Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Highly Enantioselective Recognition of a Wide Range of Carboxylic Acids Based on Enantioselectively Aggregation-Induced Emission

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Materials and Methods

Materials. All reagents and solvents were chemical pure (CP) grade or analytical reagent (AR) grade and were used as received unless otherwise indicated. $CDCl_3$ for NMR solvent was stirred for 20 min over anhydrous K_2CO_3 before used.

Measurements. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV 400 spectrometer at 298 K in $CDCl_3$. 2D NOESY spectra were measured on a Varian NMR System 600 at 600 MHz at 298 K in $CDCl_3$. Fluorescent emission spectra were collected on Shimadzu RF-5301 fluorophotometer at 298 K. Field emission scanning electron microscopy (FE-SEM) images were taken on a FEI Sirion200 electron microscope operating at 5 kV or 10 kV. Mass spectrum was measured on Bruker BioApex FTMS instrument.

^{1}H NMR titration was carried out by addition of concentrated solution of chiral acid **4** into the solution of receptor **3** in $CDCl_3$. To keep constant concentration of sensor **3** and account for dilution effects during titration, the solution of **4** was prepared with the solution of **3** at its initial concentration as a solvent. The association constants were calculated by nonlinearly curve fitting in Origin 6.1 using following equation (*Chem Eur J*. 1998, 4, 845):

$$\delta_{obs} = \delta_{\mathbf{H}} + \frac{([\mathbf{H}] + [\mathbf{G}] + 1/K_a) - \sqrt{([\mathbf{H}] + [\mathbf{G}] + 1/K_a)^2 - 4[\mathbf{H}][\mathbf{G}]}}{2[\mathbf{H}]} \cdot (\delta_{com} - \delta_{\mathbf{H}})$$

δ_{obs}: chemical shift of the proton of methine group connected with the amino group of (*R,R*)-**3** after enantiomer of **4** was gradually added;

δ_H: chemical shift of the proton of methine group connected with the amino group of (*R,R*)-**3** without **4**;

δ_{com}: chemical shift of the proton of methine group connected with the amino group of (*R,R*)-**3** in complex of **3**-**4**;

[H]: molar concentration of (*R,R*)-**3**;

[G]: molar concentration of enantiomer of **4** added during titration.

Syntheses of (*R,R*)-**3** and (*S,S*)-**3**

(*R,R*)-**3**: synthesis of (*R,R*)-N-Boc-**3**. To the flask were added (*1R,2R*)-N-Boc-N′-chloroacetyl-1,2-cyclohexanediame (*1R,2R*)-**1** (1 g, 3.5 mmol), (*E*)-α-(*p*-nitrophenyl)-β-(*p*-hydroxyphenyl) acrylonitrile **2** (0.77 g, 2.9 mmol), anhydrous K_2CO_3 (0.24 g, 1.75 mmol), KI (0.096 g, 0.58 mmol) and acetonitrile (60 mL) in order. The mixture was refluxed for about 3 h until one of reactants disappeared (monitored by TLC, dichloromethane : methanol V / V 15 : 1). The reaction mixture was cooled to room temperature and the resultant yellow precipitates were collected by filtering. The solid was dissolved into 1,2-dichloroethane and washed with water until the organic phase had *p*H 6. Upon dried over anhydrous Na_2SO_4 and filtered, the organic phase was evaporated to give a yellow solid. Remove of the Boc group of N-Boc-**3**. The obtained yellow solid was dissolved in dichloromethane (10 mL) and the solution was cooled to 0 ^oC. Trifluoroacetic acid (8.56 mL, 115.2 mmol) was dropped into the solution over 0.5 h. The solution was continued to stir for about 20 minutes at 0 ^oC (monitored by TLC, dichloromethane : methanol V / V 15 : 1). After washed two times with water, the solution was adjusted to *p*H 7—8 by 20 % (weight) of Na_2CO_3 aqueous solution and extracted with chloroform. The combined organic phase was dried over anhydrous Na_2SO_4, filtered and evaporated to afford a yellow solid (1.02 g, 85 %). Mp 125 – 127 ^oC; $[\alpha]^{20}_D$ –32.5 (*c*, 1.0, THF); IR (KBr) 3364, 3269, 3096, 2928, 2856, 2213, 1660, 1588, 1564, 1514, 1443, 1430, 1378, 1341; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.62 (s, 1H), 7.06 (d, *J* = 8.8 Hz, 2H); 6.44 (d, *J* = 8.8 Hz, 1H), 4.63, 4.58 (2d, *J* = 14.8 Hz, 2H), 3.69 – 3.56 (m, 1H), 2.54 – 2.43 (m, 1H), 2.05 – 1.98 (m, 2H), 1.75 (d, *J* = 10.4 Hz, 2H), 1.60 – 1.15 (m, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 167.4, 159.6, 147.7, 144.4, 140.7, 132.0, 127.1, 126.5, 124.4, 117.4, 115.3, 107.5, 67.4, 56.0, 55.3, 35.6, 32.4, 25.0; ESI^+ MS *m*/*z* calcd for $C_{23}H_{24}N_4O_4$ 420 [M], Found 421.1 $[(M+1)]^+$.

(*S,S*)-**3**: synthesized according to the same procedure for (*S,S*)-**3**. Mp 124 – 126 ^oC; $[\alpha]^{20}_D$ –33.6 (*c*, 1.0, THF); IR (KBr) 3366, 3270, 3099, 2933, 2859, 2215, 1661, 1588, 1565, 1515, 1446, 1430, 1342 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.62 (s, 1H), 7.06 (d, *J* = 8.8 Hz, 2H); 6.43 (d, *J* = 8.8 Hz, 1H), 4.63, 4.58 (2d, *J* = 14.8 Hz, 2H), 3.68 – 3.57 (m, 1H), 2.52 – 2.42 (m, 1H), 2.05 – 1.95 (m, 2H), 1.75 (d, *J* = 11.2 Hz, 2H), 1.45 – 1.15 (m, 6H); ^{13}C NMR (100MHz, $CDCl_3$) δ 167.4, 159.6, 147.7, 144.4, 140.7, 132.0, 127.1, 126.5, 124.4, 117.5, 115.3, 107.5, 67.4, 56.0, 55.3, 35.6, 32.4, 25.0; ESI^+ MS *m*/*z* calcd for $C_{23}H_{24}N_4O_4$ 420 [M], Found 421.1 $[(M+1)]^+$.

