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Supporting Information

Missing-linker Defects in Covalent Organic Framework Photocatalyst for highly efficient Synthesis of Tetrahydroquinoline

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Materials

2,4,6-Tris(4-aminophenyl)-1,3,5-triazine (98 %), maleimide (98.5 %), 2,5-dihydroxybenzaldehyde (99%), N,N-dimethylaniline (99 %), N,N-dimethyl-p- toluidine (99 %), 4-bromo-N,N-dimethylaniline (98 %), N-phenylmaleimide (98 %), N-methylmaleimide (97 %), $AgNO_3$ (98 %), ethylenediamine- tetraacetic acid disodium salt (99 %), 2-propanol (99 %), anhydrous acetonitrile (CH_3CN) (99. 9 %, AR), and 1,4-Benzoquinone were purchased from Adamas-beta® (Shanghai, China). Organic solvents such as acetic acid (99.7 %), N,N-Dimethylformamide (DMF) (≥ 99%)tetrahydrofuran (THF) (≥ 99%, AR), anhydrous EtOH (≥ 99.5%), acetone (≥ 99.5%) were purchased from commercially and used without further purification.

Synthesis of COF-HNU30-x

Three-component condensation strategy (TAPT/Dha/Dhb) was used to synthesize defective COF-HNU30-*x* (*x* = 0, 5, 10 and 20; *x* = 0, as defect-free COF-HNU30-*0*). Typically, 2,4,6-tris (4-aminophenyl)-1,3,5-triazine (TAPT, 0.12 mmol, 42.5 mg), 2,5-dihydroxyterephthalaldehyde (Dha) and 2,5-dihydroxybenzaldehyde (Dhb) at varied molar ratios (0.18 mmol in total, $x = [\mathrm{DHBA}]/ [\mathrm{DHBA+DHTA}]\times 100$) were charged into several glass bottles. Then 15 mL of CH_3CN was added to each bottle and sonicated for 1 min to dissolve the building blocks completely. After dispersing evenly, add 6 M acetic acid (1.35 mL), then the mixture was vigorously shaken for 10 s and stood at room temperature for 72 h. After being collected by filtration, the precipitate was washed with ethanol, tetrahydrofuran, and acetone. Finally, the solid was dried at under vacuum at 60 °C for 12 h to obtain COF-HN U30-*x* as reddish-brown powder (yield: 96.0 %).

Gram-scale synthesis of COF-HNU30-10

Typically, 2,4,6-tris (4-aminophenyl)-1,3,5-triazine (TAPT, 2.4 mmol, 850 mg), 2,5-dihydroxyter- ephthalaldehyde (Dha) and 2,5-dihydroxybenzaldehyde (Dhb) at varied molar ratios (3.6 mmol in total, $[\mathrm{DHBA}]/ [\mathrm{DHBA+DHTA}]\times 100 = 10$) were charged into a glass bottle. Then 80 mL of CH_3CN was added to the bottle and sonicated for 1 min to dissolve the building blocks completely. After dispersing evenly, add 6 M acetic acid (27 mL), then the mixture was vigorously shaken for 20 s and stood at room temperature for 72 h. After being collected by filtration, the precipitate was washed with ethanol, tetrahydrofuran, and acetone. Finally, the solid was dried at under vacuum at 60 °C for 12 h to obtain COF-HN U30-*10* as reddish-brown powder (yield: 96.0 %).

Characterization

Power X-ray diffraction (PXRD) data were obtained with an X' Pert3 powder diffractometer at 40 kV and 40 mA with Cu Kradiation from $2\theta = 2°$ to 40° in 0.05° increment. Fourier transform infrared (FT-IR) of the samples were collected on a Spectrum 400 spectrometer (Perkin-Elmer). All samples were ground into a powder with KBr and pelletized before the measurements. Nitrogen adsorption and desorption isotherms were measured at 77 K using an ASiQwin Quantachrome instrument. The samples were treated at 150 °C for 8 h before measurements. Specific surface areas were calculated from the adsorption data using Brunauer-Emmett-Teller (BET) methods. Pore size distribution data were calculated based on the nonlocal density functional theory (NLDFT) model. Field emission scanning electron microscopy (FE-SEM) observations were performed on a Hitachi SU8010 microscope operated at an accelerating voltage of 10.0 kV. In order to analyze the thermal properties of the materials, thermogravimetric analysis (TGA) data were obtained on a STA449C under N_2 atmosphere from 10°C to 800°C along with a ramp rate of 10°C min^{-1}. Nuclear magnetic resonance (NMR) spectra were recorded by a Bruker Advance III 600 MHz NMR spectrometer with chemical shift in ppm. UV-vis spectra were collected on a Shimadzu Corporation UV-2600 220V CH spectrometer. Photoluminescence and Time-resolved PL decay spectra were collected on a Horiba FluoroLog-3 in air atmosphere. EPR spectra were recorded on a EMXplus. Electrochemical tests were carried out on a CHI 760E electrochemical workstation.

General procedure for photocatalytic synthesis of 1,2,3,4- Tetrahydroquinolines

A mixture of 5 mg COF-HNU30-*x* and N,N-dimethylaniline (0.5 mmol), maleimide (0.25 mmol) was dispersed in 2 mL DMF, sonicated for 5 min, then stirred under air at room temperature over 20 W visible light LED bulb irradiation. The turbid liquid was centrifuged, the supernatant was separated and the solvent was evaporated to obtain a crude product.Yield was determined by ^{1}H-NMR analysis with 1,3,5-trimethoxybenzene as an internal standard.

Recyclability of catalysts

For the recyclability test, the catalysts were separated from the reaction mixtures by centrifugation and washed with THF for three times. After dried at 80 °C in an oven, the catalysts were reused for the next run under the optimum reaction conditions.

5-Methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3a)

White solid, mp = 77 °C [Lit. mp 77-79 °C];. ^{1}H NMR (400 MHz, $CDCl_3$) δ=8.75 (s, 1H), 7.42 (d, *J* = 7.3 Hz, 1H), 7.25 – 7.18 (m, 1H), 6.89 (td, *J* = 7.5, 0.9 Hz, 1H), 6.71 (d, *J* = 8.1 Hz, 1H), 4.02 (d, *J* = 9.5 Hz, 1H), 3.50 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.41 (ddd, *J* = 9.5, 4.4, 2.5 Hz, 1H), 3.01 (dd, *J* = 11.5, 4.3 Hz, 1H), 2.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ=179.11, 177.09, 148.52, 130.12, 128.73, 119.72, 118.42 , 112.58, 77.39, 77.08, 76.76, 50.41, 44.81, 43.25, 39.43. The mp agrees with that reported in J. Guo, D. Yang, Z. Guan, Y. He, *J. Org. Chem*., 2017, 82, 1888-1894. The NMR spectra agree with those reported in P. Huang, P. Wang, S. Wang, S. Tang, A. Lei, *Green Chem*., 2018, 20, 4870–4874. Reported as an amorphous brown solid but with no mp in Z. Song, A.P. Antonchick, *Tetrahedron*, 2016 72, 7715-7721).

8-Bromo-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3b)

Yellow solid: mp 213 °C;^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.55 (s, 1H), 7.47 (s, 1H), 7.20 (d, *J* = 14.6 Hz, 1H), 6.51 (d, *J* = 8.5 Hz, 1H), 3.90 (d, *J* = 9.2 Hz, 1H), 3.42 (d, *J* = 11.6 Hz, 1H), 3.34 (d, *J* = 4.9 Hz, 1H), 2.93 (d, *J* = 11.5 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ = 178.44, 176.16, 147.51, 132.53, 131.46, 120.25, 114.25, 111.71, 50.17, 44.52, 42.89, 39.43. HRESI-MS calcd for $C_{12}H_{11}BrN_2O_2$ $(M + H)^+$: 295.0077, found 295.0072. HRESI-MS calcd for $C_{12}H_{11}BrN_2O_2$ $(M+Na)^+$: 316.9896, found 316.9889.

8-Chloro-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3c)

White solid: mp 177 °C [Lit. mp 177-179 °C]; ^{1}H NMR (600 MHz, $CDCl_3$) δ= 8.52 (s, 1H), 7.41 (s, 1H), 7.16 (d, *J* = 8.3 Hz, 1H), 6.63 (d, *J* = 8.3 Hz, 1H), 3.98 (d, *J* = 9.1 Hz, 1H), 3.49 (d, *J* = 11.3 Hz, 1H), 3.42 (s, 1H), 3.04 – 2.99 (m, 1H), 2.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ= 178.36, 176.06, 147.08, 129.74, 128.56, 124.55, 119.83, 113.79, 50.29, 44.53, 42.99, 39.49. HRESI-MS calcd for $C_{12}H_{11}ClN_2O_2$ $(M + H)^+$: 251.0582, found 251.0581. HRESI-MS calcd for $C_{12}H_{11}ClN_2O_2$ $(M + Na)^+$: 273.0401, found 273.0396. The mp and NMR spectra agree with that reported in J. Guo, D. Yang, Z. Guan, Y. He, *J. Org. Chem*., 2017, 82, 1888-1894.

5,8-Dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3d)

White solid: mp = 82 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.21 (s, 1H), 7.25 (s, 1H), 7.03 (dd, *J* = 8.3, 1.5 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 4.00 (d, *J* = 9.5 Hz, 1H), 3.48 (dd, *J* = 11.4, 2.5 Hz, 1H), 3.41 (ddd, *J* = 9.5, 4.4, 2.5 Hz, 1H), 2.96 (dd, *J* = 11.4, 4.4 Hz, 1H), 2.79 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 179.06, 177.03, 146.37, 130.61, 129.26, 129.06, 118.41, 112.57, 50.74, 44.81, 43.32, 39.53, 20.44. HRESI-MS calcd for $C_{13}H_{14}N_2O_2$ $(M + H)^+$: 231.1128, found 231.1130. HRESI-MS calcd for $C_{13}H_{14}N_2O_2$ $(M + Na)^+$: 253.0947, found 253.0950.

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2,5-Dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3e)

White solid: mp 172 °C [Lit. mp 171-173 °C]; ^{1}H NMR (600 MHz, $CDCl_3$) δ= 7.47 (d, *J* = 7.0 Hz, 1H), 7.21 (s, 1H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 4.00 (d, *J* = 9.2 Hz, 1H), 3.53 (d, *J* = 11.4 Hz, 1H), 3.40 – 3.34 (m, 1H), 3.07 – 3.02 (m, 1H), 2.98 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ= 178.78, 176.84, 148.42, 130.21, 128.60, 119.64, 118.74, 112.50, 50.50, 43.62, 42.04, 39.42, 25.37. The mp agrees with that reported in J. Guo, D. Yang, Z. Guan, Y. He, *J. Org. Chem*., 2017, 82, 1888-1894. The NMR spectra agree with those reported in J. Tang, G. Grampp, Y. Liu, B-X Wang, F-F Tao, L-J Wang, X-Z Liang, H-Q Xiao and Y-M Shen, *J Org, Chem*. 2015, 80, 2724-2732.

2,5,8-Trimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3f)

White solid: mp 170 °C [Lit. mp 173-176 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.30 (d, *J* = 1.5 Hz, 1H), 7.02 (dd, *J* = 8.3, 1.8 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 3.96 (d, *J* = 9.4 Hz, 1H), 3.52 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.35 (ddd, *J* = 9.4, 4.4, 2.4 Hz, 1H), 2.99 (s, 4H), 2.76 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ= 178.89, 176.94, 146.27, 130.69, 129.07, 128.99, 118.67, 112.51, 50.79, 43.62, 42.10, 39.55, 25.36, 20.45. The mp and NMR spectra agree with those reported in J. Tang, G. Grampp, Y. Liu, B-X Wang, F-F Tao, L-J Wang, X-Z Liang, H-Q Xiao and Y-M Shen, *J Org, Chem*. 2015, 80, 2724-2732.

8-Bromo-2,5-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3g)

White solid: mp 191 °C [Lit. mp 188-190 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.59 (d, *J* = 2.3 Hz, 1H), 7.29 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.56 (d, *J* = 8.7 Hz, 1H), 3.95 (d, *J* = 9.5 Hz, 1H), 3.53 (dd, *J* = 11.6, 2.5 Hz, 1H), 3.37 (ddd, *J* = 9.4, 4.3, 2.5 Hz, 1H), 3.02 (dd, *J* = 10.4, 3.3 Hz, 1H), 3.00 (s, 3H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ =178.35, 176.17, 147.41, 132.59, 131.34, 120.61, 114.23, 111.68, 50.25, 43.33, 41.68, 39.48, 25.51. HRESI-MS calcd for $C_{18}H_{15}BrN_2O_2$ $(M + H)^+$: 371.0390, found 371.0392. HRESI-MS calcd for $C_{18}H_{15}BrN_2O_2$ $(M + Na)^+$:393.0209, found 393.0216. The mp and NMR spectra agree with those reported in J. Tang, G. Grampp, Y. Liu, B-X Wang, F-F Tao, L-J Wang, X-Z Liang, H-Q Xiao and Y-M Shen, *J Org, Chem*. 2015, 80, 2724-2732.

8-Bromo-5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3h)

White solid: mp 156 °C [Lit. mp 159-161 °C]; ^{1}H NMR (600 MHz, $CDCl_3$) δ= 7.64 (s, 1H), 7.43 (d, *J* = 6.3 Hz, 2H), 7.37 (s, 1H), 7.31 (d, *J* = 8.5 Hz, 1H), 7.25 (s, 1H), 6.60 (d, *J* = 5.8 Hz, 1H), 4.10 (d, *J* = 7.4 Hz, 1H), 3.60 (d, *J* = 11.4 Hz, 1H), 3.53 (d, *J* = 6.5 Hz, 1H), 3.11 (d, *J* = 11.5 Hz, 1H), 2.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ= 177.23, 175.13, 147.49, 132.75, 131.85, 131.49, 129.08, 128.66, 126.31, 120.38, 114.25, 111.74, 50.40, 43.30, 41.80, 39.48. The mp and NMR spectra agree with those reported in J. Tang, G. Grampp, Y. Liu, B-X Wang, F-F Tao, L-J Wang, X-Z Liang, H-Q Xiao and Y-M Shen, *J Org, Chem*. 2015, 80, 2724-2732.

5-Methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3i)

White solid: mp 200 °C [Lit. mp 202-204 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.54 (d, *J* = 7.3 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.39 – 7.33 (m, 1H), 7.29 – 7.24 (m, 3H), 6.93 (td, *J* = 7.5, 1.0 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 4.18 (d, *J* = 9.6 Hz, 1H), 3.63 (dd, *J* = 11.5, 2.8 Hz, 1H), 3.56 (ddd, *J* = 9.6, 4.4, 2.8 Hz, 1H), 3.15 (dd, *J* = 11.5, 4.4 Hz, 1H), 2.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 177.69, 175.77, 148.45, 134.23, 132.02, 130.37, 129.10, 128.63, 128.00, 126.38, 126.10, 119.77, 118.60, 112.63, 50.68, 43.55, 42.14, 39.50. The mp and NMR spectra agree with those reported in J. Tang, G. Grampp, Y. Liu, B-X Wang, F-F Tao, L-J Wang, X-Z Liang, H-Q Xiao and Y-M Shen, *J Org, Chem*. 2015, 80, 2724-2732.

5,8-Dimethyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3j)

White solid: mp 194 °C [Lit. mp 193-195 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.42 (dd, *J* = 10.3, 4.7 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.30 – 7.23 (m, 2H), 7.03 (dd, *J* = 8.3, 1.6 Hz, 1H), 6.65 (d, *J* = 8.3 Hz, 1H), 4.10 (d, *J* = 9.6 Hz, 1H), 3.58 (dd, *J* = 11.4, 2.6 Hz, 1H), 3.50 (ddd, *J* = 9.6, 4.3, 2.7 Hz, 1H), 3.04 (dd, *J* = 11.4, 4.4 Hz, 1H), 2.79 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 177.88, 175.93, 146.39, 132.04, 130.85, 129.27, 129.03, 128.54, 126.41, 118.65, 112.59, 50.97, 43.60, 42.21, 39.64, 20.57. The mp and NMR spectra agree with those reported in J. Tang, G. Grampp, Y. Liu, B-X Wang, F-F Tao, L-J Wang, X-Z Liang, H-Q Xiao and Y-M Shen, *J Org, Chem*. 2015, 80, 2724-2732.

2-(4-Methoxyphenyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3k)

White solid, mp = 223 °C [Lit. mp 222-224 °C]; ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.52 (d, *J* = 7.2 Hz, 1H), 7.29 – 7.10 (m, 3H), 6.91 (dd, *J* = 11.5, 8.1 Hz, 3H), 6.74 (d, *J* = 8.1 Hz, 1H), 4.13 (d, *J* = 9.5 Hz, 1H), 3.79 (s, 3H), 3.59 (d, *J* = 11.4 Hz, 1H), 3.49 (dt, *J* = 34.7, 17.3 Hz, 1H), 3.10 (dd, *J* = 11.3, 4.1 Hz, 1H), 2.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ=177.95, 176.02, 159.42, 148.51, 130.37, 128.67, 127.61, 124.69, 119.68, 118.67, 114.33, 112.55, 55.49, 50.70, 43.51, 42.08, 39.47. HRESI-MS calcd for $C_{19}H_{18}N_2O_3$ $(M + H)^+$: 323.1390, found 323.1391. HRESI-MS calcd for $C_{19}H_{18}N_2O_3$ $(M + Na)^+$: 345.1210, found 345.1211. The mp and NMR spectra agree with those reported in J. Tang, G. Grampp, Y. Liu, B-X Wang, F-F Tao, L-J Wang, X-Z Liang, H-Q Xiao and Y-M Shen, *J Org, Chem*. 2015, 80, 2724-2732.

2-(4-methoxyphenyl)-5,8-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)- dione (3l)

White solid: mp 180 °C [Lit. mp 182-183 °C]; ^{1}H NMR (600 MHz, $CDCl_3$) δ= 7.34 (s, 1H), 7.17 (d, *J* = 7.1 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 1H), 6.92 (d, *J* = 7.2 Hz, 2H), 6.64 (d, *J* = 7.1 Hz, 1H), 4.09 (d, *J* = 9.0 Hz, 1H), 3.79 (s, 3H), 3.57 (d, *J* = 11.3 Hz, 1H), 3.49 (d, *J* = 5.3 Hz, 1H), 3.04 (d, *J* = 11.2 Hz, 1H), 2.79 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ= 178.06, 176.11, 159.41, 146.37, 130.85, 129.22, 129.00, 127.62, 124.72, 118.63, 114.31, 112.54, 55.49, 50.99, 43.52, 42.14, 39.60, 30.35, 20.47.

HRESI-MS calcd for $C_{20}H_{20}N_2O_3$ (M + H)$^+$: 337.1547, found 337.3545. HRESI-MS calcd for $C_{20}H_{20}N_2O_3$ (M + Na)$^+$: 359.1366, found 359.1364. The mp and NMR spectra agree with those reported in J. Tang, G. Grampp, Y. Liu, B-X Wang, F-F Tao, L-J Wang, X-Z Liang, H-Q Xiao and Y-M Shen, *J Org, Chem*. 2015, 80, 2724-2732.

8-Chloro-5-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3m)

White solid: mp 156 °C [Lit. mp 157-159 °C]. ^{1}H NMR (600 MHz, $CDCl_3$) δ= 7.40 (d, J = 2.2 Hz, 1H), 7.33 (t, J = 7.7 Hz, 2H), 7.27 (t, J = 7.4 Hz, 1H), 7.17 (t, J = 10.7 Hz, 2H), 7.07 (dd, J = 8.7, 2.4 Hz, 1H), 6.55 (d, J = 8.8 Hz, 1H), 3.97 (d, J = 9.6 Hz, 1H), 3.48 (dd, J = 11.6, 2.7 Hz, 1H), 3.40 (ddd, J = 9.5, 4.2, 2.9 Hz, 1H), 2.98 (dd, J = 11.6, 4.4 Hz, 1H), 2.71 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ= 177.31, 175.18, 147.11, 131.91, 129.94, 129.07, 128.64, 128.53, 126.33, 124.43, 120.06, 113.80, 50.51, 43.30, 41.89, 39.52. The mp and NMR spectra agree with those reported in J. Tang, G. Grampp, Y. Liu, B-X Wang, F-F Tao, L-J Wang, X-Z Liang, H-Q Xiao and Y-M Shen, *J Org, Chem*. 2015, 80, 2724-2732.

