Supporting Information

Efficient Synthesis of Pyrrolo[1,2-*a*]indole-3-ones through Radical-Initiated Cascade Cyclization Reaction

Han Zhang,[a] Yuze Lin,[a] Gang Yang,[a] Xifa Yang*[,b] and Xiuling Cui*[,a]

[a] *Engineering Research Centre of Molecular Medicine of Ministry of Education, Key Laboratory of Fujian Molecular Medicine, Key Laboratory of Precision Medicine and Molecular Diagnosis of Fujian Universities, Key Laboratory of Xiamen Marine and Gene Drugs, School of Biomedical Sciences, Huaqiao University, Xiamen 361021, P. R. China; orcid.org/0000-0001-5759-766X; Email: cuixl@hqu.edu.cn.*

[b] *College of Plant Protection, Henan Agricultural University, Zhengzhou, 450002, China. Email: yangxifachem@163.com.*

*[,a] cuixl@hqu.edu.cn and *[,b] *yangxifachem@163.com*.

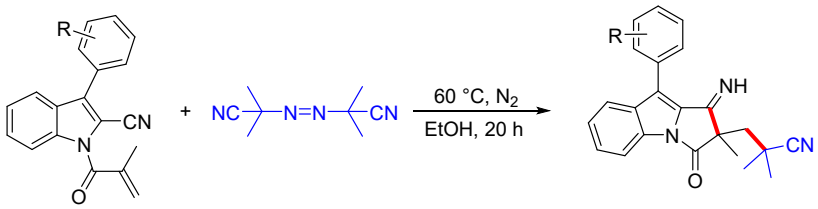
Contents

A. General information:

All chemicals were obtained from commercial sources. The reactions were monitored by TLC. Chromatographic purifications of the compounds were performed using silica gel (Mesh 100-200) and ethyl acetate and hexane as eluent. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a Bruker 400 (400, 100 and 376 MHz) advance spectrometer at room temperature in $CDCl_3$ (solvent signals, δ 7.26 and δ 77.16 ppm) using TMS as internal standard. Low-resolution mass spectra (LRMS) data were measured on GCMS-QP2010 Ultra. High-resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. IR spectra were recorded on a NICOLET iS50 FT-IR device and were recorded in the range from 4000 to 400 cm^{-1}. Digital melting point apparatus was used to record the Melting Point of the compound in degree centigrade (℃) and are uncorrected. All chemicals were obtained from commercial sources and were used as received unless otherwise noted. 1-Acryloyl-2-cyanoindoles **1** were prepared by following literature reports[1]. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA).

B. Catalytic results:

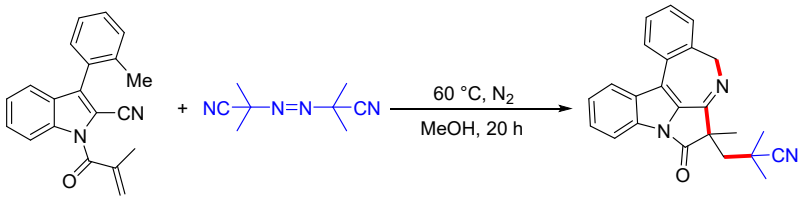
(a) General procedure for synthesis of 3.



1 **2a** **3**

To a Schlenk tube equipped with a magnetic stirring bar were added 1-methacryloyl-3-pheny l-1*H*-indole-2-carbonitrile **1** (0.2 mmol), AIBN **2a** (2.5 equiv) and absolute ethanol (2 mL). Th e mixture was stirred at 60 ℃ for 20 h under N_2. After cooled to room temperature, the solv ent was removed under reduced pressure and the crude reaction mixture was directly purified t hrough column chromatography on silica gel using PE/EA (8:1) as eluent to obtain product **3**.

(b) General procedure for synthesis of 3A.

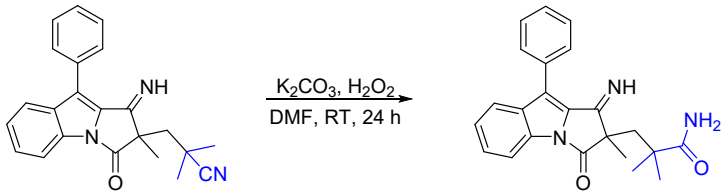


1A **2a** **3A,** 50%

To a Schlenk tube equipped with a magnetic stirring bar were added 1-methacryloyl-3-(*o*-t olyl)-1*H*-indole-2-carbonitrile **1A** (0.2 mmol), AIBN **2a** (2.5 equiv) and methanol (2 mL). The mixture was stirred at 60 ℃ for 20 h under N_2. After cooled to room temperature, the solvent

was removed under reduced pressure and the crude reaction mixture was directly purified throu gh column chromatography on silica gel using PE/EA (8:1) as eluent to obtain product **3A**.

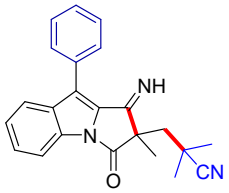
(c) General procedure for synthesis of 4[2].



3a **4**, 70%

To a Schlenk tube equipped with a magnetic stirring bar were added 3-(1-imino-2-methyl-3-oxo-9-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile **1A** (0.2 mmol), K_2CO_3 (0.2 mmol, 2.5 equiv.) and 30%H_2O_2 (2 mmol 10 equiv.) and *N*,*N*-Dimethylformamide (2 mL). The mixture was stirred at room temperature for 24 h under N_2. The solvent was rem oved under reduced pressure and the crude reaction mixture was directly purifiedthrough colum n chromatography on silica gel using PE/EA (4:1) as eluent to obtain product **4**.

(d) Characterization Data



3a

3-(1-imino-2-methyl-3-oxo-9-phenyl-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile (3a)

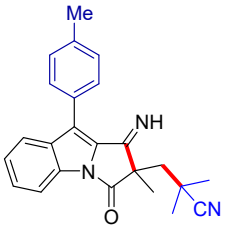
Yellow solid 85% (60.4 mg), mp: 128-129 °C. R_f = 0.6 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 7.77 (t, *J* = 7.8 Hz, 3H), 7.60 – 7.51 (m, 3H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 2.44 (d, *J* = 13.8 Hz, 1H), 2.26 (d, *J* = 14.5 Hz, 1H), 1.56 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.3, 134.1, 131.2, 131.2, 129.7, 129.0, 129.0, 127.7, 125.6, 124.0, 122.0, 121.7, 115.2, 54.5, 45.9, 30.8, 30.0, 27.9, 26.1 ppm (one signal is missing due to overlapping).

IR (ATR): $\tilde{\nu}$ = 2930, 1739, 1637, 1444, 1302, 1146, 884, 748, 700 cm^{-1}.

HRMS: $[M+Na]^+$ calculated for $C_{23}H_{21}N_3ONa^+$: 378.1578, found: 378.1577.



3b

3-(1-imino-2-methyl-3-oxo-9-(p-tolyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3b)

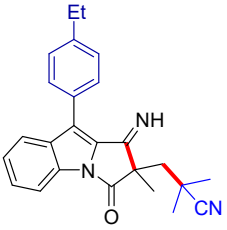
White solid 78% (57.6 mg), mp: 106-107 ℃. R_f = 0.5 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 2H), 7.55 – 7.51 (m, 1H), 7.40 (dd, *J* = 10.8, 7.8 Hz, 3H), 2.46 (s, 4H), 2.26 (d, *J* = 14.4 Hz, 1H), 1.56 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.3, 138.9, 134.2, 131.2, 130.4, 129.8, 128.8, 128.1, 127.6, 125.4, 124.0, 122.1, 121.8, 115.2, 54.5, 45.8, 30.8, 29.9, 27.9, 26.1, 21.5 ppm.

IR (ATR) : $\tilde{\nu}$ = 2975, 1745, 1643, 1447, 1384, 1306, 1140, 823, 751 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{24}H_{24}N_3O^+$: 370.1914, found: 370.1915.



3c

3-(9-(4-ethylphenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3c)

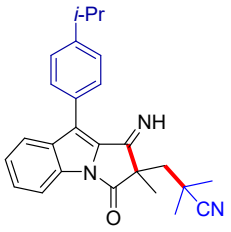
White solid 75% (57.5 mg), mp: 108-109 ℃. R_f = 0.6 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.5 Hz, 3H), 2.76 (q, *J* = 7.5 Hz, 2H), 2.43 (d, *J* = 12.3 Hz, 1H), 2.26 (d, *J* = 14.4 Hz, 1H), 1.56 (s, 3H), 1.39 (s, 3H), 1.31 (s, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.2, 145.2, 134.1, 131.2, 129.1, 128.8, 128.3, 127.5, 125.3, 123.9, 122.0, 121.8, 115.1, 54.4, 45.7, 30.7, 29.8, 28.8, 27.8, 26.0, 15.4 ppm (one signal is missing due to overlapping).

IR (ATR) : $\tilde{\nu}$ = 2930, 1737, 1644, 1452, 1145, 830, 754 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{25}H_{26}N_3O^+$: 384.2071, found: 384.2072.



3d

3-(1-imino-9-(4-isopropylphenyl)-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3d)

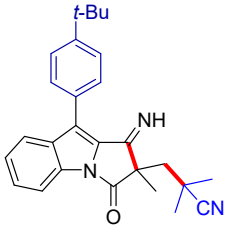
White solid 67% (53.3 mg), mp: 69-70 ℃. R_f = 0.6 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.56 – 7.52 (m, 1H), 7.44 – 7.37 (m, 1H), 2.43 (d, *J* = 14.5 Hz, 1H), 2.26 (d, *J* = 14.6 Hz, 1H), 1.56 (s, 3H), 1.40 (d, *J* = 2.8 Hz, 9H), 1.31 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.3, 152.2, 134.2, 131.3, 128.7, 128.1, 127.6, 126.6, 125.5, 124.0, 122.3, 121.9, 115.2, 54.5, 45.8, 35.0, 31.4, 30.9, 29.9, 27.9, 26.2 ppm (one signal is missing due to overlapping).

IR (ATR) : $\tilde{\nu}$ = 2966, 2233, 1739, 1643, 1444, 1384, 1140, 839, 754 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{26}H_{28}N_3O^+$: 398.2227, found: 398.2236.



3e

3-(9-(4-(tert-butyl)phenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3e)

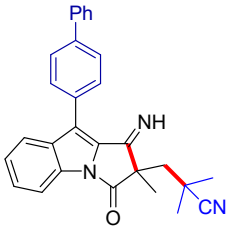
White solid 65% (53.5 mg), mp: 55-56 ℃. R_f = 0.6 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 2.43 (d, *J* = 7.4 Hz, 1H), 2.26 (d, *J* = 14.4 Hz, 1H), 1.55 (t, *J* = 7.5 Hz, 6H), 1.39 (s, 9H), 1.30 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.3, 152.2, 134.2, 131.3, 128.7, 128.1, 127.6, 126.6, 125.5, 124.0, 122.3, 121.9, 115.2, 54.5, 45.8, 35.0, 31.4, 30.9, 29.9, 27.9, 26.2 ppm (one signal is missing due to overlapping).

IR (ATR) : $\tilde{\nu}$ = 2923, 2160, 1744, 1641, 1448, 1145, 1023, 841, 748 cm^{-1}.

HRMS: $[M+H]^+$ calculated for$C_{27}H_{28}N_3O^+$: 412.2384, found: 412.2382.



3f

3-(9-([1,1'-biphenyl]-4-yl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3f)

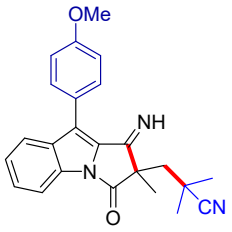
White solid 75% (64.7 mg), mp: 188-189 ℃. R_f = 0.8 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.43 (s, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 5H), 7.73 – 7.66 (m, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 15.3 Hz, 2H), 7.47 – 7.37 (m, 2H), 2.48 (d, *J* = 12.9 Hz, 1H), 2.28 (d, *J* = 14.5 Hz, 1H), 1.58 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.2, 141.7, 140.3, 134.0, 131.2, 130.0, 129.3, 129.0, 128.3, 127.8, 127.6, 127.4, 127.2, 125.5, 123.9, 122.0, 115.2, 54.4, 45.8, 30.7, 29.9, 27.8, 26.0 ppm.

IR (ATR) : $\tilde{\nu}$ = 2929, 1726, 1638, 1445, 1375, 1147, 751, 696 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{21}H_{18}NO_3^+$: 432.2071, found: 432.2072.



3g

3-(1-imino-9-(4-methoxyphenyl)-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile（3g）

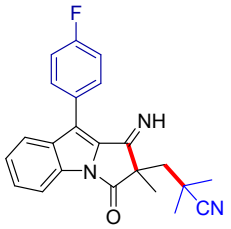
White solid 87% (67.1 mg), mp: 152-153 ℃. R_f = 0.8 (PE:EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.31 (s, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 28.3 Hz, 3H), 7.53 (t, *J* = 7.7 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.10 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 2.51 – 2.37 (m, 1H), 2.25 (d, *J* = 14.4 Hz, 1H), 1.55 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.2, 160.0, 134.2, 131.1, 130.2, 127.5, 125.3, 123.9, 123.2, 122.0, 121.5, 115.1, 55.4, 54.4, 45.7, 30.7, 29.9, 27.7, 26.0 ppm (two signals are missing due to overlapping).

IR (ATR) : $\tilde{\nu}$ = 2978, 1723, 1640, 1510, 1393, 1245, 1015, 826, 750, 576 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{24}H_{24}N_3O_2^+$: 386.1863, found: 386.1866.



3h

3-(9-(4-fluorophenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3h)

Yellow solid 93% (69.5 mg), mp: 141-142 ℃. R_f = 0.6 (PE:EA = 2:1).

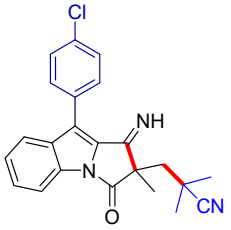
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.29 (s, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.67 (m, 3H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.30 – 7.26 (m, 2H), 2.52 – 2.36 (m, 1H), 2.27 (d, *J* = 14.5 Hz, 1H), 1.57 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.2, 162.9 (d, *J* = 249.1 Hz), 134.0, 131.1, 130.9, 130.8, 127.6, 127.0 (d, *J* = 3.3 Hz), 125.5, 123.9, 121.7, 120.4, 116.6 (d, *J* = 22.1 Hz), 115.1, 54.4, 45.8, 30.7, 30.0, 27.7, 25.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.80 ppm.

IR (ATR) : $\tilde{\nu}$ = 2921, 1739, 1634, 1510, 1380, 1144, 842, 748, 564 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{23}H_{21}FN_3O^+$: 374.1663, found: 374.1665.



3i

3-(9-(4-chlorophenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile (3i)

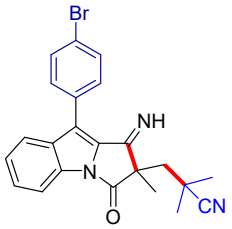
White solid 83% (64.7 mg), mp: 112-113 ℃. R_f = 0.7 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.28 (s, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 7.71 (t, *J* = 8.6 Hz, 3H), 7.58 – 7.51 (m, 3H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.26 (s, 0H), 2.44 (s, 1H), 2.24 (d, *J* = 14.2 Hz, 1H), 1.55 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.1, 134.8, 133.8, 131.1, 130.4, 129.8, 129.6, 127.7, 125.6, 123.9, 121.7, 120.2, 115.2, 54.4, 45.8, 30.6, 29.9, 27.7, 25.9 ppm.

IR (ATR) : $\tilde{\nu}$ = 2978, 1724, 1640, 1444, 1387, 1143, 827, 745 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{23}H_{21}ClN_3O^+$: 390.1368, found: 390.1371.



3j

3-(9-(4-bromophenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3j)

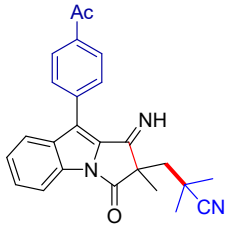
White solid 80% (69.5 mg), mp: 120-121 ℃. R_f = 0.7 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 3H), 7.65 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.7 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 2.47 – 2.34 (m, 1H), 2.25 (d, *J* = 14.4 Hz, 1H), 1.55 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.2, 133.8, 132.8, 131.2, 130.7, 130.1, 128.8, 127.8, 125.7, 123.9, 123.1, 121.8, 120.3, 115.3, 54.5, 45.9, 30.7, 30.0, 27.8, 26.0 ppm.

IR (ATR) : $\tilde{\nu}$ = 2975, 1742, 1634, 1444, 1314, 1142, 1013, 830, 747 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{23}H_{21}BrN_3O^+$: 434.0863, found: 434.0866



3k

3-(9-(4-acetylphenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3k)

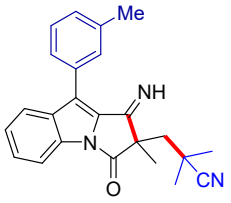
White solid 90% (71.6 mg), mp: 166-167 ℃. R_f = 0.6 (PE:EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.34 (s, 1H), 8.24 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 7.7 Hz, 2H), 7.91 (s, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 2.68 (s, 3H), 2.42 (d, *J* = 12.8 Hz, 1H), 2.25 (d, *J* = 14.5 Hz, 1H), 1.56 (s, 3H), 1.40 (s, 3H), 1.30 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 172.0, 168.9, 137.1, 136.1, 133.6, 131.1, 130.3, 129.6, 129.2, 127.8, 125.7, 123.9, 121.7, 120.1, 115.2, 54.4, 45.9, 30.7, 30.0, 27.7, 26.8, 25.9 ppm.

IR (ATR) : $\tilde{\nu}$ = 2981, 1739, 1676, 1606, 1447, 1263, 1142, 838, 729 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{25}H_{24}N_3O_2^+$: 398.1863, found: 398.1867.



3l

3-(1-imino-2-methyl-3-oxo-9-(m-tolyl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3l)

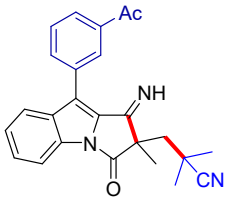
White solid 71% (52.5 mg), mp: 134-135 ℃. R_f = 0.7 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.54 (dd, *J* = 14.3, 6.6 Hz, 3H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 2.46 (s, 4H), 2.26 (d, *J* = 14.4 Hz, 1H), 1.57 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.2, 139.4, 134.0, 131.1, 131.0, 129.7, 129.6, 129.4, 127.5, 125.9, 125.4, 123.9, 122.0, 121.7, 115.1, 54.4, 45.8, 30.7, 29.9, 27.9, 26.0, 21.5 ppm (one signal is missing due to overlapping).

IR (ATR) : $\tilde{\nu}$ = 2921, 1727, 1649, 1444, 1387, 1142, 1034, 751, 700 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{24}H_{24}N_3O^+$: 370.1914, found: 370.1918.



3m

3-(9-(3-acetylphenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3m)

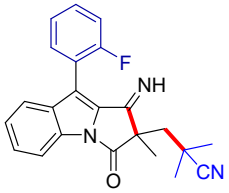
White solid 82% (65.2 mg), mp: 84-85 ℃. R_f = 0.7 (PE:EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.26 (s, 1H), 8.41 (s, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.07 (d, *J* = 7.8 Hz, 1H), 7.99 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.56 (t, *J* = 7.7 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.26 (s, 0H), 2.66 (s, 3H), 2.40 (s, 1H), 2.25 (d, *J* = 14.6 Hz, 1H), 1.55 (s, 3H), 1.40 (s, 3H), 1.29 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 172.0, 169.2, 139.5, 134.0, 131.1, 131.0, 129.7, 129.6, 129.4, 127.5, 125.9, 125.4, 123.9, 122.0, 121.7, 115.1, 54.4, 45.8, 30.7, 29.9, 27.9, 26.0, 21.5 ppm (one signal is missing due to overlapping).

IR (ATR) : $\tilde{\nu}$ = 2923, 1740, 1685, 1447, 1242, 1145, 1032, 748, 688 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{25}H_{24}N_3O_2^+$: 398.1863, found: 398.1866.



3n

3-(9-(2-fluorophenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3n)

White solid 65% (48.5 mg), mp: 115-116 ℃. R_f = 0.6 (PE:EA = 2:1).

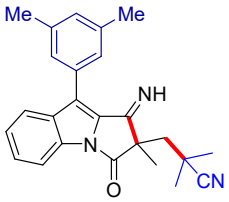
^{1}H NMR (400 MHz, $CDCl_3$) δ 11.43 (s, 1H), 9.59 (d, *J* = 8.2 Hz, 1H), 9.09 (s, 1H), 9.01 (d, *J* = 8.1 Hz, 1H), 8.94 – 8.88 (m, 1H), 8.88 – 8.82 (m, 1H), 8.79 – 8.74 (m, 1H), 8.73 – 8.64 (m, 2H), 3.87 – 3.74 (m, 1H), 3.69 (d, *J* = 7.0 Hz, 1H), 3.03 (s, 3H), 2.93 (s, 3H), 2.68 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4, 171.9, 169.1, 160.0 (d, *J* = 249.1 Hz), 134.0, 131.6 (d, *J* = 2.9 Hz), 131.1 (d, *J* = 3.8 Hz), 131.0, 127.7, 125.5, 125.2 (d, *J* = 3.6 Hz), 123.9, 122.3, 121.0, 118.8 (d, *J* = 15.4 Hz), 116.8 (d, *J* = 21.5 Hz), 115.2, 54.4, 45.7, 30.8, 27.3, 26.1, 19.4 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -111.99 ppm.

IR (ATR) : $\tilde{\nu}$ = 2933, 1742, 1640, 1447, 1384, 1145, 1022, 748, 564 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{23}H_{21}FN_3O^+$: 374.1663, found: 374.1667.



3o

3-(9-(3,5-dimethylphenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3o)

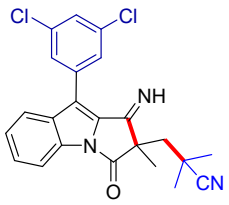
White solid 80% (61.4 mg), mp:151-152 ℃. R_f = 0.8 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.22 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.42 – 7.32 (m, 3H), 7.12 (s, 1H), 2.42 (s, 7H), 2.27 (d, *J* = 14.4 Hz, 1H), 1.57 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 169.2, 139.3, 134.1, 131.1, 130.9, 130.6, 129.8, 127.5, 126.5, 125.3, 123.9, 122.1, 122.0, 115.1, 54.4, 45.7, 30.7, 29.8, 27.9, 26.0, 21.4 ppm.

IR (ATR) : $\tilde{\nu}$ = 2930, 1722, 1643, 1450, 1387, 1149, 1056, 868, 751, 727 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{25}H_{26}N_3O^+$: 384.2071, found: 384.2072.



3p

3-(9-(3,5-dichlorophenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3p)

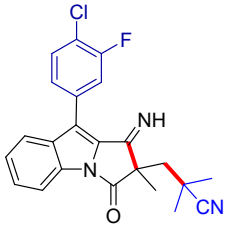
White solid 73% (61.9 mg), mp: 226-227 °C. R_f = 0.8 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 7.89 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 7.58 – 7.55 (m, 1H), 7.46 (dd, *J* = 16.2, 8.5 Hz, 2H), 2.46 (d, *J* = 14.6 Hz, 1H), 2.24 (d, *J* = 14.4 Hz, 1H), 1.58 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 168.9, 136.5, 134.3, 133.4, 131.0, 130.6, 129.1, 128.0, 127.3, 125.9, 124.0, 121.4, 118.3, 115.3, 54.5, 46.1, 30.7, 30.1, 28.0, 26.0 ppm.

IR (ATR) : $\tilde{\nu}$ = 2930, 1733, 1659, 1444, 1384, 1314, 1037, 850, 750, 679 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{23}H_{20}Cl_2N_3O^+$: 424.0978, found: 424.0987.



3q

3-(9-(4-chloro-3-fluorophenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3q)

White solid 60% (48.9 mg), mp: 148-149 °C. R_f = 0.7 (PE:EA = 2:1).

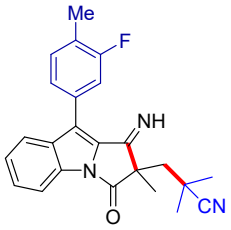
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.58 (dt, *J* = 14.8, 7.8 Hz, 4H), 7.44 (t, *J* = 7.7 Hz, 1H), 7.26 (d, *J* = 1.7 Hz, 0H), 2.53 – 2.32 (m, 1H), 2.25 (d, *J* = 14.4 Hz, 1H), 1.55 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.1, 158.7 (d, *J* = 251.1 Hz), 133.5, 131.72 (d, *J* = 7.5 Hz), 131.2, 127.9, 125.9, 125.7, 123.9, 121.8, 121.6, 119.1, 117.4 (d, *J* = 21.2 Hz), 115.3, 54.5, 45.9, 30.7, 30.0, 27.8, 25.9 ppm (two signals are missing due to overlapping).

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.88 ppm.