Supporting Figures

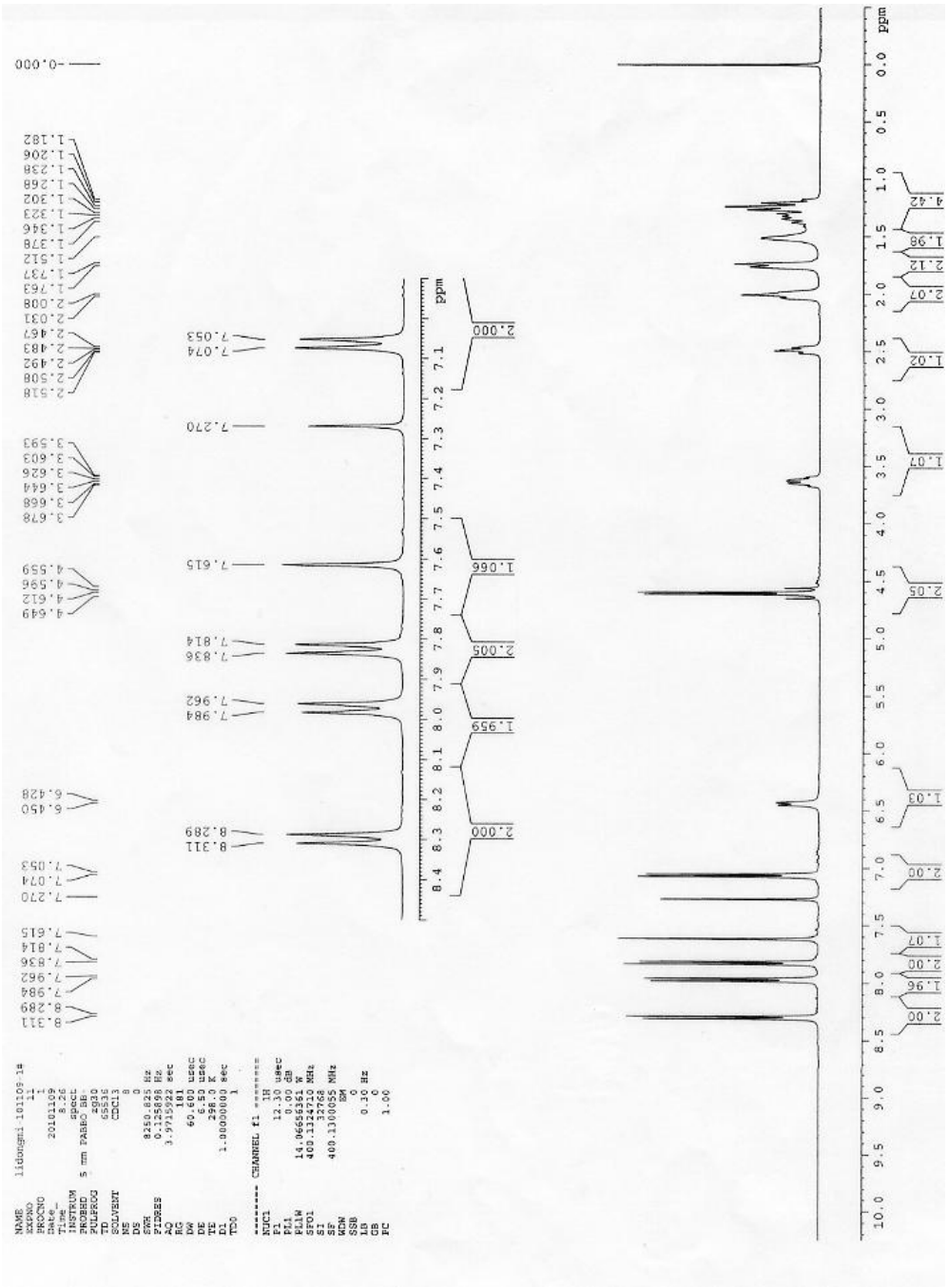


Figure S1. ^{1}H NMR spectrum of (*R,R*)-**3** in $CDCl_3$.

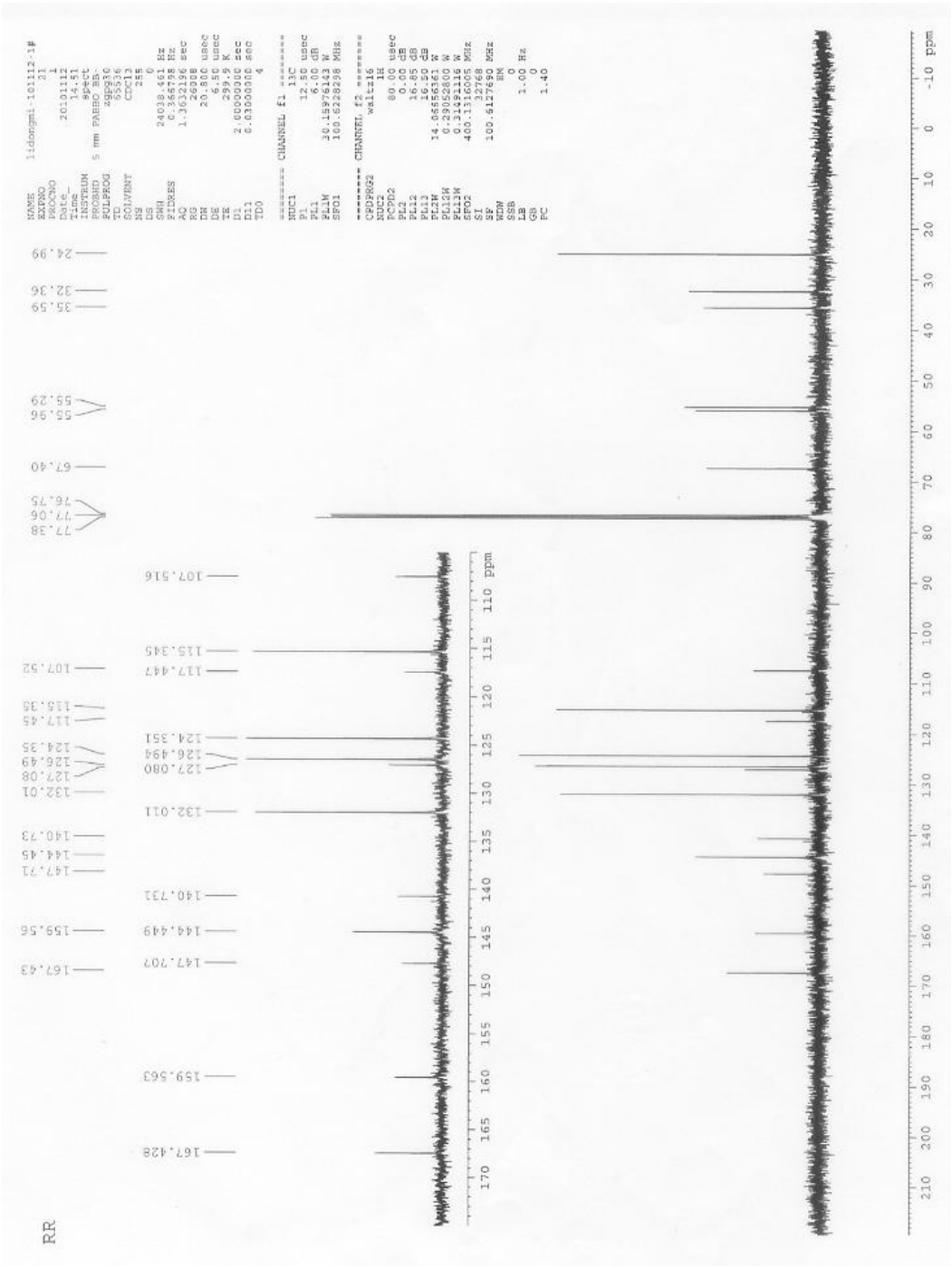


Figure S2. ^{13}C NMR spectrum of (*R,R*)-**3** in $CDCl_3$.

