

Supporting Information

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

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Contents

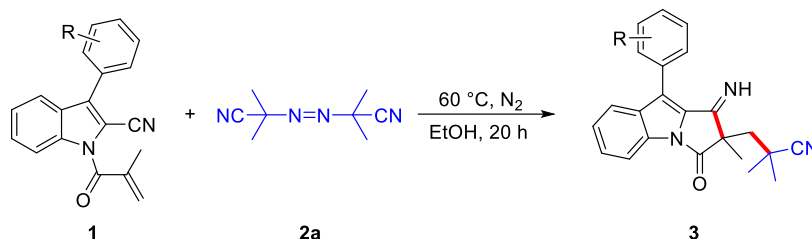
A. General information	S2
B. Catalytic results	S2
C. Scale-up reaction.	S16
D. Mechanistic studies	S16
E. Crystal structure	S18
F. NMR spectra.....	S20
G. References	S49

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. ^1H 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 ($^{\circ}\text{C}$) 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 reports¹. Column chromatography was performed on silica gel (300-400 mesh) using petroleum ether (PE)/ethyl acetate (EA).

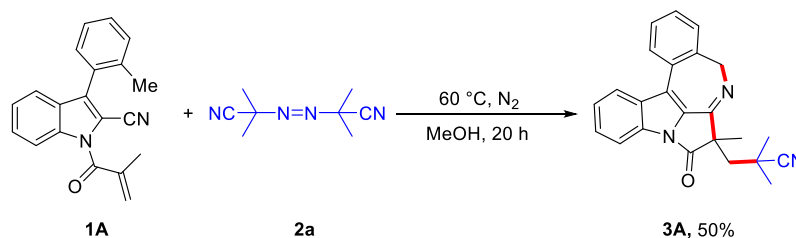
B. Catalytic results:

(a) General procedure for synthesis of **3**.



To a Schlenk tube equipped with a magnetic stirring bar were added 1-methacryloyl-3-phenyl-1H-indole-2-carbonitrile **1** (0.2 mmol), AIBN **2a** (2.5 equiv) and absolute ethanol (2 mL). The mixture was stirred at 60 $^{\circ}\text{C}$ 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 through column chromatography on silica gel using PE/EA (8:1) as eluent to obtain product **3**.

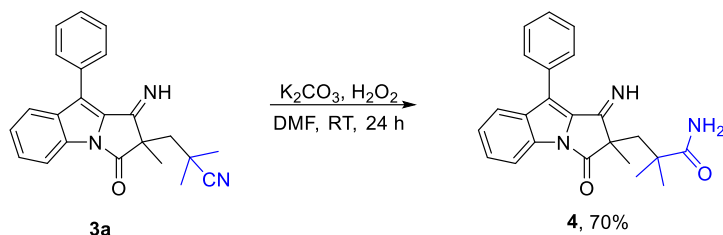
(b) General procedure for synthesis of **3A**.



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

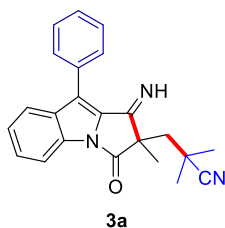
was removed under reduced pressure and the crude reaction mixture was directly purified through column chromatography on silica gel using PE/EA (8:1) as eluent to obtain product **3A**.

(c) General procedure for synthesis of **4².**



To a Schlenk tube equipped with a magnetic stirring bar were added 3-(1-imino-2-methyl-3-oxo-9-phenyl-2,3-dihydro-1H-pyrrolo[1,2-a]indol-2-yl)-2,2-dimethylpropanenitrile **1A** (0.2 mmol), K₂CO₃ (0.2 mmol, 2.5 equiv.) and 30% H₂O₂ (2 mmol 10 equiv.) and *N,N*-Dimethylformamide (2 mL). The mixture was stirred at room temperature for 24 h under N₂. The solvent was removed under reduced pressure and the crude reaction mixture was directly purified through column chromatography on silica gel using PE/EA (4:1) as eluent to obtain product **4**.

(d) Characterization Data



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

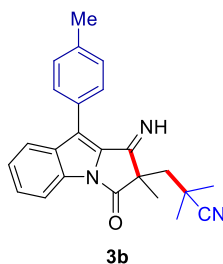
Yellow solid 85% (60.4 mg), mp: 128-129 °C. *R*_f = 0.6 (PE:EA = 2:1).

¹H NMR (400 MHz, CDCl₃) 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.

¹³C NMR (100 MHz, CDCl₃) 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 C₂₃H₂₁N₃ONa⁺: 378.1578, found: 378.1577.



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

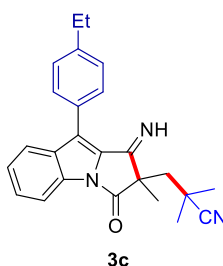
White solid 78% (57.6 mg), mp: 106-107 °C. R_f = 0.5 (PE:EA = 2:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}^+$: 370.1914, found: 370.1915.



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

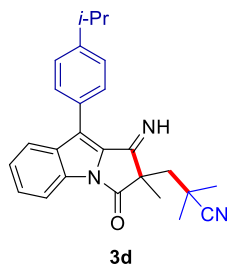
White solid 75% (57.5 mg), mp: 108-109 °C. R_f = 0.6 (PE:EA = 2:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{25}\text{H}_{26}\text{N}_3\text{O}^+$: 384.2071, found: 384.2072.



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

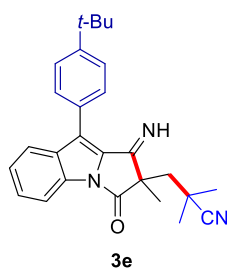
White solid 67% (53.3 mg), mp: 69-70 °C. R_f = 0.6 (PE:EA = 2:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{26}\text{H}_{28}\text{N}_3\text{O}^+$: 398.2227, found: 398.2236.



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

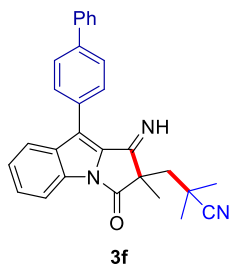
White solid 65% (53.5 mg), mp: 55-56 °C. R_f = 0.6 (PE:EA = 2:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{27}\text{H}_{28}\text{N}_3\text{O}^+$: 412.2384, found: 412.2382.



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

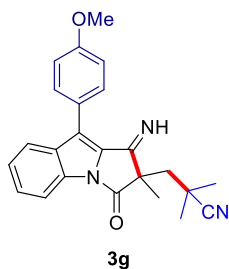
White solid 75% (64.7 mg), mp: 188-189 °C. R_f = 0.8 (PE:EA = 2:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{18}\text{NO}_3^+$: 432.2071, found: 432.2072.



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

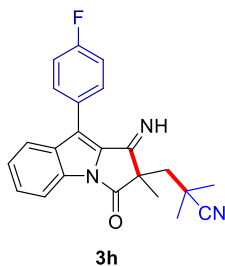
White solid 87% (67.1 mg), mp: 152-153 °C. R_f = 0.8 (PE:EA = 1:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}_2^+$: 386.1863, found: 386.1866.



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

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

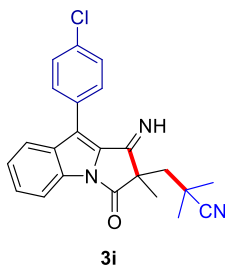
^1H NMR (400 MHz, CDCl_3) δ 10.29 (s, 1H), 8.25 (d, J = 8.2 Hz, 1H), 7.90 – 7.67 (m, 3H), 7.57 (t, J = 7.7 Hz, 1H), 7.44 (t, J = 7.7 Hz, 1H), 7.30 – 7.26 (m, 2H), 2.52 – 2.36 (m, 1H), 2.27 (d, J = 14.5 Hz, 1H), 1.57 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H) ppm.

^{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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{21}\text{FN}_3\text{O}^+$: 374.1663, found: 374.1665.



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

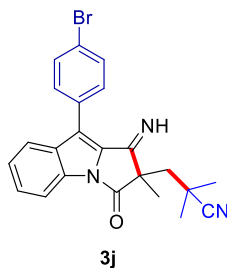
White solid 83% (64.7 mg), mp: 112-113 °C. R_f = 0.7 (PE:EA = 2:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{21}\text{ClN}_3\text{O}^+$: 390.1368, found: 390.1371.



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

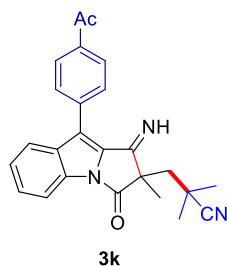
White solid 80% (69.5 mg), mp: 120-121 °C. R_f = 0.7 (PE:EA = 2:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{21}\text{BrN}_3\text{O}^+$: 434.0863, found: 434.0866



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

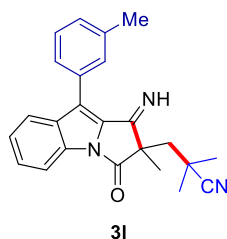
White solid 90% (71.6 mg), mp: 166-167 °C. R_f = 0.6 (PE:EA = 1:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{25}\text{H}_{24}\text{N}_3\text{O}_2^+$: 398.1863, found: 398.1867.



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

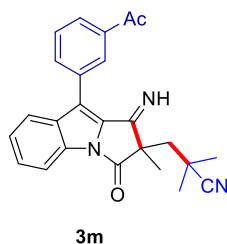
White solid 71% (52.5 mg), mp: 134-135 °C. R_f = 0.7 (PE:EA = 2:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{24}\text{N}_3\text{O}^+$: 370.1914, found: 370.1918.



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

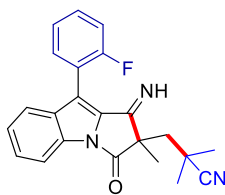
White solid 82% (65.2 mg), mp: 84-85 °C. R_f = 0.7 (PE:EA = 1:1).

^1H 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: $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{25}\text{H}_{24}\text{N}_3\text{O}_2^+$: 398.1863, found: 398.1866.



3n

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

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

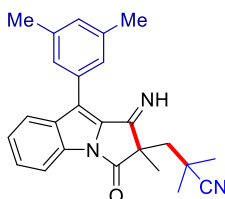
^1H NMR (400 MHz, CDCl_3) δ 11.43 (s, 1H), 9.59 (d, J = 8.2 Hz, 1H), 9.09 (s, 1H), 9.01 (d, J = 8.1 Hz, 1H), 8.94 – 8.88 (m, 1H), 8.88 – 8.82 (m, 1H), 8.79 – 8.74 (m, 1H), 8.73 – 8.64 (m, 2H), 3.87 – 3.74 (m, 1H), 3.69 (d, J = 7.0 Hz, 1H), 3.03 (s, 3H), 2.93 (s, 3H), 2.68 (s, 3H) ppm.

^{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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{21}\text{FN}_3\text{O}^+$: 374.1663, found: 374.1667.



3o

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

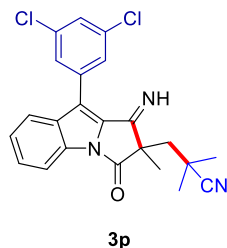
White solid 80% (61.4 mg), mp: 151-152 °C. R_f = 0.8 (PE:EA = 2:1).

^1H 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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{25}\text{H}_{26}\text{N}_3\text{O}^+$: 384.2071, found: 384.2072.



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

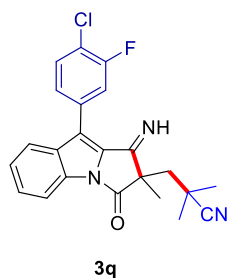
White solid 73% (61.9 mg), mp: 226-227 °C. R_f = 0.8 (PE:EA = 2:1).

^1H 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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{20}\text{Cl}_2\text{N}_3\text{O}^+$: 424.0978, found: 424.0987.



3-(9-(4-chloro-3-fluorophenyl)-1-imino-2-methyl-3-oxo-2,3-dihydro-1H-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).

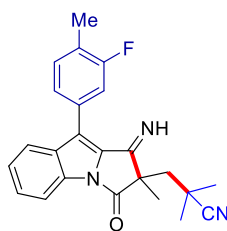
^1H NMR (400 MHz, CDCl_3) δ 10.30 (s, 1H), 8.23 (d, J = 8.2 Hz, 1H), 7.74 (d, J = 8.2 Hz, 1H), 7.58 (dt, J = 14.8, 7.8 Hz, 4H), 7.44 (t, J = 7.7 Hz, 1H), 7.26 (d, J = 1.7 Hz, 0H), 2.53 – 2.32 (m, 1H), 2.25 (d, J = 14.4 Hz, 1H), 1.55 (s, 3H), 1.39 (s, 3H), 1.29 (s, 3H) ppm.

^{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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{20}\text{ClFN}_3\text{O}^+$: 408.1274, found: 408.1278.



3r

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

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

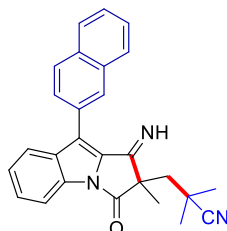
^1H NMR (400 MHz, CDCl_3) δ 10.35 (s, 1H), 8.22 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.49 – 7.35 (m, 4H), 2.38 (d, J = 2.0 Hz, 4H), 2.26 (d, J = 14.5 Hz, 1H), 1.55 (s, 3H), 1.39 (s, 3H), 1.30 (s, 3H) ppm.

^{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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{23}\text{FN}_3\text{O}^+$: 388.1820, found: 388.1824.



3s

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

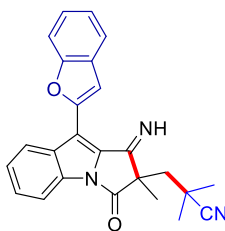
White solid 78% (63.4 mg), mp: 105-106 °C. R_f = 0.5 (PE:EA = 2:1).

^1H 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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{27}\text{H}_{24}\text{N}_3\text{O}^+$: 406.1914, found: 406.1912.



3t

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

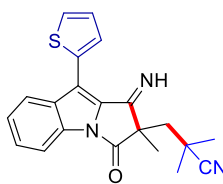
White solid 60% (47.5 mg), mp : 105-106 °C. R_f = 0.6 (PE:EA = 2:1).

^1H 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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{25}\text{H}_{22}\text{N}_3\text{O}_2^+$: 396.1707, found: 396.1711.



3u

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

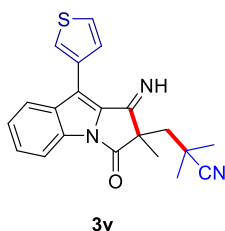
Yellow solid 65% (47.0 mg), mp: 155-156 °C. R_f = 0.6 (PE:EA = 2:1).

^1H 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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{20}\text{N}_3\text{OS}^+$: 362.1322, found: 362.1322.



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

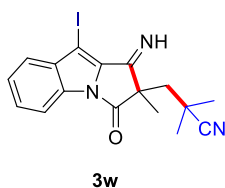
Yellow solid 61% (44.1 mg), mp: 154-155 °C. R_f = 0.6 (PE:EA = 2:1).

^1H 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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{21}\text{H}_{20}\text{N}_3\text{OS}^+$: 362.1322, found: 362.1322.



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

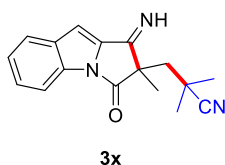
White solid 95% (77.0 mg), mp: 129-130 °C. R_f = 0.6 (PE:EA = 2:1).

^1H 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 $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{17}\text{H}_{16}\text{IN}_3\text{ONa}^+$: 428.0230, found: 428.0232.



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

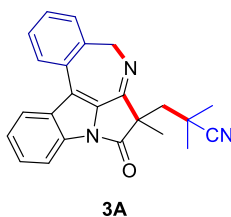
Red solid 70% (39.1 mg), mp: 120-121 °C. $R_f = 0.6$ (PE:EA = 1:1).

^1H 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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}^+$: 280.1445, found: 280.1442.



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

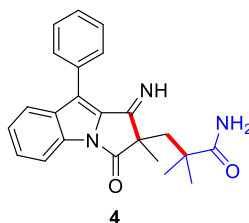
White solid 50% (36.8 mg), mp: 118-119 °C. $R_f = 0.8$ (PE:EA = 1:1).

^1H 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 $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{22}\text{N}_3\text{O}^+$: 368.1758, found: 368.1759.



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

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

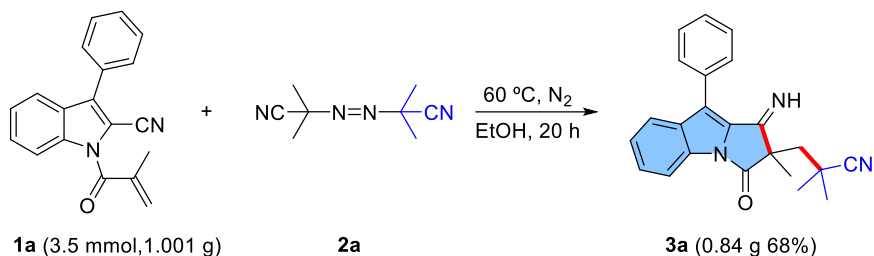
^1H NMR (400 MHz, CDCl_3) δ 10.35 (s, 1H), 8.23 (dd, $J = 8.2, 1.0$ Hz, 1H), 7.80 – 7.73 (m, 3H), 7.60 – 7.53 (m, 4H), 7.50 – 7.46 (m, 2H), 7.43 – 7.39 (m, 1H), 2.29 (d, $J = 5.6$ Hz, 1H), 2.22 (d, $J = 16.5$ Hz, 1H), 1.56 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H) ppm.

¹³C NMR (100 MHz, CDCl₃) 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 C₂₃H₂₅N₃O₂⁺: 374.1863, found: 374.1862.

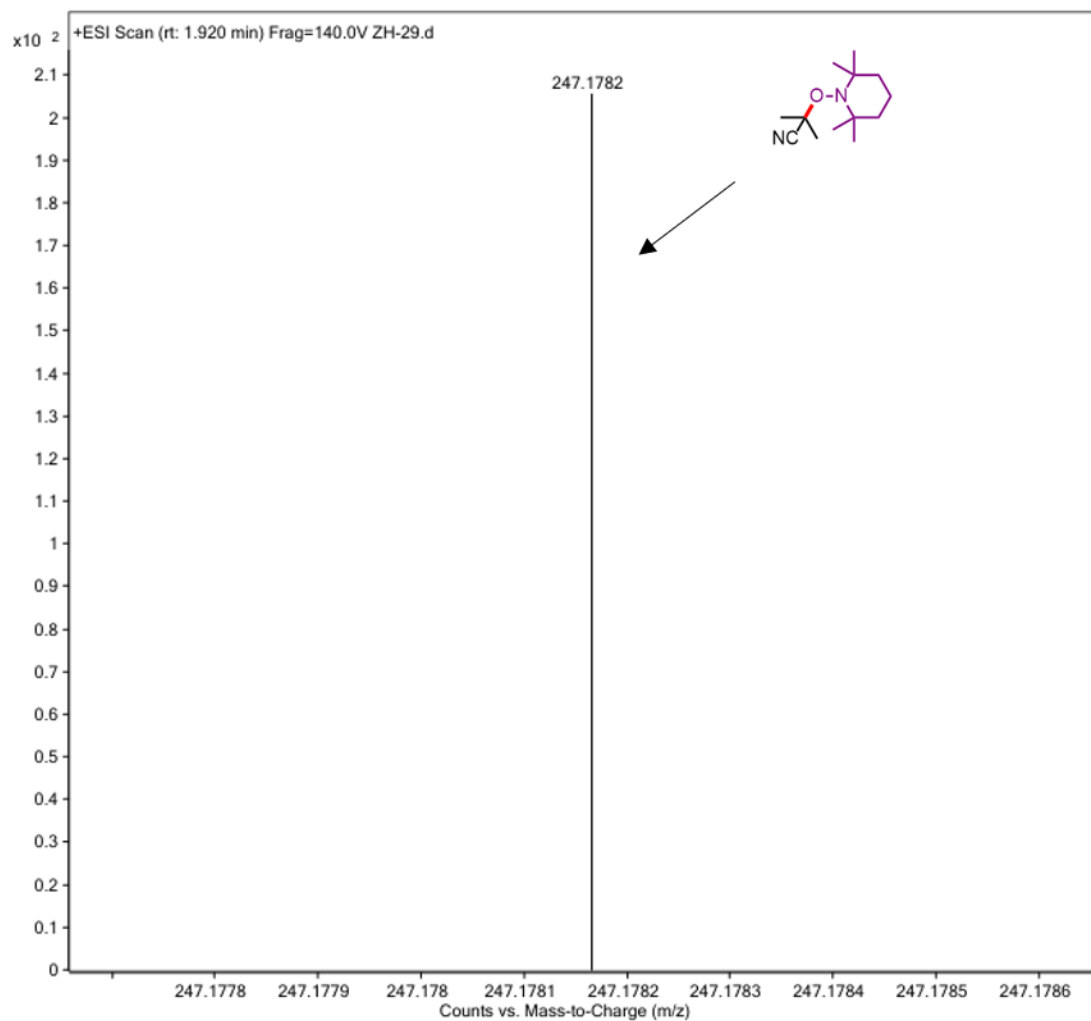
C. Scale-up reaction.