IR (ATR) : $\tilde{\nu}$ = 2918, 1719, 1637, 1450, 1391, 1309, 1145, 748, 728 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{23}H_{20}ClFN_3O^+$: 408.1274, found: 408.1278.



3r

3-(9-(3-fluoro-4-methylphenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile（3r）

White solid 90% (69.7 mg), mp: 156-157 ℃. R_f = 0.7 (PE:EA = 2:1).

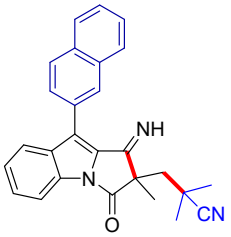
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.49 – 7.35 (m, 4H), 2.38 (d, *J* = 2.0 Hz, 4H), 2.26 (d, *J* = 14.5 Hz, 1H), 1.55 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.2, 161.9 (d, *J* = 245.3 Hz), 133.9, 132.8, 131.2, 130.5, 130.4, 127.7 126.0, 125.9(d, *J* = 17.1 Hz), 124.4, 123.9, 121.8, 120.4, 115.6 (d, *J* = 23.4 Hz), 115.2, 54.5, 45.9, 30.8, 29.9, 27.9, 26.0, 14.7 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.28 ppm.

IR (ATR) : $\tilde{\nu}$ = 2929, 1733, 1637, 1444, 1296, 1148, 745, 669, 555 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{24}H_{23}FN_3O^+$: 388.1820, found: 388.1824.



3s

3-(1-imino-2-methyl-9-(naphthalen-2-yl)-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3s)

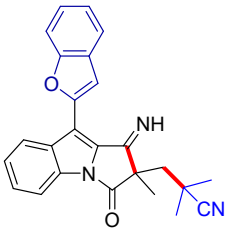
White solid 78% (63.4 mg), mp: 105-106 ℃. R_f = 0.5 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.8 Hz, 2H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.94 (dd, *J* = 6.1, 3.4 Hz, 2H), 7.86 (dd, *J* = 7.8, 3.4 Hz, 2H), 7.58 (dd, *J* = 6.4, 3.4 Hz, 3H), 7.44 (t, *J* = 7.6 Hz, 1H), 2.46 (d, *J* = 14.6 Hz, 1H), 2.29 (d, *J* = 14.6 Hz, 1H), 1.59 (s, 3H), 1.41 (s, 3H), 1.33 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.2, 134.2, 133.8, 133.3, 131.3, 130.3, 129.5, 128.6, 128.4, 128.3, 128.0, 127.7, 127.0, 126.9, 126.4, 125.6, 124.0, 122.1, 121.7, 115.2, 54.5, 45.9, 30.8, 29.9, 27.9, 26.1 ppm.

IR (ATR) : $\tilde{\nu}$ = 2926, 1745, 1643, 1441, 1306, 1142, 856, 750 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{27}H_{24}N_3O^+$: 406.1914, found: 406.1912.



3t

3-(9-(benzofuran-2-yl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3t)

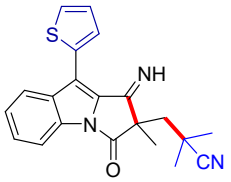
White solid 60% (47.5 mg), mp : 105-106 ℃. R_f = 0.6 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.66 (s, 1H), 8.29 (d, *J* = 8.1 Hz, 1H), 8.09 (s, 1H), 7.69 (d, *J* = 7.7 Hz, 1H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.36 (dt, *J* = 30.4, 7.2 Hz, 3H), 2.57 – 2.42 (m, 1H), 2.36 (d, *J* = 14.3 Hz, 1H), 1.62 (s, 3H), 1.35 (d, *J* = 10.2 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 167.8, 154.1, 149.0, 131.4, 131.2, 128.6, 127.9, 125.9, 125.7, 123.8, 123.7, 122.4, 121.4, 115.4, 111.2, 54.3, 45.7, 30.7, 29.3, 28.6, 26.3 ppm (three signals are missing due to overlapping).

IR (ATR) : $\tilde{\nu}$ = 2918, 1733, 1649, 1450, 1261, 1140, 817, 745 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{25}H_{22}N_3O_2^+$: 396.1707, found: 396.1711.



3u

3-(1-imino-2-methyl-3-oxo-9-(thiophen-2-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3u)

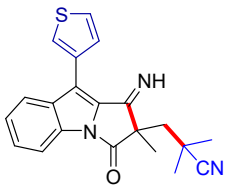
Yellow solid 65% (47.0 mg), mp: 155-156 ℃. R_f = 0.6 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.87 – 7.65 (m, 2H), 7.65 – 7.35 (m, 4H), 2.46 (d, *J* = 14.6 Hz, 1H), 2.24 (d, *J* = 14.3 Hz, 1H), 1.56 (s, 3H), 1.39 (s, 3H), 1.27 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.0, 170.4, 132.9, 132.7, 132.2, 130.7, 129.7, 129.4, 128.2, 128.2, 126.0, 124.2, 123.5, 119.2, 115.8, 56.3, 45.1, 30.9, 28.8, 28.7, 24.3 ppm.

IR (ATR) : $\tilde{\nu}$ = 2981, 1745, 1640, 1447, 1391, 1336, 745, 646 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{21}H_{20}N_3OS^+$: 362.1322, found: 362.1322.



3v

3-(1-imino-2-methyl-3-oxo-9-(thiophen-3-yl)-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3v)

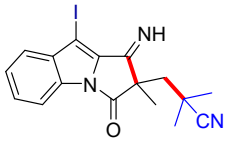
Yellow solid 61% (44.1 mg), mp: 154-155 °C. R_f = 0.6 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.42 (s, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.65 (m, 2H), 7.55 – 7.46 (m, 3H), 7.41 (t, *J* = 7.7 Hz, 1H), 2.43 (s, 1H), 2.25 (d, *J* = 13.6 Hz, 1H), 1.55 (s, 3H), 1.38 (s, 3H), 1.27 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 169.1, 134.1, 131.4, 131.1, 130.0, 127.8, 127.6, 125.5, 124.9, 123.9, 122.1, 116.5, 115.1, 54.4, 45.9, 30.8, 30.0, 27.6, 25.9 ppm (one signal is missing due to overlapping).

IR (ATR) : $\tilde{\nu}$ = 2981, 1730, 1643, 1444, 1378, 1333, 751, 643 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{21}H_{20}N_3OS^+$: 362.1322, found: 362.1322.



3w

3-(1-imino-9-iodo-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3w)

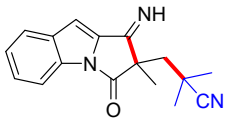
White solid 95% (77.0 mg), mp: 129-130 °C. R_f = 0.6 (PE:EA = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.40 (m, 3H), 2.40 (d, *J* = 14.6 Hz, 1H), 2.29 (d, *J* = 14.5 Hz, 1H), 1.56 (s, 3H), 1.31 (d, *J* = 20.3 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 169.3, 136.5, 131.4, 128.5, 125.9, 123.6, 123.0, 115.2, 54.6, 45.7, 30.8, 29.4, 28.5, 26.0 ppm (two signals are missing due to overlapping).

IR (ATR) : $\tilde{\nu}$ = 2984, 1730, 1640, 438, 1384, 1321, 881, 755 cm^{-1}.

HRMS $[M+Na]^+$ calculated for $C_{17}H_{16}IN_3ONa^+$: 428.0230, found: 428.0232.



3x

3-(1-imino-2-methyl-3-oxo-2,3-dihydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanenitrile(3x)

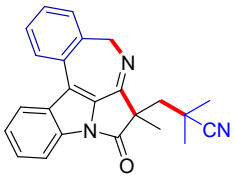
Red solid 70% (39.1 mg), mp: 120-121 ℃. R_f = 0.6 (PE:EA = 1:1).

^{1}H NMR (400 MHz,$CDCl_3$) δ 10.14 (s, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.04 (s, 1H), 2.35 (s, 1H), 2.28 (d, *J* = 14.2 Hz, 1H), 1.54 (s, 3H), 1.35 (s, 3H), 1.25 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 169.5, 134.5, 131.7, 127.3, 125.4, 123.8, 123.3, 115.2, 104.1, 54.2, 45.6, 30.8, 29.7, 27.9, 26.0 ppm (one signal is missing due to overlapping).

IR (ATR) : $\tilde{\nu}$ = 2984, 1740, 1652, 1441, 1387, 1315, 833, 757 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{17}H_{17}N_3O^+$: 280.1445, found: 280.1442.



3A

2,2-dimethyl-3-(7-methyl-6-oxo-7,9-dihydro-6*H*-benzo[b]benzo[5,6]azepino[2,3,4-*gh*]pyrrolizin-7-yl)propanenitrile(3A)

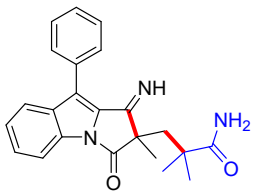
White solid 50% (36.8 mg), mp: 118-119 ℃. R_f = 0.8 (PE:EA = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.20 (m, 2H), 8.06 – 7.97 (m, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.47 (s, 3H), 5.07 (d, *J* = 13.1 Hz, 1H), 4.87 (d, *J* = 13.2 Hz, 1H), 2.43 (d, *J* = 14.6 Hz, 1H), 2.28 (d, *J* = 14.7 Hz, 1H), 1.49 (s, 3H), 1.32 (s, 3H), 1.29 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 164.8, 133.7, 133.4, 132.6, 131.9, 131.7, 130.3, 129.8, 128.5, 127.8, 125.7, 125.1, 124.2, 123.5, 122.1, 116.0, 59.7, 55.7, 46.1, 29.8, 28.4, 27.4, 25.6 ppm.

IR (ATR) : $\tilde{\nu}$ = 2930, 1742, 1649, 1450, 1315, 1146, 785, 757 cm^{-1}.

HRMS $[M+H]^+$ calculated for $C_{24}H_{22}N_3O^+$: 368.1758, found: 368.1759.



4

3-(1-imino-2-methyl-3-oxo-9-phenyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indol-2-yl)-2,2-dimethylpropanamide (4)

White solid 70% (52.6 mg), mp: 68-69 ℃. R_f = 0.5 (PE:EA = 2:1).

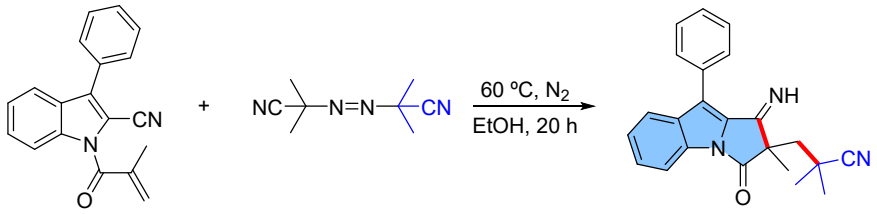
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.23 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.80 – 7.73 (m, 3H), 7.60 – 7.53 (m, 4H), 7.50 – 7.46 (m, 2H), 7.43 – 7.39 (m, 1H), 2.29 (d, *J* = 5.6 Hz, 1H), 2.22 (d, *J* = 16.5 Hz, 1H), 1.56 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 169.3, 134.8, 134.1, 132.2, 131.2, 129.8, 129.0, 128.4, 127.7, 125.6, 122.1, 120.6, 120.2, 115.2, 54.5, 45.9, 36.5, 30.8, 28.0, 26.1 ppm.

IR (ATR) : $\tilde{\nu}$ = 2921, 1637, 1523, 1447, 1302, 1258, 1140, 755, 700 cm^{-1}.

HRMS: $[M+H]^+$ calculated for $C_{23}H_{25}N_3O_2^+$: 374.1863, found: 374.1862.

C. Scale-up reaction.

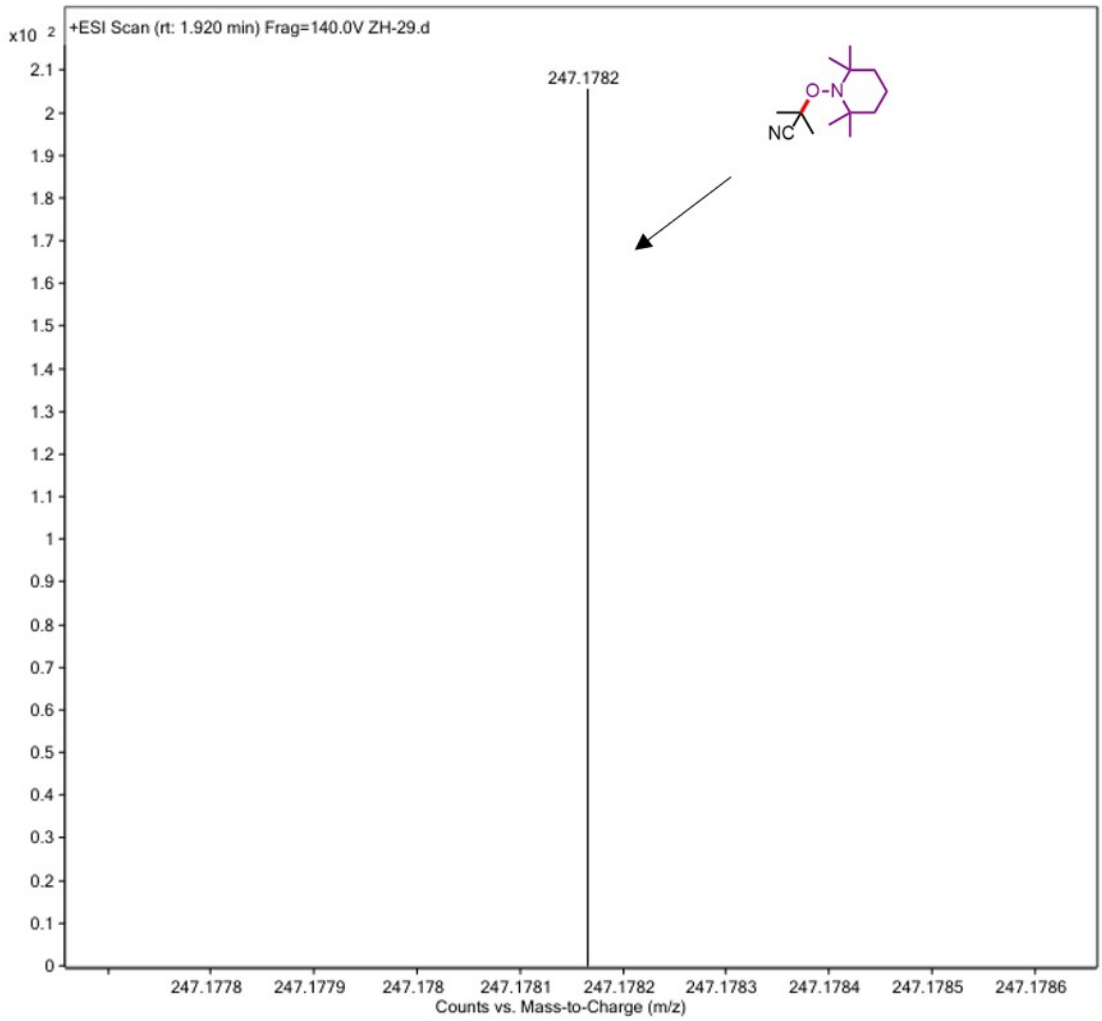


1a (3.5 mmol,1.001 g) **2a** **3a** (0.84 g 68%)

1-methacryloyl-3-phenyl-1*H*-indole-2-carbonitrile **1a** (1 mmol), AIBN **2a** (2.5 mmol) and absolute ethanole (20 mL) were charged into a pressure tube. The reaction mixture was stirred at N_2 under 60 ℃ for 20 h. After completion of the reaction, the solvent was removed under reduced pressure and the crude reaction mixture was directly purified through column chromatography on silica gel using PE/EA (8:1) as eluent to obtain product **3a** in 68% yield (0.84 g).

D. Mechanistic studies:

To a Schlenk tube under air conditions, 1-methacryloyl-3-phenyl-1*H*-indole-2-carbonitrile **1a** (0.2 mmol, 1 equiv.), AIBN **2a** (0.5 mmol, 2.5 equiv.), TEMPO/DPE (0.6 mmol, 3 equiv.) and absolute ethanole (2 mL) were successively added. Then, the tube was stirred at N_2 under 60 ℃ for 20 h. The corresponding product (**3a**) was not detected according to TLC analysis. The radical-trapping adducts **I-1** and **I-2** were detected by HRMS analysis. HRMS (ESI-TOF) Calculated for $C_{13}H_{24}N_2ONa$ ($[M+Na]^+$): 247.1782. found: 247.1782. Calculated for $C_{18}H_{17}N$ ($[M+Na]^+$): 270.1254. found: 270.1264.


+ESI Scan (rt: 1.920 min) Frag=140.0V ZH-29.d
x10 2
2.1
2
1.9
1.8
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
247.1782
O-N
NC
247.1778
247.1779
247.178
247.1781
247.1782
247.1783
247.1784
247.1785
247.1786
Counts vs. Mass-to-Charge (m/z)

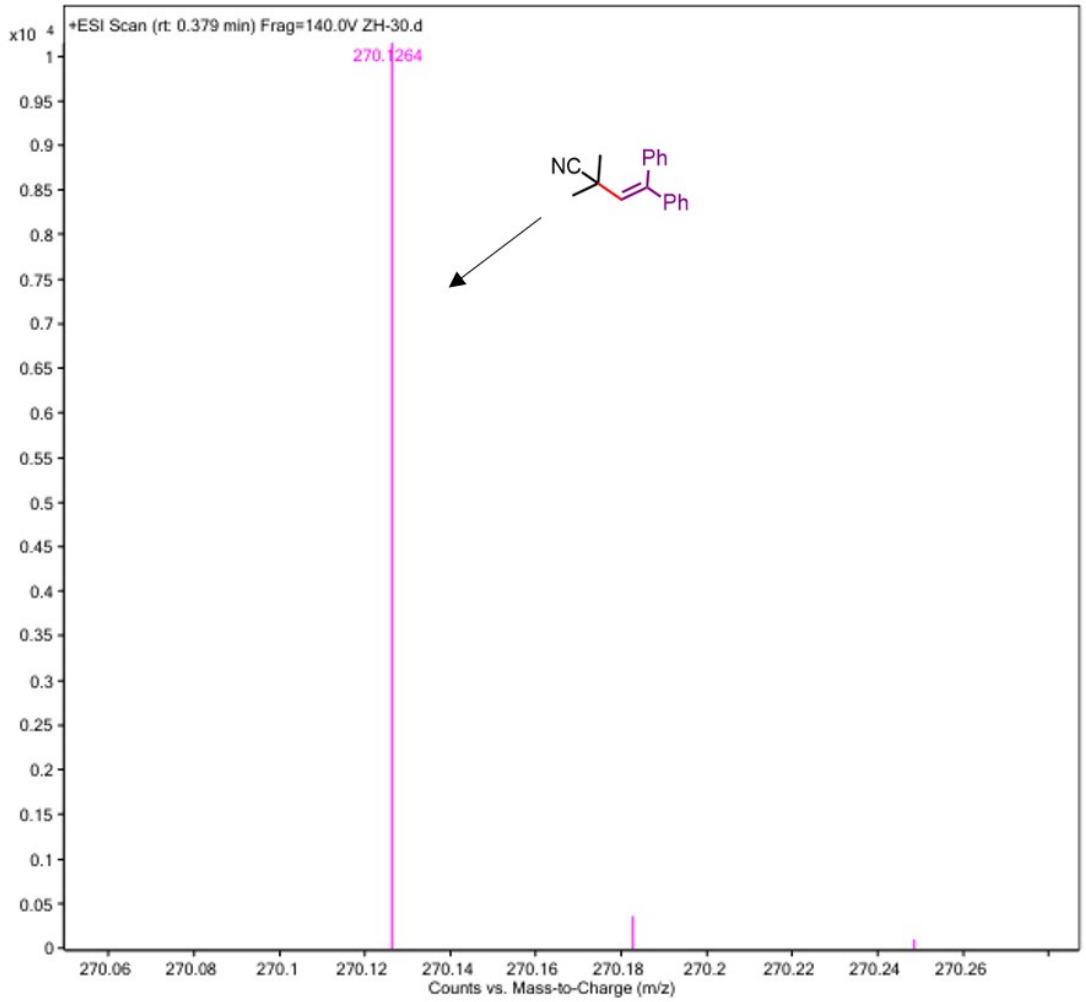


Figure S1. Copy of HRMS Spectrum of TEMPO/DPE-Br adduct

E. Crystal structure.

(a) Crystal structure of complex 3a, CCDC Number = 2413982

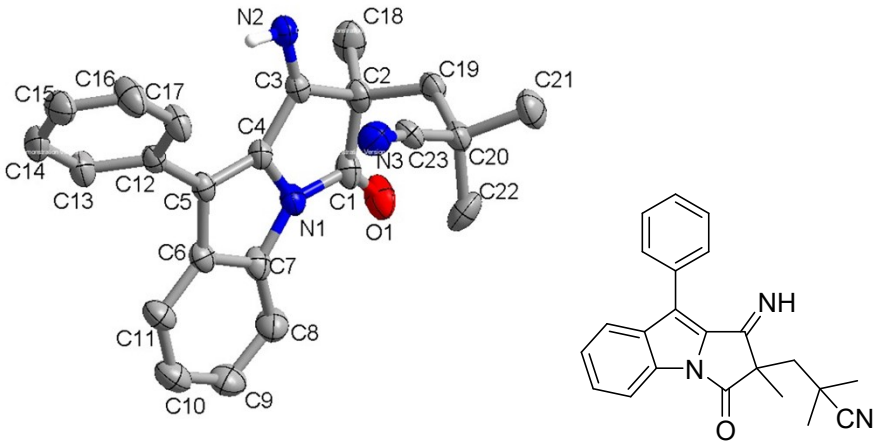


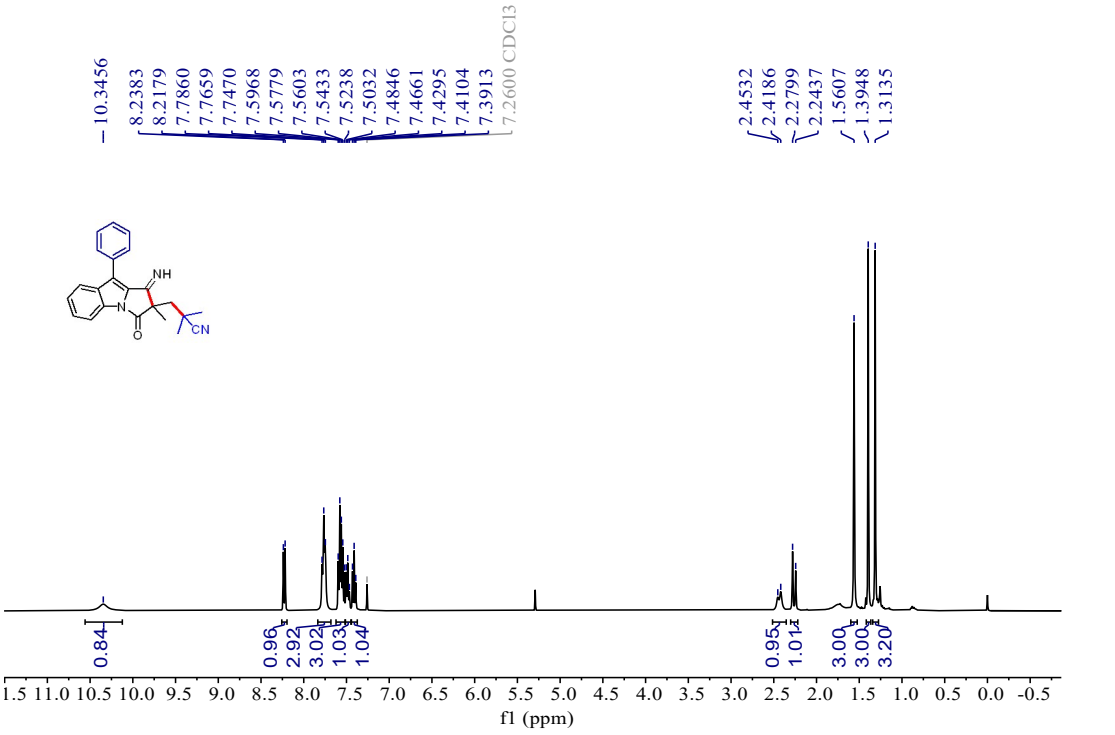
Figure S2 Crystal structure of **3a** with thermal ellipsoids at 50% probability.

