Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Dual-channel recognition of Al^{3+} and Cu^{2+} ions using a chiral pyrene-based fluorescent sensor

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1. Supplementary spectral data

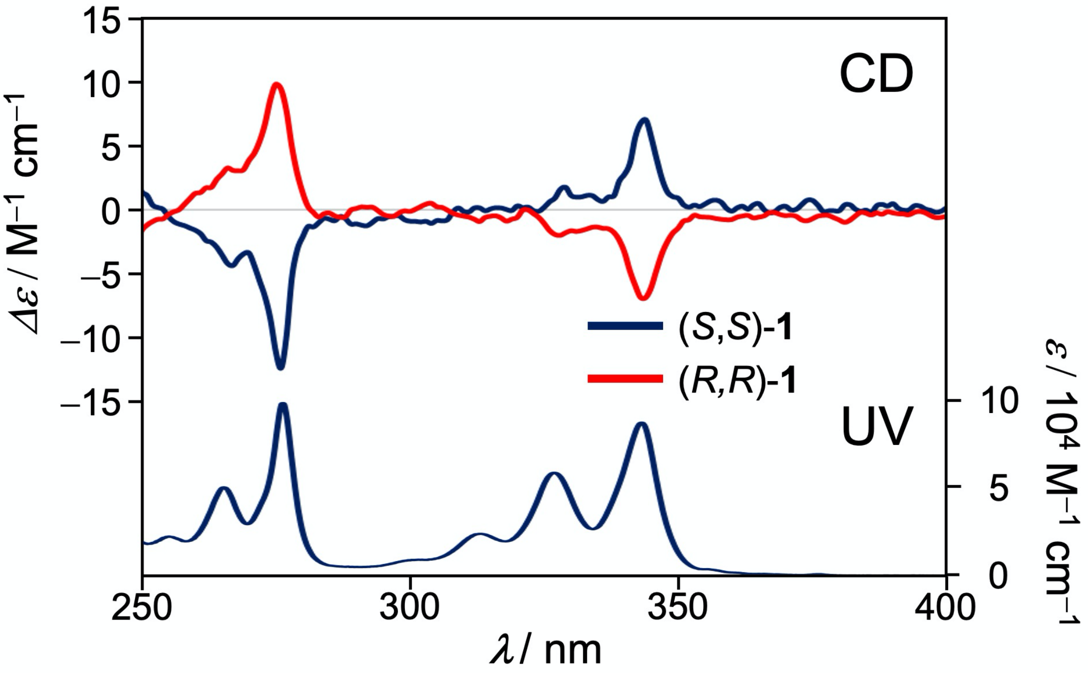


Fig. S1 UV and CD spectra of (*S*,*S*)-**1** and (*R*,*R*)-**1** in CH_3CN (1.0×10^{-5} M).

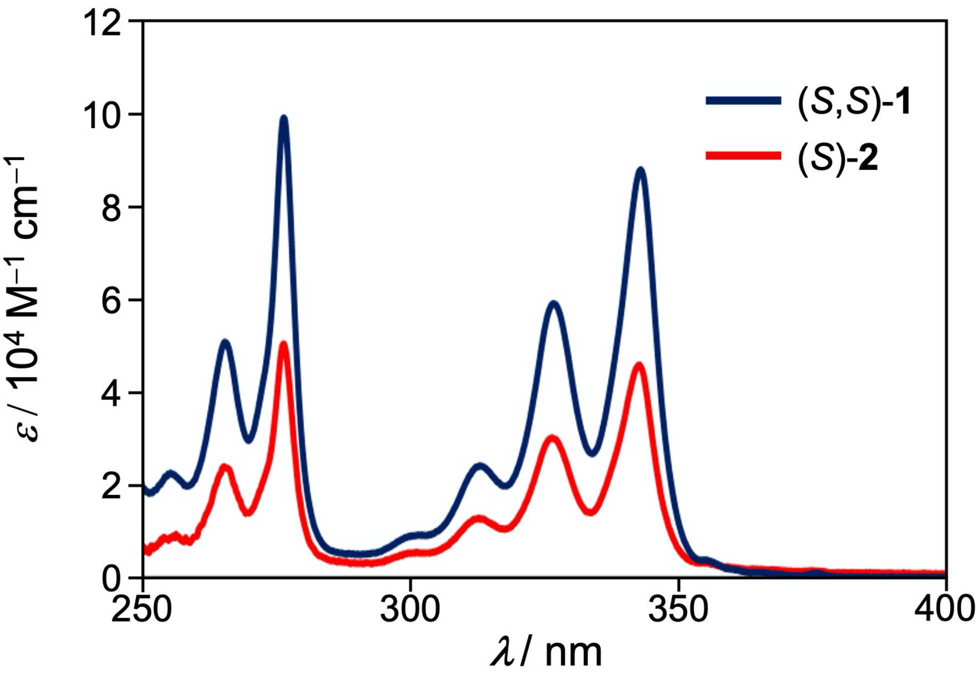


Fig. S2 UV spectra of (*S*,*S*)-**1** and (*S*)-**2** in CH_3CN (1.0×10^{-5} M).