1-methacryloyl-3-phenyl-1H-indole-2-carbonitrile **1a** (1 mmol), AIBN **2a** (2.5 mmol) and absolute ethanol (20 mL) were charged into a pressure tube. The reaction mixture was stirred at N₂ under 60 °C 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-1H-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 ethanol (2 mL) were successively added. Then, the tube was stirred at N₂ under 60 °C 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 C₁₃H₂₄N₂ONa ([M+Na]⁺): 247.1782. found: 247.1782. Calculated for C₁₈H₁₇N ([M+Na]⁺): 270.1254. found: 270.1264.



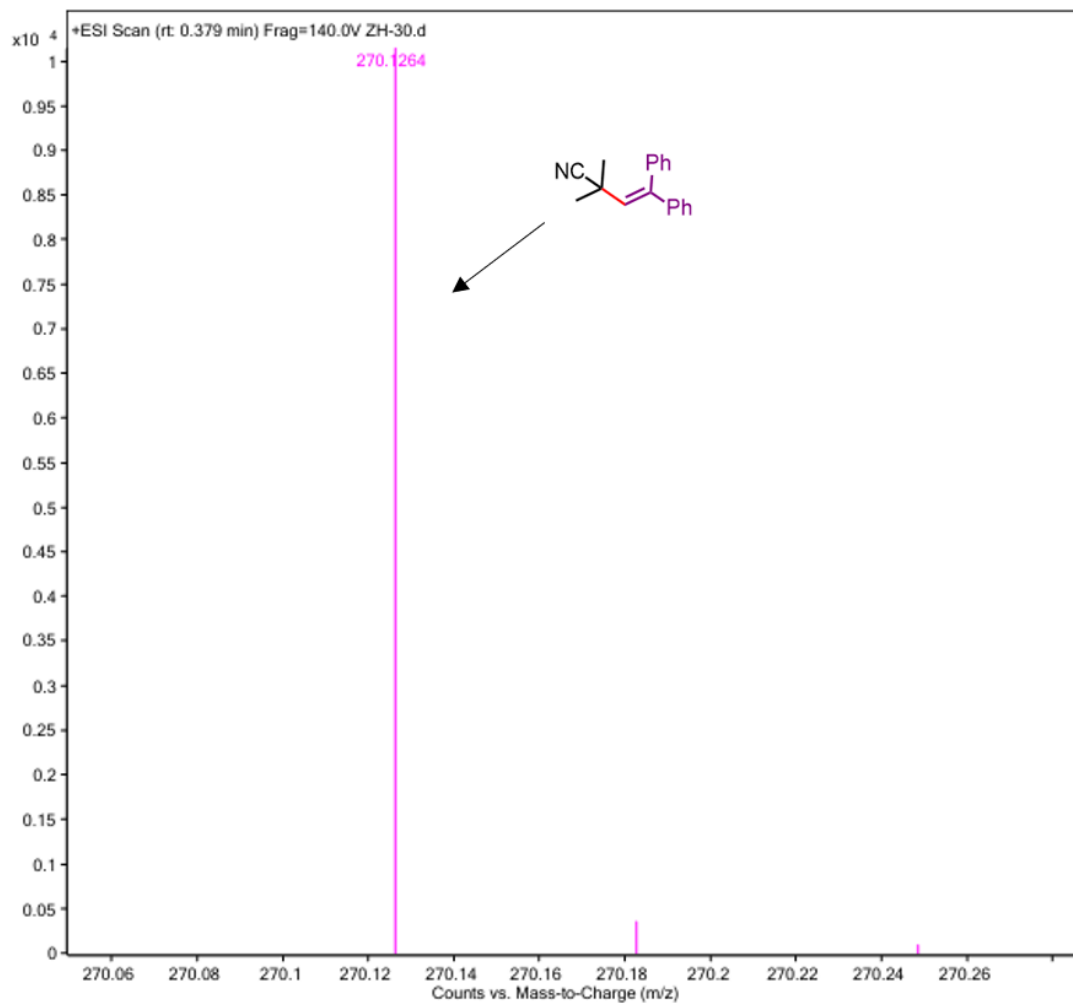


Figure S1. Copy of HRMS Spectrum of TEMPO/DPE-Br adduct

E. Crystal structure.

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

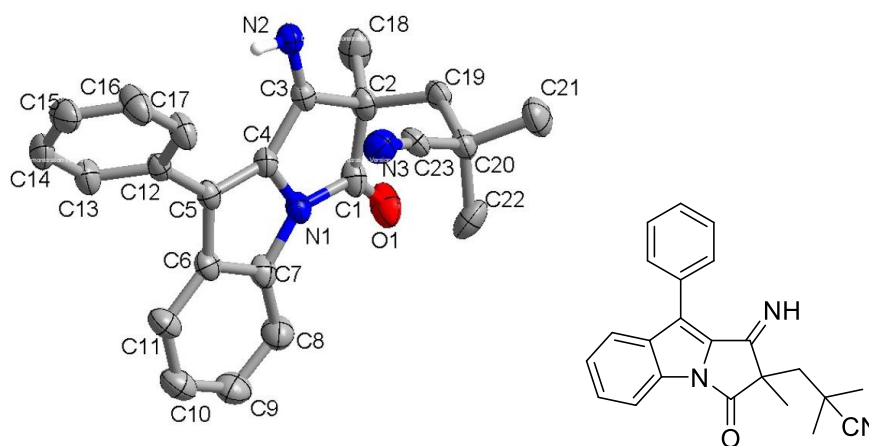


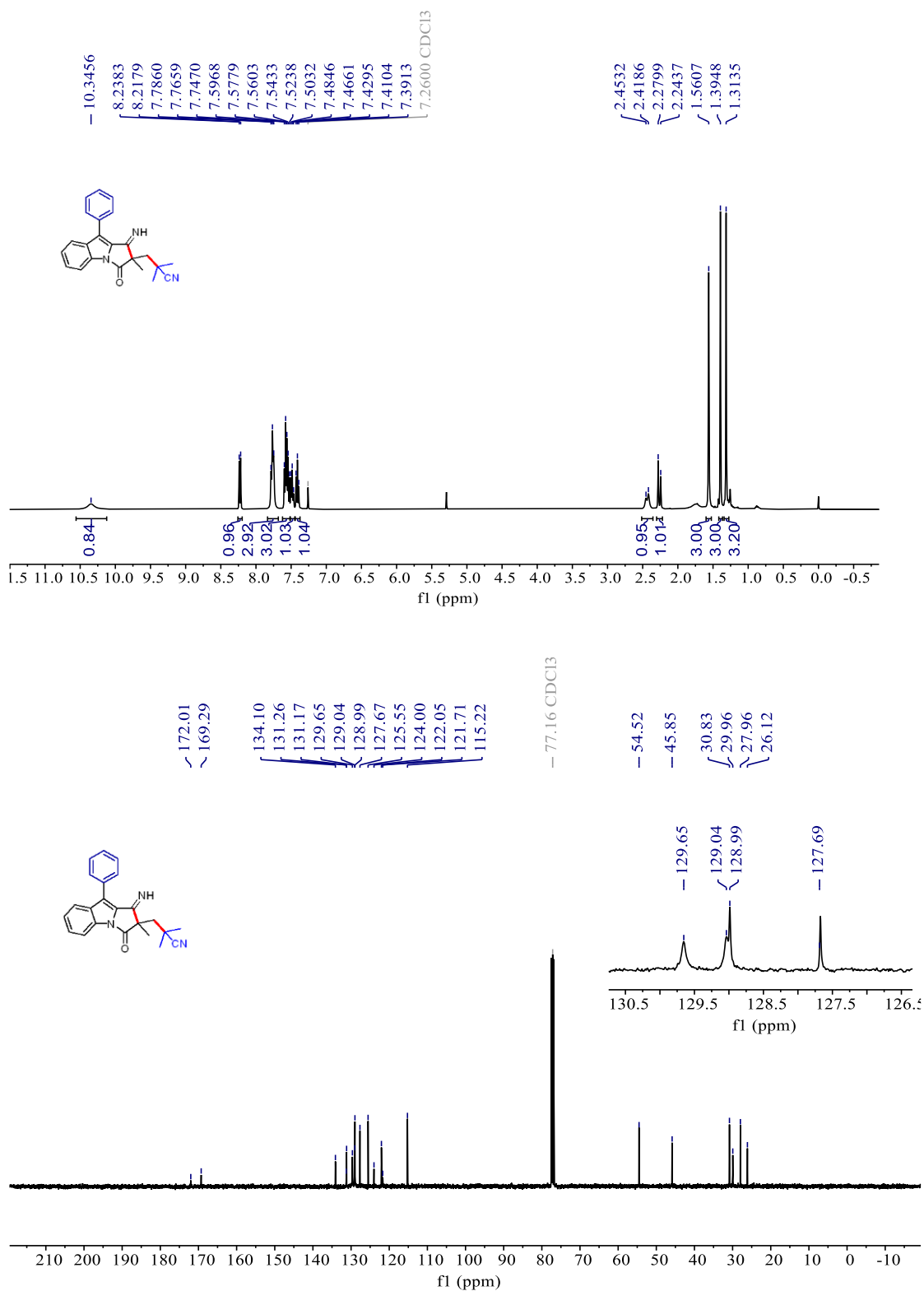
Figure S2 Crystal structure of **3a** with thermal ellipsoids at 50% probability.

Table 1 Crystal data and structure refinement for 3a

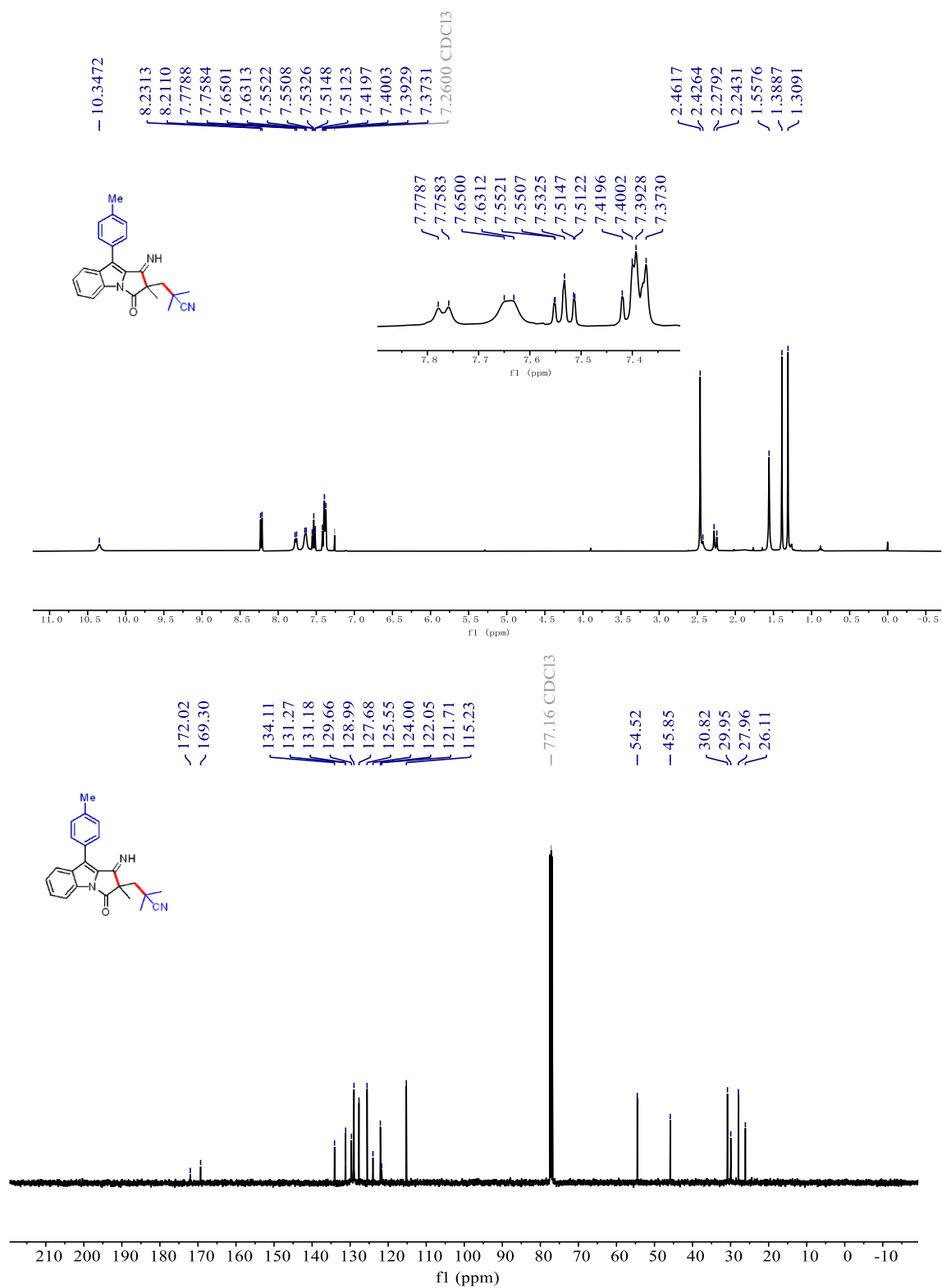
Identification code	3a
Empirical formula	C ₂₃ H ₂₁ N ₃ O
Formula weight	355.43
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	22.050(2)
b/Å	8.2245(13)
c/Å	21.735(3)
α /°	90
β /°	100.182(11)
γ /°	90
Volume/Å ³	3879.4(9)
Z	8
ρ_{calc} /cm ³	1.217
μ /mm ⁻¹	0.076
F(000)	1504.0
Crystal size/mm ³	0.17 × 0.12 × 0.1
Radiation	MoK α (λ = 0.71073)
2 Θ 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 [$I \geq 2\sigma(I)$]	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:

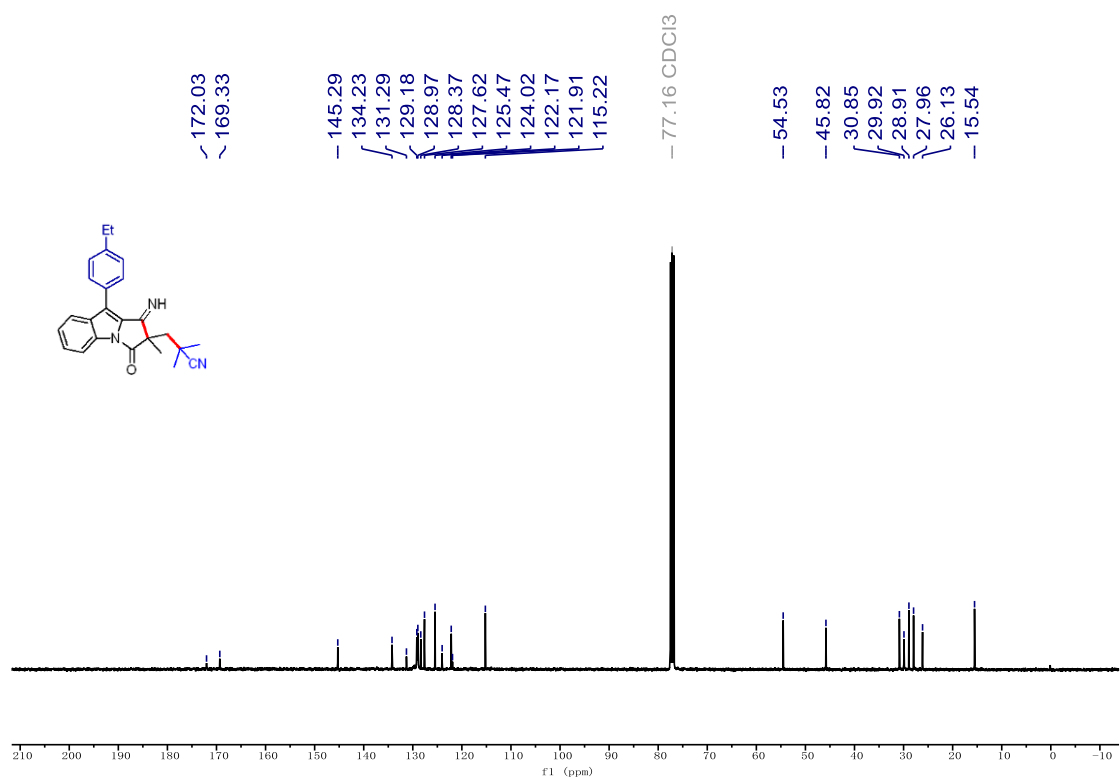
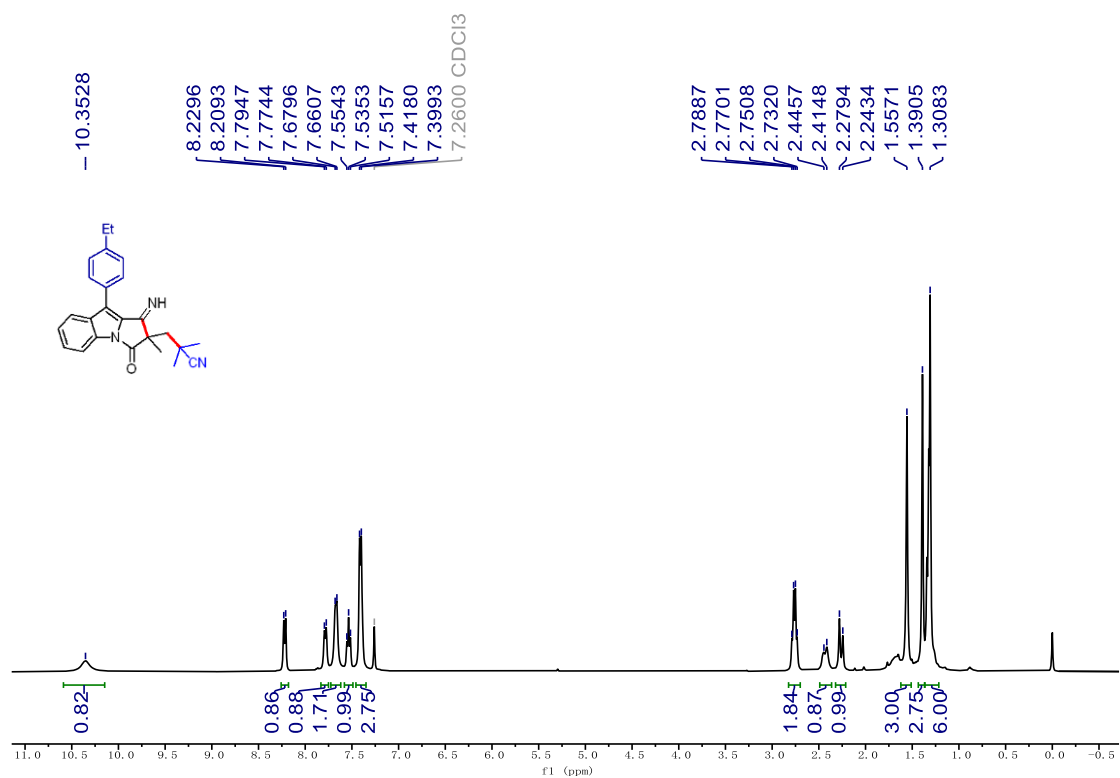
¹H and ¹³C NMR Spectra of compound 3a