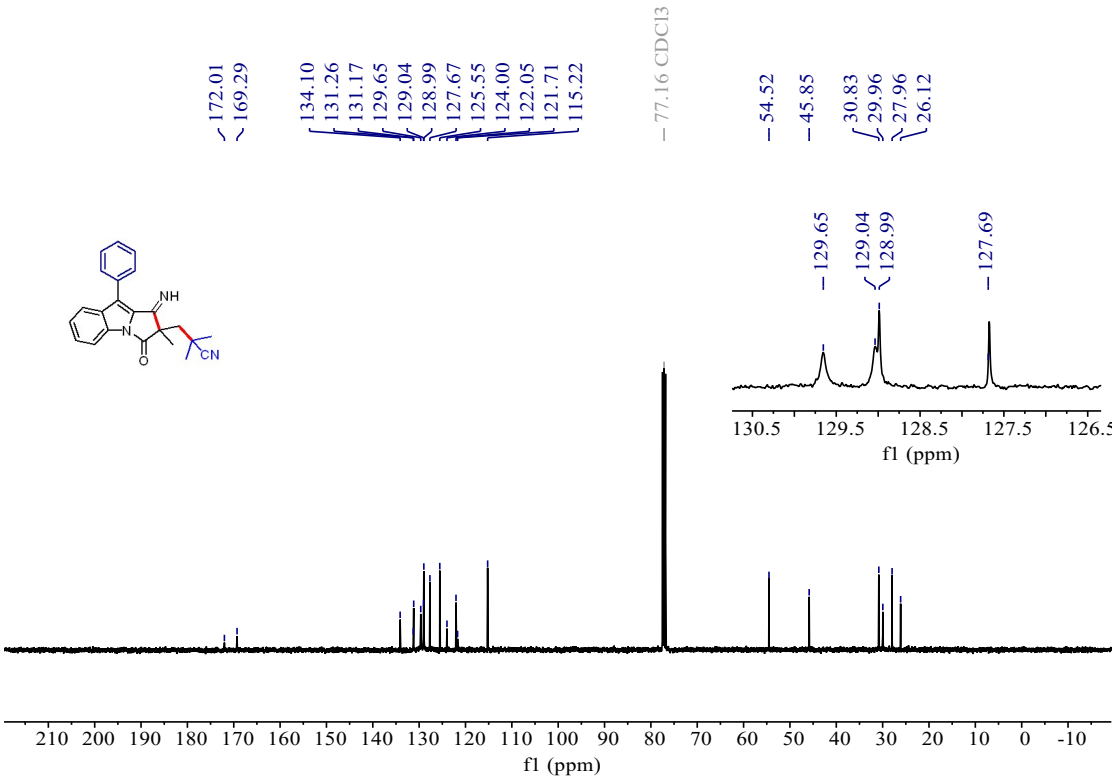
Table 1 Crystal data and structure refinement for 3a

Identification code	**3a**
Empirical formula	$C_{23}H_{21}N_3O$
Formula weight	355.43
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.050(2)
b/Å	8.2245(13)
c/Å	21.735(3)
α/°	90
β/°	100.182(11)
γ/°	90
Volume/Å^3	3879.4(9)
Z	8
ρ_{calc}g/cm^3	1.217
μ/mm^{-1}	0.076
F(000)	1504.0
Crystal size/mm^3	0.17 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.516 to 52.732
Index ranges	-24 ≤ h ≤ 27, -10 ≤ k ≤ 8, -27 ≤ l ≤ 26
Reflections collected	9870
Independent reflections	3961 [R_{int} = 0.0345, R_{sigma} = 0.0566]
Data/restraints/parameters	3961/1/262
Goodness-of-fit on F^2	1.092
Final R indexes [I>=2σ (I)]	R_1 = 0.0955, wR_2 = 0.2265
Final R indexes [all data]	R_1 = 0.1348, wR_2 = 0.2472
Largest diff. peak/hole / e Å^{-3}	0.25/-0.16

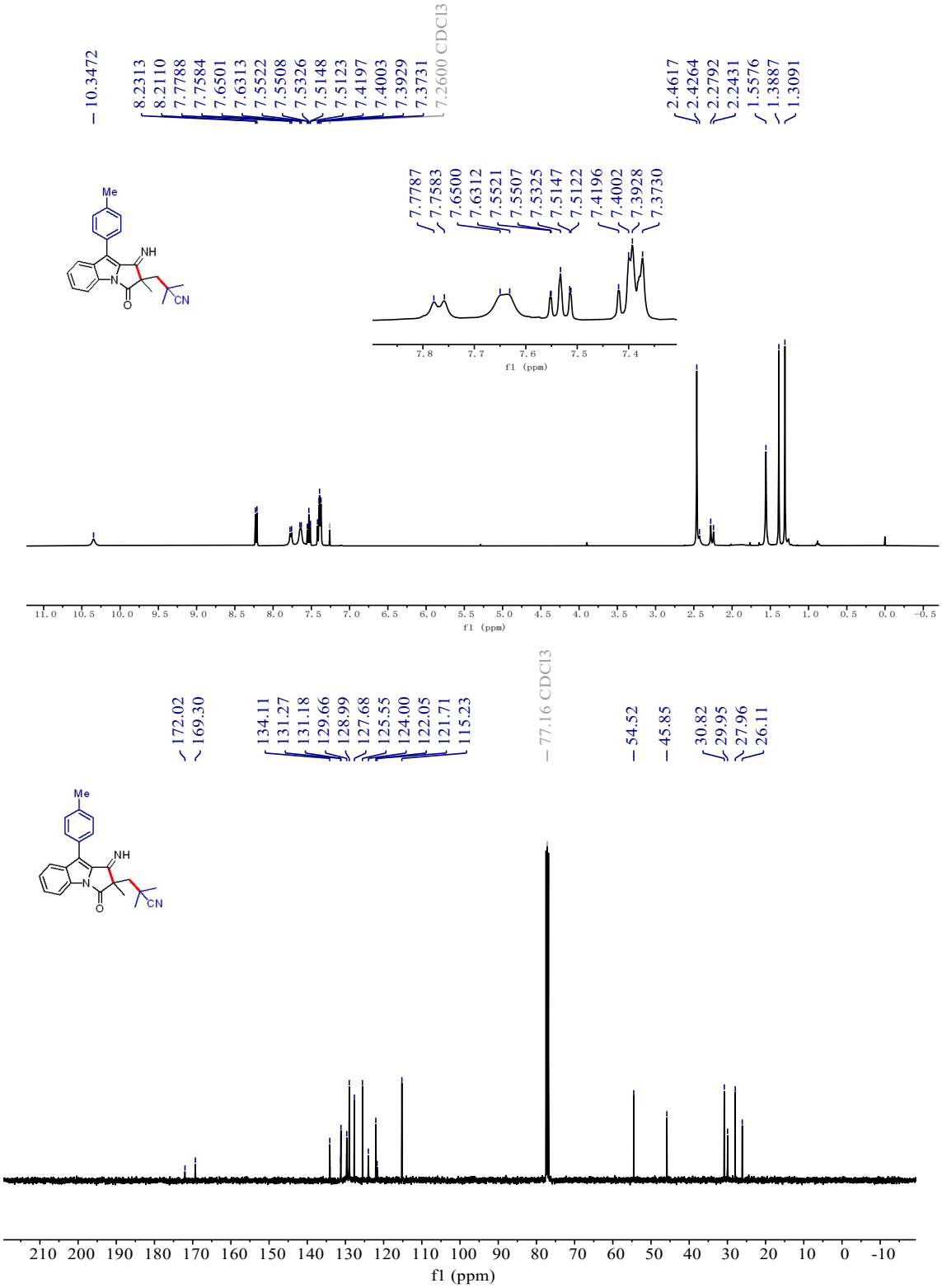
F. NMR spectra:

