Supporting Information

Metal-free Polymeric and Molecular Disorder/Order Semiconductor Heterojunction for Visible-light Photocatalytic Minisci-Type Reaction

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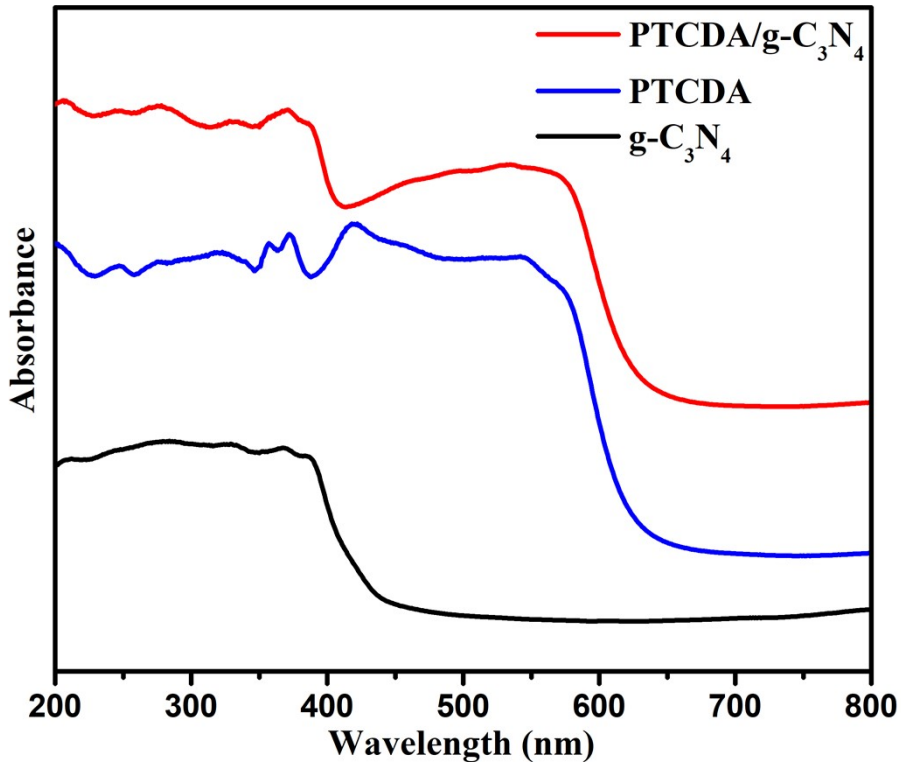


Figure S1. UV-Vis DRS spectrum of PTCDA, g-C_3N_4, and PTCDA/g-C_3N_4.

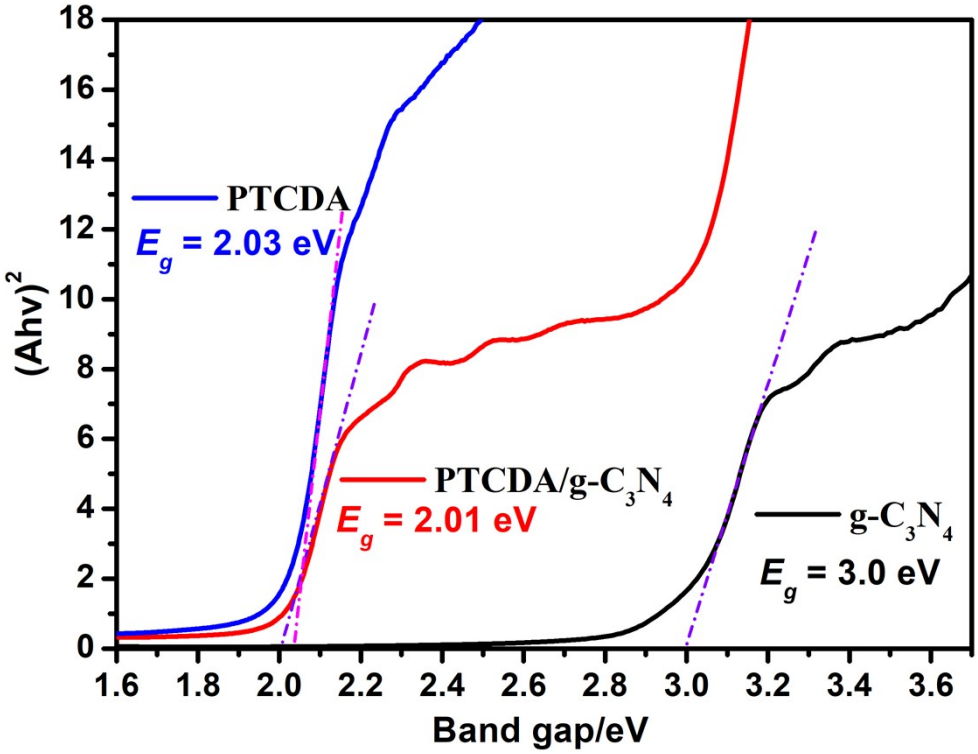


Figure S2. Tauc plot of the UV-Vis DRS spectrum of PTCDA, g-C_3N_4 and PTCDA/g-C_3N_4.

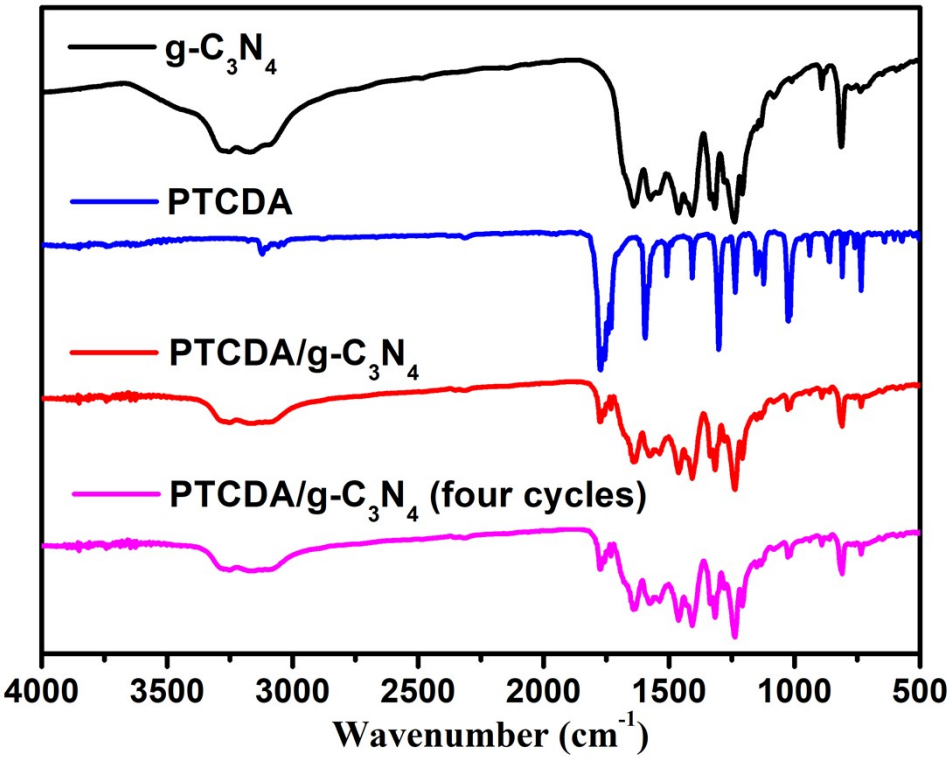


Figure S3. IR spectra of the g-C_3N_4 (black), PTCDA (blue), and as-prepared PTCDA/ g-C_3N_4 (red).

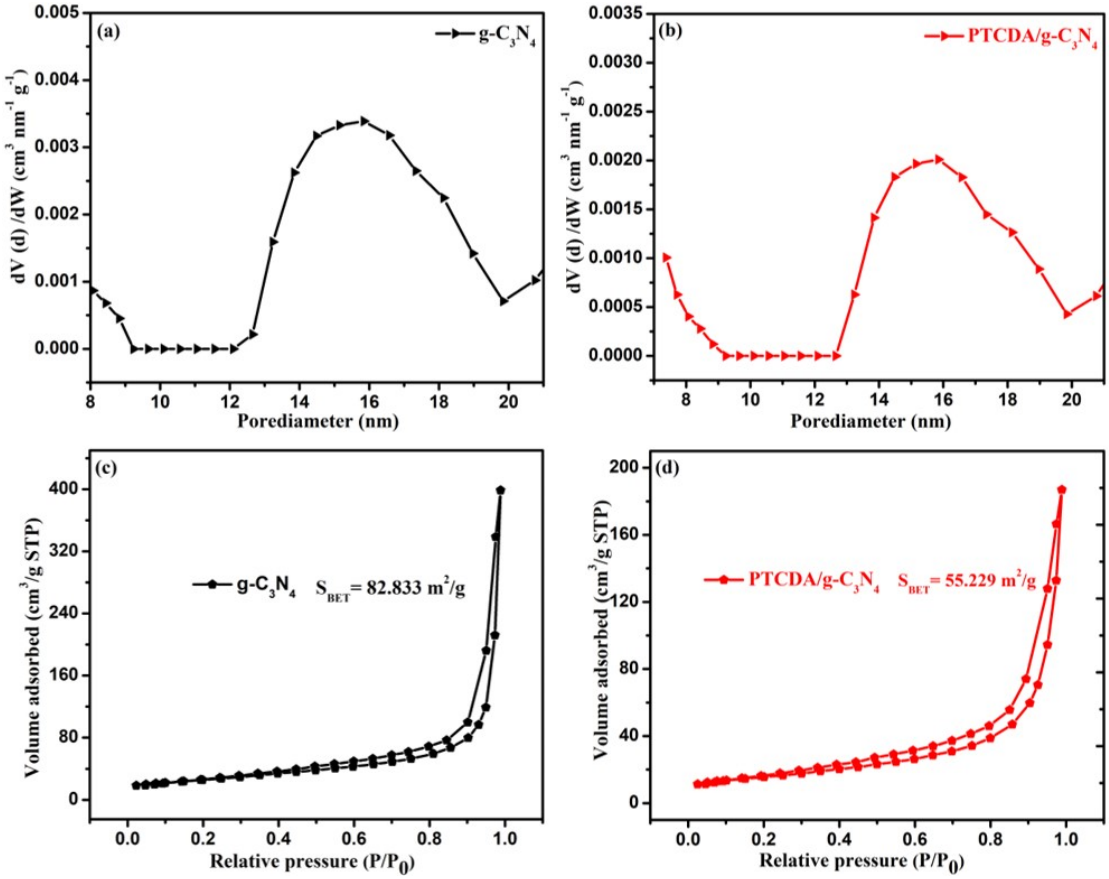


Figure S4. Specific surface area (SSA) and BJH pore size distributions for g-C_3N_4 and PTCDA/g-C_3N_4. (a) and (b) pore size distribution and pore volume analyzed according to Barret-Joyner-Halenda (BJH) method for g-C_3N_4 and PTCDA/g-C_3N_4. N_2 adsorption/desorption isotherms: (c) the SSA of g-C_3N_4 is 82.833 m^2/g, and (d) PTCDA/g-C_3N_4 is 55.229 m^2/g.