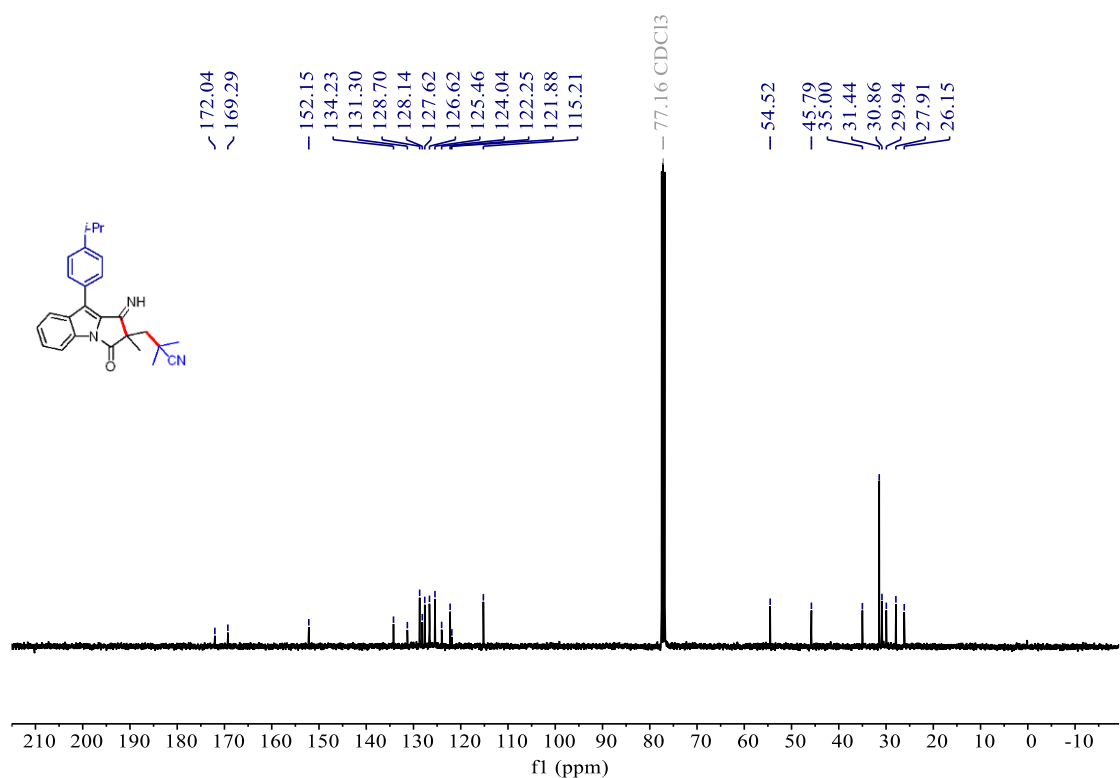
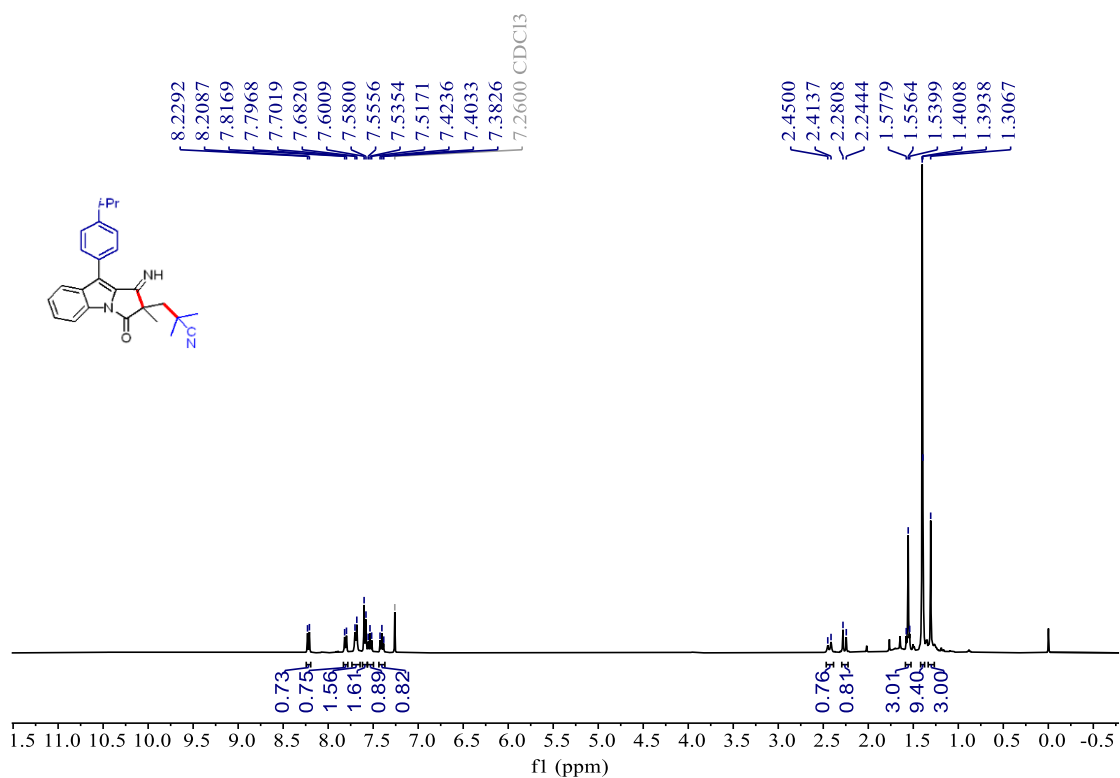
^1H and ^{13}C NMR Spectra of compound 3b



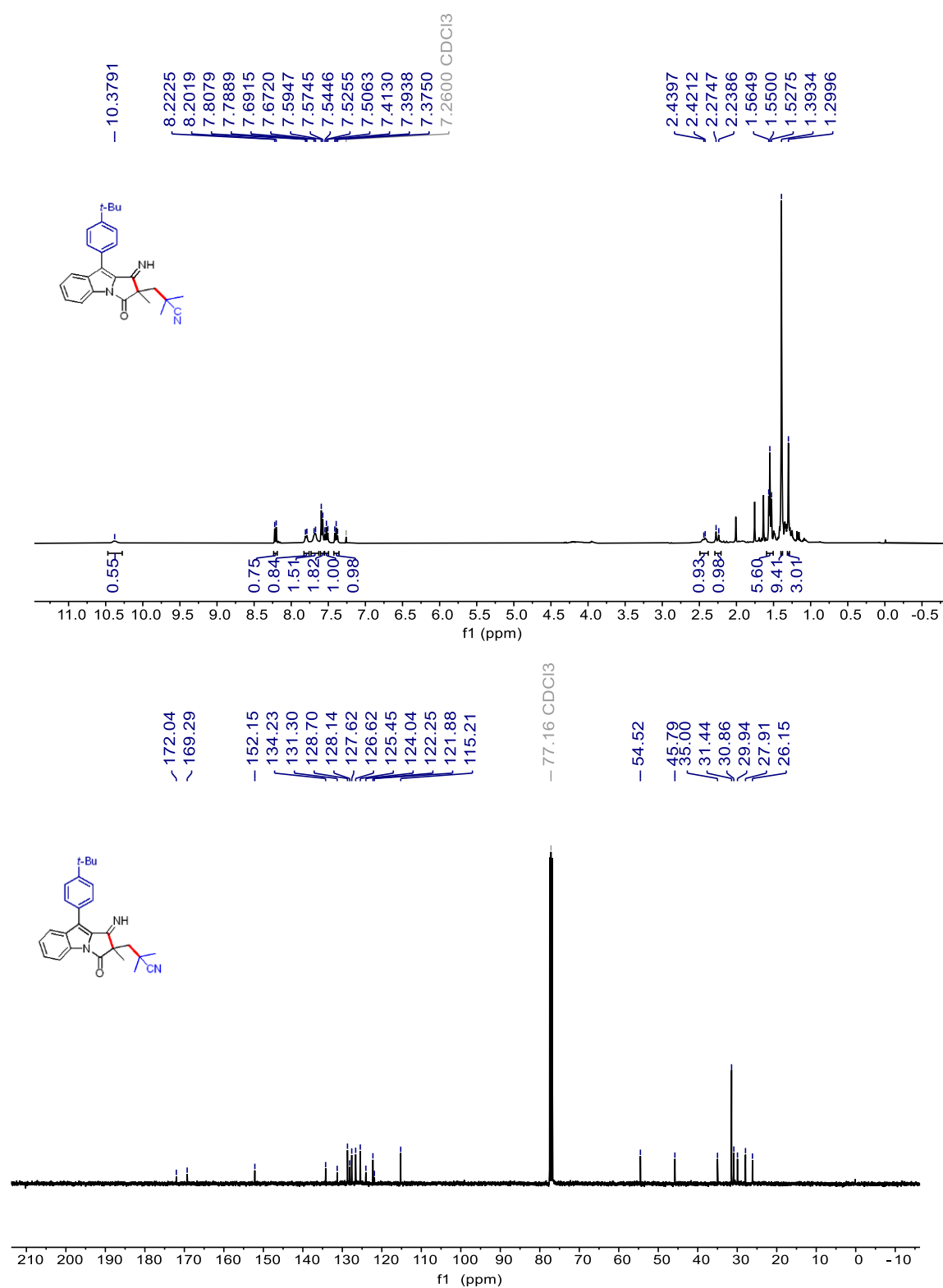
¹H and ¹³C NMR Spectra of 3c



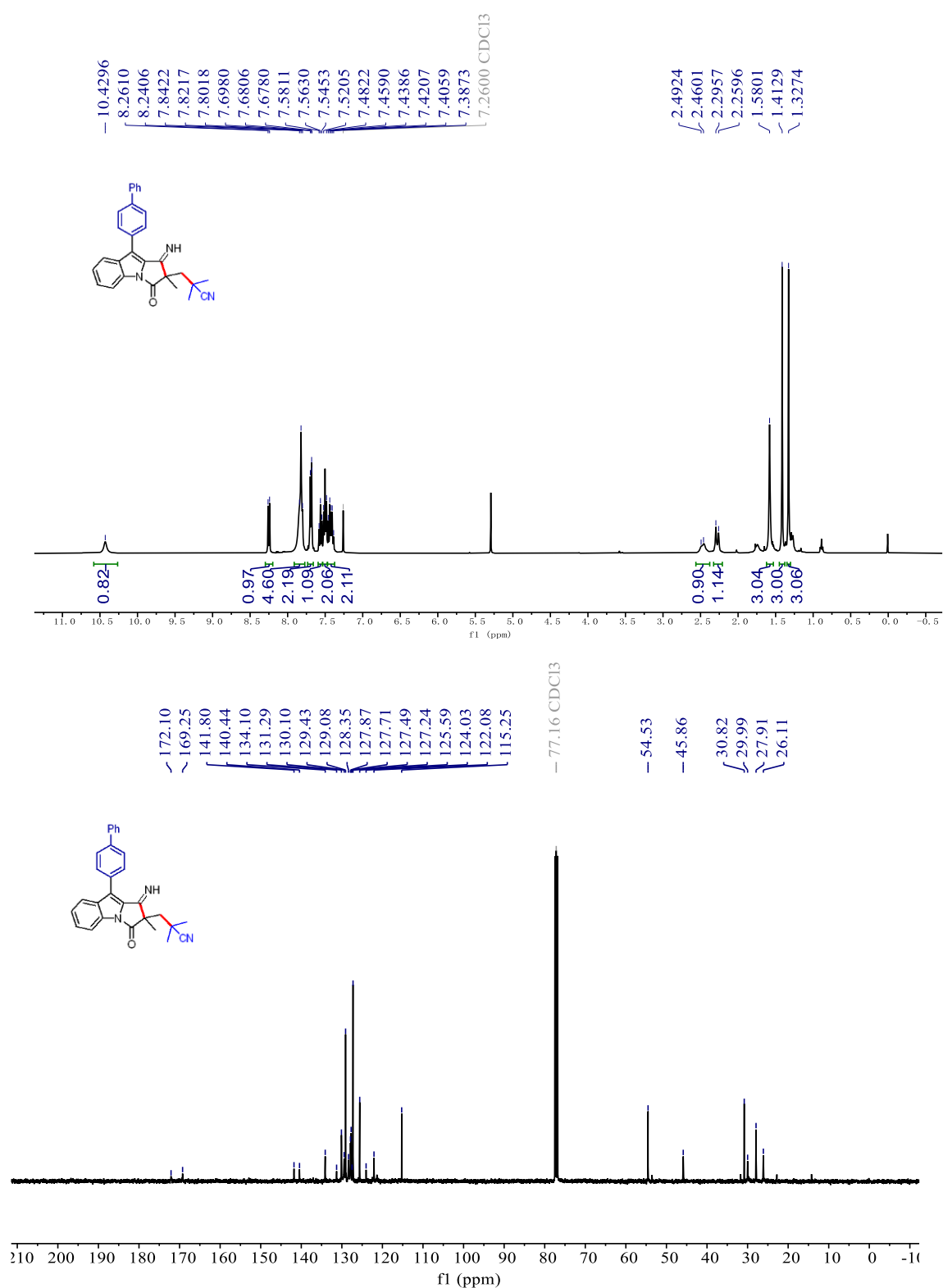
¹H and ¹³C NMR Spectra of 3d



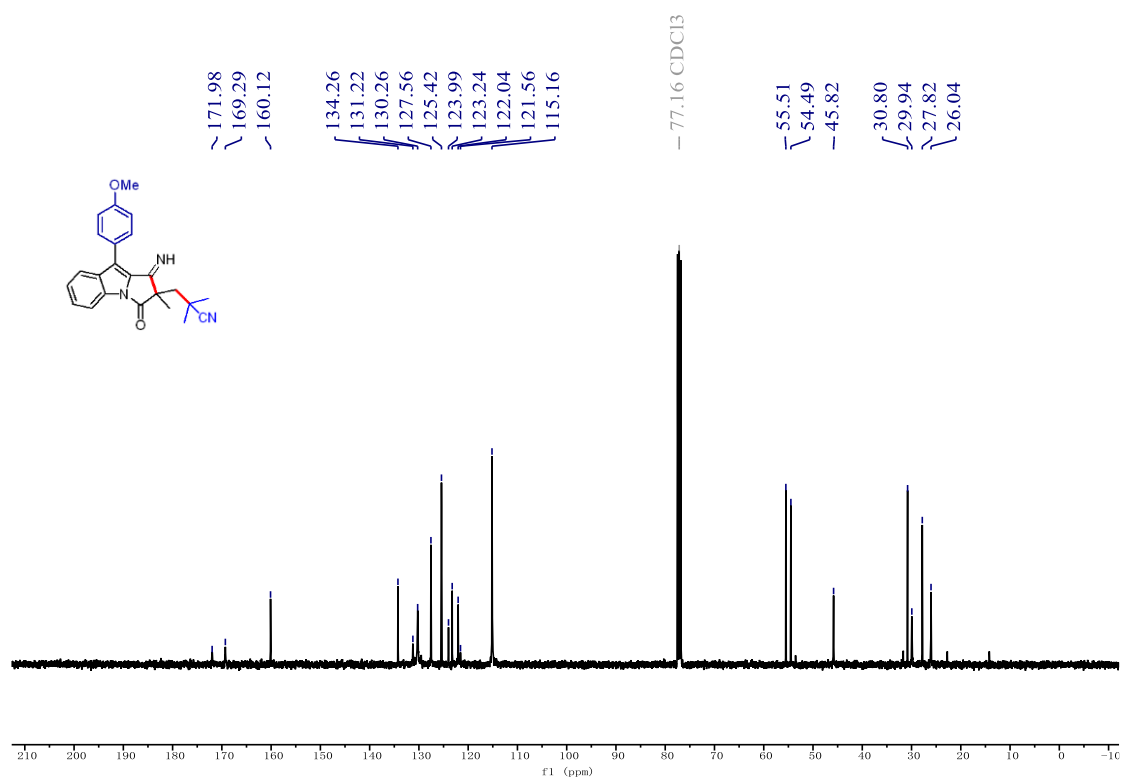
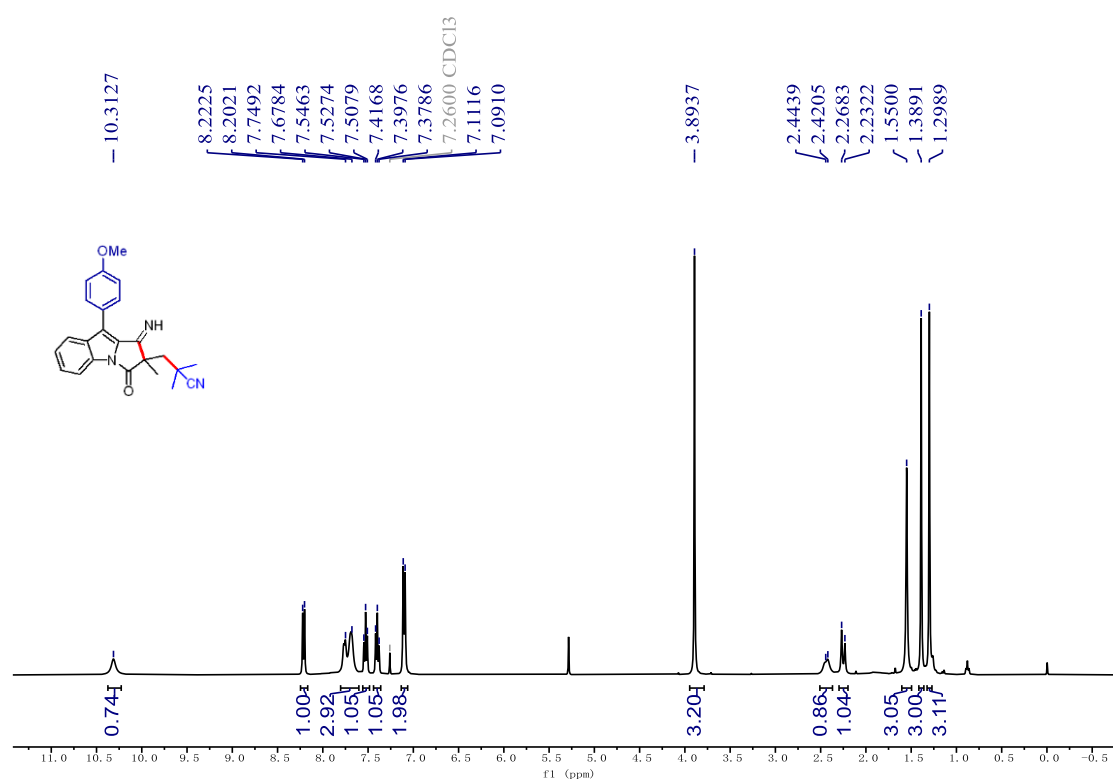
¹H and ¹³C NMR Spectra of 3e



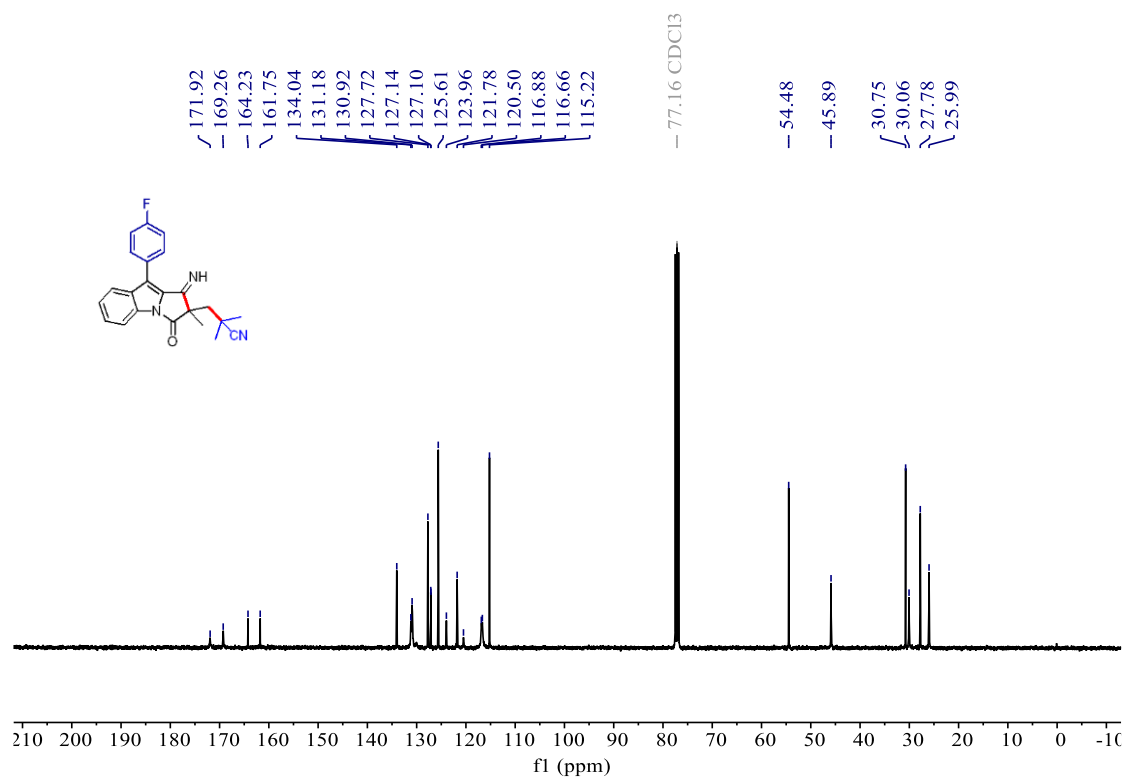
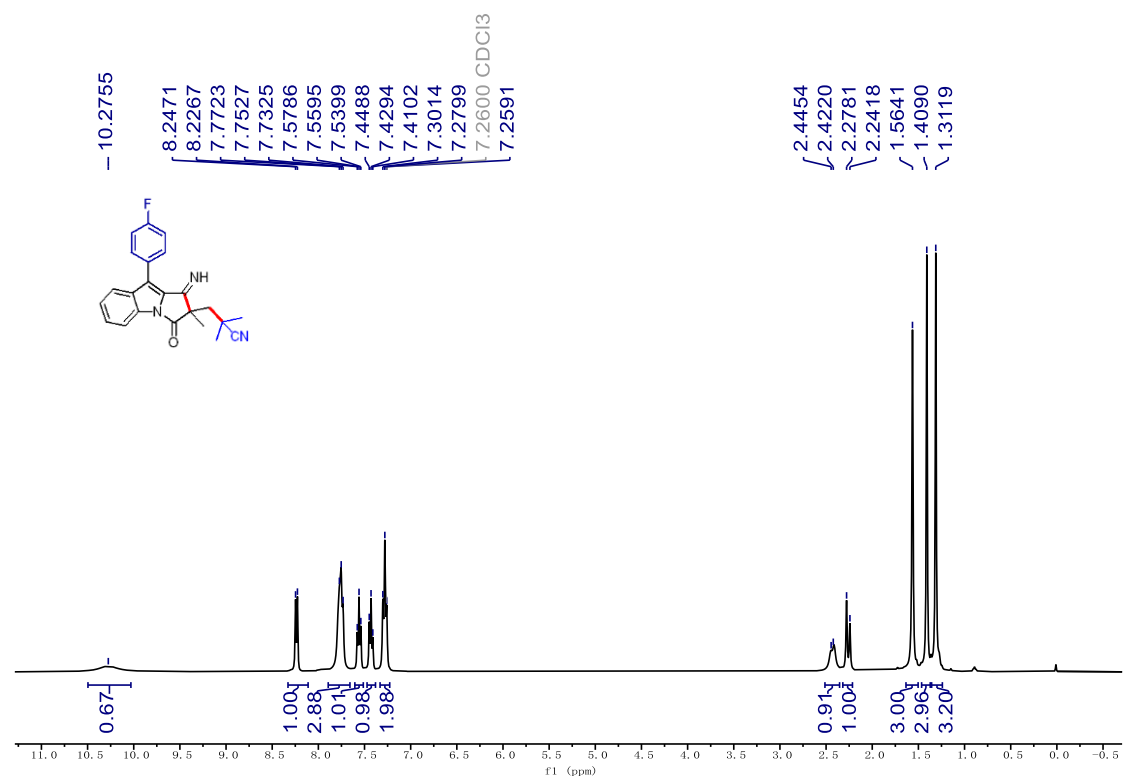
¹H and ¹³C NMR Spectra of 3f

