
Supporting Information

for

Photocatalytic Bifunctionalization of Indole to Access the Multi-substituted Benzopyrrolizidinones

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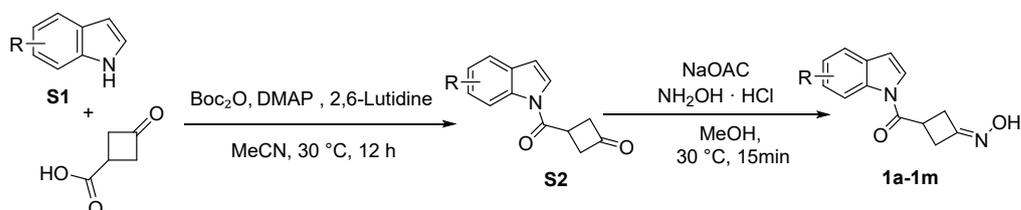
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I General Information

General remarks: ^1H and ^{13}C NMR spectra were recorded in CDCl_3 , unless otherwise noted, on a Bruker AVANCE 600 MHz or a Bruker AVANCE 400 MHz spectrometer. Chemical shifts in ^1H NMR spectra were reported in parts per million (ppm) on the δ scale from an internal standard of TMS (0.00 ppm). Data for ^1H NMR were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad), coupling constant in Hertz (Hz) and integration. Data for ^{13}C NMR spectra were reported in terms of chemical shift in ppm from the central peak of CDCl_3 (77.16 ppm). High-resolution electrospray ionization and electronic impact mass spectrometry was performed on a Thermo Scientific Q Exactive mass spectrometer (mass analyzer type: Orbitrap).

Materials and methods: Unless otherwise noted, all reactions of substrates preparation were conducted in flame dried glassware under Ar atmosphere using anhydrous solvent were re-distilled according to Purification of Laboratory Chemicals (Fifth Edition). Commercially available reagents were used without further purification. Thin layer chromatography (TLC) was performed using Jiangyou TLC silica gel plates HSG F254 and visualized using UV light, Flash column chromatography was performed over silica gel (300-400 mesh).

II Syntheses of Substrates and Characterization

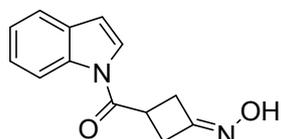


Di-tert-butyl dicarbonate (Boc_2O , 5 mmol) was added to a 50 mL single-necked flask containing a magnetic stir bar. 4-dimethylaminopyridine (DMAP, 50 mg) and 2,6-lutidine (2 drops) was added to the above solution. At room temperature, a mixed solution of 3-oxocyclobutanecarboxylic acid (5 mmol), indole derivative (S1, 5 mmol), DMAP (0.1 mmol) and 2,6-lutidine ($23.5\ \mu\text{L}$, 0.2 mmol) dissolved in 20 mL acetonitrile (MeCN) was slowly added to the aforementioned single-necked flask. Subsequently, the reaction system was heated to $30\text{ }^\circ\text{C}$ in a water bath and stirred at for 12 h. Upon completion of the reaction, the mixture was concentrated under reduced pressure to give a crude oil, which was not purified by silica gel column chromatography (eluent: n-hexane/ethyl acetate = 3:1) to afford compound S2 as a white solid^[1].

Then, compound S2 (1 eq), sodium acetate (NaOAc, 1.5 eq), hydroxylamine

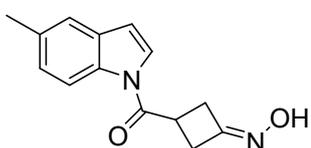
hydrochloride ($\text{NH}_2\text{OH}\cdot\text{HCl}$, 1.2 eq) and 10 mL methanol were sequentially added to a 25 mL single-necked flask. The reaction mixture was stirred at room temperature for 15 minutes. Then the mixture was concentrated under reduced pressure to give a crude oil, which was purified by silica gel column chromatography (**1a-1m**)^[2].

(3-(hydroxyimino)cyclobutyl)(1H-indol-1-yl)methanone



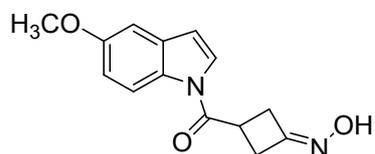
1a as white solid compound (684mg, 60%), ¹H NMR (400 MHz, Chloroform-*d*) δ 8.48 (d, $J = 7.6$ Hz, 1H), 7.58 (d, $J = 7.5$ Hz, 1H), 7.34 (dd, $J = 26.2, 7.4$ Hz, 4H), 6.76 – 6.61 (m, 1H), 3.86 (p, $J = 7.4$ Hz, 1H), 3.54 – 3.21 (m, 4H). ¹³C NMR (101 MHz, CDCl_3) δ 171.0, 153.9, 135.8, 130.5, 125.6, 124.2, 124.0, 121.1, 116.7, 110.1, 35.2, 34.5, 32.6. HR-MS (ESI-TOF) calcd for $\text{C}_{13}\text{H}_{13}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 229.0972 found 229.0971.

(3-(hydroxyimino)cyclobutyl)(5-methyl-1H-indol-1-yl)methanone



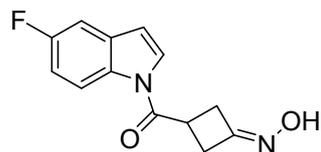
1b as white solid compound (641 mg, 53%), ¹H NMR (400 MHz, Chloroform-*d*) δ 8.57 (s, 1H), 8.25 (d, $J = 8.1$ Hz, 1H), 7.16 (d, $J = 3.1$ Hz, 1H), 7.10 (d, $J = 8.3$ Hz, 1H), 6.50 (d, $J = 3.7$ Hz, 1H), 3.69 (p, $J = 8.1, 7.2$ Hz, 1H), 3.37 (ddt, $J = 14.9, 7.1, 3.2$ Hz, 2H), 3.26 (dd, $J = 17.2, 9.4$ Hz, 1H), 3.20 – 3.12 (m, 1H), 2.36 (s, 3H). ¹³C NMR (101 MHz, CDCl_3) δ 170.8, 154.0, 133.9, 133.7, 130.7, 126.8, 124.1, 121.0, 116.3, 109.8, 35.1, 34.5, 32.4, 21.4. HR-MS (ESI-TOF) calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 243.1128 found 243.1124.

(3-(hydroxyimino)cyclobutyl)(5-methoxy-1H-indol-1-yl)methanone



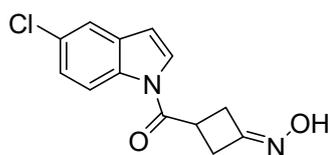
1c as white solid compound (645 mg, 50%), ¹H NMR (400 MHz, Chloroform-*d*) δ 8.36 (d, $J = 9.0$ Hz, 1H), 8.16 (s, 1H), 7.27 (d, $J = 3.6$ Hz, 1H), 7.03 (d, $J = 2.5$ Hz, 1H), 6.97 (dd, $J = 9.0, 2.6$ Hz, 1H), 6.62 – 6.57 (m, 1H), 3.85 (s, 3H), 3.83 – 3.76 (m, 1H), 3.47 (dtd, $J = 16.8, 6.8, 3.0$ Hz, 2H), 3.37 (ddt, $J = 17.3, 9.3, 2.6$ Hz, 1H), 3.30 – 3.22 (m, 1H). ¹³C NMR (101 MHz, CDCl_3) δ 170.6, 156.8, 153.9, 131.5, 130.5, 124.7, 117.5, 113.9, 109.9, 103.9, 55.8, 35.2, 34.6, 32.3. HR-MS (ESI-TOF) calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 259.1077 found 259.1073.

(5-fluoro-1H-indol-1-yl)(3-(hydroxyimino)cyclobutyl)methanone



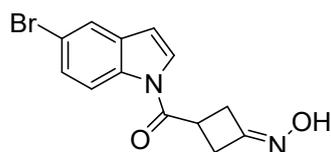
1d as white solid compound (640 mg, 52%), ¹H NMR (600 MHz, $\text{DMSO}-d_6$) δ 10.49 (s, 1H), 8.37 (dd, $J = 9.0, 4.8$ Hz, 1H), 7.89 (d, $J = 3.8$ Hz, 1H), 7.43 (dd, $J = 9.1, 2.6$ Hz, 1H), 7.18 (td, $J = 9.2, 2.6$ Hz, 1H), 6.76 (d, $J = 3.7$ Hz, 1H), 4.14 – 4.08 (m, 1H), 3.29 – 3.19 (m, 3H), 3.16 (ddd, $J = 17.9, 6.9, 2.2$ Hz, 1H). ¹³C NMR (151 MHz, DMSO) δ 172.1, 159.7, 158.1, 151.0, 131.6, 131.5, 131.4, 128.0, 117.2, 117.1, 112.3, 112.1, 108.6, 108.6, 106.5, 106.4, 34.5, 34.2, 31.7. HR-MS (ESI-TOF) calcd for $\text{C}_{13}\text{H}_{12}\text{FN}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 247.0878 found 247.0879.

(5-chloro-1*H*-indol-1-yl)(3-(hydroxyimino)cyclobutyl)methanone



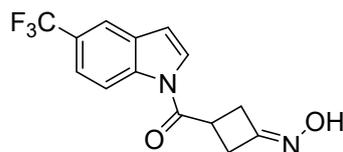
1e as white solid compound (655 mg, 50%), ¹H NMR (600 MHz, DMSO-*d*₆) δ 10.52 (s, 1H), 8.33 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 3.8 Hz, 1H), 7.65 (d, *J* = 2.0 Hz, 1H), 7.32 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.73 (d, *J* = 3.7 Hz, 1H), 4.09 (p, *J* = 8.9 Hz, 1H), 3.30 – 3.21 (m, 3H), 3.20 – 3.14 (m, 1H). ¹³C NMR (151 MHz, DMSO) δ 172.2, 150.9, 133.5, 131.7, 127.9, 127.7, 124.5, 120.3, 117.3, 108.1, 34.5, 34.2, 31.8. HR-MS (ESI-TOF) calcd for C₁₃H₁₂ClN₂O₂ [M+H]⁺ 263.0539 found 263.0535.

(5-bromo-1*H*-indol-1-yl)(3-(hydroxyimino)cyclobutyl)methanone



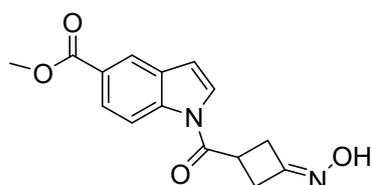
1f as white solid compound (844 mg, 55%), ¹H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 8.8 Hz, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.47 (dd, *J* = 8.8, 1.7 Hz, 1H), 7.32 (d, *J* = 3.7 Hz, 1H), 7.15 (s, 1H), 6.62 (d, *J* = 3.7 Hz, 1H), 3.84 (ddd, *J* = 16.2, 9.0, 7.0 Hz, 1H), 3.53 – 3.35 (m, 3H), 3.30 (dd, *J* = 16.8, 9.3 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 171.0, 134.5, 132.2, 128.5, 125.1, 123.8, 118.1, 117.5, 109.2, 35.2, 32.5, 29.8. HR-MS (ESI-TOF) calcd for C₁₃H₁₂BrN₂O₂ [M+H]⁺ 307.0077 found 307.0074.

(3-(hydroxyimino)cyclobutyl)(5-(trifluoromethyl)-1*H*-indol-1-yl)methanone



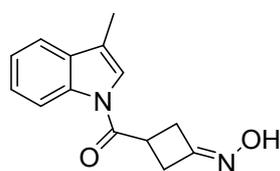
1g as white solid compound (710 mg, 48%), ¹H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 8.7 Hz, 1H), 8.06 (s, 1H), 7.86 (s, 1H), 7.64 – 7.58 (m, 1H), 7.42 (d, *J* = 3.8 Hz, 1H), 6.75 (d, *J* = 3.8 Hz, 1H), 3.91 – 3.82 (m, 1H), 3.54 – 3.37 (m, 3H), 3.36 – 3.27 (m, 1H). ¹³C NMR (151 MHz, DMSO) δ 172.1, 159.7, 158.1, 151.0, 131.6, 131.5, 131.4, 128.0, 117.2, 117.1, 112.3, 112.1, 108.6, 108.6, 106.5, 106.4, 34.5, 34.2, 31.7. HR-MS (ESI-TOF) calcd for C₁₄H₁₂F₃N₂O₂ [M+H]⁺ 297.0803 found 297.0801.

methyl 1-(3-(hydroxyimino)cyclobutane-1-carbonyl)-1*H*-indole-5-carboxylate



1h as white solid compound (558 mg, 39%), ¹H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, *J* = 8.7 Hz, 1H), 8.30 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.51 (s, 1H), 7.38 (d, *J* = 3.7 Hz, 1H), 6.75 (d, *J* = 3.8 Hz, 1H), 3.95 (s, 3H), 3.86 (ddd, *J* = 16.2, 9.1, 7.1 Hz, 1H), 3.48 (dddd, *J* = 23.5, 16.0, 8.1, 2.5 Hz, 3H), 3.35 – 3.27 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 171.2, 167.4, 153.5, 138.4, 130.3, 126.9, 126.1, 125.2, 123.3, 116.4, 110.4, 52.3, 35.2, 34.5, 32.7. HR-MS (ESI-TOF) calcd for C₁₅H₁₅N₂O₄ [M+H]⁺ 287.1027 found 287.1024.

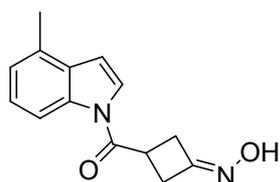
(3-(hydroxyimino)cyclobutyl)(3-methyl-1*H*-indol-1-yl)methanone



1i as white solid compound (653 mg, 54%), ¹H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 7.2 Hz, 1H), 7.63 (s, 1H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.36 (m, 1H), 7.32 (td, *J* = 7.5, 1.0 Hz, 1H), 7.07 (s, 1H), 3.80 (ddd, *J* = 16.2, 9.2, 7.0 Hz, 1H), 3.53 – 3.47 (m, 1H), 3.45 (dd, *J* = 7.0, 2.9 Hz, 1H), 3.38 (ddt, *J* = 17.2, 9.3, 2.5 Hz, 1H), 3.28

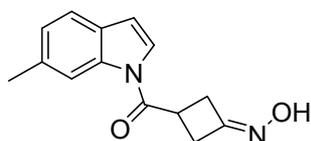
(ddt, $J = 16.8, 9.2, 2.3$ Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.5, 154.0, 136.0, 131.4, 125.5, 123.8, 120.8, 119.3, 118.9, 116.6, 35.0, 34.4, 32.4, 9.7. HR-MS (ESI-TOF) calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 243.1128 found 243.1124.

(3-(hydroxyimino)cyclobutyl)(4-methyl-1H-indol-1-yl)methanone



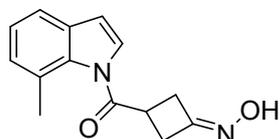
1j as white solid compound (629 mg, 52%), ^1H NMR (400 MHz, Chloroform-*d*) δ 8.31 (d, $J = 7.4$ Hz, 1H), 7.54 (s, 1H), 7.29 (d, $J = 9.4$ Hz, 2H), 7.10 (d, $J = 6.8$ Hz, 1H), 6.72 (s, 1H), 3.85 (p, $J = 8.0$ Hz, 1H), 3.52 – 3.25 (m, 4H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.0, 154.0, 135.6, 130.5, 130.1, 125.7, 124.6, 123.5, 114.2, 108.5, 35.2, 34.5, 32.6, 18.6. HR-MS (ESI-TOF) calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 243.1128 found 243.1124.

(3-(hydroxyimino)cyclobutyl)(6-methyl-1H-indol-1-yl)methanone



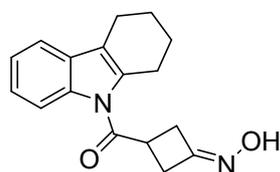
1k as white solid compound (655 mg, 55%), ^1H NMR (400 MHz, Chloroform-*d*) δ 8.33 (s, 1H), 7.70 (s, 1H), 7.45 (d, $J = 7.9$ Hz, 1H), 7.23 (d, $J = 3.0$ Hz, 1H), 7.13 (d, $J = 7.8$ Hz, 1H), 6.62 (d, $J = 3.4$ Hz, 1H), 3.83 (p, $J = 8.3$ Hz, 1H), 3.52 – 3.24 (m, 4H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 171.1, 154.0, 136.2, 135.8, 128.2, 125.6, 123.4, 120.6, 117.0, 110.0, 35.2, 34.5, 32.6, 22.1. HR-MS (ESI-TOF) calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 243.1128 found 243.1124.

(3-(hydroxyimino)cyclobutyl)(7-methyl-1H-indol-1-yl)methanone



1l as white solid compound (617 mg, 51%), ^1H NMR (400 MHz, Chloroform-*d*) δ 8.74 (s, 1H), 7.42 (d, $J = 7.5$ Hz, 1H), 7.27 – 7.21 (m, 2H), 7.18 (d, $J = 7.3$ Hz, 1H), 3.88 – 3.80 (m, 1H), 3.51 – 3.45 (m, 1H), 3.45 – 3.34 (m, 2H), 3.29 (ddt, $J = 17.0, 9.2, 2.1$ Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 170.7, 154.0, 135.2, 132.1, 128.6, 126.8, 125.3, 124.5, 118.7, 109.9, 35.8, 35.2, 33.2, 22.8. HR-MS (ESI-TOF) calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 243.1128 found 243.1124.

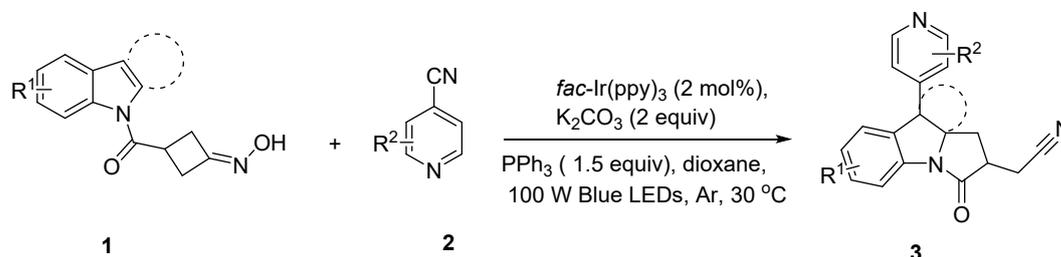
(3-(hydroxyimino)cyclobutyl)(1,2,3,4-tetrahydro-9H-carbazol-9-yl)methanone



1m as white solid compound (536 mg, 38%), ^1H NMR (400 MHz, Chloroform-*d*) δ 8.13 (s, 1H), 7.98 – 7.91 (m, 1H), 7.41 (dd, $J = 6.1, 2.7$ Hz, 1H), 7.30 – 7.23 (m, 2H), 3.95 (ddd, $J = 15.7, 8.9, 6.8$ Hz, 1H), 3.52 – 3.33 (m, 3H), 3.31 – 3.22 (m, 1H), 3.00 (t, $J = 5.6$ Hz, 2H), 2.66 (t, $J = 5.7$ Hz, 2H), 1.94 – 1.82 (m, 4H). ^{13}C NMR (101 MHz, CDCl_3) δ 172.9, 154.3, 135.8, 135.3, 130.6, 124.2, 123.3, 118.9, 118.1, 115.0, 35.7, 35.1, 34.1, 26.3, 23.9, 22.0, 21.2. HR-MS (ESI-TOF) calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 283.1398 found 283.1396.

