Cascade Reactions in Crystals through Cation-π-Controlled Reorientation on Exposure to HCl Gas

Shinji Yamada,* Yoko Tokugawa, Yuka Nojiri, and Eri Takamori

Department of Chemistry, Ochanomizu University, Bunkyo-ku, Tokyo 112-8610, Japan

Supplementary Information

1. General procedures

2. General procedure for the exposure of 4-azachalcones **1** to hydrochloric acid

3. General procedure for irradiation of 4-azachalcone hydrochlorides **2**

4. Thermogravimetric analysis of **2a** (Fig. S1)

5. ^{1}H NMR spectra for **2a**, **2b**, **3a** and **3b** before prurification (Fig. S2)

6. ^{1}H NMR spectrum for **3b** after the cascade reaction before workup (Fig. S3)

7. Schematic possible process for the orientation change from **1b** to **2b** (Fig. S4)

8. Photomicrographs of a single crystal of **2b** before and after irradiation (Fig. S5)

1. General procedures.

^{1}H NMR spectra were recorded on JEOL EX-400 and Bruker 600 spectrometers as dilute solution in $CDCl_3$, and the chemical shifts were reported relative to internal TMS. Powder X-ray diffraction profiles were recorded using a Regaku Ultima IV with monochromated Cu-Ka radiation (λ = 1.54184 A, 50 kV, 40 mA, scan speed 2.0°/min, scan range 4 - 60°) equipped with a cross-beam optics system consisting of a PSA100U parallel slip analyzer. Thermogravimetric Analyses were carried out using a TG-DTA200SA instrument manufactured by Bruker. Three to five milligrams of the crystal samples were heated from 22 to 170 °C in aluminum pans that were 5 mm in diameter. A ramping rate of 10 °C/min was used with a nitrogen purge rate of 150 mL/min.

2. General procedure for the exposure of 4-azachalcone to hydrochloric acid.

The HCl gas was generated by addition of conc hydrosulfonic acid in dropping funel to conc hydrochloric acid in two-necked flask under stirring. The evolved gas was collected to a balloon through a conc H_2SO_4 trap and a $CaCl_2$ tube. The collected dried HCl gas was introduced into a desiccator, in which the powdered crystal of **1** was placed. The powder was kept in a desiccator for 10 min. The obtained hydrochloric salt **2** was used for PXRD measurment and ^{1}H NMR analysis.

3. General procedure for irradiation of 4-azachalcone hydrochlorides.

The powdered crystals of 4-azachalcone hydrochloride **2** (30 mg) placed between two glass plates were irradiated with 250W high-pressure mercury lamp for 24h. The product was collected and was neutralized with saturated $NaHCO_3$ solution. This was extracted with CH_2Cl_2 and dried over anhydrous $MgSO_4$. Evaporation of the organic solvent gave only *syn*HT dimer **3**, the structure of which was confirmed by comparison with the ^{1}H NMR spectra with those reported.