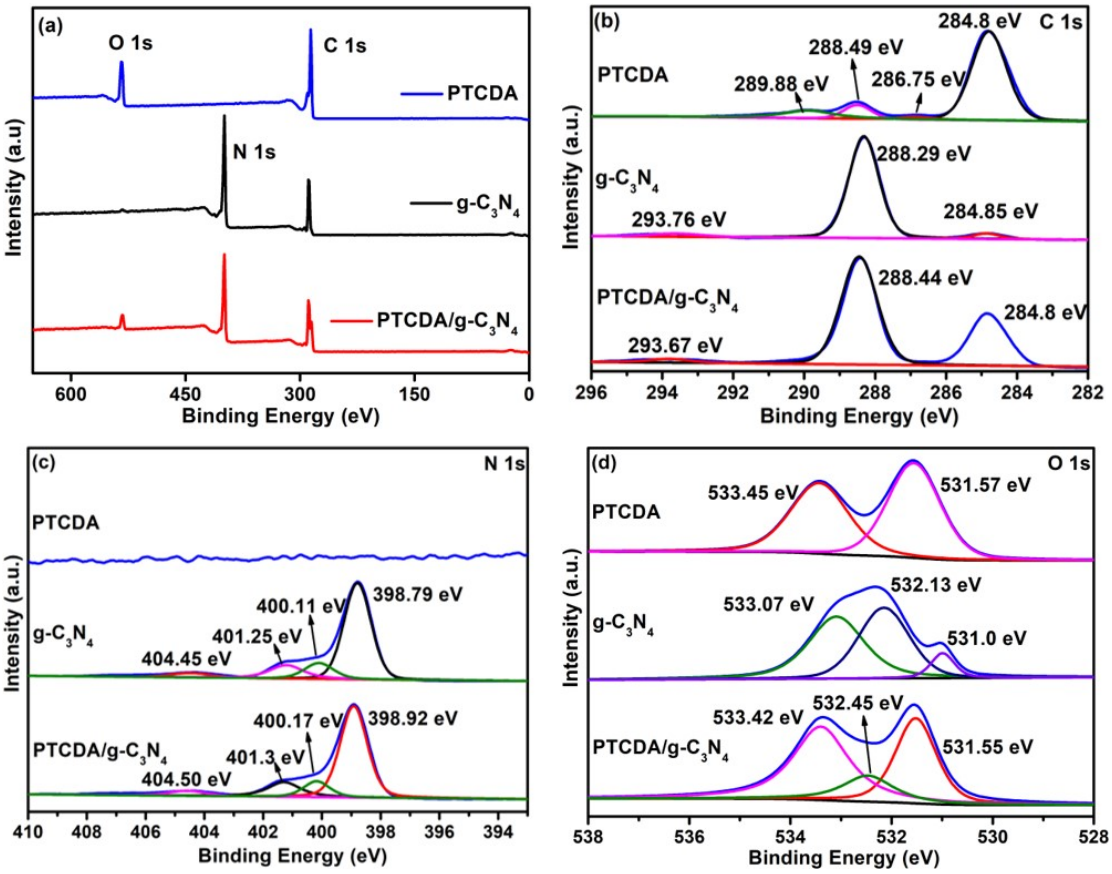


Figure S5. XPS spectra: (a) A whole scanning XPS spectra. (b) C 1s of the PTCDA, g-C_3N_4, and PTCDA/g-C_3N_4. (c) N 1s of the PTCDA, g-C_3N_4, and PTCDA/g-C_3N_4. (d) O 1s of the PTCDA, g-C_3N_4, and PTCDA/g-C_3N_4.

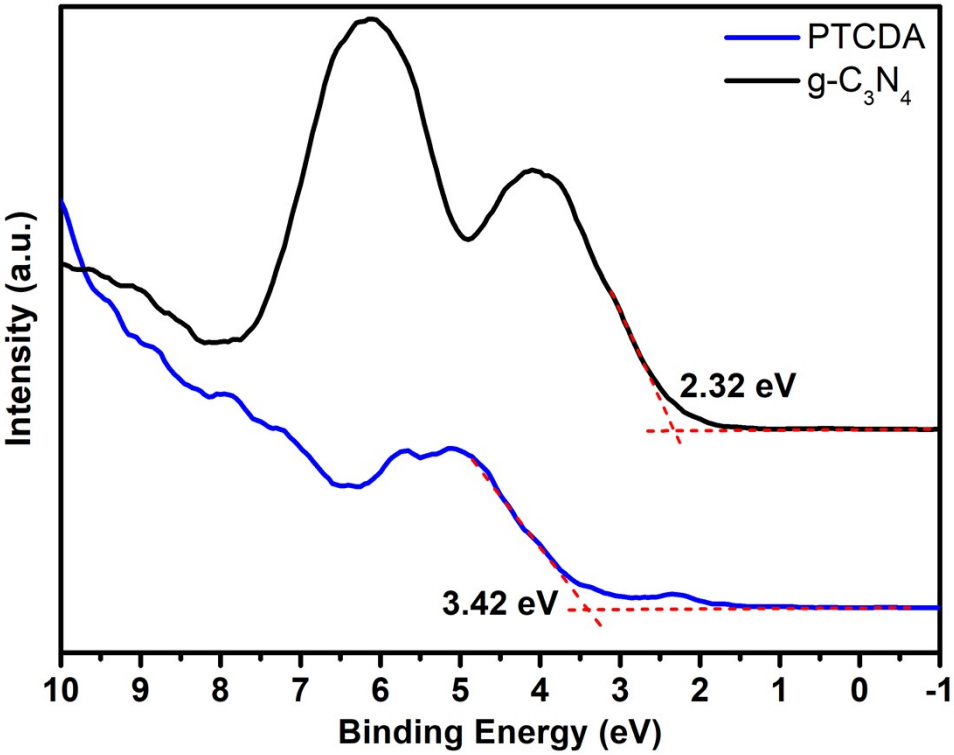


Figure S6. VB-XPS of PTCDA and g-C_3N_4.

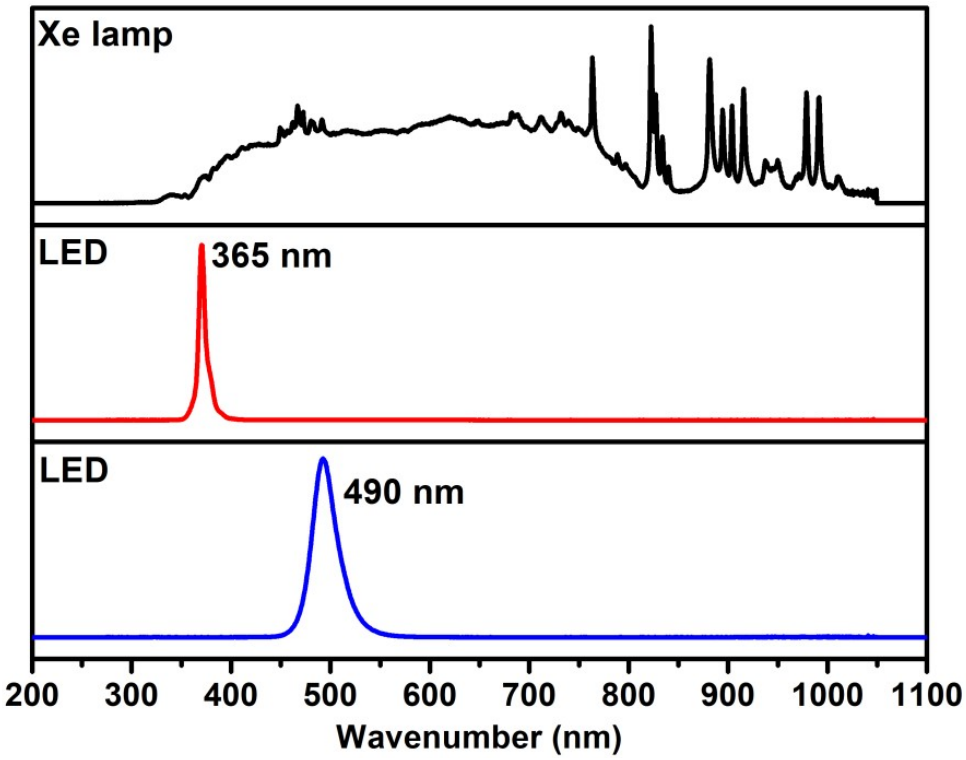


Figure S7. The emission spectrum of experiment lamps (Xe lamp and light-emitting diode (LED)).

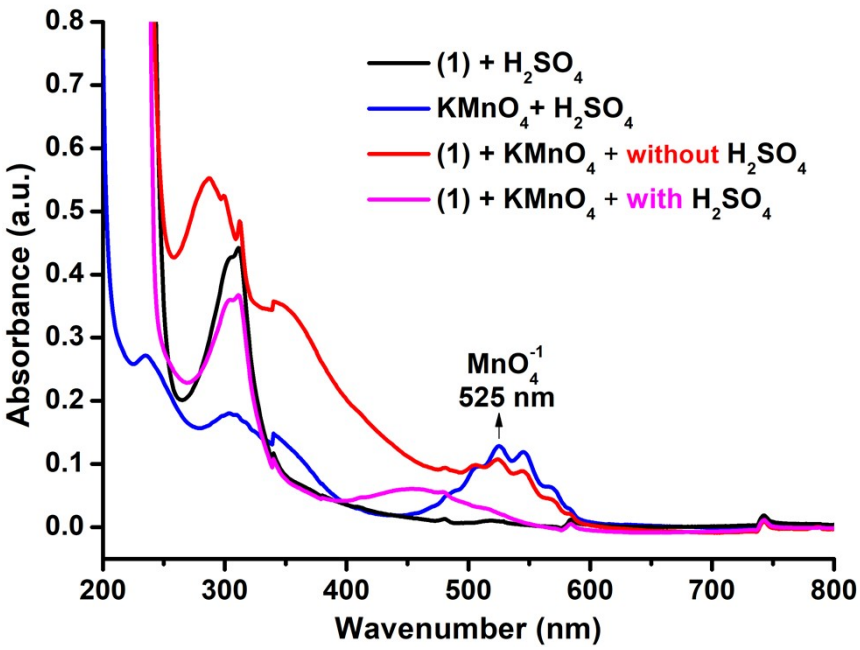
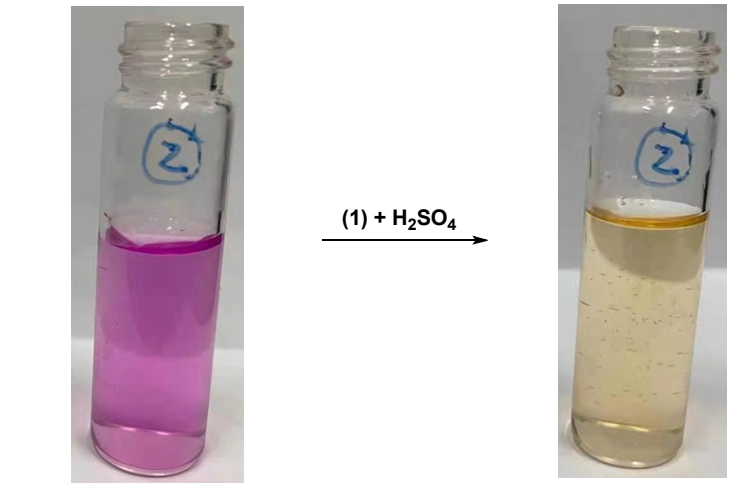


Figure S8. UV-Vis absorption spectra of the permanganate (MnO_4^{-1}) disappeared after addition the catalytic reaction solution (**(1)** = the reaction solution after photocatalysis).

We confirmed the formation of H_2O_2 by UV/Vis monitor of the disappear of the permanganate (MnO_4^{-1}) in aqueous solution. When the over amount of **(1)** (the reaction solution after photocatalysis) was added in the permanganate (MnO_4^{-1}) solution (5 ml, 0.2 mM) in the presence of hydrogen ions (H^+) (1 mL, 2M H_2SO_4), the MnO_4^- can be reduced to Mn^{2+}, which shows the disappear of the characteristic peaks at ca. 450-600 nm (maximum absorption peak at 525 ± 1 nm) in UV/Vis spectra. At the same time, the red color of potassium permanganate solution disappeared (See the following picture).

$$2MnO_4^- + 5H_2O_2 + 6H^+ = 2Mn^{2+} + 5O_2\uparrow + 8H_2O$$



MnO_4^- solution 5 mL (0.2 mM)