8-Chloro-2,5-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3n)

White solid: mp 178 °C [Lit. mp 174-177 °C]; ^{1}H NMR (600 MHz, $CDCl_3$) δ =7.46 (d, J = 2.0 Hz, 1H), 7.15 (dd, J = 8.7, 2.5 Hz, 1H), 6.61 (d, J = 8.7 Hz, 1H), 3.95 (d, J = 9.4 Hz, 1H), 3.52 (dd, J = 11.6, 2.5 Hz, 1H), 3.36 (ddd, J = 9.4, 4.4, 2.6 Hz, 1H), 3.02 (dd, J = 11.6, 4.5 Hz, 1H), 3.00 (s, 3H), 2.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ= 178.33, 176.14, 146.99, 129.82, 128.42, 124.49, 120.17, 113.71, 50.37, 43.35, 41.80, 39.49, 25.46. The mp and NMR spectra agree with that reported in J. Guo, D. Yang, Z. Guan, Y. He, *J. Org. Chem*., 2017, 82, 1888-1894.

9-Methoxy-2,5-dimethyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3o)

Yellow solid: mp 190 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (s, 1H), 6.73 (dd, J = 72.1, 8.1 Hz, 3H), 3.97 (d, J = 8.6 Hz, 1H), 3.80 (s, 4H), 3.50 (d, J = 11.0 Hz, 1H), 3.36 (s, 1H), 3.04 – 2.92 (m, 5H), 2.76 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ= 179.09 – 178.82, 176.67, 153.19 – 153.07, 142.77, 121.28, 115.82, 114.24, 113.45 – 113.30, 77.15, 76.93, 76.81 (s), 55.65, 51.33 – 50.96, 43.84 – 43.37, 42.68, 39.95, 29.33, 25.81. The NMR spectra agree with that reported in C. Hsu, H. Sunden, *Org. Lett*., 2018, 20, 2051-2054.

8-Chloro-2-(4-Methoxyphenyl)-5-methyl-3a,4,5,9b-tetrahydro-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione (3p)

Yellow solid: mp 180 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ= 7.47 (d, J = 2.2 Hz, 1H), 7.15 (d, J = 9.0 Hz, 3H), 6.91 (d, J = 9.0 Hz, 2H), 6.63 (d, J = 8.8 Hz, 1H), 4.02 (d, J = 9.6 Hz, 1H), 3.78 (s, 3H), 3.55 (dd, J = 11.6, 2.7 Hz, 1H), 3.46 (ddd, J = 9.5, 4.3, 2.9 Hz, 1H), 3.06 (dd, J = 11.6, 4.5 Hz, 1H), 2.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ= 177.56, 175.41, 159.49, 147.11, 129.93, 128.48, 127.67, 127.58, 124.54, 124.40, 120.17, 114.40, 114.36, 113.79, 55.50, 50.54, 43.22, 41.82, 39.53.

Section S2. Figures S1-32

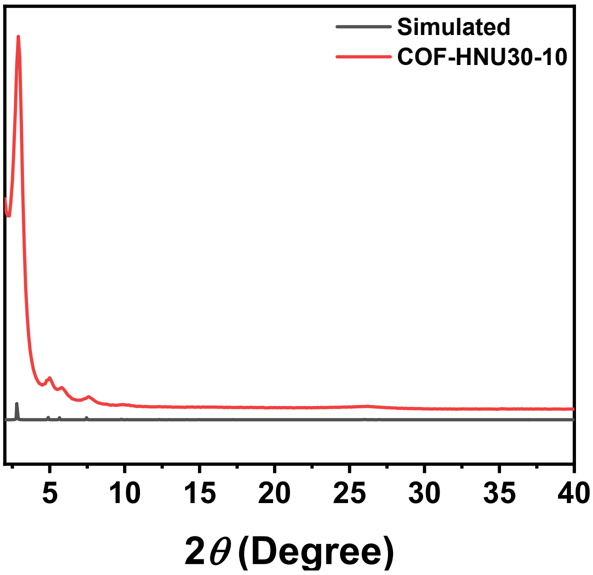


Figure S1 PXRD patterns of COF-HNU30-*10* prepared by Gram-scale synthesis.

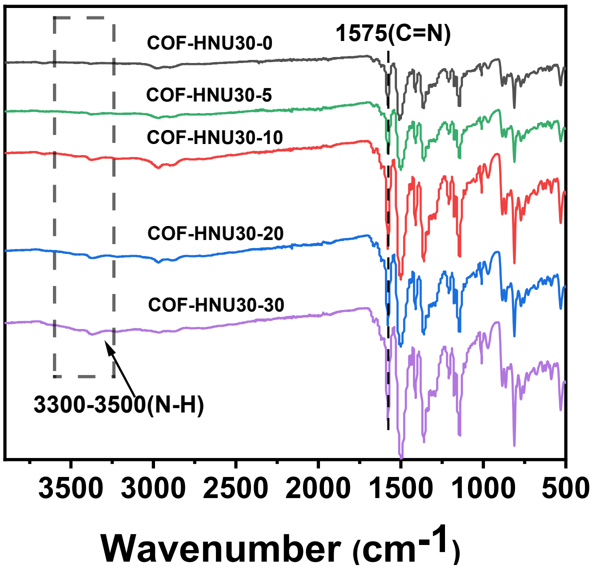


Figure S2 FT-IR spectra of COF-HNU30-*0* (black curve), COF-HNU30-*5* (green curve), COF-HNU30-*10* (red curve) , COF-HNU30-*20* (blue curve) and COF-HNU30-*30* (purple curve).

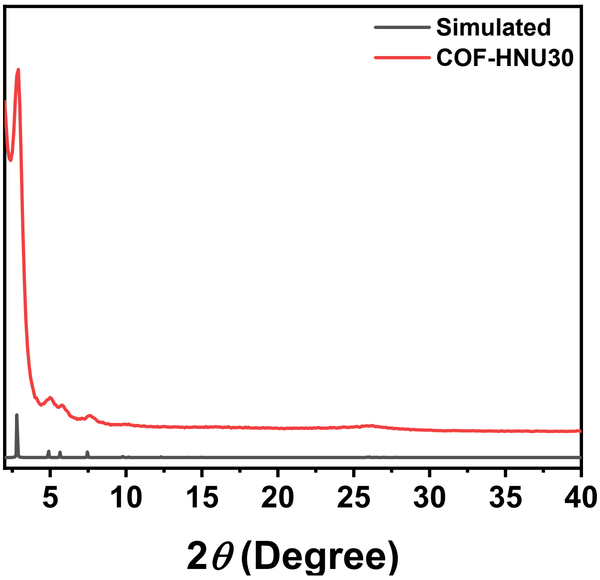


Figure S3 Experimental and simulated PXRD patterns (AA stacking) of COF-HNU30-*0*.

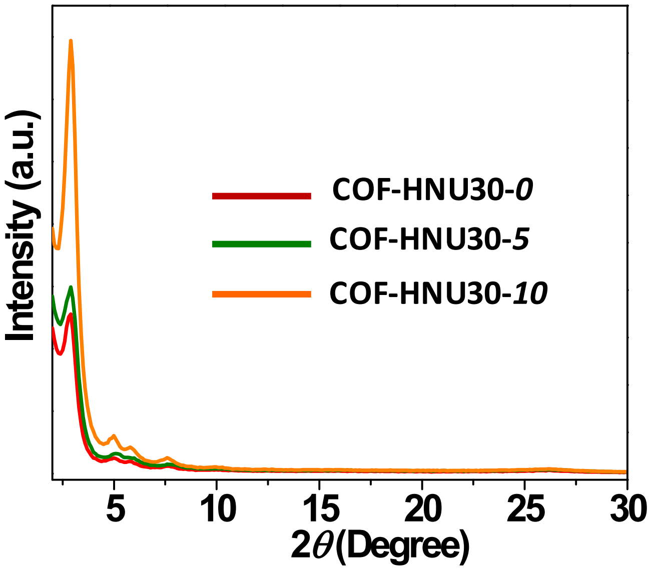


Figure S4 Powder X-ray diffraction (PXRD) pattern of COF-HNU30-*0*, COF-HNU30-*5* and COF-HNU30-*10*.

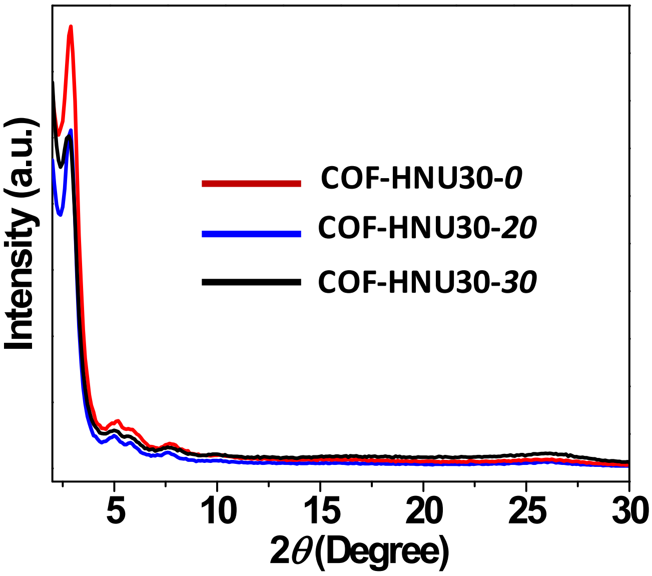


Figure S5 Powder X-ray diffraction (PXRD) pattern of COF-HNU30-*0*, COF-HNU30-*20* and COF-HNU30-*30*.

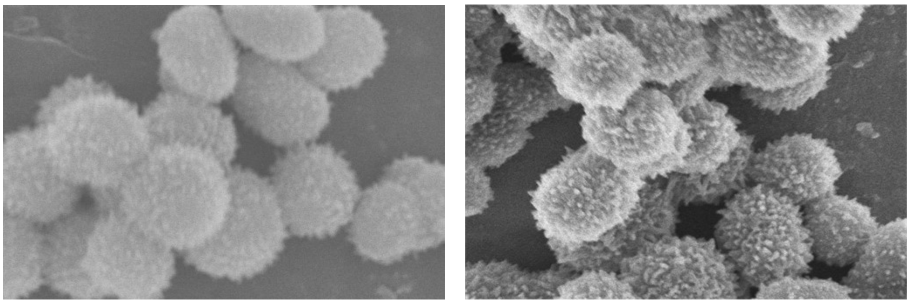


Figure S6 SEM images of COF-HNU30-*0*.

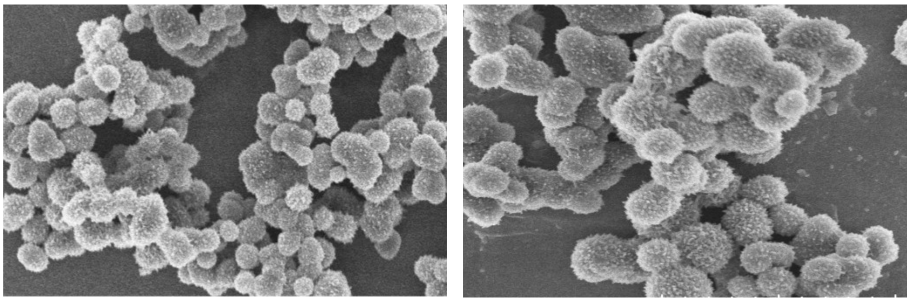


Figure S7 SEM images of COF-HNU30-*5*.

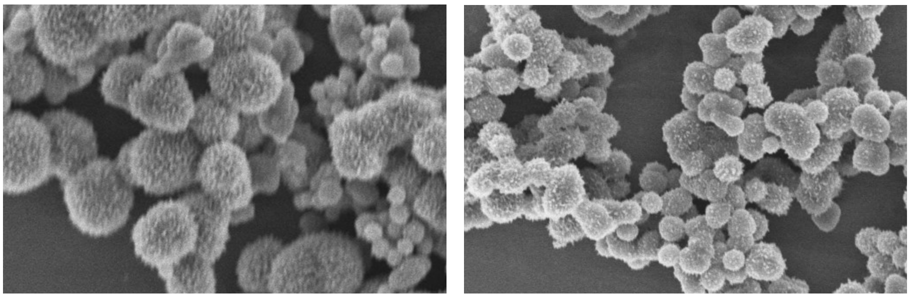


Figure S8 SEM images of COF-HNU30-*10*.

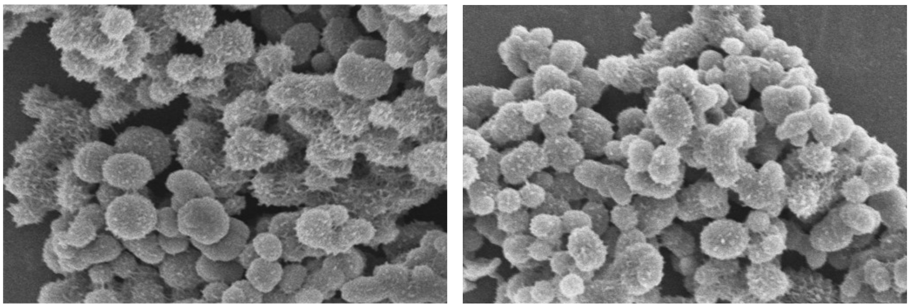


Figure S9 SEM images of COF-HNU30-*20*.

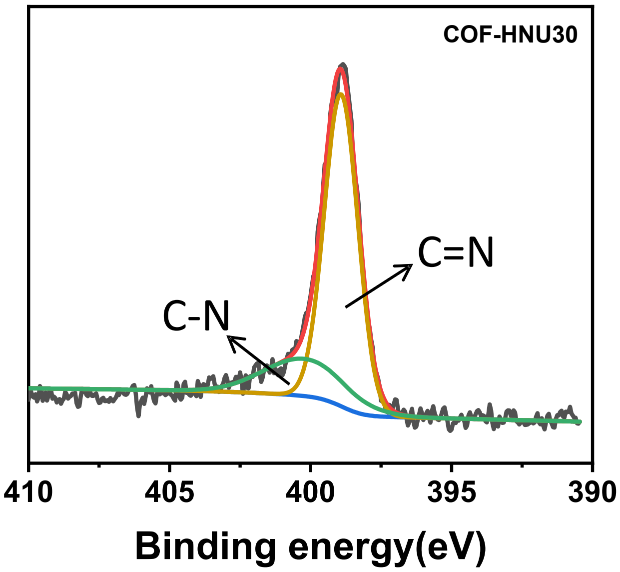


Figure S10 High resolution XPS spectra of N 1s for COF-HNU30-*0*.

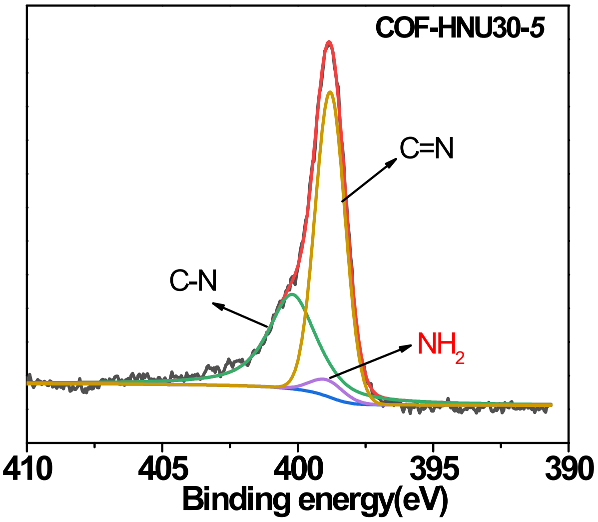


Figure S11 High resolution XPS spectra of N 1s for COF-HNU30-*5*.

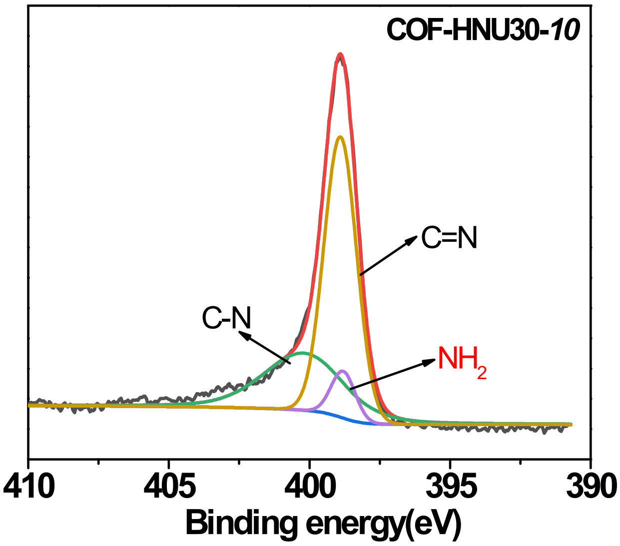


Figure S12 High resolution XPS spectra of N 1s for COF-HNU30-*10*.

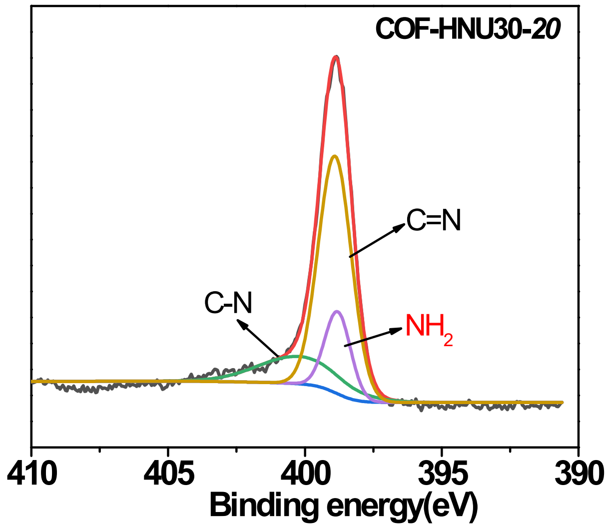


Figure S13 High resolution XPS spectra of N 1s for COF-HNU30-*20*.

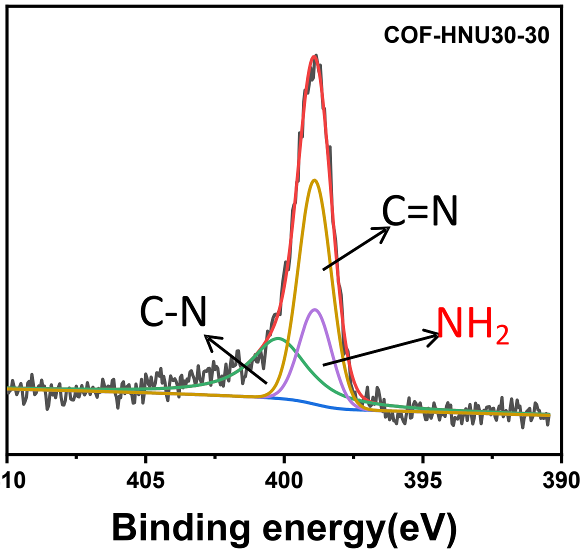


Figure S14 High resolution XPS spectra of N 1s for COF-HNU30-*30*.

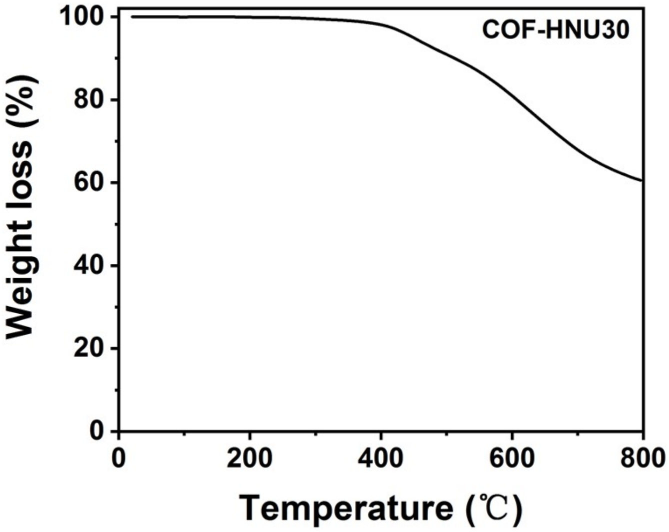


Figure S15 TGA curves of COF-HNU30-*0* under N_2 conditions.

