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Ru(II)-catalyzed C-H activation/annulation reactions of *N*-aryl-pyrazolidinones with sulfoxonium ylides: synthesis of cinnoline-fused pyrazolidinones

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1. General Methods. Solvents and reagents were used as purchased without further purification. Reactions were carried out under air in sealed tubes. Temperatures quoted are external. Reaction progress was monitored by thin-layer chromatography (TLC) on silica gel GF_{254} precoated plates. Visualization of developed plates was performed under a UV lamp. Chromatographic purification was performed on silica gel columns (100-200 mesh size). Melting points were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 and 100 MHz in $CDCl_3$ with chemical shift (δ) given in parts per million (ppm) relative to tetramethylsilane (TMS) as the internal standard. Multiplicities were indicated as followed: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), and so forth; the coupling constant (*J*) was given in hertz (Hz). High-resolution mass spectra (HRMS) were recorded on a Q-Exactive Focus Orbitrap mass spectrometer. *N*-arylpyrazolidin-3-ones **1** and sulfoxonium ylides **2** were prepared according to literature procedures.[1,2]

2. General Procedure for the Synthesis of Product 3. To a solution of *N*-arylpyrazolidin-3-ones **1** (0.3 mmol, 1.0 equiv) and sulfoxonium ylides **2** (0.45 mmol, 1.5 equiv) in DCE (2 mL) were added $[RuCl_2(p\text{-cymene})]_2$ (18.4 mg, 0.03 mmol) and $Zn(OTf)_2$ (109 mg, 0.3 mmol). The reaction mixture was stirred at 100 ℃ on a heating block for 10 min. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified using column chromatography to afford product **3**.

*5-Phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3aa**)*. Yellow solid (75 mg, 95% yield), ethyl acetate/petroleum ether = 1:4. mp 158-159 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 7.6 Hz, 2H), 7.40-7.30 (m, 3H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.45 (s, 1H), 3.96 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* =

7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 146.5, 137.3, 133.0, 129.3, 128.9, 128.4, 126.7, 126.1, 125.0, 122.6, 115.5, 111.2, 45.5, 30.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{15}N_2O$ 263.1184; found 263.1175.

*8-Fluoro-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ba**).* Yellow solid (78 mg, 93% yield), ethyl acetate/petroleum ether = 1:4. mp 152-153 ℃. ^{1}H NMR (400 MHz, CDCl3) δ: 7.51-7.49 (m, 2H), 7.41-7.34 (m, 3H), 6.84 (td *J* = 8.4 Hz, *J* = 2.8 Hz, 1H), 6.78 (dd, *J* = 8.4 Hz, *J* = 2.8 Hz, 1H), 6.64 (dd, *J* = 8.8 Hz, *J* = 4.4 Hz, 1H), 6.36 (s, 1H), 3.94 (t, *J* = 7.8 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.3, 158.7 (*J* = 239.9 Hz), 142.6 (*J* = 2.5 Hz), 138.8, 132.7, 129.4, 128.6, 126.9 (*J* = 8.3 Hz), 126.4, 115.0 (*J* = 22.8 Hz), 114.5 (*J* = 2.5 Hz), 113.4 (*J* = 23.6 Hz), 112.4 (*J* = 8.2 Hz), 45.9, 30.8. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{17}H_{12}FN_2O$ 279.0934; found 279.0925.

*8-Chloro-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ca**).* Yellow solid (80 mg, 90% yield), ethyl acetate/petroleum ether = 1:4. mp 162-163 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 8.0 Hz, 2H), 7.41-7.36 (m, 3H), 7.10 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.62 (d, *J* = 8.4 Hz, 1H), 6.34 (s, 1H), 3.94 (t, *J* = 7.8 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 2H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 145.1, 138.7, 132.7, 129.4, 128.6, 128.6, 127.9, 126.7, 126.4, 126.2, 114.2, 112.5, 45.8, 30.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}ClN_2O$ 297.0795; found 297.0783.

*8-Bromo-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3da**).* Yellow solid (101 mg, 99% yield), ethyl acetate/petroleum ether = 1:4. mp 150-151 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 2H), 7.41-7.34 (m, 3H), 7.25-7.22 (m, 1H), 7.14 (s, 1H), 6.55 (dd, *J* = 8.4 Hz, *J* = 3.2 Hz, 1H), 6.32 (s, 1H), 3.94-3.89 (m, 2H), 2.69-2.65 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 145.6, 138.6, 132.7, 131.6, 129.4, 129.0, 128.6, 127.1, 126.4, 115.2, 114.1, 112.9, 45.7, 30.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}BrN_2O$ 341.0290; found 341.0277.

*8-Methyl-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ea**).* Yellow solid (75 mg, 91% yield), ethyl acetate/petroleum ether = 1:4. mp 161-162 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (d, *J* = 7.2 Hz, 2H), 7.40-7.31 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.89 (s, 1H), 6.62 (d, *J* = 8.4 Hz, 2H), 6.43 (s, 1H), 3.95 (t, *J* = 8.0 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 144.2, 137.3, 133.2, 132.2, 129.7, 128.9, 128.5, 127.5, 126.2, 125.1, 115.7, 111.3, 45.7, 30.9, 20.6. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{18}H_{15}N_2O$ 275.1184; found 275.1171.

*8-Methoxy-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3fa**).* Yellow solid (63 mg, 72% yield), ethyl acetate/petroleum ether = 1:4. mp 138-139 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 7.6 Hz, 2H), 7.40-7.33 (m, 3H), 6.71 (dd, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H), 6.67-6.65 (m, 2H), 6.43 (s, 1H), 3.95 (t, *J* = 7.8 Hz, 2H), 3.78 (s, 3H), 2.69 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.6, 155.5, 140.1, 138.1, 133.1, 129.1, 128.5, 126.4, 126.3, 115.3, 113.7, 112.7, 112.3, 55.7, 45.9, 30.9. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{18}H_{15}N_2O_2$ 291.1134; found 291.1120.

*3-Oxo-5-phenyl-2,3-dihydro-1H-pyrazolo[1,2-a]cinnoline-8-carbonitrile (**3ga**).* Yellow solid (58 mg, 67% yield), ethyl acetate/petroleum ether = 1:4. mp 208-209 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 2H), 7.41-7.39 (m, 4H), 7.19 (s, 1H), 6.65 (d, *J* = 8.4 Hz, 1H), 6.25 (s, 1H), 3.95 (t, *J* = 8.0 Hz, 2H), 2.71 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 150.3, 139.1, 133.6, 132.3, 129.7, 129.1, 128.6, 126.4, 125.5, 118.8, 113.5, 111.2, 105.5,

45.5, 30.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{14}N_3O$ 288.1137; found 288.1124.

*5-Phenyl-8-(trifluoromethyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ha**).* Yellow solid (84 mg, 85% yield), ethyl acetate/petroleum ether = 1:4. mp 153-154 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49-7.47 (m, 2H), 7.41-7.34 (m, 4H), 7.23 (s, 1H), 6.70 (d, *J* = 8.4 Hz, 1H), 6.35 (s, 1H), 3.95 (t, *J* = 8.0 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 169.5, 149.4, 138.7, 132.6, 129.5, 128.6, 126.4, 126.4 (q, *J* = 4.0 Hz), 125.3, 124.7 (q, *J* = 32.0 Hz), 124.1 (q, *J* = 270.0 Hz), 123.2 (q, *J* = 3.8 Hz), 114.3, 111.0, 45.6, 30.7. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{13}F_3N_2NaO$ 353.0878; found 353.0863.

*10-Chloro-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ia**).* Yellow solid (63 mg, 71% yield), ethyl acetate/petroleum ether = 1:4. mp 70-71 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 7.2 Hz, 2H), 7.39-7.33 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 1H), 6.88 (d, *J* = 7.2 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 2H), 6.24 (s, 1H), 4.52 (t, *J* = 8.2 Hz, 2H), 2.70 (t, *J* = 8.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.8, 146.0, 137.2, 132.9, 132.0, 129.0, 128.5, 127.0, 126.0, 125.6, 117.8, 116.7, 49.8, 30.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}ClN_2O$ 297.0795; found 297.0782.

*10-Methyl-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ja**).* Yellow solid (67 mg, 81% yield), ethyl acetate/petroleum ether = 1:4. mp 118-119 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 7.2 Hz, 2H), 7.38-7.29 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 6.4 Hz, 1H), 6.80 (t, *J* = 7.2 Hz, 1H), 6.26 (s, 1H), 4.11 (t, *J* = 8.4 Hz, 2H), 2.68 (t, *J* = 8.4 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.9, 149.2, 135.8, 133.6, 133.4, 128.6, 128.4, 125.8, 125.2, 124.5, 122.8, 122.1, 118.1, 50.7, 30.4, 22.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}N_2O$ 277.1341; found 277.1329.

*9-Chloro-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ka**).* Yellow solid (66 mg, 74% yield), ethyl acetate/petroleum ether = 1:4. mp 196-197 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50-7.48 (m, 2H), 7.40-7.33 (m, 2H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.87 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 6.69 (s, 1H), 6.38 (s, 1H), 3.93 (t, *J* = 7.8 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.0, 147.7, 137.5, 134.7, 132.8, 129.2, 128.6, 127.5, 176.2, 123.6, 122.6, 114.6, 111.8, 45.7, 30.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}ClN_2O$ 297.0795; found 297.0783.

*9-Methyl-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3la**).* Yellow solid (68 mg, 82% yield), ethyl acetate/petroleum ether = 1:4. mp 190-191 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 7.6 Hz, 2H), 7.39-7.30 (m, 3H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.54 (s, 1H), 6.45 (s, 1H), 3.97 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.4, 146.6, 139.7, 136.3, 133.3, 128.8, 128.5, 126.8, 126.1, 123.3, 122.4, 115.8, 112.2, 45.6, 30.8, 22.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}N_2O$ 277.1341; found 277.1330.

*7, 10-Dimethyl-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ma**).* Yellow solid (44 mg, 51% yield), ethyl acetate/petroleum ether = 1:4. mp 180-181 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 7.2 Hz, 2H), 7.38-7.29 (m, 3H), 6.82 (d, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 7.6 Hz, 1H), 6.42 (s, 1H), 4.09 (t, *J* = 8.4 Hz, 2H), 2.68 (t, *J* = 8.2 Hz, 2H), 2.32 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.0, 150.1, 135.4, 133.6, 133.1, 132.4, 128.6, 128.4, 125.9, 124.1, 123.1, 119.6, 115.9, 50.8, 30.3, 22.0, 19.3. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{18}N_2NaO$ 313.1317; found 313.1303.

*8-Chloro-10-fluoro-5-phenyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3na**).*

Yellow solid (79 mg, 84% yield), ethyl acetate/petroleum ether = 1:4. mp 168-169 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47-7.45 (m, 2H), 7.41-7.37 (m, 3H), 6.89 (dd, *J* = 12.8 Hz, *J* = 2.0 Hz, 1H), 6.81 (s, 1H), 6.28 (s, 1H), 4.23 (t, *J* = 7.8 Hz, 2H), 2.69(t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.3, 148.7 (*J* = 244.0 Hz), 139.3, 132.7 (*J* = 8.1 Hz), 132.5, 129.6 (*J* = 2.4 Hz), 128.8 (*J* = 4.1 Hz), 128.6 (*J* = 2.3 Hz), 127.9 (*J* = 11.0 Hz), 126.3 (*J* = 2.1 Hz), 122.2 (*J* = 3.2 Hz), 117.2 (*J* = 26.7 Hz), 114.0 (*J* = 4.2 Hz), 48.3 (*J* = 15.0 Hz), 31.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}ClFN_2O$ 315.0700; found 315.0687.

*5-(4-Fluorophenyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ab**).* Yellow solid (66 mg, 78% yield), ethyl acetate/petroleum ether = 1:4. mp 141-142 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49-7.46 (m, 2H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.08-7.02 (m, 3H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.37 (s, 1H), 3.96 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.2, 163.1 (*J* = 247.3 Hz), 146.4, 136.4, 129.4, 129.3 (*J* = 3.3 Hz), 128.0 (*J* = 8.2 Hz), 126.6, 124.9, 122.7, 115.5 (*J* = 21.8 Hz), 115.2 (*J* = 1.6 Hz), 111.2, 45.6, 30.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}FN_2O$ 281.1090; found 281.1079.

*5-(4-Chlorophenyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ac**).* Yellow solid (75 mg, 84% yield), ethyl acetate/petroleum ether = 1:4. mp 189-190 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.4 Hz, 1H), 6.44 (s, 1H), 3.98 (t, *J* = 8.0 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 146.5, 136.2, 134.7, 131.6, 129.6, 128.8, 127.5, 126.9, 124.8, 122.8, 116.0, 111.3, 45.6, 30.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}ClN_2O$ 297.0795; found 297.0785.

*5-(4-Bromophenyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ad**).* Yellow solid

(97 mg, 95% yield), ethyl acetate/petroleum ether = 1:4. mp 139-140 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6, 1H), 6.92 (t, *J* = 7.4, 1H), 6.72 (d, *J* = 8.0, 1H), 6.45 (s, 1H), 3.98 (t, *J* = 8.0, 2H), 2.67 (t, *J* = 8.0, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 168.9, 150.3, 139.1, 133.7, 132.3, 129.7, 129.1, 128.6, 126.4, 125.5, 118.9, 113.5, 111.2, 45.5, 30.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}BrN_2O$ 341.0290; found 341.0275.

*5-(4-(Trifluoromethyl)phenyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ae**).* Yellow solid (90 mg, 91% yield), ethyl acetate/petroleum ether = 1:4. mp 182-183 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 1H), 7.07 (d, *J* = 7.2 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 6.53 (s, 1H), 3.99 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 146.8, 136.6 (*J* = 2.0 Hz), 135.8, 130.5 (q, *J* = 32.6 Hz), 130.1, 127.2, 126.4, 125.5 (q, *J* = 3.8 Hz), 124.5, 124.2 (q, *J* = 270.1 Hz), 117.6, 111.4, 45.8, 30.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{14}F_3N_2O$ 331.1058; found 331.1048.

*4-(3-Oxo-2, 3-dihydro-1H-pyrazolo[1, 2-a]cinnolin-5-yl)benzonitrile (**3af**).* Yellow solid (68 mg, 79% yield), ethyl acetate/petroleum ether = 1:4. mp 206-207 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.65 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.23 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.58 (s, 1H), 4.01 (t, *J* = 7.8 Hz, 2H), 2.69 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.8, 146.8, 137.6, 135.3, 132.3, 130.5, 127.5, 126.6, 124.3, 122.9, 118.9, 118.6, 112.0, 111.5, 45.8, 30.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{14}N_3O$ 288.1137; found 288.1126.

*5-(4-Nitrophenyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ag**).* Orange solid

(58 mg, 63% yield), ethyl acetate/petroleum ether = 1:4. mp 190-191 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8.8 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 7.2 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 6.63 (s, 1H), 4.03 (t, *J* = 7.8 Hz, 2H), 2.71 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.8, 147.6, 146.8, 139.4, 134.9, 130.7, 127.6, 126.7, 124.1, 123.9, 122.9, 119.3, 111.6, 45.9, 30.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}N_3O_3$ 308.1035; found 308.1024.

*5-(2-Bromophenyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ah**).* Yellow solid (91 mg, 89% yield), ethyl acetate/petroleum ether = 1:4. mp 177-178 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.57 (d, *J* = 7.6 Hz, 1H), 7.38 (dd, *J* = 7.2 Hz, *J* = 1.8 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.23 (td, *J* = 8.0 Hz, *J* = 2.0 Hz, 1H), 7.11(t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 6.0 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 5.83 (s, 1H), 3.71 (t, *J* = 8.4 Hz, 2H), 2.74 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.3, 148.0, 136.5, 134.7, 132.6, 130.7, 130.2, 129.6, 127.6, 125.8, 124.2, 123.0, 122.4, 116.6, 111.4, 47.5, 30.9. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{17}H_{12}BrN_2O$ 339.0133; found 339.0121.

*5-(3-Bromophenyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ai**).* Yellow solid (94 mg, 92% yield), ethyl acetate/petroleum ether = 1:4. mp 151-152 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.64 (s, 1H), 7.44 (t, *J* = 9.6 Hz, 2H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.92 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.46 (s, 1H), 3.98 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.7, 146.6, 132.8, 135.3, 131.8, 130.0, 129.8, 129.0, 127.1, 124.9, 124.7, 122.8, 122.7, 116.8, 111.4, 45.7, 30.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{14}BrN_2O$ 341.0290; found 341.0277.

*5-(4-Methoxyphenyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3aj**).* Yellow solid

(74 mg, 85% yield), ethyl acetate/petroleum ether = 1:4. mp 170-171 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, *J* = 8.4 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.04 (d, *J* = 7.2 Hz, 1H), 6.92-6.88 (m, 3H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.36 (s, 1H), 3.97 (t, *J* = 7.8 Hz, 2H), 3.82 (s, 3H), 2.67 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.5, 160.3, 146.3, 137.2, 128.9, 127.6, 126.5, 125.6, 125.5, 122.7, 114.0, 113.7, 111.2, 54.4, 45.4, 30.9. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{16}N_2NaO_2$ 315.1109; found 315.1093.

*5-(p-Tolyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ak**).* Yellow solid (77 mg, 93% yield), ethyl acetate/petroleum ether = 1:4. mp 150-151 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 6.41 (s, 1H), 3.96 (t, *J* = 8.0 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.3, 146.5, 139.1, 137.5, 130.3, 129.3, 129.1, 126.7, 126.2, 125.3, 122.7, 114.7, 111.2, 45.5, 30.9, 21.5. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{18}H_{15}N_2O$ 275.1184; found 275.1171.

*5-(o-Tolyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3al**).* Yellow solid (75 mg, 91% yield), ethyl acetate/petroleum ether = 1:4. mp 127-128 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.25 (m, 2H), 7.23-7.17 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.2 Hz, 1H), 6.85 (t, *J* = 7.2 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 5.81 (s, 1H), 3.73 (t, *J* = 8.4 Hz, 2H), 2.68 (t, *J* = 8.2 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.9, 147.5, 137.5, 136.0, 133.7, 130.0, 129.2, 128.9, 128.9, 126.0, 125.6, 124.6, 122.9, 115.8, 111.2, 47.1, 31.0, 19.9. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{18}H_{15}N_2O$ 275.1185; found 275.1172.

*5-(m-Tolyl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3am**).* Yellow solid (76 mg, 92% yield), ethyl acetate/petroleum ether = 1:4. mp 134-135 ℃. ^{1}H NMR (400 MHz, $CDCl_3$)

δ: 7.31 (d, *J* = 7.2 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.17-7.13 (m, 2H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.90 (t, *J* = 7.4 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.44(s, 1H), 3.97 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.4, 146.6, 138.1, 137.5, 133.1, 129.9, 129.3, 128.4, 126.8, 125.2, 123.5, 122.7, 115.5, 111.3, 45.6, 30.9, 21.7. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}N_2O$ 277.1341; found 277.1328.

*5-(Thiophen-2-yl)-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3an**).* Yellow solid (64 mg, 79% yield), ethyl acetate/petroleum ether = 1:4. mp 126-127 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, *J* = 4.8 Hz, 1H), 7.23 (d, *J* = 3.6 Hz, 1H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 1H), 7.03 (t, *J* = 4.6 Hz, 1H), 6.92 (t, *J* = 7.4 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.52 (s, 1H), 4.0 (t, *J* = 7.8 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.1, 146.1, 136.8, 132.0, 129.3, 127.7, 127.0, 126.4, 126.2, 125.1, 122.8, 114.7, 111.4, 45.2, 30.8. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{15}H_{13}N_2OS$ 269.0749; found 269.0736.

*5-Cyclohexyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ao**).* Yellow solid (58 mg, 72% yield), ethyl acetate/petroleum ether = 1:4. mp 96-97 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07-7.01 (m, 1H), 6.81 (s, 1H), 6.80 (s, 1H), 6.48 (d, *J* = 8.0 Hz, 1H), 5.71 (s, 1H), 3.67 (t, *J* = 8.0 Hz, 1H), 3.24 (t, *J* = 11.4 Hz, 1H), 2.69 (t, *J* = 8.4 Hz, 2H), 1.97 (d, *J* = 12.0 Hz, 2H), 1.80-1.70 (m, 3H), 1.44-1.33 (m, 2H), 1.27-1.14 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 146.7, 145.6, 128.4, 125.0, 124.3, 122.7, 110.8, 109.9, 46.4, 37.0, 31.9, 31.7, 26.5, 26.3. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{17}H_{19}N_2O$ 267.1497; found 267.1488.

*5-Isopropyl-1, 2-dihydro-3H-pyrazolo[1, 2-a]cinnolin-3-one (**3ap**).* Yellow solid (54 mg, 78% yield), ethyl acetate/petroleum ether = 1:4. mp 74-75 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.07-7.03 (m, 1H), 6.84-6.80 (m, 2H), 6.48 (d, *J* = 8.0 Hz, 1H), 5.75 (s, 1H), 3.68 (t, *J* = 8.4 Hz,

2H), 3.63-3.56 (m, 1H), 2.71(t, *J* = 8.4 Hz, 2H), 1.17 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.4, 146.6, 146.5, 128.5, 125.1, 124.2, 122.7, 110.8, 109.6, 46.4, 31.7, 27.5, 21.1. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{14}H_{15}N_2O$ 227.1184; found 227.1174.

8-Bromo-5-(4-bromophenyl)-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one ***(3dd)****.* Yellow solid (115 mg, 92% yield), ethyl acetate/petroleum ether = 1:4. mp 179-180 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.14 (s, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 6.32 (s, 1H), 3.94 (t, *J* = 8.0 Hz, 2H), 2.68 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 145.5, 137.5, 131.8, 131.7, 131.6, 129.1, 127.8, 126.7, 123.5, 115.2, 114.4, 112.9, 45.7, 30.6. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{13}Br_2N_2O$ 420.9374; found 420.9359.

8-Bromo-5-(p-tolyl)-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one ***(3dk)****.* Yellow solid (103 mg, 97% yield), ethyl acetate/petroleum ether = 1:4. mp 195-196 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 7.13 (s, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 6.29 (s, 1H), 3.92 (t, *J* = 7.8 Hz, 2H), 2.68 (t, *J* = 8.0 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 145.5, 139.6, 138.7, 131.3, 129.9, 129.3, 128.8, 127.3, 126.3, 115.2, 113.2, 112.8, 45.6, 30.8, 21.5. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{18}H_{16}BrN_2O$ 355.0446; found 355.0435.

5-(4-Bromophenyl)-9-methyl-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one ***(3ld)****.* Yellow solid (87 mg, 82% yield), ethyl acetate/petroleum ether = 1:4. mp 227-228 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 7.6 Hz, 1H), 6.55 (s, 1H), 6.45 (s, 1H), 3.98 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 146.5, 140.1, 135.2, 132.2, 131.6,

127.6, 126.9, 123.4, 122.7, 122.2, 116.2, 112.2, 45.7, 30.7, 22.0. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{18}H_{15}BrN_2NaO$ 377.0265; found 377.0254.

*9-Methyl-5-(p-tolyl)-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one (**3lk**).* Yellow solid (63 mg, 73% yield), ethyl acetate/petroleum ether = 1:4. mp 204-205 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.54 (s, 1H), 6.41 (s, 1H), 3.97 (t, *J* = 7.8 Hz, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.36 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 146.5, 139.4, 138.8, 136.4, 130.4, 129.2, 126.6, 126.0, 123.2, 122.6, 114.8, 112.1, 45.6, 30.9, 22.0, 21.5. HRMS (ESI) m/z: $[M - H]^-$ calcd for $C_{19}H_{17}N_2O$ 289.1341; found 289.1327.

*2,2-Dimethyl-5-phenyl-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one (**3oa**).* Yellow solid (84 mg, 96% yield), ethyl acetate/petroleum ether = 1:4. mp 187-188 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 5H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.22 (s, 1H), 3.66 (s, 2H), 1.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 147.8, 137.1, 133.0, 129.2, 128.9, 128.3, 126.5, 126.3, 124.2, 122.5, 115.6, 111.4, 59.9, 40.7, 23.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{19}H_{19}N_2O$ 291.1497; found 291.1484.

*5-(4-Bromophenyl)-2,2-dimethyl-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one (**3od**).* Yellow solid (107 mg, 97% yield), ethyl acetate/petroleum ether = 1:4. mp 192-193 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.13 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.22 (s, 1H), 3.67 (s, 2H), 1.29 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7, 147.7, 136.0, 132.0, 131.5, 129.5, 128.0, 126.5, 123.9, 122.9, 122. 6, 116.0, 111. 5, 59.8, 40.7, 23.8. HRMS (ESI) m/z: [M

+ H]$^+$ calcd for $C_{19}H_{18}BrN_2O$ 369.0603; found 369.0587.

*2,2-Dimethyl-5-(4-(trifluoromethyl)phenyl)-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one (**3oe**).* Yellow solid (96 mg, 90% yield), ethyl acetate/petroleum ether = 1:4. mp 146-147 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.4Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.29 (s, 1H), 3.68 (s, 2H), 1.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 147.8, 136.5 (q, *J* = 1.6 Hz), 135.5, 130.4 (q, *J* = 32.3 Hz), 129.9, 126.8, 126.7, 125.3 (q, *J* = 4.0 Hz), 124.2 (q, *J* = 270.7 Hz), 123.6, 122.6, 117.4, 111.5, 59.9, 40.7, 23.8. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{20}H_{18}F_3N_2O$ 359.1371; found 359.1356.

*4-(2,2-Dimethyl-3-oxo-2,3-dihydro-1H-pyrazolo[1,2-a]cinnolin-5-yl)benzonitrile (**3of**).* Yellow solid (86 mg, 91% yield), ethyl acetate/petroleum ether = 1:4. mp 190-191 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 1H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.36 (s, 1H), 3.70 (s, 2H), 1.30 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 147.9, 137.5, 135.0, 132.1, 130.3, 127.1, 126.9, 123.3, 122.6, 118.9, 118.4, 111.9, 111.6, 59.9, 40.6, 23.8. HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{20}H_{18}N_3O$ 316.1450; found 316.1439.

*2,2-Dimethyl-5-(thiophen-2-yl)-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one (**3on**).* Yellow solid (69 mg, 78% yield), ethyl acetate/petroleum ether = 1:4. mp 171-172 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 5.2 Hz, 1H), 7.15-7.09 (m, 2H), 7.01 (t, *J* = 4.4 Hz, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.85 (t, *J* = 7.6 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 6.38 (s, 1H), 3.70 (s, 2H), 1.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 147.5, 136.0, 131.4, 129.2, 127.4, 126.7, 126.6, 126.0, 124.0, 122.4, 115.2, 111.5, 58.9, 40.6, 24.1. HRMS (ESI) m/z: [M + H]$^+$ calcd

for $C_{17}H_{17}N_2OS$ 297.1062; found 297.1051.

*5-Cyclohexyl-2,2-dimethyl-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one (**3oo**).* Yellow solid (63 mg, 71% yield), ethyl acetate/petroleum ether = 1:4. mp 103-104 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-7.00 (m, 1H), 6.82-6.79 (m, 2H), 6.43 (d, *J* = 7.6 Hz, 1H), 5.66 (s, 1H), 3.39 (s, 2H), 3.30 (t, *J* = 11.4 Hz, 1H), 1.92 (d, *J* = 12.0 Hz, 2H), 1.80-1.70 (m, 3H), 1.44-1.33 (m, 2H), 1.28 (s, 6H), 1.26-1.16 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.77, 146.8, 145.4, 128.3, 124.8, 124.0, 122.6, 110.9, 109.1, 60.3, 41.3, 36.6, 31. 9, 26.5, 26.4, 23.4. HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{24}N_2NaO$ 319.1786; found 319.1775.

*5-Isopropyl-2,2-dimethyl-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one (**3op**).* Yellow oli (56 mg, 73% yield), ethyl acetate/petroleum ether = 1:4. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-7.44 (m, 1H), 6.80-6.77 (m, 2H), 6.44 (d, *J* = 8.0 Hz, 1H), 5.71 (s, 1H), 3.70-3.62 (m, 1H), 3.40 (s, 2H), 1.29 (s, 6H), 1.15 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 146.9, 146.3, 128.5, 124.9, 123.9, 122.6, 110.9, 109.1, 60.3, 41.3, 29.8, 27.0, 23.4, 21.0. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{16}H_{21}N_2O$ 257.1654; found 257.1642.

3. Gram-Scale Synthesis of 3aa. To a solution of compound **1a** (324 mg, 2.0 mmol) and compound **2a** (588 mg, 3.0 mmol) in DCE (14 mL) were added $[RuCl_2(p\text{-cymene})]_2$ (122.5 mg, 0.2 mmol) and $Zn(OTf)_2$ (727 mg, 2.0 mmol). The reaction mixture was stirred at 100 ℃ on a heating block for 10 min. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified using column chromatography to afford the compound **3aa** as a yellow solid (417 mg, 80% yield).

4. Procedure for the Synthesis of Compound 4. To a solution of compound **3aa** (52.4 mg, 0.2 mmol) in toluene (2 mL) was added Lawesson's reagent (162 mg, 0.4 mmol). The

reaction mixture was stirred at 100 ℃ for 2 h. After cooling to room temperature, water (5 mL) was added and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried and concentrated under reduced pressure. The residue was purified using preparative TLC to afford the compound **4**.

*5-Phenyl-1,2-dihydro-3H-pyrazolo[1,2-a]cinnoline-3-thione (**4**).* Yellow solid (30 mg, 54% yield), dichloromethane/petroleum ether = 1:2. mp 224-225 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 6.8 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.64 (s, 1H), 4.00 (t, *J* = 8.2 Hz, 2H), 3.29 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.3, 146.3, 138.2, 132.8, 129.9, 128.6, 128.4, 127.2, 126.3, 123.7, 122.9, 121.0, 110.8, 47.4, 44.2. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{15}N_2S$ 279.0956; found 279.0968.

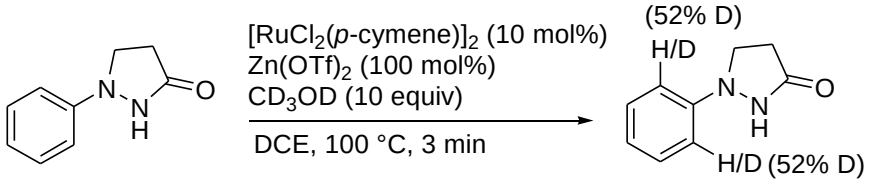
5. Procedure for the Synthesis of Compound 5. To a solution of **3da** (68 mg, 0.2 mmol) in THF/H_2O (5 mL) was added $Pd(PPh_3)_4$ (185 mg, 0.16 mmol), and K_2CO_3 (248 mg, 1.8 mmol). After 1 h at 45 ℃ in an oil bath, phenylboronic acid (30 mg, 0.24 mmol) was added. The resulting mixture was stirred at 65 ℃ in an oil bath for 8 h under N_2. After cooling to room temperature, water (5 mL) was added and the mixture was extracted with ethyl acetate (3 × 5 mL). The combined organic layers were dried and concentrated under reduced pressure followed by silica gel column chromatography purification to give the coupling product **5**.

*5,8-Diphenyl-1,2-dihydro-3H-pyrazolo[1,2-a]cinnolin-3-one (**5**).* Yellow solid (55 mg, 81% yield), ethyl acetate/petroleum ether = 1:4. mp 191-192 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55-7.52 (m, 4H), 7.45-7.32 (m, 7H), 7.30 (s, 1H), 6.79 (d, *J* = 8.4 Hz, 1H), 6.51 (s, 1H), 4.02 (t, *J* = 7.8 Hz, 2H), 2.72 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 145.9, 140.2,

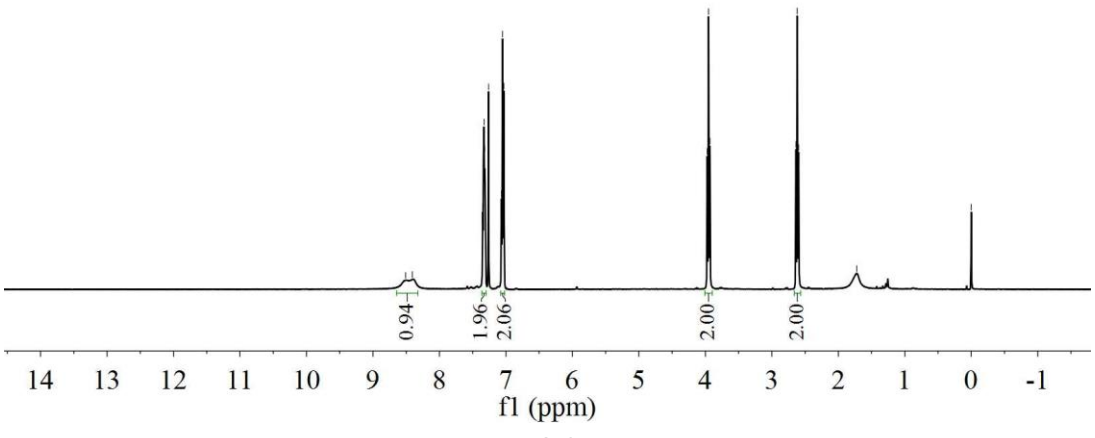
137.7, 135.8, 133.1, 129.1, 128.9, 128.5, 127.9, 127.3, 126.7, 126.3, 125.5, 125.4, 115.5, 111.7, 45.8, 30.9. HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{23}H_{19}N_2O$ 339.1497; found 339.1487.