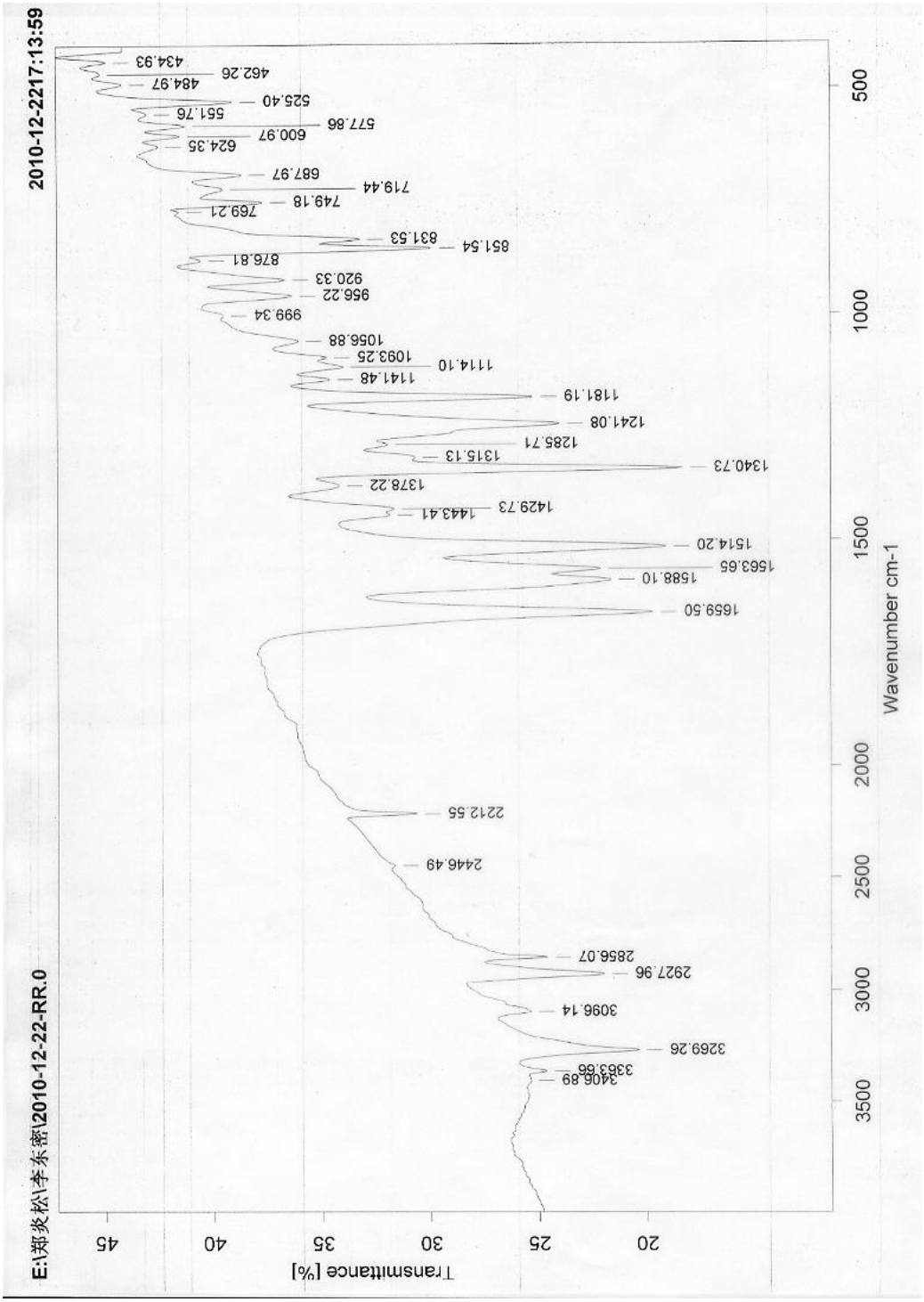


Figure S3. IR spectrum of (*R,R*)-**3**.

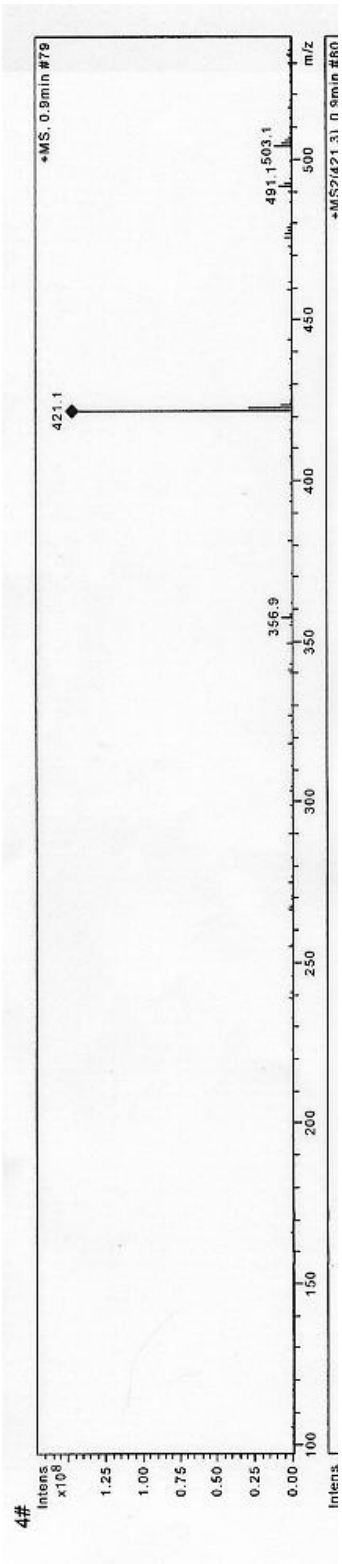


Figure S4. MS spectrum of (*R,R*)-**3**.

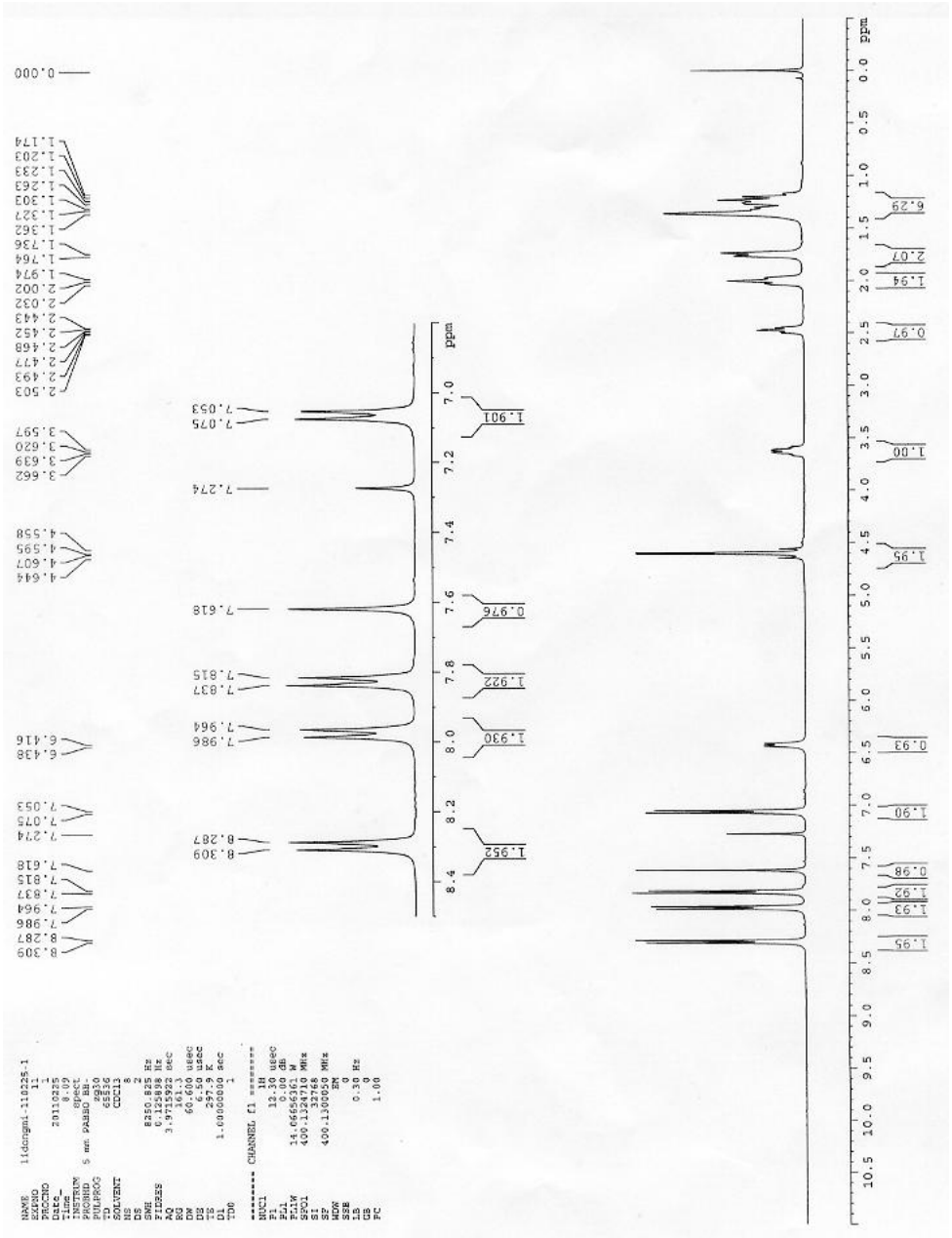


Figure S5. ^{1}H NMR spectrum of (*S,S*)-**3** in $CDCl_3$.