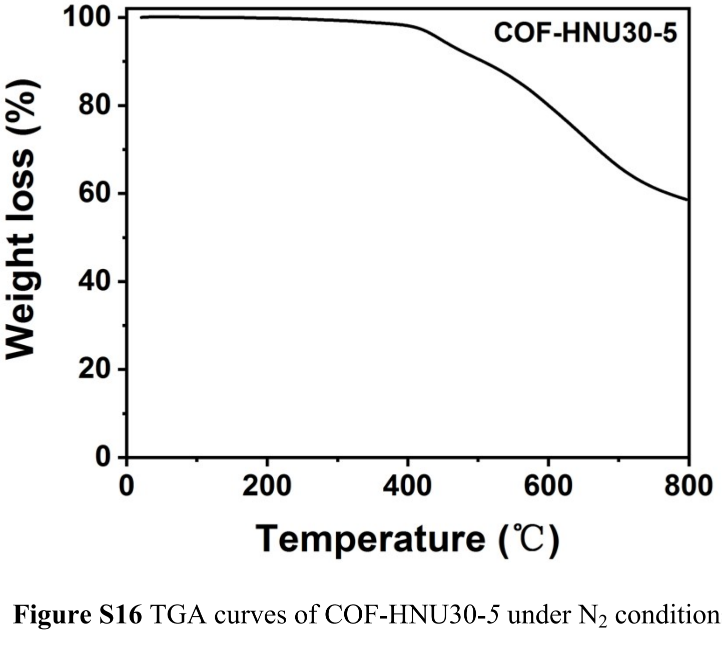


Figure S16 TGA curves of COF-HNU30-*5* under N_2 conditions.

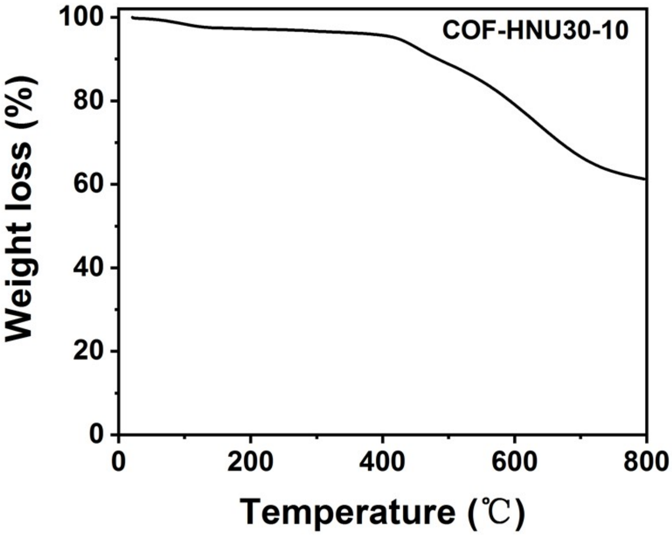


Figure S17 TGA curves of COF-HNU30-*10* under N_2 conditions. The initial drop at 50-150 ℃ corresponds to the loss of residual solvents.

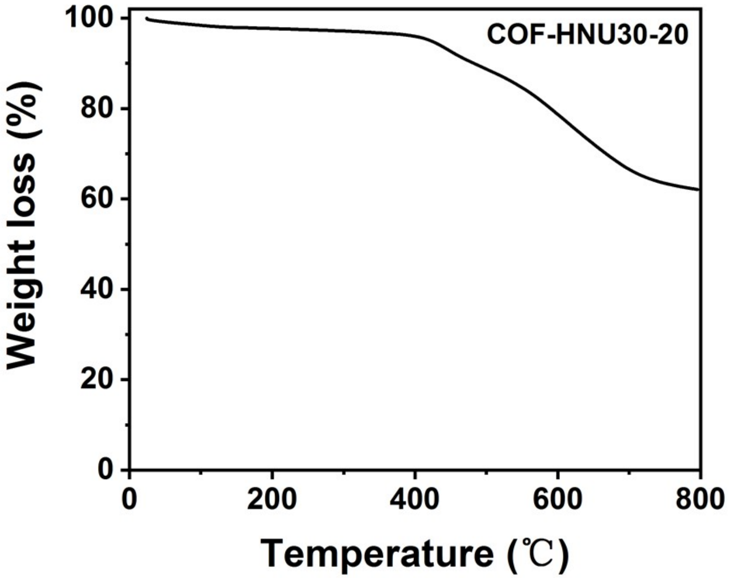


Figure S18 TGA curves ofCOF-HNU30-*20* under N_2 conditions.The initial drop at 50-150 ℃ corresponds to the loss of residual solvents.

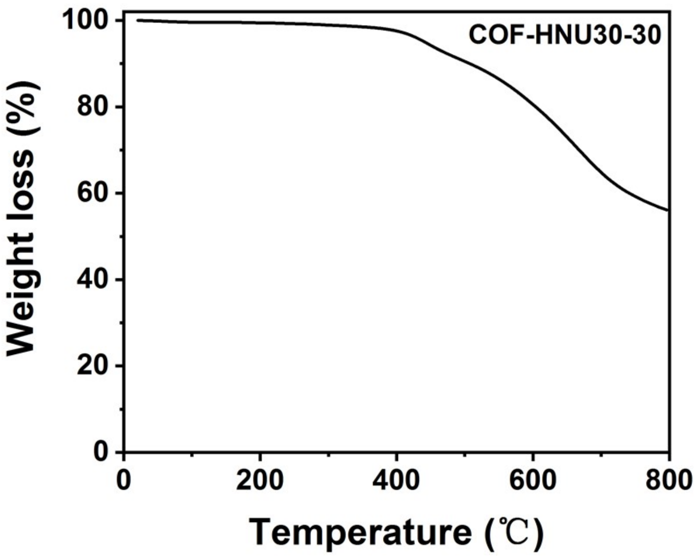


Figure S19 TGA curves of COF-HNU30-*30* under N_2 conditions.

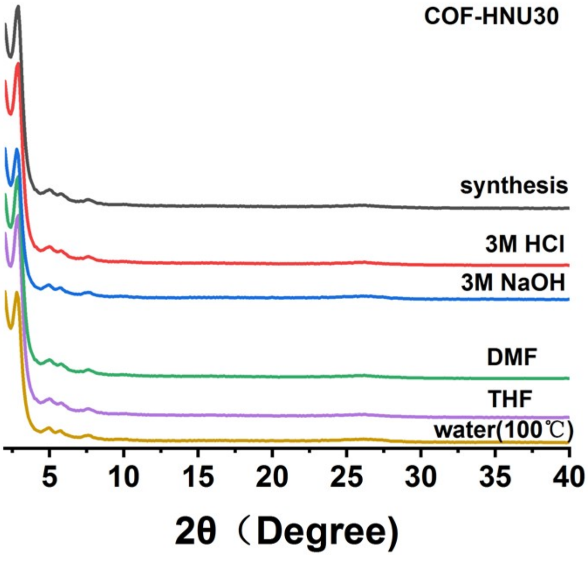


Figure S20 PXRD patterns of COF-HNU30-*0* after immersing in DMF, boiling water, 3 M NaOH, and 3 M HCl for 3 days.

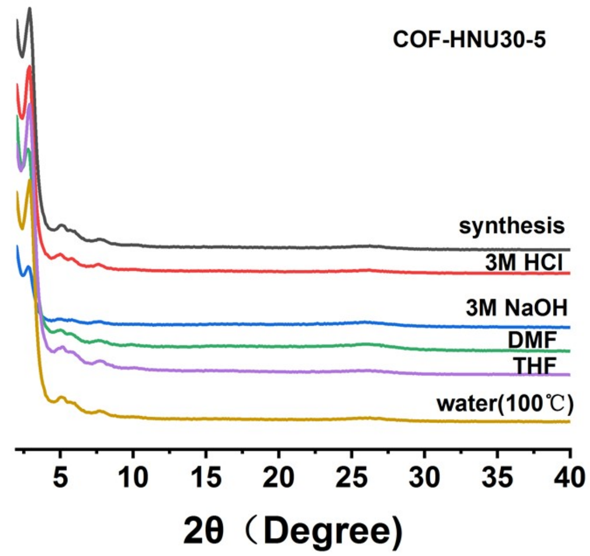


Figure S21 PXRD patterns of COF-HNU30-*5* after immersing in DMF, boiling water, 3 M NaOH, and 3 M HCl for 3 days.

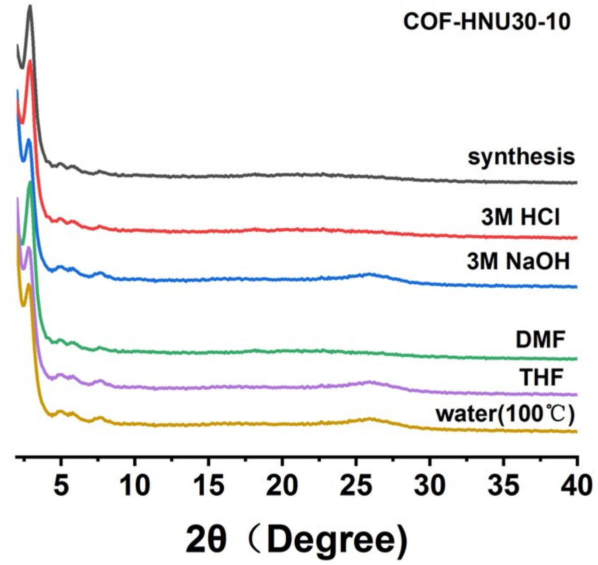


Figure S22 PXRD patterns of COF-HNU30-*10* after immersing in DMF, boiling water, 3 M NaOH, and 3 M HCl for 3 days.

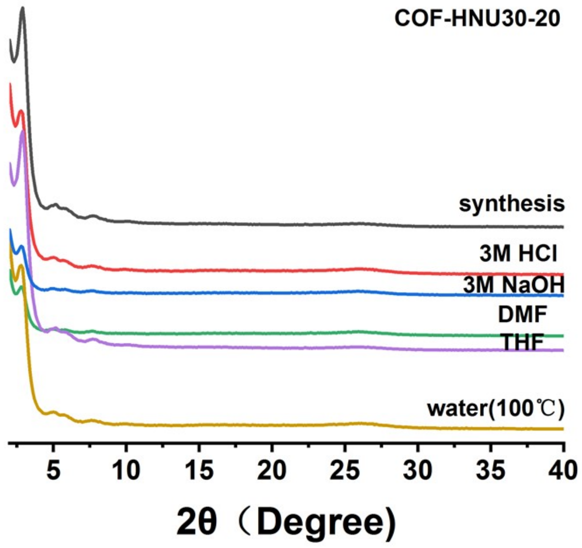


Figure S23 PXRD patterns of COF-HNU30-*20* after immersing in DMF, boiling water, 3 M NaOH, and 3 M HCl for 3 days.

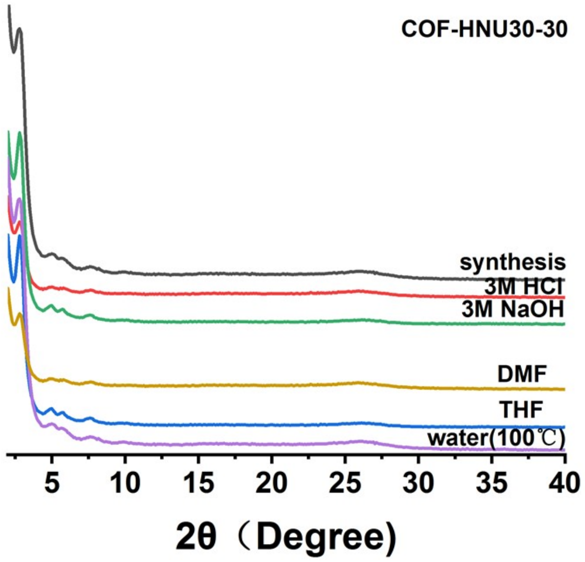


Figure S24 PXRD patterns of COF-HNU30-*30* after immersing in DMF, boiling water, 3 M NaOH, and 3 M HCl for 3 days.

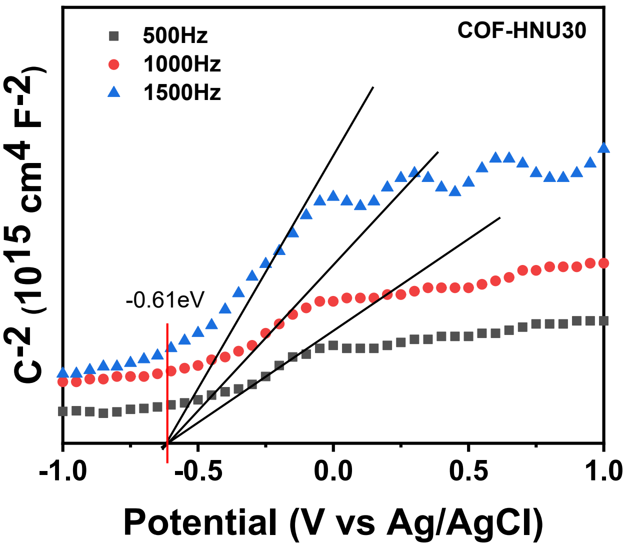


Figure S25 Mott–Schottky plots of COF-HNU30-*0* at 500, 1000 and 1500 Hz.

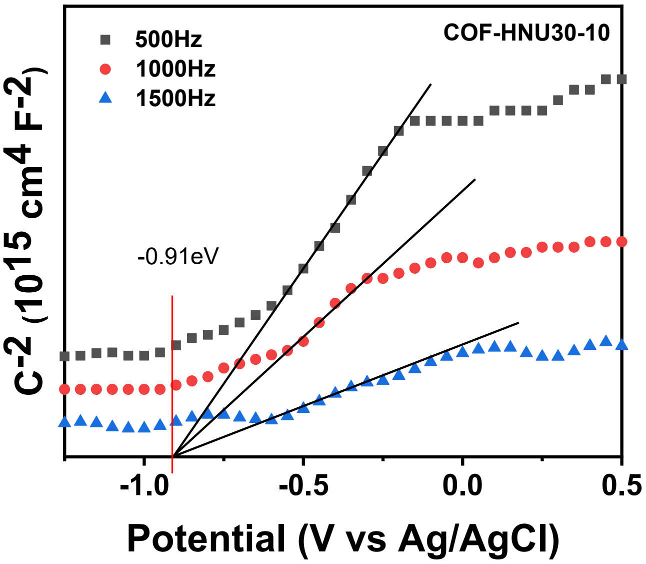


Figure S26 Mott–Schottky plots of COF-HNU30-*10* at 500, 1000 and 1500 Hz.

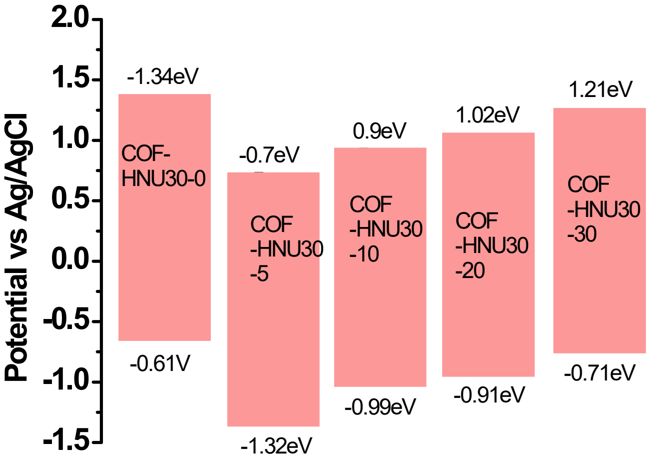


Figure S27 The band gap of COF-HNU30-*0*, COF-HNU30-*5*, COF-HNU30-*10*, COF-HNU30-*20* and COF-HNU30-*30*.

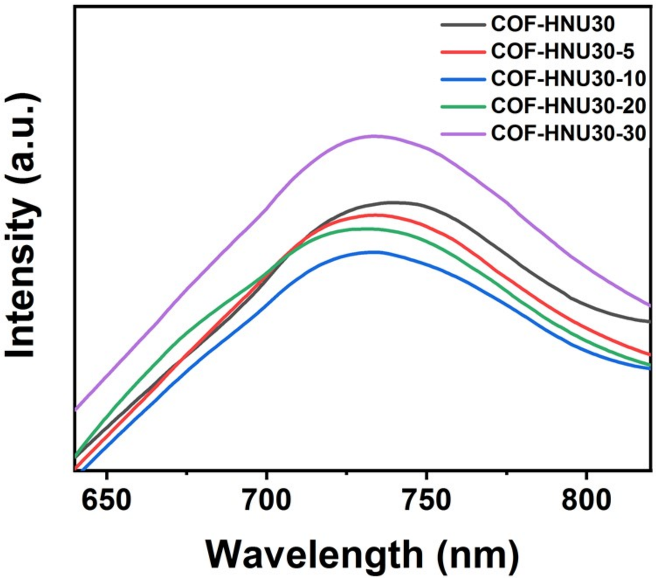


Figure S28 Photoluminescence spectra of materials with the excitation wavelength of 466 nm of COF-HNU30-*0*, COF-HNU30-*5*, COF-HNU30-*10*, COF-HNU30-*20* and COF-HNU30-*30*.

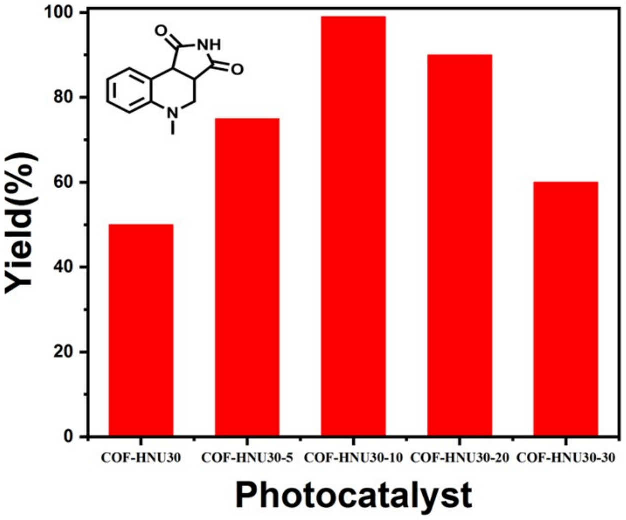


Figure S29 Yields of the Aerobic Photocatalytic Oxidative Cycloaddition by using different COF-HNU30-*x* as catalyst.

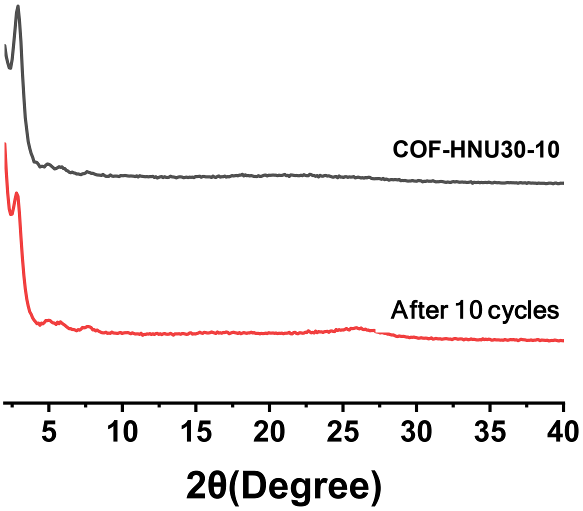


Figure S30 PXRD-patterns of COF-HNU30-*10* before and after the 10th cycles.

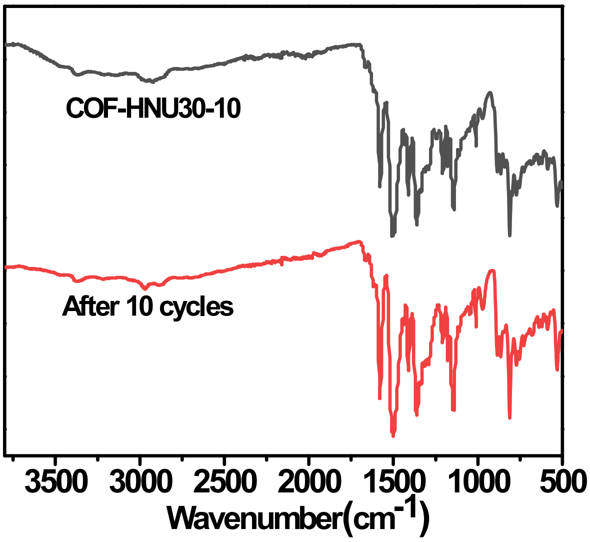


Figure S31 FT-IR of COF-HNU30-*10* before and after the 10th cycles.