6. H/D Exchange Experiments

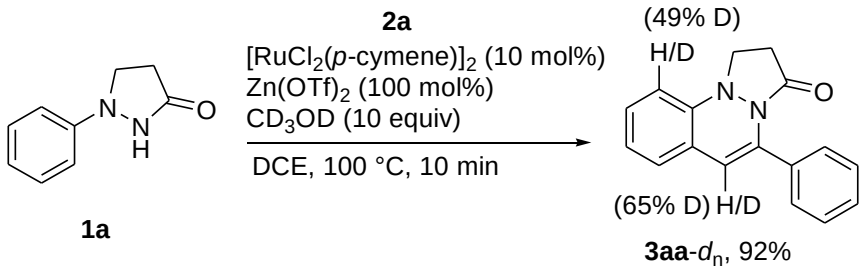
To a solution of *N*-phenylpyrazolidin-3-one **1a** (49 mg, 0.3 mmol) in DCE (2 mL) and CD_3OD (0.122 mL, 3 mmol) were added $[RuCl_2(p\text{-cymene})]_2$ (18.4 mg, 0.03 mmol) and $Zn(OTf)_2$ (109 mg, 0.3 mmol). The reaction mixture was stirred at 100 ℃ on a heating block for 3 min. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified using column chromatography (ethyl acetate/petroleum ether = 1:2) to afford **1a**-d_n in 80% yield. Upon analyzing the ^1H NMR spectrum of the product, the deuteration percentage was determined as 52%.

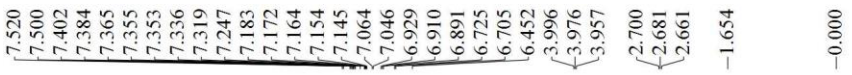


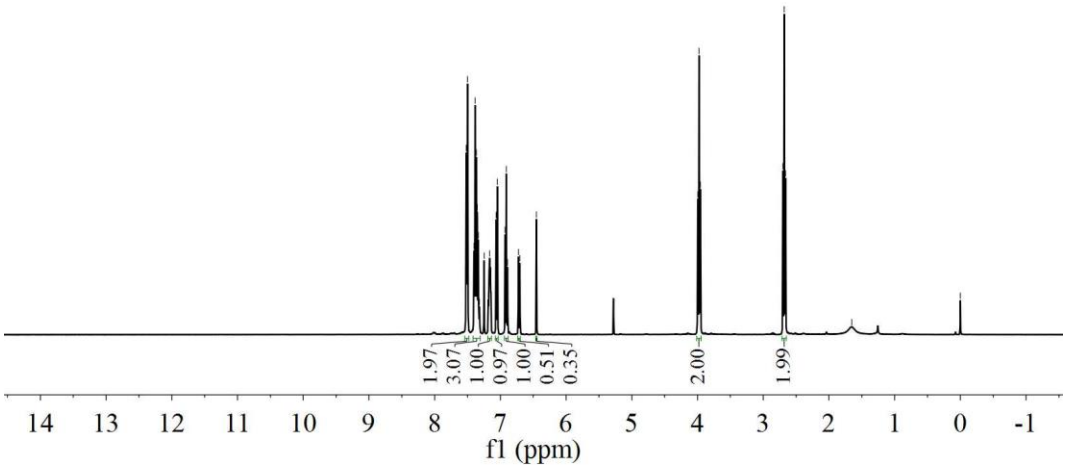
1a **1a**-$d_{n,}$ 80%



To a solution of pheylpyrazolidin-3-one **1a** (49 mg, 0.3 mmol) and sulfoxonium ylides **2** (88 mg, 0.45 mmol) in DCE (2 mL) and CD_3OD (0.122 mL, 3 mmol) were added $[RuCl_2(p\text{-cymene})]_2$ (18.4 mg, 0.03 mmol) and $Zn(OTf)_2$ (109 mg, 0.3 mmol). The reaction mixture was stirred at 100 ℃ on a heating block for 10 min. After cooling to room temperature, the solvent was removed in vacuo and the residue was purified using column chromatography (ethyl acetate/petroleum ether = 1:4) to afford **3aa**-d_n in 92% yield. Upon analyzing the ^1H NMR spectrum of the product, the deuteration percentage was determined as 65%.



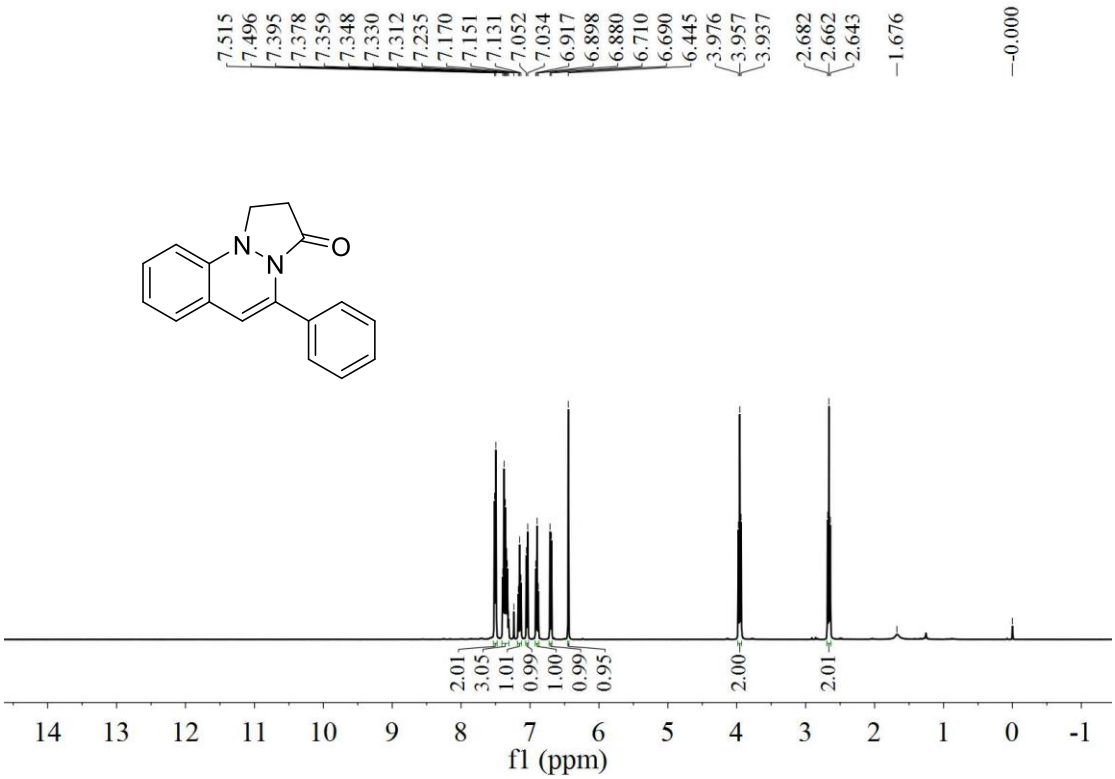




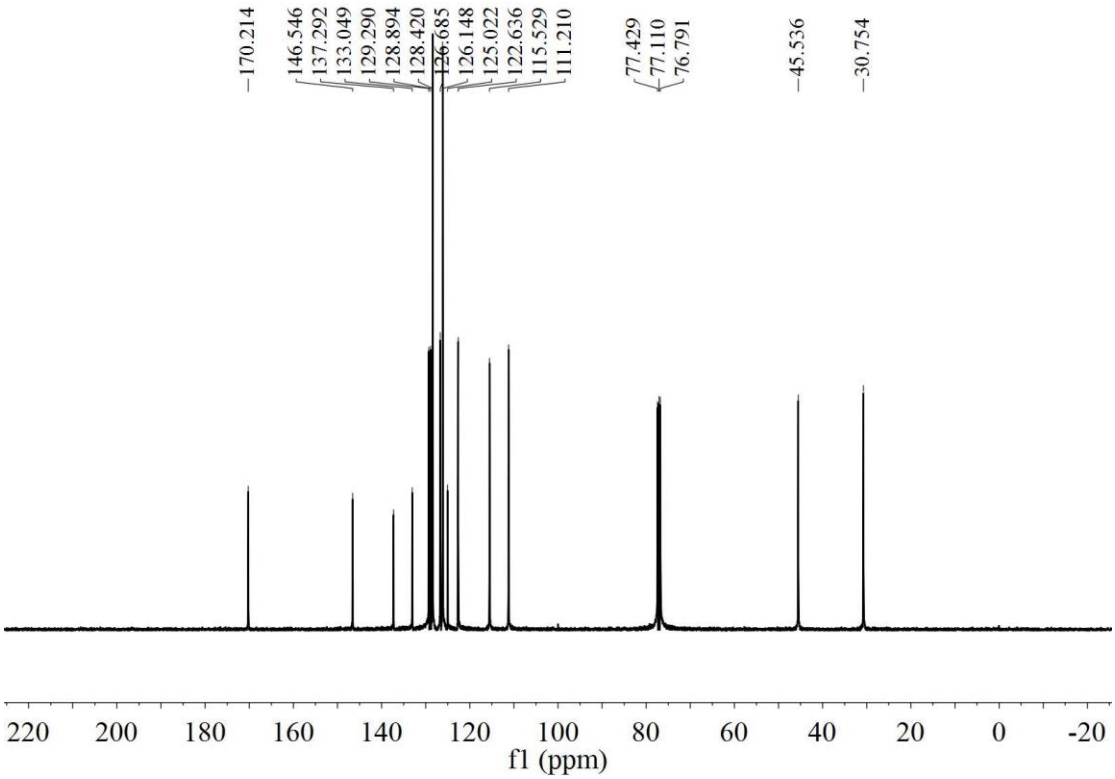
7. References

(1) Zhang, Z.; Jiang, H.; Huang, Y. *Org. Lett.* **2014**, *16*, 5976-5979.

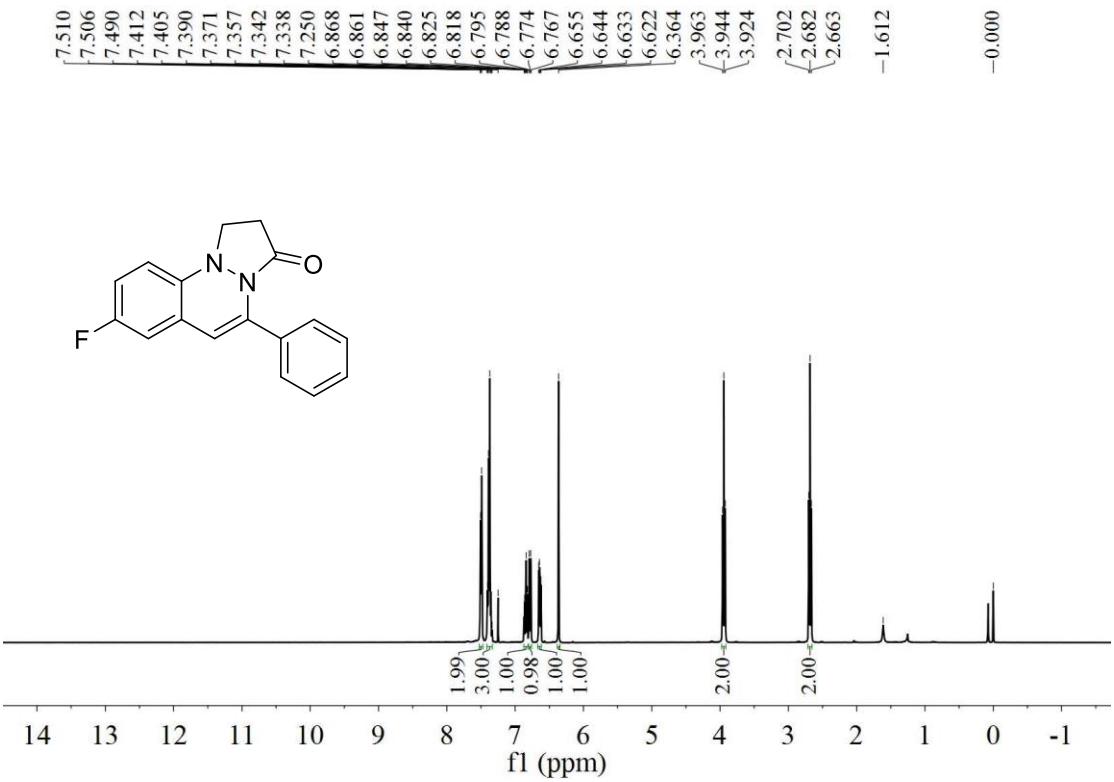
(2) Zhu, S.; Shi, K.; Zhu, H.; Jia, Z.-K.; Xia, X.-F.; Wang, D.; Zou, L.-H. *Org. Lett.* **2020**, *22*, 1504-1509.



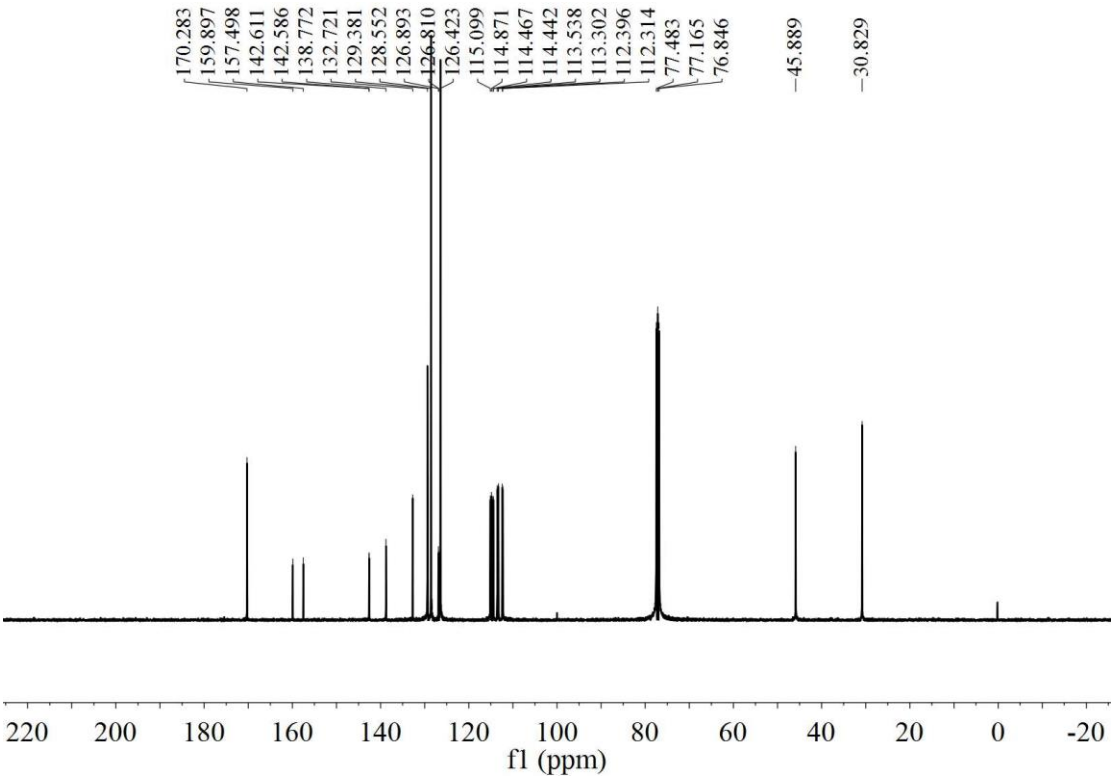
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3aa**



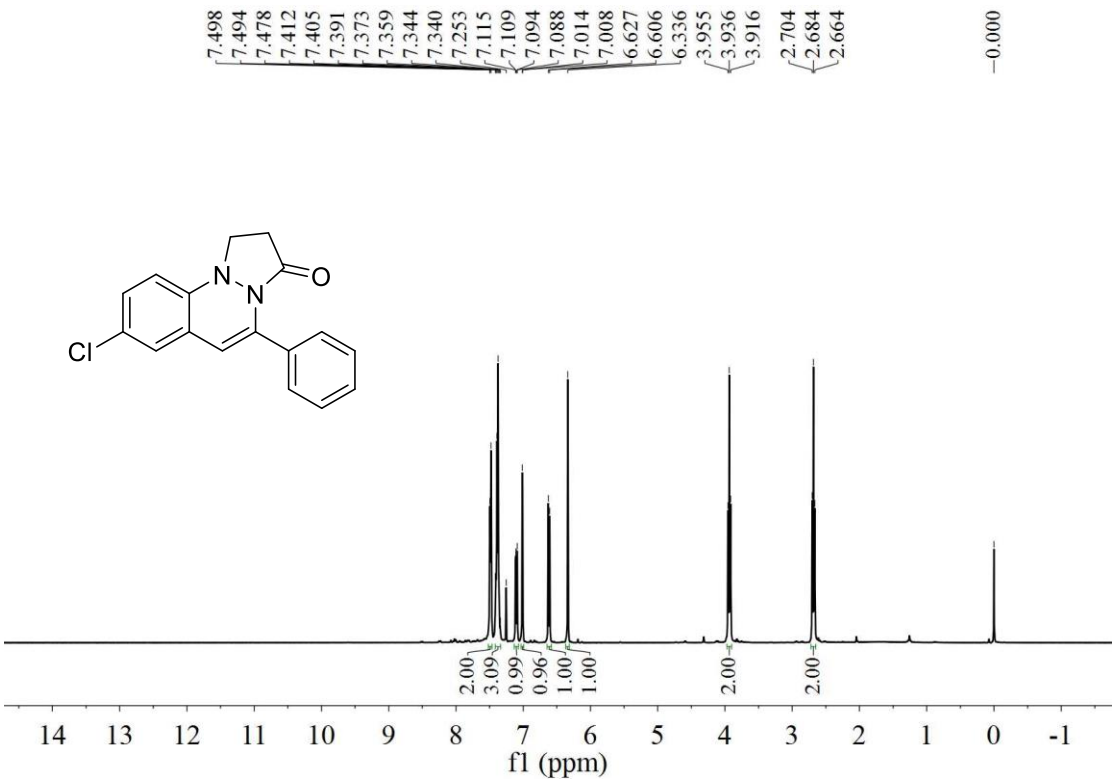
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3aa**



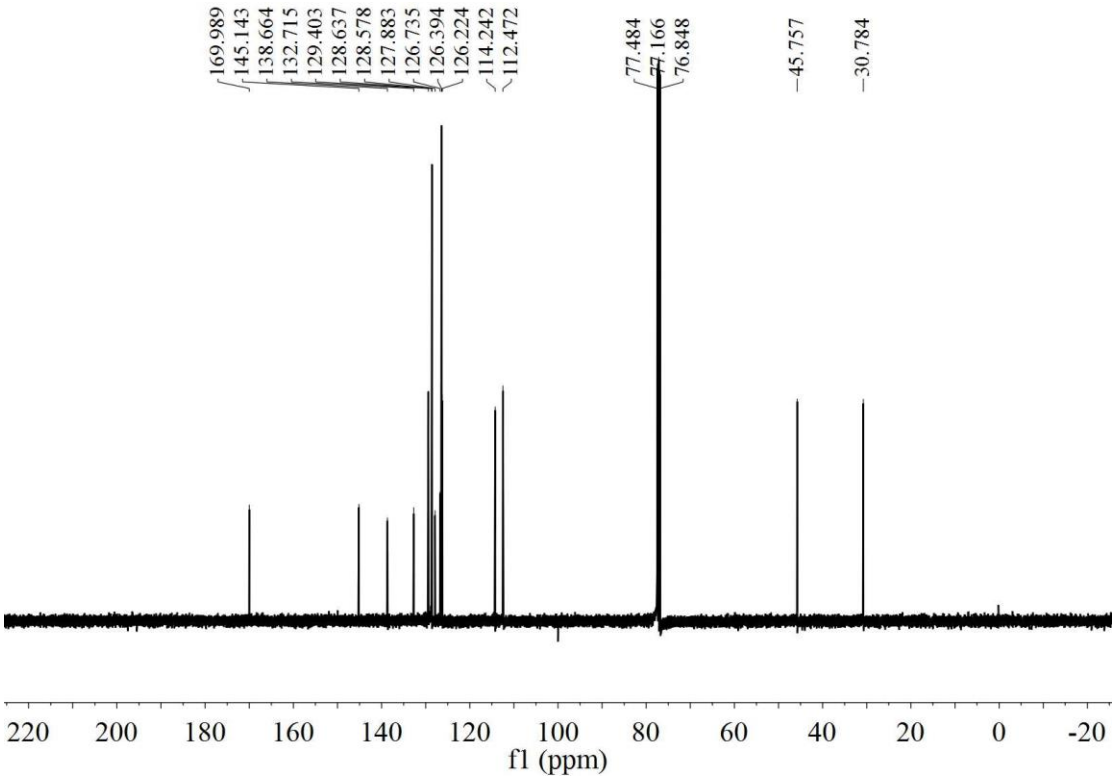
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ba**



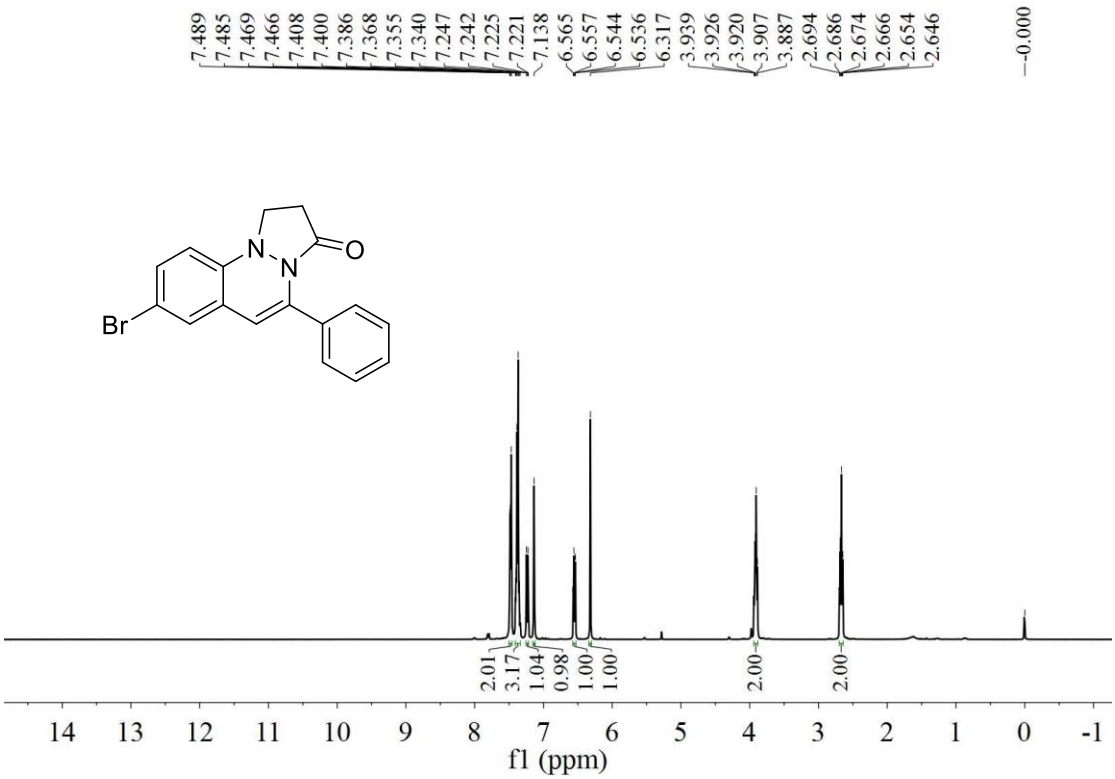
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ba**



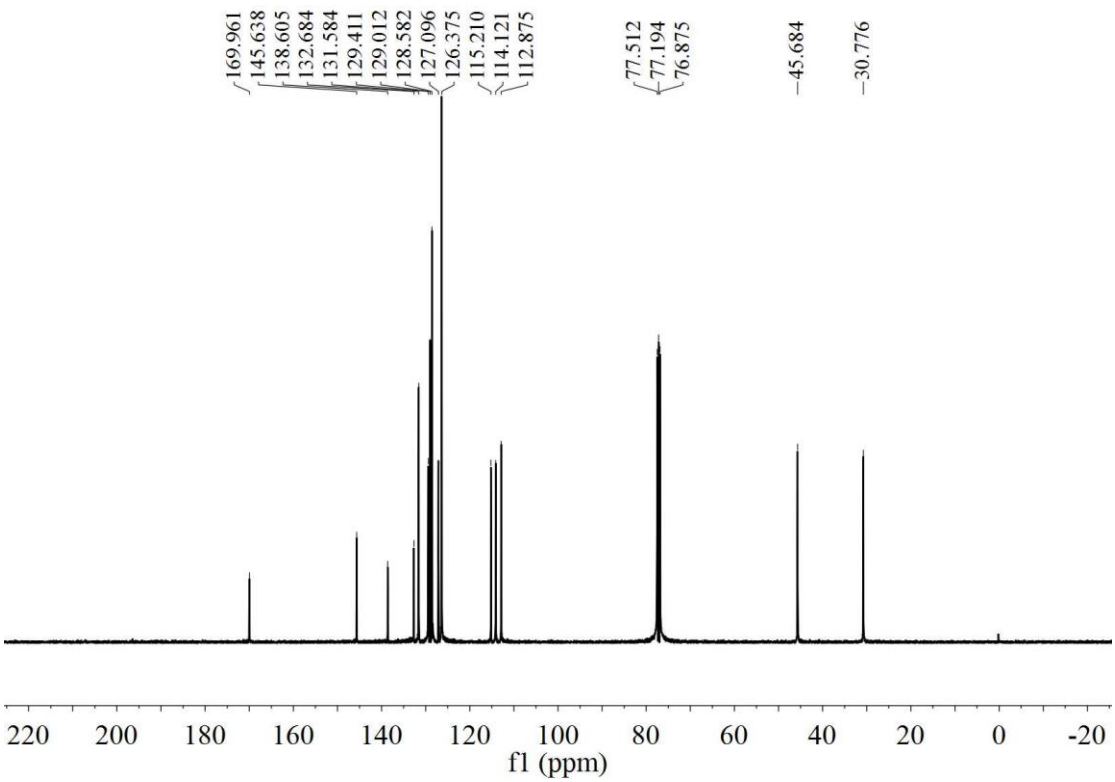
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ca**



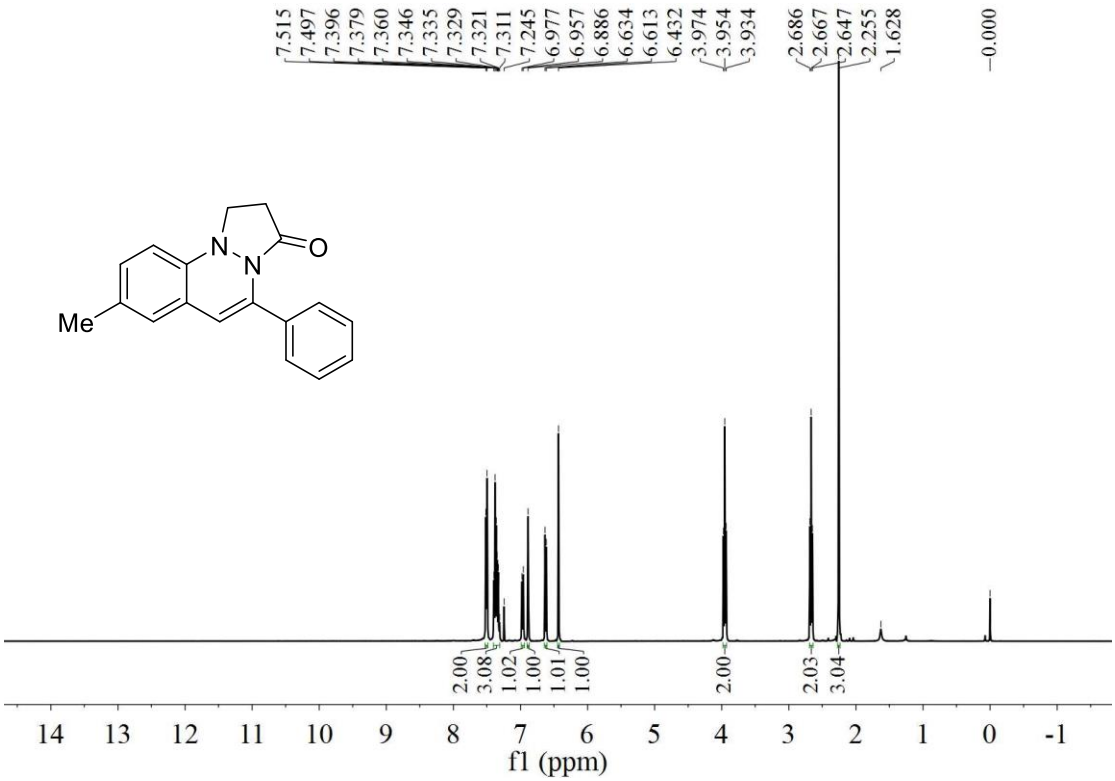
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ca**



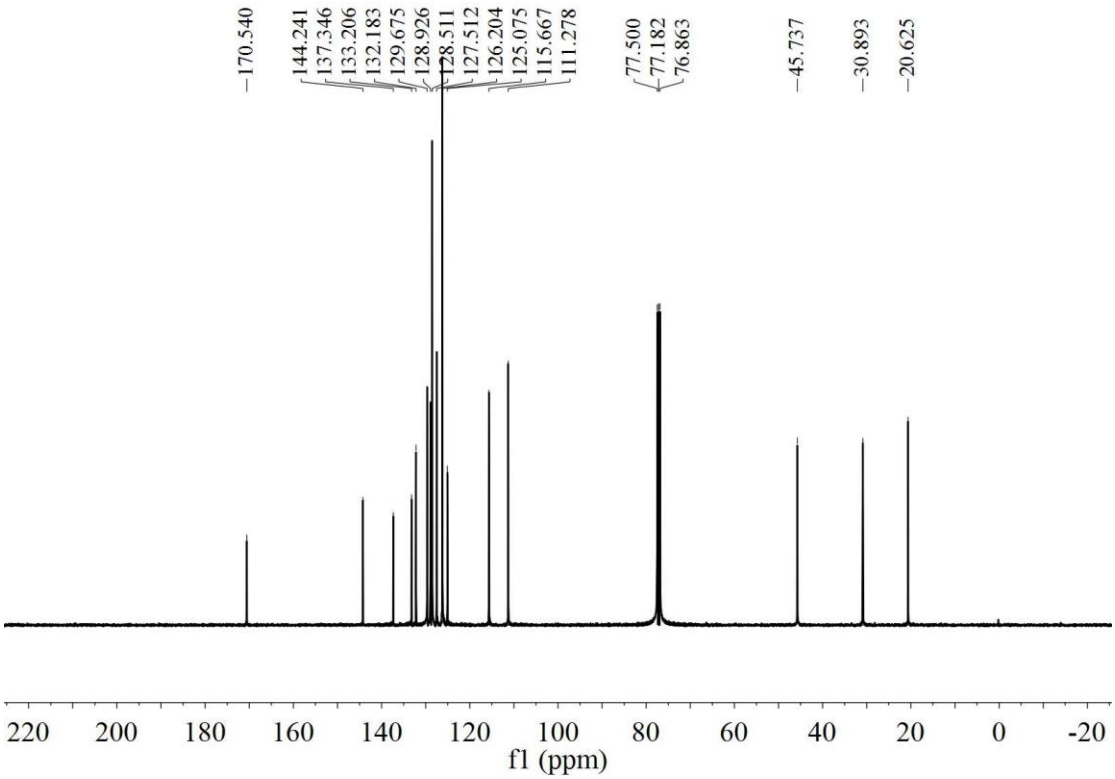
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3da**