^{1}H and ^{13}C NMR Spectra of compound 3a

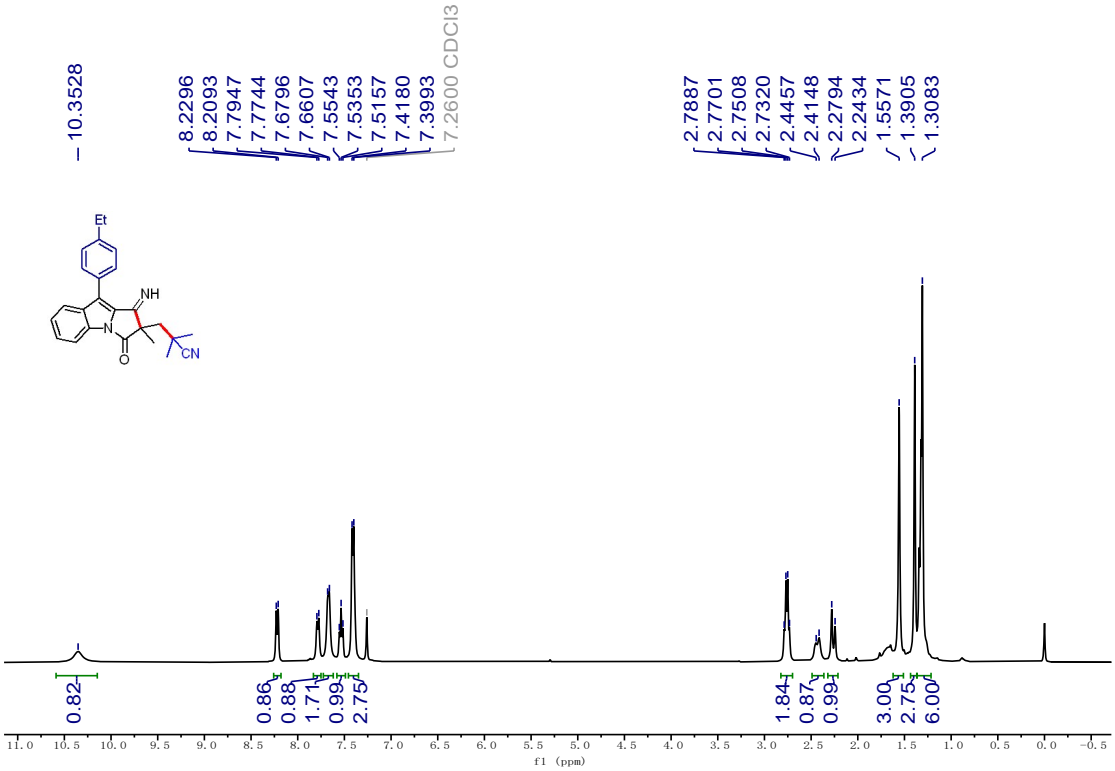


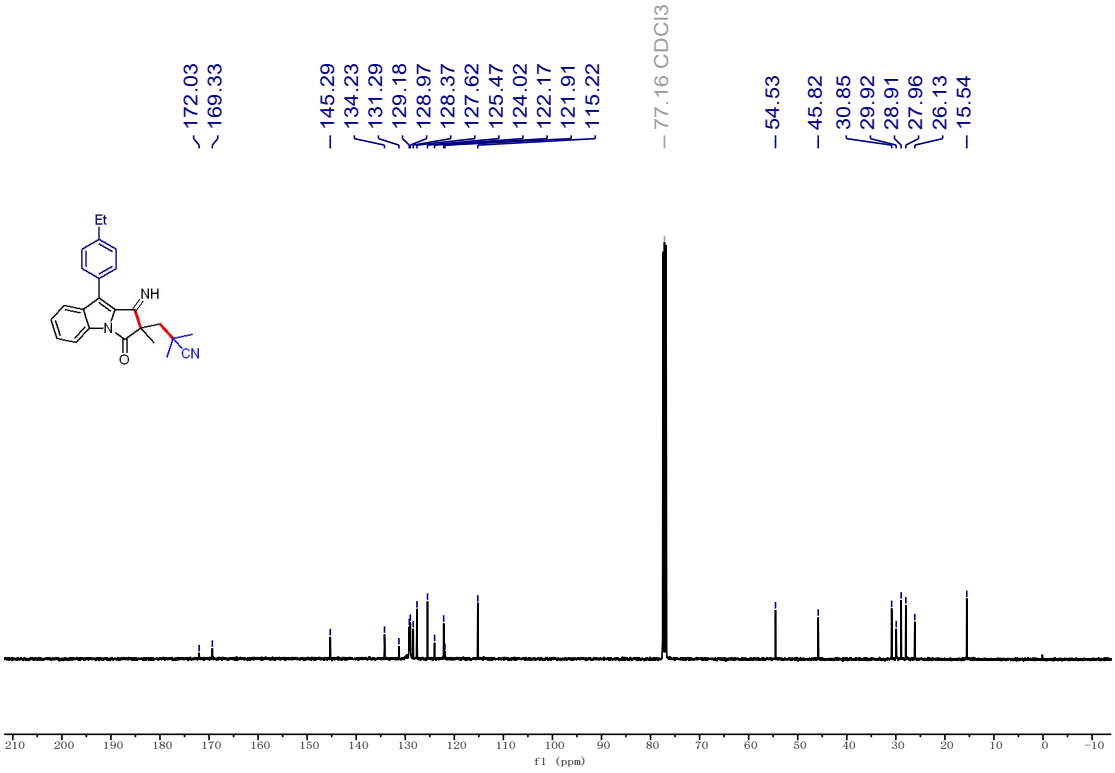


^{1}H and ^{13}C NMR Spectra of compound 3b

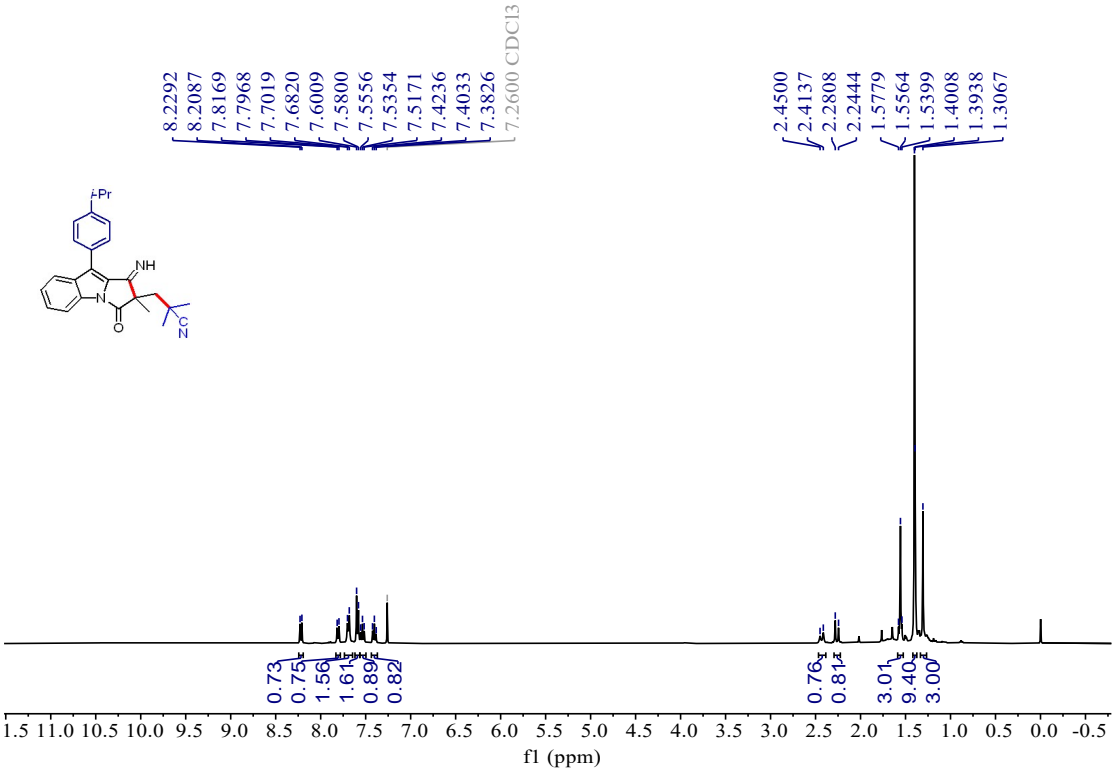


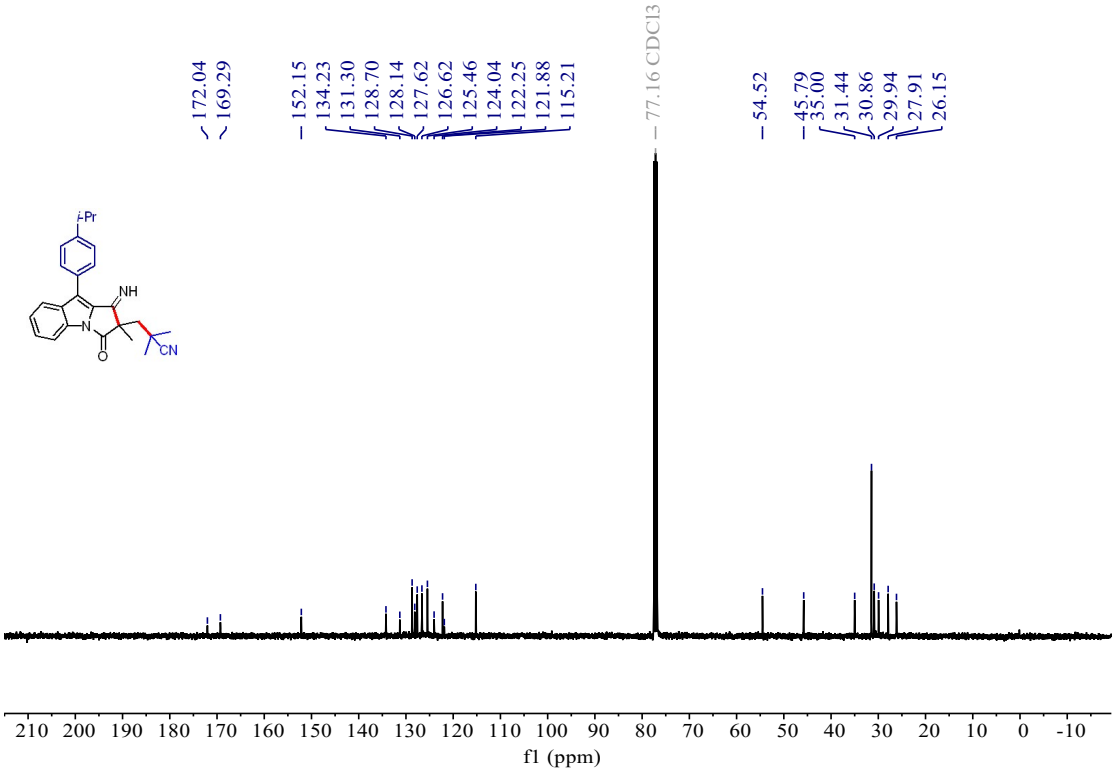
^{1}H and ^{13}C NMR Spectra of 3c



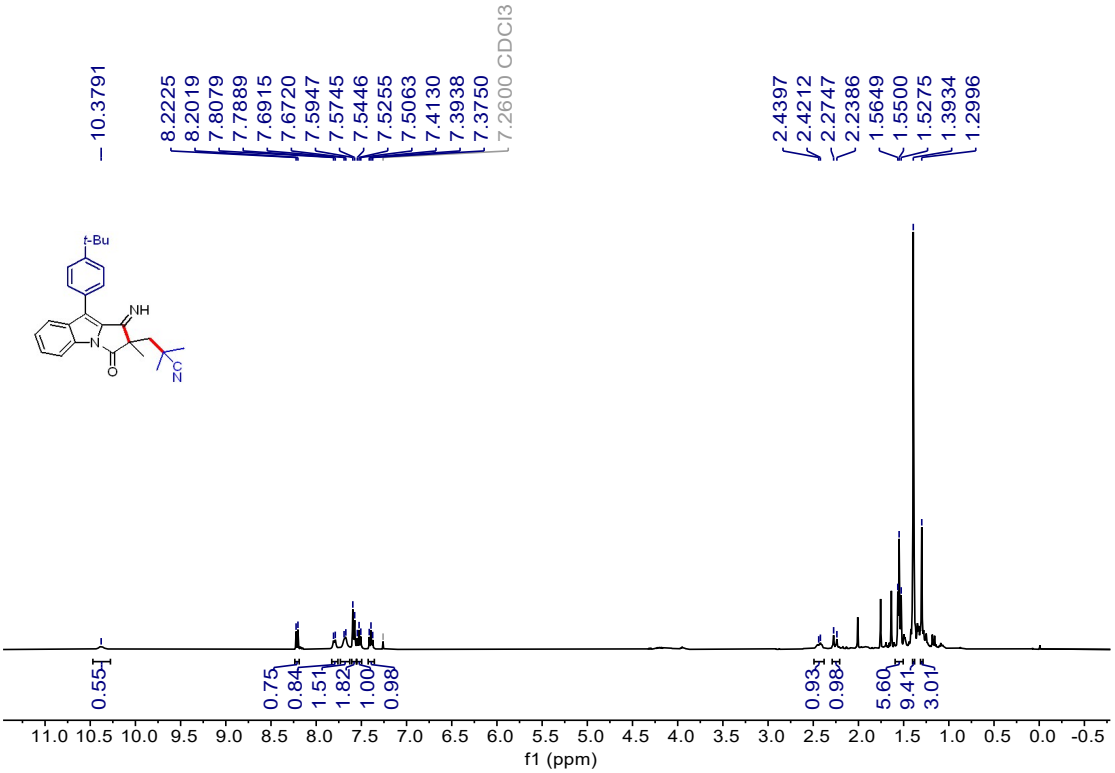


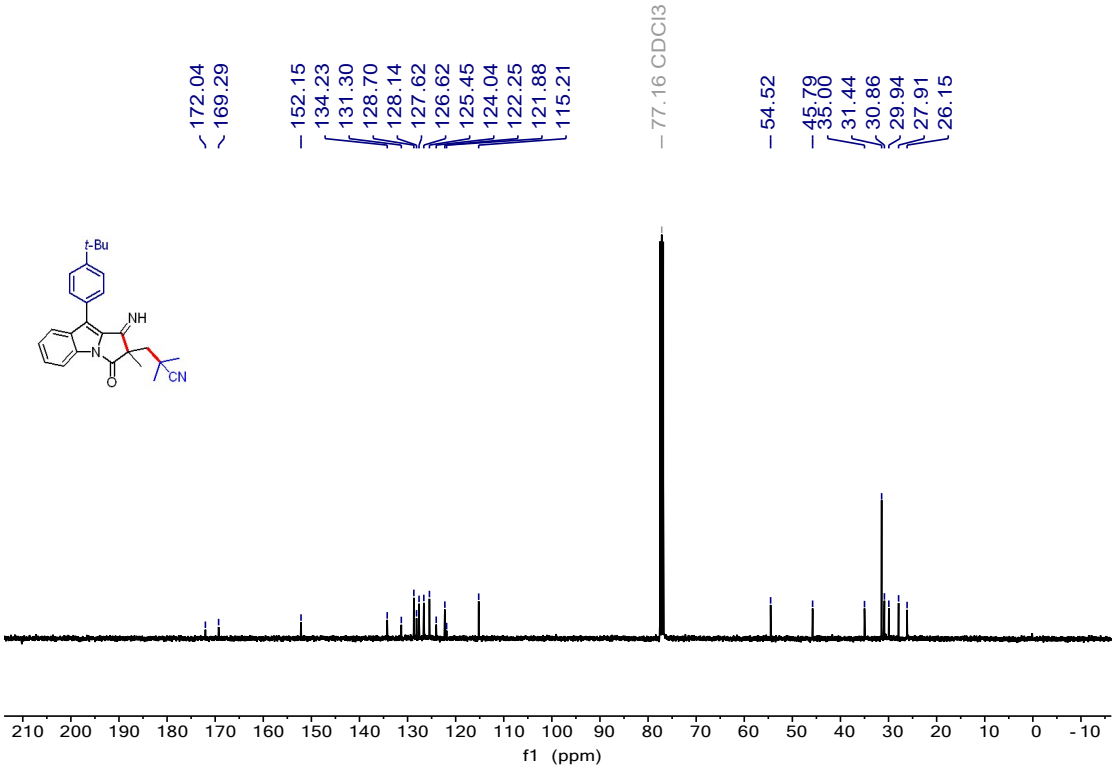
^{1}H and ^{13}C NMR Spectra of 3d



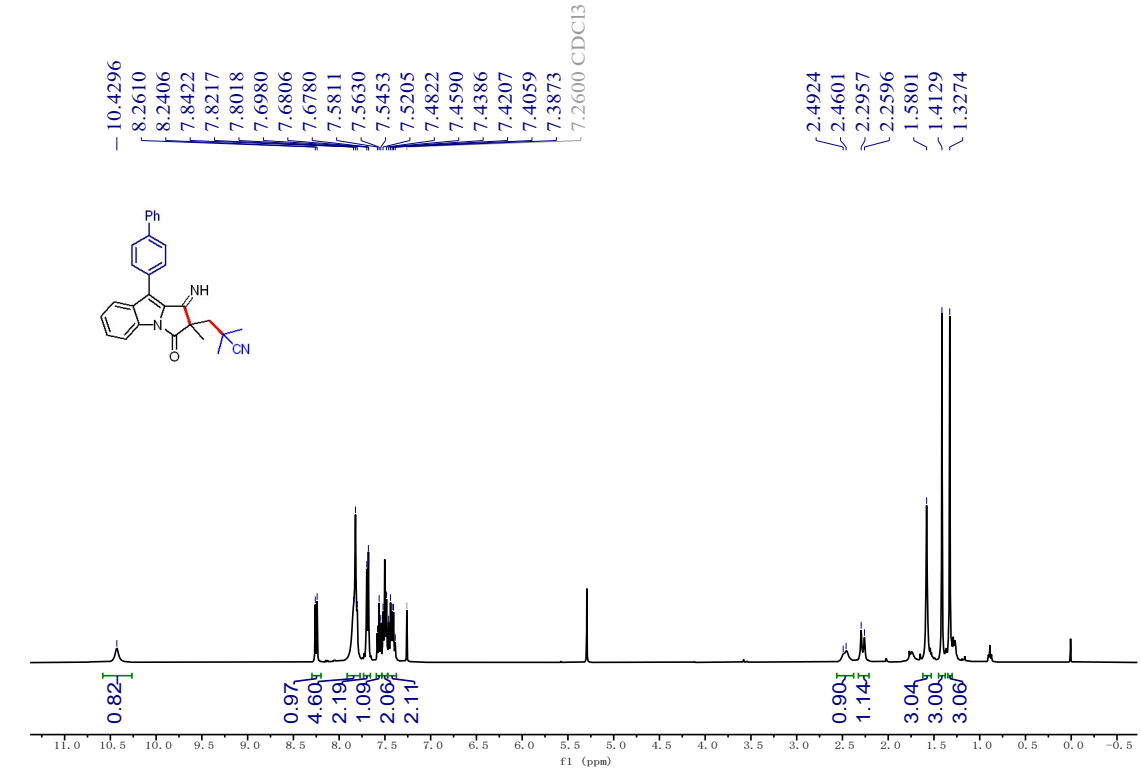


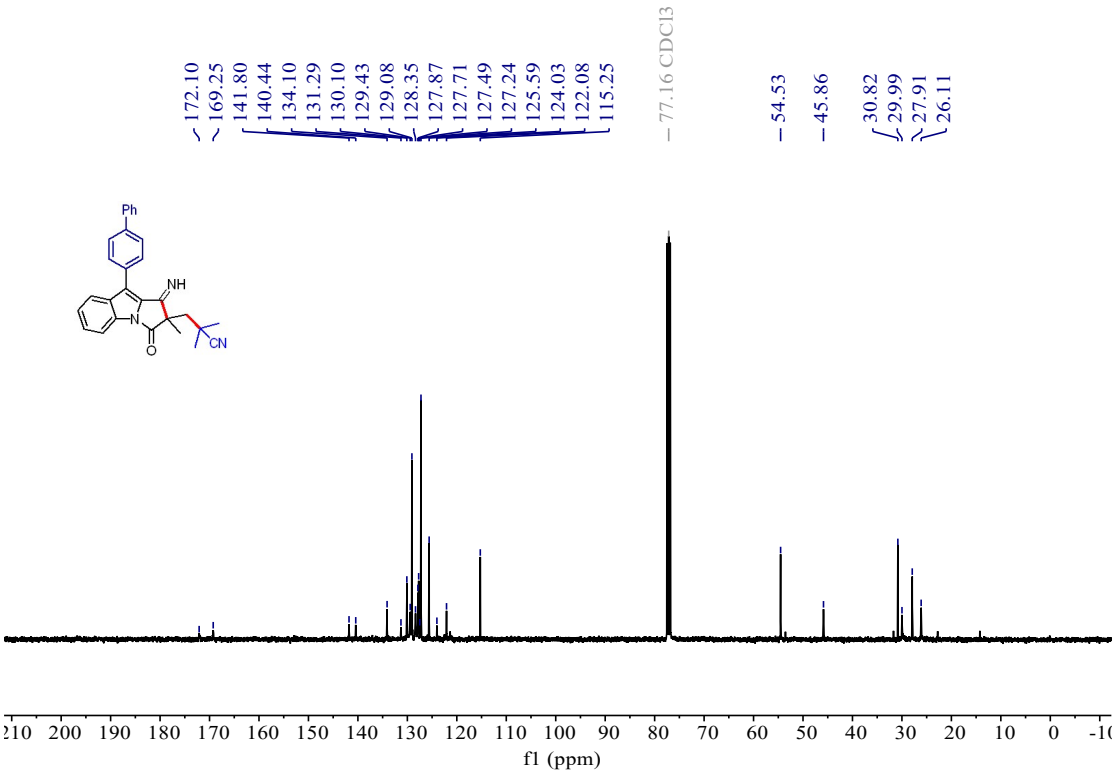
^{1}H and ^{13}C NMR Spectra of 3e