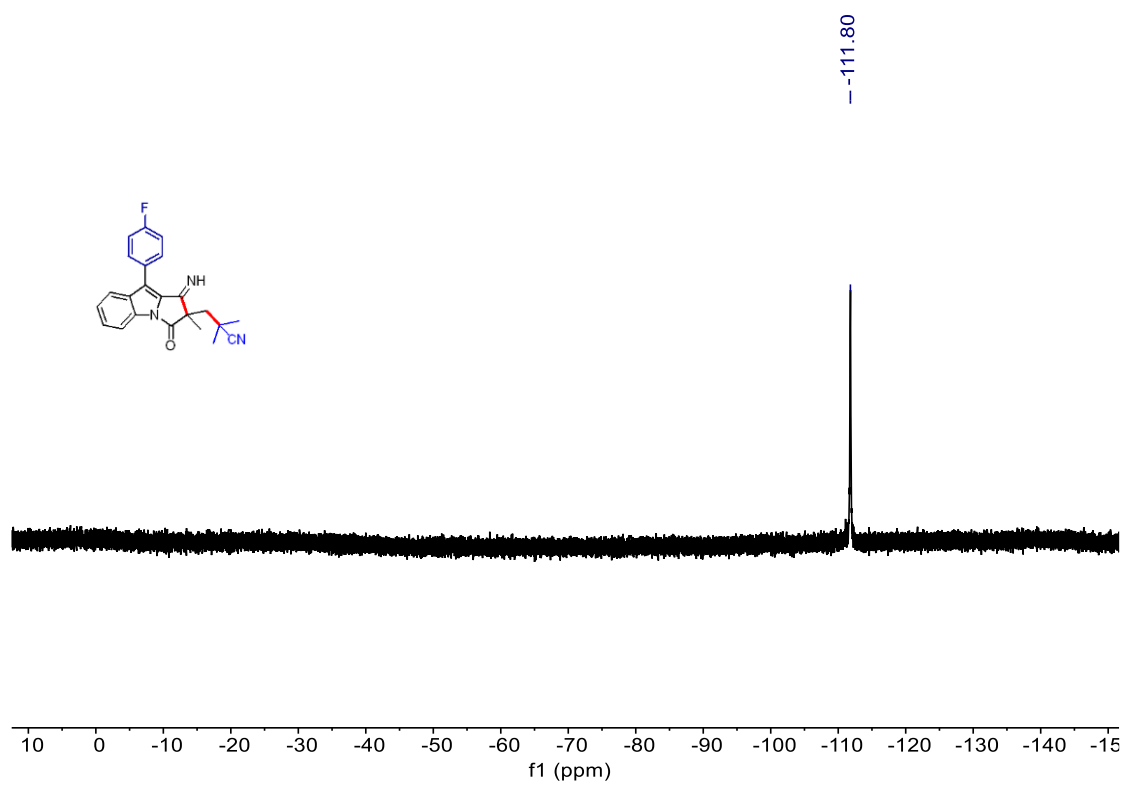


¹H and ¹³C NMR Spectra of 3g

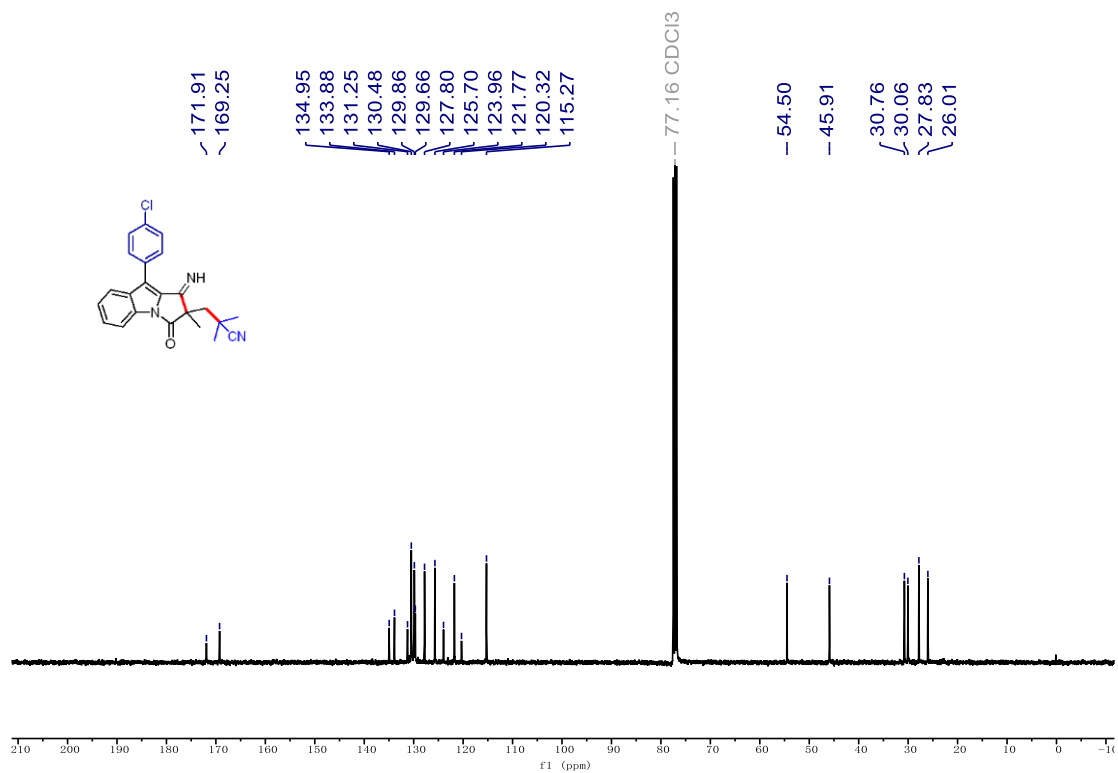
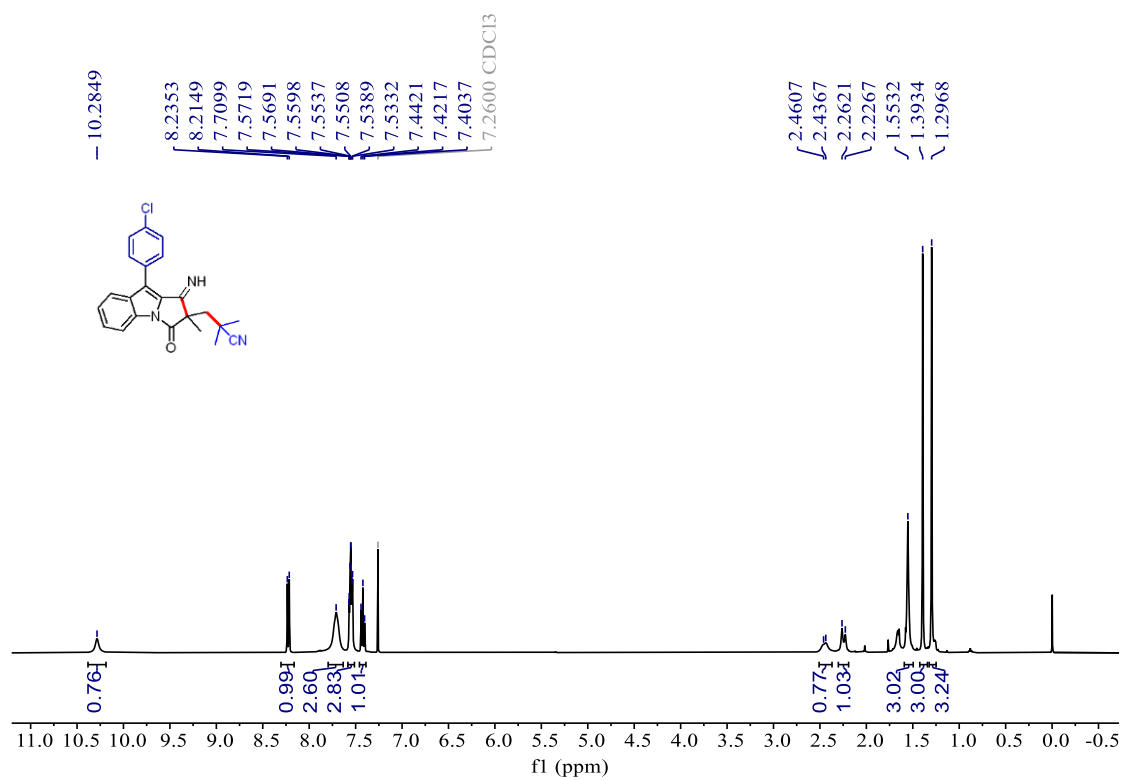


¹H and ¹³C NMR Spectra of 3h

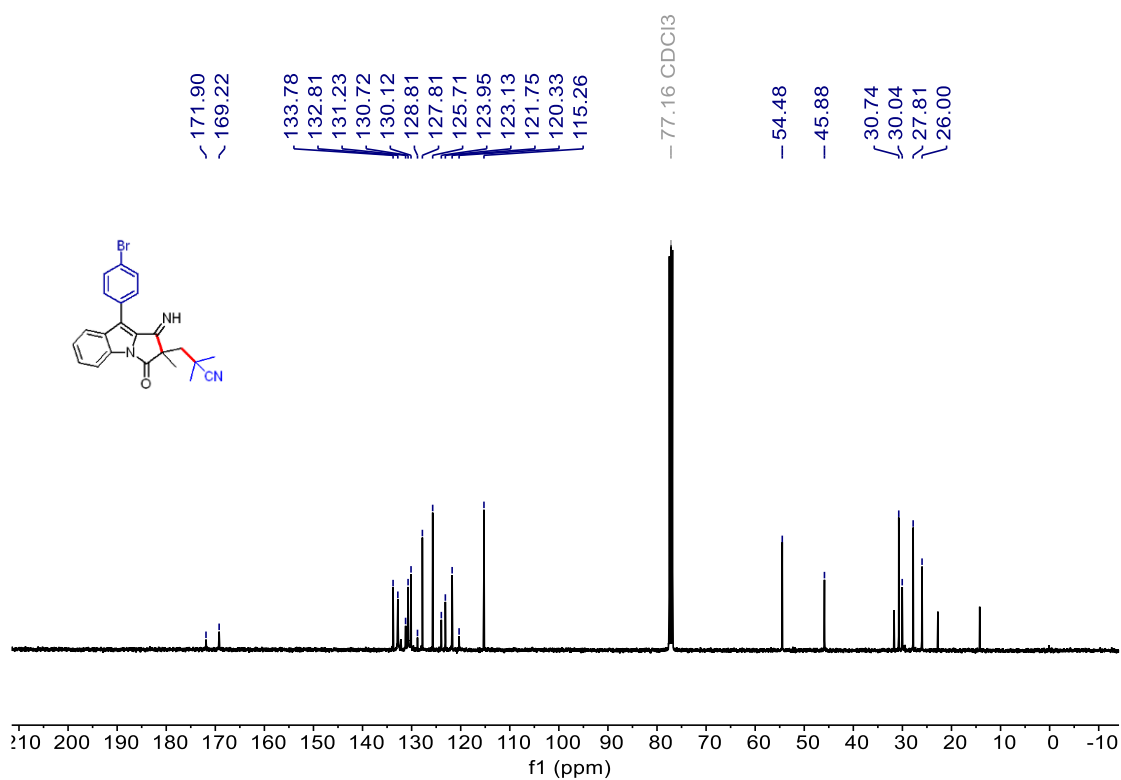
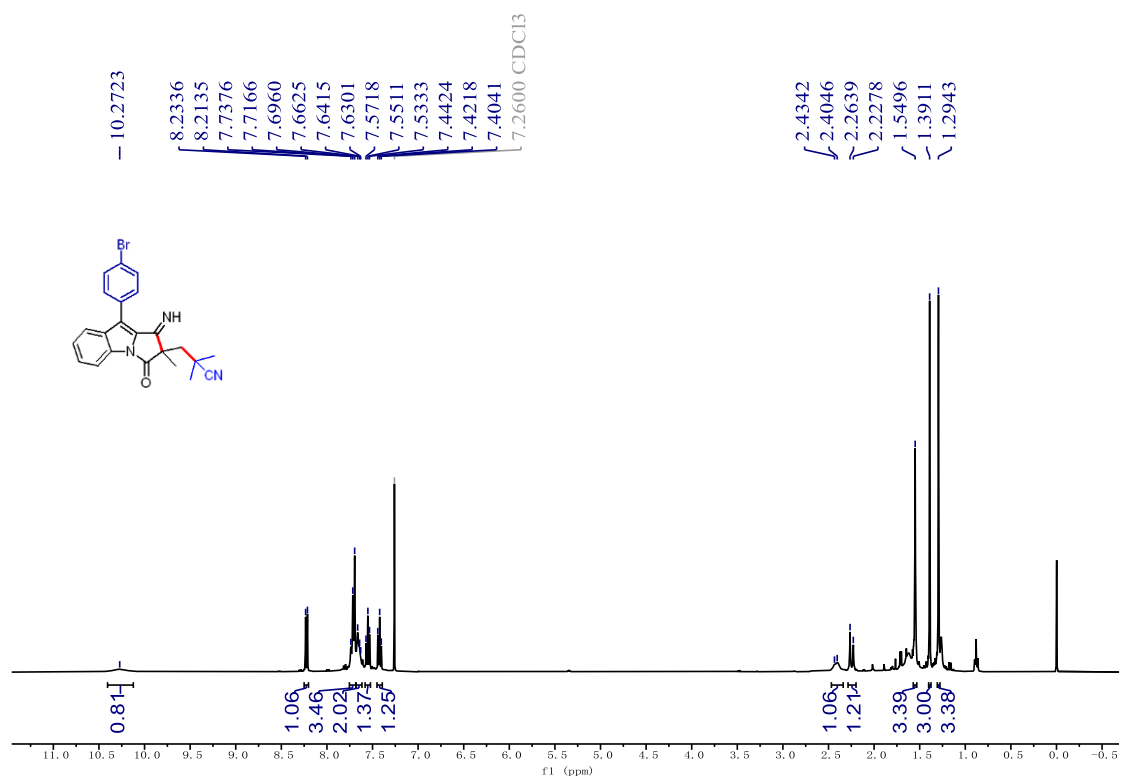