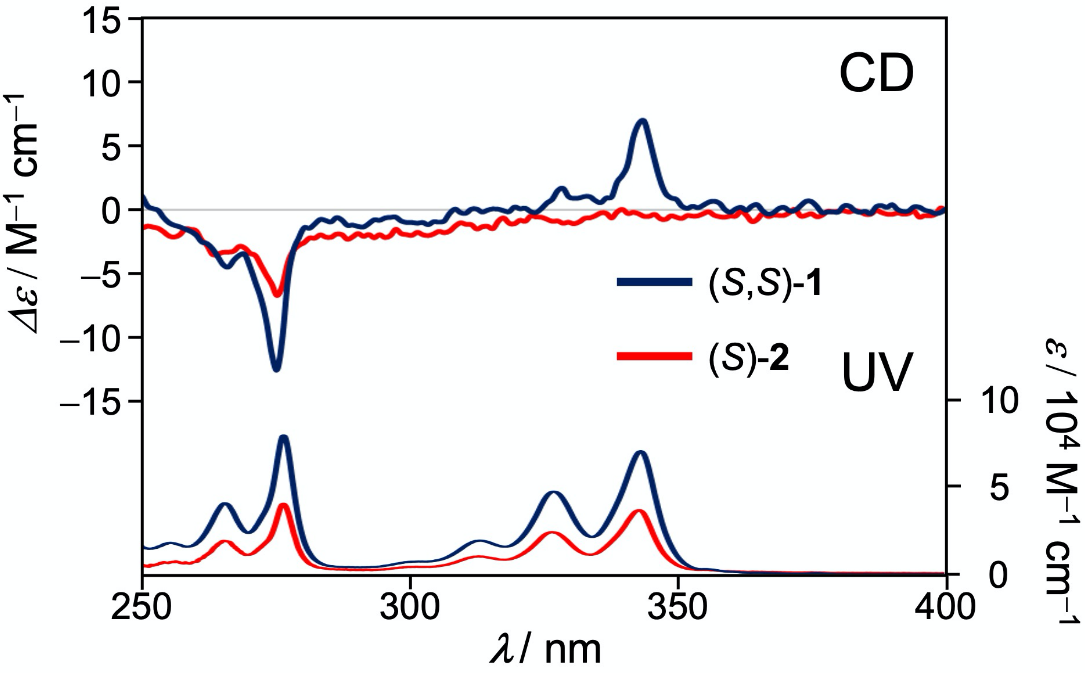


Fig. S3 UV and CD spectra of (*S*,*S*)-**1** and (*S*)-**2** in CH_3CN (1.0×10^{-5} M).

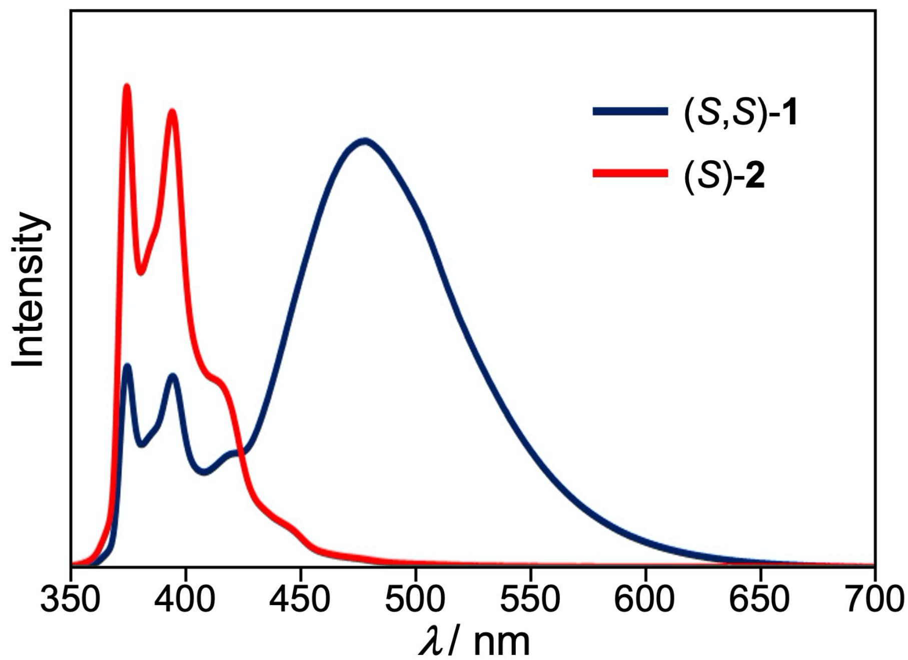


Fig. S4 Fluorescence spectra of (*S*,*S*)-**1** in CH_3CN (1.0×10^{-5} M) and (*S*)-**2** in CH_3CN (2.0×10^{-5} M) excited at 343 nm.

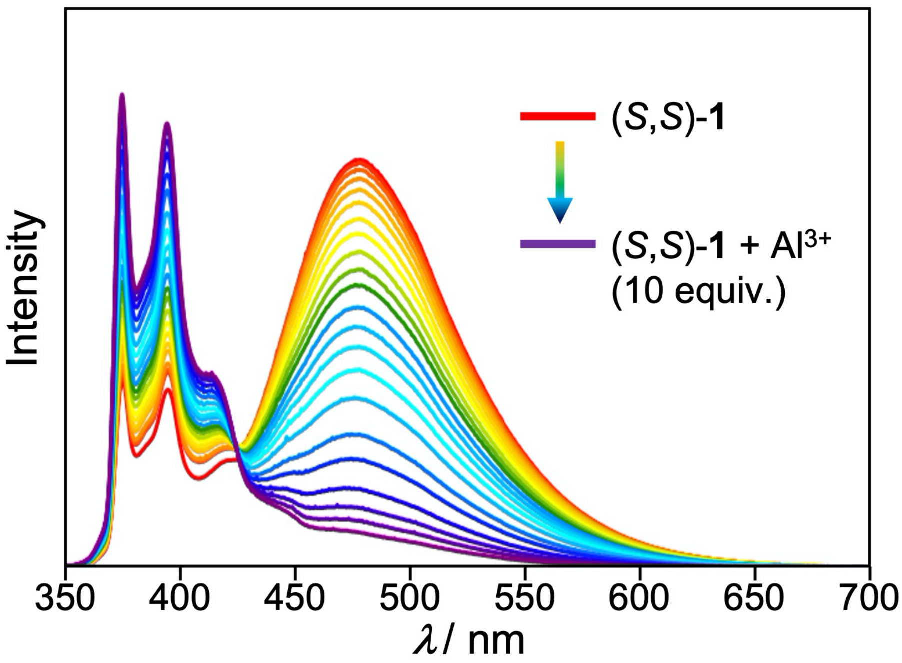


Fig. S5 Fluorescence spectra of (*S*,*S*)-**1** with Al^{3+} (0−10 equivalents) in CH_3CN (5.0×10^{-6} M) excited at 343 nm.