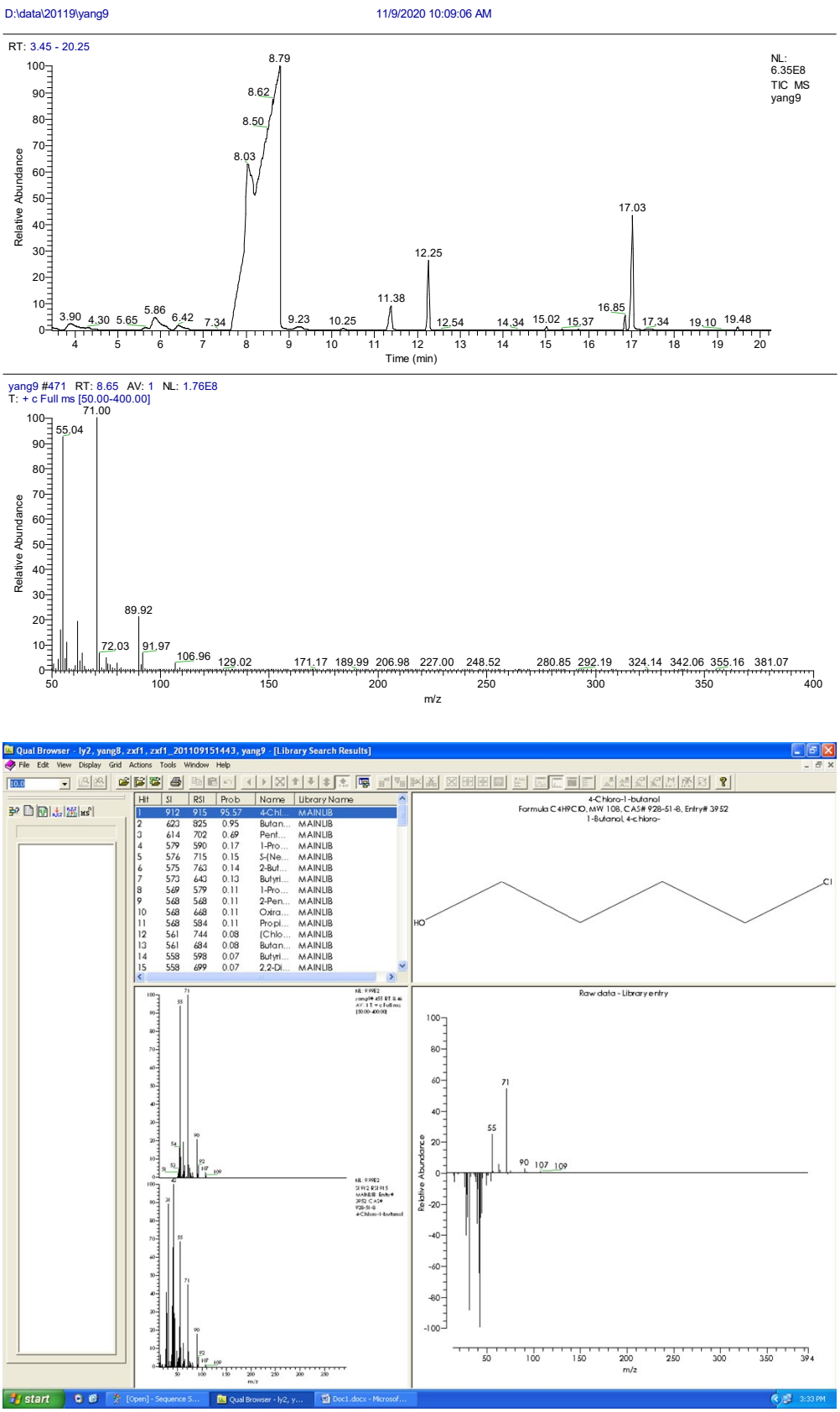


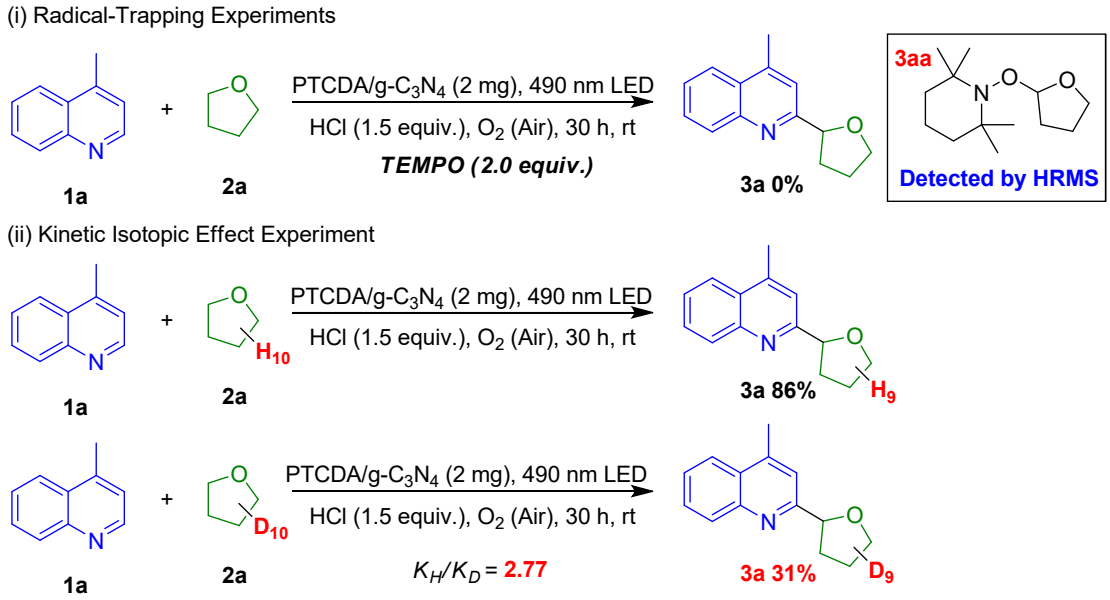
Figure S9. The open-loop of **2a** under the UV and 365 nm LED light irradiation.

Radical-trapping experiments and Kinetic isotope effect (KIE) experiment.

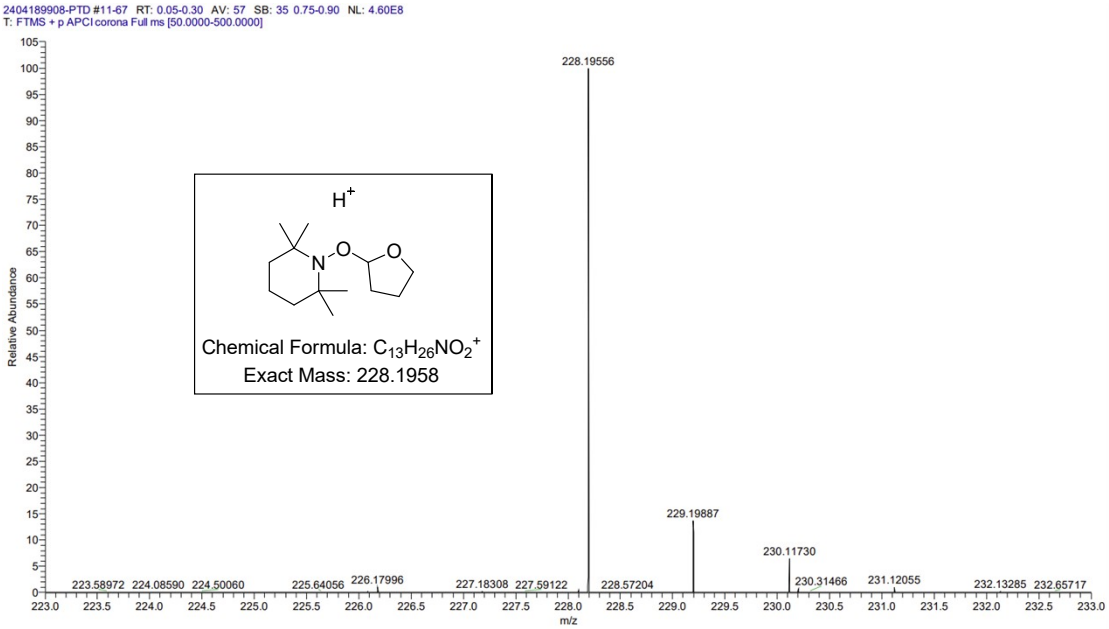
Radical-trapping experiments (i): The reaction was performed in a 20 mL quartz vial with 2 mL tetrahydrofuran containing 2 mg PTCDA/g-C_3N_4 photocatalyst, 1.5 equiv of HCl (36-38 wt%), 0.5 mmol 4-methylquinoline and 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) (2 equiv.) at room temperature under air conditions. The reactor was illuminated by a 490 nm LED light with a light intensity of 7.05 mW cm^{-2} for 30 h (**Scheme S1**).

Kinetic isotope effect (KIE) experiment (ii): The reaction was performed in a 20 mL quartz vial with 2 mL tetrahydrofuran or tetrahydrofuran-D8 (CAS: 1693-74-9) containing 2 mg PTCDA/g-C_3N_4 photocatalyst, 1.5 equiv of HCl (36-38 wt%), 0.5 mmol 4-methylquinoline at room temperature under air conditions. The reactor was illuminated by a 490 nm LED light with a light intensity of 7.05 mW cm^{-2} for 30 h (**Scheme S1**). After completion of the reaction, the catalyst was separated by centrifugation and washed with ethyl acetate. The reaction was quenched with 5 mL saturated ammonium chloride, 5 mL saturated sodium bicarbonate, and extracted with ethyl acetate (3×10 mL), the organic layer was washed with H_2O, brine, dried over $MgSO_4$, and purified by silica gel flash chromatography using a mixture of petroleum ether and ethyl acetate to provide the desired product.

Scheme S1. Mechanistic experiments.



TEMPO trapped product **3aa** is confirmed by HRMS



Quantum efficiency calculations.

The QE determination at λ_0 = 490 nm. The catalyst solution was irradiated by a 15 W LED with a λ_0±20 nm band-pass filter for 30 hours. The average intensity of irradiation was determined to be 7.05 mW/cm^2 by an ILT 950 spectroradiometer (International Light Technologies) and the irradiation area was 3.02 cm^2. The number of incident photons (N) is 5.668 × 10^{21} as calculated by equation (1). The yield of **3a** is 86%, The amount of **3a** molecules generated in 30 hours was 0.5 × 86% mmol. The quantum efficiency is calculated from equation (2).

$$N = \frac{E\lambda}{hc} = \frac{7.05 \times 10^{-3} \times 3.02 \times 30 \times 3600 \times 490 \times 10^{-9}}{6.626 \times 10^{-34} \times 3 \times 10^{8}} \left(\frac{W/cm^2 \times cm^2 \times s \times m}{J \cdot s \times m/s} \right) = 5.668 \times 10^{21} \quad \textbf{(1)}$$

$$QE = \frac{2 \times \text{the number of evolved } H_2 \text{ molecules}}{\text{the number of incident photons}} \times 100\%$$

$$= \frac{2 \times 6.02 \times 10^{23} \times 0.5 \times 0.86 \times 10^{-3}}{5.668 \times 10^{21}} \times 100\% = 9.13\ \% \quad \textbf{(2)}$$

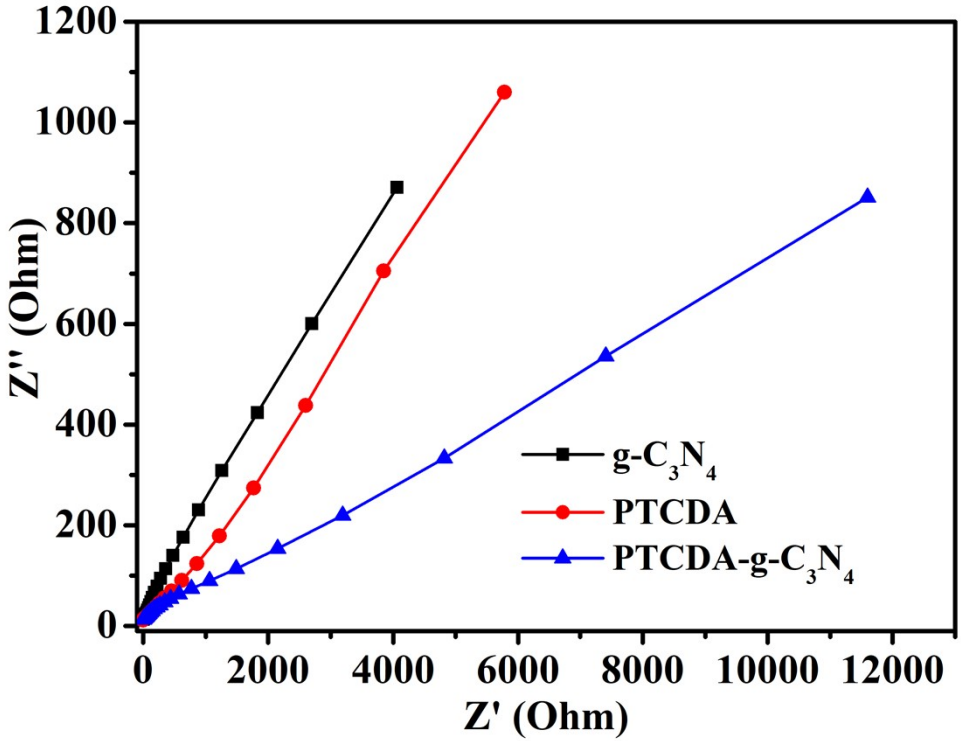


Figure S10. Electrochemical impedance spectroscopy (EIS) spectra of g-C_3N_4, PTCDA and PTCDA/g-C_3N_4.

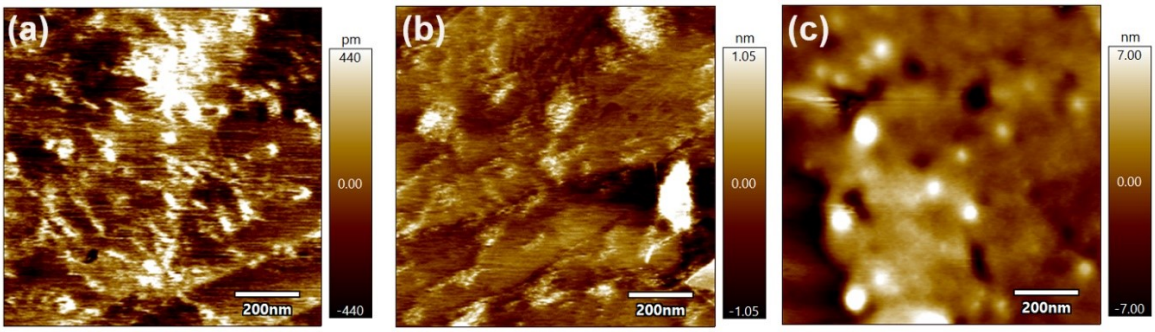


Figure S11. Tapping-mode AFM images in air for the electrode surface. (a) g-C_3N_4, (b) PTCDA, (c) PTCDA/g-C_3N_4.