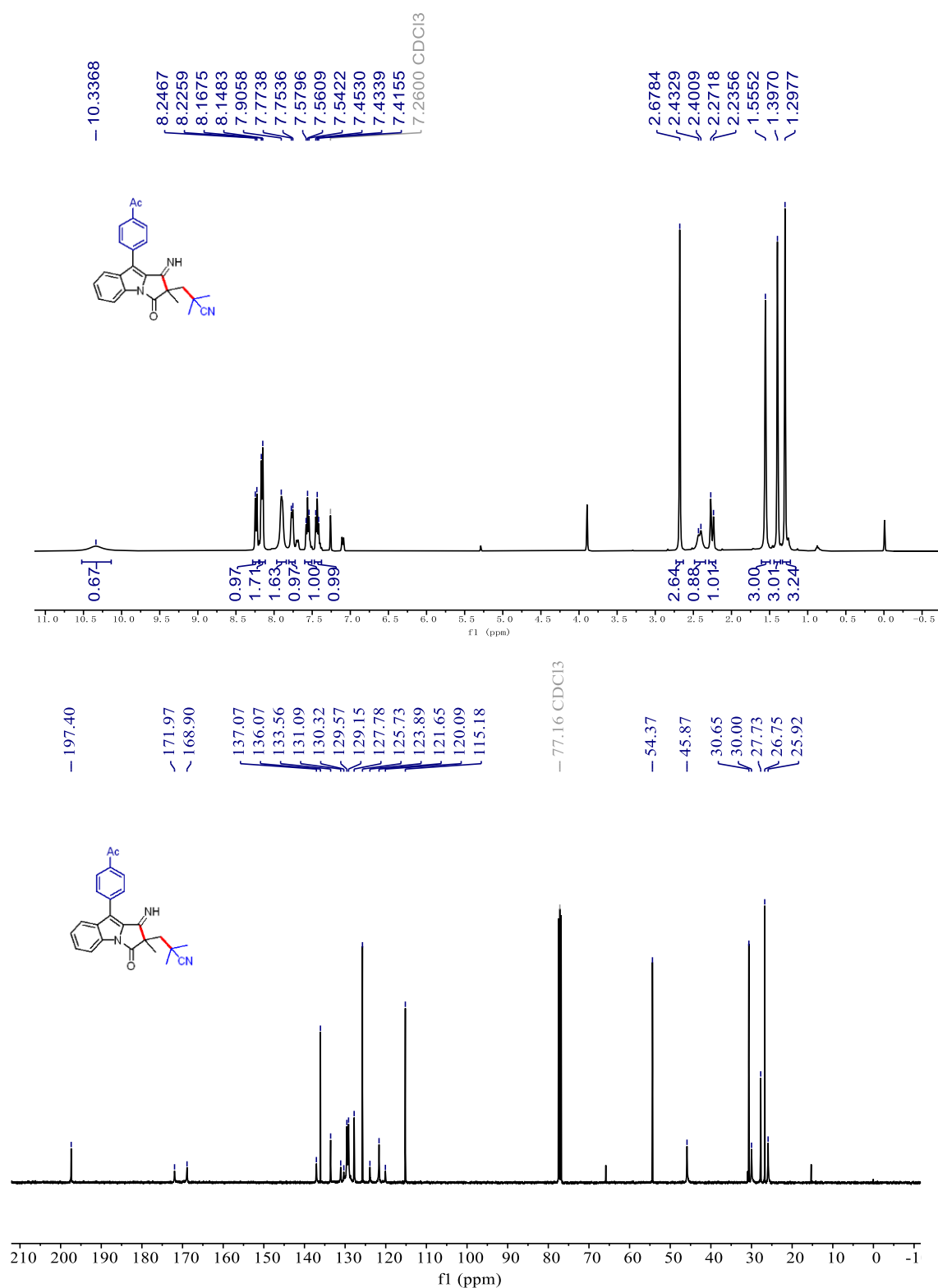
¹H and ¹³C NMR Spectra of 3i



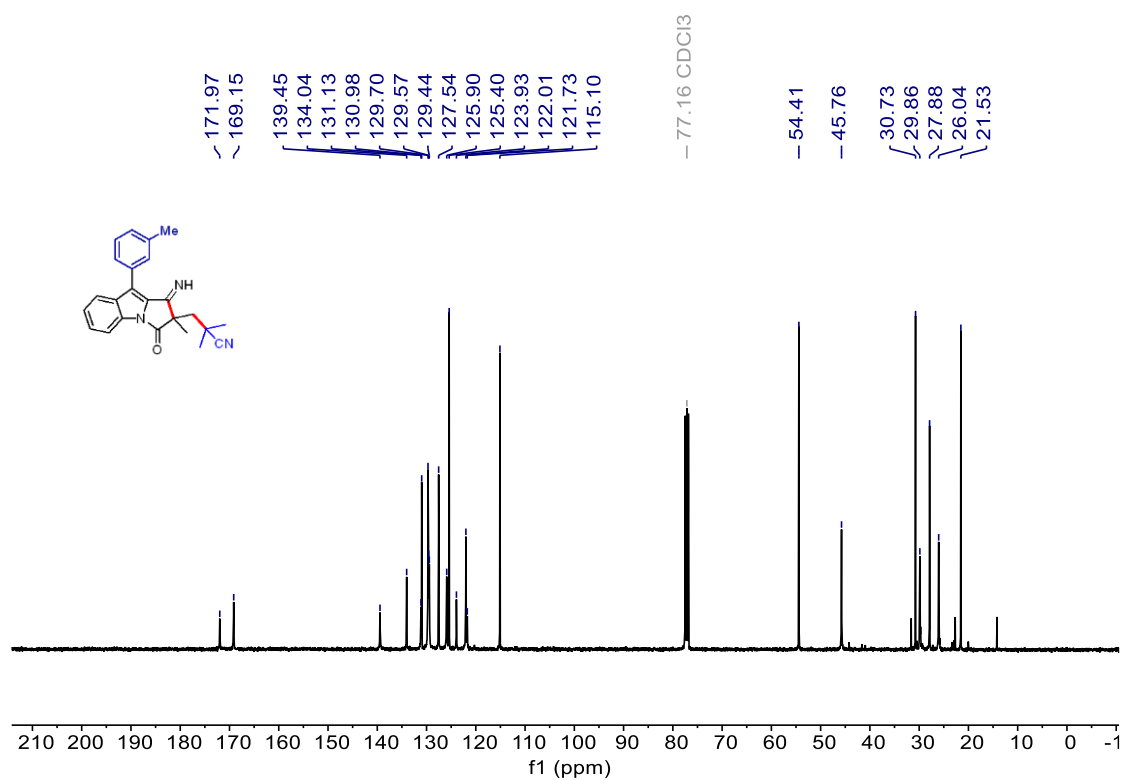
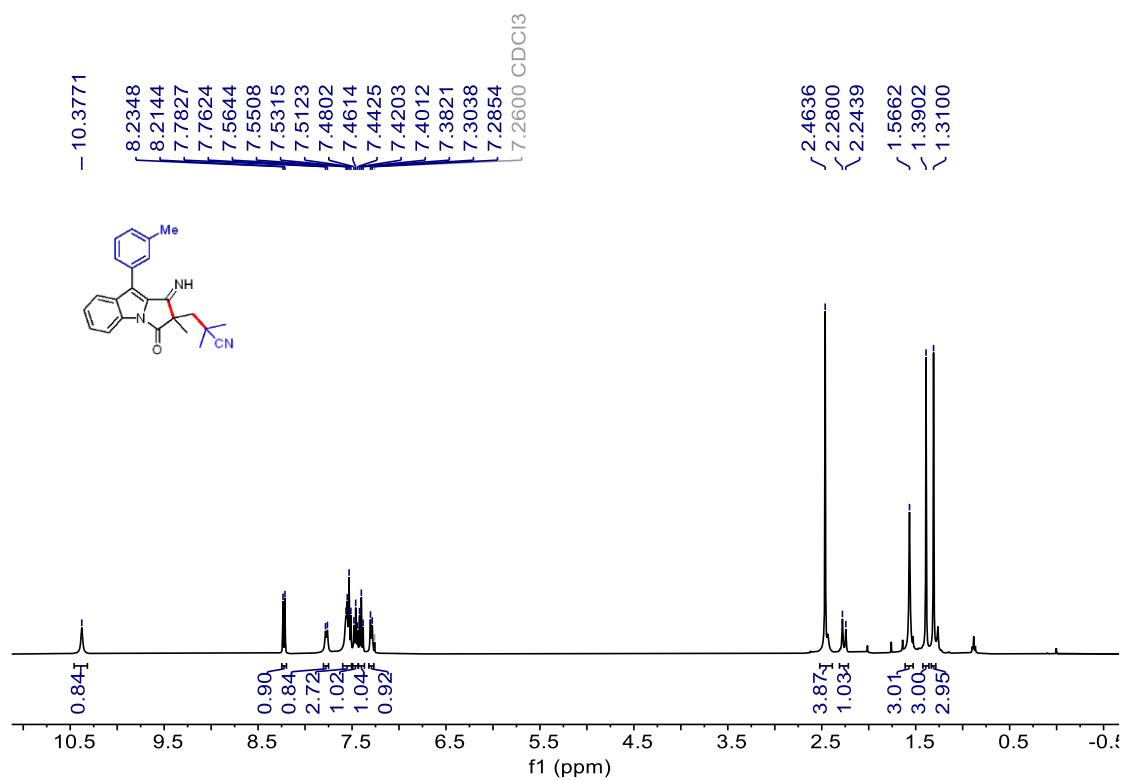
¹H and ¹³C NMR Spectra of 3j



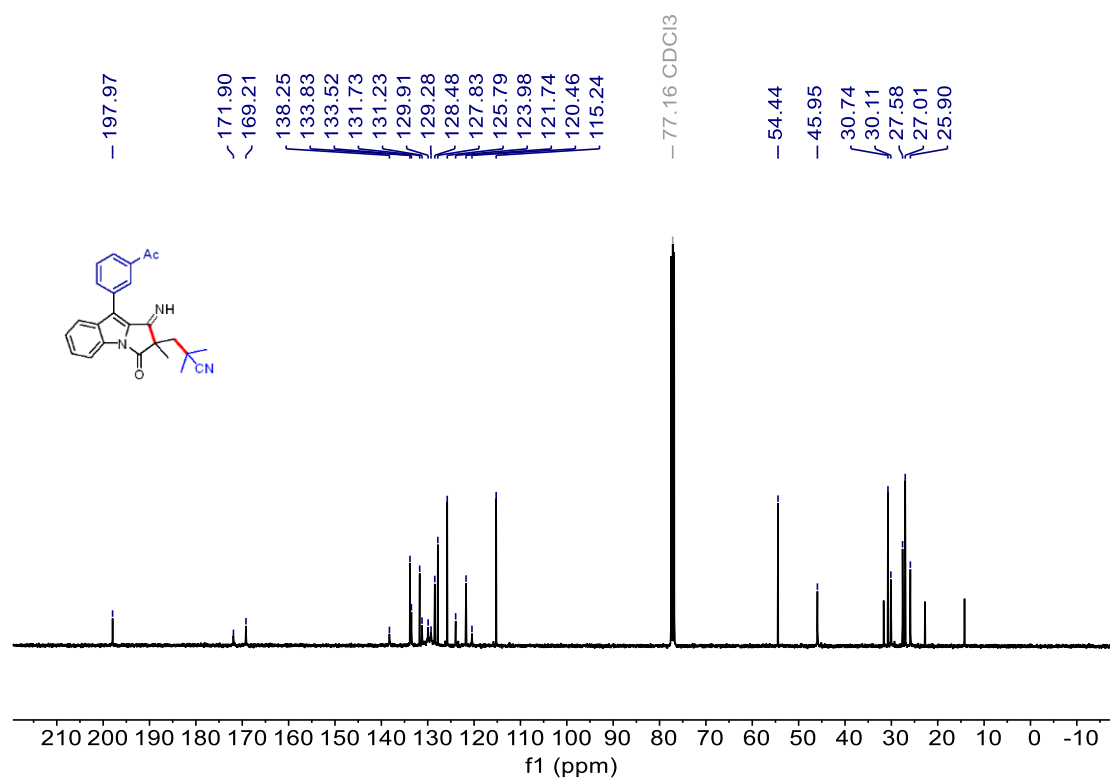
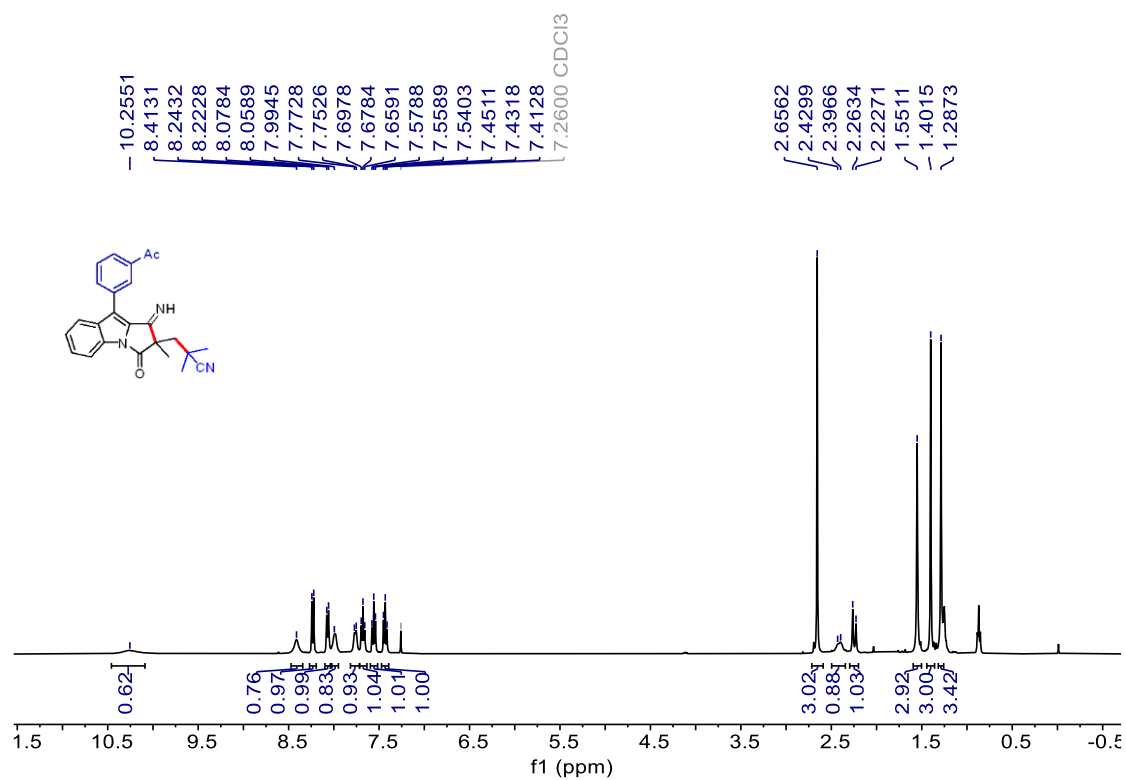
¹H and ¹³C NMR Spectra of 3k



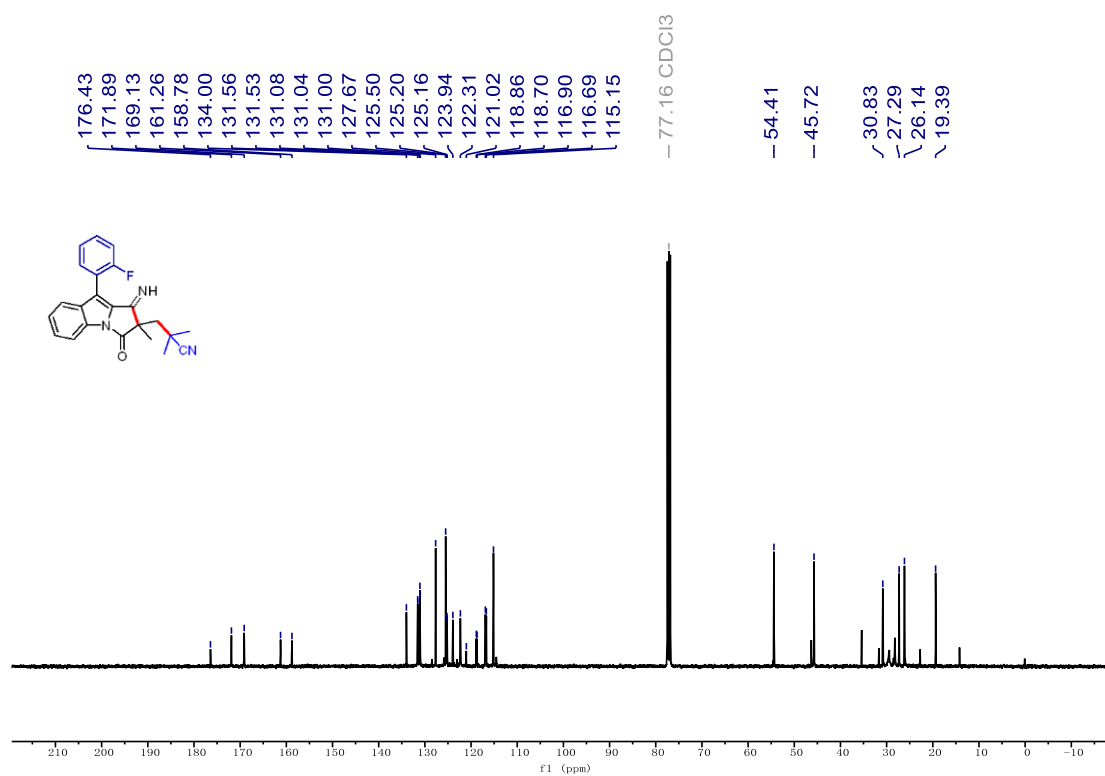
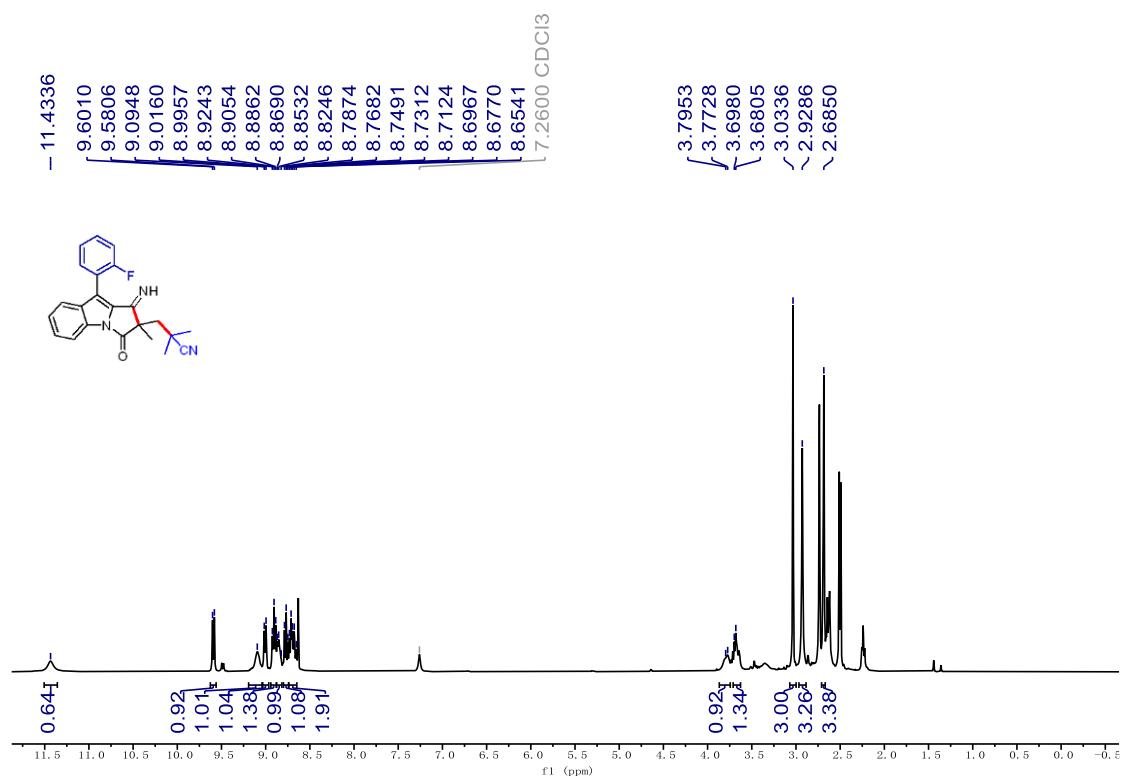
¹H and ¹³C NMR Spectra of 3l

