

### *Supplementary Information*

## **Crystallization-induced Diastereomer Transformation of 2-Quinolone-4-carboxamide Followed by Stereoselective Intermolecular Photocycloaddition Reaction**

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### **Experimental**

General. NMR spectra were recorded on CDCl<sub>3</sub> solutions on a BRUKER 300 operating 300 MHz, respectively, for <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy. Chemical shifts are reported in parts per million (ppm) relative to TMS as internal standards. IR spectra were recorded on JASCO FT/IR-230 spectrometers as KBr disks.

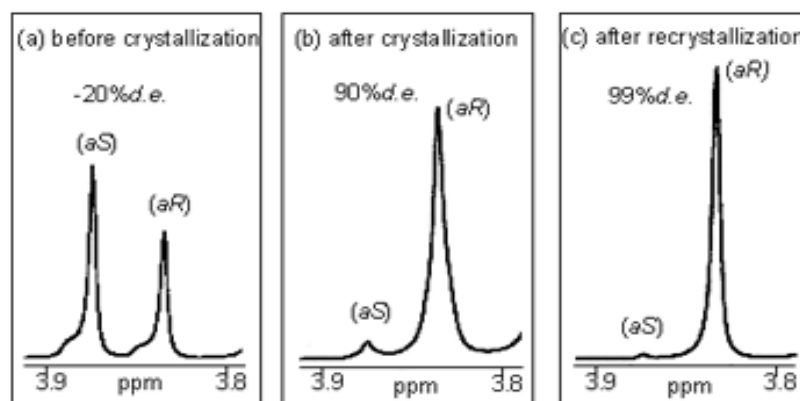
**General procedure for preparation of 1,3-dimethyl-2-quinolone-4-carboxamide 1.** The amide **1** was prepared from the corresponding 1,3-dimethyl-2-quinolone-4-carboxylic acid and (*S*)-proline methyl ester. To a THF solution containing 1.13 g (5.5 mmol) of carboxylic acid and triethylamine 0.67g (6.6 mmol) was added 0.79 g (6.6 mmol) of thionyl chloride at 0°C. The reaction mixture was stirred for 0.5 h, and then a THF solution containing 1.68 g of (*S*)-proline methyl ester (13.0 mmol) was added dropwise. After the reaction mixture was stirred for 2 h, water and ethyl acetate were added, and the organic layer was extracted in the usual manner. After the organic solvent was evaporated in *vacuo*, the residual mixture was subjected to chromatography on silica gel and the amide **1** was separated. The structure was determined on the basis of spectral data and mass spectroscopy.

**(*S*)-1-(1,3-Dimethyl-2-oxo-1,2-dihydro-quinoline-4-carbonyl)-pyrrolidine-2-carboxylic acid methyl ester 1:** m.p. 137-142°C; IR (cm<sup>-1</sup>, KBr) 1648, 1741; <sup>1</sup>H-NMR: (CDCl<sub>3</sub>) δ 1.82-2.21 (m, 3H), 2.30-2.43(m, 4H), 3.14-3.22 (m, 1H), 3.36-3.44 (m, 1H), 3.77 (s, 3H), 3.83 (s, 3H), 4.79-4.83(m, 1H), 7.20-7.28 (m, 1H), 7.37-7.41 (m, 2H), 7.55 (td, *J* = 1.4 and 7.8 Hz, 1H), <sup>13</sup>C NMR (75 Mz, CDCl<sub>3</sub>) δ 14.6, 25.1, 30.0, 30.4, 48.0, 52.9, 58.6, 114.8, 117.4, 123.0, 125.7, 127.2, 130.5, 139.5, 141.7, 162.8, 166.5, 172.5; EI-MS *m/z* (rel intensity): 309 (M<sup>+</sup>, 96); HRMS (FABMS) *m/z* calcd for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>4</sub>+H: 329.1501, found 329.1485.

### **Crystallization-induced diastereomer transformation of amide 1.**

A solution of the amide **1** (200 mg) in THF (10 ml) in a test tube was heated at 70°C in an oil bath,

and the THF was gradually evaporated with stirring by using magnetic stir. Resulting solid was analyzed by NMR, which showed the solid was composed of 95% of (*S*, *aR*)-**1** and 5% of (*S*, *aS*)-**1**. When the solid was recrystallized from ether, 99% *de* of (*S*, *aR*)-**1a** was obtained (Fig. S1).