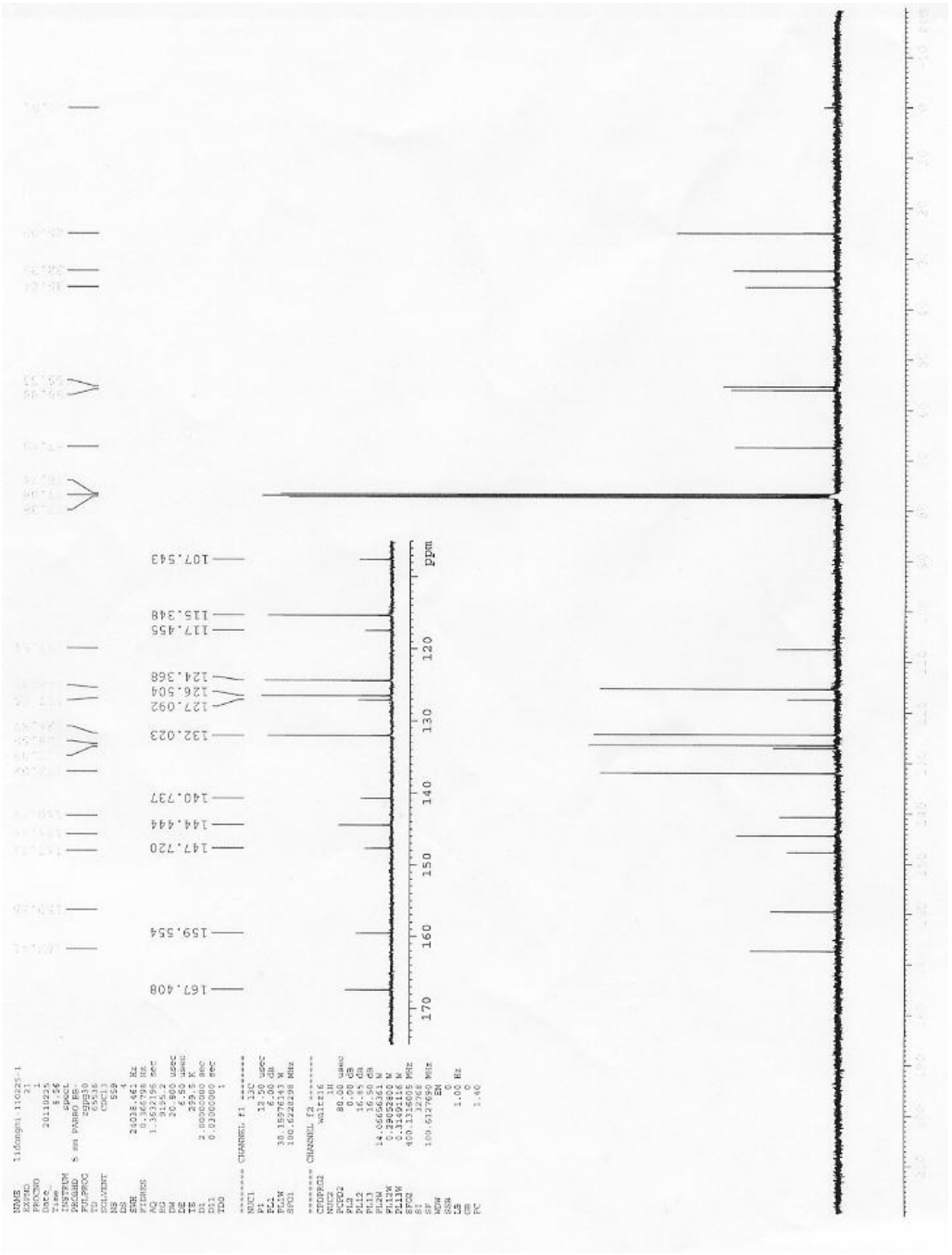


Figure S6. ^{13}C NMR spectrum of (*S,S*)-**3** in $CDCl_3$.

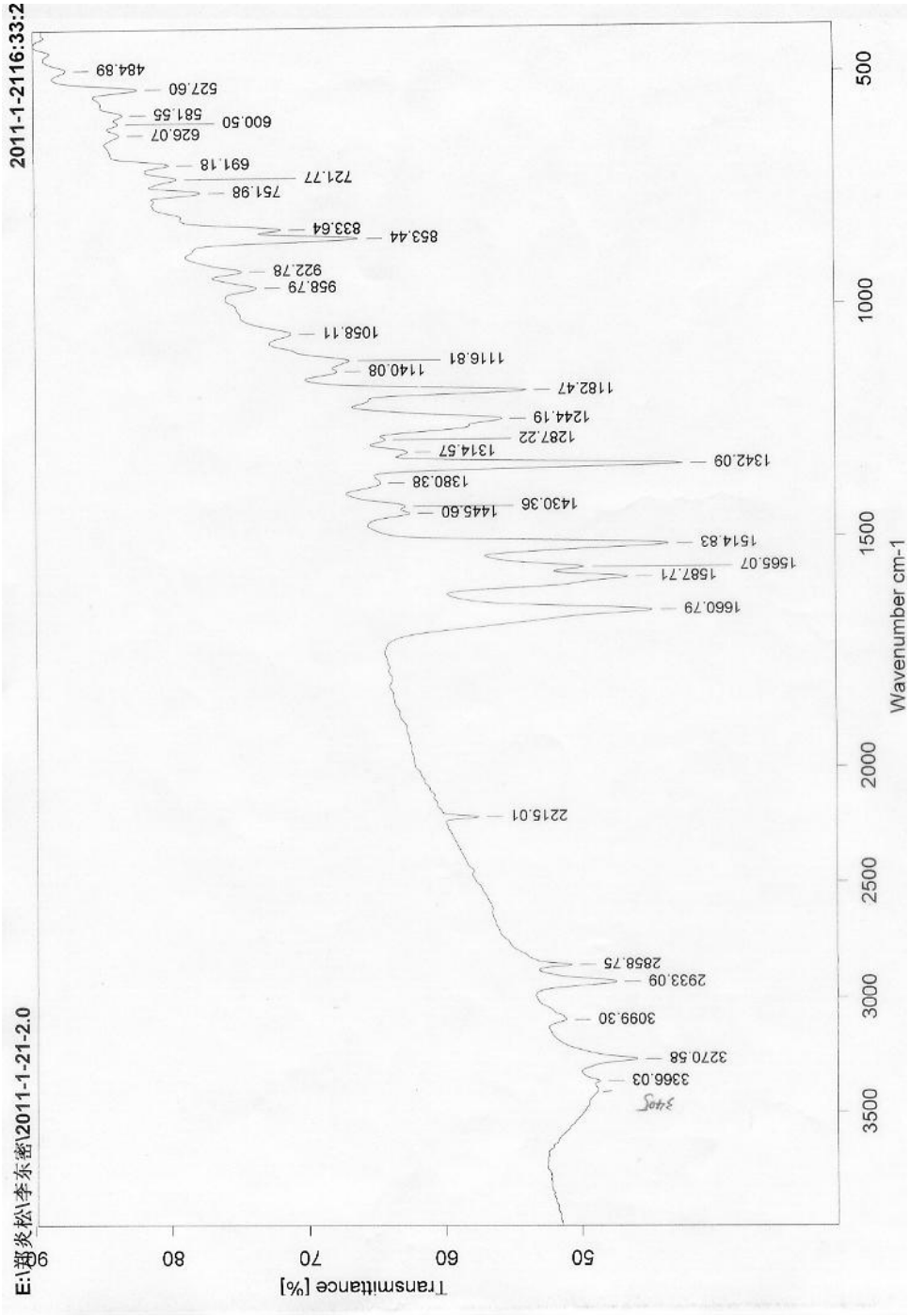


Figure S7. IR spectrum of (*S,S*)-**3**.

