Supplementary Information for

# Pressure-dependent Helix Inversion of Poly(quinoxaline2,3-diyl)s Containing Chiral Side Chains in Non-aqueous Solvents

Yuuya Nagata,\*a Ryohei Takeda,a and Michinori Suginome\*ab

<sup>*a*</sup> Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

> <sup>b</sup> CREST, Japan Science and Technology Agency (JST), Katsura, Nishikyo-ku, Kyoto 615-8510, Japan

E-mail: nagata@sbchem.kyoto-u.ac.jp, suginome@sbchem.kyoto-u.ac.jp

## 1. General

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. <sup>1</sup>H NMR spectra were recorded on a Varian 400-MR spectrometer at ambient temperature. <sup>1</sup>H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane ( $\delta$  scale), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and br = broad), coupling constant (Hz), and integration. The GPC analysis was carried out with TSKgel G4000H<sub>HR</sub> or TSKgel GMH<sub>XL</sub> (CHCl<sub>3</sub>, polystyrene standards). Preparative GPC was performed on JAI LC-908 equipped with JAIGEL-1H and - 2H columns in a series (CHCl<sub>3</sub>). CD spectra were recorded on a JASCO J-750 spectrometer equipped with a high-pressure cell at room temperature. UV spectra were calculated from HT voltage measured with spectrometer.

*o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub>,<sup>1</sup> 1m,<sup>2</sup> 2m,<sup>3</sup> 3m,<sup>3</sup> and 4m,<sup>4</sup> were prepared according to the reported procedures. Tetrahydrofurane (THF) were dried and deoxygenized using an alumina/catalyst column system (Glass Contour Co.). Other chemical reagents were purchased from the commercial sources and were used without further purification.

### 2. Experimental Procedures and Spectral Data for Synthesized Compounds

Synthesis of 1 : A THF solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub> (50.0 mM, 45.7 µL, 2.28 µmol) was diluted with THF (3 mL). 1m (30.0 mg, 91.3 µmol) were dissolved in THF (3 mL). A THF solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub> (6.43 mM, 391.9 µL, 2.52 µmol) was added to the monomer solution. After 19.5 h, A THF solution of LiBH<sub>4</sub> (2.00 M, 182.7 µL, 91.3 µmol) was added to the reaction mixture and stirred for 1 h. Saturated NH<sub>4</sub>Cl aq (10 mL) was added to the solution and extracted with and CH<sub>2</sub>Cl<sub>2</sub> (10 ml). The organic extract was washed with water (10 mL) and brine (10 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was evaporated. The residue was subjected to preparative GPC to give 1 as a beige solid (29.9 mg, >99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.62 (2H, br s), 4.53 (2H, br s), 3.40 (2H, br s), 2.31 (6H, br s), 1.21 (6H, br, d *J* = 4.8 Hz), 0.87(6H, br, t *J* = 6.6 Hz); GPC (CHCl<sub>3</sub>, g/mol):  $M_n = 7.35 \times 10^3$ ,  $M_w/M_n = 1.13$ .

Scheme S1. Synthesis of 1.



Synthesis of 2 : A THF solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub> (50.6 mM, 34.6  $\mu$ L, 1.75  $\mu$ mol) was diluted with THF (3 mL). **2m** (25.0 mg, 70.1  $\mu$ mol) was dissolved in THF (3 mL). A THF solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub> (9.34 mM, 223.6  $\mu$ L, 2.09  $\mu$ mol) was added to the monomer solution. After stirring for 17 h, a NaBH<sub>4</sub> (5.30 mg, 140  $\mu$ mol) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH<sub>4</sub>Claq (1 mL) was added. Extraction with CH<sub>2</sub>Cl<sub>2</sub> (10mL) followed by preparative GPC gave **2** as a beige solid (24.9 mg, >99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.65 (2H, br s), 4.48 (2H, br s), 3.46 (2H, br s),

2.57–2.01 (14H, m), 1.79–1.03 (14H, m), 0.99–0.73 (6H, m); GPC (CHCl<sub>3</sub>, g/mol):  $M_n = 6.59 \times 10^3$ ,  $M_w/M_n = 1.14$ .