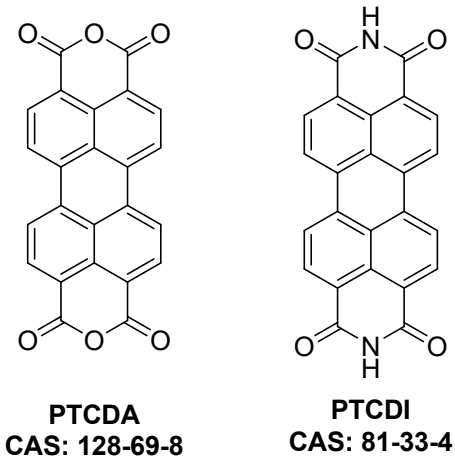


Figure S12. The molecular structure of PTCDA and PTCDI.

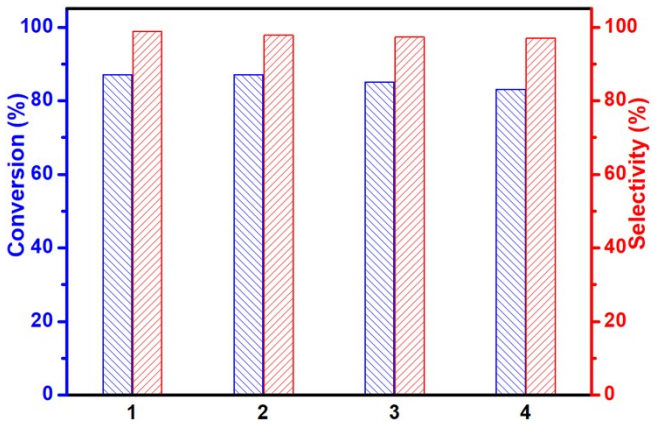
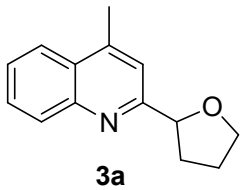


Figure S13. Reusability tests using the isolated PTCDA/g-C_3N_4 photocatalyst (Legend: blue bar, **1a** conversion; red bar, **3a** selectivity.).

Spectroscopic data of products

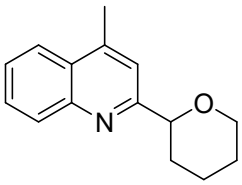
Table 3, entry 1



3a

4-methyl-2-(tetrahydrofuran-2-yl)quinolone (3a). Oil; R_f = 0.5 (hexane:EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.96 (d, J = 8.3 Hz, 1H), 7.68 (t, J = 7.1 Hz, 1H), 7.52 (t, J = 7.1 Hz, 1H), 7.44 (s, 1H), 5.13 (t, J = 7.0 Hz, 1H), 4.17 (dd, J = 14.8, 6.7 Hz, 1H), 4.03 (dd, J = 14.8, 6.8 Hz, 1H), 2.70 (s, 3H), 2.50 (dd, J = 11.8, 5.5 Hz, 1H), 2.23-1.81 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 147.7, 145.3, 129.9, 129.5, 127.8, 126.2, 124.0, 119.0, 82.4, 69.6, 33.7, 26.3, 19.3. (Spectra data are consistent with those reported in the literature: H. Zhao, Z. Li and J. Jin*, New J. Chem.,* **2019***, 43,* 12533-12537.)

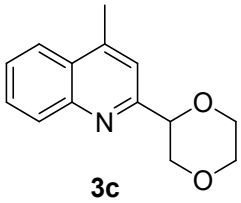
Table 3, entry 2



3b

4-methyl-2-(tetrahydro-2*H*-pyran-2-yl)quinolon (3b). Oil; R_f = 0.5 (hexane:EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.68 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.46 (s, 1H), 4.60 (d, J = 11.1 Hz, 1H), 4.21 (d, J = 11.2 Hz, 1H), 3.69 (t, J = 11.1 Hz, 1H), 2.71 (s, 3H), 2.09 (d, J = 13.0 Hz, 1H), 1.98 (s, 1H), 1.76 (t, J = 9.2 Hz, 2H), 1.64 (t, J = 11.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0, 147.0, 144.9, 129.5, 128.9, 127.4, 125.7, 123.5, 118.7, 81.5, 68.8, 32.7, 25.7, 23.6, 18.7. (Spectra data are consistent with those reported in the literature: H. Zhao, Z. Li and J. Jin*, New J. Chem.,* **2019***, 43,* 12533-12537.)

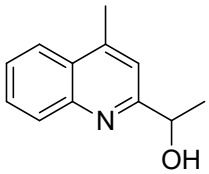
Table 3, entry 3



3c

2-(1,4-dioxan-2-yl)-4-methylquinoline (3c). White solid; R_f = 0.5 (hexane:EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.70 (t, J = 8.3 Hz, 1H), 7.55 (t, J = 7.0 Hz, 1H), 7.46 (s, 1H), 4.90 (dd, J = 10.1, 2.8 Hz, 1H), 4.23 (dd, J = 11.6, 2.7 Hz, 1H), 4.01 (dd, J = 10.4, 2.7 Hz, 2H), 3.82 (dd, 2H), 3.63 (t, 1H), 2.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2, 147.6, 145.6, 130.1, 129.7, 128.0, 126.6, 124.1, 119.5, 79.2, 71.5, 67.5, 66.8, 19.3. (Spectra data are consistent with those reported in the literature: H. Zhao, Z. Li and J. Jin*, New J. Chem.,* **2019***, 43,* 12533-12537.)

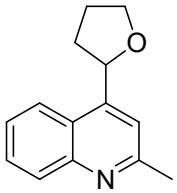
Table 3, entry 4



3d

1-(4-methylquinolin-2-yl)ethanol (3d). Oil; R_f = 0.6 (hexane:EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 8.3 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.56 (t, J = 7.6 Hz, 1H), 7.18 (s, 1H), 5.14 (br s, 1H), 4.99 (dd, J = 6.6 Hz, 1H), 2.72 (s, 3H), 1.57 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 146.1, 145.3, 129.5, 129.3, 127.5, 126.2, 123.8, 118.6, 68.6, 24.1, 19.0. (Spectra data are consistent with those reported in the literature: H. Zhao, Z. Li and J. Jin*, New J. Chem.,* **2019***, 43,* 12533-12537.)

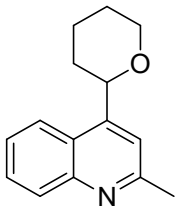
Tabel 3, entry 5



3e

2-methyl-4-(tetrahydrofuran-2-yl)quinolone (3e). Oil; R_f = 0.5 (hexane:EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J = 8.4 Hz, 1H), 7.85 (d, J = 8.3 Hz, 1H), 7.67 (t, J = 7.6 Hz, 1H), 7.49 (t, J = 7.2 Hz, 1H), 7.45 (s, 1H), 5.58 (t, J = 7.1 Hz, 1H), 4.23 (td, J = 7.6, 5.7 Hz, 1H), 4.05 (dd, J = 15.3, 7.2 Hz, 1H), 2.74 (s, 3H), 2.65–2.58 (m, 1H), 2.21–1.97 (m, 2H), 1.88–1.81 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 148.1, 129.7, 129.6, 129.4, 125.9, 124.2, 123.4, 117.6, 75.7, 69.4, 34.3, 26.4, 25.8. (Spectra data are consistent with those reported in the literature: A. Vijeta and E. Reisner, *Chem. Commun.,* ***2019****, 55,* 14007-14010.)

Table 3, entry 6



3f

2-methyl-4-(tetrahydro-2H-pyran-2-yl)quinolone (3f). Oil; R_f = 0.45 (hexane:EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.4 Hz, 1H), 7.92 (d, J = 8.4 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.45 (s, 1H), 5.02 (d, J = 10.0 Hz, 1H), 4.26 (d, J = 10.0 Hz, 1H), 3.77 (d, J = 11.8 Hz, 1H), 2.74 (s, 3H), 2.07–1.99 (m, 2H), 1.82–1.76 (m, 2H), 1.69–1.58 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 149.0, 148.2, 129.7, 129.3, 125.9, 123.9, 123.1, 118.6, 76.5, 69.6, 34.0, 26.3, 25.8, 24.4. (Spectra data are consistent with those reported in the literature: J. Jin and D. W. C. MacMillan, *Angew. Chem. Int. Ed.,* **2015**, *54*, 1565-1569.)

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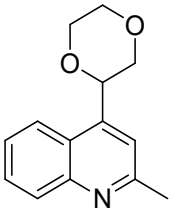
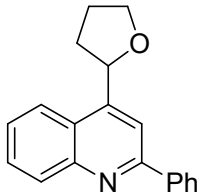


3g

4-(1,4-dioxan-2-yl)-2-methylquinoline (3g). Oil; R_f = 0.5 (hexane:EtOAc = 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 8.5 Hz, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.68 (t, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.49 (s, 1H), 5.36 (d, *J* = 9.3 Hz, 1H), 4.12 (d, *J* = 11.8 Hz, 1H), 4.07–4.05 (m, 2H), 3.91–3.88 (m, 1H), 3.84–3.74 (m, 1H), 3.46 (t, J = 10.5 Hz, 1H), 2.75 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.2, 147.9, 143.5, 129.7, 129.3, 126.0, 123.6, 122.4, 119.1, 74.2, 72.1, 67.4, 66.7, 25.6. (Spectra data are consistent with those reported in the literature: M. C. Quattrini, S. Fujii, K. Yamada, T. Fukuyama, D. Ravelli, M. Fagnoni and L. Ryu, *Chem. Commun.* **2017**, *53*, 2335-2338.)

Table 3, entry 8



3h

2-phenyl-4-(tetrahydrofuran-2-yl)quinolone (3h). Oil; R_f = 0.35 (hexane:EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.8, 4.7 Hz, 3H), 8.06 (s, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.53 (dd, *J* = 14.0, 6.8 Hz, 3H), 7.47 (t, *J* = 6.9 Hz, 1H), 5.66 (t, *J* = 7.1 Hz, 1H), 4.28 (dd, *J* = 15.0, 5.7 Hz, 1H), 4.08 (dd, *J* = 15.0, 7.4 Hz, 1H), 2.68–2.62 (m, 1H), 2.11–1.98 (m, 2H), 1.93–1.86 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 150.0, 148.5, 140.0, 130.7, 129.3, 129.2, 128.8, 127.7, 126.1, 124.6, 123.1, 114.4, 77.1, 69.1, 34.1, 26.1. (Spectra data are consistent with those reported in the literature: C.-Y. Huang, J. Li, W. Liu and C.-J. Li, *Chem. Sci.* **2019**, *10*, 5018-5024.)

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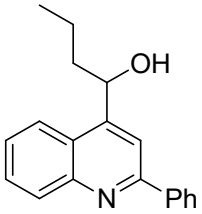
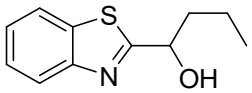


3i

1-(2-phenylquinolin-4-yl)butan-1-ol (3i). Oil; R_f = 0.35 (hexane:EtOAc = 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 (d, J = 8.4 Hz, 1H), 8.00-7.98 (m, 2H), 7.83-7.77 (m, 2H), 7.66 (t, 1H), 7.44-7.42 (m, 4H), 5.31-5.23 (m, 1H), 4.26 (br s, 1H), 1.79-1.74 (m, 2H), 1.55-1.46 (m, 2H), 0.96-0.92 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.2, 151.5, 148.1, 139.4, 130.3, 129.5, 129.3, 128.8, 127.6, 126.1, 124.5, 122.9, 115.2, 69.9, 40.5, 19.3, 13.9; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{20}NO$ 278.154; found 278.151.