**Fig. S1** Change of  $^1\text{H}$  NMR spectra of **1** followed by crystallization-induced diastereomer transformation. (a) Before crystallization; (b) after crystallization by evaporating THF at  $70^\circ\text{C}$ ; (c) after recrystallization of the solid obtained by CIDT.

### General procedure for the photochemical cycloaddition reaction of quinolonecarboxamide **1** with methacrylonitrile.

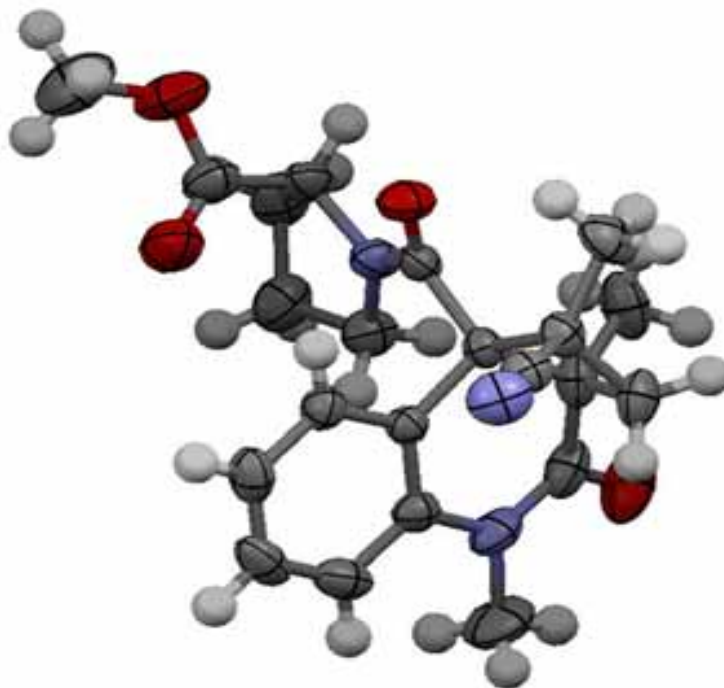
A THF solution containing amide **1** (0.02 M) and methacrylonitrile (0.1 M) was irradiated with a 500-W high pressure mercury lamp under argon atmosphere until the starting material disappeared by checking with TLC, it needed 2hrs to be consumed perfectly. After removing the solvent in vacuo, the crude photolysate was subjected to chromatography on silica gel. The 4+4 cycloadducts (*1S*,*2aR*,*8bR*)-**2** and (*1R*,*2aS*,*8bS*)-**2** were isolated.

**(*S*)-1-((*1S*,*2aR*,*8bR*)-1-Cyano-1,2a,4-trimethyl-3-oxo-2,2a,3,4-tetrahydro-1H-cyclobuta[*c*]quinoline-8b-carbonyl)-pyrrolidine-2-carboxylic acid methyl ester, (*1S*,*2aR*,*8bR*)-**2**** was obtained as colorless prisms from hexane-chloroform; m.p.  $153\text{--}158^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{25} = -208.6$  (c 0.50  $\text{CHCl}_3$ ); IR (KBr)  $1747, 1644\text{ cm}^{-1}$ ;  $^1\text{H}$  NMR (300 Mz,  $\text{CDCl}_3$ )  $\delta$  1.53-2.10 (m, 11H), 2.50-2.57 (m, 1H), 2.85 (d,  $J = 12.2\text{ Hz}$ , 1H), 3.04-3.14 (m, 1H), 3.48 (s, 3H), 3.75 (s, 3H), 4.47 (dd,  $J = 8.3$  and  $4.3\text{ Hz}$ , 1H), 7.10 (d,  $J = 8.3\text{ Hz}$ , 1H), 7.16-7.23 (m, 1H), 7.34 (dd,  $J = 7.8$  and  $1.5\text{ Hz}$ , 1H), 7.39-7.45 (m, 1H);  $^{13}\text{C}$  NMR (75 Mz,  $\text{CDCl}_3$ )  $\delta$  22.0, 25.7, 26.6, 28.6, 30.5, 41.6, 43.7, 44.2, 45.4, 52.7, 57.2, 60.2, 115.4, 120.0, 122.9, 124.5, 130.1, 130.6, 139.0, 168.6, 170.2, 172.7; FAB-MS  $m/z$  (rel intensity) 395 ( $\text{M}^+ + 1$ , 11); HRMS (FAB-MS)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{25}\text{N}_3\text{O}_4 + \text{H}$  396.1923, found 396.1910.