4. TG-DTA chart for 2a

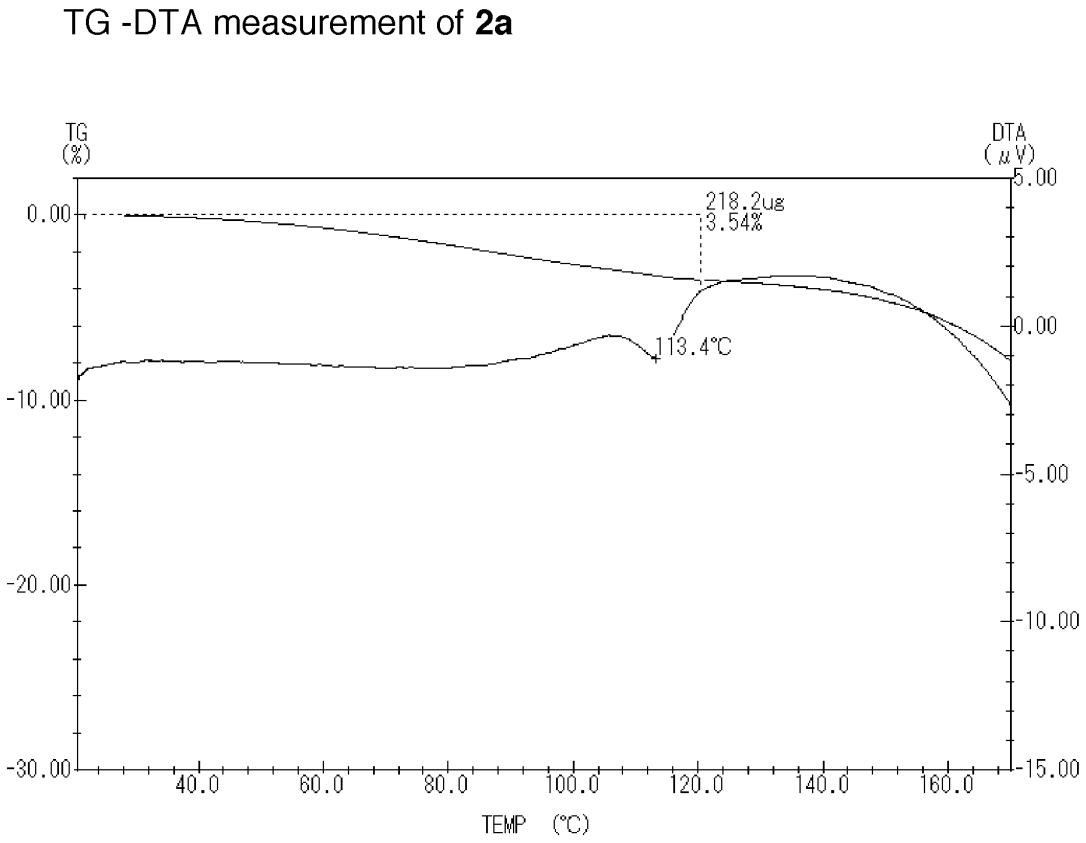
