Electronic Supplementary Information

Facets in metal halide perovskite nanocrystals for photoinduced electron transfer annulation reaction

Qing Guo,[+*a] Jun-Lin Lu,[+a] Bin Qin,[b] Qi-Chao Shan,[a] Le Liu,[a] Jin-Dan Zhang,[a] Xi Liu,*[c] Xin-Hua Duan[a] and Li-Na Guo*[a]

[a]Xi'an Key Laboratory of Sustainable Energy Material Chemistry and Engineering Research Center of Energy Storage Materials and Devices, *School of Chemistry, Xi'an Jiaotong University, Xi'an, 710049, P. R. China.*

[b]*Department of Chemistry, The University of Hong Kong, Hong Kong, 999077, P. R. China.*

[c]*Research Center for Tissue Repair and Regeneration affiliated to the Medical Innovation Research Department, PLA General Hospital and PLA Medical College, Beijing 100048, P. R. China.*

[+]These authors contributed equally to this work.

*To whom correspondence should be addressed.

E-mail: guoqing92@xjtu.edu.cn; liuxipla@163.com; guoln81@xjtu.edu.cn

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1. General Information

High-resolution transmission electron microscopy (HRTEM) was performed by JEM 2100F (operated at an accelerating voltage of 200 kV). UV-vis absorption spectra and PL spectra of $CsPbBr_3$ NCs hexane solution were recorded by Lambd950 and LS-55, respectively. The X-ray photoelectron spectra (XPS) measurements were performed by an ESCALAB 250 spectrophotometer with Al-Kα radiation. And the binding energy scale was using C 1s peak at 284.8 eV. X-ray powder diffraction pattern (XRD) was conducted on a Bruker AXS D8 X-ray diffractometer (parameters: Cu Kα, λ = 1.5406 Å, 100 mA, and 40 kV), and the $CsPbBr_3$ NCs dispersed in hexane were dropped on the surface of clean glass and measured. FT-IR spectra was recorded on a FT-IR spectrometer (Nicolet) with a KBr disk. PL spectrum and time-resolved PL decay curves for $CsPbBr_3$ powers capped with BF_4^- were conducted on a FLS-920 fluorescence lifetime spectrophotometer (Edinburgh Instruments, UK) under the excitation of 405 nm. ^1H NMR, ^{13}C NMR and ^{19}F NMR were recorded using a JEOL 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in ppm from TMS with the solvent resonance. Standard abbreviations indicating multiplicity were used as following: s = singlet, d = doublet, t = triplet, dd = double doublet, q = quartet, m = multiplet. HRMS was obtained on a WATERS I-Class VION IMS Q-Tof with an ESI source. All reagents were purchased from commercial suppliers and used without further purification.

2. Synthesis of $CsPbBr_3$ NCs

$CsPbBr_3$ NCs were synthesized by reported methods, which involved following steps:

(1) Synthesis of Cs-oleate stock solution: Cs-oleate solution was synthesized according to previously reports.[1, 2] In a typical synthesis, ODE (8.75 mL) and OA (1.25 mL) were added to a 25 mL three-necked flask with Cs_2CO_3 (0.326 g, 1.0 mmol), which was degassed with purging N_2 at 120 °C for 1 h. The temperature was raised to 150 °C using a mantle and kept for several minutes until the complete dissolution of Cs_2CO_3. After that, a light-yellow clear solution was obtained, which should be preheated to above 80 °C before use.

(2) Synthesis of $CsPbBr_3$ seed clusters: $CsPbBr_3$ seed clusters were prepared by reported methods.[1, 2] Briefly, ODE (9.6 mL), OA (1.8 mL) and OLA (1.8 mL) were introduced to a 25 mL three-necked flask with $PbBr_2$ (0.22 g, 0.6 mmol). The reaction flask was degassed with purging N_2 at 120 °C for 1 h. The solution

was cooled down to room temperature naturally. Subsequently, the above prepared Cs-oleate solution (0.66 mL) was quickly injected into the flask with severely stirring under N_2 at room temperature. After 10 min stirring, a turbid solution was obtained. The precipitate was collected by centrifugation (7500 rpm, 10 min). After that, the seed clusters solution was obtained by dispersing the precipitate into 3 mL ODE for further use.

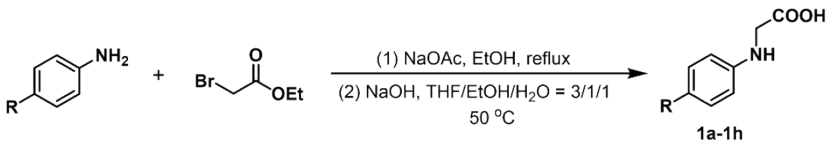
(3) Synthesis of $CsPbBr_3$ nanocubes (Cube): $CsPbBr_3$ nanocubes were synthesized according to reported method.[1, 2] 14 mL ODE was added into a 25 mL three-necked flask and degassed under vacuum for 30 min. The flask was filled with purging N_2 and heated at 120 °C for 1 h. Then the temperature was increased to 180 °C using a mantle. The above obtained seed clusters solution (4.0 mL) was quickly injected under N_2 and heated for 5 min. Then, the solution was cooled down to room temperature naturally. The nanocrystals were collected by centrifugation (7500 rpm, 10 min) and washed twice with hexane.

(4) Synthesis of $CsPbBr_3$ nanocube polyhedron nanocrystals (Poly): $CsPbBr_3$ polyhedron nanocrystals were synthesized by reported methods.[1, 2] 14 mL ODE was introduced into a 25 mL three-necked flask and degassed under vacuum for 30 min. It was heated to 120 °C under N_2 for 1 h. The temperature was increased to 230 °C, and the prepared seed clusters solution (4.0 mL) was quickly injected under N_2 and kept for 10 min. The solution was cooled down to room temperature naturally. The solution was centrifuged (7500 rpm, 10 min) and the precipitate was collected, which was washed twice with hexane. After that, $CsPbBr_3$ polyhedron nanocrystals were obtained.

Ligand exchange of NCs: Ligand exchange was performed by reported methods.[3, 4] $CsPbBr_3$ nanocrystals (250 mg) were dispersed in 10 mL ethyl acetate. NH_4BF_4 (30 mg) was dispersed in 1 mL ethyl acetate, which was slowly added into the $CsPbBr_3$ ethyl acetate solution under vigorous stirring. After stirring for 30 min, the solution was centrifuged (7500 rpm, 10 min), and the precipitate was collected. It was dried at 60 °C under vacuum and $CsPbBr_3$ capped with BF_4^- was obtained.

3. Synthesis of Starting Materials

3.1 General procedure for the synthesis of *N*-aryl amino acids **1a**-**1h**

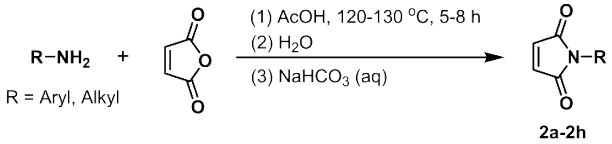


1a-1h

Compounds **1a-1h** were prepared according to the **General Procedure 1** (**GP1**).[5] Para-substituted

substituted aniline (5 mmol, 1.0 equiv), ethyl bromoacetate (6 mmol, 1.2 equiv) and anhydrous sodium acetate (10 mmol, 2.0 equiv) were added into a 100 mL reaction tube with 20 mL anhydrous ethanol and refluxed for 12 h. The reaction solution was filtered to remove the precipitate and the solvent was rotary removed by evaporation. The product was purified by column chromatography (petroleum ether/EtOAc = 10/1) to give *N*-phenylglycine ester. *N*-phenylglycine ester (1.0 mmol, 1.0 equiv), NaOH (3.3 mmol, 3.3 equiv), H_2O (10 mL), EtOH (10 mL) and THF (30 mL) were added to a 100 mL reaction tube and stirred at 50 °C for 3 h. Then the reaction solution was concentrated to remove organic solution, and the resulted aqueous layer was extracted with EA (3 × 10 mL) to remove the organic waste. After that, hydrochloric acid was added into the aqueous layer to acidify until pH = 2~3. It was extracted with ethyl acetate (3 × 20 mL). The combined organic layer was washed with NaCl aqueous solution and dried over Na_2SO_4. The solution was concentrated to give the target products **1a**-**1h** (Yields: 72-92%).

3.2 General procedure for synthesis of *N*-aryl maleimides **2a**-**2h**



Compounds **2a-2h** were prepared according to the **General procedure 2** (**GP2**).[6] Maleic anhydride (6 mmol, 2.0 equiv) was added to 30 mL acetic acid and stirred until maleic anhydride was completely dissolved. Aniline (3 mmol, 1.0 equiv) was added to above mixture at room temperature and reacted at 125 °C for 5-8 h. Then the solution was transferred to a 500 mL beaker and saturated sodium bicarbonate aqueous solution was slowly dropped until no bubble was produced. Subsequently, ethyl acetate (3 × 30 mL) was added to extract organics. The combined organic layer was washed with NaCl aqueous solution and dried with Na_2SO_4. After that, organic layer was concentrated to afford residue, which was purified by column chromatography on silica gel to obtain high purity substituted maleimide (yellow solid) in good yields (Yields: 80-94 %).

4. General Experimental Procedure

Compounds **3** were prepared according to the **General Procedure 3** (**GP3**): $CsPbBr_3$ powders capped with $BF4^-$ (3.0 mg) were added into a 25 mL reaction tube with magnetic stirring bar, which

were dispersed in 3.0 mL EA. Then substrates **1** (0.4 mmol, 2.0 equiv) and **2** (0.2 mmol, 1.0 equiv) were introduced into the above solution. The reaction tube was sealed and irradiated by 10 W blue LEDs (λ = 450 nm) at room temperature for 1.0 h. After reaction, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to give the target product **3**.

5. Photoelectrochemical Measurements

All measurements were conducted on a Zennium electrochemical workstation (Germany, Zahner Company) in a conventional three-electrode system. The resultant electrode served as the working electrode, platinum as the counter electrode and Ag/AgCl electrode as the reference electrode. A 0.1 M $TBAPF_6$ (tetrabutylamine hexafluorophosphate) acetonitrile solution was used as the electrolyte. The working electrodes were prepared by adding 10 μL Nafion (5%) aqueous solution into a 2 mL $CsPbBr_3$ NCs (3.5 mg) ethyl acetate solution. Then 200.0 μL obtained solution was dropped onto a clean ITO conductive glass with an active area of about 1.0 cm^2, which was washed by ultrasonication with distilled water, ethanol, and isopropanol for 15 s, and dried in a vacuum oven before experiments. The obtained electrode was dried under inert atmosphere. For photocurrent response versus time (i-t curve), a 300 W Xe lamp was used as the light source with switching on and off mode. The electrochemical impedance spectroscopy (EIS) results were recorded at the open circuit potential using a frequency ranged from 10^5 Hz to 10^{-2} Hz.

6. DFT Calculations

Density functional theory was performed using the Vienna ab initio simulation package (VASP).[7, 8] Exchange-correlation interactions were described by the generalized gradient approximation (GGA) in the form of Perdew-Burke-Ernzerhof (PBE) function,[9] and the ion-electron interactions were treated by the projector augmented wave (PAW) method.[10] The cut-off energy for the plane wave basis was set to be 400 eV. Brillouin zone integration was sampled with a K-mesh of 0.04 2π/Å for structure optimization. The convergence criteria for energy and force were set to be 10^{-7} eV/atom and 0.02 eV/Å, respectively. Dimer method was used to find the transition states.[11, 12]

To build the adsorption models, the $CsPbBr_3$ (002), $CsPbBr_3$ (110) and $CsPbBr_3$ (112) planes were initially cleaved and expanded into 2 × 2 supercell. The $CsPbBr_3$ (012) plane was initially cleaved and

expanded into 3 × 1 supercell. The $CsPbBr_3$ (100) plane was cleaved, and the resultant was the same to that of (002) plane. Vacuum above lattice plane was set to be 14 Å.

7. The selected area fast Fourier transform (FFT) pattern of Cube

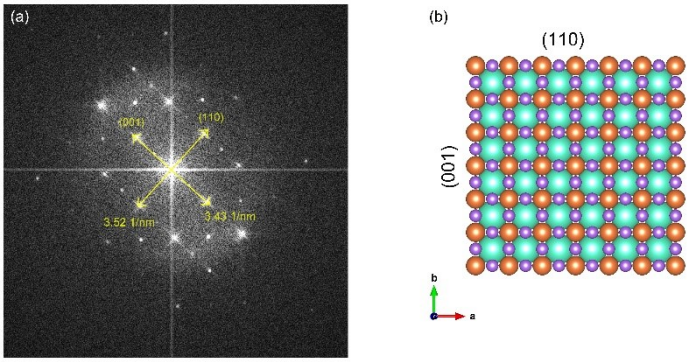


Fig. S1 FFT pattern (a) and the alternative atomic model (b) of Cube.

8. UV-vis absorption spectra of Cube and Poly

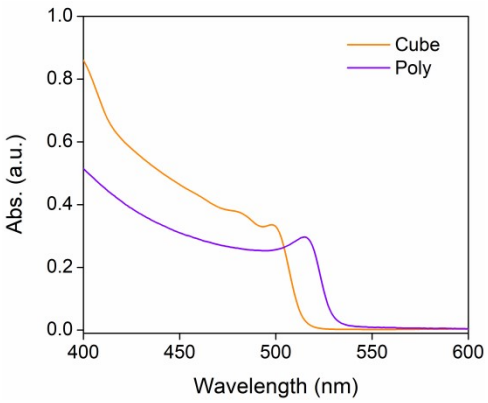


Fig. S2 UV-vis absorption spectra of Cube and Poly dispersed in hexane solution at room temperature.

9. PL spectra of Cube and Poly

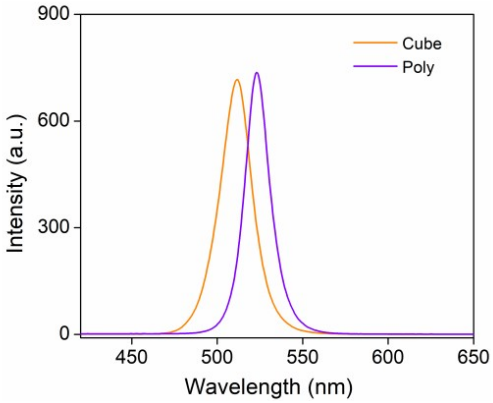


Fig. S3 PL spectra of Cube and Poly dispersed in hexane solution at room temperature.

10. FFT pattern of Poly

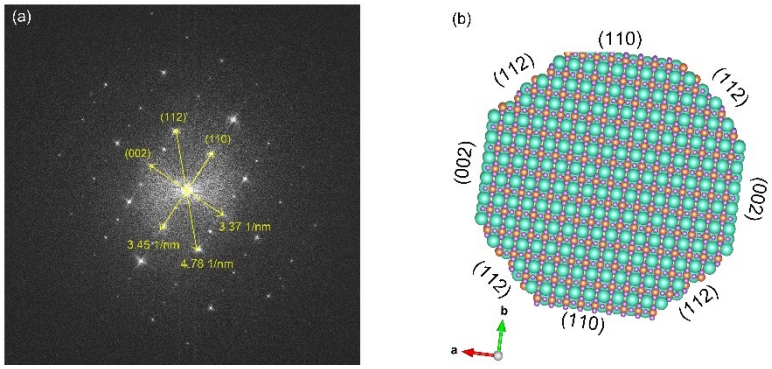


Fig. S4 FFT pattern (a) and the alternative atomic model (b) of Cube.

11. Full XPS spectra of Cube and Poly

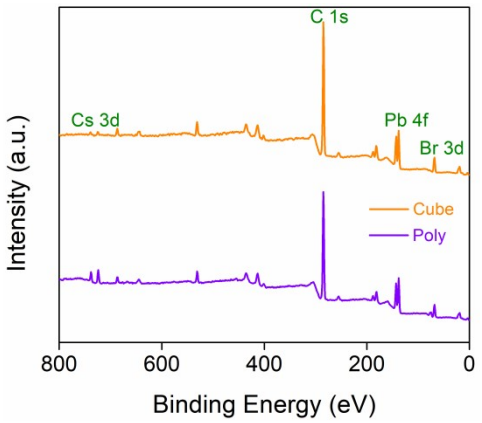


Fig. S5 Full XPS spectra of Cube and Poly.