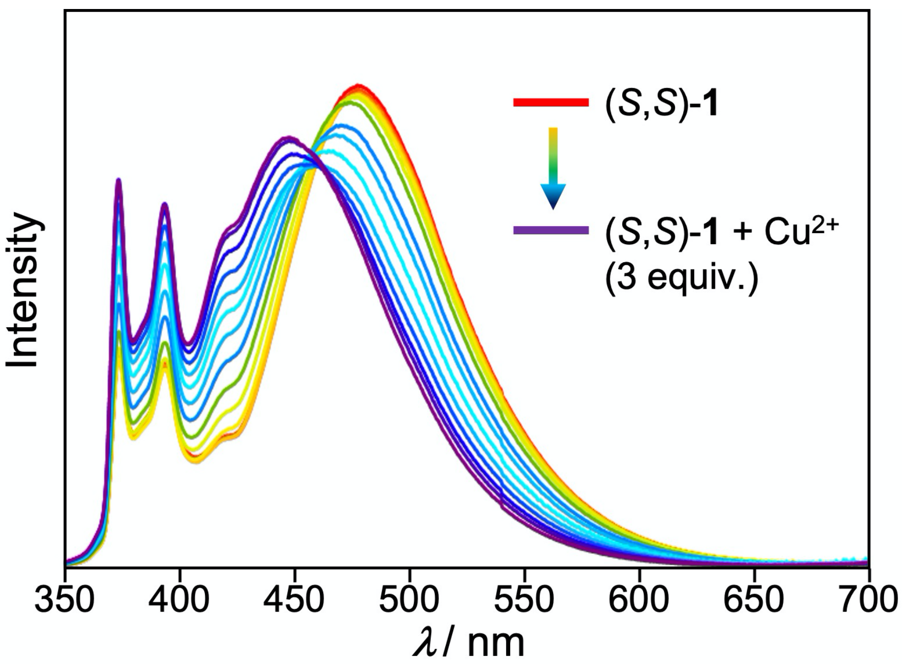


Fig. S6 Fluorescence spectra of (*S*,*S*)-**1** with Cu^{2+} (0−3 equivalents) in CH_3CN (5.0×10^{-6} M) excited at 343 nm.

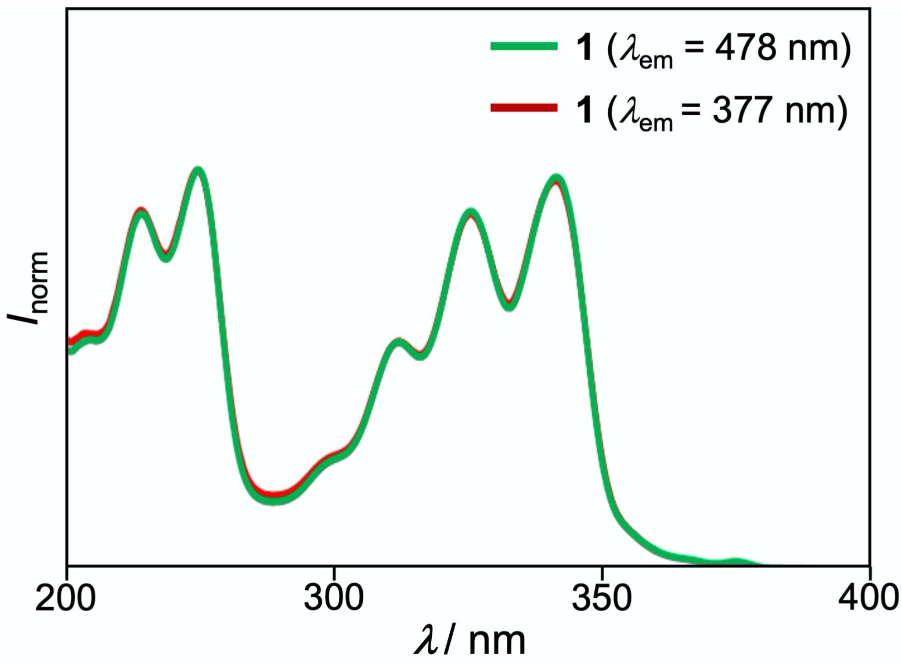


Fig. S7 Excitation spectra of (*S*,*S*)-**1** observed at 377 nm or 478 nm in CH_3CN (1.0×10^{-5} M).

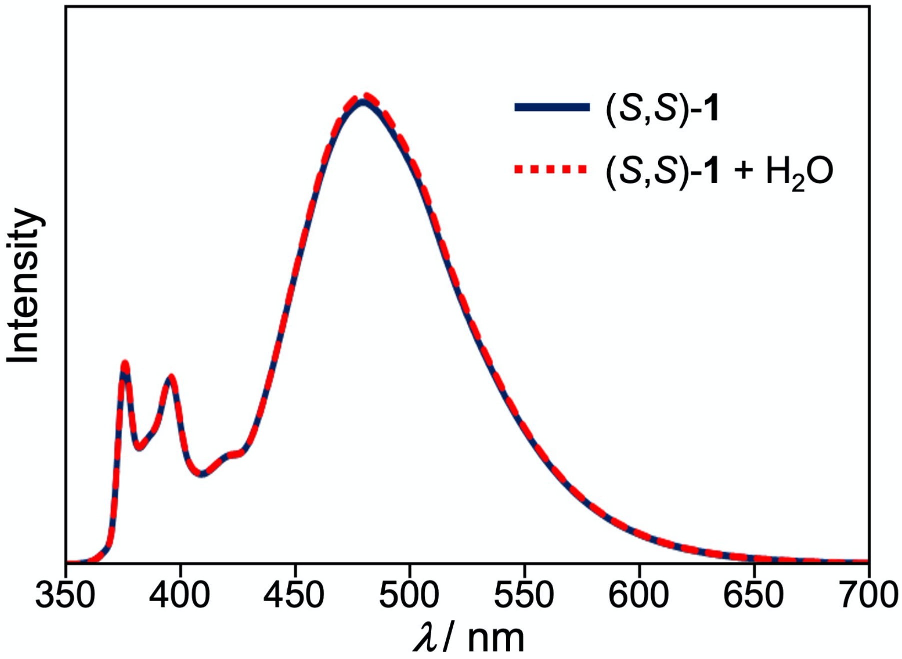


Fig. S8 Fluorescence spectra of (*S*,*S*)-**1** and (*S*,*S*)-**1** with H_2O (90 equiv.) in CH_3CN (5.0×10^{-6} M) excited at 343 nm.