**(*S*)-1-((*1R*,*2aS*,*8bS*)-1-Cyano-1,2a,4-trimethyl-3-oxo-2,2a,3,4-tetrahydro-1H-cyclobuta[*c*]quinoline-8b-carbonyl)-pyrrolidine-2-carboxylic acid methyl ester, (*1R*,*2aS*,*8bS*)-**2**** was obtained as colorless prisms from hexane-chloroform; m.p.  $179\text{--}180^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{25} = +121.2$  (c 1.00

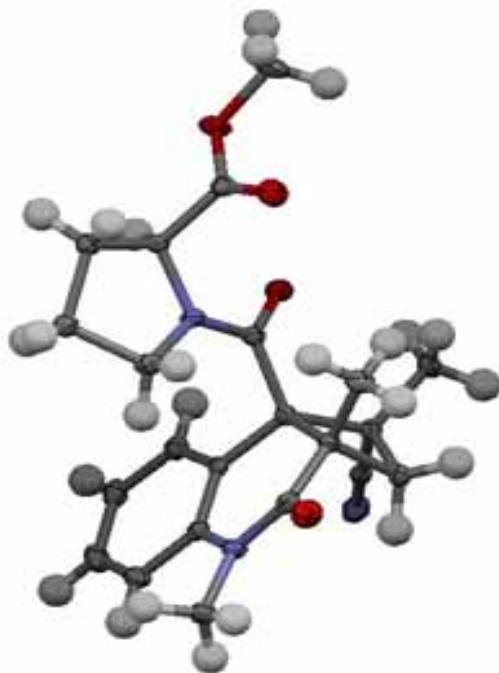
CHCl<sub>3</sub>); IR (KBr) 1750, 1659 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 Mz, CDCl<sub>3</sub>) δ 1.67-1.80 (m, 6H), 2.07-2.17 (m, 5H), 2.53-2.61 (m, 1H), 2.86-2.97 (m, 2H), 3.48 (s, 3H), 3.72 (s, 3H), 4.43-4.47 (m, 1H), 7.11 (d, *J* = 8.3 Hz, 1H), 7.23-7.28 (m, 1H), 7.34 (dd, *J* = 7.8 and 1.7 Hz, 1H), 7.42-7.47 (m, 1H); <sup>13</sup>C NMR (75 Mz, CDCl<sub>3</sub>) δ 22.1, 25.9, 26.2, 28.5, 30.5, 41.3, 43.7, 44.2, 45.6, 52.5, 57.3, 60.4, 115.2, 120.1, 122.9, 124.3, 130.7 130.9, 138.8, 168.2, 170.1, 172.6; FAB-MS *m/z* (rel intensity) 395 (M<sup>+</sup> + 1, 73); HRMS (FAB-MS) *m/z* calcd for C<sub>22</sub>H<sub>25</sub>N<sub>3</sub>O<sub>4</sub> + H 396.1923, found 396.1910.

**Crystal data for (1*S*,2*aR*,8*bR*)-2** (recrystallized from CHCl<sub>3</sub>-hexane): Orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 11.32160(10) Å, *b* = 13.26990(10) Å, *c* = 13.7391(2) Å, *V* = 2064.11(4) Å<sup>3</sup>, *Z* = 4, ρ = 1.273 Mg m<sup>-3</sup>; in the final least-square refinement cycles on *F*<sup>2</sup>, the model converged to *R*<sub>1</sub> = 0.0480, *wR*<sub>2</sub> = 0.1187 for 5281 reflections, CCDC 667898 contains crystallographic data.



**Fig. S2** ORTEP drawing of 2+2 photocycloadduct (1*S*,2*aR*,8*bR*)-2 with 50% probability.

**Crystal data for (1*R*,2*aS*,8*bS*)-2** (recrystallized from CHCl<sub>3</sub>–hexane): Orthorhombic, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 8.0817(10) Å, *b* = 14.5195(18) Å, *c* = 17.141(2) Å, *V* = 2011.4(4) Å<sup>3</sup>, *Z* = 4,  $\rho$  = 1.306 Mg m<sup>-3</sup>; in the final least-square refinement cycles on *F*<sup>2</sup>, the model converged to *R*<sub>1</sub> = 0.0330, *wR*<sub>2</sub> = 0.0809 for 4309 reflections, CCDC 667899 contains crystallographic data.



**Fig. S3** ORTEP drawing of 2+2 photocycloadduct (1*R*,2*aS*,8*bS*)-2 with 50% probability.