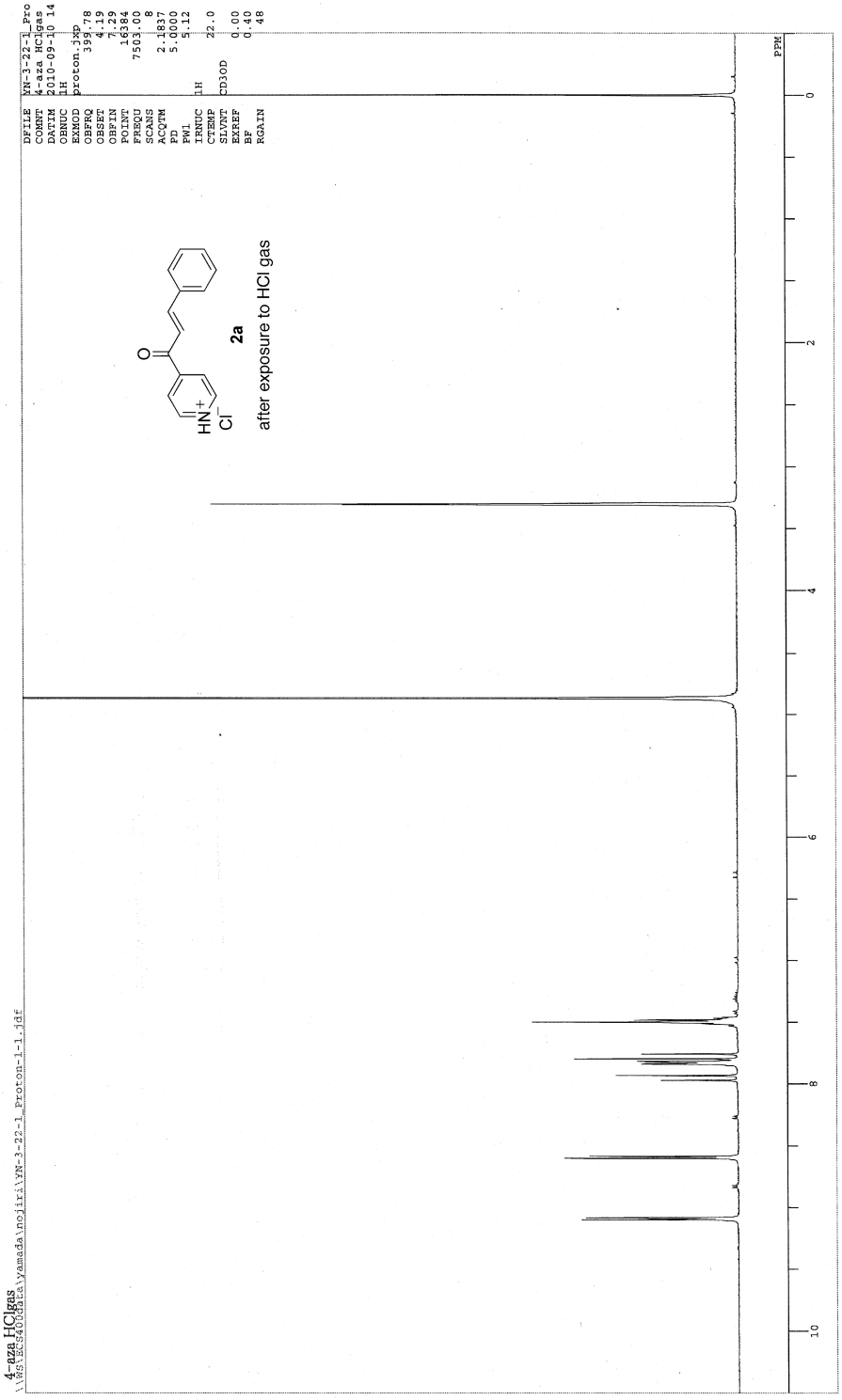
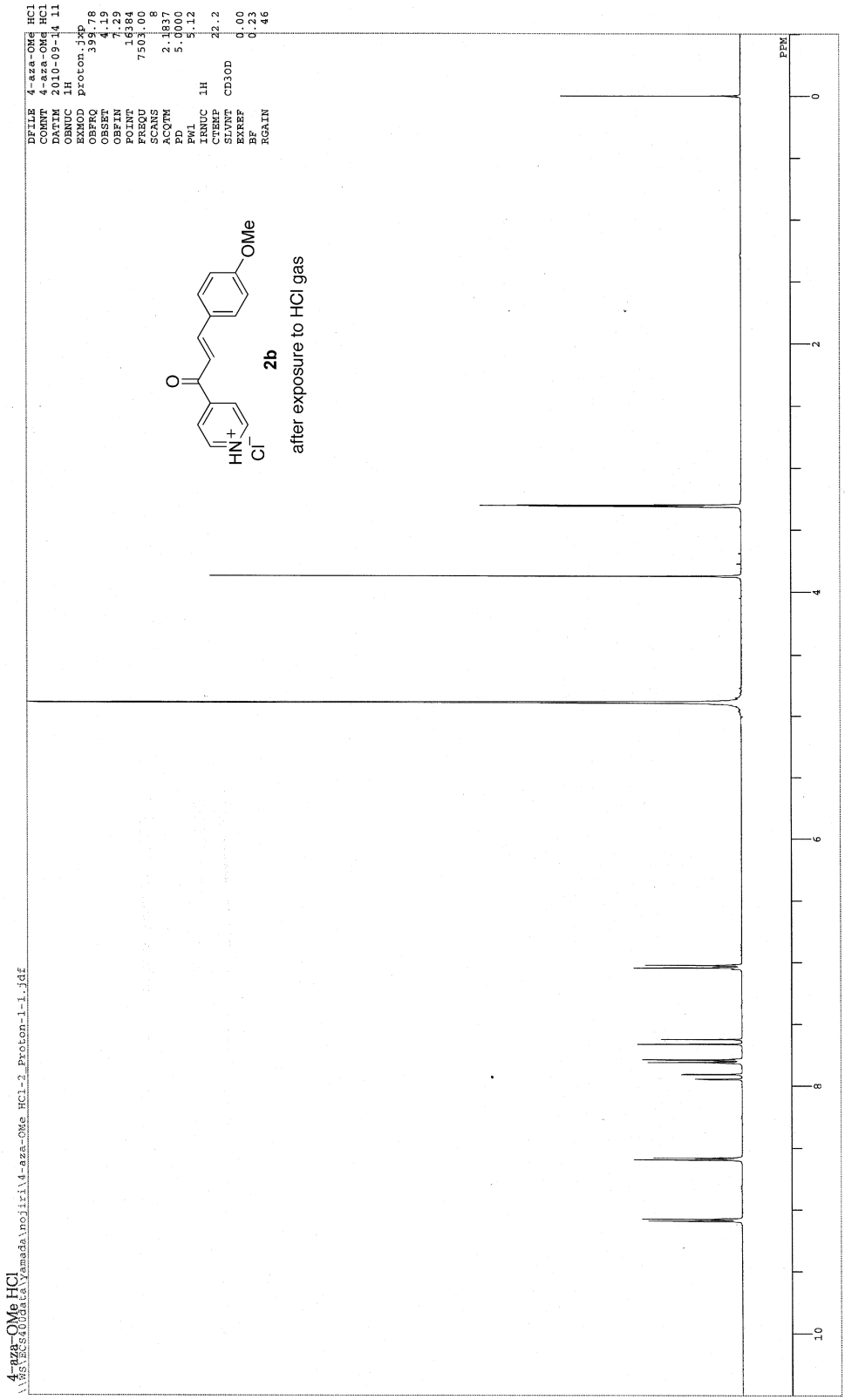