12. High-resolution XPS spectrum of Cube and Poly

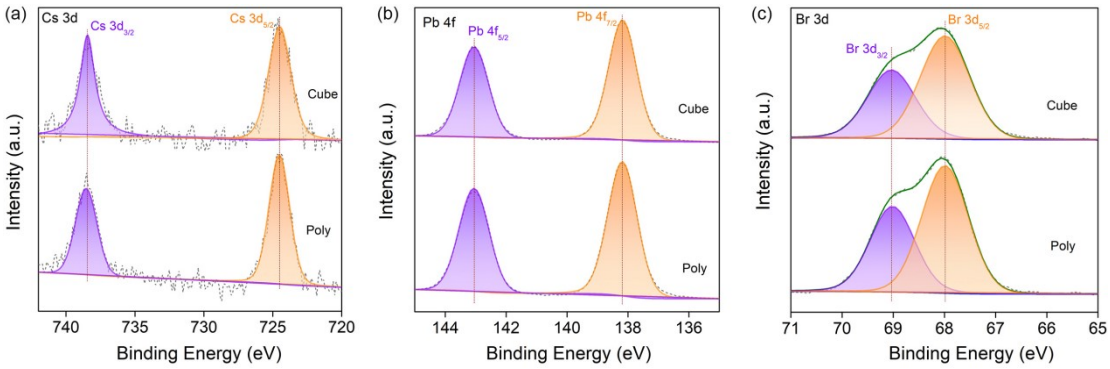


Fig. S6 High-resolution XPS spectrum of (a) Cs 3d, (b) Pb 4f and (c) Br 3d for Cube and Poly.

13. XRD patterns of Cube and Poly

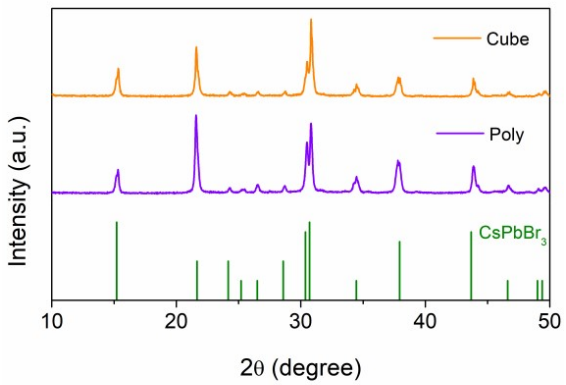


Fig. S7 XRD patterns of Cube and Poly.

14. FT-IR spectra of Cube

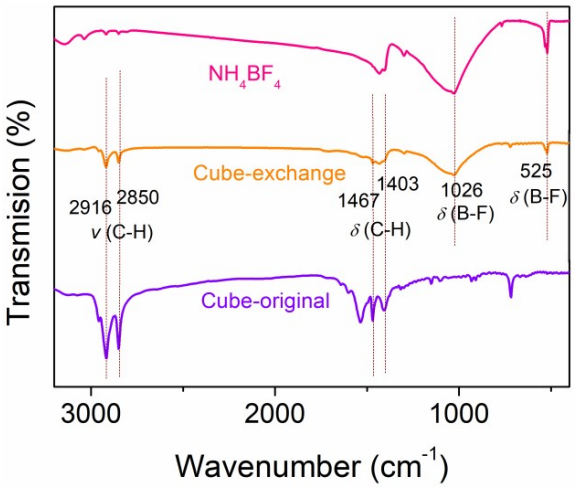
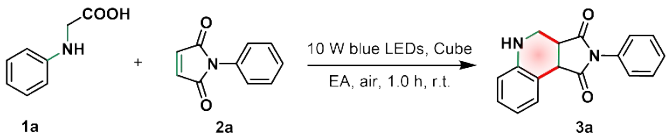


Fig. S8 FT-IR spectra of Cube before (Cube-original) and after ligand exchange (Cube-exchange).

15. Table S1. The ratio of 1a and 2a in cascade cyclization



Entry	Ratio of **1a**:**2a**	**Yield of 3a** (%)
1	1.0:1	60
2	1.5:1	63
3	2.0:1	75
4	2.5:1	75
5	3.0:1	78

Reaction conditions: **1a**, 0.2 mmol **2a**, and Cube (6.0 mg) which was dispersed in 3.0 mL EA, were added into 25 mL reaction tube under room temperature. The solution was irradiated by 10 W blue LEDs (λ = 450 nm) for 1.0 h. Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard based on **2a**.

16. Table S2. The amount optimization of Cube for cascade cyclization

Entry	Amount (mg)	**3a** Yield (%)
1	1.0	18
2	3.0	75
3	6.0	75

Reaction conditions: 0.4 mmol **1a**, 0.2 mmol **2a**, and Cube which was dispersed in 3.0 mL EA, were added into 25 mL reaction tube under room temperature. The solution was irradiated by 10 W blue LEDs (λ = 450 nm) for 1.0 h. Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard based on **2a**.

17. *Tauc* plots of Cube and Poly

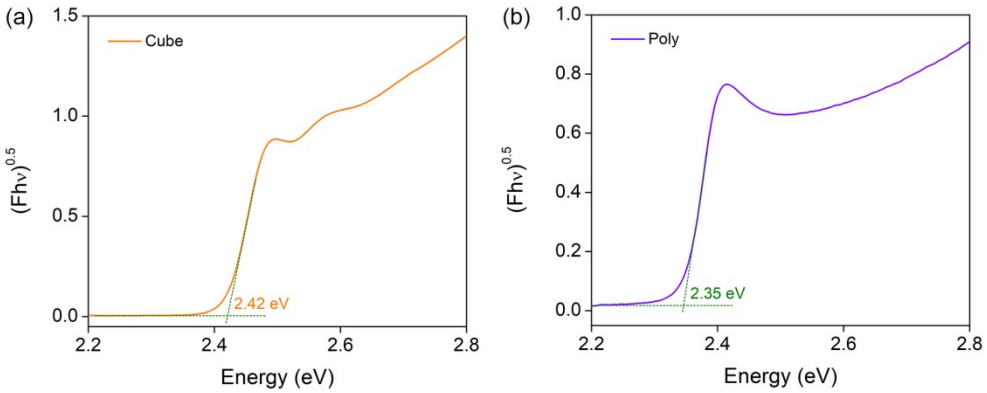


Fig. S9 The corresponding *Tauc* plots of (a) Cube and (b) Poly. As shown in Fig. S9, Cube exhibits a wide bandgap of ~2.42 eV, while Poly possesses a narrower bandgap of ~2.35 eV.

18. Calculation of VB band potentials of Cube and Poly

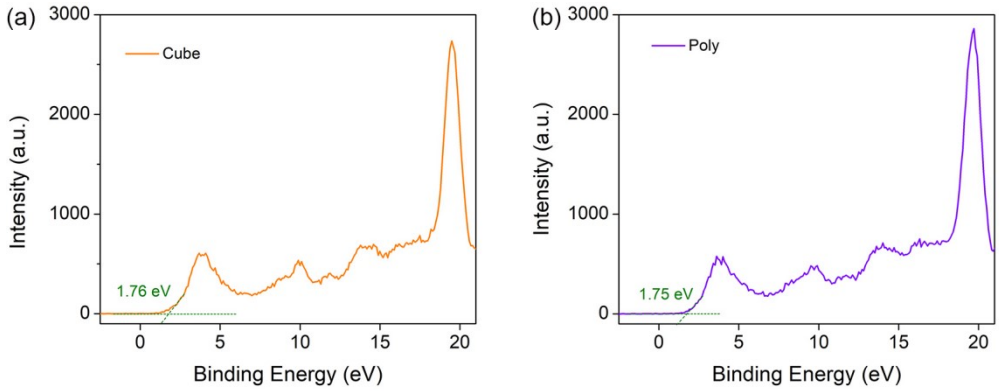


Fig. S10 High-resolution VB XPS spectra of (a) Cube and (b) Poly. As shown in Fig. S10, the valence bands of Cube and Poly are +1.76 and +1.75 V *vs* NHE, respectively.

19. Band structure of Cube and Poly

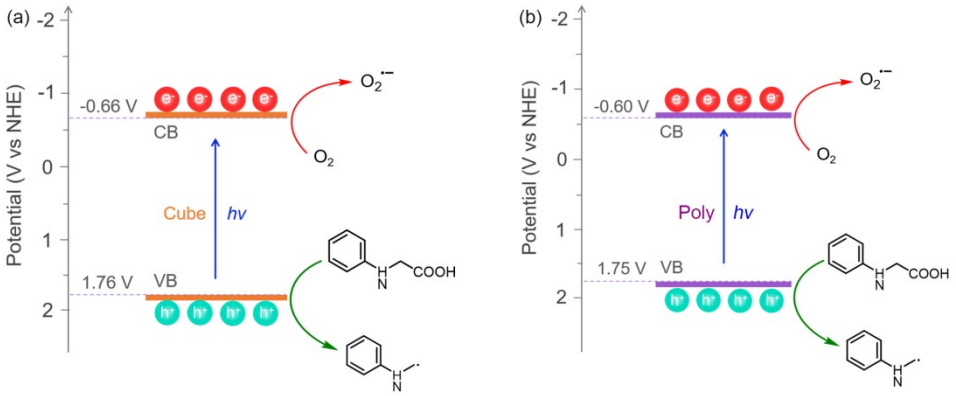


Fig. S11 Schematic illustration for the band structure of (a) Cube and (b) Poly. As shown in Fig. S11, it is both thermodynamically feasible for the redox reaction.

20. Table S3. Fitted parameter of PL lifetime in Fig. 3b

Sample	B_1	B_2	B_3	τ_1 / ns	τ_2 / ns	τ_3 / ns	τ / ns
Cube	1492.64	323.55	138.73	3.79	15.19	100	60.67
Poly	2315.4	414.60	95.76	0.19	6.73	71.14	50.12

The emission decays of Cube and Poly were studied and the decay curves for the samples were well fitted with three-exponential function *Y*(t) based on nonlinear least-squares, using the following equation:

$$Y(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$$

Where B_1, B_2, B_3 are fractional contributions from time-resolved emission decay lifetime τ_1, τ_2, τ_3 as shown in **Table S3**, which are assigned to (1) trap-assisted exciton recombination (τ_1), (2) exciton recombination (τ_2), and (3) free-carrier recombination (τ_3). The average lifetime τ could be obtained from the following equation:

$$<\tau> = \frac{B_1\tau_1^2 + B_2\tau_2^2 + B_3\tau_3^2}{B_1\tau_1 + B_2\tau_2 + B_3\tau_3}$$

21. Table S4. Resistance values in fitted equivalent circuit of EIS plots for Cube and Poly

Sample	Rs (Ω)	Rct (Ω)
Cube	21.5	2319
Poly	23.46	3927

22. Time-resolved PL spectra of Cube and Poly before ligand exchange

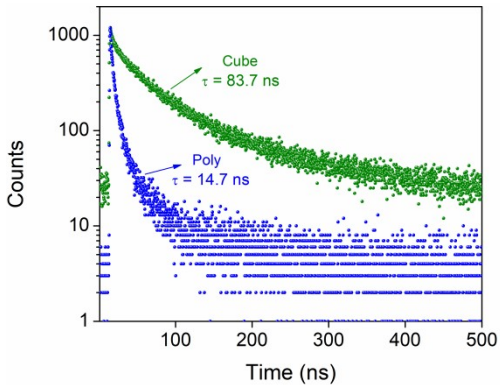


Fig. S12 Time-resolved PL spectra of Cube and Poly before ligand exchange (excitation laser: 405 nm).

23. Table S5. Fitted parameter of PL lifetime in Fig. S12

Sample	B_1	B_2	B_3	τ_1 / ns	τ_2 / ns	τ_3 / ns	τ / ns
Cube	339.61	578.36	205.88	4.02	37.89	126.49	83.7
Poly	775.60	273.99	20.43	2.84	11.53	50.00	14.7

The emission decays of Cube and Poly were studied and the decay curves for the samples were well fitted with three-exponential function *Y*(t) based on nonlinear least-squares, using the following equation:

$$Y(t) = B_1 \exp(-t/\tau_1) + B_2 \exp(-t/\tau_2) + B_3 \exp(-t/\tau_3)$$

Where B_1, B_2, B_3 are fractional contributions from time-resolved emission decay lifetime τ_1, τ_2, τ_3 as shown in **Table S5**. The average lifetime τ could be obtained from the following equation:

$$<\tau> = \frac{B_1\tau_1^2 + B_2\tau_2^2 + B_3\tau_3^2}{B_1\tau_1 + B_2\tau_2 + B_3\tau_3}$$

24. Electrochemical measurements of Cube and Poly with organic ligands

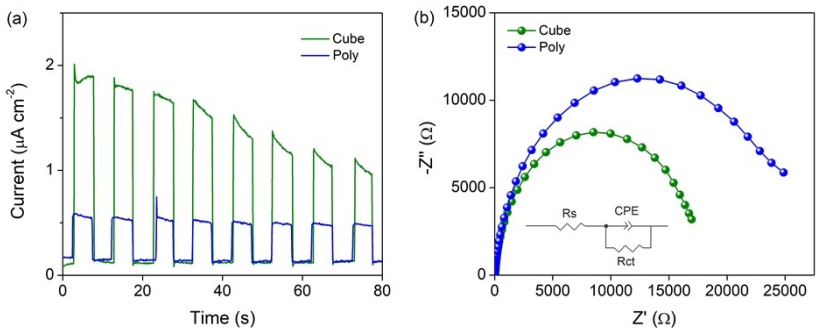


Fig. S13 (a) Photocurrent responses and (b) EIS Nyquist plots of Cube and Poly with organic ligands (inset is the equivalent curve), respectively.

25. Table S6. Resistance values in fitted equivalent circuit of EIS plots for Cube and Poly with organic ligands

Sample	Rs (Ω)	Rct (Ω)
Cube	26.56	18733
Poly	32.24	26976

26. HRMS spectrum of reaction system with addition BHT

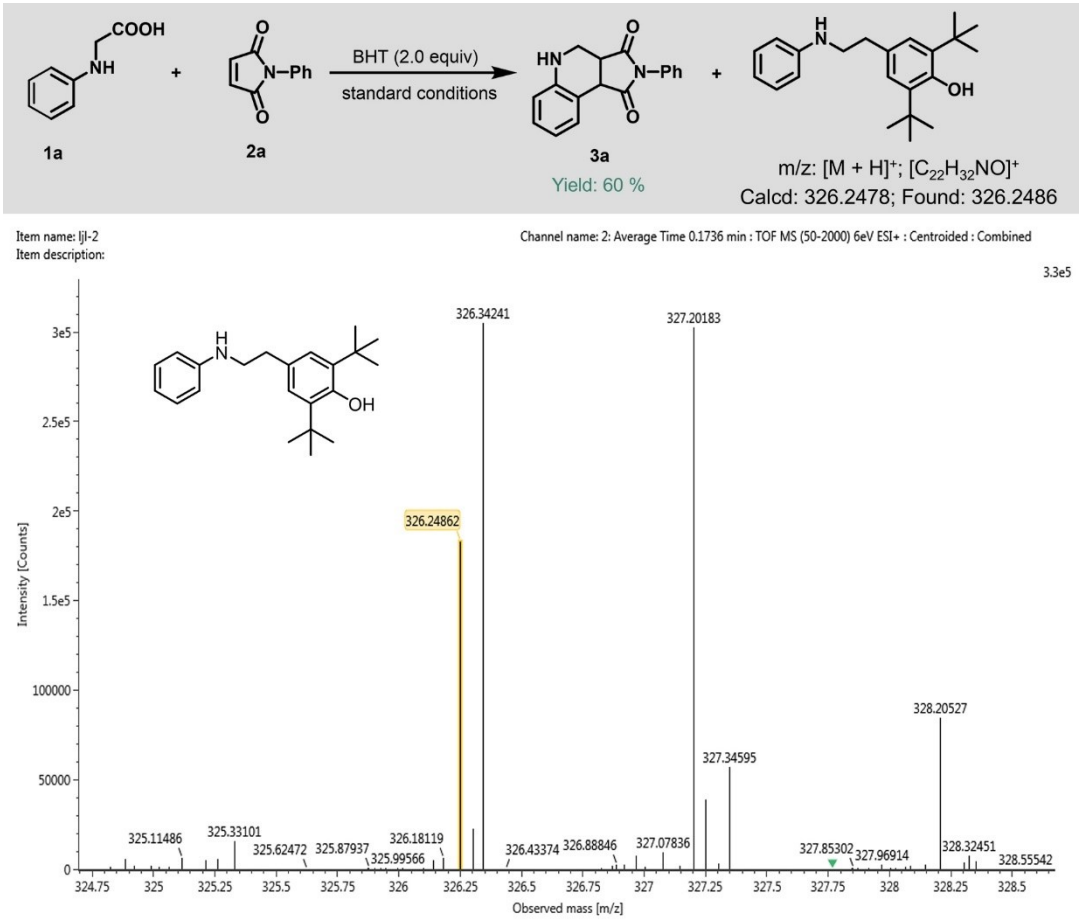
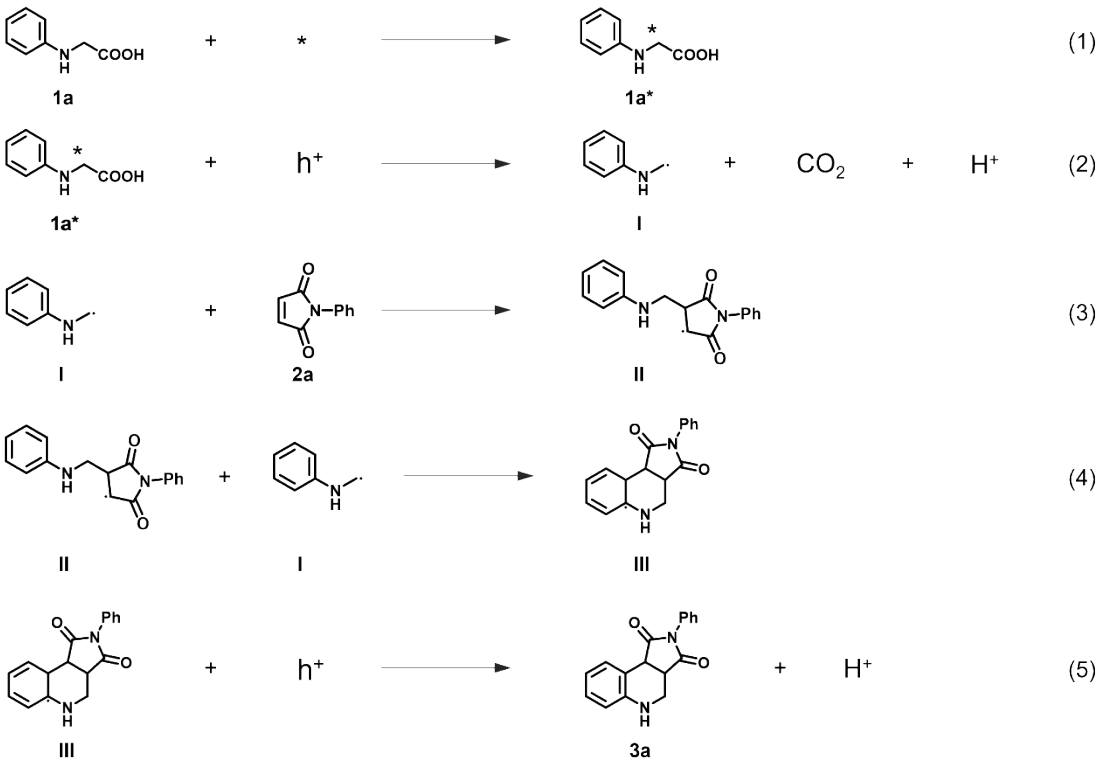


