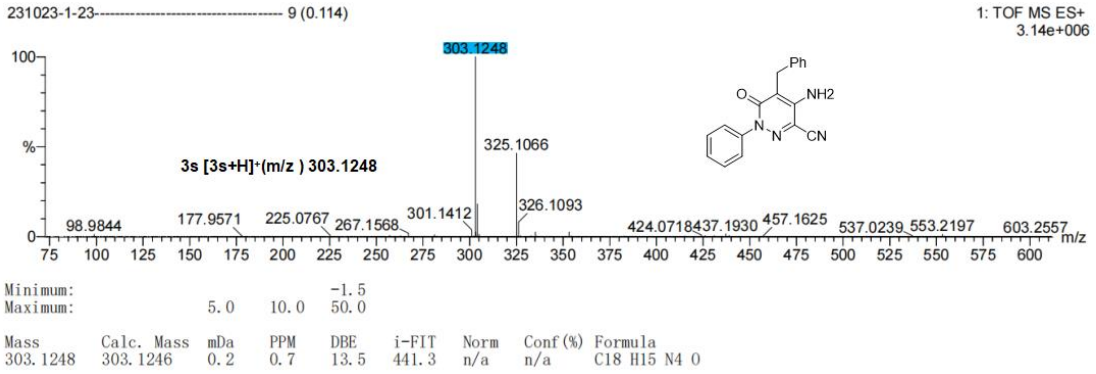
HRMS spectrum of **3p**



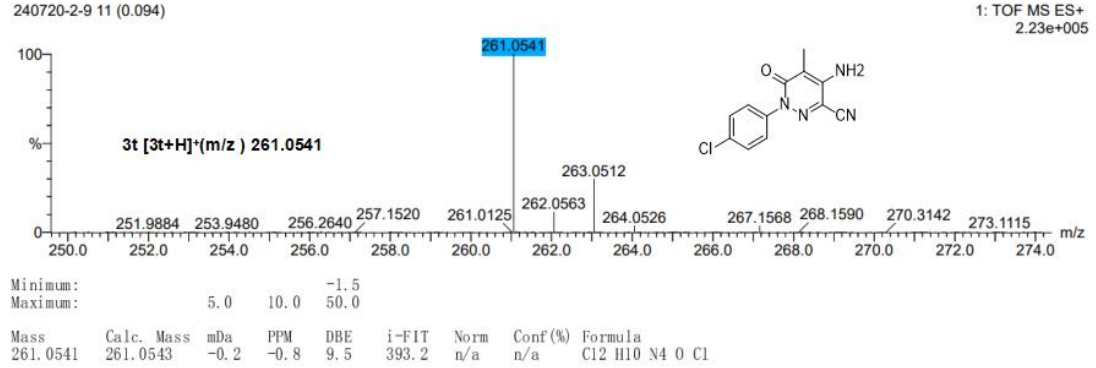
HRMS spectrum of **3q**



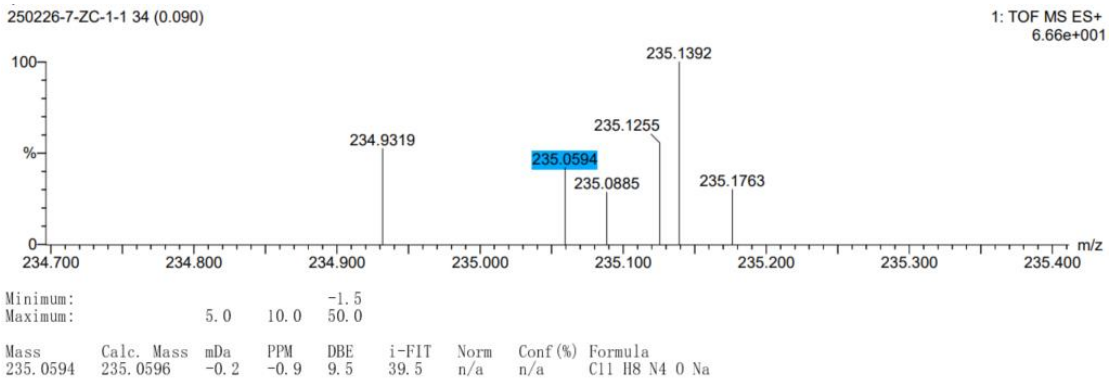
HRMS spectrum of **3r**



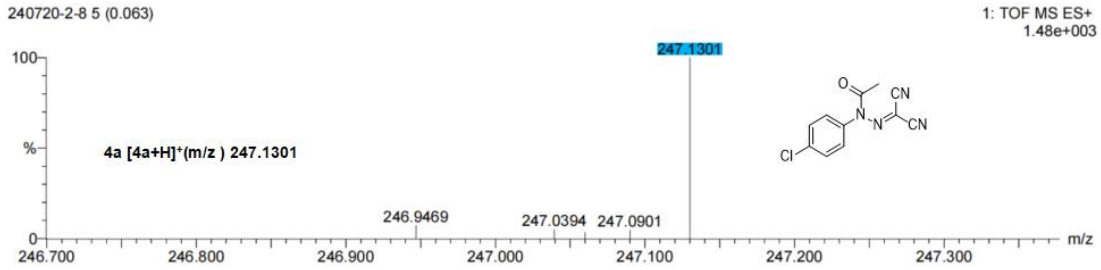
HRMS spectrum of **3s**



HRMS spectrum of **3t**



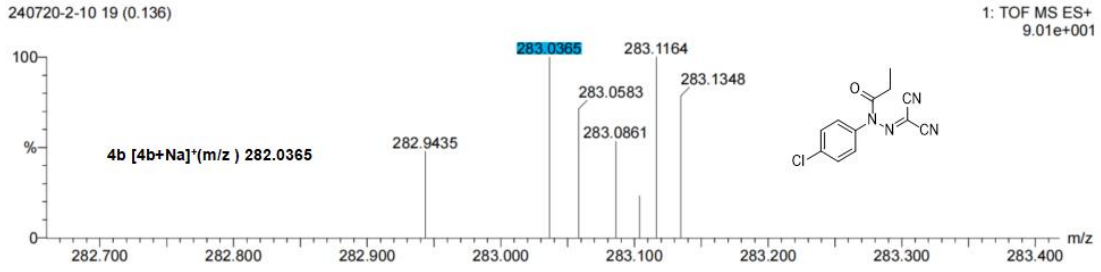
HRMS spectrum of **4a**



Minimum: −1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
247.0394	247.0387	0.7	2.8	9.5	47.8	n/a	n/a	C11 H8 N4 O Cl

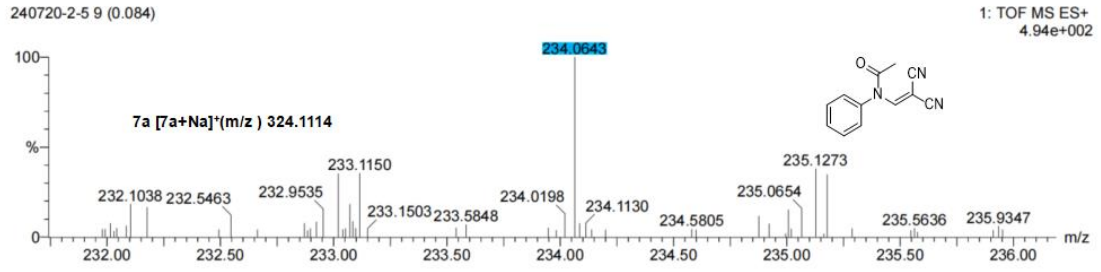
HRMS spectrum of **4b**