2. Determination of association constants by fluorescence titration

Association constant K_a of host–guest complexes is defined

$$\mathrm{H} + \mathrm{G} \xrightleftharpoons{K_a} \mathrm{HG} \qquad (1)$$

$$K_a = \frac{[\mathrm{HG}]}{[\mathrm{H}][\mathrm{G}]} \qquad (2)$$

$$[\mathrm{H}] = [\mathrm{H}]_0 - [\mathrm{HG}] \quad [\mathrm{G}] = [\mathrm{G}]_0 - [\mathrm{HG}]$$

$$K_a = \frac{[\mathrm{HG}]}{[\mathrm{H}][\mathrm{G}]} = \frac{[\mathrm{HG}]}{([\mathrm{H}]_0 - [\mathrm{HG}])([\mathrm{G}]_0 - [\mathrm{HG}])} \qquad (3)$$

where [H], [G], and [HG], and [HG_2] represent molar concentrations of the host, guest, and 1:1 complex of host–guest, respectively.

The results were analysed by the nonlinear curve fitting program using Bindfit.[1–3] Each titration experiment was carried out three times. The results are summarized in Tables S1 and S2.

Table S1. Data tables for fluorescence titration of (*S*,*S*)-**1** with Al^{3+}.

1st titration

$[Al^{3+}]_0$ 10^{-6} M	$I_{377\ nm}$ (a.u.)	$I_{412\ nm}$ (a.u.)	$I_{447\ nm}$ (a.u.)	$I_{520\ nm}$ (a.u.)
0.00	175.98	101.25	267.52	254.94
0.53	183.45	117.87	270.27	251.54
1.01	186.30	118.40	265.77	247.60
1.52	192.15	120.48	261.32	242.09
2.05	201.95	127.86	256.31	234.09
2.54	208.83	129.93	249.17	226.50
3.05	218.70	133.23	238.95	216.74
3.59	228.01	138.04	230.70	206.93
4.08	240.36	142.18	220.64	195.03
4.59	252.52	147.58	212.77	184.84
5.10	263.82	150.43	201.78	174.16
6.38	276.72	154.66	189.22	161.41
7.66	292.44	163.10	179.12	148.49
10.08	303.83	164.95	167.00	136.51
15.39	320.25	171.67	154.18	121.20
20.36	338.10	178.66	138.58	103.70
25.50	359.95	184.73	116.40	80.73
30.55	376.80	190.39	102.56	65.60
35.76	396.80	196.57	86.11	47.15
40.89	410.85	202.97	75.15	35.60
45.92	420.34	206.62	67.50	27.04
51.10	426.86	208.51	61.28	20.00
101.12	437.59	211.68	54.50	12.85
152.78	443.10	214.07	50.39	7.83
203.58	446.96	215.44	49.60	5.14
255.89	450.40	216.44	47.41	3.98
510.90	452.94	220.87	49.05	4.15

[(*S*,*S*)-**1**]$_0$ = 5.1×10^{-6} M

2nd titration

$[Al^{3+}]_0$ 10^{-6} M	$I_{377\ nm}$ (a.u.)	$I_{412\ nm}$ (a.u.)	$I_{447\ nm}$ (a.u.)	$I_{520\ nm}$ (a.u.)
0.00	174.65	100.67	269.16	255.77
0.50	173.92	99.42	260.87	247.18
1.00	177.20	101.30	257.82	244.16
1.51	183.76	104.15	253.57	238.70
2.01	190.31	106.41	247.22	231.75
2.52	199.05	109.84	239.50	222.50
3.02	207.88	112.88	228.76	211.70
3.53	217.61	116.91	219.54	201.06
4.04	227.67	120.58	209.37	191.08
4.53	240.16	124.94	200.66	180.85
5.03	250.21	128.98	189.86	168.04
6.30	266.78	136.47	177.17	154.46
7.55	283.65	143.50	163.40	138.47
10.11	299.13	148.90	148.45	122.84
15.13	317.71	156.06	136.58	108.98
20.06	338.13	163.29	118.63	89.08
25.09	365.17	172.21	97.34	65.75
30.21	382.72	178.58	82.61	49.27
35.23	398.97	184.25	66.75	32.43
40.33	414.00	189.86	56.55	21.76
45.32	424.53	193.76	50.63	14.67
50.38	430.55	196.11	46.70	10.36
100.97	436.79	198.89	43.39	6.49
150.56	440.56	200.57	41.80	4.72
201.02	443.65	202.71	42.16	4.42
252.27	443.94	204.63	42.46	4.47
503.03	447.72	210.72	44.81	4.81

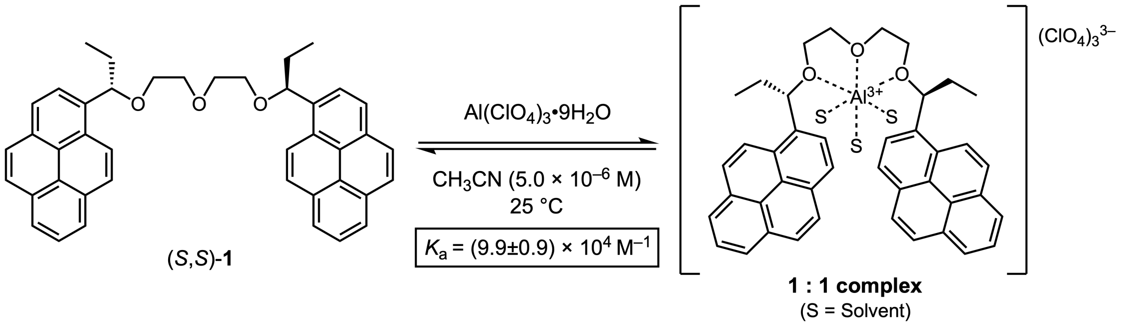
$[(S,S)\text{-}\mathbf{1}]_0 = 5.0 \times 10^{-6}$ M