Fig. S14 Mass spectrum (ESI, positive) of reaction system with addition BHT (2.0 equiv) upon 1.0 h irradiation. HRMS (ESI+) Calcd. for $C_{22}H_{32}NO$ $[M + H]^+$: 326.2478, Found: 326.2486. The result indicated the formation of phenylaminomethyl radical.

27. Proposed mechanism of 1a reacted with 2a



Note: * represents the active sites on NC surface.

Fig. S15 The detailed mechanism of **1a** reacted with **2a** to produce **3a**.

28. The adsorption models of 1a and intermediate I on various facets

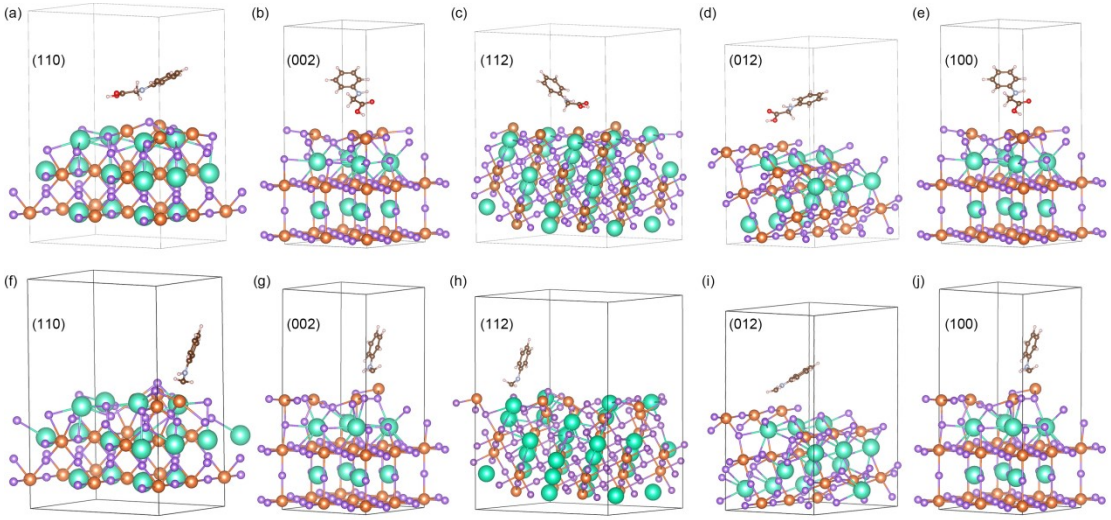


Fig. S16 The adsorption behavious of substrate **1a** (a-e) and intermediate **I** (f-j) on various facets of $CsPbBr_3$ nanocrystals.

29. Table S7. Calculated adsorption energies of 1a on series facets of NC

Facet	Adsorption energy (eV)
(110)	-0.26
(002)	-0.38
(112)	0.07
(012)	-0.03
(100)	-0.38

30. Table S8. BET surface areas of Cube and Poly

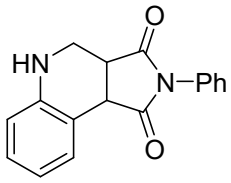
Sample	BET surface area ($m^2 g^{-1}$)
Cube	0.65
Poly	1.50

31. Table S9. Calculated adsorption energies of intermediate I on series facets

Facet	Adsorption energy (eV)
(110)	-1.88
(002)	-0.89
(112)	-2.46
(012)	-2.35
(100)	-0.89

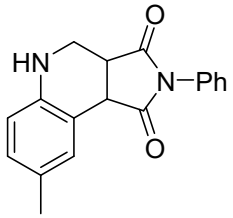
32. Characterization Data for All Compounds

2-phenyl-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3aa)



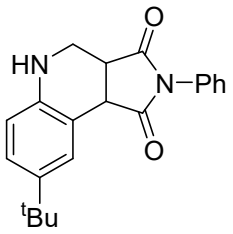
The compound was prepared according to **GP3** and isolated as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.44-7.40 (m, 2H), 7.37-7.33 (m, 1H), 7.27-7.25 (m, 2H), 7.11 (td, *J* = 8, 1.2 Hz, 1H), 6.87 (td, *J* = 8, 0.8 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.15 (d, *J* = 9.2 Hz, 1H), 3.75 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.55-3.51 (m, 1H), 3.30 (dd, *J* = 11.6, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.5, 175.8, 146.0, 132.0, 130.6, 129.1, 128.7, 128.5, 126.5, 120.3, 116.9, 115.9, 43.3, 41.7, 41.6. The spectral data matched those reported previously.[13]

8-methyl-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3ba)



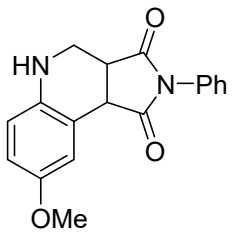
The compound was prepared according to **GP3** and isolated as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.44-7.40 (m, 2H), 7.36-7.33 (m, 2H), 7.27-7.25 (m, 2H), 6.93-6.91 (m, 1H), 6.53 (d, *J* = 8.0 Hz, 1H), 4.11 (d, *J* = 9.2 Hz, 1H), 3.74 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.53-3.49 (m, 1H), 3.27 (dd, *J* = 11.2, 4.4 Hz, 1H), 2.27(s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.7, 176.0, 143.8, 132.1, 130.8, 129.5, 129.2, 129.1, 128.6, 126.5, 116.8, 115.8, 43.4, 42.0, 41.6, 20.7. The spectral data matched those reported previously.[13]

8-(tert-butyl)-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3ca)



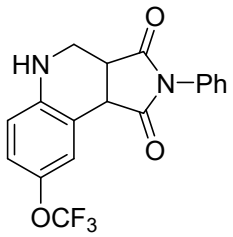
The compound was prepared according to **GP3** and isolated as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 (d, *J* = 2.0 Hz, 1H), 7.44-7.40 (m, 2H), 7.37-7.33 (m, 1H), 7.29-7.25 (m, 2H), 7.14 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 4.15 (d, *J* = 9.2 Hz, 1H), 3.72 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.53-3.49 (m, 1H), 3.30 (dd, *J* = 11.2, 4.4 Hz, 1H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.6, 175.9, 143.5, 143.1, 132.1, 129.1, 128.6, 127.4, 126.5, 125.5, 116.3, 115.5, 43.3, 41.9, 41.7, 34.2, 31.6. HRMS (ESI) calcd for $C_{21}H_{22}N_2O_2$ $[M+H]^+$ 335.1754, found 335.1765.

8-methoxy-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3da)



The compound was prepared according to **GP3** and isolated as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.45-7.40 (m, 2H), 7.38-7.33 (m, 1H), 7.28-7.26 (m, 2H), 7.12-7.11 (m, 1H), 6.72 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.56 (d, *J* = 9.2 Hz, 1H), 4.11 (d, *J* = 9.2 Hz, 1H), 3.78 (s, 3H), 3.71 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.51-3.47 (m, 1H), 3.24 (dd, *J* = 11.2, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.6, 175.8, 153.6, 140.0, 132.0, 129.1, 128.7, 126.5, 117.7, 116.8, 115.3, 114.9, 55.8, 43.3, 42.3, 41.9. HRMS (ESI) calcd for $C_{18}H_{16}N_2O_3$ $[M+H]^+$ 309.1234, found 309.1241.

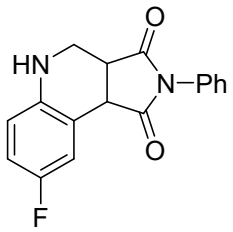
2-phenyl-8-(trifluoromethoxy)-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3ea)



The compound was prepared according to **GP3** and isolated as a yellow paste solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.44-7.40 (m, 3H), 7.37-7.33 (m, 1H), 7.25-7.23 (m, 2H), 6.95 (dd, *J* = 8.8, 2.0 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 4.08 (d, *J* = 9.6 Hz, 1H), 4.00 (s, 1H), 3.67 (dd, *J* = 11.2, 2.4 Hz, 1H), 3.49-3.45 (m, 1H), 3.23 (dd, *J* = 11.6, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.2, 175.2, 144.9, 141.9 (q, *J* = 2.0 Hz), 131.8, 129.2, 128.8, 126.4, 123.5, 121.7, 120.7 (q, *J* = 257.3 Hz), 117.5, 116.3, 42.8, 41.5, 41.3. ^{19}F NMR (376 MHz, Chloroform-d) δ -58.17. HRMS (ESI) calcd

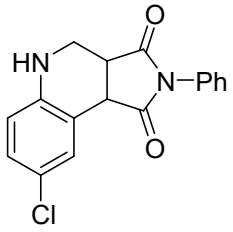
for $C_{18}H_{13}F_3N_2O_3$ $[M+H]^+$ 363.0951, found 363.0947.

8-fluoro-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3fa)



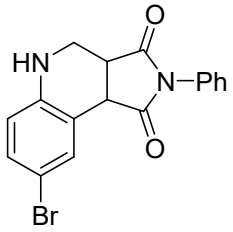
The compound was prepared according to **GP3** and isolated as a reddish yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.44-7.40 (m, 2H), 7.37-7.34 (m, 1H), 7.26-7.24 (m, 3H), 6.84-6.80 (m, 1H), 6.56-6.52 (m, 1H), 4.07 (d, *J* = 9.2 Hz, 1H), 3.70-3.67 (m, 1H), 3.49-3.46 (m, 1H), 3.25-3.20 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.3, 175.4, 156.8 (d, *J* = 239.5 Hz), 142.4 (d, *J* = 2.5 Hz), 131.9, 129.2, 128.8, 126.5, 118.0 (d, *J* = 7.8 Hz), 116.9 (d, *J* = 23.3 Hz), 116.6 (d, *J* = 7.8 Hz), 115.5 (d, *J* = 22.8 Hz), 43.0, 42.1, 41.6. ^{19}F NMR (376 MHz, Chloroform-d) δ -123.68. HRMS (ESI) calcd for $C_{17}H_{13}FN_2O_2$ $[M+H]^+$ 297.1034, found 297.1045.

8-chloro-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3ga)



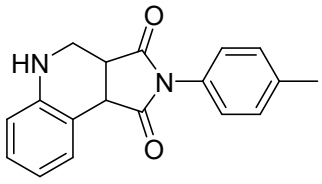
The compound was prepared according to **GP3** and isolated as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.52-7.51 (m, 1H), 7.45-7.40 (m, 2H), 7.38-7.34 (m, 1H), 7.26-7.24 (m, 2H), 7.05 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.55 (d, *J* = 8.4 Hz, 1H), 4.10 (d, *J* = 9.2 Hz, 1H), 3.74 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.54-3.49 (m, 1H), 3.28 (dd, *J* = 11.2, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.2, 175.3, 144.7, 131.9, 130.2, 129.2, 128.8, 128.6, 126.5, 124.7, 118.2, 116.9, 43.0, 41.6, 41.4. HRMS (ESI) calcd for $C_{17}H_{10}ClN_2O_2$ $[M+H]^+$ 313.0738, found 313.0750.

8-bromo-2-phenyl-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3ha)



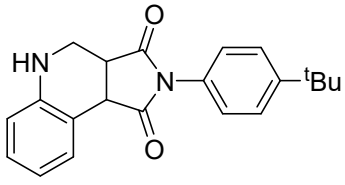
The compound was prepared according to **GP3** and isolated as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.67-7.66 (m, 1H), 7.46-7.41 (m, 2H), 7.39-7.35 (m, 1H), 7.27-7.25 (m, 2H), 7.20 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 4.11 (d, *J* = 9.2 Hz, 1H), 3.76 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.53-3.51 (m, 1H), 3.30 (dd, *J* = 11.2, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.1, 175.3, 145.1, 133.1, 131.9, 131.4, 129.2, 128.8, 126.5, 118.7, 117.4, 111.9, 43.0, 41.5, 41.3. HRMS (ESI) calcd for $C_{17}H_{13}BrN_2O_2$ $[M+H]^+$ 337.0233, found 357.0243.

2-(p-tolyl)-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3ab)



The compound was prepared according to **GP3** and isolated as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.24-7.22 (m, 2H), 7.14-7.12 (m, 2H), 7.11-7.09 (m, 1H), 6.87 (td, *J* = 7.6, 0.8 Hz, 1H), 6.62 (dd, *J* = 7.6, 0.8 Hz, 1H), 4.14 (d, *J* = 9.2 Hz, 1H), 3.74 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.53-3.49 (m, 1H), 3.30 (dd, *J* = 11.2, 4.4 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.7, 176.0, 146.1, 138.7, 130.6, 129.8, 129.4, 128.5, 126.3, 120.2, 116.9, 115.8, 43.3, 41.7, 41.6, 21.3. HRMS (ESI) calcd for $C_{18}H_{16}N_2O_2$ $[M+H]^+$ 293.1284, found 293.1284.

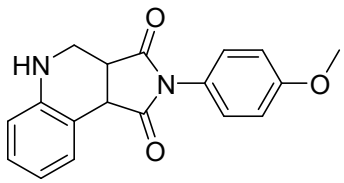
2-(4-(tert-butyl)phenyl)-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3ac)



The compound was prepared according to **GP3** and isolated as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.46-7.42 (m, 2H), 7.21-7.17 (m, 2H), 7.10 (td, *J* = 8.4, 1.2 Hz, 1H), 6.86 (td, *J* = 7.6, 0.8 Hz, 1H), 6.61 (d, *J* = 8.0 Hz, 1H), 4.13 (d, *J* = 9.6 Hz, 1H), 3.72 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.52-3.48 (m, 1H), 3.27 (dd, *J* = 11.2, 4.4 Hz, 1H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.7, 176.0, 151.6, 146.1,

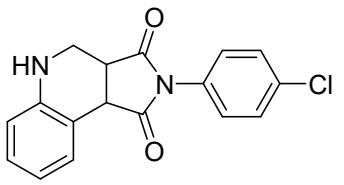
130.6, 129.3, 128.4, 126.1, 125.9, 120.1, 116.8, 115.7, 43.3, 41.6, 41.5, 34.8, 31.3. HRMS (ESI) calcd for $C_{21}H_{22}N_2O_2$ $[M+H]^+$ 335.1754, found 335.1753.