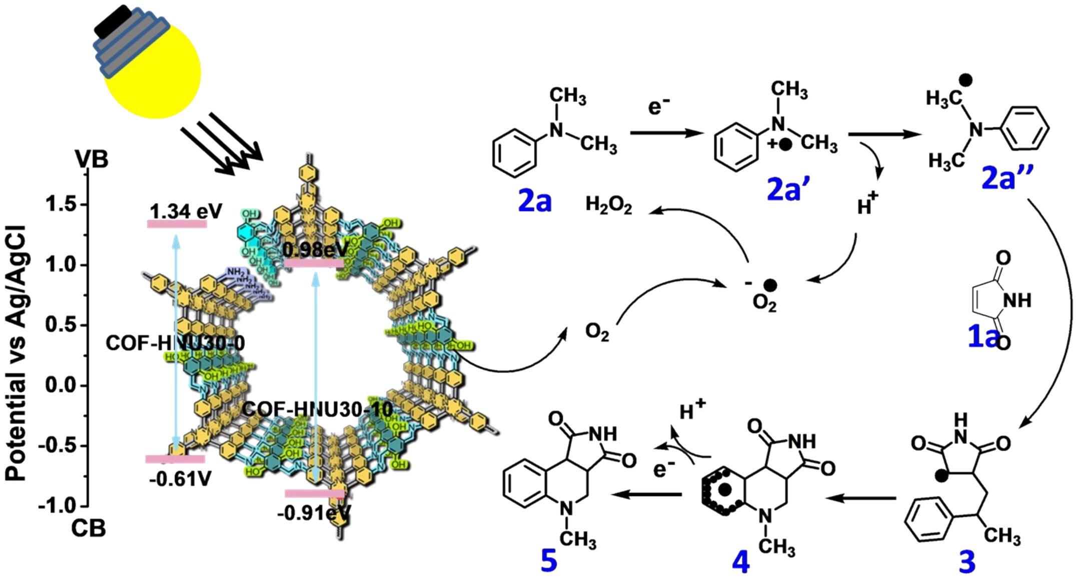
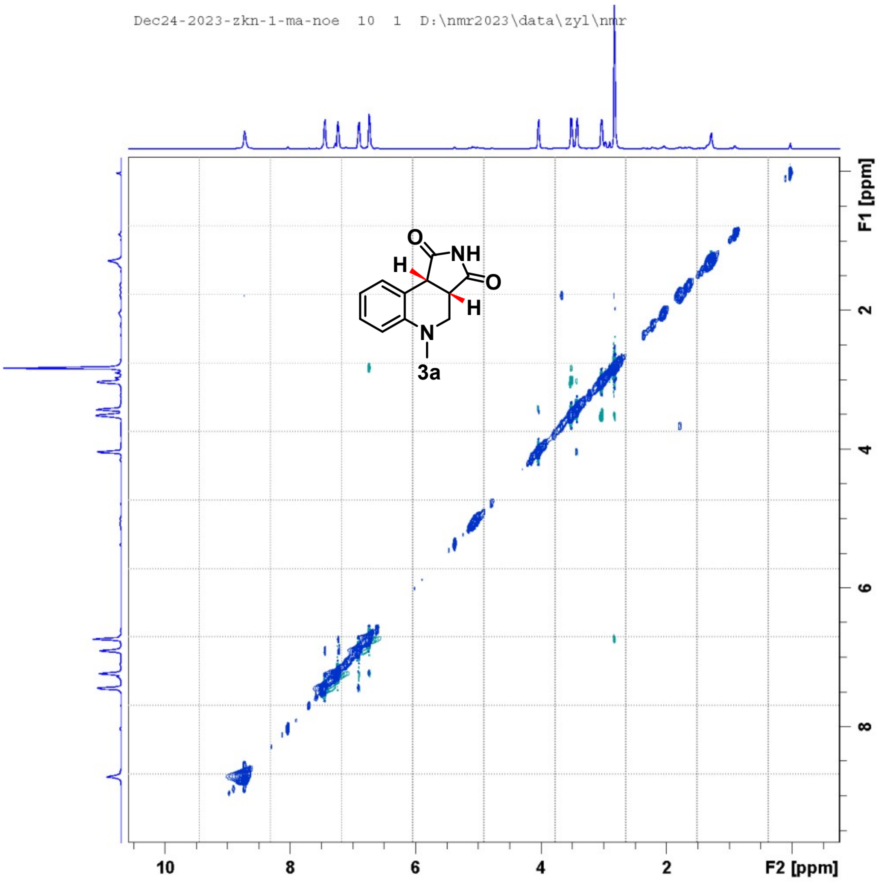
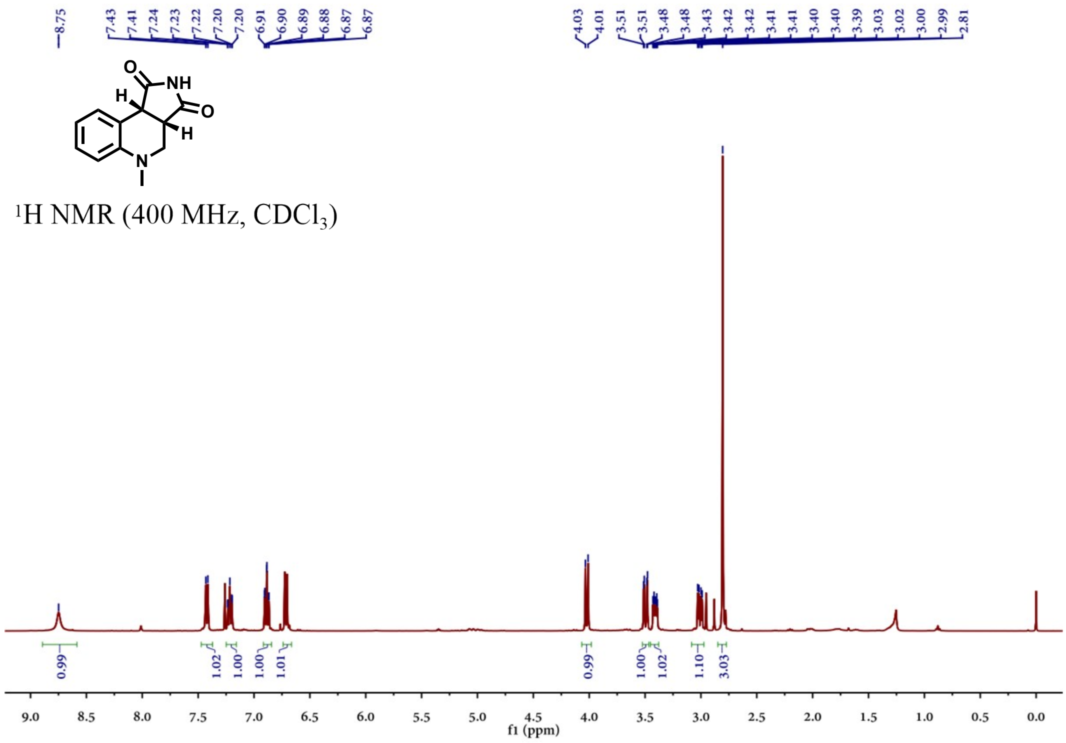


Figure 32 Possible reaction mechanism for the photocatalytic synthesis of tetrahydroquinoline over COF-HNU30-*10*.

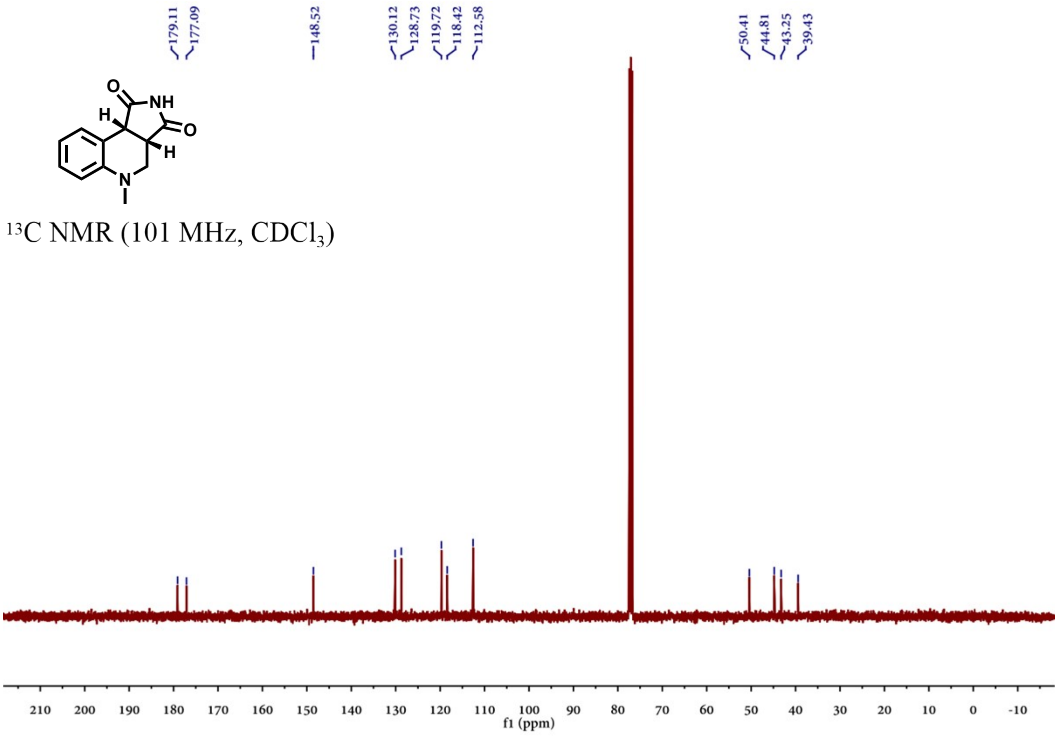
Section 3 NMR spectra of the products



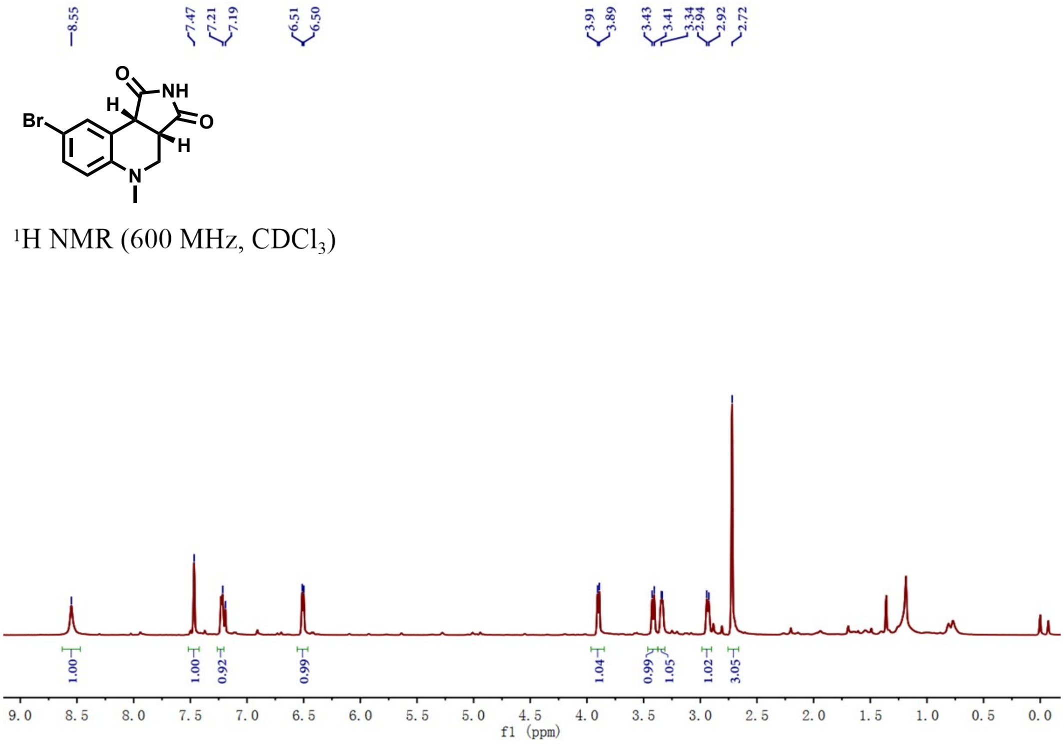
^{1}H-^{1}H NOESY of 3a,4,5,9b-Tetrahydro-5-methyl-1H-pyrrolo[3,4-c]quinoline-1,3(2H)-dione.