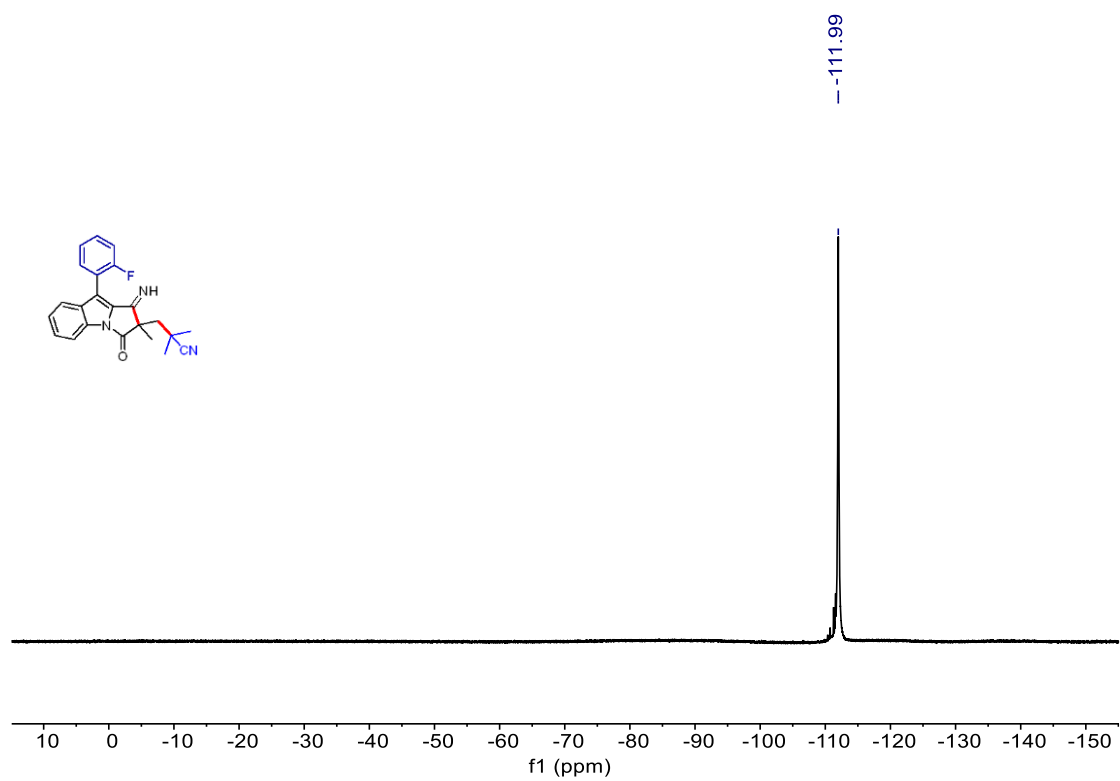


¹H and ¹³C NMR Spectra of 3m

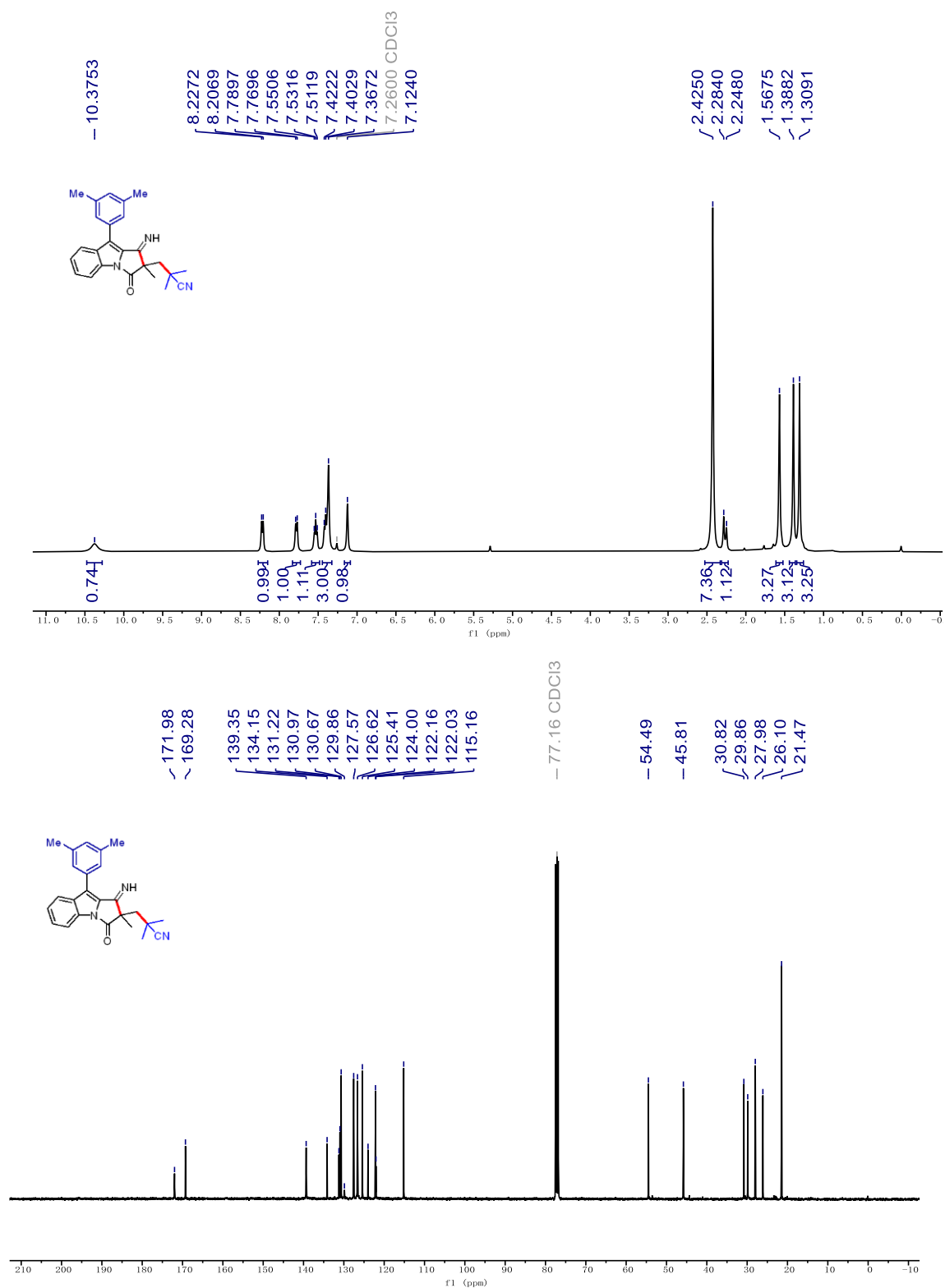


¹H and ¹³C NMR Spectra of 3n

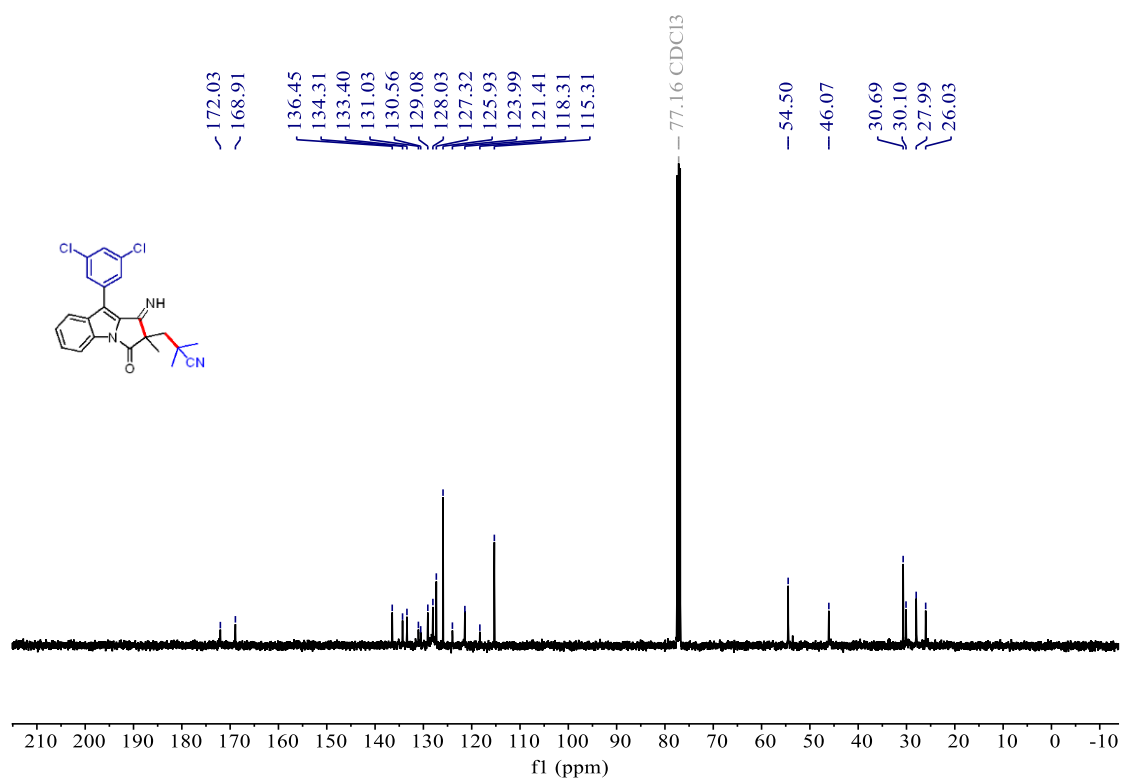
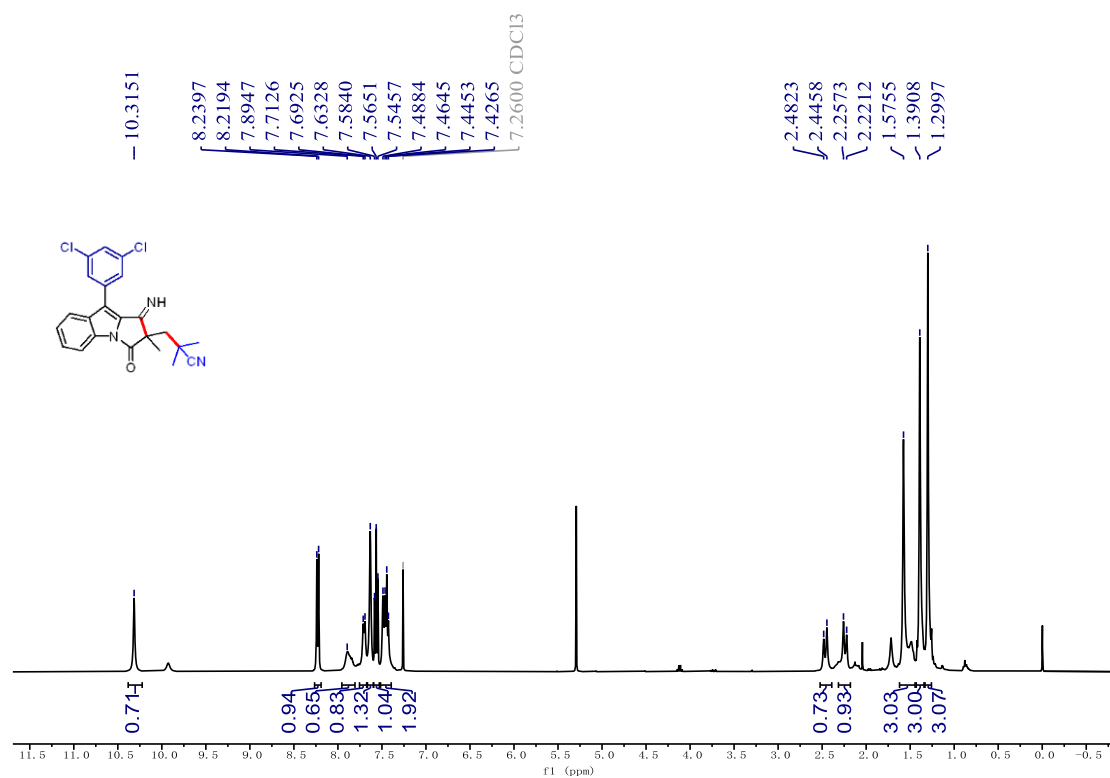




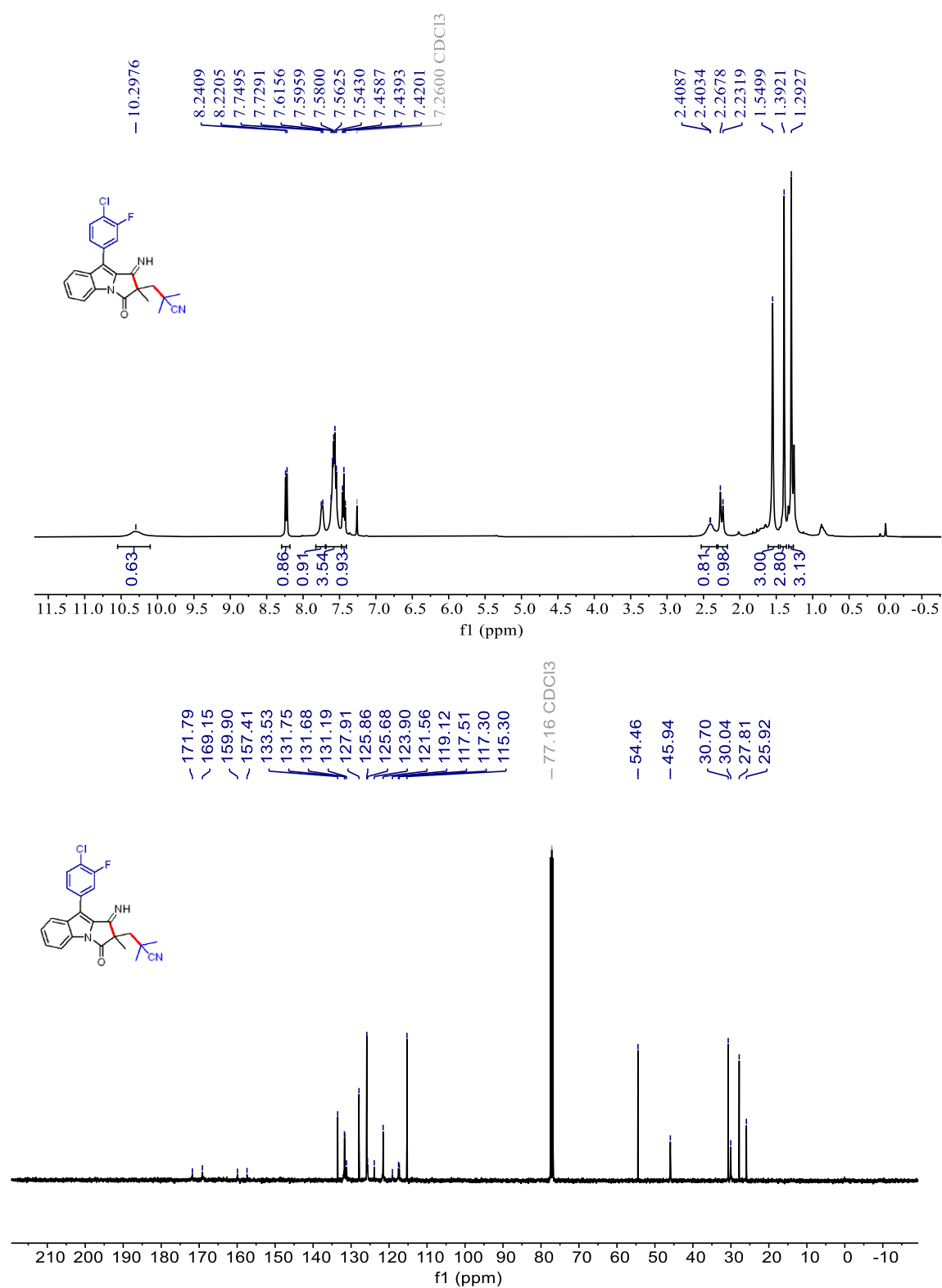
¹H and ¹³C NMR Spectra of 3o



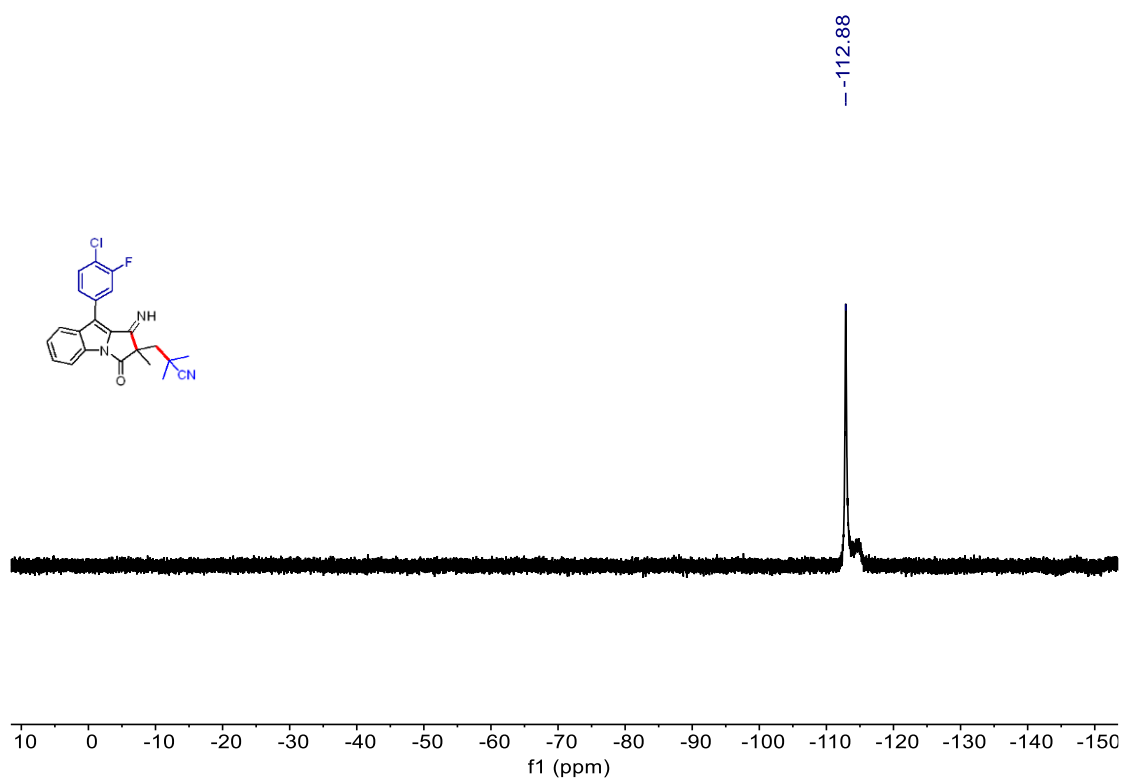
¹H and ¹³C NMR Spectra of 3p



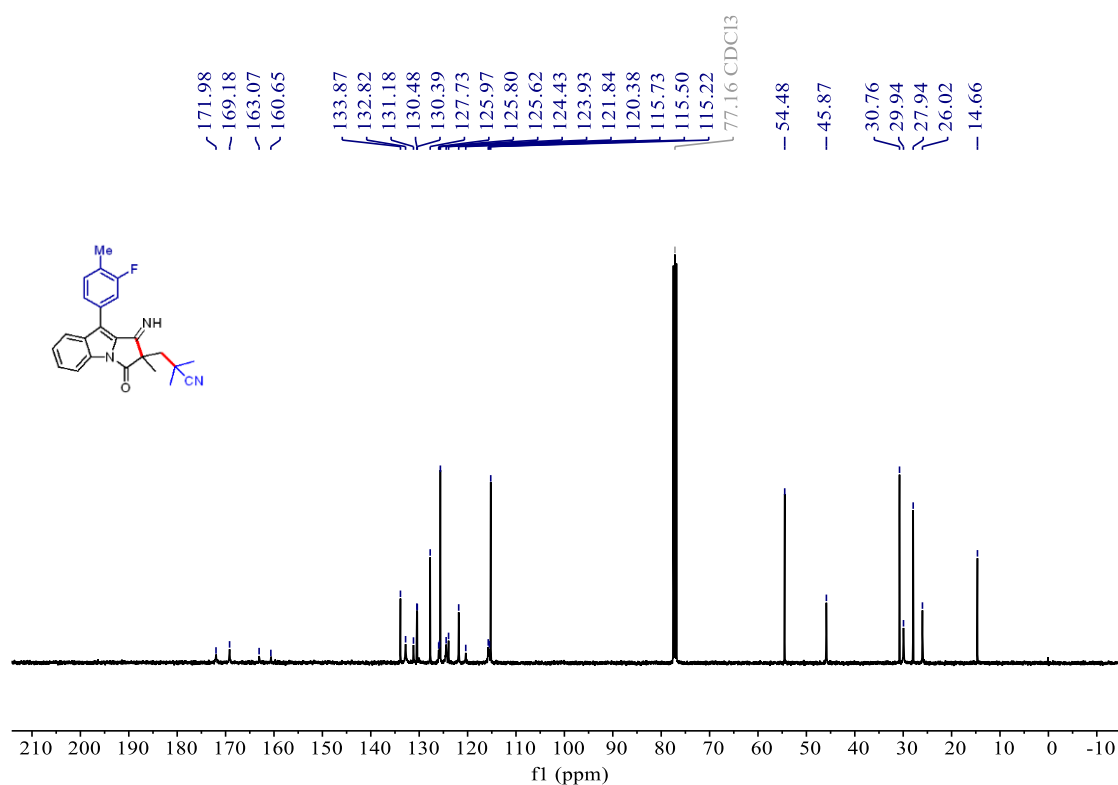
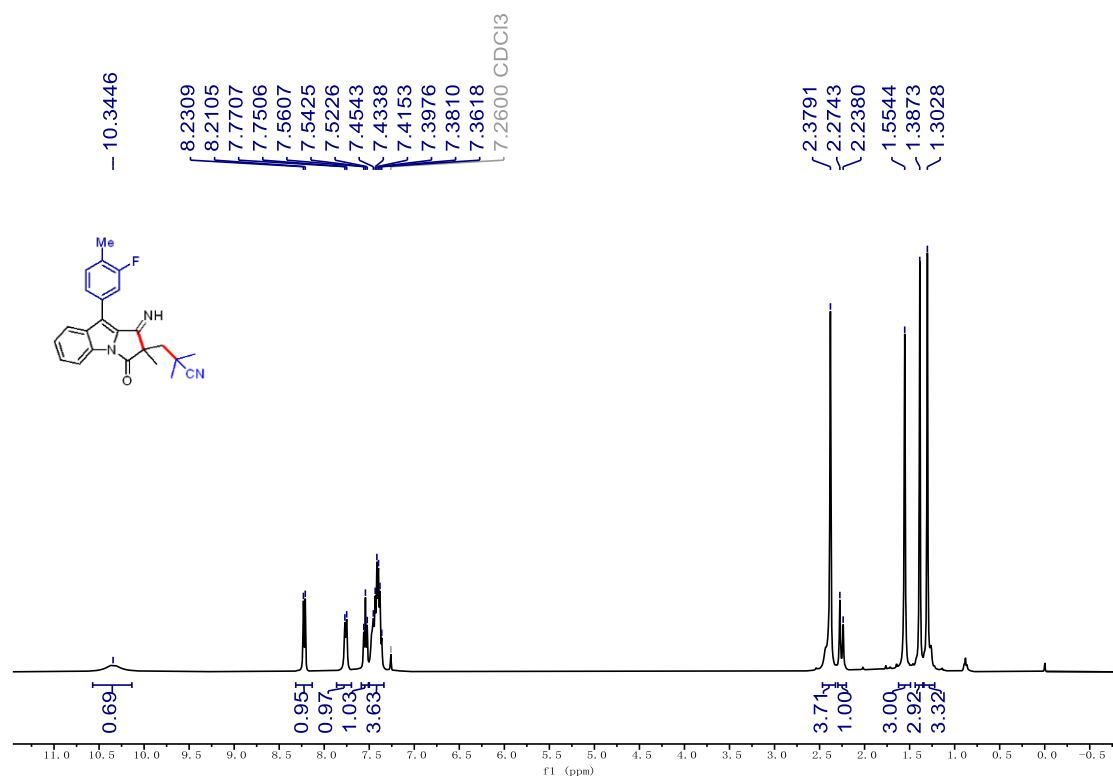
¹H and ¹³C NMR Spectra of 3q



