Supporting Information

Tuning the Thermo- and Mechanoresponsive Behavior of Luminescent Cyclophanes

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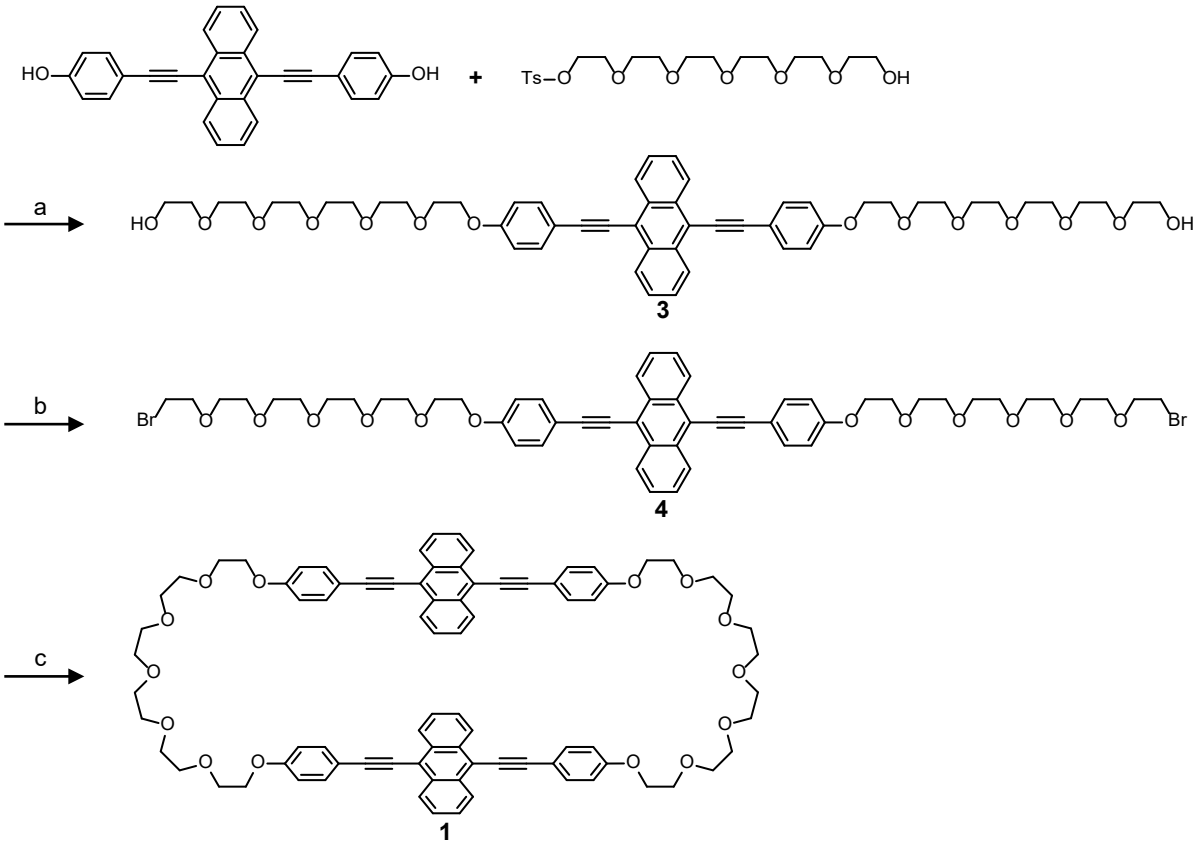
Synthesis of compound 1 and 2

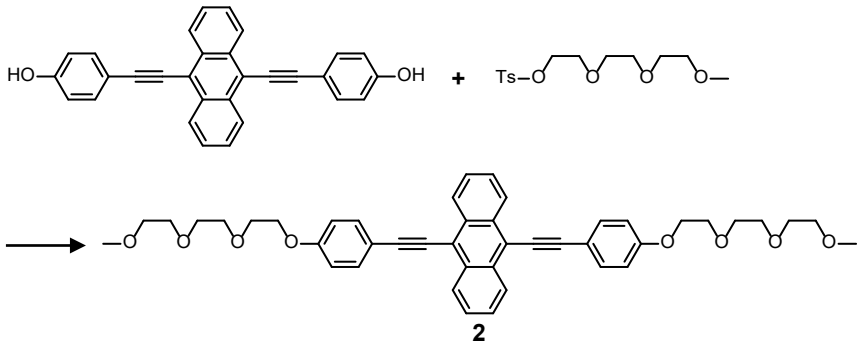
The synthetic routes used to prepare compounds **1** and **2** are shown in Schemes S1 and S2, respectively. 9,10-Bis(4-hydroxyphenylethynyl)anthracene, hexaethyleneglycol mono-tosylate, and 2-(2-(2-methoxy-ethoxy)ethoxy)ethyl tosylate were prepared according to previously reported procedures.[S1-S3]