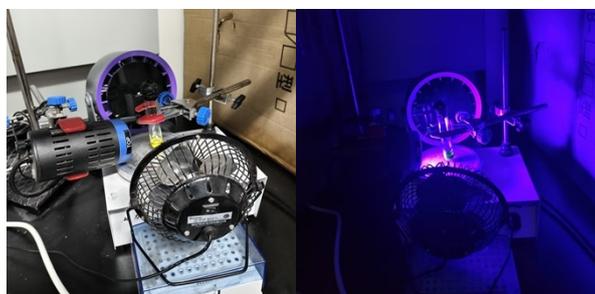
III General Procedures

Typical Procedure A



A 15 mL of reaction tube was charged with **1** (0.2 mmol), **2** (0.2 mmol), *fac*-Ir(ppy)₃ (2%), K₂CO₃ (0.4 mmol), PPh₃ (0.3 mmol) and dioxane (2 mL) under argon atmosphere. The tube was placed approximately 2 cm from 100 W blue LEDs (427 nm), and stirred at room 30 °C for 12 h. The corresponding reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silical gel using 100% (v/v) ethyl acetate in petroleum ether as eluent to afford the desired product.

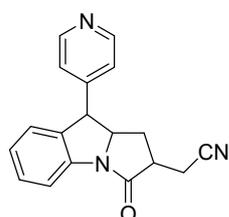
Reaction Setup



The reaction was carried out using the above setup with one 100W of blue LEDs (LEDDRIVER YJ-100W, $\lambda=427 \text{ nm}$). There is 2.5 cm distance between the reactor and LEDs at 30 °C, which is monitored by a thermometer.

IV Characterization of Multisubstituted Indoline

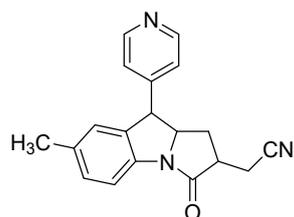
2-(3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (**3a**)



3a as oil compound (49.2 mg, 85%), d.r. > 19:1. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.61 (d, $J = 3.9 \text{ Hz}$, 2H), 7.64 (d, $J = 7.7 \text{ Hz}$, 1H), 7.32 (t, $J = 7.6 \text{ Hz}$, 1H), 7.24 (d, $J = 4.4 \text{ Hz}$, 2H), 7.10 (t, $J = 7.4 \text{ Hz}$, 1H), 6.92 (d, $J = 7.4 \text{ Hz}$, 1H), 4.47 (q, $J = 9.4 \text{ Hz}$, 1H), 4.37 (s, 1H), 3.20 (dq, $J = 12.0, 7.4 \text{ Hz}$, 1H), 2.89 (dd, $J = 17.2, 4.4 \text{ Hz}$, 1H), 2.81 (dt, $J = 12.3, 6.4 \text{ Hz}$, 1H),

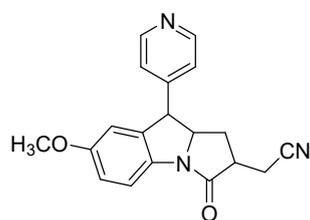
2.68 (dd, $J = 17.2, 8.1$ Hz, 1H), 2.07 (q, $J = 11.7$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 168.5, 150.4, 149.3, 138.8, 135.5, 129.0, 125.4, 123.6, 117.4, 115.2, 68.7, 67.1, 54.9, 43.2, 34.1, 18.4. HR-MS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{16}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 290.1288 found 290.1283.

2-(7-methyl-3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3b)



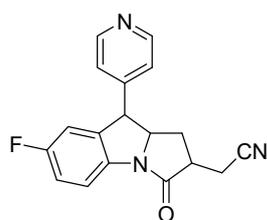
3b as oil compound (54.0 mg, 89%), d.r. 1.63:1. ^1H NMR (600 MHz, Chloroform- d) δ 8.57 (d, $J = 58.6$ Hz, 2H), 7.54 (dd, $J = 39.3, 7.8$ Hz, 1H), 7.31 – 6.64 (m, 4H), 4.92 – 4.31 (m, 2H), 3.18 (dt, $J = 12.9, 8.5, 4.0$ Hz, 1H), 2.89 – 2.65 (m, 2H), 2.57 – 2.32 (m, 1H), 2.26 (s, 3H), 2.05 (q, $J = 11.3, 10.6$ Hz, 0.62H), 1.14 (q, $J = 12.1, 11.4$ Hz, 0.38H). ^{13}C NMR (151 MHz, CDCl_3) δ 168.31, 168.06, 150.48, 150.43, 149.35, 147.29, 136.54, 136.21, 135.79, 135.75, 135.55, 135.42, 129.79, 129.42, 127.05, 126.00, 123.82, 123.67, 117.59, 117.48, 114.79, 114.72, 68.88, 63.48, 60.43, 54.91, 48.31, 43.55, 43.23, 34.10, 30.03, 21.28, 21.27, 21.09, 18.44, 18.41, 14.24. HR-MS (ESI-TOF) calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 304.1444 found 304.1440.

2-(7-methoxy-3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3c)



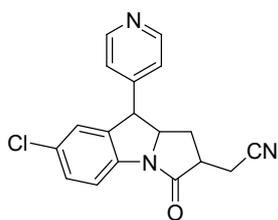
3c as oil compound (52.4 mg, 82%), d.r. 4:1. ^1H NMR (600 MHz, Chloroform- d) δ 8.58 (dd, $J = 54.8, 4.0$ Hz, 2H), 7.58 (dd, $J = 41.2, 8.7$ Hz, 1H), 7.25 – 6.41 (m, 4H), 4.94 – 4.32 (m, 2H), 3.74 – 3.68 (m, 3H), 3.18 (dq, $J = 12.0, 7.7$ Hz, 1H), 2.90 – 2.28 (m, 3H), 2.05 (q, $J = 11.8$ Hz, 0.8H), 1.14 (td, $J = 12.2, 10.1$ Hz, 0.2H). ^{13}C NMR (151 MHz, CDCl_3) δ 168.03, 157.85, 150.55, 150.48, 149.14, 137.17, 132.55, 123.86, 123.70, 117.61, 115.83, 115.80, 114.30, 113.72, 112.47, 111.78, 69.15, 67.18, 63.75, 55.87, 55.82, 55.26, 48.72, 43.49, 43.17, 34.06, 18.54. HR-MS (ESI-TOF) calcd for $\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+$ 320.1394 found 320.1390.

2-(7-fluoro-3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3d)



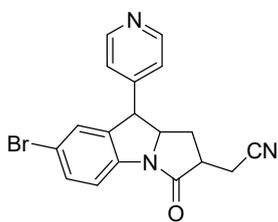
3d as oil compound (46.7 mg, 76%), d.r. 2.85:1. ^1H NMR (600 MHz, Chloroform- d) δ 8.74 – 8.44 (m, 2H), 7.67 – 7.51 (m, 1H), 7.25 – 6.55 (m, 4H), 4.96 – 4.35 (m, 2H), 3.25 – 3.09 (m, 1H), 2.87 – 2.36 (m, 3H), 2.07 (q, $J = 11.1$ Hz, 0.74H), 1.16 (q, $J = 11.5$ Hz, 0.26H). ^{13}C NMR (151 MHz, CDCl_3) δ 168.46, 161.17, 159.55, 150.64, 148.42, 137.61, 137.56, 135.07, 135.06, 123.48, 117.45, 116.04, 115.99, 115.71, 115.55, 113.14, 112.98, 69.02, 63.60, 54.97, 48.38, 43.30, 43.01, 34.01, 18.34. HR-MS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{15}\text{FN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 308.1194 found 308.1189.

2-(7-chloro-3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3e)



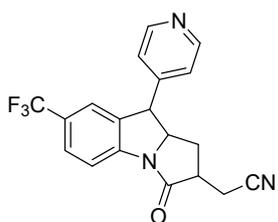
3e as oil compound (51 mg, 79%), d.r. 2.85:1. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.59 (dd, $J = 53.5, 5.4$ Hz, 2H), 7.65 – 7.53 (m, 1H), 7.33 – 6.73 (m, 4H), 4.95 – 4.35 (m, 2H), 3.19 (td, $J = 12.1, 7.6$ Hz, 1H), 2.88 – 2.29 (m, 3H), 2.10 – 2.04 (q, 0.74H), 1.17 (q, $J = 12.1$ Hz, 0.26H). ^{13}C NMR (151 MHz, CDCl_3) δ 168.63, 168.45, 150.70, 150.64, 148.38, 137.49, 137.46, 137.35, 130.68, 129.49, 129.17, 126.85, 125.81, 123.70, 123.54, 117.39, 116.06, 115.99, 68.85, 63.45, 54.86, 48.23, 43.46, 43.17, 34.14, 18.37. HR-MS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{15}\text{ClN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 324.0898 found 324.0893.

2-(7-bromo-3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3f)



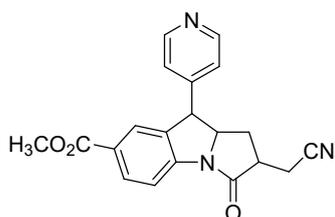
3f as oil (55.2 mg, 75%), d.r. 2.7:1. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.61 (dd, $J = 52.4, 4.1$ Hz, 2H), 7.56 (dd, $J = 41.8, 8.3$ Hz, 1H), 7.50 – 6.77 (m, 4H), 4.96 – 4.38 (m, 2H), 3.26 – 3.15 (m, 1H), 2.95 – 2.36 (m, 3H), 2.09 (q, $J = 11.4$ Hz, 0.73H), 1.19 (q, $J = 11.6$ Hz, 0.27H). ^{13}C NMR (151 MHz, CDCl_3) δ 168.66, 150.67, 150.59, 148.48, 137.97, 137.77, 132.44, 132.13, 129.75, 128.69, 123.76, 123.59, 118.18, 117.38, 116.54, 116.47, 68.80, 63.40, 54.86, 48.20, 43.52, 43.23, 34.16, 18.40. HR-MS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{15}\text{BrN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 368.0393 found 368.0389.

2-(3-oxo-9-(pyridin-4-yl)-7-(trifluoromethyl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3g)



3g as oil compound (51.4 mg, 72%), d.r. 9:1. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.61 (dd, $J = 56.0, 4.5$ Hz, 2H), 7.87 – 7.65 (m, 1H), 7.61 – 6.74 (m, 4H), 5.01 – 4.37 (m, 2H), 3.22 (dq, $J = 12.1, 7.4$ Hz, 1H), 2.90 – 2.32 (m, 3H), 2.13 – 2.08 (m, 0.9H), 1.32 – 1.28 (m, 0.1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.08, 150.82, 148.24, 141.62, 136.43, 127.77, 127.56, 126.91, 126.89, 124.80, 123.54, 122.99, 122.70, 122.68, 117.27, 115.14, 68.83, 54.72, 43.29, 34.33, 18.32. HR-MS (ESI-TOF) calcd for $\text{C}_{19}\text{H}_{15}\text{F}_3\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 358.1162 found 358.1157.

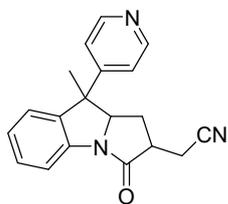
Methyl 2-(cyanomethyl)-3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indole-7-carboxylate (3h)



3h as oil compound (47.2 mg, 68%), d.r. 4:1. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.65 – 8.51 (m, 2H), 8.25 (d, $J = 43.1$ Hz, 1H), 7.87 – 7.74 (m, 1H), 7.23 – 6.73 (m, 3H), 4.99 – 4.40 (m, 2H), 3.90 (d, $J = 9.2$ Hz, 3H), 3.21 (dq, $J = 12.2, 7.6, 6.1$ Hz, 1H), 2.90 – 2.41 (m, 3H), 2.10 (q, $J = 12.0$ Hz, 0.8H), 1.21 – 1.17 (m, 0.2H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.83, 166.24, 150.65,

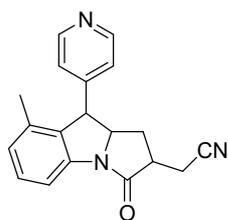
148.52, 140.65, 139.16, 131.35, 127.20, 125.38, 123.62, 117.42, 115.86, 68.79, 54.95, 52.46, 43.21, 34.26, 18.37. HR-MS (ESI-TOF) calcd for C₂₀H₁₉N₃O [M+H]⁺ 348.1343 found 348.1349.

2-(9-methyl-3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3i)



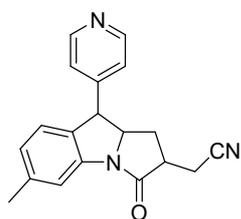
3i as oil compound (54.5 mg, 90%), d.r. 4:1. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.54 (dd, *J* = 52.3, 5.7 Hz, 2H), 7.67 (dd, *J* = 18.3, 7.9 Hz, 1H), 7.37 – 6.71 (m, 5H), 4.53 – 4.08 (m, 1H), 3.23 (dtd, *J* = 12.1, 7.6, 4.9 Hz, 1H), 2.93 – 2.33 (m, 3H), 2.09 (q, *J* = 11.8 Hz, 0.8H), 1.70 (d, *J* = 219.1 Hz, 3H), 0.95 (q, *J* = 11.9 Hz, 0.2H). ¹³C NMR (151 MHz, Chloroform-*d*) δ 167.83, 154.07, 150.23, 141.74, 137.27, 128.81, 125.60, 124.95, 122.23, 117.54, 114.99, 71.37, 50.80, 43.55, 28.04, 21.60, 18.63. HR-MS (ESI-TOF) calcd for C₁₉H₁₇N₃O [M+H]⁺ 304.1444 found 304.1440.

2-(8-methyl-3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3j)



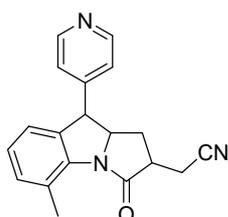
3j as oil compound (46.1 mg, 76%), d.r. 3:1. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 4.8 Hz, 2H), 7.70 – 7.54 (m, 1H), 7.53 – 6.76 (m, 4H), 4.98 – 4.40 (m, 2H), 3.31 – 3.14 (m, 1H), 2.95 – 2.36 (m, 3H), 2.14 – 2.07 (q, 0.75H), 1.93 (d, *J* = 116.3 Hz, 3H), 1.21 (q, *J* = 11.7 Hz, 0.25H). ¹³C NMR (151 MHz, CDCl₃) δ 169.15, 168.17, 150.87, 150.86, 150.60, 146.20, 139.49, 138.27, 136.17, 136.05, 134.17, 132.63, 129.49, 129.35, 127.48, 126.95, 123.34, 117.56, 117.49, 112.81, 112.59, 69.26, 67.17, 63.28, 54.68, 47.43, 43.76, 42.93, 34.75, 19.34, 18.37. HR-MS (ESI-TOF) calcd for C₁₉H₁₇N₃O [M+H]⁺ 304.1444 found 304.1440.

2-(6-methyl-3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3k)



3k as oil compound (47.3 mg, 78%), d.r. 1.78:1. ¹H NMR (600 MHz, Chloroform-*d*) δ 8.55 (dd, *J* = 54.7, 5.3 Hz, 2H), 7.51 (d, *J* = 36.6 Hz, 1H), 7.24 – 6.71 (m, 4H), 4.93 – 4.32 (m, 2H), 3.18 (dt, *J* = 12.1, 6.0 Hz, 1H), 2.90 – 2.79 (m, 1H), 2.77 – 2.65 (m, 1H), 2.38 (d, *J* = 14.6 Hz, 3H), 2.35 – 2.25 (m, 1H), 2.06 (q, *J* = 12.0 Hz, 0.64H), 1.14 (q, *J* = 12.0 Hz, 0.36H). ¹³C NMR (151 MHz, CDCl₃) δ 168.54, 168.32, 150.47, 150.41, 149.57, 147.52, 139.75, 139.47, 138.97, 138.67, 132.62, 126.45, 126.21, 125.14, 123.83, 123.62, 117.54, 117.45, 115.84, 115.69, 69.06, 63.64, 54.64, 48.02, 43.67, 43.33, 34.21, 21.62, 21.54, 18.48, 18.45. HR-MS (ESI-TOF) calcd for C₁₉H₁₇N₃O [M+H]⁺ 304.1444 found 304.1440.

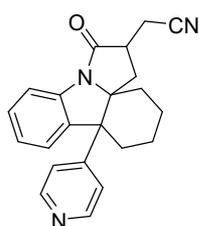
2-(5-methyl-3-oxo-9-(pyridin-4-yl)-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3l)



3l as oil compound (50.9 mg, 84%), d.r. 1.5:1. ¹H NMR (600 MHz,

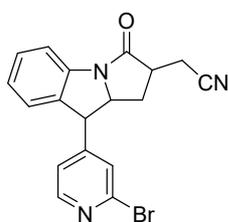
Chloroform-*d*) δ 8.57 (dd, $J = 41.6, 4.9$ Hz, 2H), 7.73 – 7.01 (m, 4H), 6.93 (d, $J = 7.4$ Hz, 1H), 6.69 (d, $J = 7.4$ Hz, 0H), 4.99 – 4.31 (m, 2H), 3.27 (ddtd, $J = 17.1, 13.0, 8.8, 8.4, 4.7$ Hz, 1H), 3.00 – 2.26 (m, 6H), 2.18 (dd, $J = 17.2, 9.0$ Hz, 0.6H), 1.18 (dd, $J = 12.3, 3.0$ Hz, 0.4H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 169.19, 150.48, 147.39, 138.30, 137.00, 131.68, 127.73, 126.68, 123.82, 123.50, 117.60, 64.2, 49.21, 42.94, 28.47, 20.35, 18.78. HR-MS (ESI-TOF) calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 304.1444 found 304.1440.

2-(7-oxo-12b-(pyridin-4-yl)-1,3,4,6,7,12b-hexahydro-2H,5H-pyrrolo[2,1-k]carbazol-6-yl)acetonitrile (3m)



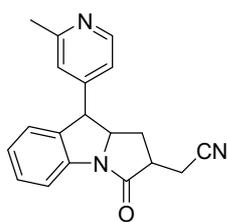
3m as white solid (37.1 mg, 54%), d.r. >19:1. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.48 (d, $J = 4.9$ Hz, 2H), 7.70 (d, $J = 7.8$ Hz, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.21 (t, $J = 7.5$ Hz, 1H), 7.09 (d, $J = 7.5$ Hz, 1H), 6.70 (s, 2H), 3.24 (td, $J = 11.3, 4.4$ Hz, 1H), 2.72 (dd, $J = 17.1, 4.1$ Hz, 1H), 2.51 – 2.45 (m, 1H), 2.33 (d, $J = 14.1$ Hz, 1H), 2.21 (dd, $J = 12.4, 7.8$ Hz, 1H), 2.03 (dd, $J = 17.0, 9.8$ Hz, 2H), 1.84 – 1.74 (m, 2H), 1.67 (d, $J = 12.7$ Hz, 1H), 1.46 (p, $J = 13.6, 12.1$ Hz, 2H), 1.31 (t, $J = 11.8$ Hz, 1H). ^{13}C NMR (151 MHz, CDCl_3) δ 169.28, 169.19, 150.57, 150.48, 149.33, 147.39, 138.66, 138.30, 137.00, 136.93, 132.22, 132.16, 131.67, 131.36, 128.66, 128.58, 127.73, 127.37, 126.68, 126.43, 124.05, 123.82, 123.50, 122.37, 117.69, 117.60, 69.88, 64.29, 56.41, 49.21, 42.94, 42.87, 32.81, 28.47, 20.35, 20.13, 18.88, 18.78. HR-MS (ESI-TOF) calcd for $\text{C}_{22}\text{H}_{22}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 344.1757 found 344.1753.

