**Supporting Information for:**

# Conformational Polymorphism and Optical Properties in the Solid State of 1,4,7,10-Tetra(*n*-butyl)tetracene

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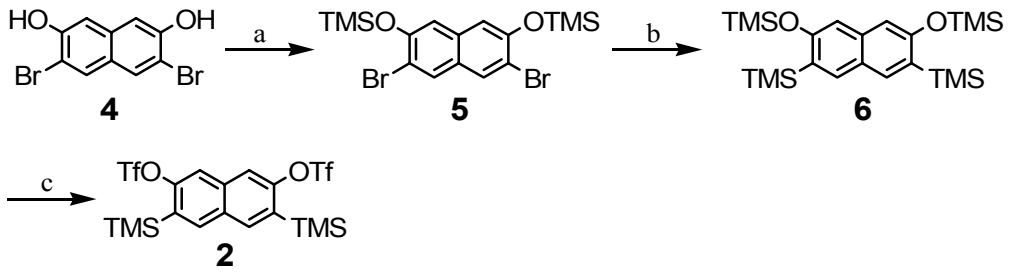
**General.** Melting points were measured on a Yanaco Melting Point apparatus and are uncorrected. Elemental analysis was carried out on a Yanaco MT-5 CHN corder. $^{1}H$ and $^{13}C$ spectra were recorded on a Bruker-Biospin DRX500 FT spectrometer at 500 and 126 MHz, respectively. THF was distilled from $LiAlH_4$ prior to use. $Et_2O$ and toluene were distilled from NaH prior to use. Commercially available reagents were used as supplied unless otherwise stated. All reactions were carried out under nitrogen atmosphere unless otherwise noted. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 $F_{254}$ 0.25 mm aluminium plates, and components were visualized by UV light. Column chromatography was performed on silica gel (Wako C-300, 45-75 μm).

**Preparation of 3,6-bis(trimethylsilyl)-2,7-bis(trifluoromethanesulfonate)naphthalene (2)**




**Scheme 1.** Reagents and conditions: (a) TMSCl, pyridine, toluene, reflux, 87%; (b) *n*-BuLi, THF, -80 ˚C: TMSCl, -80 ˚C to rt, 74%; (c) , THF, -80 ˚C: $Tf_2O$, -80 ˚C to rt, quantitatively

**Synthesis of 3,6-dibroromo-2,7-bis(trimethylsiloxy)naphthalene (5)**

A mixture of 3,6-dibromo-2,7-dihydoroxynaphthalene[1] **4** (978 mg, 3.03 mmol) and toluene (10 mL) was heated until **4** dissolved completely. After addition of a solution of TMSCl (3 mL) and pyridine (3 mL), the mixture was stirred at reflux for 6 h. Then the mixture was cooled to room temperature. Water was cautiously added, and the organic layer was separated. The organic phase was washed with brine, and dried over $Na_2SO_4$. *n*-Hexane was added to the organic solution, and the mixture was filtered to remove salts deposited. After removal of solvents and vacuum drying, **5** was obtained as a creamy white solid (1.24 g, 87% yield). **5** was used in the next reaction without

further purification. Mp 83-85 ˚C. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$0.36 (s, 18H), 7.05 (s, 2H), 7.89 (s, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$0.34, 114.29, 115.67, 126.58, 130.79, 133.76, 150.48.