Scheme S1



Conditions: (a) LiBr, K_2CO_3, CH_3CN, reflux, 1 day; (b) CBr_4, PPh_3, CH_2Cl_2, 0 °C → r.t., 3 h; (c) 9,10-bis(4-hydroxyphenylethynyl)anthracene, K_2CO_3, DMF, 70 °C, 28 h.

Scheme S2



Condition: K_2CO_3, DMF, 80 °C, 8 h.

Compound 3. A suspension of 9,10-bis(4-hydroxyphenylethynyl)anthracene (940 mg, 2.29 mmol), hexaethyleneglycol mono-tosylate (2.20 g, 5.04 mmol), K_2CO_3 (1.59 g, 11.5 mmol), and lithium bromide (19.9 mg, 0.229 mmol) in acetonitrile (200 mL) was stirred for 1 day under reflux. After cooling to room temperature, most of the acetonitrile was evaporated and 5% aq. HCl (100 mL) was added to the suspension. After the mixture was extracted with chloroform (3 × 100 mL), the combined organic layers were washed with saturated aq. $NaHCO_3$ solution (1 × 50 mL), then washed with saturated aq. NaCl solution (1 × 100 mL), dried over $MgSO_4$, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: stepwise gradient from dichloromethane/methanol = 30:1 to dichloromethane/methanol = 15:1) to afford compound **3** (1.55 g, 1.65 mmol) as an orange solid in 72% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.73 (t, J = 6.4 Hz, 2H), 3.57–3.76 (m, 40H), 3.89 (t, J = 4.8 Hz, 4H), 4.19 (t, J = 4.8 Hz, 4H), 6.98 (d, J = 8.8 Hz, 4H), 7.59–7.64 (m, 4H), 7.69 (d, J = 8.8 Hz, 4H), 8.65–8.69 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 61.83, 67.64, 69.75, 70.41, 70.67, 70.73, 70.96, 72.63, 85.52, 102.56, 114.97, 115.83, 118.52, 126.74, 127.39, 132.04, 133.24, 159.32. MS (MALDI-TOF): m/z: 938.57 (calcd. $[M]^+$ = 938.45).

Compound 4. To a solution of **3** (1.35 g, 1.44 mmol) and triphenylphosphine (1.10 g, 4.18 mmol) in dichloromethane (200 mL) was added dropwise a solution of tetrabromomethane (1.43 g, 4.31 mmol) in dichloromethane (15 mL) at 0 °C. The reaction mixture was subsequently stirred for 3 h at room temperature before most of the dichloromethane was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/acetone = 7:1), then purified by another flash column chromatography (dichloromethane/acetone = 1:1) to afford compound **4** (1.53 g, 1.44 mmol) as an orange solid in quantitative yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.47 (t, J = 6.4 Hz, 4H), 3.66–3.77 (m, 32H), 3.80 (t, J = 6.4 Hz, 4H), 3.91 (t, J = 4.8 Hz, 4H), 4.21 (t, J = 4.8 Hz, 4H), 6.70 (d, J = 8.8 Hz, 4H), 7.61–7.65 (m, 4H), 7.71 (d, J = 8.8 Hz, 4H), 8.66–8.71 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.47, 67.65, 69.76, 70.62, 70.69, 70.70, 70.75, 70.76, 71.00, 71.29, 85.53, 102.56, 114.97, 115.84, 118.53, 126.75, 127.39, 132.05, 133.25, 159.31. MS (MALDI-TOF): m/z: 1062.42 (calcd. $[M]^+$ = 1062.28).