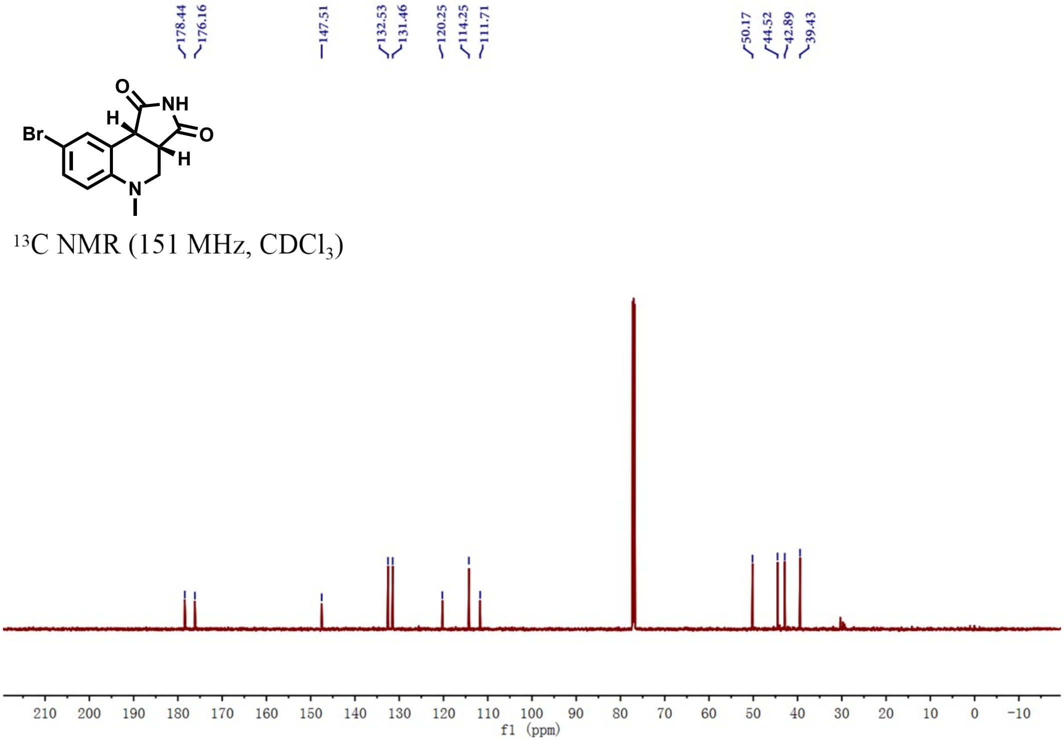
^{1}H-NMR of 3a



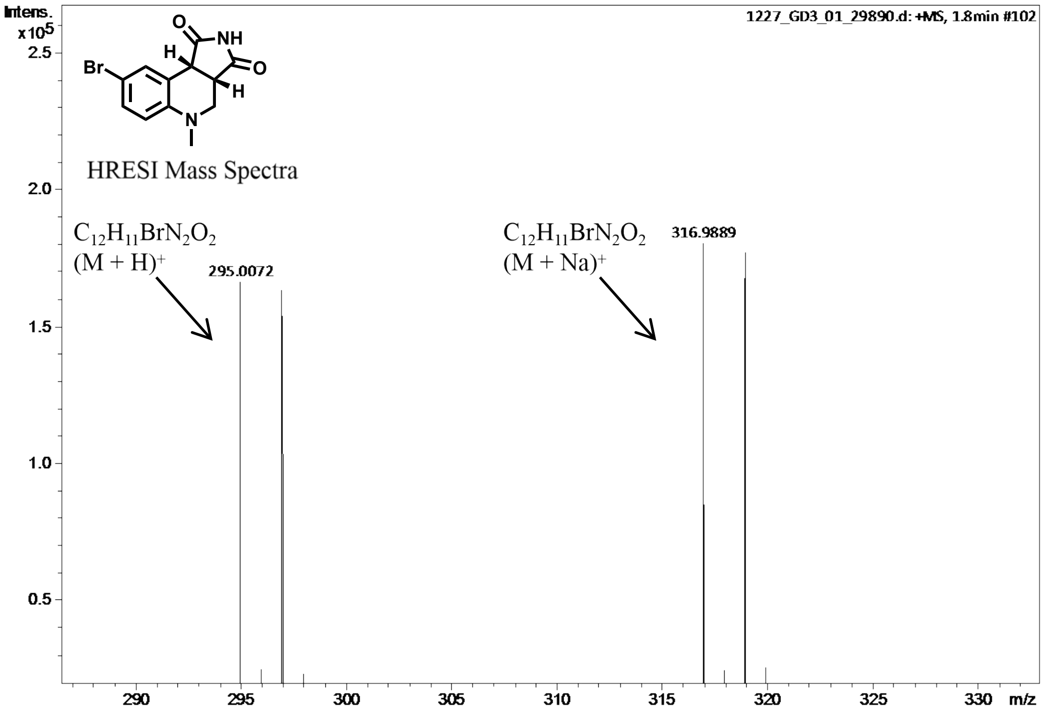
^{13}C-NMR of 3a



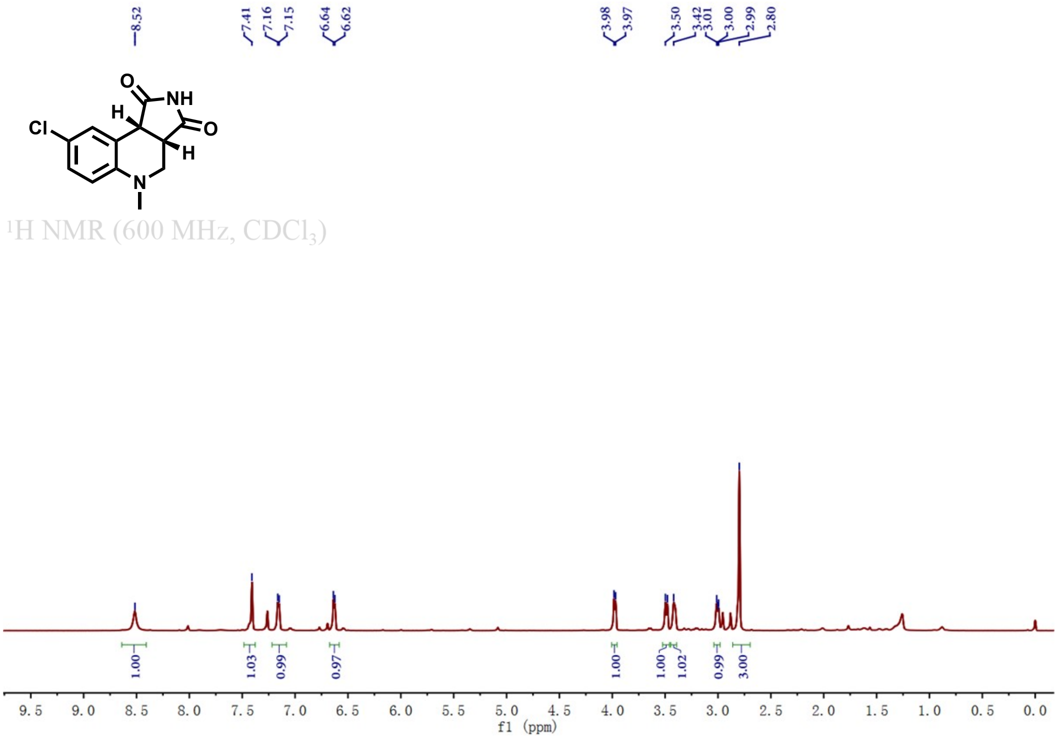
^{1}H-NMR of 3b



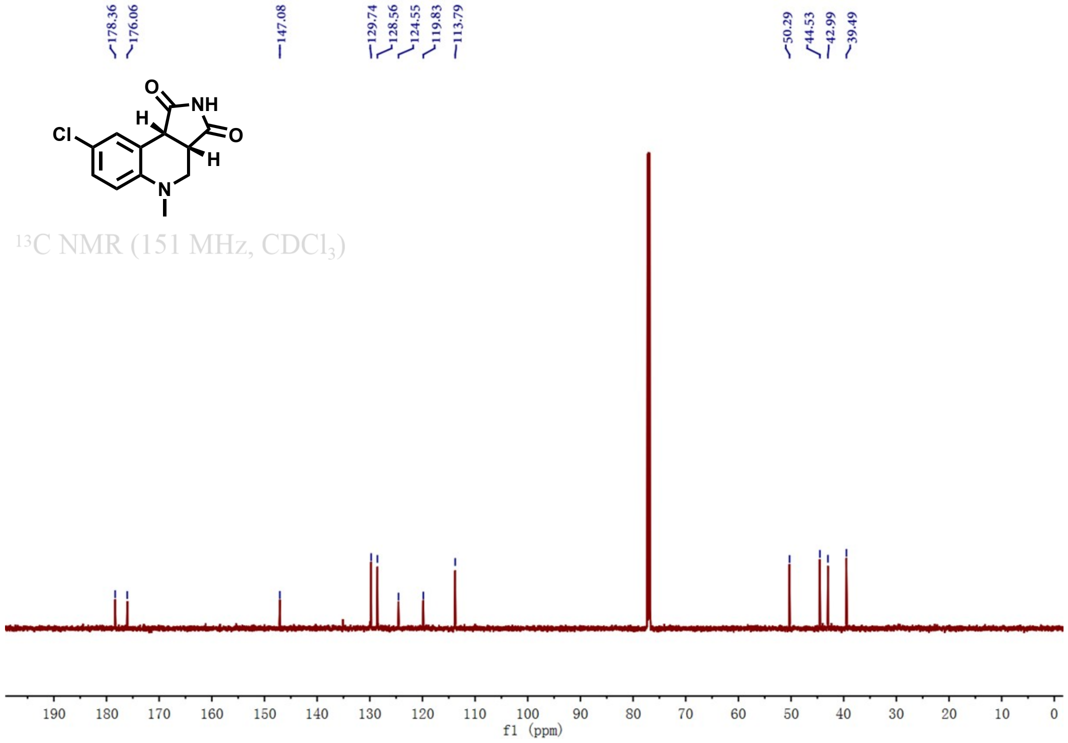
^{13}C-NMR of 3b



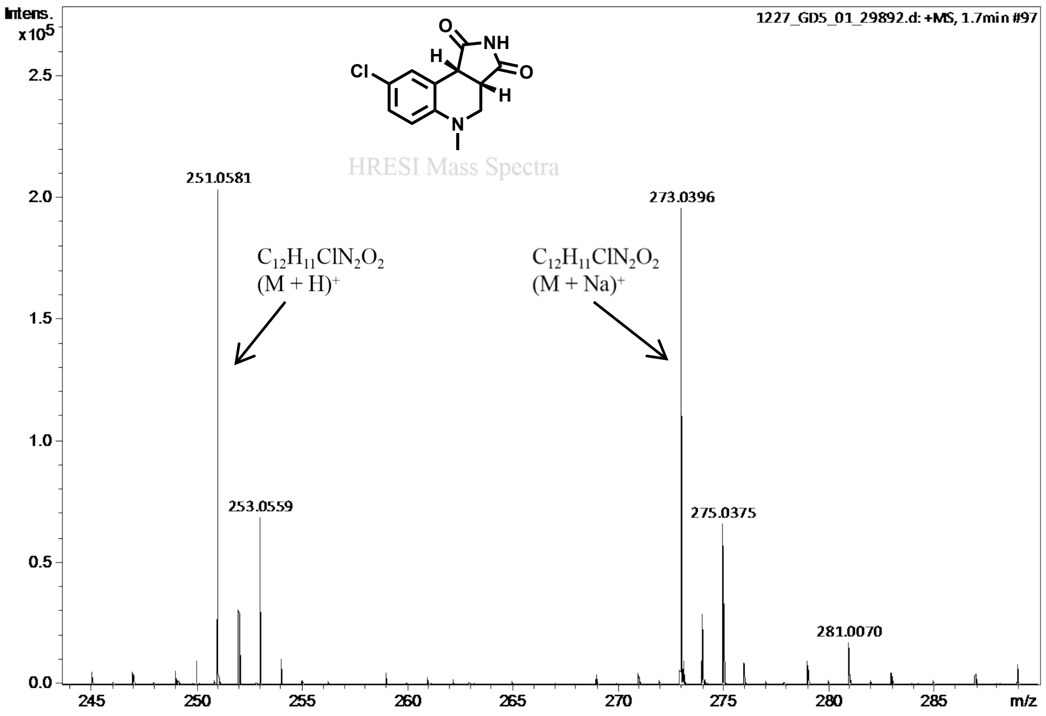
HRESI-MS of 3b



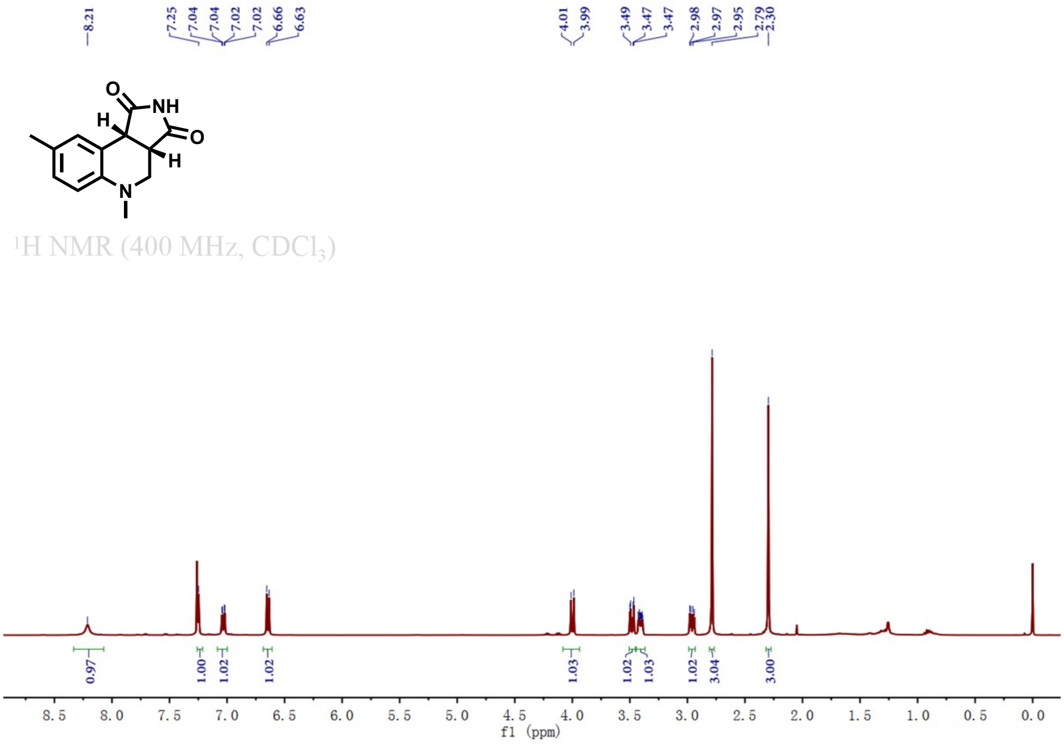
^{1}H-NMR of 3c



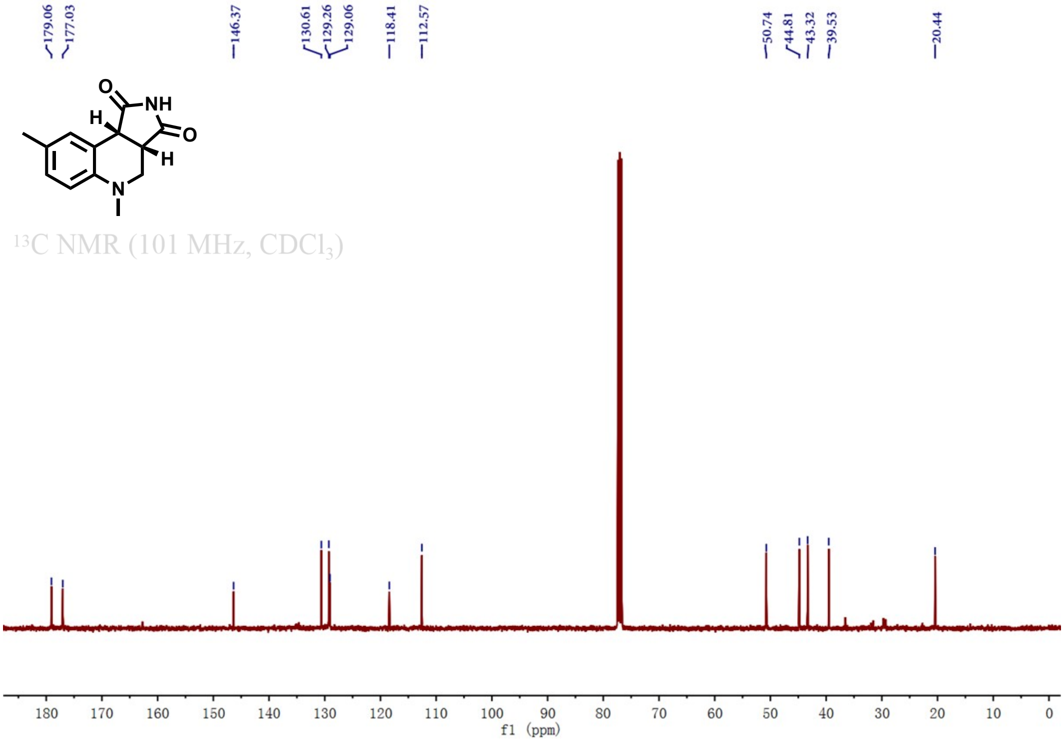
^{13}C-NMR of 3c



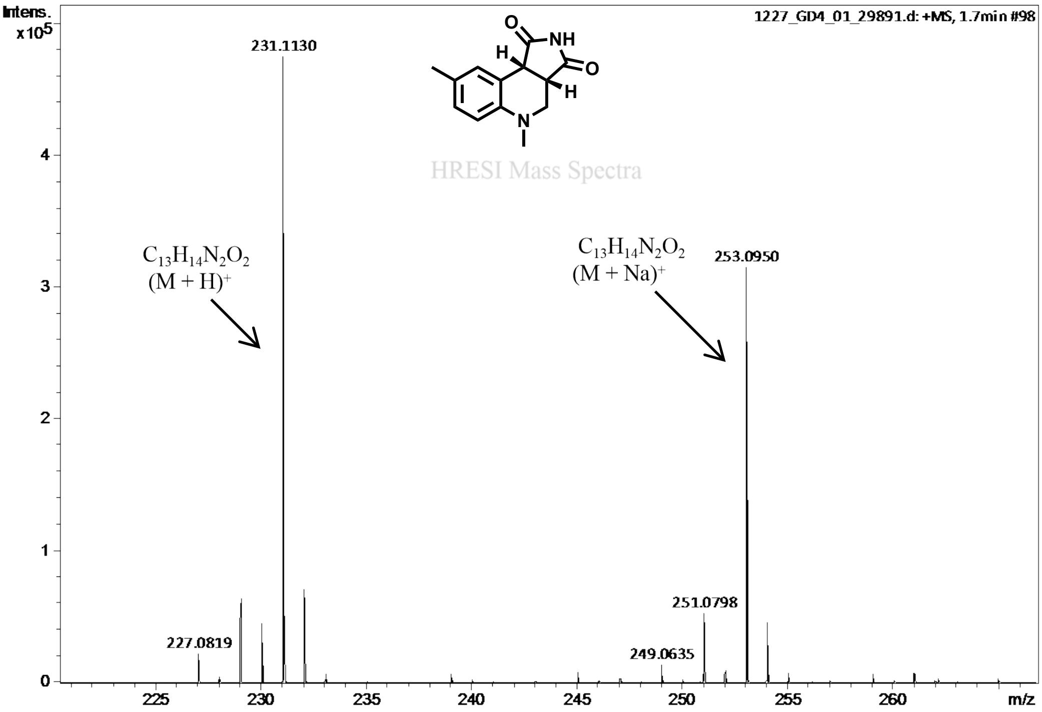
HRESI-MS of 3c



^{1}H-NMR of 3d



^{13}C-NMR of 3d



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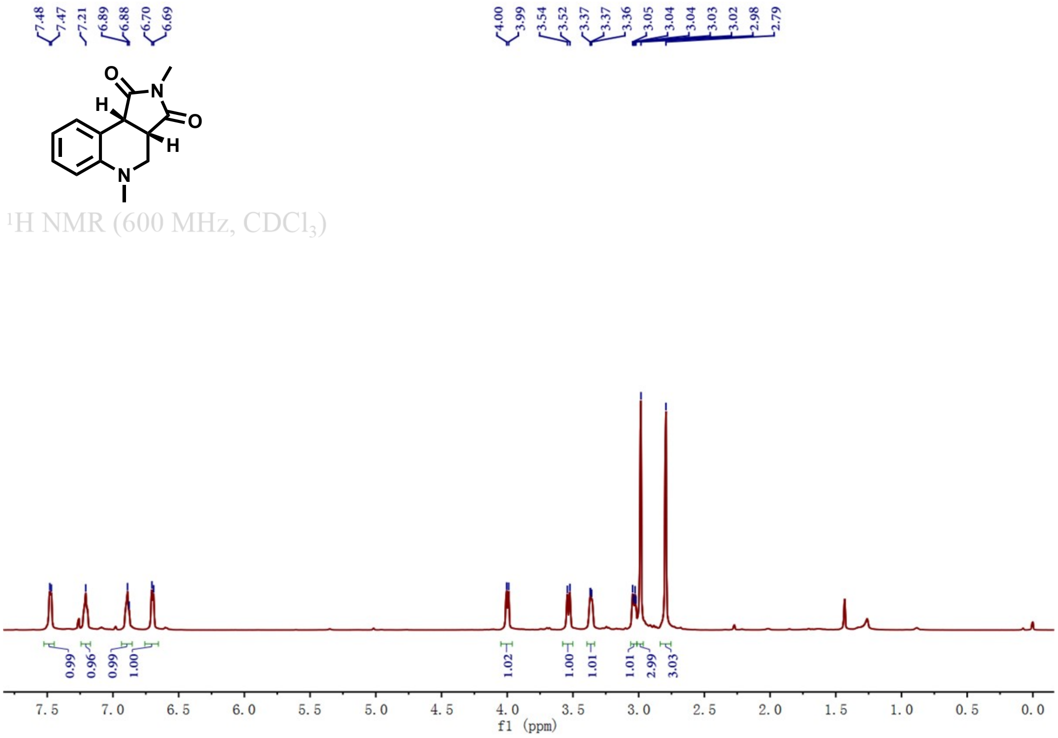
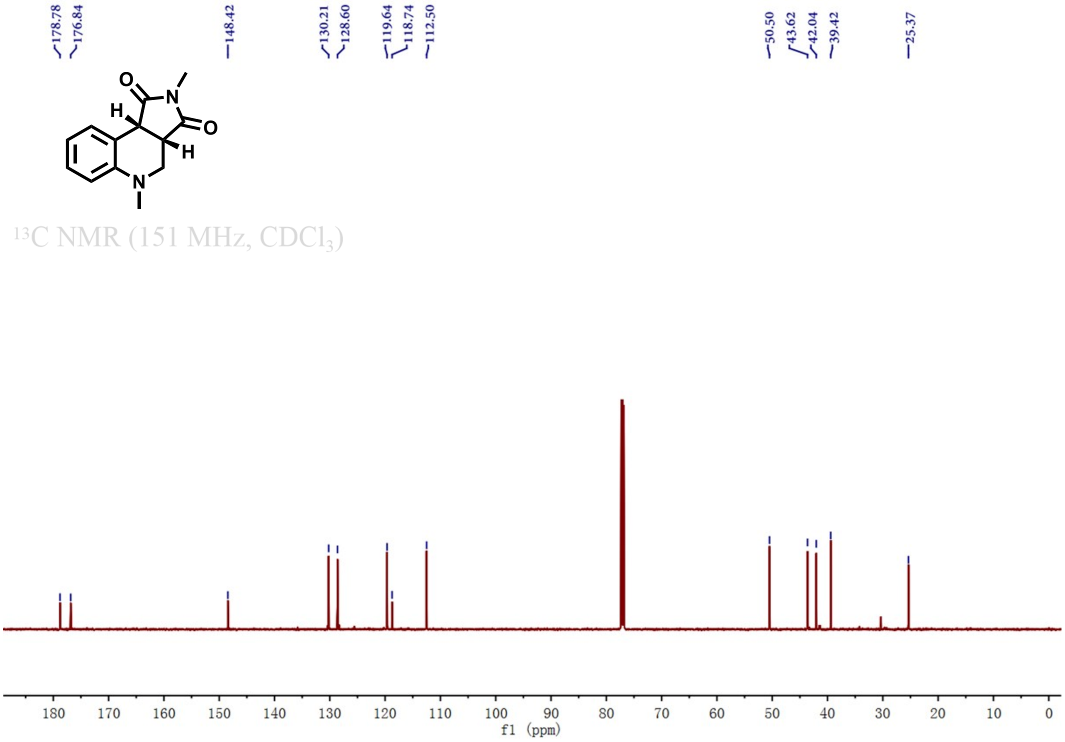
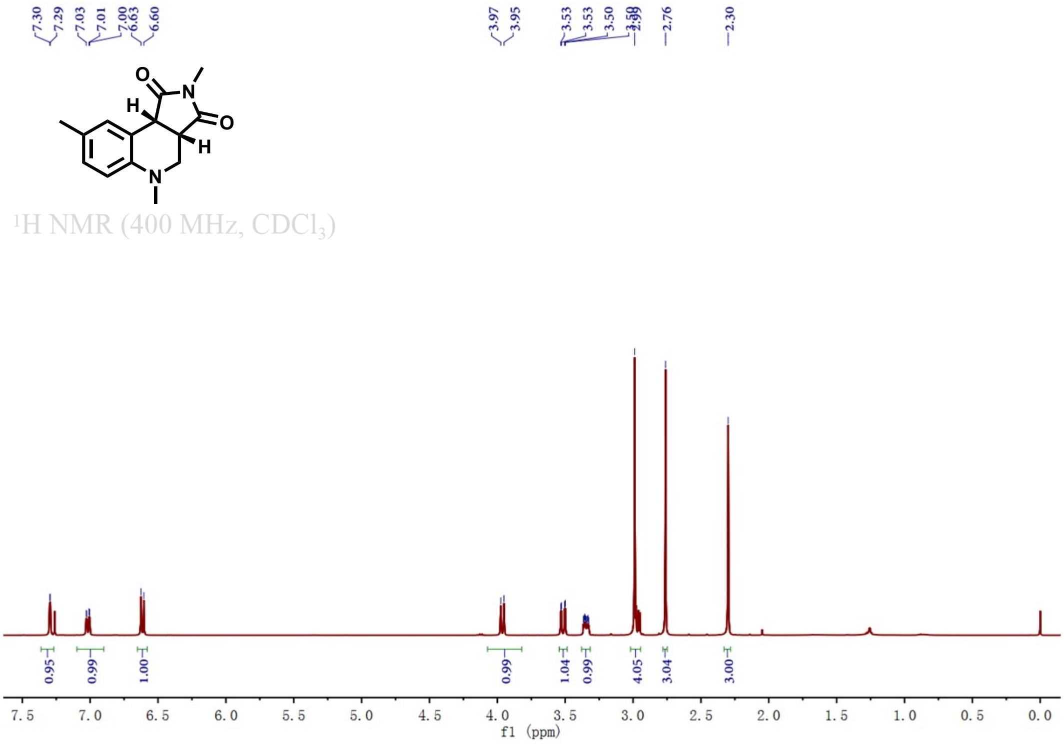