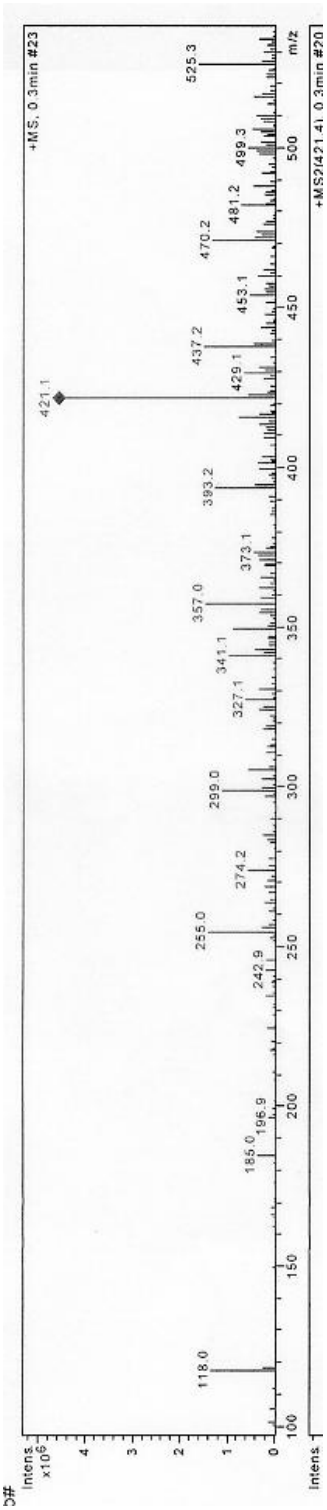


Figure S8. MS spectrum of (*S,S*)-**3**.

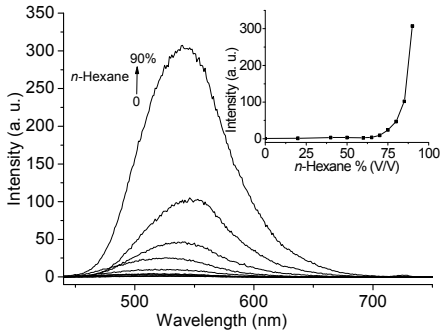


Figure S9. Changes of the fluorescence spectra of (*R,R*)-**3** (5.0×10^{-4} M) with *n*-hexane added in 1,2-dichloroethane. λ_{ex} = 320 nm, ex/em slits = 5/3 nm. Inset: curve of the fluorescence intensity vs *n*-hexane percentage measured at 550 nm.

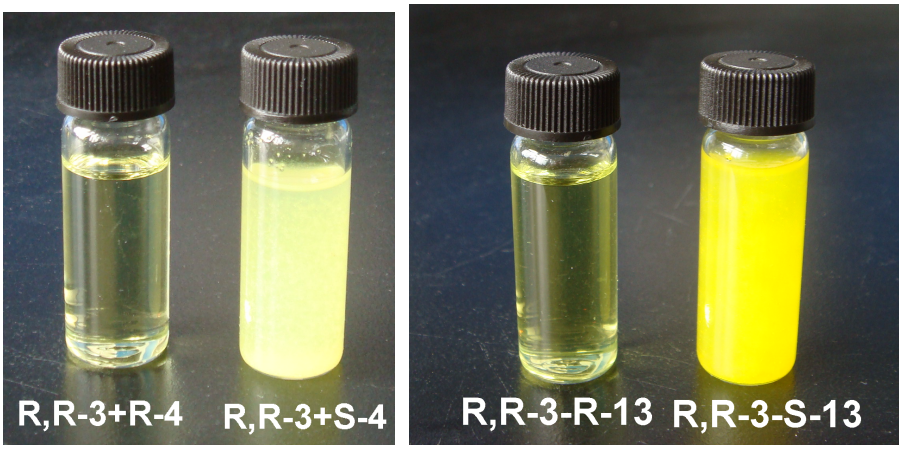
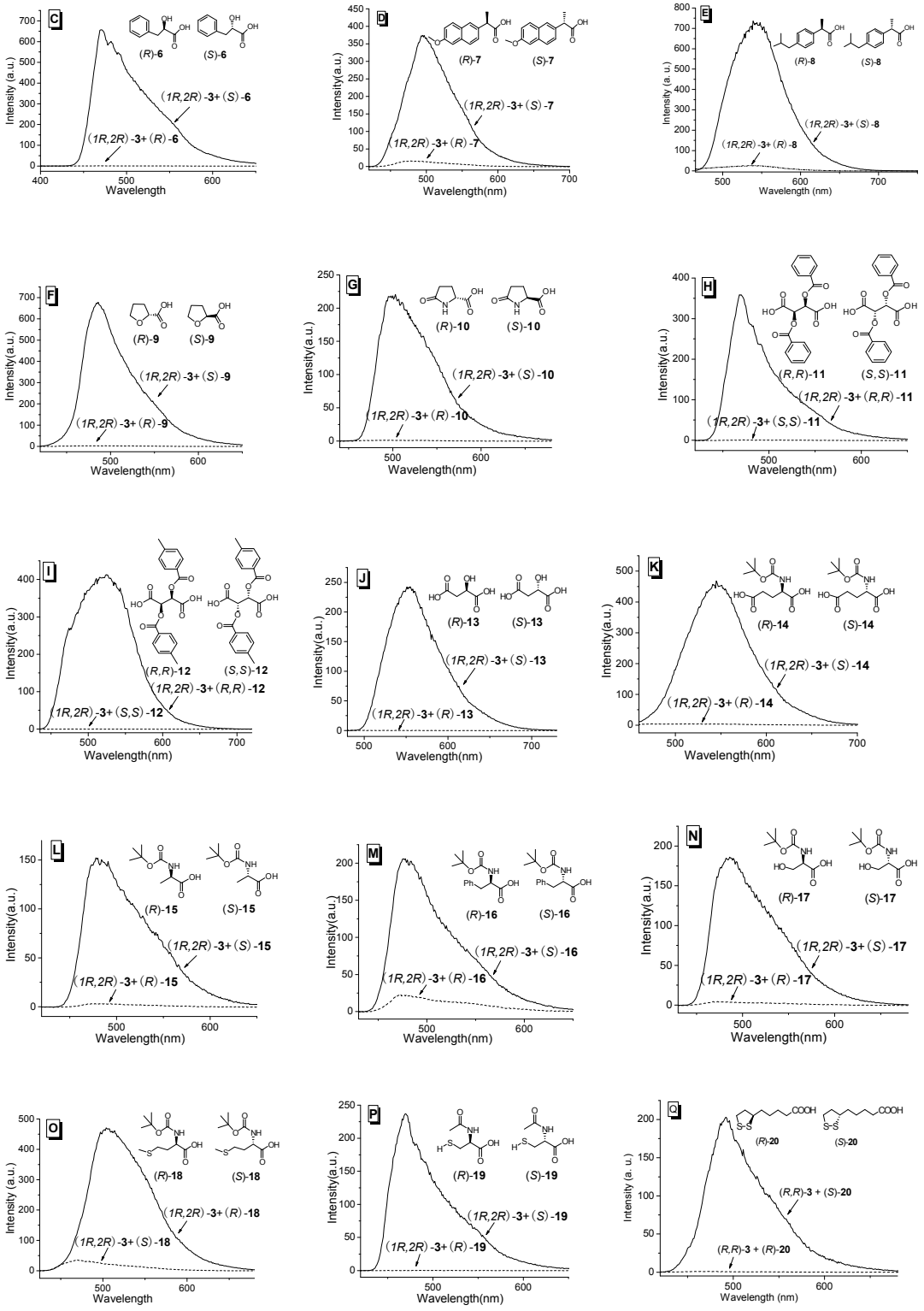


Figure S10. Photos of a mixture of *(R,R*-**3**) and enantiomers of acids in solvent under daylight.