**Synthesis of 3,6-bis(trimethylsilyl)-2,7-bis(trimethylsiloxy)naphthalene (6)**

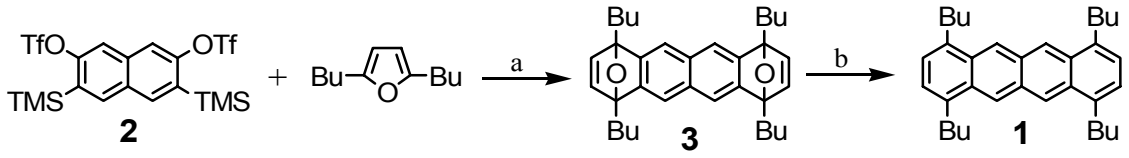
To a solution of **5** (2.83 g, 6.11 mmol) in THF (15 mL), 9 mL of 1.6 M *n*-BuLi in *n*-hexane (14.4 mmol) was added dropwise at -80 ˚C. The mixture was stirred for 30 min at -80 ˚C. Then, TMSCl (2.5 mL, 19.6 mmol) was added dropwise. The mixture was allowed to be warmed to room temperature, and stirred for additional 17 h. Water was cautiously added, and the resulting mixture was extracted with $Et_2O$. The combined organic layers were washed with brine, and dried over $Na_2SO_4$. After removal of solvents, MeOH was added to the residue, and the resulting solid was filtered off. After vacuum drying, **6** was obtained as a white solid (2.01 g, 74% yield). **6** was used in the next reaction without further purification. Mp 142-144 ˚C. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$0.30 (s, 18H), 0.39 (s, 18H), 6.84 (s, 2H), 7.76 (s, 2H). $^{13}$C NMR (126 MH, $CDCl_3$) $\delta$-0.74, 0.68, 109.58, 124.38, 129.77, 136.25, 137.60, 158.58.

**Synthesis of 3,6-bis(trimethylsilyl)-2,7-bis(trifluoromethanesulfonate)naphthalene (2)**

To a solution of **6** (2.76 g, 6.15 mmol) in $Et_2O$, 9 mL of 1.6 M *n*-BuLi in *n*-hexane (14.4 mmol) was added dropwise at 0 ˚C. The mixture was warmed at room temperature for 4h, and cooled to 0 ˚C again. $Tf_2O$ (3.3 mL, 19.6 mmol) was added dropwise, and the mixture was stirred at 0 ˚C for additional 40 min. A saturated solution of $NaHCO_3$ in water was cautiously added, and the resulting mixture was extracted with $Et_2O$. The combined organic layers were washed with brine, and dried over $Na_2SO_4$. After removal of solvents and drying under vacuum, **2** was obtained as a brown solid (3.5 g) quantitatively. *Caution! **2** was slightly unstable at room temperature.* Therefore, **2** should be stored in refrigerator. We could use **2** that was stored in refrigerator for 4 months in the next Diels-Alder reaction. Mp 70-72 ˚C. $^{1}$H NMR (500 MHz, $CDCl_3$) $\delta$0.44 (s, 18H), 7.80 (s, 2H), 8.04 (s, 2H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ -0.86, 116.27, 118.69 (q, $J$ = 320 Hz), 130.02, 132.76,

135.03, 137.63, 153.70. Anal. Calcd for $C_{18}H_{22}F_6O_6S_2Si_2$: C, 38.02; H, 3.90. Found: C, 38.32; H, 3.84.

**Preparation of 1,4,7,10-tetra(*n*-butyl)tetracene (1)**




**Scheme 2.** Reagents and conditions: (a) KF, 18-crown-6, THF, rt, 47%; (b) $H_2$, 10% Pd/C, *n*-BuOH, rt: conc HCl, $Ac_2O$, rt, 42%

KF (496 mg, 8.53 mmol) was added to a solution of **2** (1.00 g, 1.76 mmol), 2,5-di(*n*-butyl)furan[2] (680 mg, 3.77 mmol), and 18-crown-6 (1.98 g, 7.50 mmol) in THF (10 mL), and the mixture was stirred at room temperature for 20 h. Water was added, and the resulting mixture was extracted with $Et_2O$. The combined organic layers were washed with brine, and dried over $Na_2SO_4$. After removal of solvents, the residue was purified by column chromatography ($CHCl_3$/*n*-hexane = 1/1) to afford a mixture of *syn*- and *anti*-isomers of **3** (404 mg, 47% yield) as a pale brown oil. Then, the product **3** in *n*-BuOH (15 mL) was hydrogenated over 10% Pd/C (84 mg) under atmospheric pressure at room temperature for 2 h. The catalyst was removed by filtration, and the filtrate was concentrated under reduced pressure. To the residue was added a cold solution of conc HCl (1.5 mL) and $Ac_2O$ (7.5 mL) at 0 ˚C, and the mixture was stirred at room temperature for 1 h. Water was added, and the resulting mixture was extracted with $CHCl_3$. The combined organic layers were washed with brine, and dried over $Na_2SO_4$. After removal of solvents, column chromatography of the residue (*n*-hexane) and recrystallization with $Et_2O$ afforded **1** (157 mg, 42% yield) as a mixture of red and yellow solids. Mp 128-131 ˚C. $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 1.03 (t, $J$ = 7.3 Hz, 12H), 1.53-1.57 (m, 8H), 1.84-1.90 (m, 8H), 3.19 (t, $J$ = 7.8 Hz, 8H), 7.14 (s, 4H), 8.81 (s, 4H). $^{13}$C NMR (126 MHz, $CDCl_3$) $\delta$ 14.16, 23.03, 32.31, 32.95, 123.22, 123.87, 128.99, 131.00, 136.67. Anal. Calcd for $C_{34}H_{44}$: C, 90.20; H, 9.80. Found: C, 90.27; H, 9.71.