2-(9-(2-bromopyridin-4-yl)-3-oxo-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3n)



3n as oil compound (47.7 mg, 65%), d.r. 1.7:1. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.60 (dd, $J = 54.2, 4.6$ Hz, 1H), 7.69 (dd, $J = 38.8, 7.7$ Hz, 1H), 7.56 – 6.64 (m, 5H), 5.00 – 4.26 (m, 2H), 3.21 (dq, $J = 12.1, 7.6, 6.0$ Hz, 1H), 2.93 – 2.18 (m, 3H), 2.09 (q, $J = 12.0$ Hz, 0.63H), 1.18 (dd, $J = 22.7, 12.0$ Hz, 0.37H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.60, 150.33, 138.96, 135.52, 129.21, 125.61, 125.56, 123.82, 117.52, 115.34, 68.82, 55.10, 43.39, 34.31, 18.53. HR-MS (ESI-TOF) calcd for $\text{C}_{18}\text{H}_{15}\text{BrN}_3\text{O}$ $[\text{M}+\text{H}]^+$ 368.0393 found 368.0386.

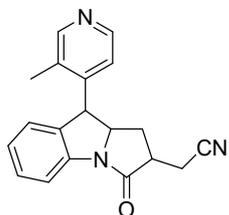
2-(9-(2-methylpyridin-4-yl)-3-oxo-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3o)



3o as oil compound (44.8 mg, 74%), d.r. 9:1. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.66 – 8.54 (m, 1H), 7.87 – 7.77 (m, 1H), 7.52 – 7.07 (m, 5H), 5.08 – 4.47 (m, 2H), 3.34 (td, $J = 12.2, 7.6$ Hz, 1H), 3.07 – 2.80 (m, 3H), 2.72 (s, 3H), 2.21 (q, $J = 12.1$ Hz, 0.9H), 1.05 – 0.97 (m, 0.1H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.60, 159.43, 149.86, 149.59, 138.90, 135.78, 129.02, 125.56, 125.50, 123.22, 120.76, 117.56, 115.22, 68.75, 54.99, 43.36, 34.30, 24.50, 18.48. HR-MS (ESI-TOF) calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 304.1444

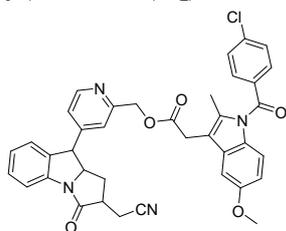
found 304.1440.

2-(9-(3-methylpyridin-4-yl)-3-oxo-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-2-yl)acetonitrile (3p)



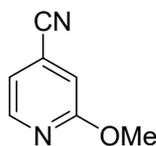
3p as oil compound (42.4 mg, 70%), d.r. 3:1. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.53 – 8.26 (m, 2H), 7.69 (dd, $J = 31.6, 7.9$ Hz, 1H), 7.32 (t, $J = 7.5$ Hz, 1H), 7.20 – 7.02 (m, 2H), 6.89 (d, $J = 7.4$ Hz, 1H), 6.22 (s, 0H), 5.00 – 4.47 (m, 2H), 3.26 – 3.13 (m, 1H), 2.97 – 2.45 (m, 3H), 2.41 – 2.25 (m, 3H), 2.15 – 2.09 (q, 0.75H), 1.06 (q, $J = 11.3$ Hz, 0.25H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 168.63, 148.23, 139.09, 135.81, 132.42, 129.38, 129.01, 126.72, 125.77, 125.55, 125.47, 117.54, 115.27, 62.93, 43.50, 35.09, 30.08, 18.46, 16.97. HR-MS (ESI-TOF) calcd for $\text{C}_{19}\text{H}_{17}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$ 304.1444 found 304.1440.

(4-(2-(cyanomethyl)-3-oxo-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-9-yl)pyridin-2-yl)methyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (3q)



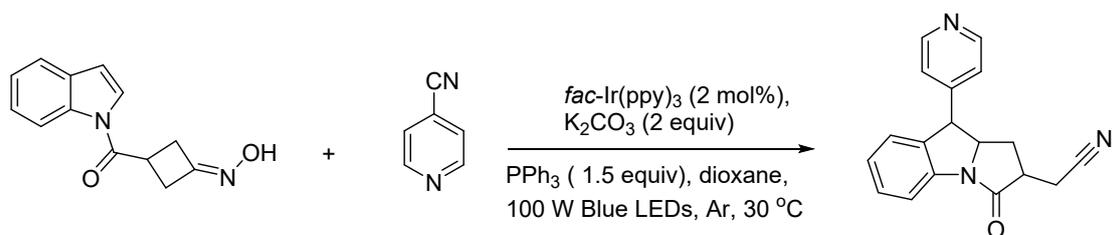
3q as white solid (82.9 mg, 63%), d.r. 2.3:1. ^1H NMR (600 MHz, Chloroform-*d*) δ 8.71 – 8.25 (m, 1H), 7.63 (dt, $J = 32.2, 9.2$ Hz, 4H), 7.54 – 7.43 (m, 4H), 7.33 (dt, $J = 33.2, 7.3$ Hz, 1H), 7.12 – 7.05 (m, 1H), 6.92 (dd, $J = 72.2, 8.0$ Hz, 2H), 6.78 – 6.43 (m, 2H), 5.26 (d, $J = 30.1$ Hz, 1H), 4.80 – 4.10 (m, 2H), 3.82 – 3.69 (m, 4H), 3.33 – 3.07 (m, 1H), 2.94 – 2.65 (m, 2H), 2.35 (d, $J = 8.8$ Hz, 3H), 1.99 (q, $J = 11.1$ Hz, 0.7H), 1.01 (q, $J = 10.2$ Hz, 0.3H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.28, 168.55, 168.28, 156.61, 156.02, 149.95, 139.47, 138.64, 136.00, 135.51, 133.63, 132.13, 132.06, 131.19, 129.16, 128.97, 128.55, 128.47, 125.38, 125.22, 122.48, 121.21, 115.13, 115.01, 112.18, 111.68, 101.47, 68.40, 66.70, 55.71, 54.86, 43.29, 33.96, 30.41, 18.39, 13.42. ^{13}C NMR (151 MHz, CDCl_3) δ 170.3, 168.5, 168.3, 156.6, 156.0, 150.0, 139.5, 138.6, 136.0, 135.5, 133.6, 132.1, 132.1, 131.2, 129.2, 129.0, 128.6, 128.5, 125.4, 125.2, 122.5, 121.2, 115.1, 115.0, 112.2, 111.7, 101.5, 68.4, 66.7, 55.7, 54.9, 43.3, 34.0, 30.4, 18.4, 13.4. HR-MS (ESI-TOF) calcd for $\text{C}_{38}\text{H}_{32}\text{ClN}_4\text{O}_5$ $[\text{M}+\text{H}]^+$ 659.2056 found 659.2052.

Unsuccessful Substrates



V Mechanistic Study

4.1 Time profile for the transformation with the light ON-OFF over time



Standard reactions were set up parallel on a 0.2 mmol scale according to the standard conditions, The reaction started with successive irradiation and black periods to study the influence of continuous irradiation of the visible-light for the progress. This on-off cycling of the light source (2 h on/2 h off) was repeated until the final batch was sampled after a total reaction time of 12 h. All of yields were isolated yield. These results revealed that light irradiation is a necessary component of the reaction (Figure 1).

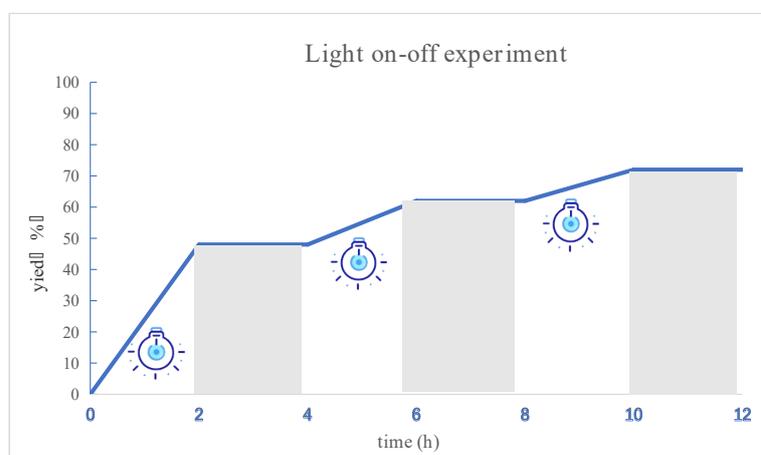
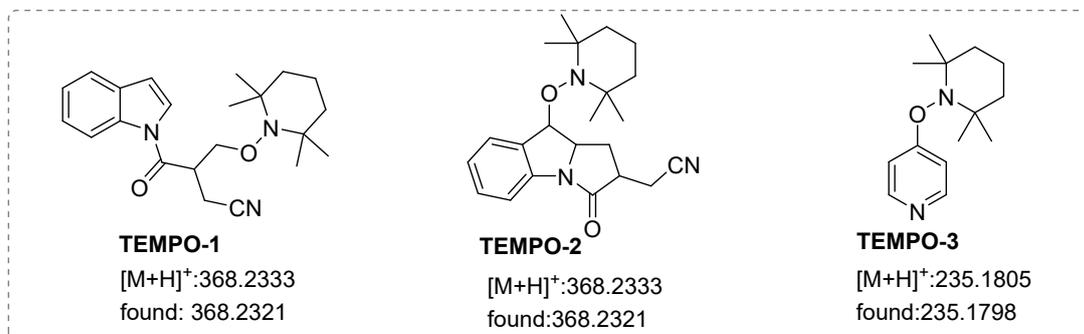
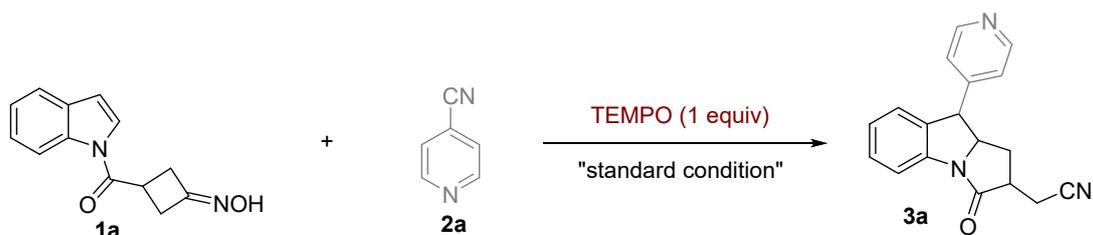
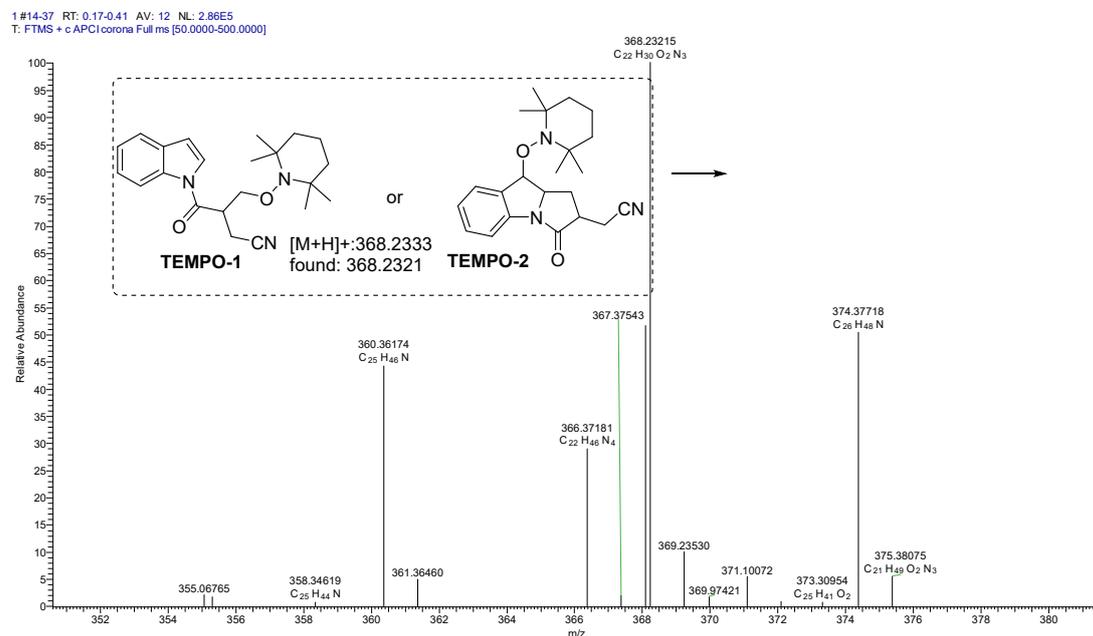


Figure 1. light on-off experiment

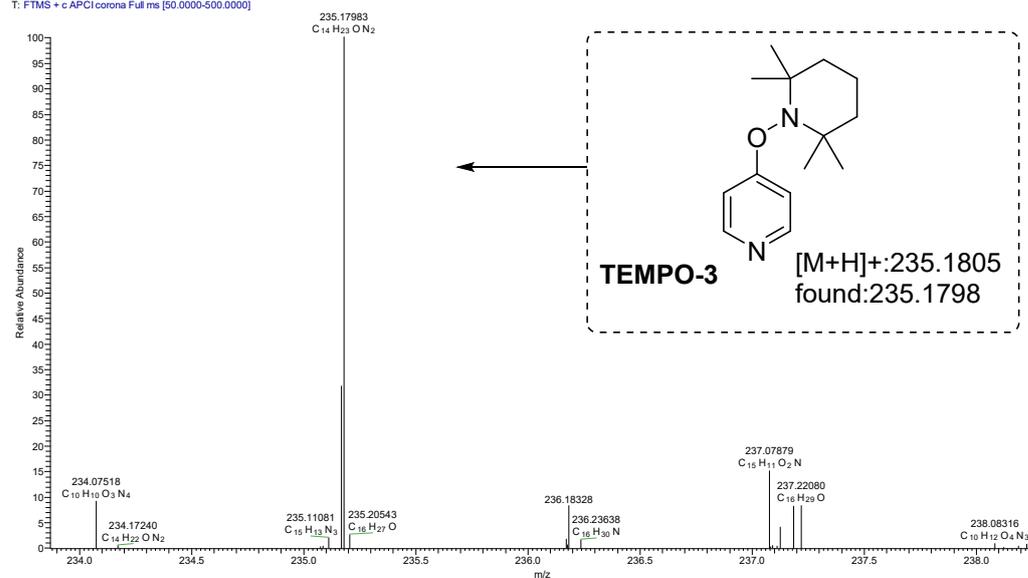
4.2 TEMPO captured reaction



A 15 mL of reaction tube was charged with **1** (0.2 mmol), **2** (0.2 mmol), *fac*-Ir(ppy)₃ (2%), K₂CO₃ (0.4 mmol), PPh₃ (0.3 mmol), TEMPO (0.2 mmol) and dioxane (2 mL) under argon atmosphere. The tube was placed approximately 2 cm from 30 W blue LEDs, and stirred at room 30 °C for 12 h. The corresponding derived TEMPO-trapped adduct **TEMPO-1**, **TEMPO-2** and **TEMPO-3** was detected through ESI-HRMS analysis.



1#14-37 RT: 0.17-0.41 AV: 12 NL: 1,24E6
T: FTMS + c AP-Cl corona Full ms [50.0000-500.0000]



4.3 Stern-Volmer Fluorescence Quenching Experiments

Stern-Volmer fluorescence quenching experiments were performed using freshly prepared 0.1 mM *fac*-Ir(ppy)₃ solutions in degassed dry 1,4-dioxane at room temperature. The solutions were irradiated at a wavelength of 395 nm, and the fluorescence intensity was measured over the wavelength range of 450–700 nm. Control experiment results indicated that the excited-state facial *fac*-Ir(ppy)₃ was mainly quenched by 4-cyanopyridine **2a**.

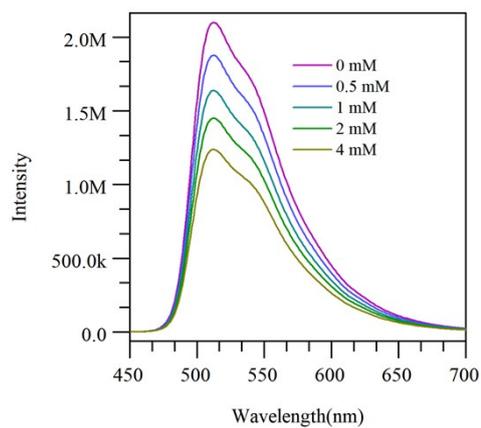


Figure 2. Fluorescence quenching data with *fac*-Ir(ppy)₃ and isonicotinonitrile **2a** (4×10^{-2} M)

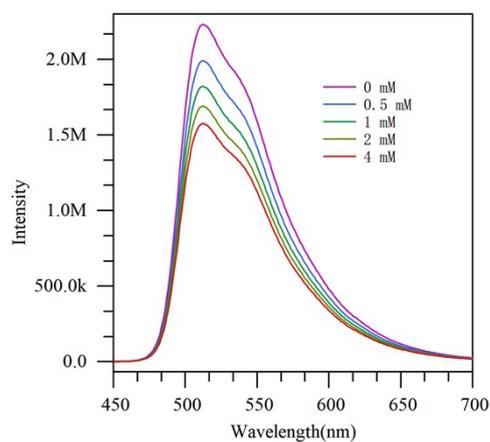


Figure 3. Fluorescence quenching data with *fac*-Ir(ppy)₃ and (3-(hydroxyimino)cyclobutyl)(1*H*-indol-1-yl)methanone **1a** (4×10^{-2} M)

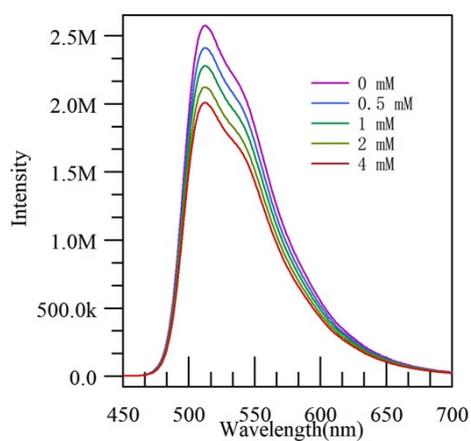


Figure 4. Fluorescence quenching data with *fac*-Ir(ppy)₃ and PPh₃ (4×10^{-2} M)

