

## Supporting Information

### Stereomutation and chiroptical bias in the kinetically controlled supramolecular polymerization of cyano-luminogens

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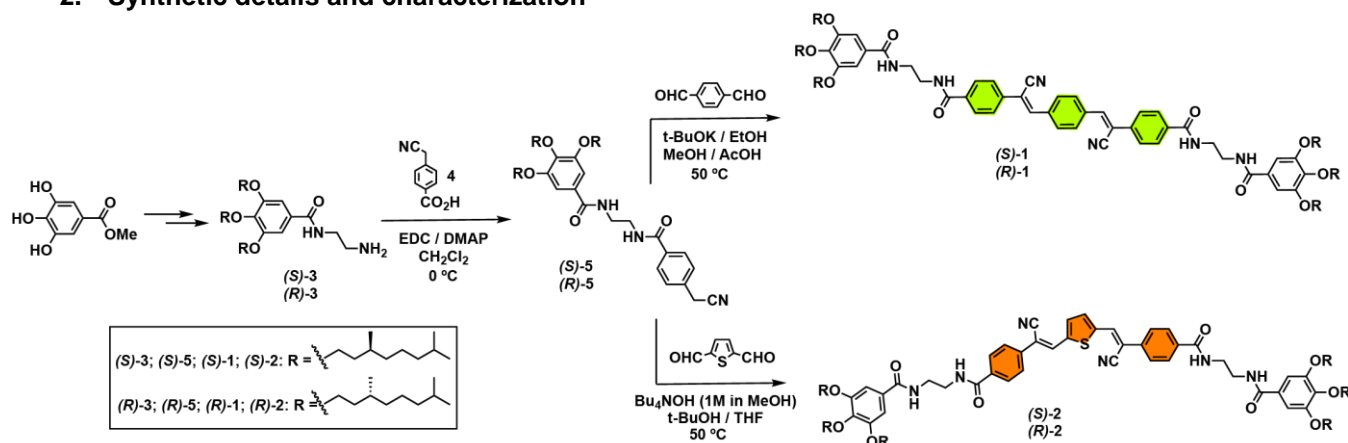
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## 1. Experimental Procedures

**General.** All solvents were dried according to standard procedures. Reagents were used as purchased. All air-sensitive reactions were carried out under argon atmosphere. Flash chromatography was performed using silica gel (Merck, Kieselgel 60, 230-240 mesh or Scharlau 60, 230-240 mesh). Analytical thin layer chromatography (TLC) was performed using aluminium-coated Merck Kieselgel 60 F254 plates. NMR spectra were recorded on a Bruker Avance 300 ( $^1\text{H}$ : 300 MHz;  $^{13}\text{C}$ : 75 MHz) spectrometer using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts ( $\delta$ ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad. FT-IR spectra in film were recorded on a Bruker Tensor 27 (ATR device) spectrometer. The samples for the FTIR experiments were prepared as follows: a 1 mM solution of the corresponding cyano-luminogen in  $\text{CHCl}_3$  was deposited in the ATR device and the solvent was gently evaporated under a nitrogen stream. UV-Vis spectra were registered on a Jasco-V630 spectrophotometer equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 280 and 550 nm, with a wavelength increment of 1 nm, a response time of 4 s, and a bandwidth of 1 nm, by using a quartz cuvette (Hellma). Circular dichroism (CD) measurements were performed on a JASCO-1500 dichrograph equipped with a Peltier thermoelectric temperature controller. The spectra were recorded in the continuous mode between 280 and 550 nm, with a wavelength increment of 0.2 nm, a response time of 1 s, and a bandwidth of 2 nm using a quartz cuvette (Hellma). Matrix Assisted Laser Desorption Ionization (coupled to a Time-Of-Flight analyzer) experiments (MALDI-TOF) were recorded on a Bruker REFLEX spectrometer detecting cationic species. AFM measurements were performed under ambient conditions using a MultiMode 8HR SPM from Bruker operating in tapping mode in air. Silicon cantilevers with a resonance frequency of 300 kHz were used. Solutions of compounds **(S)-1**, **2** and **(R)-1**, **2** were spin-coated onto HOPG. Circularly polarized luminescence (CPL) measurements were performed in a spectrofluoropolarimeter, using a green InGaN LED (LuckyLight Electronics Co., LTD,  $\lambda_{\text{max}} = 517$  nm, HWHM = 15 nm) (3 mm, 2 V) as excitation source at  $90^\circ$  of the samples (parameters used: emission slot width  $\approx 10$  nm, integration time = 4 s, scanning speed = 50 nm/min, 3 accumulations). Photoluminescence (PL) measurements were recorded on a Jasco-FP8300 or a Edinburgh Instruments FS5

**Preparation of solutions of Aggl and AgglI species for spectroscopic measurements.** Firstly, one stock solution of each enantiomer in  $\text{CHCl}_3$  (1 mM) is prepared, slightly heating it up to ensure the complete solution of the solid. Afterwards, two 10  $\mu\text{M}$  solutions are prepared from that previous one, one in  $\text{CHCl}_3$  and the other one in MCH. Both of these solutions must be stocked away from daylight, since the product isomerizes under the presence of light. Aggl is obtained as soon as both solutions are mixed in the right proportion. After 24 h, Aggl has completely turned into AgglI for all of the molar fractions in which Aggl was found.

## 2. Synthetic details and characterization

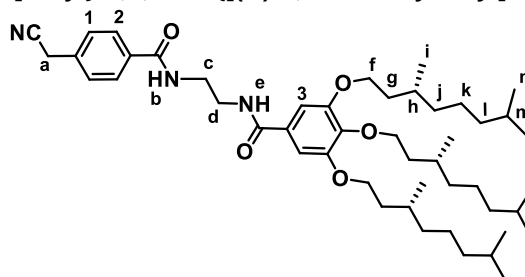


Compounds **(R)-3**, **(S)-3**, **(R)-4** and **(S)-4**<sup>S1</sup> were prepared following the procedures previously described in the literature and presented identical spectroscopic features.<sup>S1</sup>

### General procedure for the preparation of 5

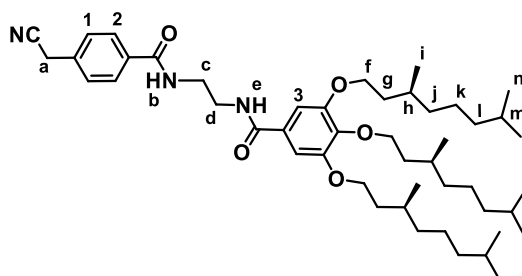
To a solution of **4** (70 mg, 0.043 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (5 mL), a mixture of EDC (91 mg, 0.47 mmol) and DMAP (58 mg, 0.47 mmol) is added slowly under argon atmosphere at 0 °C. The mixture is stirred for 30 min and, after, **3** (300 mg, 0.47 mmol) is slowly added at 0 °C. The solution is stirred at room temperature for 18 h. After this time, the reaction mixture is washed with HCl (1 M) and a saturated solution of K<sub>2</sub>CO<sub>3</sub>, dried under MgSO<sub>4</sub> and the solvent is removed under reduced pressure. The crude is purified by column chromatography (silica gel, CHCl<sub>3</sub>/MeOH 10:0.05) obtaining product **5**.

### *N*-{2-[4-(cyanomethyl)benzamide]ethyl}-3,4,5-tris{[(*R*)-3,7-dimethyloctyl]oxy}benzamide ((*R*)-5)



63 % yield. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.84 (2H, H<sub>1</sub>, d, *J*=8.2 Hz), 7.56 (1H, H<sub>b</sub>, br), 7.37 (2H, H<sub>2</sub>, d, *J*=8.1 Hz), 7.28 (1H, H<sub>e</sub>, br), 7.04 (2H, H<sub>3</sub>, s), 4.02 (6H, H<sub>f</sub>, m), 3.78 (2H, H<sub>a</sub>, s), 3.68 (4H, H<sub>c+d</sub>, br), 1.84 (3H, H<sub>h</sub>, m), 1.67 (3H, H<sub>m</sub>, br), 1.52 (6H, H<sub>g</sub>, m), 1.38-1.07 (18H, H<sub>j-l</sub>, br), 0.92 (9H, H<sub>i</sub>, m), 0.85 (18H, H<sub>n</sub>, d, *J*=6.6 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ: 169.1, 168.0, 153.3, 141.3, 133.8, 133.7, 128.5, 128.3, 128.1, 117.3, 105.6, 71.9, 67.6, 39.5, 39.4, 37.6, 37.5, 37.4, 36.5, 30.0, 29.8, 28.1, 24.9, 24.8, 23.7, 22.8, 22.7, 19.7. FT-IR (cm<sup>-1</sup>): 1117, 1231, 1340, 1382, 1427, 1466, 1499, 1542, 1580, 1635, 2250, 2870, 2925, 2954, 3298. HRMS (MALDI-TOF) *m/z*: calculated for C<sub>48</sub>H<sub>77</sub>N<sub>3</sub>O<sub>5</sub> [M]<sup>+</sup> 775.5863; found [M]<sup>+</sup> 775.4050.

### *N*-{2-[4-(cyanomethyl)benzamide]ethyl}-3,4,5-tris{[(*S*)-3,7-dimethyloctyl]oxy}benzamide ((*S*)-5)

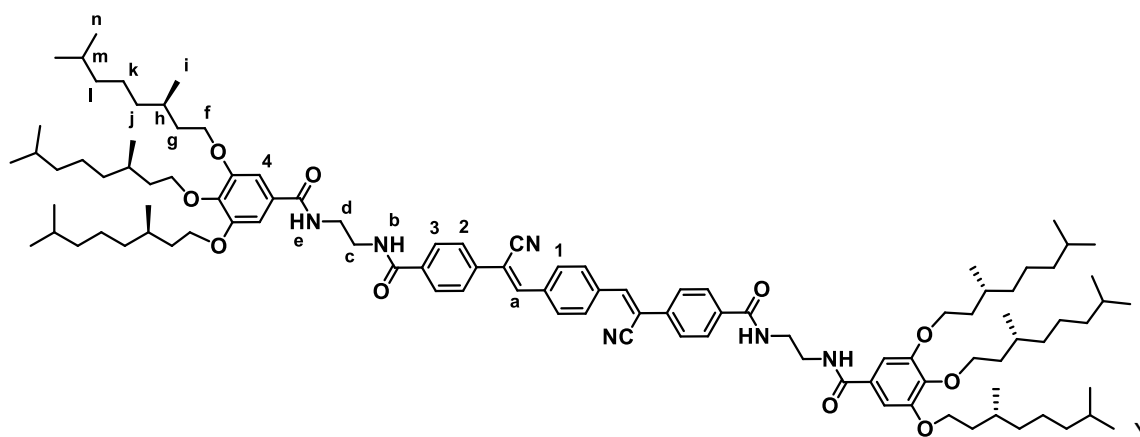


71 % yield. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.83 (2H, H<sub>1</sub>, d, *J*=8.2 Hz), 7.54 (1H, H<sub>b</sub>, br), 7.32 (2H, H<sub>2</sub>, d, *J*=8.1 Hz), 7.30 (1H, H<sub>e</sub>, br), 7.02 (2H, H<sub>3</sub>, s), 4.05 (6H, H<sub>f</sub>, m), 3.81 (2H, H<sub>a</sub>, s), 3.65 (4H, H<sub>c+d</sub>, br), 1.83 (3H, H<sub>h</sub>, m), 1.68 (3H, H<sub>m</sub>, br), 1.52 (6H, H<sub>g</sub>, m), 1.38-1.05 (18H, H<sub>j-l</sub>, br), 0.95 (9H, H<sub>i</sub>, m), 0.85 (18H, H<sub>n</sub>, d, *J*=6.6 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ: 169.3, 168.4, 153.0, 141.2, 133.5, 133.9, 128.6, 128.3, 128.1, 117.4, 105.8, 72.0, 67.5, 39.5, 39.3, 37.9, 37.4, 37.3, 36.8, 30.0, 29.7, 28.0, 24.8, 24.7, 23.7, 22.8, 22.7, 19.5. FT-IR (cm<sup>-1</sup>): 1118, 1235, 1343, 1379, 1425, 1464, 1501, 1546, 1580, 1632, 2258, 2871, 2926, 2954, 3299. HRMS (MALDI-TOF) *m/z*: calculated for C<sub>48</sub>H<sub>77</sub>N<sub>3</sub>O<sub>5</sub> [M]<sup>+</sup> 775.5863; found [M]<sup>+</sup> 775.4145.

### Synthesis of cyano- luminogens **1**. General procedure

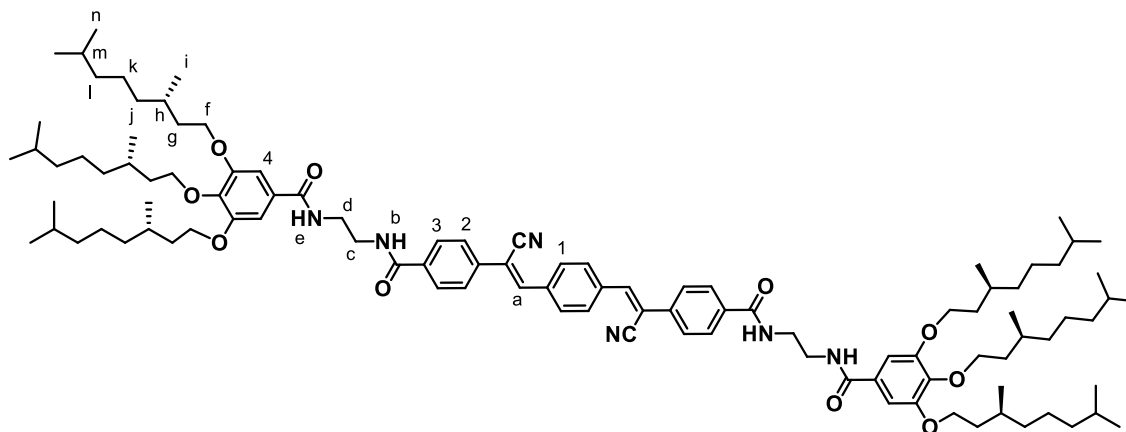
To a solution of **5** (120 mg, 0.155 mmol) and thereftaldehyde (10.5 mg, 0.078 mmol) in <sup>t</sup>BuOH (8 mL), 3 mg of <sup>t</sup>BuOK are added and the mixture is stirred at 50 °C for 5 h in the absence of light. After this time, the resulting solid is filtered and washed with cold MeOH. Finally, it is dried under vacuum to obtain product **1** as a yellow solid.