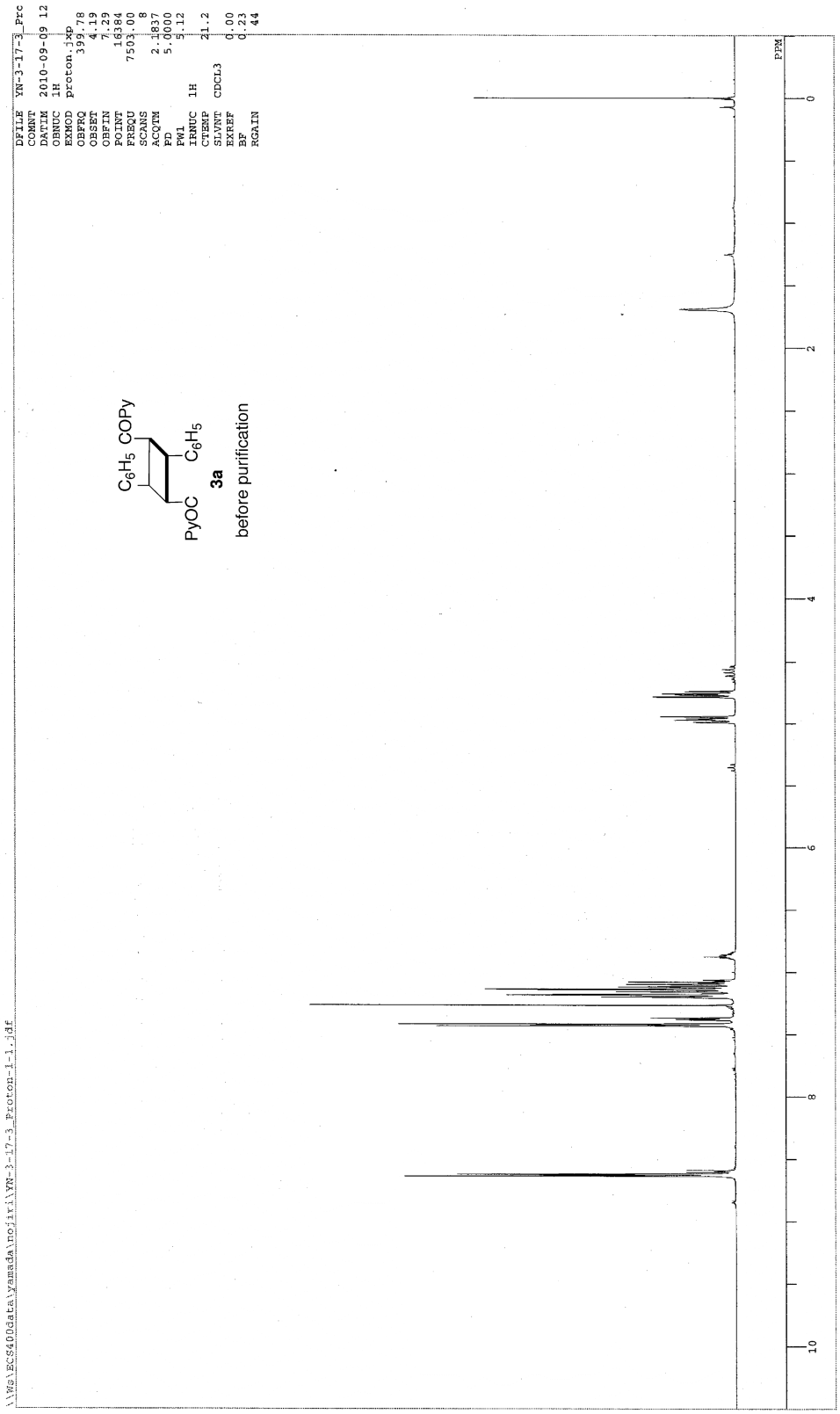