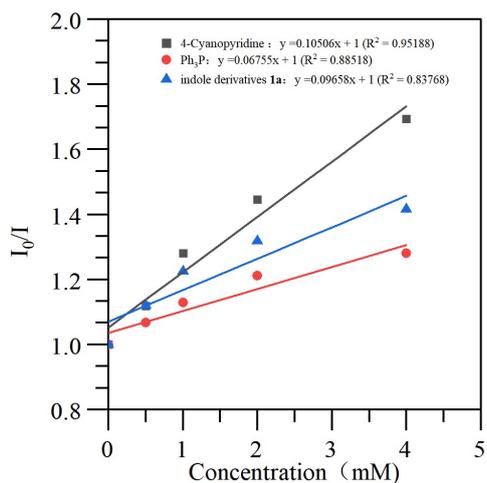
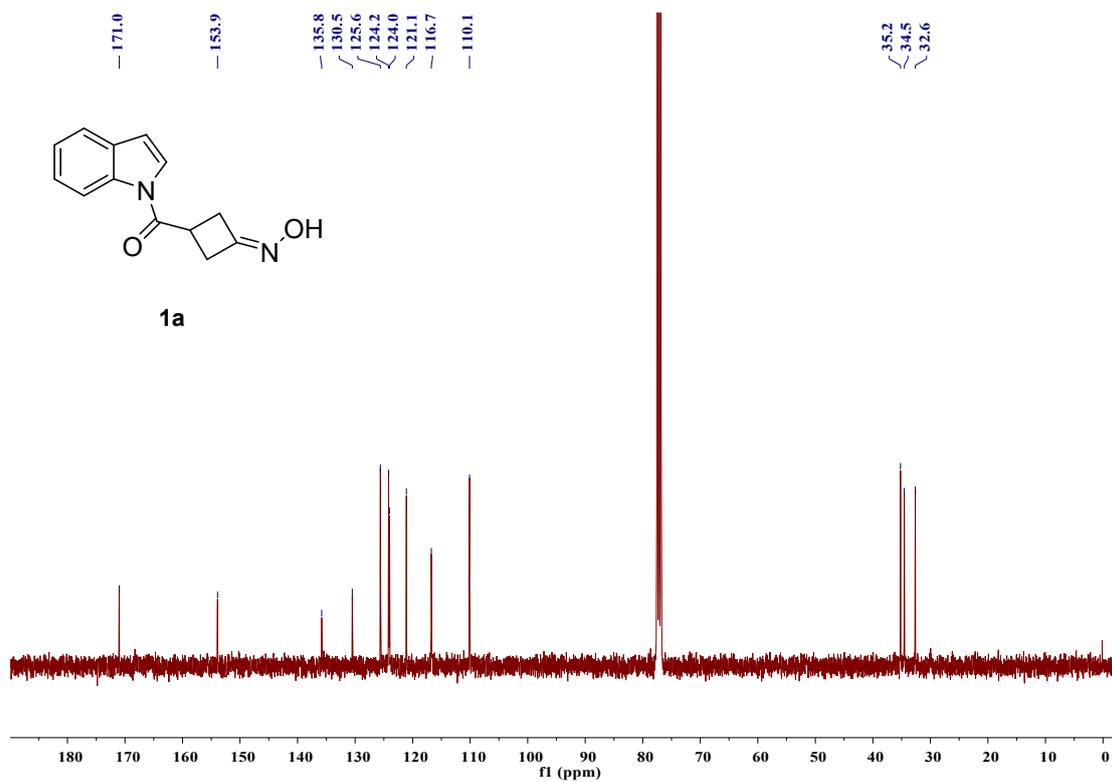
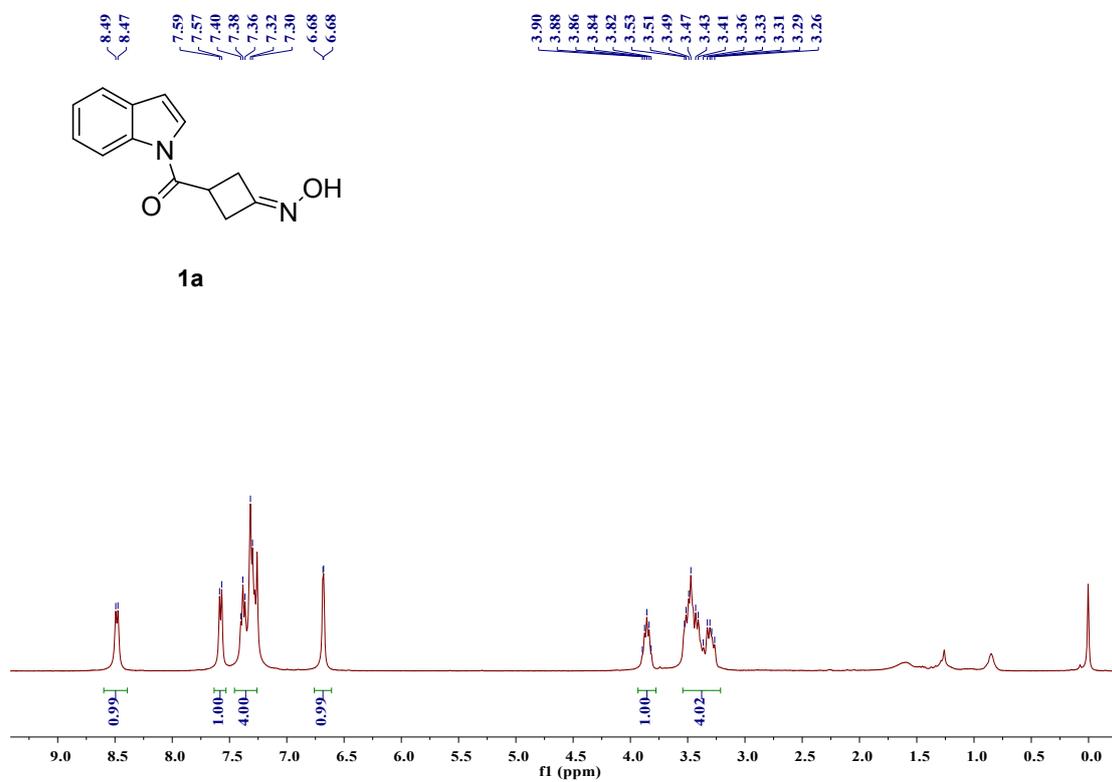


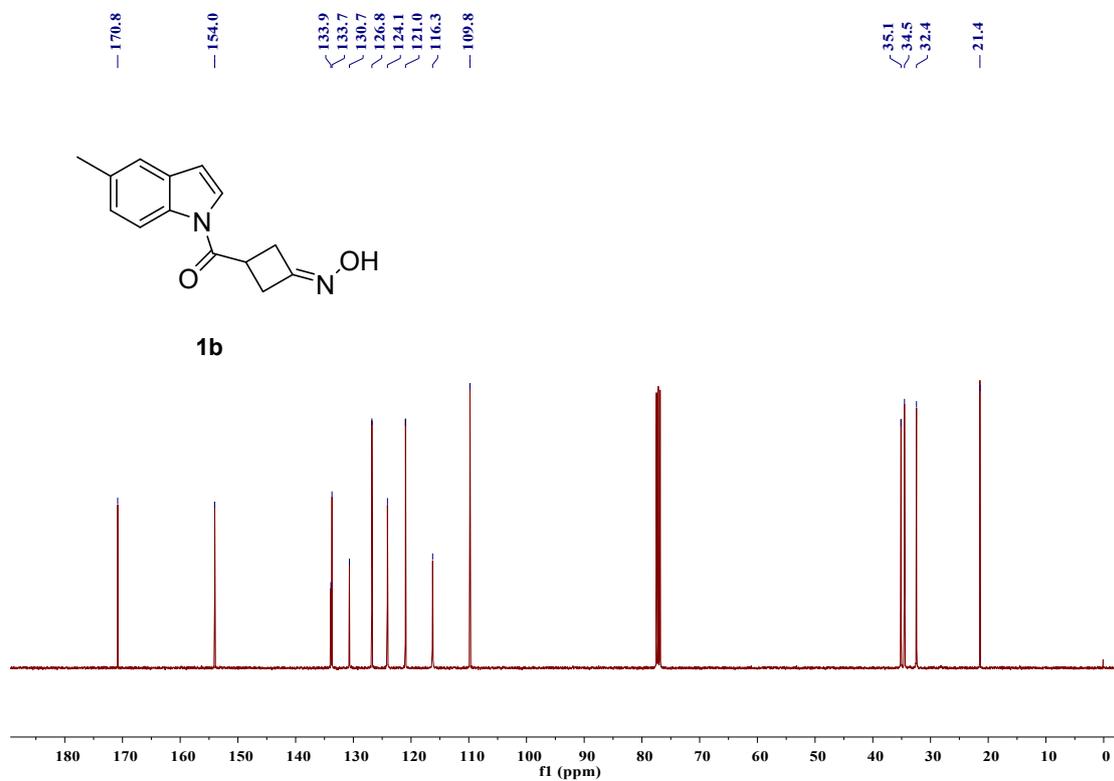
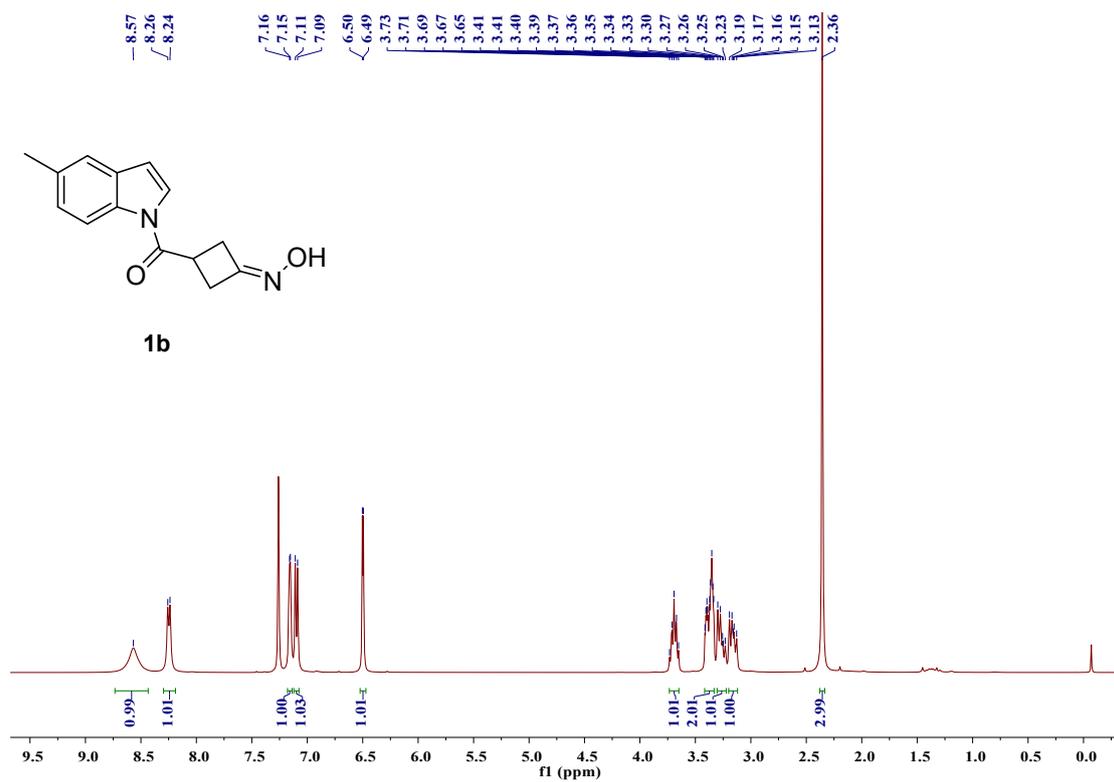
Figure 5. Stern-Volmer plots of *fac*-(ppy)₃ and three quenchers

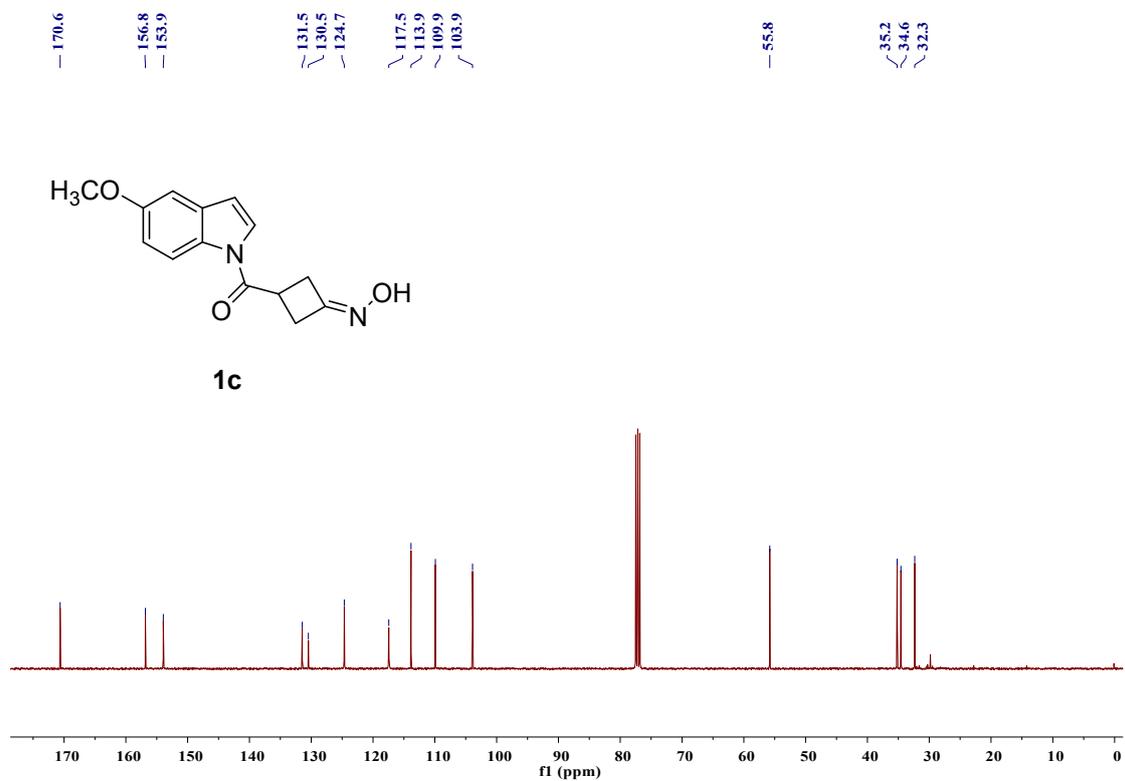
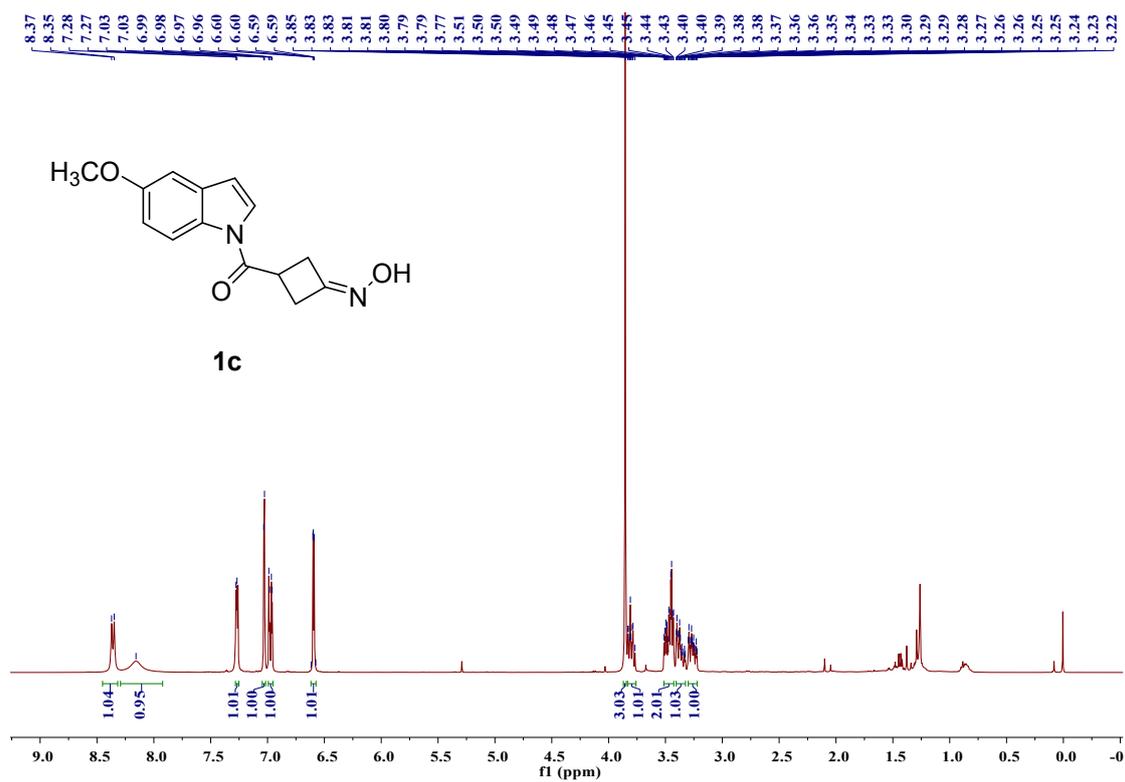
VI References