***N,N'*-[({4,4'-[(1*Z*,1'*Z*)-1,4-phenylenbis(1-cyanoethene-2,1-diyl)]bis(benzoyl)}bis(azanodiyl))bis(ethene-2,1-diyl)]bis(3,4,5-tris[[(*R*)-3,7-dimethyloctyl]oxy]benzamide) ((*R*)-1)**



60 % yield. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.99 (4H, H<sub>1</sub>, s), 7.88 (4H, H<sub>3</sub>, d, *J*=8.2 Hz), 7.70 (4H, H<sub>2</sub>, d, *J*=8.2 Hz), 7.59 (2H, H<sub>a</sub>, s), 7.56 (2H, H<sub>b</sub>, br), 7.16 (2H, H<sub>e</sub>, br), 7.05 (4H, H<sub>4</sub>, s), 4.03 (12H, H<sub>f</sub>, m), 3.72 (8H, H<sub>c+d</sub>, br), 1.85 (6H, H<sub>n</sub>, m), 1.68 (6H, H<sub>m</sub>, br), 1.51 (12H, H<sub>g</sub>, m), 1.38-1.08 (36H, H<sub>j-l</sub>, br), 0.91 (18H, H<sub>i</sub>, m), 0.85 (36H, H<sub>n</sub>, d, *J*=5.3 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ: 169.1, 167.7, 153.3, 141.8, 141.4, 137.1, 135.6, 134.9, 130.2, 128.8, 128.1, 126.3, 112.3, 109.1, 105.7, 71.9, 67.7, 39.5, 39.4, 37.7, 37.5, 36.5, 31.4, 30.0, 29.8, 28.1, 24.9, 24.8, 22.9, 22.8, 19.7. FT-IR (cm<sup>-1</sup>): 766, 851, 1114, 1229, 1335, 1365, 1381, 1426, 1465, 1497, 1543, 1580, 1638, 2218, 2869, 2925, 2953, 3308. HRMS (MALDI-TOF) *m/z*: calculated for C<sub>104</sub>H<sub>157</sub>N<sub>6</sub>O<sub>10</sub> [M+H]<sup>+</sup> 1650.1883; found [M+H]<sup>+</sup> 1650.1510.

***N,N'*-[({4,4'-[(1*Z*,1'*Z*)-1,4-phenylenbis(1-cyanoethene-2,1-diyl)]bis(benzoyl)}bis(azanodiyl))bis(ethene-2,1-diyl)]bis(3,4,5-tris[[(*S*)-3,7-dimethyloctyl]oxy]benzamide) ((*S*)-1)**

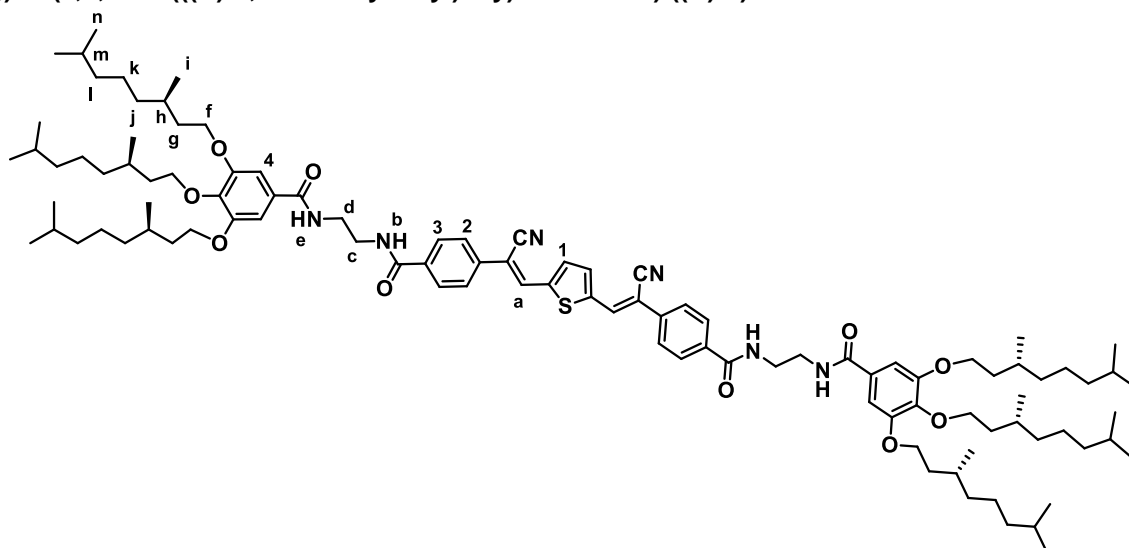


72 % yield. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) δ: 7.88 (4H, H<sub>1</sub>, s), 7.80 (4H, H<sub>3</sub>, d, *J*=8.2 Hz), 7.57 (4H, H<sub>2</sub>, d, *J*=8.2 Hz), 7.51 (2H, H<sub>a</sub>, s), 7.63 (2H, H<sub>b</sub>, br), 7.30 (2H, H<sub>e</sub>, br), 7.01 (4H, H<sub>4</sub>, s), 3.95 (12H, H<sub>f</sub>, m), 3.65 (8H, H<sub>c+d</sub>, br), 1.76 (6H, H<sub>n</sub>, m), 1.45 (6H, H<sub>m</sub>, br), 1.22 (12H, H<sub>g</sub>, m), 1.07 (36H, H<sub>j-l</sub>, br), 0.83 (18H, H<sub>i</sub>, d, *J* = 6.5 Hz), 0.77 (36H, H<sub>n</sub>, d, *J*=5.3 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) δ: 169.0, 167.6, 153.2, 141.5, 141.2, 136.7, 135.4, 134.7, 130.0, 128.6, 128.0, 126.1, 117.3, 111.9, 105.6, 71.8, 67.5, 39.4, 39.3, 37.5, 37.4, 36.4, 29.83, 29.67, 29.8, 28.0, 24.8, 24.7, 22.7, 22.6, 19.5. FT-IR (cm<sup>-1</sup>): 765, 851, 1115, 1229, 1335, 1364, 1381, 1426, 1466, 1497, 1543, 1579, 1638, 2215, 2869, 2928, 2953, 3307. HRMS (MALDI-TOF) *m/z*: calculated for C<sub>104</sub>H<sub>156</sub>N<sub>6</sub>O<sub>10</sub>K [M+K]<sup>+</sup> 1689.1883; found [M+K]<sup>+</sup> 1689.1941.

**Synthesis of cyano- luminogens 2. General procedure**

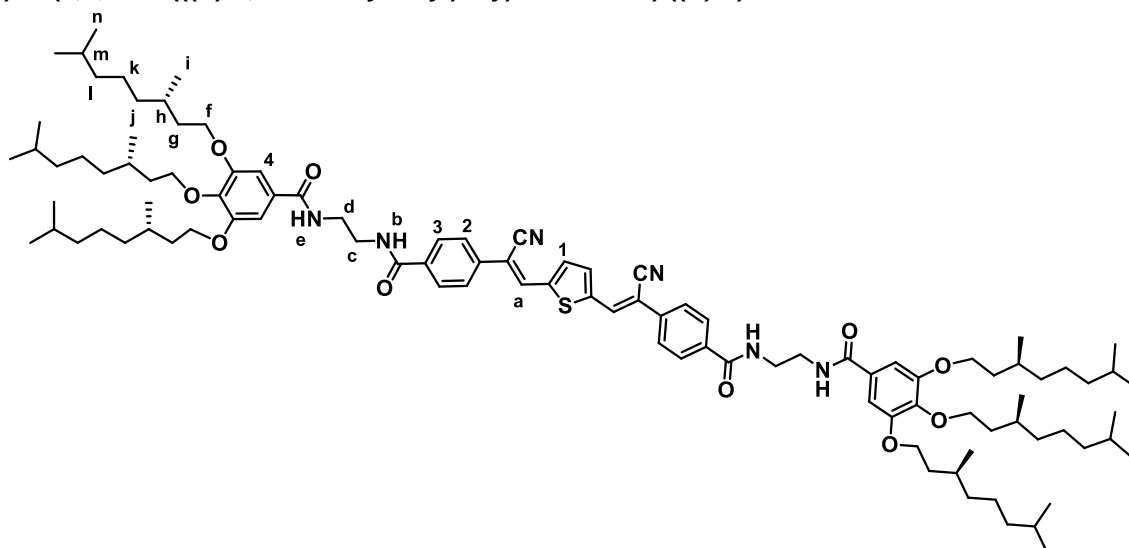
A solution of **5** (200 mg, 0.258 mmol) and thiophene-2,5-dicarbaldehyde (18.1 mg, 0.129 mmol) is prepared in 5 – 6 mL of <sup>t</sup>BuOH. Then, a small amount of <sup>t</sup>BuOK is added, observing the apparition of an orange solid in suspension. The mixture is covered to prevent it from light exposure and stirred at 50 °C for 5 h. After this time, the orange solid is extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water, dried over MgSO<sub>4</sub> and filtered. The solvent is removed under reduced pressure and the resulting product is precipitated and washed with MeOH. Finally, it is dried under vacuum to obtain product **2** as an orange solid.

**N,N'-(((4,4'-((1Z,1'Z)-thiophene-2,5-diylbis(1-cyanoethene-2,1-diyl))bis(benzoyl))bis(azanediy))bis(ethane-2,1-diyl))bis(3,4,5-tris(((R)-3,7-dimethyloctyl)oxy)benzamide) ((R)-2)**



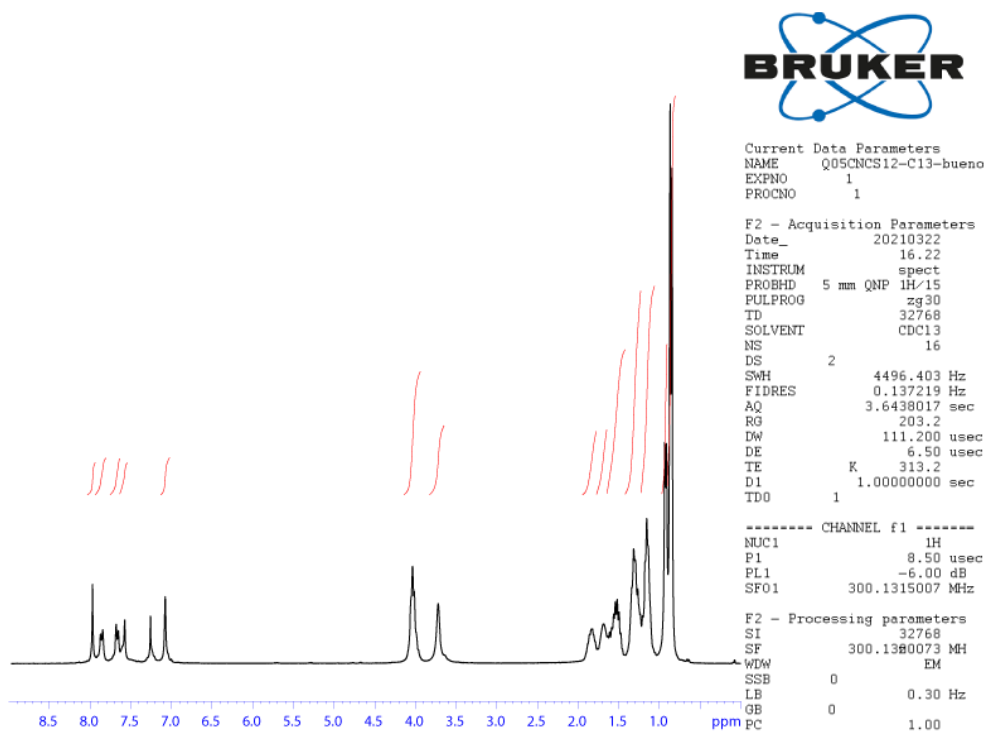
65 % yield. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, TFA) δ: 7.85 (4H, H<sub>3</sub>, d, *J*=8.2 Hz), 7.81 (4H, H<sub>a+1</sub>, s), 7.75 (4H, H<sub>2</sub>, d, *J*=8.2 Hz), 7.60 (4H, H<sub>b+e</sub>, br), 6.95 (4H, H<sub>4</sub>, s), 4.15 (12H, H<sub>f</sub>, m), 4.00 (4H, H<sub>d</sub>, br), 3.83 (4H, H<sub>c</sub>, br), 1.83 (6H, H<sub>h</sub>, m), 1.61 (6H, H<sub>m</sub>, br), 1.52 (12H, H<sub>g</sub>, m), 1.37-1.21 (24H, H<sub>j,k</sub>, br), 1.21-1.07 (12H, H<sub>i</sub>, br), 0.91 (18H, H<sub>i</sub>, m), 0.85 (36H, H<sub>n</sub>, d, *J*=5.3 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, TFA) δ: 171.6, 171.1, 153.2, 141.7, 140.4, 137.5, 135.6, 134.0, 132.8, 128.4, 127.5, 126.4, 116.9, 109.1, 105.6, 73.3, 67.9, 40.5, 40.3, 39.4, 39.3, 37.5, 37.4, 36.8, 36.2, 29.9, 29.8, 28.1, 24.8, 24.8, 22.7, 22.6, 22.6, 19.6, 18.4. FT-IR (cm<sup>-1</sup>): 665, 764, 852, 994, 1113, 1230, 1305, 1334, 1365, 1381, 1427, 1465, 1496, 1540, 1581, 1637, 2210, 2869, 2926, 2953, 3072, 3335. (MALDI-TOF) *m/z*: calculated for C<sub>102</sub>H<sub>154</sub>N<sub>6</sub>O<sub>10</sub>S [M]<sup>+</sup> 1655.1447; found [M]<sup>+</sup> 1655.1349.