Compound 1. A solution of compound **4** (450 mg, 0.423 mmol) and 9,10-bis(4-hydroxyphenylethynyl)anthracene (173 mg, 0.423 mmol) in DMF (25 mL) was added to a suspension of K_2CO_3 (1.17 g, 8.46 mmol) in DMF (150 mL) dropwise at 70 °C over 4 h under vigorous stirring. After 24 h, the reaction suspension was cooled and most of the DMF was evaporated in vacuo. The crude product was dissolved in chloroform and washed with saturated aq. NH_4Cl solution (3 × 100 mL), followed by saturated aq. NaCl solution, the organic layer was dried over $MgSO_4$, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/acetone = 5:2) and subsequent re-precipitated from a mixture of dichloromethane and hexane to afford compound **1** (151 mg, 0.115 mmol) as a yellow powder in 27% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.68–3.75 (m, 32H), 3.85 (t, J = 4.8 Hz, 8H), 4.08 (t, J = 4.8 Hz, 8H), 6.82 (d, J = 8.8 Hz, 8H), 7.40–7.44 (m, 8H), 7.50 (d, J = 8.8 Hz, 8H), 8.41–8.45 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 67.63, 69.79, 70.84, 70.86, 70.90, 71.06, 85.65, 102.40, 114.77, 115.92, 118.34, 126.45, 127.20, 131.81, 133.15, 159.11. MS (MALDI-TOF): m/z: 1312.73 (calcd. $[M]^+$ = 1312.55). Elemental analysis (%) calcd. for $C_{84}H_{80}O_{14}$: C 76.81, H 6.14, N 0.00; found: C 76.58, H 6.06, N 0.30.

Compound 2. A suspension of 9,10-bis(4-hydroxyphenylethynyl)anthracene (300 mg, 0.731 mmol), 2-(2-(2-methoxyethoxy)ethoxy)ethyl tosylate (582 mg, 1.83 mmol), and K_2CO_3 (505 mg, 3.66 mmol) in DMF (150 mL) was stirred for 8 h at 80 °C. The reaction suspension was poured into ethyl acetate and the organic phase was washed with saturated aq. NH_4Cl solution (4 × 100 mL), followed by saturated aq. NaCl solution. The organic layer was dried over $MgSO_4$, filtered, and the solvent was evaporated. The crude product was purified by flash column chromatography on silica gel (eluent: dichloromethane/acetone = 5:1) and subsequent re-precipitated from a mixture of dichloromethane and hexane (483 mg, 0.687 mmol) as a yellow solid in 94% yield.
^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.39 (s, 6H), 3.55–3.57 (m, 4H), 3.66–3.68 (m, 4H), 3.69–3.71 (m, 4H), 3.75–3.78 (m, 4H), 3.89–3.91 (m, 4H), 4.19–4.21 (m, 4H), 6.99 (d, J = 8.8 Hz, 4H), 7.60–7.63 (m, 4H), 7.69 (d, J = 9.2 Hz, 8H), 8.66–8.68 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 59.16, 67.62, 69.74, 70.69, 70.76, 70.96, 72.03, 85.52, 102.57, 114.95, 115.82, 118.52, 126.72, 127.38, 132.03, 133.22, 159.30. MS (MALDI-TOF): m/z: 702.43 (calcd. $[M]^+$ = 702.32). Elemental analysis (%) calcd. for $C_{44}H_{46}O_8$: C 75.19, H 6.60, N 0.00; found: C 75.07, H 6.58, N 0.30.

Sample preparation for XRD measurements

The powder Y-form was carefully put on an XRD sample holder to conduct the XRD measurement for the Y-form. The subsequent thermal treatment for the sample holder with the Y-form at 150 °C resulted in the conversion to the YG-form on the sample holder. The sample holder was used for the XRD measurement for the YG-form. As for the Am-form, compound **1** was carefully ground on the glass substrates and the resultant solid (Am-form) was transferred onto the XRD sample holder and the XRD pattern of **1** in the Am-form was obtained. Then, after annealing the sample holder with the Am-form, the XRD measurement for the annealed Am-form was carried out.