**Fluorescence measurements in the solid state**

For fluorescence measurements in the solid state, the samples were excited by He-Cd laser (Kimmon, IK3301R-G) and the spectra were recorded using a calibrated optical multichannel analyzer (Hamamatsu Photonics, PMA11). The measurement of the absolute quantum yield $\Phi_F$ was performed using an integrating sphere (Labsphere, IS-040-SF) and showed the $\Phi_F$ values of 0.16 and 0.34 for the red **1** and the yellow **1**, respectively.

**References**

(1) Cooke, R. G.; Johnson, B. L.; Owen, W. R. *Aust. J. Chem*. **1960**, *13*, 256.

(2) McKeown, N. B.; Chambrier, I.; Cook, M. J. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1169.

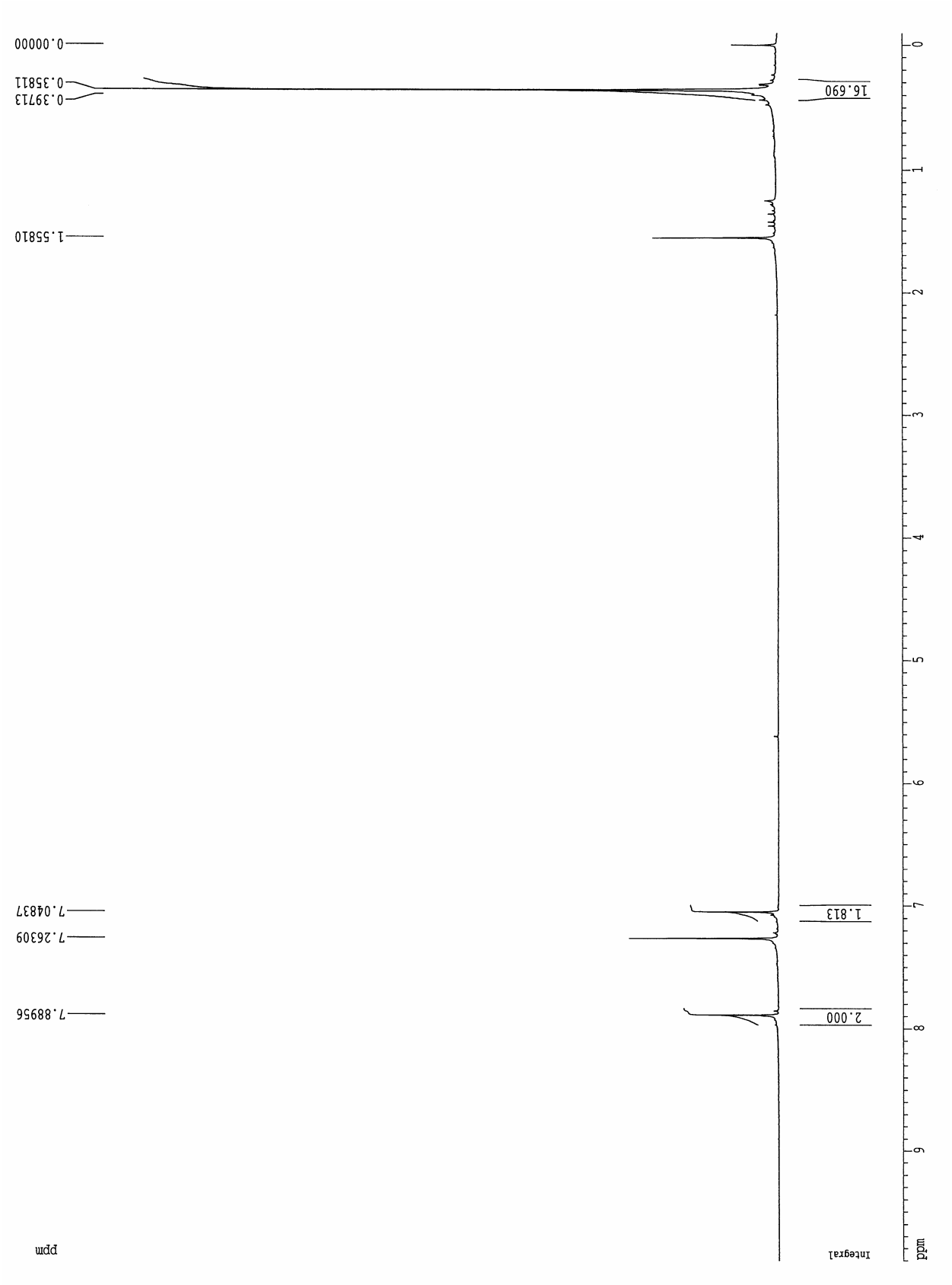



**Figure S-1.** $^{1}$H NMR spectrum of **5**.

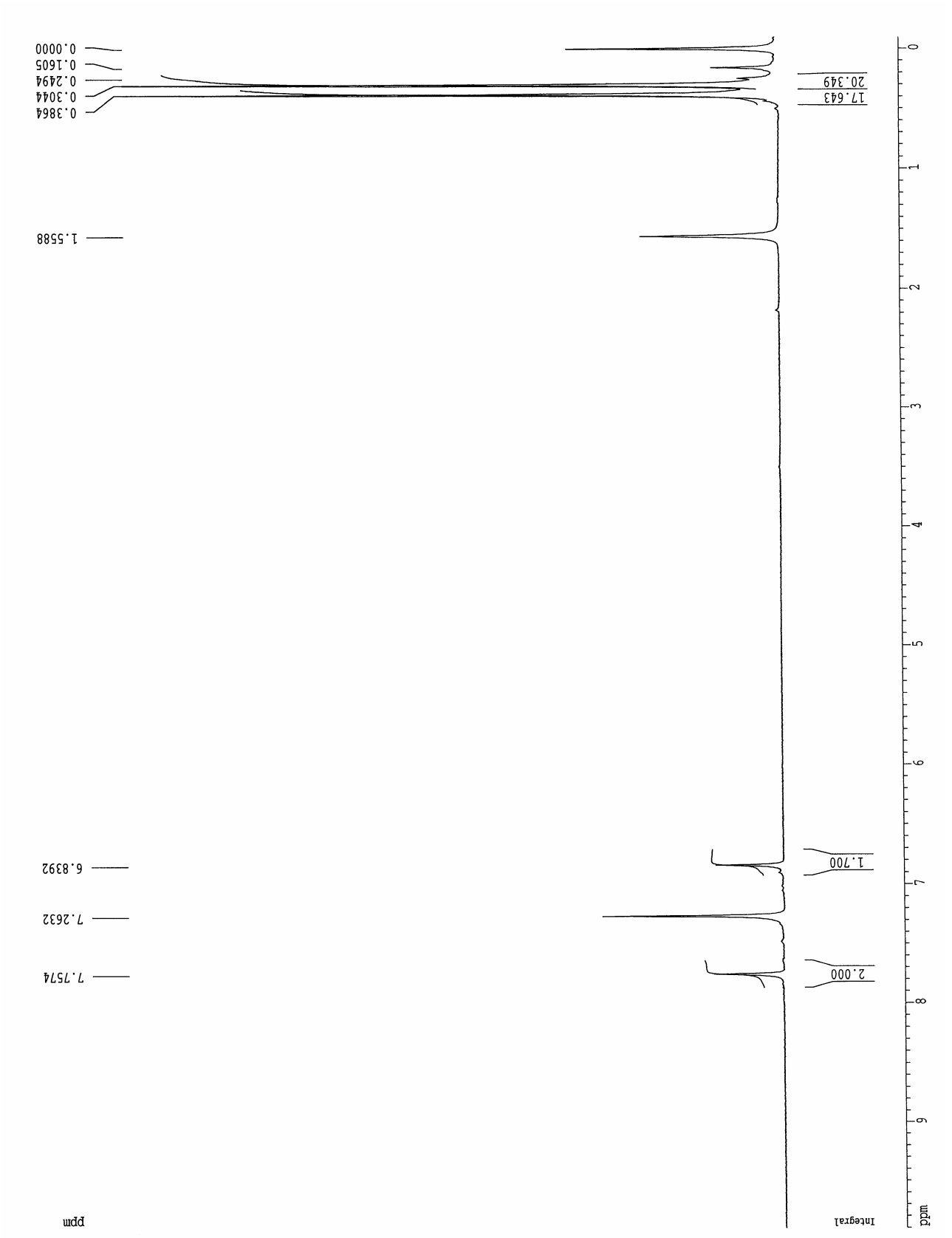