Fig. S1 Thermogravimetric analysis of **2a.**

5. ^{1}H NMR spectra for 2a and 2b (in CD_3OD), and 3a and 3b (in $CDCl_3$) before purification




4-aza-OMe HCl
\\WS\EC400data\Yamada\nojiri\4-aza-OMe HCl-2_Proton-1-1.jdf
DFILE 4-aza-OMe HCl
COMNT 4-aza-OMe HCl
DATIM 2010-09-14 11
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78
OBSET 4.19
OBFIN 7.29
POINT 16384
FREQU 7503.00
SCANS 8
ACQTM 2.1837
PD 5.0000
PW1 5.12
IRNUC 1H
CTEMP 22.2
SLVNT CD3OD
EXREF 0.00
BF 0.23
RGAIN 46
OMe
O
HN+
Cl−
2b
after exposure to HCl gas
PPM
0
2
4
6
8
10


\\Ws\ECS400data\yamada\nojiri\YN-3-17-3_Proton-1-1.jdf
DFILE YN-3-17-3_Prc
COMNT
DATIM 2010-09-09 12
OBNUC 1H
EXMOD proton.jxp
OBFRQ 399.78
OBSET 4.19
OBFIN 7.29
POINT 16384
FREQU 7503.00
SCANS 8
ACQTM 2.1837
PD 5.0000
PW1 5.12
IRNUC 1H
CTEMP 21.2
SLVNT CDCL3
EXREF 0.00
BF 0.23
RGAIN 44
C6H5 COPy
C6H5
PyOC
3a
before purification
PPM
0
2
4
6
8
10