Concentration dependence of the absorption and photoluminescence spectra

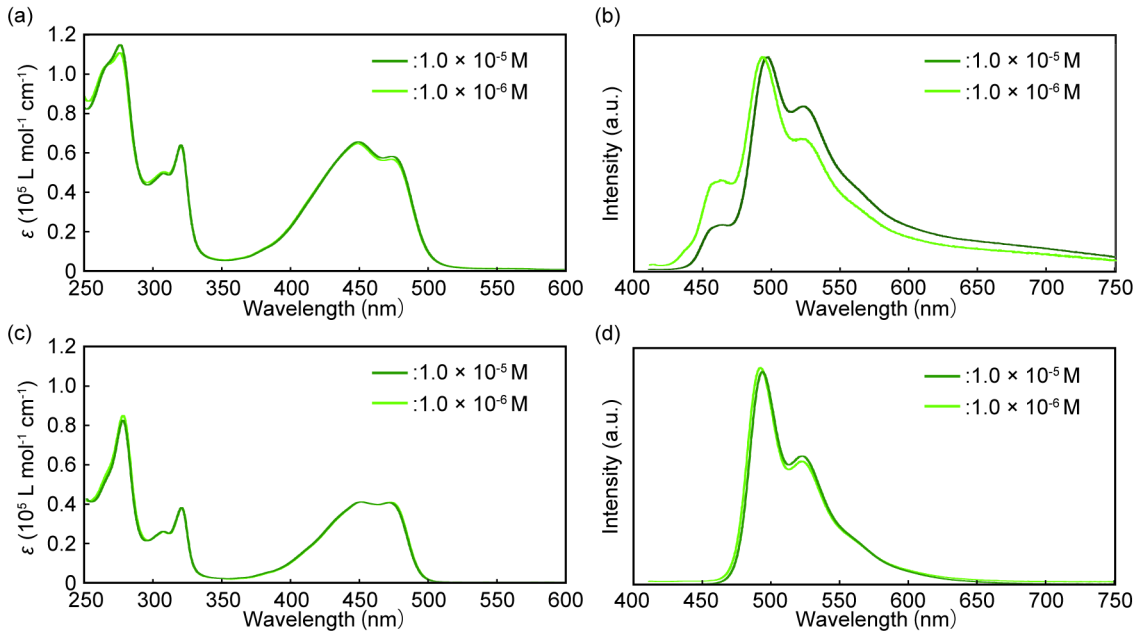


Figure S1. Absorption and emission spectra of compounds **1** (a,b) and **2** (c,d) in chloroform at the concentration of 1.0×10^{-5} M and 1.0×10^{-6} M.