3rd titration

$[Al^{3+}]_0$ 10^{-6} M	$I_{377\ nm}$ (a.u.)	$I_{412\ nm}$ (a.u.)	$I_{447\ nm}$ (a.u.)	$I_{520\ nm}$ (a.u.)
0.00	176.65	122.54	254.92	237.48
0.51	177.62	121.90	252.36	234.82
1.03	180.92	122.44	251.44	233.58
1.52	182.96	122.38	244.68	227.40
2.06	187.71	124.48	240.13	222.75
2.55	193.63	125.65	234.59	215.87
3.07	203.24	126.95	220.68	201.08
3.57	210.60	130.93	216.98	197.05
4.09	220.04	134.13	209.69	188.70
4.60	229.08	137.63	201.74	179.24
5.10	238.87	140.74	192.71	169.25
6.39	255.65	147.14	180.22	155.66
7.67	270.64	151.94	164.75	137.88
10.33	286.64	157.43	150.03	122.51
15.33	306.43	164.46	134.43	105.10
20.48	331.79	173.19	114.04	82.58
25.53	355.43	181.20	95.55	62.07
30.71	376.75	188.91	77.33	42.60
35.79	394.72	194.76	63.91	27.95
40.78	404.92	197.35	55.80	19.39
45.89	415.40	201.52	49.65	12.82
51.10	425.64	205.76	47.17	9.01
102.35	429.01	205.91	44.25	6.40
152.68	429.96	206.95	44.17	5.80
204.24	432.20	208.03	44.09	5.94
254.84	433.55	209.44	44.52	5.84
511.60	437.07	214.49	45.94	5.67

$[(S,S)\text{-}\mathbf{1}]_0 = 5.1 \times 10^{-6}$ M

Table S2. Association constants and error values obtained by the curve-fitting analysis of fluorescence titration data of (*S*,*S*)-**1** with Al^{3+} using Bindfit calculator.



Entry	K_a (M^{-1})	Error (%)
1st titration[a]	98201	±5.4723
2nd titration[b]	107357	±5.7539
3rd titration[c]	90651	±6.6794
Average	$(9.9\pm0.9)\times10^4$	

[a] Bindfit URL: http://app.supramolecular.org/bindfit/view/fea2eab5-7ed3-481e-a790-bc8dcbdfb38a

[b] Bindfit URL: http://app.supramolecular.org/bindfit/view/c7ba8225-cbde-43e3-9376-c50b89416e30

[c] Bindfit URL: http://app.supramolecular.org/bindfit/view/f035a784-7074-4e68-8168-b5b7aff8df54

3. The reaction of (*S*,*S*)-1 with Cu^{2+}

Fluorescence spectral change

To a CH_3CN solution of (*S*,*S*)-**1** (1.0×10^{-4} M) were added 1.5 molar equivalents of $Cu(ClO_4)_2{\bullet}6H_2O$, and the mixture was stirred at room temperature. The maximum emission wavelength of the mixture was changed from 478 nm to 455 nm within 0.5 min (Fig. S9).

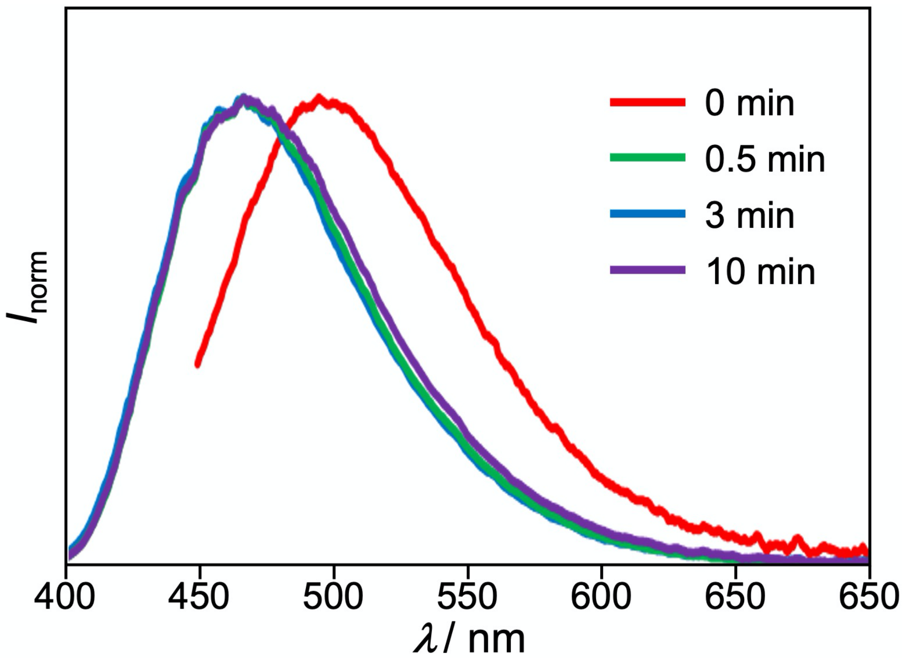
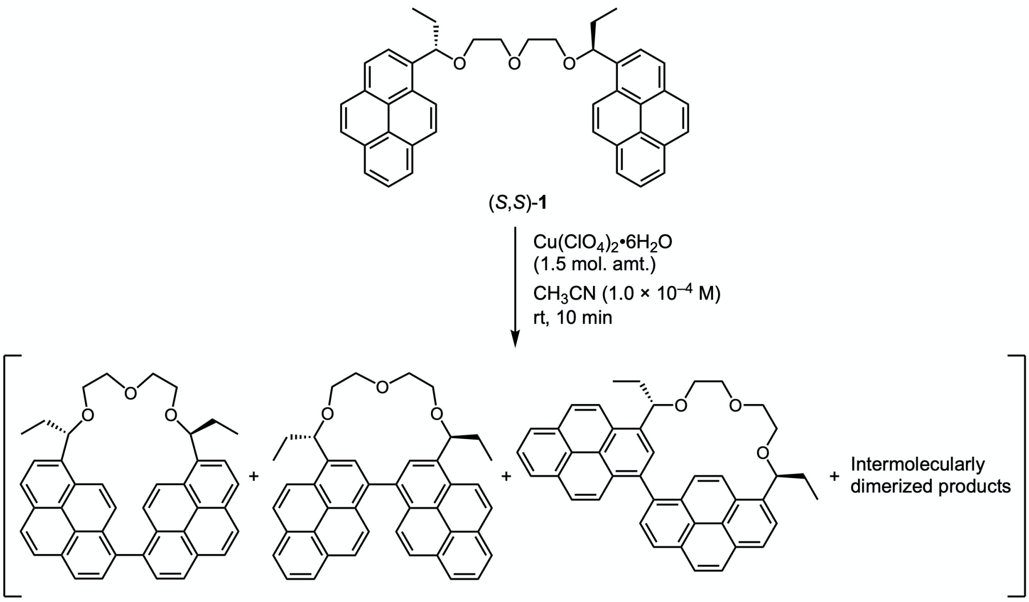


Fig. S9 Fluorescence spectral change in the reaction of (*S*,*S*)-**1** with $Cu(ClO_4)_2{\bullet}6H_2O$ (1.5 equiv.) in CH_3CN (1.0×10^{-4} M) excited at 365 nm.