2-(4-methoxyphenyl)-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3ad)



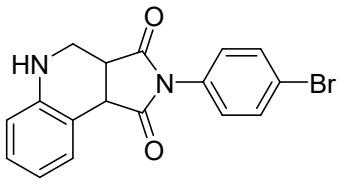
The compound was prepared according to **GP3** and isolated as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34 (d, *J* = 7.6 Hz, 1H), 7.12-7.08 (m, 2H), 7.04-7.02 (m, 1H), 7.01-6.98 (m, 2H), 6.73-6.67 (m, 2H), 4.16 (d, *J* = 9.2 Hz, 1H), 3.76 (s, 3H), 3.60-3.56 (m, 1H), 3.45 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.10 (dd, *J* = 11.6, 4.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.1, 176.5, 158.9, 147.2, 130.2, 128.1, 127.6, 125.0, 118.2, 116.9, 115.3, 114.2, 55.4, 42.7, 41.1, 40.9. HRMS (ESI) calcd for $C_{18}H_{16}N_2O_3$ $[M+H]^+$ 309.1234, found 309.1242.

2-(4-chlorophenyl)-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3ae)



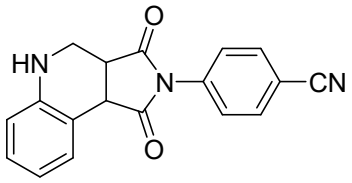
The compound was prepared according to **GP3** and isolated as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.42-7.38 (m, 2H), 7.26-7.22 (m, 2H), 7.15-7.11 (m, 1H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.16 (d, *J* = 9.6 Hz, 1H), 3.77 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.56-3.52 (m, 1H), 3.31 (dd, *J* = 11.2, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.3, 175.6, 146.1, 134.4, 130.6, 130.5, 129.3, 128.6, 127.7, 120.3, 116.7, 115.9, 43.5, 41.7, 41.6. HRMS (ESI) calcd for $C_{17}H_{13}ClN_2O_2$ $[M+H]^+$ 313.0738, found 313.0746.

2-(4-bromophenyl)-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3af)



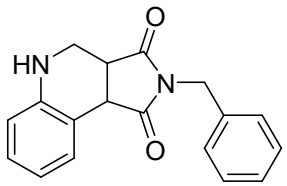
The compound was prepared according to **GP3** and isolated as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.56-7.54 (m, 1H), 7.53-7.51 (m, 2H), 7.19-7.17 (m, 1H), 7.16-7.15 (m, 1H), 7.11 (td, *J* = 7.6, 1.2 Hz, 1H), 6.87 (td, *J* = 7.6, 1.2 Hz, 1H), 6.62 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.15 (d, *J* = 9.2 Hz, 1H), 3.76 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.55-3.50 (m, 1H), 3.30 (dd, *J* = 12.0, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 177.3, 175.6, 146.1, 132.3, 131.0, 130.6, 128.6, 128.0, 122.5, 120.4, 116.7, 115.9, 43.5, 41.7, 41.6. HRMS (ESI) calcd for $C_{17}H_{13}BrN_2O_2$ $[M+H]^+$ 357.0233, found 357.0244.

4-(1,3-dioxo-2,3,3a,4,5,9b-hexahydro-1*H*-cyclopenta[*c*]quinolin-2-yl)benzonitrile (3ag)



The compound was prepared according to **GP3** and isolated as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.72-7.70 (m, 2H), 7.52-7.47 (m, 3H), 7.14-7.10 (m, 1H), 6.88 (td, *J* = 7.6, 0.8 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 4.19 (d, *J* = 9.6 Hz, 1H), 3.78 (dd, *J* = 11.2, 2.8 Hz, 1H), 3.59-3.55 (m, 1H), 3.30 (dd, *J* = 11.6, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 176.9, 175.2, 146.1, 136.0, 132.9, 130.5, 128.8, 126.9, 120.5, 118.2, 116.4, 116.0, 112.1, 43.5, 41.7, 29.8. HRMS (ESI) calcd for $C_{18}H_{13}N_3O_2$ $[M+H]^+$ 304.1080, found 304.1080.

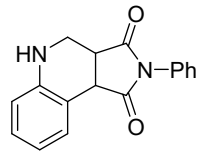
2-benzyl-3a,4,5,9b-tetrahydro-1*H*-cyclopenta[*c*]quinoline-1,3(2*H*)-dione (3ah)



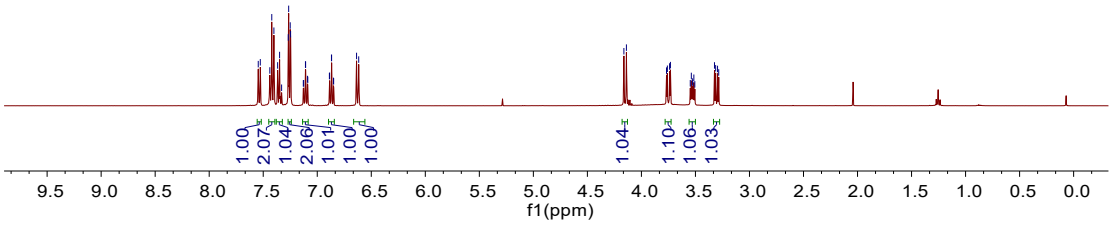
The compound was prepared according to **GP3** and isolated as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.48 (d, *J* = 7.6 Hz, 1H), 7.30-7.22 (m, 5H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 6.54 (td, *J* = 7.6, 1.2 Hz, 1H), 6.58 (dd, *J* = 8.0, 1.2 Hz, 1H), 4.63 (q, *J* = 14.4 Hz, 2H), 3.98 (d, *J* = 9.2 Hz, 1H), 3.63 (dd, *J* = 11.2, 3.2 Hz, 1H), 3.36-3.32 (m, 1H), 3.22 (dd, *J* = 11.2, 4.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 178.2, 176.5, 146.0, 135.7, 130.5, 128.7, 128.5, 128.4, 127.9, 120.2,

117.1, 115.8, 43.4, 42.9, 41.7, 41.5. The spectral data matched those reported previously.[13]

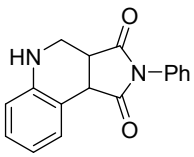
33. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR



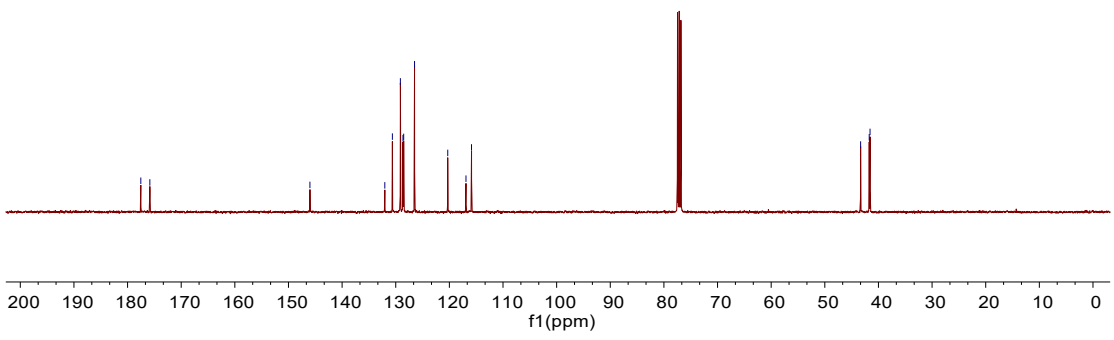
3aa



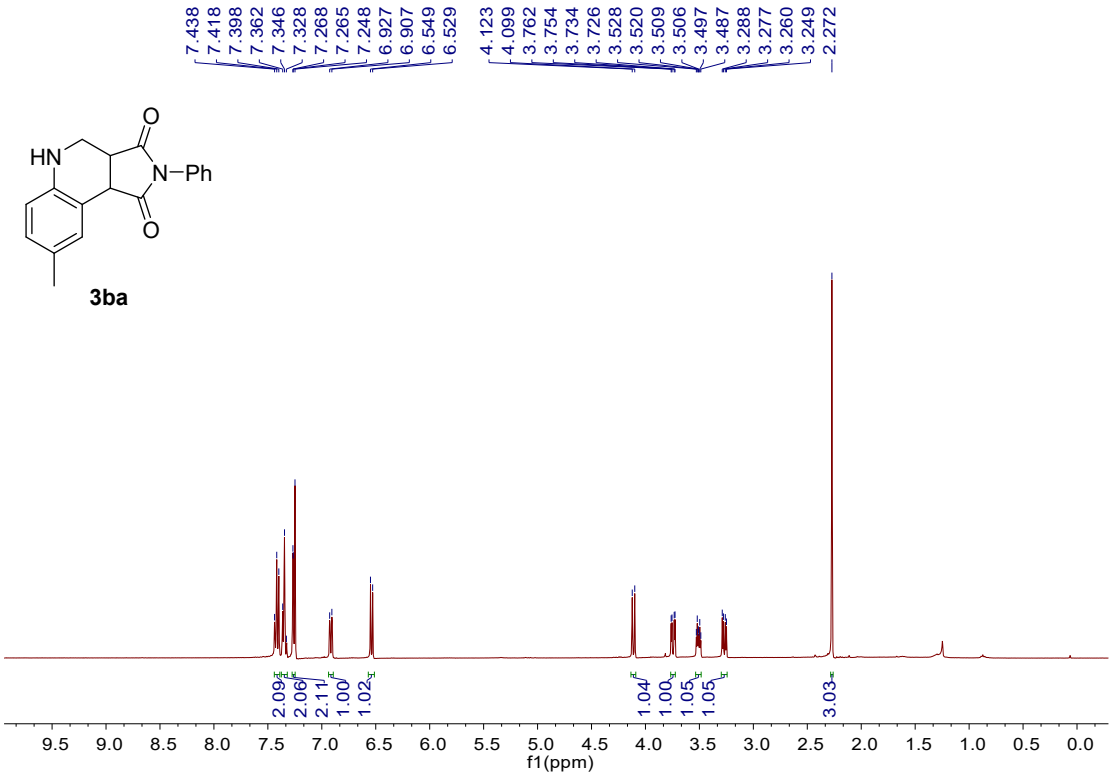
^{1}H NMR (400 MHz, $CDCl_3$) of **3aa**



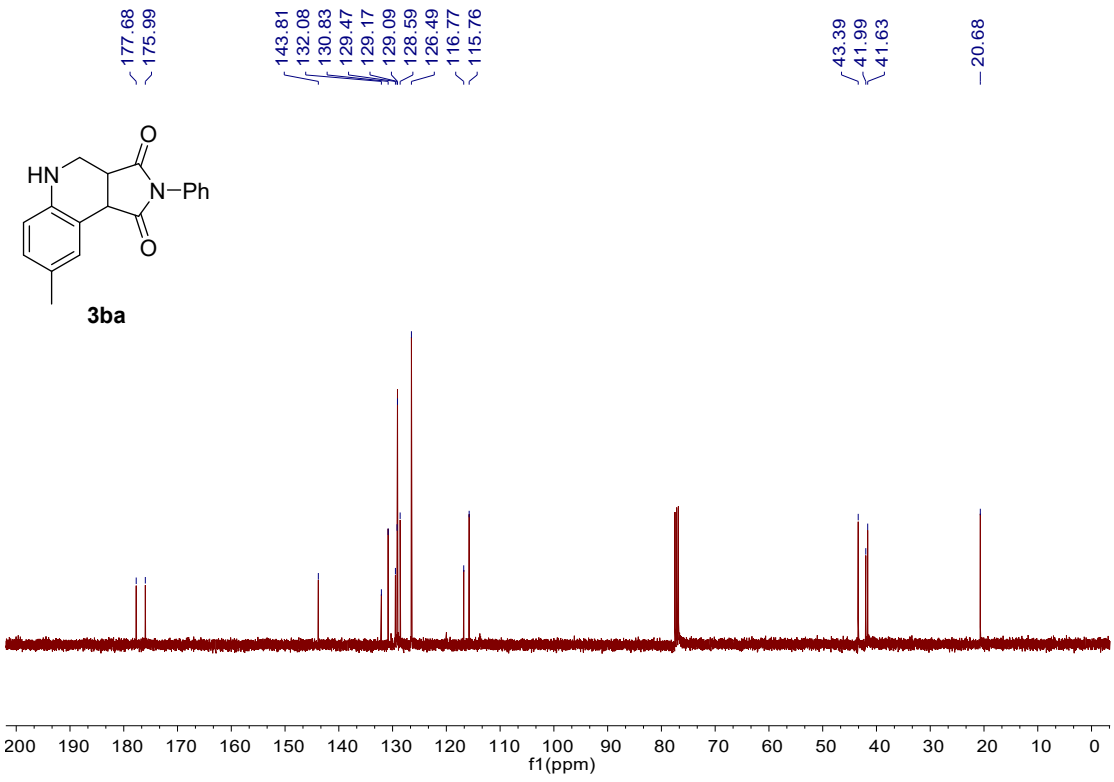
3aa



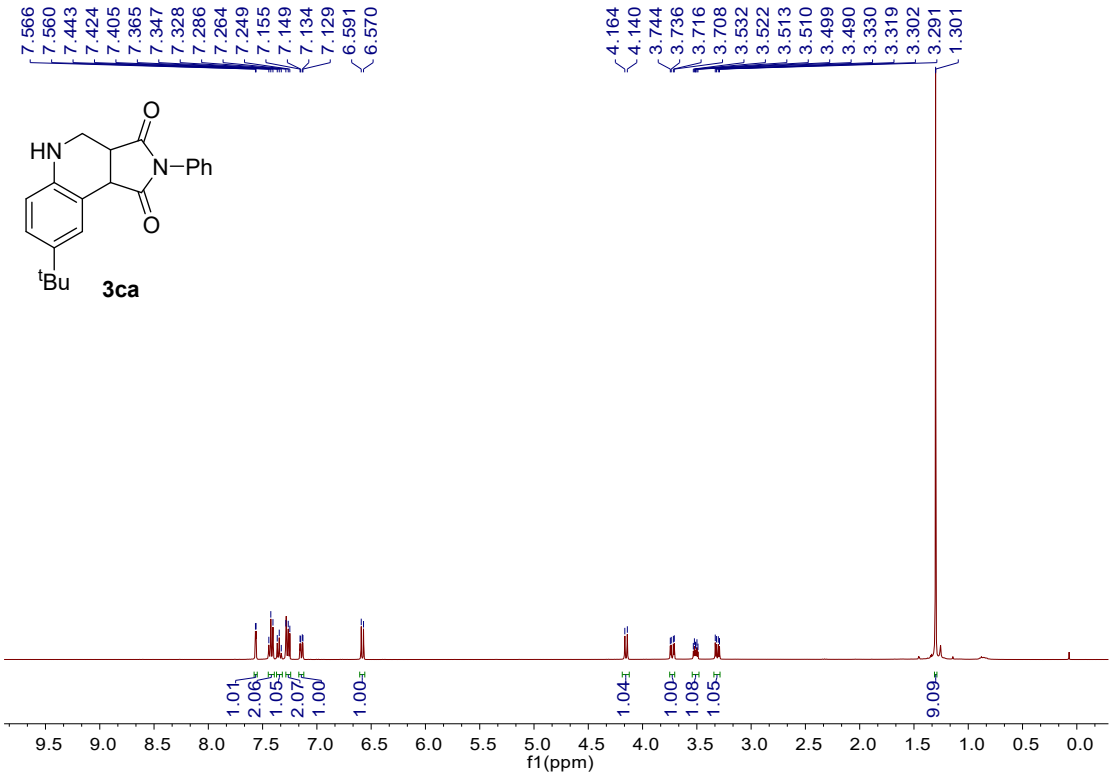
^{13}C NMR (101 MHz, $CDCl_3$) of **3aa**