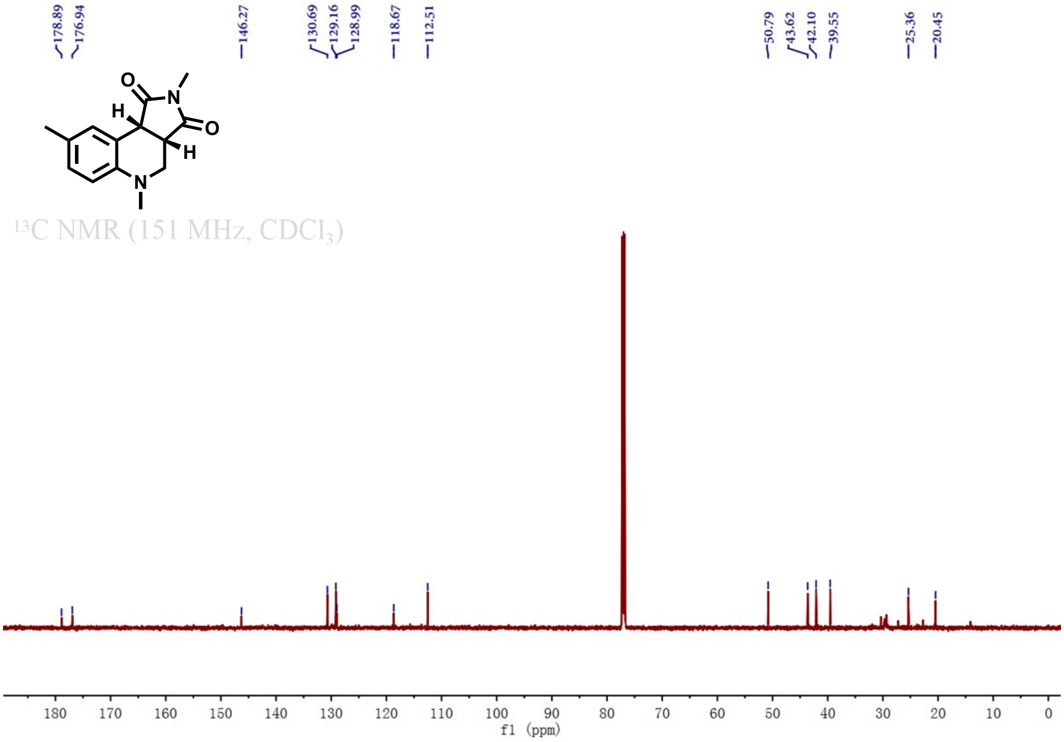
^{1}H-NMR of 3e



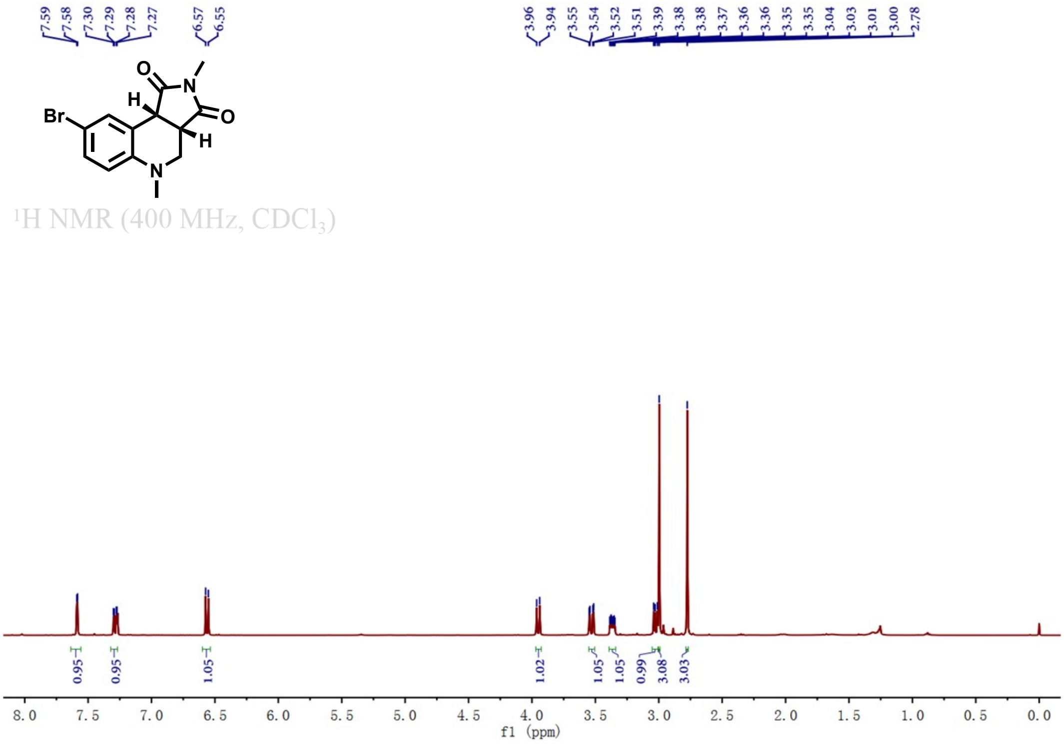
^{13}C-NMR of 3e



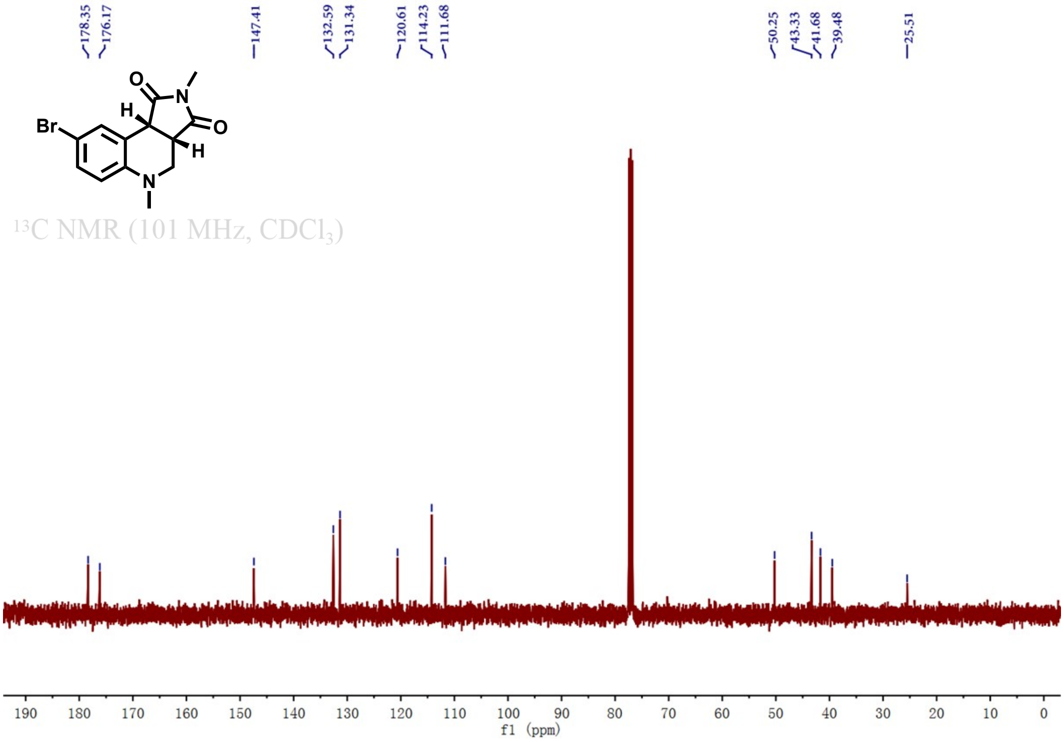
^{1}H-NMR of 3f



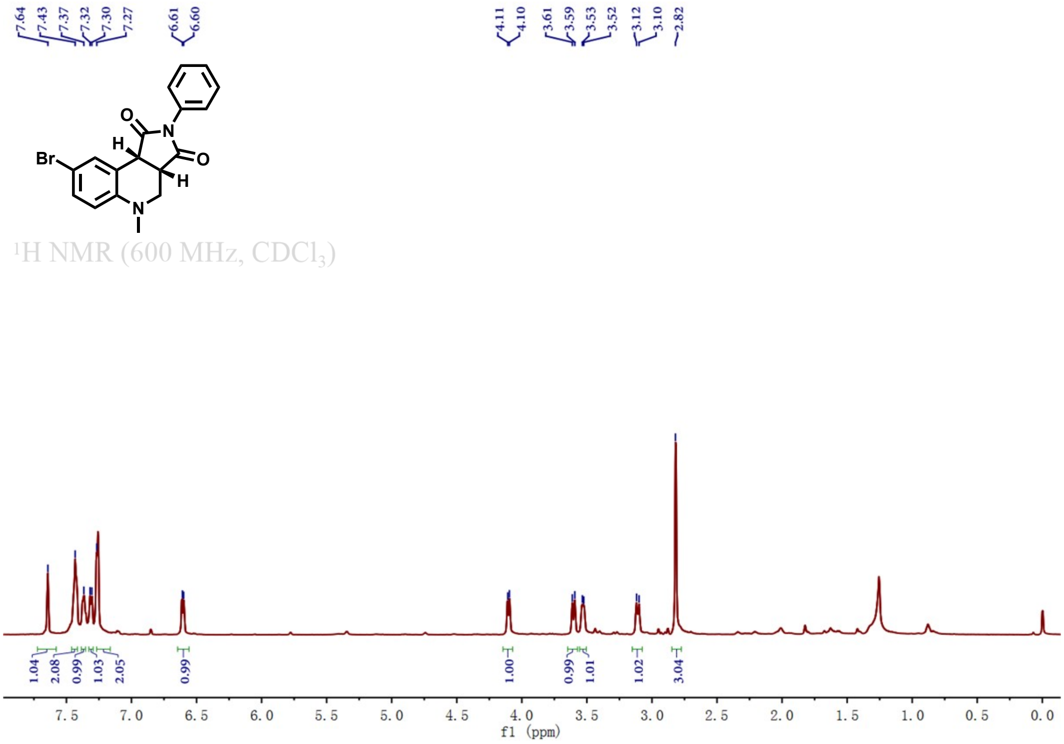
^{13}C-NMR of 3f



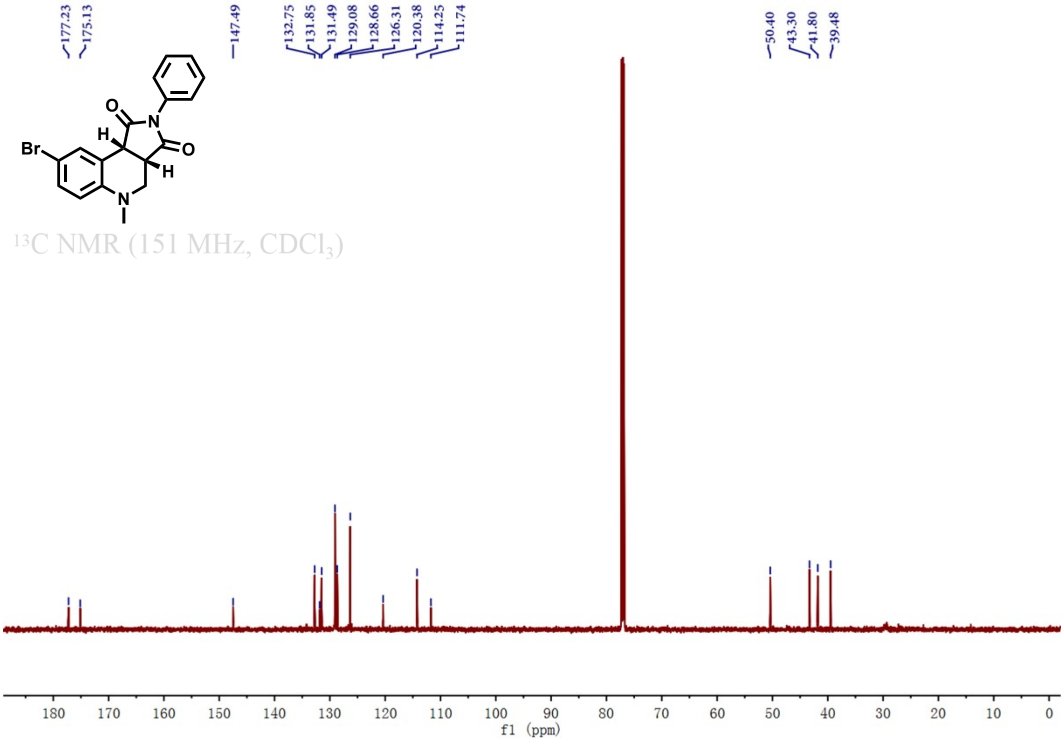
^{1}H-NMR of 3g



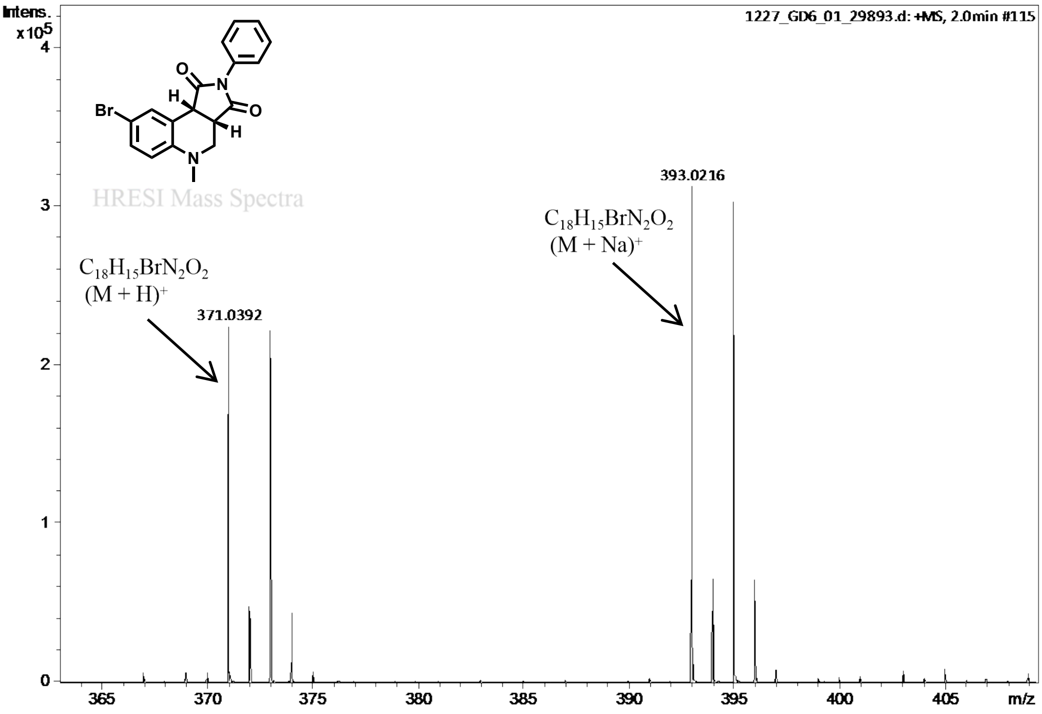
^{13}C-NMR of 3g



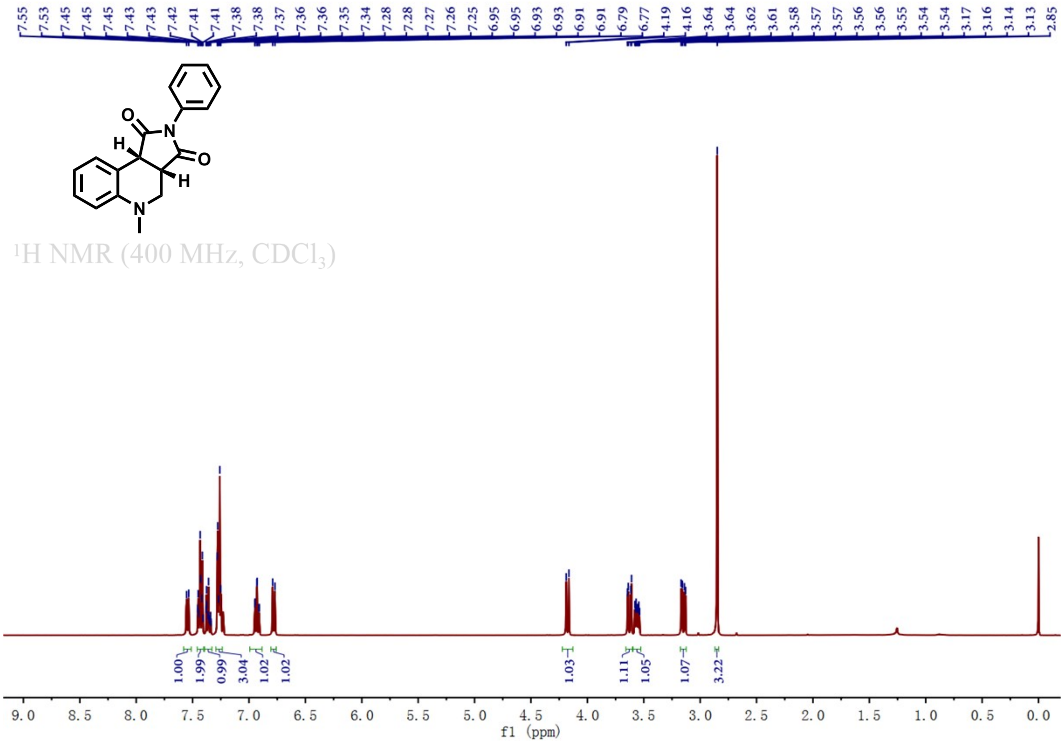
^{1}H-NMR of 3h



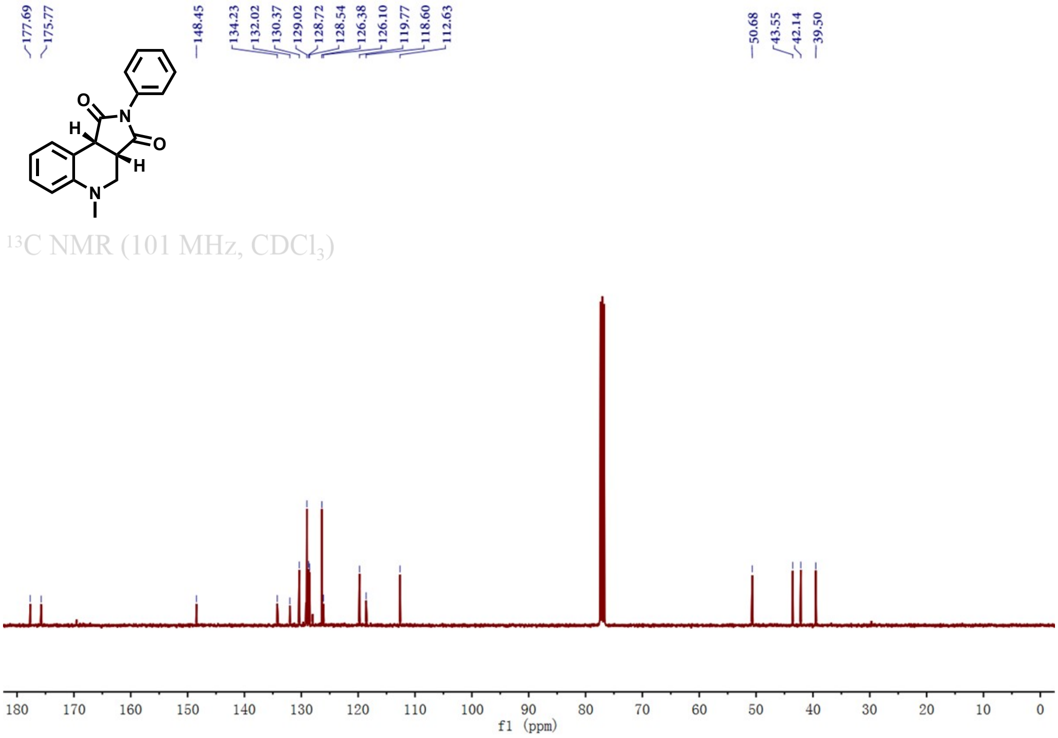
^{13}C-NMR of 3h



HRESI-MS of 3h



^{1}H-NMR of 3i



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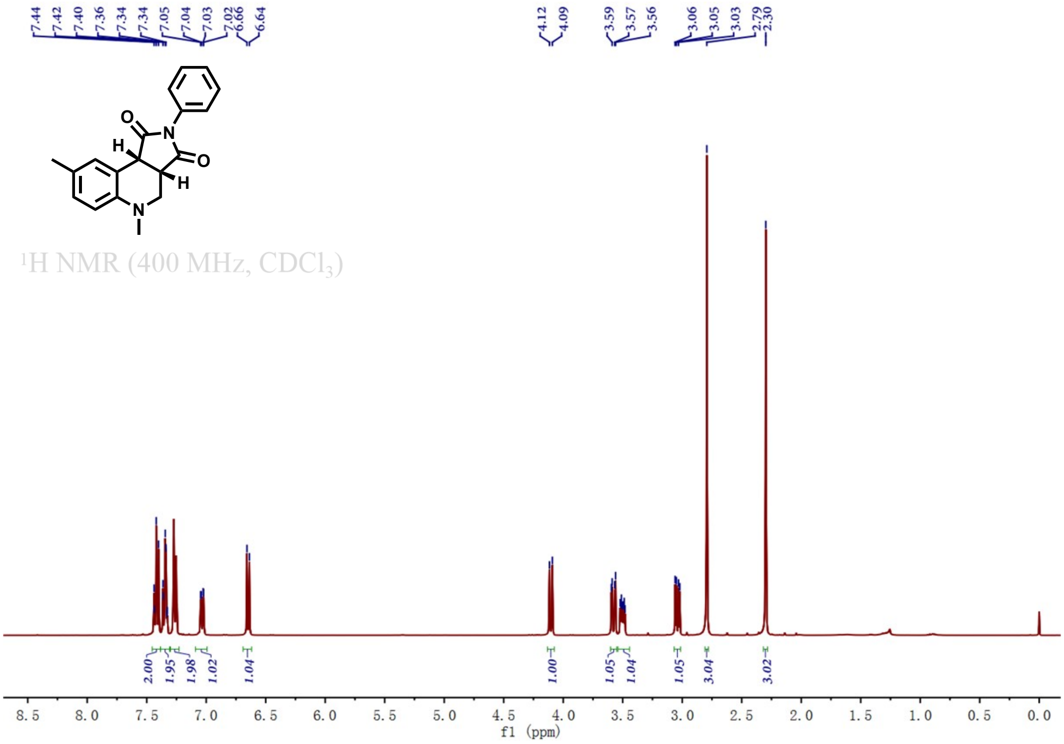