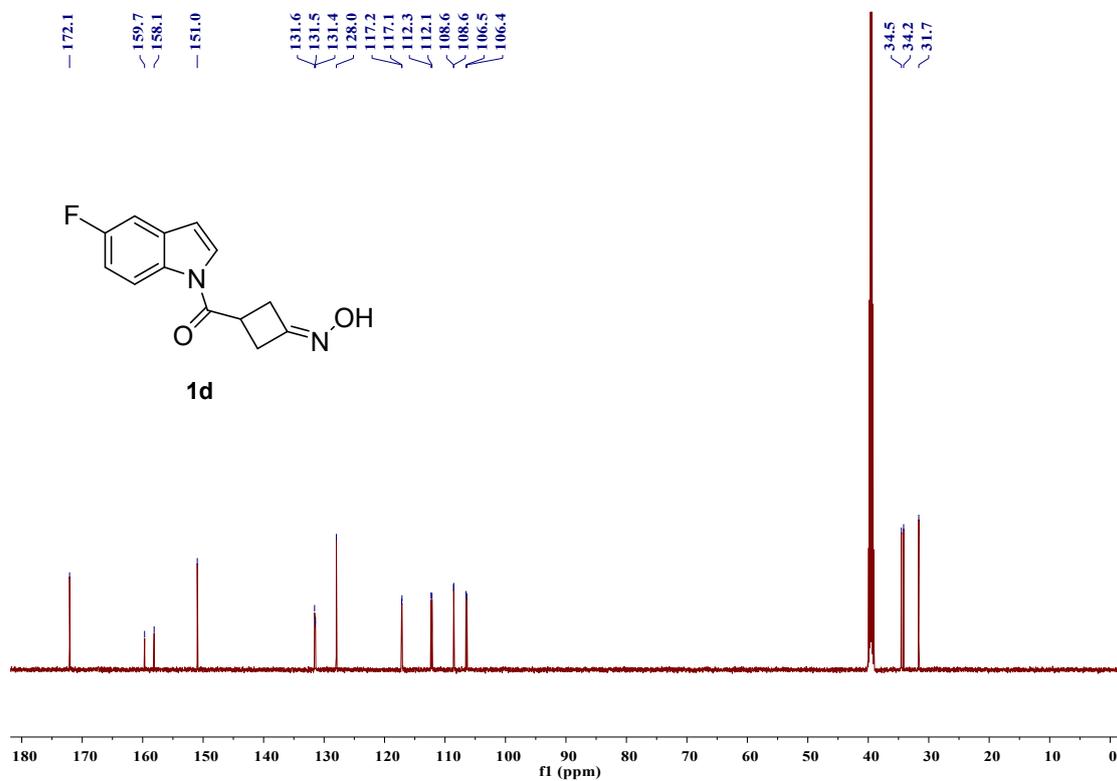
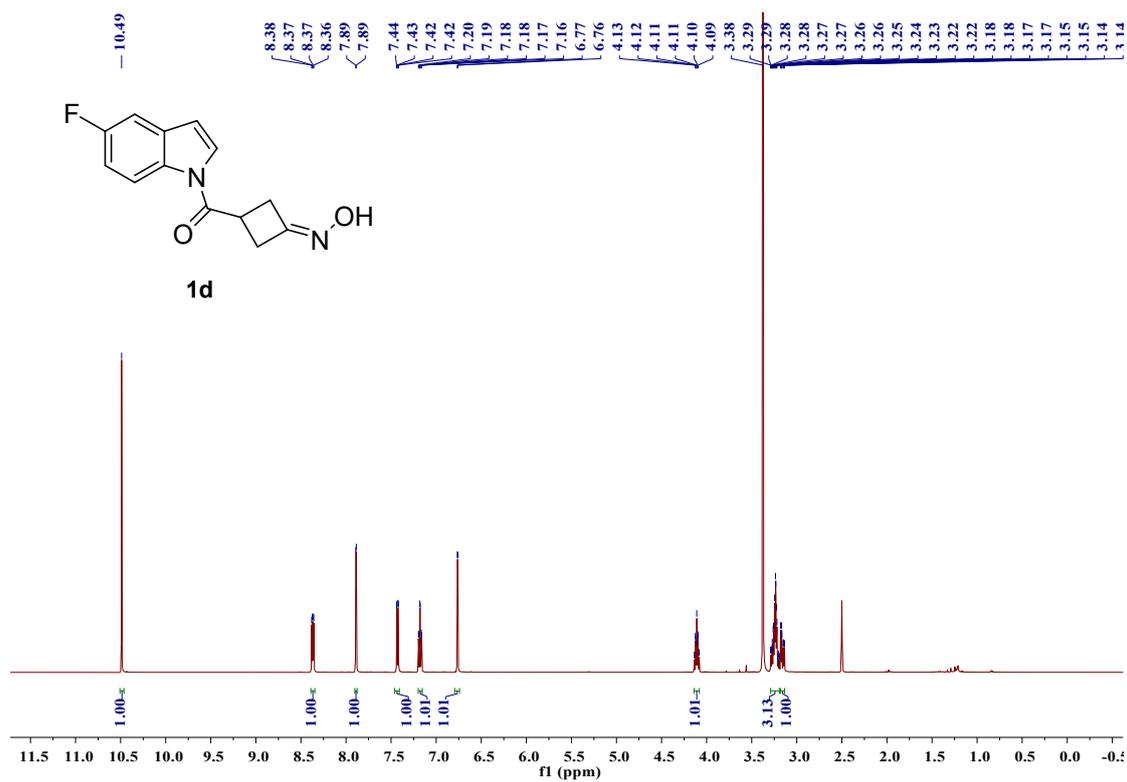
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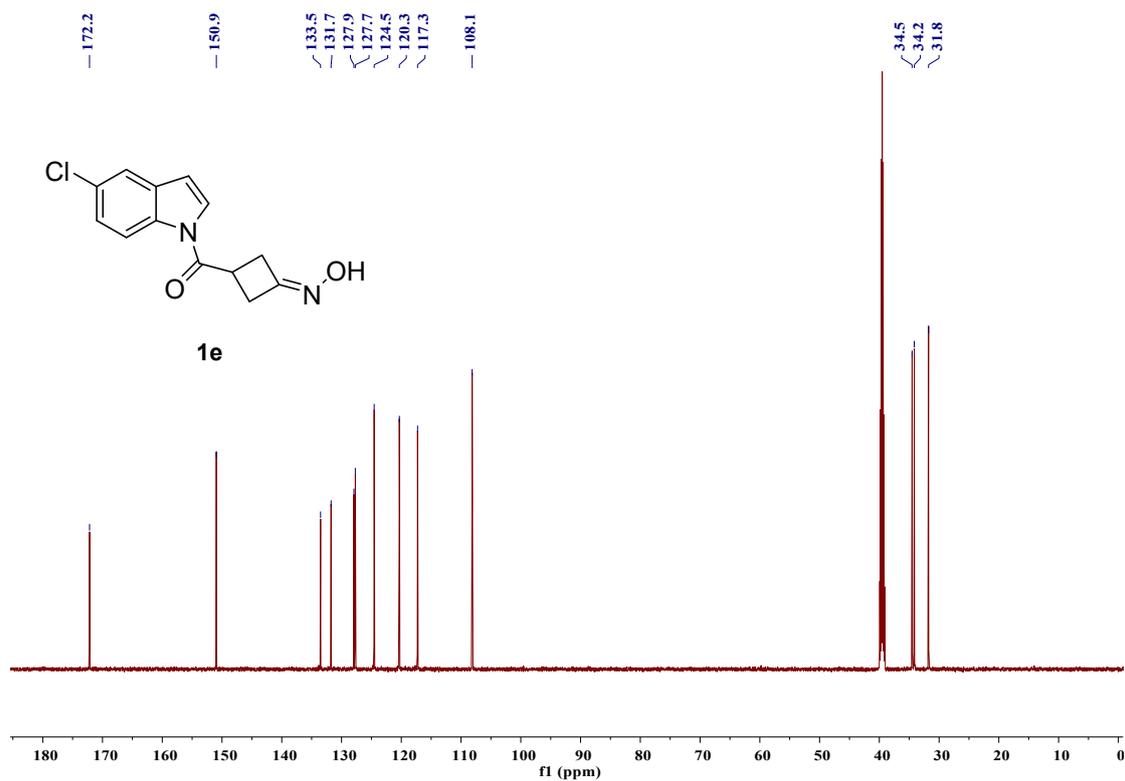
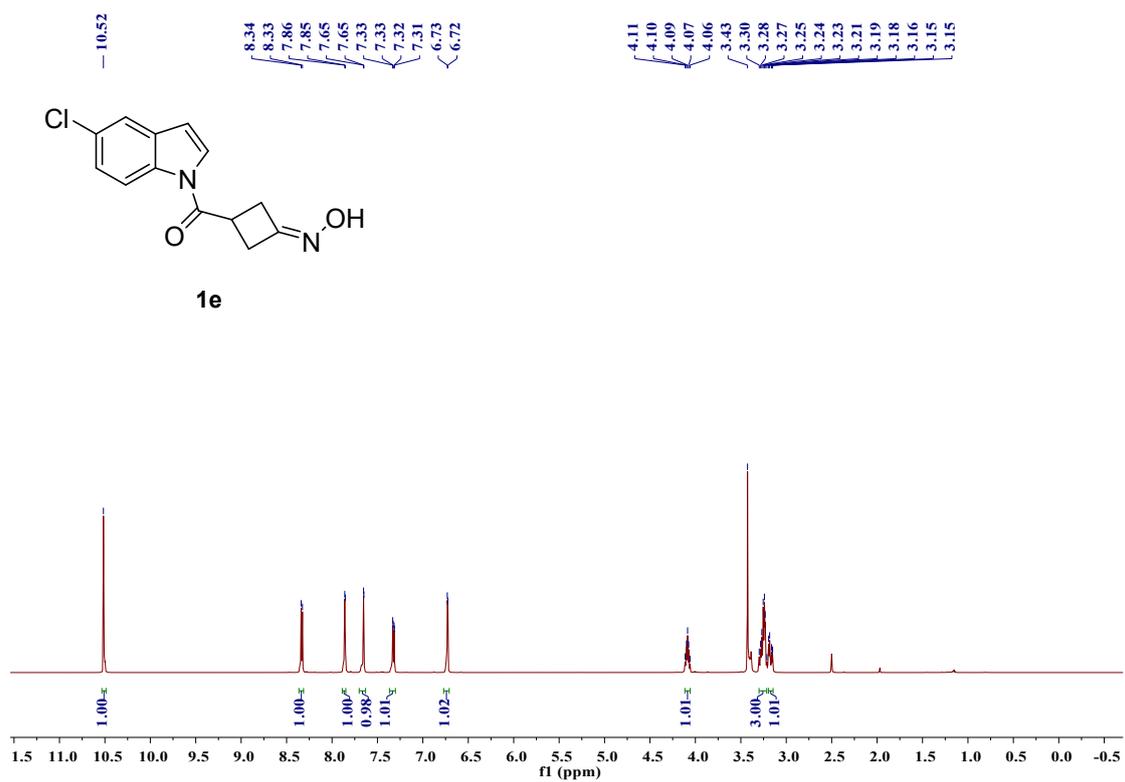
VII ^1H , ^{13}C Spectra of Compounds

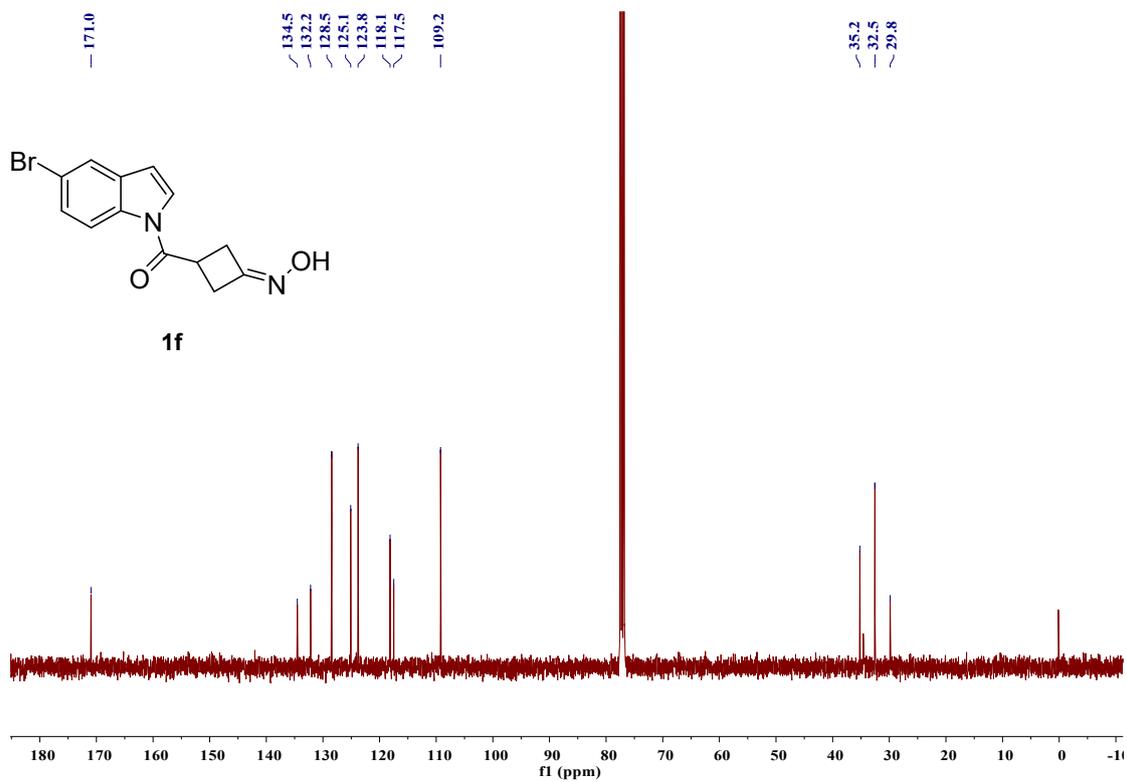
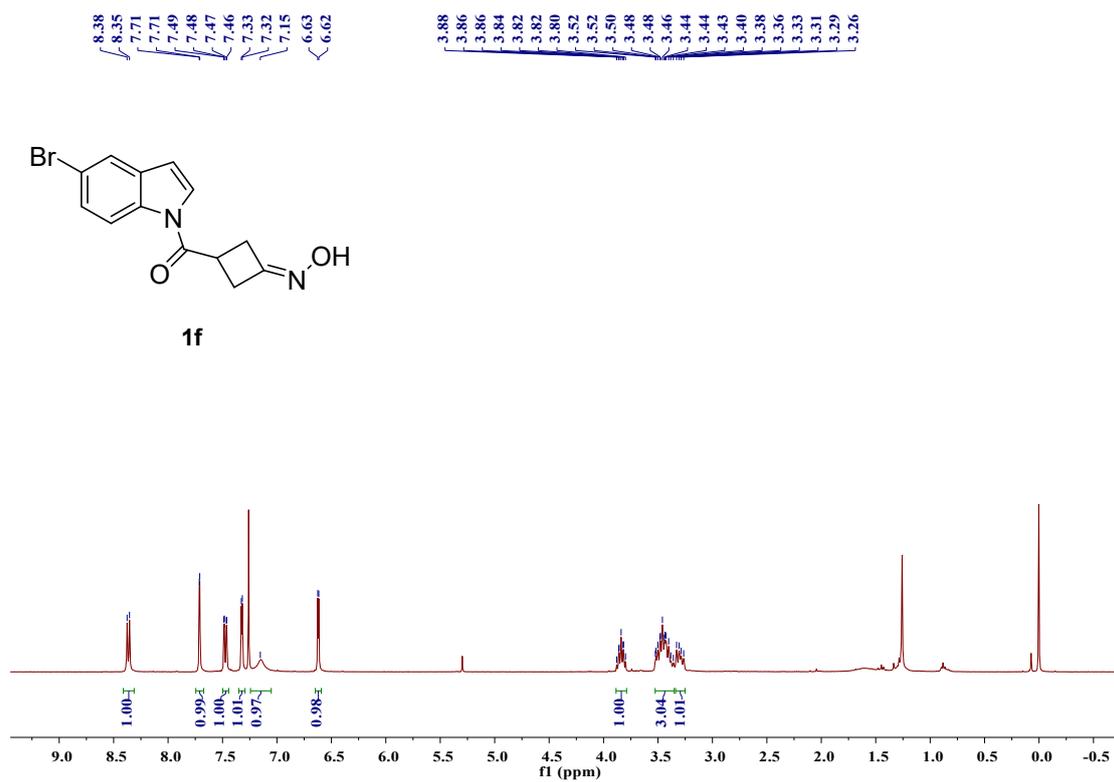


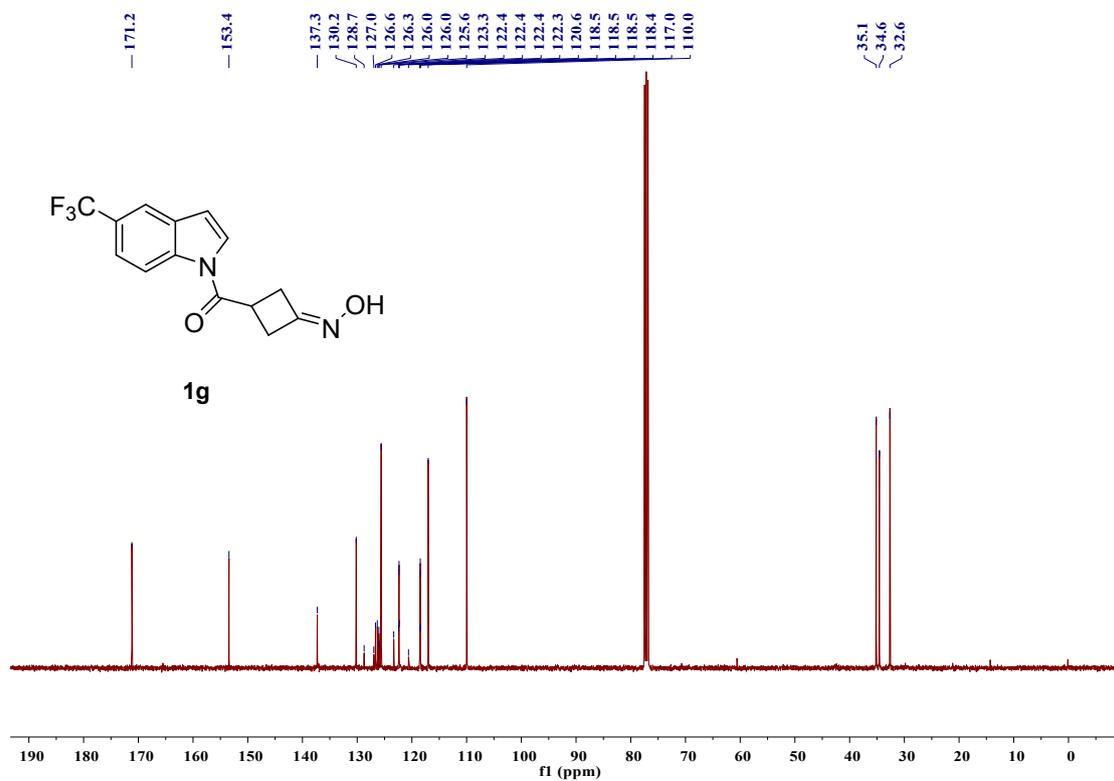
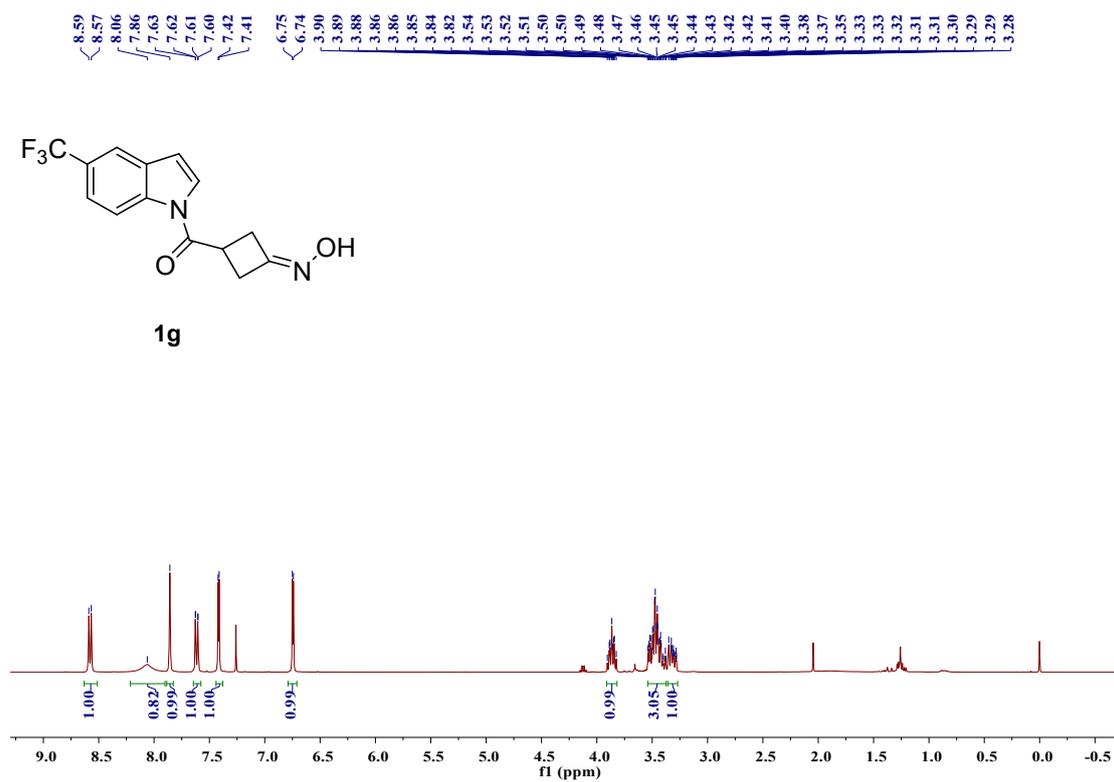