<u>[1]H NMR spectrum</u>

The [1]H NMR spectrum of the crude mixture for the reaction of (*S*,*S*)-**1** with $Cu(ClO_4)_2{\bullet}6H_2O$ suggested the conversion of (*S*,*S*)-**1** to intramolecularly cyclized products and intermolecularly dimerized products.



Potential structures of intramolecularly cyclized products

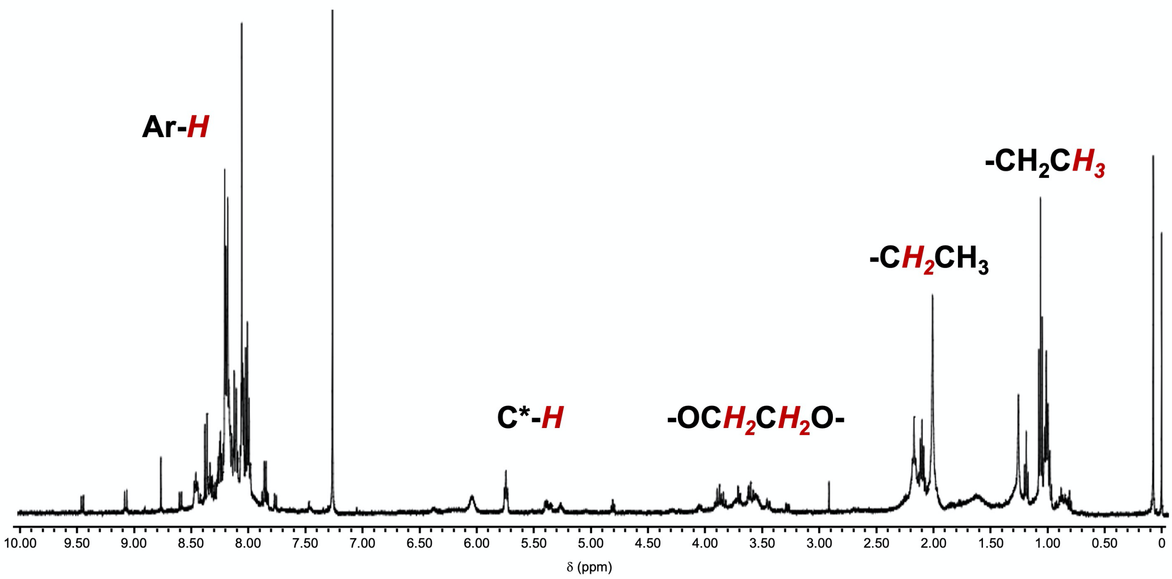


Fig. 10 [1]H NMR spectrum of the crude mixture of (*S*,*S*)-**1** with $Cu(ClO_4)_2{\bullet}6H_2O$.

ESI-HRMS analysis

The formation of intramolecularly cyclized product of (*S*,*S*)-**1** was suggested by the ESI-MS analysis of the mixture obtained by the reaction of (*S*,*S*)-**1** with $Cu(ClO_4)_2 \bullet 6H_2O$ (Fig. S10).

Sample preparation.

A 2.1 mM 0.1vol%-AcOH/CH_3CN solution of (*S*,*S*)-**1** (solution A) was prepared in a 10 mL volumetric flask by dissolving (*S*,*S*)-**1** (12.6 mg, 0.021 mmol) into 0.1vol%-AcOH/CH_3CN. A 5.6 mM 0.1vol%-AcOH/CH_3CN solution of $Cu(ClO_4)_2 \bullet 6H_2O$ (solution B) was prepared in a 5 mL volumetric flask by dissolving $Cu(ClO_4)_2 \bullet 6H_2O$ (10.5 mg, 0.028 mmol) into 0.1vol%-AcOH/CH_3CN. A 1.0×10^{-4} M 0.1vol%-AcOH/CH_3CN solution of $Cu(ClO_4)_2 \bullet 6H_2O$ containing 1.0×10^{-5} M of (*S*,*S*)-**1** (solutions C) was prepared in a 5 mL volumetric flask by dilution of solution A (23 μL) and solution B (89 μL) with 0.1vol%-AcOH/CH_3CN.

Eluent of LC.

0.1vol%-AcOH/CH_3CN (95%)/water (5%)

Result.

HRMS-ESI (*m*/*z*): [(*S*,*S*)-**1**–2H]$^+$ calcd for $C_{42}H_{36}O_3$, 588.2659; found, 588.2664.

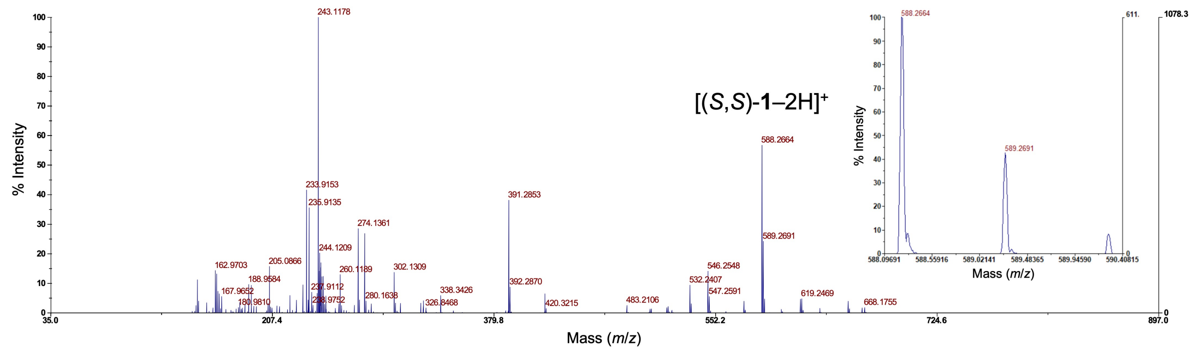


Fig. S11 ESI-MS spectrum of the mixture obtained by the reaction of (*S*,*S*)-**1** with $Cu(ClO_4)_2 \bullet 6H_2O$.