Table 3, entry 10

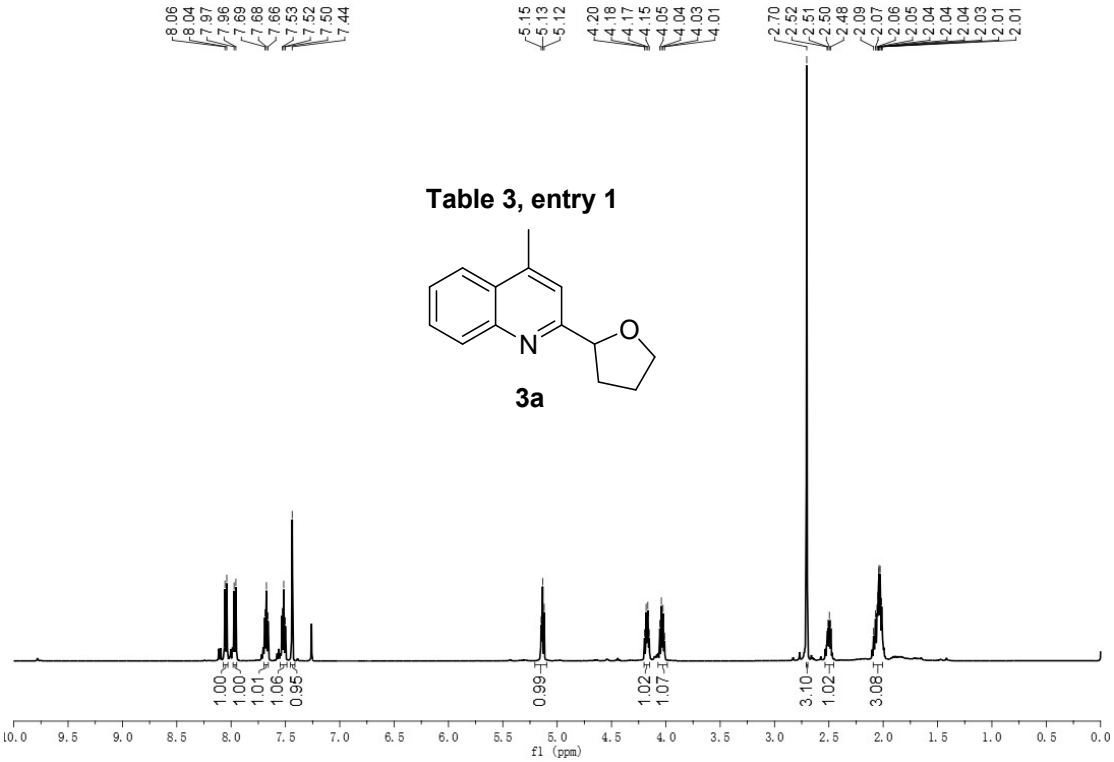


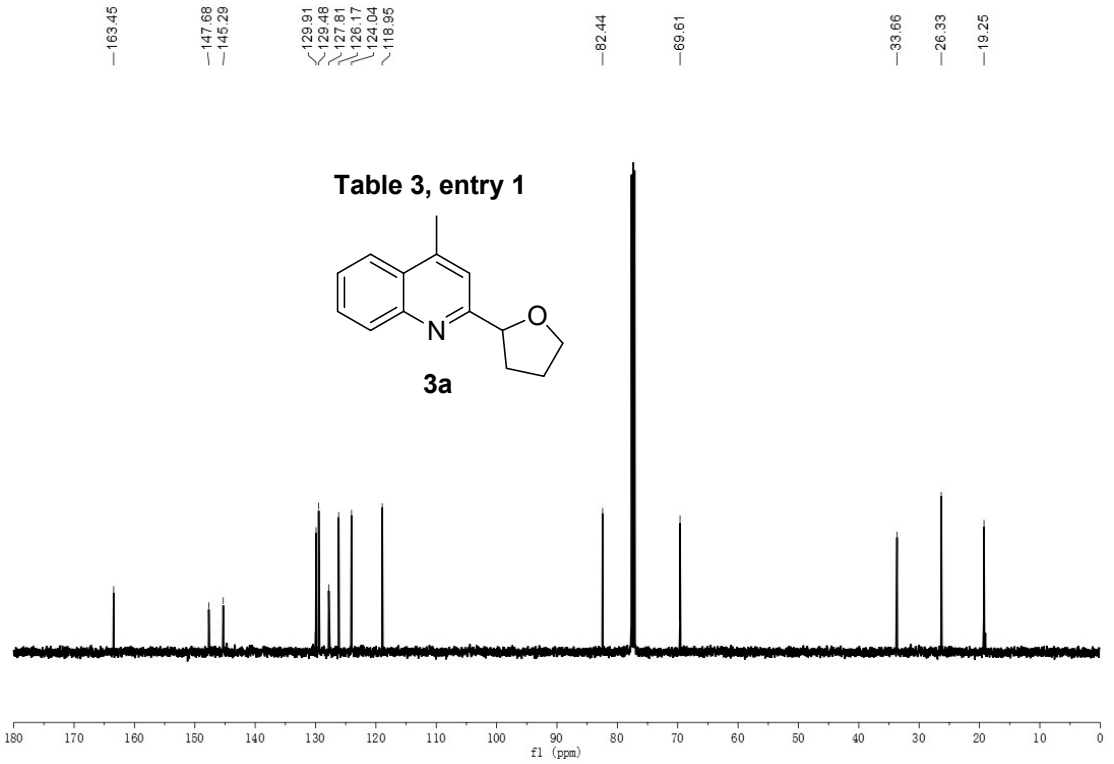
3j

1-(benzo[d]thiazol-2-yl)butan-1-ol (3j). Oil; R_f = 0.35 (hexane:EtOAc = 5:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.0 Hz, 1H), 7.48 (t, J = 7.7 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 5.13-5.10 (m, 1H), 3.06 (d, J = 7.6 Hz, 1H), 2.05-1.98 (m, 1H), 1.95-1.88 (m, 1H), 1.59-1.52 (m, 2H), 0.99 (t, J = 10.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.1, 152.8, 134.9, 126.1, 125.0, 122.9, 121.9, 72.2, 40.2, 18.4, 13.9. (Spectra data are consistent with those reported in the literature: T. He, L. Yu, L. Zhang, L. Wang and M. Wang, *Org. Lett.,* **2011***, 13,* 5016-5019.)

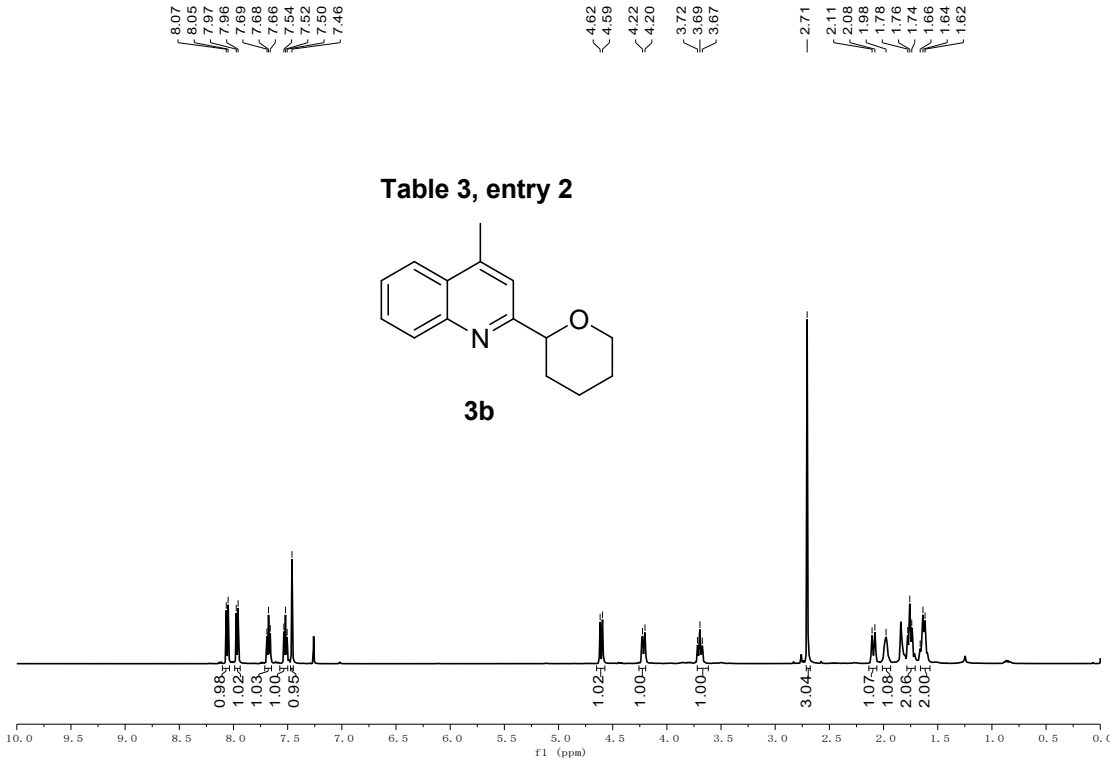
NMR Spectra

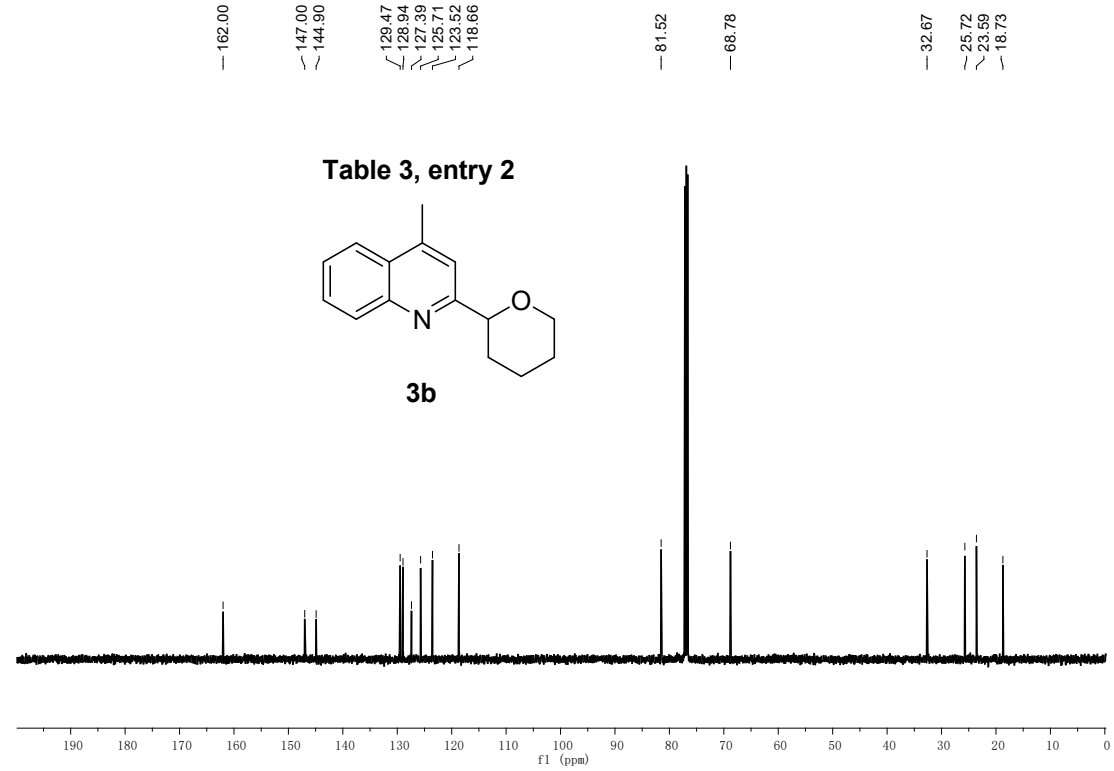
^{1}H NMR and ^{13}C NMR Spectrum of **3a**