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3da**



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ea**



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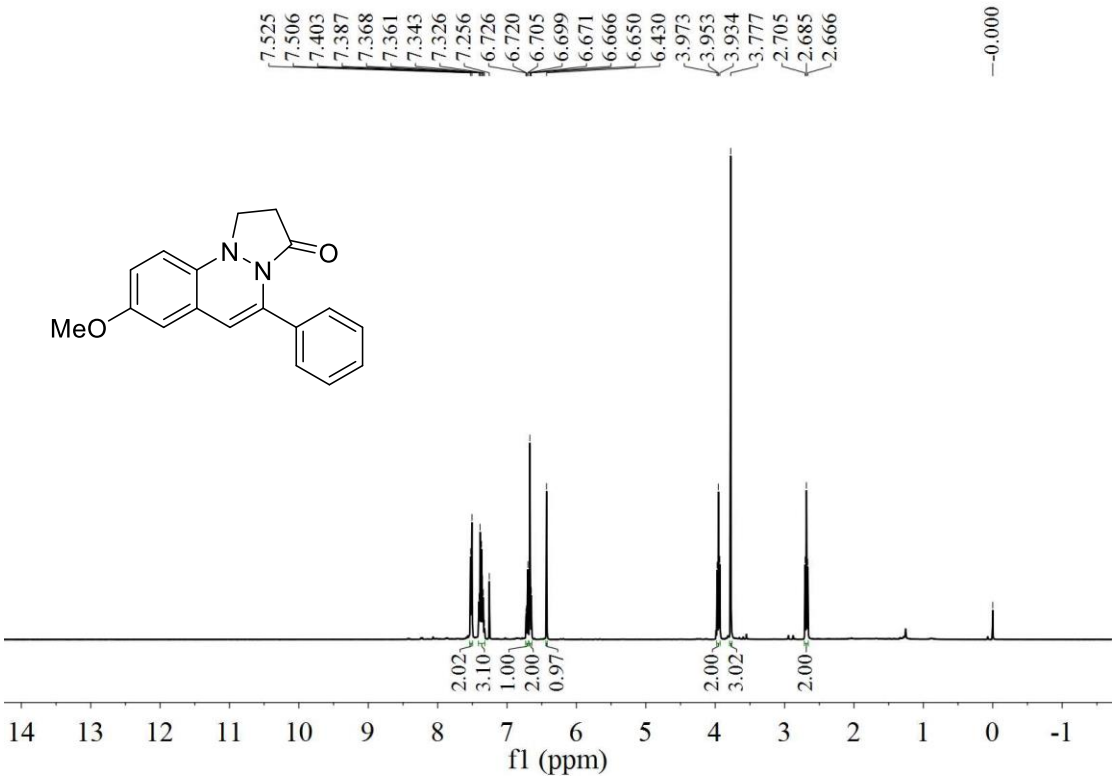
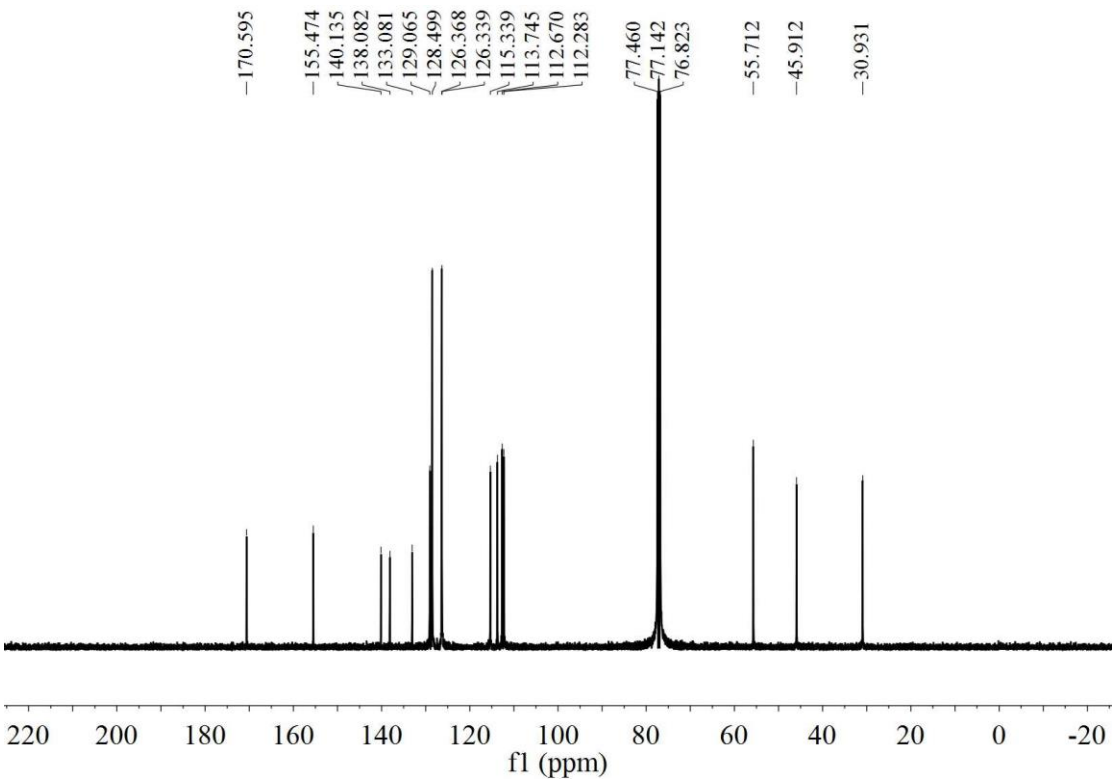
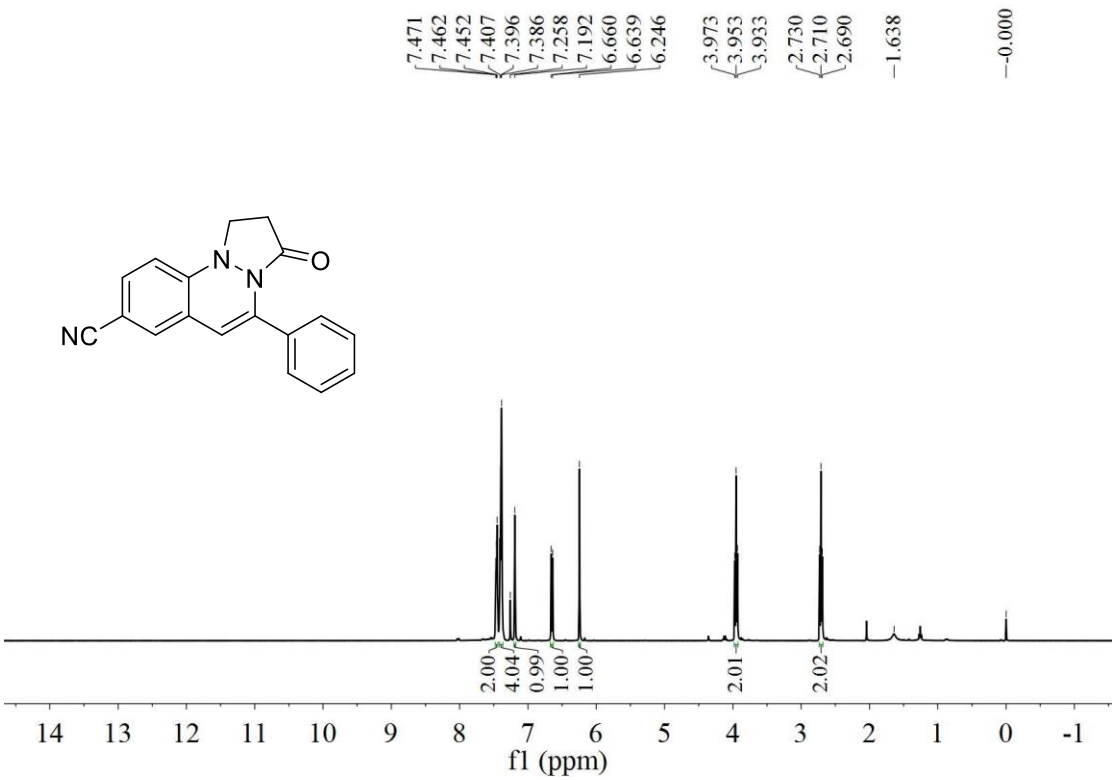


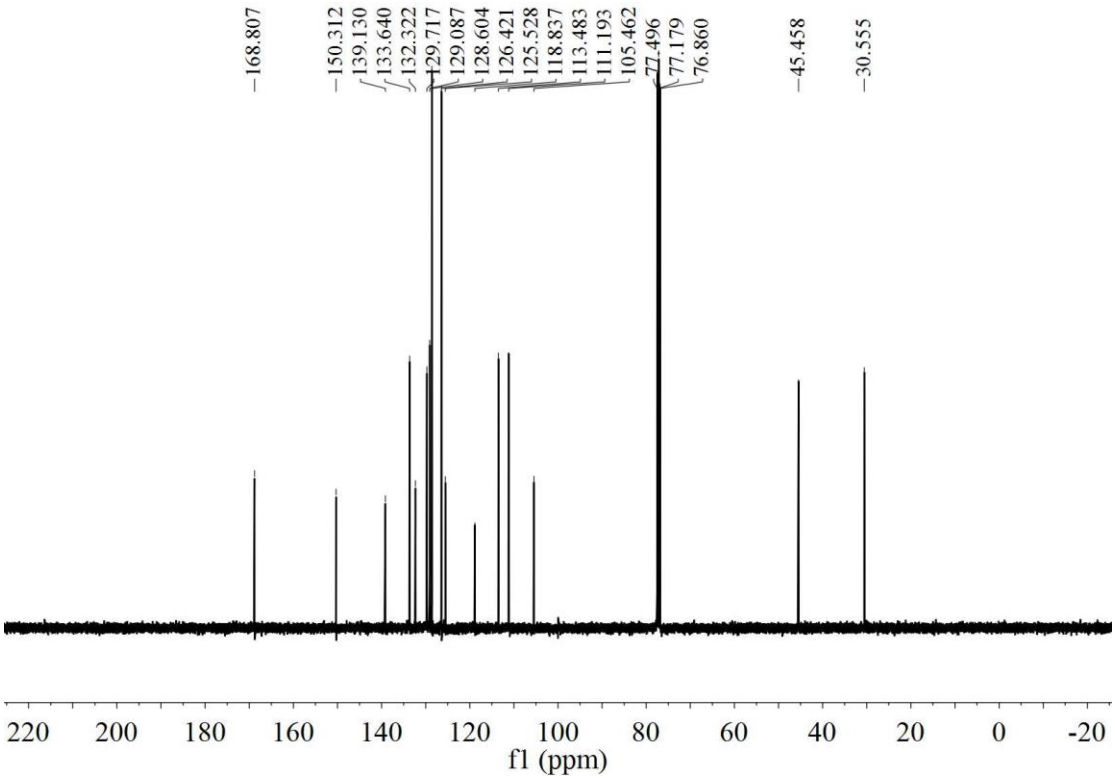
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3fa**



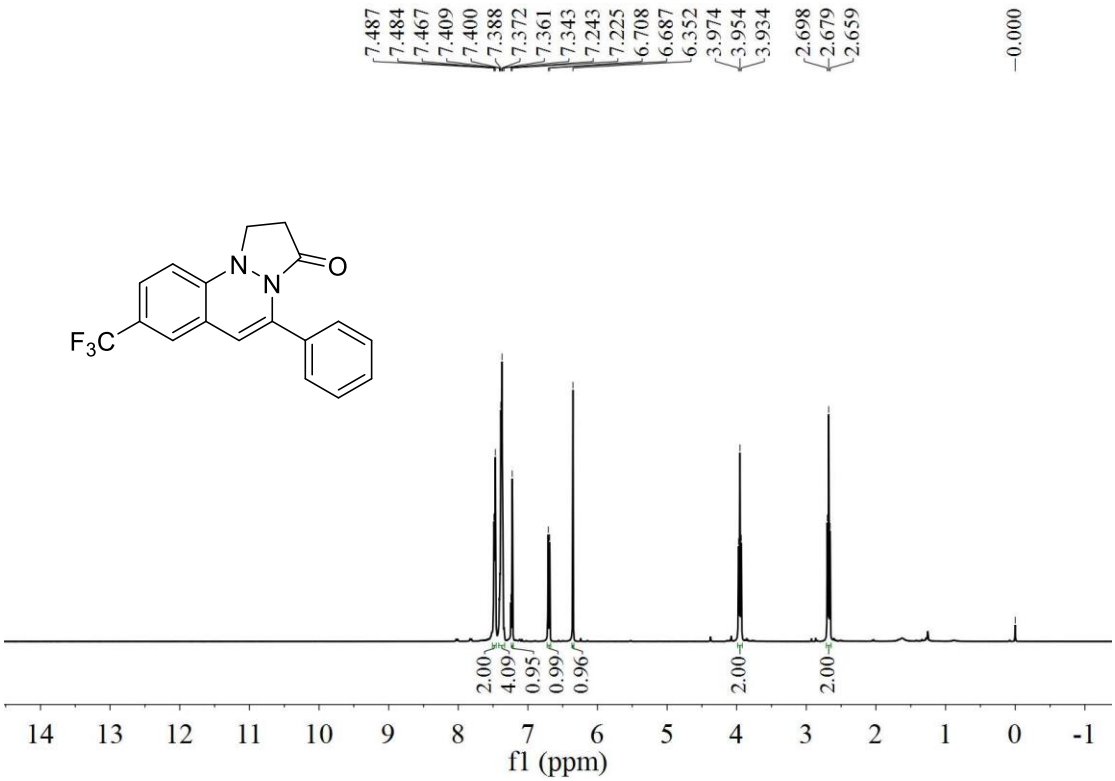
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3fa**



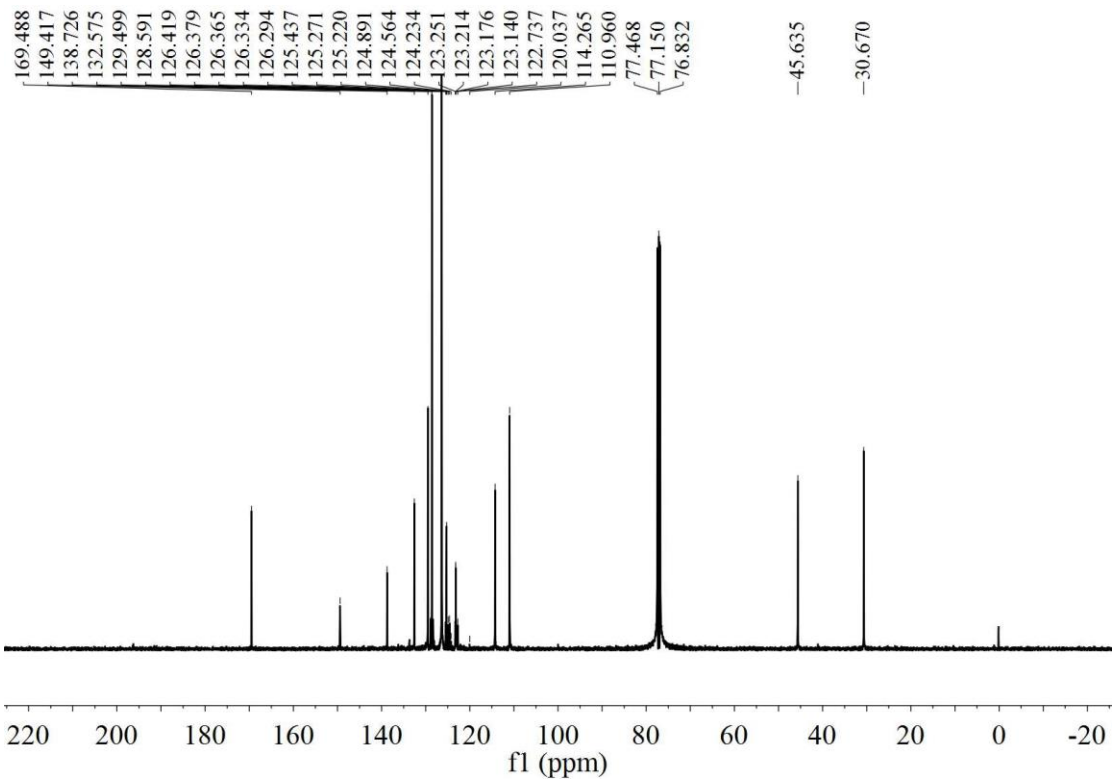
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ga**



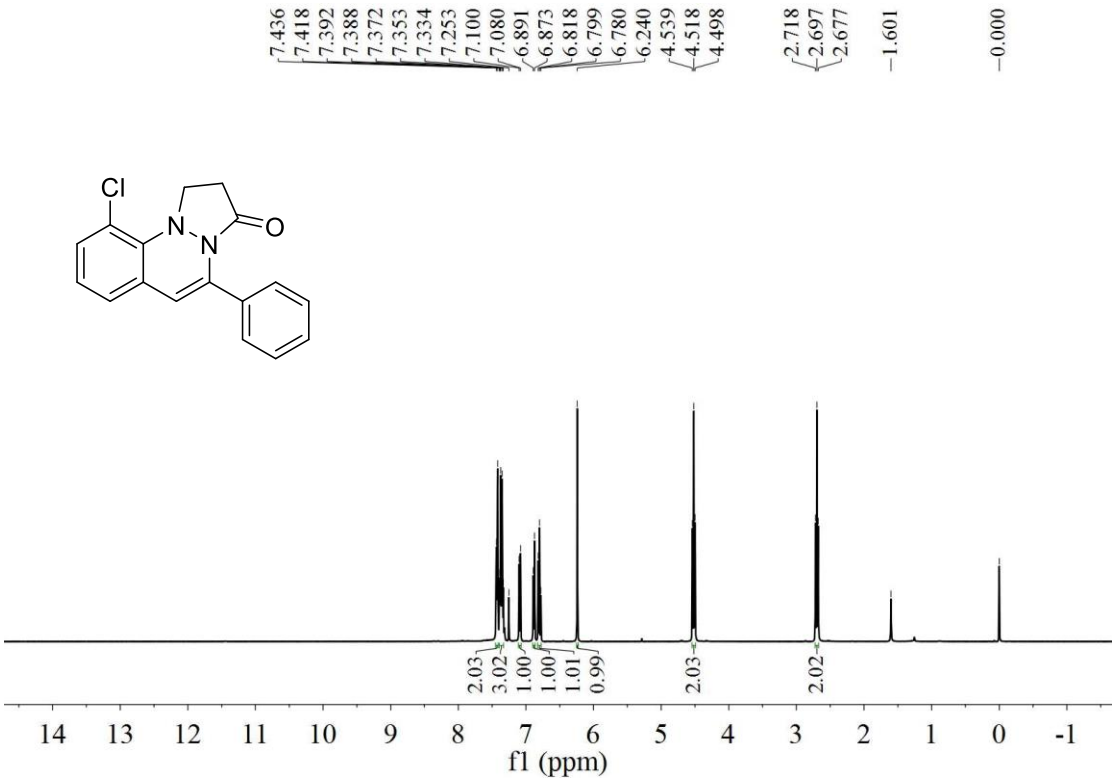
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ga**



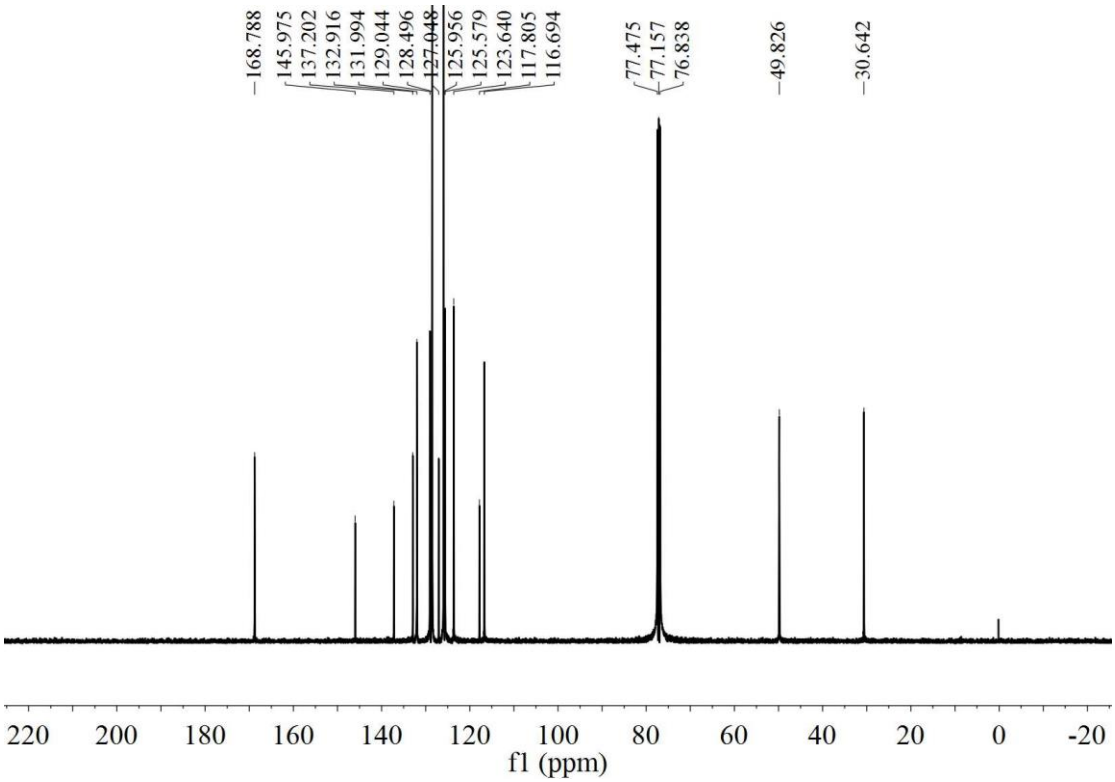
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ha**



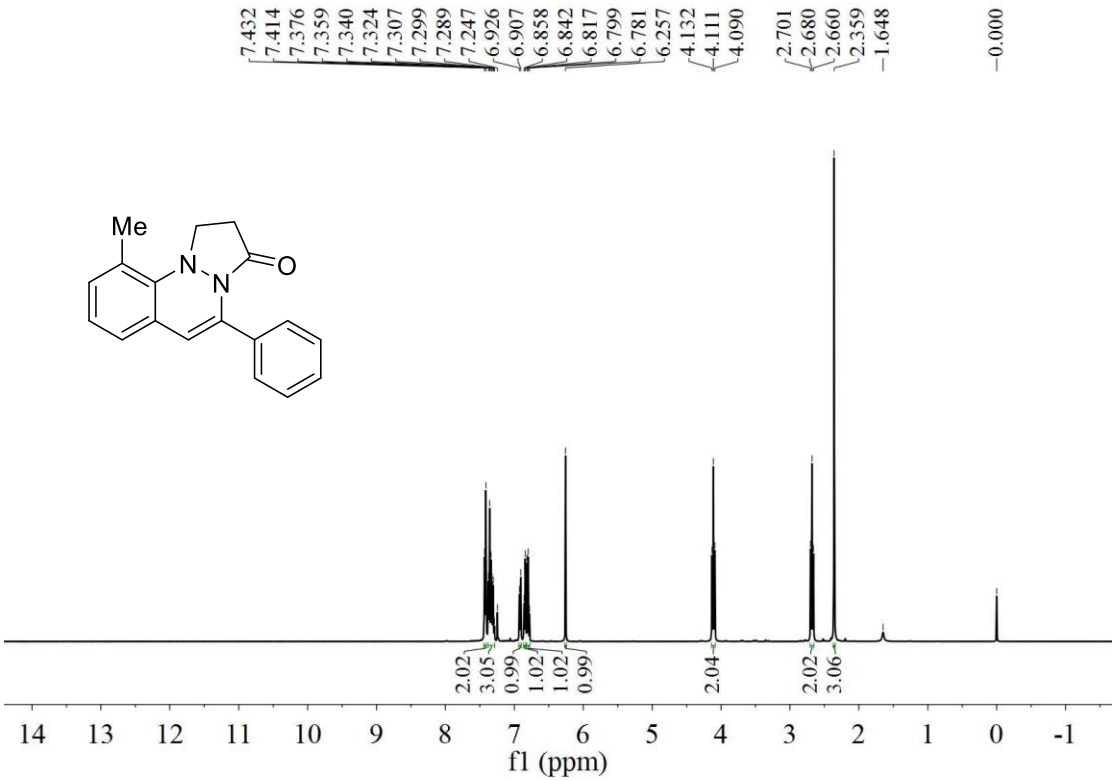
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ha**



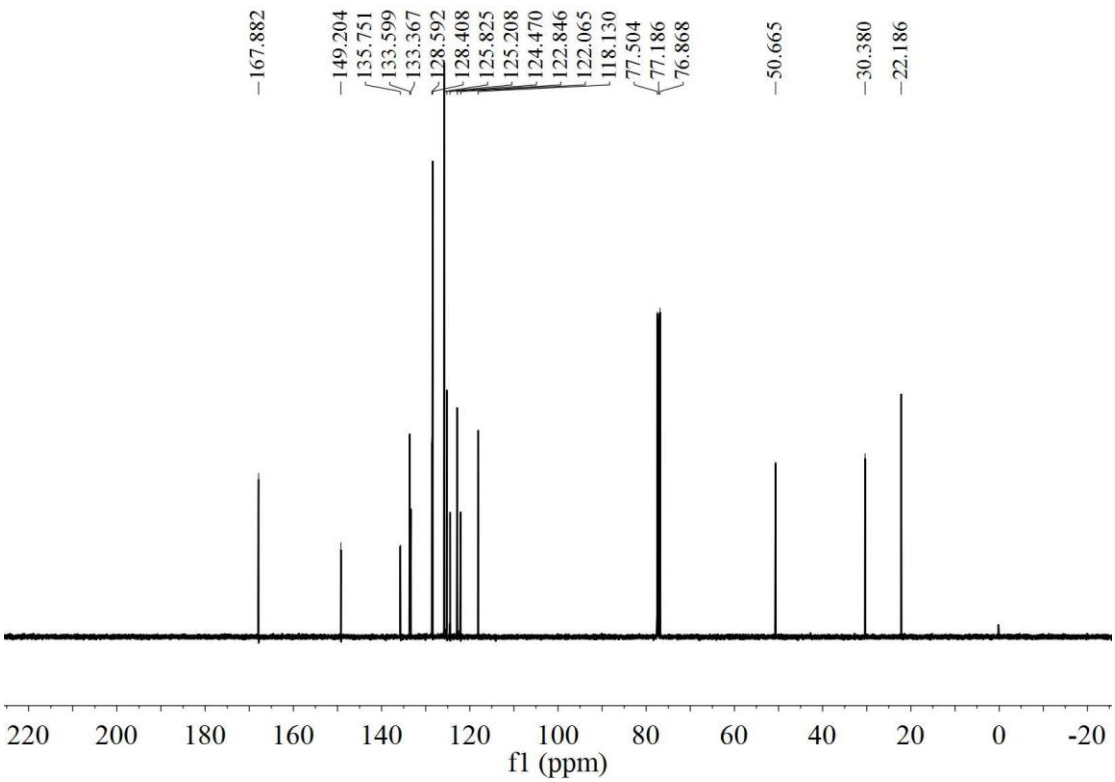
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ia**



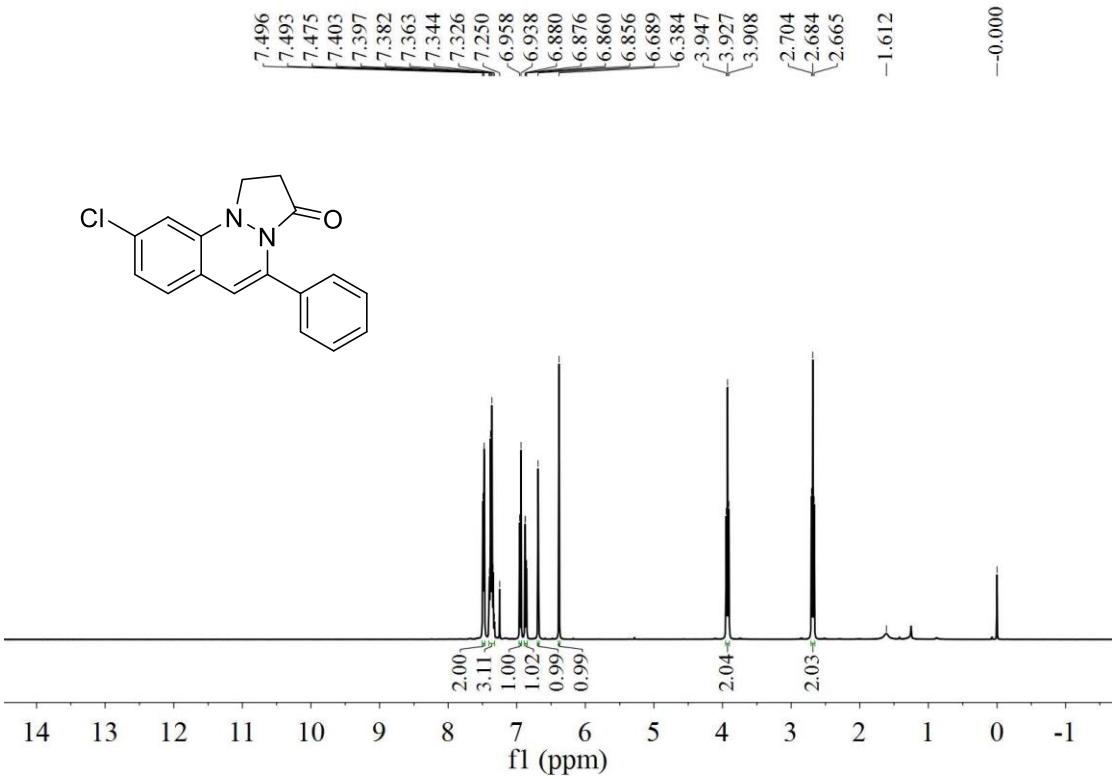
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ia**



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ja**



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ja**



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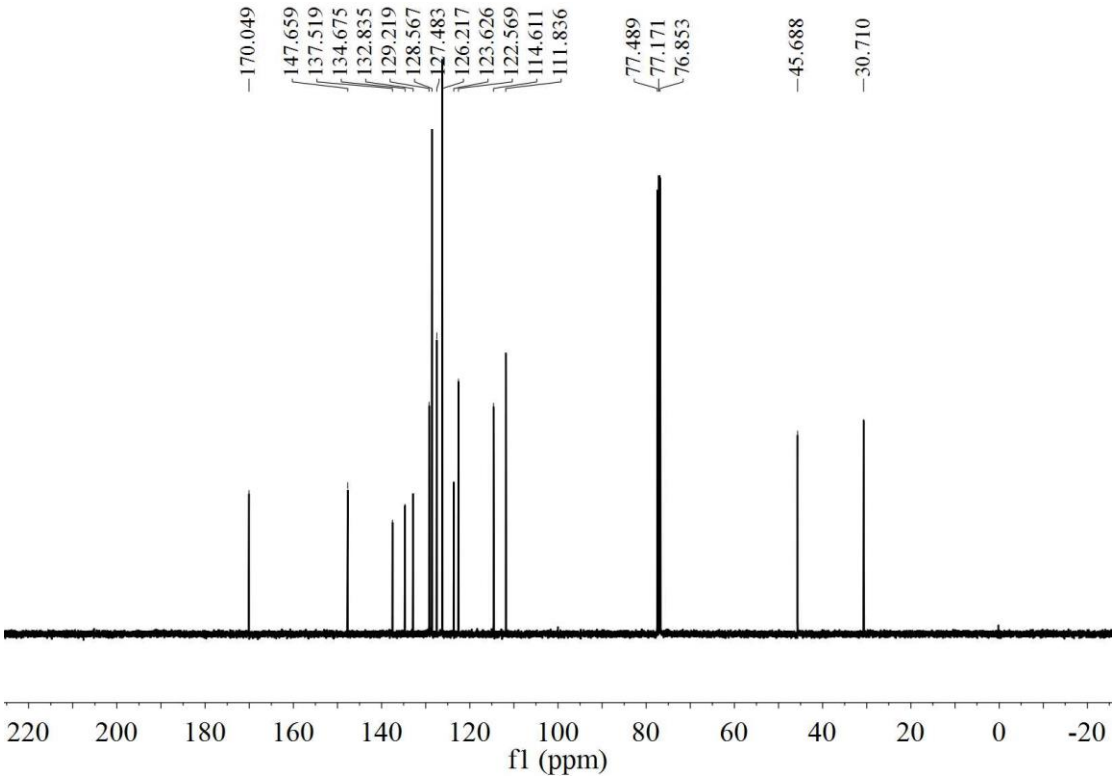
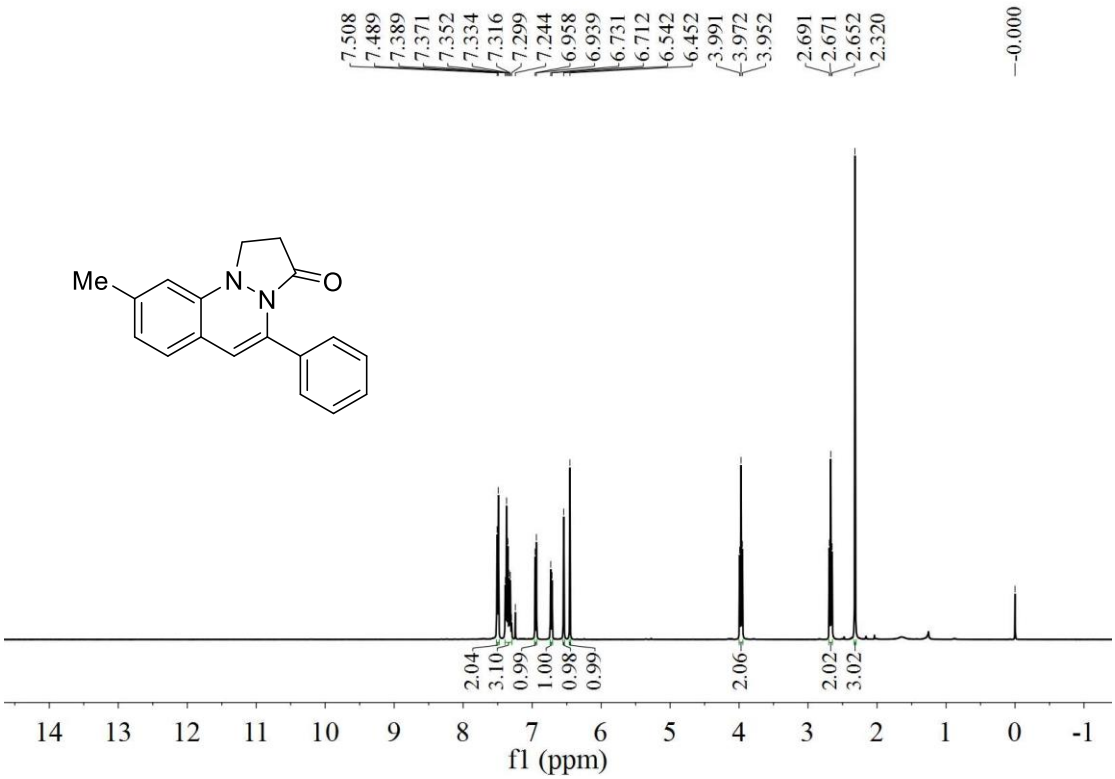
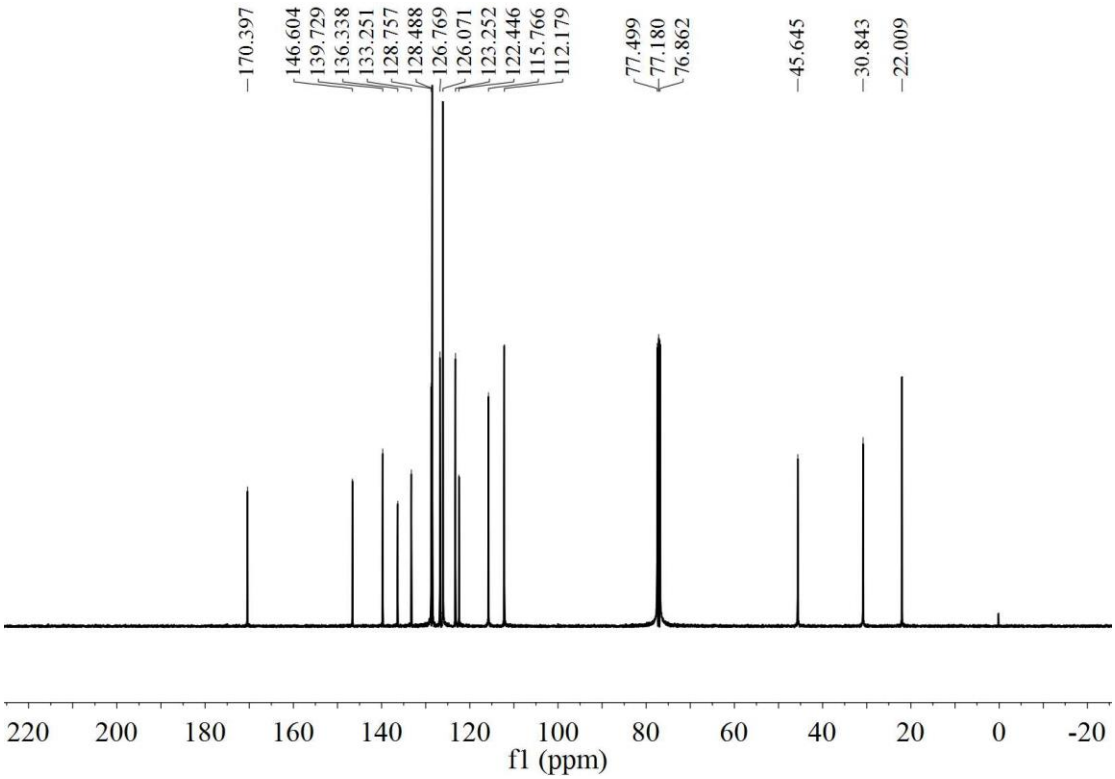