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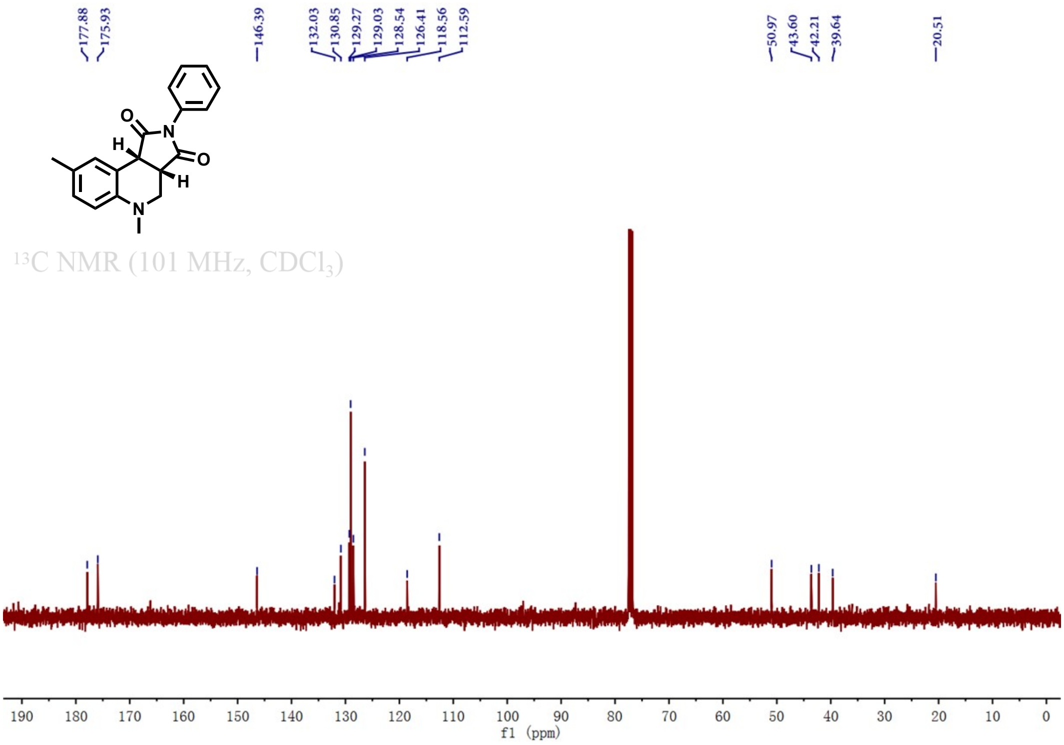
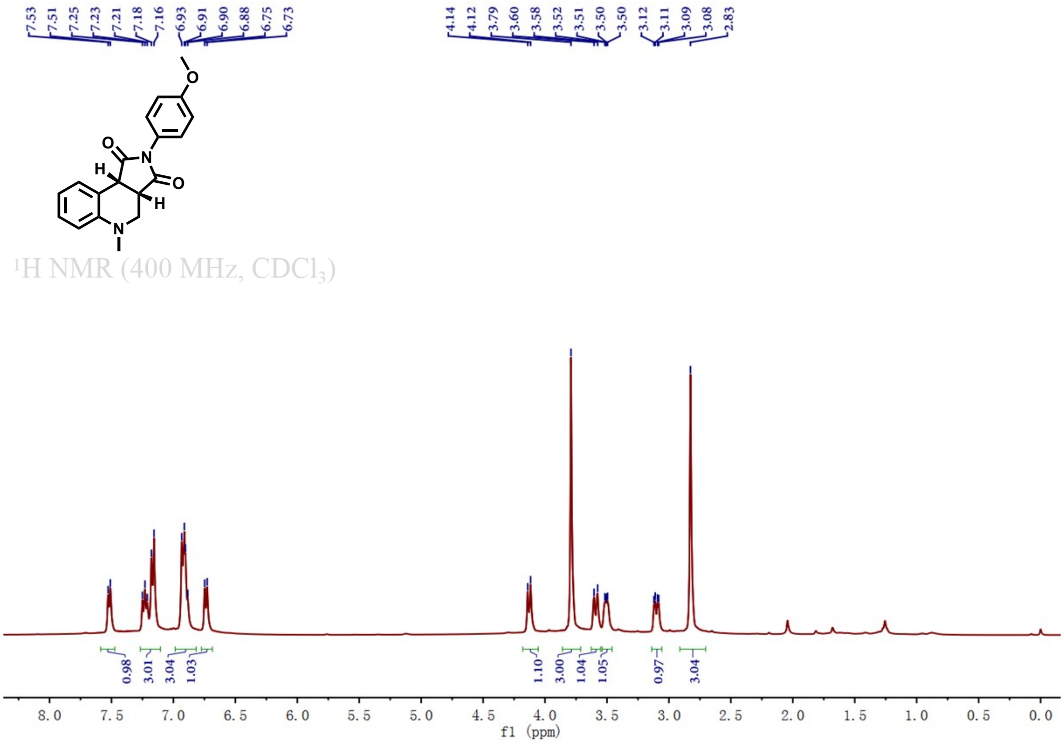
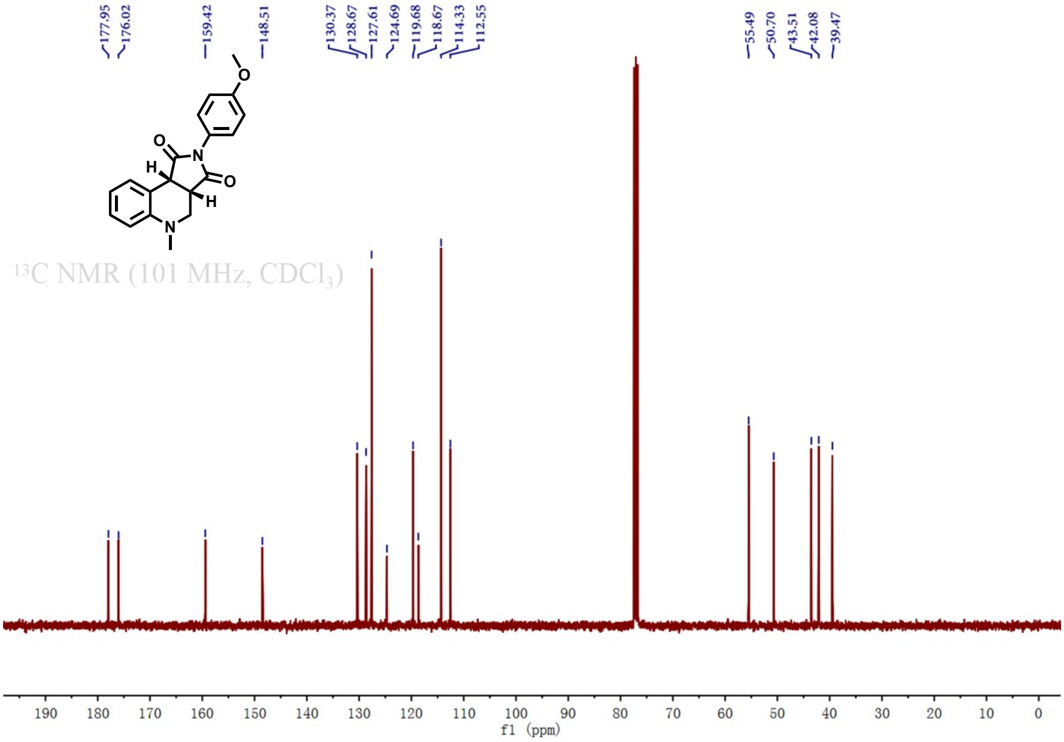