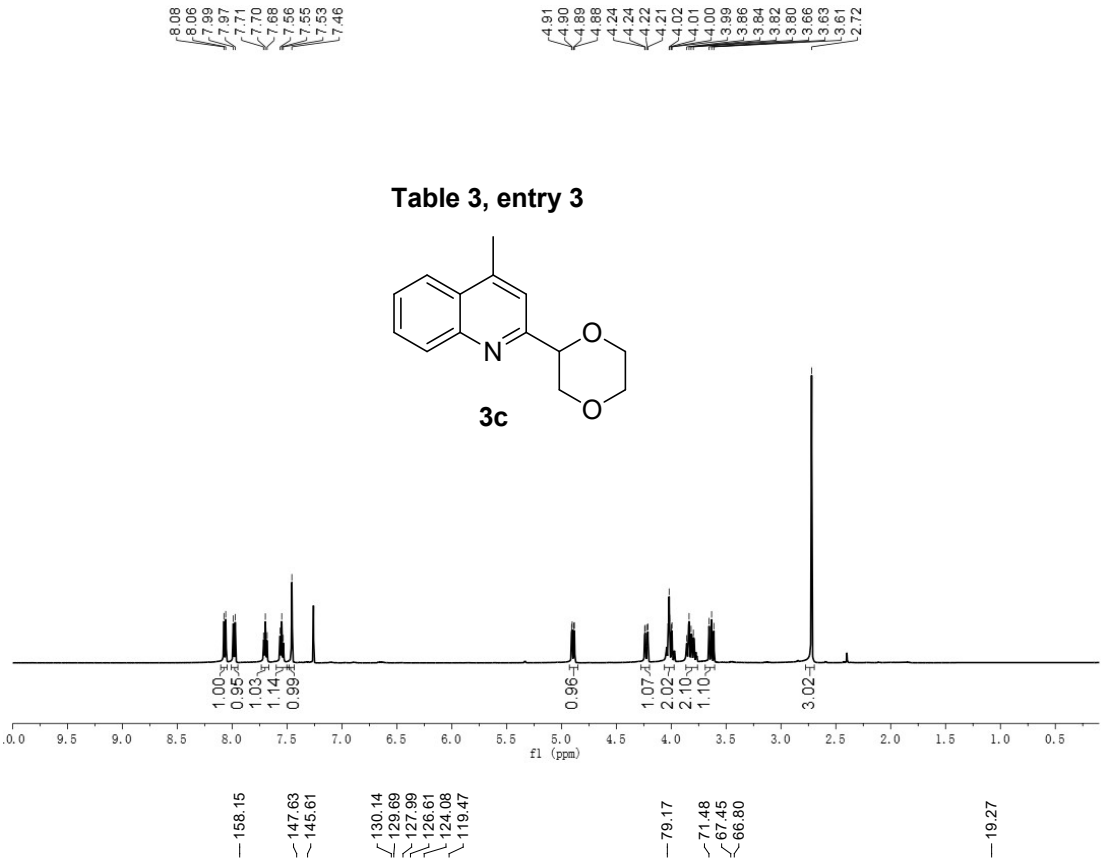


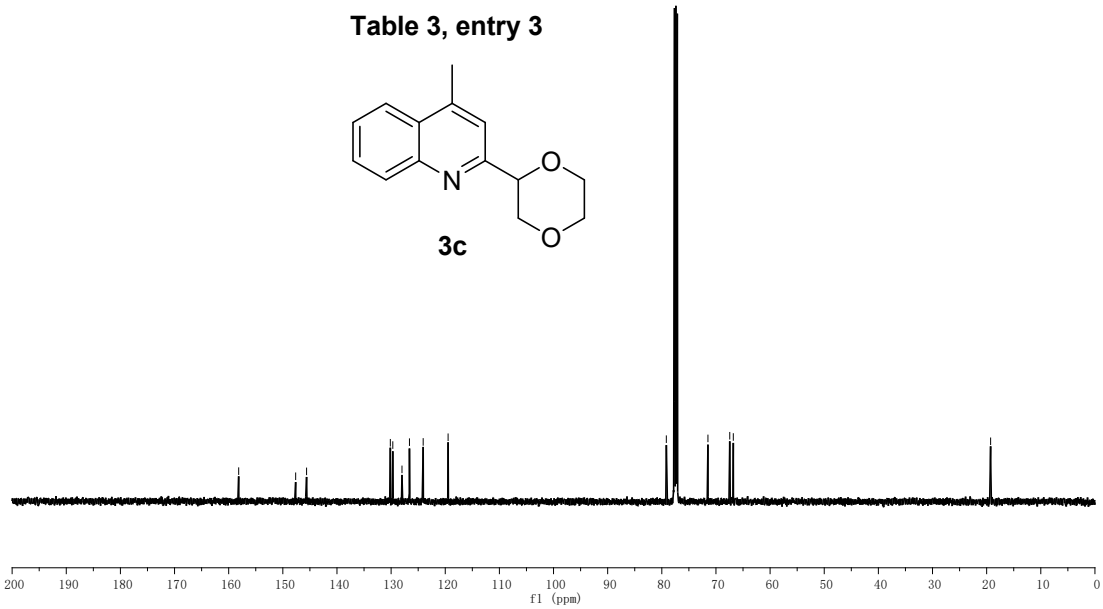
^{1}H NMR and ^{13}C NMR Spectrum of **3b**



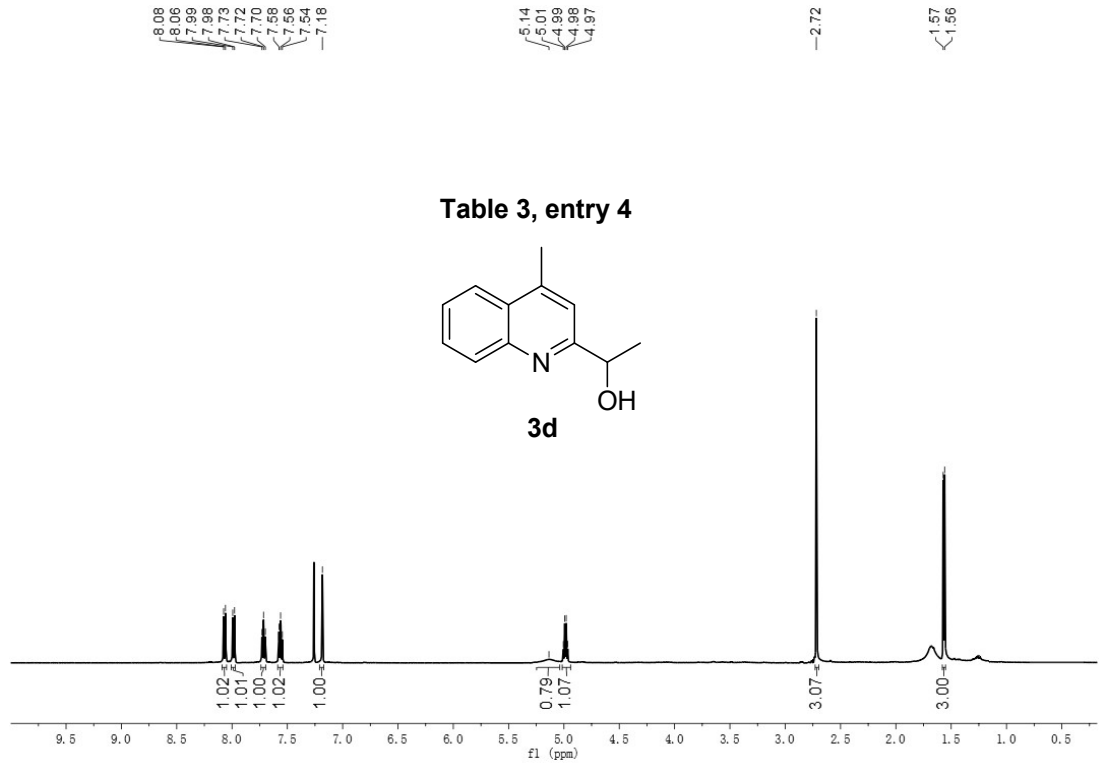


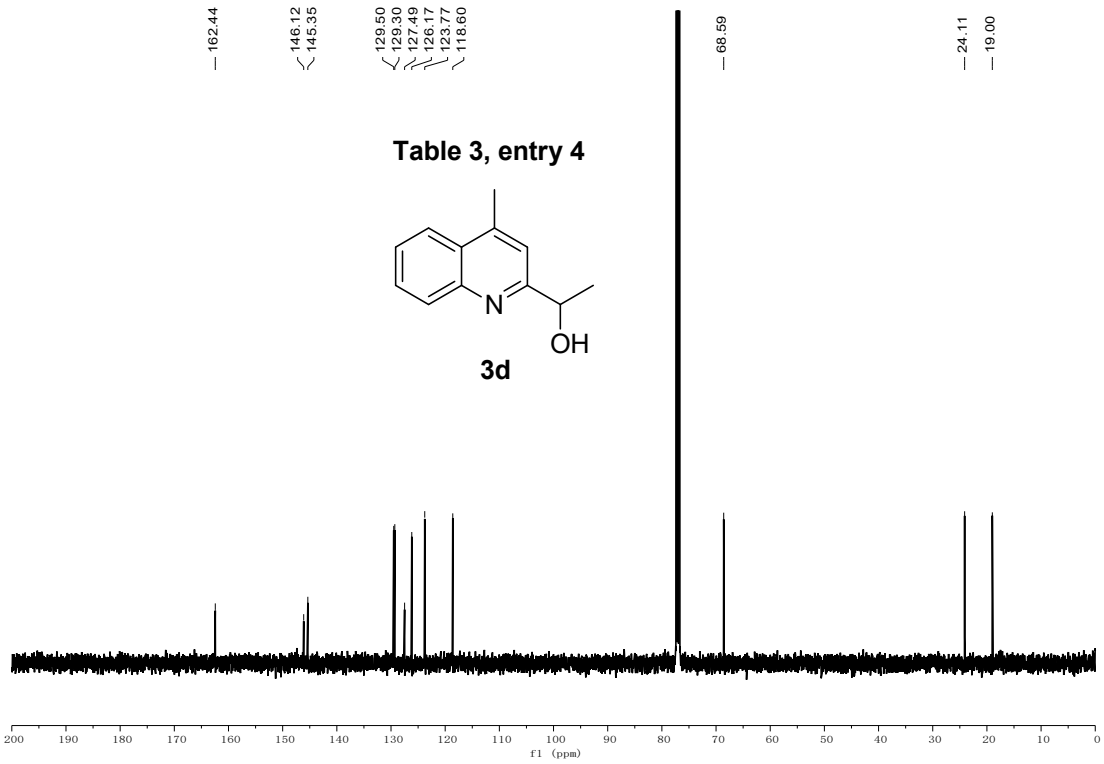
^{1}H NMR and ^{13}C NMR Spectrum of **3c**