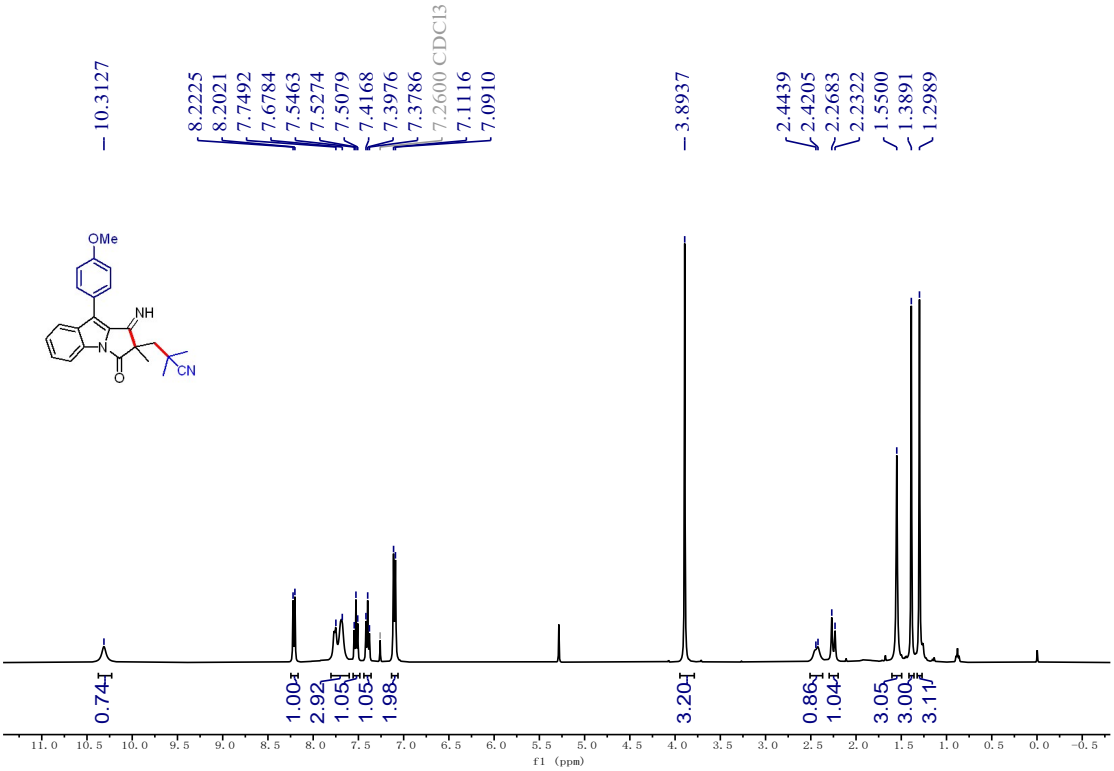


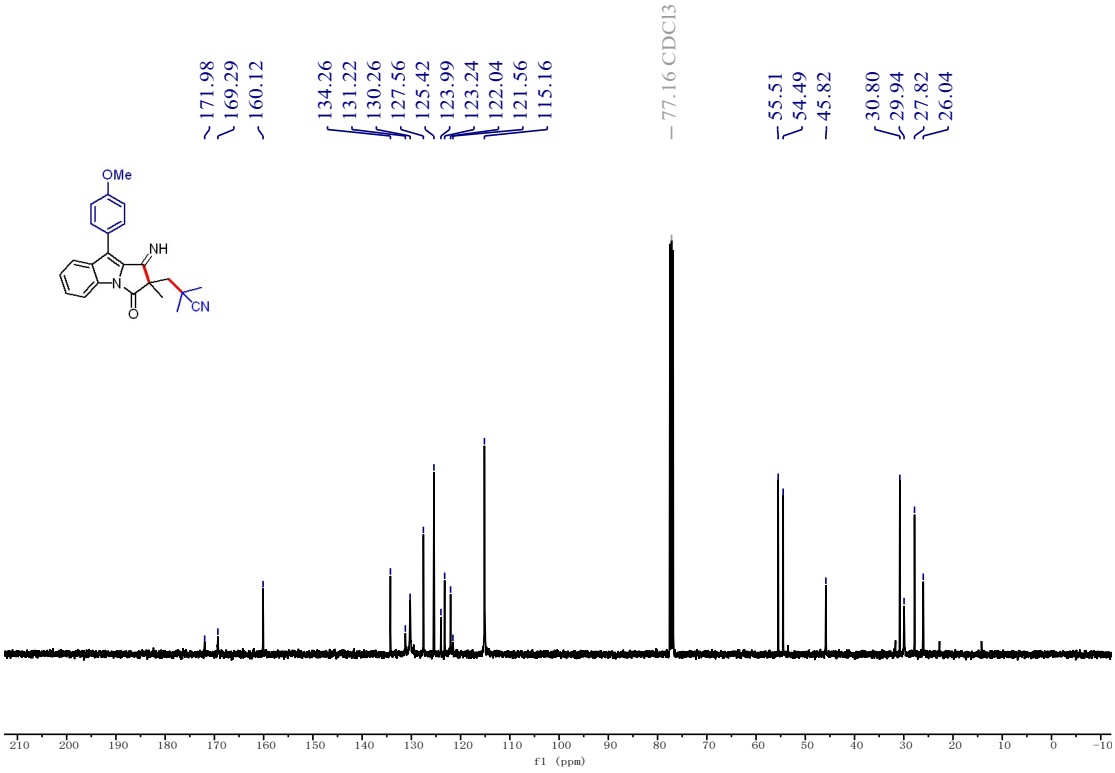
^{1}H and ^{13}C NMR Spectra of 3f



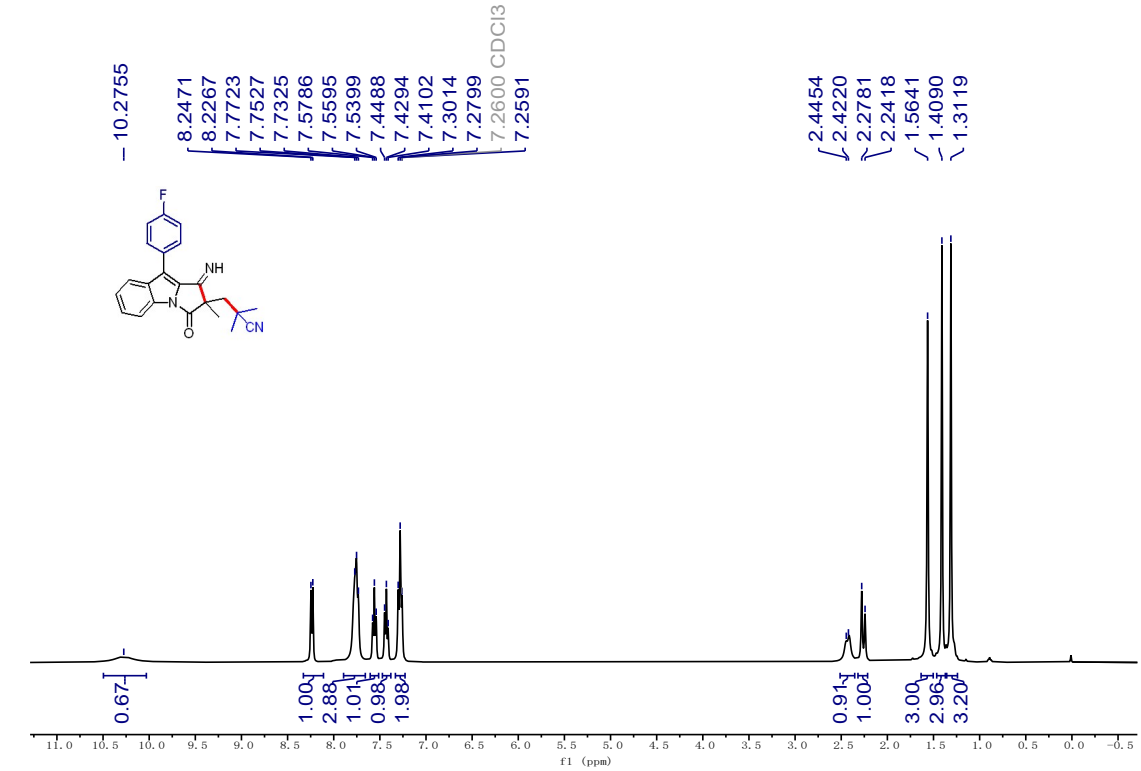


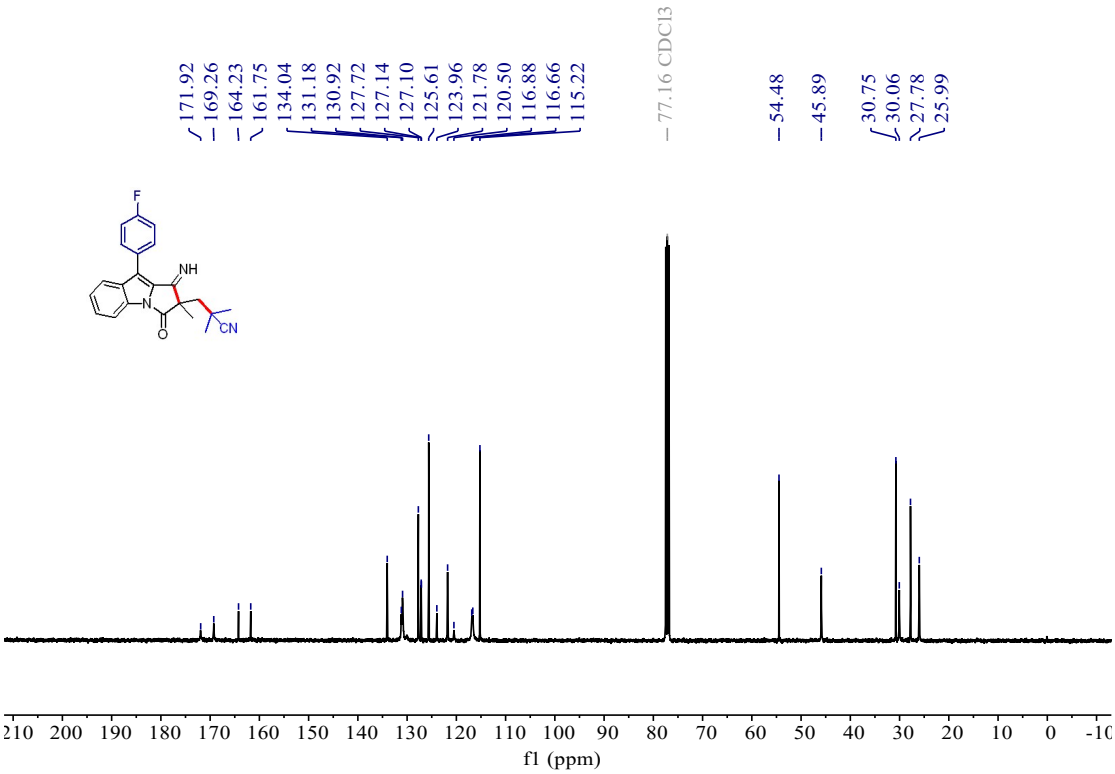
^{1}H and ^{13}C NMR Spectra of 3g

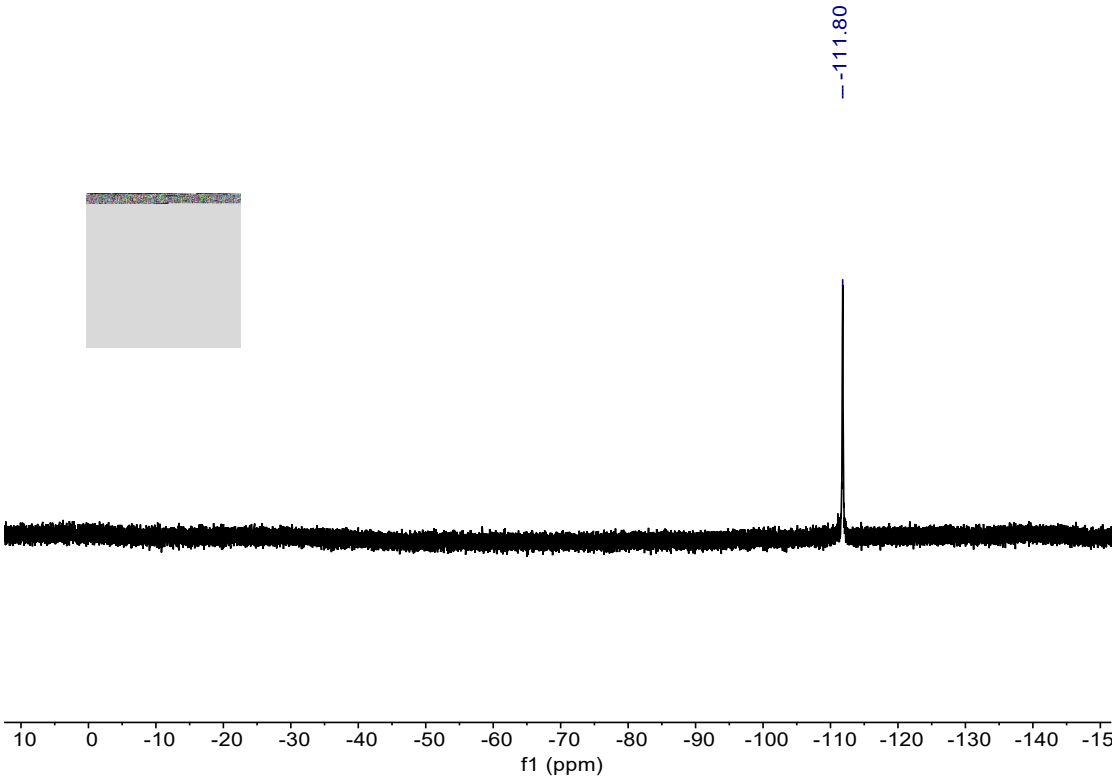




^{1}H and ^{13}C NMR Spectra of 3h



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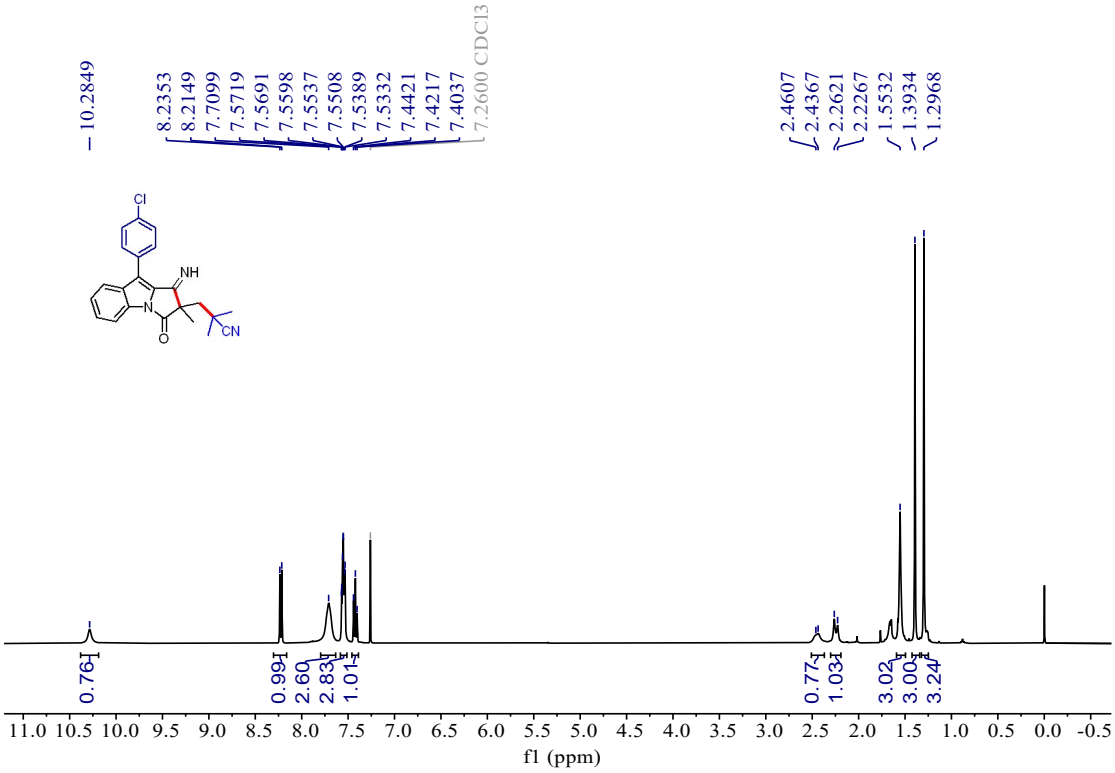
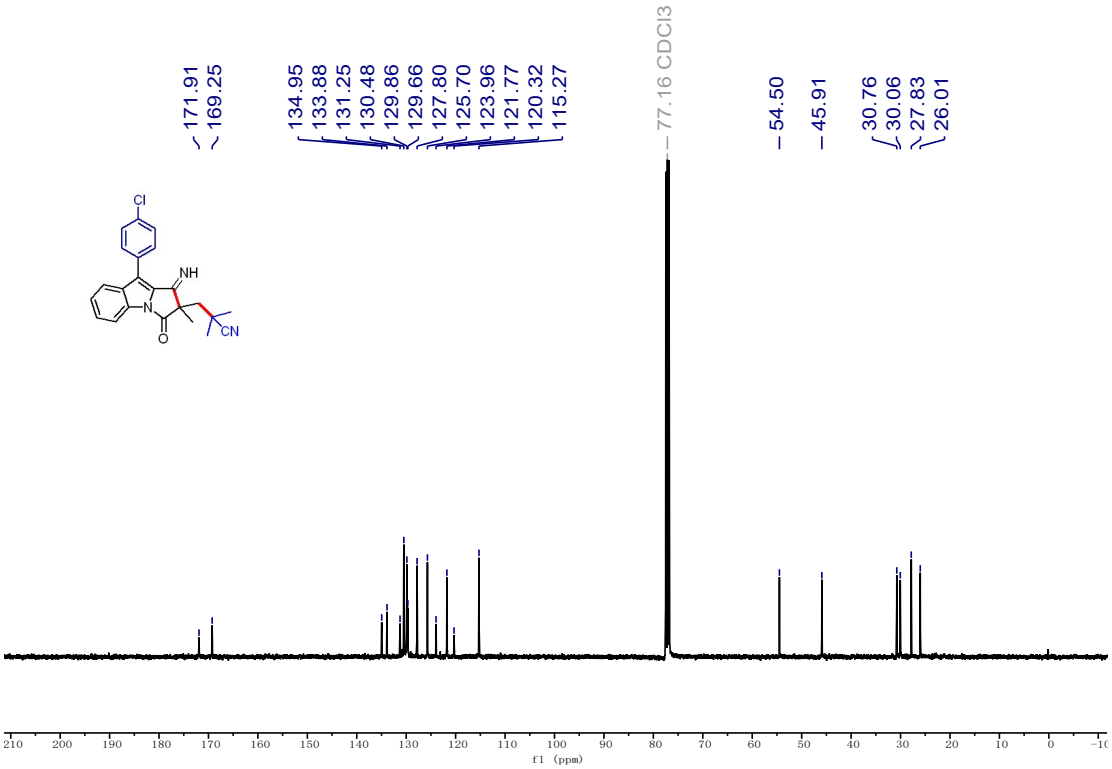
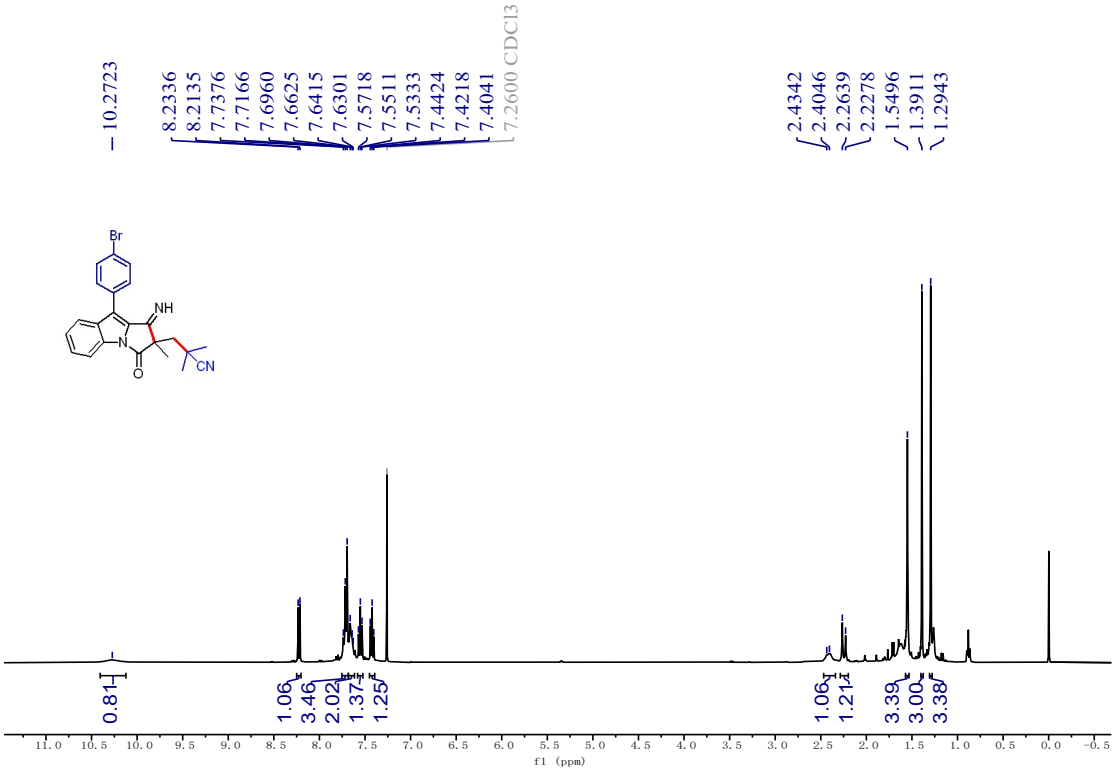
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-15
f1 (ppm)