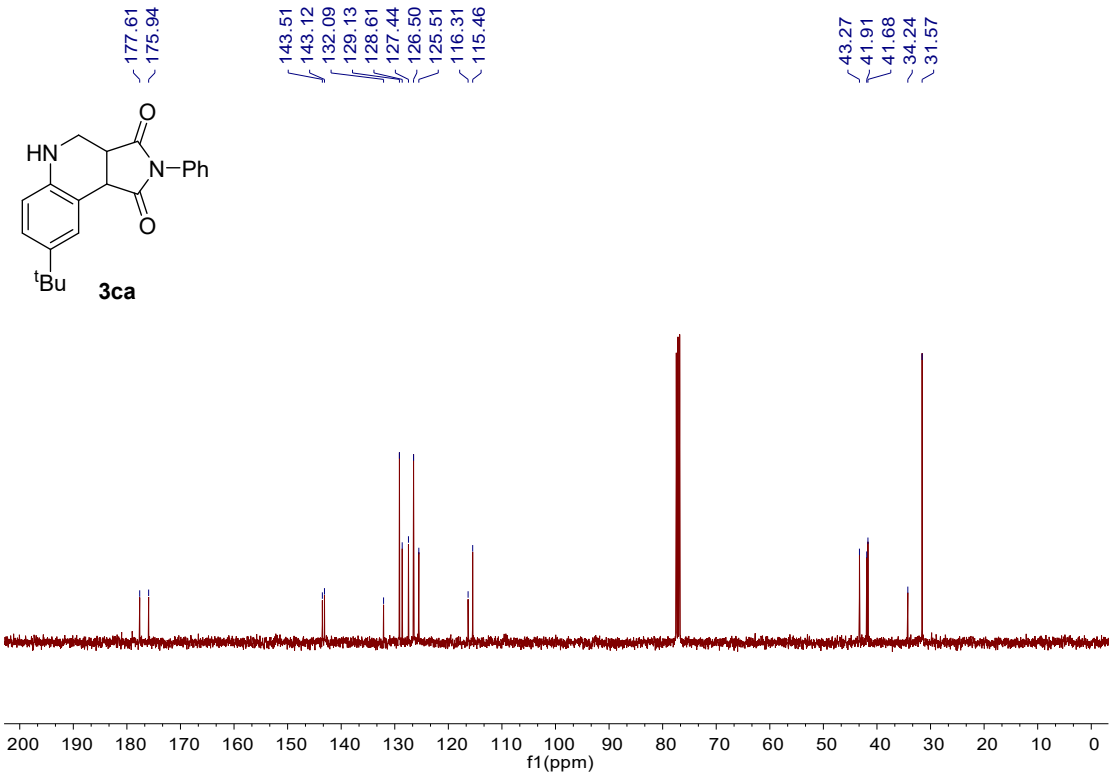
^{1}H NMR (400 MHz, $CDCl_3$) of **3ba**



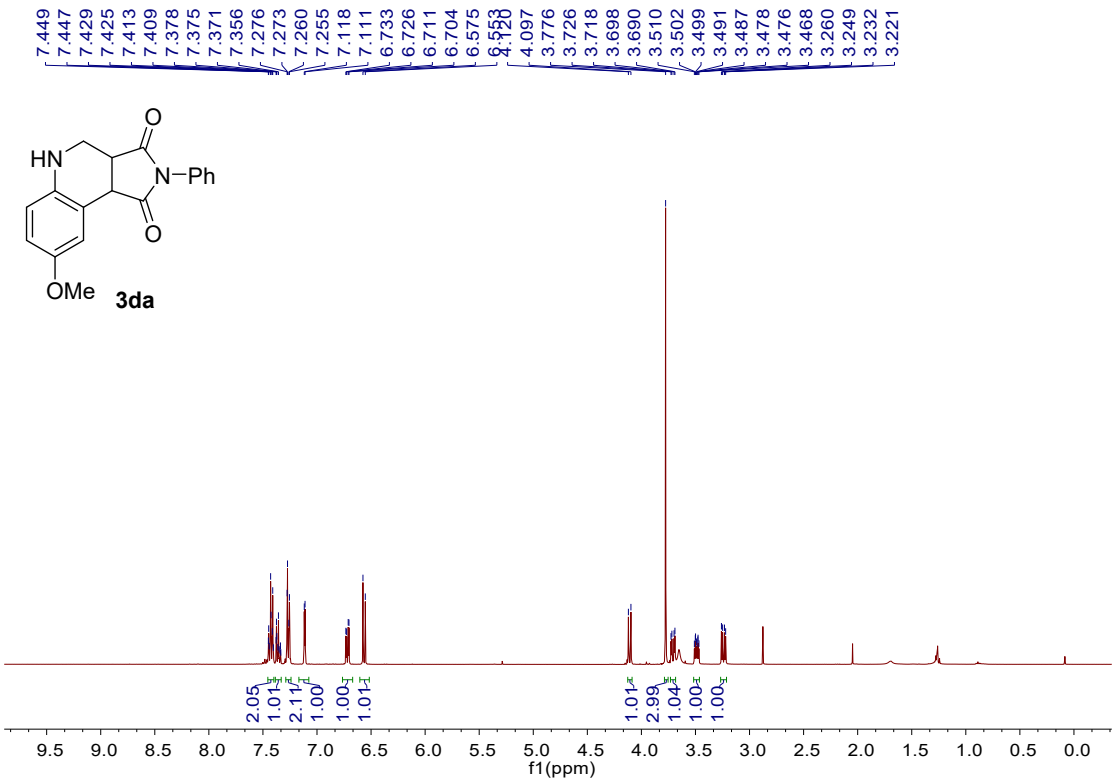
^{13}C NMR (101 MHz, $CDCl_3$) of **3ba**



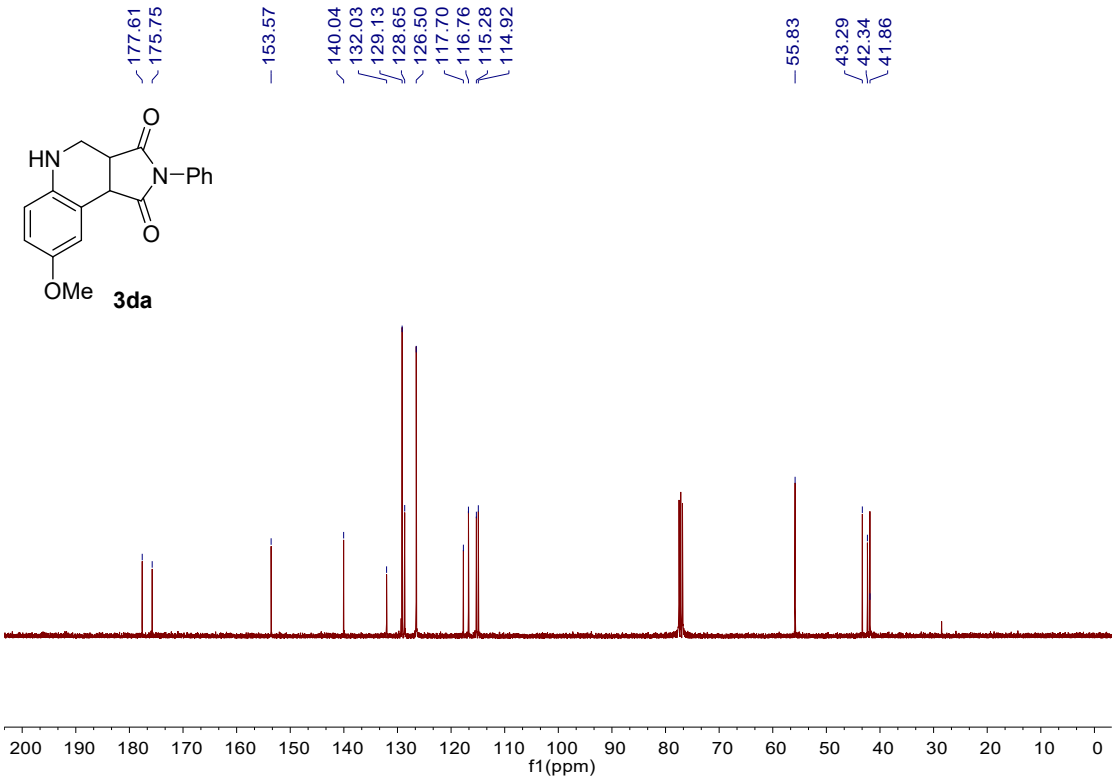
^{1}H NMR (400 MHz, $CDCl_3$) of **3ca**



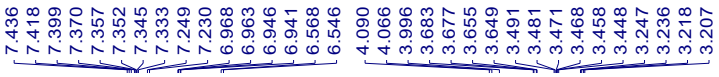
^{13}C NMR (101 MHz, $CDCl_3$) of **3ca**

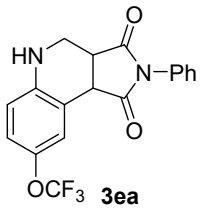


^{1}H NMR (400 MHz, $CDCl_3$) of **3da**

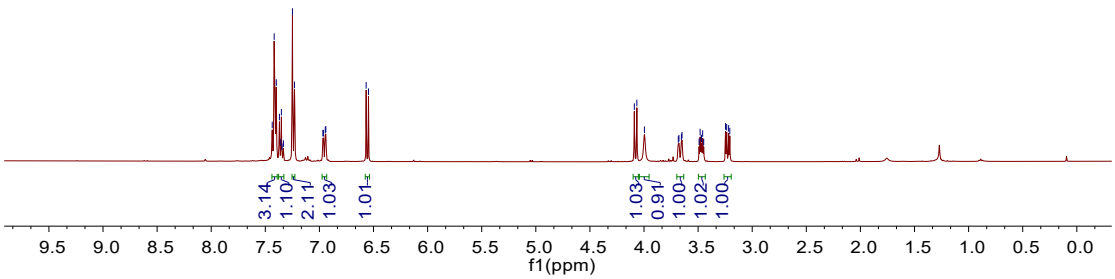


^{13}C NMR (101 MHz, $CDCl_3$) of **3da**

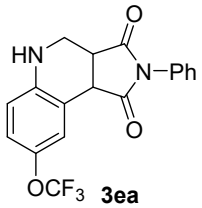




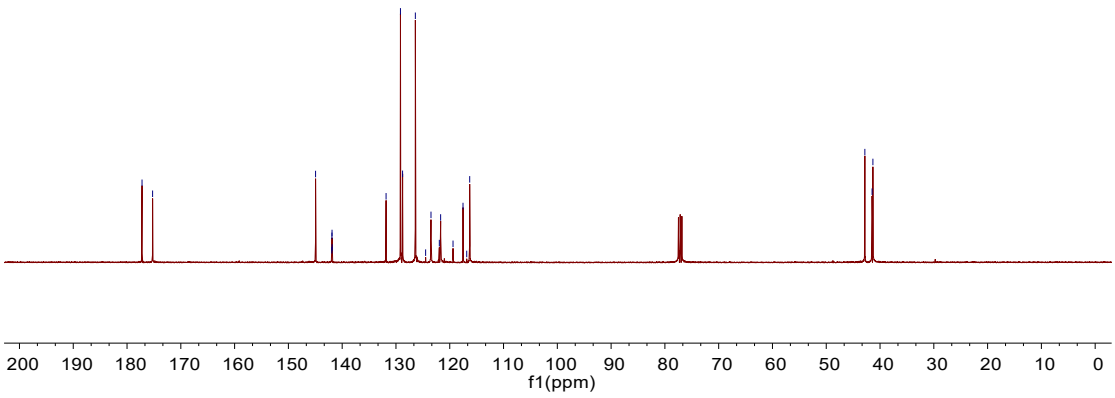
3ea



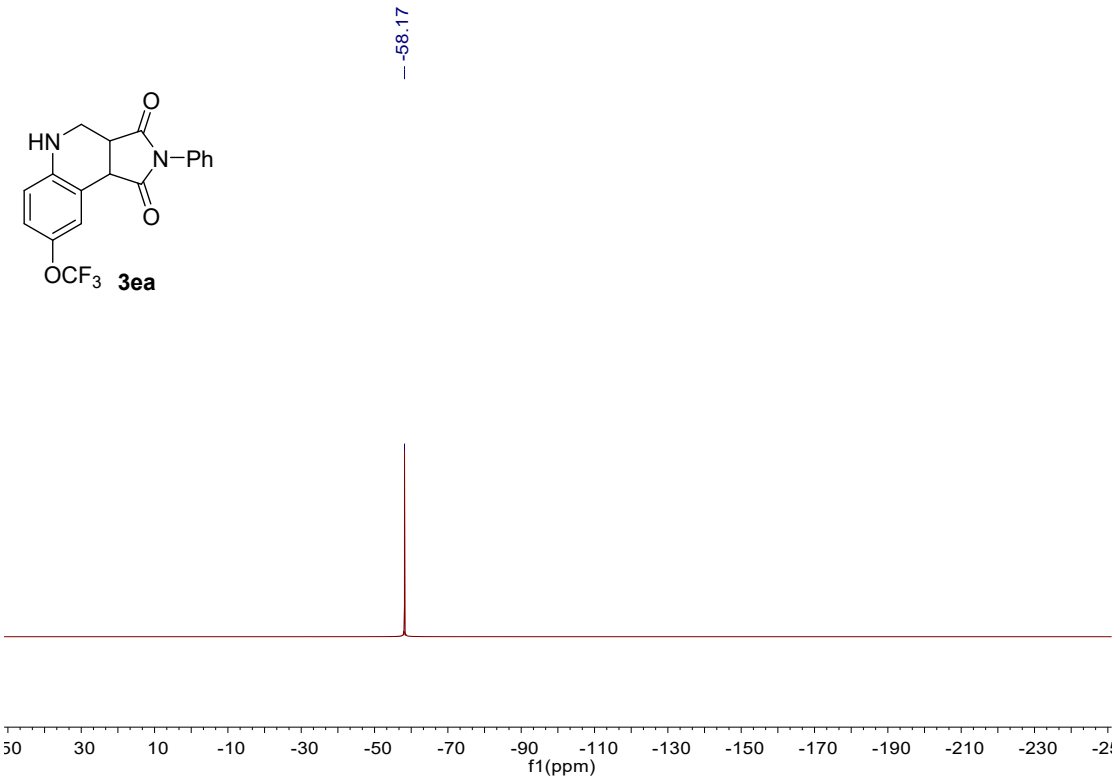
^{1}H NMR (400 MHz, $CDCl_3$) of **3ea**



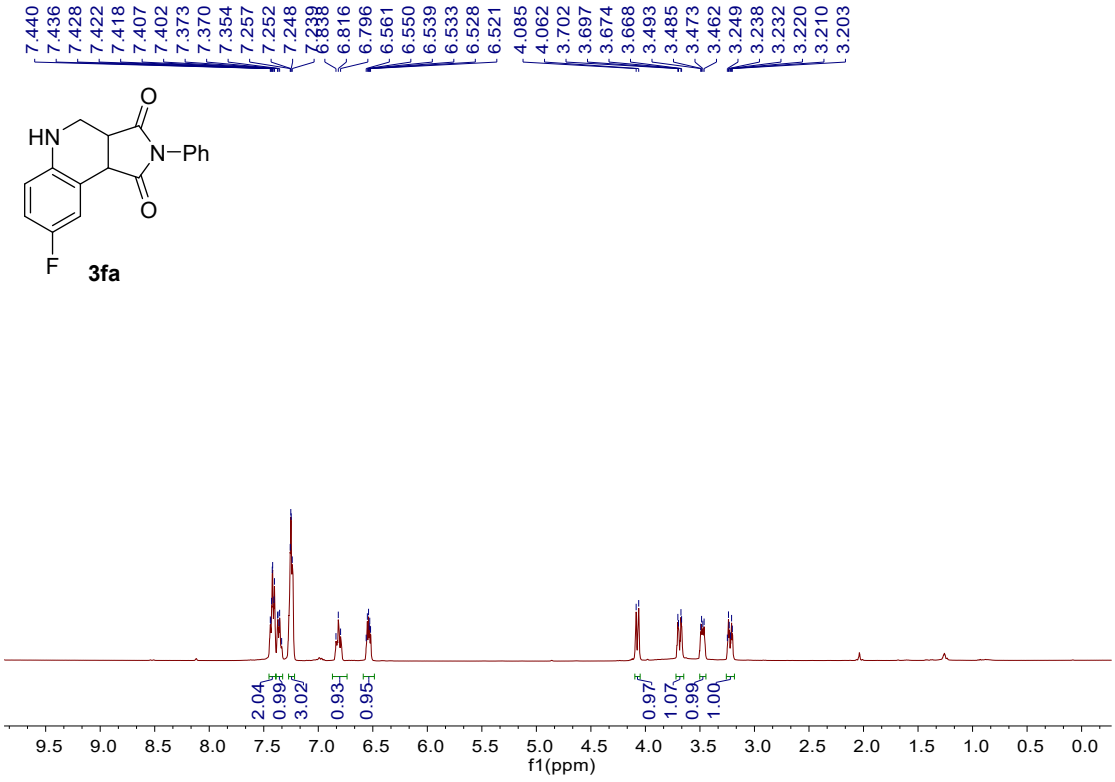
3ea



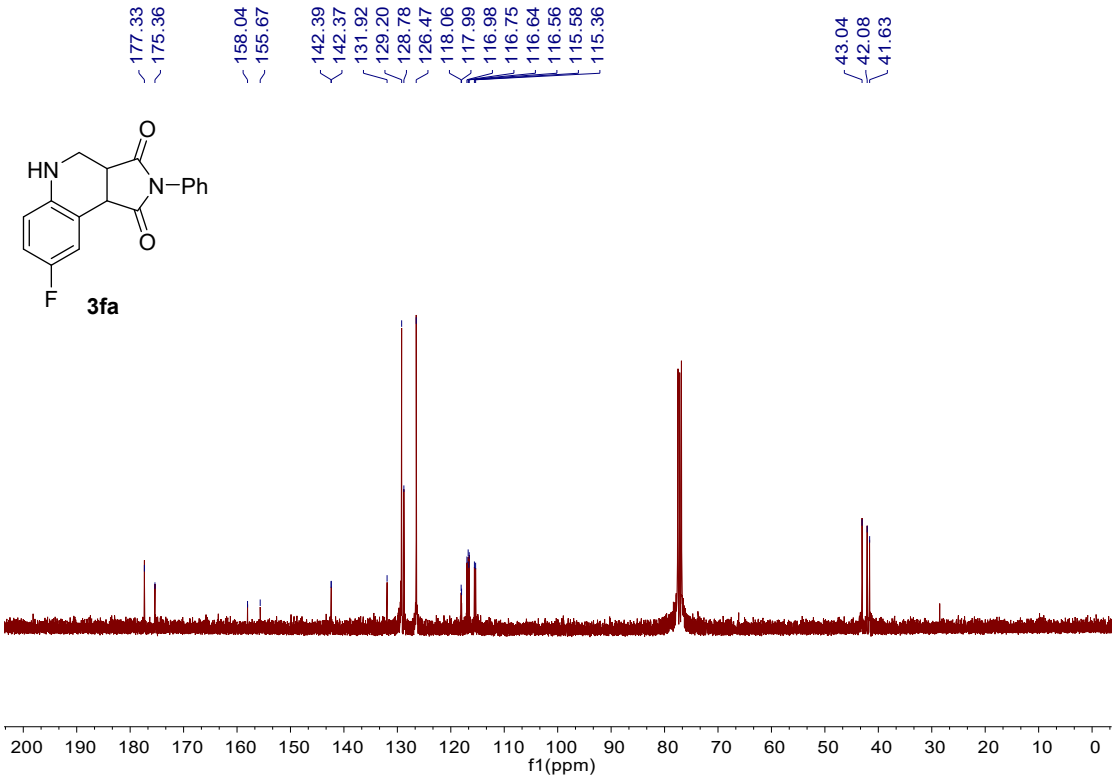
^{13}C NMR (101 MHz, $CDCl_3$) of **3ea**