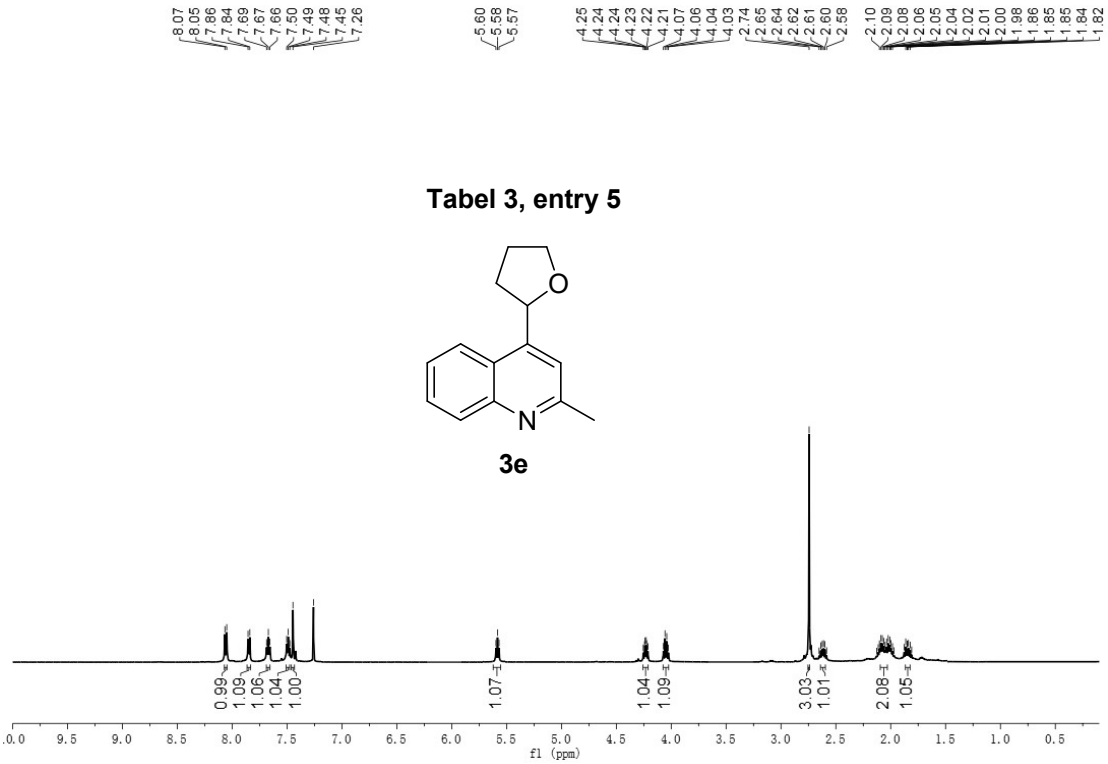


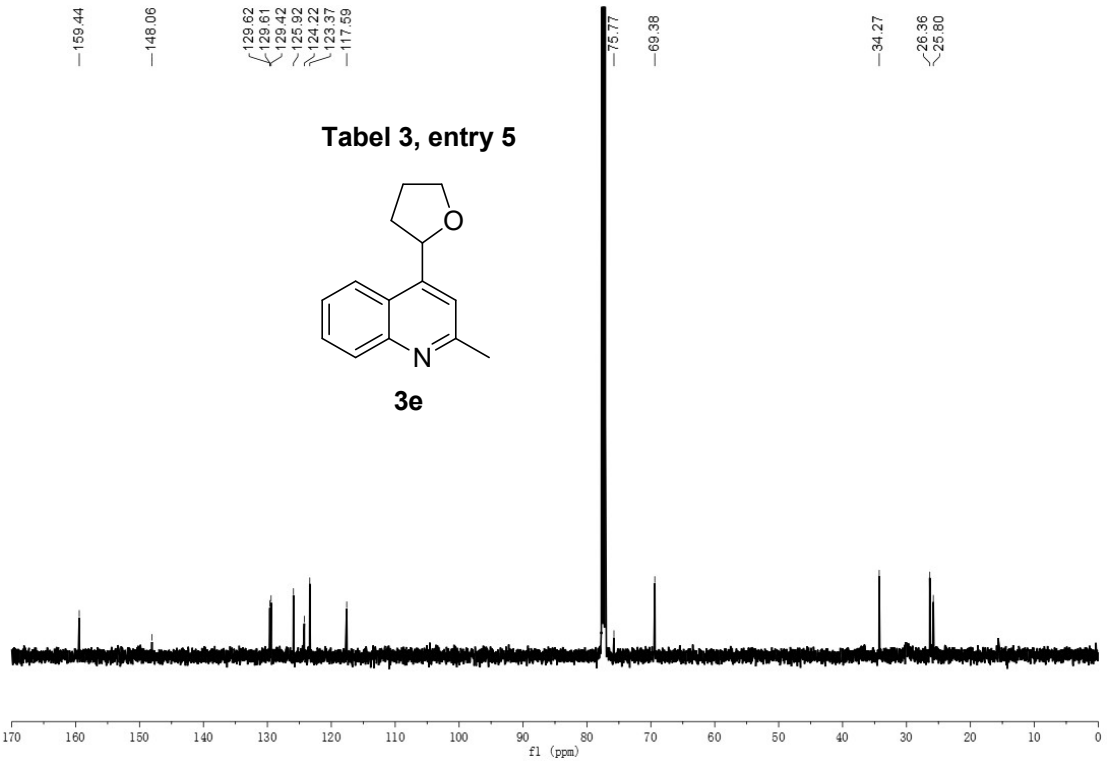
^{1}H NMR and ^{13}C NMR Spectrum of **3d**



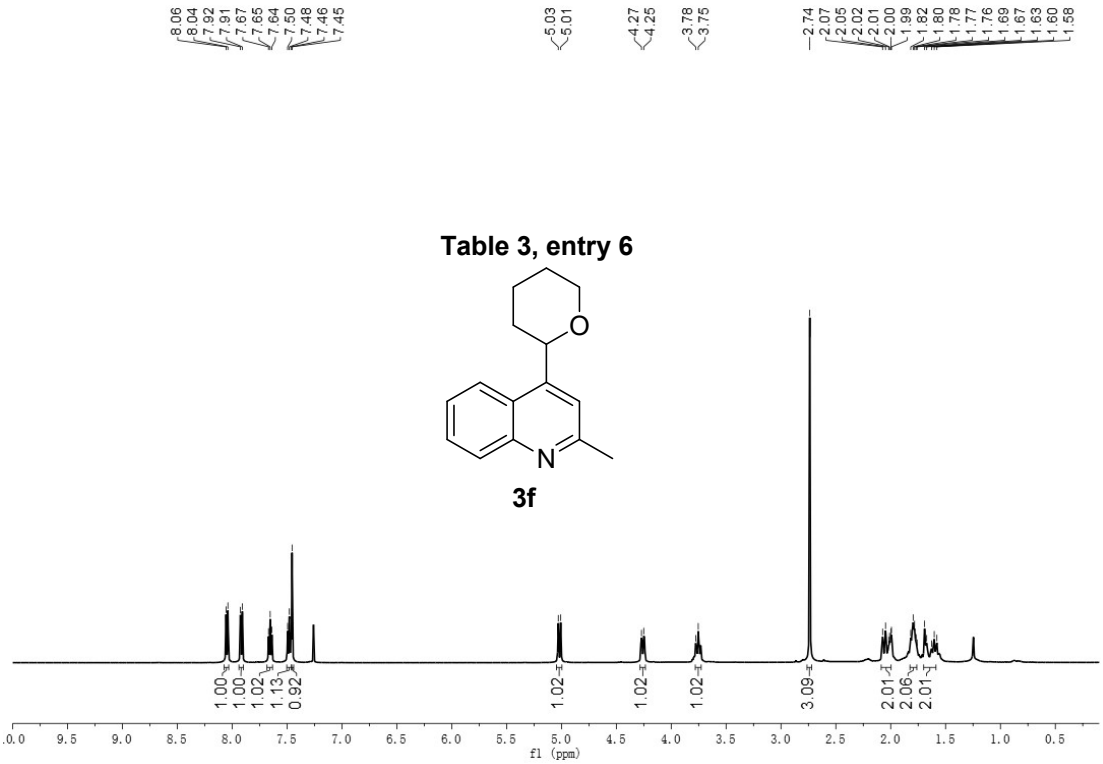


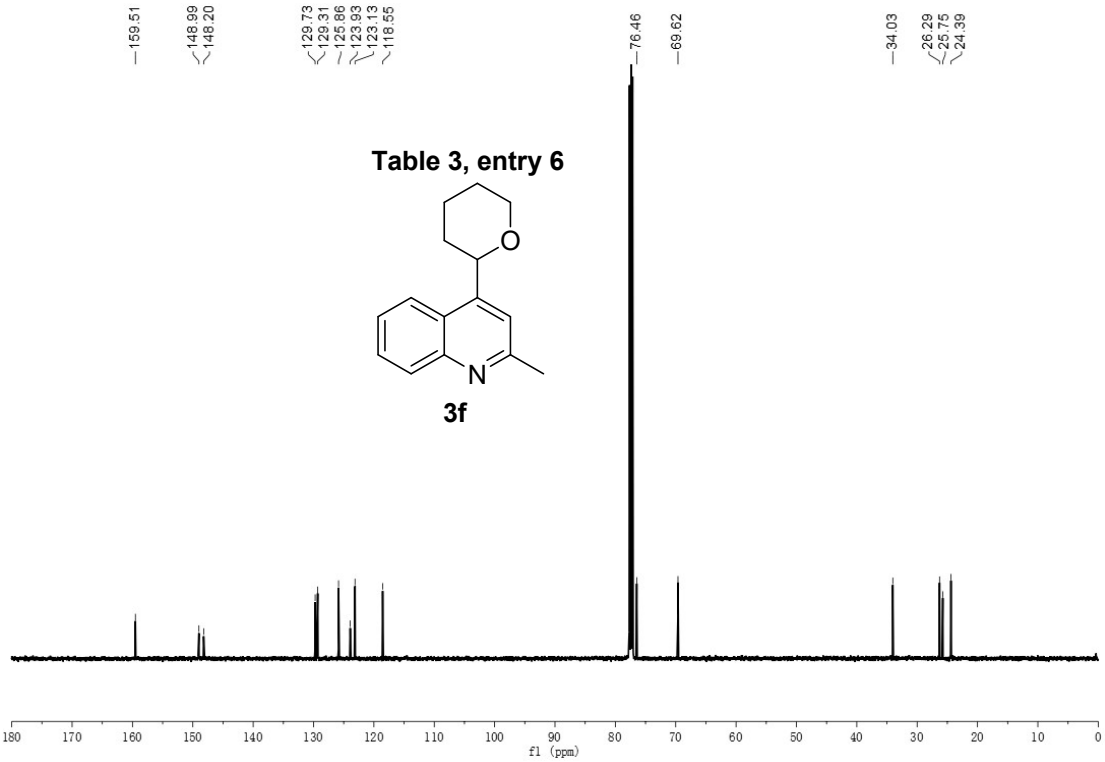
^{1}H NMR and ^{13}C NMR Spectrum of **3e**