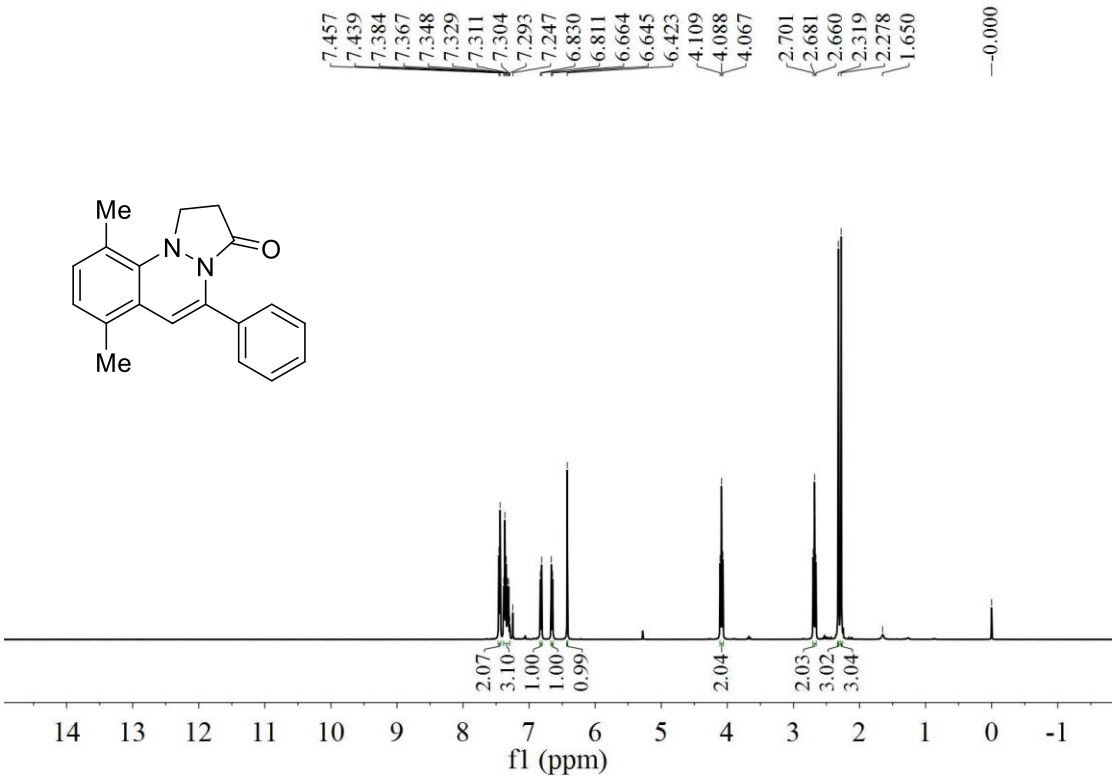
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ka**



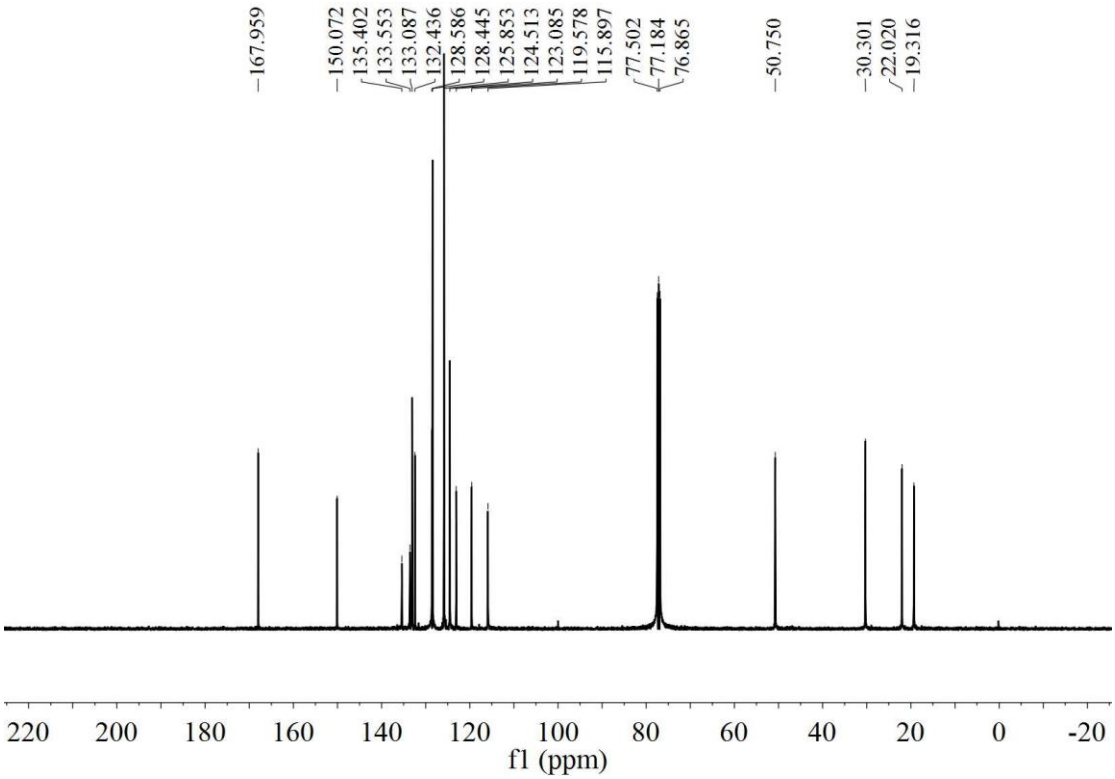
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3la**



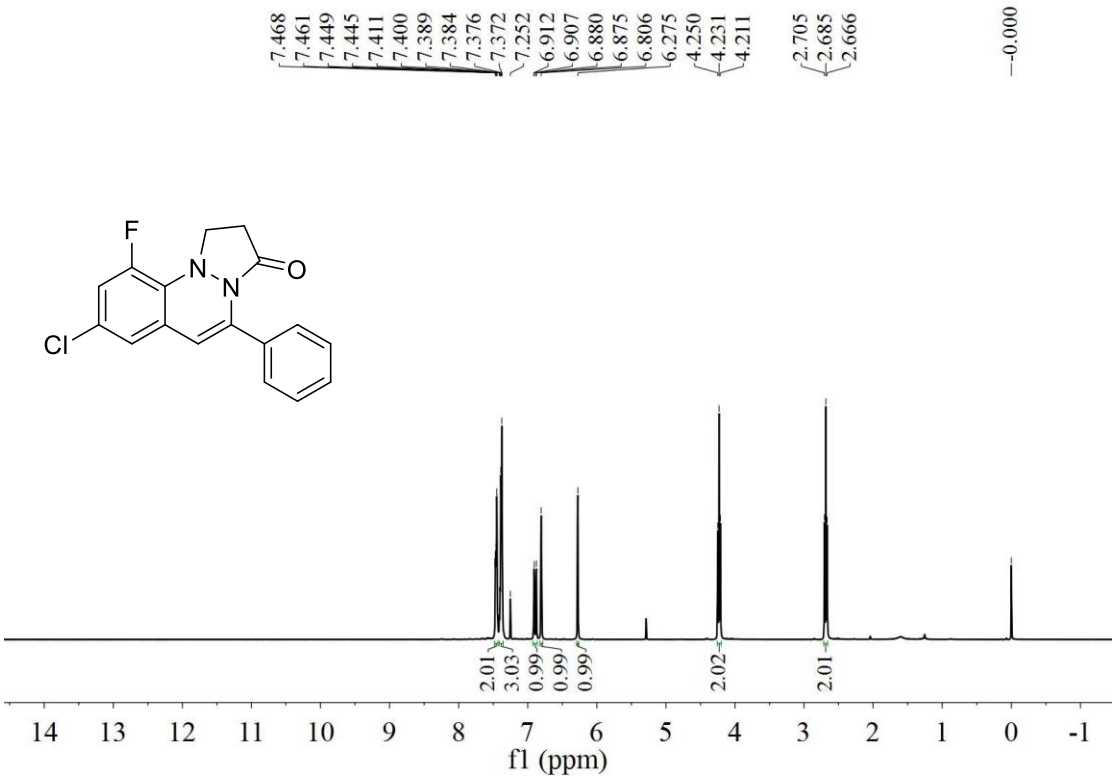
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3la**



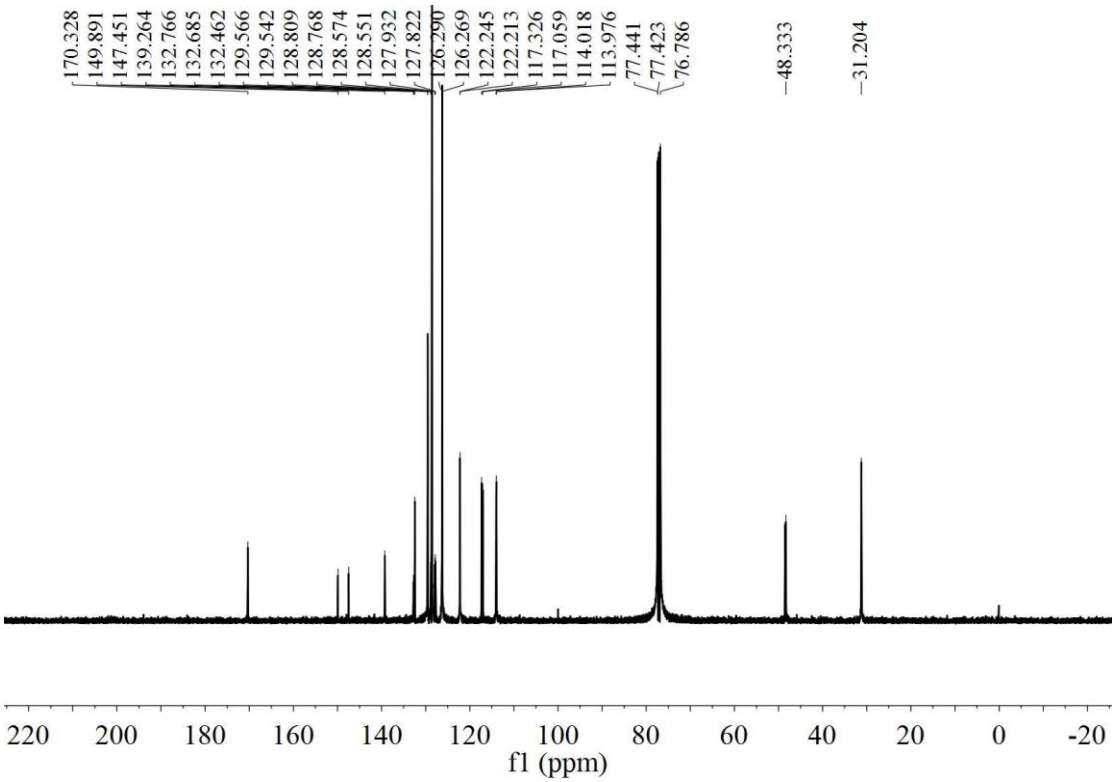
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ma**



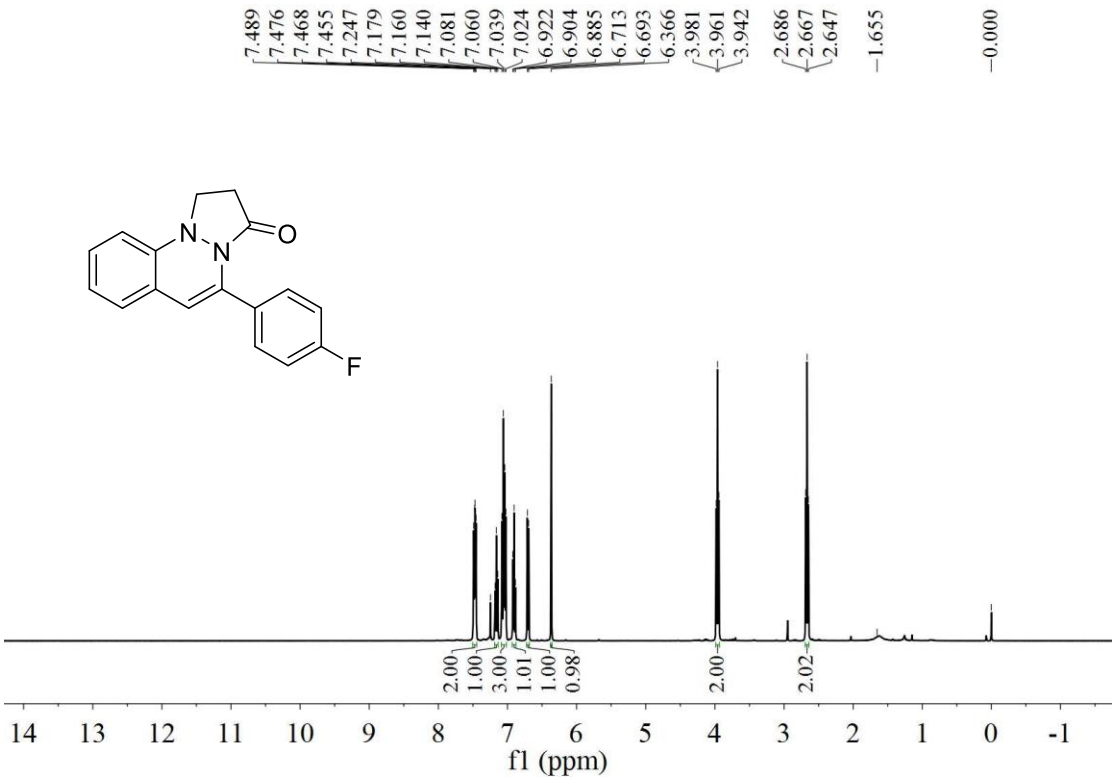
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ma**



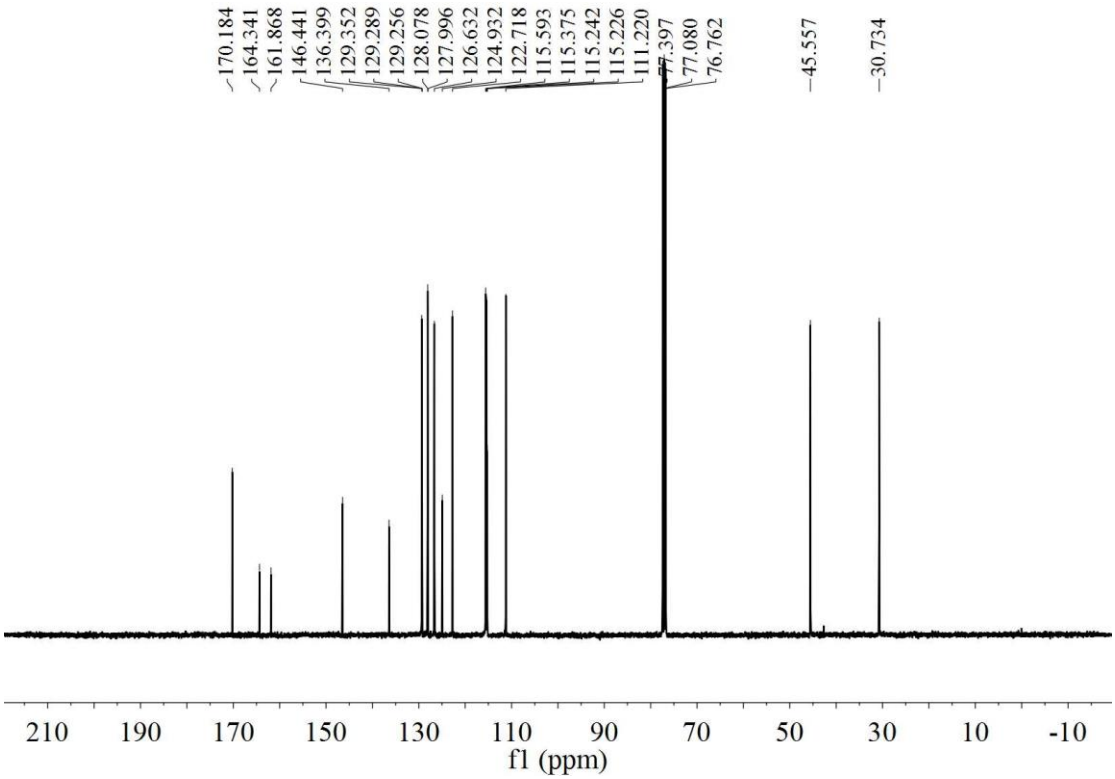
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3na**



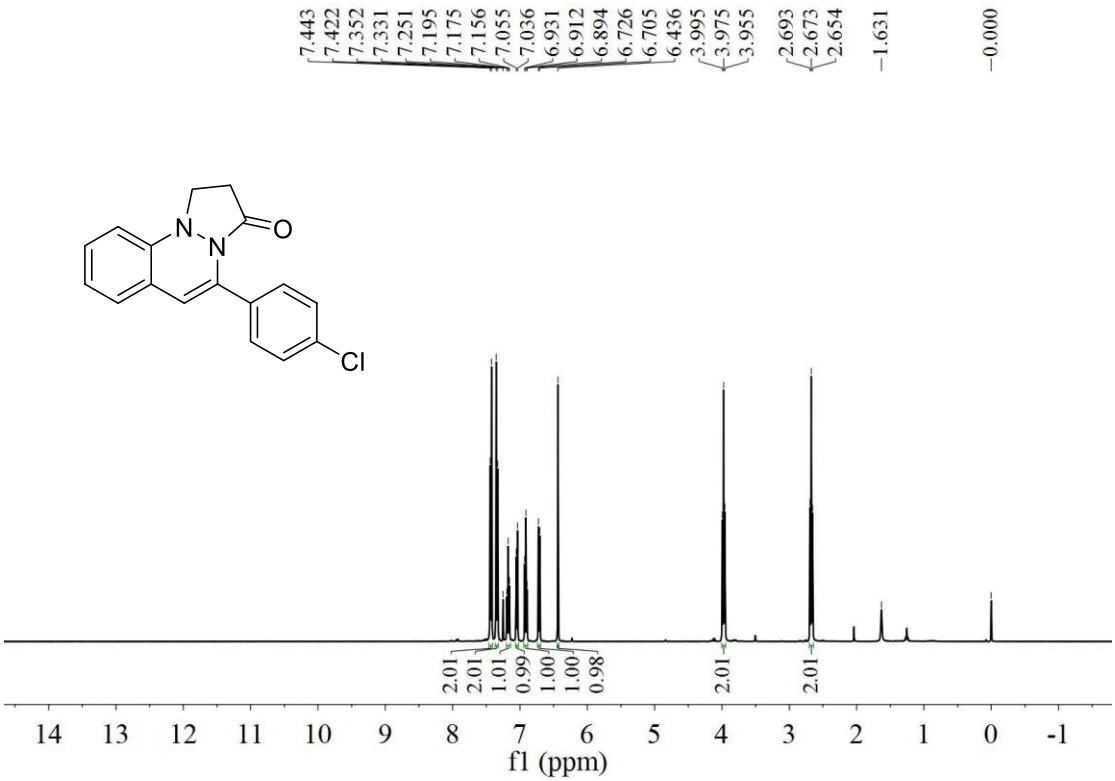
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3na**



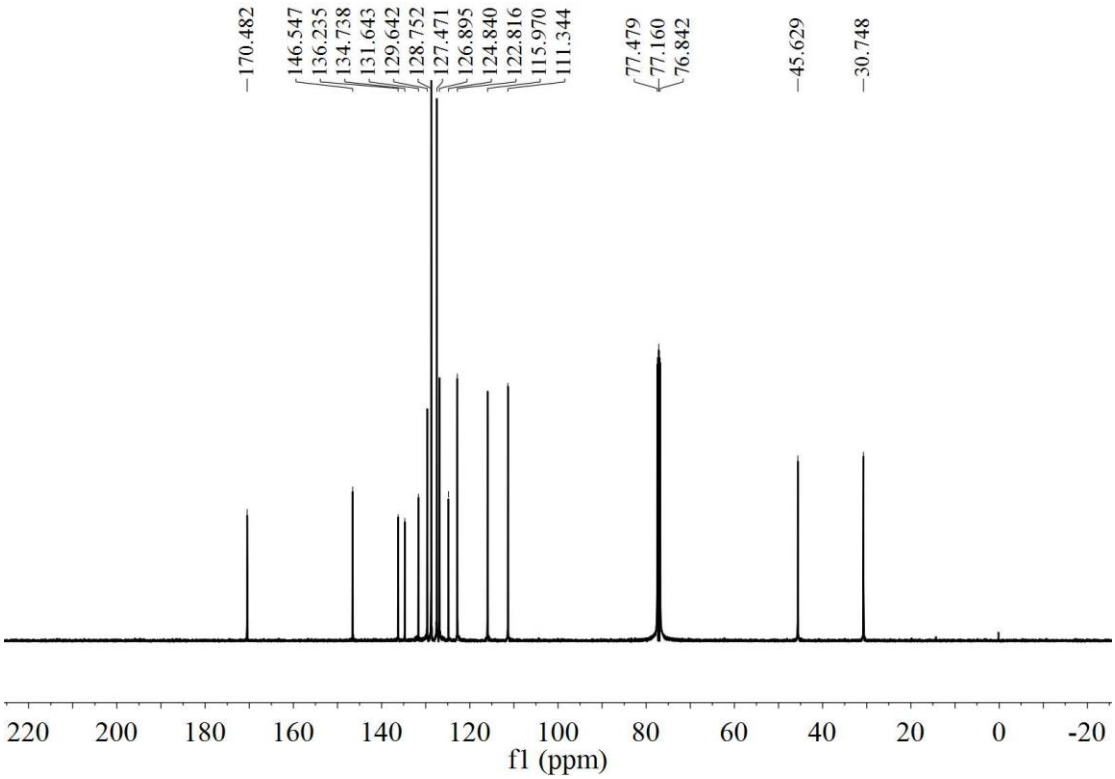
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ab**



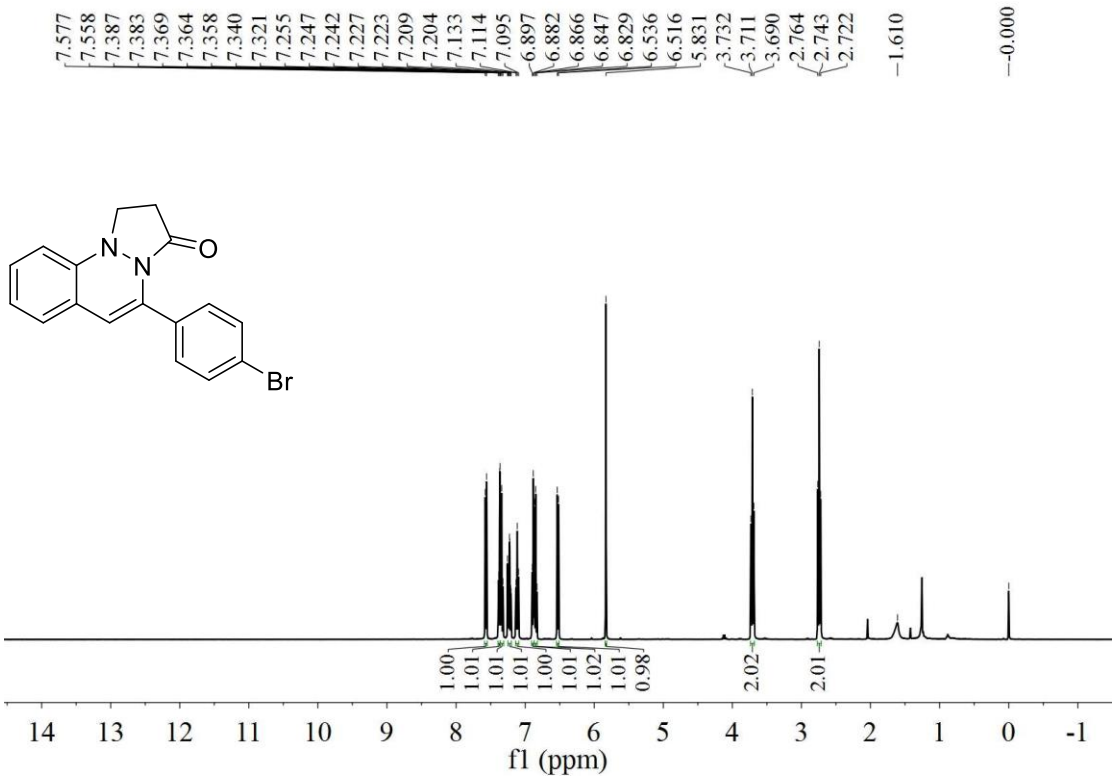
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ab**



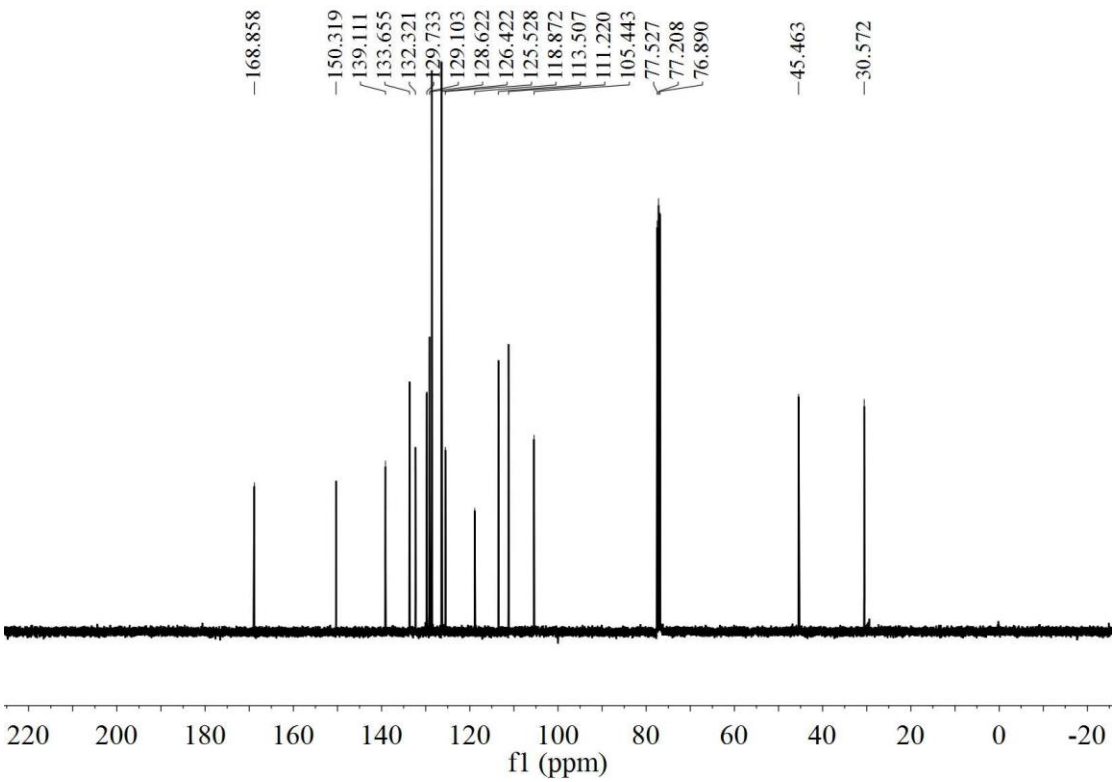
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ac**



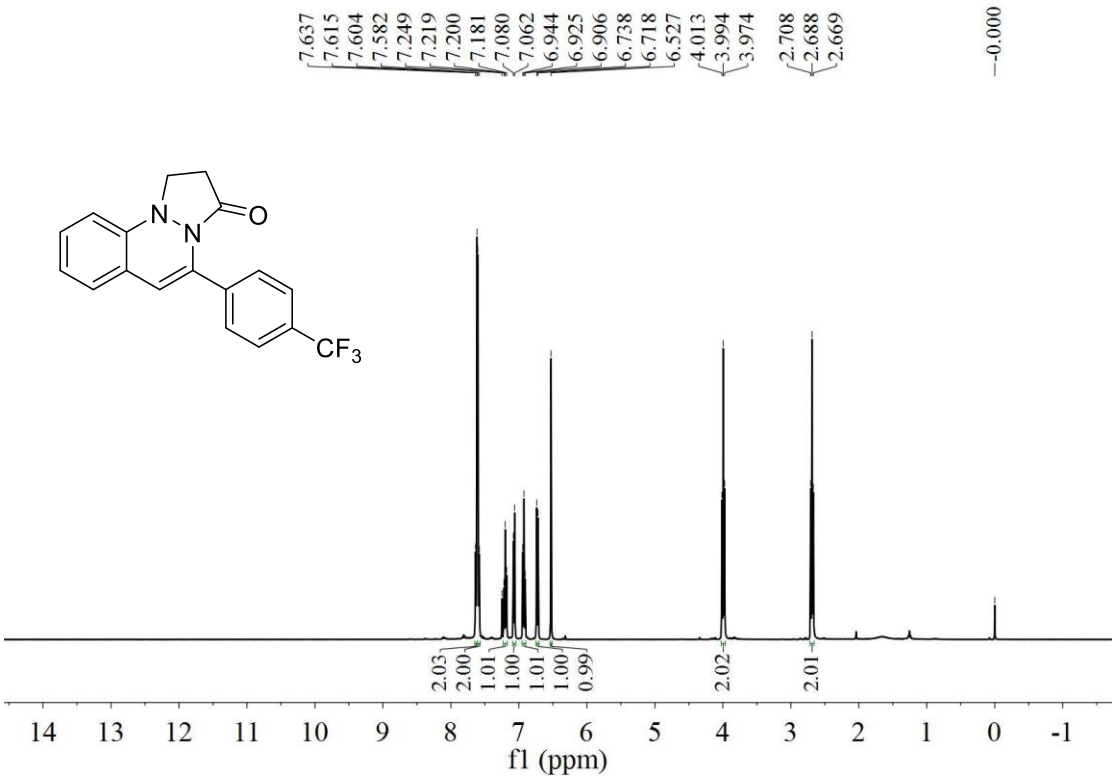
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ac**



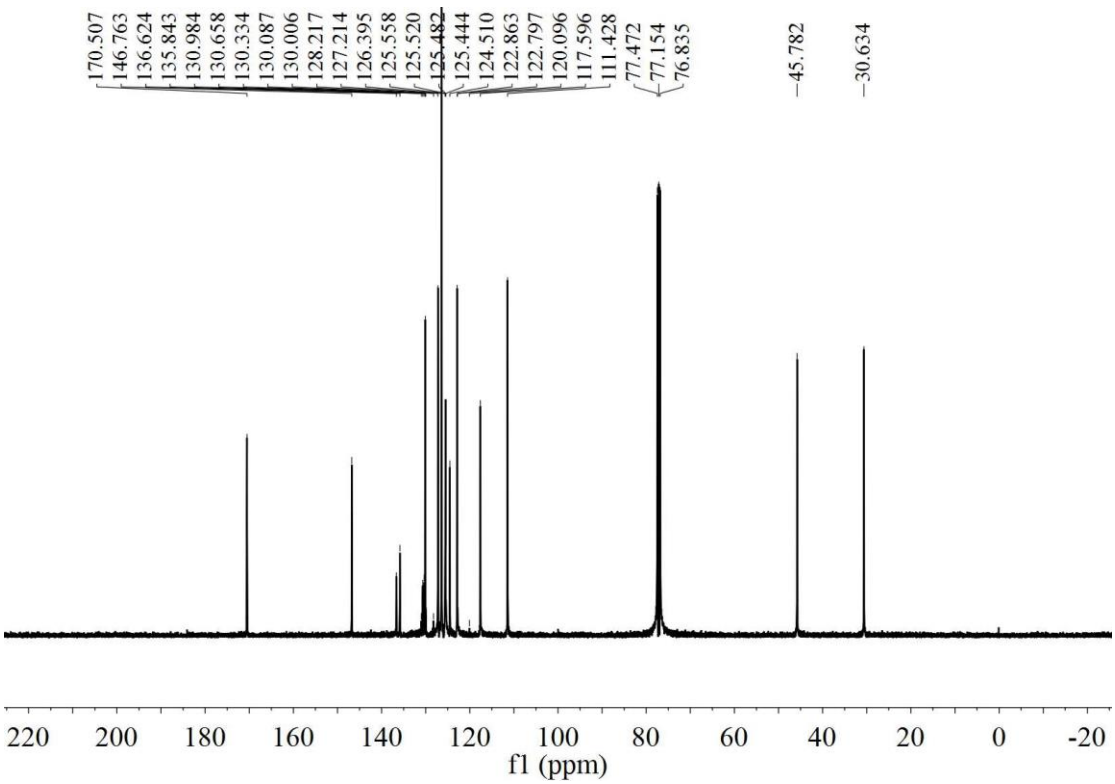
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ad**