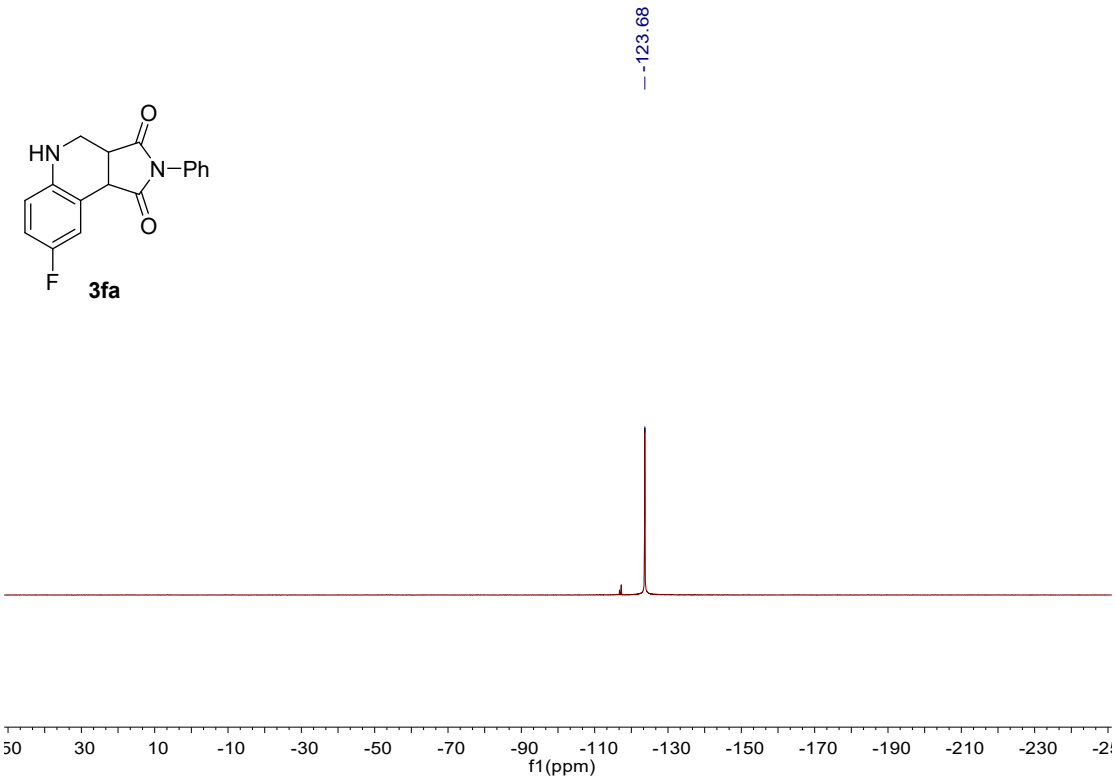
^{19}F NMR (376 MHz, $CDCl_3$) of **3ea**



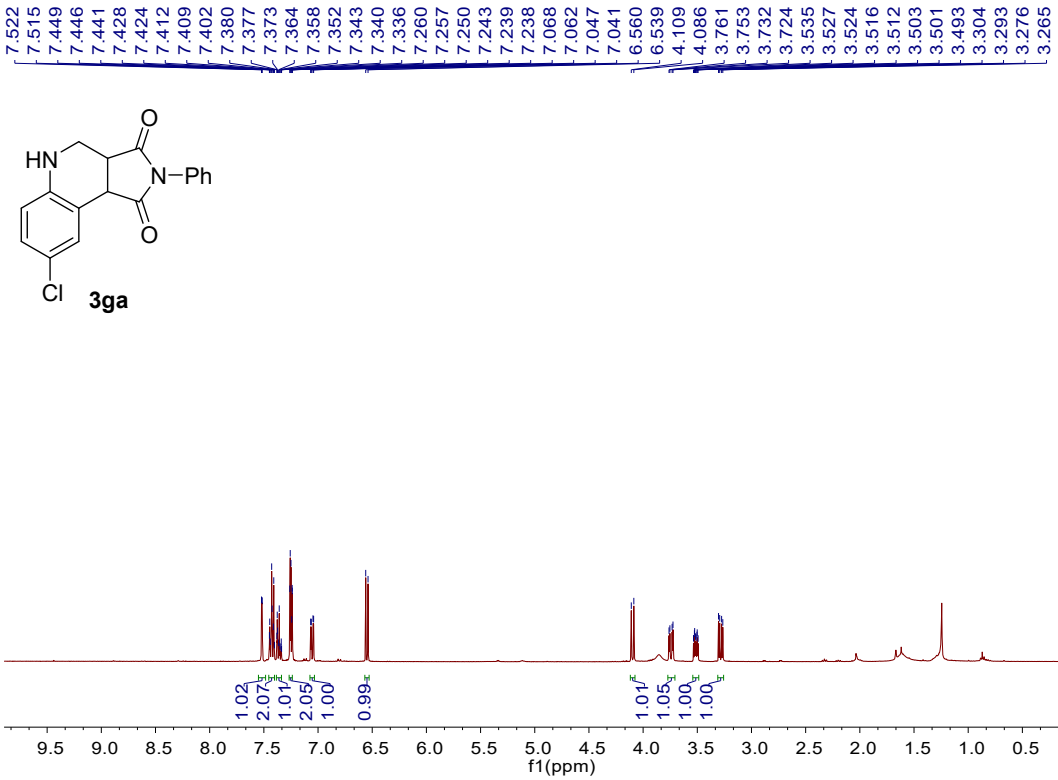
^{1}H NMR (400 MHz, $CDCl_3$) of **3fa**



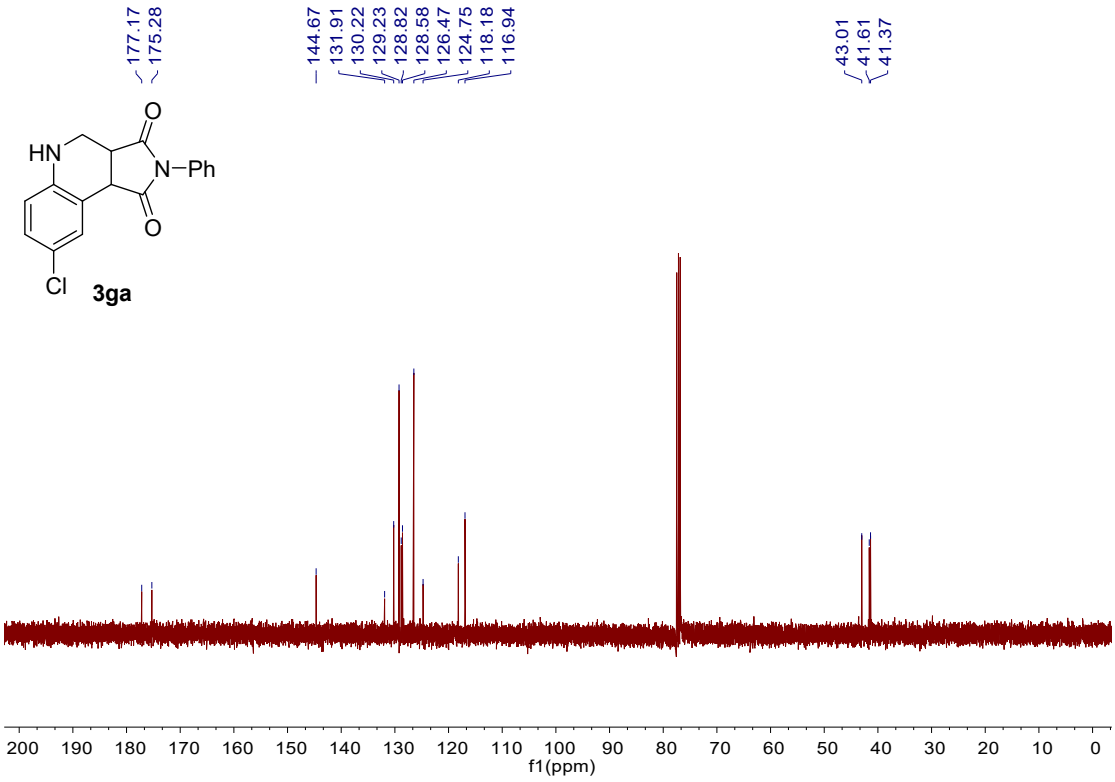
^{13}C NMR (101 MHz, $CDCl_3$) of **3fa**



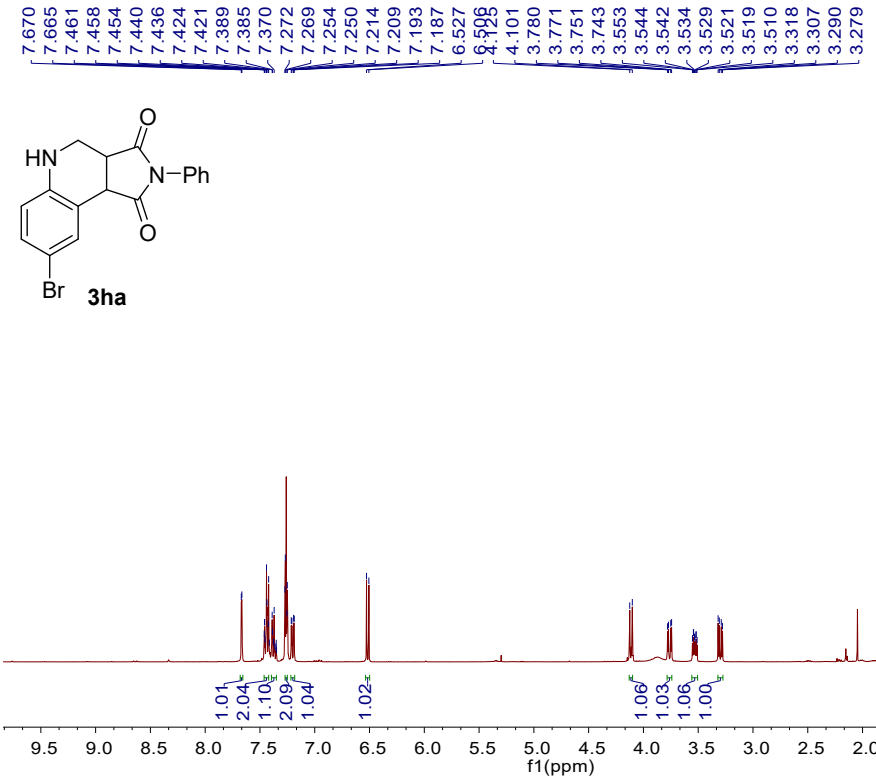
^{19}F NMR (376 MHz, $CDCl_3$) of **3fa**



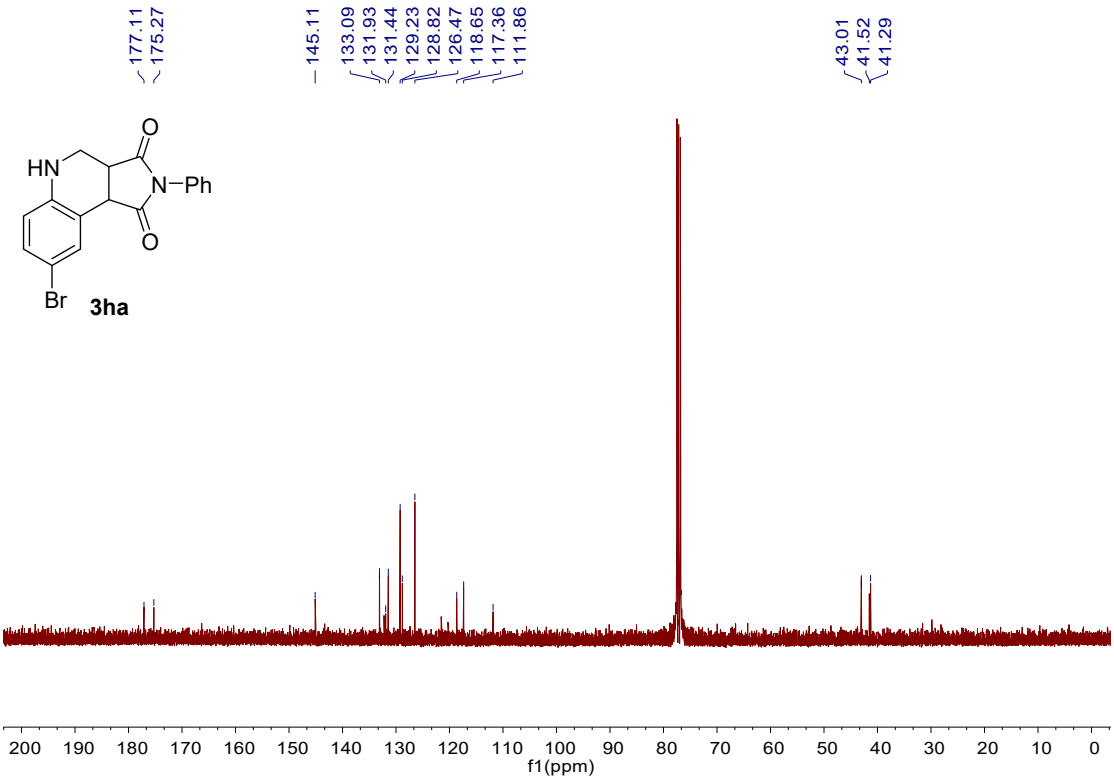
^{1}H NMR (400 MHz, $CDCl_3$) of **3ga**



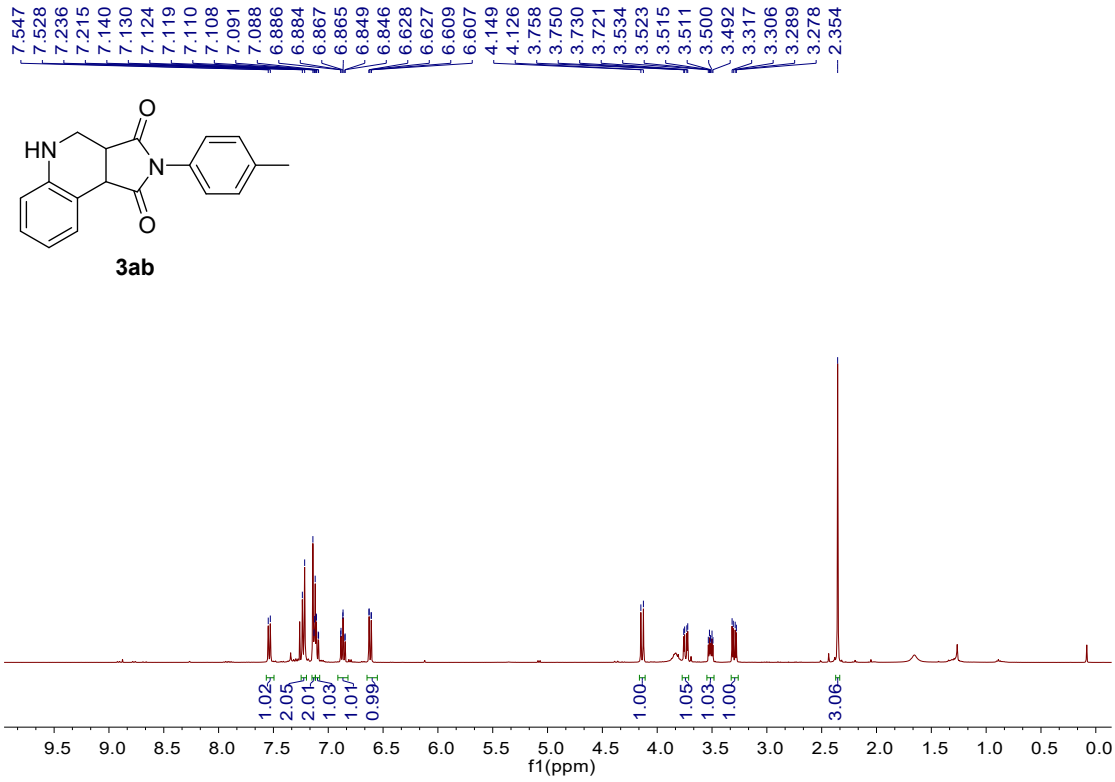
^{13}C NMR (101 MHz, $CDCl_3$) of **3ga**