C
(R)-6
(S)-6
(1R,2R)-3+(S)-6
(1R,2R)-3+(R)-6
Intensity (a.u.)
Wavelength
D
(R)-7
(S)-7
(1R,2R)-3+(S)-7
(1R,2R)-3+(R)-7
Intensity(a.u.)
Wavelength(nm)
E
(R)-8
(S)-8
(1R,2R)-3+(S)-8
(1R,2R)-3+(R)-8
Intensity (a. u.)
Wavelength (nm)
F
(R)-9
(S)-9
(1R,2R)-3+(S)-9
(1R,2R)-3+(R)-9
Intensity(a.u.)
Wavelength(nm)
G
(R)-10
(S)-10
(1R,2R)-3+(S)-10
(1R,2R)-3+(R)-10
Intensity(a.u.)
Wavelength(nm)
H
(R,R)-11
(S,S)-11
(1R,2R)-3+(R,R)-11
(1R,2R)-3+(S,S)-11
Intensity(a.u.)
Wavelength(nm)
I
(R,R)-12
(S,S)-12
(1R,2R)-3+(R,R)-12
(1R,2R)-3+(S,S)-12
Intensity(a.u.)
Wavelength(nm)
J
(R)-13
(S)-13
(1R,2R)-3+(S)-13
(1R,2R)-3+(R)-13
Intensity(a.u.)
Wavelength(nm)
K
(R)-14
(S)-14
(1R,2R)-3+(S)-14
(1R,2R)-3+(R)-14
Intensity(a.u.)
Wavelength(nm)
L
(R)-15
(S)-15
(1R,2R)-3+(S)-15
(1R,2R)-3+(R)-15
Intensity(a.u.)
Wavelength(nm)
M
(R)-16
(S)-16
(1R,2R)-3+(S)-16
(1R,2R)-3+(R)-16
Intensity(a.u.)
Wavelength(nm)
N
(R)-17
(S)-17
(1R,2R)-3+(S)-17
(1R,2R)-3+(R)-17
Intensity(a.u.)
Wavelength(nm)
O
(R)-18
(S)-18
(1R,2R)-3+(R)-18
(1R,2R)-3+(S)-18
Intensity (a.u.)
Wavelength
P
(R)-19
(S)-19
(1R,2R)-3+(S)-19
(1R,2R)-3+(R)-19
Intensity(a.u.)
Wavelength(nm)
Q
(R)-20
(S)-20
(R,R)-3 + (S)-20
(R,R)-3 + (R)-20
Intensity (a. u.)
Wavelength (nm)

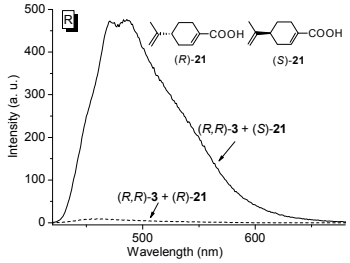
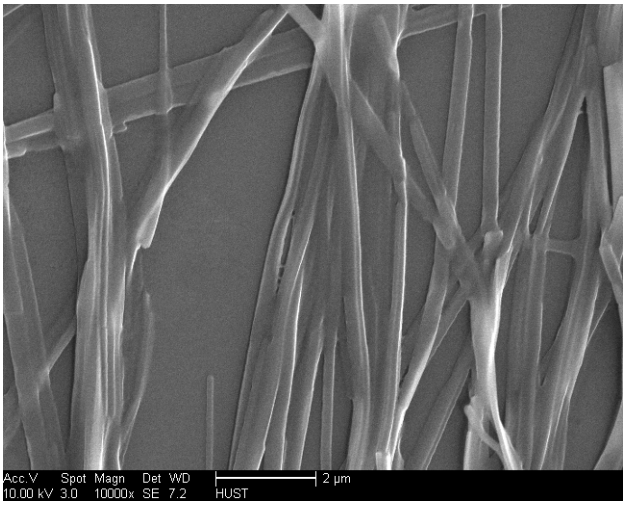
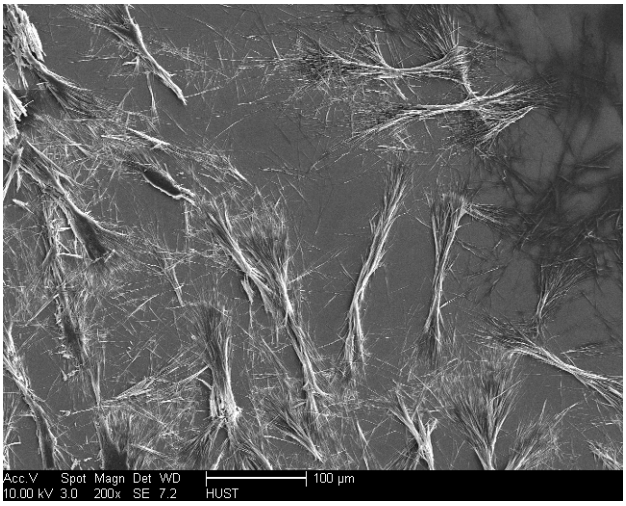


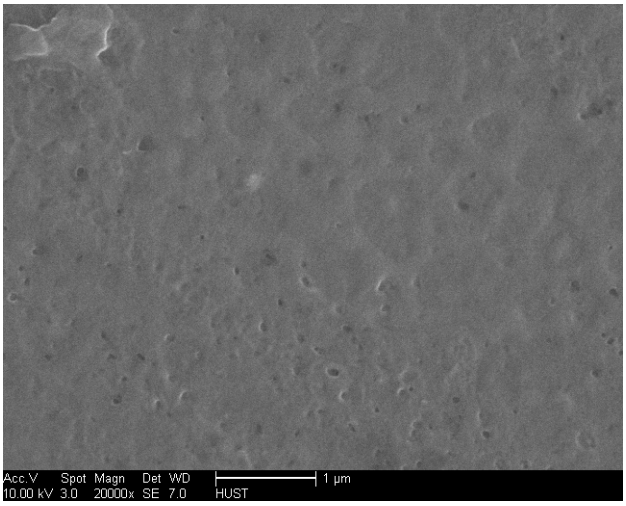
Figure S11. The fluorescence spectra of the mixture of acid enantiomer and (*R,R*)-**3** in solvent(s). C) 5×10-3 M in ethanol. D) 5×10-3 M in 1,2-dichloroethane and n-hexane 1.2:0.8. E) 2.0×10-3 M in 1,2-dichloroethane and n-hexane 2.0:2.5. F) 2×10-3 M in 1,2-dichloroethane. G) 5×10^{-3} M in 1,2-dichloroethane. H, I) 2.5×10^{-3} M in 1,2-dichloroethane. J) [(*R,R*)-**3**] = 2 [**13**] = 5×10^{-3} M in ethanol and water 1:1. K) 2.2×10^{-3} M in ethanol and water 1:3.5. L) 2.5×10^{-3} M in ethanol and water 1:3. M) 3.3×10^{-3} M in ethanol and water 1:1. N) 2.8×10^{-3} M in ethanol and water 1:2.5. O) 5×10^{-3} M in 1,2-dichloroethane and *n*-hexane 1.7 : 1.1. P) 2.2×10^{-3} M in 1,2-dichloroethane and ethanol 4:0.5. Q) 5×10^{-3} M in 1,2-dichloroethane and *n*-hexane 1.2 : 0.8. R) 5.3×10^{-3} M in 1,2-dichloroethane and *n*-hexane 1.0 : 0.9. [(*R,R*)-**3**] = **[**acid] unless indicated.



(a)



(b)



(c)

Figure S12. (a) and (b) FE-SEM images of precipitates from the mixture of (*R,R*)-**3** and (*S*)-**4** in 1,2-dichloroethane. (c) FE-SEM images of the solid obtained by evaporation of solution of (*R,R*)-**3** and (*R*)-**4** in 1,2-dichloroethane.

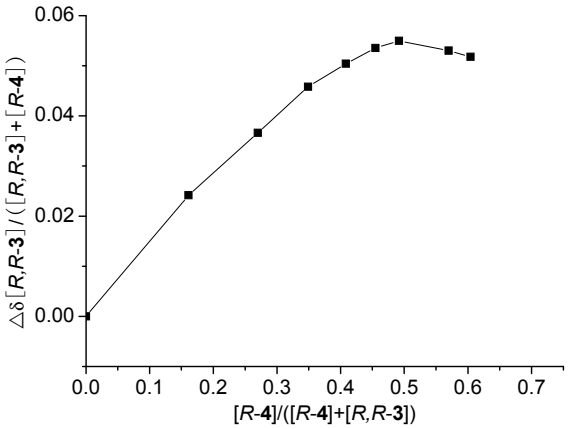


Figure S13. Job plot for ^{1}H NMR titration of (*R,R*)-**3** ([(*R,R*)-**3**] = 0.005 M) with (*R*)-**4** in $CDCl_3$.