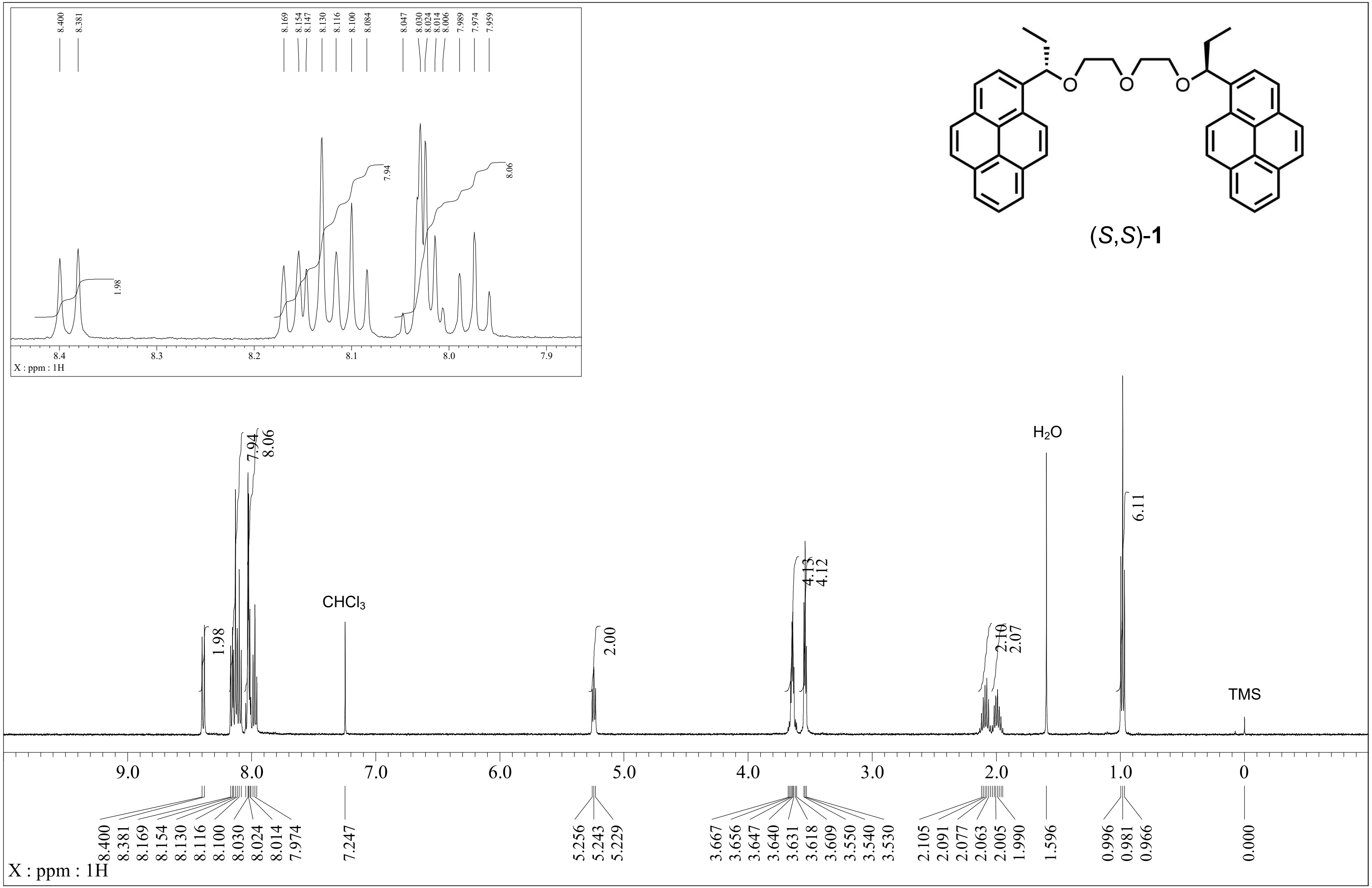
4. References

1) Bindfit. http://app.supramolecular.org/bindfit/, accessed Jan 5, 2022.

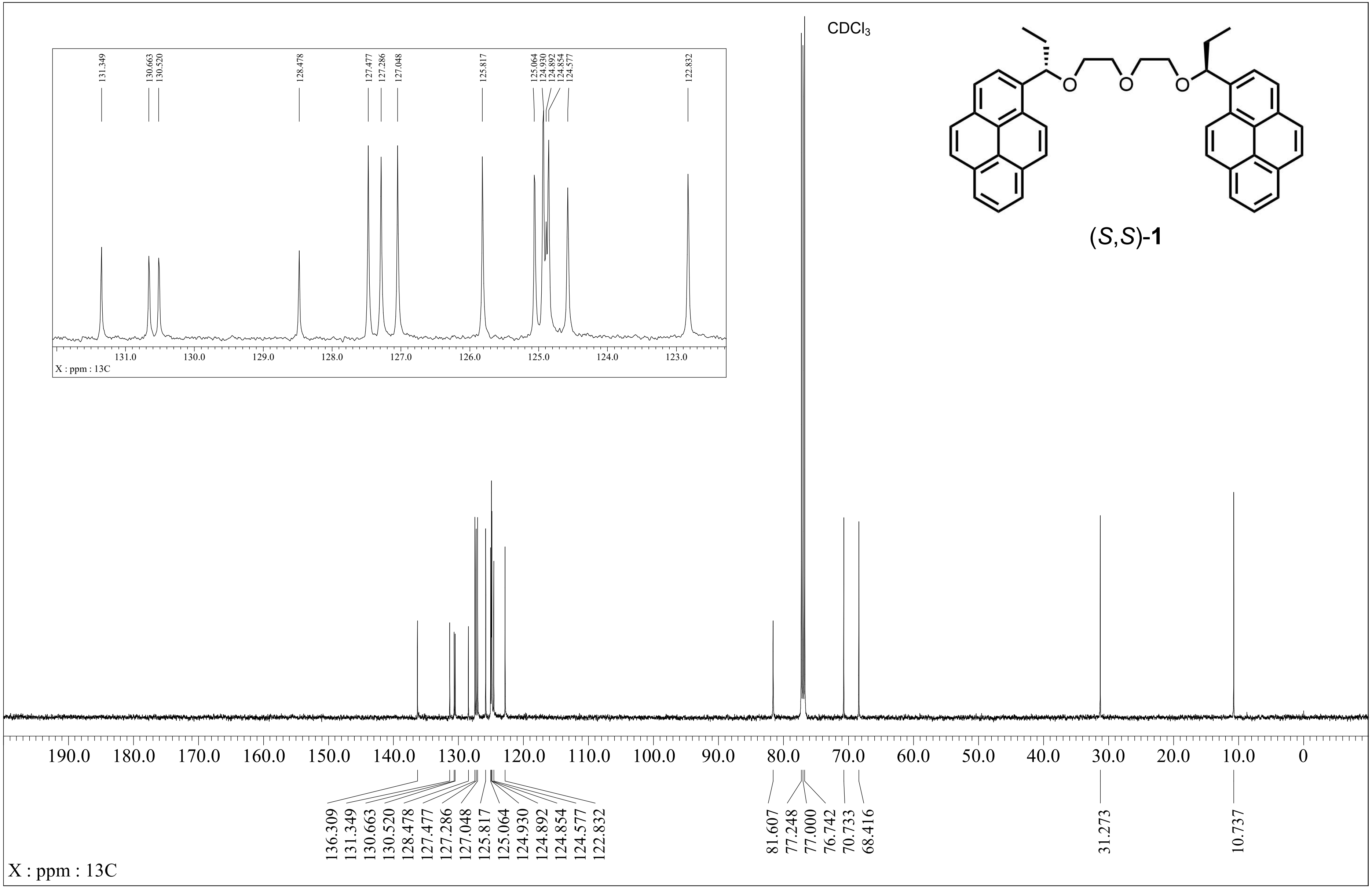
2) P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305−1323.