**N,N'-(((4,4'-((1Z,1'Z)-thiophene-2,5-diylbis(1-cyanoethene-2,1-diyl))bis(benzoyl))bis(azanediy))bis(ethane-2,1-diyl))bis(3,4,5-tris(((S)-3,7-dimethyloctyl)oxy)benzamide) ((S)-2)**

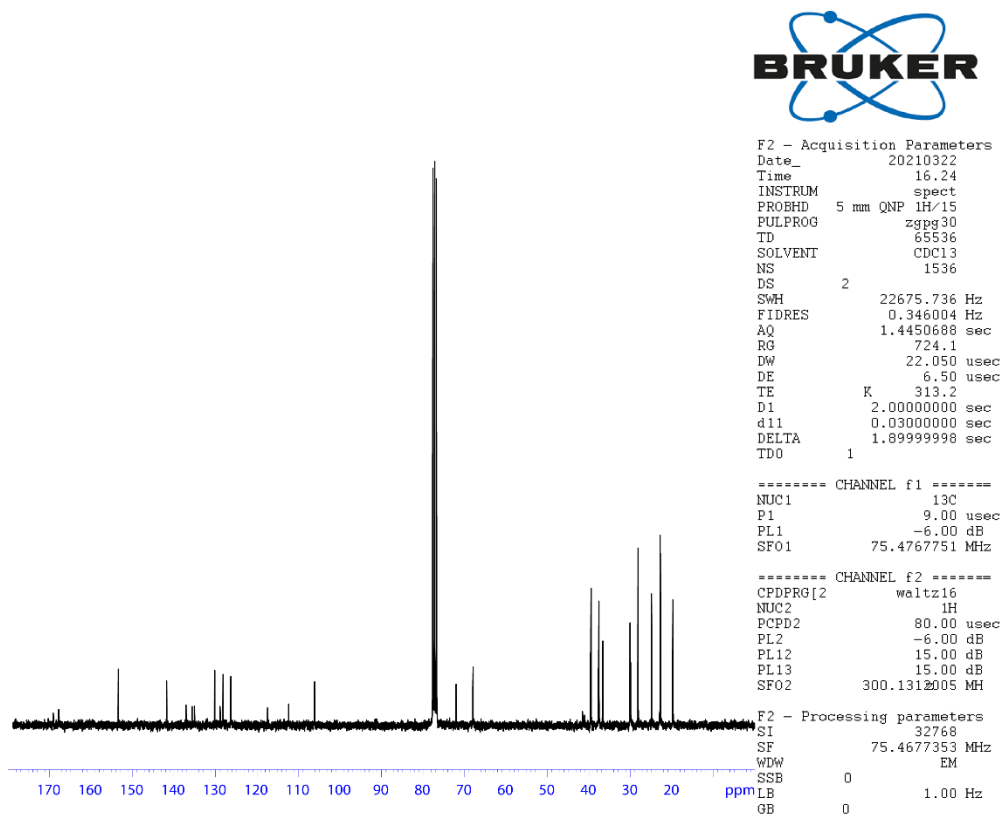


61 % yield. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, TFA) δ: 7.84 (4H, H<sub>3</sub>, d, *J*=8.95), 7.79 (2H, H<sub>a</sub>, s), 7.77 (2H, H<sub>1</sub>, s), 7.73 (4H, H<sub>2</sub>, d, *J*=8.95 Hz), 6.97 (4H, H<sub>4</sub>, s), 4.19 (12H, H<sub>f</sub>, m), 4.03 (4H, H<sub>d</sub>, br), 3.85 (4H, H<sub>c</sub>, br), 1.83 (6H, H<sub>h</sub>, m), 1.66 (6H, H<sub>m</sub>, br), 1.51 (12H, H<sub>g</sub>, m), 1.37-1.21 (24H, H<sub>j,k</sub>, br), 1.21-1.07 (12H, H<sub>i</sub>, br), 0.91 (18H, H<sub>i</sub>, m), 0.85 (36H, H<sub>n</sub>, d, *J*=5.3 Hz). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, TFA) δ: 171.4, 169.8, 153.2, 141.7, 140.6, 137.5, 135.3, 133.9, 132.9, 128.4, 127.4, 126.4, 115.8, 109.2, 105.6, 73.1, 67.8, 40.5, 40.3, 39.4, 39.3, 37.5, 37.4, 36.9, 36.3, 29.9, 29.8, 28.1, 24.8, 24.8, 22.8, 22.7, 22.7, 19.6, 19.4. FT-IR (cm<sup>-1</sup>): 624, 647, 667, 732, 765, 803, 850, 908, 988, 1065, 1112, 1229, 1999, 1365, 1381, 1426, 1466, 1495, 1538, 1581, 1635, 2210, 2869, 2925, 2952, 3320. HRMS (MALDI-TOF) *m/z*: calculated for C<sub>102</sub>H<sub>154</sub>N<sub>6</sub>O<sub>10</sub>S [M+H]<sup>+</sup> 1656.1447; found [M+H]<sup>+</sup> 1656.1421.

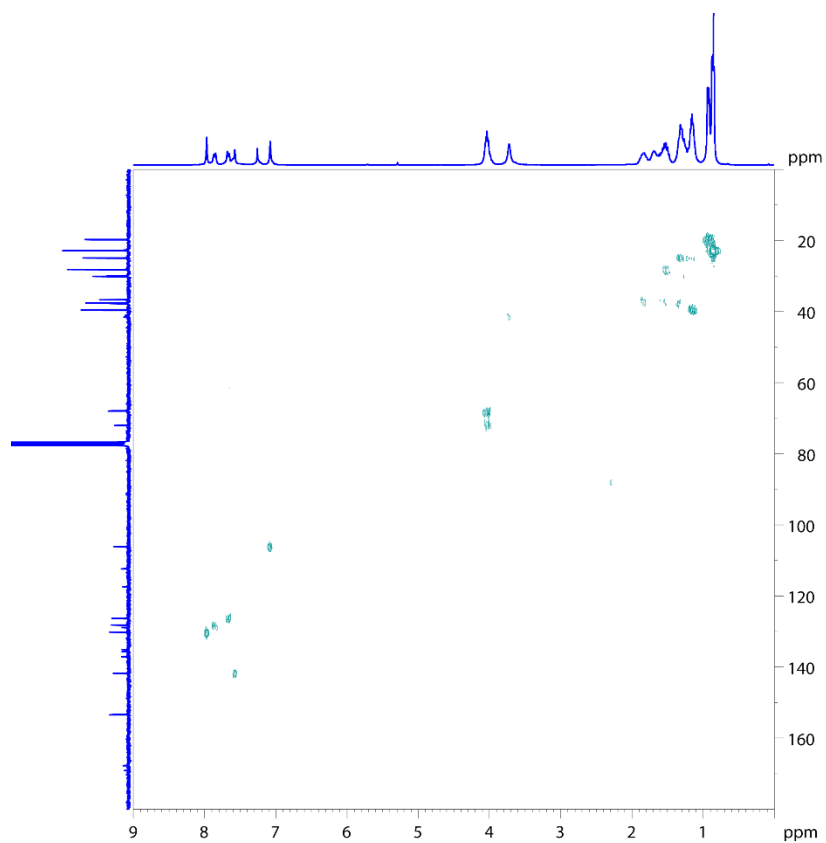
### 3. Collection of spectra



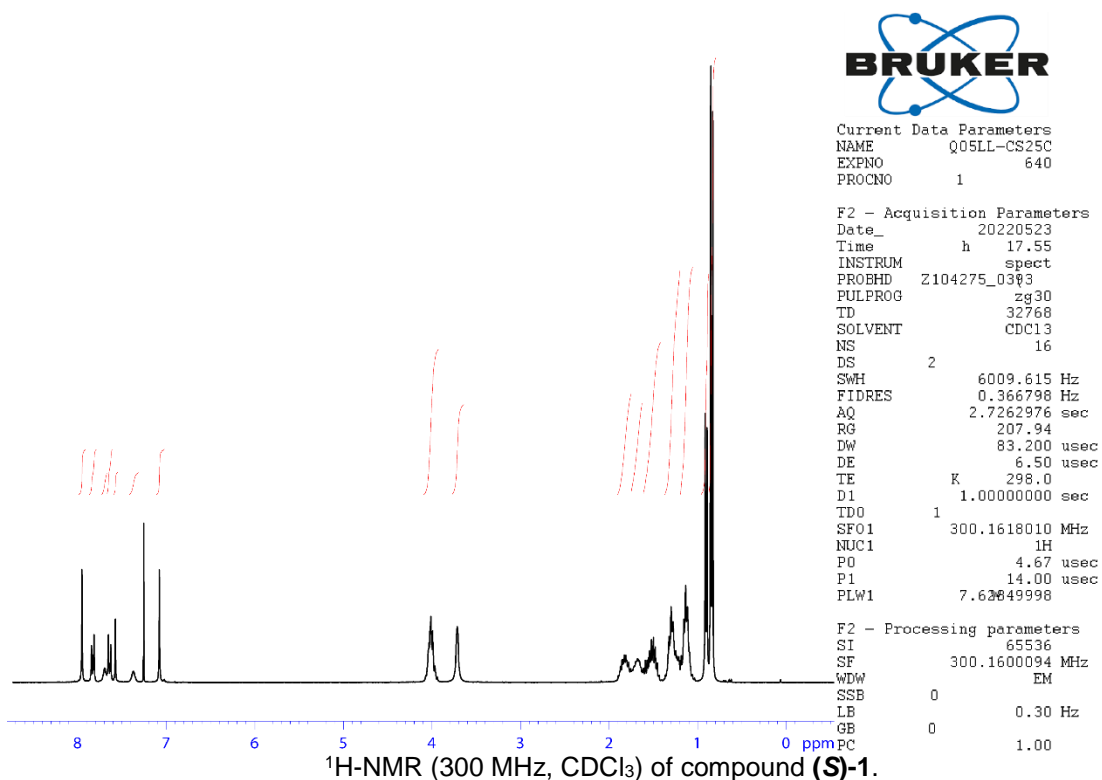
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) of compound (**R**)-1.



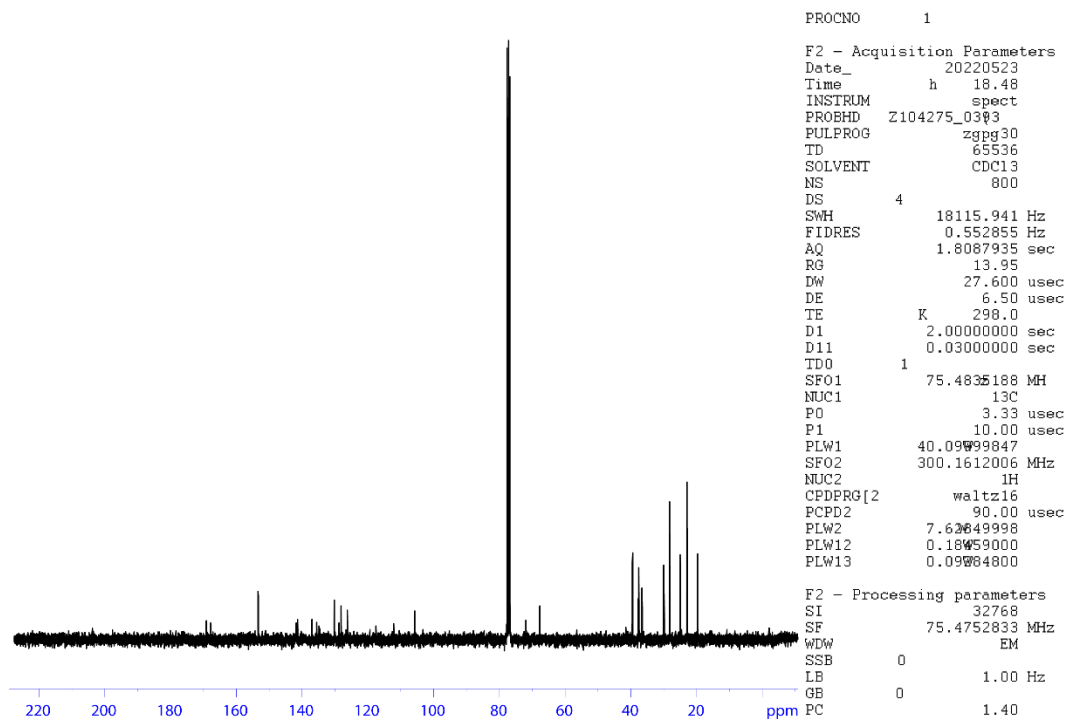
<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) of compound (**R**)-1.



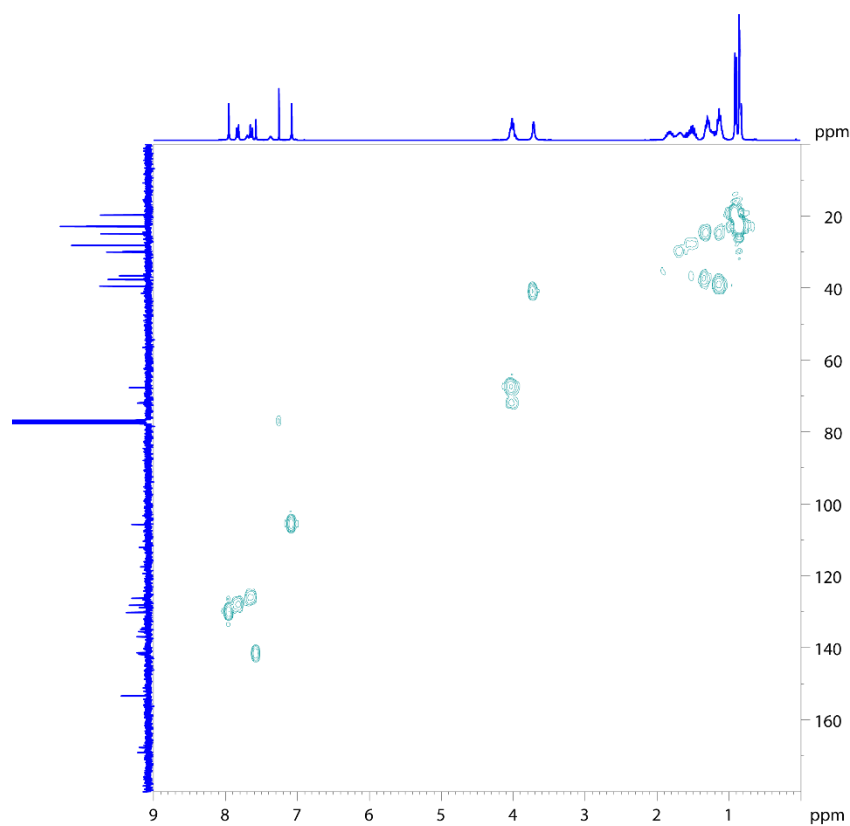
$^1\text{H}$ ,  $^{13}\text{C}$ -HMQC ( $\text{CDCl}_3$ ) of compound (*R*)-1.



$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ) of compound (*S*)-1.

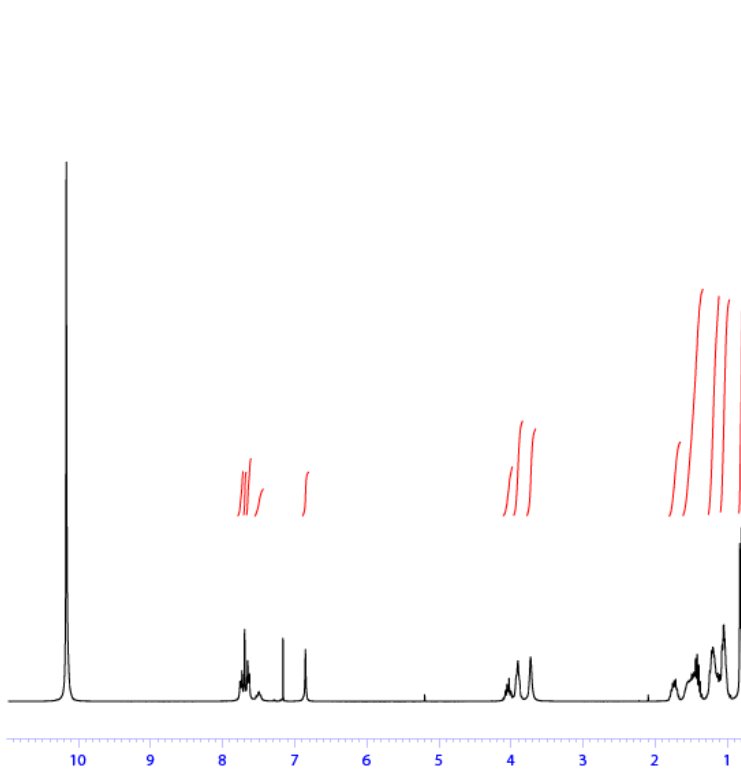


$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ ) of compound (S)-1.