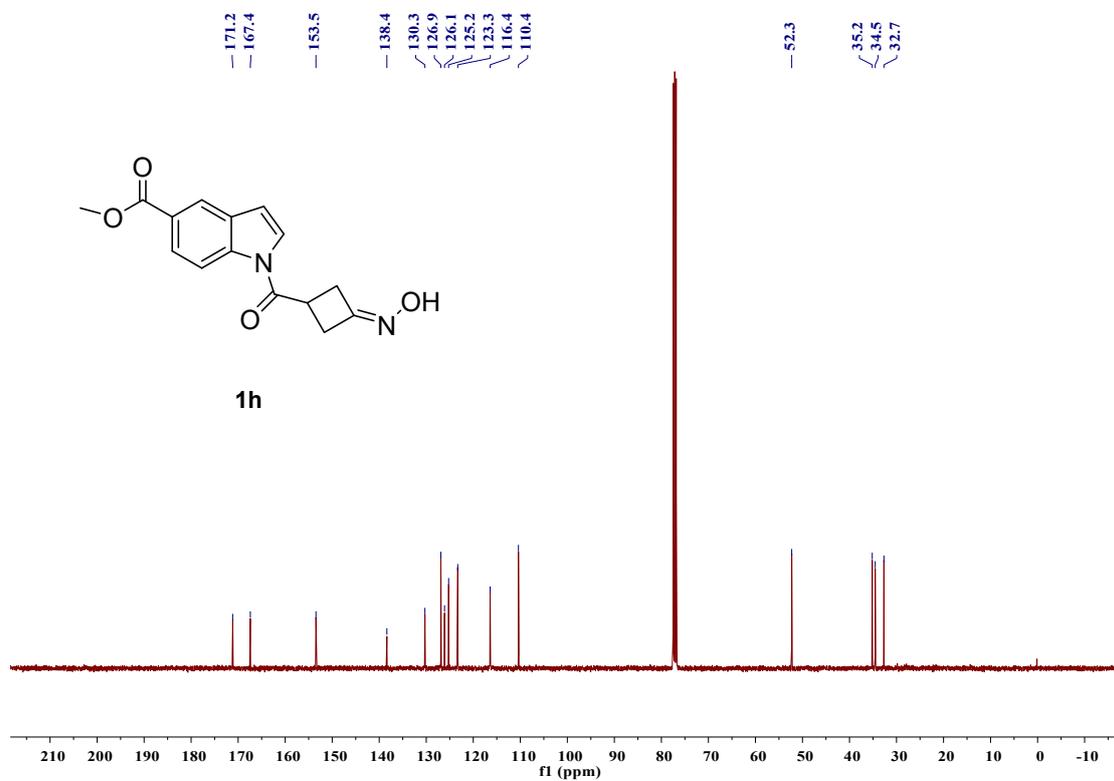
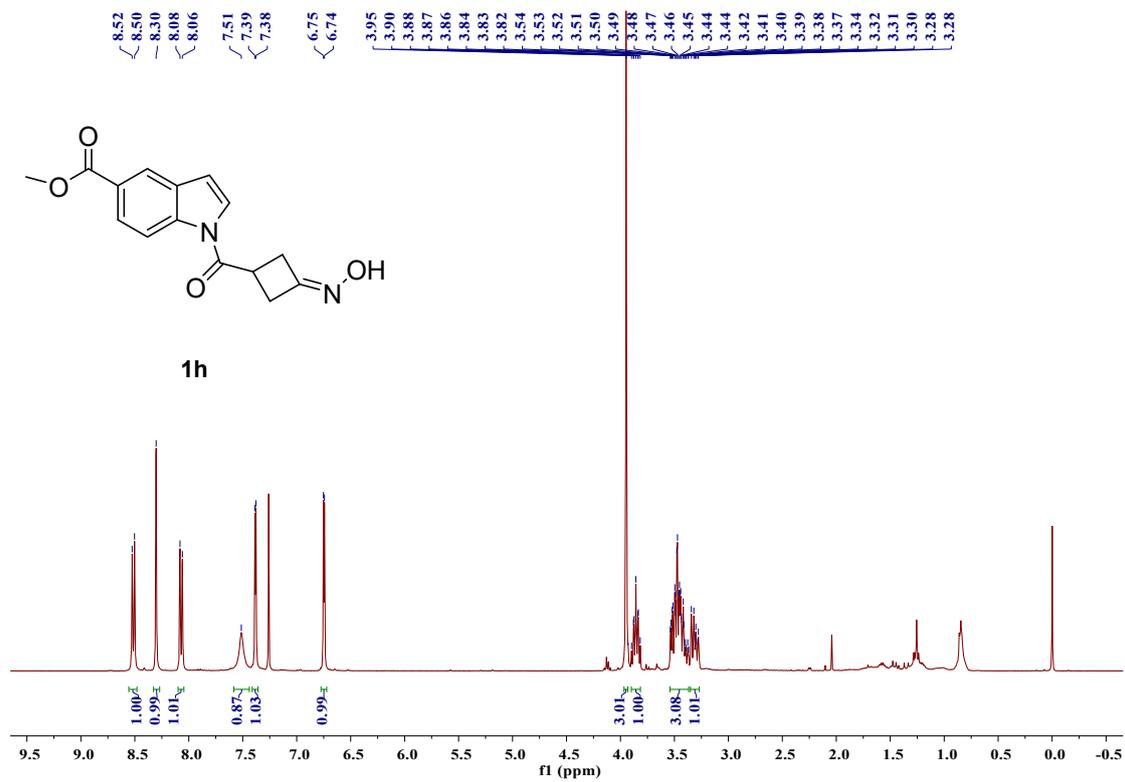


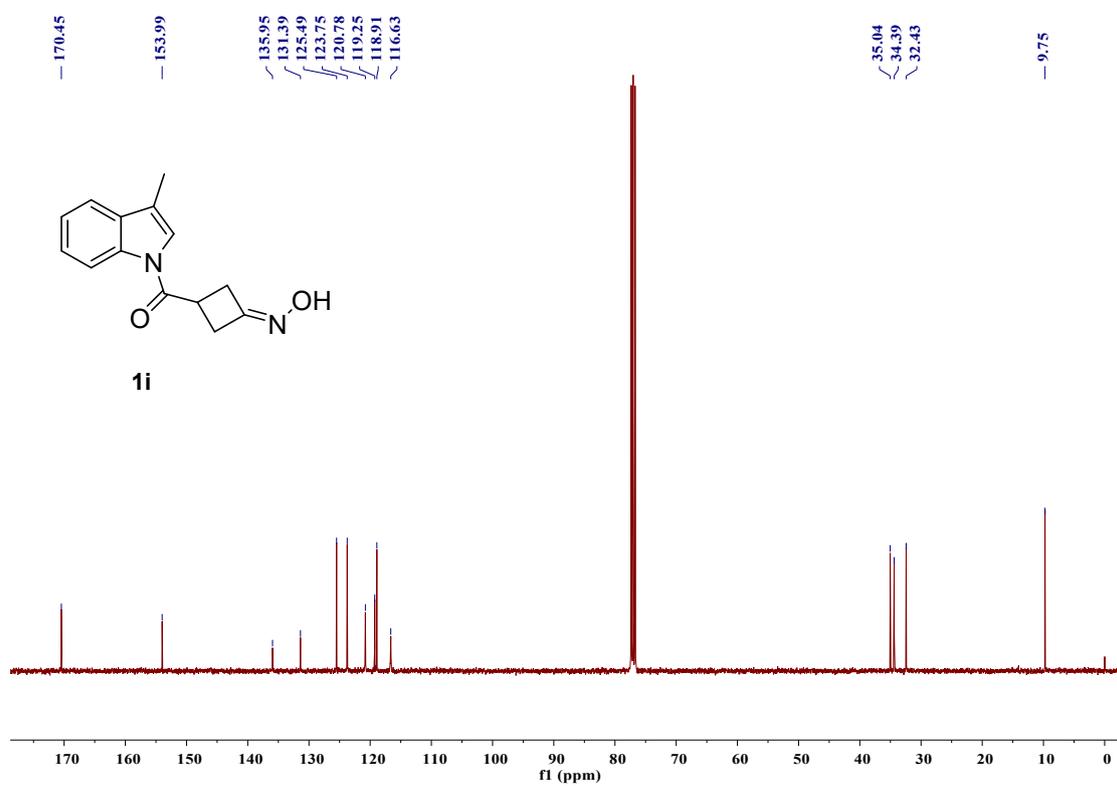
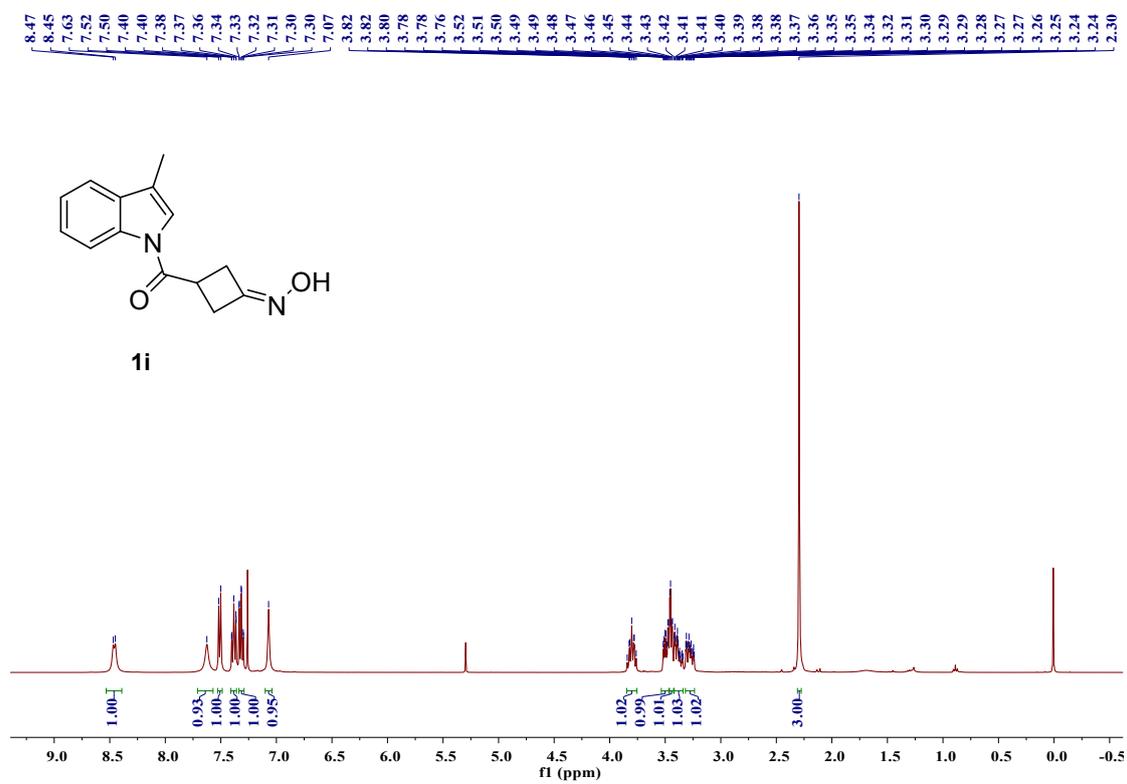


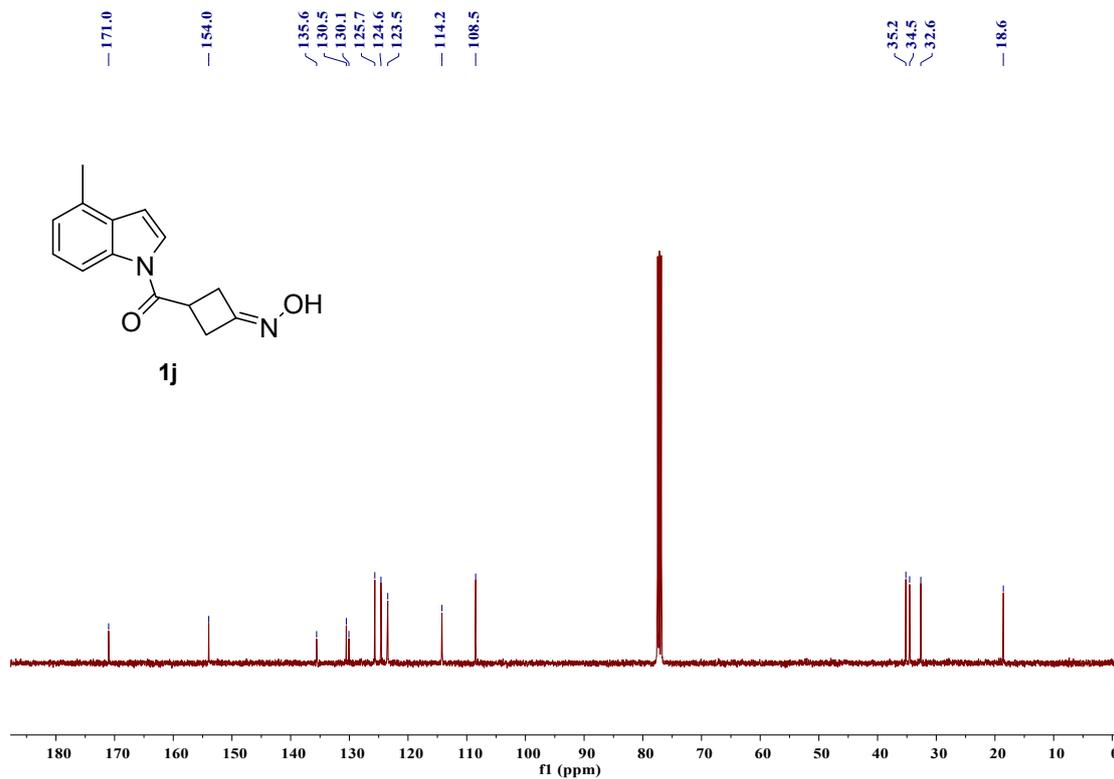
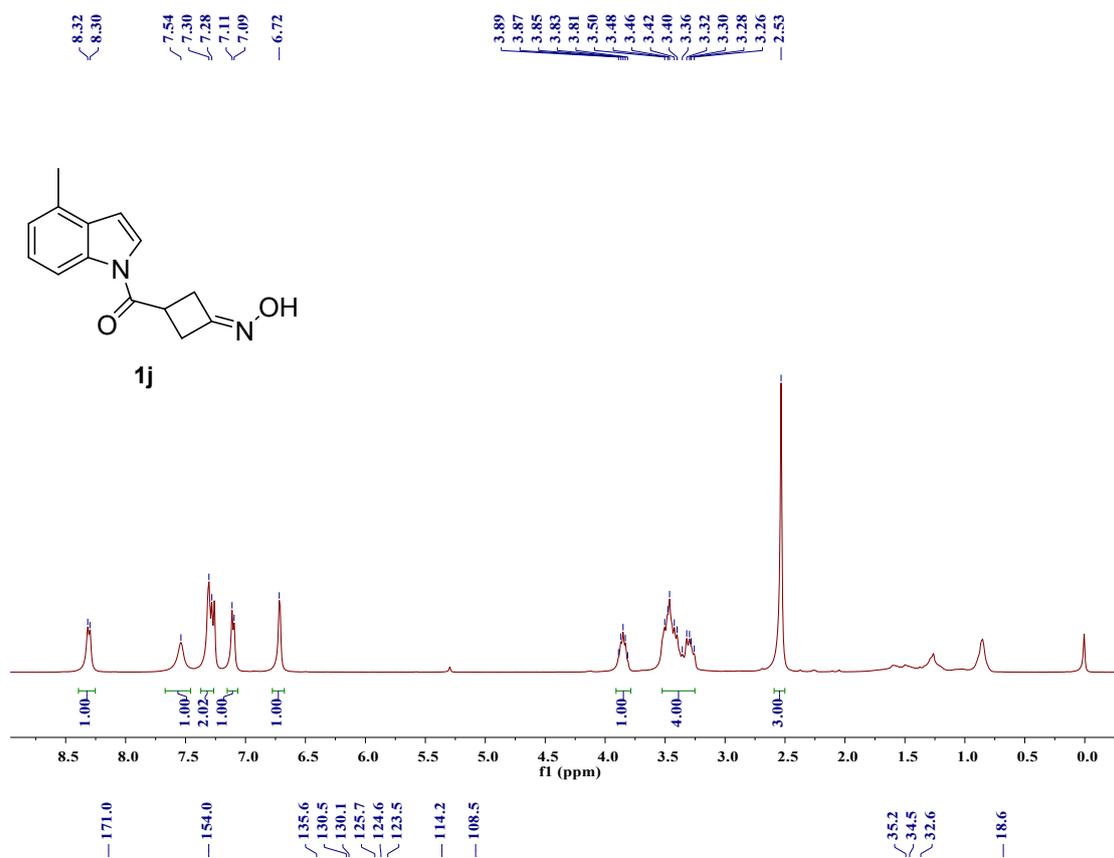