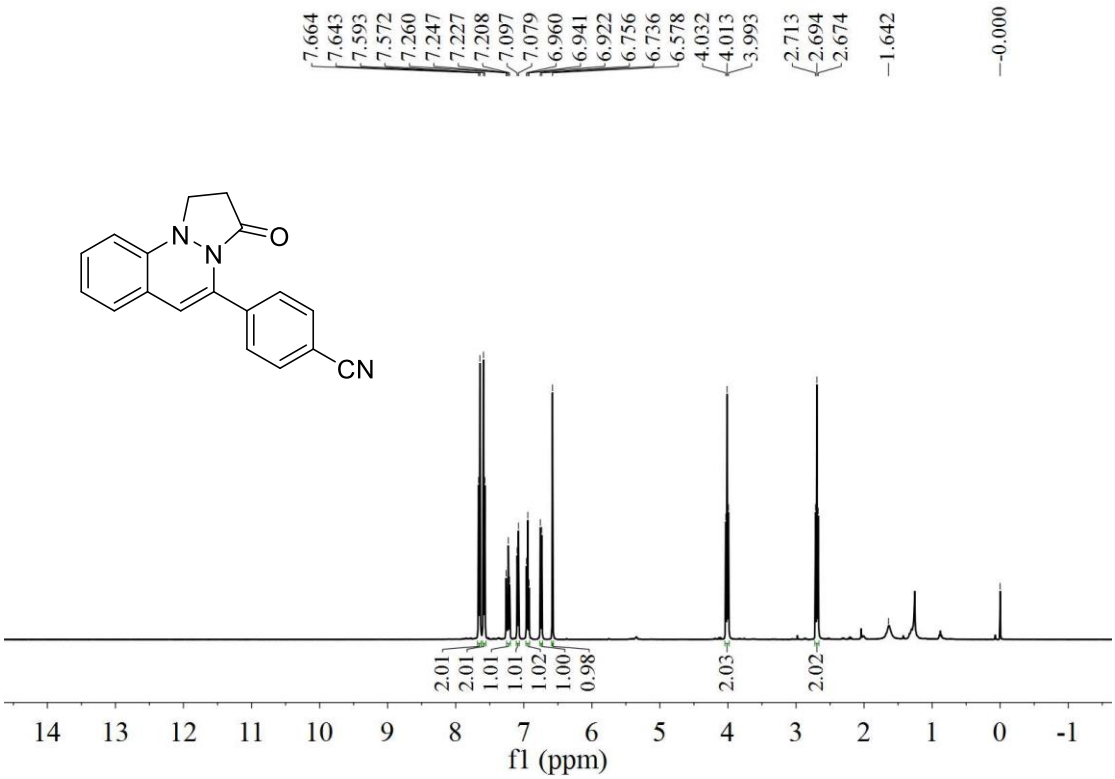
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ad**



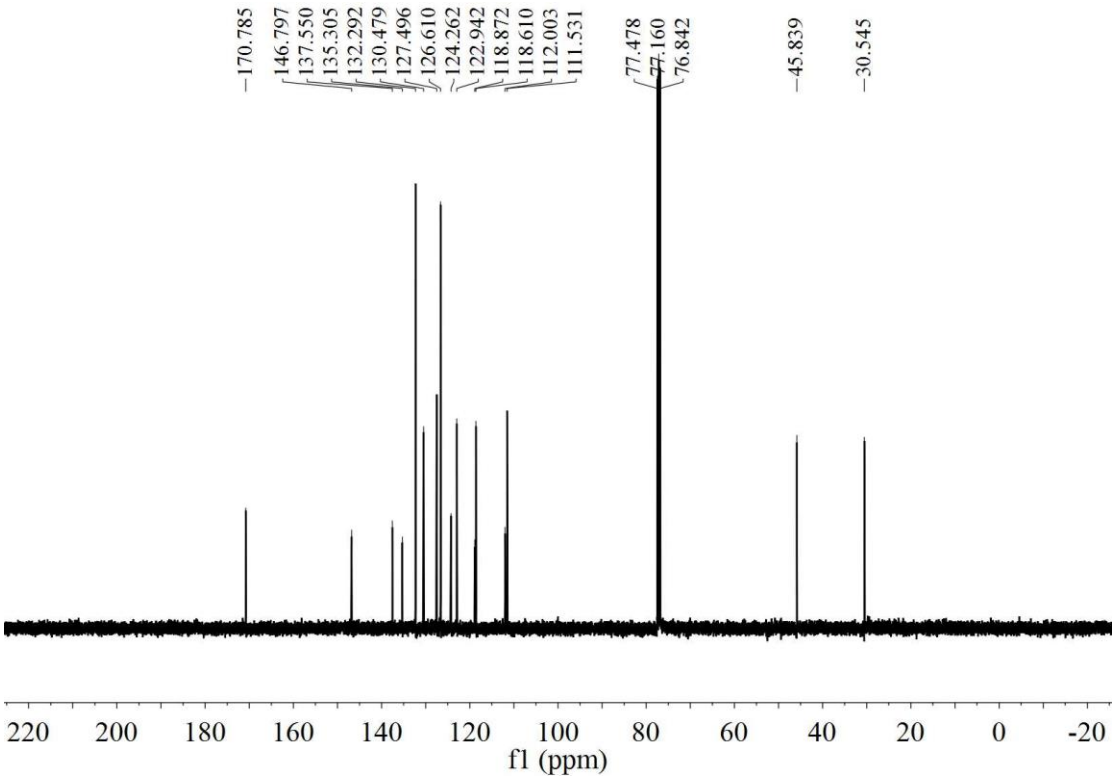
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ae**



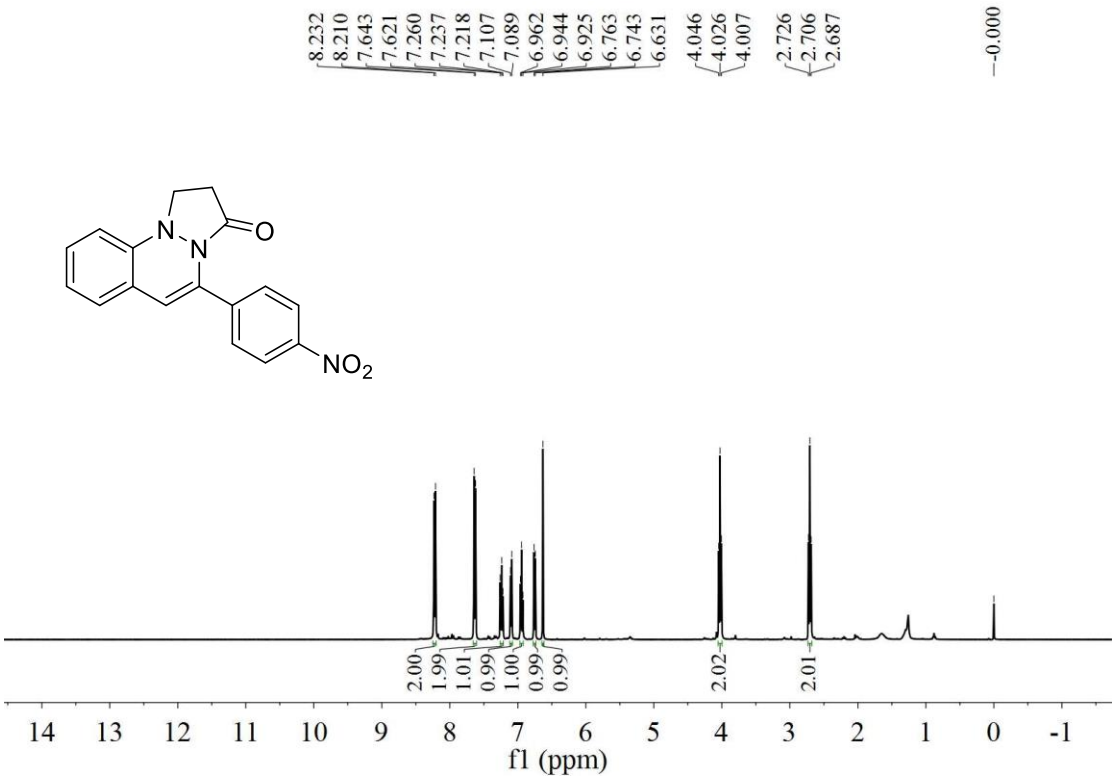
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ae**



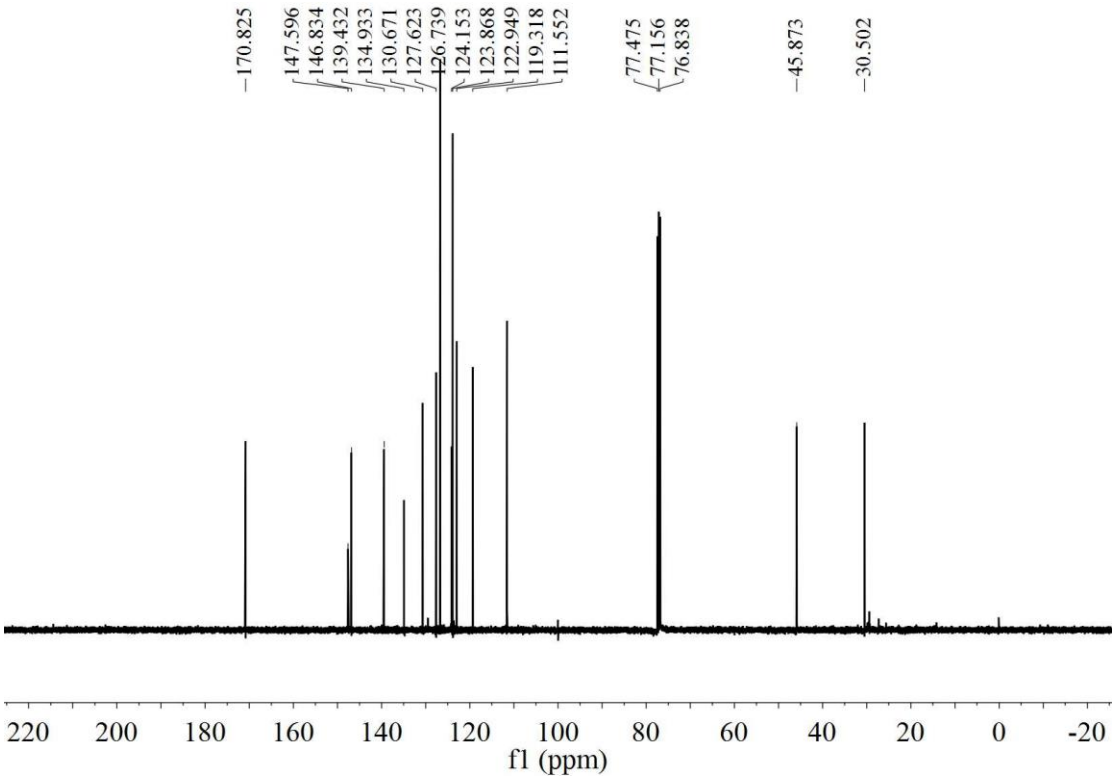
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3af**



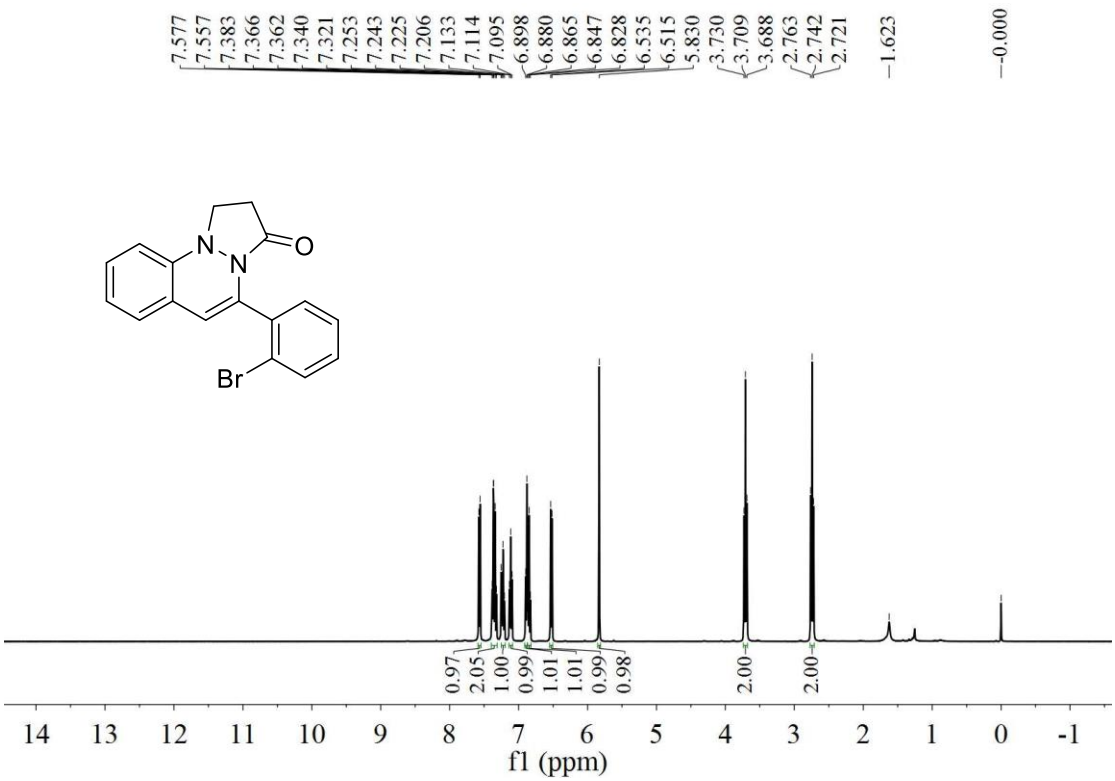
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3af**



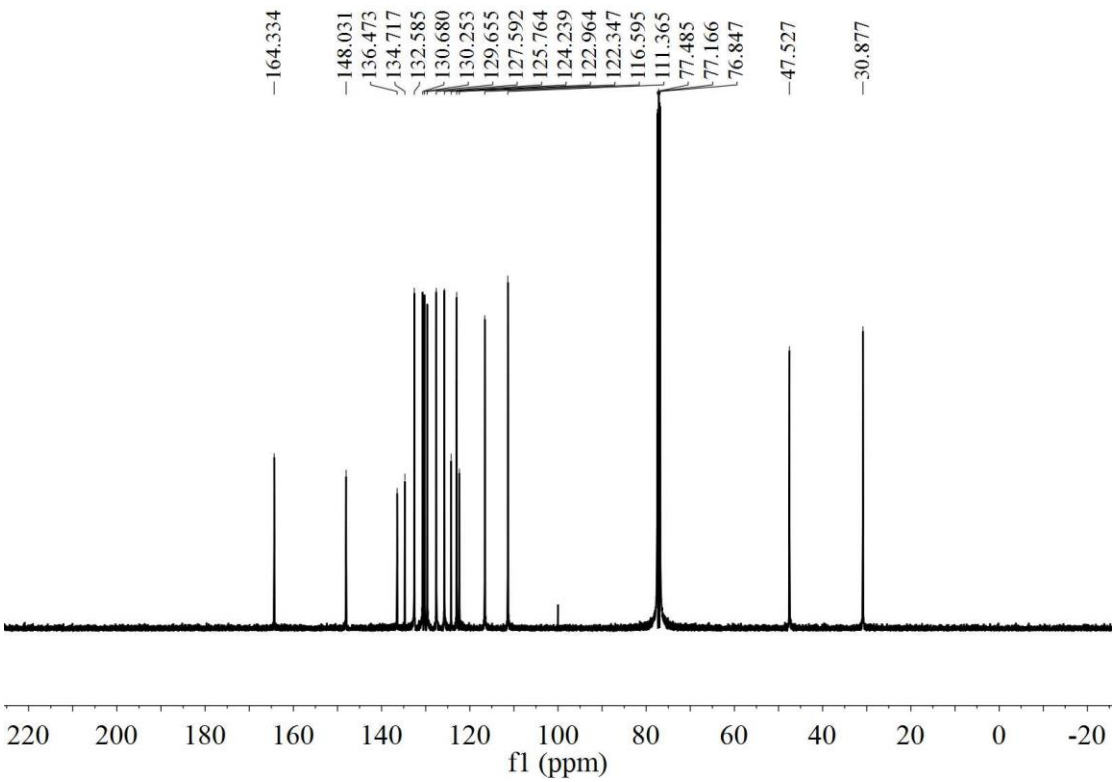
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ag**



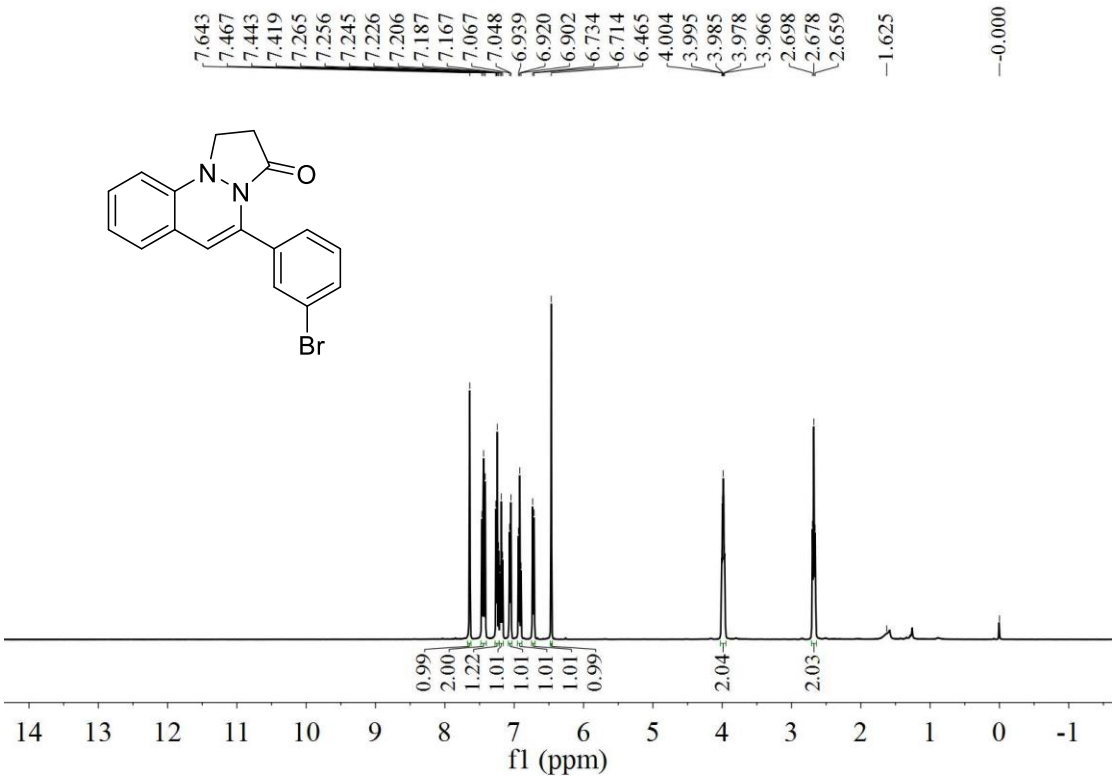
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ag**



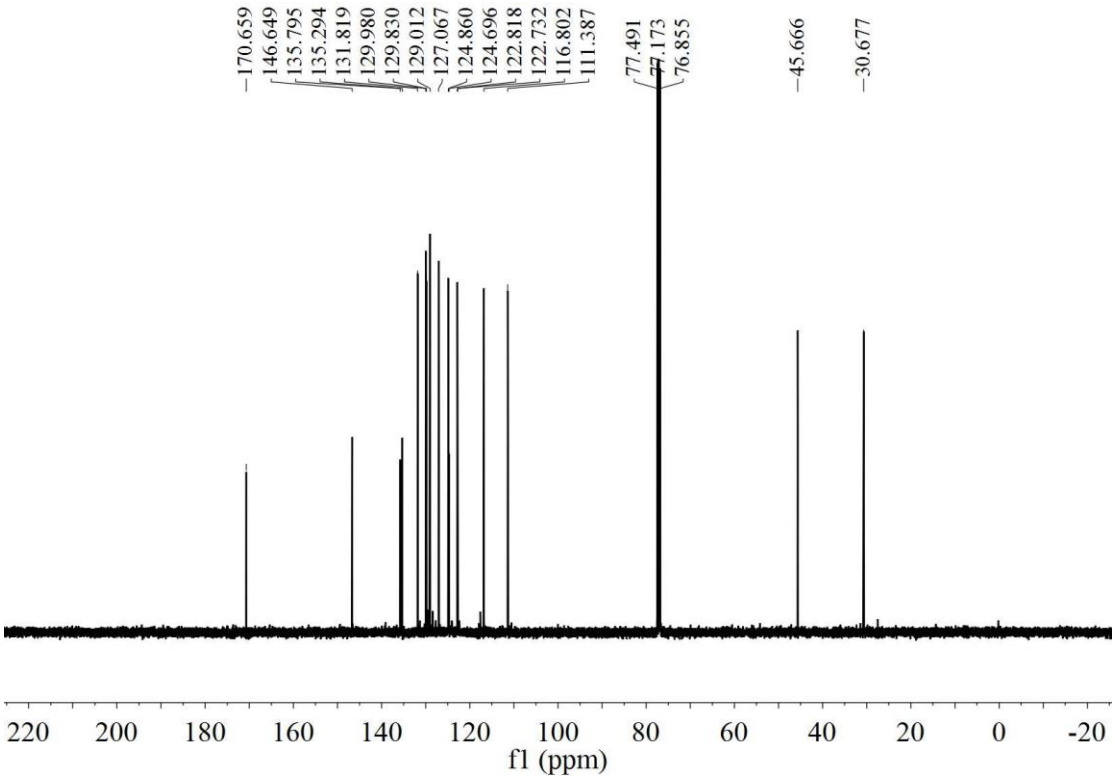
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ah**



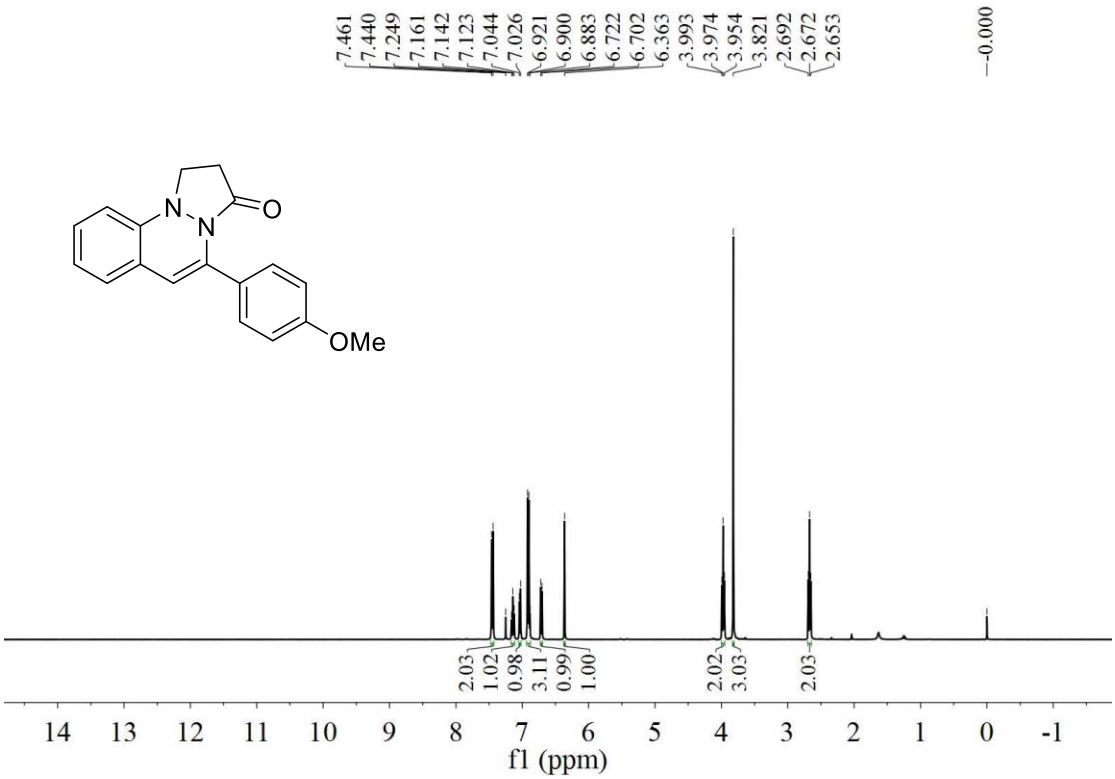
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ah**



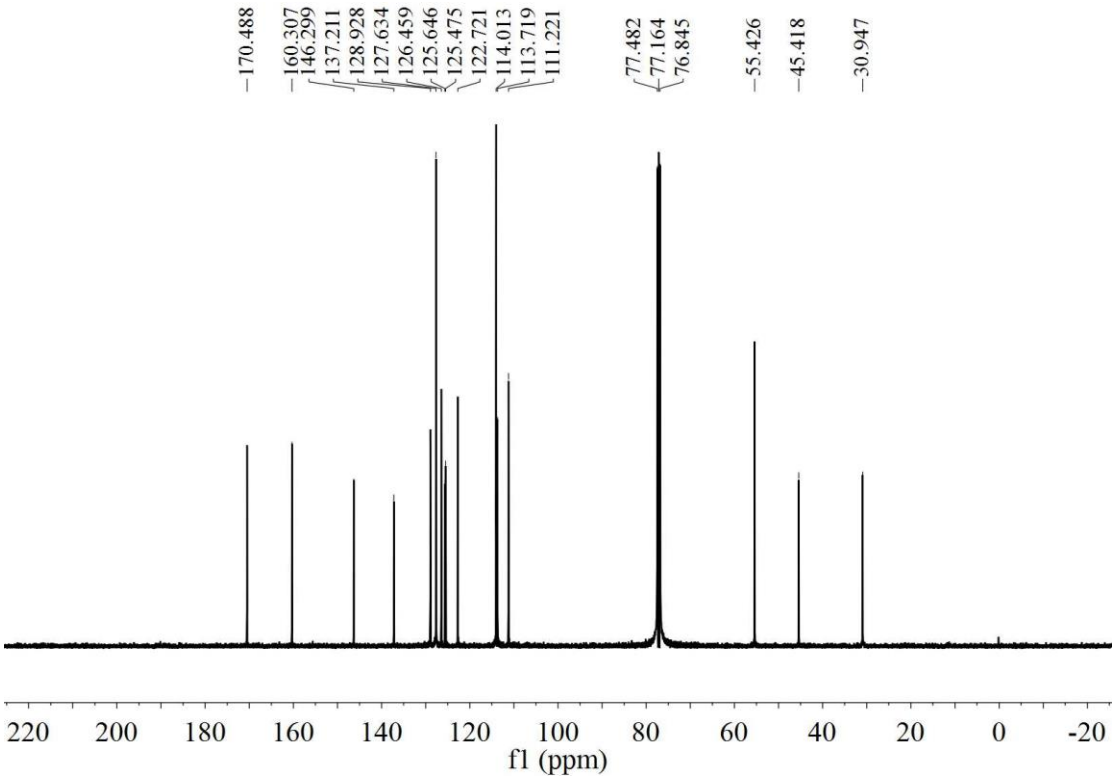
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ai**



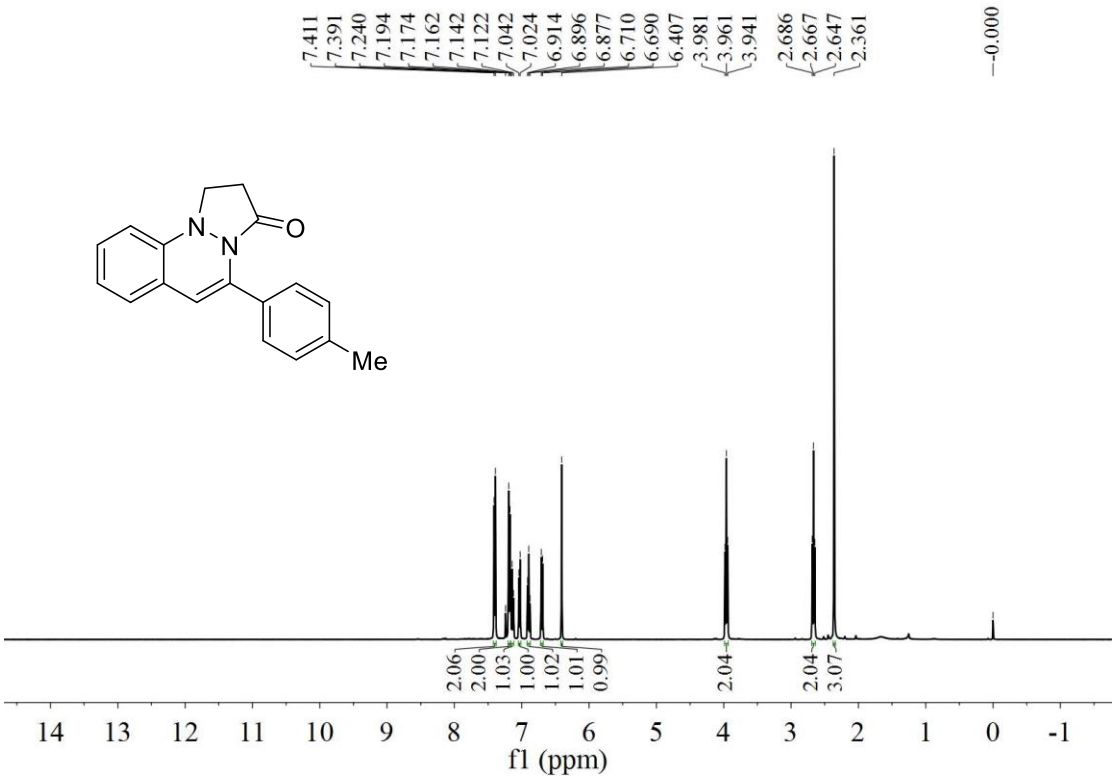
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ai**



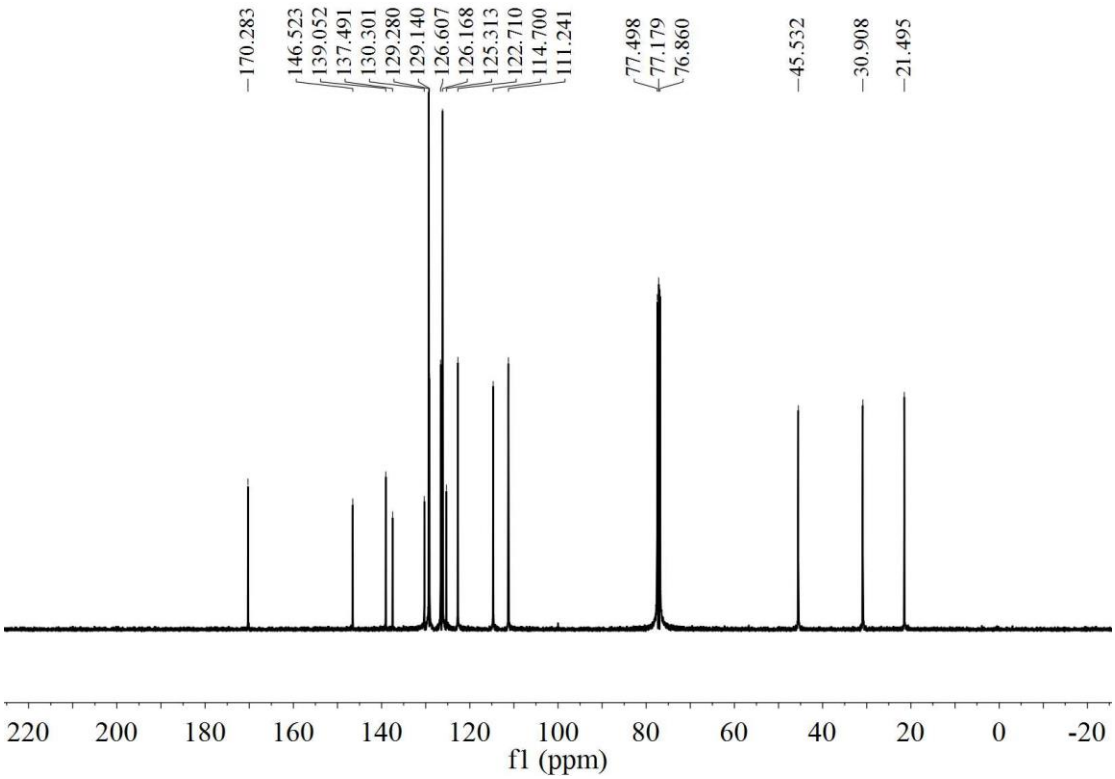
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3aj**