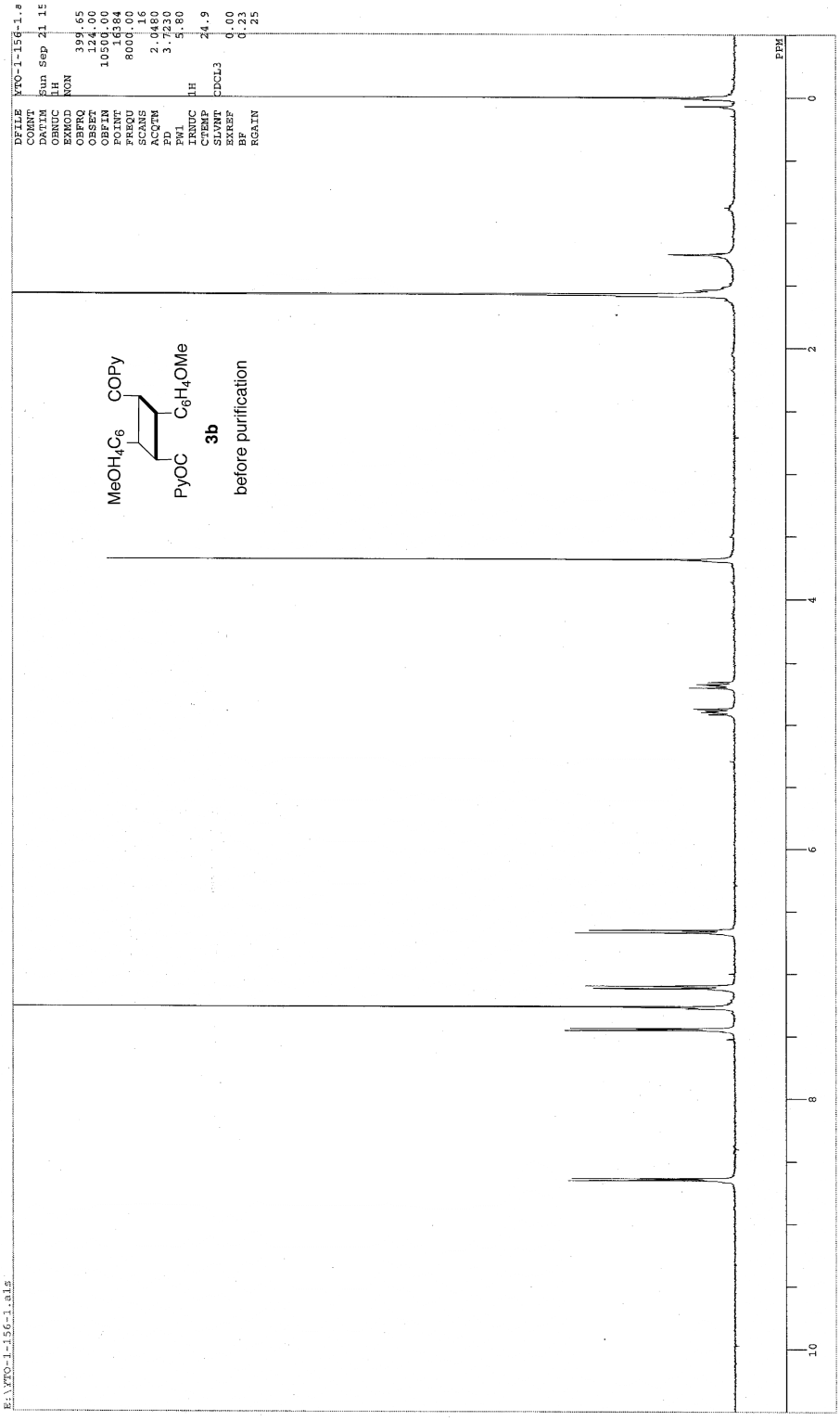


Fig. S2 ^{1}H NMR spectra for **2a** and **2b** (in CD_3OD), and **3a** and **3b** (in $CDCl_3$) before purification

6. ^{1}H NMR spectrum for 3b (CD_3OD) after the cascade reaction before workup.