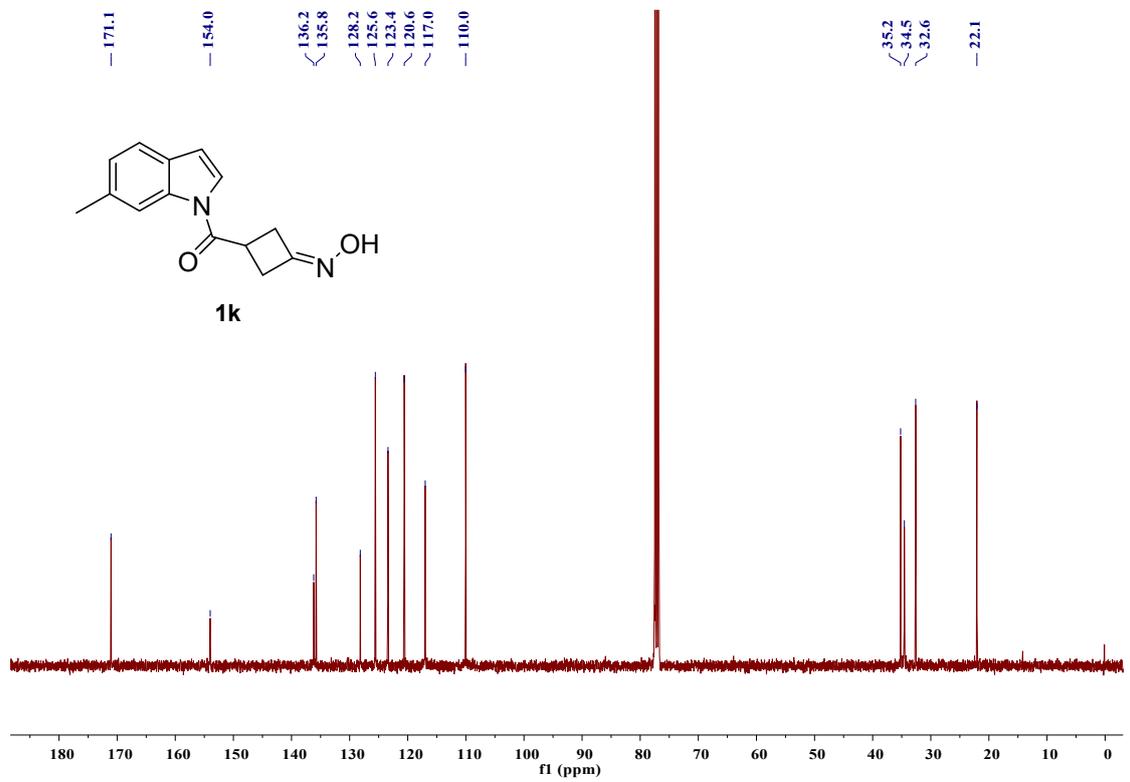
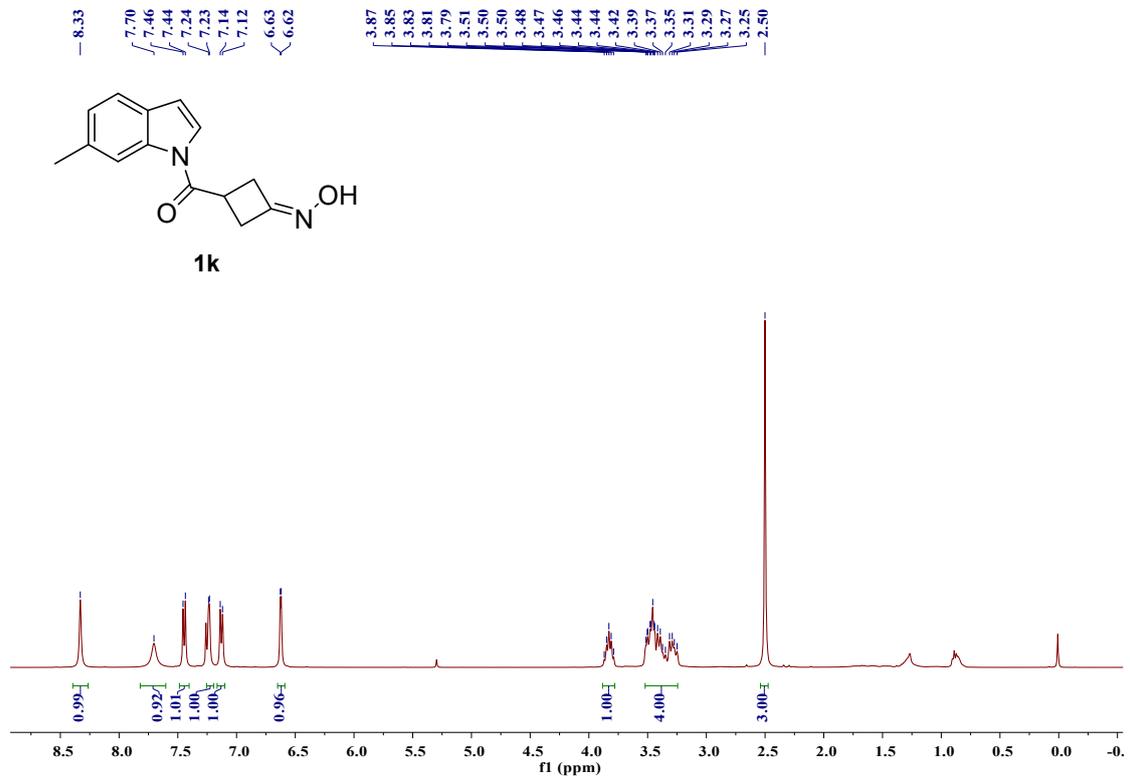


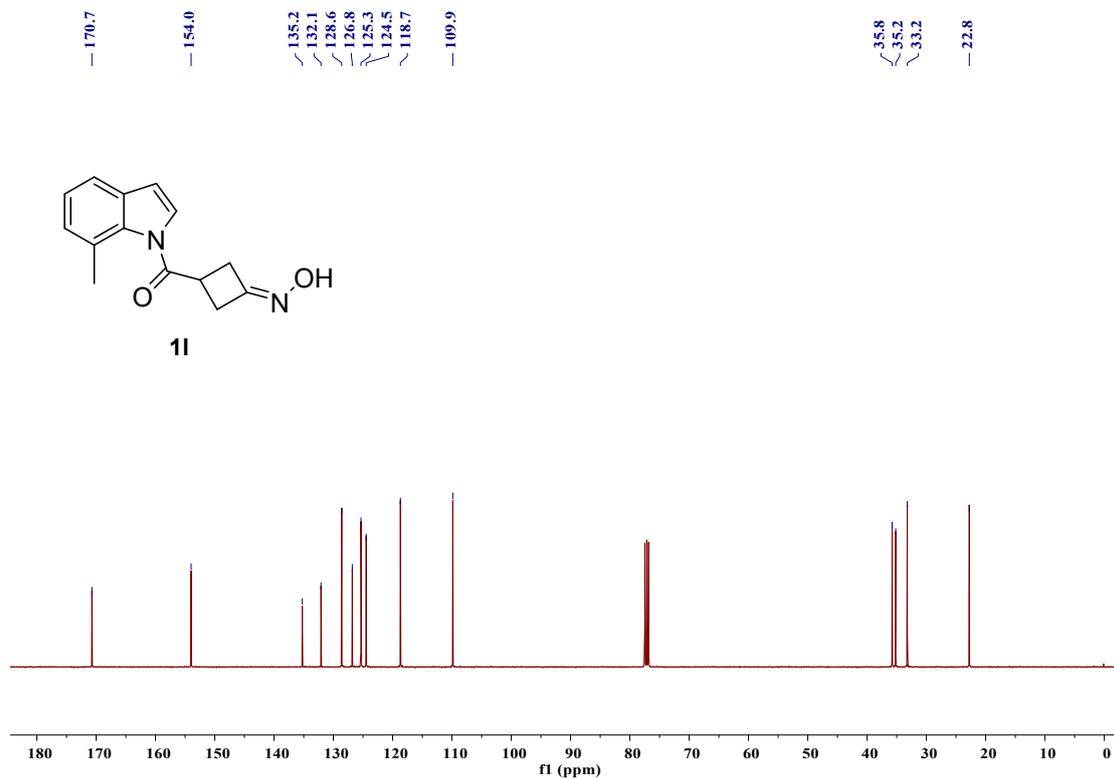
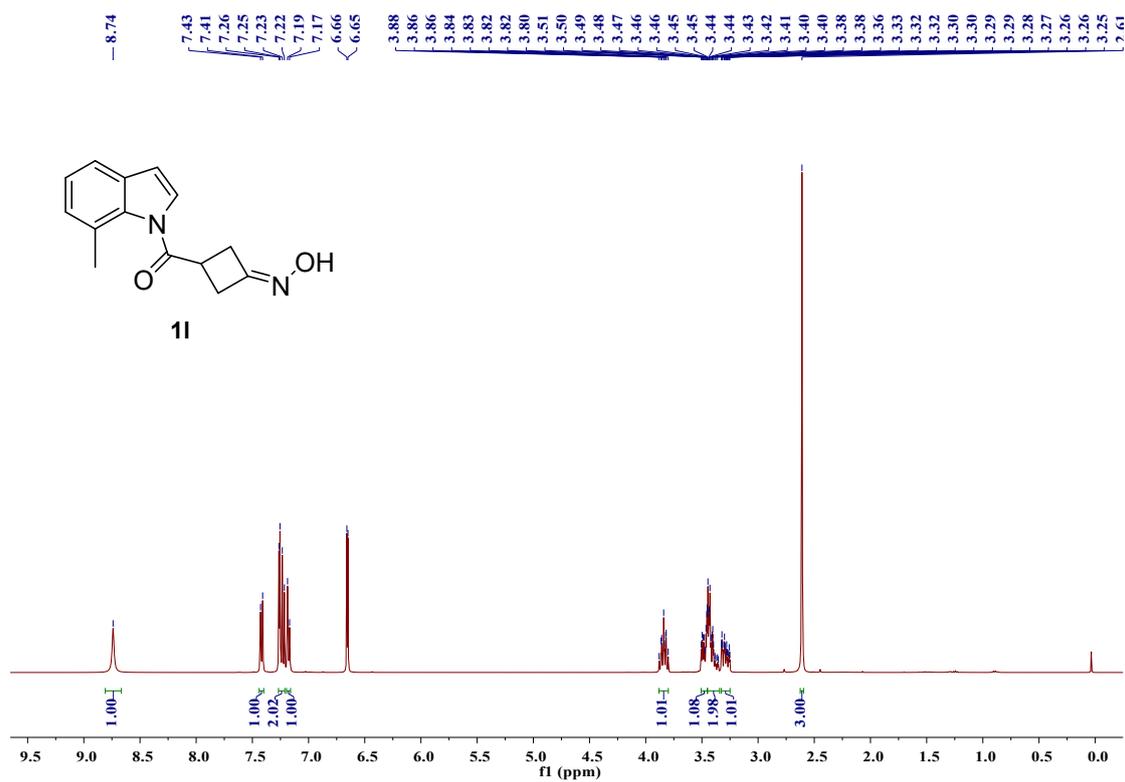


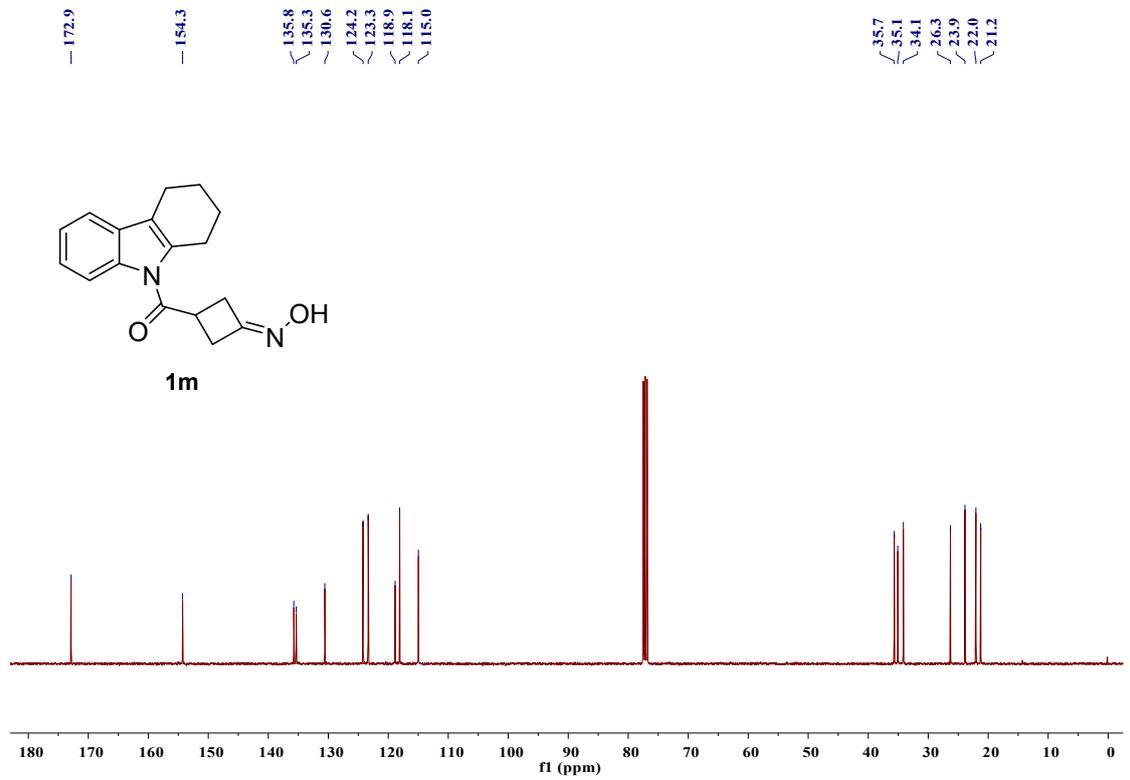
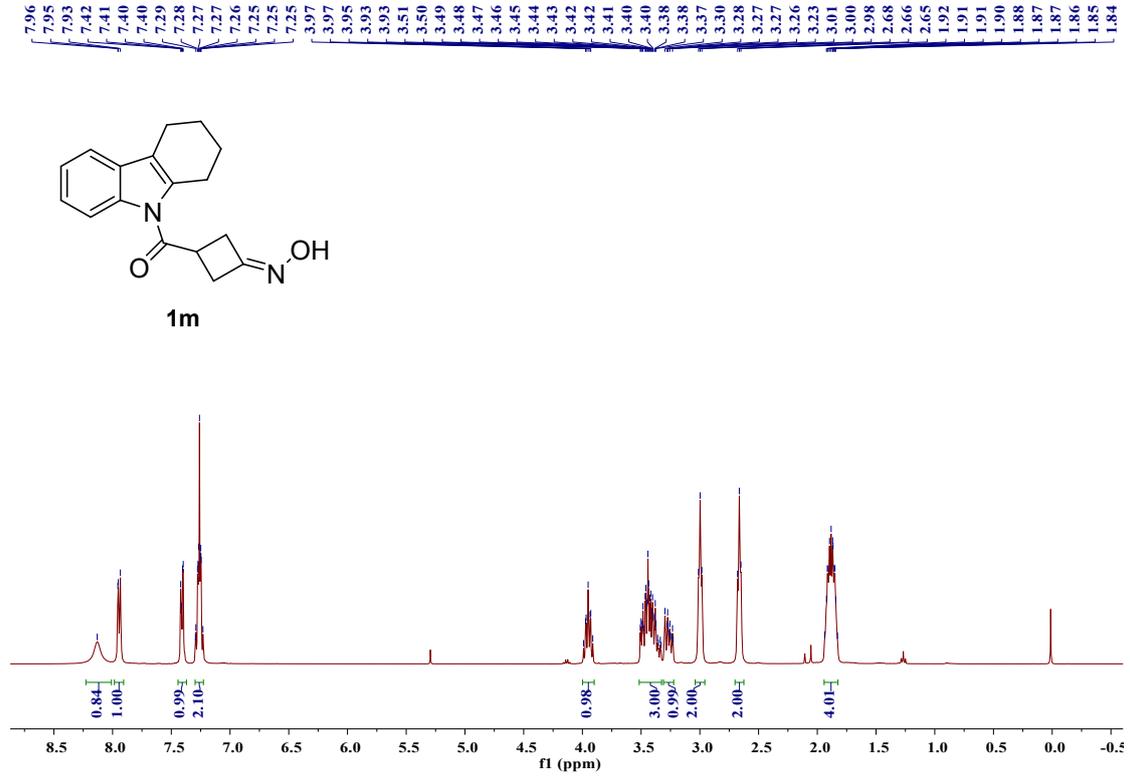


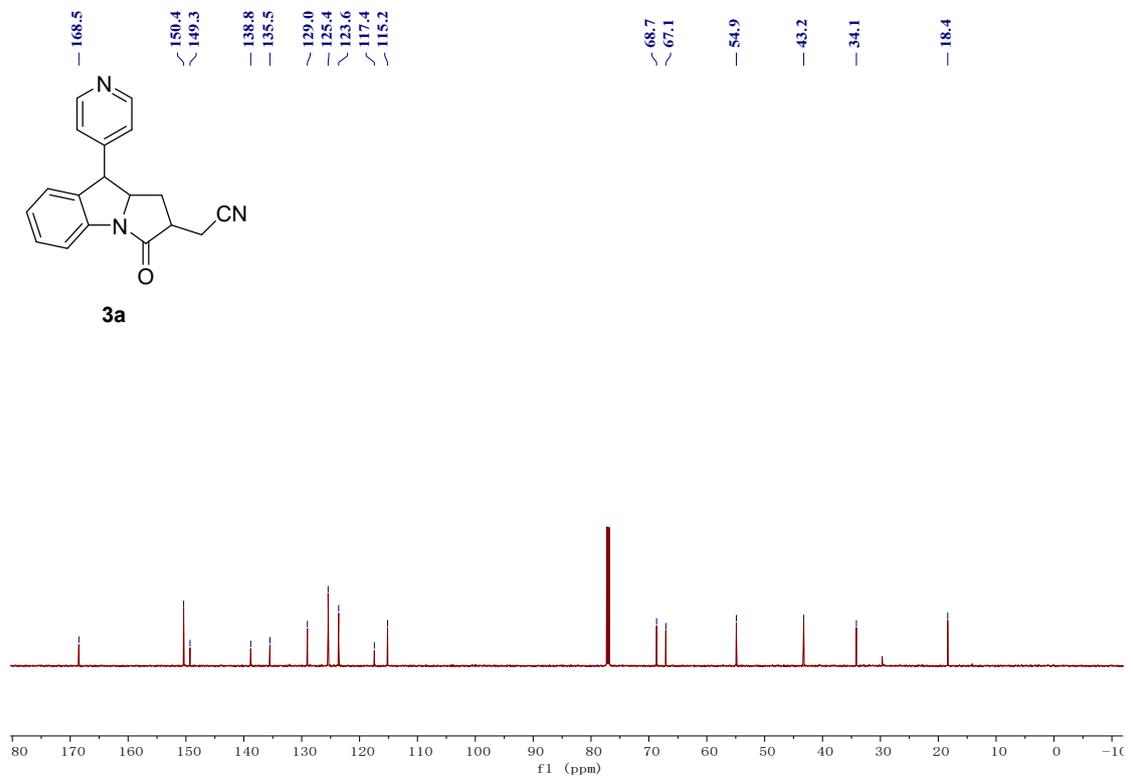
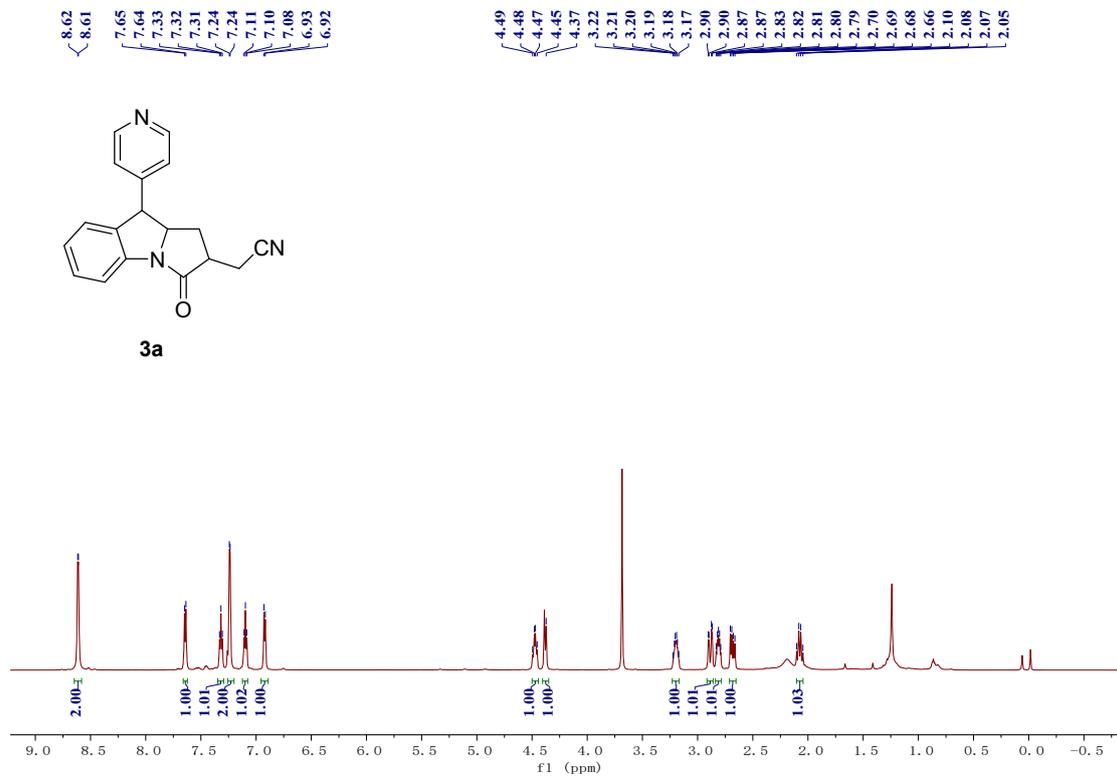