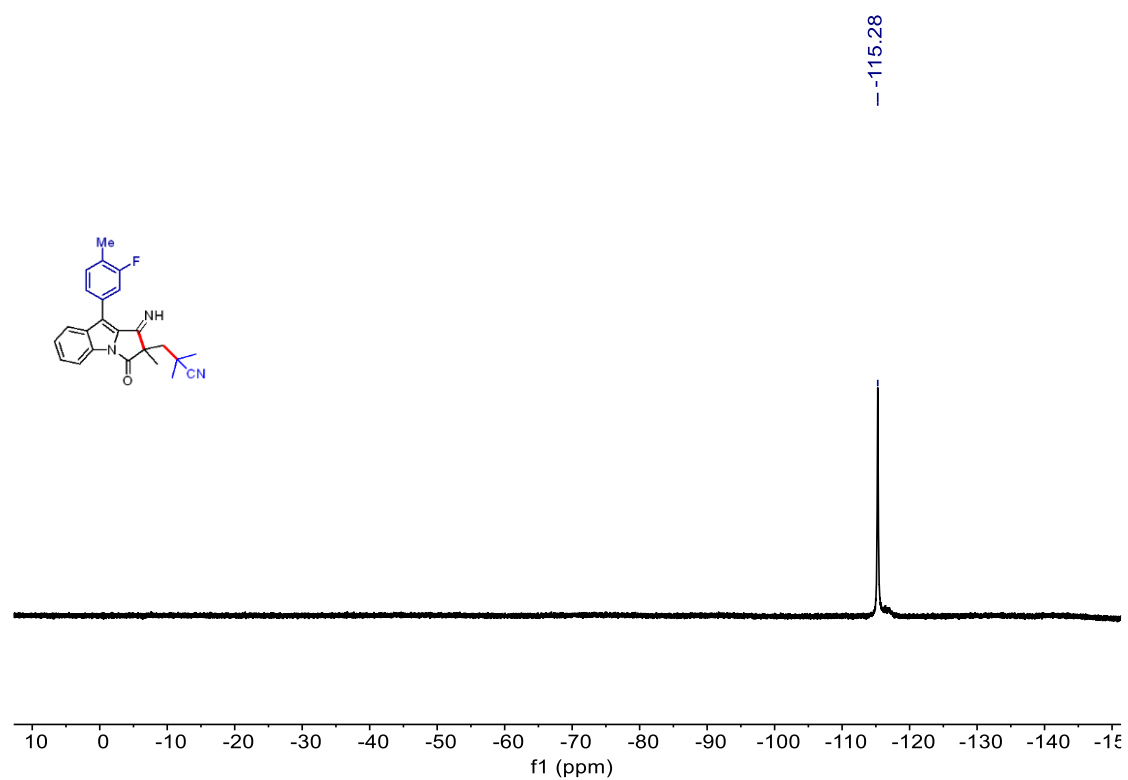
¹⁹F NMR spectrum of **3q**



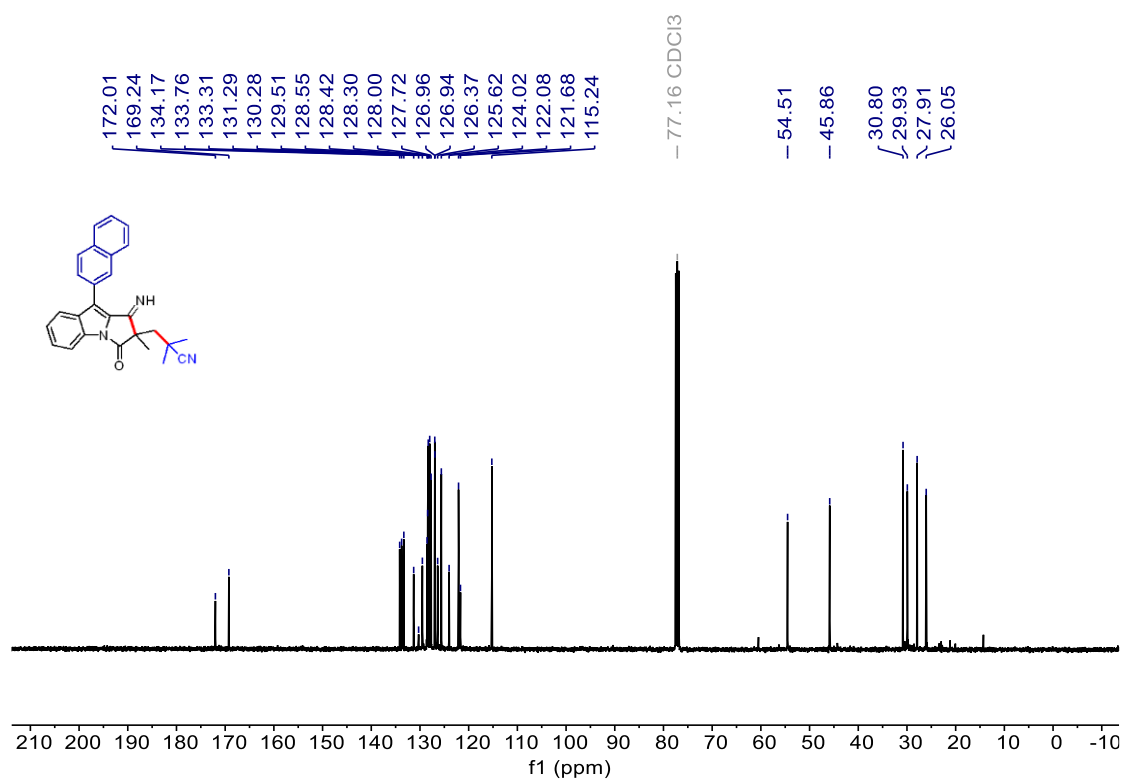
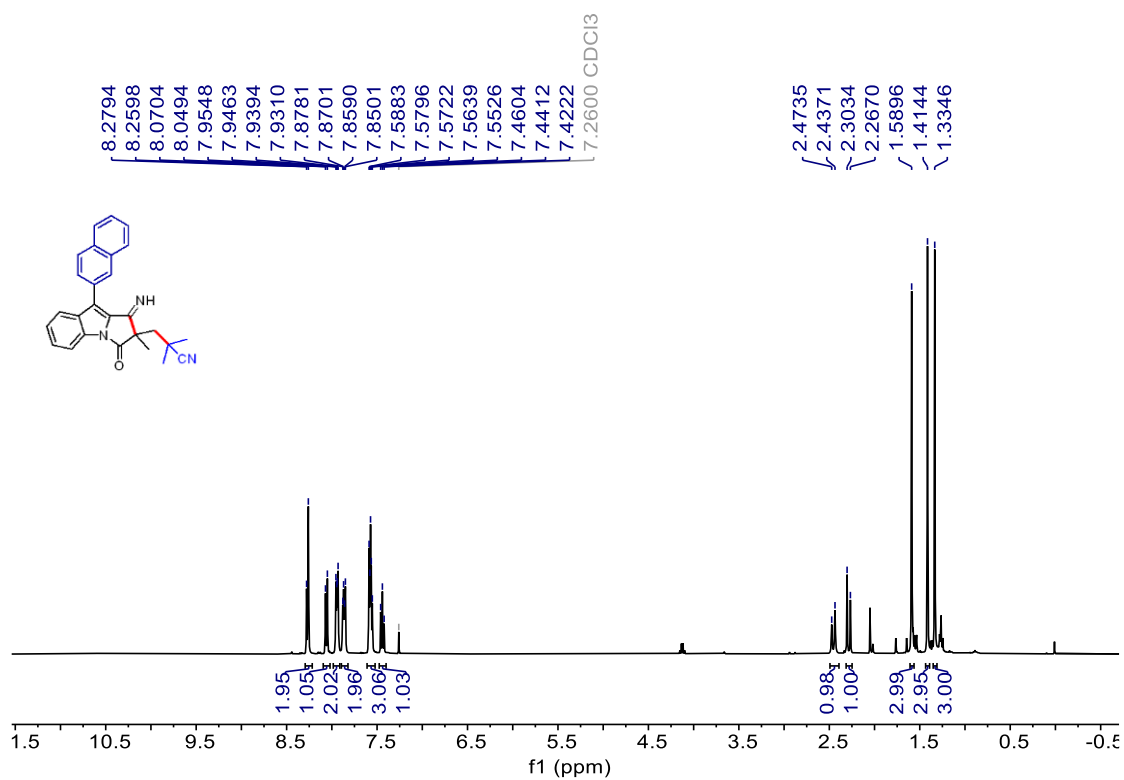
¹H and ¹³C NMR Spectra of 3r



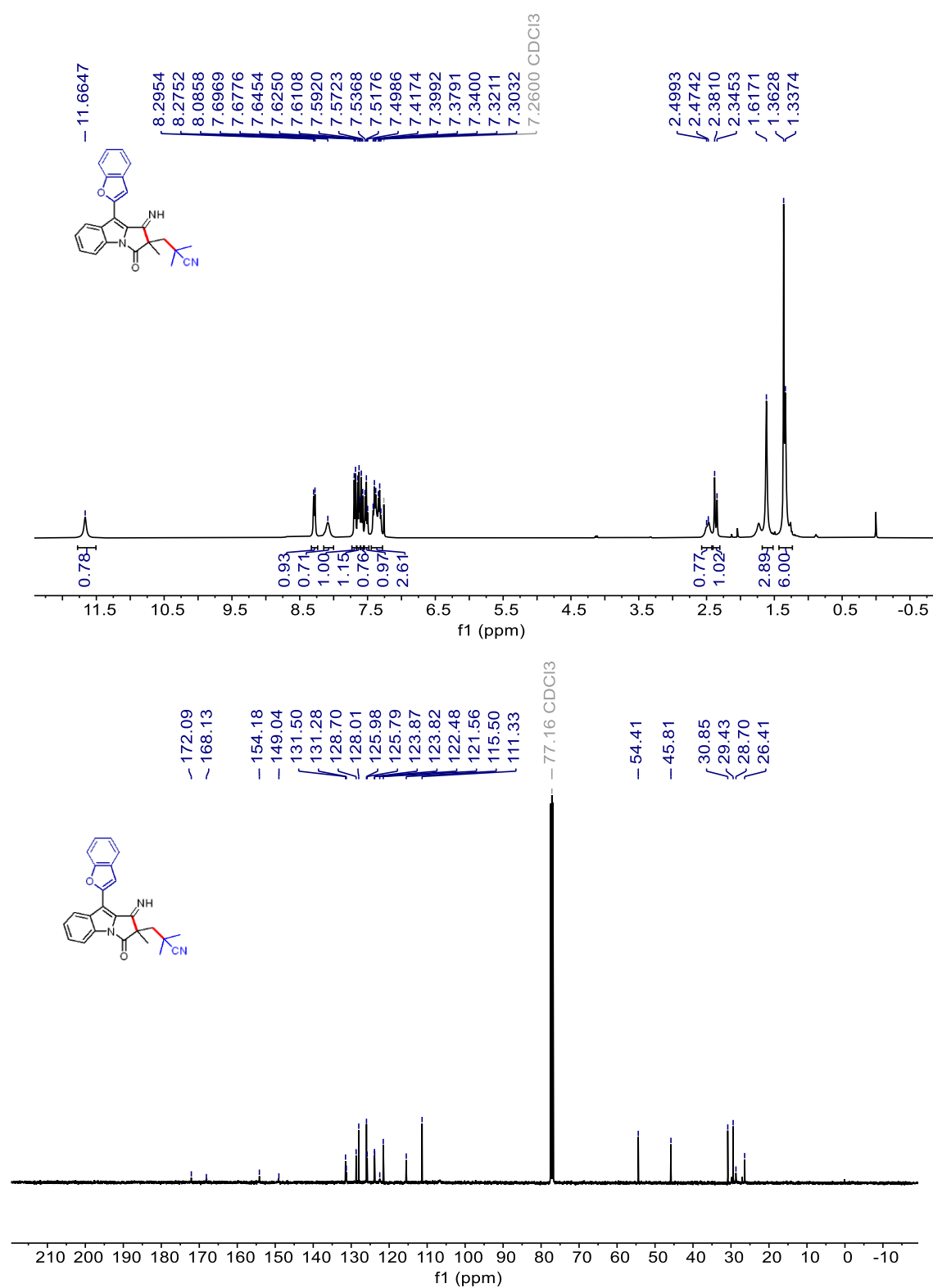
¹⁹F NMR spectrum of **3r**



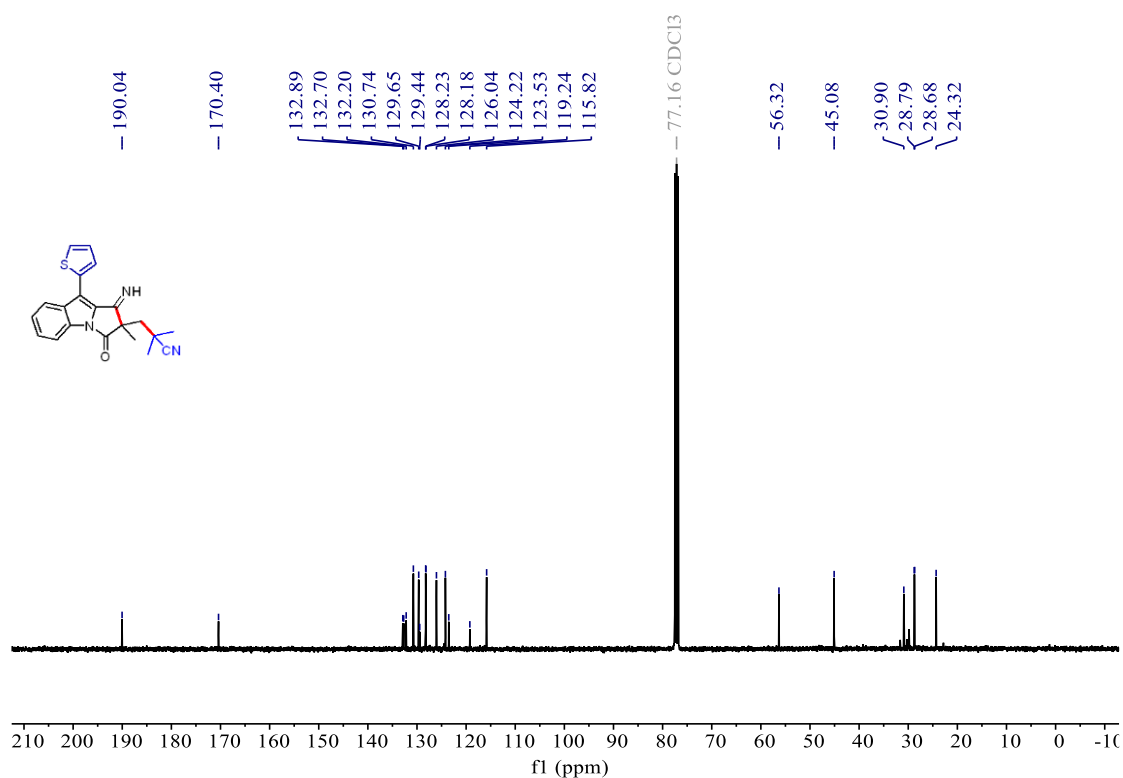
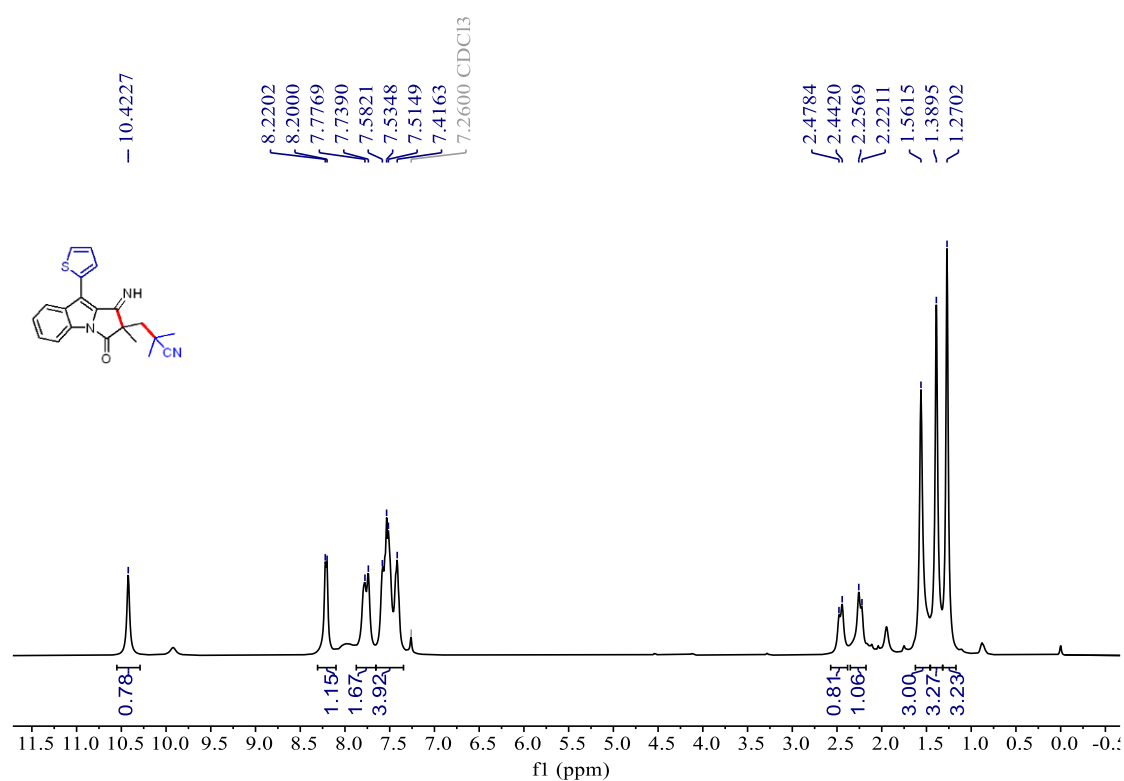
^1H and ^{13}C NMR Spectra of 3s



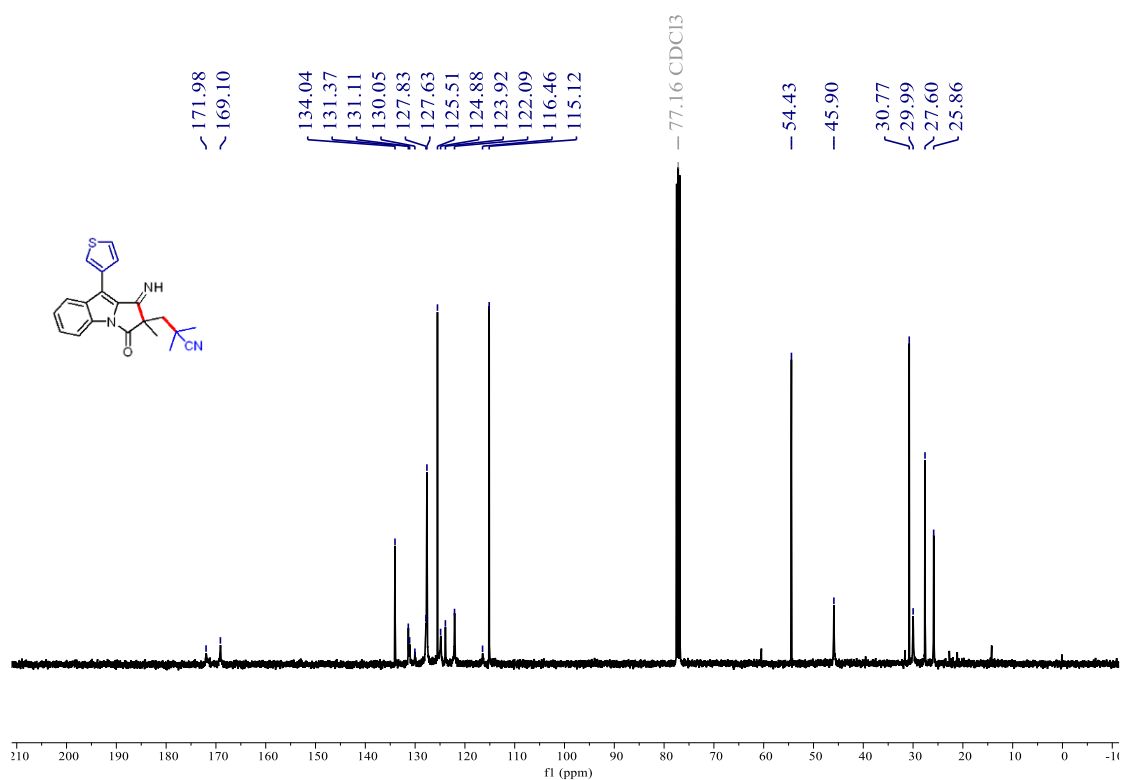
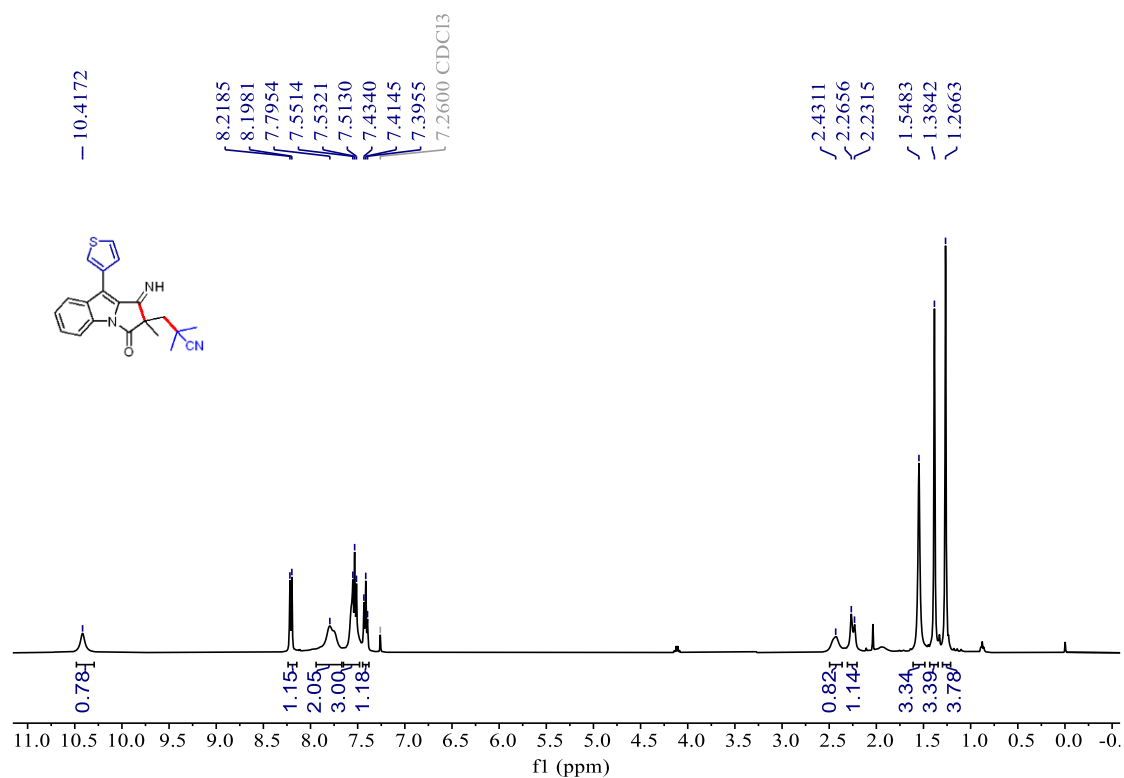
¹H and ¹³C NMR Spectra of 3t