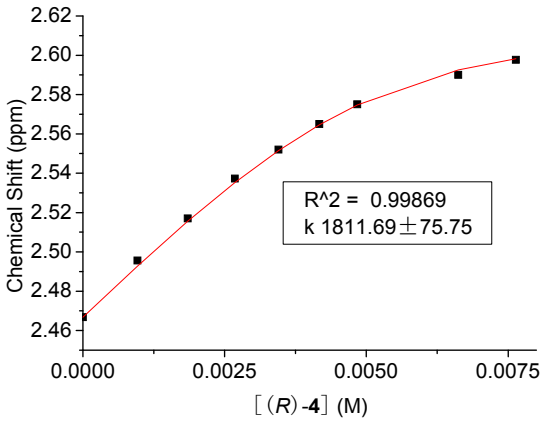


Figure S14. Chemical shift of (*R,R*)-**3** ([(*R,R*)-**3**] = 0.005 M) with concentration of (*R*)-**4** added. The red curve is the result by fitting.

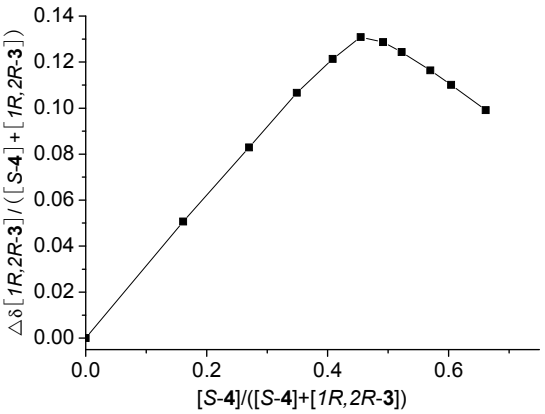


Figure S15. Job plot for ^{1}H NMR titration of (*R,R*)-**3** ([(*R,R*)-**3**] = 0.005 M) with (*S*)-**4** in $CDCl_3$.

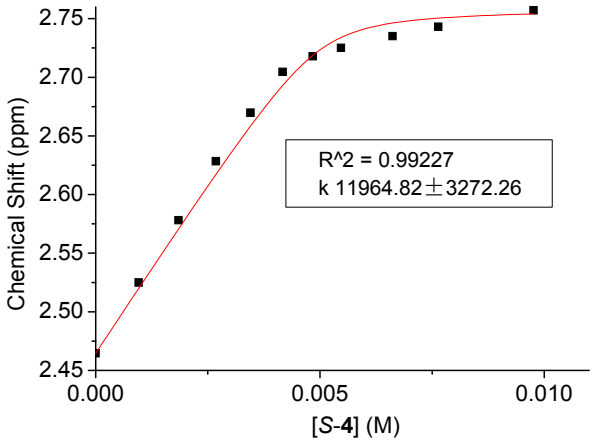
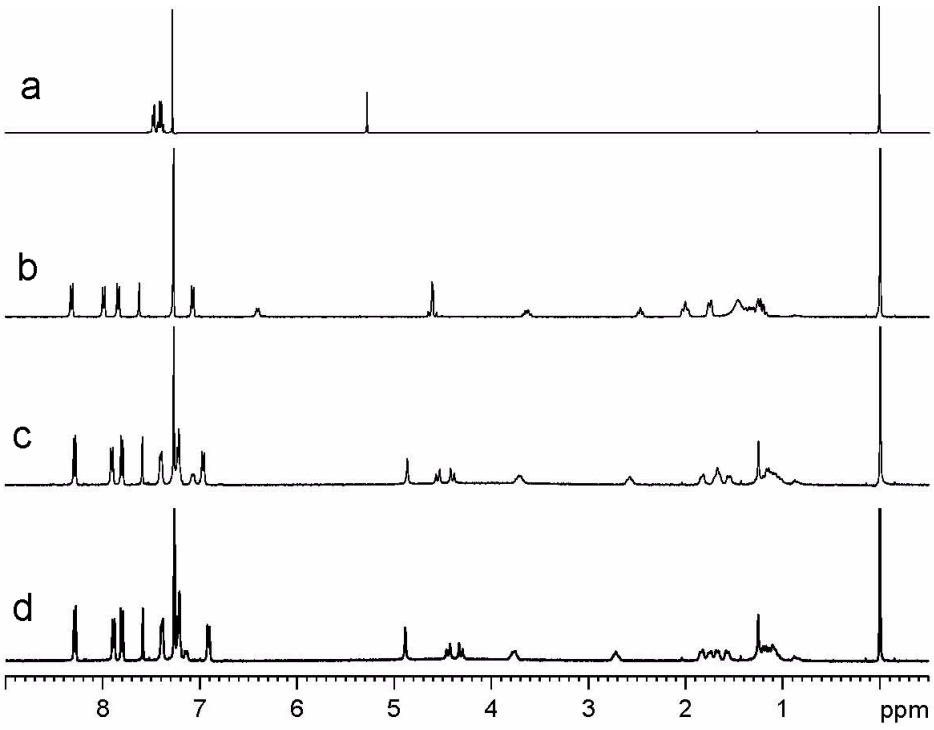
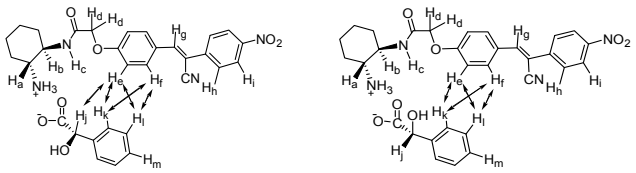


Figure S16. Chemical shift of (*R,R*)-**3** ([(*R,R*)-**3**] = 0.005 M) with concentration of (*S*)-**4** added. The red curve is the result by fitting.





	H_a	H_b	H_c	H_d	H_e	H_f
(*R*,*R*)-**3**+(*R*)-**4**	+0.11	+0.08	+0.67	-0.21	-0.10	-0.08
(*R*,*R*)-**3**+(*S*)-**4**	+0.24	+0.14	+0.75	-0.30	-0.16	-0.09
	H_g	H_h	H_i	H_j	H_k	H_l
(*R*,*R*)-**3**+(*R*)-**4**	-0.03	-0.04	-0.03	-0.42	-0.08	-0.18
(*R*,*R*)-**3**+(*S*)-**4**	-0.03	-0.04	-0.03	-0.39	-0.08	-0.18

Figure S17. ^{1}H NMR spectrum of (*S*)-**4** (a); of (*R*,*R*)-**3** (b); (c) of a 1:1 mixture of (*R*)-**4** and (*R*,*R*)-**3** (c); of a 1:1 mixture of (*S*)-**4** and (*R*,*R*)-**3** (d). [(*R*,*R*)-**3**] = [(*R*)-**4**] = [(*S*)-**4**] = 5 mM in $CDCl_3$. And the difference of chemical shift of the mixture of (*R*,*R*)-**3** and enantiomers of **4** vs that of free ones (Δδ ppm) that was put in the table.