$^1\text{H}$ ,  $^{13}\text{C}$ -HMQC ( $\text{CDCl}_3$ ) of compound (S)-1.



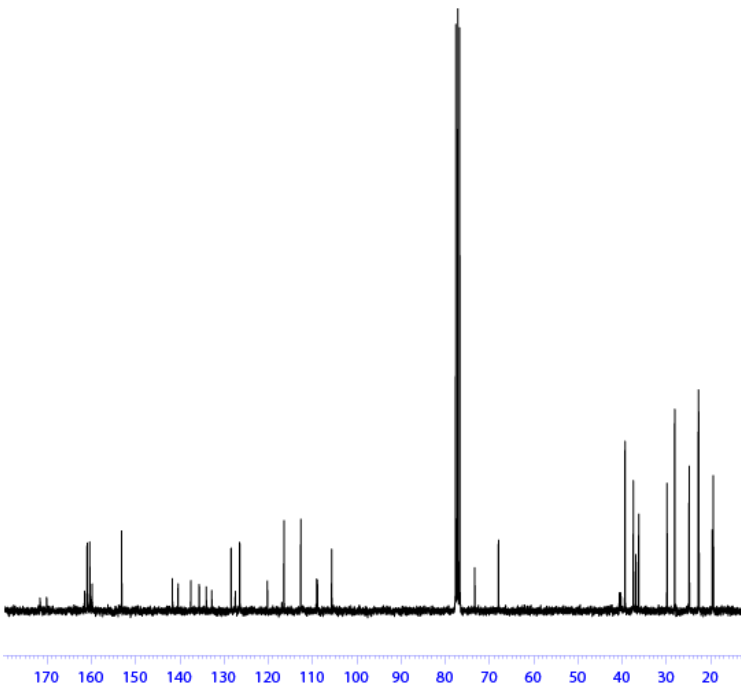


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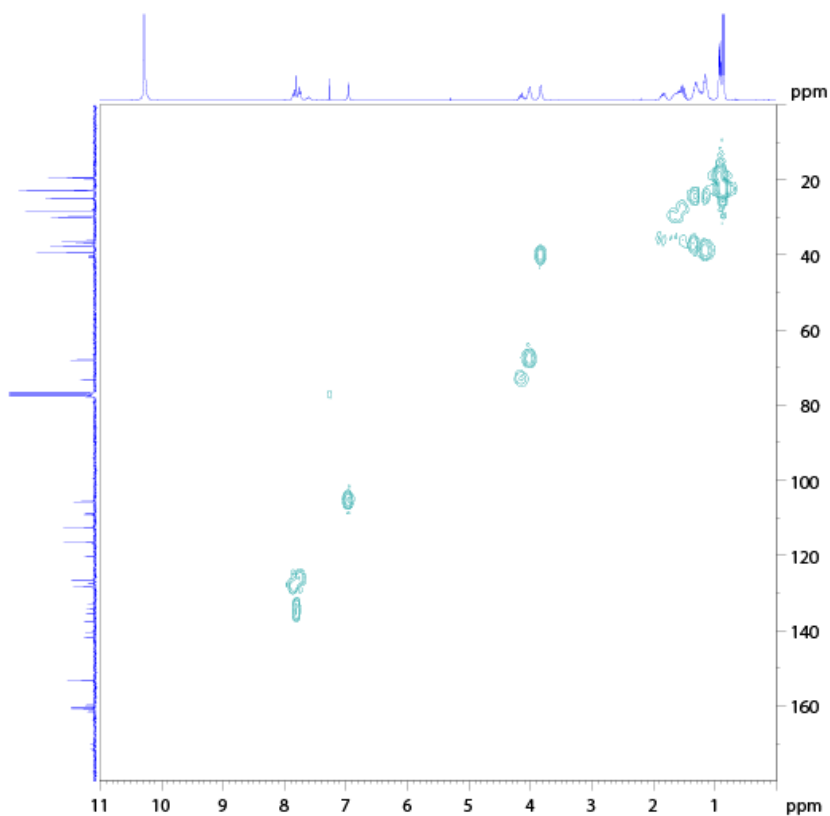
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, TFA) of compound (*R*)-2.



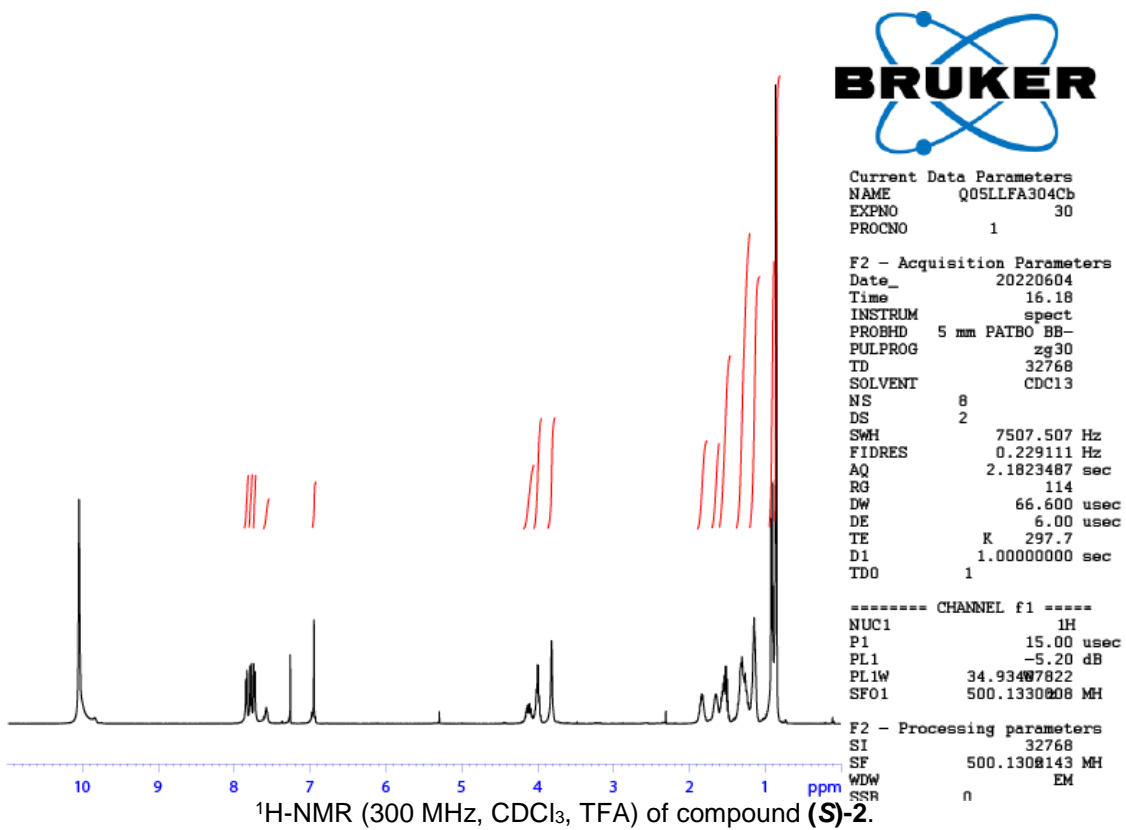
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SWH 18115.941 Hz  
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RG 13.95  
DW 27.600 usec  
DE 6.50 usec  
TE K 298.2  
D1 2.00000000 sec  
D11 0.03000000 sec  
TDO 1  
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NUC1 13C  
P0 3.33 usec  
P1 10.00 usec  
PLW1 39.59999847  
SFO2 300.1612006 MH  
NUC2 1H  
CPDPRG[2] waltz16  
PCPD2 90.00 usec  
PLW2 7.8600013  
PLW12 0.19009000  
PRW13 0.09566000

<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>, TFA) of compound (*R*)-2.



$^1\text{H}$ ,  $^{13}\text{C}$ -HMQC ( $\text{CDCl}_3$ , TFA) of compound (*R*)-2.



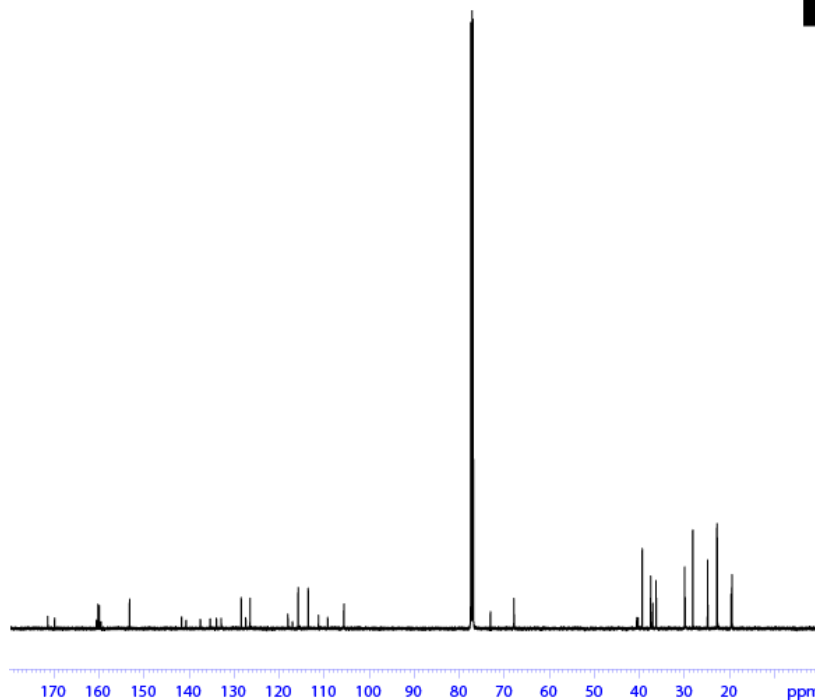


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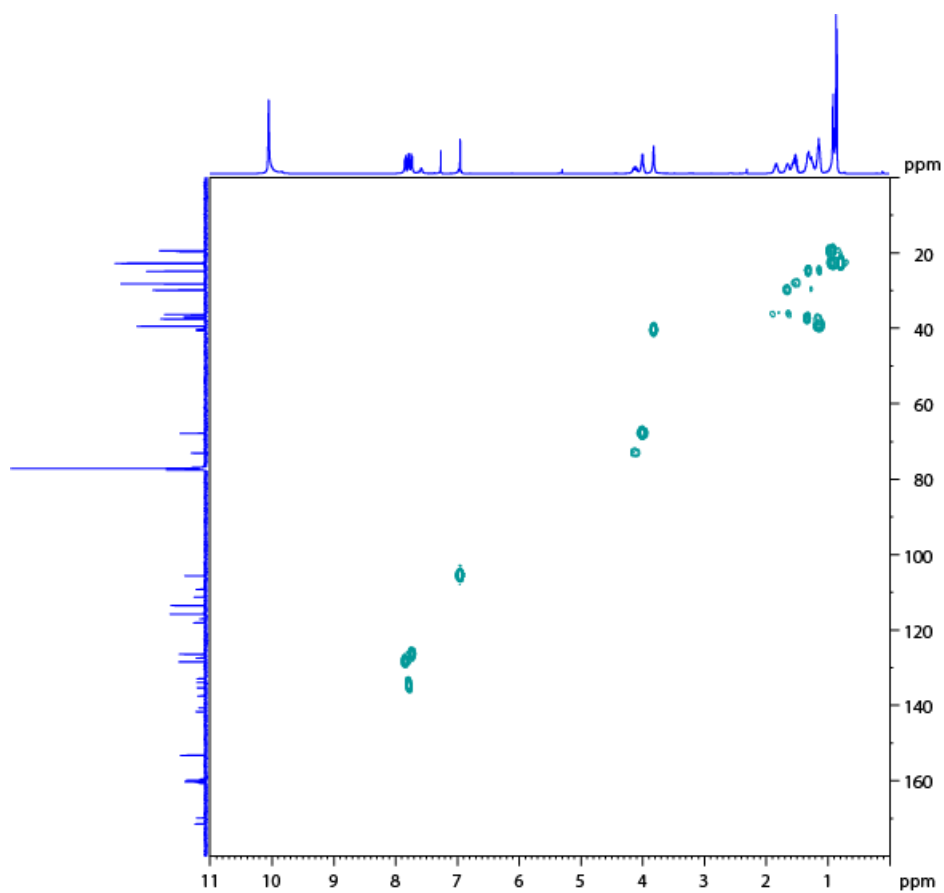
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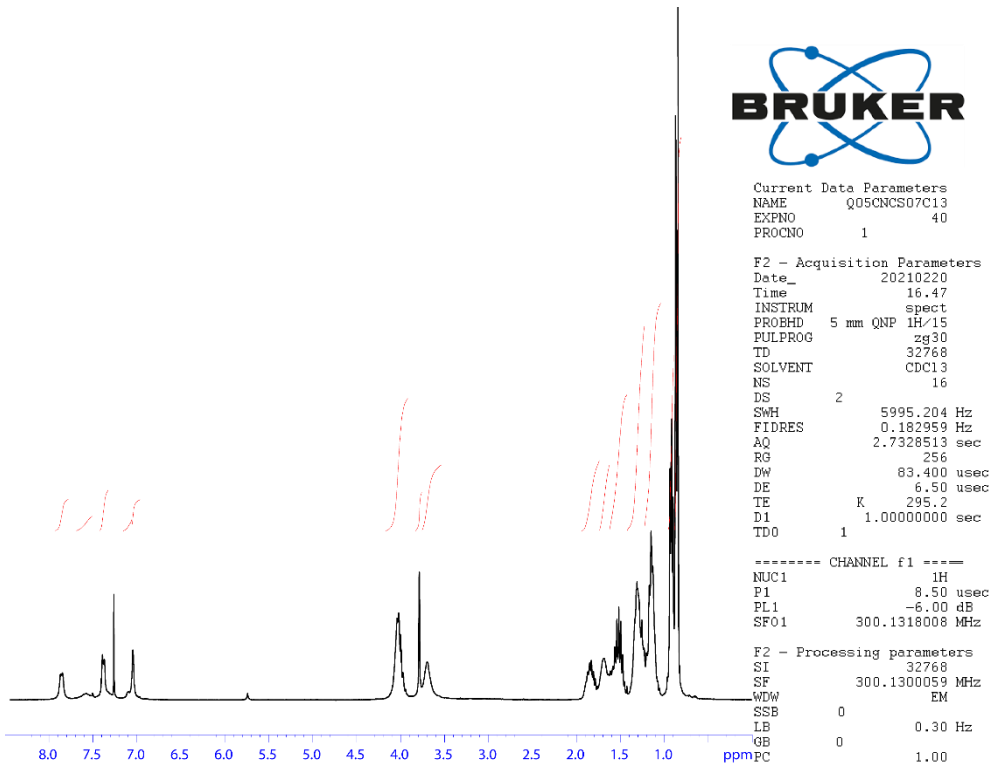
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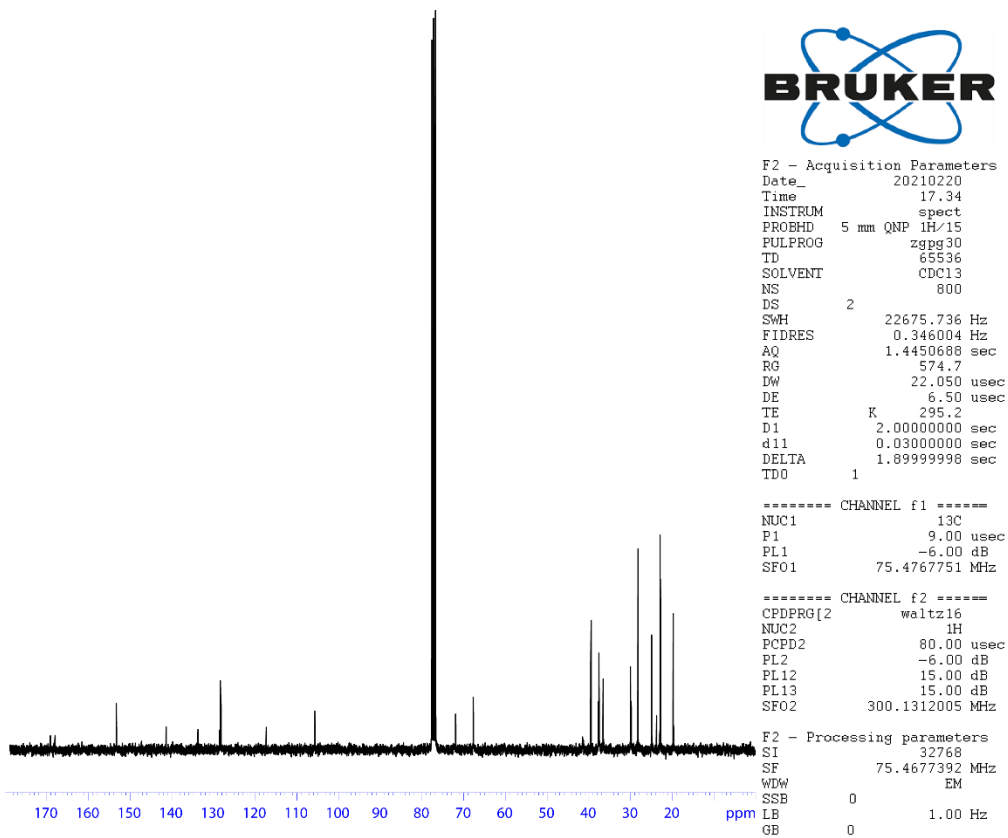
$^{13}\text{C}$ -NMR (75 MHz,  $\text{CDCl}_3$ , TFA) of compound (S)-2.