Scheme S2. Synthesis of 2.



Synthesis of 3 : A THF solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub> (50.0 mM, 52.3 µL, 2.61 µmol) was diluted with THF (3 mL). A THF solution of **3m** (46.0 mg, 104 µmol) was diluted with THF (3 mL). The monomer solution was added to the solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub>. After stirring for 12 h, NaBH<sub>4</sub> (7.87 mg, 208 µmol) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH<sub>4</sub>Cl aq (10 mL) was added and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The organic extract was washed with water (10 mL) and brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> followed by preparative GPC gave **3** as a beige solid (43.2 mg, 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.62 (2H, br s), 4.50 (2H, br s), 3.47 (2H, br s), 2.54–1.97 (6H, m), 1.75–0.99 (28H, m), 0.84 (6H, br s); GPC (CHCl<sub>3</sub>, g/mol): M<sub>n</sub> = 8.06 × 10<sup>3</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.13.

#### Scheme S3. Synthesis of 3.



**Synthesis of 4** : A THF solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub> (50.0 mM, 15.2  $\mu$ L, 0.76  $\mu$ mol) was diluted with THF (3 mL). A THF solution of **4m** (11.8 mg, 30.4  $\mu$ mol) was diluted with THF (3 mL). The monomer solution was added to the solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub>. After stirring for 11 h, NaBH<sub>4</sub> (2.31 mg, 61  $\mu$ mol) was added to the reaction mixture at room temperature. After

stirring for 1 h at room temperature, saturated NH<sub>4</sub>Cl aq (10 mL) was added and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The organic extract was washed with water (10 mL) and brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> followed by preparative GPC gave **4** as a beige solid (10.7 mg, 91%). <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  4.98 (2H, br s), 4.63 (2H, br s), 4.13 (2H, br s), 3.74–3.53 (6H, m), 2.60–2.07 (6H, m), 1.36 (6H, br s); GPC (CHCl<sub>3</sub>, g/mol): M<sub>n</sub> = 9.39 × 10<sup>3</sup>, M<sub>w</sub>/M<sub>n</sub> = 1.17.

Scheme S4. Synthesis of 4.



Synthesis of 1(60) : A THF solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub> (50.0 mM, 50.8 µL, 2.54 µmol) was diluted with THF (3 mL). A THF solution of **1m** (50.0 mg, 152 µmol) was diluted with THF (3 mL). The monomer solution was added to the solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub>. After stirring for 12 h, LiBH<sub>4</sub> (2.00 M, 304 µL, 152 µmol) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH<sub>4</sub>Cl aq (10 mL) was added and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The organic extract was washed with water (10 mL) and brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> followed by preparative GPC gave **1(60)** as a beige solid (49.4 mg, 99%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.64 (2H, br s), 4.51 (2H, br s), 3.39 (2H, br s), 2.32 (6H, br s), 1.68–1.31 (4H, m), 1.21 (6H, br, d *J* = 4.56 Hz), 0.87(6H, br, t *J* = 6.72 Hz); GPC (CHCl<sub>3</sub>, g/mol):  $M_n$  = 12.2 × 10<sup>3</sup>,  $M_w/M_n$  = 1.11. **1(60)** was soluble in 1,2-DCE under 0.1 MPa and insoluble in 1,2-DCE under 200 MPa.