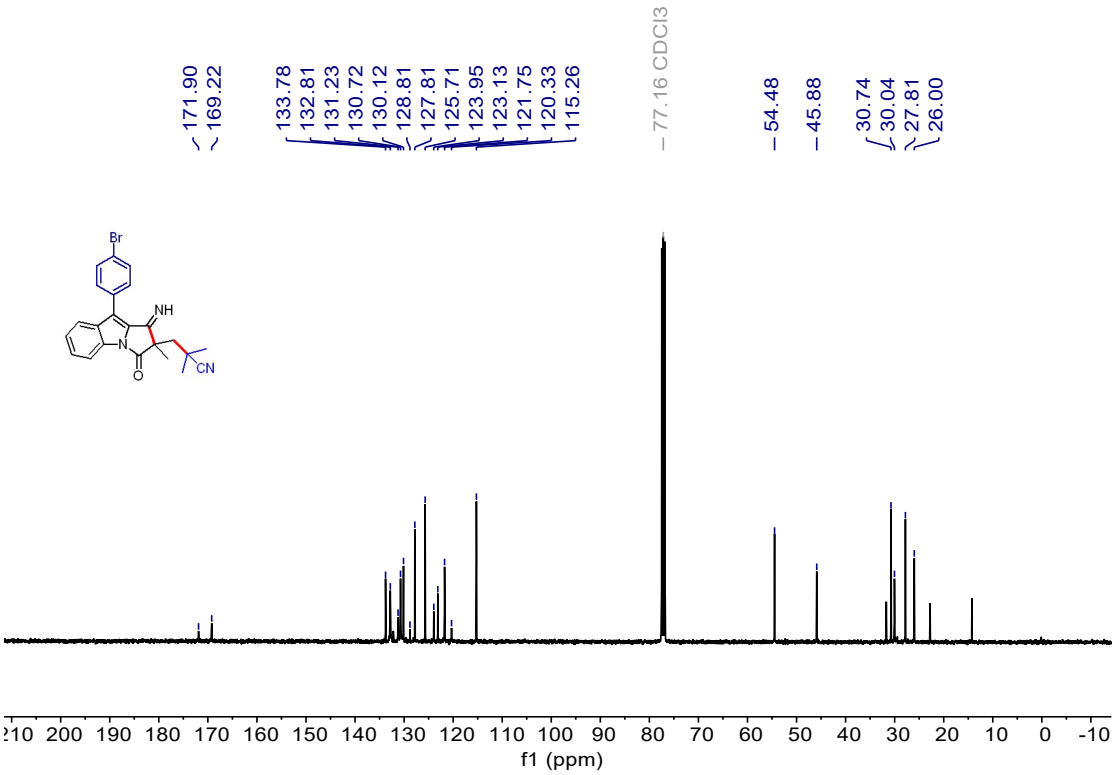
^{1}H and ^{13}C NMR Spectra of 3i



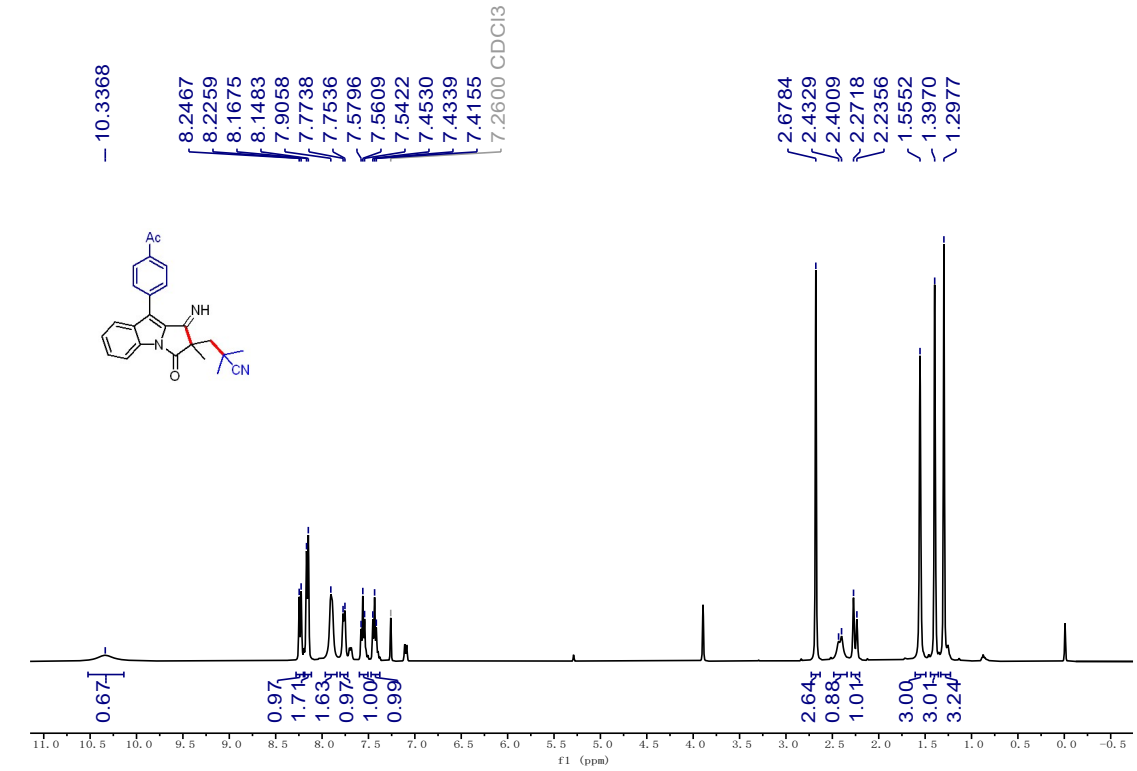


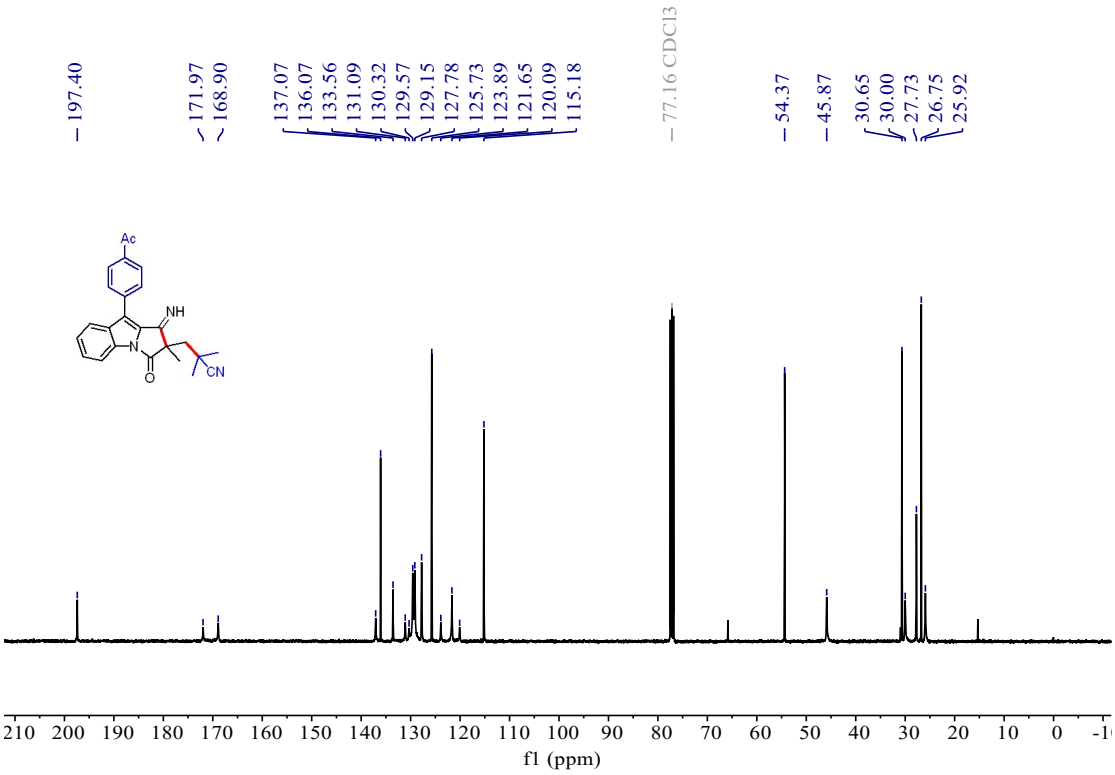
^{1}H and ^{13}C NMR Spectra of 3j



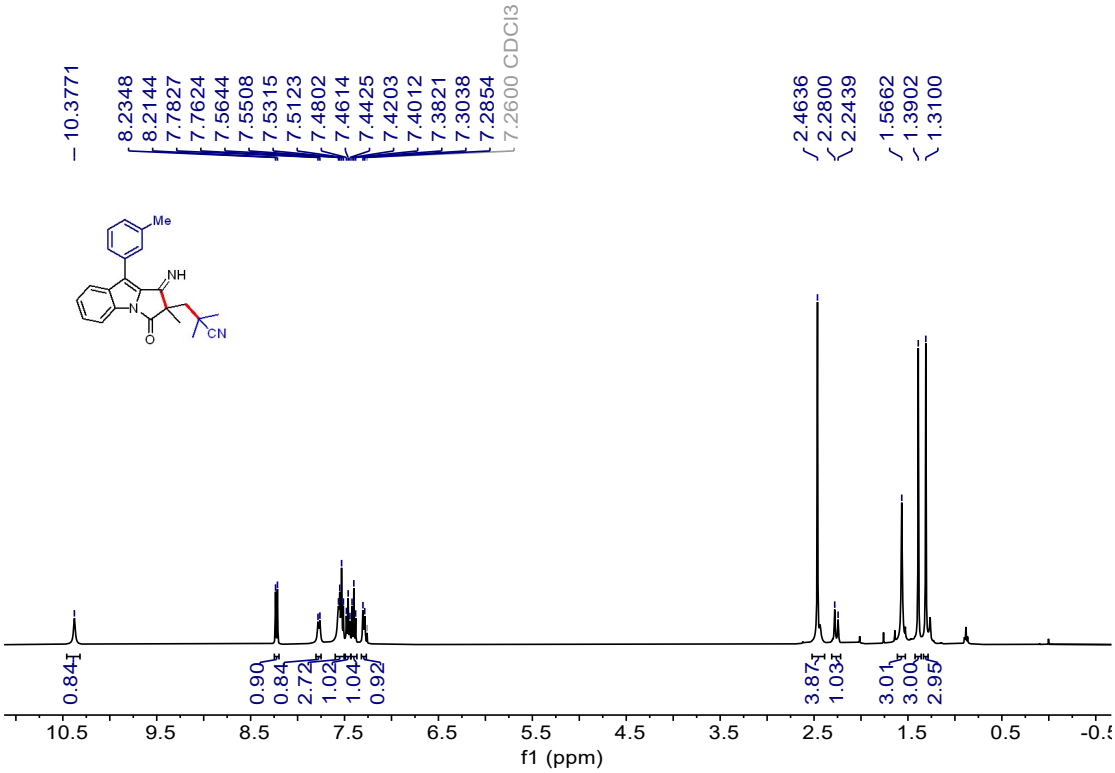


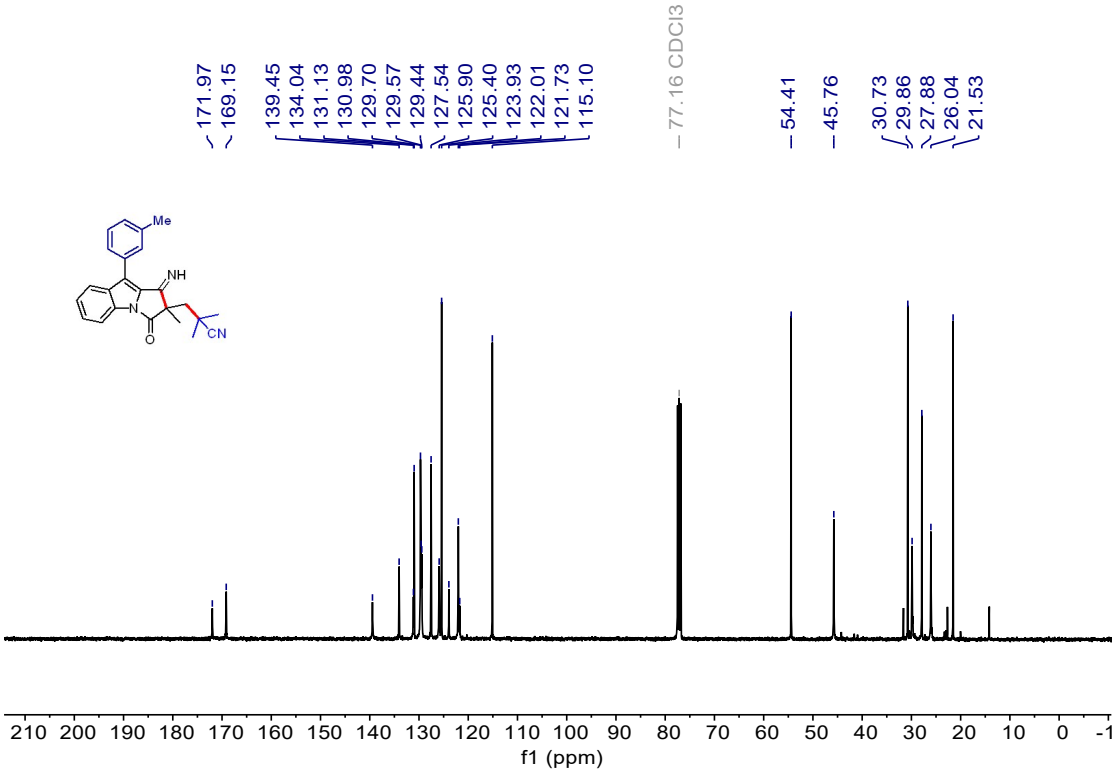
^{1}H and ^{13}C NMR Spectra of 3k



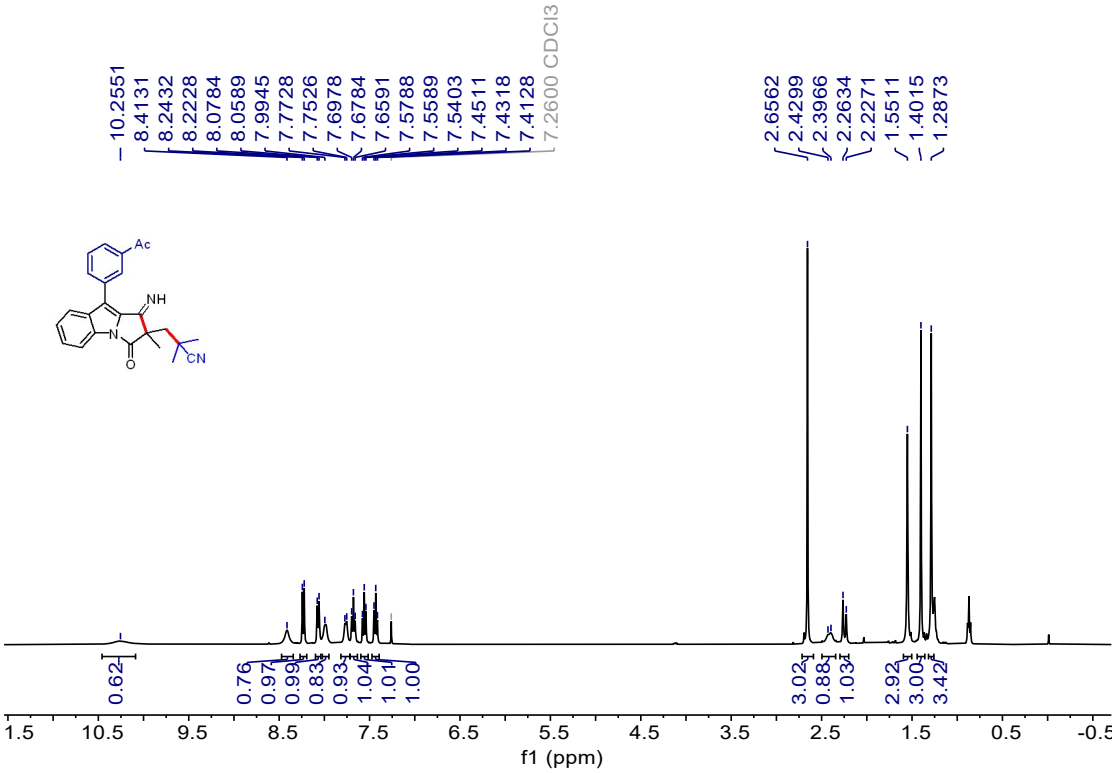


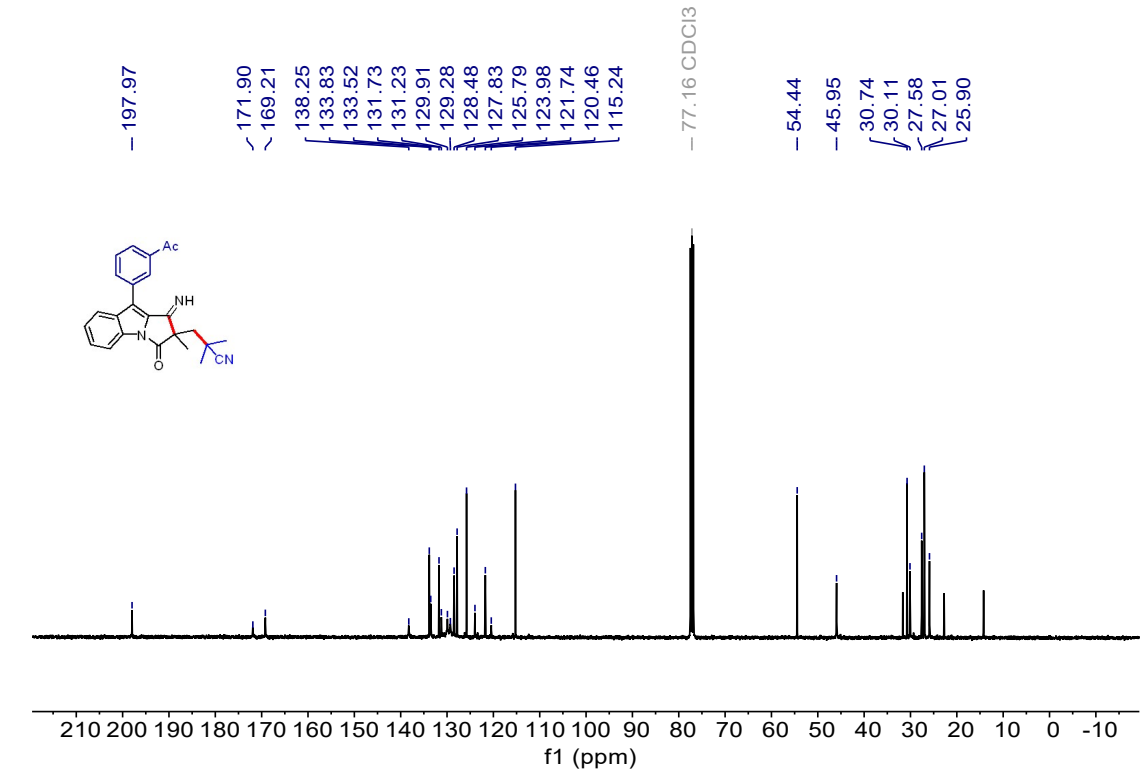
^{1}H and ^{13}C NMR Spectra of 3l



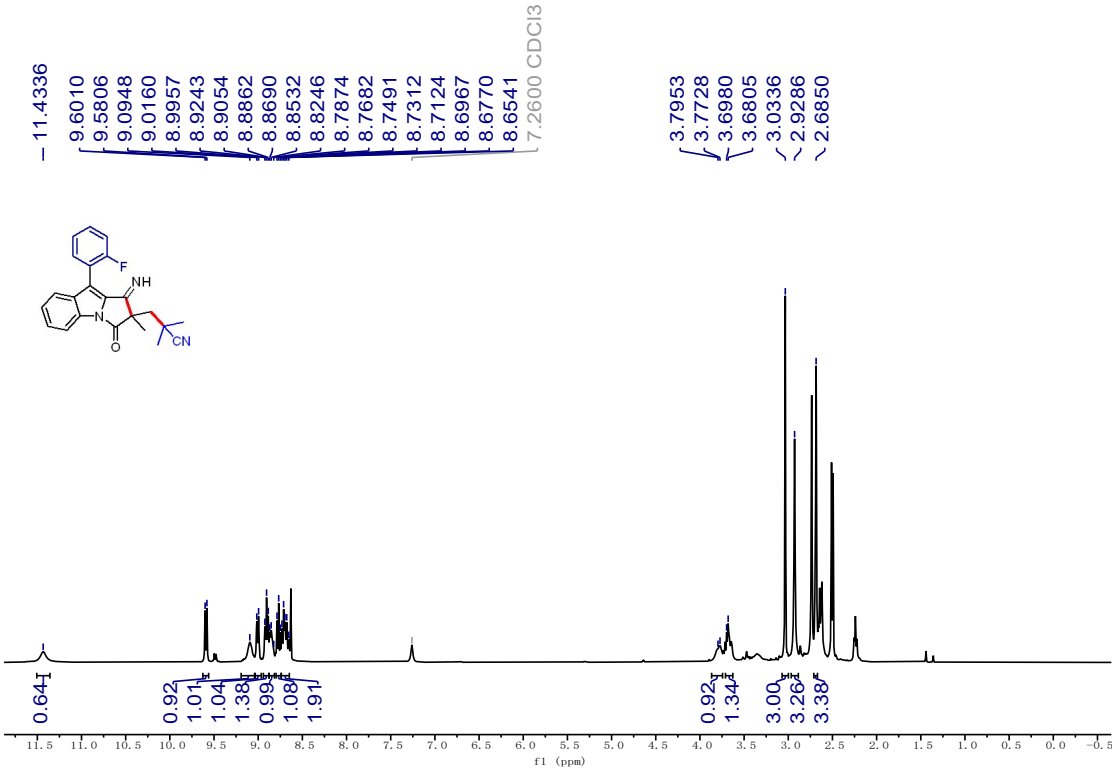


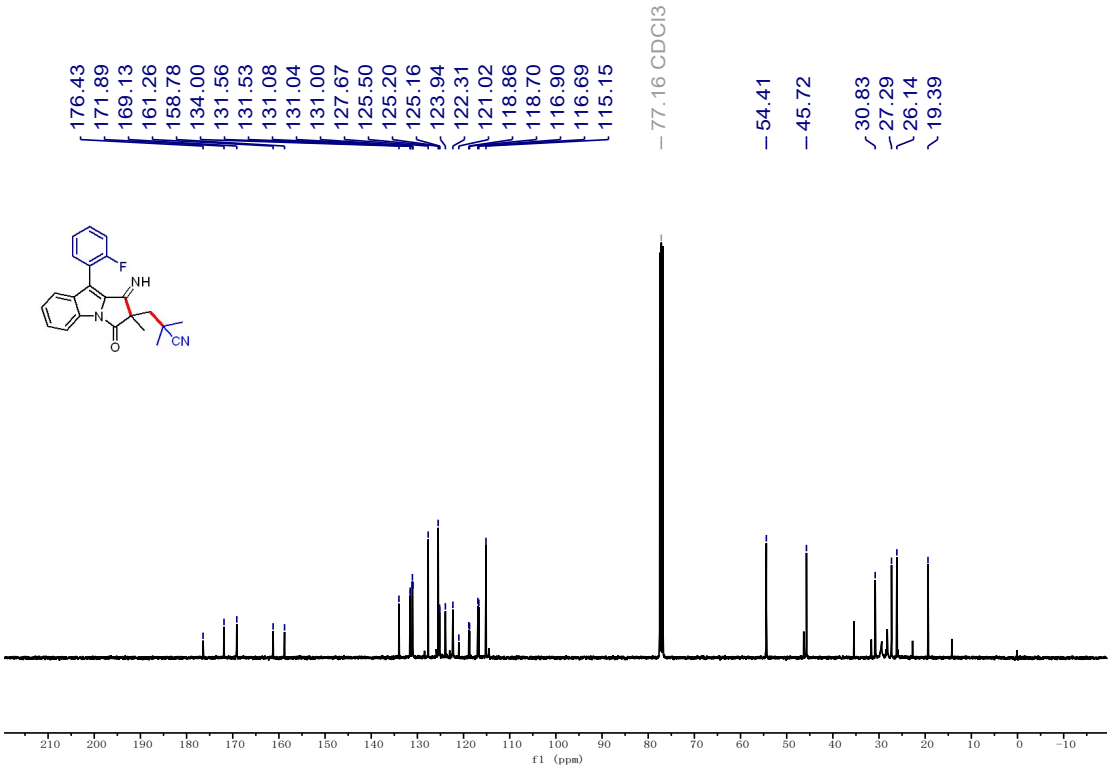
^{1}H and ^{13}C NMR Spectra of 3m

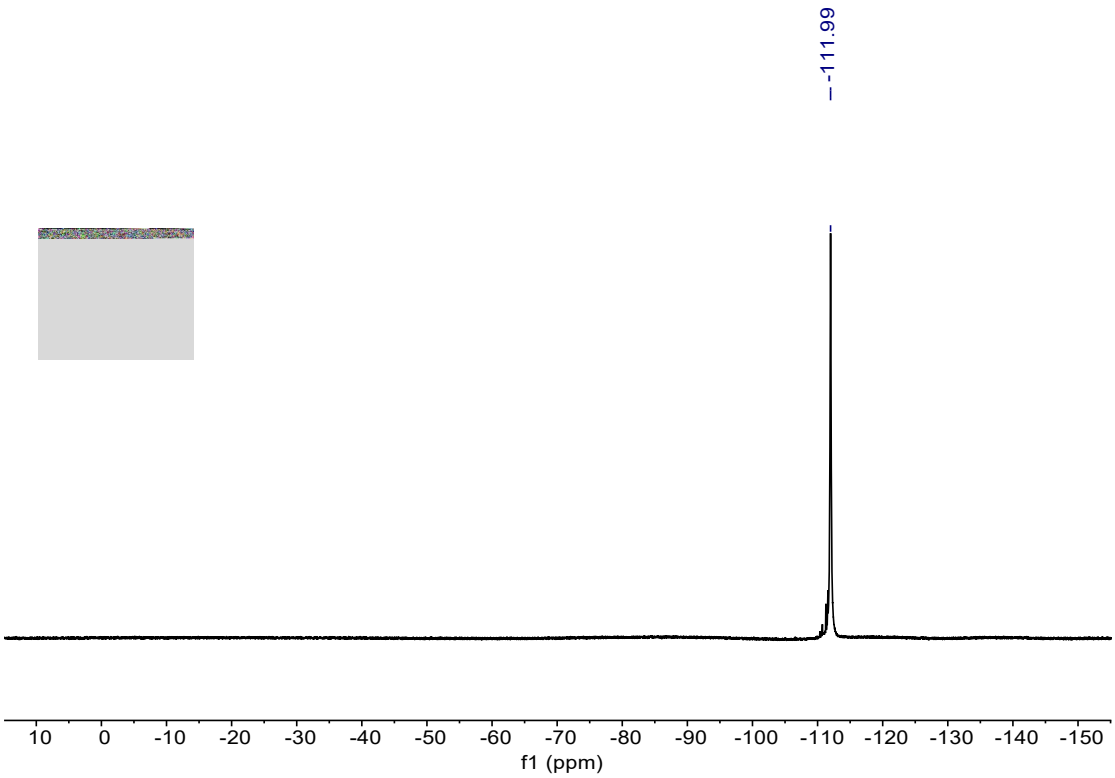




^{1}H and ^{13}C NMR Spectra of 3n






-111.99
10
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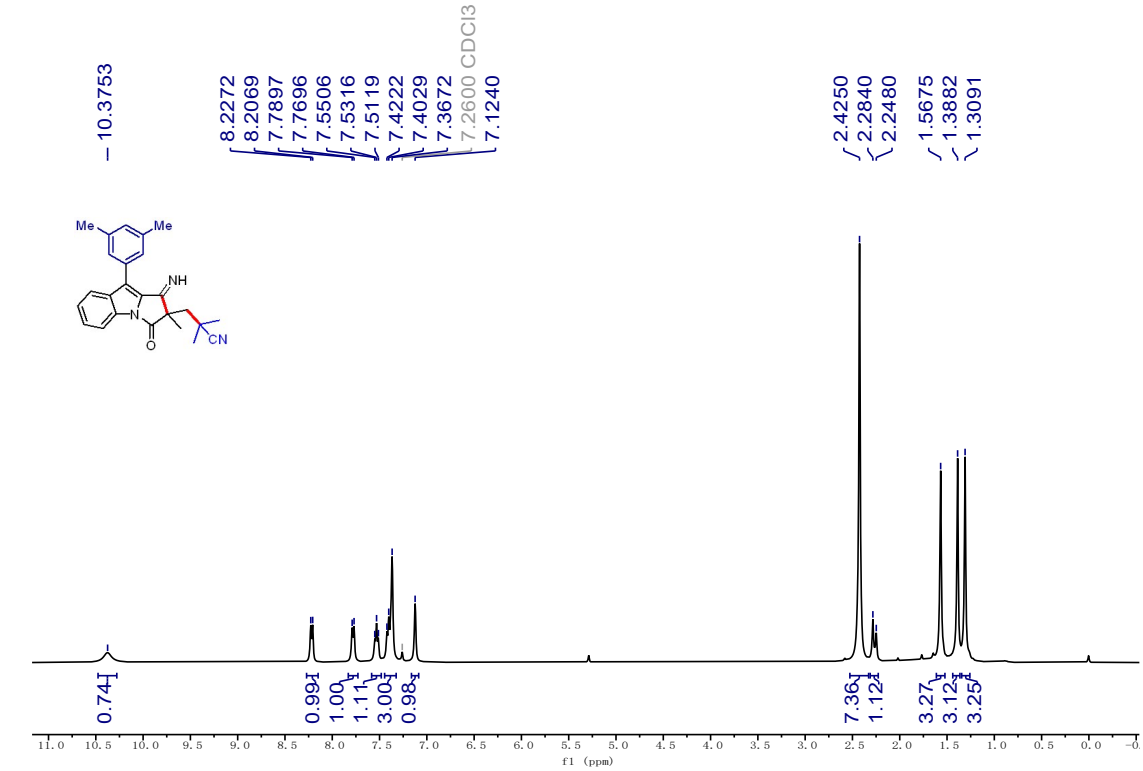
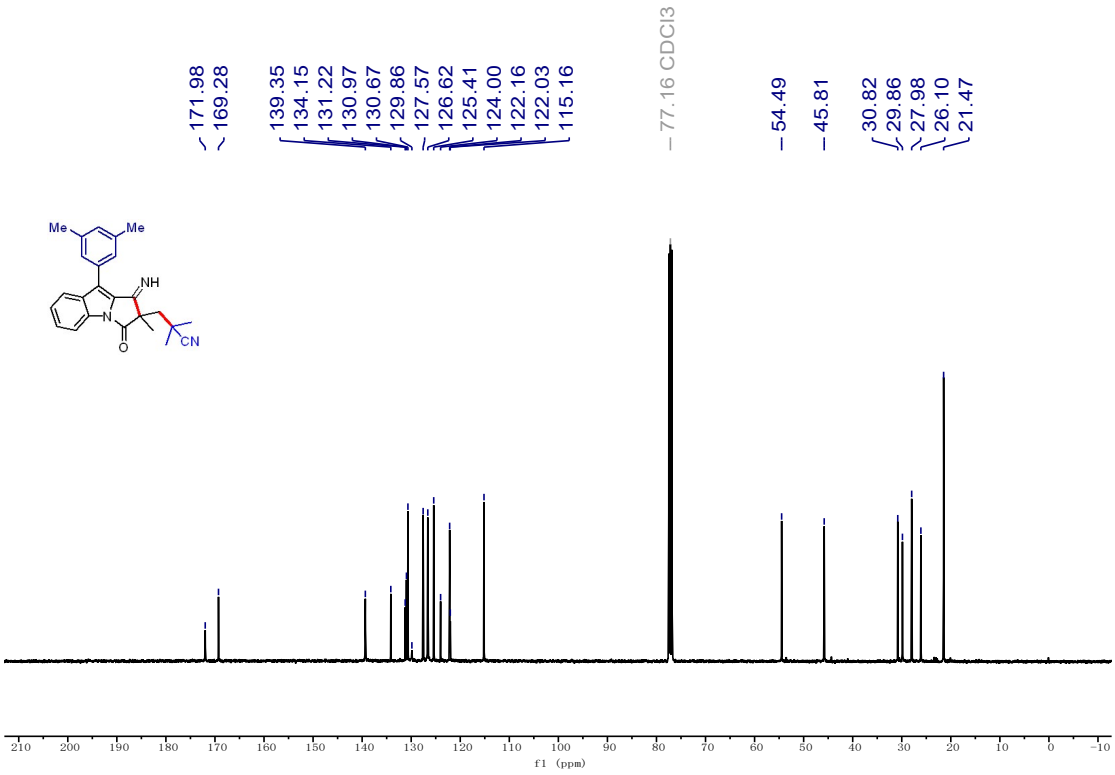
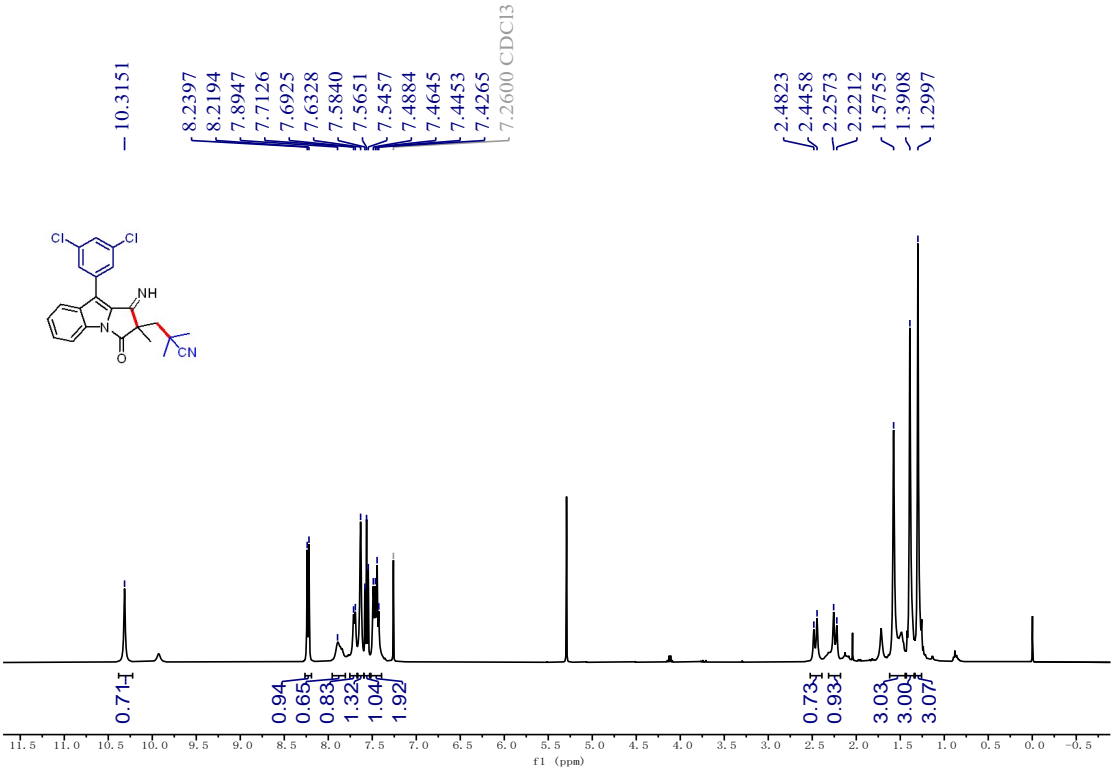
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
f1 (ppm)