**Figure S-2.** $^{1}$H NMR spectrum of **6**.

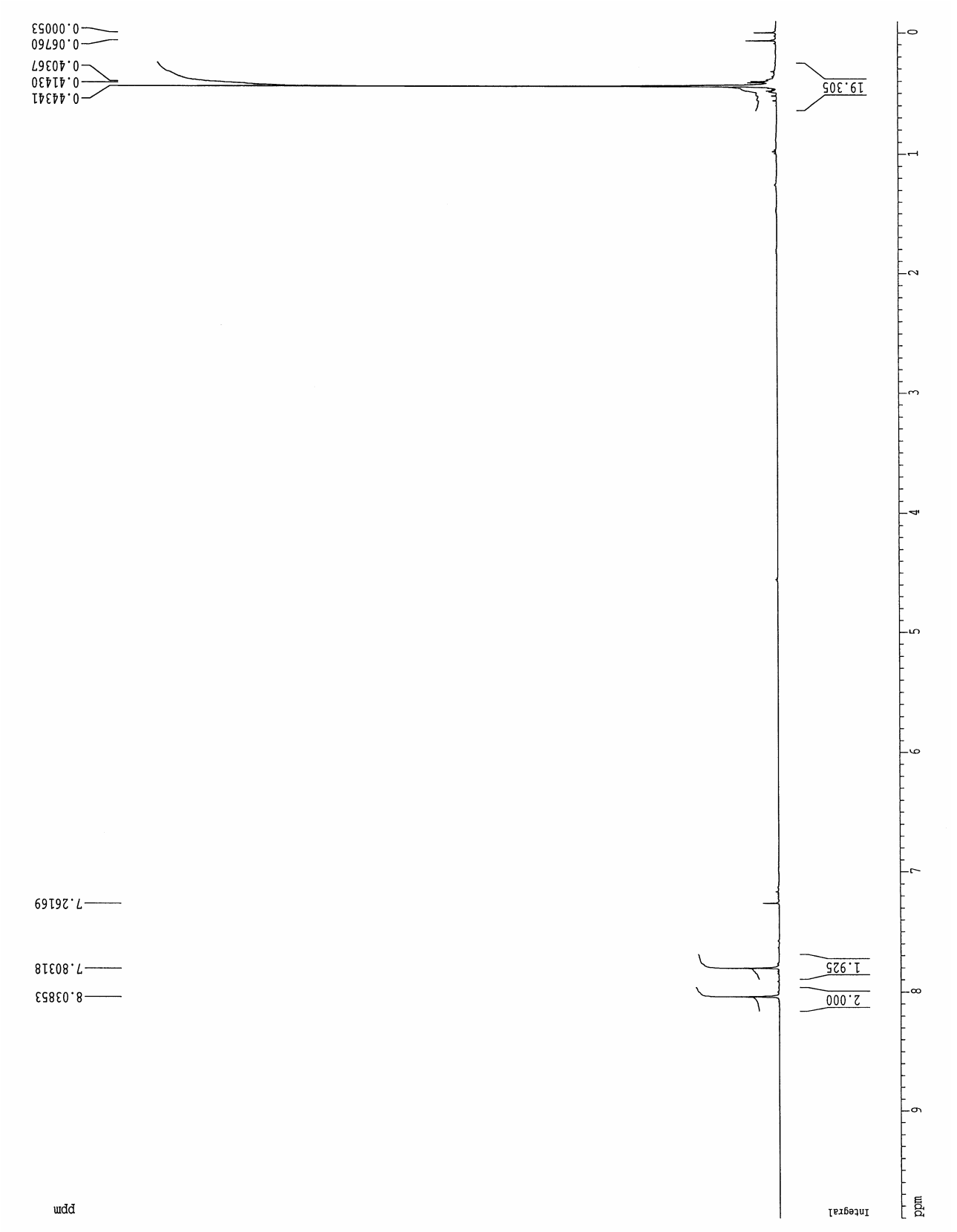



**Figure S-3.** $^{1}$H NMR spectrum of **2**.

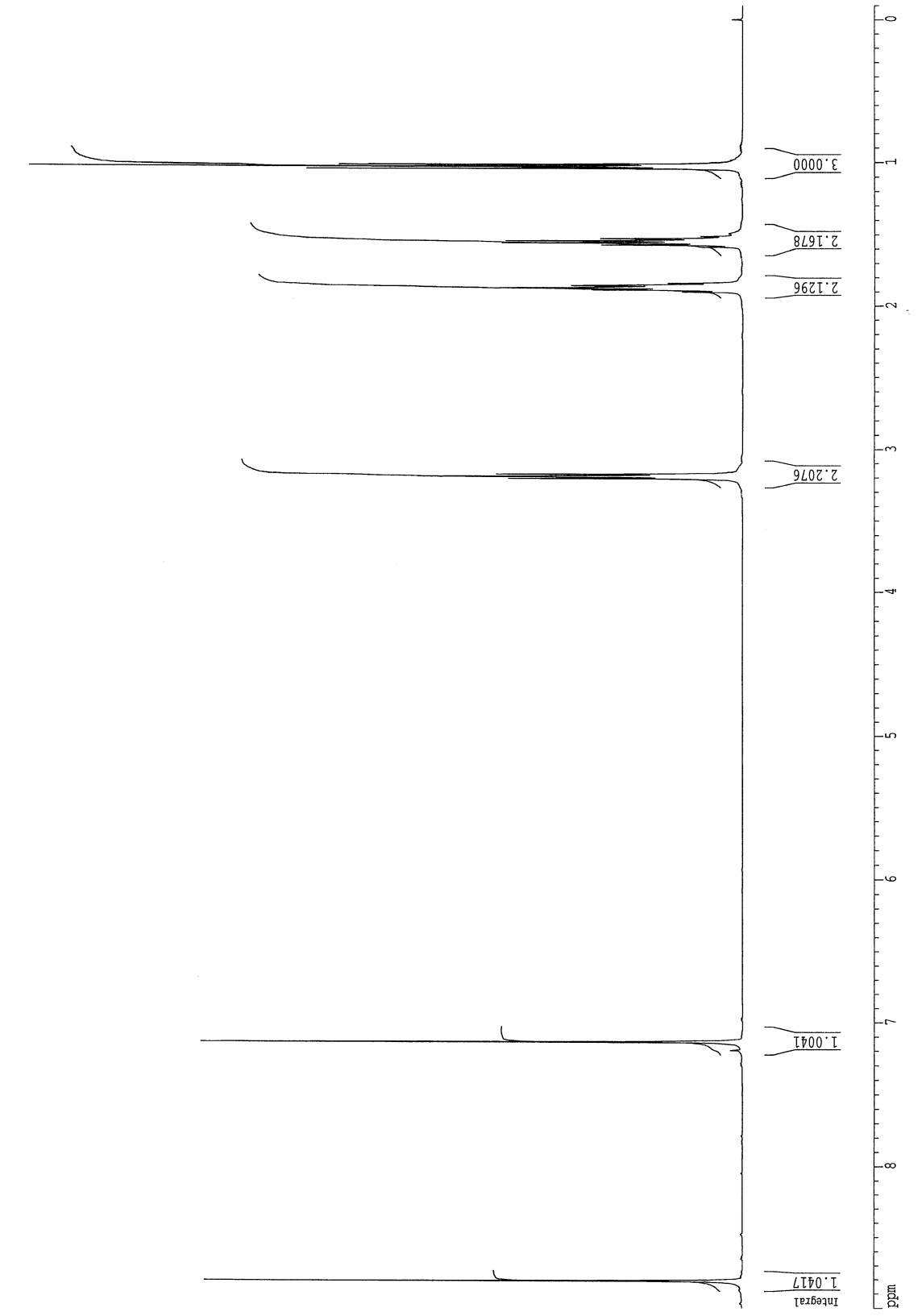



**Figure S-4.** $^{1}$H NMR spectrum of **1**.