#### Scheme S5. Synthesis of 1(60).



Synthesis of 1(100) : A THF solution of *o*-TolNiCl(PMe3)<sub>2</sub> (50.0 mM, 62.4 µL, 3.12 µmol) was diluted with THF (3 mL). A THF solution of 1m (102 mg, 312 µmol) was diluted with THF (3 mL). The monomer solution was added to the solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub>. After stirring for 18h, LiBH<sub>4</sub> (2.00 M, 623 µL, 312 µmol) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH<sub>4</sub>Cl aq (10 mL) was added and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The organic extract was washed with water (10 mL) and brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> followed by preparative GPC gave 1(100) as a beige solid (98.5 mg, 96%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.64 (2H, br s), 4.55 (2H, br s), 3.40 (2H, br s), 2.32 (6H, br s), 1.72–1.33 (4H, m), 1.21 (6H, br s), 0.88(6H, br s); GPC (CHCl<sub>3</sub>, g/mol):  $M_n = 27.8 \times 10^3$ ,  $M_w/M_n = 1.08$ . 1(100) was insoluble in 1,2-DCE.

Scheme S6. Synthesis of 1(100).



Synthesis of 1(200) : A THF solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub> (50.0 mM, 30.4 µL, 1.52 µmol) was diluted with THF (3 mL). A THF solution of 1m (99.8 mg, 303 µmol) was diluted with THF (3 mL). The monomer solution was added to the solution of *o*-TolNiCl(PMe<sub>3</sub>)<sub>2</sub>. After stirring for 19 h, LiBH<sub>4</sub> (2.00 M, 608 µL, 304 µmol) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH<sub>4</sub>Cl aq (10 mL) was added and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The organic extract was washed with water (10 mL) and brine (10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> followed by preparative GPC gave 1(200) as a beige solid (94.3 mg, 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.65 (4H, br s), 3.41 (2H, br s), 2.32 (6H, br s), 1.78–1.34 (4H, m), 1.34–1.05 (6H, m), 0.88(6H, br s); GPC (CHCl<sub>3</sub>, g/mol):  $M_n = 55.1 \times 10^3$ ,  $M_w/M_n = 1.25$ . 1(200) was insoluble in 1,2-DCE.

#### Scheme S7. Synthesis of 1(200).



### 3. High-pressure CD and UV-vis measurement

**General procedure:** A polymer was dissolved in solvent (ca. 0.1 g/L) to enclose a quartz inner cell (volume = 300  $\mu$ L, light path length = 2 mm) with a diaphragm tube. The inner cell was placed in a high-pressure vessel with quartz windows (PCI-500, Syn Corporation, Kyoto, Japan) to be pressurized by a high-pressure hand pump (HP-500, Syn Corporation, Kyoto, Japan) using water as pressure medium. The high-pressure vessel was set in JASCO J-750 spectrometer to measure CD and UV-vis spectra. Absorbance (*A*) was calculated from voltage value (HT) of a photomultiplier tube in the spectrometer according to the following equation, whose validity was also confirmed by comparing the obtained spectra with UV-vis spectra measured by JASCO V-770 UV-Visible/NIR spectrophotometer.

$$A = \{a \times (HT)^4\} + \{b \times (HT)^3\} + \{c \times (HT)^2\} + \{d \times HT\} + e, \quad (1)$$
  
Here,  $a = -5.933 \times 10^{-12}$ ,  $b = 2.265 \times 10^{-8}$ ,  $c = -3.179 \times 10^{-5}$ ,  $d = 2.424 \times 10^{-2}$ ,  $e = -3.720$ .



Figure S1. Photographs of (a) a quartz inner cell and a cell holder (b) a high-pressure vessel with quartz windows (c) a high-pressure hand pump with a pressure gauge.

**Determination of rate constants:** We supposed that the helix inversion induced by pressure is a first order reaction to determine the rate constants, i.e., we adopted following equation for curve fittings. The  $g_{abs}$  plot against time was subjected to a nonlinear, least-squares fitting of the parameters *a*, *c*, *t*<sub>0</sub>, and *k* (the rate constant) using the following equation.

$$g_{abs} = a \times \exp\{-k \times (t - t_0)\} + c, (2)$$

These parameters were successfully converged (Figure S2) and the final values are summarized in Table 1. We concluded that rate constants for the helix inversion reaction were determined as  $2.40 \times 10^{-2}$  s<sup>-1</sup> (*P* to *M* at 200 MPa) and  $5.41 \times 10^{-3}$  s<sup>-1</sup> (*M* to *P* at 0.1 MPa) after averaging the obtained values.