3) D. B. Hibbert and P. Thordarson, *Chem. Commun.*, 2016, **52**, 12792–12805.

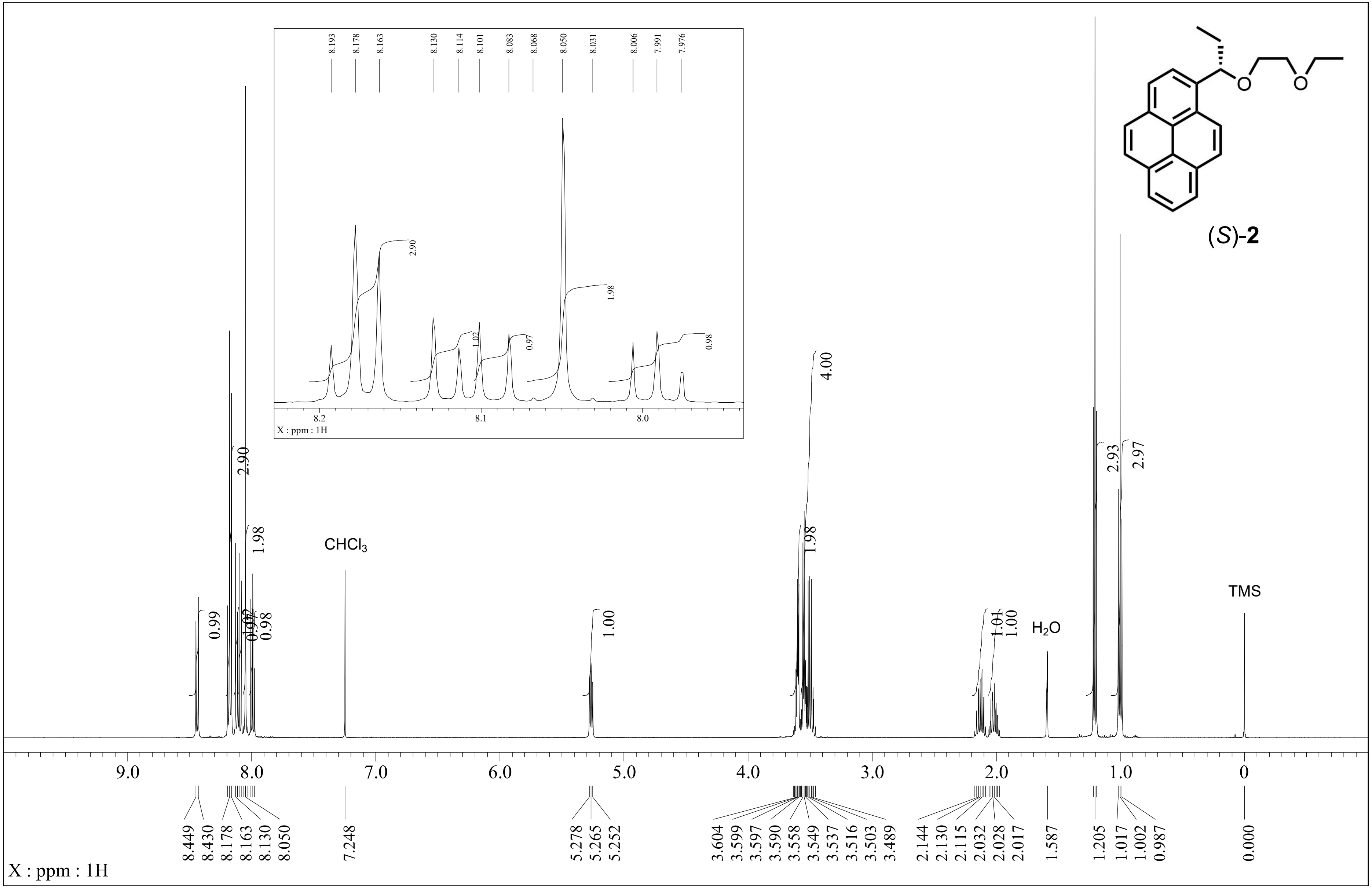
^{1}H NMR spectrum of (*S*,*S*)-**1** (500 MHz, $CDCl_3$, rt)



^{13}C NMR spectrum of (*S*,*S*)-**1** (126 MHz, $CDCl_3$,rt)



^1H NMR spectrum of (*S*)-**2** (500 MHz, $CDCl_3$, rt)



^{13}C NMR of spectrum of (*S*)-**2** (126 MHz, $CDCl_3$,rt)