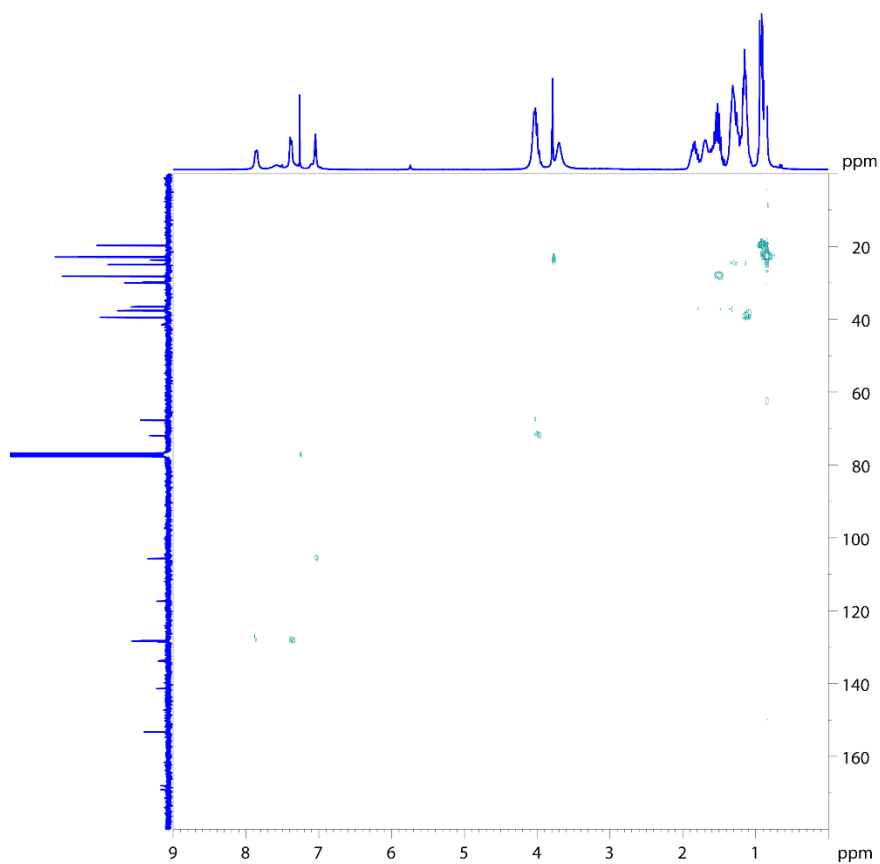
$^1\text{H}$ ,  $^{13}\text{C}$ -HMQC ( $\text{CDCl}_3$ , TFA) of compound (S)-2.



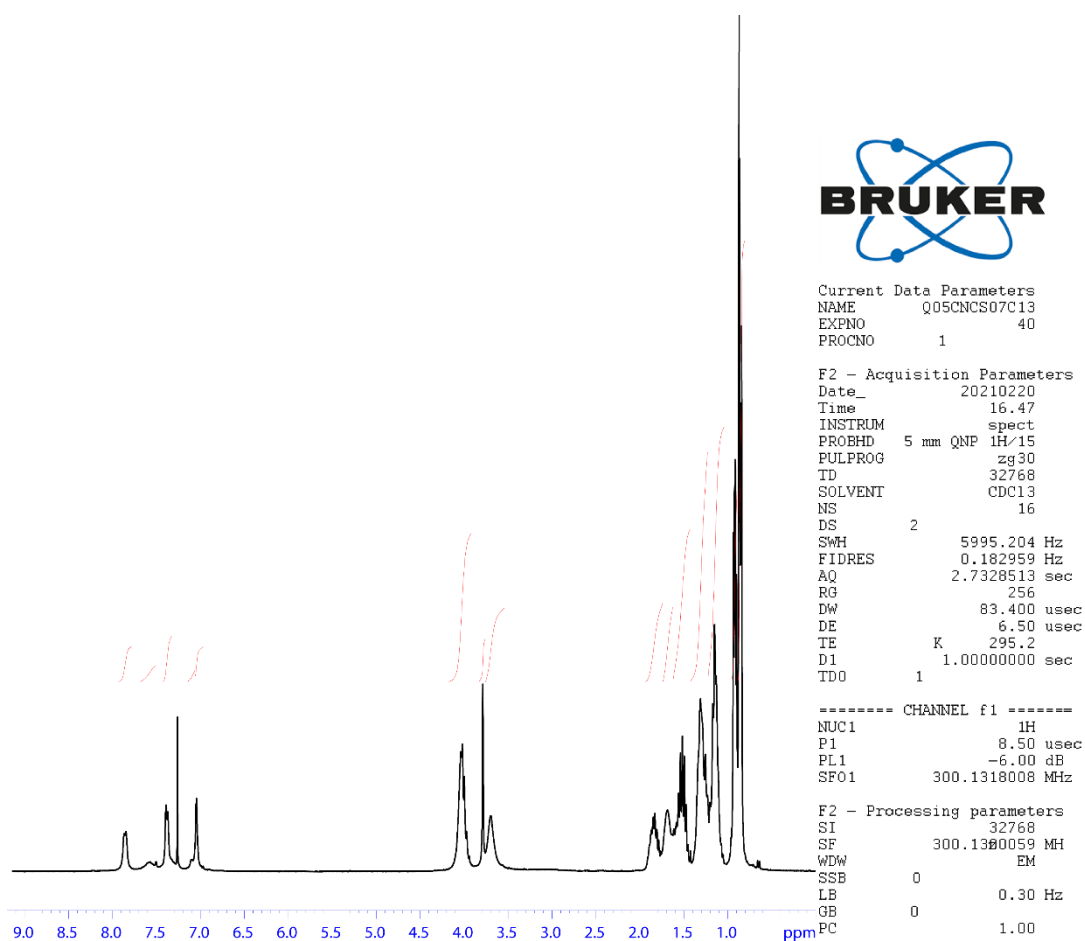
<sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>) of compound (*R*)-5.



<sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>) of compound (*R*)-5.



$^1\text{H}$ ,  $^{13}\text{C}$ -HMQC ( $\text{CDCl}_3$ ) of compound (**R**)-5.



$^1\text{H}$ -NMR (300 MHz,  $\text{CDCl}_3$ ) of compound (**S**)-5.

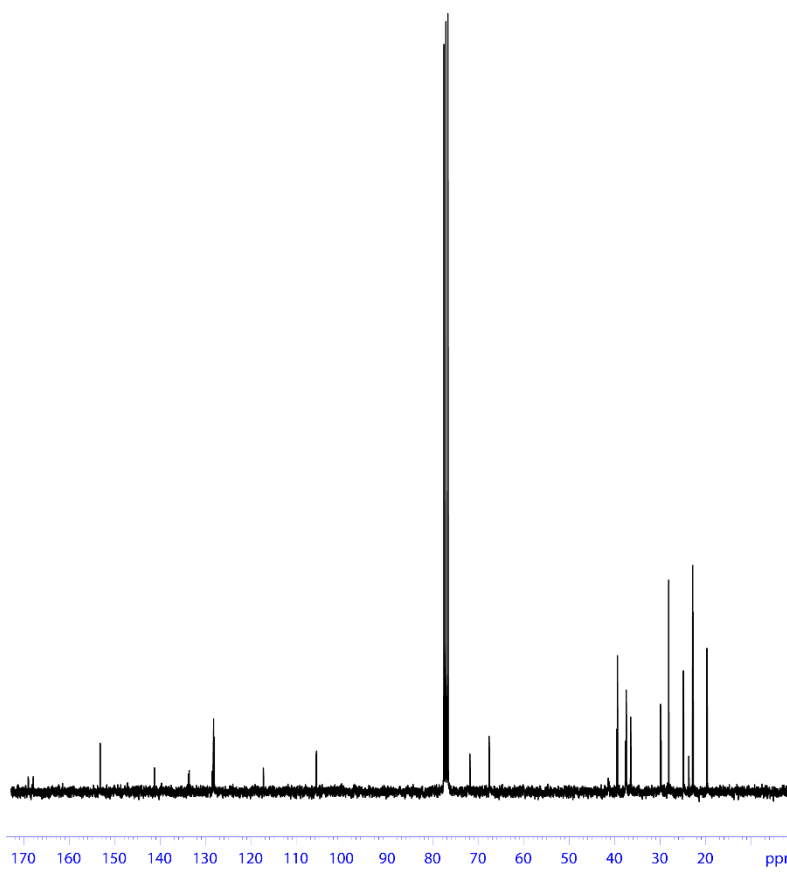


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FIDRES 0.346004 Hz  
AQ 1.4450688 sec  
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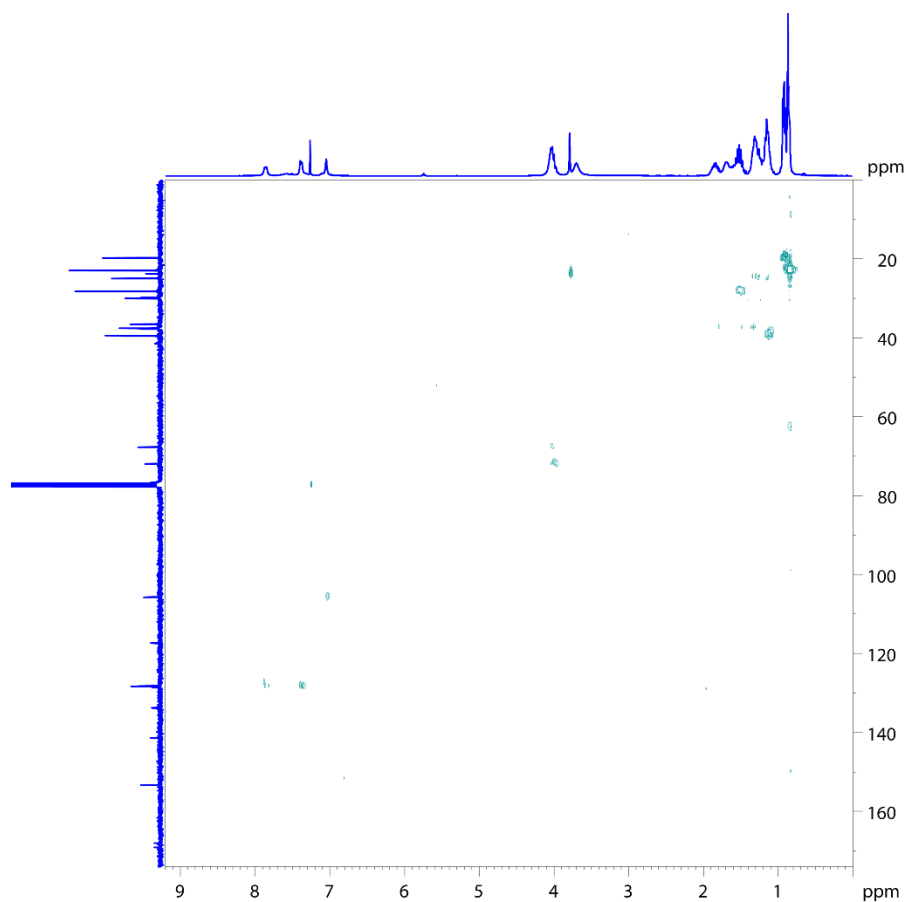
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PL12 15.00 dB  
PL13 15.00 dB  
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F2 - Processing parameters  
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WDW EM  
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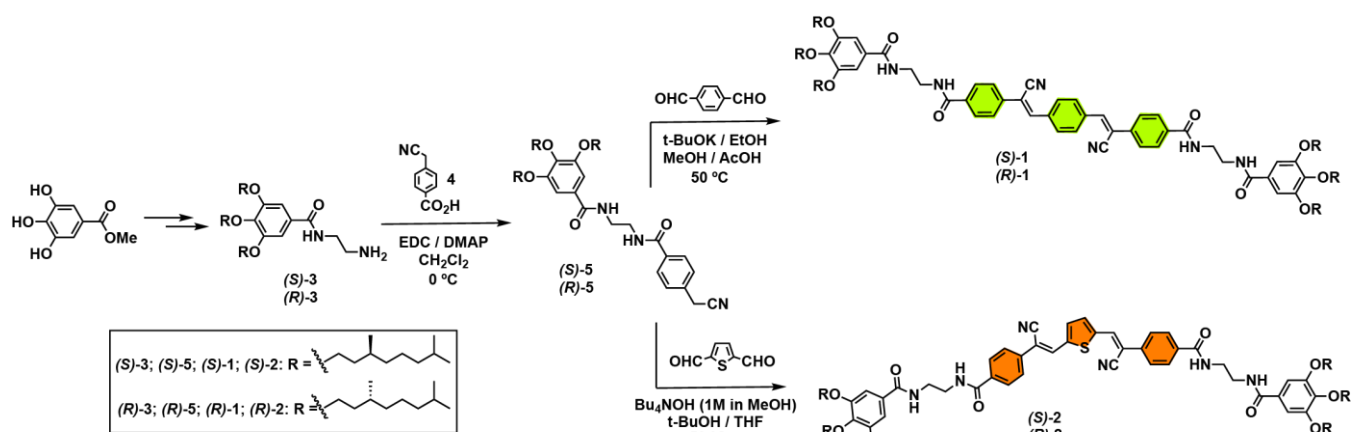


<sup>13</sup>C-NMR (300 MHz, CDCl<sub>3</sub>) of compound (S)-5.