Figure S2. Time-resolved CD intensity change of 1 in 1,2-DCE at 368.0 nm exposed to pressurization (200 MPa) and depressurization (0.1 MPa) cycles. Fitting curves are also presented. Data points observed within a few seconds after pressurization were omitted from the curve fittings to exclude errors arising from the time of the pressurization and the temporal temperature change.

Fitting	<i>a</i> (/10 <sup>3</sup> )	$c(10^3)$	$t_0$ (min)	k (s <sup>-1</sup> )
1 (Press.)	1.03	-1.41	4.15	$2.43 \times 10^{-2}$
2 (Depress.)	-1.97	0.91	15.38	$5.33 \times 10^{-3}$
<b>3</b> (Press.)	1.00	-1.39	51.26	$2.37  imes 10^{-2}$
4 (Depress.)	-2.04	0.90	63.85	$5.49\times10^{3}$

**Table 1.** Converged values of a, c,  $t_0$ , and k in pressurization (200 MPa) and depressurization (0.1 MPa) cycles.

Determination of the difference of the partial molar volume of the dissolved polymer and the compressibility factor: According to Hawley,<sup>5</sup> the Gibbs energy difference ( $\Delta G$ ) in an isothermal process before and after pressurization can be expressed as

$$\Delta G = \Delta V \times (P - P_0) - \Delta \beta / 2 \times (P - P_0)^2, \qquad (3)$$

where  $\Delta V$  and  $\Delta\beta$  represent the difference of the partial molar volume of the dissolved polymer and the compressibility factor, respectively. According to Green's theory,<sup>6</sup>  $\Delta G$  of the helix inversion may also be expressed as

$$\Delta G = -2RT_0 \times \{\operatorname{atanh}(g_{\operatorname{abs}} / g_{\operatorname{max}}) - \operatorname{atanh}(g_{\operatorname{abs},0} / g_{\operatorname{max}})\}, \qquad (4)$$

wherein  $g_{abs,0}$  and  $g_{abs}$  refer to the dissymmetry factor before and after pressurization, respectively,  $g_{max}$  to the dissymmetry factor for the purely single-handed polymer (*P*-helix, 100%, 2.31 × 10<sup>-3</sup> was used here),  $T_0$  to the operating temperature (298.15 K), and *R* to the gas constant (8.314 J K<sup>-1</sup> mol<sup>-1</sup>). Therefore,  $g_{abs}$  can be expressed using *P* as

$$g_{abs} = \tanh[\{\Delta V \times (P - P_0) - \Delta \beta / 2 \times (P - P_0)^2\} / (-2RT_0) + \tanh(g_{abs,0} / g_{max})], \quad (4)$$

After nonlinear least-squares fitting, convergence of these parameters at  $\Delta V = -36.8 \text{ cm}^3 \text{ mol}^{-1}$ and  $\Delta \beta = -0.103 \text{ cm}^3 \text{ mol}^{-1} \text{ MPa}^{-1}$  were observed.



Figure S3. Correlation between pressure and  $g_{abs}$  of 1 in 1,2-DCE at 368.0 nm. A fitted curve was also presented.



Figure S4. CD spectra of 1 in 1,2-DCE at various pressures  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 

## 4. References

- 1. Carmona, E.; Paneque, M.; Poveda, M. L. Polyhedron 1989, 8, 285.
- 2. Yamada, T; Nagata, Y.; Suginome, M. Chem. Commun. 2010, 46, 4914
- 3. Nagata, Y.; Yamada, T.; Adachi, T.; Akai, Y.; Yamamoto, T.; Suginome, M. J. Am. Chem. Soc., **2013**, *135*, 10104.
- 4. Nagata, Y.; Kuroda, T.; Takagi, K.; Suginome, M. Chem. Sci. 2014, 5, 4953.
- 5. Hawley, S. A. *Biochemistry*, **1971**, *10*, 2436.

 Lifson, S.; Andreola, C.; Peterson, N. C.; Green, M. M. J. Am. Chem. Soc., 1989, 111, 8850.