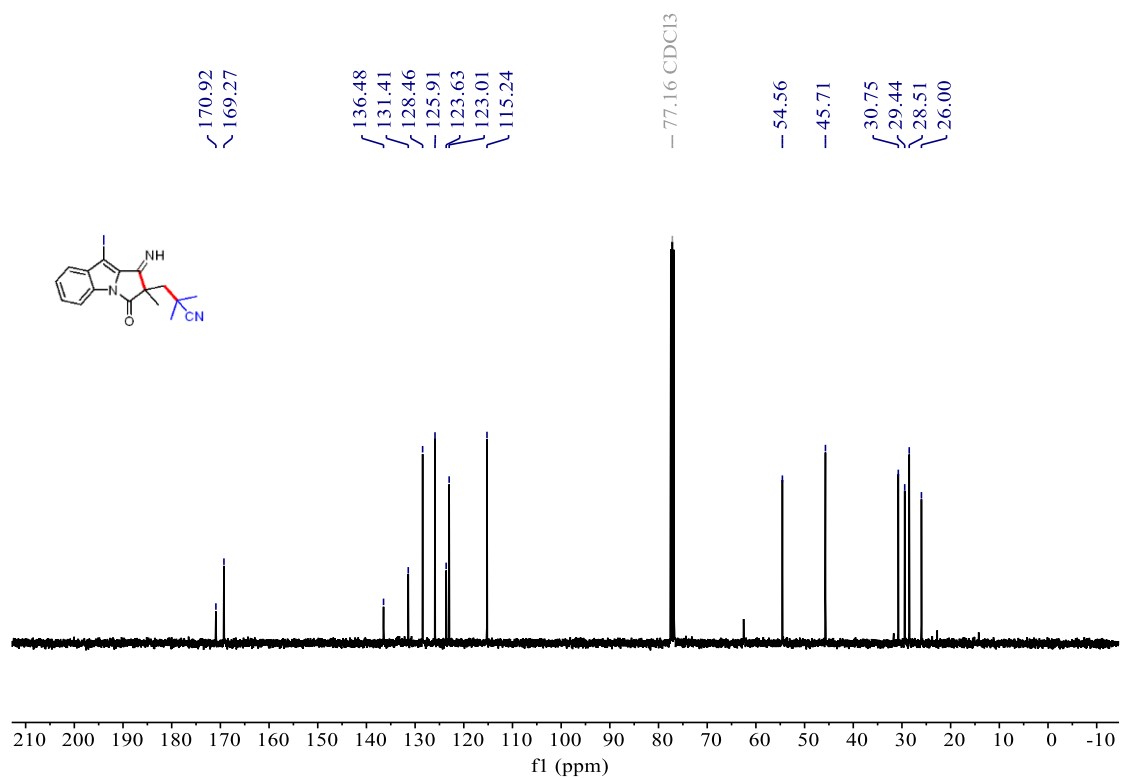
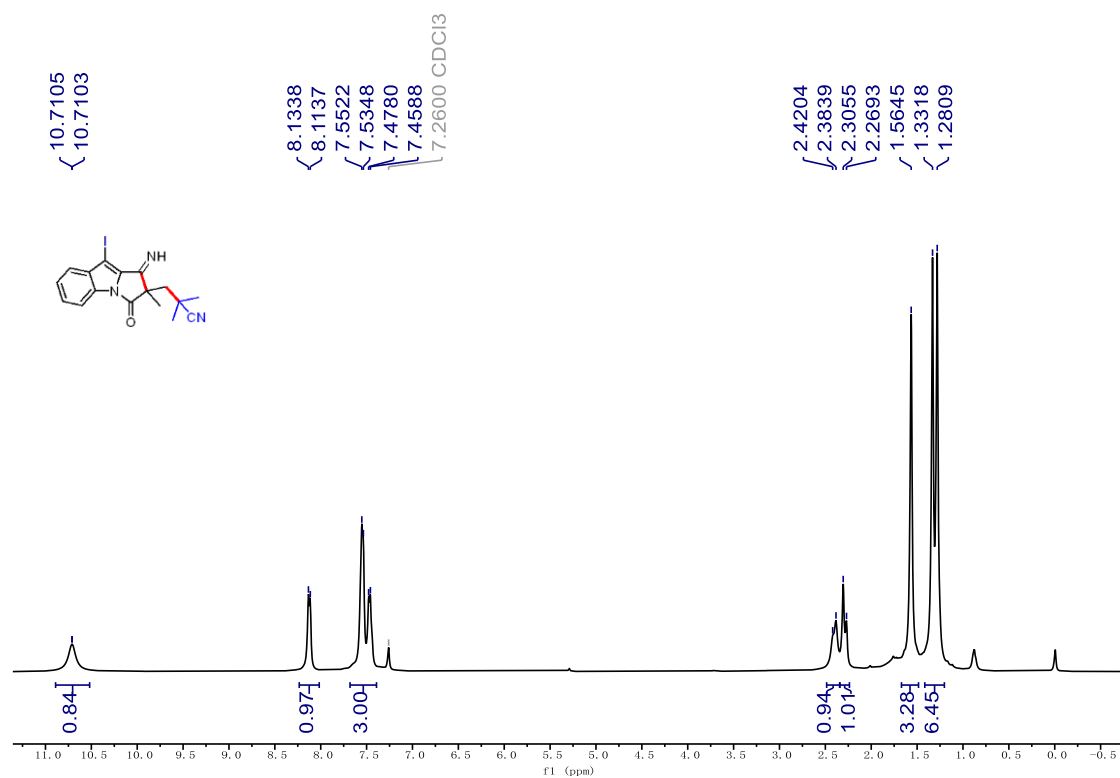
¹H and ¹³C NMR Spectra of 3u



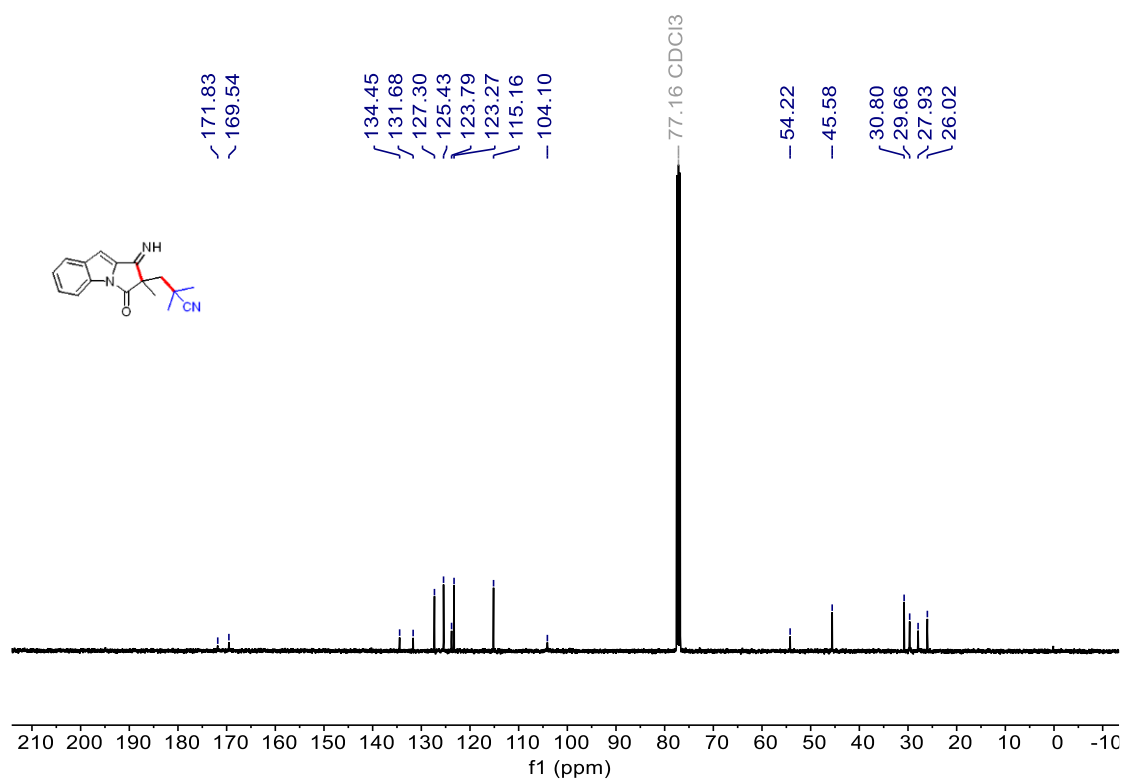
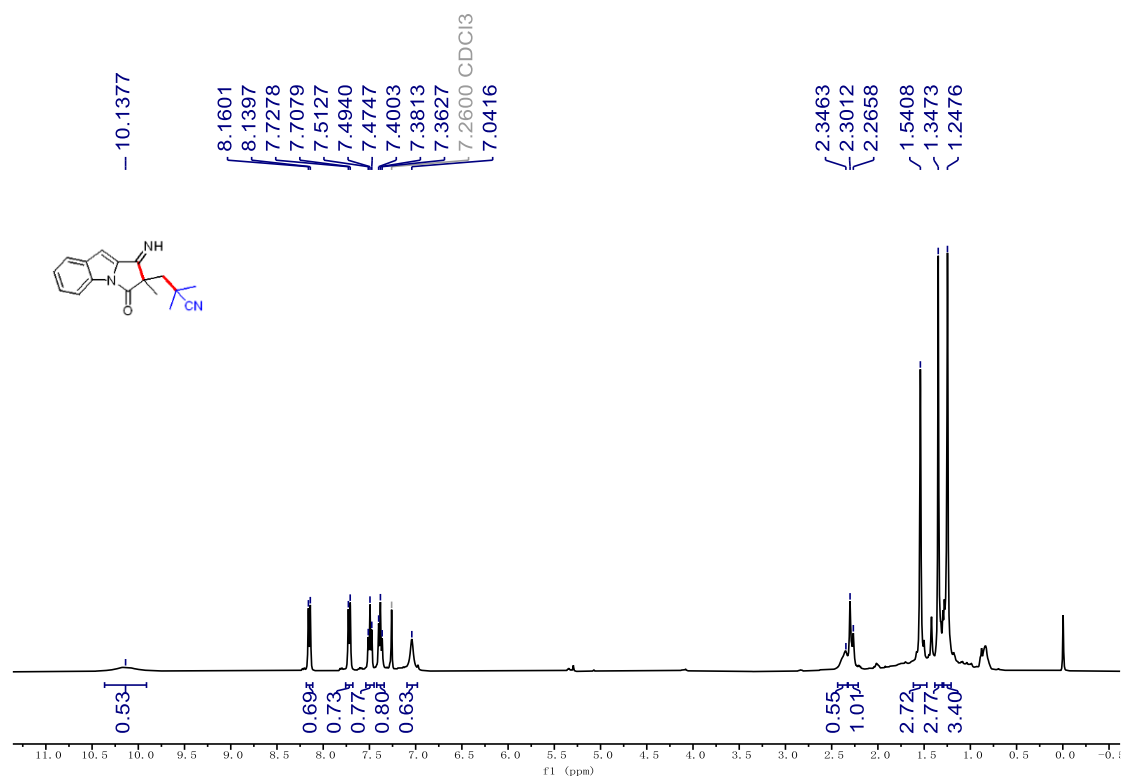
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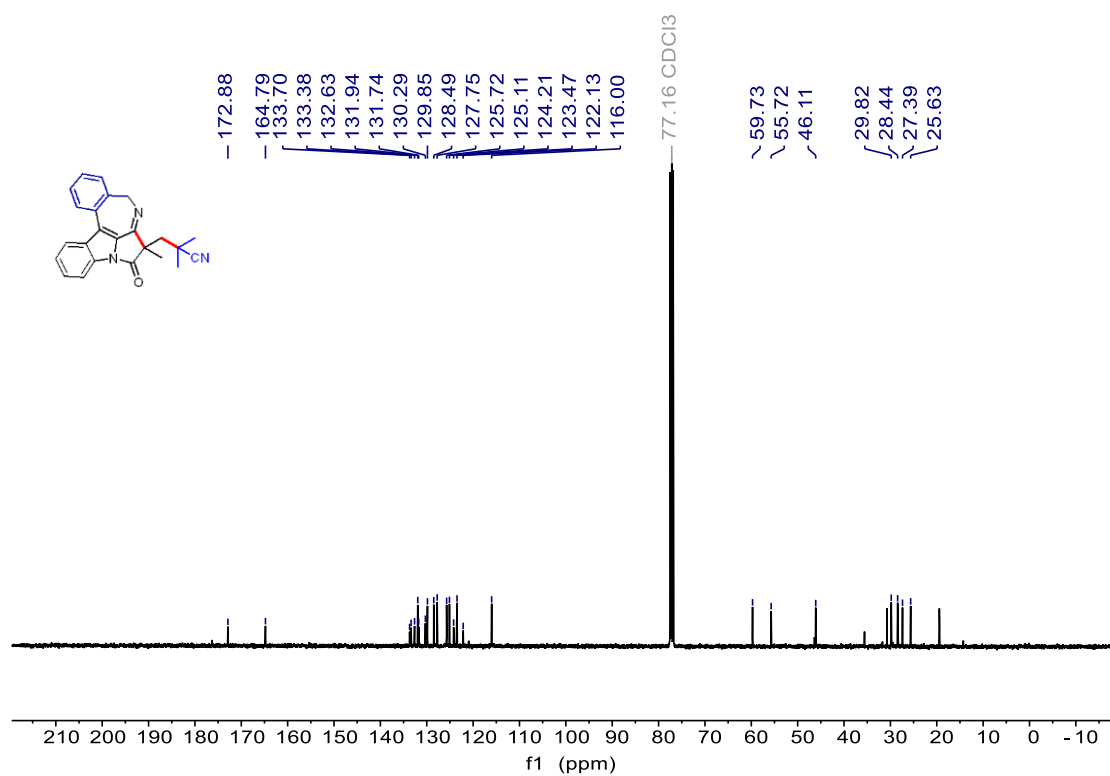
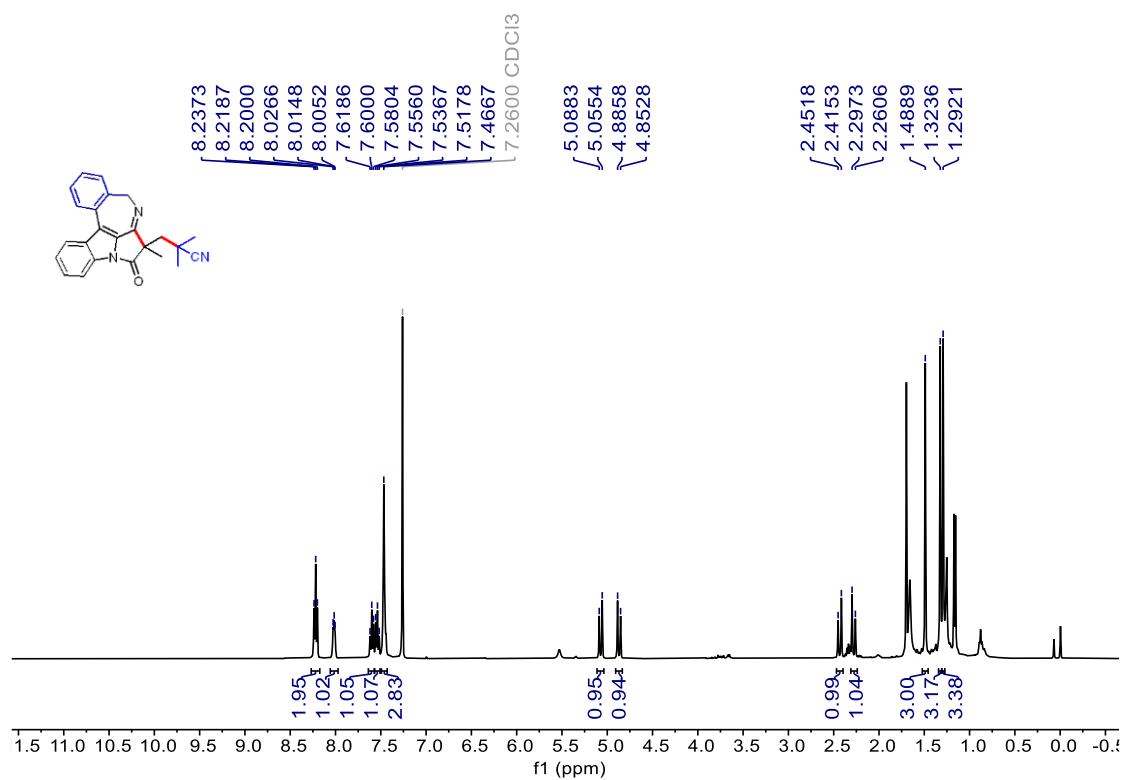
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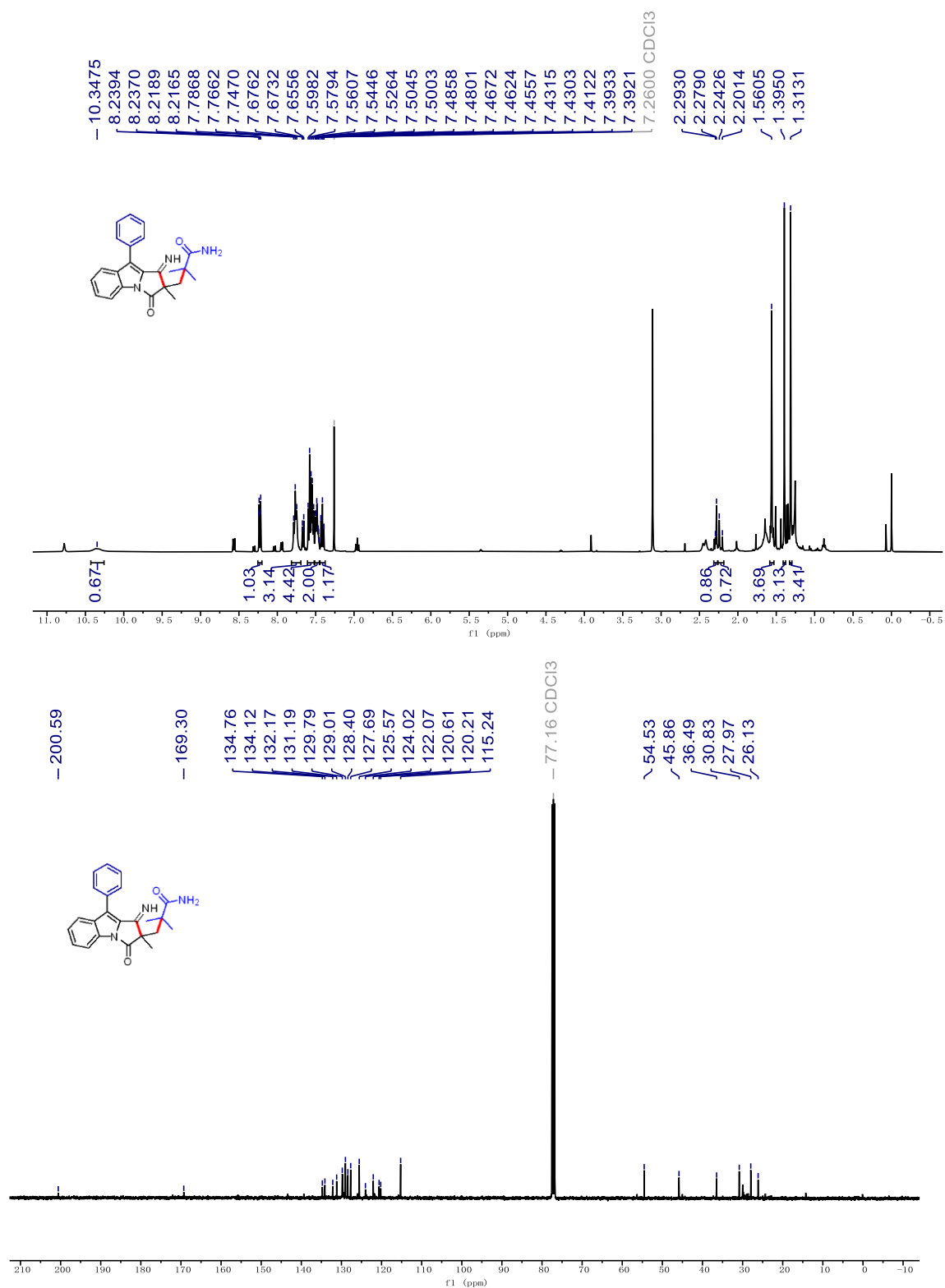
¹H and ¹³C NMR Spectra of 3x



¹H and ¹³C NMR Spectra of 3A



¹H and ¹³C NMR Spectra of 4



G. References

- 1 J. Yuan, L. Shen, N. Guo, Y. Yin, P. Yang, L. Yang, Y. Xiao and S. Zhang, *The Journal of Organic Chemistry*, 2023, **88**, 16598-16608.
- 2 R. Wang and W. Bao, *RSC Advances*, 2015, **5**, 57469-57471.