Minimum: −1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
283.0365	283.0363	0.2	0.7	9.5	57.4	n/a	n/a	C12 H9 N4 O Na Cl

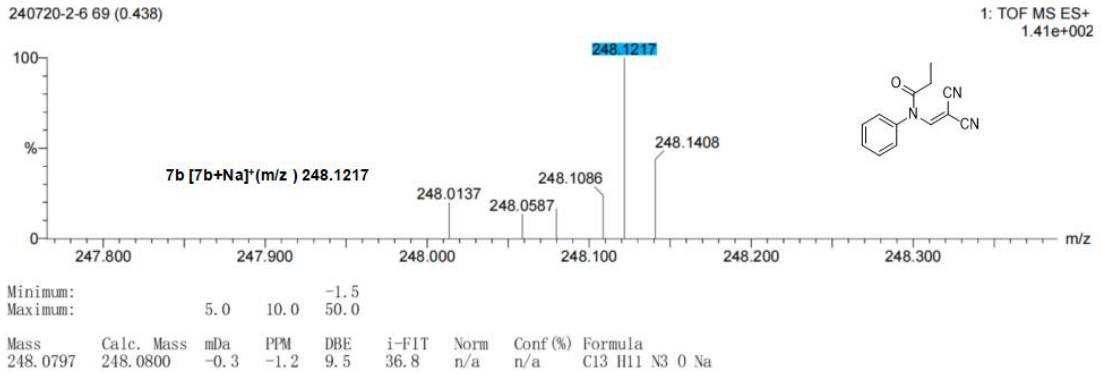
HRMS spectrum of **4c**



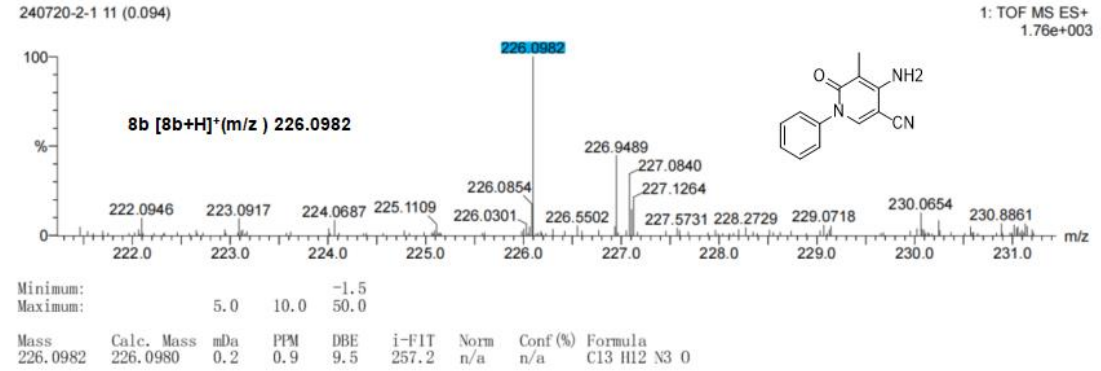
Minimum: −1.5
Maximum: 5.0 10.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
234.0643	234.0643	0.0	0.0	9.5	153.8	n/a	n/a	C12 H9 N3 O Na

HRMS spectrum of **7a**



HRMS spectrum of **7b**



HRMS spectrum of **8b**

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Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

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