# 5. NMR Spectra of New Compounds

Figure S5. <sup>1</sup>H NMR spectrum of 1 in CDCl<sub>3</sub>.



Figure S6. <sup>1</sup>H NMR spectrum of 2 in CDCl<sub>3</sub>.



Figure S7. <sup>1</sup>H NMR spectrum of 3 in CDCl<sub>3</sub>.



Figure S8. <sup>1</sup>H NMR spectrum of 4 in CDCl<sub>3</sub>.



Figure S9. <sup>1</sup>H NMR spectrum of **1\_60** in CDCl<sub>3</sub>.



Figure S10. <sup>1</sup>H NMR spectrum of 1\_100 in CDCl<sub>3</sub>.



Figure S11. <sup>1</sup>H NMR spectrum of 1\_200 in CDCl<sub>3</sub>.

## 6. UV-vis and CD spectra of New Compounds



Figure S12. UV-vis absorption of 1(60) in 1,2-DCE under 0.1 MPa ( $8.60 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S13. CD spectrum of 1(60) in 1,2-DCE under 0.1 MPa ( $8.60 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S14. UV-vis absorption of 1(60) in 1,2-DCE under 200 MPa ( $8.60 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S15. CD spectrum of 1(60) in 1,2-DCE under 200 MPa ( $8.60 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S16 UV-vis absorption of 1 in CHCl<sub>3</sub> under 0.1 MPa  $(12.2 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S17. CD spectrum of 1 in CHCl<sub>3</sub> under 0.1 MPa  $(12.2 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S18. UV-vis absorption of 1 in CHCl<sub>3</sub> under 200 MPa  $(12.2 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S19. CD spectrum of 1 in CHCl<sub>3</sub> under 200 MPa  $(12.2 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S20. UV-vis absorption of 1 in 1,1,2-TCE under 0.1 MPa  $(16.3 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S21. CD spectrum of 1 in 1,1,2-TCE under 0.1 MPa ( $16.3 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S22. UV-vis absorption of 1 in 1,1,2-TCE under 200 MPa ( $16.3 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S23. CD spectrum of 1 in 1,1,2-TCE under 200 MPa ( $16.3 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S24. UV-vis absorption of 1 in the 80/20 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S25. CD spectrum of 1 in the 80/20 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S26. UV-vis absorption of 1 in the 80/20 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S27. CD spectrum of 1 in the 80/20 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S28. UV-vis absorption of 1 in the 60/40 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S29. CD spectrum of 1 in the 60/40 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S30. UV-vis absorption of 1 in the 60/40 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S31. CD spectrum of 1 in the 60/40 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S32. UV-vis absorption of 1 in the 50/50 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S33. CD spectrum of 1 in the 50/50 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S34. UV-vis absorption of 1 in the 50/50 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S35. CD spectrum of 1 in the 50/50 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S36. UV-vis absorption of 1 in the 40/60 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S37. CD spectrum of 1 in the 40/60 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S38. UV-vis absorption of 1 in the 40/60 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S39. CD spectrum of 1 in the 40/60 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S40. UV-vis absorption of 1 in the 35/65 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S41. CD spectrum of 1 in the 35/65 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S42. UV-vis absorption of 1 in the 35/65 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S43. CD spectrum of 1 in the 35/65 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S44. UV-vis absorption of 1 in the 30/70 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S45. CD spectrum of 1 in the 30/70 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S46. UV-vis absorption of 1 in the 30/70 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S47. CD spectrum of 1 in the 30/70 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S48. UV-vis absorption of 1 in the 20/80 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S49. CD spectrum of 1 in the 20/80 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S50. UV-vis absorption of 1 in the 20/80 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S51. CD spectrum of 1 in the 20/80 mixture of CHCl<sub>3</sub>/1,1,2-TCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S52. UV-vis absorption of 1 in toluene under 0.1 MPa ( $15.5 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S53. CD spectrum of 1 in toluene under 0.1 MPa ( $15.5 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S54. UV-vis absorption of 1 in toluene under 200 MPa  $(15.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S55. CD spectrum of 1 in toluene under 200 MPa  $(15.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 