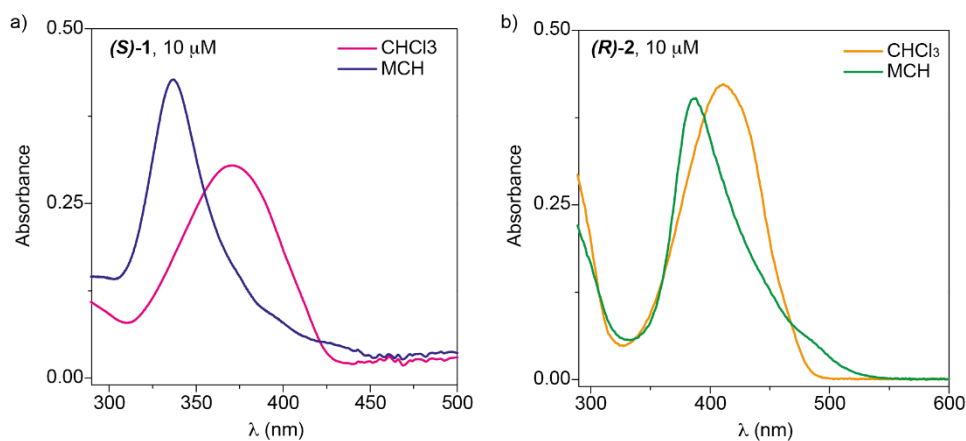


<sup>1</sup>H, <sup>13</sup>C-HMQC (CDCl<sub>3</sub>) of compound (S)-5.

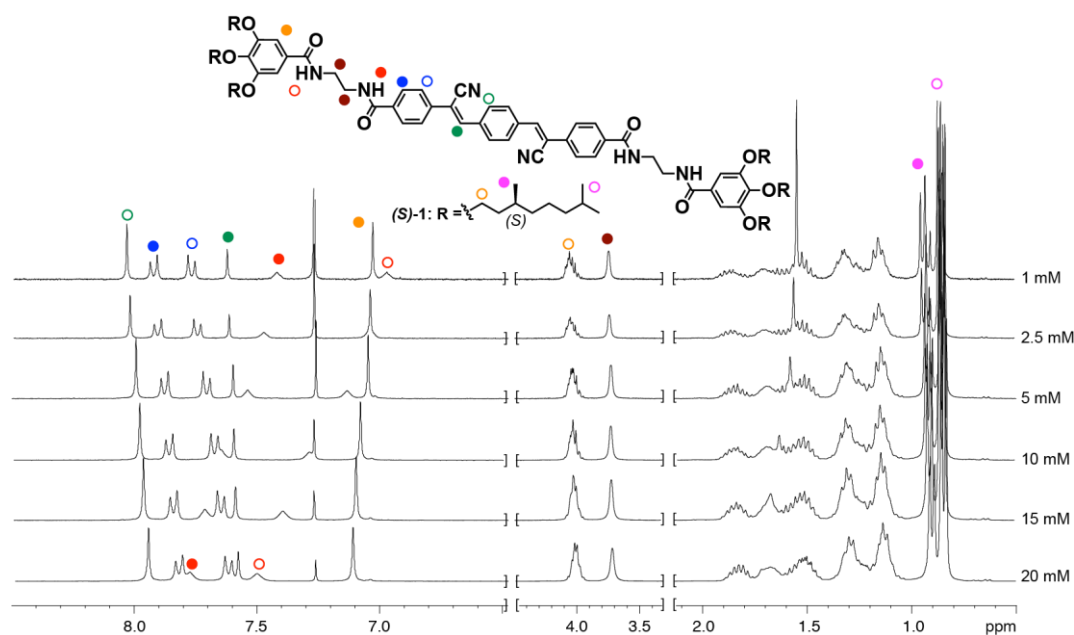
#### 4. Supplementary Figures and Tables



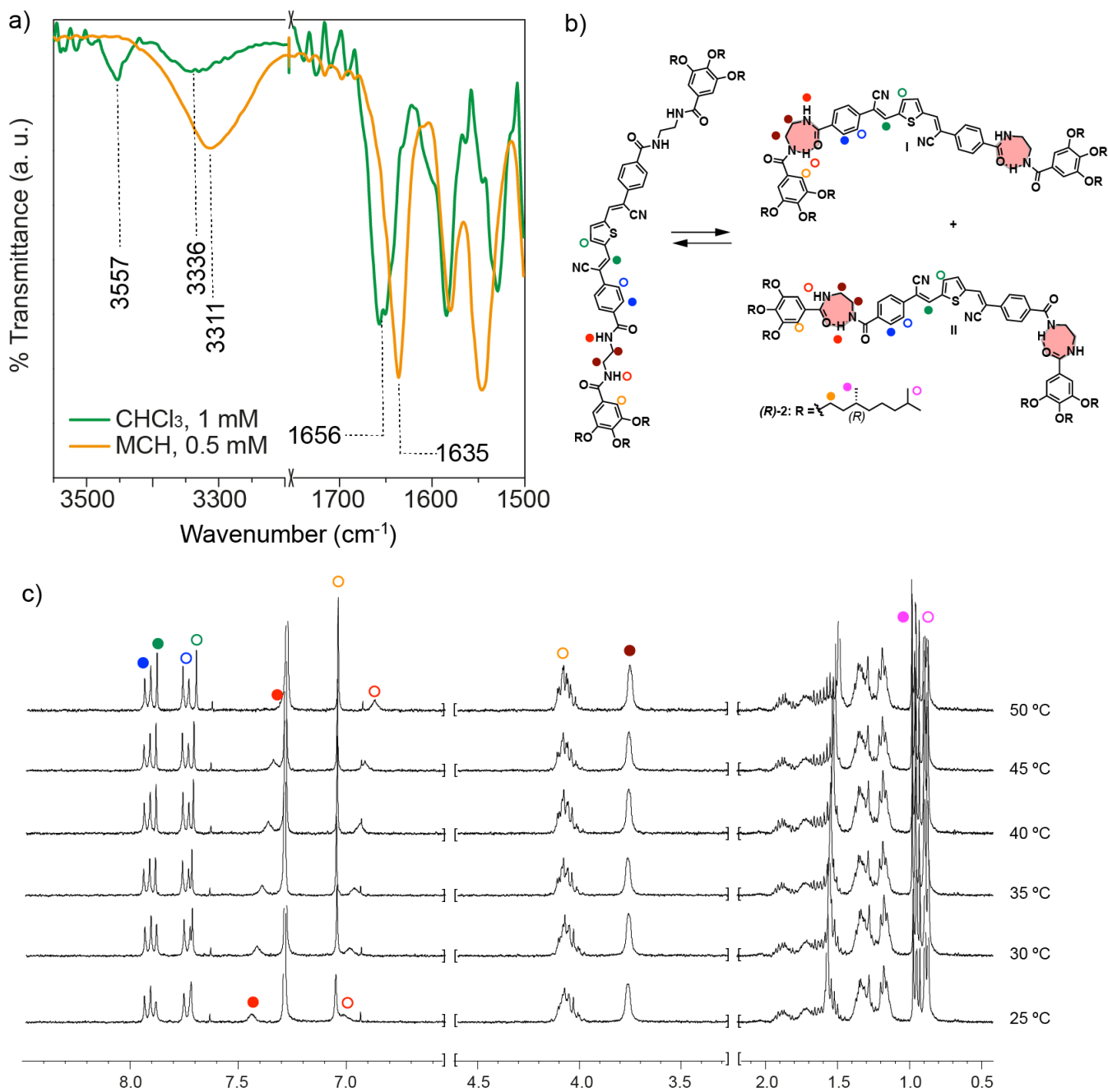
**Scheme S1.** Synthetic protocol followed to prepare the cyano-luminogens **1** and **2**.



**Figure S1.** UV-Vis spectra of **(S)-1** (a) and **(R)-2** (b) in  $\text{CHCl}_3$  and MCH ( $c_T = 10 \mu\text{M}$ ,  $20^\circ\text{C}$ ).

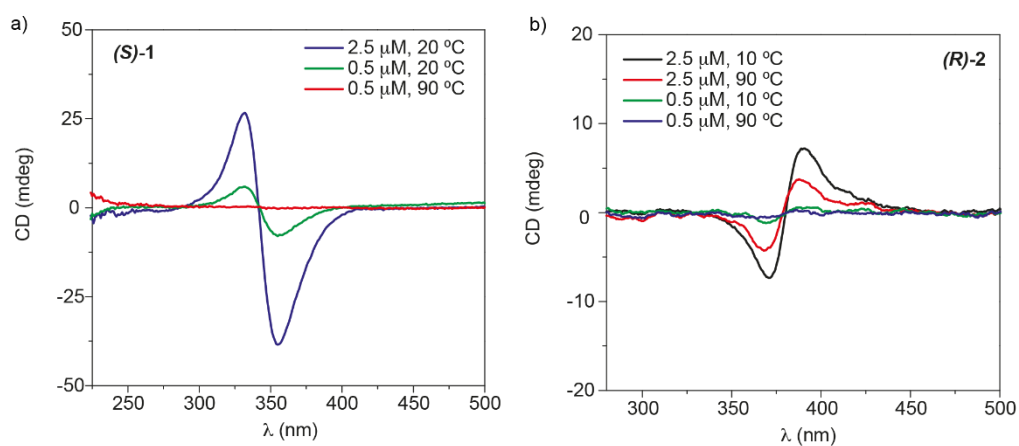


**Figure S2.** Partial  $^1\text{H}$  NMR spectra of **(S)-1** showing the aromatic, the amide and the paraffinic protons (300 MHz,  $\text{CDCl}_3$ ,  $20^\circ\text{C}$ ).

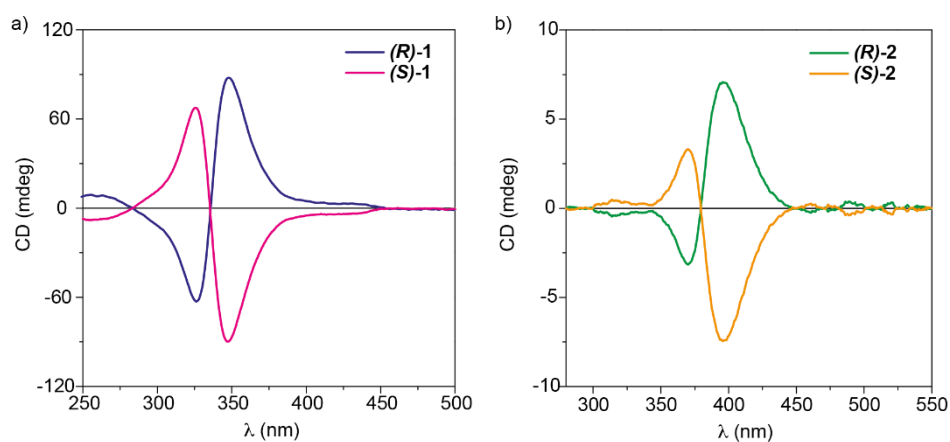


**Figure S3.** a) Partial FTIR spectra of **(R)-2** in  $\text{CHCl}_3$  and MCH; b) Schematic illustration of the equilibrium between the two monomeric species, the totally unbounded and the intramolecularly H-bonded, of cyano luminogens **2**; c) Partial  $^1\text{H}$  NMR spectra of **(R)-2** at different temperatures (300 MHz,  $\text{CDCl}_3$ ,  $c_T = 1$  mM).

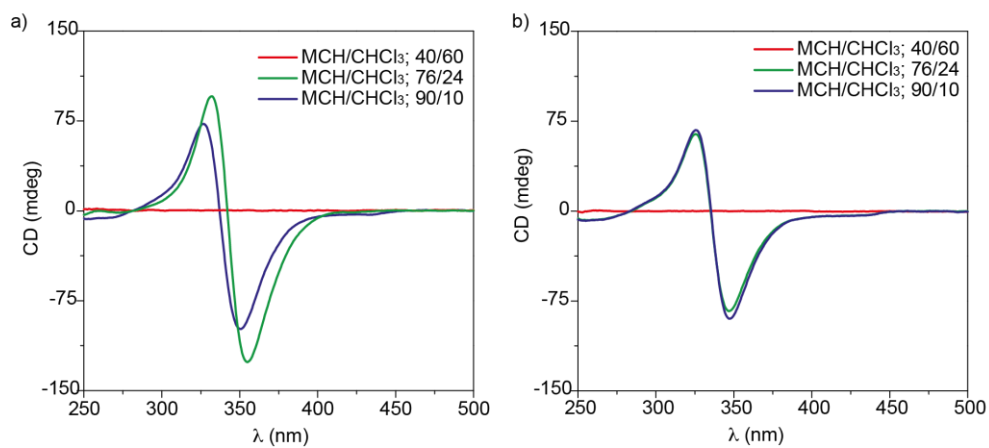




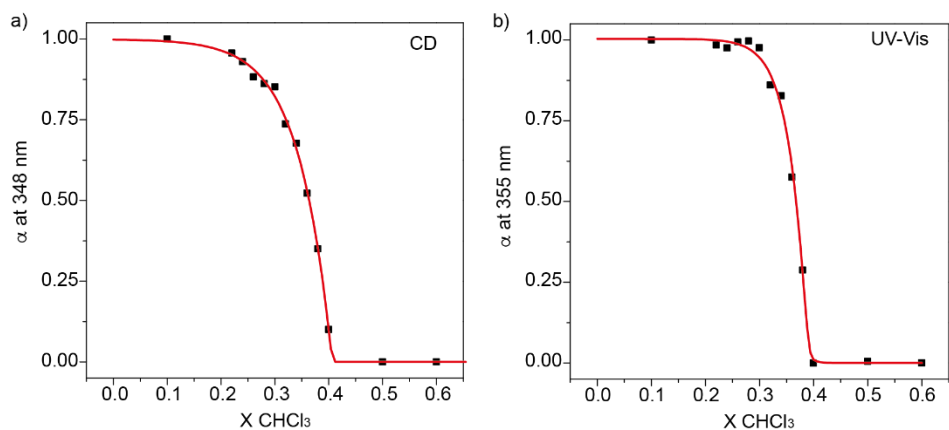
**Figure S4.** CD spectra of **(S)-1** (a) and **(R)-2** (b) in MCH ( $c_T = 2.5$  and  $0.5 \mu\text{M}$ ).