DSC trace of the Am-form

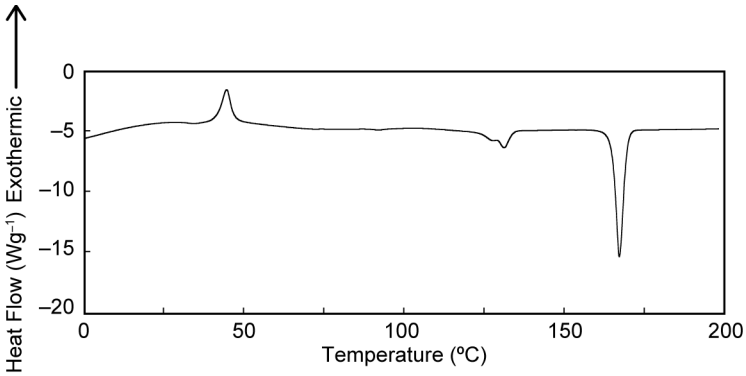


Figure S2. First heating DSC trace of the Am-form

References

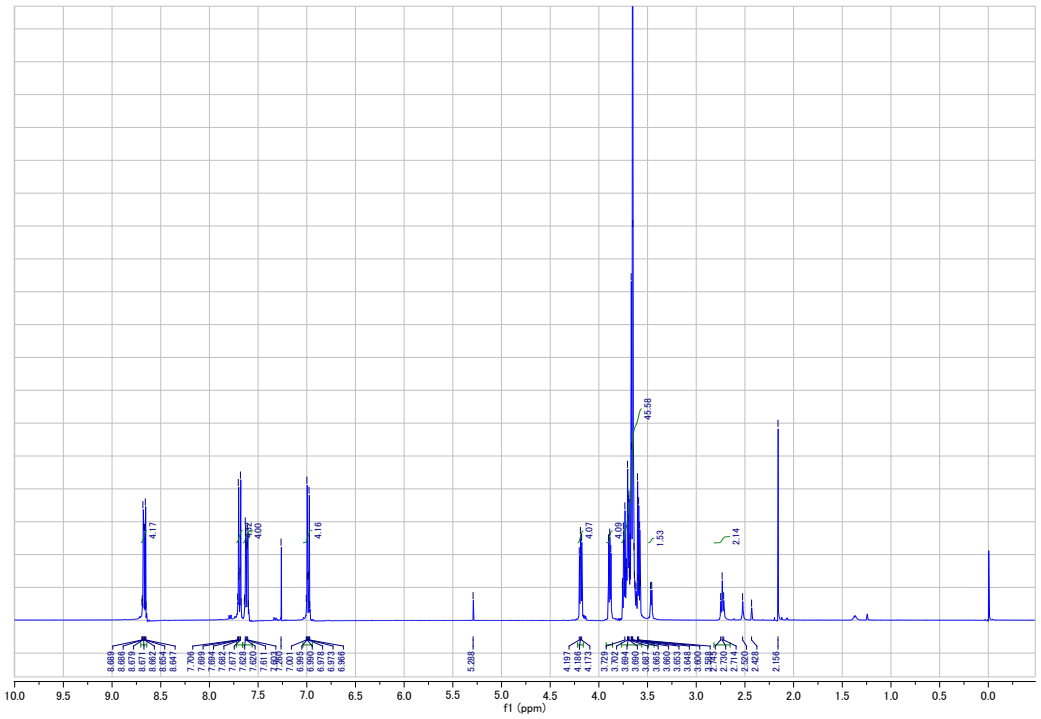
S1. Y. Sagara, Y. C. Simon, N. Tamaoki and C. Weder, *Chem. Commun.*, 2016, **52**, 5694−5697.

S2. A. Dif, F. Boulmedais, M. Pinot, V. Roullier, M. Baudy-Floc'h, F. M. Coquelle, S. Clarke, P. Neveu, F. Vignaux, R. Le Borgne, M. Dahan, Z. Gueroui and V. Marchi-Artzner, *J. Am. Chem. Soc.*, 2009, **131**, 14738–14746.

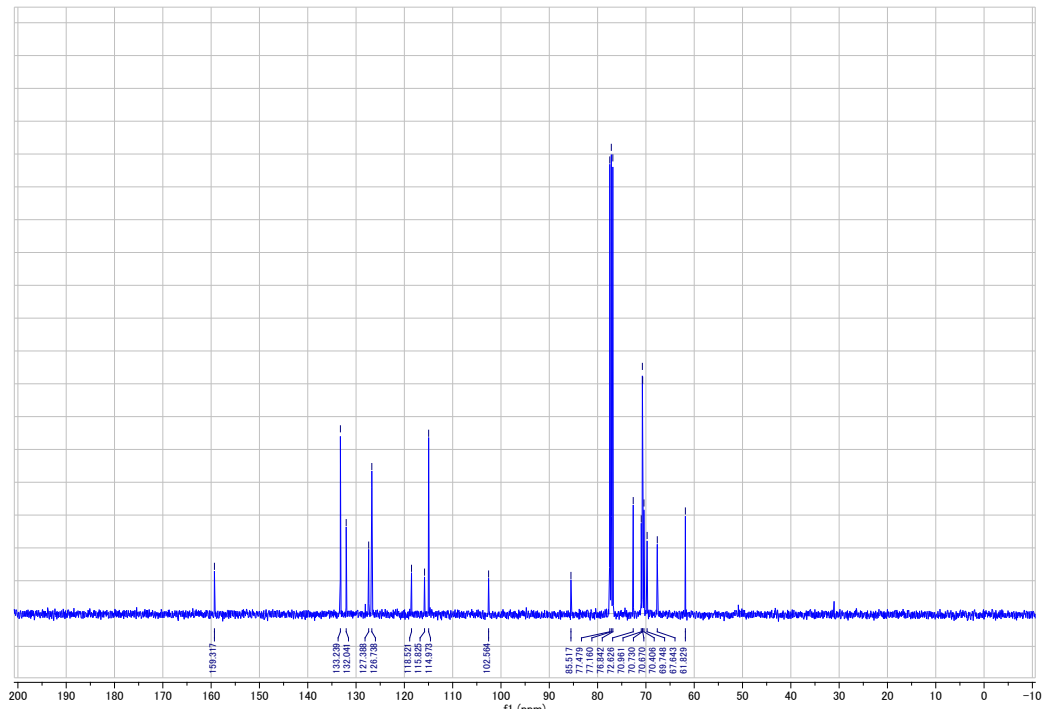
S3. T. Wei, J. H. Jung and T. F. Scott, *J. Am. Chem. Soc.*, 2015, **137**, 16196−16202.