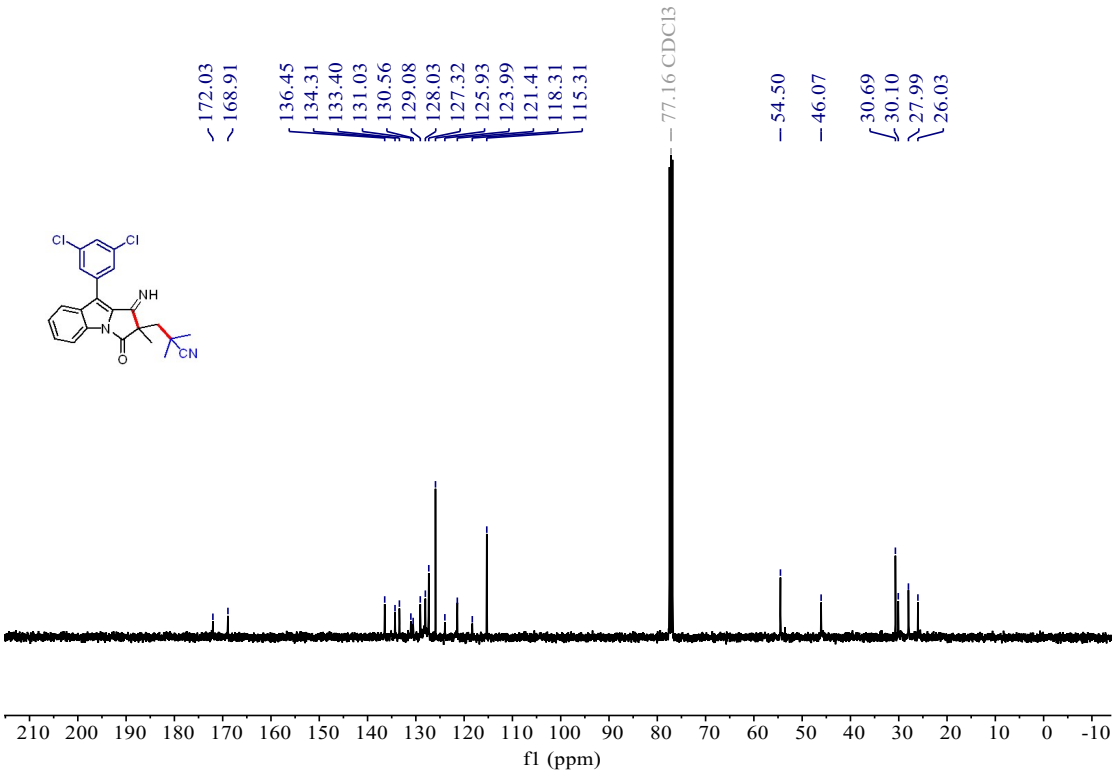
^{1}H and ^{13}C NMR Spectra of 3o



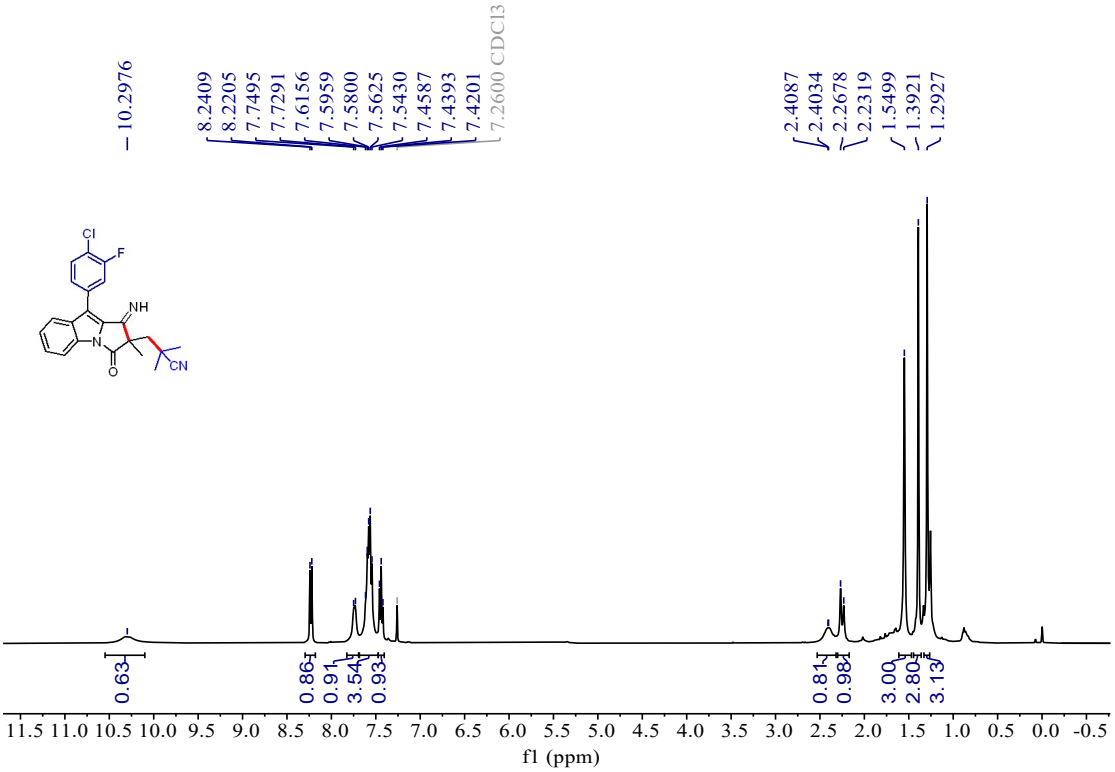


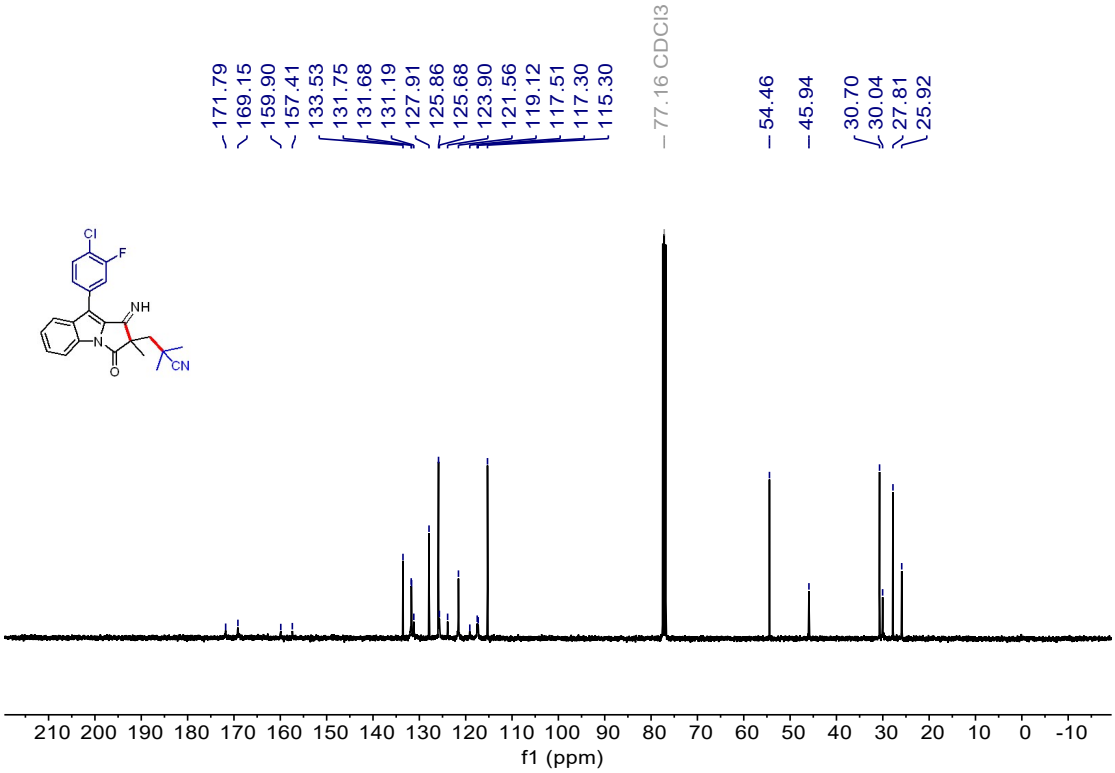
^{1}H and ^{13}C NMR Spectra of 3p



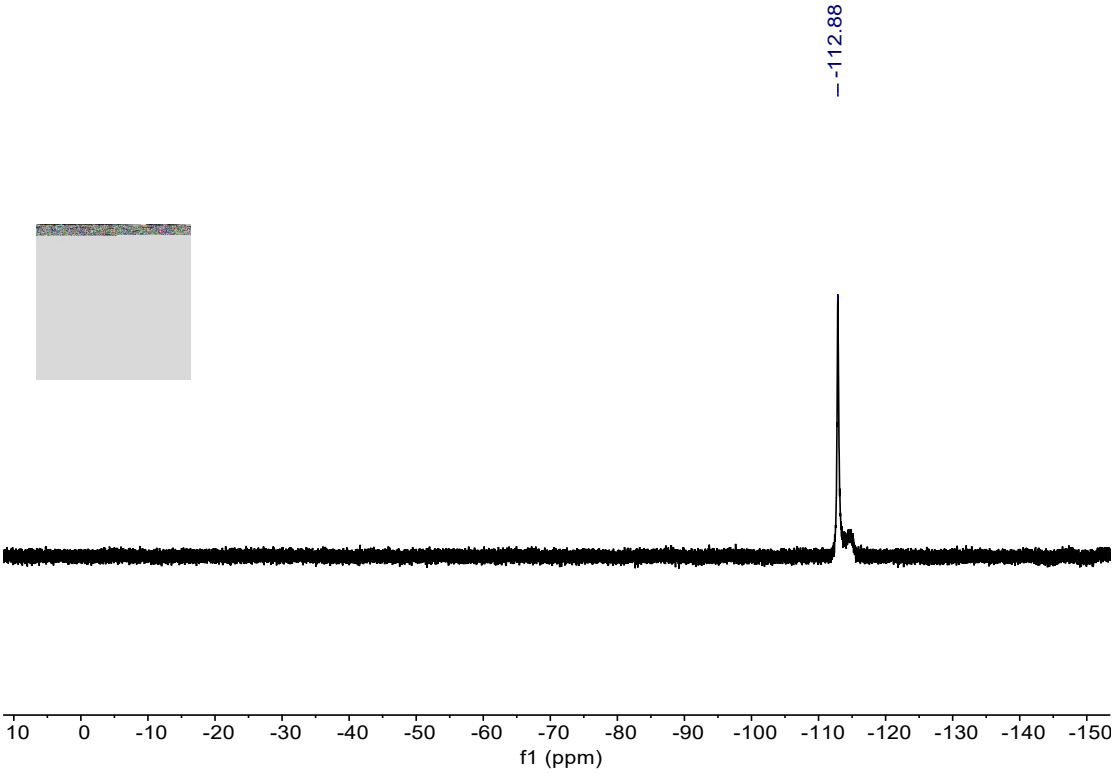


^{1}H and ^{13}C NMR Spectra of 3q

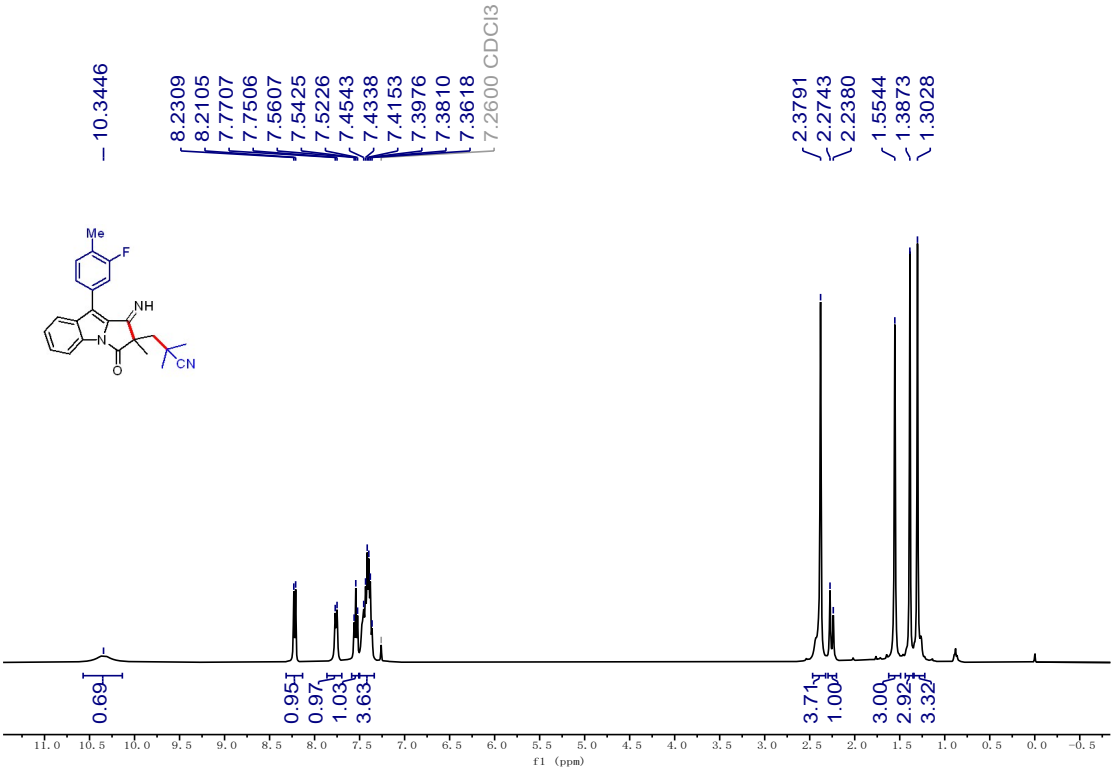


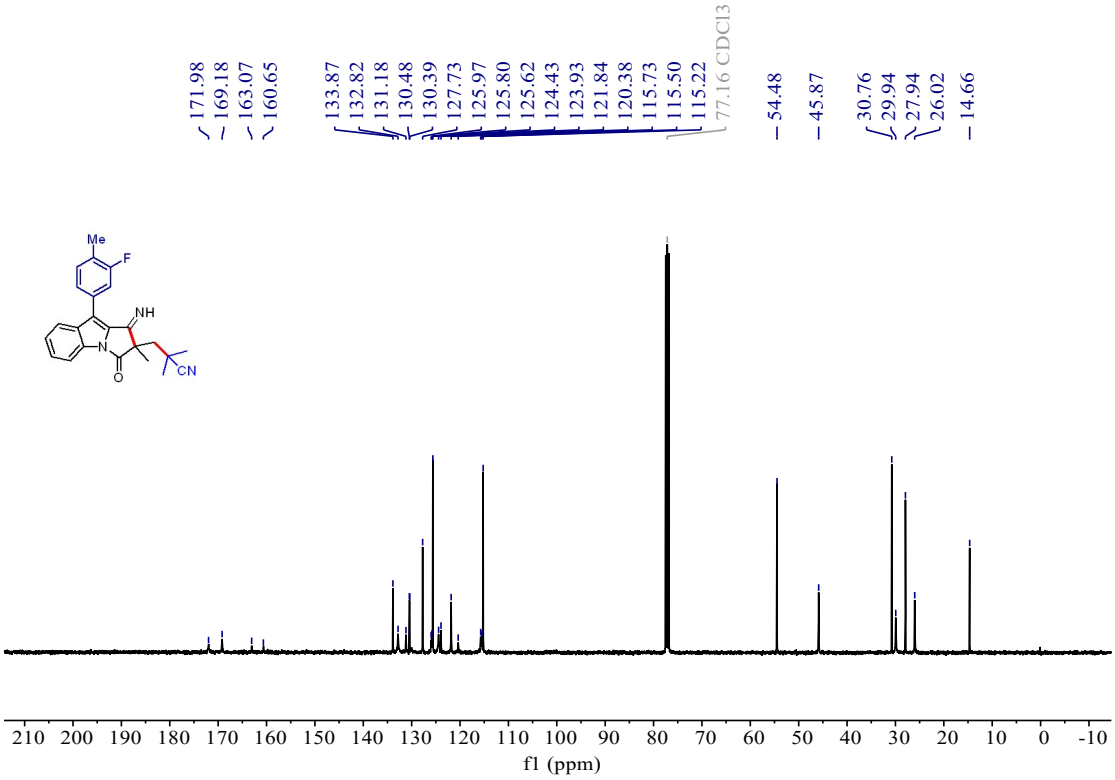


^{19}F NMR spectrum of **3q**

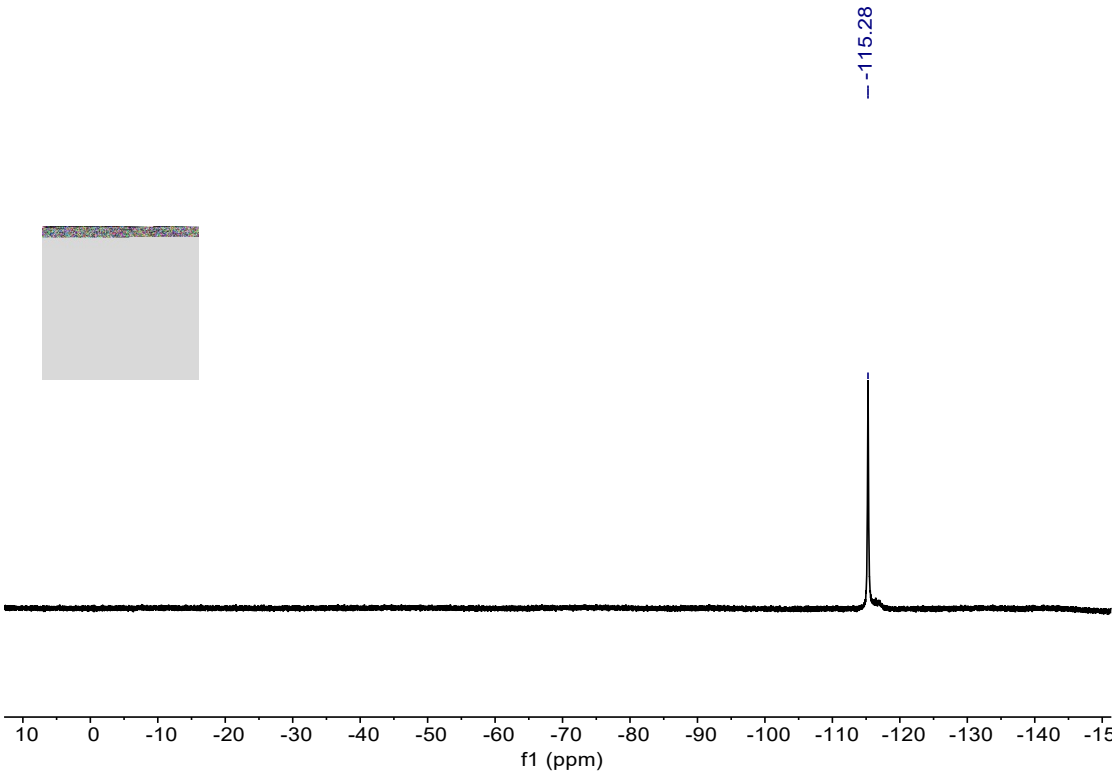


^{1}H and ^{13}C NMR Spectra of 3r

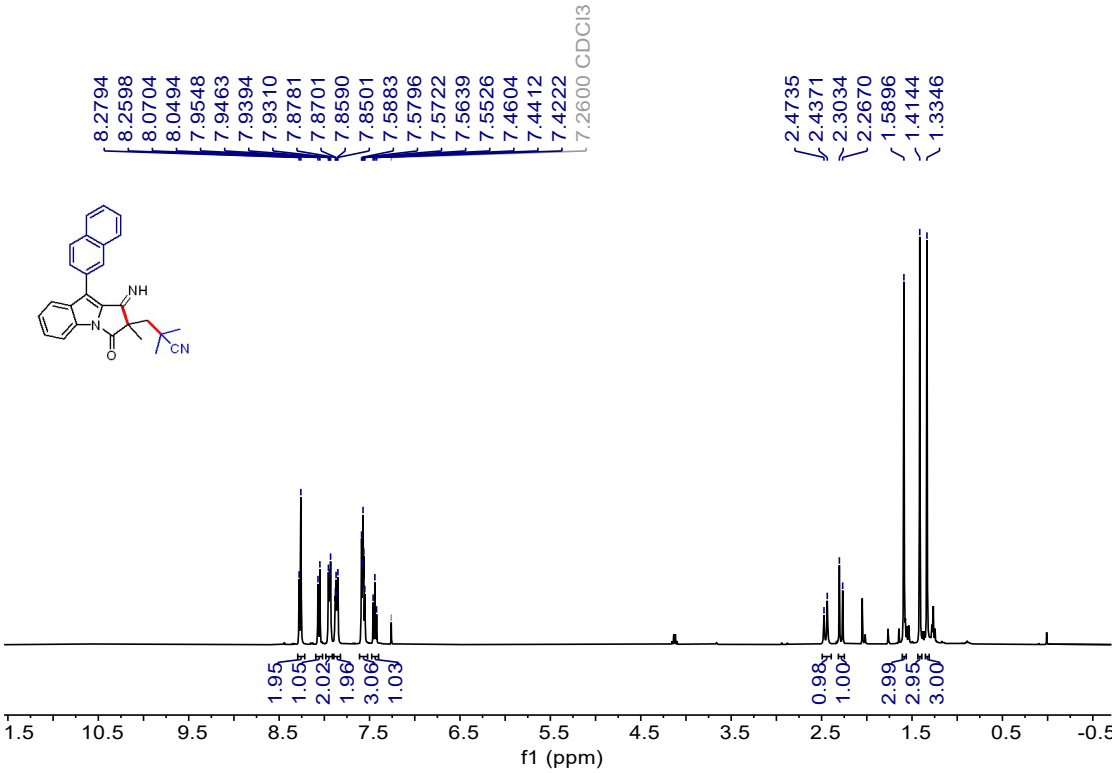


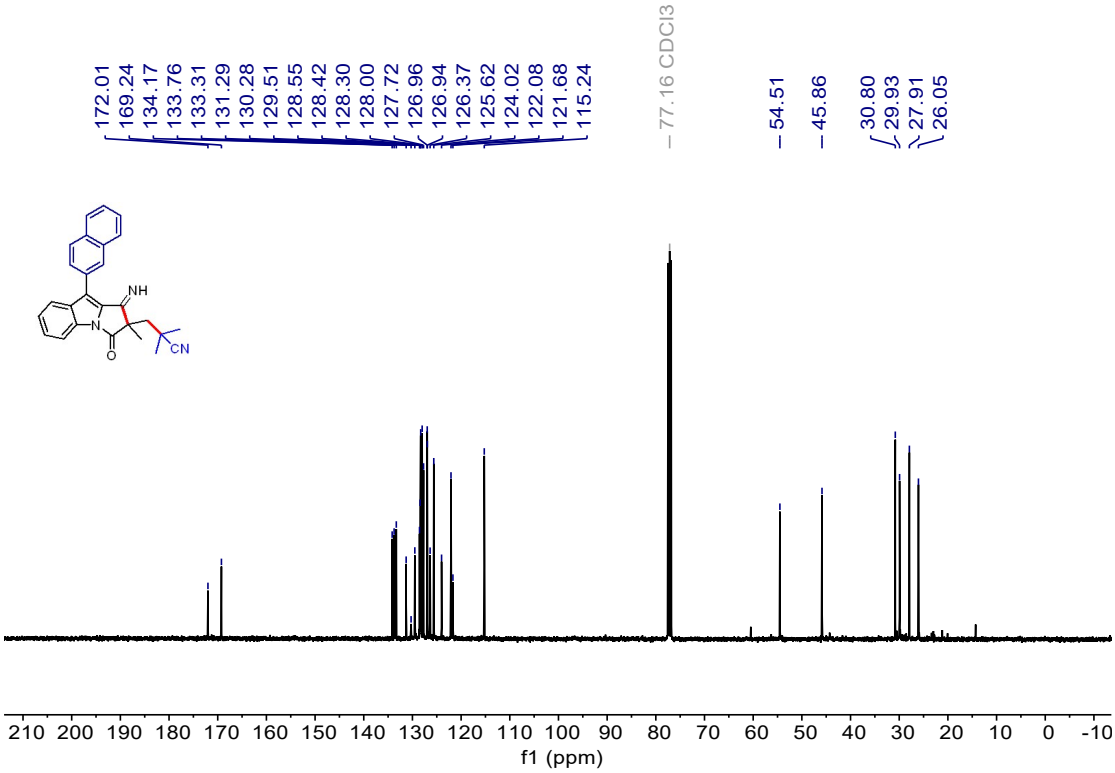


^{19}F NMR spectrum of **3r**

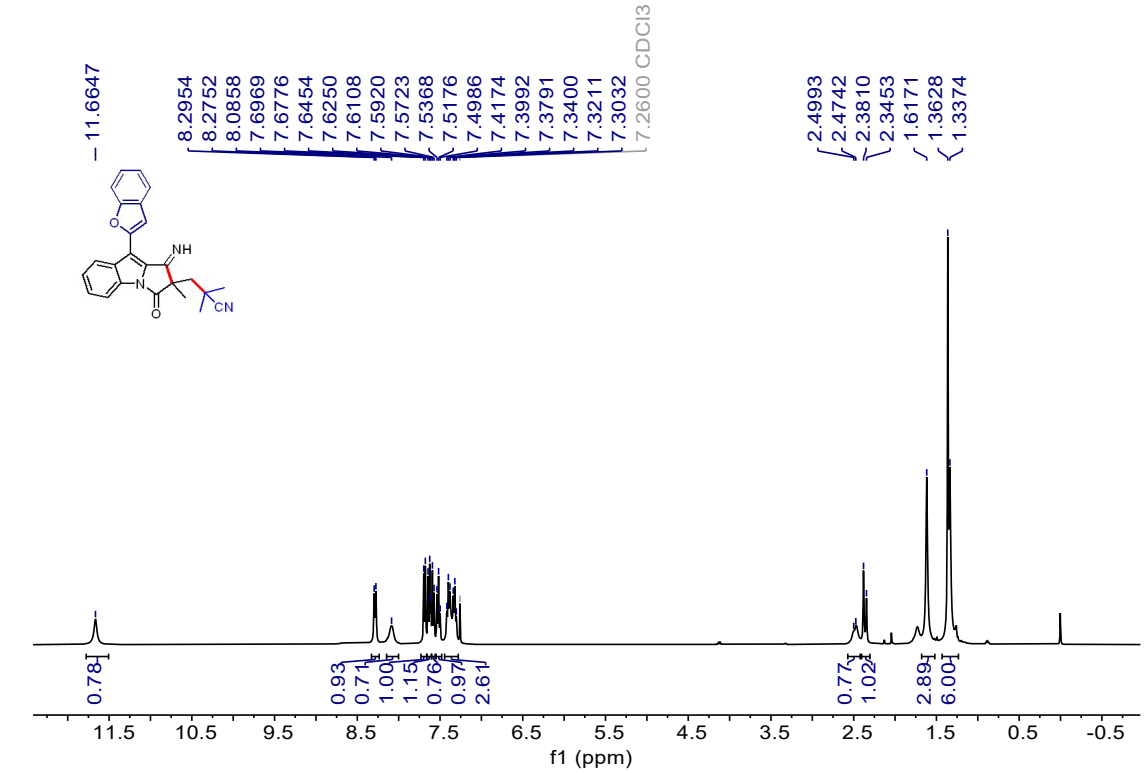


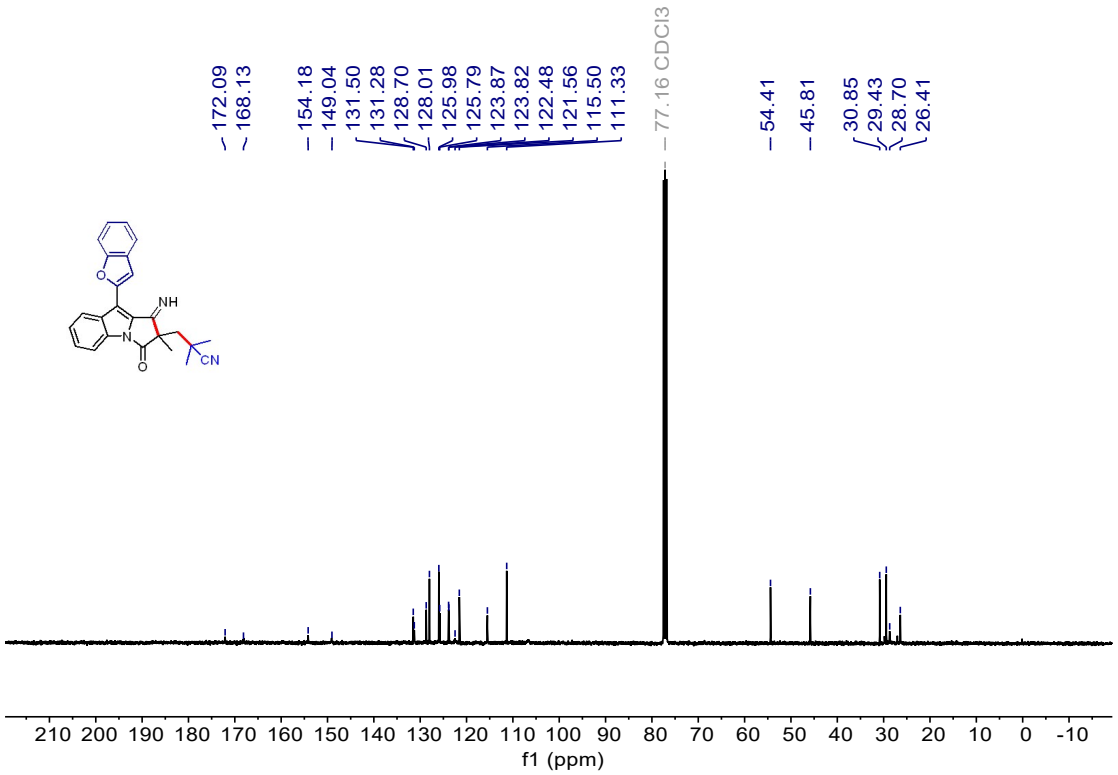
^{1}H and ^{13}C NMR Spectra of 3s



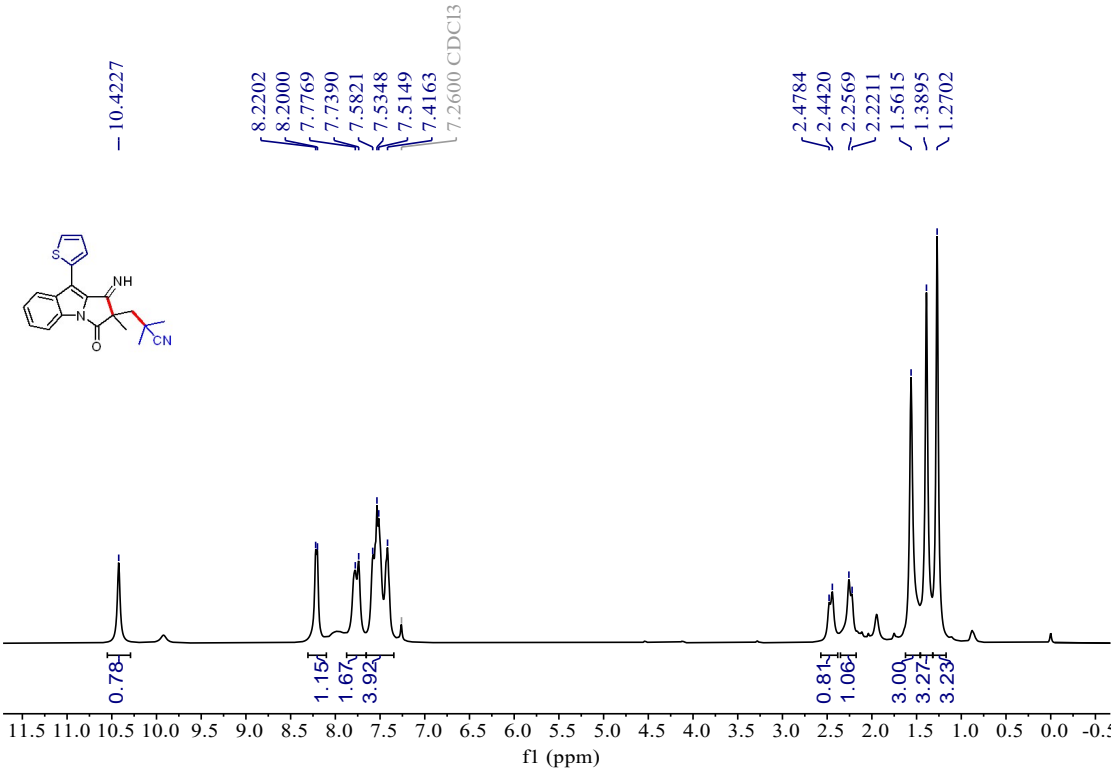


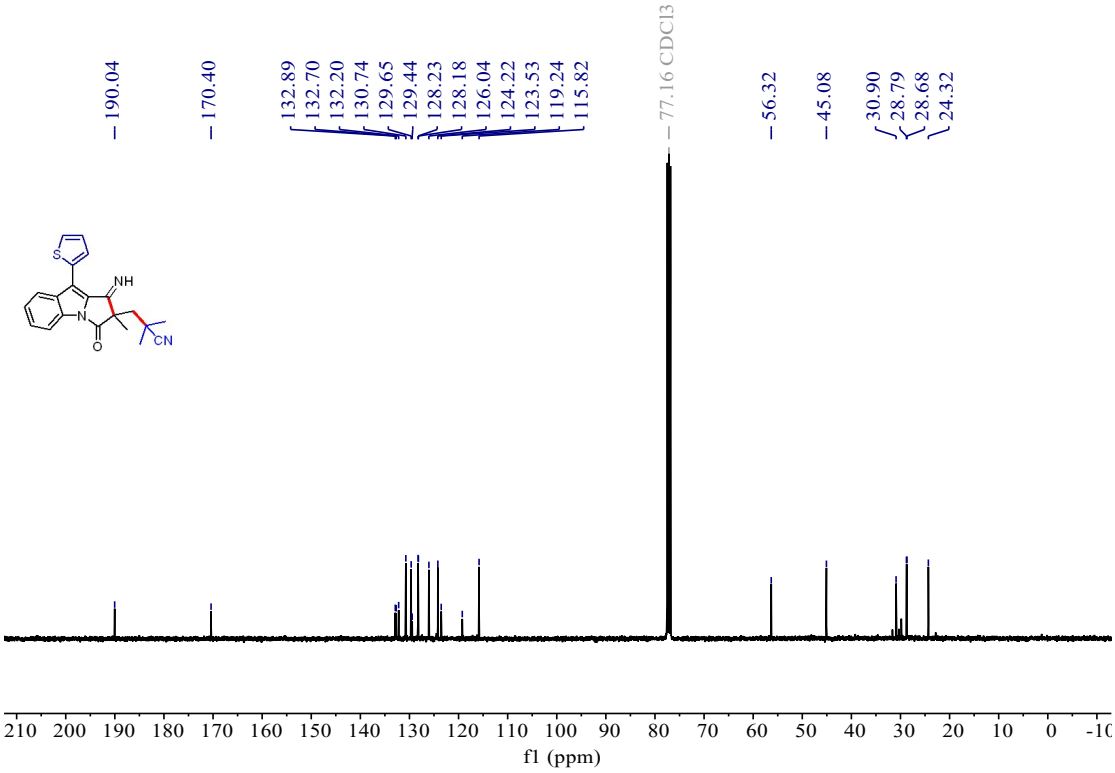