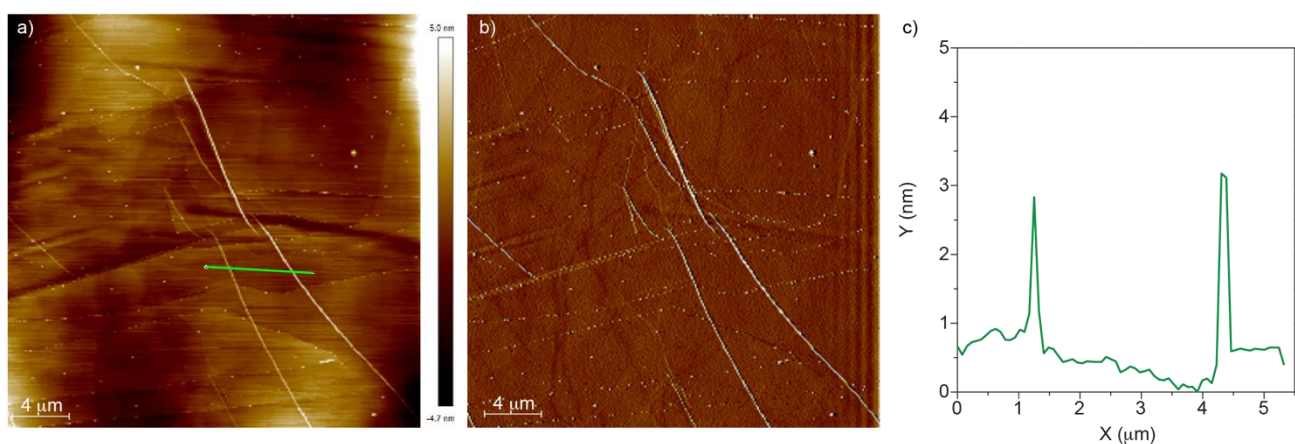
**Figure S5.** CD spectra of chiral luminogens **1** (a) and **2** (b) in MCH (10 °C;  $c_T = 10 \mu\text{M}$ ).



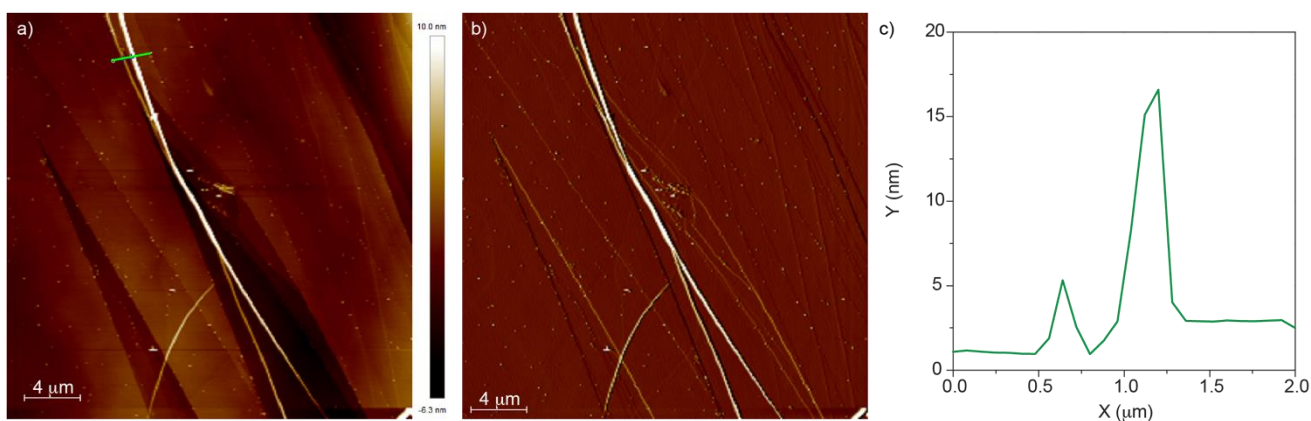
**Figure S6.** Selected CD spectra of **(S)-1** in MCH/CHCl<sub>3</sub> mixtures freshly prepared (a) and upon aging for 24 h (b) (20 °C;  $c_T = 10 \mu\text{M}$ )



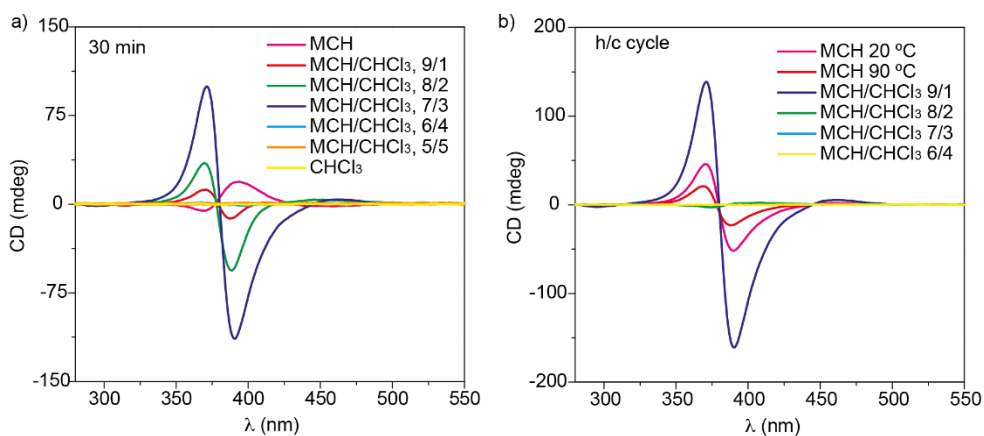
**Figure S7.** Denaturalization curves of **(S)-1** in MCH/CHCl<sub>3</sub> mixtures attained by CD (a) and UV-Vis (b) experiments (20 °C;  $c_T = 10 \mu\text{M}$ ). Red lines in panels (a) and (b) depict the fit to the SD model.



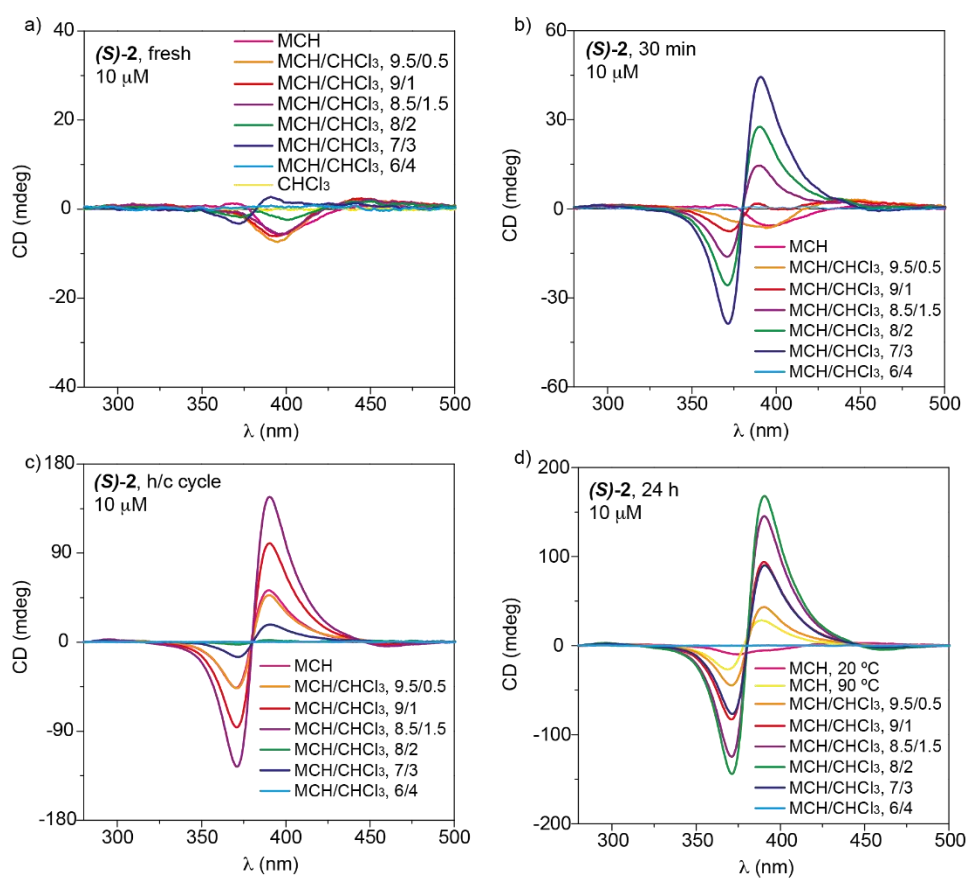
**Figure S8.** Height (a) and phase (b) AFM images of the Aggl of luminogen **(S)-1** formed from a freshly prepared MCH/CHCl<sub>3</sub> 9/1 mixture (HOPG as surface,  $c_T = 10 \mu\text{M}$ ). Panel (c) shows the height profile along the green line in panel (a).



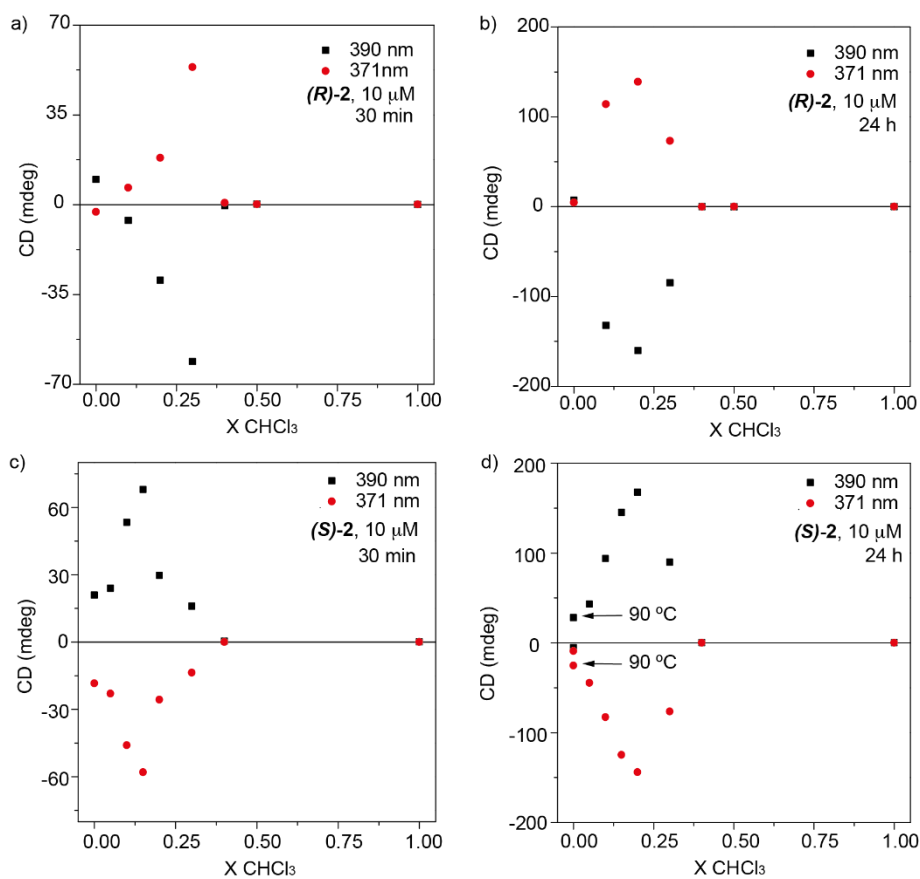
**Figure S9.** Height (a) and phase (b) AFM images of the AgglI of luminogen **(S)-1** formed from a freshly prepared MCH/CHCl<sub>3</sub> 9/1 mixture (HOPG as surface,  $c_T = 10 \mu\text{M}$ ). Panel (c) shows the height profile along the green line in panel (a).



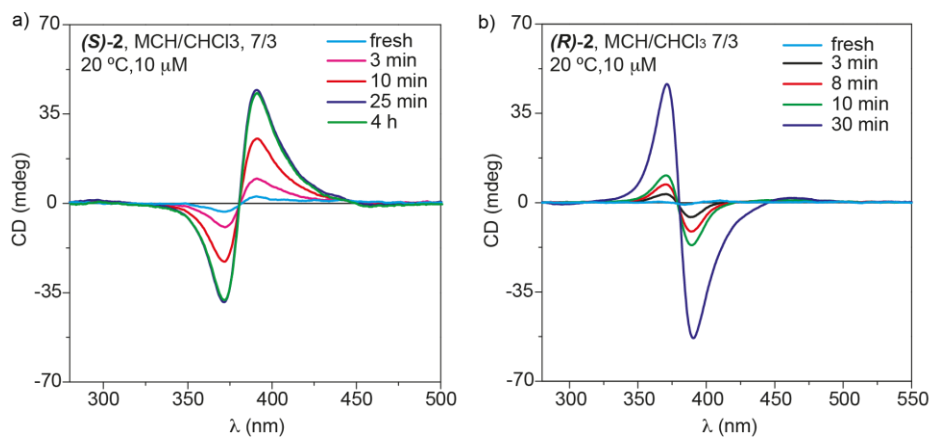
**Figure S10.** CD spectra of **(R)-2** at different conditions of time and solvent composition after 30 min (a) and upon heating/cooling cycle (b) (20 °C,  $c_T = 10 \mu\text{M}$ ).



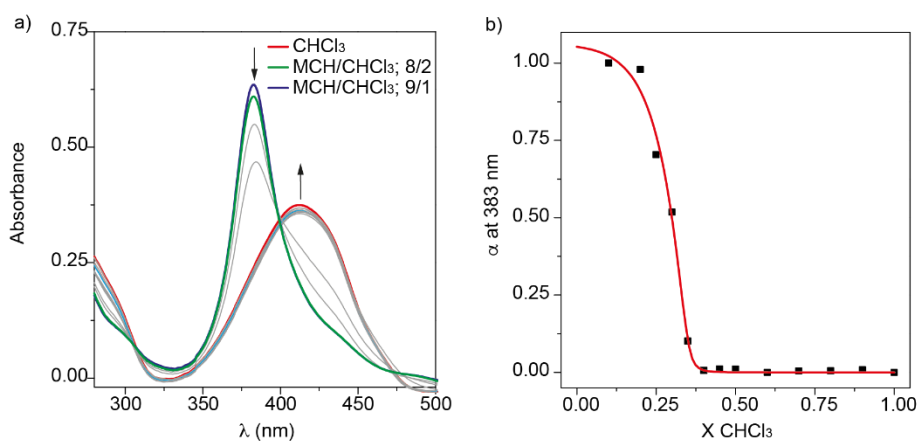
**Figure S11.** CD spectra of **(S)-2** at different conditions of time and solvent composition (20 °C,  $c_T = 10 \mu\text{M}$ ).