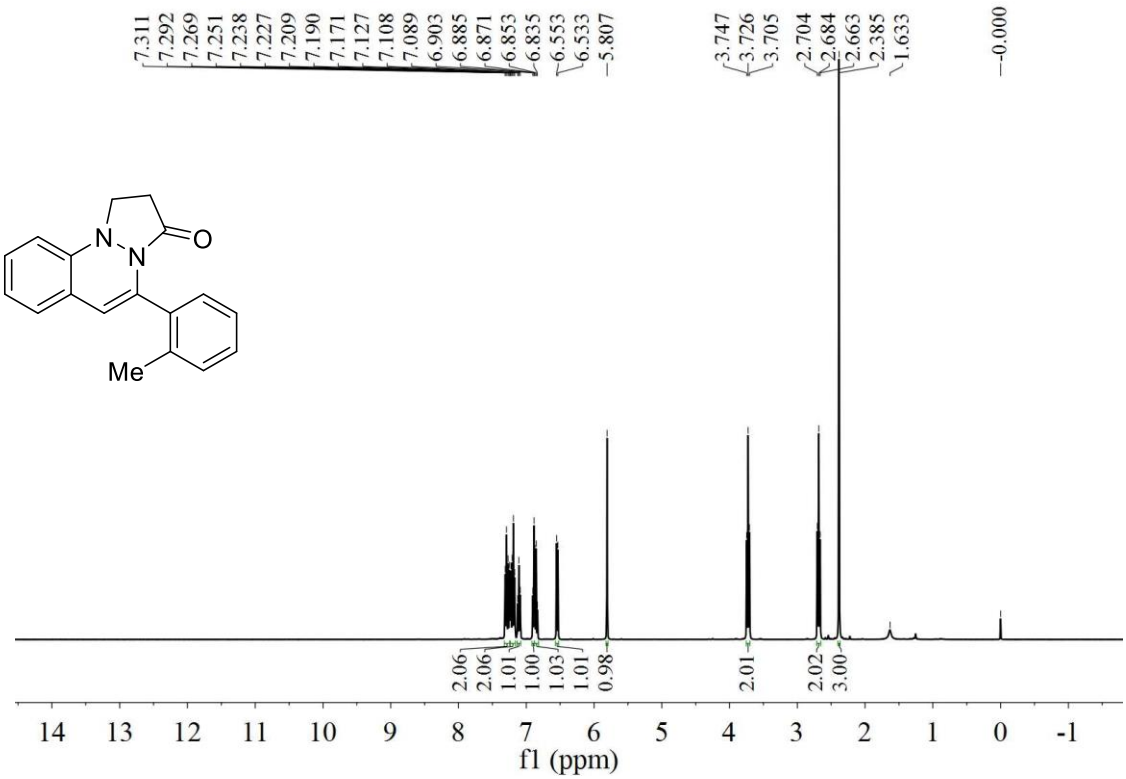
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3aj**



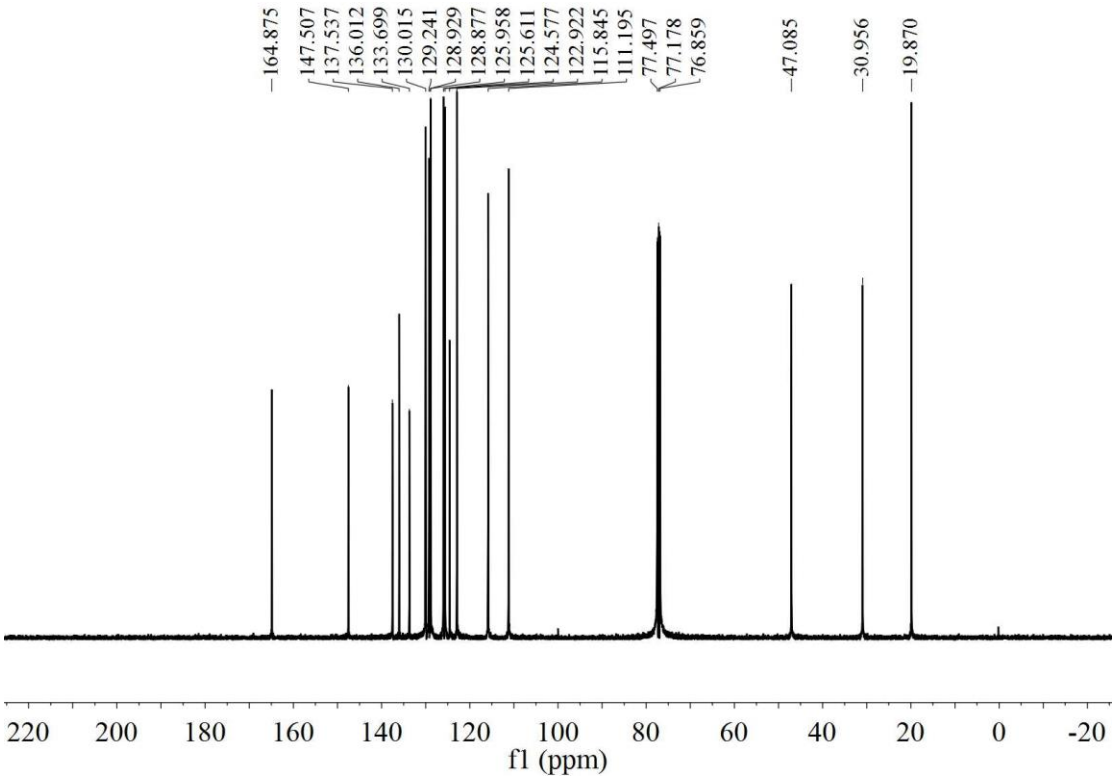
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ak**



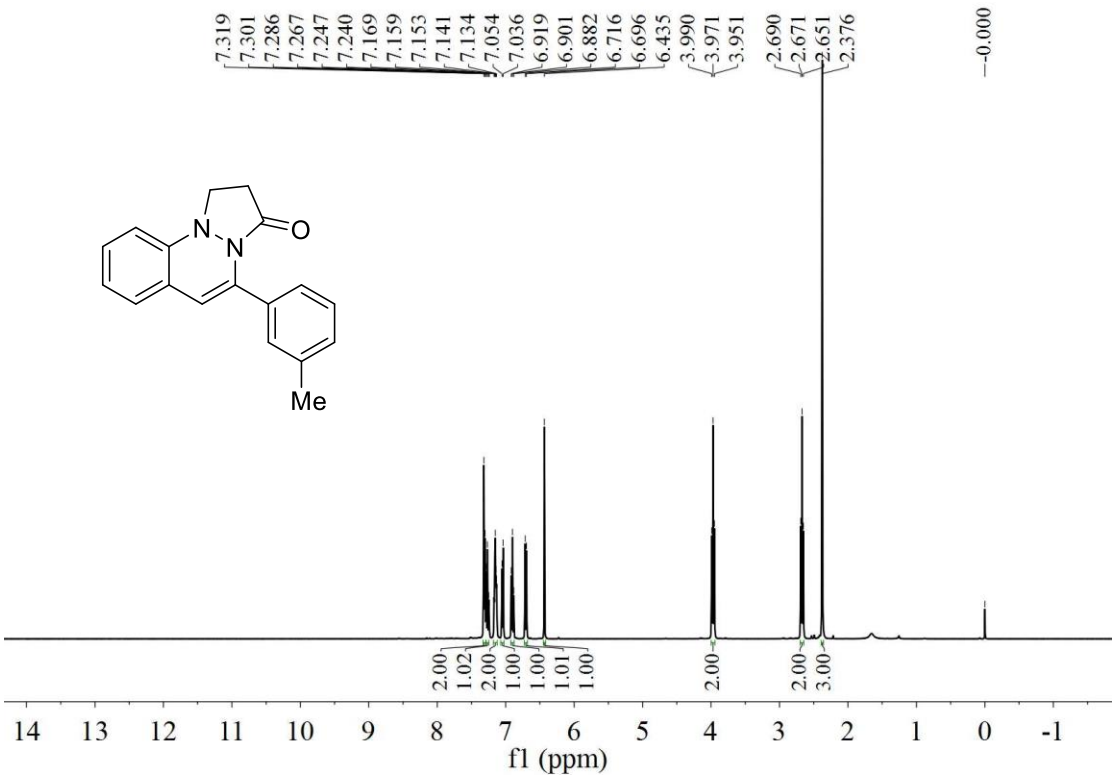
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ak**



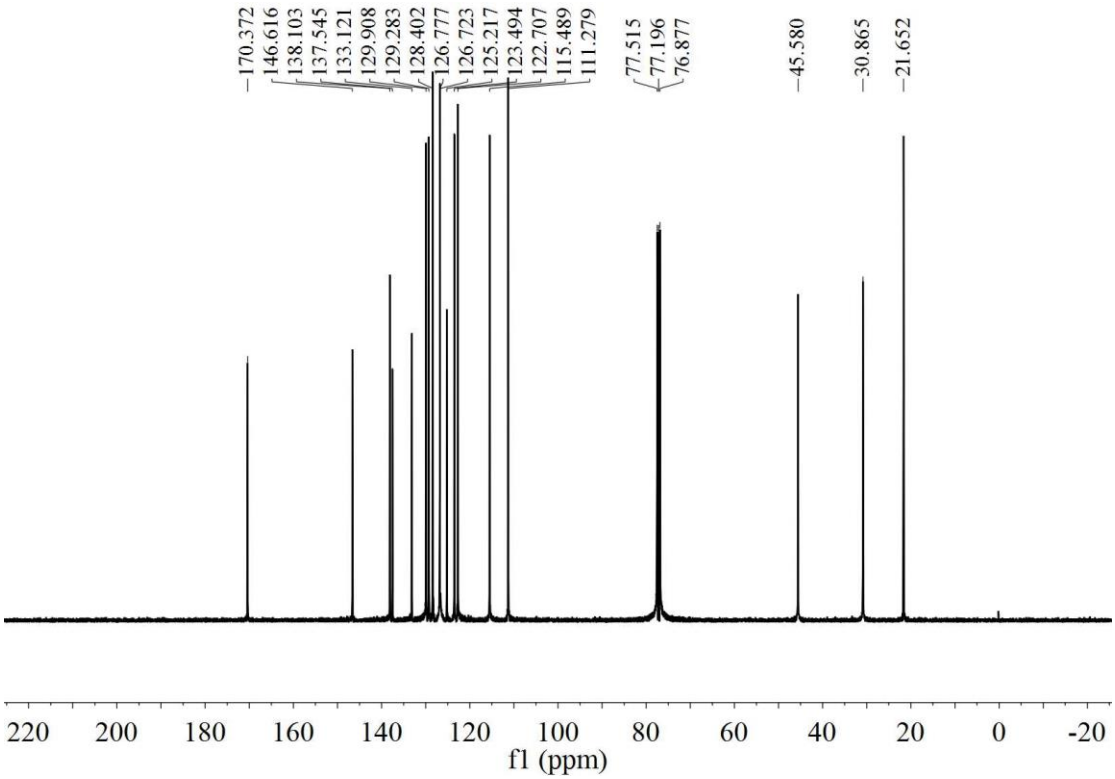
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3al**



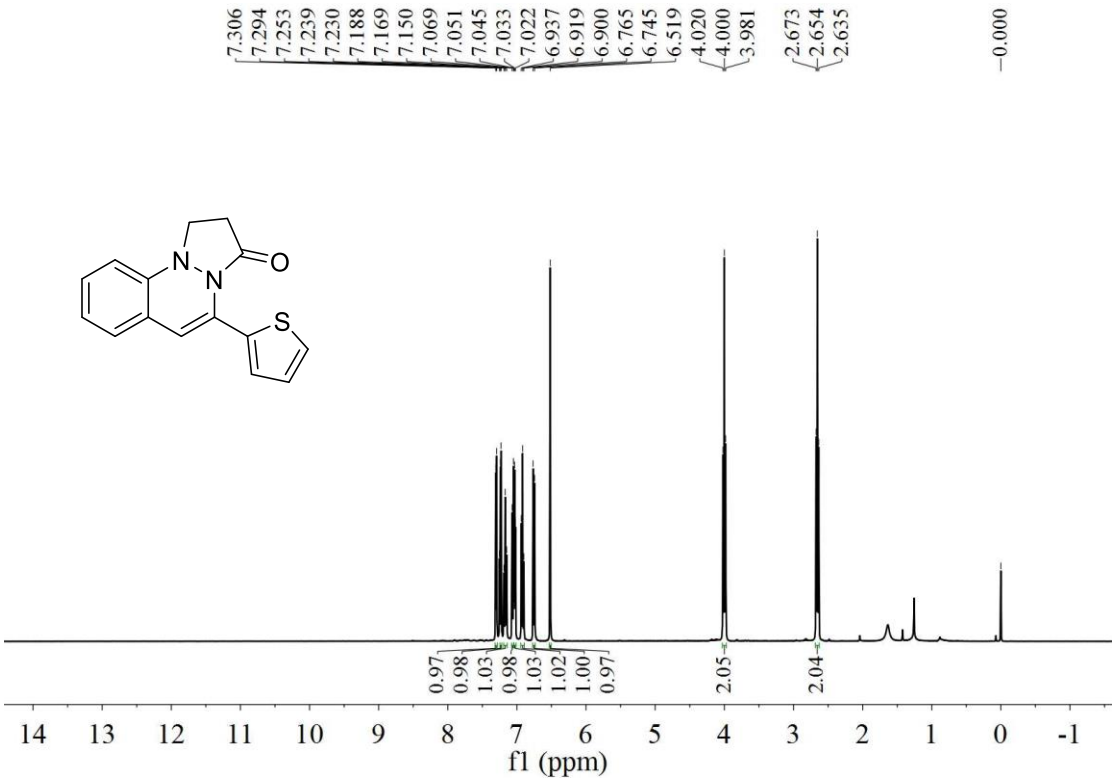
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3al**



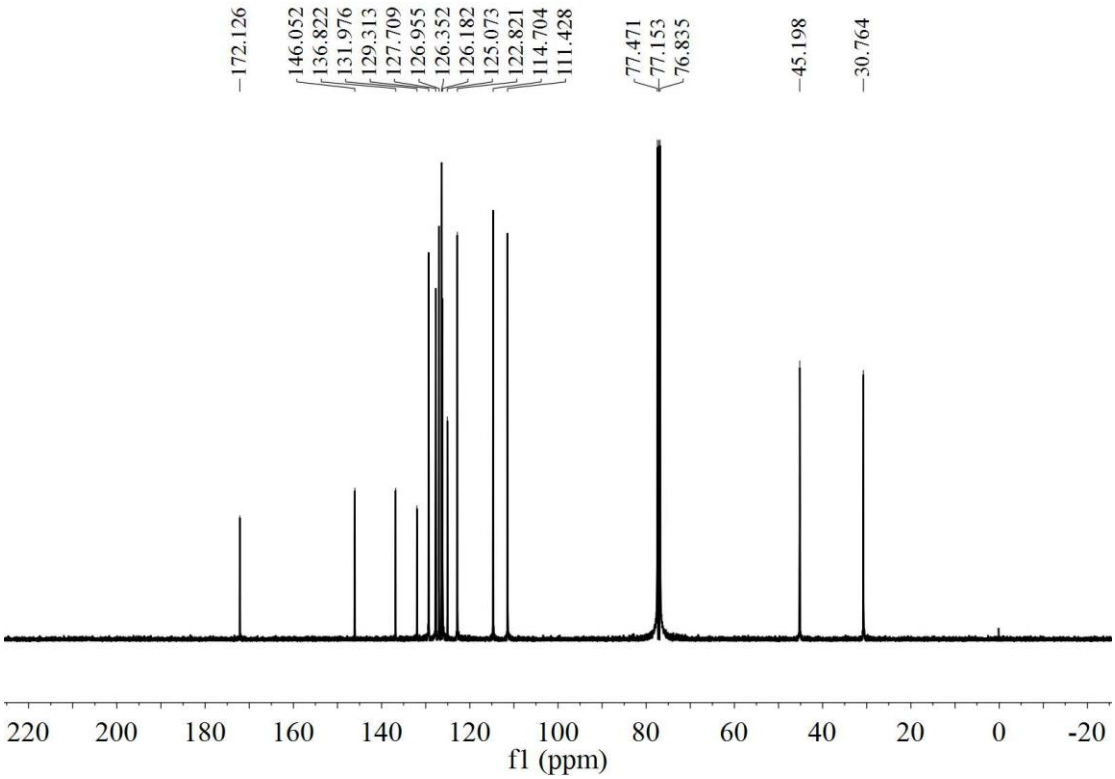
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3am**



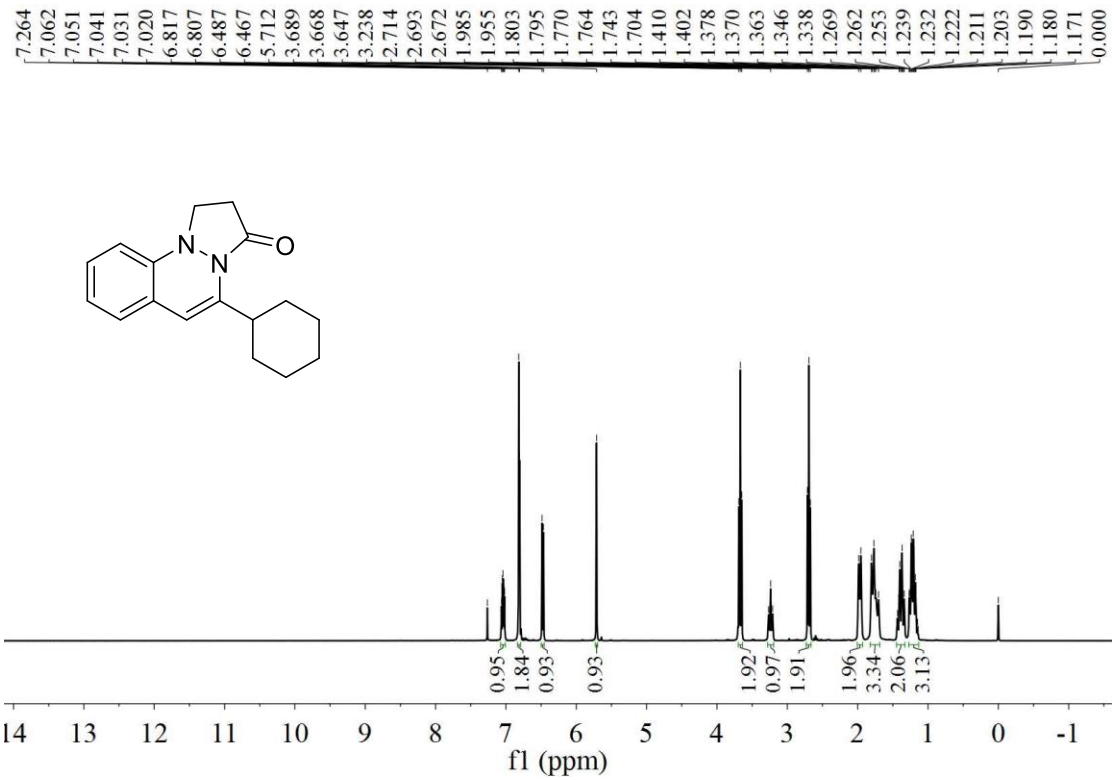
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3am**



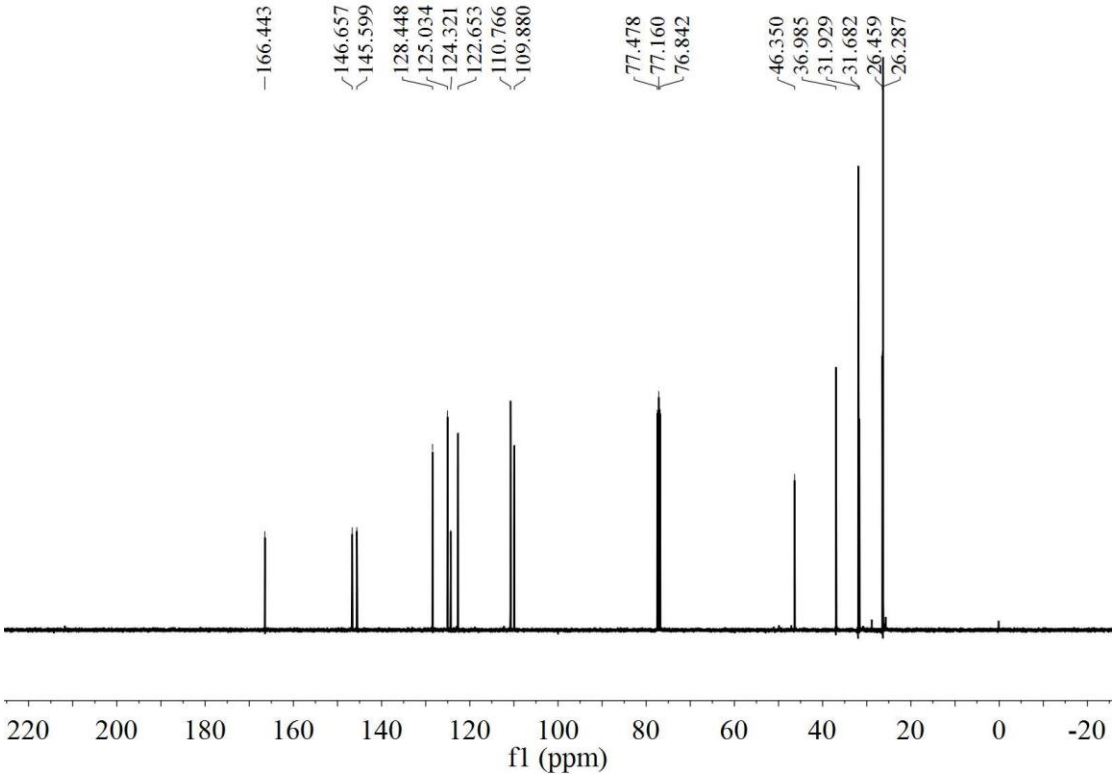
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3an**



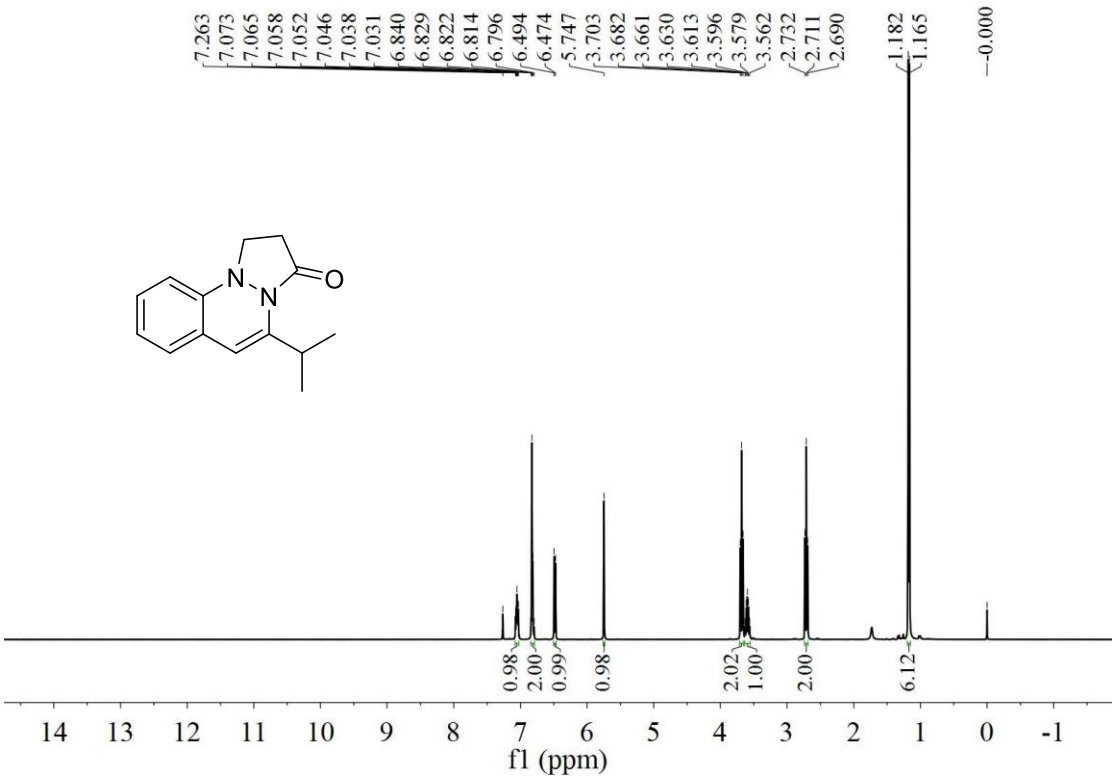
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3an**



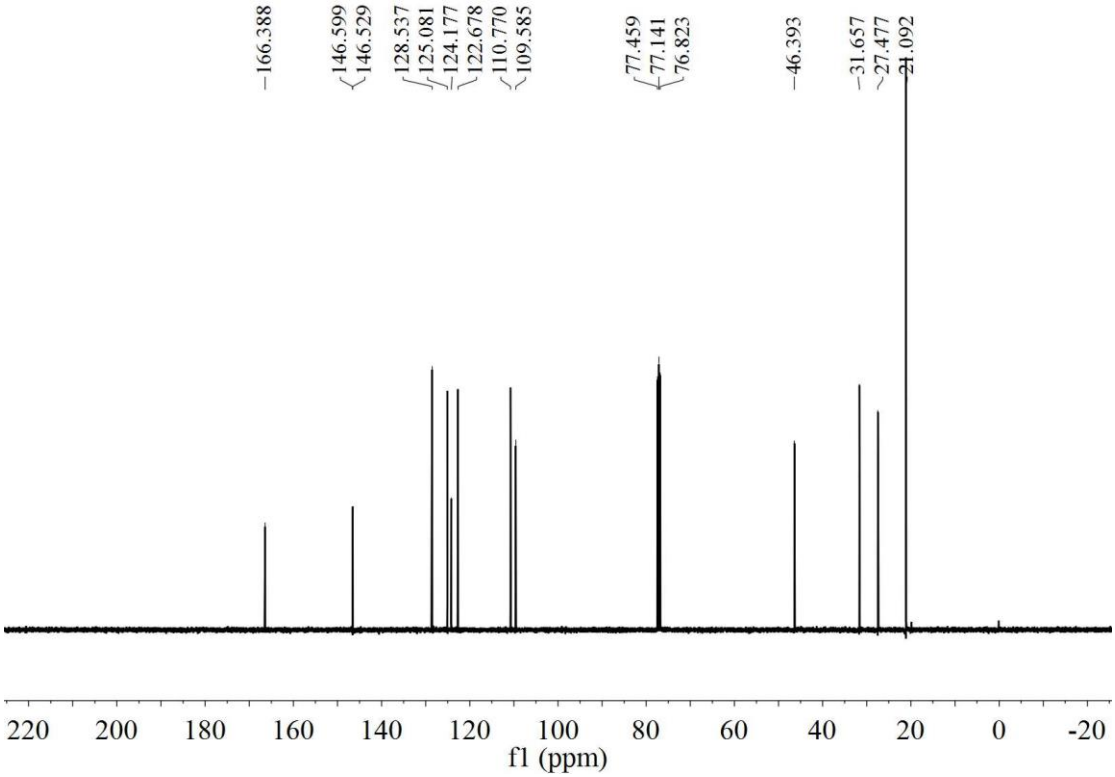
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ao**



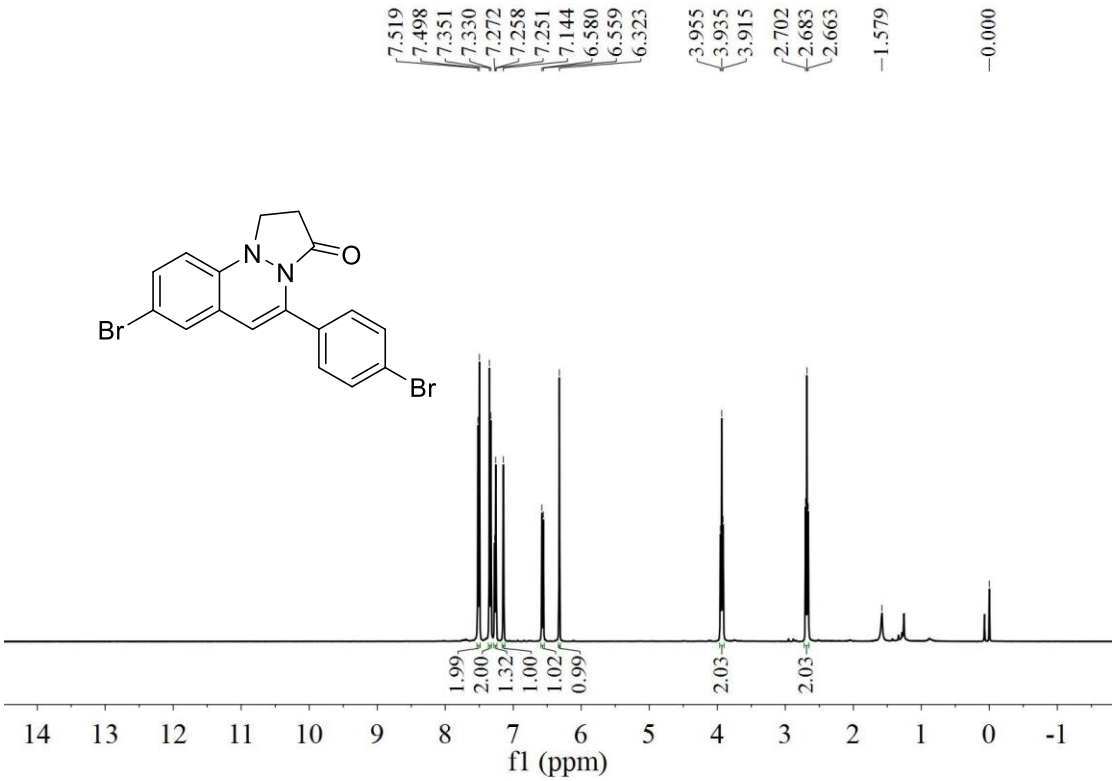
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ao**



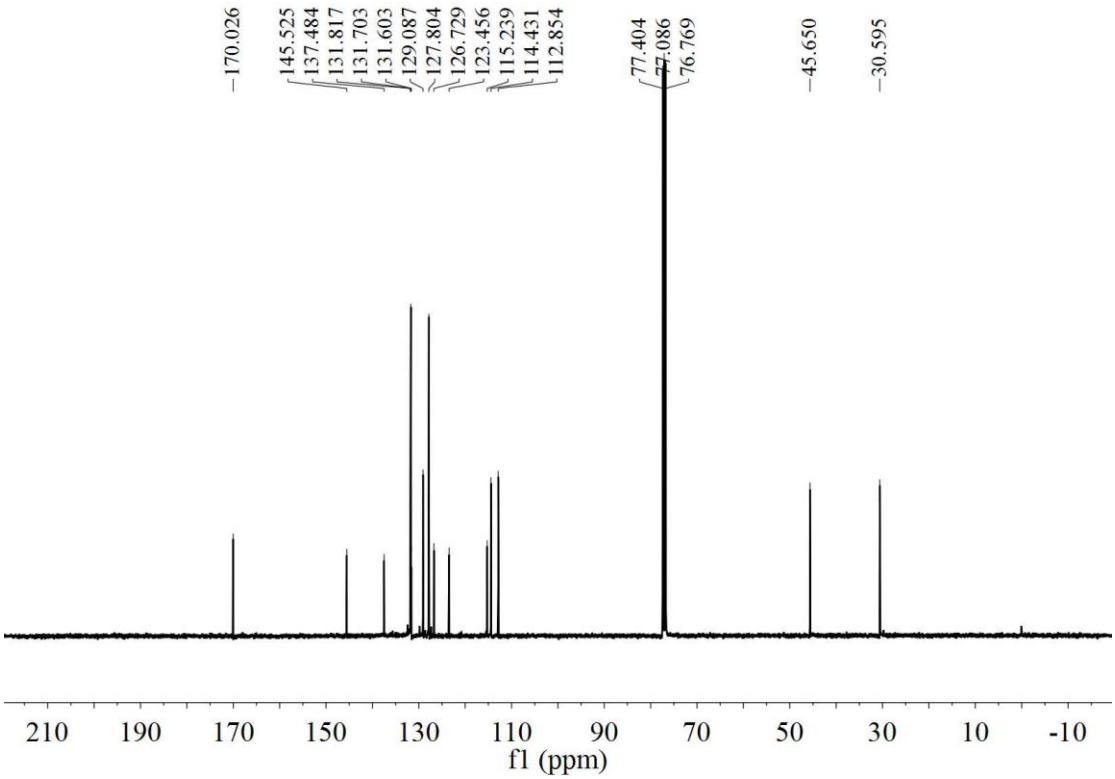
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ap**



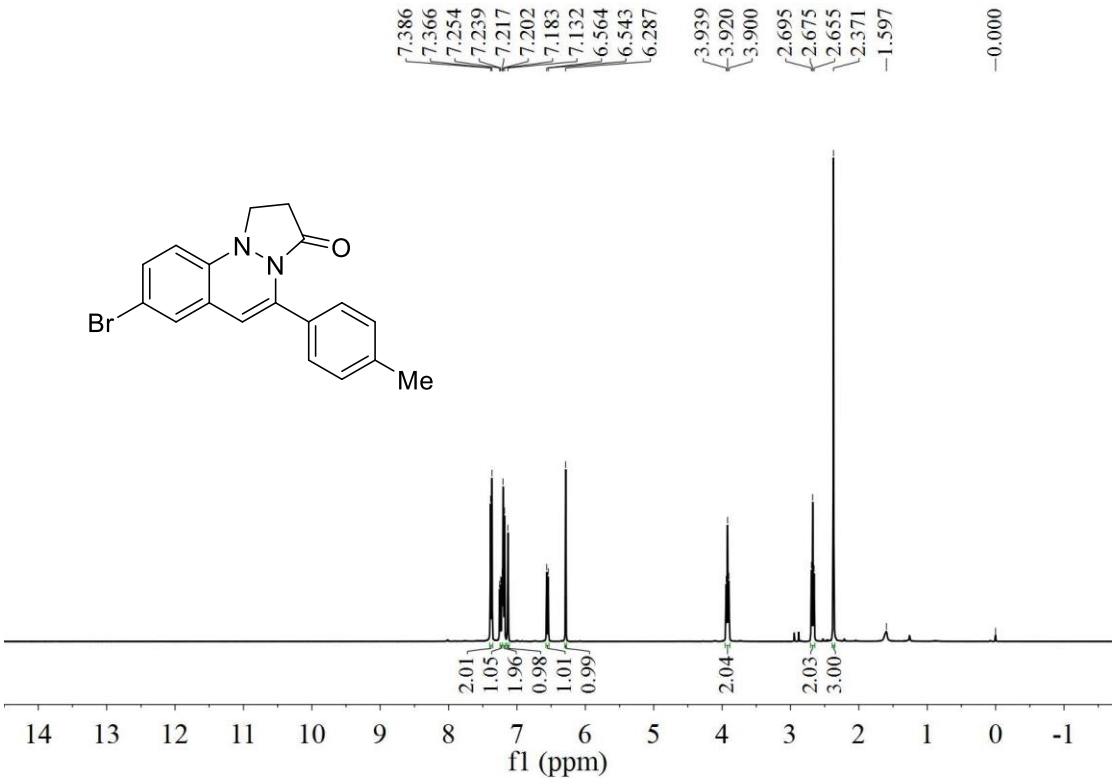
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ap**