NMR spectra of compounds

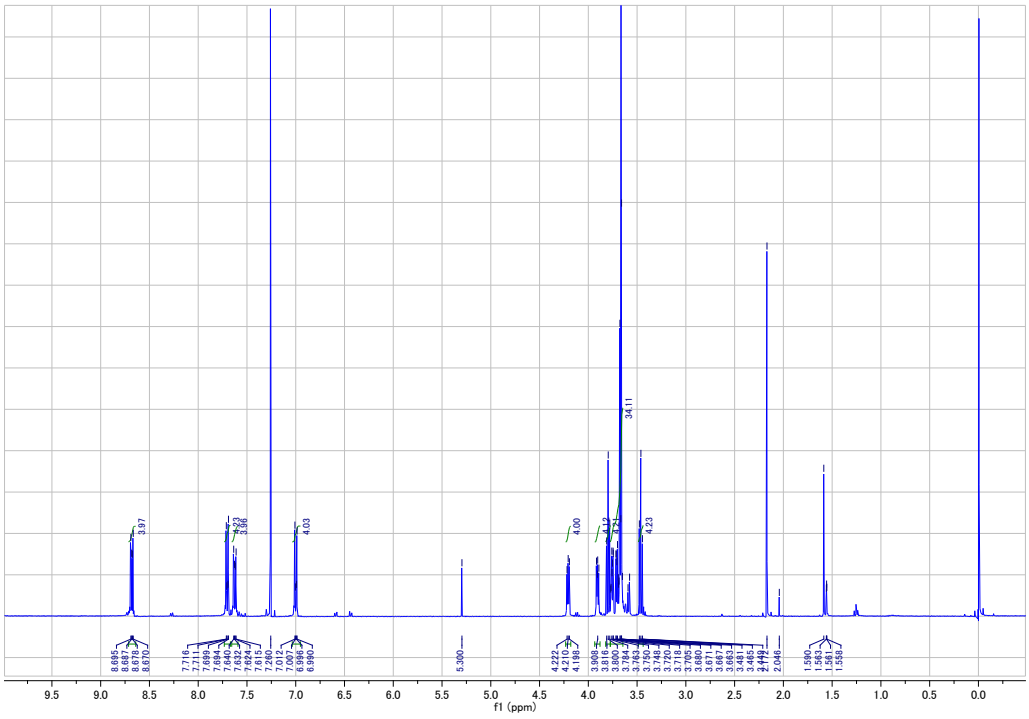
^{1}H NMR spectrum of Compound **3**



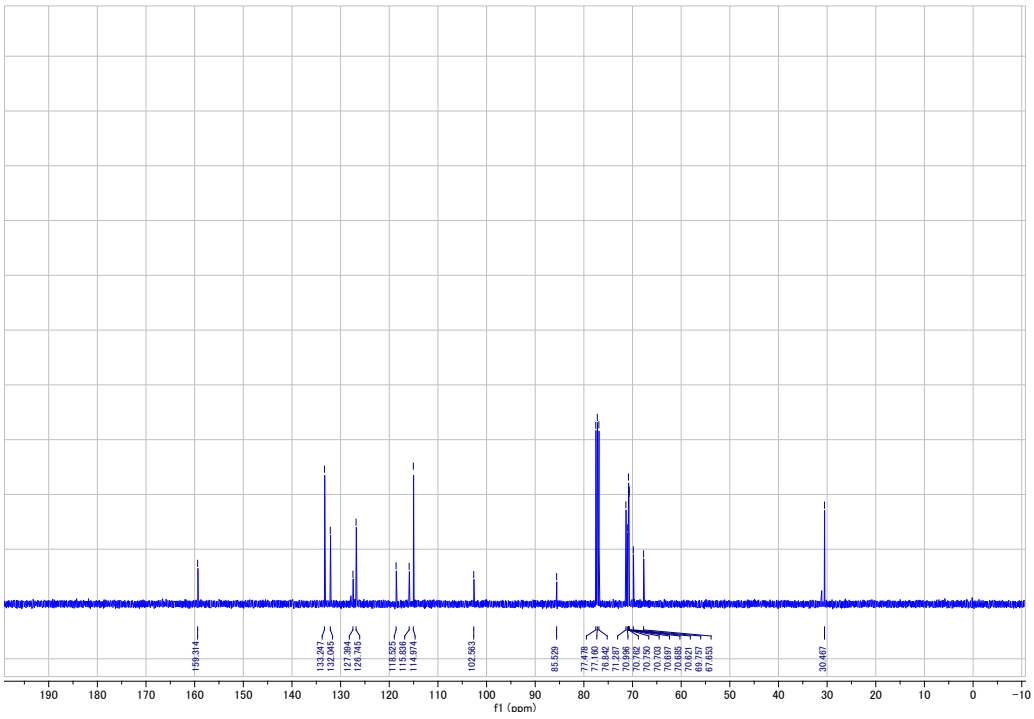
^{13}C NMR spectrum of Compound **3**