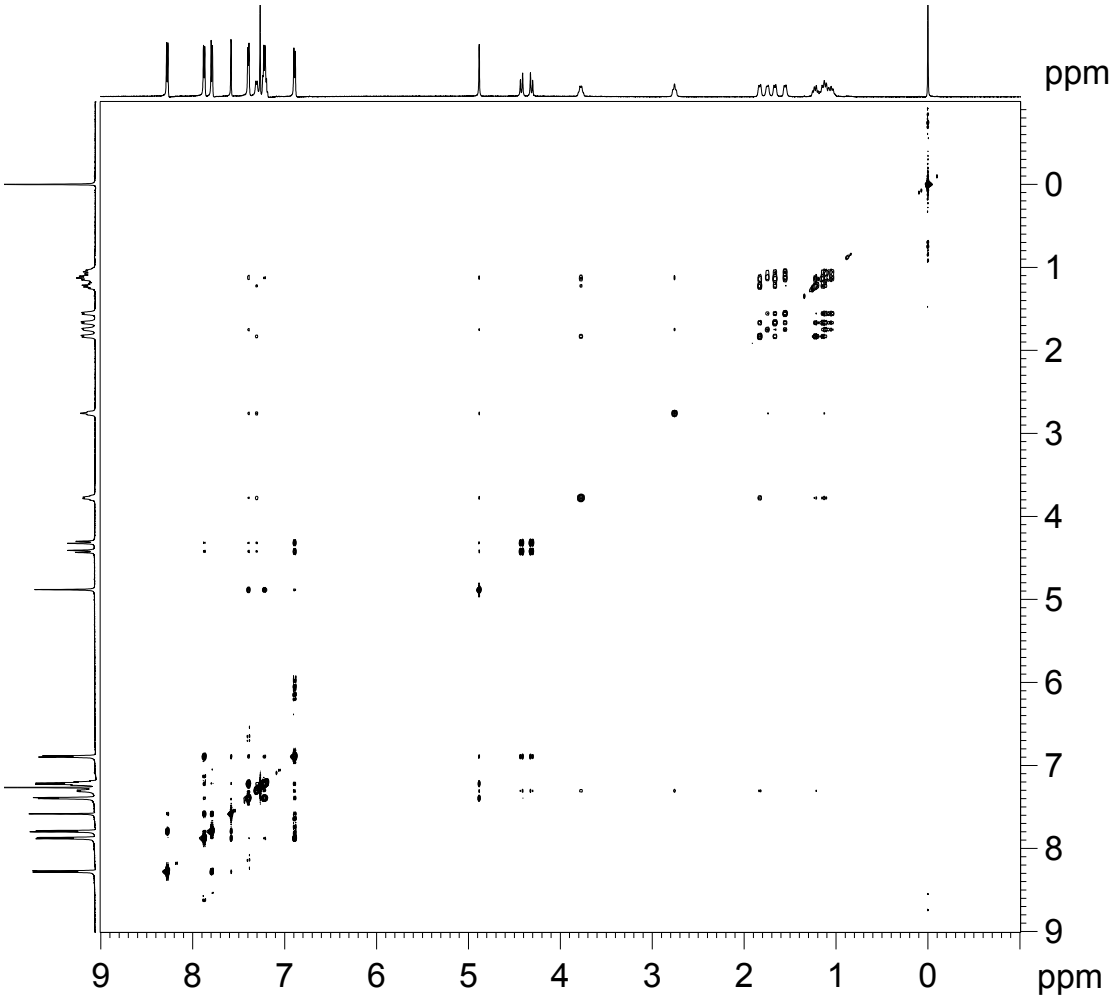


Figure S18. 2D NOESY spectrum of a 1:1 mixture of (*S*)-**4** and (*R,R*)-**3** in $CDCl_3$. It was measured in 5 h at 25 ^{o}C. [(*R,R*)-**3**] = [(*S*)-**4**] = 10 mM.

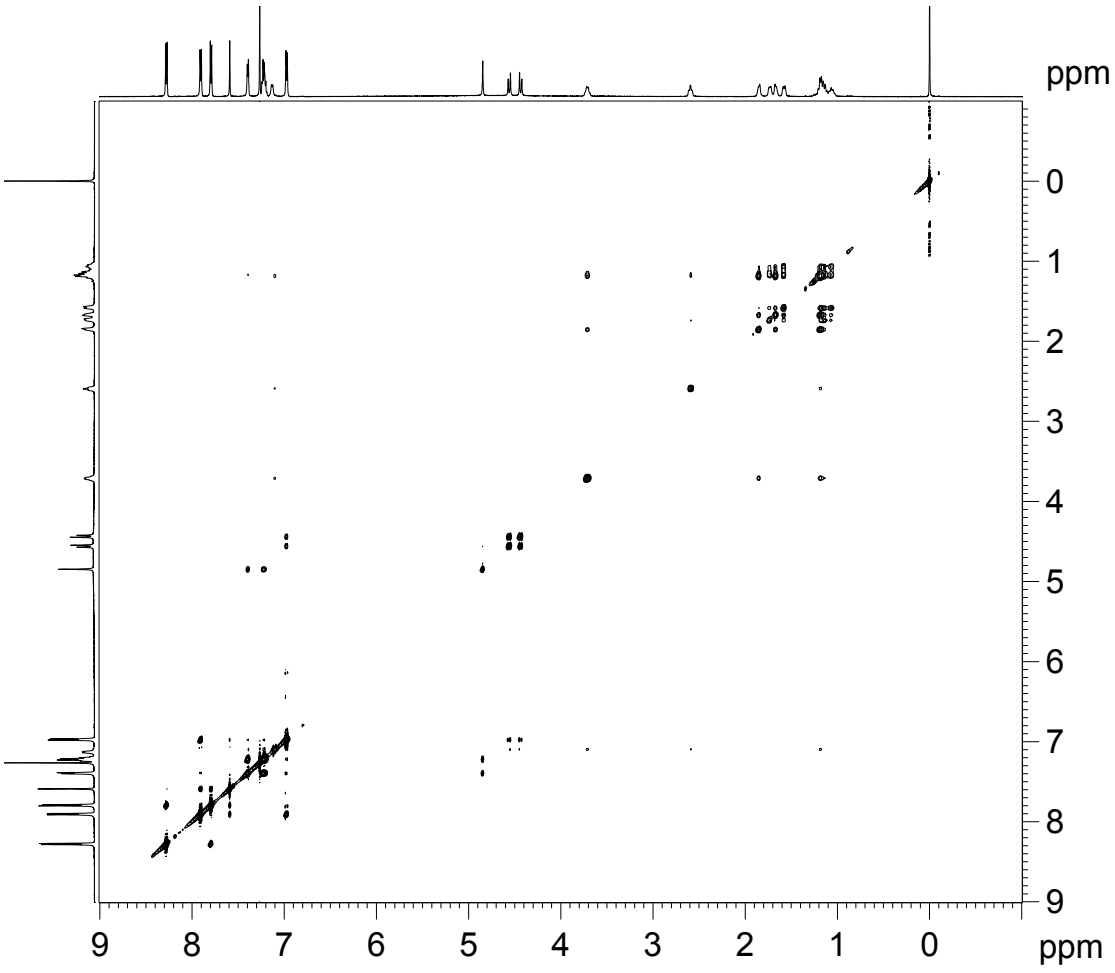
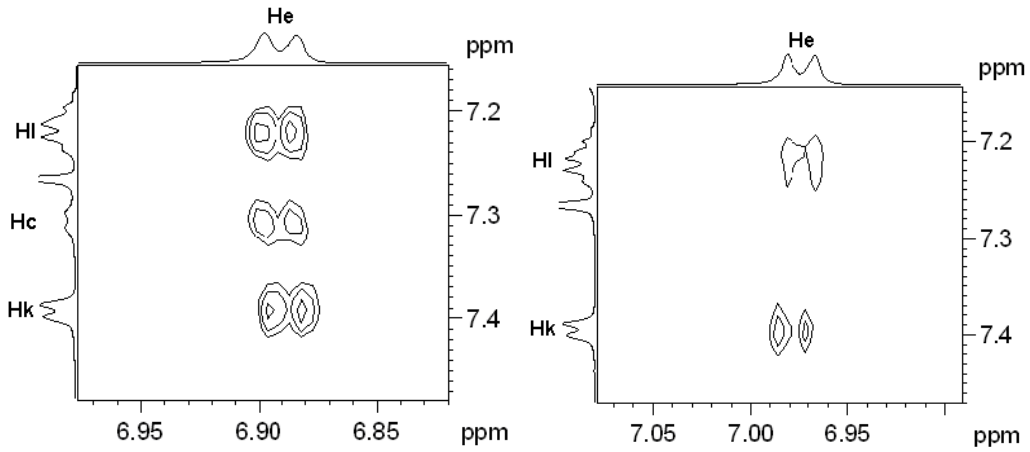


Figure S19. 2D NOESY spectrum of a 1:1 mixture of (*R*)-**4** and (*R,R*)-**3** in $CDCl_3$. It was measured in 5 h at 25 ^{o}C. [(*R,R*)-**3**] = [(*R*)-**4**] = 10 mM.



(a) (b)

Figure S20. (a) Portion of the 2D NOESY spectrum of a 1:1 mixture of (*R,R*)-**3** and (*S*)-**4**, and (b) that of (*R*)-**4**.