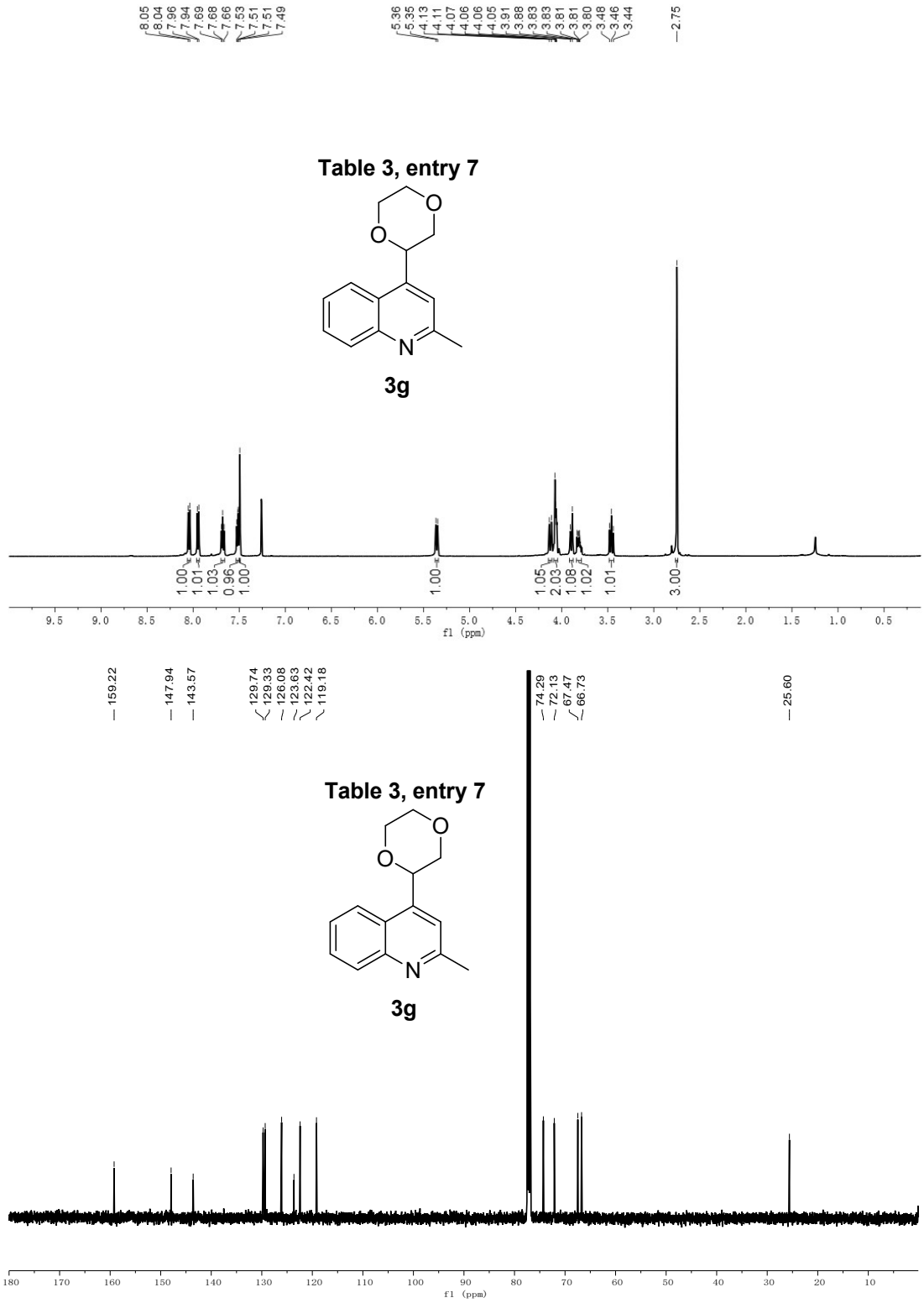


^{1}H NMR and ^{13}C NMR Spectrum of **3f**

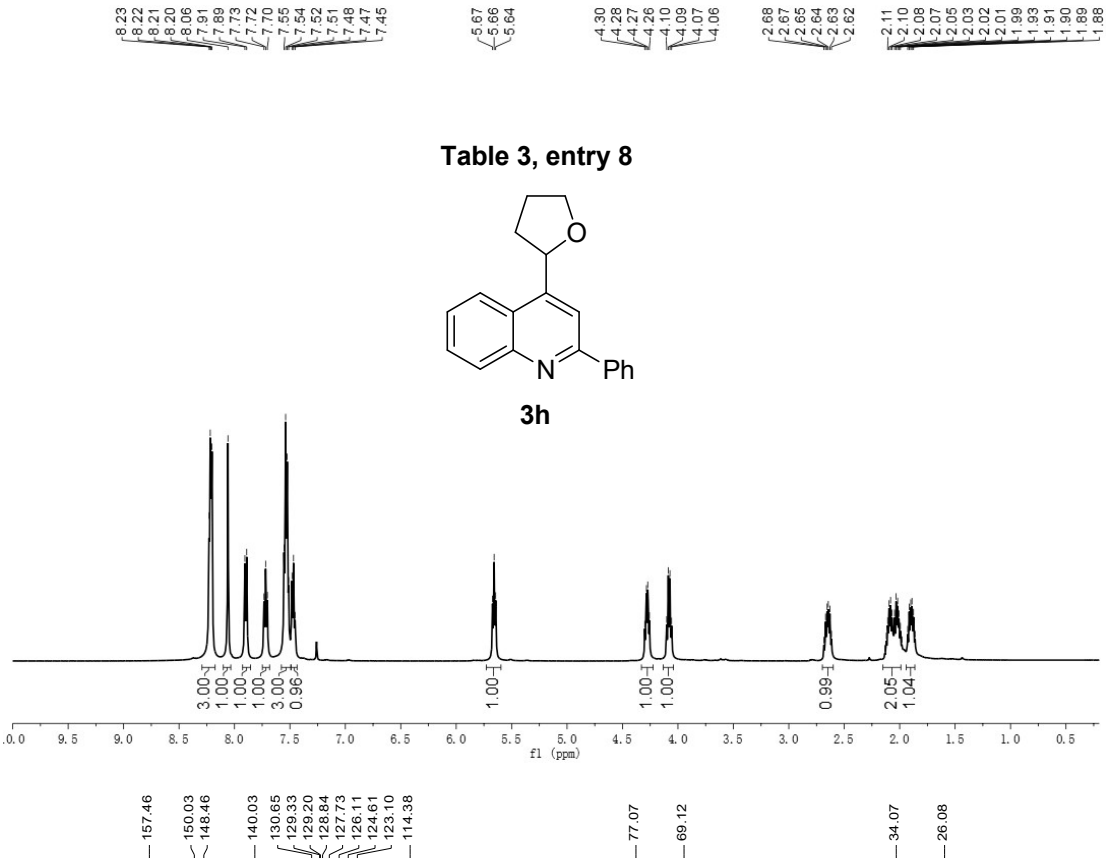


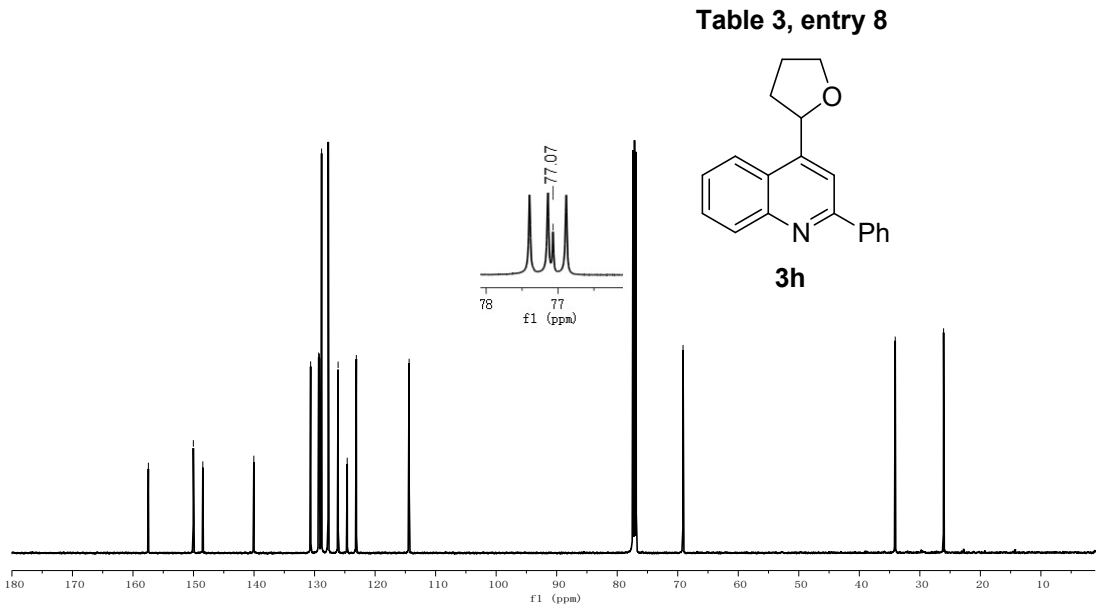


^{1}H NMR and ^{13}C NMR Spectrum of **3g**

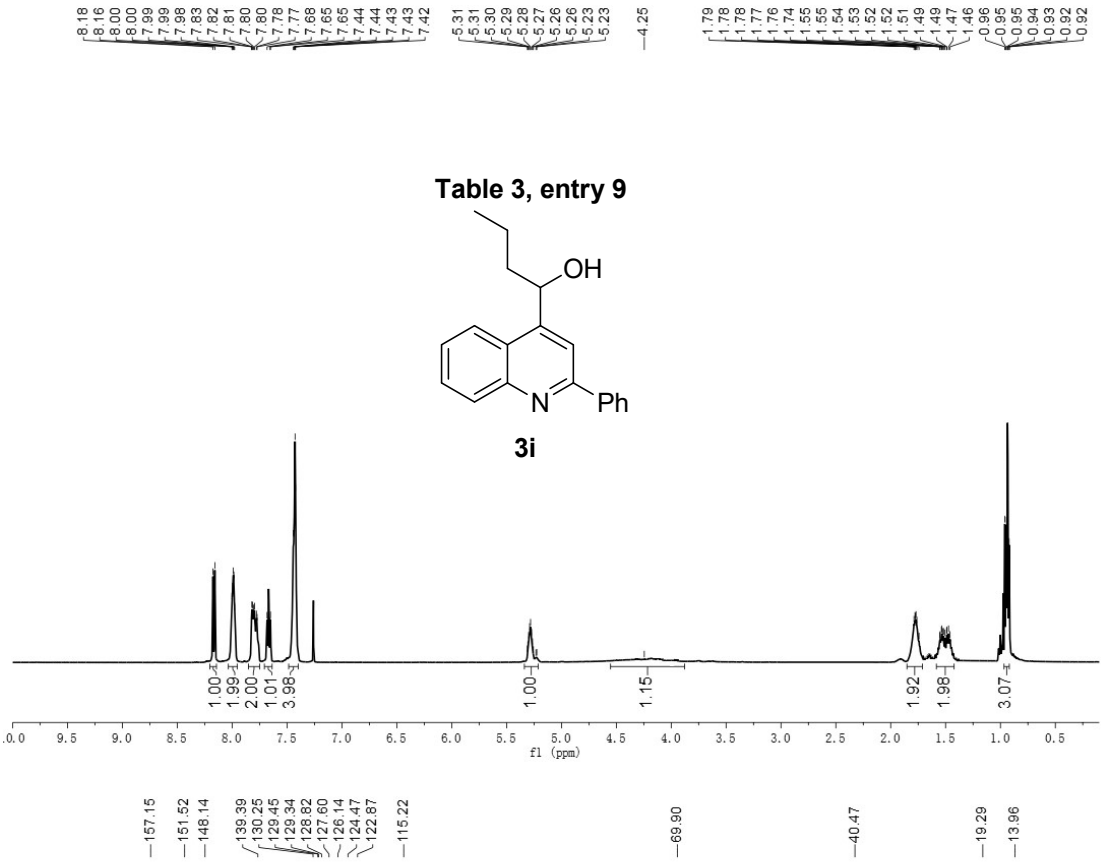


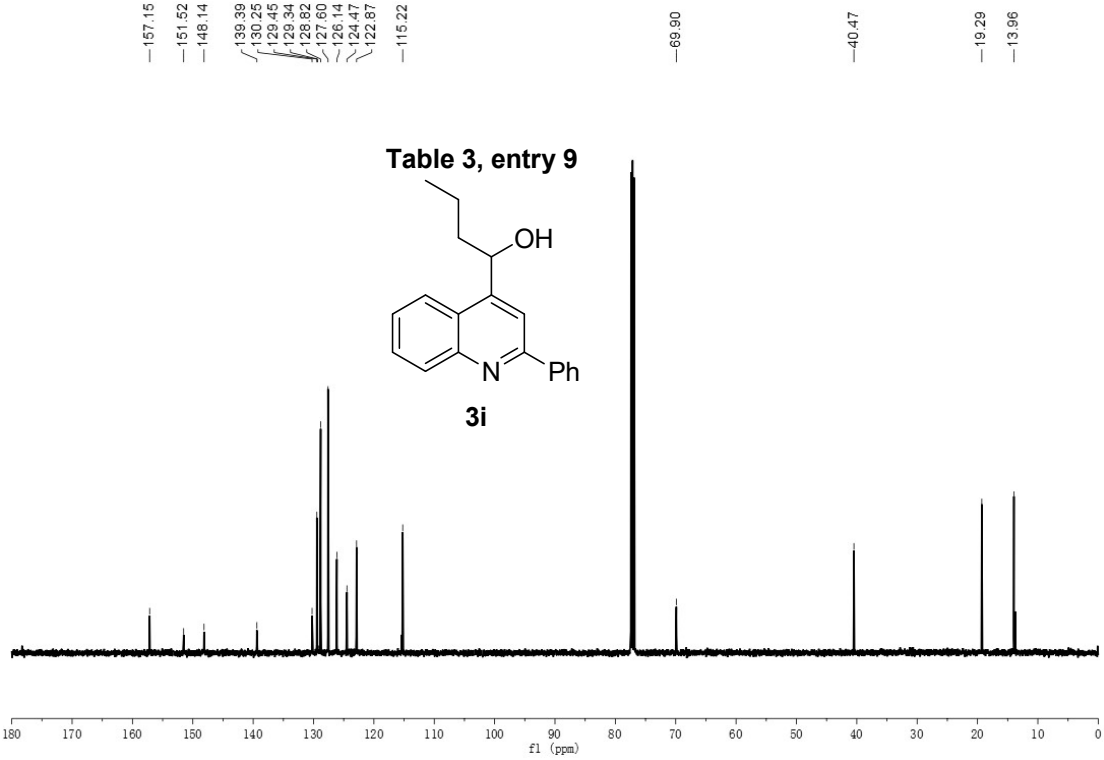
^{1}H NMR and ^{13}C NMR Spectrum of **3h**



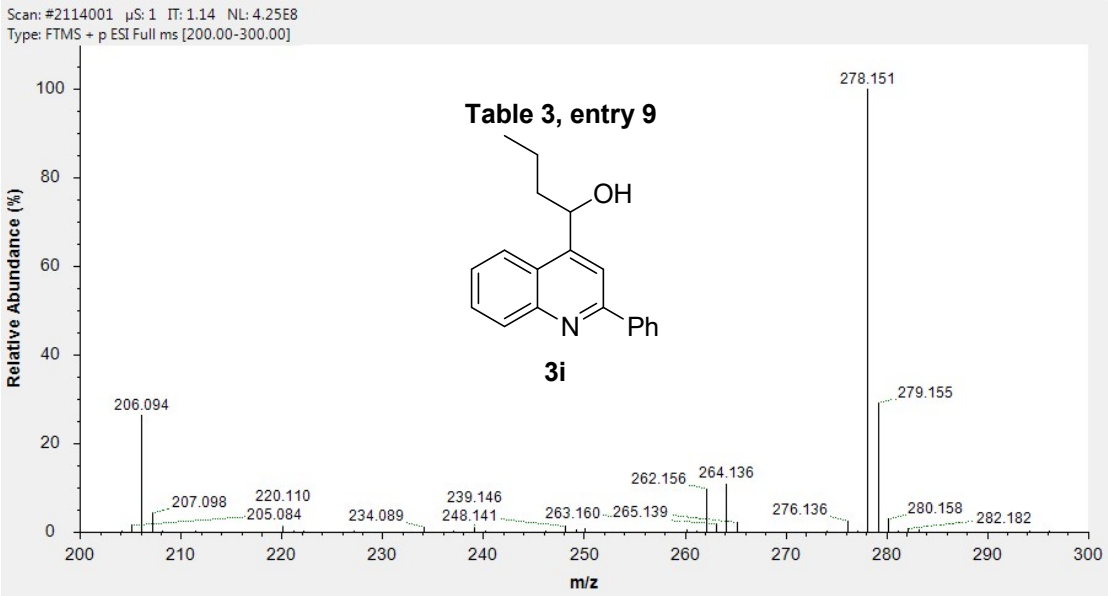


^{1}H NMR and ^{13}C NMR Spectrum of **3i**





HRMS of **3i**


Scan: #2114001 µS: 1 IT: 1.14 NL: 4.25E8
Type: FTMS + p ESI Full ms [200.00-300.00]
Table 3, entry 9
OH
N
Ph
3i
Relative Abundance (%)
m/z
278.151
279.155
206.094
207.098
220.110
205.084
234.089
239.146
248.141
263.160
265.139
262.156
264.136
276.136
280.158
282.182

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