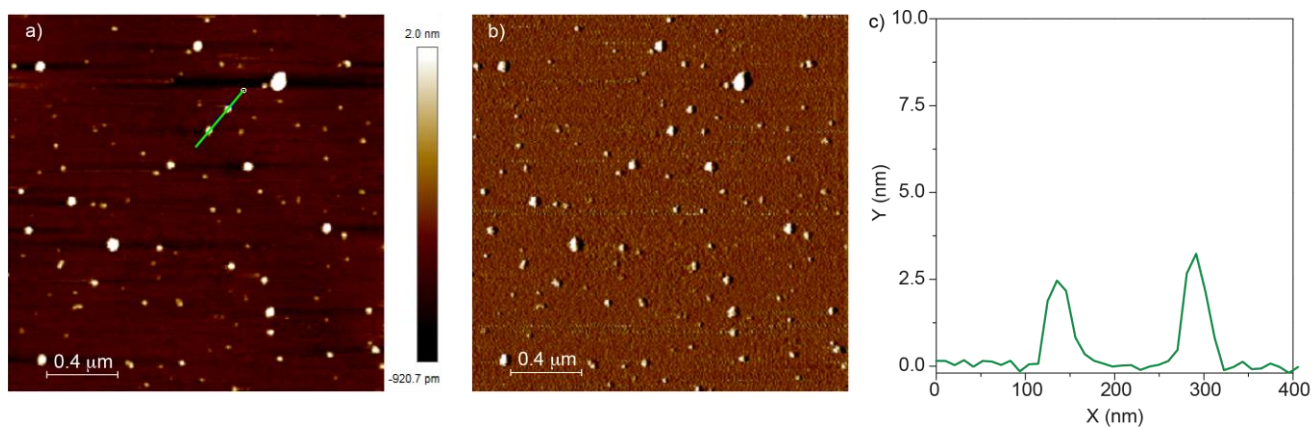
**Figure S12.** Plot of the variation of the dichroic response of **(R)-2** and **(S)-2** versus the molar fraction of  $\text{CHCl}_3$  at different times ( $20\text{ }^\circ\text{C}$ ,  $c_T = 10\text{ }\mu\text{M}$ ).



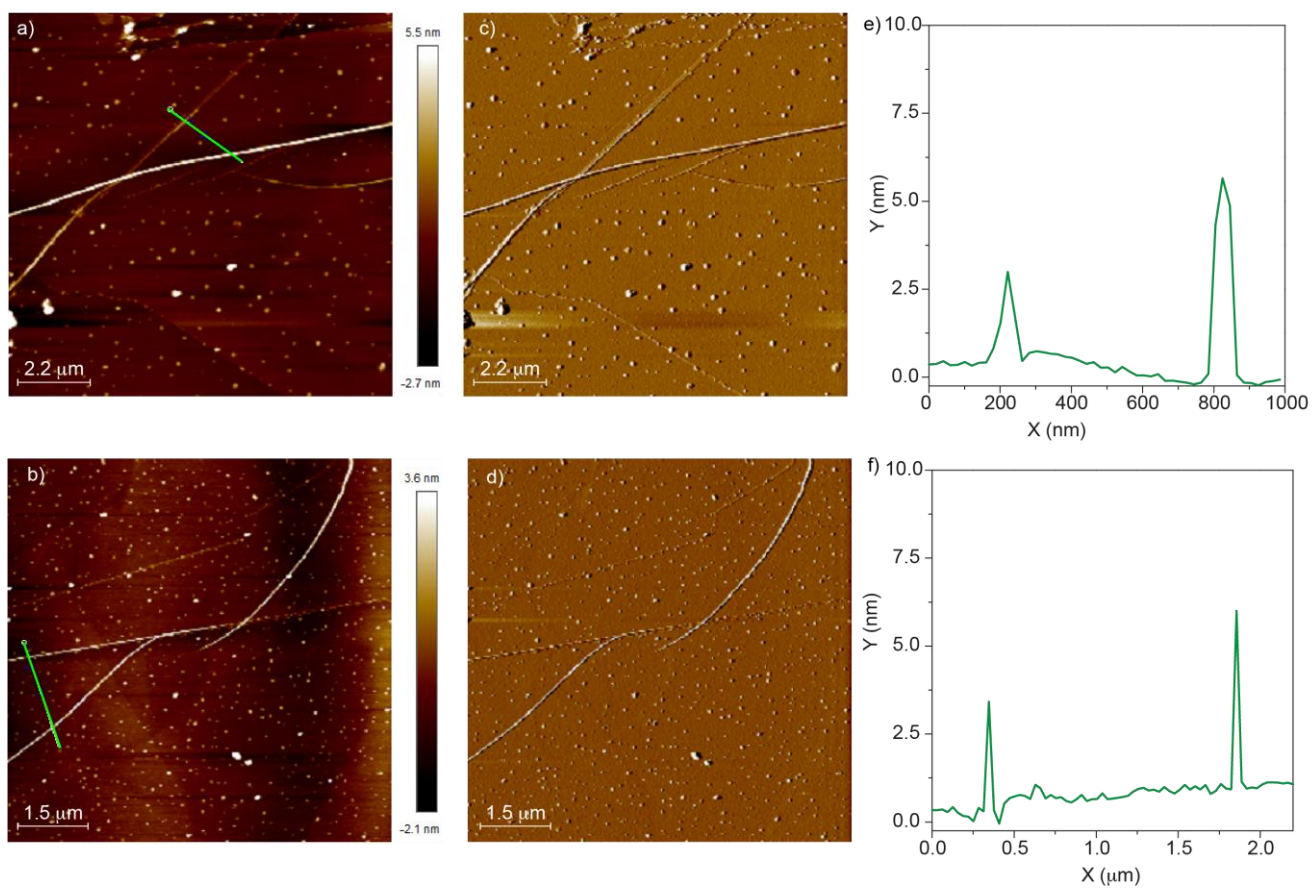
**Figure S13.** CD spectra of **(S)-2** and **(R)-2** at different times (MCH/ $\text{CHCl}_3$  7/3;  $20\text{ }^\circ\text{C}$ ,  $c_T = 10\text{ }\mu\text{M}$ ).



**Figure S14.** UV-Vis spectra and denaturalization curves of **(S)-2** in MCH/ $\text{CHCl}_3$  mixtures (20 °C;  $c_T = 10 \mu\text{M}$ ). The red line in panel (b) depicts the fit to the SD model.

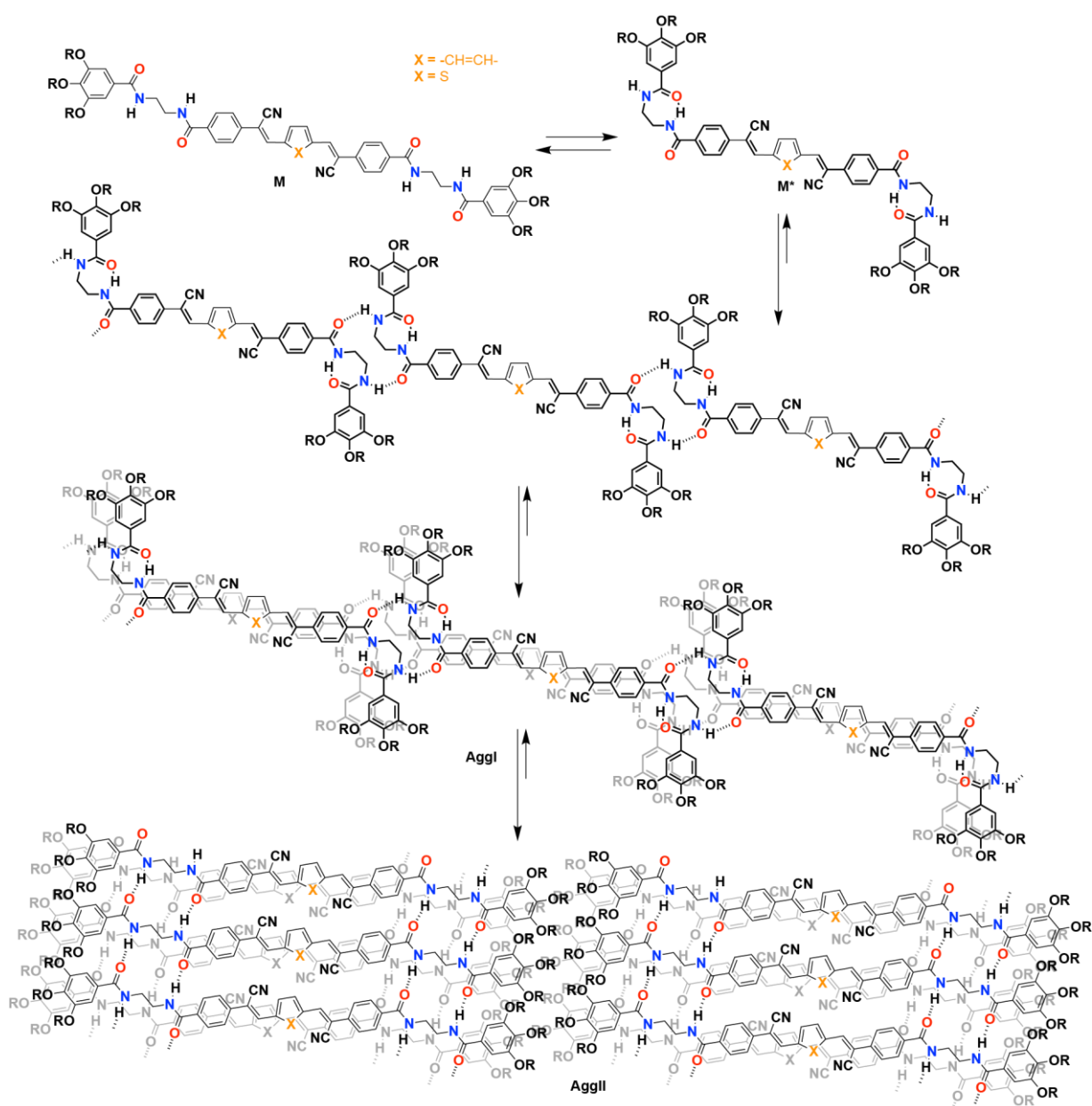


**Figure S15.** Height (a) and phase (b) AFM images of the Aggl of luminogen **(S)-2** formed from a freshly prepared MCH/ $\text{CHCl}_3$  9/1 mixture (HOPG as surface,  $c_T = 10 \mu\text{M}$ ). Panel (c) shows the height profile along the green line in panel (a).

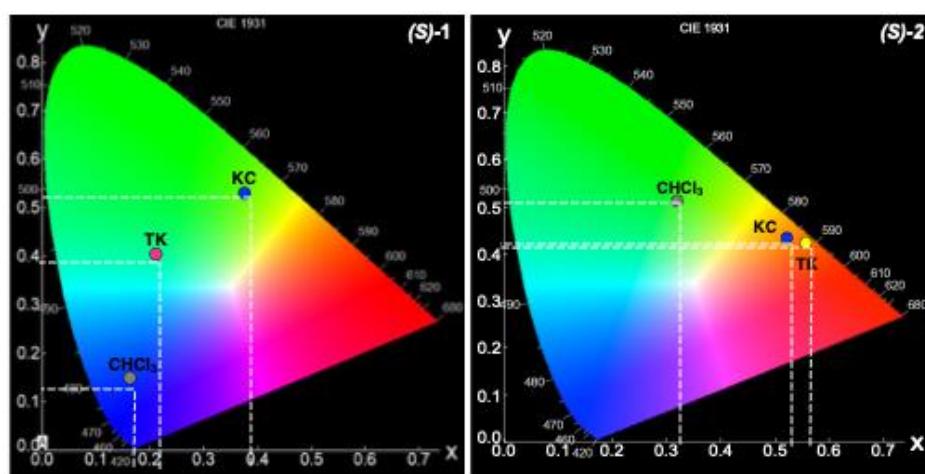


**Figure S16.** Height (a,b) and phase (c,d) AFM images of the AggII of luminogen **(S)-2** formed from an aged prepared MCH/CHCl<sub>3</sub> 9/1 mixture (HOPG as surface,  $c_T = 10 \mu\text{M}$ ). Panels (e) and (f) show the height profile along the green line in panels (a) and (b).

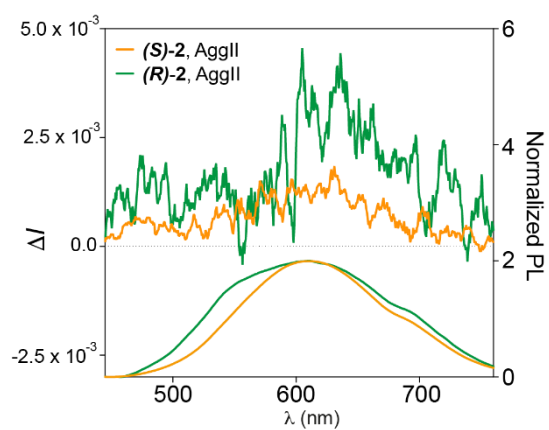




**Figure S17.** Schematic illustration of the self-assembly process yielding the kinetically controlled AggI and the thermodynamically controlled AggII species from compounds 1 and 2.



**Figure S18.** CIE chromaticity diagrams for the monomeric and aggregated species of compounds (S)-1 and (S)-2 ( $c_T = 10 \mu\text{M}$ ).



**Figure S19.** CPL/PL spectra of the thermodynamically controlled aggregated species (AggII) of compound **(S)-2** (experimental conditions: 9/1 MCH/ $\text{CHCl}_3$  mixture;  $c_T = 10 \mu\text{M}$ ,  $\lambda_{\text{exc}} = 390 \text{ nm}$ ).



## 5. References

- [S1] Greciano, E. E.; Rodríguez, R.; Maeda, K.; Sánchez, L. Disclosing chirality in consecutive supramolecular polymerizations: chiral induction by light in N-annulated perylenetetracarboxamides. *Chem. Commun.* 2020, 56, 2244-2247.
- [S2] Aparicio, F.; Cherumukkil, S.; Ajayaghosh, A.; Sánchez, L. Color-Tunable Cyano-Substituted Divinylene Arene Luminogens as Fluorescent  $\pi$ -Gelators. *Langmuir* 2016, 32, 284-289.