^{1}H and ^{13}C NMR Spectra of 3t



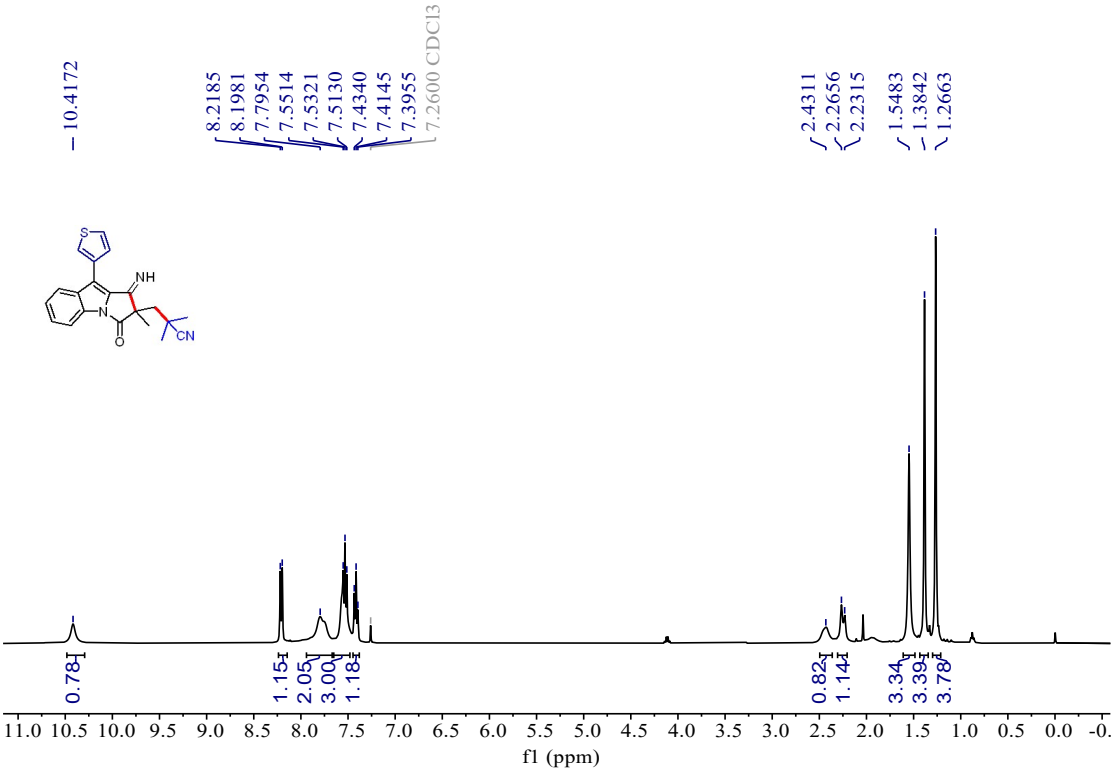


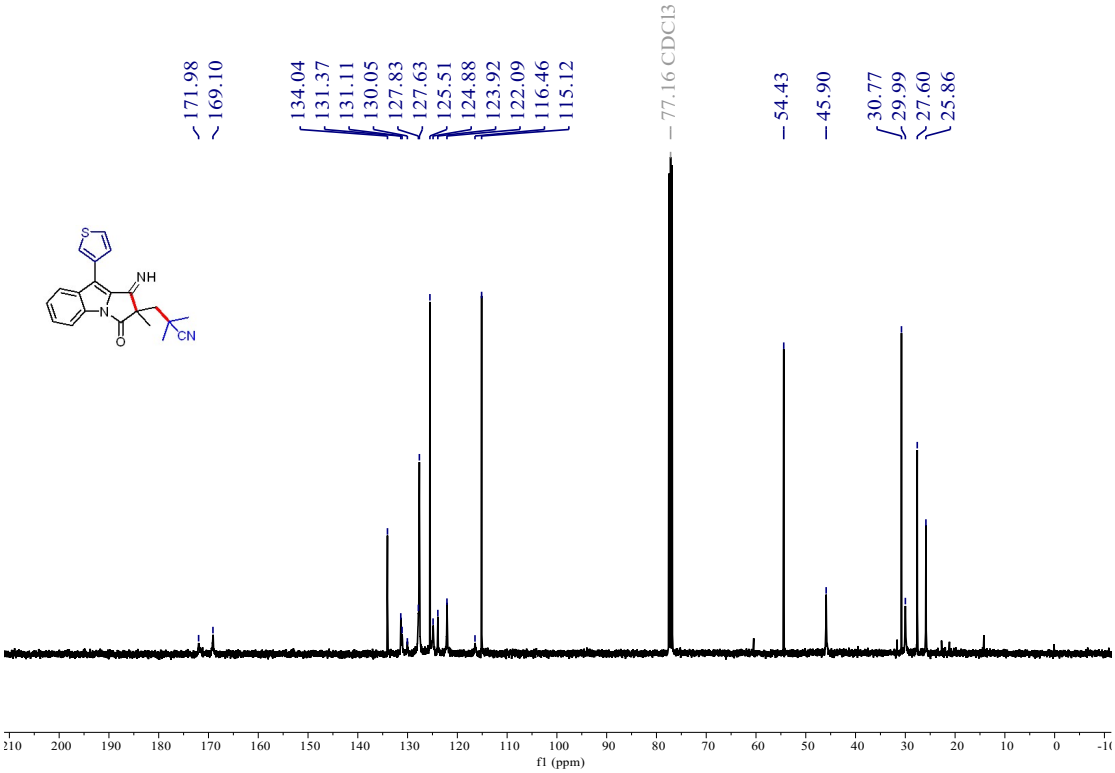
^{1}H and ^{13}C NMR Spectra of 3u



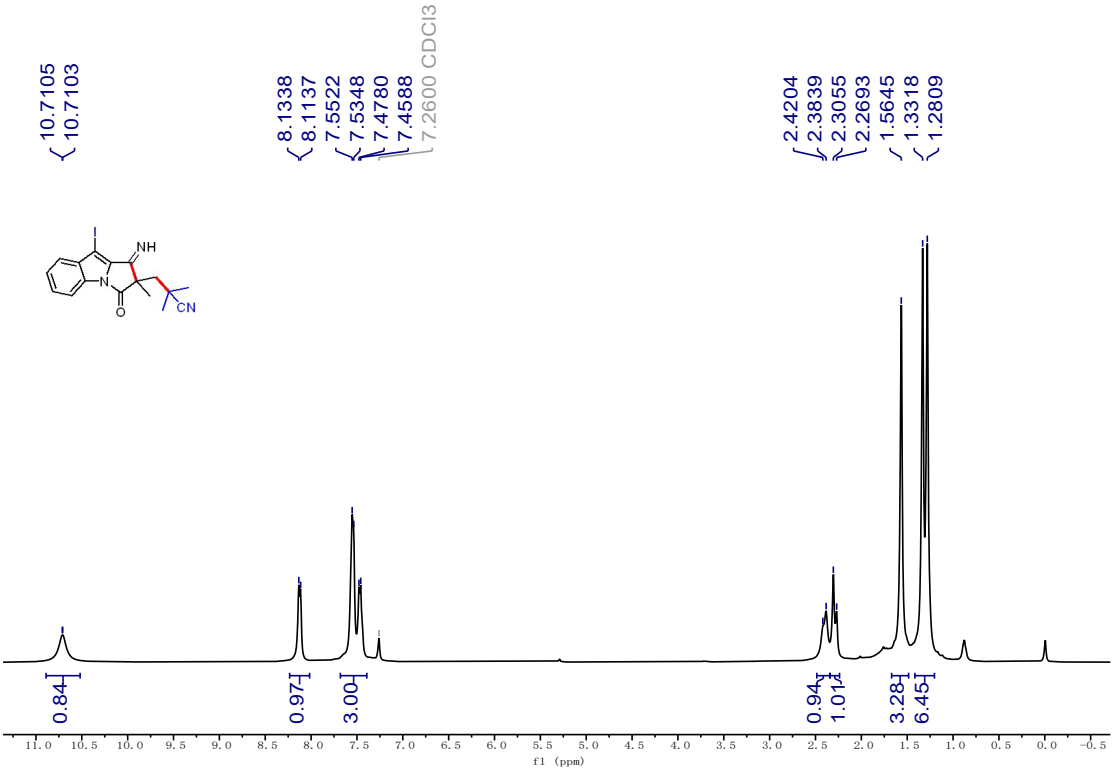


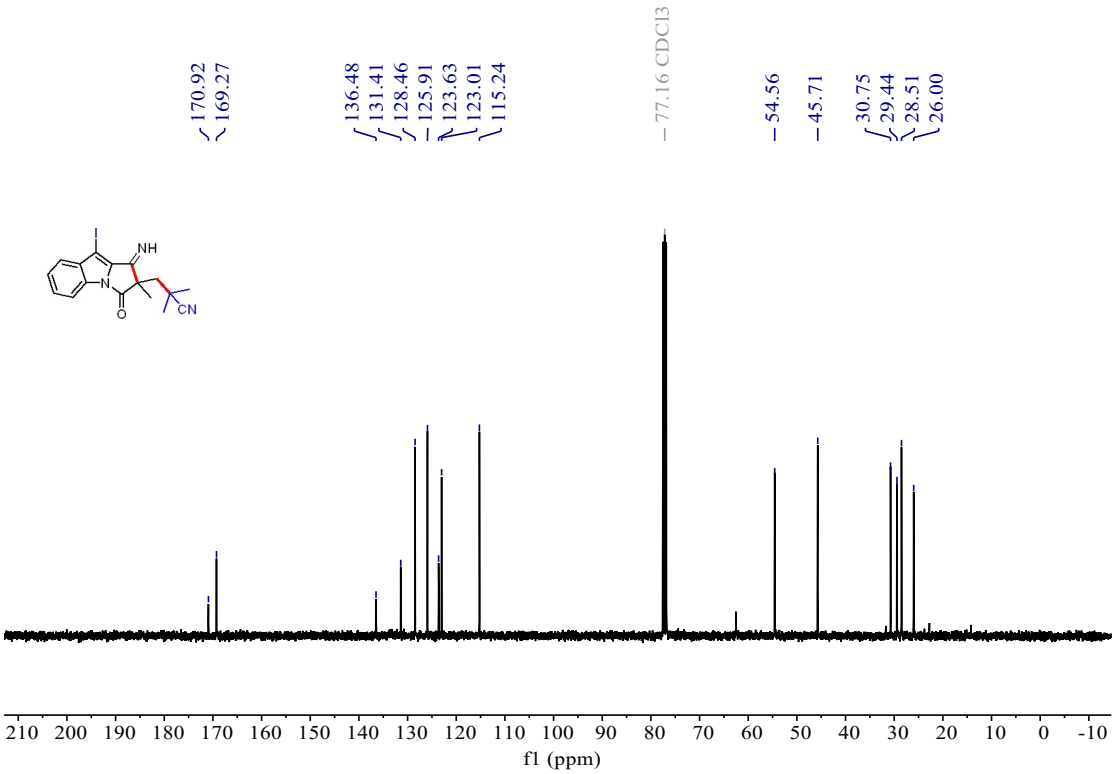
^{1}H and ^{13}C NMR Spectra of 3v



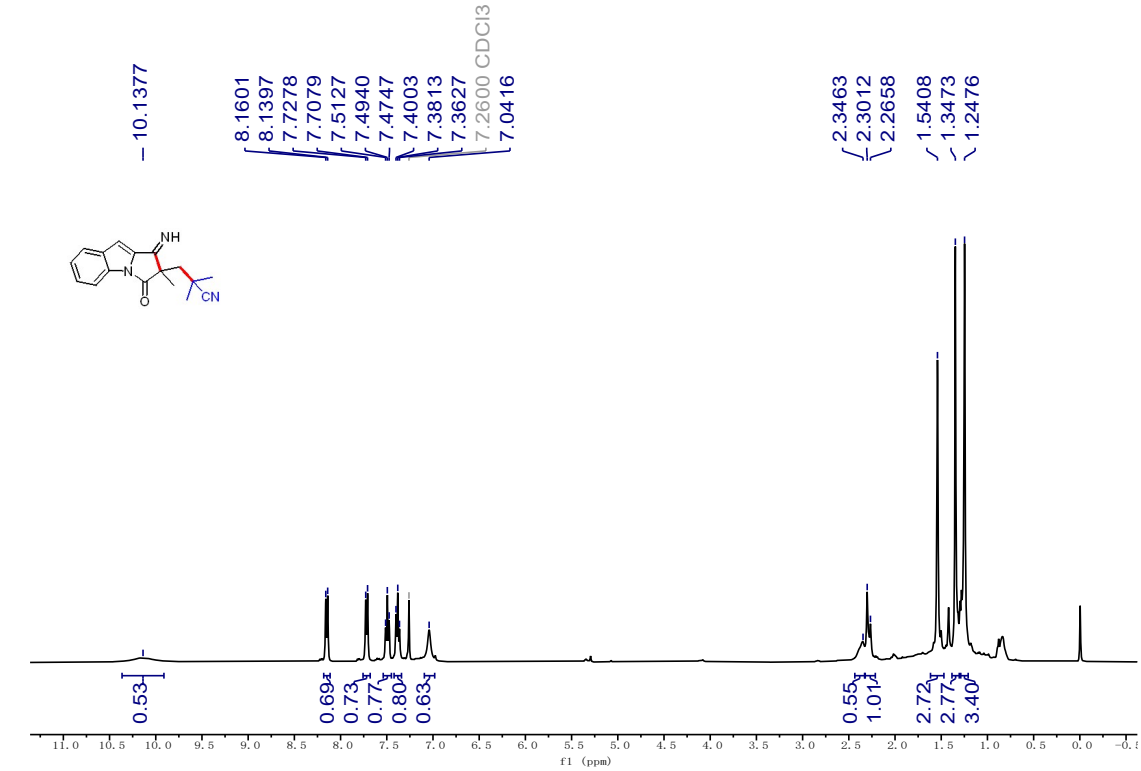


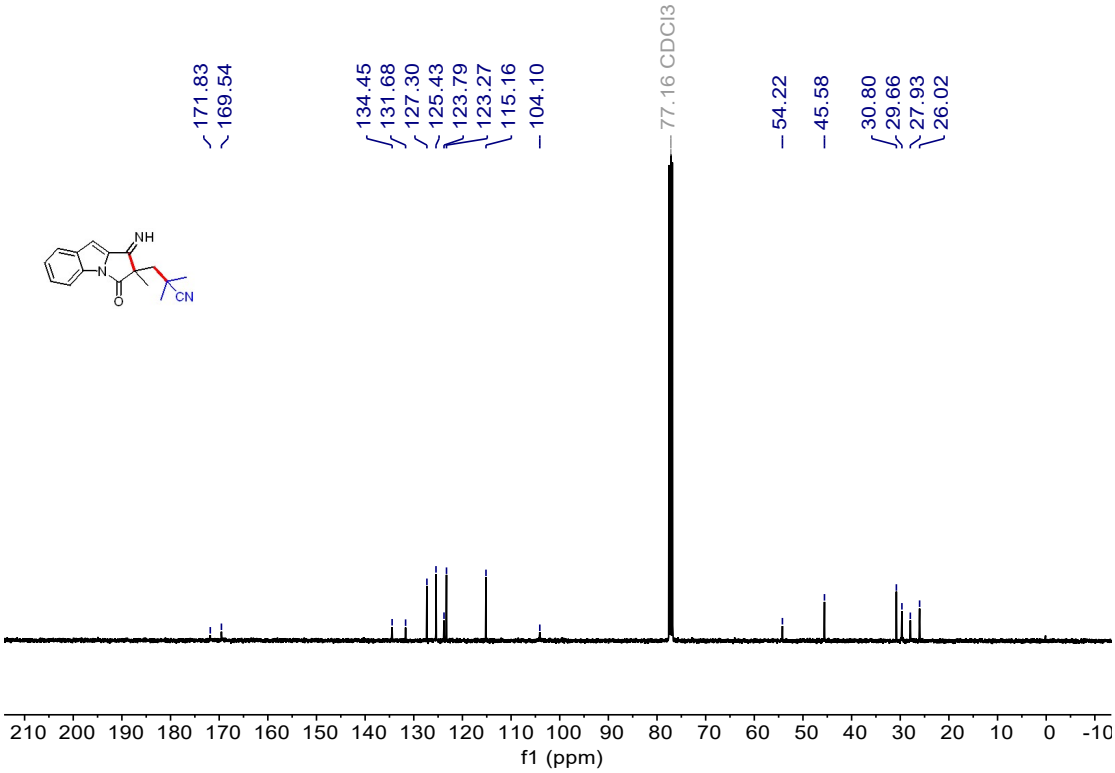
^{1}H and ^{13}C NMR Spectra of 3w



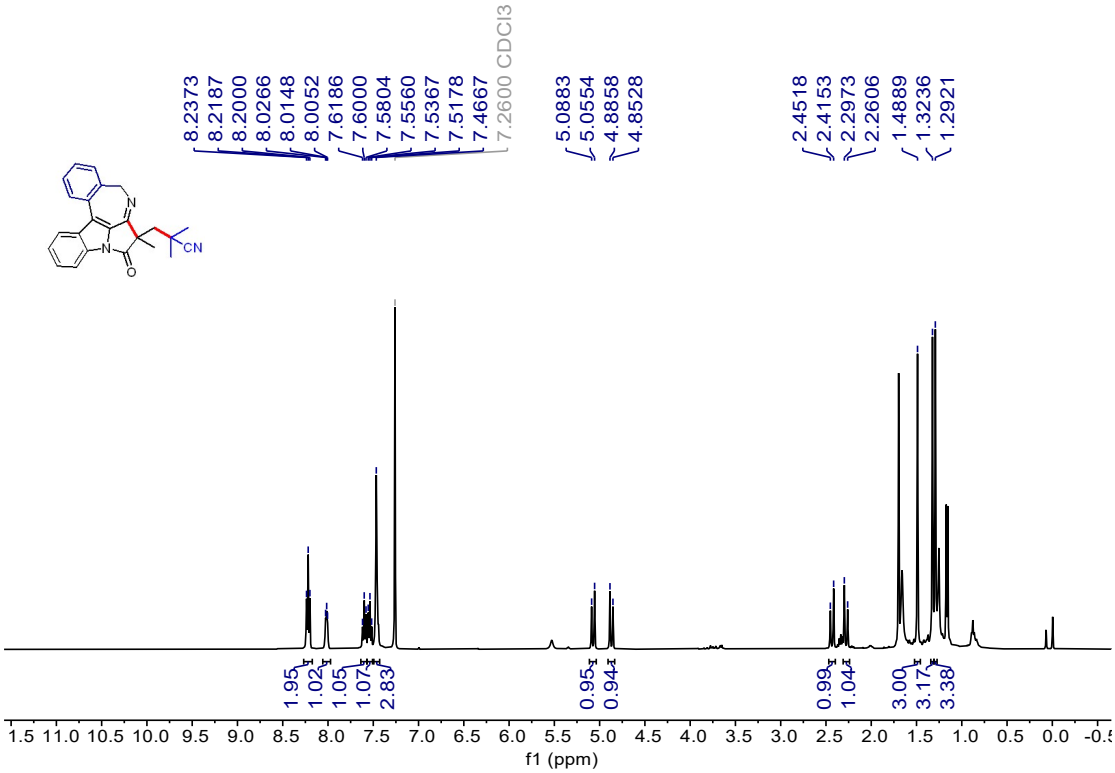


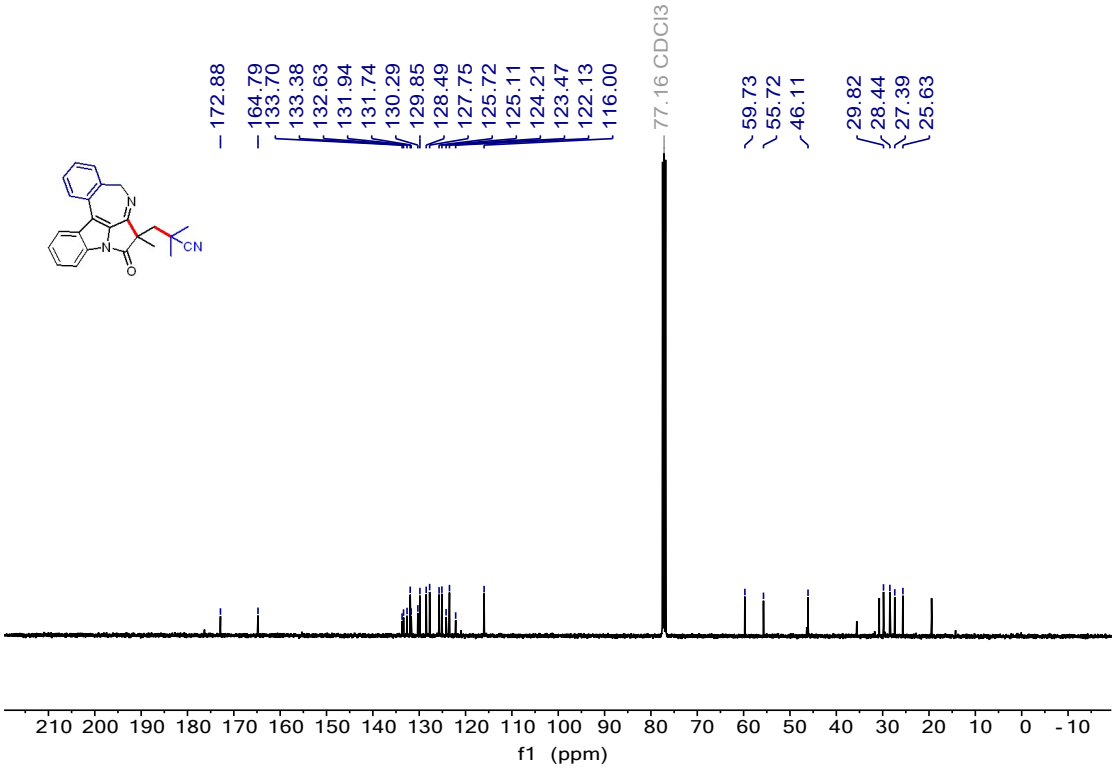
^{1}H and ^{13}C NMR Spectra of 3x



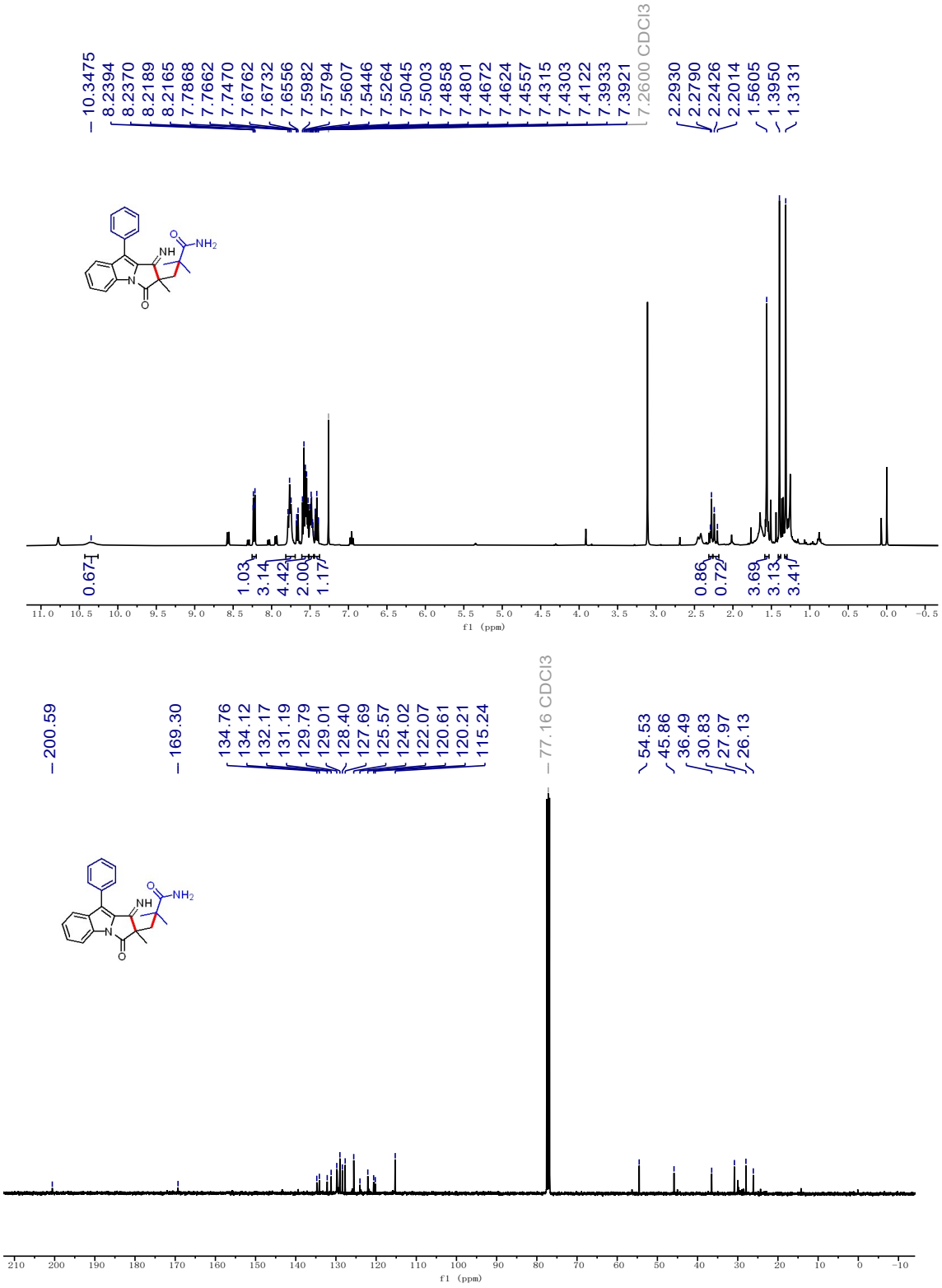


^{1}H and ^{13}C NMR Spectra of 3A





^{1}H and ^{13}C NMR Spectra of 4



G. References

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2 R. Wang and W. Bao, *RSC Advances*, 2015, **5**, 57469-57471.