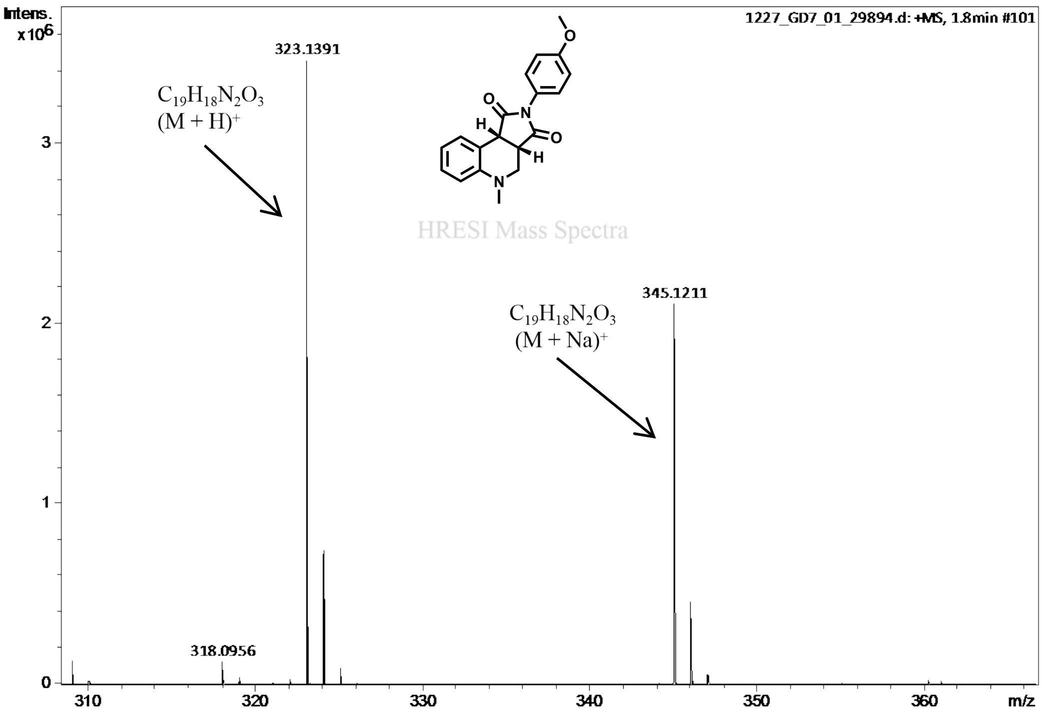
^{13}C-NMR of 3j



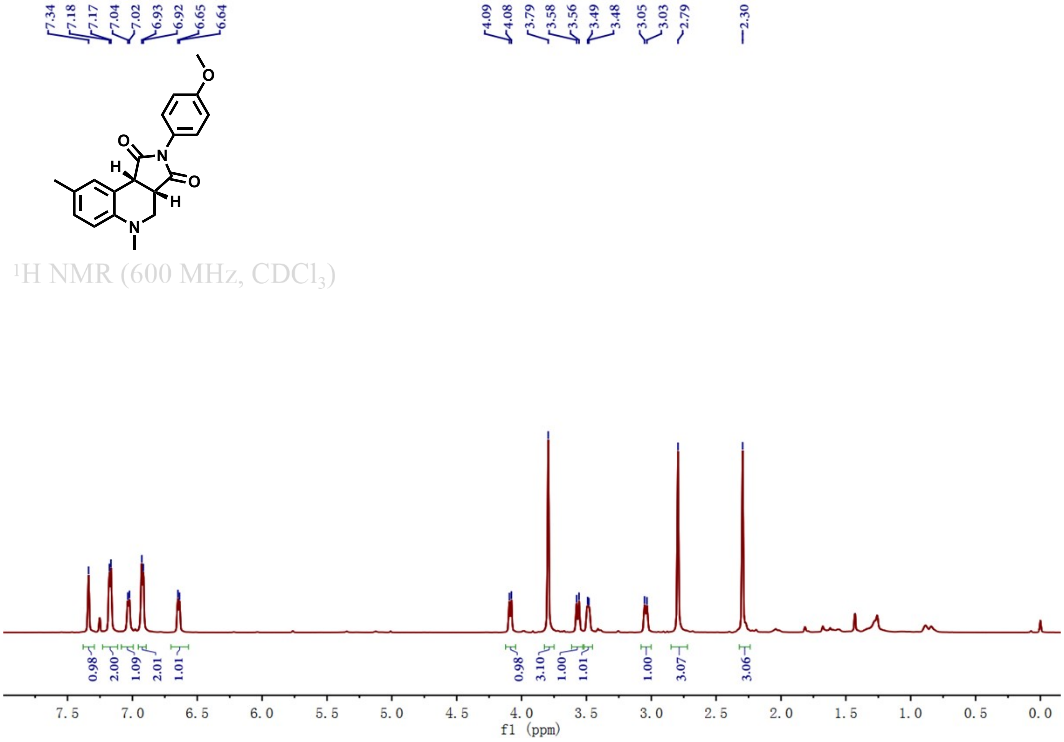
^{1}H-NMR of 3k



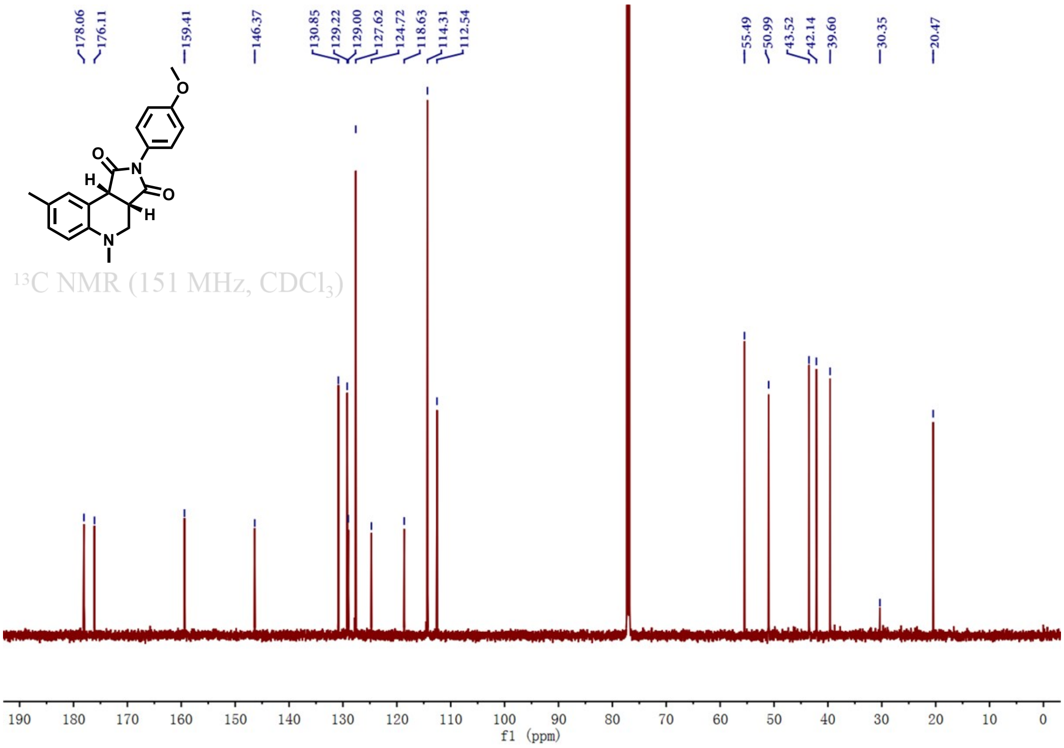
^{13}C-NMR of 3k



HRESI-MS of 3k



^{1}H-NMR of 3l



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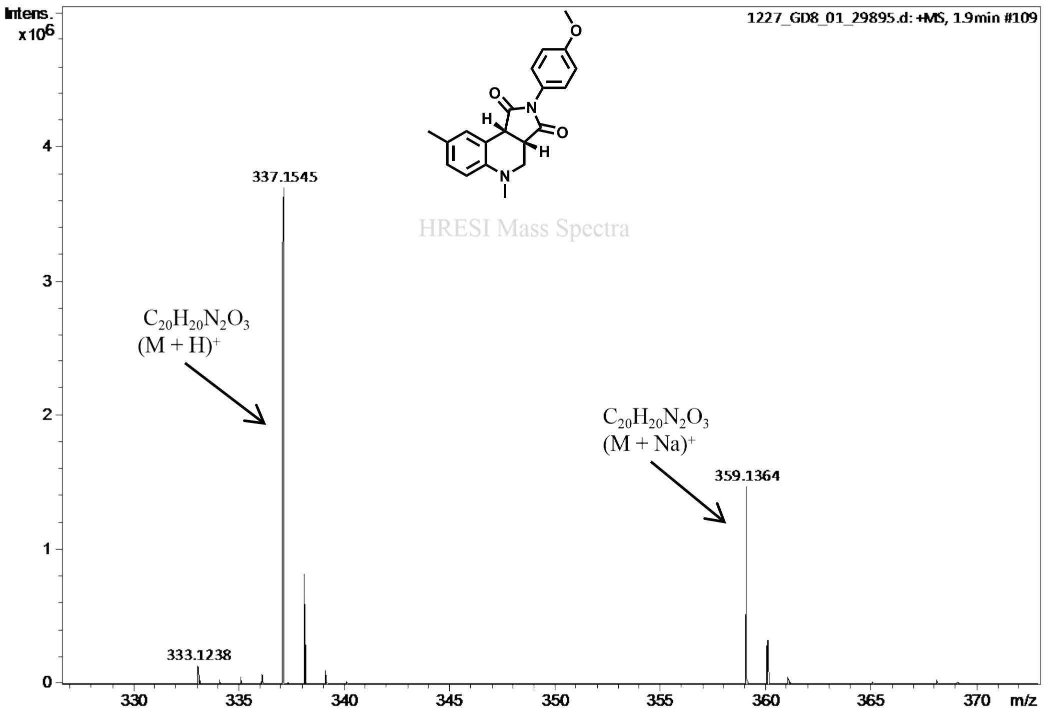
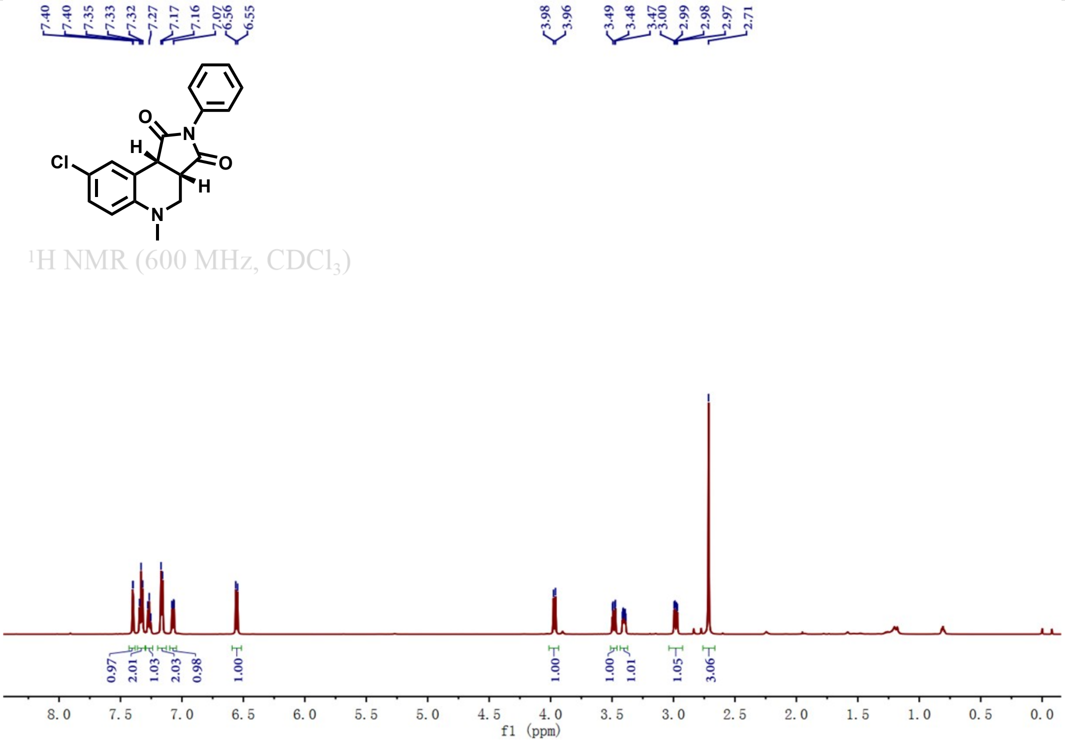
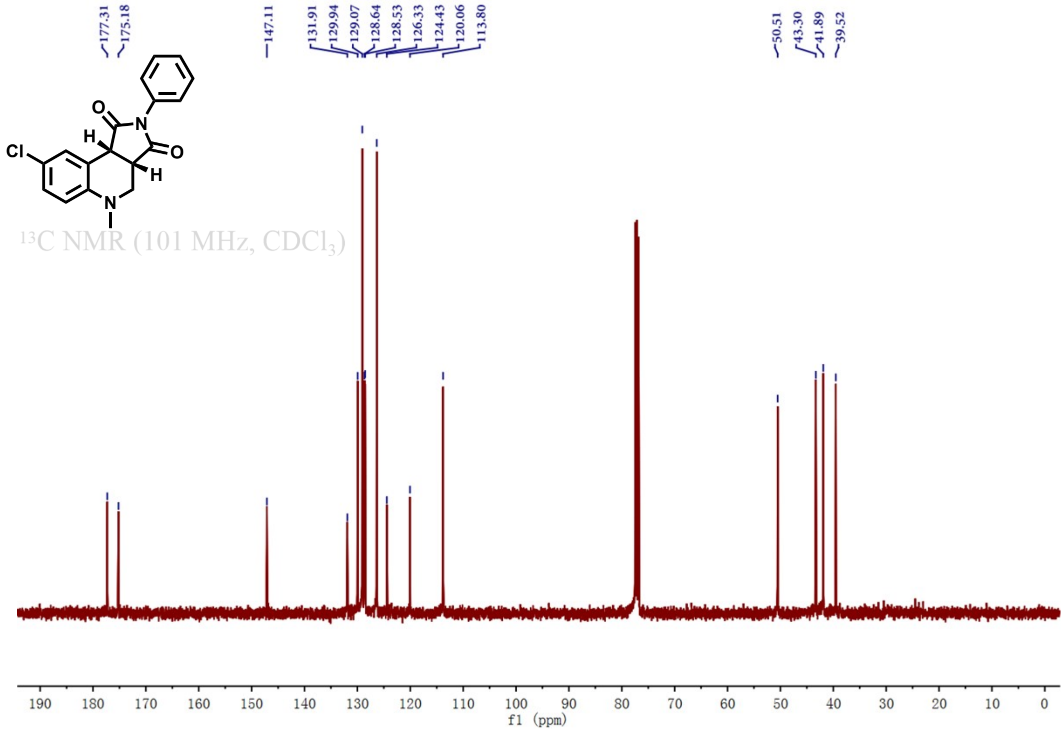


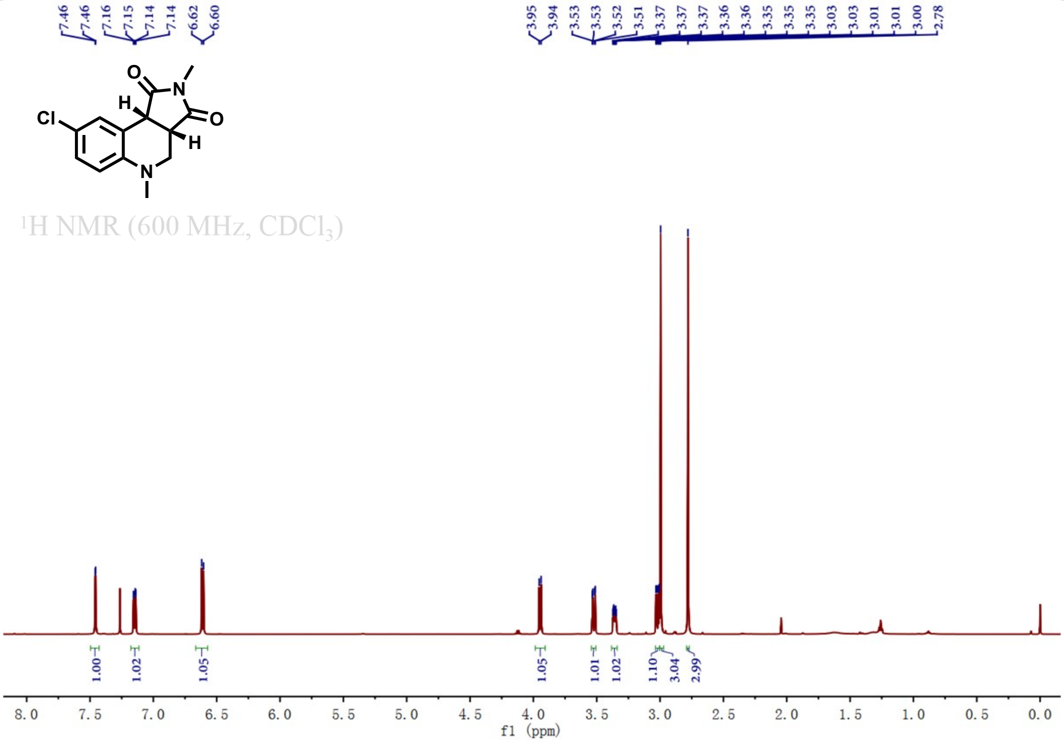
HRESI-MS of 3l



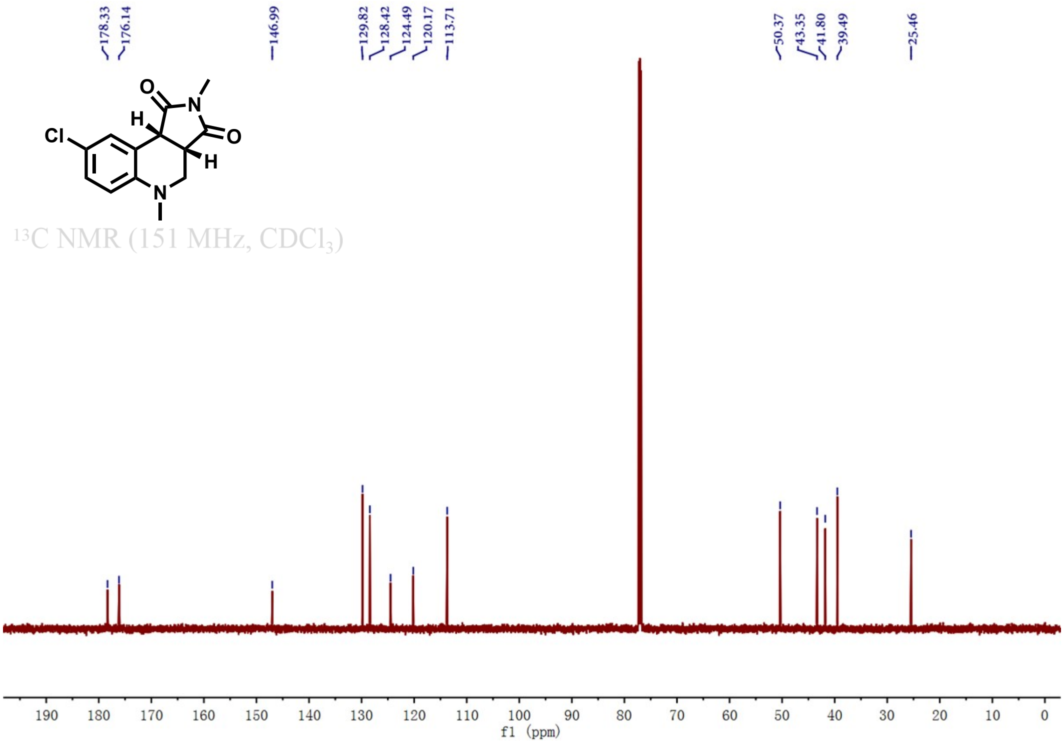
^{1}H-NMR of 3m



^{13}C-NMR of 3m



^{1}H-NMR of 3n



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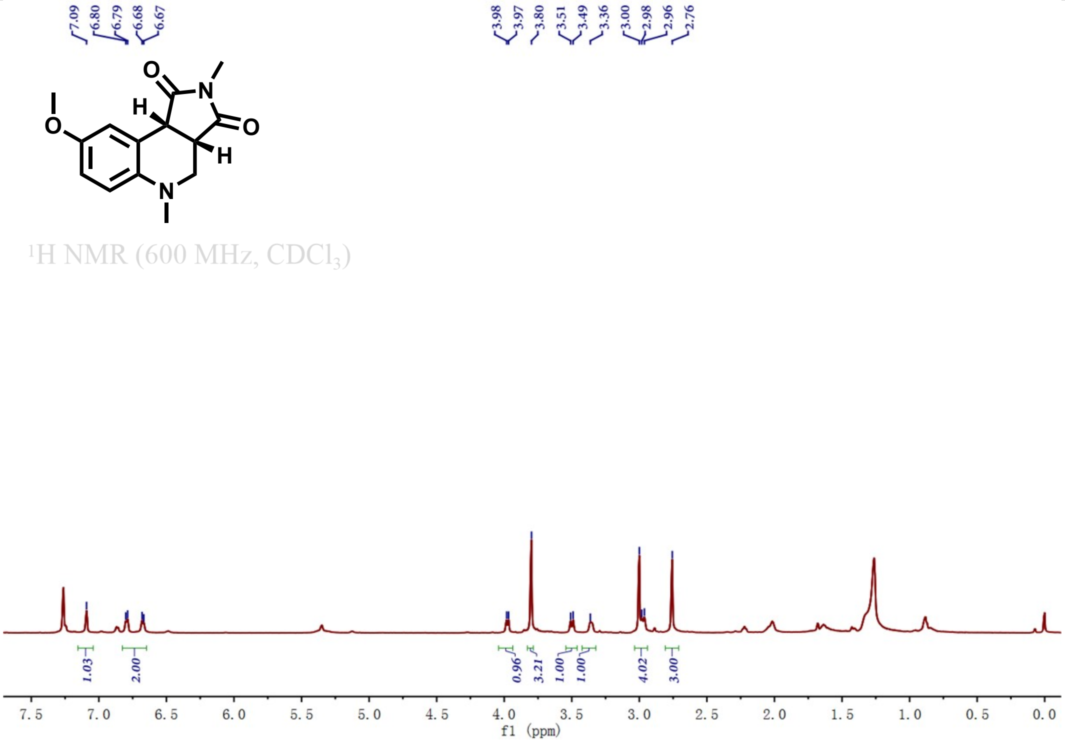
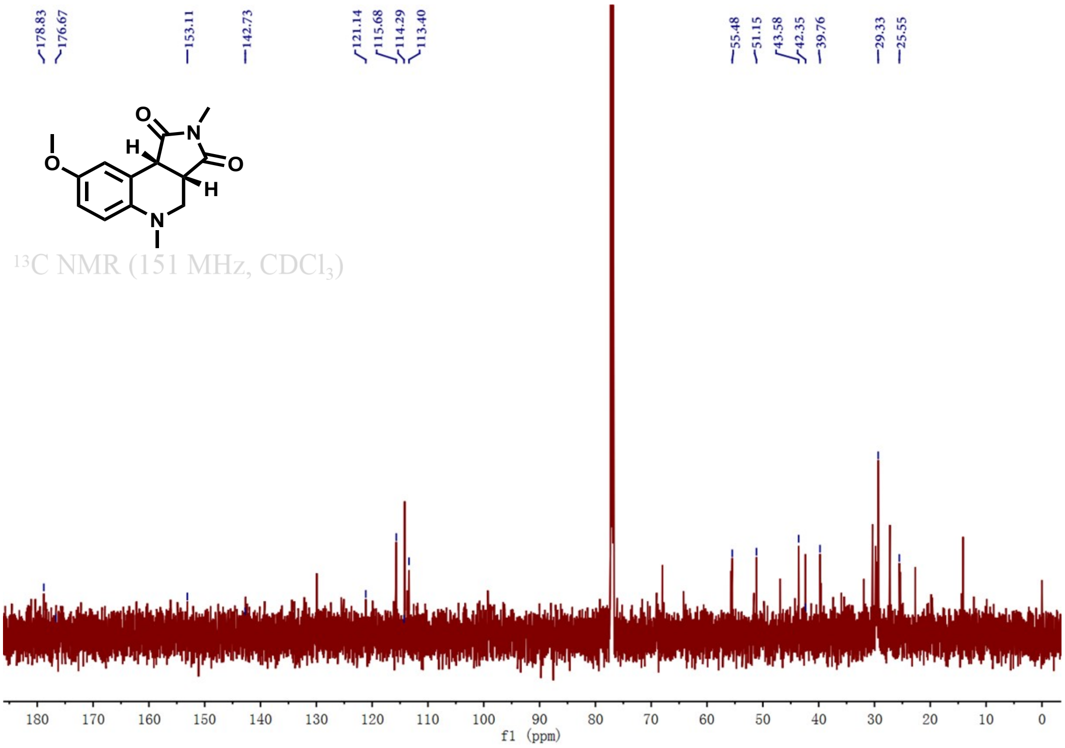
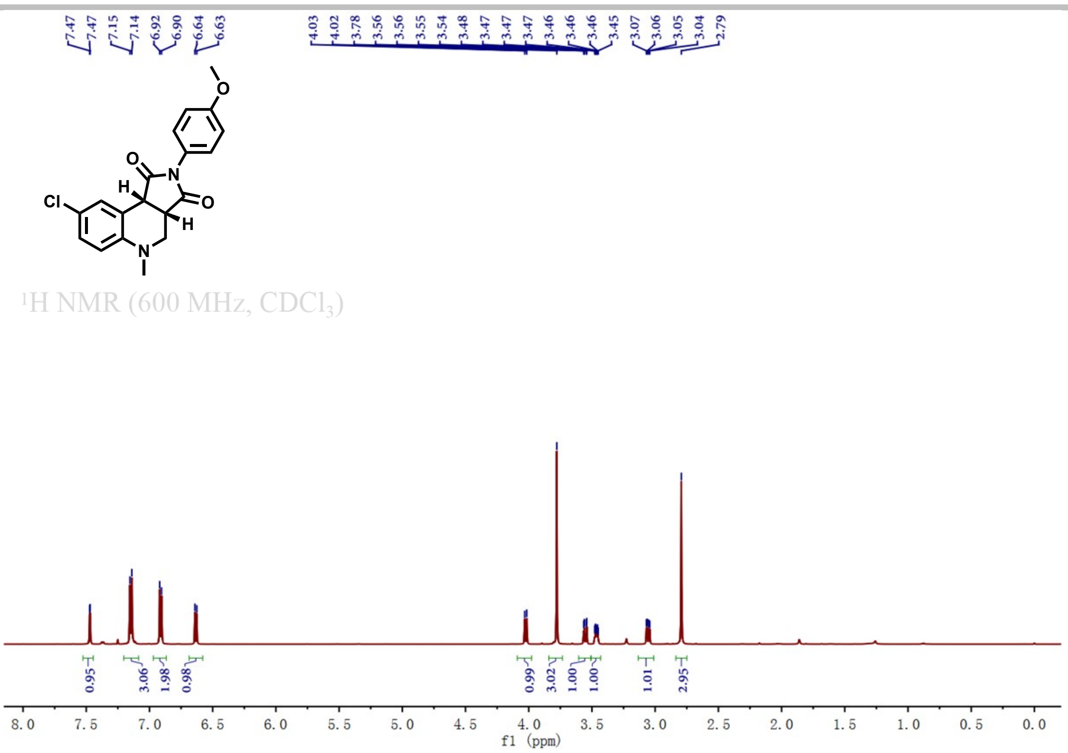


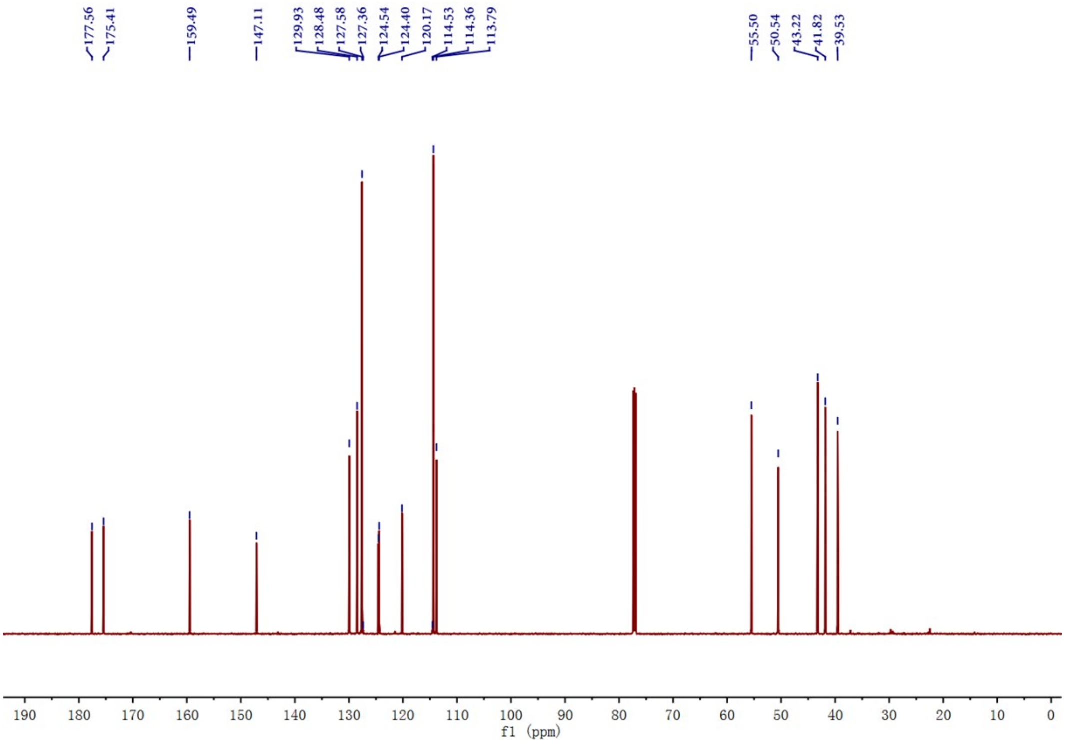
^{1}H-NMR of 3o



^{13}C-NMR of 3o



^{1}H-NMR of 3p



^{13}C-NMR of 3p