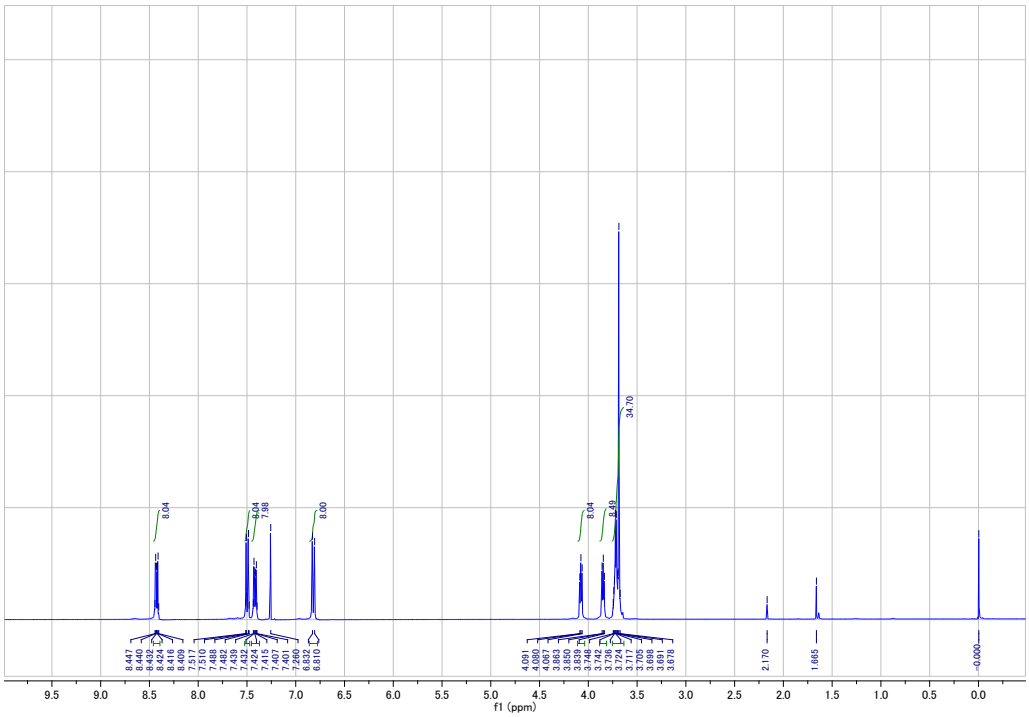
^{1}H NMR spectrum of Compound **4**



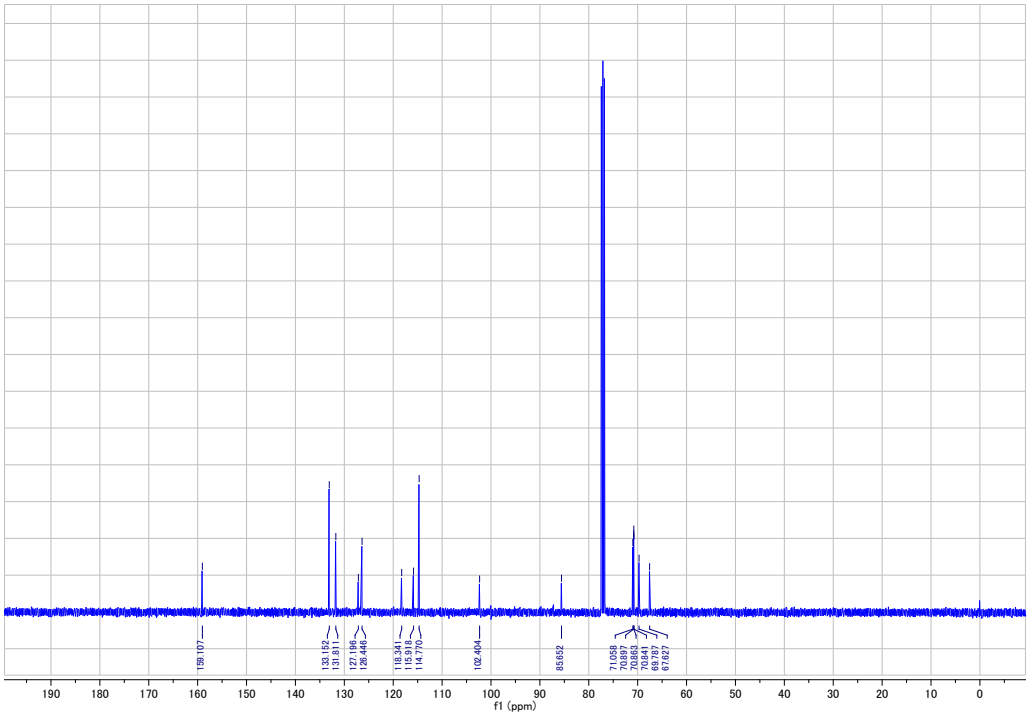
^{13}C NMR spectrum of Compound **4**