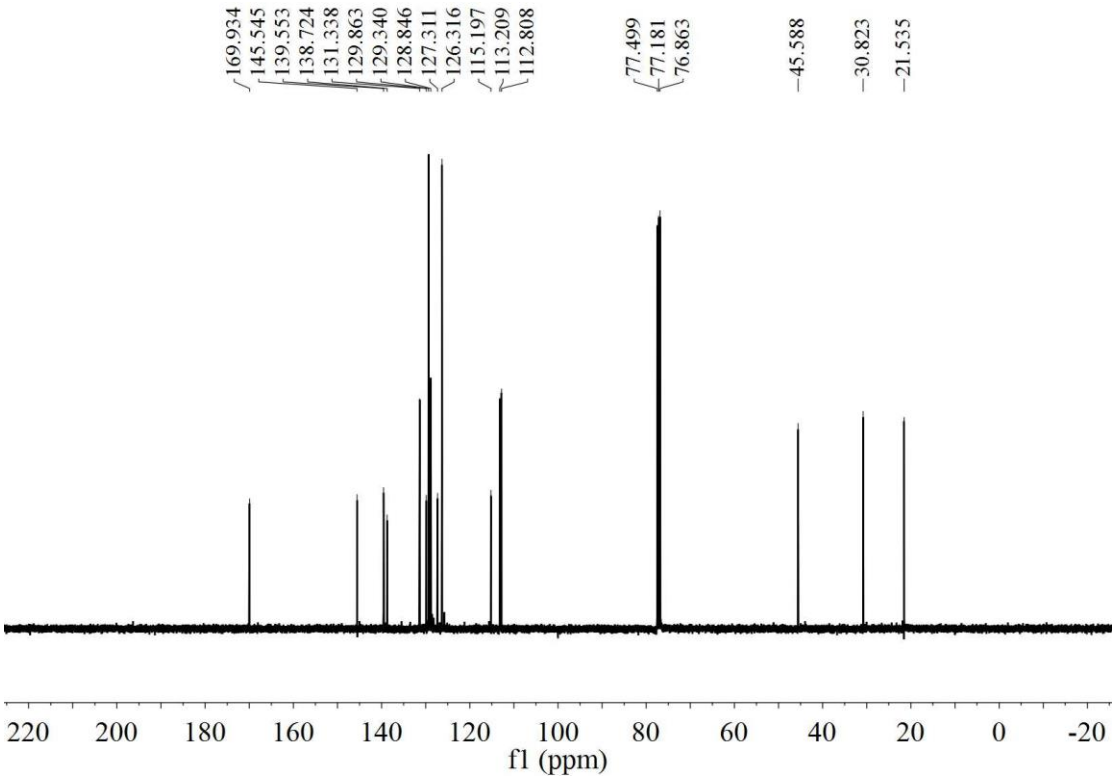
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3dd**



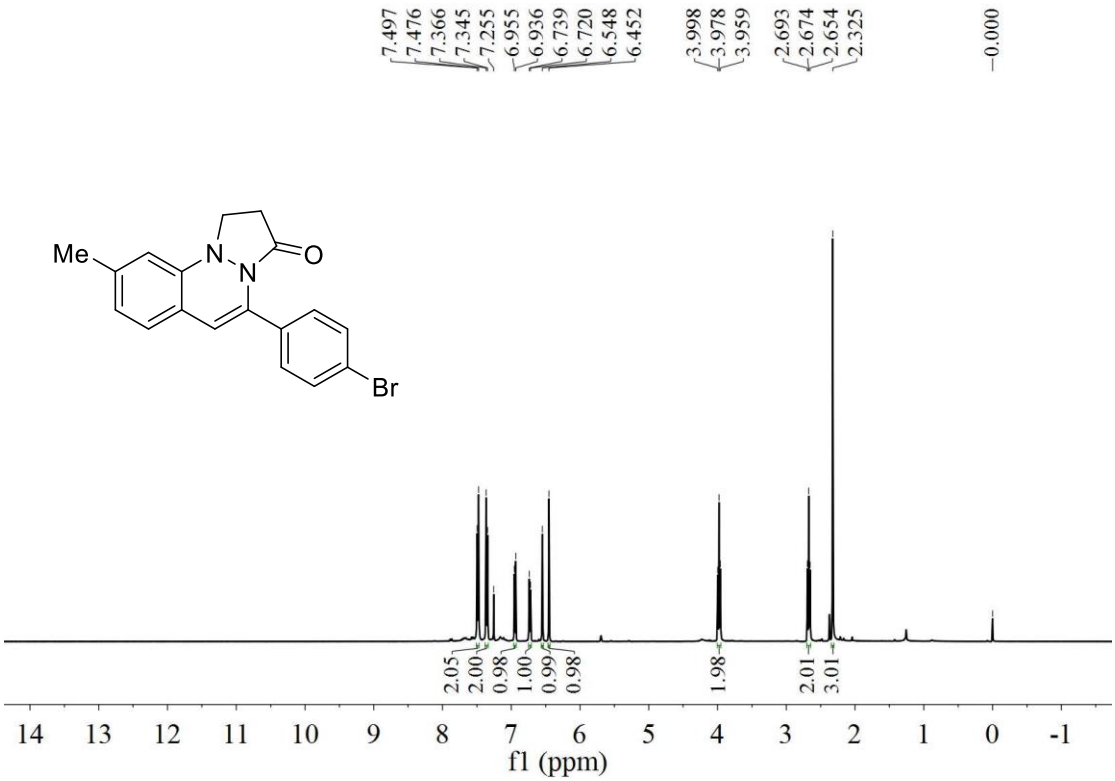
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3dd**



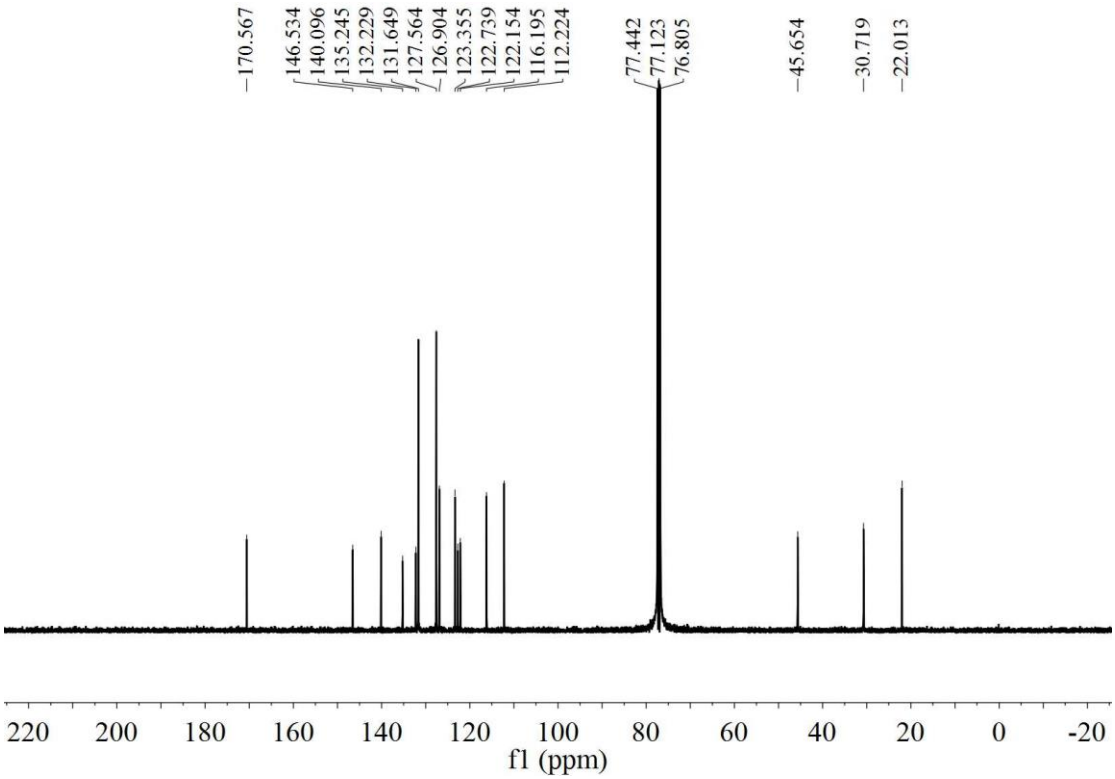
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3dk**



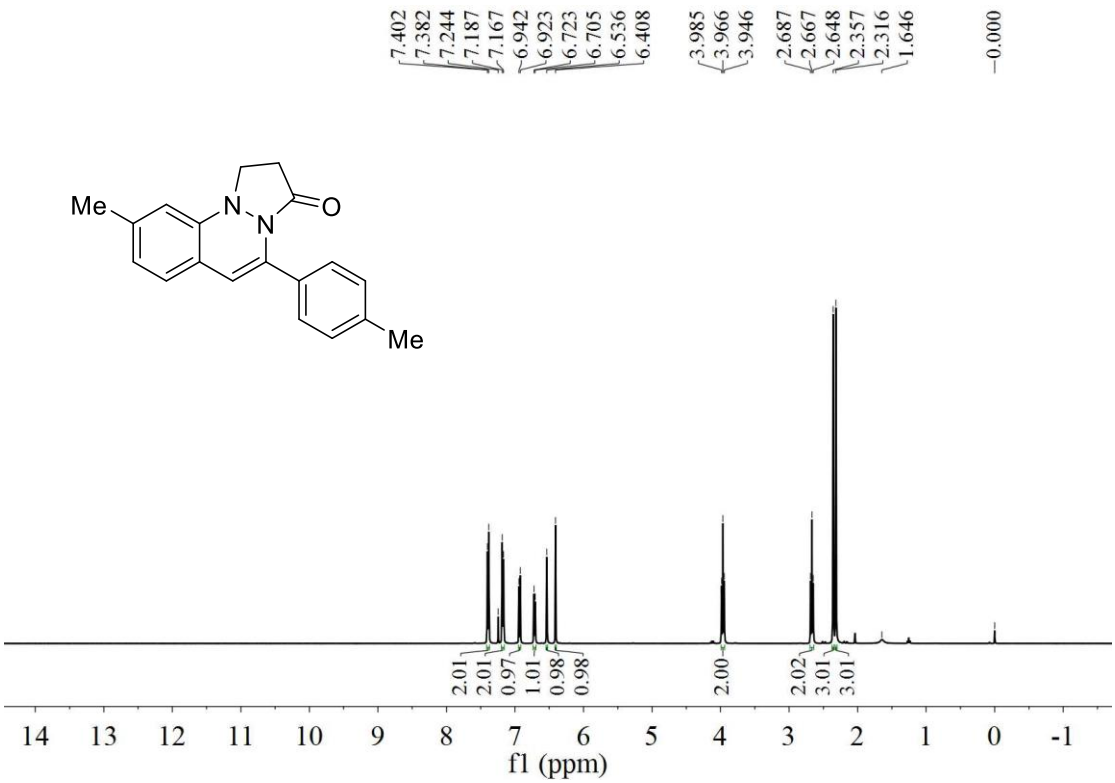
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3dk**



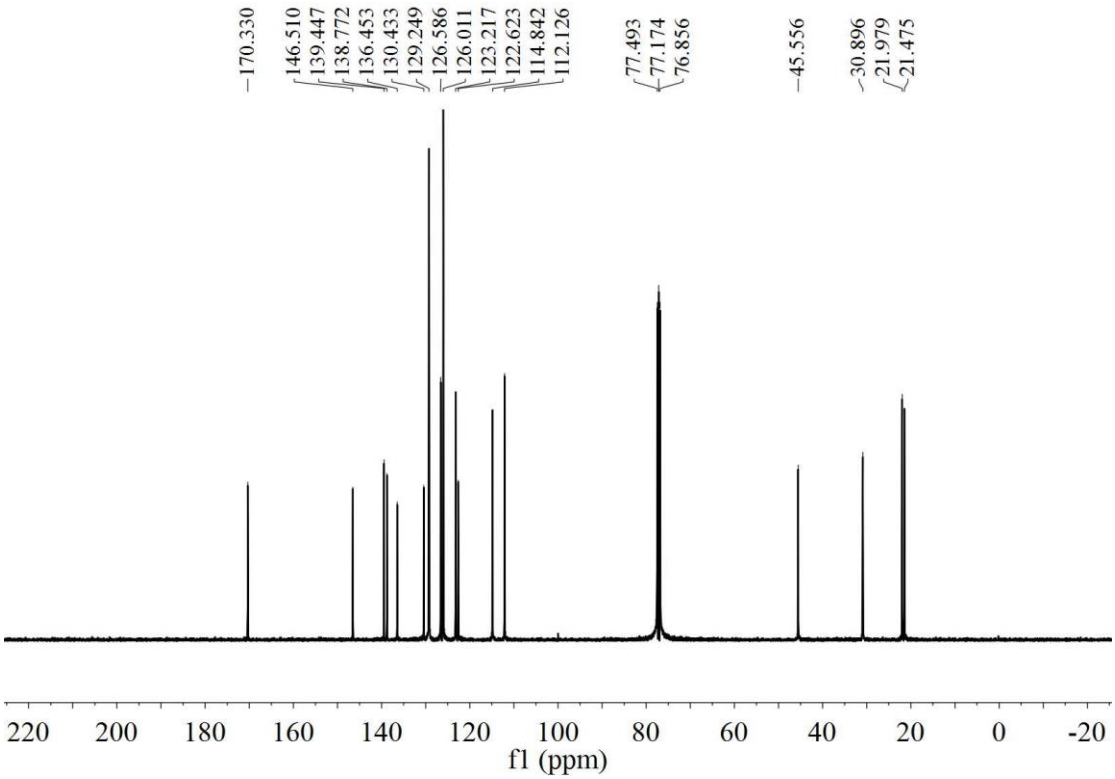
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3ld**



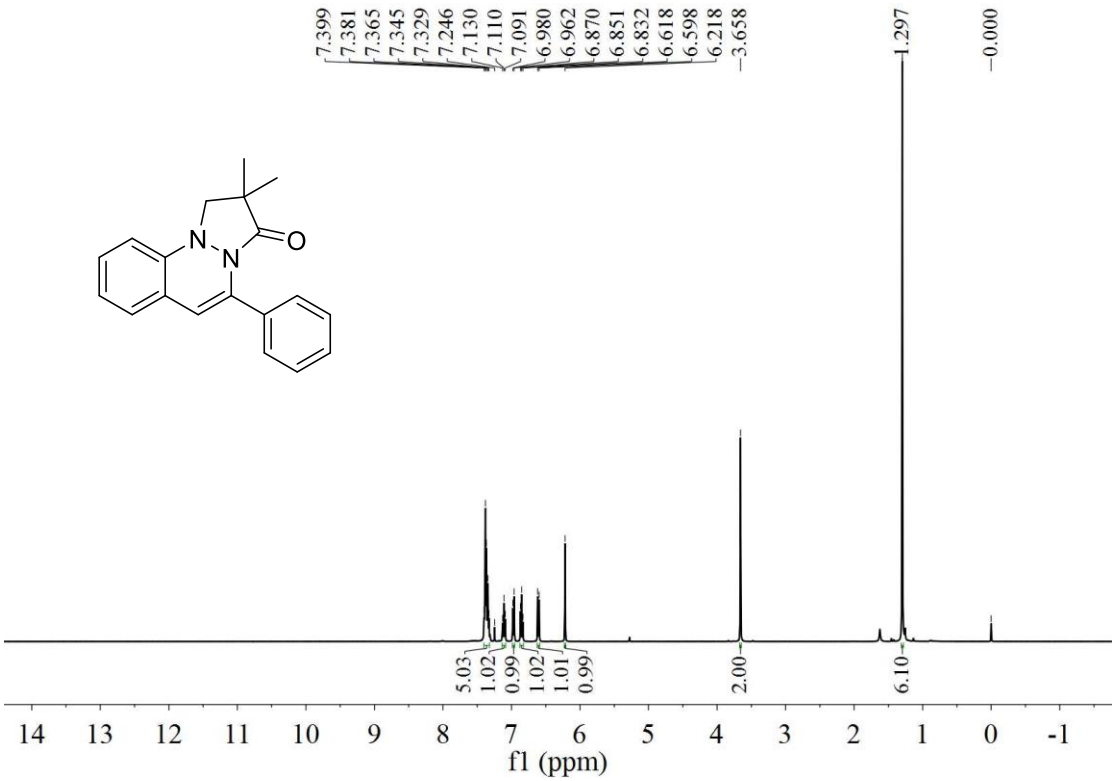
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3ld**



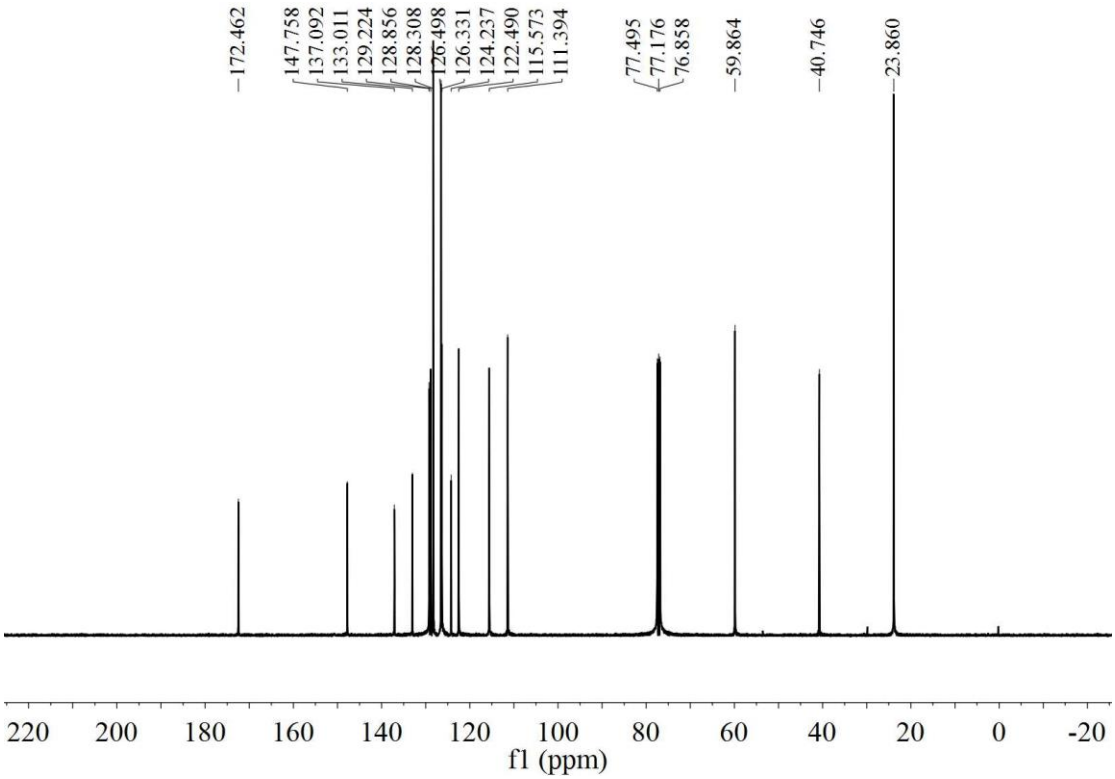
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3lk**



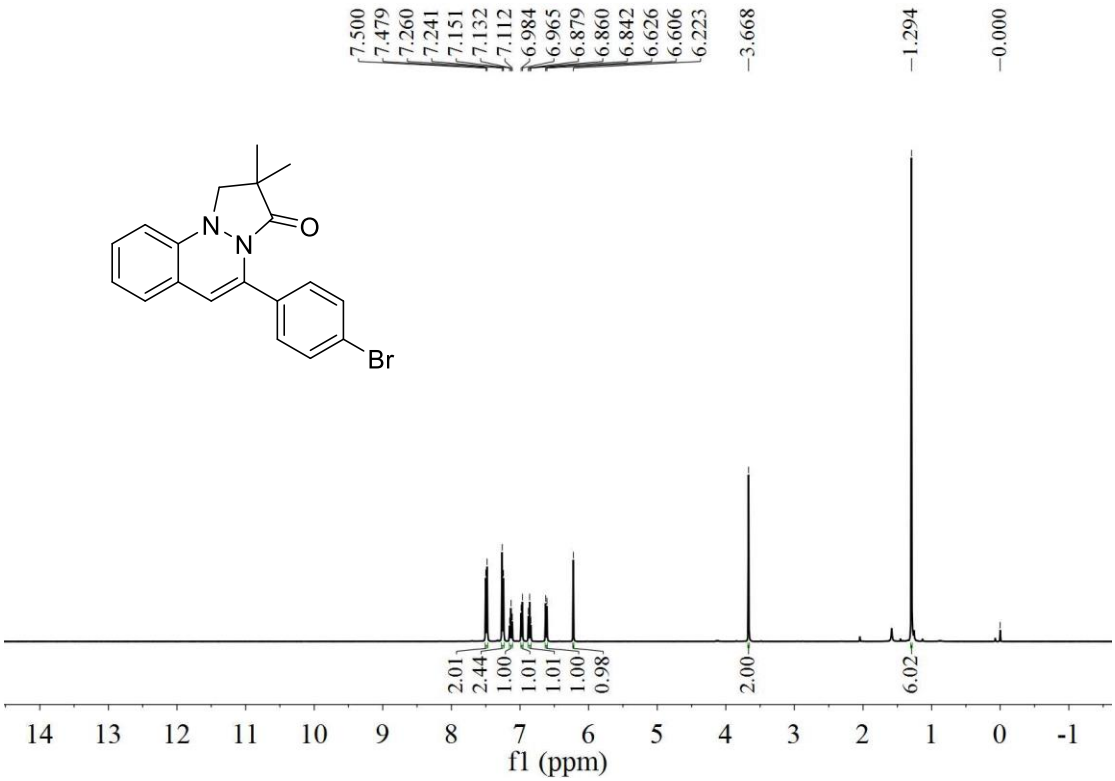
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3lk**



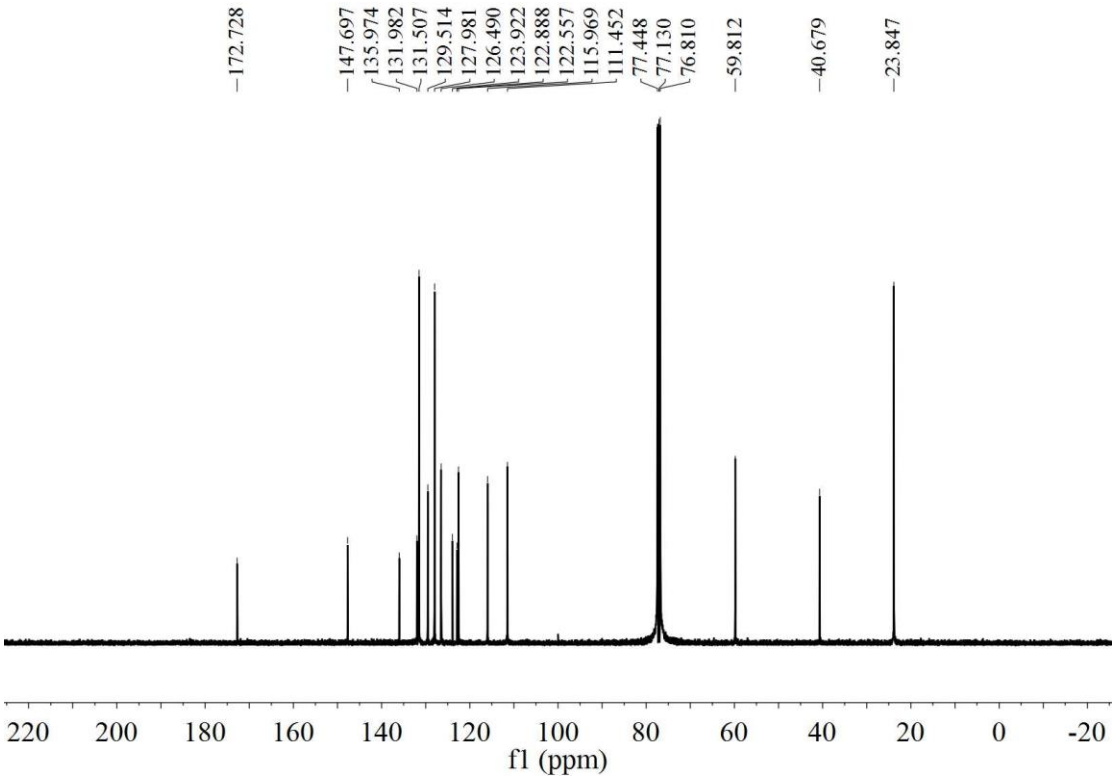
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3oa**



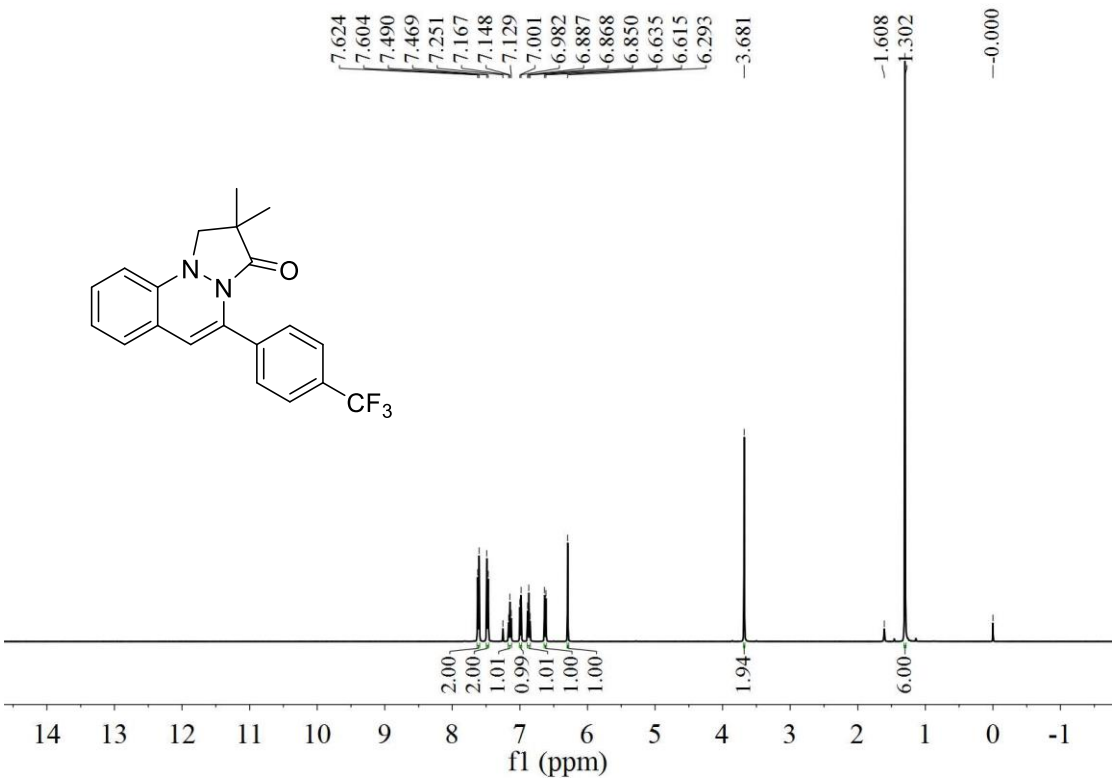
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3oa**



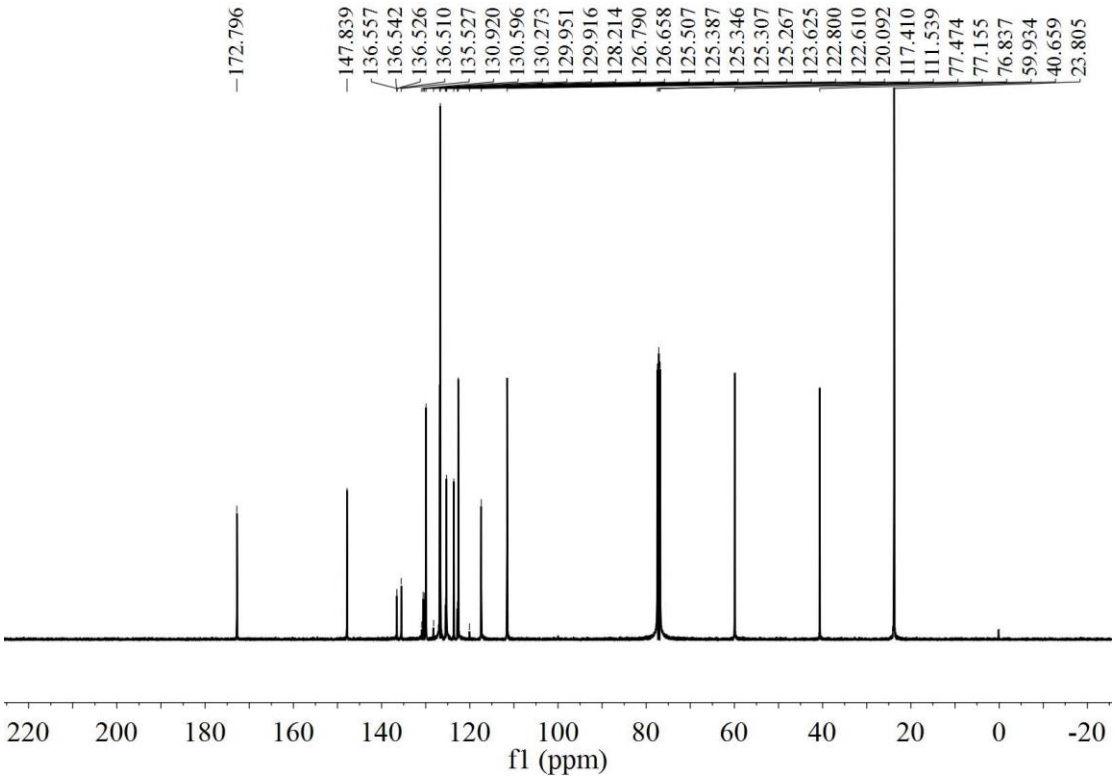
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3od**



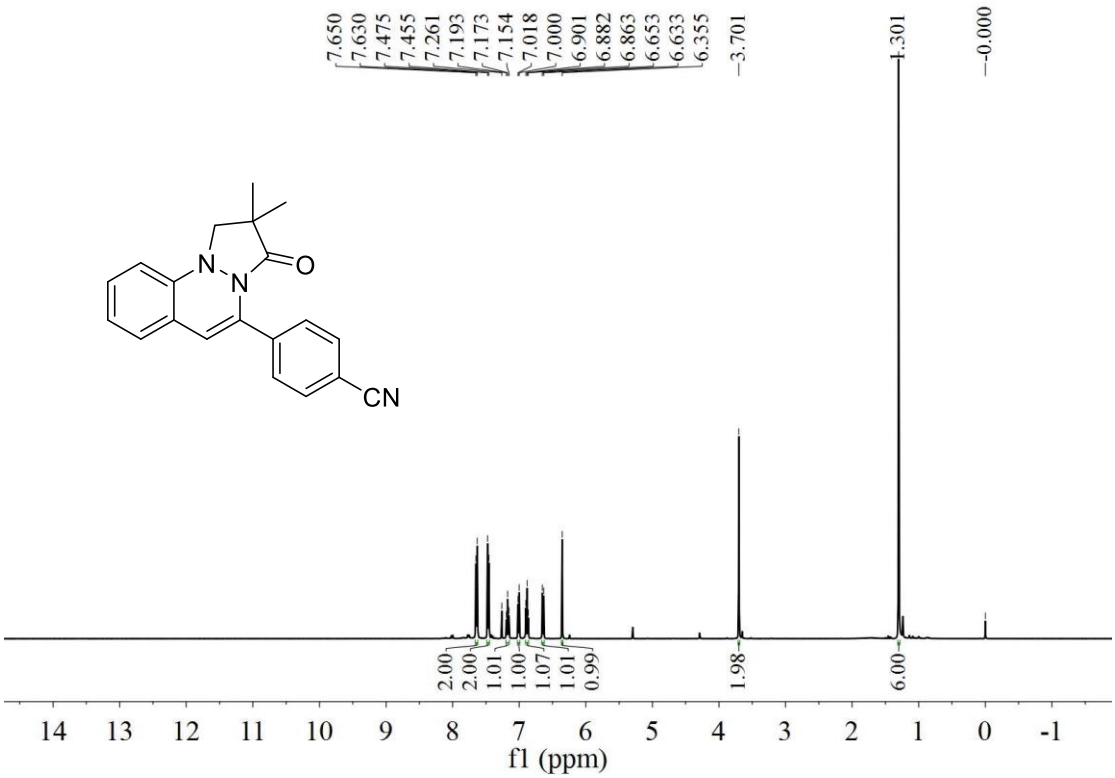
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3od**