Figure S59. CD spectrum of **1** in CH<sub>2</sub>Cl<sub>2</sub> under 200 MPa  $(14.6 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S60. UV-vis absorption of **1** in 1,1,1-TCE under 0.1 MPa  $(14.0 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S61. CD spectrum of **1** in 1,1,1-TCE under 0.1 MPa  $(14.0 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S62. UV-vis absorption of 1 in 1,1,1-TCE under 200 MPa  $(14.0 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S63. CD spectrum of **1** in 1,1,1-TCE under 200 MPa  $(14.0 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



















Figure S68. UV-vis absorption of **1** in 1-BuCl under 0.1 MPa  $(14.3 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S69. CD spectrum of 1 in 1-BuCl under 0.1 MPa ( $14.3 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S70. UV-vis absorption of **1** in 1-BuCl under 200 MPa  $(14.3 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S71. CD spectrum of **1** in 1-BuCl under 200 MPa  $(14.3 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S72. UV-vis absorption of **1** in 1-BuCN under 0.1 MPa  $(12.8 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S73. CD spectrum of 1 in 1-BuCN under 0.1 MPa  $(12.8 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S74. UV-vis absorption of 1 in 1-BuCN under 200 MPa  $(12.8 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S75. CD spectrum of **1** in 1-BuCN under 200 MPa  $(12.8 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S76. UV-vis absorption of 1 in 1,2-DCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S77. CD spectrum of **1** in 1,2-DCE under 0.1 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S78. UV-vis absorption of **1** in 1,2-DCE under 50 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S79. CD spectrum of 1 in 1,2-DCE under 50 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S80. UV-vis absorption of 1 in 1,2-DCE under 100 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S81. CD spectrum of 1 in 1,2-DCE under 100 MPa ( $14.5 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S82. UV-vis absorption of 1 in 1,2-DCE under 150 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm})$ 



Figure S83. CD spectrum of 1 in 1,2-DCE under 150 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S84. UV-vis absorption of 1 in 1,2-DCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S85. CD spectrum of 1 in 1,2-DCE under 200 MPa  $(14.5 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S86. UV-vis absorption of **1** in 1,3-dichloropropane under 0.1 MPa  $(15.1 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S87. CD spectrum of **1** in 1,3-dichloropropane under 0.1 MPa  $(15.1 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S88. UV-vis absorption of **1** in 1,3-dichloropropane under 200 MPa  $(15.1 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S89. CD spectrum of **1** in 1,3-dichloropropane under 200 MPa  $(15.1 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S90. UV-vis absorption of **2** in 1,2-DCE under 0.1 MPa  $(15.1 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S91. CD spectrum of **2** in 1,2-DCE under 0.1 MPa  $(15.1 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S92. UV-vis absorption of **2** in 1,2-DCE under 200 MPa  $(15.1 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S93. CD spectrum of **2** in 1,2-DCE under 200 MPa  $(15.1 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S94. UV-vis absorption of **3** in 1,2-DCE under 0.1 MPa  $(16.7 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S95. CD spectrum of **3** in 1,2-DCE under 0.1 MPa ( $16.7 \times 10^{-2}$  g/L, light path length = 2 mm).



Figure S96. UV-vis absorption of **3** in 1,2-DCE under 200 MPa  $(16.7 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S97. CD spectrum of **3** in 1,2-DCE under 200 MPa  $(16.7 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S98. UV-vis absorption of **4** in 1,2-DCE under 0.1 MPa  $(13.2 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S99. CD spectrum of 4 in 1,2-DCE under 0.1 MPa  $(13.2 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S100. UV-vis absorption of 4 in 1,2-DCE under 200 MPa  $(13.2 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$ 



Figure S101. CD spectrum of **4** in 1,2-DCE under 200 MPa  $(13.2 \times 10^{-2} \text{ g/L}, \text{ light path length} = 2 \text{ mm}).$