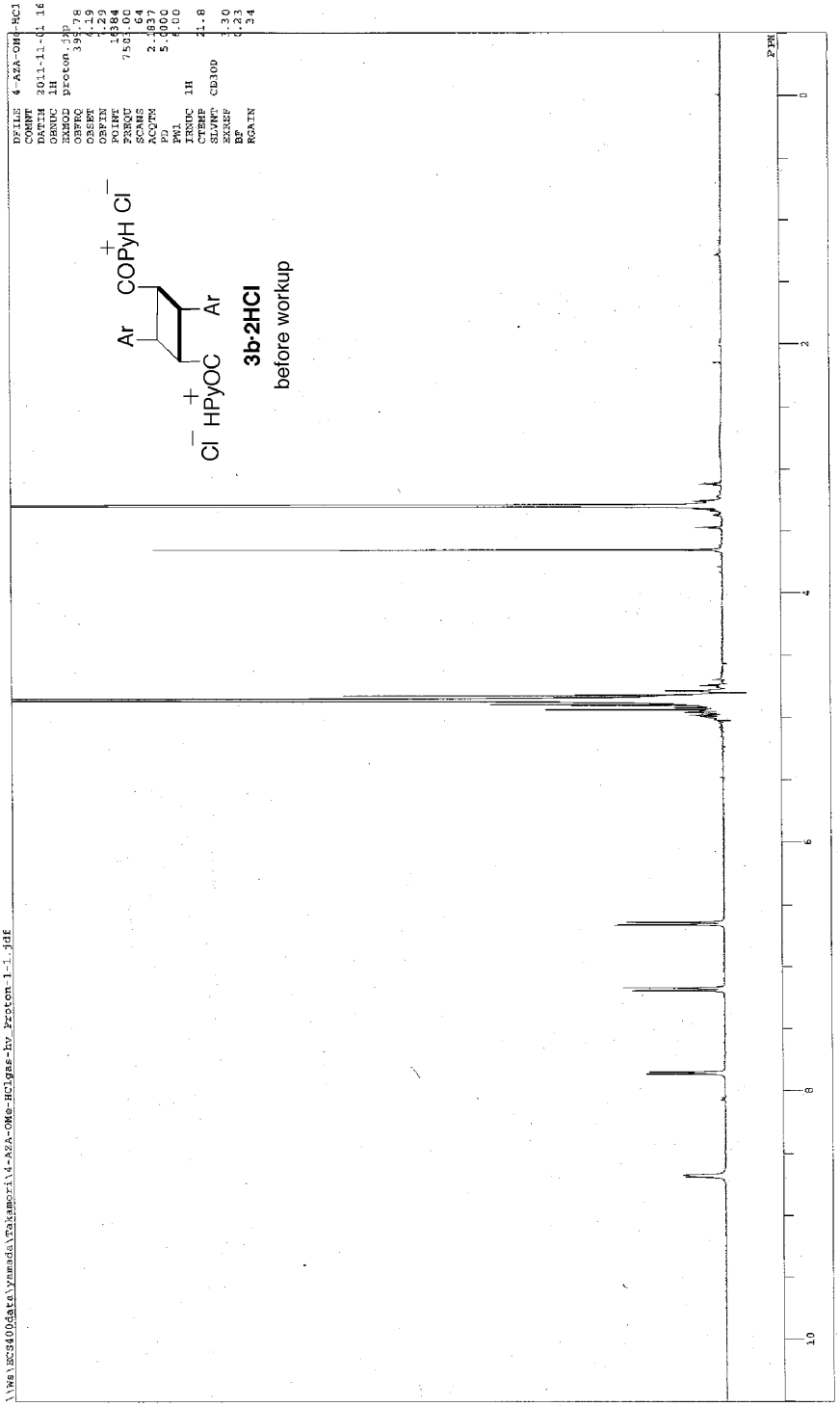


Fig. S3 ^{1}H NMR Spectrum for **3b** (in CD_3OD) after the cascade reaction before workup.