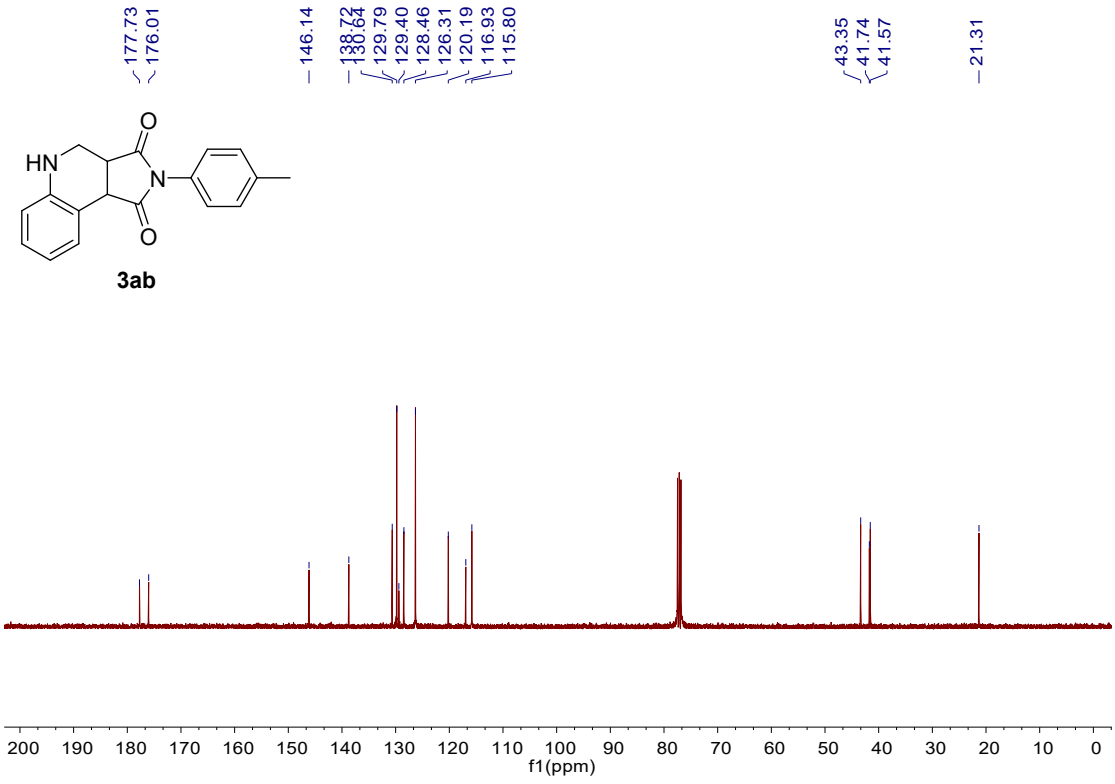
^{1}H NMR (400 MHz, $CDCl_3$) of **3ha**



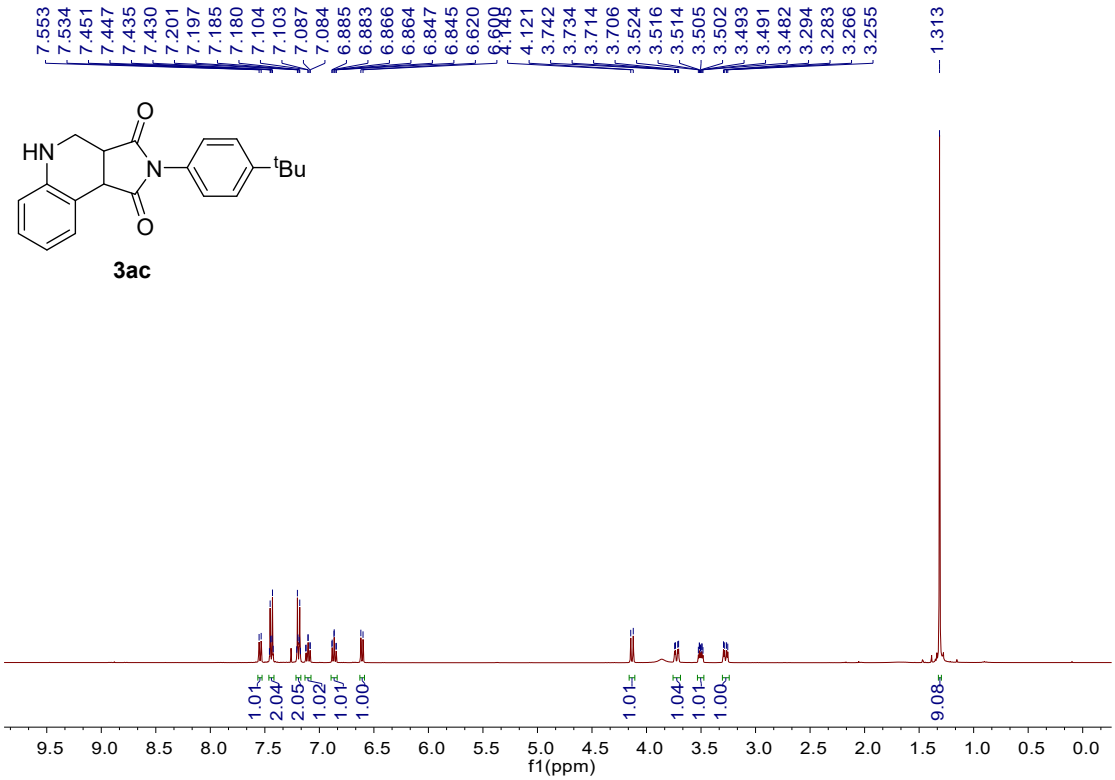
^{13}C NMR (101 MHz, $CDCl_3$) of **3ha**



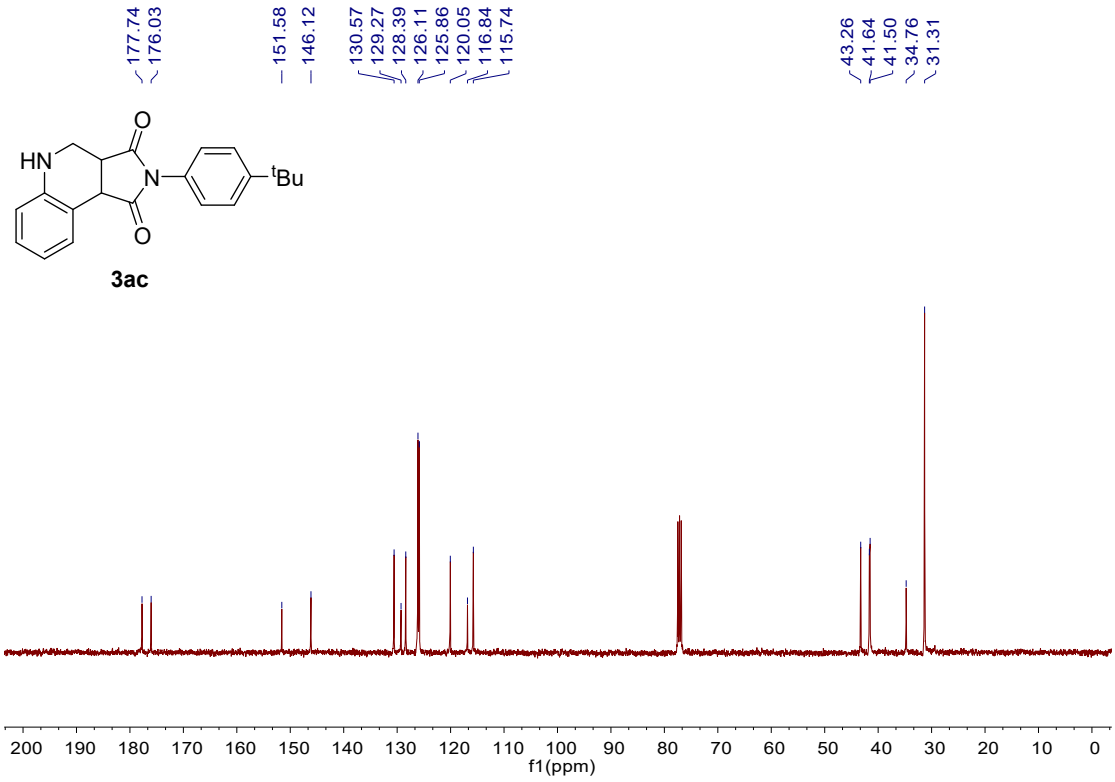
^{1}H NMR (400 MHz, $CDCl_3$) of **3ab**



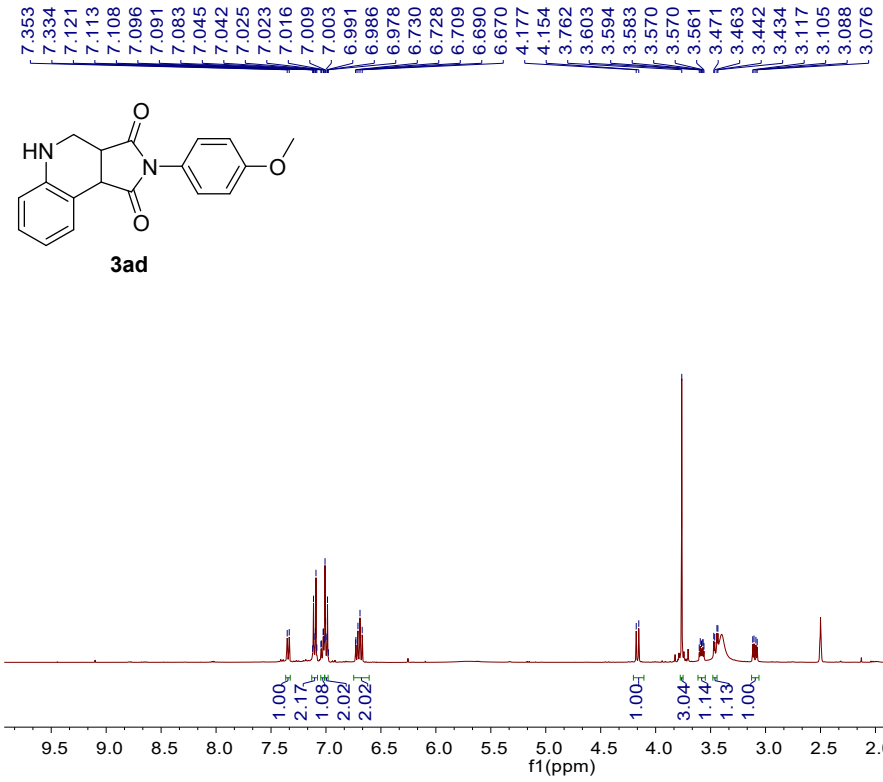
^{13}C NMR (101 MHz, $CDCl_3$) of **3ab**