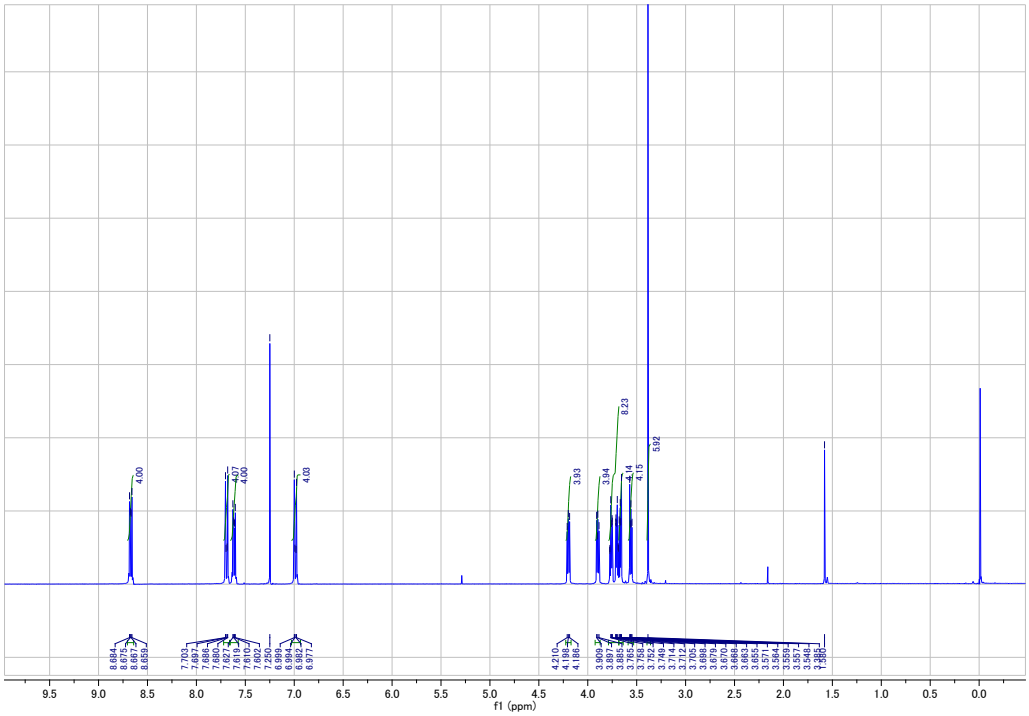
^{1}H NMR spectrum of Compound **1**



^{13}C NMR spectrum of Compound **1**



^{1}H NMR spectrum of Compound **2**



^{13}C NMR spectrum of Compound **2**