7. Schematic possible process for the orientation change from 1b to 2b.

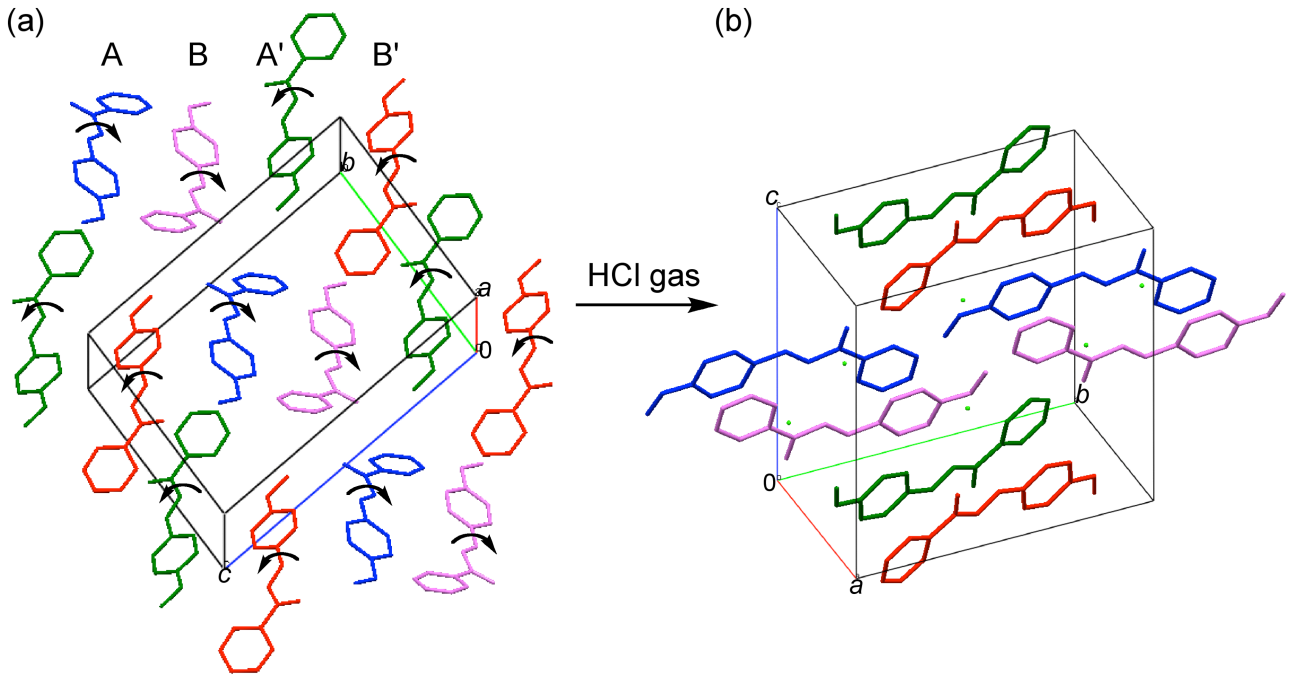


Fig. S4 Possible process for the orientation change from **1b** (a) to **2b** (b) on exposure to HCl gas.

8. Photomicrographs of a single crystal of 2b (a) before and (b) after irradiation for 24h.

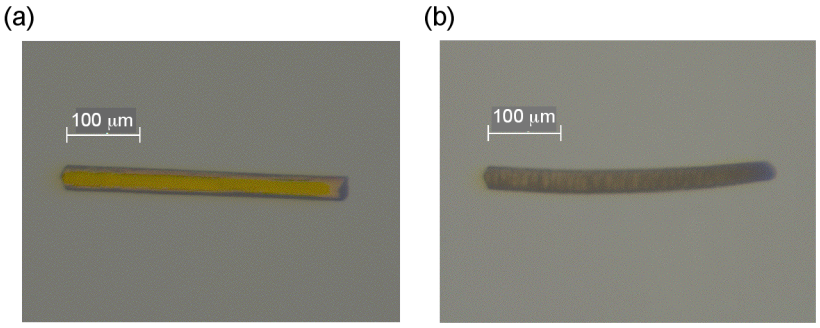


Fig. S5 Photomicrographs of a single crystal of **2b** (a) before and (b) after irradiation for 24h.