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

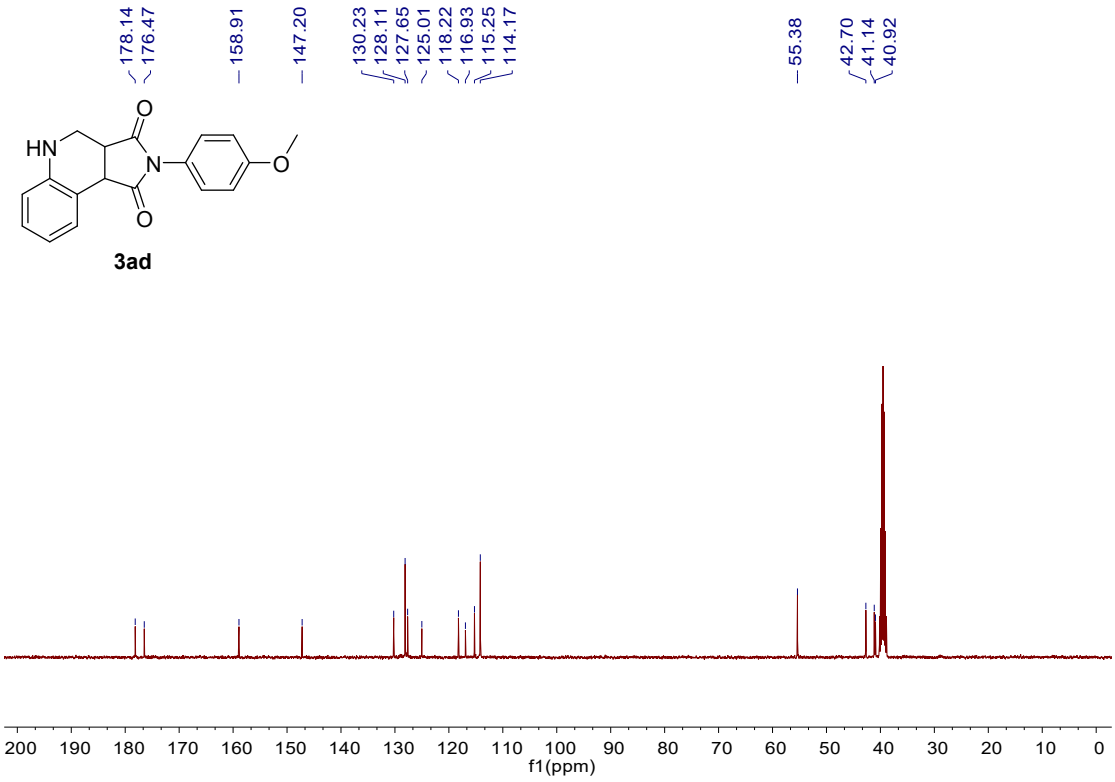


^{13}C NMR (101 MHz, $CDCl_3$) of **3ac**



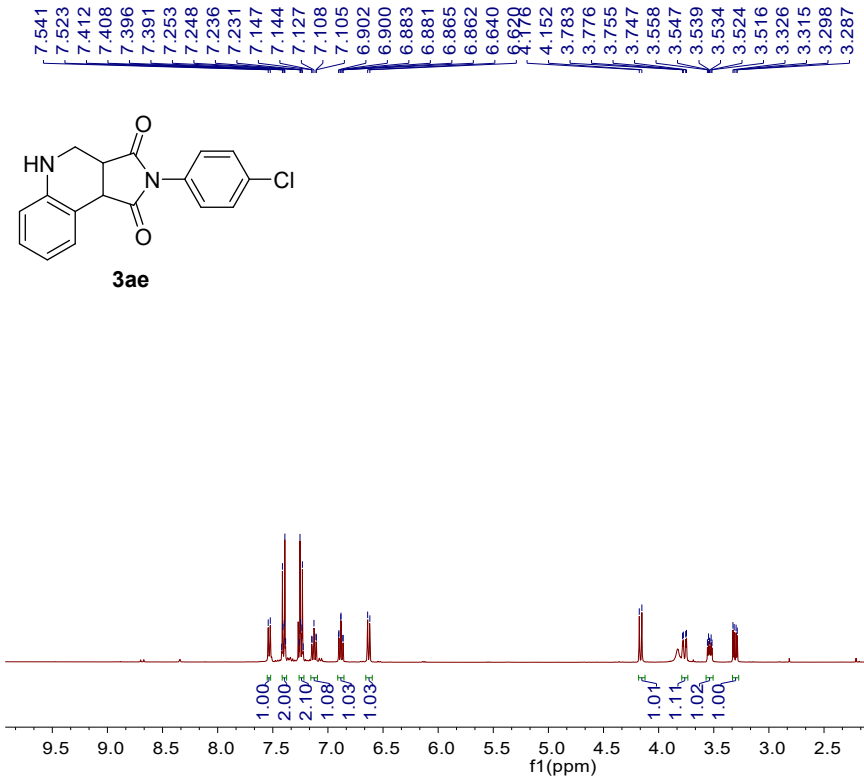
3ad

^{1}H NMR (400 MHz, DMSO-d_6) of **3ad**

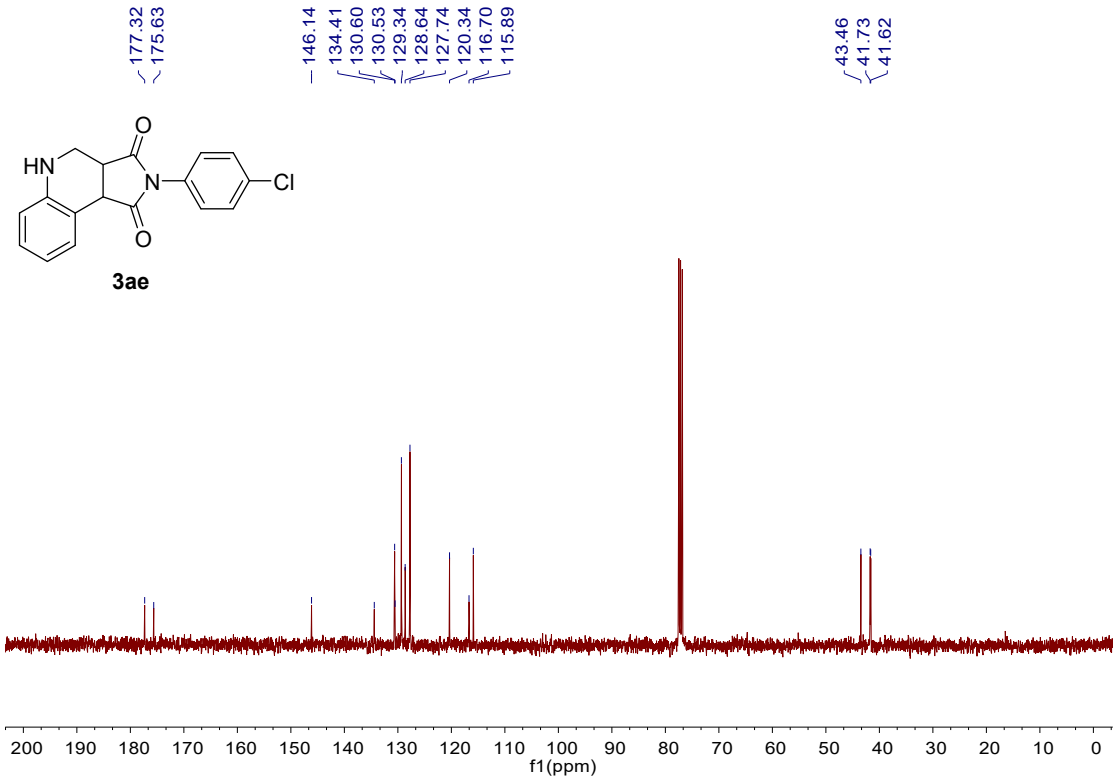


3ad

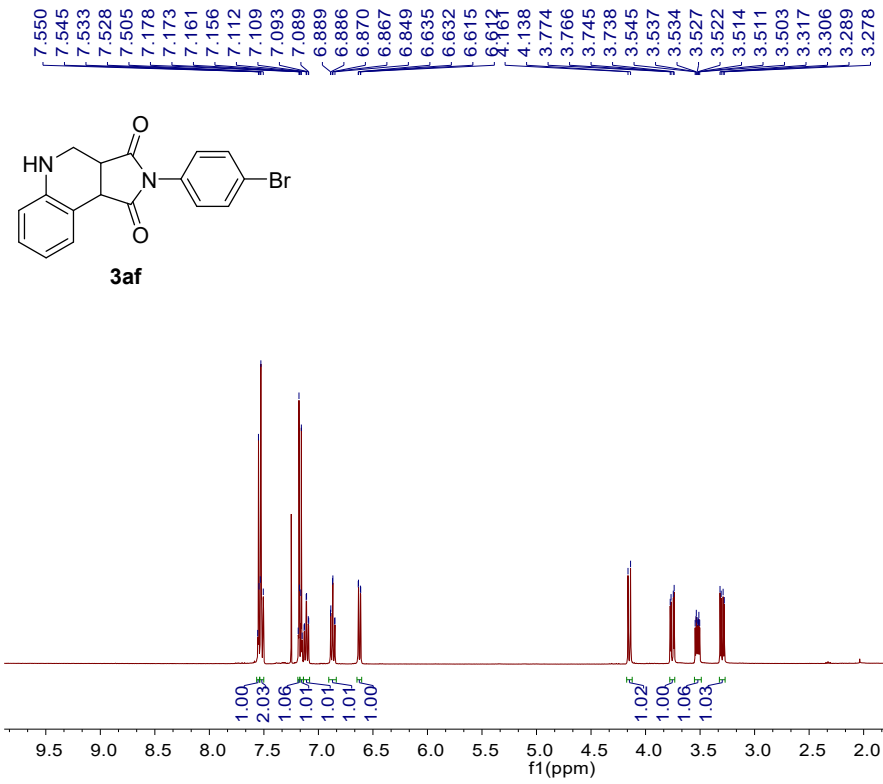
^{13}C NMR (101 MHz, DMSO-d_6) of **3ad**



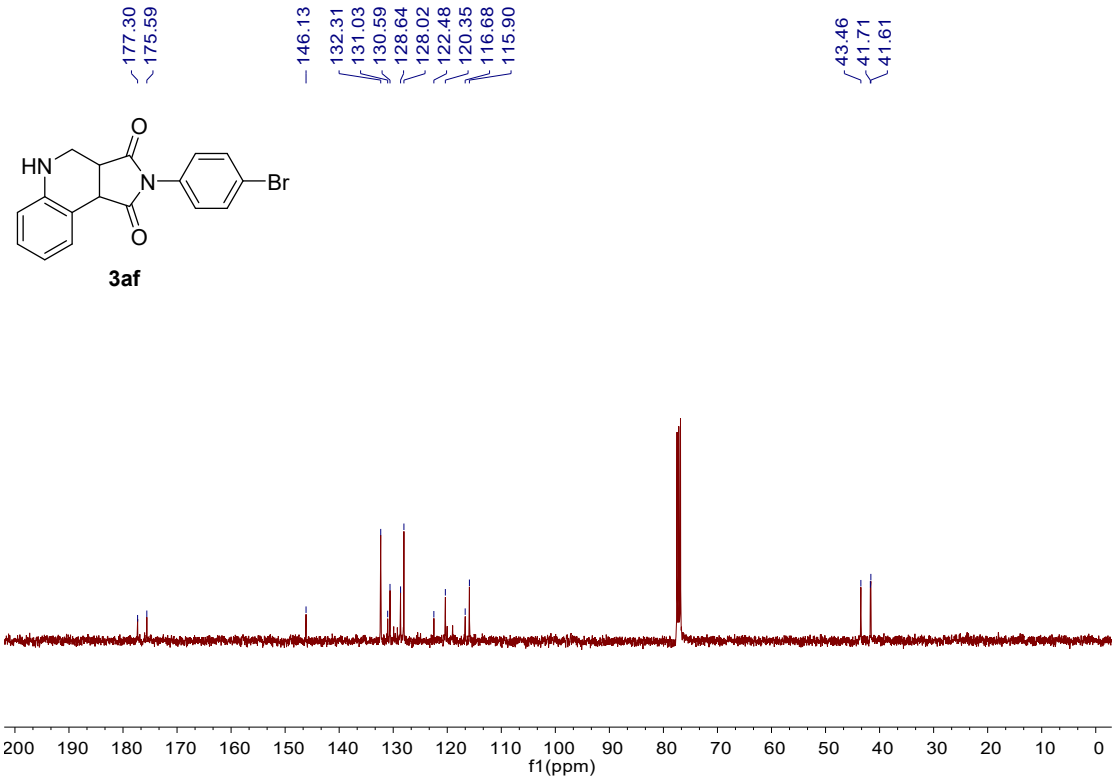
^{1}H NMR (400 MHz, $CDCl_3$) of **3ae**



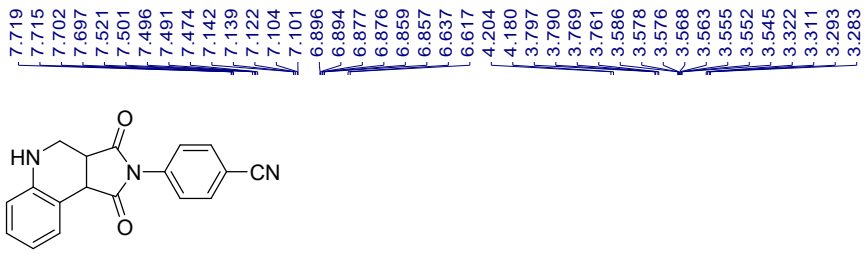
^{13}C NMR (101 MHz, $CDCl_3$) of **3ae**



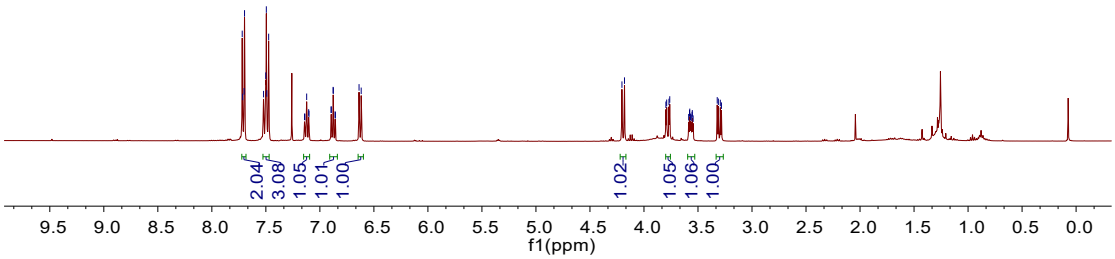
^{1}H NMR (400 MHz, $CDCl_3$) of **3af**



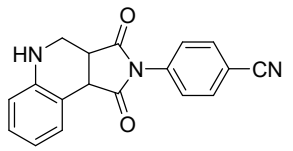
^{13}C NMR (101 MHz, $CDCl_3$) of **3af**



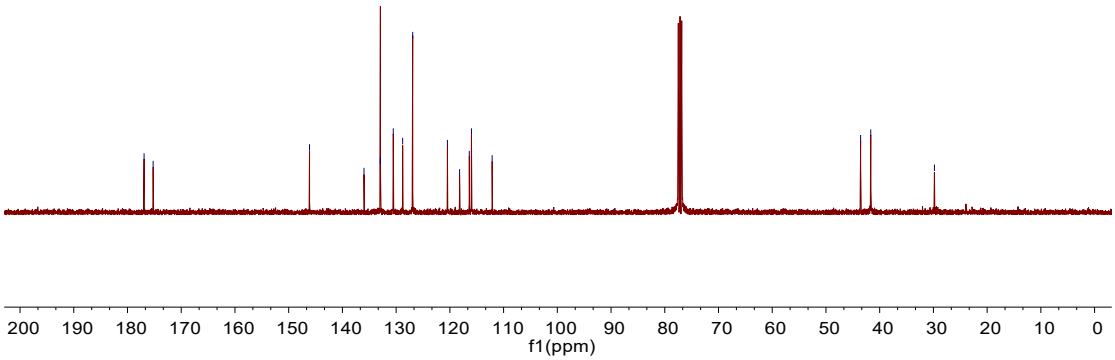
3ag



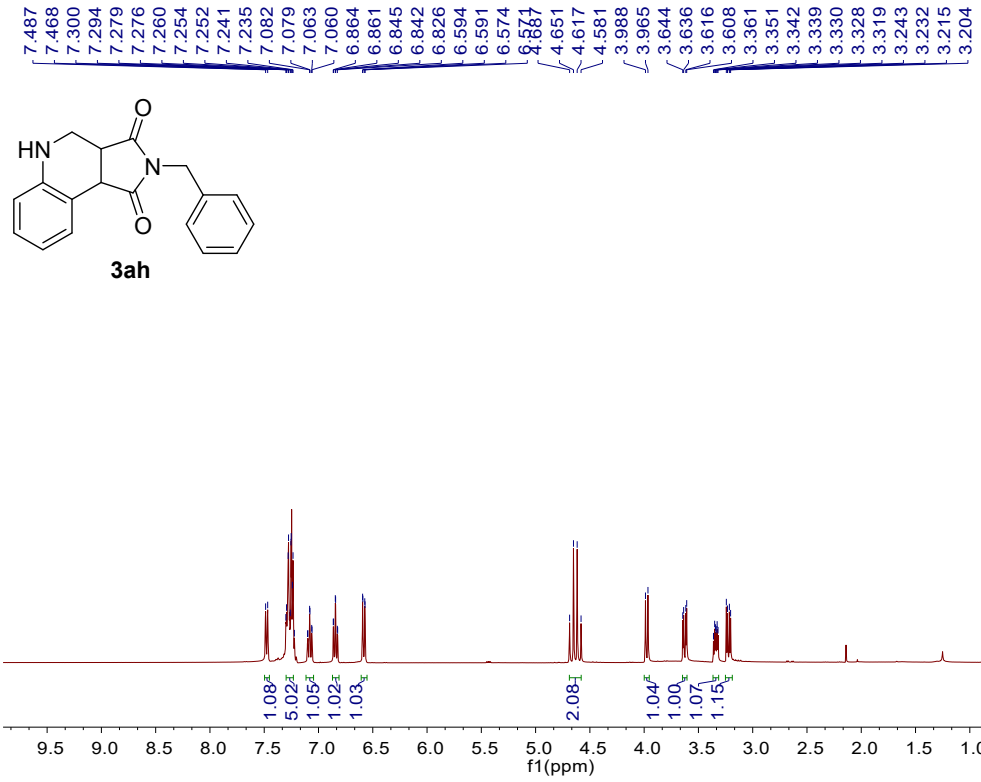
^{1}H NMR (400 MHz, $CDCl_3$) of **3ag**



3ag

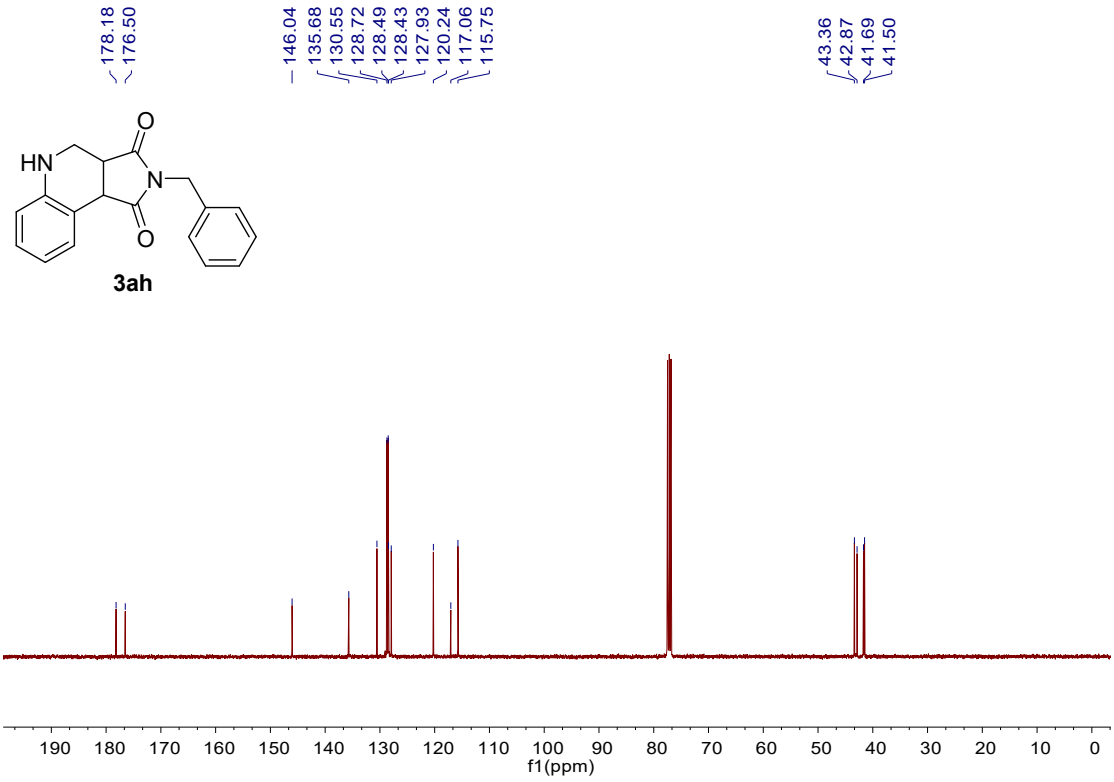


^{13}C NMR (101 MHz, $CDCl_3$) of **3ag**



3ah

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



3ah

^{13}C NMR (101 MHz, $CDCl_3$) of **3ah**

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