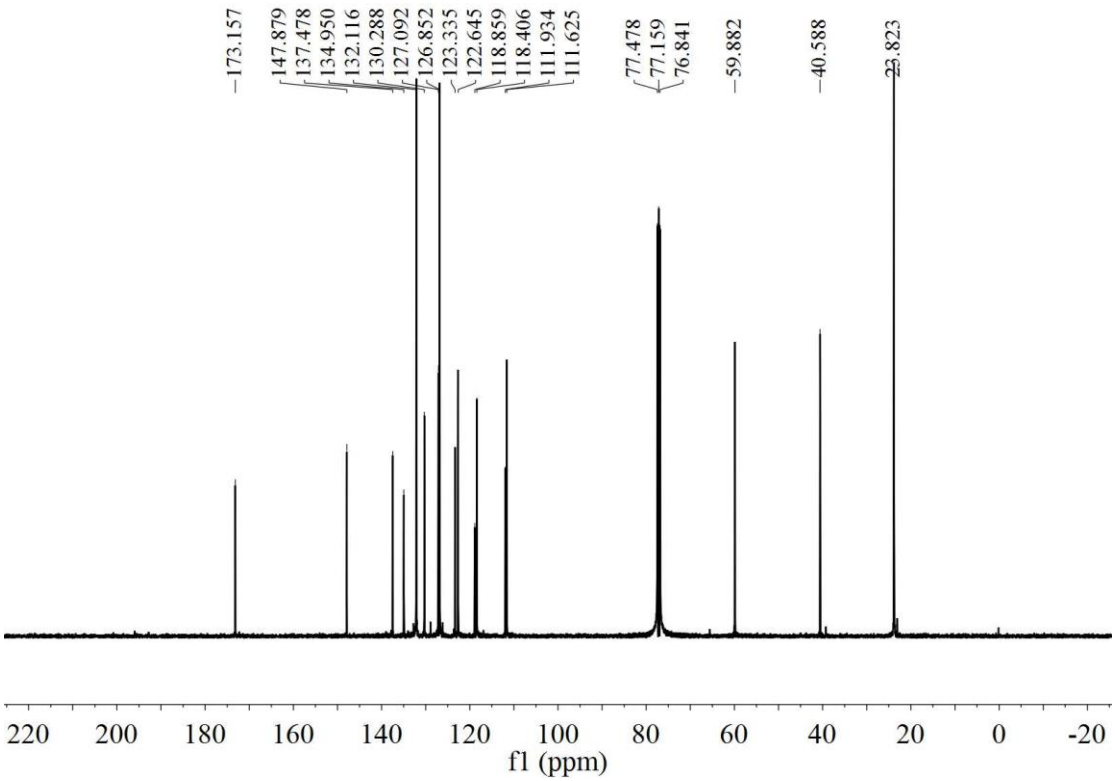
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3oe**



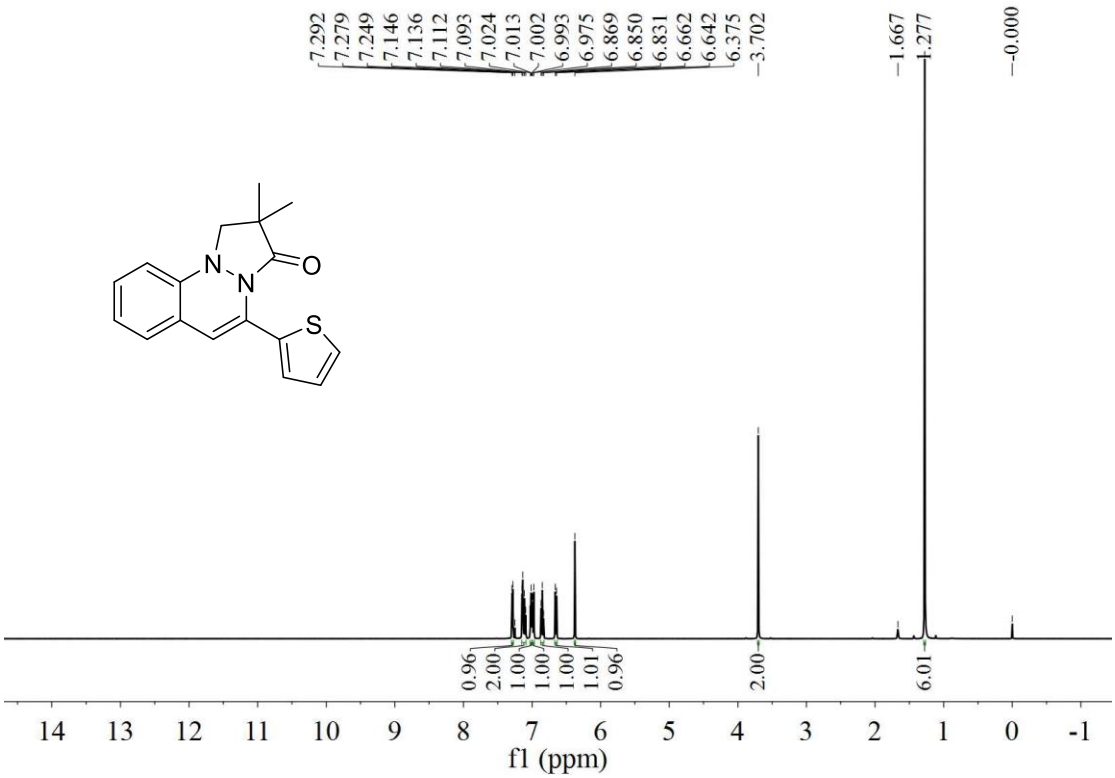
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3oe**



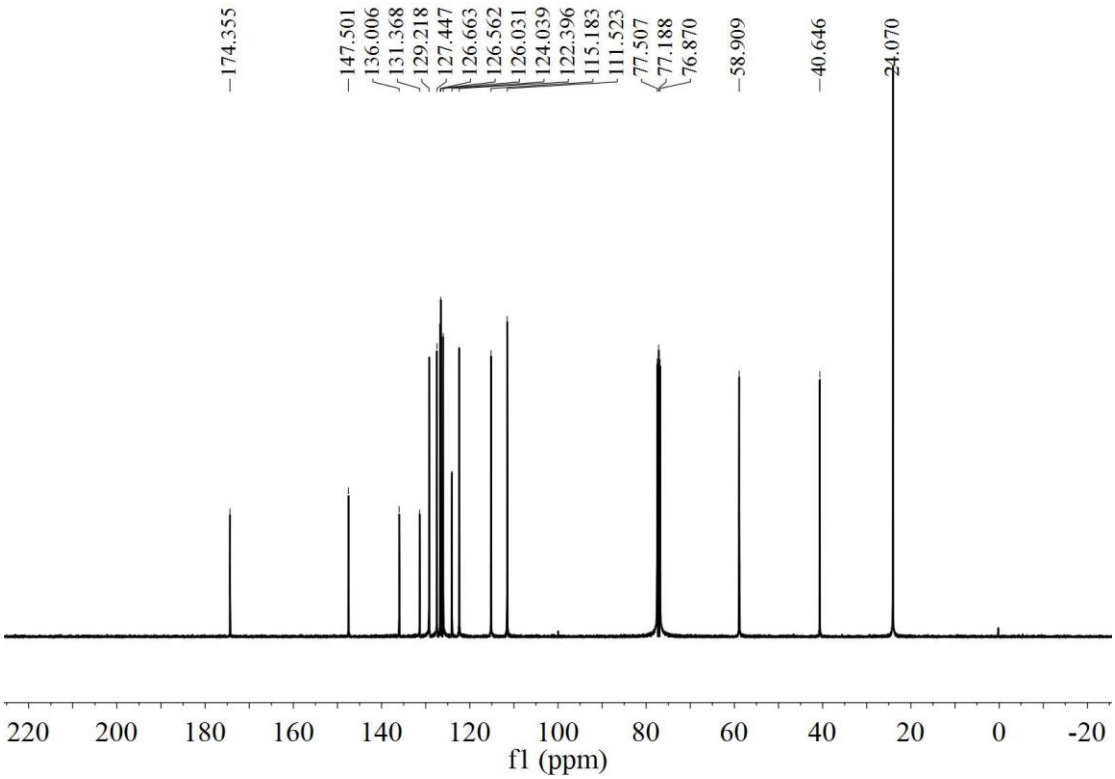
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3of**



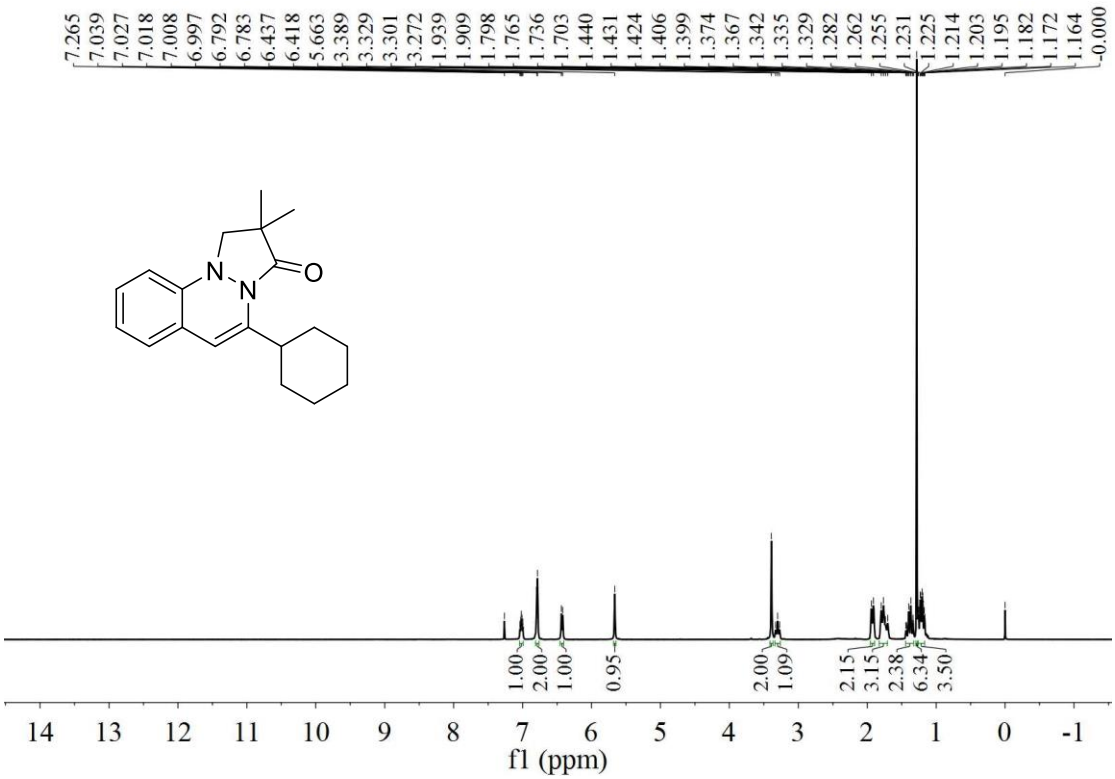
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3of**



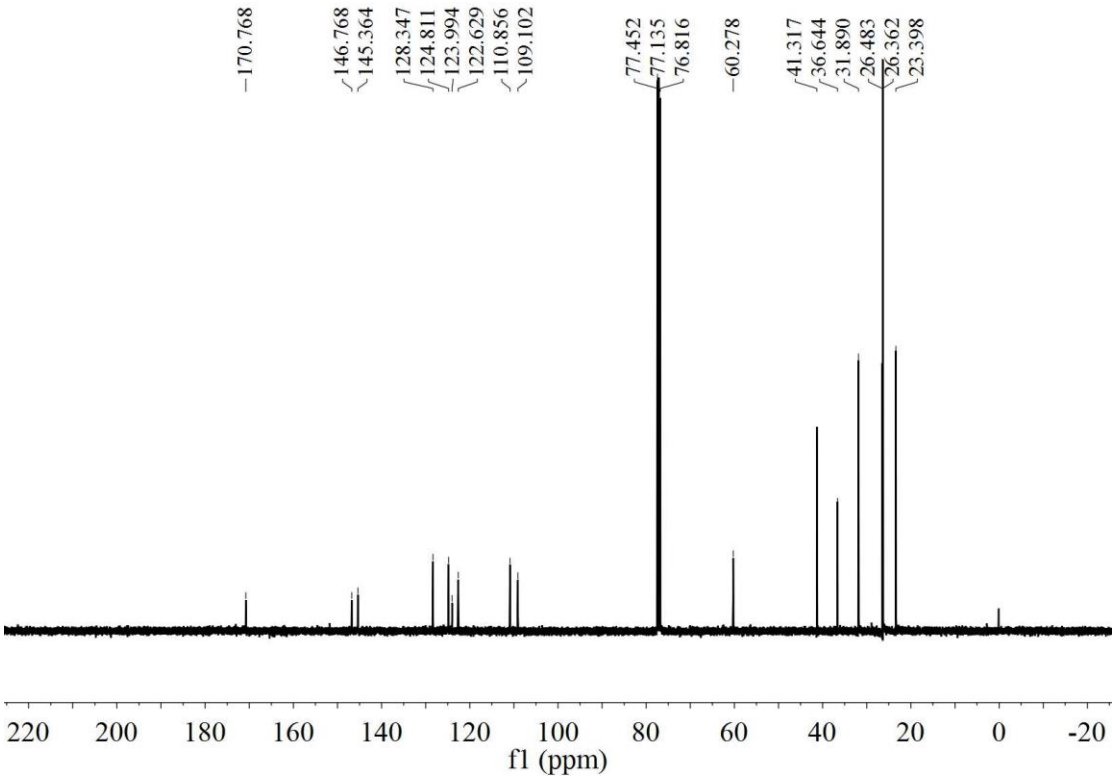
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3on**



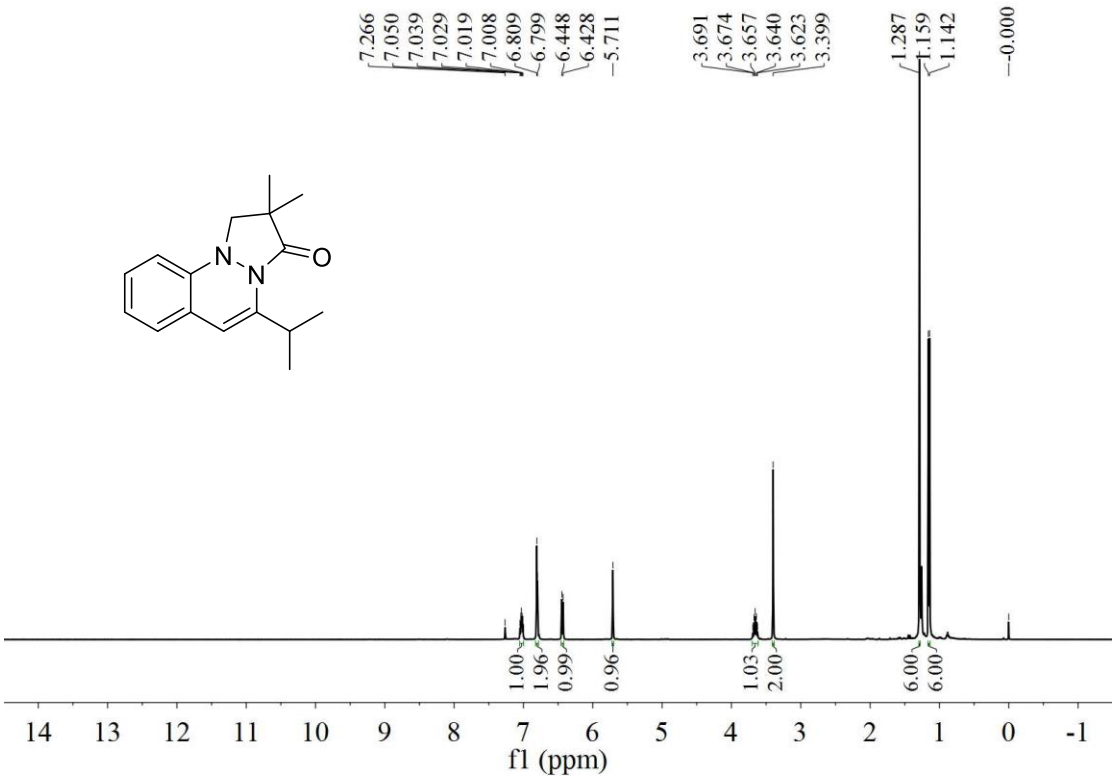
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3on**



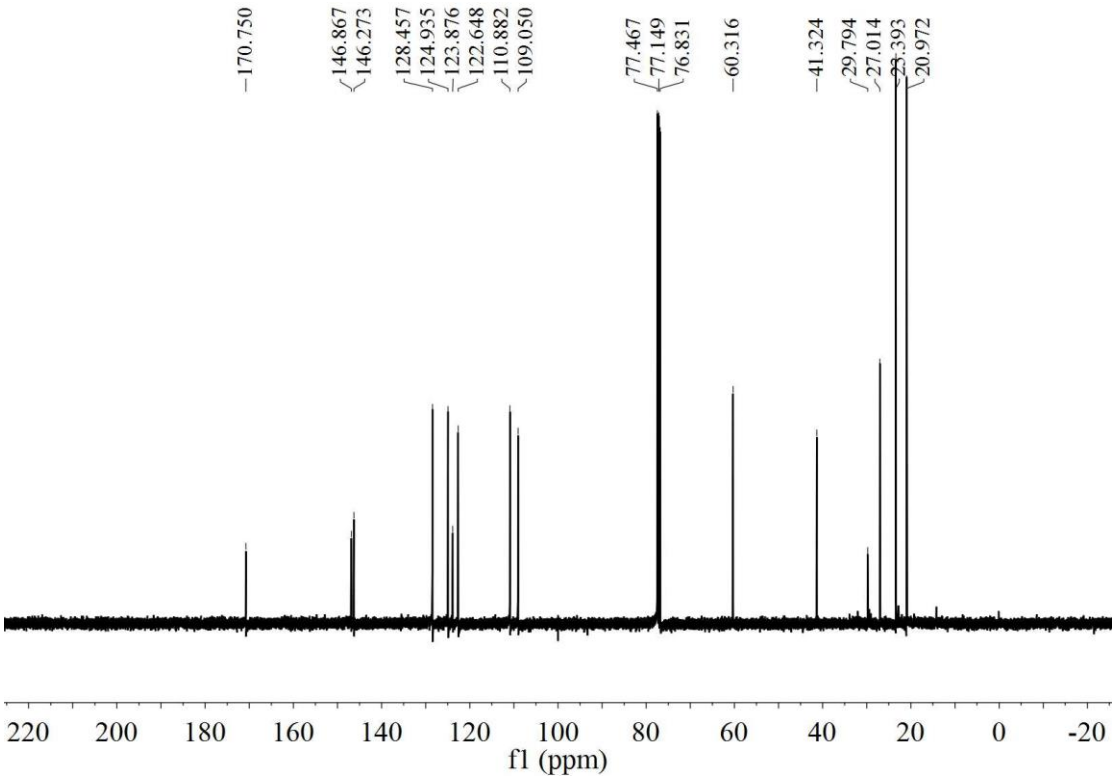
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3oo**



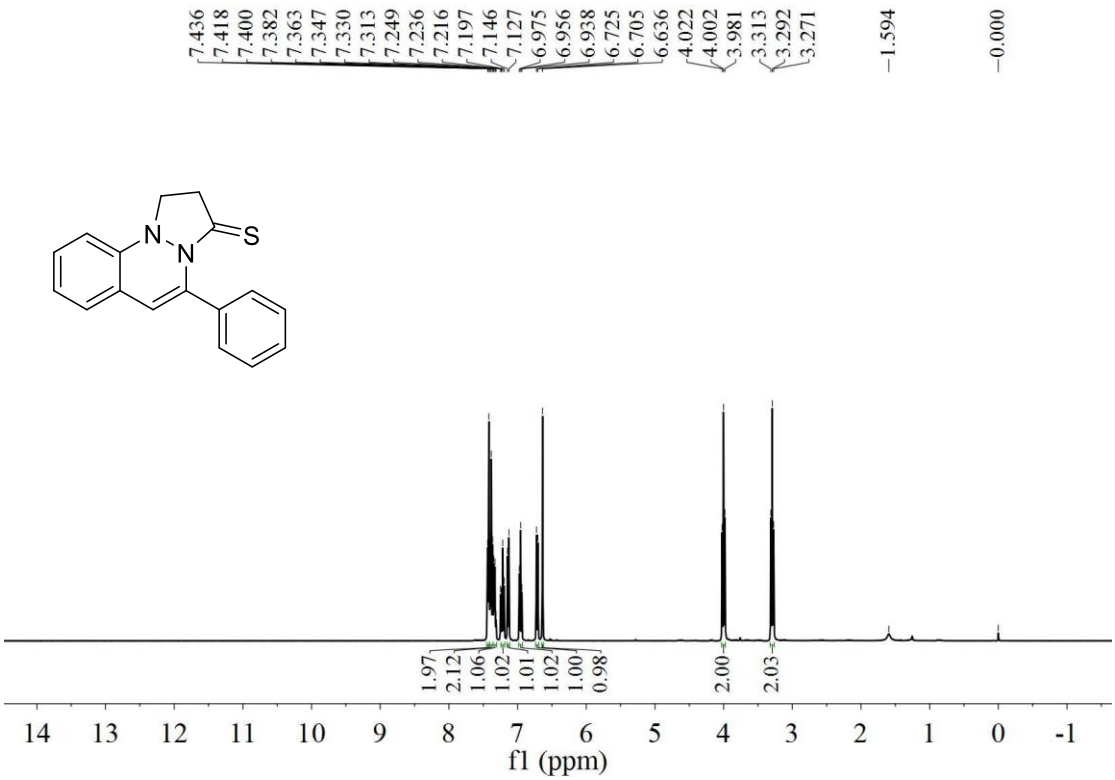
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound 3**oo**



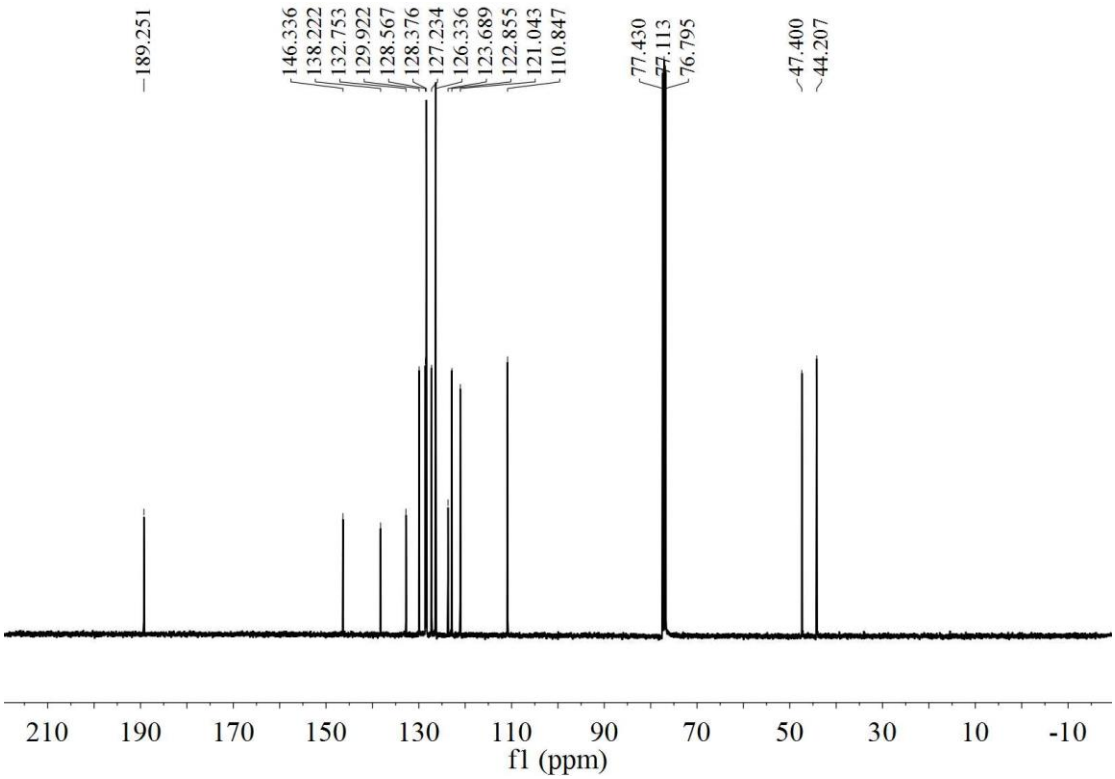
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **3op**



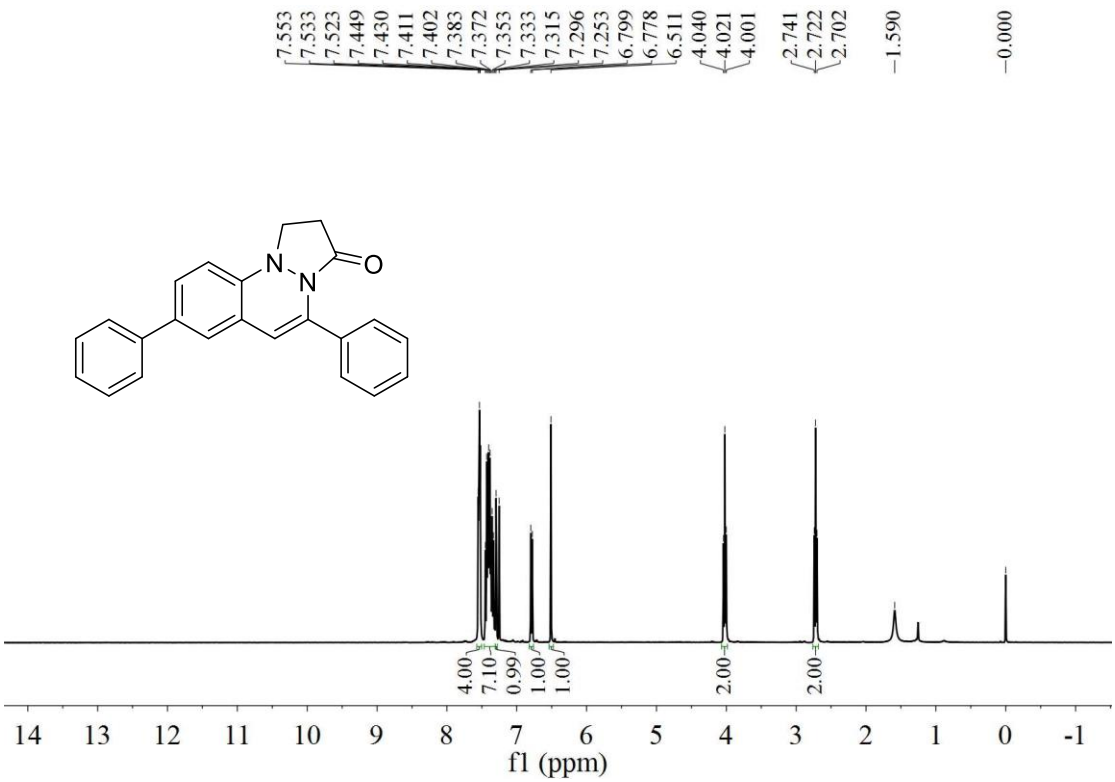
^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **3op**



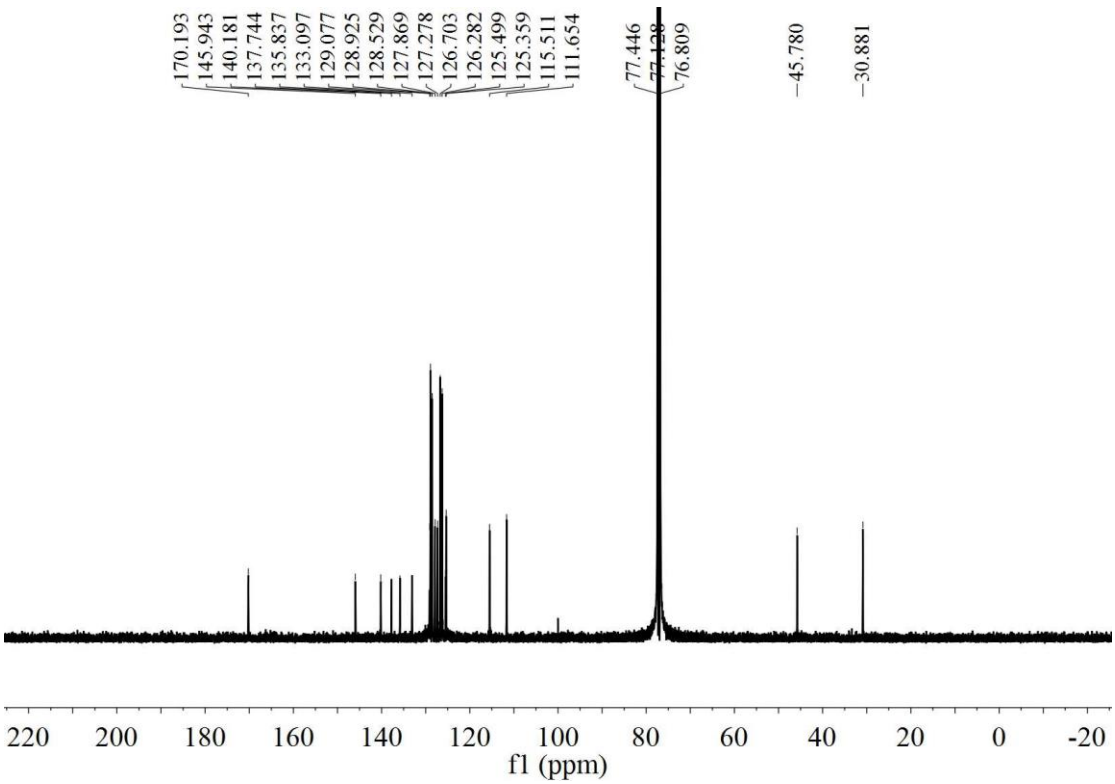
^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **4**



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **4**



^{1}H NMR Spectrum (400 MHz, $CDCl_3$) of Compound **5**



^{13}C NMR Spectrum (100 MHz, $CDCl_3$) of Compound **5**

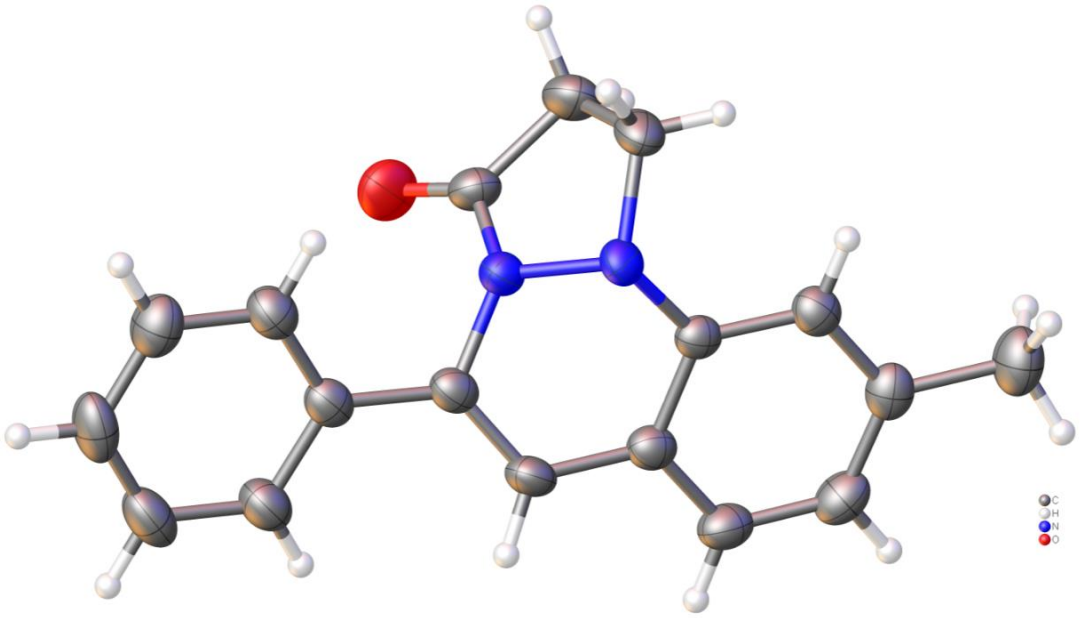


Figure S1. Crystal structure of **3la** (35% probability level for the thermal ellipsoids).

Table S1. Crystal Data for Compound **3la**

Formula	$C_{18}H_{16}N_2O$
Formula weight	276.33
Temperature	293 (2) K
Wavelength	0.71000 Å
Crystal system	triclinic
Space group	P1
Unit cell dimensions	a = 5.8988(4) Å, α = 106.781(6) deg.
	b = 11.1914(8) Å, β = 101.292(6) deg.
	c = 11.6421(8) Å, γ = 96.496(6) deg.
Volume	709.71(9) $Å^3$
Z	4
Density (calculated)	1.293 g / cm^3
Absorption coefficient	0.081 mm^{-1}
F(000)	292.0
Crystal	0.27 x 0.19 x 0.15 mm
Theta range for data collection	7.154 to 58.19 deg
Limiting indices	-7<=h<=7, -13<=k<=9, -13<=l<=15
Reflections collected	5511
Independent reflections	4066 [R(int) = 0.0241]
Data / restraints / parameters	4066 / 3 / 381
Goodness-of-fit on F^2	1.045
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0450, wR_2 = 0.0992
R indices (all data)	R_1 = 0.0529, wR_2 = 0.1046
Largest diff. peak and hole	0.18 and -0.23 e. $Å^{-3}$