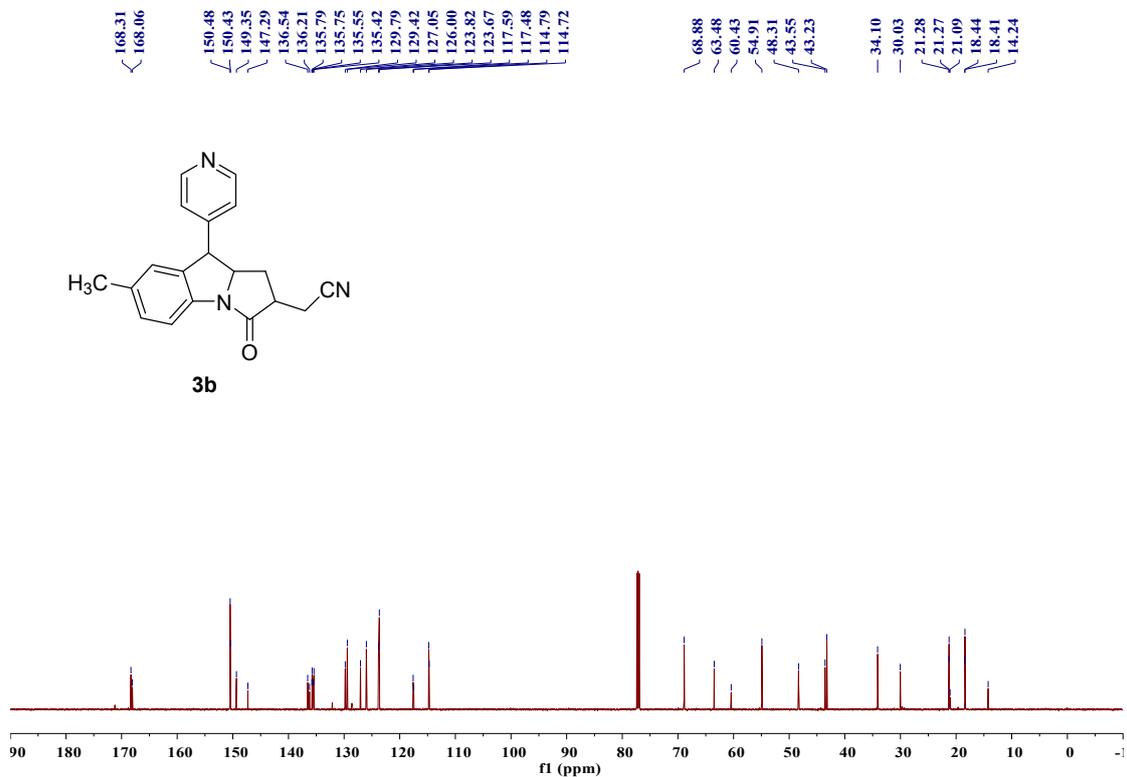
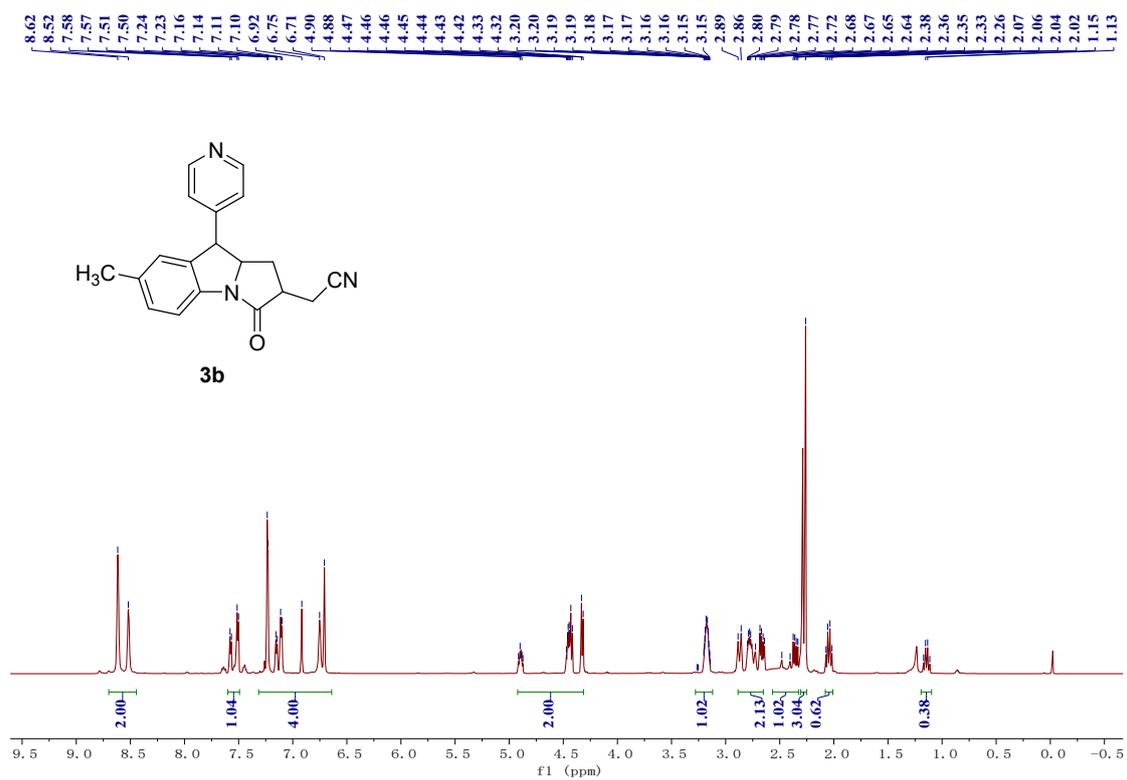


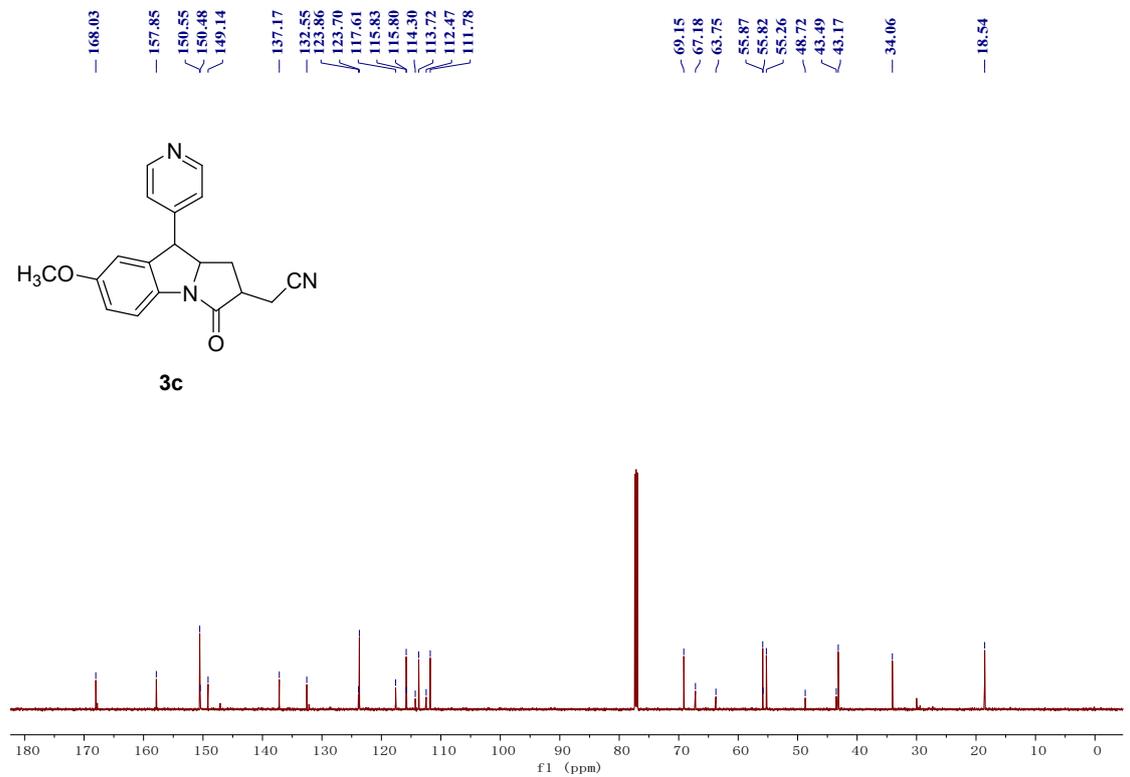
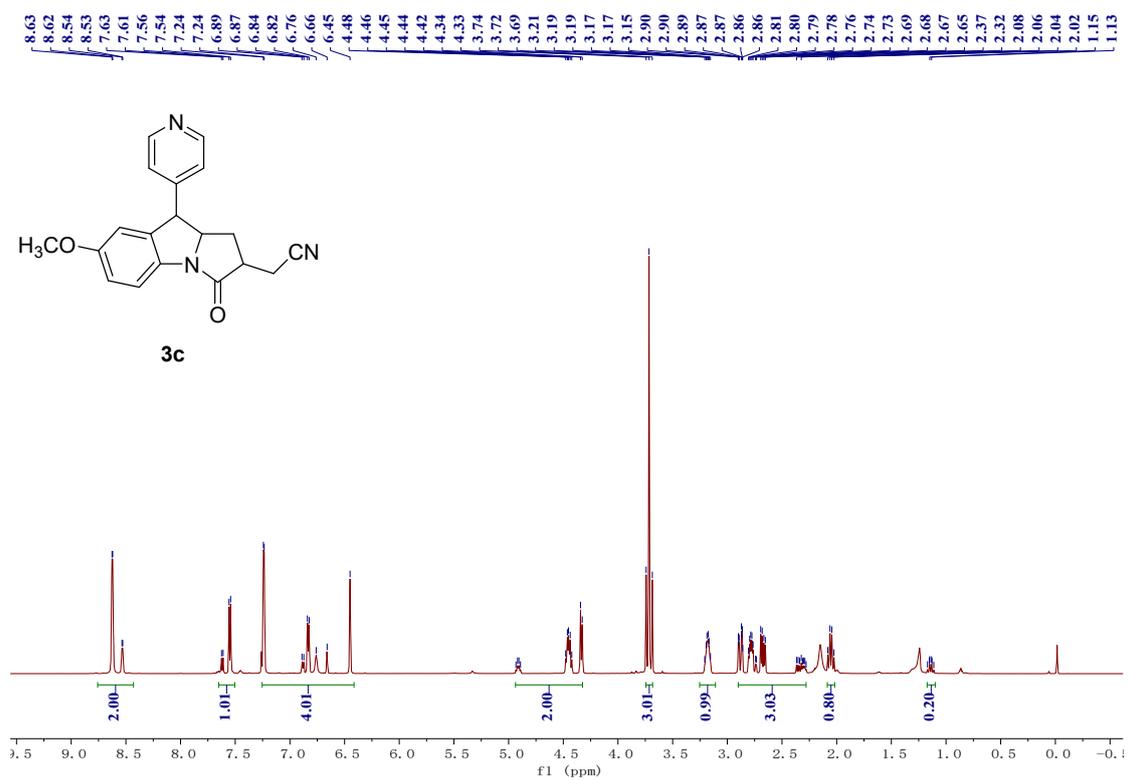


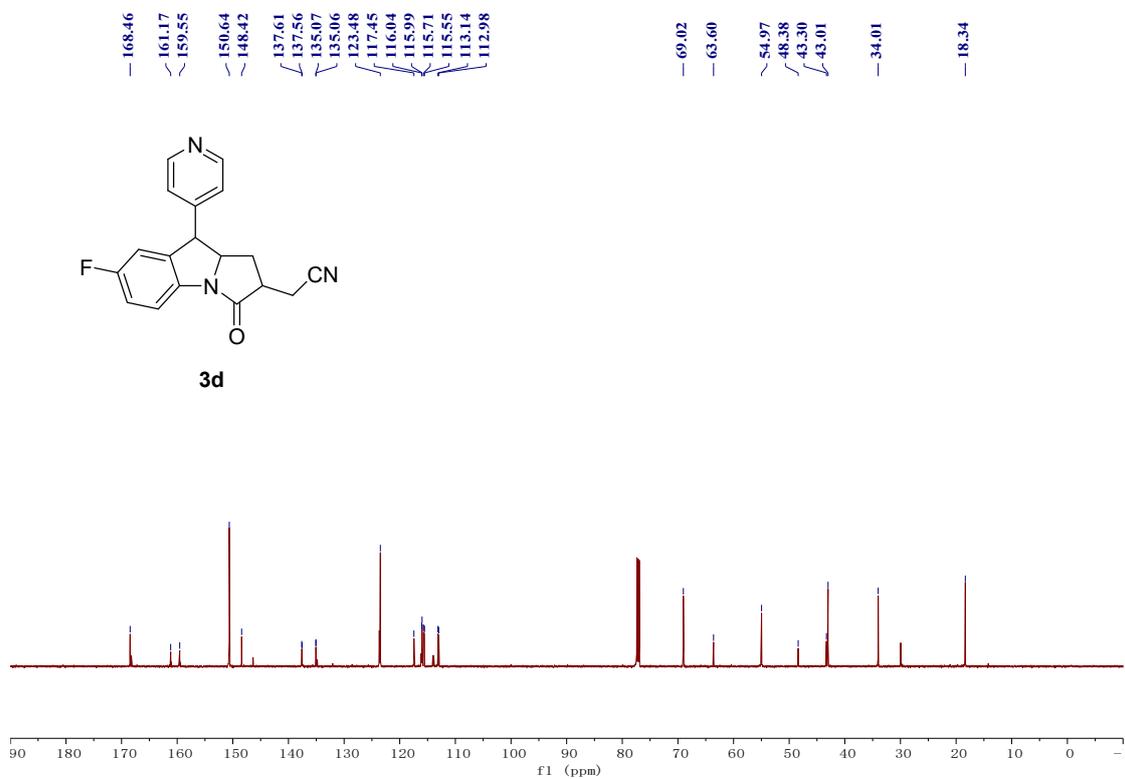
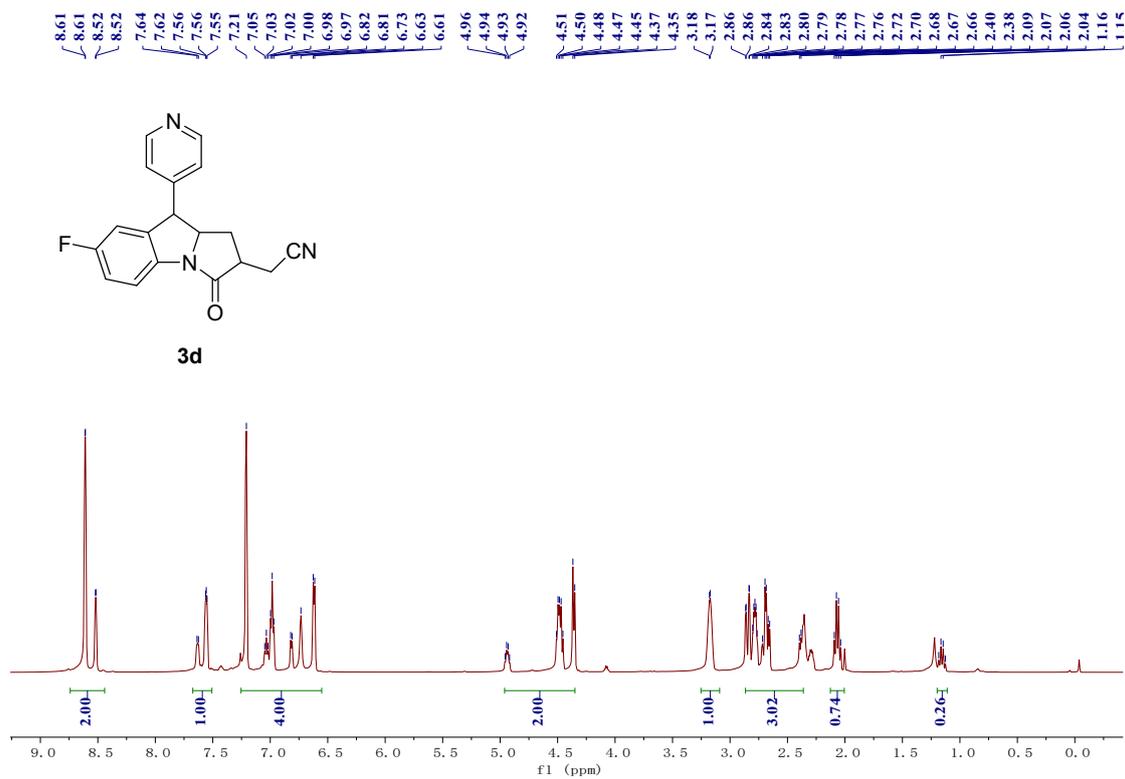


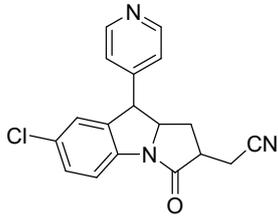




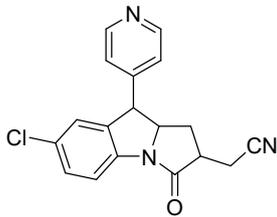
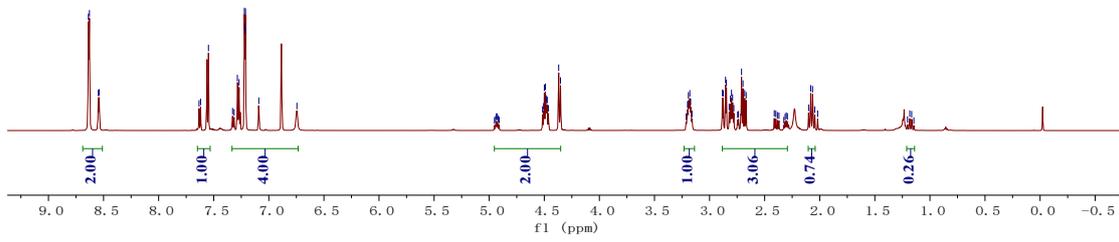








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